Electronic Supplementary Material (ESI) for ChemComm.

Palladium-catalyzed stereocontrolled ring-opening of 7-oxabenzonorbornadienes with organic carboxylic acids

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Electronic Supporting Information (ESI)

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Experimental Section

General Information: All reactions were carried out under the air atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use (three times). Dry solvents were used for the reaction. Column chromatography purifications were performed using SiO_2 (100-200 mesh ASTM) from Merck if not indicated otherwise. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Starting Materials: carboxylic acid,[1] 7-oxabenzonorbornadienes,[2] $Pd_2(dba)_3$, were prepared according to literature procedures. Commercially available metal salts and other chemicals were purchased from Sigma-Aldrich and Spectrochem. Pvt. Ltd., India and used without further purification.

Preparation of Starting Materials

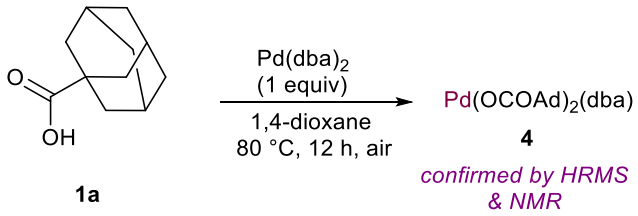
7-Oxabenzonorbornadienes and substituted 7-Oxabenzonorbornadienes (**2a–g**) were prepared by the known reported procedure.[2]

Procedure for the Palladium-Catalyzed Reaction of 7-Oxabenzonorbornadienes 2a with Carboxylic Acid 1a

A 15-mL pressure tube with septum containing $Pd(dba)_2$ (0.017 mmol, 5 mol %), and Oxabenzonorbornadienes **2a** (100 mg, 0.694 mmol, 2 equiv) was added under the open-air conditions. To the tube, were then added 1-admantanecarboxylic acid **1a** (62.5 mg, 0.347 mmol, 1 equiv) in 1,4-dioxane (2 mL, 0.17 M) *via* syringe sequentially and the reaction mixture was stirred at room temperature for 5 minutes. Then the reaction mixture was allowed to stir at 80 °C for 12 h in an oil bath. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure desired product **3aa** (127 mg, 78%).

Intermediate Isolation

a) Intermediate isolation

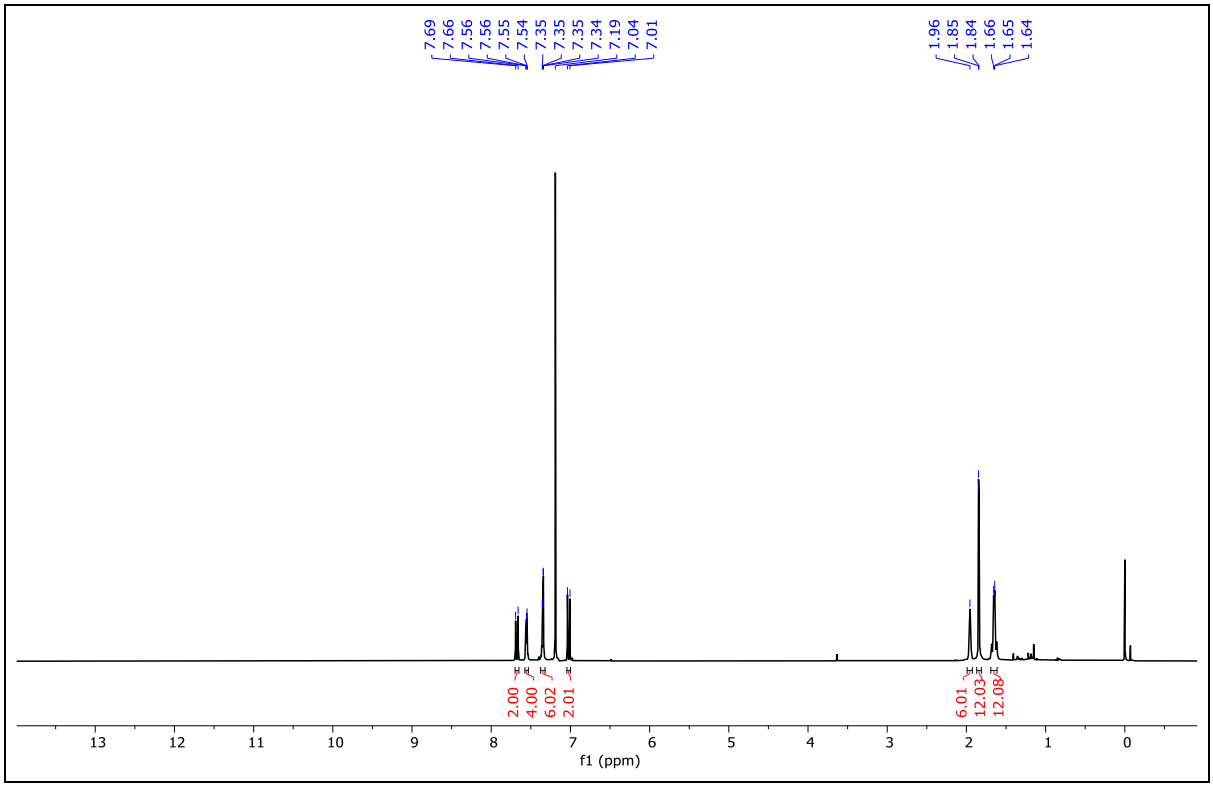


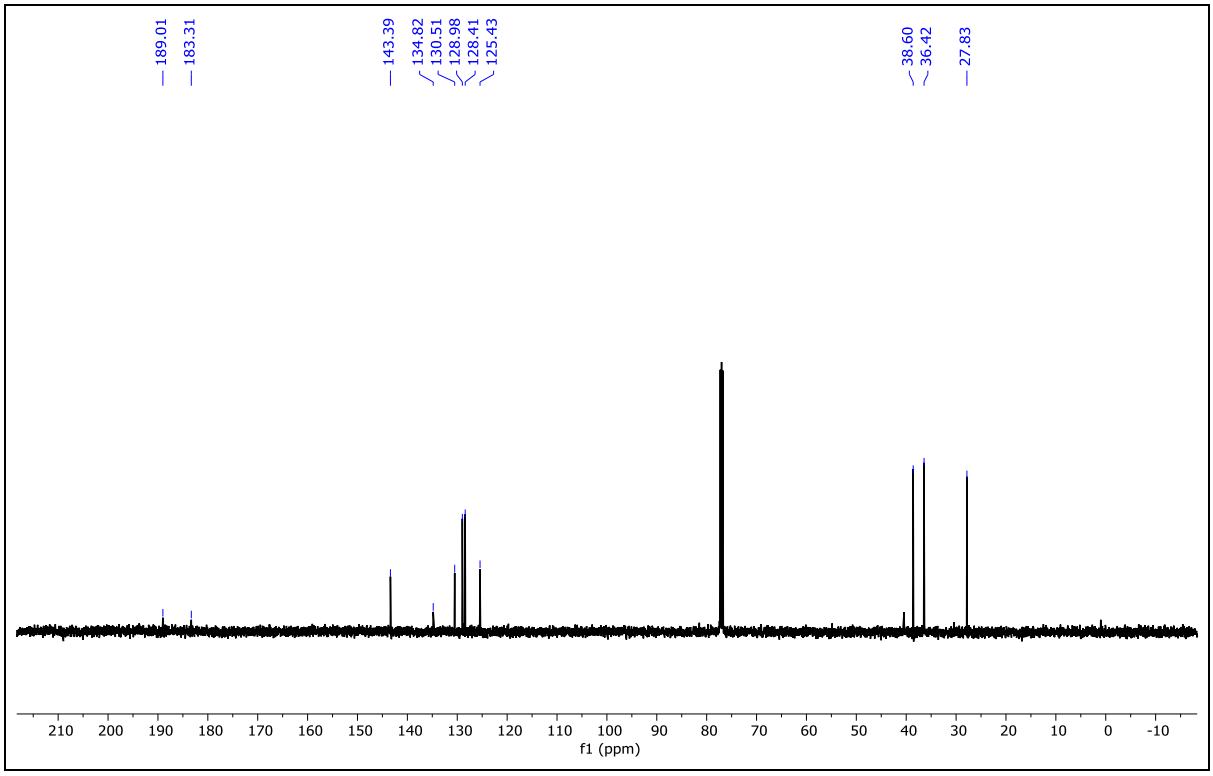
1a

Chemical formula of complex **9a:** $C_{39}H_{44}O_5Pd$

HRMS (ESI/Q-TOF): $[M + H]^+$ Calcd for $C_{39}H_{48}NO_5Pd$ 718.2566; Found 718.2431.

^1H and ^{13}C NMR Spectra of Compound **4** ($CDCl_3$, 400 MHz)

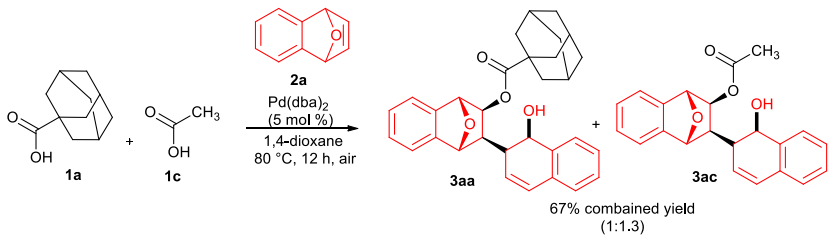




Mechanistic Studies

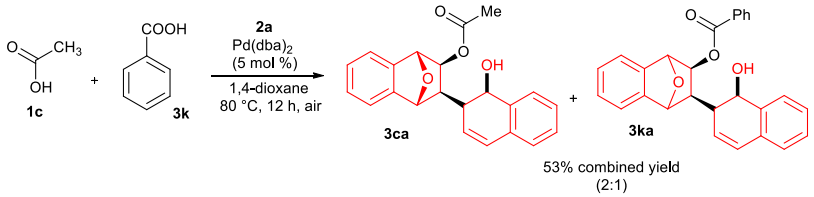
Procedure for Competition Reaction between Aliphatic Acids.

A 15-mL pressure tube with septum containing $Pd(dba)_2$ (5 mol %), and Oxabenzonorbornadienes **2** (0.25 mmol, 1.0 equiv) was added under the open air conditions. To the tube, were then added 1-adamantecarboxylic acid **1a** (0.25 mmol, 1.0 equiv) and acetic acid **1c** (0.25 mmol, 1.0 equiv) in 1,4-dioxane (0.17 M) *via* syringe sequentially and the reaction mixture was stirred at room temperature for 5 minutes. Then the reaction mixture was allowed to stir at 80 °C for 12 h in an oil bath. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure desired product to give products **3aa** and **3ac** in 33% and 25% yields, respectively.



Procedure for Competition Reaction between Acetic acid and Benzoic acid.

A 15-mL pressure tube with septum containing $Pd(dba)_2$ (5 mol %), and Oxabenzonorbornadienes **2** (0.25 mmol, 1.0 equiv) was added under the open air conditions. To the tube, were then added acetic acid **1c** (0.25 mmol, 1.0 equiv) and benzoic acid (0.25 mmol, 1.0 equiv) in 1,4-dioxane (0.17 M) *via* syringe sequentially and the reaction mixture was stirred at room temperature for 5 minutes. Then the reaction mixture was allowed to stir at 80 °C for 12 h in an oil bath. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure desired product to give products **3ca** and **3ka** in 18% and 35% yields, respectively.



Procedure for Competition Reaction between Benzoic acids.

A 15-mL pressure tube with septum containing $Pd(dba)_2$ (5 mol %), and Oxabenzonorbornadienes **2** (0.25 mmol, 1.0 equiv) was added under the open air conditions. To the tube, were then added p-toluic acid **1c** (0.25 mmol, 1.0 equiv) and 4-nitrobenzoic acid (0.25 mmol, 1.0 equiv) in 1,4-dioxane (0.17 M) *via* syringe sequentially and the reaction mixture was stirred at room temperature for 5 minutes. Then the reaction mixture was allowed to stir at 80 °C for 12 h in an oil bath. Then, the reaction mixture was diluted with CH_2Cl_2, filtered through celite, and the filtrate was concentrated. The crude residue was purified through a silica gel column using petroleum ether and ethyl acetate as eluent to give pure desired product to give products **3la** and **3na** in 35% and 25% yields, respectively.

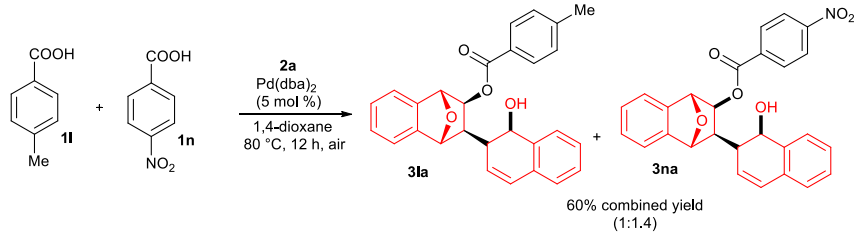
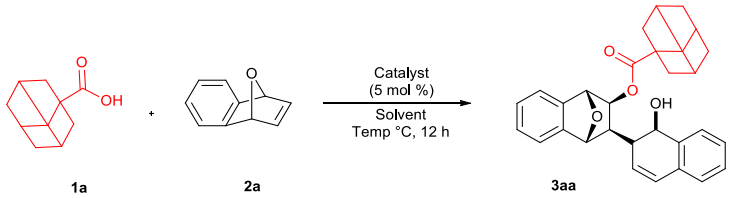


Table S1. Optimization studies[a]



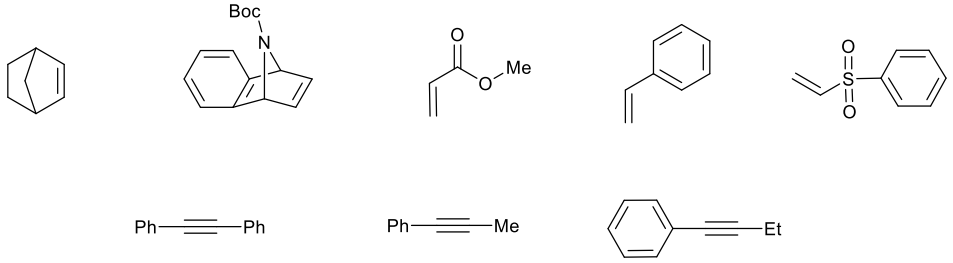
1a 2a 3aa

Entry	Catalyst	Solvent	Temp °C	Yield % (3aa)	dr
1	$Cu(OAc)_2$ $2H_2O$	1,4-dioxane	80	NR	
2	$CuCl_2$	1,4-dioxane	80	NR	
3	$Pd(OAc)_2$	1,4-dioxane	80	53	14:1
4	**$Pd(dba)_2$**	**1,4-dioxane**	**80**	**78**	**18:1**
5	$PdCl_2$	1,4-dioxane	80	47	16:1
6	$[Pd(PPh_3)_2Cl_2]$	1,4-dioxane	80	trace	
7	$Pd(dba)_2$	1,2-DCE	80	45	16:1
8	$Pd(dba)_2$	THF	80	NA	
9	$Pd(dba)_2$	DMF	80	NR	
10	$Pd(dba)_2$	MeOH	80	15	
11	$Pd(dba)_2$	TFE	80	20	
12	$Pd(dba)_2$	CH_3CN	80	37	10:1
13	$Pd(dba)_2$	toluene	80	50	5:1
14	$Pd(dba)_2$	benzene	80	45	4:1
15	$Pd(dba)_2$	DMA	80	24	
16	$Pd(dba)_2$	DMSO	80	12	
17	$Pd(dba)_2$	CF_3CH_2OH	80	26	
18	$Pd(dba)_2$	tBuOH	80	19	
19	$Pd(dba)_2$	1,4-dioxane	rt	NR	
20	$Pd(dba)_2$	1,4-dioxane	60	61	
21	$Pd(dba)_2$	1,4-dioxane	100	56	
22	$Pd(dba)_2$	1,4-dioxane	120	39	
23	$Pd(dba)_2$	1,4-dioxane	80	12[b]	
24	$Pd(dba)_2$	1,4-dioxane	80	15[c]	
25	$Pd(dba)_2$	1,4-dioxane	80	25[d]	
26	$Pd(dba)_2$	1,4-dioxane	80	12[e]	

[a]All reactions were carried out using Oxabenzonorbornadienes **2a** (100 mg), 1-adamantanecarboxylic acid **1a** (1 equiv), catalyst (5 mol %), and solvent (2 mL) for 12 h. [b]1,10-phenanthroline (10 mol%) was added. [c] 1,2-

bis(diphenylphosphino)ethane (10 mol%) was added. [d]2-acetamido-3-methylbutanoic acid (10 mol%) was added. [e]1 mol% of $Pd_2(dba)_3$ was used.

Unsuccessful substrates 1

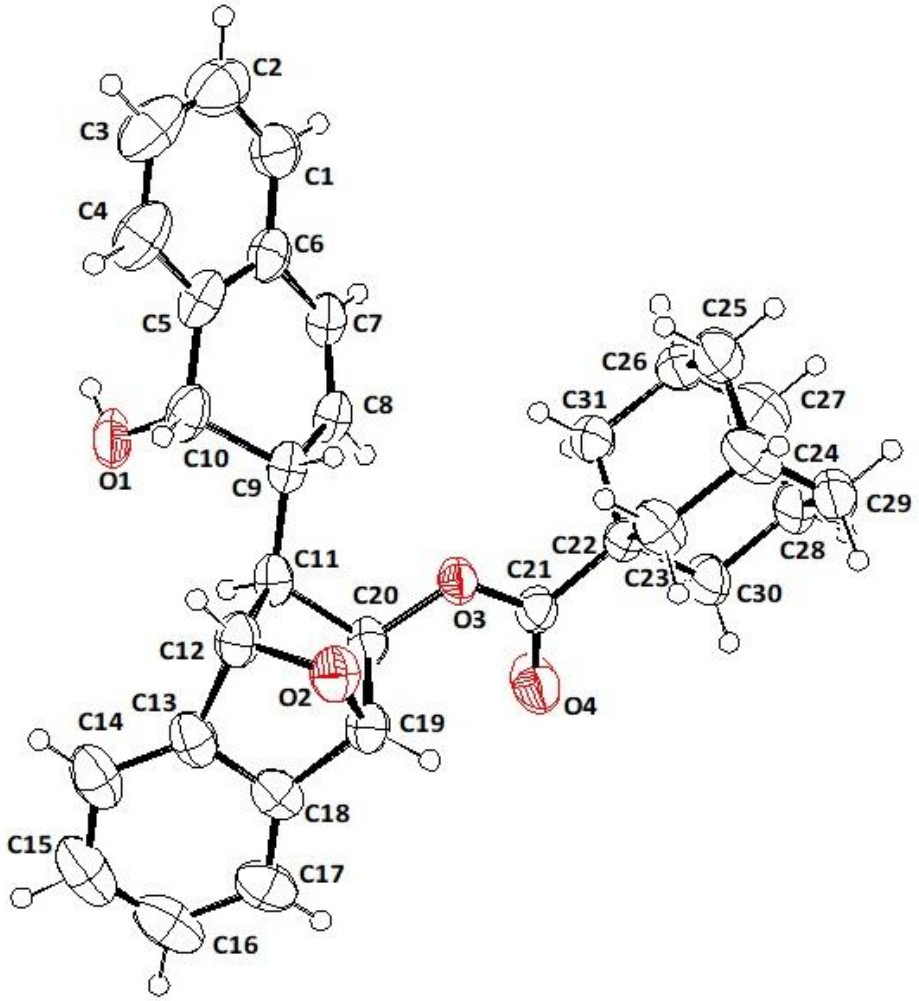


X-Ray Analysis of Compounds aba (the crystal is having dimeric compound).

Identification code	**3aa**
Empirical formula	C31 H32 O4
Formula weight	468.56
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system,	Orthorhombic
Space group	P b c a
Unit cell dimensions	a = 12.880(4) A alpha = 90 deg. b = 18.325(7) A beta = 90 deg. c = 21.134(8) A gamma = 90 deg.
Volume	4988(3) A^3
Z, Calculated density	8, 1.248 Mg/m^3
Absorption coefficient	0.081 mm^-1
F (000)	2000
Crystal size	0.200 x 0.180 x 0.150 mm
Theta range for data collection	3.341 to 24.997 deg.
Limiting indices	-15<=h<=15, -21<=k<=21, -25<=l<=25
Reflections collected / unique	103399 / 4373 [R (int) = 0.0562]
Completeness to theta = 24.997	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. And min. transmission	0.7457 and 0.6743
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4373 / 354 / 422
Goodness-of-fit on F^2	1.137
Final R indices [I>2sigma (I)]	R1 = 0.0550, wR2 = 0.1356
R indices (all data)	R1 = 0.0784, wR2 = 0.1644

Extinction coefficient	N/A
Largest diff. peak and hole	0.367 and -0.237 e.A^-3

X-ray crystal structure of 3aa.

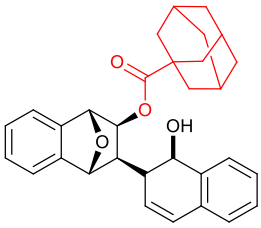


References:

1. Y. –F. Liang, X. Wang, C. Tang, T. Shen, J. Liu and N. Jiao, *Chem. Commun*. 2016, **52**, 1416.
2. Y. Otani, O. Nagae, Y. Naruse, S. Inagaki, M. Ohno, K. Yamaguchi, G. Yamamoto, M. Uchiyama and T. Ohwada, *J. Am. Chem. Soc*. 2003, **125**, 15191−15199.
3. M. P. Huestis, *J. Org. Chem*. 2016, **81**, 12545

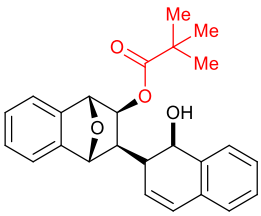
Spectral Data of All Compounds.

(2S,3S)-3-((2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl adamantane-1-carboxylate (3aa)



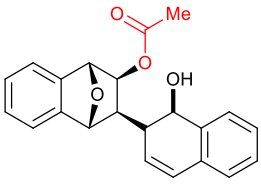
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 127 mg was isolated, and the yield was 78%. Mp: 161-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.28 – 7.17 (m, 3H), 7.15 – 7.10 (m, 3H), 6.45 (d, *J* = 9.5 Hz, 1H), 5.61 (s, 1H), 5.45 (d, *J* = 9.6 Hz, 1H), 5.20 – 5.04 (m, 2H), 4.88 (s, 1H), 2.91 (d, *J* = 11.3 Hz, 1H), 2.41 (dd, *J* = 11.4, 7.1 Hz, 1H), 1.91 (s, 3H), 1.82 (s, 6H), 164 – 1.59 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 147.1, 141.1, 136.1, 132.4, 130.3, 129.1, 128.5, 127.8, 127.7, 127.0, 126.8, 126.5, 120.9, 119.2, 84.8, 80.7, 74.4, 69.6, 44.9, 38.6, 38.3, 36.4, 27.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{31}H_{32}O_4Na$ 491.2193; Found 491.2198.

(2S,3S)-3-((2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl pivalate (3ba)



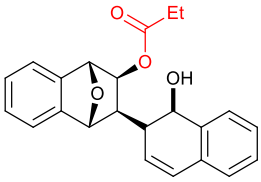
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 101 mg was isolated, and the yield was 75%. Mp: 97-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.4 Hz, 2H), 7.29 – 7.20 (m, 3H), 7.16 – 7.05 (m, 3H), 6.44 (dd, *J* = 9.6, 2.6 Hz, 1H), 5.60 (s, 1H), 5.44 (d, *J* = 9.6 Hz, 1H), 5.17 (s, 1H), 5.10 (d, *J* = 7.0 Hz, 1H), 4.87 (d, *J* = 3.7 Hz, 1H), 2.90 (s, 1H), 2.42 (dd, *J* = 11.6, 7.1 Hz, 1H), 1.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 147.1, 141.0, 136.1, 132.3, 130.2, 129.1, 128.5, 127.9, 127.8, 127.0, 126.8, 126.5, 120.9, 119.3, 84.7, 80.6, 74.8, 69.5, 44.8, 38.3, 27.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}O_4Na$ 413.1723; Found 413.1726.

(2S,3S)-3-((2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl acetate (3ca)



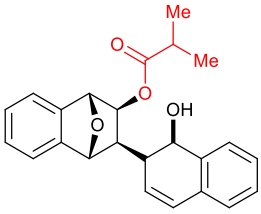
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 82 mg was isolated, and the yield was 68%. Mp: 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.31 (dd, *J* = 14.1, 8.3 Hz, 3H), 7.24 – 7.12 (m, 3H), 6.52 (dd, *J* = 9.6, 2.5 Hz, 1H), 5.68 (s, 1H), 5.52 (d, *J* = 9.7 Hz, 1H), 5.30 (s, 1H), 5.25 (d, *J* = 7.0 Hz, 1H), 4.93 (s, 1H), 2.96 (d, *J* = 11.8 Hz, 1H), 2.47 (dd, *J* = 11.6, 7.0 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 147.1, 140.8, 129.7, 129.1, 128.4, 127.9, 127.8, 127.0, 126.7, 121.0, 119.2, 84.7, 80.7, 74.7, 69.6, 44.7, 38.4, 21.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{20}O_4Na$ 371.1259; Found 371.1254.

(2S,3S)-3-((2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl propionate (3da)



White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 90 mg was isolated, and the yield was 72%.p: 112-113 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 7.23 – 7.18 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.52 (dd, *J* = 9.7, 2.8 Hz, 1H), 5.68 (s, 1H), 5.52 (d, *J* = 9.7 Hz, 1H), 5.29 (s, 1H), 5.25 (d, *J* = 7.0 Hz, 1H), 4.93 (s, 1H), 3.01 – 2.93 (m, 1H), 2.48 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.43 – 2.32 (m, 2H), 1.68 (d, *J* = 7.3 Hz, 1H), 1.15 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.4, 147.1, 140.9, 136.1, 132.3, 129.9, 129.1, 128.4, 127.9, 127.8, 127.0, 126.7, 126.7, 120.9, 119.2, 84.7, 80.7, 74.6, 69.6, 44.8, 38.4, 27.9, 9.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{22}O_4Na$ 385.1410; Found 385.1411.

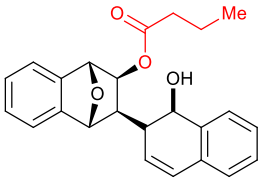
(2S,3S)-3-((2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl isobutyrate (3ea)



White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 86 mg was isolated, and the yield was 66%. Mp: 170-171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.35 – 7.27 (m, 3H), 7.23 – 7.19 (m, 2H), 7.15 (d, *J* = 6.9 Hz, 1H), 6.52 (dd, *J*

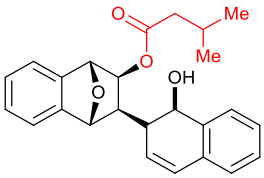
= 9.6, 2.8 Hz, 1H), 5.68 (s, 1H), 5.52 (dt, *J* = 9.6, 1.6 Hz, 1H), 5.27 (s, 1H), 5.22 (d, *J* = 7.0 Hz, 1H), 3.03 – 2.95 (m, 1H), 2.58 (dd, *J* = 14.0, 7.0 Hz, 1H), 2.49 (dd, *J* = 11.6, 7.0 Hz, 1H), 1.68 (d, *J* = 7.7 Hz, 1H), 1.17 (dd, *J* = 10.2, 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.1, 147.1, 140.9, 136.1, 132.3, 130.1, 129.1, 128.5, 127.9, 127.8, 127.0, 126.7, 126.6, 120.9, 119.2, 84.7, 80.6, 74.5, 69.6, 44.8, 38.3, 34.3, 18.9, 18.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{24}O_4Na$ 399.1567; Found 399.1566.

(2S,3S)-3-((1R,2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl butyrate (3fa)



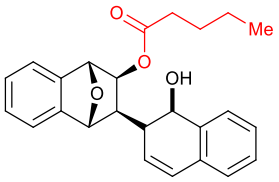
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 95 mg was isolated, and the yield was 73%. Mp: 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.30 (ddd, *J* = 14.6, 7.3, 1.2 Hz, 3H), 7.22 – 7.18 (m, 2H), 7.15 (d, *J* = 6.8 Hz, 1H), 6.51 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.67 (s, 1H), 5.52 (d, *J* = 9.7 Hz, 1H), 5.29 (s, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 4.93 (s, 1H), 3.01 – 2.93 (m, 1H), 2.47 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.33 (td, *J* = 7.4, 3.9 Hz, 2H), 1.67 (dt, *J* = 14.8, 7.3 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 147.1, 140.9, 136.1, 132.3, 129.9, 129.1, 128.4, 127.9, 127.8, 127.0, 126.7, 120.9, 119.2, 84.7, 80.7, 74.5, 69.6, 44.7, 38.4, 36.4, 18.3, 13.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{24}H_{24}O_4Na$ 399.1567; Found 399.1563.

(2S,3S)-3-((1R,2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 3-methylbutanoate (3ga)



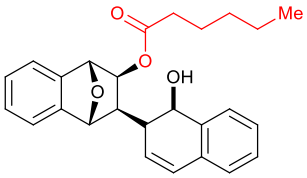
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 86 mg was isolated, and the yield was 64%. Mp: 163-164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 4.5, 2.6 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 7.15 (d, *J* = 7.1 Hz, 1H), 6.51 (dd, *J* = 9.7, 2.8 Hz, 1H), 5.67 (s, 1H), 5.55 – 5.49 (m, 1H), 5.29 (s, 1H), 5.22 (d, *J* = 7.0 Hz, 1H), 4.93 (s, 1H), 3.01 – 2.91 (m, 1H), 2.47 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.27 – 2.20 (m, 2H), 2.12 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.70 (d, *J* = 6.4 Hz, 1H), 0.96 (dd, *J* = 6.6, 2.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 147.1, 140.9, 136.1, 132.3, 129.9, 129.1, 128.4, 127.9, 127.8, 127.0, 126.7, 126.6, 120.9, 119.2, 84.7, 80.7, 74.5, 69.6, 44.7, 43.6, 38.4, 29.7, 25.7, 22.5, 22.4. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}O_4$ 391.1904; Found 391.1920.

