

國立臺灣師範大學理學院化學系

碩士論文

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利用一價銠金屬催化劑催化具高鏡像選擇性之不對稱串聯

合環反應

Highly Enantioselective Rhodium(I)-Catalyzed Asymmetric

Cascade Cyclization Reactions

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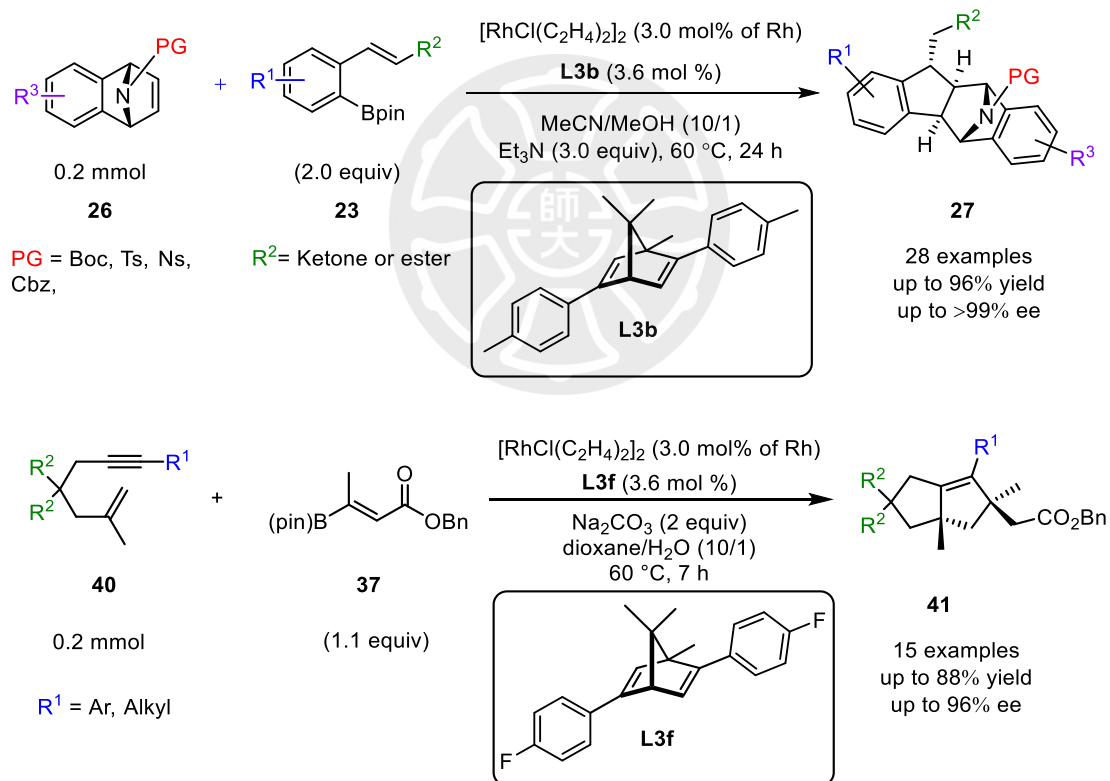
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摘要

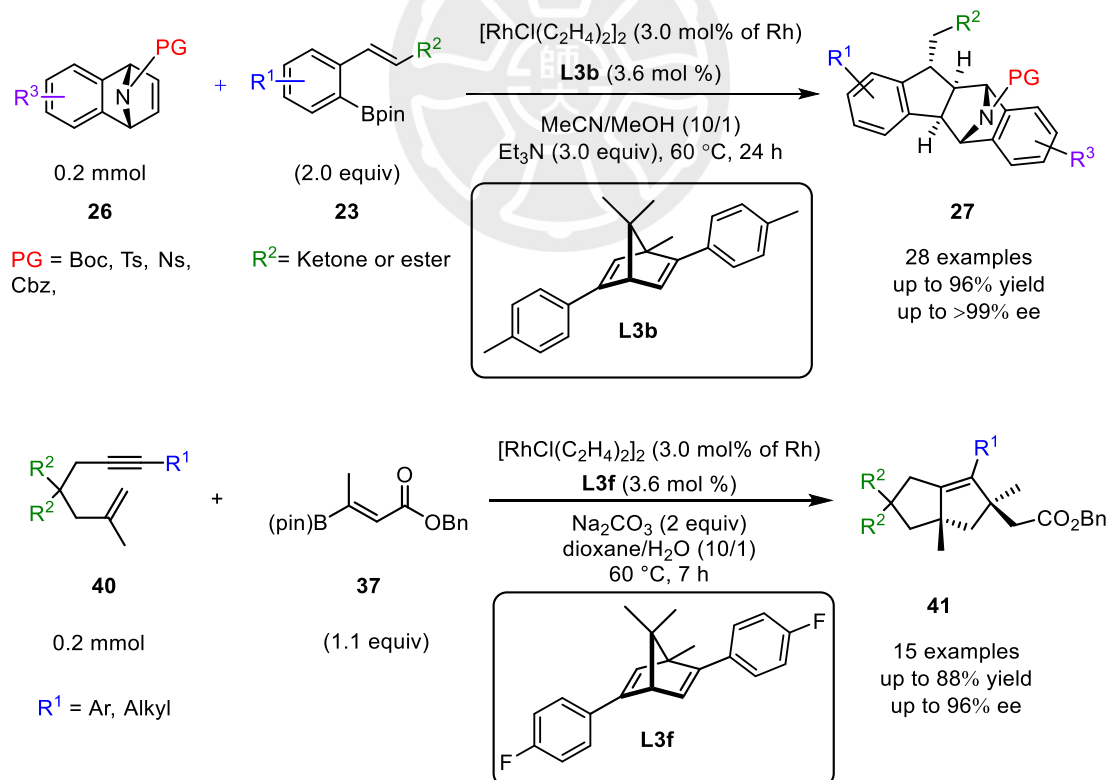
本論文敘述以一價銦金屬及掌性雙環[2.2.1]雙烯配基 **L3b** 形成之催化劑，催化具有不同取代基的芳基硼酯化合物 **23** 與 7-氮苯駢降冰片烯化合物 **26** 進行不對稱串聯合環反應，生成一系列具有茛烷(indane)結構的掌性環化產物 **27**，共 28 個例子，最高產率達 96%，以及高達 99% 的鏡像超越值。此反應在形成兩個新的碳-碳鍵的同時，亦可有效地建立三個連續的掌性中心。此外本論文亦探討以烯基硼試劑 **37** 與 1,6-烯炔起始物 **40** 進行不對稱串聯合環反應，合成一系列具有(diquinene)結構的掌性環化產物 **41**，有 15 個例子，產率、鏡像超越值皆有良好的表現 (88% yield, 96% ee)。



關鍵詞：一價銦金屬催化、掌性雙環[2.2.1]雙烯配基、不對稱串聯合環反應、鏡像選擇性、芳香基硼酯化合物、7-氮苯駢降冰片烯化合物、1,6-烯炔

Abstract

This thesis describes a highly enantioselective cascade cyclization of arylboronate esters **23** and 1,4-dihydro-1,4-iminonaphthalene **26** in the presence of a rhodium(I)-catalyst prepared *in situ* from $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ and the chiral bicyclo[2.2.1]heptadiene ligand **L3b**. Under the optimal conditions, the annulated products **27** bearing an indane skeleton were generated in up to 96% yield and 99% ee as demonstrated in 28 examples featuring with three consecutive chiral centers. The second part of this thesis aims for studying enantioselective cascade cyclization reaction of 1,6-eynes **40** and arylboronate esters **37**. In the presence of rhodium(I)-catalyst *in situ* generated from **L3f** under optimal conditions, the annulated products **41** comprising a diquinene skeleton were produced in up to 88% yield and 96% ee, as demonstrated in 15 examples.



Key words: rhodium(I)-catalyzed, chiral bicyclo[2.2.1]diene ligands, asymmetric cascade cyclization, enantioselective, arylboronic ester, 1,4-dihydro-1,4-iminonaphthalene, 1,6-Enyne.



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¹³ C NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromophenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ag).....	371
¹ H NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)	372
¹³ C NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)	373
¹⁹ F NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)	374
¹ H NMR spectrum of di-tert-butyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (44ae)	375
¹³ C NMR spectrum of di-tert-butyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (44ae)	376
¹ H NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ai)	377
¹³ C NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ai)	378

¹H NMR spectrum of 4-bromobenzyl 2-(6-(4-bromophenyl)-2',2',3a,5-tetramethyl-3,3a,4,5-tetrahydro-1H-spiro[pentalene-2,5'-[1,3]dioxan]-5-yl)acetate (44af).....	379
¹³C NMR spectrum of 4-bromobenzyl 2-(6-(4-bromophenyl)-2',2',3a,5-tetramethyl-3,3a,4,5-tetrahydro-1H-spiro[pentalene-2,5'-[1,3]dioxan]-5-yl)acetate (44af).....	380



縮寫對照表

縮寫	全名
Ac	acetyl
aq	aqueous
Ar	aryl
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Bn	benzyl
Boc	<i>tert</i> -Butyloxycarbonyl
BPE	1,2-bis(diphenylphospholano)ethane
br	broad (NMR)
Bu	butyl
calcd	calculated
cat	catalyst
Cbz	benzyloxycarbonyl
COD	1,5-cyclooctadiene
d	doublet (NMR)
dil	diluted
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane
dr	diastereomeric ratio
ee	enantiomeric excess
equiv	equivalent
Et	ethyl
EtOAc	Ethyl acetate

h	hour
HPLC	high-performance liquid chromatography
Hz	Hertz
<i>i</i>	<i>iso</i>
IPA	isopropyl alcohol
KHMDS	potassium bis(trimethylsilyl)amide
LDA	lithium diisopropylamide
m	multiplet (NMR)
M	molarity
Me	methyl
min	minute
mol	mole
m.p.	melting point
<i>n</i>	normal (unbranched alkyl chain)
NHC	<i>N</i> -heterocyclic carbene
NMR	Nuclear Magnetic Resonance Spectroscopy
N.R.	No reaction
Nu	nucleophile
OMe	methoxy
ORTEP	Oak Ridge Thermal-Ellipsoid Plot Program
OTf	trifluoromethanesulfonate
<i>p</i>	<i>para</i>
PCC	pyridinium chlorochromate
PG	Protecting group

Ph	phenyl
pin	pinacolato
Pr	propyl
quint	quintet (NMR)
R_f	retention factor
rt	room temperature
s	singlet (NMR)
SDS	sodium dodecyl sulfate
sept	septet (NMR)
t	triplet (NMR)
<i>t</i>	<i>tert</i>
TEA	triethylamine
Temp.	temperature
THF	tetrahydrofuran
TLC	thin-layer chromatography
TPPDS	Trisodium 3,3',3''-phosphanetriyltri(benzene-1-sulfonate)
α	alpha
β	beta

第一章 緒論

掌性(chirality)分子的需求日益增長，合成複雜的掌性分子有許多不同的策略，眾多策略的考量中，合成具有良好位向選擇性(regioselectivity)、鏡像選擇性(enantioselectivity)，以生成具有高光學純度(enantiopurity) 的產物為重要目標。其中，過渡金屬催化的不對稱串聯反應，非常具有研究價值，串聯反應的主要優點包括原子經濟性高(high atom economy)、減少過多的合成步驟所產生的廢棄物，以及執行這些過程所需的時間和次數。良好的實驗設計，可以利用串聯反應在一步操作中，形成多個碳-碳鍵的有效策略，為構建天然和產物生物活性分子的核心結構提供了經濟有效的方法。

本論文綜述探討了銦(I)催化的不對稱串聯反應，本內容分為二個部分：1) 7-氮苯駢降冰片烯化合物與鄰位共軛烯酯取代的芳基硼酯試劑進行不對稱串聯環化反應；2) 由烯炔化合物與烯基硼試劑之反應，進行不對稱環化反應的串聯反應。這類的反應是相當具有合成效益的。我們預期透過銦金屬與不同掌性雙烯配基所生成的掌性催化劑，進行不對稱催化串聯反應，可以得到好的位向選擇性與鏡像選擇性。

第二章 第一部分文獻回顧與研究動機

隨著掌性分子需求的不斷增長，高效的合成方法取得了顯著進展。其中，不對稱過渡金屬催化的串聯反應已被廣泛認可為一種具高度潛力的合成策略，能夠在單一操作中高效地構建多個碳-碳鍵，從而以具經濟效益的方式實現天然產物與生物活性分子核心骨架的構築。串聯反應可以根據起始物的官能基不同而細分如：(1)雙鍵或參鍵化合物與具拉電子基取代的芳基硼試劑之反應；(2)烯炔化合物與芳基硼試劑之反應；(3)炔酮化合物與芳基硼試劑之反應。本篇論文兩大主題包含：第一部分研究主題；7-氯苯駢降冰片烯化合物與鄰位共軛烯酯取代的芳基硼試劑進行不對稱串聯環化反應和第二部分研究主題；由烯炔化合物與烯基硼試劑之反應，進行不對稱環化反應的串聯反應進行文獻回顧之討論。

一、銦金屬催化之串聯合環反應

Hayashi 教授於 2002 年(圖 2-1)，使用銦金屬催化劑催化 α,β -不飽和酮 **1** 與 *B*-Ar-9-BBN (**2**) 進行共軛加成後生成 π -allyl 銦烯醇鹽中間體 **IT-1**，接著與醛 **3** 經由醛醇反應(aldol reaction)，產生 rhodium aldolate **IT-2**。經由轉移金屬化(transmetalation)生成產物 boron aldolate **5**。在催化反應結束後，經由水解反應生成醇化合物 **4**，產率高達 99%，並且有良好的選擇性 (*syn:anti* = 20:1)。若是上述反應中的兩個參與反應的官能基(化合物 **1** 與 **3**)位於同一個分子內，則可以進行經由銦烯醇鹽中間體的環化反應，為合環反應增添更廣泛的應用，此後諸多反應也參照此概念設計起始物分子。^[1]

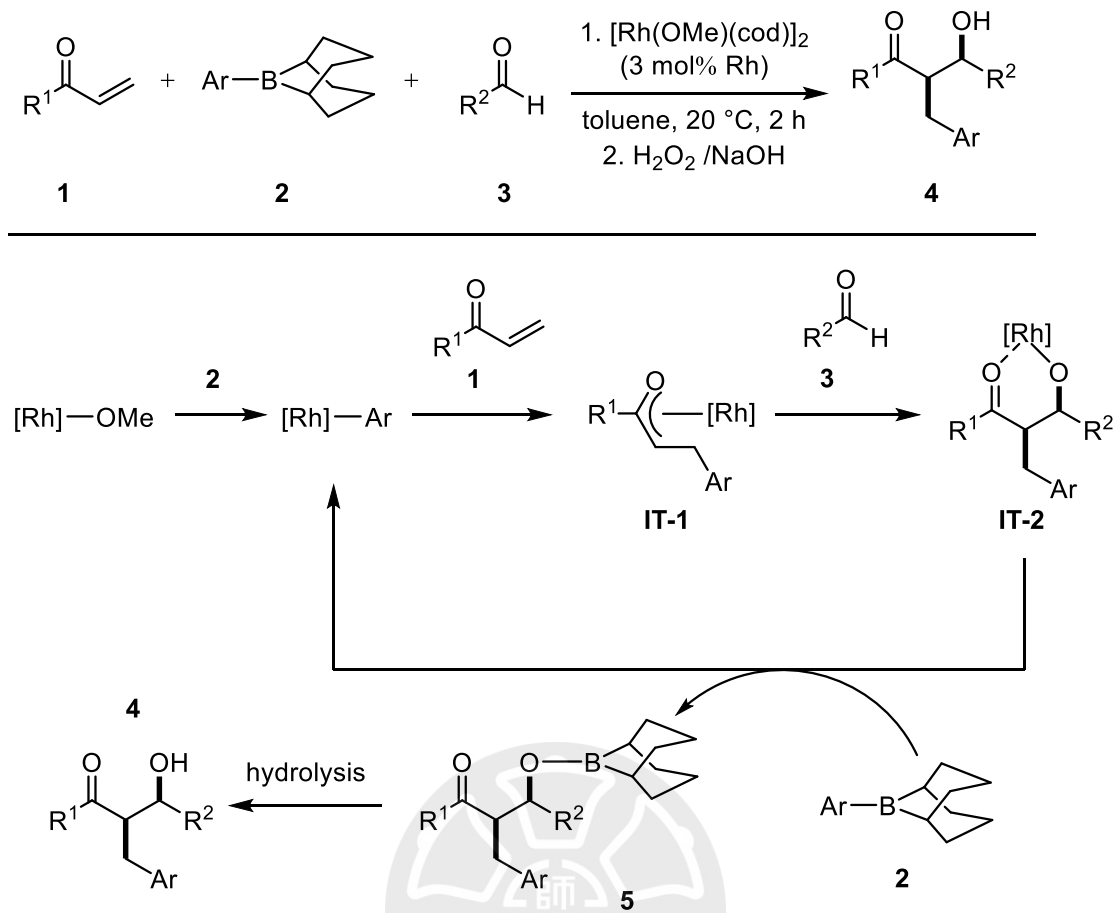


圖 2-1 Hayashi 教授研究銠金屬催化醛醇反應

二、利用環張力釋放之反應活性進行合環反應

Goddard 教授於 2009 年對具有雙環[2.2.1]結構的化合物的環張力進行深入的研究(圖 2-2)。若分別以化合物 **6a-6d**、**7a-7d**、**8a-8d** 以及 **9a-9d** 為一組，進行環張力相對能量之比較，由以上四組化合物可發現，隨著環內雙鍵的增加，環張力有增加的趨勢；由此可知，若對環內雙鍵進行加成，使雙鍵減少，則能夠釋放一部份的環張力。另外，當 7 號位置有不同取代基時，造成環張力差異。而本論文旨在探討具有雙環[2.2.1]結構的化合物 **9d** (以下稱 7-氮苯駢降冰片烯化合物，7-aza-benzonorbornene)與其衍生物的雙鍵進行串聯合環反應。^[2]

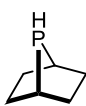

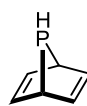
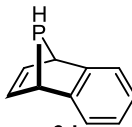



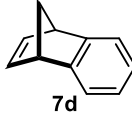
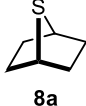
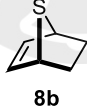
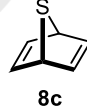
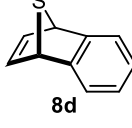
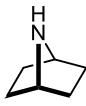
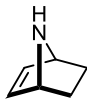
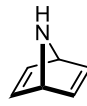
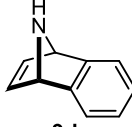
				
6a	6b	6c	6d	
RSE (kcal/mol)	12.5	14.4	21.3	-7.5
				
7a	7b	7c	7d	
RSE (kcal/mol)	15.1	18.8	27.6	0.0
				
8a	8b	8c	8d	
RSE (kcal/mol)	11.5	18.3	30.7	1.6
				
9a	9b	9c	9d	
RSE (kcal/mol)	15.1	19.8	33.0	5.2

圖 2-2 Goddard 教授計算具雙環[2.2.1]結構化合物的環張力相對能量

於 2005 年時，Murakami 教授使用芳基硼酸 **10** 作為起始物，經一價銦金屬前催化劑與掌性雙環[2.2.2]雙烯配基 **L1** 所形成的催化劑，對苯駢降冰片烯衍生物 **11** 進行不對稱合環反應，藉由環張力之釋放作為驅動力，促使串聯合環反應的進行，反應機構為，一價銦金屬錯合物與起始 2-氰基苯硼酸 **10** 進行轉移金屬反應生成中間體 **IT-3**、並進行 5-*exo* 加成至降冰片烯衍生物 **11** 的雙鍵之後，因苯環的鄰位尚有一親電基團—氰基，故在進行雙鍵加成以後形成的銦金屬中間體 **IT-4**，銦金屬中間體 **IT-4** 與苯環上的氰基進行分子內的加成，產生銦金屬與亞胺的中間體 **IT-5**，經水解反應生成環化產物 **12**，產率為 62% 鏡像超越值為 80% ee (圖 2-3)。[3]



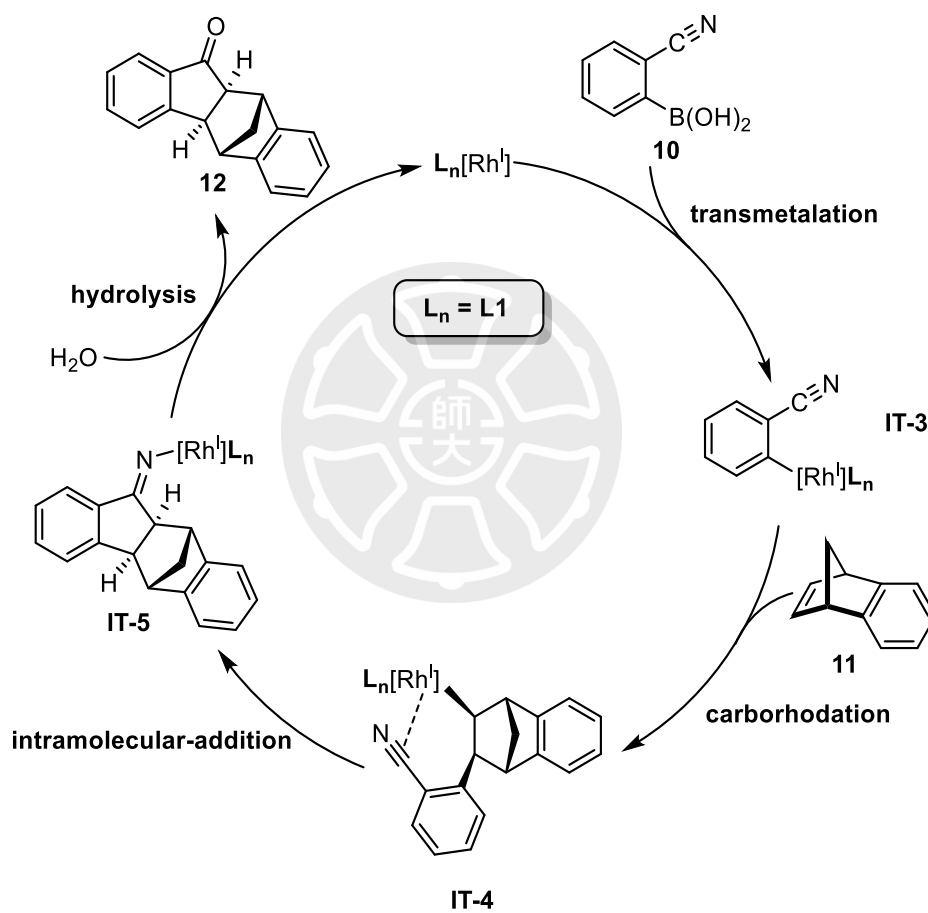
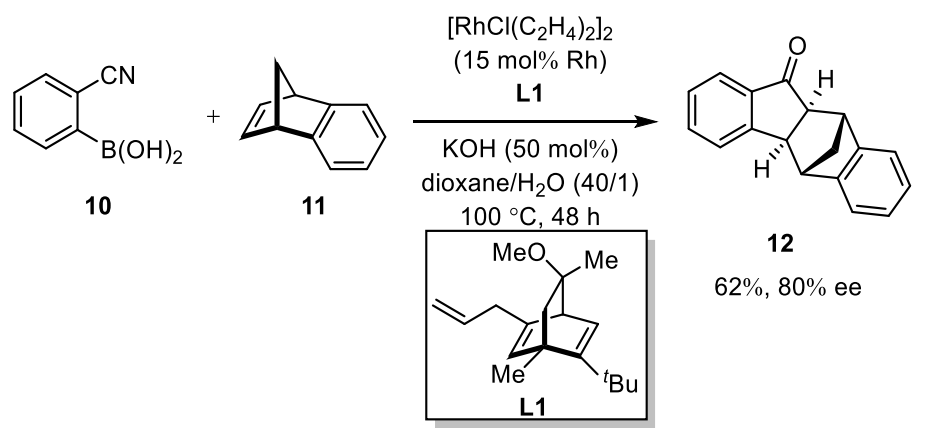


圖 2-3 Murakami 教授推測反應機構

Radhakrishnan 教授於 2011 年使用銨金屬結合(±)-BINAP 雙膦配基形成之催化劑，催化 2-氰基苯硼酸 **10** 與 2,3-二氮雜二環[2.2.1]-5-庚烯化合物 **13** 進行串聯合環反應，也是藉由環張力之釋放作為驅動力，促使串聯合環反應的進行。反應機構為，一價銨金屬與 2 號位置接上氰基的芳基硼酸化合物 **10** 進行金屬轉移反應生成中間體 **IT-6**、並以 *exo* 位向加成至二氮雜二環[2.2.1]庚烯 **13** 的雙鍵，因苯環的鄰位尚有一親電基團—氰基，故在進行雙鍵加成以後形成的銨金屬中間體 **IT-7**，與苯環上的氰基進行分子內的加成反應，產生銨金屬與亞胺的中間體 **IT-8**，其後經水解反應生成環化產物 **14**。共 4 個例子，產率為 61–69%。通過觀察發現，起始物 2,3-二氮雜二環[2.2.1]-5-庚烯 **13**，氮上保護基會影響產物產率。隨著基團變大，立體效應也隨之增加，產率有略為下降的趨勢(圖 2-4)。^[4]



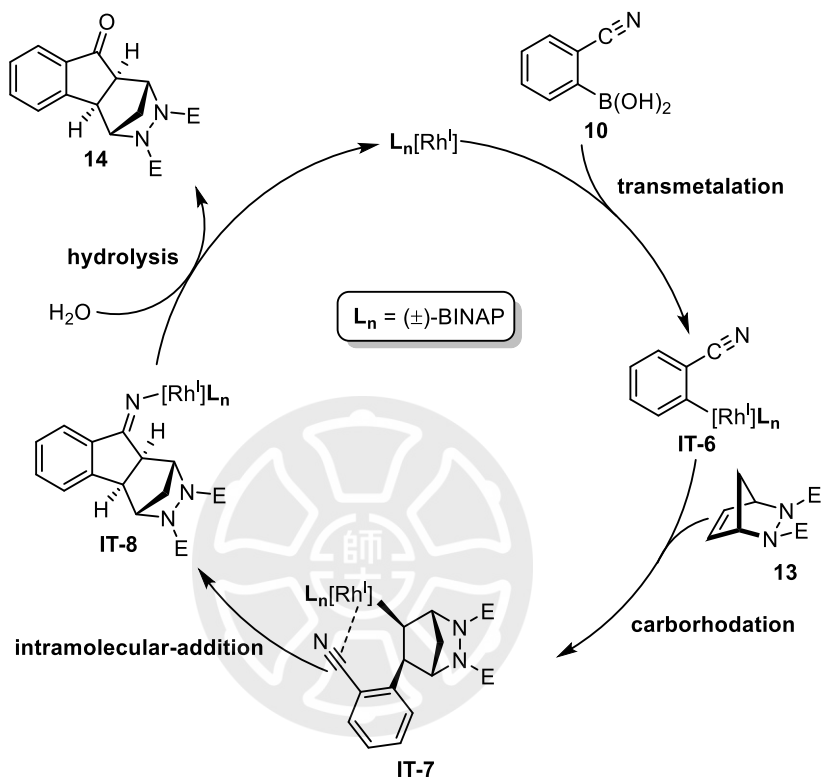
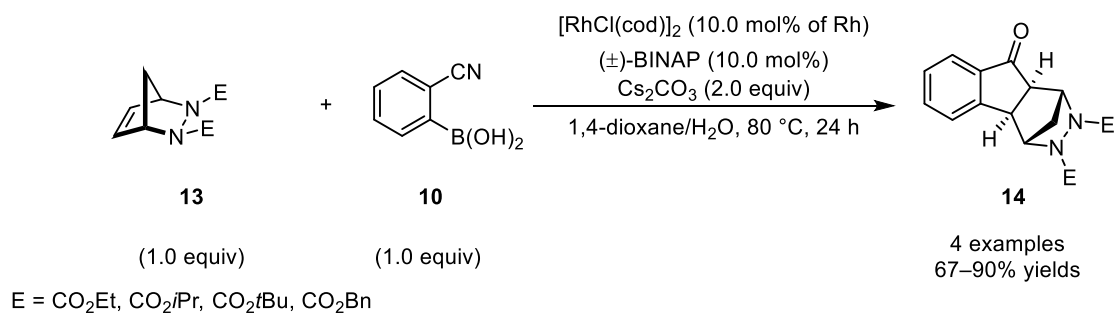


圖 2-4 Radhakrishnan 教授的研究

以上所敘述的兩則文獻回顧中，銻金屬催化劑會先與反應中所加入的試劑經由金屬轉移反應形成中間體並加成至降冰片烯與其衍生物的雙鍵，若加入反應中的試劑除了有可與金屬形成中間體的官能團(硼酸或硼酯)以外，尚有親電基團位於鄰位，則反應在形成銻金屬中間體並加成至降冰片烯與其衍生物的雙鍵以後，做為親核試劑的銻金屬中間體，易與具有親電性的官能基做第二次的加成，進行合環的反應，進而產生環化的產物，此種反應類型屬於串聯合環反應(tandem annulation)。

於 2002 年時，Lautens 教授使用一價銻金屬前催化劑與水溶性含磷配基 **L2** 所形成之催化劑，催化具有 α,β -不飽和酯基取代的苯硼酯 **16**，與降冰片烯(norbornene)衍生物 **15** 進行合環反應，得到具茚烷(indane)結構之合環產物 **17**，其反應機構為，一價銻金屬錯合物先與芳基硼酯 **16** 進行轉移金屬反應，生成 arylrhodium 中間體 **IT-9**，隨後，中間體 **IT-9** 進行 carborhodation 加成至降冰片烯 **15** 的雙鍵，產生中間體 **IT-10**。硼酯官能基所在的鄰位上 α,β -不飽和酯基，可做為親電基團引導一價銻金屬中間體進行加成，因此中間體 **IT-10** 經由 5-exo-trig 的加成反應，產生 oxa- π -allylrhodium 中間體 **IT-11**，再進行質子去金屬化(protodemetalation)，生成環化產物 **17**。共 7 個例子，產率為 62–95% 且有大於 20:1 的非鏡像異構物比例。(圖 2-5)。^[5]

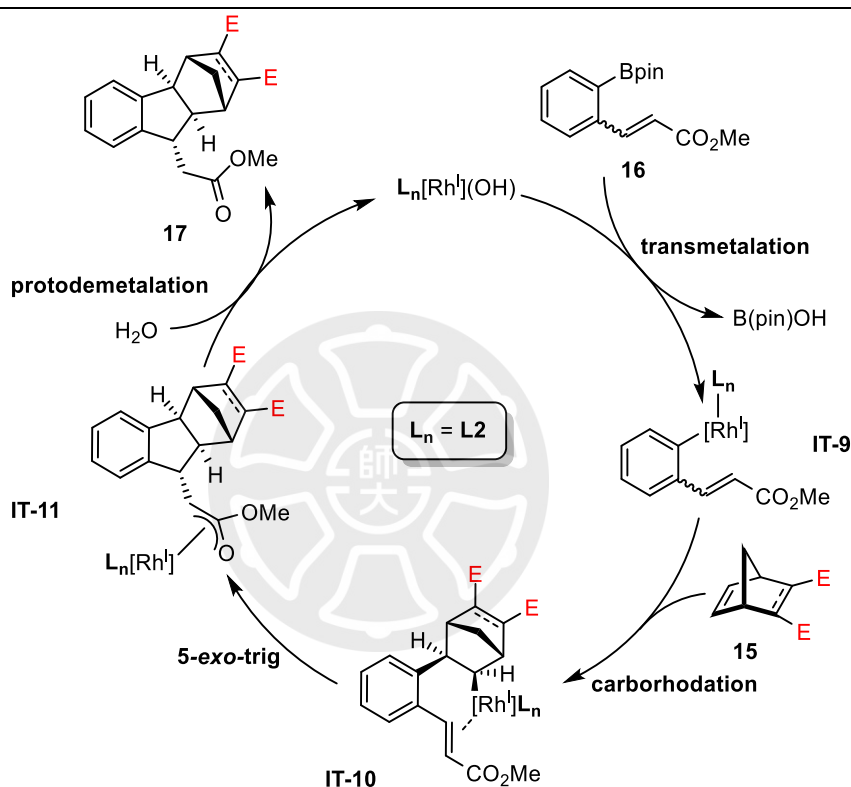
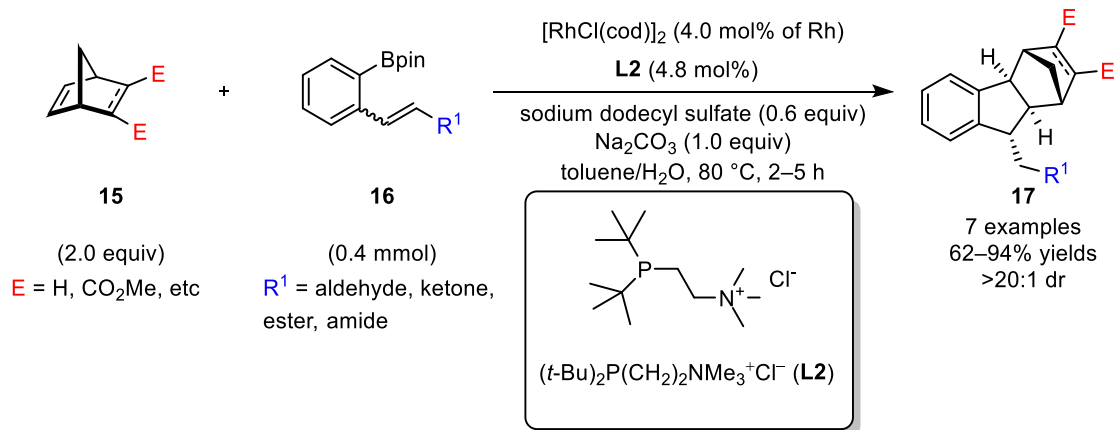


圖 2-5 Lautens 教授的研究

Lautens 教授又於 2009 年使用具有 α, β -不飽和酯基取代的雜環芳基硼酯 **19** 作為起始物，經一價銦金屬前催化劑(precatalyst)與水溶性含磷配基形成的銦金屬催化劑，降冰片烯衍生物 **18** 進行合環反應，最終得到環化產物 **20**，共 10 個例子，且產率為 22–98%，於此反應中，即便化合物 **19** 的結構裡含有可作為離去基的雜原子，反應仍傾向於生成合環的產物 (圖 2-6)。^[6]

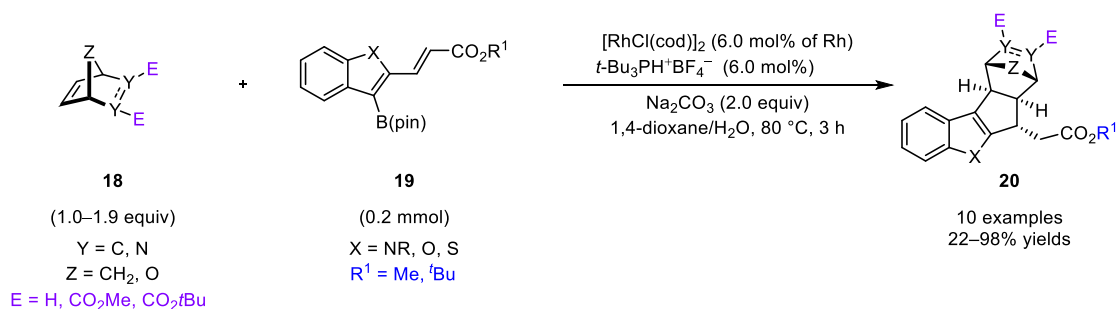
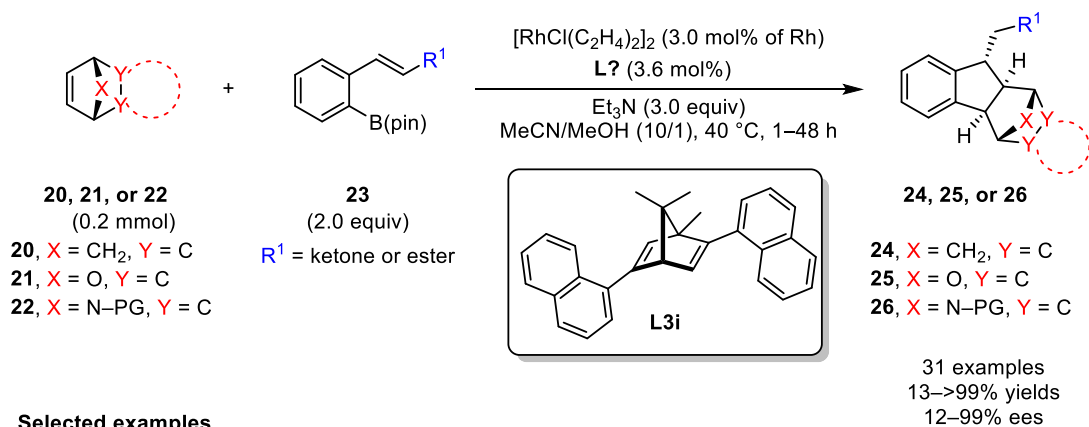
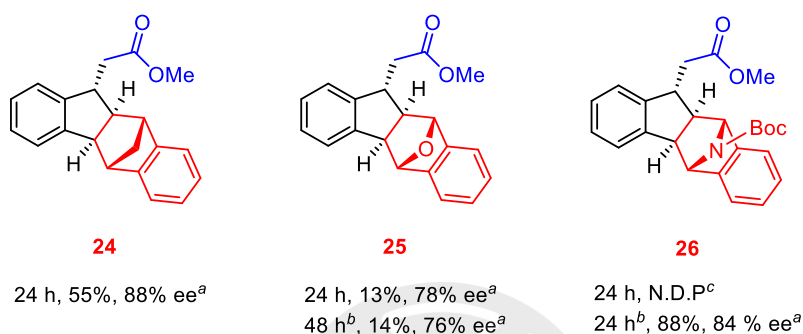


圖 2-6 Lautens 教授雜環芳基硼酯催化

本實驗室的郭瑀潔同學於 2022 年，發表以一價銨金屬前催化劑與掌性雙環 [2.2.1]雙烯配基 **L3i** 形成錯合物，催化 α,β -不飽和酯基取代的芳基硼酯 **23** 與不同的降冰片烯衍生物 **20–22** 進行不對稱串聯合環反應，生成合環產物 **24–26**，共 31 個例子、產率為 13–99%，鏡像超越值為 12–99% ees。在嘗試以含有雜原子且容易進行開環的一類降冰片烯衍生物 **20–22** 為起始物進行反應，僅得到合環的產物 (**24**、**25**、**26**, 13–88% yields, 78–88% ees)，並無任何開環產物的生成。氮上保護基為第三丁氧羰基(Boc)的 1,4-dihydro-1,4-iminonaphthalene 在最佳反應條件下反應並不會進行，嘗試將溫度提升至 60 °C 後，經 24 小時可得到合環產物 **26**，產率為 88%，鏡像超越值為 84%。由化合物 **24**、**25** 及 **26** 三者結果進行比較，可以看到將橋環化合物架橋上的碳原子替換為雜原子時，反應性會大幅下降，甚至不會進行反應，必須將溫度提高才得以增加其反應性。推測是因為雜原子的孤對電子可能會與銨金屬進行配位，進而導致加成反應不易進行 (圖 2-7)。



Selected examples



^a Determined by HPLC analysis on a chiral column. ^b Reaction temperature is 60 °C. ^cN.D.P. = No Desired Product.

圖 2-7 郭瑤潔同學研究成果

由以上文獻回顧可知，化學家在以降冰片烯衍生物為起始物進行不對稱合環反應的探討中已取得不錯的成果，而氮上保護基為第三丁氧羰基(Boc)的 7-氮苯駢降冰片烯化合物的雙鍵進行串聯合環反應的研究則相對較少。因此，本論文欲延續郭瑤潔同學的研究成果，以一價銨金屬前催化劑與掌性雙環[2.2.1]雙烯配基 **L3b** 形成之錯合物，催化芳基硼酯 **23** 與氮上保護基為第三丁氧羰基(Boc)的 7-氮苯駢降冰片烯化合物 **26** 進行不對稱串聯合環反應，形成合環產物 **27**，並且進一步探討其反應性 (圖 2-8)。

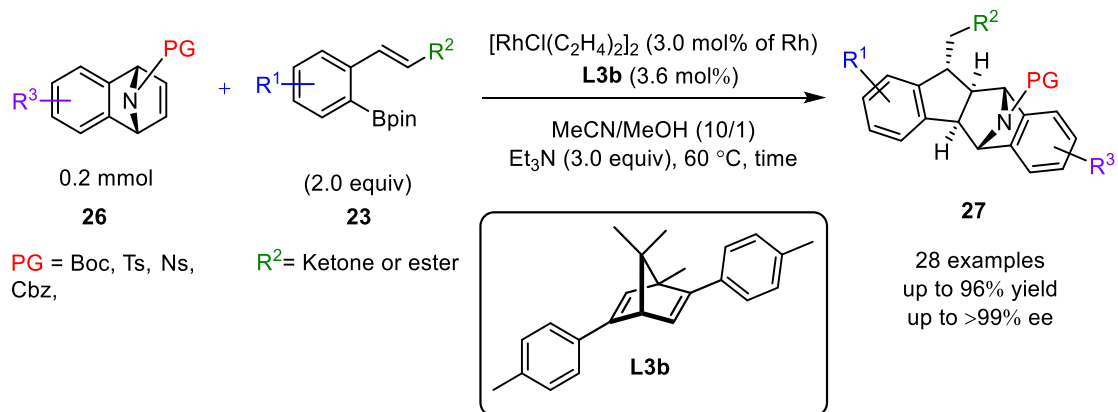


圖 2-8 本論文研究目標



第三章 掌性雙環[2.2.1]雙烯配體的合成

本實驗室於 2011 年發表，由高光學純度起始物:左旋醋酸冰片酯(L-bornyl acetate, **27**)，經由(圖 3-1)之步驟，製備出一系列在 2、5 號位具有不同芳香基團取代的掌性雙環[2.2.1]雙烯配基 **L3**。如(圖 三-1)所示，5-ketobornyl acetate **28**，可由左旋醋酸冰片酯 **27** 在立即生成(*in situ*)之四氧化鈦(ruthenium tetraoxide, RuO₄)的催化下，與加入的過一硫酸氫鉀複合鹽(Oxone)進行氧化反應得到。對 5-ketobornyl acetate **28** 進行皂化反應(saponification reaction)，在不經純化下，將所生成之酮醇化合物 **29** 的粗產物溶於二氯甲烷中，與氯鉻酸吡啶鹽(pyridinium chlorochromate, PCC)進行氧化反應，所生成之雙酮化合物 **30**，在經由純化後，得到三步之總產率為 14%。將雙酮化合物 **30** 與 Comins' 試劑於真空下攪拌至混溶後，將兩者的混合物溶於四氫呋喃，並於-78 °C 下緩慢滴入 KHMDS (potassium bis(trimethylsilyl) amide)，反應 2 小時後，生成雙三氟甲磺酸酯 **31**，產率為 65%。之後於鈀金屬的催化下，催化雙三氟甲磺酸酯 **75** 與不同取代的芳香基硼酸進行鈴木-宮浦反應(Suzuki-Miyaura reaction)，生成 2、5 號位具有不同芳香基團取代的掌性雙環[2.2.1]雙烯配基 **L3a-L3j**，產率為 72%–98%。^[7]

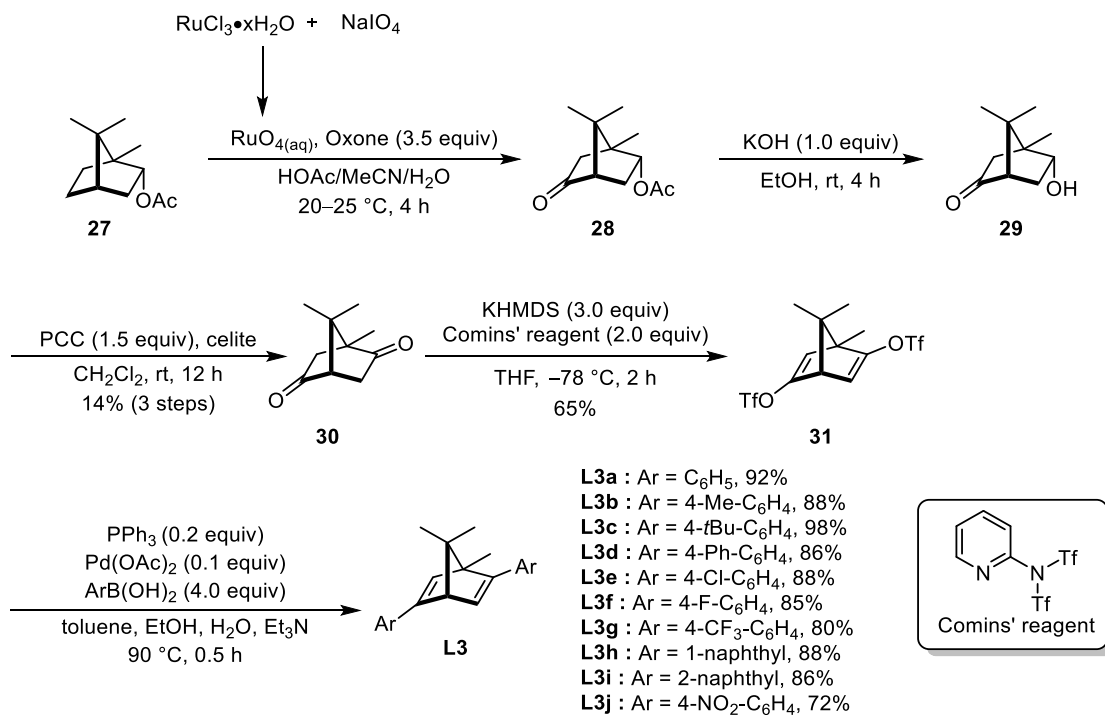


圖 3-1 本實驗室製備掌性雙環[2.2.1]雙烯配基 **L3** 之合成路徑



第四章 第一部分實驗結果與討論

本論文欲探討以氮上有保護基的 7-氮苯駢降冰片烯化合物 **26a** 與芳基硼酯 **23a** 進行不對稱串聯合環反應之反應性。依據本實驗室郭瑀潔同學的實驗結果，以 1.5 mol% 的一價銠金屬二聚體 $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3 mol% of Rh) 與 3.6 mol% 的掌性雙環[2.2.1]雙烯配基 **L3i** 所形成的為催化劑，催化 0.2 毫莫耳的 7-氮苯駢降冰片烯化合物 **26a** 與 2.0 當量的芳基硼酯 **23a**，在加入 3.0 當量的三乙胺為鹼性添加劑、並以乙腈與甲醇比例為 10:1 的混合溶劑條件下，於反應溫度 40 °C 進行不對稱串聯合環反應。使用薄層層析術(thin-layer chromatography, TLC)追蹤反應，以氮上保護基為第三丁氧羰基(Boc)的 7-氮苯駢降冰片烯化合物 **26a** 或芳基硼酯 **23a** 其一完全反應時為反應終點，生成合環產物 **27a** (88% yield, 84% ee) (圖 4-1)。以此作為基礎，後續將對溶劑、配基以及溫度，分別進行探討，期望優化出此反應之最佳化條件。

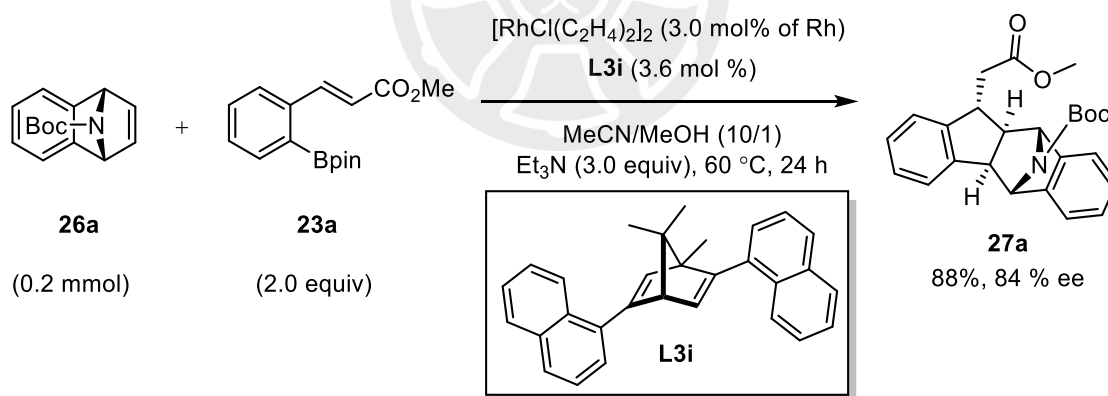
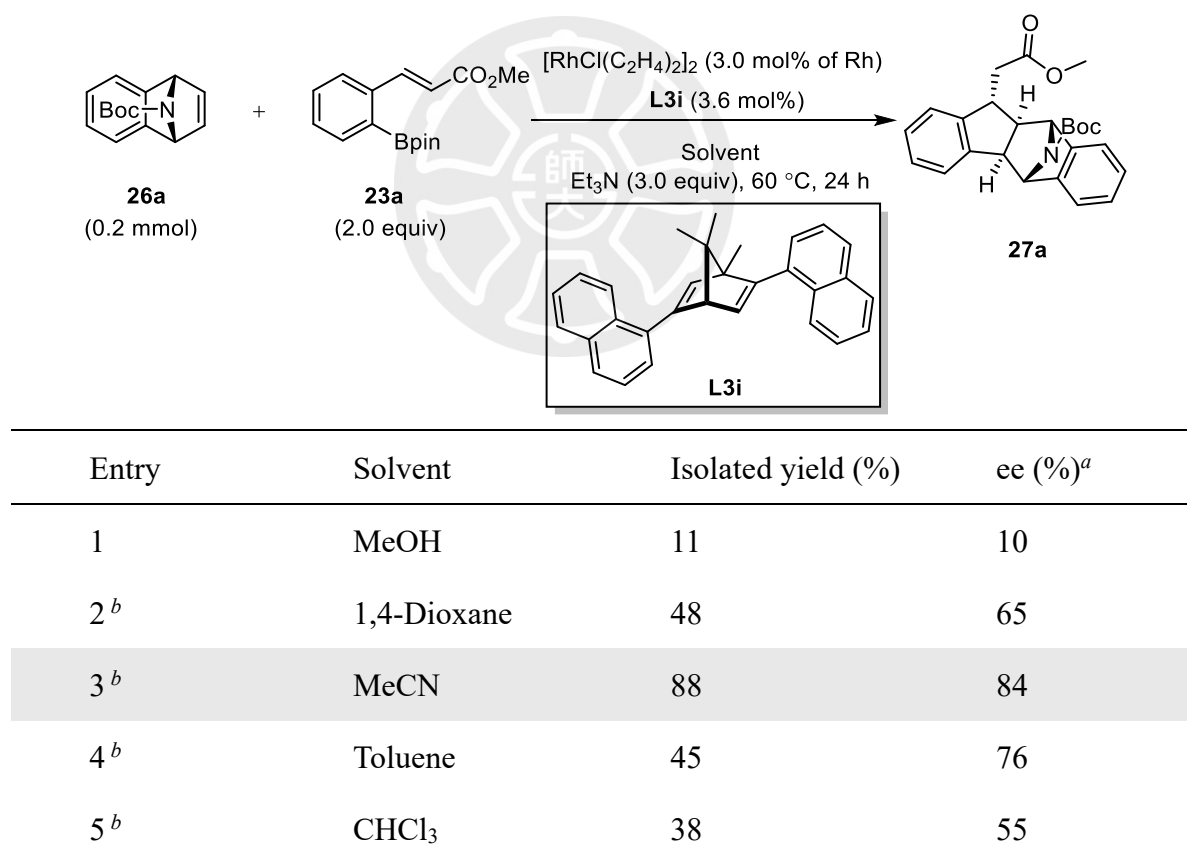


圖 4-1 郭瑀潔同學研究成果

一、溶劑效應

溶劑的溶解度、極性、質子性以及氫鍵效應等皆會對反應有所影響。因此，我們嘗試使用不同性質之溶劑進行優化。當極性質子溶劑甲醇做為溶劑時只得到 11% 合環產物 **27a** 並且鏡像超越值為 10% (**Entry 1**)，並觀察到生成大量加成產物，推測當反應進行時甲醇溶劑可當作質子來源，會造成反應快速質子化並止步於最初加成反應，而只有少量的中間體進行合環反應，後續四種極性由高至低的非質子溶劑，添加甲醇作為質子添加劑，比例為 10:1 的條件進行反應(**Entry 2-5**)，可以看到鏡像超越值以乙腈(MeCN)表現較好(**Entry 3**, 84% ee)，最後選用了乙腈作為最佳化溶劑進行後續實驗探討。(如 表 1)

表 1 溶劑效應



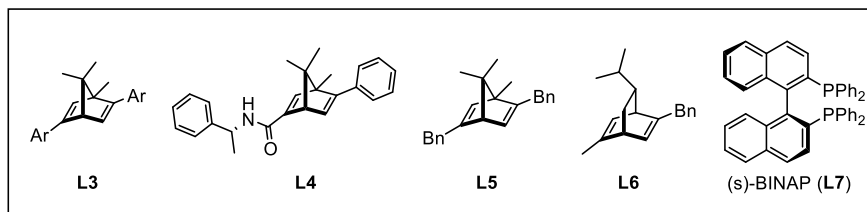
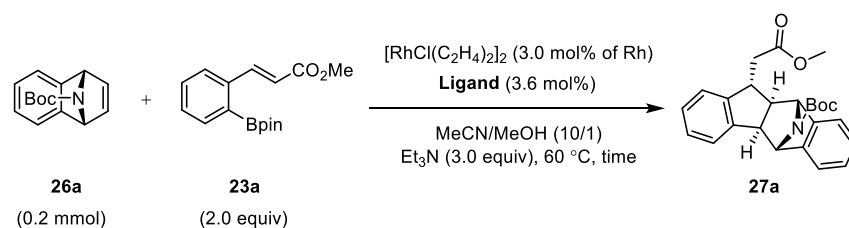
^a Determined by HPLC analysis on a Chiralpak IA column. ^b MeOH was added as proton source (solvent/MeOH = 10/1).

二、配基效應

本節探討以一價銻金屬與不同掌性雙烯配基形成的催化劑，催化不對稱環化反應生成產物的反應性與鏡像選擇性之差異。

以下十種於 2,5 號位具有不同芳香基取代的掌性雙環[2.2.1]雙烯配基 **L3a-L3j**、掌性雙環[2.2.1]雙烯醯胺類配基 **L4**，以及其他三種易於製備或市售可得的掌性配基 **L5**、**L6** 及 **L7** 進行不對稱合環反應的反應性探討，結果如(表 2)所述。在先前本實驗室的郭瑀潔同學的反應中，使用苯環取代的配體 **L3i** 反應 24 小時後，生成環化產物 **27a** 的產率為 88% (鏡像超越值為 84%)，(如圖 4-1)。經過相同樣條件嘗試後，產率提升至 94% (鏡像超越值為 99%)，當配體上的芳香取代具有較大立體障礙((**L3c**, **L3d**, **L3h**, **L3i**)，除了使用配體 **L3h** 時，環化產物 **27a** 產率和鏡像超越值皆有良好表現(Entry 3-4, 8-9, 87–96% yield, 87-99% ee)。當配體的苯環上對位具有拉電子基時(**L3e-3g**, **L3j**)，產率 80–95%，鏡像超越值皆維持在 80–92%。若使用掌性雙環[2.2.1]雙烯醯胺配體(**L4**)進行反應，生成環化產物 **27a** 的產率和鏡像超越值(Entry 11, 89% yield, 96% ee)。而以 2,5 號位具有苄基取代的掌性雙環[2.2.1]雙烯配體 **L5** 進行反應，產率和鏡像超越值(Entry 12, 71% yield, 92% ee)，嘗試以 2,5 號位分別具有甲基和苄基取代的掌性雙環[2.2.2]雙烯配體 **L6** 行反應，產率和鏡像超越值(Entry 13, 73% yield, 58% ee)。將掌性雙烯配體改為掌性雙膦配體(*S*)-BINAP (**L7**)進行反應，經過 24 小時後，幾乎沒有目標環化產物 **27a** 的生成，觀察粗產物 ¹H NMR 光譜中發現加成產物。綜合上述，使用配體 **L3b** 進行反應時環化產物 **27a** 的 ¹H NMR 產率和鏡像超越值提升，最後選用 **L3b** 作為反應的最佳配體。

表 2 配基效應



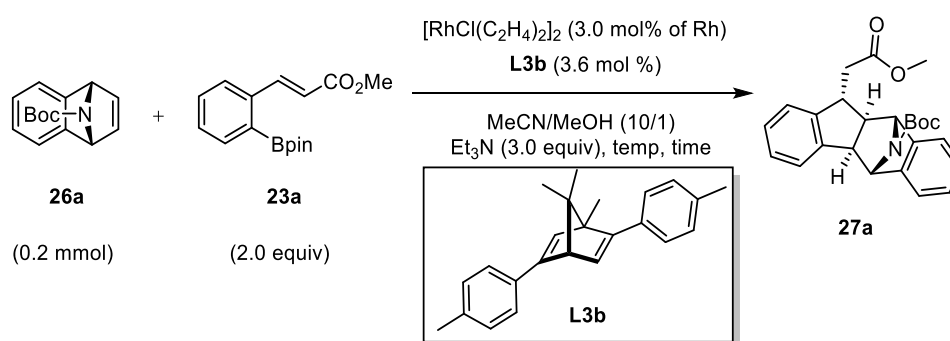
Entry	Ligand	Ar	Yield (%) ^a	ee (%) ^b
1	L3a	C ₆ H ₅	91	90
2	L3b	4-Me-C ₆ H ₄	95	99
3	L3c	4- <i>t</i> -Bu-C ₆ H ₄	87	99
4	L3d	4-biphenyl	87	96
5	L3e	4-Cl-C ₆ H ₄	88	92
6	L3f	4-F-C ₆ H ₄	95	84
7	L3g	4-CF ₃ -C ₆ H ₄	96	80
8	L3h	1-naphthyl	83	87
9	L3i	2-naphthyl	94	99
10	L3j	4-NO ₂ -C ₆ H ₄	80	89
11	L4	-	89	96
12	L5	-	71	92
13	L6	-	73	58
14	L7	-	0	N.A. ^c

^a Isolated yield. ^b Determined by HPLC analysis on a Chiralpak IA column. ^c N.A. = Not Available.

三、溫度效應

篩選出適當的配基後，緊接著進行反應溫度的優化。依據(表 3)的結果，反應溫度下降使合環反應速率減緩，提升反應溫度會使合環產物之鏡像選擇性降低。

表 3 溫度效應

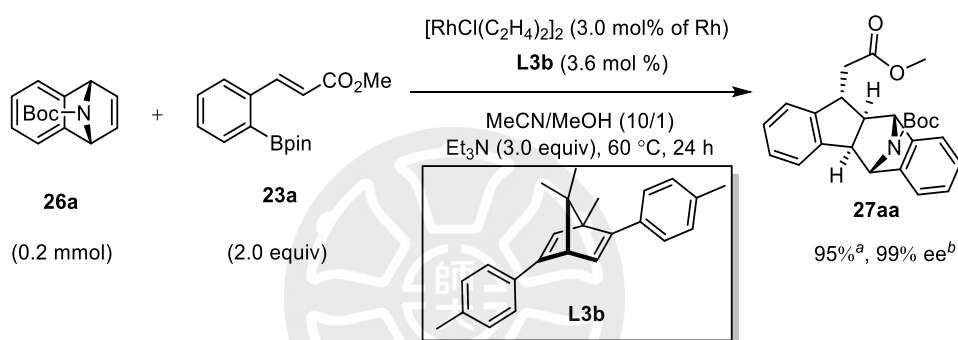


Entry	Temp(°C)	Time (h)	Yield (%)	ee (%) ^a
1	50	36	90	99
2	60	24	94	99
3	80	18	91	89

^a Isolated yield. ^b The ee was determined by HPLC analysis on a chiral column.

四、最優化條件

經過條件優化後，最佳反應的條件為：以 1.5 mol% 的一價銠金屬二聚體 $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.0 mol% of Rh) 與 3.6 mol% 的掌性雙環[2.2.1]雙烯配基 **L3b** 所形成的錯合物為催化劑，催化 0.2 毫莫耳的 7-氯苯駢降冰片烯化合物 **26a** 與 2.0 當量的芳基硼酯 **23a**，在加入 3.0 當量的三乙胺為鹼性添加劑、並以乙腈與甲醇比例為 10:1 的條件下，於反應溫度 60°C 催化芳基硼酯 **23a** 與氮上有保護基的 1,4-亞氮-1,4-二氫茶 **26a** 進行不對稱合環反應，得到具掌性環化產物 **27aa**，可以得到優良的反應性及鏡像選擇性(95% yield, 99% ee) (圖 4-2)。

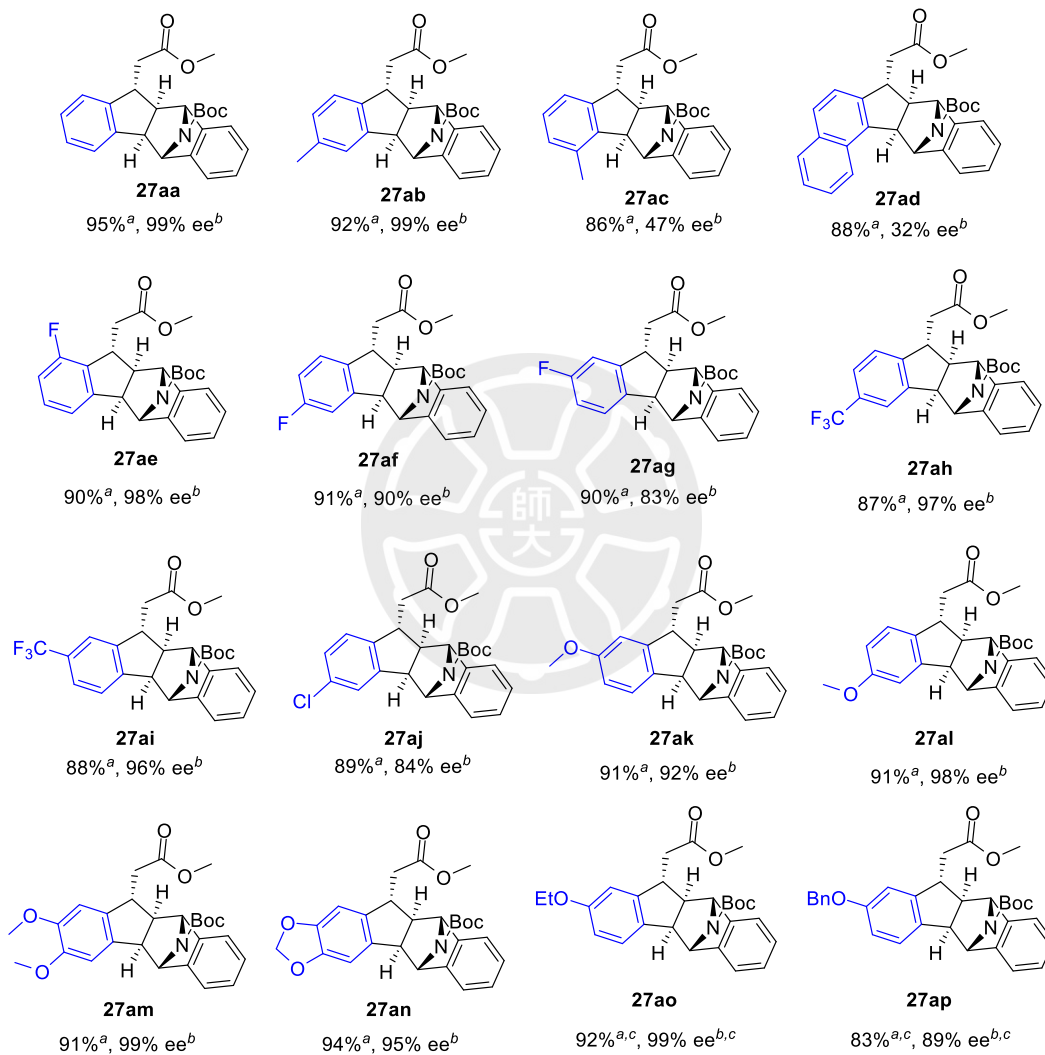
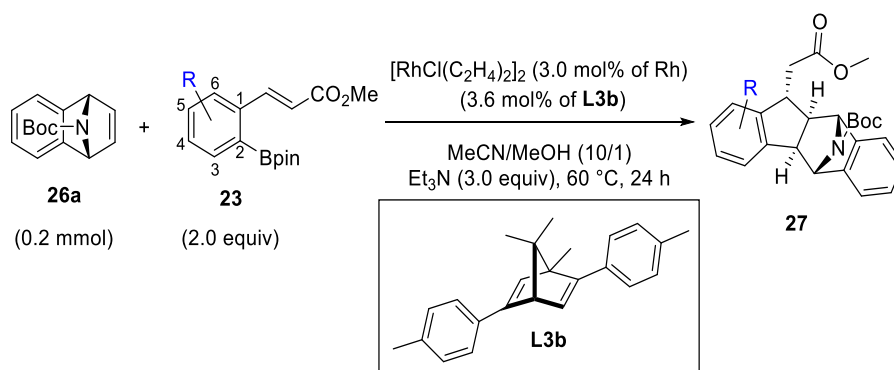


^a Isolated yield. ^b The ee was determined by HPLC analysis on a chiral column.

圖 4-2 優化條件

五、不同芳基硼酯作為親核試劑之反應性探討

接下來使用苯環上具有不同取代基的芳基硼酯 **23** 與起始物 **26a** 進行不對稱合環反應的探討，並將結果與苯環上未接有任何取代基的環化產物 **27aa** (95% yield, 99% ee) 進行比較(圖 4-3)。由實驗結果發現，若是位於苯環的 4 號及 5 號接上取代基 (**27ab**, **27af-27an**)，則除了 (**27ag**, 90% yield, 83% ee、**27aj**, 89% yield, 84% ee) 鏡像超越值略微下降，皆可維持良好的產率(**27ab**, **27af-27an**, 83-94% yields)，並且都有良好的鏡像超越值(90-99% ees)。在 α,β -不飽和甲酯的鄰位接上取代基，可維持良好的產率及鏡像超越值(**27ae**, 90% yield, 98% ees)。而(**27ao**, **27ap**)則需提升反應溫度至 80 度才會獲得合環產物而非加成產物。綜合以上所得反應結果，在 α,β -不飽和甲酯上之芳香環取代基推拉電子效應具有一定影響因素。另外，若在硼酯官能團的鄰位接上取代基，可觀察到產率降低並且鏡像超越值下降(**27ac**, 86% yield, 47% ee、**27ad**, 88% yield, 32% ee)，其 3 號位置靠近進行轉移金屬反應的反應中心—硼酯，除了推拉電子效應的影響外，取代基所造成的立體效應也是影響的因素，其所造成的立體效應亦使得鄰近的硼酯難以和配基極大的銦金屬催化劑接近。



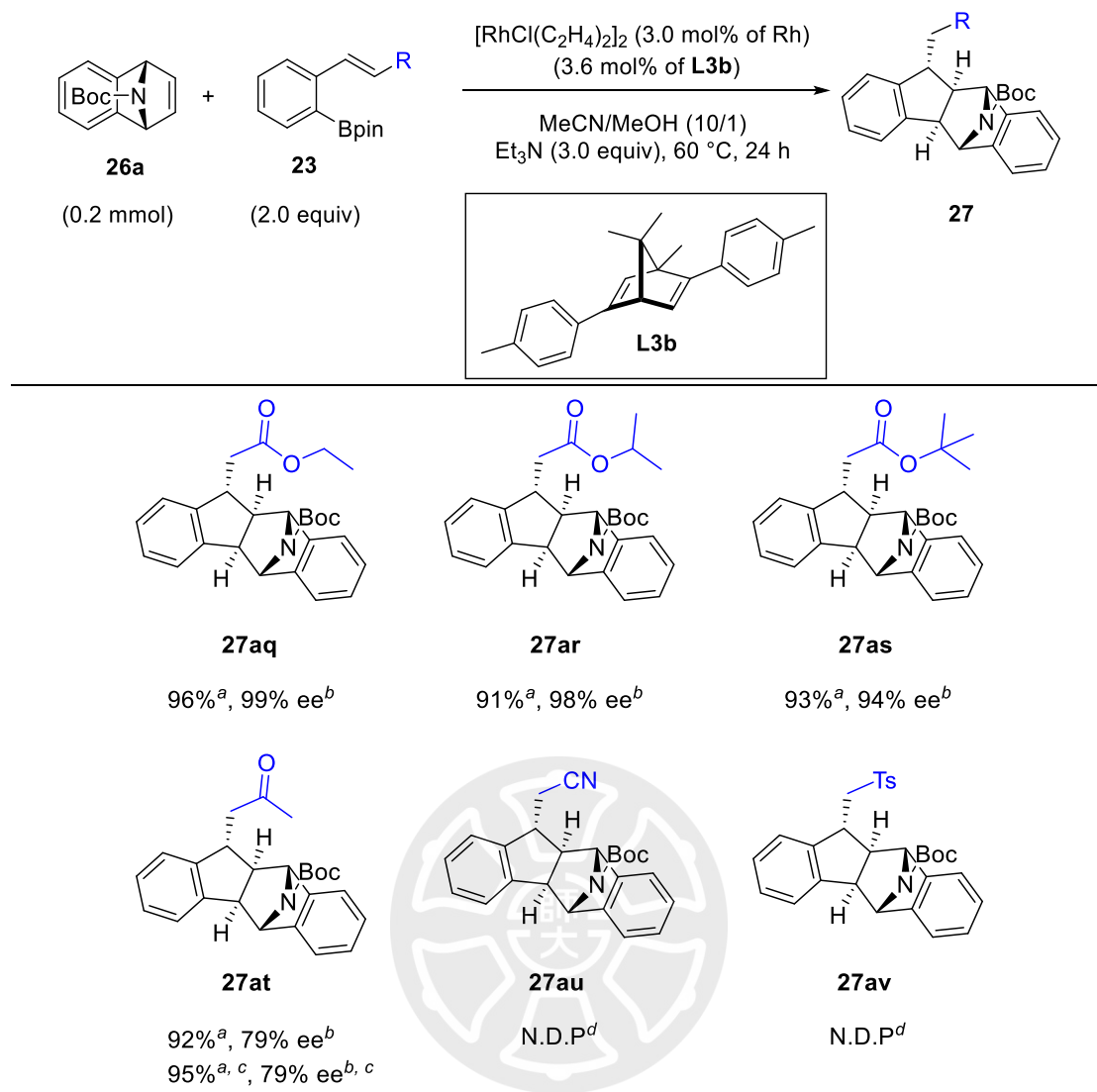
^a Isolated yield. ^b The ee value were determined by HPLC analysis on a chiral column. ^c 80 °C.

圖 4-3 不同芳基硼酯之受質效應

六、不同酯基、酮基或拉電子基的芳基硼酯之反應性探討之反應性探討

在(圖 四-4)的 6 個例子中(**27aq–27as**)，以具有不同酯基、酮基或拉電子基的芳基硼酯 **23**，與起始物 **26a** 進行反應，由合環產物 **27aq–27as** 之產率與鏡像超越值，可發現當酯基為乙酯時(**27aq**)，鏡像超越值 (99% ee)，爾後隨著酯基立體效應之增大，鏡像超越值有下降的趨勢(**27ar**, 98% ee), (**27as**, 94% ee)，並且相較於共軛酯基較缺電子的共軛酮基時鏡像超越值有明顯下降的趨勢(**27at**, 79% ee)，最後嘗試以具有 α,β -不飽和氰基(cyano group)和對甲苯磺醯基(tosyl group)的芳基硼酯，與起始物 **26a** 進行反應，經過 24 小時後，皆觀察到少量加成產物而非合環產物(**27au**，**27av**)。





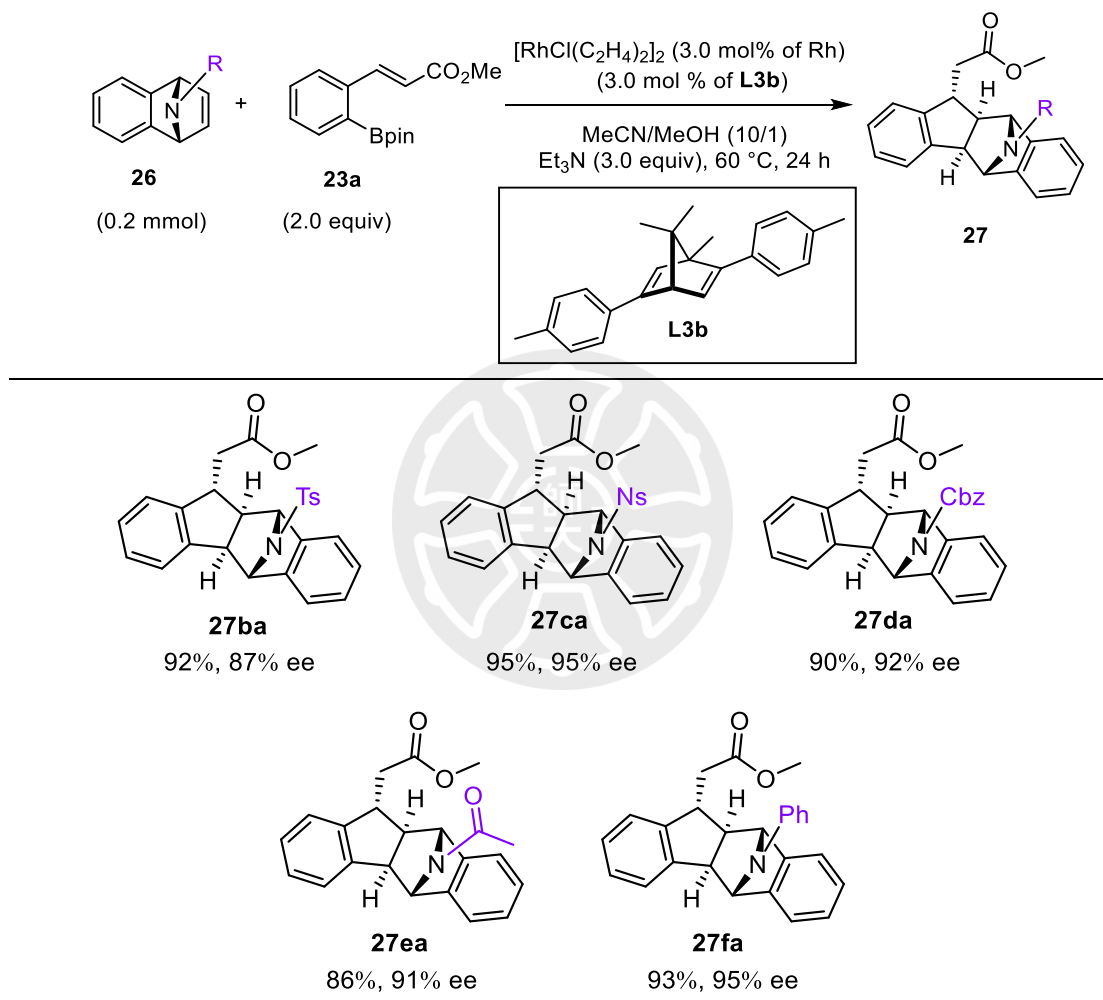
^a Isolated yield. ^b The ee value were determined by HPLC analysis on a chiral column. ^c 50 °C.

^d N.D.P. = No desired product.

圖 4-4 不同酯基、酮基或拉電子基的芳基硼酯之受質效應

七、氮上不同保護基的 7-氮苯駢降冰片烯化合物之反應性探討

在(圖 4-5)的 5 個例子中(27ba–27fa)，以氮上具有不同保護基的起始物 **26**，與芳基硼酯 **23a** 進行反應，發現除了環化產物(27ba)的鏡像超越值(87% ee)略為下降，皆可維持良好的產率(27ba–27fa, 86–95% yields)，並且都有良好的鏡像超越值(91–95% ees)。

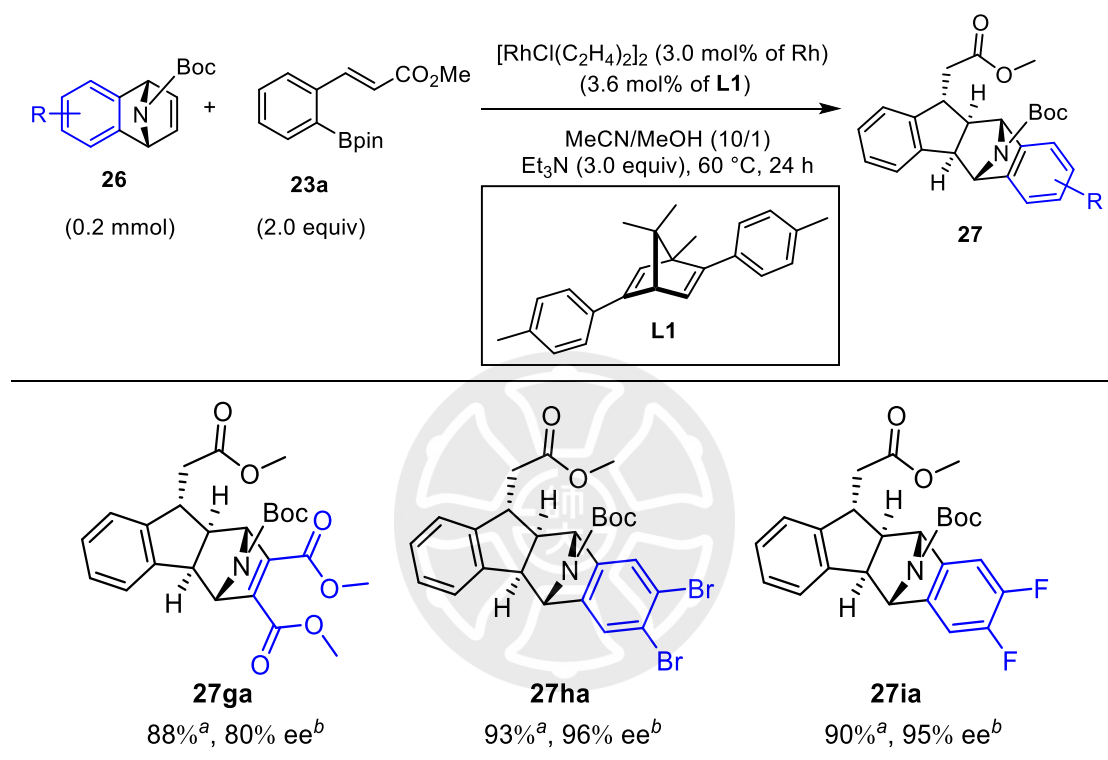


^a Isolated yield. ^b The ee value were determined by HPLC analysis on a chiral column.

圖 4-5 不同氮上保護基受質效應

八、不同結構的降冰片烯衍生物之反應性探討

在(圖 4-6)的 3 個例子中(27ga–27ia)，以不同結構的降冰片烯衍生物的起始物 **26**，與芳基硼酯 **23a** 進行反應，發現產物結構 **27ga** 的取代基拉電子效應具有一定影響因素，使其較不易和富含電子的銨金屬進行反應，造成產率和鏡像超越值有下降的趨勢(88% yield, 80% ee)。



^a Isolated yield. ^b The ee value were determined by HPLC analysis on a chiral column.

圖 4-6 不同結構的降冰片烯衍生物之受質效應

第五章 絕對立體組態與反應機構探討

一、環化產物之絕對立體組態探討

本篇論文係利用一價銠金屬催化，芳基硼酯 **23a** 與氮上有保護基的 7-氮苯駢降冰片烯化合物 **26a** 進行不對稱合環反應，生成環化產物 **27aa**。為了探討其絕對立體組態，使用乙醚對環化產物 **27aa** 進行再結晶，所得晶體經由 X-ray 單晶繞射解析，鑑定其三個連續的立體中心皆為(*R*)-組態。(圖 5-1)。

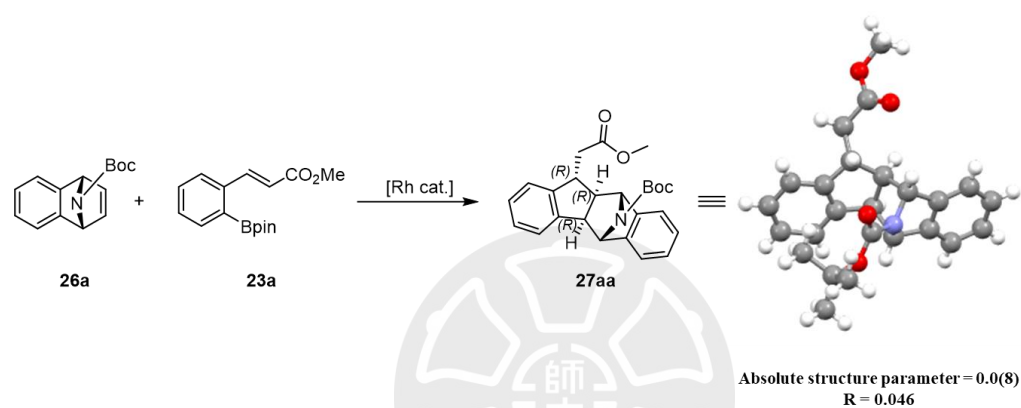


圖 5-1 絕對立體組態

二、反應機構探討

依 X-ray 單晶繞射解析之結果，推測此不對稱串聯合環反應的反應機構，如(圖 5-2)所示。一價銠金屬前催化劑(precatalyst)[RhCl(C₂H₄)₂]₂與掌性雙環[2.2.1]雙烯配基 **L3b** 形成錯合物，錯合物與芳基硼酯 **23a** 進行轉移金屬反應(transmetalation)，生成 arylrhodium 中間體 **IT-12**。中間體 **IT-12** 與氮上有(Boc)保護基的 7-氮苯駢降冰片烯化合物 **26a** 進行配位，形成中間體 **IT-14**。形成的中間體 **IT-14**，arylrhodium 在由 *exo* 位向進行加成時，兩種過渡態 **TS-I** 與 **TS-I'** (圖 5-3) 可分別討論：在過渡態 (一) **TS-I** 當中，arylrhodium 上的芳香基團會經由 *exo*-addition 加成至氮上有(Boc)保護基的 7-氮苯駢降冰片烯化合物的 carbon A，生成中間體 **IT-14** 和 **IT-14'**。此時，氮上有(Boc)保護基的 7-氮苯駢降冰片烯化合物位於較空曠處，無立體效應的影響。在過渡態(二) **TS-I'** 當中，arylrhodium 上的芳香基團會經由 *exo*-addition 加成至氮上有(Boc)保護基的 7-氮苯駢降冰片烯化合物的 carbon B，氮上有(Boc)保護基的 7-氮苯駢降冰片烯化合物上的取代基會與芳基硼酯的酯基之間有立體效應。綜合以上(一)與(二)兩點，過渡態 **TS-I'** 因受到立體效應之影響，在能量上相較於過渡態 **TS-I** 為高，反應傾向經由能量較低的過渡態 **TS-I** 進行，生成中間體 **IT-14** 和 **IT-14'** (圖 5-3)。如(圖 5-4)，形成中間體 **IT-14** 後，鄰位的共軛酯基在由同向進行 1,4-加成時，若由 *re*-face 進行加成， α,β -不飽和酯基會與氮上有(Boc)保護基 7-氮苯駢降冰片烯化合物 **26a** 上的保護基結構有立體阻礙，因此，反應會傾向從 *si*-face 進行加成，生成(圖 5-4)中的中間體 **IT-15**。中間體 **IT-15** 進行水解反應，生成合環產物 **27a**(圖 5-2)。

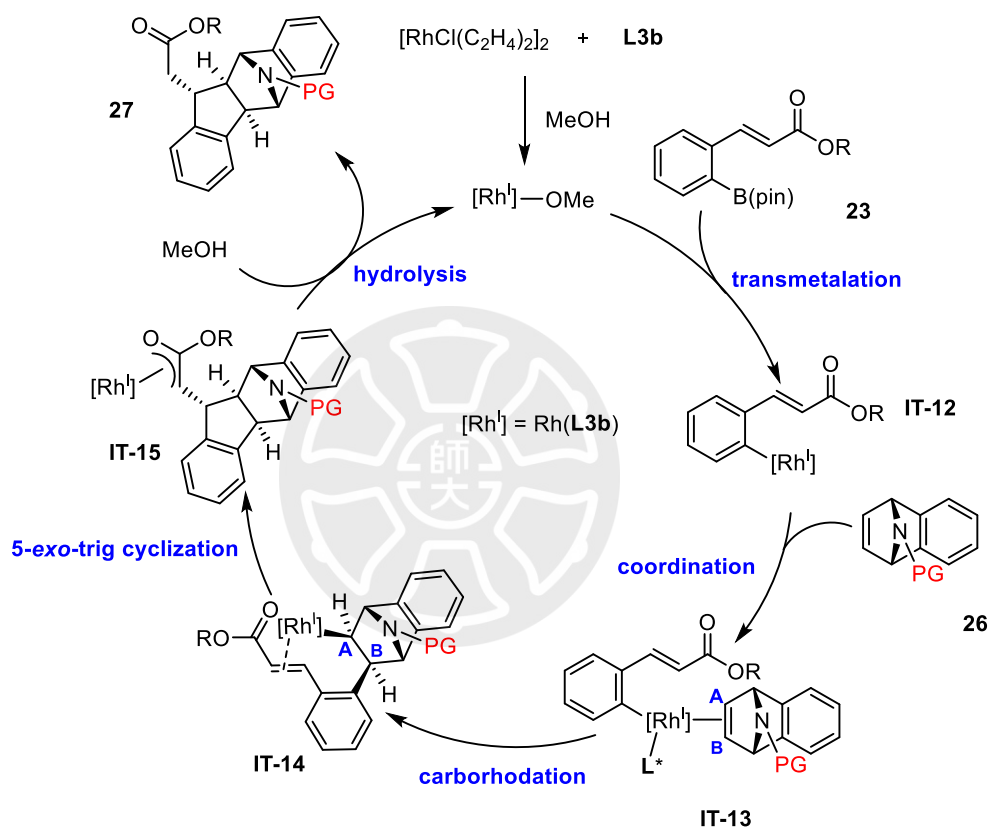
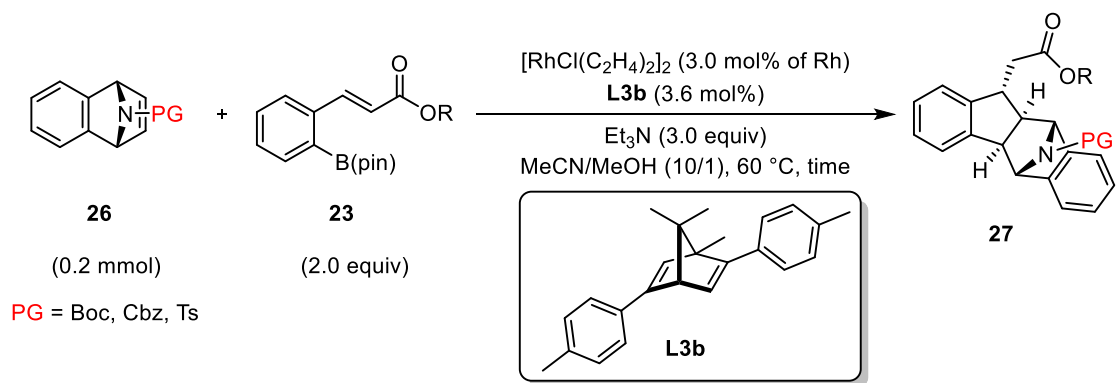


圖 5-2 推測反應機構

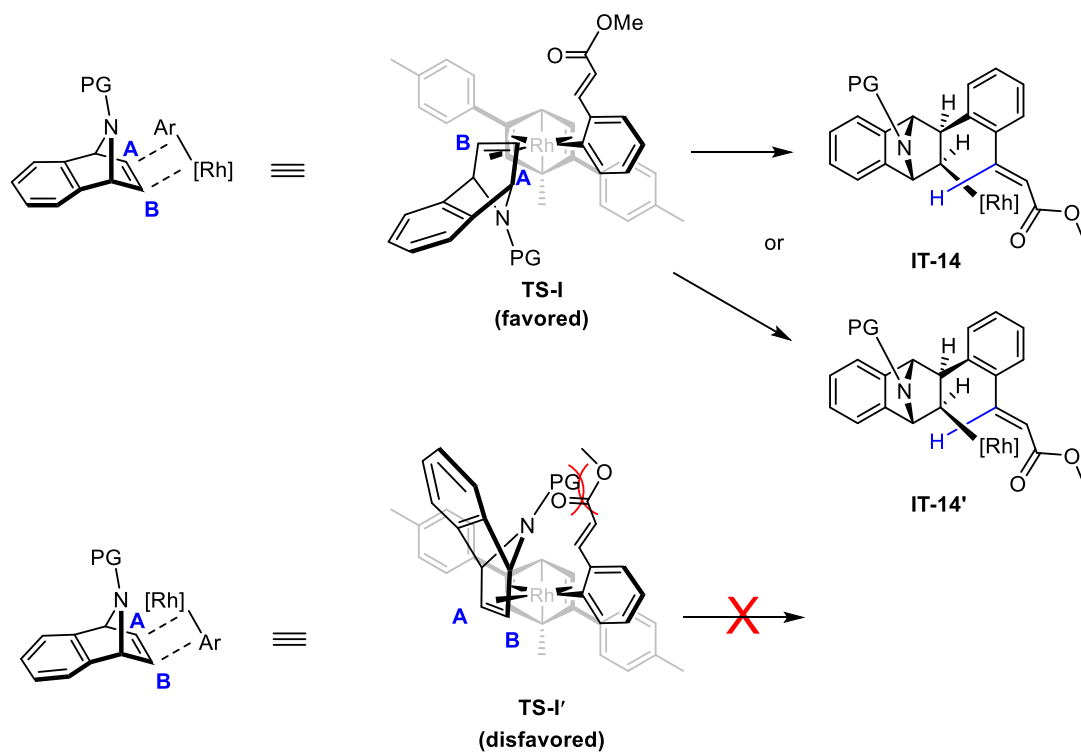


圖 5-3 進行 *exo* 位向加成 TSII 與 TSII' 過度態探討

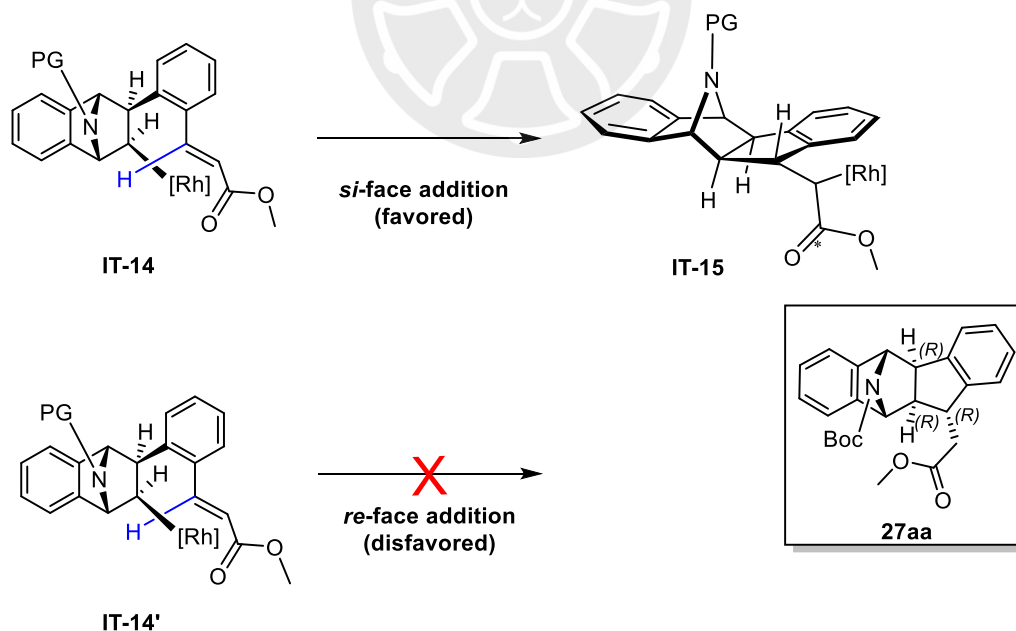
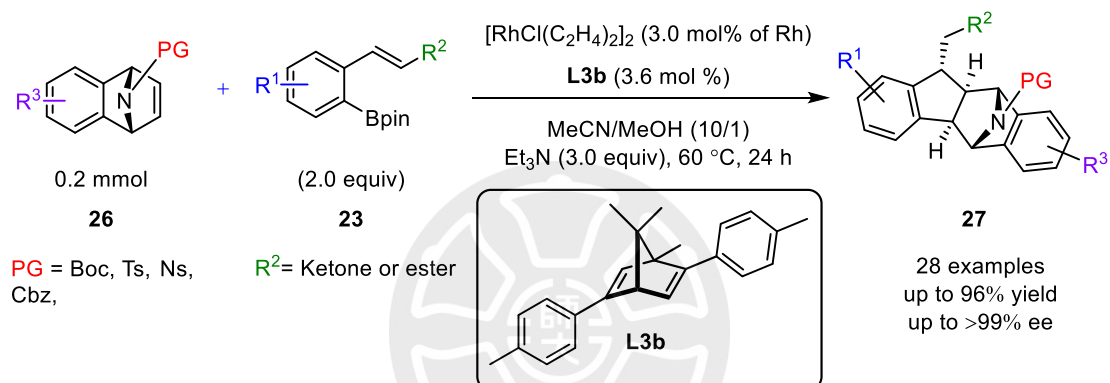


圖 5-4 共軛烯酯進行 1,4-同向加成

第六章 結論

本論文以 1.5 mol% 的一價銑金屬二聚體 $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.0 mol% of Rh) 與 3.6 mol% 的掌性雙環[2.2.1]雙烯配基 **L3b** 形成的催化劑，以 3.0 當量的三乙胺為鹼性添加劑，使用比例為 10:1 的乙腈與甲醇為溶劑，於 60 °C 下催化具有不同取代基的芳基硼酯 **23** 與 7-氮苯駢降冰片烯化合物 **26** 進行不對稱串聯合環反應，所生成之一系列具有莜烷結構的掌性環化產物 **27**，有 28 個例子，最高產率為 96%，以及高達 99% 的鏡像超越值。



第七章 第二部分文獻回顧與研究動機

一、烯炔化合物串聯合環反應

Murakami 教授等人於 2005 年研究一價銻金屬催化劑催化烯炔化合物與芳基硼酸進行串聯合環反應。此反應透過芳基銻試劑(aryl rhodium(I))啟動，經由具位向選擇性的加成(regioselective addition)於起始物 **28** 的三鍵上，形成烯基銻中間體 **IT-15** (alkenyl rhodium intermediate)，再和雙鍵進行 5-*exo-trig* 環化反應並形成五員環中間體 **IT-16**，最後烷基銻錯合物以及甲氧基 (methoxy group) 行 β -消去反應(β -alkoxide elimination)並形成五員環目標產物 **29**，具有 18 個例子，產率最高為 82% (圖 7-1)。^[8]



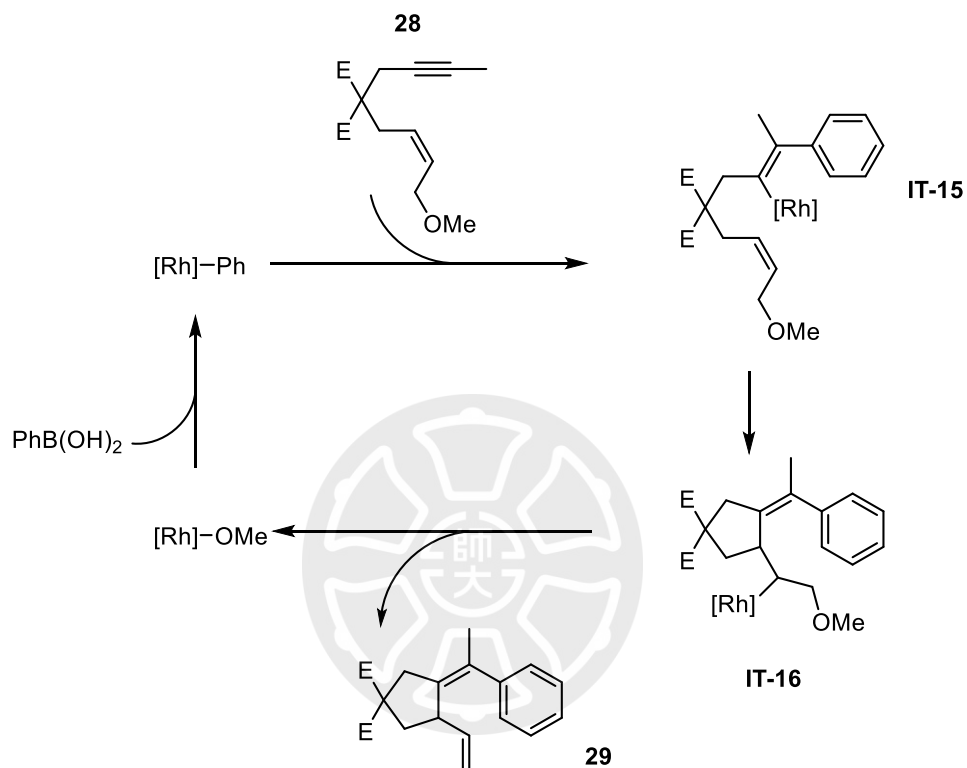
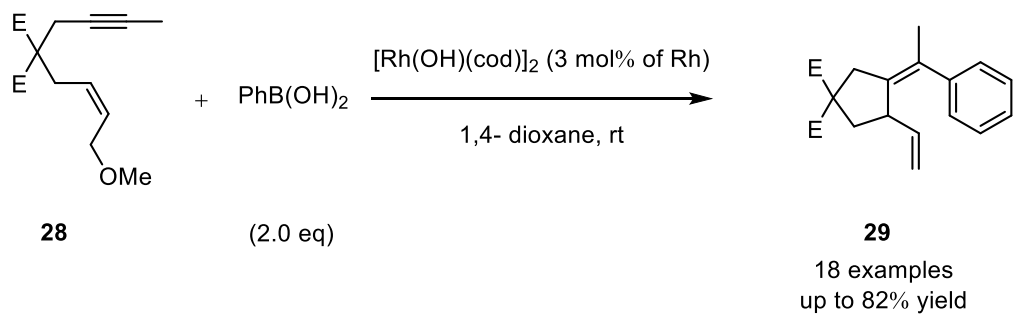


圖 7-1 Murakami 教授利用烯炔化合物 **28** 串聯反應

Hayashi 教授等人於 2005 年利用具有 1,6-烯炔起始物 **30** 以及芳基硼酸試劑和雙鍵進行 5-*exo-trig* 環化反應並最終形成五環中間體 **IT-18**，最後五環中間體 **IT-18** 和水進行質子化反應後獲得目標產物，此研究應用了一價銦金屬以及掌性雙環[2.2.2]雙烯配基 **L8** 進行反應，生成具有高鏡像純度(enantiopurity)產物，反應機構如(圖 7-2)，一價銦金屬催化劑與芳基硼酸試劑進行轉移金屬反應(Transmetalation)反應，形成芳基銦試劑(Aryl rhodium)並選擇性加成於三鍵上形成中間體 **IT-17**，進行 5-*exo-trig* 環化反應並形成五員環中間體 **IT-18**，此時位於甲酯(拉電子基)的 α 位上的銦金屬和水進行質子化反應後，形成五員環產物 **31**，總共具有 11 個例子，產率最高為 83%，鏡像超越值最高為 99% ee，並成為第一個於此反應使用掌性雙烯配基進行不對稱串聯合環反應的例子。^[9]



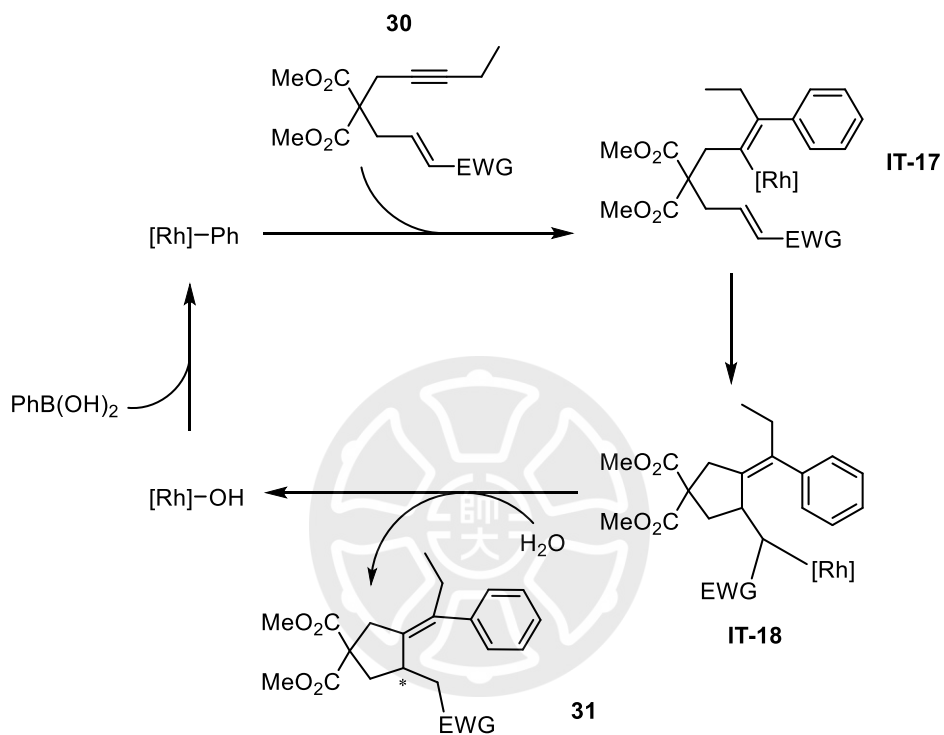
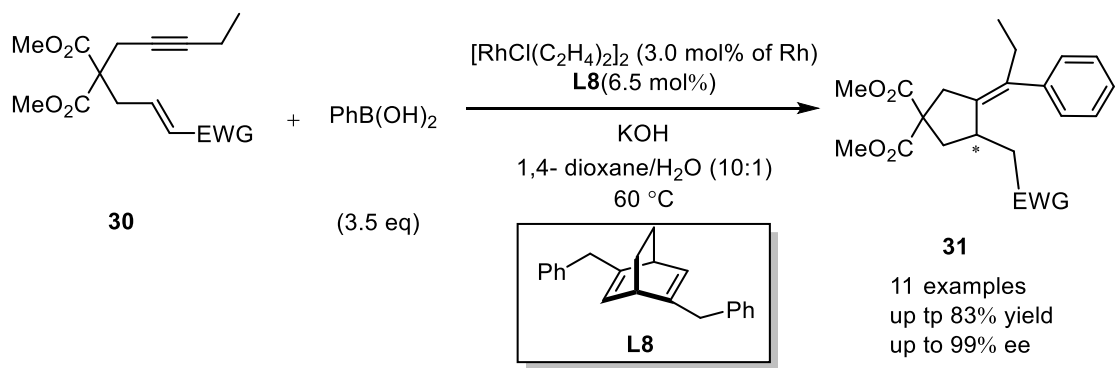


圖 7-2 Hayashi 教授利用掌性雙烯配基進行不對稱串聯合環反應

Darses 教授於 2017 年之發表中，利用三鍵上取代基為苯環的 1,6-烯炔起始物 **32**，在銻金屬結合掌性雙烯配基 **L9** 形成的催化劑的催化下，進行合環反應得到產物 **33**。反應機構為銻金屬錯合物和苯硼酸進行轉移金屬反應後，和起始物 **32** 上的三鍵進行選擇性 1,2-加成反應產生中間體 **IT-19**，再經由 1,4-轉移反應 (1,4-shift) 產生芳基銻中間體 **IT-20**，進行 7-*exo-trig* 的共軛加成反應產生中間體 **IT-21** 後和甲醇進行質子化反應，最終產生目標產物 **33** (圖 7-3)。^[10]



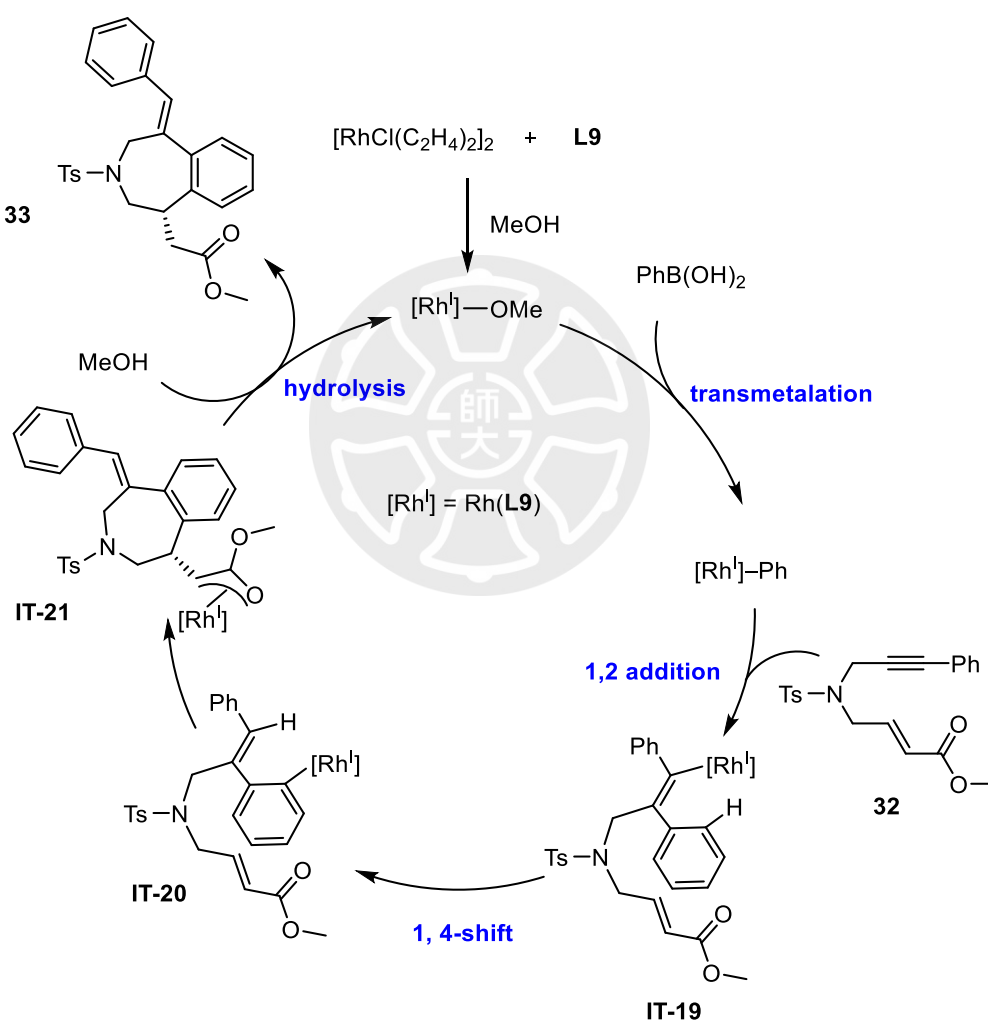
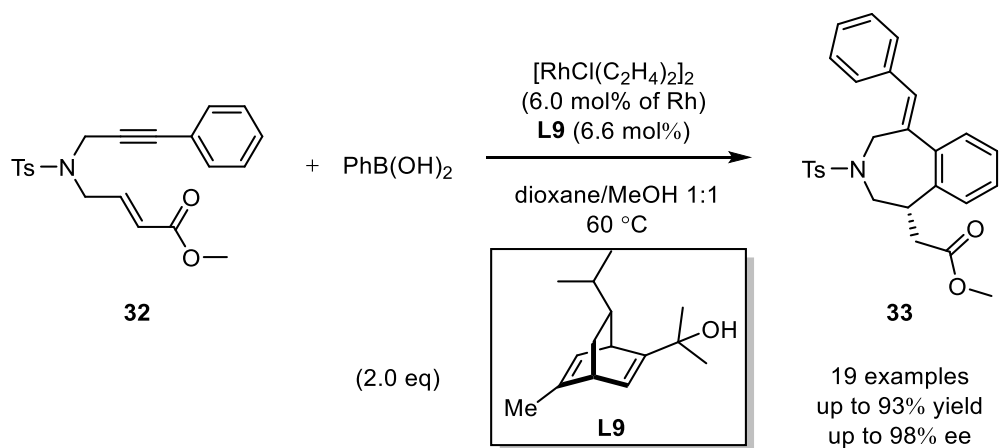


圖 7-3 Darses 教授銦金屬進行不對稱串聯合環反應

Darses 教授於 2019 年發表中，反應機構為起始物 **34** 以及苯硼酸在銦金屬結合掌性雙烯配基 **L10** 所形成之錯合物的催化下進行不對稱還化反應，進行合環得到產物 **35**。銦金屬錯合物和苯硼酸進行轉移金屬反應後，和起始物 **34** 上的三鍵進行選擇性 1,2-加成反應產生中間體 **IT-22**，再經由 1,4-轉移反應(1,4-shift) 產生芳基銦中間體 **IT-23**，再選擇性加成於丙二酸二甲酯上的酯基上，形成銦醇鹽中間體 **IT-24** (rhodium alkoxide)，最後 **IT-24** 進行 β -消去反應，形成目標產物 **35**。
(圖 7-4)^[11]



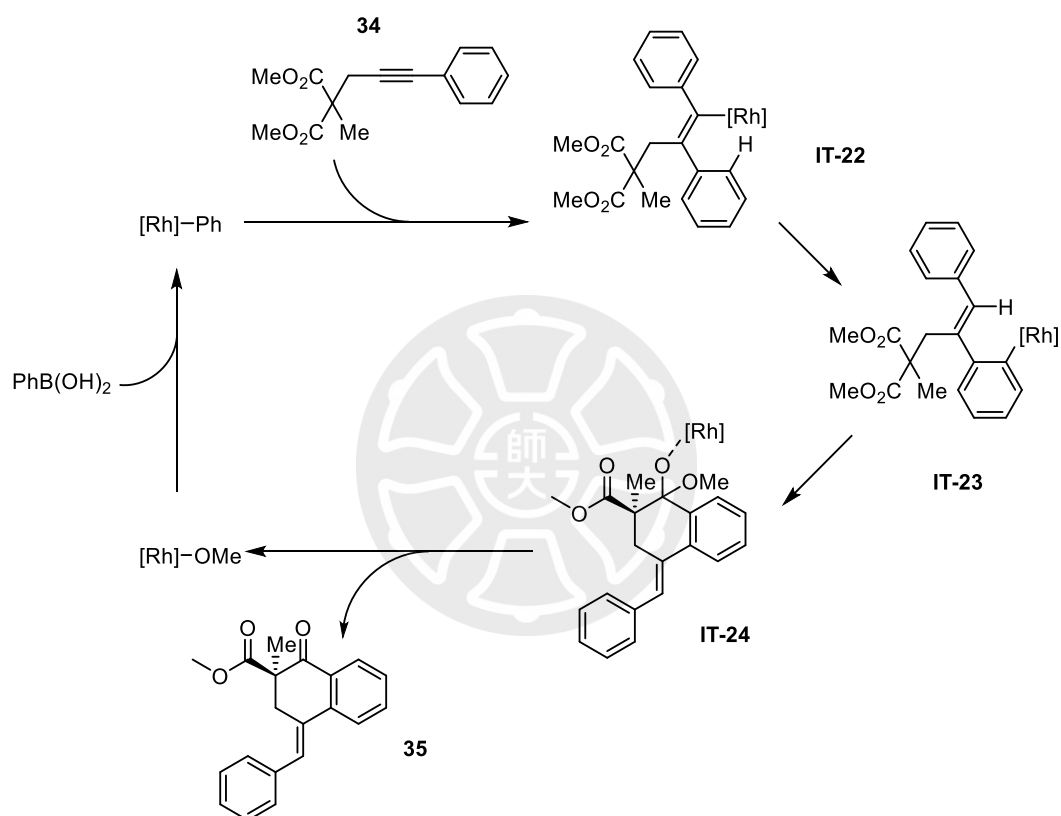
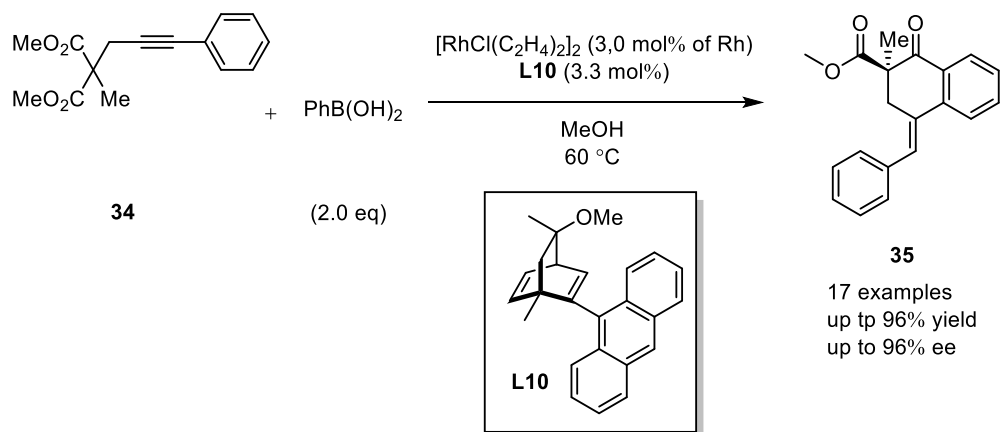
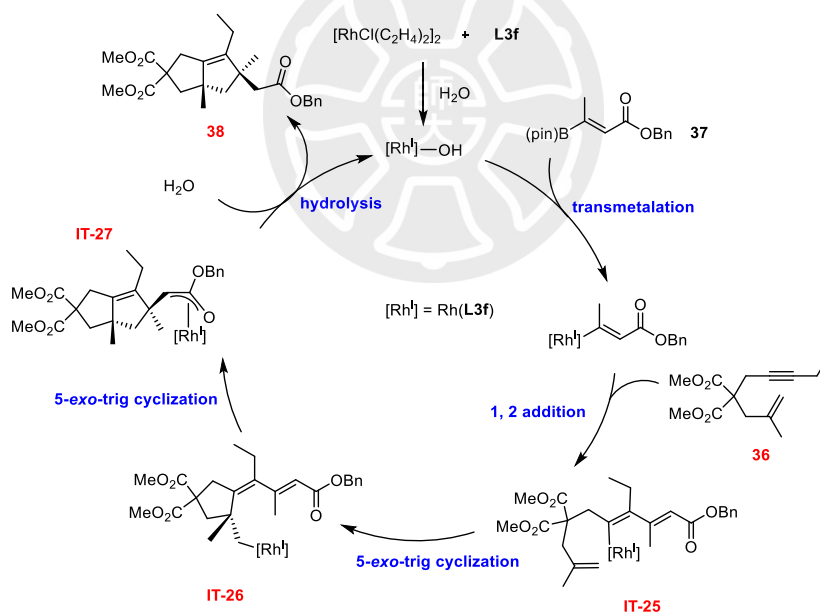
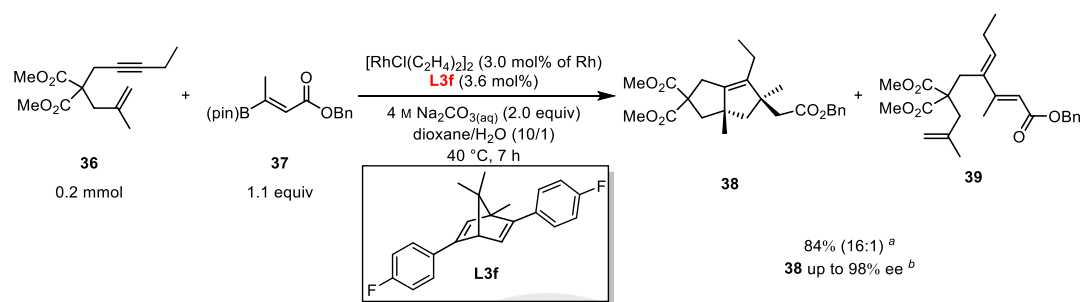


圖 7-4 Darses 教授進行不對稱環化反應的研究

以上兩則文獻，三鍵上的取代基為芳香環時，觀察到銨金屬錯合物和苯硼酸進行轉移金屬反應後，進行區域選擇性(regioselective) 1,2-加成。接著介紹本實驗室博士生楊玉珠利用 β 位硼酯取代的 α,β -不飽和酯 **37** 和具有 1,6-烯炔結構的起始物 **36** 藉由一價銨金屬催化劑的催化下進行雙合環反應，形成具有雙五環結構

的產物 **38** (圖 7-5)，反應機構如下：一價銨金屬與掌性雙環[2.2.1]雙烯配基 **L3f** 所形成的銨金屬錯合物和硼酯化合物 **37** 進行金屬轉移反應後，進行選擇性 1,2-加成於起始物上的三鍵，形成烯基銨(alkenyl rhodium)中間體 **IT-25**，接下來與雙鍵進行 5-*exo-trig* 環化反應後形成了中間體 **IT-26**，再和 α,β -不飽和酯 **37** 的雙鍵進行一次 5-*exo-trig* 環化反應，形成銨烯醇鹽(rhodium enolate)中間體 **IT-27** 後和水進行質子化反應，最後形成了雙五圓環結構產物 **38**。



^a Isolated yield of **38**+**39** and isolated ratio of **38**:**39**. ^b The % ee was determined by HPLC analysis on a chiral stationary phase column.

圖 7-5 博士生楊玉珠研究成果

綜合上述，化學家在以 1,6-烯炔(1,6-enyne)結構的為起始物進行合環反應的探討中已取得不錯的成果，並且觀察到三鍵上的取代基為芳香環時，1,2-加成時銨金屬選擇性加成於靠近苯環的位置，後續進行 1,4-轉移反應(1,4-shift)。而利用 β 位硼酯取代的 α,β -不飽和酯進行雙合環反應的研究則相對較少， α,β -不飽和酯可做為親電基團引導一價銨金屬中間體進行共軛加成，能順利進行二次 5-*exo-trig* 環化反應，也是探討方向之一。因此，本論文欲延續博士生楊玉珠的研究成果，以一價銨金屬催化劑與掌性雙環[2.2.1]雙烯配基 **L1f** 形成之錯合物，在 1,4-dioxane 與水比例為 10:1、碳酸鈉為鹼性添加劑的條件之下，催化 β -位硼酯取代 α,β -不飽和酯 **37** 與 1,6-烯炔結構的起始物 **36** 進行不對稱串聯合環反應，進一步探討其反應性(圖 7-6)。

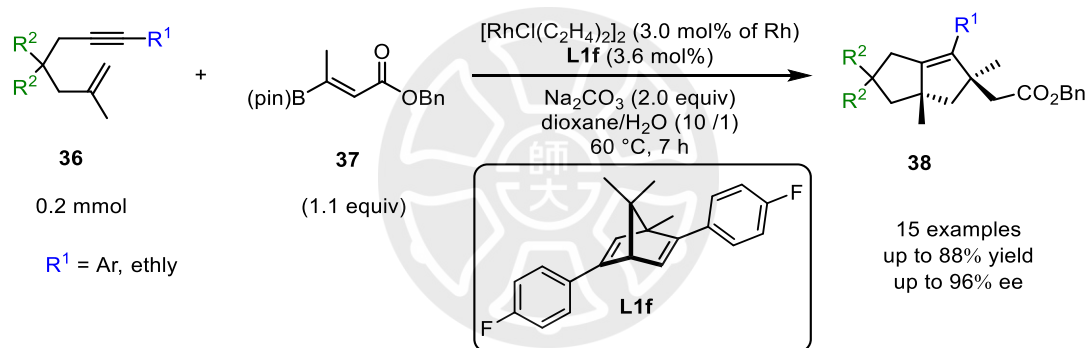
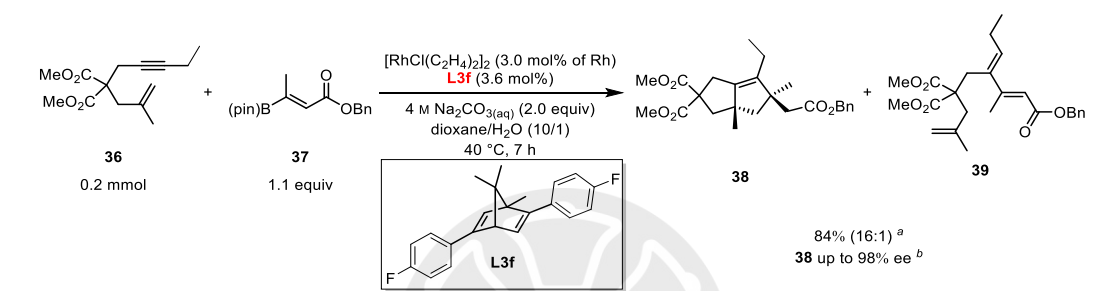


圖 7-6 串聯合環反應

第八章 第二部分實驗結果與討論

如(圖 8-1)當中所敘述，本論文欲探討以 β -位硼酯取代的 α,β -不飽和酯 **37** 與 1,6-烯炔結構的起始物 **36** 進行不對稱串聯合環反應，進一步探討其反應性。依博士生楊玉珠的研究成果，以一價銨金屬催化劑與掌性雙環[2.2.1]雙烯配基 **L3f** 形成之錯合物，在醚類的 1,4-dioxane 與水比例為 10:1、碳酸鈉為鹼性添加劑的條件之下，催化 β 位硼酯取代的 α,β -不飽和酯 **37** 與 1,6-烯炔結構的起始物 **36** 進行不對稱串聯合環反應。



^a Isolated yield of **38+39** and isolated ratio of **38:39**. ^b The % ee was determined by HPLC analysis on a chiral stationary phase column.

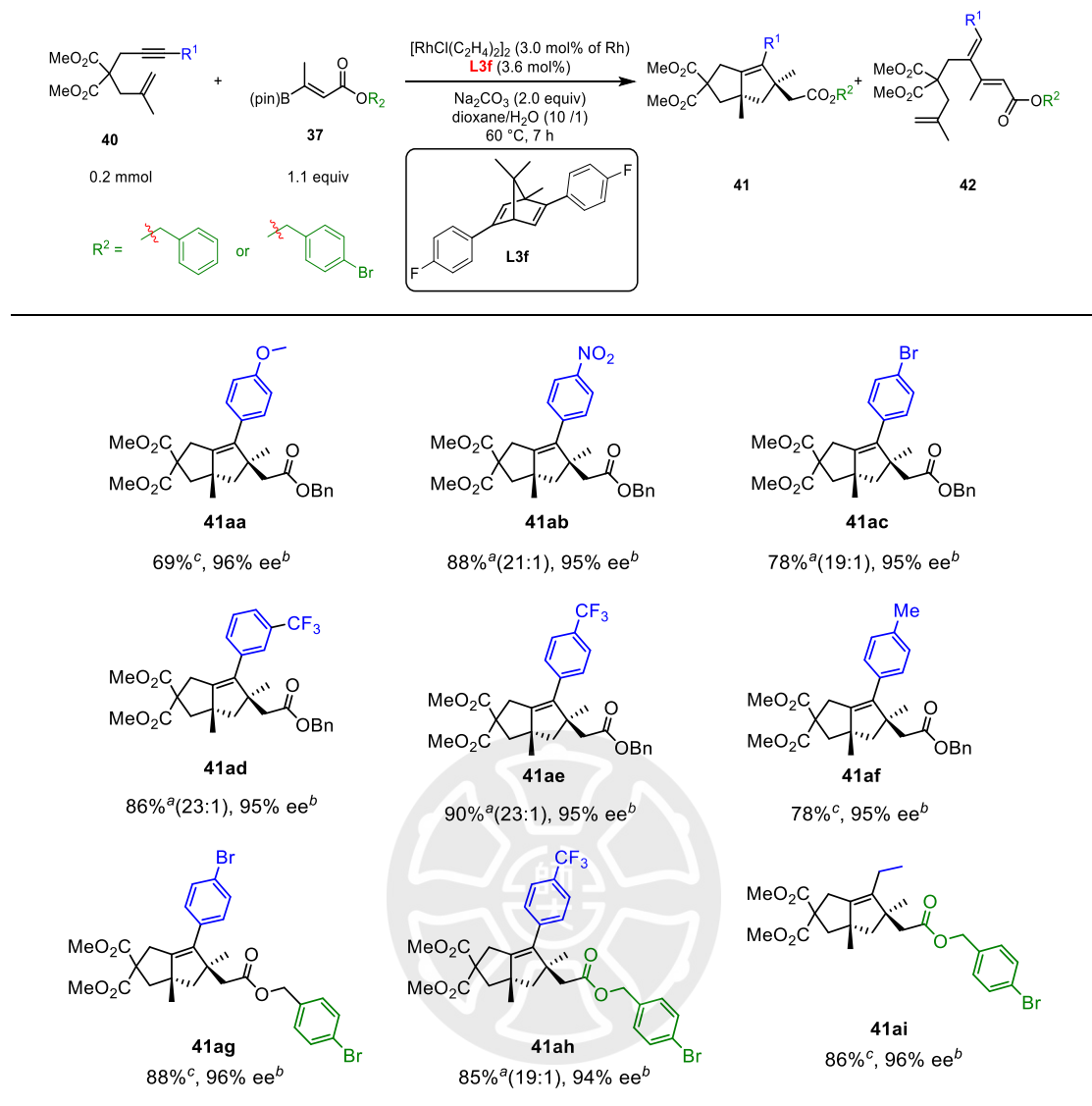
圖 8-1 博士生楊玉珠研究成果

以相同的反應條件，探討 1,6-烯炔結構並且三鍵上的取代基為芳香環的起始物 **36** 與 β 位硼酯取代的 α,β -不飽和酯 **37** 進行不對稱串聯合環反應的反應性之影響(圖 8-1)。

一、以苯環上具有不同取代基進行反應性之探討

在(圖 8-2)的 9 個例子中(**41aa–41ai**)，以三鍵上的取代基為芳香環的起始物 **40**，與 β 位硼酯取代的 α,β -不飽和酯 **37** 進行反應，並將結果與三鍵上的取代為乙基的環化產物 **41ai** (86% yield, 94% ee) 進行比較，除 **41aa** 產率(69% yield) 經多次純化造成產率下降以外，與三鍵末端為乙基的產物 **41ai** 反應結果比較，發現可維持良好的產率(**41ab–41ah**, 78–90% yields, 區位異構物比例大於 19:1)，並且都有良好的鏡像超越值(94–96% ees)。





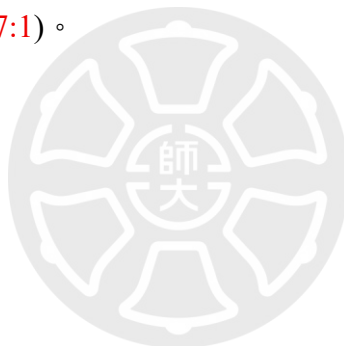
^a Isolated yield (**41**+**42**). ^b The ee value were determined by HPLC analysis on a chiral column. ^c

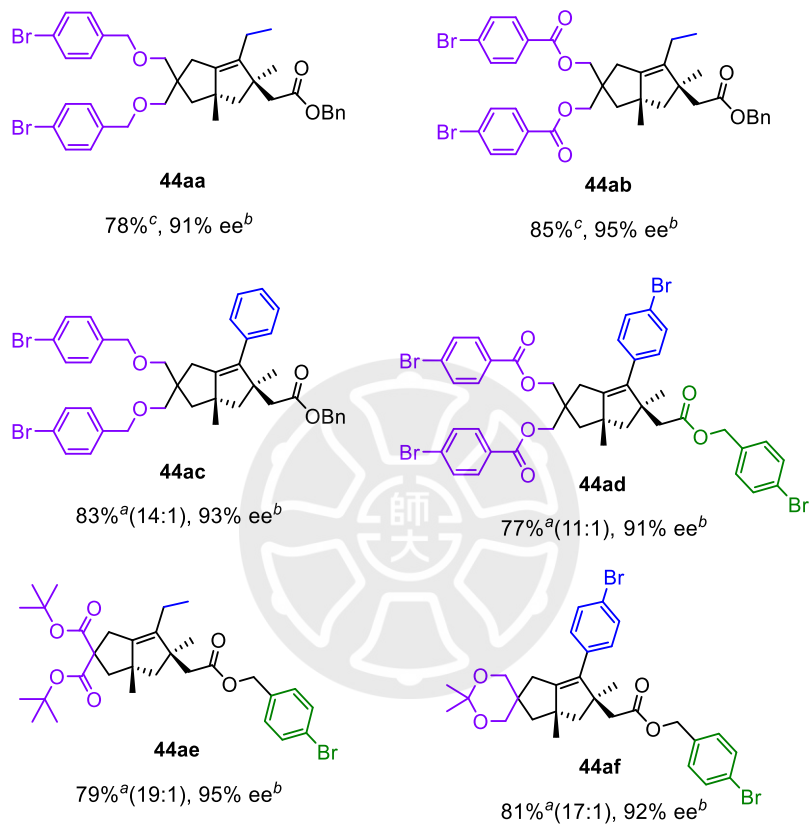
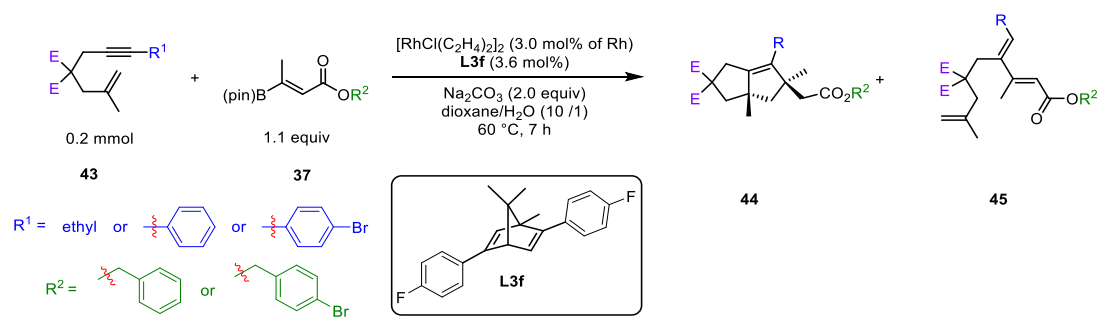
Isolated yield.

圖 8-2 苯環上具有不同取代基

二、丙二酯類進行不同取代之反應性探討

在(圖 8-3)的 6 個例子中(44aa–44af)，以 1,6-烯炔結構中不同取代 43，與 β 位硼酯取代的 α,β -不飽和酯 37 進行反應，發現將丙二酸酯進行還原形成二元醇 (diol) 中間體後，和不同的鹵代烷烴進行反應，形成二苄醚基(Benzyl)取代的起始物 43a 進行反應，可得到良好的產率(44aa, 78% yield; 44ac, 83% yield, 區位異構物(regioisomer)比例 14:1)，並且都有良好的鏡像超越值(91–93% ees)，而苯甲醯基(Benzoyl) 取代的起始物進行反應，與 44ab (85% yield, 95% ee)進行比較，會得到產率和鏡像超越值下降的結果 44ad (77% yield, 91% ee, 區位異構物比例 11:1)，酯基為第三丁基和縮醛(Acetal) 取代的起始物進行反應，有良好的產率和鏡像超越值 44ae (79% yield, 95% ee, 區位異構物比例 19:1)，44af (81% yield, 92% ee, 區位異構物比例 17:1)。





^a Isolated yield (**44**+**45**). ^b The ee value were determined by HPLC analysis on a chiral column. ^c

Isolated yield.

圖 8-3 丙二酯類進行不同取代

三、反應機構探討

推測反應機構如下(圖 8-4):首先一價銦金屬催化劑與親核性試劑 **37** 進行金屬交換反應(Transmetalation), 形成烯基銦中間體 **IT-28** (Alkenylrhodium intermediate), 之後和起始物 **40** 上的三鍵進行選擇性 1,2-加成, 形成烯基銦中間體 **IT-28** (Alkenylrhodium intermediate)。接著中間體 **IT-28** 上的銦金屬會和雙鍵進行 5-*exo-trig* 環化反應, 並形成五環中間體 **IT-29** 以及第一個立體中心, 接著中間體 **IT-29** 上的銦金屬會和 α,β -不飽和酯的雙鍵進行 5-*exo-trig* 環化反應, 並形成銦烯醇鹽(rhodium enolate)五環中間體 **IT-30**, 最後經由與水的質子化反應而產生目標產物 **41aj**。



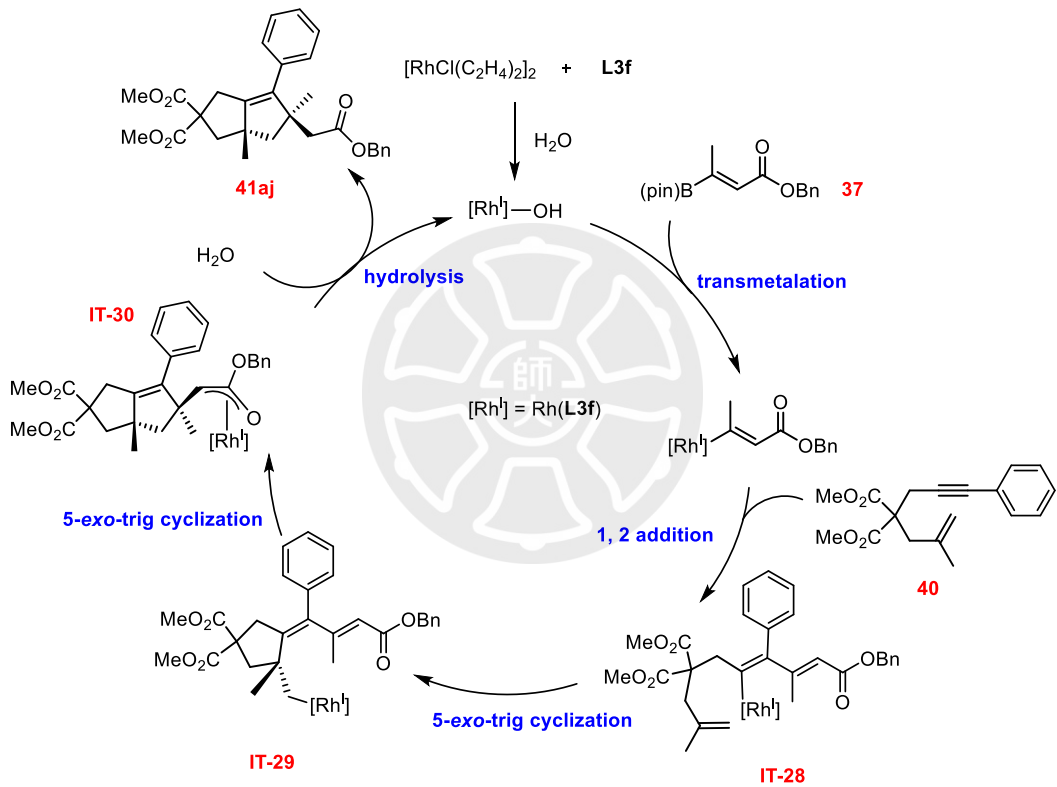
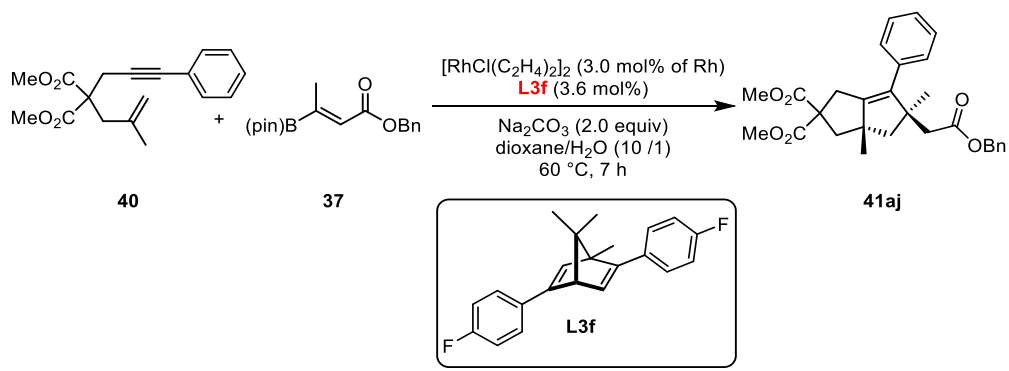


圖 8-4 推測反應機構

第九章 合成應用

在本次研究的最後，對環化產物 **41aj** 進行了官能基轉換的探討，如(圖 9-1)所示。以二異丁基氫化鋁對進行還原反應得到產物 **46**。接著也嘗試以鈀金屬催化對 diquinene 結構的雙鍵進行氫解反應(hydrogenolysis Reaction)得到產物 **47**。

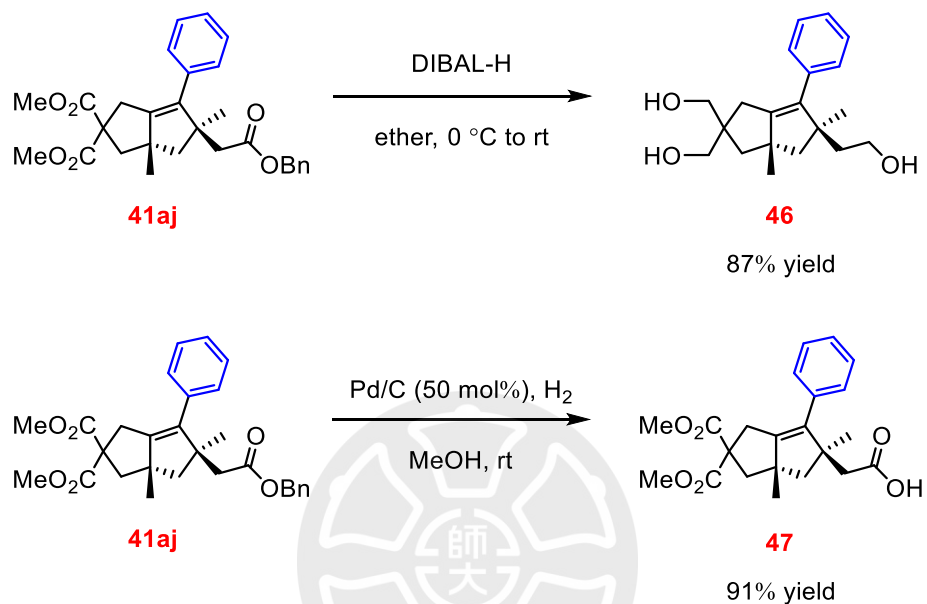


圖 9-1 合成應用

第十章 結論

本論文第二部分，以 1.5 mol% 的一價銠金屬二聚體 $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (3.0 mol% of Rh) 與 3.6 mol% 的掌性雙環[2.2.1]雙烯配基 **L3f** 形成的催化劑，在醚類的 1,4-dioxane 與水比例為 10:1、碳酸鈉為鹼性添加劑的條件之下，催化 β -位硼酯取代的 α,β -不飽和酯 **37** 與 1,6-烯炔結構的起始物 **40** 進行不對稱串聯合環反應，所生成之一系列具有 diquinene 結構的掌性環化產物 **41**，有 15 個例子，最高產率為 88%，以及高達 96% 的鏡像超越值(圖 10-1)。

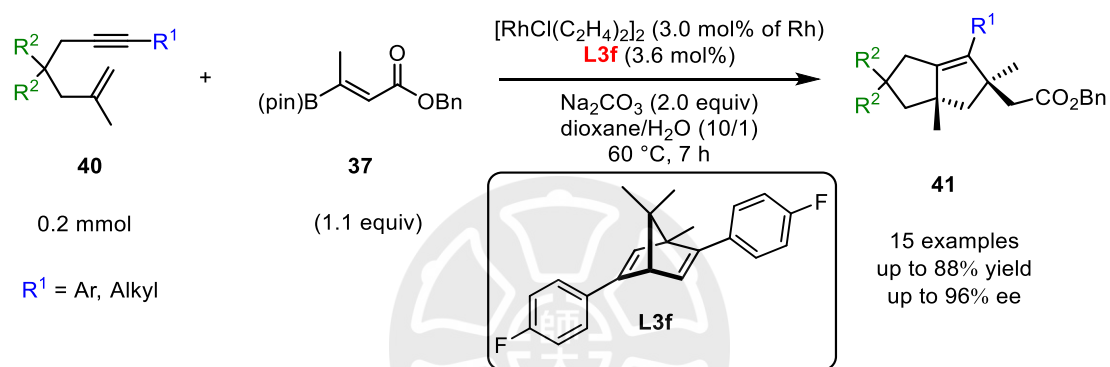


圖 10-1 第二部分研究成果

第十一章 實驗部分

一、分析儀器及基本實驗

核磁共振光譜儀 (Nuclear Magnetic Resonance Spectroscopy, NMR) :

以 Bruker AVIII HD-400 MHz NMR 和 Bruker AV-400 核磁共振光譜儀所測定樣品以氘化氯仿(chloroform-d, CDCl₃)為溶劑，化學位移(chemical shift)以 ppm 為單位。氫核磁共振光譜(¹H NMR)的化學位移以氯仿(chloroform)為內標準品，定義其化學位移 7.26 ppm，或以四甲基矽烷(tetramethyl silane, TMS)為內標準品，定義其化學位移為 0 ppm。分裂形式(splitting pattern)定義如下：單峰(s, singlet)、雙重峰(d, doublet)、三重峰(t, triplet)、四重峰(q, quartet)、五重峰(quint, quintet)、七重峰(sept, septet)、多重峰(m, multiplet)、寬峰(br, broad)；耦合常數(coupling constant)以 *J* 表示，單位為 Hz。光譜數據紀錄依序：化學位移(分裂形式，耦合常數，氫數)。碳核磁共振光譜(¹³C NMR)亦以同型儀器操作，其化學位移以氘化氯仿(chloroform-d, CDCl₃)為內標準品，並定義其化學位移為 77.0 ppm。氟核磁共振光譜(¹⁹F NMR)也是以同型儀器操作。

高解析質譜分析儀 (High Resolution Mass Spectrometer, HRMS) :

使用 JEOL JMS-700 型質譜儀做為測定儀器。以飛行式正離子電灑游離法(time-of-flight-electrospray ionization, TOF-ESI)進行分析，係委託國立臺灣師範大學貴重儀器使用中心技術專員鐘琬茹小姐及王瀟瀾小姐代測。

X-Ray 單晶繞射儀 (X-ray Single Crystal Diffractometer, SC-XRD) :

使用 Bruker D8 Venture 雙鈮單晶繞射儀做為測定儀器，係委託國立臺灣師範大學化學系助教郭頂審先生代測。

薄層色層分析 (Thin-layer Chromatography, TLC) :

使用 MACHEREY-NAGEL, Silica gel pore size 60 Å with fluorescent indicator UV₂₅₄, 0.20 mm 厚度的鋁箔薄片進行溶劑的展開, 並以紫外光、磷鉬酸(phosphomolybdic acid, PMA)或過錳酸鉀(KMnO₄)等顯色劑檢視。

管柱層析 (Column Chromatography) :

使用 KM3 SCIENTIFIC CORPORATION, Silica gel 45–75 μm 做為填充物。

比旋光度 (Specific Rotation) :

使用 JASCO P-2000 Polarimeter 作為測定儀器。測量前先以溶劑進行背景校正。

比旋光度記錄為 $[\alpha]_D^T$ (T: 溫度/ °C, D: 鈉 D 線)。

熔點 (Melting Point, M.p.) :

使用 Mel-Temp 熔點測定儀測定。

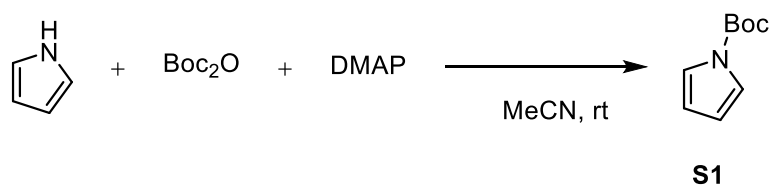
高效能液相層析 (High-Performance Liquid Chromatography, HPLC) :

使用 Hitachi 7000 系列高效能液相層析系統, 包括自動取樣器(Hitachi L-7200 Autosampler)、幫浦(Hitachi L-7100 Pump)、介面控制器(Hitachi D-7000 Interface)、偵測器(Hitachi L-7450H Diode Array Detector)。使用 CHIRALPAK 管柱(Daicel Chemical Ind., Ltd., IA 4.6 mm×250 mm、IB 4.6 mm×250 mm、IC 4.6 mm×250 mm、ID 4.6 mm×250 mm、IE 4.6 mm×250 mm、IF 4.6 mm×250 mm、IG 4.6 mm×250 mm)。

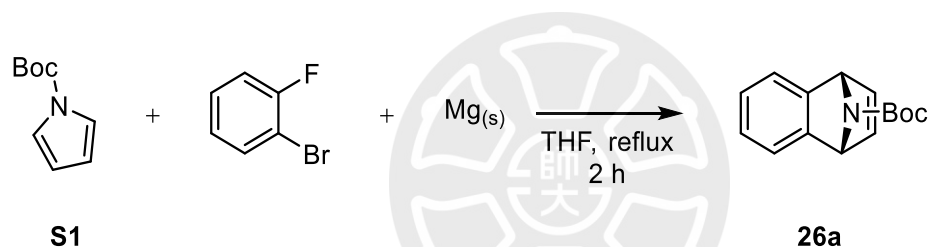
所有實驗所使用之市售化學藥品及溶劑均為分析級或試藥級。純化、除水乾燥皆依標準處理手續進行。反應均於氬氣環境下以磁石攪拌子攪拌之, 並在加熱攪拌器上進行。反應瓶於真空系統下經高溫烘槍烘烤, 冷卻後再填充氬氣使用。

Preparation of 1,4-dihydro-1,4-epiminonaphthalene derivatives

Procedure A



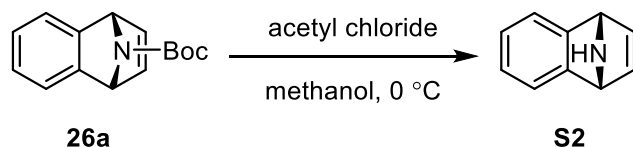
Di-*tert*-butyl dicarbonate (1.4 equiv) and 4-(*N,N* dimethyl amino) pyridine, (0.15 equiv) were added to pyrrole (1.0 equiv) in acetonitrile (1 M) under argon. After the addition was completed, the mixture was stirred at room temperature for 24 hours. Evaporation of the solvent and subsequent column chromatography affords the desired product **S1** as a colorless oil (2.1 g, 85% yield).^[12]



To a two-necked flask was added activated magnesium turning (0.4 g) and the flask was flame dried under vacuum. The system was flushed with argon and allowed to cool. *N*-Boc-pyrrole (1.17 g, 6.99 mmol, 1.0 equiv) in 5.0 mL of dry THF was introduced into the flask and heated to gentle reflux. *o*-Fluorobromobenzene (0.84 mL, 7.69 mmol, 1.1 equiv) dissolved in 4.0 mL of dry THF was added dropwise over a period of 10 min and refluxed for 1.5 h. The initiation of reaction was indicated by the solution turning turbid followed by it turning yellow in color. After completion of the reaction, the solution was cooled and poured into a flask containing 10 mL aqueous solution of ammonium chloride. The aqueous layer was extracted with petroleum ether, and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated.

