Nitrogen atom insertion into arenols to access benazepines

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1. General information

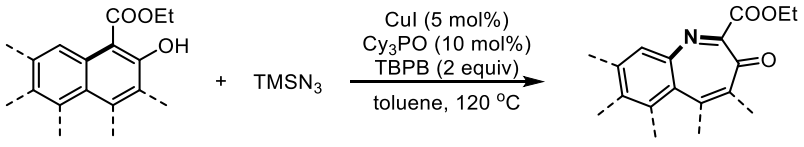
Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. All reactions were carried out under an atmosphere of nitrogen using standard schlenk techniques unless otherwise noted. Glass wares were heat-dried and cooled down under vacuum prior to use. Column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. Flash column chromatography was carried out using silica gel (200–300 mesh) at increased pressure. ^{1}H NMR, ^{13}C NMR spectra were recorded on a WNMR-I spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as the solvent at room temperature. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) or TMS (^{1}H) as an internal standard. HRMS were performed on Bruker Daltonics MicroTof-Q II mass spectrometer. Cyclic Voltammetry studies were performed using a Shanghai Chenhua CHI760E workstation.

Caution!

The azide and peroxide compounds involved in the experiments are potentially dangerous, and all compounds must be synthesized on a small scale. The operation must be carried out in the cover behind the blast shield. Always wear protective goggles and leather gloves.

2. Experimental procedures

2.1 General procedure of copper-catalyzed nitrogen atom insertion into arenols

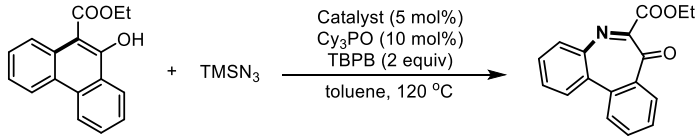


In a sealed 10 mL vial equipped with a magnetic stir bar was charged with the arenols (0.1 mmol), CuI (1.0 mg, 0.005 mmol, 5 mol%), Cy_3PO (3.0 mg, 0.01 mmol, 10

mol%), TBPB (38.0 μL, 0.2 mmol, 2.0 equiv), and $TMSN_3$ (39.0 μL, 0.3 mmol, 3.0 equiv) in toluene (1.0 mL) was premixed and added before the vial was briefly flushed with nitrogen. Subsequently the vial was capped and closed tightly. Then the reaction was stirred at 120 ℃ for 12 h. After the reaction was completed, the organic phase was washed with saturated sodium bicarbonate solution for three times, dried over $MgSO_4$, concentrated, and purified by flash chromatography to afford desired products.

2.2 Optimization of reaction conditions

Table S1. Screening for catalysts[a]

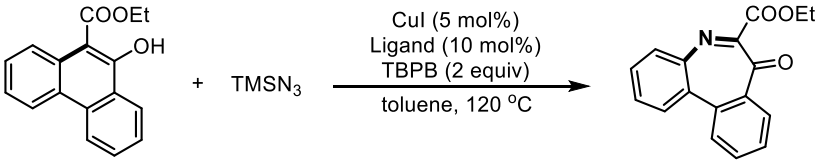


1a 1

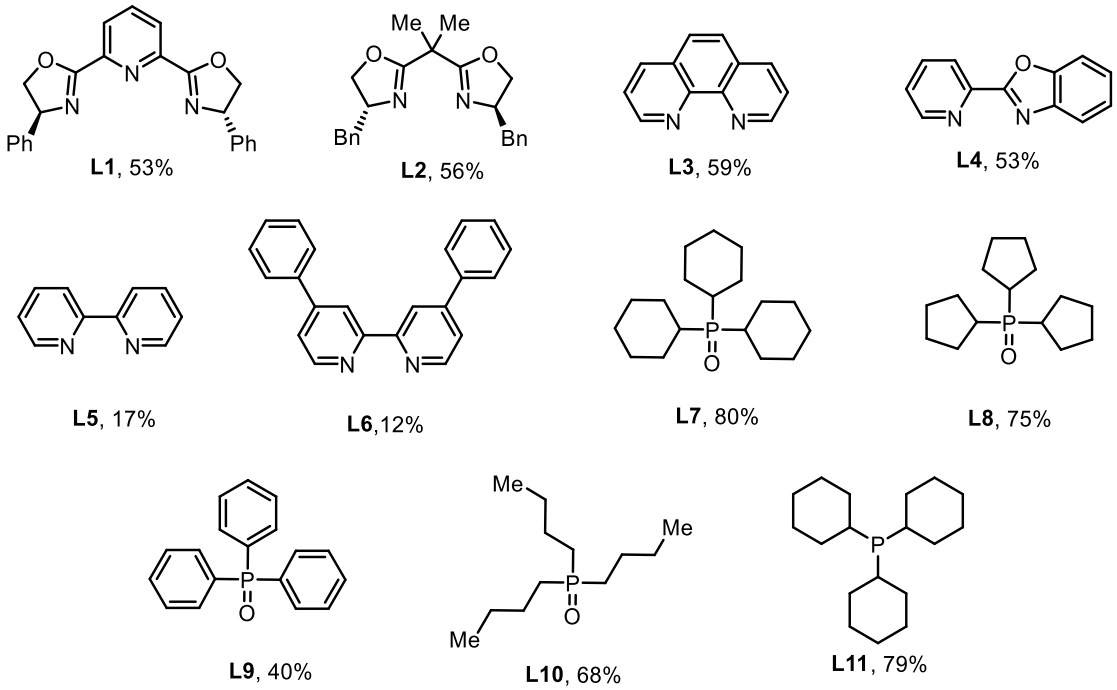
Entry	Catalyst	Yield[b]
1	**CuI**	**80%**
2	CuCl	72%
3	CuBr	65%
4	$Cu(OAc)_2$	60%
5	CuCN	61%
6	Cu_2O	62%
7	$Cu_2(OH)_2CO_3$	21%
8	$Cu(CF_3SO_3)(CH_3CN)_4$	67%
9	$Ni(acac)_2$	n.r
10	$Pd(PPh_3)_4$	n.r
11	$Ru(bpy)_3Cl_2$	n.r

[a]Unless otherwise specified, all reactions were carried out using 1a (0.1 mmol) and $TMSN_3$ (0.3 mmol), with catalyst (5 mol%), Cy_3PO (10 mol%) and TBPB (2.0 equiv) in toluene at 120 ℃ for 12 h. [b]Isolated yields after chromatography.

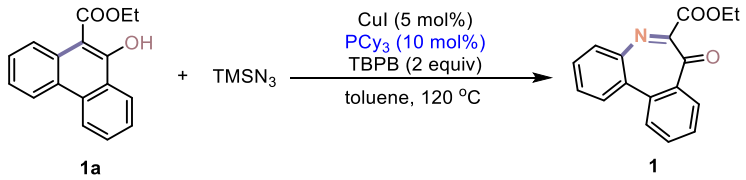
Table S2. Screening for ligands[a]



1a 1



Ligand PCy_3 can afford desired product in 79% yield. However, PCy_3 was oxidized to the Cy_3PO under these condition.



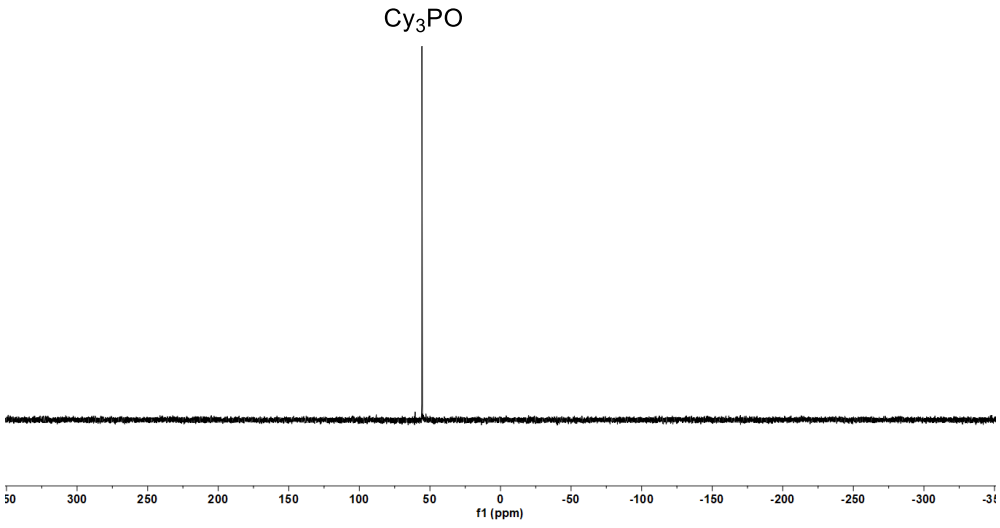
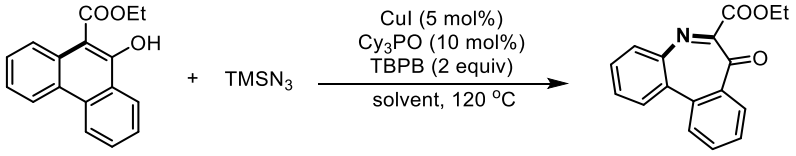


Figure S1. ^{31}P-NMR of the reaction mixture after the reaction.

Table S3. Screening for solvents[a]

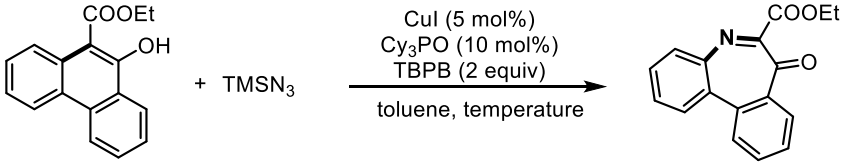


1a 1

Entry	Solvent	Yield[b]
1	**toluene**	**80%**
2	DCE	50%
3	PhCl	72%
4	DME	30%
5	DMF	n.r
6	DMSO	n.r
7	1,4-dioxane	n.r
8	MeCN	n.r

[a]Unless otherwise specified, all reactions were carried out using **1a** (0.1 mmol) and $TMSN_3$ (0.3 mmol), with CuI (5 mol%), Cy_3PO (10 mol%) and TBPB (2.0 equiv) in solvent at 120 ℃ for 12 h. [b]Isolated yields after chromatography.

Table S4. Screening for temperatures[a].



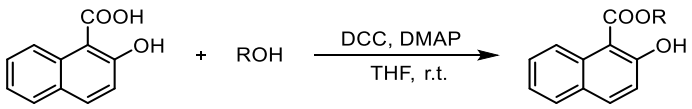
1a 1

Entry	Temperature(°C)	Yield[b]
1	90	6%
2	100	11%
3	110	54%
4	**120**	**80%**
5	130	63%
6	140	39%

[a]Unless otherwise specified, all reactions were carried out using **1a** (0.1 mmol) and $TMSN_3$ (0.3 mmol), with CuI (5 mol%), Cy_3PO (10 mol%) and TBPB (2.0 equiv) in toluene at temperature for 12 h. [b]Isolated yields after chromatography.

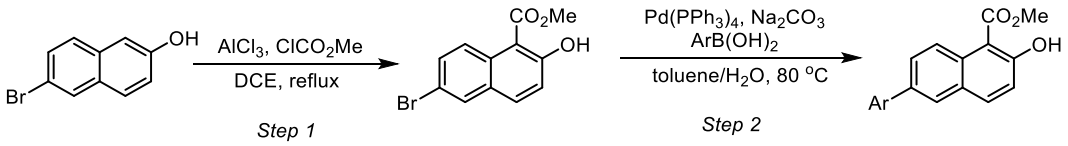
2.3 Synthesis of starting materials

2.3.1 General procedure for preparation of substrate 20a, 22a-24a, 26a-33a[1]



Step 1: To a stirred solution of 2-hydroxy-1-naphthoic acid (10.0 mmol, 1.0 equiv), alcohol derivatives (10.0 mmol, 1.0 equiv) and DMAP (0.1 mmol, 0.1 equiv) in THF (15 mL), a solution of DCC (15 mmol, 1.5 equiv) in THF (15 mL) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. Then the mixture was filtered through a pad of celite and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography to afford the desired products.

2.3.2 General procedure for preparation of substrate 5a-17a[1]

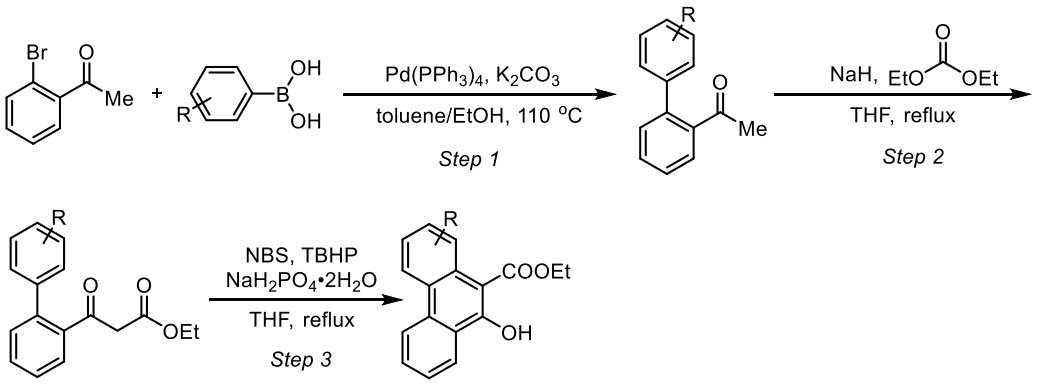


Step 1: To a 50 mL three-neck round-bottomed flask equipped with a condenser, $AlCl_3$ (5.0 mmol, 1.0 equiv) and DCE (10 mL) were added successively. Then methyl chloroformate (12.5 mmol, 2.5 equiv) was added and the mixture was stirred for 10 min at room temperature. 7-methyl-2-naphthol (5.0 mmol, 1.0 equiv) was added and the mixture was stirred under reflux for 10 h. Then ice water was added. Then the mixture was filtered through a pad of celite. The aqueous layer was extracted with DCM for three times. The organic layer was washed with brine, dried over $MgSO_4$, filtered and then concentrated. The residue was purified by silica gel column chromatography to afford desired products.

Step 2: To a 100 mL schlenk flask, methyl-6-bromo-2-hydroxy-1-naphthoate (2.0 mmol, 1.0 equiv), aryl boronic acid (2.4 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (0.2 mmol, 0.1 equiv), Na_2CO_3 (4.0 mmol, 2.0 equiv), toluene (5.0 mL) and H_2O (5.0 mL) were added successively. The mixture was reacted at 80 ℃ under nitrogen

atmosphere for 12 h. The reaction mixture was allowed to cool down to room temperature, filtered through a pad of celite and the solution was extracted with DCM. The organic layer was dried over $MgSO_4$, concentrated, and purified by flash chromatography to afford desired products.

2.3.3 General procedure for Preparation of substrate 34a-42a, 45a-47a[2]



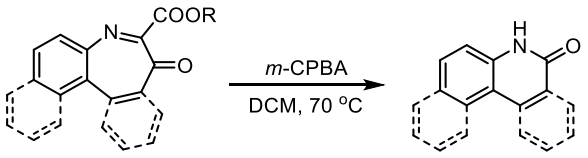
Step 1: To a stirred solution of aryl bromide (5.0 mmol, 1.0 equiv) and aryl boronic acid (5.0 mmol, 1.2 equiv) in a toluene/ethanol (3:1) mixture was added K_2CO_3 (15.0 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (0.5 mmol, 0.1 equiv). The resulting suspension was heated at 110 ℃ under nitrogen atmosphere for 11 h. The solvent was removed under reduced pressure and the crude residue was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$, concentrated, and purified by flash chromatography to afford desired products.

Step 2: To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (5.0 mmol, 2.8 equiv), diethyl carbonate (5.0 mmol, 2.8 equiv), and anhydrous THF (1.0 M). The mixture was heated to 80 ℃. Then a solution of ketone (5.0 mmol, 1.0 equiv) in anhydrous THF (20.0 mL) was added dropwise from the dropping funnel over 30 min. After the addition, the mixture was heated to reflux until the ketone was completely consumed (1-3 h).

When the reaction was cooled to room temperature, glacial acetic acid was added dropwise. Later, ice-water was added until the solid was dissolved completely. The organic layer was separated, and the water layer was extracted with ethyl acetate. The combined organic solution was washed with water and brine, then dried over $MgSO_4$, concentrated, and purified by flash chromatography to afford desired products.

Step 3: Products of step 2 (2.0 mmol, 1.0 equiv) was added to a mixture of NBS (0.8 mmol, 0.4 equiv) and NaH_2PO_4 $2H_2O$ (2.0 mmol, 1.0 equiv) under air, and then TBHP (7.0 mmol, 3.5 equiv, in 70% H_2O) and THF (16 mL) were added. After the mixture was stirred under reflux for 15 h, the resulting mixture was purified by silica gel column chromatography to give desired products.

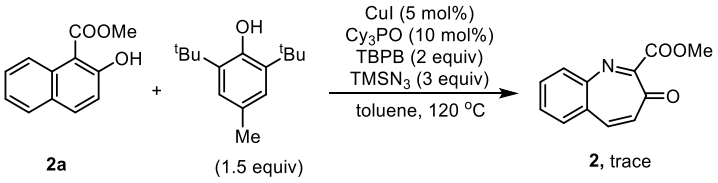
2.4 Procedure for derivatization of products



To a 25 mL round-bottom flask were added nitrogen atom insertion product (0.1 mmol, 1,0 equiv), *m*-CPBA (0.3 mmol, 3.0 equiv) and DCM. The reaction mixture was stirred at 70 ℃ until the raw materials had been completely consumed monitored by TLC. The organic layers were washed with saturated sodium bicarbonate solution and dried over $MgSO_4$, concentrated, and purified by flash chromatography to afford desired products.

3. Mechanism studies

3.1 Radical inhibition experiment



2a (0.1 mmol), CuI (1.0 mg, 0.005 mmol, 5 mol%), were added to an oven dried high pressure tube. Cy_3PO (3.0 mg, 0.01 mmol, 10 mol%), BHT (33.0 mg, 0.15 mmol, 1.5 equiv), toluene (1.0 mL), TBPB (38.0 μL, 0.2 mmol, 2.0 equiv), $TMSN_3$ (39.0 μL, 0.3 mmol, 3.0 equiv), were added in glovebox. Then the reaction was stirred at 120 ℃ for 12 h. After cooling down to room temperature (monitored by TLC), only trace of product **2** was detected.

3.2 Cyclic Voltammetry

The cyclic voltammetry was carried out with a Shanghai Chenhua CHI760E workstation. A glassy-carbon(GC) electrode (3mm-diameter, disc-electrode) was used as the working electrode, a Pt plate was used as the auxiliary electrode and an Ag/Ag^+ electrode was used as a reference electrode, respectively. The measurements were carried out at a scan rate of 50 mV s^{-1}, if not indicated otherwise. The operation temperature was 298 K.

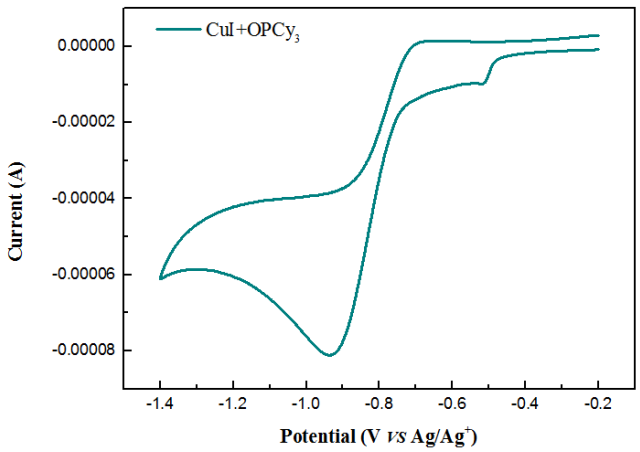


Figure S2. Cyclic voltammograms of CuI and Cy_3PO system at 50 mVs^{-1} in MeCN, $^nBu_4NBF_4$ (0.1 M in MeCN), CuI and Cy_3PO (1 mM).

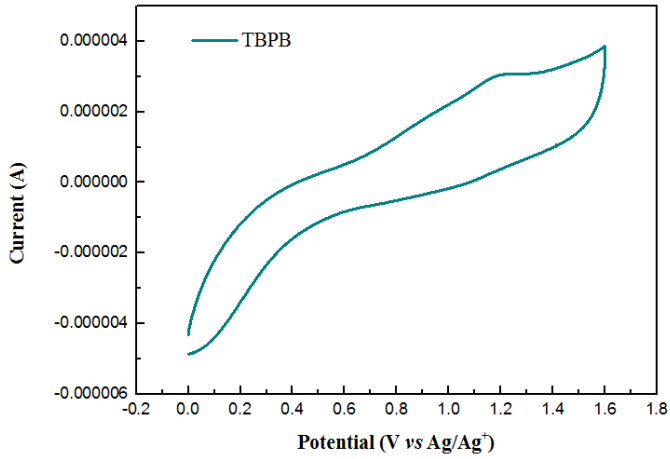


Figure S3. Cyclic voltammograms of TBPB at 50 mVs^{-1} in MeCN, $^{n}Bu_4NBF_4$ (0.1 M in MeCN), TBPB (10 mM).

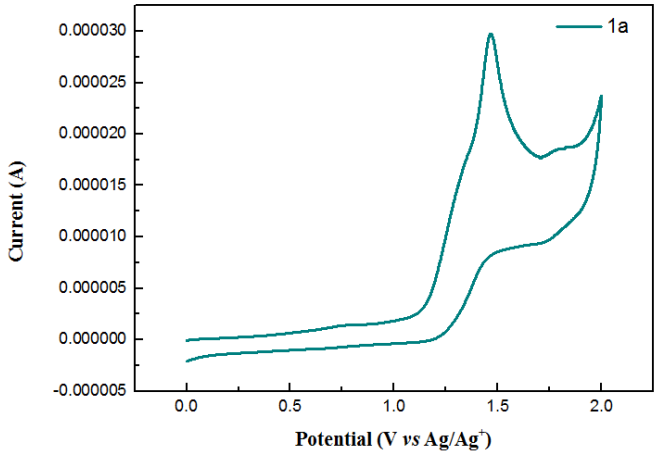
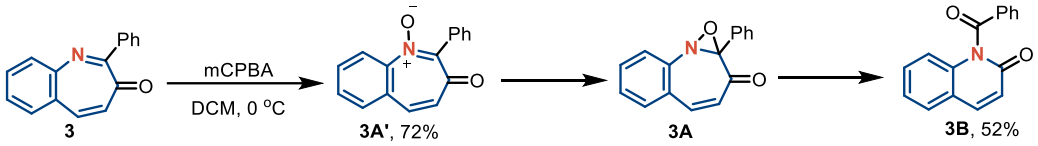


Figure S4. Cyclic voltammograms of 1a at 50 mVs^{-1} in MeCN, $^{n}Bu_4NBF_4$ (0.1 M in MeCN), 1a (1 mM).

To gain further insights into the reaction mechanism, mechanistic studies were performed by means of cyclic voltammetry (CV). An irreversible reduction peak of the mixture CuI and Cy_3PO at -0.94 V (vs Ag/Ag+ in MeCN) was observed. Moreover, CV experiments on substrate **1a** and TBPB gave the irreversible oxidation peaks at +1.46 V (vs Ag/Ag+ in MeCN) and +1.19 V (vs Ag/Ag+ in MeCN) respectively. These results suggested TBPB underwent reduction preferentially, which was consistent with the plausible mechanism that a single-electron transfer between Cu(I) and TBPB.

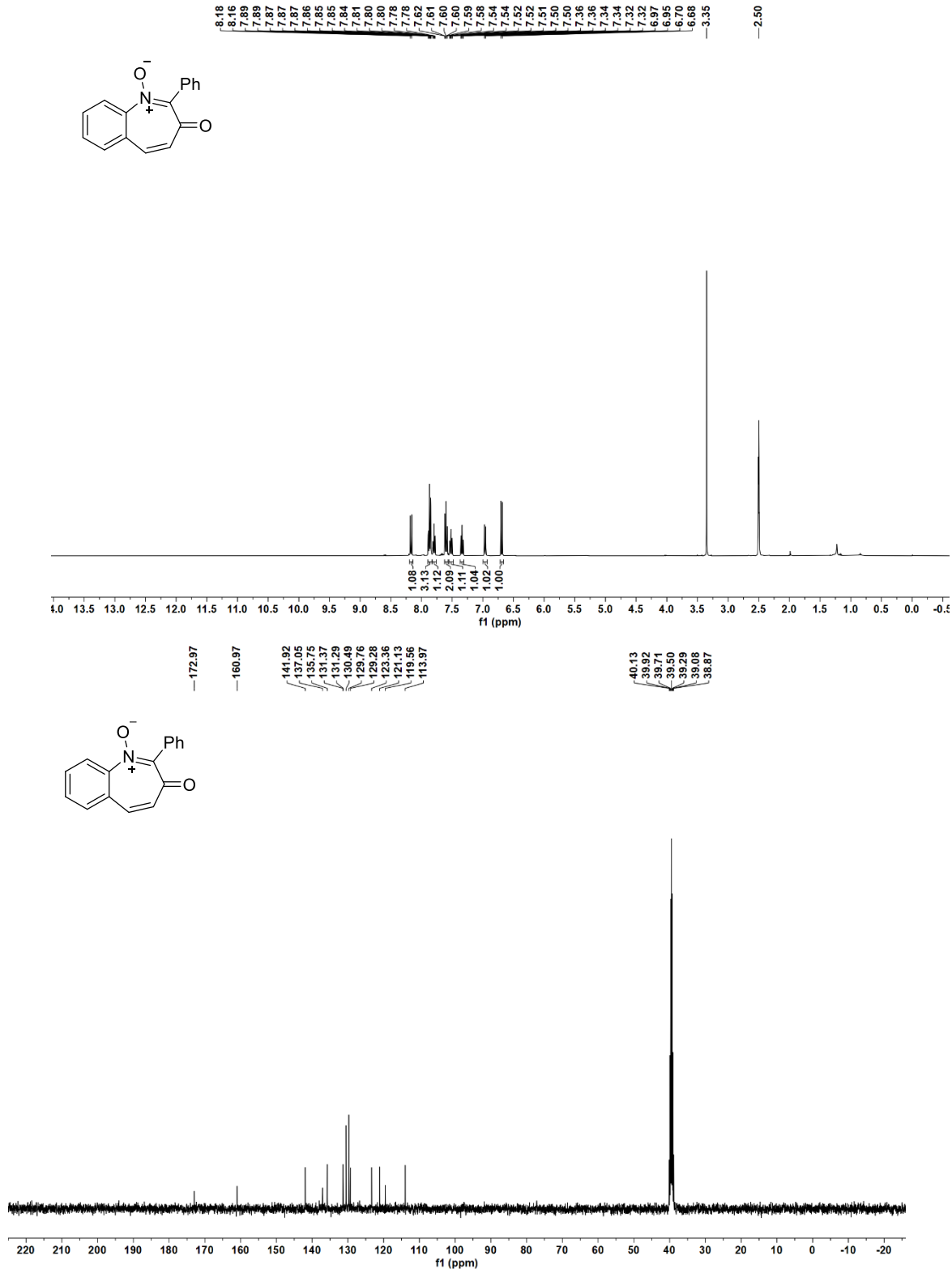
3.3 Mechanistic studies for carbon atom deletion



A series of control experiments were performed to investigate the reaction pathway. The reaction of **3** was initially conducted with mCPBA at 0 ^{o}C, which resulted in nitrone intermediate **3A'** in 72% yield. Isomerization of **3A'** propels the formation of **3A**. Furthermore, heating **3A'** in DCM led to intermediate **3B** without the need for additional reagents. These results indicated that the reaction proceeded via oxaziridine intermediate **3A** and amide intermediate **3B**.

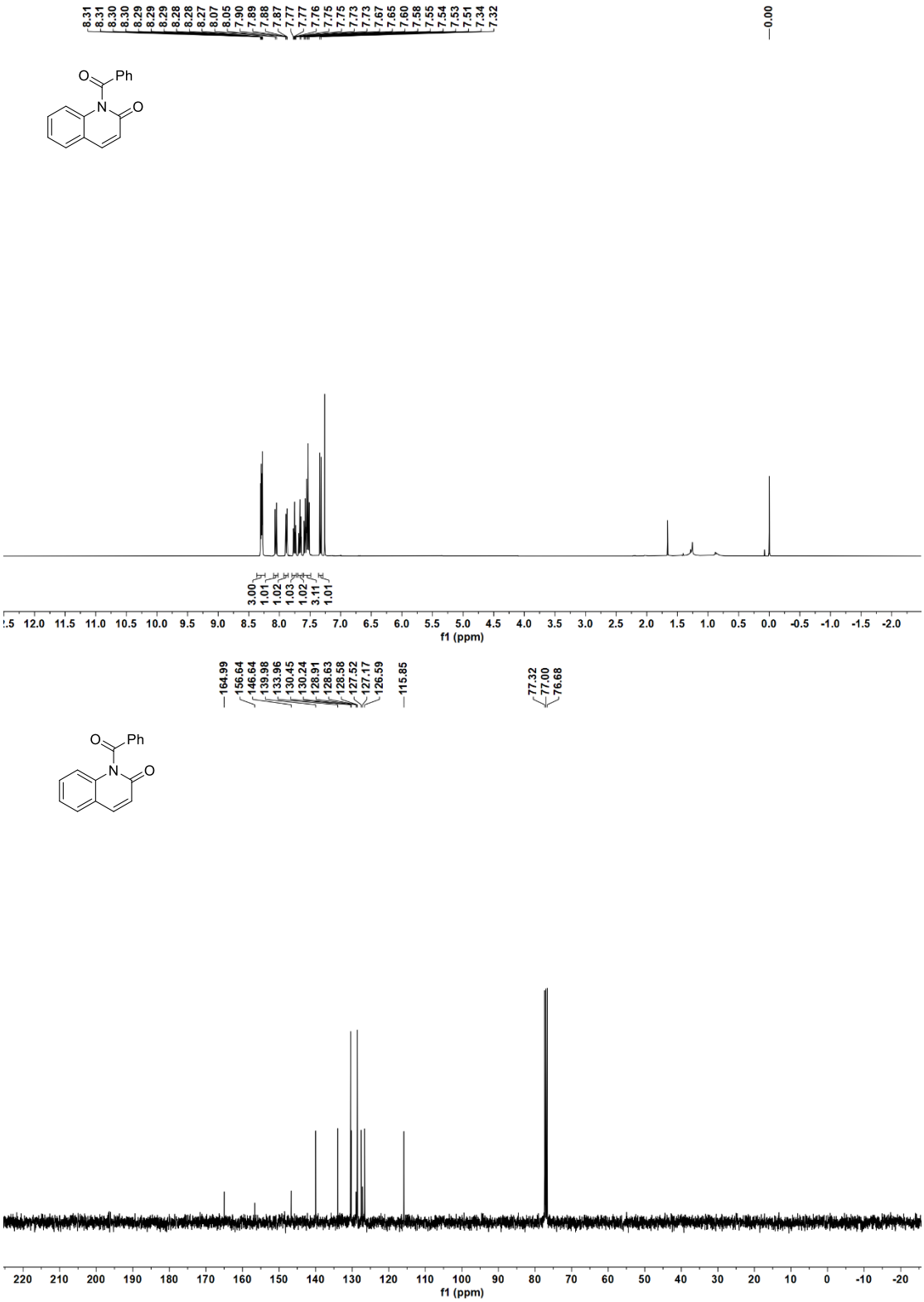
3-oxo-2-phenyl-3H-benzo[b]azepine 1-oxide (3A').

Colorless solid (17.9 mg, 72% yield). Mp = 111.9 – 112.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J = 9.0 Hz, 1H), 7.87 (m, 3H), 7.82 – 7.76 (m, 1H), 7.62 – 7.57 (m, 2H), 7.52 (m, 1H), 7.34 (m, 1H), 6.96 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 161.0, 142.0, 137.1, 135.8, 131.4, 131.3, 130.5, 129.8, 129.3, 123.4, 121.1, 119.6, 114.0. HRMS (ESI) Calculated for $C_{16}H_{12}NO_2$ $[M+H]^+$: 250.0862; Found: 250.0854.

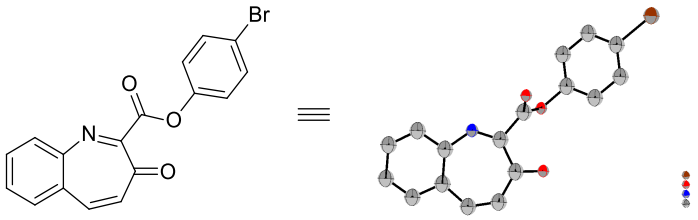


N-Acyl quinolin-2(1*H*)-ones (3B). Colorless solid. Mp = 122.3 – 123.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (m, 3H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* =

8.1Hz, 1H), 7.75 (m, 1H), 7.70 – 7.63 (m, 1H), 7.56 (m, 3H), 7.33 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 156.6, 146.6, 140.0, 134.0, 130.5, 130.2, 128.9, 128.6, 128.6, 127.5, 127.2, 126.6, 115.9. HRMS (ESI) Calculated for $C_{16}H_{12}NO_2$ $[M+H]^+$: 250.0862; Found: 250.0857.



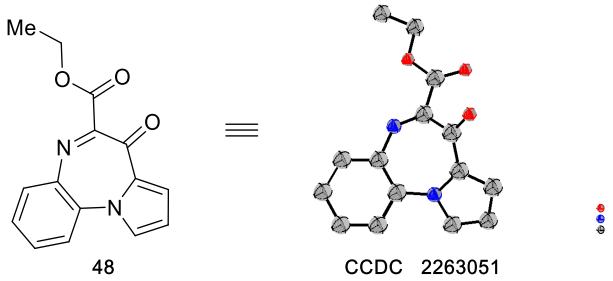
4. X-Ray crystallographic data



20 CCDC 2263048

Table S5 Crystal data and structure refinement for **20**

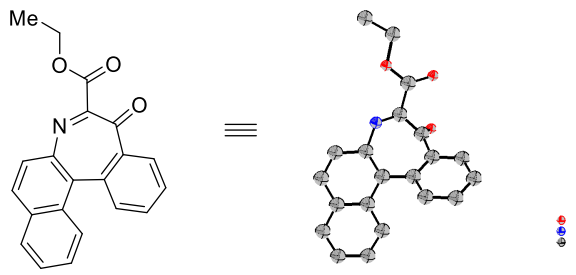
Empirical formula	$C_{17}H_{10}BrNO_3$
Formula weight	356.17
Temperature/K	220.0K
Crystal system	Monoclinic
Space group	P 21/c
a/Å	5.4496(2)
b/Å	20.6183(6)
c/Å	13.2918(4)
α/°	90
β/°	99.8540(10) °
γ/°	90
Volume/Å^3	1471.45(8)
Z	4
Density (calculated) g/cm^3	1.608
μ/mm^{-1}	2.584
F(000)	712
Crystal size/mm^3	0.180 ×0.130 ×0.120
Radiation	MoK\a（wavelength = 1.34138）
Index ranges	-4 ≤ h ≤ 6, -25 ≤ k ≤ 24 -15 ≤ l ≤ 16
Reflections collected	14842
Independent reflections	2964 [R_{int} = 0.0464]
Data/restraints/parameters	2964 / 0 / 199
Goodness-of-fit on F^2	1.081
Final R indexes [I>=2σ (I)]	R_1= 0.0344, wR_2= 0.0934
Final R indexes [all data]	R_1= 0.0374, wR_2= 0.0962
Largest diff. peak/hole / e Å^{-3}	0.427 and -0.711



48 CCDC 2263051

Table S6 Crystal data and structure refinement for **48**

Empirical formula	$C_{15}H_{12}N_2O_3$
Formula weight	268.27
Temperature/K	298.0K
Crystal system	Monoclinic
Space group	P 21/n
a/Å	7.7369(6)
b/Å	9.7927(9)
c/Å	16.8291(16)
α/°	90
β/°	100.727(4)
γ/°	90
Volume/Å^3	1252.78(19)
Z	4
Density (calculated) g/cm^3	1.422
μ/mm^{-1}	0.535
F(000)	560
Crystal size/mm^3	0.130 ×0.120 ×0.100
Radiation	MoK\a（wavelength = 1.34138）
Index ranges	-9 ≤ h ≤ 9, -9 ≤ k ≤ 11, -19 ≤ l ≤ 19
Reflections collected	16086
Independent reflections	2215 [R_{int} = 0.1040]
Data/restraints/parameters	2215 / 0 / 163
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1= 0.0935, wR_2= 0.2433
Final R indexes [all data]	R_1= 0.1478, wR_2= 0.3017
Largest diff. peak/hole / e Å^{-3}	1.125 and -0.448

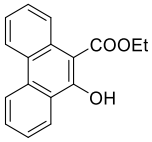


46 CCDC 2263052

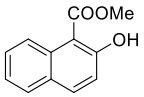
Table S7 Crystal data and structure refinement for **46**

Empirical formula	$C_{21}H_{15}NO_3$
Formula weight	329.34
Temperature/K	200.0K
Crystal system	Monoclinic
Space group	P 21/n
a/Å	7.7620(5)
b/Å	12.9308(9)
c/Å	15.9453(10)
α/°	90
β/°	94.829(2)
γ/°	90
Volume/Å^3	1594.73(18)
Z	4
Density (calculated) g/cm^3	1.372
μ/mm^{-1}	0.476
F(000)	688
Crystal size/mm^3	0.180 ×0.130 ×0.100
Radiation	MoK\a（wavelength = 1.34138）
Index ranges	$-9 \le h \le 9$, $-14 \le k \le 16$, $-19 \le l \le 19$
Reflections collected	15353
Independent reflections	3266 [R_{int} = 0.1532]
Data/restraints/parameters	3266 / 0 / 227
Goodness-of-fit on F^2	0.947
Final R indexes [I>=2σ (I)]	R_1= 0.0477, wR_2= 0.0962
Final R indexes [all data]	R_1= 0.1257, wR_2= 0.1195
Largest diff. peak/hole / e Å^{-3}	0.248 and -0.309

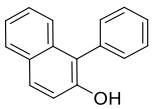
5. NMR spectra data of compounds



Ethyl 10-hydroxyphenanthrene-9-carboxylate (1a).[2] Colorless solid. Mp = 132.4 – 133.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.24 (s, 1H), 8.70 (dd, *J* = 8.4, *J* = 1.3 Hz, 1H), 8.50 – 8.44 (m, 3H), 7.69 – 7.63 (m, 1H), 7.56 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 4.51 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 162.7, 133.6, 130.4, 129.4, 127.5, 126.8, 126.0, 125.9, 125.2, 124.9, 124.2, 122.8, 122.4, 101.5, 62.0, 14.3. HRMS (ESI): Calculated for $C_{17}H_{13}O_3$ $[M-H]^-$: 265.0859; Found: 265.0870.

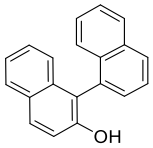


Methyl 2-hydroxy-1-naphthoate (2a).[1] Colorless solid. Mp = 92.6 – 94.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.27 (s, 1H), 8.70 (d, *J* = 8.9 Hz, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.70 (dd, *J* = 8.1, *J* = 1.6 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.37 – 7.29 (m, 1H), 7.13 (dd, *J* = 9.0, *J* = 1.1 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.3, 136.7, 131.6, 128.9, 128.5, 128.3, 125.2, 123.5, 119.1, 104.4, 52.2. HRMS (ESI): Calculated for $C_{12}H_9O_3$ $[M-H]^-$: 201.0546; Found: 201.1544.

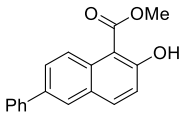


1-Phenylnaphthalen-2-ol (3a).[5] Colorless solid. Mp = 97.8 – 101.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.43 – 7.36 (m, 2H), 7.33 – 7.24 (m, 4H), 7.21 – 7.14 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.08 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 134.2, 133.2, 131.1, 129.5, 129.4, 128.8, 128.3, 128.0, 126.4, 124.5,

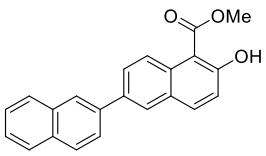
123.2, 120.9, 117.3. HRMS (ESI): Calculated for $C_{16}H_{11}O$ $[M-H]^-$: 219.0804; Found: 219.0823.



[1,1'-Binaphthalen]-2-ol (4a).[5] Colorless solid. Mp = 118.6 – 120.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.79 – 7.71 (m, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.12 – 7.07 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 134.1, 133.8, 132.8, 131.4, 131.1, 129.8, 129.6, 129.2, 128.9, 128.4, 128.0, 126.8, 126.5, 126.0, 125.7, 124.9, 123.3, 118.7, 117.4. HRMS (ESI): Calculated for $C_{20}H_{13}O$ $[M-H]^-$: 269.0961; Found: 269.0961.

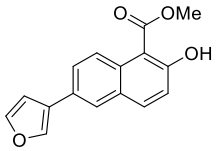


Methyl 2-hydroxy-6-phenyl-1-naphthoate (5a).[3] Colorless solid. Mp = 158.6 – 159.3 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.20 (s, 1H), 8.61 (d, *J* = 8.9 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.65 (dd, *J* = 8.7, *J* = 2.2 Hz, 1H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 9.1 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.3, 140.1, 137.0, 136.0, 130.7, 128.8, 127.7, 127.3, 127.1, 126.9, 126.6, 126.8, 119.6, 104.4, 52.3. HRMS (ESI): Calculated for $C_{18}H_{13}O_3$ $[M-H]^-$: 277.0859; Found: 277.0876.

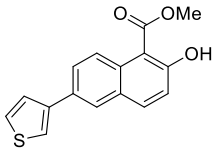


Methyl 6-hydroxy-[2,2'-binaphthalene]-5-carboxylate (6a). Colorless solid. Mp = 214.6 – 215.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.33 (s, 1H), 8.80 (d, *J* = 9.0 Hz, 1H), 8.12 – 8.02 (m, 2H), 7.95 – 7.90 (m, 4H), 7.87 – 7.80 (m, 2H), 7.52 – 7.46 (m, 2H), 7.18 (d, *J* = 8.9 Hz, 1H), 4.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8,

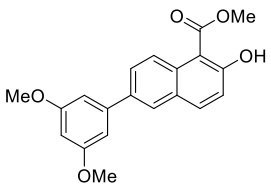
164.4, 137.5, 137.1, 136.0, 133.7, 132.6, 130.9, 129.0, 128.5, 128.2, 127.9, 127.6, 127.0, 126.4, 126.0, 125.9, 125.7, 125.3, 119.7, 104.6, 52.5. HRMS (ESI): Calculated for $C_{22}H_{15}O_3$ $[M-H]^-$: 327.1016; Found: 327.1015.



Methyl 6-(furan-3-yl)-2-hydroxy-1-naphthoate (7a). Colorless solid. Mp = 112.0 – 112.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.17 (s, 1H), 8.61 (d, *J* = 9.0 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 9.1, *J* = 2.2 Hz, 1H), 7.42 (s, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 6.70 (s, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.1, 143.8, 138.6, 136.7, 130.6, 128.9, 127.6, 126.7, 125.8, 125.7, 125.2, 119.7, 108.7, 104.7, 52.4. HRMS (ESI): Calculated for $C_{16}H_{11}O_4$ $[M-H]^-$: 267.0652; Found: 267.0650.

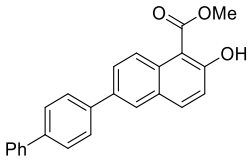


Methyl 2-hydroxy-6-(thiophen-3-yl)-1-naphthoate (8a). Colorless solid. Mp = 138.2 – 139.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.28 (s, 1H), 8.78 – 8.73 (m, 1H), 7.94 – 7.88 (m, 2H), 7.83 – 7.78 (m, 1H), 7.56 – 7.53 (m, 1H), 7.51 – 7.48 (m, 1H), 7.45 – 7.41 (m, 1H), 7.18 (dd, *J* = 9.0, *J* = 0.9 Hz, 1H), 4.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.3, 141.5, 136.9, 131.0, 130.7, 128.9, 127.2, 126.4, 126.2, 125.9, 125.8, 120.3, 119.7, 104.7, 52.5. HRMS (ESI): Calculated for $C_{16}H_{11}O_3S$ $[M-H]^-$: 283.0423; Found: 283.0417.

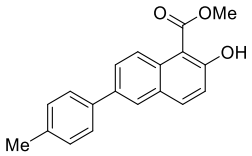


Methyl 6-(3,5-dimethoxyphenyl)-2-hydroxy-1-naphthoate (9a). Colorless solid. Mp = 165.4 – 166.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.37 – 12.22 (m, 1H), 8.77

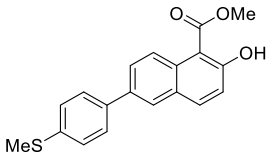
(d, *J* = 9.1 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.78 (dd, *J* = 9.1, *J* = 2.1 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 2H), 6.49 (t, *J* = 2.3 Hz, 1H), 4.11 (s, 3H), 3.86 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.4, 161.1, 142.5, 137.1, 136.1, 131.0, 128.8, 127.7, 126.8, 125.8, 119.7, 105.3, 104.5, 99.2, 55.4, 52.4. HRMS (ESI): Calculated for $C_{20}H_{17}O_5$ $[M-H]^-$: 337.1071; Found: 337.1071.



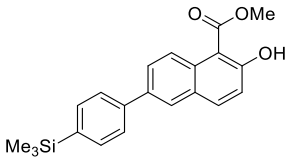
Methyl 6-([1,1'-biphenyl]-4-yl)-2-hydroxy-1-naphthoate (10a). Colorless solid. Mp = 258.7 – 259.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.23 (s, 1H), 8.74 (d, *J* = 9.1 Hz, 1H), 7.92 – 7.86 (m, 2H), 7.79 (dd, *J* = 9.0, *J* = 2.2 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 164.4, 140.6, 140.2, 139.1, 137.1, 135.6, 130.9, 129.0, 128.8, 127.6, 127.5, 127.4, 127.0, 126.7, 126.6, 125.9, 119.8, 104.6, 52.5. HRMS (ESI): Calculated for $C_{24}H_{17}O_3$ $[M-H]^-$: 353.1172; Found: 353.1190.



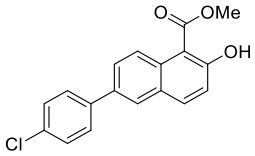
Methyl 2-hydroxy-6-(p-tolyl)-1-naphthoate (11a). Colorless solid. Mp = 158.0 – 159.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.29 (s, 1H), 8.73 (d, *J* = 9.1 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.76 (dd, *J* = 9.0, *J* = 2.1 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 9.0 Hz, 1H), 4.06 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.3, 137.3, 137.1, 137.0, 136.0, 130.6, 129.6, 128.9, 127.6, 126.8, 126.3, 125.7, 119.5, 104.5, 52.3, 21.1. HRMS (ESI): Calculated for $C_{19}H_{15}O_3$ $[M-H]^-$: 291.1016; Found: 291.1027.



Methyl 2-hydroxy-6-(4-(methylthio)phenyl)-1-naphthoate (12a). Colorless solid. Mp = 160.1 – 161.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.29 (s, 1H), 8.72 (d, *J* = 9.1 Hz, 1H), 7.86 – 7.82 (m, 2H), 7.75 – 7.70 (m, 1H), 7.58 – 7.54 (m, 2H), 7.33 – 7.29 (m, 2H), 7.13 (dd, *J* = 9.1, *J* = 1.1 Hz, 1H), 4.06 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 164.3, 137.7, 136.9, 136.8, 135.3, 130.7, 128.8, 127.3, 127.2, 126.8, 126.2, 125.8, 119.6, 104.4, 52.3, 15.7. HRMS (ESI): Calculated for $C_{19}H_{15}O_3S$ $[M-H]^-$: 323.0736, Found: 323.0729.

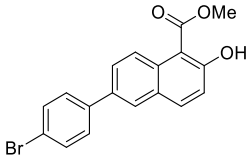


Methyl 2-hydroxy-6-(4-(trimethylsilyl)phenyl)-1-naphthoate (13a). Colorless solid. Mp = 113.8 – 114.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (s, 1H), 8.73 (d, *J* = 9.3 Hz, 1H), 7.89 – 7.84 (m, 2H), 7.77 (dd, *J* = 9.0, *J* = 2.1 Hz, 1H), 7.63 (t, *J* = 8.1 Hz, 4H), 7.13 (d, *J* = 9.0 Hz, 1H), 4.04 (s, 3H), 0.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.4, 140.6, 139.3, 137.0, 136.0, 133.9, 130.8, 128.9, 127.6, 126.7, 126.3, 125.8, 119.6, 104.5, 52.3, -1.1. HRMS (ESI): Calculated for $C_{21}H_{21}O_3Si$ $[M-H]^-$: 349.1254; Found: 349.1253.

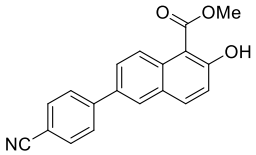


Methyl 6-(4-chlorophenyl)-2-hydroxy-1-naphthoate (14a). Colorless solid. Mp = 175.9 – 176.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.31 (s, 1H), 8.79 (d, *J* = 9.2 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.76 (dd, *J* = 9.1, *J* = 2.4 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.46 – 7.42 (m, 2H), 7.20 (d, *J* = 8.7 Hz, 1H), 4.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.5, 138.7, 137.0, 134.9, 133.4, 131.0, 129.0, 128.9, 128.3, 127.4,

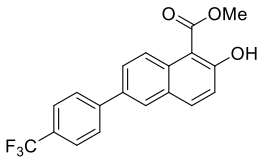
126.7, 126.0, 119.9, 104.6, 52.5. HRMS (ESI): Calculated for $C_{18}H_{12}ClO_3$ $[M-H]^-$: 311.0469; Found: 311.0486.



Methyl 6-(4-bromophenyl)-2-hydroxy-1-naphthoate (15a). Colorless solid. Mp = 139.2 – 140.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.30 (s, 1H), 8.70 (d, *J* = 8.9 Hz, 1H), 7.85 – 7.77 (m, 2H), 7.67 (dd, *J* = 8.7, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 8.7 Hz, 1H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 164.4, 139.0, 136.9, 134.7, 131.9, 130.9, 128.8, 128.4, 127.1, 126.5, 125.9, 121.5, 119.8, 104.4, 52.4. HRMS (ESI): Calculated for $C_{18}H_{12}BrO_3$ $[M-H]^-$: 354.9964; Found: 354.9977.

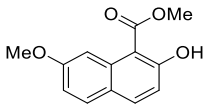


Methyl 6-(4-cyanophenyl)-2-hydroxy-1-naphthoate (16a). Colorless solid. Mp = 262.2 – 262.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.35 (s, 1H), 8.84 (d, *J* = 9.1 Hz, 1H), 7.95 (t, *J* = 4.6 Hz, 2H), 7.82 – 7.69 (m, 5H), 7.22 (d, *J* = 9.0 Hz, 1H), 4.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 164.9, 144.7, 137.1, 134.0, 132.7, 131.6, 128.8, 127.5, 127.3, 127.1, 126.3, 120.2, 118.9, 110.8, 104.6, 52.6. HRMS (ESI): Calculated for $C_{19}H_{12}NO_3$ $[M-H]^-$: 302.0812; Found: 302.0797.

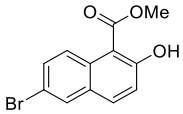


Methyl 2-hydroxy-6-(4-(trifluoromethyl)phenyl)-1-naphthoate (17a). Colorless solid. Mp = 130.9 – 131.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.33 (s, 1H), 8.67 (d, *J* = 9.0 Hz, 1H), 7.78 – 7.75 (m, 2H), 7.67 – 7.61 (m, 5H), 7.09 (d, *J* = 9.0 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.7, 143.6, 137.0, 134.2, 131.2,

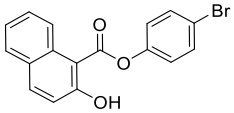
129.6 (q, J = 32.4 Hz), 129.3, 127.2 (t, J = 8.5 Hz), 126.0, 125.9 (q, J = 3.8 Hz), 124.5 (q, J = 270.6 Hz), 119.8, 104.4, 52.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI): Calculated for $C_{19}H_{12}F_3O_3$ $[M-H]^-$: 345.0733; Found: 345.0735.



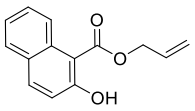
Methyl 2-hydroxy-7-methoxy-1-naphthoate (18a).[3] Colorless solid. Mp = 135.2 – 137.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.21 (s, 1H), 8.06 (d, J = 2.5 Hz, 1H), 7.68 (d, J = 8.9 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 6.95 – 6.85 (m, 2H), 3.98 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 165.0, 159.8, 136.6, 133.4, 130.5, 123.8, 116.5, 114.4, 106.1, 103.8, 55.1, 52.3. HRMS (ESI): Calculated for $C_{13}H_{11}O_4$ $[M-H]^-$: 231.0652; Found: 231.0656.



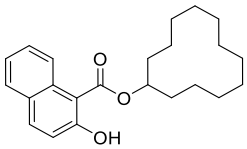
Methyl 6-bromo-2-hydroxy-1-naphthoate (19a).[1] Colorless solid. Mp = 102.2 – 103.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.18 (s, 1H), 8.48 (d, J = 9.3 Hz, 1H), 7.75 (d, J = 2.3 Hz, 1H), 7.65 (dd, J = 9.1, J = 0.7 Hz, 1H), 7.48 (dd, J = 9.3, J = 2.3 Hz, 1H), 7.06 (d, J = 9.1 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 164.4, 135.6, 131.3, 130.8, 130.2, 129.8, 127.1, 120.5, 117.2, 104.7, 52.5. HRMS (ESI): Calculated for $C_{12}H_8BrO_3$ $[M-H]^-$: 278.9651; Found: 278.9664.



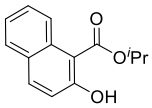
4-Bromophenyl 2-hydroxy-1-naphthoate (20a). Colorless solid. Mp = 147.1 – 148.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.93 (s, 1H), 8.84 (d, J = 8.8 Hz, 1H), 7.96 (d, J = 9.1 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.63 – 7.58 (m, 3H), 7.44 – 7.38 (m, 1H), 7.22 – 7.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 165.5, 148.8, 138.0, 132.8, 131.5, 129.4, 128.9, 128.7, 125.2, 124.0, 123.7, 119.7, 119.3, 103.7. HRMS (ESI): Calculated for $C_{17}H_{10}BrO_3$ $[M-H]^-$: 340.9808; Found: 340.9815.



Allyl 2-hydroxy-1-naphthoate (21a).[3] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H), 8.75 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 9.1 Hz, 1H), 7.71 – 7.64 (m, 1H), 7.56 – 7.48 (m, 1H), 7.35 – 7.29 (m, 1H), 7.13 (d, *J* = 1.0 Hz, 1H), 6.17 – 6.05 (m, 1H), 5.51 – 5.41 (m, 1H), 5.38 – 5.31 (m, 1H), 4.98 – 4.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 164.4, 136.8, 131.7, 131.5, 129.0, 128.5, 128.4, 125.2, 123.5, 119.2, 119.2, 104.4, 66.3. HRMS (ESI): Calculated for $C_{14}H_{11}O_3$ $[M-H]^-$: 227.0703; Found: 227.0707.

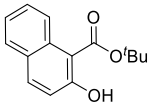


Cyclododecyl 2-hydroxy-1-naphthoate (22a). Colorless solid. Mp = 155.0 – 155.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.38 (s, 1H), 8.71 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 9.1 Hz, 1H), 5.42 – 5.32 (m, 1H), 1.88 – 1.80 (m, 2H), 1.67 (dd, *J* = 13.9, *J* = 5.6 Hz, 2H), 1.42 – 1.37 (m, 6H), 1.34 – 1.24 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 164.3, 136.5, 132.0, 129.0, 128.6, 128.2, 125.2, 123.4, 119.3, 105.0, 74.8, 29.0, 24.2, 24.0, 23.2, 23.0, 20.8. HRMS (ESI): Calculated for $C_{23}H_{29}O_3$ $[M-H]^-$: 353.2111; Found: 353.2109.

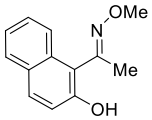


Isopropyl 2-hydroxy-1-naphthoate (23a).[1] Colorless solid. Mp = 69.6 – 70.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.33 (s, 1H), 8.73 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.63 (m, 1H), 7.51 – 7.43 (m, 1H), 7.31 – 7.25 (m, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 5.46 – 5.34 (m, 1H), 1.44 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 164.3, 136.6, 131.9, 129.0, 128.6, 128.3, 125.2, 123.5, 119.3, 105.0,

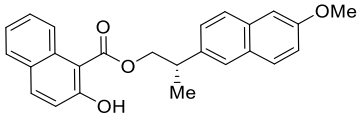
70.0, 22.1. HRMS (ESI): Calculated for $C_{14}H_{13}O_3$ $[M-H]^-$: 229.0859; Found: 229.0859.