(2S,3S)-3-((1R,2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl pentanoate (3ha)



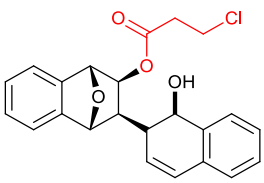
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 90 mg was isolated, and the yield was 67%. Mp: 120-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.31 (ddd, *J* = 12.7, 7.8, 4.3 Hz, 3H), 7.20 (dt, *J* = 7.9, 2.4 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.51 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.67 (s, 1H), 5.52 (d, *J* = 9.6 Hz, 1H), 5.29 (s, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 4.93 (s, 1H), 3.02 – 2.93 (m, 1H), 2.47 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.34 (td, *J* = 7.5, 4.7 Hz, 2H), 1.65 – 1.59 (m, 3H), 1.34 (d, *J* = 7.9 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 147.1, 140.9, 136.1, 132.3, 129.9, 129.1, 128.4, 127.9, 127.8, 127.0, 126.7, 126.7, 120.9, 119.2, 84.7, 80.7, 74.5, 69.6, 44.7, 38.4, 34.3, 26.8, 22.2, 13.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{25}H_{26}O_4Na$ 413.1723; Found 413.1725.

(2S,3S)-3-((1R,2S)ydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl hexanoate (3ia)



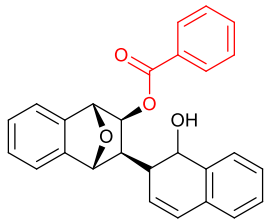
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 105 mg was isolated, and the yield was 75%. Mp: 128-129 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.51 (dd, *J* = 9.6, 2.8 Hz, 1H), 5.68 (s, 1H), 5.52 (d, *J* = 9.6 Hz, 1H), 5.29 (s, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 4.93 (s, 1H), 3.01 – 2.91 (m, 1H), 2.47 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.34 (td, *J* = 7.5, 5.0 Hz, 2H), 1.71 (s, 1H), 1.32 – 1.27 (m, 4H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 147.1, 140.9, 136.0, 132.3, 129.9, 129.1, 128.4, 127.9, 127.8, 127.0, 126.7, 126.7, 120.9, 119.2, 84.7, 80.6, 74.5, 69.6, 44.7, 38.4, 34.5, 31.3, 24.5, 22.3, 14.2, 13.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{26}H_{28}O_4Na$ 427.1880; Found 427.1881.

(2S,3S)-3-((1R,2S)-1-hydroxy-1,2-dihydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 3-chloropropanoate (3ja)



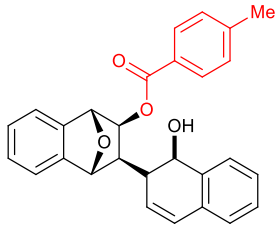
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 79 mg was isolated, and the yield was 58%. Mp: 124-125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 4.7, 2.6 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.21 (dt, *J* = 8.1, 2.4 Hz, 2H), 7.16 (d, *J* = 6.8 Hz, 1H), 6.53 (dd, *J* = 9.7, 2.8 Hz, 1H), 5.68 (s, 1H), 5.53 (d, *J* = 9.7 Hz, 1H), 5.33 – 5.28 (m, 2H), 4.93 (d, *J* = 3.7 Hz, 1H), 3.75 (dd, *J* = 9.5, 3.6 Hz, 2H), 2.98 – 2.93 (m, 1H), 2.86 – 2.81 (m, 2H), 2.50 (dd, *J* = 11.6, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 147.0, 140.6, 136.0, 132.2, 129.5, 129.1, 128.4, 127.9, 127.9, 127.8, 127.0, 126.9, 126.8, 121.0, 119.3, 84.6, 80.7, 75.4, 69.5, 44.7, 38.8, 38.4, 37.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{23}H_{21}ClO_4Na$ 419.1021; Found 419.1008.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl benzoate (3ka)



Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 112 mg was isolated, and the yield was 78%. Mp: 122-123 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 1H), 8.01 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.47 – 7.38 (m, 5H), 7.36 – 7.29 (m, 3H), 7.24 – 7.21 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.49 (dd, *J* = 9.7, 2.8 Hz, 1H), 5.75 (s, 1H), 5.64 (dd, *J* = 9.6, 1.6 Hz, 1H), 5.48 – 5.40 (m, 2H), 5.07 – 4.97 (m, 1H), 3.22 – 3.12 (m, 1H), 2.61 (dd, *J* = 11.5, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 147.1, 141.0, 136.1, 133.6, 133.3, 132.4, 130.2, 129.8, 129.7, 129.1, 128.5, 128.5, 128.4, 127.9, 127.8, 127.0, 126.9, 126.8, 121.0, 119.3, 84.8, 80.8, 75.7, 69.7, 44.9, 38.6. HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{24}O_4$ 433.1410; Found 433.1417.

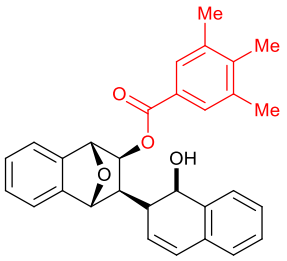
(2S,3S)-3-((2R)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 4-methylbenzoate (3la)



Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 96 mg was isolated, and the yield was 65%. Mp: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.38 (t, *J* = 6.5 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.22 (m, 2H), 7.16 (d, *J* = 7.1 Hz, 1H), 6.52 (dd, *J* = 9.7, 2.7 Hz, 1H), 5.77 (s, 1H), 5.68 (d, *J* = 9.7 Hz, 1H), 5.51 – 5.42 (m, 2H), 5.04 (d, *J* = 4.2 Hz, 1H), 3.19 (d, *J* = 11.3 Hz, 1H), 2.63 (dd, *J* = 11.4, 7.1 Hz, 1H), 2.38 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 166.8,

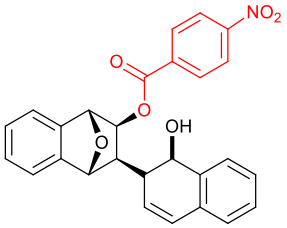
147.0, 141.0, 138.3, 136.1, 134.1, 132.3, 130.3, 129.9, 129.7, 129.1, 128.4, 127.9, 127.8, 127.0, 126.9, 126.7, 121.0, 119.3, 84.8, 80.8, 75.6, 69.7, 44.8, 38.7, 21.2. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}O_4Na$ 447.1567; Found 447.1566.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 3,4,5-trimethylbenzoate (3ma)



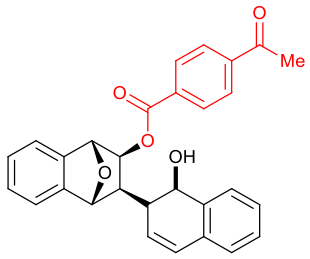
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 91 mg was isolated, and the yield was 58%. Mp: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 2H), 7.61 (s, 1H) 7.56 (s, 1H), 7.37 (dd, *J* = 12.2, 5.6 Hz, 2H), 7.26 (dd, *J* = 10.6, 6.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.10 (s, 1H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.42 (d, *J* = 9.7 Hz, 1H), 5.69 (s, 1H), 5.60 (d, *J* = 9.7 Hz, 1H), 5.36 (d, *J* = 7.1 Hz, 2H), 4.95 (d, *J* = 4.2 Hz, 1H), 3.83 – 3.67 (m, 1H), 3.08 (d, *J* = 10.4 Hz, 1H), 2.53 (dd, *J* = 11.2, 7.1 Hz, 1H), 2.30 (s, 9H), 2.23 (s, 6H). 13C NMR (126 MHz, $CDCl_3$) δ 171.5, 166.9, 147.0, 141.1, 138.2, 135.4, 130.0, 129.1, 128.4, 127.9, 127.5, 127.1, 126.9, 126.7, 121.0, 119.3, 84.8, 809, 75.5, 45.0, 38.8, 21.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{30}H_{30}O_4Na$ 475.1880; Found 475.1880.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 4-nitrobenzoate (3na)



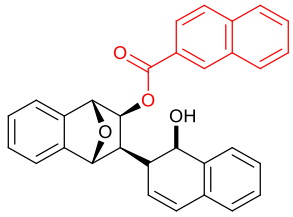
Half White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 123 mg was isolated, and the yield was 78%. 190-191 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.37 – 7.29 (m, 3H), 7.25 (dd, *J* = 5.3, 2.9 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.49 (dd, *J* = 9.7, 2.6 Hz, 1H), 5.75 (s, 1H), 5.59 (d, *J* = 9.6 Hz, 1H), 5.46 (d, *J* = 5.8 Hz, 2H), 5.00 (s, 1H), 3.21 – 3.04 (m, 1H), 2.64 (dd, *J* = 11.6, 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.7, 147.0, 140.6, 136.0, 135.2, 132.2, 130.8, 129.2, 128.4, 128.1, 128.0, 127.2, 127.2, 126.9, 123.7, 121.0, 119.4, 84.6, 80.8, 69.5, 45.0, 38.6. HRMS (ESI-QTOF) m/z: $[M+ Na]^+$ calcd for $C_{27}H_{23}NO_6Na$ 478.1261; Found 478.1252.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 4-acetylbenzoate (3oa)



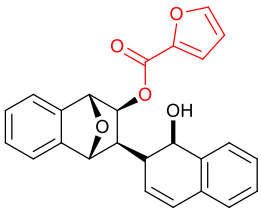
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 116 mg was isolated, and the yield was 74%. Mp: 108-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.56 – 7.39 (m, 3H), 7.38 – 7.30 (m, 3H), 7.25 – 7.21 (m, 2H), 7.15 (d, *J* = 7.1 Hz, 1H), 6.49 (d, *J* = 9.6 Hz, 1H), 5.76 (s, 1H), 5.62 (d, *J* = 9.7 Hz, 1H), 5.45 (d, *J* = 10.2 Hz, 2H), 5.02 (d, *J* = 4.2 Hz, 1H), 3.16 (d, *J* = 11.6 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 165.7, 147.0, 140.8, 140.5, 136.1, 133.6, 132.3, 130.4, 129.9, 129.5, 129.2, 128.4, 128.3, 128.3, 128.0, 127.9, 127.1, 127.0, 126.8, 121.0, 119.4, 84.7, 80.8, 76.2, 69.6, 44.9, 38.6, 26.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{26}O_5Na$ 475.1516; Found 475.1516.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 2-naphthoate (3pa)



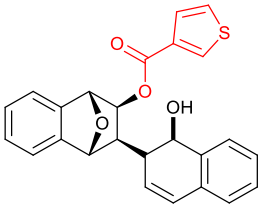
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 111 mg was isolated, and the yield was 70%. Mp: 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 2H), 8.32 (d, *J* = 7.3 Hz, 2H), 8.10 (d, *J* = 7.4 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.34 (d, *J* = 5.1 Hz, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.42 (dd, *J* = 9.7, 2.3 Hz, 1H), 5.71 (s, 1H), 5.64 (d, *J* = 9.6 Hz, 1H), 5.50 – 5.46 (m, 2H), 4.96 (d, *J* = 4.3 Hz, 1H), 3.11 (d, *J* = 11.6 Hz, 1H), 2.58 (dd, *J* = 11.5, 7.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 166.8, 147.1, 141.0, 136.2, 135.9, 135.7, 132.4, 132.4, 132.1, 131.5, 129.9, 129.5, 129.4, 129.1, 128.6, 128.4, 128.3, 128.3, 127.9, 127.8, 127.8, 127.7, 127.1, 127.0, 126.8, 126.7, 126.5, 125.4, 125.1, 121.0, 119.3, 84.8, 83.5, 80.9, 76.5, 75.8, 69.7, 45.0, 38.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}O_5Na$ 483.1567; Found 483.1570.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl furan-2-carboxylate (3qa)



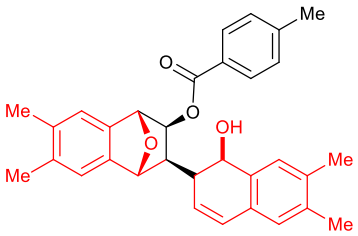
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 112 mg was isolated, and the yield was 81%. Mp: 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.15 (m, 5H), 7.07 (d, *J* = 11.5 Hz, 2H), 6.42 (d, *J* = 12.5 Hz, 2H), 5.66 (s, 1H), 5.56 (d, *J* = 9.7 Hz, 1H), 5.37 (s, 1H), 5.33 (d, *J* = 6.6 Hz, 1H), 4.93 (s, 1H), 3.02 (d, *J* = 11.1 Hz, 1H), 2.56 – 2.45 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 153.5, 147.0, 146.9, 140.8, 136.1, 132.3, 129.8, 129.0, 128.4, 127.9, 127.7, 126.8, 126.7, 121.0, 119.3, 118.6, 111.9, 84.6, 80.8, 75.5, 69.7, 44.9, 38.6. HRMS (ESI-QTOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{20}O_5$ 423.1203; Found 423.1196.

(2S,3S)-3-((2S)-1-hydroxy-1,2,4a,8a-tetrahydronaphthalen-2-yl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl thiophene-3-carboxylate (3ra)



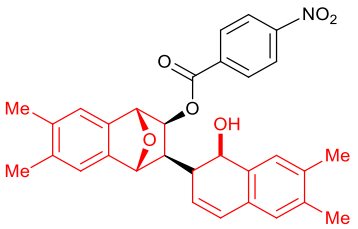
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2a**), 107 mg was isolated, and the yield was 74%. Mp: 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.43 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.29 – 7.25 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 – 7.13 (m, 2H), 7.09 (d, *J* = 6.9 Hz, 1H), 6.44 (dd, *J* = 9.7, 2.8 Hz, 1H), 5.66 (s, 1H), 5.58 (d, *J* = 9.7 Hz, 1H), 5.38 (s, 1H), 5.28 (d, *J* = 7.0 Hz, 1H), 4.93 (d, *J* = 3.9 Hz, 1H), 3.05 (s, 1H), 2.52 (dd, *J* = 11.5, 7.1 Hz, 1H). 13C NMR (126 MHz, $CDCl_3$) δ 162.6, 146.9, 140.9, 136.1, 133.4, 133.2, 132.3, 129.9, 129.1, 128.4, 127.9, 127.9, 127.8, 127.4, 127.1, 126.8, 126.8, 126.3, 121.0, 119.3, 84.7, 80.8, 75.5, 69.6, 44.6, 38.7. HRMS (ESI-QTOF) m/z: $[M+NH_4]^+$ calcd for $C_{25}H_{26}O_4NS$ 434.1421; Found 434.1411.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethyl-1,2,4a,8a-tetrahydronaphthalen-2-yl)-6,7-dimethyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 4-methylbenzoate (3lb)



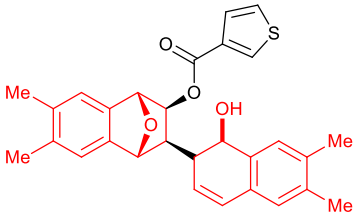
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2b**), 77 mg was isolated, and the yield was 55%. Mp: 100-101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.7 Hz, 3H), 7.76 (s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.36 (s, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.12 (s, 1H), 7.06 (s, 1H), 6.84 (s, 1H), 6.35 (dd, J = 9.7, 2.8 Hz, 1H), 5.60 (s, 1H), 5.48 (d, J = 9.5 Hz, 1H), 5.31 (d, J = 7.0 Hz, 2H), 4.87 (d, J = 4.1 Hz, 1H), 3.03 (d, J = 11.1 Hz, 1H), 2.48 (dd, J = 11.4, 7.0 Hz, 1H), 2.35 (s, 3H), 2.27 (s, 3H), 2.22 (s, 3H), 2.20 – 2.15 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 145.0, 140.8, 138.7, 137.3, 136.3, 135.9, 135.1, 133.8, 132.2, 131.9, 131.7, 130.8, 130.0, 129.8, 128.9, 128.0, 126.6, 125.8, 125.8, 122.2, 120.6, 84.8, 80.7, 75.69, 69.4, 45.4, 38.9, 21.9, 20.0, 19.9, 19.6, 19.5. HRMS (ESI-QTOF) m/z: [M+ Na]+ calcd for $C_{32}H_{32}O_4Na$ 503.2193; Found 503.2190.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethyl-1,2,4a,8a-tetrahydronaphthalen-2-yl)-6,7-dimethyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 4-nitrobenzoate (3nb)



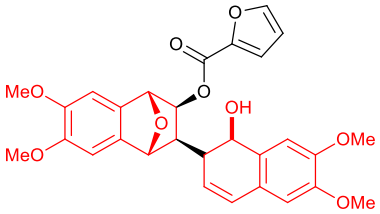
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2b**), 101 mg was isolated, and the yield was 68%. Mp: 141-142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.7 Hz, 2H), 7.24 (s, 1H), 7.21 (s, 1H), 7.15 (s, 1H), 6.94 (s, 1H), 6.43 (dd, *J* = 9.6, 2.6 Hz, 1H), 5.67 (s, 1H), 5.49 (d, *J* = 9.6 Hz, 1H), 5.42 (d, *J* = 6.9 Hz, 1H), 5.39 (s, 1H), 4.92 (s, 1H), 3.08 (d, *J* = 11.5 Hz, 1H), 2.60 (dd, *J* = 11.7, 6.9 Hz, 1H), 2.31 (s, 3H), 2.30 – 2.26 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 150.7, 144.8, 138.3, 137.6, 136.6, 136.3, 135.3, 133.7, 130.8, 129.8, 129.8, 128.3, 128.2, 127.0, 123.6, 122.3, 120.7, 84.5, 80.7, 69.3, 45.5, 38.9, 20.0, 19.9, 19.6, 19.5. HRMS (ESI-QTOF) m/z: $[M+ Na]^+$ calcd for $C_{31}H_{29}NO_6Na$ 534.1887; Found 534.1883.

(2S,3S)-3-((2S)-1-Hydroxy-6,7-dimethyl-1,2,4a,8a-tetrahydronaphthalen-2-yl)-6,7-dimethyl-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl furan-3-carboxylate (3rb)



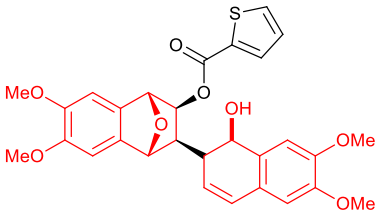
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2b**), 93 mg was isolated, and the yield was 68%. Mp: 104-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.5 Hz, 1H), 7.52 (d, *J* = 4.9 Hz, 1H), 7.21 – 7.19, 2H, 7.12 (s, 1H), 7.08 – 7.03 (m, 1H), 6.93 (s, 1H), 6.44 (d, *J* = 2.6 Hz, 1H), 5.65 (s, 1H), 5.54 (d, *J* = 9.6 Hz, 1H), 5.39 (s, 1H), 5.32 (d, *J* = 7.0 Hz, 1H), 4.92 (s, 1H), 3.07 (d, *J* = 11.6 Hz, 1H), 2.53 (dd, *J* = 11.5, 7.0 Hz, 1H), 2.30 (s, 3H), 2.26 (d, *J* = 5.3 Hz, 9H). 13C NMR (126 MHz, $CDCl_3$) δ 162.2, 144.9, 138.6, 137.3, 136.2, 136.0, 135.1, 133.8, 133.8, 133.5, 132.9, 130.0, 129.8, 128.9, 128.0, 127.8, 126.6, 122.3, 120.6, 84.5, 80.7, 76.2, 69.5, 45.3, 38.9, 20.1, 20.0, 19.9, 19.6, 19.5. HRMS (ESI-QTOF) m/z: $[M+K]^+$ calcd for $C_{29}H_{28}O_4SK$ 511.1340; Found 511.1343.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-2-yl)-6,7-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl furan-2-carboxylate (3qc)



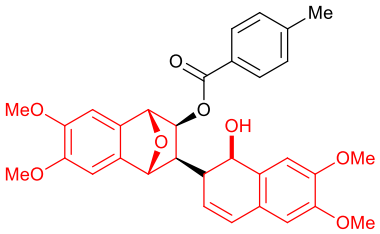
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2c**), 91 mg was isolated, and the yield was 71%. Mp: 110-111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.63 (d, *J* = 0.7 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.34 (s, 1H), 7.31 (d, *J* = 3.5 Hz, 1H), 7.08 (d, *J* = 2.5 Hz, 2H), 7.05 (s, 1H), 6.93 (s, 1H), 6.55 (dd, *J* = 3.5, 1.7 Hz, 1H), 6.45 (d, *J* = 3.2 Hz, 1H), 6.18 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.50 (s, 2H), 5.34 (d, *J* = 7.0 Hz, 1H), 3.98 (d, *J* = 1.9 Hz, 6H), 3.91 (d, *J* = 11.0 Hz, 6H), 3.44 (d, *J* = 7.0 Hz, 1H). 13C NMR (101 MHz, $CDCl_3$) δ 158.1, 149.4, 148.3, 147.2, 146.3, 143.9, 139.3, 133.9, 133.6, 128.8, 128.0, 126.9, 126.2, 125.7, 119.8, 117.8, 112.2, 111.4, 106.2, 105.9, 105.5, 103.2, 85.4, 83.4, 76.7, 76.4, 56.4, 56.3, 55.8, 51.4. HRMS (ESI-QTOF) m/z: $[M+K]^+$ calcd for $C_{29}H_{28}O_9K$ 559.1265; Found 559.1282.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-2-yl)-6,7-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl thiophene-2-carboxylate (3rc)



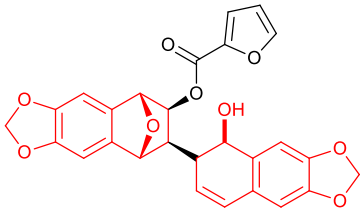
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2c**), 74 mg was isolated, and the yield was 56%. Mp: 106-107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 1.5 Hz, 1H), 7.31 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.27 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.09 (d, *J* = 6.2 Hz, 2H), 7.06 (s, 1H), 6.93 (s, 1H), 6.81 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.50 (d, *J* = 4.6 Hz, 2H), 5.31 (d, *J* = 7.1 Hz, 1H), 3.98 (d, *J* = 2.7 Hz, 6H), 3.93 (s, 3H), 3.91 (s, 3H), 3.44 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 149.4, 149.2, 148.9, 148.4, 139.3, 134.1, 133.8, 133.3, 133.1, 132.5, 129.0, 128.1, 127.3, 127.0, 126.2, 125.9, 106.3, 106.0, 105.5, 103.9, 85.4, 83.5, 56.4, 56.3, 55.8, 55.8, 51.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{28}NO_8SNa$ 599.1397; Found 599.1399.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-2-yl)-6,7-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl 4-methylbenzoate (3lc)



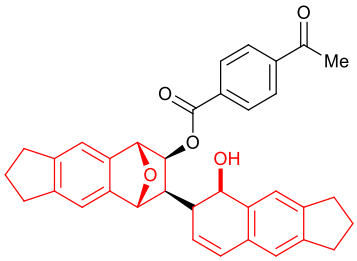
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2c**), 77 mg was isolated, and the yield was 58%. Mp: 131-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 19.8, 8.1 Hz, 2H), 7.10 (dd, *J* = 13.8, 8.3 Hz, 4H), 7.05 – 6.99 (m, 2H), 6.95 (s, 1H), 5.58 (s, 1H), 5.50 (s, 1H), 5.32 (d, *J* = 7.1 Hz, 1H), 4.13 – 4.11 (m, 1H), 3.98 (d, *J* = 1.7 Hz, 6H), 3.95 – 3.90 (m, 6H), 3.47 (d, *J* = 7.1 Hz, 1H), 2.04 (s, 1H), 1.99 (s, 3H). 13C NMR (101 MHz, $CDCl_3$) δ 166.4, 149.4, 149.2, 148.8, 148.3, 139.2, 137.6, 134.1, 134.1, 133.4, 129.9, 129.5, 129.0, 128.0, 127.8, 126.6, 126.4, 126.3, 125.9, 106.2, 106.0, 105.5, 103.8, 85.1, 83.5, 76.4, 56.3, 55.8, 55.8, 51.1, 20.7. HRMS (ESI-QTOF) m/z: $[M+]^+$ calcd for $C_{32}H_{32}O_8$ 544.2097; Found 544.2046.

(6S,7S)-7-((6S)-5-hydroxy-4a,5,6,8a-tetrahydronaphtho[2,3-d][1,3]dioxol-6-yl)-5,6,7,8-tetrahydro-5,8-epoxynaphtho[2,3-d][1,3]dioxol-6-yl furan-2-carboxylate (3qd)



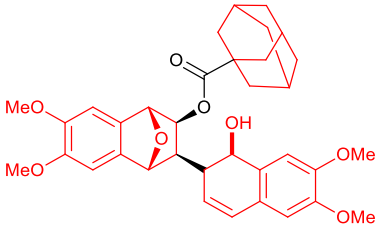
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**2d**), 94 mg was isolated, and the yield was 72%. Mp: 148-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.7 Hz, 15H), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.27 (d, *J* = 3.4 Hz, 1H), 7.05 (s, 1H), 6.73 (s, 1H), 6.59 (dd, *J* = 4.8, 3.1 Hz, 2H), 6.47 (s, 1H), 5.99 (d, *J* = 4.7 Hz, 2H), 5.86 (d, *J* = 8.8 Hz, 2H), 5.73 (d, *J* = 3.2 Hz, 2H), 5.66 (s, 1H), 5.49 (s, 1H), 5.31 (s, 1H), 5.08 (s, 1H), 4.62 (d, *J* = 19.0 Hz, 1H), 3.14 (d, *J* = 8.8 Hz, 1H), 2.33 (dd, *J* = 8.8, 4.3 Hz, 1H), 1.97 (s, 1H), 1.85 – 1.78 (m, 1H). 13C NMR (126 MHz, $CDCl_3$) δ 169.6, 147.2, 146.9, 145.8, 142.0, 141.0, 140.8, 138.7, 133.4, 132.2, 131.6, 131.4, 130.6, 129.9, 128.4, 128.3, 127.9, 127.7, 127.5, 127.4, 127.1, 126.5, 126.4, 126.1, 125.8, 120.5, 119.2, 119.1, 118.2, 84.0, 82.5, 80.9, 80.0, 48.8, 44.2, 43.5, 29.7. HRMS (ESI-QTOF) m/z: $[M+K]^+$ calcd for $C_{27}H_{20}O_9K$ 527.0739; Found 527.0735.

(6S,7S)-7-((6S)-5-hydroxy-2,3,4a,5,6,8a-hexahydro-1H-cyclopenta[b]naphthalen-6-yl)-2,3,5,6,7,8-hexahydro-1H-5,8-epoxycyclopenta[b]naphthalen-6-yl 4-acetylbenzoate (3oe)



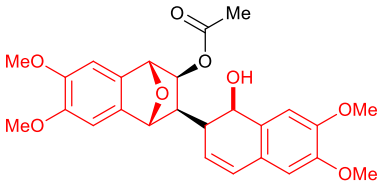
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**1e**), 84 mg was isolated, and the yield was 58% Mp: 148-149 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.69 – 7.51 (m, 7H), 7.33 (s, 1H), 7.12 (d, *J* = 1.9 Hz, 1H), 5.55 (ddd, *J* = 14.6, 9.6, 3.9 Hz, 2H), 5.48 – 5.38 (m, 1H), 3.64 – 3.48 (m, 1H), 3.24 – 3.13 (m, 1H), 3.08 – 2.81 (m, 8H), 2.52 (s, 3H), 2.22 – 2.09 (m, 4H). 13C NMR (126 MHz, CDCl3) δ 197.6, 165.3, 145.4, 144.9, 144.1, 143.5, 143.3, 143.2, 139.8, 139.1, 137.4, 135.6, 134.4, 133.4, 132.6, 131.8, 131.4, 129.5, 128.9, 128.0, 127.9, 127.7, 127.0, 126.7, 126.4, 126.2, 125.1, 123.9, 123.4, 123.0, 121.8, 121.7, 118.7, 117.4, 116.9, 115.6, 51.7, 51.4, 32.7, 32.6, 32.5, 31.0, 30.7, 30.6, 26.7, 26.1, 25.7, 24.6, 24.5. HRMS (ESI-QTOF) m/z: $[M+K]^+$ calcd for $C_{35}H_{32}O_5K$ 571.1881; Found 571.1896.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-2-yl)-6,7-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl adamantane-1-carboxylate (3ac)



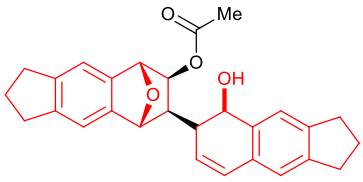
White Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**1c**), 100 mg was isolated, and the yield was 69%. Mp: 180-181 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.01 (d, *J* = 9.7 Hz, 2H), 6.90 (s, 1H), 6.69 (s, 1H), 5.75 (s, 1H), 5.58 (s, 2H), 4.91 (s, 1H), 3.96 (s, 1H), 3.91 (s, 3H), 3.82 (s, 6H), 3.65 (s, 3H), 3.27 (d, *J* = 8.8 Hz, 1H), 2.43 (dd, *J* = 8.8, 2.3 Hz, 1H), 2.04 (s, 3H), 1.95 (s, 6H), 1.71 (d, *J* = 13.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.1, 149.4, 149.2, 148.7, 148.3, 139.3, 134.3, 133.7, 129.0, 128.1, 127.1, 126.6, 125.7, 106.2, 105.9, 105.3, 103.9, 85.4, 83.4, 75.4, 56.3, 55.8, 51.3, 40.3, 38.0, 36.2, 27.6. HRMS (ESI-QTOF) m/z: [M+Na]+ calcd for $C_{35}H_{40}O_8Na$ 611.2615; Found 611.2640.