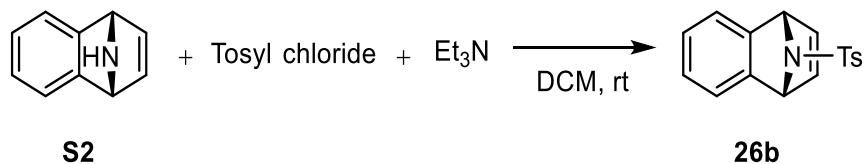
The resulting dark oil on column chromatography followed by crystallization from hexane afforded **26a** as a white crystalline solid (0.86 g, 51% yield).^{[13][14]}

Procedure B



To a 50 ml flame-dried flask, MeOH (5.9 mL) was added dropwise freshly distilled acetyl chloride (6.43 g, 82 mmol) at 0 °C under a nitrogen atmosphere. The resulting solution was stirred for 5 min at 0 °C and **26a** (14.4 mmol) was added. The solution was allowed to reach room temperature and stirred for additional 2 h. Water (200 mL) was added and the mixture was extracted with diethyl ether two times. The aqueous layer was subsequently adjusted to pH ~ 10 with solid potassium carbonate and extracted three times with each 100 mL diethyl ether. The combined extracts were dried over Na₂SO₄ and the solvent was removed in vacuo to give free amine (1.83 g, 89% yield).^[15]

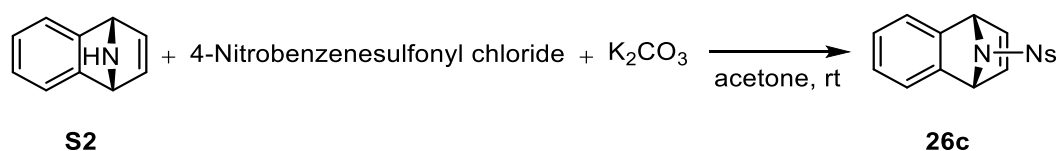
Procedure C



Free amine (10 mmol) was dissolved in 50 mL CH₂Cl₂ followed by the addition of Et₃N (2 mL), tosyl chloride (12 mmol) was added. The reaction was stirred at room temperature for 4 h. Water (100 mL) and CH₂Cl₂ was added until all precipitates

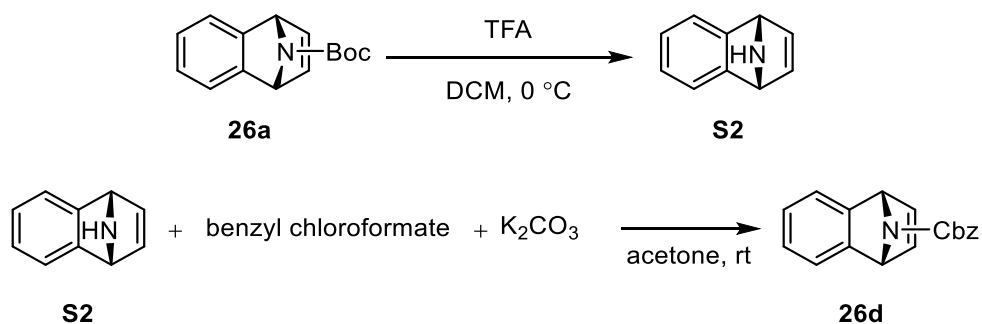
dissolved. The organic and aqueous phases were separated and the aqueous phase was extracted twice with CH_2Cl_2 . The organic fractions were combined, dried over Na_2SO_4 and concentrated. Recrystallization from ethyl acetate gave **26b** as a crystalline solid (1.54 g, 52% yield).^[16]

Procedure D



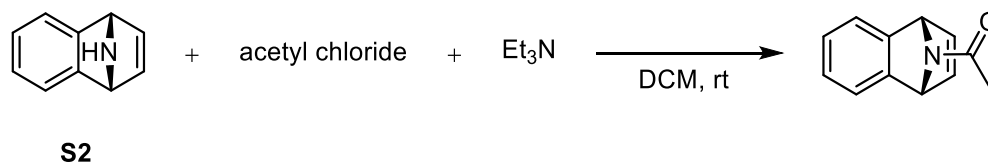
free amine (1.0 equiv) was dissolved in acetone (35 mL) and K_2CO_3 (1.5 equiv) was added. A condenser was attached and 4-Nitrobenzenesulfonyl chloride (1.4 equiv) was added heating. After the addition of 4-Nitrobenzenesulfonyl chloride, the temperature was raised to $65\text{ }^\circ\text{C}$ and refluxed for 18 h. The mixture was then quenched with water and partitioned in diethyl ether. The aqueous layer was extracted with diethyl ether ($2 \times 50\text{ mL}$). The organic layer was dried with Na_2SO_4 , filtered and concentrated. The crude product was purified by column chromatography (EtOAc:Hexanes = 1:5) and then recrystallized in hexanes to provide the product **26c** as white solid (0.8 g, 48% yield).^[17]

Procedure E



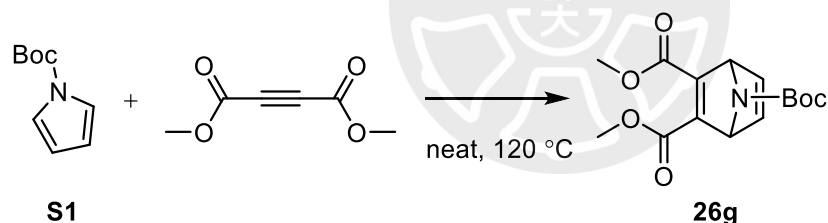
To a flame-dried flask, **26a** (6.20 mmol) was added and dissolved in CH_2Cl_2 (40 mL). The flask was purged with N_2 and trifluoroacetic acid (110.9 mmol) was added dropwise and the mixture was stirred for 1 h. Solvent was removed by rotary evaporation and the crude mixture was diluted with toluene (50 mL) and concentrated by rotary evaporation. This process was repeated 3 times to azeotropically remove excess TFA. Upon removal of the last portion of toluene, a brown salt was formed. The salt was dissolved in acetone (35 mL) and K_2CO_3 (12.4 mmol) was added. A condenser was attached and benzyl chloroformate (9.3 mmol) was added dropwise while heating. After the addition of benzyl chloroformate, the temperature was raised to $65\text{ }^\circ\text{C}$ and refluxed for 18 h. The mixture was then quenched with water and partitioned in diethyl ether. The aqueous layer was extracted with diethyl ether ($2 \times 50\text{ mL}$). The organic layer was dried with Na_2SO_4 , filtered and concentrated. The crude product was purified by column chromatography (EtOAc:Hexane = 1:5) and then recrystallized in hexanes to provide the product **26d** as an off white solid (0.94 g, 55% yield), compared with literature.^[18]

Procedure F



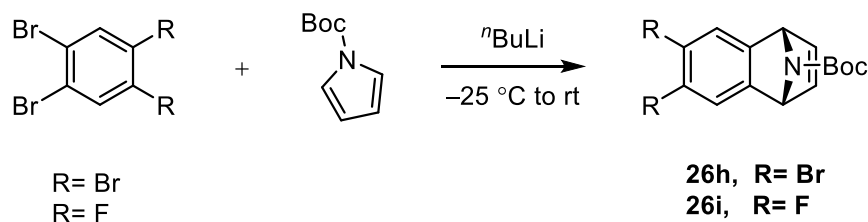
free amine (10 mmol) was dissolved in 50 mL CH₂Cl₂ followed by the addition of Et₃N (2 mL), acetyl chloride (12 mmol) was added. The reaction was stirred at room temperature for 4 h. Water (100 mL) and CH₂Cl₂ was added until all precipitates dissolved. The organic and aqueous phases were separated and the aqueous phase was extracted twice with CH₂Cl₂. The organic fractions were combined, dried over Na₂SO₄ and concentrated. Recrystallization from ethyl acetate gave product as a crystalline solid (0.59 g, 32% yield).^[19]

Procedure G



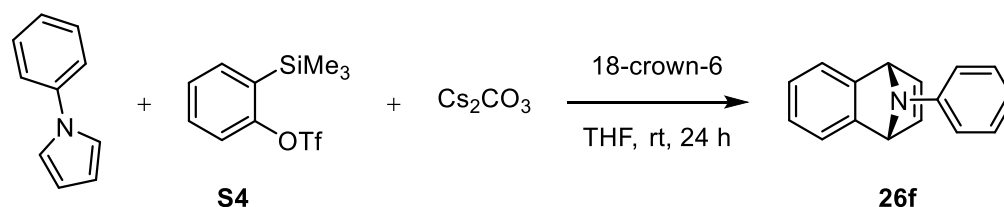
Boc-pyrrole (14.9 mmol, 2.50 g) and dimethyl acetylenedicarboxylate (124.2 mmol, 17.6 g) were heated for 45 min (open vessel, 120 °C). The crude was then purified by flash chromatography, eluting with Hexane/Et₂O 6:4 to recover excess acetylene dicarboxylate and with Hexane/Et₂O 4:6 to collect the desired product (3.69 g, 80%) as a white solid **26g** (4.04 g, 88% yield) compared with literature.^[20]

General procedure H



To an oven-dried round bottom flask was added bromobenzene (1.02 g, 2.59 mmol), toluene (25 mL), and tert-butyl-1-pyrrole carboxylate (0.55 mL, 3.29 mmol). The mixture was purged with argon and cooled to $-25\text{ }^{\circ}\text{C}$. A solution of *n*-butyllithium in hexanes (1.0 M, 2.80 mL) was added dropwise over 20 minutes. The mixture was warmed to room temperature slowly and stirred vigorously for 23 hours, quenched with water when reaction completed. The aqueous phase was extracted three times with diethyl ether. The combined organic layers were washed with water then brine, dried with Na_2SO_4 , filtered, and concentrated using rotary evaporation. The crude product was purified using column chromatography (diethyl ether:hexanes 1:9) to obtain **26h** (0.33 g, 33% yield), **26i** (0.35 g, 48% yield) as a light orange solid. ^[21]

Procedure I

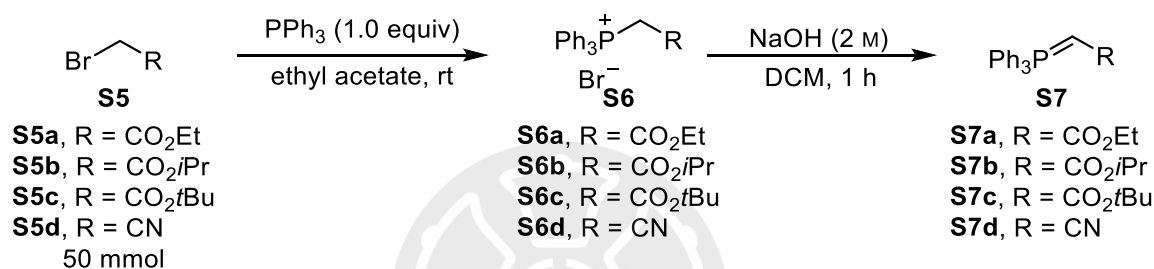


To a mixture of 2-(trimethylsilyl)phenyl triflate (**S4**, 0.503 mmol) and benzyl azide (2.50 mmol) dissolved in THF (2.5 mL) was added cesium carbonate (1.00 mmol) and 18-crown-6-ether (1.00 mmol) at room temperature. After stirred vigorously for 24 h at

25 °C, water (10 mL) was added to the mixture. The mixture was then extracted with ethyl acetate (15 mL × 3), and the combined organic extract was washed with brine (10 mL), dried with Na₂SO₄, and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (Hexane/EtOAc = 5/1) to give **26f** as a colorless solid (0.38 g, 70% yield).^[22]

General Procedures for the Synthesis of Wittig Reagent

General Procedure J



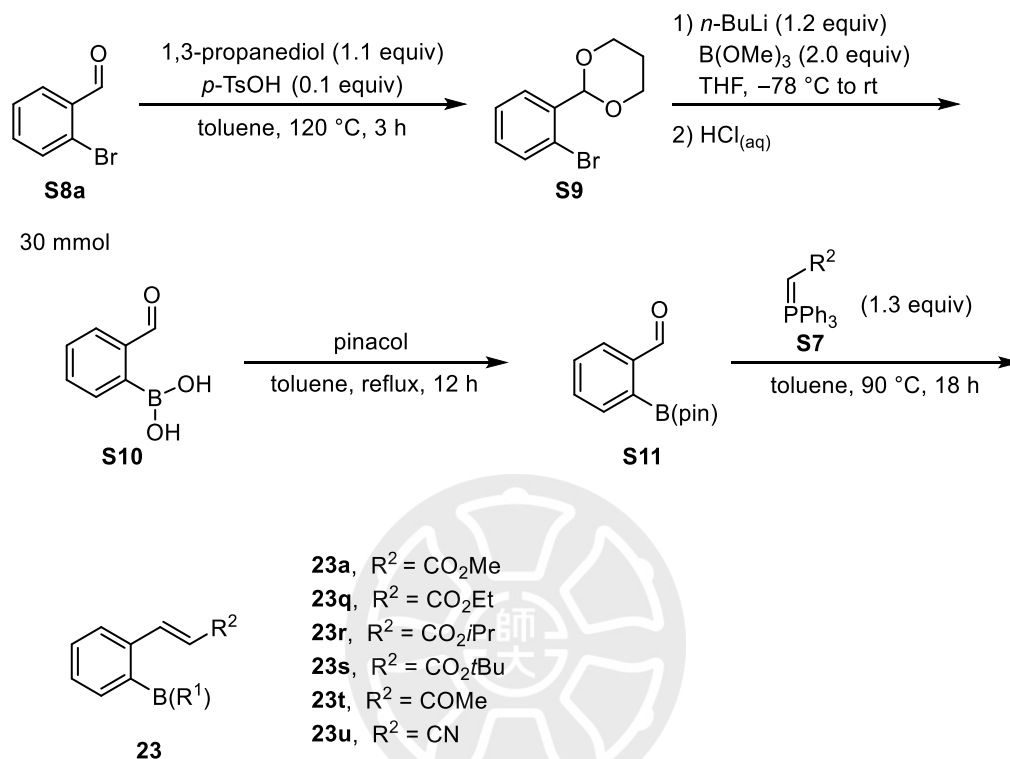
Compound **S5** (50 mmol) was dissolved in ethyl acetate, and then triphenylphosphine (1.0 equiv) was added, the reaction was stirred at room temperature overnight. The reaction mixture was filtered and the precipitate was washed with ethyl acetate to give **S6** as white solid (up to 80% yield), compared with literatures.^{[23] [24]}
[25]

General Procedure K

S6 was dissolved in dichloromethane (50 mL), and NaOH (2 M) solution was added. The reaction was stirred vigorously for 1 h. Then, the aqueous layer was extracted with dichloromethane, and the organic phase was washed with brine, dried with Na₂SO₄. After removal of the solvent, the solid obtained was washed with hexanes to afford the pure product **S7** (up to 85% yield) compared with literature.^[25]

Synthesis of Unsubstituted Arylboronic Esters

General Procedure L



To a solution of **S8a** (30 mmol) in toluene was added *p*-TsOH (0.1 equiv) and 1,3-diol, the mixture was heated at 120 °C with azeotropic removal of water using Dean-Stark apparatus for 3 h. The organic layer was washed with brine and dried with Na₂SO₄. After removing the solvent under reduced pressure, the crude product was purified by column chromatography to give the pure product **S9** (88% yield), compared with literature.^[26]

General Procedure M

To a solution of **S9** in THF, *n*-BuLi (1.6 M in hexanes, 1.2 equiv) was added dropwise at -78 °C, the mixture was stirred at this temperature for 2.5 h. After that, B(OMe)₃ (2.0 equiv) was added dropwise, and the mixture was stirred for another half

hour at $-78\text{ }^{\circ}\text{C}$. Then, the reaction was warm to room temperature and stirred overnight. A solution of HCl in water (10%) was added to the reaction mass and stirred vigorously for 1 h. The aqueous layer was extracted with ethyl acetate, and the organic layer was dried with Na_2SO_4 . The crude product was purified by recrystallization with dichloromethane after column chromatography to yield **S10** as white needle (55% yield), compared with literature.^[27]

General Procedure N

To a solution of **S10** in toluene (0.25 M) was added pinacol or neopentyl glycol (1.1 equiv), the mixture was heated to reflux for 12 h, with azeotropic removal of water using Dean-Stark apparatus. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (ethyl acetate / hexanes) to give compound **S11** (76% yield) were compared with literatures.^{[28][29]}

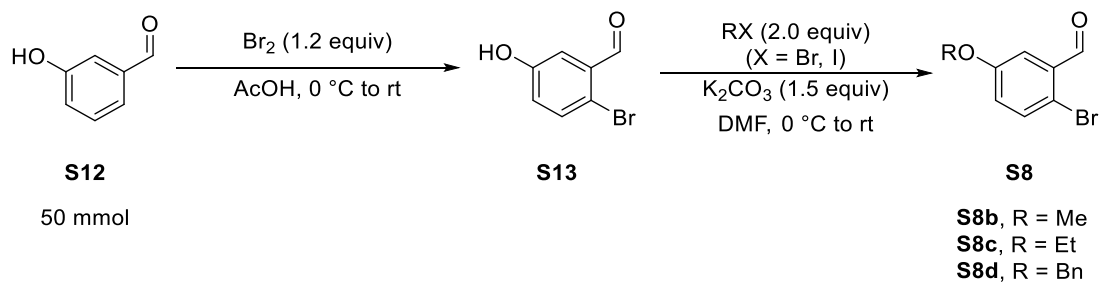
General Procedure O

Compound **S11** (2.0 mmol) was dissolved in toluene (0.65 M), and appropriate Wittig reagent **S7** (1.3 equiv) was added. The mixture was stirred at $90\text{ }^{\circ}\text{C}$. After 18 h, the solvent was evaporated, and the crude product was filtered through column (ethyl acetate/hexanes, 1/40). The pure *trans* isomer **23** (up to 65% yield) is obtained by recrystallization from boiling hexanes.^{[30][31]}

Synthesis of Substituted Arylboronic Esters

Preparation of Substituted 2-bromobenzaldehyde

General Procedure P



General Procedure Q

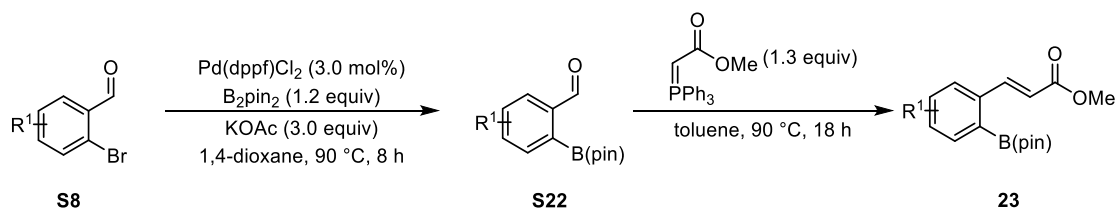
To a solution of **S12** (50 mmol) in acetic acid, bromine (1.2 equiv) was added dropwise via a dropping funnel at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was washed with water and hexanes. The solid obtained was dried under vacuum to afford **S13** (64% yield), which is used without any further purification in the next step. **S13** was compared with literature.^[32]

General Procedure R

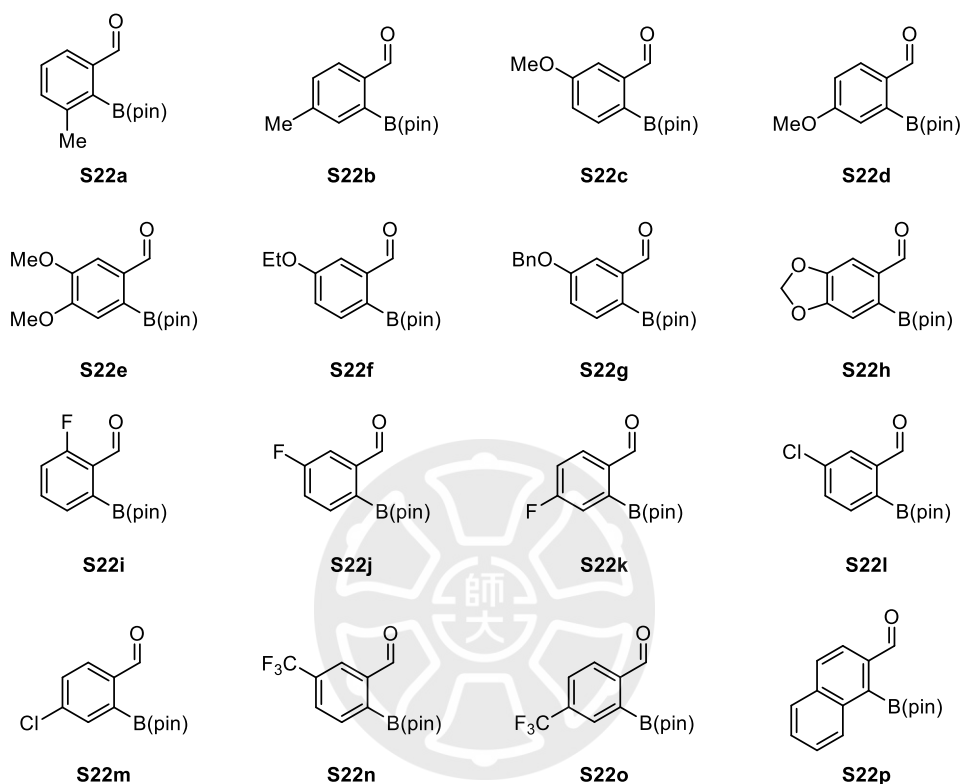
Compound **S13** was dissolved in anhydrous DMF (0.8 M), and K₂CO₃ (1.5 equiv) was added at 0 °C. The mixture was stirred at room temperature for 30 min, then, the appropriate alkyl halide was added dropwise to the reaction and the mixture was stirred overnight. The reaction was quenched with HCl (3 M), and the aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by column chromatography (ethyl acetate / hexanes, 1/20) to afford **S8b** (67% yield),^[33] **S8c** (57% yield),^[34] and **S8d** (58% yield)^[35] compared with literature.

Preparation of Substituted Arylboronic Esters

Arylboronic ester **23** were prepared according to known procedures described below:



General Procedure S



To a two-necked round bottom flask equipped with a condenser, Pd(dppf)Cl₂ (0.12 mmol, 3.0 mol%), B₂pin₂ (4.8 mmol, 1.2 equiv), substituted 2-bromobenzaldehyde **S8** (4.0 mmol, 1.0 equiv), KOAc (12.0 mmol, 3.0 equiv) and 1,4-dioxane (15.0 mL) were added. The resulting mixture was heated at 90 °C for 8 h. Then, the mixture was diluted with ethyl acetate, washed with brine and dried with Na₂SO₄. Solvent was evaporated under reduced pressure and the residue was purified by column chromatography (diethyl ether /hexane) to afford **S22**(up to 74% yield).^[36]

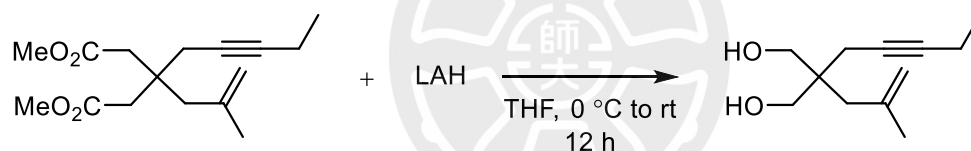
General Procedure T

Compound **S22** was dissolved in toluene (0.65 M), and methyl (triphenylphosphoranylidene) acetate (1.3 equiv) was added. The resulting mixture was heated at 90 °C for 18 h. After that, the solvent was evaporated, and the crude product was filtered through a short column (diethyl ether / hexanes, 1/40), to get rid of the side product $\text{Ph}_3\text{P}=\text{O}$. The pure *trans* isomer of compound **23** (up to 65% yield) was obtained by recrystallization from boiling hexanes. [37]

Preparation of 1,6-Enynes

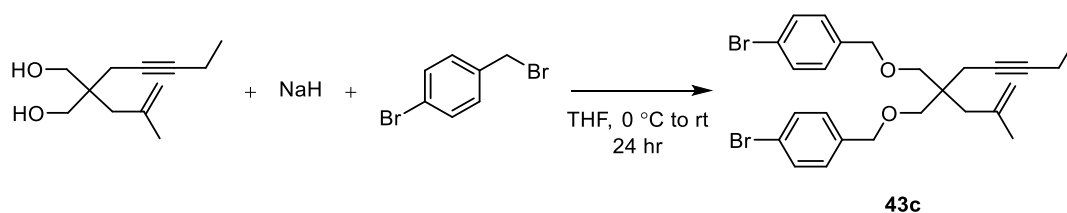
Preparation of 2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diol

Procedure U



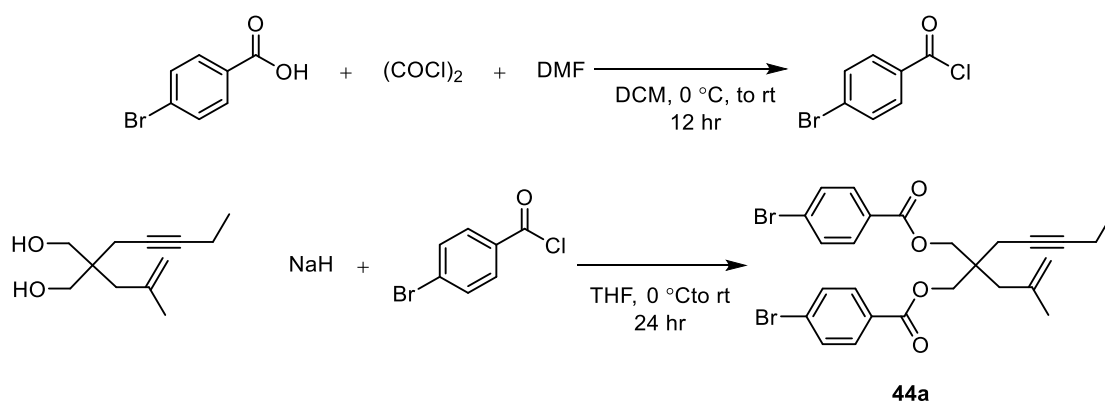
A solution of dimethyl methyl(2-pentynyl)malonate (5.0 mmol) in THF (8 mL) was added to a suspension of LiAlH_4 (10.0 mmol) in THF (12 mL) at 0 °C. The mixture was stirred for 9 h at room temperature and the reaction was quenched with water. The precipitate was removed by filtration, and the remaining solution was dried over MgSO_4 , filtered, and concentrated under vacuum to afford diol as a colorless oil (0.93 g, 95% yield). [38]

Procedure for Benzyl 1,6-Enyne (43c)



To a suspension of NaH (60%, 7.67 mmol) in THF (15 mL) was added a solution of 2-allyl-2-but-2-ynylpropane-1,3-diol (2.56 mmol) in THF (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min. To the mixture was slowly added benzyl bromide (7.67 mmol). The mixture was warmed to room temperature, and stirred overnight. The reaction was quenched with H₂O, and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by a column chromatography (hexane/ethyl acetate = 6:1) to afford **43c** (1.15 g, 85% yield) as a colorless oil. [39]

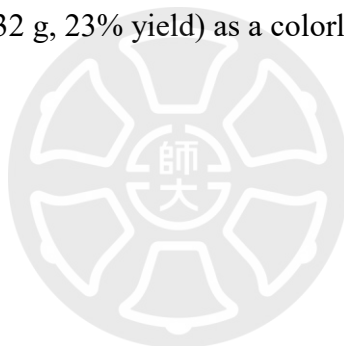
Procedure for Benzoyl 1,6-Enyne (44a)



A round-bottom flask (25.0 mL) was charged with 4-bromobenzoic acid (7.67 mmol, 1.0 equiv), dry DCM (6.0 mL) and catalytic amount of DMF (2.0 drops). The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then, (COCl)₂ (1.5 equiv)

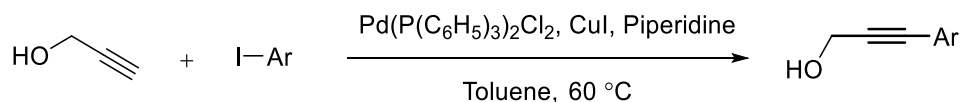
was added dropwise to the reaction mixture and stirred at 25 °C for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

To a suspension of NaH (60%, 7.67 mmol) in THF (15 mL) was added a solution of -allyl-2-but-2-ynylpropane-1,3-diol (2.56 mmol) in THF (10 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 15 min. To the mixture was slowly added benzoyl chloride (7.67 mmol). The mixture was warmed to room temperature, and stirred overnight. The reaction was quenched with H₂O, and the mixture was extracted with diethyl ether. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated. The residue was purified by a column chromatography (hexane/ diethyl ether = 6:1) to afford **44a** (0.32 g, 23% yield) as a colorless oil. ^[40]



Sonogashira Coupling of Aryl Iodides with Propargyl Alcohol

General Procedure:



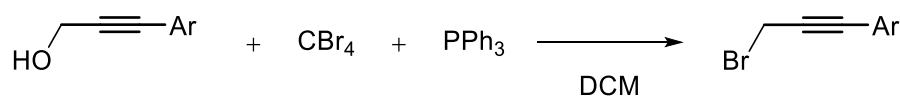
S23a Ar = 4-Me-C₆H₄, **S23d** Ar = 4-OMe-C₆H₄

S23b Ar = 4-Br-C₆H₄, **S23e** Ar = 4-NO₂-C₆H₄

S23c Ar = 4-CF₃-C₆H₄, **S23f** Ar = 3-CF₃-C₆H₄

Aryl Iodides (1.0 equiv) in toluene (1.0 M) at rt was added Pd(PPh₃)₂Cl₂ (0.03 equiv), followed by CuI (0.06 equiv) and piperidine (1.91 equiv). The yellow mixture was stirred at rt for 2 min, then propargyl alcohol (1.02 equiv) was added dropwise (Caution: exothermic reaction!). The deep brown reaction mixture was stirred at 60 °C for 4 h (complete consumption of starting material according to TLC). After cooling to rt, the reaction was filtered through a plug of silica and eluted with dichloromethane (200 ml, analysis by TLC for complete elution of the product). Concentration in vacuo provided a viscous oil, which was purified by chromatography on silica gel (hexane: dichloromethane 6:1 to 2:1 gradient) to afford propargyl alcohol **S23a** (1.2 g, 77% yield), **S23b** (1.3 g, 75% yield), **S23c** (1.2 g, 75% yield), **S23d** (1.5 g, 87% yield), **S23e** (1.0 g, 55% yield), **S23f** (1.1 g, 84% yield), compared with literature. ^[41]

General procedure for the synthesis of derivatives of (3-bromoprop-1-ynyl) benzene



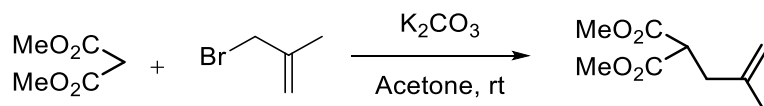
S24a Ar = 4-Me-C₆H₄, **S24d** Ar = 4-OMe-C₆H₄

S24b Ar = 4-Br-C₆H₄, **S24e** Ar = 4-NO₂-C₆H₄

S24c Ar = 4-CF₃-C₆H₄, **S24f** Ar = 3-CF₃-C₆H₄

To a solution of the corresponding propargyl alcohol (3.83 mmol) in anhydrous DCM (15 ml) under Ar, CBr₄ (5.75 mmol) was added and the reaction mixture was cooled at 0 °C. PPh₃ (5.94 mmol) was added slowly. The reaction mixture was allowed to reach room temperature and stirred for 16 hours. Ethanol (2 ml) was added and the reaction mixture stirred for 20 min. The solvent was removed under reduced pressure and the crude purified by flash chromatography on silica gel (hexane: diethyl ether 100:1 to 50:1 gradient) to afford final product **S24a**(67% yield), **S24b**(88% yield), **S24c**(73% yield), **S24d**(85% yield), **S24e**(56% yield), **S24f**(85% yield), compared with literature.^[42]

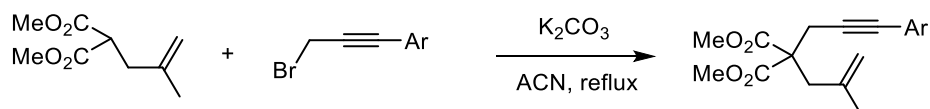
Procedure of dimethyl (2-methyl-2-propenyl)-propanedioate



To a flame-dried round bottom flask with a magnetic stir bar, K₂CO₃ (3.0 equiv) was added to a solution of dimethylmalonate (1.0 equiv) and propargyl bromides (1.3 equiv) in acetone (0.6 M). The reaction was left stirring for 24 h. Once the reaction was deemed complete via TLC, which was purified by chromatography on silica gel (hexane:

diethyl ether 100:1 to 50:1 gradient) to afford the dimethyl 2-allyl malonate product (2.2 g, 77% yield) compared with literature. ^[43]

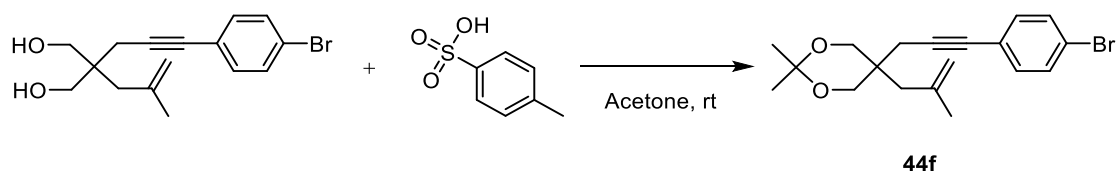
General procedure for the synthesis of 1,6-Enynes



40a Ar = 4-OMe-C₆H₄, **40d** Ar = 3-CF₃-C₆H₄
40b Ar = 4-NO₂-C₆H₄, **40e** Ar = 4-CF₃-C₆H₄
40c Ar = 4-Br-C₆H₄, **40f** Ar = 4-Me-C₆H₄

To a flame-dried round bottom flask with a magnetic stir bar, K₂CO₃ (3.0 equiv) was added to a solution of dimethyl 2-allyl malonate (1.0 equiv) and allyl bromide in acetonitrile (0.6 M). The reaction was left stirring with reflux for 24 h at room temperature. Once the reaction was deemed complete via TLC, which was purified by chromatography on silica gel (hexane: diethyl ether 100:1 to 50:1 gradient) to afford the 1,6-enyne products **40a** (0.45 g, 55% yield), **40b** (0.66 g, 38% yield), **40c** (0.65 g, 34% yield), **40d** (0.46 g, 55% yield), **40e** (0.86 g, 56% yield), **40f** (0.63 g, 67% yield).

Procedure for the synthesis of Acetal 1,6-Enynes

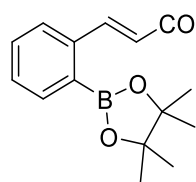


2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diol (1.2 mmol) and *p*-toluenesulfonic acid monohydrate (1.0 mol%) in acetone (10 mL) and the mixture was stirred at room temperature for 12 h. A small amount of NaHCO₃ was

added to neutralize the acid, followed by addition of water, and the resulting mixture was extracted with diethyl ether. The combined ether extracts were washed with brine, dried over Na_2SO_4 , filtered and concentrated. The crude oil was chromatographed on silica gel using (hexanes/diethyl ether 20/1) as eluent to give **44f** (0.42 mmol, 35% yield) as a viscous colorless oil.



**methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate
(23a)**



Isolated as a white solid: 71% yield

m.p. = 78.6–83.1 °C.

R_f 0.25(ethyl acetate/hexanes, 1/20).

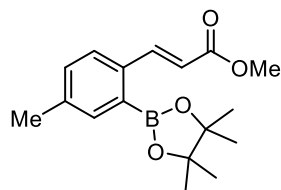
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.58 (d, $J = 16.0$ Hz, 1H), 7.84 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.44 (td, $J = 7.6, 1.2$ Hz, 1H), 7.36 (t, $J = 7.2$, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 3.81 (s, 3H), 1.38 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.6, 145.9, 140.1, 136.1, 131.0, 129.0, 125.6, 118.5, 84.1, 51.5, 24.8.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{B}$ 289.1524; Found 289.1557



Methyl (E)-3-(4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) acrylate (23b)



Isolated as a white solid: 75% yield

m.p. = 120.0 °C.

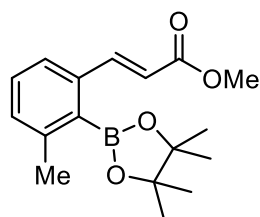
R_f0.30(ethyl acetate/hexanes, 1/20).

¹H NMR (CDCl₃, 400 MHz): δ 8.56 (d, *J* = 16.0 Hz, 1H), 7.64 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.26–7.24 (m, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 2.36 (s, 3H), 1.38 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.8, 145.8, 139.2, 137.4, 136.6, 131.9, 125.7, 117.5, 84.1, 51.5, 24.8, 21.2.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₇H₂₄O₄B 303.1768; Found 303.1769

methyl (E)-3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23c)



Isolated as a white solid: 61% yield

m.p. = 80.7–81.1 °C.

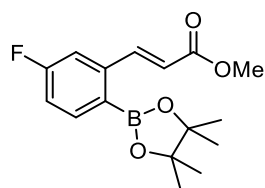
R_f 0.30 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.04 (d, $J = 15.6$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.7$ Hz, 1H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 15.6$ Hz, 1H), 3.78 (s, 3H), 2.44 (s, 3H), 1.43 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.5, 146.1, 142.5, 138.6, 130.7, 129.6, 122.8, 118.3, 84.4, 51.5, 24.9, 22.1.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4\text{B}$ 303.1768; Found 303.1778

methyl (E)-3-(5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23g)



Isolated as white solid: 76% yield

m.p. = 59.0–59.5 °C.

R_f 0.50 (ethyl acetate/hexanes, 1/10).

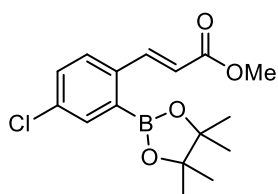
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.57 (dd, $J = 16.0, 1.6$ Hz, 1H), 7.84 (dd, $J = 8.4, 6.8$ Hz, 1H), 7.34 (dd, $J = 10.4, 2.4$ Hz, 1H), 7.07 (td, $J = 8.4, 2.4$ Hz, 1H), 6.36 (d, $J = 16.0$ Hz, 1H), 3.81 (s, 3H), 1.37 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.3, 164.7 (d, $J_{\text{C-F}} = 249.2$ Hz), 144.6, 142.5 (d, $J_{\text{C-F}} = 7.6$ Hz), 138.5 (d, $J_{\text{C-F}} = 8.3$ Hz), 119.7, 116.1 (d, $J_{\text{C-F}} = 20.1$ Hz), 112.3 (d, $J_{\text{C-F}} = 21.2$ Hz), 84.2, 51.7, 24.8.

$^{19}\text{F NMR}$ (CDCl_3 , 376 MHz): δ -108.7

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_4\text{FB}$ 307.1517; Found 307.1526

methyl (E)-3-(4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23j)



Isolated as white solid: 64% yield

m.p. = 126.5–127.5 °C.

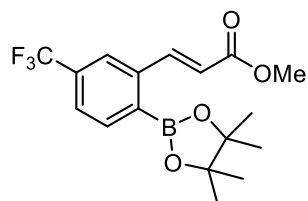
R_f 0.2 (ethyl acetate/hexanes, 1/10)

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.51 (d, $J = 16.0$ Hz, 1H), 7.80 (d, $J = 2.4$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.40 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.36 (d, $J = 15.6$ Hz, 1H), 3.81 (s, 3H), 1.38 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.4, 144.5, 138.5, 135.8, 135.3, 131.1, 127.0, 119.0, 84.5, 51.6, 24.8.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_4\text{ClB}$ 323.1221; Found 323.1223

methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl)acrylate (23i)



Isolated as a white solid: 56% yield

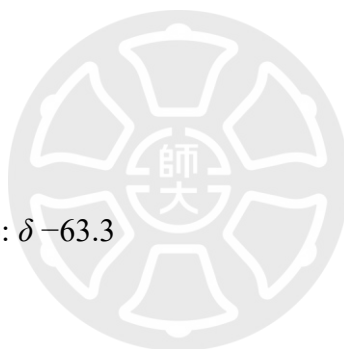
m.p. = 114.1–114.4 °C.

R_f 0.4 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.55 (d, $J = 16.0$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.88 (s, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 3.82 (s, 3H), 1.39 (s, 12H).

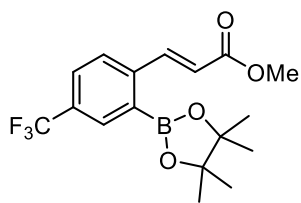
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.1, 144.4, 141.0, 136.7, 133.0 (q, $J_{\text{C-F}} = 32.1$ Hz), 125.0 (q, $J_{\text{C-F}} = 3.3$ Hz), 123.7 (q, $J_{\text{C-F}} = 271.0$ Hz), 122.2 (q, $J_{\text{C-F}} = 3.7$ Hz), 120.3, 84.6, 51.7, 24.8.

$^{19}\text{F NMR}$ (CDCl_3 , 376 MHz): δ -63.3



HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{21}\text{O}_4\text{F}_3\text{B}$ 357.1485; Found 357.1486

methyl(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenyl) acrylate (23h)



Isolated as a white solid: 54% yield

m.p. = 120.1–121.5 °C.

R_f 0.40 (ethyl acetate/hexanes, 1/10).

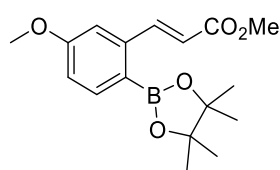
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.57 (d, $J = 15.6$ Hz, 1H), 8.09 (s, 1H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.68 (dd, $J = 8.3, 1.6$ Hz, 1H), 6.43 (d, $J = 15.6$ Hz, 1H), 3.83 (s, 3H), 1.39 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.1, 144.3, 143.6, 132.9 (q, $J_{\text{C-F}} = 3.7$ Hz), 130.6 (q, $J_{\text{C-F}} = 32.3$ Hz), 127.7 (q, $J_{\text{C-F}} = 3.6$ Hz), 126.0, 124.0 (q, $J_{\text{C-F}} = 270.7$ Hz), 120.9, 84.6, 51.7, 24.8.

$^{19}\text{F NMR}$ (CDCl_3 , 376 MHz): δ -62.8

HRMS (EI-TOF) m/z : [M] Calcd for $\text{C}_{17}\text{H}_{20}\text{F}_3\text{O}_4\text{B}$ 356.1407; Found 356.1398

methyl(E)-3-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23k)



Isolated as a white solid: 44% yield

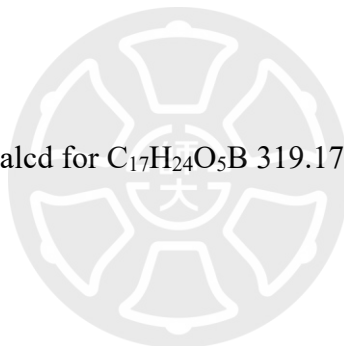
m.p. = 117.9–118.5 °C.

R_f 0.40 (ethyl acetate/hexanes, 1/10).

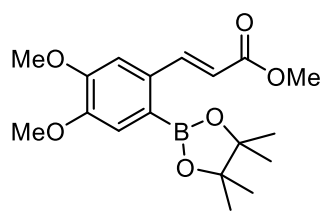
¹H NMR (CDCl₃, 400 MHz): δ 8.60 (d, *J* = 15.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.17 (d, *J* = 2.4 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.36 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.5, 161.7, 145.8, 142.1, 138.0, 118.6, 114.9, 110.6, 120.9, 83.7, 55.1, 51.5, 24.8.

HRMS (EI-TOF) *m/z*: [M] Calcd for C₁₇H₂₄O₅B 319.1717; Found 319.1720



methyl(E)-3-(4,5-dimethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) acrylate (23m)



Isolated as a white solid: 64% yield

m.p. = 92.6–92.9 °C.

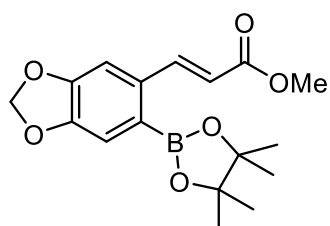
R_f 0.38 (ethyl acetate/hexanes, 1/4).

¹H NMR (CDCl₃, 400 MHz): δ 8.63 (d, *J* = 16.0 Hz, 1H), 7.29 (s, 1H), 7.18 (s, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 3.95 (s, 3H), 3.94 (s, 3H), 3.81 (s, 3H), 1.38 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.8, 151.1, 149.9, 145.6, 134.1, 117.5, 116.3, 107.8, 83.9, 55.9, 55.8, 51.5, 24.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₈H₂₆O₆B 349.1822; Found 349.1821

methyl (E)-3-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d][1,3]dioxol-5-yl) acrylate (23n)



Isolated as a white solid: 60% yield

m.p. = 148.6 °C.

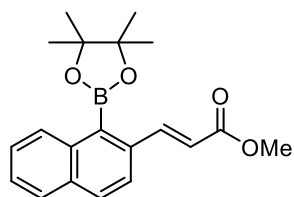
R_f0.2 (ethyl acetate/hexanes, 1/20).

¹H NMR (CDCl₃, 400 MHz): δ 8.59 (d, *J* = 16.0 Hz, 1H), 7.26 (s, 1H), 7.15 (s, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 6.00 (s, 2H), 3.79 (s, 3H), 1.37 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.8, 150.3, 148.7, 145.3, 135.8, 116.7, 114.9, 105.5, 101.4, 84.1, 51.5, 24.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₇H₂₂O₆B 333.1509; Found 333.1516

methyl (E)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-yl)acrylate (23d)



Isolated as a white solid: 65% yield

m.p. = 107.0–107.1 °C.

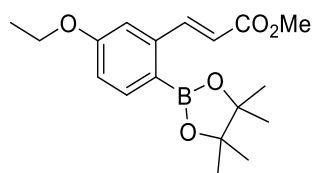
R_f 0.45 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.32 (d, $J = 16.0$ Hz, 1H), 8.17–8.15 (m, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.82–7.76 (m, 1H), 7.70 (d, $J = 8.8$ Hz, 1H), 7.51–7.44 (m, 2H), 6.48 (d, $J = 16.0$ Hz, 1H), 3.80 (s, 3H), 1.52 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 167.5, 145.7, 137.1, 136.2, 133.4, 130.2, 128.6, 128.2, 126.7, 122.4, 118.6, 84.7, 51.5, 25.0.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_4\text{B}$ 339.1768; Found 339.1776

methyl(E)-3-(5-ethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23o)



Isolated as a white solid: 54% yield

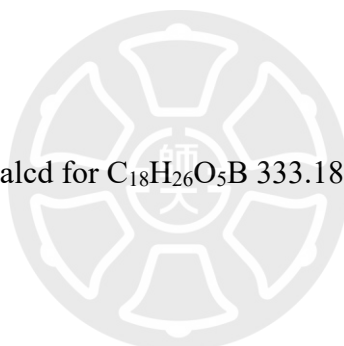
m.p. = 118.9–120.5 °C.

R_f 0.40 (ethyl acetate/hexanes, 1/10).

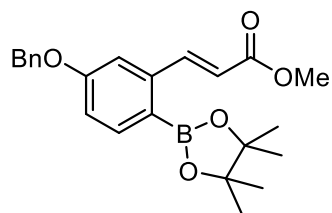
¹H NMR (CDCl₃, 400 MHz): δ 8.59 (d, *J* = 16.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 6.90 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.08 (q, 2H), 3.80 (s, 3H), 1.43 (t, 3H), 1.36 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.6, 161.1, 146.0, 142.1, 138.0, 118.6, 115.4, 111.3, 120.9, 83.8, 51.6, 24.8, 14.7.

HRMS (EI-TOF) *m/z*: [M] Calcd for C₁₈H₂₆O₅B 333.1873; Found 333.1876



methyl (E)-3-(5-(benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23p)



Isolated as a white solid: 68% yield

m.p. = 101.2–101.3 °C.

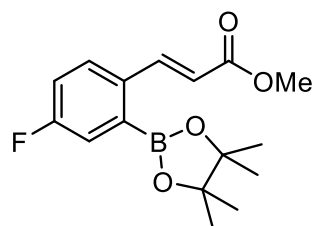
R_f 0.33 (ethyl acetate/hexanes, 1/10).

¹H NMR (CDCl₃, 400 MHz): δ 8.60 (d, *J* = 15.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.44–7.30 (m, 5H), 7.25 (s, 1H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 5.10 (s, 2H), 3.80 (s, 3H), 1.35 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.6, 160.9, 145.8, 142.2, 138.1, 136.4, 128.6, 128.0, 127.4, 118.7, 115.7, 111.7, 83.8, 69.8, 51.6, 24.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₃H₂₈O₅B 395.2030; Found 395.2032

methyl (E)-3-(4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23f)



Isolated as a white solid: 66% yield.

m.p. = 72.3–73.3 °C.

R_f 0.45 (ethyl acetate/hexanes, 1/10).

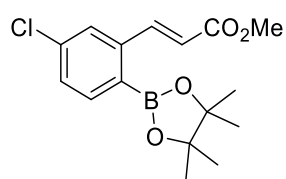
¹H NMR (CDCl₃, 400 MHz): δ 8.52 (d, *J* = 16.0 Hz, 1H), 7.67 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.51 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.13 (td, *J* = 8.4, 2.9 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 1.38 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.5, 163.1 (d, *J*_{C-F} = 250.0 Hz), 144.6, 136.3 (d, *J*_{C-F} = 3.1 Hz), 127.8 (d, *J*_{C-F} = 7.7 Hz), 122.3 (d, *J*_{C-F} = 19.8 Hz), 118.3, 118.2 (d, *J*_{C-F} = 21.6 Hz), 84.5, 51.6, 24.8.

¹⁹F NMR (CDCl₃, 376 MHz): δ -111.8

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₆H₂₁O₄FB 307.1517; Found 307.1515

methyl(E)-3-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate AC16



Isolated as a white solid: 41% yield

m.p. = 110.9–112.5 °C.

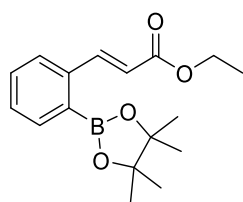
R_f 0.35 (ethyl acetate/hexanes, 1/10).

¹H NMR (CDCl₃, 400 MHz): δ 8.52 (d, *J* = 16.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 1.37 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.2, 144.5, 142.1, 137.6, 137.5, 125.7, 119.8, 84.3, 51.7, 24.8.

HRMS (EI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₇H₂₄O₄B 323.1153; Found 323.1166

ethyl(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23q)



Isolated as a white solid: 44% yield

m.p. = 117.1–118.8 °C.

R_f 0.30 (ethyl acetate/hexanes, 1/10).

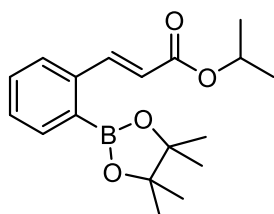
¹H NMR (CDCl₃, 400 MHz): δ 8.58 (d, *J* = 16.0 Hz, 1H), 7.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.45–7.41 (m, 1H), 7.37–7.33 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.26 (q, 2H), 1.38 (s, 12H), 1.34 (t, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.1, 145.5, 140.2, 136.0, 131.0, 128.9, 125.5, 119.0, 84.0, 60.2, 24.8, 14.3.

HRMS (EI-TOF) *m/z*: [M] Calcd for C₁₇H₂₄O₄B 303.1768; Found 303.1765



**isopropyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate
(23r)**



Isolated as white solid: 40% yield

m.p. = 60.5–61.2 °C.

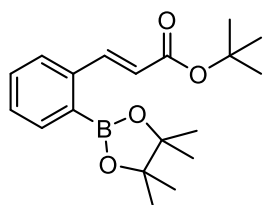
R_f 0.44 (ethyl acetate/hexanes, 1/10).

¹H NMR (CDCl₃, 400 MHz): δ 8.56 (d, *J* = 16.0 Hz, 1H), 7.83 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.44 (td, *J* = 7.7, 1.1 Hz, 1H), 7.35 (td, *J* = 7.4, 1.1 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 5.14 (sept, *J* = 6.3 Hz, 1H), 1.38 (s, 12H), 1.32 (d, *J* = 6.4 Hz, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 166.7, 145.2, 140.4, 136.1, 131.0, 128.9, 125.6, 119.6, 84.1, 67.5, 24.9, 22.0.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₈H₂₆O₄B 317.1924; Found 317.1932

tert-butyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23s)



Isolated as white solid: 41% yield

m.p. = 66.5–67.2 °C.

R_f 0.50 (diethyl ether/hexanes, 1/5).

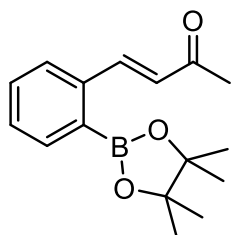
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.44 (d, $J = 16.0$ Hz, 1H), 7.83 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.67 (d, $J = 7.6$ Hz, 1H), 7.43 (td, $J = 8.0$, 0.8 Hz, 1H), 7.33 (td, $J = 7.2$, 1.2 Hz, 1H), 6.30 (d, $J = 16.0$ Hz, 1H), 1.55 (s, 9H), 1.38 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 166.4, 144.2, 140.5, 136.1, 131.0, 128.6, 125.5, 121.2, 84.0, 80.0, 28.2, 24.8.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{27}\text{O}_4\text{BNa}$ 353.1900; Found 353.1911



(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-2-one (23t)



Isolated as white solid: 30% yield

m.p. = 86.8–90.0 °C.

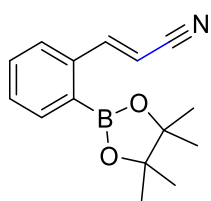
R_f 0.34 (ethyl acetate/hexanes, 1/20).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.52 (d, $J = 16.4$ Hz, 1H), 7.88 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.46 (td, $J = 7.6, 1.2$ Hz, 1H), 7.37 (td, $J = 7.4, 1.1$ Hz, 1H), 6.58 (d, $J = 18.0$ Hz, 1H), 2.41 (s, 3H), 1.38 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 199.5, 145.4, 140.4, 136.5, 131.3, 129.1, 128.6, 125.5, 84.0, 26.1, 24.9.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{B}$ 287.1819; Found 287.1825

(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (23u)



Isolated as a white solid: 44% yield

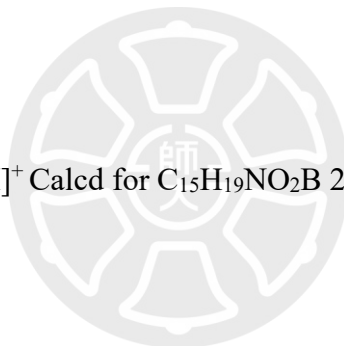
m.p. = 117.9–118.5 °C.

R_f 0.45 (ethyl acetate/hexanes, 1/10).

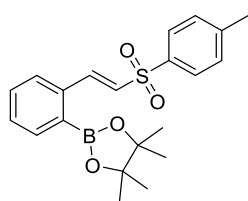
¹H NMR (CDCl₃, 400 MHz): δ 8.37 (d, *J* = 16.8 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.6 Hz, 1H), 7.41 (td, *J* = 7.2, 0.8 Hz, 1H), 5.83 (d, *J* = 16.4 Hz, 1H), 1.36 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 151.7, 139.4, 136.8, 131.3, 129.8, 124.7, 118.7, 96.8, 84.3, 24.8.

HRMS (EI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₉NO₂B 256.1509; Found 256.1508



(E)-4,4,5,5-tetramethyl-2-(2-(2-tosylvinyl)phenyl)-1,3,2-dioxaborolane (23v)



Isolated as a white solid: 44% yield

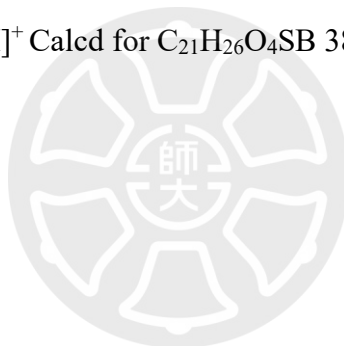
m.p. = 117.9–118.5 °C.

R_f 0.35 (ethyl acetate/hexanes, 1/10).

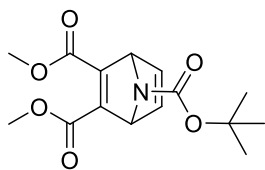
¹H NMR (CDCl₃, 400 MHz): δ 8.55 (d, *J* = 15.2 Hz, 1H), 7.87-7.84 (m, 3H), 6.76 (d, *J* = 7.6 Hz, 1H), 7.44-7.31 (m, 4H), 6.76 (d, *J* = 15.2 Hz, 1H), 2.42 (s, 3H), 1.39 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 144.0, 143.9, 138.6, 138.1, 136.3, 131.2, 129.8, 129.5, 128.7, 127.8, 126.2, 84.2, 24.8, 21.5.

HRMS (EI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₁H₂₆O₄SB 385.1645; Found 385.1638



7-(tert-butyl) 2,3-dimethyl 7-azabicyclo[2.2.1]hepta-2,5-diene-2,3,7-tricarboxylate (26g)



Isolated as a white solid: 88% yield:

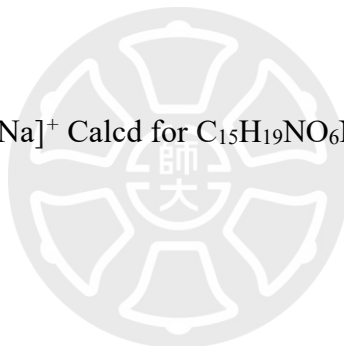
m.p. = 107.0–108.0 °C

R_f 0.40 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.14 (s, 2H), 5.46 (s, 2H), 3.82 (s, 6H), 1.41 (s, 9H).

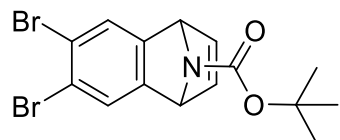
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 163.2, 153.9, 152.4, 143.2, 142.3, 81.3, 68.9, 52.2, 28.0.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_6\text{Na}$ 332.1110; Found 332.1105



tert-butyl 6,7-dibromo-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26h)

Isolated as a white solid: 33% yield:



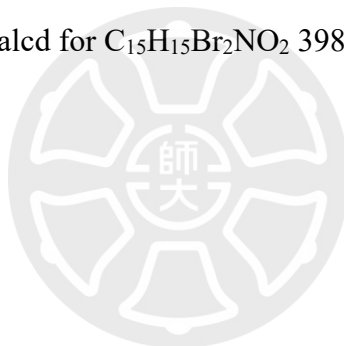
m.p. = 111.2–112.8 °C.

R_f 0.45 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.47-7.08 (s, 2H), 6.92 (s, 2H), 5.43 (s, 2H), 1.37 (s, 9H).

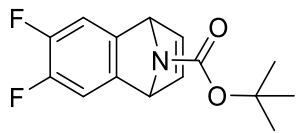
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 154.3, 149.3, 142.9, 142.1, 126.0, 125.7, 120.4, 80.9, 65.9, 28.0.

HRMS (EI-TOF) m/z : [M] Calcd for $\text{C}_{15}\text{H}_{15}\text{Br}_2\text{NO}_2$ 398.9470; Found 398.9461



tert-butyl 6,7-difluoro-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26i)

Isolated as a white solid: 48% yield:



m.p. = 100.2–102.6°C.

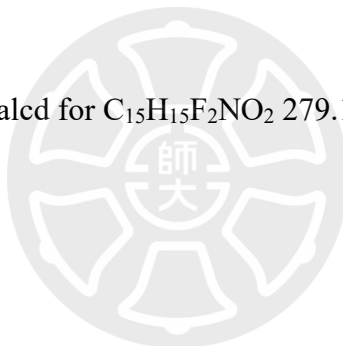
R_f 0.5 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.47–7.08 (s, 2H), 6.97 (s, 2H), 5.45 (s, 2H), 1.38 (s, 9H).

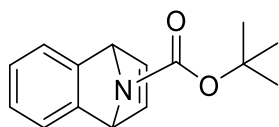
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 154.7, 148.4, 146.0, 143.3, 142.4, 126.0, 125.7, 111.3, 81.0, 66.3, 65.9, 28.0.

$^{19}\text{F NMR}$ (CDCl_3 , 376 MHz): δ -142.3, -142.4.

HRMS (EI-TOF) m/z : [M] Calcd for $\text{C}_{15}\text{H}_{15}\text{F}_2\text{NO}_2$ 279.1071; Found 279.1063



tert-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26a)



Isolated as a white solid: 51% yield:

m.p. = 100.2–100.9 °C.

R_f 0.50 (ethyl acetate/hexanes, 1/10).

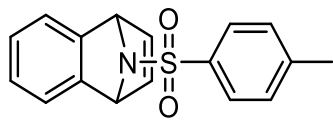
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.25 (br, 2H), 6.94 (br, 4H), 5.48 (br, 2H), 1.37 (s, 9H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 155.1, 148.2, 143.4, 142.3, 124.9, 121.1, 81.5, 66.7, 66.1, 28.1.

HRMS (EI-TOF) m/z : [M] Calcd for $\text{C}_{15}\text{H}_{17}\text{NO}_2$ 243.1259; Found 243.1248



9-tosyl-1,4-dihydro-1,4-epiminonaphthalene (26b)



Isolated as a white solid: 52% yield:

m.p. = 115.2–118.9 °C.

R_f 0.25 (ethyl acetate/hexanes, 1/10).

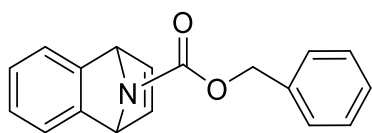
¹H NMR (CDCl₃, 400 MHz): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04–7.02 (br, 2H), 6.78–6.76 (br, 4H), 5.44 (br, 2H), 2.33 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 147.2, 143.2, 142.1, 135.1, 124.3, 128.2, 124.9, 121.1, 67.6, 21.4.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₇H₁₆NO₂S 298.0902; Found 298.0905



benzyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26d)



Isolated as a white solid: 55% yield:

m.p. =114.0–117.4 °C.

R_f 0.30 (ethyl acetate/hexanes, 1/10).

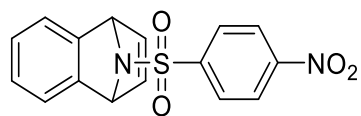
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.87-7.84 (br, 3H), 7.67 (d, $J = 8.0$ Hz, 2H), 7.53-7.33 (br, 8H), 7.01 (br, 1H), 5.26 (s, 2H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 154.2, 136.1, 134.1, 132.4, 128.8, 128.6, 128.4, 126.3, 126.0, 125.8, 125.1, 120.4, 67.3.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{16}\text{NO}_2$ 278.1181; Found 278.1189



9-((4-nitrophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene (26c)



Isolated as a white solid: 48% yield:

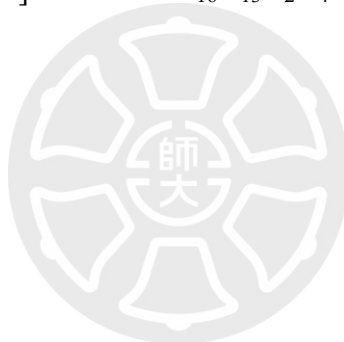
m.p. =134.0–136.9 °C.

R_f 0.10 (ethyl acetate/hexanes, 1/10).

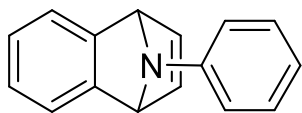
$^1\text{H NMR}$ ($(\text{CD}_3)_2\text{SO}$, 400 MHz): δ 8.17-8.15 (m, 2H), 7.78-7.54 (m, 2H), 7.11-7.08 (m, 2H), 6.91 (t, $J = 1.6$ Hz, 2H), 6.773-6.69 (m, 2H), 5.64 (br, 2H).

$^{13}\text{C NMR}$ ($(\text{CD}_3)_2\text{SO}$, 100 MHz): δ 149.9, 147.5, 143.5, 143.2, 130.3, 125.3, 124.5, 122.1, 67.9.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_4\text{S}$ 329.0596; Found 329.0591



9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (26f)



Isolated as a white solid: 54% yield:

m.p. = 110.0–112.2 °C.

R_f 0.50 (ethyl acetate/hexanes, 1/10).

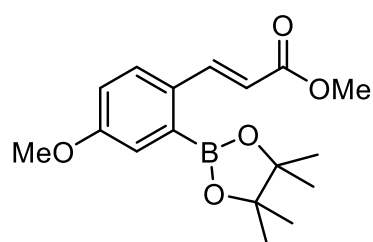
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.23–7.21 (m, 2H), 7.16–7.12 (m, 2H), 6.90–6.88 (m, 4H), 6.81–6.79 (m, 3H), 5.39 (s, 2H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 148.4, 146.8, 141.7, 128.7, 124.8, 121.3, 120.7, 117.8, 69.1.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{14}\text{N}$ 220.1126; Found 220.1122



methyl (E)-3-(4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23i)



Isolated as a white solid: 63% yield

m.p. = 92.2–92.6 °C.

R_f 0.25 (ethyl acetate/hexanes, 1/10).

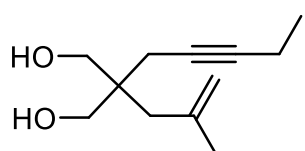
¹H NMR (CDCl₃, 400 MHz): δ 8.53 (d, *J* = 16.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 2.8 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 1.38 (s, 12H).

¹³C NMR (CDCl₃, 100 MHz): δ 167.9, 160.2, 145.4, 132.7, 127.3, 119.9, 117.4, 116.1, 84.2, 55.3, 51.4, 24.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₇H₂₄O₅B 319.1717; Found 319.1726



2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diol (SC1)



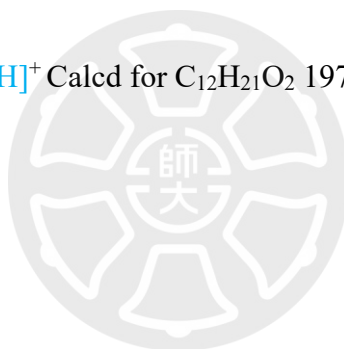
Isolated as a colorless oil: 88% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

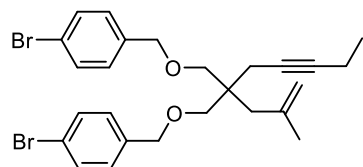
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 4.91 (s, 1H), 4.81 (s, 1H), 3.63 (dd, $J = 16.4, 10.8$ Hz, 1H), 3.07 (s, 2H), 2.22-2.14 (m, 4H), 2.11 (s, 2H), 1.82 (s, 3H), 1.30 (t, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 141.9, 115.1, 84.6, 75.8, 67.1, 42.6, 38.6, 25.0, 21.9, 14.1, 12.3.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ 197.1542; Found 197.1538



4,4'-(((2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diyl)bis(oxy))bis (methylene))bis(bromobenzene) (43c)



Isolated as a colorless oil: 71% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

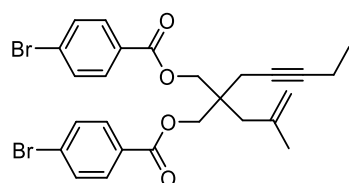
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.41-7.39 (m, 4H), 7.16-7.14 (m, 4H), 4.88 (s, 1H), 4.77 (s, 1H), 4.41 (s, 4H), 3.34 (dd, $J = 13.2, 8.8$ Hz, 4H), 2.22 (s, 2H), 2.17-2.10 (m, 4H), 1.76 (s, 3H), 1.08 (t, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 141.8, 137.7, 131.2, 128.9, 121.1, 114.9, 84.0, 76.7, 72.3, 71.9, 42.6, 38.3, 25.1, 22.6, 14.4, 12.4.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{31}\text{O}_2\text{Br}_2$ 533.0691; Found 533.0685



2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diyl bis(4-bromobenzoate) (44a)



Isolated as a colorless oil: 23% yield

R_f 0.25 (ethyl acetate/hexanes, 1/10).

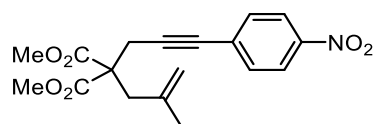
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.87-7.85 (m, 4H), 7.56-7.54 (m, 4H), 4.99 (s, 1H), 4.84 (s, 1H), 4.36 (dd, $J = 17.2, 11.2$ Hz, 4H), 2.44 (t, 2H), 2.39 (s, 2H), 2.15 (qt, $J = 14.8, 7.6$ Hz, 2H), 1.83 (s, 3H), 1.10 (t, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 165.4, 140.2, 131.8, 131.0, 128.8, 128.2, 116.5, 85.5, 74.1, 66.7, 41.3, 39.2, 25.1, 23.3, 14.1, 12.4.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{26}\text{H}_{27}\text{O}_4\text{Br}_2$ 561.0276; Found 561.0281



dimethyl 2-(2-methylallyl)-2-(3-(4-nitrophenyl)prop-2-yn-1-yl)malonate (40b)



Isolated as a colorless oil: 38% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

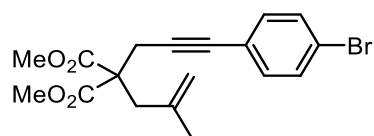
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 8.16-8.14 (m, 2H), 7.51-7.48 (m, 2H), 4.95 (s, 1H), 4.86 (s, 1H), 3.77 (s, 6H), 3.09 (s, 2H), 2.89 (s, 2H), 1.68 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 170.4, 146.9, 139.6, 132.3, 130.3, 123.5, 116.5, 90.7, 82.2, 56.5, 52.8, 39.9, 25.1, 23.7, 23.1.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{NO}_6$ 346.1295; Found 346.1246



dimethyl 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)malonate (40c)



Isolated as a colorless oil: 34% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

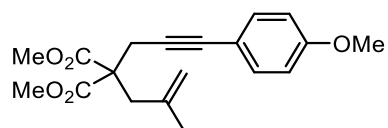
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.41-7.39 (m, 2H), 7.23-7.20 (m, 2H), 4.93 (s, 1H), 4.85 (s, 1H), 3.75 (s, 6H), 3.03 (s, 2H), 2.88 (s, 2H), 1.67 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 170.5, 139.7, 133.0, 131.4, 122.1, 116.3, 85.9, 82.7, 56.6, 52.7, 39.8, 25.1, 23.5, 23.1.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{BrO}_4$ 379.0545; Found 379.0467



dimethyl2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2-(2-methylallyl)malonate (40a)



Isolated as a colorless oil: 45% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

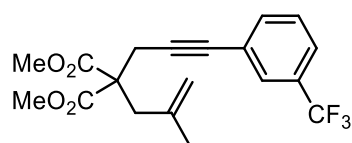
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.31-7.29 (m, 2H), 6.81-6.79 (m, 2H), 4.93 (s, 1H), 4.88 (s, 1H), 3.78 (s, 3H), 3.75 (s, 6H), 3.03 (s, 2H), 2.90 (s, 2H), 1.69 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 170.7, 159.3, 139.9, 132.9, 116.2, 115.3, 113.8, 83.6, 82.9, 56.8, 55.2, 52.7, 39.7, 25.1, 23.6, 23.2.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_5$ 331.1543; Found 331.1501



dimethyl2-(2-methylallyl)-2-(3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl) malonate (40d)



Isolated as a colorless oil: 55% yield:

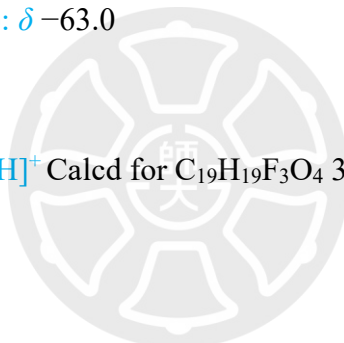
R_f 0.25 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.61 (s, 1H), 7.55-7.51 (m, 2H), 7.42-7.38 (m, 1H), 4.95 (s, 1H), 4.89 (s, 1H), 3.77 (s, 6H), 3.08 (s, 2H), 2.92 (s, 2H), 1.69 (s, 3H).

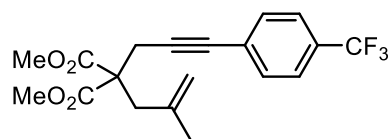
$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 170.5, 139.7, 134.7, 130.7 (dd, $J_{\text{C-F}} = 65.0, 33.0$ Hz), 128.7, 128.1 (d, $J_{\text{C-F}} = 4.0$ Hz), 124.5 (d, $J_{\text{C-F}} = 4.0$ Hz), 127.8 (d, $J_{\text{C-F}} = 7.7$ Hz), 124.1, 123.6 (dd, $J_{\text{C-F}} = 542.0, 217.0$ Hz), 116.3, 86.4, 82.3, 56.6, 52.7, 39.8, 23.5, 23.0.

$^{19}\text{F NMR}$ (CDCl_3 , 376 MHz): δ -63.0

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{O}_4$ 369.1320; Found 369.1269



**dimethyl2-(2-methylallyl)-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)
malonate (40e)**



Isolated as a colorless oil: 56% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

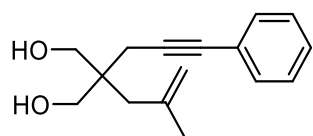
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.54-7.52 (m, 2H), 7.48-7.46 (m, 2H), 4.95 (s, 1H), 4.88 (s, 1H), 3.77 (s, 6H), 3.08 (s, 2H), 2.91 (s, 2H), 1.69 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 170.5, 139.7, 131.8, 129.7 (dd, $J_{\text{C-F}} = 65.0, 32.0$ Hz), 127.0, 125.1 (d, $J_{\text{C-F}} = 4.0$ Hz), 123.9 (dd, $J_{\text{C-F}} = 271.0, 95.0$ Hz), 116.3, 87.5, 82.6, 56.6, 52.7, 39.8, 23.6, 23.1.

$^{19}\text{F NMR}$ (CDCl_3 , 376 MHz): δ -62.9

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{O}_4$ 369.1235 Found 369.1294

2-(2-methylallyl)-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diol (SC9)



Isolated as a white solid: 65% yield:

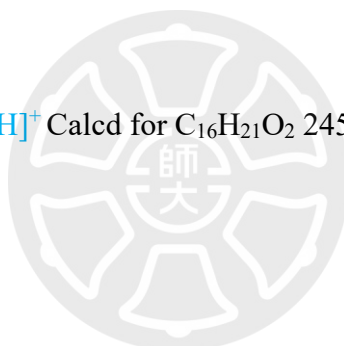
m.p. = 79.0 – 81.2 °C.

R_f 0.15 (ethyl acetate/hexanes, 1/10).

¹H NMR (CDCl₃, 400 MHz): δ 7.40-7.38 (m, 2H), 7.29-7.26 (m, 3H), 4.94 (t, 1H), 4.85 (s, 1H), 3.71 (dd, *J* = 16.8, 10.8 Hz, 4H), 2.83 (s, 2H), 2.49 (s, 2H), 2.19 (s, 2H), 1.84 (s, 3H).

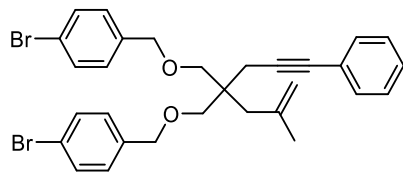
¹³C NMR (CDCl₃, 100 MHz): δ 141.9, 131.5, 128.2, 127.8, 123.5, 115.5, 86.7, 83.4, 67.7, 43.1, 39.0, 25.1, 22.7.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₆H₂₁O₂ 245.1542; Found 245.1541



4,4'-(((2-(2-methylallyl)-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diyl)bis(oxy))bis(methylene))bis(bromobenzene) (44c)

Isolated as a colorless oil: 76% yield:

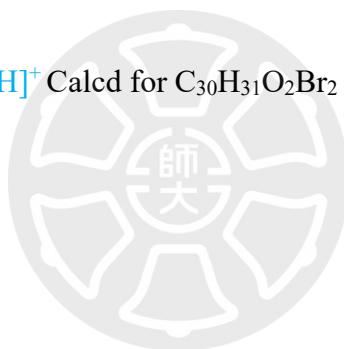


R_f 0.25 (ethyl acetate/hexanes, 1/10).

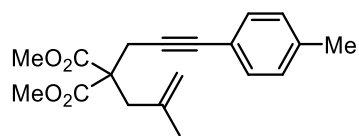
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.41-7.39 (m, 4H), 7.31-7.26 (m, 4H), 7.18-7.68 (m, 4H), 4.92 (t, 1H), 4.81 (s, 1H), 4.43 (s, 4H), 3.42 (dd, $J = 9.6, 1.6$ Hz, 4H), 2.49 (s, 2H), 2.25 (s, 2H), 1.80 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 141.7, 137.6, 131.5, 131.4, 129.0, 128.2, 127.6, 123.8, 121.2, 115.2, 87.1, 82.9, 72.4, 71.9, 43.0, 38.6, 25.1, 23.4.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{31}\text{O}_2\text{Br}_2$ 581.0691; Found 581.0692



dimethyl 2-(2-methylallyl)-2-(3-(p-tolyl)prop-2-yn-1-yl)malonate (40f)



Isolated as a colorless oil: 67% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

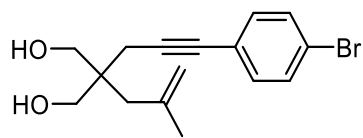
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.27-7.25 (m, 2H), 7.09-7.06 (m, 2H), 4.93 (t, 1H), 4.88 (s, 1H), 3.75 (s, 6H), 3.04 (s, 2H), 2.90 (s, 2H), 2.32 (s, 3H), 1.69 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 170.7, 139.9, 138.0, 131.4, 128.9, 120.1, 116.3, 83.9, 83.7, 56.8, 52.7, 39.7, 23.6, 23.2, 21.4.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{23}\text{O}_4$ 315.1596; Found 315.1591



2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diol (SC12)



Isolated as a white solid: 77% yield:

m.p. =101.0–102.6 °C.

R_f 0.20 (ethyl acetate/hexanes, 1/10).

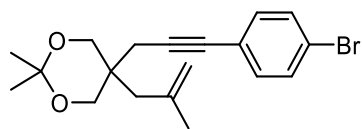
¹H NMR (CDCl₃, 400 MHz): δ 7.42-7.40 (m, 2H), 7.26-7.24 (m, 2H), 4.95 (s, 1H), 4.85 (s, 1H), 3.71 (m, 4H), 2.50 (m, 4H), 2.18 (s, 2H), 1.85 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 141.9, 133.0, 131.5, 122.5, 121.9, 115.6, 88.0, 82.4, 67.8, 43.1, 39.2, 25.1, 22.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₁₆H₂₀O₂Br 323.0647; Found 323.0637



5-(3-(4-bromophenyl)prop-2-yn-1-yl)-2,2-dimethyl-5-(2-methylallyl)-1,3-dioxane (44f)



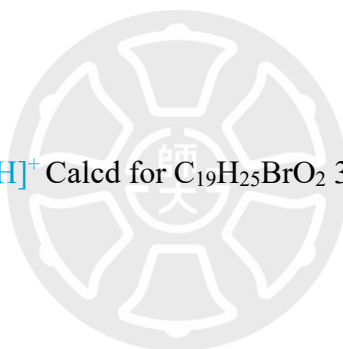
Isolated as a colorless oil: 35% yield:

R_f 0.55 (ethyl acetate/hexanes, 1/10).

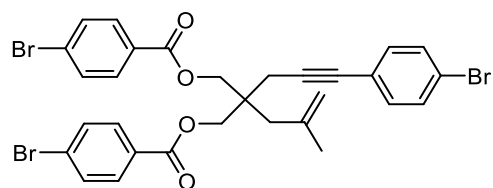
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.41-7.38 (m, 2H), 7.25-7.23 (m, 2H), 4.94 (s, 1H), 4.81 (s, 1H), 3.72 (dd, $J = 14.8, 11.6$ Hz, 4H), 2.65 (s, 2H), 2.14 (s, 2H), 1.81 (s, 3H), 1.43 (s, 6H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 140.6, 132.9, 131.4, 122.7, 121.7, 115.5, 98.0, 88.3, 82.4, 67.1, 40.1, 36.4, 26.5, 25.1, 23.3, 21.0.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{25}\text{BrO}_2$ 362.0881; Found 362.0896



2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diylbis(4-bromo benzoate) (44d)



Isolated as a white solid: 28% yield:

m.p. = 120.2–121.7 °C.

R_f 0.25 (ethyl acetate/hexanes, 1/10).

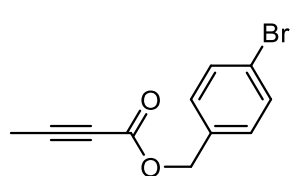
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.87-7.85 (m, 4H), 7.55-7.53 (m, 4H) 7.40-7.38 (m, 2H), 7.21-7.19 (m, 2H), 5.03 (s, 1H), 4.89 (s, 1H), 4.44 (dd, $J = 20.0, 11.6$ Hz, 4H), 2.69 (s, 2H), 2.45 (s, 2H), 1.86 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 165.4, 140.0, 133.0, 131.8, 131.5, 131.0, 128.6, 128.4, 122.2, 122.1, 116.9, 86.2, 83.1, 66.7, 41.6, 39.5, 26.5, 25.2, 24.1.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4\text{Br}_3$ 686.9381; Found 686.9357



4-bromobenzyl but-2-ynoate (DC1)



Isolated as a white solid: 95% yield:

m.p. = 101.2–102.3 °C.

R_f 0.25 (ethyl acetate/hexanes, 1/10).

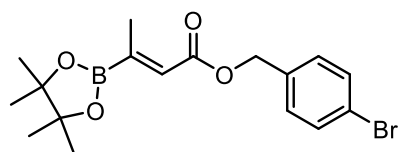
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.49–7.47 (m, 2H), 7.24–7.22 (m, 2H), 5.11 (s, 2H), 1.97 (s, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 153.2, 134.0, 131.7, 130.0, 122.5, 72.0, 66.4, 3.7.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_9\text{BrO}_2$ 252.9786; Found 252.9864



**4-bromobenzyl(Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate
(37b)**



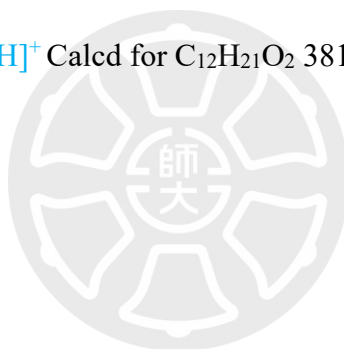
Isolated as a colorless oil: 54% yield:

R_f 0.25 (ethyl acetate/hexanes, 1/10).

$^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.49-7.46 (m, 2H), 7.26-7.23 (m, 2H), 6.49 (q, 1H), 5.10 (s, 2H), 2.19 (d, $J = 1.6$ Hz, 3H), 1.27 (s, 12H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): δ 165.7, 135.2, 131.6, 129.7, 122.1, 84.2, 83.1, 64.8, 24.8, 16.5.

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{21}\text{O}_2$ 381.0795; Found 381.0803



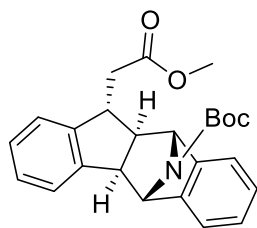
General Procedure for Rh(I)-Catalyzed Achiral Tandem Annulation

To a 4 mL sample vial, $[\text{RhCl}(\text{cod})_2]$ (1.5 mg, 1.5 mol%), acetonitrile (0.5 mL), methanol (0.1 mL), and triethylamine (0.6 mmol, 84 μL , 3.0 equiv) were added under inert atmosphere. Then, to the mixture were added arylboronic esters **23** (0.4 mmol, 2.0 equiv), followed by 1,4-dihydro-1,4-iminonaphthalene **26** (0.2 mmol, 1.0 equiv) and acetonitrile (0.5 mL). The reaction was stirred at 60 °C and monitored by TLC. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography (hexanes / ethyl acetate or hexanes / diethyl ether) to afford the desired product **27**.

General Procedure for Rh(I)-Catalyzed Asymmetric Tandem Annulation

To a 4 mL sample vial, $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (1.2 mg, 1.5 mol%), chiral diene **L5b**, acetonitrile (0.5 mL), methanol (0.1 mL), and triethylamine (0.6 mmol, 84 μL , 3.0 equiv) were added successively under inert atmosphere. The resulting mixture was stirred for 5–10 min. After that, arylboronic esters **23** (0.4 mmol, 2.0 equiv), followed by 1,4-dihydro-1,4-iminonaphthalene **26** (0.2 mmol, 1.0 equiv) and acetonitrile (0.5 mL) were added to the reaction. The reaction was stirred at 60 °C and monitored by TLC. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography (hexanes / ethyl acetate or hexanes / diethyl ether) to afford the desired product **27**.

tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)



Isolated as a white solid: 95% yield:

HPLC: 99% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 200 nm. Retention times: 12.15 min [(R)-enantiomer], 26.70 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.17$ (c 0.5, CHCl₃). m.p. = 140.2–145.8 °C. R_f = 0.3 (ether/hexanes, 1/5).

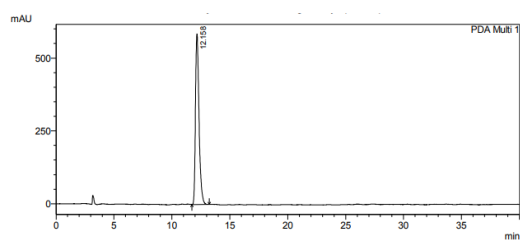
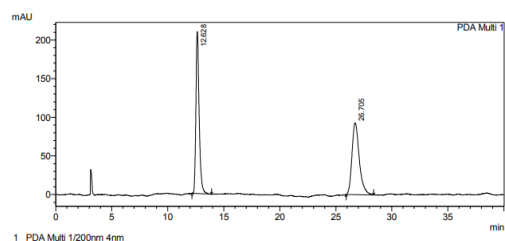
¹H NMR (CDCl₃, 500 MHz): δ 7.42 (d, *J* = 7.0 Hz, 1H), 7.35–7.31 (m, 2H), 7.29–7.22 (m, 2H), 7.19–7.13 (m, 3H), 5.28–5.12 (br, 2H), 3.84 (br, 1H), 3.75 (s, 3H), 3.47 (d, *J* = 7.0 Hz, 1H), 2.83 (dd, *J* = 16.5, 5.0 Hz, 1H), 2.49 (dd, *J* = 16.5, 10.5 Hz, 1H), 2.40 (br, 1H), 1.13 (br, 9H).

¹H NMR (DMSO-*d*₆, 500 MHz): δ 7.46 (d, *J* = 7.5 Hz, 1H), 7.43–7.41 (m, 1H), 7.34–7.32 (m, 1H), 7.26–7.23 (m, 1H), 7.21–7.14 (m, 4H), 5.11–5.07 (br, 2H), 3.67 (s, 3H), 3.61 (br, 1H), 3.36 (d, *J* = 7.5 Hz, 1H), 2.83 (dd, *J* = 16.0, 5.0 Hz, 1H), 2.54 (dd, *J* = 16.5, 9.5 Hz, 1H), 2.27 (dd, *J* = 7.5, 3.5 Hz, 1H), 1.06 (br, 9H).

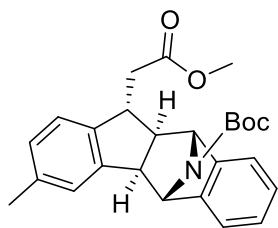
¹³C NMR (CDCl₃, 125 MHz): δ 172.6, 153.5, 147.4, 145.6, 141.7, 127.7, 127.4, 126.5, 126.4, 125.1, 124.1, 119.9, 79.4, 66.7, 66.3, 54.7, 53.7, 51.5, 44.7, 41.7, 28.0.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₅H₂₈NO₄ 406.2018; Found 406.2021

HPLC chromatogram:



tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-methyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ab)



Isolated as a white solid: 92% yield:

HPLC: 99% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 10.75 min [(R)-enantiomer], 30.92 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.10$ (c 0.5, CHCl₃). m.p. = 135.2–135.8 °C. $R_f = 0.3$ (ether/hexanes,

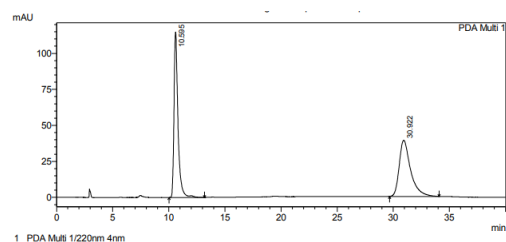
1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.41 (d, $J = 7.4$ Hz, 1H), 7.31–7.20 (m, 4H), 7.16–7.10 (m, 3H), 5.31–5.09 (br, 2H), 3.79 (br, 1H), 3.72 (s, 3H), 3.40 (br, 1H), 2.79 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.45–2.42 (br, 2H), 2.36 (s, 3H), 1.13 (br, 9H).

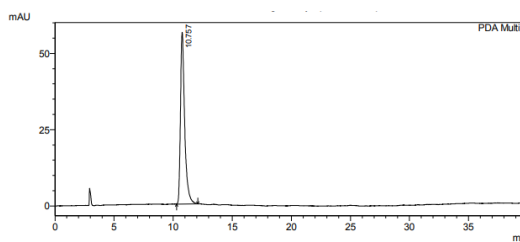
¹³C NMR (CDCl₃, 100 MHz): δ 172.6, 153.5, 147.5, 145.1, 141.6, 136.9, 128.6, 126.4, 125.6, 123.9, 119.8, 119.4, 79.0, 66.5, 65.9, 54.8, 53.8, 51.5, 43.9, 41.5, 27.8, 21.3.

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₂₆H₃₀NO₄ 420.2175; Found 420.2181

HPLC chromatogram:

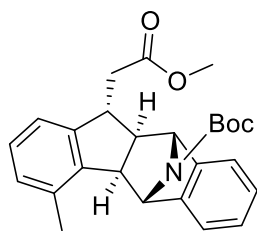


PeakTable			
Peak#	Ret. Time	Area	Area %
1	10.595	2813959	50.527
2	30.922	2755297	49.473
Total		5569257	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	10.757	1390854	100.000
Total		1390854	100.000

tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4-methyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ac)



Isolated as a white solid: 86% yield:

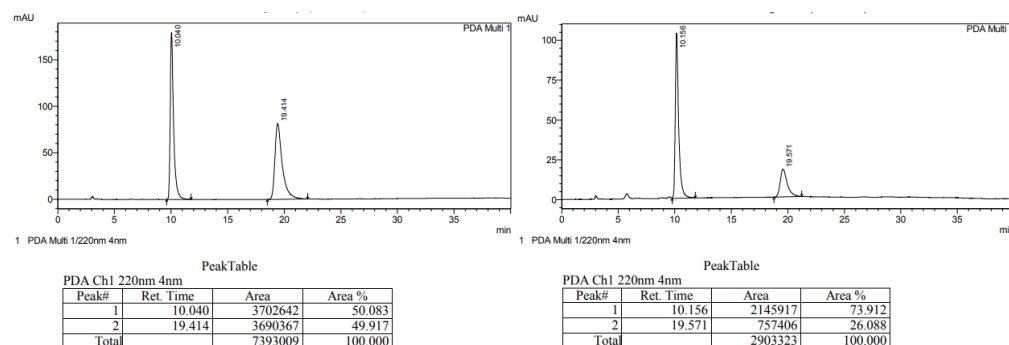
HPLC: 47% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 10.15 min [(R)-enantiomer], 19.57 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.13$ (c 0.5, CHCl₃). m.p. = 130.2–133.8 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.31–7.20 (m, 4H), 7.16–7.10 (m, 3H), 5.31–5.09 (br, 2H), 3.89 (br, 1H), 3.47 (s, 3H), 3.44 (br, 1H), 2.80 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.39 (s, 3H), 2.37 (br, 2H), 1.13 (br, 9H).

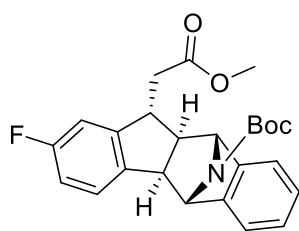
¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 153.3, 145.3, 139.8, 134.4, 128.0, 126.5, 126.4, 121.6, 119.8, 119.4, 79.1, 65.7, 64.0, 53.5, 51.5, 44.2, 41.5, 27.7, 18.9.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₆H₃₀NO₄ 420.2175; Found 420.2176

HPLC chromatogram:



tert-butyl (4bR,10aR,11R)-2-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ag)



Isolated as a white solid: 90% yield:

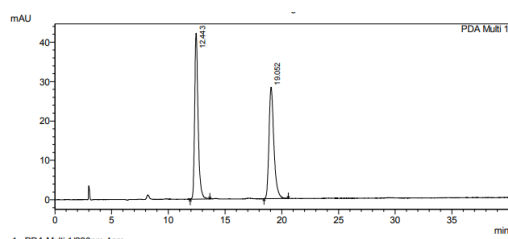
HPLC: 83% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 12.46 min [(R)-enantiomer], 19.14 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.18$ (c 0.5, CHCl₃). m.p. = 141.4–144.3 °C. $R_f = 0.3$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.41 (d, $J = 7.4$ Hz, 1H), 7.31–7.20 (m, 4H), 7.16–7.10 (m, 3H), 5.32–5.06 (br, 2H), 3.82 (br, 1H), 3.71 (s, 3H), 3.39 (br, 1H), 2.77 (dd, $J = 16.4, 4.8$ Hz, 1H), 2.46 (br, 2H), 1.16 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.1, 164.0, 161.6, 153.5, 149.5, 145.1, 144.8, 137.1, 137.1, 126.5, 126.1, 126.0, 119.9, 114.7, 110.7, 79.3, 66.5, 65.8, 54.1, 53.9, 51.6, 44.2, 41.1, 27.8.

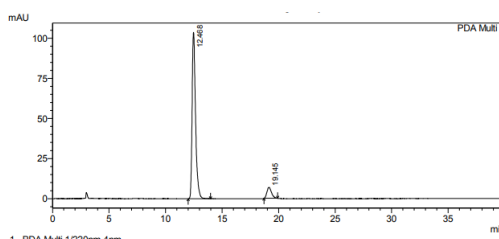
HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₂₇NO₄F 424.1924; Found 424.1914

HPLC chromatogram:



PeakTable

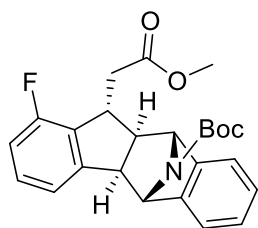
Peak#	Ret. Time	Area	Area %
1	12.443	884824	51.063
2	19.052	847981	48.937
Total		1732805	100.000



PeakTable

Peak#	Ret. Time	Area	Area %
1	12.468	2177501	91.925
2	19.145	191287	8.075
Total		2368789	100.000

tert-butyl (4bR,10aR,11R)-1-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ae)



Isolated as a white solid: 90% yield:

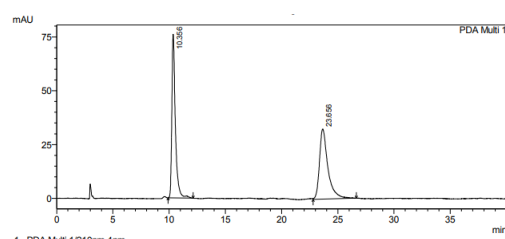
HPLC: 98% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 10.64 min [(R)-enantiomer], 24.59 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.21$ (c 0.5, CHCl₃). m.p. = 143.2–145.1 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.31–7.20 (m, 4H), 7.16–7.10 (m, 3H), 5.36–5.07 (br, 2H), 3.95 (br, 1H), 3.69 (s, 3H), 3.49 (br, 1H), 3.07 (dd, *J* = 16.4, 3.2 Hz, 1H), 2.44 (br, 2H), 1.15 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 160.6, 158.0, 153.5, 145.3, 145.1, 133.0, 129.4, 126.5, 120.7, 119.8, 114.0, 110.7, 79.9, 66.4, 65.9, 55.2, 53.9, 51.5, 42.2, 39.1, 27.7.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₅H₂₇O₄F 424.1924; Found 424.1927

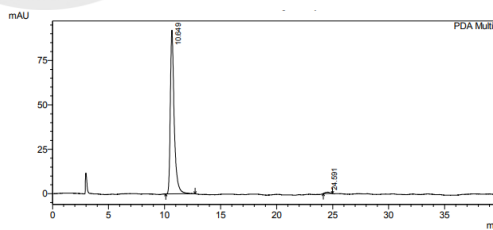
HPLC chromatogram:



1 PDA Multi 1/210nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	10.356	1651570	49.478
2	23.656	1686397	50.522
Total		3337967	100.000

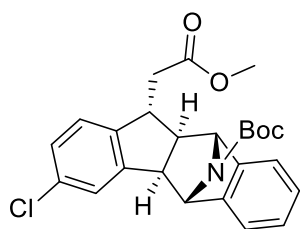


1 PDA Multi 1/210nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	10.649	2207500	99.011
2	24.591	22055	0.989
Total		2229555	100.000

tert-butyl (4bR,10aR,11R)-3-chloro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aj)



Isolated as a white solid: 89% yield:

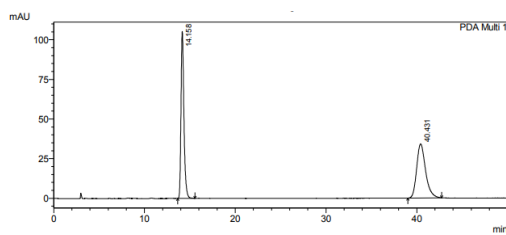
HPLC: 84% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 14.17 min [(R)-enantiomer], 40.36 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.24$ (c 0.5, CHCl₃). m.p. = 130.2–135.0 °C. $R_f = 0.3$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.39 (s, 1H), 7.31–7.29 (m, 2H), 7.19–7.14 (m, 3H), 7.04–7.02 (d, $J = 8.4$, 1H), 5.30–5.08 (br, 2H), 3.78 (br, 1H), 3.70 (s, 3H), 3.42 (br, 1H), 2.76 (dd, $J = 16.0, 4.4$ Hz, 1H), 2.46 (dd, $J = 16.4, 10.0$ Hz, 1H), 2.40 (br, 1H), 1.16 (br, 9H).

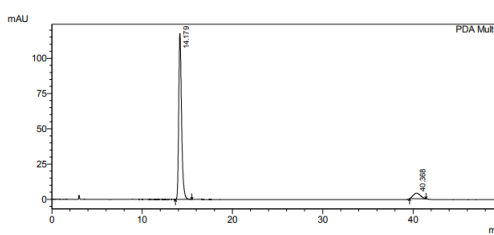
¹³C NMR (CDCl₃, 100 MHz): δ 172.2, 153.5, 145.8, 145.6, 143.6, 133.1, 127.9, 126.6, 126.5, 125.2, 119.9, 66.4, 65.9, 53.9, 51.6, 43.8, 41.2, 27.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₂₇NO₄Cl 440.1629; Found 440.1631

HPLC chromatogram:

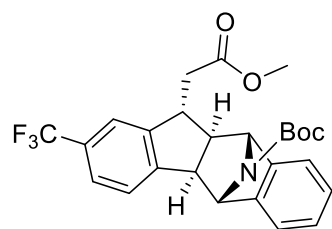


PeakTable			
Peak#	Ret. Time	Area	Area %
1	14.158	2350427	50.190
2	40.431	2332671	49.810
Total		4683099	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	14.179	2566619	92.119
2	40.368	219572	7.881
Total		2786191	100.000

tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-2-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)



Isolated as a white solid: 88% yield:

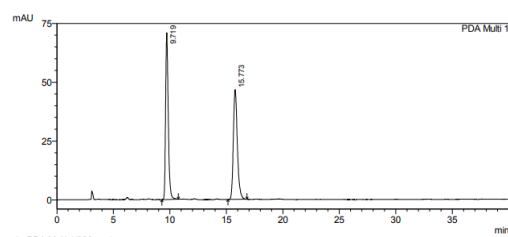
HPLC: 96% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 9.75 min [(R)- enantiomer], 15.93 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.33$ (c 0.5, CHCl₃). m.p. = 140.2–142.1 °C. $R_f = 0.3$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.41 (d, $J = 7.4$ Hz, 1H), 7.31–7.20 (m, 4H), 7.16–7.10 (m, 3H), 5.35–5.13 (br, 2H), 3.89 (br, 1H), 3.71 (s, 3H), 3.52 (br, 1H), 2.82 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.51 (br, 2H), 1.12 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.0, 153.2, 151.4, 145.1, 144.6, 142.5, 129.9 (q, $J_{C-F} = 31.8$ Hz), 126.7, 126.6, 124.6, 124.8 (q, $J_{C-F} = 3.1$ Hz), 124.6, 124.3 (q, $J_{C-F} = 270.5$ Hz), 122.1 (q, $J_{C-F} = 2.8$ Hz), 119.9, 119.7, 79.4, 66.3, 65.7, 53.8, 51.6, 44.1, 40.9, 27.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₆H₂₇NO₄F₃ 474.1892; Found 474.1888

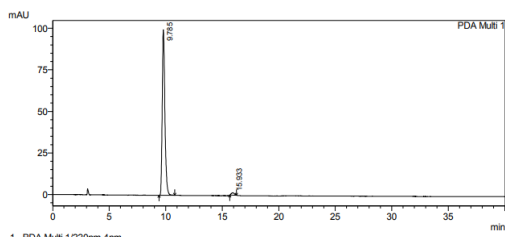
HPLC chromatogram:



1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	9.719	1156751	50.072
2	15.773	1153424	49.928
Total		2310175	100.000

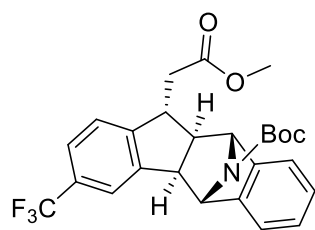


1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	9.785	1641348	98.330
2	15.933	27880	1.670
Total		1669227	100.000

tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ah)



Isolated as a white solid: 87% yield:

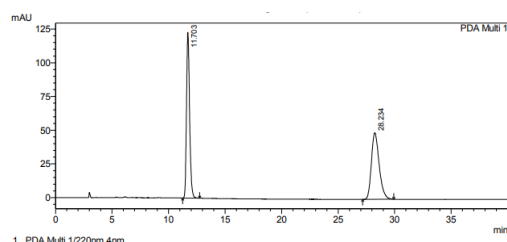
HPLC: 97% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 11.58 min [(R)-enantiomer], 28.58 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.25$ (c 0.5, CHCl₃). m.p. = 136.2–137.3 °C. $R_f = 0.3$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.69 (s, 1H), 7.49 (d, $J = 8.0$ Hz, 1H), 7.33–7.30 (m, 2H), 7.25–7.18 (m, 1H), 7.18–7.14 (m, 2H), 5.35–5.13 (br, 2H), 3.89 (br, 1H), 3.71 (s, 3H), 3.51 (br, 1H), 2.81 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.53–2.46 (br, 2H), 1.12 (br, 9H).

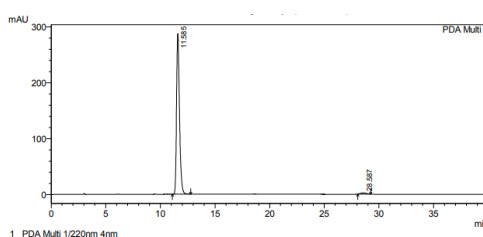
¹³C NMR (CDCl₃, 100 MHz): δ 172.1, 151.4, 145.1, 142.6, 129.9 (q, $J_{C-F} = 31.7$ Hz), 126.7, 126.6, 124.8 (q, $J_{C-F} = 3.2$ Hz), 124.5, 124.3 (q, $J_{C-F} = 270.5$ Hz), 122.0 (q, $J_{C-F} = 3.2$ Hz), 119.9, 119.7, 79.4, 66.3, 65.7, 53.8, 51.6, 44.2, 40.9, 27.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₆H₂₇NO₄F₃ 474.1892; Found 474.1887

HPLC chromatogram:

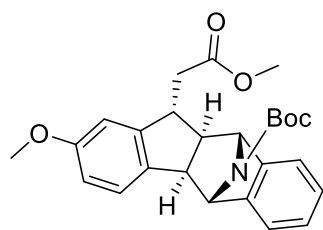


PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.703	2344985	49.842
2	28.234	2359835	50.158
Total		4704820	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.585	5394212	98.603
2	28.587	76400	1.397
Total		5470613	100.000

tert-butyl (4bR,10aR,11R)-2-methoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ak)



Isolated as a white solid: 91% yield:

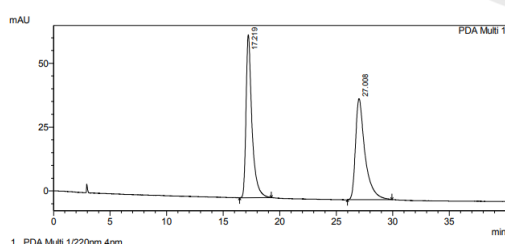
HPLC: 92% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 16.98 min [(R)-enantiomer], 26.73 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.44$ (c 0.5, CHCl₃). m.p. = 148.2–152.0 °C. $R_f = 0.25$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.30–7.27 (m, 3H), 7.14–7.12 (m, 2H), 6.83 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.63 (d, $J = 2.0$, 1H), 5.30–5.04 (br, 2H), 3.81 (br, 1H), 3.76 (s, 3H), 3.72 (br, 3H), 3.37 (br, 1H), 2.79 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.47–2.32 (br, 2H), 1.14 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.4, 159.8, 153.6, 148.8, 145.3, 133.6, 126.4, 125.6, 119.8, 119.5, 114.2, 108.6, 79.1, 66.5, 65.8, 55.3, 54.1, 53.9, 51.5, 44.4, 41.4, 27.8.

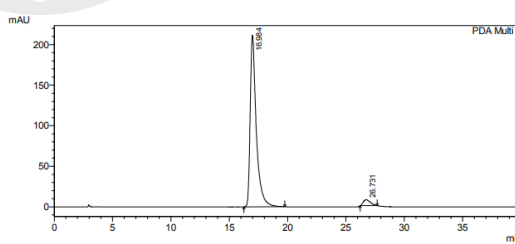
HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₆H₃₀NO₅ 436.2124; Found 436.2126

HPLC chromatogram:



PeakTable

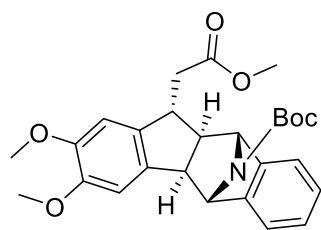
Peak#	Ret. Time	Area	Area %
1	17.219	2322904	50.214
2	27.008	2303136	49.786
Total		4626041	100.000



PeakTable

Peak#	Ret. Time	Area	Area %
1	16.984	7688198	96.147
2	26.731	308084	3.853
Total		7996281	100.000

tert-butyl (4bR,10aR,11R)-2,3-dimethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27am)



Isolated as a white solid: 91% yield:

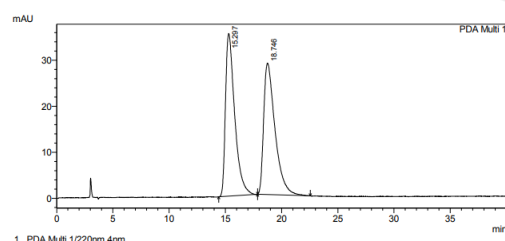
HPLC: 99% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 15.29 min [(R)- enantiomer], 18.74 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.12$ (c 0.5, CHCl₃). m.p. = 155.2–158.7 °C. $R_f = 0.3$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.30–7.28 (m, 2H), 7.16–7.12 (m, 2H), 6.89 (s, 1H), 6.61 (s, 1H), 5.31–5.08 (br, 2H), 3.91 (s, 3H) 3.82–3.71 (br, 1H), 3.71 (br, 3H), 3.39 (br, 1H), 2.77 (dd, $J = 16.6, 4.4$ Hz, 1H), 2.45–2.33 (br, 2H), 1.16 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.4, 153.2, 148.9, 145.1, 144.7, 132.9, 126.3, 119.6, 119.4, 107.2, 106.5, 78.9, 66.0, 65.6, 55.8, 54.0, 51.4, 44.1, 41.5, 27.7.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₇H₃₂NO₆ 466.2230; Found 466.2224

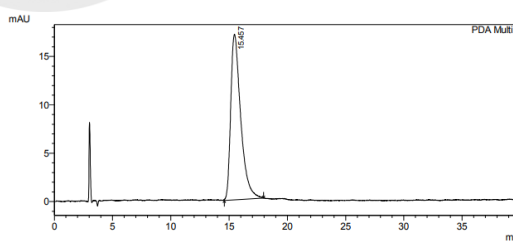
HPLC chromatogram:



1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	15.297	2011864	50.074
2	18.746	2005884	49.926
Total		4017747	100.000

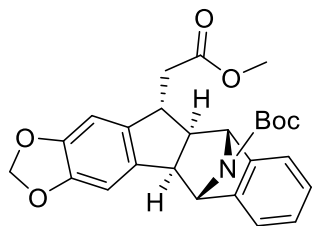


1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	15.457	1018265	100.000
Total		1018265	100.000

tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[6,7]fluoreno[2,3-d][1,3]dioxole-13-carboxylate (27an)



Isolated as a white solid: 94% yield:

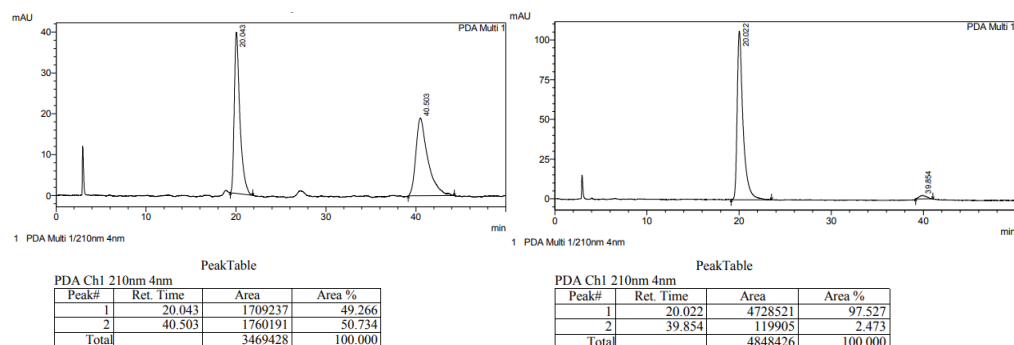
HPLC: 95% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 20.02 min [(R)-enantiomer], 39.85 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.12$ (c 0.5, CHCl₃). m.p. = 150.1–152.4 °C. $R_f = 0.1$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.29–7.26 (m, 2H), 7.14–7.12 (m, 2H), 6.82 (s, 1H), 6.54 (s, 1H), 5.93–5.91 (s, 2H), 5.27–5.02 (br, 2H), 3.71 (s, 3H), 3.63 (br, 1H), 3.32 (br, 1H), 2.72 (dd, $J = 16.0, 4.4$ Hz, 1H), 2.43–2.37 (br, 2H), 1.19 (br, 9H).

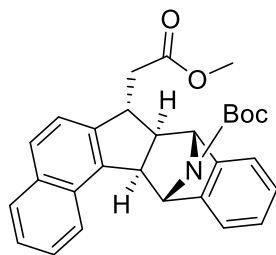
¹³C NMR (CDCl₃, 100 MHz): δ 172.4, 153.7, 147.7, 147.5, 145.2, 144.8, 140.1, 134.2, 126.4, 119.8, 104.8, 104.1, 101.1, 79.1, 66.3, 65.8, 54.3, 54.0, 51.5, 44.0, 41.6, 27.9.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₆H₂₈NO₆ 450.1917; Found 450.1911

HPLC chromatogram:



tert-butyl (7R,7aR,13aR)-7-(2-methoxy-2-oxoethyl)-7a,8,13,13a-tetrahydro-7H-8,13-epiminodibenzo[b,g]fluorene-14-carboxylate (27ad)



Isolated as a white solid: 88% yield:

HPLC: 32% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 11.07 min [(R)-enantiomer], 46.48 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.66$ (c 0.5, CHCl₃). m.p. = 120.2–125.5 °C. $R_f = 0.4$ (ether/hexanes,

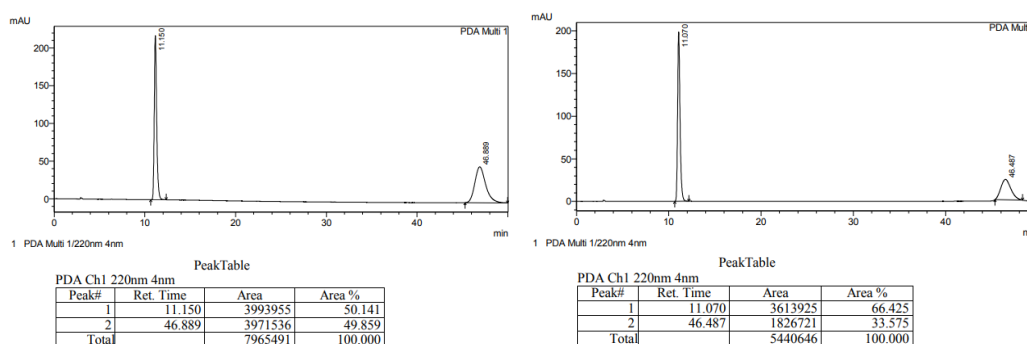
1/5).

¹H NMR (CDCl₃, 400 MHz): δ 8.05 (d, $J = 7.6$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.61–7.59 (m, 1H), 7.50–7.43 (m, 2H), 7.35–7.32 (m, 1H), 7.25–7.15 (m, 3H), 5.42–5.23 (br, 2H), 4.04 (br, 1H), 3.87 (br, 1H), 3.72 (s, 3H), 2.89 (dd, $J = 16.0, 4.0$ Hz, 1H), 2.53 (br, 1H), 2.46 (dd, $J = 16.0, 4.0$ Hz, 1H), 0.95 (br, 9H).

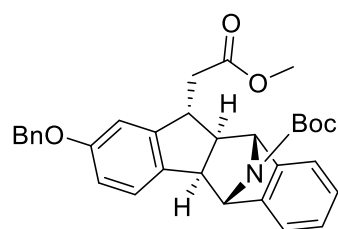
¹³C NMR (CDCl₃, 100 MHz): δ 172.4, 153.1, 145.2, 145.0, 144.2, 136.3, 133.2, 130.3, 128.8, 128.7, 126.5, 126.5, 126.5, 125.3, 123.7, 122.3, 119.8, 119.6, 78.7, 65.6, 64.4, 53.9, 51.5, 44.9, 41.4, 27.4.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₉H₃₀NO₄ 456.2175; Found 456.2170

HPLC chromatogram:



tert-butyl (4bR,10aR,11R)-2-(benzyloxy)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ap)



Isolated as a white solid: 83% yield:

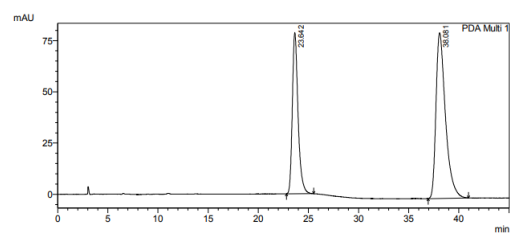
HPLC: 89% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 22.49 min [(R)- enantiomer], 36.72 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.43$ (c 0.5, CHCl₃). m.p. = 140.8–145.8 °C. $R_f = 0.2$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.43-7.36 (m, 4H), 7.34-7.27 (m, 4H), 7.16–7.11 (m, 4H), 6.90 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.71 (d, $J = 2.0$, 1H), 5.30–4.98 (br, 4H), 3.80 (br, 1H), 3.71 (s, 3H), 3.37 (br, 1H), 2.77 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.46-2.33 (br, 2H), 1.15 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 159.7, 153.7, 148.9, 145.4, 145.1, 137.0, 134.0, 128.6, 127.9, 127.4, 126.4, 125.7, 119.9, 119.6, 115.0, 79.2, 70.2, 66.6, 65.9, 54.1, 54.0, 51.6, 44.4, 41.4, 29.7, 27.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₂H₃₄NO₅ 512.2437; Found 512.2436

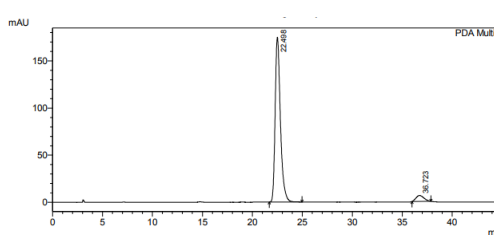
HPLC chromatogram :



1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	23.642	3119257	37.039
2	38.081	5302216	62.961
Total		8421473	100.000

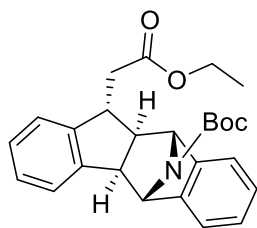


1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	22.498	6406964	94.828
2	36.723	349414	5.172
Total		6756379	100.000

tert-butyl (4bR,10aR,11R)-11-(2-ethoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aq)



Isolated as a white solid: 96% yield:

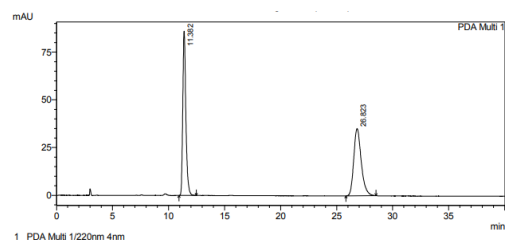
HPLC: 99% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 11.17 min [(R)-enantiomer], 26.82 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.11$ (c 0.5, CHCl₃). m.p. = 130.2–136.6 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.32–7.19 (m, 4H), 7.16–7.10 (m, 3H), 5.33–5.09 (br, 2H), 4.21–4.17 (s, 2H), 3.84–3.74 (br, 1H), 3.48–3.44 (br, 1H), 2.81 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.45–2.39 (br, 2H), 1.29 (t, 3H), 1.31–1.01 (br, 9H).

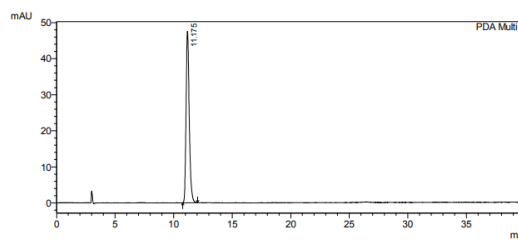
¹³C NMR (CDCl₃, 100 MHz): δ 172.0, 153.5, 147.5, 145.4, 145.2, 141.5, 127.6, 126.4, 125.0, 124.2, 119.8, 79.2, 77.3, 77.0, 76.7, 66.5, 65.8, 60.4, 54.7, 53.5, 44.3, 41.8, 27.8, 14.3.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₆H₃₀NO₄ 420.2175; Found 420.2174

HPLC chromatogram :

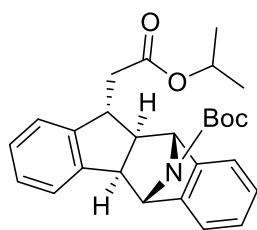


PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.382	1652598	50.177
2	26.823	1640938	49.823
Total		3293536	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.175	893773	100.000
Total		893773	100.000

tert-butyl (4bR,10aR,11R)-11-(2-isopropoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ar)



Isolated as a white solid: 91% yield:

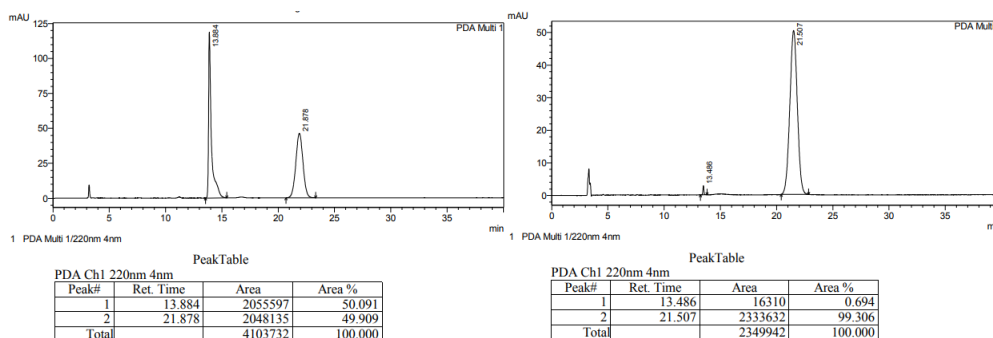
HPLC: 98% ee. The ee was determined on a Chiralpak IC column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 8.78 min [(R)-enantiomer], 18.44 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.19$ (c 0.5, CHCl₃). m.p. = 128.2–135.8 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.40 (d, *J* = 7.2 Hz, 1H), 7.32–7.19 (m, 4H), 7.16–7.11 (m, 3H), 5.32–5.09 (br, 3H), 3.83–3.73 (br, 1H), 3.49–3.44 (br, 1H), 2.79 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.40 (br, 1H), 1.30 (br, 3H), 1.26 (d, 3H), 1.29 (t, 3H), 1.13 (br, 9H).

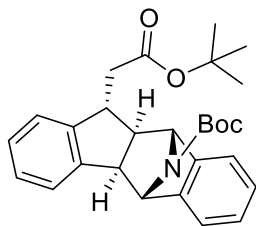
¹³C NMR (CDCl₃, 100 MHz): δ 171.5, 153.4, 147.5, 145.8, 145.4, 145.1, 141.4, 127.6, 126.4, 125.0, 124.2, 119.7, 119.6, 79.1, 66.4, 65.8, 54.7, 53.3, 44.4, 42.2, 27.7, 21.9, 21.9.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₇H₃₂NO₄ 434.2331; Found 434.2327

HPLC chromatogram :



tert-butyl (4bR,10aR,11R)-11-(2-(tert-butoxy)-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27as)



Isolated as a white solid: 93% yield:

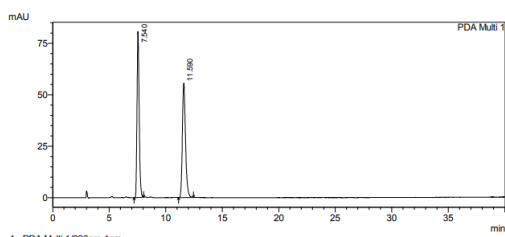
HPLC: 94% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 7.57 min [(R)-enantiomer], 11.71 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.17$ (c 0.5, CHCl₃). m.p. = 128.1–133.8 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.32 (m, 1H), 7.26–7.18 (m, 3H), 7.15–7.11 (m, 3H), 5.31–5.09 (br, 2H), 3.81–3.71 (br, 1H), 3.43 (br, 1H), 2.74 (dd, *J* = 15.2, 4.0 Hz, 1H), 2.41–2.28 (br, 2H), 1.48 (s, 9H), 1.13 (br, 9H).

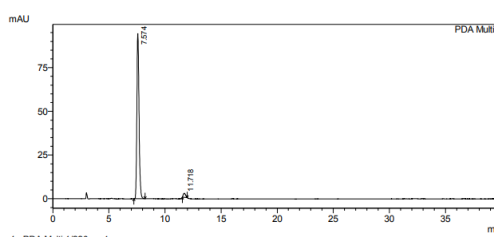
¹³C NMR (CDCl₃, 100 MHz): δ 171.3, 153.4, 147.6, 145.4, 145.1, 141.4, 127.6, 126.4, 124.9, 124.2, 119.7, 119.6, 80.5, 79.1, 66.4, 65.9, 54.7, 53.1, 44.6, 43.1, 28.1.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₈H₃₄NO₄ 448.2488; Found 448.2478

HPLC chromatogram :

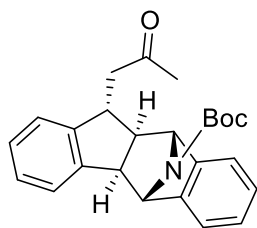


PeakTable			
Peak#	Ret. Time	Area	Area %
1	7.540	1070714	49.897
2	11.590	1075145	50.103
Total		2145859	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	7.574	1260146	97.439
2	11.718	33115	2.561
Total		1293261	100.000

tert-butyl (4bR,10aR,11R)-11-(2-oxopropyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27at)



Isolated as a white solid: 95% yield:

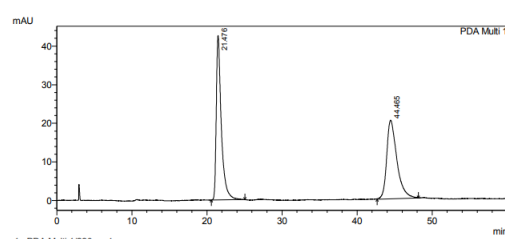
HPLC: 79% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 21.23 min [(R)-enantiomer], 43.53 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.24$ (c 0.5, CHCl₃). m.p. = 160.7–162.6 °C. R_f = 0.1 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, *J* = 7.2 Hz, 1H), 7.31 (m, 2H), 7.26–7.18 (m, 1H), 7.15–7.10 (m, 2H), 7.08–7.07 (m, 1H), 5.45–5.09 (br, 2H), 3.85–3.76 (br, 1H), 3.40 (br, 1H), 2.93 (dd, *J* = 17.6, 3.6 Hz, 1H), 2.60–2.58 (br, 1H), 2.19 (s, 1H), 2.14 (s, 3H), 1.12 (br, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 207.2, 153.4, 147.8, 145.5, 145.0, 141.5, 127.6, 126.4, 126.3, 125.0, 124.0, 119.9, 79.0, 66.5, 53.8, 51.4, 43.4, 30.2, 27.7.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₅H₂₈NO₃ 390.2069; Found 390.2059

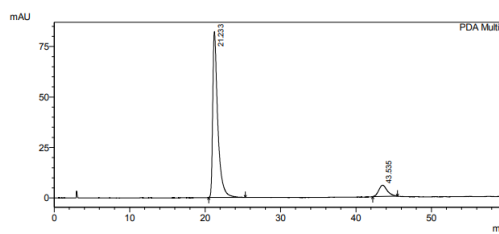
HPLC chromatogram :



1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	21.476	1982654	50.809
2	44.465	1919524	49.191
Total		3902178	100.000

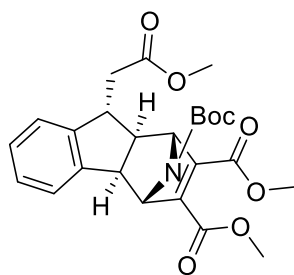


1 PDA Multi 1/220nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	21.233	3817882	89.748
2	43.535	436113	10.252
Total		4253995	100.000

10-(tert-butyl) 2,3-dimethyl (4aR,9R,9aR)-9-(2-methoxy-2-oxoethyl)-4,4a,9,9a-tetrahydro-1H-1,4-epiminofluorene-2,3,10-tricarboxylate (27ga)



Isolated as a white solid: 88% yield:

HPLC: 80% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 18.75 min [(R)-enantiomer], 23.17 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.33$ (c 0.5, CHCl₃). m.p. = 100.9–105.5 °C. $R_f = 0.2$ (ether/hexanes,

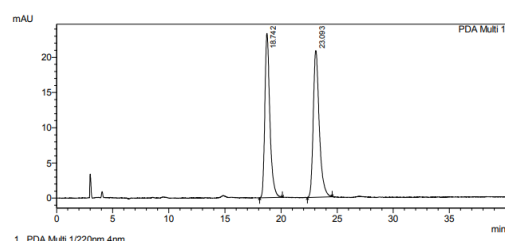
1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.36–7.34 (m, 1H), 7.27–7.20 (m, 2H), 7.10–7.08 (m, 1H), 5.13–4.94 (br, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H), 3.65–3.60 (br, 2H), 2.83 (dd, $J = 16.0, 4.8$ Hz, 1H), 2.53–2.47 (br, 2H), 1.20 (br, 9H).

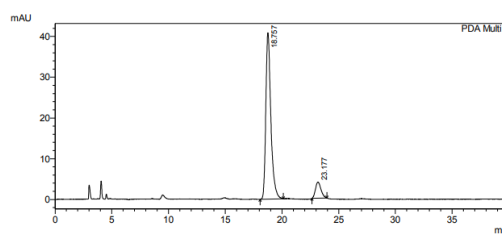
¹³C NMR (CDCl₃, 100 MHz): δ 174.6, 172.2, 163.3, 163.0, 147.3, 144.7, 140.2, 128.0, 127.5, 124.9, 124.1, 80.4, 67.9, 67.3, 52.4, 52.3, 51.6, 43.8, 41.3, 27.9.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₃₀NO₈ 472.1971; Found 472.1978

HPLC chromatogram :

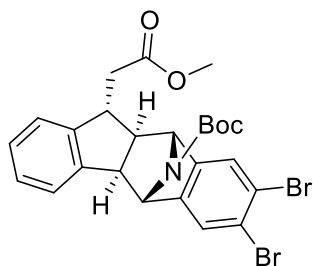


PeakTable			
Peak#	Ret. Time	Area	Area %
1	18.742	722777	48.341
2	23.093	772374	51.659
Total		1495151	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	18.757	1259135	90.312
2	23.177	135065	9.688
Total		1394200	100.000

tert-butyl (4bR,10aR,11R)-7,8-dibromo-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ha)



Isolated as a white solid: 93% yield:

HPLC: 95% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 10.72 min [(R)- enantiomer], 17.86 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.15$ (c 0.5, CHCl₃). m.p. = 131.2–137.8 °C. $R_f = 0.3$

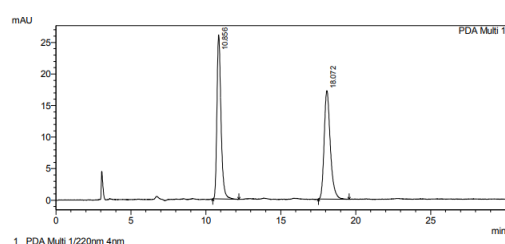
(ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.59 (m, 1H), 7.37 (d, $J = 6.8$, 1H), 7.28–7.21 (m, 2H), 7.10 (d, $J = 7.2$, 1H), 6.93–6.91 (m, 1H), 5.29–5.04 (br, 2H), 3.78 (br, 1H), 3.79 (br, 1H), 3.72 (s, 3H), 3.42 (br, 1H), 2.83 (dd, $J = 16.4, 4.0$ Hz, 1H), 2.47 (dd, $J = 16.4, 10.8$ Hz, 1H), 2.35 (br, 2H), 1.15 (br, 9H).

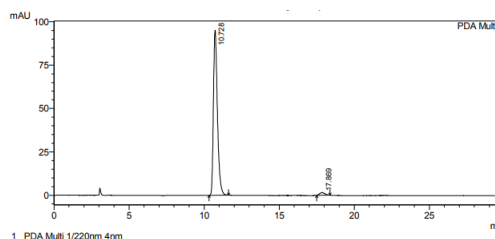
¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 153.6, 146.4, 140.8, 127.9, 124.9, 124.1, 122.4, 80.0, 66.1, 65.4, 54.4, 53.2, 51.6, 44.4, 41.1, 27.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₂₆NO₄Br₂ 562.0229; Found 562.0223

HPLC chromatogram :

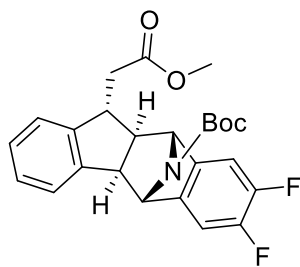


PDA Ch1 220nm 4nm			
Peak#	Ret. Time	Area	Area %
1	10.856	490706	50.045
2	18.072	489820	49.955
Total		980526	100.000



PDA Ch1 220nm 4nm			
Peak#	Ret. Time	Area	Area %
1	10.728	1754703	97.930
2	17.869	37091	2.070
Total		1791795	100.000

tert-butyl (4bR,10aR,11R)-7,8-difluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ia)



Isolated as a white solid: 90% yield:

HPLC: 95% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 14.02 min [(R)-enantiomer], 25.01 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.18$ (c 0.5, CHCl₃). m.p. = 139.2–141.1 °C. $R_f = 0.3$ (ether/hexanes,

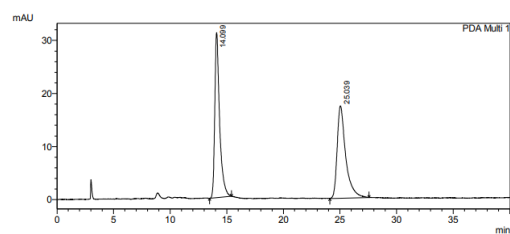
1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.38 (d, $J = 7.2$, 1H), 7.27–7.10 (m, 5H), 5.30–5.06 (br, 2H), 3.78 (br, 1H), 3.78 (br, 1H), 3.72 (s, 3H), 3.41 (br, 1H), 2.83 (dd, $J = 16.4$, 4.0 Hz, 1H), 2.47 (dd, $J = 16.4$, 10.8 Hz, 1H), 2.34 (br, 2H), 1.15 (br, 9H).

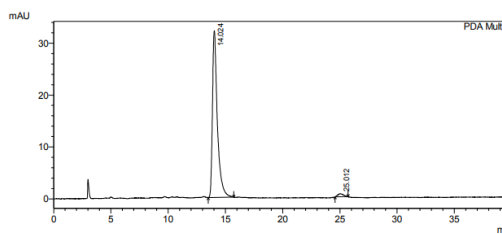
¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 153.6, 150.1 (dd, $J_{C-F} = 15.0$, 4.0 Hz), 147.7 (dd, $J_{C-F} = 15.0$, 4.0 Hz), 147.1, 141.4, 140.9, 127.8, 127.5, 124.9, 124.0, 110.0, 79.7, 66.3, 65.8, 54.6, 53.4, 51.6, 44.3, 41.1, 27.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₂₆NO₄F₂ 442.1830; Found 442.1820

HPLC chromatogram :

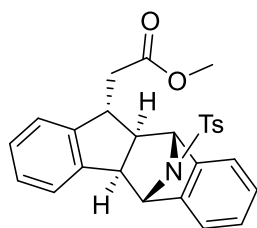


PeakTable			
Peak#	Ret. Time	Area	Area %
1	14.024	919645	50.244
2	25.012	910712	49.756
Total		1830357	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	14.024	954604	97.919
2	25.012	20287	2.081
Total		974891	100.000

methyl 2-((4bR,10aR,11R)-12-tosyl-4b,10,10a,11-tetrahydro-5H-5,10-epimino benzo [b]fluoren-11-yl)acetate (27ba)



Isolated as a white solid: 92% yield:

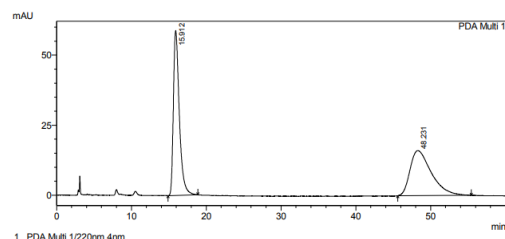
HPLC: 87% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 16.28 min [(R)-enantiomer], 48.29 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.26$ (c 0.5, CHCl₃). m.p. = 148.7–151.1 °C. R_f = 0.2 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.34–7.31 (m, 1H), 7.27–7.22 (m, 2H), 7.18 (d, *J* = 8.4, 2H), 7.15–7.13 (m, 1H), 7.06 (d, *J* = 6.8, 1H), 6.99 (d, *J* = 7.6, 1H), 6.95–6.88 (m, 2H), 6.86 (d, *J* = 8.0, 2H), 5.08 (s, 1H), 4.93 (s, 1H), 3.70 (s, 3H), 3.67 (ddd, *J* = 10.8, 4.0 Hz, 1H), 3.39 (d, *J* = 7.2, 1H), 2.86 (dd, *J* = 16.4, 4.0 Hz, 1H), 2.48 (dd, *J* = 16.4, 10.4 Hz, 1H), 2.37 (dd, *J* = 7.2, 3.2 Hz, 1H), 2.22 (s, 3H).

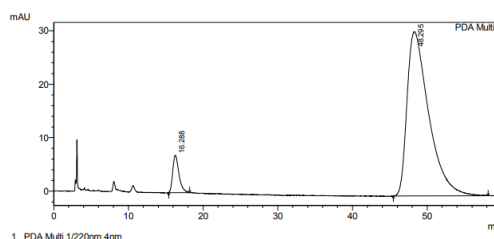
¹³C NMR (CDCl₃, 100 MHz): δ 172.7, 147.4, 143.6, 142.6, 140.9, 135.4, 128.7, 127.7, 127.6, 127.5, 126.6, 124.5, 123.8, 120.4, 120.2, 69.7, 69.7, 55.0, 53.3, 51.6, 45.0, 40.7, 21.3.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₇H₂₆NO₄S 460.1583; Found 460.1589

HPLC chromatogram :

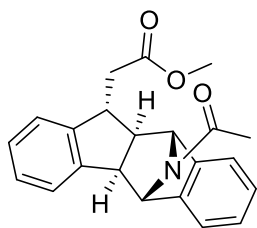


PeakTable			
Peak#	Ret. Time	Area	Area %
1	15.912	3252327	50.632
2	48.231	3171138	49.368
Total		6423464	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	16.288	406705	6.152
2	48.295	6204214	93.848
Total		6610919	100.000

methyl 2-((4bR,10aR,11R)-12-acetyl-4b,10,10a,11-tetrahydro-5H-5,10-epimino benzo[b]fluoren-11-yl)acetate (27ea)



Isolated as a white solid: 86% yield:

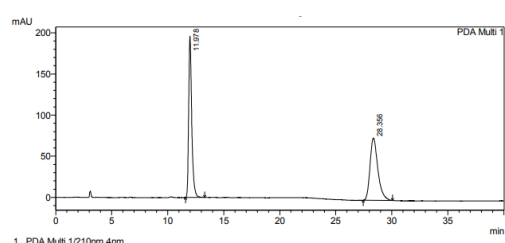
HPLC: 99% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 11.91 min [(R)-enantiomer], 28.70 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.24$ (c 0.5, CHCl₃). m.p. = 144.0–147.6 °C. R_f = 0.15 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.42–7.38 (m, 2H), 7.38–7.30 (m, 2H), 7.28–7.20 (m, 2H), 7.20–7.09 (m, 4H), 7.06 (d, *J* = 6.8, 1H), 6.99 (d, *J* = 7.6, 1H), 6.95–6.88 (m, 2H), 5.70 (s, 1H), 4.98 (s, 1H), 3.78 (ddd, *J* = 9.6, 3.6 Hz, 1H), 3.69 (s, 3H), 3.54 (d, *J* = 7.2, 1H), 2.75 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.44–2.39 (m, 2H), 1.34 (s, 3H).

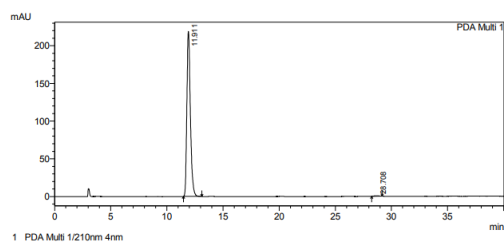
¹³C NMR (CDCl₃, 100 MHz): δ 172.2, 166.0, 147.3, 144.6, 144.2, 140.5, 128.1, 127.5, 126.8, 126.6, 124.5, 123.8, 120.1, 119.4, 67.4, 63.9, 54.6, 52.7, 51.4, 44.1, 41.0, 20.1.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ C₂₂H₂₂NO₃ 348.1600; Found 348.1607

HPLC chromatogram :

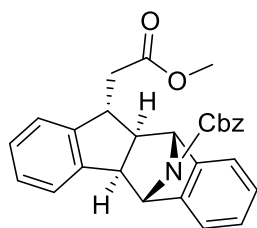


PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.978	3723318	50.323
2	28.356	3675470	49.677
Total		7398788	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.911	4766197	99.692
2	28.708	14733	0.308
Total		4780930	100.000

benzyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27da)



Isolated as a white solid: 90% yield:

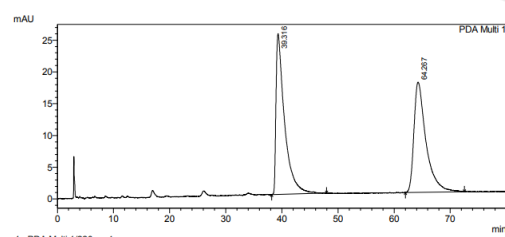
HPLC: 92% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 38.49 min [(R)-enantiomer], 63.76 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.20$ (c 0.5, CHCl₃). m.p. = 141.3–143.7 °C. R_f = 0.2 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.13 (m, 12H), 6.94 (m, 1H), 5.36-5.18 (br, 2H), 4.87-4.50 (br, 2H), 3.70 (s, 3H), 3.80-3.66 (br, 1H), 3.46 (s, 1H), 2.80 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.47 (dd, *J* = 16.4, 10.4 Hz, 1H), 2.38 (br, 1H).

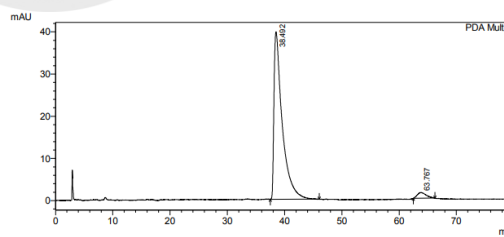
¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 155.0, 147.2, 145.2, 141.3, 136.4, 128.2, 127.7, 127.5, 126.7, 124.9, 124.0, 120.2, 66.9, 66.5, 54.6, 53.0, 51.6, 44.7, 41.3, 30.3.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₈H₂₆NO₄ 440.1862; Found 440.1862

HPLC chromatogram :

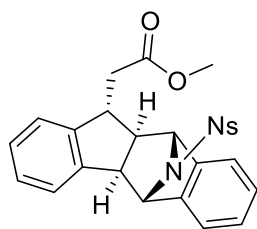


PeakTable			
Peak#	Ret. Time	Area	Area %
1	39.316	2679249	50.825
2	64.267	2592320	49.175
Total		5271569	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	38.492	3983466	96.477
2	63.767	145457	3.523
Total		4128923	100.000

methyl 2-((4bR,10aR,11R)-12-((4-nitrophenyl)sulfonyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl)acetate (27ca)



Isolated as a white solid: 95% yield:

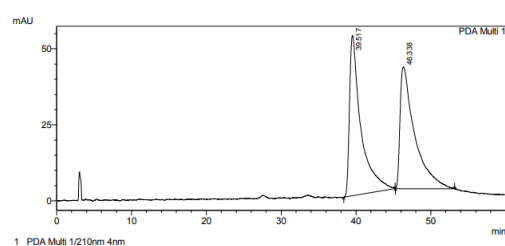
HPLC: 95% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 38.66 min [(R)-enantiomer], 46.29 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.13$ (c 0.5, CHCl₃). m.p. = 166.5–168.8 °C. R_f = 0.1 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.90 (d, *J* = 8.8, 2H), 7.50 (d, *J* = 8.8, 2H), 7.36–7.34 (m, 1H), 7.29–7.25 (m, 2H), 7.17–7.14 (m, 1H), 7.08 (d, *J* = 6.8, 1H), 7.01 (d, *J* = 6.8, 1H), 6.95–6.88 (m, 2H), 5.18 (s, 1H), 5.00 (s, 1H), 3.72 (s, 3H), 3.68 (ddd, *J* = 11.2, 3.2 Hz, 1H), 3.44 (d, *J* = 7.2, 1H), 2.89 (dd, *J* = 16.8, 4.0 Hz, 1H), 2.49 (dd, *J* = 17.2, 11.2 Hz, 1H), 2.41 (dd, *J* = 7.6, 3.6 Hz, 1H).

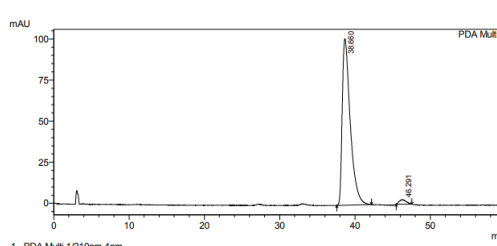
¹³C NMR (CDCl₃, 100 MHz): δ 172.7, 149.3, 147.2, 144.4, 143.4, 140.5, 128.8, 128.1, 127.7, 127.0, 124.5, 123.3, 120.6, 120.4, 70.2, 70.0, 54.9, 53.3, 51.6, 45.0, 40.6.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ C₂₆H₂₃N O₆S 491.1277; Found 491.1271

HPLC chromatogram :

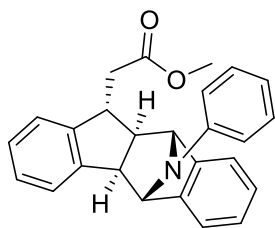


PeakTable			
Peak#	Ret. Time	Area	Area %
1	38.660	5567736	50.568
2	46.291	5442669	49.432
Total		11010405	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	38.660	7503328	97.765
2	46.291	171502	2.235
Total		7674829	100.000

methyl 2-((4bR,10aR,11R)-12-benzoyl-4b,10,10a,11-tetrahydro-5H-5,10-epimino benzo[b]fluoren-11-yl)acetate (27fa)



Isolated as a white solid: 93% yield:

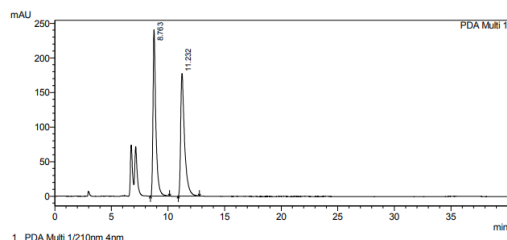
HPLC: 95% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 8.73 min [(R)-enantiomer], 11.16 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.17$ (c 0.5, CHCl₃). m.p. = 151.3–155.6 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, *J* = 7.6, 2H), 7.31–7.15 (m, 4H), 7.29–7.25 (m, 2H), 7.10–7.04 (m, 3H), 7.01–6.97 (m, 2H), 6.65–6.62 (m, 1H), 5.06 (s, 1H), 4.89 (s, 1H), 3.74 (s, 3H), 3.72 (br, 1H), 3.44 (d, *J* = 7.6, 1H), 2.89 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.54 (dd, *J* = 16.4, 10.8 Hz, 1H), 2.40 (dd, *J* = 7.6, 3.6 Hz, 1H).

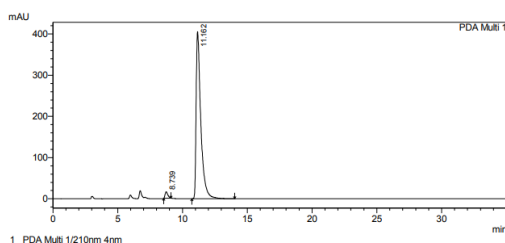
¹³C NMR (CDCl₃, 100 MHz): δ 173.1, 148.0, 147.8, 145.5, 145.1, 142.8, 128.5, 127.3, 127.2, 126.6, 124.2, 121.3, 121.0, 119.9, 118.1, 70.9, 70.5, 54.4, 53.1, 51.6, 45.7, 40.1.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₆H₂₃NO₂ 382.1801; Found 382.1729

HPLC chromatogram :

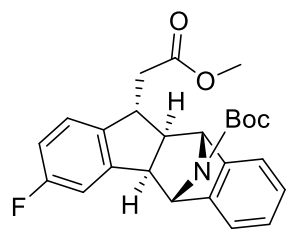


PeakTable			
Peak#	Ret. Time	Area	Area %
1	8.763	4236370	50.123
2	11.232	4215569	49.877
Total		8451940	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	8.739	231598	2.226
2	11.162	10173053	97.774
Total		10404652	100.000

tert-butyl (4bR,10aR,11R)-3-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27af)



Isolated as a white solid: 91% yield:

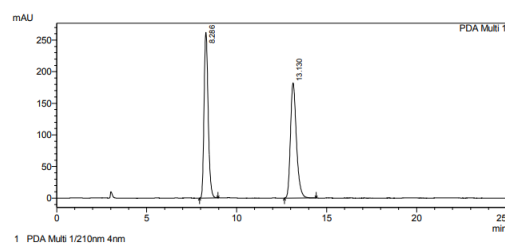
HPLC: 90% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 8.26 min [(R)-enantiomer], 13.05 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.21$ (c 0.5, CHCl₃). m.p. = 141.8–143.8 °C. $R_f = 0.3$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.31-7.29 (m, 2H), 7.16–7.14 (m, 2H), 7.09–7.02 (m, 2H), 6.93–6.91 (m, 1H), 5.31–5.08 (br, 2H), 3.78 (br, 1H), 3.70 (s, 3H), 3.41 (br, 1H), 2.77 (dd, $J = 16.4, 4.8$ Hz, 1H), 2.48-2.42 (br, 2H), 1.16 (br, 9H).

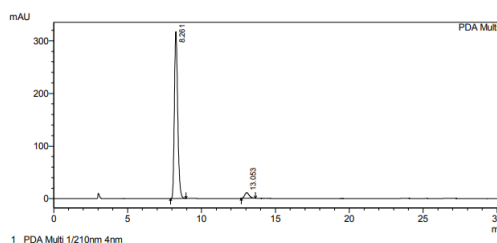
¹³C NMR (CDCl₃, 100 MHz): δ 172.3, 162.6 (d, $J_{C-F} = 242.0$ Hz), 155.0, 144.5 (d, $J_{C-F} = 153.0$ Hz), 144.8, 143.6, 142.8, 126.5 (d, $J_{C-F} = 20.0$ Hz), 125.2, 119.9, 114.9 (d, $J_{C-F} = 22.0$ Hz), 111.6 (d, $J_{C-F} = 23.0$ Hz), 79.3, 66.3, 65.8, 54.5, 54.1, 51.5, 43.6, 41.4, 27.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₂₇NO₄F 424.1924; Found 424.1923

HPLC chromatogram :

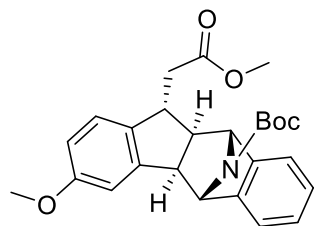


PeakTable			
Peak#	Ret. Time	Area	Area %
1	8.286	4148294	49.764
2	13.130	4187656	50.236
Total		8335950	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	8.261	4975211	95.484
2	13.053	235330	4.516
Total		5210541	100.000

tert-butyl (4bR,10aR,11R)-3-methoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)



Isolated as a white solid: 91% yield:

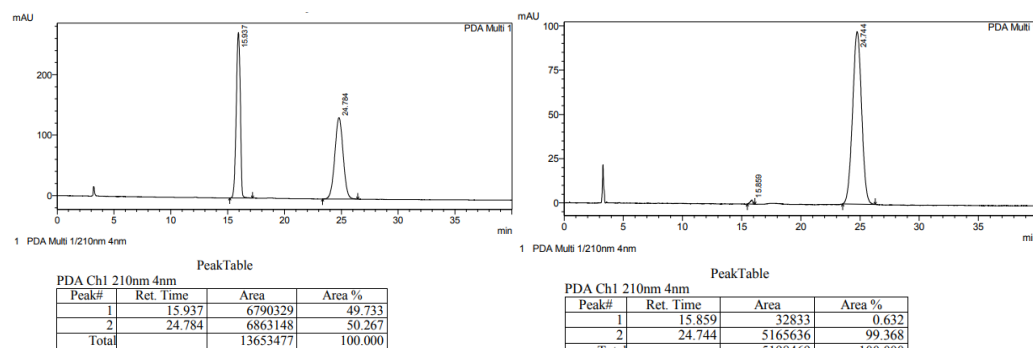
HPLC: 98% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 10.70 min [(R)-enantiomer], 18.08 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.20$ (c 0.5, CHCl₃). m.p. = 148.9–152.7 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.30–7.25 (m, 2H), 7.14–7.12 (m, 2H), 6.99 (d, *J* = 8.4, 1H), 6.91 (s, 1H), 6.79 (d, *J* = 6.0, 1H), 5.31–5.10 (br, 2H), 3.81 (s, 3H), 3.81–3.70 (br, 1H), 3.70 (s, 3H), 3.39 (br, 1H), 2.76 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.45–2.38 (br, 2H), 1.15 (br, 9H).

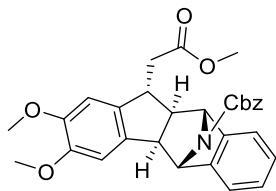
¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 159.4, 153.4, 145.3, 144.9, 142.8, 139.3, 126.4, 126.3, 124.7, 119.8, 111.4, 109.4, 79.1, 66.3, 65.8, 55.3, 54.1, 51.4, 43.5, 41.5, 27.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₆H₃₀NO₅ 436.2124; Found 436.2128

HPLC chromatogram :



benzyl (4bR,10aR,11R)-2,3-dimethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate BC28



Isolated as a white solid: 90% yield:

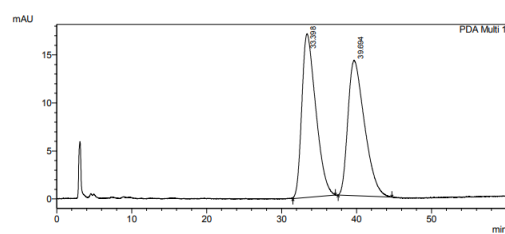
HPLC: 92% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 33.18 min [(R)-enantiomer], 39.47 min [(S)-enantiomer]. $[\alpha]_{\text{D}}^{28} = -0.11$ (c 0.5, CHCl₃). m.p. = 165.2–168.0 °C. $R_f = 0.2$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.30-7.23 (m, 5H), 7.17–7.13 (m, 3H), 6.96 (m, 1H), 6.85 (d, $J = 20.0$, 1H), 6.60 (d, $J = 24.8$, 1H), 5.36–5.16 (br, 2H), 4.79 (d, $J = 12.0$, 1H), 4.54 (d, $J = 12.0$, 1H), 3.89-3.60 (br, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.71 (s, 3H), 3.40 (br, 1H), 2.77 (dd, $J = 16.4, 4.4$ Hz, 1H), 2.46-2.40 (br, 2H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 154.6, 149.1, 149.0, 138.8, 136.2, 132.7, 128.1, 127.6, 127.4, 126.6, 119.9, 119.6, 107.0, 106.3, 66.6, 66.3, 55.8, 55.7, 54.5, 53.6, 51.5, 44.5, 41.6.