***Tert*-butyl 2-hydroxy-1-naphthoate (24a).**[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.39 (s, 1H), 8.71 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.49 – 7.42 (m, 1H), 7.29 – 7.22 (m, 1H), 7.07 (d, *J* = 9.0 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 164.2, 136.2, 132.0, 129.0, 128.6, 128.1, 125.2, 123.4, 119.4, 105.9, 84.1, 28.5. HRMS (ESI): Calculated for $C_{15}H_{15}O_3$ $[M-H]^-$: 243.1016; Found: 243.1028.

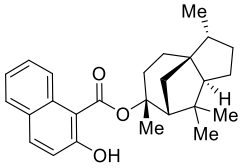


(2-Hydroxynaphthalen-1-yl)ethan-1-one O-methyl oxime (25a).[4] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.69 – 7.56 (m, 3H), 7.38 – 7.30 (m, 1H), 7.26 – 7.20 (m, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 3.97 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 152.7, 131.7, 131.2, 129.1, 128.7, 126.6, 124.3, 123.3, 118.3, 114.4, 62.3, 17.9. HRMS (ESI): Calculated for $C_{13}H_{12}NO_2$ $[M-H]^-$: 214.0863; Found: 214.0880.

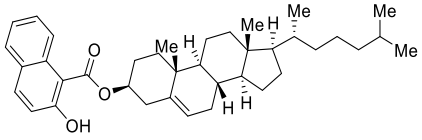


(*S*)-2-(6-Methoxynaphthalen-2-yl)propyl 2-hydroxy-1-naphthoate (26a). Colorless solid. Mp = 119.5 – 120.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.14 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.66 – 7.57 (m, 4H), 7.49 (dd, *J* = 8.1, *J* = 1.6 Hz, 1H), 7.30 (dd, *J* = 8.5, *J* = 1.9 Hz, 1H), 7.11 – 7.03 (m, 2H), 7.00 – 6.95 (m, 2H), 6.94 – 6.89 (m, 1H), 4.58 – 4.50 (m, 2H), 3.76 (s, 3H), 3.33 (q, *J* = 7.1 Hz, 1H), 1.36 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 164.2, 157.5, 138.1, 136.7, 133.6,

131.6, 129.1, 129.0, 128.8, 128.4, 128.1, 127.3, 125.9, 125.8, 125.3, 123.4, 119.1, 118.9, 105.5, 104.6, 71.0, 55.2, 38.8, 18.3. HRMS (ESI): Calculated for $C_{25}H_{21}O_4$ $[M-H]^-$: 385.1434; Found 385.1433.

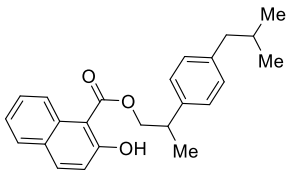


(3*R*,3a*S*,6*R*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl 2-hydroxy-1-naphthoate (27a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, 1H), 8.87 – 8.78 (m, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.66 (dd, *J* = 8.1, *J* = 1.5 Hz, 1H), 7.48 – 7.38 (m, 1H), 7.31 – 7.25 (m, 1H), 7.08 (d, *J* = 9.0 Hz, 1H), 2.78 (d, *J* = 5.2 Hz, 1H), 2.32 – 2.18 (m, 2H), 1.85 – 1.78 (m, 2H), 1.74 (d, *J* = 0.9 Hz, 3H), 1.70 – 1.62 (m, 2H), 1.54 – 1.43 (m, 4H), 1.41 – 1.37 (m, 1H), 1.36 – 1.29 (m, 1H), 1.26 – 1.18 (m, 1H), 0.97 (s, 3H), 0.92 (s, 3H), 0.80 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 164.4, 136.3, 129.0, 128.7, 128.0, 125.4, 123.3, 119.5, 105.9, 90.7, 56.8, 54.0, 43.5, 41.2, 41.2, 36.9, 33.9, 31.3, 31.2, 28.5, 26.8, 26.7, 25.3, 15.5. HRMS (ESI): Calculated for $C_{26}H_{31}O_3$ $[M-H]^-$: 391.2268; Found: 391.2267.

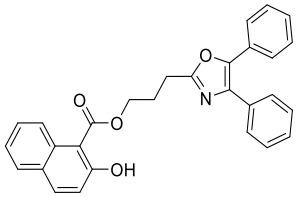


(3*S*, 8*S*, 9*S*, 10*R*, 13*R*, 14*S*, 17*R*)-10, 13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2, 3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 2-hydroxy-1-naphthoate (28a). Colorless solid. Mp = 206.8 – 207.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.33 (s, 1H), 8.69 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 5.32 (d, *J* = 4.8 Hz, 1H), 4.99 – 4.85 (m, 1H), 2.49 (d, *J* = 8.1 Hz, 2H), 2.02 (d, *J* = 10.0 Hz, 1H), 1.92 – 1.71 (m, 5H), 1.43 – 1.32 (m, 5H), 1.28 – 1.21 (m, 3H), 1.17 – 1.12 (m, 2H), 1.07 – 1.01 (m, 4H), 0.96 (s, 4H), 0.83 –

0.80 (m, 4H), 0.79 – 0.75 (m, 10H), 0.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 164.5, 139.2, 136.5, 131.9, 129.0, 128.6, 128.3, 125.3, 123.4, 123.2, 119.3, 104.8, 76.2, 56.6, 56.1, 50.0, 42.2, 39.6, 39.5, 38.3, 37.0, 36.6, 36.2, 35.8, 31.8, 31.7, 28.0, 26.9, 24.2, 23.9, 22.8, 22.6, 21.0, 19.3, 18.7, 14.1, 11.8. HRMS (ESI): Calculated for $C_{38}H_{51}O_3$ $[M-H]^-$: 555.3833; Found: 555.3835.

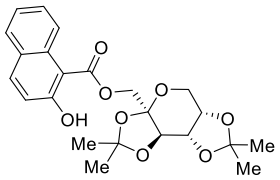


2-(4-Isobutylphenyl)propyl 2-hydroxy-1-naphthoate (29a). Colorless solid. Mp = 54.7 – 55.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.24 (s, 1H), 8.34 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.20 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.10 – 7.03 (m, 3H), 4.55 – 4.47 (m, 2H), 3.23 (q, *J* = 7.1 Hz, 1H), 2.41 (d, *J* = 7.3 Hz, 2H), 1.84 – 1.76 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H), 0.85 (s, 3H), 0.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 164.3, 140.2, 140.1, 136.6, 131.7, 129.3, 128.8, 128.4, 128.1, 126.9, 125.4, 123.4, 119.1, 104.6, 71.1, 45.0, 38.5, 30.1, 22.3, 18.3. HRMS (ESI): Calculated for $C_{24}H_{25}O_3$ $[M-H]^-$: 361.1798; Found: 361.1803.

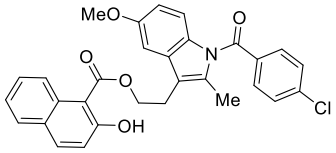


3-(4,5-Diphenyloxazol-2-yl)propyl 2-hydroxy-1-naphthoate (30a). Colorless solid. Mp = 106.4 – 107.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.23 (s, 1H), 8.64 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.44 – 7.40 (m, 3H), 7.25 – 7.17 (m, 7H), 7.02 (d, *J* = 9.1 Hz, 1H), 4.56 (t, *J* = 6.3 Hz, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.39 – 2.33 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 164.5, 162.0, 145.3, 136.8, 135.0, 132.3, 131.7, 129.0, 128.8, 128.5, 128.5,

128.4, 128.3, 128.0, 127.8, 126.3, 125.0, 123.5, 119.2, 118.9, 104.5, 64.8, 25.9, 25.0. HRMS (ESI): Calculated for $C_{29}H_{22}NO_4$ [M-H]$^-$: 448.1543; Found: 448.1541.

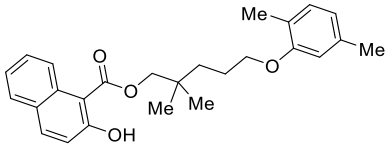


((3aR,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-3a-yl)methyl 2-hydroxy-1-naphthoate (31a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 8.67 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.56 (dd, *J* = 8.0, *J* = 1.5 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.26 – 7.17 (m, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.50 (dd, *J* = 7.9, *J* = 2.7 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.27 (d, *J* = 2.7 Hz, 1H), 4.10 (dd, *J* = 7.9, *J* = 1.6 Hz, 1H), 3.82 (dd, *J* = 13.0, *J* = 1.9 Hz, 1H), 3.69 (dd, *J* = 13.0, *J* = 0.8 Hz, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 1.21 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 163.5, 136.6, 131.5, 128.7, 128.4, 128.3, 125.3, 123.5, 119.0, 108.9, 108.9, 104.8, 101.1, 70.8, 70.5, 69.8, 65.6, 61.3, 26.3, 25.6, 24.9, 23.8. HRMS (ESI): Calculated for $C_{23}H_{25}O_8$ [M-H]$^-$: 429.1544; Found: 429.1546.

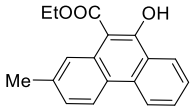


2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)ethyl 2-hydroxy-1-naphthoate (32a). Colorless solid. Mp = 159.2 – 160.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.13 (s, 1H), 8.49 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.22 (m, 3H), 7.05 – 7.01 (m, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.61 – 6.56 (m, 1H), 4.65 (t, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 168.2, 164.3, 156.0, 139.0, 136.9, 135.4, 133.8, 131.6, 131.0, 130.9, 130.5, 129.0, 128.9, 128.5, 128.4, 125.1, 123.6,

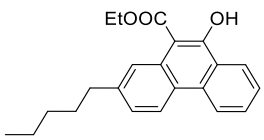
119.2, 115.1, 114.9, 111.5, 104.5, 101.0, 64.4, 55.6, 23.7, 13.3. HRMS (ESI): Calculated for $C_{30}H_{23}ClNO_5$ [M-H]$^-$: 512.1259; Found: 512.1257.



5-(2,5-Dimethylphenoxy)-2,2-dimethylpentyl 2-hydroxy-1-naphthoate (33a). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.32 (s, 1H), 8.75 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.32 – 7.23 (m, 1H), 7.13 – 7.05 (m, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 4.23 (s, 2H), 3.85 (t, *J* = 6.2 Hz, 2H), 2.20 (s, 3H), 2.01 (s, 3H), 1.81 – 1.73 (m, 2H), 1.58 – 1.52 (m, 2H), 1.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 164.5, 156.9, 136.8, 136.4, 131.8, 130.2, 129.1, 128.6, 128.3, 125.2, 123.6, 123.5, 120.6, 119.4, 111.9, 104.8, 74.0, 68.1, 35.7, 34.9, 33.8, 24.7, 24.1, 21.4, 15.7. HRMS (ESI): Calculated for $C_{26}H_{29}O_4$ [M-H]$^-$: 405.2060; Found: 405.2070.

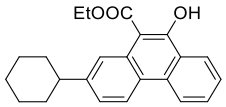


Ethyl 10-hydroxy-7-methylphenanthrene-9-carboxylate (34a).[2] Colorless solid. Mp = 131.6 – 133.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.25 (s, 1H), 8.55 (s, 1H), 8.48 (t, *J* = 8.3 Hz, 2H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.60 – 7.53 (m, 1H), 7.28 – 7.23 (m, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 162.7, 137.2, 133.6, 130.3, 129.4, 126.3, 125.9, 125.6, 124.8, 124.8, 123.8, 122.6, 122.1, 101.3, 61.9, 22.1, 14.2. HRMS (ESI): Calculated for $C_{18}H_{15}O_3$ [M-H]$^-$: 279.1016; Found: 279.1020.

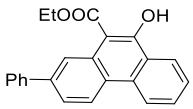


Ethyl 10-hydroxy-7-pentylphenanthrene-9-carboxylate (35a).[6] Colorless solid. Mp = 75.1 – 76.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.17 (s, 1H), 8.52 (d, *J* = 1.8

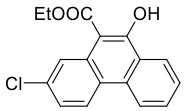
Hz, 1H), 8.42 (dd, *J* = 8.2, *J* =1.5 Hz, 2H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.51 – 7.47 (m, 1H), 7.21 (dd, *J* = 8.4, *J* =1.8 Hz, 1H), 4.52 – 4.45 (m, 2H), 2.68 (t, *J* = 7.7 Hz, 2H), 1.68 – 1.60 (m, 2H), 1.48 – 1.44 (m, 3H), 1.31 – 1.27 (m, 4H), 0.84 – 0.81 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 162.7, 142.1, 133.7, 130.3, 129.4, 126.3, 125.3, 125.1, 124.9, 124.8, 124.05, 122.7, 122.2, 101.4, 61.9, 36.4, 31.5, 31.0, 22.6, 14.2, 14.0. HRMS (ESI): Calculated for $C_{22}H_{23}O_3$ $[M-H]^-$: 335.1642; Found: 335.1642.



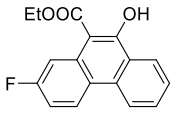
Ethyl 7-cyclohexyl-10-hydroxyphenanthrene-9-carboxylate (36a).[6] Colorless solid. Mp = 156.6 – 158.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.19 (s, 1H), 8.57 (d, *J* = 1.8 Hz, 1H), 8.46 – 8.38 (m, 2H), 8.36 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.52 – 7.44 (m, 1H), 7.24 (dd, *J* = 8.5, *J* = 1.8 Hz, 1H), 4.49 (q, *J* = 7.2 Hz, 2H), 2.61 – 2.51 (m, 1H), 1.96 – 1.86 (m, 2H), 1.84 – 1.76 (m, 2H), 1.76 – 1.66 (m, 1H), 1.50 – 1.45 (m, 4H), 1.43 – 1.38 (m, 2H), 1.37 – 1.31 (m, 1H), 1.25 – 1.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 162.7, 147.2, 133.7, 130.3, 129.5, 126.3, 124.9, 124.8, 124.2, 123.8, 123.6, 122.7, 122.2, 101.5, 61.9, 44.9, 34.6, 26.9, 26.3, 14.3. HRMS (ESI): Calculated for $C_{23}H_{23}O_3$ $[M-H]^-$: 347.1642; Found: 347.1643.



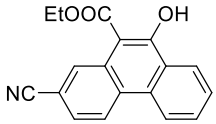
Ethyl 10-hydroxy-7-phenylphenanthrene-9-carboxylate (37a).[7] Colorless solid. Mp = 204.4 – 205.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.31 (s, 1H), 8.98 (d, *J* = 1.9 Hz, 1H), 8.48 – 8.41 (m, 3H), 7.66 – 7.59 (m, 4H), 7.54 – 7.49 (m, 1H), 7.43 – 7.37 (m, 2H), 7.33 – 7.27 (m, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 163.2, 141.4, 139.8, 133.4, 130.5, 129.7, 128.8, 127.3, 127.2, 126.8, 125.2, 125.1, 125.0, 124.5, 123.3, 123.1, 122.4, 101.4, 62.0, 14.3. HRMS (ESI): Calculated for $C_{23}H_{17}O_3$ $[M-H]^-$: 341.1172; Found: 341.1172.



Ethyl 7-chloro-10-hydroxyphenanthrene-9-carboxylate (38a).[6] Colorless solid. Mp = 150.9 – 151.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.43 (s, 1H), 8.76 – 8.66 (m, 1H), 8.44 (d, *J* = 8.3 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.31 (d, *J* = 8.9 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.60 – 7.55 (m, 1H), 7.36 – 7.29 (m, 1H), 4.56 (q, *J* = 7.1, 6.7 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 163.6, 133.6, 132.9, 130.6, 130.4, 126.9, 125.4, 125.4, 125.0, 124.3, 124.2, 124.0, 122.2, 100.4, 62.3, 14.2. HRMS (ESI): Calculated for $C_{17}H_{12}ClO_3$ $[M-H]^-$: 299.0469; Found: 299.0470.

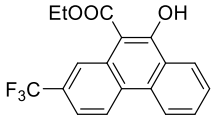


Ethyl 7-fluoro-10-hydroxyphenanthrene-9-carboxylate (39a).[6] Colorless solid. Mp = 152.1 – 152.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.41 (s, 1H), 8.37 – 8.25 (m, 4H), 7.63 – 7.56 (m, 1H), 7.48 – 7.44 (m, 1H), 7.07 – 7.01 (m, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 163.9, 162.1 (d, *J* = 244.0 Hz), 133.2, 131.0 (d, *J* = 13.0 Hz), 130.6, 126.5, 125.0, 124.7 (d, *J* = 9.6 Hz), 124.6, 122.4, 122.1, 112.4 (d, *J* = 23.5 Hz), 111.4 (d, *J* = 25.6 Hz), 100.8 (d, *J* = 2.0 Hz),), 62.2, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2. HRMS (ESI): Calculated for $C_{17}H_{12}FO_3$ $[M-H]^-$: 283.0765; Found: 283.0783.

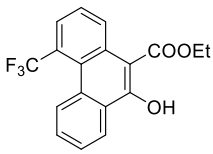


Ethyl 7-cyano-10-hydroxyphenanthrene-9-carboxylate (40a).[6] Colorless solid. Mp = 232.6 – 233.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.48 (s, 1H), 8.99 (s, 1H), 8.46 – 8.35 (m, 3H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz,

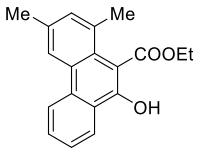
$CDCl_3$) δ 172.2, 164.1, 132.3, 131.1, 131.0, 129.3, 128.6, 128.5, 126.2, 125.8, 125.3, 123.7, 122.9, 119.7, 110.9, 100.5, 62.7, 14.3. HRMS (ESI) Calculated for $C_{18}H_{12}NO_3$ $[M-H]^-$: 290.0812; Found: 290.0819.



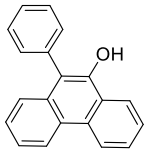
Ethyl 10-hydroxy-7-(trifluoromethyl)phenanthrene-9-carboxylate (41a).[6] Colorless solid. Mp = 183.0 – 184.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.41 (s, 1H), 9.06 (s, 1H), 8.49 – 8.41 (m, 3H), 7.73 – 7.66 (m, 1H), 7.62 – 7.52 (m, 2H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 163.6, 132.4, 130.7, 129.1, 128.8, 128.8 (d, *J* = 32.0 Hz), 127.8, 127.7, 125.9, 125.7, 125.0 (q, *J* = 261.3 Hz), 123.2, 122.5, 119.9 (q, *J* = 4.0 Hz), 100.8, 62.3, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3. HRMS (ESI): Calculated for $C_{18}H_{12}F_3O_3$ $[M-H]^-$: 333.0733; Found: 333.0754.



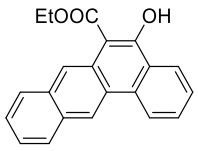
Ethyl 10-hydroxy-5-(trifluoromethyl)phenanthrene-9-carboxylate (42a). Colorless solid. Mp = 105.6 – 106.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.09 (s, 1H), 8.74 (d, *J* = 8.3 Hz, 1H), 8.44 (dd, *J* = 7.4, 2.5 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.58 (m, 2H), 7.41 (t, *J* = 8.1 Hz, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 162.4, 131.4, 131.1, 129.1, 129.0, 128.3 (q, *J* = 7.8 Hz), 126.9, 126.1, 126.0 (d, *J* = 30.5 Hz), 125.7 (d, *J* = 366.0 Hz), 125.7, 124.9 (q, *J* = 6.9 Hz), 124.5 (q, *J* = 1.5 Hz), 124.2, 101.3, 62.2, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.9. HRMS (ESI) Calculated for $C_{18}H_{12}F_3O_3$ $[M-H]^-$: 333.0733; Found: 333.0739.



Ethyl 10-hydroxy-6,8-dimethylphenanthrene-9-carboxylate (43a).[2] Colorless solid. Mp = 141.5 – 142.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.72 (s, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 8.1 Hz, 1H), 8.10 (s, 1H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.50 (t, 1H), 7.14 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 157.6, 133.9, 133.5, 132.0, 129.8, 127.2, 126.7, 126.5, 124.6, 124.4, 122.7, 120.3, 103.6, 61.7, 22.8, 21.4, 14.1. HRMS (ESI): Calculated for $C_{19}H_{17}O_3$ [M-H]$^-$: 293.1172; Found: 293.1172.

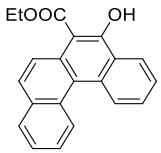


10-Phenylphenanthren-9-ol (44a).[8] Pink solid. Mp = 182.2 – 183.2 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 – 8.55 (m, 2H), 8.30 (d, *J* = 8.0 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 6.8 Hz, 1H), 7.38 (t, *J* = 6.2 Hz, 3H), 7.34 – 7.28 (m, 2H), 5.37 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 134.4, 132.4, 131.4, 131.0, 129.8, 128.6, 127.2, 126.8, 126.6, 126.3, 125.3, 124.9, 124.0, 123.0, 122.6, 122.5, 117.2. HRMS (ESI): Calculated for $C_{20}H_{13}O$ [M-H]$^-$: 269.0961; Found: 269.0970.

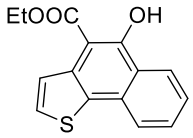


Ethyl 5-hydroxytetraphene-6-carboxylate (45a).[2] Colorless solid. Mp = 153.4 – 154.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 8.56 – 8.50 (m, 2H), 8.42 (d, *J* = 8.9 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.74 – 7.70 (m, 1H), 7.64 – 7.59 (m, 1H), 7.52 – 7.47 (m, 1H), 7.46 – 7.41 (m, 1H), 4.31 (q, 2H), 1.10 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4,

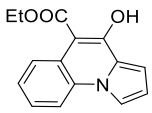
158.5, 133.1, 132.9, 130.0, 129.4, 128.9, 127.7, 126.7, 126.6, 126.0, 125.8, 124.6, 124.6, 124.2, 123.9, 122.9, 120.1, 103.7, 61.6, 13.7. HRMS (ESI): Calculated for $C_{21}H_{15}O_3$ $[M-H]^-$: 315.1016; Found: 315.1021.



Ethyl 5-hydroxybenzo[c]phenanthrene-6-carboxylate (46a).[2] Colorless solid. Mp = 124.9 – 125.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.99 (s, 1H), 8.66 – 8.60 (m, 2H), 8.54 – 8.48 (m, 2H), 7.79 – 7.75 (m, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.50 – 7.44 (m, 1H), 7.43 – 7.38 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 161.6, 132.9, 131.5, 129.6, 129.0, 128.2, 128.0, 127.6, 127.6, 127.2, 125.8, 125.6, 125.4, 125.0, 124.2, 123.7, 122.3, 102.2, 61.9, 14.1. HRMS (ESI): Calculated for $C_{21}H_{15}O_3$ $[M-H]^-$: 315.1016; Found: 315.1026.

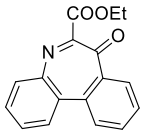


Ethyl 5-hydroxynaphtho[1,2-b]thiophene-4-carboxylate (47a).[6] Colorless solid. Mp = 104.6 – 106.1 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.70 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 5.4 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.30 – 7.22 (m, 1H), 7.17 (d, *J* = 5.5 Hz, 1H), 4.26 (q, *J* = 6.7 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 161.5, 133.3, 131.3, 129.9, 129.9, 126.2, 125.2, 125.0, 124.9, 123.0, 123.0, 101.3, 61.6, 14.1. HRMS (ESI): Calculated for $C_{15}H_{11}O_3S$ $[M-H]^-$: 271.0423; Found: 271.0423.

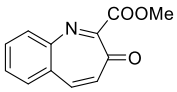


Ethyl 4-hydroxypyrrolo[1,2-a]quinoline-5-carboxylate (48a).[2] Colorless solid. Mp = 123.2 – 124.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.32 (s, 1H), 8.49 – 8.41 (m,

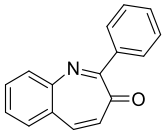
1H), 7.70 – 7.66 (m, 1H), 7.60 – 7.54 (m, 1H), 7.17 – 7.11 (m, 2H), 6.97 – 6.92 (m, 1H), 6.65 – 6.61 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 159.5, 129.1, 126.6, 124.9, 124.5, 124.3, 121.1, 116.0, 114.0, 113.4, 107.3, 94.0, 61.6, 14.2. HRMS (ESI): Calculated for $C_{15}H_{12}NO_3$ $[M-H]^-$: 254.0812; Found: 254.0823.



Ethyl 7-oxo-7*H*-dibenzo[b,d]azepine-6-carboxylate (1). Yellow solid (22.6 mg, 80% yield). Mp = 138.2 – 140.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 162.5, 154.7, 142.3, 141.5, 135.6, 132.7, 131.6, 130.7, 130.4, 129.1, 129.0, 128.7, 128.5, 126.1, 62.6, 14.0. HRMS (ESI): Calculated for $C_{17}H_{14}NO_3$ $[M+H]^+$: 280.0968; Found: 280.0981.

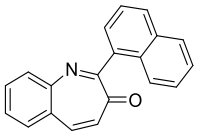


Methyl 3-oxo-3*H*-benzo[b]azepine-2-carboxylate (2). Yellow solid (14.2 mg, 68% yield). Mp = 78.2 – 80.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 1H), 7.68 – 7.61 (m, 2H), 7.58 – 7.51 (m, 2H), 6.77 (d, *J* = 12.1 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.2, 156.1, 144.7, 143.8, 135.4, 133.4, 132.9, 132.2, 131.5, 131.2, 52.9. HRMS (ESI): Calculated for $C_{12}H_9NO_3Na$ $[M+Na]^+$: 238.0475; Found: 238.0474.

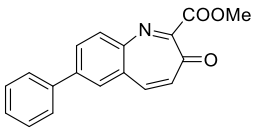


2-Phenyl-3*H*-benzo[*b*]azepin-3-one (3). Brown solid (10.3 mg, 46% yield). Mp = 82.4 – 84.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.01 (m, 2H), 7.94 (d, *J* = 8.0

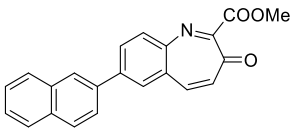
Hz, 1H), 7.66 – 7.64 (m, 2H), 7.53 (d, *J* = 12.0 Hz, 1H), 7.39 – 7.36 (m, 4H), 6.73 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 160.3, 145.7, 141.5, 137.1, 133.1, 131.8, 131.5, 131.0, 130.8, 129.4, 129.3, 128.3, 127.9. HRMS (ESI): Calculated for $C_{16}H_{11}NONa$ $[M+Na]^+$: 256.0733; Found: 256.0733.



2-(Naphthalen-1-yl)-3*H*-benzo[b]azepin-3-one (4). Yellow solid (12.2 mg, 44% yield). Mp = 206.8 – 208.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.77 (m, 4H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.62 – 7.53 (m, 3H), 7.51 – 7.35 (m, 4H), 6.82 (d, *J* = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 164.1, 145.7, 142.7, 137.5, 134.2, 133.7, 132.4, 132.0, 131.5, 130.6, 130.1, 129.8, 129.1, 128.6, 127.7, 126.5, 125.9, 125.2, 124.8. HRMS (ESI): Calculated for $C_{20}H_{13}NONa$ $[M+Na]^+$: 306.0889; Found: 306.0888.

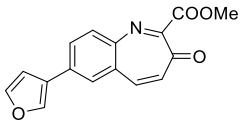


Methyl 3-oxo-7-phenyl-3*H*-benzo[*b*]azepine-2-carboxylate (5). Yellow solid (22.7 mg, 78% yield). Mp = 139.8 – 142.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.58 – 7.51 (m, 3H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 1H), 6.75 (d, *J* = 12.1 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 166.3, 155.7, 143.9, 143.8, 143.6, 138.3, 136.0, 133.0, 131.8, 131.5, 130.5, 129.1, 128.7, 127.1, 52.8. HRMS (ESI): Calculated for $C_{18}H_{13}NO_3Na$ $[M+Na]^+$: 314.0787; Found: 314.0782.

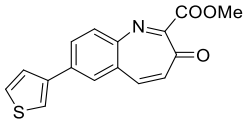


Methyl 7-(naphthalen-2-yl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (6).

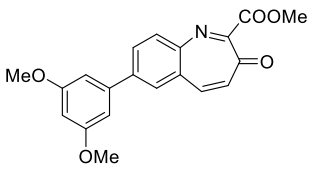
Yellow solid (20.1 mg, 59% yield). Mp = 206.2 – 208.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H), 8.07 – 8.01 (m, 1H), 7.99 – 7.94 (m, 2H), 7.94 – 7.86 (m, 2H), 7.80 – 7.74 (m, 1H), 7.65 (d, *J* = 12.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 6.86 (d, *J* = 12.1 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.3, 155.7, 143.7, 143.6, 143.7, 136.1, 135.6, 133.4, 133.1, 133.0, 131.9, 131.7, 130.7, 129.0, 128.3, 127.7, 126.8, 126.7, 126.5, 124.7, 52.9. HRMS (ESI): Calculated for $C_{22}H_{16}NO_3$ $[M+H]^+$: 342.1125; Found: 342.1124.



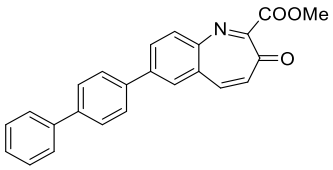
Methyl 7-(furan-3-yl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (7). Yellow solid (11.8 mg, 42% yield). Mp = 227.2 – 229.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.78 – 7.73 (m, 1H), 7.71 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 12.1 Hz, 1H), 7.51 – 7.46 (m, 1H), 6.79 (d, *J* = 12.1 Hz, 1H), 6.74 – 6.70 (m, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 166.4, 155.4, 144.5, 143.6, 143.4, 140.1, 136.2, 135.7, 133.3, 132.2, 129.9, 129.2, 124.7, 108.4, 52.9. HRMS (ESI): Calculated for $C_{16}H_{12}NO_4$ $[M+H]^+$: 282.0760; Found: 282.0755.



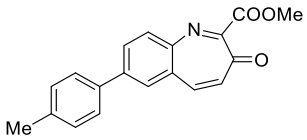
Methyl 3-oxo-7-(thiophen-3-yl)-3*H*-benzo[*b*]azepine-2-carboxylate (8) . Yellow solid (21.4 mg, 72% yield). Mp = 230.4 – 232.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.87 (m, 2H), 7.68 – 7.61 (m, 2H), 7.48 (d, *J* = 2.2 Hz, 2H), 6.86 (d, *J* = 12.1 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.3, 155.4, 143.7, 143.4, 139.7, 138.5, 136.2, 133.2, 132.1, 130.6, 129.8, 127.3, 125.9, 122.8, 52.9. HRMS (ESI): Calculated for $C_{16}H_{12}NO_3S$ $[M+H]^+$: 298.0532; Found: 298.0532.



Methyl 7-(3,5-dimethoxyphenyl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (9). Yellow solid (22.8 mg, 66% yield). Mp = 241.6 – 243.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.79 (d, *J* = 2.2 Hz, 1H), 7.58 (d, *J* = 12.1 Hz, 1H), 6.80 (d, *J* = 12.2 Hz, 1H), 6.71 (d, *J* = 2.2 Hz, 2H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.3, 161.3, 155.8, 144.0, 143.9, 143.8, 140.6, 136.0, 133.2, 131.9, 131.7, 130.7, 105.6, 100.4, 55.5, 53.0. HRMS (ESI): Calculated for $C_{20}H_{18}NO_5$ $[M+H]^+$: 352.1179; Found: 352.1184.

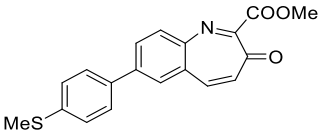


Methyl 7-([1,1'-biphenyl]-4-yl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (10). Yellow solid (16.1 mg, 44% yield). Mp = 237.8 – 239.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.88 (m, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.70 – 7.65 (m, 4H), 7.61 – 7.56 (m, 3H), 7.43 – 7.38 (m, 2H), 7.35 – 7.29 (m, 1H), 6.80 (d, *J* = 12.1 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 166.3, 155.7, 143.8, 143.8, 143.5, 141.6, 140.1, 137.2, 136.2, 133.2, 132.0, 131.4, 130.5, 128.9, 127.8, 127.8, 127.6, 127.0, 52.9. HRMS (ESI): Calculated for $C_{24}H_{17}NO_3Na$ $[M+Na]^+$: 390.1100; Found: 390.1099.

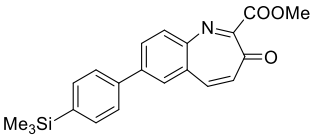


Methyl 3-oxo-7-(p-tolyl)-3*H*-benzo[*b*]azepine-2-carboxylate (11). Yellow solid (22.0 mg, 72% yield). Mp = 192.8 – 194.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.89 (m, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.64 (d, *J* = 12.2 Hz,

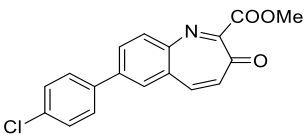
1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 12.1 Hz, 1H), 3.99 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.4, 155.5, 143.9, 143.9, 143.5, 138.9, 136.1, 135.5, 133.1, 131.9, 131.3, 130.4, 129.9, 127.0, 52.9, 21.2. HRMS (ESI): Calculated for $C_{19}H_{15}NO_3Na$ $[M+Na]^+$: 328.0944; Found: 328.0937.



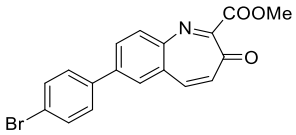
Methyl 7-(4-(methylthio)phenyl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (12). Yellow solid (18.5 mg, 56% yield). Mp = 192.6 – 194.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.3 Hz, 1H), 7.91 – 7.83 (m, 2H), 7.66 – 7.56 (m, 3H), 7.38 – 7.31 (m, 2H), 6.85 (d, *J* = 12.1 Hz, 1H), 3.99 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.3, 155.6, 143.7, 143.5, 143.2, 140.0, 136.1, 134.7, 133.1, 132.0, 131.0, 130.1, 127.4, 126.5, 52.9, 15.3. HRMS (ESI): Calculated for $C_{19}H_{16}NO_3S$ $[M+H]^+$: 338.0845; Found: 338.0847.



Methyl 3-oxo-7-(4-(trimethylsilyl)phenyl)-3*H*-benzo[*b*]azepine-2-carboxylate (13). Yellow solid (24.3 mg, 68% yield). Mp = 205.6 – 207.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 1H), 7.97 – 7.86 (m, 2H), 7.73 – 7.62 (m, 5H), 6.86 (d, *J* = 12.1 Hz, 1H), 3.99 (s, 3H), 0.32 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.3, 155.7, 143.9, 143.8, 143.7, 141.4, 138.7, 136.1, 134.1, 133.1, 131.9, 131.6, 130.5, 126.4, 52.8, -1.2. HRMS (ESI): Calculated for $C_{21}H_{22}NO_3Si$ $[M+H]^+$: 364.1363; Found: 364.1364.

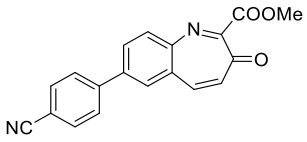


Methyl 7-(4-chlorophenyl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (14). Yellow solid (17.9 mg, 56% yield). Mp = 238.2 – 240.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.82 (m, 2H), 7.67 – 7.57 (m, 3H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 12.1 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 166.2, 155.8, 143.8, 143.6, 142.6, 136.8, 136.1, 135.0, 133.2, 131.9, 131.4, 130.3, 129.3, 128.4, 52.9. HRMS (ESI): Calculated for $C_{18}H_{13}ClNO_3$ $[M+H]^+$: 326.0578; Found: 326.0577.



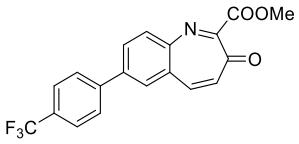
Methyl 7-(4-bromophenyl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (15).

Yellow solid (19.6 mg, 53% yield). Mp = 208.8 – 210.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.78 (d, *J* = 2.2 Hz, 1H), 7.60 – 7.54 (m, 3H), 7.49 – 7.45 (m, 2H), 6.81 (d, *J* = 12.2 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 166.2, 155.9, 143.9, 143.6, 142.7, 137.4, 136.2, 133.4, 132.3, 132.0, 131.4, 130.3, 128.8, 123.3, 51.0. HRMS (ESI): Calculated for $C_{18}H_{12}BrNO_3Na$ $[M+Na]^+$: 391.9893; Found: 391.9880.

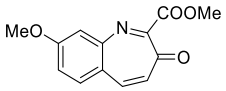


Methyl 7-(4-cyanophenyl)-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (16).

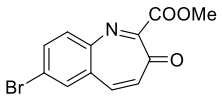
Yellow solid (9.5 mg, 32% yield). Mp = 296.4 – 298.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.76 – 7.70 (m, 4H), 7.60 (d, *J* = 12.1 Hz, 1H), 6.83 (d, *J* = 12.0 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 166.0, 156.3, 144.6, 143.2, 142.9, 141.7, 136.3, 133.6, 132.9, 132.0, 131.8, 130.5, 128.0, 118.4, 112.4, 53.0. HRMS (ESI): Calculated for $C_{19}H_{13}N_2O_3$ $[M+H]^+$: 317.0921; Found: 317.0918.



Methyl 3-oxo-7-(4-(trifluoromethyl)phenyl)-3*H*-benzo[*b*]azepine-2-carboxylate (17). Yellow solid (25.5 mg, 71% yield). Mp = 225.8 – 227.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.82 – 7.75 (m, 4H), 7.67 (d, *J* = 12.2 Hz, 1H), 6.88 (d, *J* = 12.1 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 166.1, 156.2, 144.3, 143.4, 142.3, 142.0, 136.2, 133.4, 132.0, 131.8, 130.8, 130.6, 130.5, 127.6, 126.1 (q, *J* = 3.9 Hz), 53.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9. HRMS (ESI): Calculated for $C_{19}H_{12}F_3NO_3Na$ $[M+Na]^+$: 382.0662; Found: 382.0650.

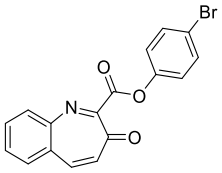


Methyl 8-methoxy-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (18). Yellow solid (13.5 mg, 55% yield). Mp = 138.0 – 140.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 12.0 Hz, 1H), 7.38 (d, *J* = 2.8 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.64 (d, *J* = 11.9 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 166.5, 162.4, 157.2, 146.5, 143.7, 134.9, 130.2, 125.1, 119.5, 117.5, 55.8, 52.8. HRMS (ESI): Calculated for $C_{13}H_{11}NO_4Na$ $[M+Na]^+$: 268.0580; Found: 268.0578.

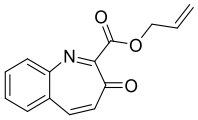


Methyl 7-bromo-3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (19). Yellow solid (16.6 mg, 58% yield). Mp = 174.2 – 175.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 3H), 7.42 (d, *J* = 12.2 Hz, 1H), 6.80 (d, *J* = 12.2 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 165.9, 156.1, 143.5, 142.1, 136.8, 135.5, 135.1,

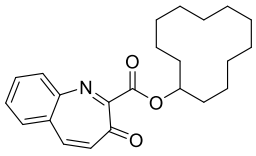
134.1, 132.7, 125.3, 53.0. HRMS (ESI): Calculated for $C_{12}H_8BrNO_3Na$ $[M+Na]^+$: 315.9579; Found: 315.9573.



4-Bromophenyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (20). Yellow solid (14.5 mg, 41% yield). Mp = 191.6 – 193.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.71 – 7.63 (m, 2H), 7.60 – 7.51 (m, 2H), 7.25 – 7.20 (m, 2H), 6.90 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 164.1, 155.6, 149.5, 144.7, 144.3, 135.8, 133.7, 133.0, 132.6, 132.4, 131.7, 131.7, 123.4, 119.5. HRMS (ESI): Calculated for $C_{17}H_{10}BrNO_3Na$ $[M+Na]^+$: 377.9736; Found: 377.9743.

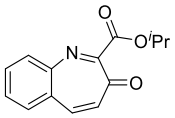


Allyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (21). Yellow solid (12.1 mg, 52% yield). Mp = 96.4 – 98.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.58 – 7.50 (m, 2H), 6.77 (d, *J* = 12.0 Hz, 1H), 6.02 – 5.88 (m, 1H), 5.45 – 5.36 (m, 1H), 5.28 – 5.21 (m, 1H), 4.85 – 4.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 165.5, 156.2, 144.8, 143.9, 135.5, 133.4, 132.9, 132.2, 131.5, 131.3, 131.2, 119.1, 66.5. HRMS (ESI): Calculated for $C_{14}H_{12}NO_3$ $[M+H]^+$: 242.0812; Found: 242.0808.

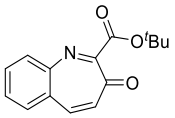


Cyclododecyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (22). Yellow solid (22.8 mg, 62% yield). Mp = 171.8 – 173.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.55 – 7.48 (m, 2H), 6.73 (d, *J* = 12.1 Hz, 1H),

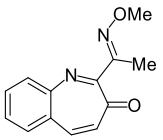
5.32 – 5.18 (m, 1H), 1.82 – 1.73 (m, 2H), 1.64 – 1.56 (m, 2H), 1.43 – 1.25 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 165.7, 157.0, 144.9, 143.8, 135.5, 133.3, 132.9, 132.0, 131.4, 130.9, 74.7, 28.7, 24.1, 24.0, 23.2, 23.0, 20.6. HRMS (ESI): Calculated for $C_{23}H_{29}NO_3Na$ $[M+Na]^+$: 390.2039; Found: 390.2039.



Isopropyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (23). Yellow oil (18.0 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.56 – 7.49 (m, 2H), 6.75 (d, *J* = 12.2 Hz, 1H), 5.31 – 5.20 (m, 1H), 1.33 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 165.6, 156.8, 144.9, 143.8, 135.5, 133.4, 133.0, 132.1, 131.5, 131.0, 70.1, 21.6. HRMS (ESI): Calculated for $C_{14}H_{14}NO_3$ $[M+H]^+$: 244.0968; Found: 244.0968.

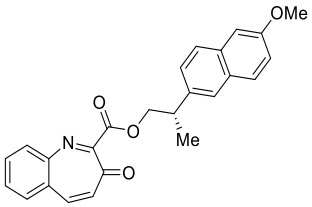


Tert-butyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (24). Brown solid (14.9 mg, 58% yield). Mp = 66.4 – 68.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.55 – 7.45 (m, 2H), 6.73 (d, *J* = 12.1 Hz, 1H), 1.55 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 165.2, 157.1, 145.0, 143.7, 135.3, 133.3, 133.0, 132.0, 131.4, 130.8, 83.6, 28.0. HRMS (ESI): Calculated for $C_{15}H_{16}NO_3$ $[M+H]^+$: 258.1125; Found: 258.1124.

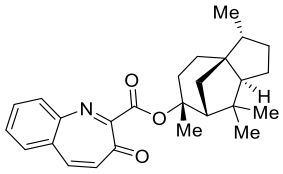


2-(1-(Methoxyimino)ethyl)-3*H*-benzo[*b*]azepin-3-one (25). Yellow solid (10.9 mg, 48% yield). Mp = 64.4 – 66.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 1H), 7.53 – 7.48 (m, 2H), 7.37 – 7.32 (m, 2H), 6.63 (d, *J* = 12.1 Hz, 1H), 3.95 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.9, 157.9, 156.1, 145.2, 140.1, 132.6,

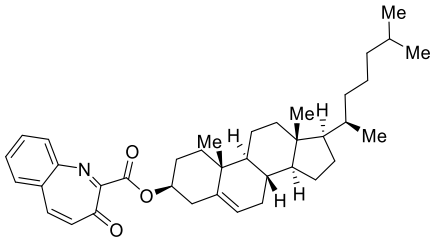
131.8, 131.6, 130.6, 129.3, 128.1, 62.7, 11.4. HRMS (ESI): Calculated for $C_{13}H_{12}N_2O_2Na$ $[M+Na]^+$: 251.0790; Found: 251.0793.



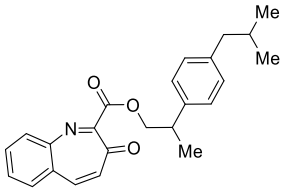
(*S*)-2-(6-methoxynaphthalen-2-yl)propyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (26). Yellow solid (12.8 mg, 33% yield). Mp = 144.6 – 146.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 1H), 7.63 – 7.55 (m, 5H), 7.52 – 7.43 (m, 2H), 7.34 – 7.29 (m, 1H), 7.10 – 6.96 (m, 2H), 6.71 (d, *J* = 12.1 Hz, 1H), 4.52 – 4.41 (m, 2H), 3.81 (s, 3H), 3.41 – 3.26 (m, 1H), 1.39 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 165.9, 157.4, 156.3, 144.7, 143.8, 137.8, 135.5, 133.5, 133.4, 132.8, 132.1, 131.5, 131.1, 129.1, 128.9, 127.0, 126.3, 125.7, 118.8, 105.5, 70.7, 55.2, 38.8, 18.0. HRMS (ESI): Calculated for $C_{25}H_{21}NO_4Na$ $[M+Na]^+$: 422.1362; Found: 422.1362.



(3*R*,3a*S*,6R,7R,8aS)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (27). Yellow solid (18.6 mg, 46% yield). Mp = 197.4 – 199.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.46 (m, 2H), 6.73 (d, *J* = 11.9 Hz, 1H), 2.38 (d, *J* = 5.0 Hz, 1H), 2.23 – 2.15 (m, 1H), 2.09 – 1.99 (m, 1H), 1.83 – 1.73 (m, 2H), 1.70 (s, 3H), 1.66 – 1.58 (m, 2H), 1.55 – 1.26 (m, 6H), 1.19 (s, 3H), 0.93 (s, 3H), 0.77 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 164.8, 157.0, 145.1, 143.6, 135.3, 133.2, 133.0, 131.9, 131.5, 130.6, 90.0, 57.8, 56.7, 53.8, 43.5, 41.2, 41.0, 36.9, 32.8, 31.3, 28.5, 27.2, 25.5, 25.3, 15.5. HRMS (ESI): Calculated for $C_{26}H_{31}NO_3Na$ $[M+Na]^+$: 428.2196; Found: 428.2199.

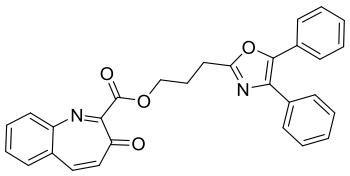


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (28). Yellow solid (25.0 mg, 44% yield). Mp = 175.4 – 177.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.56 – 7.49 (m, 2H), 6.76 (d, *J* = 12.2 Hz, 1H), 5.39 – 5.33 (m, 1H), 4.95 – 4.81 (m, 1H), 2.52 – 2.35 (m, 2H), 2.06 – 1.61 (m, 7H), 1.57 – 1.35 (m, 7H), 1.31 – 1.02 (m, 12H), 0.97 (s, 3H), 0.85 (d, *J* = 6.4 Hz, 3H), 0.79 (dd, *J* = 6.7, *J* =1.9 Hz, 6H), 0.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 165.4, 156.8, 144.9, 143.8, 139.4, 135.5, 133.4, 132.9, 132.1, 131.5, 131.0, 122.9, 76.1, 56.6, 56.1, 49.9, 42.2, 39.7, 39.5, 37.8, 36.9, 36.5, 36.1, 35.7, 31.9, 31.8, 28.2, 28.0, 27.5, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. HRMS (ESI): Calculated for $C_{38}H_{52}NO_3$ $[M+H]^+$: 570.3941; Found: 570.3941.

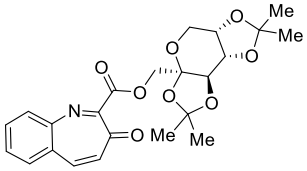


2-(4-Isobutylphenyl)propyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (29). Yellow oil (19.1 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.53 – 7.44 (m, 2H), 7.13 – 7.07 (m, 2H), 7.04 – 6.98 (m, 2H), 6.71 (d, *J* = 12.1 Hz, 1H), 4.45 – 4.36 (m, 1H), 4.38 – 4.27 (m, 1H), 3.21 – 3.10 (m, 1H), 2.35 (d, *J* = 7.1 Hz, 2H), 1.81 – 1.71 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 165.8, 156.3, 144.7, 143.7, 140.0, 139.8, 135.4, 133.4, 132.8, 132.0, 131.4, 131.1, 129.2, 127.0, 70.8, 44.9, 38.4,

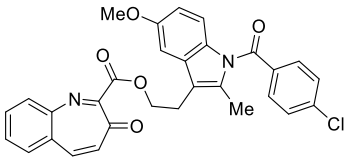
30.1, 22.3, 17.9. HRMS (ESI): Calculated for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907; Found: 376.1917.



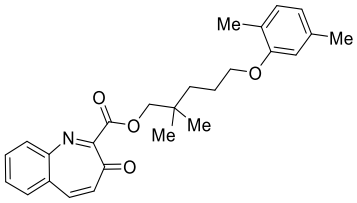
3-(4,5-Diphenyloxazol-2-yl)propyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (30). Yellow solid (31.4 mg, 68% yield). Mp = 68.2 – 70.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.40 (m, 8H), 7.25 – 7.16 (m, 6H), 6.67 (d, *J* = 12.1 Hz, 1H), 4.47 (t, *J* = 6.2 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.30 – 2.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.2, 165.8, 162.2, 156.2, 145.1, 144.5, 143.8, 135.3, 134.9, 133.3, 132.6, 132.3, 132.0, 131.3, 131.1, 128.8, 128.4, 128.3, 128.2, 127.8, 127.7, 126.2, 64.8, 25.8, 24.6. HRMS (ESI): Calculated for $C_{29}H_{23}N_2O_4$ $[M+H]^+$: 463.1652; Found: 463.1653.



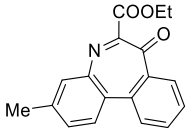
((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (31). Yellow solid (26.6 mg, 60% yield). Mp = 88.2 – 90.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.58 – 7.50 (m, 2H), 6.73 (d, *J* = 12.1 Hz, 1H), 4.60 – 4.47 (m, 2H), 4.41 – 4.31 (m, 2H), 4.20 – 4.14 (m, 1H), 3.92 – 3.82 (m, 1H), 3.70 (d, *J* = 13.0 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 164.7, 155.2, 144.4, 143.7, 135.1, 133.4, 132.7, 132.1, 131.4, 131.2, 109.0, 108.9, 101.2, 70.6, 70.0, 69.9, 65.4, 61.2, 26.4, 25.7, 25.2, 24.0. HRMS (ESI): Calculated for $C_{23}H_{25}NO_8Na$ $[M+Na]^+$: 466.1472; Found: 466.1470.



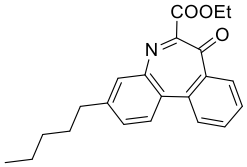
2-(1-(4-Chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)ethyl 3-oxo-3*H*-benzo[*b*]azepine-2-carboxylate (32). Yellow solid (38.9 mg, 74% yield). Mp = 154.2 – 156.8 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.66 – 7.51 (m, 6H), 7.40 – 7.31 (m, 2H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 1H), 6.74 (d, *J* = 12.2 Hz, 1H), 6.62 – 6.55 (m, 1H), 4.50 (t, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 3.09 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 168.3, 165.7, 156.0, 155.9, 144.7, 143.8, 139.0, 135.5, 135.4, 134.0, 133.4, 132.8, 132.2, 131.5, 131.2, 131.1, 130.9, 130.8, 129.0, 115.0, 114.9, 111.5, 100.9, 64.8, 55.6, 23.5, 13.3. HRMS (ESI): Calculated for $C_{30}H_{24}ClN_2O_5$ $[M+H]^+$: 527.1368; Found: 527.1364.



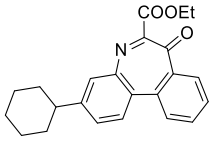
5-(2,5-Dimethylphenoxy)-2,2-dimethylpentyl 3-oxo-3*H*-benzo[*b*] azepine-2-carboxylate (33). Yellow oil (22.2 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.52 – 7.42 (m, 2H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.75 – 6.68 (m, 1H), 6.53 (d, *J* = 8.9 Hz, 2H), 4.08 (s, 2H), 3.87 – 3.79 (m, 2H), 2.19 (s, 3H), 2.05 (s, 3H), 1.77 – 1.67 (m, 2H), 1.47 – 1.39 (m, 2H), 0.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 166.0, 156.9, 156.5, 144.7, 143.7, 136.3, 135.4, 133.3, 132.7, 132.0, 131.4, 131.0, 130.1, 123.4, 120.5, 111.8, 73.3, 68.2, 35.2, 33.9, 24.1, 24.0, 21.3, 15.7. HRMS (ESI): Calculated for $C_{26}H_{29}NO_4Na$ $[M+Na]^+$: 442.1988; Found: 422.1987.



Ethyl 3-methyl-7-oxo-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (34). Yellow solid (22.3 mg, 76% yield). Mp = 152.2 – 154.4 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 1H), 7.77 – 7.65 (m, 4H), 7.63 – 7.58 (m, 1H), 7.31 – 7.27 (m, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 162.7, 154.5, 142.2, 141.2, 139.3, 135.8, 132.7, 130.7, 130.5, 129.9, 129.0, 128.9, 128.3, 126.3, 62.6, 20.8, 14.0. HRMS (ESI): Calculated for $C_{18}H_{16}NO_3$ $[M+H]^+$: 294.1125; Found: 294.1138.

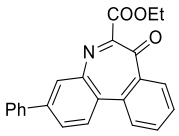


Ethyl 7-oxo-3-pentyl-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (35). Yellow oil (24.4 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.70 – 7.57 (m, 4H), 7.56 – 7.51 (m, 1H), 7.25 – 7.20 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.57 (m, 2H), 1.36 – 1.24 (m, 7H), 0.86 – 0.78 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 162.7, 154.5, 144.4, 142.3, 141.2, 135.9, 132.7, 130.6, 130.2, 129.3, 129.2, 128.9, 128.4, 126.3, 62.7, 35.2, 31.3, 30.6, 22.5, 14.1, 14.0. HRMS (ESI): Calculated for $C_{22}H_{24}NO_3$ $[M+H]^+$: 350.1751; Found: 350.1754.

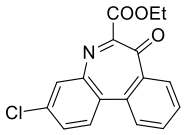


Ethyl 3-cyclohexyl-7-oxo-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (36). Yellow solid (22.0 mg, 61% yield). Mp = 142.4 – 144.6 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.58 (m, 4H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.22 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.59 – 2.47 (m, 1H), 1.88 – 1.76 (m, 4H), 1.73 – 1.66 (m, 1H), 1.44 – 1.29 (m, 7H), 1.22 – 1.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 162.8, 154.4, 149.4, 142.4, 141.2, 135.9, 132.7, 130.6, 129.3, 128.9, 128.6,

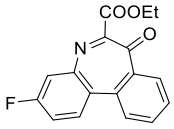
128.4, 127.9, 126.3, 62.6, 43.9, 34.1, 26.7, 26.0, 14.0. HRMS (ESI): Calculated for $C_{23}H_{23}NO_3Na$ $[M+Na]^+$: 384.1570; Found: 384.1571.



Ethyl 7-oxo-3-phenyl-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (37). Yellow solid (24.9 mg, 72% yield). Mp = 200.2 – 202.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.69 – 7.59 (m, 5H), 7.55 (dd, *J* = 7.5, *J* =1.0 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 162.6, 155.0, 142.8, 141.8, 141.3, 138.8, 135.5, 132.8, 131.2, 130.5, 129.2, 129.0, 128.7, 128.5, 128.1, 127.2, 127.0, 126.4, 62.7, 14.0. HRMS (ESI): Calculated for $C_{23}H_{17}NO_3Na$ $[M+Na]^+$: 378.1100; Found: 378.1100.

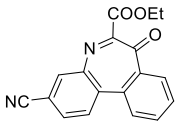


Ethyl 3-chloro-7-oxo-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (38). Yellow solid (26.3 mg, 84% yield). Mp = 138.8 – 141.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.81 (m, 2H), 7.79 – 7.71 (m, 3H), 7.69 – 7.63 (m, 1H), 7.47 – 7.41 (m, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 1.40 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 162.3, 155.8, 143.2, 141.3, 134.8, 134.7, 132.9, 131.9, 130.2, 129.8, 129.5, 128.8, 128.4, 126.4, 62.9, 14.0. HRMS (ESI): Calculated for $C_{17}H_{13}ClNO_3$ $[M+H]^+$: 314.0578; Found: 314.0579.