(2S,3S)-3-((2S)-1-hydroxy-6,7-dimethoxy-1,2-dihydronaphthalen-2-yl)-6,7-dimethoxy-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl acetate (3cc)



Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**1c**), 80 mg was isolated, and the yield was 70%. Mp: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 5.4 Hz, 2H), 7.01 (d, *J* = 3.1 Hz, 1H), 6.91 (s, 1H), 5.45 (s, 1H), 5.39 (s, 1H), 5.20 (d, *J* = 6.9 Hz, 1H), 4.04 (s, 1H), 4.00 (d, *J* = 3.9 Hz, 7H), 3.90 (d, *J* = 6.9 Hz, 7H), 3.37 (d, *J* = 6.9 Hz, 1H), 1.47 (s, 1H), 1.43 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 170.4, 148.8, 148.3, 133.7, 128.8, 127.0, 126.4, 125.7, 106.4, 106.0, 105.4, 103.9, 85.4, 83.1, 56.4, 56.3, 55.8, 51.6, 20.4. HRMS (ESI-QTOF) m/z: [M+H]+ calcd for $C_{26}H_{28}O_8$ 468.1779; Found 468.1733.

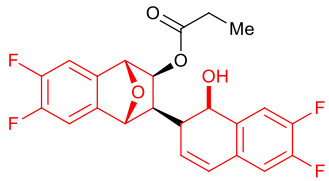
(6S,7S)-7-((6S)-5-hydroxy-2,3,4a,5,6,8a-hexahydro-1H-cyclopenta[b]naphthalen-6-yl)-2,3,5,6,7,8-hexahydro-1H-5,8-epoxycyclopenta[b]naphthalen-6-yl acetate (3ce)



Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**1e**), 72 mg was isolated, and the yield was 62%. Mp: 106-107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.54 (s, 1H), 7.41 – 7.30 (m, 1H), 7.07 (s, 1H), 7.04 – 6.97 (m, 1H), 5.44 (s, 1H), 5.35 (d, *J* = 15.4 Hz, 1H), 5.20 – 5.14 (m, 1H), 3.39 – 3.32 (m, 1H), 3.18 (s, 1H), 2.99 –

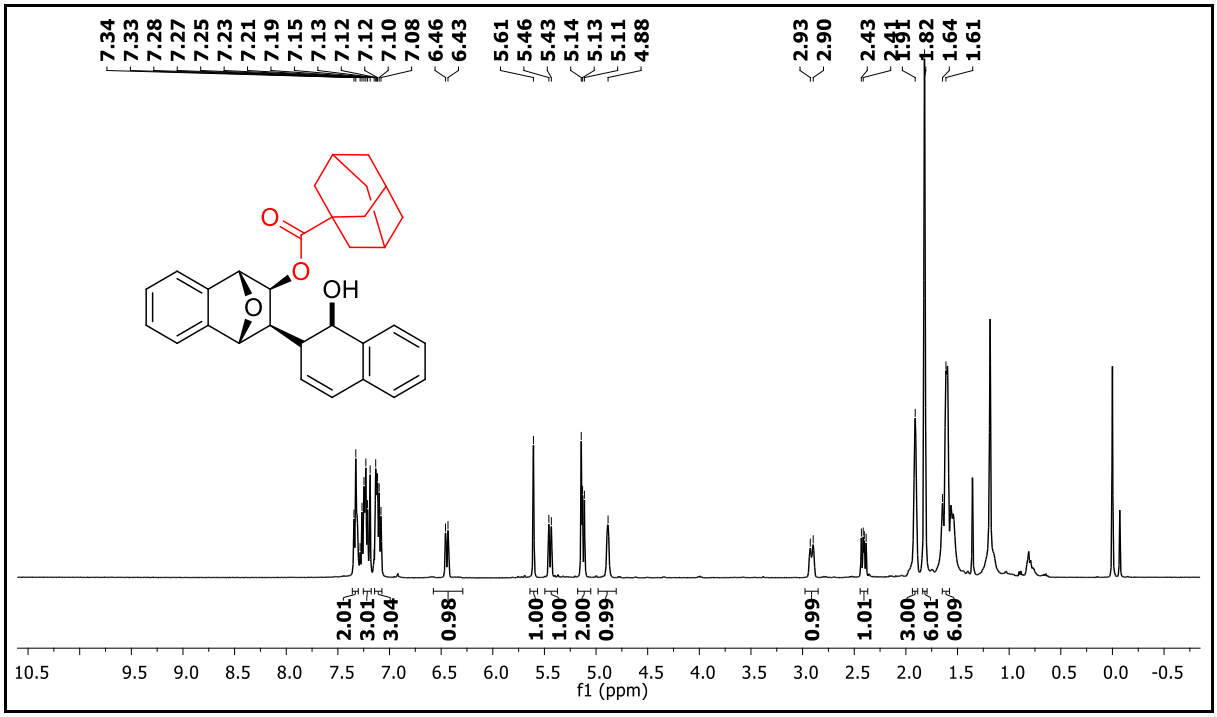
2.79 (m, 8H), 2.10 – 2.01 (m, 4H), 1.35 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 145.5, 143.9, 143.4, 143.2, 140.4, 135.3, 134.4, 132.5, 131.8, 129.3, 129.0, 128.2, 127.0, 126.7, 126.6, 123.6, 123.3, 122.6, 122.1, 121.7, 118.5, 117.2, 116.8, 115.5, 85.2, 85.1, 83.9, 83.0, 82.9, 81.8, 76.3, 51.6, 50.8, 33.7, 32.6, 31.0, 30.6, 30.5, 26.1, 25.7, 24.5, 20.4. HRMS (ESI-QTOF) m/z: [M+ Na]+ calcd for $C_{28}H_{28}O_4Na$ 451.1880; Found 451.1861.

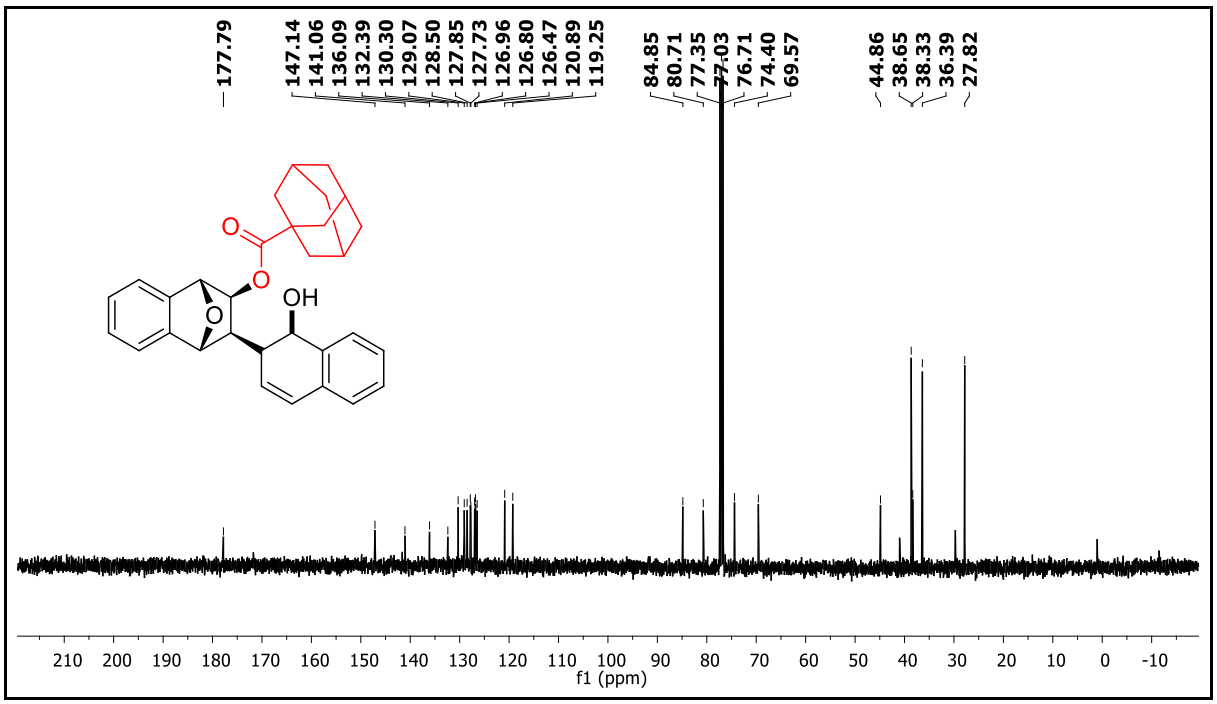
(2S,3S)-3-((2S)-6,7-Difluoro-1-hydroxy-1,2-dihydronaphthalen-2-yl)-6,7-difluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl propionate (3df)



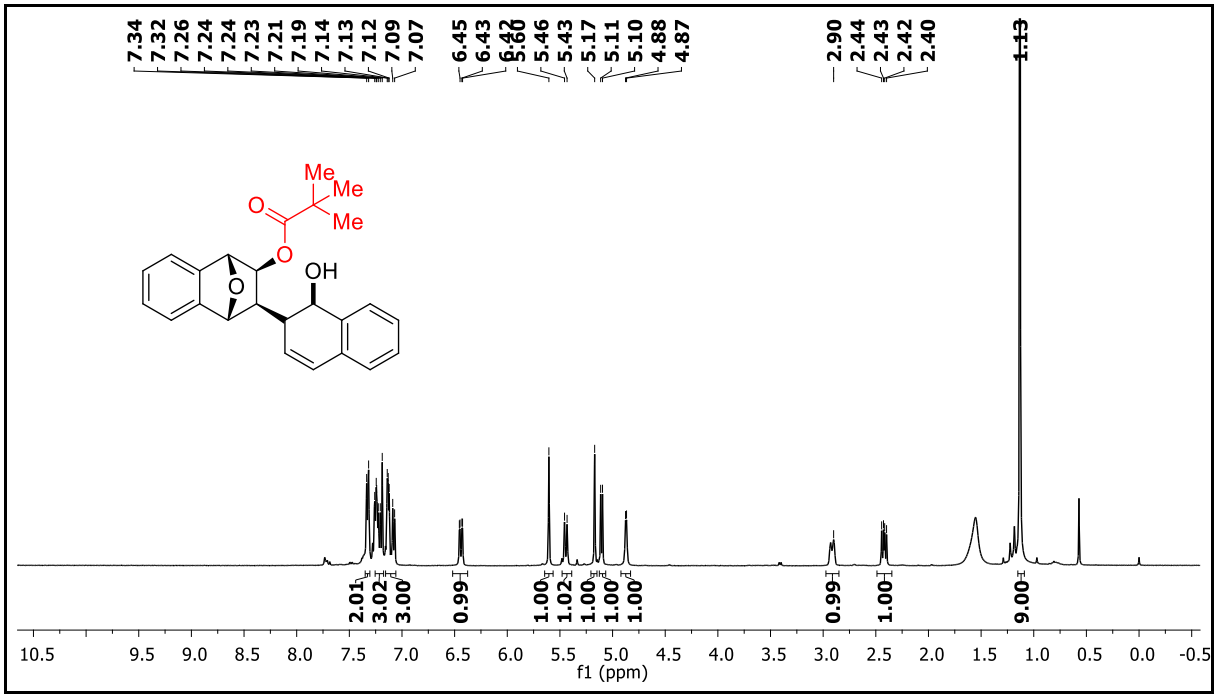
Brown Solid; eluent (5 % ethyl acetate in hexane). The reaction scale is 100 mg (**1f**), 78 mg was isolated, and the yield was 65%. Mp: 114-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (ddd, *J* = 10.8, 7.3, 3.2 Hz, 2H), 7.12 (dd, *J* = 8.6, 6.8 Hz, 1H), 6.96 (dd, *J* = 10.4, 7.7 Hz, 1H), 6.43 (dd, *J* = 9.7, 2.7 Hz, 1H), 5.61 (s, 1H), 5.56 (d, *J* = 9.7 Hz, 1H), 5.26 (s, 1H), 5.16 (d, *J* = 7.0 Hz, 1H), 4.84 (s, 1H), 2.94 – 2.85 (m, 1H), 2.45 – 2.34 (m, 3H), 1.75 (s, 1H), 1.15 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 148.1, 142.8, 136.8, 132.5, 130.2, 129.1, 129.1, 125.3, 117.5, 117.3, 115.5, 115.4, 111.1, 110.9, 109.5, 109.3, 84.3, 80.4, 74.1, 68.6, 44.6, 38.0, 27.8, 8.9. HRMS (ESI-QTOF) m/z: [M+H]+ calcd for $C_{23}H_{19}F_4O_4$ 435.1214; Found 435.1198.

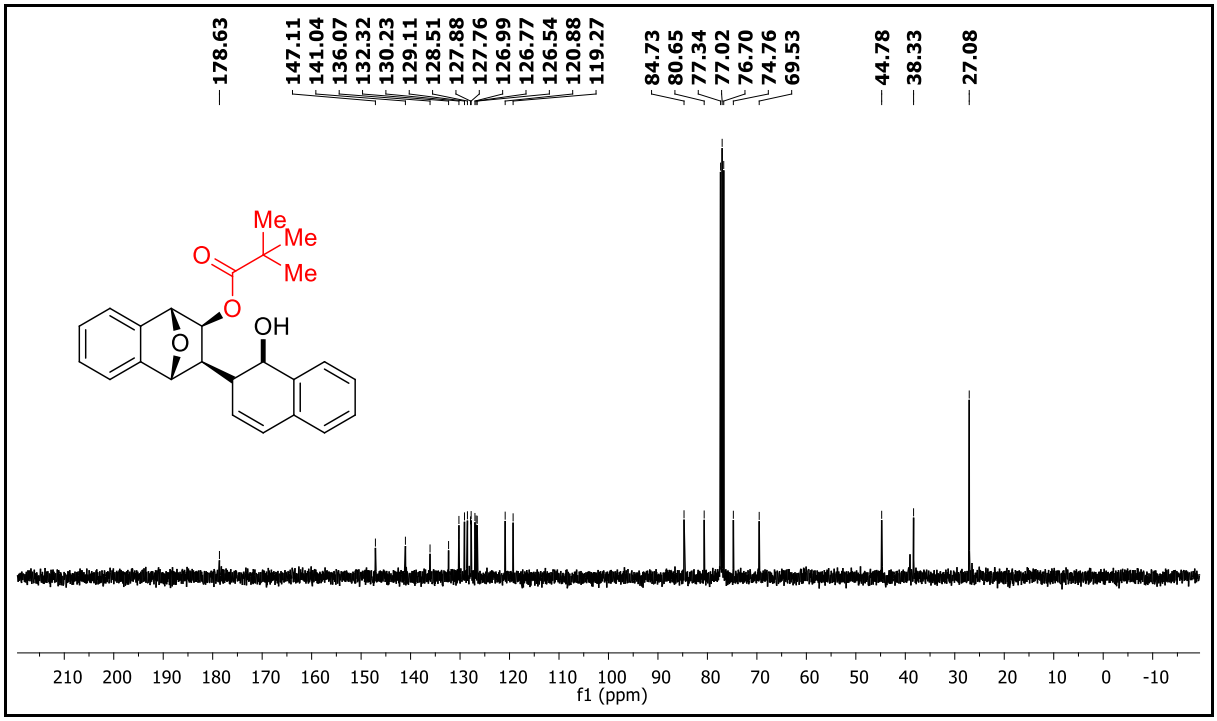
^{1}H and ^{13}C NMR Spectra of Compound **3aa** ($CDCl_3$, 400 MHz)



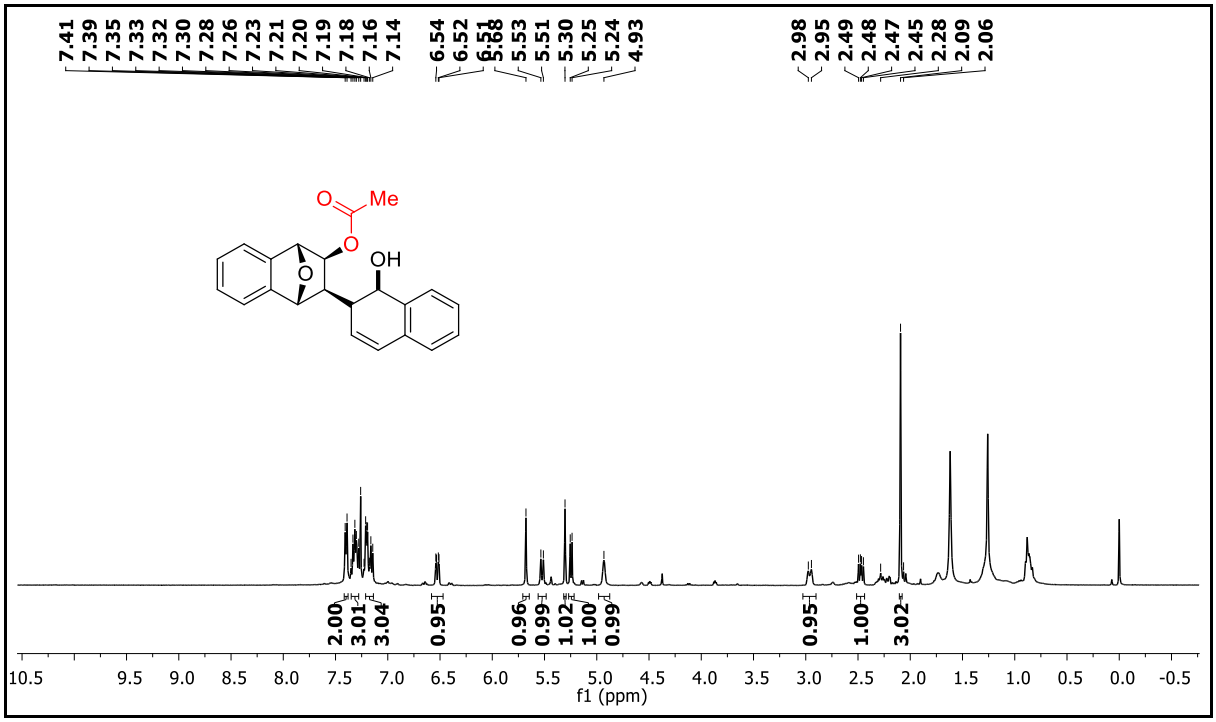


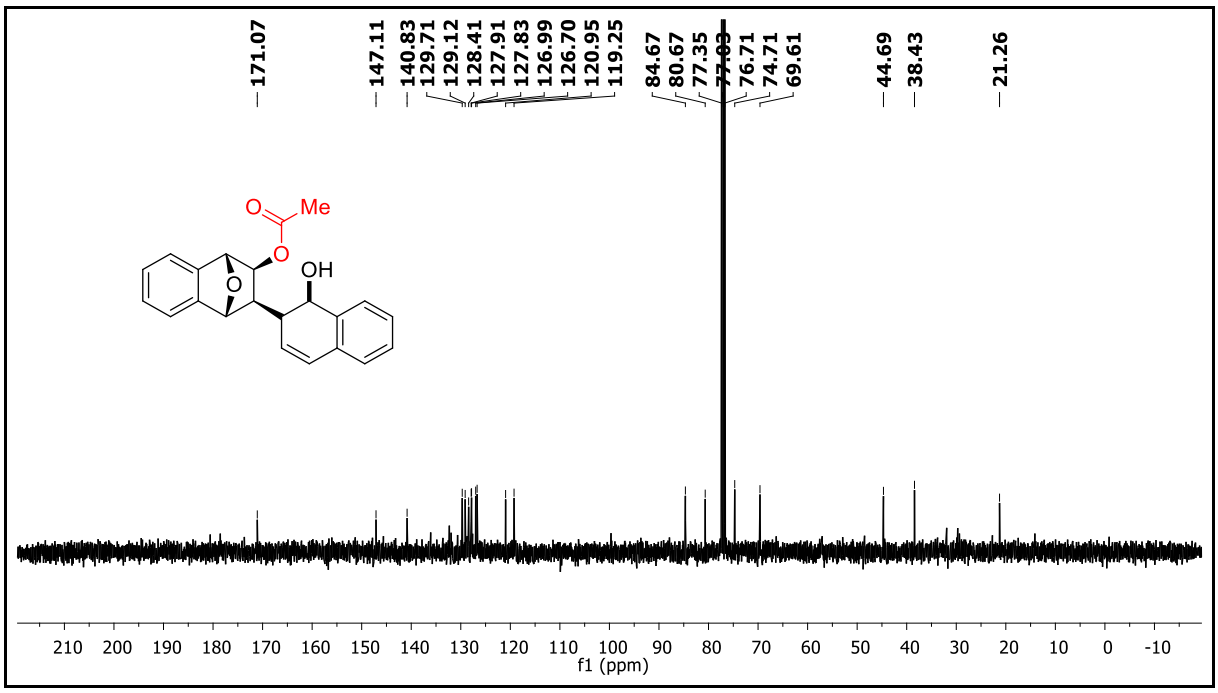
^{1}H and ^{13}C NMR Spectra of Compound **3ba** ($CDCl_3$, 400 MHz)



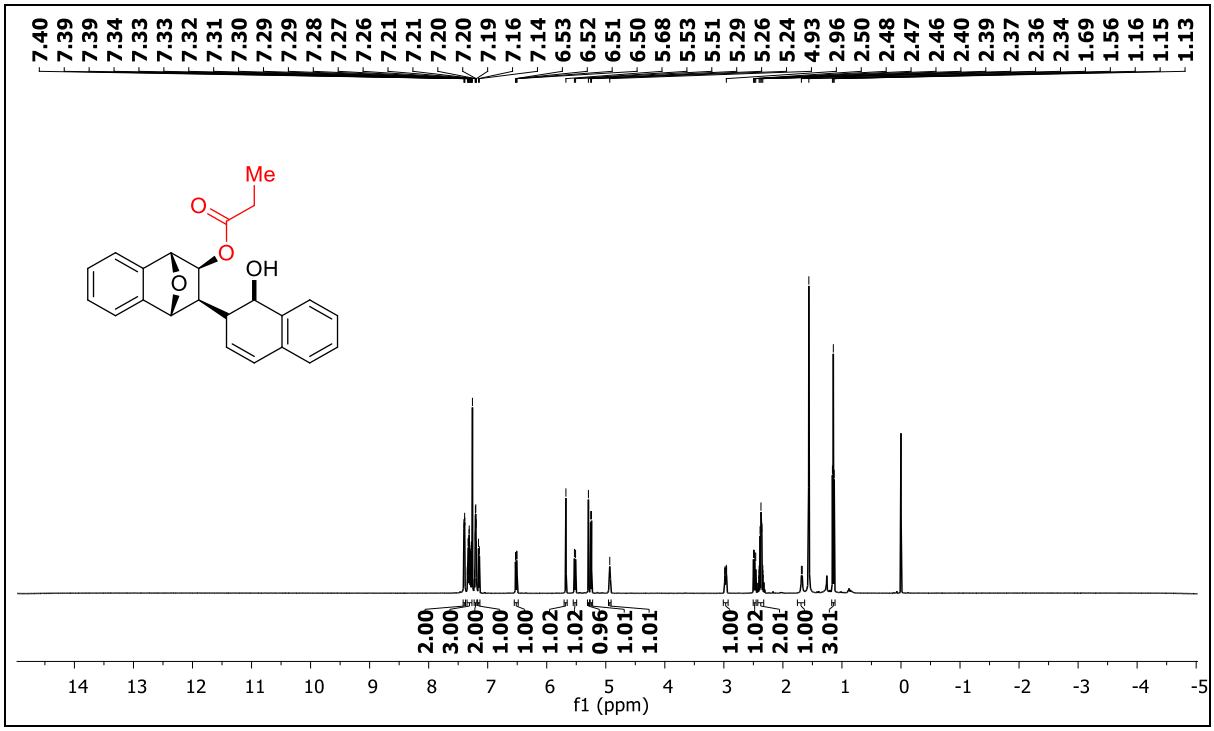


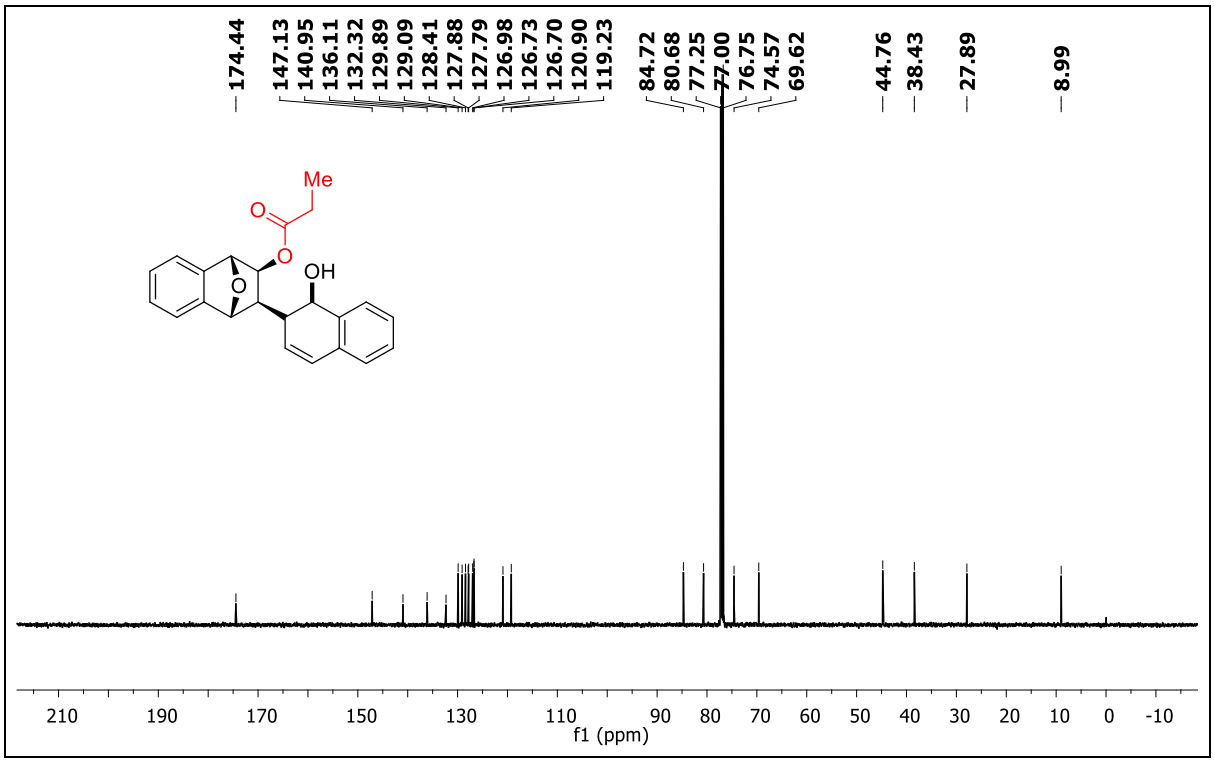
^{1}H and ^{13}C NMR Spectra of Compound **3ca** ($CDCl_3$, 400 MHz)



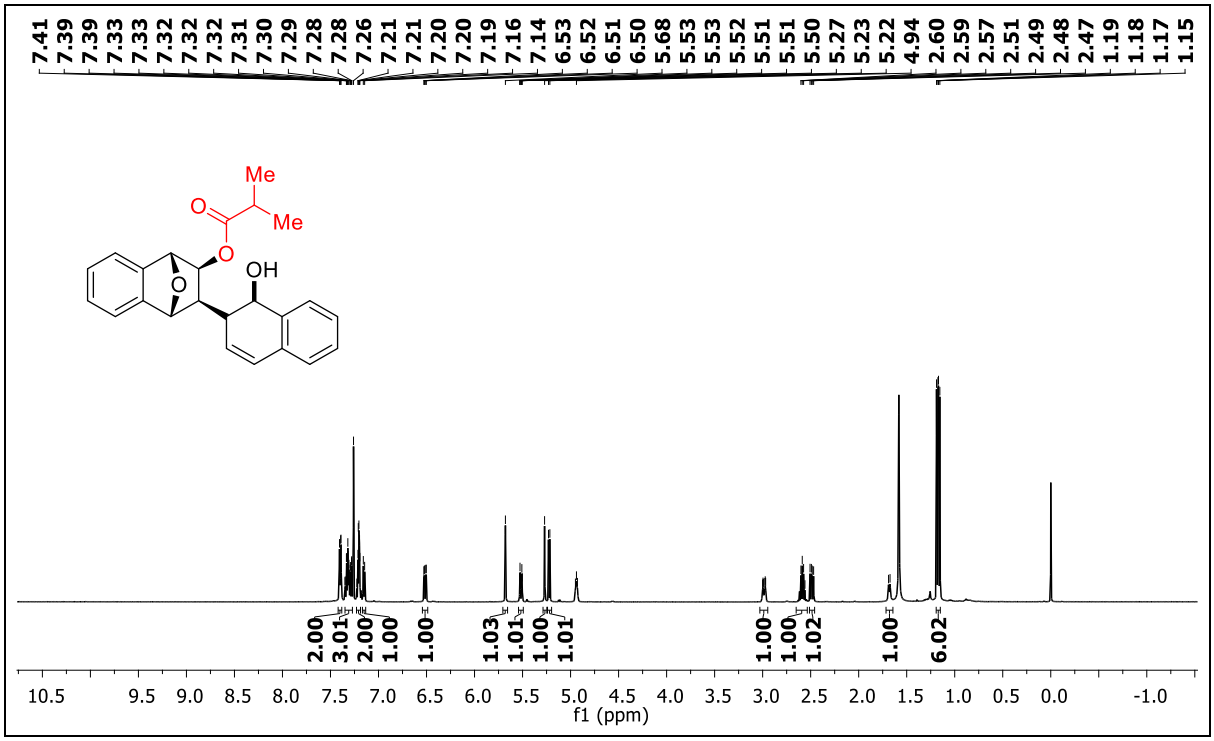


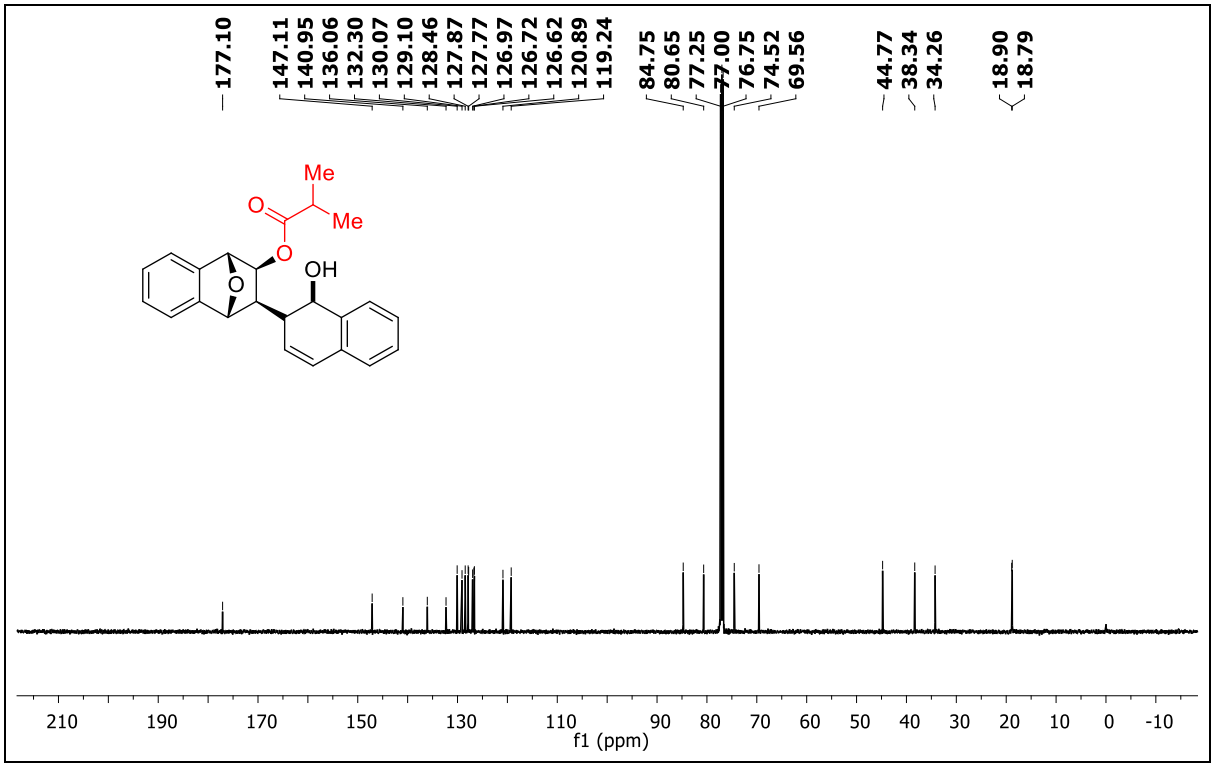
^{1}H and ^{13}C NMR Spectra of Compound **3da** ($CDCl_3$, 500 MHz)