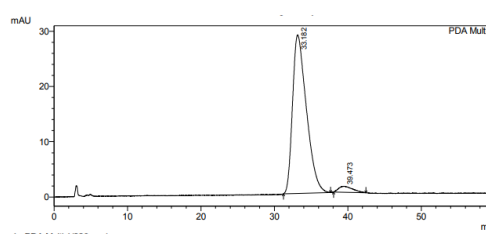
HRMS (ESI-TOF) m/z : $[M+H]^+$ C₃₀H₃₀NO₆ 500.2073; Found 500.2065

HPLC chromatogram :



1 PDA Multi 1/220nm 4nm

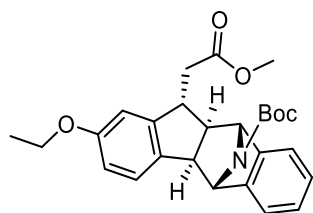
Peak#	Ret. Time	Area	Area %
1	33.398	2207102	50.449
2	39.694	2167781	49.551
Total		4374883	100.000



1 PDA Multi 1/220nm 4nm

Peak#	Ret. Time	Area	Area %
1	33.182	3762618	96.327
2	39.473	143476	3.673
Total		3906094	100.000

tert-butyl (4bR,10aR,11R)-3-ethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetra hydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ao)



Isolated as a white solid: 92% yield:

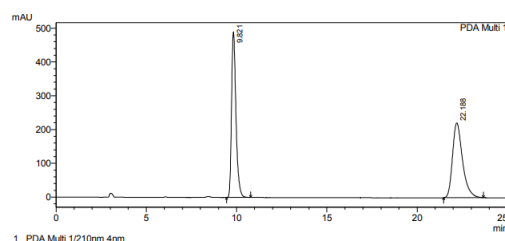
HPLC: 99% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 9.95 min [(R)-enantiomer], 22.34 min [(S)-enantiomer]. $[\alpha]_D^{28} = -0.21$ (c 0.5, CHCl₃). m.p. = 140.8–142.6 °C. R_f = 0.3 (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.29–7.25 (m, 3H), 7.15–7.11 (m, 2H), 6.81 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.64 (d, *J* = 2.0, 1H), 5.30–5.03 (br, 2H), 2.74 (qdd, *J* = 16.0, 4.4 Hz, 1H), 3.80 (br, 1H), 3.72 (s, 3H), 3.36 (br, 1H), 2.74 (dd, *J* = 16.0, 4.4 Hz, 1H), 2.46–2.32 (br, 2H), 1.38 (t, *J* = 6.8, 3H), 1.16 (br, 9H).

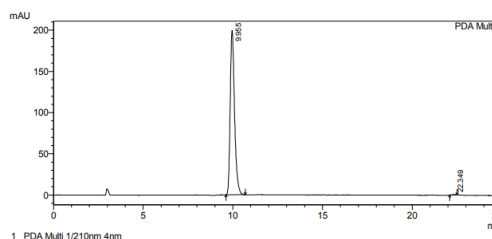
¹³C NMR (CDCl₃, 100 MHz): δ 172.5, 159.1, 153.6, 148.8, 145.3, 145.1, 133.5, 126.4, 125.6, 119.8, 114.7, 109.2, 79.1, 66.5, 65.8, 63.5, 54.1, 53.9, 51.5, 44.4, 41.4, 27.8, 14.8.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₅H₂₈NO₄ 406.2018; Found 406.2021

HPLC chromatogram :



PeakTable			
Peak#	Ret. Time	Area	Area %
1	9.821	8336484	49.486
2	22.188	8509611	50.514
Total		16846094	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	9.955	3350468	99.879
2	22.349	4073	0.121
Total		3354541	100.000

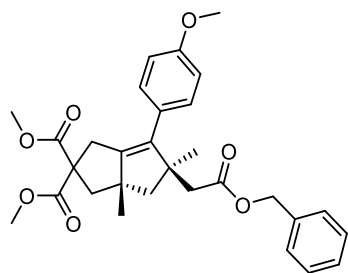
General Procedure for Rh(I)-Catalyzed Achiral Tandem Annulation

To a 4 mL sample vial, [RhCl(cod)]₂ (1.5 mg, 1.5 mol%), 1,4-dioxane (0.5 mL), H₂O (0.1 mL), and Sodium carbonate (2.0 equiv) were added under inert atmosphere. Then, to the mixture were added boronic esters **37** (0.4 mmol, 2.0 equiv), followed by 1,6-enynes **40** (0.2 mmol, 1.0 equiv) and 1,4-dioxane (0.5 mL). The reaction was stirred at 60 °C and monitored by TLC. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography (hexanes / ethyl acetate or hexanes / diethyl ether) to afford the desired product **41**.

General Procedure for Rh(I)-Catalyzed Asymmetric Tandem Annulation

To a 4 mL sample vial, [RhCl(C₂H₄)₂]₂ (1.2 mg, 1.5 mol%), chiral diene **L3f**, 1,4-dioxane (0.5 mL), H₂O (0.1 mL), and Sodium carbonate (2.0 equiv) were added successively under inert atmosphere. The resulting mixture was stirred for 5–10 min. After that, boronic esters **37** (0.4 mmol, 2.0 equiv), followed by 1,6-enynes **40** (0.2 mmol, 1.0 equiv) and 1,4-dioxane (0.5 mL) were added to the reaction. The reaction was stirred at 60 °C and monitored by TLC. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography (hexanes / ethyl acetate or hexanes / diethyl ether) to afford the desired product **41**.

dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-6-(4-methoxyphenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41aa)



Isolated as a colorless oil: 69% yield:

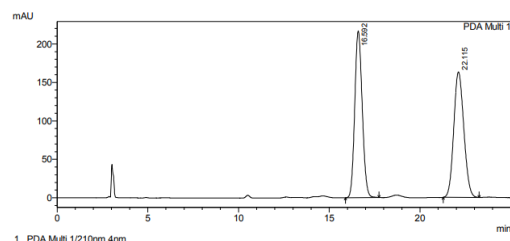
HPLC: 96% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 16.78 min [(*R*)-enantiomer], 22.19 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.13$ (c 0.5, CHCl₃). $R_f = 0.5$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.35–7.27 (m, 2H), 7.09–7.05 (m, 2H), 6.85–6.81 (m, 2H), 5.06 (d, $J = 12.6$ Hz, 1H), 4.99 (d, $J = 12.6$ Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.66 (s, 3H), 2.94 (d, $J = 16.0$ Hz, 1H), 2.60 (d, $J = 16.0$ Hz, 1H), 2.58 (d, $J = 13.6$ Hz, 1H), 2.47 (d, $J = 13.6$ Hz, 1H), 2.37 (d, $J = 13.6$ Hz, 1H), 2.31 (d, $J = 13.2$ Hz, 1H), 2.19 (d, $J = 13.2$ Hz, 1H), 1.80 (d, $J = 14.0$ Hz, 1H), 1.20 (s, 3H), 1.18 (s, 3H).

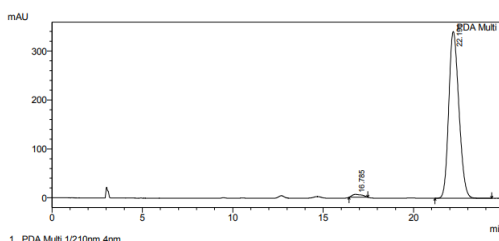
¹³C NMR (CDCl₃, 100 MHz): δ 172.8, 172.7, 171.8, 158.6, 148.0, 139.5, 135.9, 130.4, 128.4, 128.3, 128.2, 128.1, 113.3, 65.9, 60.8, 55.1, 54.7, 52.8, 52.7, 52.1, 50.6, 47.9, 45.0, 32.1, 28.2, 26.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₀H₃₅O₇ 507.2383; Found 507.2382

HPLC chromatogram :

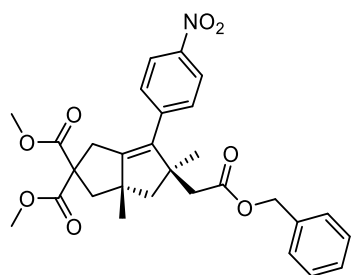


PeakTable			
Peak#	Ret. Time	Area	Area %
1	16.592	6214582	49.749
2	22.115	6277260	50.251
Total		12491842	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	16.785	234474	1.730
2	22.191	13320062	98.270
Total		13554536	100.000

dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-nitrophenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ab)



Isolated as a colorless oil: 88% yield:

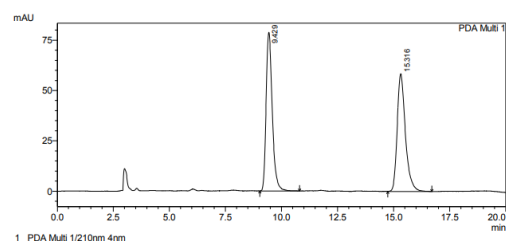
HPLC: 95% ee. The ee was determined on a Chiralpak AS-H column with hexanes/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 9.38 min [(*R*)- enantiomer], 15.30 min [(*S*)-enantiomer] . $[\alpha]_D^{27} = -0.12$ (c 0.5, CHCl₃). $R_f = 0.5$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 8.16–8.14 (m, 2H), 7.36–7.26 (m, 7H), 5.07 (d, $J = 12.4$ Hz, 1H), 5.00 (d, $J = 12.6$ Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.92 (d, $J = 16.0$ Hz, 1H), 2.60 (d, $J = 14.0$ Hz, 1H), 2.59 (d, $J = 16.0$ Hz, 1H), 2.41 (d, $J = 13.6$ Hz, 1H), 2.39 (d, $J = 13.6$ Hz, 1H), 2.39 (d, $J = 13.6$ Hz, 1H), 2.16 (d, $J = 13.6$ Hz, 1H), 1.87 (d, $J = 13.6$ Hz, 1H), 1.22 (s, 3H), 1.19 (s, 3H).

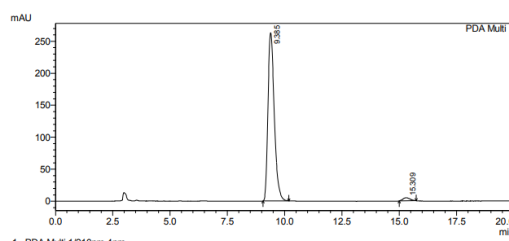
¹³C NMR (CDCl₃, 100 MHz): δ 172.6, 172.4, 171.3, 151.1, 146.9, 143.7, 137.9, 135.7, 130.2, 128.5, 128.3, 123.2, 66.2, 60.6, 55.2, 53.0, 52.8, 50.9, 47.8, 45.2, 32.1, 28.6, 26.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₉H₃₂NO₈ 522.2128; Found 522.2132

HPLC chromatogram :

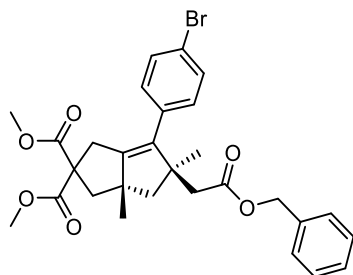


PeakTable			
Peak#	Ret. Time	Area	Area %
1	9.429	1502272	50.153
2	15.316	1493082	49.847
Total		2995354	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	9.385	5025804	97.937
2	15.309	105856	2.063
Total		5131660	100.000

dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-6-(4-bromophenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ac)



Isolated as a colorless oil: 78% yield:

HPLC: 93% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 97/3, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 20.19 min [(*R*)- enantiomer], 20.12 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.14$ (c 0.5, CHCl₃). $R_f = 0.5$ (ether/hexanes,

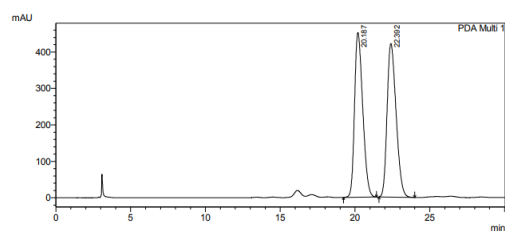
1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.42–7.40 (m, 2H), 7.34–7.30 (m, 2H), 7.03–7.01 (m, 2H), 5.07 (d, $J = 12.4$ Hz, 1H), 5.00 (d, $J = 12.4$ Hz, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 2.91 (d, $J = 16.0$ Hz, 1H), 2.57 (d, $J = 16.4$ Hz, 1H), 2.56 (d, $J = 13.2$ Hz, 1H), 2.46 (d, $J = 13.6$ Hz, 1H), 2.37 (d, $J = 13.6$ Hz, 1H), 2.34 (d, $J = 14.0$ Hz, 1H), 2.17 (d, $J = 13.6$ Hz, 1H), 1.82 (d, $J = 13.6$ Hz, 1H), 1.18 (s, 3H), 1.17 (s, 3H).

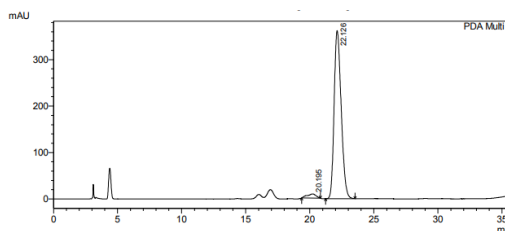
¹³C NMR (CDCl₃, 100 MHz): δ 172.6, 172.6, 171.6, 149.2, 138.7, 135.8, 131.1, 131.0, 128.5, 128.2, 128.1, 121.2, 66.1, 60.7, 54.8, 52.8, 52.7, 52.4, 50.7, 47.9, 45.0, 32.0, 28.3, 26.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₉H₃₂O₆Br 555.1382; Found 555.1375

HPLC chromatogram :

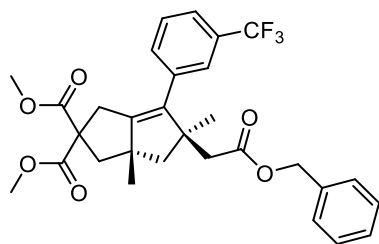


PeakTable			
Peak#	Ret. Time	Area	Area %
1	20.187	17211074	49.423
2	22.392	17613081	50.577
Total		34824155	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	20.195	432412	3.029
2	22.126	13843607	96.971
Total		14276019	100.000

dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(3-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ad)



Isolated as a colorless oil: 86% yield:

HPLC: 95% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 97/3, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 15.61 min [(*R*)- enantiomer], 28.72 min [(*S*)-enantiomer].

$[\alpha]_D^{27} = -0.13$ (c 0.5, CHCl₃). $R_f = 0.5$ (ether/hexanes, 1/5).

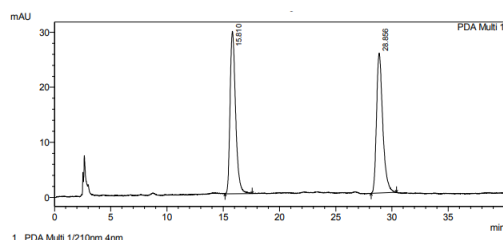
¹H NMR (CDCl₃, 400 MHz): δ 7.56–7.54 (m, 2H), 7.36–7.28 (m, 5H), 5.07 (d, $J = 12.4$ Hz, 1H), 5.00 (d, $J = 12.4$ Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.91 (d, $J = 16.0$ Hz, 1H), 2.60 (d, $J = 13.6$ Hz, 1H), 2.58 (d, $J = 16.0$ Hz, 1H), 2.47 (d, $J = 13.6$ Hz, 1H), 2.40 (d, $J = 13.6$ Hz, 1H), 2.37 (d, $J = 13.2$ Hz, 1H), 2.18 (d, $J = 13.6$ Hz, 1H), 1.84 (d, $J = 13.6$ Hz, 1H), 1.19 (s, 3H), 1.19 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.7, 172.6, 171.5, 149.9, 140.2, 138.7, 135.8, 129.7, 129.2 (q, $J_{C-F} = 32.2$), 128.5, 128.3, 128.2, 124.9 (q, $J_{C-F} = 3.5$), 124.2 (q, $J_{C-F} = 270.5$), 66.1, 60.7, 55.0, 52.9, 52.8, 52.6, 50.7, 45.1, 32.0, 28.4, 26.6.

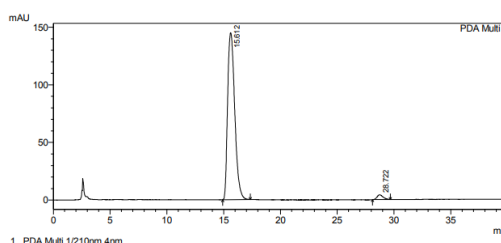
¹⁹F NMR (CDCl₃, 376 MHz): δ -62.5

HRMS (ESI-TOF) m/z : [M+H]⁺ Calcd for C₃₀H₃₂O₆F₃ 545.2151; Found 545.2143

HPLC chromatogram :

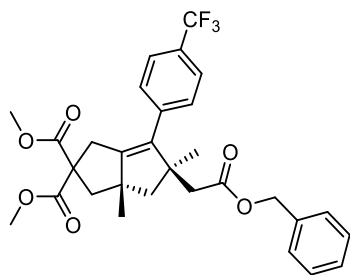


PeakTable			
Peak#	Ret. Time	Area	Area %
1	15.810	1002977	50.610
2	28.856	978803	49.390
Total		1981780	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	15.612	6293840	97.649
2	28.722	151516	2.351
Total		6445356	100.000

dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ae)



Isolated as a colorless oil: 90% yield:

HPLC: 95% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 10.99 min [(*R*)- enantiomer], 26.15 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.12$ (c 0.5, CHCl₃). $R_f = 0.5$ (ether/hexanes, 1/5).

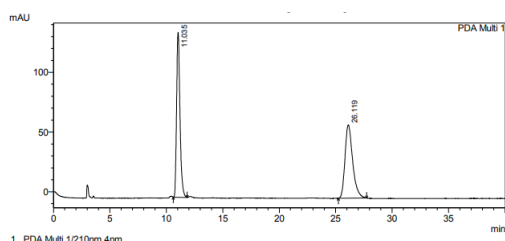
¹H NMR (CDCl₃, 400 MHz): δ 7.56–7.54 (m, 2H), 7.37–7.28 (m, 7H), 5.07 (d, $J = 12.4$ Hz, 1H), 5.00 (d, $J = 12.4$ Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.91 (d, $J = 16.0$ Hz, 1H), 2.59 (d, $J = 16.0$ Hz, 1H), 2.47 (d, $J = 14.0$ Hz, 1H), 2.40 (d, $J = 13.6$ Hz, 1H), 2.37 (d, $J = 13.2$ Hz, 1H), 2.31 (d, $J = 13.2$ Hz, 1H), 2.18 (d, $J = 13.6$ Hz, 1H), 1.84 (d, $J = 13.2$ Hz, 1H), 1.94 (s, 3H), 1.19 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.7, 172.6, 171.5, 149.9, 140.2, 138.6, 135.8, 129.7, 129.2 (q, $J_{C-F} = 32.2$), 128.5, 128.3, 128.2, 124.9 (q, $J_{C-F} = 3.6$), 124.2 (q, $J_{C-F} = 270.2$), 66.1, 60.7, 55.0, 52.9, 52.8, 52.6, 50.7, 47.9, 45.1, 32.0, 28.4, 26.5.

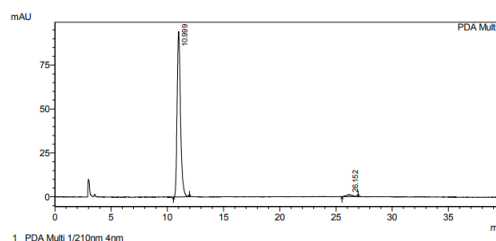
¹⁹F NMR (CDCl₃, 376 MHz): δ -62.5

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₀H₃₂O₆F₃ 545.2151; Found 545.2152

HPLC chromatogram :

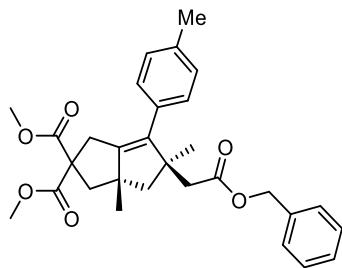


Peak#	Ret. Time	Area	Area %
1	11.035	2878172	49.872
2	26.119	2892982	50.128
Total		5771154	100.000



Peak#	Ret. Time	Area	Area %
1	10.999	1987037	97.919
2	26.152	42221	2.081
Total		2029258	100.000

dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(p-tolyl)-3,3a,4,5-tetrahydro pentalene-2,2(1H)-dicarboxylate (41af)



Isolated as a colorless oil: 78% yield:

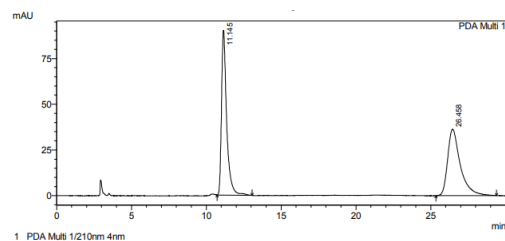
HPLC: 97% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 99/1, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 11.05 min [(*R*)-enantiomer], 26.25 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.14$ (c 0.5, CHCl₃). $R_f = 0.6$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.35–7.29 (m, 5H), 7.10 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 5.06 (d, $J = 12.4$ Hz, 1H), 5.00 (d, $J = 12.4$ Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 2.94 (d, $J = 16.0$ Hz, 1H), 2.59 (d, $J = 16.8$ Hz, 1H), 2.59 (d, $J = 13.2$ Hz, 1H), 2.47 (d, $J = 13.2$ Hz, 1H), 2.38 (d, $J = 13.2$ Hz, 1H), 2.32 (s, 3H), 2.30 (d, $J = 13.6$ Hz, 1H), 2.21 (d, $J = 13.6$ Hz, 1H), 1.80 (d, $J = 13.6$ Hz, 1H), 1.20 (s, 3H), 1.18 (s, 3H).

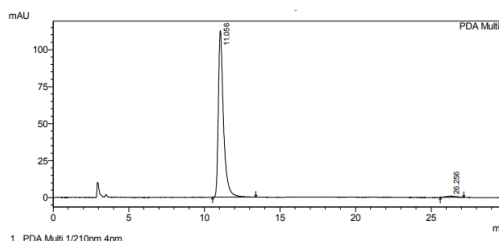
¹³C NMR (CDCl₃, 100 MHz): δ 172.8, 172.7, 171.8, 148.0, 139.9, 136.5, 135.9, 133.1, 129.2, 128.6, 128.4, 128.2, 128.1, 65.9, 60.8, 54.7, 52.8, 52.7, 52.2, 50.6, 47.9, 45.0, 32.1, 28.1, 26.5, 21.1.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₀H₃₅O₆ 491.2434; Found 491.2437

HPLC chromatogram :

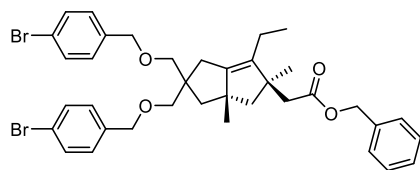


PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.145	2149261	50.154
2	26.458	2136071	49.846
Total		4285333	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.056	2668934	98.602
2	26.256	37847	1.398
Total		2706781	100.000

benzyl 2-(5,5-bis(((4-bromobenzyl)oxy)methyl)-3-ethyl-2,6a-dimethyl-1,2,4,5,6,6a-hexahydropentalen-2-yl)acetate (44aa)



Isolated as a colorless oil: 78% yield:

HPLC: 91% ee. The ee was determined on a Chiralpak IC column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 220 nm.

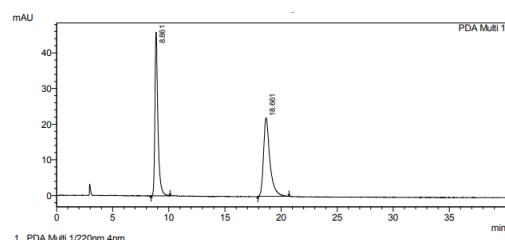
Retention times: 15.61 min [(R)- enantiomer], 28.72 min [(S)-enantiomer]. $[\alpha]_D^{27} = -0.04$ (c 0.5, CHCl₃). $R_f = 0.55$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.42–7.39 (m, 4H), 7.35–7.29 (m, 5H), 7.16–7.11 (m, 4H), 5.12 (d, $J = 12.4$ Hz, 1H), 5.06 (d, $J = 12.4$ Hz, 1H), 4.44 (s, 2H), 4.37 (s, 2H), 3.47 (d, $J = 8.4$ Hz, 1H), 3.42 (d, $J = 8.8$ Hz, 1H), 3.17 (d, $J = 8.4$ Hz, 1H), 3.13 (d, $J = 8.4$ Hz, 1H), 2.45 (s, 2H), 2.20 (d, $J = 13.6$ Hz, 2H), 1.99 (d, $J = 14.8$ Hz, 1H), 1.92 (dq, $J = 15.6, 8.0$ Hz, 1H), 1.85 (dq, $J = 15.6, 8.0$ Hz, 1H), 1.72 (d, $J = 13.6$ Hz, 1H), 1.55 (d, $J = 13.6$ Hz, 1H), 1.43 (d, $J = 13.6$ Hz, 1H), 1.10 (s, 3H), 1.08 (s, 3H), 0.96 (t, $J = 7.6, 3H$).

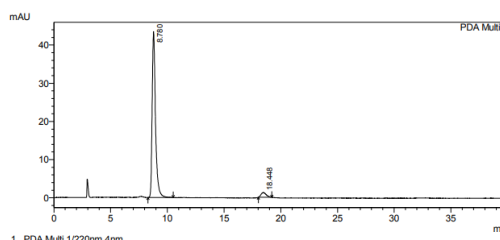
¹³C NMR (CDCl₃, 100 MHz): δ 172.1, 146.2, 139.0, 137.7, 137.6, 136.1, 131.3, 129.1, 128.9, 128.4, 128.2, 128.0, 121.2, 121.1, 75.1, 74.0, 72.3, 72.2, 65.9, 53.6, 52.0, 51.3, 49.2, 47.0, 44.9, 29.9, 28.1, 27.6, 18.5, 14.8.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₇H₄₃O₄Br₂ 709.1528; Found 709.1528

HPLC chromatogram :

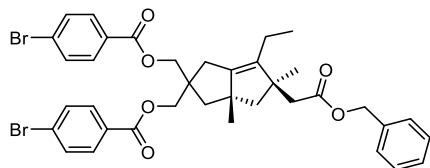


PeakTable			
Peak#	Ret. Time	Area	Area %
1	8.861	859295	49.791
2	18.661	866518	50.209
Total		1725813	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	8.780	890018	95.776
2	18.448	39252	4.224
Total		929270	100.000

(5-(2-(benzyloxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-1,2,3,3a,4,5-hexahydropentane-2,2-diyl)bis(methylene) bis(4-bromobenzoate) (44ab)



Isolated as a colorless oil: 85% yield:

HPLC: 95% ee. The ee was determined on a Chiralpak IC column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 210 nm.

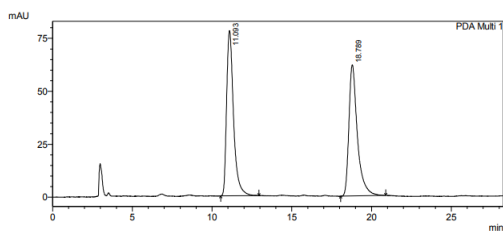
Retention times: 11.04 min [(*R*)-enantiomer], 18.76 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.06$ (c 0.5, CHCl₃). $R_f = 0.65$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.87–7.83 (m, 4H), 7.57–7.54 (m, 4H), 7.36–7.31 (m, 5H), 5.14 (d, $J = 12.4$ Hz, 1H), 5.08 (d, $J = 12.4$ Hz, 1H), 4.45 (d, $J = 11.2$ Hz, 1H), 4.39 (d, $J = 11.2$ Hz, 1H), 4.15 (s, 2H), 2.49 (s, 2H), 2.37 (d, $J = 14.8$ Hz, 1H), 2.30 (d, $J = 13.6$ Hz, 1H), 2.24 (d, $J = 14.8$ Hz, 1H), 1.99 (d, $J = 8.0$ Hz, 1H), 1.95 (d, $J = 7.6$ Hz, 1H), 1.72 (d, $J = 13.6$ Hz, 1H), 1.54 (d, $J = 13.2$ Hz, 1H), 1.38 (d, $J = 14.0$ Hz, 1H), 1.21 (s, 3H), 1.16 (s, 3H), 1.00 (t, $J = 7.6$ Hz, 3H).

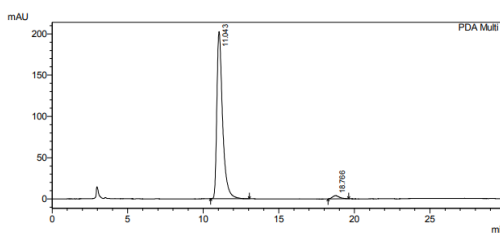
¹³C NMR (CDCl₃, 100 MHz): δ 172.0, 165.7, 144.6, 140.5, 136.0, 131.8, 131.0, 128.8, 128.5, 128.3, 128.1, 69.1, 68.2, 66.0, 53.9, 51.8, 51.7, 47.9, 46.7, 44.9, 29.9, 28.1, 27.6, 18.7, 14.9.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₇H₃₉O₆Br₂ 737.1113; Found 737.1096

HPLC chromatogram :

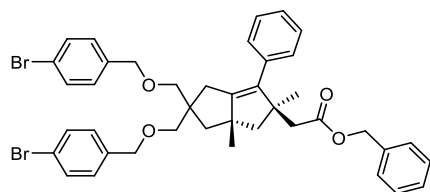


PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.093	2335749	50.416
2	18.789	2297228	49.584
Total		4632977	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.043	5336281	97.754
2	18.766	122616	2.246
Total		5458897	100.000

benzyl 2-(5,5-bis(((4-bromobenzyl)oxy)methyl)-2,6a-dimethyl-3-phenyl-1,2,4,5,6,6a-hexahydropentalen-2-yl)acetate (44ac)



Isolated as a colorless oil:83% yield:

HPLC: 92% ee. The ee was determined on a Chiralpak IC column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 220 nm.

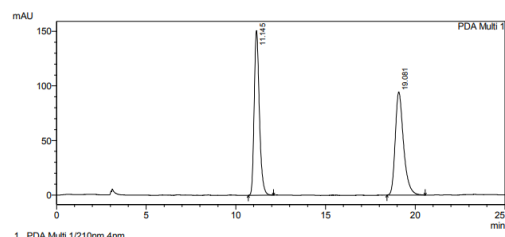
Retention times: 9.71 min [(*R*)-enantiomer], 15.99 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.04$ (c 0.5, CHCl₃). $R_f = 0.55$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.47–7.38 (m, 7H), 7.27–7.24 (m, 2H), 7.19–7.13 (m, 5H), 7.07–7.05 (m, 4H), 4.98 (d, $J = 12.8$ Hz, 1H), 4.92 (d, $J = 12.4$ Hz, 1H), 4.42 (s, 2H), 4.35 (s, 2H), 3.44 (d, $J = 8.8$ Hz, 1H), 3.41 (d, $J = 8.8$ Hz, 1H), 3.20 (d, $J = 8.4$ Hz, 1H), 3.16 (d, $J = 8.8$ Hz, 1H), 2.58 (d, $J = 13.6$ Hz, 1H), 2.47 (d, $J = 13.6$ Hz, 1H), 2.33 (d, $J = 13.2$ Hz, 1H), 2.08 (d, $J = 15.2$ Hz, 1H), 1.97 (d, $J = 14.8$ Hz, 1H), 1.63 (d, $J = 13.6$ Hz, 1H), 1.62 (d, $J = 15.6$ Hz, 1H), 1.28 (d, $J = 13.6$ Hz, 1H), 1.21 (s, 3H), 1.16 (s, 3H).

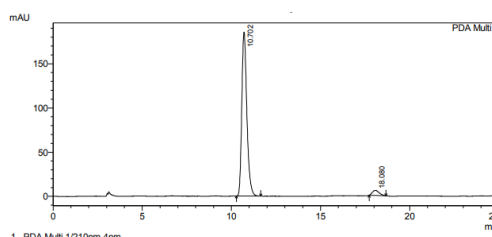
¹³C NMR (CDCl₃, 100 MHz): δ 171.8, 150.8, 138.9, 137.7, 137.5, 136.8, 135.0, 131.6, 131.4, 129.9, 129.4, 129.2, 129.0, 127.9, 126.8, 122.1, 121.3, 121.2, 75.1, 74.2, 72.4, 72.3, 65.1, 54.3, 52.3, 51.6, 49.1, 46.9, 45.1, 30.6, 28.6, 28.1.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₅H₂₈NO₄ 406.2018; Found 406.2021

HPLC chromatogram :

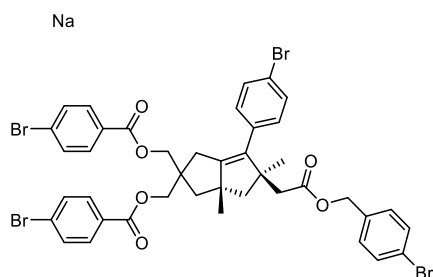


PeakTable			
Peak#	Ret. Time	Area	Area %
1	11.145	3017936	49.863
2	19.081	3034483	50.137
Total		6052418	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	10.702	3643552	96.085
2	18.080	148450	3.915
Total		3792002	100.000

(5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromophenyl)-3a,5-dimethyl-1,2,3,3a,4,5-hexahydropentalene-2,2-diyl)bis(methylene) bis(4-bromobenzoate)
(44ad)



Isolated as a colorless oil: 77% yield:

HPLC: 91% ee. The ee was determined on a Chiralpak AS-H column with hexanes/2-propanol = 96/4, flow = 1.0 mL/min, wavelength = 210 nm.

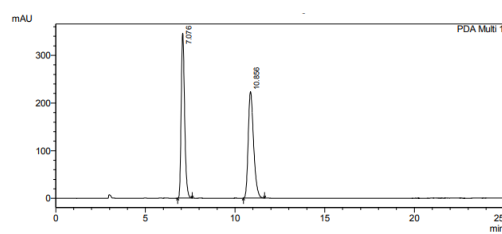
Retention times: 7.09 min [(*R*)-enantiomer], 10.87 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.03$ (c 0.5, CHCl₃). $R_f = 0.35$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.83–7.77 (m, 4H), 7.55–7.52 (m, 4H), 7.48–7.44 (m, 2H), 7.27–7.24 (m, 2H), 7.19–7.17 (m, 2H), 7.12–7.09 (m, 2H), 5.00 (d, $J = 12.4$ Hz, 1H), 4.93 (d, $J = 12.4$ Hz, 1H), 4.43 (d, $J = 11.2$ Hz, 1H), 4.40 (d, $J = 11.2$ Hz, 1H), 4.20 (d, $J = 11.2$ Hz, 1H), 4.17 (d, $J = 11.2$ Hz, 1H), 2.61 (d, $J = 14.0$ Hz, 1H), 2.49 (d, $J = 14.0$ Hz, 1H), 2.44 (d, $J = 13.6$ Hz, 1H), 2.30 (d, $J = 14.8$ Hz, 1H), 2.13 (d, $J = 15.2$ Hz, 1H), 1.80 (d, $J = 13.6$ Hz, 1H), 1.76 (d, $J = 13.6$ Hz, 1H), 1.55 (d, $J = 14.0$ Hz, 1H), 1.33 (s, 3H), 1.23 (s, 3H).

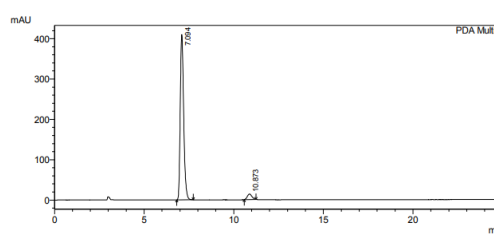
¹³C NMR (CDCl₃, 100 MHz): δ 171.6, 165.7, 148.9, 140.6, 136.1, 134.9, 131.8, 131.7, 131.6, 131.0, 129.9, 129.4, 129.2, 128.7, 128.3, 128.0, 127.9, 127.1, 122.2, 69.0, 68.0, 65.2, 54.6, 52.0, 51.8, 47.7, 46.7, 45.9, 30.6, 28.5, 28.2.

HRMS (ESI-TOF) m/z : $[M+Na]^+$ Calcd for C₄₁H₃₆Br₄NaO₆ 967.3388; Found 970.7259

HPLC chromatogram:

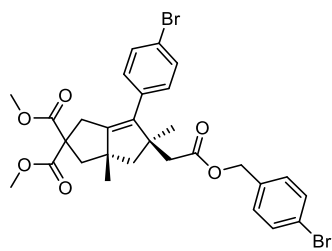


PeakTable			
Peak#	Ret. Time	Area	Area %
1	7.076	4598101	49.676
2	10.856	4658157	50.324
Total		9256258	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	7.094	5426541	95.819
2	10.873	236777	4.181
Total		5663318	100.000

dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromophenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ag)



Isolated as a colorless oil: 88% yield:

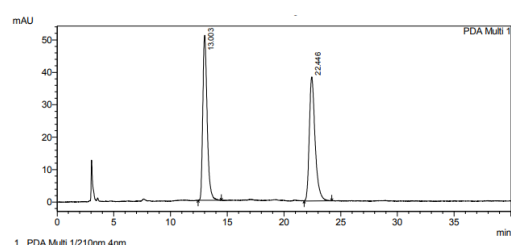
HPLC: 96% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 12.97 min [(*R*)- enantiomer], 22.49 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.16$ (c 0.5, CHCl₃). $R_f = 0.45$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.47–7.41 (m, 4H), 7.19–7.17 (m, 2H), 7.03–7.01 (m, 2H), 5.00 (d, $J = 12.8$ Hz, 1H), 4.94 (d, $J = 12.4$ Hz, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 2.91 (d, $J = 16.0$ Hz, 1H), 2.58 (d, $J = 16.0$ Hz, 1H), 2.56 (d, $J = 13.2$ Hz, 1H), 2.56 (d, $J = 13.6$ Hz, 1H), 2.45 (d, $J = 13.6$ Hz, 1H), 2.34 (d, $J = 14.0$ Hz, 2H), 2.18 (d, $J = 13.6$ Hz, 1H), 1.82 (d, $J = 13.6$ Hz, 1H), 1.18 (s, 3H), 1.17 (s, 3H).

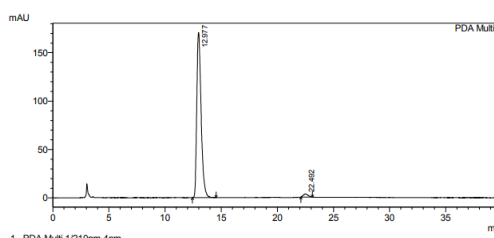
¹³C NMR (CDCl₃, 100 MHz): δ 172.6, 172.5, 171.4, 149.3, 138.6, 135.0, 134.8, 131.6, 131.1, 131.0, 129.9, 122.2, 121.2, 65.2, 60.7, 54.7, 52.9, 52.8, 52.7, 52.3, 50.7, 47.8, 45.0, 32.0, 28.2, 26.5.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₂₉H₃₁O₆Br₂ 633.0487; Found 633.0476

HPLC chromatogram:

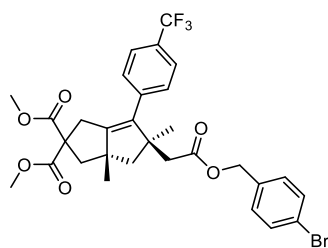


PeakTable			
Peak#	Ret. Time	Area	Area %
1	13.003	1360865	50.117
2	22.446	1354505	49.883
Total		2715370	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	12.977	4606107	98.036
2	22.492	92288	1.964
Total		4698395	100.000

dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)



Isolated as a colorless oil: 85% yield:

HPLC: 94% ee. The ee was determined on a Chiralpak IG column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 17.25 min [(*R*)-enantiomer], 31.06 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.14$ (c 0.5, CHCl₃). $R_f = 0.45$ (ether/hexanes, 1/5).

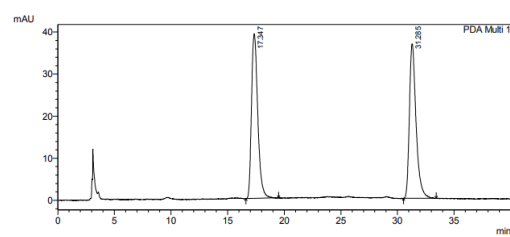
¹H NMR (CDCl₃, 400 MHz): δ 7.57–7.55 (m, 2H), 7.47–7.45 (m, 2H), 7.28–7.26 (m, 2H), 7.19–7.17 (m, 2H), 5.00 (d, $J = 12.4$ Hz, 1H), 4.94 (d, $J = 12.8$ Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 2.91 (d, $J = 16.0$ Hz, 1H), 2.60 (d, $J = 14.0$ Hz, 1H), 2.59 (d, $J = 16.0$ Hz, 1H), 2.47 (d, $J = 13.6$ Hz, 1H), 2.37 (d, $J = 13.2$ Hz, 1H), 2.36 (d, $J = 13.2$ Hz, 1H), 2.37 (d, $J = 13.2$ Hz, 1H), 2.18 (d, $J = 13.6$ Hz, 1H), 1.85 (d, $J = 13.6$ Hz, 1H), 1.19 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 172.6, 172.5, 171.3, 150.0, 140.1, 138.6, 134.8, 131.7, 129.9, 129.6, 129.2 (q, $J_{C-F} = 32.1$ Hz), 124.9 (q, $J_{C-F} = 3.6$ Hz), 124.2 (q, $J_{C-F} = 270.5$ Hz), 122.2, 65.3, 60.7, 55.0, 52.9, 52.8, 52.6, 50.8, 47.8, 45.0, 32.0, 28.3, 26.5.

¹⁹F NMR (CDCl₃, 376 MHz): δ -62.5

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₀H₃₁O₆F₃Br 623.1256; Found 623.1266

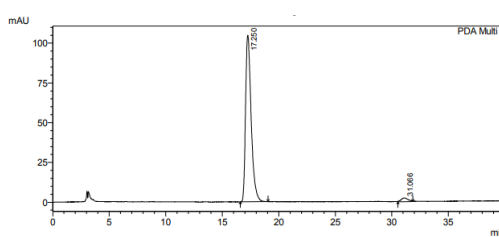
HPLC chromatogram :



1 PDA Multi 1/210nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	17.347	1503111	50.128
2	31.285	1495427	49.872
Total		2998537	100.000

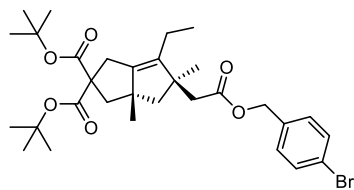


1 PDA Multi 1/210nm 4nm

PeakTable

Peak#	Ret. Time	Area	Area %
1	17.250	3605793	97.254
2	31.066	101813	2.746
Total		3707606	100.000

di-tert-butyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (44ae)



Isolated as a colorless oil: 79% yield:

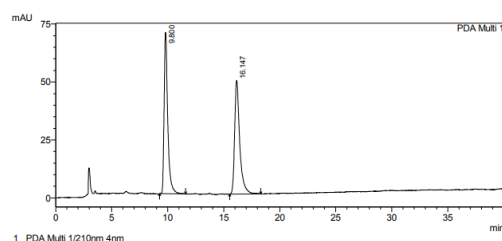
HPLC: 95% ee. The ee was determined on a Chiralpak IC column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 210 nm. Retention times: 9.71 min [(*R*)- enantiomer], 15.99 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.21$ (c 0.5, CHCl₃). $R_f = 0.65$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.49–7.46 (m, 2H), 7.24–7.22 (m, 2H), 5.07 (d, *J* = 12.8 Hz, 1H), 5.02 (d, *J* = 12.8 Hz, 1H), 2.82 (d, *J* = 15.6 Hz, 1H), 2.72 (d, *J* = 15.6 Hz, 1H), 2.47 (s, 2H), 2.17 (d, *J* = 13.2 Hz, 1H), 2.10 (d, *J* = 13.6 Hz, 1H), 1.98 (d, *J* = 13.6 Hz, 1H), 1.58 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 9H), 1.42 (s, 9H), 1.10 (s, 3H), 1.07 (s, 3H), 1.01 (t, *J* = 7.6 Hz 3H).

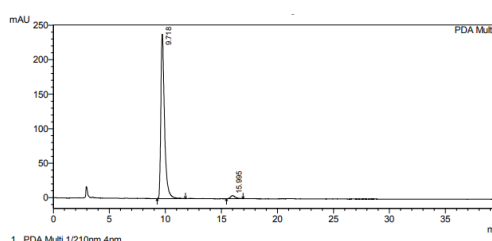
¹³C NMR (CDCl₃, 100 MHz): δ 171.9, 171.6, 171.5, 145.0, 139.2, 135.1, 131.6, 129.9, 122.1, 80.9, 65.1, 62.8, 54.0, 52.2, 50.6, 47.8, 44.9, 31.3, 27.8, 27.2, 26.5, 18.6, 14.6.

HRMS (ESI-TOF) *m/z*: [M+Na]⁺ Calcd for C₃₁H₄₃O₆BrNa 613.2141; Found 613.2136

HPLC chromatogram :

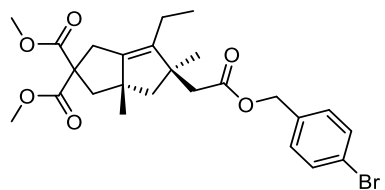


PeakTable			
Peak#	Ret. Time	Area	Area %
1	9.800	1566807	50.308
2	16.147	1547600	49.692
Total		3114407	100.000



PeakTable			
Peak#	Ret. Time	Area	Area %
1	9.718	5432409	97.581
2	15.995	134670	2.419
Total		5567079	100.000

dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ai)



Isolated as a colorless oil: 88% yield:

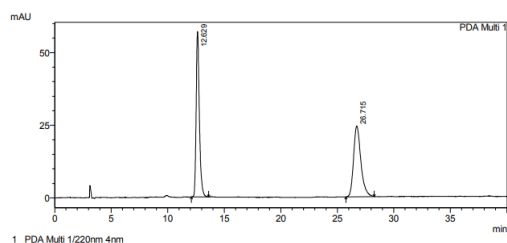
HPLC: 96% ee. The ee was determined on a Chiralpak IA column with hexanes/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 9.71 min [(*R*)- enantiomer], 15.99 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.16$ (c 0.5, CHCl₃). $R_f = 0.55$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.49–7.47 (m, 2H), 7.24–7.22 (m, 2H), 5.07 (d, *J* = 12.4 Hz, 1H), 5.02 (d, *J* = 12.4 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 2.87 (s, 2H), 2.46 (s, 2H), 2.24 (d, *J* = 13.2 Hz, 1H), 2.19 (d, *J* = 13.2 Hz, 1H), 2.04 (d, *J* = 13.6 Hz, 1H), 1.96 (d, *J* = 7.6 Hz, 1H), 1.93 (d, *J* = 7.6 Hz, 1H), 1.58 (d, *J* = 14.0 Hz, 1H), 1.10 (s, 3H), 1.06 (s, 3H), 1.01 (t, *J* = 7.6 Hz, 3H).

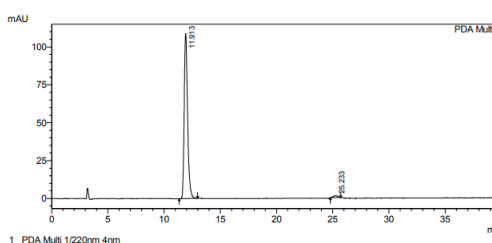
¹³C NMR (CDCl₃, 100 MHz): δ 172.9, 172.8, 171.8, 144.3, 139.9, 135.0, 131.6, 129.9, 122.1, 65.2, 61.3, 54.1, 52.8, 52.7, 52.2, 50.5, 47.9, 44.9, 31.6, 27.2, 26.5, 18.6, 14.5.

HRMS (ESI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₅H₃₂O₆Br 507.1382; Found 507.1380

HPLC chromatogram :

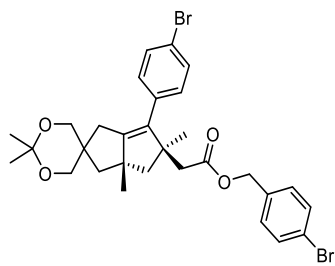


Peak#	Ret. Time	Area	Area %
1	12.629	1127147	50.751
2	26.715	1093767	49.249
Total		2220914	100.000



Peak#	Ret. Time	Area	Area %
1	11.913	2291875	98.387
2	25.233	37400	1.613
Total		2319276	100.000

4-bromobenzyl 2-(6-(4-bromophenyl)-2',2',3a,5-tetramethyl-3,3a,4,5-tetrahydro-1H-spiro[pentalene-2,5'-[1,3]dioxan]-5-yl)acetate (44af)



Isolated as a colorless oil: 81% yield:

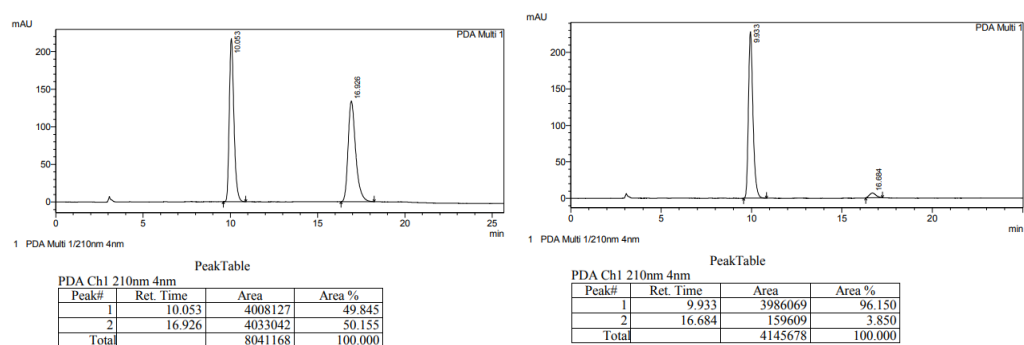
HPLC: 92% ee. The ee was determined on a Chiralpak OJ-H column with hexanes/2-propanol = 98/2, flow = 1.2 mL/min, wavelength = 210 nm. Retention times: 9.93 min [(*R*)- enantiomer], 16.68 min [(*S*)-enantiomer]. $[\alpha]_D^{27} = -0.09$ (c 0.5, CHCl₃). $R_f = 0.56$ (ether/hexanes, 1/5).

¹H NMR (CDCl₃, 400 MHz): δ 7.48–7.47 (m, 2H), 7.46–7.45 (m, 2H), 7.18–7.16 (m, 2H), 7.01–6.98 (m, 2H), 4.98 (d, $J = 12.4$ Hz, 1H), 4.92 (d, $J = 12.4$ Hz, 1H), 3.77 (d, $J = 11.2$ Hz, 1H), 3.70 (dd, $J = 10.8, 0.8$ Hz, 1H), 3.48 (d, $J = 11.2$ Hz, 1H), 3.34 (dd, $J = 10.8, 0.8$ Hz, 1H), 2.54 (d, $J = 13.6$ Hz, 1H), 2.33 (d, $J = 13.6$ Hz, 1H), 2.20 (d, $J = 15.6$ Hz, 1H), 2.10 (d, $J = 15.2$ Hz, 1H), 1.69 (d, $J = 13.6$ Hz, 1H), 1.56 (d, $J = 13.6$ Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 1.20 (s, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 171.6, 151.0, 138.1, 135.4, 134.9, 131.6, 131.2, 129.9, 122.2, 122.1, 97.6, 70.8, 69.3, 65.2, 54.4, 51.8, 51.4, 47.7, 45.0, 43.1, 32.2, 28.7, 27.9, 25.8, 21.6.

HRMS (ESI-TOF) m/z : $[M+H]^+$ Calcd for C₃₀H₃₅O₄Br₂ 617.0902; Found 617.0905

HPLC chromatogram :



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附錄一 X-ray 單晶數據



tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate **BC1**

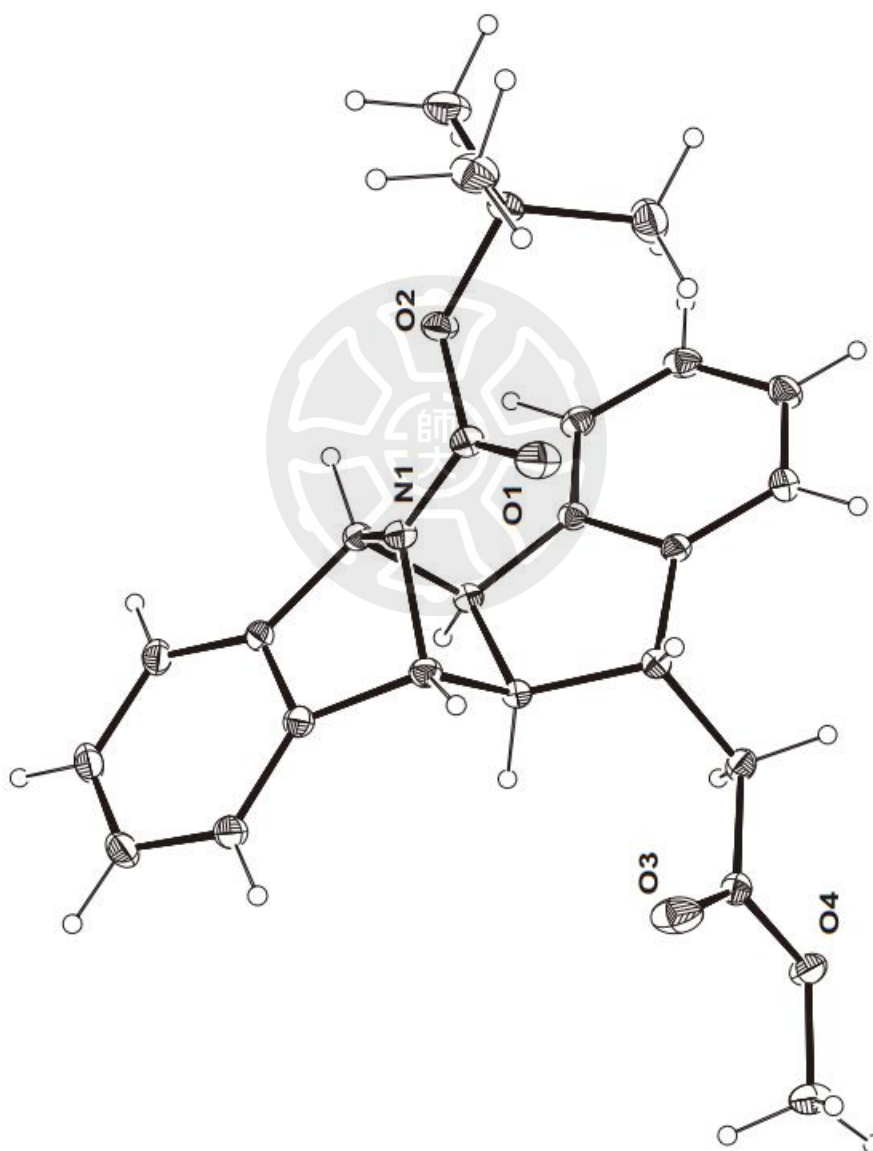
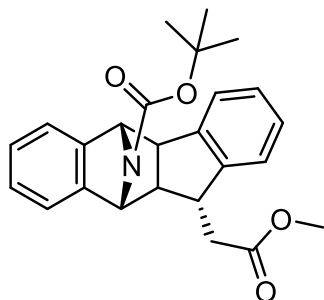


Table 1. Crystal data and structure refinement for d25033a.

Identification code	d25033a	
Empirical formula	C ₂₅ H ₂₇ N O ₄	
Formula weight	405.48	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.9970(3) Å	α = 90°.
	b = 9.8493(4) Å	β = 90°.
	c = 27.1106(8) Å	γ = 90°.
Volume	2135.36(13) Å ³	
Z	4	
Density (calculated)	1.261 Mg/m ³	
Absorption coefficient	0.085 mm ⁻¹	
F(000)	864	
Crystal size	0.39 x 0.25 x 0.20 mm ³	
Theta range for data collection	2.20 to 25.06°.	
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 8, -32 ≤ l ≤ 27	
Reflections collected	13294	
Independent reflections	3767 [R(int) = 0.0466]	
Completeness to theta = 25.06°	99.4 %	
Absorption correction	None	
Max. and min. transmission	0.9832 and 0.9676	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3767 / 0 / 275	
Goodness-of-fit on F ²	1.063	
Final R indices [I > 2σ(I)]	R1 = 0.0315, wR2 = 0.0800	
R indices (all data)	R1 = 0.0330, wR2 = 0.0813	
Absolute structure parameter	0.0(8)	
Largest diff. peak and hole	0.167 and -0.151 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

for d25033a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	5528(2)	3869(2)	6566(1)	28(1)
C(2)	4435(2)	1668(2)	6839(1)	31(1)
C(3)	5210(2)	570(2)	7160(1)	49(1)
C(4)	2880(2)	2239(2)	7082(1)	46(1)
C(5)	4110(2)	1147(2)	6322(1)	48(1)
C(6)	8693(2)	4239(1)	6640(1)	25(1)
C(7)	9238(2)	4089(1)	6086(1)	26(1)
C(8)	8648(2)	2803(1)	5844(1)	26(1)
C(9)	9193(2)	1477(2)	5933(1)	33(1)
C(10)	8541(2)	426(2)	5651(1)	37(1)
C(11)	7355(2)	681(2)	5291(1)	38(1)
C(12)	6794(2)	1995(2)	5208(1)	35(1)
C(13)	7454(2)	3053(1)	5485(1)	27(1)
C(14)	7112(2)	4555(1)	5423(1)	26(1)
C(15)	8195(2)	5244(1)	5827(1)	26(1)
C(16)	7197(2)	5851(1)	6270(1)	27(1)
C(17)	8473(2)	6587(2)	6583(1)	29(1)
C(18)	8856(2)	7943(2)	6642(1)	36(1)
C(19)	10221(2)	8272(2)	6939(1)	42(1)
C(20)	11180(2)	7273(2)	7159(1)	40(1)
C(21)	10802(2)	5904(2)	7095(1)	34(1)
C(22)	9419(2)	5579(2)	6811(1)	28(1)
C(23)	7607(2)	4995(2)	4902(1)	29(1)
C(24)	7254(2)	6456(2)	4784(1)	29(1)
C(25)	7662(2)	8125(2)	4167(1)	42(1)
N(1)	6924(2)	4653(1)	6585(1)	27(1)
O(1)	4237(1)	4216(1)	6371(1)	41(1)
O(2)	5771(1)	2704(1)	6822(1)	31(1)
O(3)	6564(2)	7260(1)	5043(1)	54(1)

O(4)

7817(2)

6743(1)

4332(1)

37(1)

-



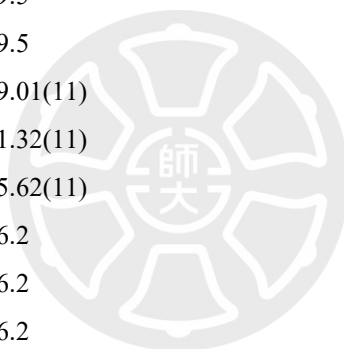
Table 3. Bond lengths [Å] and angles [°] for d25033a.

C(1)-O(1)	1.2094(18)
C(1)-O(2)	1.3547(17)
C(1)-N(1)	1.3589(19)
C(2)-O(2)	1.4782(17)
C(2)-C(5)	1.515(2)
C(2)-C(4)	1.515(2)
C(2)-C(3)	1.521(2)
C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800
C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-N(1)	1.4795(18)
C(6)-C(22)	1.5146(19)
C(6)-C(7)	1.5688(18)
C(6)-H(6)	1.0000
C(7)-C(8)	1.5033(19)
C(7)-C(15)	1.5754(18)
C(7)-H(7)	1.0000
C(8)-C(13)	1.3858(19)
C(8)-C(9)	1.397(2)
C(9)-C(10)	1.389(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.384(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.388(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.389(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.514(2)
C(14)-C(23)	1.5295(18)

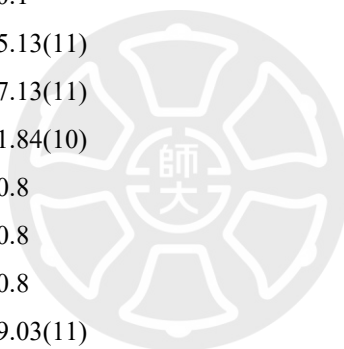
C(14)-C(15)	1.5526(19)
C(14)-H(14)	1.0000
C(15)-C(16)	1.5592(19)
C(15)-H(15)	1.0000
C(16)-N(1)	1.4733(18)
C(16)-C(17)	1.513(2)
C(16)-H(16)	1.0000
C(17)-C(18)	1.379(2)
C(17)-C(22)	1.393(2)
C(18)-C(19)	1.393(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.383(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.392(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.386(2)
C(21)-H(21)	0.9500
C(23)-C(24)	1.501(2)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-O(3)	1.1935(18)
C(24)-O(4)	1.3361(17)
C(25)-O(4)	1.4374(19)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800

O(1)-C(1)-O(2)	125.85(13)
O(1)-C(1)-N(1)	123.87(13)
O(2)-C(1)-N(1)	110.14(12)
O(2)-C(2)-C(5)	109.28(12)
O(2)-C(2)-C(4)	110.50(12)
C(5)-C(2)-C(4)	112.78(14)
O(2)-C(2)-C(3)	102.35(12)
C(5)-C(2)-C(3)	110.98(14)
C(4)-C(2)-C(3)	110.46(14)
C(2)-C(3)-H(3A)	109.5

C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(22)	99.01(11)
N(1)-C(6)-C(7)	101.32(11)
C(22)-C(6)-C(7)	105.62(11)
N(1)-C(6)-H(6)	116.2
C(22)-C(6)-H(6)	116.2
C(7)-C(6)-H(6)	116.2
C(8)-C(7)-C(6)	114.24(11)
C(8)-C(7)-C(15)	104.32(11)
C(6)-C(7)-C(15)	102.18(10)
C(8)-C(7)-H(7)	111.8
C(6)-C(7)-H(7)	111.8
C(15)-C(7)-H(7)	111.8
C(13)-C(8)-C(9)	120.19(13)
C(13)-C(8)-C(7)	111.92(12)
C(9)-C(8)-C(7)	127.87(12)
C(10)-C(9)-C(8)	118.92(14)
C(10)-C(9)-H(9)	120.5
C(8)-C(9)-H(9)	120.5
C(11)-C(10)-C(9)	120.74(14)
C(11)-C(10)-H(10)	119.6



C(9)-C(10)-H(10)	119.6
C(10)-C(11)-C(12)	120.28(14)
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-C(13)	119.31(14)
C(11)-C(12)-H(12)	120.3
C(13)-C(12)-H(12)	120.3
C(8)-C(13)-C(12)	120.55(14)
C(8)-C(13)-C(14)	112.09(12)
C(12)-C(13)-C(14)	127.23(13)
C(13)-C(14)-C(23)	109.39(11)
C(13)-C(14)-C(15)	104.37(11)
C(23)-C(14)-C(15)	112.54(12)
C(13)-C(14)-H(14)	110.1
C(23)-C(14)-H(14)	110.1
C(15)-C(14)-H(14)	110.1
C(14)-C(15)-C(16)	115.13(11)
C(14)-C(15)-C(7)	107.13(11)
C(16)-C(15)-C(7)	101.84(10)
C(14)-C(15)-H(15)	110.8
C(16)-C(15)-H(15)	110.8
C(7)-C(15)-H(15)	110.8
N(1)-C(16)-C(17)	99.03(11)
N(1)-C(16)-C(15)	102.44(11)
C(17)-C(16)-C(15)	105.70(11)
N(1)-C(16)-H(16)	115.8
C(17)-C(16)-H(16)	115.8
C(15)-C(16)-H(16)	115.8
C(18)-C(17)-C(22)	121.20(14)
C(18)-C(17)-C(16)	132.77(14)
C(22)-C(17)-C(16)	105.88(12)
C(17)-C(18)-C(19)	117.78(15)
C(17)-C(18)-H(18)	121.1
C(19)-C(18)-H(18)	121.1
C(20)-C(19)-C(18)	121.20(15)
C(20)-C(19)-H(19)	119.4
C(18)-C(19)-H(19)	119.4



C(19)-C(20)-C(21)	120.99(15)
C(19)-C(20)-H(20)	119.5
C(21)-C(20)-H(20)	119.5
C(22)-C(21)-C(20)	117.77(15)
C(22)-C(21)-H(21)	121.1
C(20)-C(21)-H(21)	121.1
C(21)-C(22)-C(17)	121.03(14)
C(21)-C(22)-C(6)	132.68(14)
C(17)-C(22)-C(6)	106.08(12)
C(24)-C(23)-C(14)	114.86(12)
C(24)-C(23)-H(23A)	108.6
C(14)-C(23)-H(23A)	108.6
C(24)-C(23)-H(23B)	108.6
C(14)-C(23)-H(23B)	108.6
H(23A)-C(23)-H(23B)	107.5
O(3)-C(24)-O(4)	123.79(14)
O(3)-C(24)-C(23)	126.61(13)
O(4)-C(24)-C(23)	109.60(12)
O(4)-C(25)-H(25A)	109.5
O(4)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
O(4)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(1)-N(1)-C(16)	123.68(11)
C(1)-N(1)-C(6)	129.23(12)
C(16)-N(1)-C(6)	97.88(10)
C(1)-O(2)-C(2)	119.76(11)
C(24)-O(4)-C(25)	117.10(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d25033a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	29(1)	29(1)	27(1)	2(1)	2(1)	-1(1)
C(2)	28(1)	28(1)	36(1)	2(1)	3(1)	-6(1)
C(3)	50(1)	36(1)	62(1)	16(1)	-5(1)	-8(1)
C(4)	39(1)	45(1)	52(1)	-2(1)	17(1)	-6(1)
C(5)	52(1)	50(1)	42(1)	-11(1)	2(1)	-9(1)
C(6)	25(1)	26(1)	25(1)	3(1)	-2(1)	-2(1)
C(7)	26(1)	25(1)	26(1)	1(1)	0(1)	1(1)
C(8)	27(1)	26(1)	25(1)	0(1)	5(1)	-1(1)
C(9)	36(1)	31(1)	31(1)	4(1)	3(1)	6(1)
C(10)	46(1)	25(1)	40(1)	1(1)	11(1)	3(1)
C(11)	50(1)	28(1)	38(1)	-7(1)	4(1)	-7(1)
C(12)	43(1)	33(1)	29(1)	-4(1)	-3(1)	-6(1)
C(13)	31(1)	26(1)	24(1)	1(1)	3(1)	-2(1)
C(14)	28(1)	25(1)	26(1)	0(1)	-2(1)	-1(1)
C(15)	28(1)	24(1)	24(1)	2(1)	-1(1)	-2(1)
C(16)	32(1)	23(1)	28(1)	2(1)	1(1)	1(1)
C(17)	36(1)	27(1)	23(1)	-2(1)	6(1)	-1(1)
C(18)	52(1)	28(1)	28(1)	-3(1)	8(1)	-2(1)
C(19)	54(1)	34(1)	36(1)	-11(1)	9(1)	-14(1)
C(20)	43(1)	46(1)	31(1)	-12(1)	2(1)	-13(1)
C(21)	36(1)	41(1)	26(1)	-5(1)	0(1)	-5(1)
C(22)	33(1)	29(1)	22(1)	-2(1)	3(1)	-6(1)
C(23)	36(1)	28(1)	25(1)	-1(1)	-2(1)	5(1)
C(24)	32(1)	29(1)	28(1)	-1(1)	-4(1)	1(1)
C(25)	47(1)	33(1)	46(1)	13(1)	2(1)	-1(1)
N(1)	28(1)	24(1)	28(1)	4(1)	0(1)	0(1)
O(1)	28(1)	40(1)	54(1)	14(1)	-6(1)	1(1)
O(2)	27(1)	30(1)	37(1)	8(1)	-2(1)	-6(1)
O(3)	80(1)	32(1)	49(1)	3(1)	23(1)	13(1)
O(4)	50(1)	32(1)	29(1)	6(1)	4(1)	5(1)

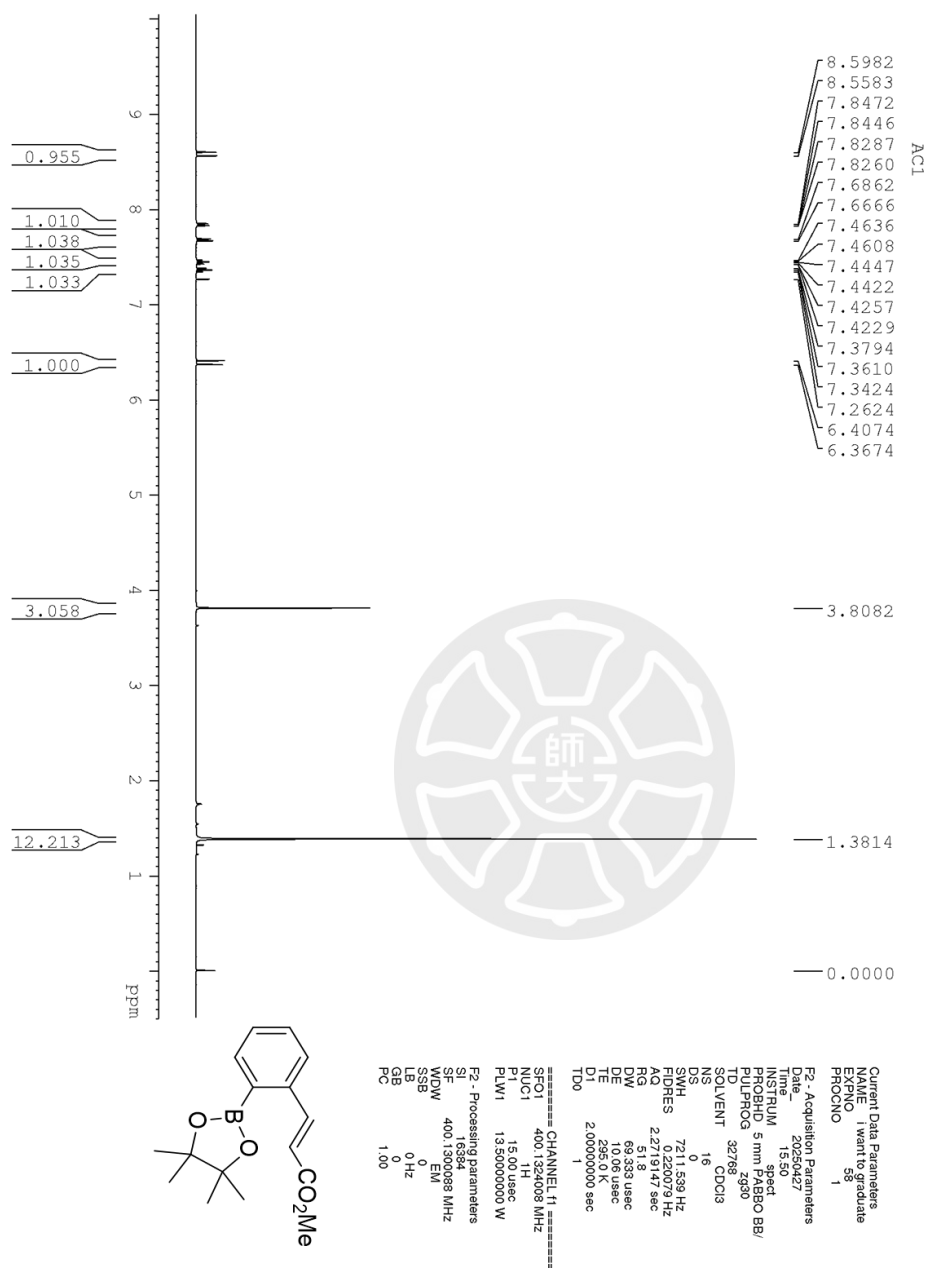
Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for d25033a.

	x	y	z	U(eq)
H(3A)	4448	-208	7179	74
H(3B)	5407	930	7492	74
H(3C)	6275	279	7015	74
H(4A)	2098	1498	7153	68
H(4B)	2348	2894	6860	68
H(4C)	3189	2693	7390	68
H(5A)	3322	386	6336	72
H(5B)	5164	840	6175	72
H(5C)	3634	1877	6121	72
H(6)	8909	3438	6857	30
H(7)	10468	4226	6043	31
H(9)	9996	1298	6183	39
H(10)	8912	-478	5705	44
H(11)	6923	-47	5099	46
H(12)	5967	2169	4964	42
H(14)	5901	4749	5482	31
H(15)	8951	5942	5679	31
H(16)	6173	6381	6181	33
H(18)	8211	8629	6486	43
H(19)	10497	9199	6990	50
H(20)	12110	7525	7357	48
H(21)	11471	5216	7242	41
H(23A)	8819	4828	4858	35
H(23B)	7004	4418	4662	35
H(25A)	7993	8187	3820	63
H(25B)	8389	8709	4367	63
H(25C)	6498	8422	4203	63

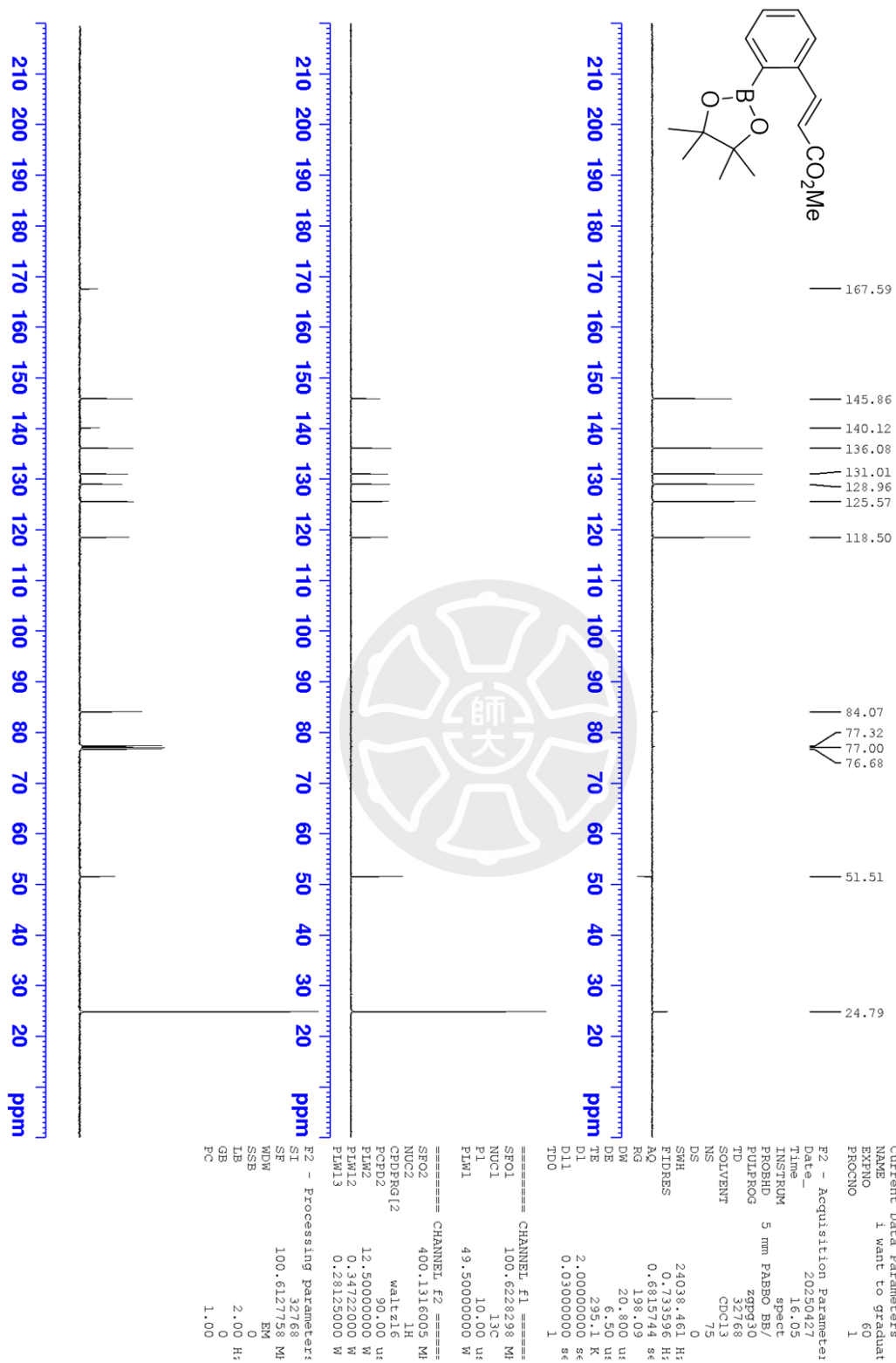
附錄二 核磁共振光譜



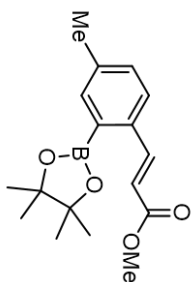
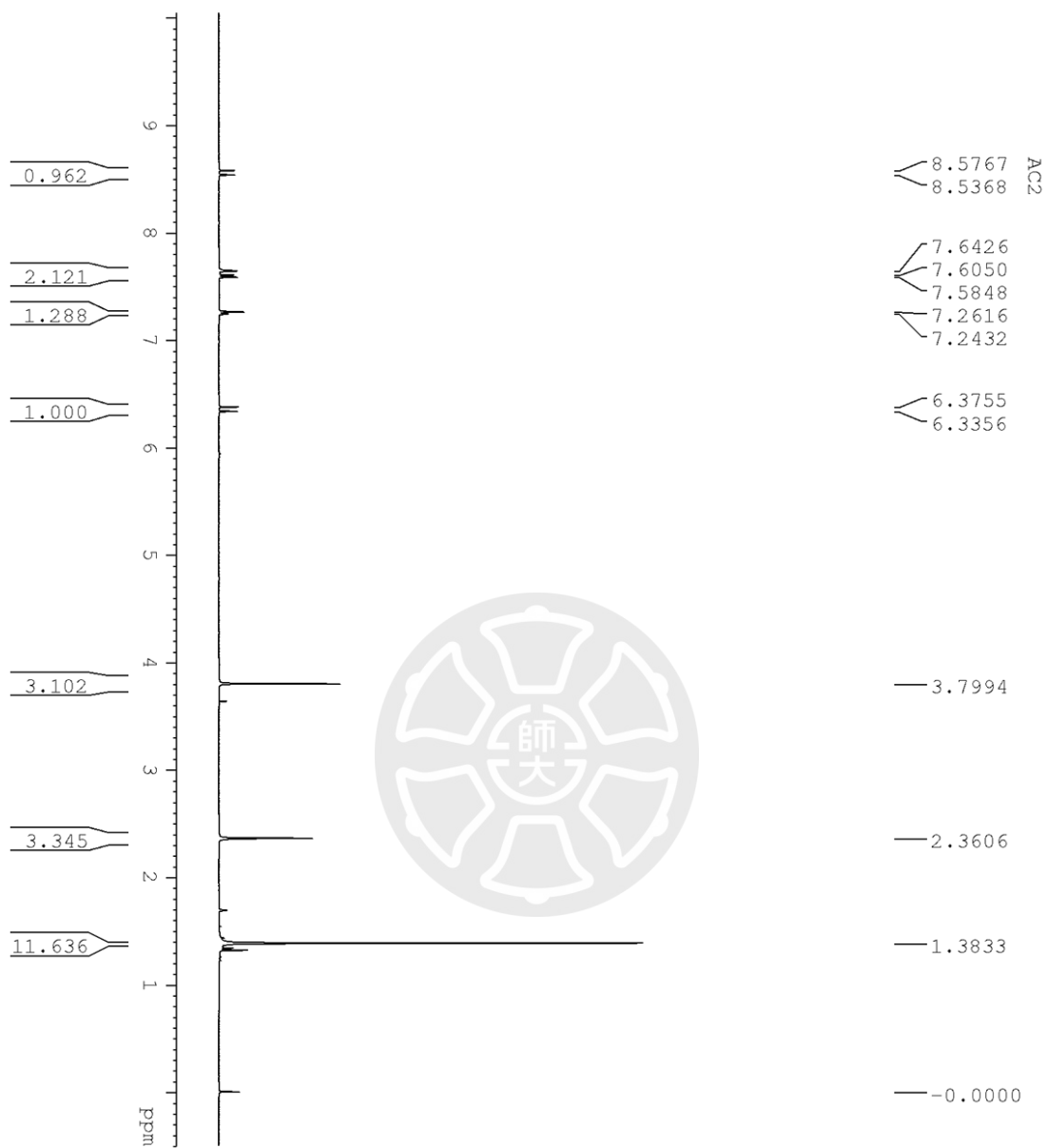
¹H NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23a)



¹³C NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23a)



¹H NMR spectrum of methyl (E)-3-(4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23b)



```

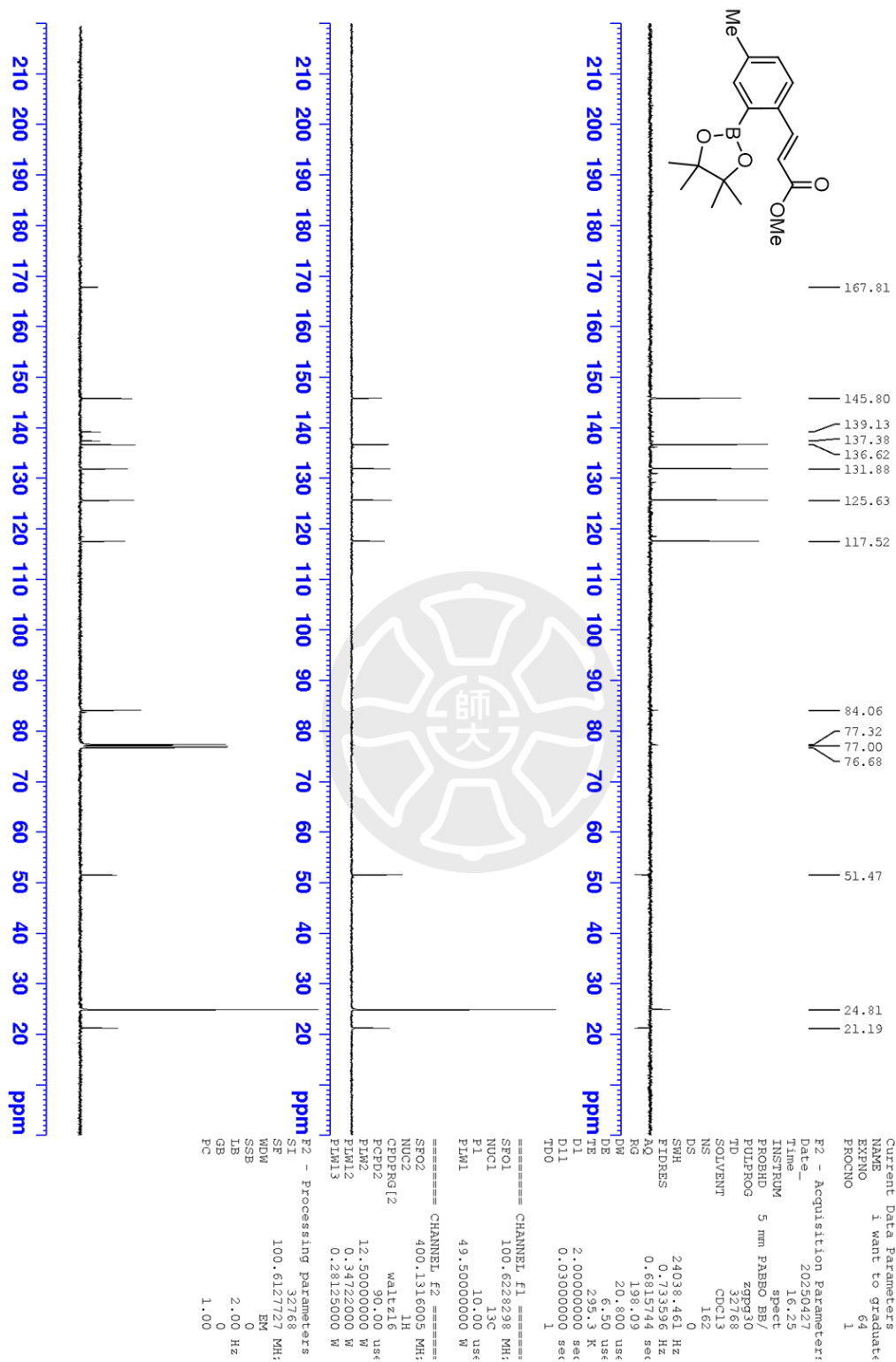
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PROCNO   1

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PULPROG zgpg30
SOLVENT  CDCl3
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NS        0
SMW       721.539 Hz
FIDRES    0.220079 Hz
AQ        2.2719147 sec
RG         63.58
DW         69.393 usec
DE         10.06 usec
TE        295.2 K
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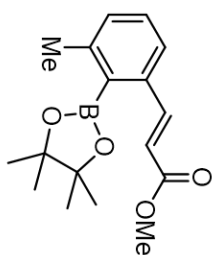
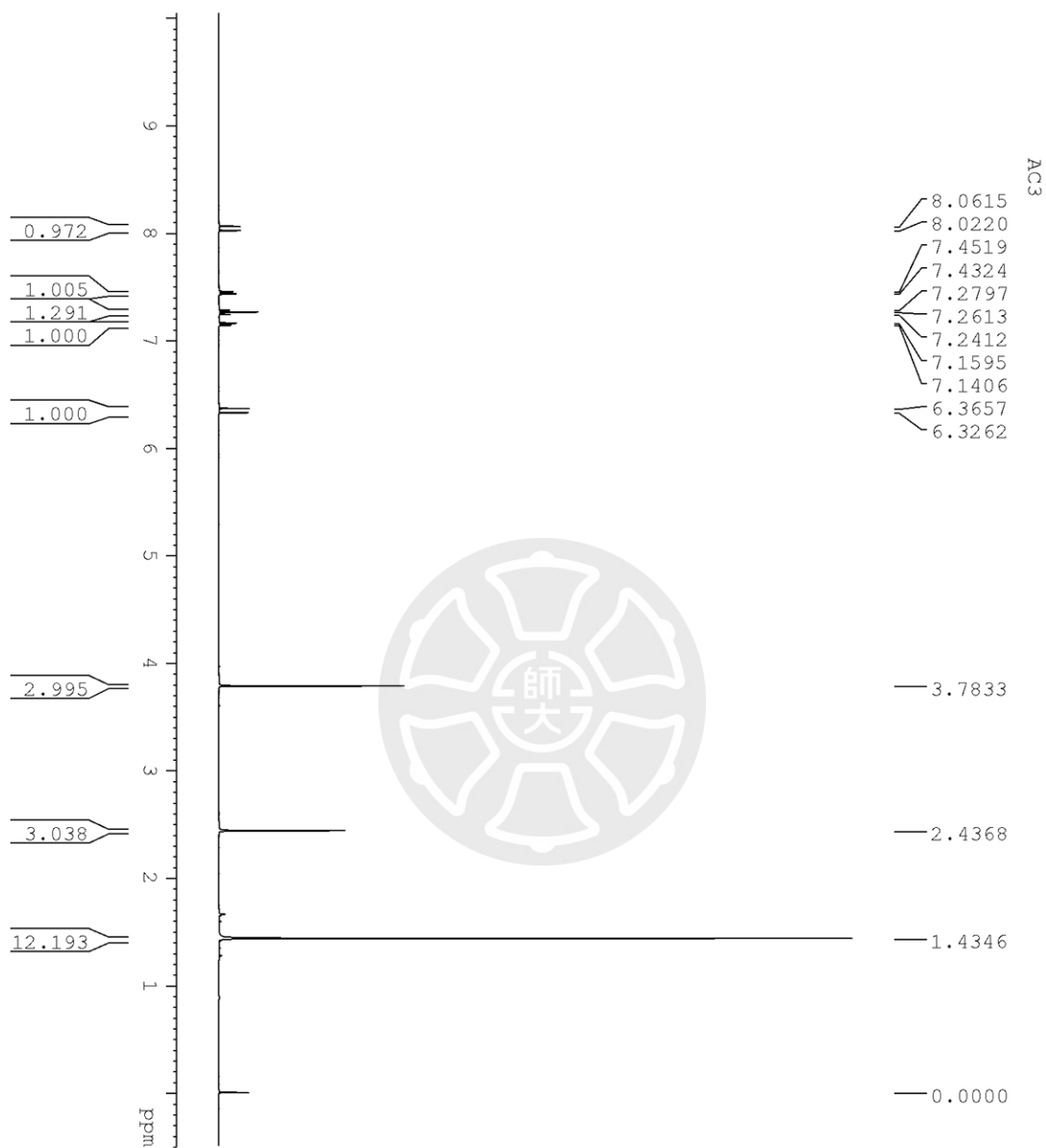
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P1         15.00 usec
PLW1      13.50000000 W

F2 - Processing parameters
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WDW        EM
SSB        0
LB         0 Hz
GB         0
PC         1.00
    
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¹³C NMR spectrum of methyl (E)-3-(4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23b)



¹H NMR spectrum of methyl (E)-3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) acrylate (23c)



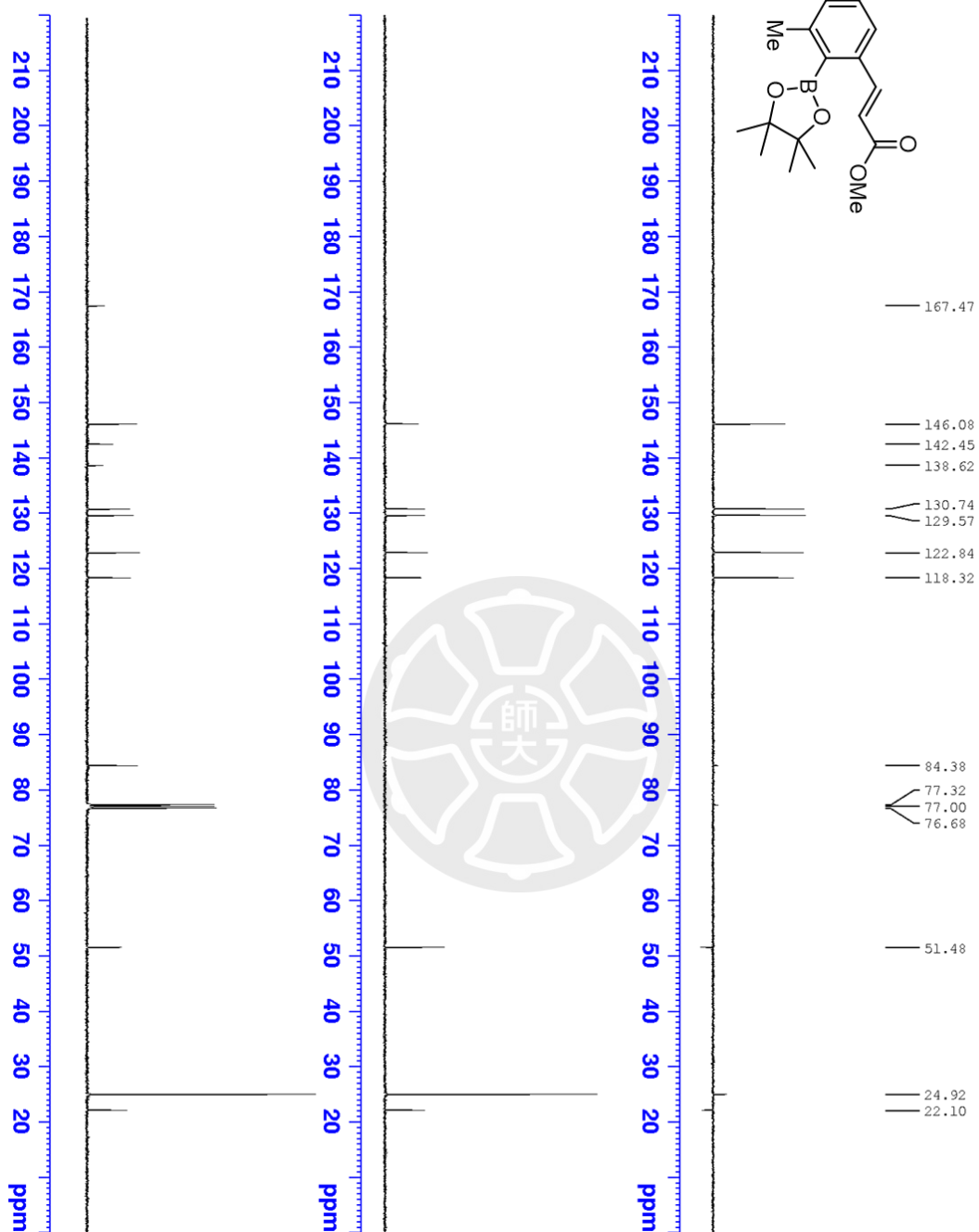
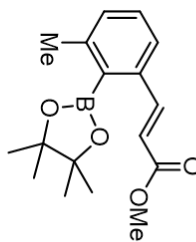
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 PROCNO: 1

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 NS: 4
 DS: 0
 SWH: 7211.539 Hz
 FIDRES: 0.220079 Hz
 AQ: 2.2719147 sec
 RG: 57.42
 DW: 69.383 usec
 DE: 10.06 usec
 TE: 295.4 K
 D1: 2.00000000 sec
 TDO: 1

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 NUC1: 1H
 P1: 15.00 usec
 PLW1: 13.50000000 W

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 SI: 16384
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 WDW: EM
 SSB: 0
 LB: 0 Hz
 GB: 0
 PC: 1.00

¹³C NMR spectrum of methyl (E)-3-(3-methyl-2-(4,4,5,5-tetramethyl-1,3-dioxaborolan-2-yl)phenyl) acrylate (23c)



Current Data Parameters
 NAME I want to graduate.
 EXPNO 68
 PROCNO 1

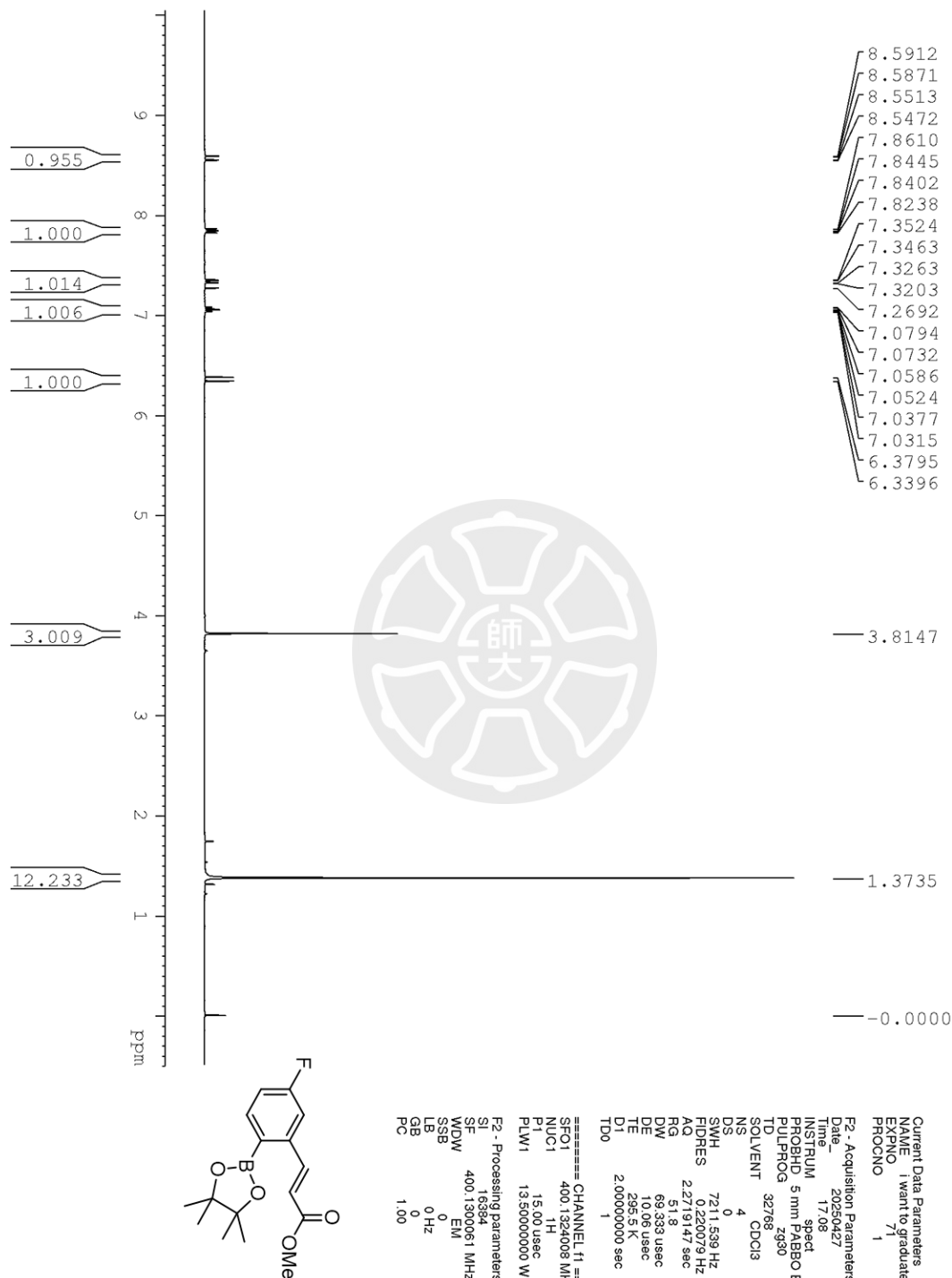
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 PULPROG zgpg30
 TD 32768
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 NS 107
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 se
 RG 198.09
 DW 20.800 us.
 DE 6.50 us.
 TE 295.5 K
 D1 2.00000000 se
 D11 0.03000000 se
 TDO 1

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 PL1 49.50000000 W

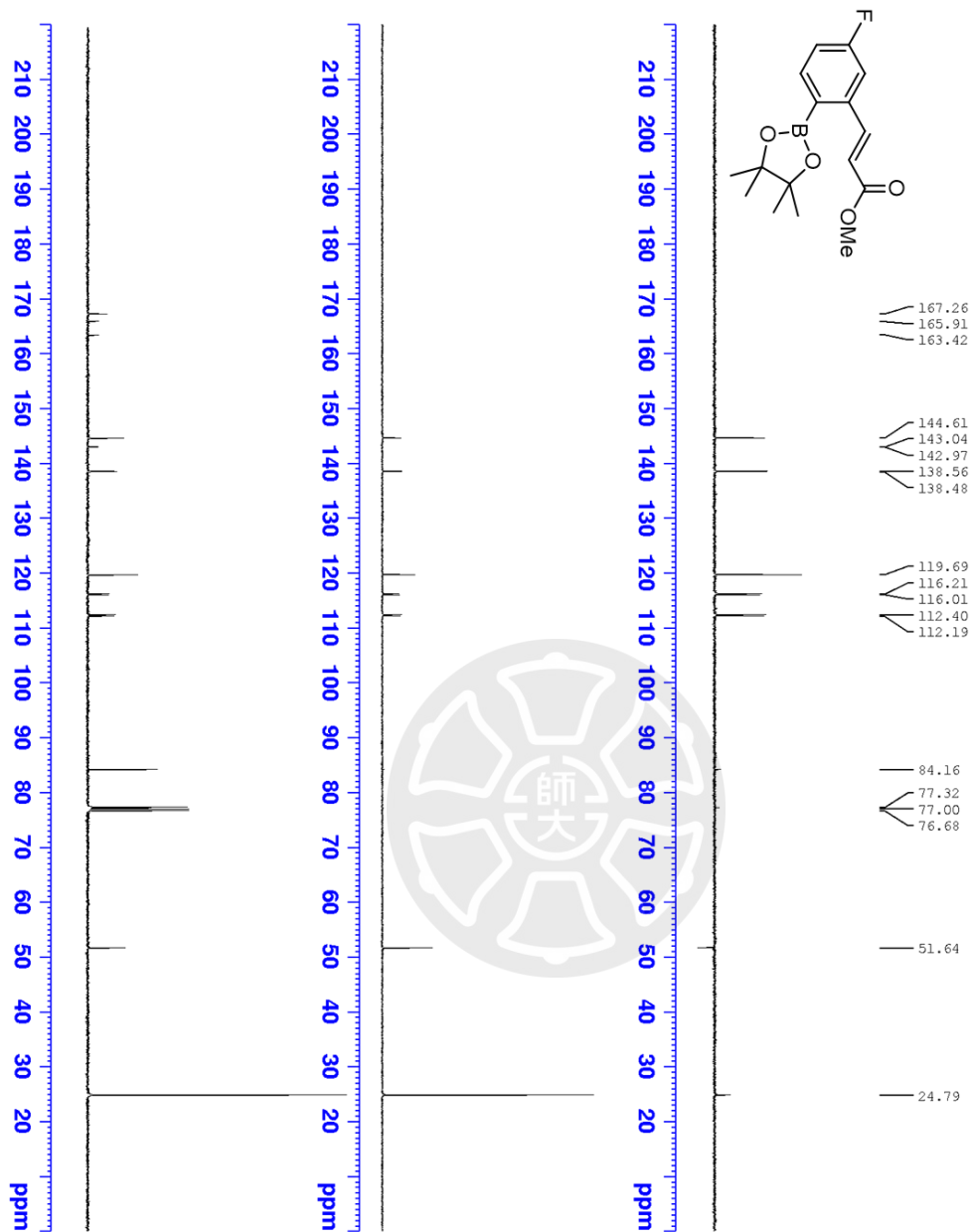
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 CEPRPG12 waltz16
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 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127732 MH
 WDM 0
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of methyl (E)-3-(5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23g)



¹³C NMR spectrum of methyl (E)-3-(5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23g)



```

Current Data Parameters
NAME          i want to graduate
EXPNO         72
PROCNO        1

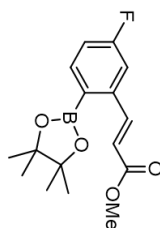
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PULPROG      zgpg30
TD           32768
SOLVENT      CDCl3
NS           97
DS           0
SWH          24038.461 Hz
FIDRES      0.733596 Hz
AQ          0.6815744 sec
RG          198.09
DW          20.800 usec
DE          6.50 usec
TE          295.8 K
D1          2.00000000 sec
D11         0.03000000 sec
TDO         1

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NUC1       13C
P1         10.00 usec
PL1       49.50000000 W
PLM1

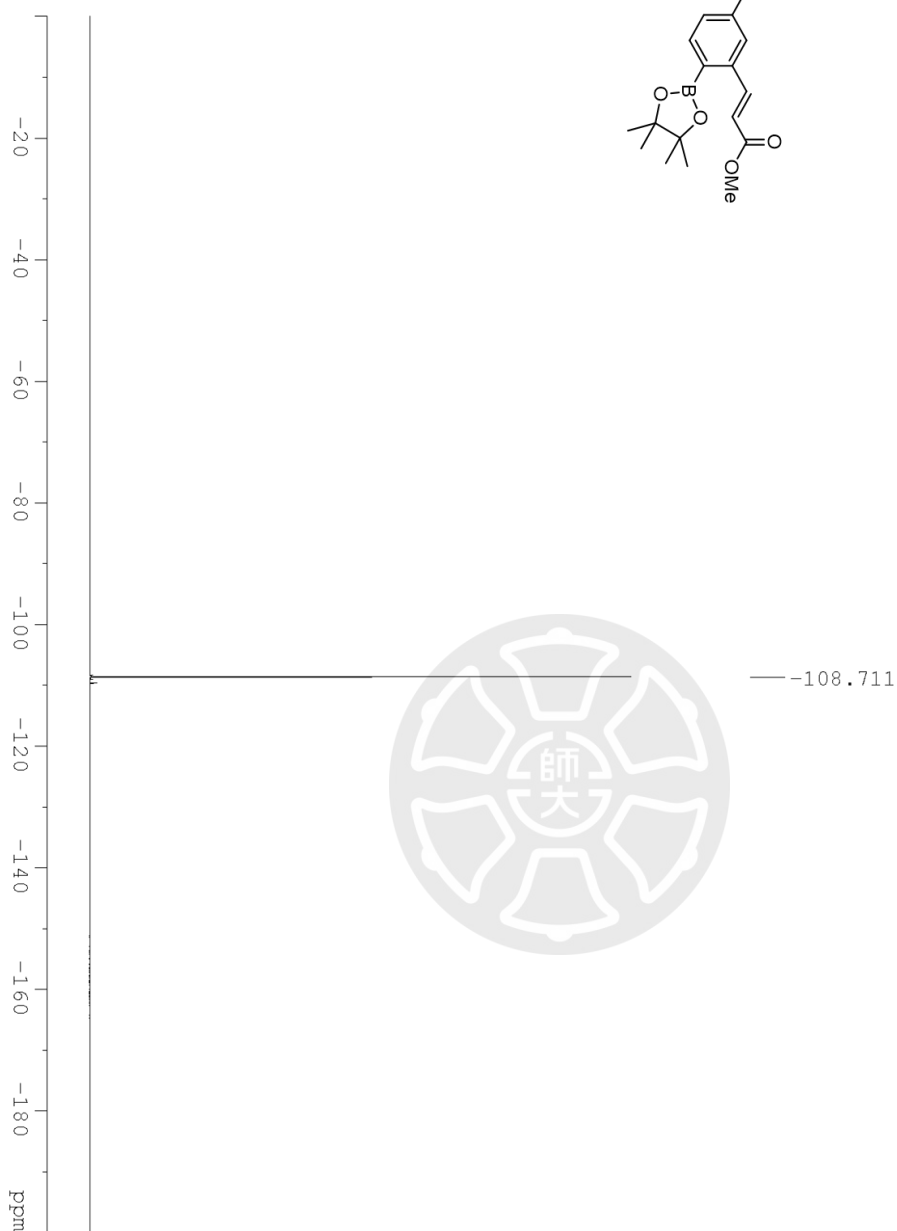
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NUC2       1H
CPDPRG2    waltz16
PCPD2      90.00 usec
PLM2       12.50000000 W
PLM12     0.34722000 W
PLM13     0.28125000 W

F2 - Processing parameters:
SI         32768
SF         100.6127727 MHz
WDW        EM
SSB        0
LB         2.00 Hz
GB         0
PC         1.00
  
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¹⁹F NMR spectrum of methyl (E)-3-(5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23g)



AC4 19F



Current Data Parameters
 NAME I went to graduate
 EXPNO 75
 PROCNO 1

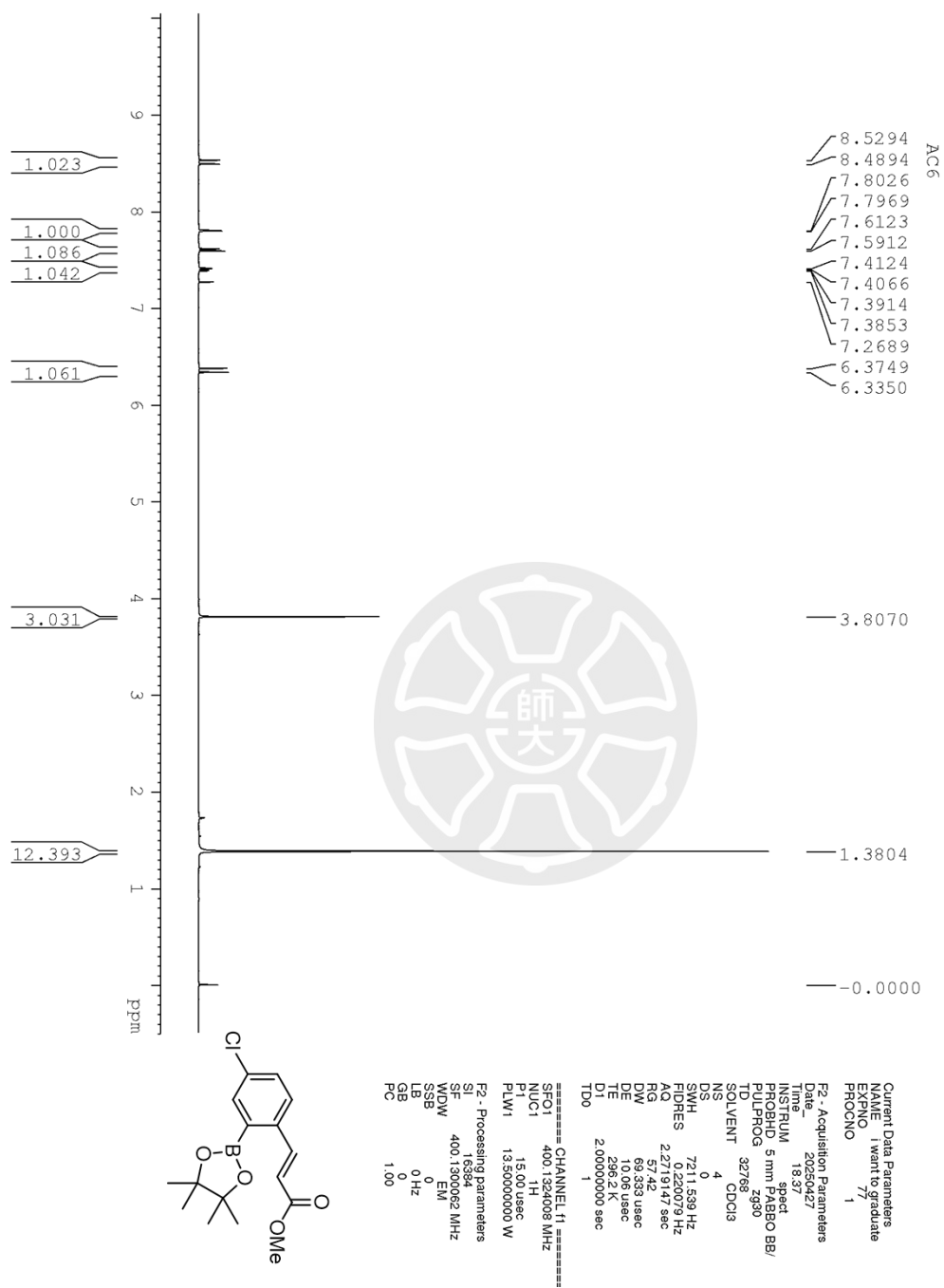
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 PULPROG zgpg
 TD 131072
 SOLVENT CDCl3
 NS 4
 DS 4
 SWH 89295.711 Hz
 FIDRES 0.6981196 Hz
 AQ 0.7240032 sec
 RG 198.09
 DW 5.600 usec
 DE 6.50 usec
 TE 295.9 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDO 1

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 PLW1 16.50000000 W

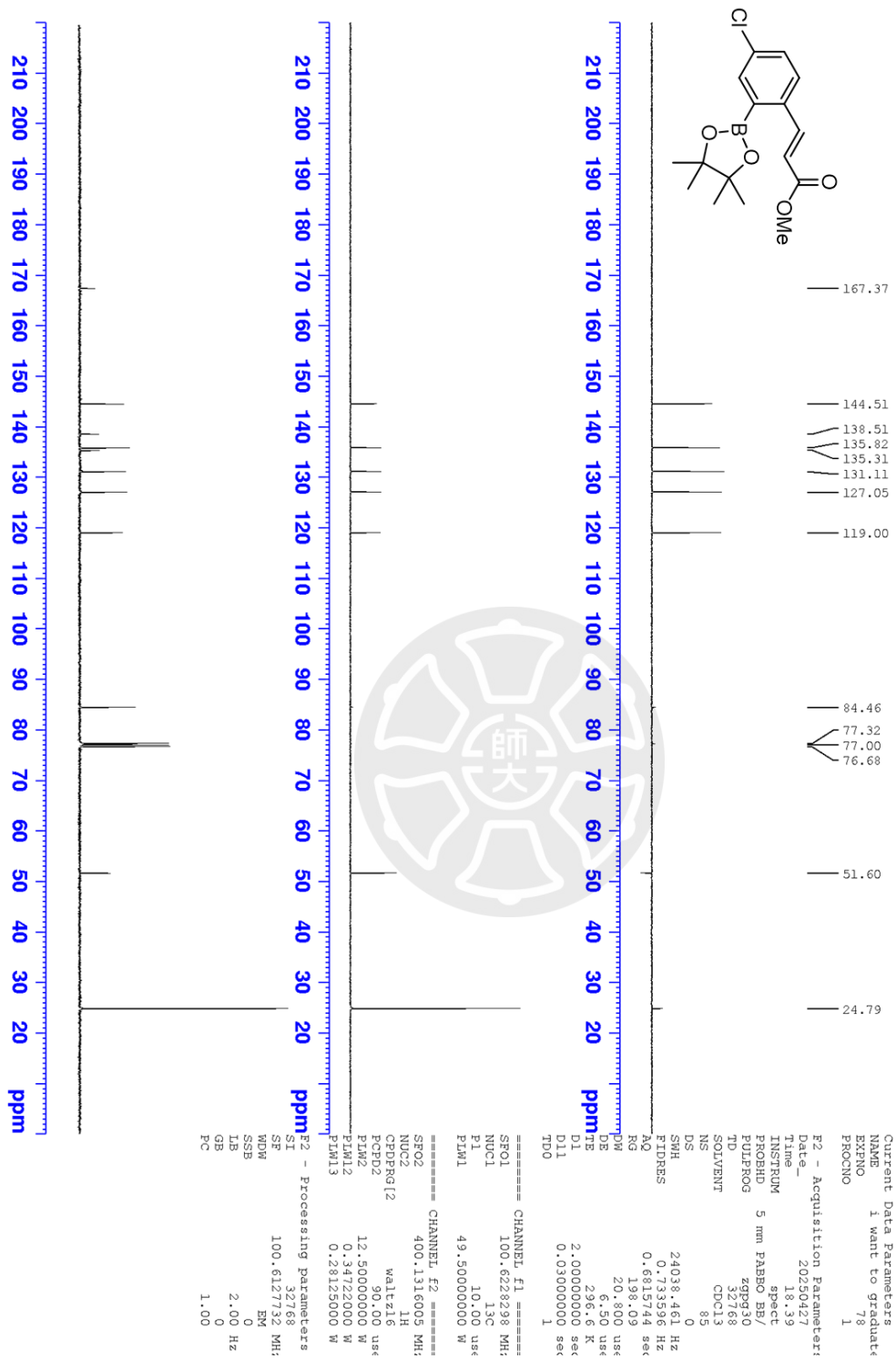
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 CPDPRGf2 waltz16
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 PLW2 12.50000000 W
 PLW12 0.34722000 W

F2 - Processing parameters

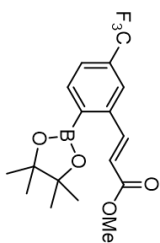
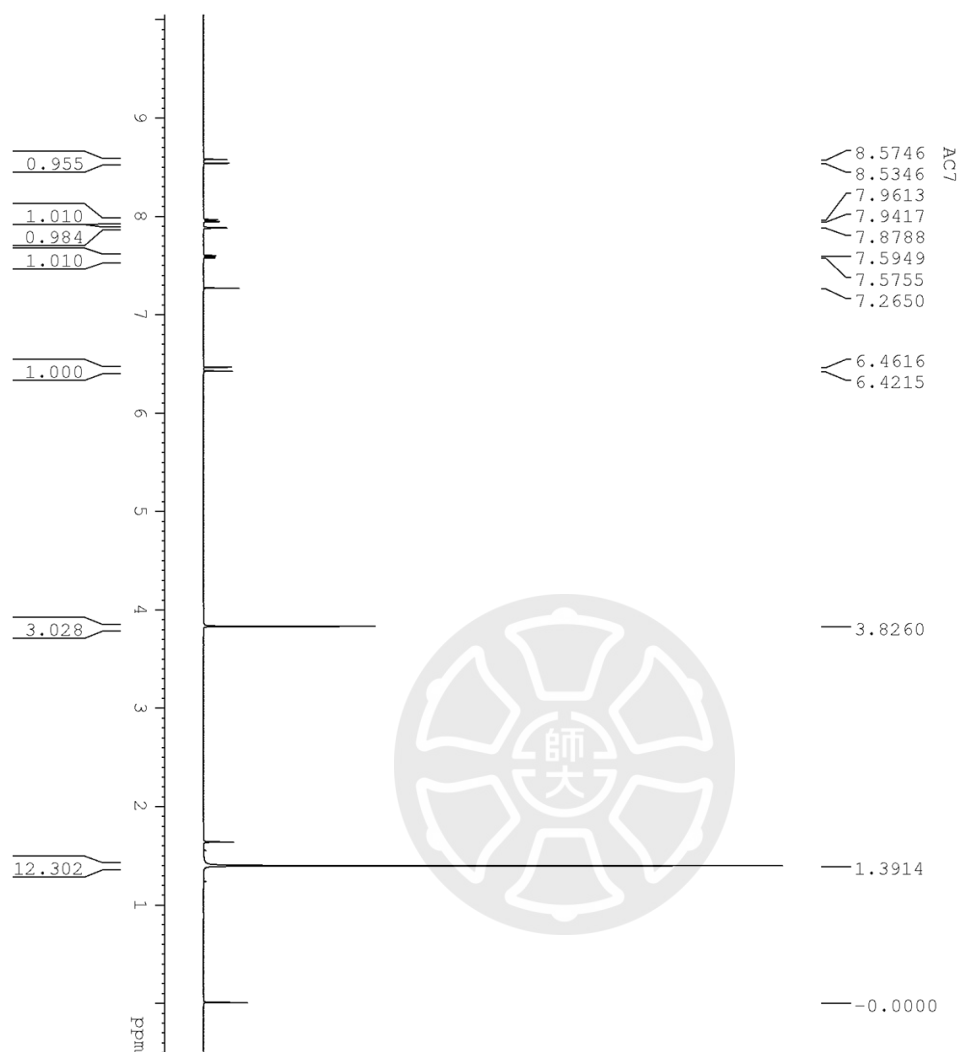
¹H NMR spectrum of methyl (E)-3-(4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23j)



¹³C NMR spectrum of methyl (E)-3-(4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23j)



¹H NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl) phenyl) acrylate (23i)



```

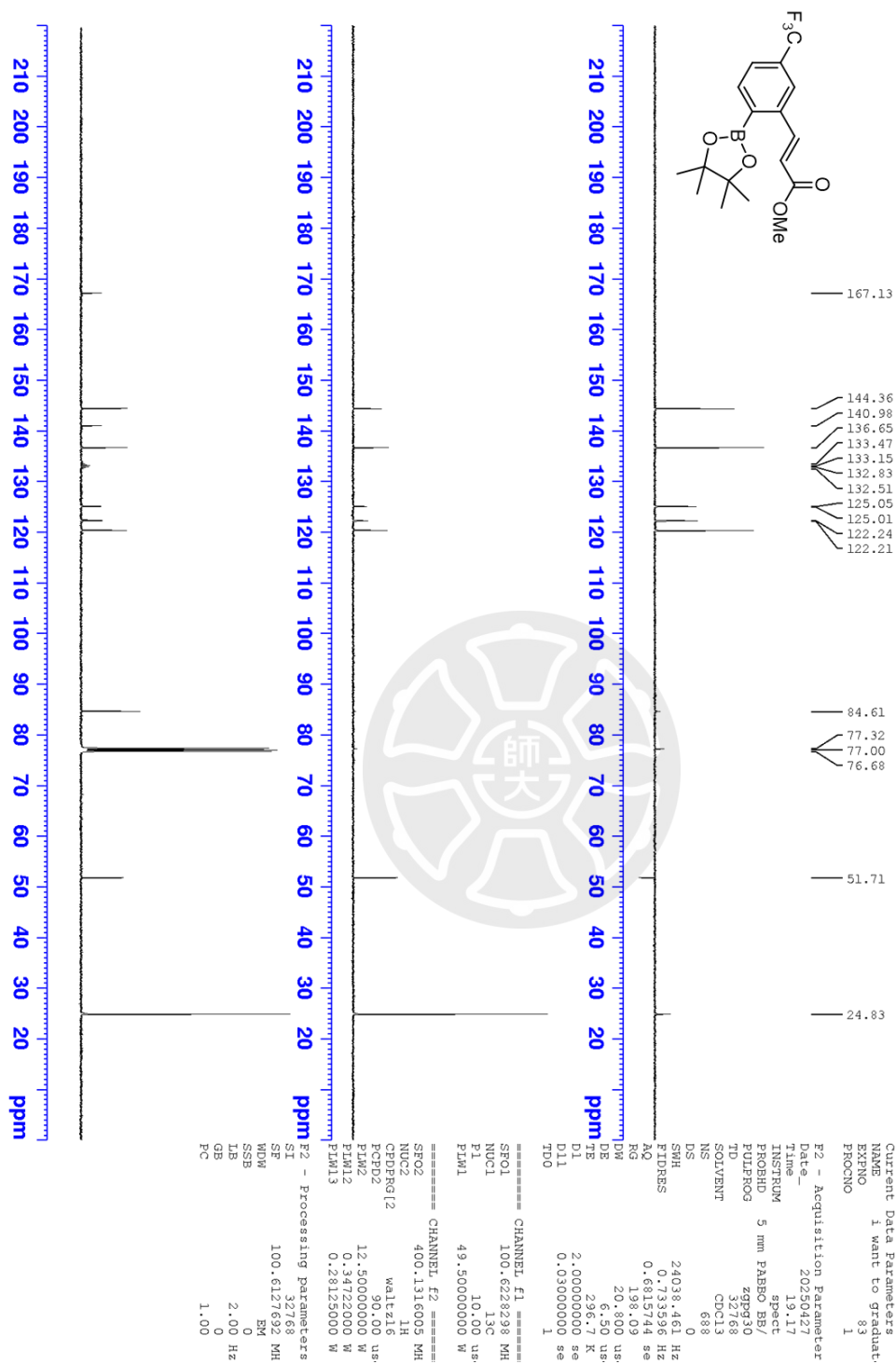
Current Data Parameters
NAME i want to graduate
EXPNO 81
PROCNO 1

F2 - Acquisition Parameters
Date_ 20250427
Time 19.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWHES 7211.539 Hz
FIDRES 0.22742079 Hz
AQ 2.2715447 sec
RG 39.08
DE 69.335 usec
TE 296.4 K
TD0 2.00000000 sec

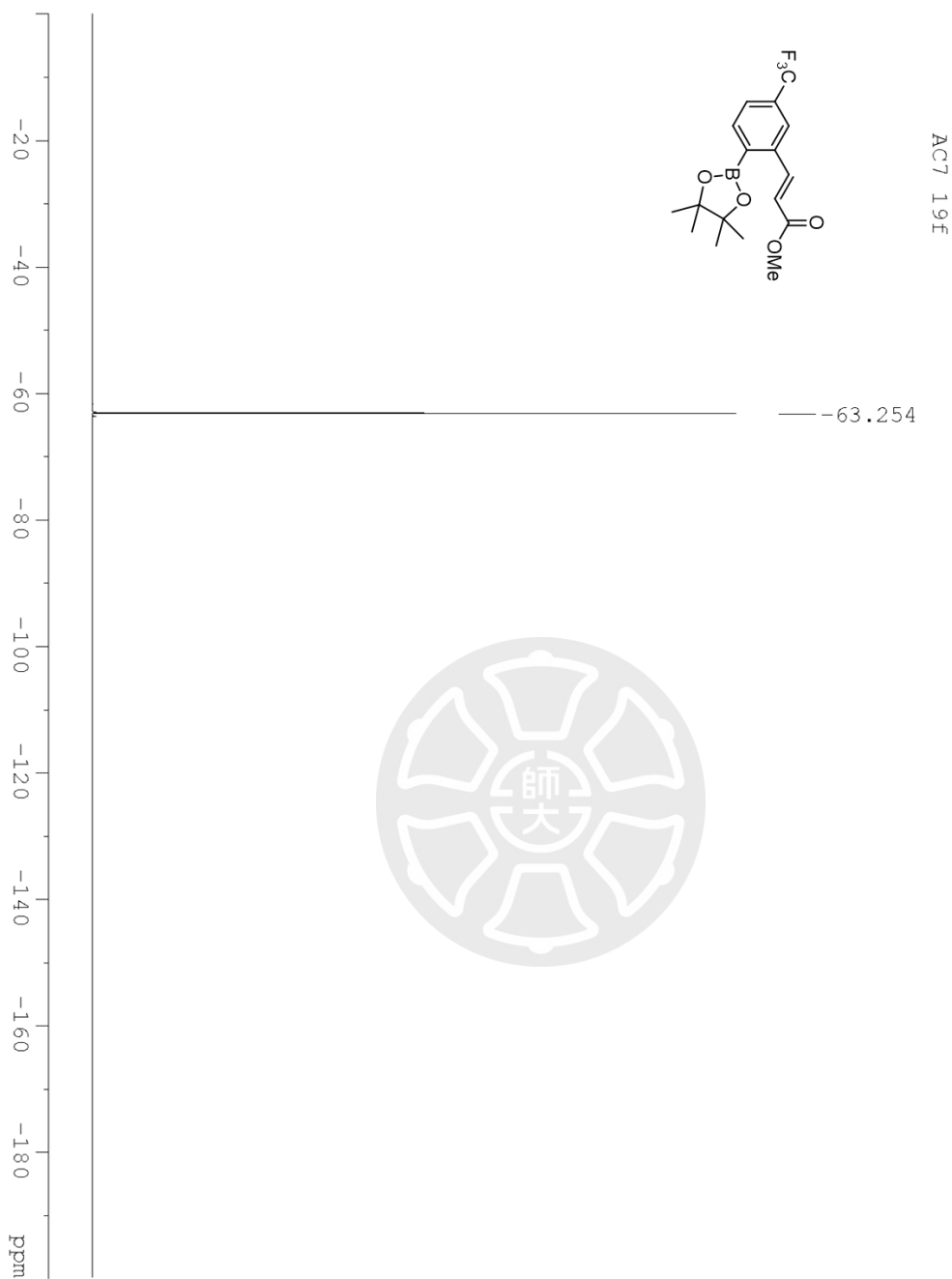
===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 16384
SF 400.1300077 MHz
WDW EM
SSB 0
GB 0
PC 1.00
    
```

¹³C NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl) phenyl) acrylate (23i)



¹⁹F NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl) phenyl) acrylate (23i)



ACT7 19F

Current Data Parameters
 NAME I want to graduate
 EXPNO 96
 PROCNO 1

F2 - Acquisition Parameters

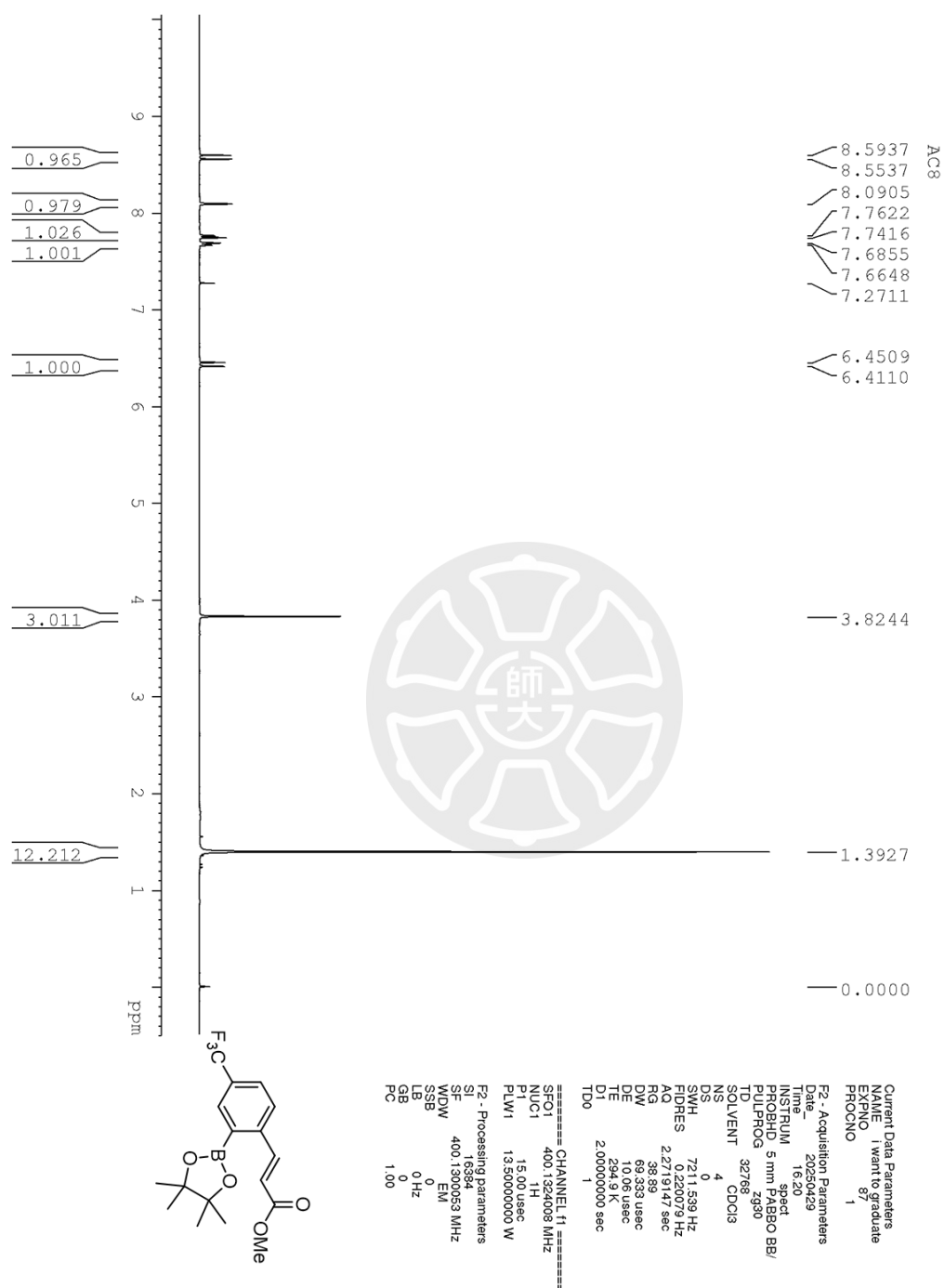
Date 20250427
 Time 20:31
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg
 TD 131072
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 89285.711 Hz
 FIDRES 0.681196 Hz
 AQ 0.7340032 sec
 RG 198.09
 DW 5.600 usec
 DE 6.50 usec
 TE 296.9 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
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 NUC1 19F
 P1 15.00 usec
 PLW1 16.50000000 W

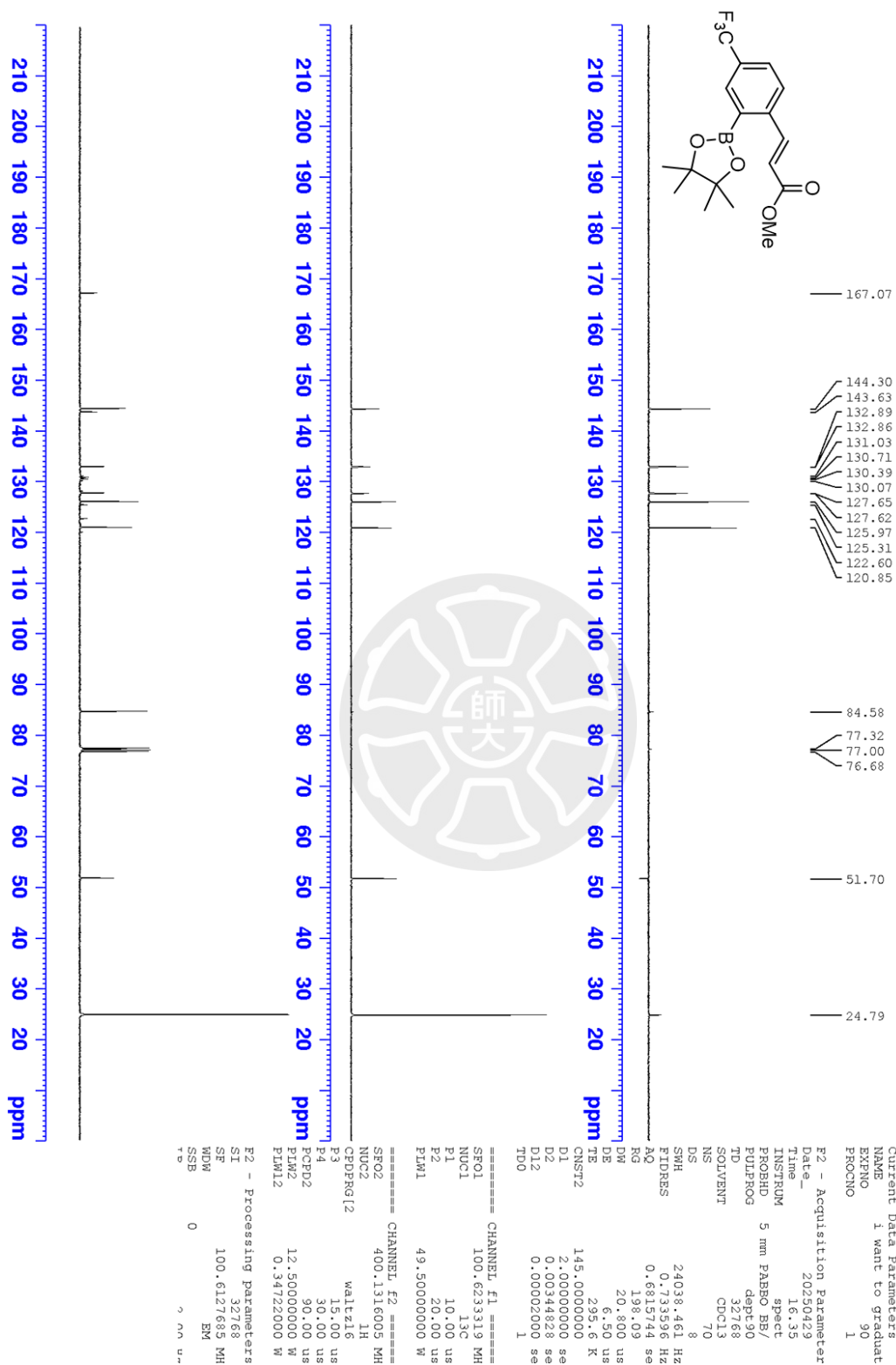
===== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRGf2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLWf2 0.34722000 W

F2 - Processing parameters

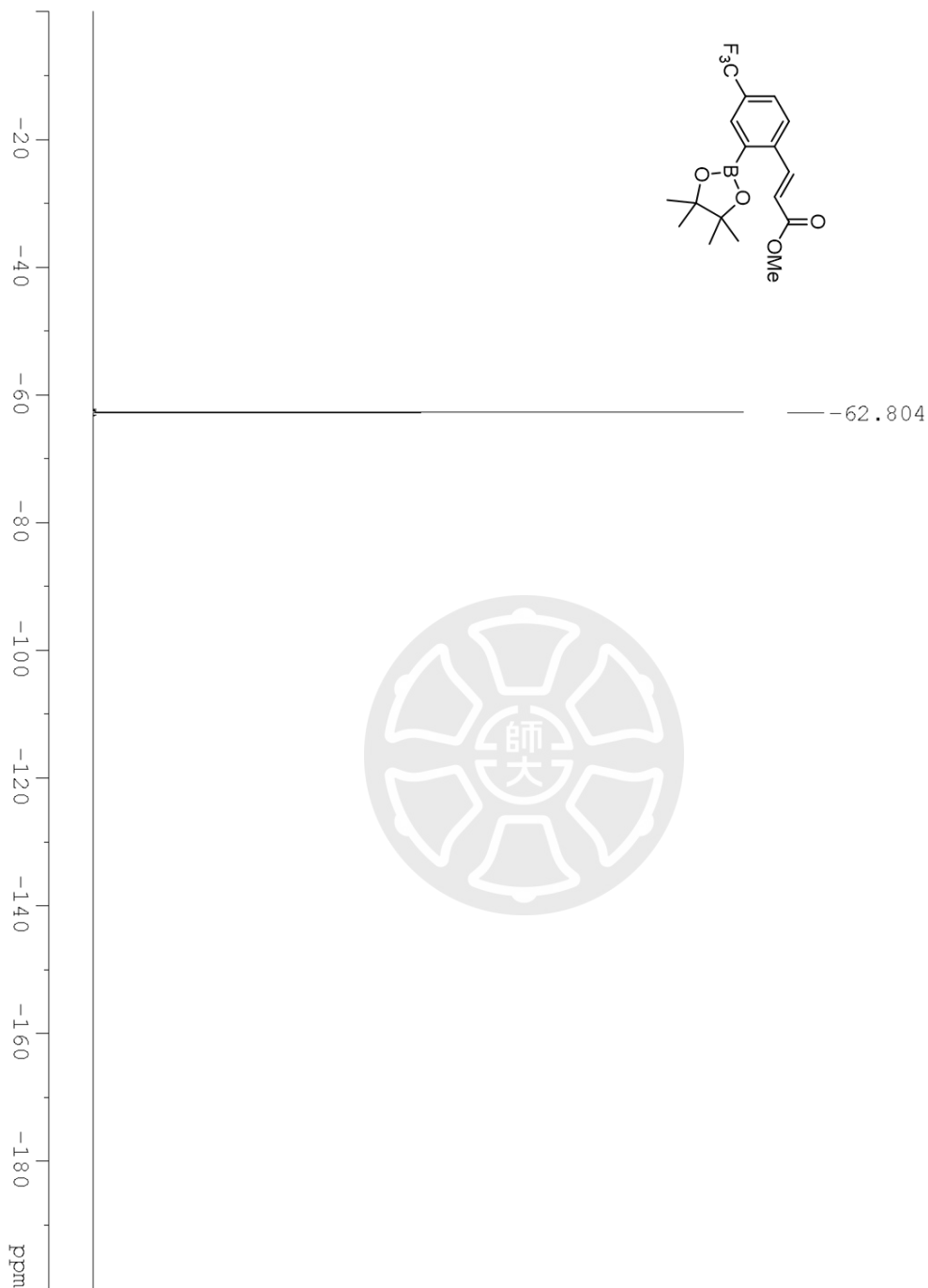
¹H NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenyl) acrylate (23h)



¹³C NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenyl) acrylate (23h)



^{19}F NMR spectrum of methyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)phenyl) acrylate (23h)



AC8 19F

Current Data Parameters
 NAME i want to graduate
 EXPNO 91
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20250429
 Time 16.42
 INSTRUM spect
 PROBHID 5 mm PABBO BB/
 PULPROG zgpg
 TD 131072
 SOLVENT CDC13
 NS 8
 DS 0
 SWH 89285.711 Hz
 FIDRES 0.681196 Hz
 AQ 0.7340032 sec
 RG 198.09
 DW 5.600 usec
 DE 6.50 usec
 TE 295.3 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====

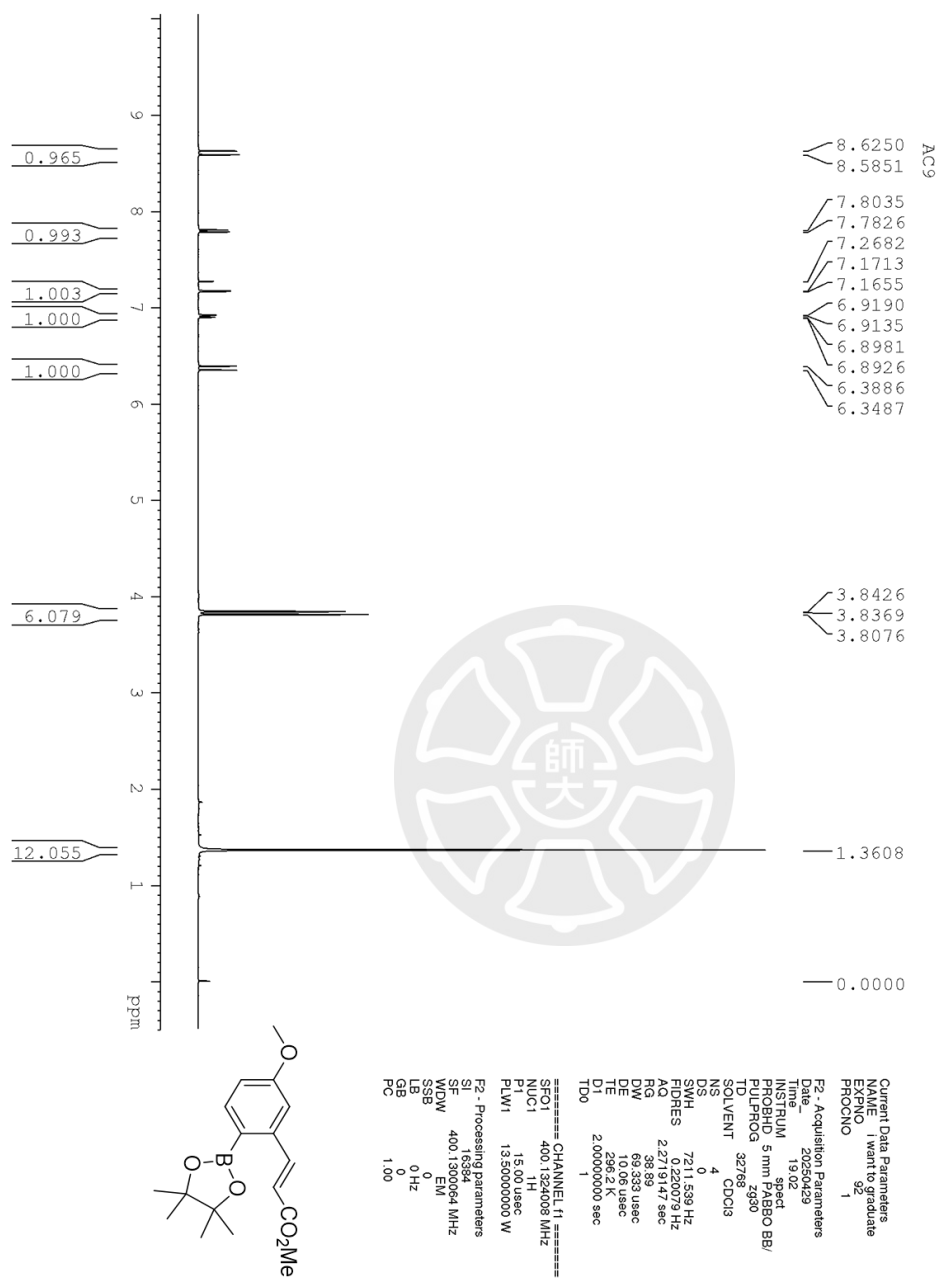
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 NUC1 ^{19}F
 P1 15.00 usec
 PLW1 16.50000000 W

===== CHANNEL f2 =====

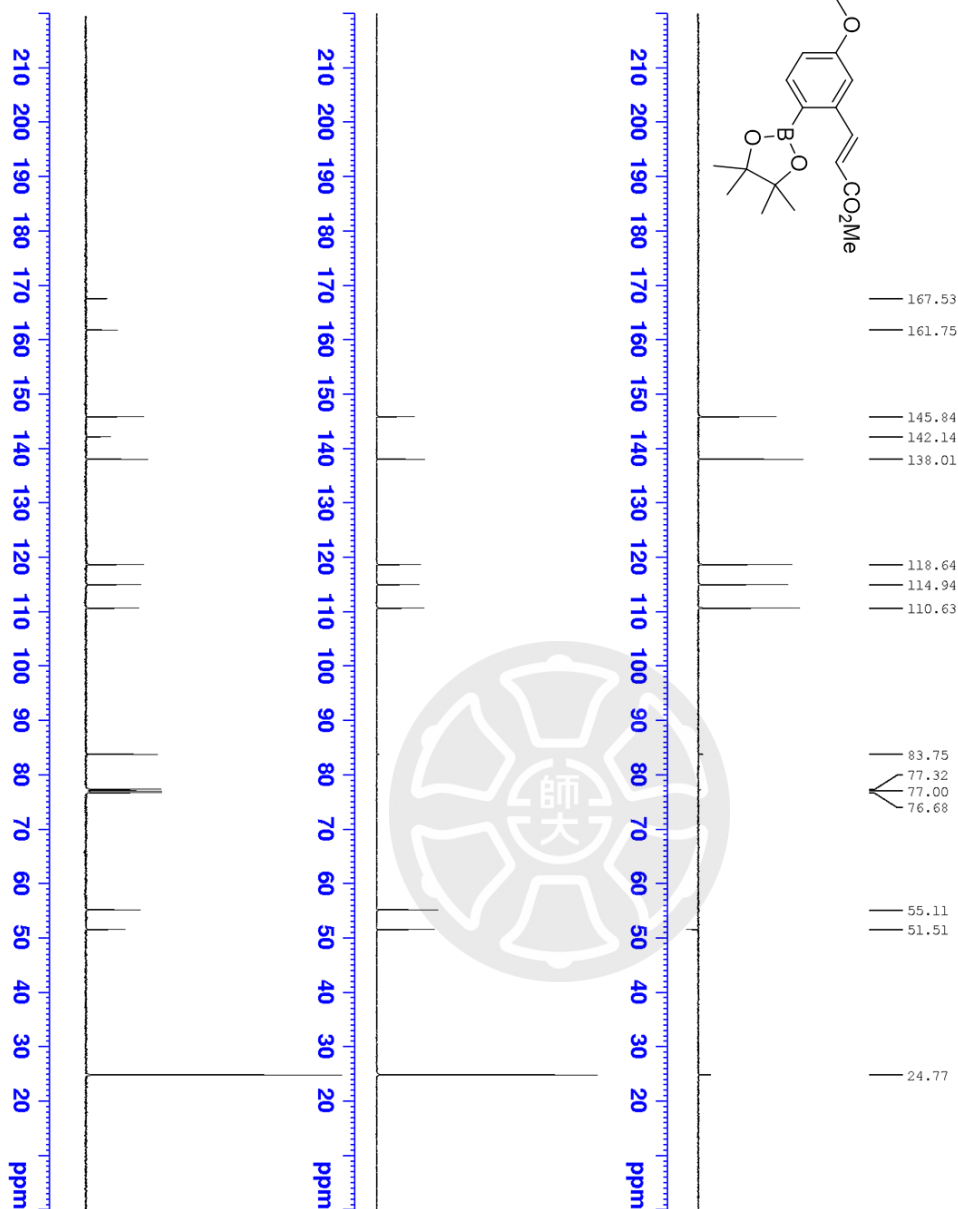
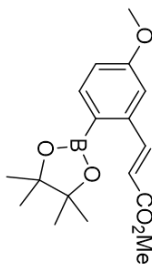
SFO2 400.1316005 MHz
 NUC2 ^1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLW12 0.34722000 W

F2 - Processing parameters

¹H NMR spectrum of methyl(E)-3-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)acrylate (23k)