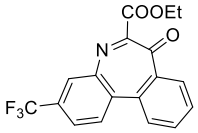


Ethyl 3-fluoro-7-oxo-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (39). Yellow solid (14.3 mg, 48% yield). Mp = 196.2 – 198.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d,

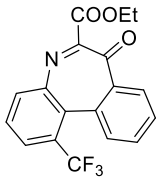
J = 7.9 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.68 – 7.61 (m, 1H), 7.56 – 7.51 (m, 1H), 7.25 – 7.17 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.1, 163.4, 162.2 (d, *J* = 250.7 Hz), 155.7, 143.8 (d, *J* = 10.2 Hz), 141.2, 135.0, 132.9, 132.6 (d, *J* = 8.8 Hz), 129.2, 128.5, 128.1 (d, *J* = 3.6 Hz), 127.0, 126.3, 116.3 (d, *J* = 22.2 Hz), 62.9, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.9. HRMS (ESI): Calculated for $C_{17}H_{13}FNO_3$ $[M+H]^+$: 298.0874; Found: 298.0882.



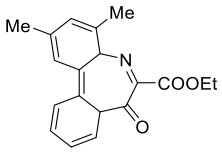
Ethyl 3-cyano-7-oxo-7*H*-dibenzo[b,d]azepine-6-carboxylate (40). Yellow solid (10.0 mg, 33% yield). Mp = 170.2 – 171.9 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.8 Hz, 1H), 7.96 – 7.89 (m, 2H), 7.84 – 7.71 (m, 4H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 162.0, 156.8, 142.8, 142.0, 135.9, 134.2, 134.1, 133.2, 131.9, 130.9, 130.6, 128.8, 126.6, 117.4, 112.9, 63.1, 14.0. HRMS (ESI) Calculated for $C_{18}H_{12}N_2O_3Na$ $[M+Na]^+$: 327.0740; Found: 327.0738.



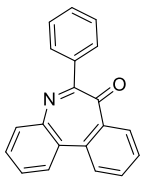
Ethyl 7-oxo-3-(trifluoromethyl)-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (41). Yellow solid (14.5 mg, 42% yield). Mp = 180.0 – 182.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 1.8 Hz, 1H), 7.94 (m, 2H), 7.84 – 7.76 (m, 2H), 7.74 – 7.69 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.7, 162.1, 156.2, 142.5, 141.9, 134.8, 134.5, 131.7 (d, *J* = 284.9 Hz), 131.6, 131.2 (d, *J* = 33.6 Hz), 129.9, 128.8, 127.7(m), 126.5, 124.8 (q, *J* = 3.8 Hz), 124.7, 63.0, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7. HRMS (ESI) Calculated for $C_{18}H_{12}F_3NO_3Na$ $[M+Na]^+$: 370.0661; Found: 370.0676.



Ethyl 7-oxo-1-(trifluoromethyl)-7*H*-dibenzo[*b,d*]azepine-6-carboxylate(42). Yellow liquid (10.7 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 1H), 7.80 (m, 2H), 7.69 – 7.57 (m, 4H), 4.40 (qd, *J* = 7.1, 2.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 161.5, 158.2, 143.4 (d, *J* = 53.8 Hz), 140.4, 137.9, 131.9 (d, *J* = 1.3 Hz), 131.3 (d, *J* = 4.8 Hz), 130.8, 130.5, 130.4, 130.4 (d, *J* = 1.5 Hz), 129.4 (d, *J* = 131.8 Hz), 127.7 (m), 125.2, 123.7, 63.0, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -53.2. HRMS (ESI) Calculated for $C_{18}H_{12}F_3NO_3Na$ $[M+Na]^+$: 370.0661; Found: 370.0661.

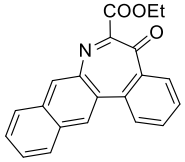


Ethyl 2,4-dimethyl-7-oxo-4a,7a-dihydro-7*H*-dibenzo[*b,d*]azepine-6-carboxylate (43). Yellow solid (15.2 mg, 51% yield). Mp = 139.4 – 141.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.54 – 7.48 (m, 1H), 7.32 (s, 1H), 7.16 (s, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 2.34 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 162.5, 152.0, 141.6, 138.9, 138.4, 138.1, 136.3, 132.4, 131.6, 131.4, 129.0, 128.9, 128.8, 125.8, 62.3, 21.4, 19.1, 14.0. HRMS (ESI): Calculated for $C_{19}H_{19}NO_3Na$ $[M+Na]^+$: 330.1100; Found: 330.1105.

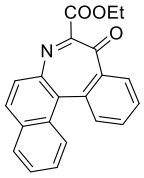


6-Phenyl-7*H*-dibenzo[*b,d*]azepin-7-one (44). Yellow solid (6.8 mg, 26% yield). Mp = 174.6 – 176.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.95 (m, 2H), 7.85 (d,

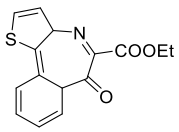
J = 8.1 Hz, 1H), 7.70 – 7.59 (m, 4H), 7.54 – 7.49 (m, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.36 (m, 3H), 7.32 – 7.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 162.5, 144.3, 142.2, 136.2, 134.2, 132.2, 131.3, 130.5, 130.4, 129.4, 128.8, 128.7, 128.6, 128.5, 128.1, 126.4, 125.2. HRMS (ESI): Calculated for $C_{20}H_{14}NO$ $[M+H]^+$: 284.1070; Found: 284.1077.



Ethyl 5-oxo-5*H*-benzo[d]naphtho[2,3-*b*]azepine-6-carboxylate (45). Yellow solid (22.0 mg, 68% yield). Mp = 140.2 – 142.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.72 (m, 4H), 7.71 – 7.66 (m, 1H), 7.62 – 7.52 (m, 3H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6, 162.4, 152.2, 141.6, 138.3, 135.9, 133.0, 132.5, 130.9, 129.3, 129.1, 129.1, 127.8, 127.7, 127.5, 127.4, 127.2, 126.0, 125.4, 62.6, 14.1. HRMS (ESI): Calculated for $C_{21}H_{16}NO_3$ $[M+H]^+$: 330.1125; Found: 330.1136.

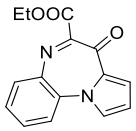


Ethyl 9-oxo-9*H*-benzo[d]naphtho[2,1-*b*]azepine-8-carboxylate (46). Yellow solid (21.7 mg, 66% yield). Mp = 162.0 – 164.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.93 – 7.88 (m, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.75 – 7.67 (m, 3H), 7.57 – 7.51 (m, 1H), 7.50 – 7.45 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 161.9, 155.3, 143.6, 140.4, 133.1, 132.8, 131.8, 131.6, 130.3, 129.6, 129.5, 128.4, 128.2, 127.8, 126.9, 126.9, 126.3, 124.3, 62.8, 14.0. HRMS (ESI): Calculated for $C_{21}H_{16}NO_3$ $[M+H]^+$: 330.1125; Found: 330.1128.

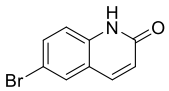


Ethyl 6-oxo-3a,6a-dihydro-6*H*-benzo[*d*]thieno[3,2-*b*]azepine-5-carboxylate (47).

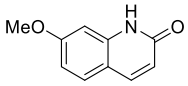
Yellow solid (17.4 mg, 62% yield). Mp = 139.3 – 140.7 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.56 (t, 1H), 7.43 (d, *J* = 5.5 Hz, 1H), 7.36 (d, *J* = 5.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.4, 164.6, 151.8, 143.3, 137.0, 136.3, 133.8, 131.4, 131.3, 130.1, 129.3, 127.4, 125.0, 62.5, 14.0. HRMS (ESI): Calculated for $C_{15}H_{13}NO_3SNa$ $[M+Na]^+$: 308.0352; Found: 308.0351.



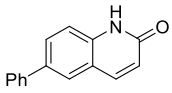
Ethyl 7-oxo-7*H*-benzo[b]pyrrolo[1,2-*d*][1,4]diazepine-6-carboxylate (48). Yellow solid (15.8 mg, 60% yield). Mp = 120.8 – 122.2 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 1H), 7.73 – 7.67 (m, 1H), 7.54 – 7.41 (m, 3H), 7.32 – 7.27 (m, 1H), 6.73 – 6.67 (m, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 164.5, 155.2, 139.9, 135.1, 133.8, 133.1, 131.1, 127.2, 127.0, 122.5, 119.5, 114.7, 62.4, 14.0. HRMS (ESI): Calculated for $C_{15}H_{13}N_2O_3$ $[M+H]^+$: 269.0921; Found: 269.0927.



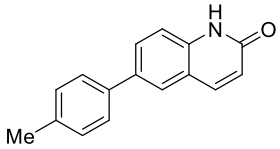
6-Bromoquinolin-2(1*H*)-one (49). Colorless solid (8.0 mg, 36% yield). Mp = 244.9 – 246.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.87 (s, 1H), 7.93 – 7.82 (m, 2H), 7.68 – 7.57 (m, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.7, 139.1, 137.9, 132.8, 129.9, 123.1, 120.8, 117.3, 113.3. HRMS (ESI): Calculated for C_9H_5BrNO $[M-H]^-$: 221.9549; Found: 221.9536.



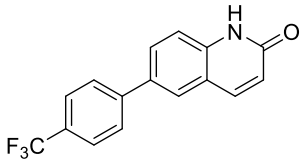
7-Methoxyquinolin-2(1*H*)-one (50). Colorless solid (6.6 mg, 38% yield). Mp = 216.8 – 217.9 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.60 (s, 1H), 7.80 (d, J = 9.5 Hz, 1H), 7.55 (d, J = 8.3 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.30 (d, J = 9.4 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.2, 161.0, 140.7, 140.0, 129.3, 118.6, 113.3, 110.6, 98.0, 55.3. HRMS (ESI): Calculated for $C_{10}H_8NO_2$ $[M-H]^-$: 174.0550; Found: 174.0538.



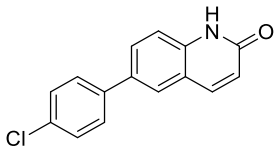
6-Phenylquinolin-2(1*H*)-one (51). Colorless solid (9.0 mg, 41% yield). Mp = 272.9 – 273.4 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (s, 1H), 7.97 (d, J = 11.0 Hz, 2H), 7.83 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.8 Hz, 2H), 7.47 (t, J = 6.9 Hz, 2H), 7.42 – 7.31 (m, 2H), 6.54 (d, J = 9.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.9, 140.4, 139.3, 138.3, 133.7, 129.0, 127.2, 126.4, 125.6, 122.3, 119.5, 115.7. HRMS (ESI): Calculated for $C_{15}H_{10}NO$ $[M-H]^-$: 220.0757; Found: 220.0745.



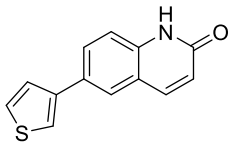
6-(*p*-Tolyl)quinolin-2(1*H*)-one (52). Colorless solid (9.5 mg, 42% yield). Mp = 304.4 – 305.7 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 8.01 – 7.89 (m, 2H), 7.80 (m, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.6 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 9.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 140.4, 138.1, 136.5, 136.5, 133.6, 129.6, 128.8, 126.3, 125.3, 122.3, 119.5, 115.7, 20.7. HRMS (ESI): Calculated for $C_{16}H_{13}NONa$ $[M+Na]^+$: 258.0889; Found: 258.0873.



6-(4-((Difluoro-λ^3-methyl)-λ^2-fluoranyl)phenyl)quinolin-2(1*H*)-one (53). Colorless solid (18.8 mg, 65% yield). Mp = 281.3 – 282.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.91 (s, 1H), 8.06 – 7.75 (m, 7H), 7.41 (d, *J* = 8.6 Hz, 1H), 6.55 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 143.3, 140.4, 139.0, 133.0, 129.1, 128.9, 127.6 (d, *J* = 31.7 Hz), 127.1, 126.3, 125.8 (q, *J* = 4.0 Hz), 123.1, 121.0 (d, *J* = 301.1 Hz), 116.0. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.8. HRMS (ESI): Calculated for $C_{16}H_{10}NOF_3Na$ $[M+Na]^+$: 312.0606; Found: 312.0606.

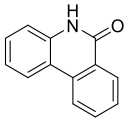


6-(4-Chlorophenyl)quinolin-2(1*H*)-one (54). Colorless solid (16.3 mg, 64% yield). Mp = 307.5 – 308.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.00 (d, *J* = 2.2 Hz, 1H), 7.96 (d, *J* = 9.5 Hz, 1H), 7.84 – 7.81 (m, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 1H), 6.54 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.0, 140.4, 138.5, 138.2, 132.3, 132.1, 128.9, 128.8, 128.2, 125.7, 122.4, 119.5, 115.8. HRMS (ESI): Calculated for $C_{15}H_{10}ClNONa$ $[M+Na]^+$: 278.0343; Found: 278.0327.

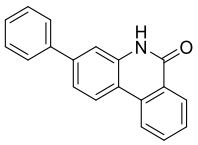


6-(Thiophen-3-yl)quinolin-2(1*H*)-one (55). Colorless solid (6.6 mg, 29% yield). Mp = 280.3 – 281.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.79 (s, 1H), 8.02 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 9.3 Hz, 1H), 7.88 (m, 1H), 7.85 (m, 1H), 7.66 (m, 1H), 7.58 (m, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 9.5 Hz, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 161.9, 140.7, 140.3, 138.0, 129.0, 128.6, 127.2, 126.1, 124.9, 122.4,

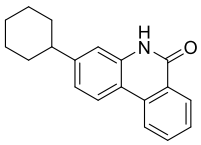
120.3, 119.4, 115.6. HRMS (ESI): Calculated for $C_{13}H_9NOSNa$ $[M+Na]^+$: 250.0297; Found: 250.0285.



Phenanthridin-6(5*H*)-one (56).[9] Colorless solid (10.3 mg, 53% yield). Mp = 280.6 – 282.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 136.6, 134.3, 132.8, 129.6, 127.9, 127.5, 125.7, 123.3, 122.6, 122.3, 117.6, 116.1. HRMS (ESI): Calculated for $C_{13}H_9NONa$ $[M+Na]^+$: 218.0576; Found: 218.0576.

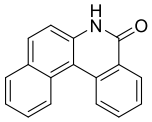


3-Phenylphenanthridin-6(5*H*)-one (57). Colorless solid (11.7 mg, 43% yield). Mp > 320 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.77 (s, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 2H), 7.55 – 7.49 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.0, 141.2, 139.3, 137.1, 134.0, 132.9, 129.1, 128.1, 128.0, 127.5, 126.7, 125.6, 124.0, 122.7, 120.9, 116.9, 113.8. HRMS (ESI): Calculated for $C_{19}H_{13}NONa$ $[M+Na]^+$: 294.0889; Found: 294.0890.

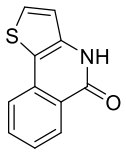


3-Cyclohexylphenanthridin-6(5*H*)-one (58). Colorless solid (11.1 mg, 40% yield). Mp = 277.8 – 279.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.62 (s, 1H), 8.43 (d, *J* = 8.0 Hz, 1H), 8.31 – 8.24 (m, 2H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H),

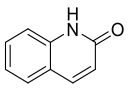
7.18 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 2.55 (d, *J* = 11.0 Hz, 1H), 1.84 – 1.78 (m, 4H), 1.43 – 1.34 (m, 4H), 1.22 (d, *J* = 17.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.0, 149.3, 136.6, 134.4, 132.7, 127.4, 127.3, 125.3, 123.2, 122.4, 121.3, 115.6, 113.7, 43.6, 33.8, 26.2, 25.6. HRMS (ESI): Calculated for $C_{19}H_{19}NONa$ $[M+Na]^+$: 300.1359; Found: 300.1359.



Benzo[a]phenanthridin-5(6*H*)-one (59).[11] Colorless solid (8.3 mg, 34%). Mp = 296.5 – 298.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.00 (s, 1H), 8.79 (t, *J* = 8.4 Hz, 2H), 8.48 – 8.41 (m, 1H), 8.05 – 8.00 (m, 2H), 7.95 – 7.90 (m, 1H), 7.7 yield 1 – 7.66 (m, 2H), 7.57 – 7.50 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 135.7, 134.6, 132.5, 130.7, 130.4, 129.4, 129.2, 129.0, 127.7, 127.7, 127.2, 126.7, 124.9, 124.4, 117.0, 110.9. HRMS (ESI): Calculated for $C_{17}H_{11}NONa$ $[M+Na]^+$: 268.0733; Found: 268.0733.



Thieno[3,2-c]isoquinolin-5(4*H*)-one (60). Colorless solid (6.4 mg, 32% yield). Mp = 256.7 – 258.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.02 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 7.82 – 7.73 (m, 3H), 7.52 (m 1H), 7.06 (d, *J* = 5.3 Hz, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ 161.4, 138.4, 133.2, 133.1, 128.2, 127.8, 126.4, 123.6, 122.4, 118.0, 115.0. HRMS (ESI): Calculated for $C_{11}H_7NOSNa$ $[M+Na]^+$: 224.0140; Found: 224.0127.



Quinolin-2(1*H*)-one (61).[9] Colorless solid. Mp = 234.6 – 236.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.87 (s, 1H), 7.74 (d, *J* = 9.4 Hz, 1H), 7.51 – 7.38 (m, 3H), 7.19 – 7.09 (m, 1H), 6.66 (d, *J* = 9.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 141.1, 138.4, 130.6, 127.7, 122.7, 121.1, 119.9, 116.3. HRMS (ESI): Calculated for C_9H_6NO $[M-H]^-$: 144.0443; Found: 144.0443.

6. References

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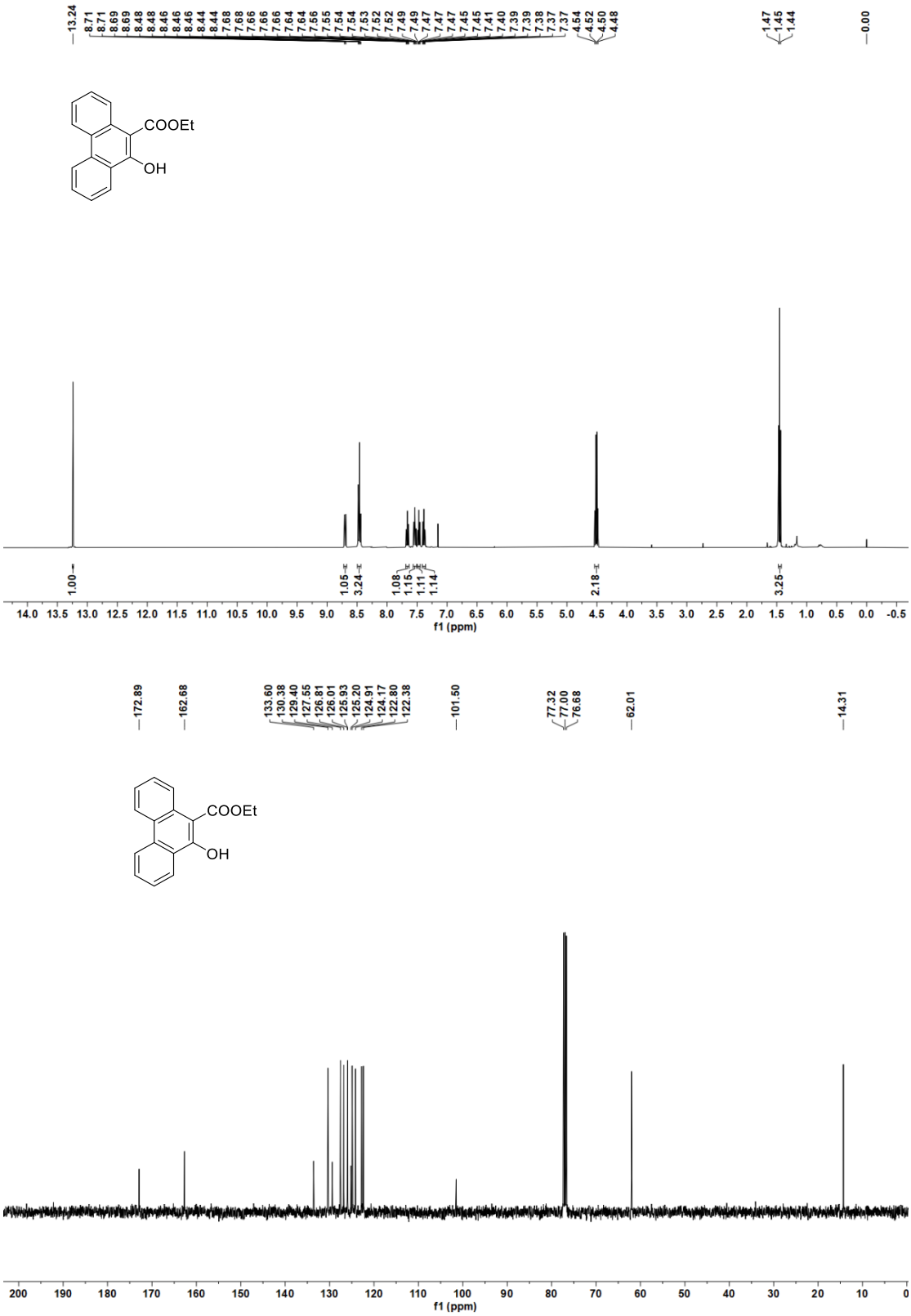
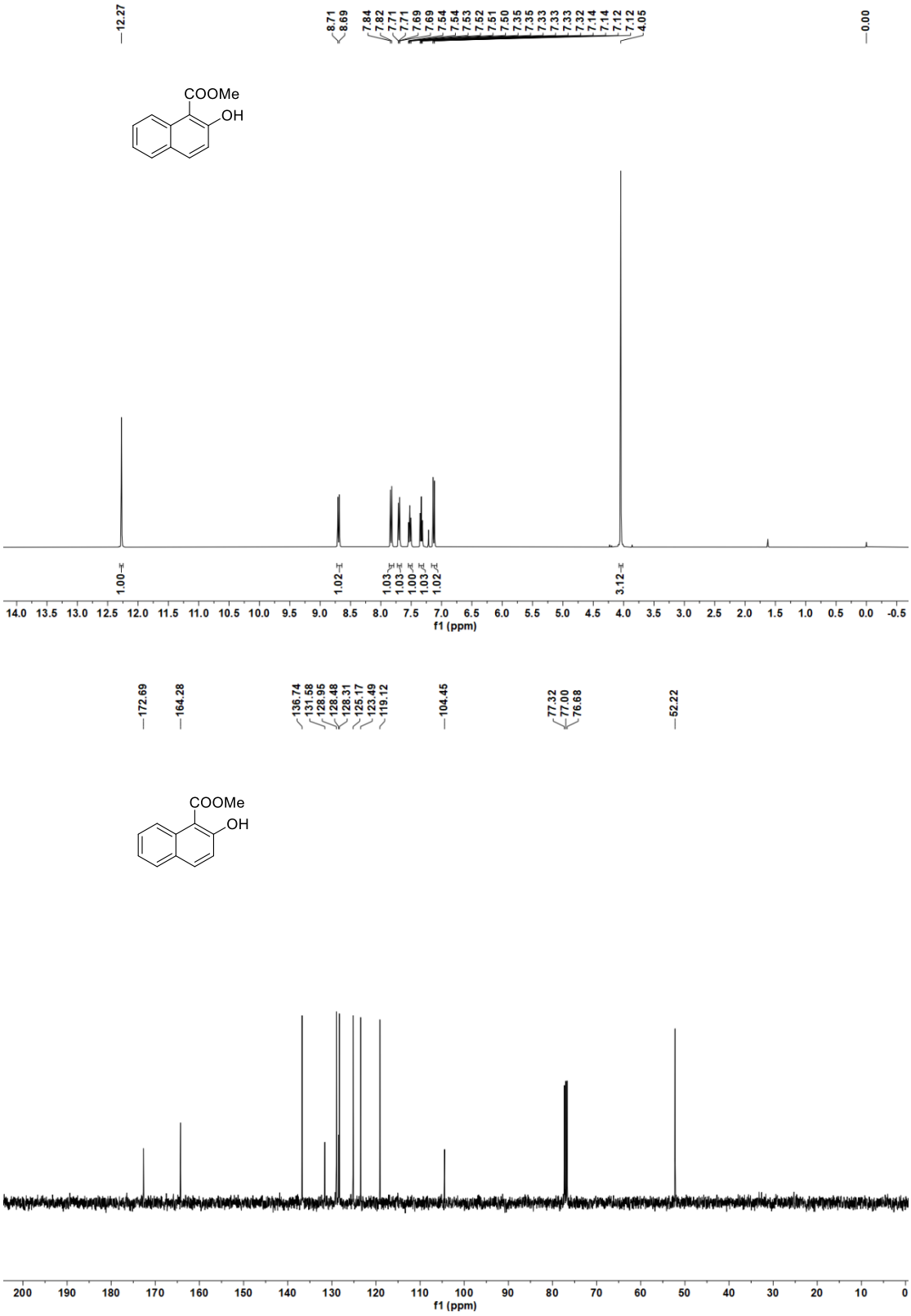
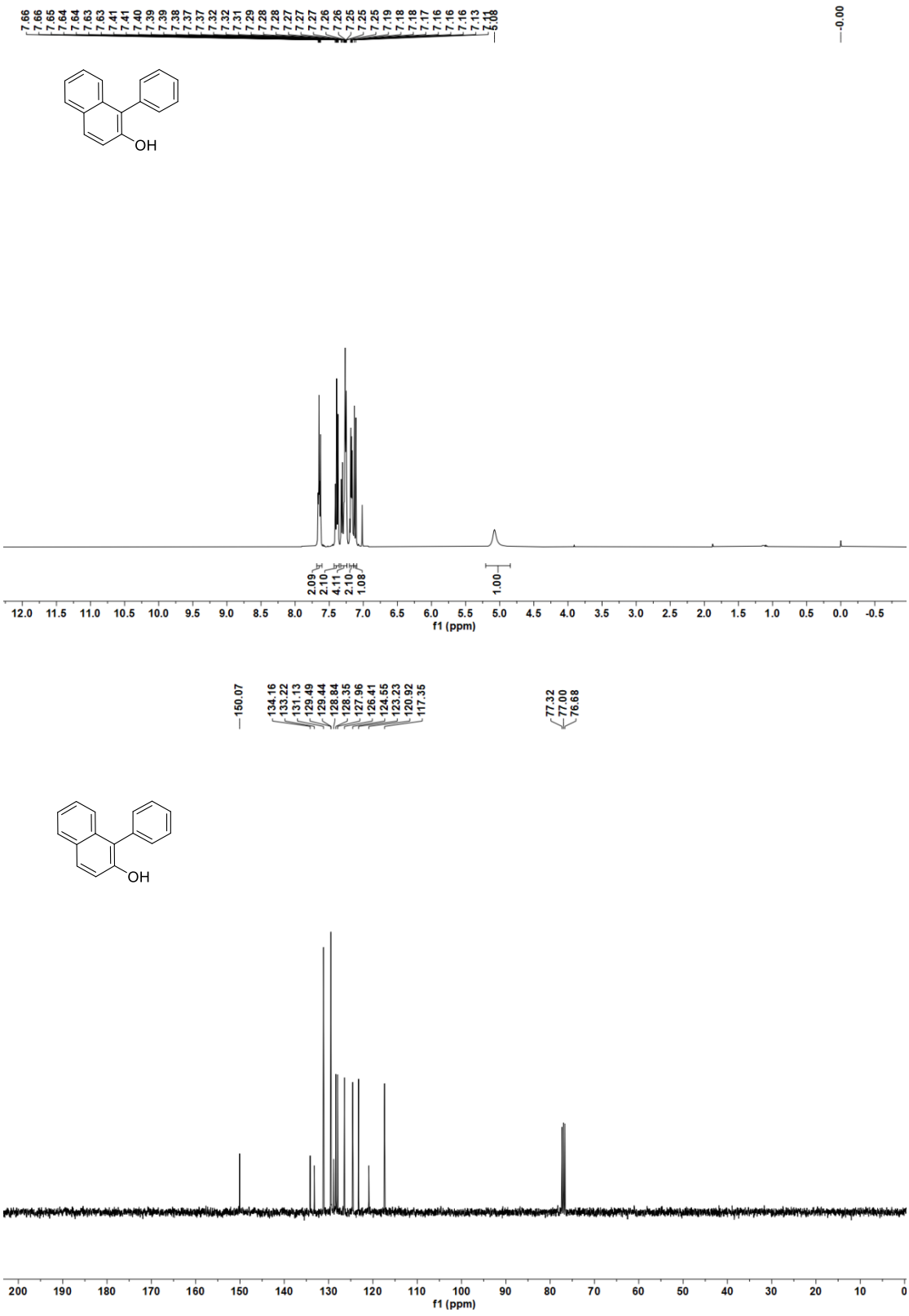
7. Spectra of Compunds



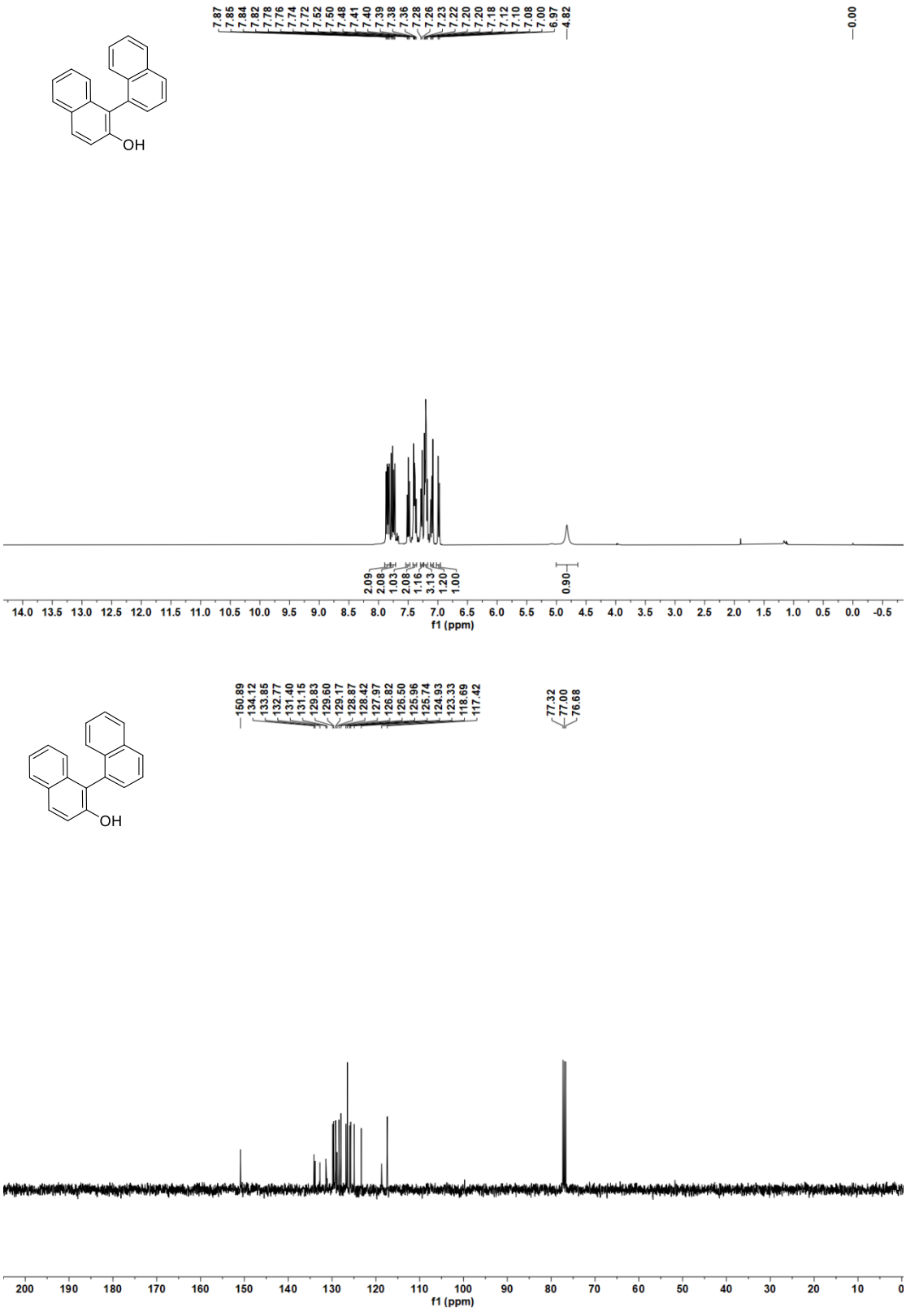
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **1a**



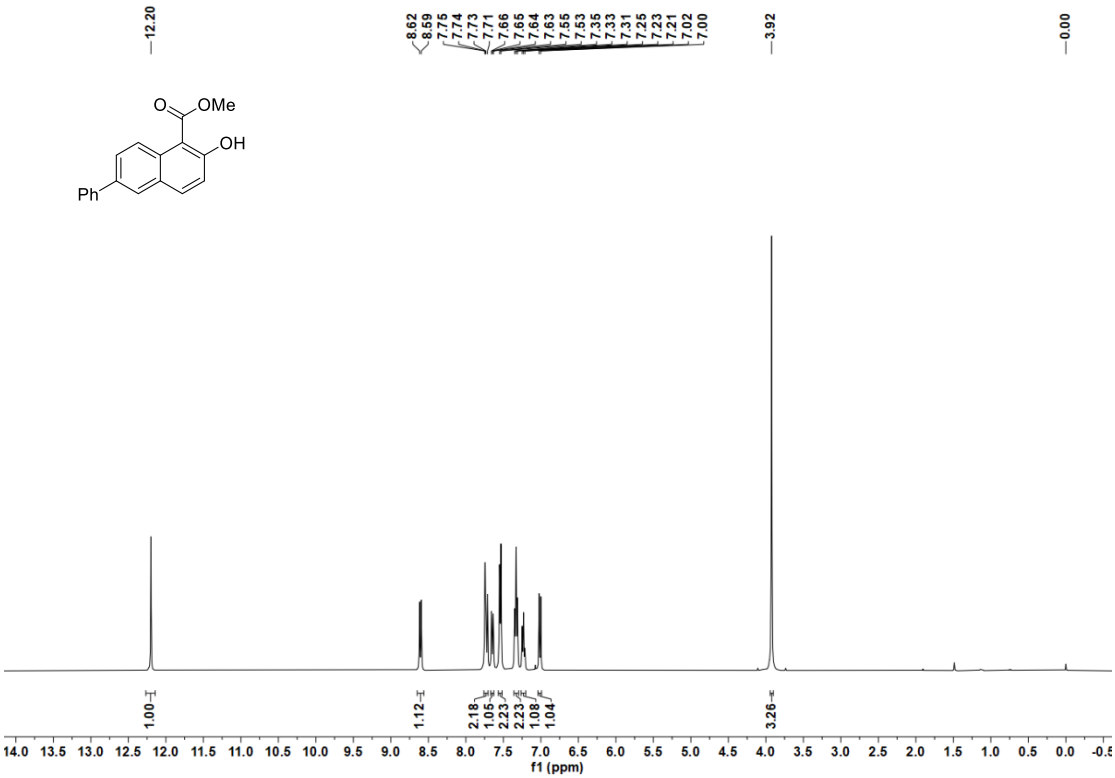
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **2a**

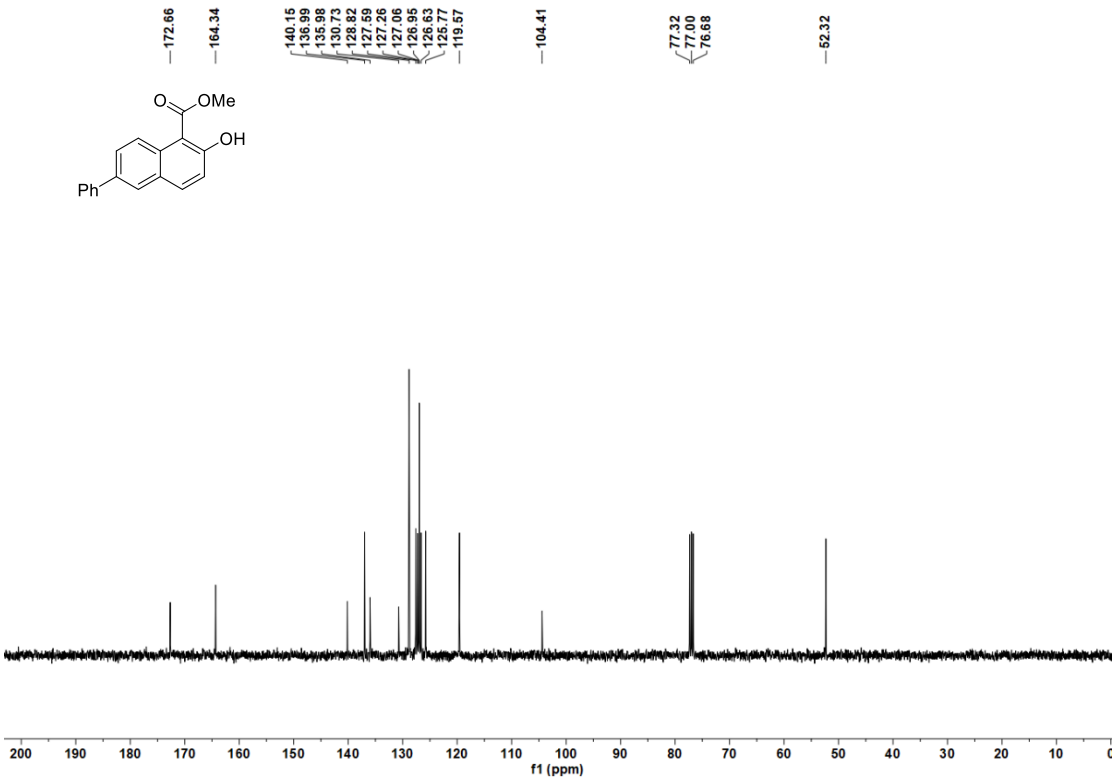


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **3a**

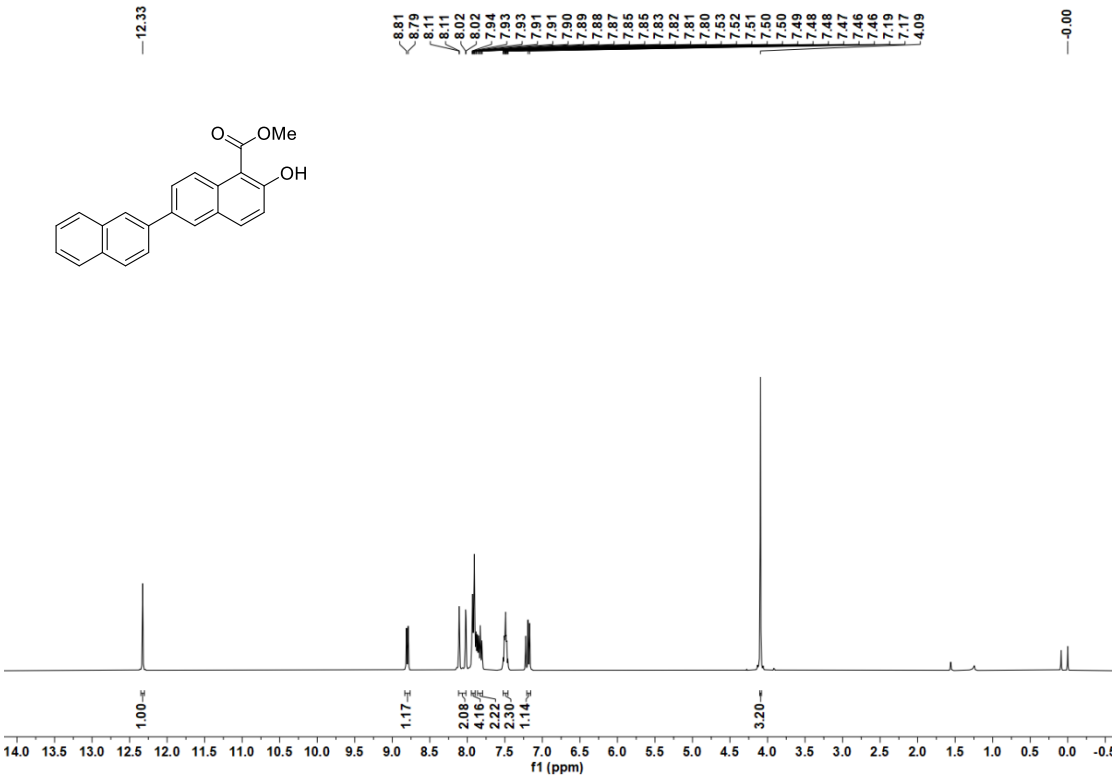


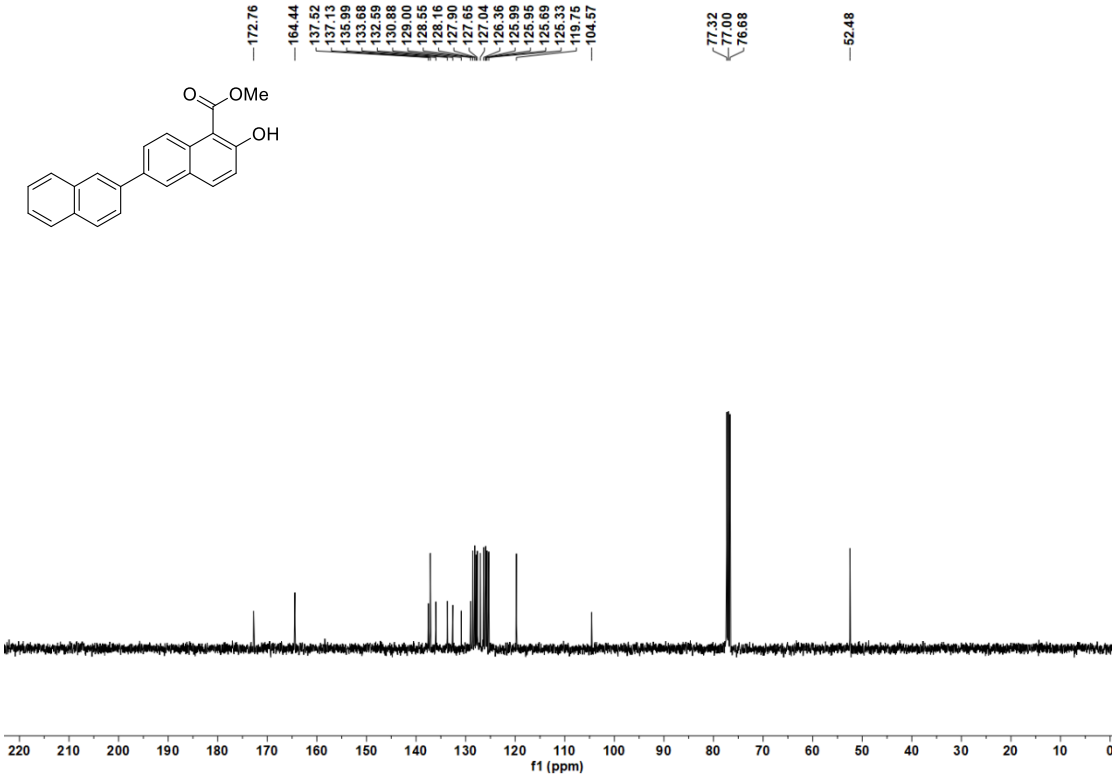
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **4a**



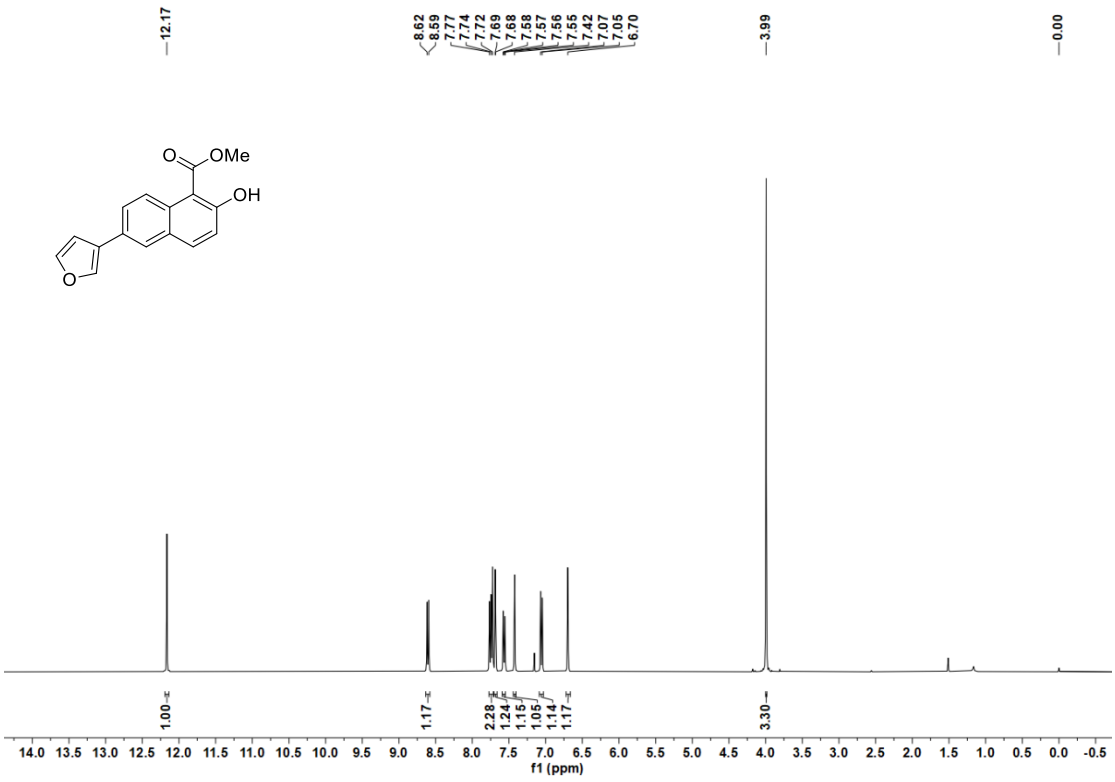


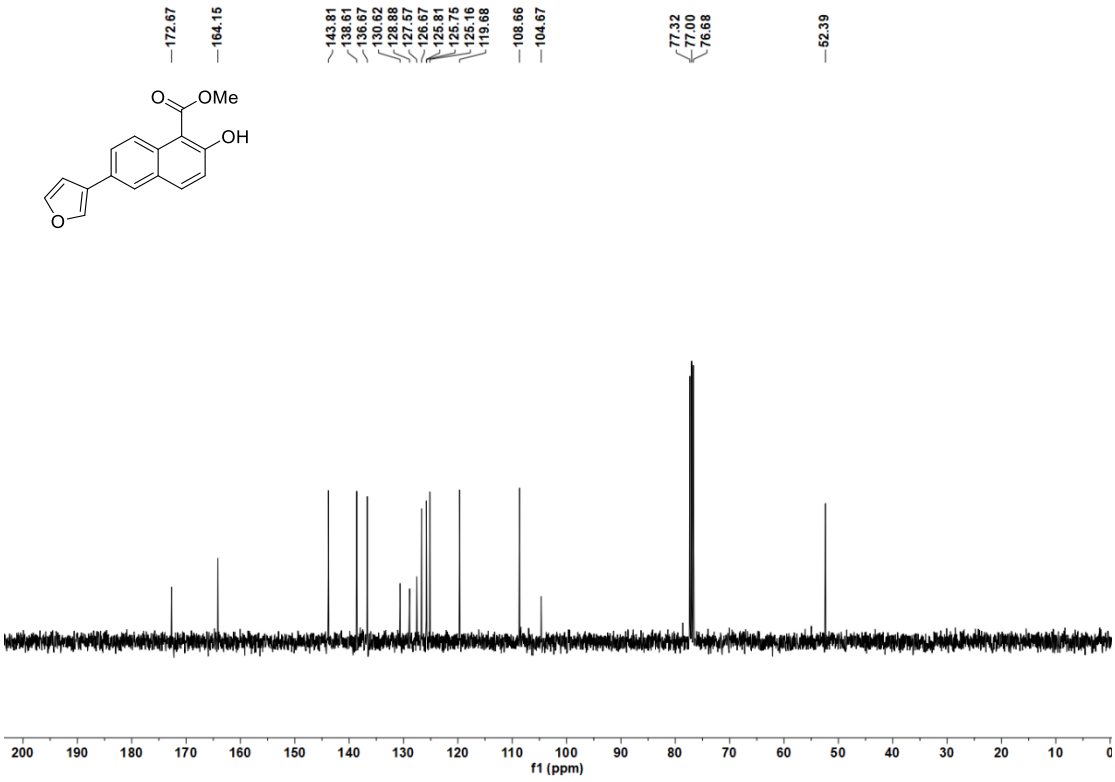
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **5a**



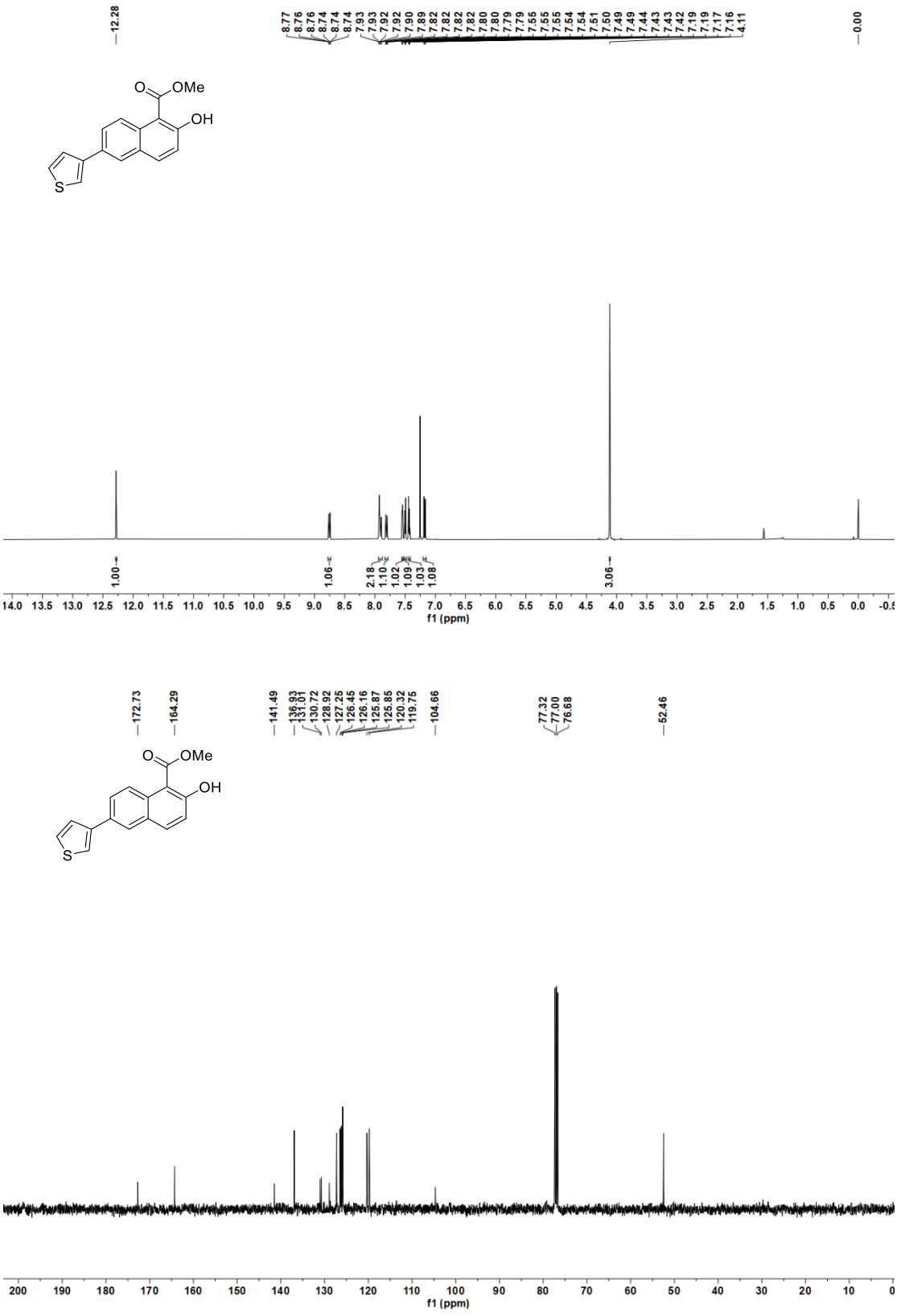


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **6a**

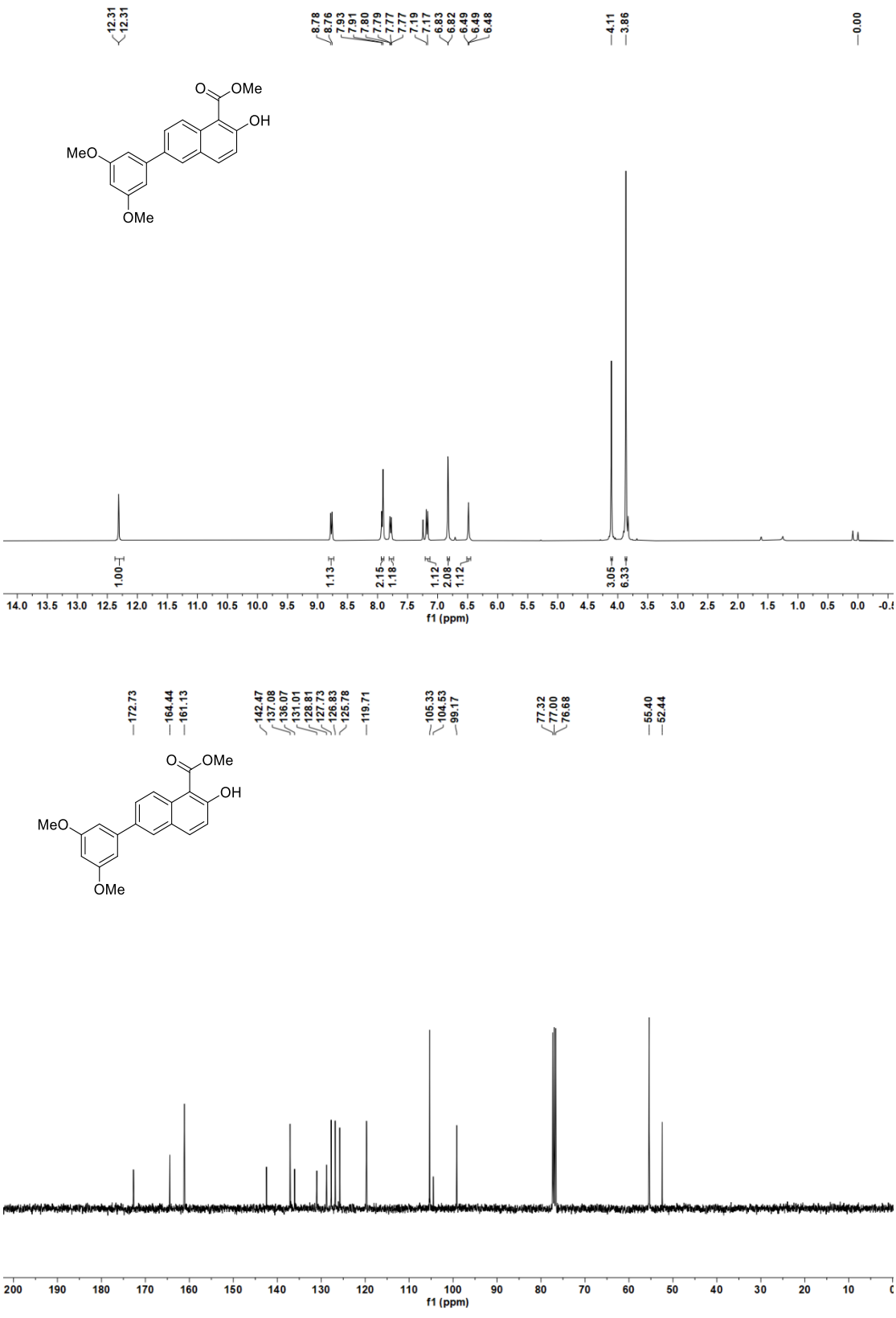




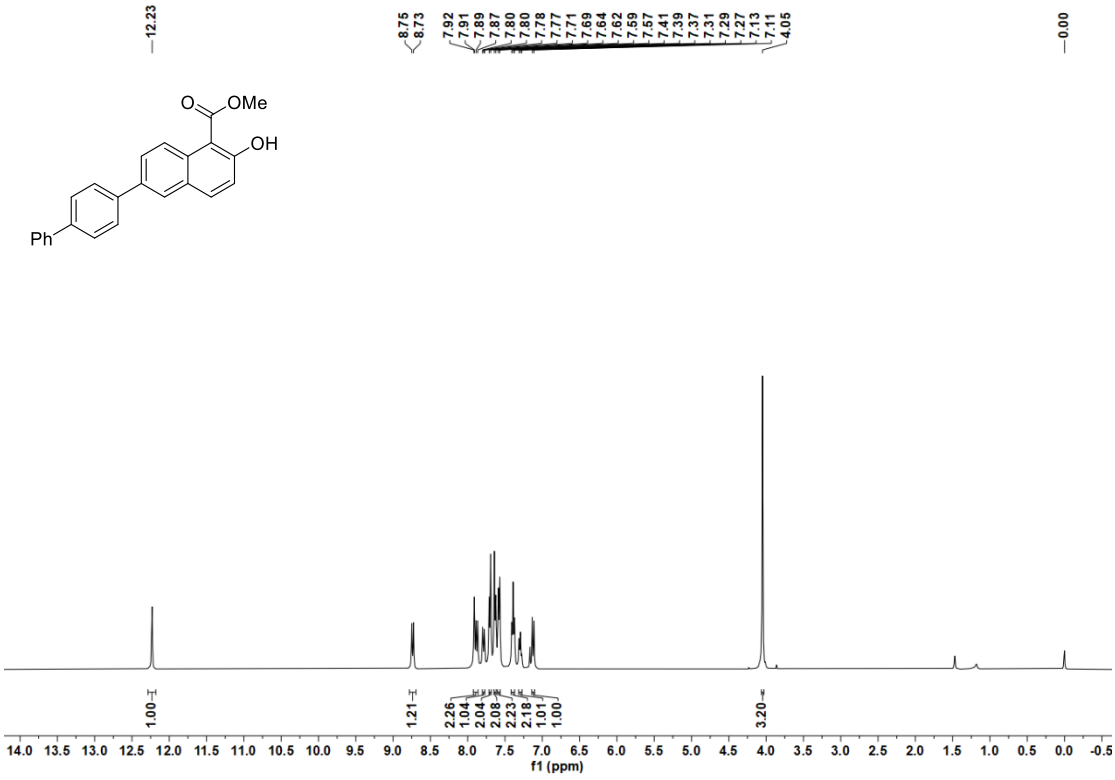
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **7a**