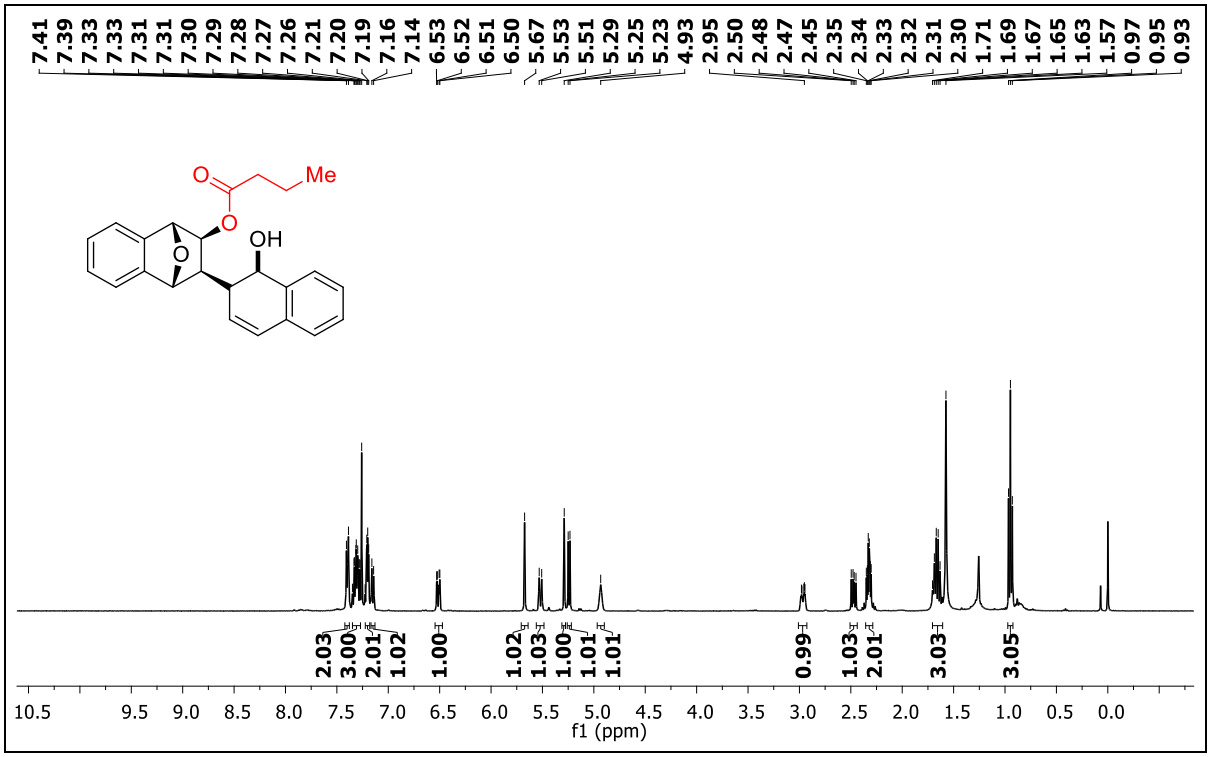


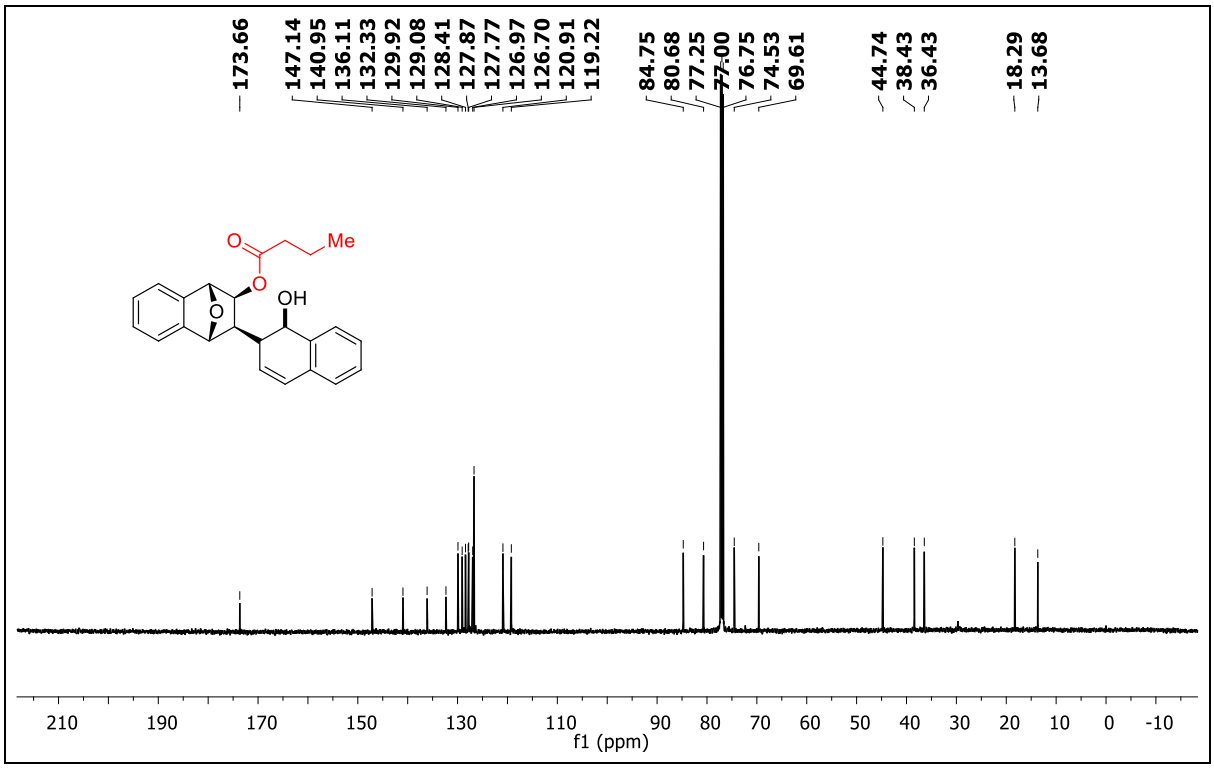
^{1}H and ^{13}C NMR Spectra of Compound **3ea** ($CDCl_3$, 500 MHz)



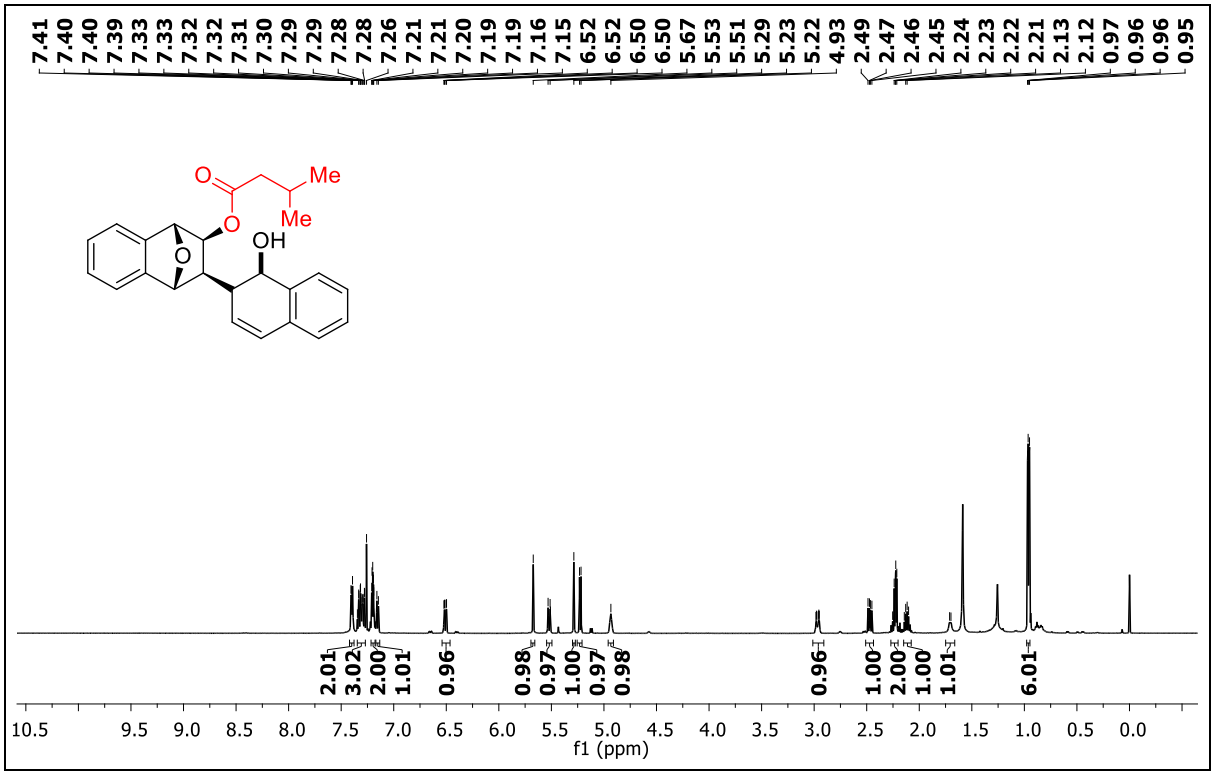


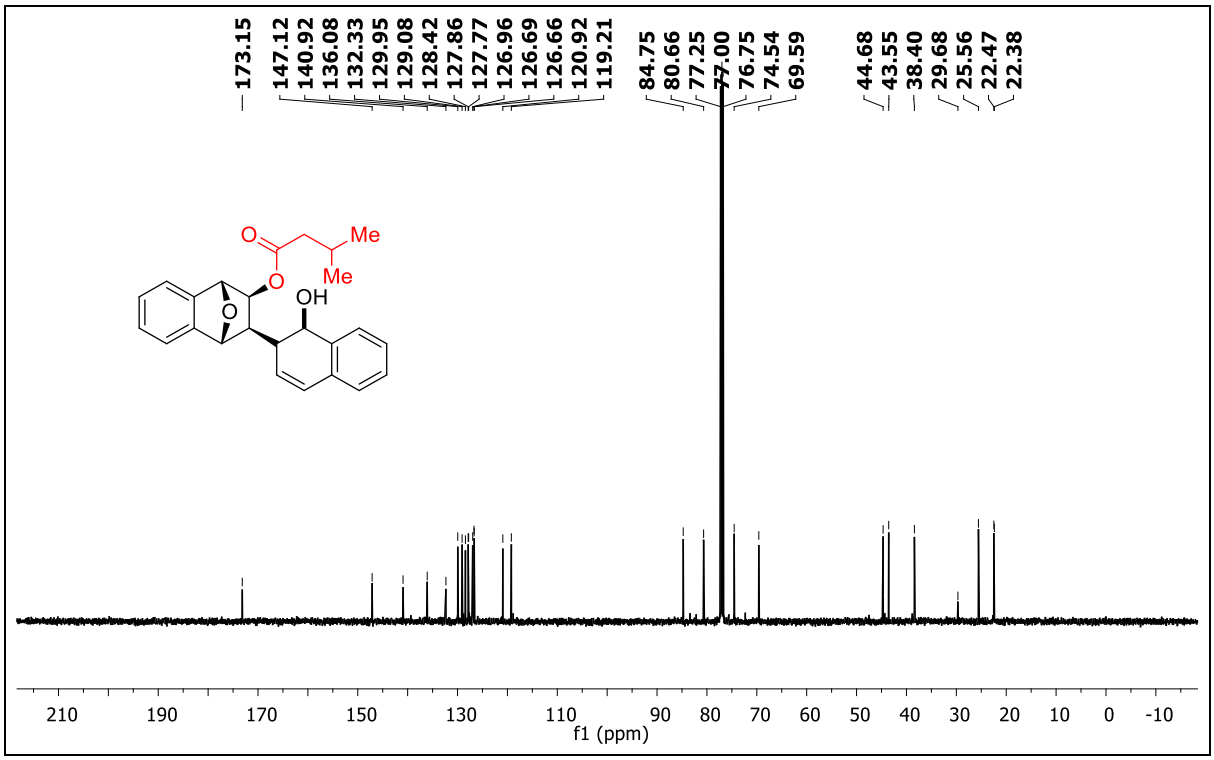
^{1}H and ^{13}C NMR Spectra of Compound **3fa** ($CDCl_3$, 400 MHz)



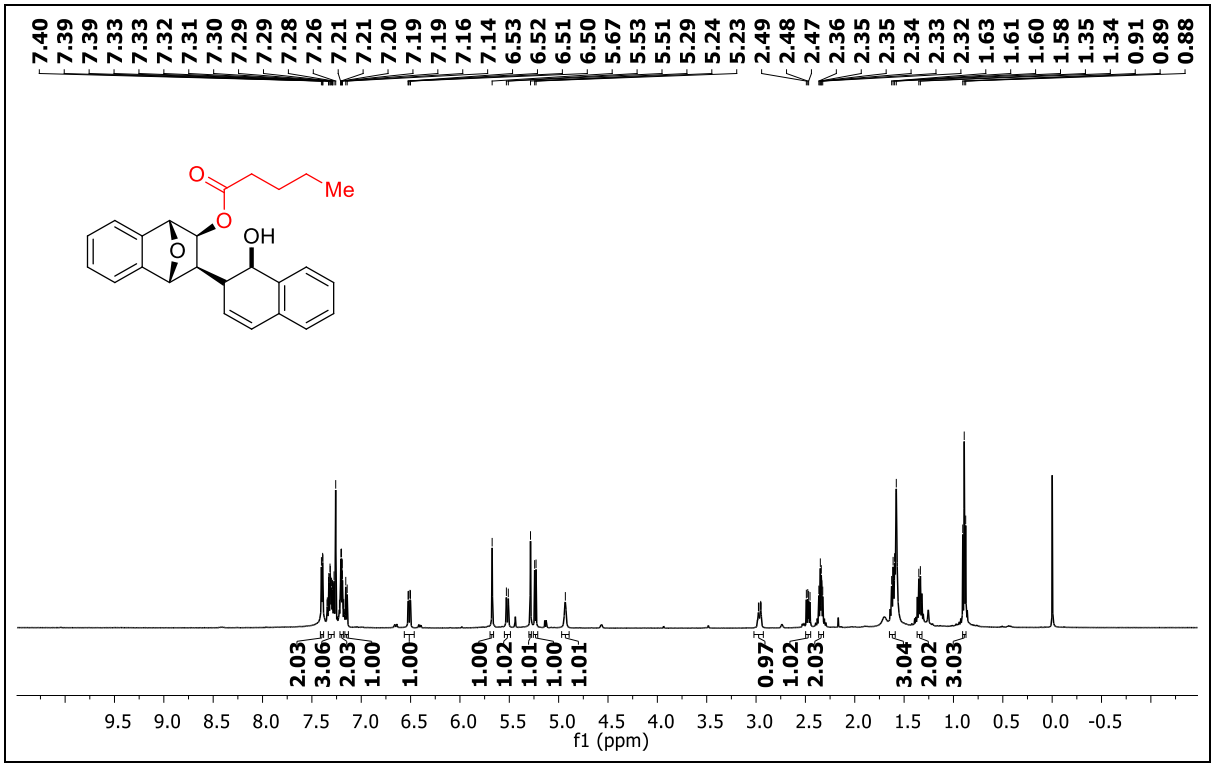


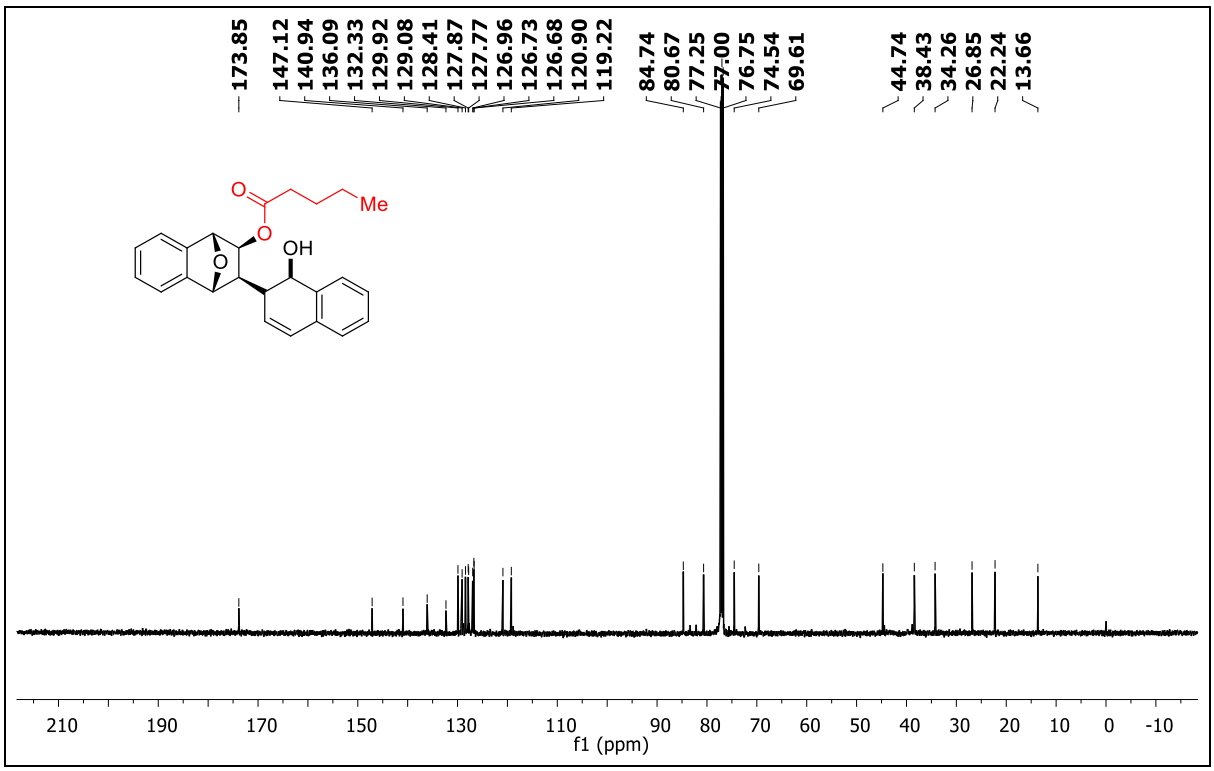
^{1}H and ^{13}C NMR Spectra of Compound **3ga** ($CDCl_3$, 500 MHz)



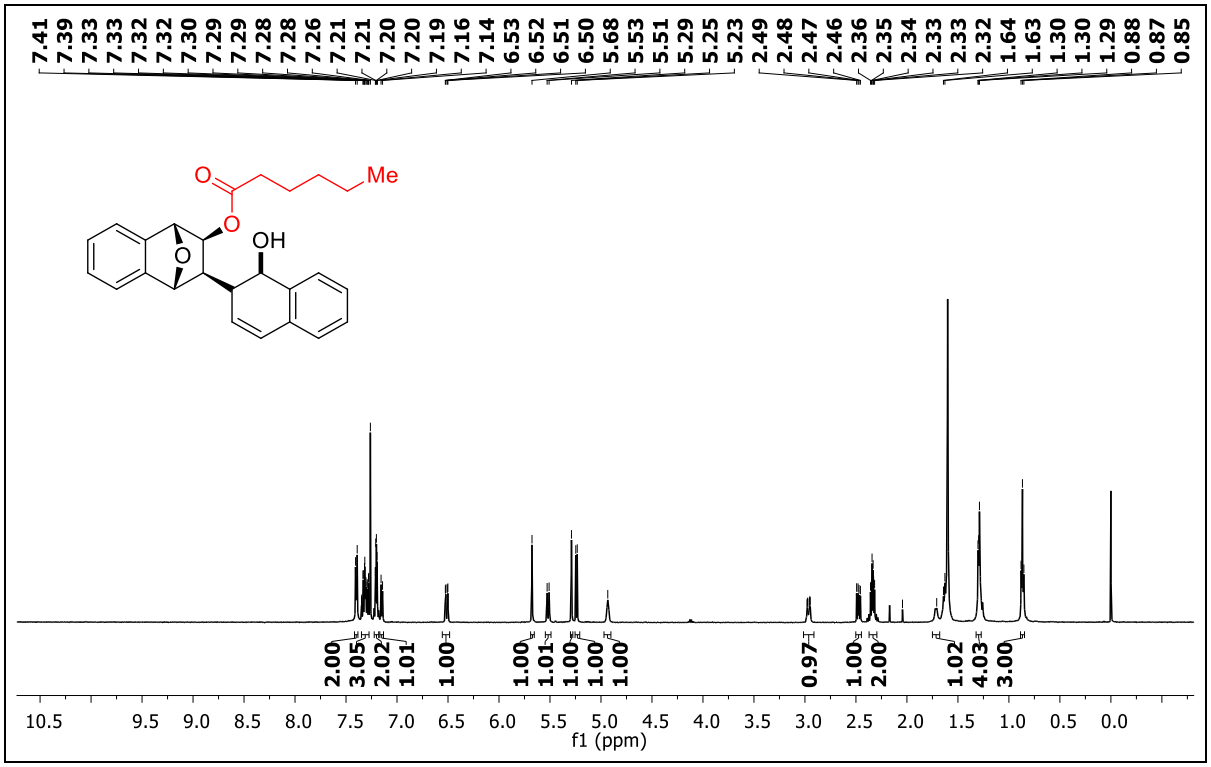


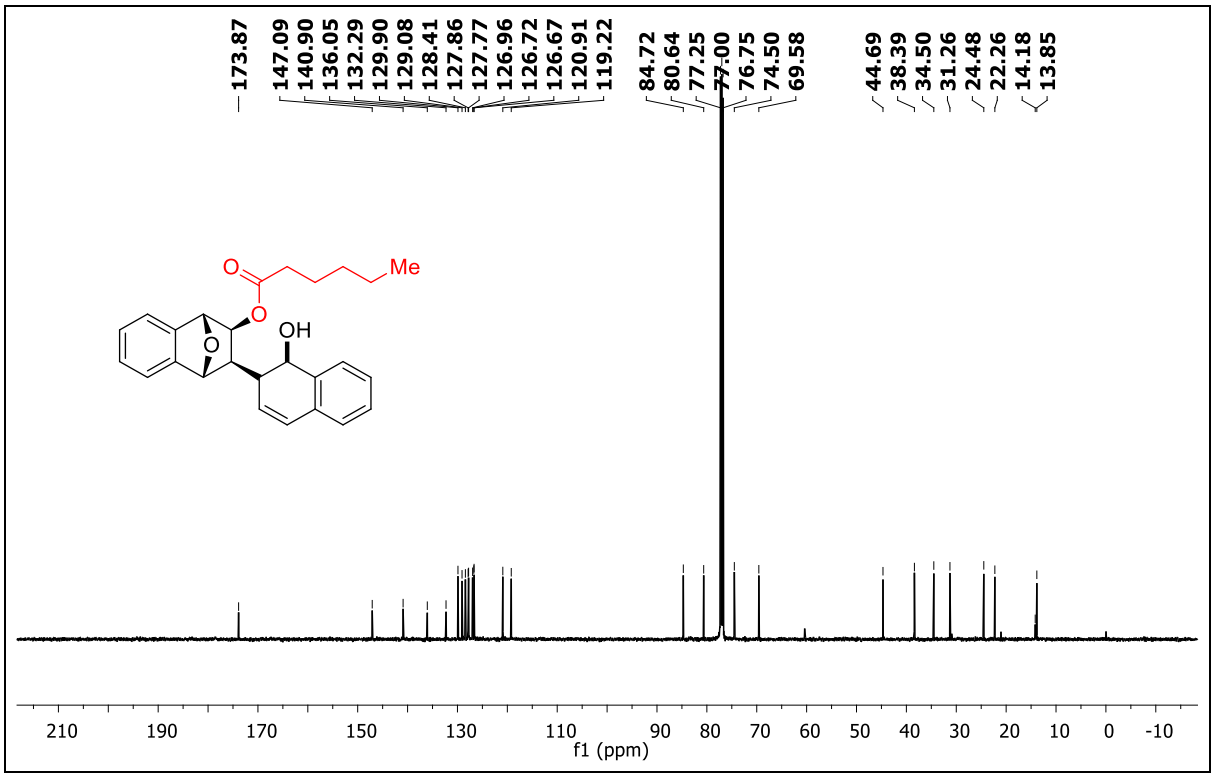
^{1}H and ^{13}C NMR Spectra of Compound **3ha** ($CDCl_3$, 500 MHz)