¹³C NMR spectrum of methyl(E)-3-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)acrylate (23k)



```

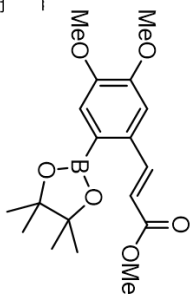
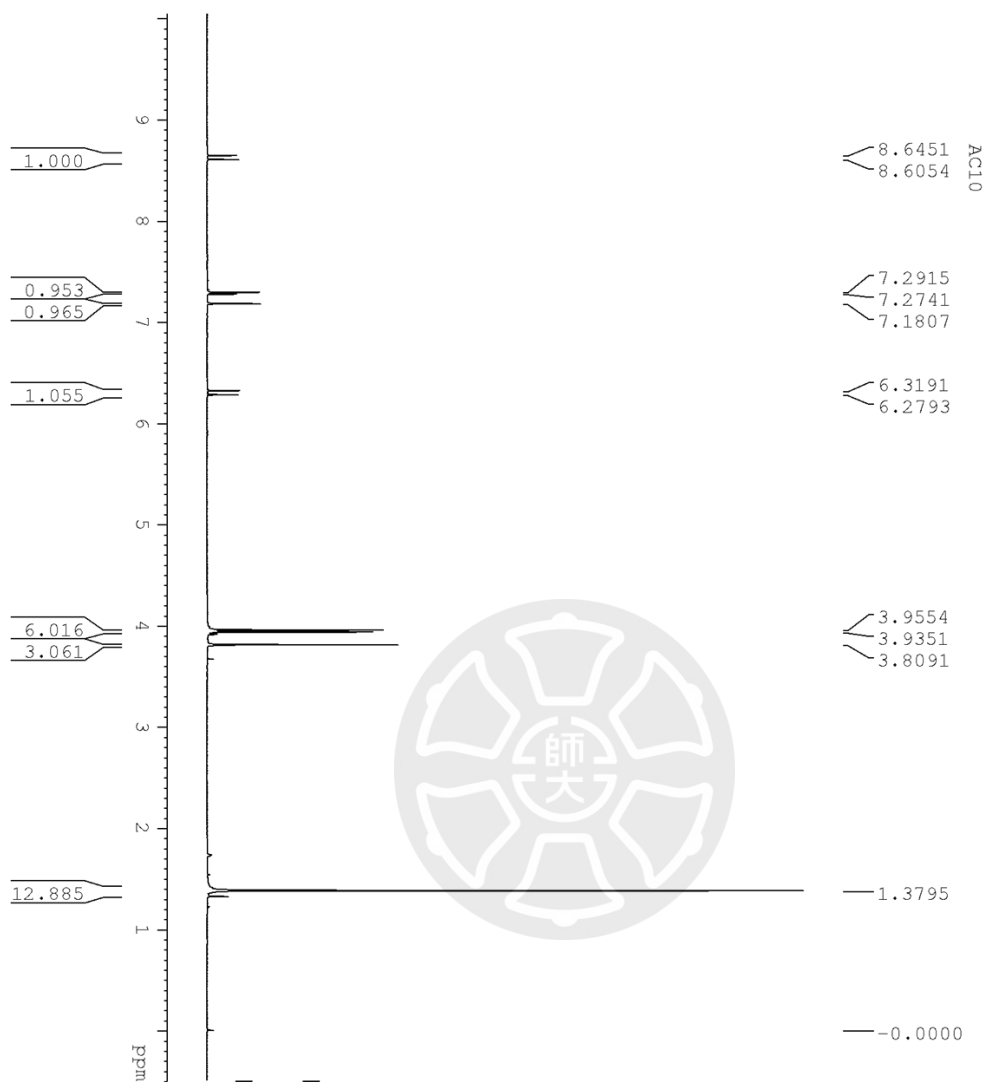
Current Data Parameters
NAME          I want to graduat
EXPNO         93
PROCNO        1
F2 - Acquisition Parameters
Date_         20230429
Time         19.09
INSTRUM       5 mm F400
PROBHD        BBO
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
NS            79
DS            0
SWH           24038.461 Hz
FIDRES       0.733596 Hz
AQ           0.6815744 se
RG           198.09
DM           20.800 us
DE           6.50 us
TE           296.5 K
D1           2.00000000 se
D11          0.03000000 se
TDO          1

===== CHANNEL f1 =====
SFO1         100.6228238 MH
NUC1         13C
P1           10.00 us
PLM1         49.50000000 W

===== CHANNEL f2 =====
SFO2         400.1316005 MH
NUC2         1H
CPDPRG2      waltz16
FREQ2       12.50030000 W
P2           30.00 us
PLM2         0.34725000 W
PLM3         0.28125000 W

===== CHANNEL f3 - Processing parameters =====
SF           100.6127758 MH
SI           32768
WDW          EM
SSB          0
GB           0
PC           1.00
    
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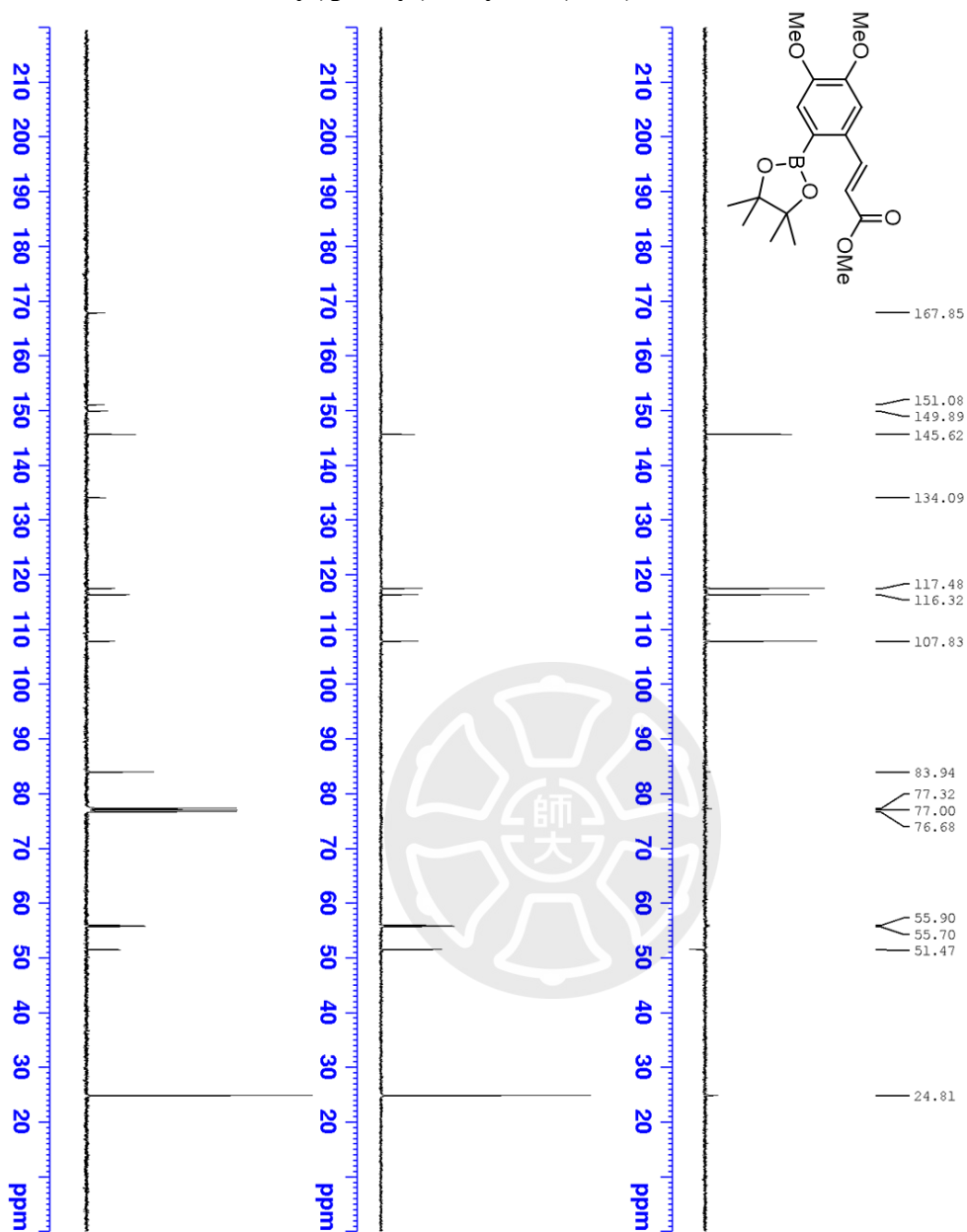
¹H NMR spectrum of methyl (E)-3-(4,5-dimethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) acrylate (23m)



```

Current Data Parameters
Name: 1 Wante 023diate
EXPNO: 98
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20250430
Time: 16.32
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 4
DS: 0
SWH: 721.539 Hz
F1: 0.22029 Hz
F2: 2.2719147 sec
RG: 63.58
DE: 69.333 usec
TE: 10.06 usec
T1: 295.1 K
T2: 2.00000000 sec
TD0: 1
===== CHANNEL f1 =====
SFO1: 400.1324008 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.50000000 W
F2 - Processing parameters
SI: 400.1300040 MHz
SF: 16384
WDW: EM
SSB: 0
LB: 0 Hz
GB: 0
PC: 1.00
  
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¹³C NMR spectrum of methyl (E)-3-(4,5-dimethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) acrylate (23m)



Current Data Parameters
 NAME 1 want to graduat
 EXPNO 97
 PROCNO 1

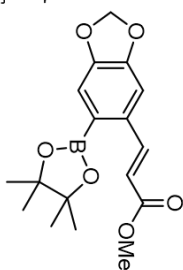
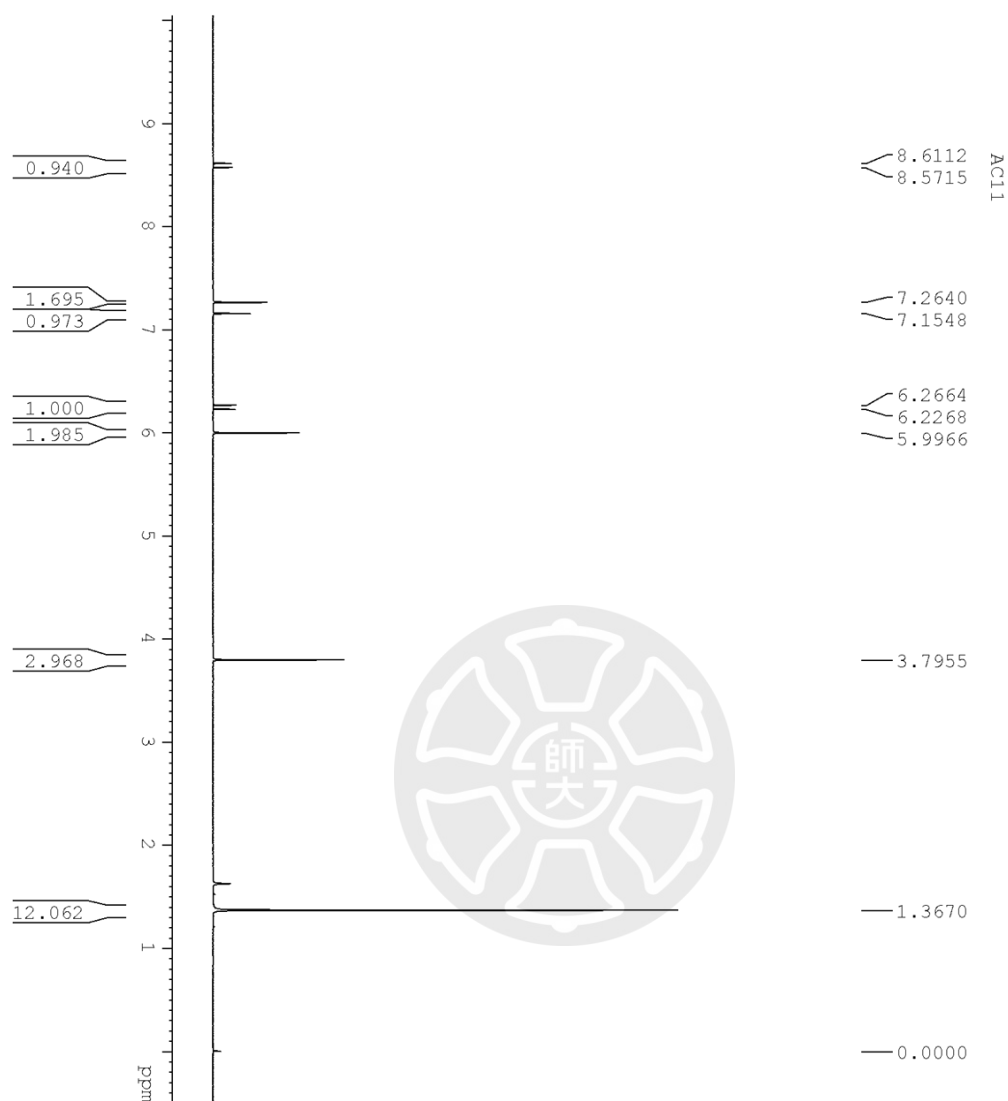
F2 - Acquisition Parameters:
 Date_ 20250430
 Time 16.35
 INSTRUM spect
 PROBD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 84
 DS 0
 SMH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 198.09
 DW 20.800 usec
 DE 6.50 usec
 TE 295.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

==== CHANNEL f1 =====
 SF01 100.6228298 MH:
 NUCL 13C
 P1 10.00 usec
 P1M1 49.50000000 W

==== CHANNEL f2 =====
 SF02 400.1316005 MH:
 NUCL 1H
 P2 30.00 usec
 P2M1 12.50000000 W
 P2M2 0.34722000 W
 P2M13 0.28125000 W

F2 - Processing parameters:
 SI 32768
 SF 100.6127740 MH:
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 FC 1.00

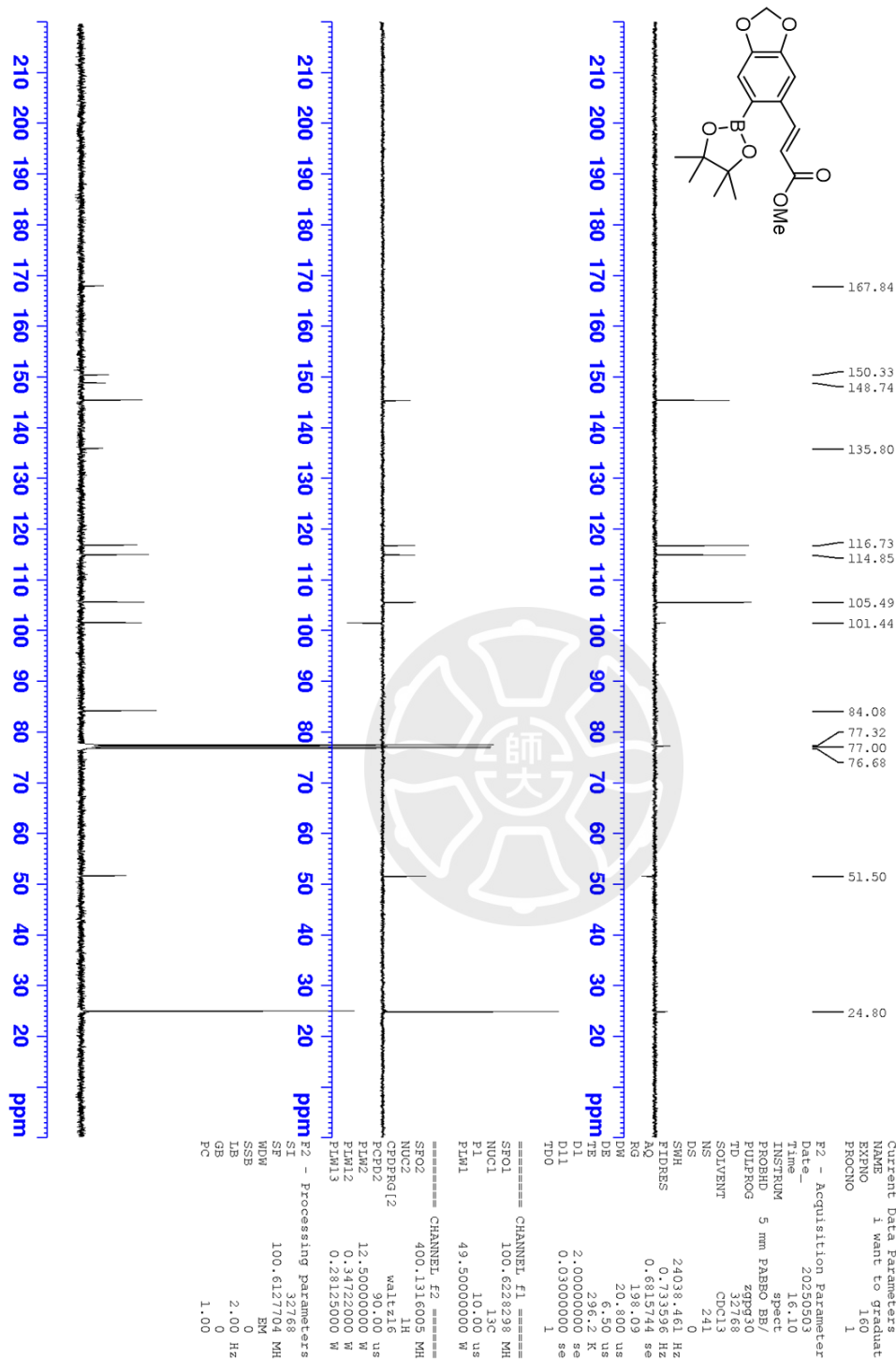
¹H NMR spectrum of methyl (E)-3-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d][1,3]dioxol-5-yl) acrylate (23n)



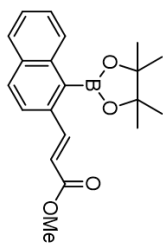
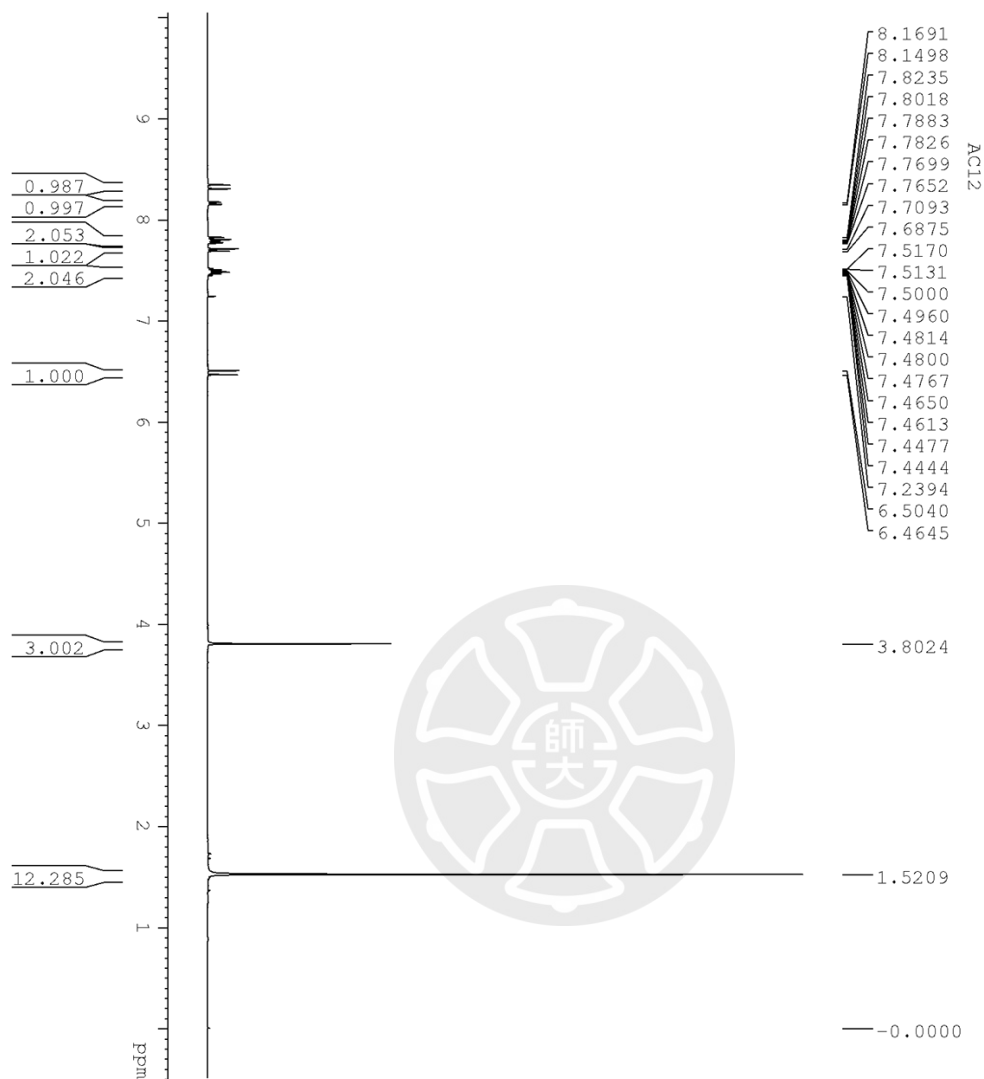
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Current Data Parameters
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EXPNO: 159
PROCNO: 1
F2 - Acquisition Parameters
Date_ : 20250303
Time: 18
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 4
DS: 0
SI: 0
SF: 721.4530 Hz
FIDRES: 6.220079 Hz
AQ: 2.2719147 sec
RG: 113.31
DE: 69.333 usec
TE: 295.7 K
DT0: 2.00000000 sec
===== CHANNEL f1 =====
SFO1: 400.1324008 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.50000000 W
F2 - Processing parameters
SF: 400.1324008 MHz
WDW: EM
SSB: 0 Hz
LB: 0 Hz
GB: 0 Hz
PC: 1.00
  
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¹³C NMR spectrum of methyl(E)-3-(6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d][1,3]dioxol-5-yl) acrylate (23n)



¹H NMR spectrum of methyl (E)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-yl) acrylate (23d)



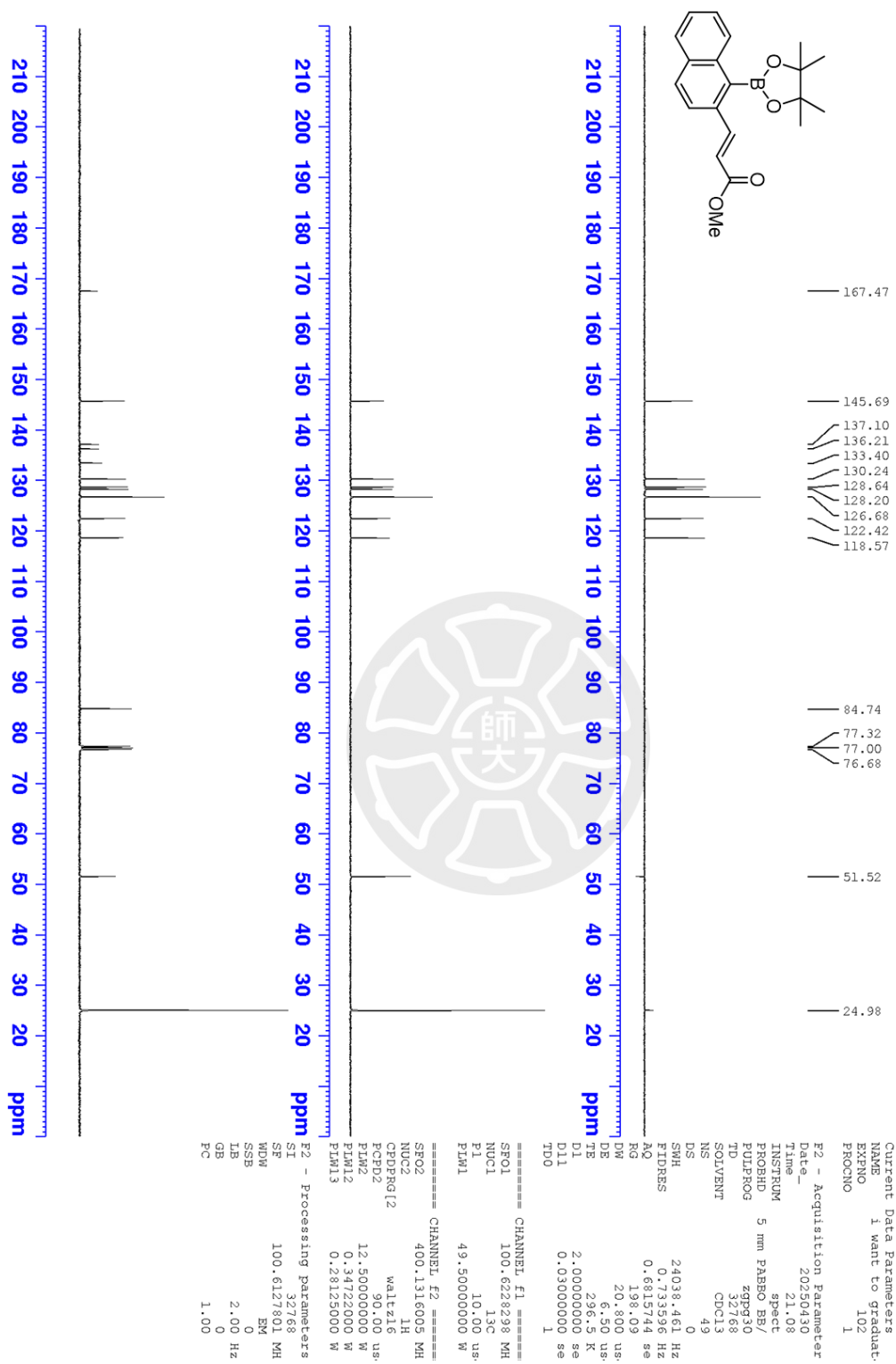
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Current Data Parameters
NAME_          1 wairto graduate
EXPNO          10
PROCNO         1

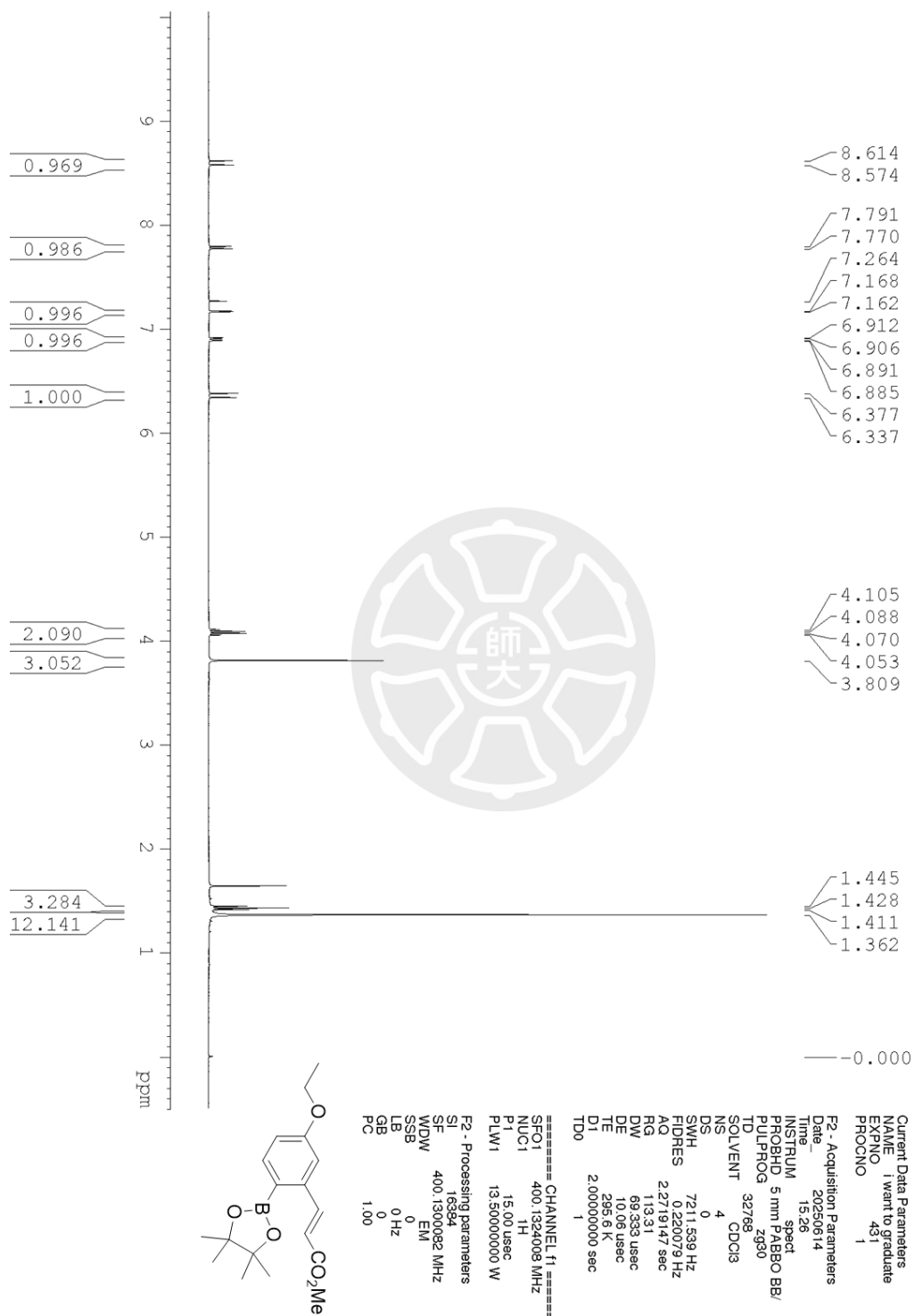
F2 - Acquisition Parameters
Date_          20250430
Time           18:46
INSTRUM        spect
PROBHD         5 mm 1ABBO BB/
PULPROG        zgpg30
TD             32768
SOLVENT        CDCl3
NS             4
DS             0
SWH            721.539147
FIDRES         0.12409717
AQ             2.2719147 sec
RG             31.16
DE             69.333 usec
TE             296.2 K
D1             2.00000000 sec
TD0            1

===== CHANNEL f1 =====
SFO1           400.1324008 MHz
NUC1           1H
P1             15.00 usec
PLW1           13.50000000 W
F2 - Processing parameters
SI             16384
SF             400.1300178 MHz
WDW            EM
SSB            0
LB             0 Hz
GB             0
PC             1.00
  
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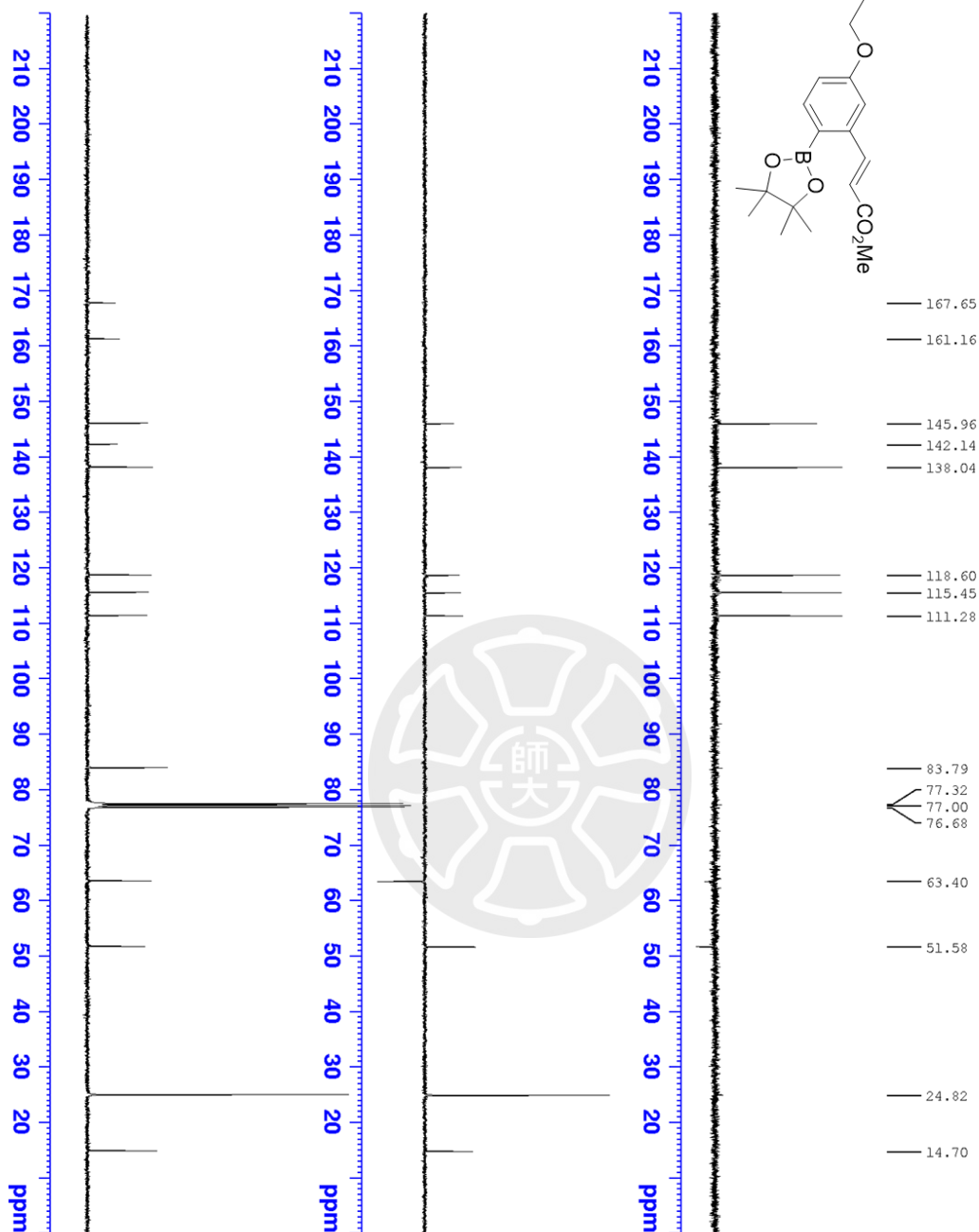
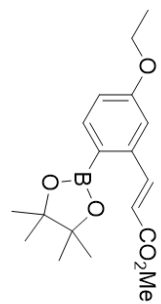
¹³C NMR spectrum of methyl (E)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-yl) acrylate (23d)



¹H NMR spectrum of methyl(E)-3-(5-ethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23o)



¹³C NMR spectrum of methyl(E)-3-(5-ethoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) acrylate (23o)

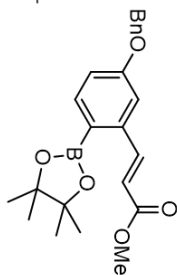
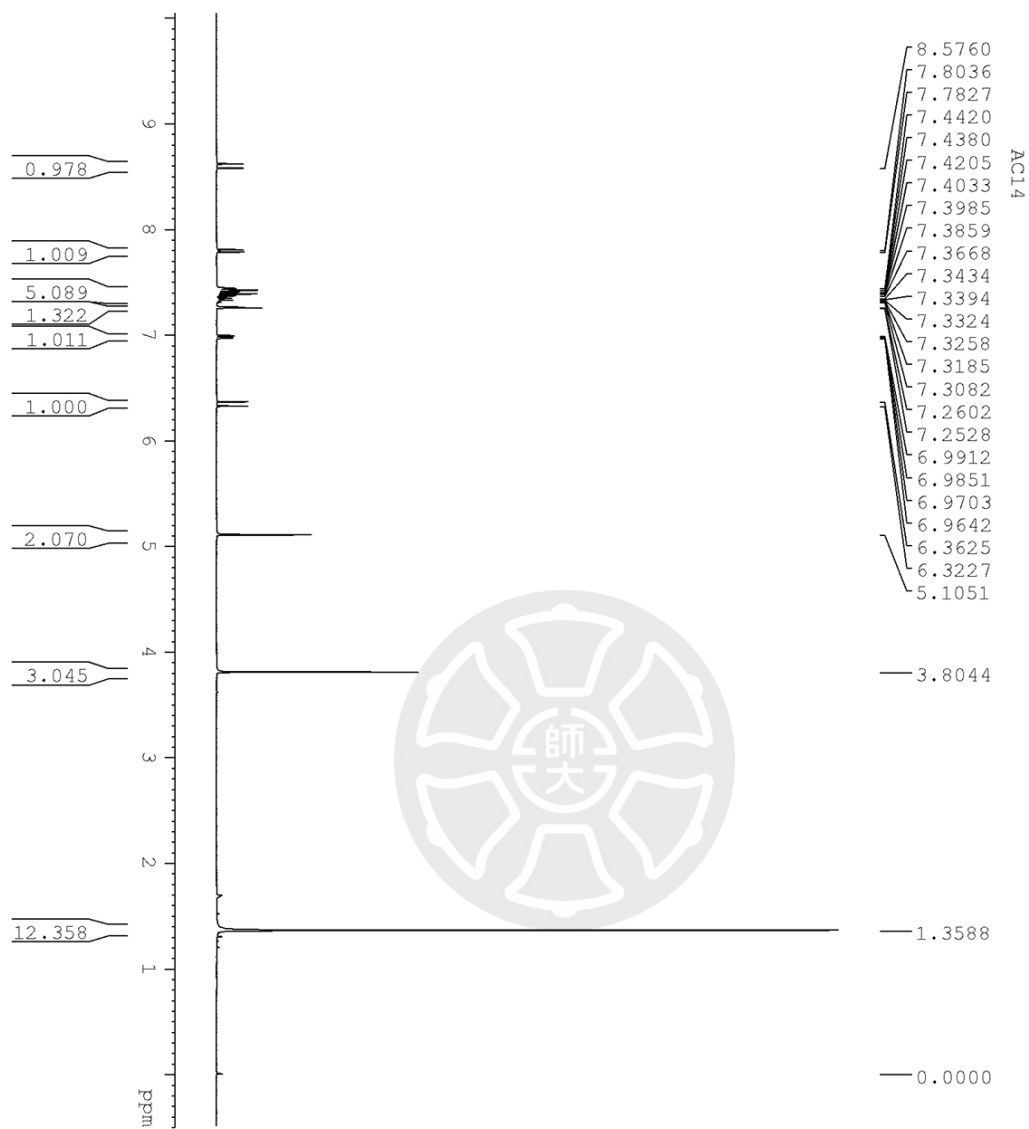


- 167.65
- 161.16
- 145.96
- 142.14
- 138.04
- 118.60
- 115.45
- 111.28
- 83.79
- 77.32
- 77.00
- 76.68
- 63.40
- 51.58
- 24.82
- 14.70

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Current Data Parameters
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EXPNO     432
PROCNO    1
===== Acquisition Parameters
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Time      15.23
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         611
DS         0
SWH        24038.461 Hz
FIDRES    0.733596 Hz
AQ         0.6815744 se
RG         198.09
DW         20.800 us
DE         6.50 us
TE         296.0 K
D1         2.00000000 se
D11        0.03000000 se
TDO        1
===== CHANNEL F1 =====
SFO1      100.6228298 MHz
NUC1       13C
P1         10.00 us
PL1        49.50000000 W
===== CHANNEL F2 =====
SFO2      400.1316005 MHz
NUC2       1H
P2         90.00 us
PL2        12.50000000 W
PLM12     0.34722000 W
PLM13     0.28125000 W
===== Processing parameters =====
SI         32768
SF         100.6127713 MHz
WDW         EM
SSB         0
LB         2.00 Hz
GB         0
PC         1.00
  
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¹H NMR spectrum of methyl (E)-3-(5-(benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23p)

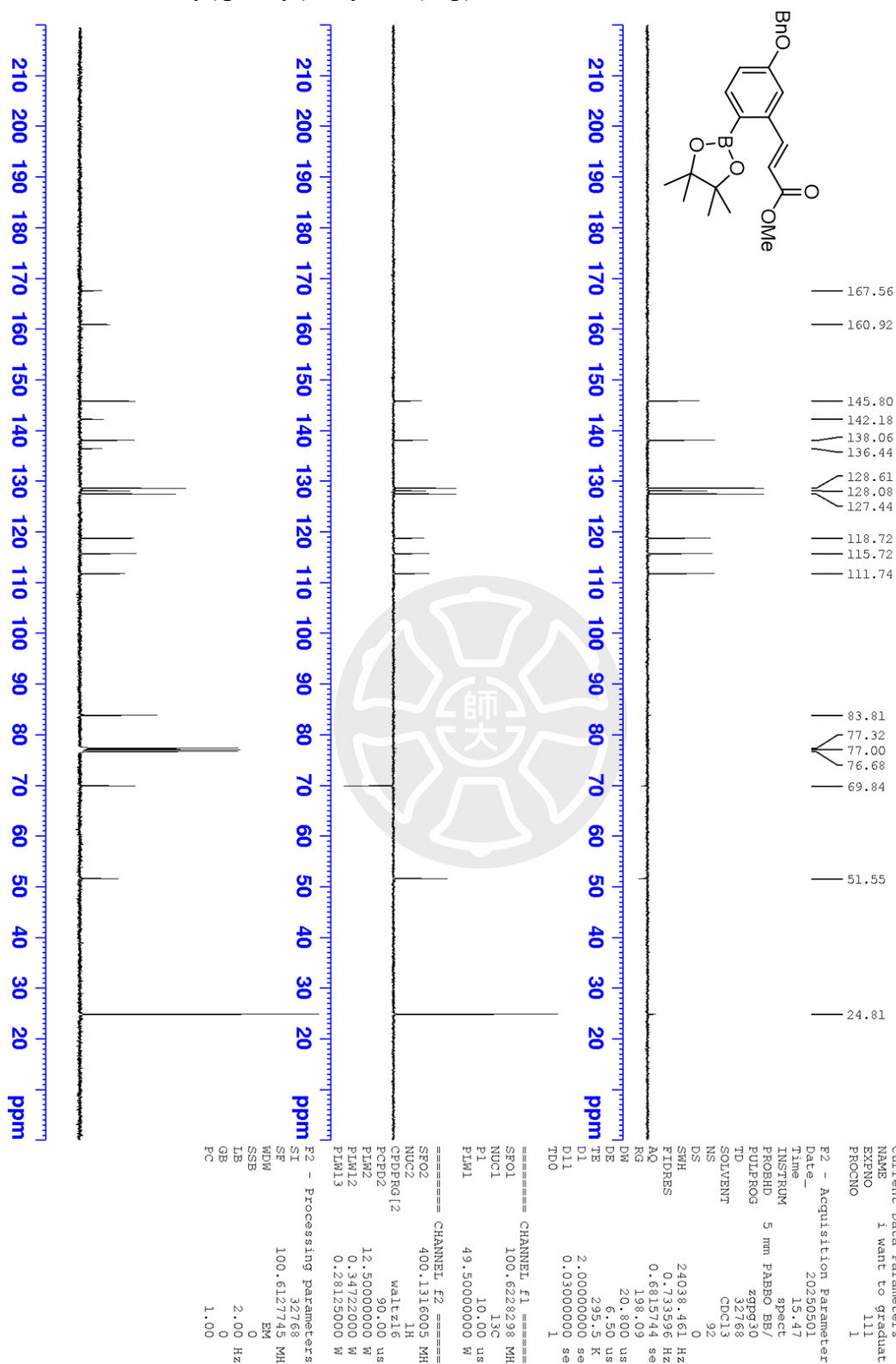


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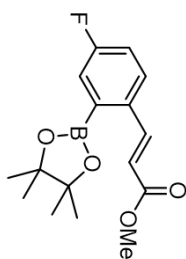
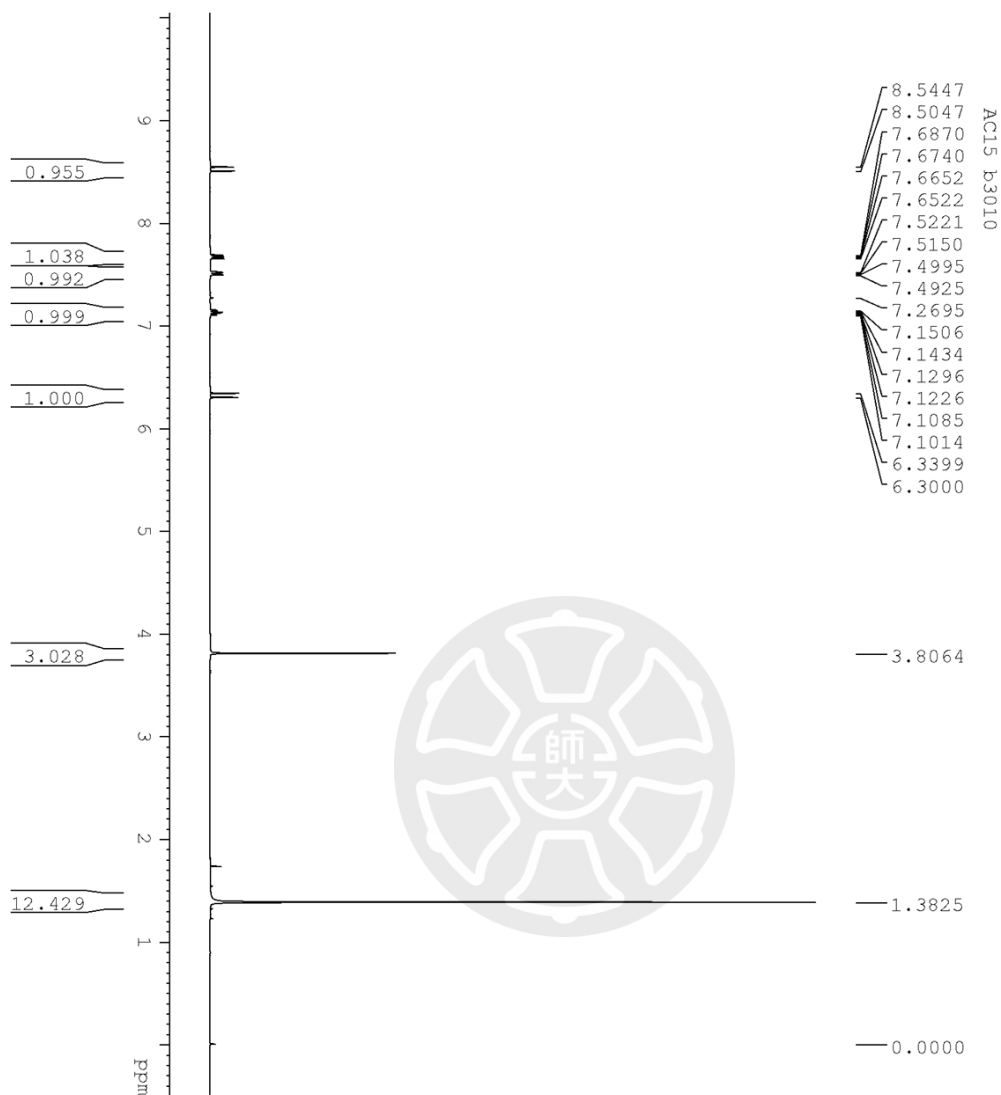
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NAME      i want to graduate
EXPNO    110
PROCNO   1
===== CHANNEL f1 =====
SFO1     400.130068 MHz
NUC1     13C
P1       15.00 usec
PLW1     13.50000000 W
F2 - Processing parameters
SI       16384
SF       400.1300129 MHz
WDW      EM
SSB      0
LB       0 Hz
GB       0
PC       1.00
===== Acquisition Parameters =====
Date_    20250101
Time     15:46
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       4
DS       0
SINH1    721.5391 Hz
FIDRES   0.12200000 Hz
AQ       2.2719147 sec
RG       63.58
DW       68.333 usec
DE       10.06 usec
TE       295.3 K
D1       2.00000000 sec
TDO      1

```

¹³C NMR spectrum of methyl(E)-3-(5-(benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23p)



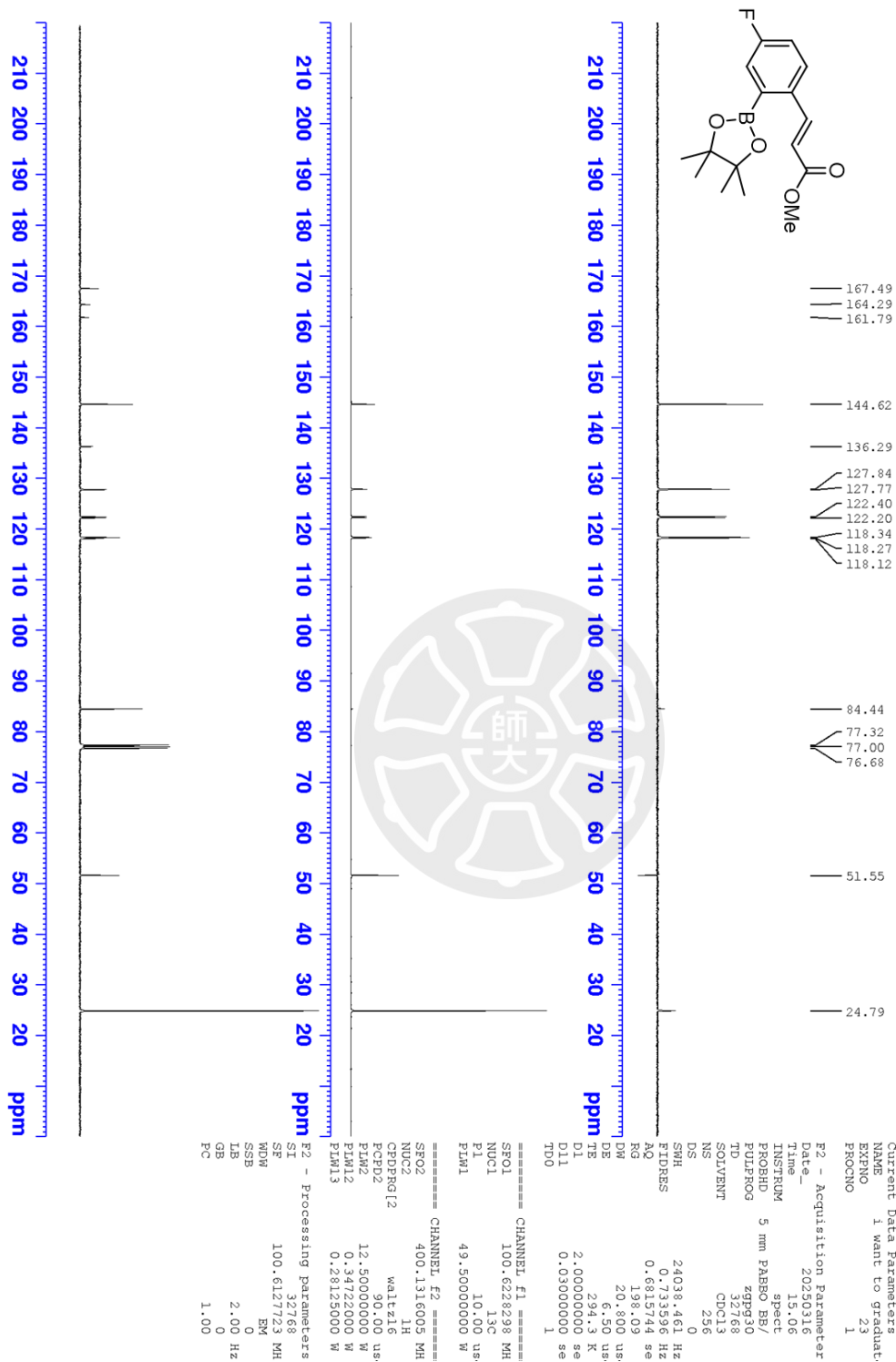
¹H NMR spectrum of methyl (E)-3-(4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23f)



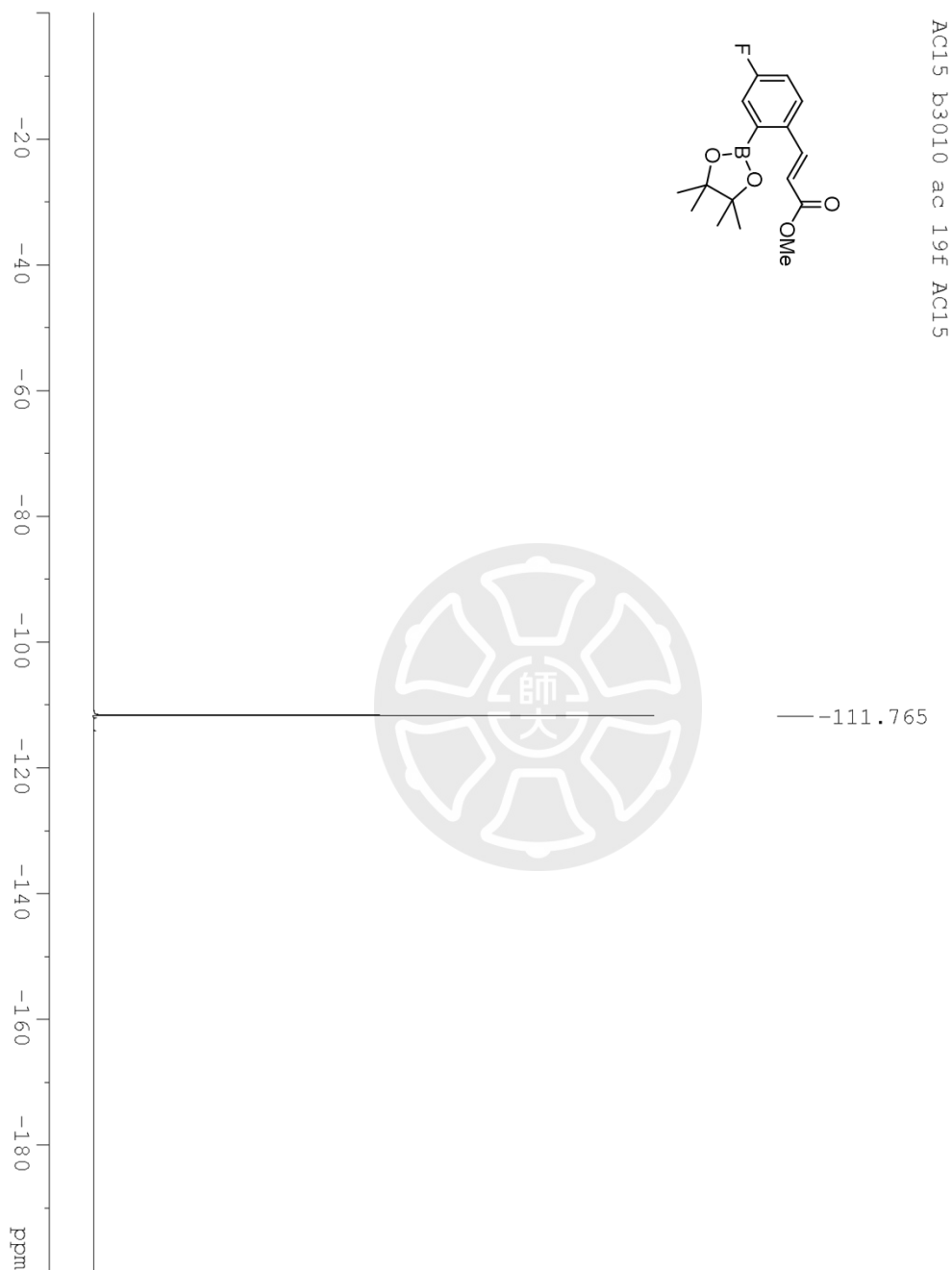
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Current Data Parameters
NAME: Iwant to graduate
EXPNO: 2
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20250316
Time: 15:04
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zgpg30
TD: 32768
SOLVENT: CDCl3
NS: 16
DS: 0
SWH: 7211.539 Hz
FIDRES: 0.220079 Hz
AQ: 2.2719147 sec
RG: 68.333 usec
DE: 10.06 usec
TE: 294.1 K
D1: 2.00000000 sec
TD0: 1
===== CHANNEL f1 =====
SFO1: 400.1324008 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.50000000 W
F2 - Processing parameters
SI: 16384
SF: 400.1300060 MHz
SFO2: EM
SCB: 0
LB: 0 Hz
GB: 0
PC: 1.00
  
```

¹³C NMR spectrum of methyl (E)-3-(4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23f)



¹⁹F NMR spectrum of methyl (E)-3-(4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23f)



Current Data Parameters
 NAME I want to graduate
 EXPNO 28
 PROCNO 1

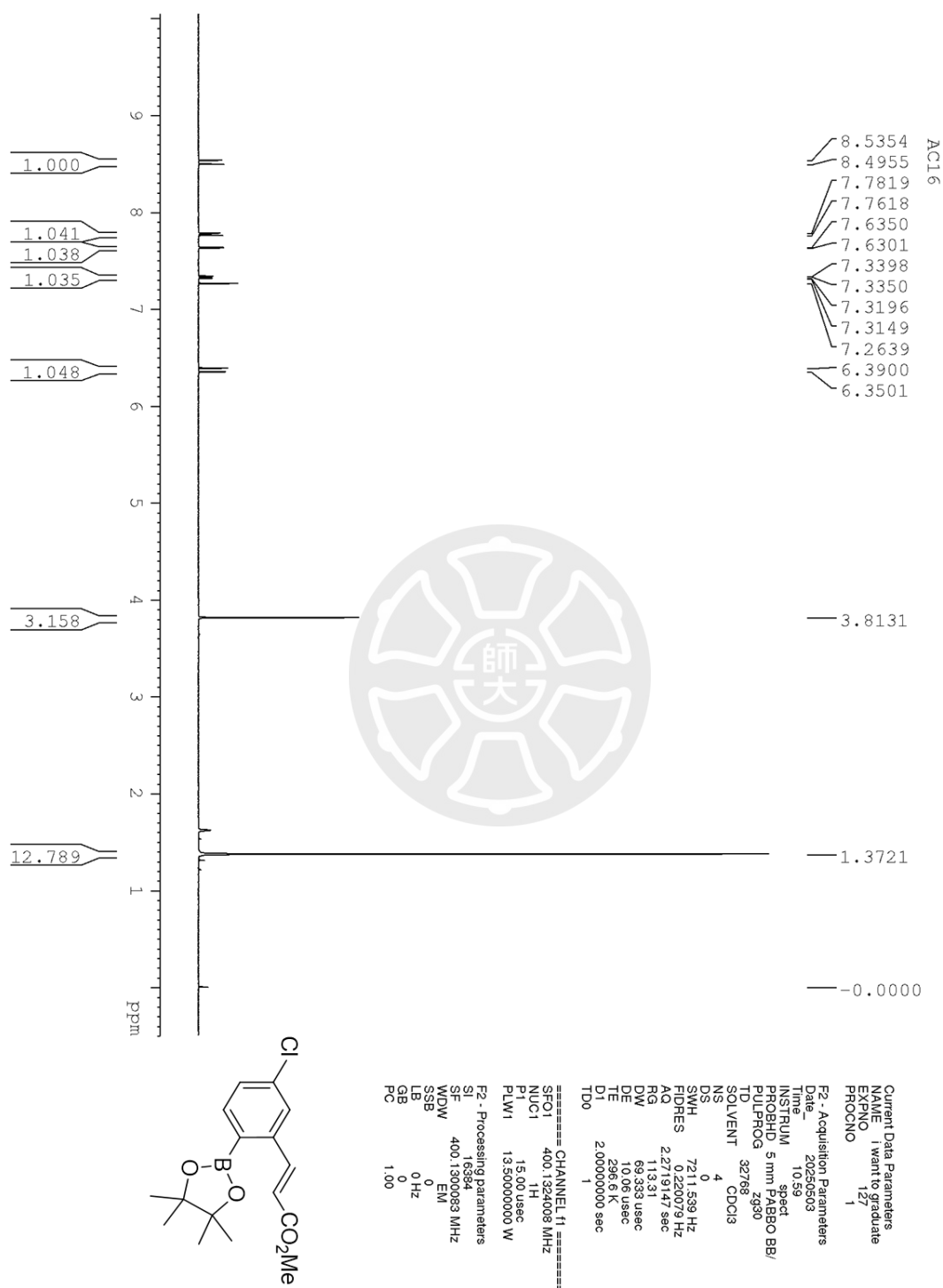
F2 - Acquisition Parameters
 Date_ 20250316
 Time 18:51
 INSTRUM spect
 PROBD 5 mm PABBO BB/
 PULPROG zgpg
 TD 131072
 SOLVENT CDCl3
 NS 32
 DS 0
 SWH 8926.711 Hz
 FIDRES 0.681196 Hz
 AQ 0.7340032 sec
 RG 198.09
 DW 5.600 usec
 DE 6.50 usec
 TE 295.0 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 376.4607168 MHz
 NUC1 19F
 P1 15.00 usec
 PLW1 16.50000000 W

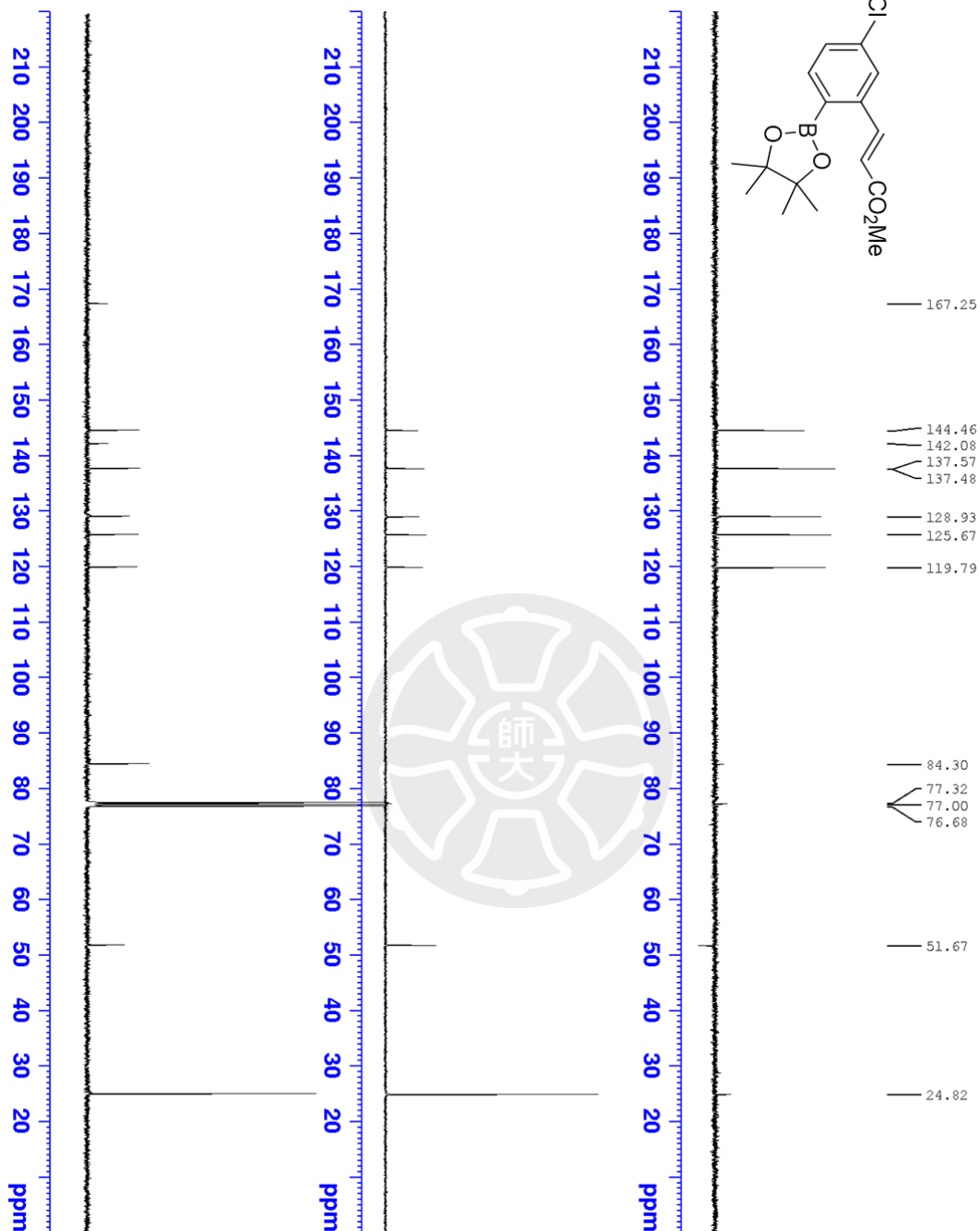
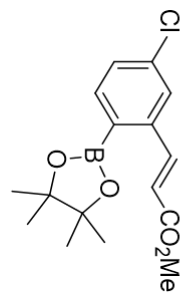
===== CHANNEL f2 =====
 SFO2 400.1319005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLW12 0.34722000 W

F2 - Processing parameters

¹H NMR spectrum of methyl(E)-3-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)acrylate AC16



¹³C NMR spectrum of methyl(E)-3-(5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)acrylate AC16



Current Data Parameters
 NAME i want to graduat
 EXPNO 128
 PROCNO 1

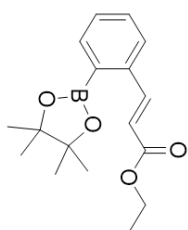
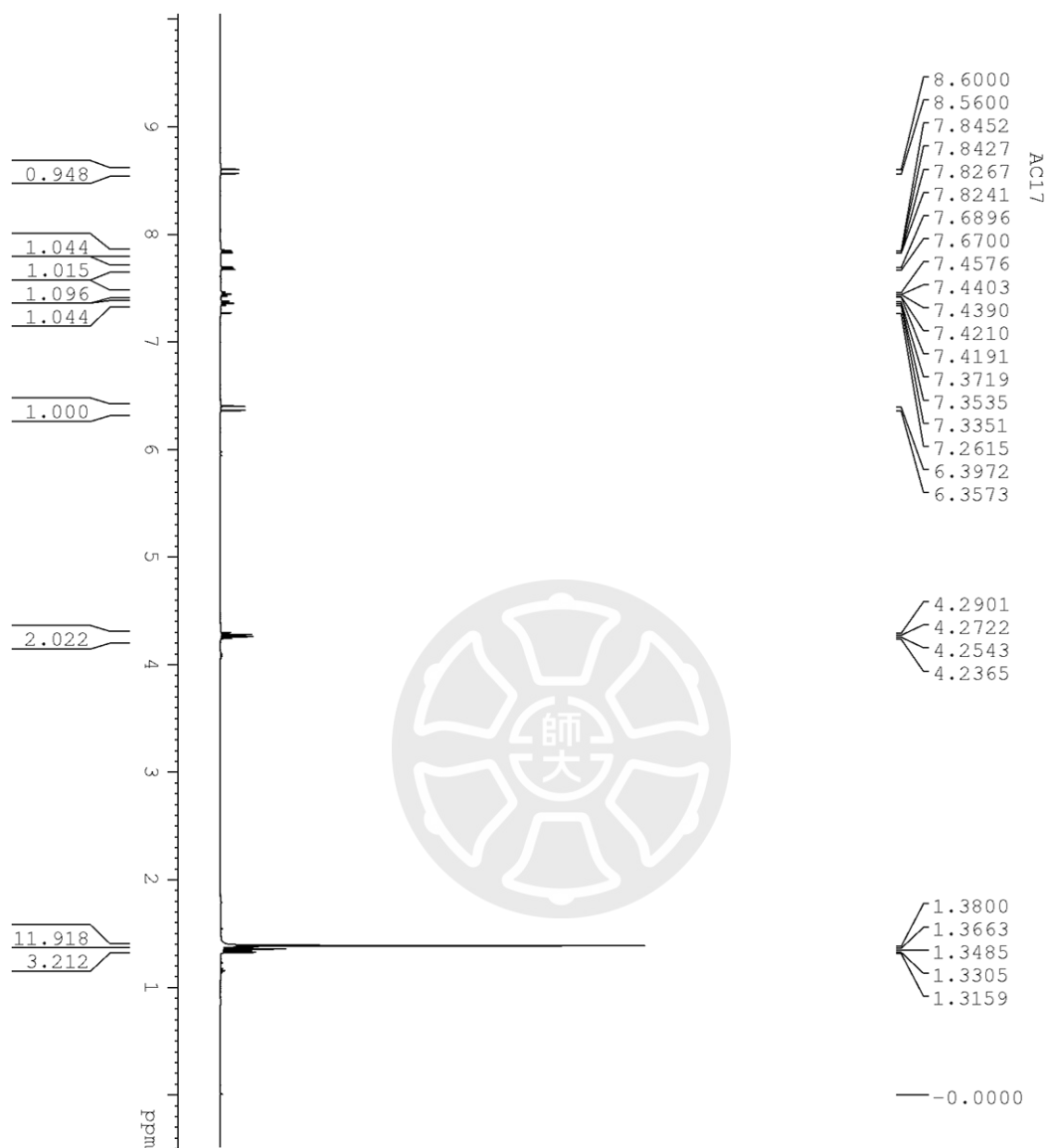
F2 - Acquisition Parameters
 Date_ 20250503
 Time 11.00
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 190
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.73356 Hz
 AQ 0.6815744 sec
 RG 198.09
 DM 20.800 us
 DE 6.50 us
 TE 296.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TPO 1

==== CHANNEL F1 =====
 SFO1 100.6282898 MH
 NUC1 13C
 P1 10.00 us
 PLM1 49.50000000 W

==== CHANNEL F2 =====
 SFO2 400.1316005 MH
 NUC2 1H
 CPDPRG12 waltz16
 PCPDZ 90.00 us
 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127703 MH
 WDW EM
 SSB 0
 GB 2.00 Hz
 PC 1.00

¹H NMR spectrum of ethyl(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23q)



```

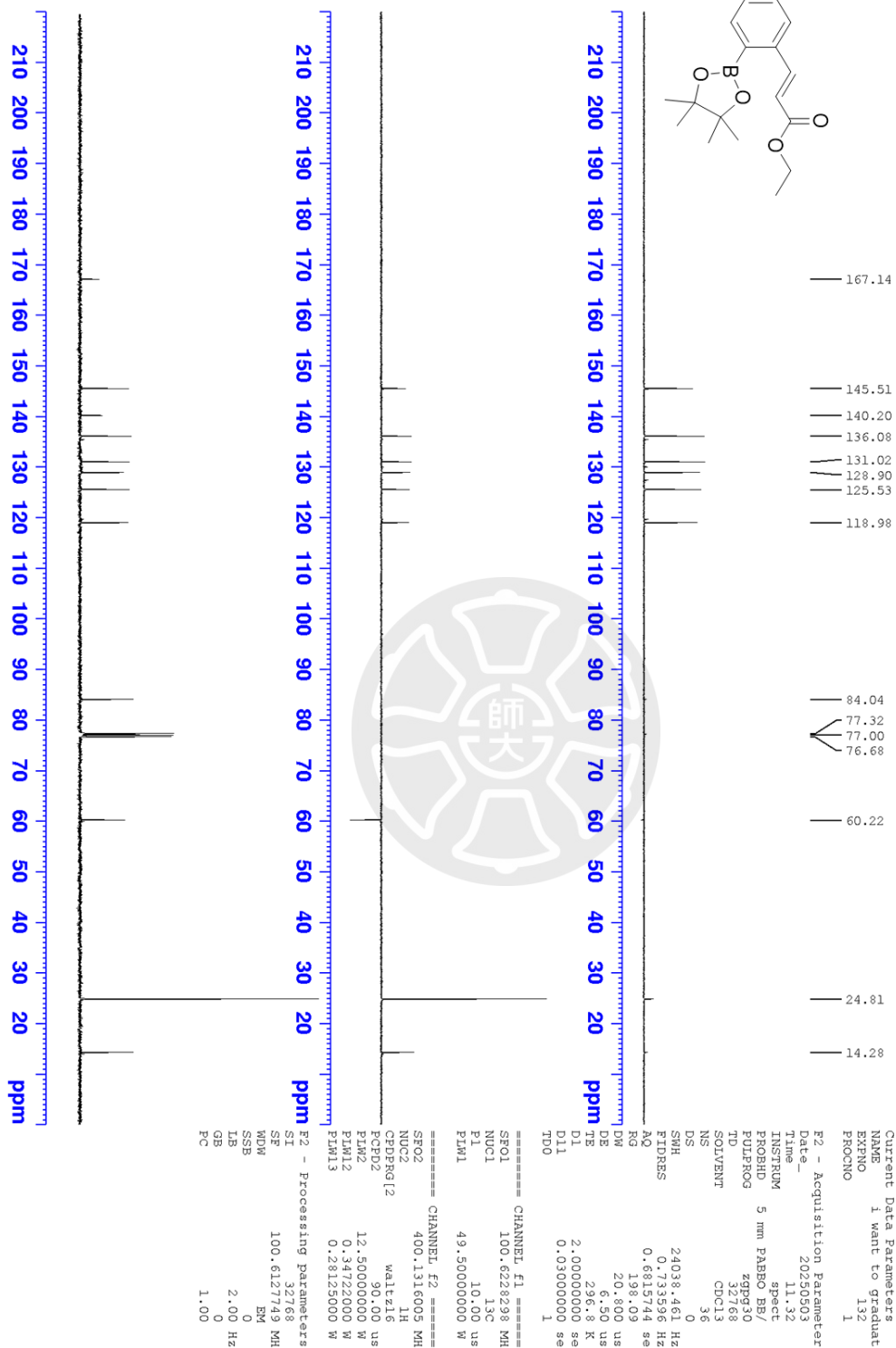
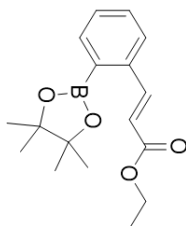
Current Data Parameters
Name: I want to graduate
EXPNO 131
PROCNO 1

F2 - Acquisition Parameters
Date_ 20250503
Time 11:31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 721.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 45.15
DW 69.333 usec
DE 10.06 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1

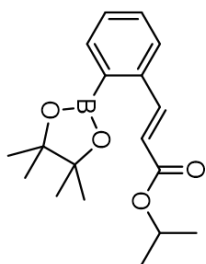
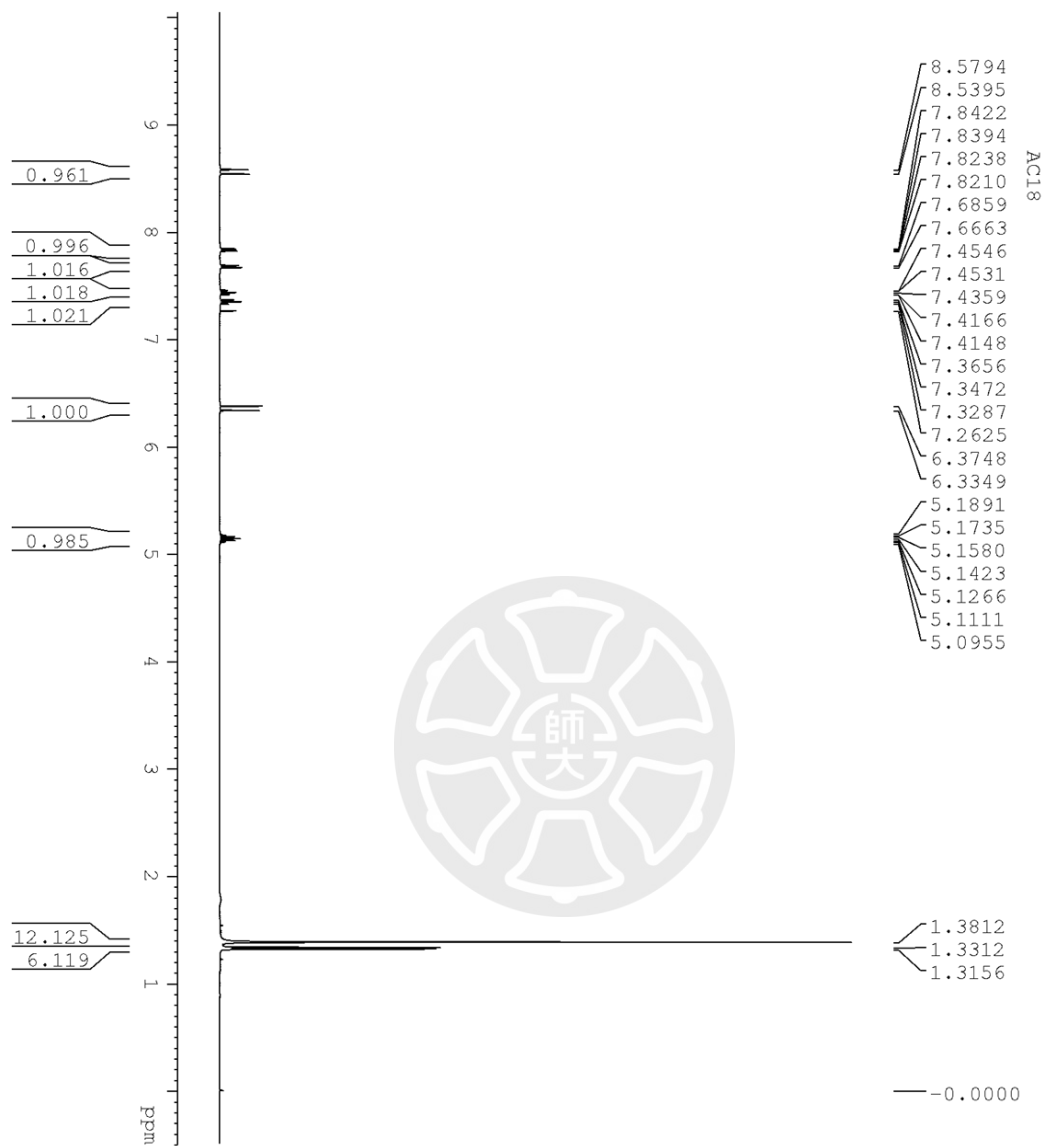
===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
PULC1 15.00 usec
PLW1 13.50000000 W

F2 - Processing parameters
SI 16384
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
    
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¹³C NMR spectrum of ethyl(E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23q)



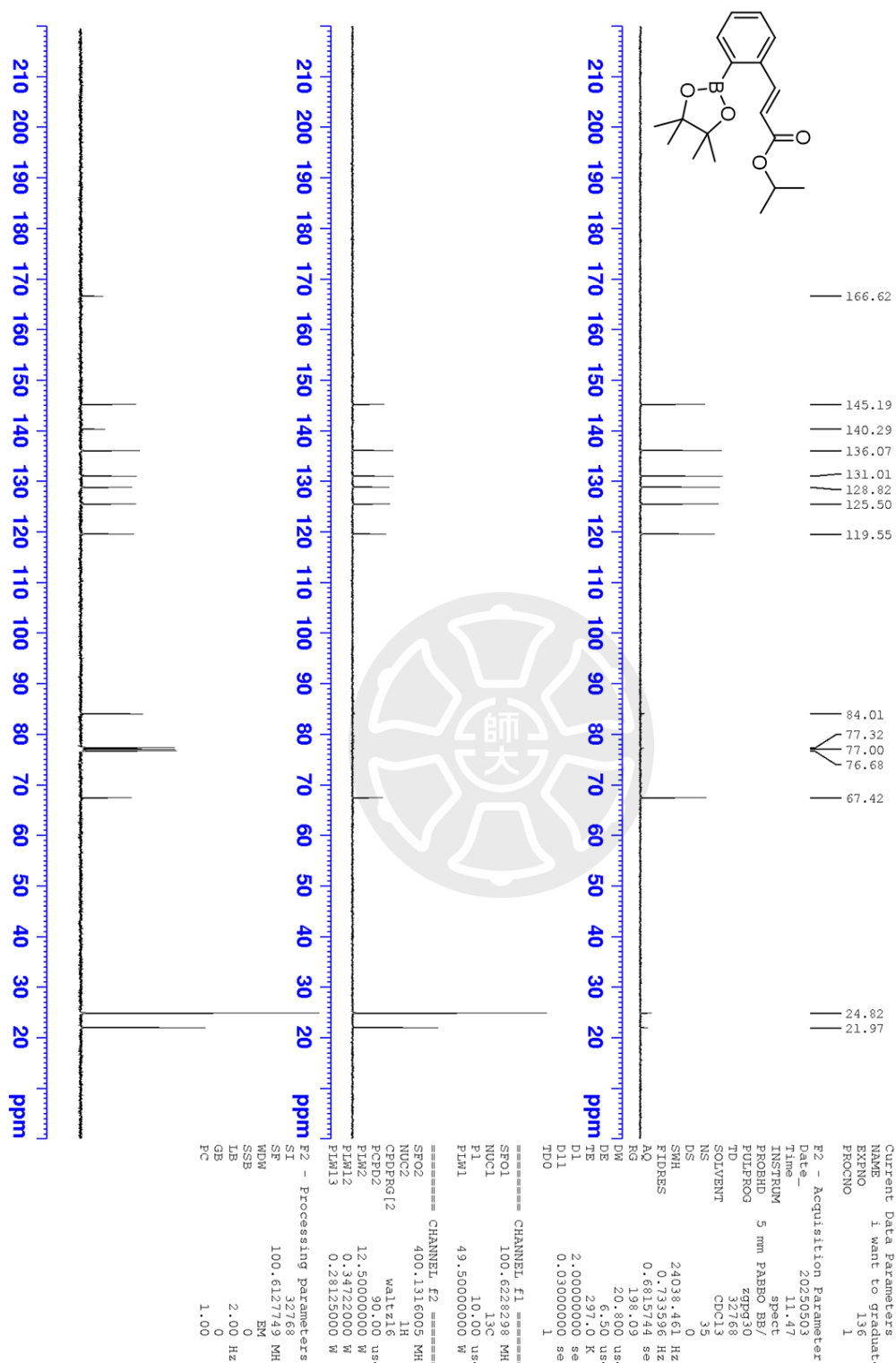
¹H NMR spectrum of isopropyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23r)



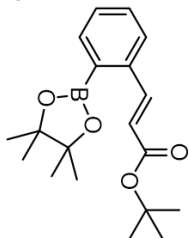
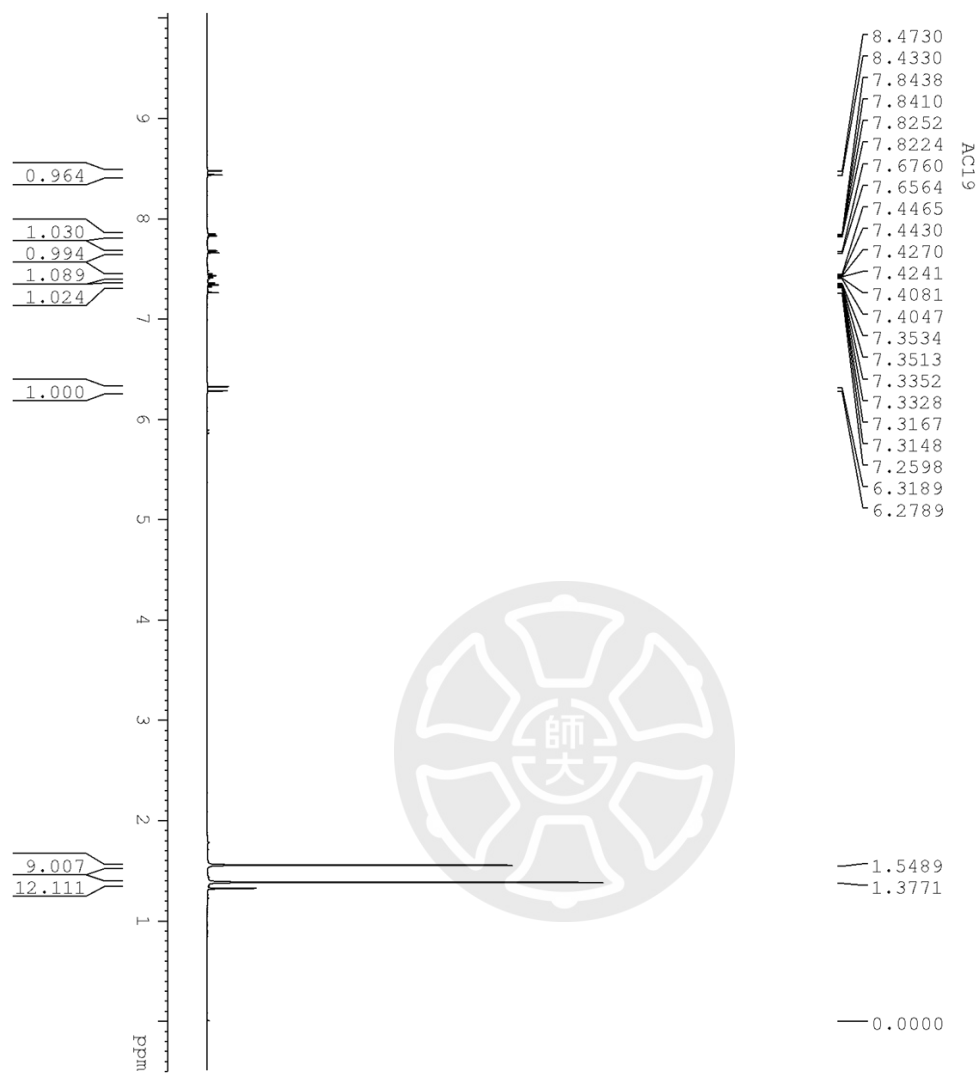
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Current Data Parameters
NAME 1-want to graduate
EXPNO 135
PROCNO 1
F2 - Acquisition Parameters
Date_ 20230303
Time 11:45
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 38.89
RW 19.024 usec
DE 10.94 usec
TE 296.8 K
D1 2.00000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.50000000 W
F2 - Processing Parameters
SI 32768
SF 400.1300087 MHz
EM 0 Hz
SSB 0 Hz
LB 0 Hz
GB 0 Hz
PC 1.00
  
```

¹³C NMR spectrum of isopropyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23r)



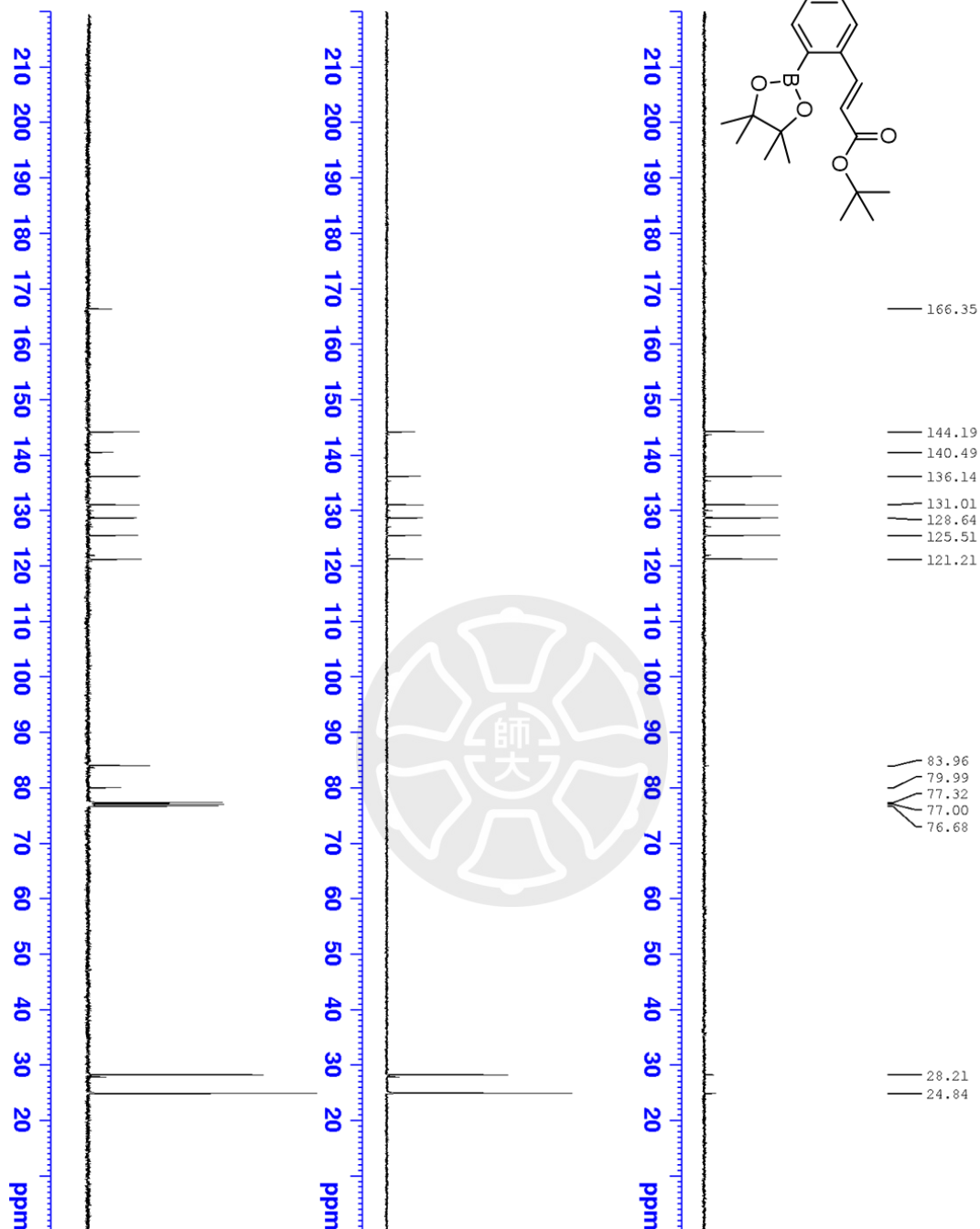
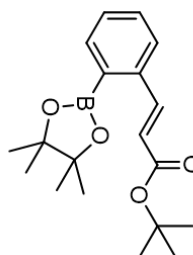
¹H NMR spectrum of tert-butyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23s)



```

Current Data Parameters
NAME: I want to graduate
EXPNO: 139
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20250503
Time: 12.06
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
P1: 13.980
TD: 65536
SOLVENT: CDCl3
NS: 4
DS: 0
SWH: 7211.539 Hz
FIDRES: 0.220079 Hz
AQ: 2.27181 sec
RG: 327.68
DE: 69.333 usec
TE: 296.7 K
D1: 2.00000000 sec
TD0: 1
===== CHANNEL f1 =====
SFO1: 400.1324098 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.50000000 W
F2 - Processing parameters
SI: 32768
SF: 400.1300968 MHz
WDW: EM
SSB: 0 Hz
LB: 0 Hz
GB: 0
PC: 1.00
    
```

¹³C NMR spectrum of tert-butyl (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23s)



Current Data Parameters
 NAME I want to graduate
 EXPNO 140
 PROCNO 1

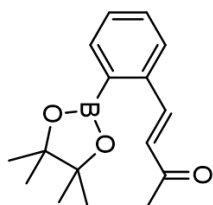
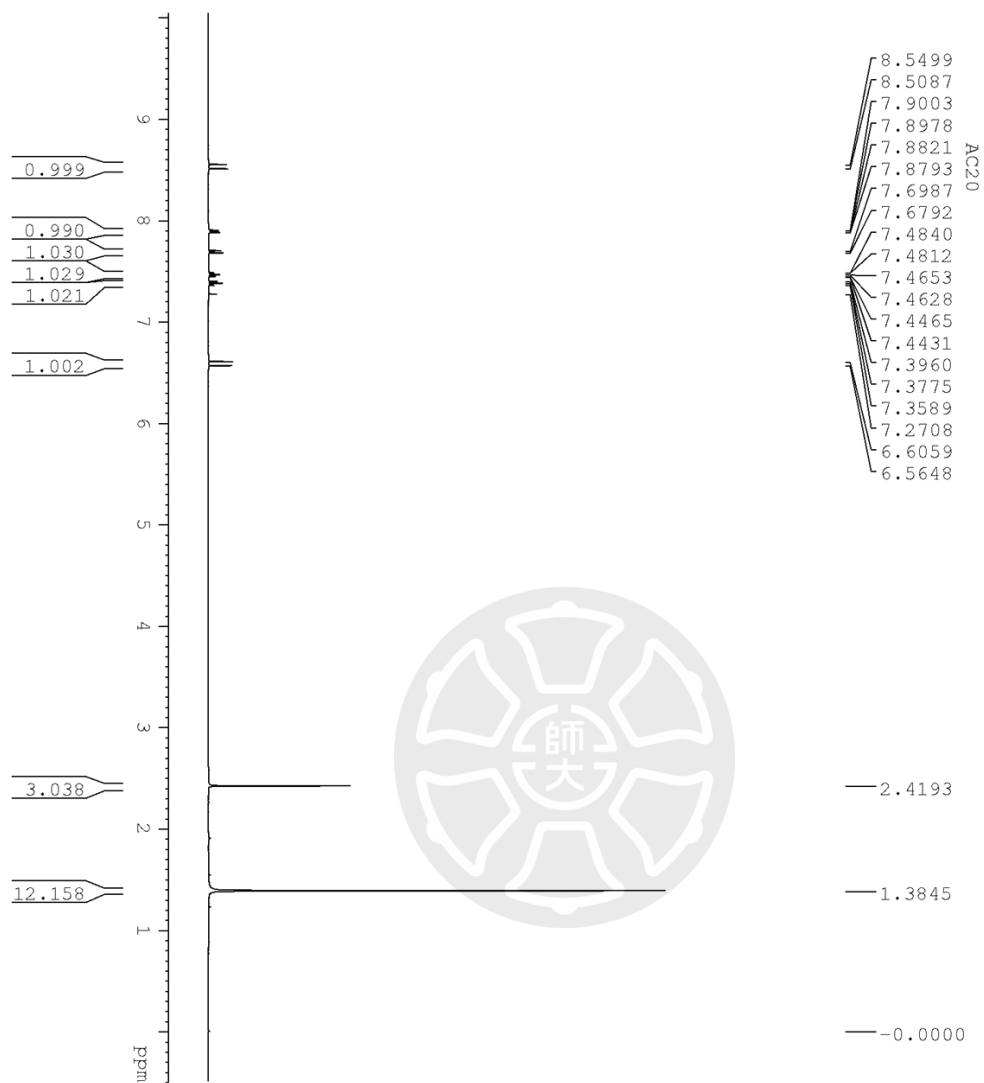
F2 - Acquisition Parameters:
 Date_ 20250503
 Time 12.07
 INSTRUM spect
 PROBD 5 mm PABBO BB/
 PULPROG zgpg30
 TP 32768
 SOLVENT CDCl3
 NS 21
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733996 Hz
 AQ 0.6815744 sec
 RG 198.09
 DE 20.800 use
 TE 296.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SFO1 100.6228298 MHz
 NUC1 13C
 P1 10.00 use
 PL1 49.50000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 P2 90.00 use
 PL2 12.50000000 W
 PL12 0.34722000 W
 PL13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127745 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

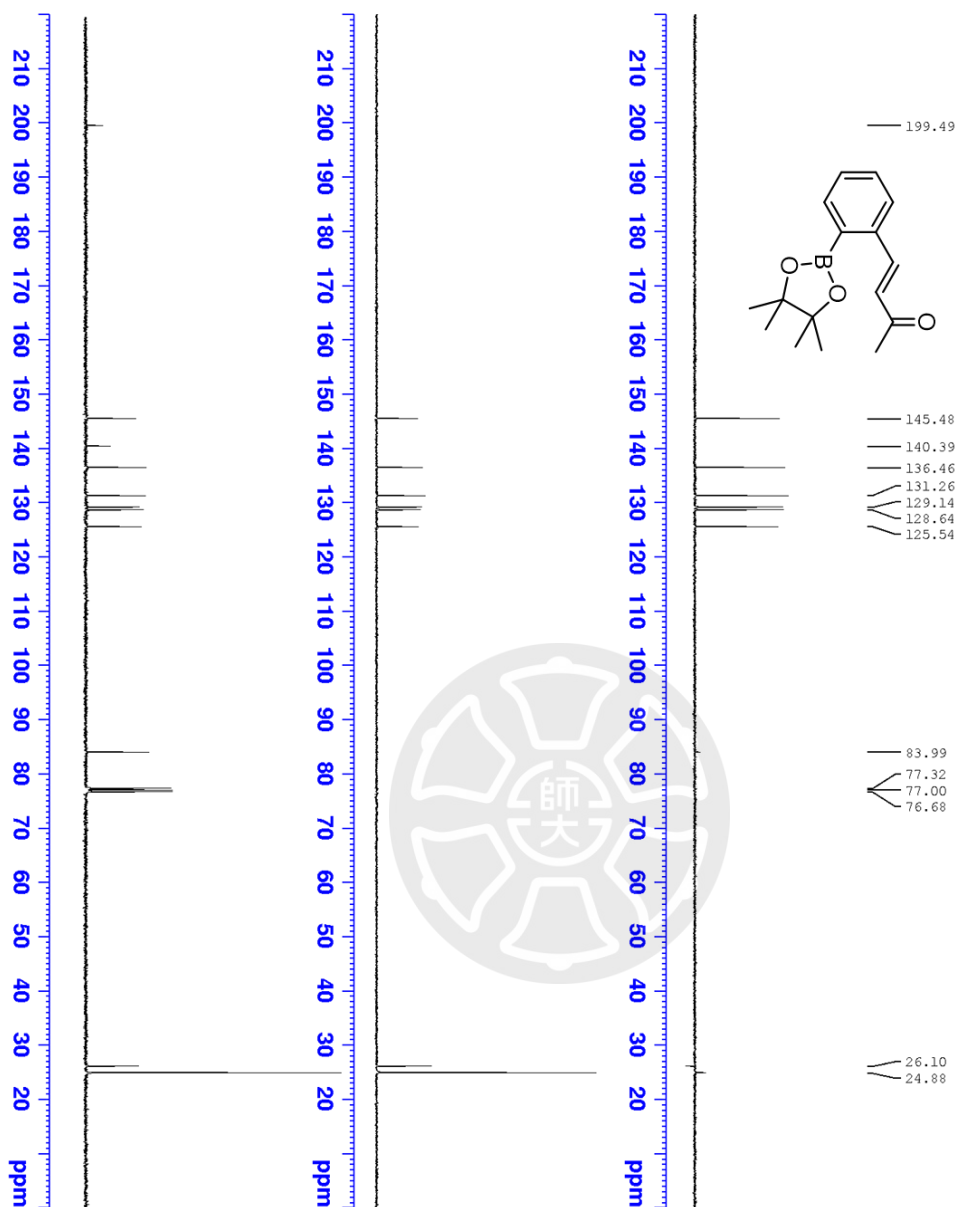
¹H NMR spectrum of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-2-one (23t)



```

Current Data Parameters
NAME      1 wanto graduate
EXPNO     143
PROCNO    1
F2 - Acquisition Parameters
Date_     20250503
Time      12.44
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         4
DS         0
SWH        7211.539 Hz
FIDRES     0.220079 Hz
AQ         2.278147 sec
RG         60.333 usec
DE         10.06 usec
TE         297.0 K
D1         2.00000000 sec
TD0        1
===== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1       1H
P1         15.00 usec
PLW1      13.50000000 W
F2 - Processing parameters
SI         65536
SF         400.1324008 MHz
WDW        EM
SSB        0
LB         0 Hz
GB         0
PC         1.00
  
```

¹³C NMR spectrum of (E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-2-one (23t)



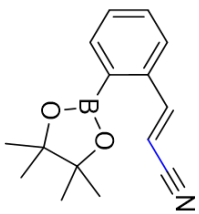
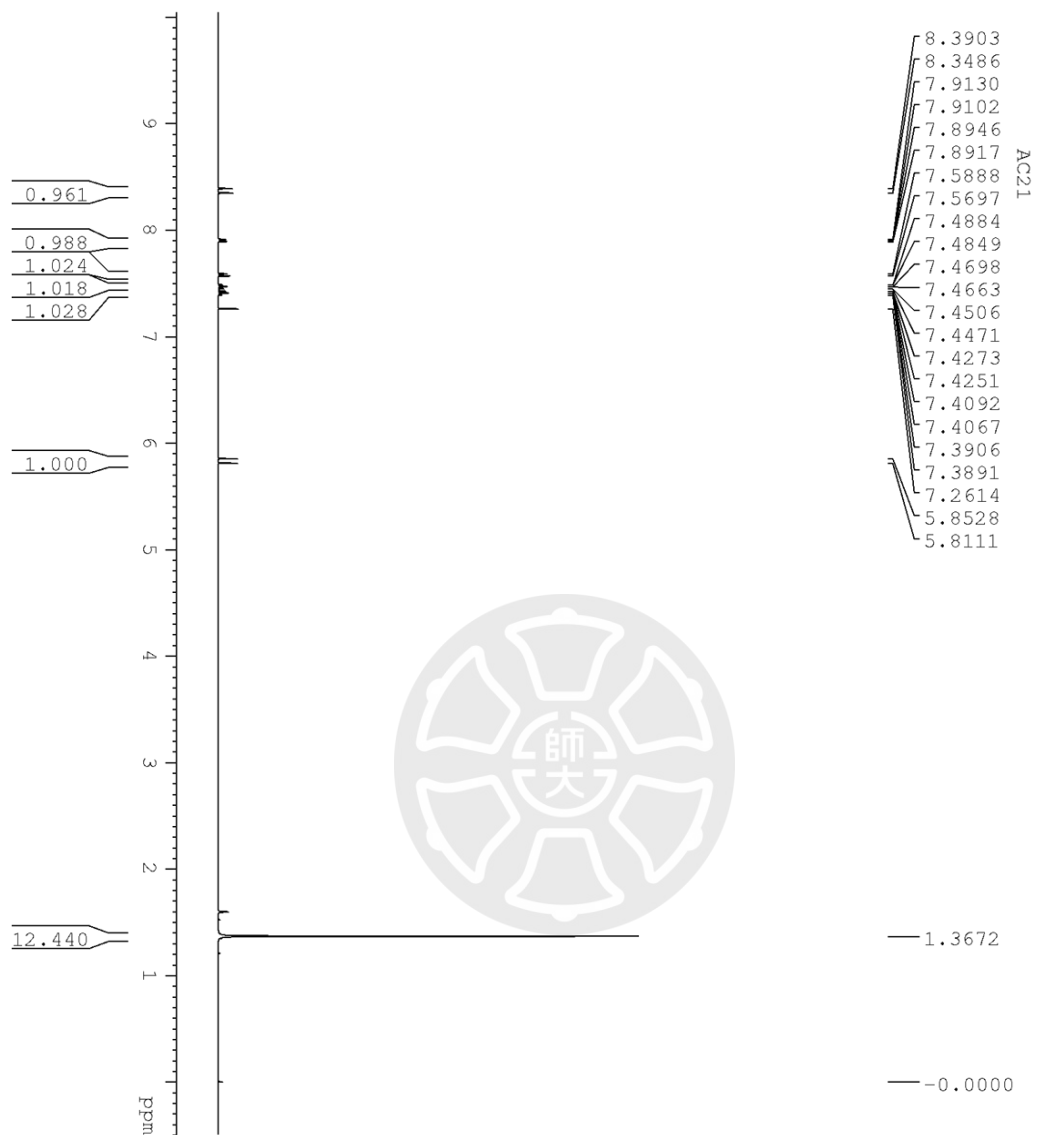
Current Data Parameters
 NAME I want to graduat.
 EXPNO 144
 F2 - Acquisition Parameters
 Date_ 20250503
 Time_ 12:45
 INSTRUM spect
 PROBRD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 25
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 se
 RG 198.09
 DE 20.800 us
 TE 6.50 us
 D1 297.1 K
 D11 2.00000000 se
 D12 0.03000000 se
 TDO 1

==== CHANNEL F1 =====
 SFO1 100.6228298 MH
 NUCL 13C
 P1 10.00 us
 PLM1 49.50000000 W

==== CHANNEL F2 =====
 SFO2 400.1316005 MH
 NUCL 1H
 P1 19.00 us
 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127778 MH
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (23u)



```

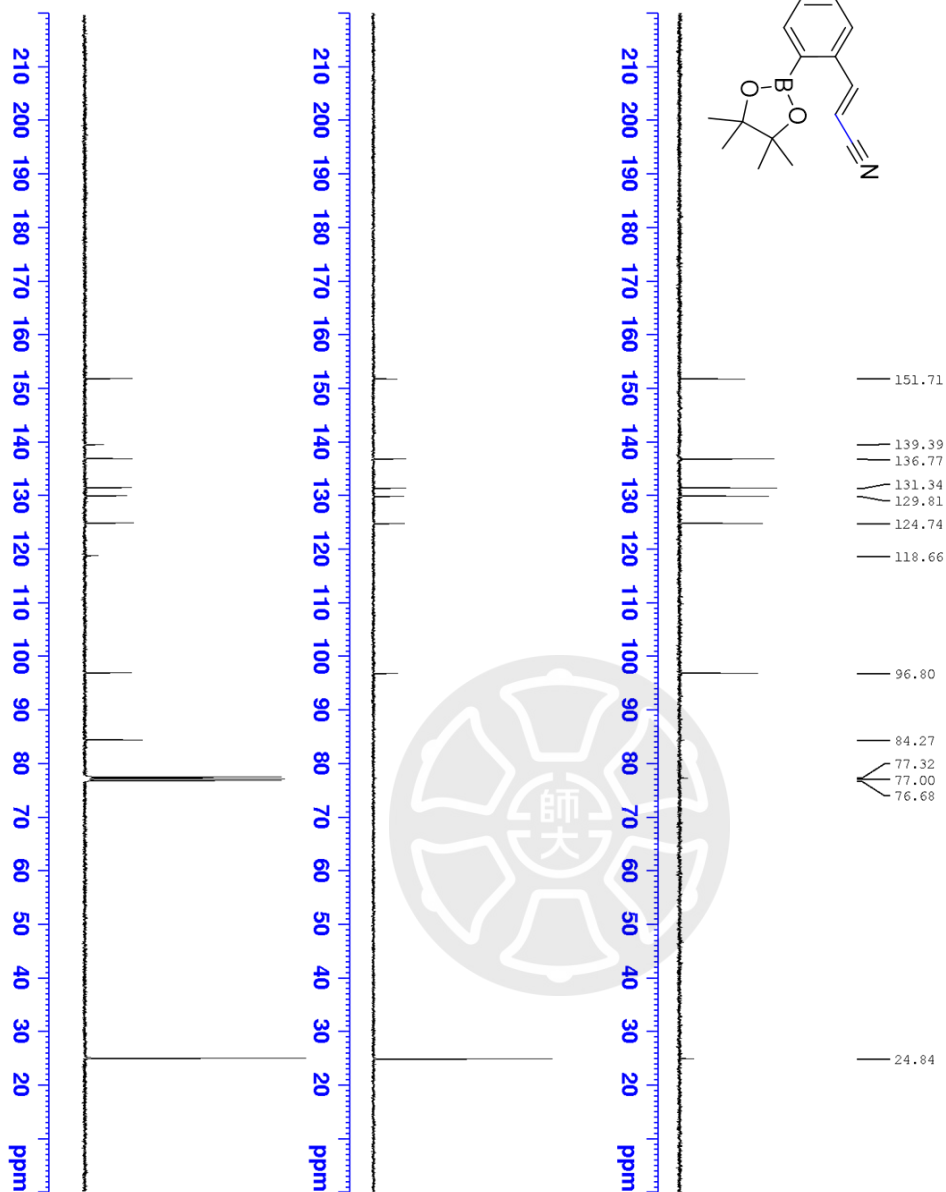
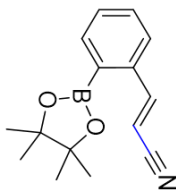
Current Data Parameters
NAME: I want to graduate
EXPNO: 147
PROCNO: 1

F2 - Acquisition Parameters
Date_   20250503
Time    14:43
INSTRUM spect
PROBHD  5 mm F4BBO BB/
PULPROG zg30
TD      32768
SOLVENT CDCl3
NS      4
DS      0
SWH     7211.539 Hz
FIDRES 0.220079 Hz
AQ      2.2719147 sec
RG      99.72
DW      69.333 usec
DE      10.06 usec
TE      296.4 K
D1      2.00000000 sec
D10     1

===== CHANNEL f1 =====
SFO1   400.1324081 MHz
NUC1    1H
P1     15.00 usec
PLW1   13.50000000 W

F2 - Processing Parameters
SI      16384
SF      400.1300092 MHz
WDW     EM
SSB     0
LB      0 Hz
GB      0
PC      1.00
    
```

¹³C NMR spectrum of (E)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylonitrile (23u)



Current Data Parameters
 NAME 1 want to 94
 EXPNO 148
 PROCNO 1

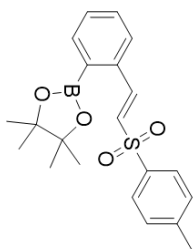
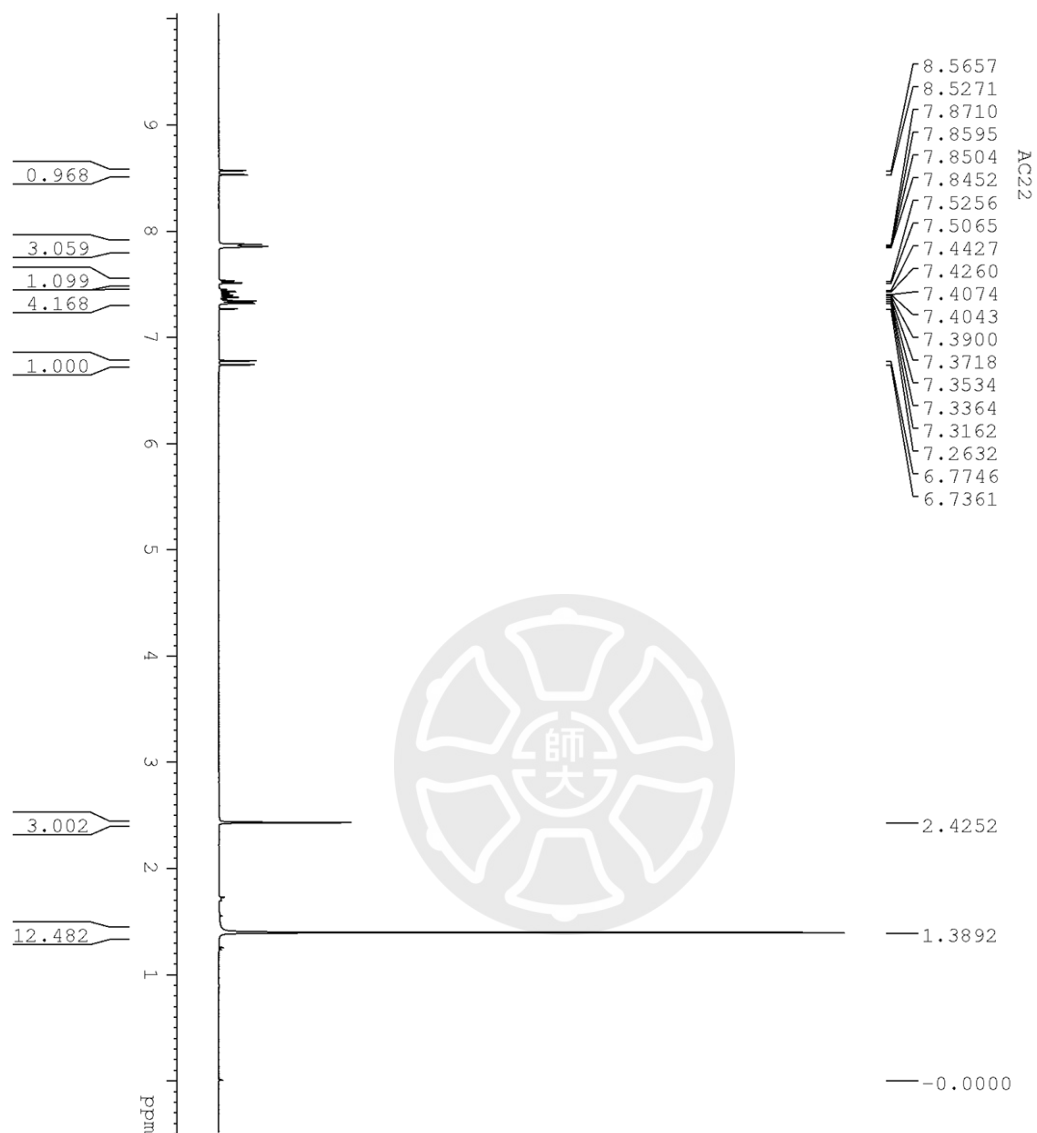
F2 - Acquisition Parameters
 Date_ 20250503
 Time 14.46
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 202
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6915744 se
 RG 198.09
 DM 20.809 us
 DE 28.09 us
 DI 0.03000000 se
 D11 0.03000000 se
 TDO 1

==== CHANNEL f1 =====
 SFO1 100.6228298 MH
 NUC1 13C
 P1 10.00 us
 P1M1 49.50000000 W

==== CHANNEL f2 =====
 SFO2 400.1316005 MH
 NUC2 1H
 CPDPRG12 waltz16
 PCDZ 90.00 us
 PFMZ 12.50000000 W
 PFM12 0.34722000 W
 PFM13 0.28125000 W

F2 - Processing Parameters
 SF 100.6127716 MH
 SFO 400.1316005 MH
 RMW 0
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

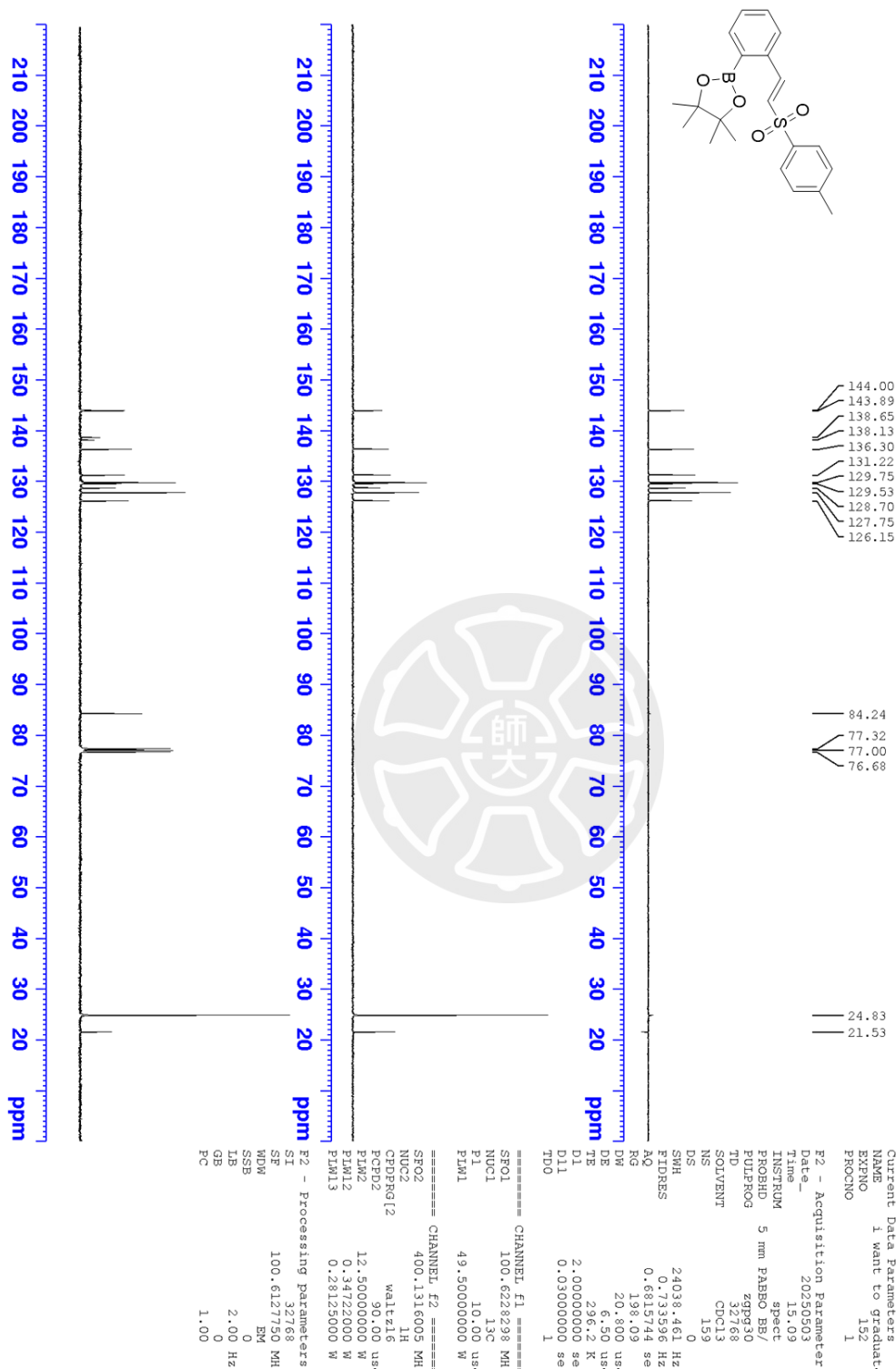
¹H NMR spectrum of (E)-4,4,5,5-tetramethyl-2-(2-(2-tosylvinyl)phenyl)-1,3,2-dioxaborolane (23v)



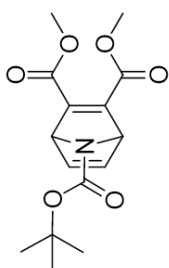
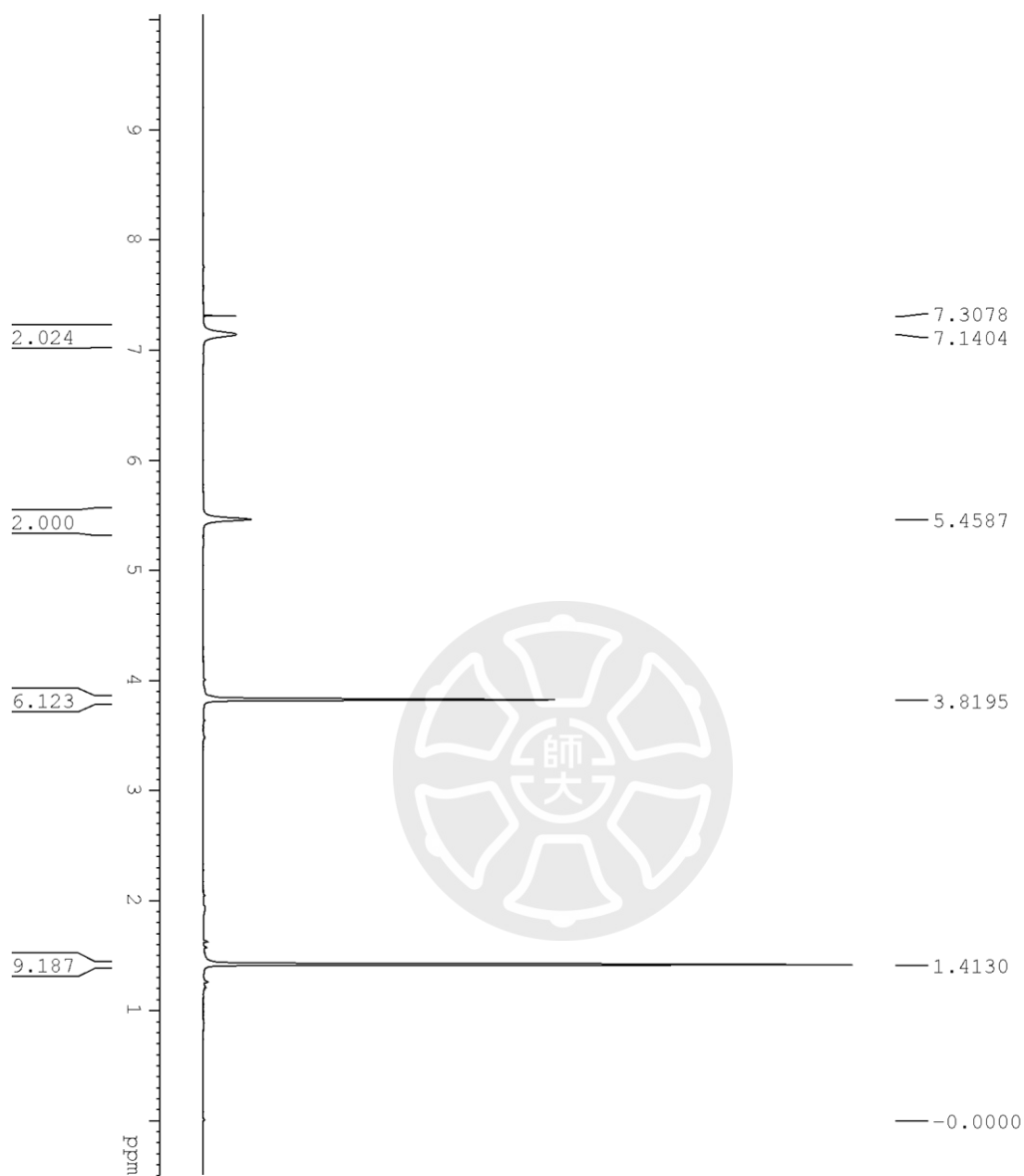
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Current Data Parameters
=====
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20250503
Time 15:07
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
SOLVENT CDCl3
NS 4
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 57.42
DW 69.333 usec
DE 10.06 usec
TE 296.0 K
D1 2.00000000 sec
TD0 1
===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 16384
SF 400.1300085 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
  
```

¹³C NMR spectrum of (E)-4,4,5,5-tetramethyl-2-(2-(2-tosylvinyl)phenyl)-1,3,2-dioxaborolane (23v)



¹H NMR spectrum of 7-(tert-butyl) 2,3-dimethyl 7-azabicyclo[2.2.1]hepta-2,5-diene-2,3,7-tricarboxylate (26g)



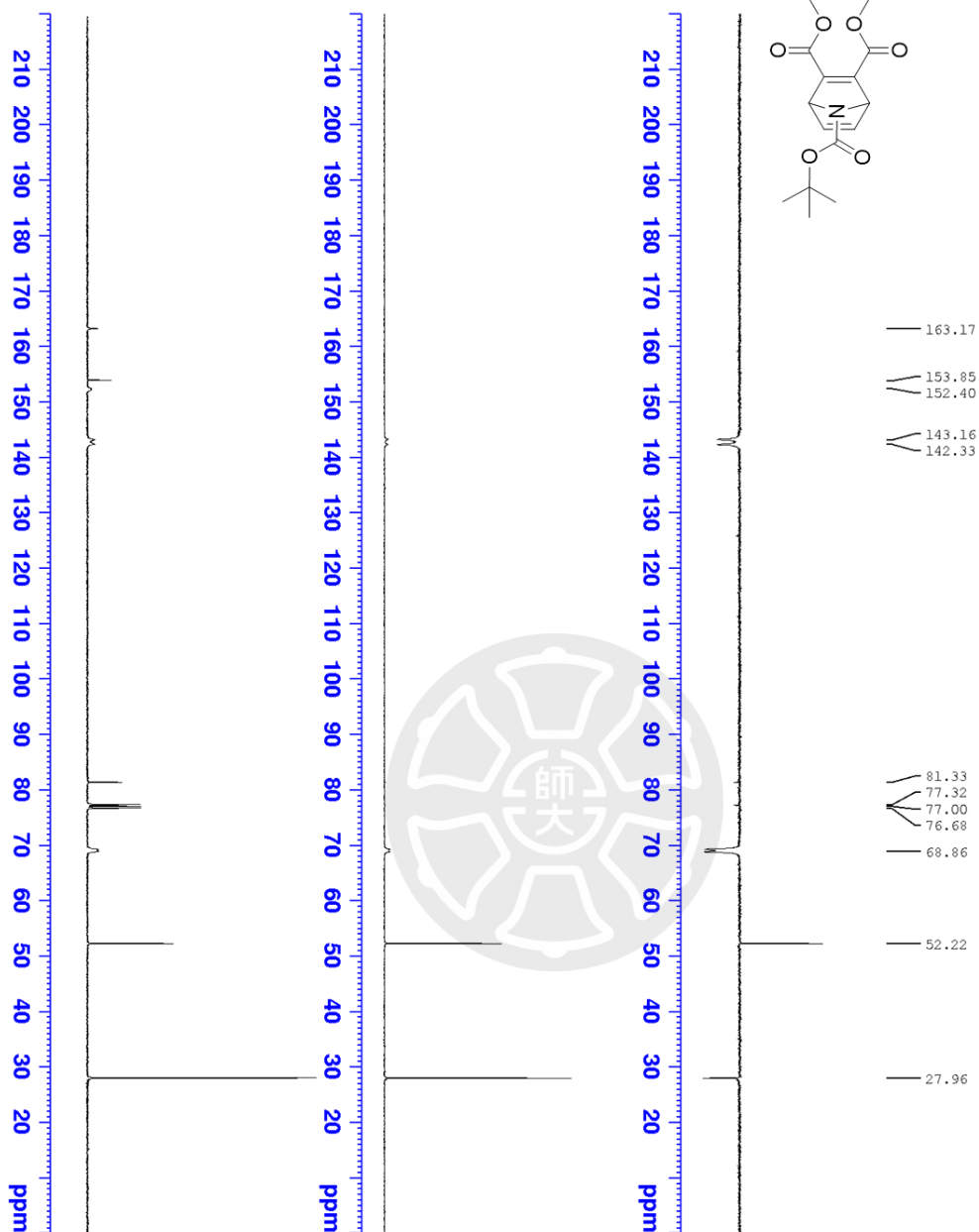
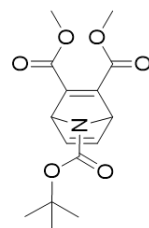
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===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PLW1 13.50000000 W
F2 - Processing parameters
SI 16384
SF 400.129905 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
  
```

```

Current Data Parameters
Name 1 want to graduate
EXPNO 155
PROCNO 1
F2 - Acquisition Parameters
Date_ 20250503
Time 15:31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 31.16
DE 60.053 usec
TE 296.0 K
TD0 2.00000000 sec
  
```

¹³C NMR spectrum of 7-(tert-butyl) 2,3-dimethyl 7-azabicyclo[2.2.1]hepta-2,5-diene-2,3,7-tricarboxylate (26g)



Current Data Parameters
 NAME I want to graduat
 EXPNO 196
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20250503
 Time 15.33
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 166
 DS 0

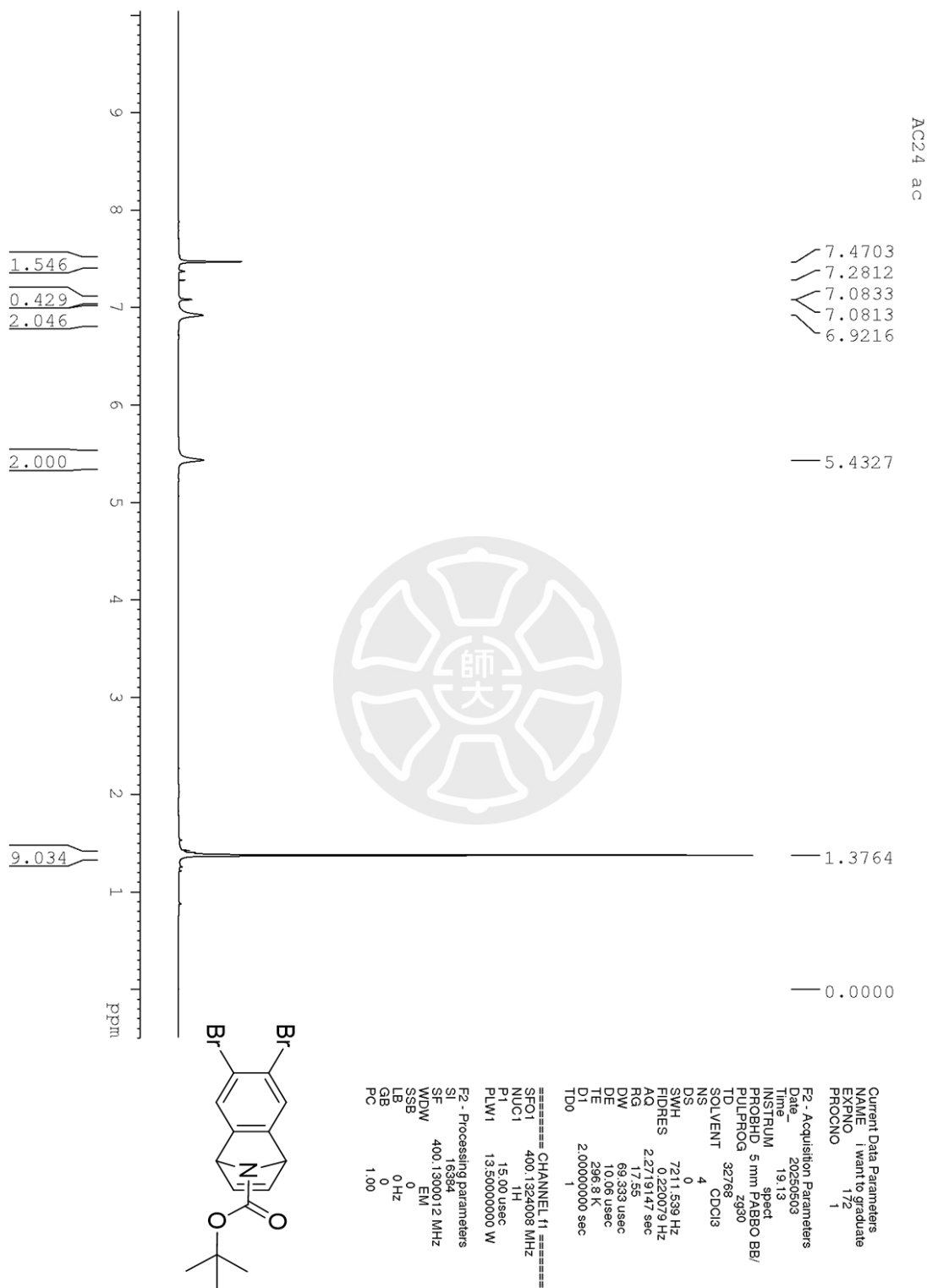
SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6819744 se
 RG 198.09
 DW 20.800 us
 DE 6.50 us
 TE 296.2 K
 D1 2.0000000 se
 D11 0.0300000 se
 TDO 1

===== CHANNEL f1 =====
 SF01 100.628298 MH
 NUCL1 13C
 P1 10.00 us
 PL1 49.50000000 W
 PLM1

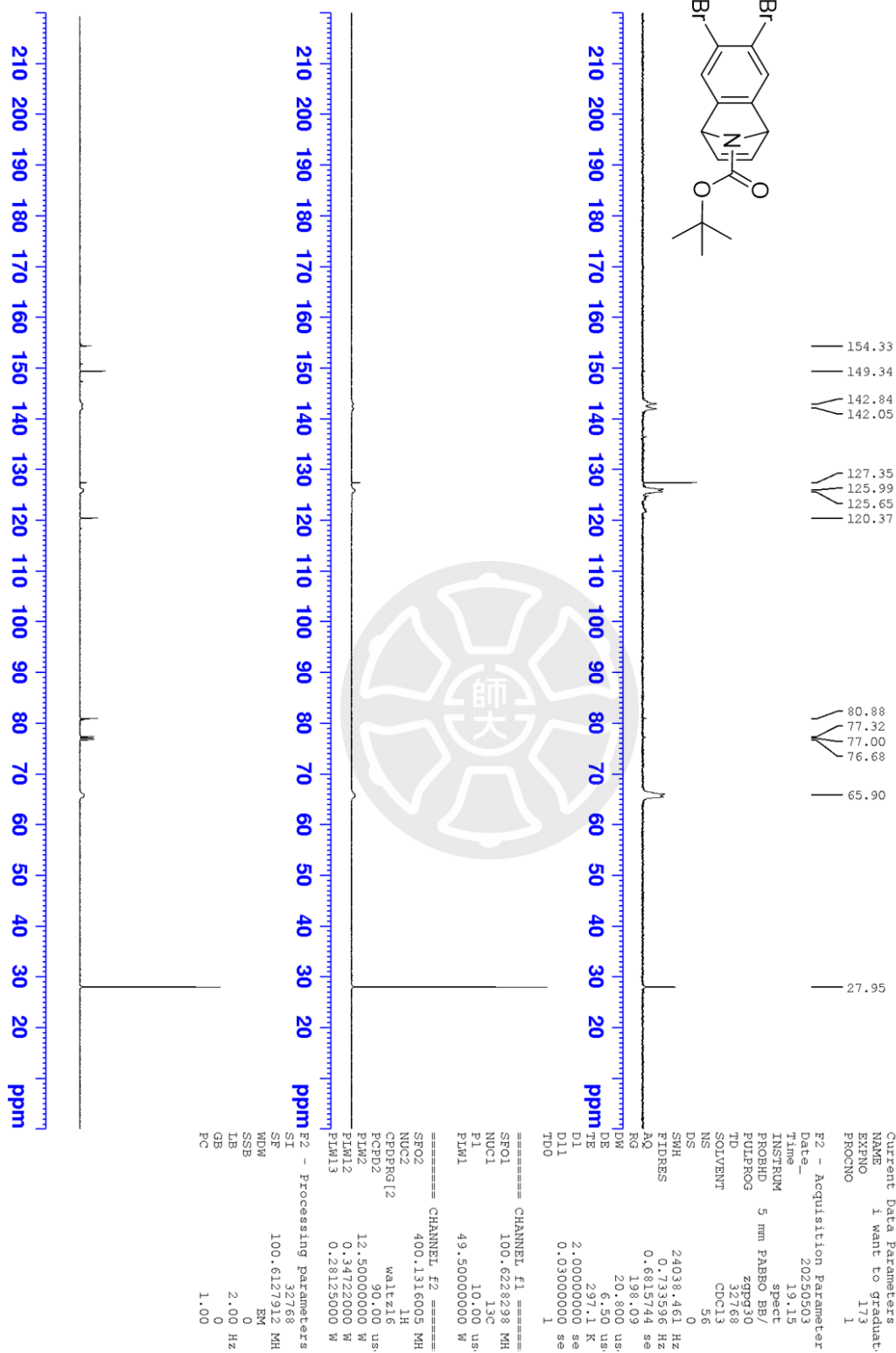
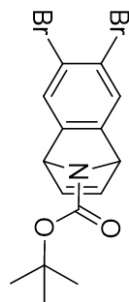
===== CHANNEL f2 =====
 SF02 400.1316005 MH
 NUCL2 1H
 CPDPRG12 waltz16
 PCPD2 90.00 us
 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127776 MH
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 FC 1.00

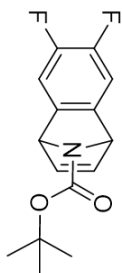
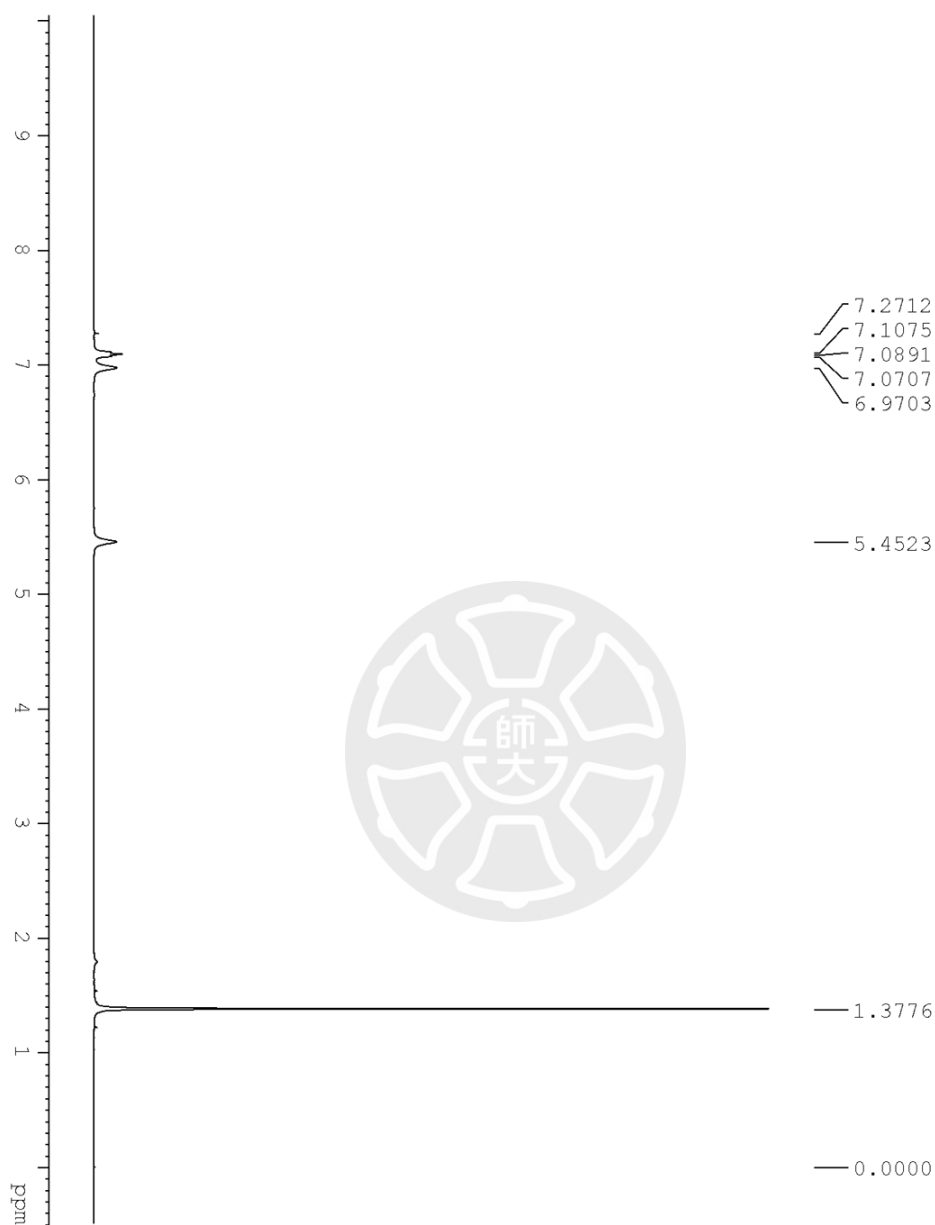
¹H NMR spectrum of tert-butyl 6,7-dibromo-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26h)



¹³C NMR spectrum of tert-butyl 6,7-dibromo-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26h)



¹H NMR spectrum of tert-butyl 6,7-difluoro-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26i)



```

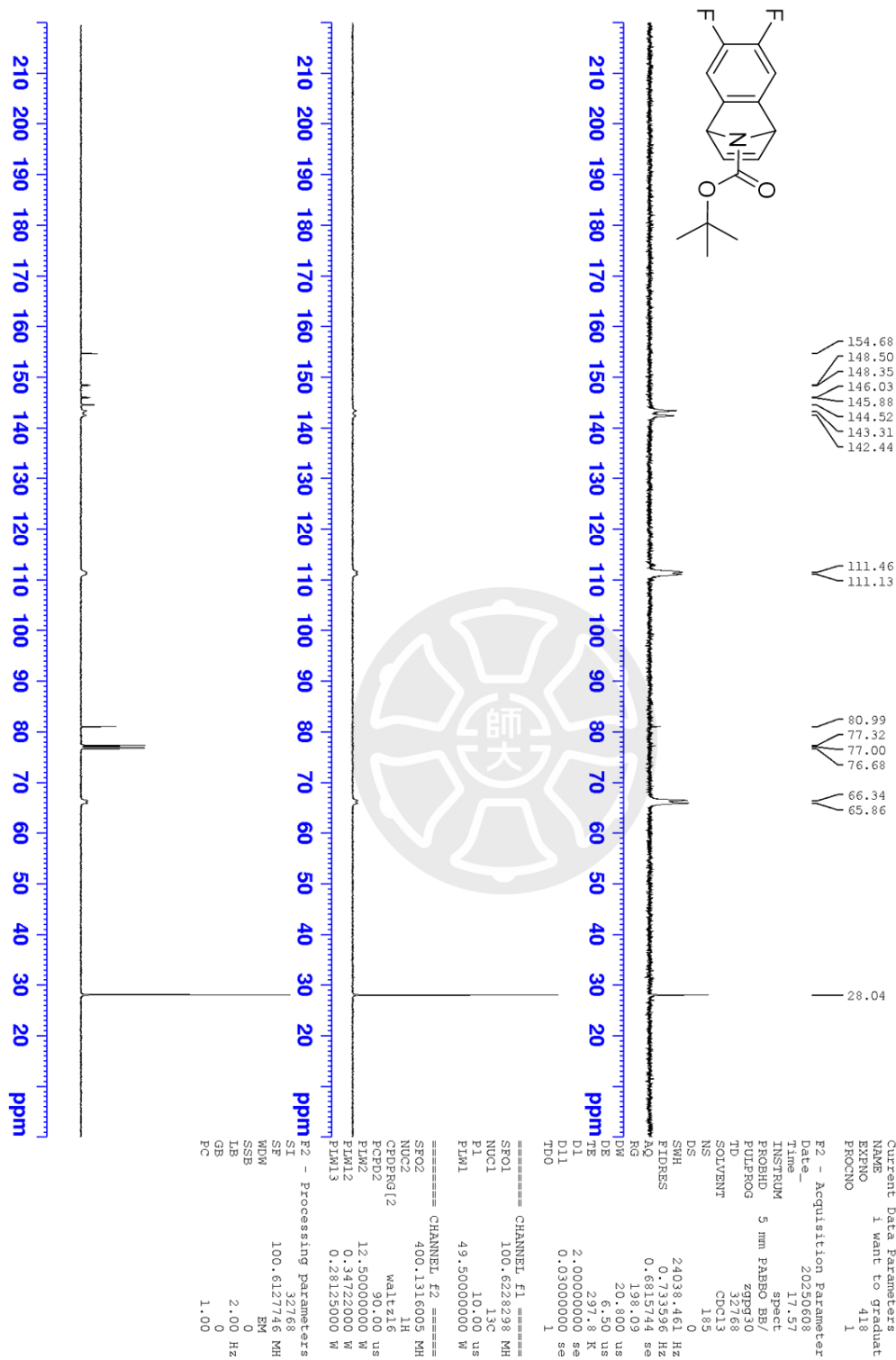
Current Data Parameters
NAME      I want to graduate
EXPNO     417
PROCNO    1

F2 - Acquisition Parameters
Date_     20250609
Time      17:55
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         4
DS         0
SWH        7211.539 Hz
FIDRES     0.220079 Hz
AQ         2.2719147 sec
RG         51.8
DW         69.333 usec
DE         10.08 usec
TE         297.1 K
D1         2.00000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1      1H
P1        15.00 usec
PLW1      13.50000000 W

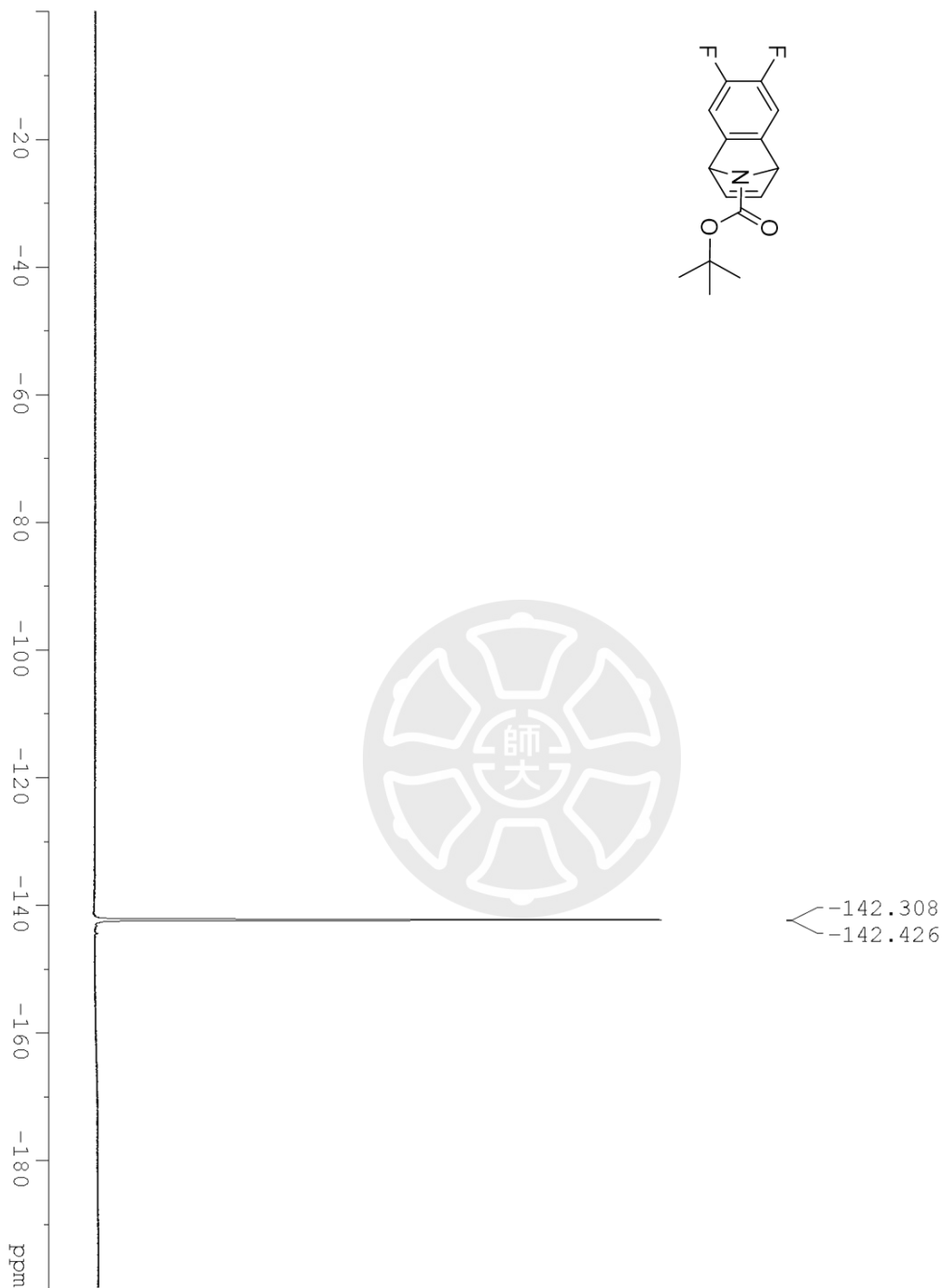
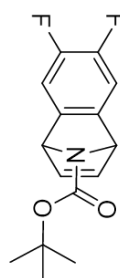
F2 - Processing parameters
SI        16384
SF        400.1300053 MHz
WDW       EM
SSB       0
LB        0 Hz
GB        0
PC        1.00
    
```

¹³C NMR spectrum of tert-butyl 6,7-difluoro-1,4-dihydro-1,4-iminonaphthalene-9-carboxylate (26i)



¹⁹F NMR spectrum of tert-butyl 6,7-difluoro-1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26i)

AC25 19F



Current Data Parameters
 NAME i want to graduate
 EXPNO 421
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20230608
 Time 18.19

INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg

TD 131072
 SOLVENT CDCl3

NS 8
 DS 0

SWH 89285.711 Hz
 FIDRES 0.681196 Hz

AQ 0.7340032 sec
 RG 198.09

DW 5.600 usec
 DE 6.50 usec

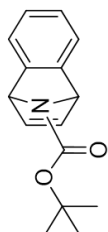
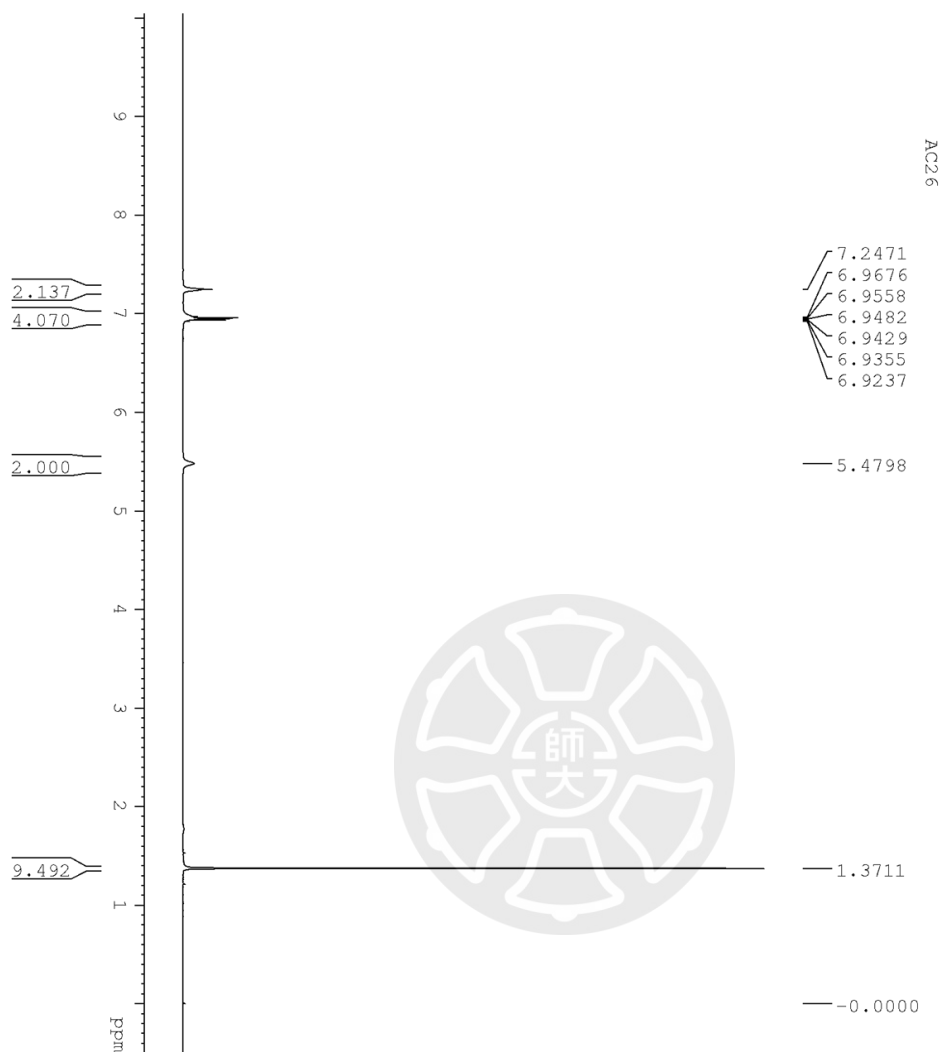
TE 297.3 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TDO 1

=====
 CHANNEL f1
 SFO1 376.4607168 MHz
 NUC1 19F
 P1 15.00 usec
 PLW1 16.50000000 W

=====
 CHANNEL f2
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLW12 0.34722000 W

F2 - Processing parameters

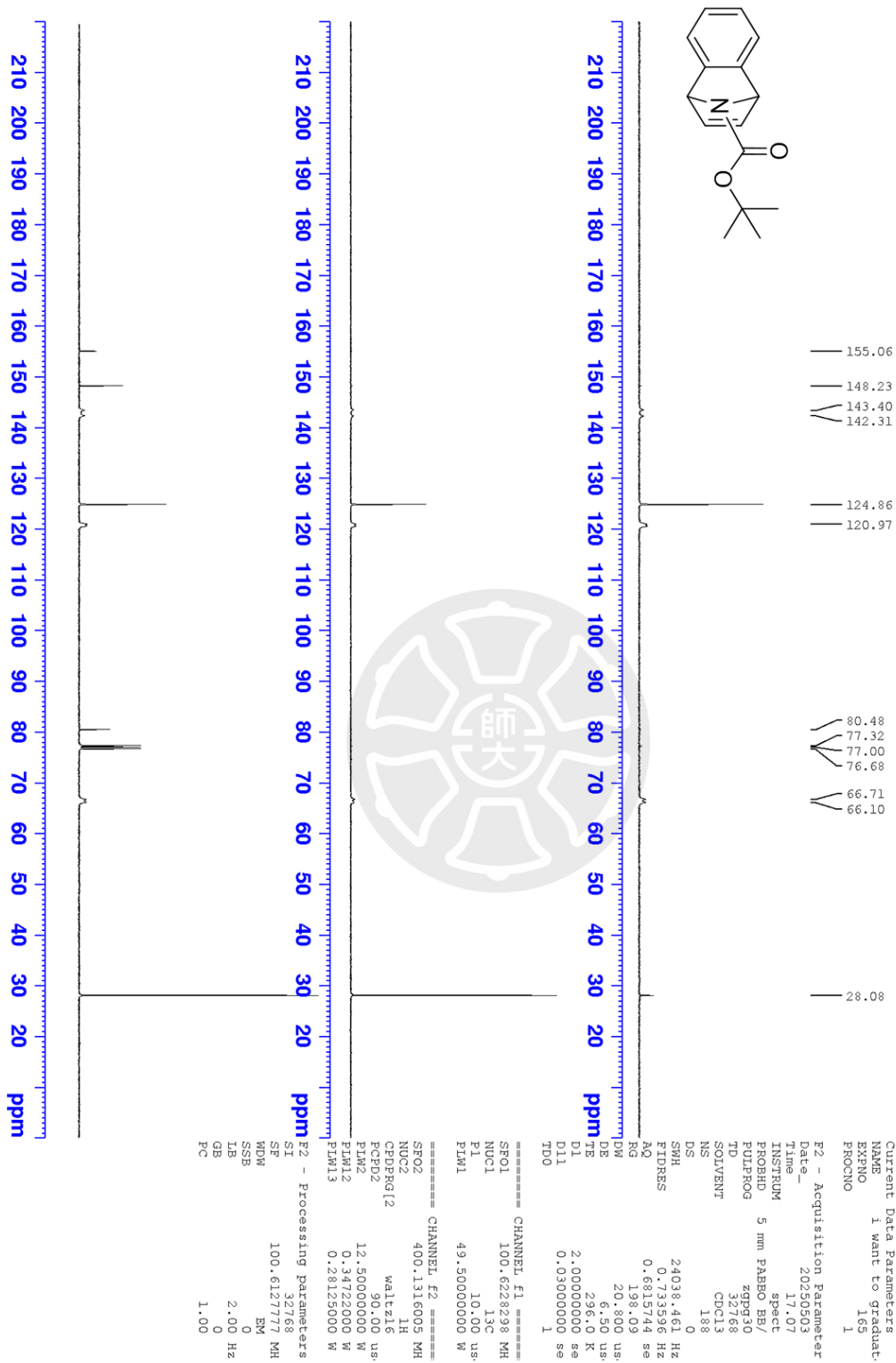
¹H NMR spectrum of tert-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26a)