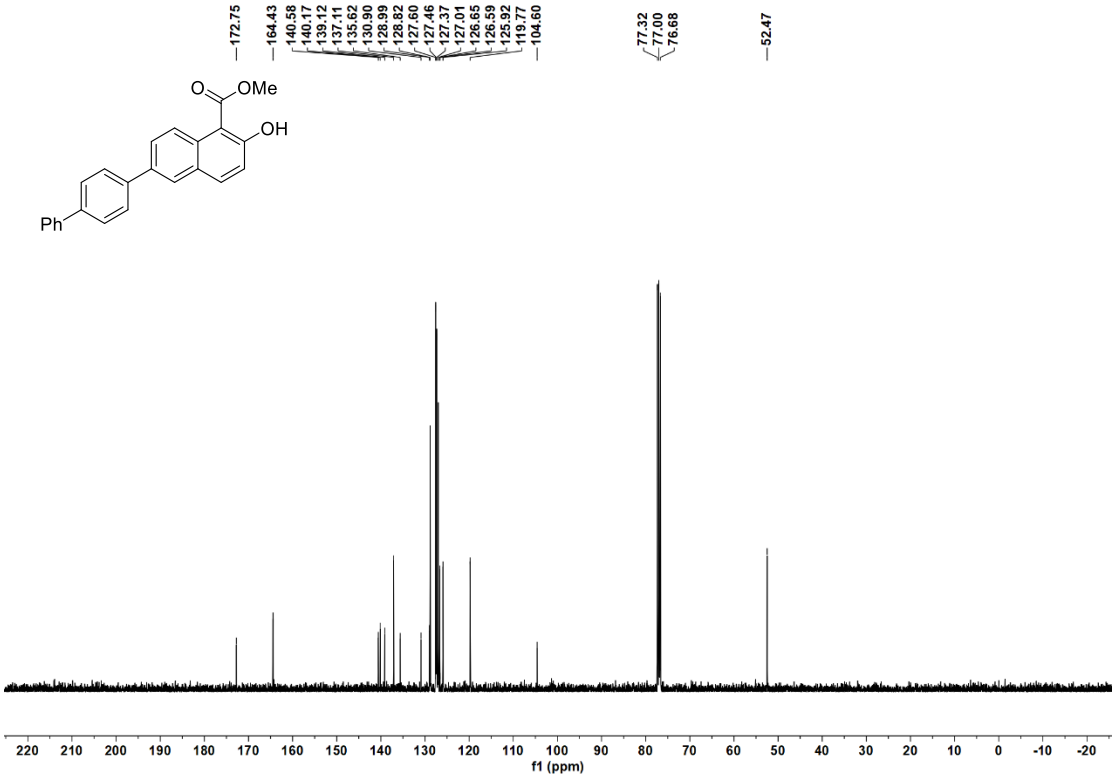


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **8a**



^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **9a**





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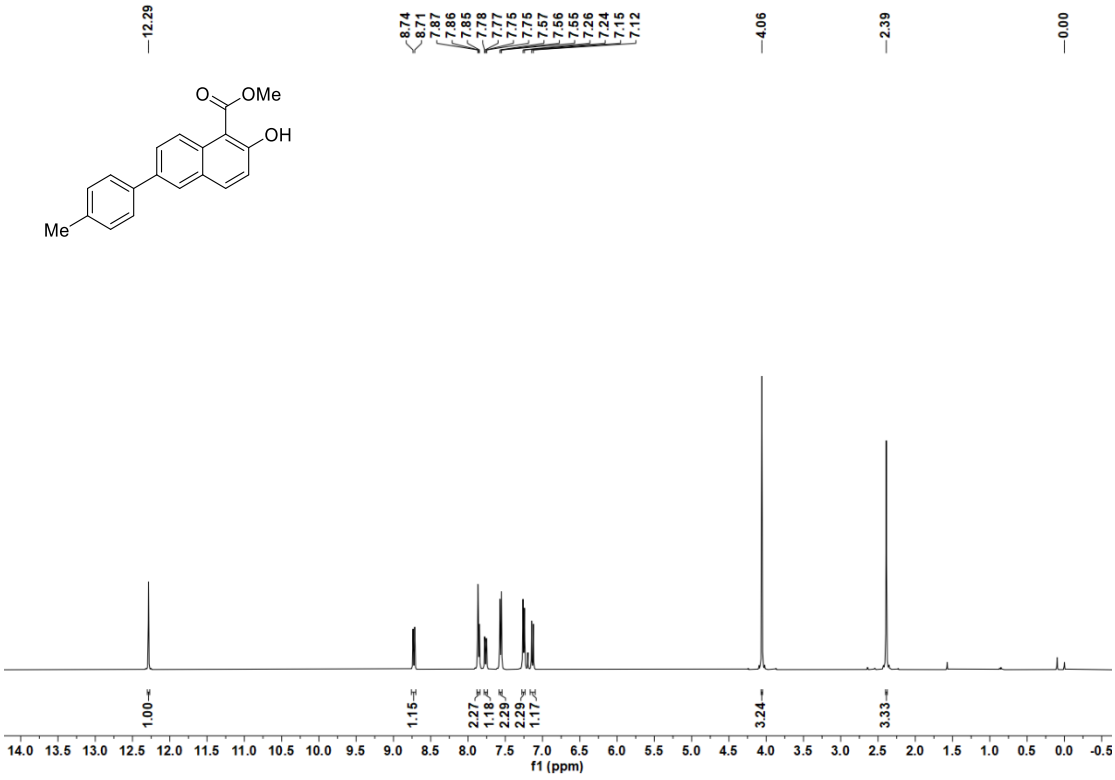
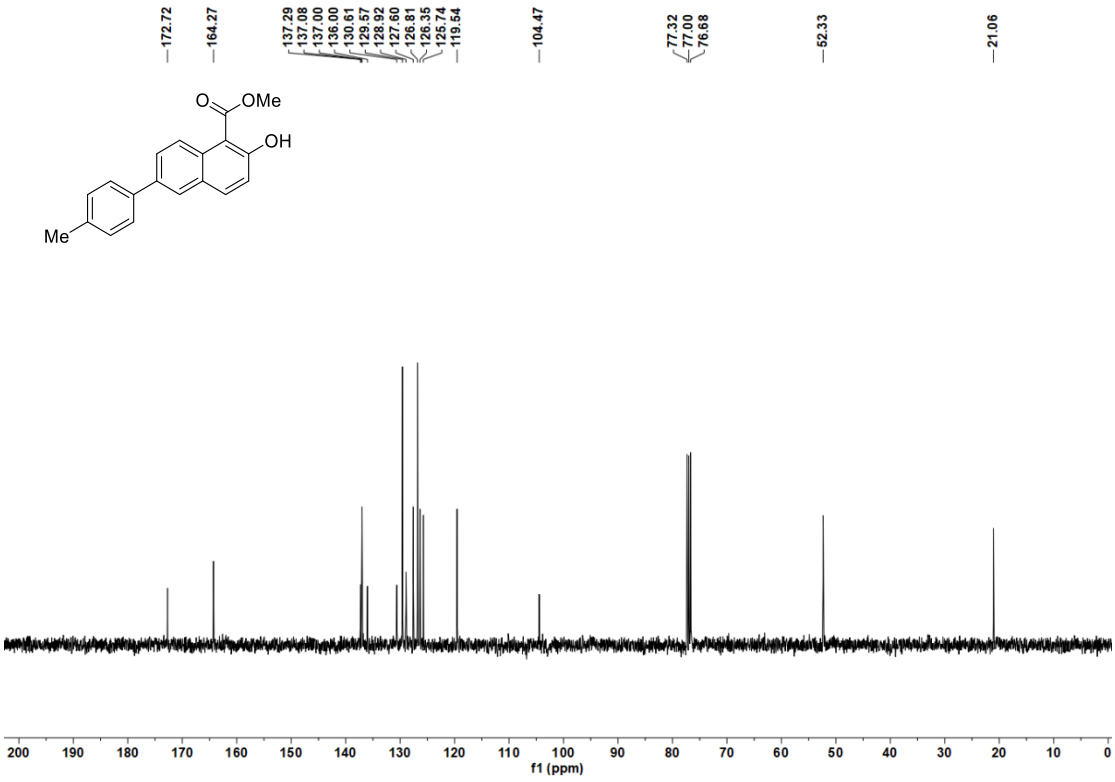
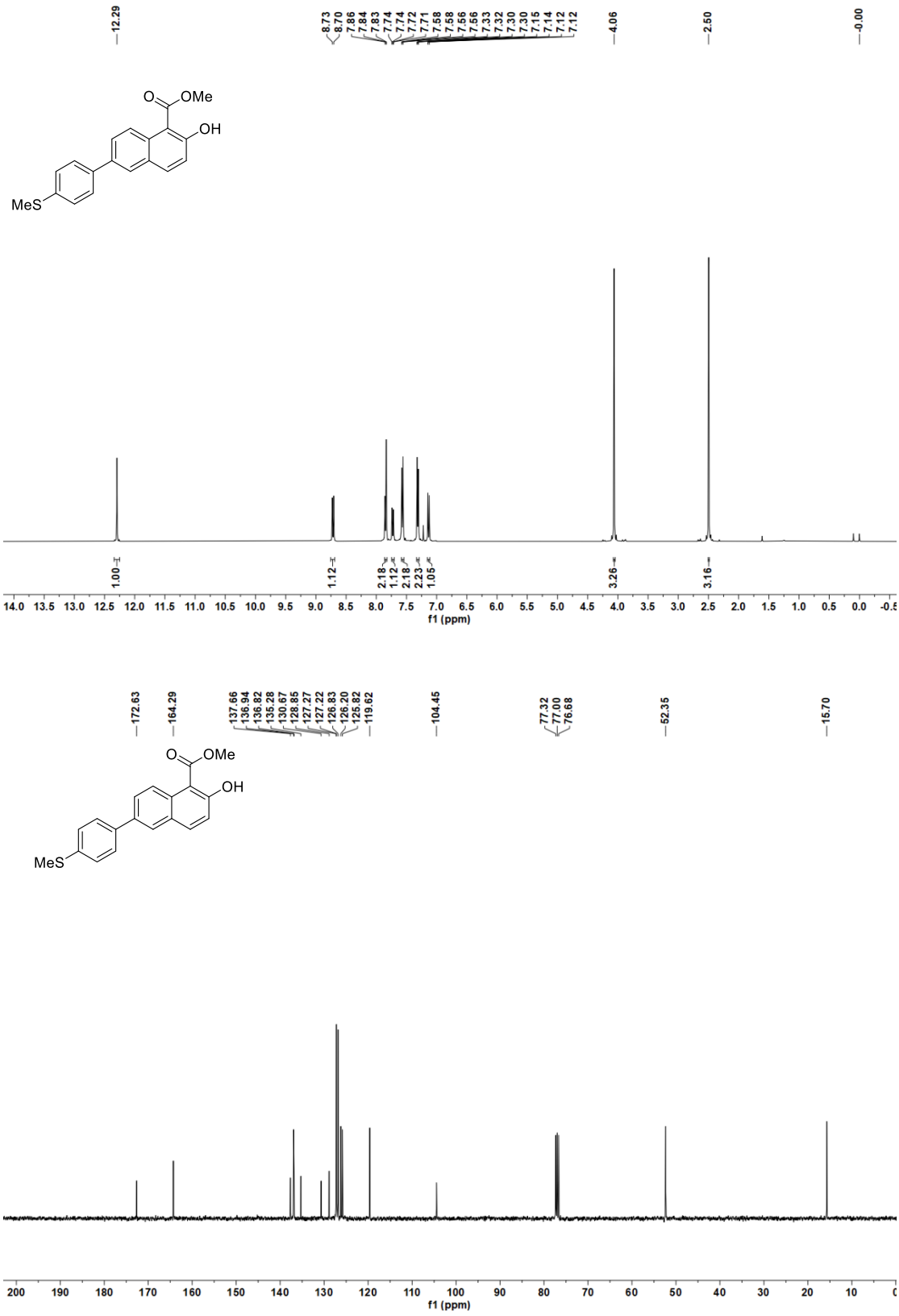
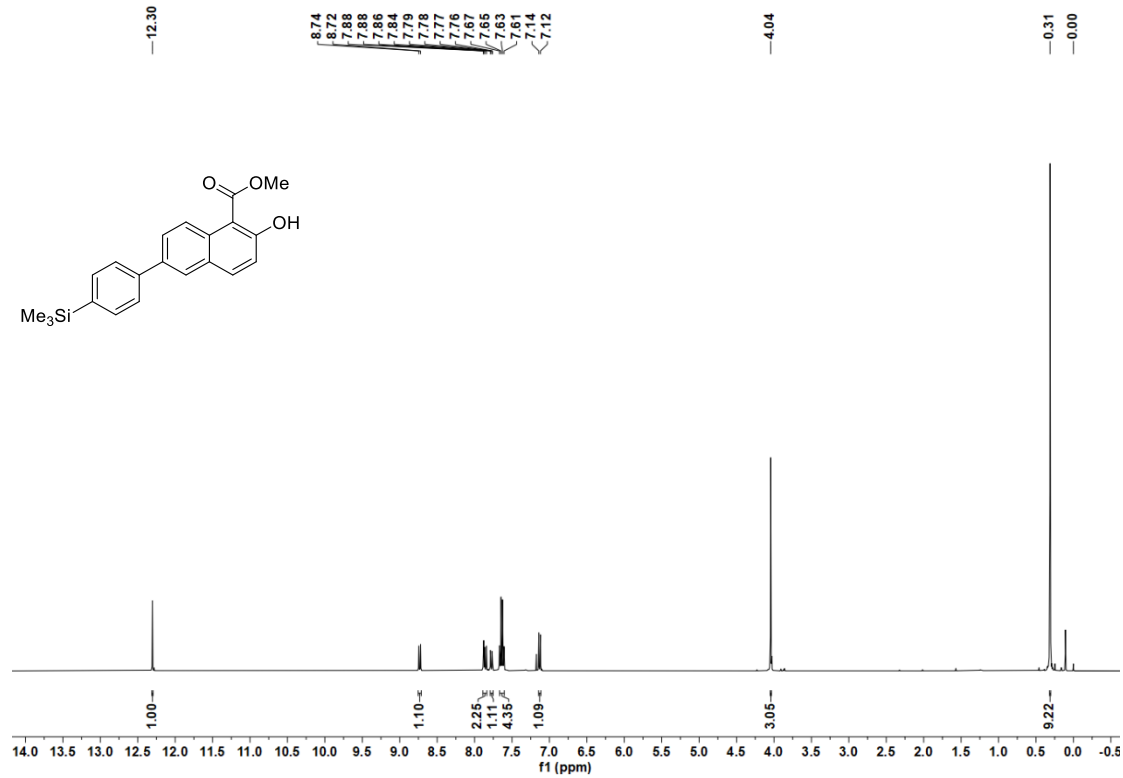


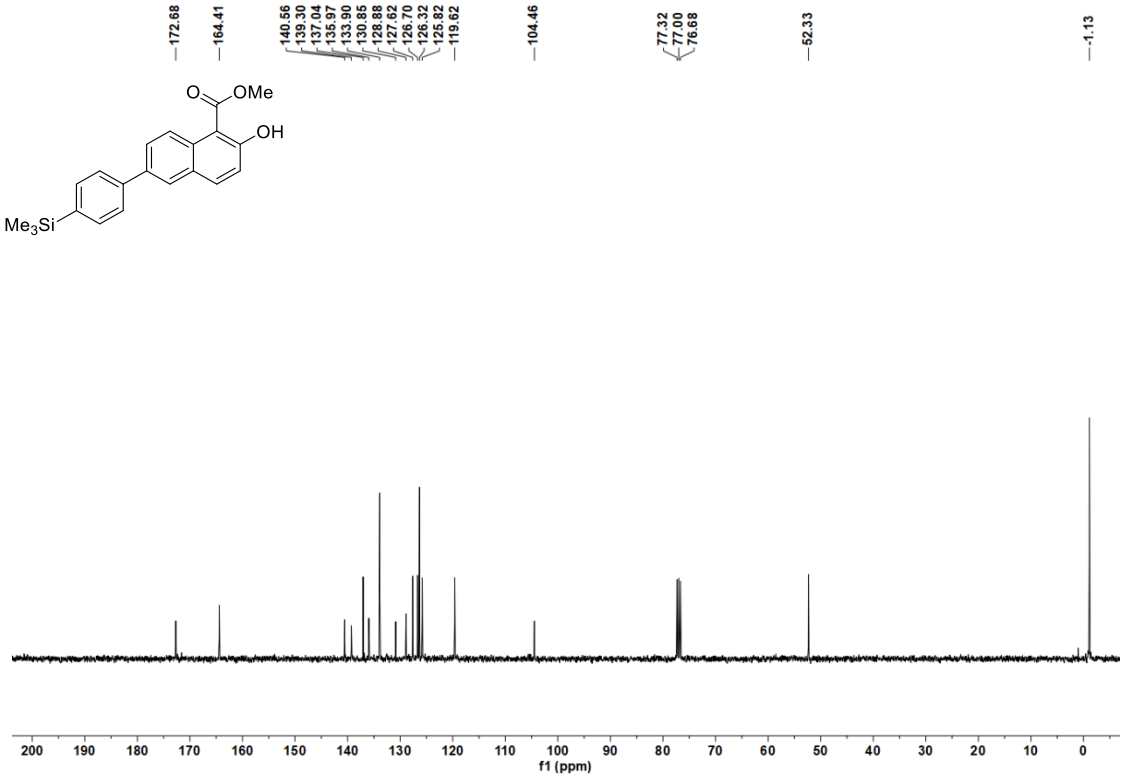


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **11a**

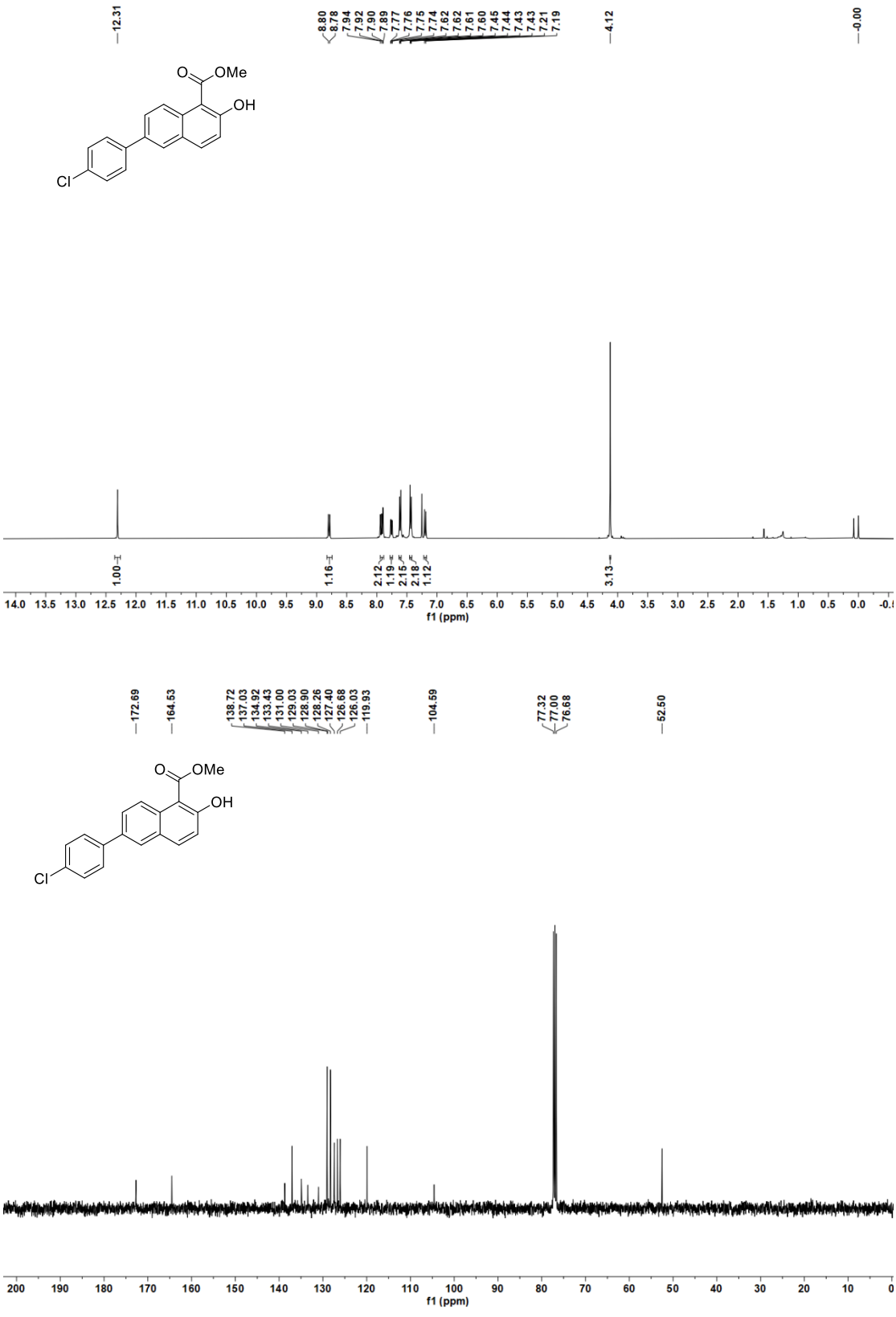


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **12a**

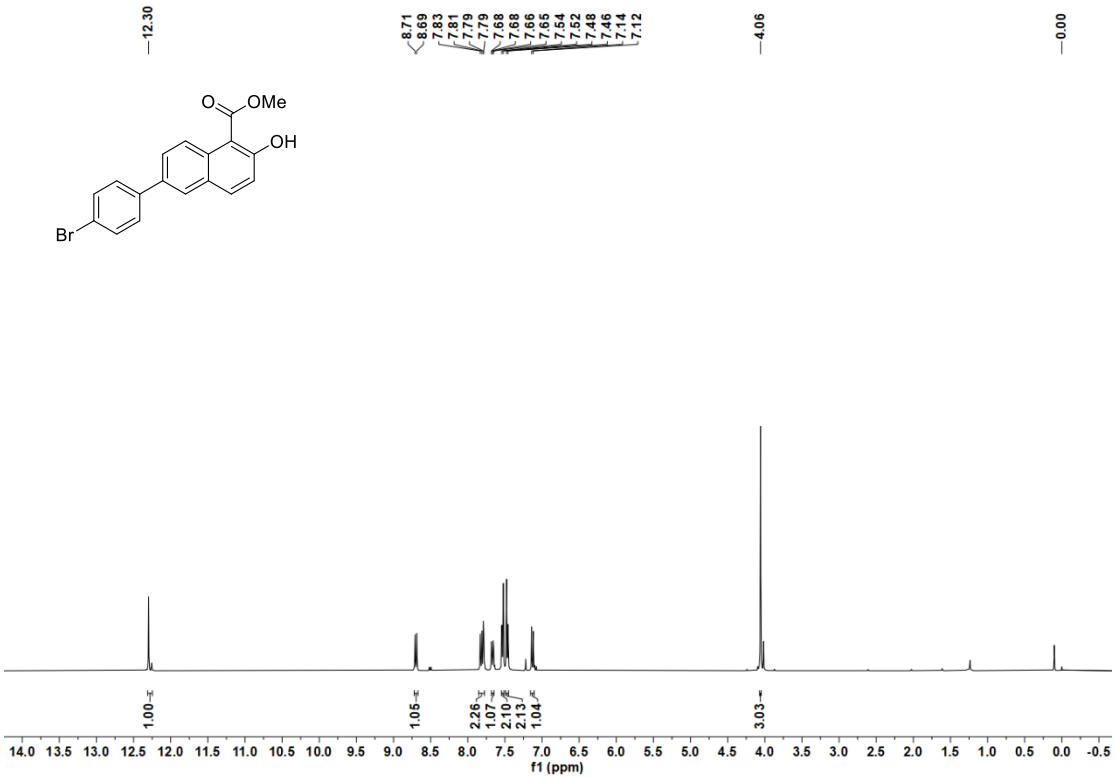


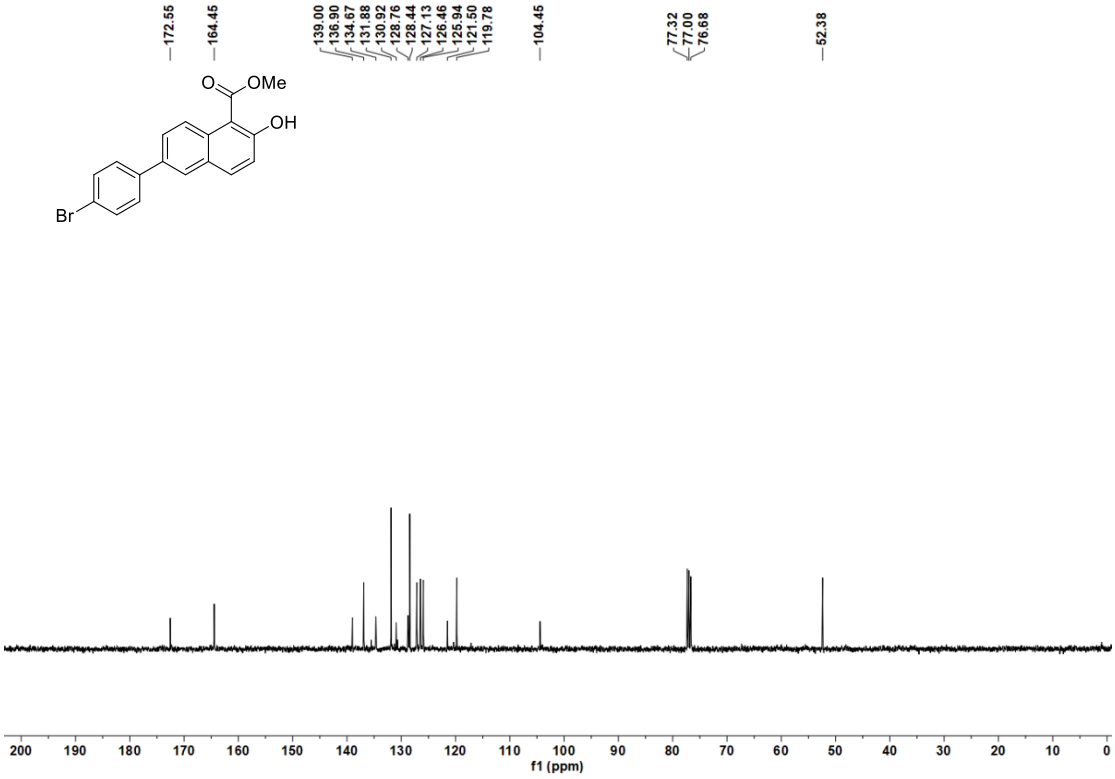


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **13a**

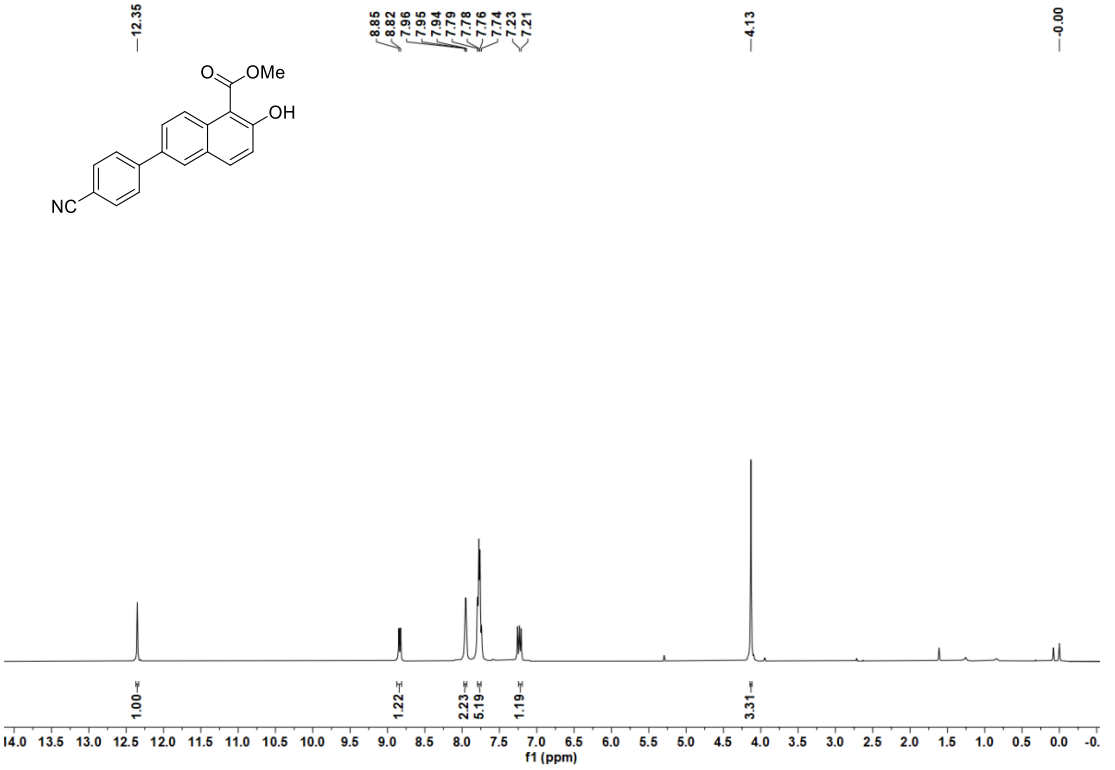


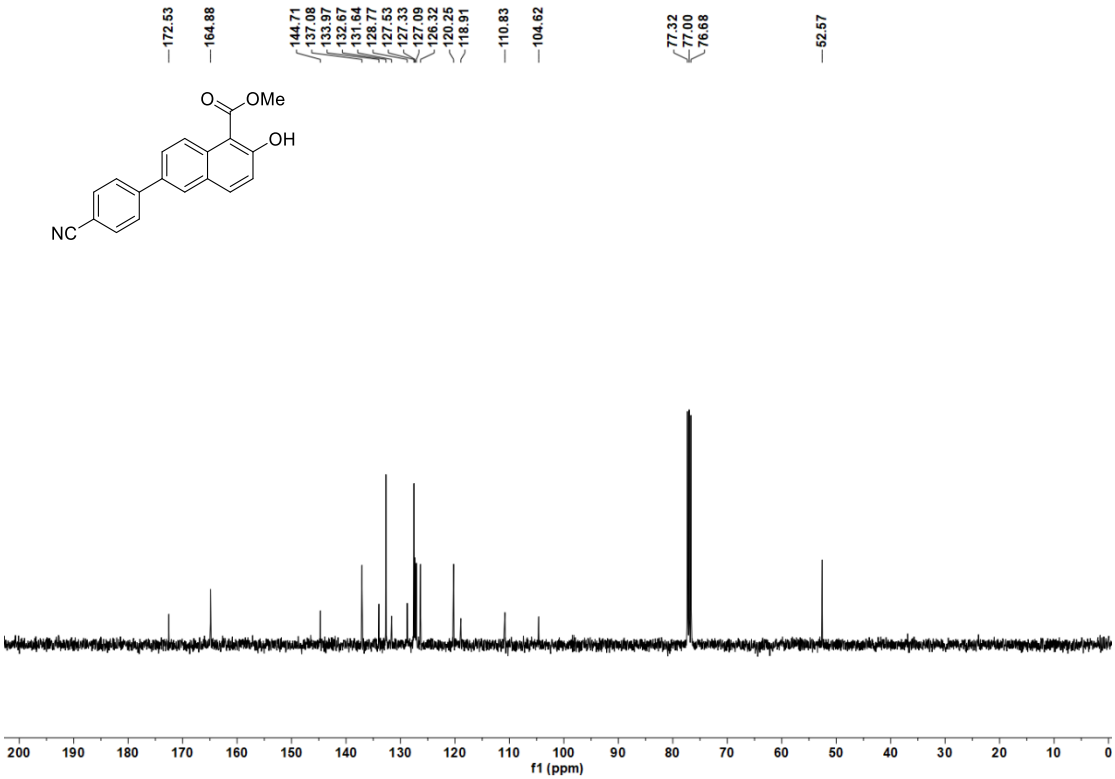
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **14a**



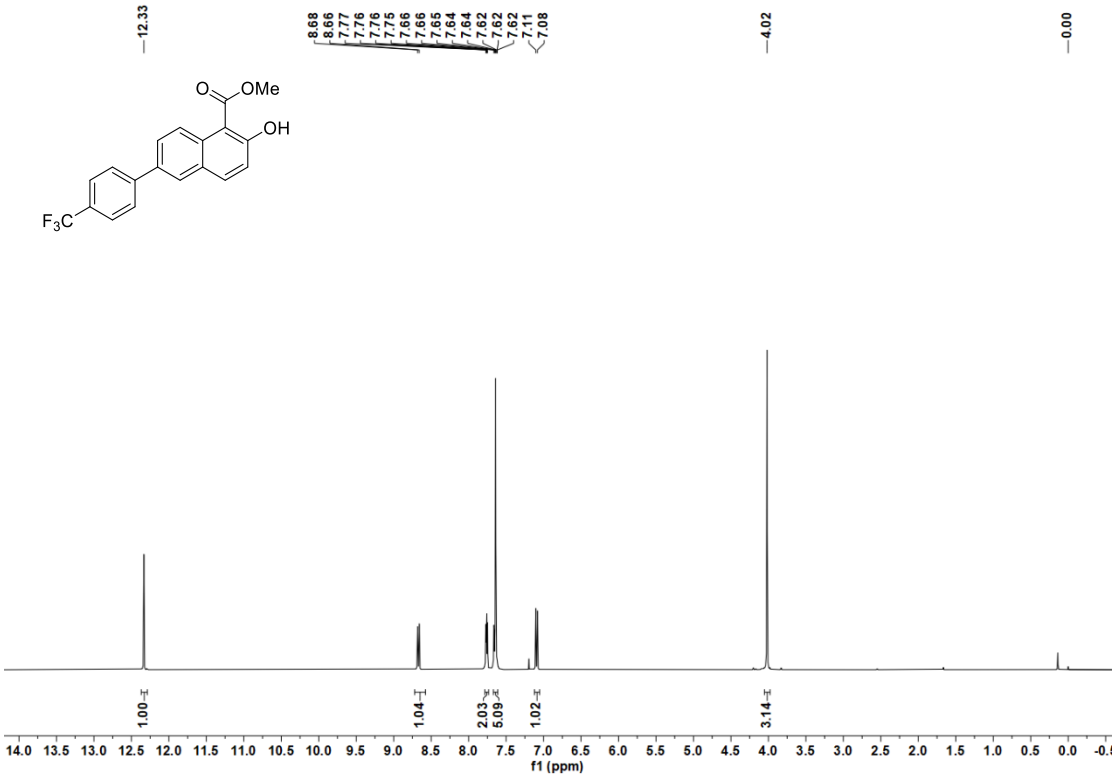


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **15a**





^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **16a**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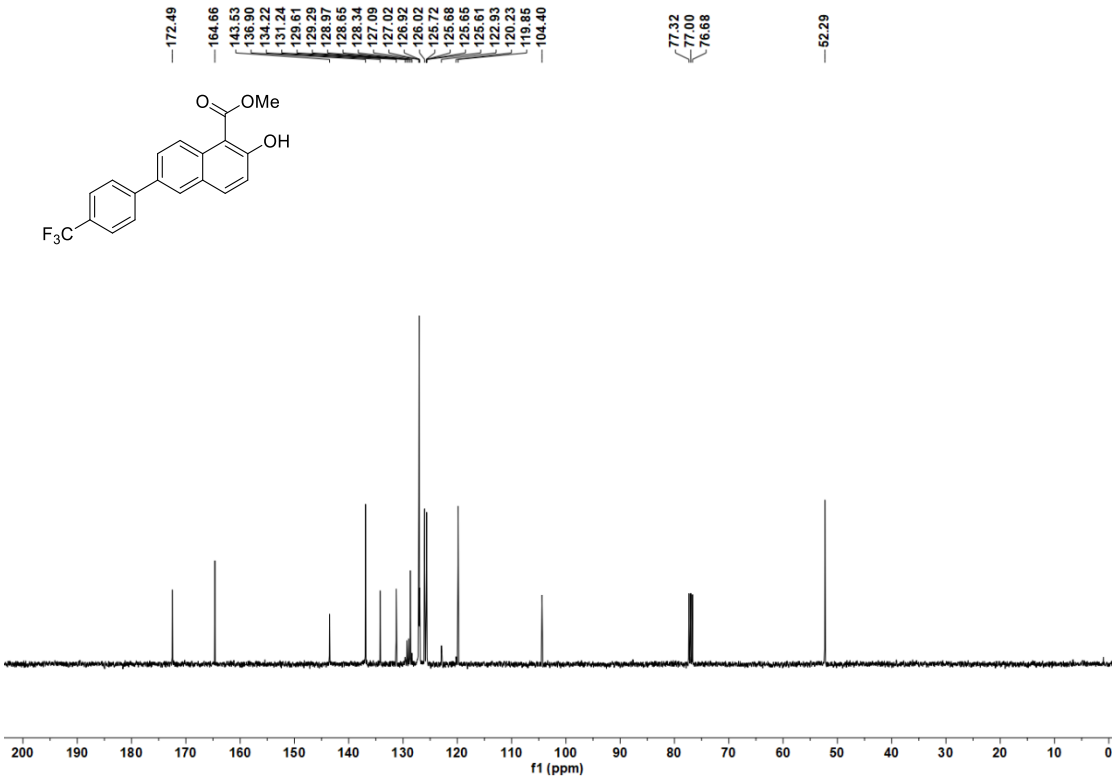
8.68
8.66
7.77
7.76
7.76
7.75
7.66
7.66
7.65
7.64
7.64
7.62
7.62
7.62
7.11
7.08
4.02
0.00
O
OMe
OH
F3C
1.00
1.04
2.03
5.09
1.02
3.14
f1 (ppm)


172.49
164.66
143.53
136.90
134.22
131.24
129.61
129.29
128.97
128.65
128.34
127.09
127.02
126.92
126.02
125.72
125.68
125.65
125.61
122.93
120.23
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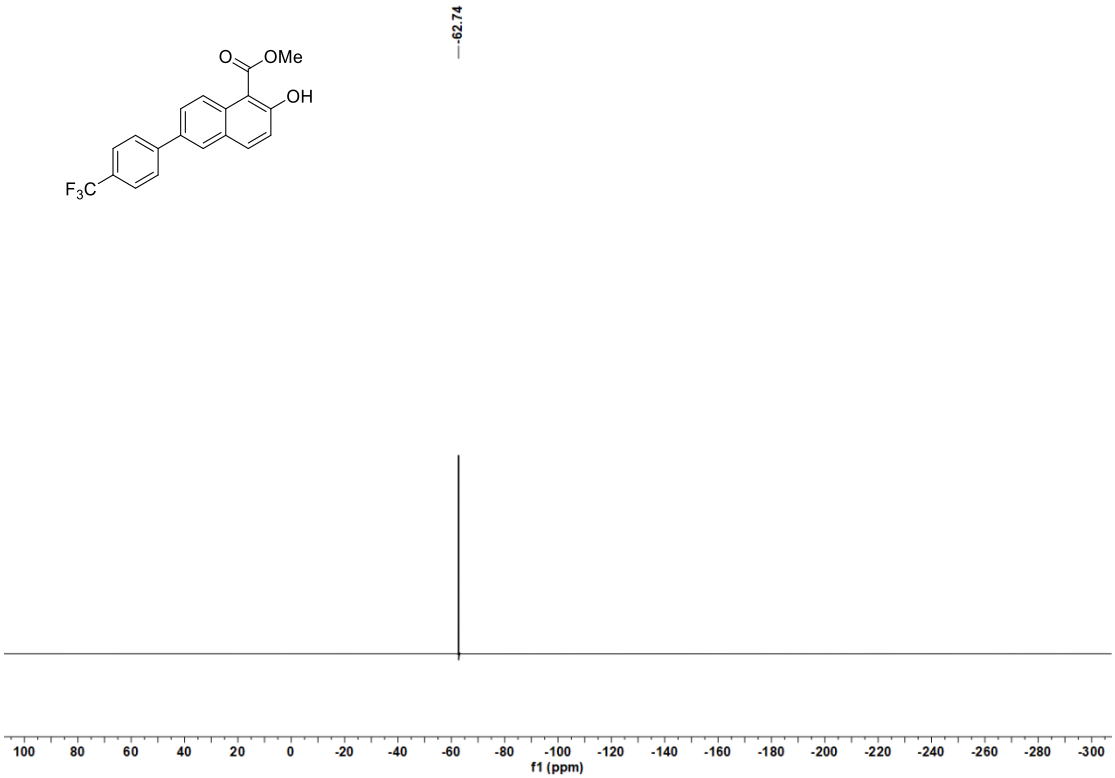
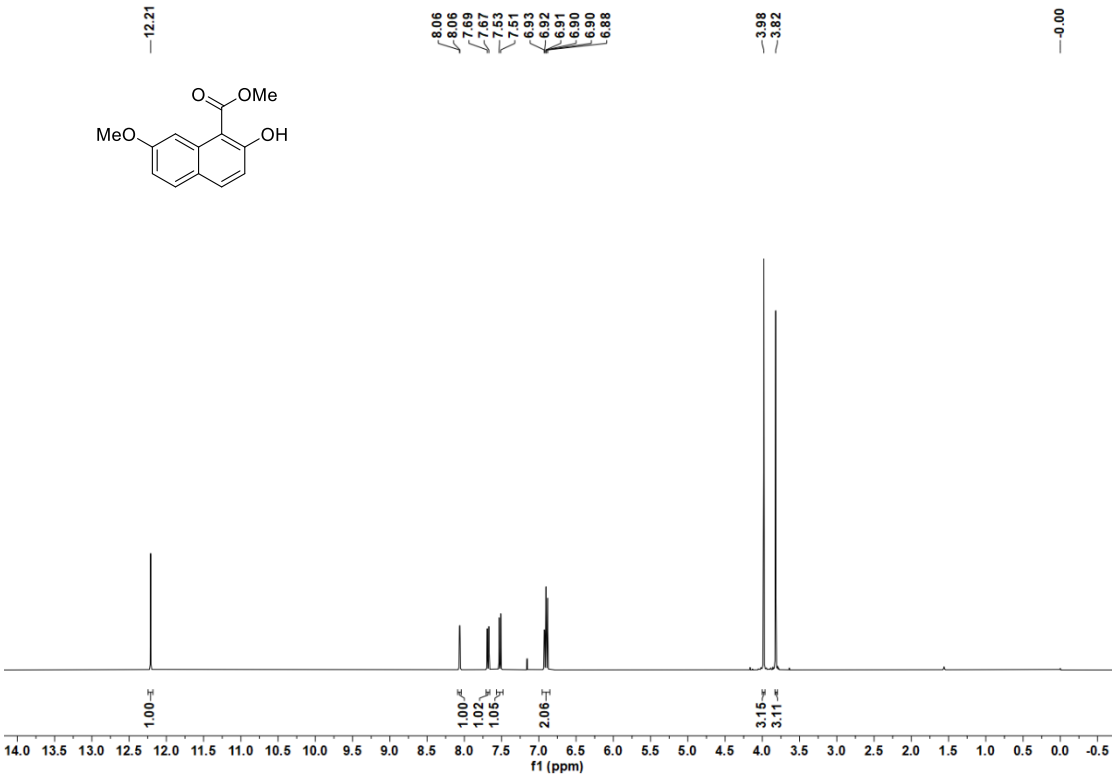
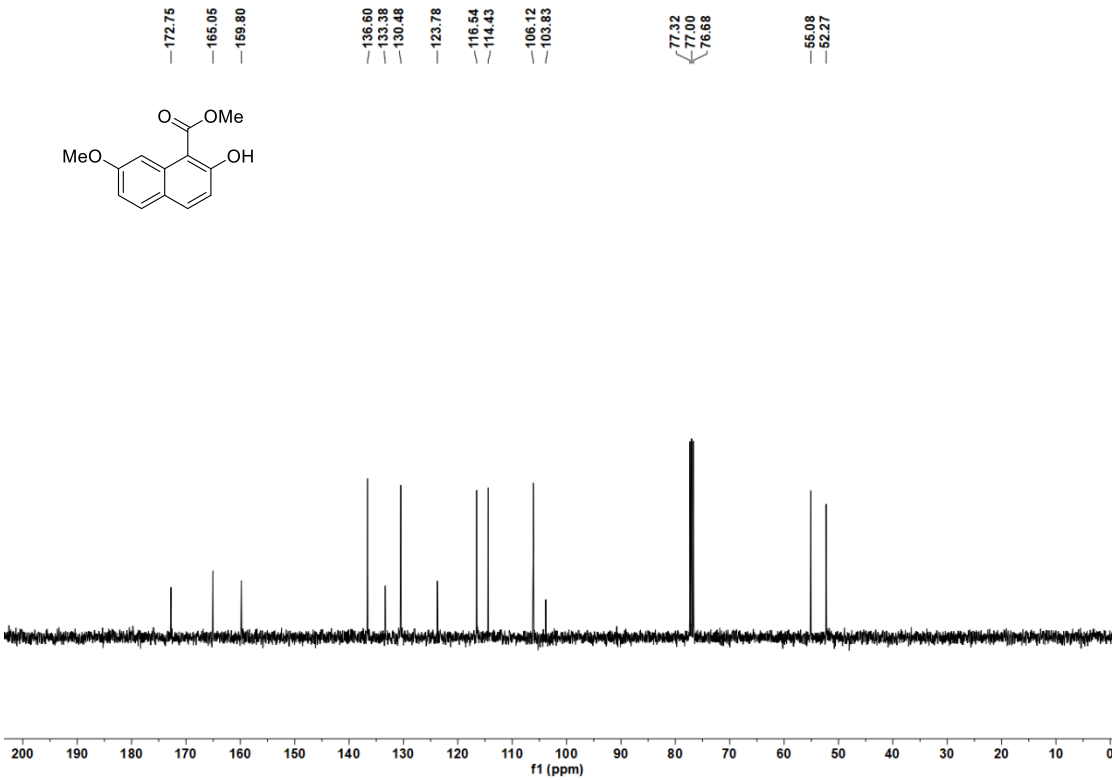
104.40
77.32
77.00
76.68
52.29
O
OMe
OH
F3C
f1 (ppm)

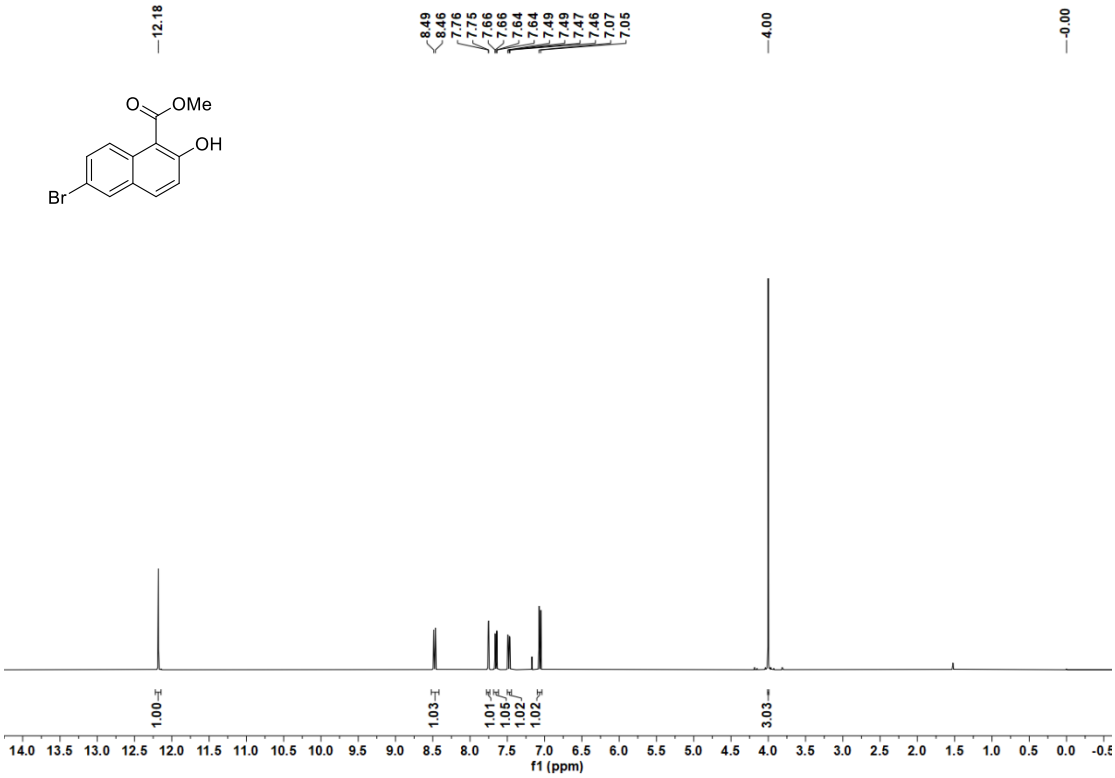


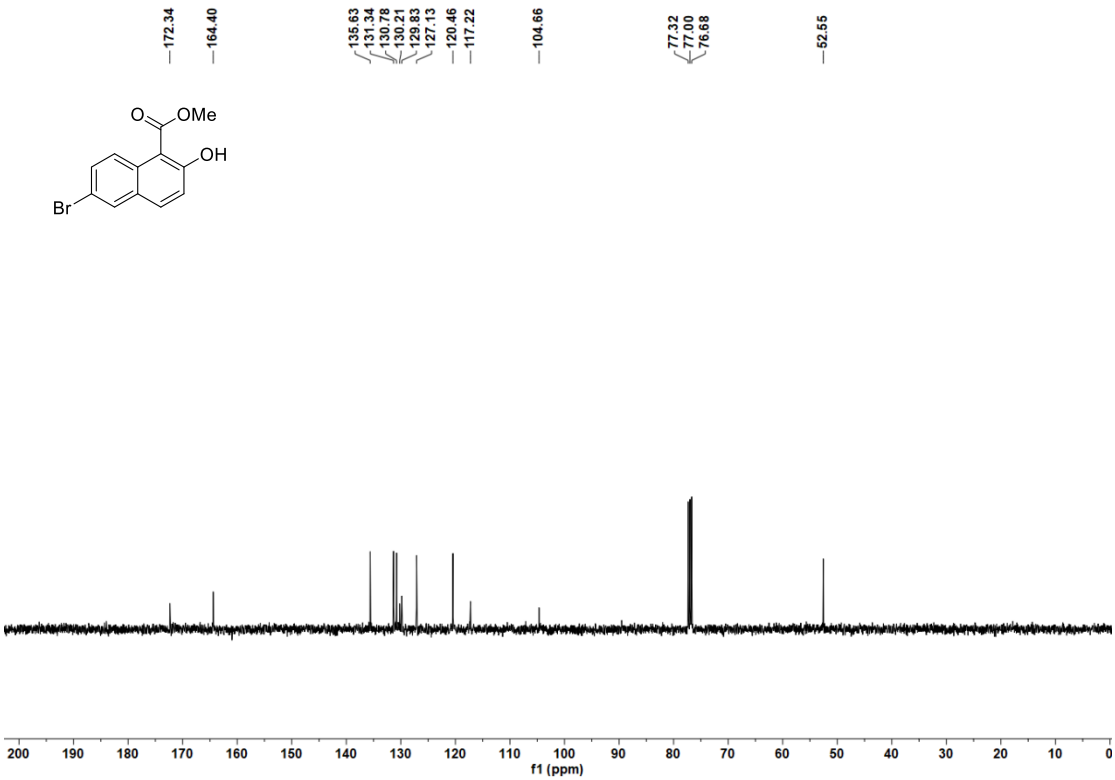
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$), of **17a**