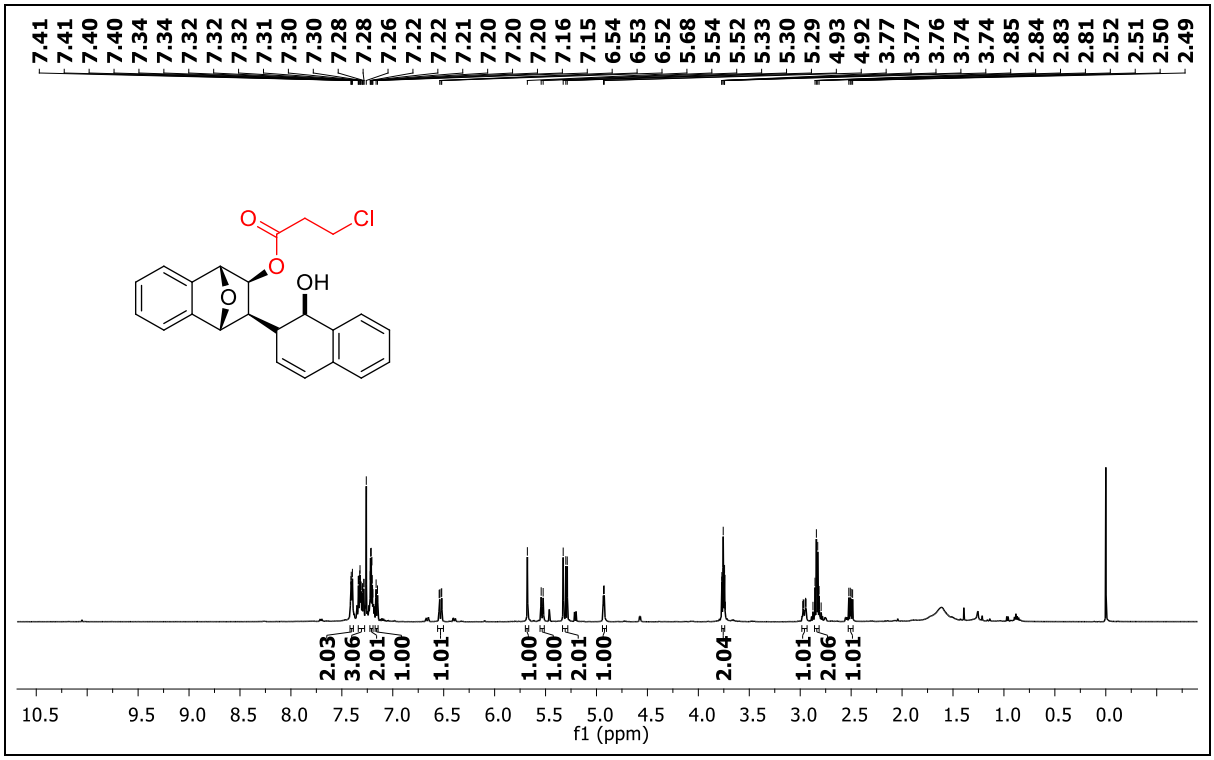


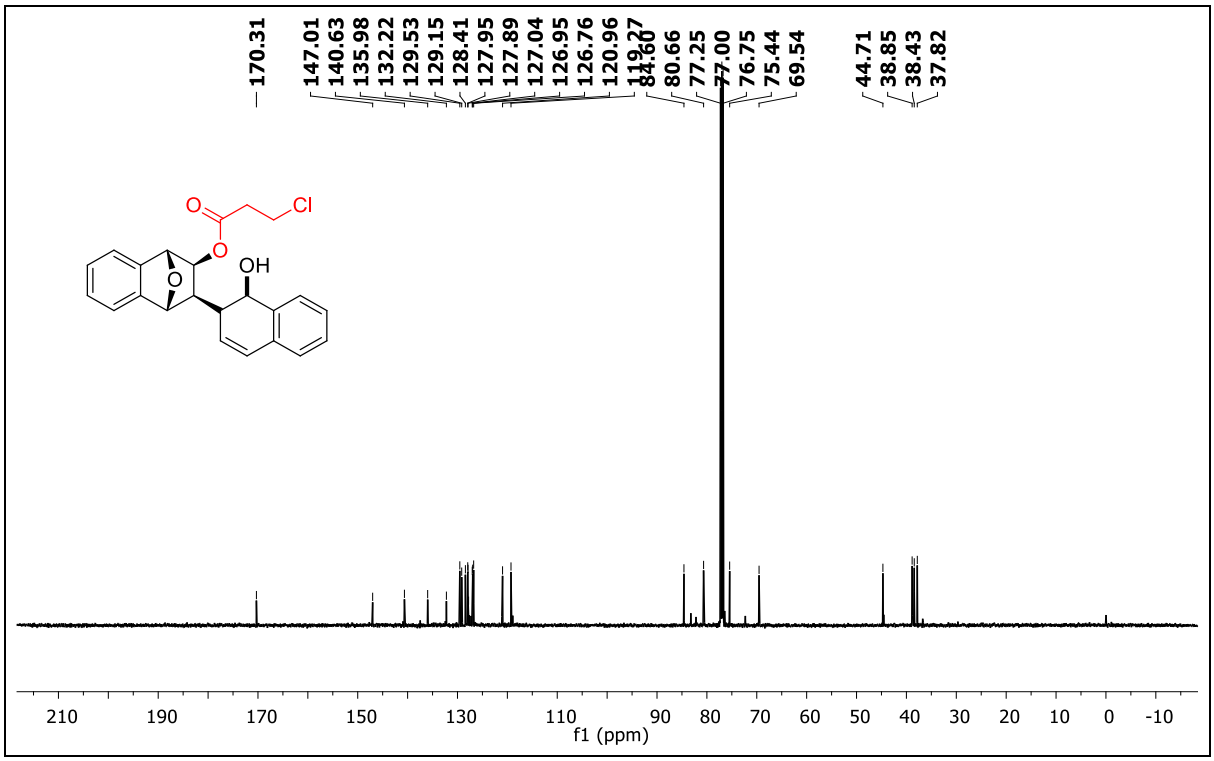
^{1}H and ^{13}C NMR Spectra of Compound **3ia** ($CDCl_3$, 500 MHz)



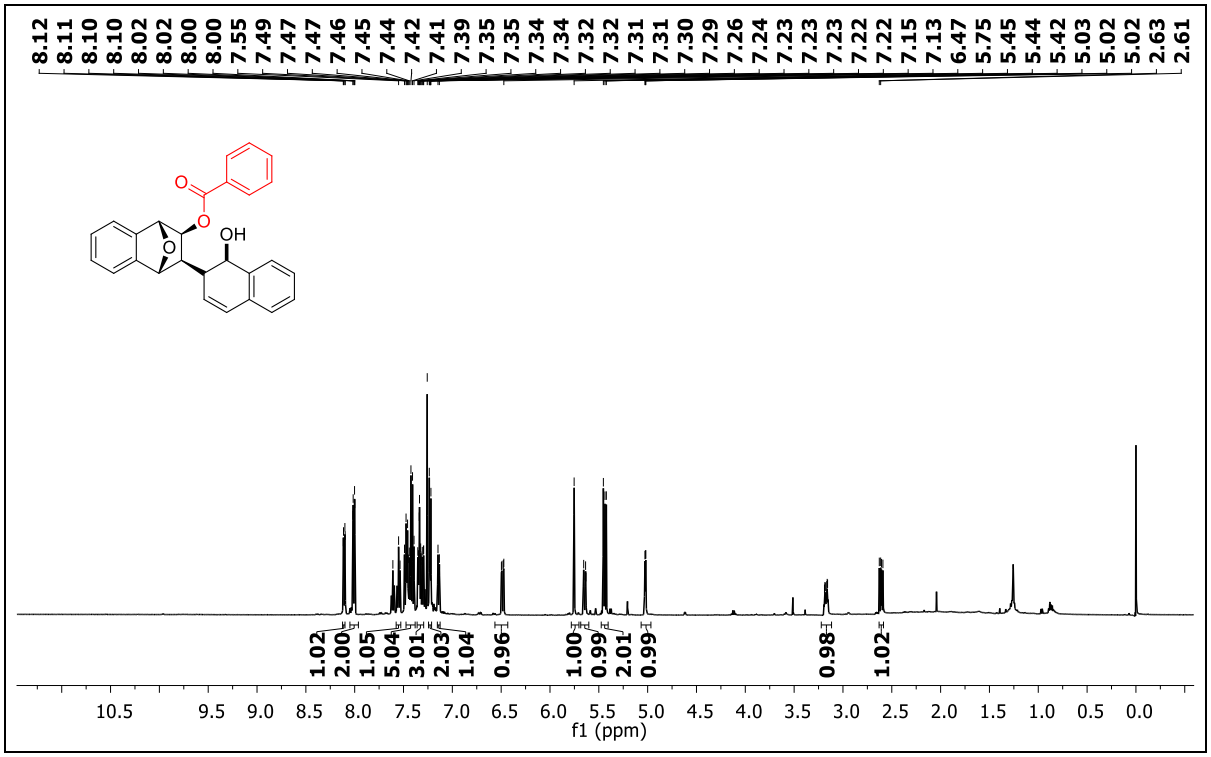


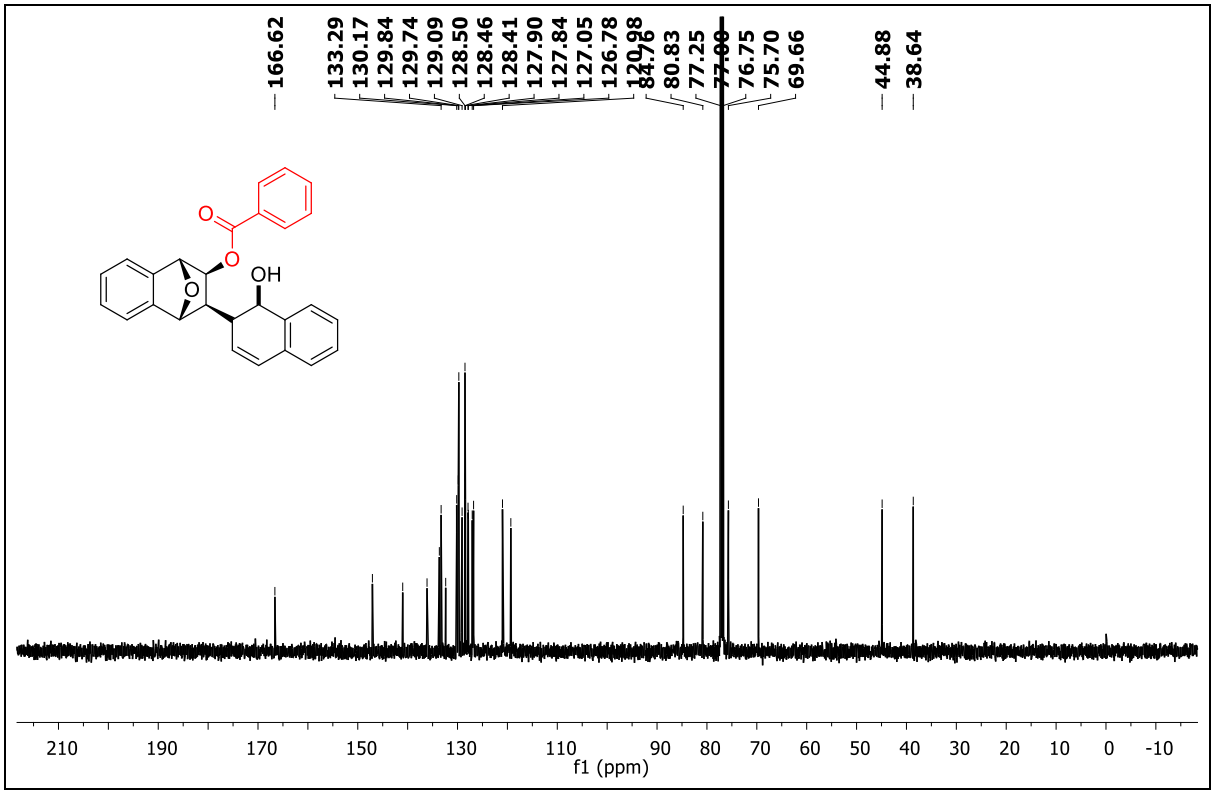
^{1}H and ^{13}C NMR Spectra of Compound **3ja** ($CDCl_3$, 500 MHz)



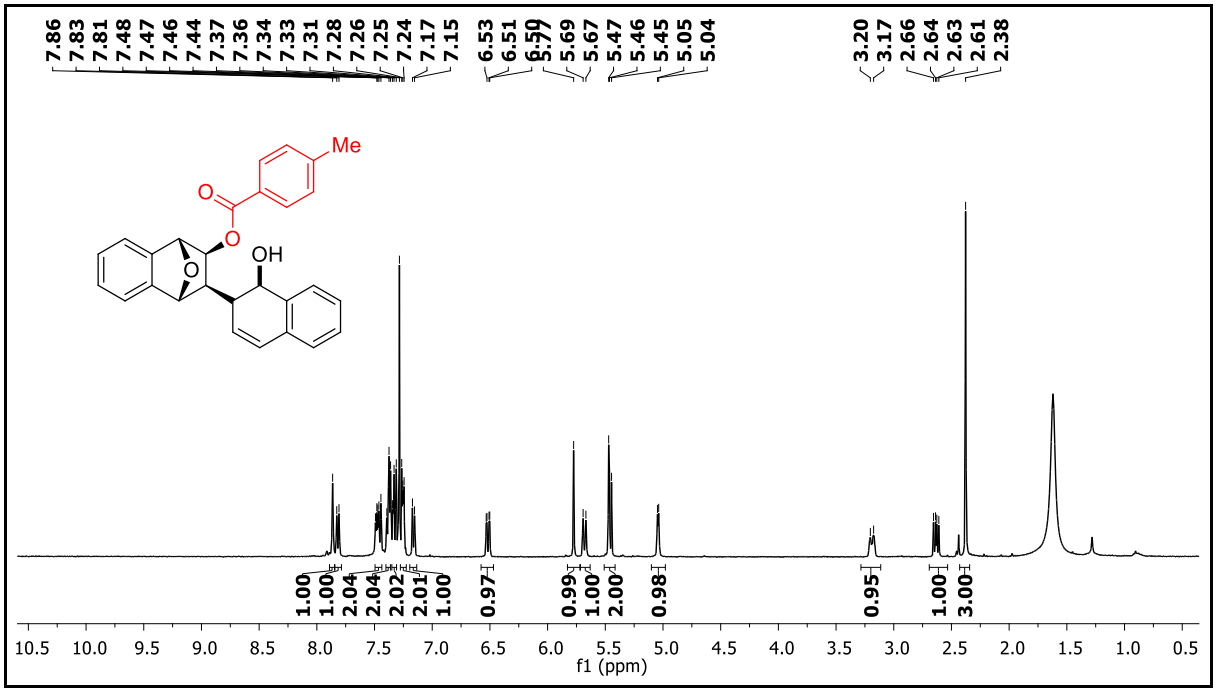


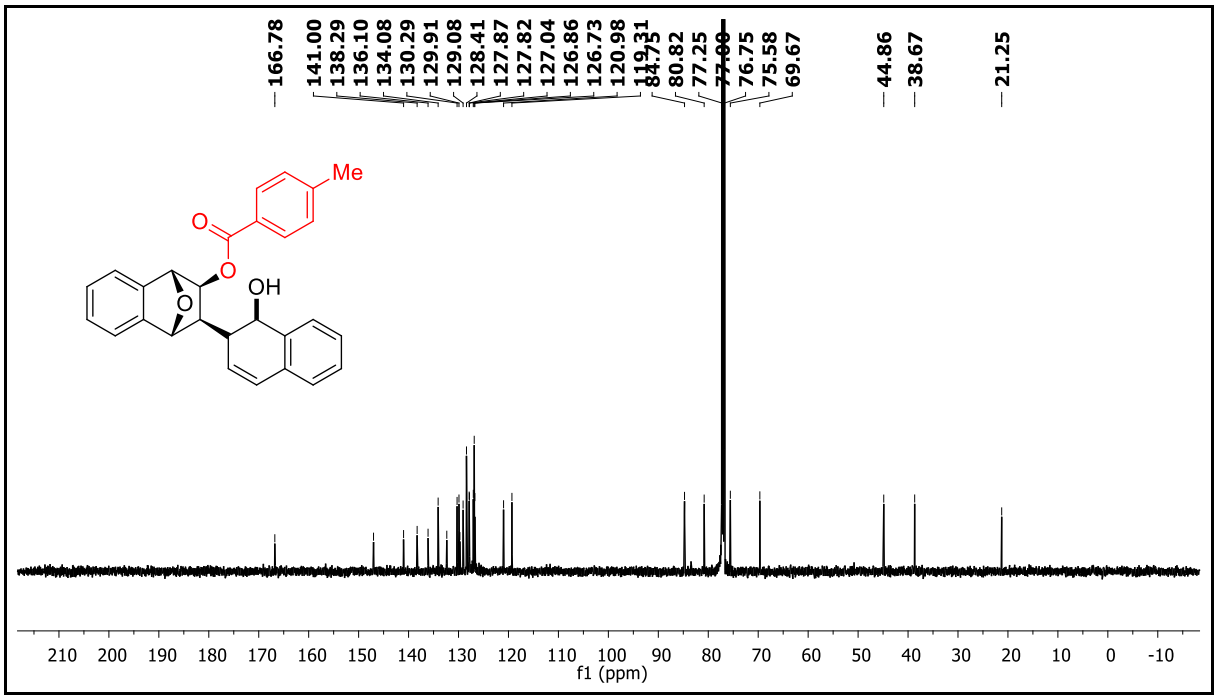
^{1}H and ^{13}C NMR Spectra of Compound **3ka** ($CDCl_3$, 400 MHz)



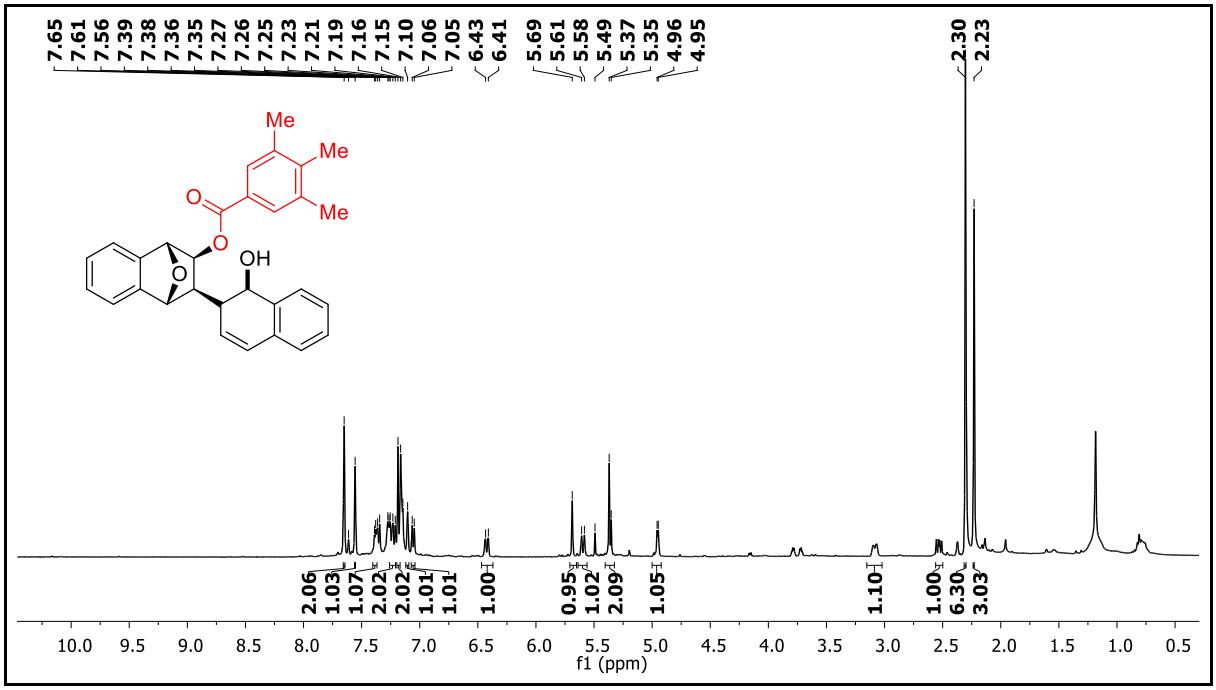


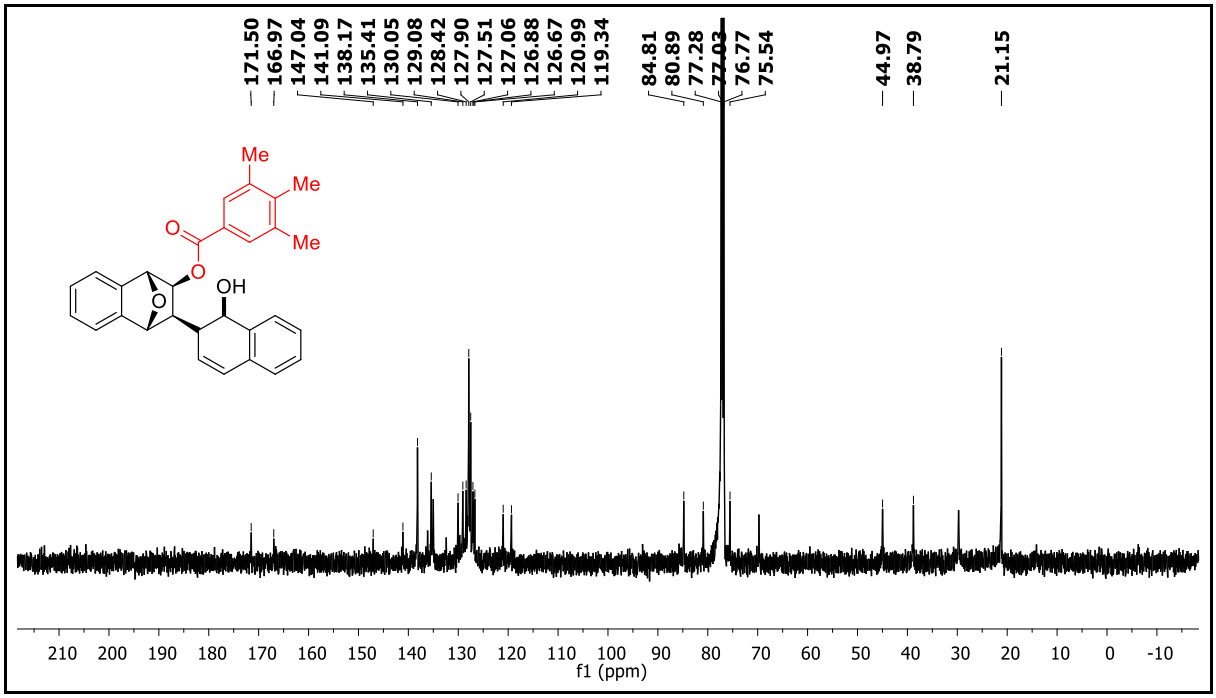
^{1}H and ^{13}C NMR Spectra of Compound **3la** ($CDCl_3$, 400 MHz)



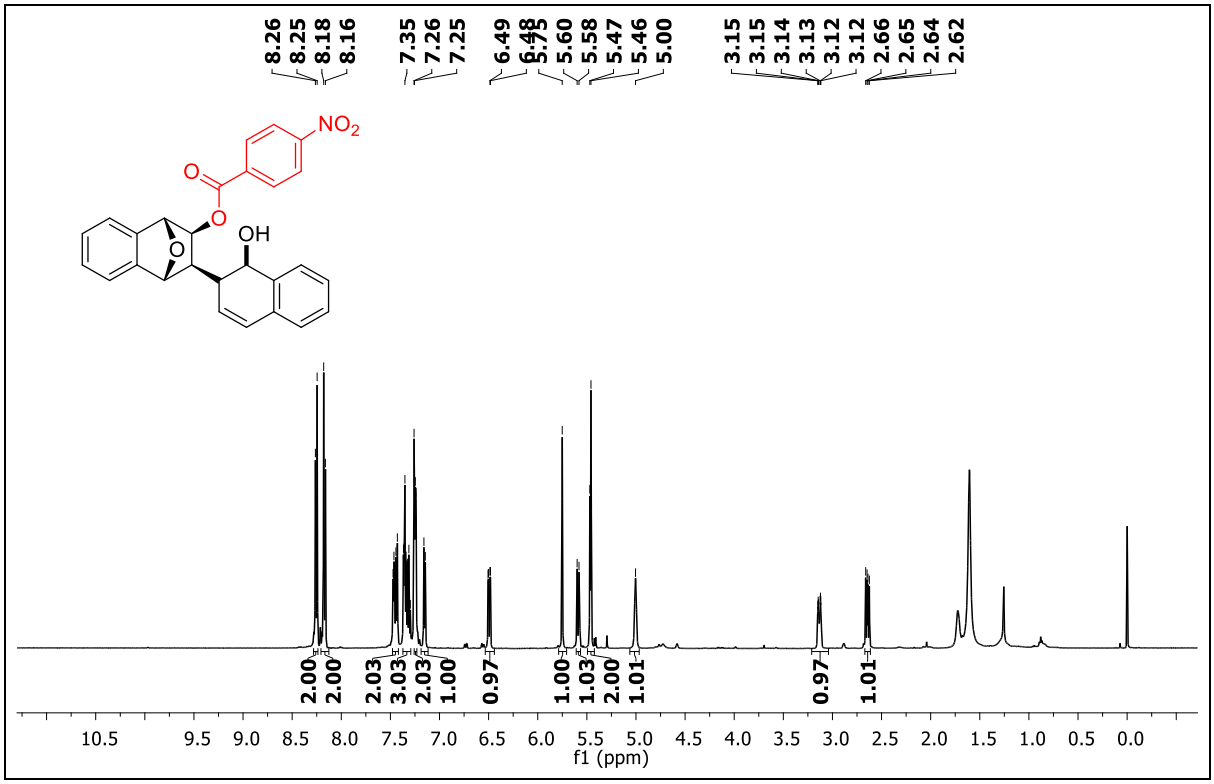


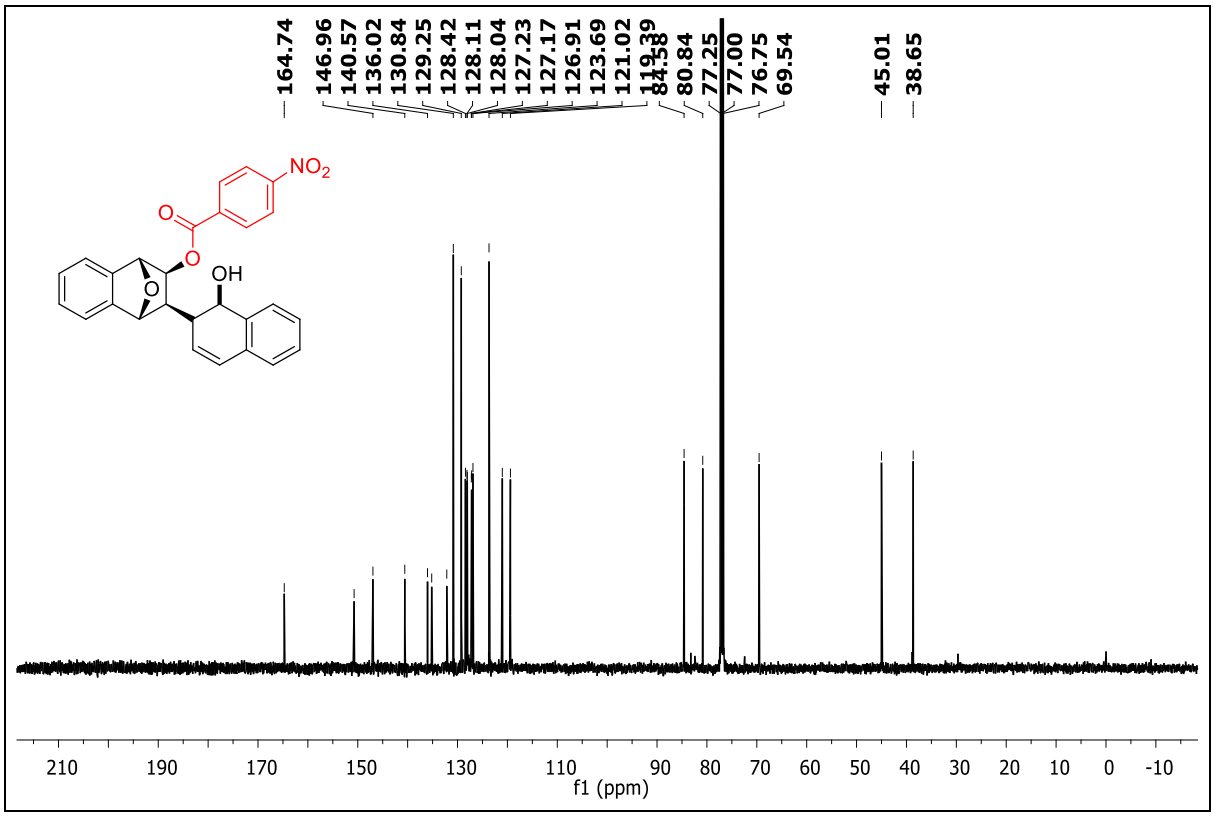
^{1}H and ^{13}C NMR Spectra of Compound **3ma** ($CDCl_3$, 400 MHz)



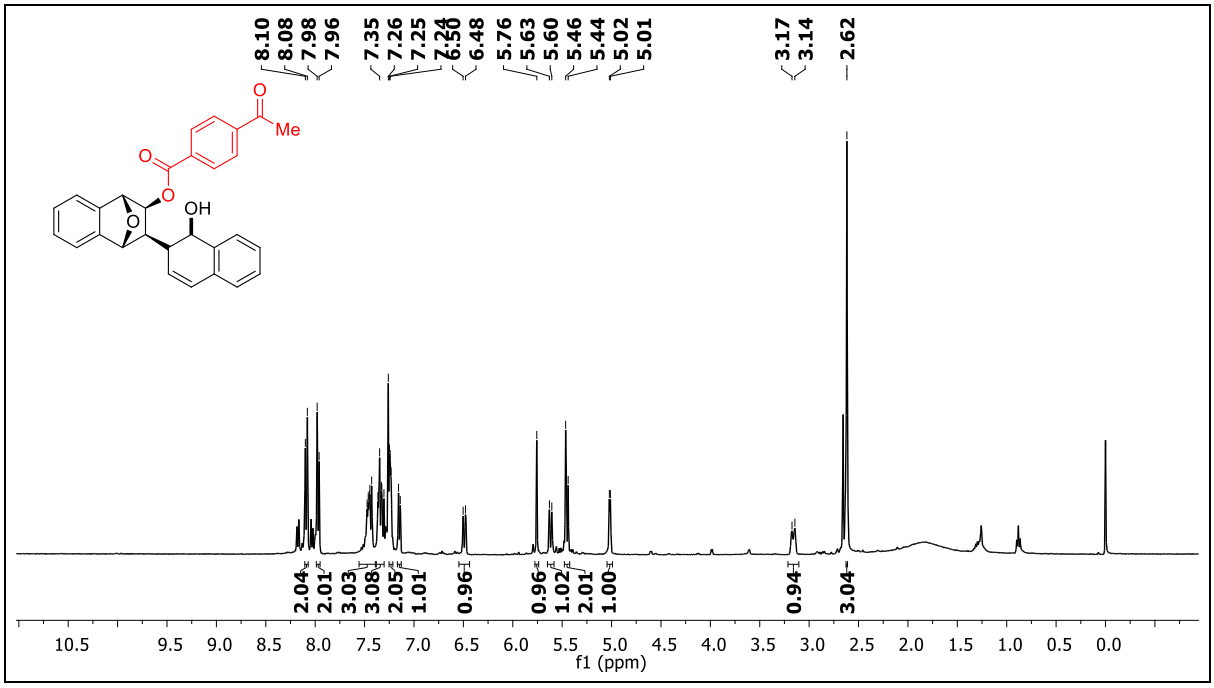


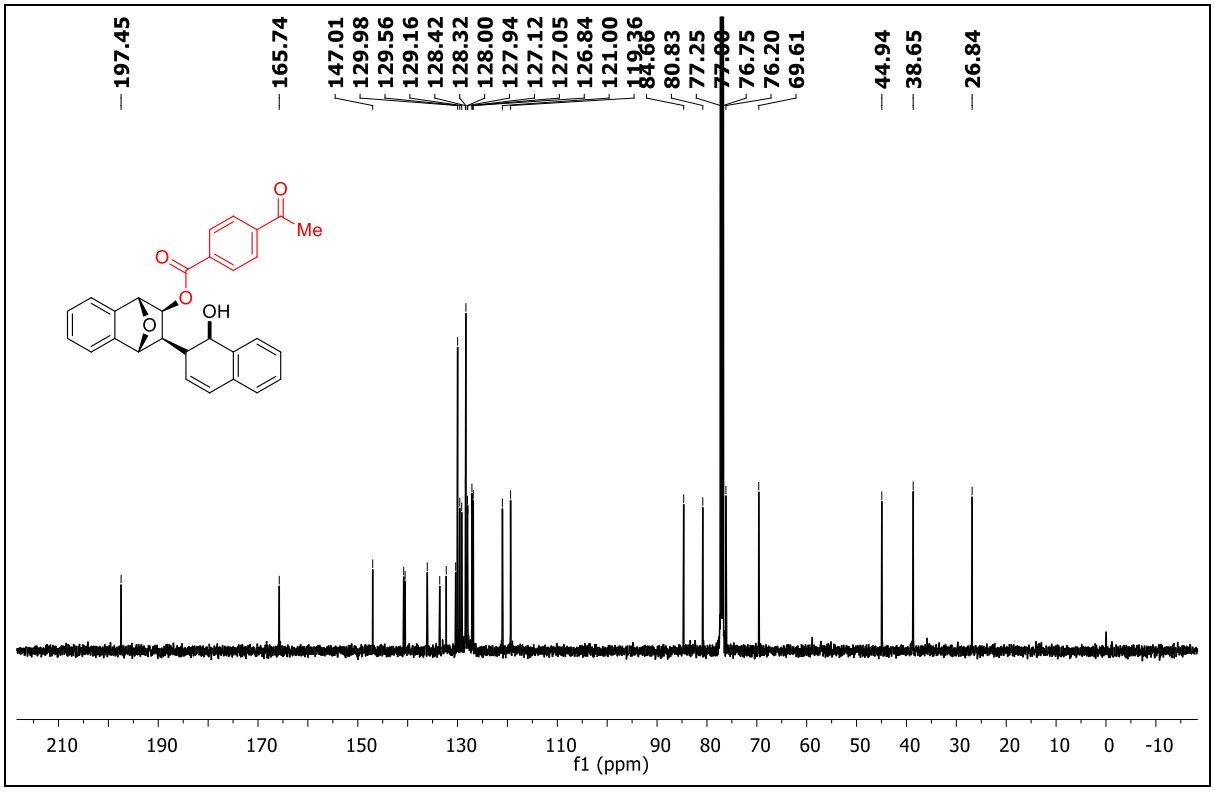
^{1}H and ^{13}C NMR Spectra of Compound **3na** ($CDCl_3$, 400 MHz)