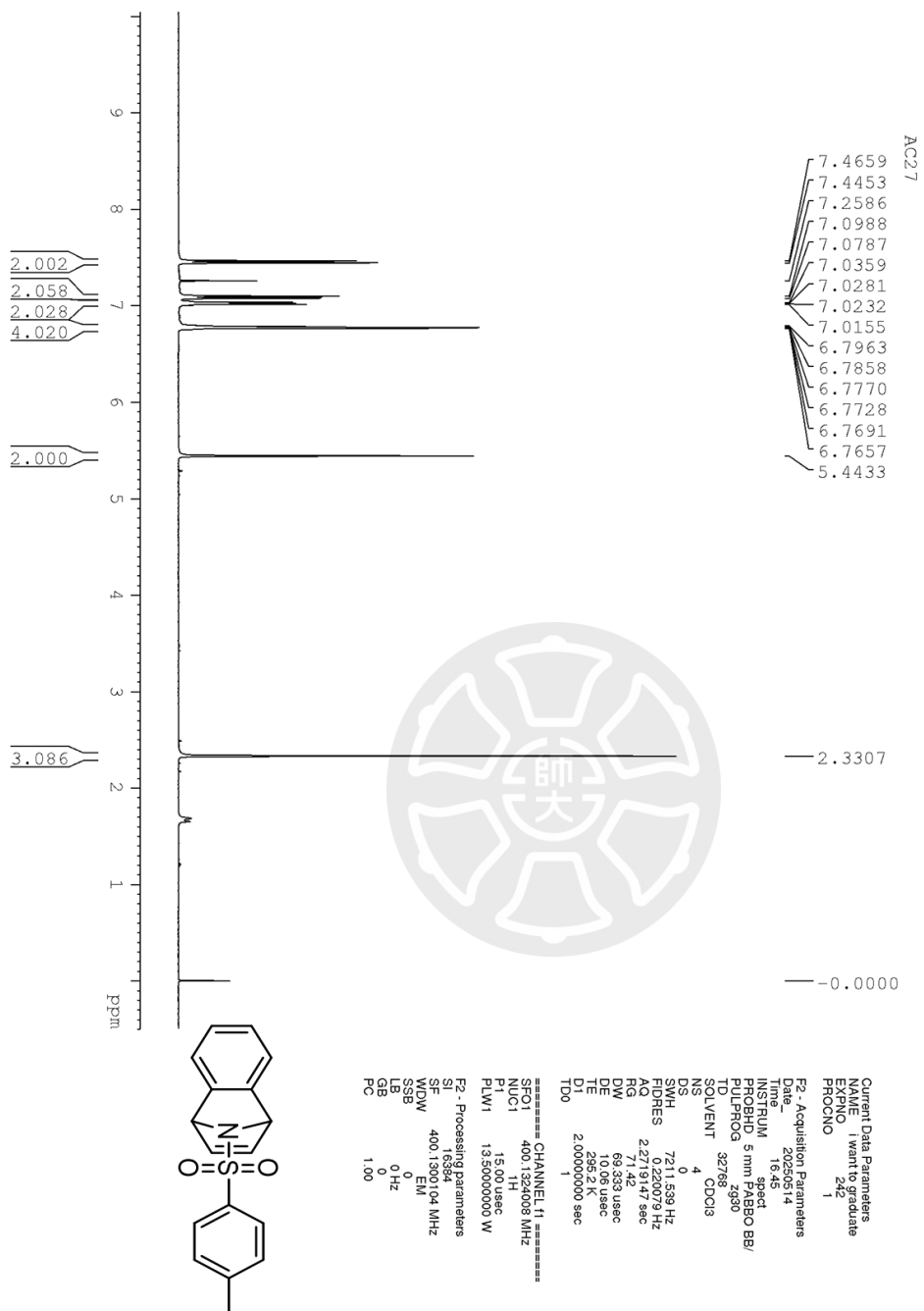
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Current Data Parameters
NAME      I want to graduate
EXPNO    164
PROCNO   1
F2 - Acquisition Parameters
Date_    20250903
Time     17.06
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
SOLVENT  CDCl3
NS       4
DS       0
SWH      7211.539 Hz
FDRS     0.220079 Hz
AQ       2.2781947 sec
RG       69.333 usec
DE       10.06 usec
TE       295.6 K
D1       2.00000000 sec
TD0      1
===== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1     1H
P1       15.00 usec W
PLW1     13.50000000 W
F2 - Processing parameters
SI       16384
SF       400.1300148 MHz
WDW      EM
SSB      0
LB       0 Hz
GB       0 Hz
PC       1.00
  
```

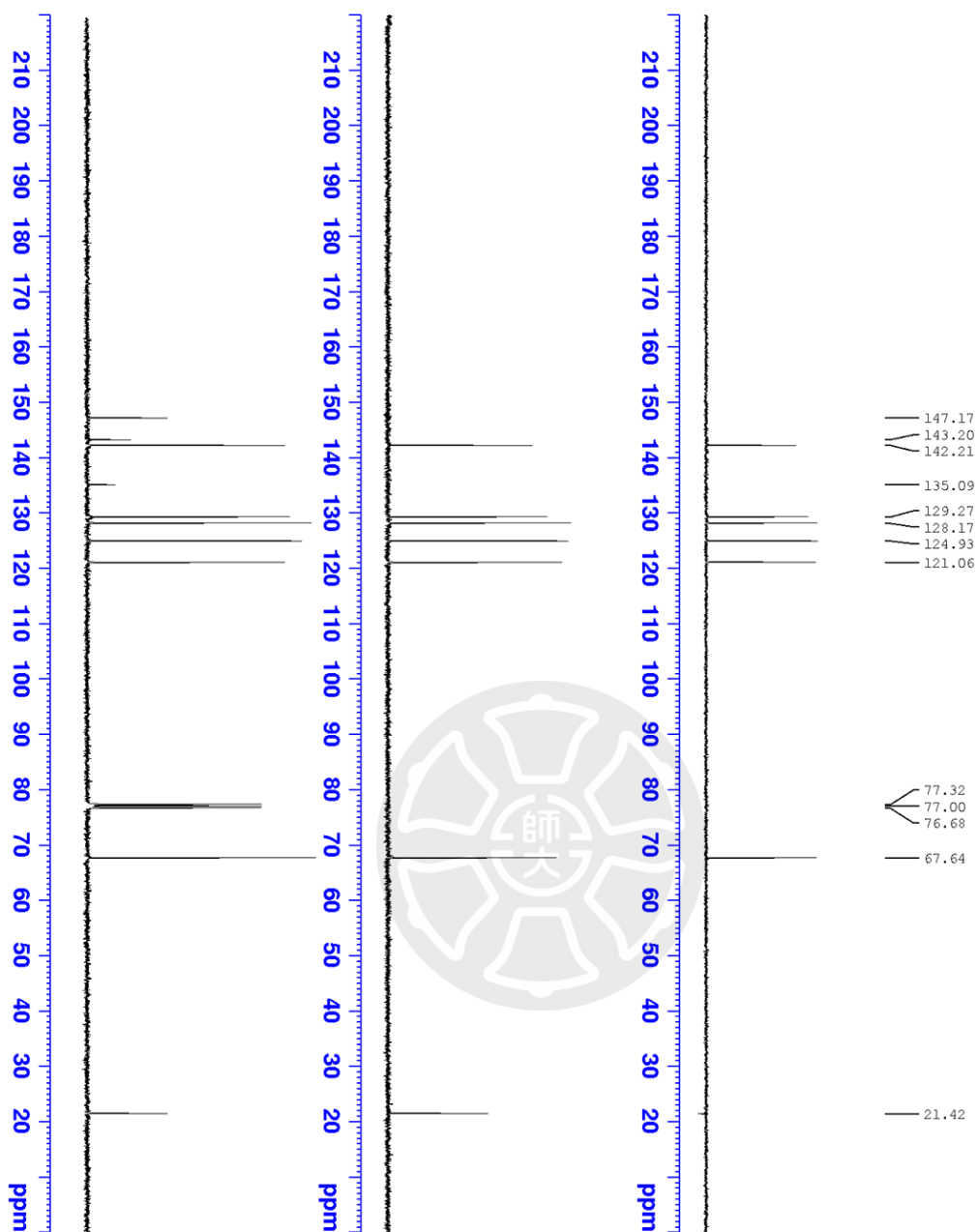
¹³C NMR spectrum of tert-butyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26a)



¹H NMR spectrum of 9-tosyl-1,4-dihydro-1,4-epiminonaphthalene (26b)



¹³C NMR spectrum of 9-tosyl-1,4-dihydro-1,4-epiminonaphthalene (26b)



```

Current Data Parameters
NAME      1 want to graduat
EXPNO    246
PROCNO   1

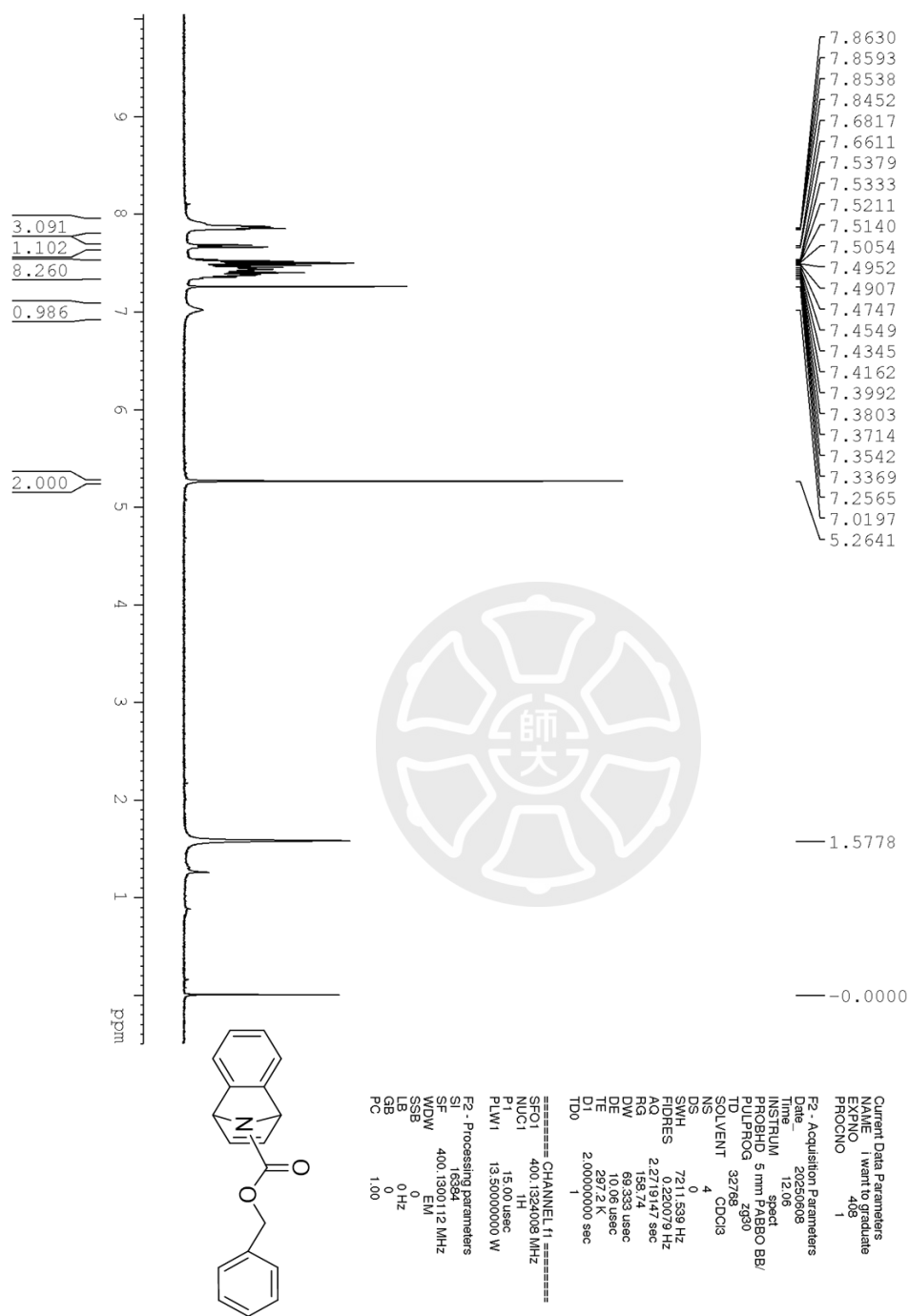
F2 - Acquisition Parameters
Date_    20250514
Time     17.06
INSTRUM spect
PROBHD   5 mm PABBO/BE/
PULPROG zgpg30
TD       32768
SOLVENT  CDCl3
NS       106
DS
SWH      24038.461 Hz
FIDRES   0.735396 Hz
AQ        0.681974 sec
RG        198.09
DE        20.800 us
TE        285.7 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1

===== CHANNEL f1 =====
SF01     100.628298 MH
NUC1     13C
PI       10.00 us
PLM1     49.50000000 W

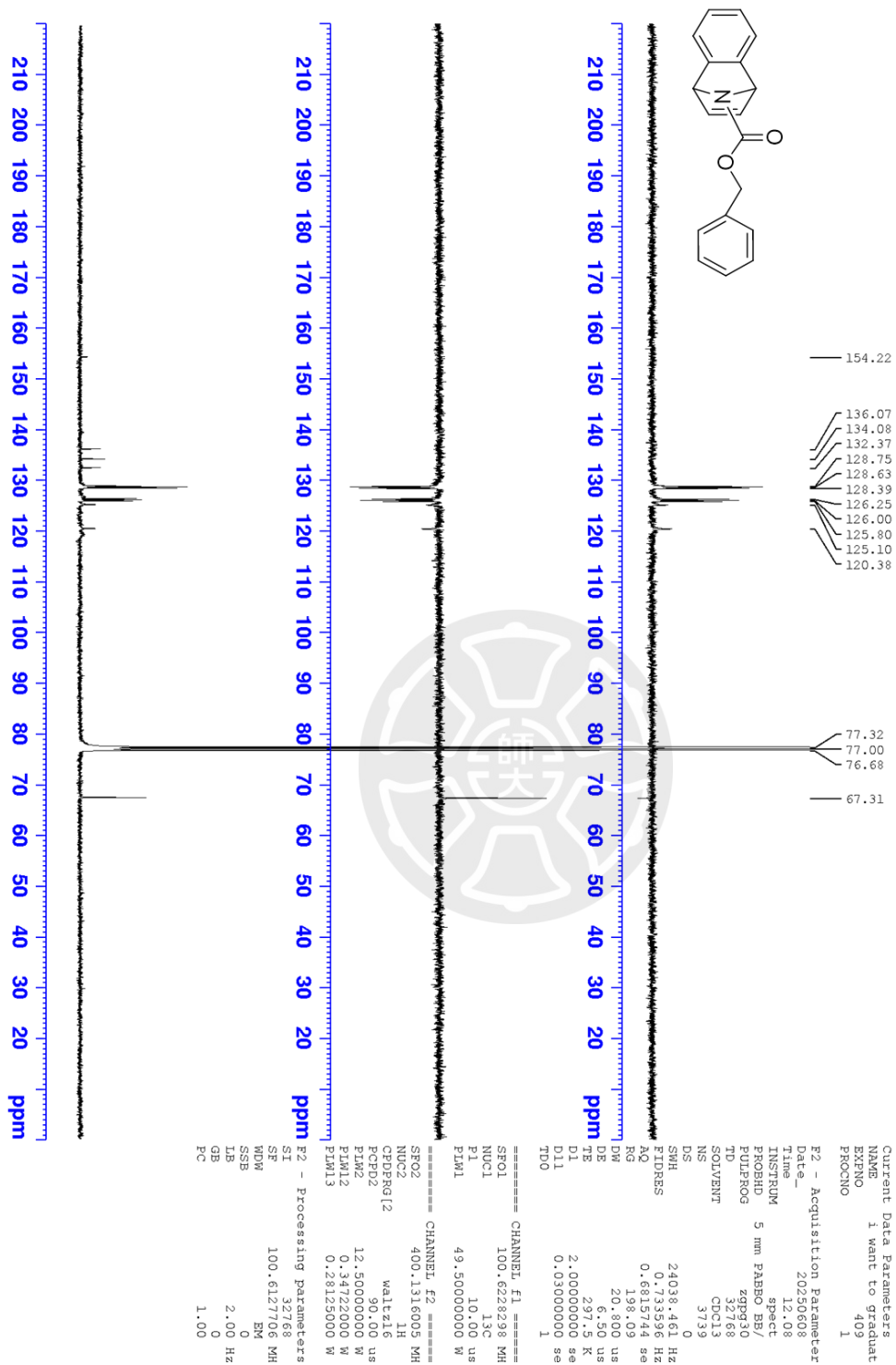
===== CHANNEL f2 =====
SF02     400.1316005 MH
NUC2     1H
CPDPRG12 waltz16
PCPD2    90.00 us
PLM2     12.50000000 W
PLM12    0.34722000 W
PLM13    0.28125000 W

F2 - Processing Parameters
SI
SE       100.6127775 MH
WDW      EM
SSB      0
LB       2.00 Hz
GB       0
PC       1.00
    
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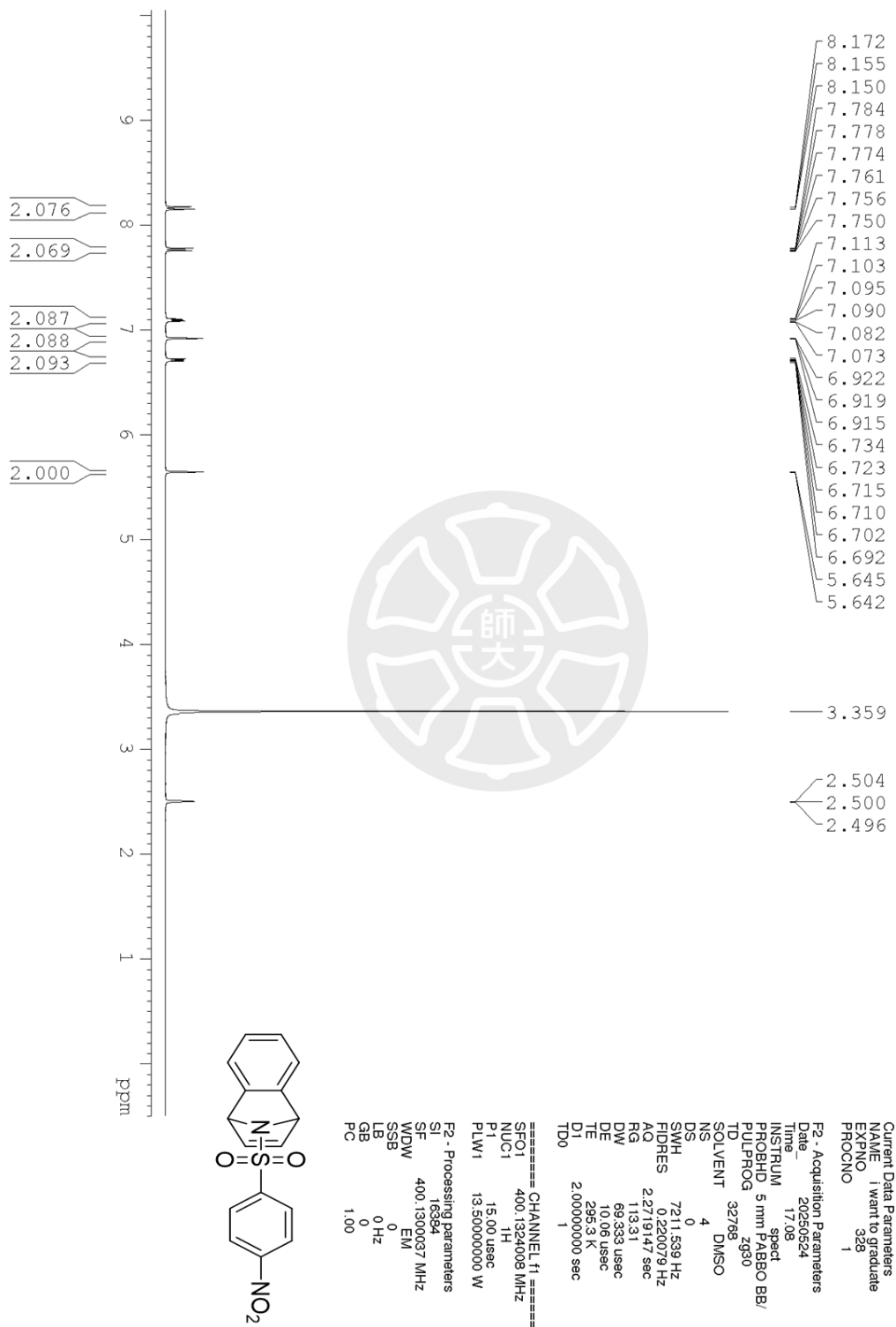
¹H NMR spectrum of benzyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26d)



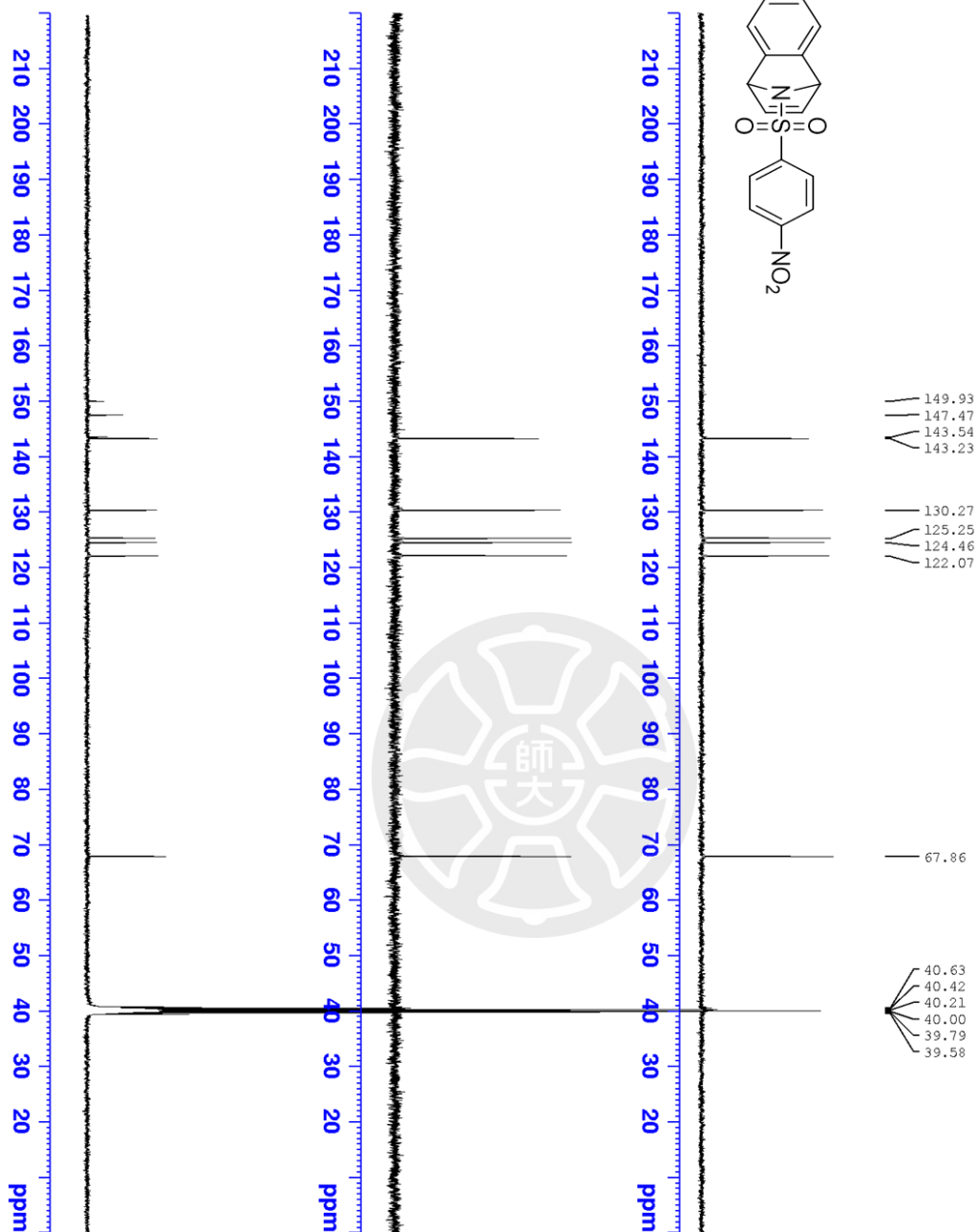
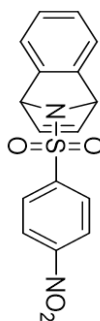
¹³C NMR spectrum of benzyl 1,4-dihydro-1,4-epiminonaphthalene-9-carboxylate (26d)



¹H NMR spectrum of 9-((4-nitrophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene (26c)



¹³C NMR spectrum of 9-((4-nitrophenyl)sulfonyl)-1,4-dihydro-1,4-epiminonaphthalene (26c)



149.93
147.47
143.54
143.23
130.27
125.25
124.46
122.07

67.86
40.63
40.42
40.21
40.00
39.79
39.58

Current Data Parameters
NAME I want to graduate
EXPNO 329
PROCNO 1

F2 - Acquisition Parameter

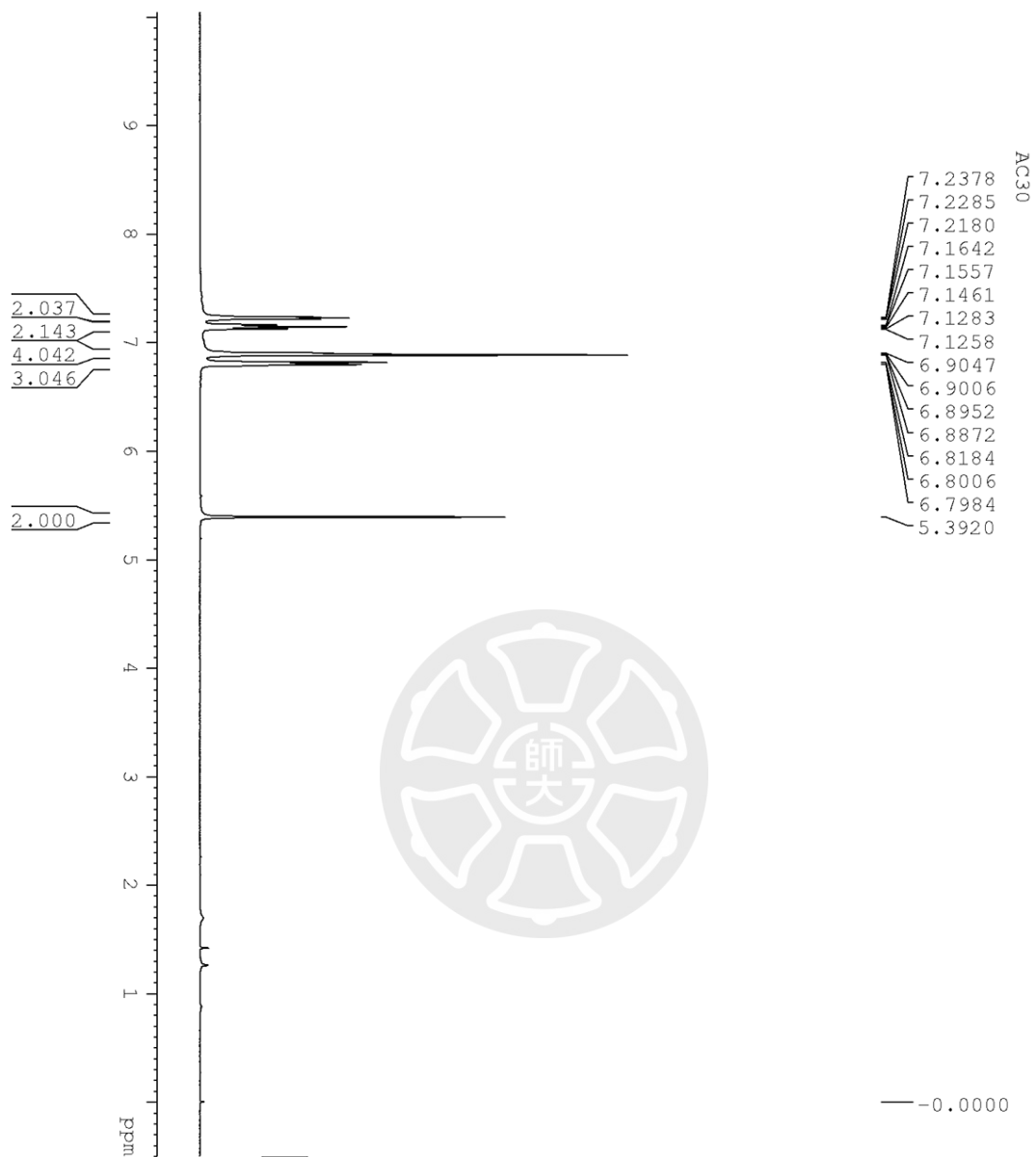
Date_ 20250524
Time 17.11
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT DMSO
NS 589
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 se
RG 198.09
DE 20.800 us
TE 6.50 us
D1 296.0 K
D11 2.00000000 se
TD0 0.03000000 se
1

CHANNEL F1
SFO1 100.622629 MHz
NUC1 13C
P1 10.00 us
PL1 49.50000000 W
FLM1

CHANNEL F2
SFO2 400.1316005 MHz
NUC2 1H
P2 90.00 us
PLM2 12.50000000 W
PLM1 0.34722000 W
PLM3 0.28129000 W

F2 - Processing parameters
SI 32768
SF 100.6127661 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

¹H NMR spectrum of 9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (26f)



```

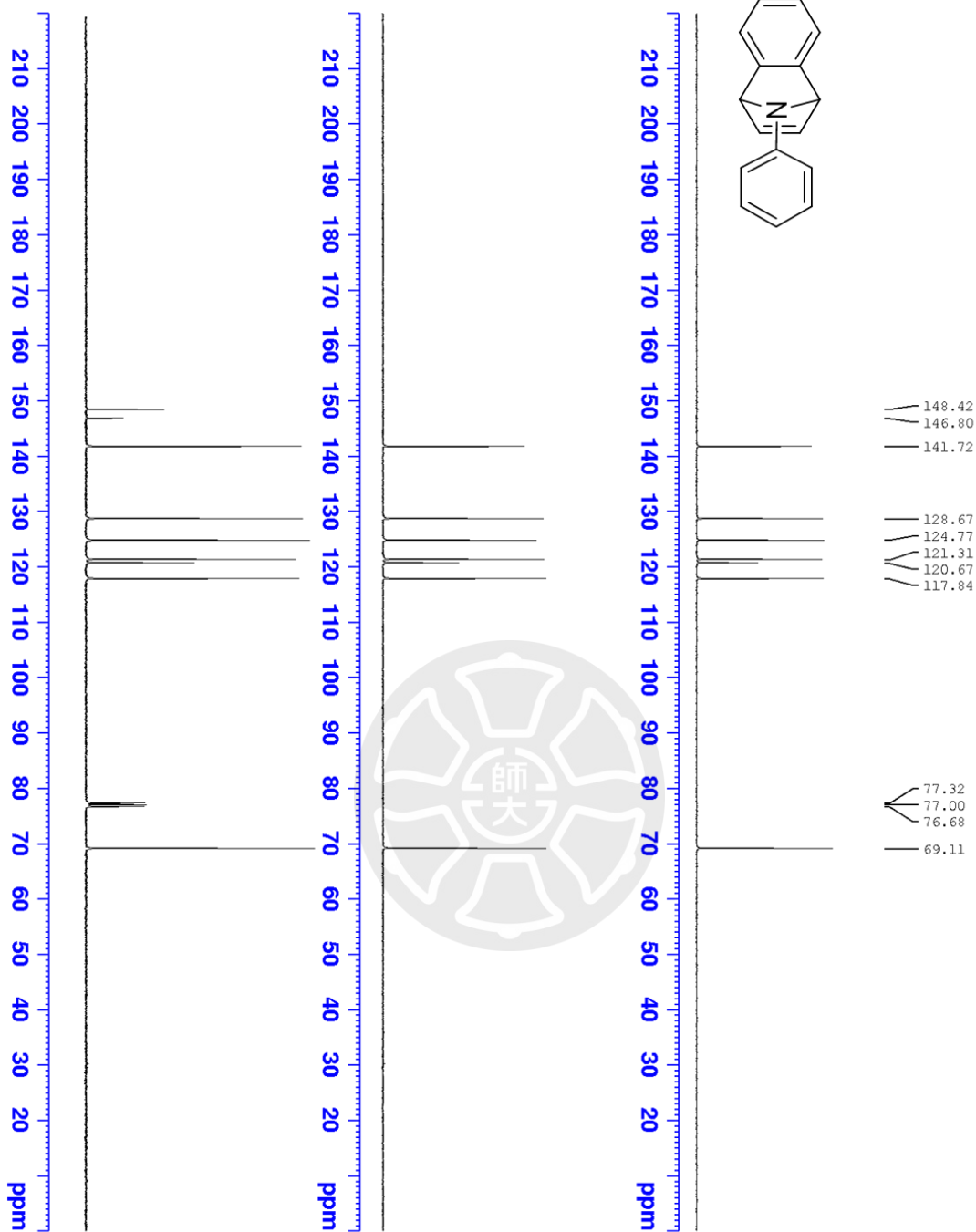
Current Data Parameters
NAME      I want to graduate
EXPNO     241
PROCNO    1

F2 - Acquisition Parameters
Date_     20250514
Time      21:07
INSTRUM   spect
PROBHD    5 mm F4BBO BB/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         4
DS         0
SWH        7211.539 Hz
FIDRES     0.220079 Hz
AQ         2.2719147 sec
RG         31.16
DW         69.333 usec
DE         10.06 usec
TE         295.6 K
D1         2.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       400.132003 MHz
P1         15.00 usec
PLW1       13.50000000 W

F2 - Processing parameters
SI         18354
SF         400.1300514 MHz
WDW        EM
SSB        0
LB         0 Hz
GB         0
PC         1.00
    
```

¹³C NMR spectrum of 9-phenyl-1,4-dihydro-1,4-epiminonaphthalene (26f)



148.42
146.80
141.72
128.67
124.77
121.31
120.67
117.84

77.32
77.00
76.68
69.11

Current Data Parameters
NAME I want to graduat.
EXPNO 248
PROCNO 1

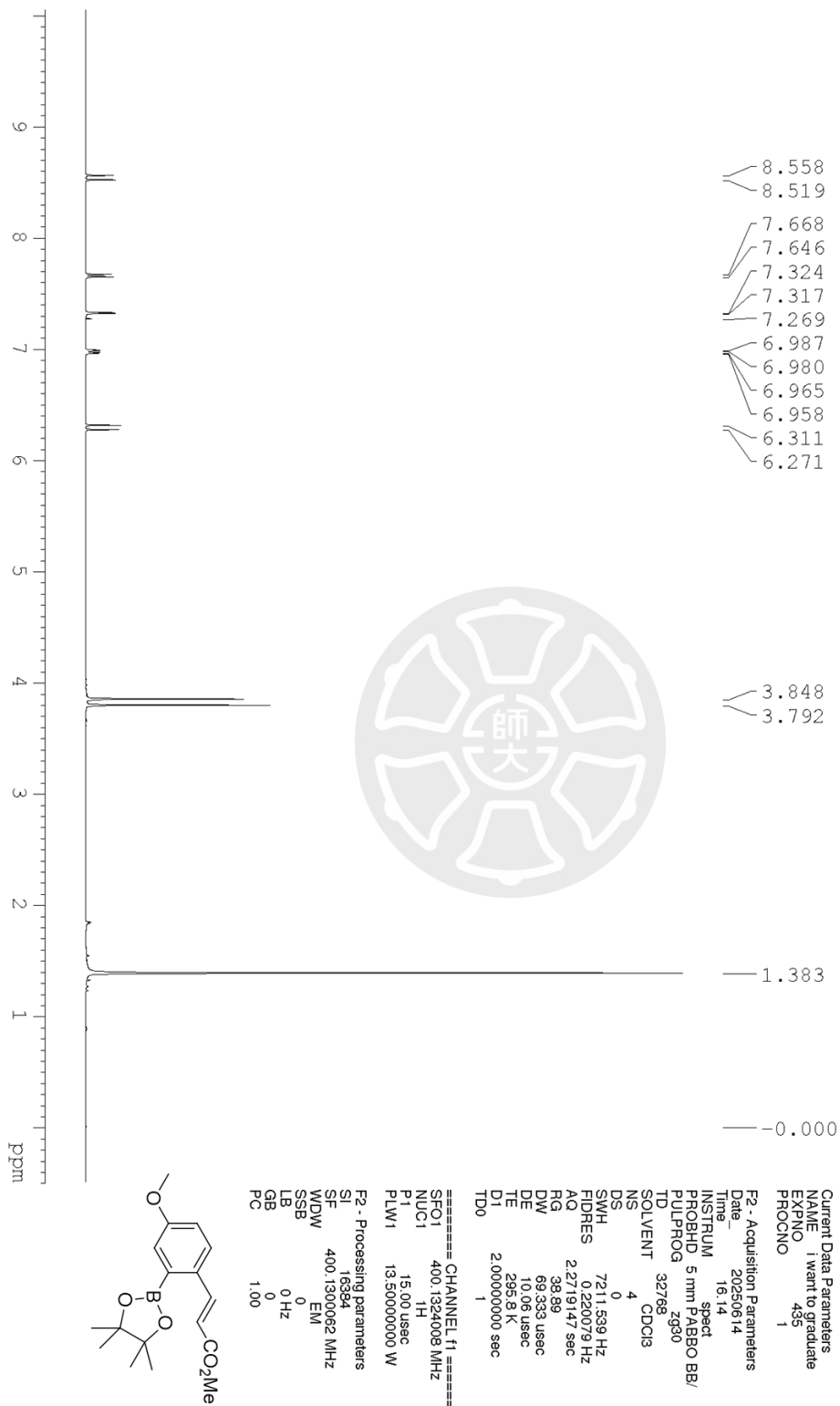
F2 - Acquisition Parameters
Date_ 20250614
Time 21.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 90
DS 0
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 se
RG 198.09
DW 20.800 us
DE 6.50 us
TE 296.0 K
D1 2.00000000 se
D11 0.03000000 se
TDO 1

==== CHANNEL f1 =====
SFO1 100.6228298 MH
NUC1 13C
P1 10.00 us
P1M1 49.50000000 W

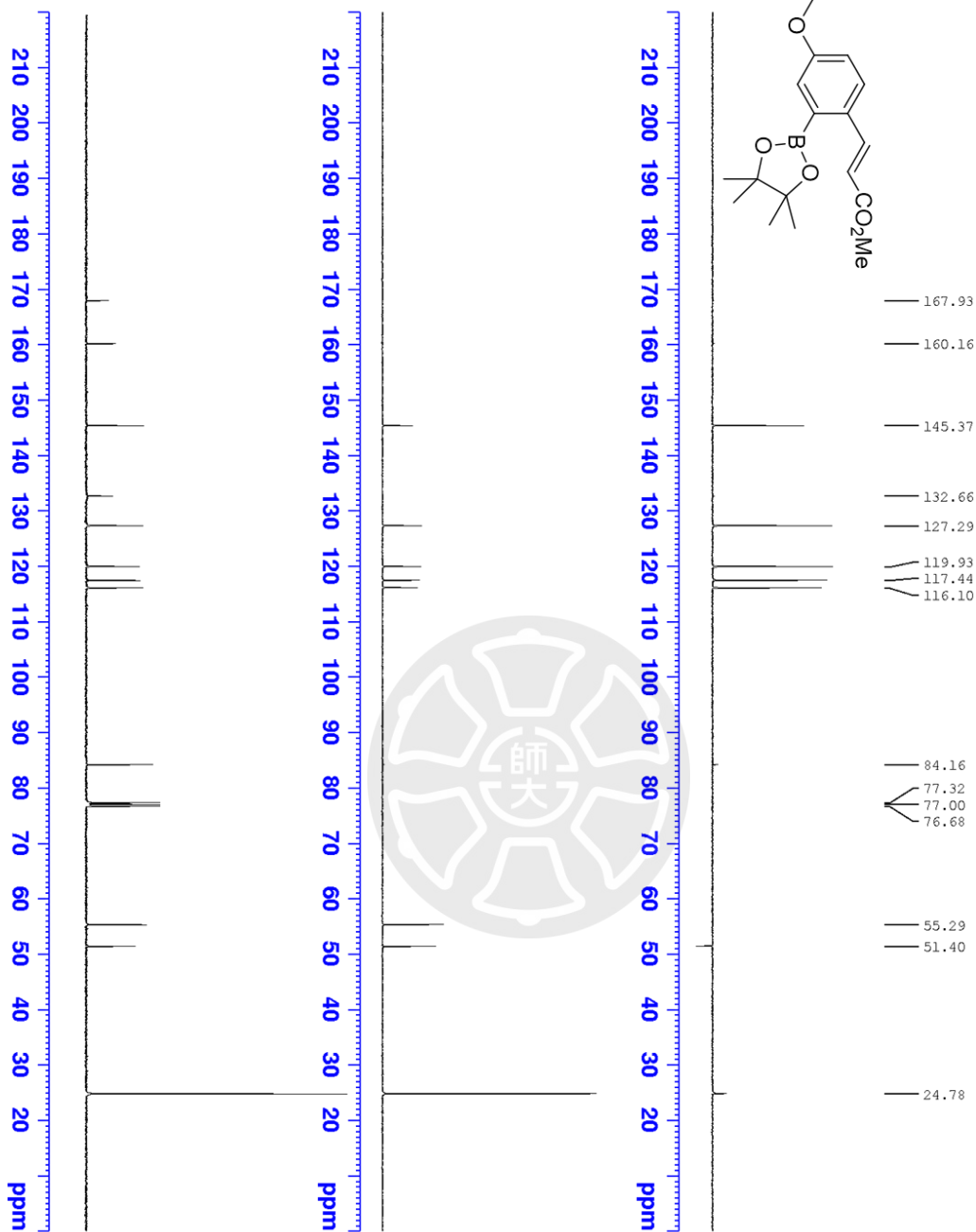
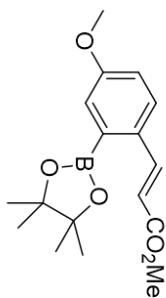
==== CHANNEL f2 =====
SFO2 400.1316005 MH
NUC2 1H
CPEPRG12 waltz16
PCPD2 90.00 us
P1M2 12.50000000 W
P1M12 0.34722000 W
P1M13 0.28125000 W

F2 - Processing parameters
SI 32768
SF 100.6127922 MH
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.00

¹H NMR spectrum of methyl (E)-3-(4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23l)



¹³C NMR spectrum of methyl (E)-3-(4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acrylate (23l)



Current Data Parameters
 NAME I want to graduate
 EXPNO 436
 PROCNO 1

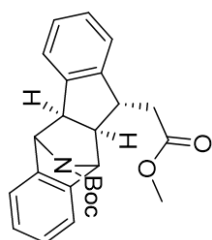
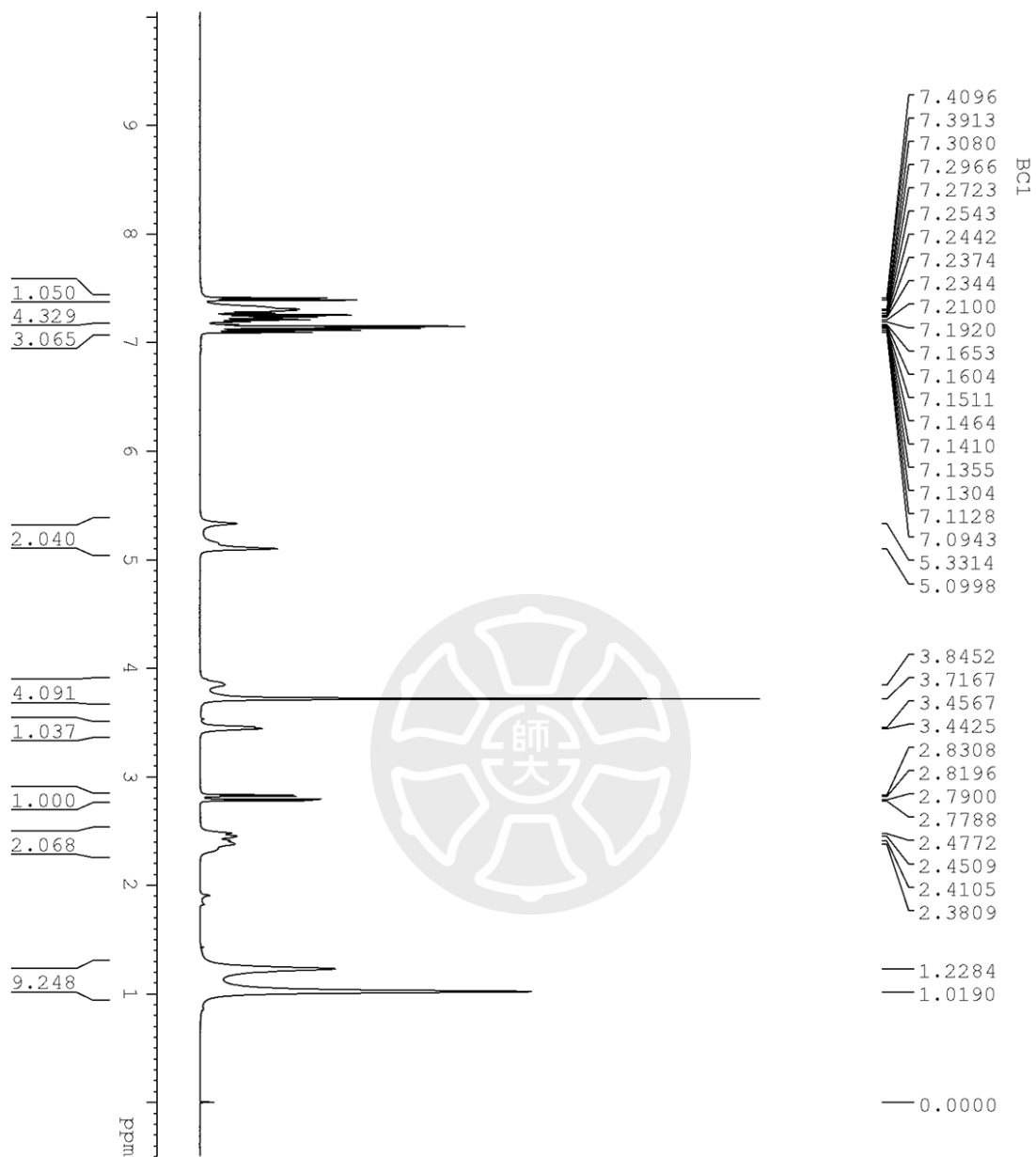
F2 - Acquisition Parameters:
 Date_ 20250614
 Time 16.16
 INSTRUM spect
 PROBHD 5 mm F4BBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 126
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 198.09
 DM 20.800 use
 DE 6.50 use
 TE 296.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 SF01 100.6228298 MHz;
 NUC1 13C
 P1 10.00 use
 PLW1 49.50000000 W

==== CHANNEL f2 =====
 SF02 400.1316005 MHz;
 NUC2 1H
 CPDPRG12 waltz16
 PCPD2 90.00 use
 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127154 MHz;
 NDM 0 BM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

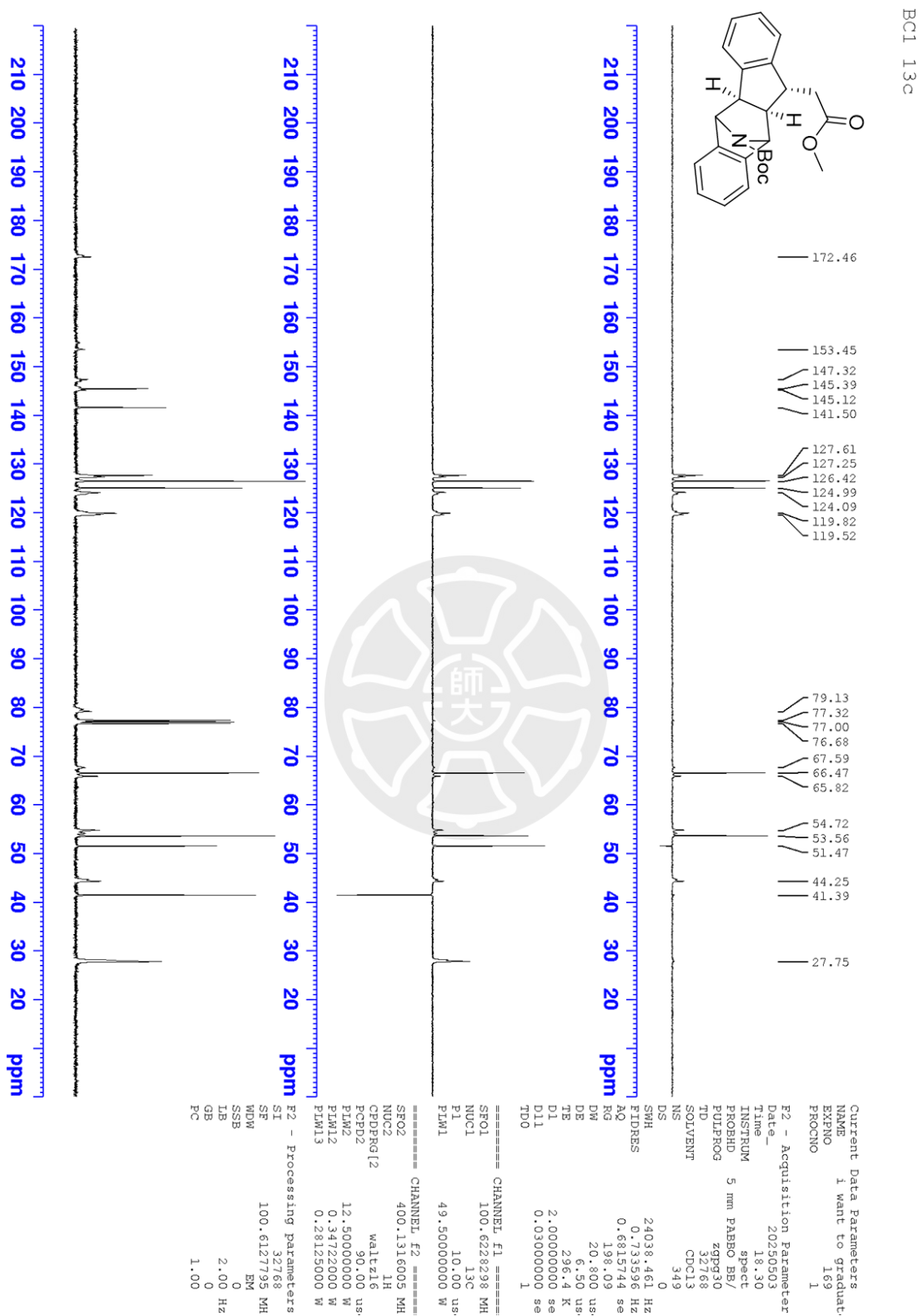
¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)



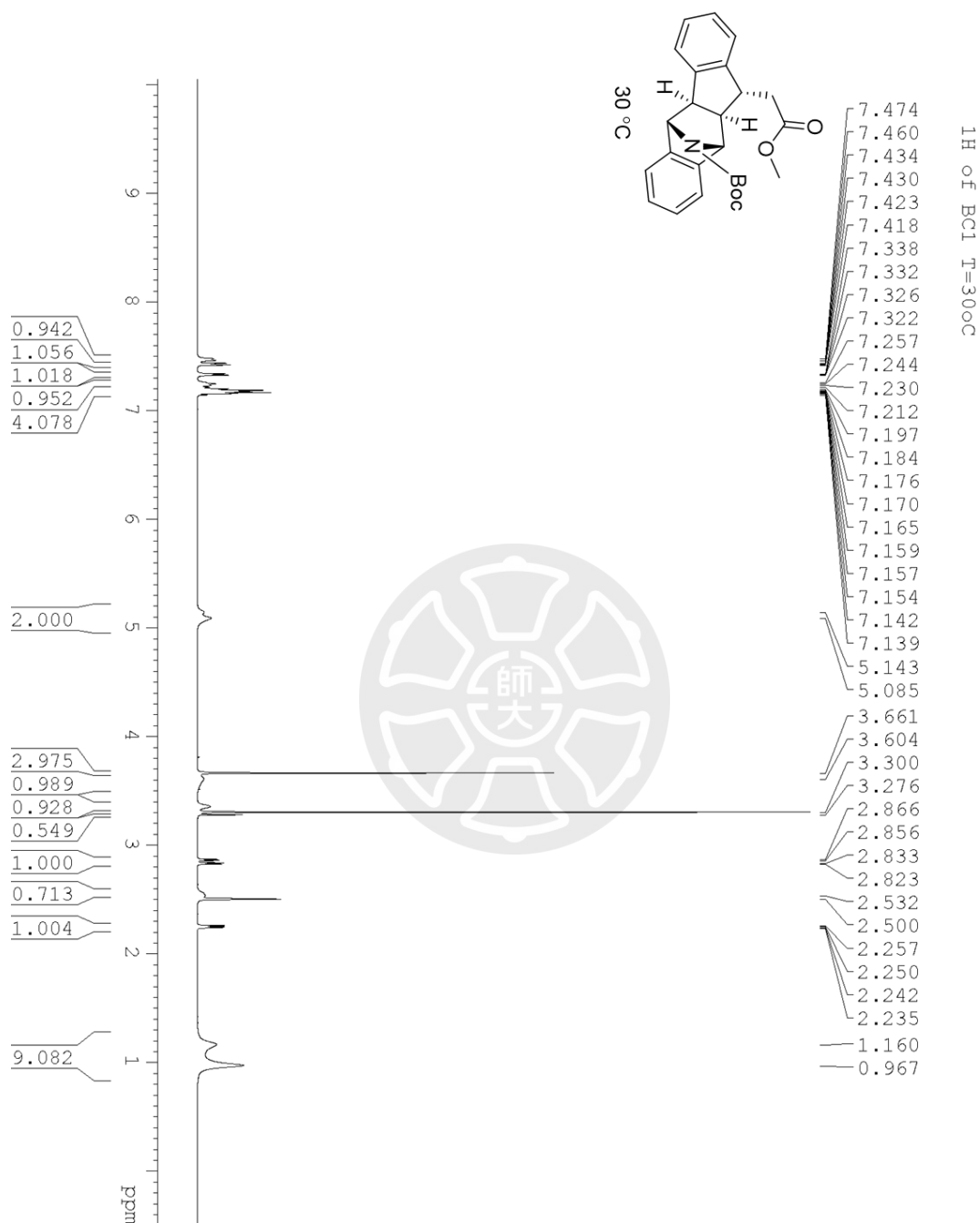
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Current Data Parameters
NAME      I want to graduate
EXPNO    168
PROCNO   1
F2 - Acquisition Parameters
Date_    20250503
Time     18:29
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       4
DS       0
SWH      7211.539 Hz
FIDRES   0.222079 Hz
AQ       2.2719147 sec
RG       31.16
DW       69.353 usec
DE       10.06 usec
TE       296.3 K
D1       2.00000000 sec
TD0      1
===== CHANNEL f1 =====
SFO1    400.1324008 MHz
NUC1    1H
P1      15.00 usec
PLW1    13.30000000 W
F2 - Processing parameters
SI      32768
SF      400.1300160 MHz
WDW     EM
SSB     0
LB      0 Hz
GB      0
PC      1.00
    
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)

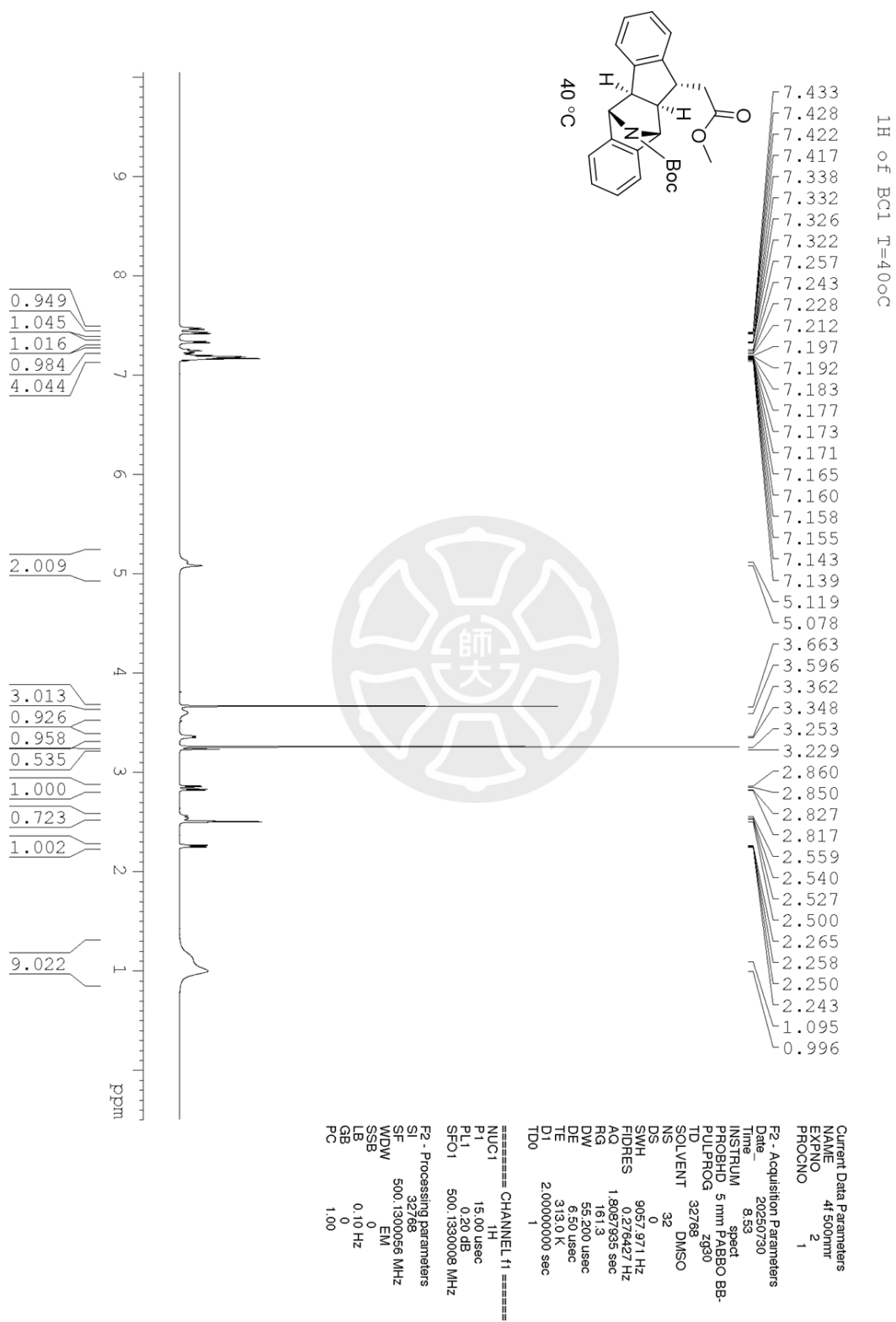


¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)

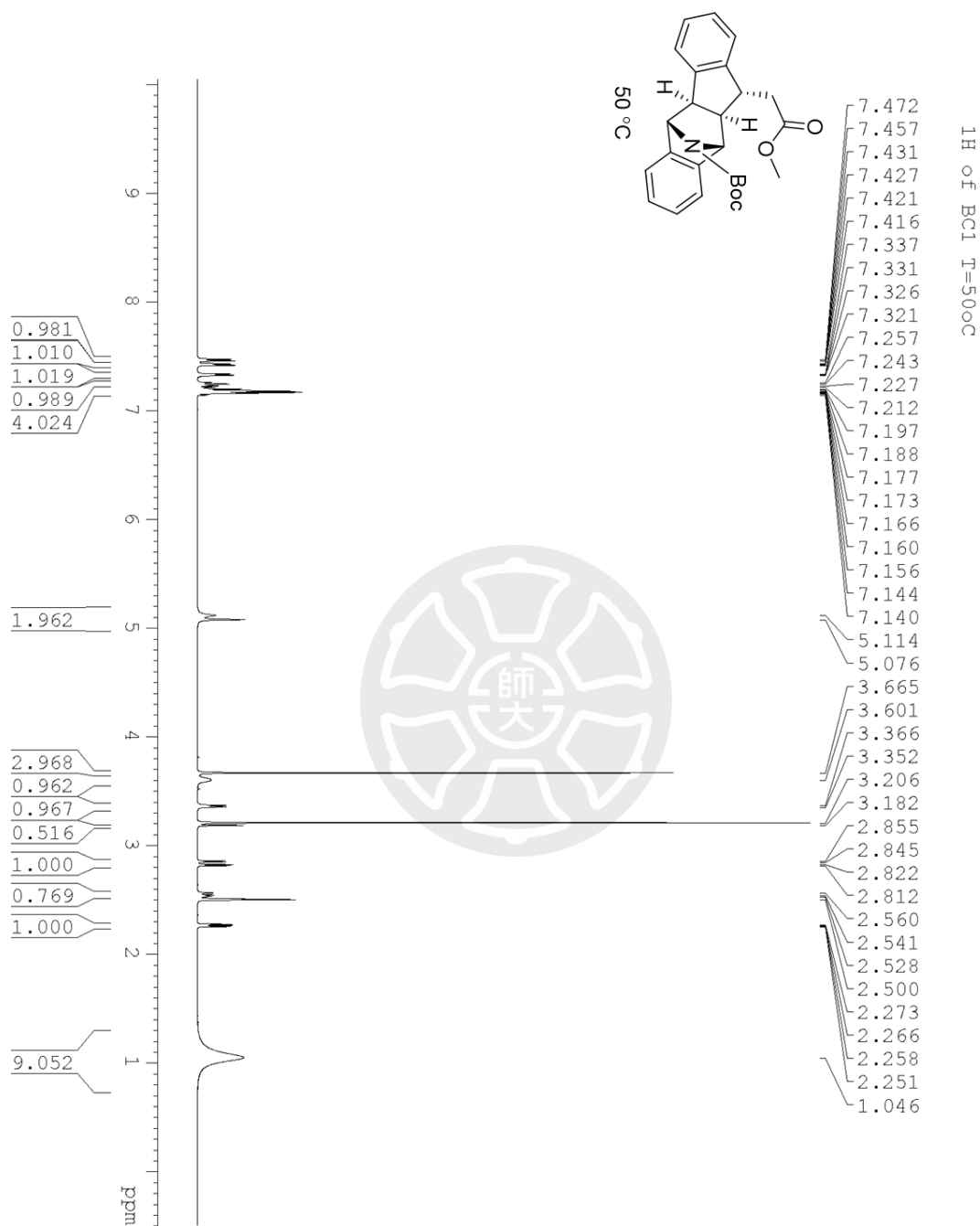


Current Data Parameters
 NAME 4f500mm
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20250730
 Time 7:57:30
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 32768
 SOLVENT 32 DMSO
 NS 0
 DS 0
 SWH 9057.971 Hz
 FIDRES 0.276427 Hz
 AQ 1.8087935 sec
 RG 161.3
 DW 55.200 usec
 DE 6.50 usec
 TE 303.0 K
 D1 2.00000000 sec
 TDO 1
 CHANNEL f1
 NUC1 ¹H
 P1 15.00 usec
 PL1 0.20 dB
 SFO1 500.1330008 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.1300055 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)

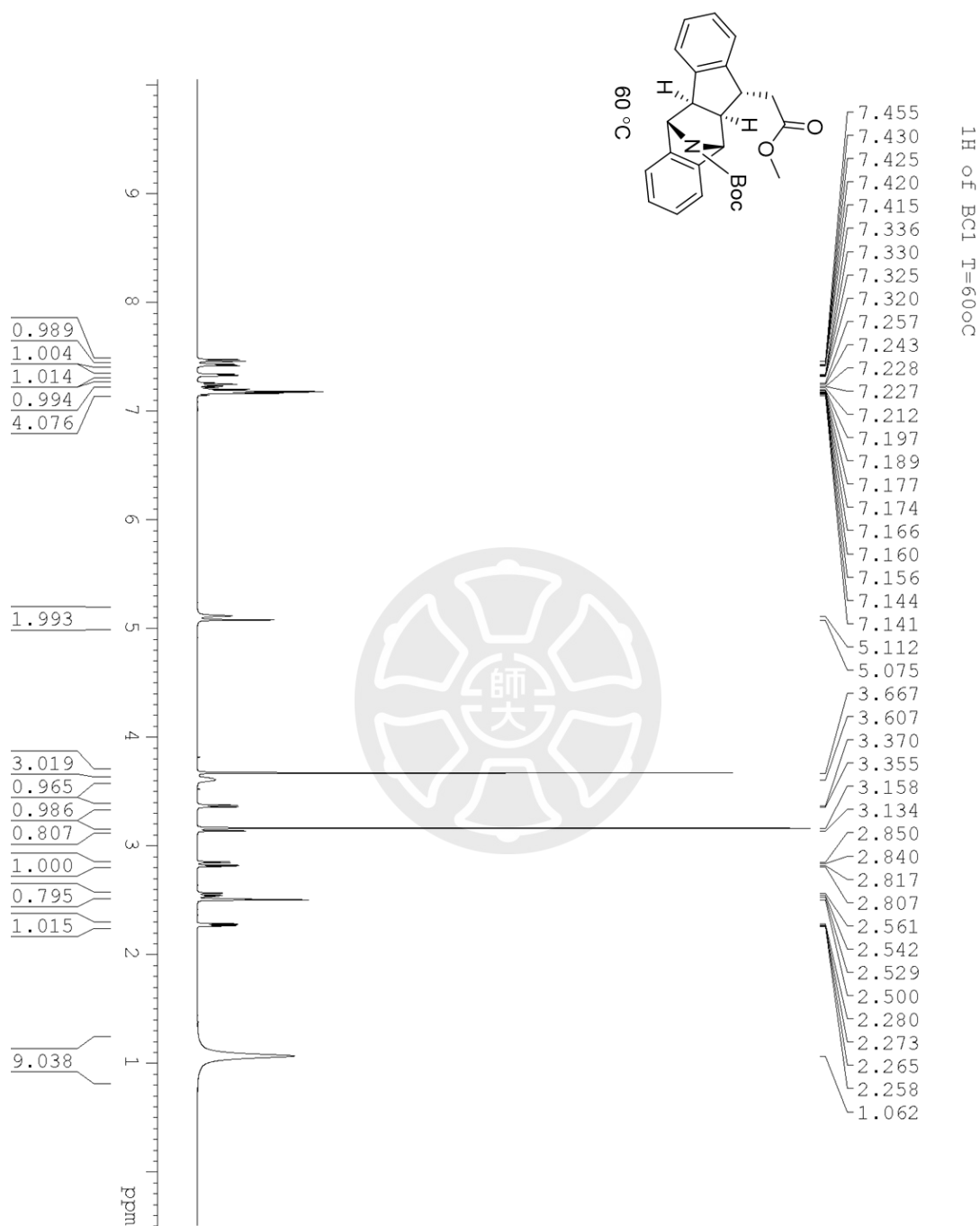


¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)



Current Data Parameters
 NAME 4f500nmr
 EXPNO 3
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20250730
 Time 9:22
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 32768
 SOLVENT DMSO
 NS 32
 DS 0
 SWH 9057.971 Hz
 FIDRES 0.276427 Hz
 AQ 1.8087935 sec
 RG 161.3
 DW 55.200 usec
 DE 6.50 usec
 TE 323.0 K
 D1 2.00000000 sec
 TDO 1
 ===== CHANNEL f1 =====
 NUC1 ¹H
 P1 15.00 usec
 PL1 0.20 dB
 SFO1 500.1330008 MHz
 F2 - Processing parameters
 SI 32768
 SF 500.1300055 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aa)



```

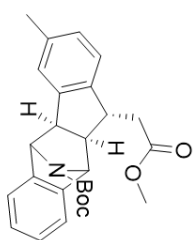
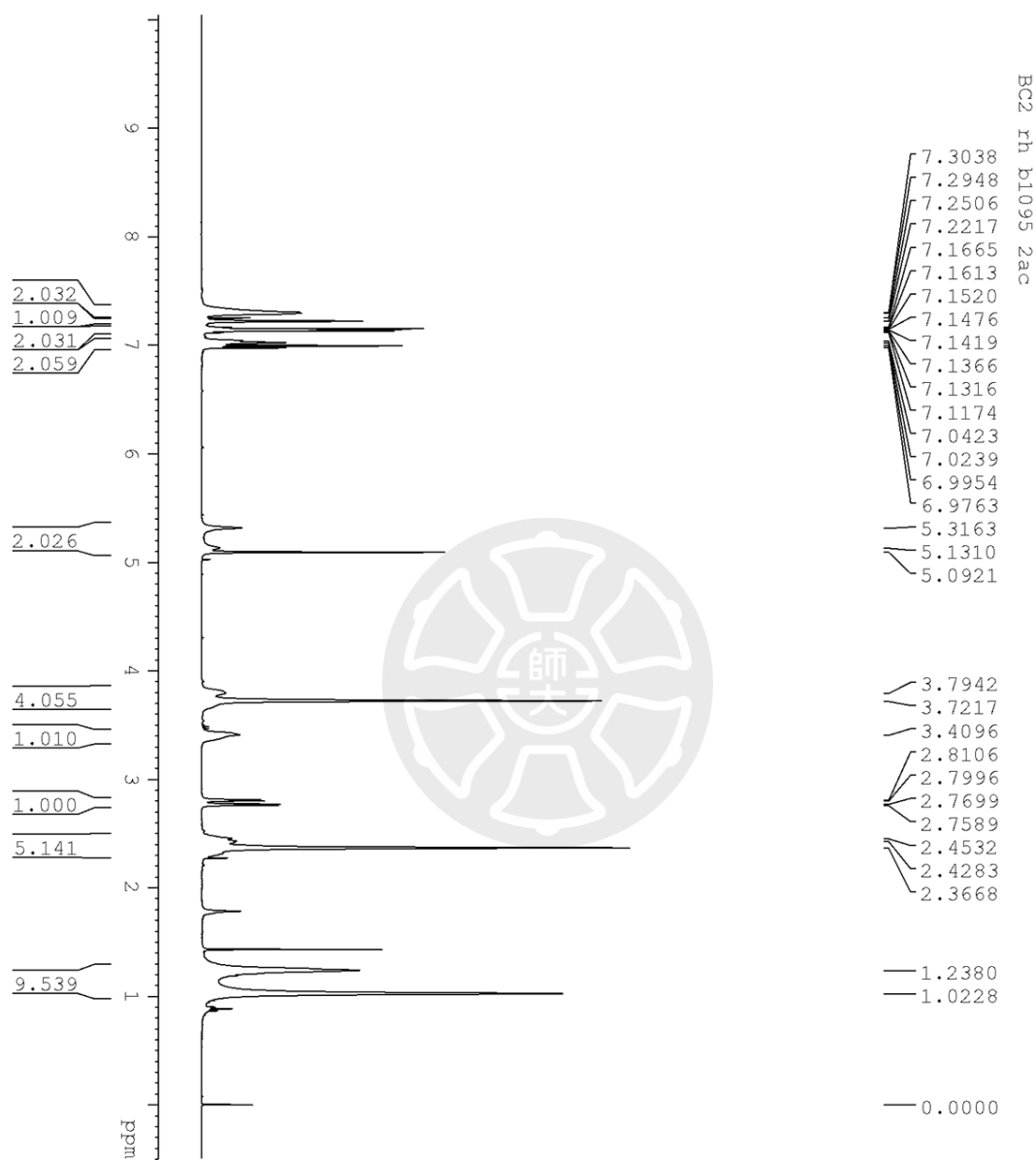
Current Data Parameters
NAME          41500nmr
EXPNO         4
PROCNO        1

F2 - Acquisition Parameters
Date_         20250730
Time          9:50
INSTRUM       spect
PROBHD        5 mm PABBO BB-
PULPROG       zg30
TD            32768
SOLVENT       DMSO
NS            32
DS            0
SWH           9057.971 Hz
FIDRES        0.276427 Hz
AQ            1.8087935 sec
RG            161.3
DW            55.200 usec
DE            6.50 usec
TE            333.0 K
D1            2.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1           1H
P1            15.00 usec
PL1           0.20 dB
SFO1          500.1330008 MHz

F2 - Processing parameters
SI            32768
SF            500.1300055 MHz
WDW           EM
SSB           0
GB            0.10 Hz
LB            0
PC            1.00
  
```


¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-methyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ab)



```

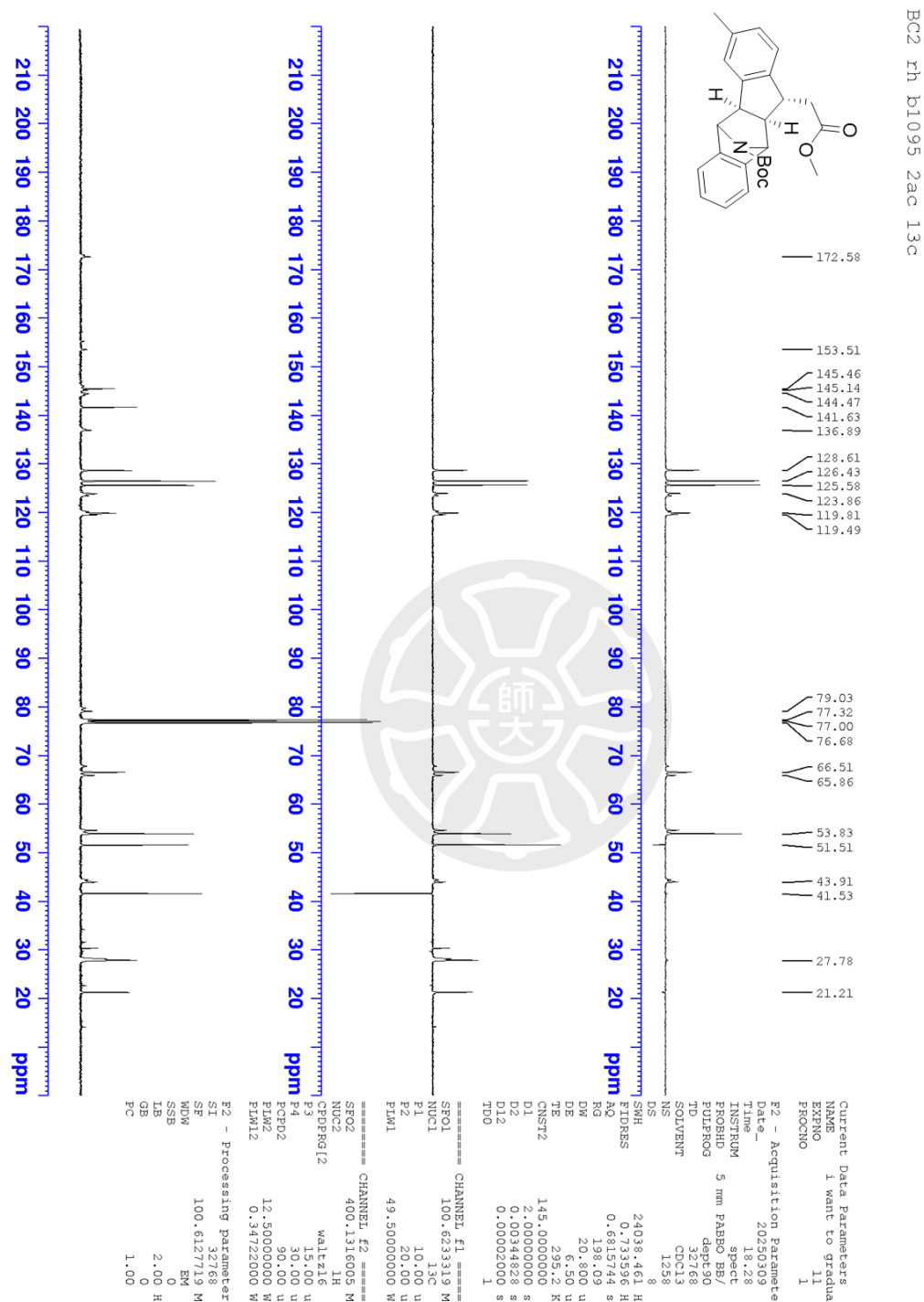
Current Data Parameters
NAME 1 want to graduate
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 202509
Time 18:50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 45.15
DW 69.333 usec
DE 10.06 usec
TE 293.7 K
D1 2.00000000 sec
TD0 1

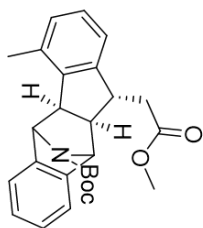
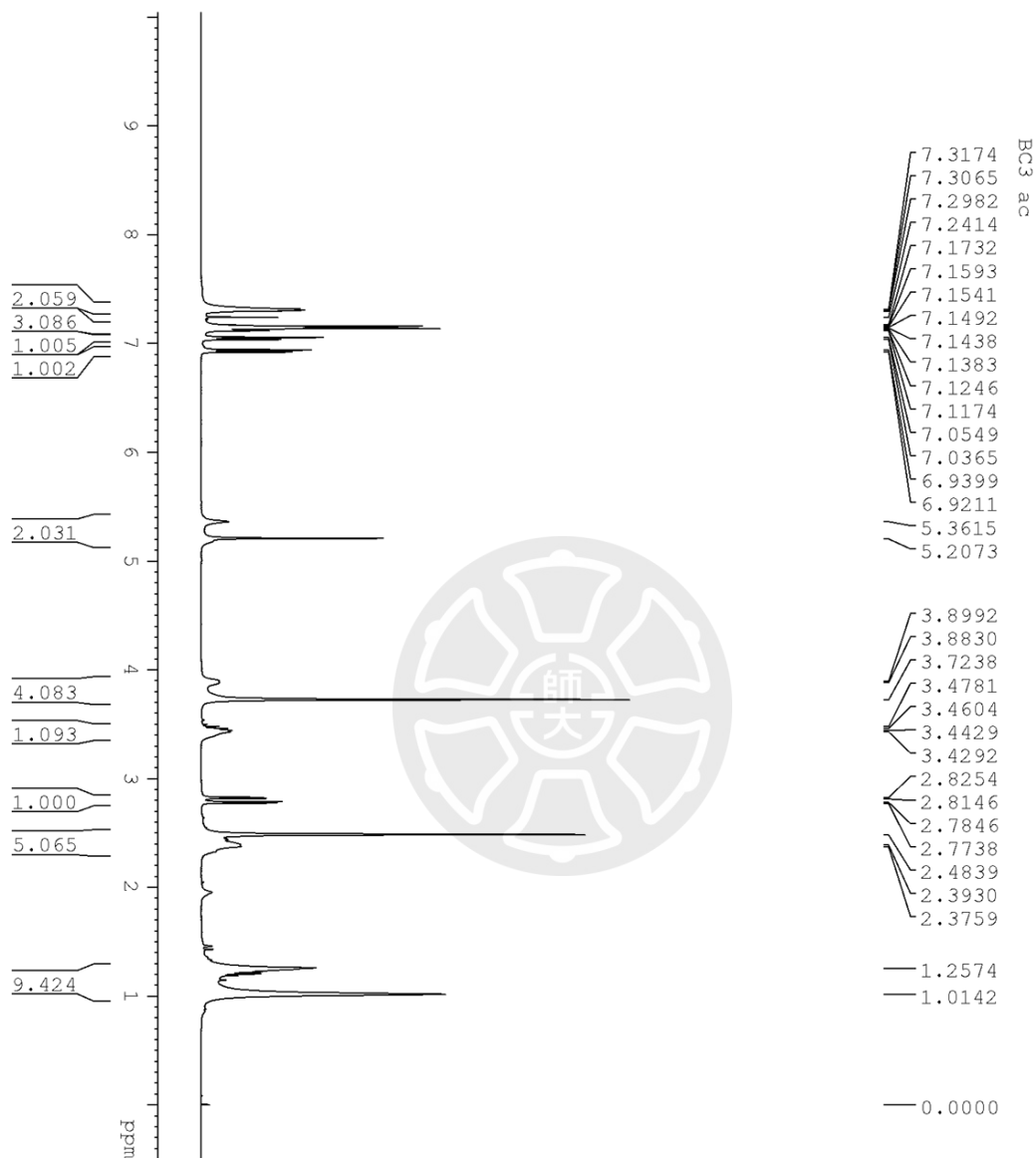
===== CHANNEL f1 =====
SFO1 400.1324008 MHz
NUC1 1H
P1 15.00 usec
PL1 0.00 dB
FLW1 13.50000000 W

F2 - Processing parameters
SI 16384
SF 400.1300135 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-methyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ab)



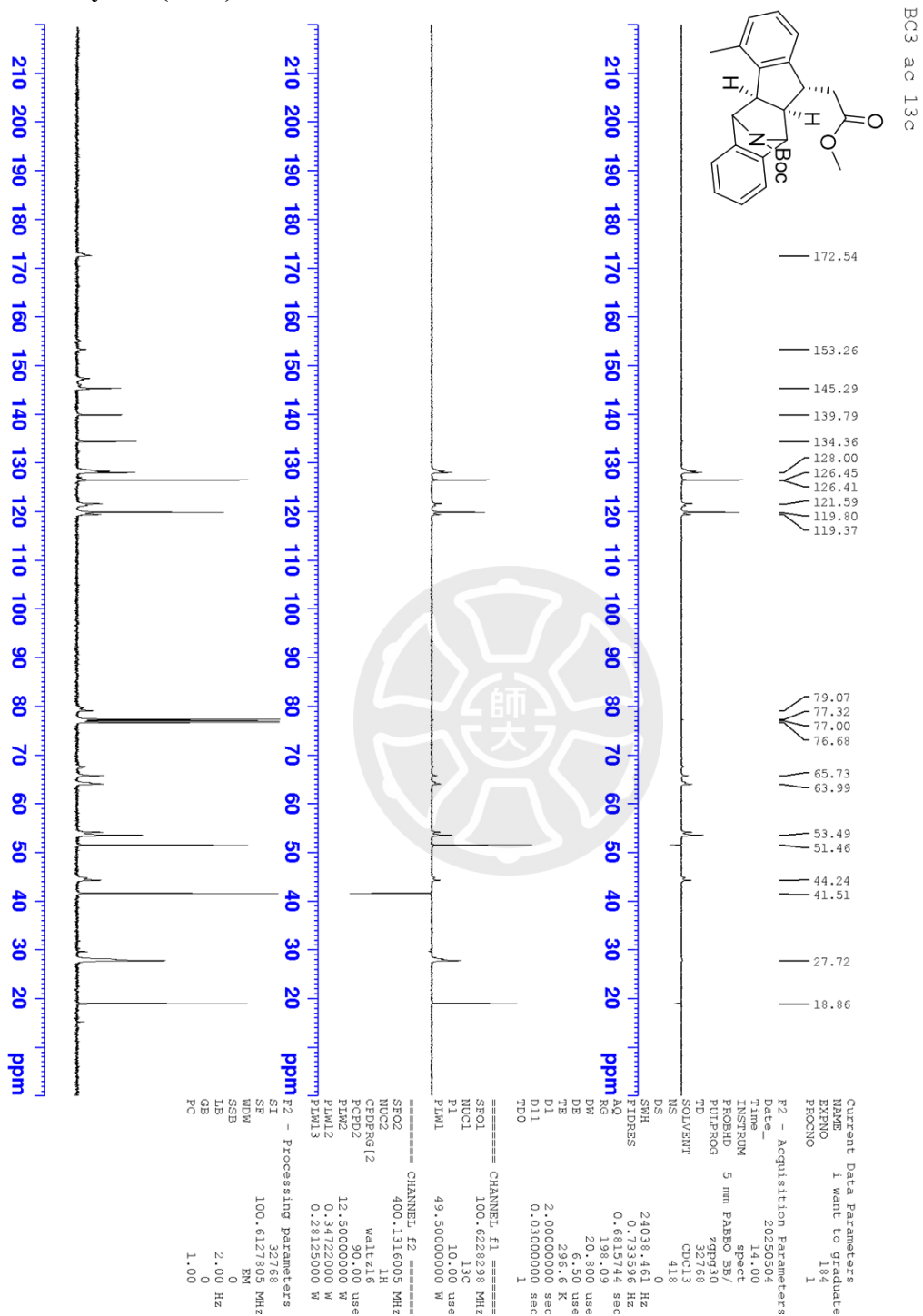
¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4-methyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ac)



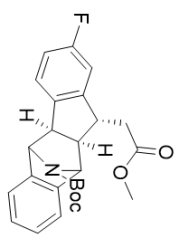
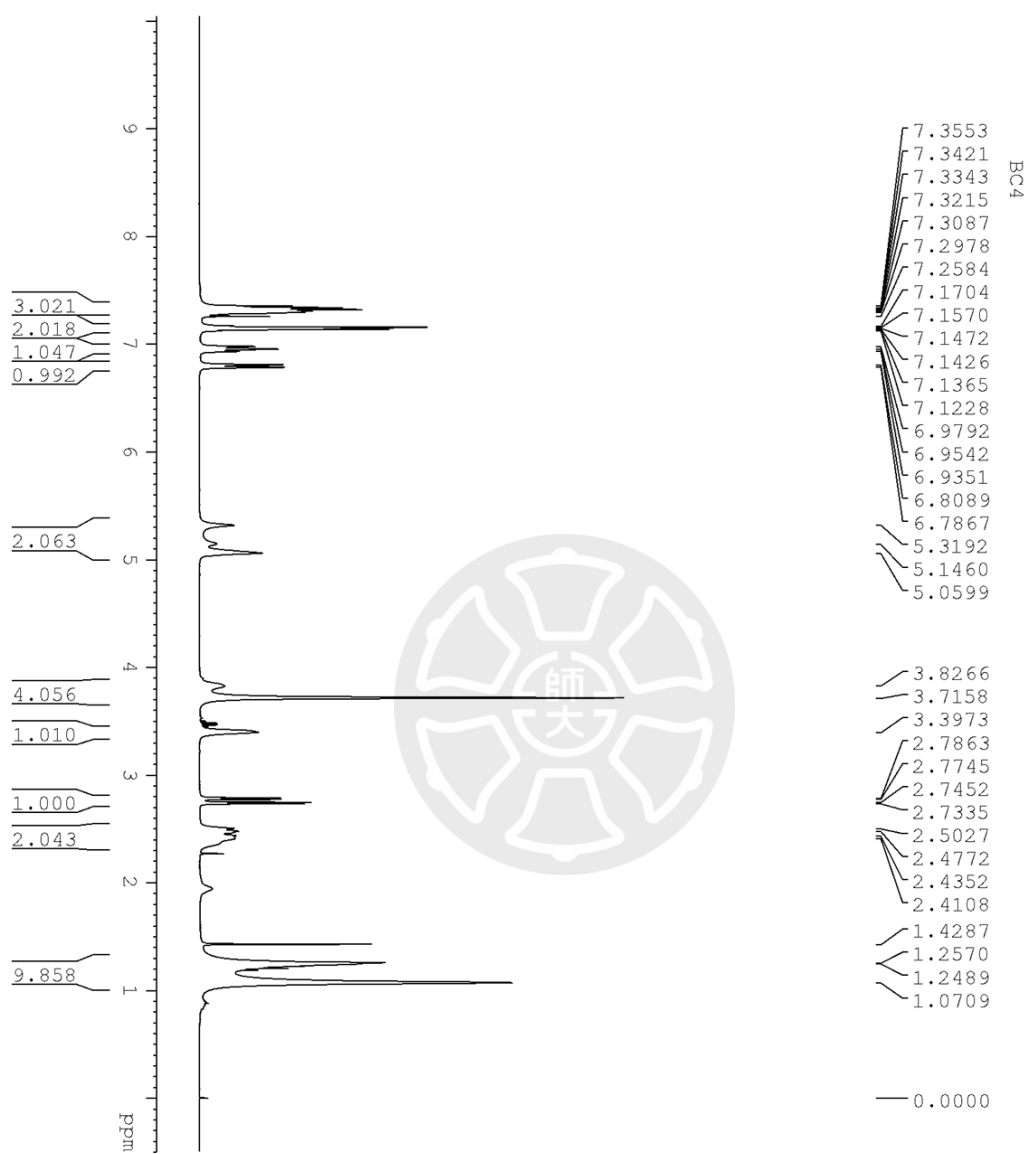
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Current Data Parameters
NAME | wanto graduate
EXPNO | 183
PROCNO | 1
F2 - Acquisition Parameters
Date_ | 20250504
Time | 13:58
INSTRUM | spect
PROBHD | 5 mm PABBO BB/
PULPROG | zg30
TD | 32768
SOLVENT | 4 CDCl3
NS | 4
DS | 4
SWH | 7211.539 Hz
FIDRES | 0.220079 Hz
AQ | 2.2719147 sec
RG | 29.06
DE | 69.333 usec
TE | 10.06 usec
D1 | 296.5 K
D10 | 2.00000000 sec
===== CHANNEL f1 =====
NUC1 | 4001324008 MHz
P1 | 15.00 usec
PLW1 | 13.30000000 W
F2 - Processing parameters
SI | 16384
SF | 400.1300171 MHz
WDW | EM
SSB | 0
LB | 0 Hz
GB | 0
PC | 1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4-methyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ac)



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-2-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ag)

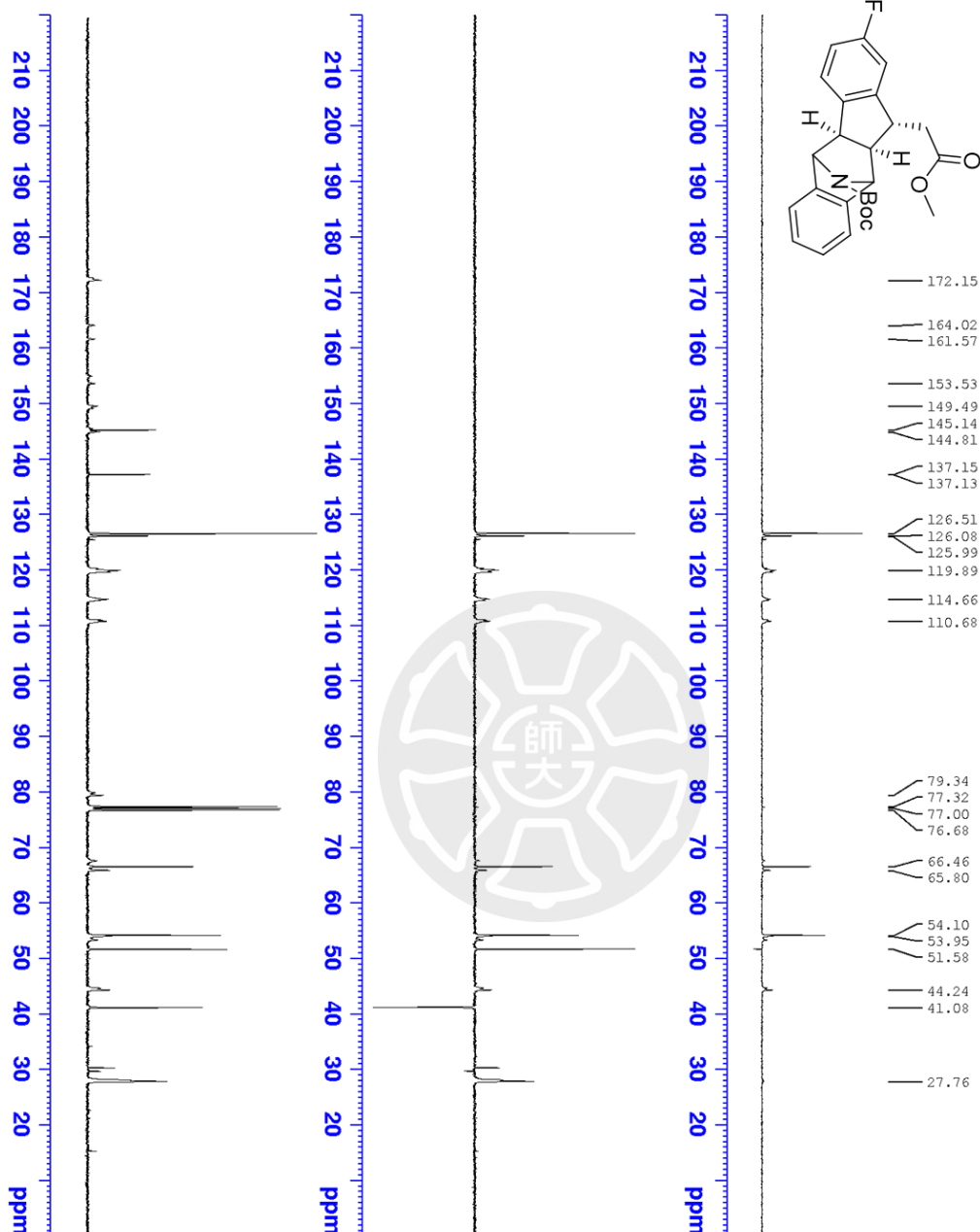
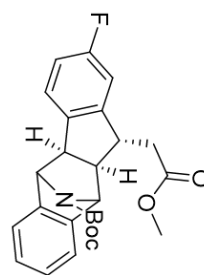


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Current Data Parameters
NAME      I want to graduate
EXPNO    213
PROCNO   1
F2 - Acquisition Parameters
Date_    20250511
Time     15:42
INSTRUM  spect
PROBHD   5 mm 1H1
PULPROG  zgpg30
TD        32768
SOLVENT  CDCl3
NS        4
DS        0
SWH       7211.539 Hz
FIDRES    0.220079 Hz
AQ         2.2719147 sec
RG         31.16
DW         69.833 usec
DE         1.006 usec
TE         294.6 K
D1         2.0000000 sec
TD0
===== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1     1H
P1       15.00 usec
PLW1     13.50000000 W
F2 - Processing parameters
SI       16384
SF       400.1300102 MHz
WDW      EM
SSB      0
LB       0 Hz
GB       0
PC       1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-2-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ag)

BC4 13C



- 172.15
- 164.02
- 161.57
- 153.53
- 149.49
- 145.14
- 144.81
- 137.15
- 137.13
- 126.51
- 126.08
- 125.99
- 119.89
- 114.66
- 110.68
- 79.34
- 77.32
- 77.00
- 76.68
- 66.46
- 65.80
- 54.10
- 53.95
- 51.58
- 44.24
- 41.08
- 27.76

```

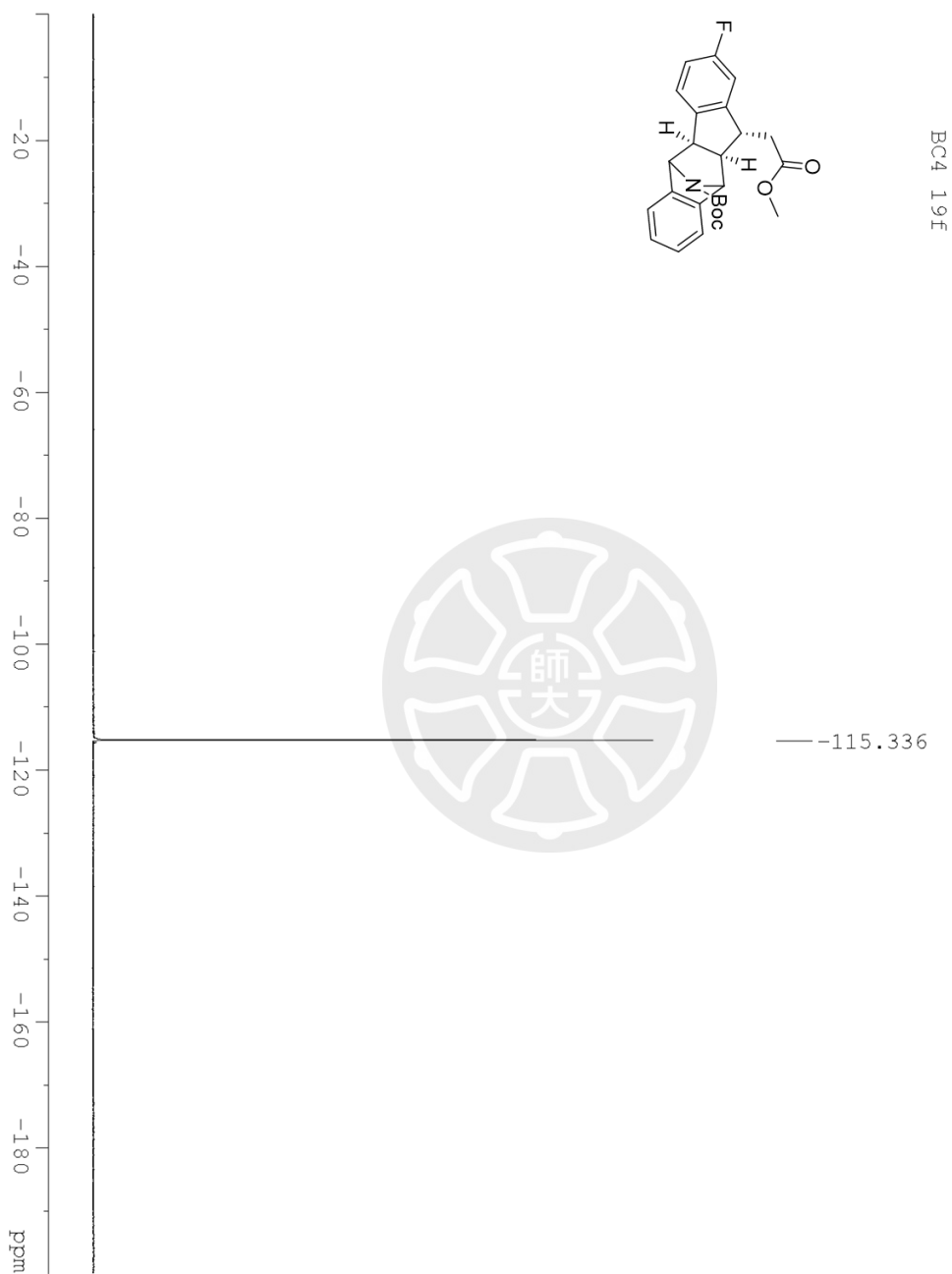
Current Data Parameters
NAME          I want to graduat.
EXPNO        214
PROCNO       1
F2 - Acquisition Parameters
Date_        20250511
Time         16:01
INSTRUM     5 mm PABBO BR/
PROBHD      zgpg30
PULPROG     32768
TD          32768
SOLVENT     CDCl3
NS          389
DS          0
SWH         24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6815744 se
RG         198.09
DE         20.800 us
TE         6.50 us
D1         295.7 K
D11        2.00000000 se
D12        0.03000000 se
TD0         1

===== CHANNEL f1 =====
SFO1       100.6228298 MH
NUC1       13C
P1         10.00 us
P1M1       49.50000000 W

===== CHANNEL f2 =====
SFO2       400.1316005 MH
NUC2       1H
CPDPRG12  waltz16
PCPD2     90.00 us
P1M2     12.50000000 W
P1M12    0.34722000 W
P1M13    0.28125000 W

F2 - Processing Parameters
SI         100.6127800 MH
SF         32768
WDW        0
SSB        0
LB         2.00 Hz
GB         0
PC         1.00
    
```

¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-2-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ag)



Current Data Parameters
 NAME 1 want to graduate
 EXPNO 217
 PROCNO 1

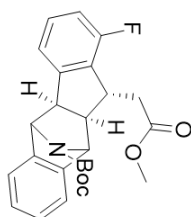
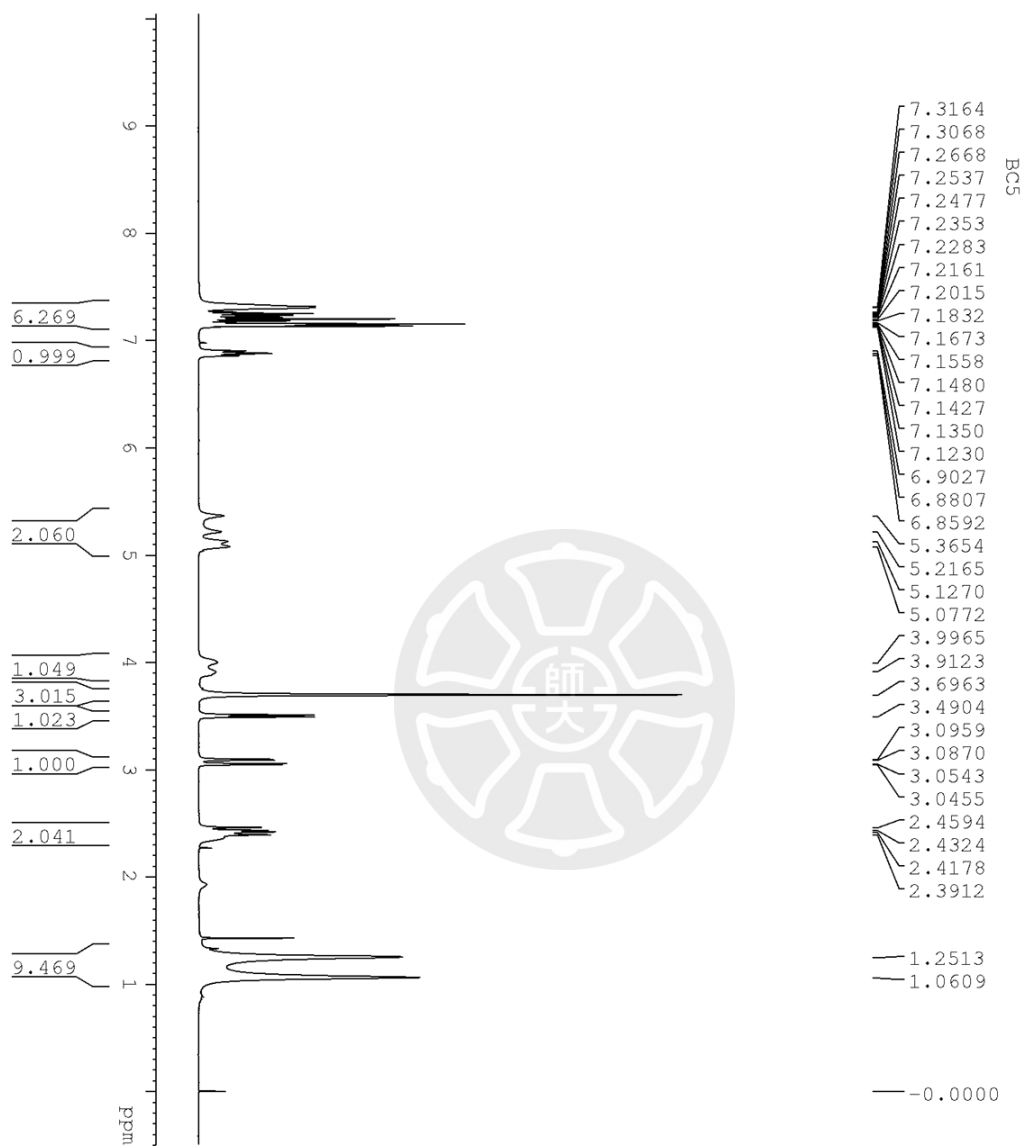
F2 - Acquisition Parameters
 Date_ 20250511
 Time 16.21
 INSTRUM spect
 PROBHD 5 mm F4BBO BB/
 PULPROG zgpg
 TD 131072
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 89295.711 Hz
 FIDRES 0.581196 Hz
 AQ 0.7340092 sec
 RG 198.09
 DE 6.50 usec
 TE 294.6 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 376.4607168 MHz
 NUC1 19F
 P1 15.00 usec
 PLW1 16.500000000 W

===== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG12 waltz16
 PCPD2 90.00 usec
 PLW2 12.500000000 W
 PLW12 0.34722000 W

F2 - Processing parameters

¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-1-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ae)



```

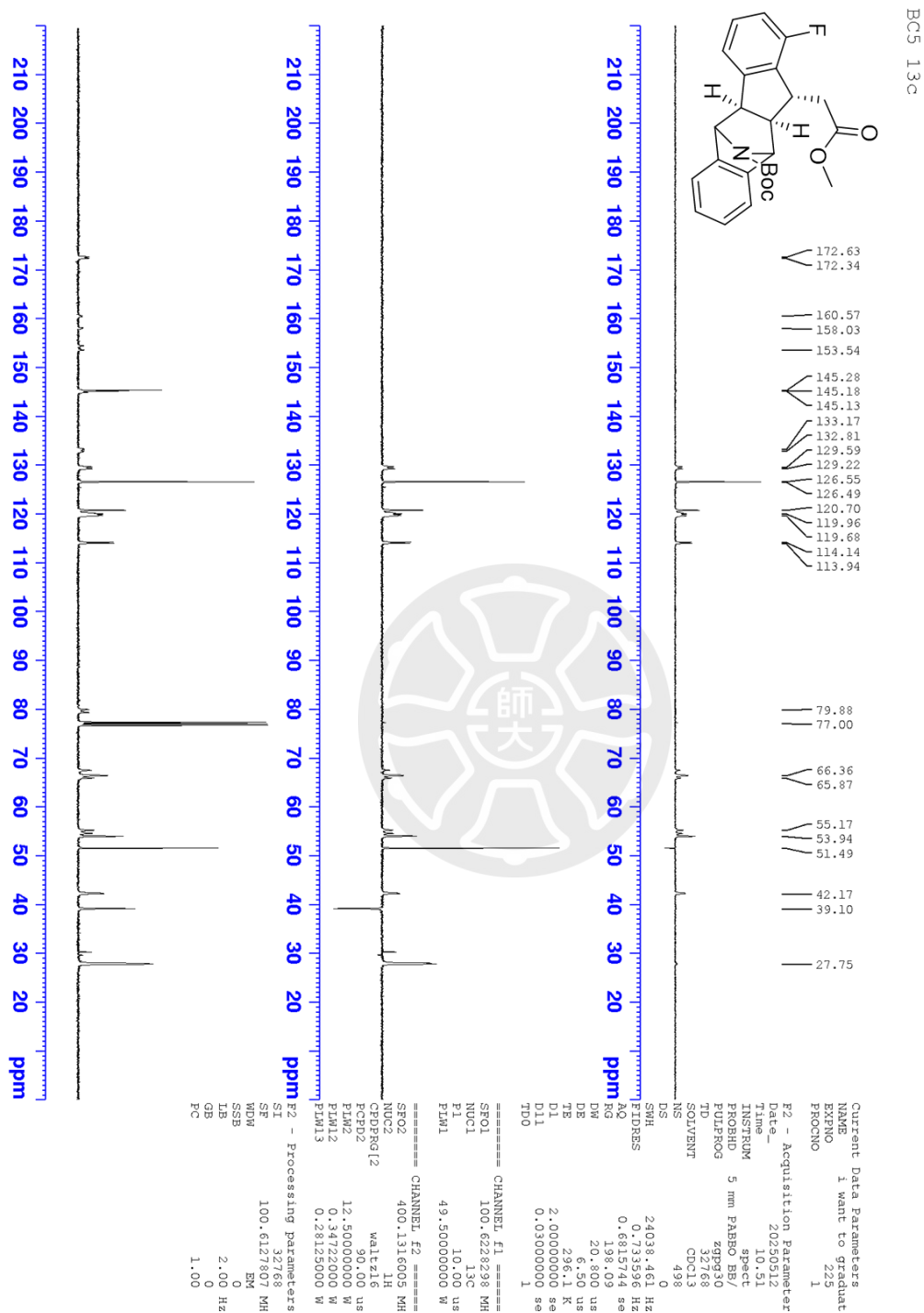
Current Data Parameters
NAME: iwantto graduate
EXPNO: 224
PROCNO: 1

F2 - Acquisition Parameters
Date_   20250512
Time    10.40
INSTRUM spect
PROBHD  5 mm PABBO BB/
PULPROG zg30
TD       32768
SOLVENT CDCl3
NS       4
DS       0
SWH      7211.539 Hz
FIDRES   0.220079 Hz
AQ       2.2719147 sec
RG       29.06
DW       69.333 usec
DE       10.06 usec
TE       295.0 K
DQ       2.0000000 sec
TD0      1

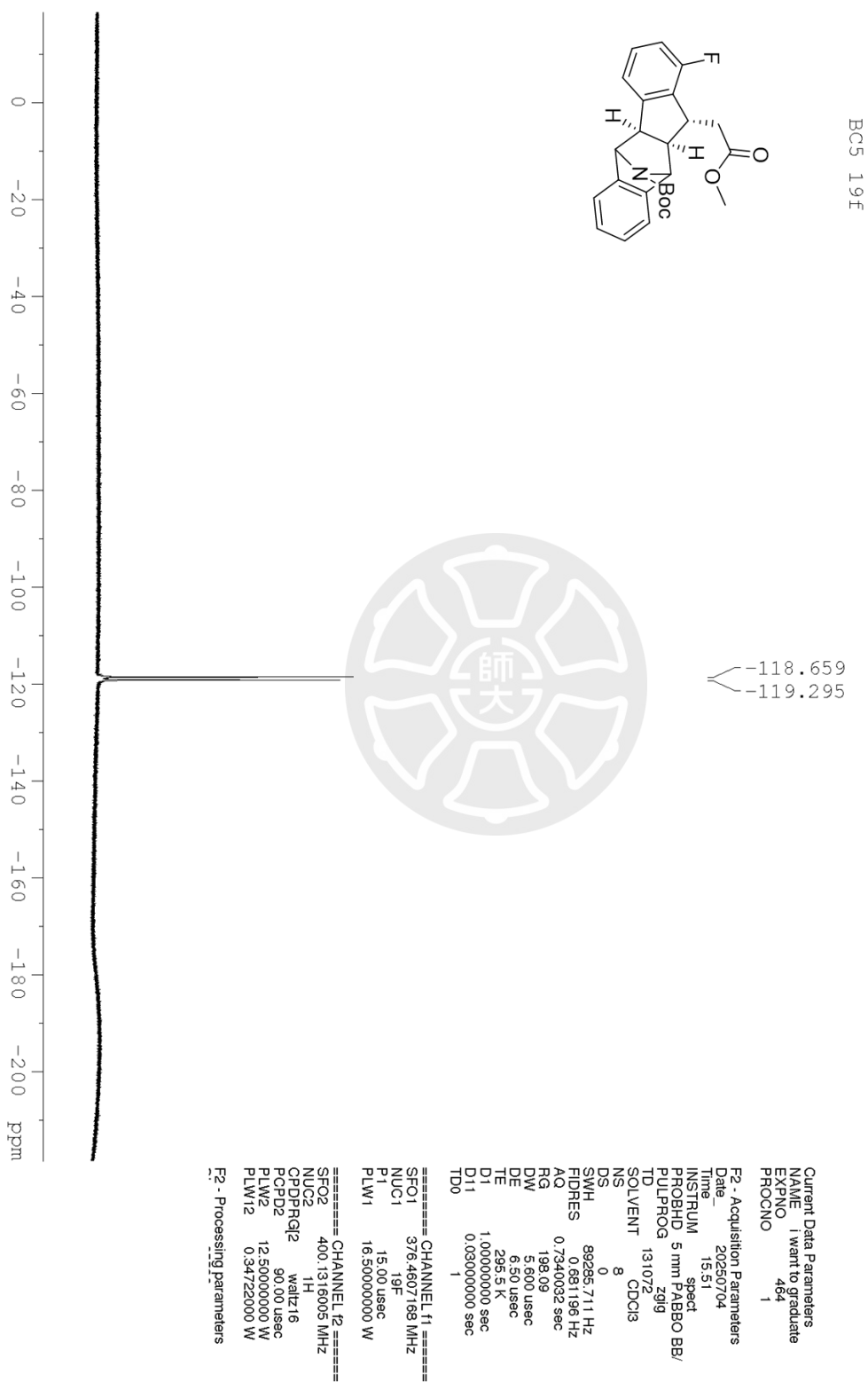
===== CHANNEL f1 =====
SFO1    400.1324008 MHz
NUC1    1H
P1      15.00 usec
PLW1    13.5000000 W

F2 - Processing parameters
SI      16384
SF      400.1300122 MHz
WDW     EM
SSB     0
GB      0
PC      1.00
  
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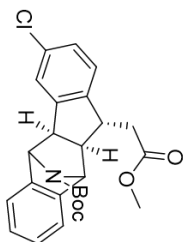
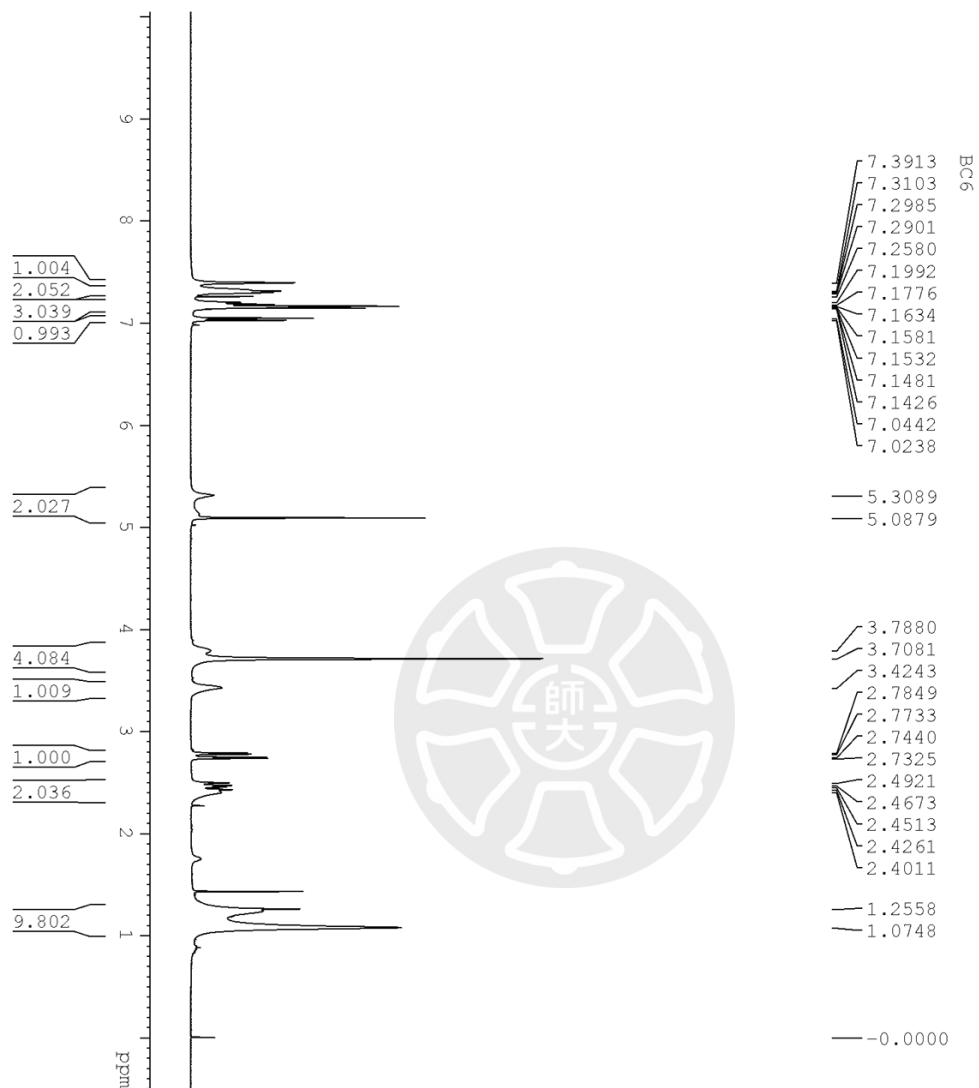
¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-1-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ae)



¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-1-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ae)



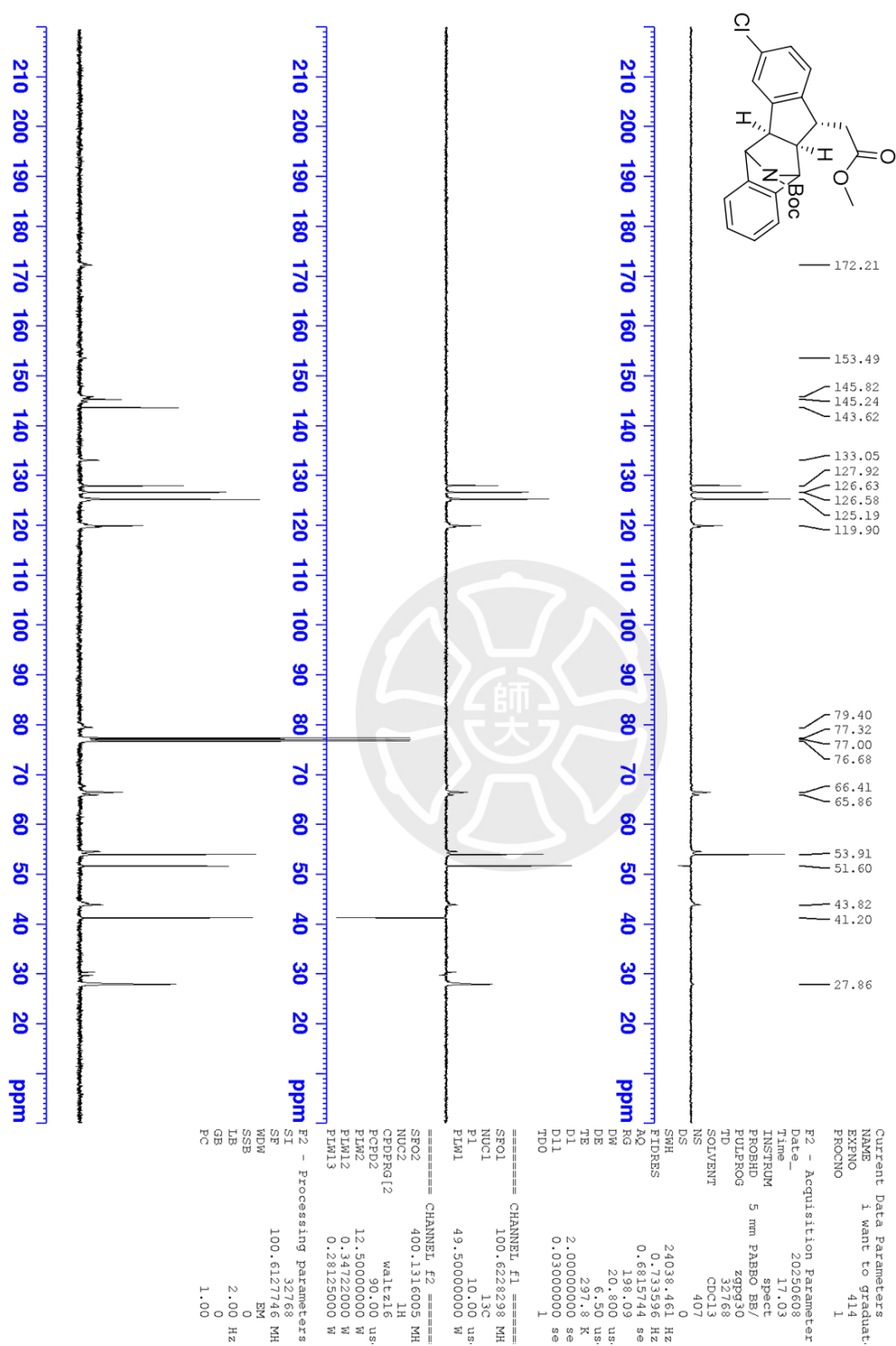
¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-3-chloro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aj)



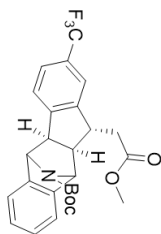
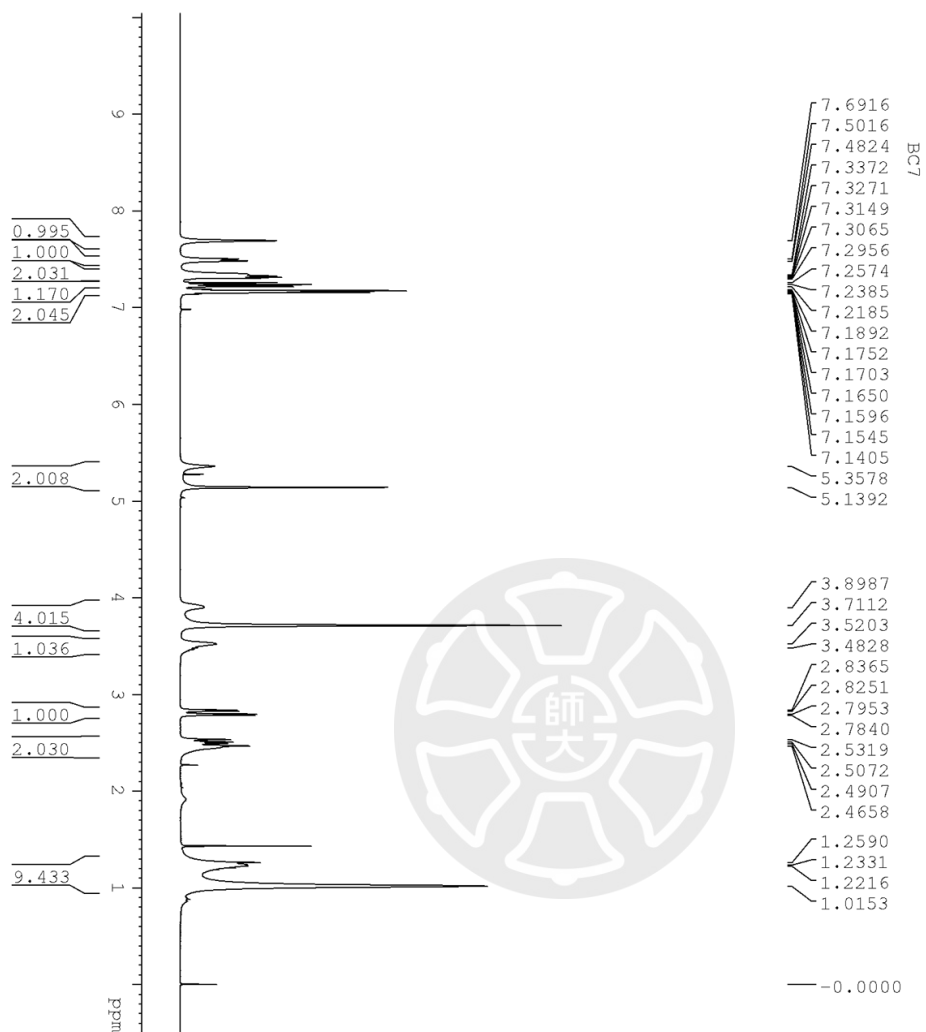
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Current Data Parameters
NAME      I want to graduate
EXPNO     413
PROCNO    1
F2 - Acquisition Parameters
Date_     20250303
Time      17:02
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         32768
SOLVENT   4 CDCl3
NS         0
DS         0
SWH        7211.539 Hz
FIDRES     0.220079 Hz
AQ         2.2719147 sec
RG         51.8
DW         69.833 usec
DE         10.09 usec
TE         299.2 K
D          2.0000000 sec
TDO
===== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1      1H
P1         15.00 usec
PLW1      13.50000000 W
F2 - Processing parameters
SI         16384
SF         400.1300105 MHz
WDW        EM
SSB        0
LB         0 Hz
GB         0
PC         1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-3-chloro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aj)



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-2-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)



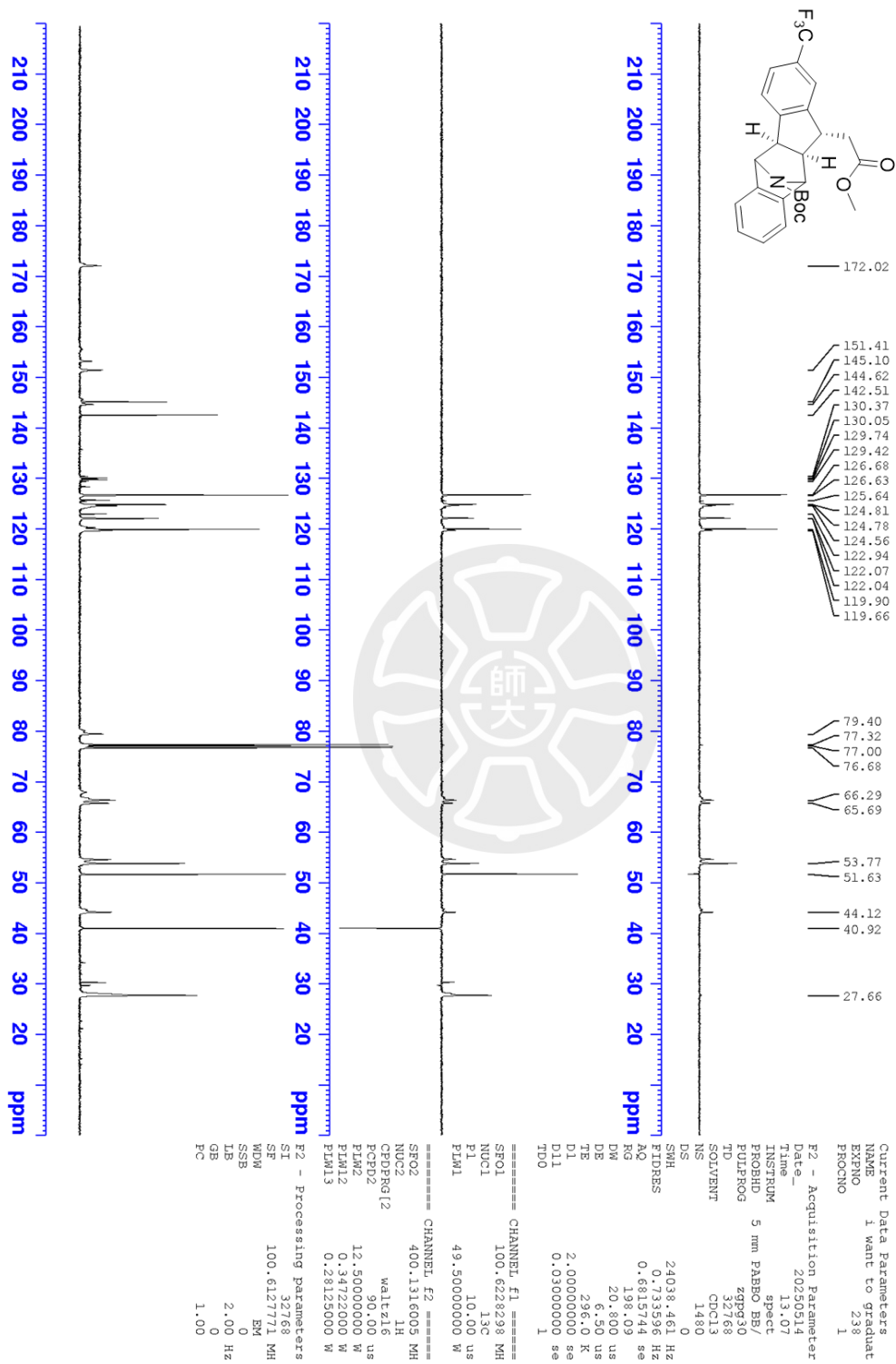
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Current Data Parameters
NAME      1 want to graduate
EXPNO     235
PROCNO    1
F2 - Acquisition Parameters
Date_     20250514
Time      12:53
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         4
DS         0
SWH        7211.5391 Hz
FIDRES     0.22079 Hz
AQ         2.27547 sec
RG         36.64
DE         69.333 usec
TE         295.91 K
TD0        2.00000000 sec

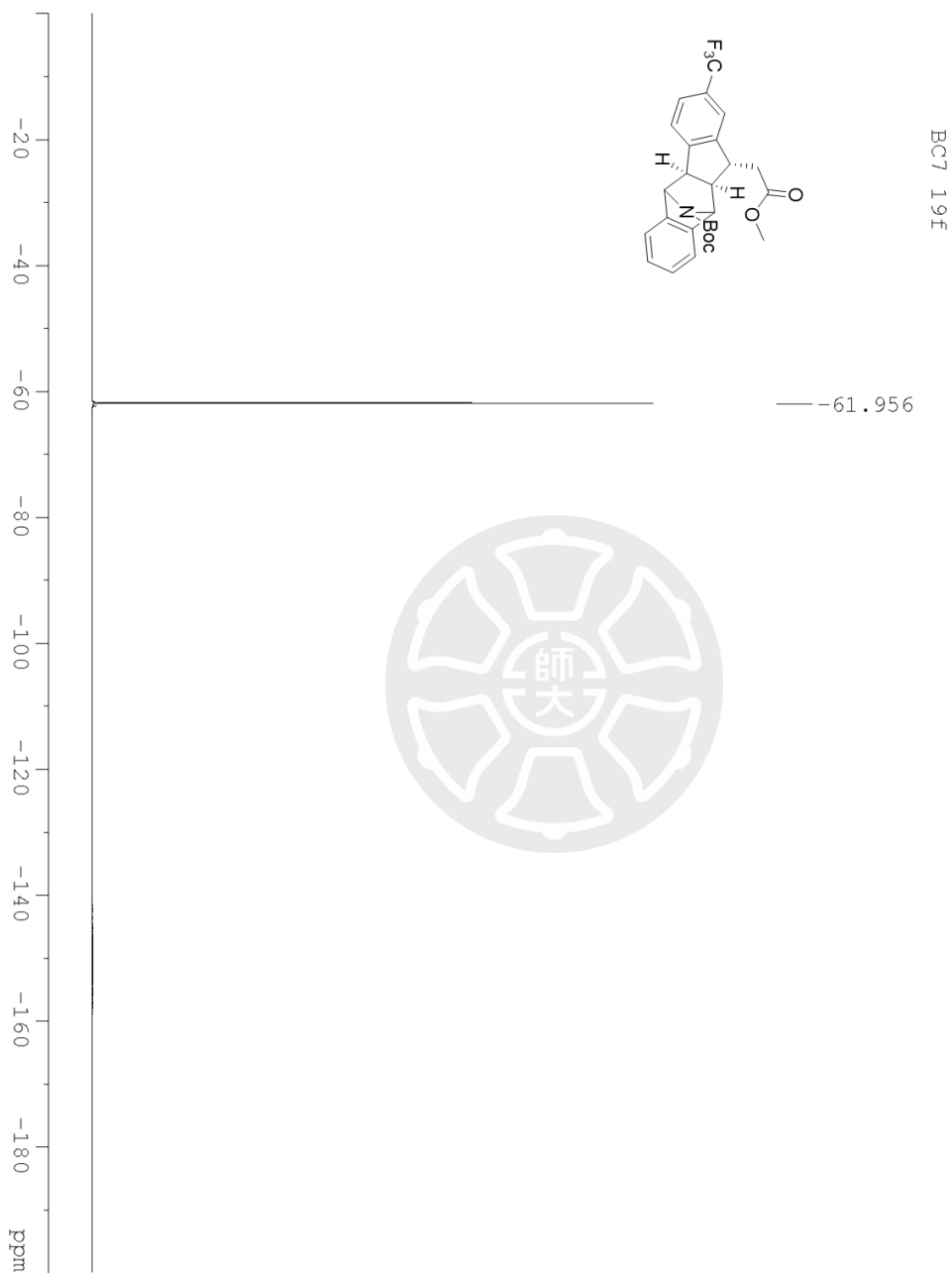
===== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1       1H
P1         15.00 usec
PLW1      13.50000000 W
F2 - Processing parameters
SI         16384
SF         400.1300107 MHz
WDW        0
SSB        0 Hz
LB         0 Hz
GB         0 Hz
PC         1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-2-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)

BC7 13C



¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-2-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)



BC7 19F

— 61.956

```

Current Data Parameters
NAME      i want to graduate
EXPNO    236
PROCNO   1

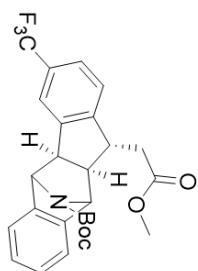
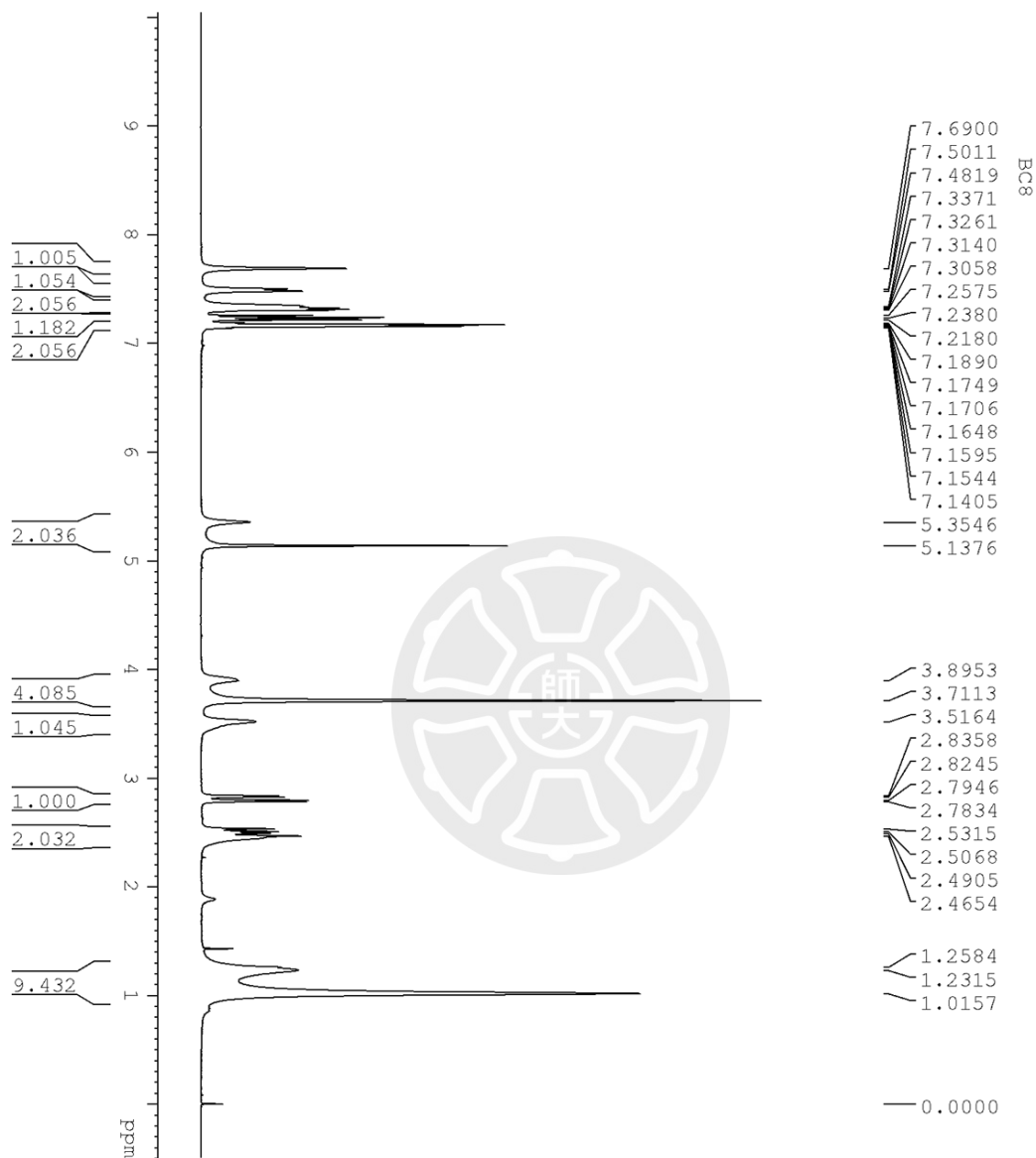
F2 - Acquisition Parameters
Date_    20250514
Time     12:56
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zgpg
TD        131072
SOLVENT  CDCl3
NS        16
DS         0
SWH       89285.711 Hz
FIDRES    0.681196 Hz
AQ         0.7340032 sec
RG         198.09
DW         5.600 usec
DE         6.50 usec
TE         295.9 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1     376.4607168 MHz
NUC1      19F
P1        15.00 usec
PLW1     16.50000000 W

===== CHANNEL f2 =====
SFO2     400.1316005 MHz
NUC2      1H
CPDPRG2  waltz16
PCPD2     90.00 usec
PLW2     12.50000000 W
PLW12    0.34722000 W

F2 - Processing parameters
    
```

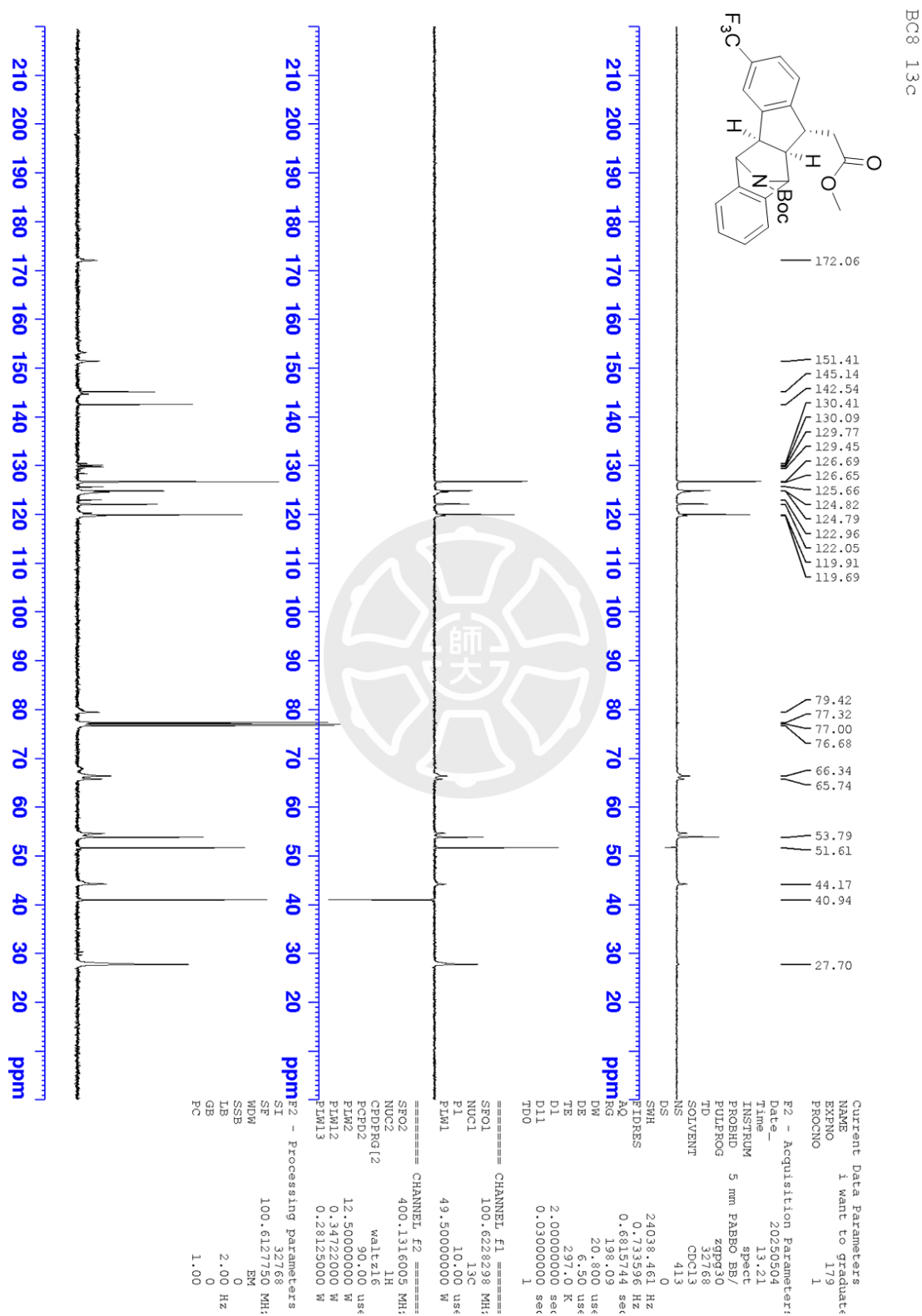
¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ah)



```

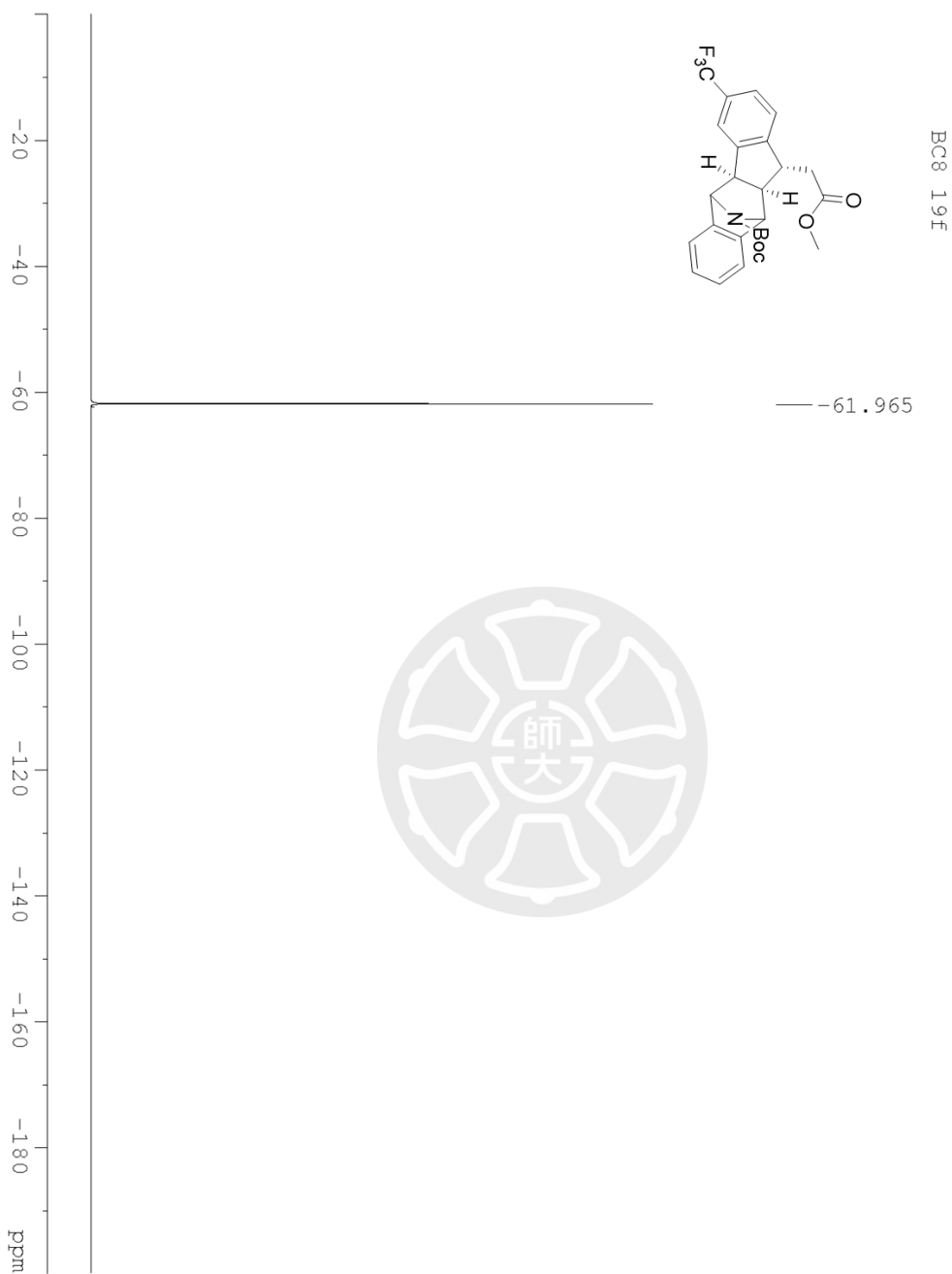
Current Data Parameters
NAME      I want to graduate
EXPNO    178
PROCNO   1
F2 - Acquisition Parameters
Date_    20250504
Time     13.18
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD        32768
SOLVENT  4 CDCl3
NS        4
DS        0
SWH       7211.539 Hz
FIDRES    0.220079 Hz
AQ         2.2719147 sec
RG         36.64
DE         69.333 usec
TE         10.06 usec
TD0        296.5 K
===== CHANNEL f1 =====
NUC1       13C
P1         15.00 usec
PLW1       13.50000000 W
F2 - Processing parameters
SI         16384
SF         400.1300108 MHz
WDW        EM
SSB        0
LB         0 Hz
GB         0
PC         1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ah)



¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-

¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-3-(trifluoromethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ah)



```

Current Data Parameters
NAME      i want to graduate
EXPNO    182
PROCNO   1

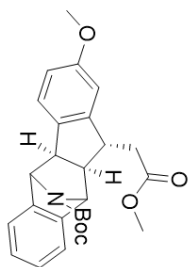
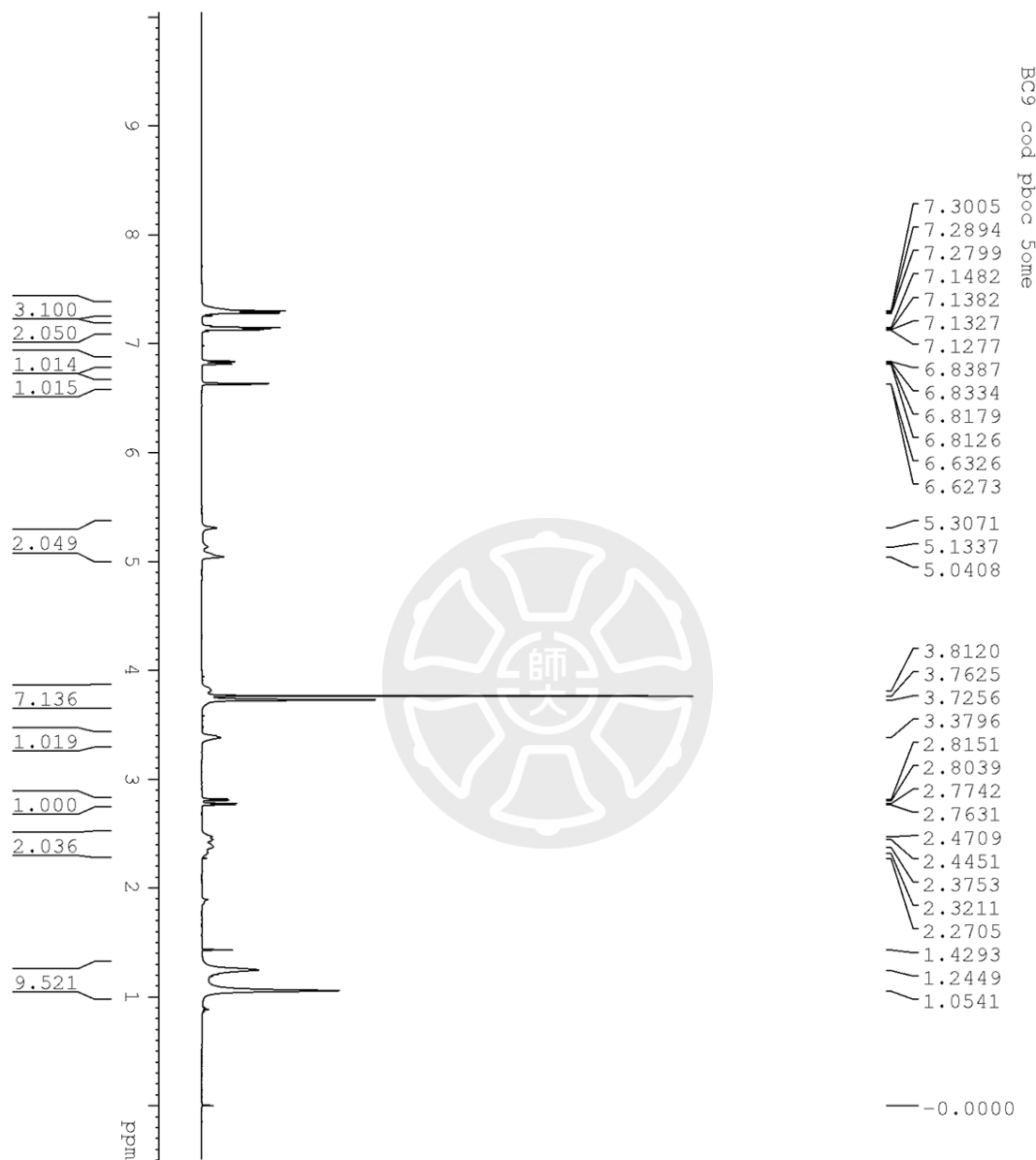
F2 - Acquisition Parameters
Date_    20250504
Time     13:54
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zgpg
TD       131072
SOLVENT  CDCl3
NS       8
DS       0
SWH      89285.711 Hz
FIDRES   0.681196 Hz
AQ       0.7340032 sec
RG       198.09
DW       5.600 usec
DE       6.50 usec
TE       296.7 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0      1

===== CHANNEL f1 =====
SFO1    376.4607168 MHz
NUC1     19F
P1      15.00 usec
PLW1    16.50000000 W

===== CHANNEL f2 =====
SFO2    400.1316005 MHz
NUC2     1H
CPDPRG2  waltz16
PCPD2    90.00 usec
PLW2    12.50000000 W
PLW12   0.34722000 W