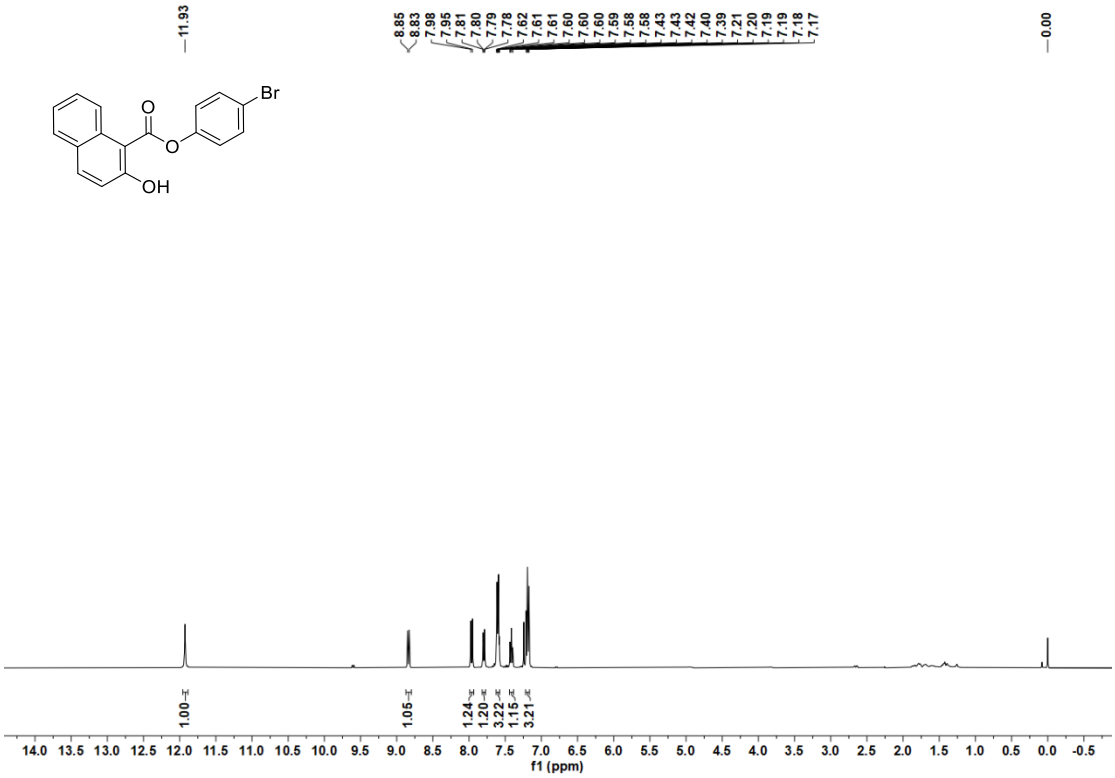


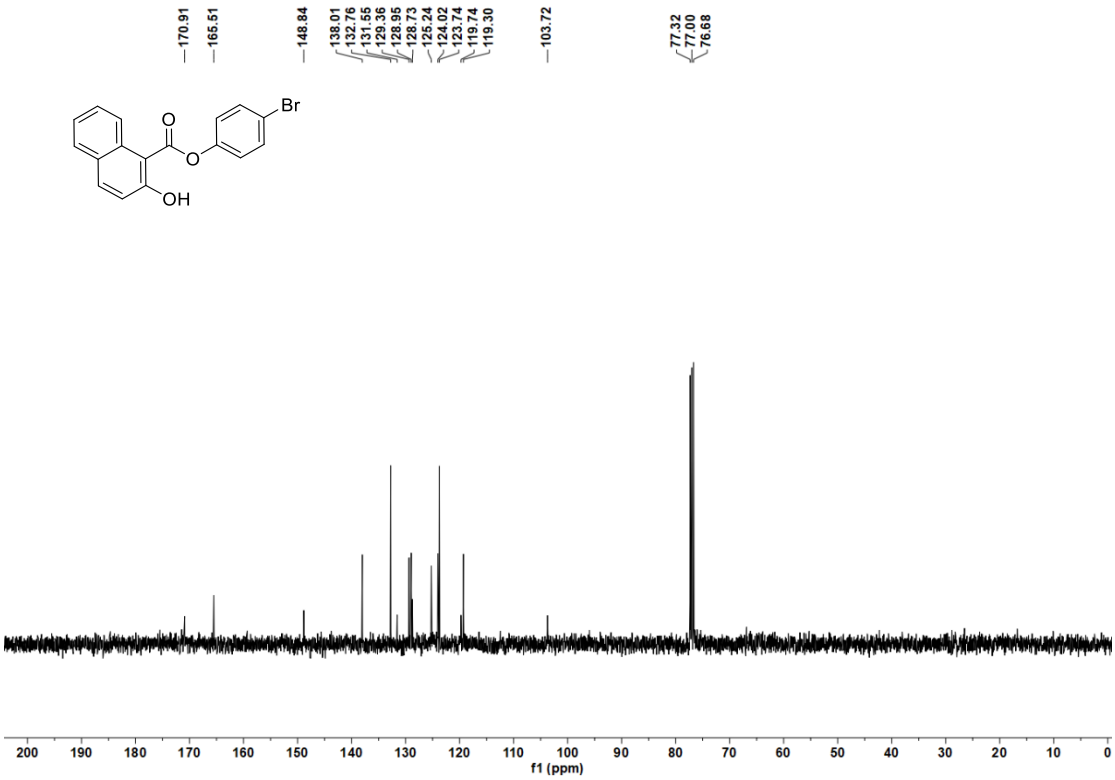
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **18a**



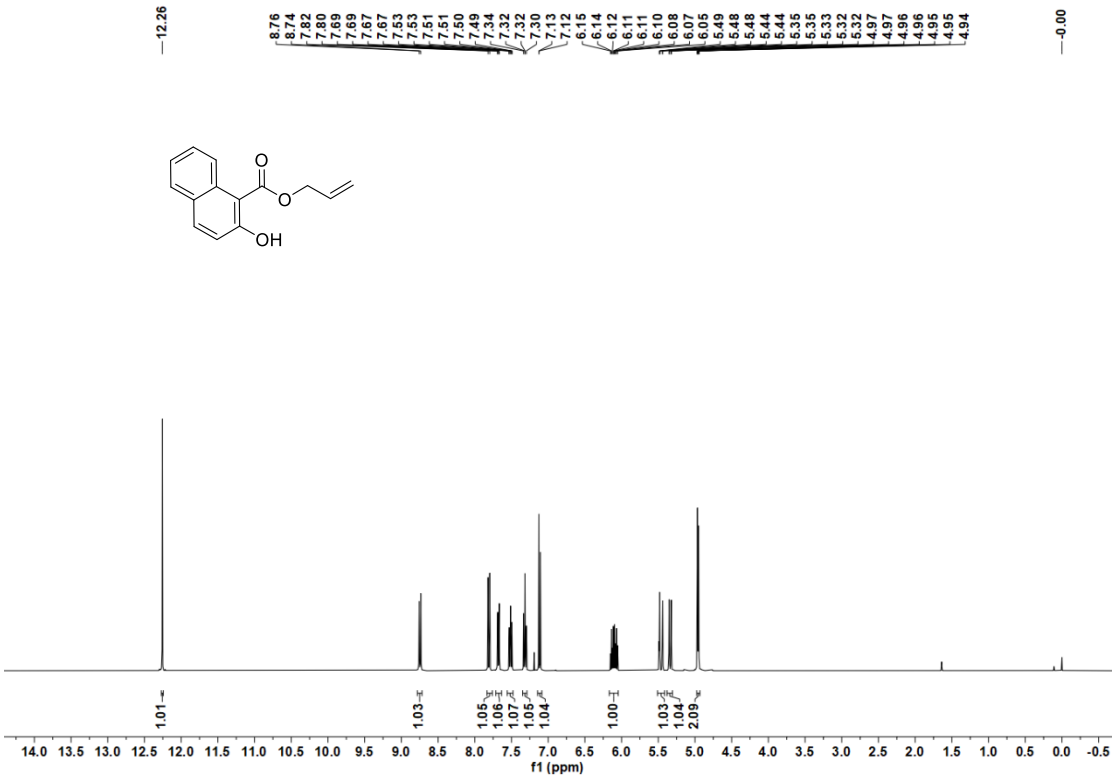


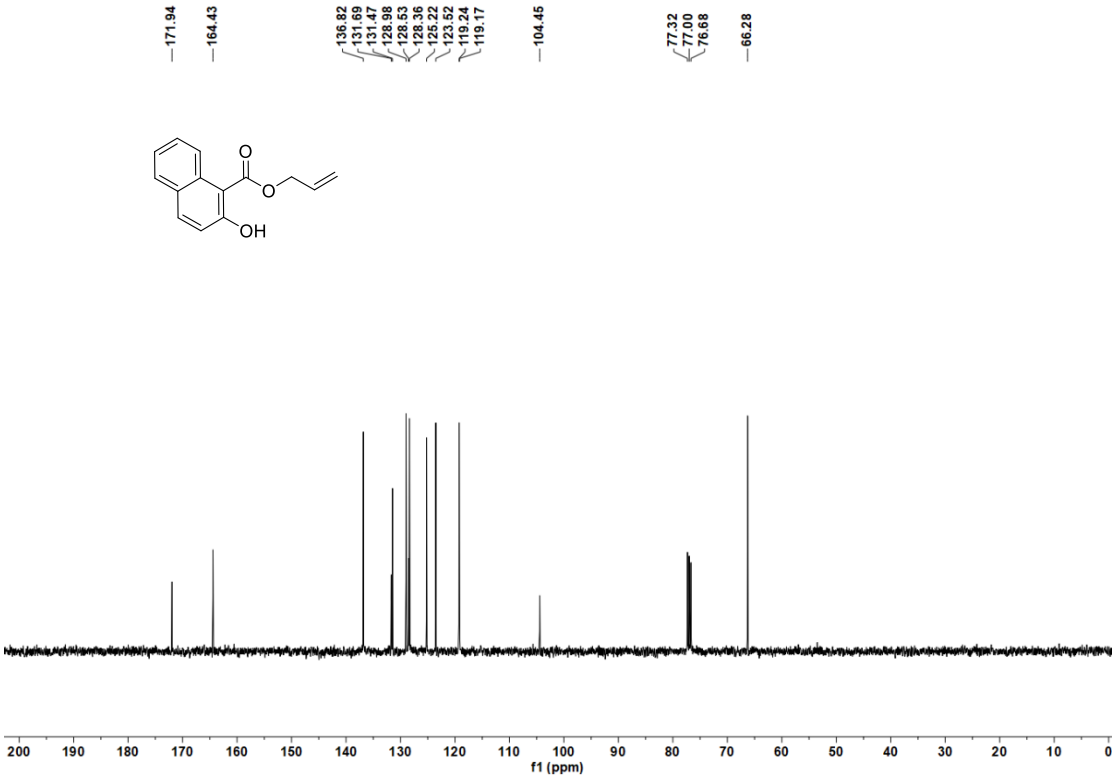
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **19a**



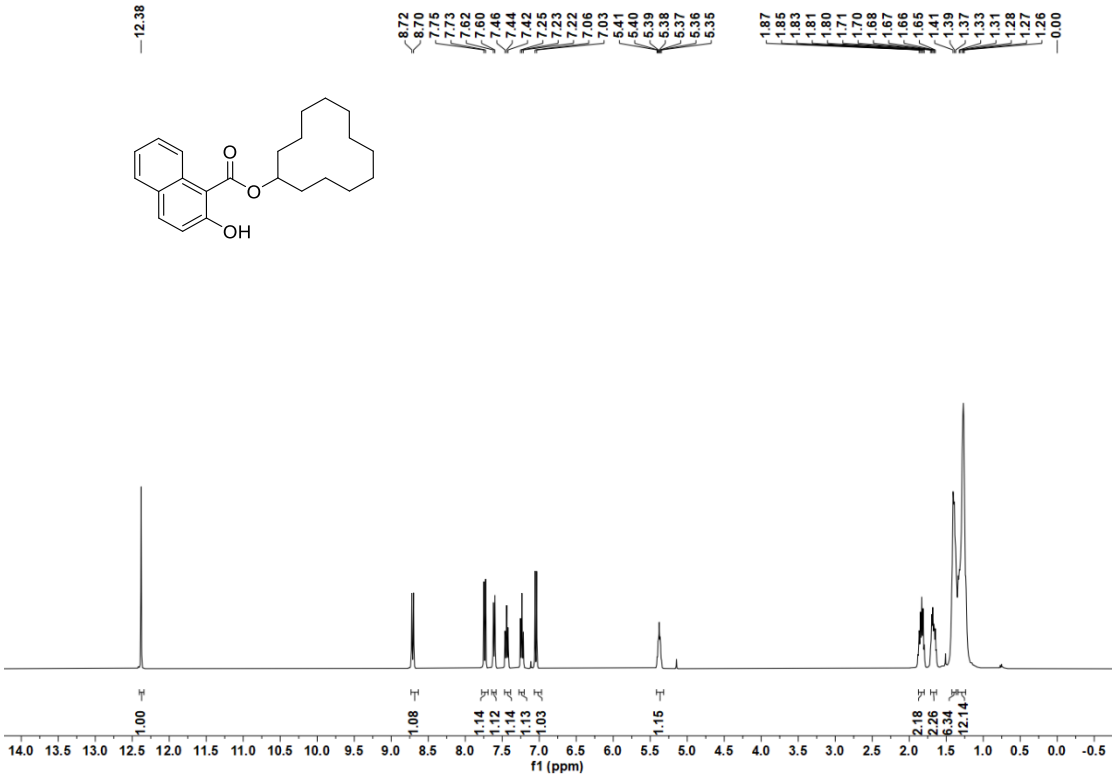


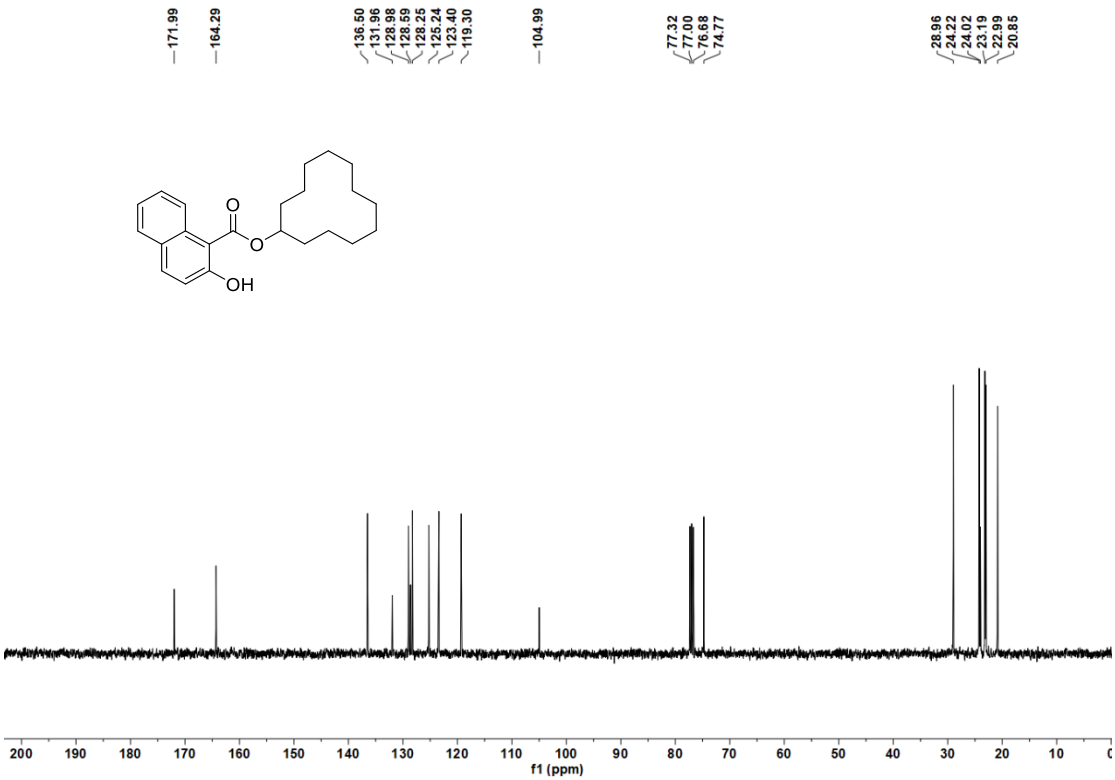
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **20a**



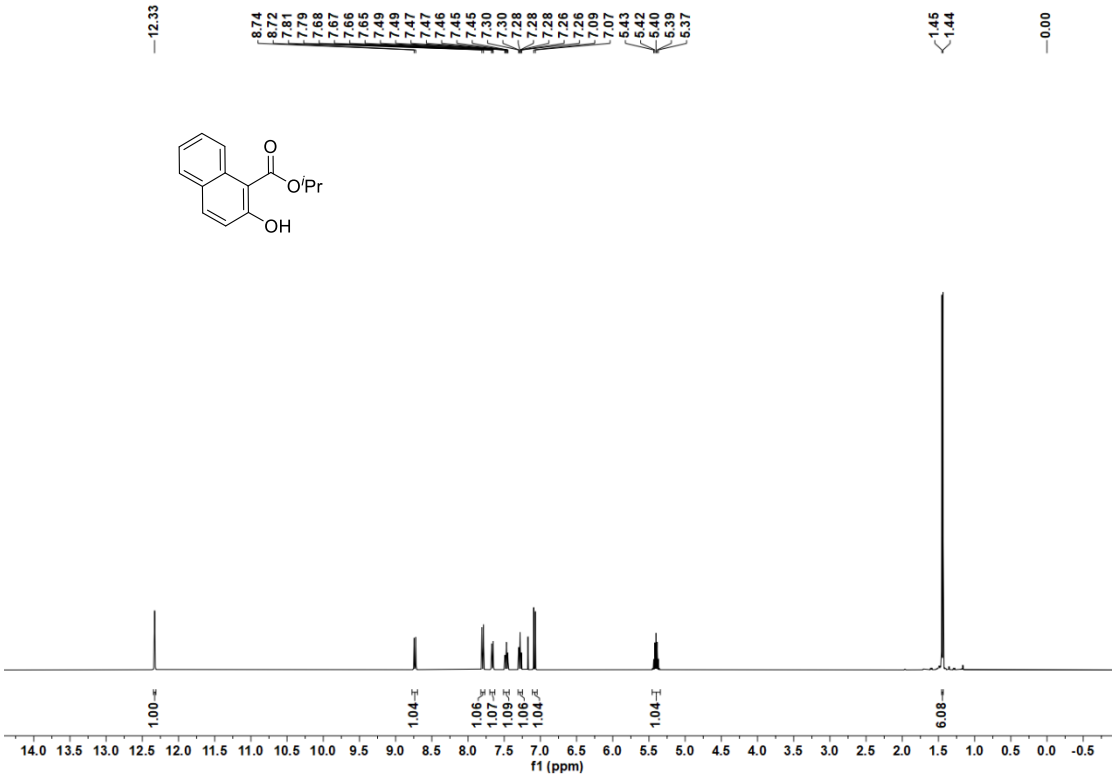


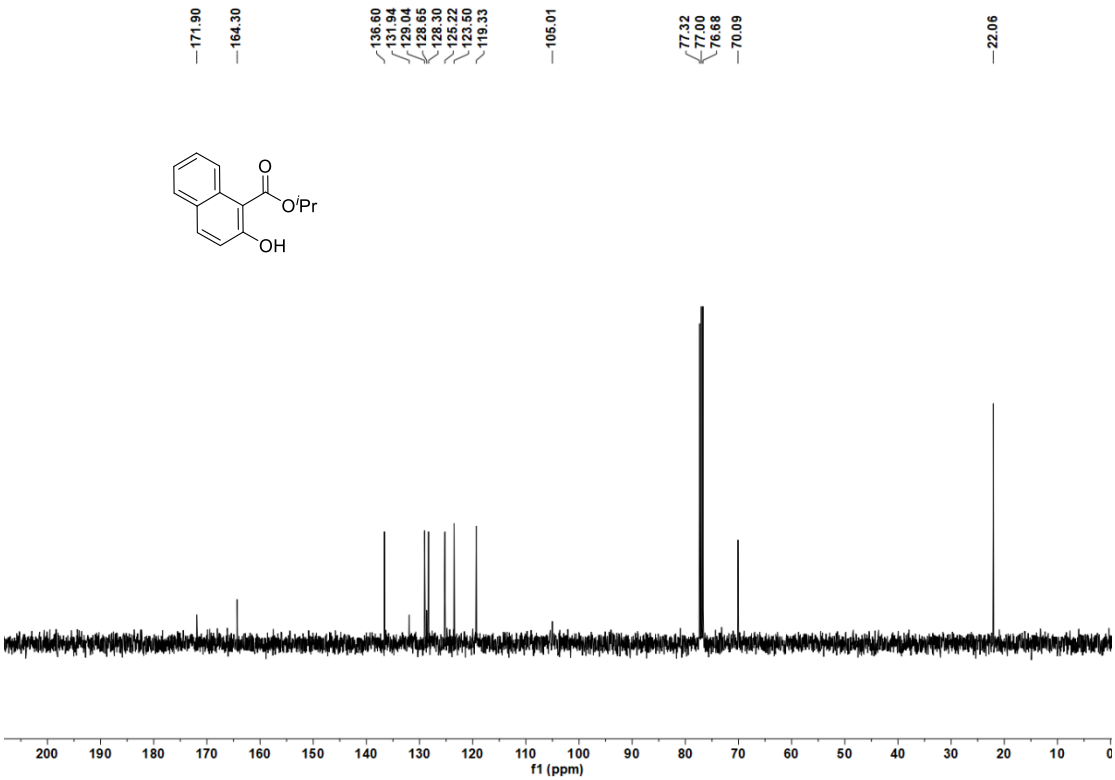
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **21a**



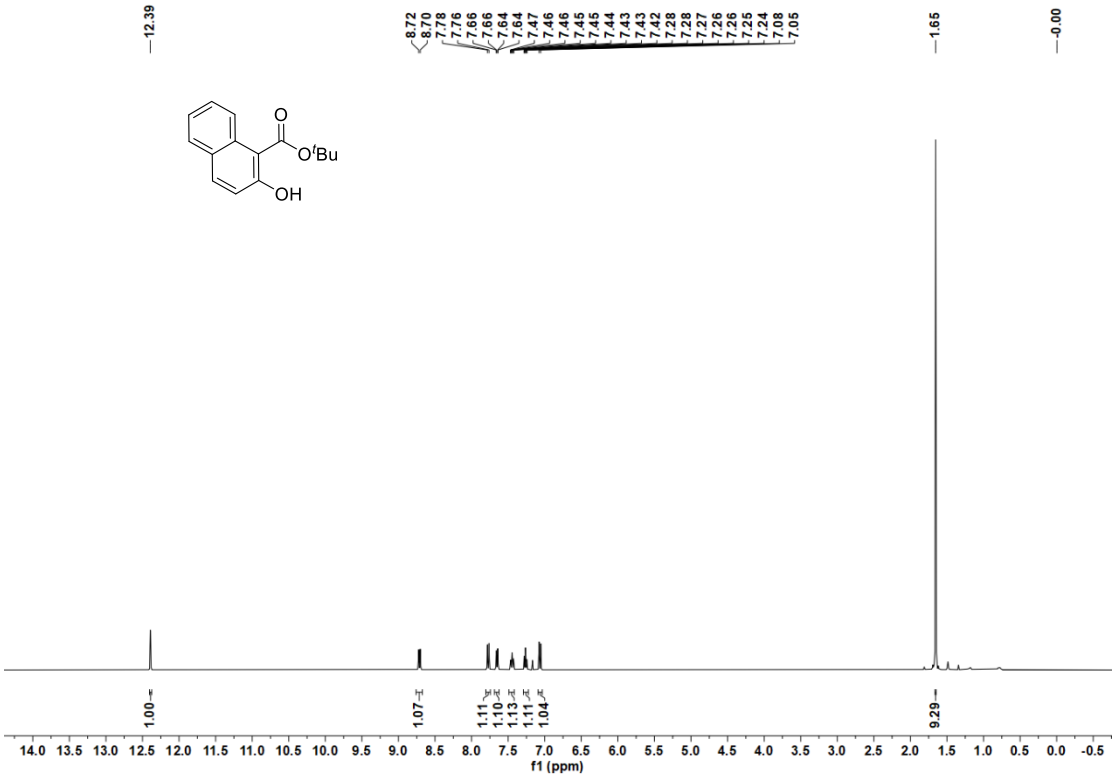


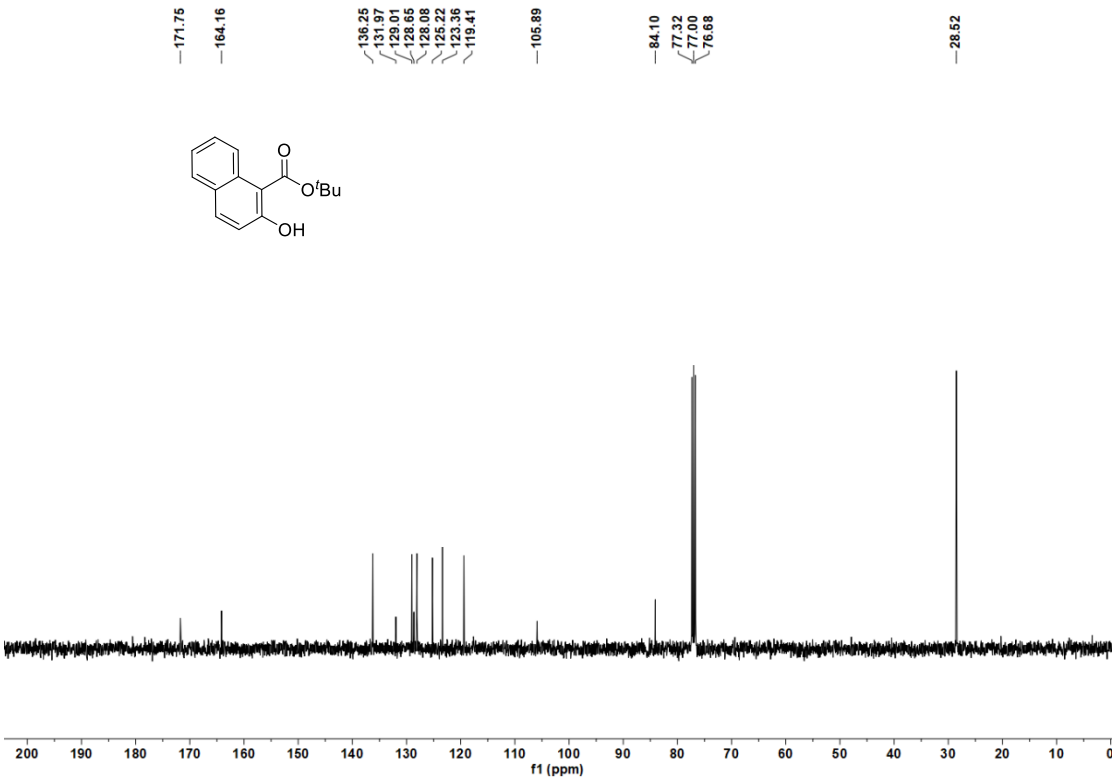
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **22a**



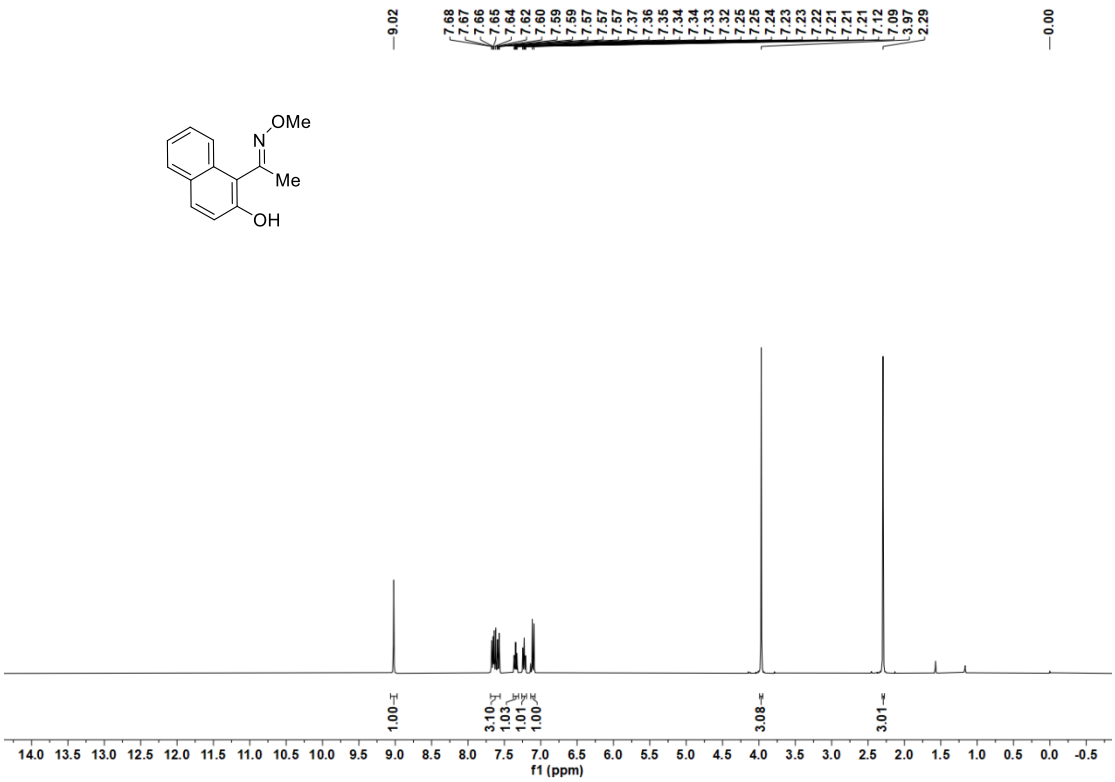


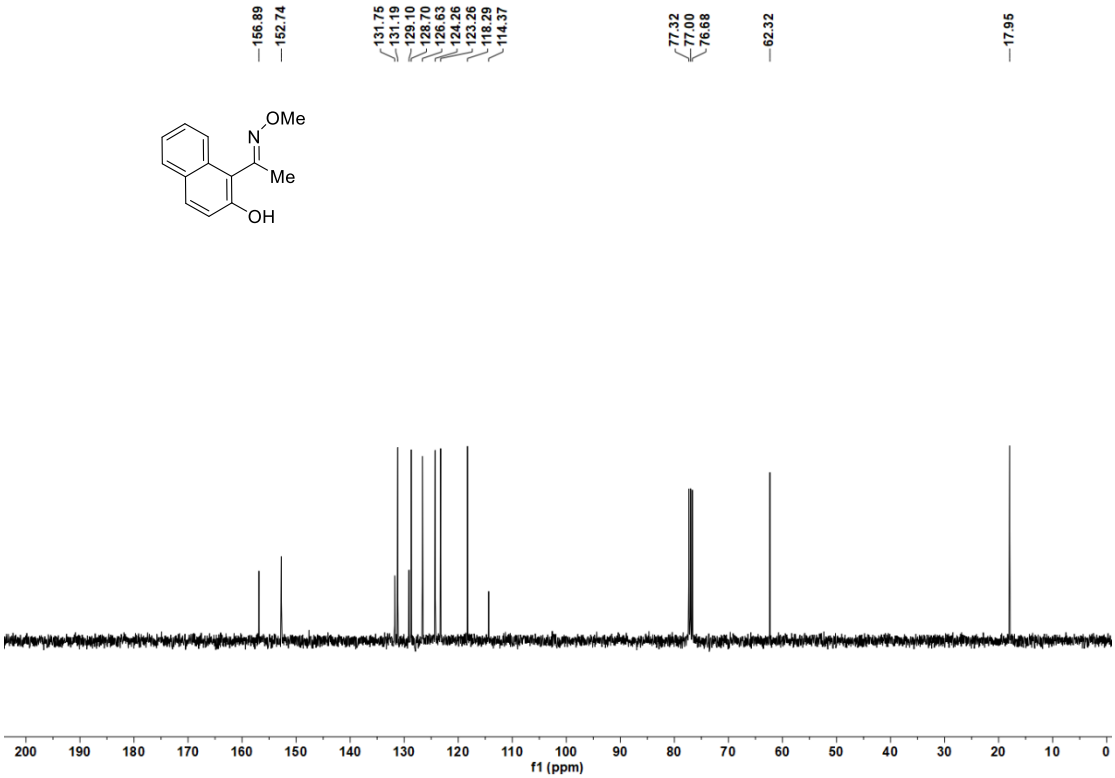
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **23a**



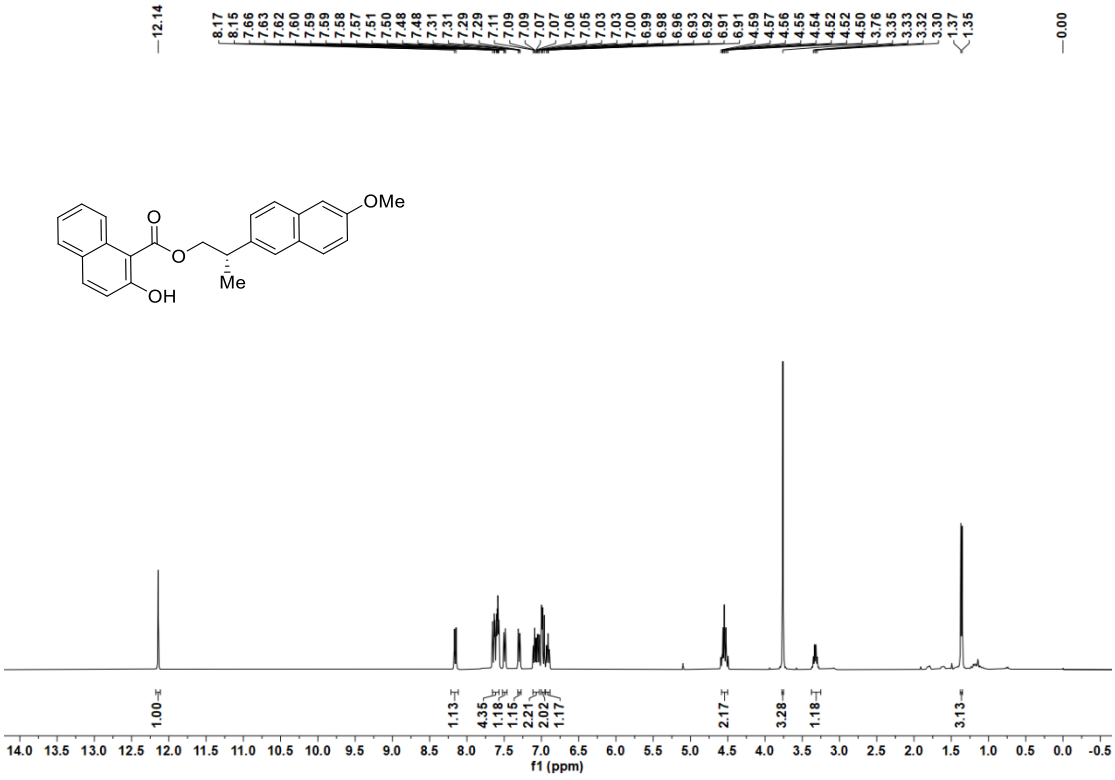


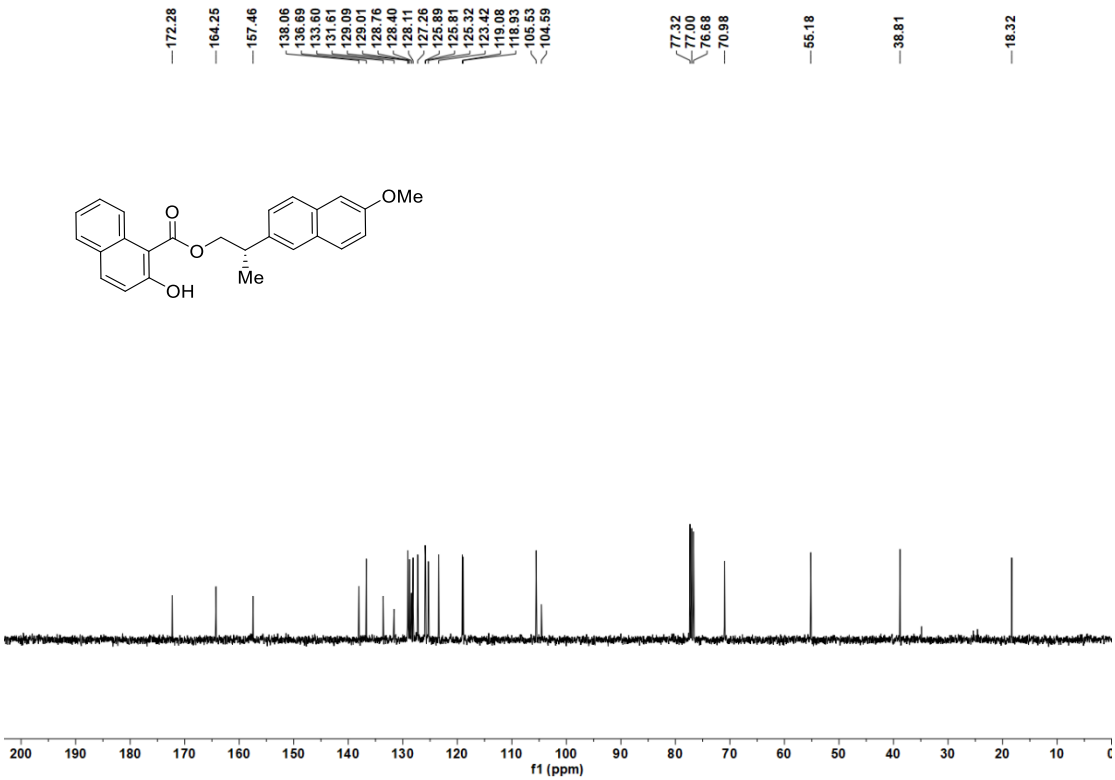
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **24a**



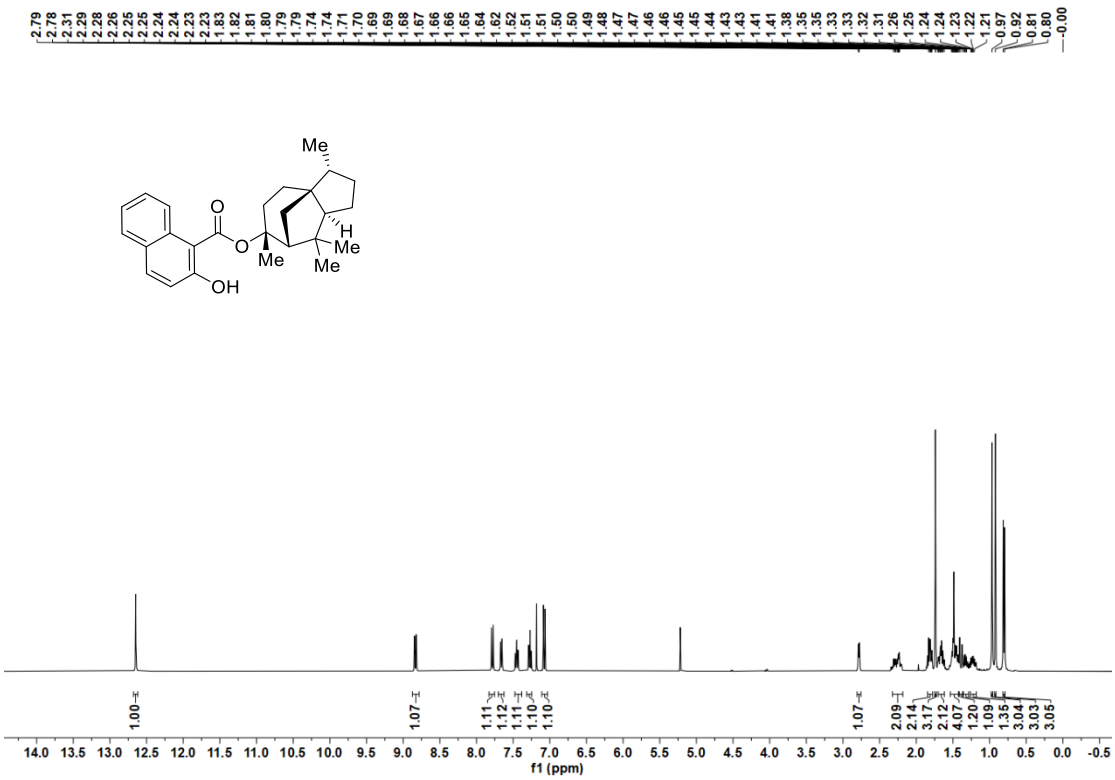


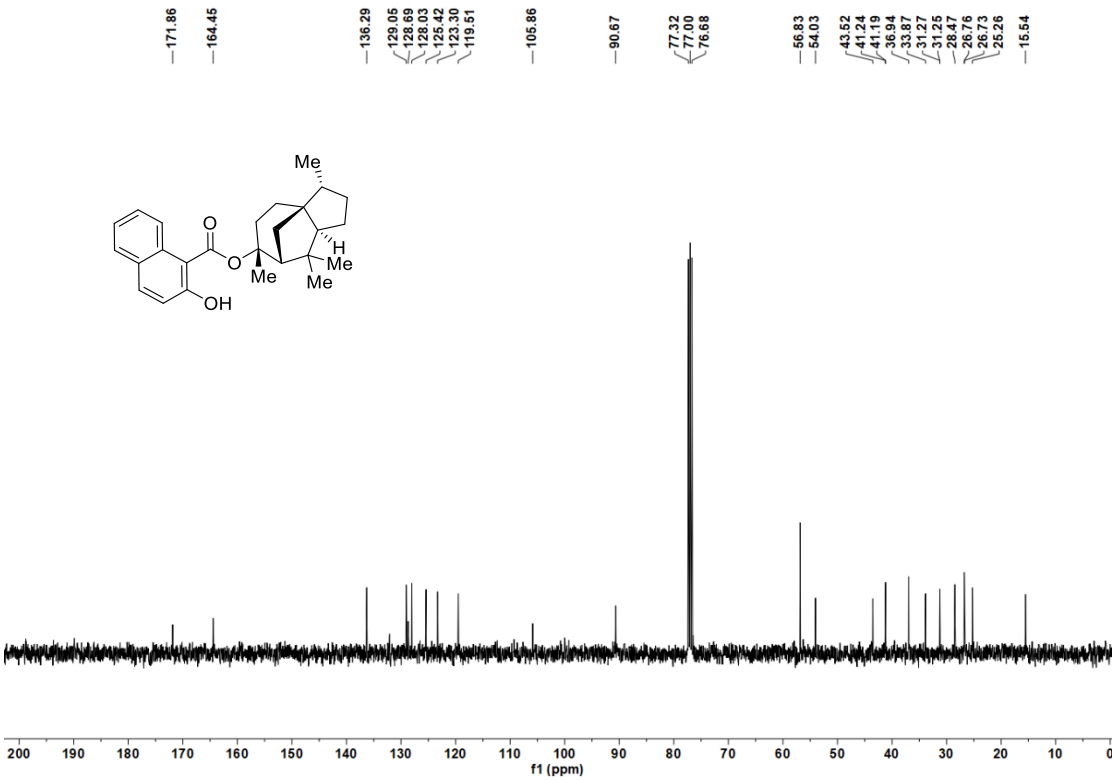
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **25a**



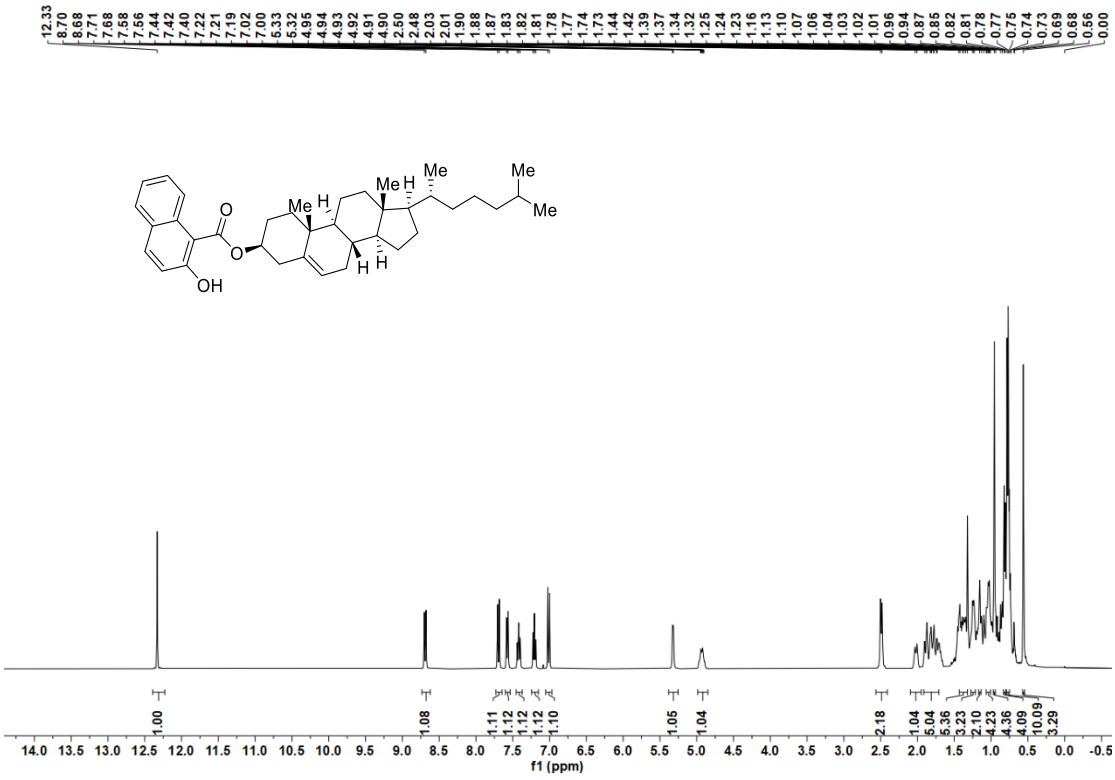


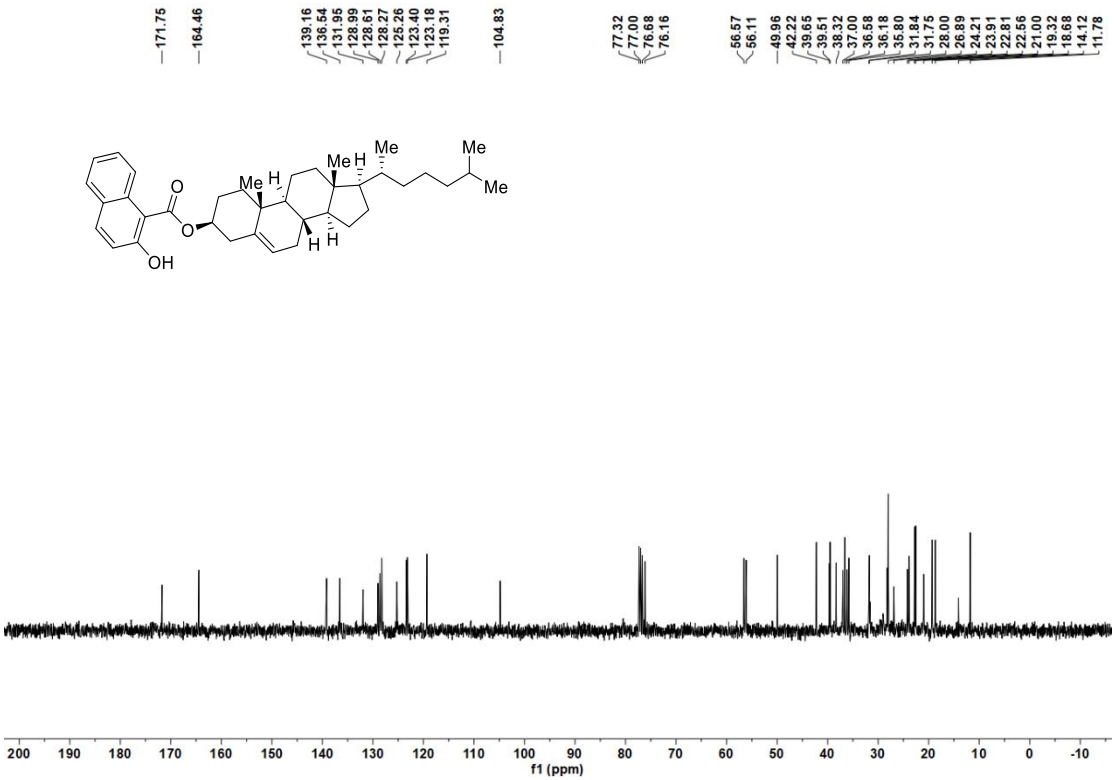
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **26a**



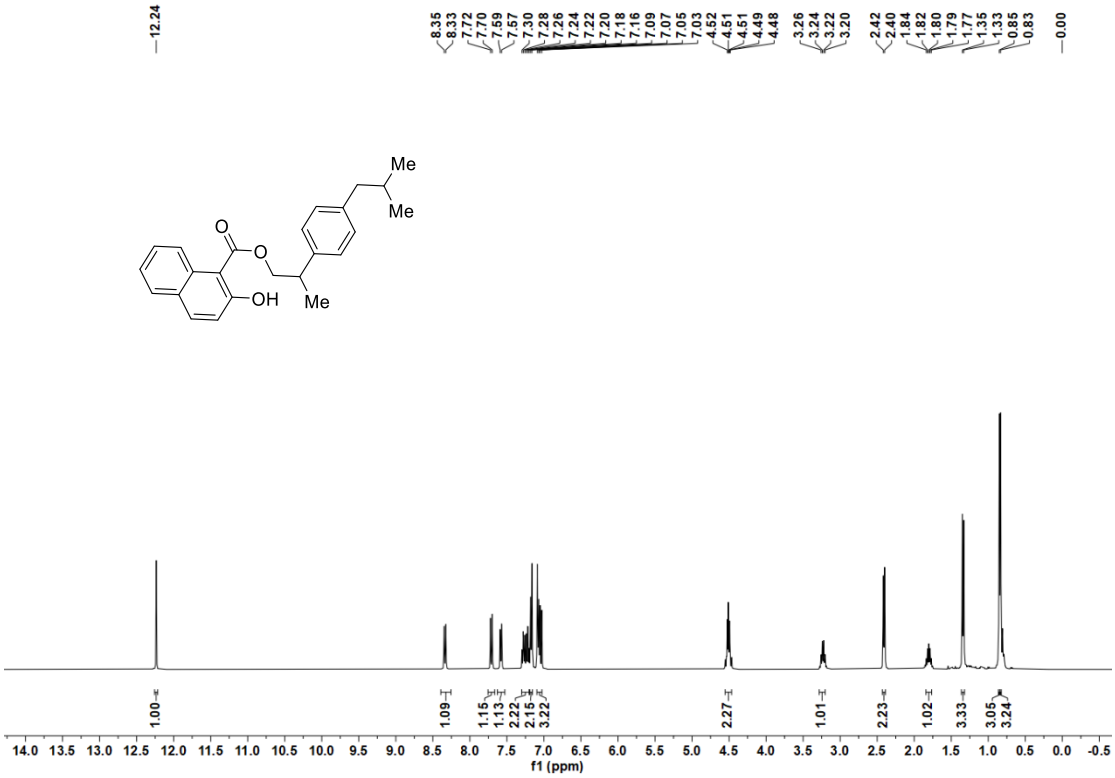


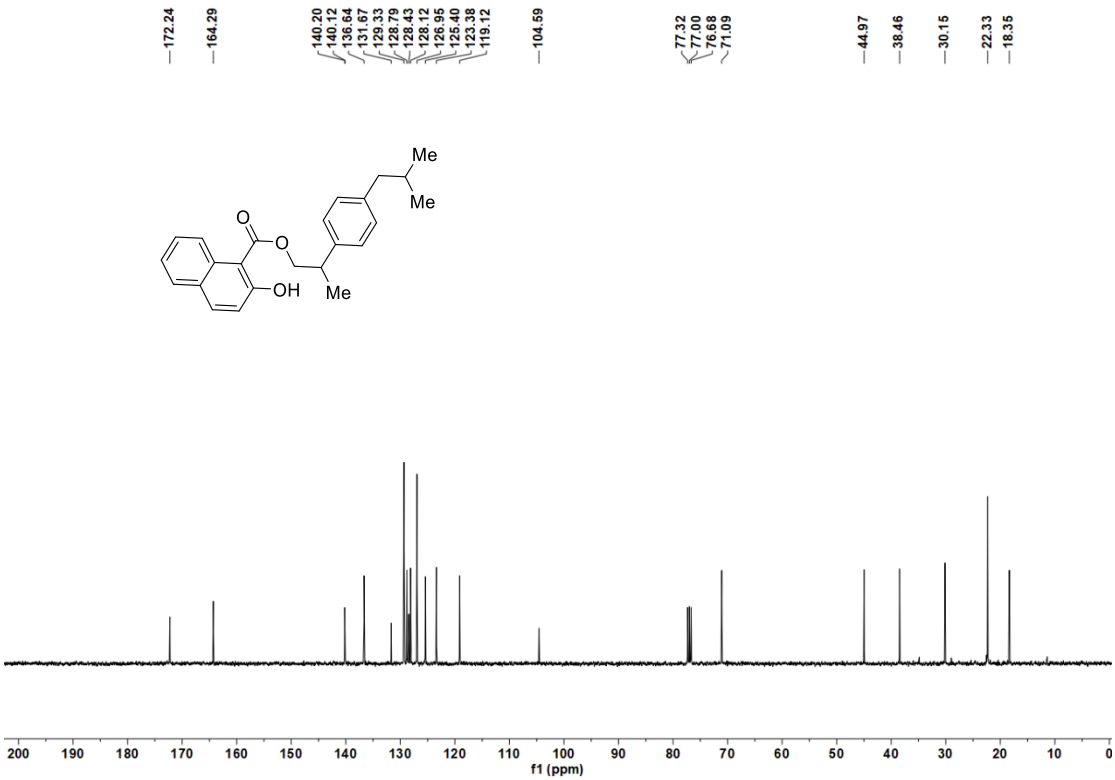
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **27a**



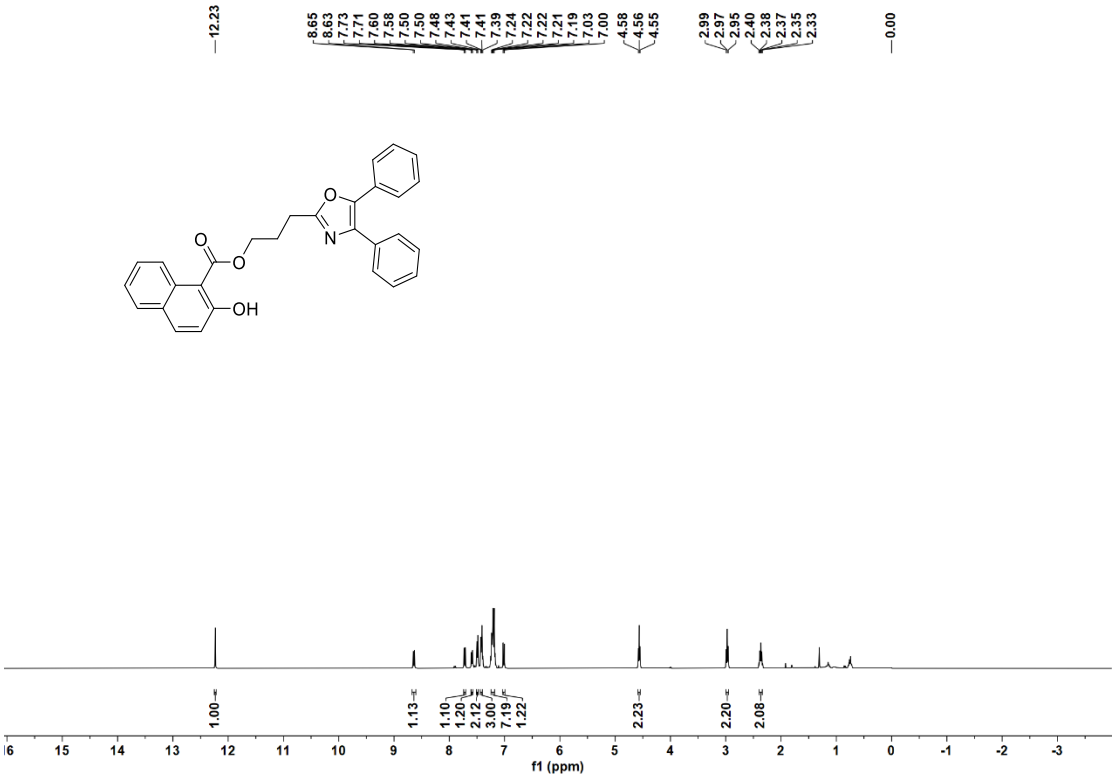


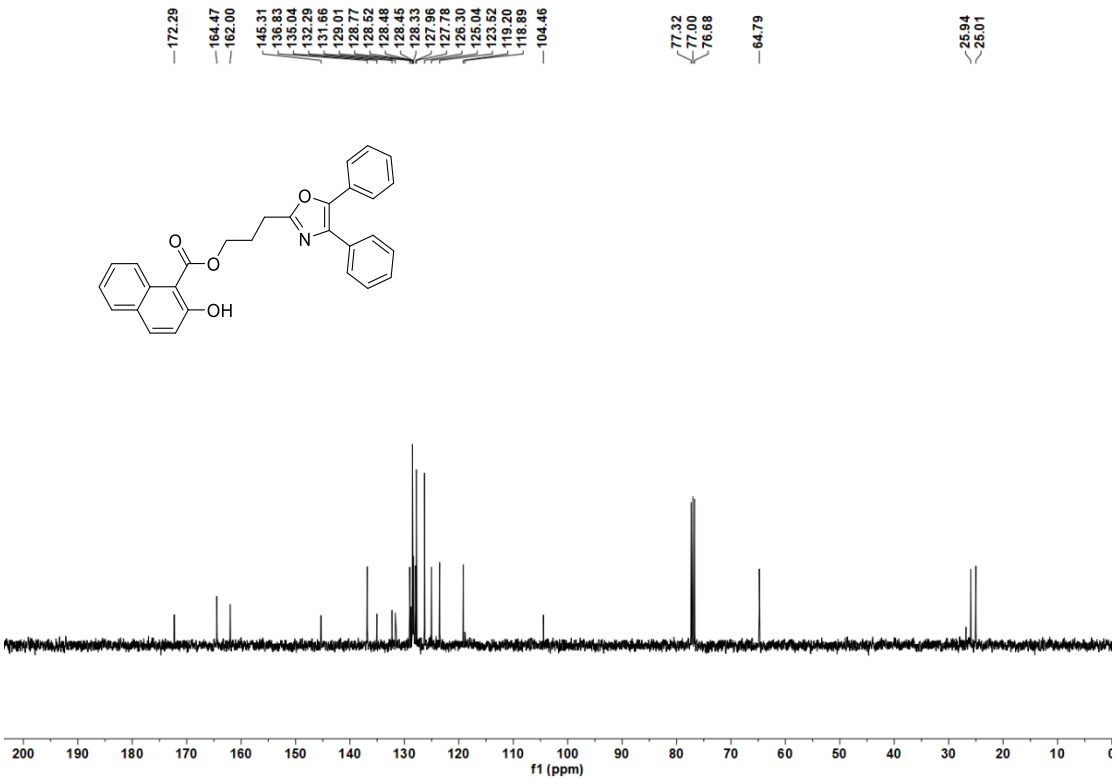
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **28a**