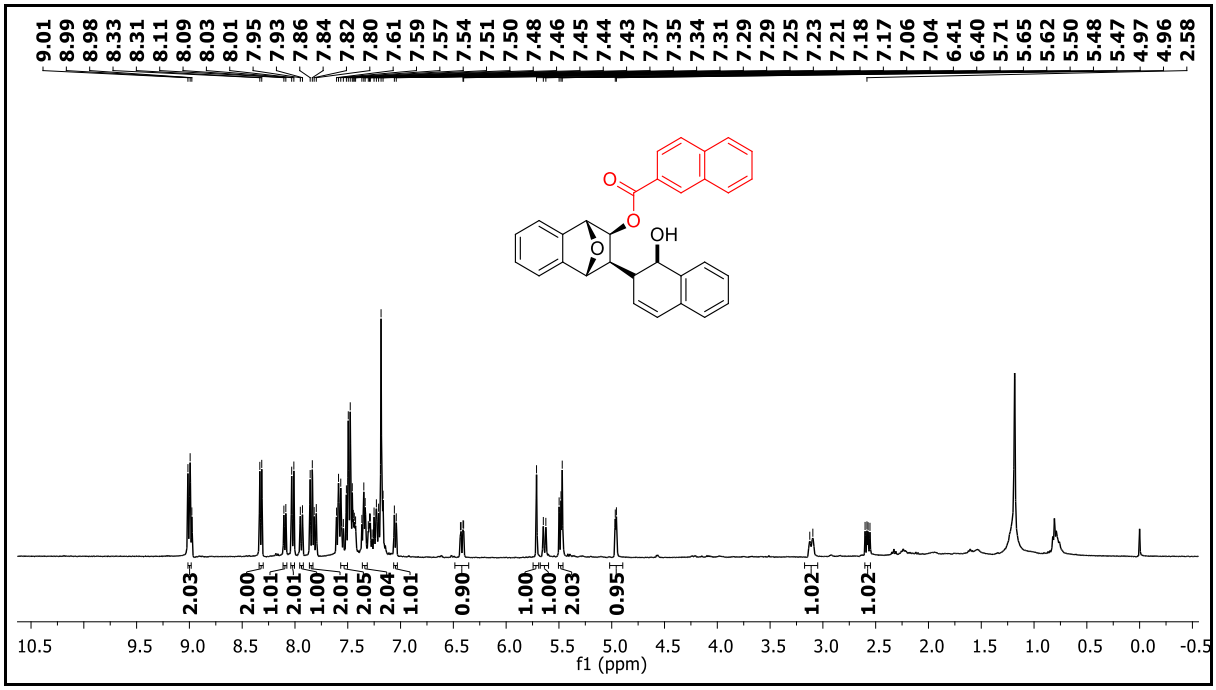


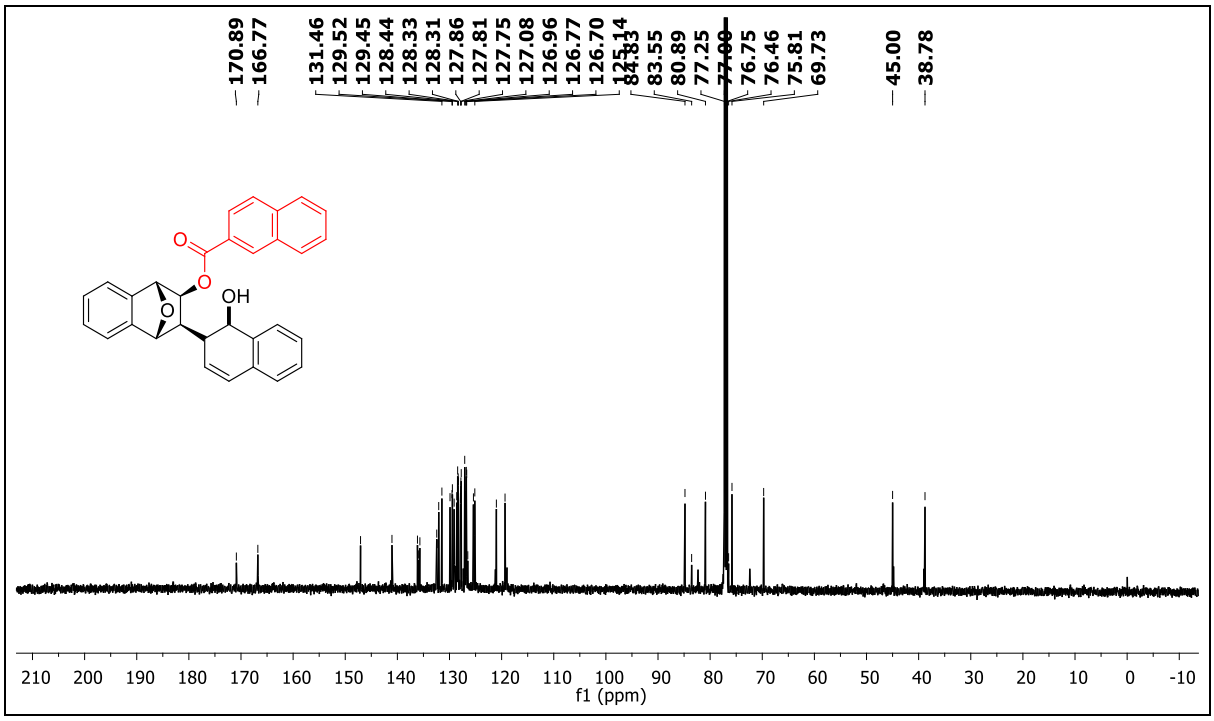
^{1}H and ^{13}C NMR Spectra of Compound **3oa** ($CDCl_3$, 400 MHz)



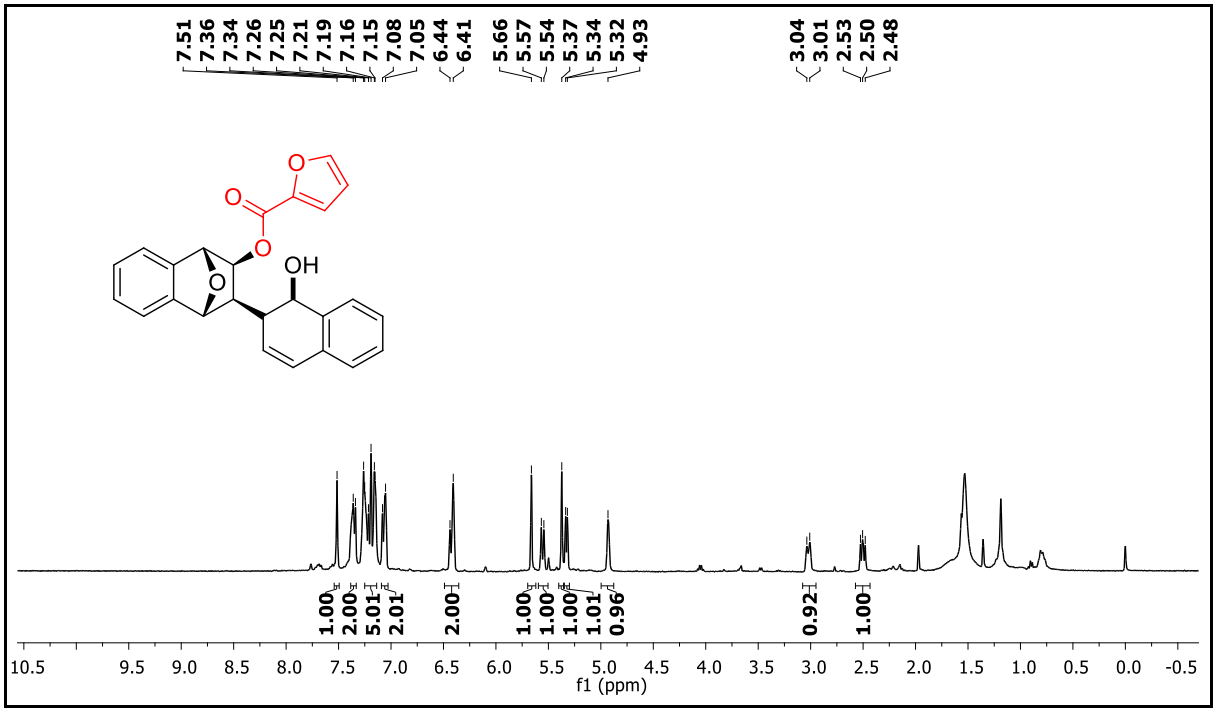


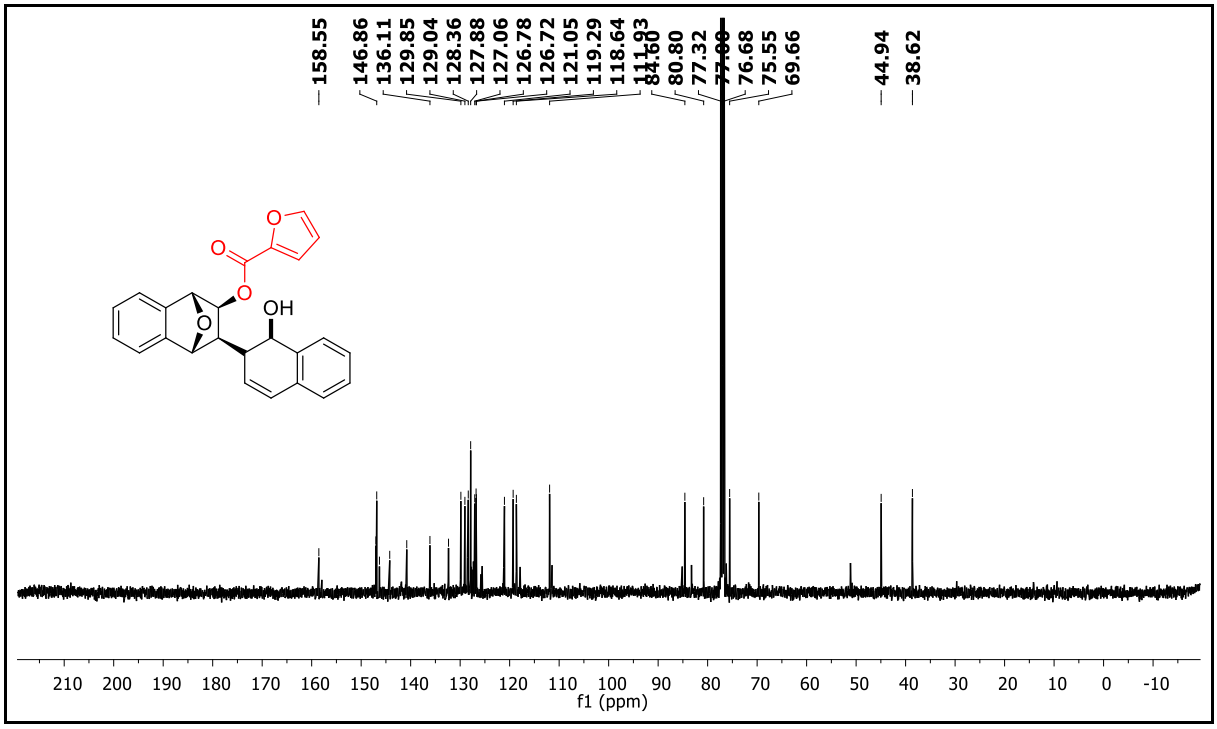
^{1}H and ^{13}C NMR Spectra of Compound **3pa** ($CDCl_3$, 400 MHz)



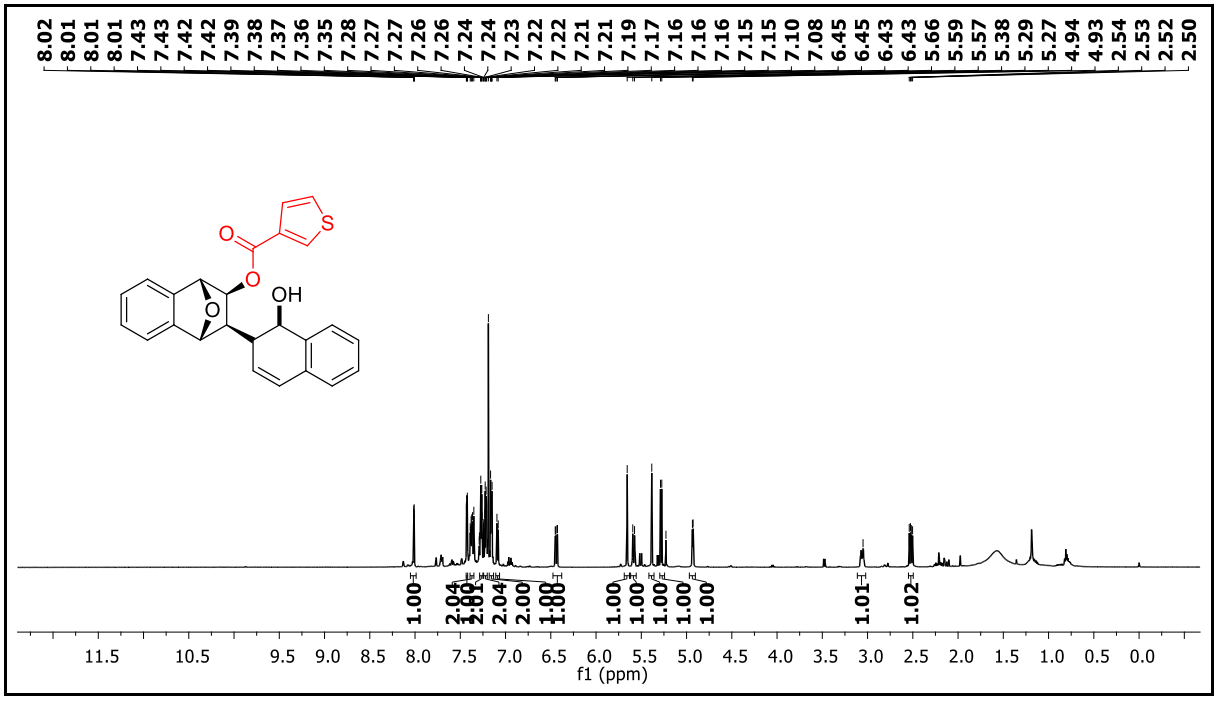


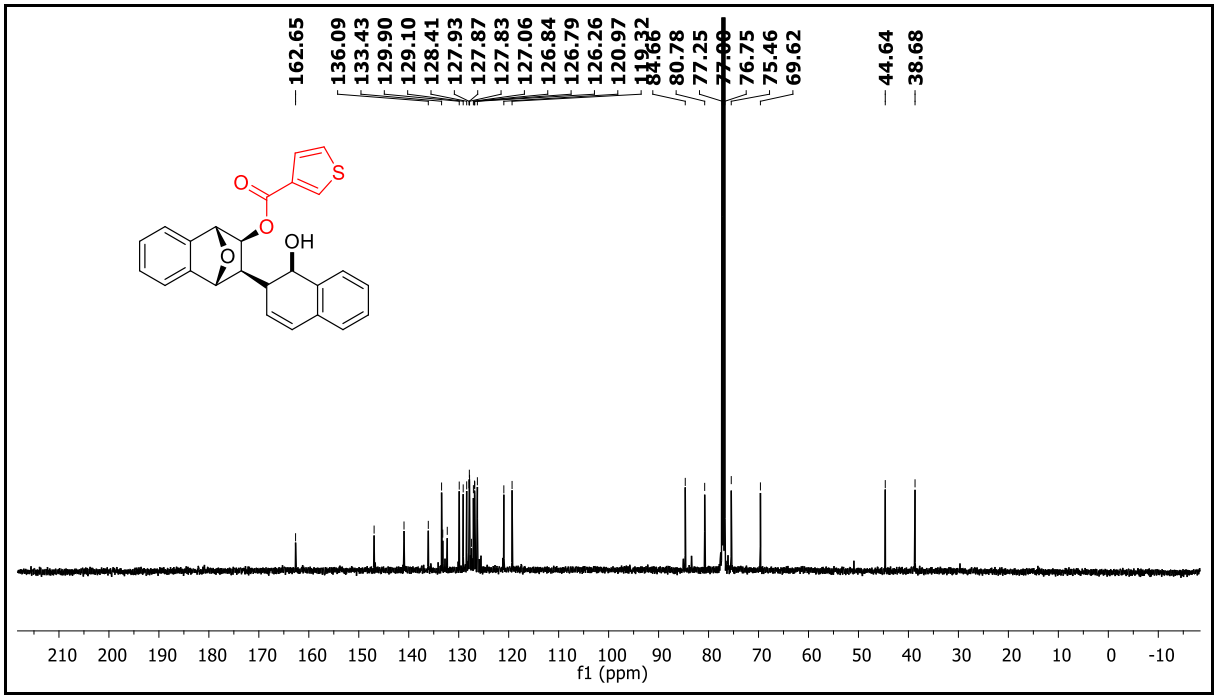
^{1}H and ^{13}C NMR Spectra of Compound **3qa** ($CDCl_3$, 400 MHz)



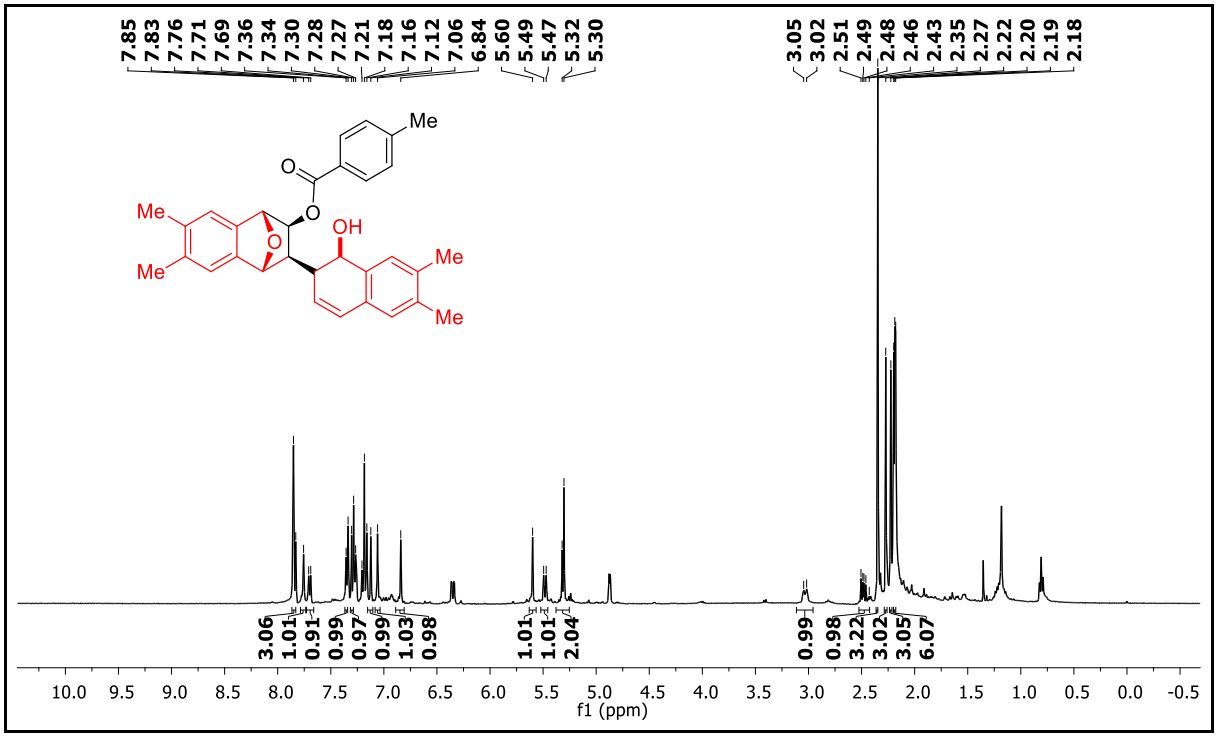


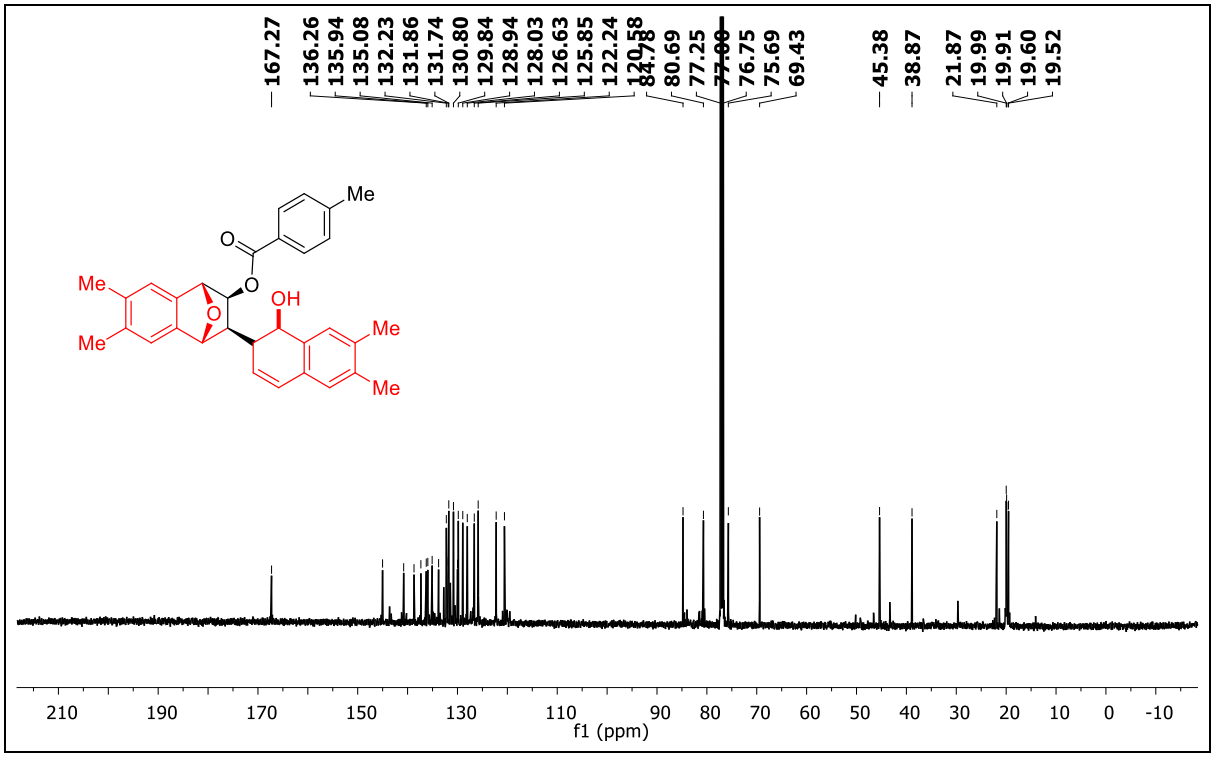
^{1}H and ^{13}C NMR Spectra of Compound **3ra** ($CDCl_3$, 400 MHz)



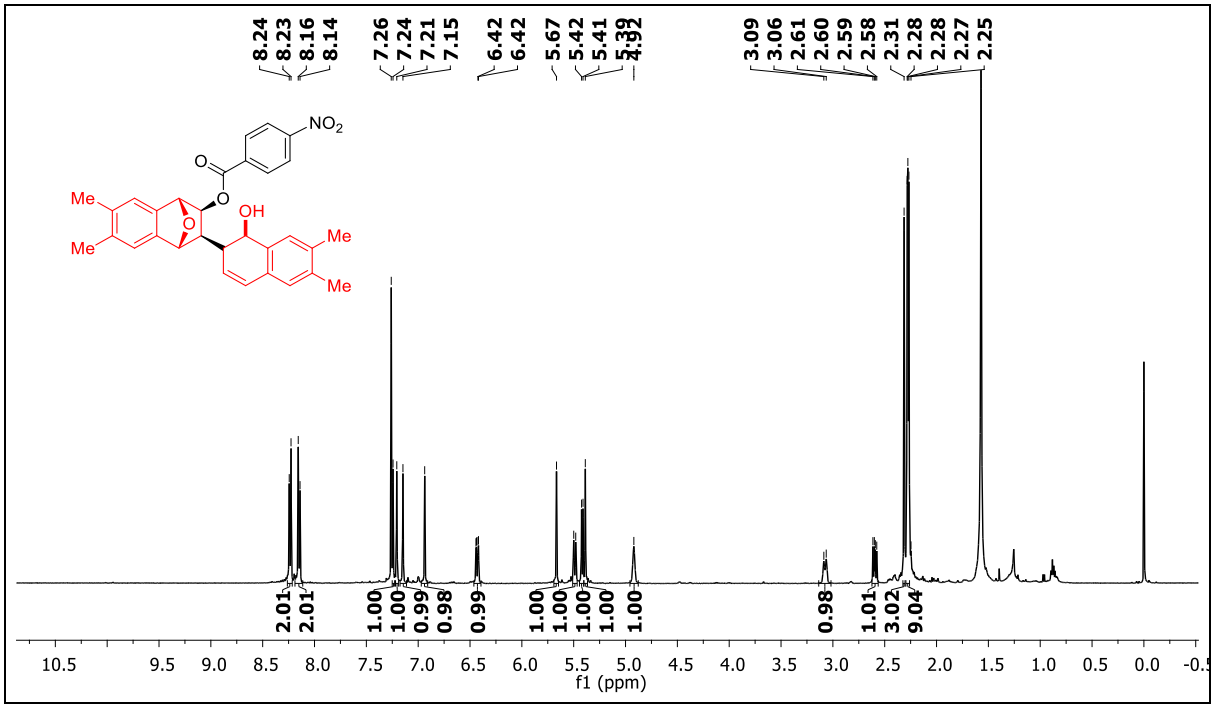


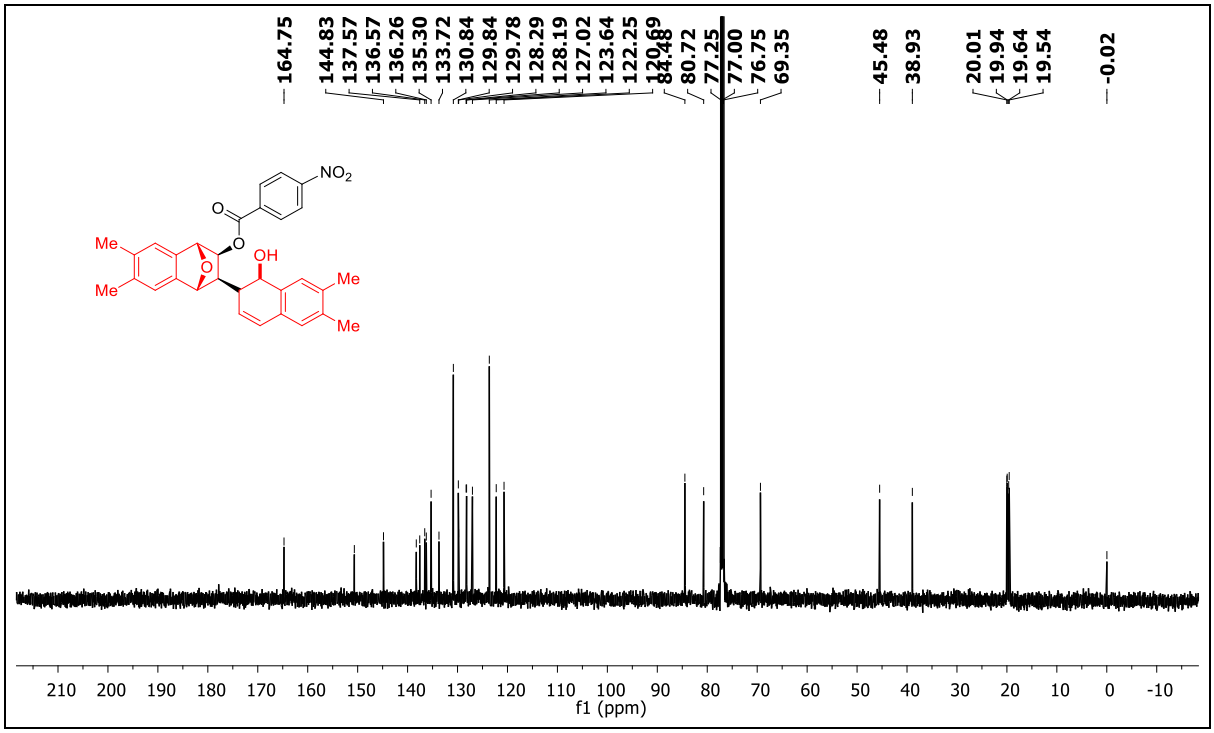
^{1}H and ^{13}C NMR Spectra of Compound **3lb** ($CDCl_3$, 400 MHz)