F2 - Processing parameters
    
```

¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-2-methoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ak)

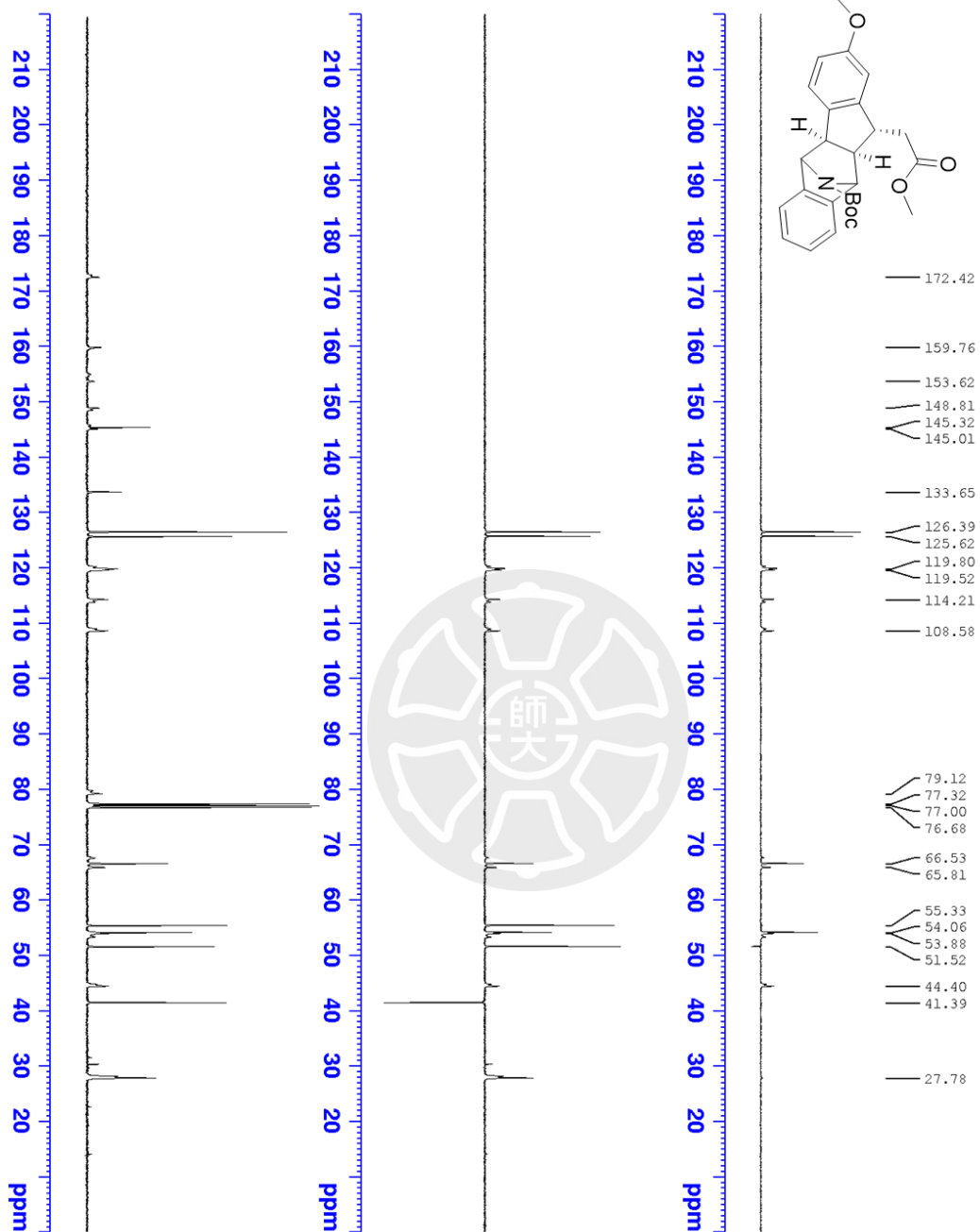
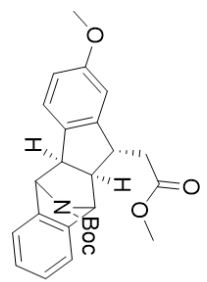


```

Current Data Parameters
NAME      1 want to graduate
EXPNO    1
PROCNO   1
===== CHANNEL f1 =====
SIUC1    400.1324005 MHz
NUC1     15.00 usec
PLW1     13.50000000 W
F2 - Processing parameters
SI       16384
SF       400.1300113 MHz
WDW      EM
SSB      0
LB        0 Hz
GB        0
PC        1.00
=====
Date_      20250308
Time      15.52
INSTRUM   spect
PROBHD    5 mm F4BBO BB/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         0
SWH        7211.539 Hz
FIDRES     0.220079 Hz
AQ         2.2719147 sec
RG         36.64
DE         69.333 usec
TE         10.06 usec
TD0        293.8 K
=====
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-2-methoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ak)

BC9 cod pboc Some 13c

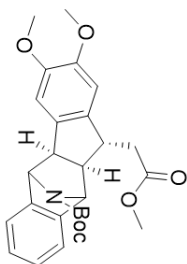
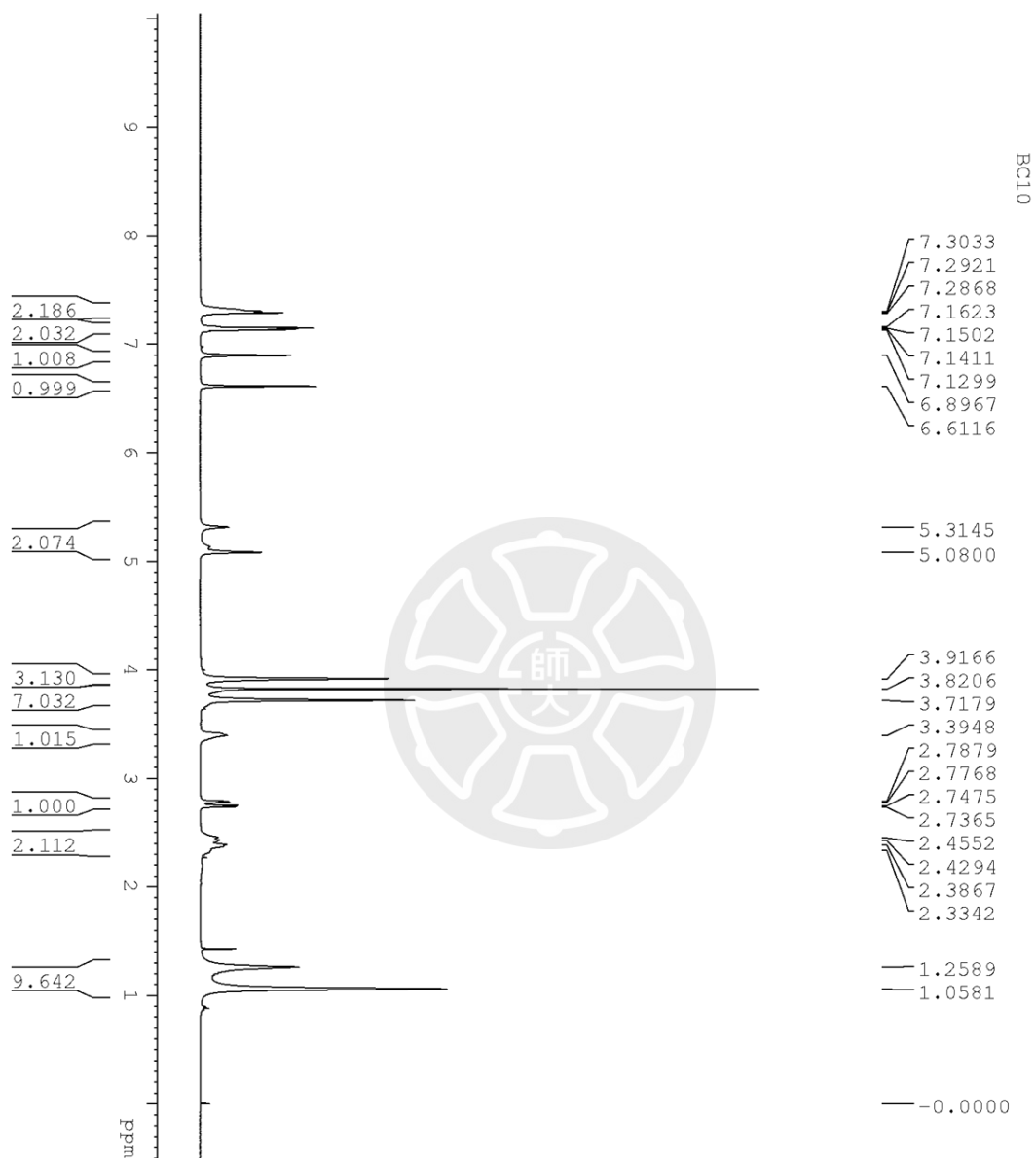


Chemical Shift (ppm)
172.42
159.76
153.62
148.81
145.32
145.01
133.65
126.39
125.62
119.80
119.52
114.21
108.58
79.12
77.32
77.00
76.68
66.53
65.81
55.33
54.06
53.88
51.52
44.40
41.39
27.78

```

Current Data Parameters
NAME          1 want to graduat-
EXPNO         2
PROCNO        1
F2 - Acquisition Parameters
Date_         20250308
Time          15.56
INSTRUM      spect
PROBHD       5 mm PABBO BB/
PULPROG      zgpg30
TD            32768
SOLVENT      CDCl3
NS            792
DS            1
===== CHANNEL f1 =====
SFO1          100.6228298 MH
NUC1           13C
P1             10.00 us-
P1M1          49.50000000 W
===== CHANNEL f2 =====
SFO2          400.1316005 MH
NUC2           1H
P2             90.00 us-
P2M1          12.50000000 W
P2M2          0.34722000 W
P2M3          0.28125000 W
===== Processing parameters =====
SI            32768
SF            100.6127780 MH
WDW           EM
SSB           0
LB            2.00 Hz
GB            0
PC            1.00
  
```

¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-2,3-dimethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27am)



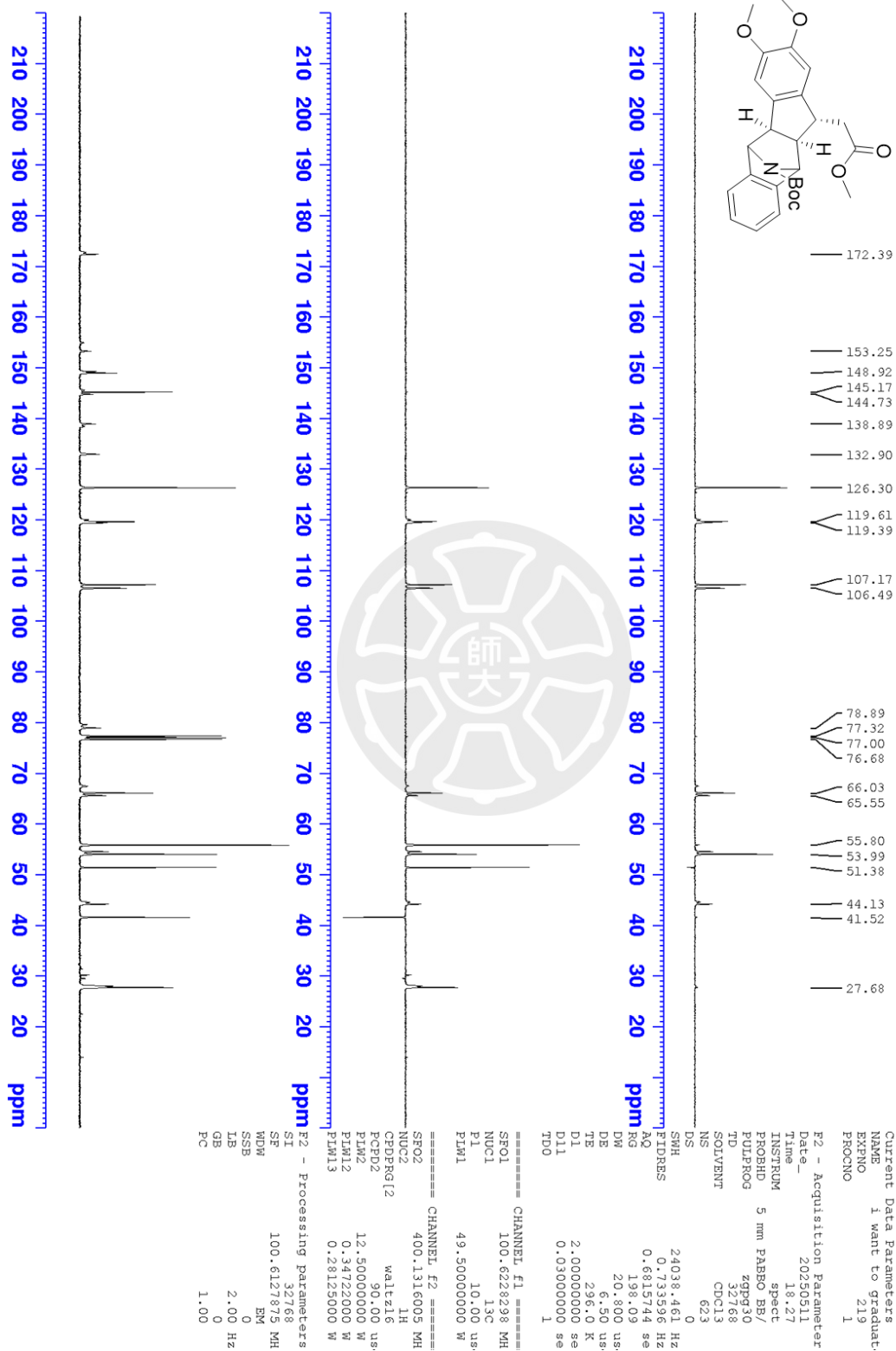
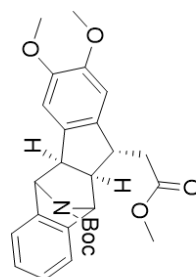
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Current Data Parameters
NAME      I want to graduate
EXPNO    218
PROCNO   1
F2 - Acquisition Parameters
Date_    20250511
Time     18.25
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       4
DS       0
SMH      7211.599 Hz
FIDRES   0.220079 Hz
AQ       2.2719147 sec
RG       22.82
DE       69.333 usec
DW       10.06 usec
TE       295.5 K
D1       2.00000000 sec
TD0      1

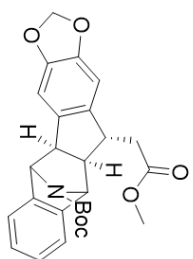
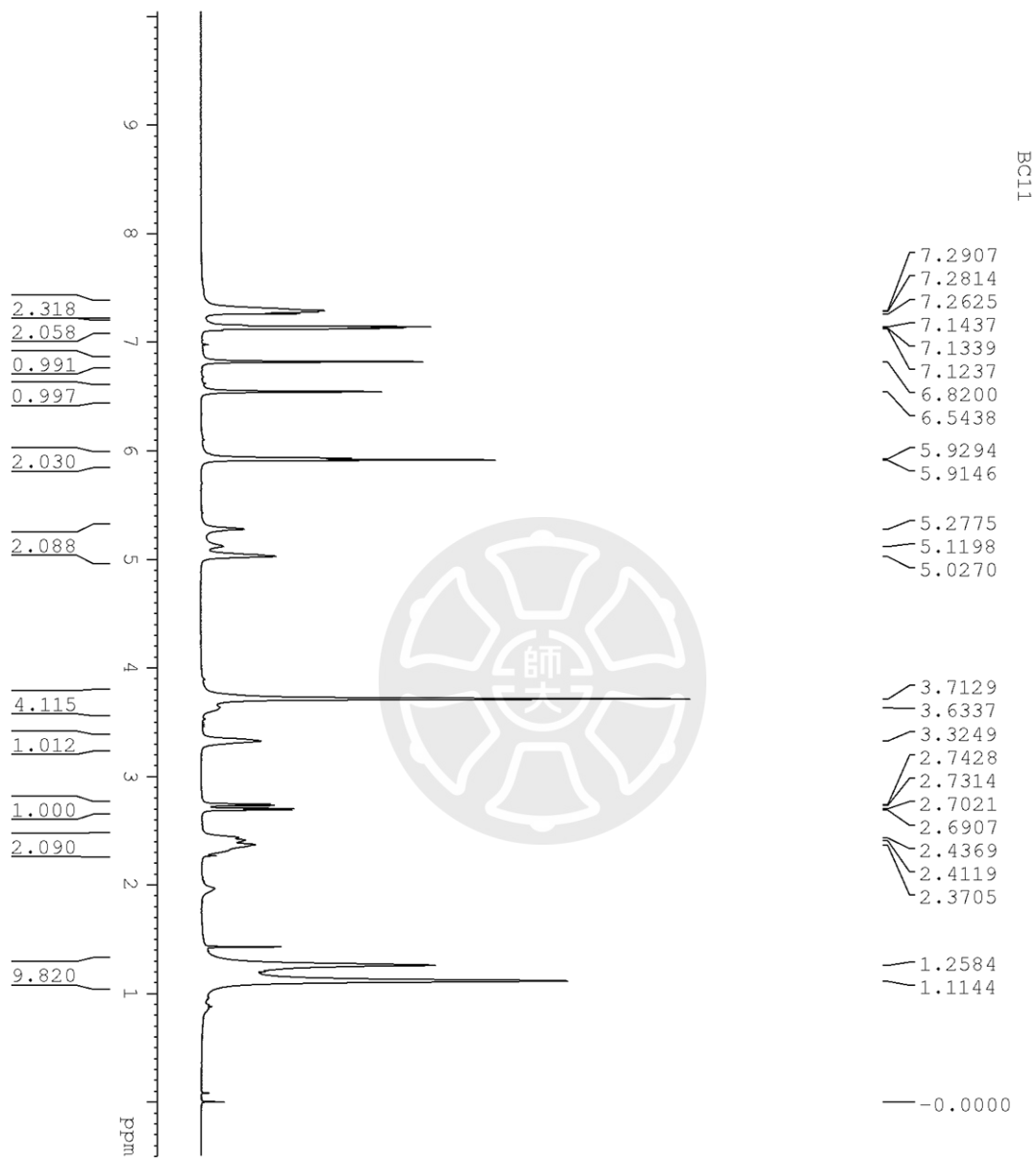
===== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1     1H
P1       15.00 usec
PLW1     13.50000000 W
F2 - Processing parameters
SI       16394
WDW      400.1299987 MHz
SSB      0
LB       0 Hz
GB       0
PC       1.00
  
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-2,3-dimethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27am)

BC10 13C



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[6,7]fluoreno[2,3-d][1,3]dioxole-13-carboxylate (27an)



```

Current Data Parameters
NAME      i want to graduate
EXPNO    251
PROCNO    1

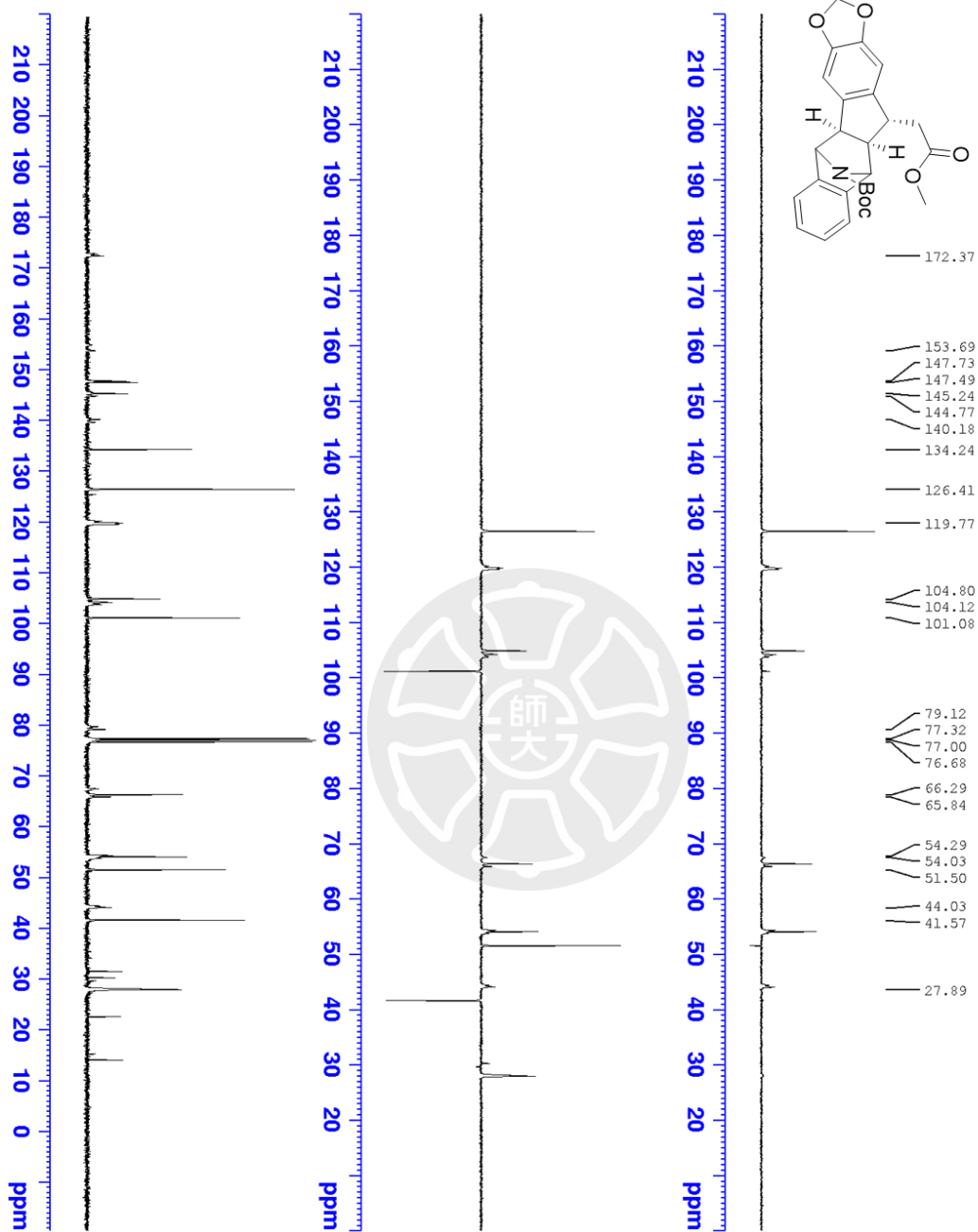
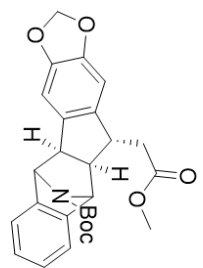
F2 - Acquisition Parameters
Date_     20250515
Time      10.23
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         32768
SOLVENT    CDCl3
NS         4
DS         0
SWH        7211.539 Hz
FIDRES     0.1220079 Hz
AQ         2.2719147 sec
RG         29.06
DW         69.333 usec
DE         10.06 usec
TE         295.3 K
D1         2.0000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1      1H
P1        15.00 usec
PLW1      13.50000000 W

F2 - Processing parameters
SI        16394
SF        400.1300088 MHz
WDW       EM
SSB       0
LB        0 Hz
GB        0
PC        1.00
    
```

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[6,7]fluoreno[2,3-d][1,3]dioxole-13-carboxylate (27an)

BC11 13C



```

Current Data Parameters
NAME          1 want to graduat
EXPNO         223
PROCNO        1

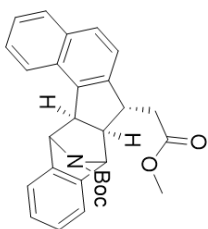
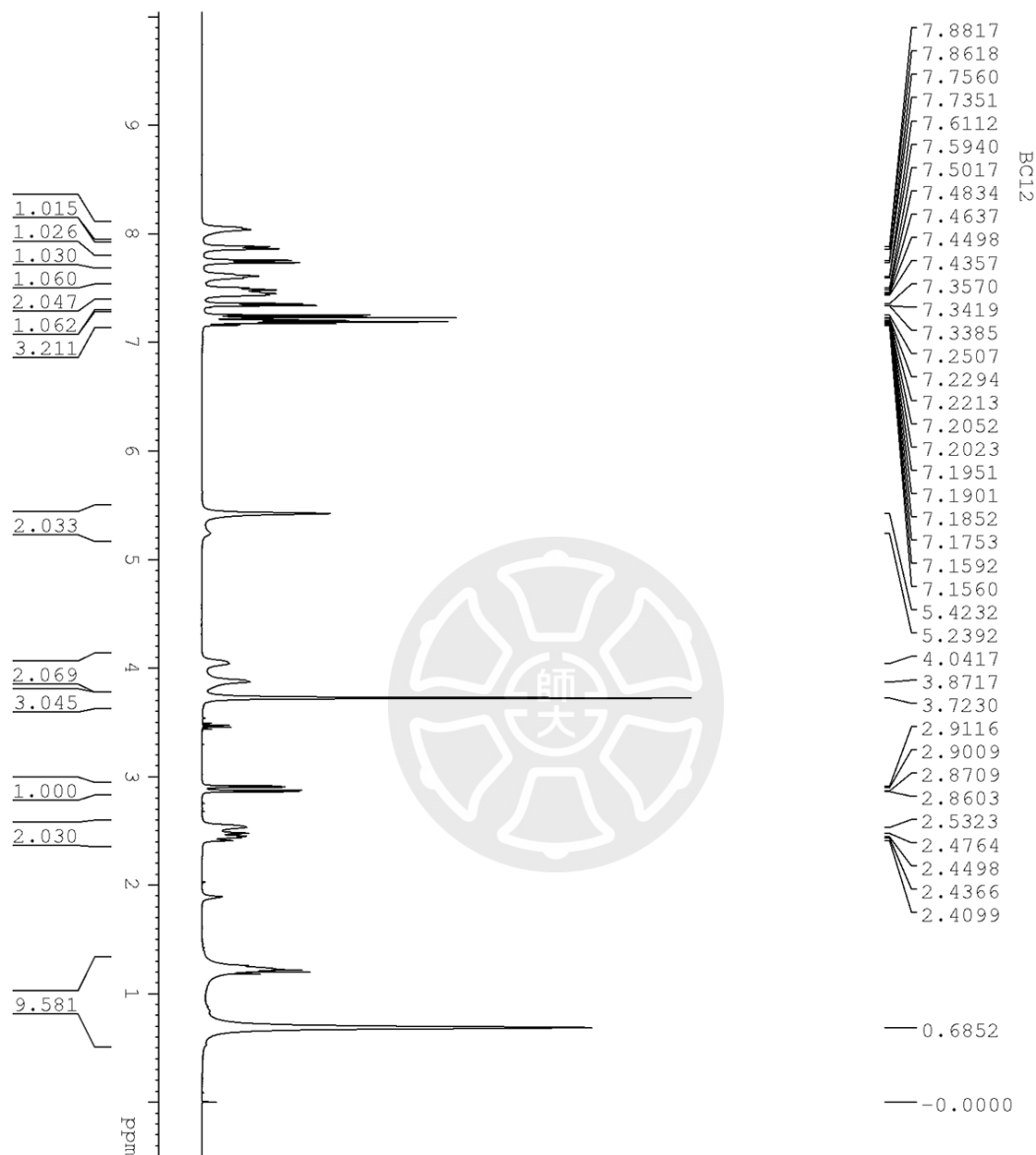
F2 - Acquisition Parameters
Date_         20250511
Time_         19.47
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
NS            152
DS            0
SWH           24038.461 Hz
FIDRES       0.733596 Hz
AQ           0.6815744 se
RG           198.09
DE           20.800 us
TE           6.50 us
D1           296.5 K
D11          2.00000000 se
D12          0.03000000 se
TD0          1

===== CHANNEL f1 =====
SFO1         100.62828298 MHz
NUC1         13C
P1           10.00 us
PL1         49.500000000 W
PLM1

===== CHANNEL f2 =====
SFO2         400.1316005 MHz
NUC2         1H
P2           90.00 us
PL2         12.50000000 W
PLM2
PLM13       0.28125000 W

F2 - Processing parameters
SI           32768
SF           100.6127800 MHz
WDW          EM
SSB          0
LB           2.00 Hz
GB           0
PC           1.00
  
```

¹H NMR spectrum of tert-butyl (7R,7aR,13aR)-7-(2-methoxy-2-oxoethyl)-7a,8,13,13a-tetrahydro-7H-8,13-epiminodibenzo[b,g]fluorene-14-carboxylate (27ad)

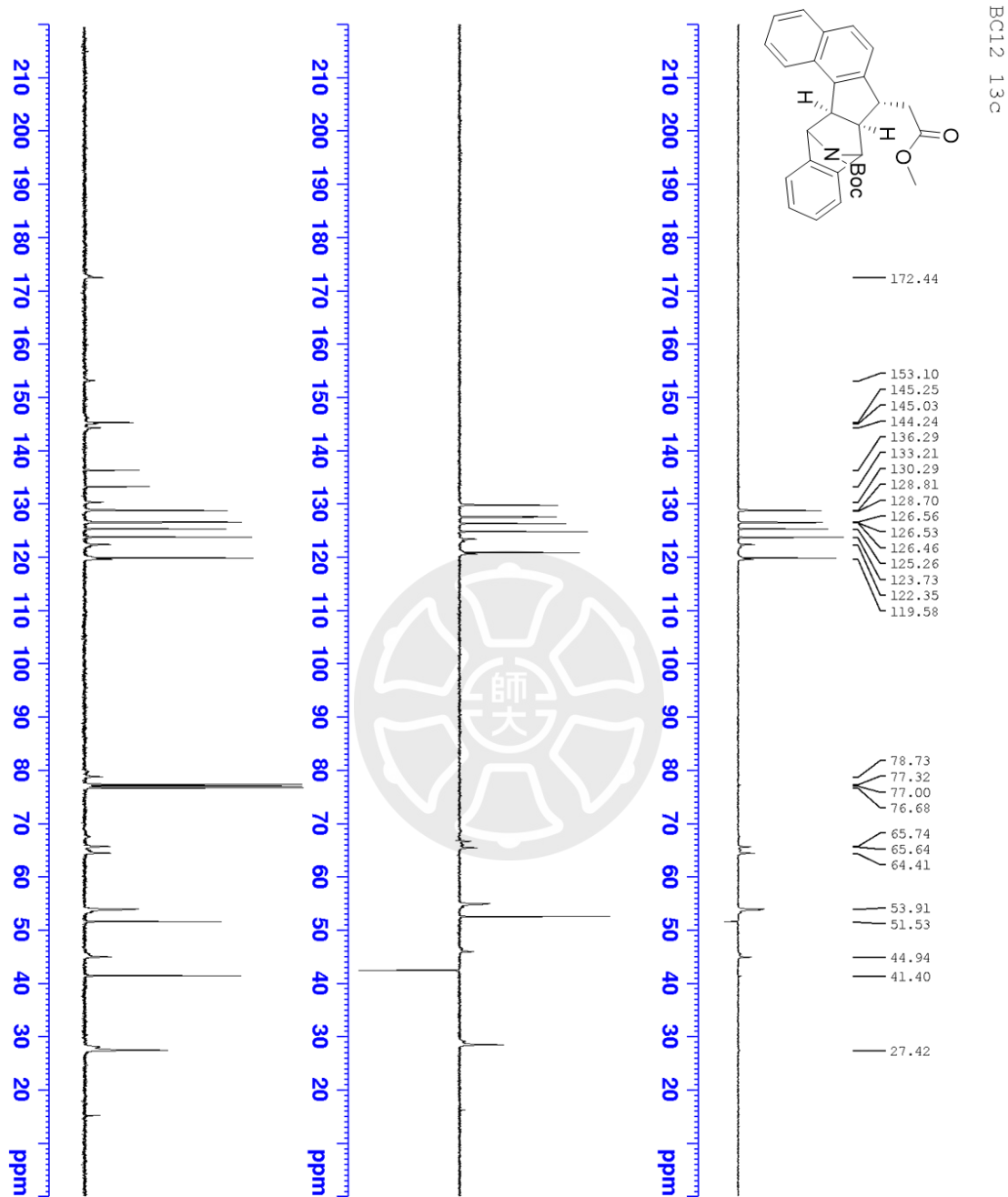


Current Data Parameters
 Name 1 want to graduate
 ExpNO 188
 F2 - Acquisition Parameters
 Date_ 20250504
 Time 16:59
 INSTRUM spect
 PROBHD 5 mm PABBO BE/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 7211.539 Hz
 FIDRES 0.220079 Hz
 AQ 2.2719147 sec
 RG 29.06
 DW 69.833 usec
 DE 19.078 usec
 TE 29.9
 D1 2.0000000 sec
 TDO 1

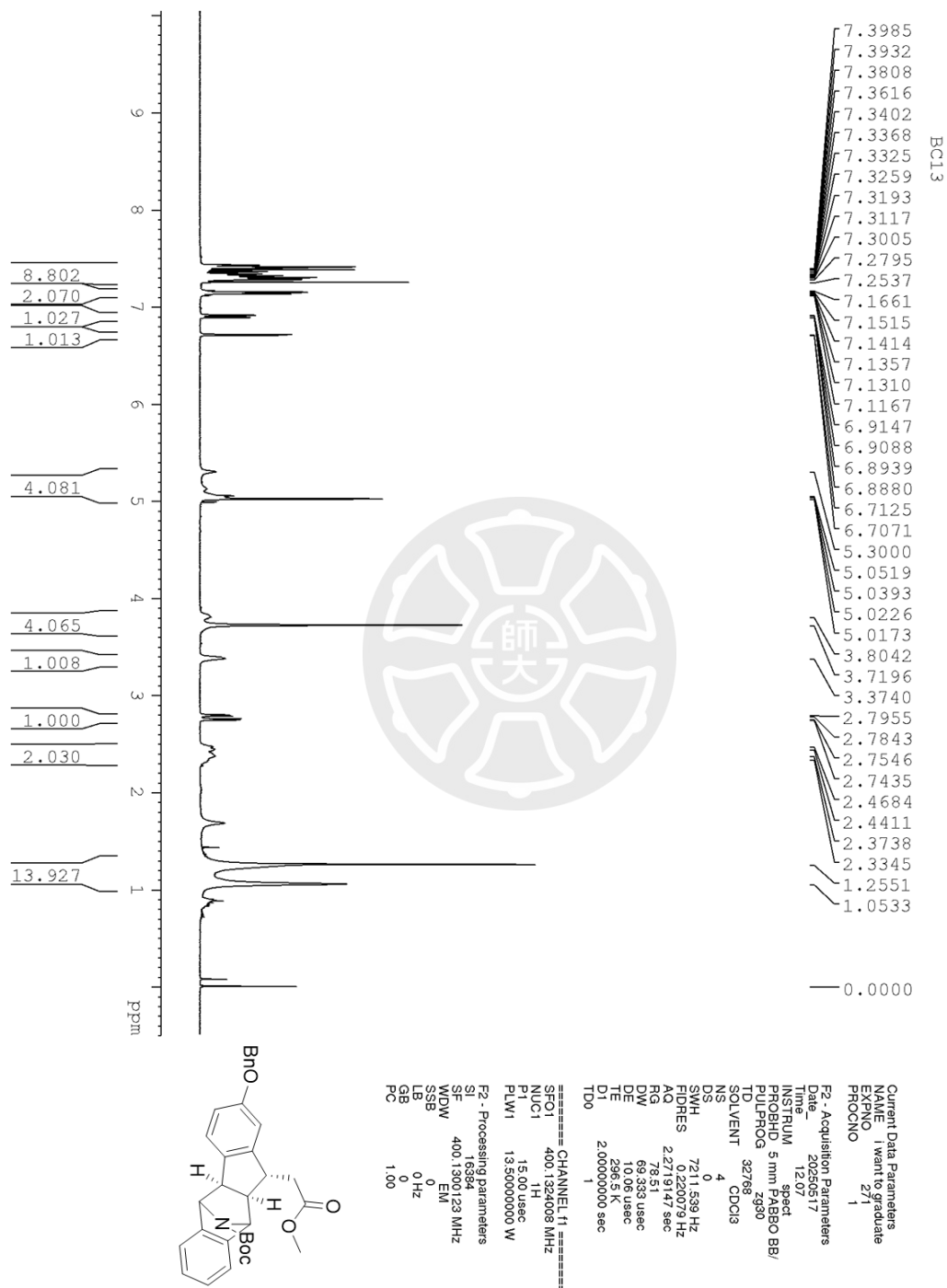
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 NUC1 1H
 P1 15.00 usec
 PLW1 13.50000000 W

F2 - Processing parameters
 SI 16384
 SF 400.1300220 MHz
 WDW EM
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.00

¹³C NMR spectrum of tert-butyl (7R,7aR,13aR)-7-(2-methoxy-2-oxoethyl)-7a,8,13,13a-tetrahydro-7H-8,13-epiminodibenzo[b,g]fluorene-14-carboxylate (27ad)

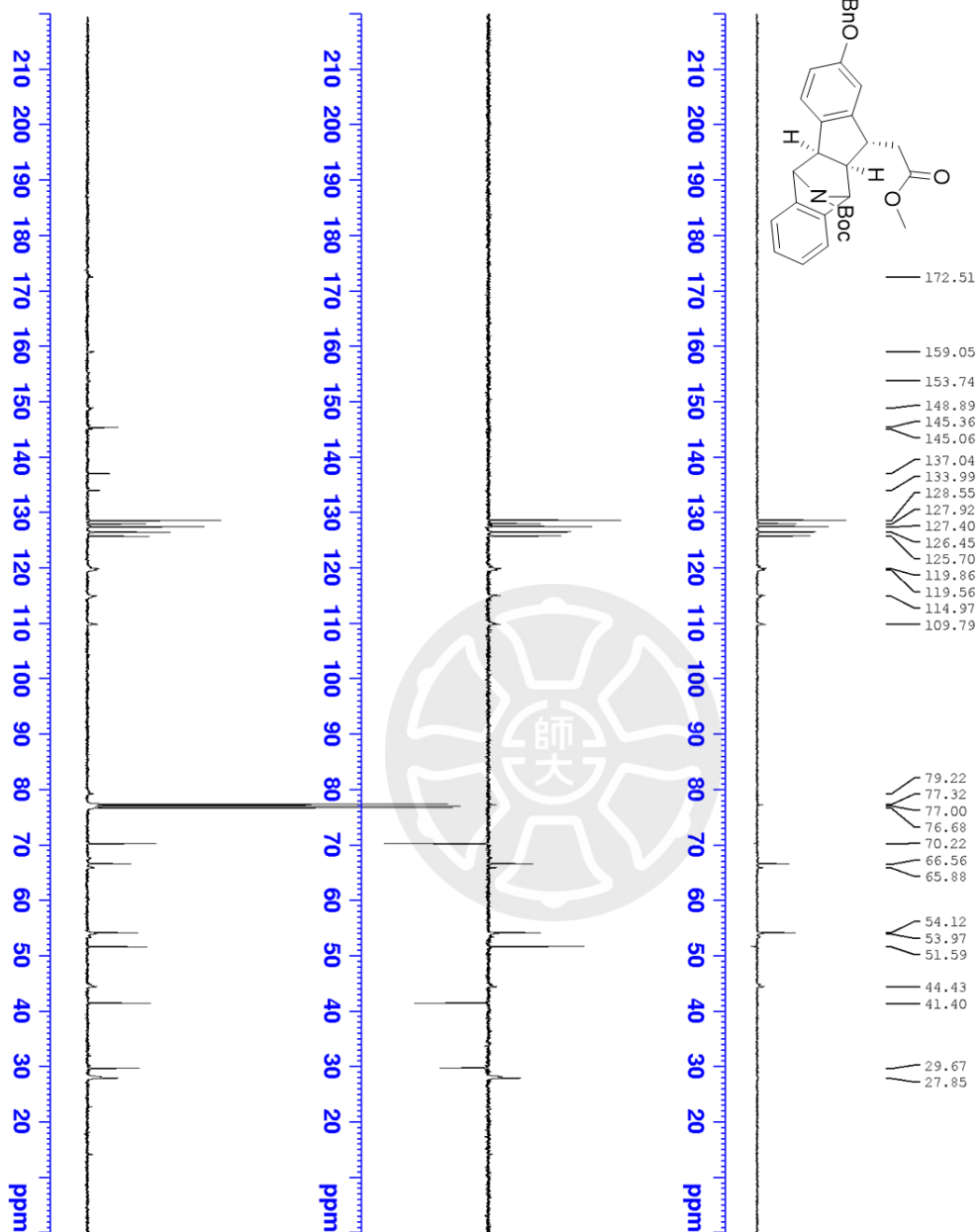
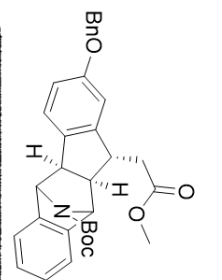


¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-2-(benzyloxy)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ap)



¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-2-(benzyloxy)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ap)

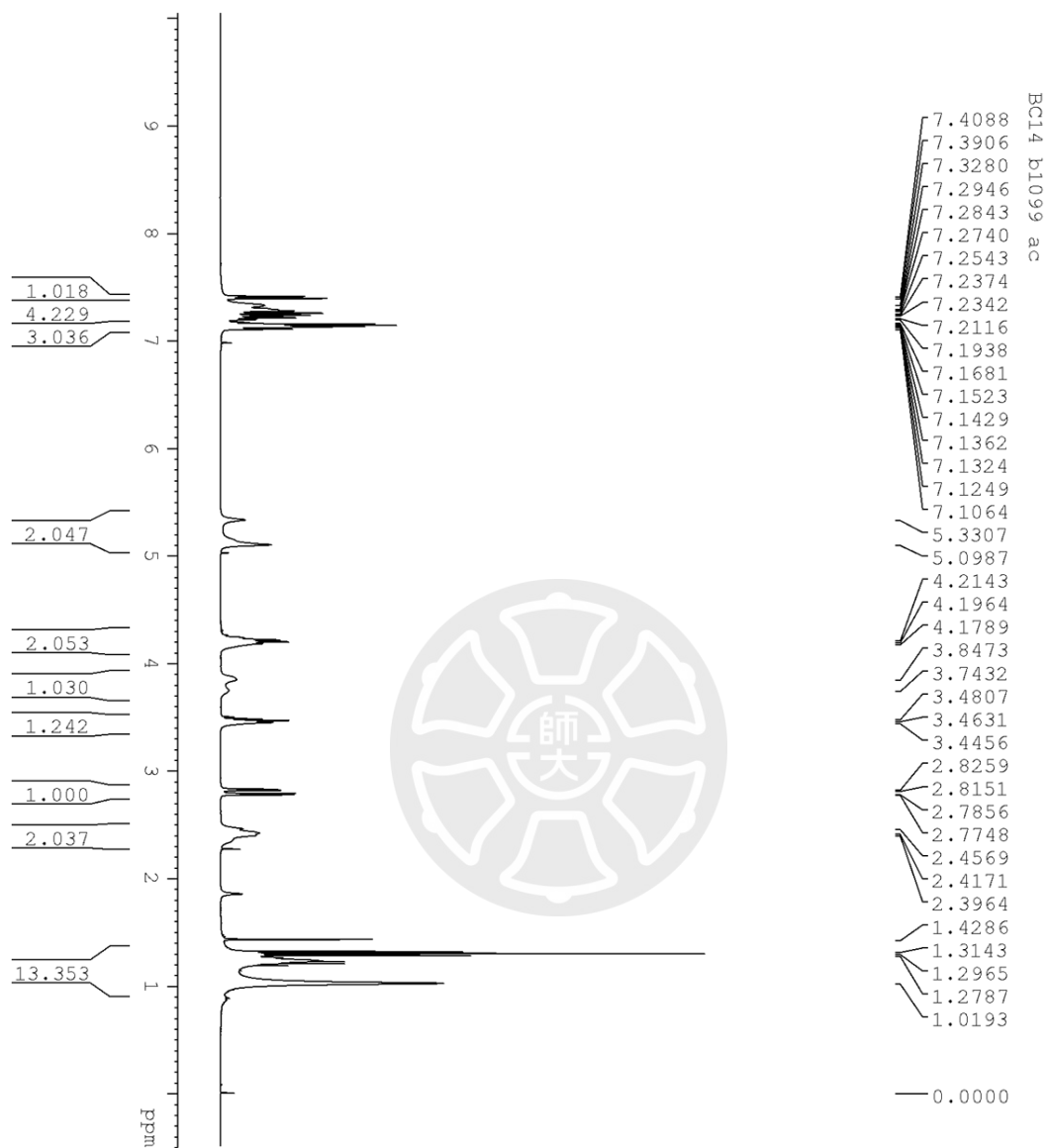
BC13 13C



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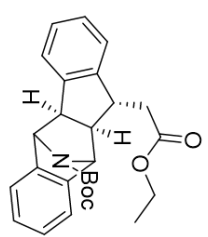
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NAME      1 want to graduat
EXPNO    272
PROCNO   1
F2 - Acquisition Parameters
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Time     12.09
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zgpg30
TD       32768
SOLVENT  CDCl3
NS       1034
DS       0
SWH      24038.461 Hz
FIDRES   0.733596 Hz
AQ       0.6815744 se
RG       198.09
DM       20.800 us-
DE       6.50 us-
TE       296.9 K
D1       2.00000000 se
D11      0.03000000 se
TD0      1
===== CHANNEL f1 =====
SFO1    100.628298 MH
NUC1     13C
P1       10.00 us-
PLW1    49.50000000 W
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SFO2    400.1316005 MH
NUC2     1H
CPDPRG2  waltz16
PCPD2    90.00 us-
PLW2    12.50000000 W
PLW12   0.34722000 W
PLW13   0.28125000 W
F2 - Processing Parameters
SI       32768
SF       100.6127728 MH
WDW      EM
SSB      0
GB       0
PC       1.00
  
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¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-ethoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aq)



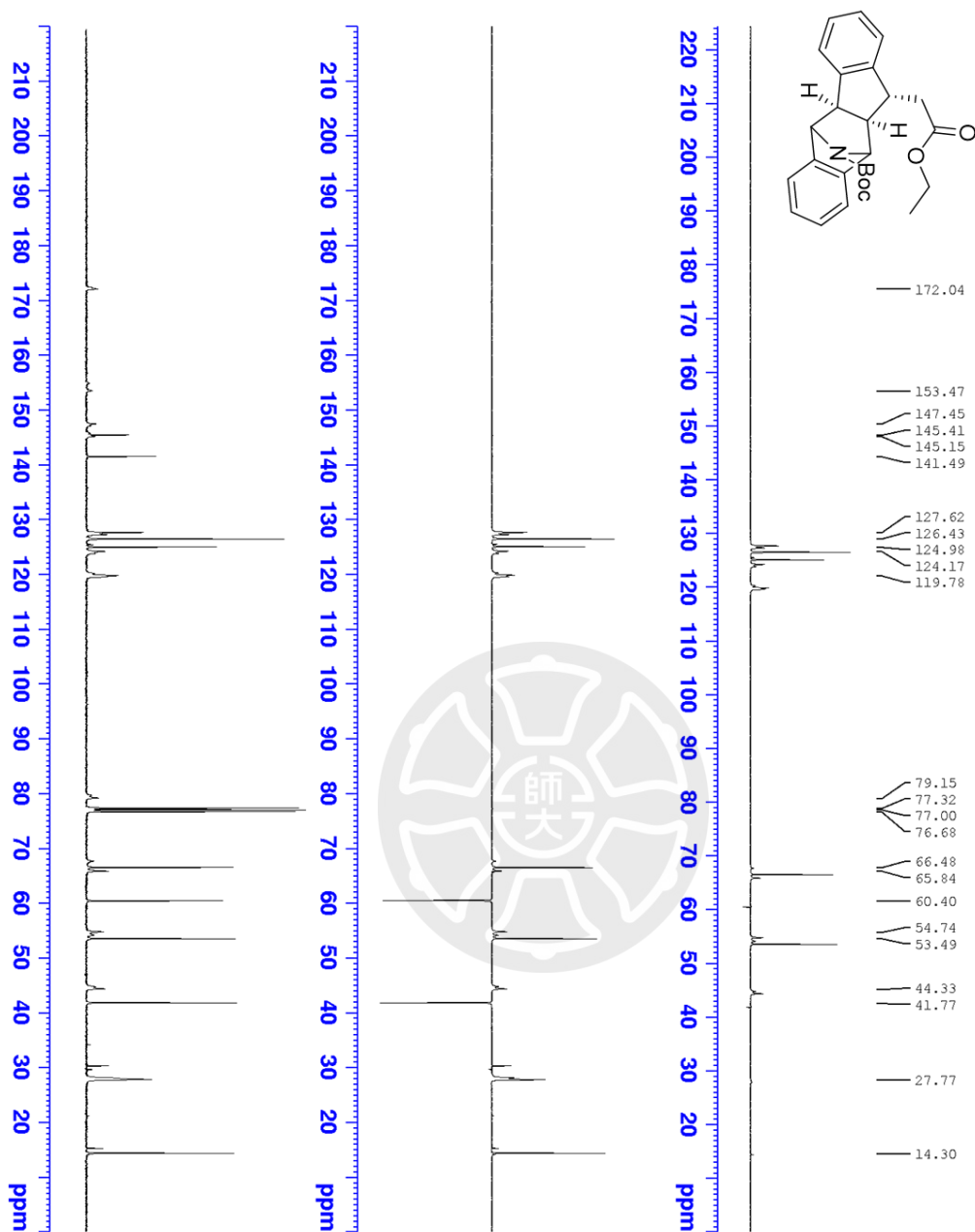
BC14 b1099 ac

- 7.4088
- 7.3906
- 7.3280
- 7.2946
- 7.2843
- 7.2740
- 7.2543
- 7.2374
- 7.2342
- 7.2116
- 7.1938
- 7.1681
- 7.1523
- 7.1429
- 7.1362
- 7.1324
- 7.1249
- 7.1064
- 5.3307
- 5.0987
- 4.2143
- 4.1964
- 4.1789
- 3.8473
- 3.7432
- 3.4807
- 3.4631
- 3.4456
- 2.8259
- 2.8151
- 2.7856
- 2.7748
- 2.4569
- 2.4171
- 2.3964
- 1.4286
- 1.3143
- 1.2965
- 1.2787
- 1.0193
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Current Data Parameters
 NAME: i want to graduate
 EXPNO: 18
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 20250316
 Time: 11:09
 INSTRUM: spect
 PROBHD: 5 mm PABBO BB/
 PULPROG: zg30
 TULPROG: 32768
 SOLVENT: CDCl3
 NS: 16
 DS: 0
 SWH: 7211.539 Hz
 FIDRES: 0.220079 Hz
 AQ: 2.2719147 sec
 RG: 36.64
 DW: 69.333 usec
 DE: 10.06 usec
 TE: 296.1 K
 D1: 2.00000000 sec
 TD0: 1
 ===== CHANNEL f1 =====
 SFO1: 400.130003 MHz
 NUC1: ¹H
 P1: 15.00 usec
 PLW1: 13.50000000 W
 F2 - Processing parameters
 SI: 16384
 SF: 400.1300142 MHz
 WDW: EM
 SSB: 0
 LB: 0 Hz
 GB: 0
 PC: 1.00

¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-ethoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27aq)



BC14 b1099 ac 13c

Current Data Parameters
 NAME I want to graduate
 EXPNO 19
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20250316
 Time 11:16
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 PULPROG zgpg30
 TD 492930
 SFO 492968
 SOLVENT CDCl3
 NS 1392
 DS 0

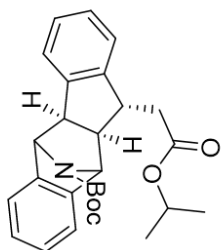
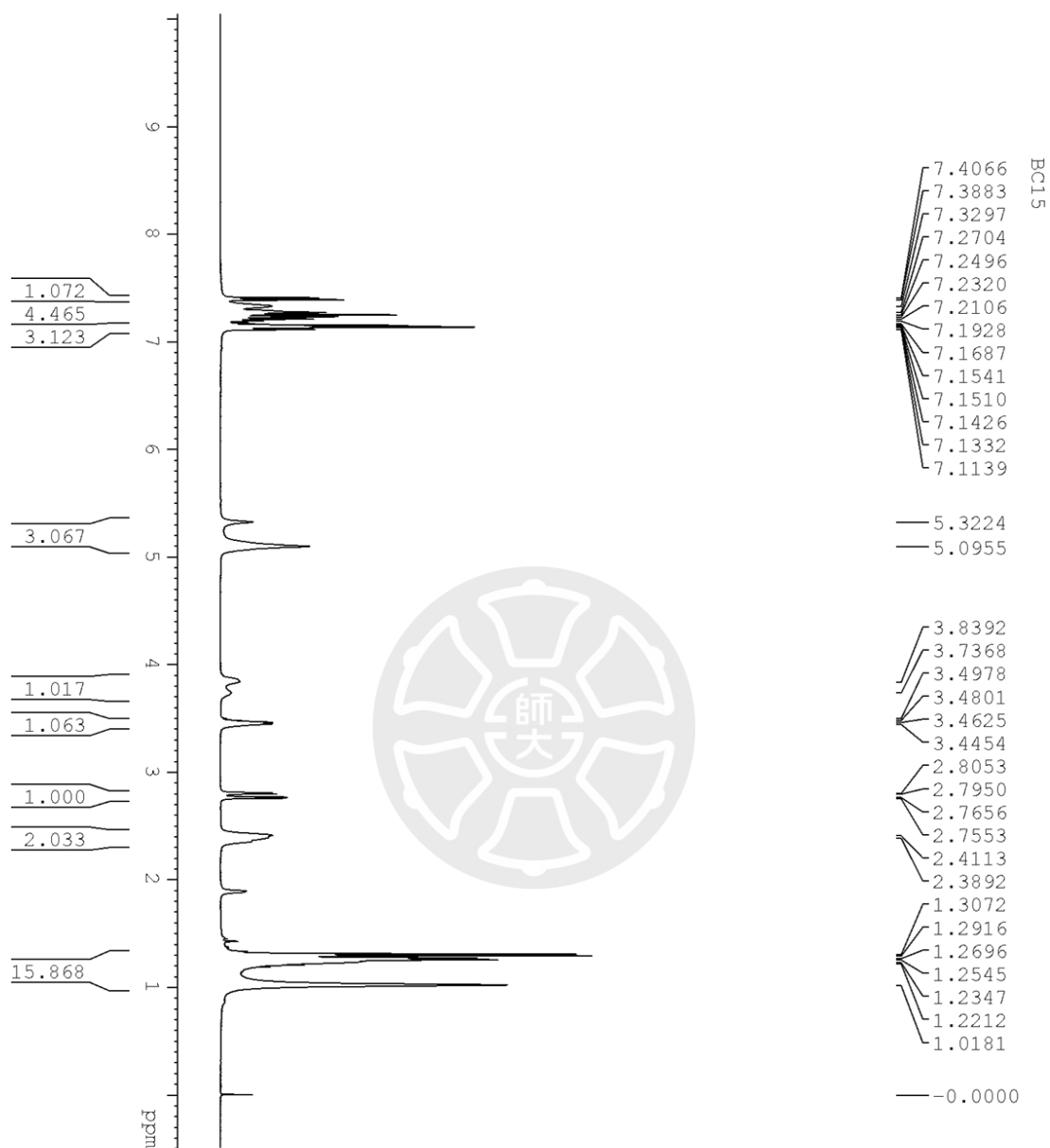
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 FIDRES 0.73396 Hz
 AQ 0.6815744 ss
 RG 198.09
 DW 20.800 us
 DE 6.50 us
 TE 296.2 K
 D1 2.00000000 ss
 D11 0.03000000 ss
 TDO 1

===== CHANNEL f2 =====
 SFO2 100.6228298 MHz
 NUC1 13C
 P1 10.00 us
 FLM1 49.50000000 W

===== CHANNEL f3 =====
 SFO3 400.1316005 MHz
 NUC2 1H
 WALTZ16
 GPDPRG12 waltz16
 PCPD2 90.00 us
 PPR2 12.50000000 W
 PPR12 0.34722000 W
 FLM13 0.28125000 W

F2 - Processing Parameters
 SI 0
 SF 100.6127774 MHz
 WSRW 27.68
 SSB 0
 LB 2.00 Hz
 GB 0
 FC 1.00

¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-isopropoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ar)



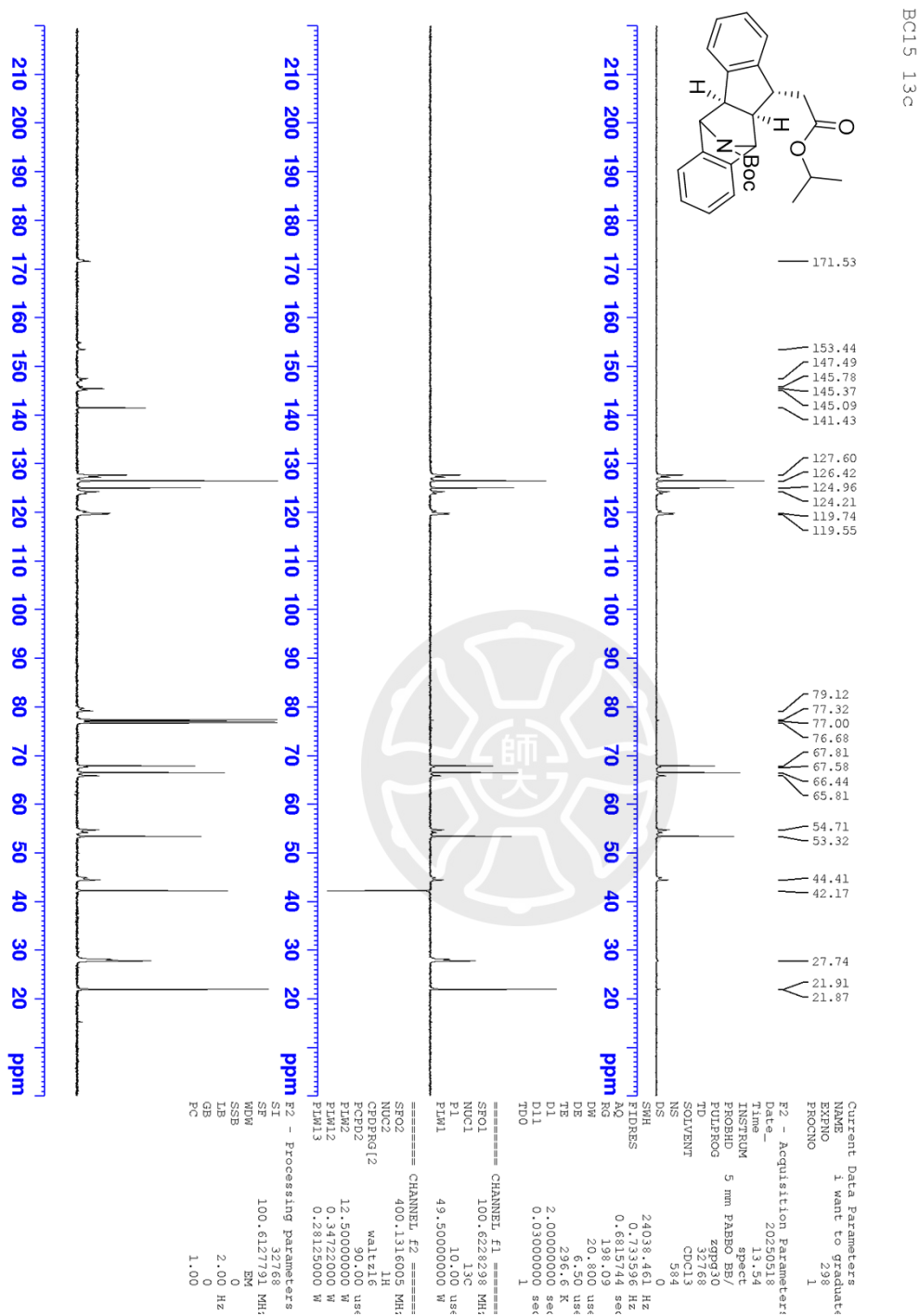
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Current Data Parameters
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EXPNO: 297
PROCNO: 1

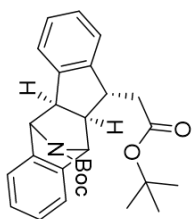
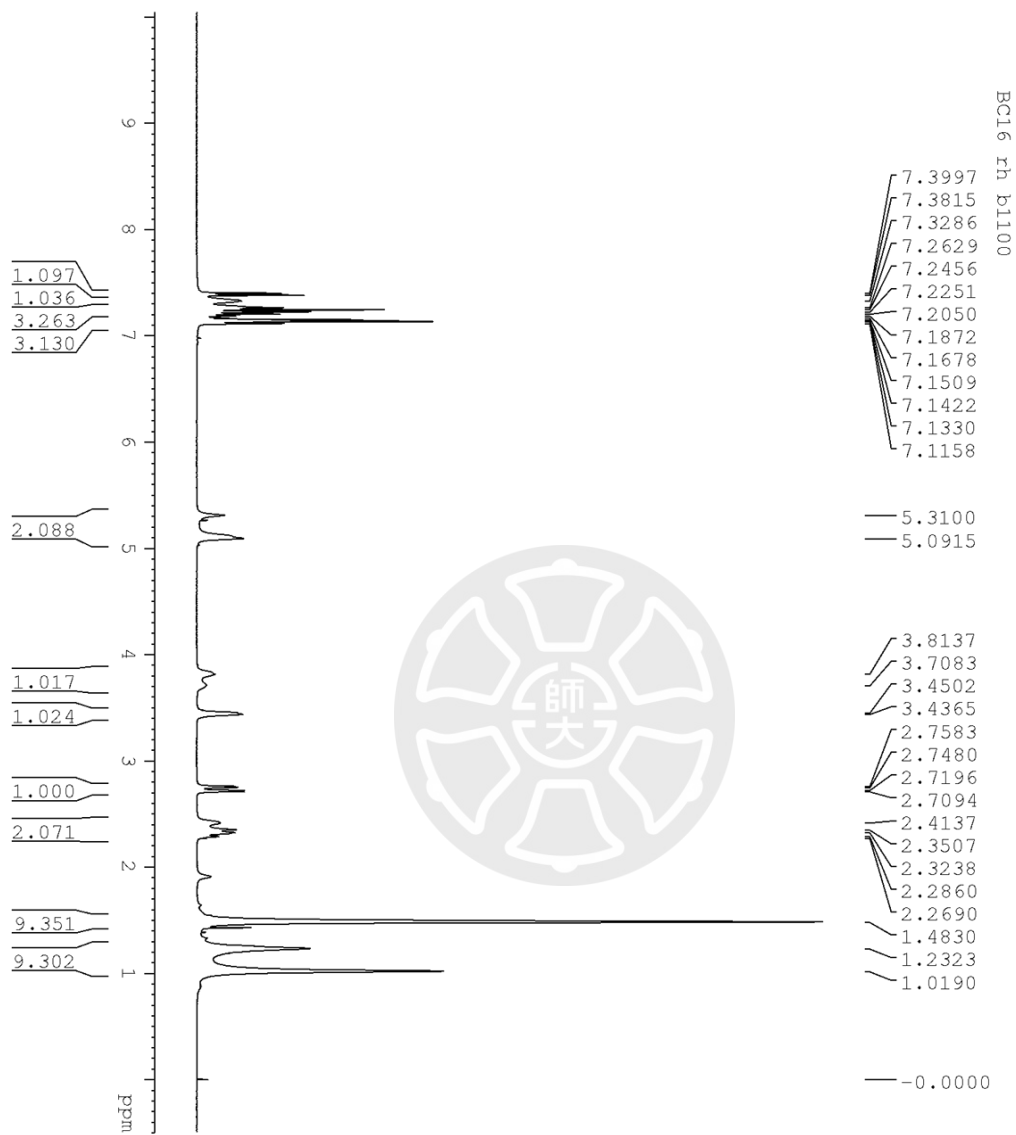
F2 - Acquisition Parameters
Date_ : 20250518
Time: 13.48
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 4
DS: 0
SWH: 7211.539 Hz
FIDRES: 0.220079 Hz
AQ: 2.2719147 sec
RG: 31.16
DE: 69.333 usec
TE: 295.7 K
D1: 2.00000000 sec
TD0: 1

===== CHANNEL f1 =====
SFO1: 400.1324008 MHz
NUC1: 13C
P1: 15.00 usec
PLW1: 13.30000000 W
F2 - Processing parameters
SI: 32768
SF: 400.1300140 MHz
WDW: EM
SSB: 0
LB: 0 Hz
GB: 0
PC: 1.00
    
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¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-ethoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ar)



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-(tert-butoxy)-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27as)



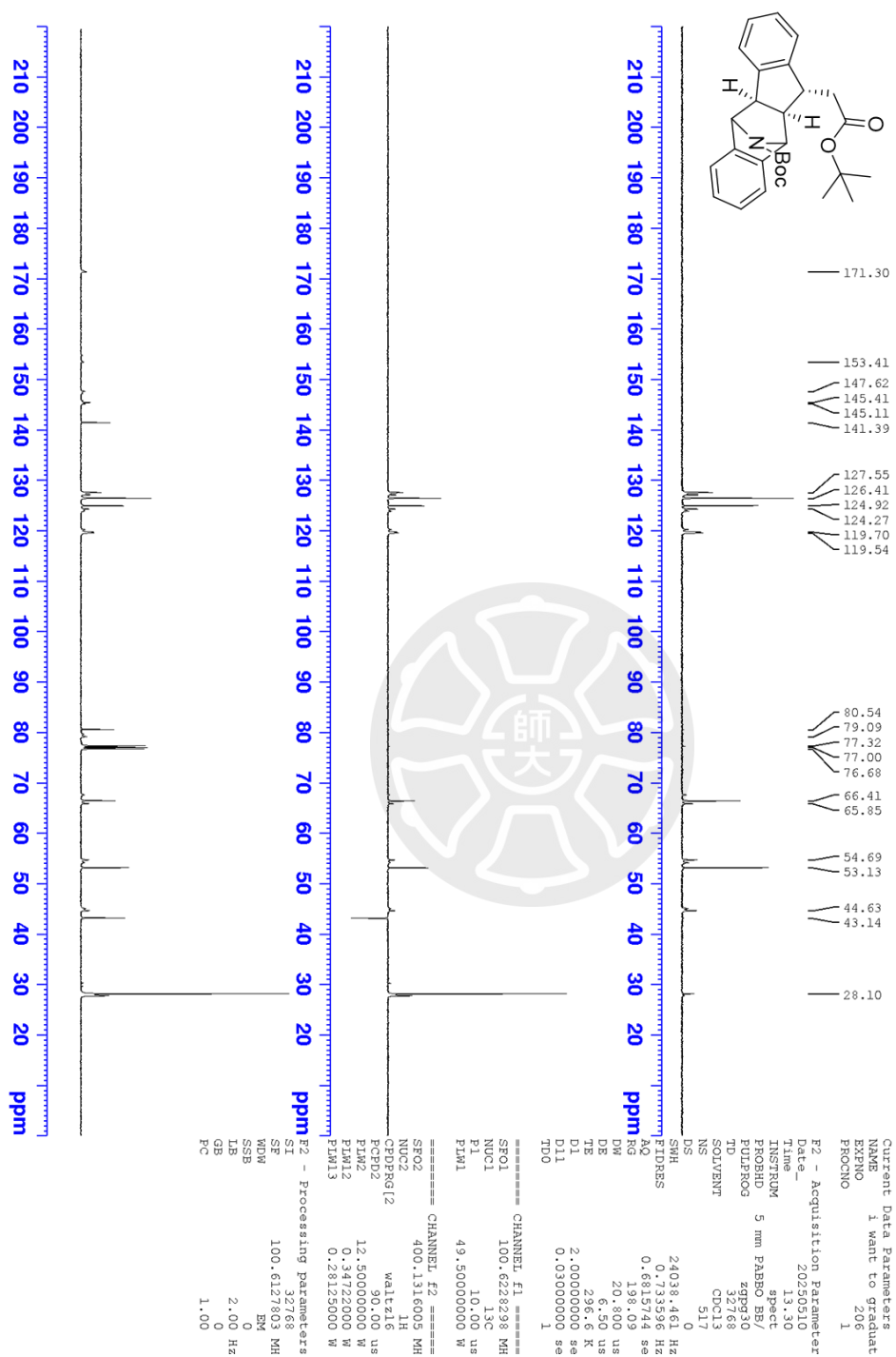
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===== CHANNEL f1 =====
SFO1 400.1324008 MHz
P1 15.00 usec
PLW1 13.50000000 W
F2 - Processing Parameters
SI 16384
SF 400.1300155 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

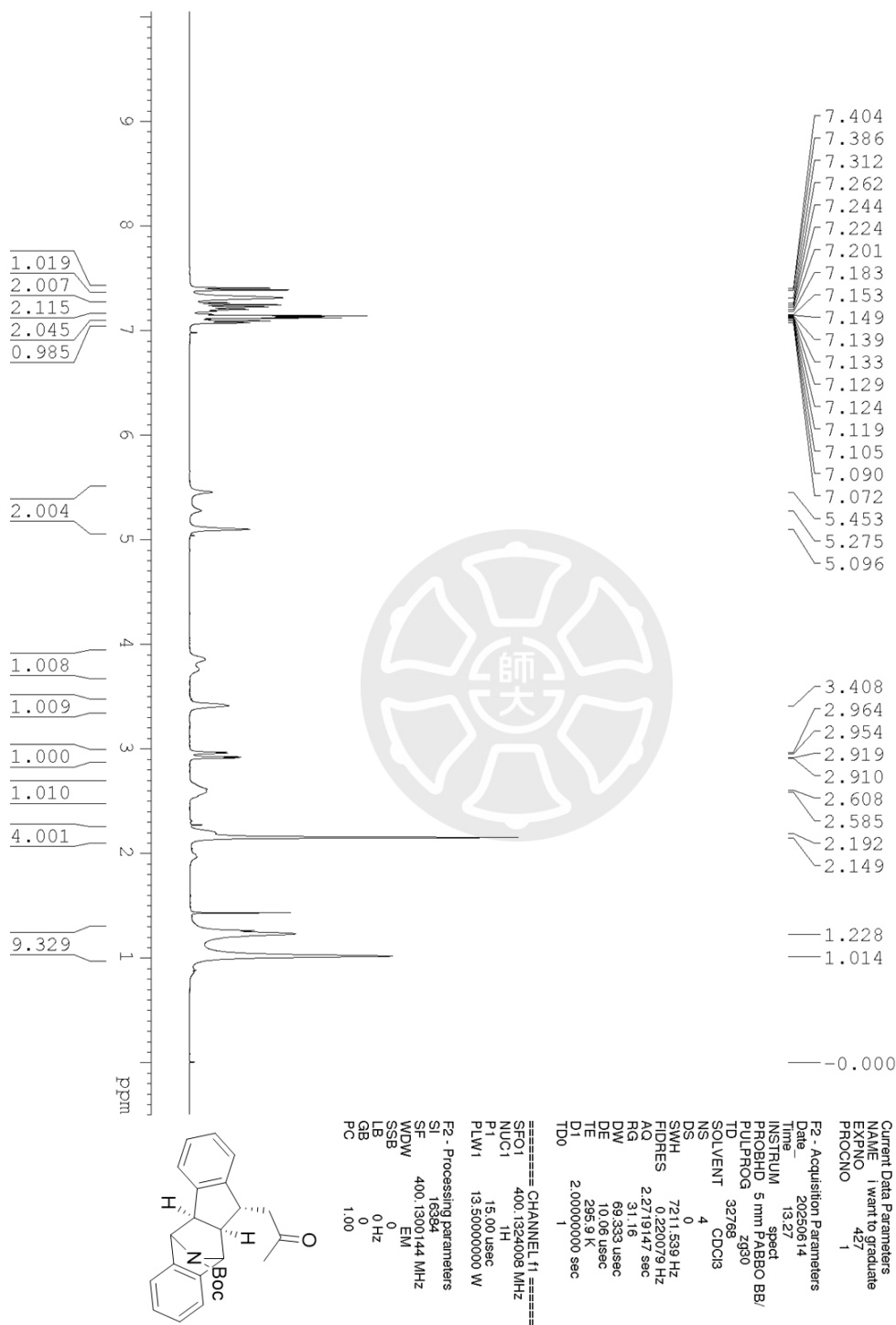
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Date_ 20250509
Time_ 10.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 721.539 Hz
AQ 0.12197 Hz
RG 2271547 sec
DE 69.333 usec
TE 295.9 K
D1 2.000000000 sec
TD0 1

Current Data Parameters
NAME I want to graduate
EXPNO 195
PROCNO 1
    
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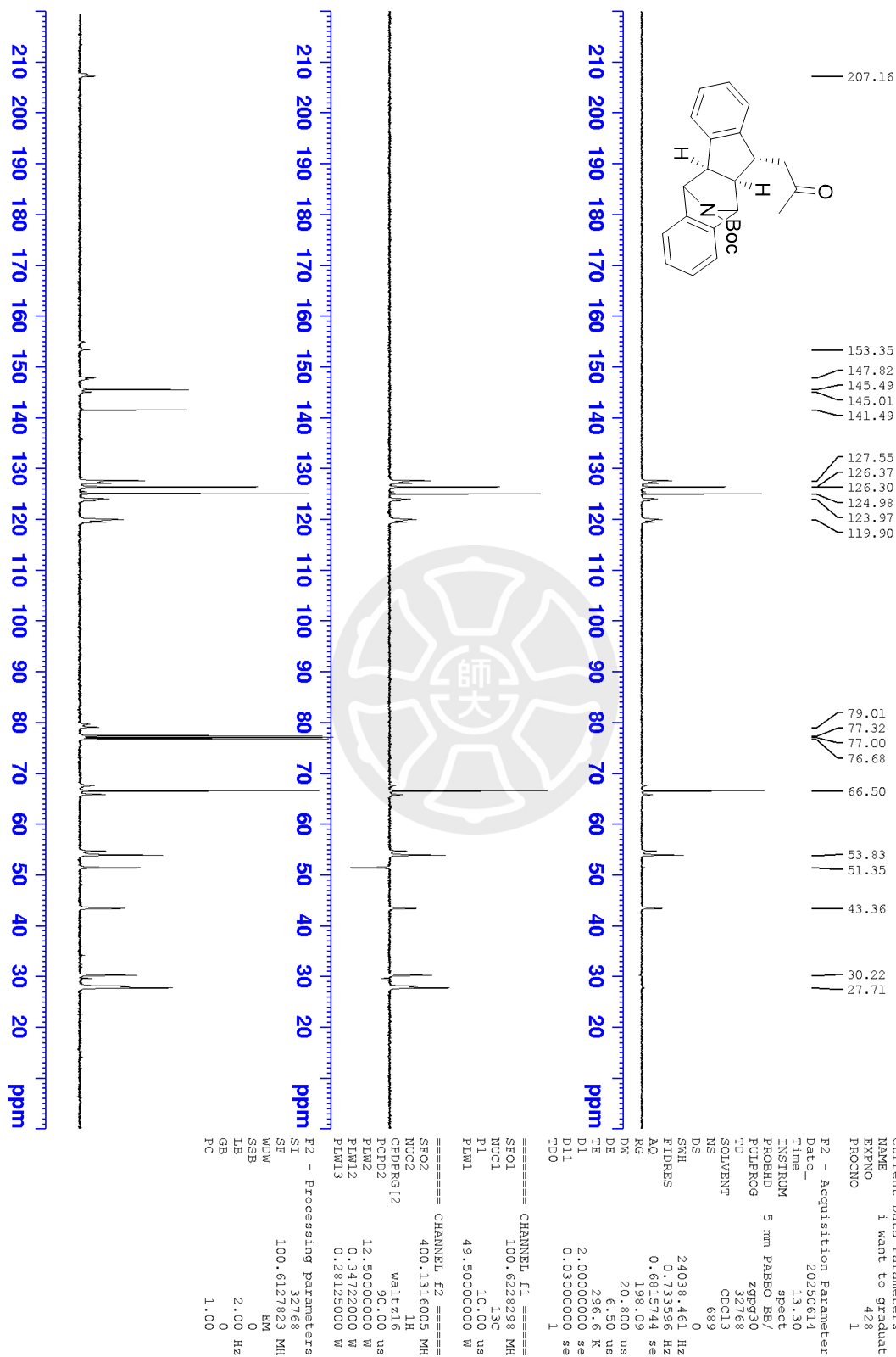
¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-(tert-butoxy)-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27as)



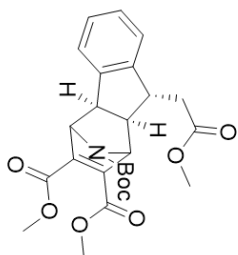
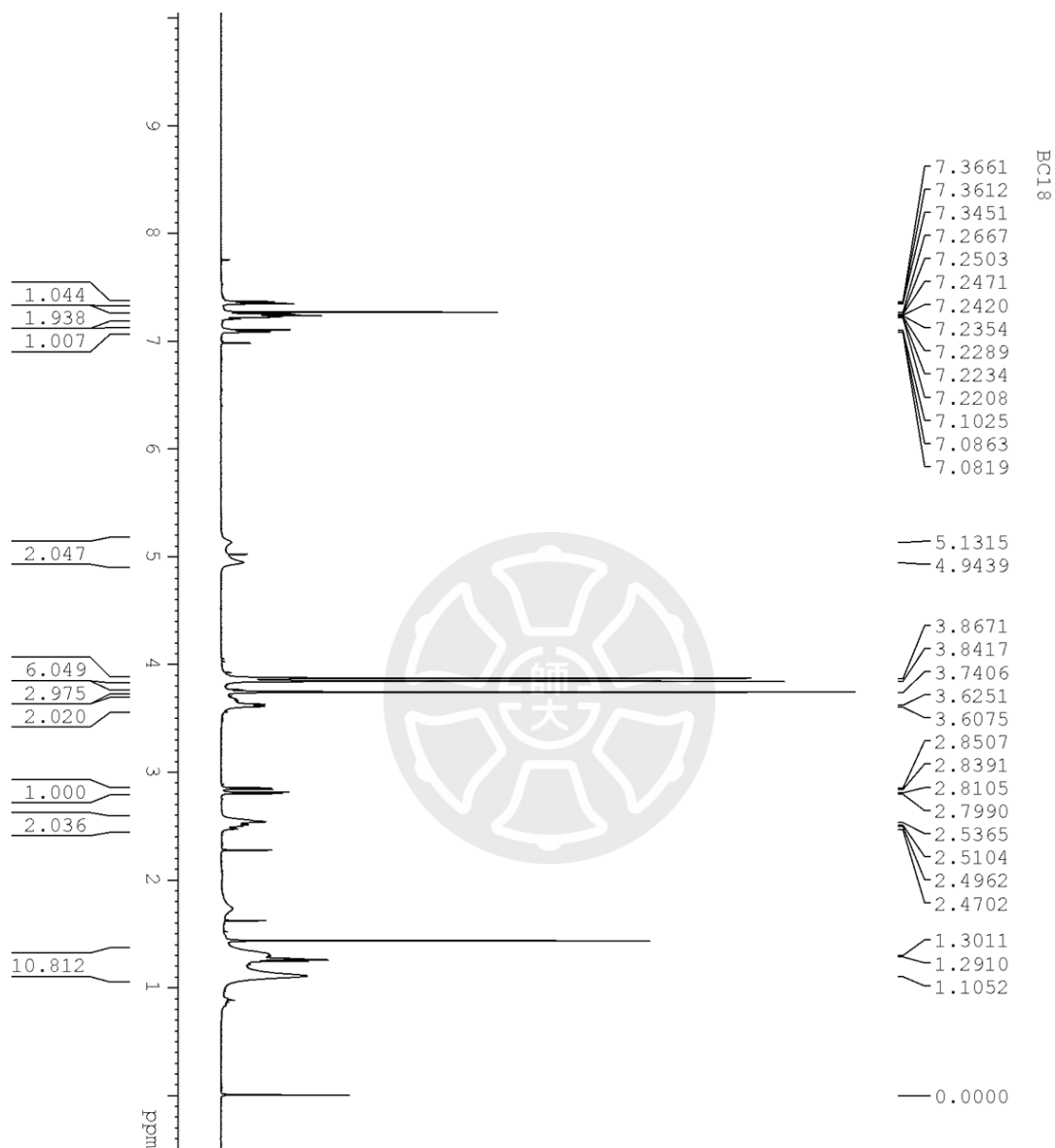
¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-oxopropyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27at)



¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-11-(2-oxopropyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27at)



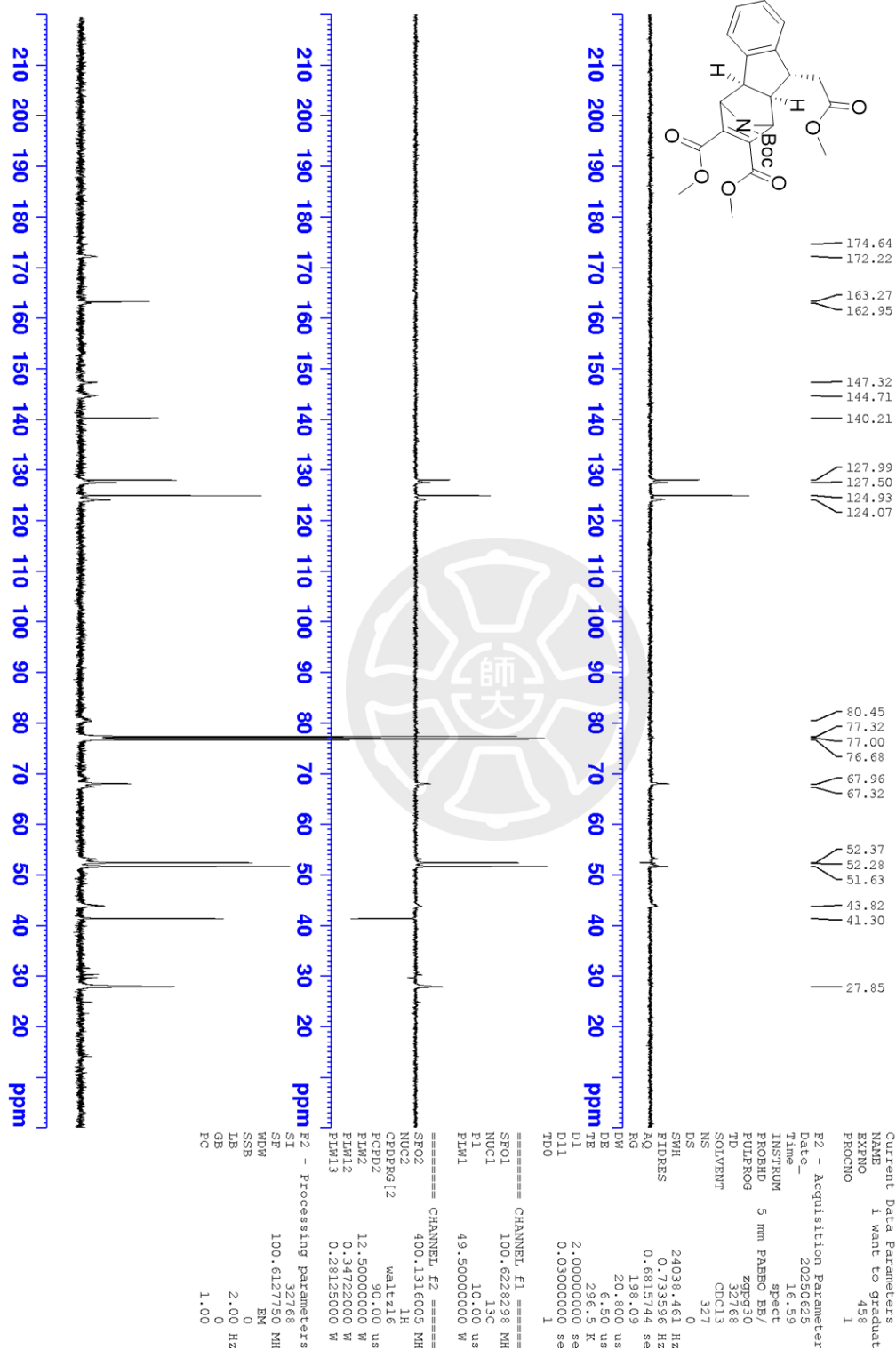
¹H NMR spectrum of 10-(tert-butyl) 2,3-dimethyl (4aR,9R,9aR)-9-(2-methoxy-2-oxoethyl)-4,4a,9,9a-tetrahydro-1H-1,4-epiminofluorene-2,3,10-tricarboxylate (27ga)



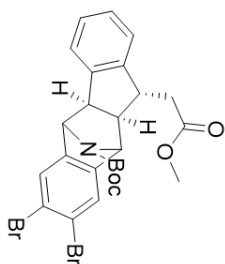
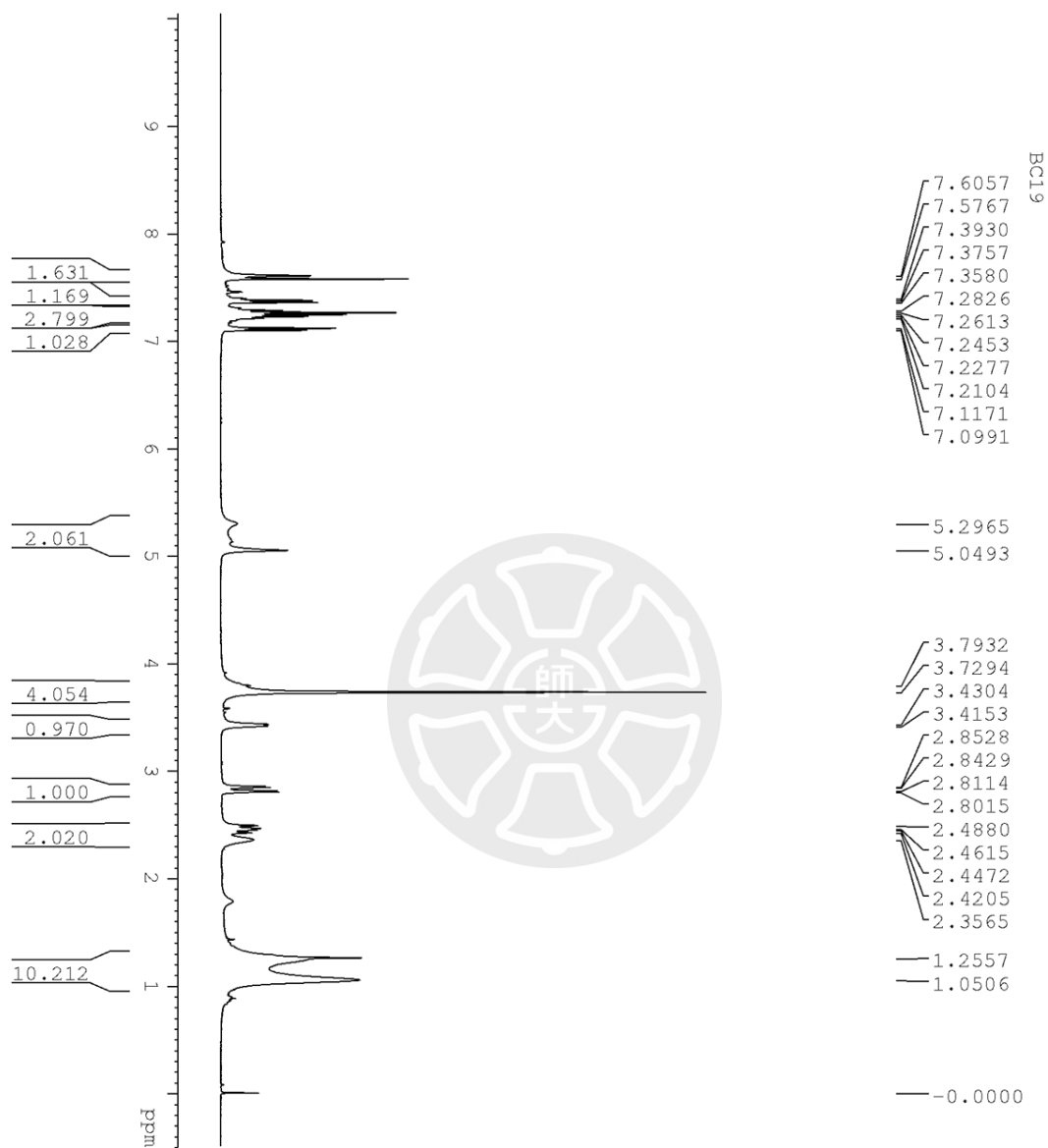
Current Data Parameters
 NAME 1 want to graduate
 EXPNO 256
 PROCNO 1
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 Date_ 20250119
 Time 13:39
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 PROBHD 5 mm PARBO BB/
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 7211.539 Hz
 FIDRES 0.220079 Hz
 AQ 2.2719147 sec
 RG 78.51
 DW 69.333 usec
 DE 10.06 usec
 TE 295.7 K
 D1 2.00000000 sec
 TDO -
 ===== CHANNEL f1 =====
 SFO 400.1324093 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 13.50000000 W
 F2 - Processing parameters
 SI 16384
 SF 400.1300071 MHz
 WDW EM
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.00

¹³C NMR spectrum of 10-(tert-butyl) 2,3-dimethyl (4aR,9R,9aR)-9-(2-methoxy-2-oxoethyl)-4,4a,9,9a-tetrahydro-1H-1,4-epiminofluorene-2,3,10-tricarboxylate (27ga)

b2088 13c



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-7,8-dibromo-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ha)



```

Current Data Parameters
NAME: I want to graduate
EXPNO: 279
PROCNO: 1

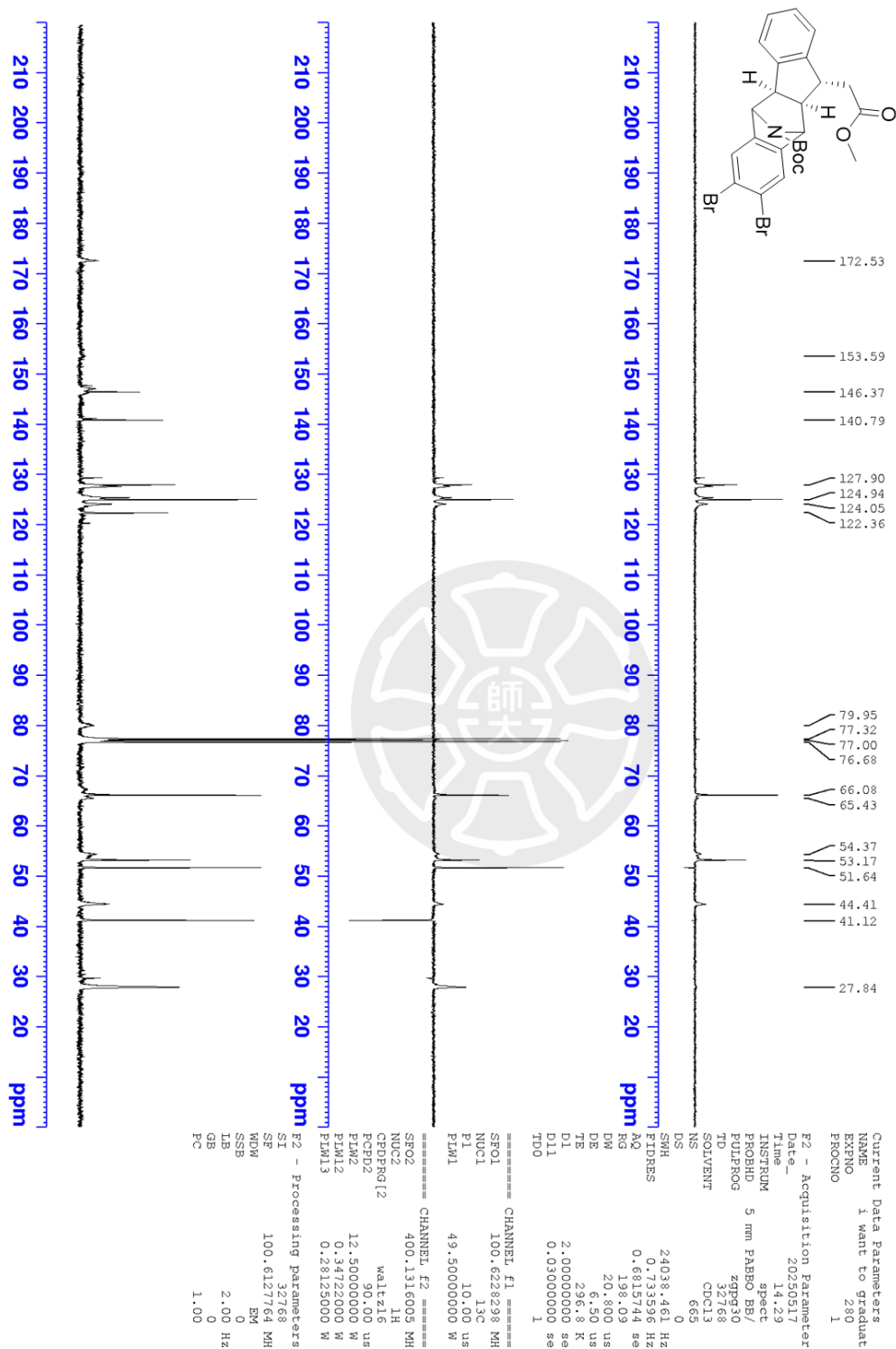
F2 - Acquisition Parameters
Date_: 20250517
Time: 13.59
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 4
DS: 0
SWH: 7211.539 Hz
FIDRES: 0.220079 Hz
AQ: 2.2719147 sec
RG: 48.15
DW: 69.330 usec
DE: 296.8 K
TE: 296.8 K
D1: 2.0000000 sec
TD0: 1

===== CHANNEL f1 =====
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NUC1: 1H
P1: 15.00 usec
PLW1: 13.50000000 W

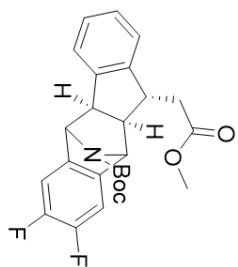
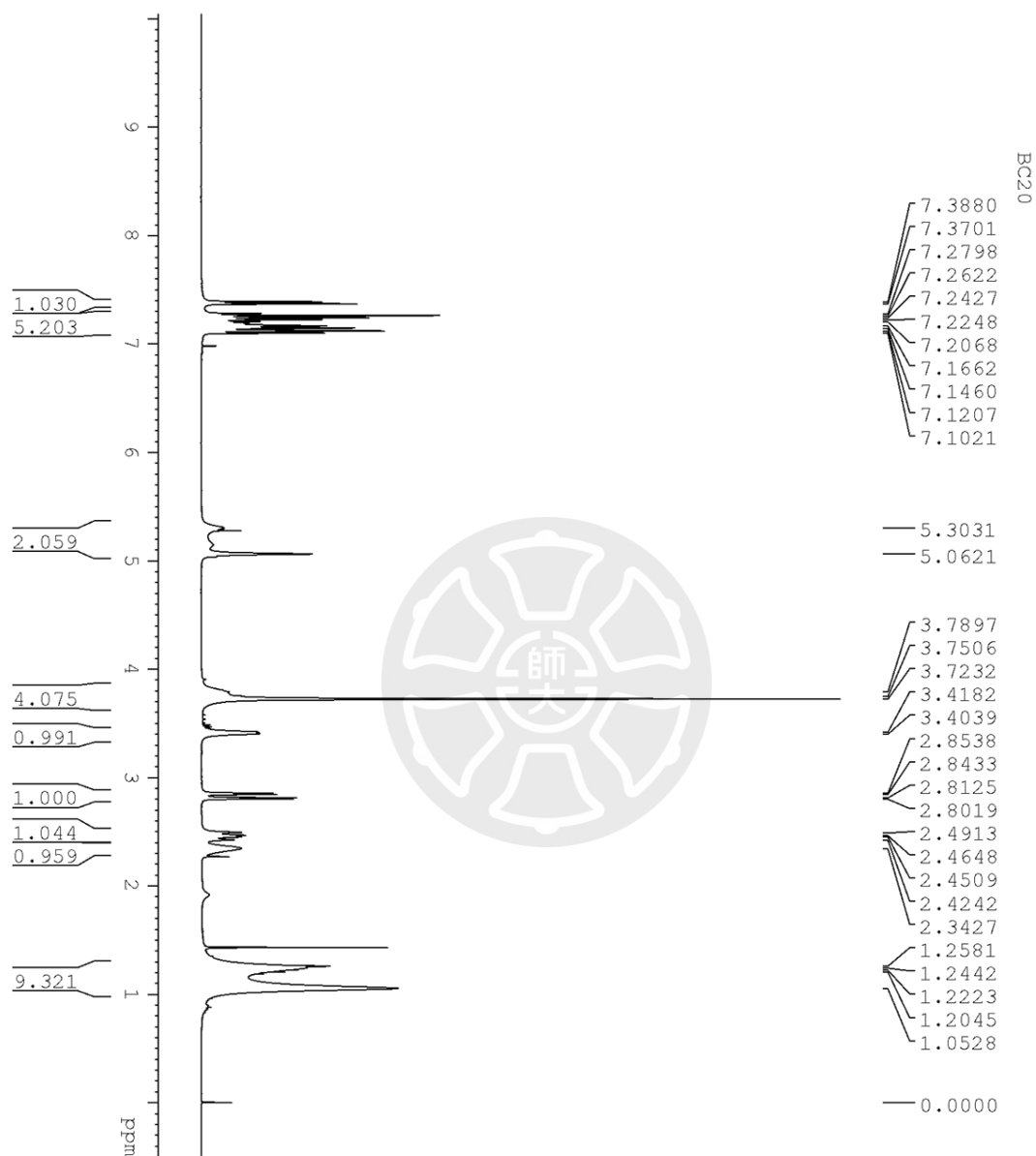
F2 - Processing parameters
SI: 16384
SF: 400.1300094 MHz
WDW: EM
SSB: 0
GB: 0
PC: 1.00
  
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¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-7,8-dibromo-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ha)

BC19_13c



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-7,8-difluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ia)



```

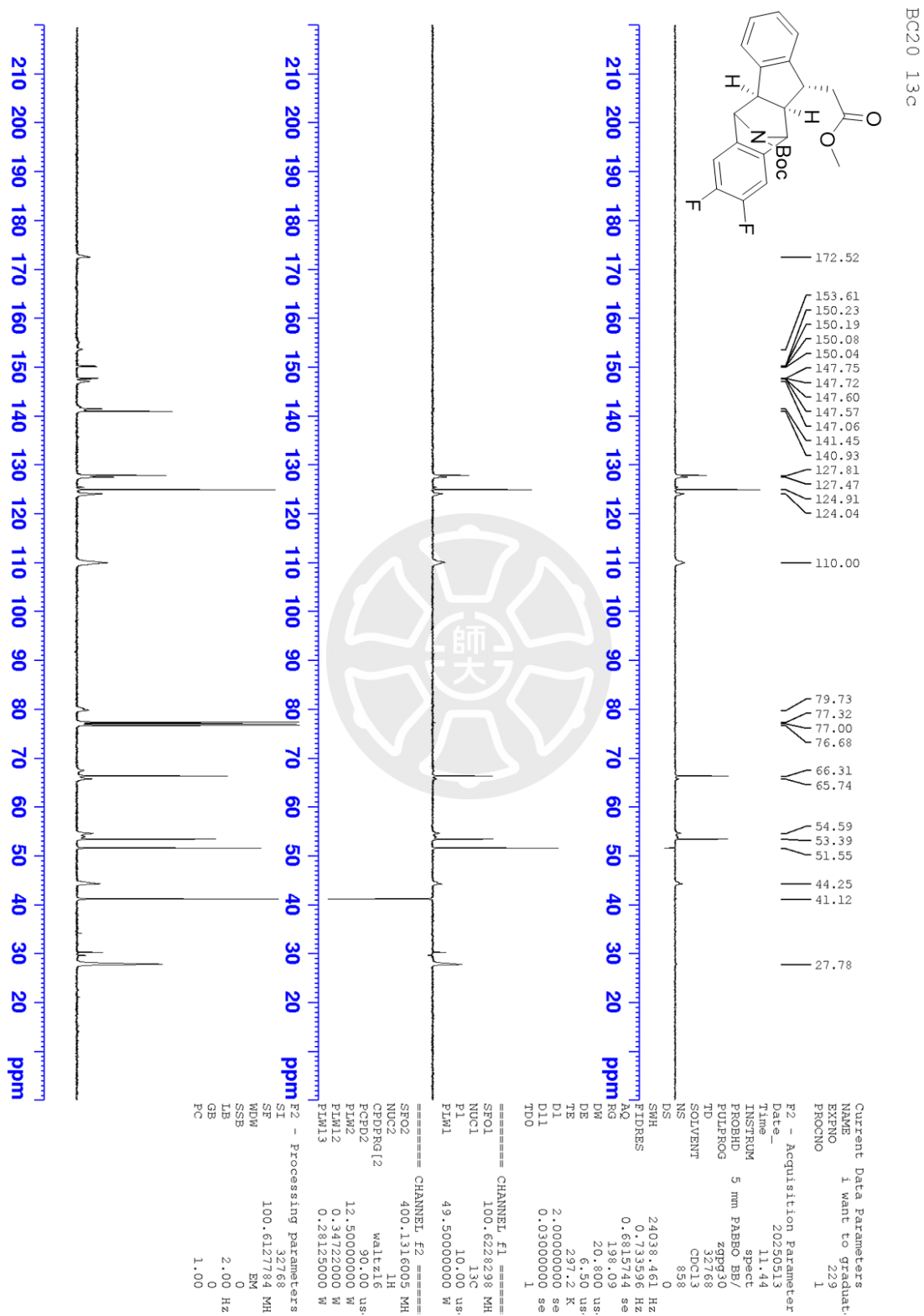
Current Data Parameters
NAME 1 want to graduate
EXPNO 228
PROCNO 1

F2 - Acquisition Parameters
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Time 11:05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 7211.539 Hz
FIDRES 0.220079 Hz
AQ 2.2719147 sec
RG 31.16
DW 69.333 usec
DE 10.06 usec
TE 295.8 K
D1 2.00000000 sec
TD0 1

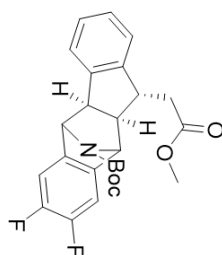
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NUC1 1H
PULC1 15.00 usec
FLW1 13.50000000 W

F2 - Processing parameters
SI 16384
SF 400.1300088 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00
  
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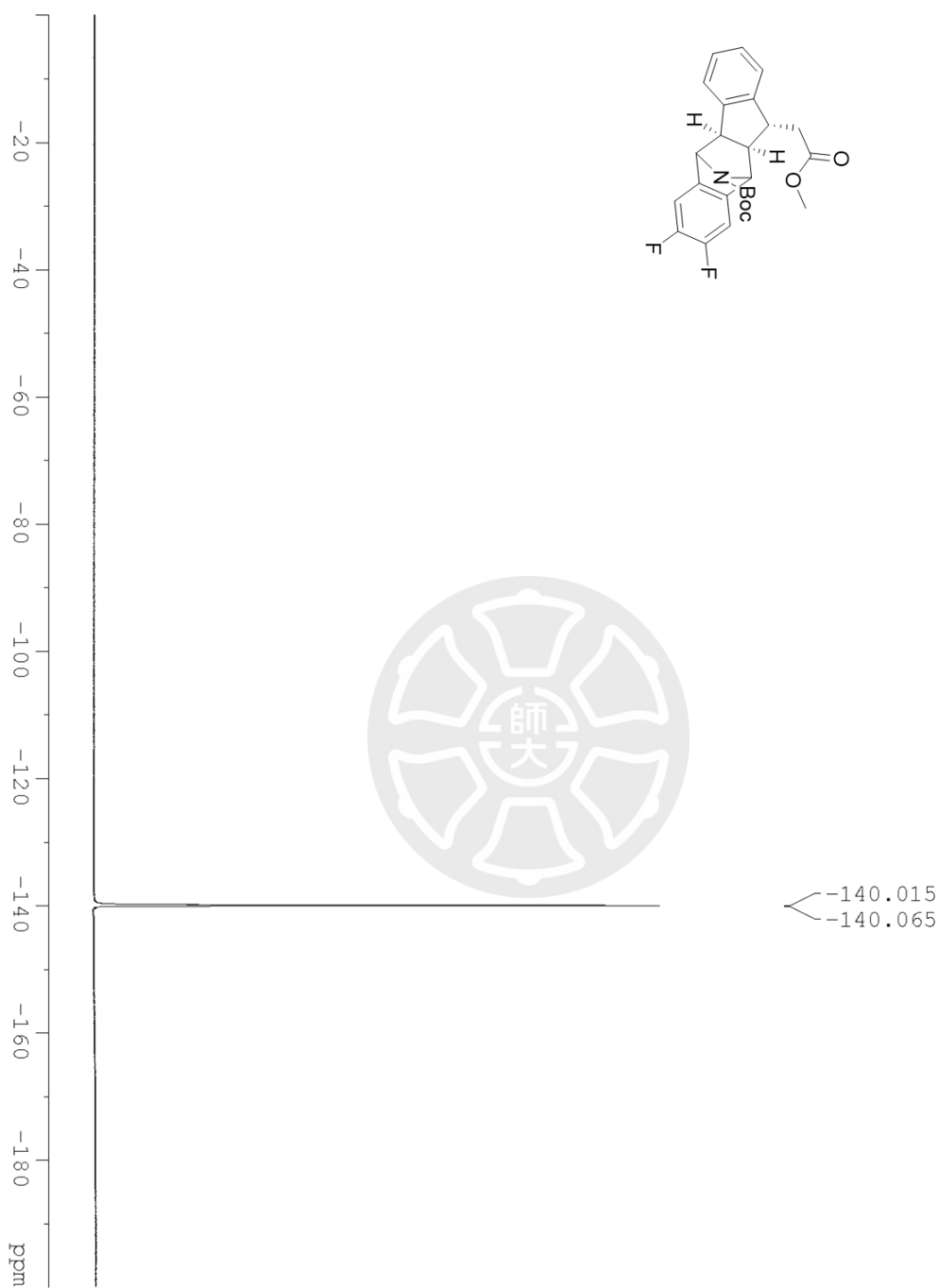
¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-7,8-difluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ia)



¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-7,8-difluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ia)



BC20 19F



Current Data Parameters
 NAME i went to graduate
 EXPNO 233
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20250513
 Time 16.05

INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg

TD 131072
 SOLVENT CDCl3
 NS 4

DS 0
 SWH 89285.711 Hz
 FIDRES 0.681196 Hz

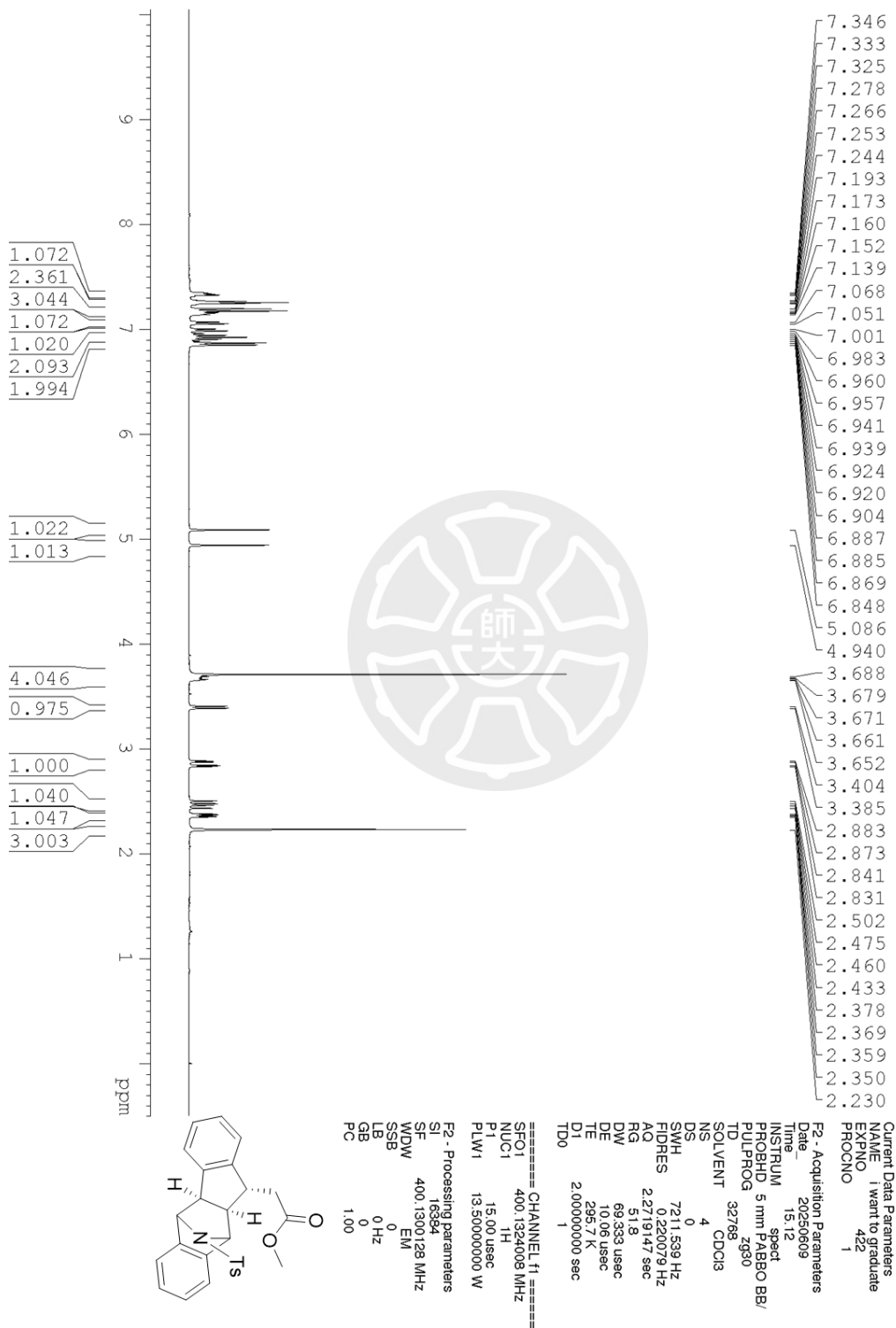
AQ 0.7340032 sec
 RG 198.09
 DE 5.600 usec
 TE 294.5 K
 D1 1.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
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 NUC1 19F
 P1 15.00 usec
 PLW1 16.50000000 W

===== CHANNEL f2 =====
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 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLW12 0.34722000 W

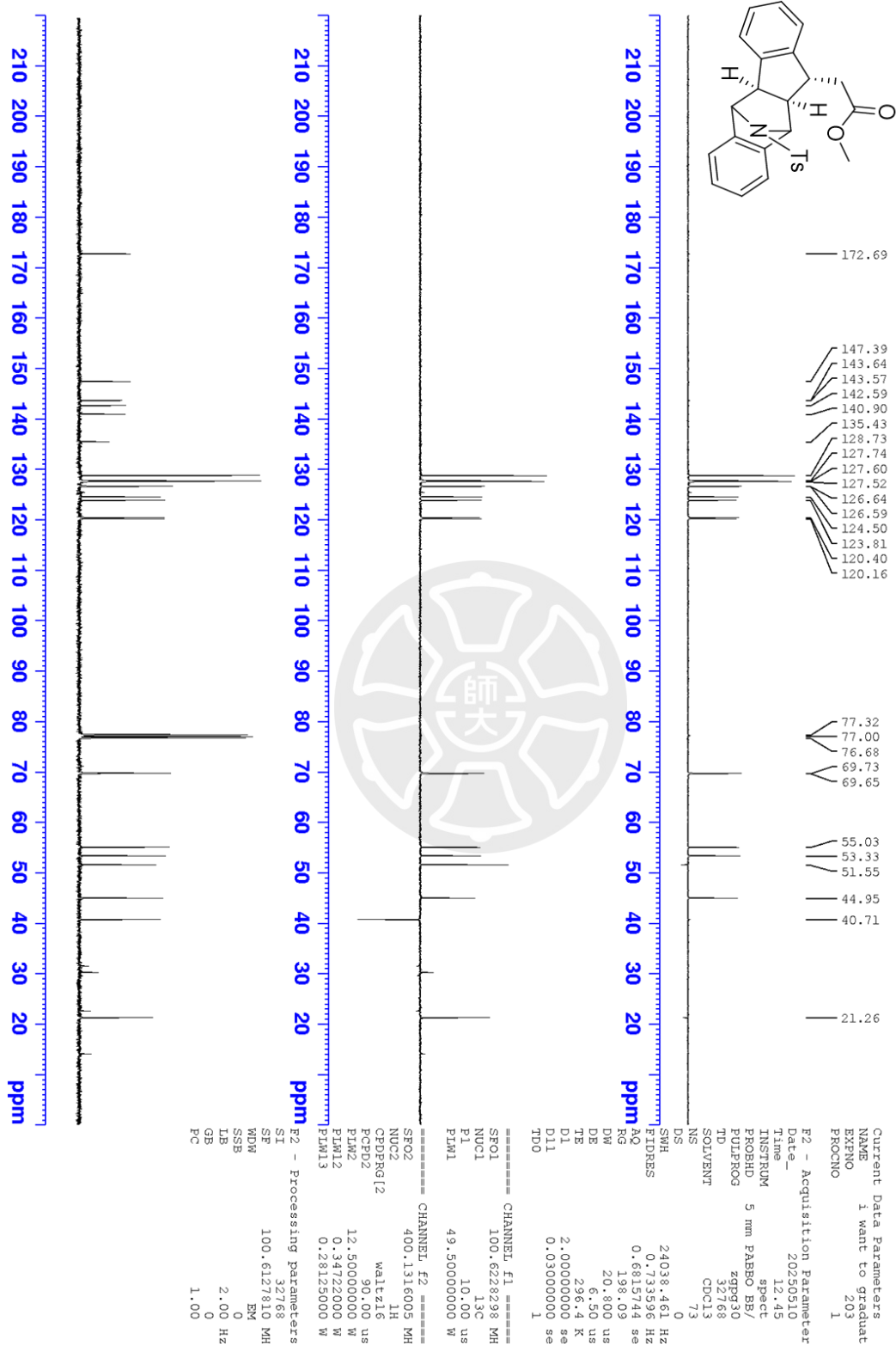
F2 - Processing parameters

¹H NMR spectrum of methyl 2-((4bR,10aR,11R)-12-tosyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl) acetate (27ba)

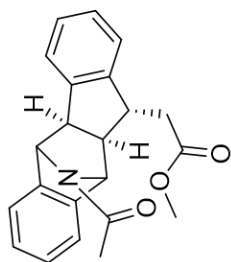
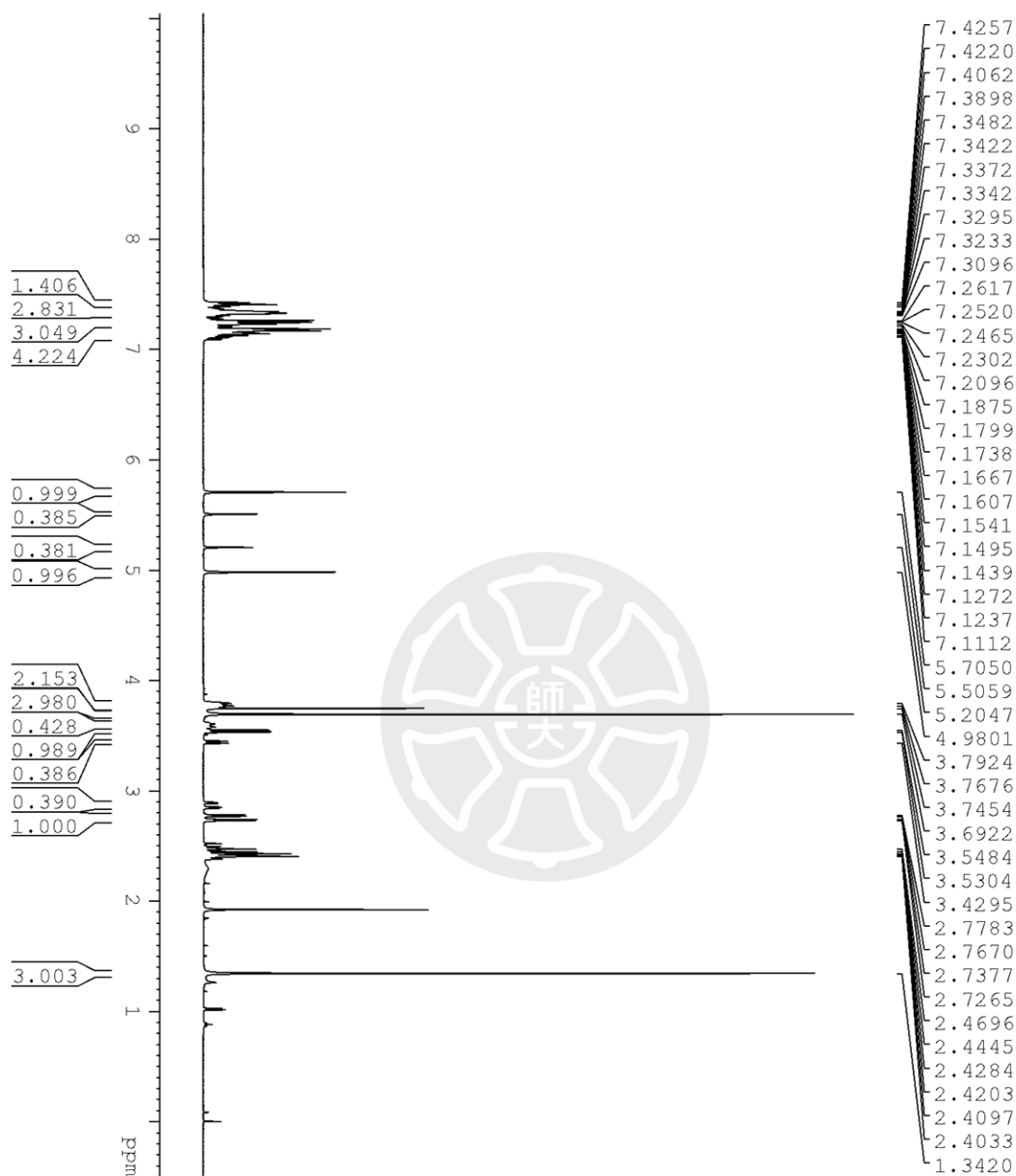


¹³C NMR spectrum of methyl 2-((4bR,10aR,11R)-12-tosyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl) acetate (27ba)

BC21 13C



¹H NMR spectrum of methyl 2-((4bR,10aR,11R)-12-acetyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl) acetate (27ea)



```

Current Data Parameters
NAME      Iwantto graduate
EXPNO    289
PROCNO   1

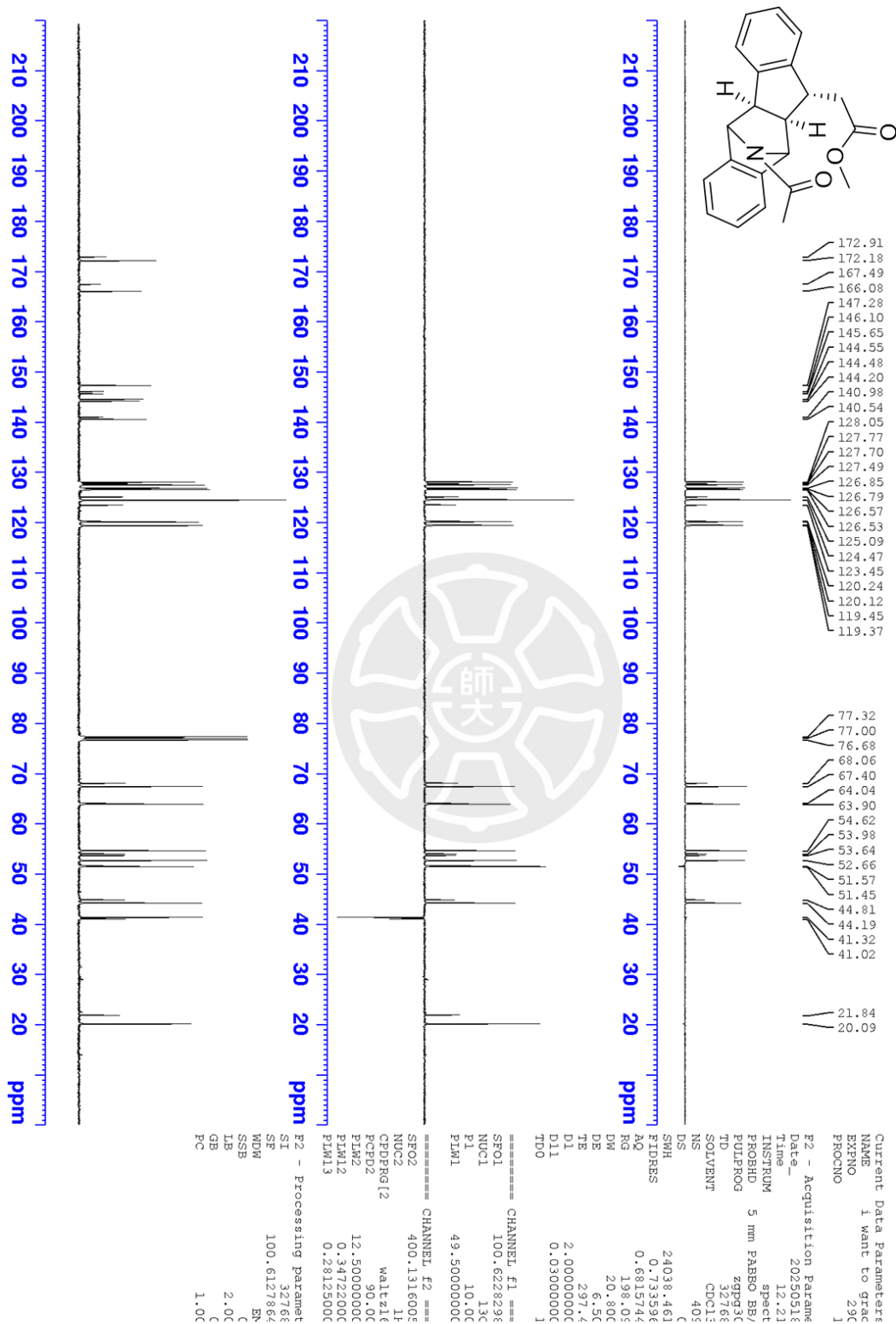
F2 - Acquisition Parameters
Date_    20250518
Time     12:19
INSTRUM  spect
PROBHD   5 mm PARBO BB/
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        4
DS        0
SWH       7211.539 Hz
FIDRES   0.220079 Hz
AQ        2.2719147 sec
RG        36.64
DW        69.333 usec
DE        10.06 usec
TE        297.1 K
D1        2.00000000 sec
TD0       1

===== CHANNEL f1 =====
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NUC1     1H
P1       15.00 usec
PLW1    13.50000000 W

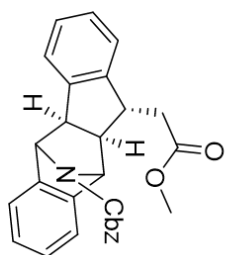
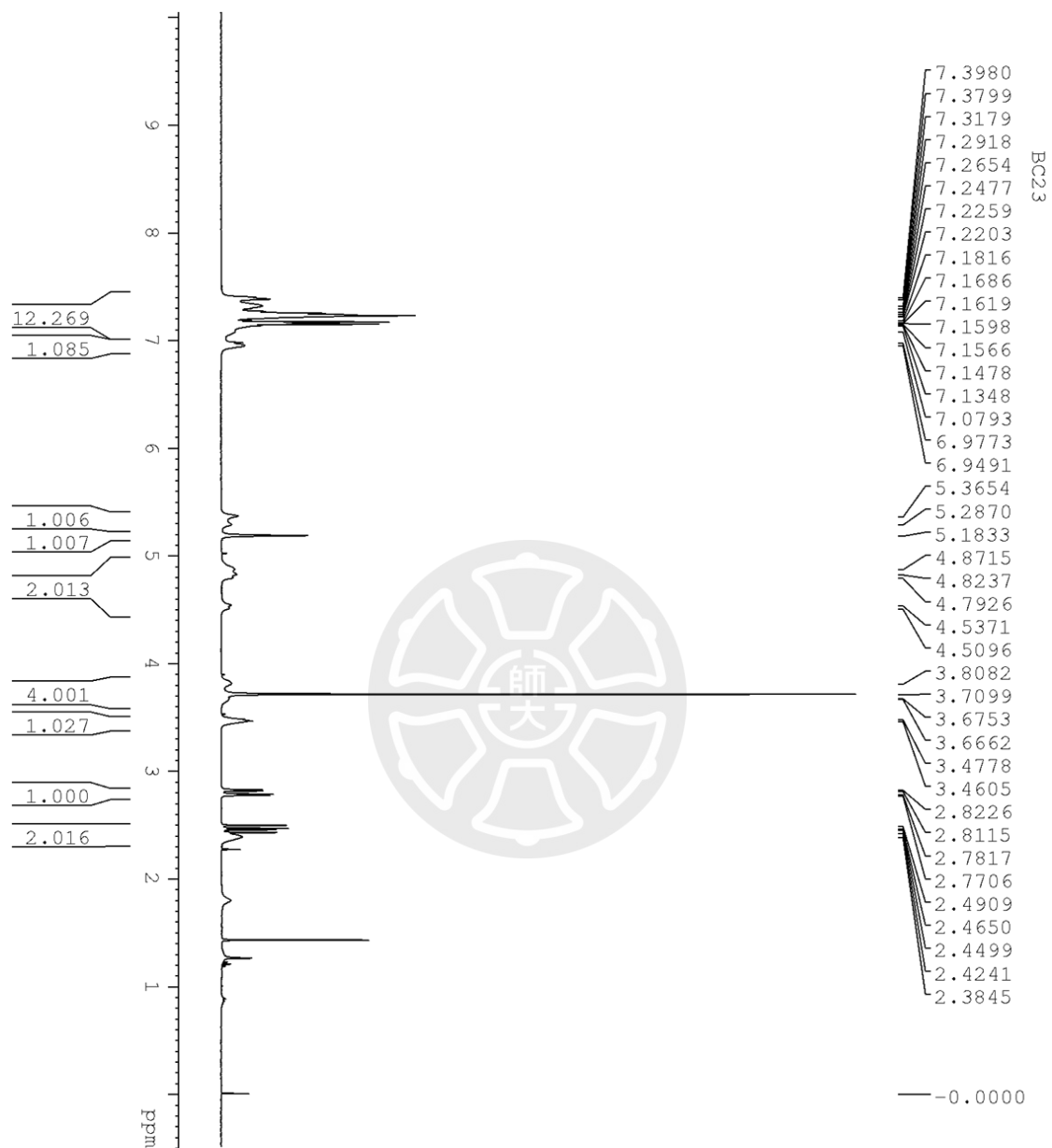
F2 - Processing parameters
SI       16384
SF       400.130090 MHz
WDW      EM
SSB      0
LB       0 Hz
GB       0
PC       1.00
    
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¹³C NMR spectrum of methyl 2-((4bR,10aR,11R)-12-acetyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl) acetate (27ea)

BC22 13c



¹H NMR spectrum of benzyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27da)

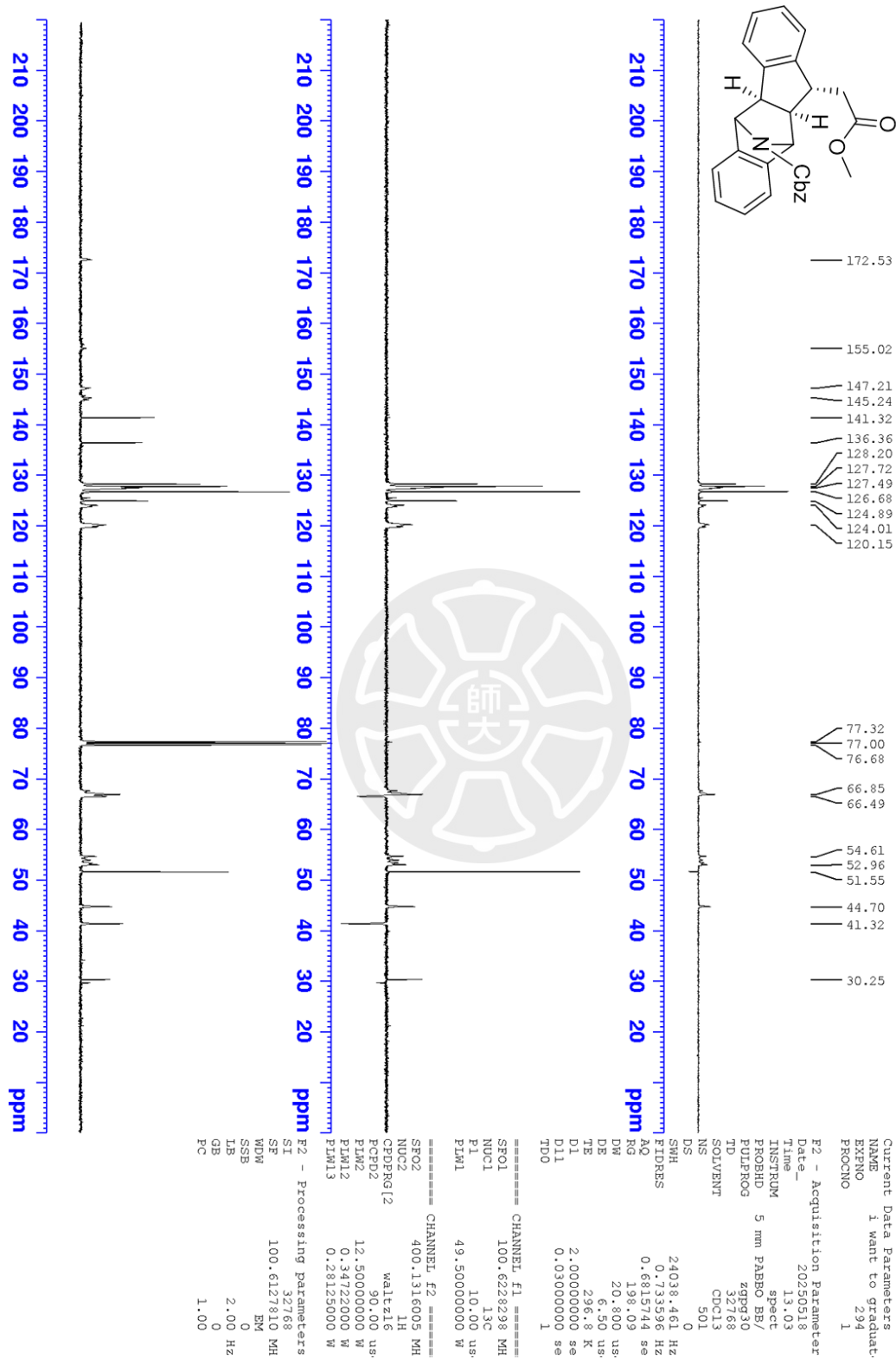


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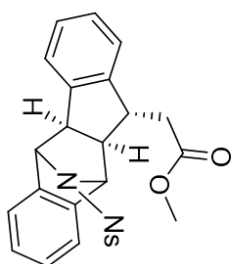
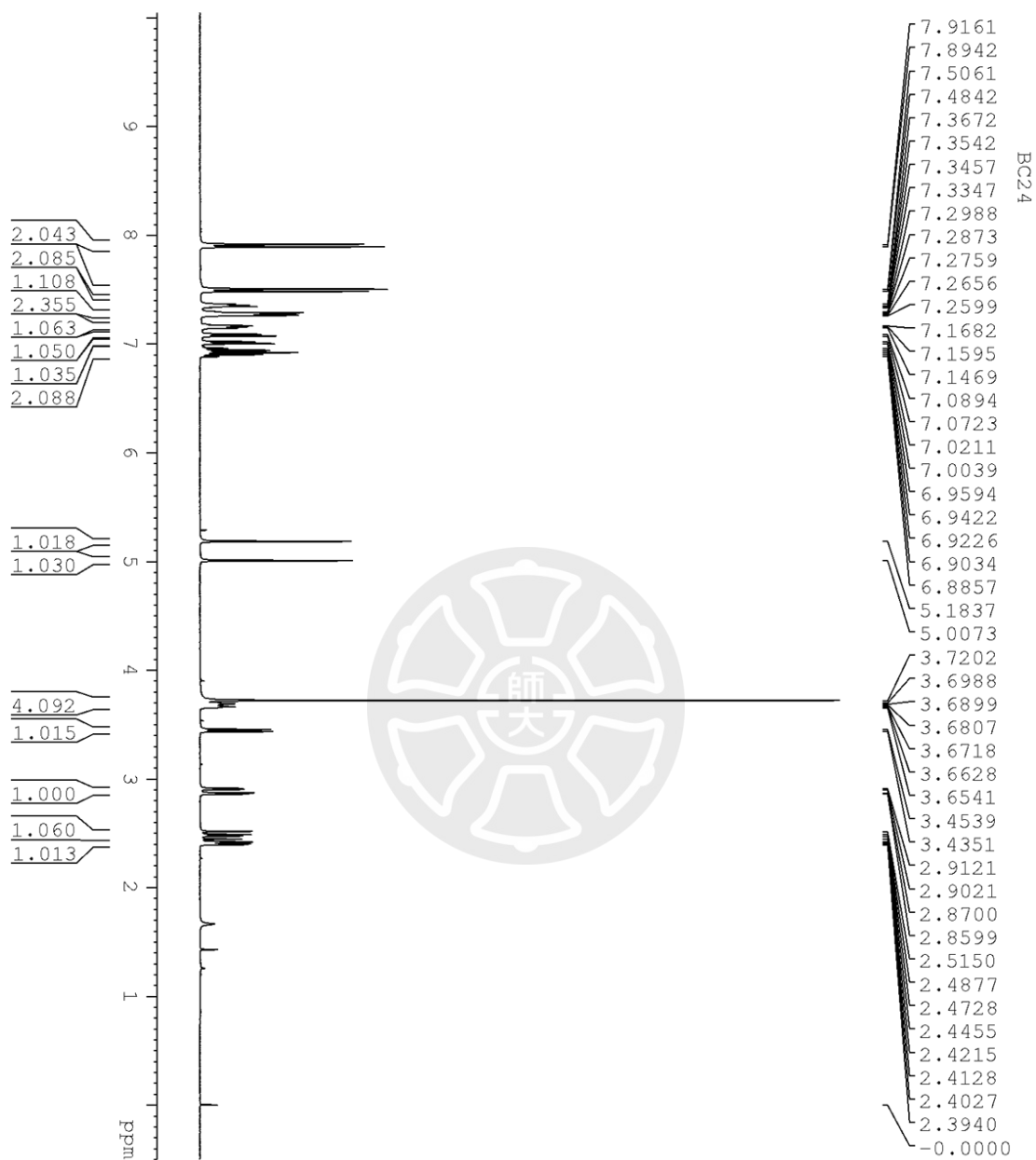
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EXPNO: 283
PROCNO: 1
F2 - Acquisition Parameters
Date_   : 20250518
Time    : 13 01
INSTRUM : spect
PROBHD  : 5 mm PABBO BB/
PULPROG : zg30
TD      : 32768
SOLVENT : CDCl3
NS      : 4
DS      : 0
SWH     : 7211.539 Hz
FIDRES  : 0.220079 Hz
AQ      : 2.2719147 sec
RG      : 45.15
DW      : 69.333 usec
DE      : 10.06 usec
TE      : 296.2 K
D1      : 2.00000000 sec
TD0     : 1
===== CHANNEL f1 =====
SFO1    : 400.1324008 MHz
NUC1    : 1H
P1      : 15.00 usec
PLW1    : 13.50000000 W
F2 - Processing parameters
SI      : 16384
SF      : 400.1300233 MHz
WDW     : EM
SSB     : 0
LB      : 0 Hz
GB      : 0
PC      : 1.00
  
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¹³C NMR spectrum of benzyl (4bR,10aR,11R)-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27da)

BC23 13c



¹H NMR spectrum of methyl 2-((4bR,10aR,11R)-12-((4-nitrophenyl)sulfonyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl)acetate (27ca)



```

Current Data Parameters
NAME      i want to graduate
EXPNO    119
PROCNO   1

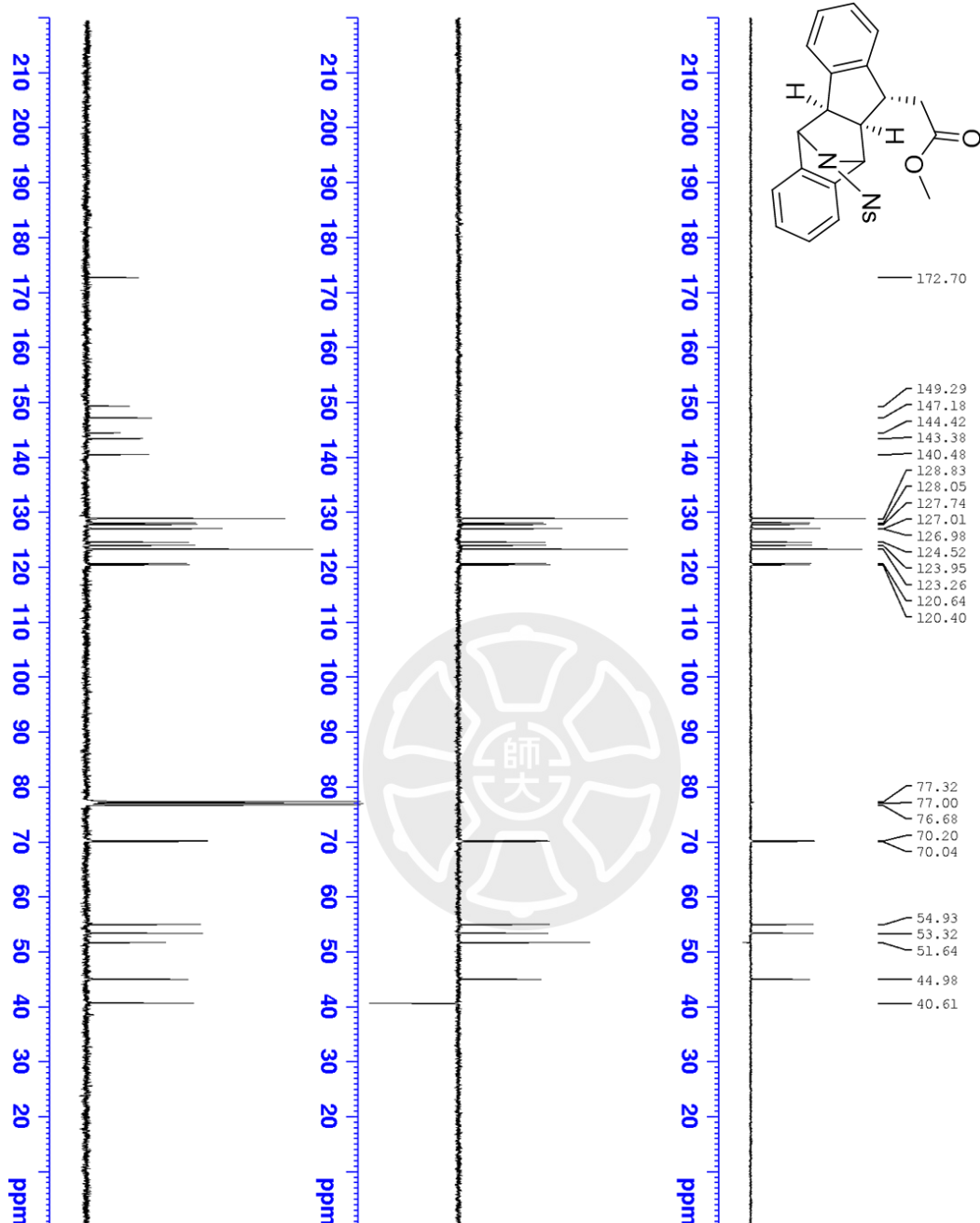
F2 - Acquisition Parameters
Date_    20250502
Time     19.17
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zg30
TD       32768
SOLVENT  CDCl3
NS       4
DS       0
SWH      7211.539 Hz
FIDRES   0.220079 Hz
AQ       2.2719147 sec
RG       63.58
DW       69.333 usec
DE       10.06 usec
TE       296.5 K
D1       2.00000000 sec
TD0      1

===== CHANNEL f1 =====
SFO1     400.1324008 MHz
NUC1     1H
P1       15.00 usec
PLW1     13.50000000 W

F2 - Processing parameters
SI       16384
SF       400.130099 MHz
WDW      EM
SSB      0
LB       0 Hz
GB       0
PC       1.00
    
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¹³C NMR spectrum of methyl 2-((4bR,10aR,11R)-12-((4-nitrophenyl)sulfonyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl)acetate (27ca)

BC24 13C



Current Data Parameters
 NAME I want to graduat
 EXNO 120
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20250502
 Time 19.18
 INSTRUM spect
 PROBHD 5 mm PABO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 91
 DS 0

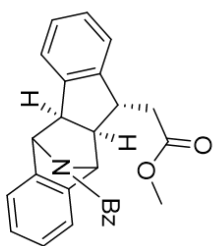
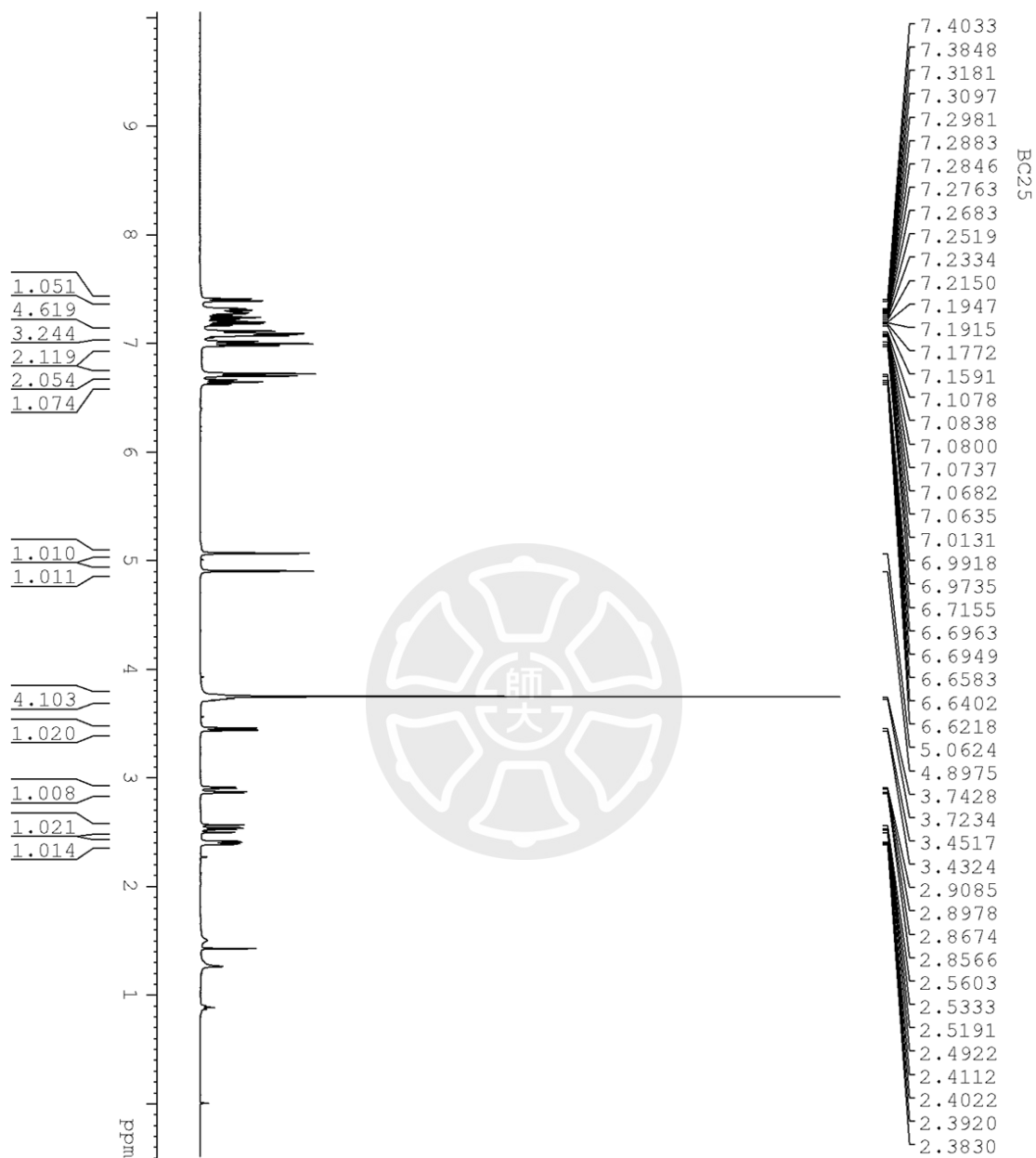
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 TE 286.6 K
 D1 2.00000000 s
 D11 0.03000000 s
 TDO 1

==== CHANNEL F1 =====
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 NUCL1 13C
 P1 10.00 us
 PLM1 49.50000000 W

==== CHANNEL F2 =====
 SFO2 400.1316005 MHz
 NUCL2 1H
 CPDPRG12 waltz16
 PCPD2 90.00 us
 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing parameters:
 SI 39768
 SF 100.6127771 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of methyl 2-((4bR,10aR,11R)-12-benzoyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl)acetate (27fa)



Current Data Parameters
 NAME i want to graduate
 EXPNO 259
 PROCNO 1

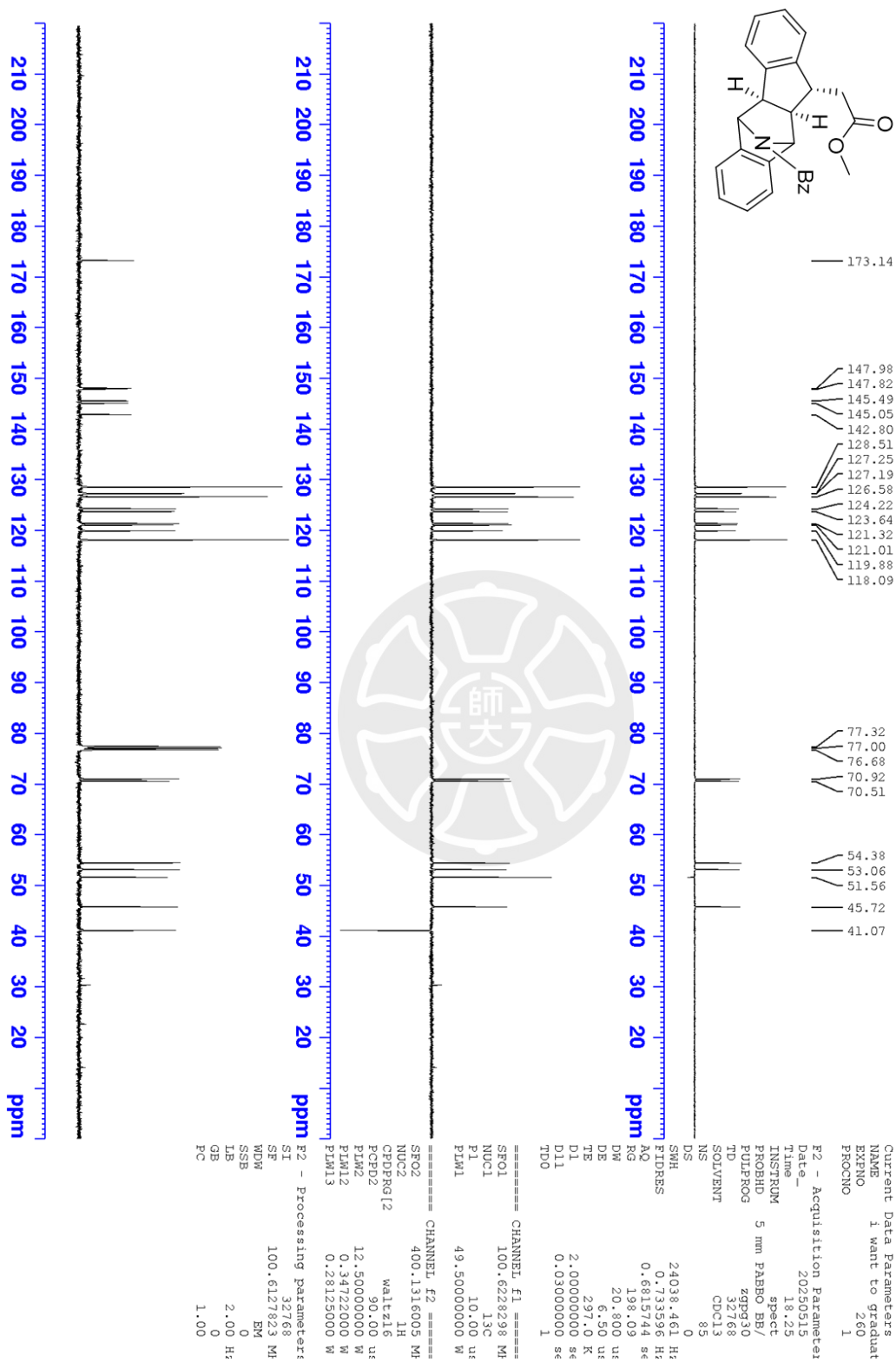
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 Time 18.23
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 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 7211.539 Hz
 FIDRES 0.220079 Hz
 AQ 2.2719147 sec
 RG 38.89
 DW 69.333 usec
 DE 10.06 usec
 TE 296.3 K
 D1 2.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 400.1324008 MHz
 NUC1 1H
 P1 15.00 usec
 PLW1 13.500000000 W

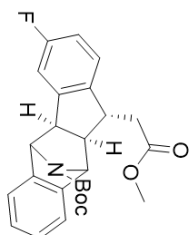
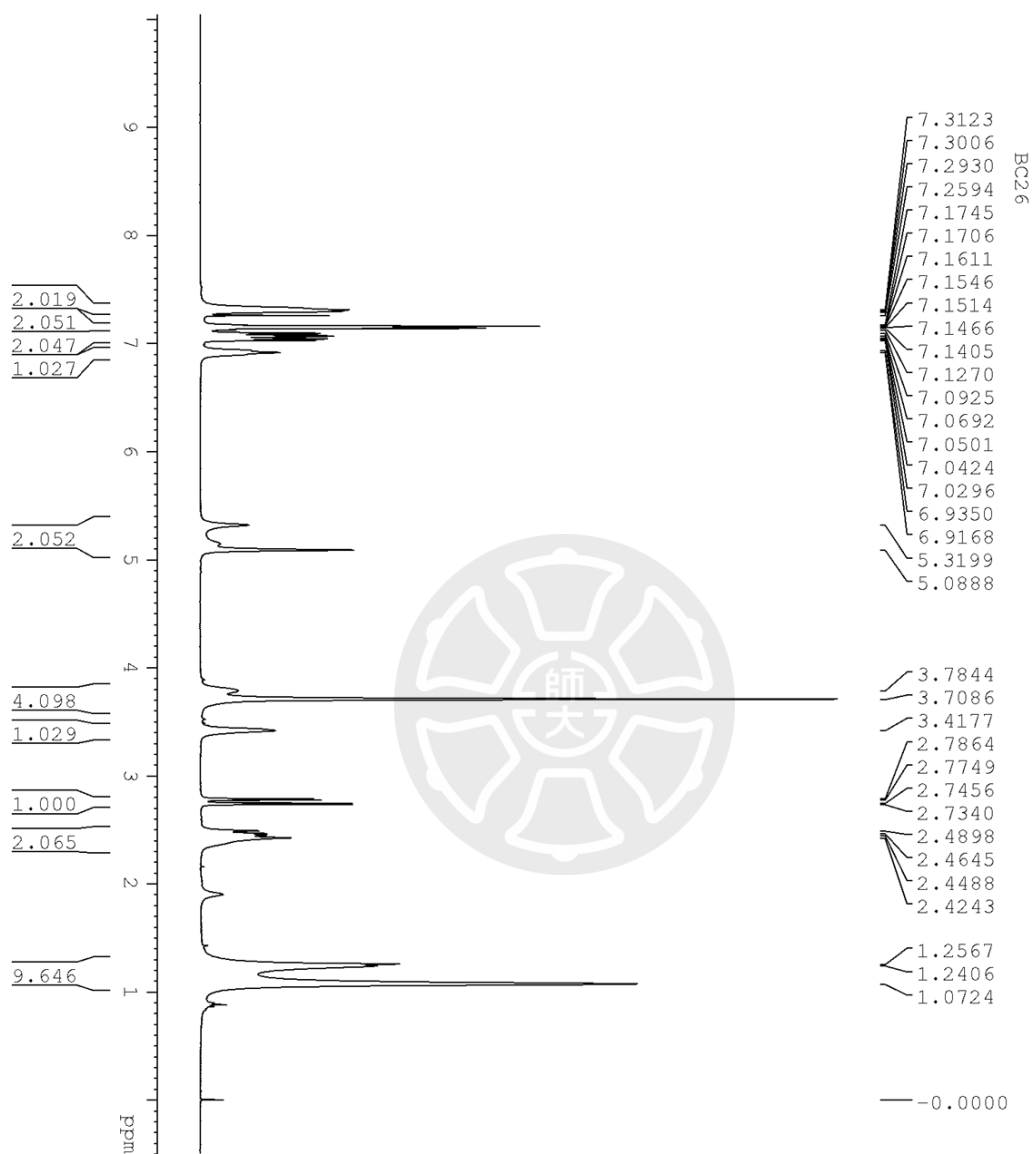
F2 - Processing parameters
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 SF 400.1300371 MHz
 WDW EM
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.00