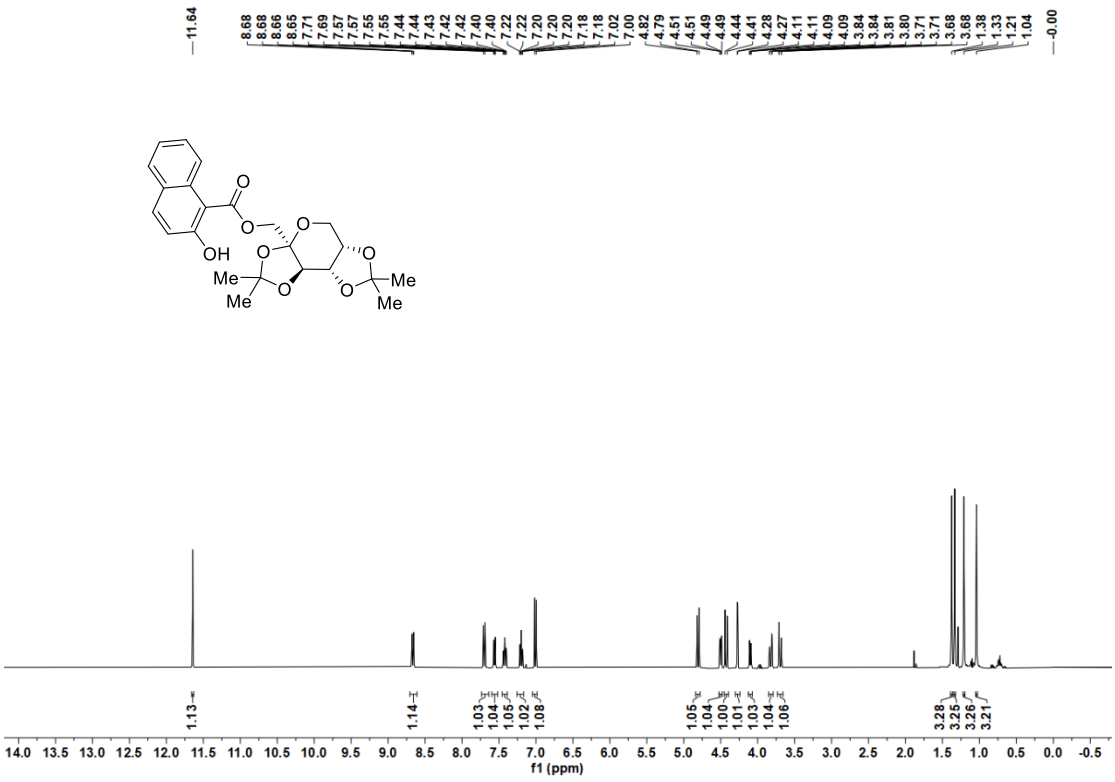


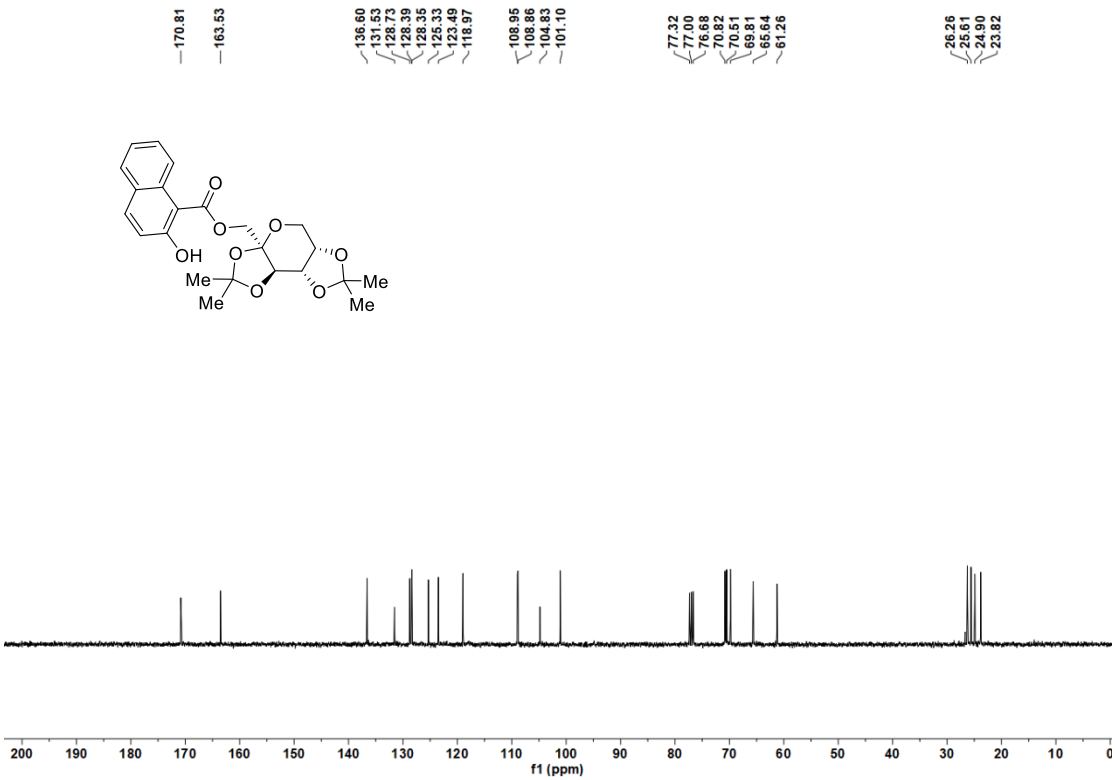
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **29a**



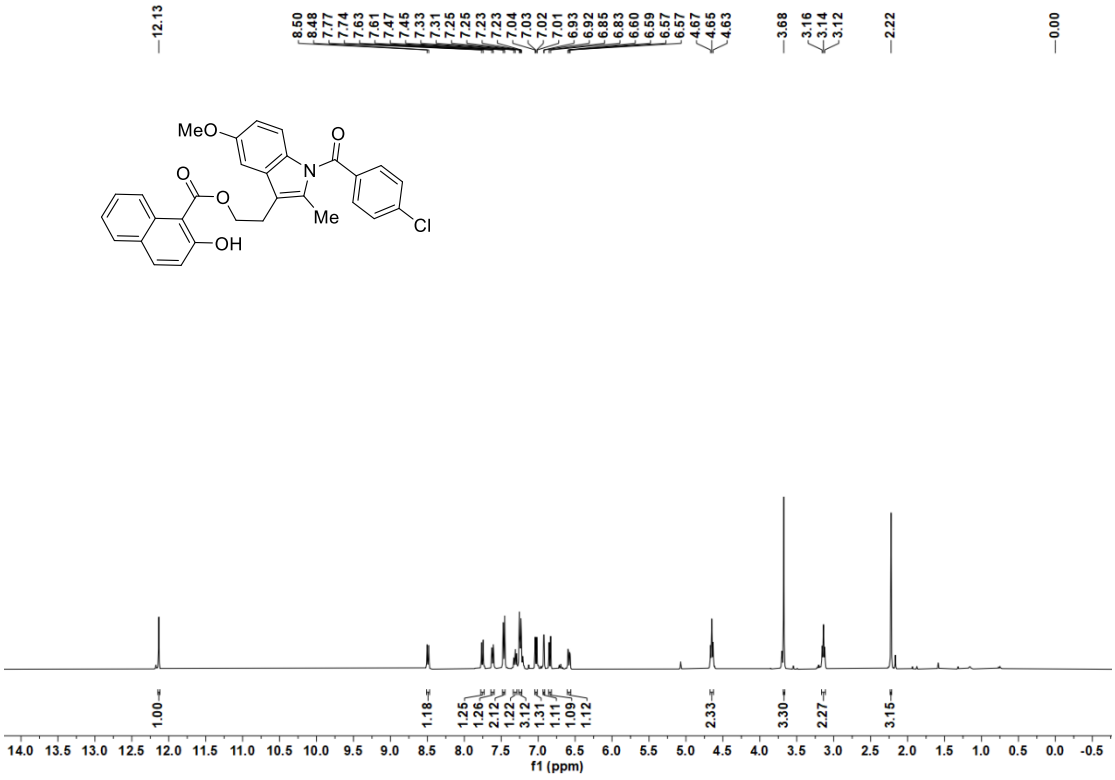


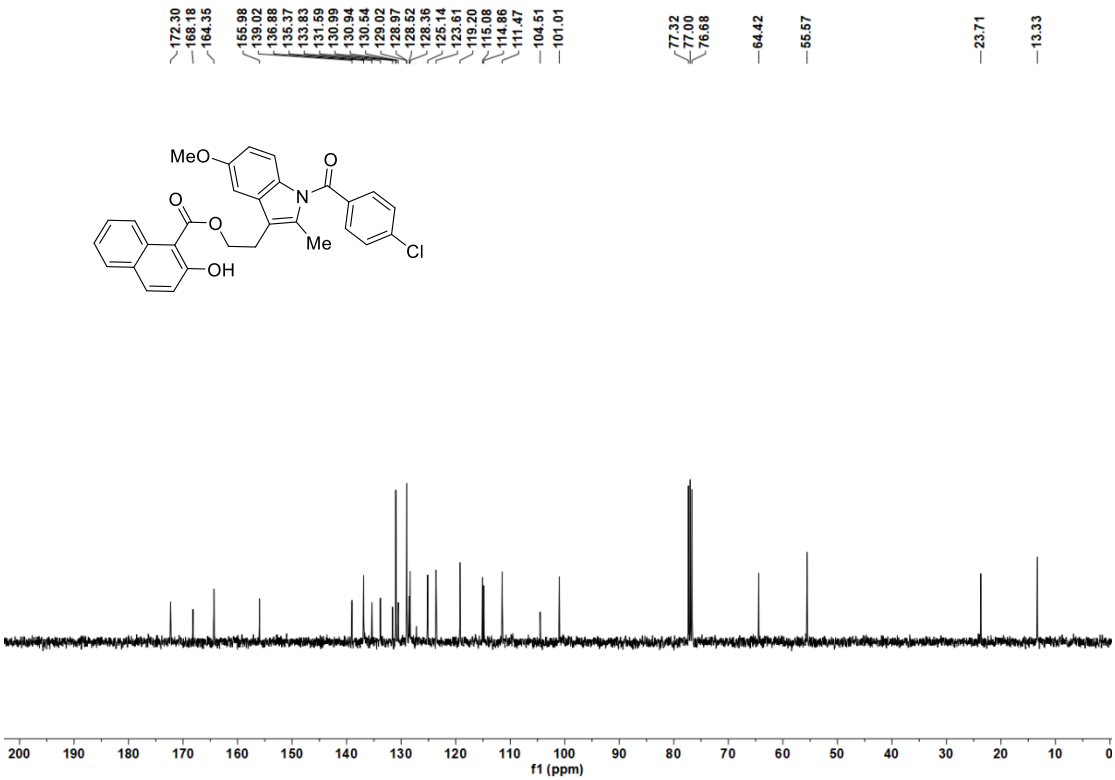
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **30a**



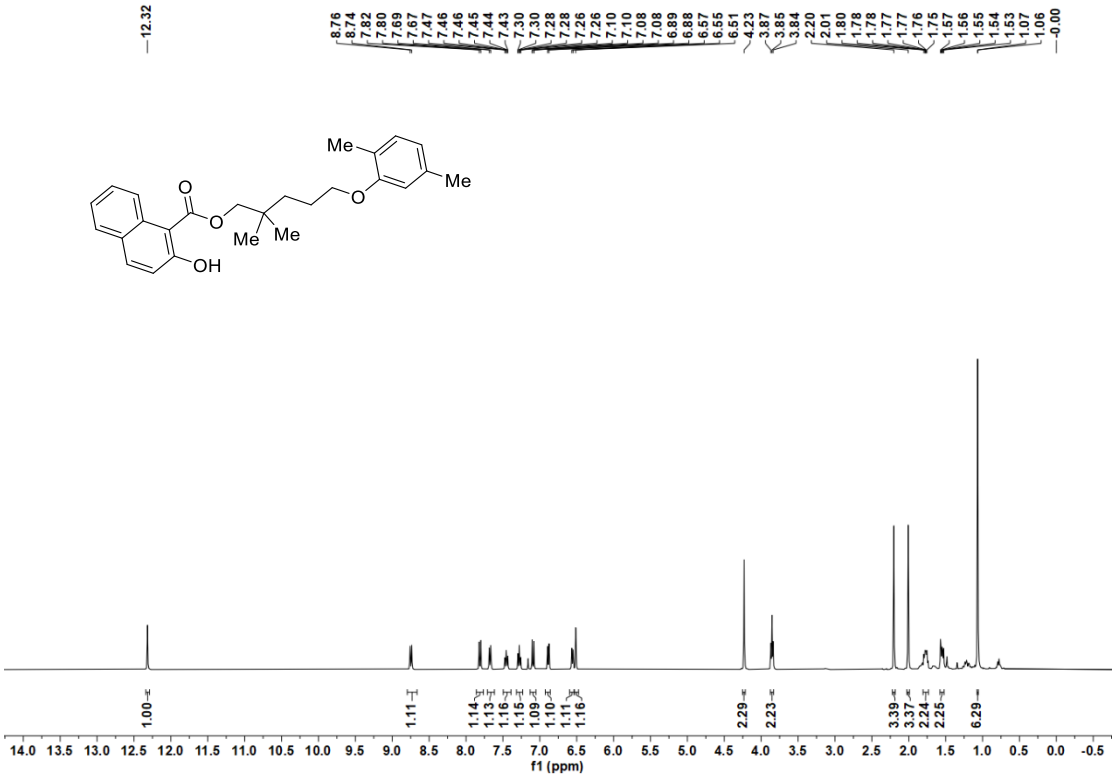


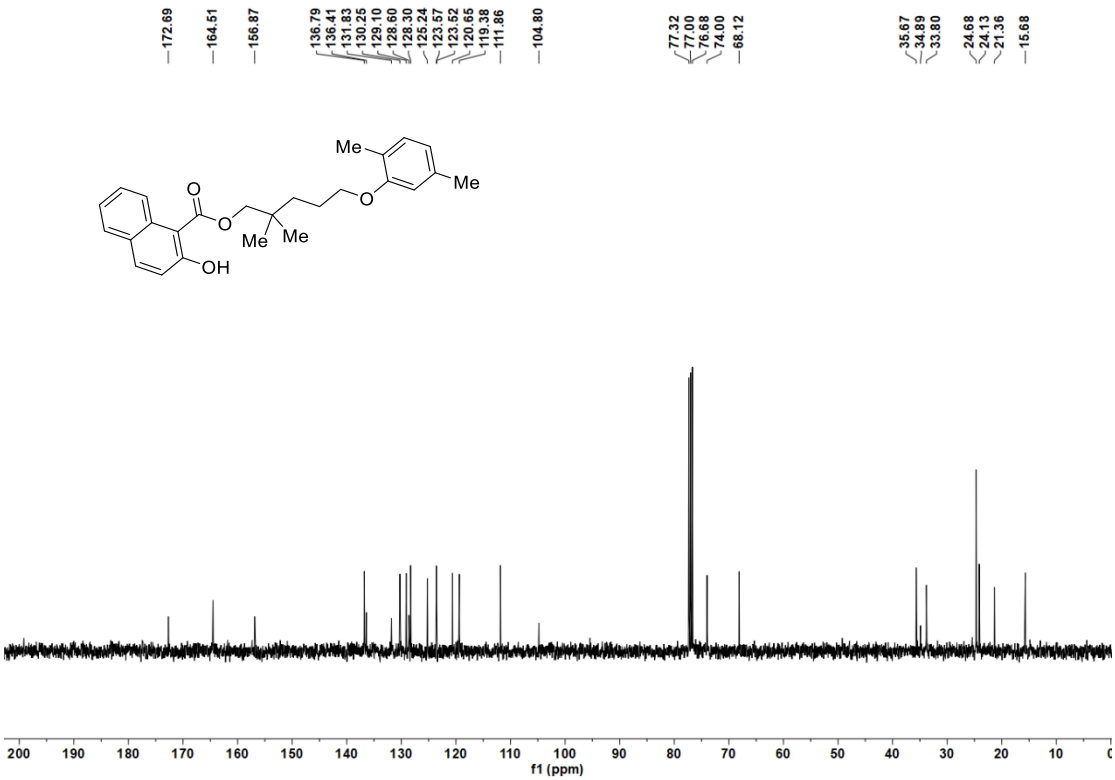
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **31a**



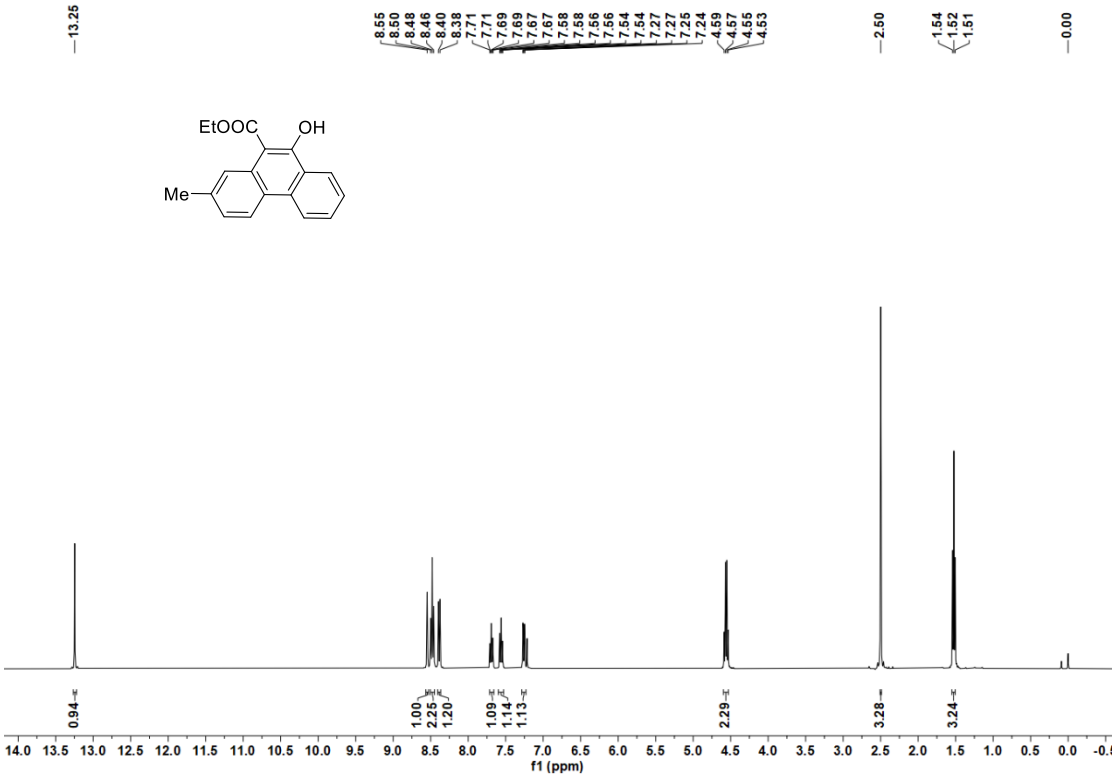


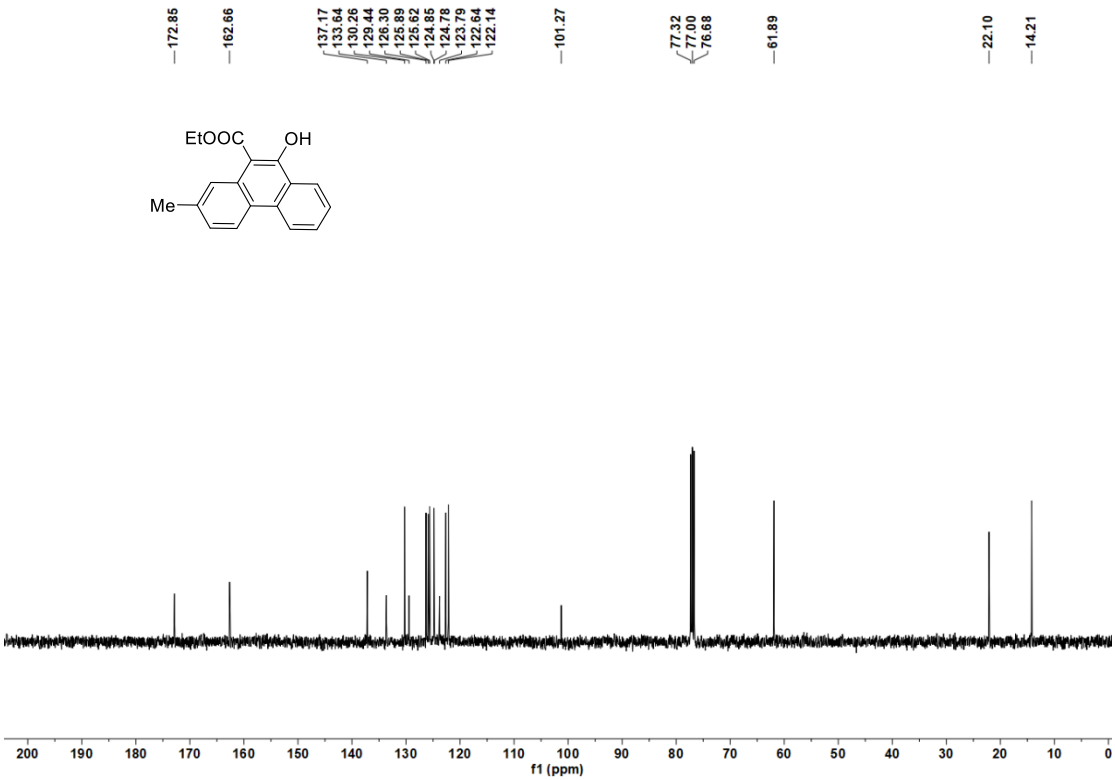
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **32a**



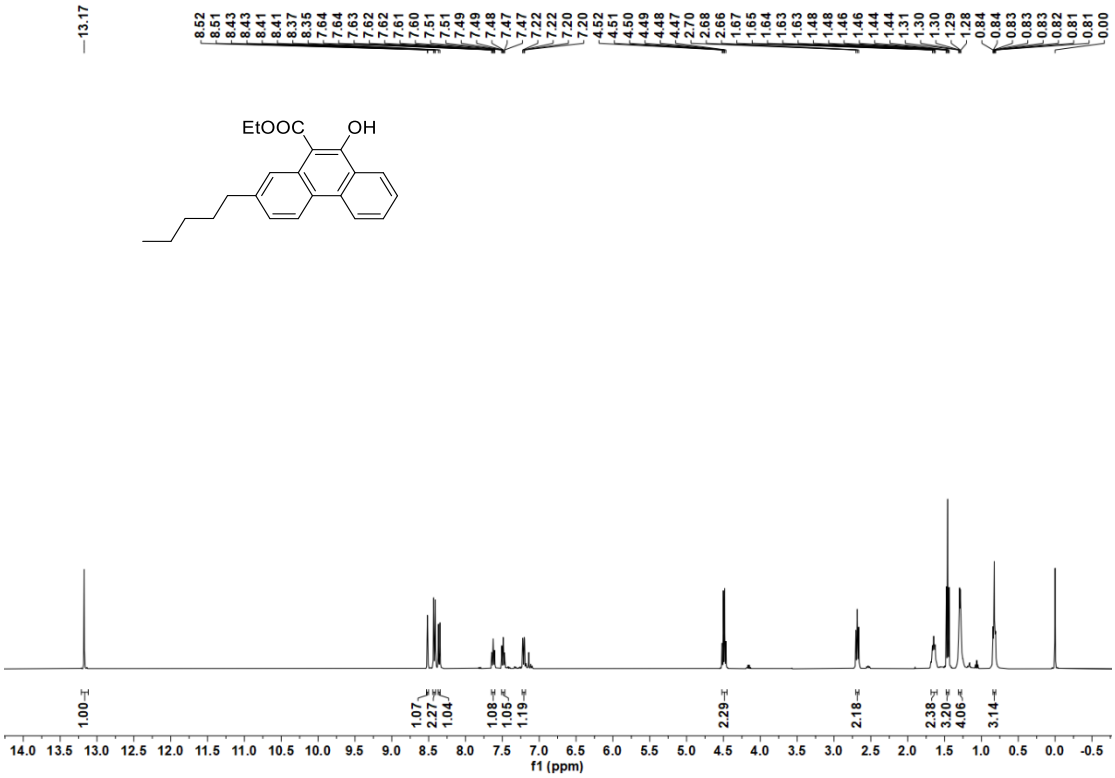


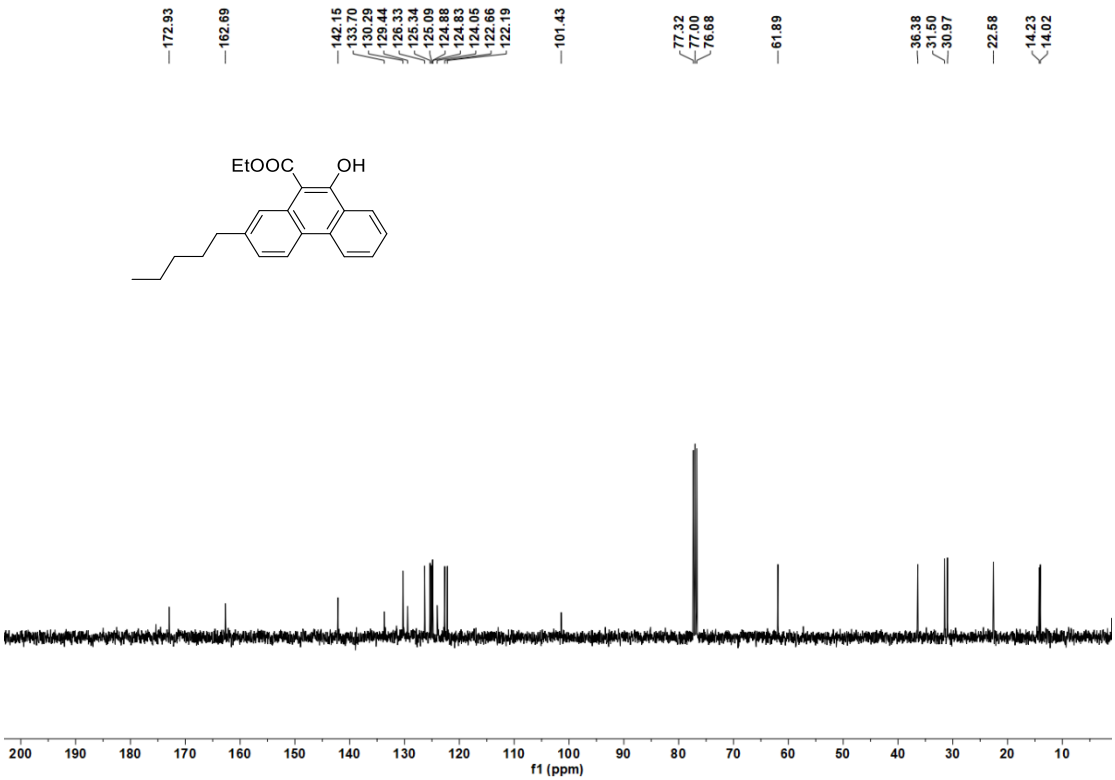
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **33a**



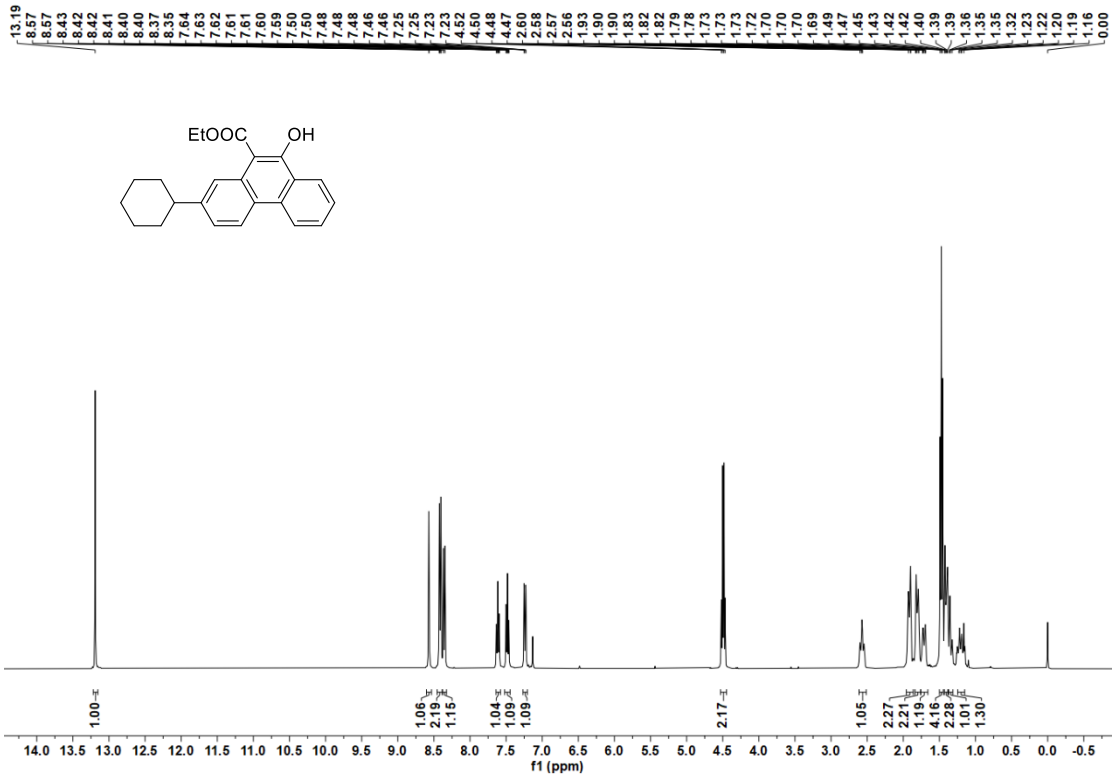


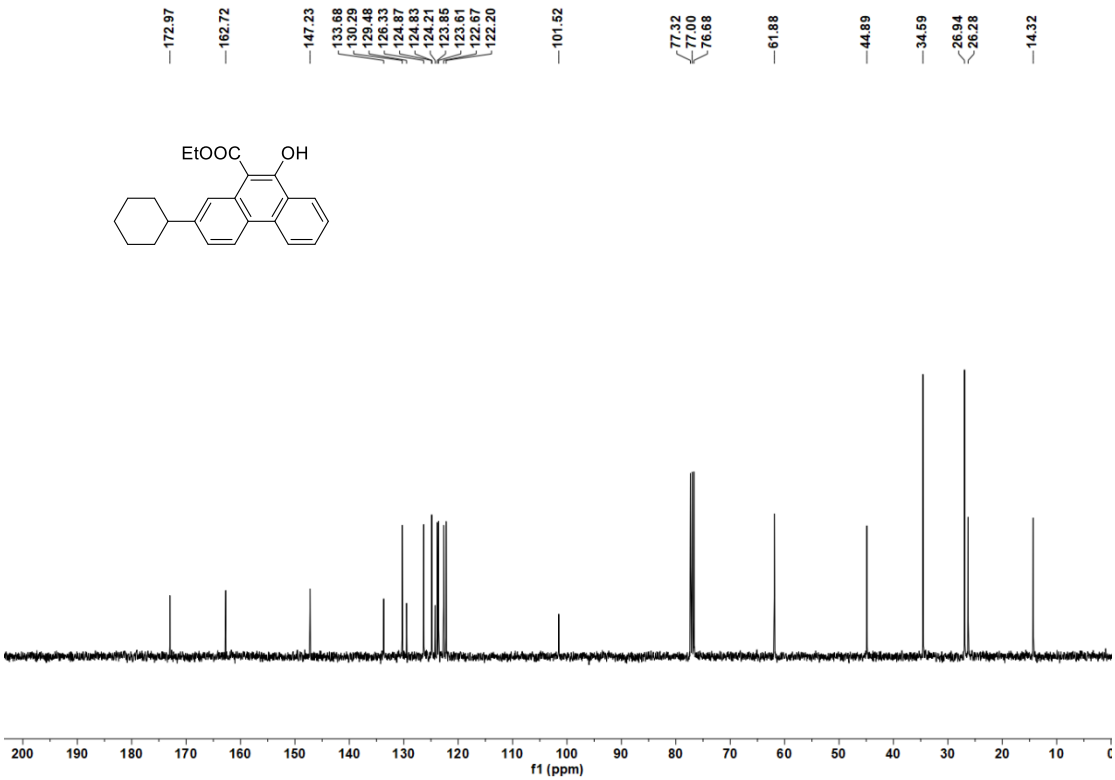
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **34a**



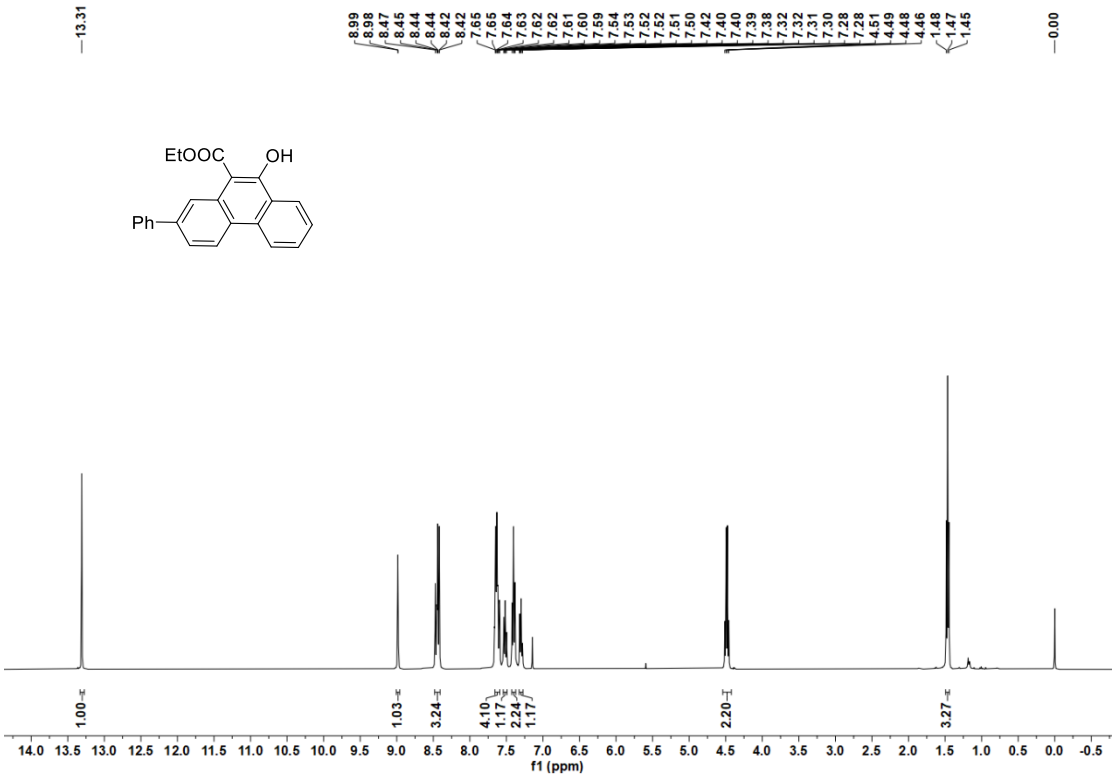


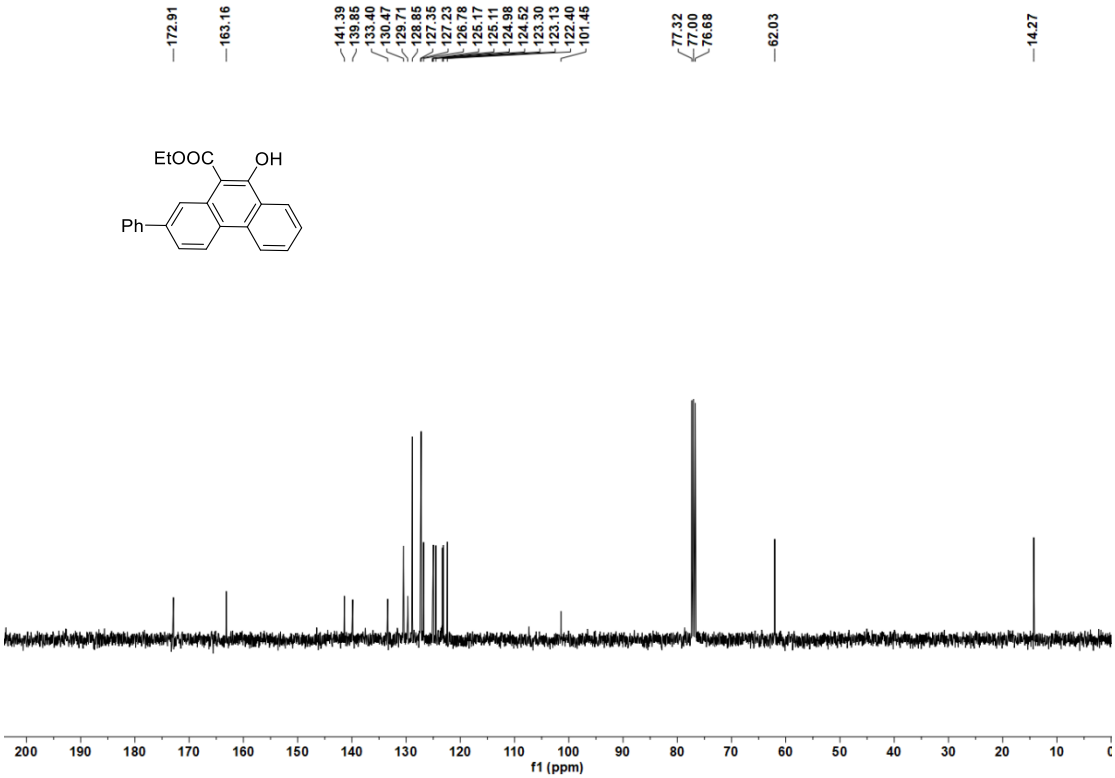
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **35a**



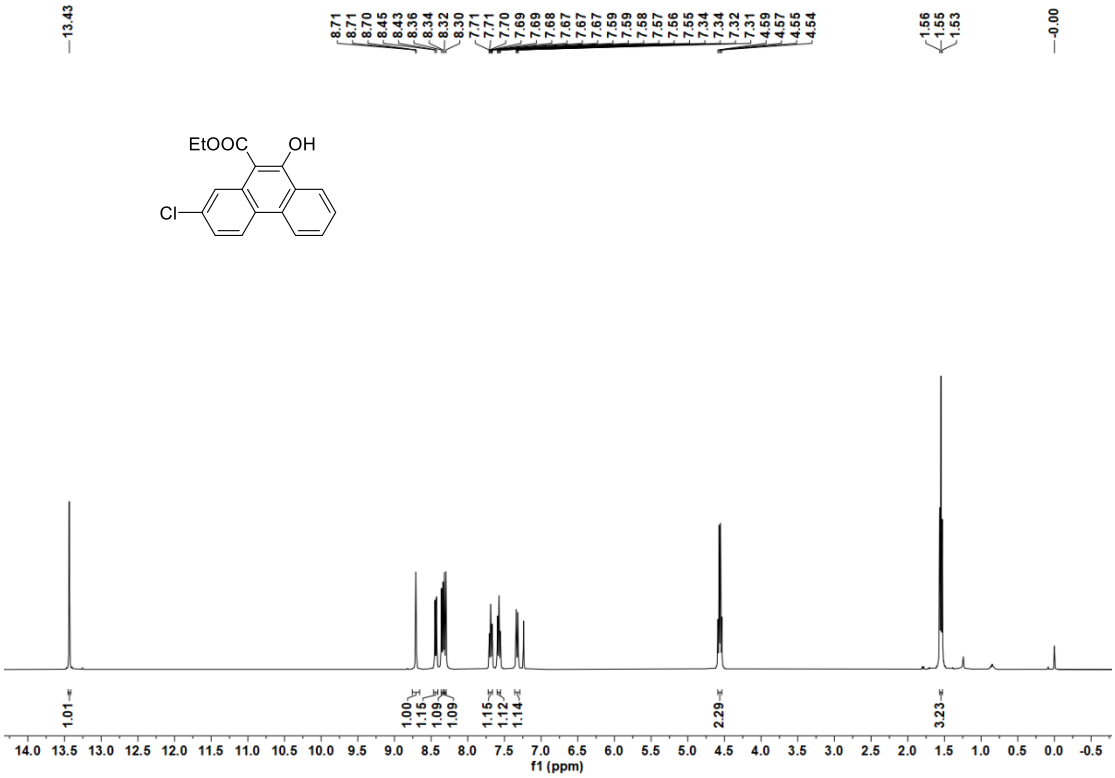


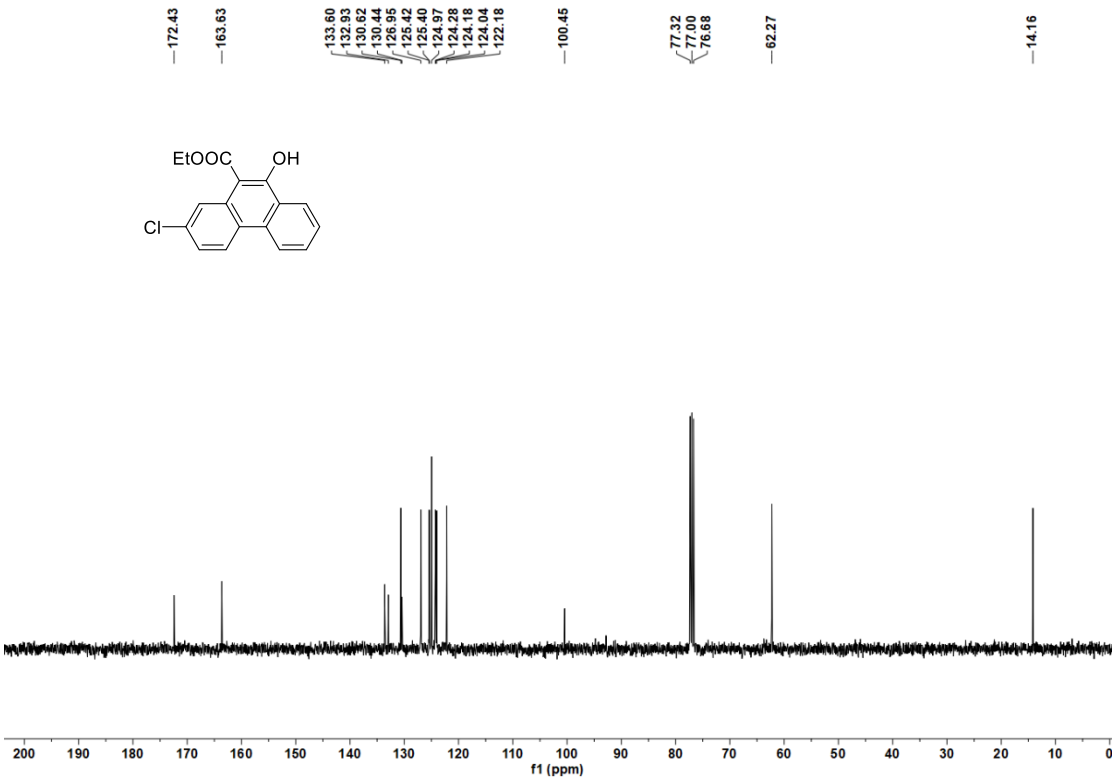
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **36a**



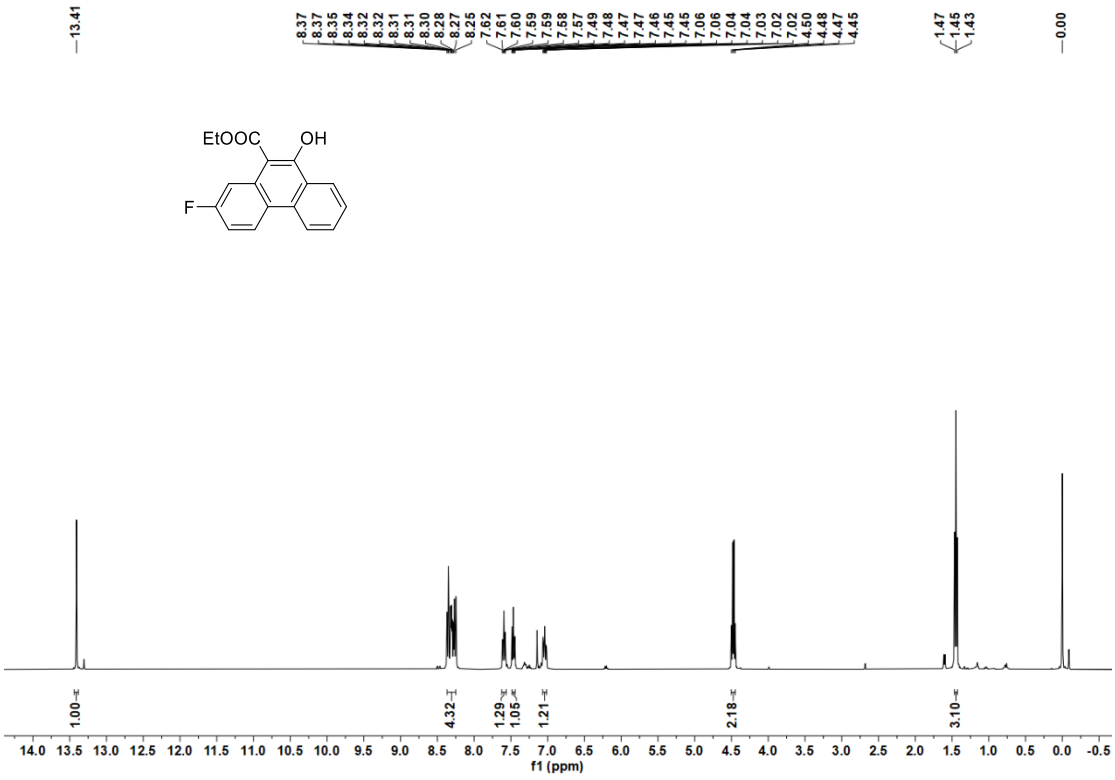


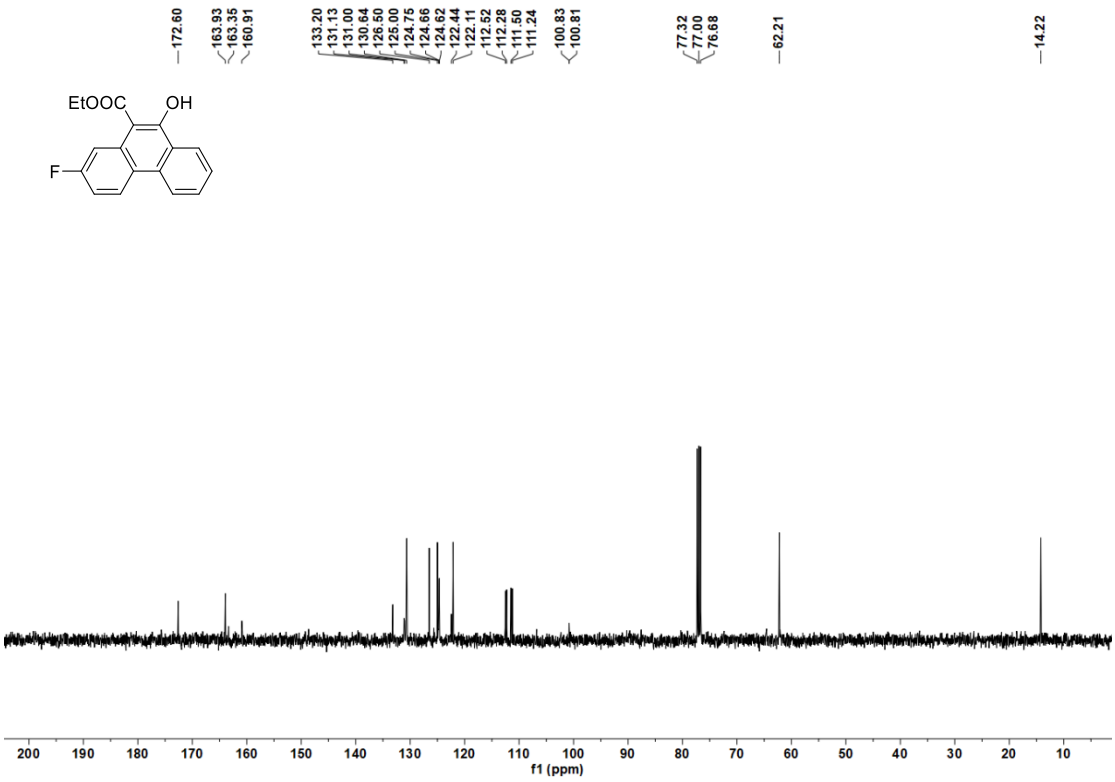
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **37a**

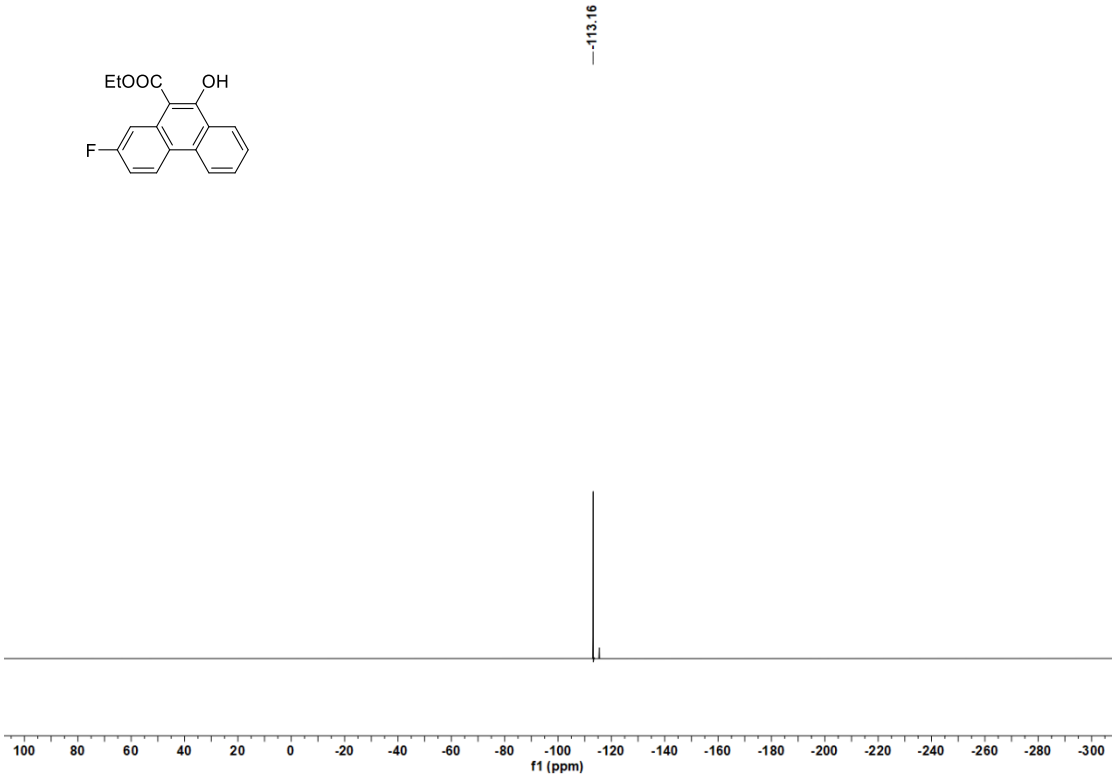




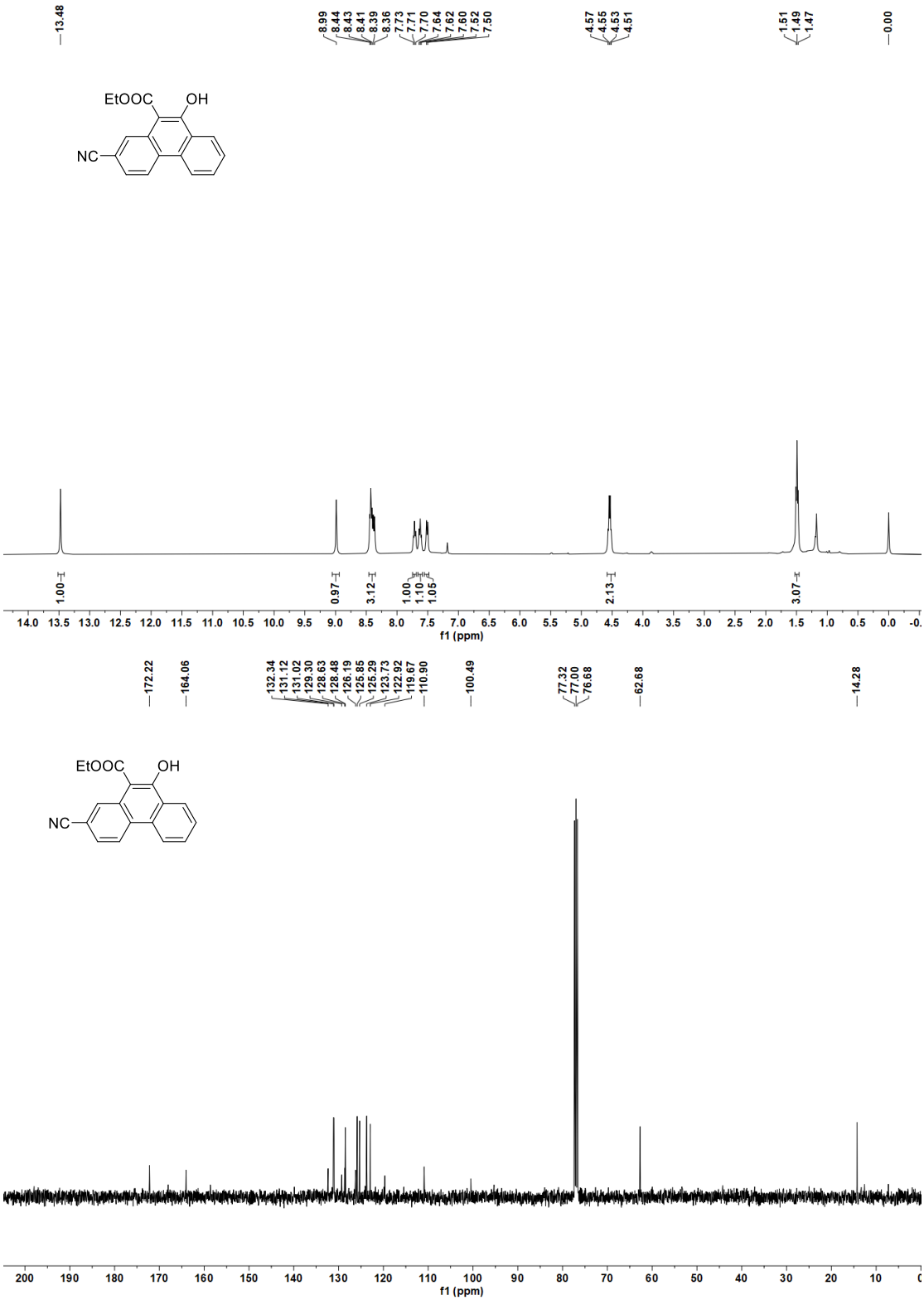
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **38a**