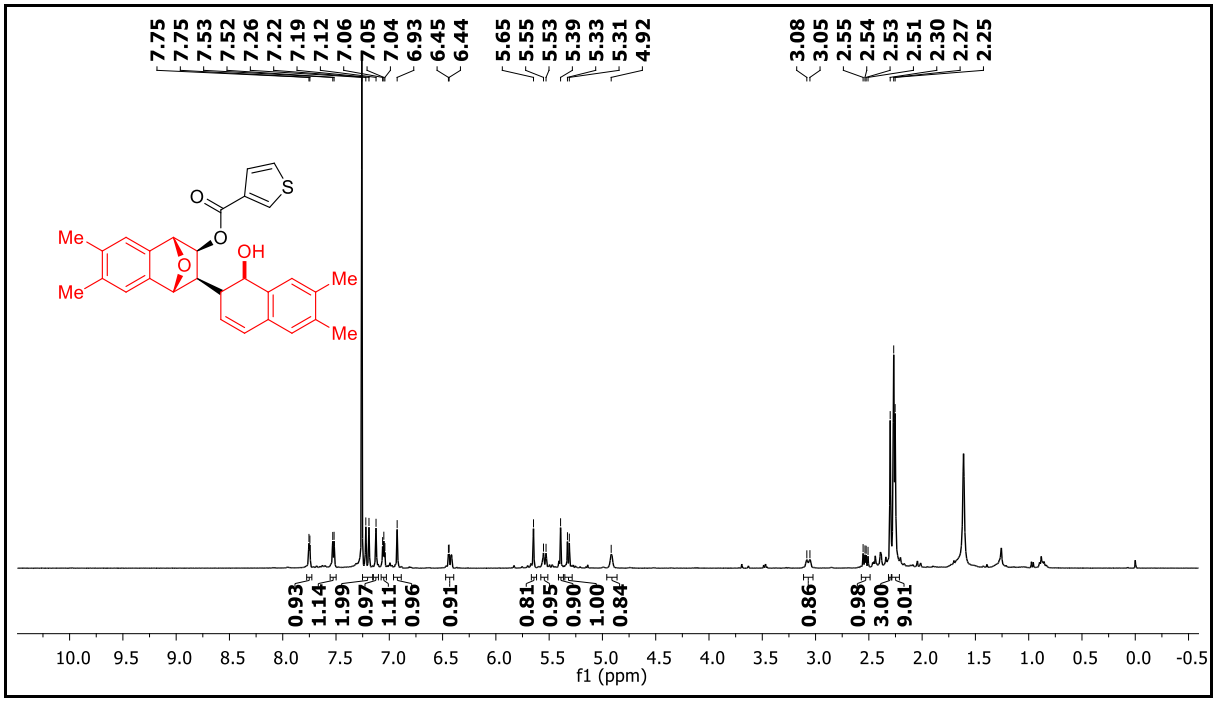


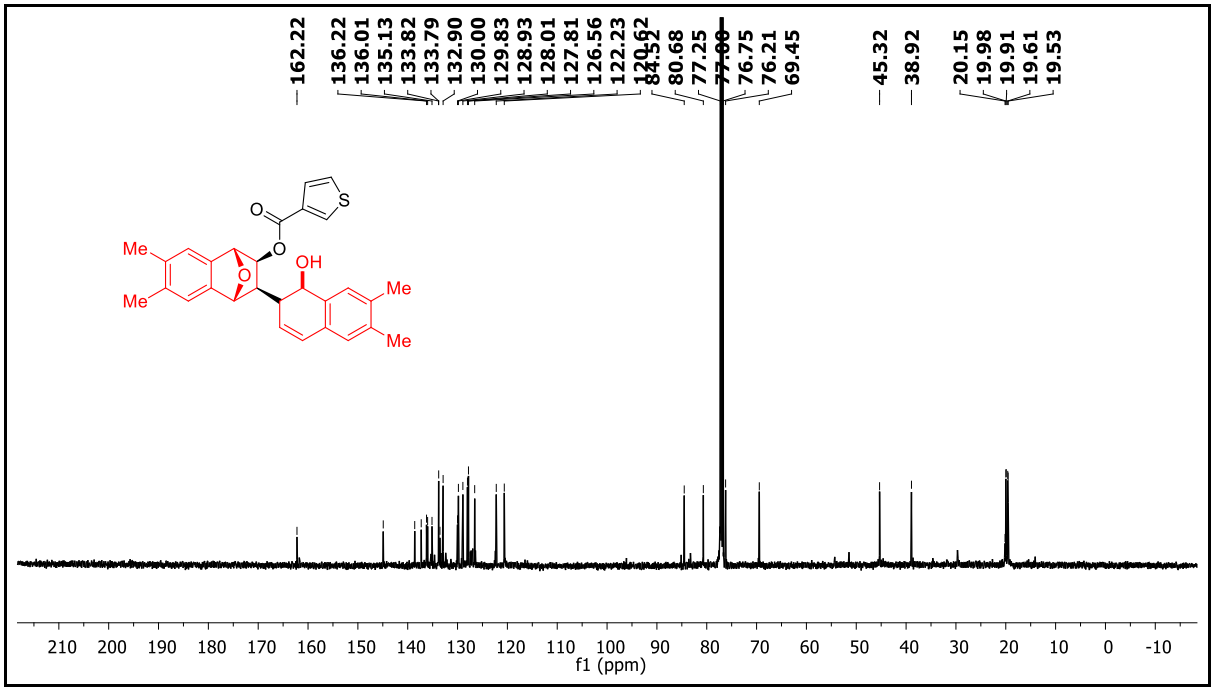
^{1}H and ^{13}C NMR Spectra of Compound **3nb** ($CDCl_3$, 400 MHz)



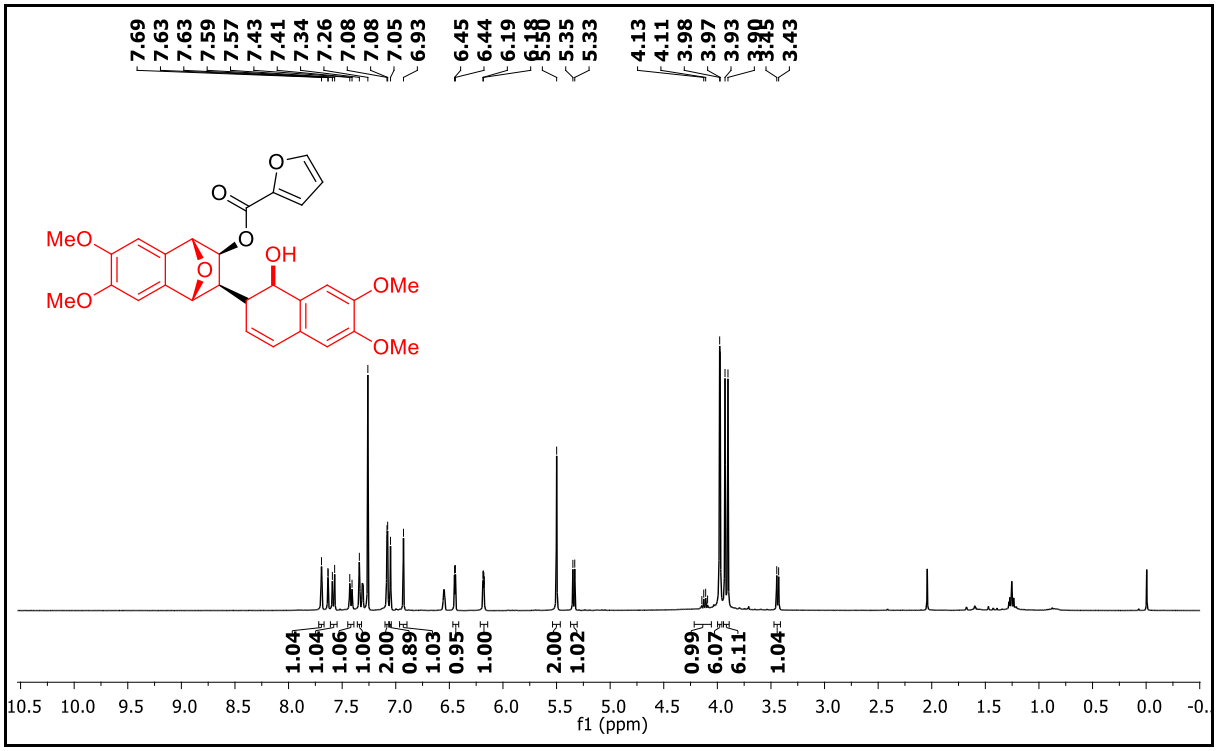


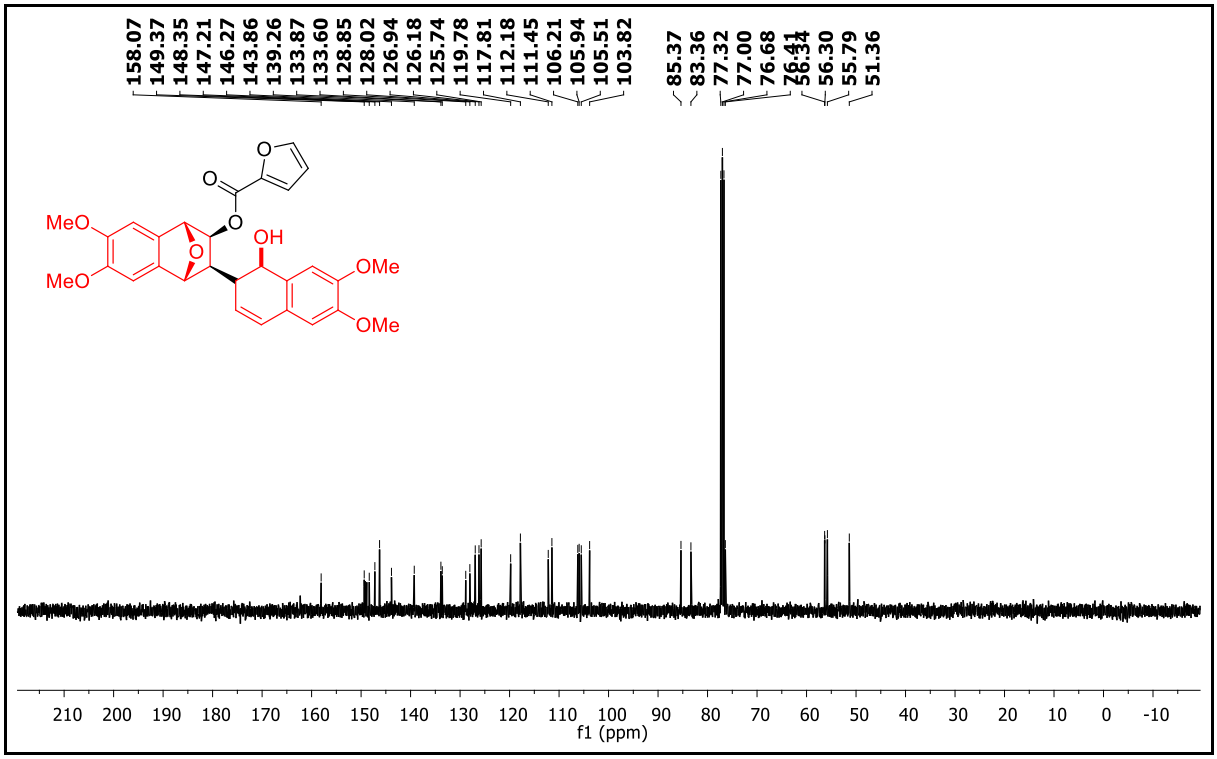
^{1}H and ^{13}C NMR Spectra of Compound **3rb** ($CDCl_3$, 400 MHz)



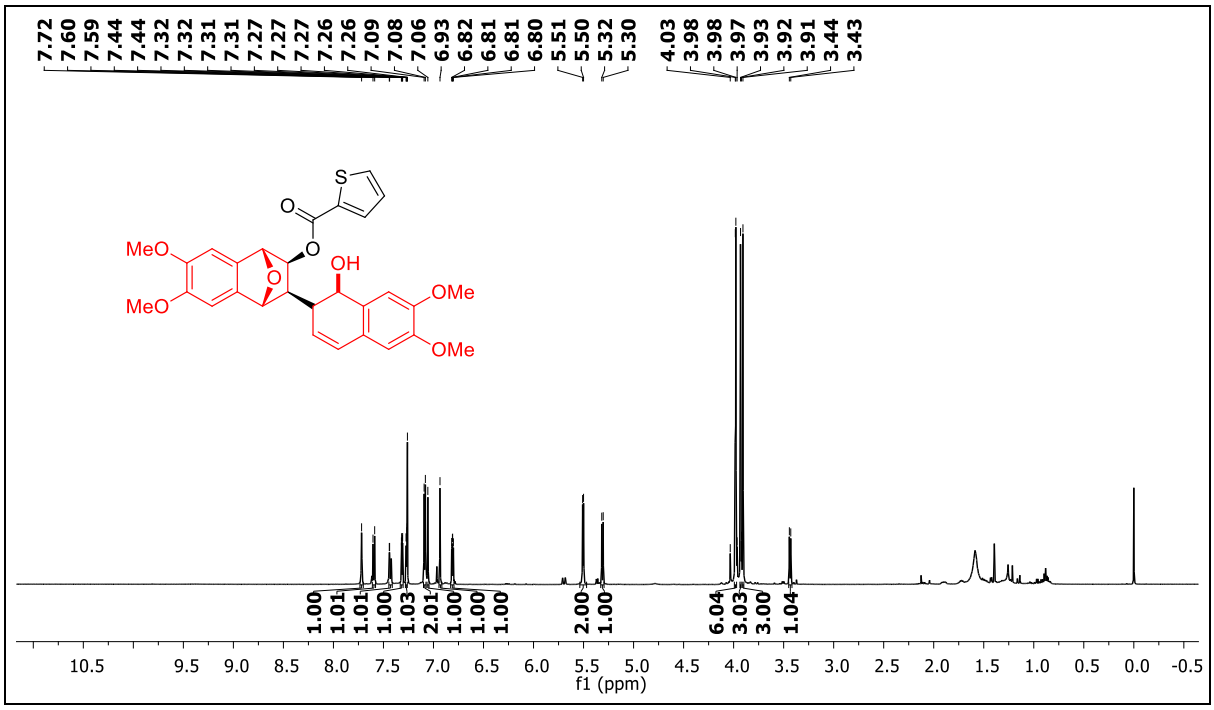


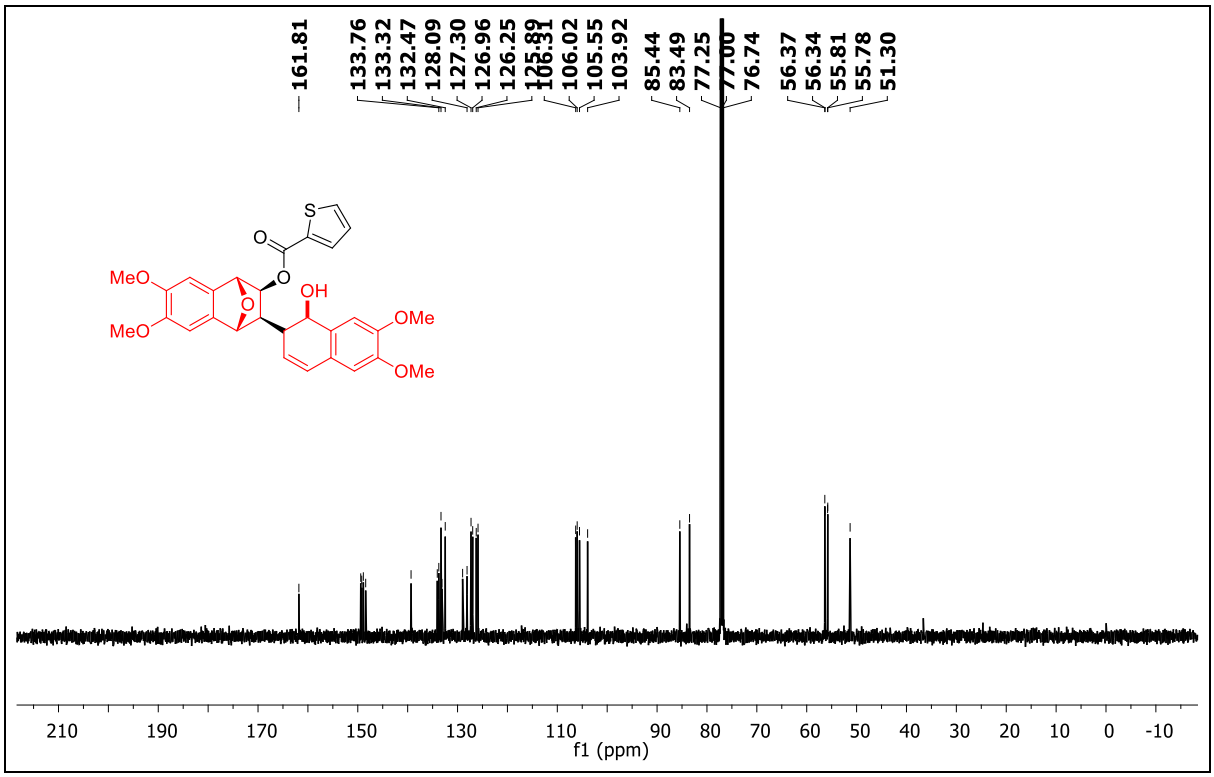
^{1}H and ^{13}C NMR Spectra of Compound **3qc** ($CDCl_3$, 400 MHz)



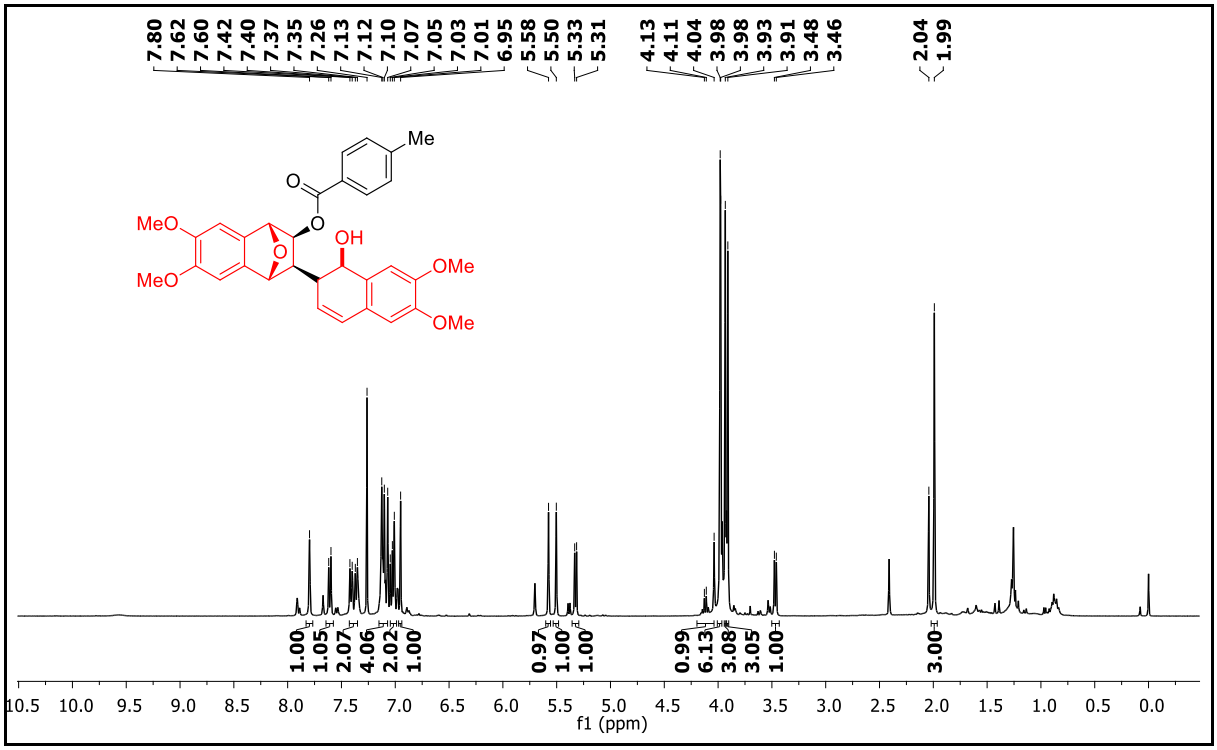


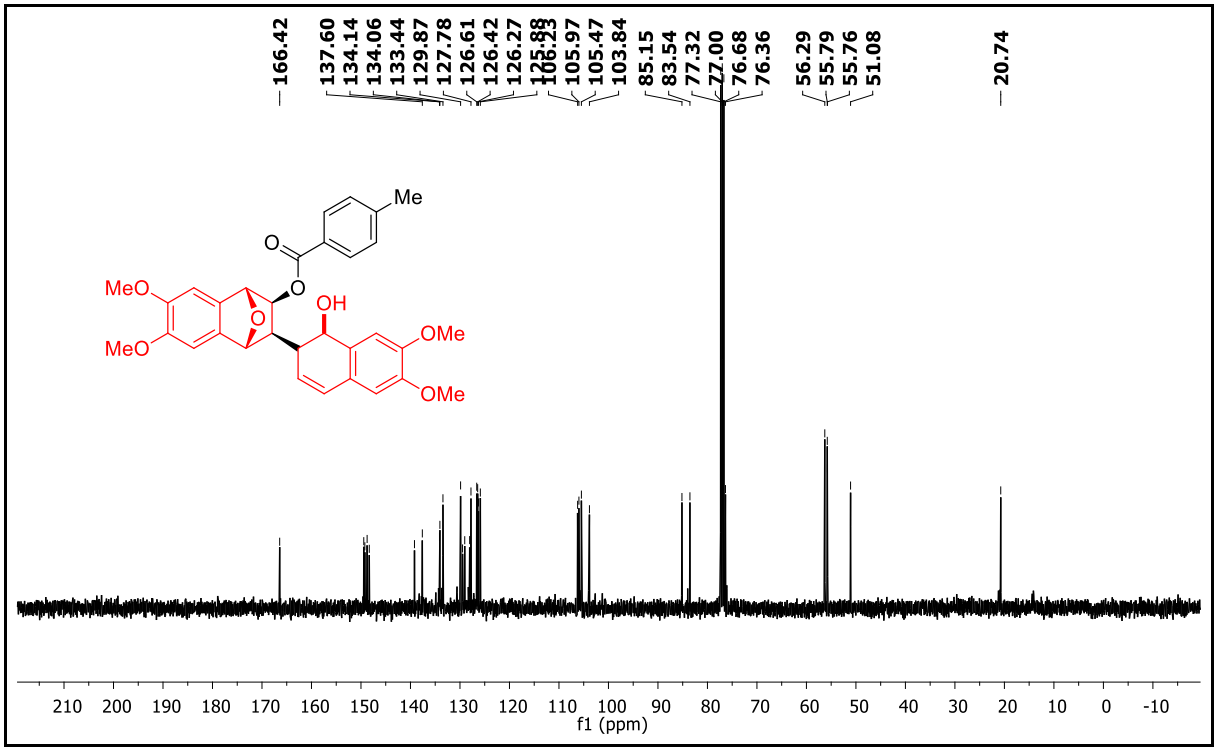
^{1}H and ^{13}C NMR Spectra of Compound **3rc** ($CDCl_3$, 400 MHz)



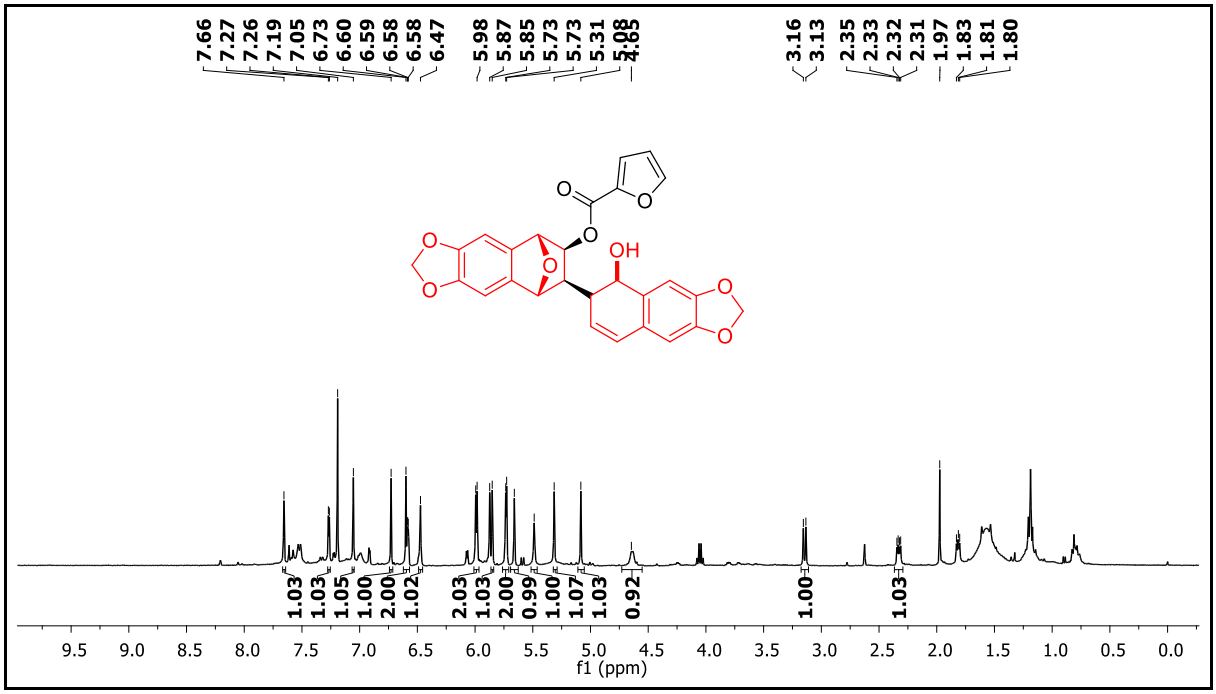


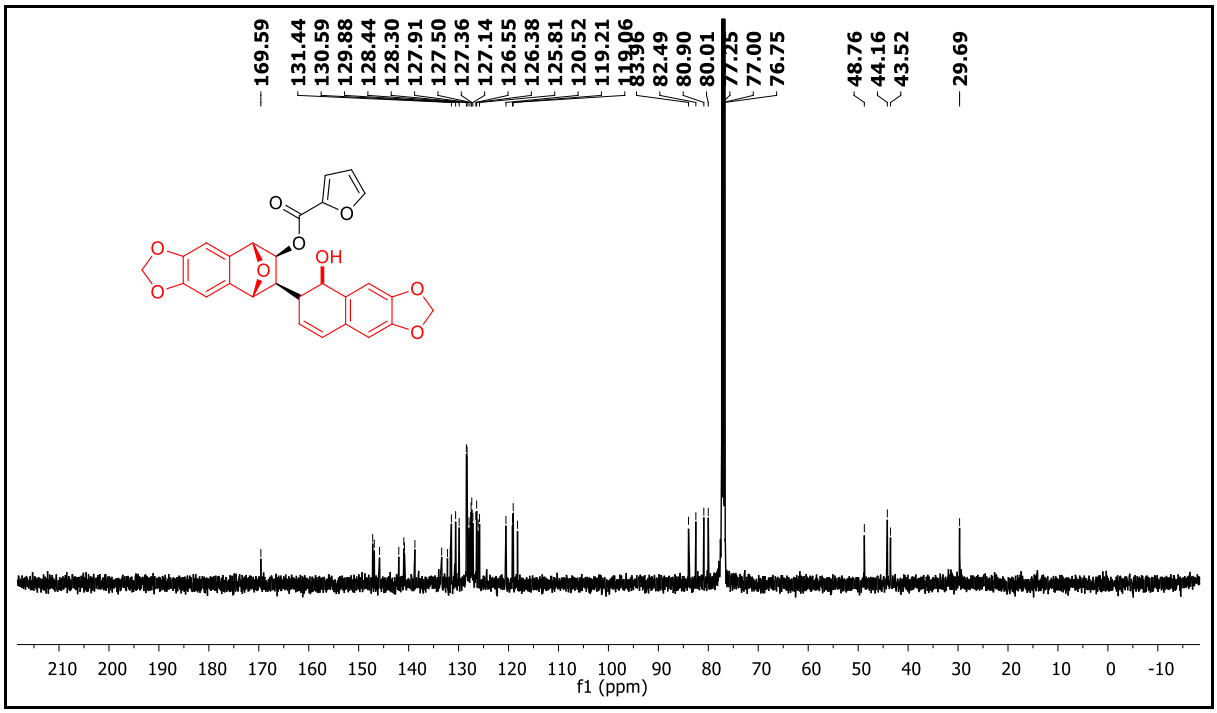
^{1}H and ^{13}C NMR Spectra of Compound **3lc** ($CDCl_3$, 400 MHz)