¹³C NMR spectrum of methyl 2-((4bR,10aR,11R)-12-benzoyl-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluoren-11-yl)acetate (27fa)

BC25 13c



¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-3-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27af)



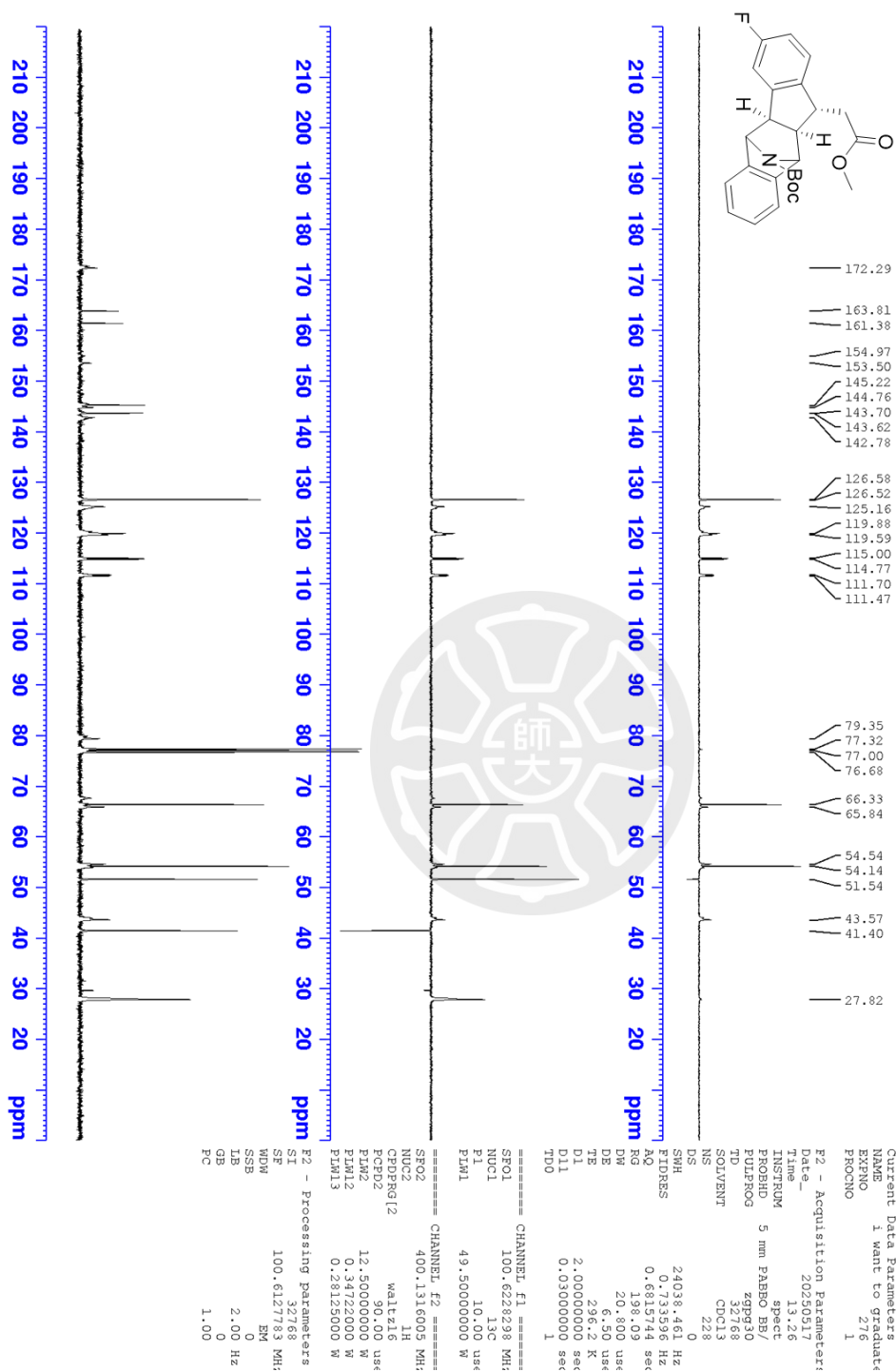
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Current Data Parameters
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EXPNO    2/5
PROCNO   1
F2 - Acquisition Parameters
Date_    20250717
Time     13:25
INSTRUM  spect
PROBHD   5 mm F4BBO BB/
PULPROG  zg30
TD        32768
SOLVENT  CDCl3
NS        4
DS        0
SWH       7211.539 Hz
FIDRES    0.220079 Hz
AQ        2.2719147 sec
RG        683.639
DWDW      683.639 usec
DE        10.06 usec
TE        296.9 K
D1        2.00000000 sec
TD0       1

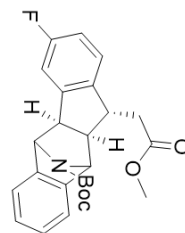
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NUC1     1H
P1       15.00 usec
PLW1     13.50000000 W

F2 - Processing parameters
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WDW       EM
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LB        0 Hz
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PC        1.00
  
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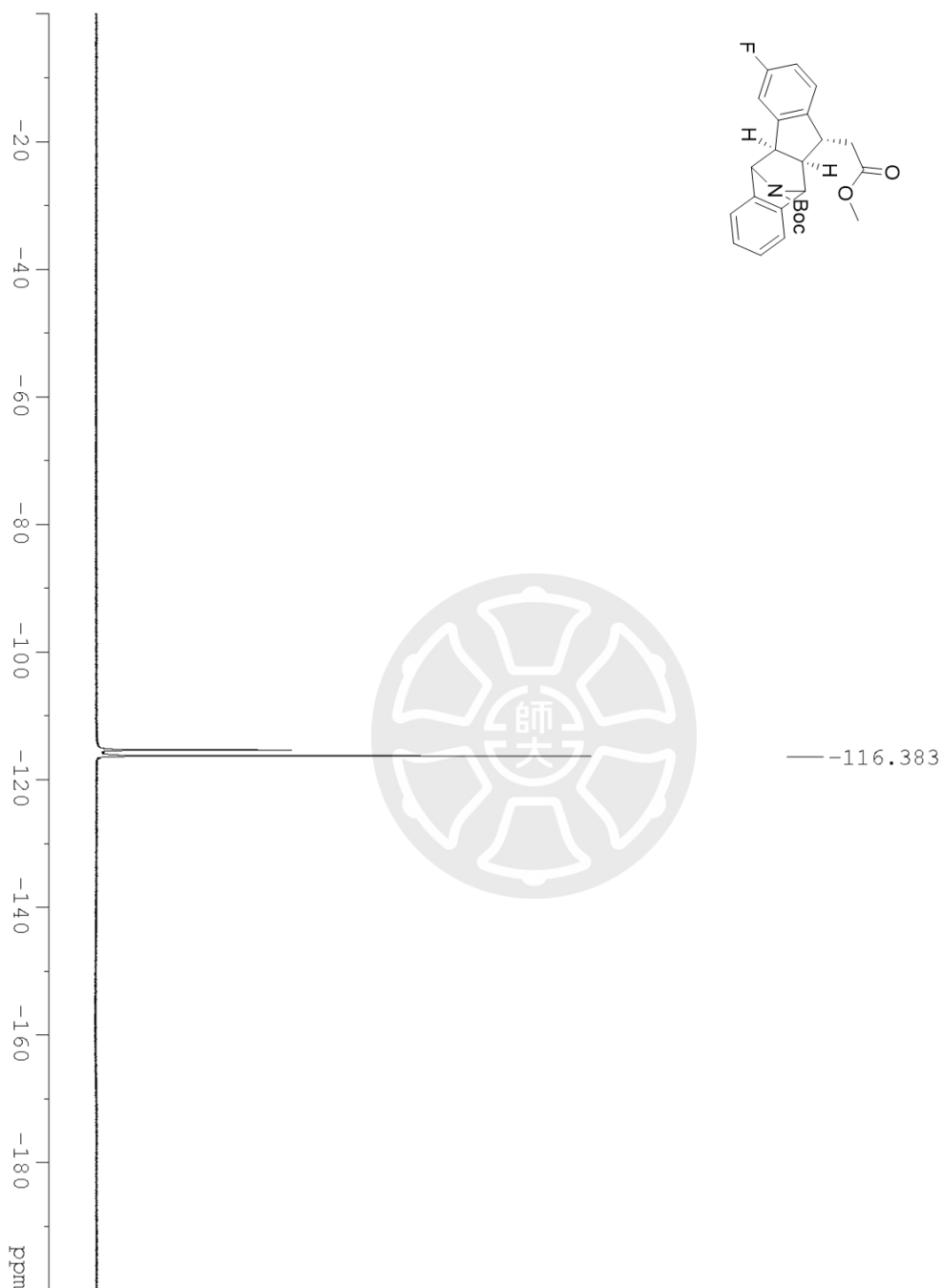
¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-3-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27af)



¹⁹F NMR spectrum of tert-butyl (4bR,10aR,11R)-3-fluoro-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27af)



BC27 19F



— -116.383

```

Current Data Parameters
NAME      I want to graduate
EXPNO     288
PROCNO    1

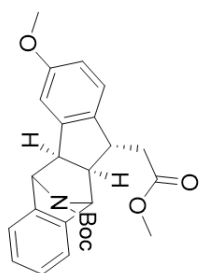
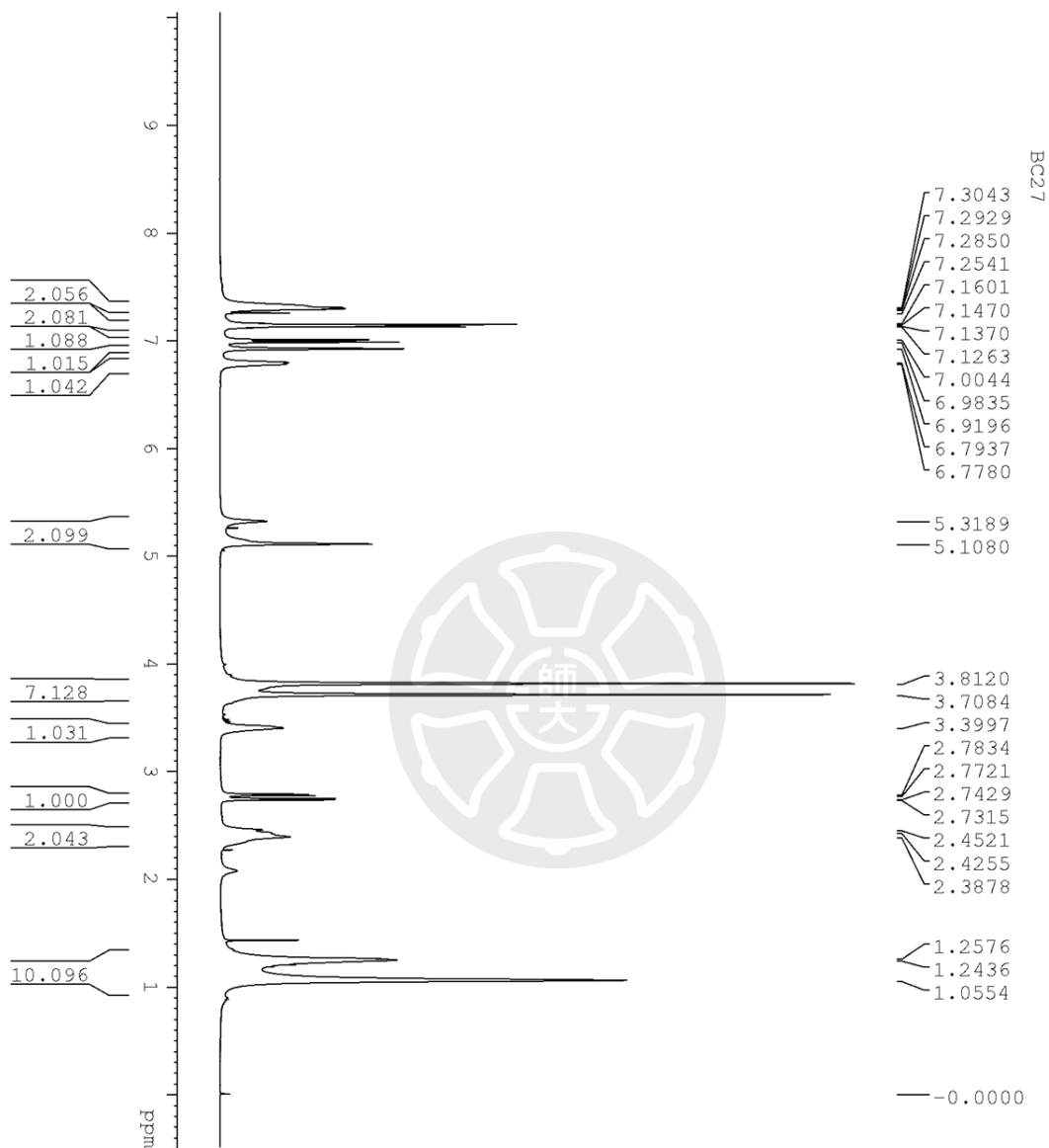
F2 - Acquisition Parameters
Date_     20250518
Time      12.08
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg
TD         131072
SOLVENT   CDCl3
NS         4
DS         0
SWH        89285.711 Hz
FIDRES     0.681196 Hz
AQ         0.7340032 sec
RG         198.09
DW         5.600 usec
DE         6.50 usec
TE         297.1 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      376.4807168 MHz
NUC1      19F
P1         15.00 usec
PLW1      16.50000000 W

===== CHANNEL f2 =====
SFO2      400.1316005 MHz
NUC2      1H
CPDPRG2   waltz16
PCPD2     90.00 usec
PLW2      12.50000000 W
PLW12     0.34722000 W

F2 - Processing parameters
    
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¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-3-methoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)



```

===== CHANNEL f1 =====
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NUC1 1H
P1 15.00 usec
PLW1 13.50000000 W

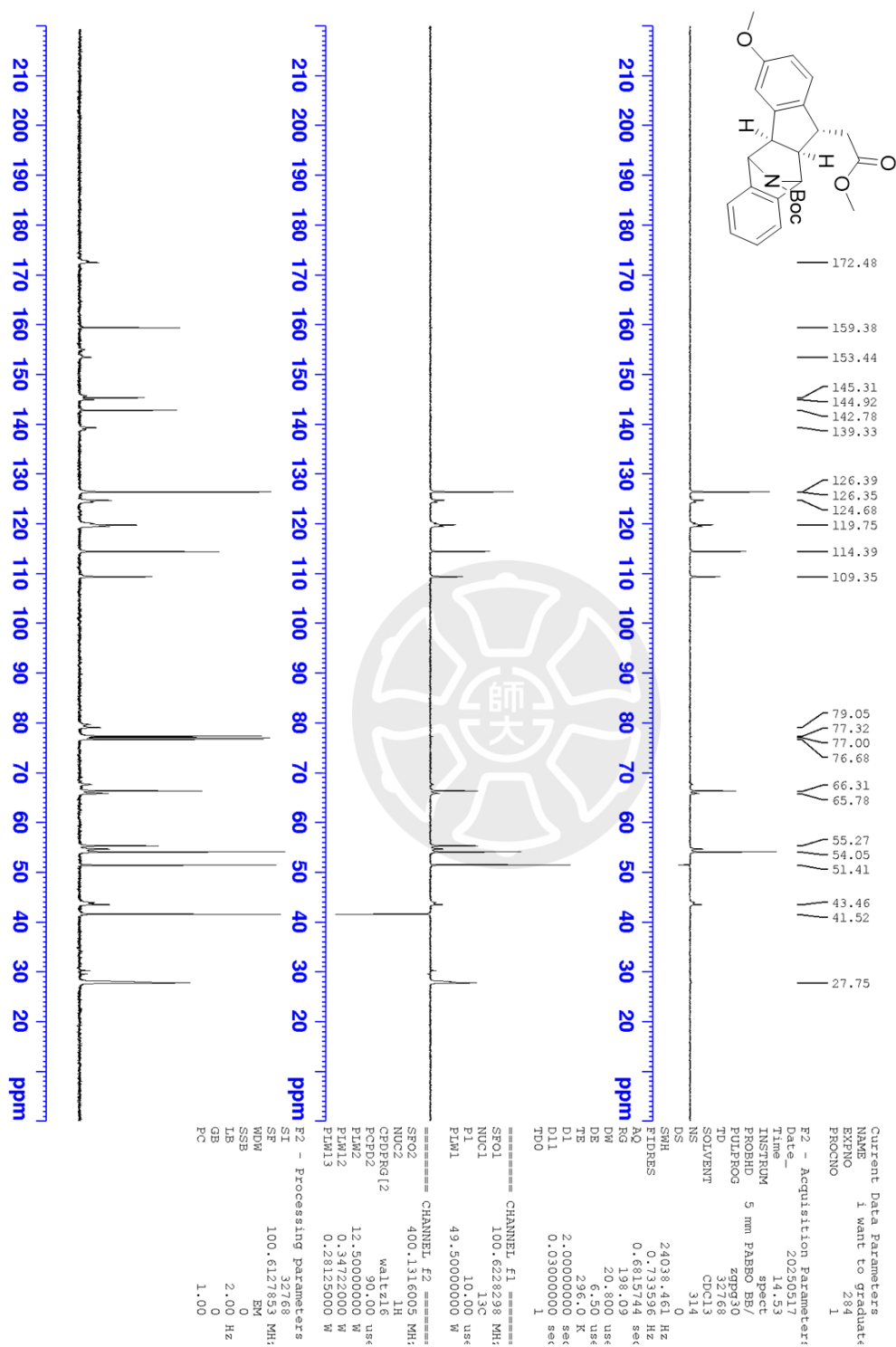
F2 - Processing parameters
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WDW EM
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LB 0 Hz
GB 0
PC 1.00
    
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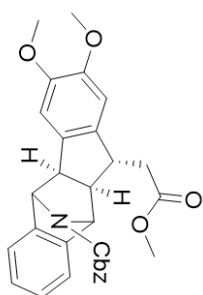
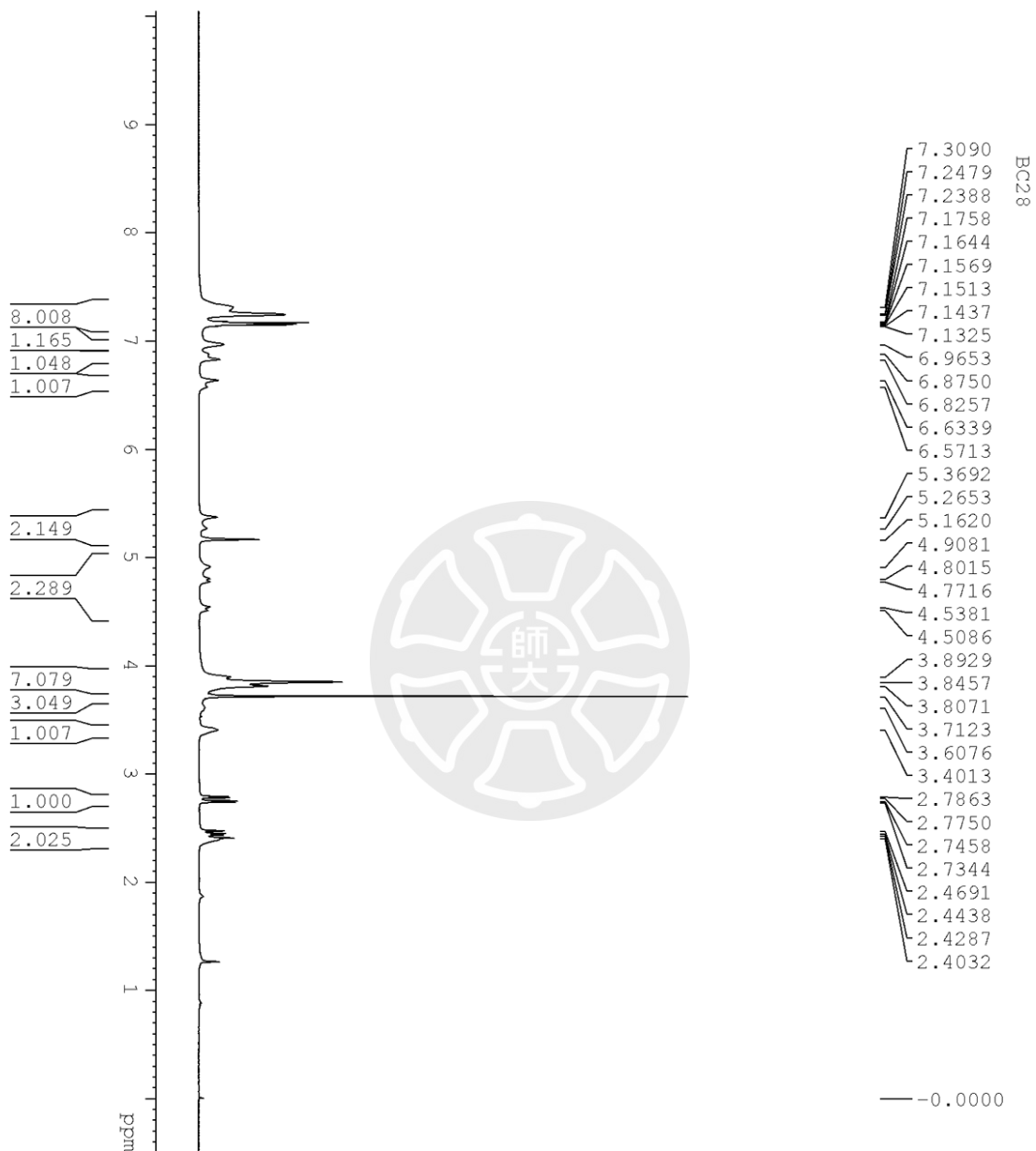
Current Data Parameters
NAME i want to graduate
EXPNO 283
PROCNO 1

F2 - Acquisition Parameters
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4
DS 0
SWH 7211.539 Hz
FDRS 0.220079 Hz
AQ 2.2719147 sec
RG 22.62
DE 69.333 usec
TE 285.7 K
D1 2.00000000 sec
TD0 1
    
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¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-3-methoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ai)



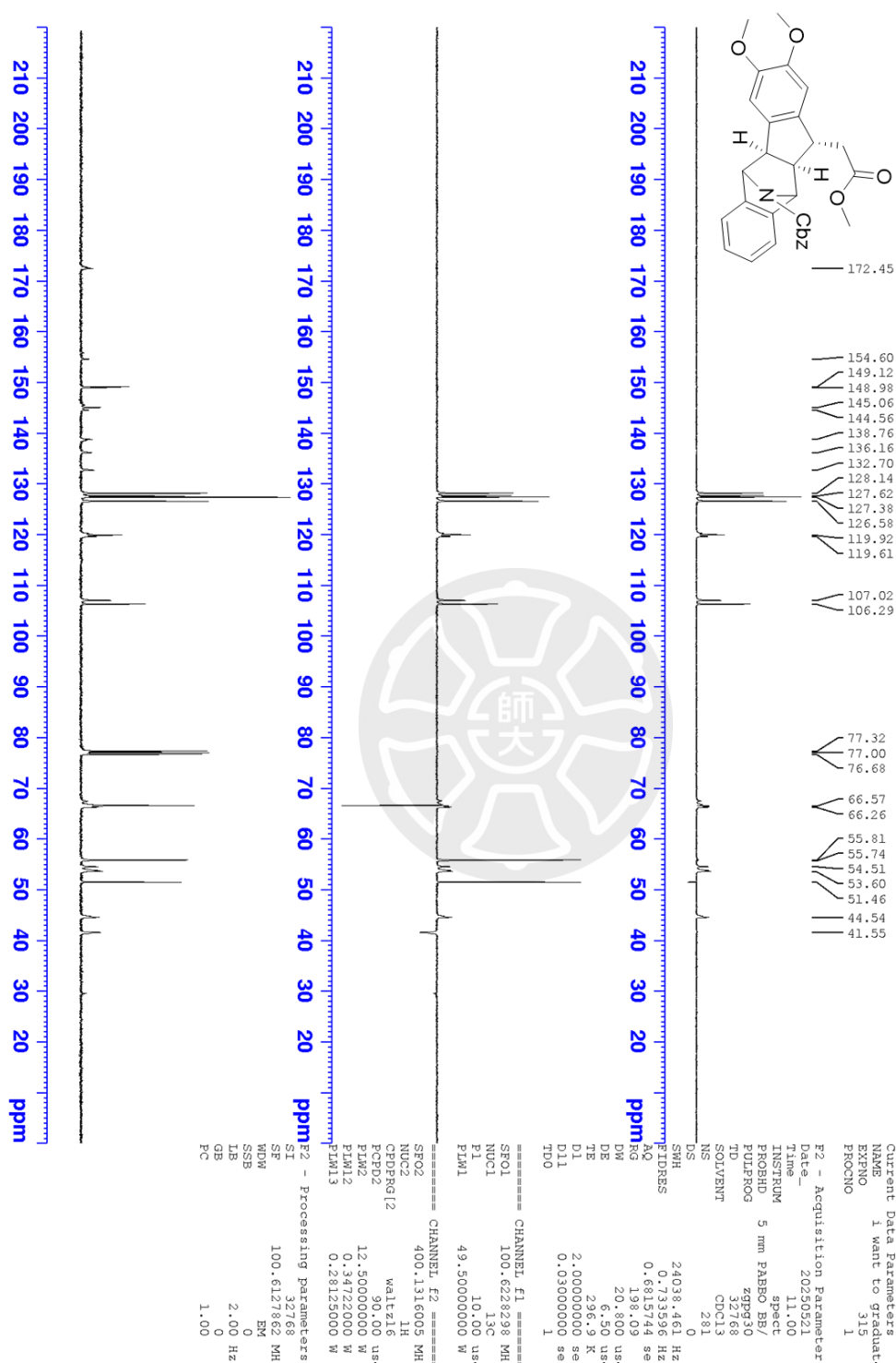
¹H NMR spectrum of benzyl (4bR,10aR,11R)-2,3-dimethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate **BC28**



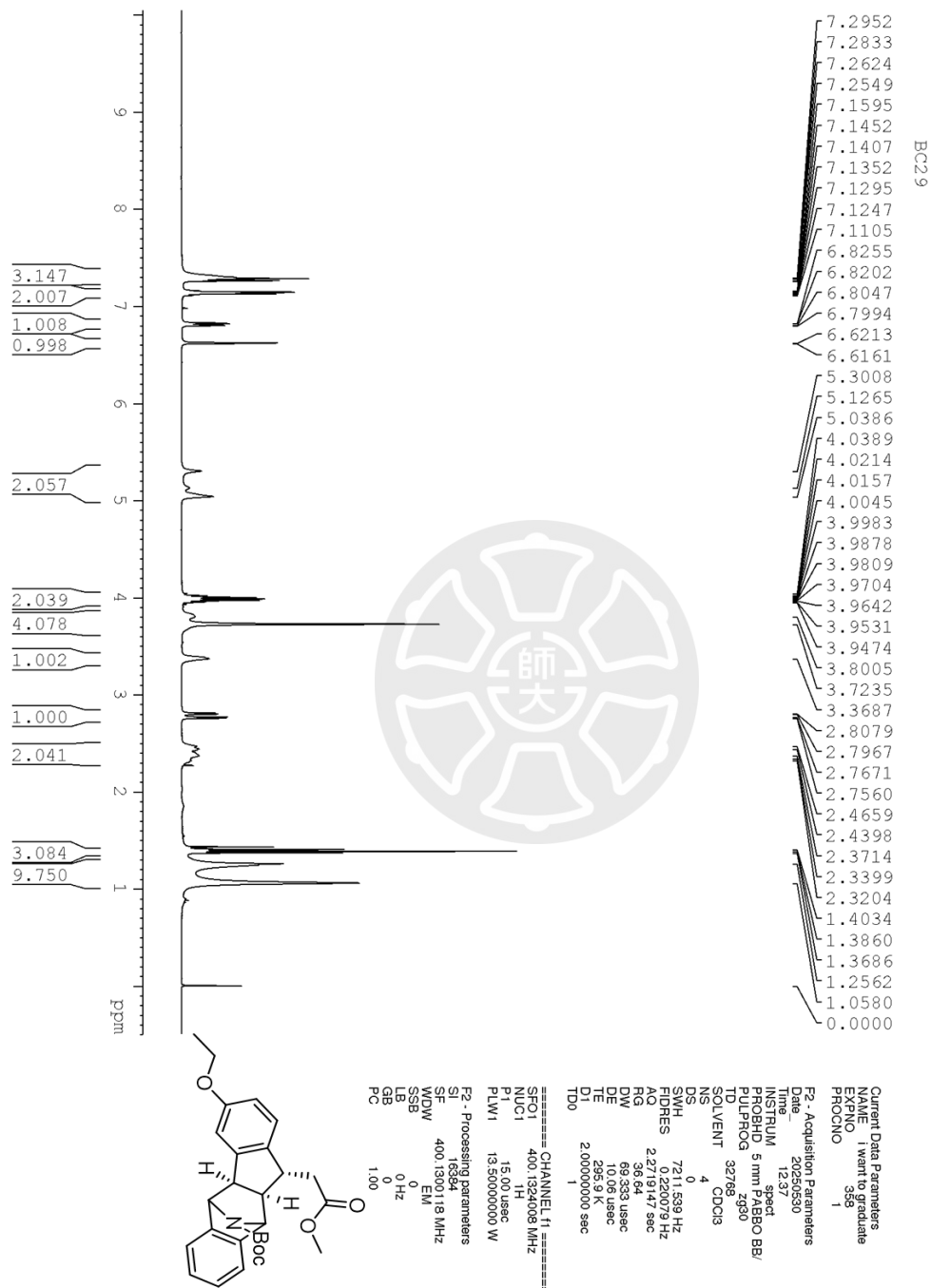
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EXPNO: 314
PROCNO: 1
F2 - Acquisition Parameters
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Time: 10.59
INSTRUM: spect
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 4
DS: 0
SWH: 7211.539 Hz
FIDRES: 0.22079 Hz
AQ: 2.2719147 sec
RG: 31.16
DVI: 68.333 usec
DE: 10.09 usec
TE: 296.3 K
D1: 2.00000000 sec
TD0: 1
===== CHANNEL f1 =====
SFO1: 400.1324008 MHz
NUC1: 1H
P1: 15.00 usec
PLW1: 13.50000000 W
F2 - Processing parameters
SI: 6584
SF: 400.1300142 MHz
WDW: EM
SSB: 0 Hz
LB: 0 Hz
GB: 0
PC: 1.00
  
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¹³C NMR spectrum of benzyl (4bR,10aR,11R)-2,3-dimethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate **BC28**

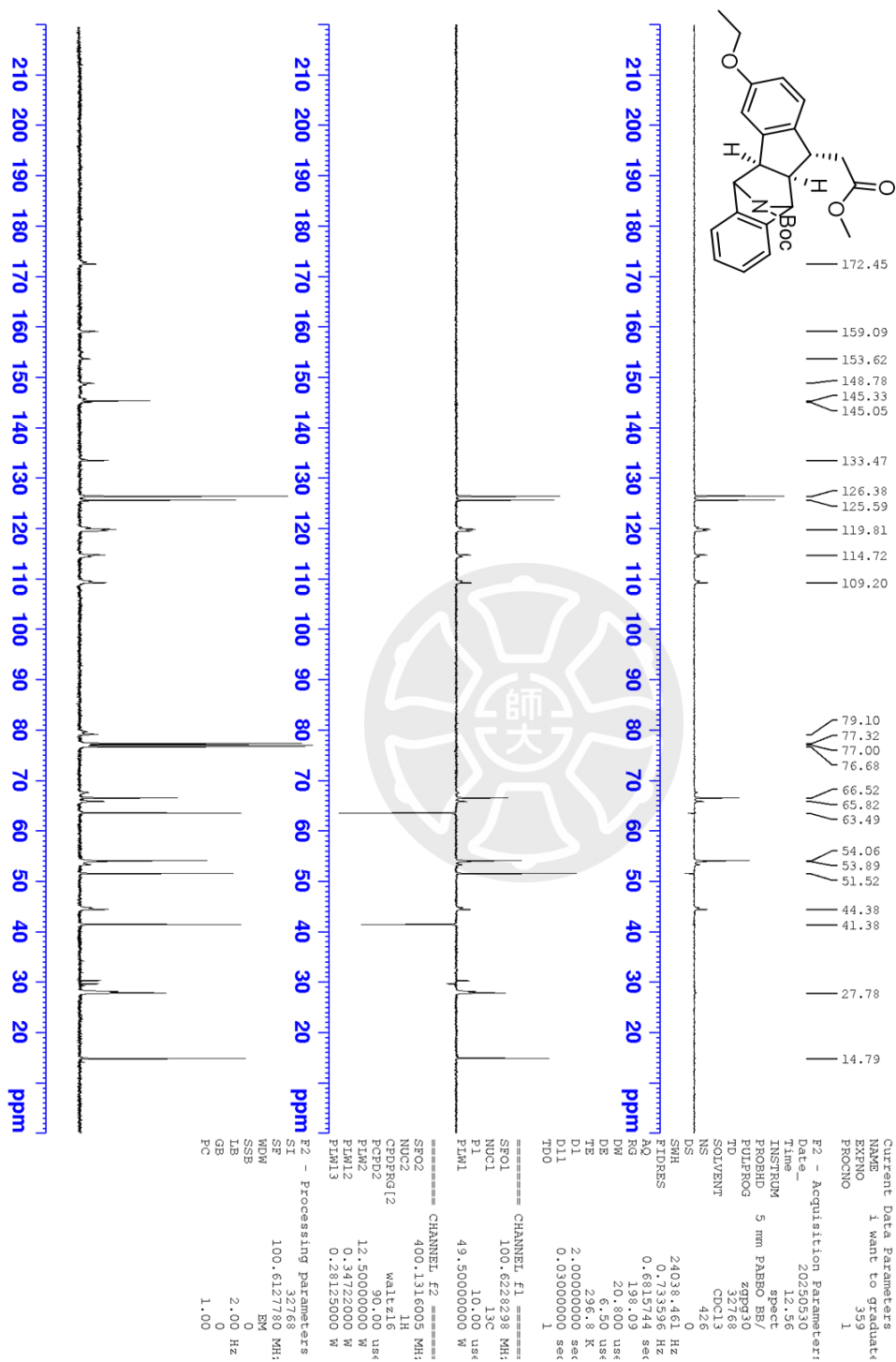


¹H NMR spectrum of tert-butyl (4bR,10aR,11R)-3-ethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ao)

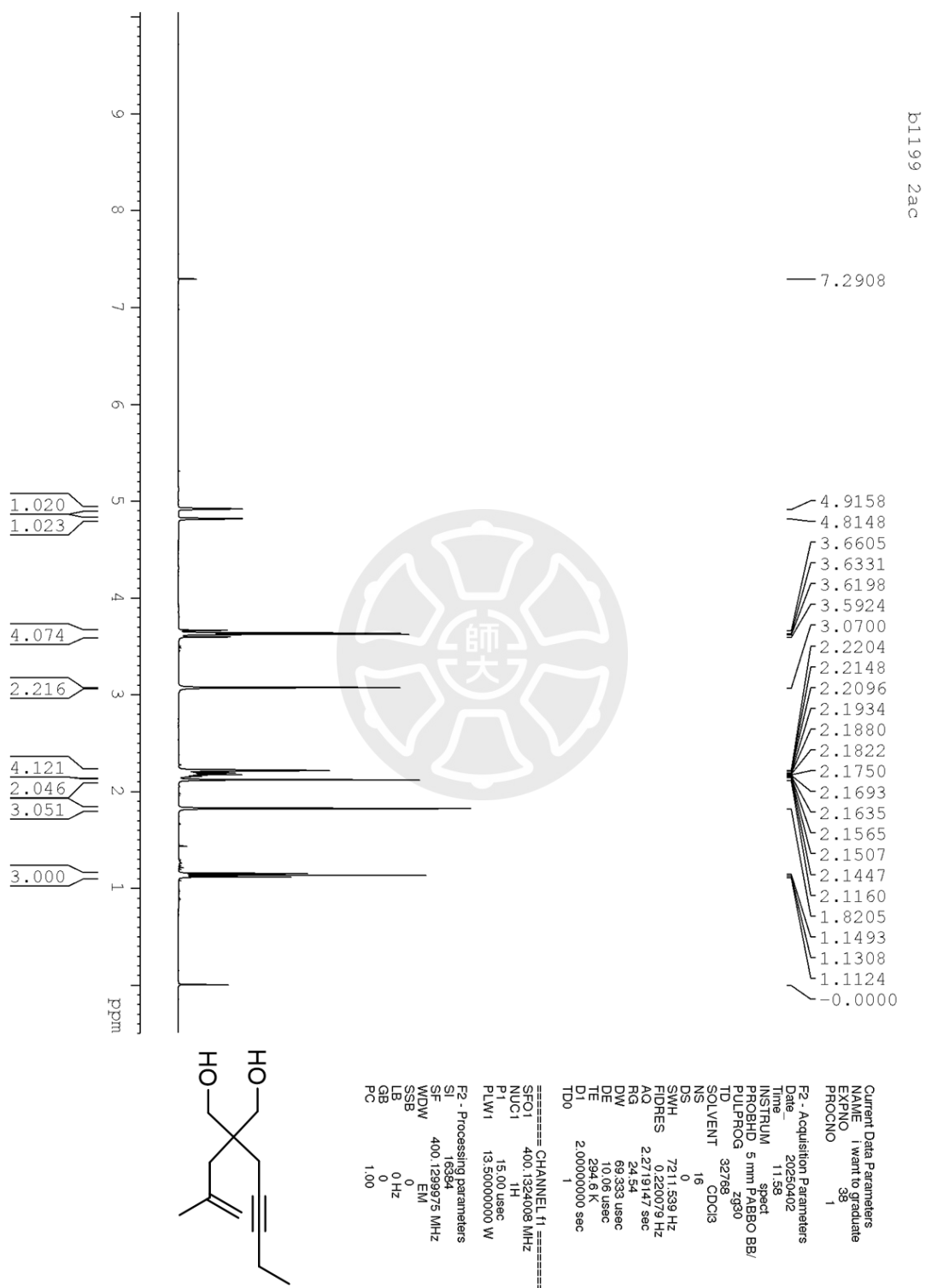


¹³C NMR spectrum of tert-butyl (4bR,10aR,11R)-3-ethoxy-11-(2-methoxy-2-oxoethyl)-4b,10,10a,11-tetrahydro-5H-5,10-epiminobenzo[b]fluorene-12-carboxylate (27ao)

BC29 13C

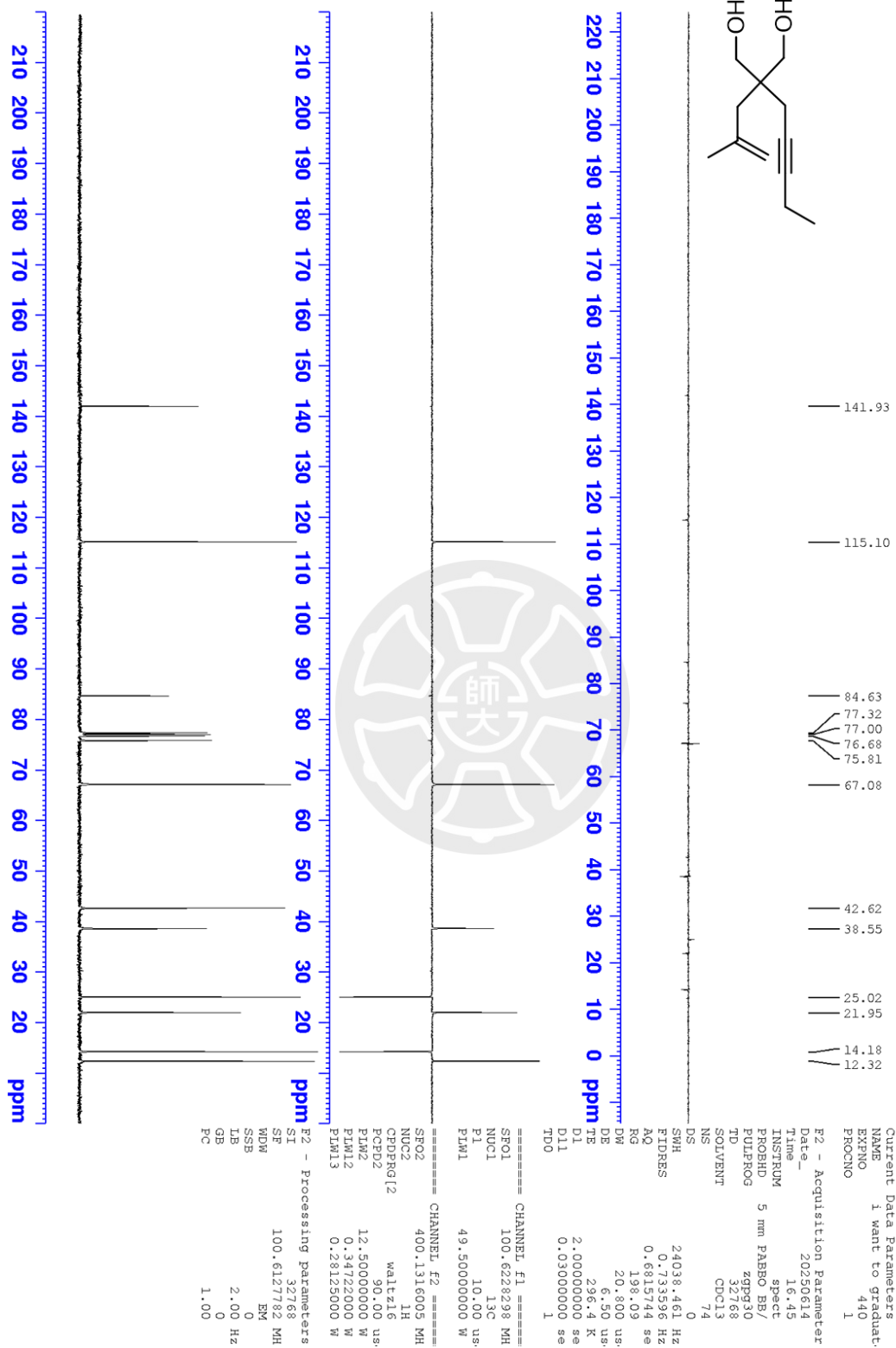
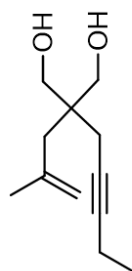


¹H NMR spectrum of 2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diol
(SC1)

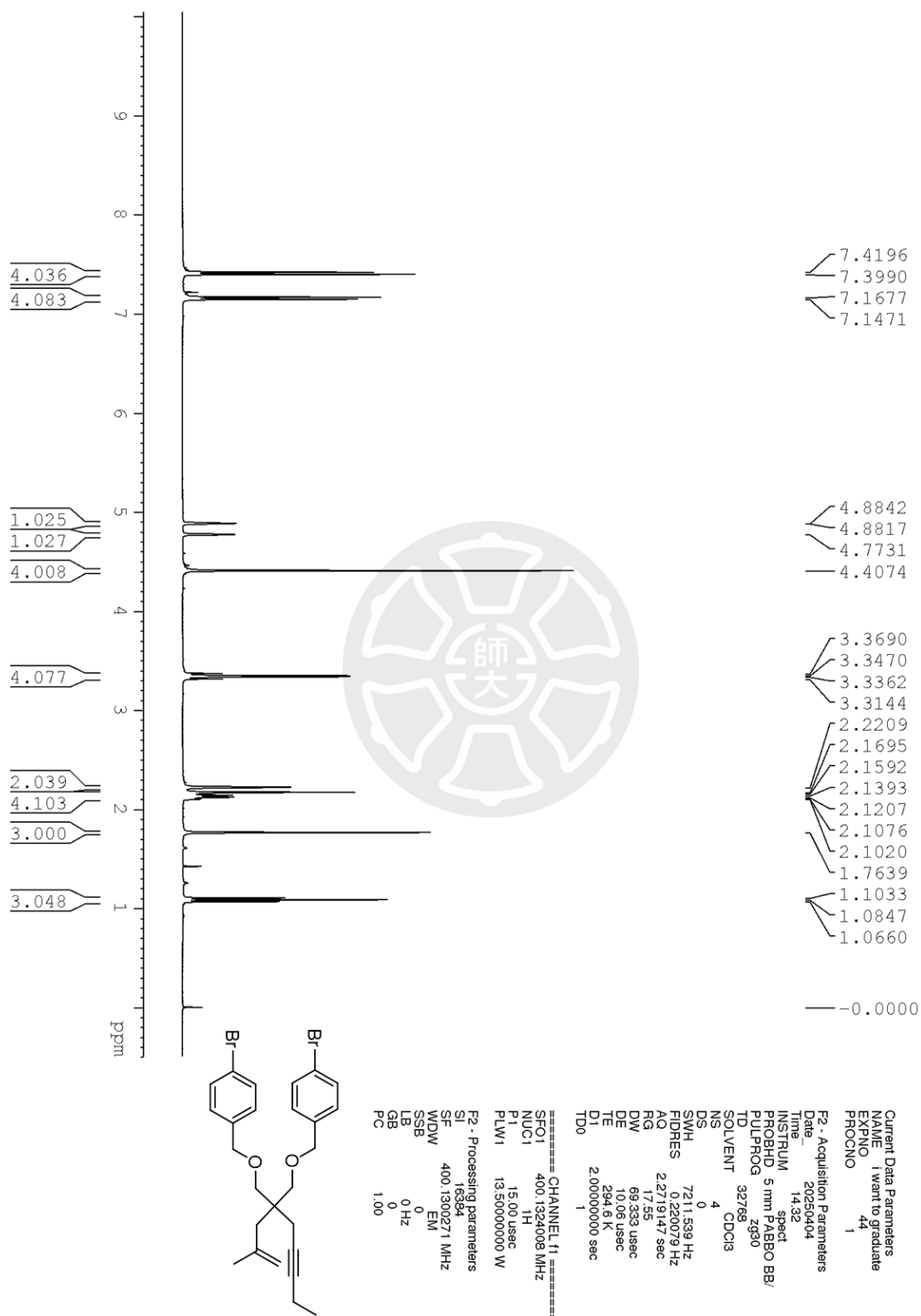


¹³C NMR spectrum of 2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diol (SC1)

b1199 13c

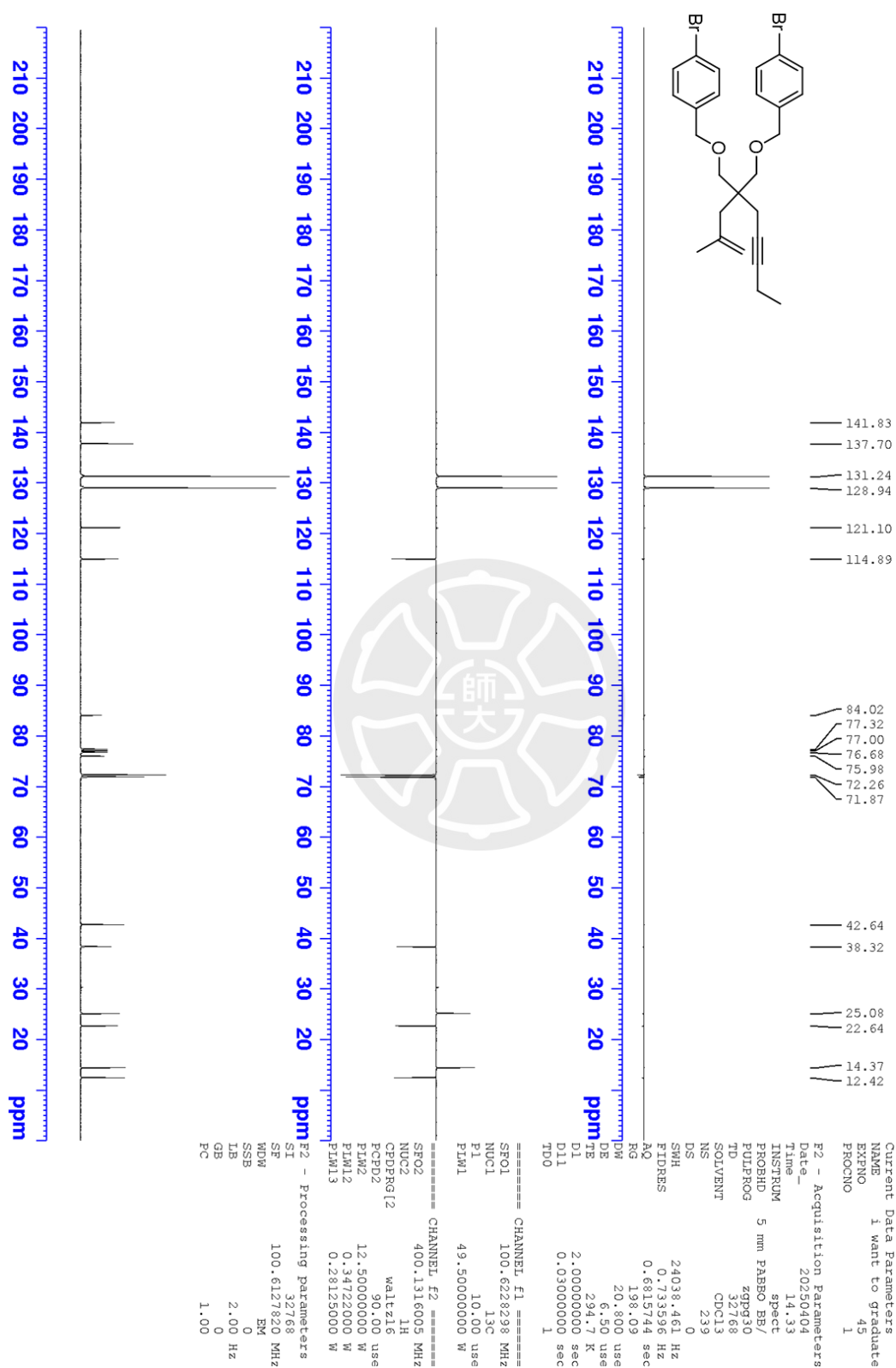


¹H NMR spectrum of 4,4'-(((2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diyl)bis(oxy)) bis(methylene))bis(bromobenzene) (43a)

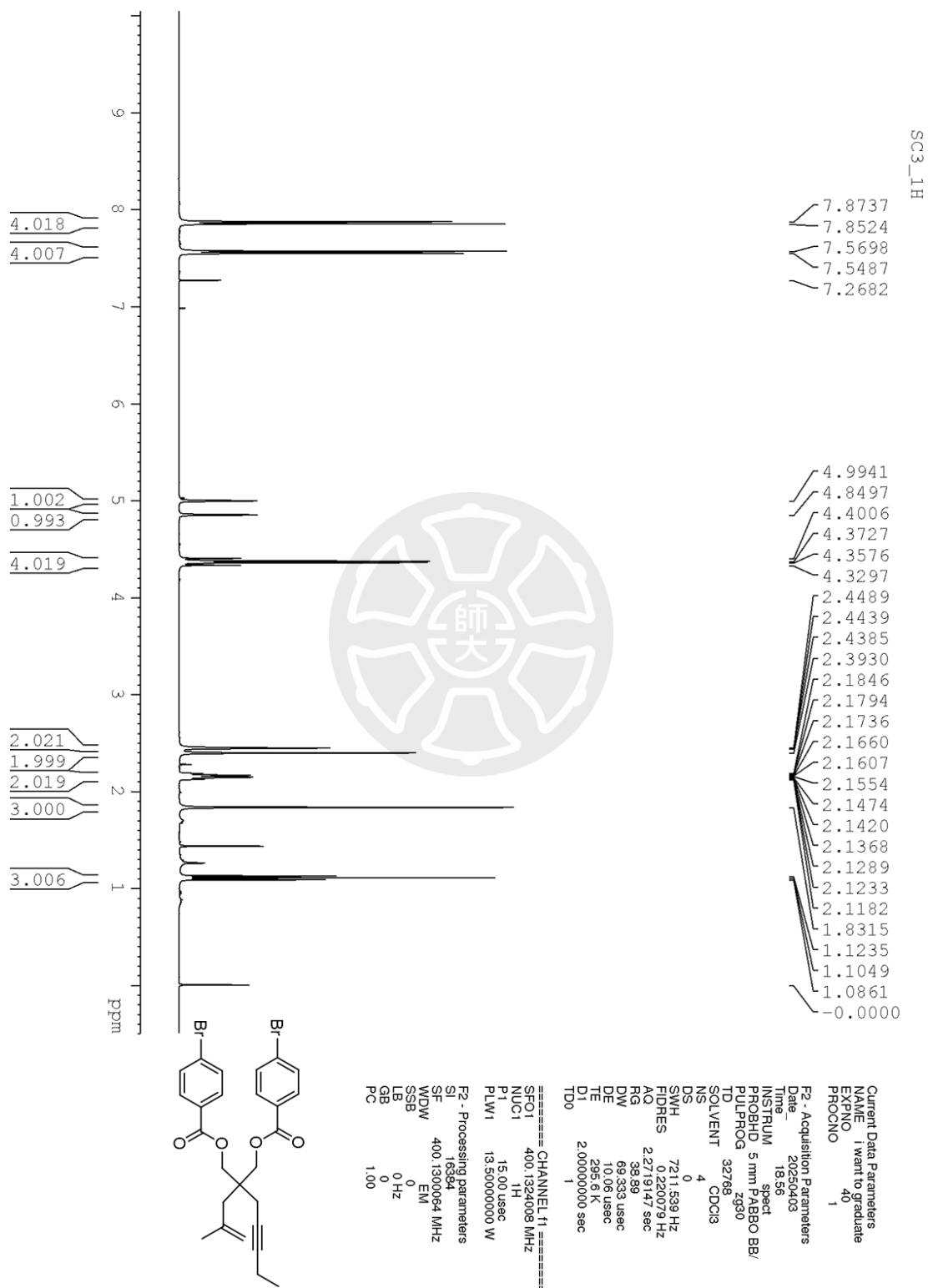


¹³C NMR spectrum of 4,4'-(((2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diyl)bis(oxy)) bis(methylene))bis(bromobenzene) (43a)

SC2_13c

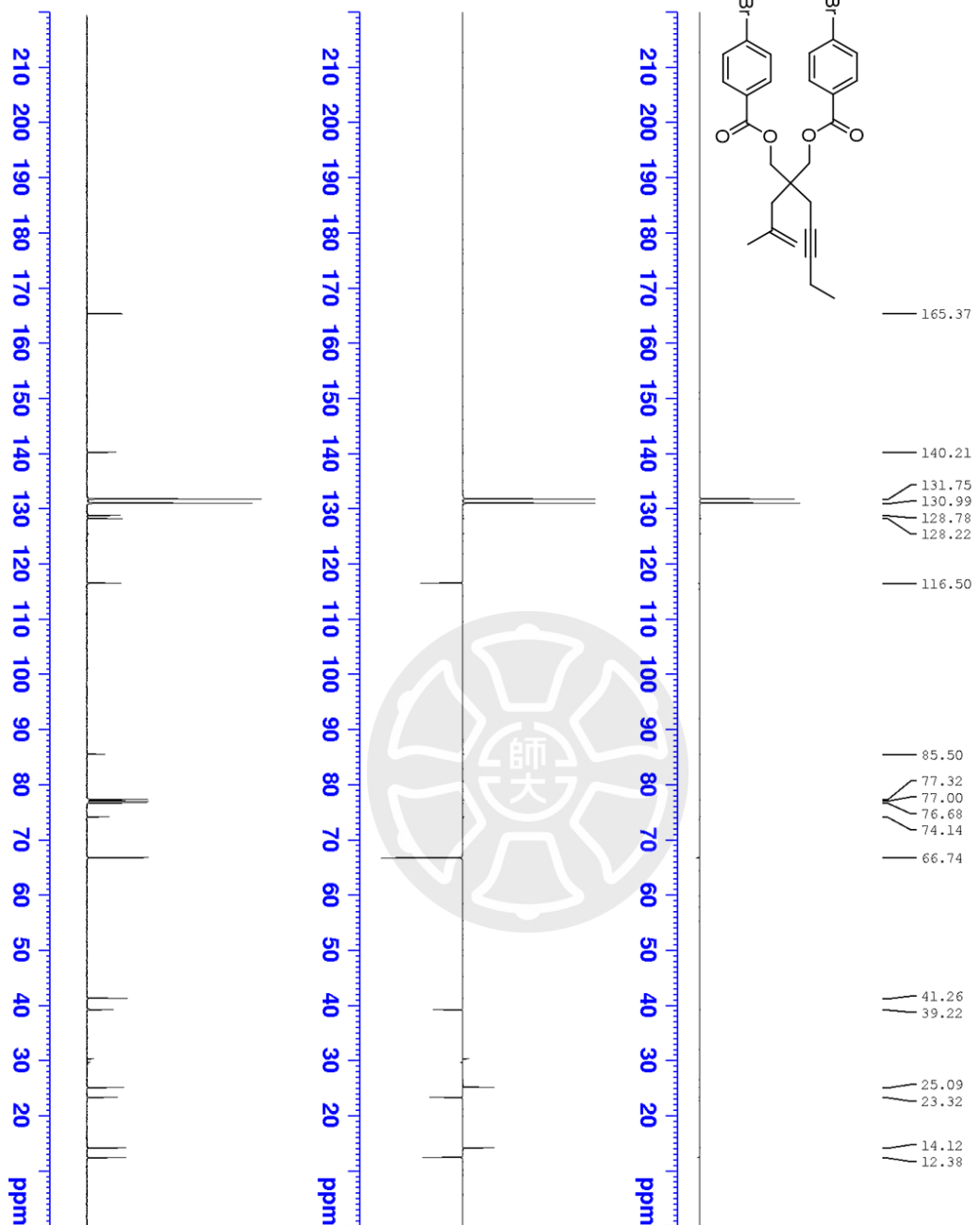
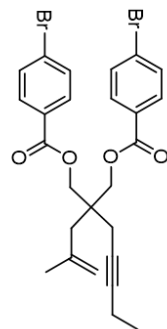


¹H NMR spectrum of 2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diyl bis(4-bromobenzoate) (43b)



¹³C NMR spectrum of 2-(2-methylallyl)-2-(pent-2-yn-1-yl)propane-1,3-diyl bis(4-bromobenzoate) (43b)

SC3_13c



Current Data Parameters
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 EXPNO 41
 PROCNO 1

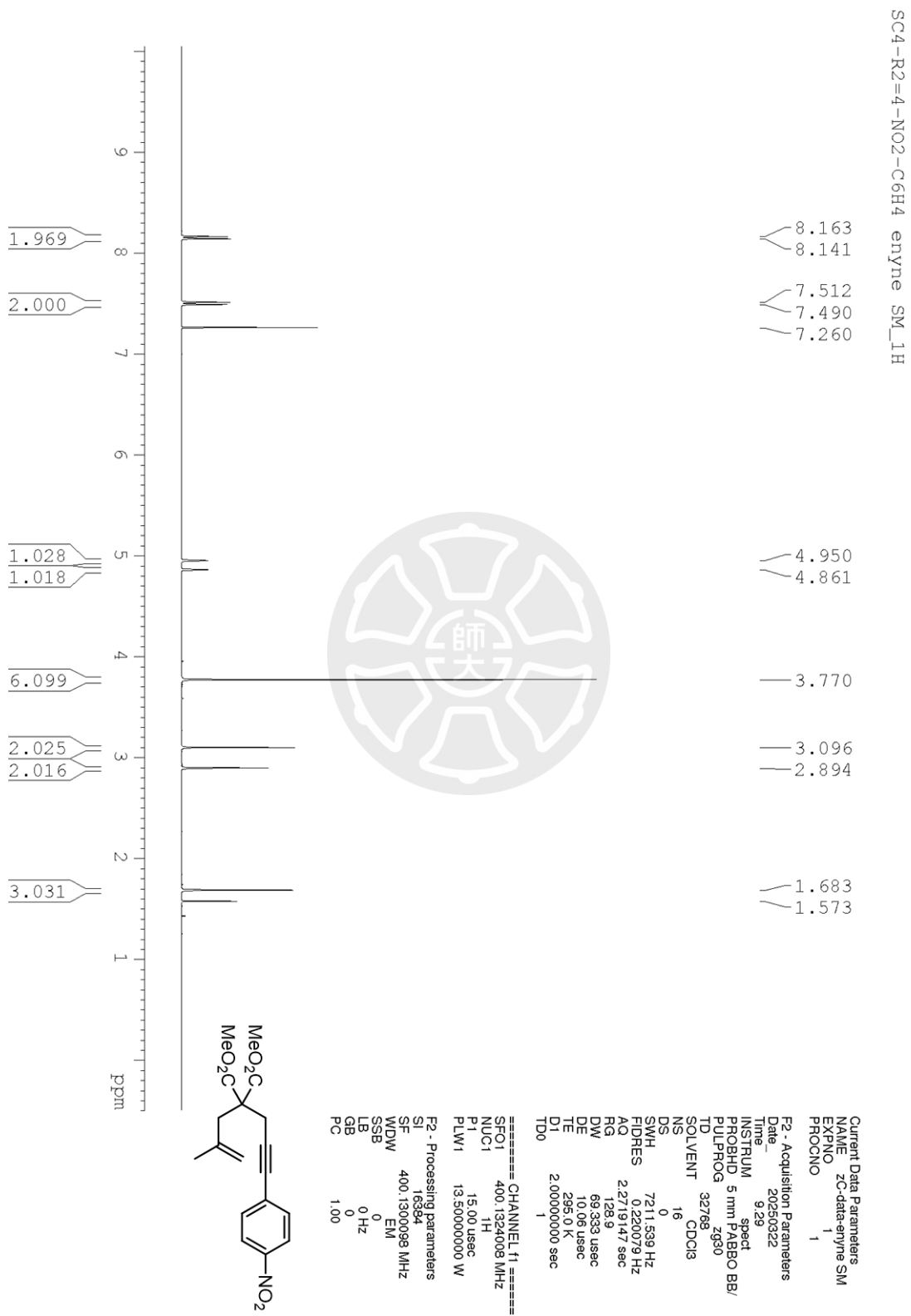
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 Time 18.58
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 PULPROG zgpg30
 TD 32768
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 NS 278
 DS 0
 SFO1 24038.461 HZ
 FIDRES 0.733598 HZ
 AQ 0.6935744 se
 RG 138.09
 DW 20.800 us
 DE 6.50 us
 TE 295.8 K
 D1 2.00000000 se
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 TDO 1

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 P1M1 49.50000000 W

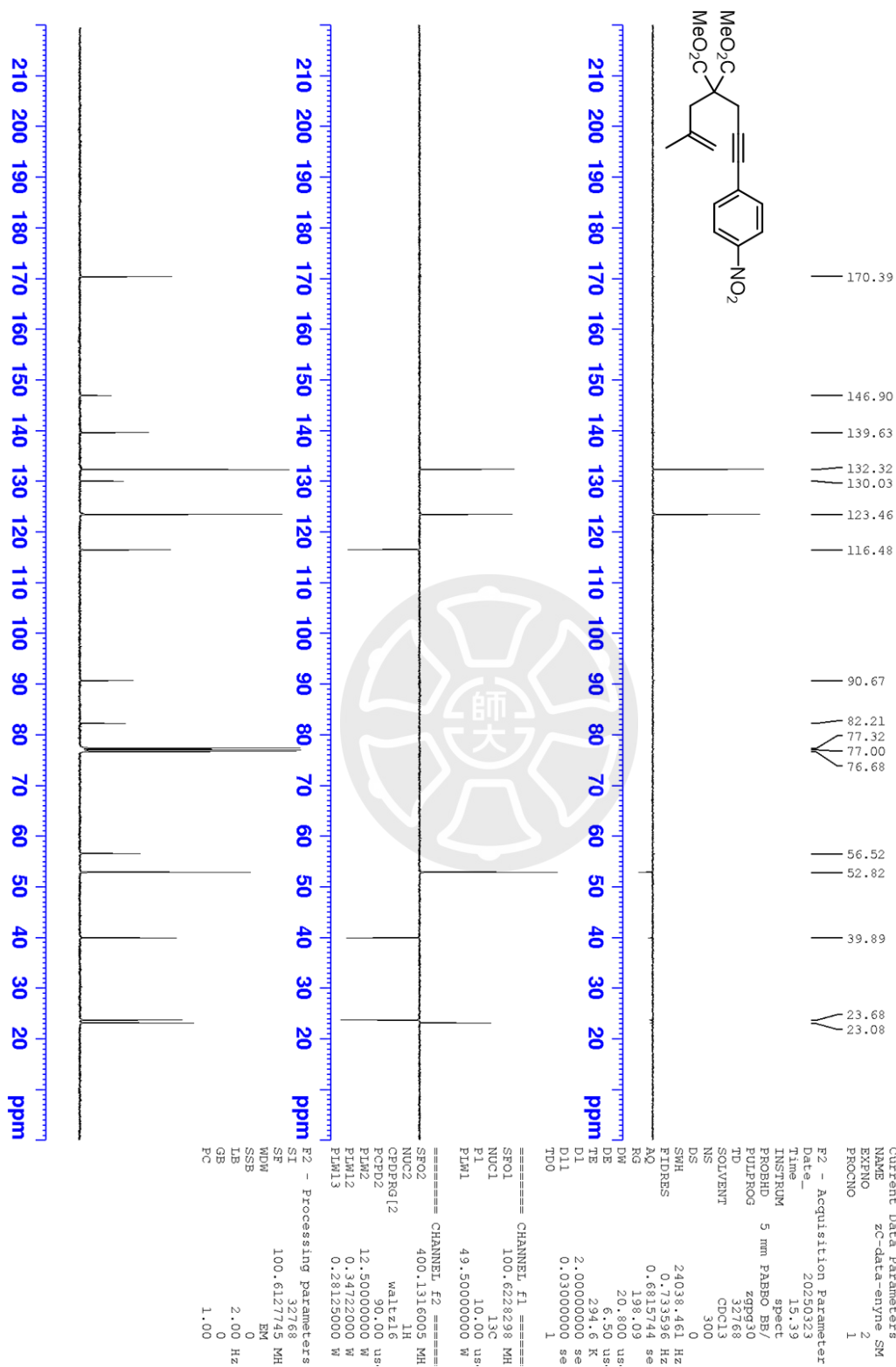
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 P1M3 0.34722000 W
 P1M4 0.28125000 W

F2 - Processing Parameters
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 SE 32768
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

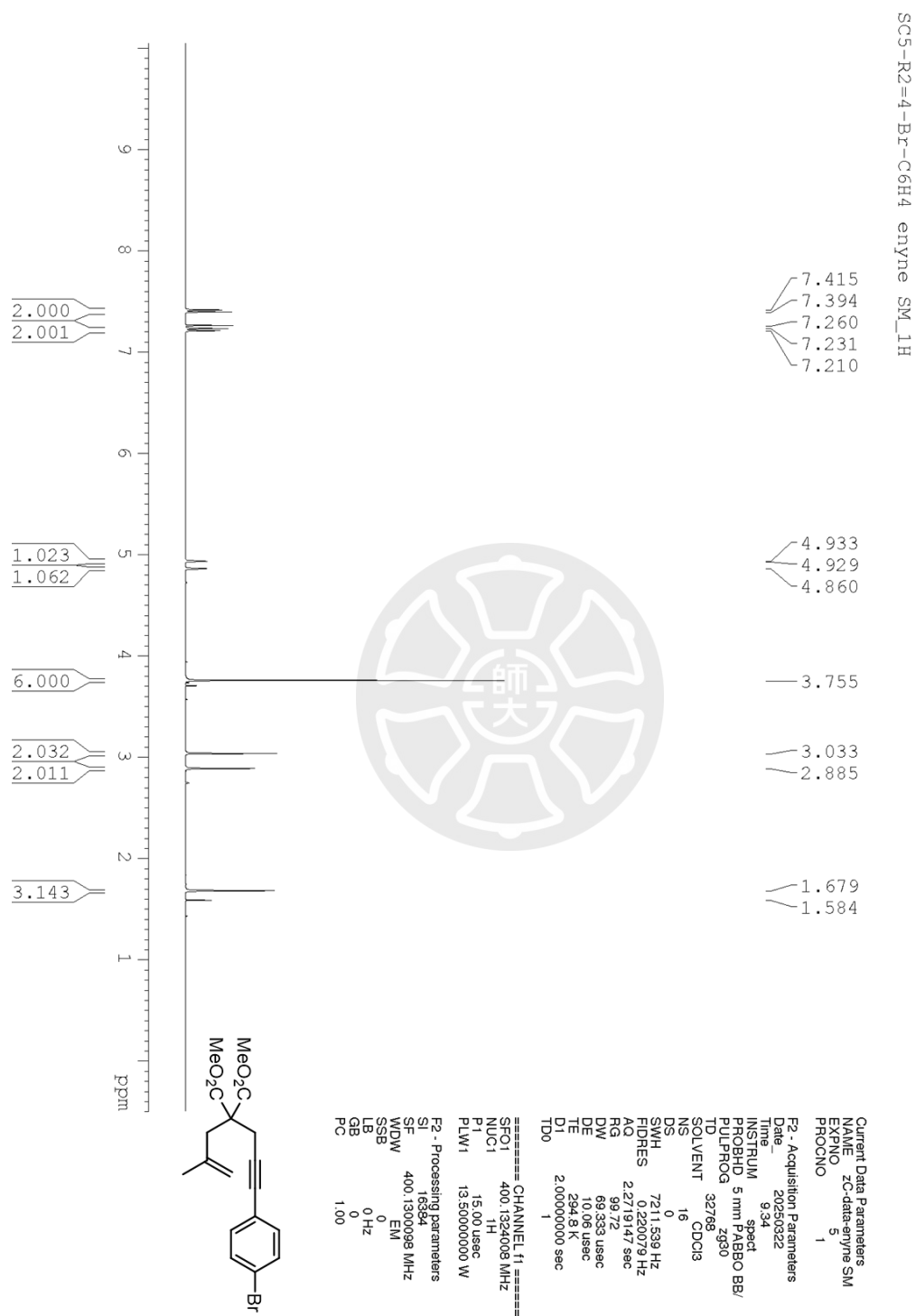
¹H NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(4-nitrophenyl)prop-2-yn-1-yl)malonate (40a)



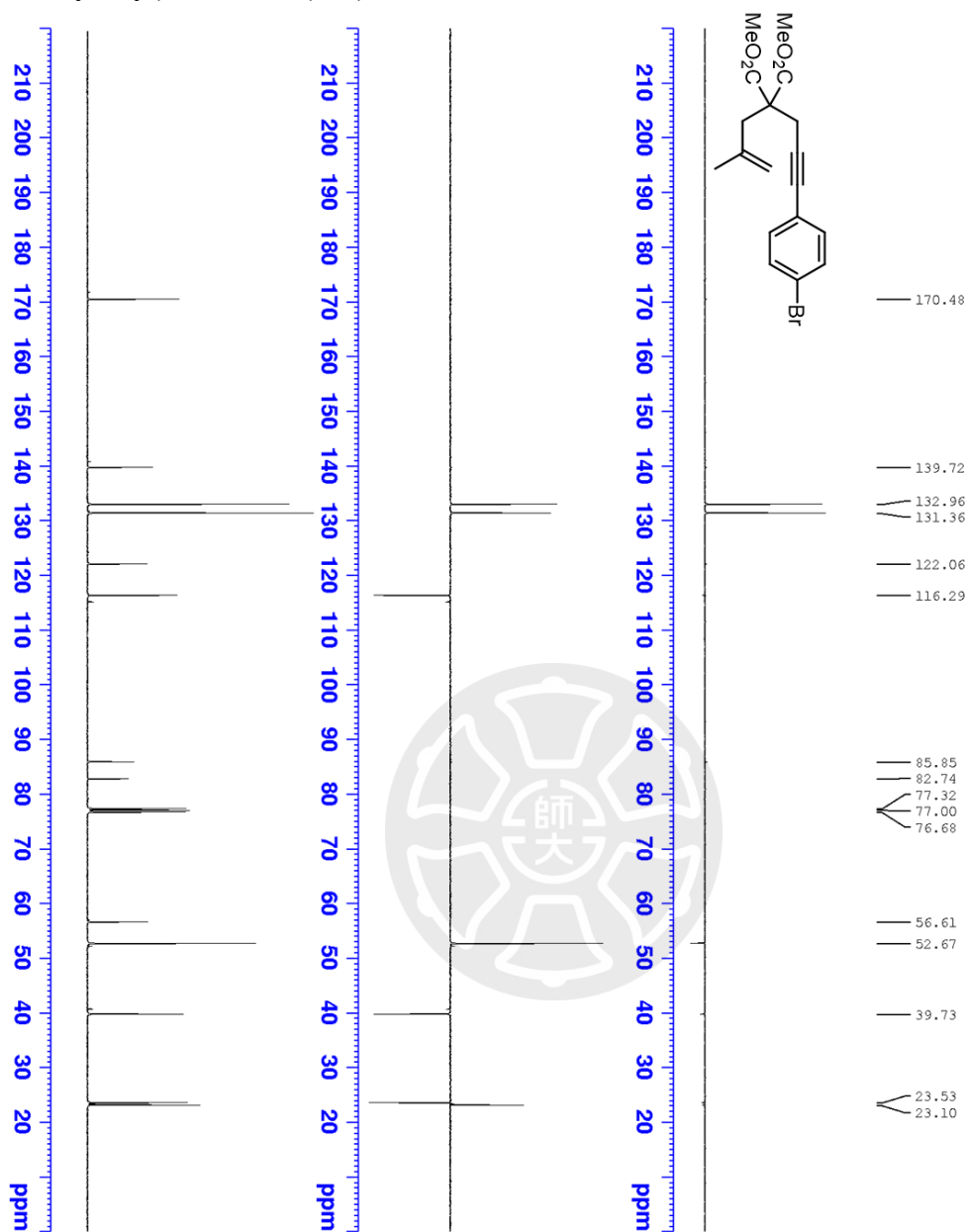
¹³C NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(4-nitrophenyl)prop-2-yn-1-yl)malonate (40a)



¹H NMR spectrum of dimethyl 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)malonate (40c)



¹³C NMR spectrum of dimethyl 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)malonate (40c)



SC5-R2=4-Br-C6H4 enyne SM_13C

Current Data Parameters
 NAME Zc-data-ene-yne SM
 EXPNO 1
 F2PROCNO 1

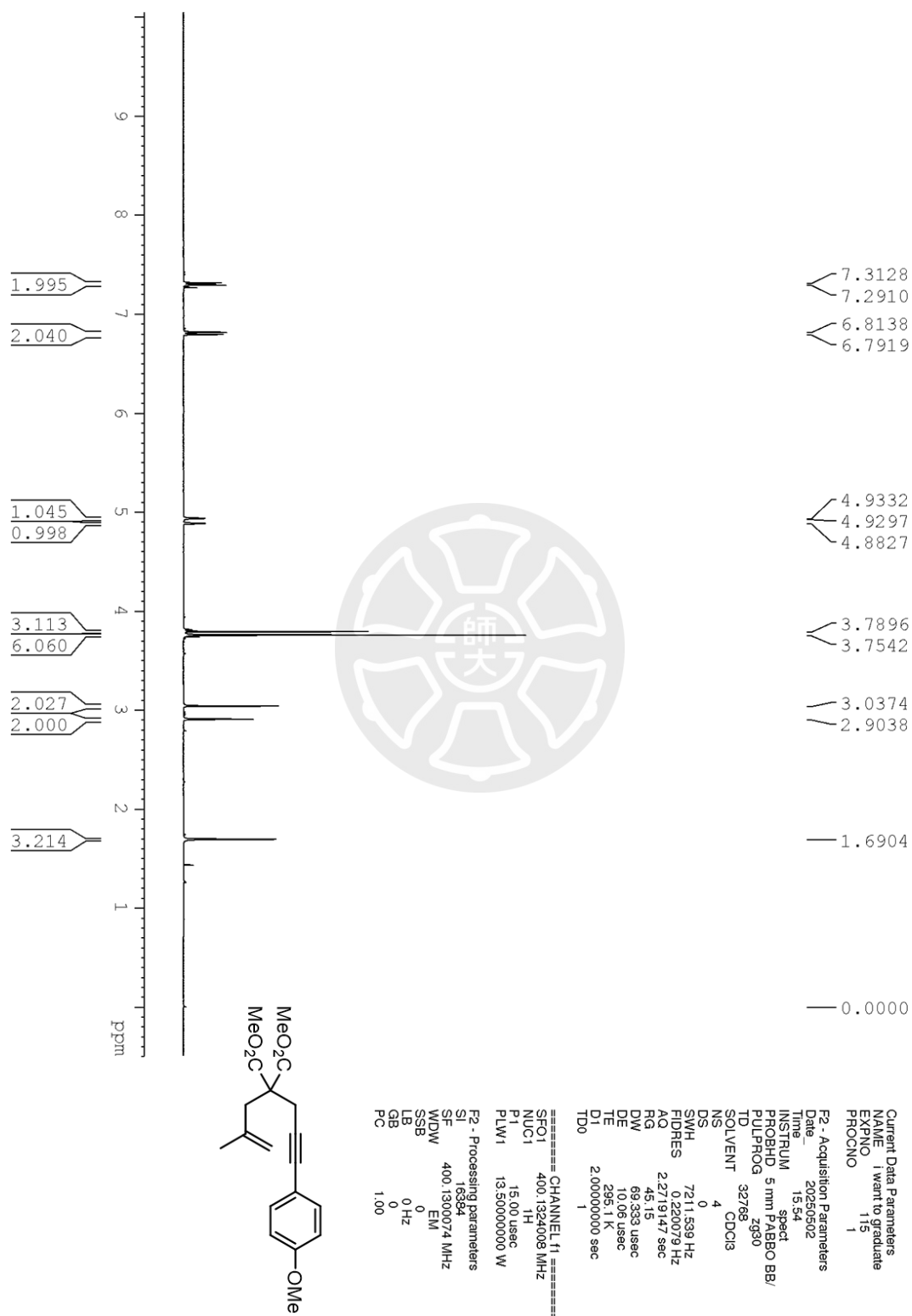
F2 - Acquisition Parameters
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 Time_ 16:00
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 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 300
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 se
 RG 198.09
 DW 20.800 us
 DE 6.50 us
 TE 294.7 K
 D1 2.00000000 se
 D11 0.03000000 se
 TDO 1

===== CHANNEL F1 =====
 SFO1 100.628298 MH
 NUC1 13C
 P1 10.00 us
 P1M1 49.50000000 W

===== CHANNEL F2 =====
 SFO2 400.1316005 MH
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 us
 P1M2 12.50000000 W
 P1M12 0.34722000 W
 P1M13 0.28125000 W

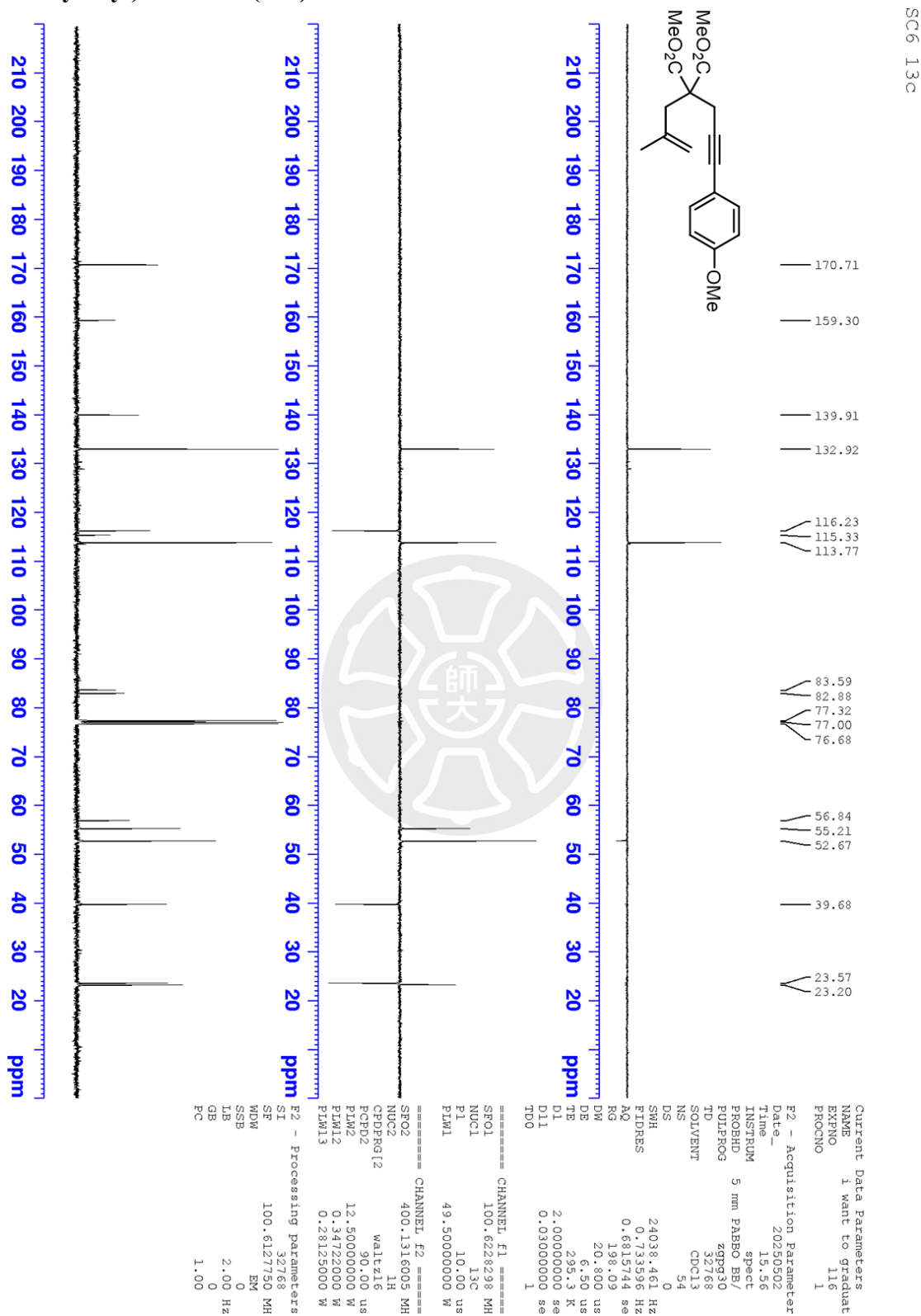
F2 - Processing parameters
 SI 32768
 SF 100.6127788 MH
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of dimethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2-(2-methylallyl)malonate (40a)

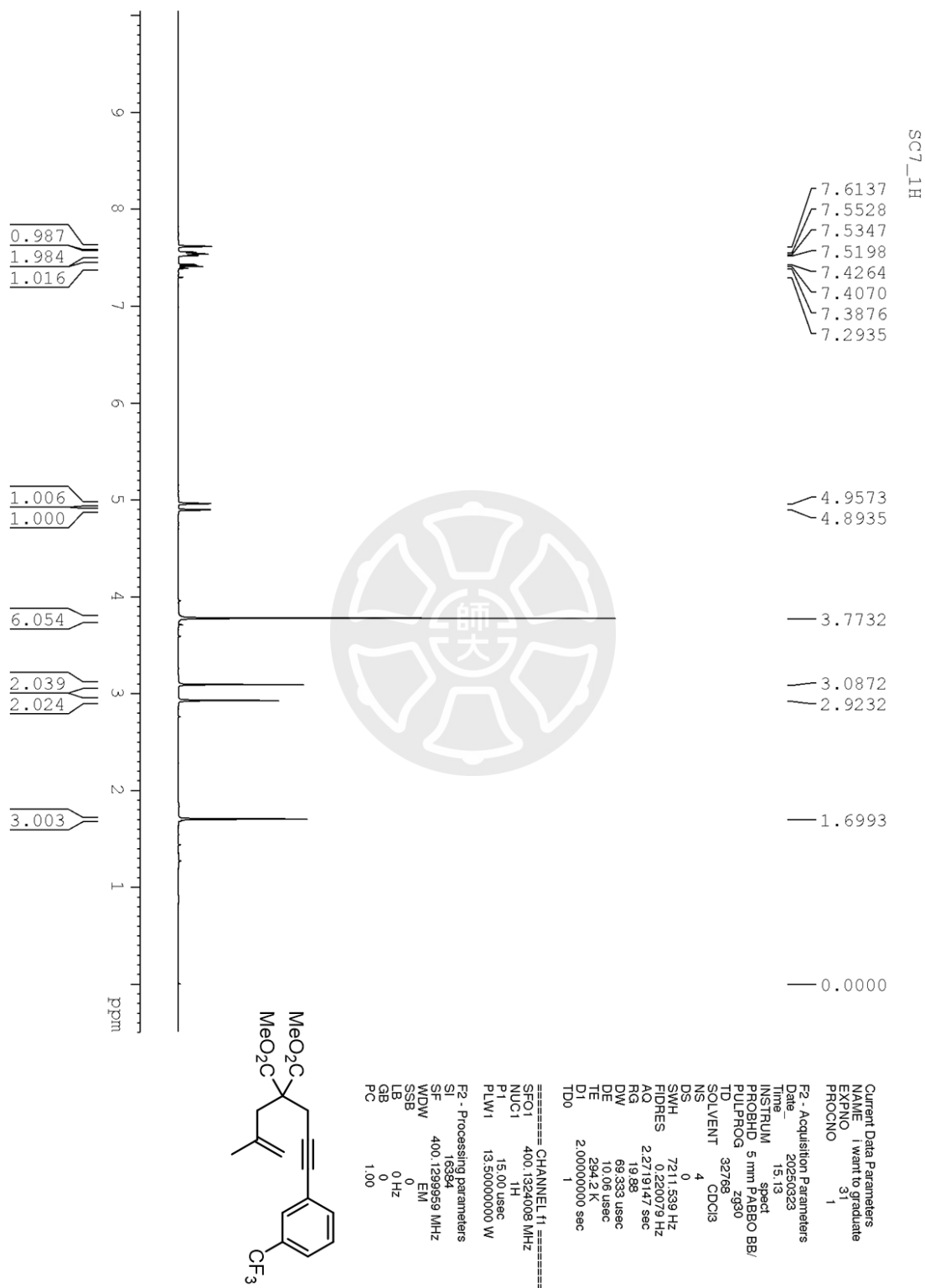


SC6

¹³C NMR spectrum of dimethyl 2-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-2-(2-methylallyl)malonate (40a)

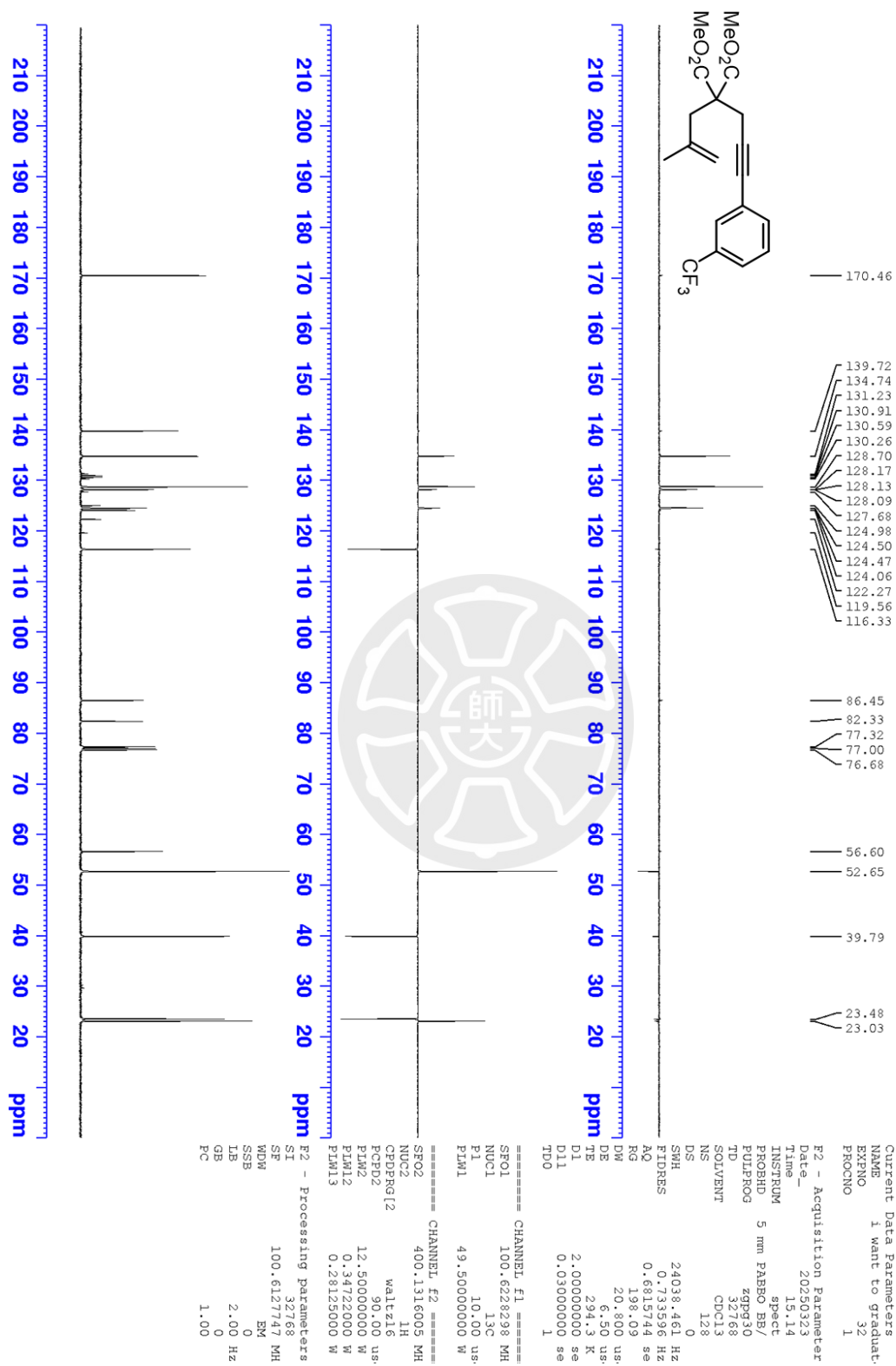


¹H NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (40d)

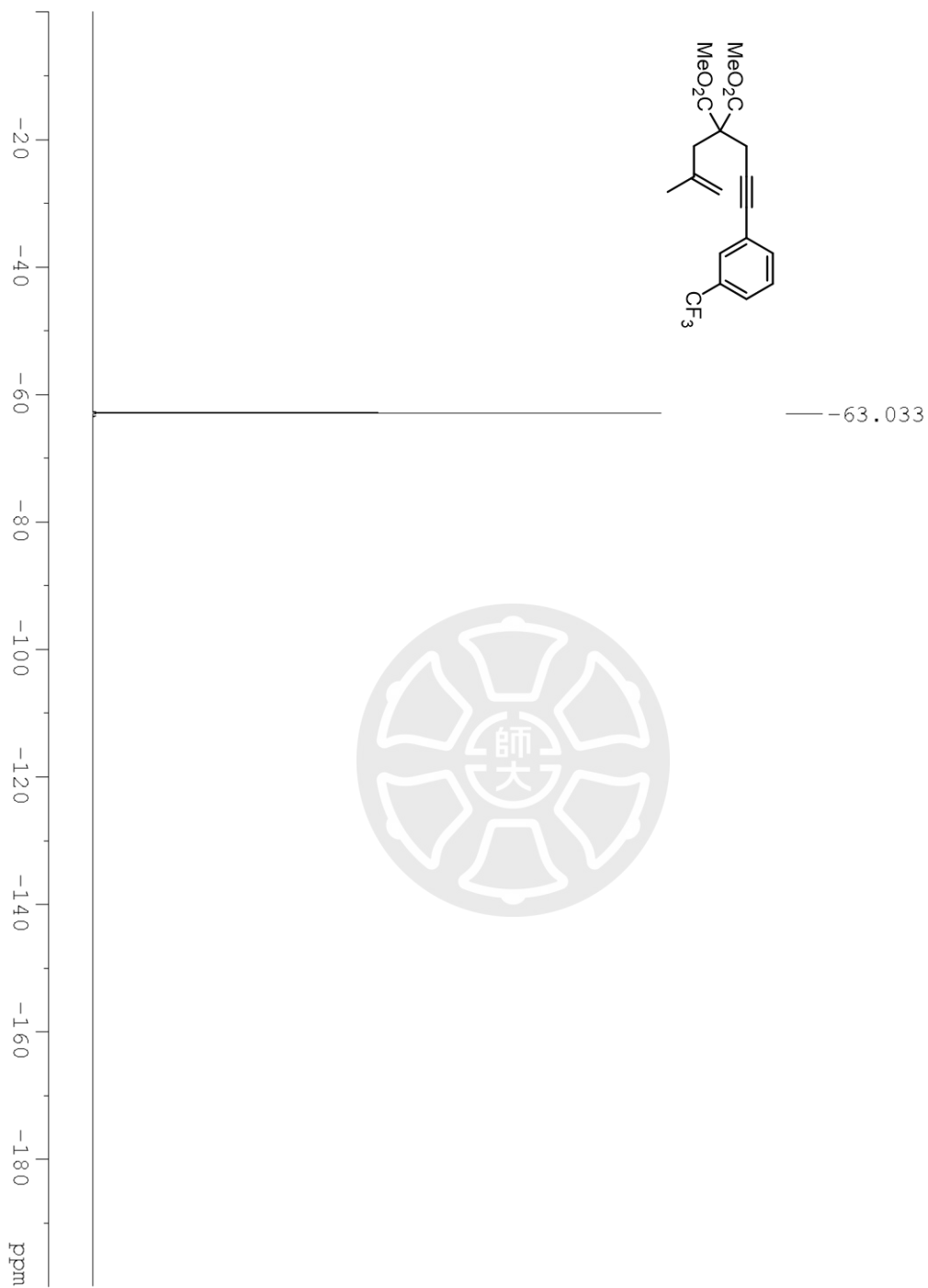


¹³C NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (40d)

SC7_13c



¹⁹F NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (40d)



SC7_19F

Current Data Parameters
 NAME I want to graduate
 EXPNO 35
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20250323
 Time 15:34

INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg

TD 131072
 SOLVENT CDCl3

DS 16
 NS 0

SWH 89285.711 Hz
 FIDRES 0.681196 Hz

AQ 0.7340032 sec
 RG 198.09

DW 5.600 usec
 DE 6.50 usec

TE 294.5 K
 D1 1.00000000 sec

D11 0.03000000 sec
 TD0 1

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 NUC1 19F

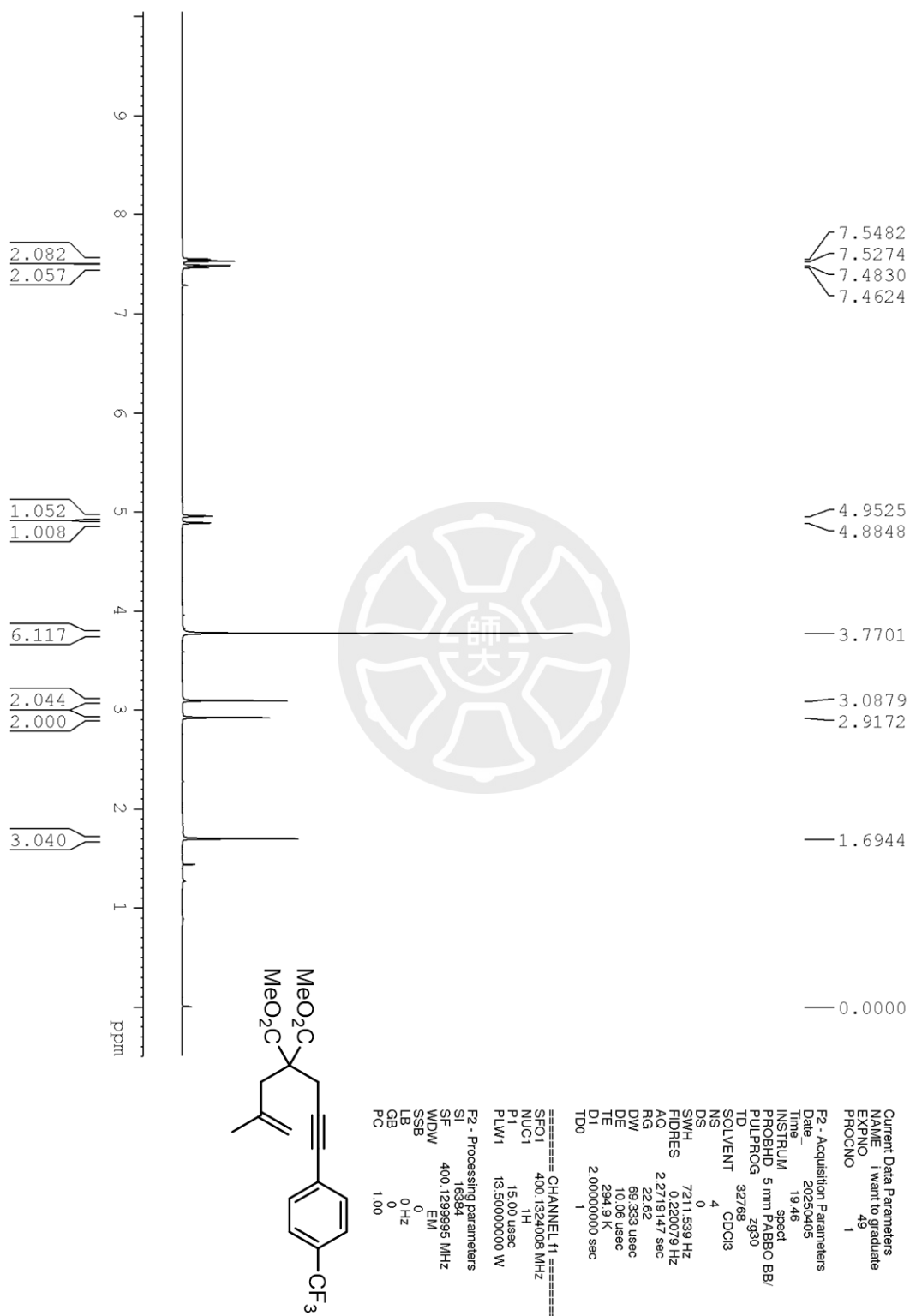
P1 15.00 usec
 PLW1 15.50000000 W

==== CHANNEL f2 =====
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 NUC2 1H

CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLWT2 0.34722000 W

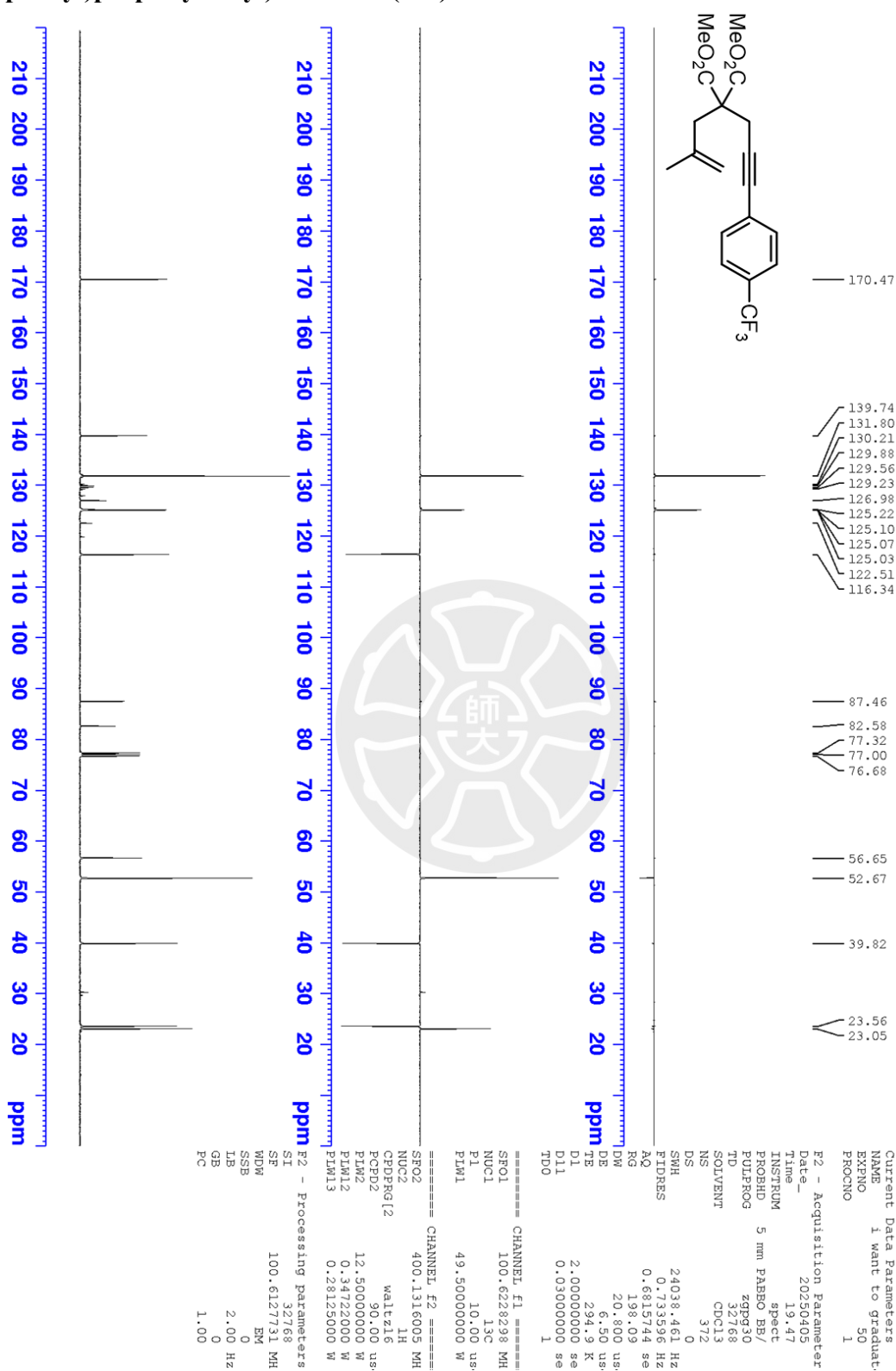
F2 - Processing parameters

¹H NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (40e)

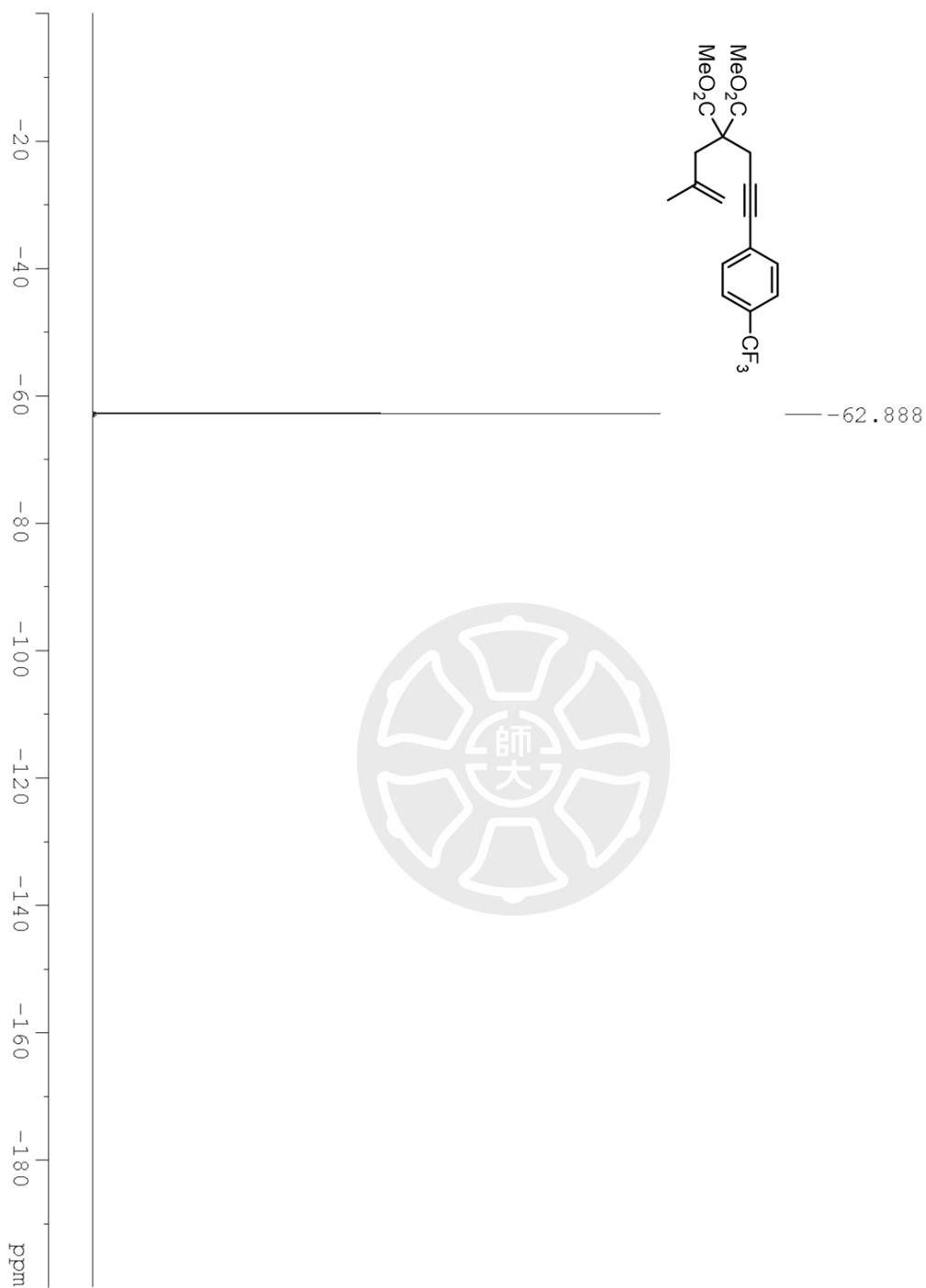


¹³C NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (40e)

SC8_13c



¹⁹F NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)malonate (40e)



SC8_19F

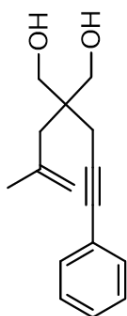
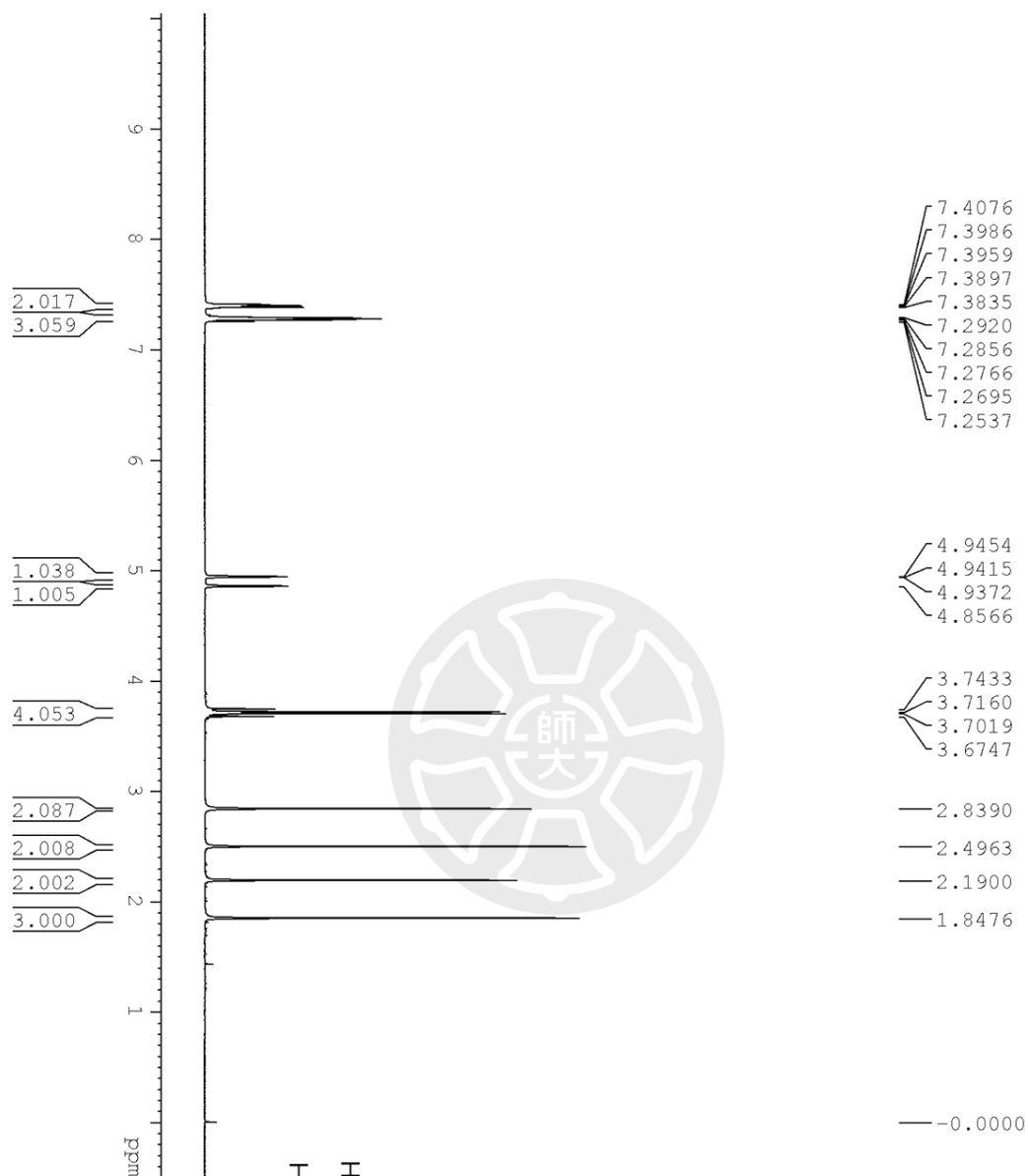
Current Data Parameters
 NAME: i want to graduate
 EXPNO: 53
 PROCNO: 1

F2 - Acquisition Parameters
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 Time: 20:33
 INSTRUM: spect
 PROBHD: 5 mm PABBO BB/
 PULPROG: zgpg
 TD: 131072
 SOLVENT: CDCl3
 NS: 16
 DS: 0
 SWH: 89285.711 Hz
 FIDRES: 0.681196 Hz
 AQ: 0.7340032 sec
 RG: 198.09
 DW: 5.600 usec
 DE: 6.50 usec
 TE: 295.3 K
 D1: 1.00000000 sec
 D11: 0.03000000 sec
 TD0: 1

===== CHANNEL f1 =====
 SFO1 376.4607168 MHz
 NUC1 19F
 P1 15.00 usec
 PLW1 16.50000000 W

 ===== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.50000000 W
 PLW12 0.34722000 W
 F2 - Processing parameters

¹H NMR spectrum of 2-(2-methylallyl)-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diol (SC9)

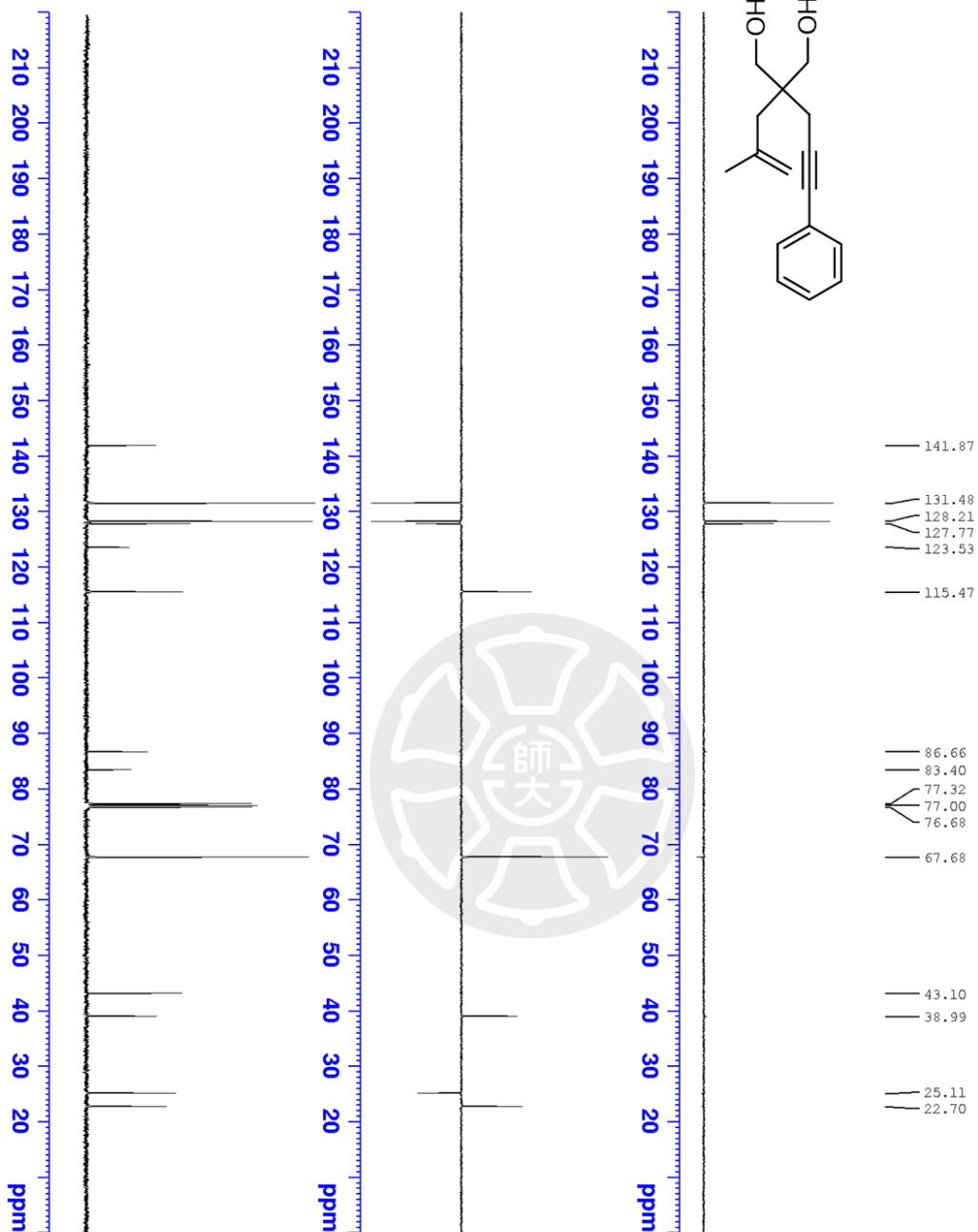
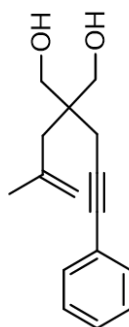


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Current Data Parameters
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EXPNO     123
PROCNO    1
F2 - Acquisition Parameters
Date_     20250502
Time      19.55
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PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         4
DS         0
SWMH      7211.539 Hz
FIDRES    0.220079 Hz
AQ         2.2719147 sec
RG         38.89
DE         69.533 usec
TE         10.06 usec
TD0        296.5 K
D1         2.00000000 sec
===== CHANNEL f1 =====
SFO1      400.1324008 MHz
NUC1       1H
P1         15.00 usec
PLW1      13.50000000 W
F2 - Processing parameters
SI         16384
SF         400.1300123 MHz
WDW        EM
SSB        0
LB         0 Hz
GB         0
PC         1.00
  
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¹³C NMR spectrum of 2-(2-methylallyl)-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diol (SC9)

SC9 b2070 13C



Current Data Parameters
 NAME 1 want to graduat
 EXPRNO 124
 PROCNO 1

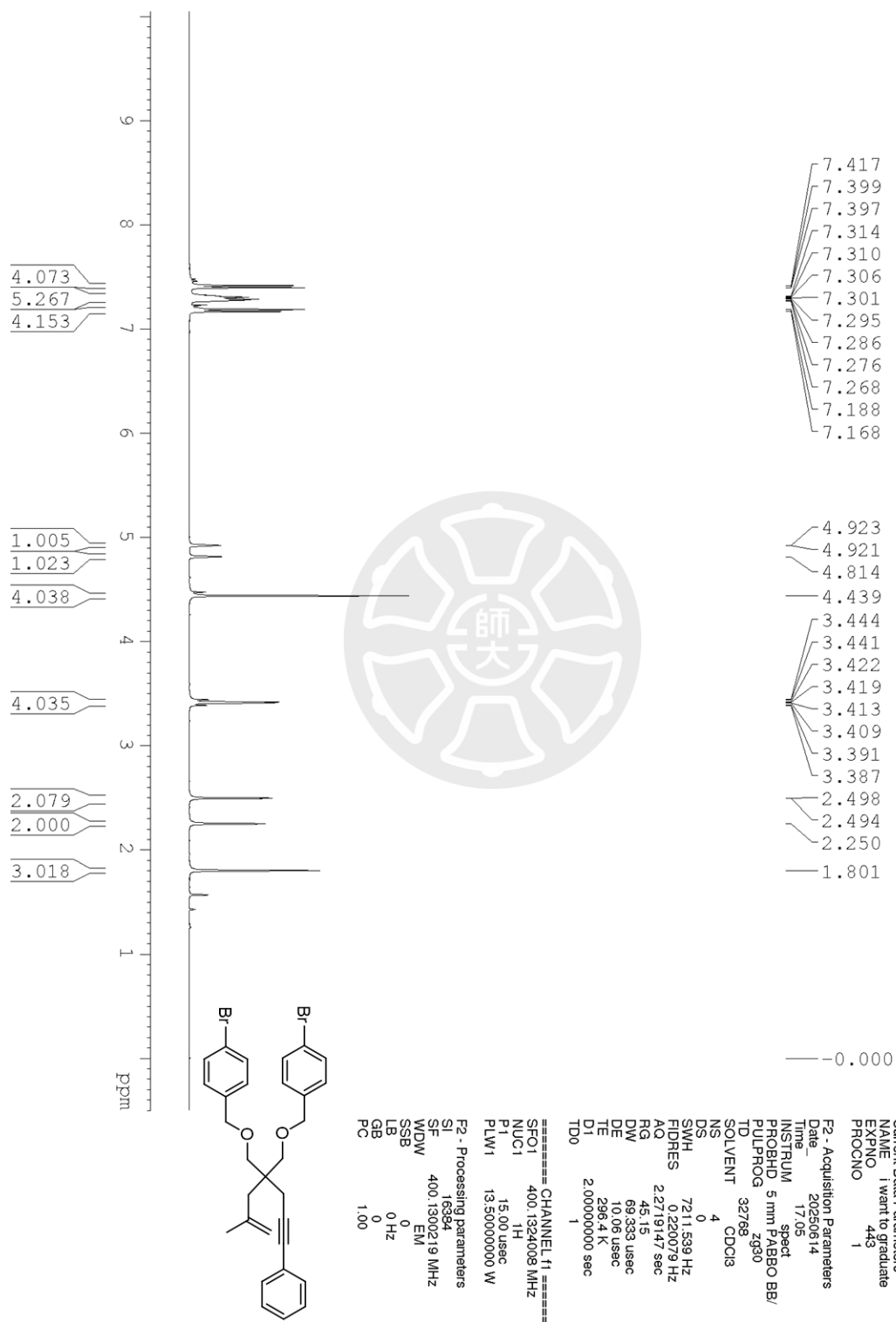
F2 - Acquisition Parameters
 Date_ 20250502
 Time_ 19:56
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 PULPROG zgpg30
 FULPROG zgpg30
 ID 32768
 SOLVENT CDCl3
 NS 61
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 se
 RG 198.09
 DW 20.800 us
 DE 6.50 us
 TE 296.7 K
 D1 2.00000000 se
 D11 0.03000000 se
 TDO 1

==== CHANNEL F1 =====
 SF01 100.6228298 MH
 NUC1 13C
 P1 10.00 us
 PL1 49.50000000 W

==== CHANNEL F2 =====
 SFO2 400.1316095 MH
 NUC2 1H
 CPDPRG12 waltz16
 PCPD2 90.00 us
 PLM2 12.50000000 W
 PLM12 0.3472000 W
 PLM13 0.28125000 W

F2 - Processing parameters
 SI 32768
 SF 100.6127766 MH
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

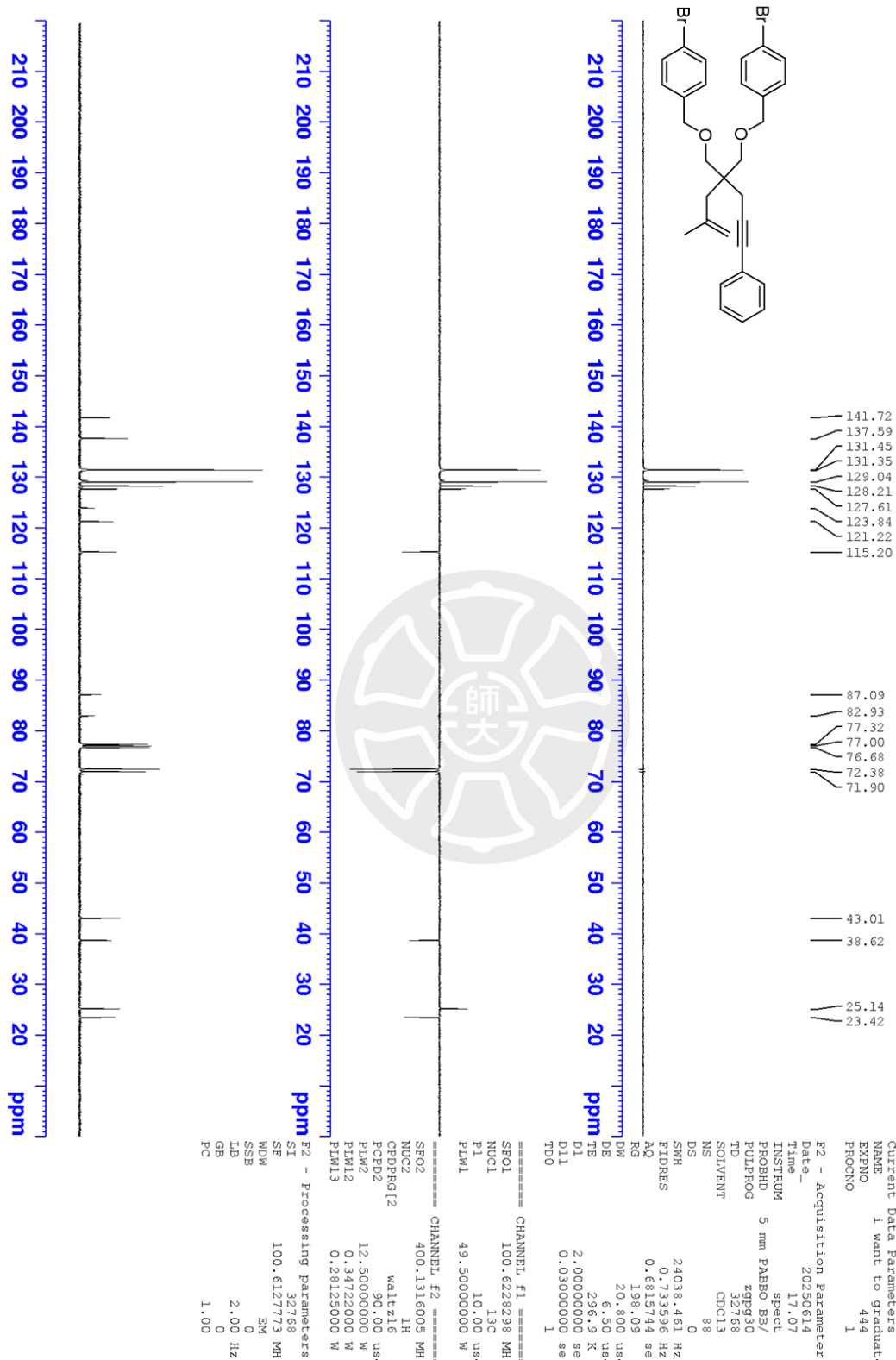
¹H NMR spectrum of 4,4'-(((2-(2-methylallyl)-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diyl)bis(oxy)) bis(methylene))bis(bromobenzene) (43c)



b2078

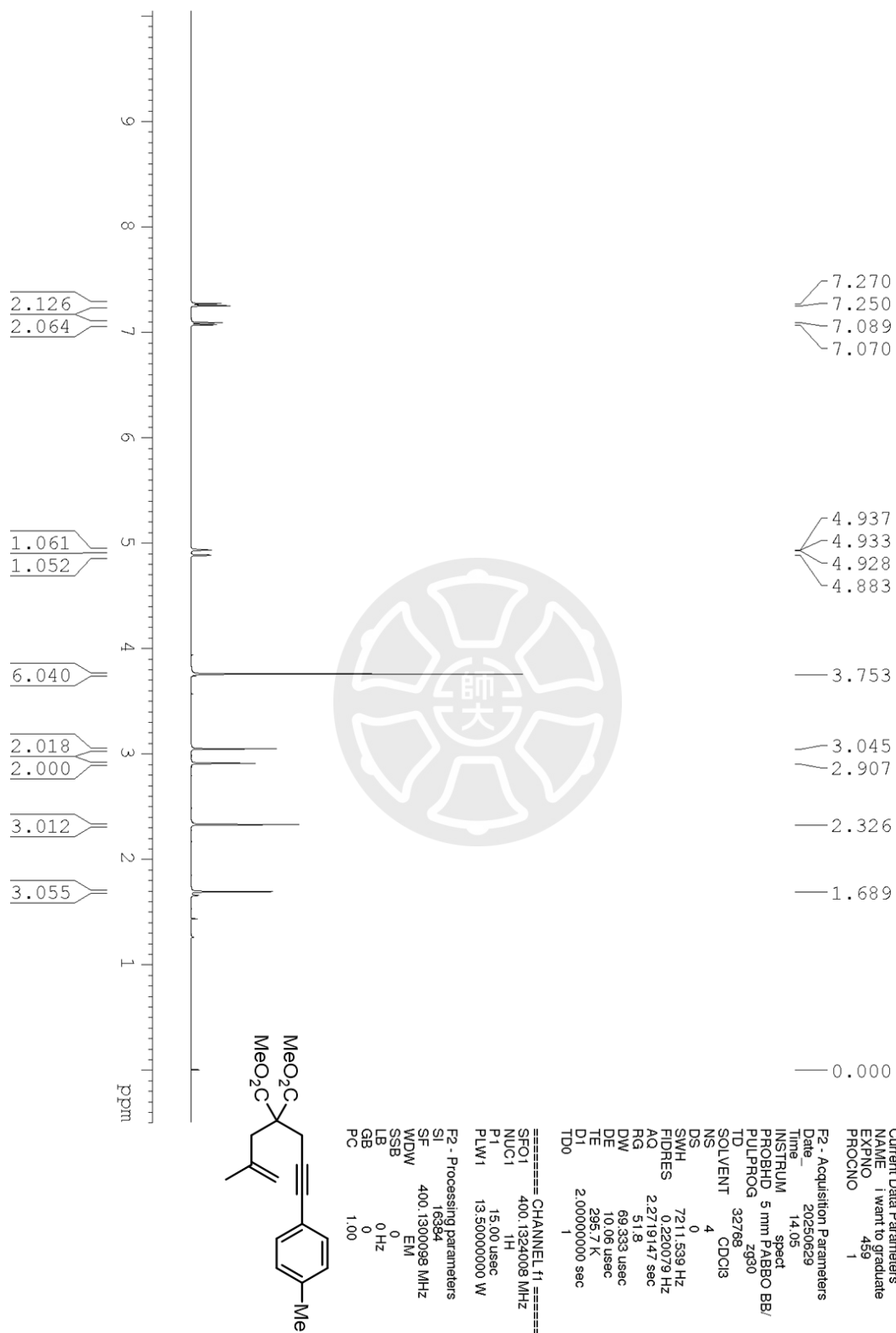
¹³C NMR spectrum of 4,4'-(((2-(2-methylallyl)-2-(3-phenylprop-2-yn-1-yl)propane-1,3-diyl)bis(oxy)) bis(methylene))bis(bromobenzene) (43c)

b2078 13c



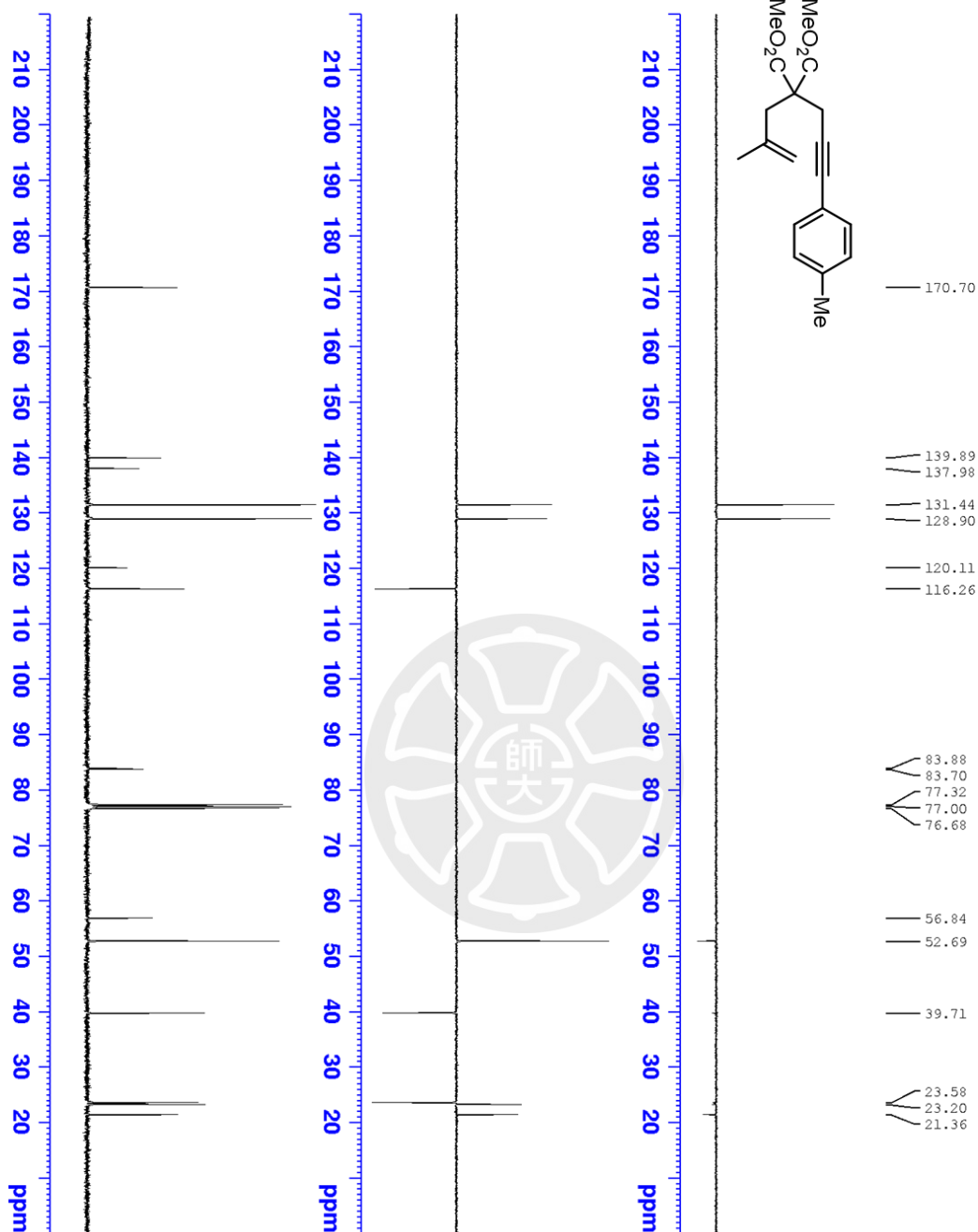
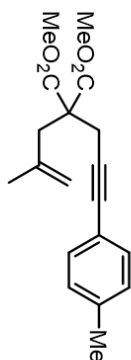
¹H NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(p-tolyl)prop-2-yn-1-yl) malonate (40f)

b2068



¹³C NMR spectrum of dimethyl 2-(2-methylallyl)-2-(3-(p-tolyl)prop-2-yn-1-yl) malonate (40f)

b2068 13c



Current Data Parameters
 NAME 1 want to graduat
 EXPNO 460
 PROCNO 1

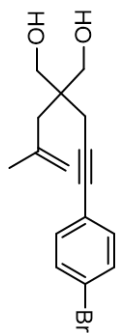
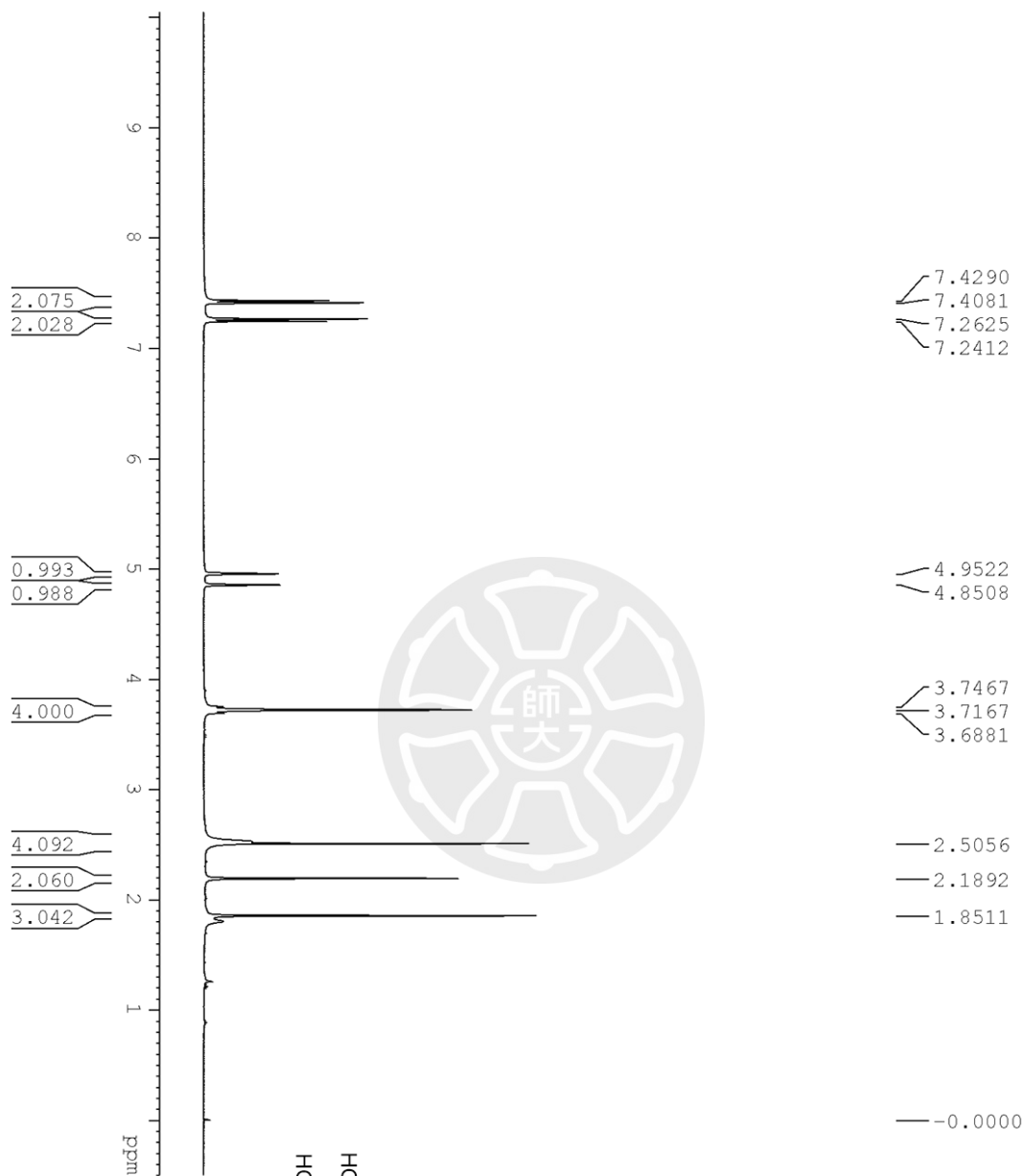
F2 - Acquisition Parameters
 Date_ 20250629
 Time 14:08
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 104
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 s
 RG 198.09
 DW 20.800 us
 DE 6.50 us
 TE 296.3 K
 D1 2.00000000 s
 D11 0.03000000 s
 TPO 1

==== CHANNEL f1 =====
 SFO1 100.628298 MHz
 NUO1 13C
 P1 10.00 us
 PL1 49.50000000 W
 ===== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUO2 1H
 CPDPRG12 waltz16
 PCPD2 90.00 us
 PLM2 12.50000000 W
 PLM12 0.34722000 W
 PLM13 0.28125000 W

F2 - Processing Parameters:
 SI 32768
 SF 100.6127744 MHz
 RFR 0 MHz
 SSB 2.00 Hz
 LB 0
 GB 0
 PC 1.00

¹H NMR spectrum of 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diol (SC12)

SC12_b2078

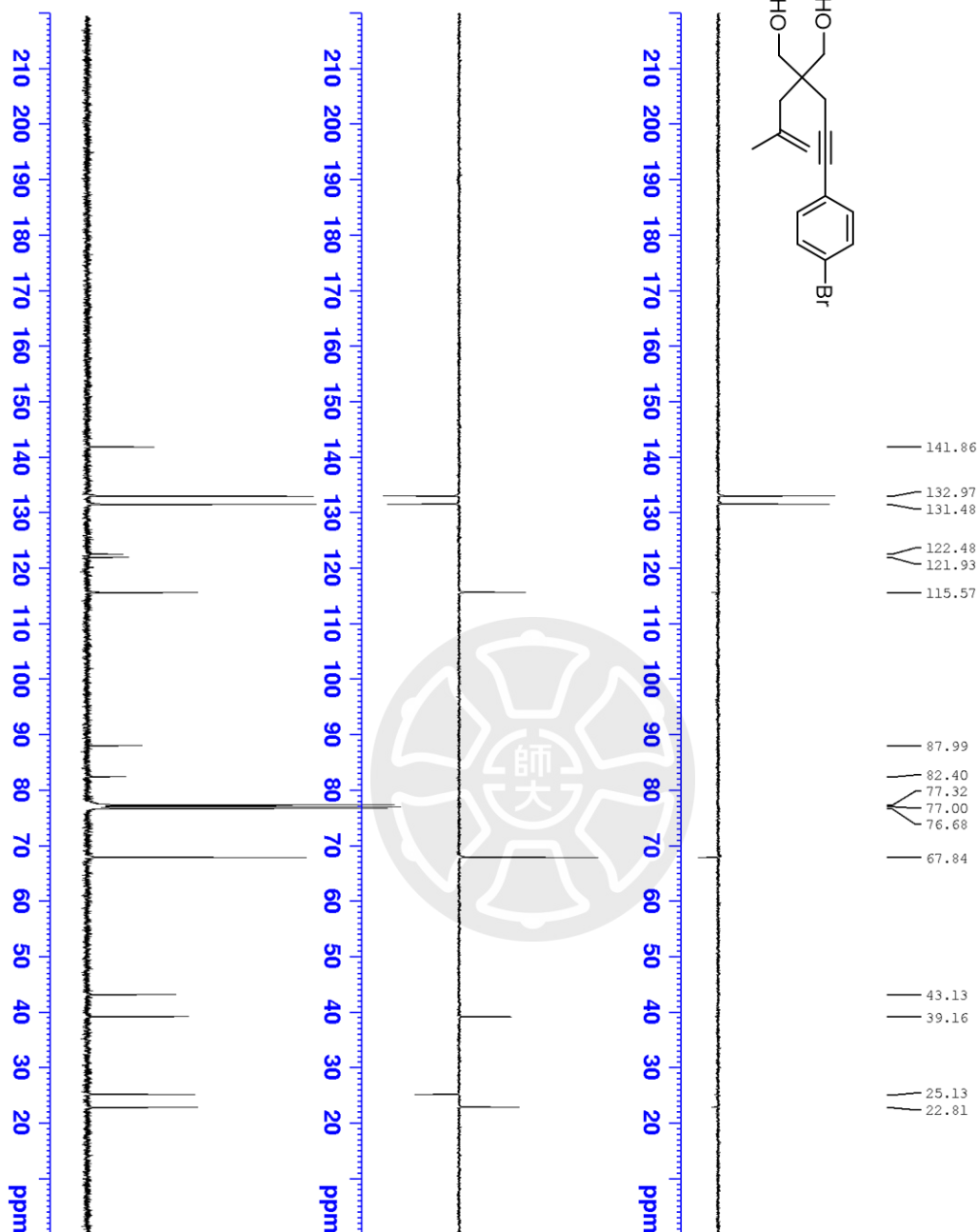
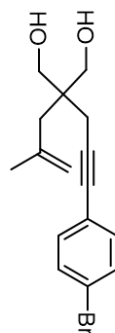


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Current Data Parameters
NAME      i want to graduate
EXPNO    322
PROCNO   1
F2 - Acquisition Parameters
Date_    20250524
Time     14.40
INSTRUM spect
PROBHD   5 mm PABO BB/
PULPROG zg30
TD       32768
SOLVENT  CDCl3
NS       4
DS       0
SWH      7211.539 Hz
FIDRES   0.220079 Hz
AQ       2.2719147 sec
RG       89.08
DW       69.333 usec
DE       10.06 usec
TE       296.5 K
D1       2.00000000 sec
TD0      1
===== CHANNEL f1 =====
SFO1    400.1324008 MHz
NUC1    1H
P1      15.00 usec
PLW1    13.50000000 W
F2 - Processing parameters
SI      32768
SF      400.1324008 MHz
WDW     EM
SSB     0
LB      0.1 Hz
GB      0
PC      1.00
    