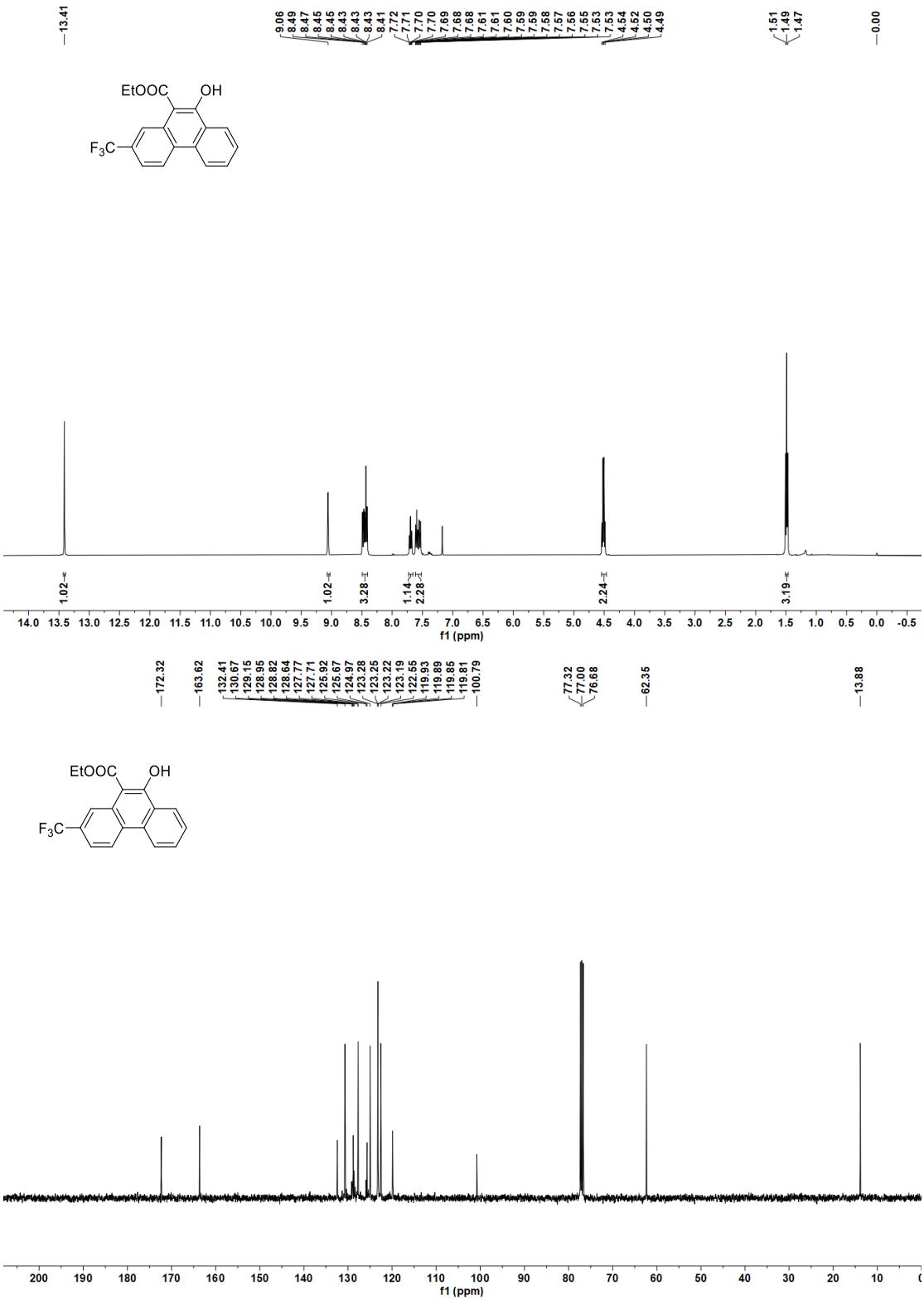




^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **39a**



^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **40a**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8.49
8.47
8.45
8.45
8.43
8.43
8.43
8.41
7.72
7.71
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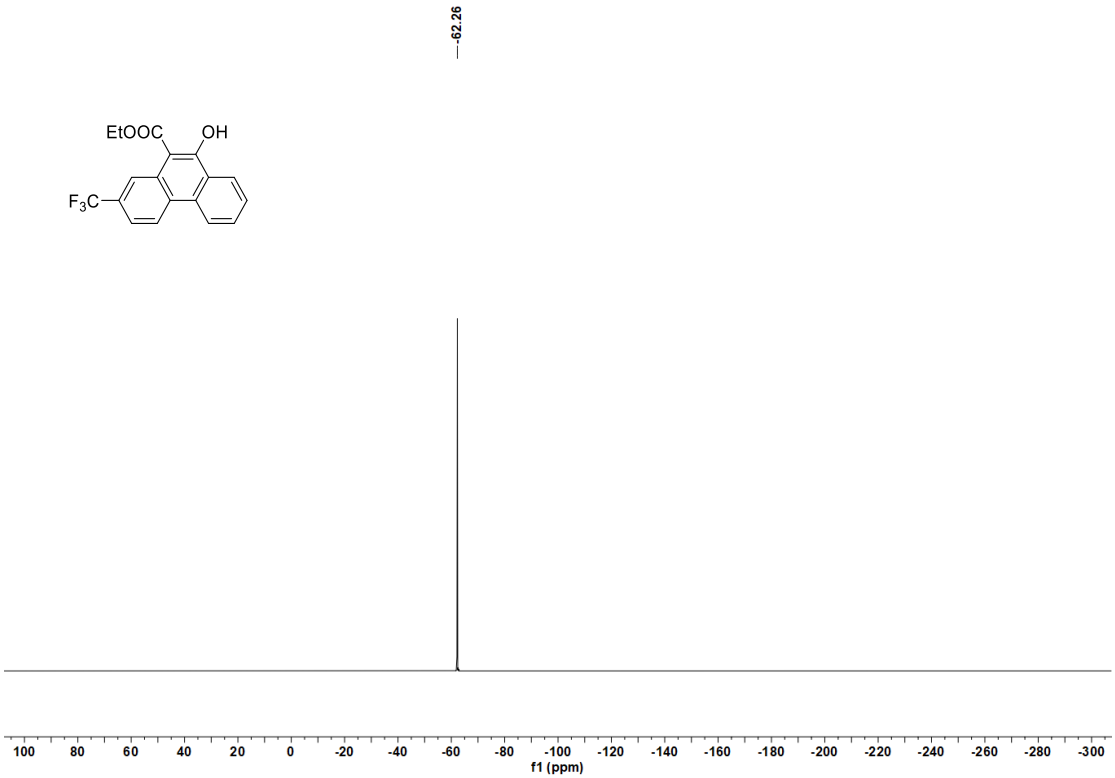
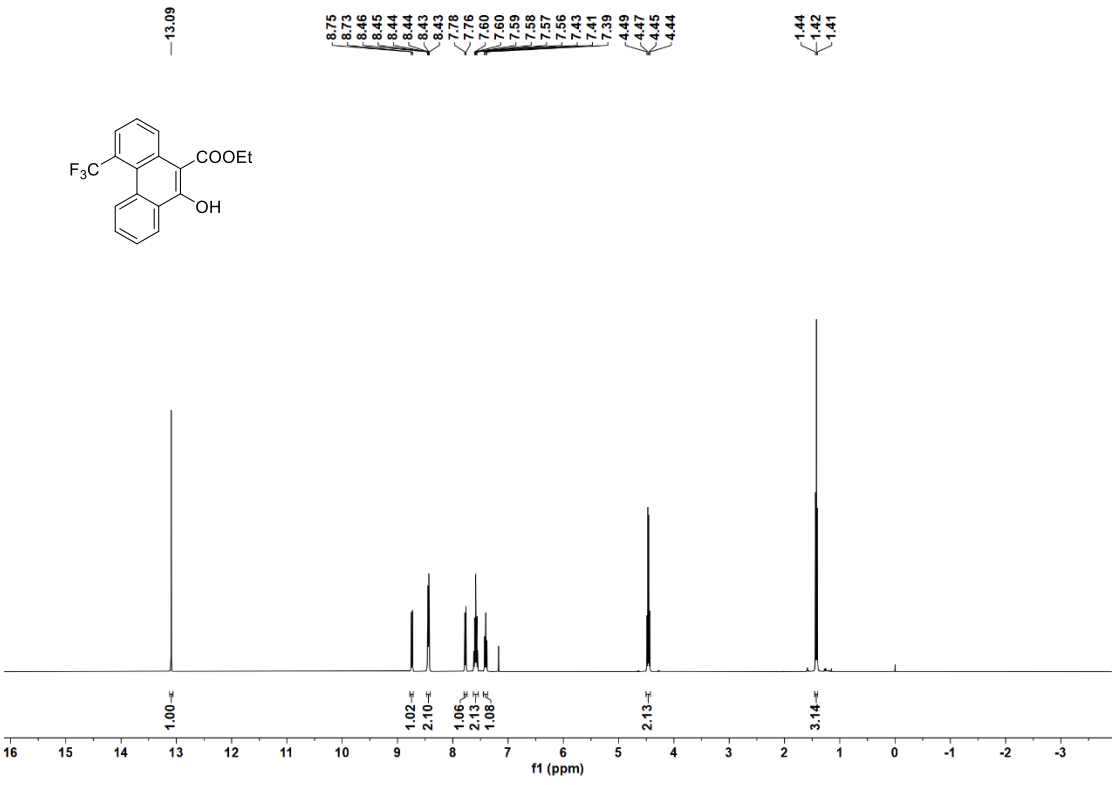
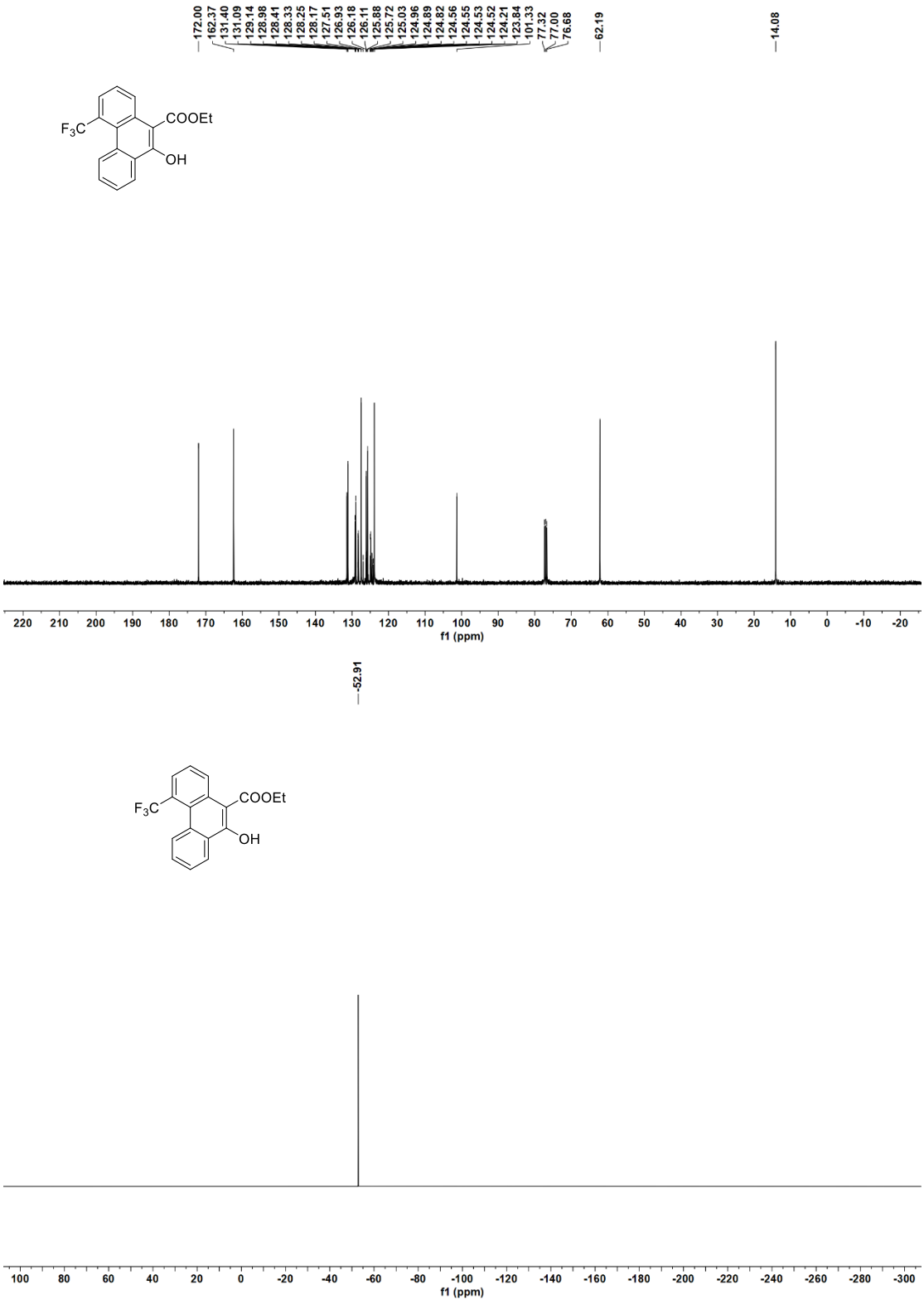
7.70
7.69
7.68
7.68
7.61
7.61
7.60
7.59
7.59
7.58
7.57
7.56
7.55
7.53
7.53
4.54
4.52
4.50
4.49
1.51
1.49
1.47
0.00
EtOOC
OH
F3C
1.02
1.02
3.28
1.14
2.28
2.24
3.19
f1 (ppm)
172.32
163.62
132.41
130.67
129.15
128.95
128.82
128.64
127.77
127.71
125.92
125.67
124.97
123.28
123.25
123.22
123.19
122.55
119.93
119.89
119.85
119.81
100.79
77.32
77.00
76.68
62.35
13.88
EtOOC
OH
F3C
f1 (ppm)

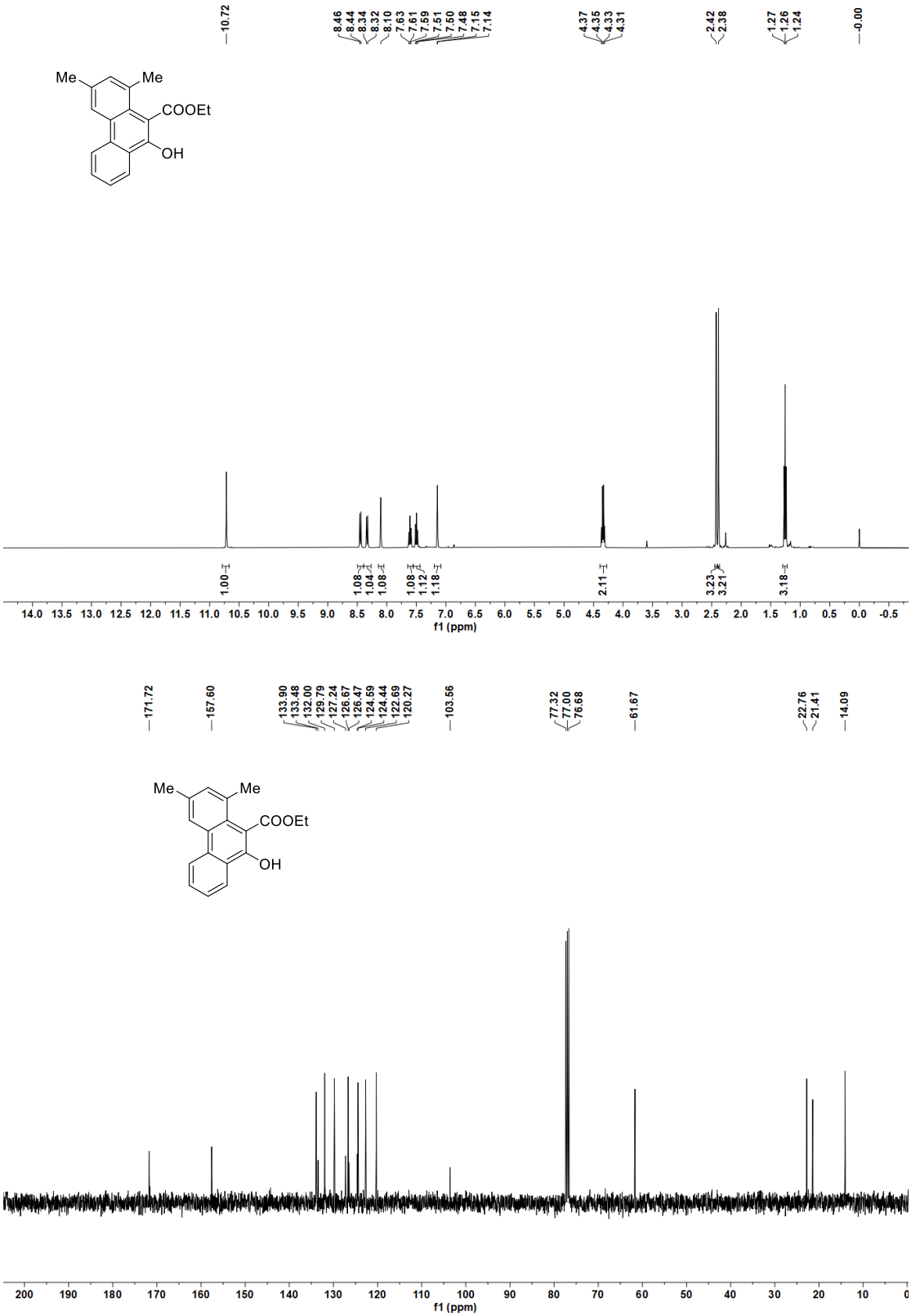


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **41a**

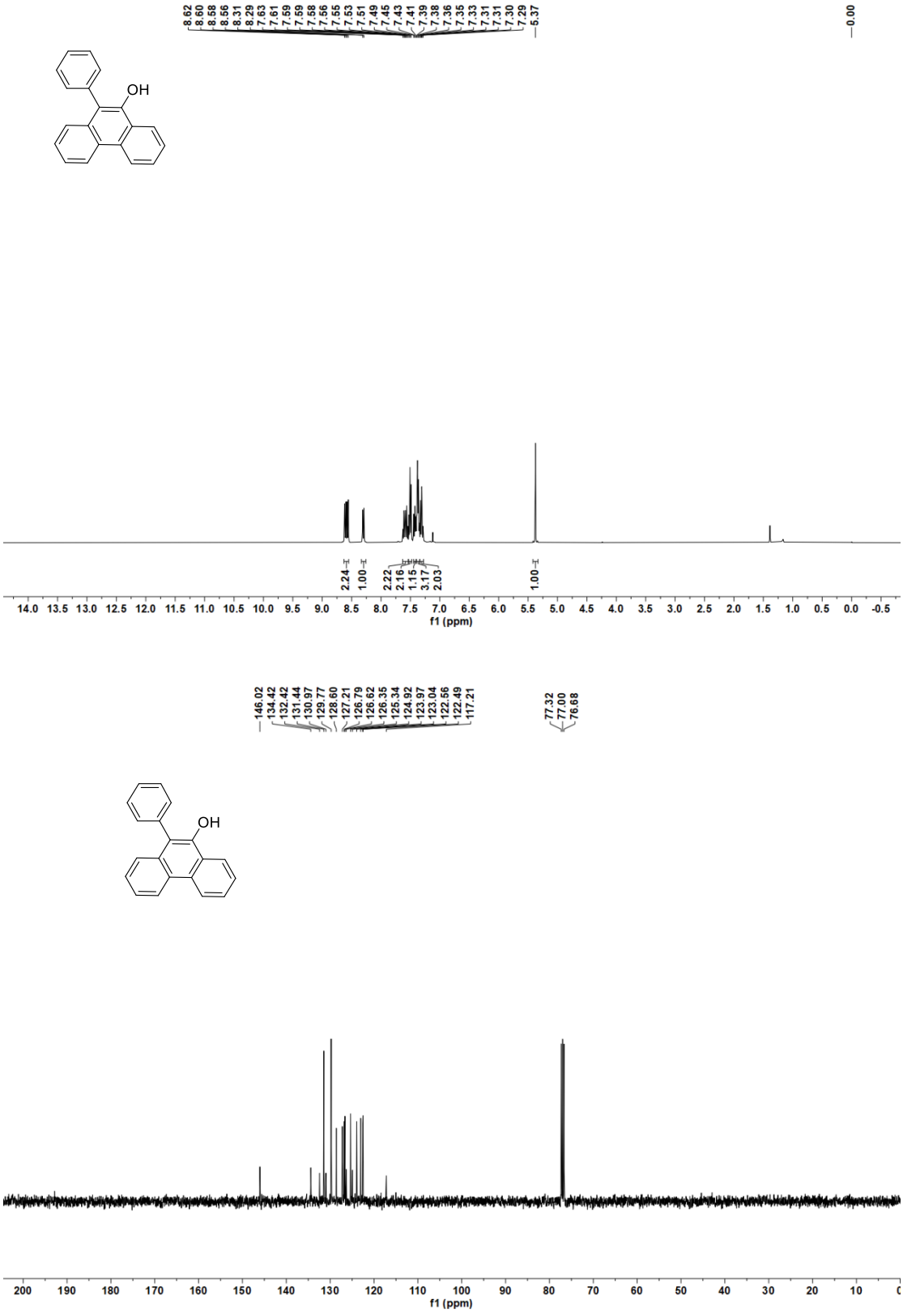




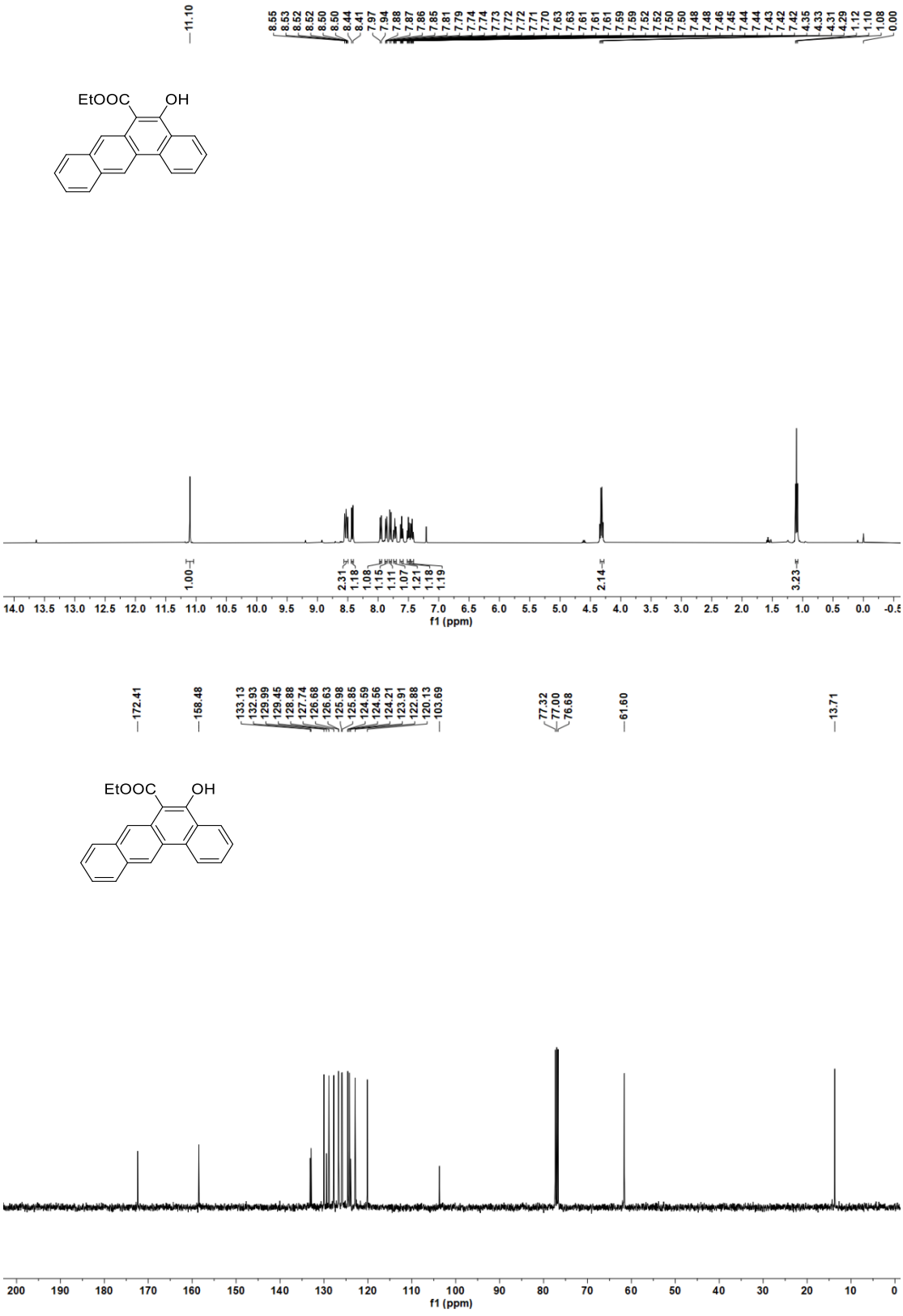
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **42a**



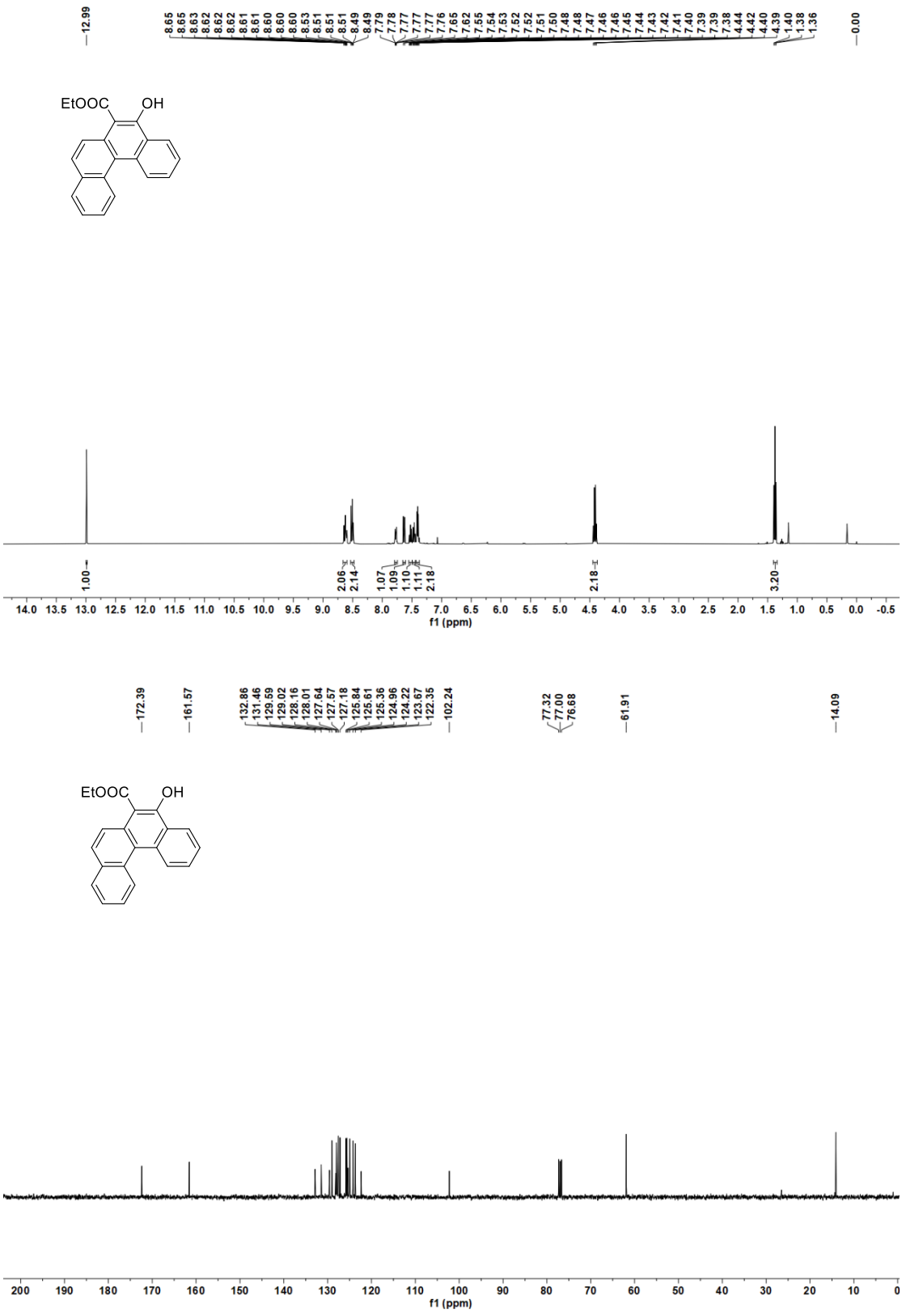
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **43a**



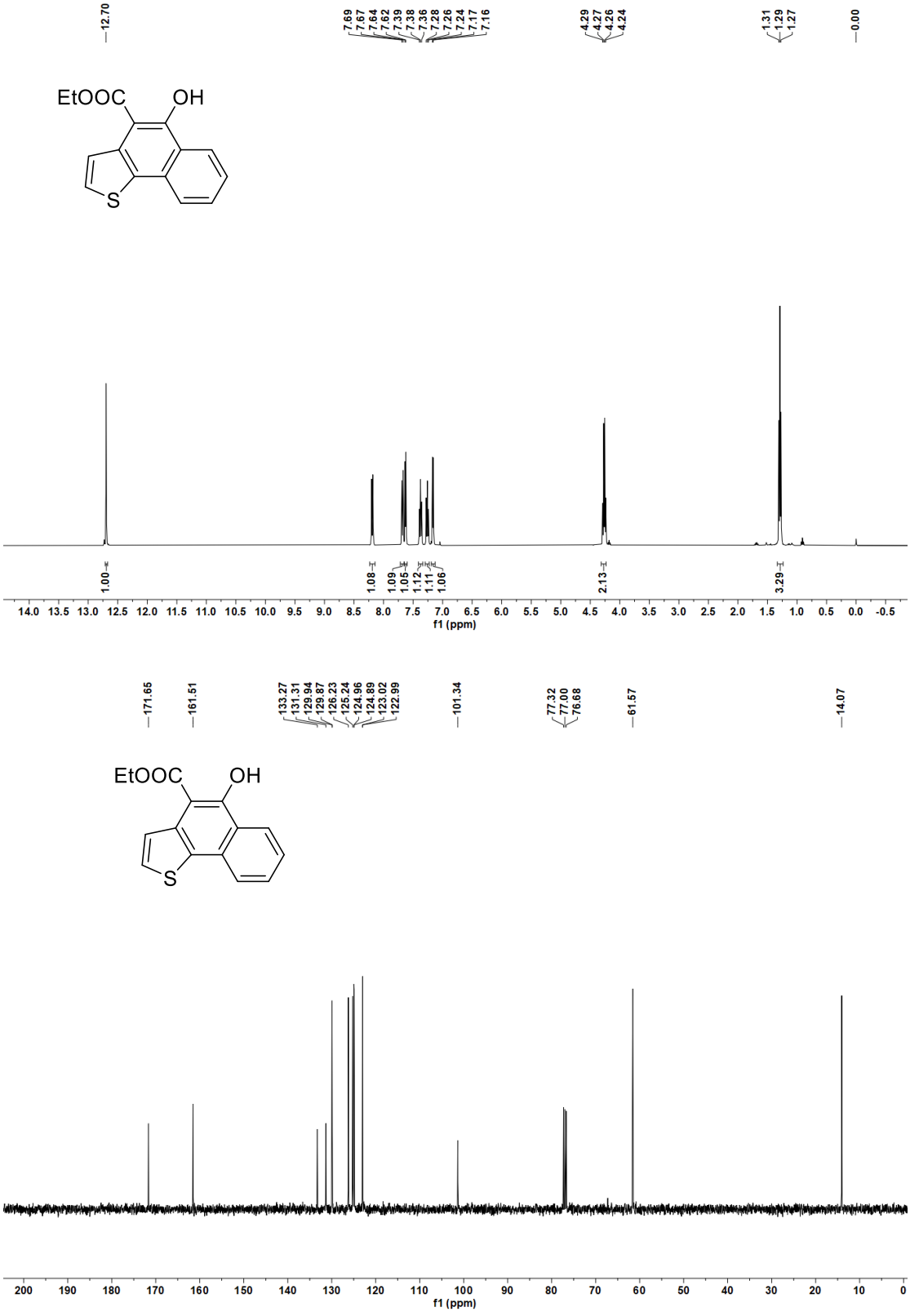
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **44a**



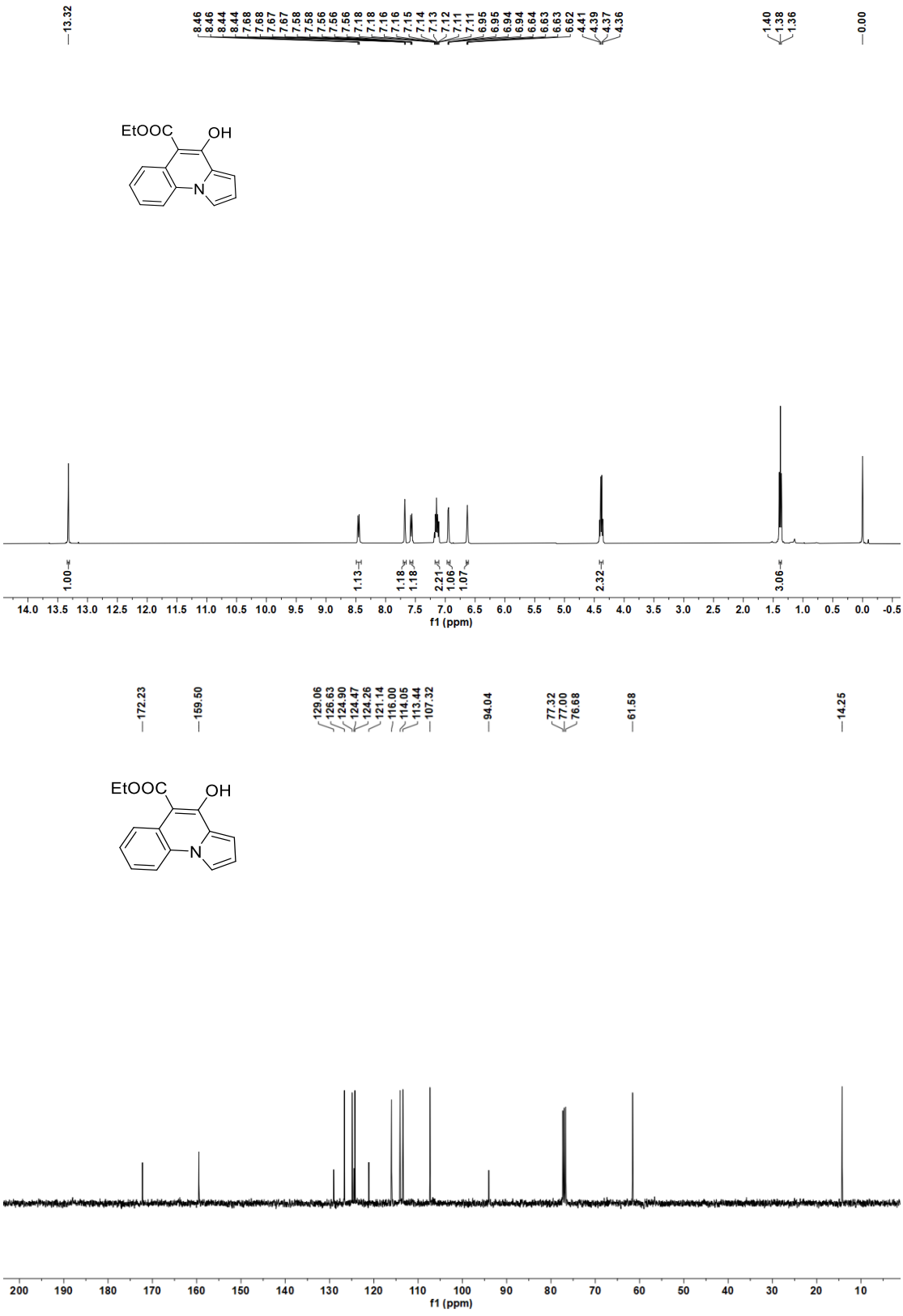
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **45a**



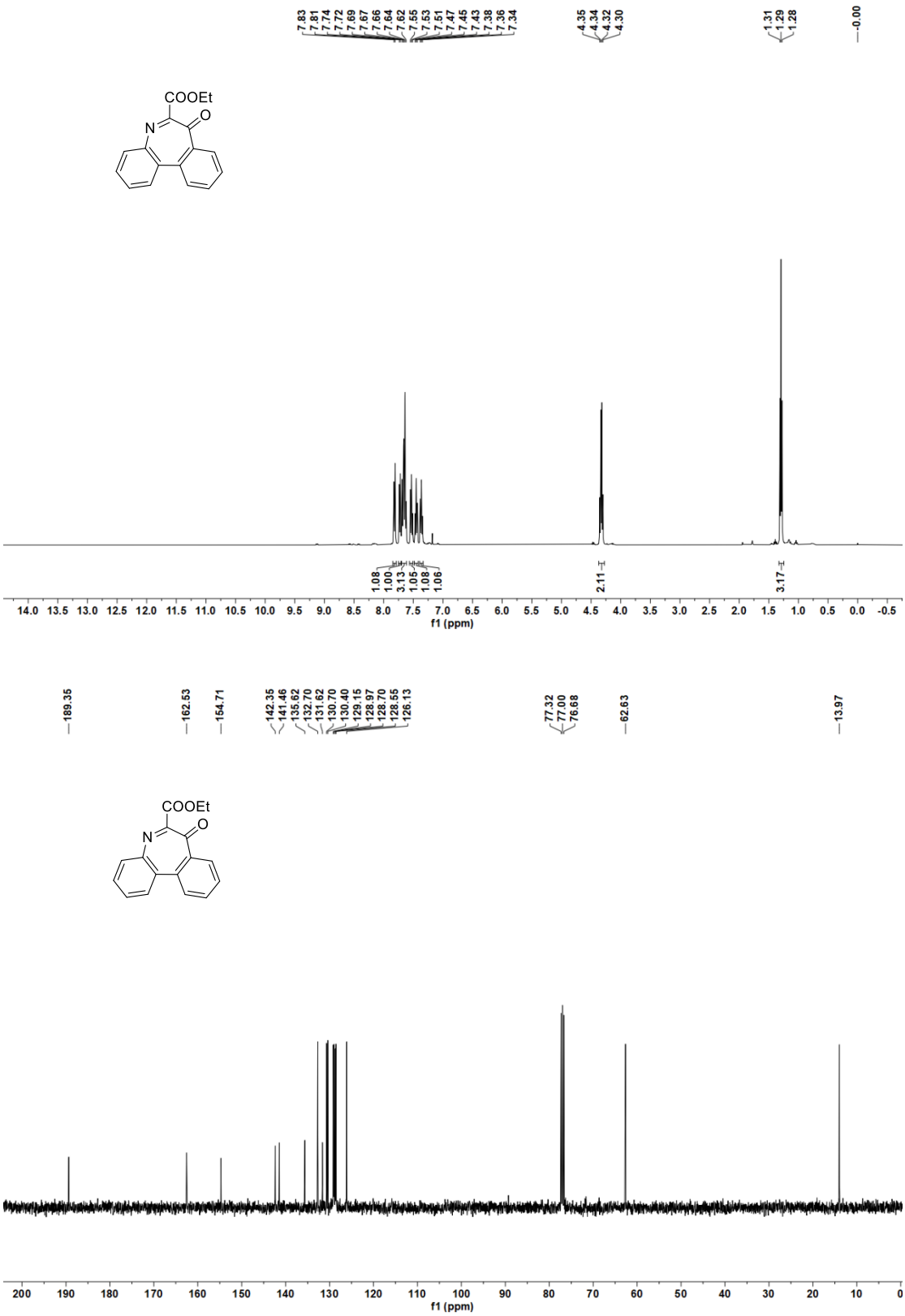
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **46a**



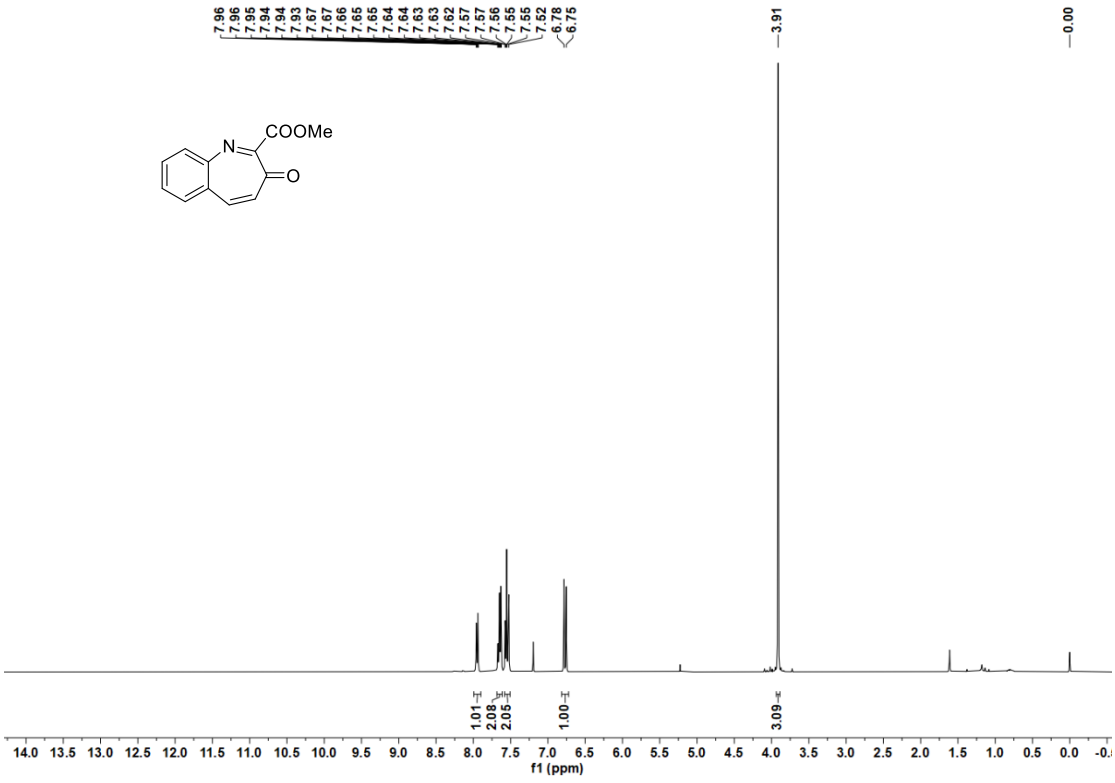
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **47a**

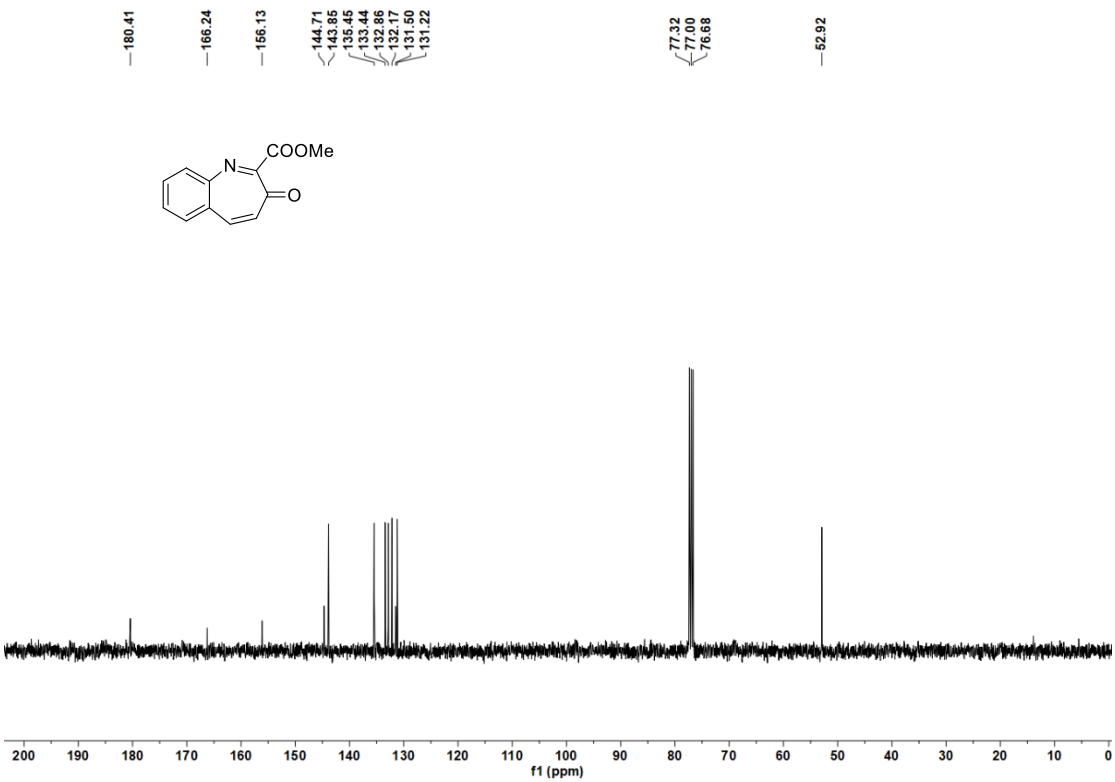


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **48a**

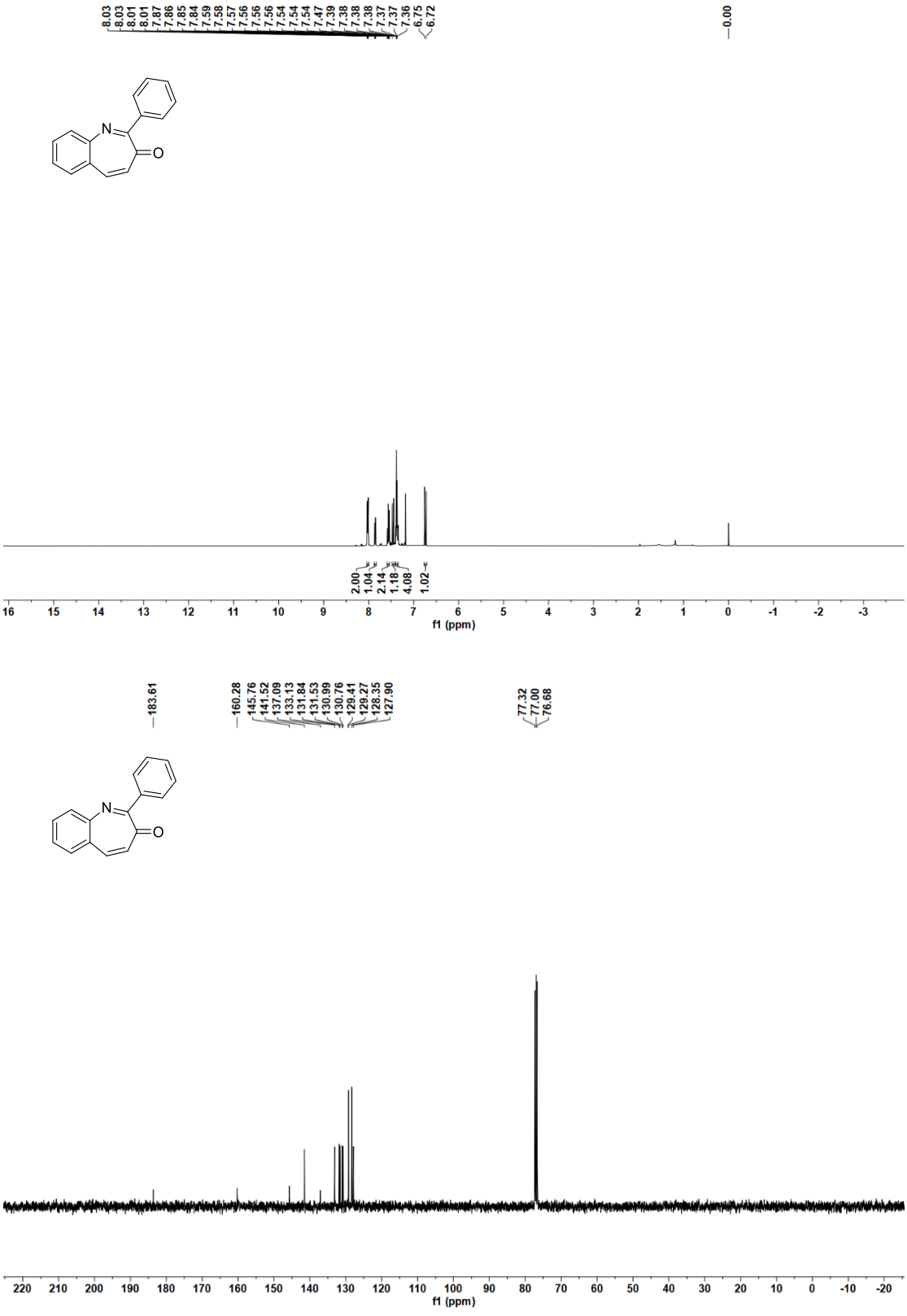


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **1**

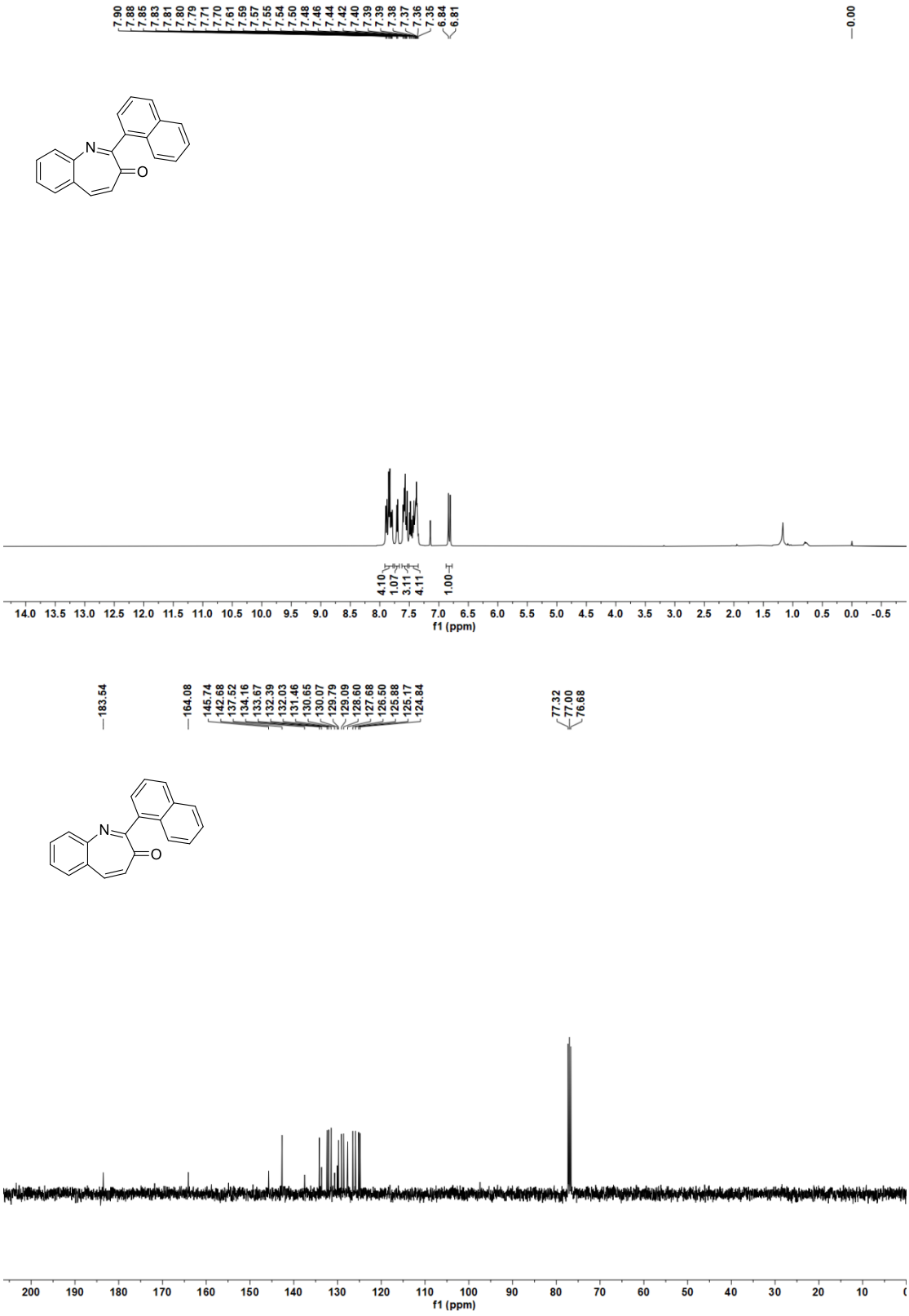




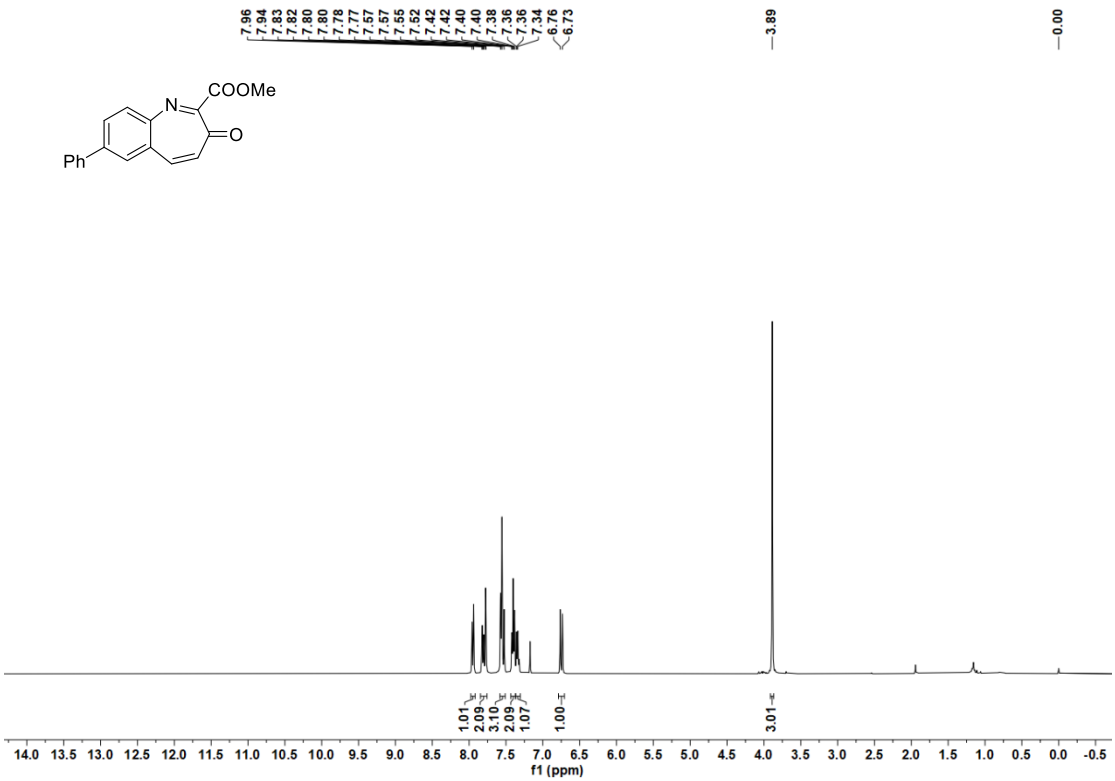
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **2**