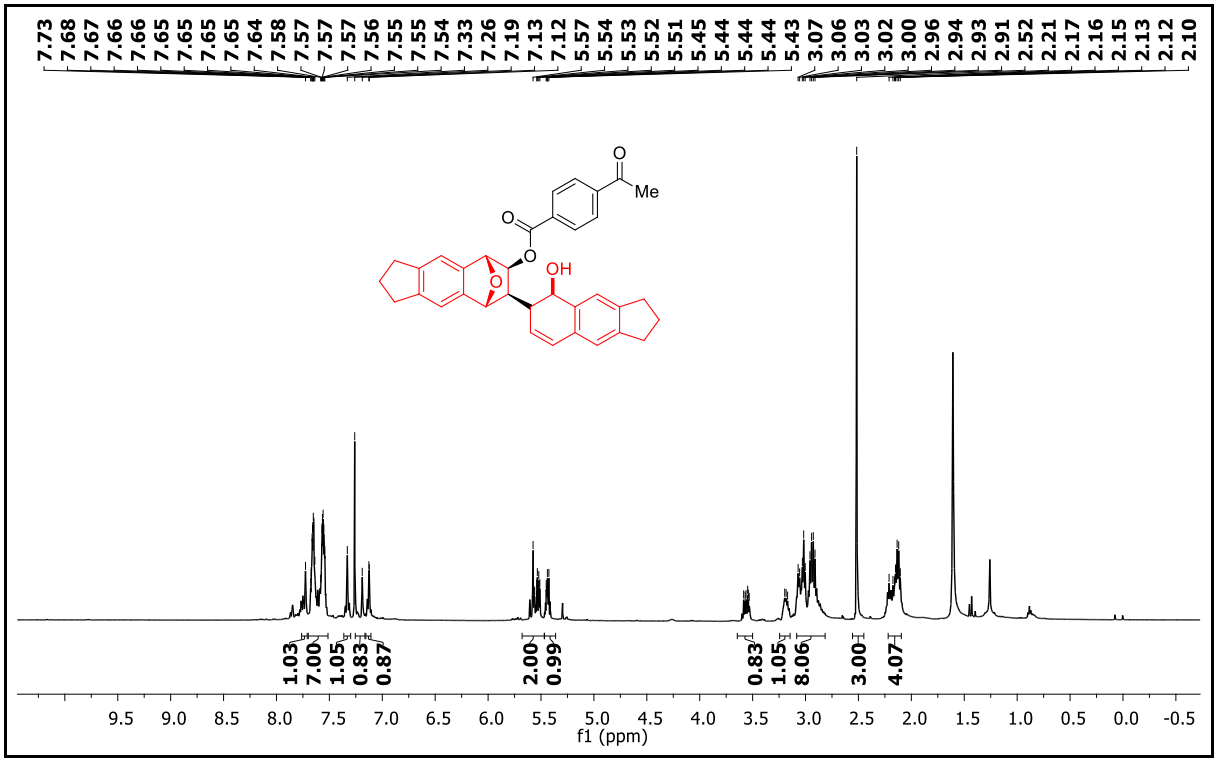


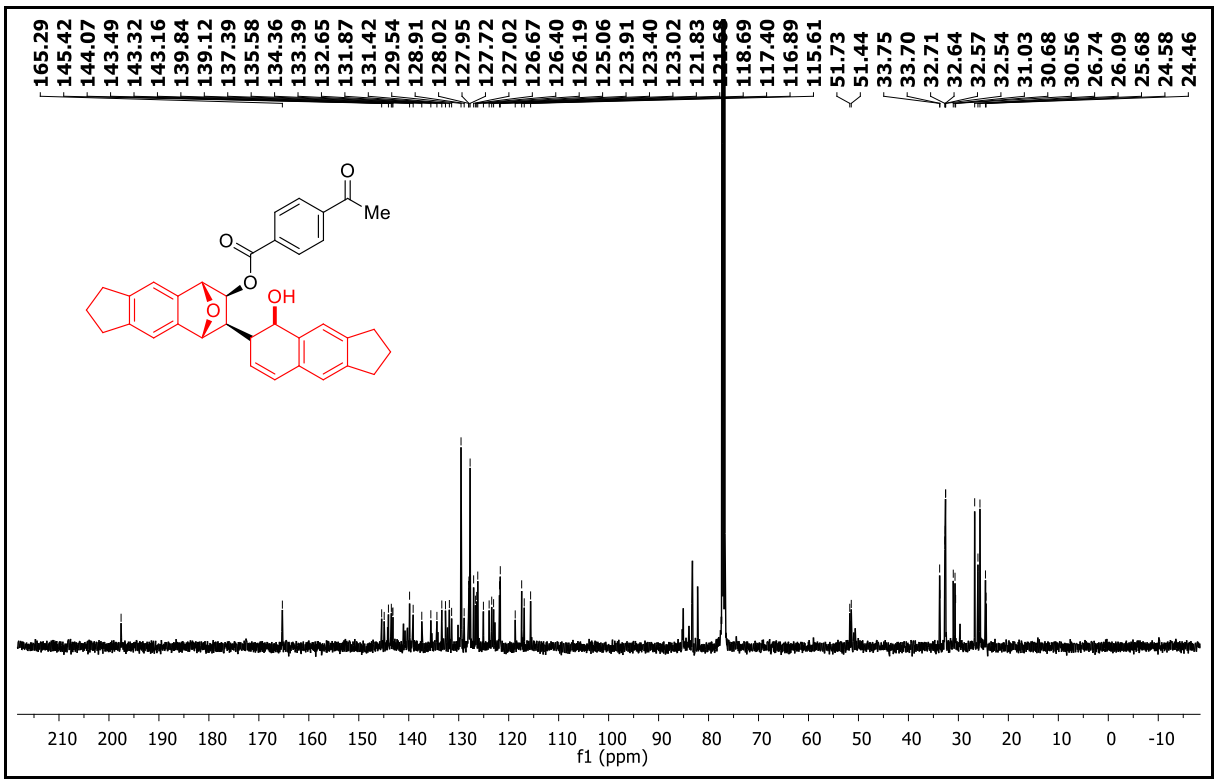
^{1}H and ^{13}C NMR Spectra of Compound **3qd** ($CDCl_3$, 400 MHz)



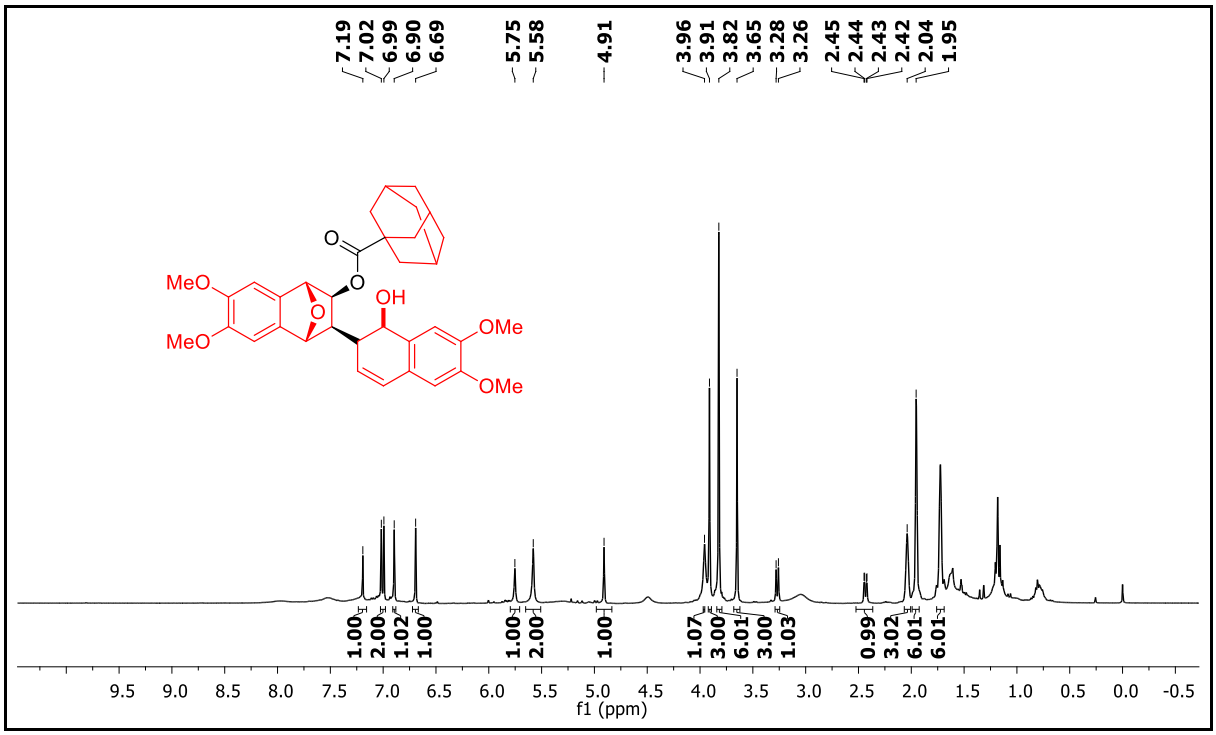


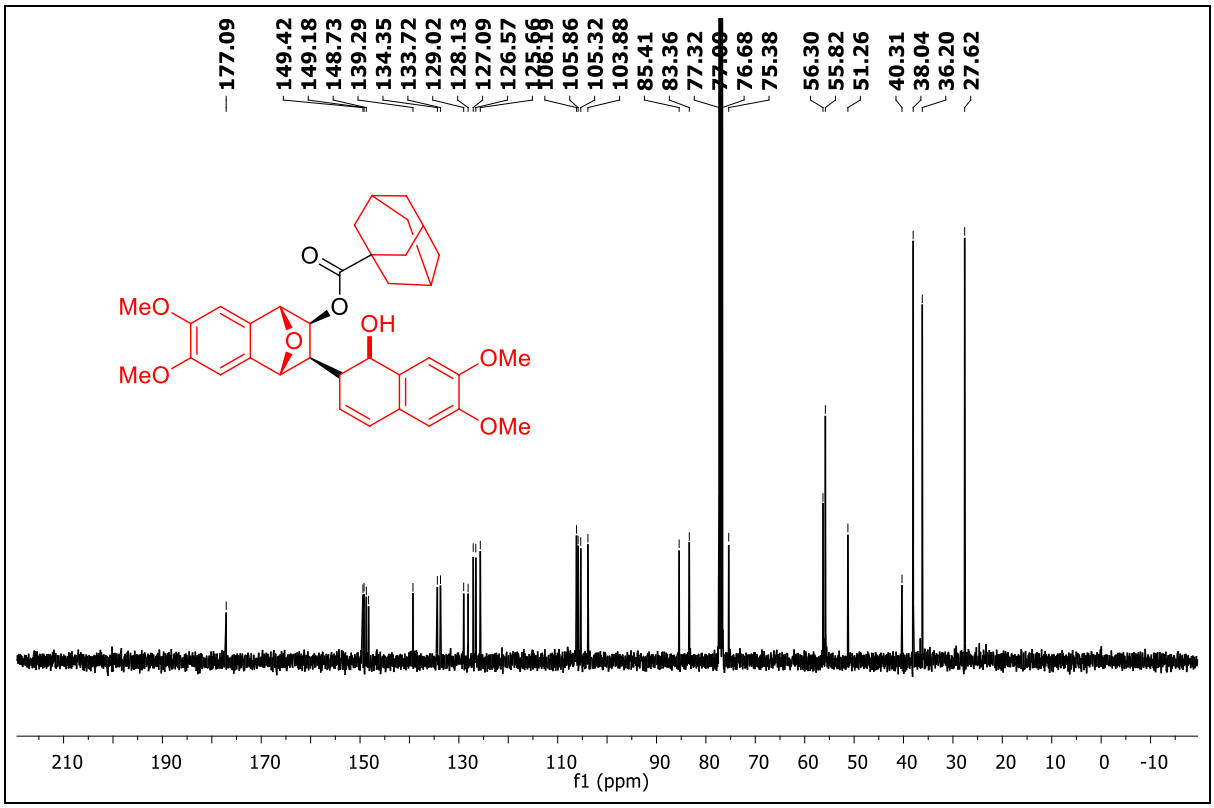
^{1}H and ^{13}C NMR Spectra of Compound **3oe** ($CDCl_3$, 400 MHz)



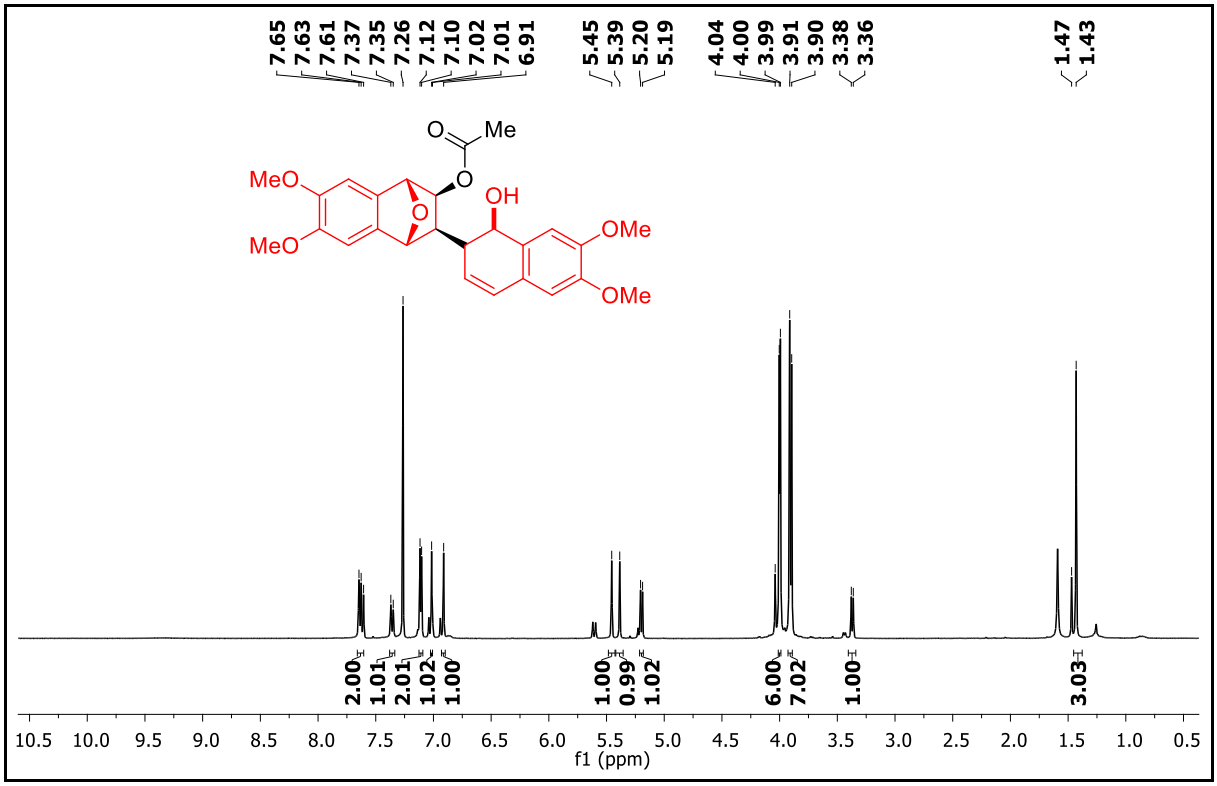


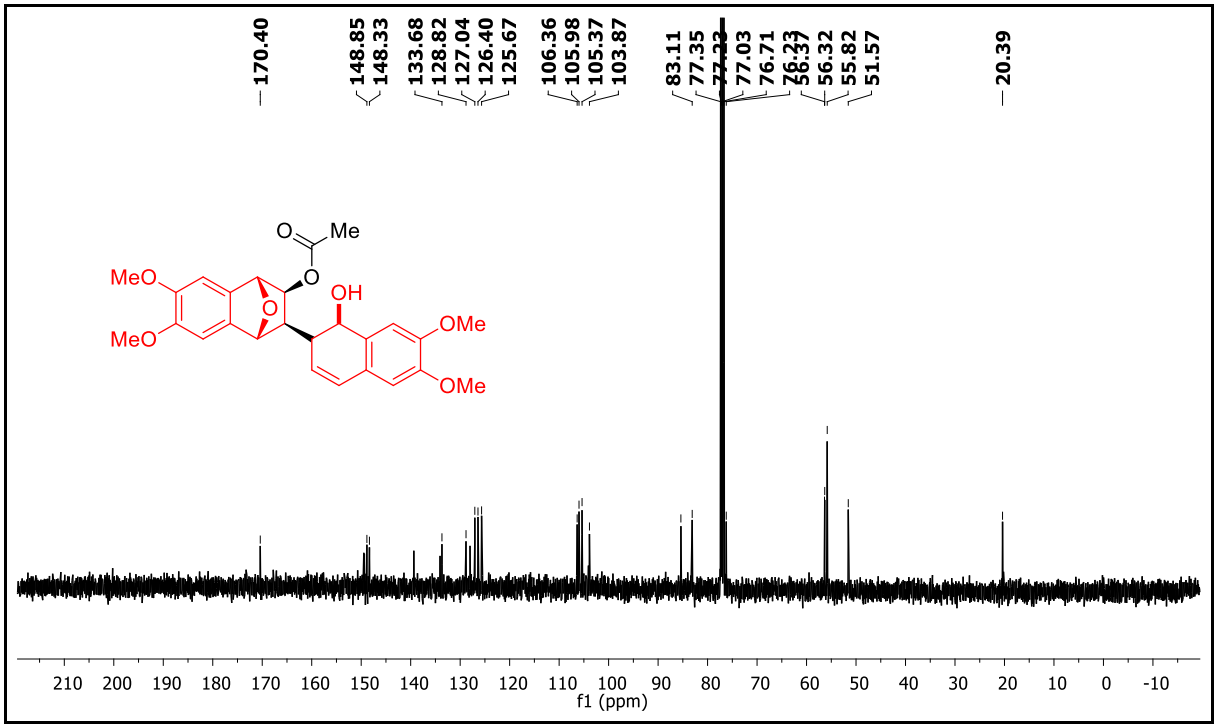
^{1}H and ^{13}C NMR Spectra of Compound **3ac** ($CDCl_3$, 400 MHz)



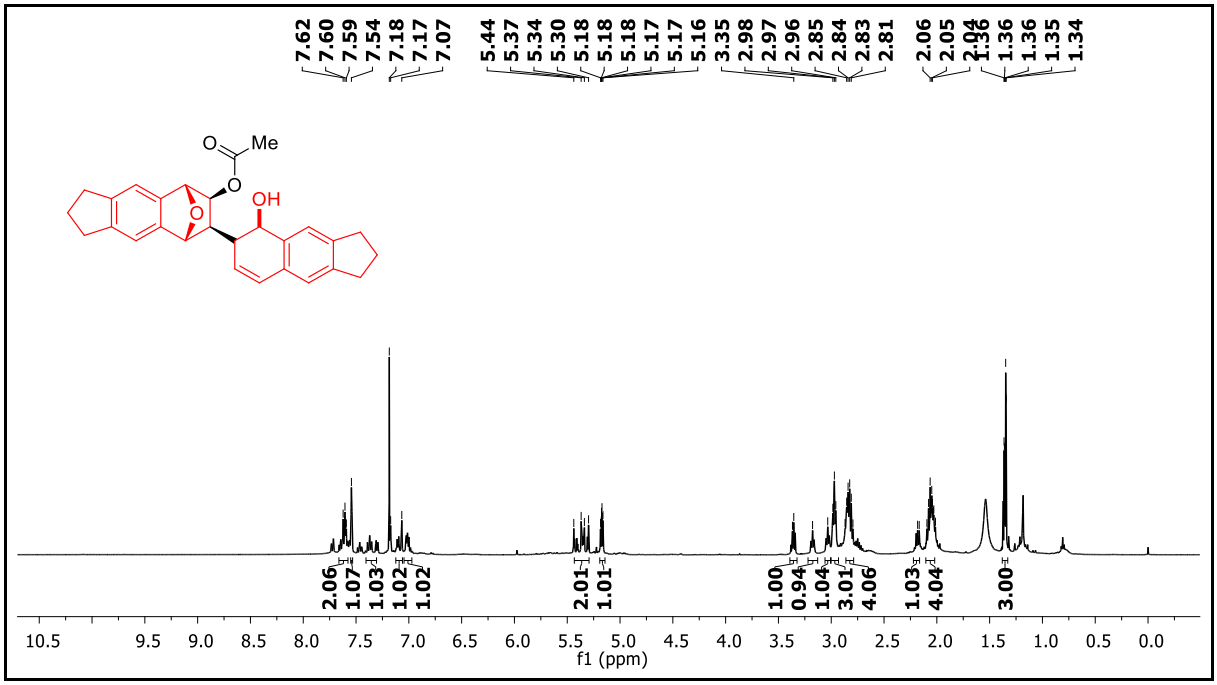


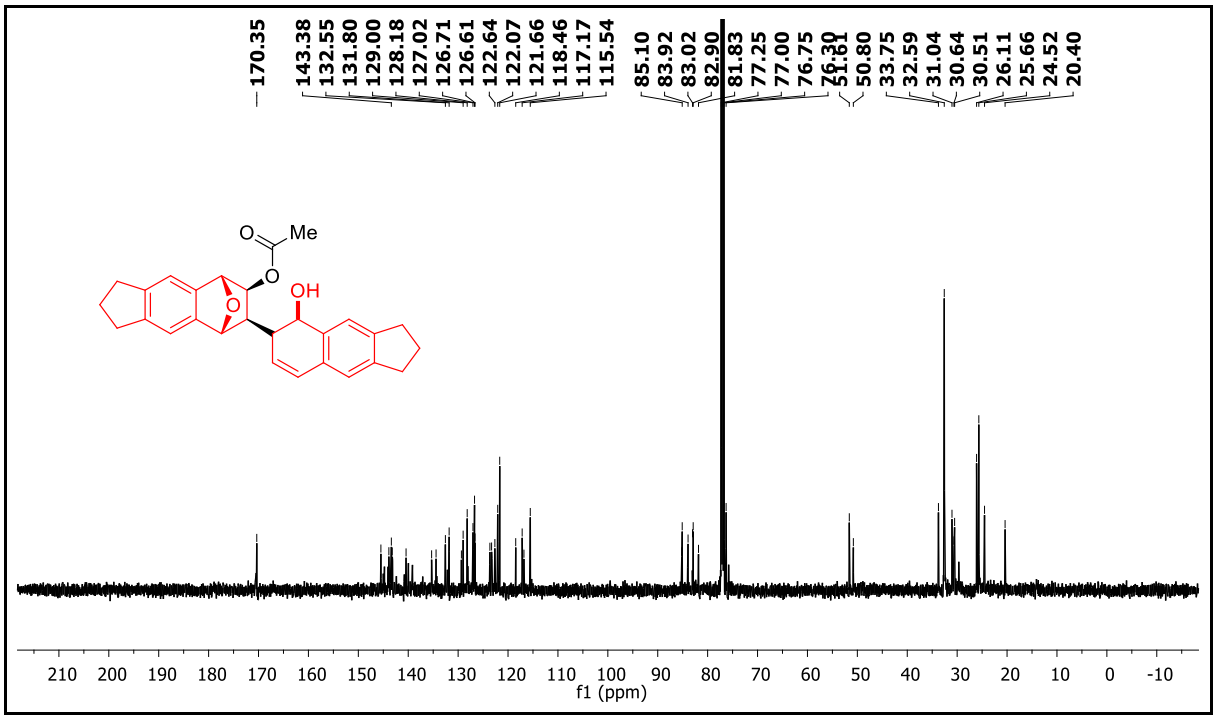
^{1}H and ^{13}C NMR Spectra of Compound **3cc** ($CDCl_3$, 400 MHz)



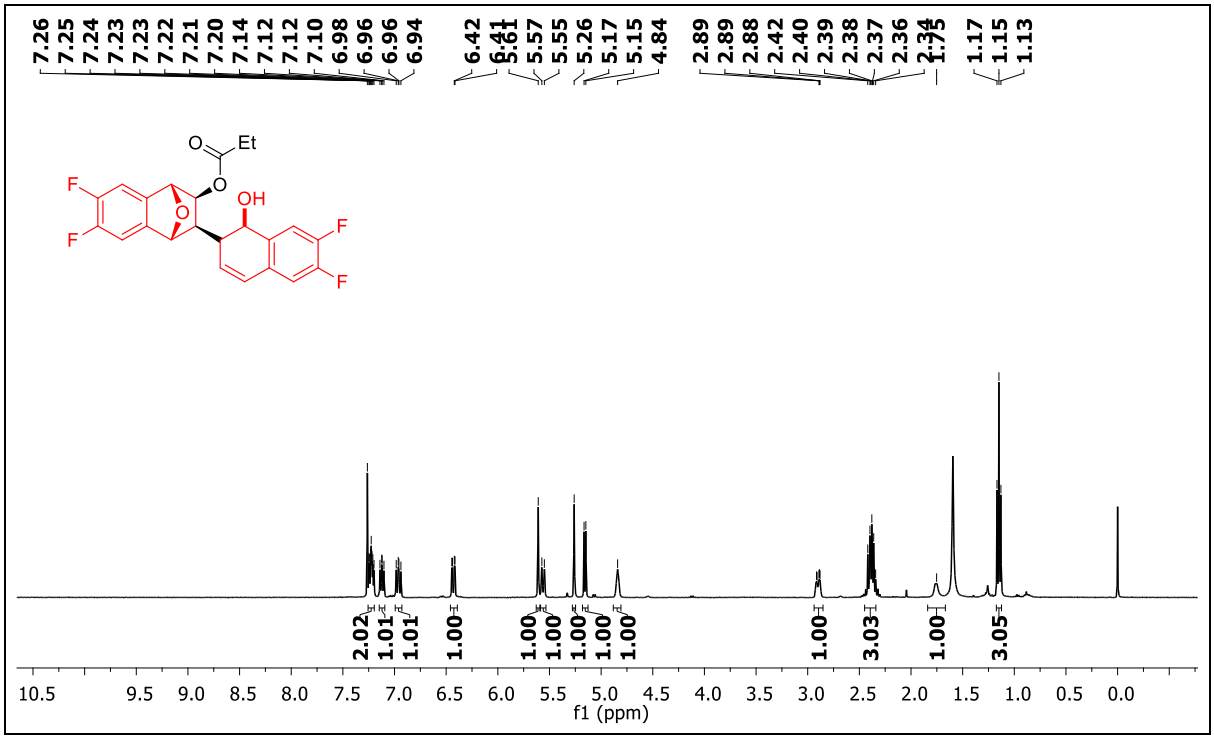


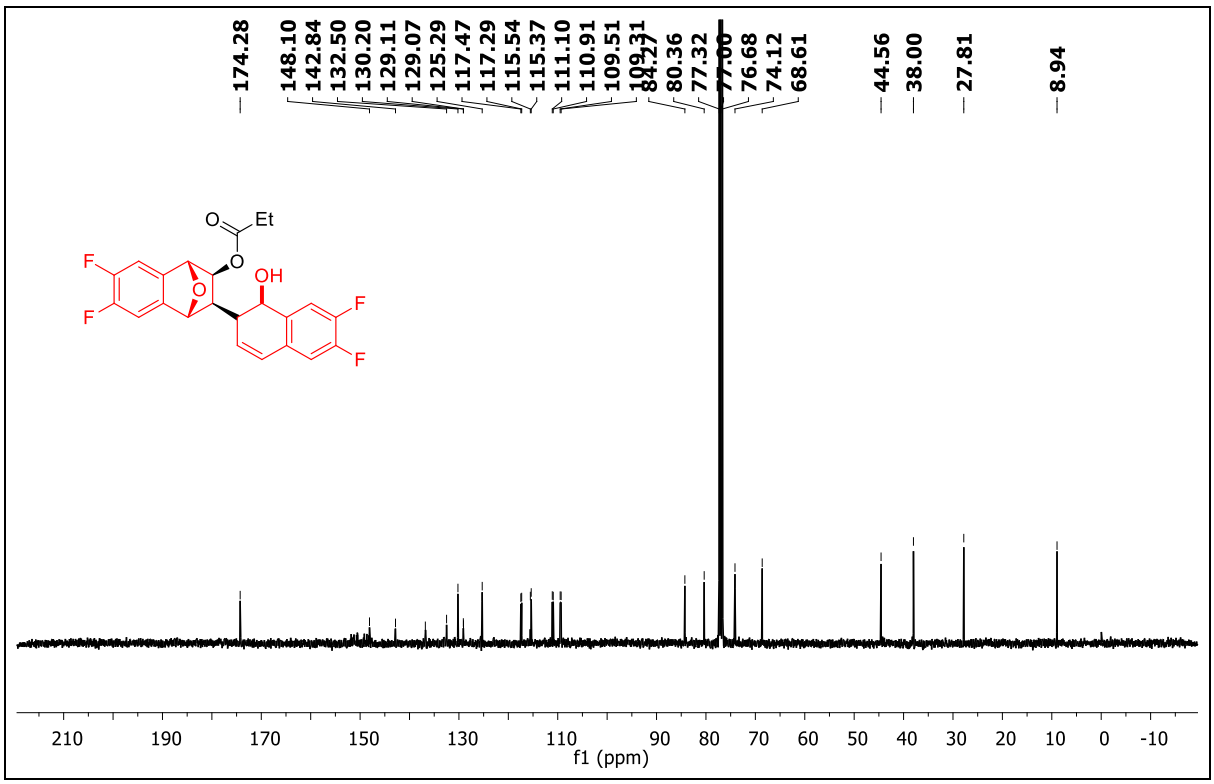
^{1}H and ^{13}C NMR Spectra of Compound **3ce** ($CDCl_3$, 400 MHz)





^{1}H and ^{13}C NMR Spectra of Compound **3df** ($CDCl_3$, 400 MHz)





^{19}F NMR Spectra of Compound **3df** ($CDCl_3$, 471 MHz)