```

¹³C NMR spectrum of 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diol (SC12)

SC12 b2078 13C



Current Data Parameters
 NAME i want to graduate
 EXPNO 323
 PROCNO 1

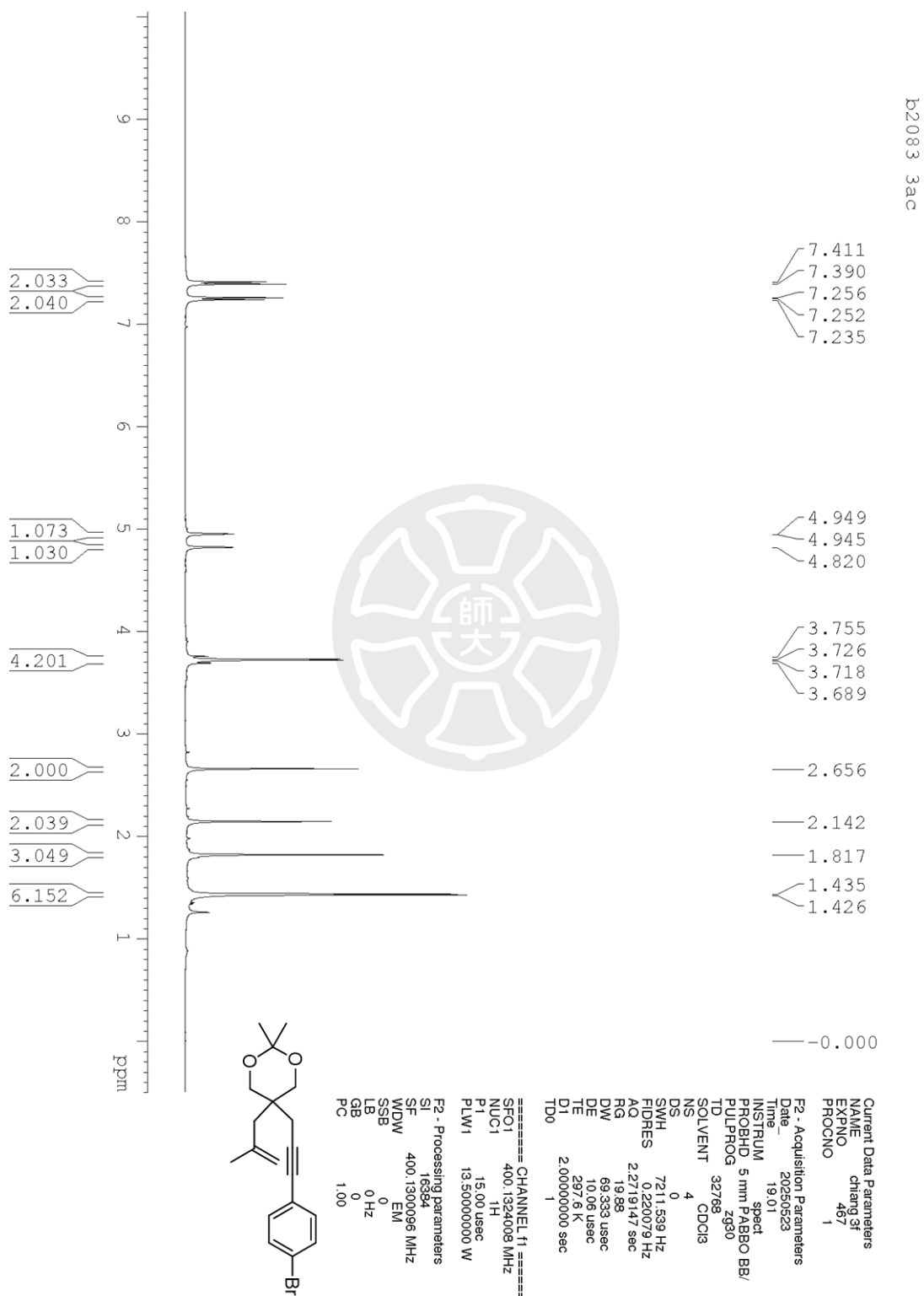
F2 - Acquisition Parameters
 Date_ 20250524
 Time_ 14:42
 INSTRUM spect
 PROBD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 492768
 SFO1 125.7618
 SOLVENT CDCl3
 NS 192
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 198.09
 DW 20.800 us
 DE 6.50 us
 TE 295.8 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6228298 MHz
 NUC1 13C
 P1 10.00 us
 P1M1 49.50000000 W

===== CHANNEL f2 =====
 SFO2 400.1316005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 us
 P1M2 12.50000000 W
 P1M12 0.34722000 W
 P1M13 0.28125000 W

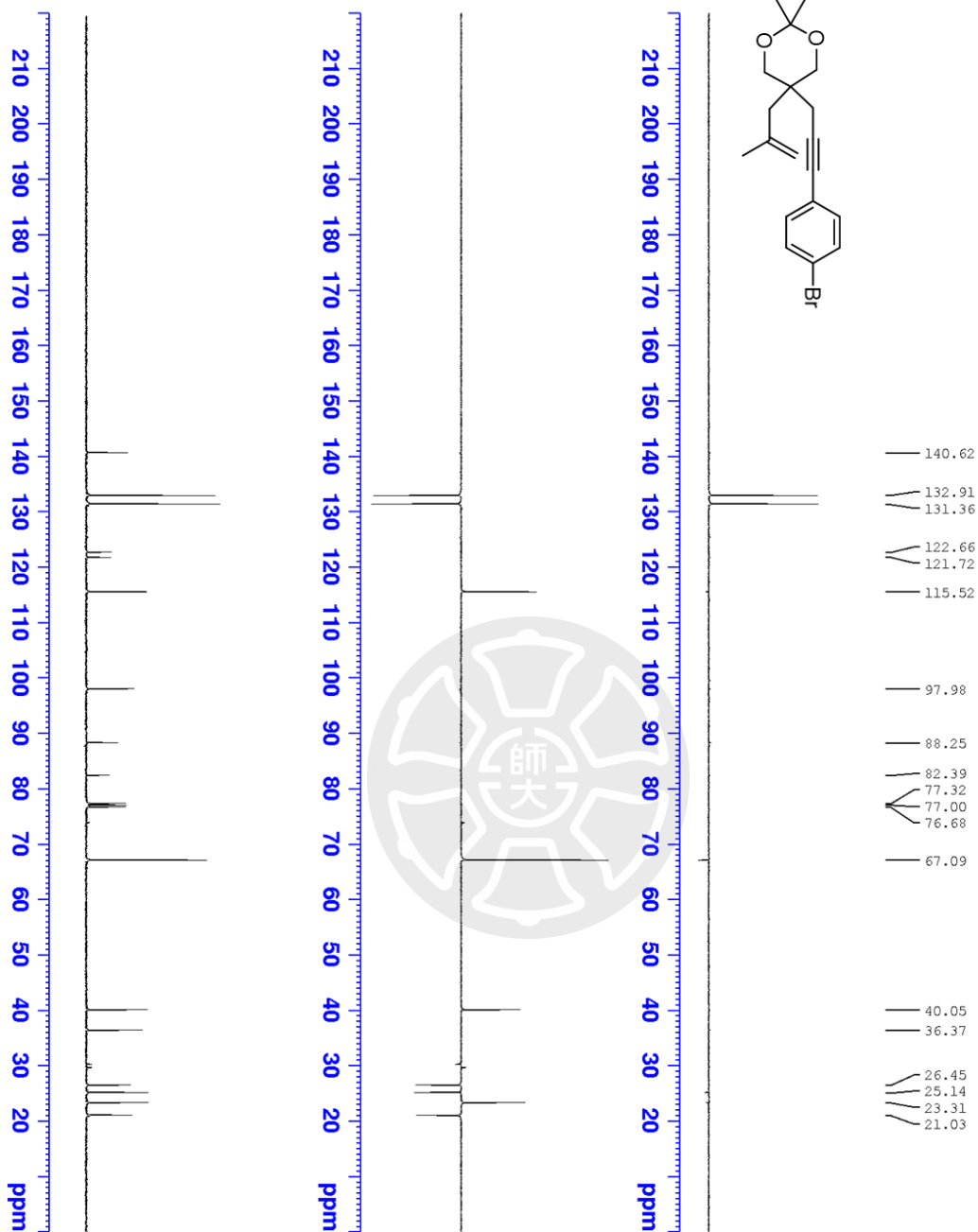
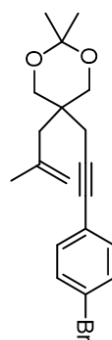
F2 - Processing parameters
 SI 32768
 SF 100.6127730 MHz
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of 5-(3-(4-bromophenyl)prop-2-yn-1-yl)-2,2-dimethyl-5-(2-methylallyl)-1,3-dioxane (43f)



¹³C NMR spectrum of 5-(3-(4-bromophenyl)prop-2-yn-1-yl)-2,2-dimethyl-5-(2-methylallyl)-1,3-dioxane (43f)

SCI3 b2083 13c



Current Data Parameters
 NAME I want to graduat.
 EXPNO 319
 PROCNO 1

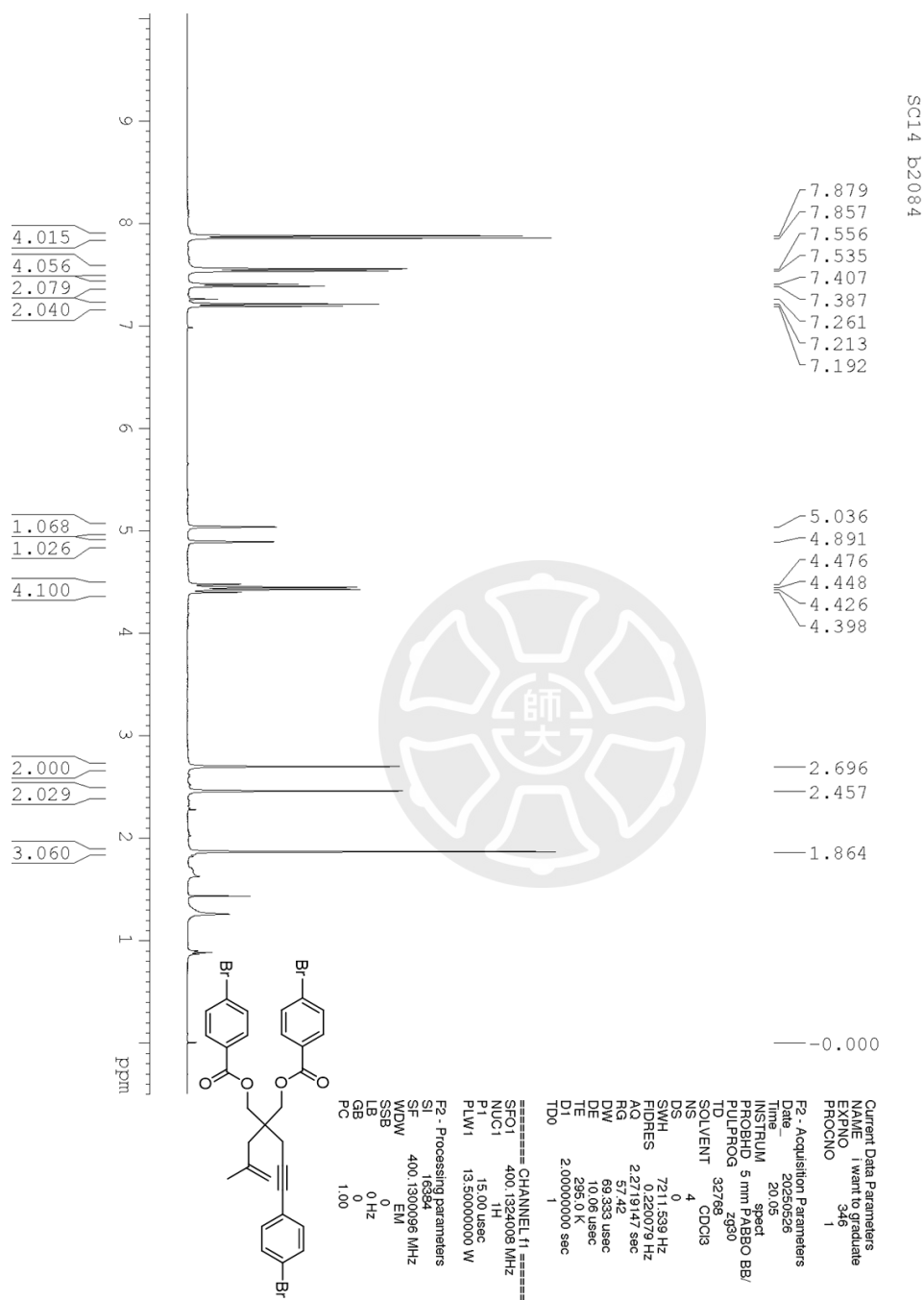
F2 - Acquisition Parameters
 Date_ 20250523
 Time 19.14
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 42
 DS 0
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 se
 RG 198.09
 DM 20.800 us
 DE 298.4 K
 TE 2.00000000 se
 D1 0.03000000 se
 D11 1
 TDO

==== CHANNEL F1 =====
 SFO1 100.6228298 MH
 NUCl 13C
 P1 10.00 us
 P1M1 49.50000000 W

==== CHANNEL F2 =====
 SFO2 400.1316005 MH
 NUCl 1H
 CPDPRG [2] waltz16
 PCPD2 90.00 us
 P1M2 12.50000000 W
 P1M12 0.34722000 W
 P1M13 0.28125000 W

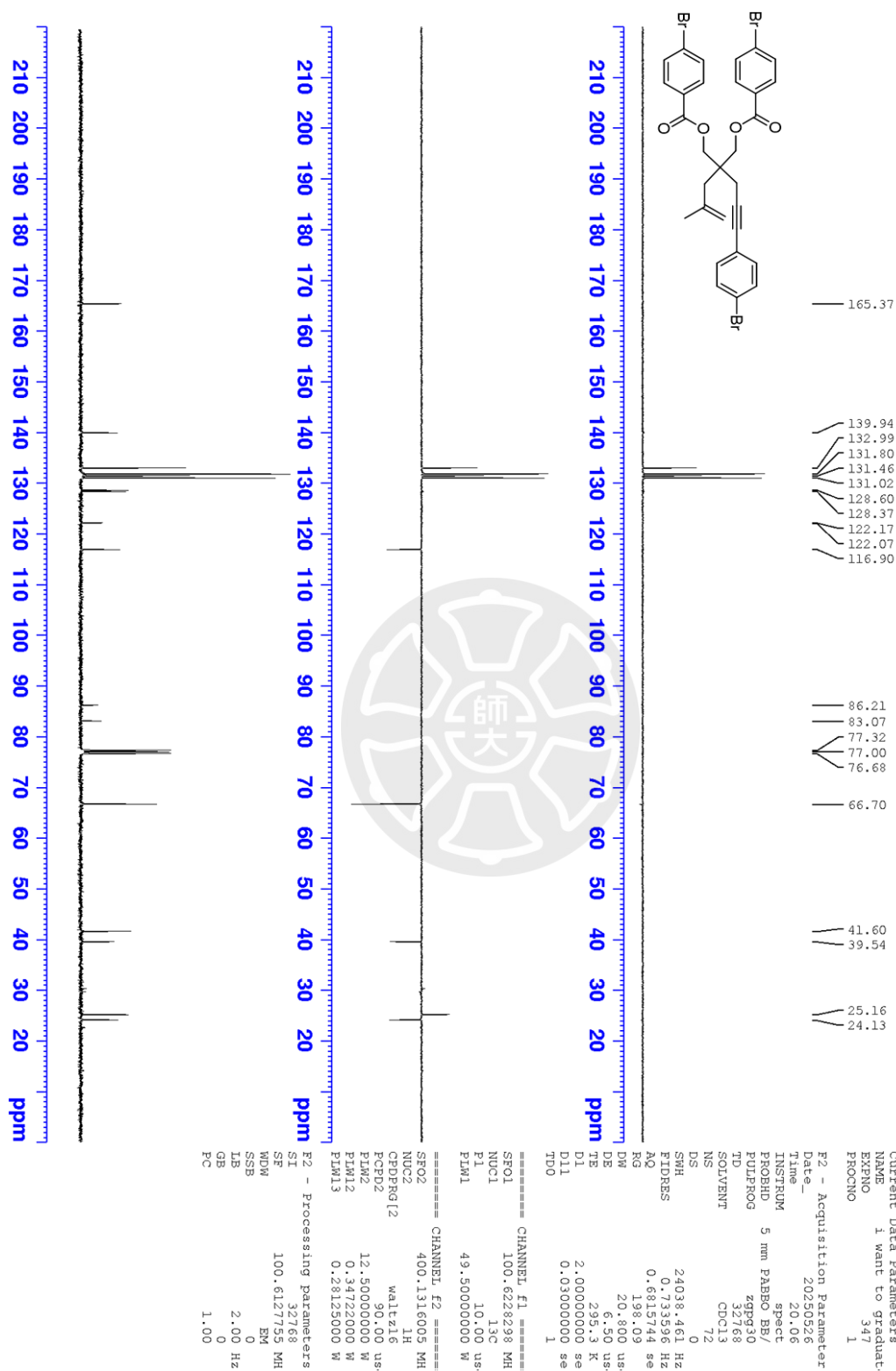
F2 - Processing parameters
 SI 32768
 SF 100.6127797 MH
 WDW EM
 SSB 0
 LB 2.00 Hz
 GB 0
 PC 1.00

¹H NMR spectrum of 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diyl bis(4-bromobenzoate) (43d)

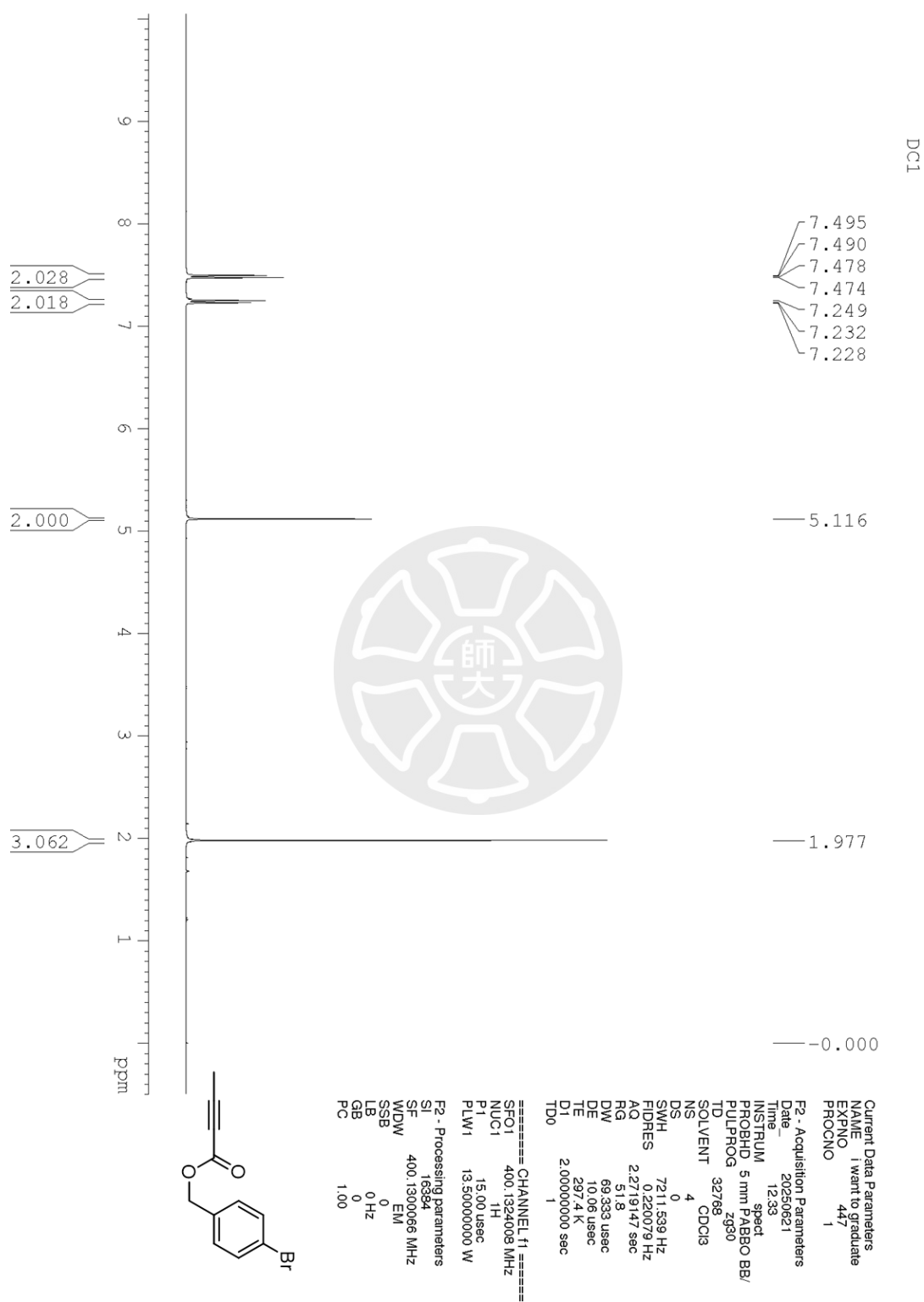


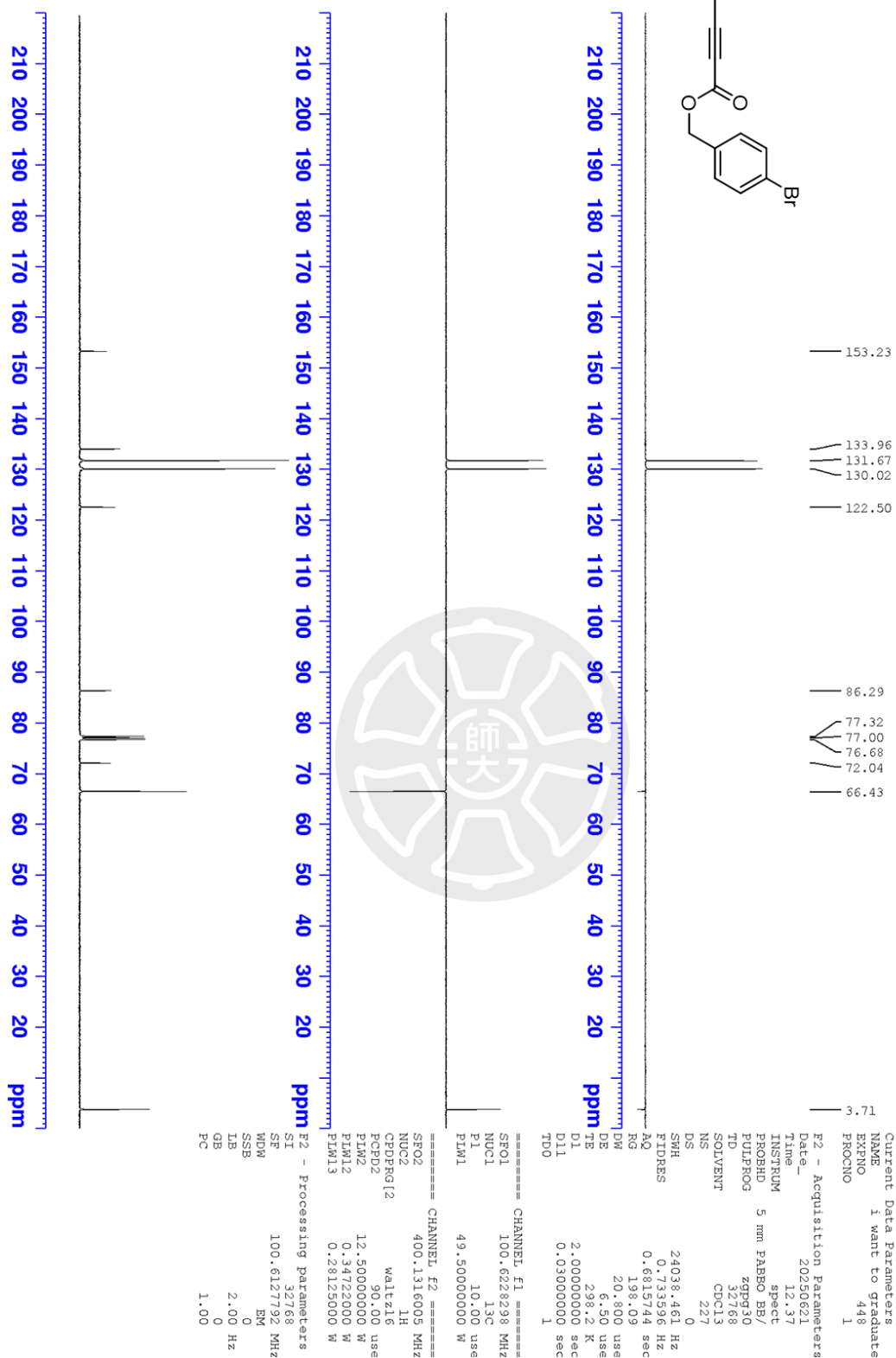
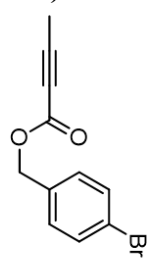
¹³C NMR spectrum of 2-(3-(4-bromophenyl)prop-2-yn-1-yl)-2-(2-methylallyl)propane-1,3-diyl bis(4-bromobenzoate) (43d)

SC14_b2084_13c

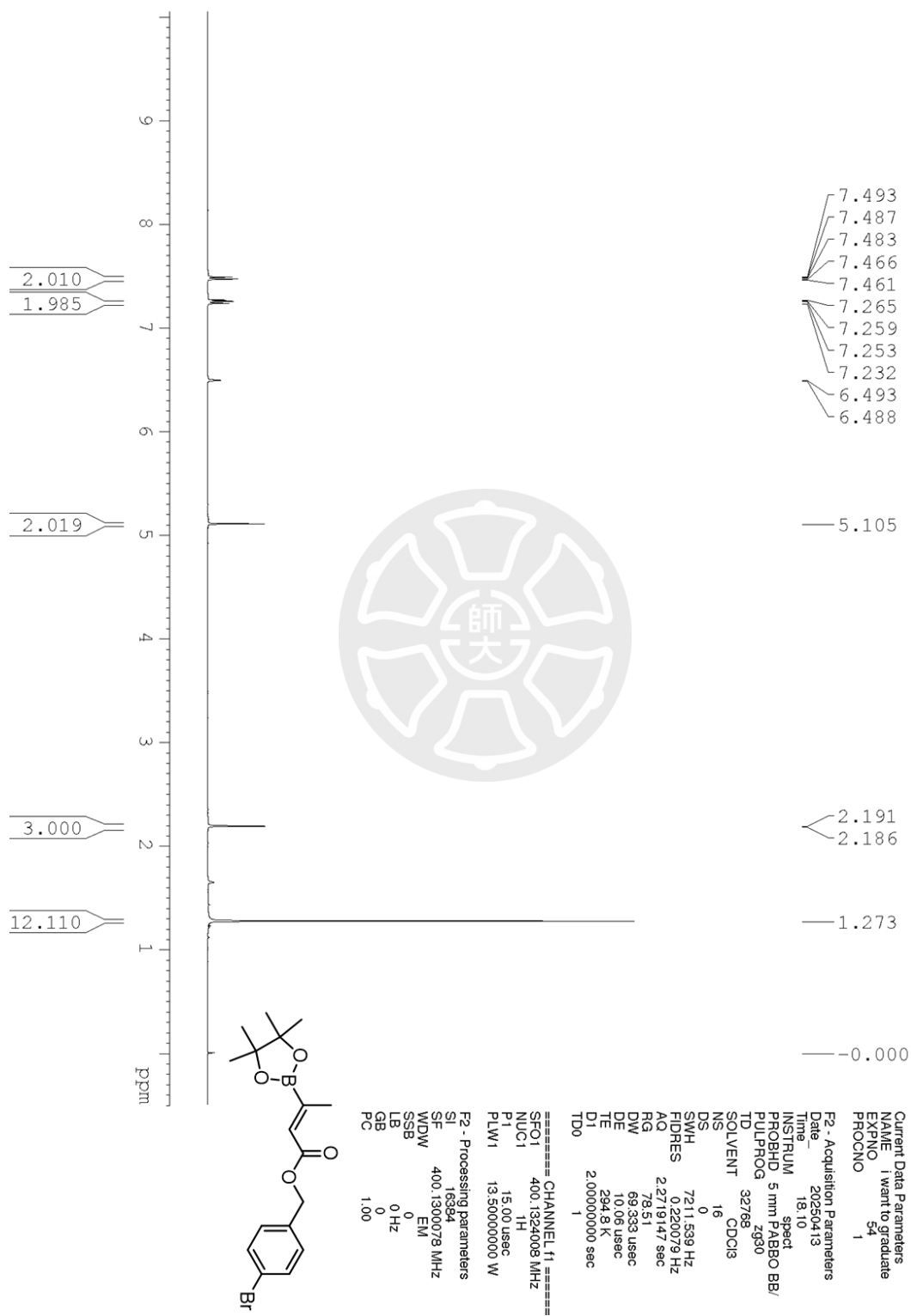


¹H NMR spectrum of 4-bromobenzyl but-2-ynoate (DC1)



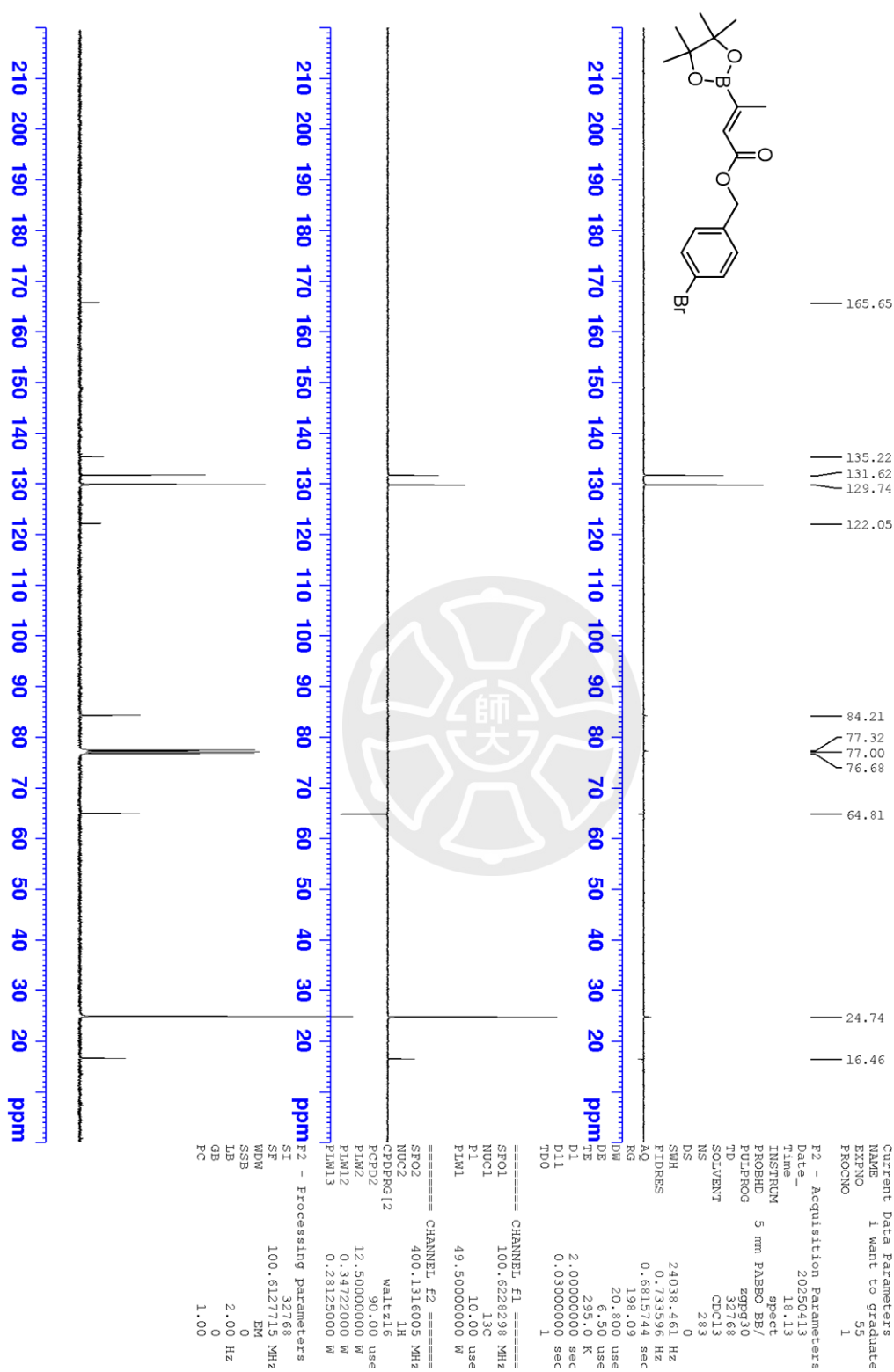
¹³C NMR spectrum of 4-bromobenzyl but-2-ynoate (DC1)

¹H NMR spectrum of 4-bromobenzyl (Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (37b)

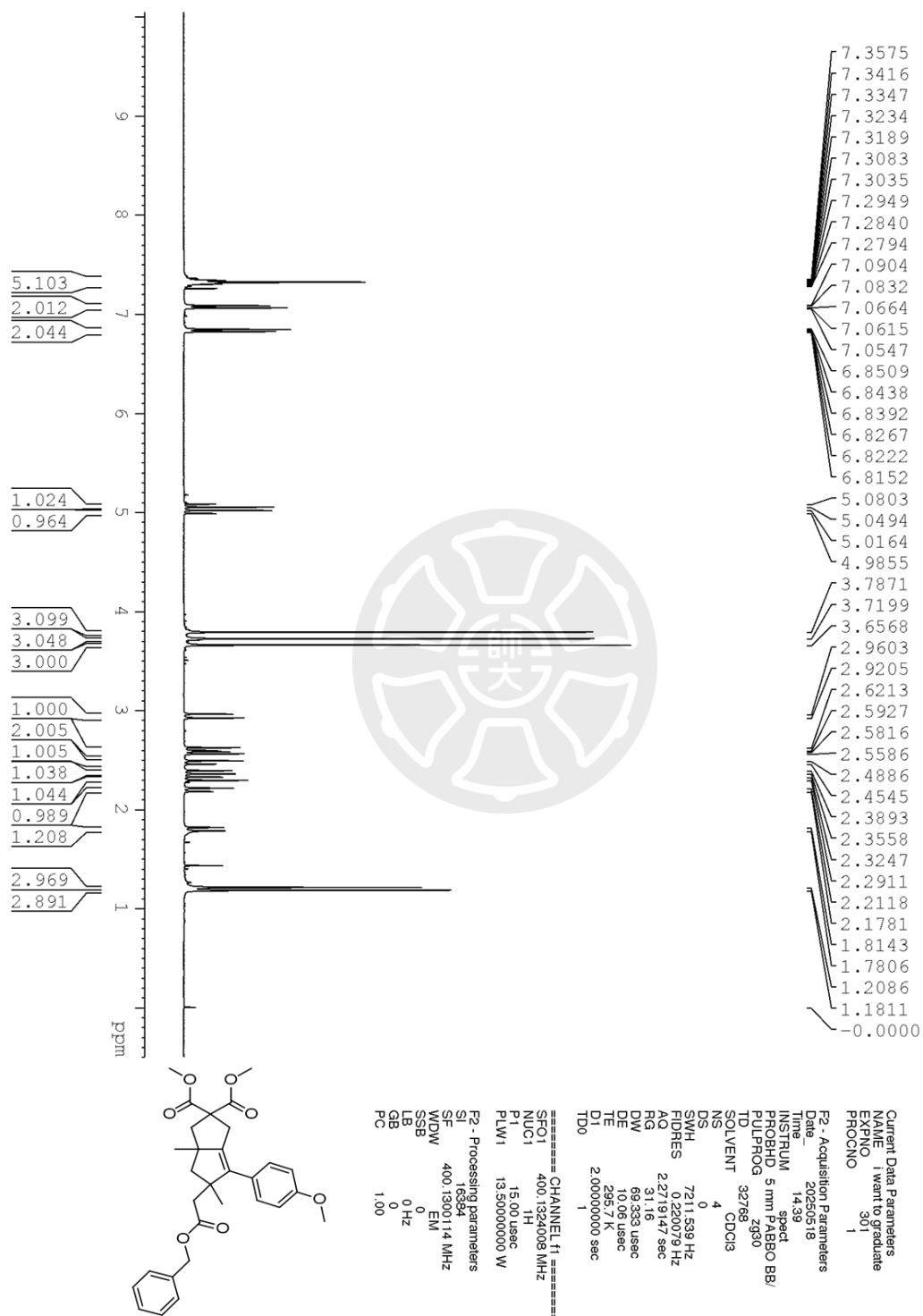


¹³C NMR spectrum of 4-bromobenzyl (Z)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-enoate (**37b**)

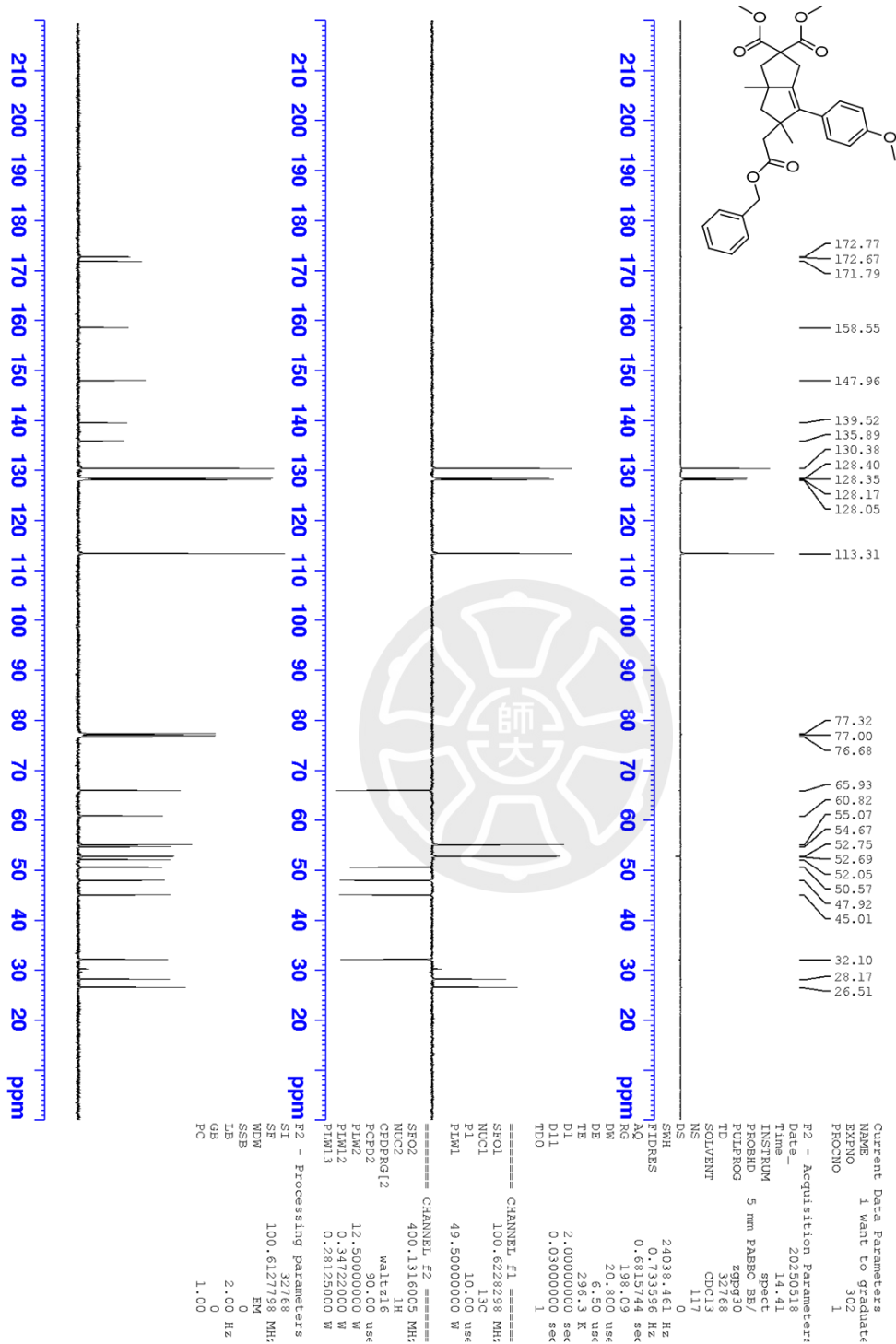
DC2 b2011 13c



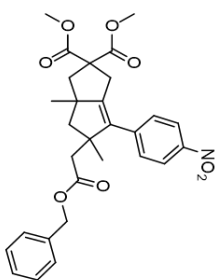
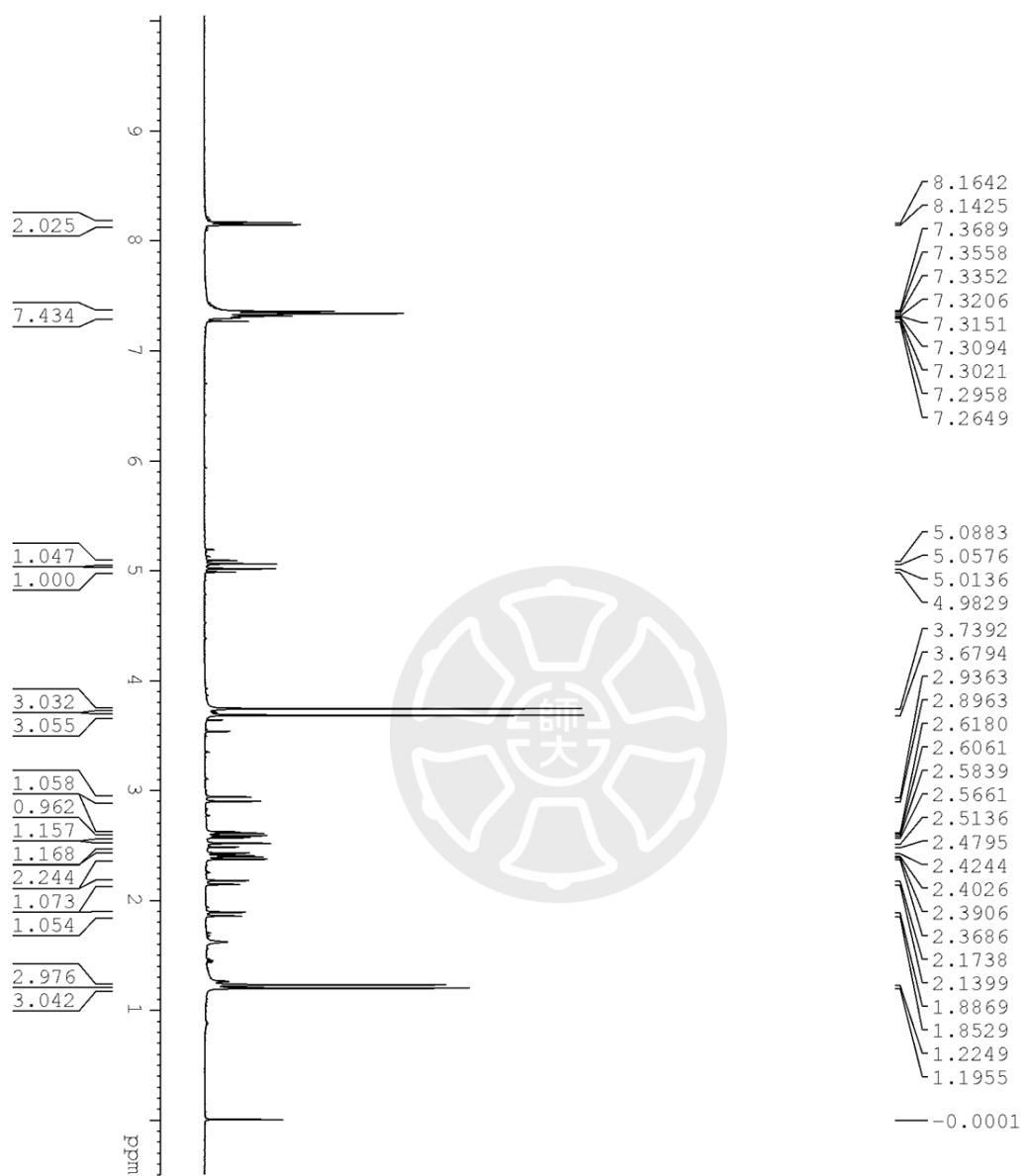
¹H NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-6-(4-methoxyphenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate(41aa)



¹³C NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-6-(4-methoxyphenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate(41aa)



¹H NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-nitrophenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ab)



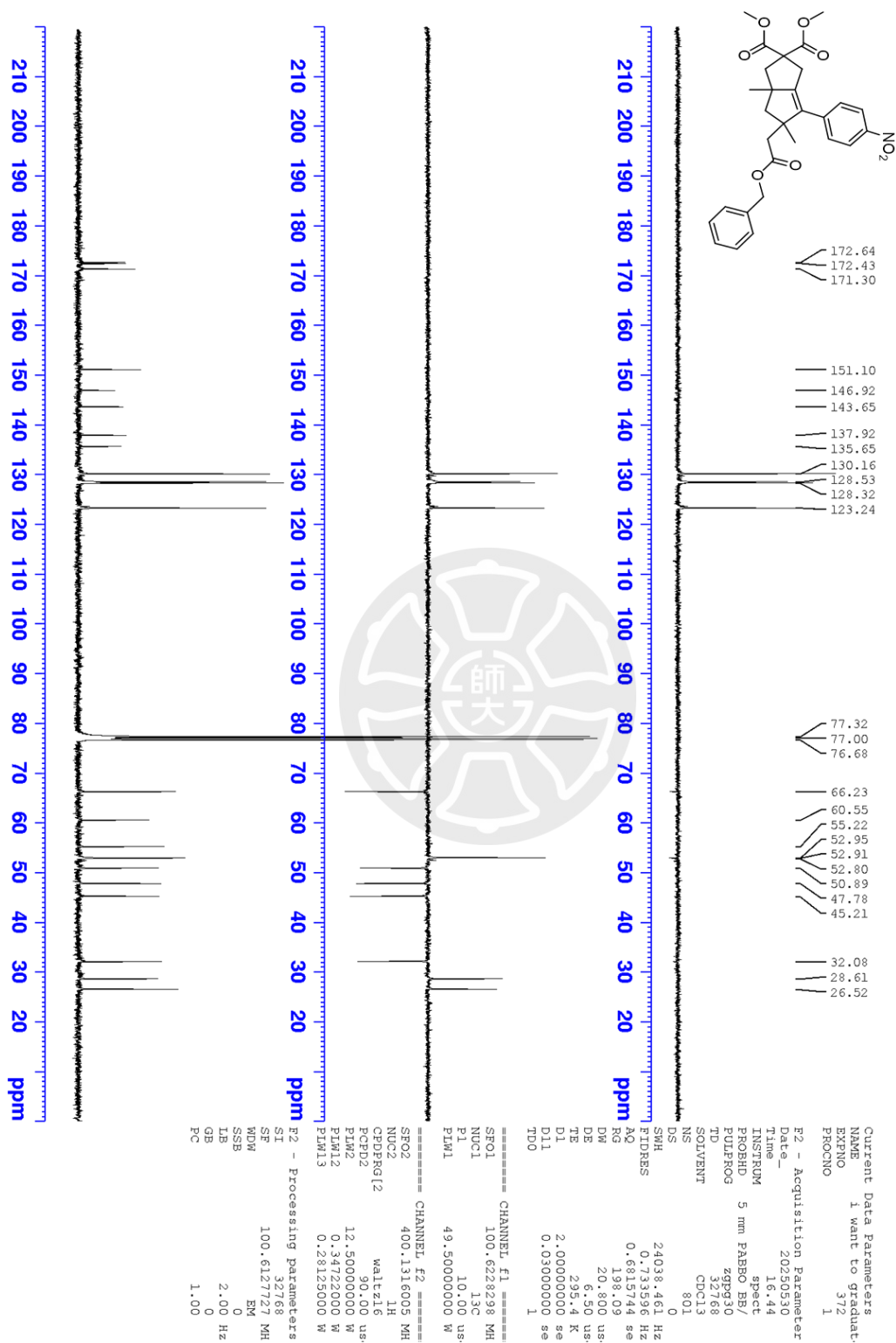
Current Data Parameters
 NAME i want to graduate
 EXPNO 371
 PROCNO 1

F2 - Acquisition Parameters
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 PULPROG zg30
 TD 32768
 SOLVENT 4 CDCl3
 NS 4
 DS 0
 SMH 721.539 Hz
 FIDRES 0.220079 Hz
 AQ 2.2719147 sec
 RG 89.08
 DW 69.333 usec
 DE 10.06 usec
 TE 294.7 K
 D1 2.00000000 sec
 TDO 1

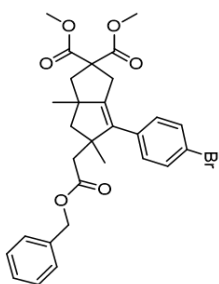
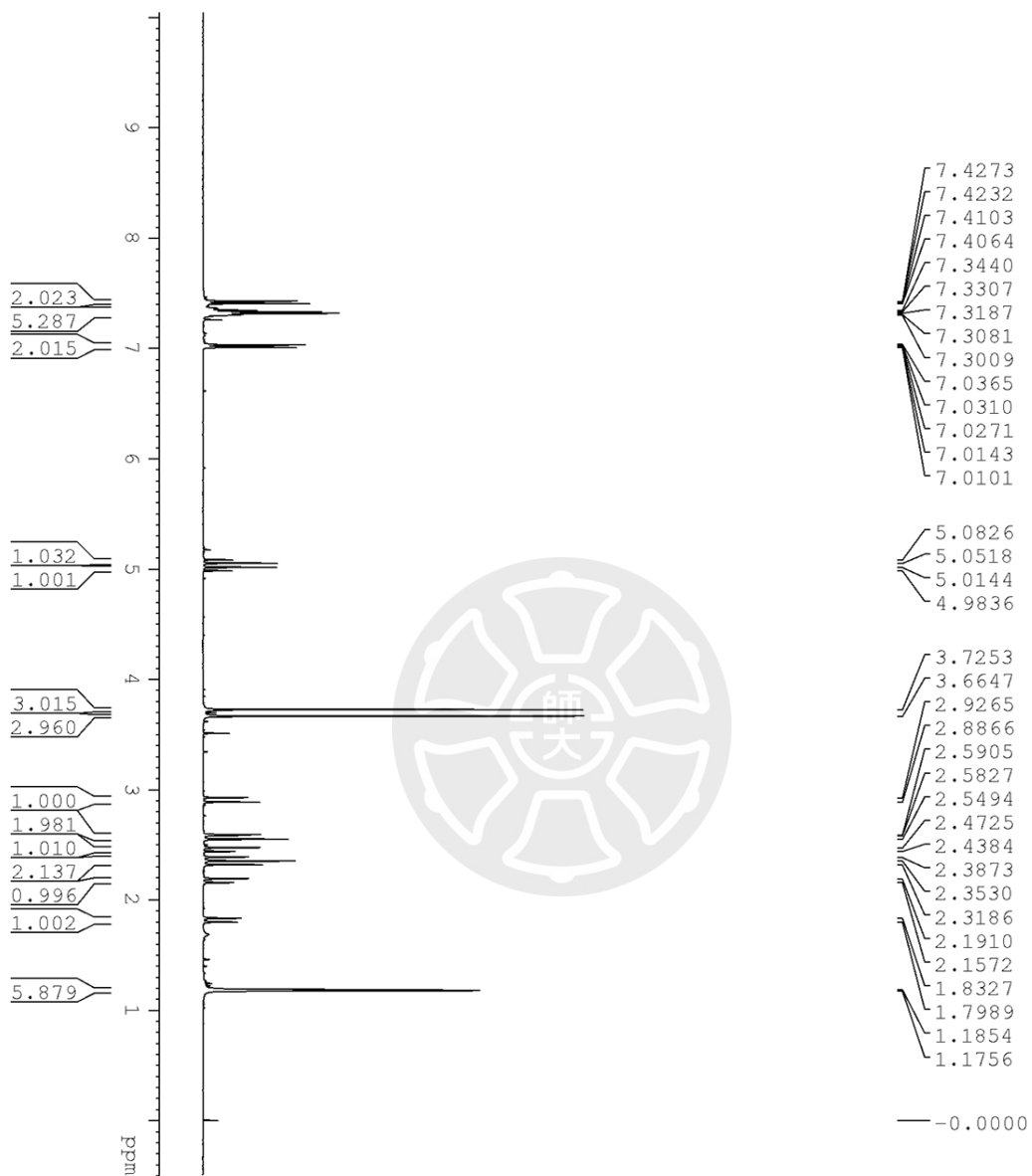
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 NUC1 1H
 P1 15.00 usec
 PLW1 13.50000000 W

F2 - Processing parameters
 SF 400.1324008 MHz
 SE 16384
 WIDW 400.1324008 MHz
 SSB 0
 LB 0 Hz
 GB 0
 PC 1.00

¹³C NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-nitrophenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ab)



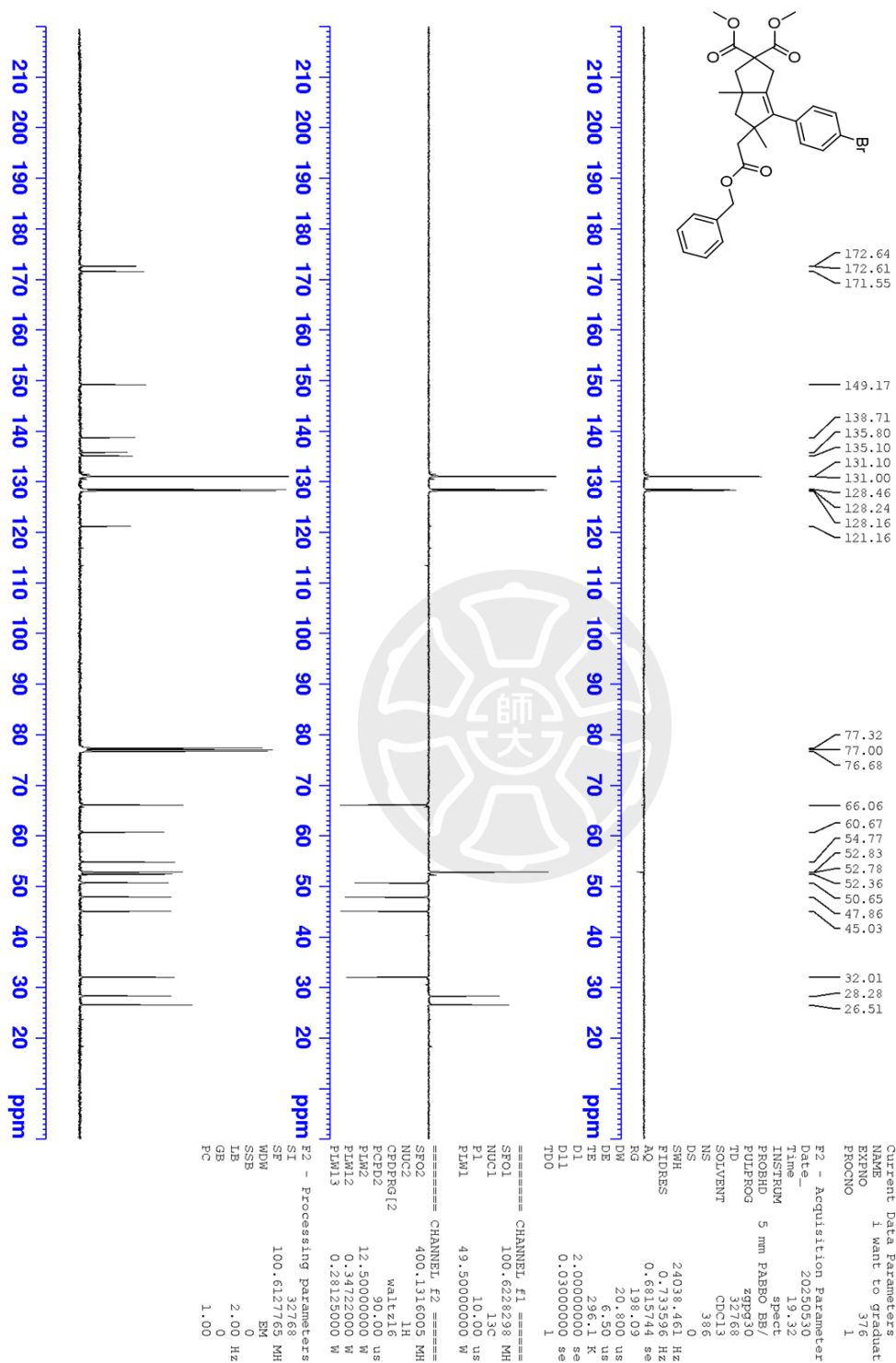
¹H NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-6-(4-bromo phenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ac)



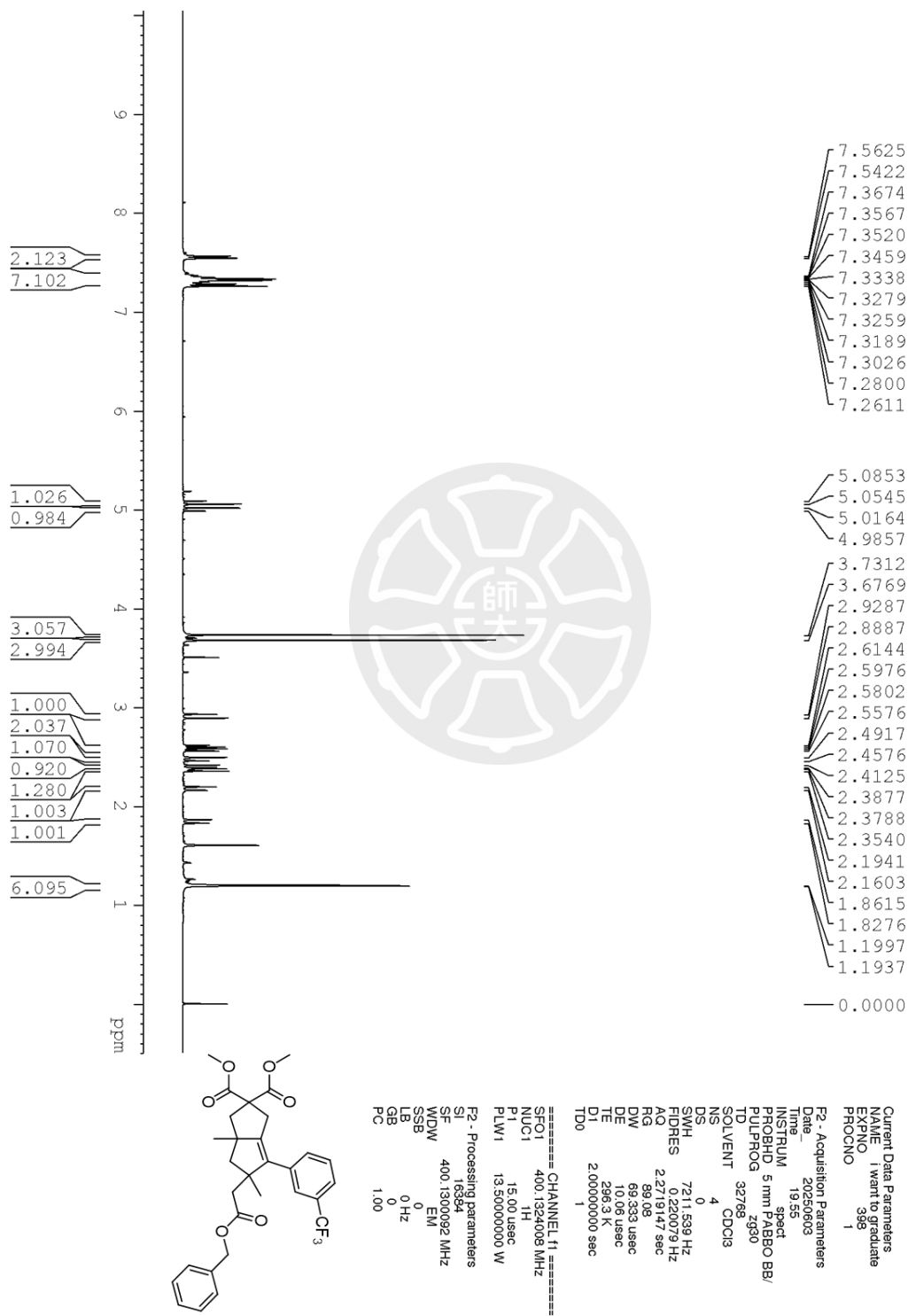
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Current Data Parameters
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EXPNO: 375
PROCNO: 1
F2 - Acquisition Parameters
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Time    19:30
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PROBHD  5 mm PABBO BB/
PULPROG zg30
TD       32768
SOLVENT CDCl3
NS       4
DS       0
SWH      7211.5391 Hz
FIDRES   2.271420079 Hz
AQ       2.271417 sec
RG       481
DE       69.329 usec
TE       296.9 K
D1       2.00000000 sec
TD0      1
===== CHANNEL f1 =====
SFO1    400.1324008 MHz
NUC1    1H
P1      15.00 usec
PLW1    13.500000000 W
F2 - Processing parameters
SI       16384
SF       400.1300102 MHz
WDW      EM
SSB      0
GB       0 Hz
PC       1.00
  
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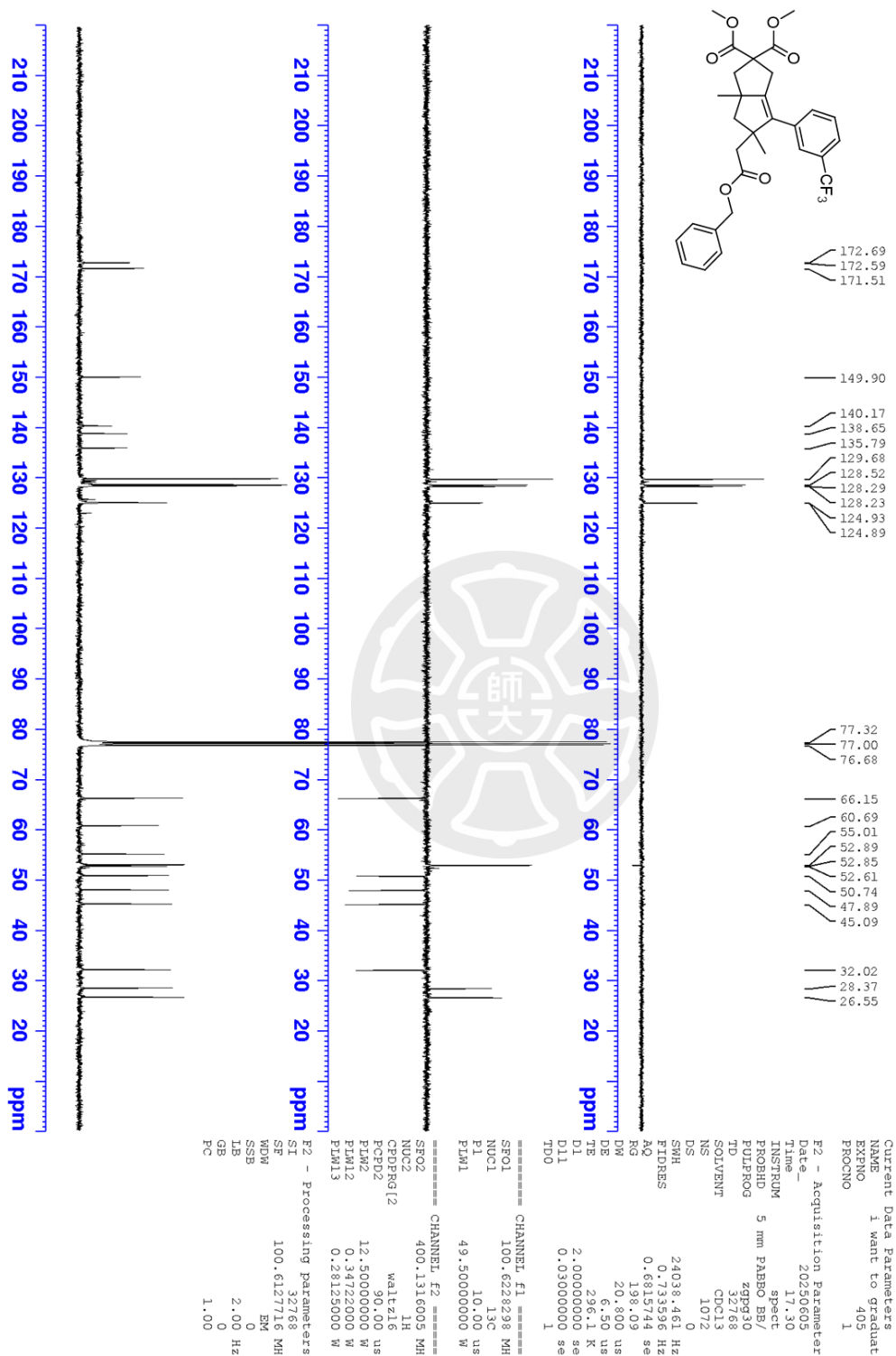
¹³C NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-6-(4-bromo phenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ac)



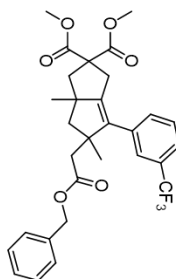
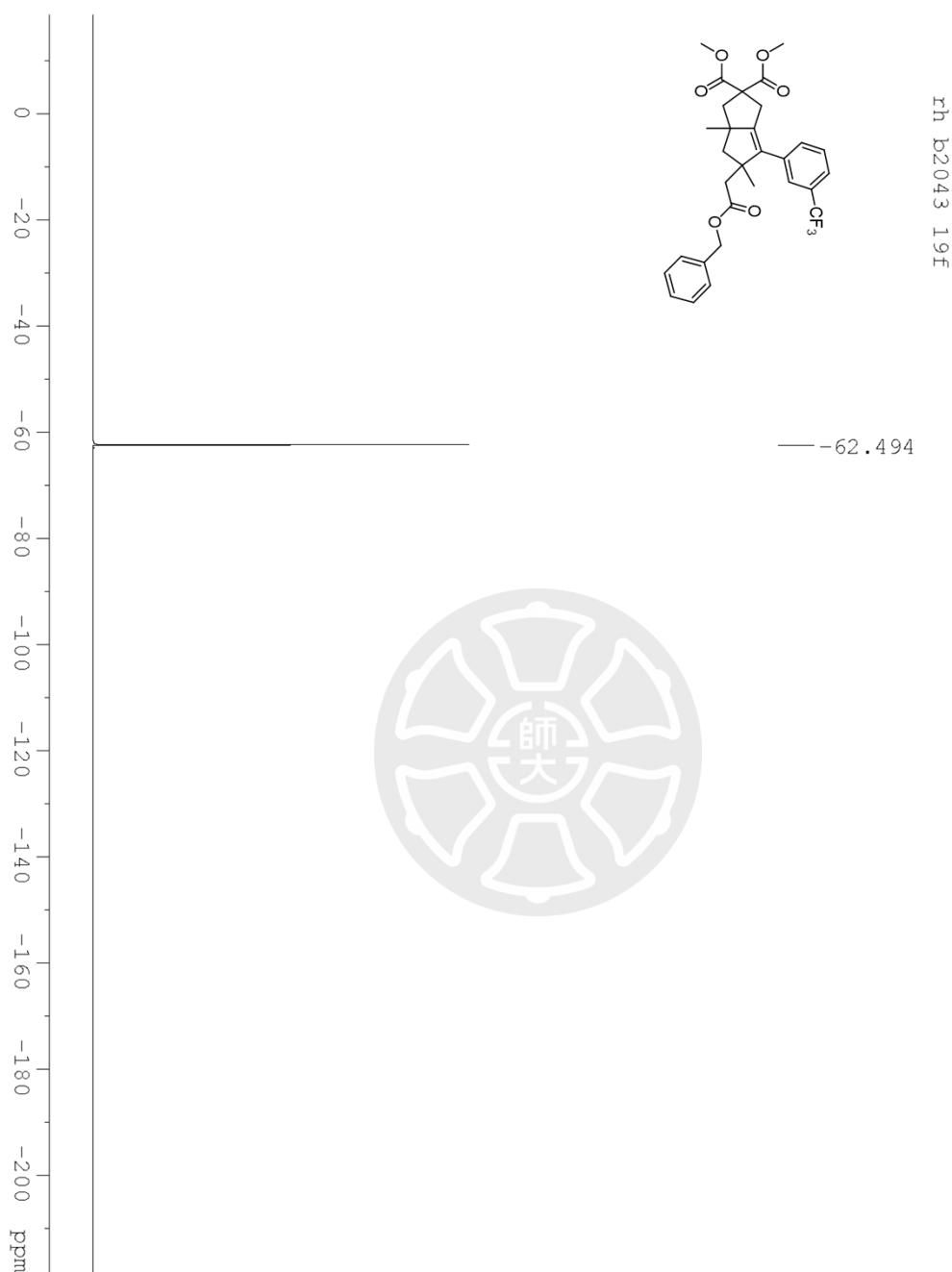
¹H NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(3-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ad)



¹³C NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(3-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ad)



¹⁹F NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(3-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ad)



```

Current Data Parameters
NAME      I want to graduate
EXPNO     486
PROCNO    1

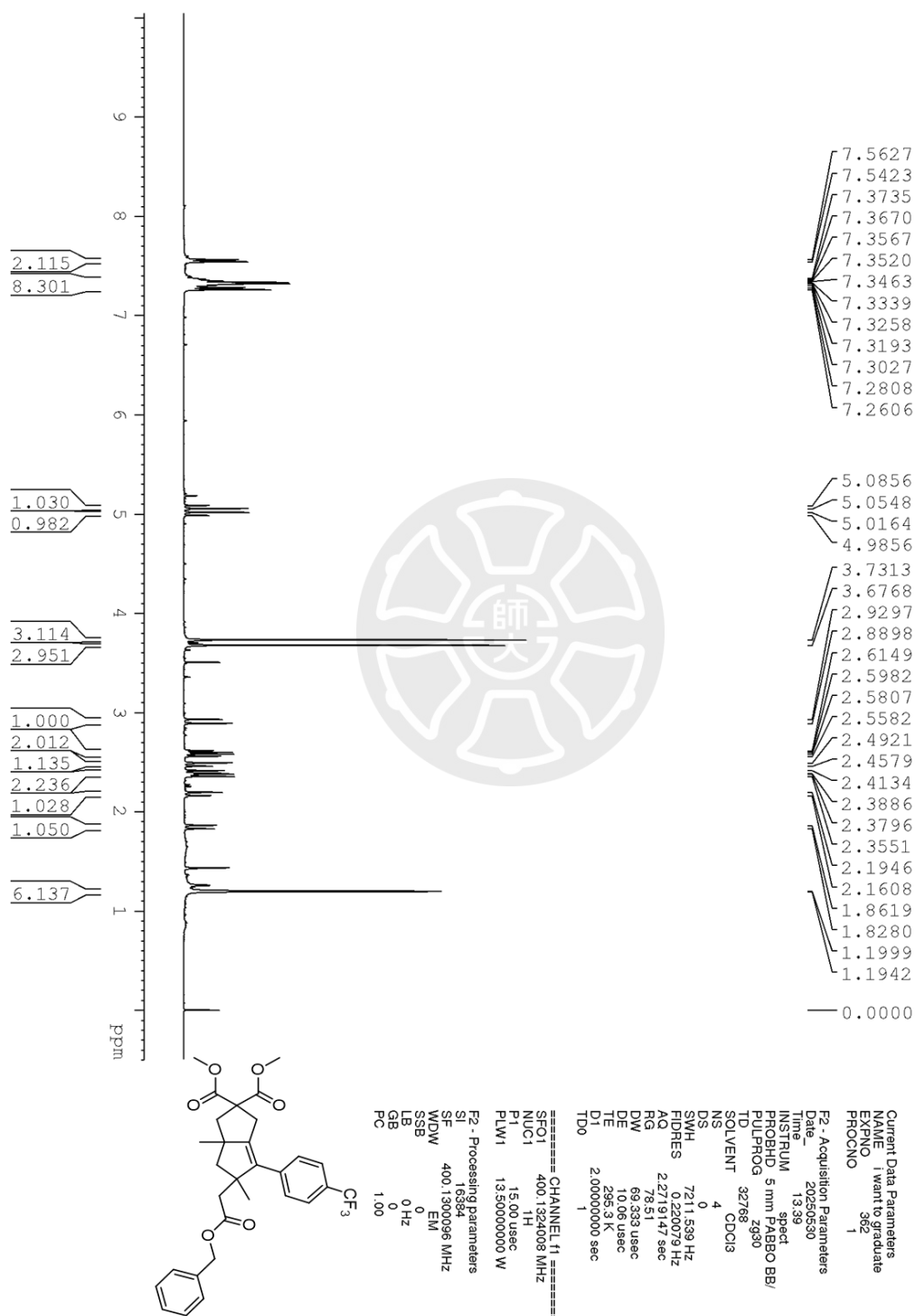
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TD         131072
SOLVENT   CDCl3
NS         16
DS         0
SWH        8925.711 Hz
FIDRES     0.691196 Hz
AQ         0.7340082 sec
RG         198.09
DW         5.60 usec
DE         295.5 K
TE         1.00000000 sec
D1         0.03000000 sec
TD0        1

===== CHANNEL f1 =====
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NUC1       19F
P1         15.00 usec
PLW1      16.50000000 W

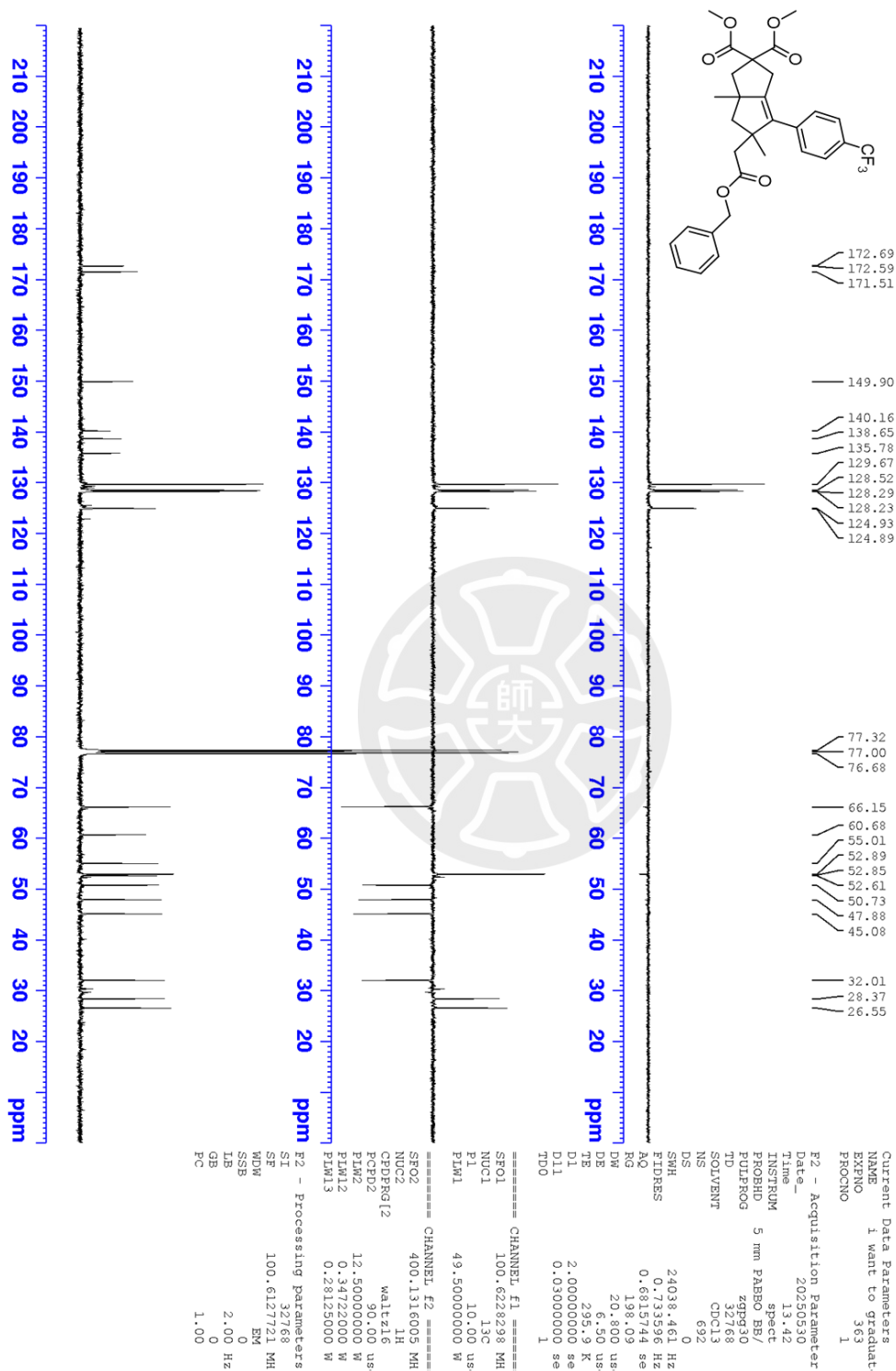
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PLW12     0.34722000 W

F2 - Processing parameters
    
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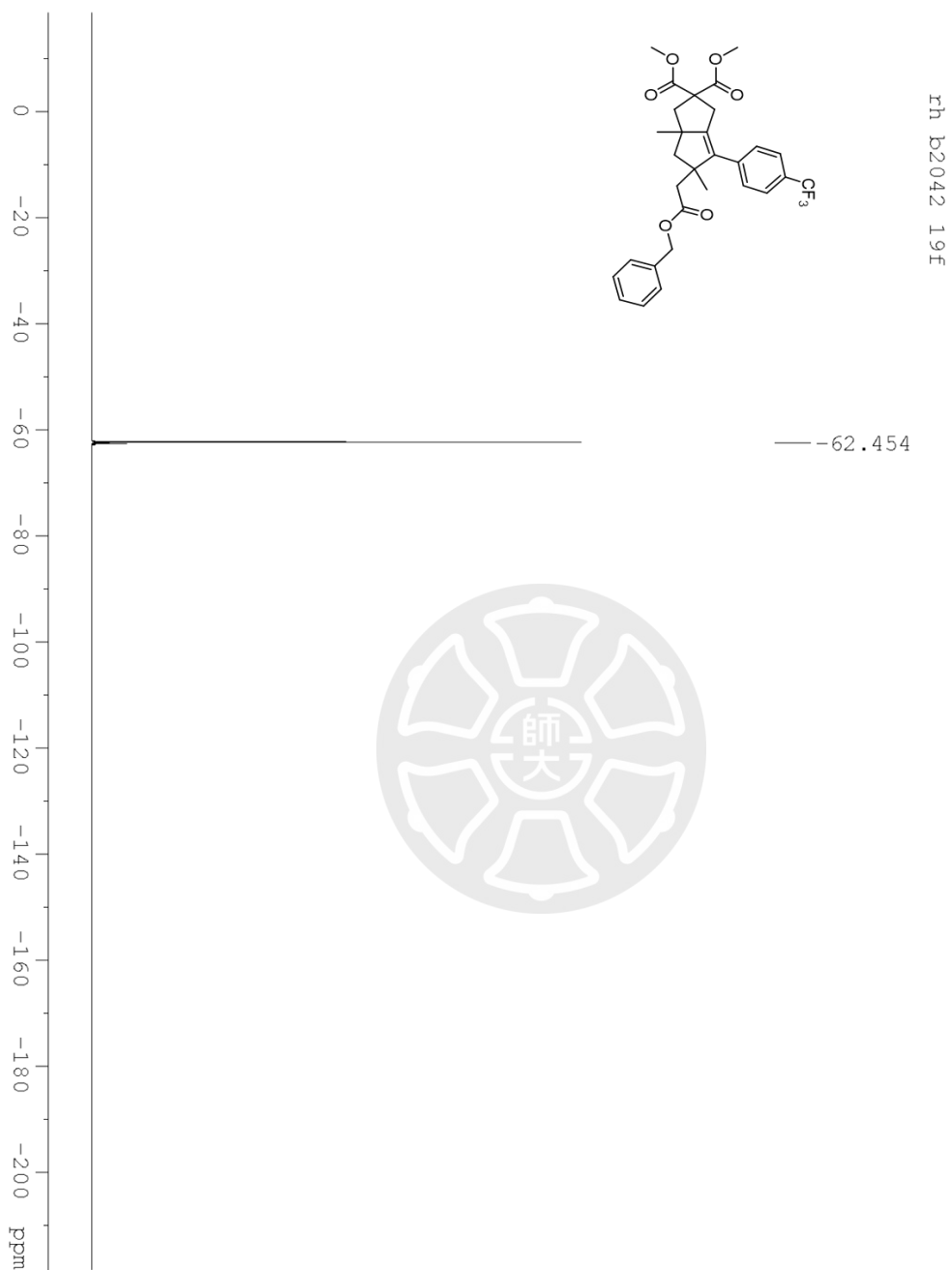
¹H NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ae)



¹³C NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ae)



¹⁹F NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ae)



rh b2042 19F

-62.454

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Current Data Parameters
NAME      i want to graduate
EXPNO    468
PROCNO   1

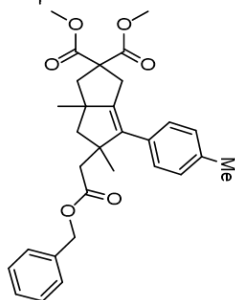
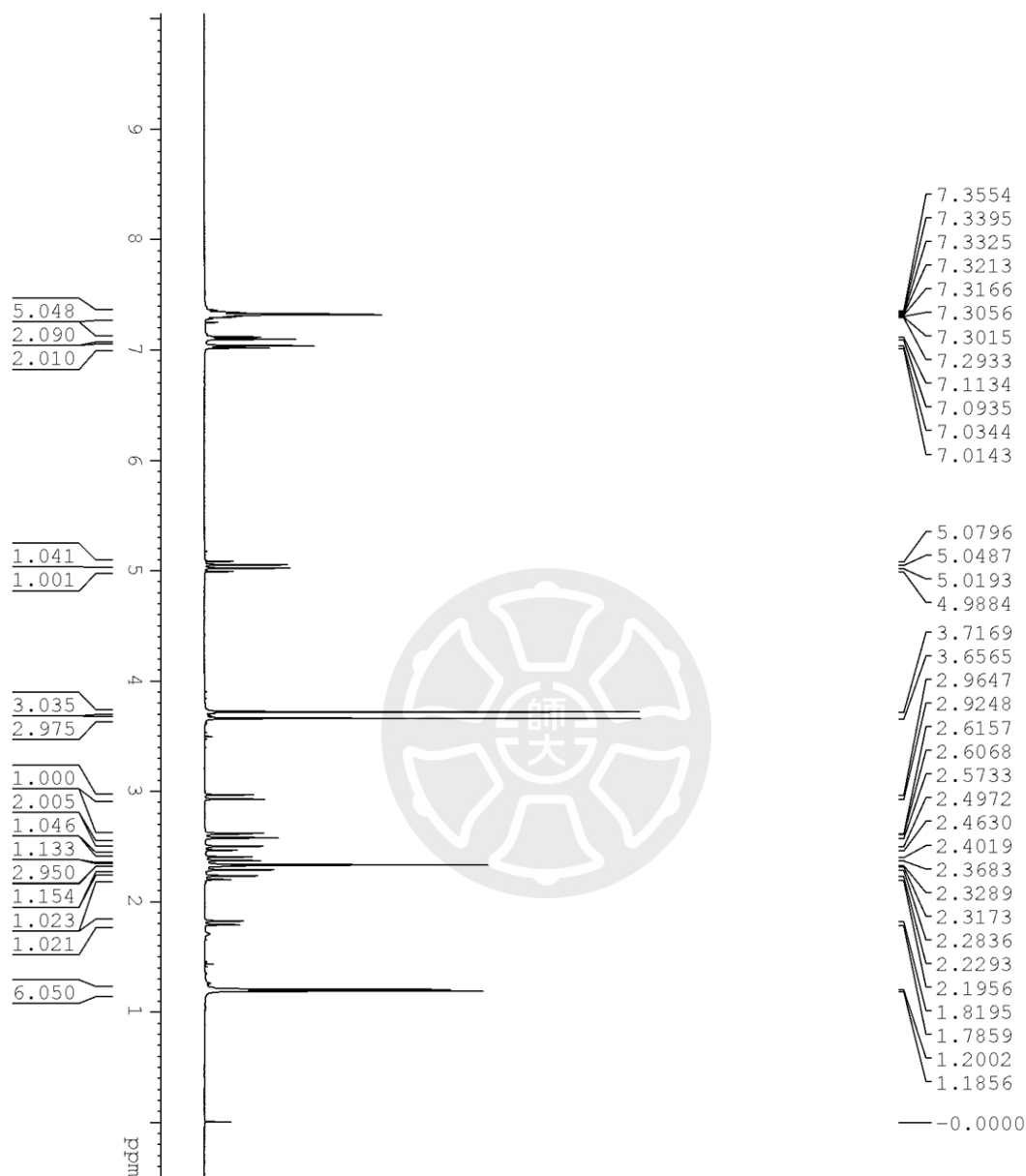
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SWH      89285.711 Hz
FIDRES   0.681196 Hz
AQ       0.7340032 sec
RG       198.09
DW       5.600 usec
DE       6.50 usec
TE       295.9 K
D1       1.000000000 sec
D11      0.030000000 sec
TD0      1

===== CHANNEL f1 =====
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NUC1     19F
P1       15.00 usec
PLW1    16.500000000 W

===== CHANNEL f2 =====
SFO2     400.1316005 MHz
NUC2     1H
CPDPRG2  waltz16
PCPD2    90.00 usec
PLW2    12.500000000 W
PLW12   0.34722000 W

F2 - Processing parameters
    
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¹H NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(p-tolyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41af)



```

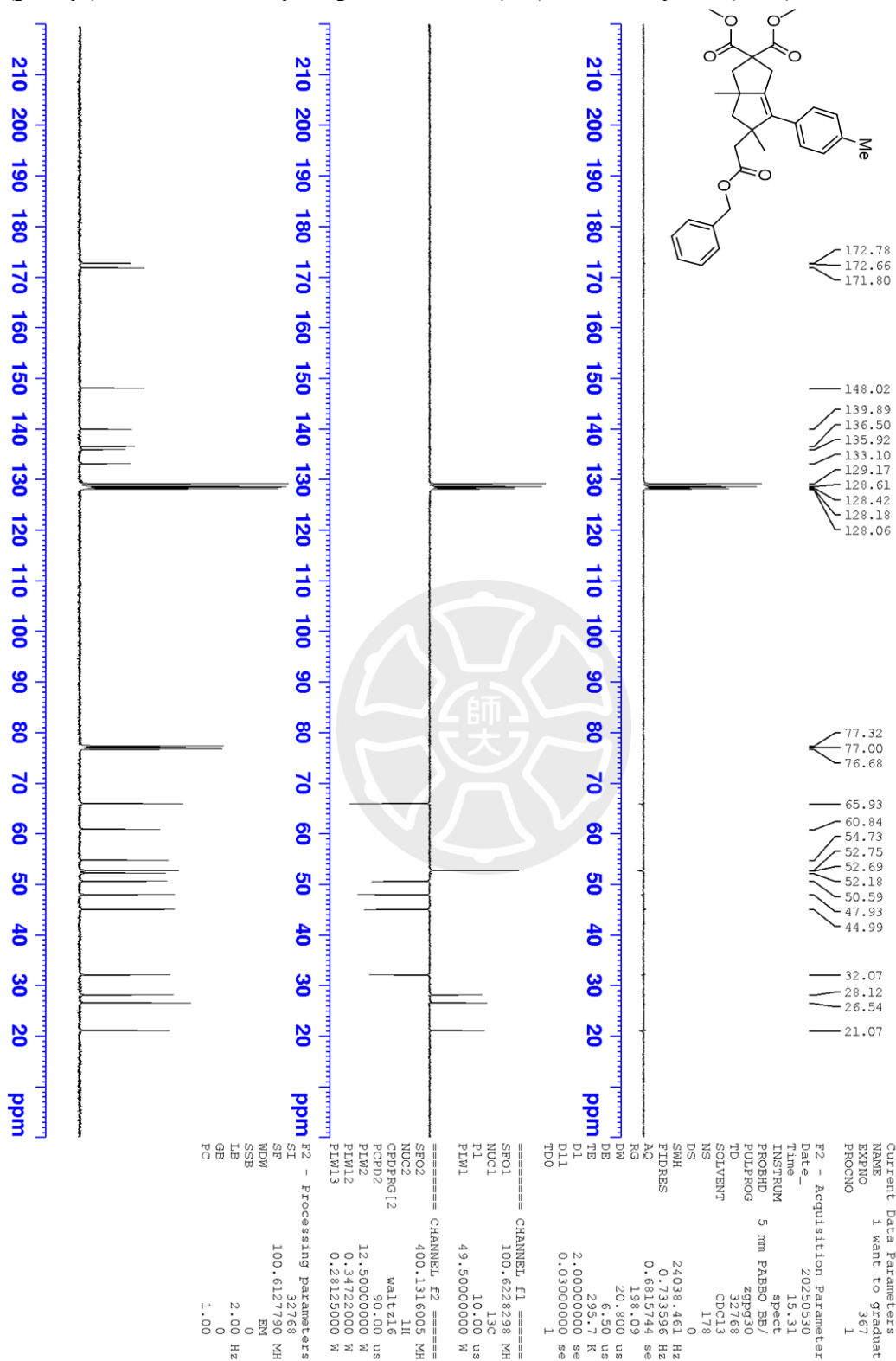
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EXPNO: 359
PROCNO: 1

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TD       32768
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DS       0
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DW       69.333 usec
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TE       295.1 K
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TD0      1

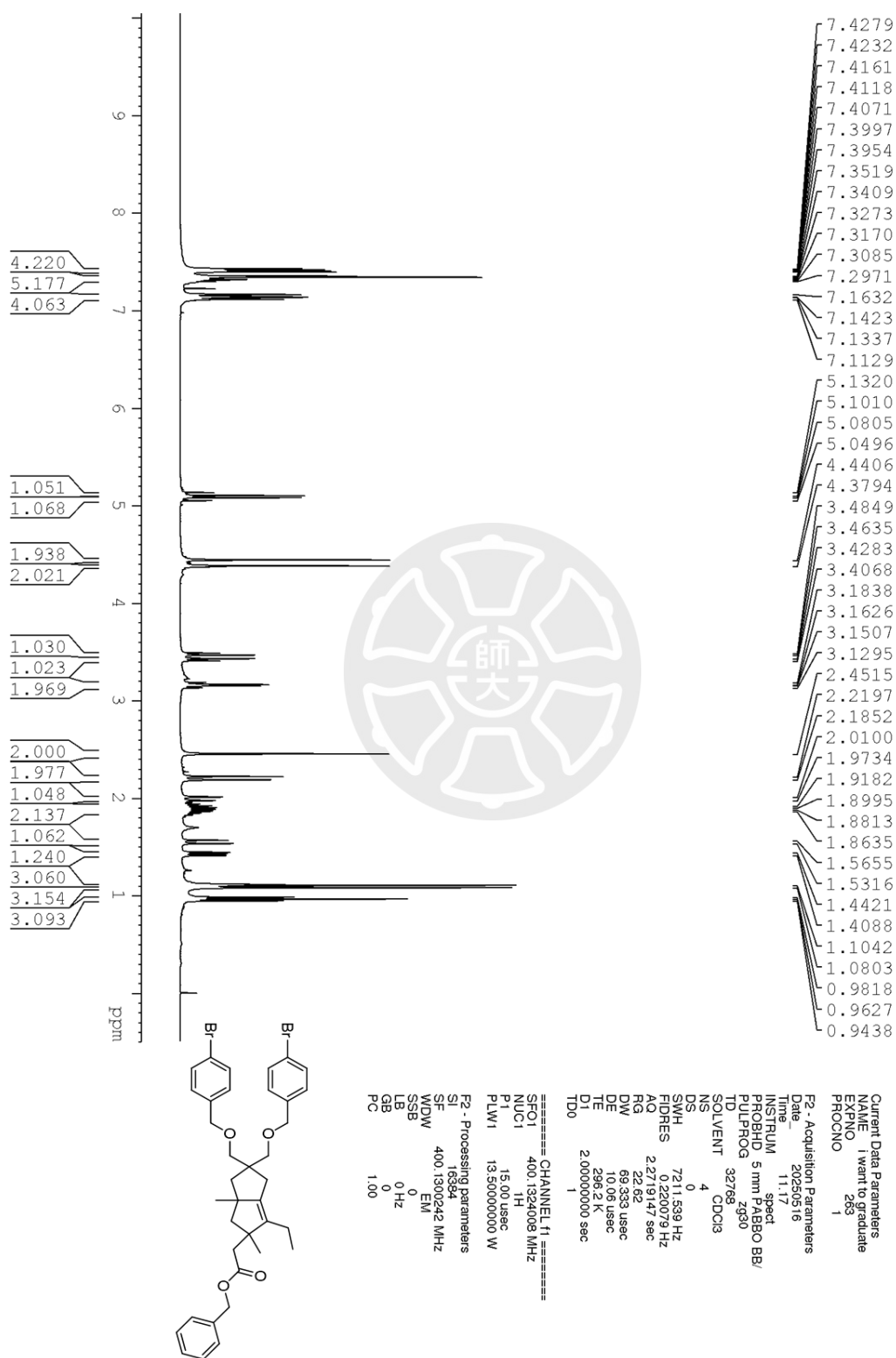
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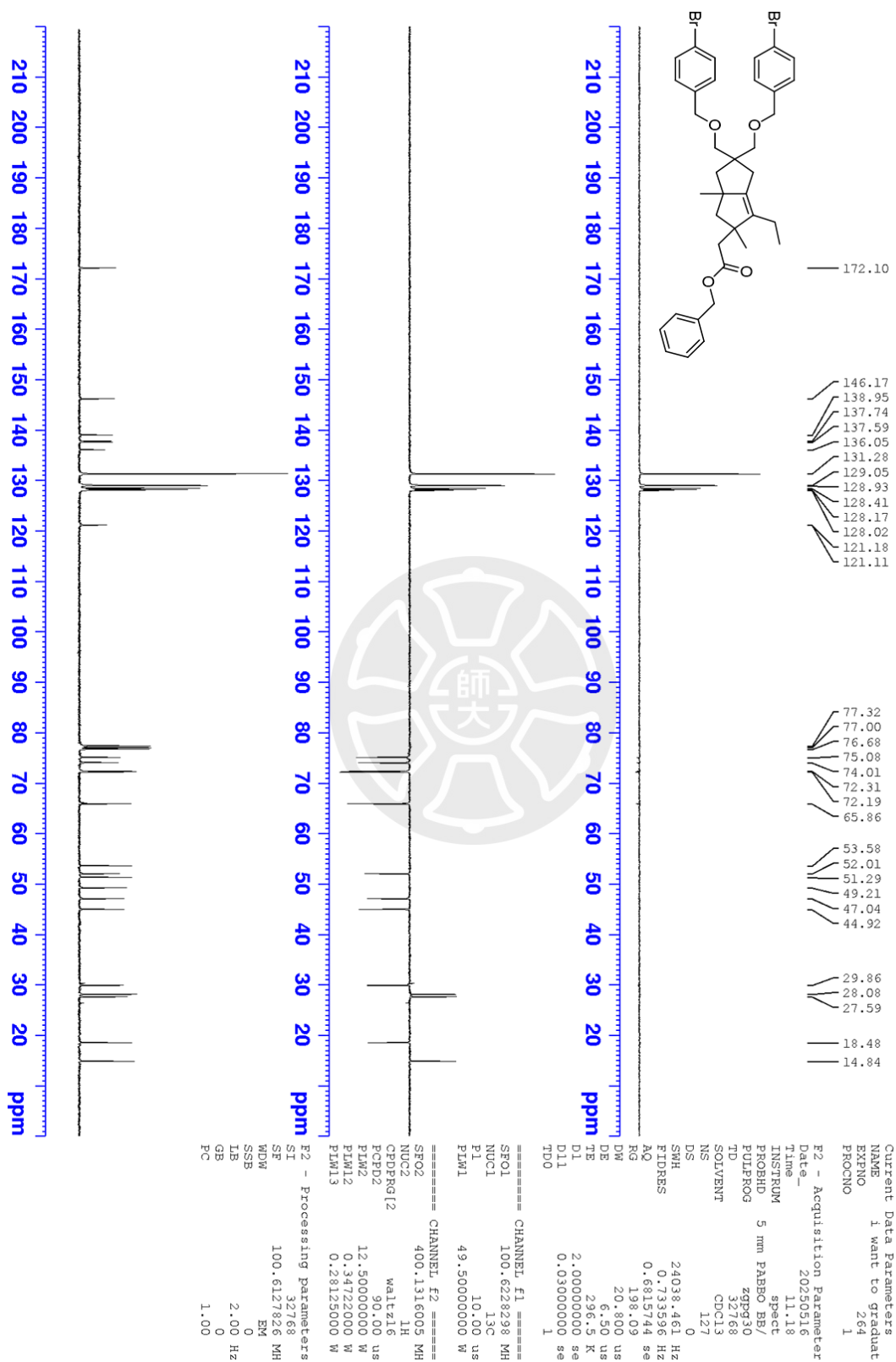
¹³C NMR spectrum of dimethyl 5-(2-(benzyloxy)-2-oxoethyl)-3a,5-dimethyl-6-(p-tolyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (44af)



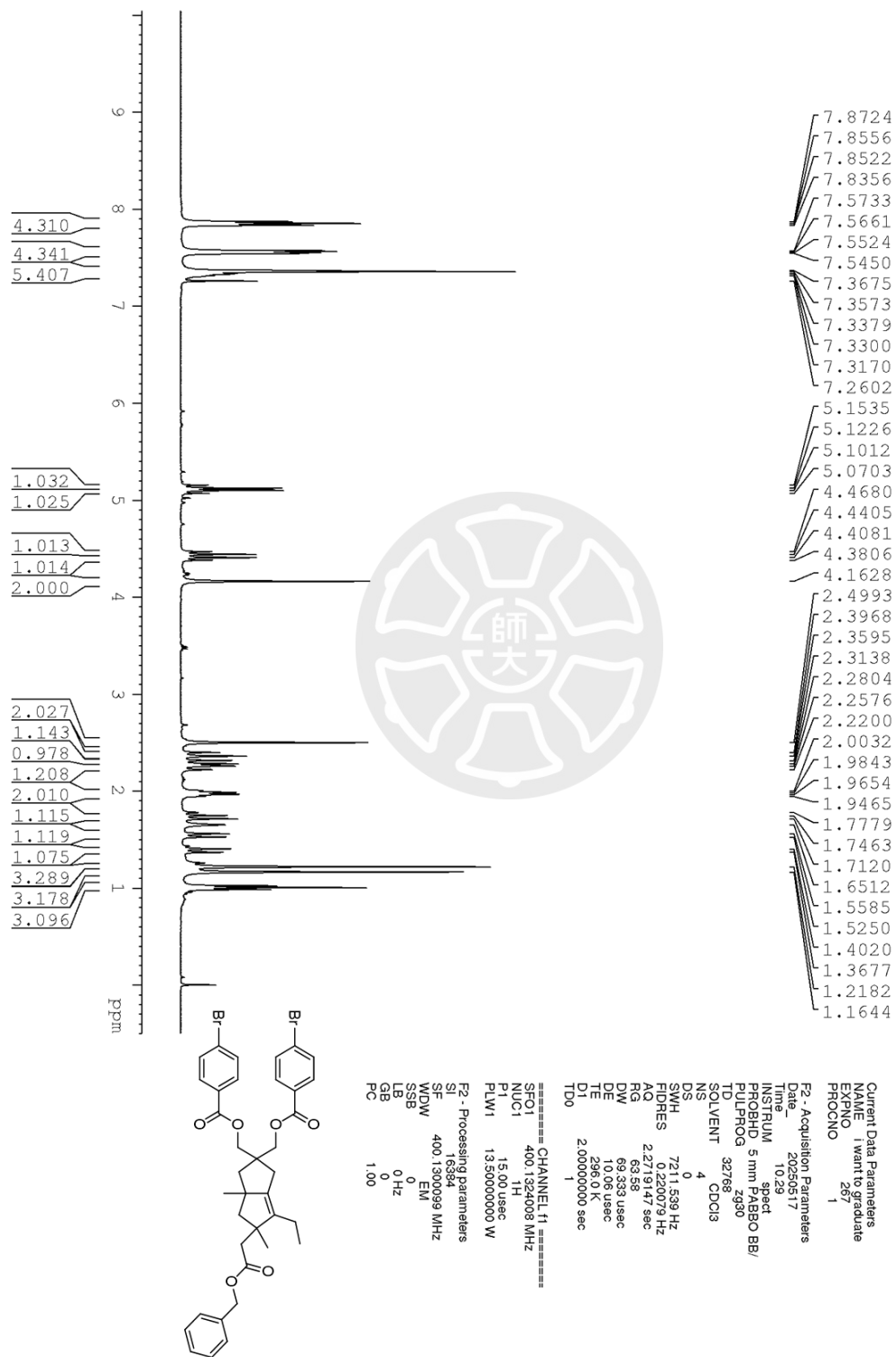
¹H NMR spectrum of benzyl 2-(5,5-bis(((4-bromobenzyl)oxy)methyl)-3-ethyl-2,6a-dimethyl-1,2,4,5,6,6a-hexahydropentalen-2-yl)acetate (44aa)



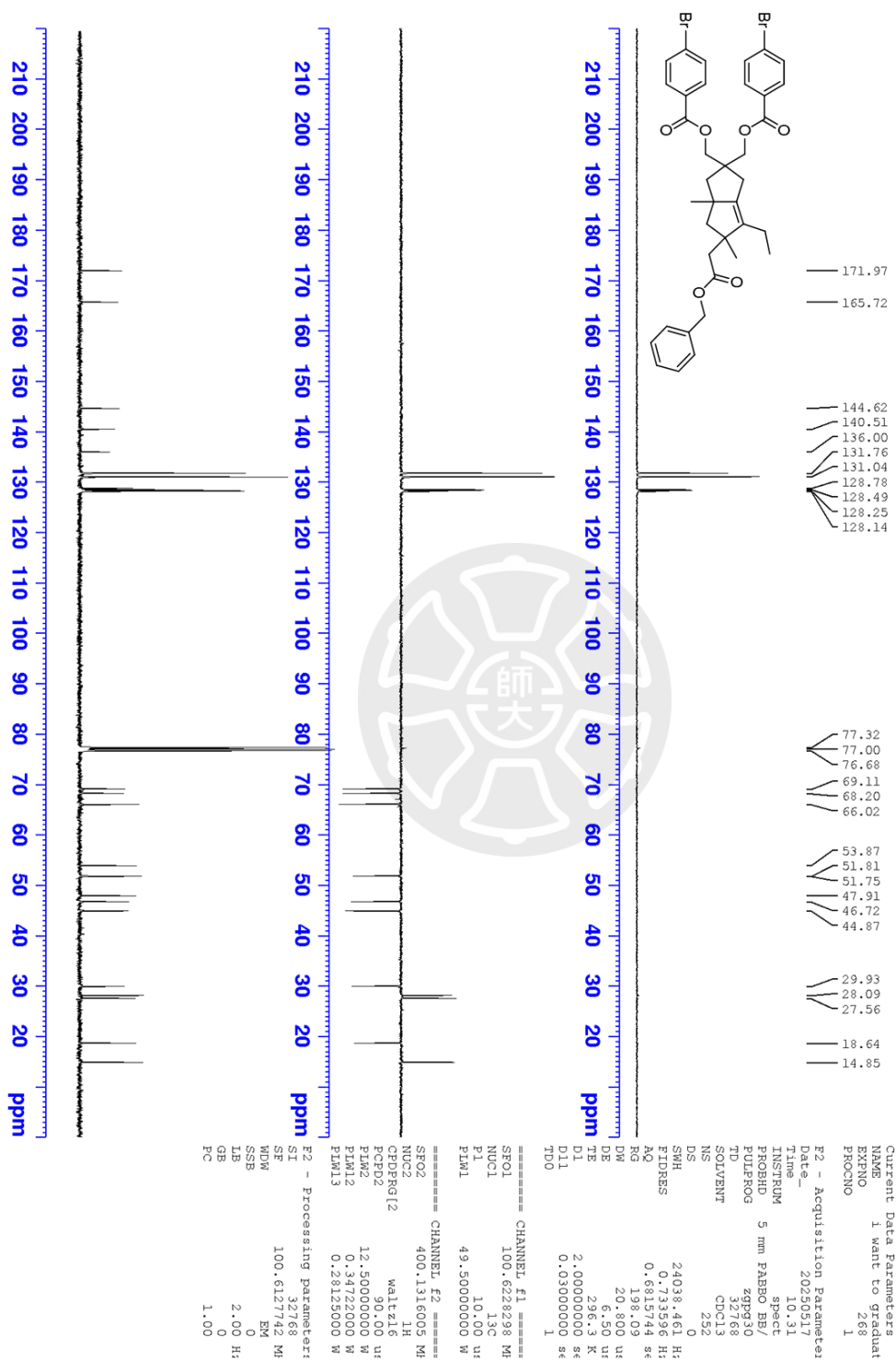
¹³C NMR spectrum of benzyl 2-(5,5-bis(((4-bromobenzyl)oxy)methyl)-3-ethyl-2,6a-dimethyl-1,2,4,5,6,6a-hexahydropentalen-2-yl)acetate (44aa)



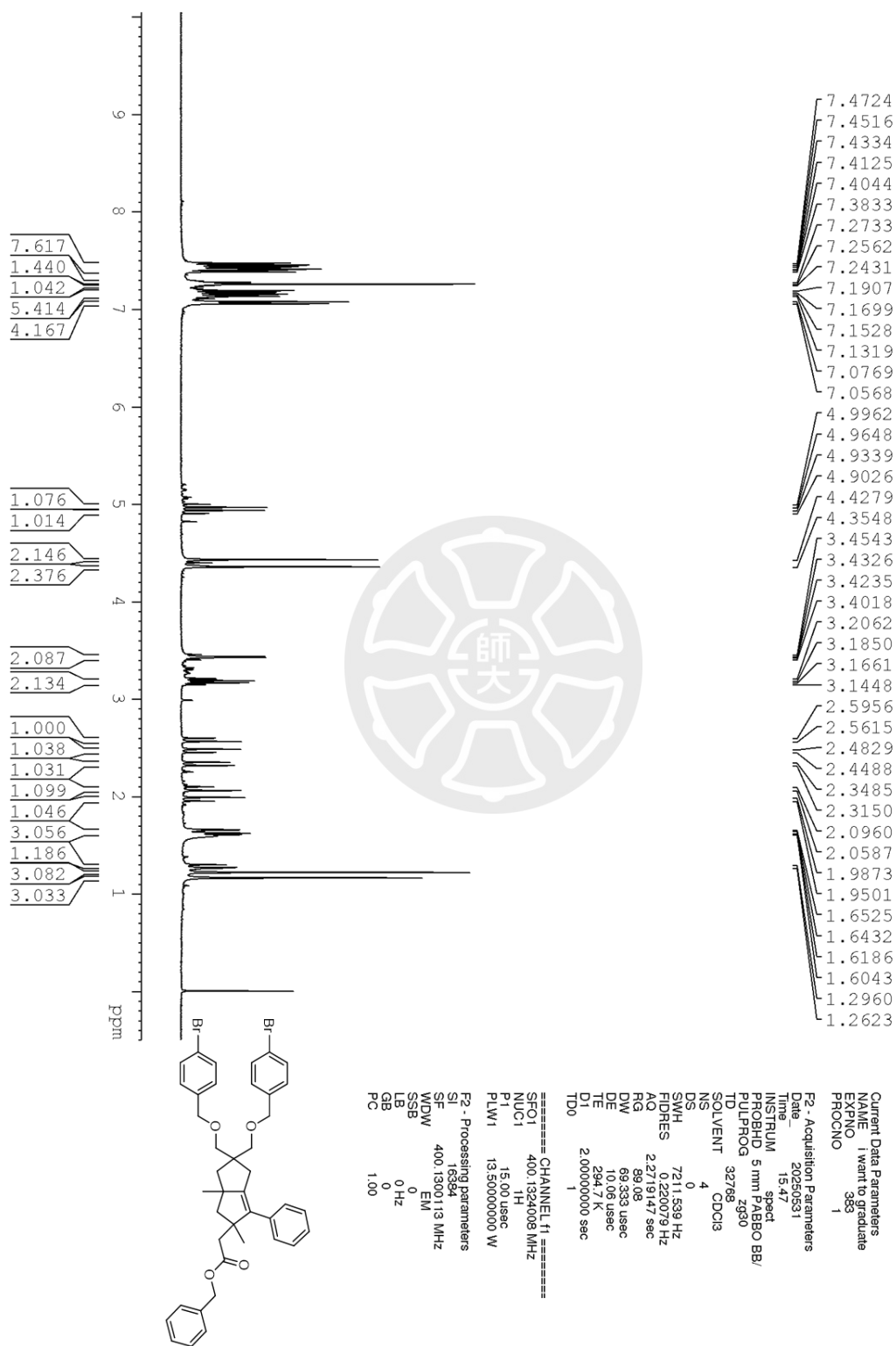
¹H NMR spectrum of (5-(2-(benzyloxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-1,2,3,3a,4,5-hexahydropentalene-2,2-diyl)bis(methylene) bis(4-bromobenzoate) (44ab)



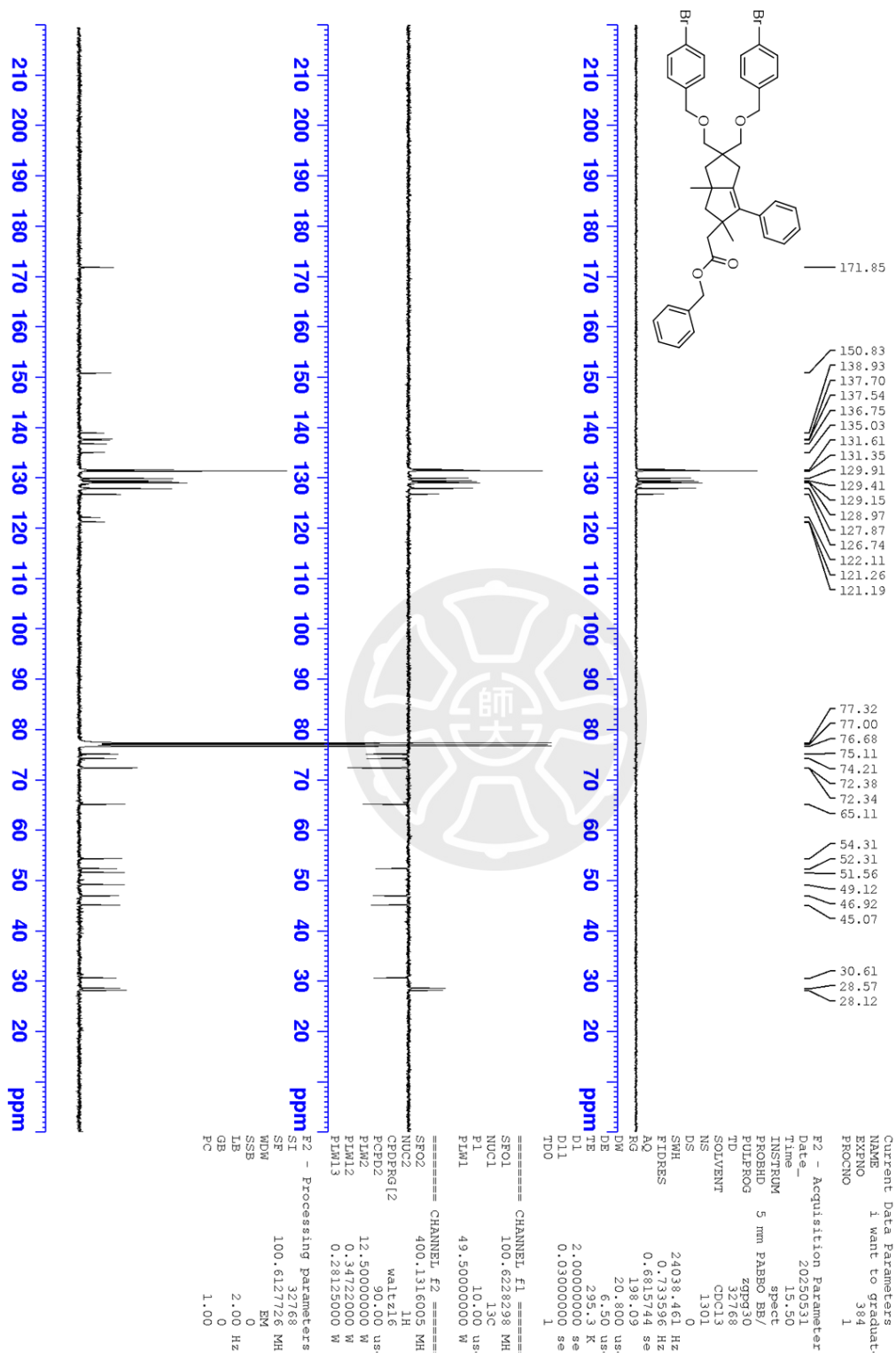
¹³C NMR spectrum of (5-(2-(benzyloxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-1,2,3,3a,4,5-hexahydropentalene-2,2-diyl)bis(methylene) bis(4-bromobenzoate) (44ab)



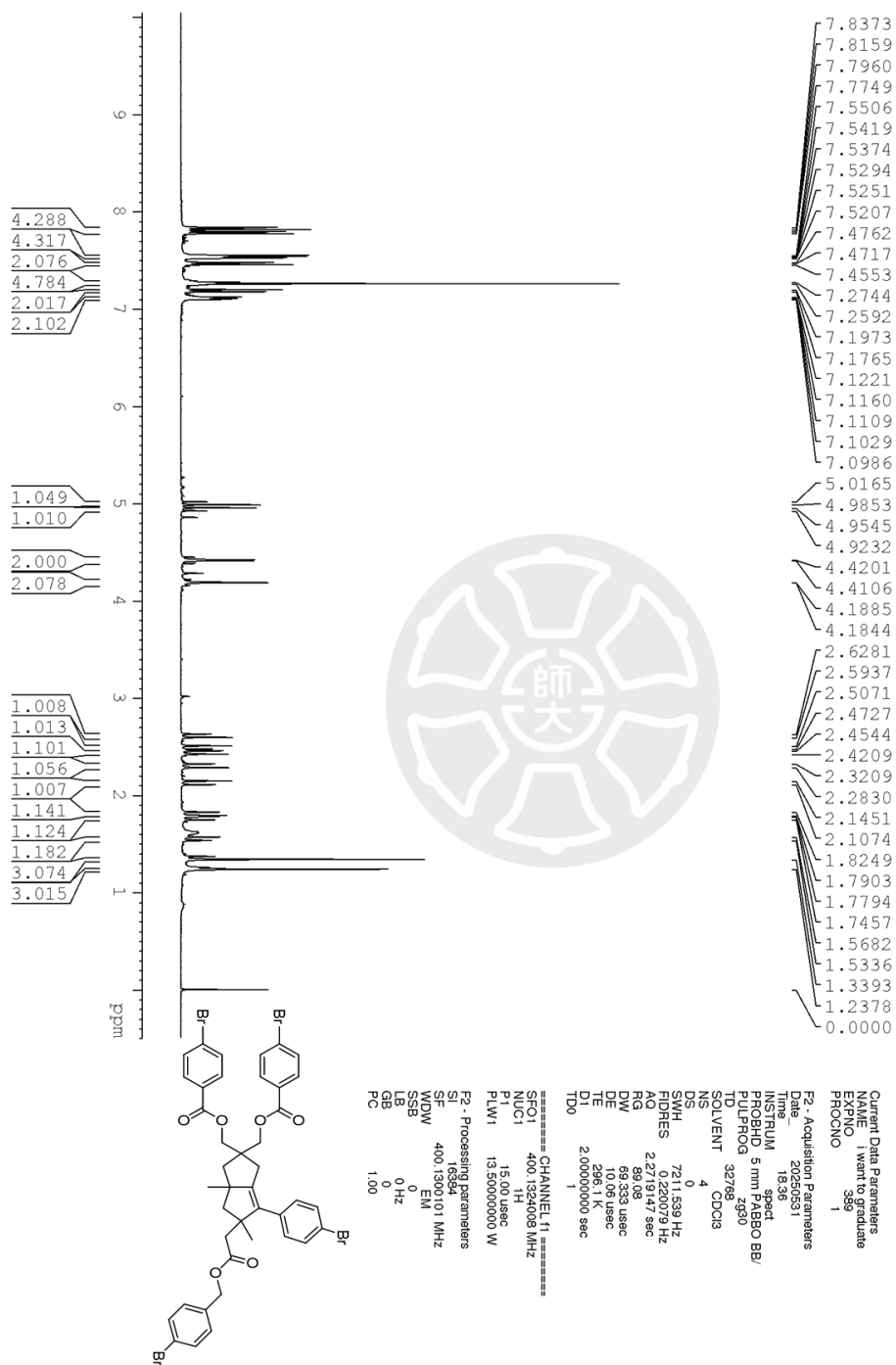
¹H NMR spectrum of benzyl 2-(5,5-bis(((4-bromobenzyl)oxy)methyl)-2,6a-dimethyl-3-phenyl-1,2,4,5,6,6a-hexahydropentalen-2-yl)acetate (44ac)



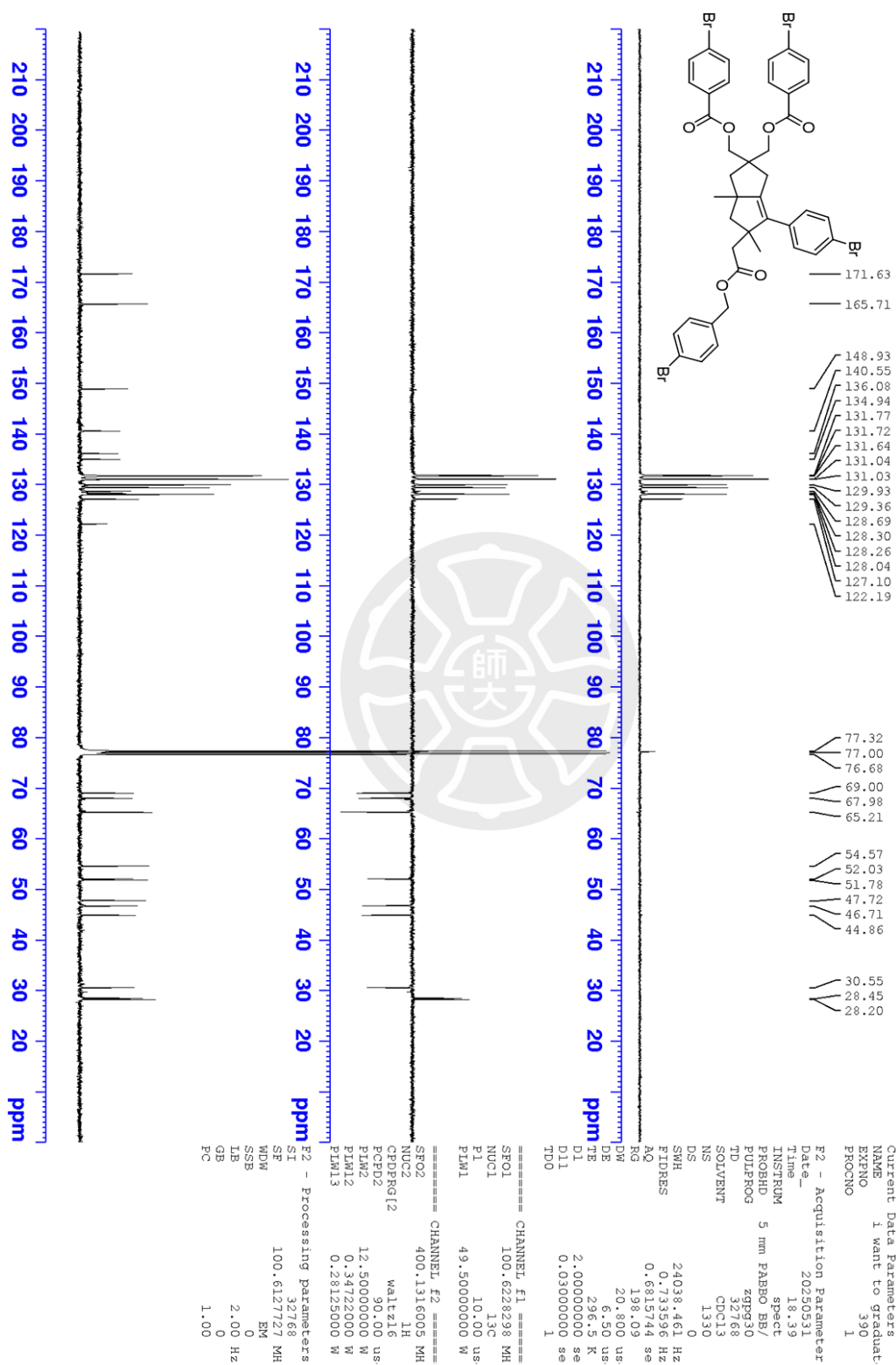
¹³C NMR spectrum of benzyl 2-(5,5-bis(((4-bromobenzyl)oxy)methyl)-2,6a-dimethyl-3-phenyl-1,2,4,5,6,6a-hexahydropentalen-2-yl)acetate (44ac)



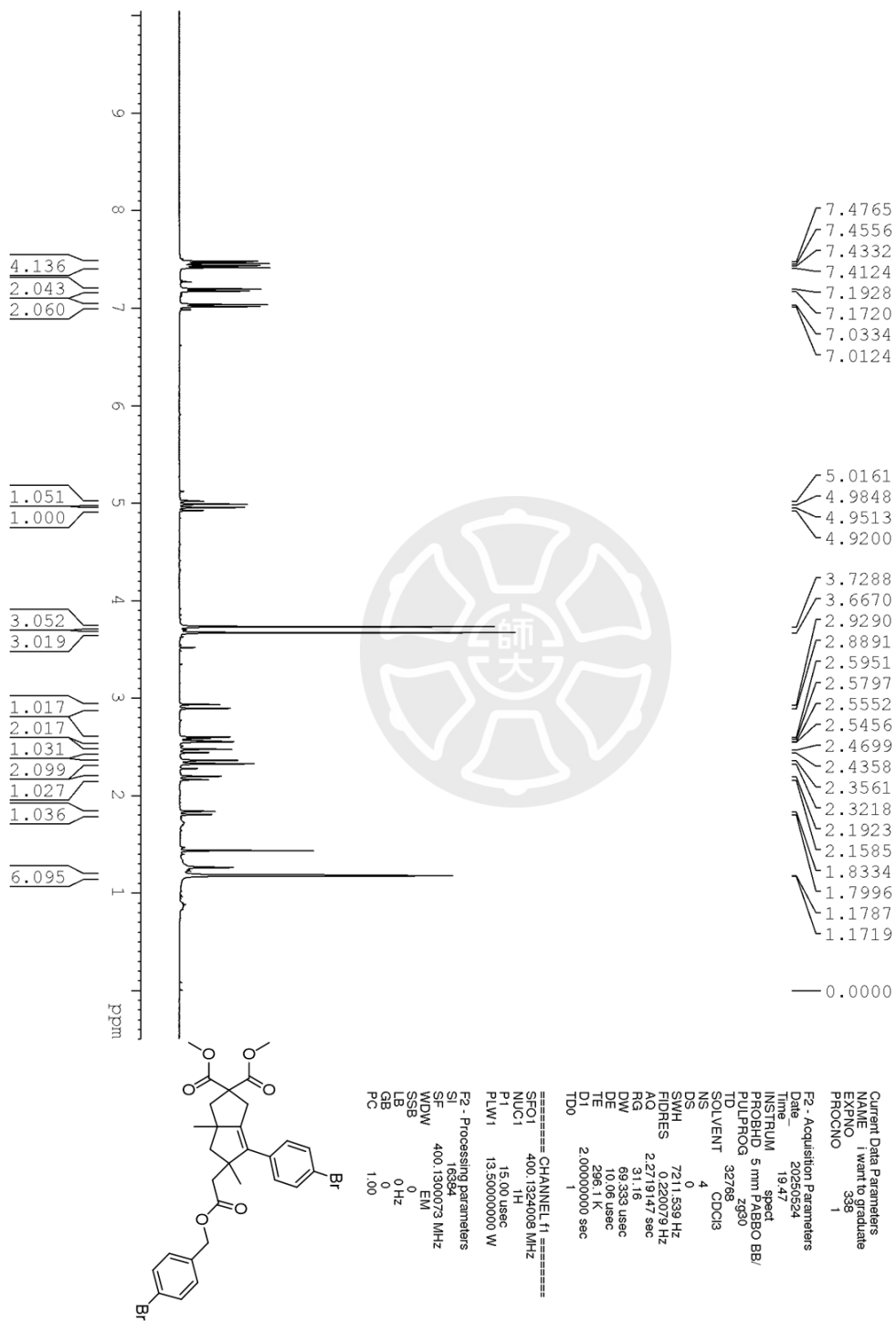
¹H NMR spectrum of (5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromo phenyl)-3a,5-dimethyl-1,2,3,3a,4,5-hexahydropentalene-2,2-diyl)bis(methylene) bis(4-bromobenzoate) (44ad)



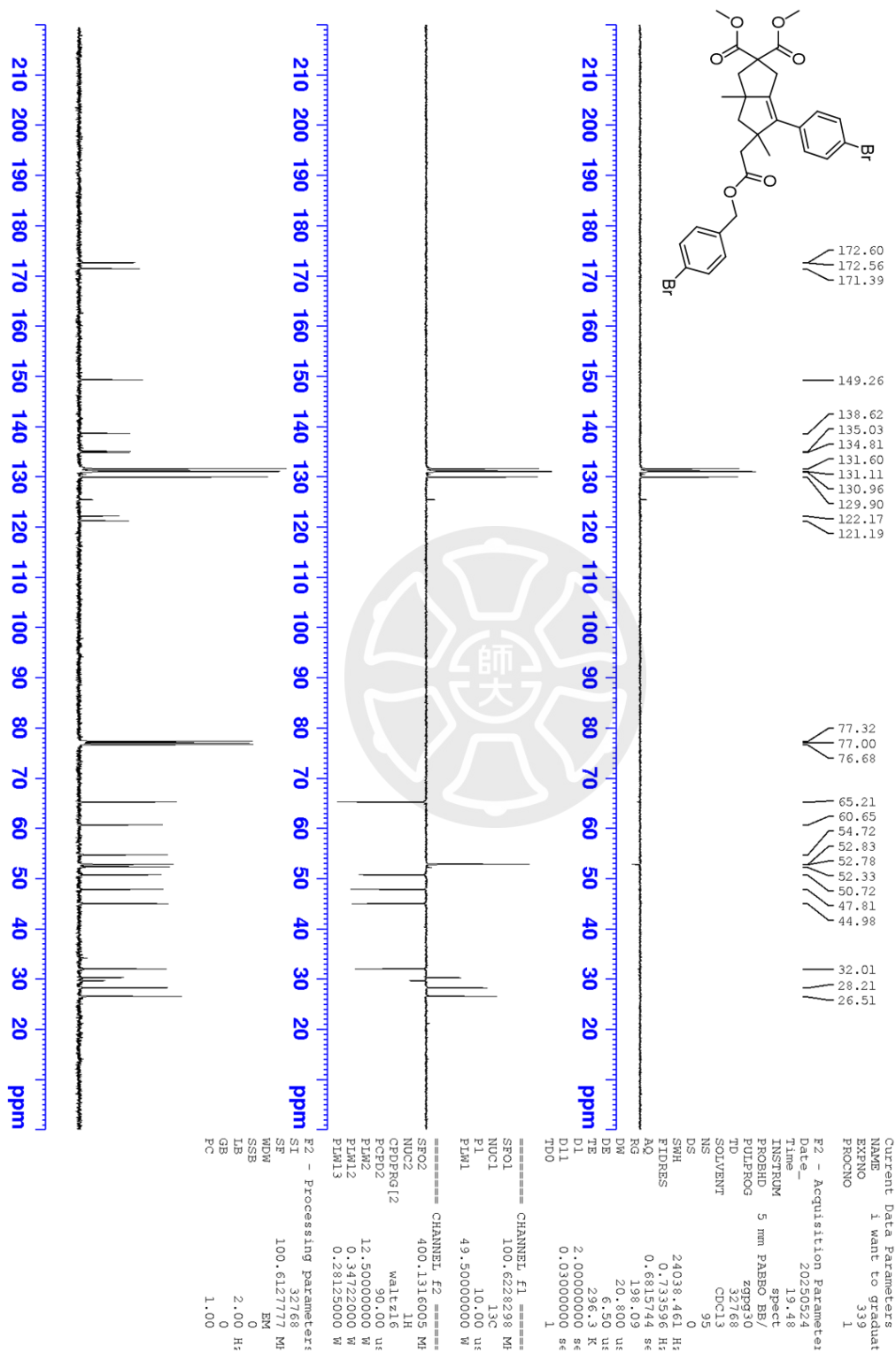
¹³C NMR spectrum of (5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromo phenyl)-3a,5-dimethyl-1,2,3,3a,4,5-hexahydropentalene-2,2-diyl)bis(methylene) bis(4-bromobenzoate) (44ad)



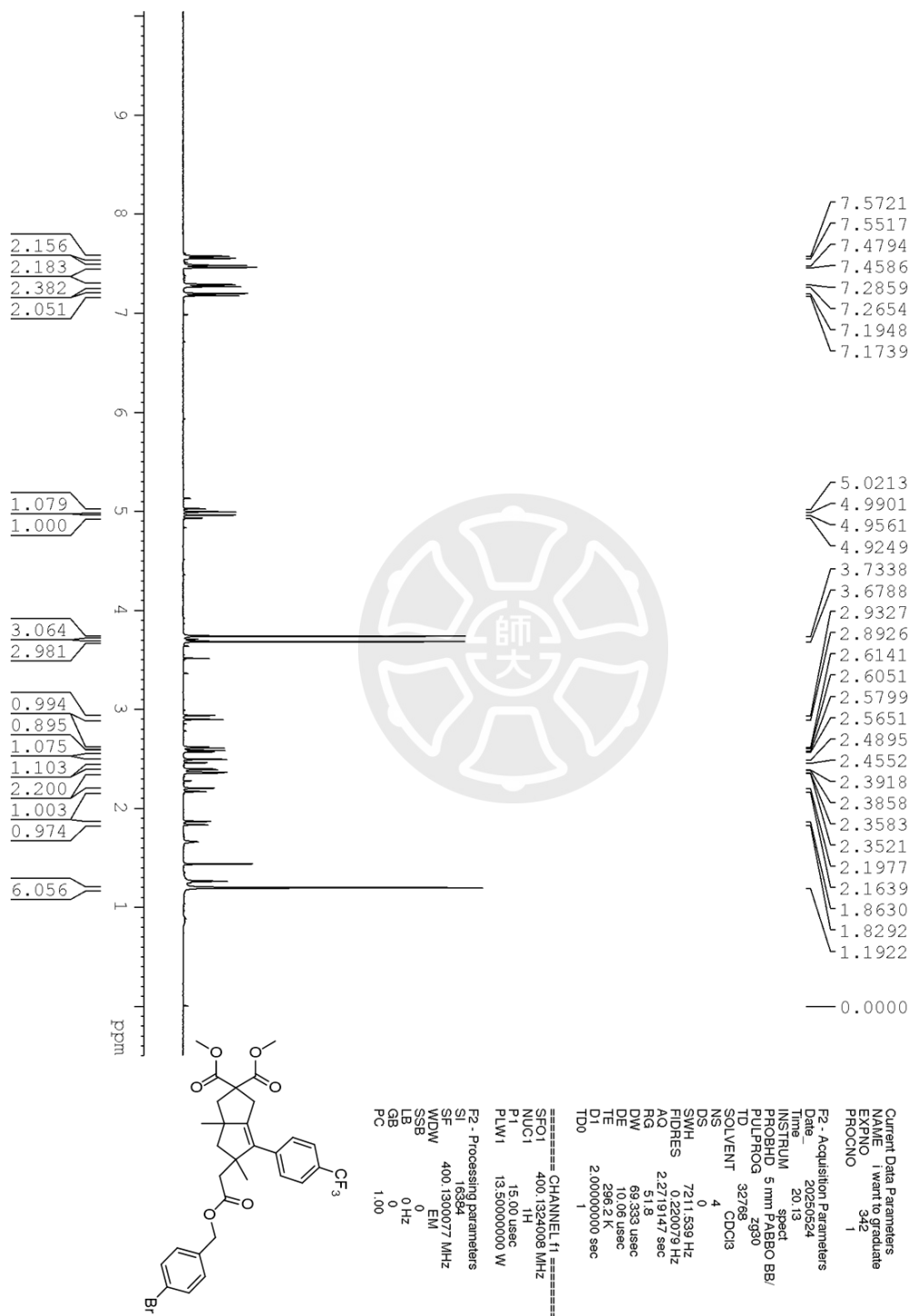
¹H NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromophenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ag)



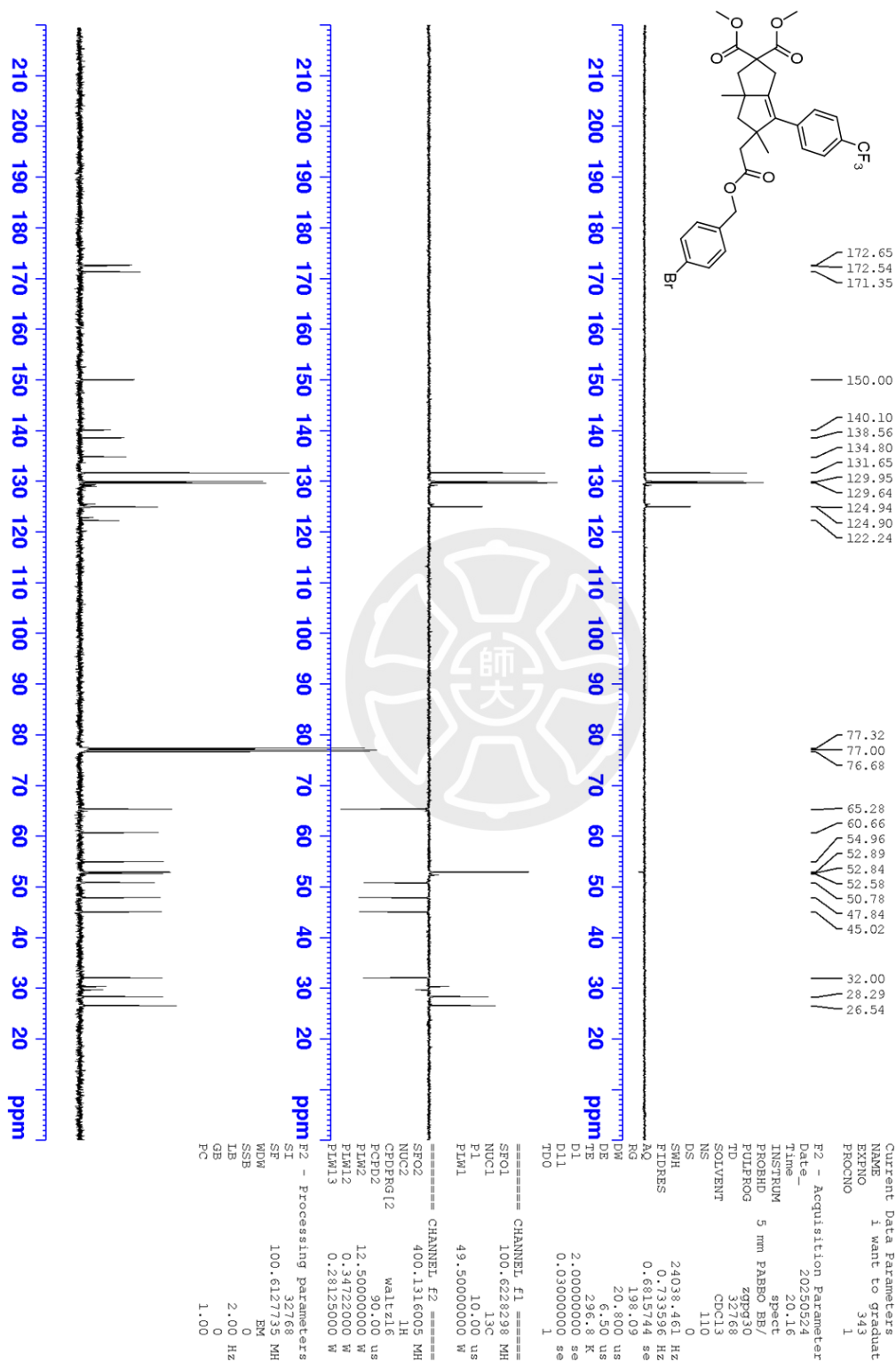
¹³C NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-(4-bromophenyl)-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ag)



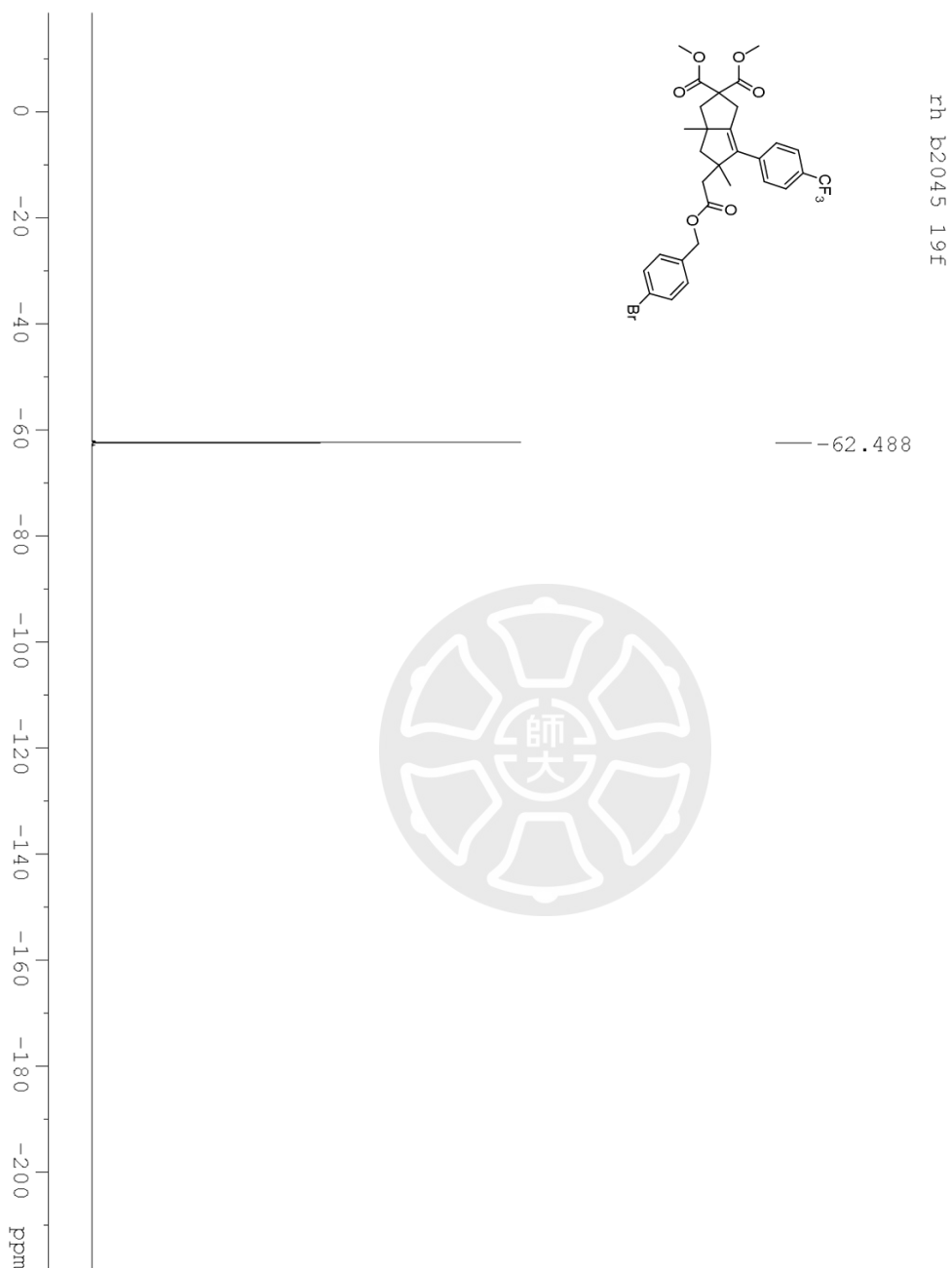
¹H NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)



¹³C NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)



¹⁹F NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-3a,5-dimethyl-6-(4-(trifluoromethyl)phenyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ah)



-62.488



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Current Data Parameters
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EXPNO     4/0
PROCNO    1

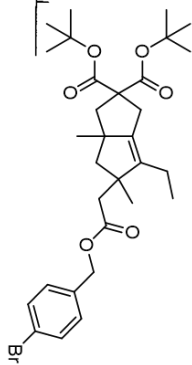
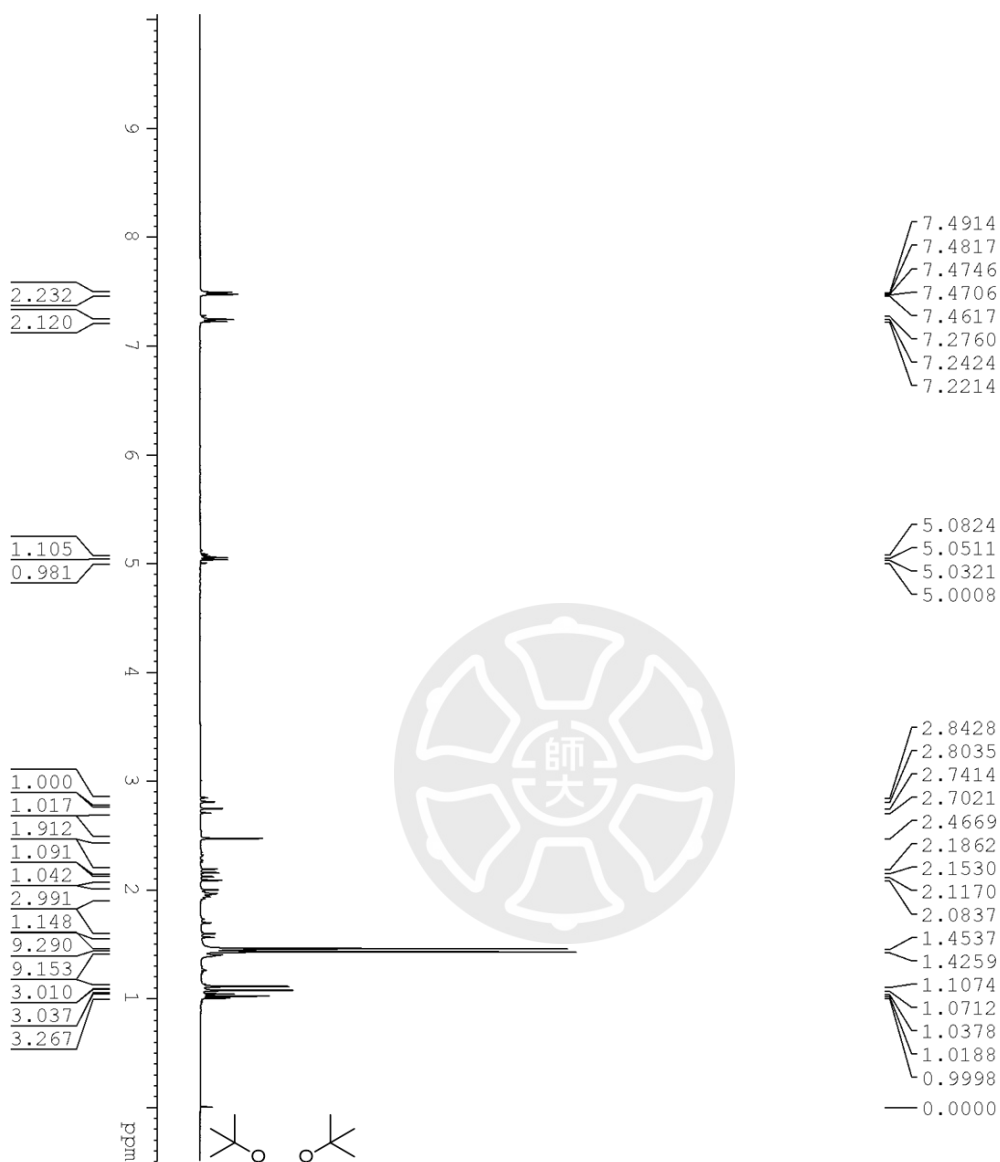
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SWH        89235.711 Hz
FIDRES     0.681196 Hz
AQ         0.7340032 sec
RG         198.09
DE         5.600 usec
TE         296.1 K
D1         1.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      376.4607168 MHz
NUC1       19F
P1         15.00 usec
PLW1      16.50000000 W

===== CHANNEL f2 =====
SFO2      400.1316005 MHz
NUC2       1H
CPDPRGf2  waltz16
PCPD2     90.00 usec
PLW2     12.50000000 W
PLW12    0.34722000 W

F2 - Processing parameters
    
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¹H NMR spectrum of di-tert-butyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (44ae)



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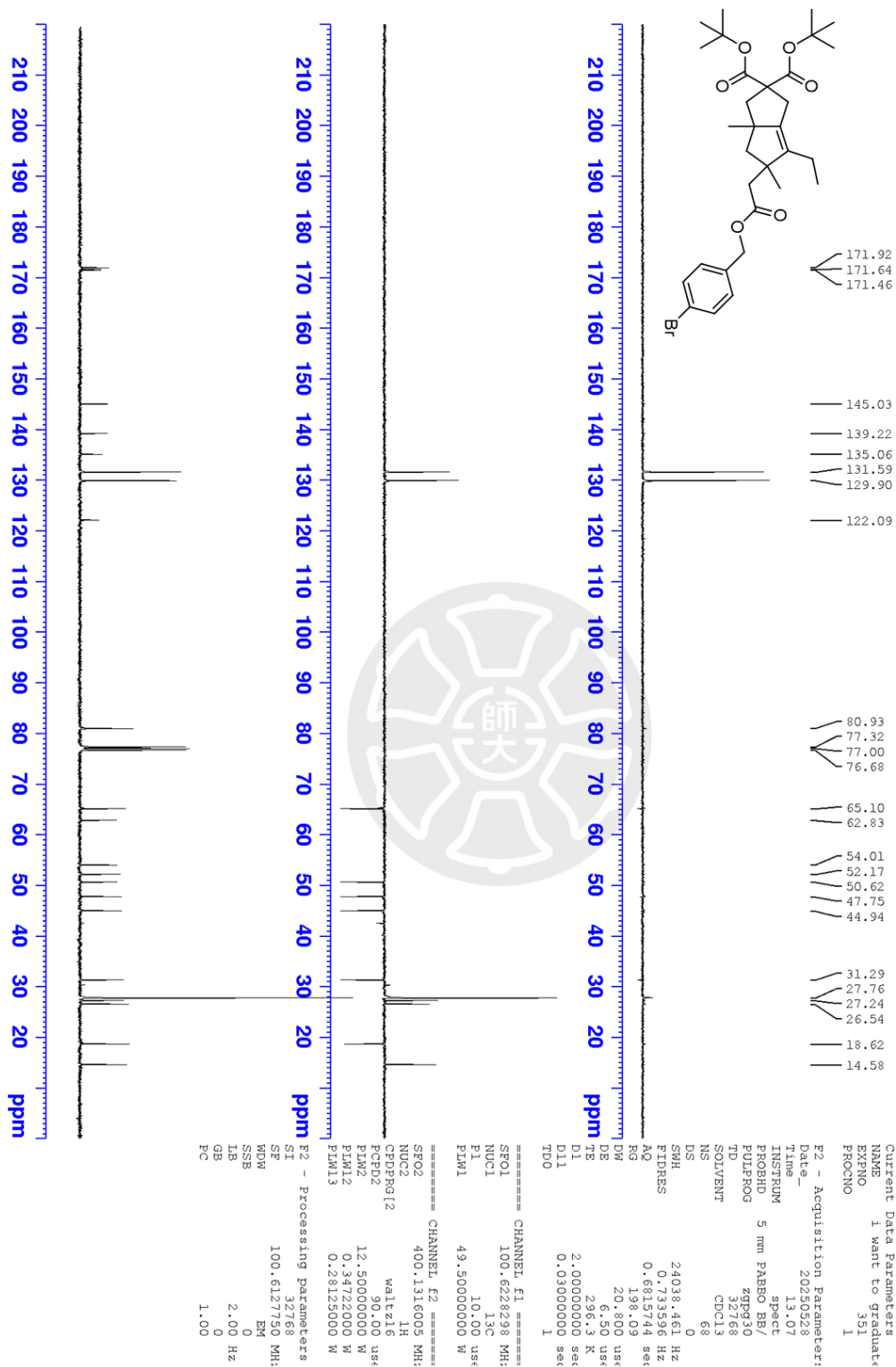
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DS       0
SI/Hz    721.599 Hz
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TD0      1

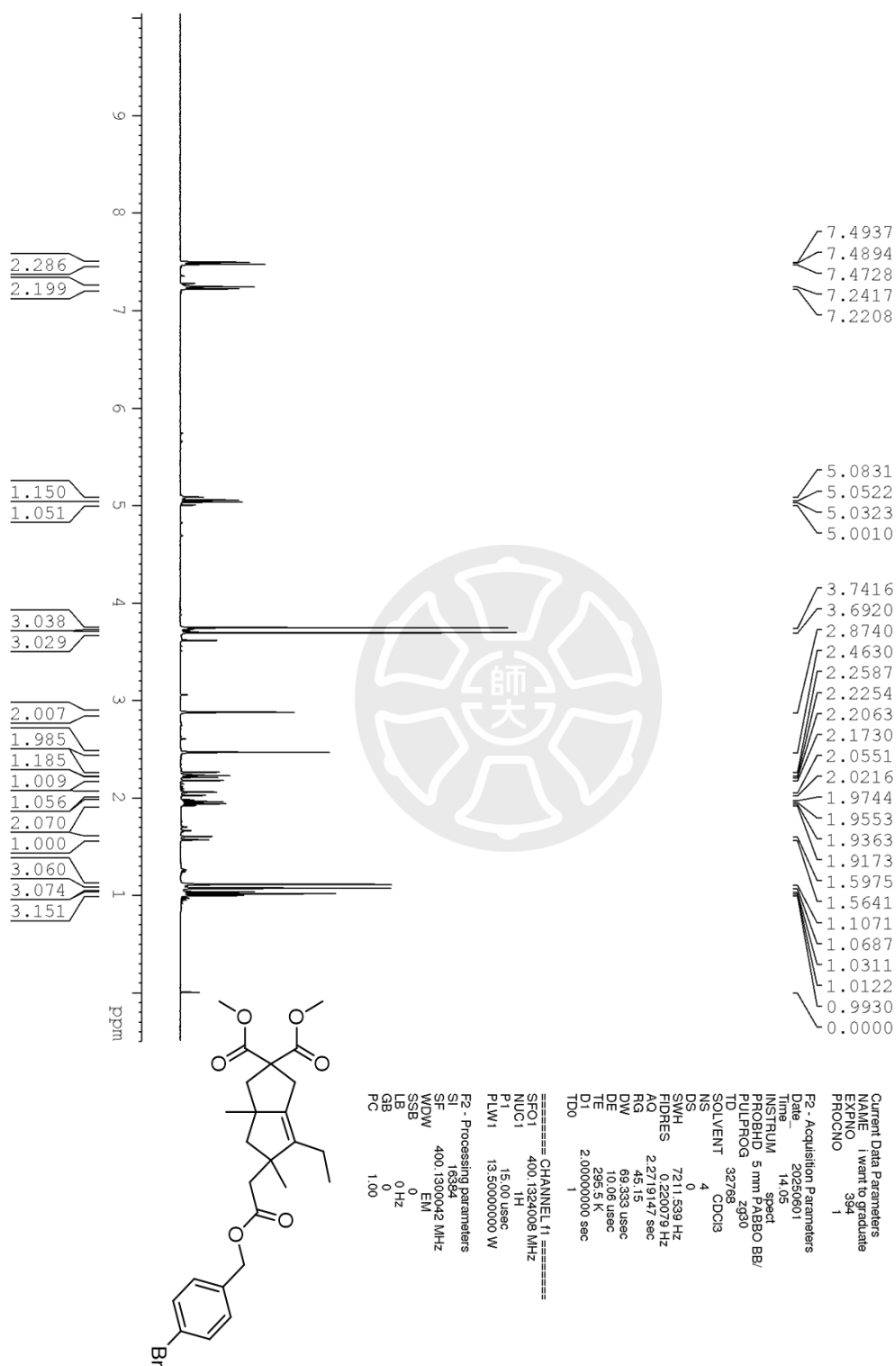
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NUC1     1H
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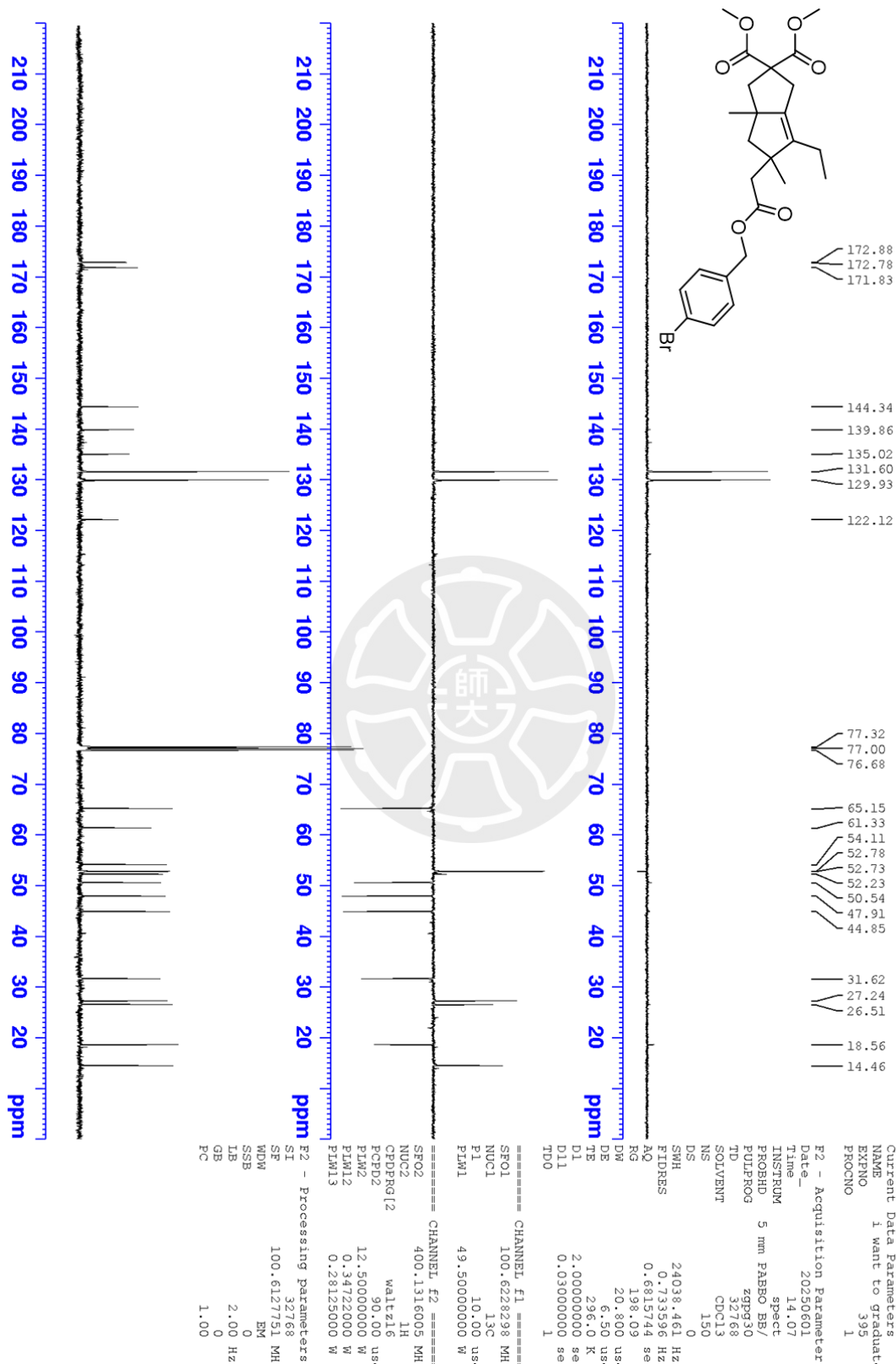
¹³C NMR spectrum of di-tert-butyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (44ae)



¹H NMR spectrum of dimethyl 5-(2-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ai)



¹³C NMR spectrum of dimethyl 5-((4-bromobenzyl)oxy)-2-oxoethyl)-6-ethyl-3a,5-dimethyl-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate (41ai)



¹³C NMR spectrum of 4-bromobenzyl 2-(6-(4-bromophenyl)-2',2',3a,5-tetra methyl-3,3a,4,5-tetrahydro-1H-spiro[pentalene-2,5'-[1,3]dioxan]-5-yl)acetate (44af)