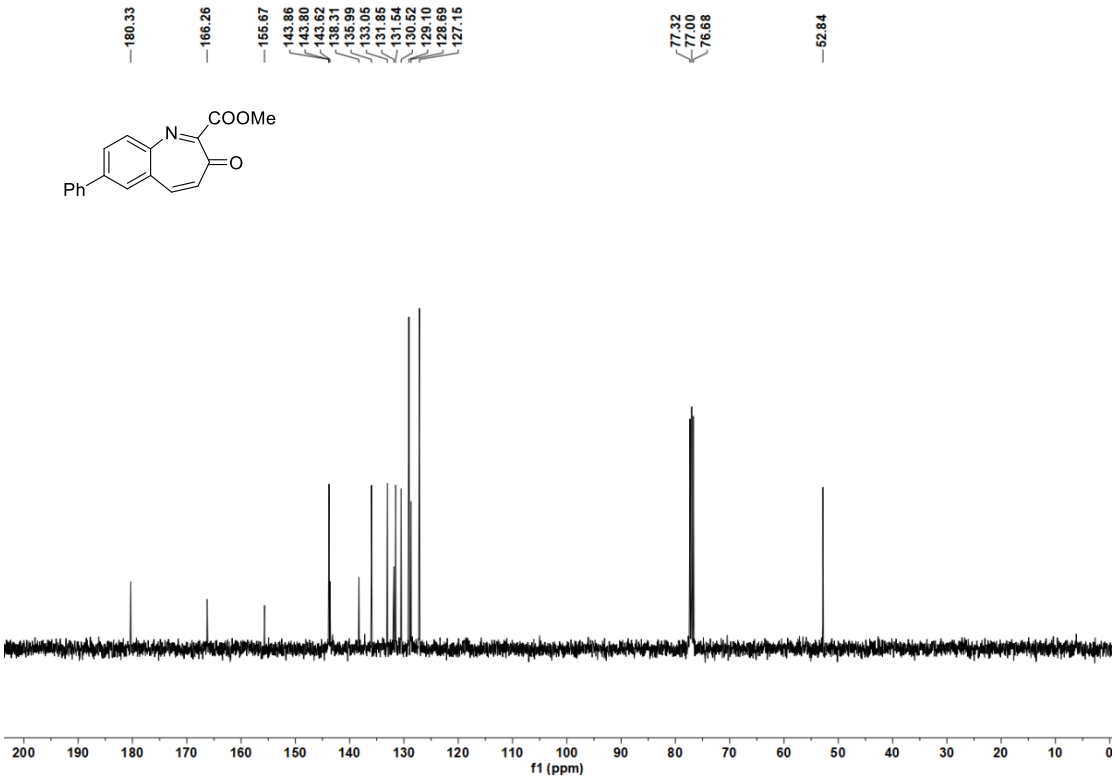


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **3**

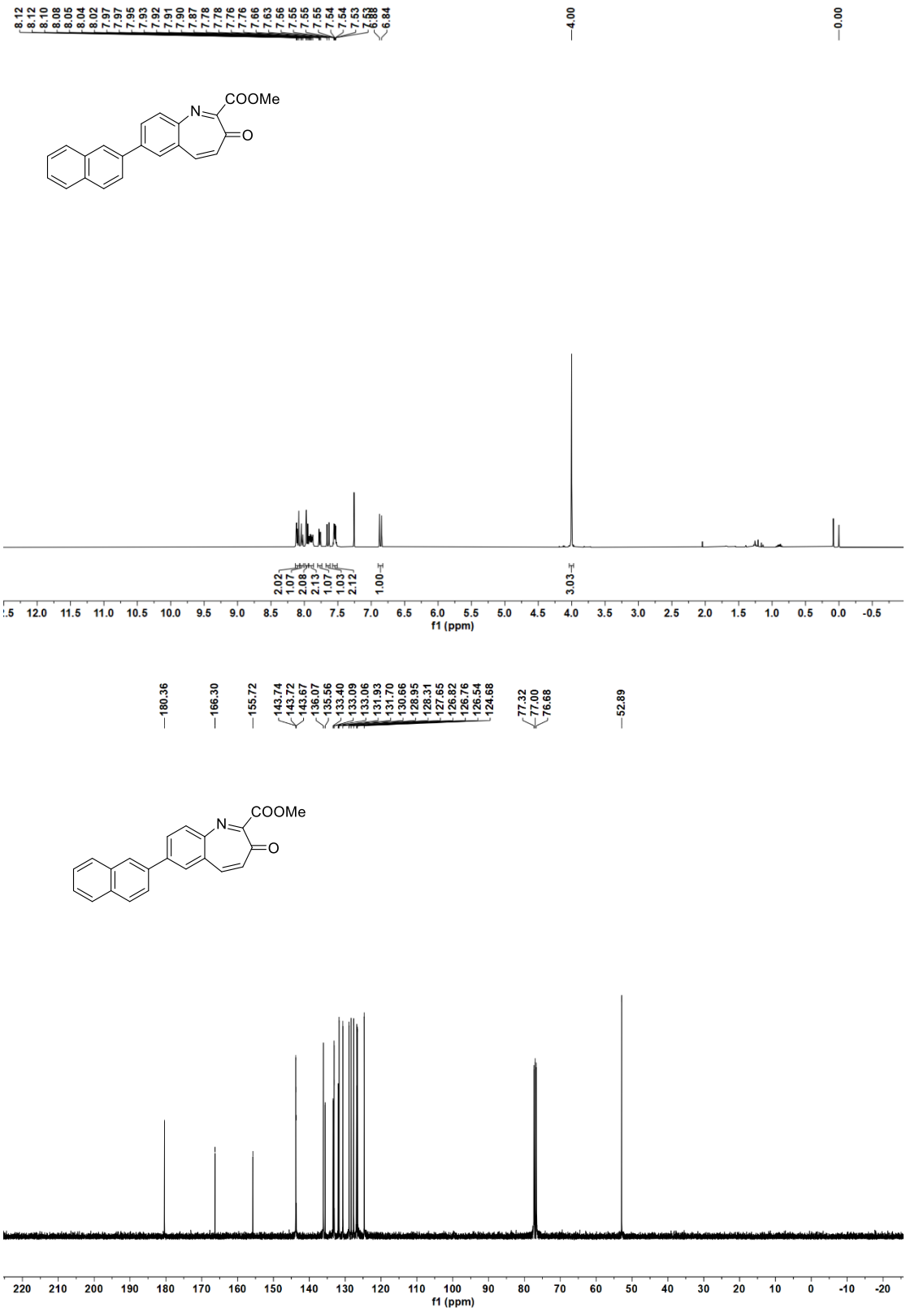


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **4**

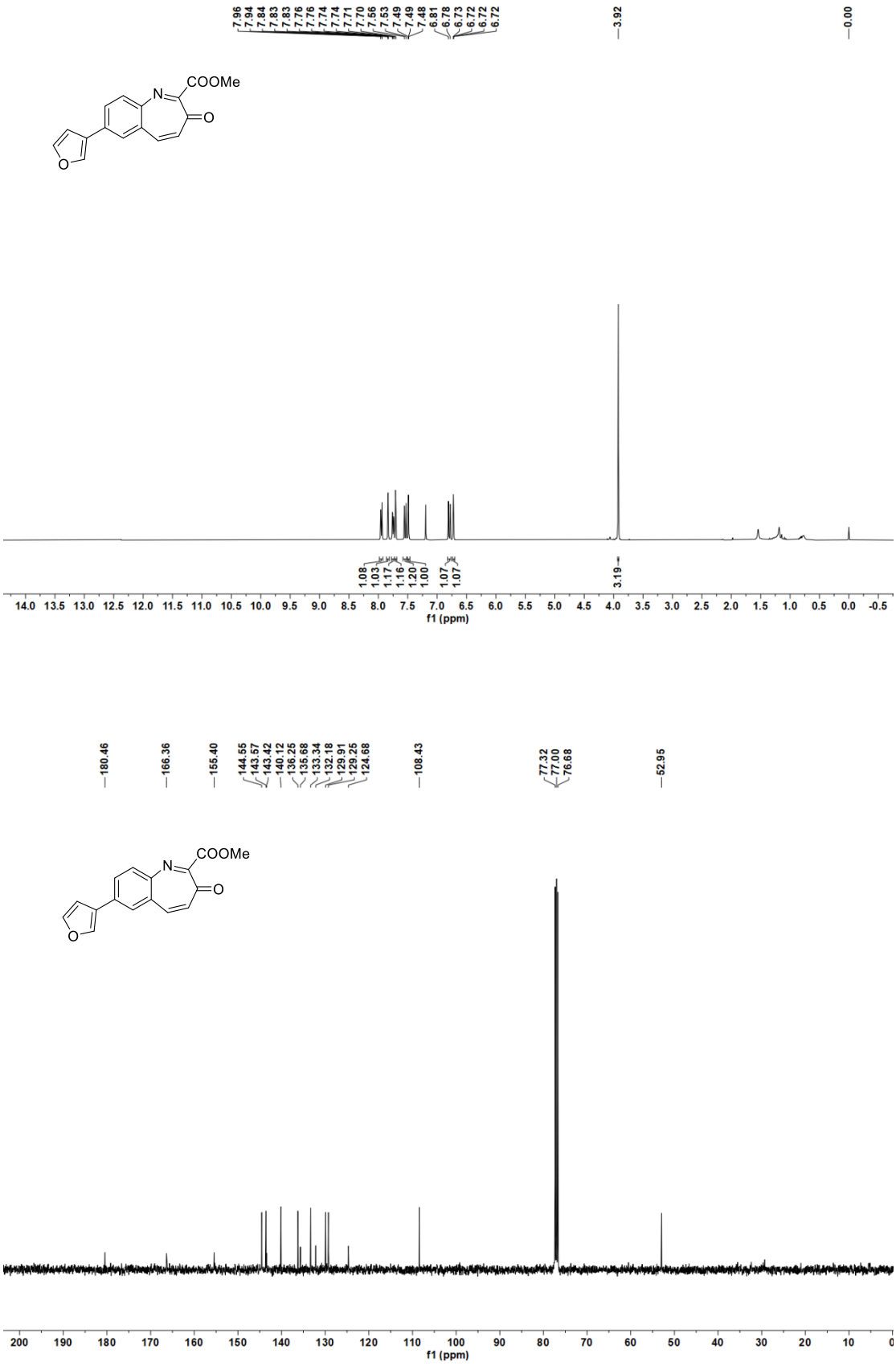




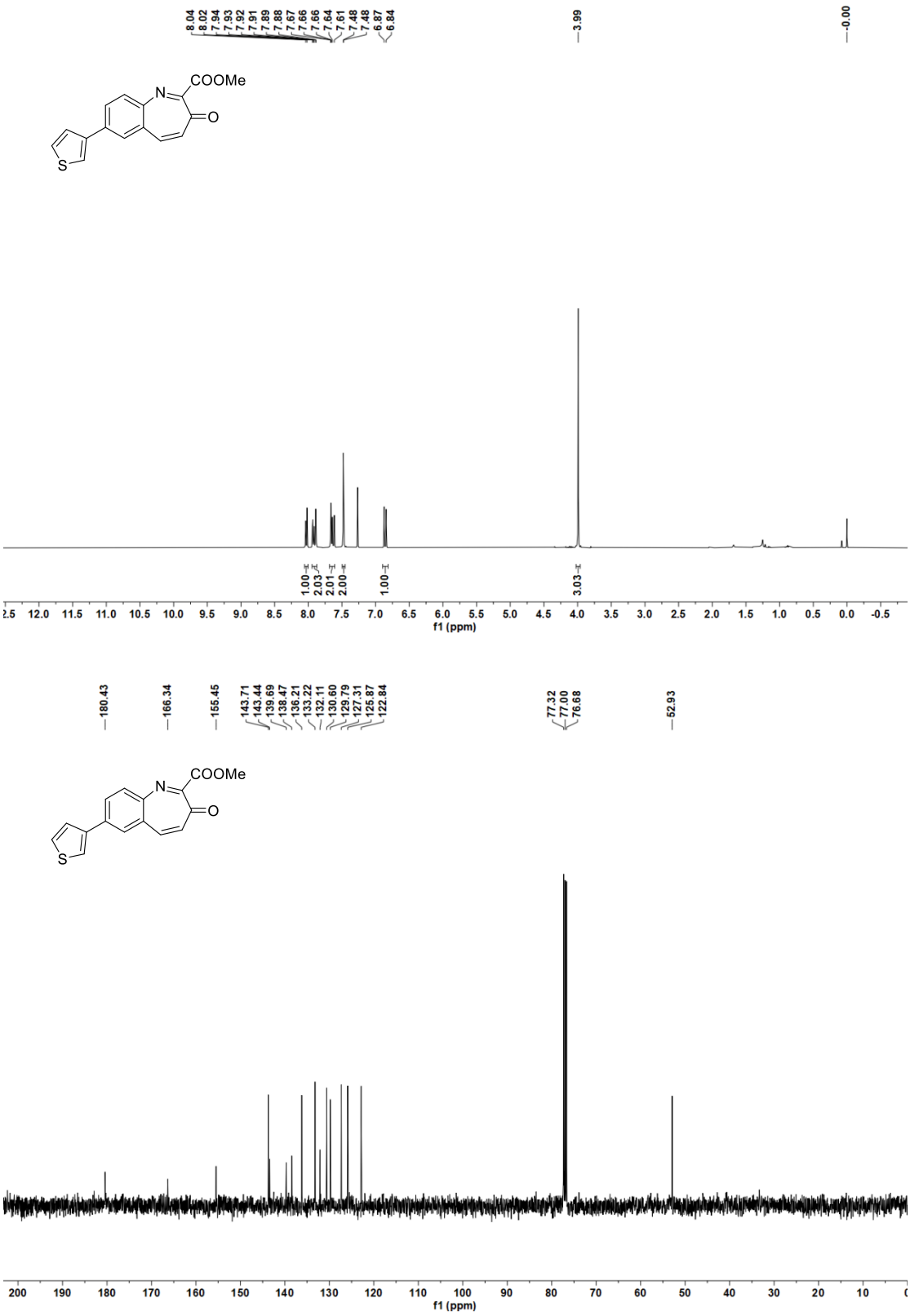
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **5**



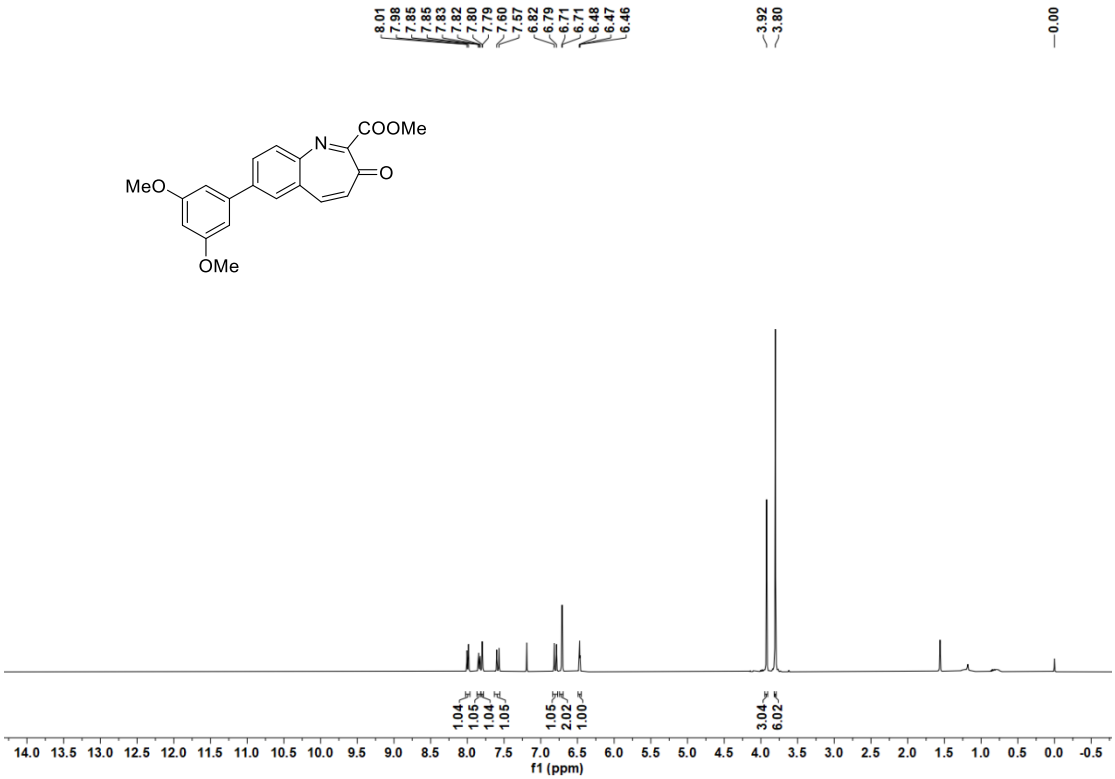
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **6**

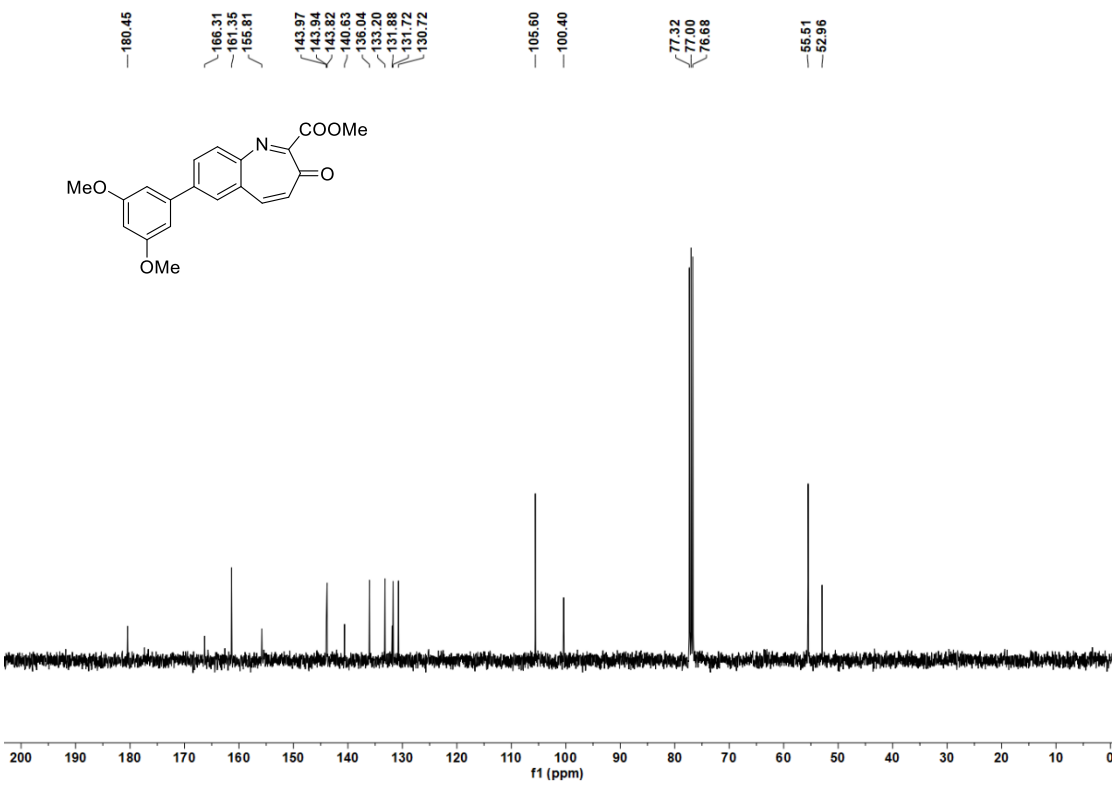


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **7**

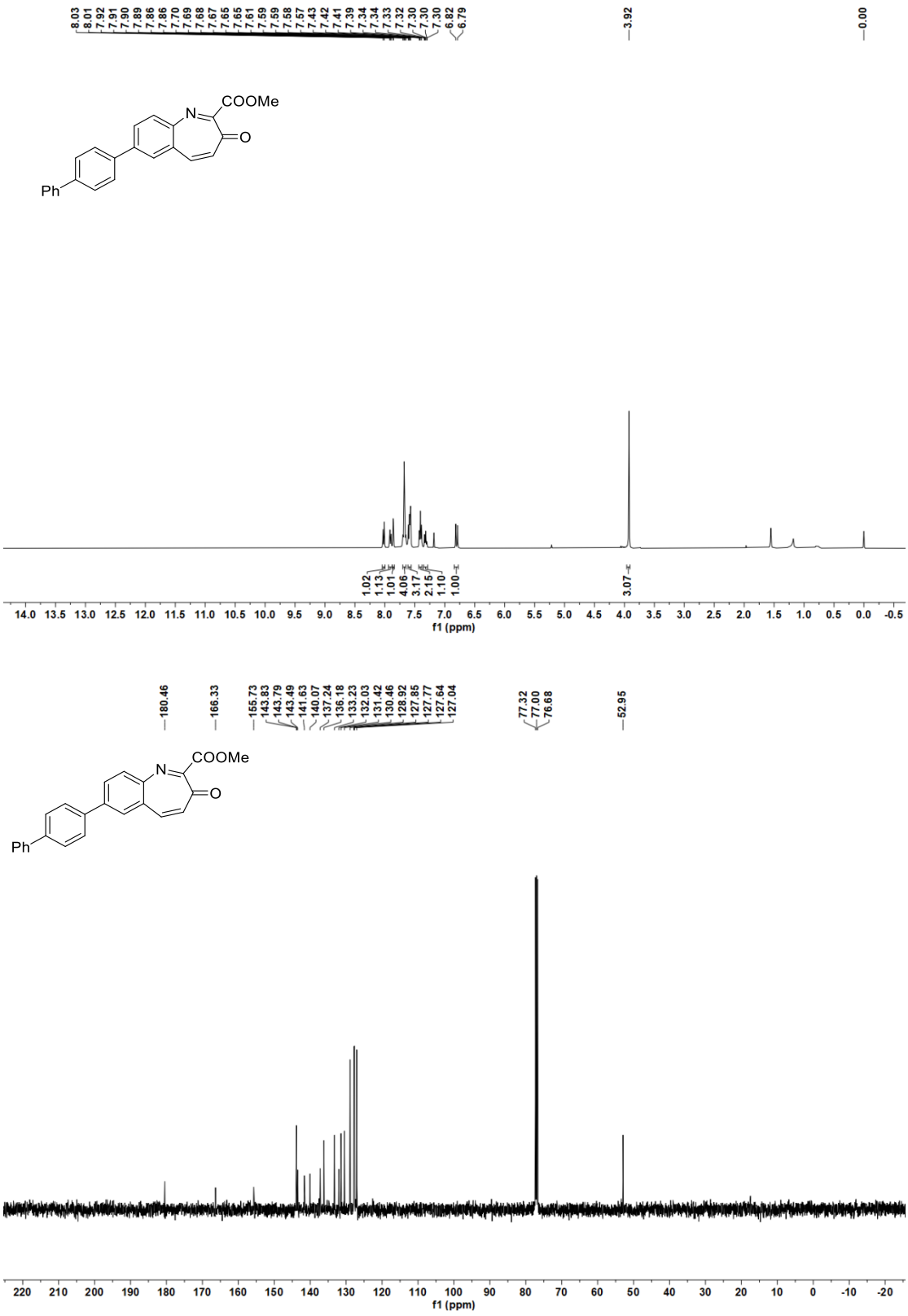


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **8**

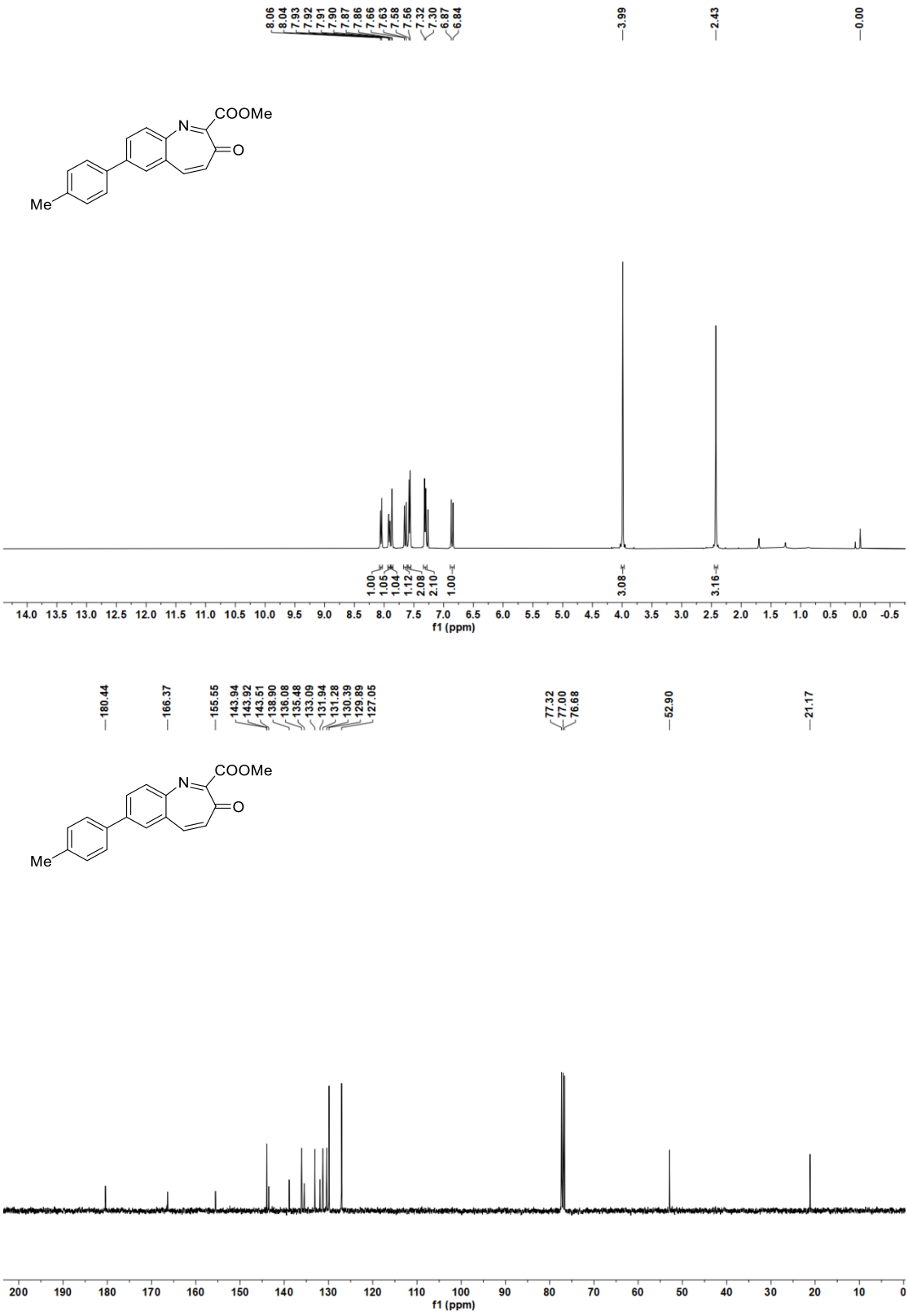




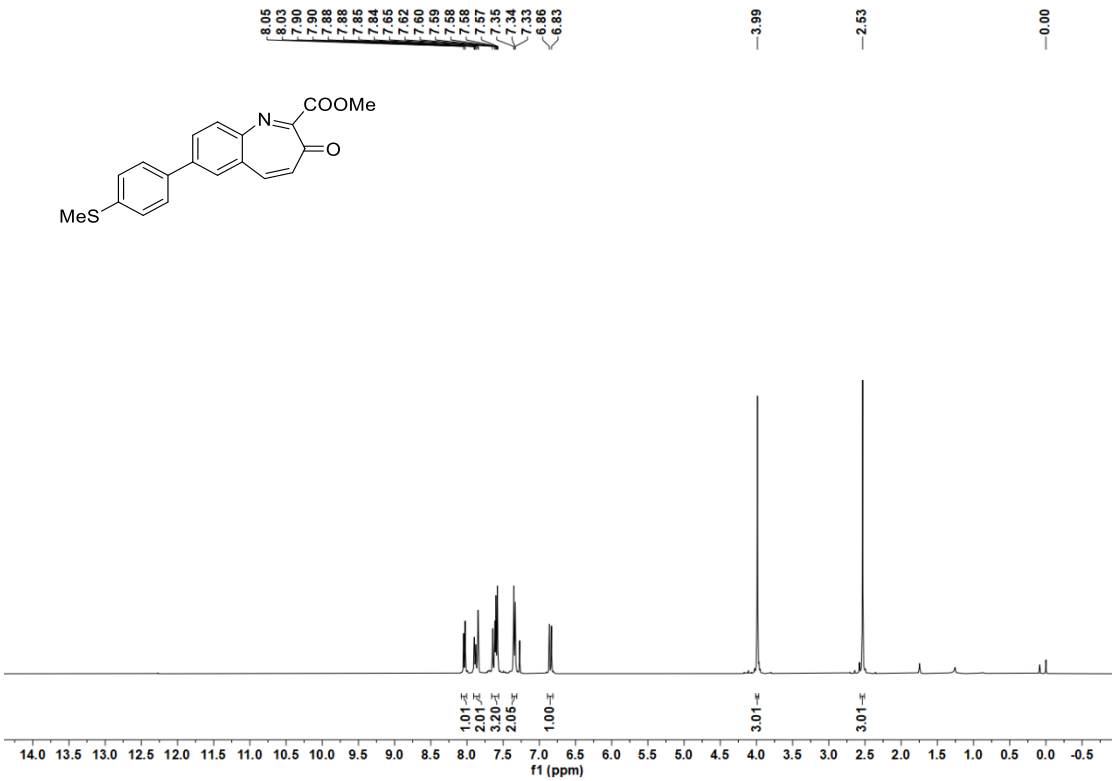
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **9**

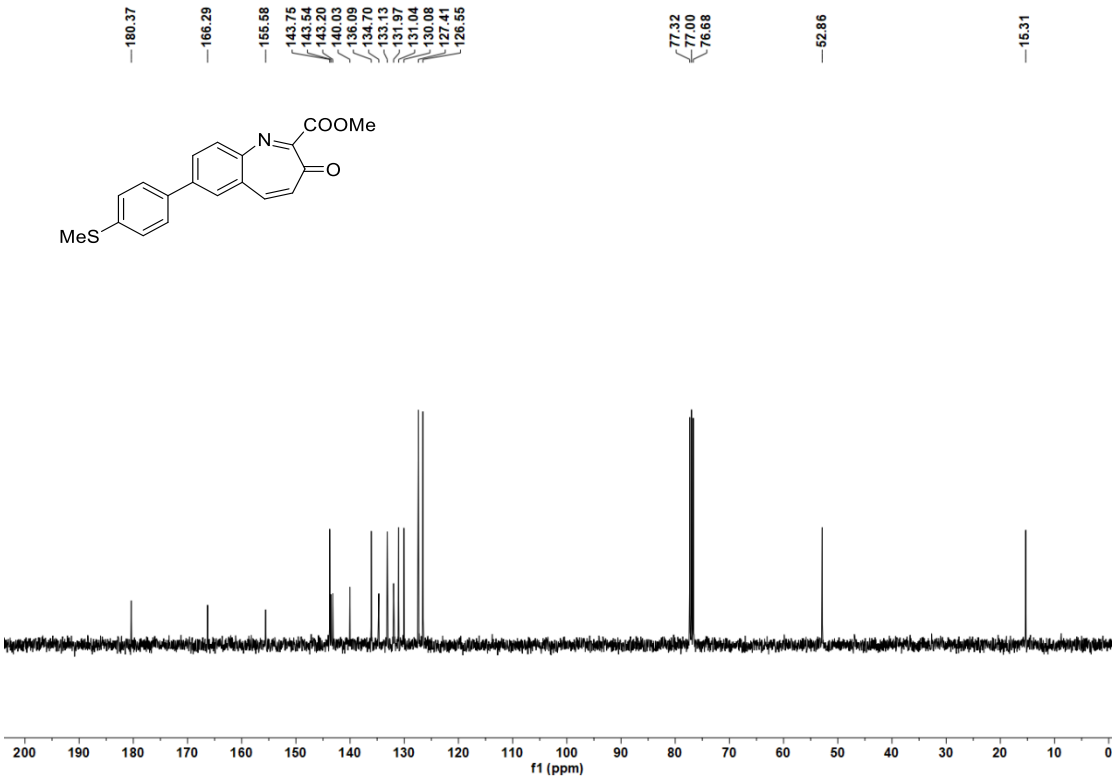


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **10**

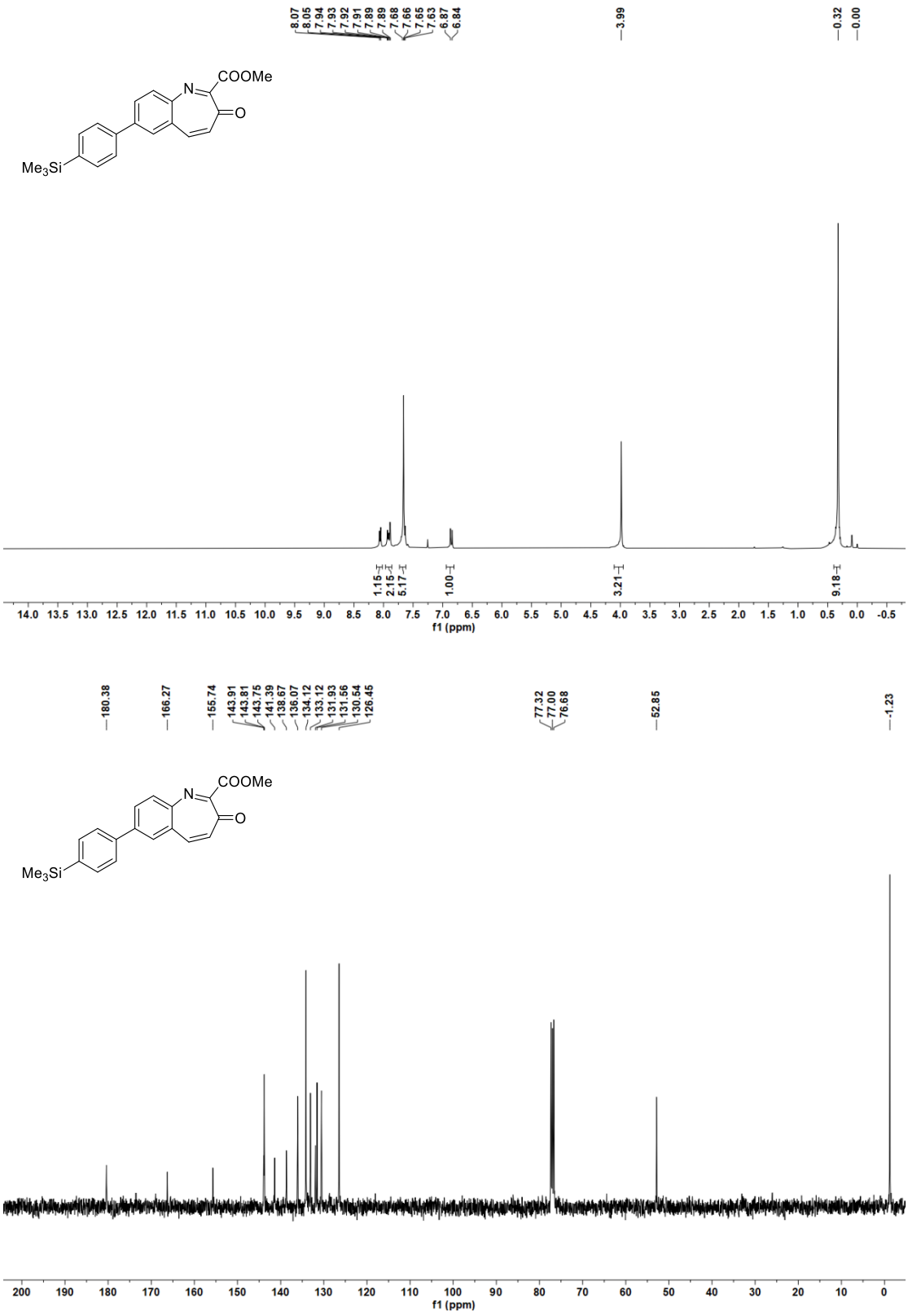


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **11**

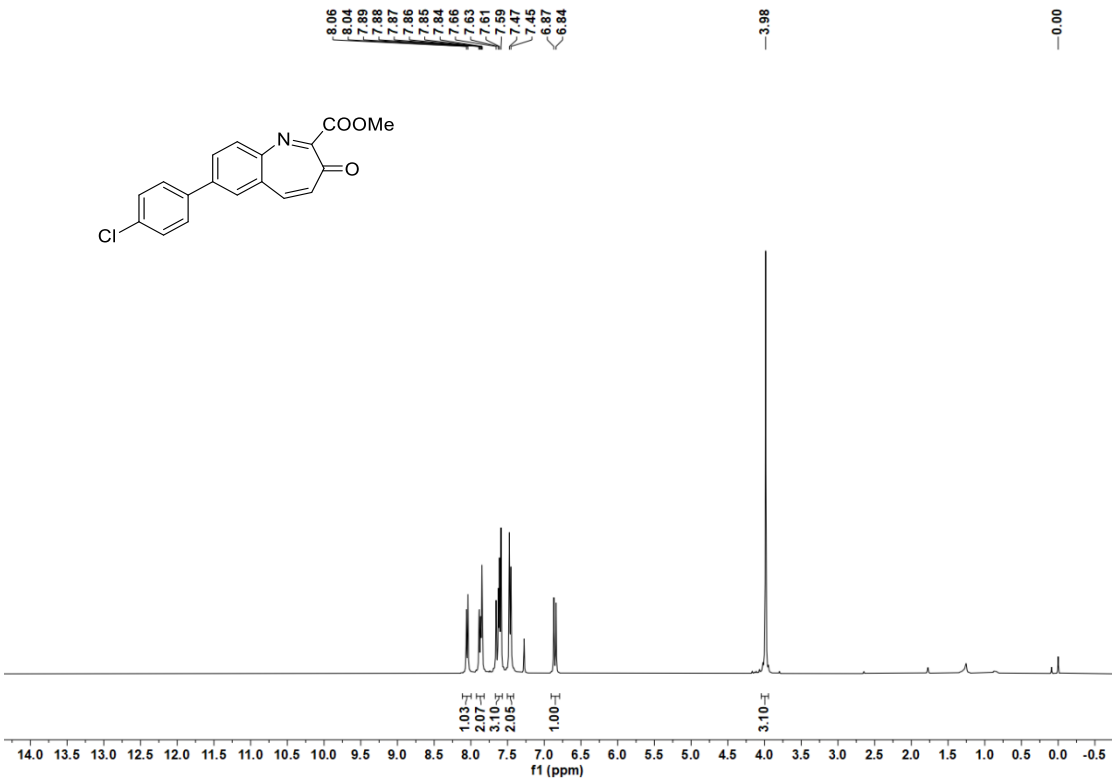


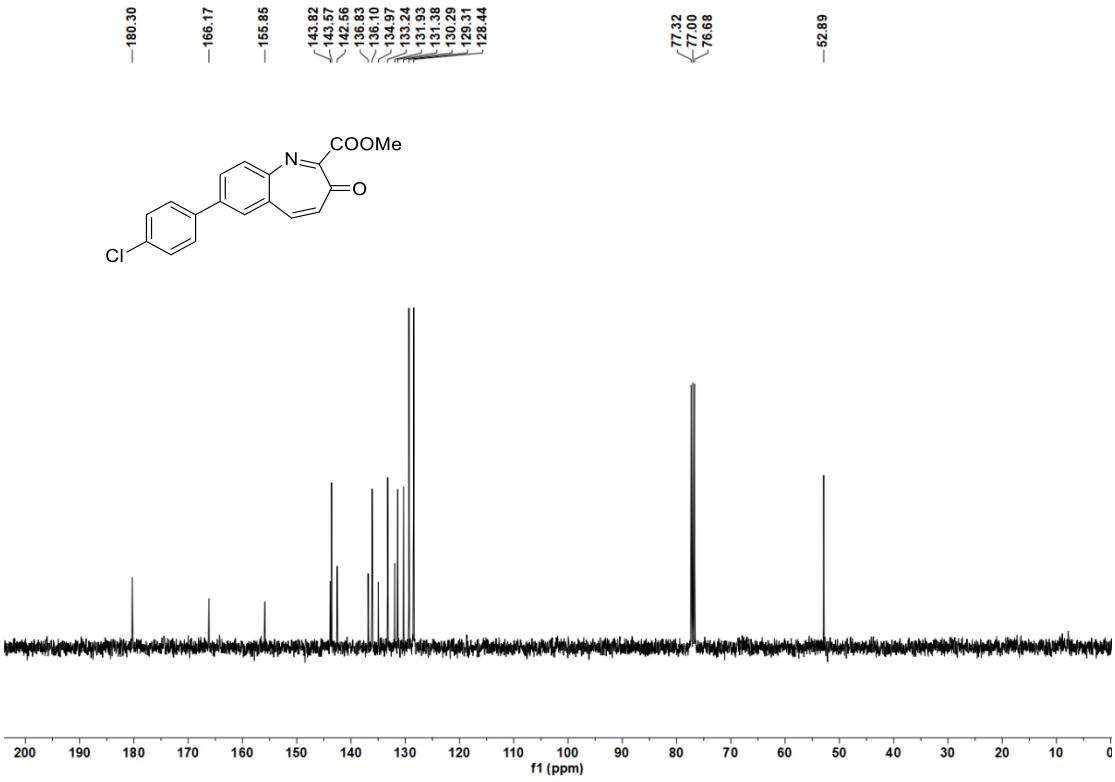


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **12**

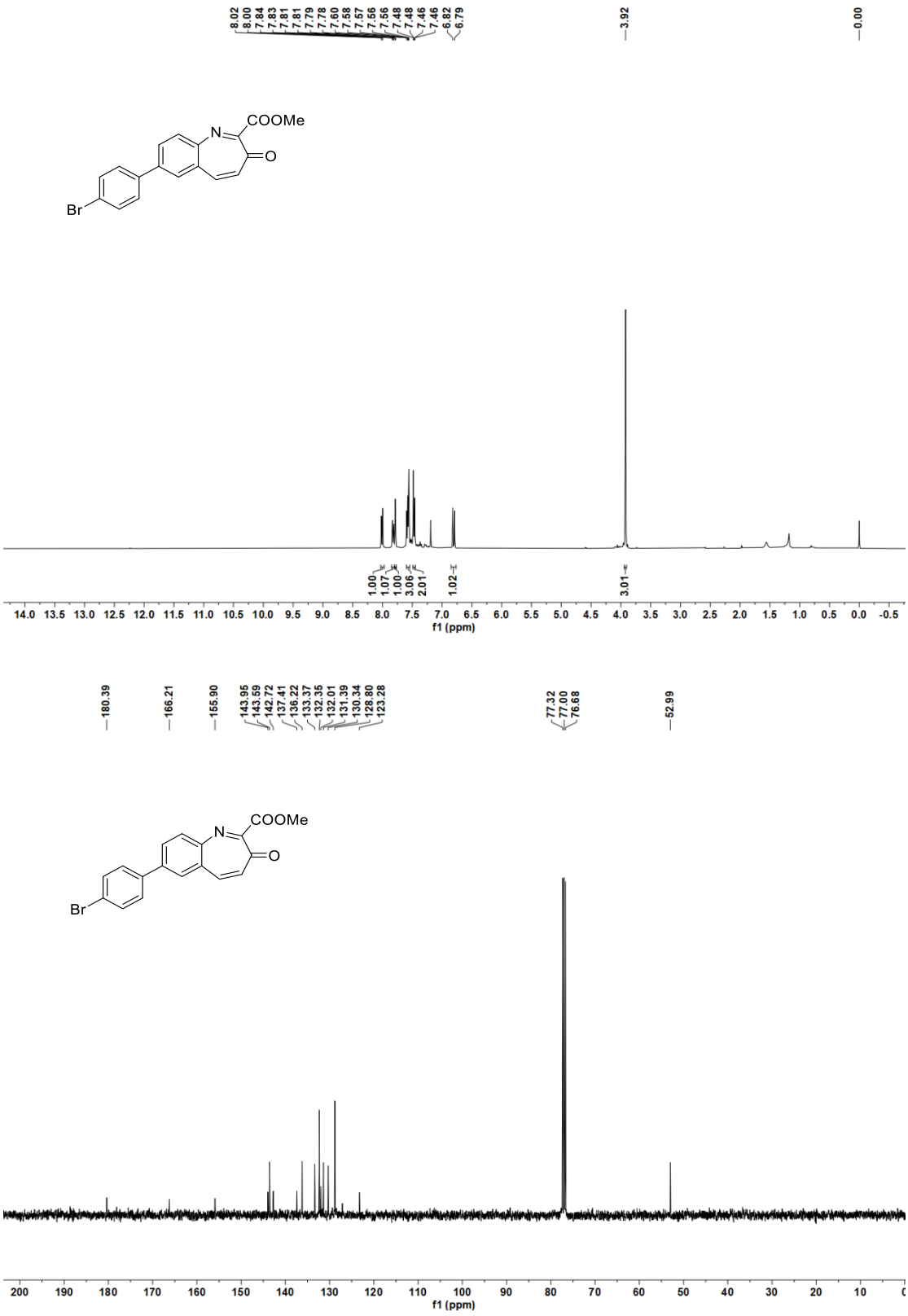


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **13**

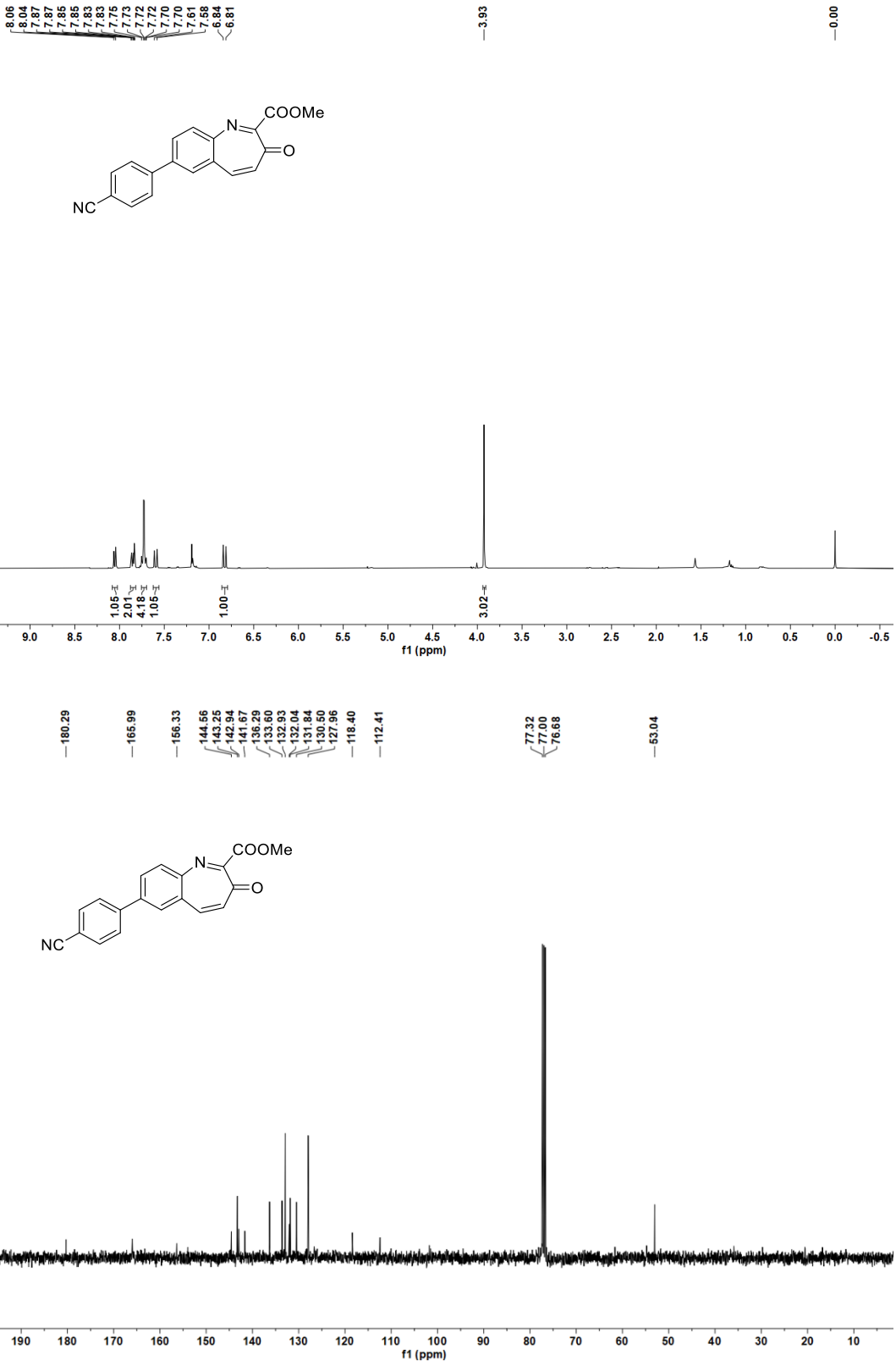




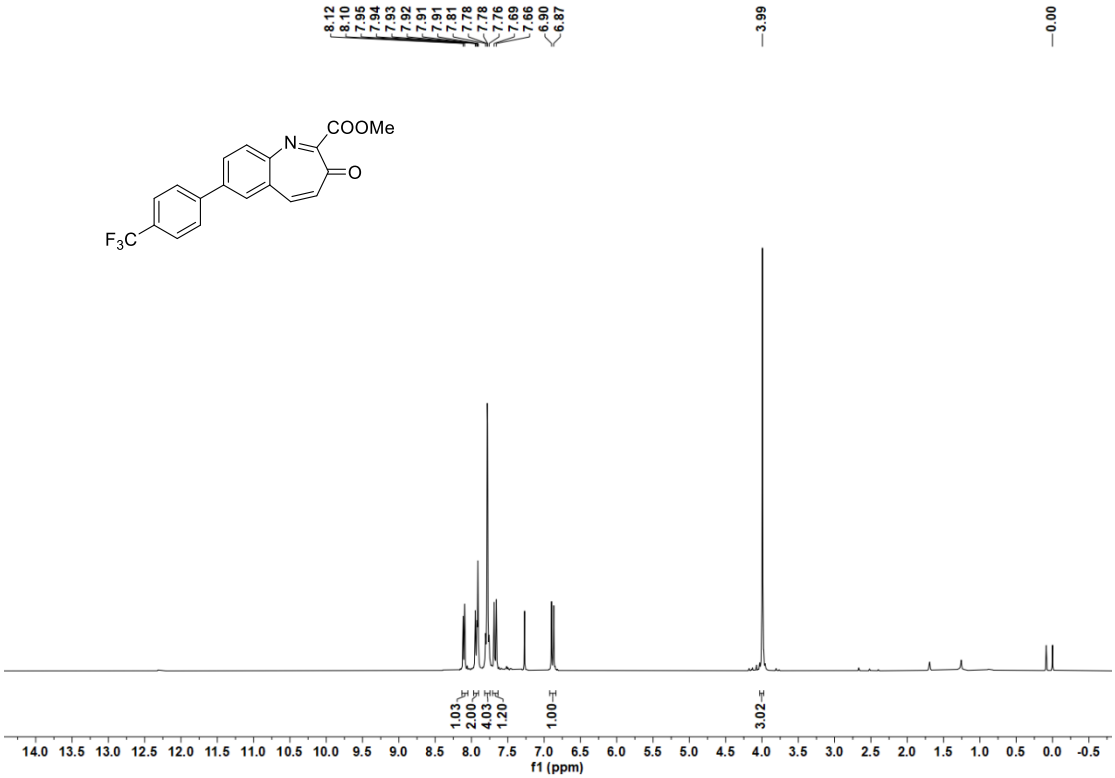
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **14**



^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **15**



^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **16**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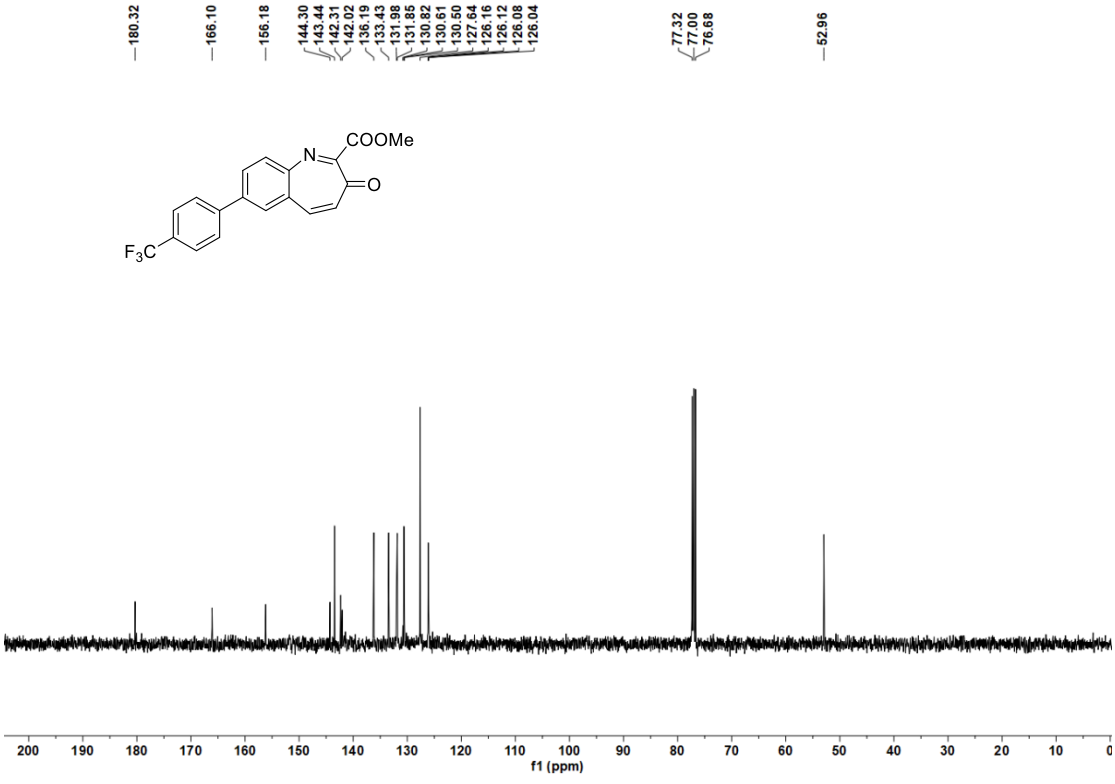
7.92
7.91
7.91
7.81
7.78
7.78
7.76
7.69
7.66
6.90
6.87
3.99
0.00
COOMe
N
O
F3C
1.03
2.00
4.03
1.20
1.00
3.02
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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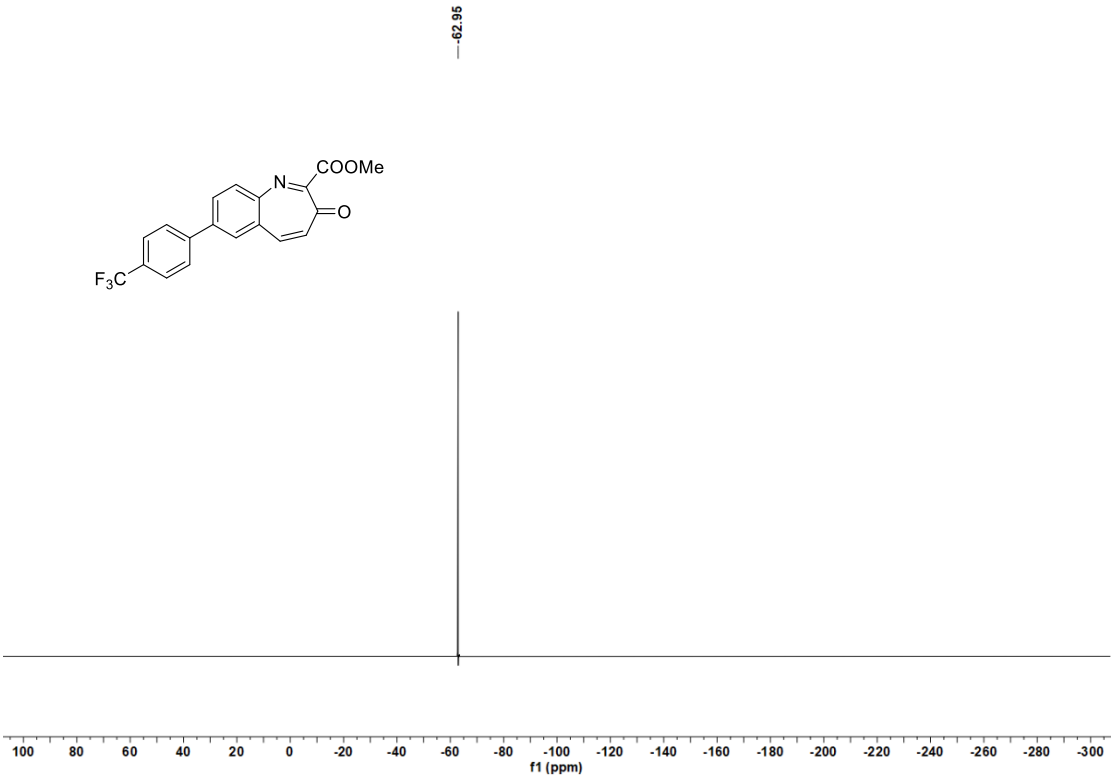
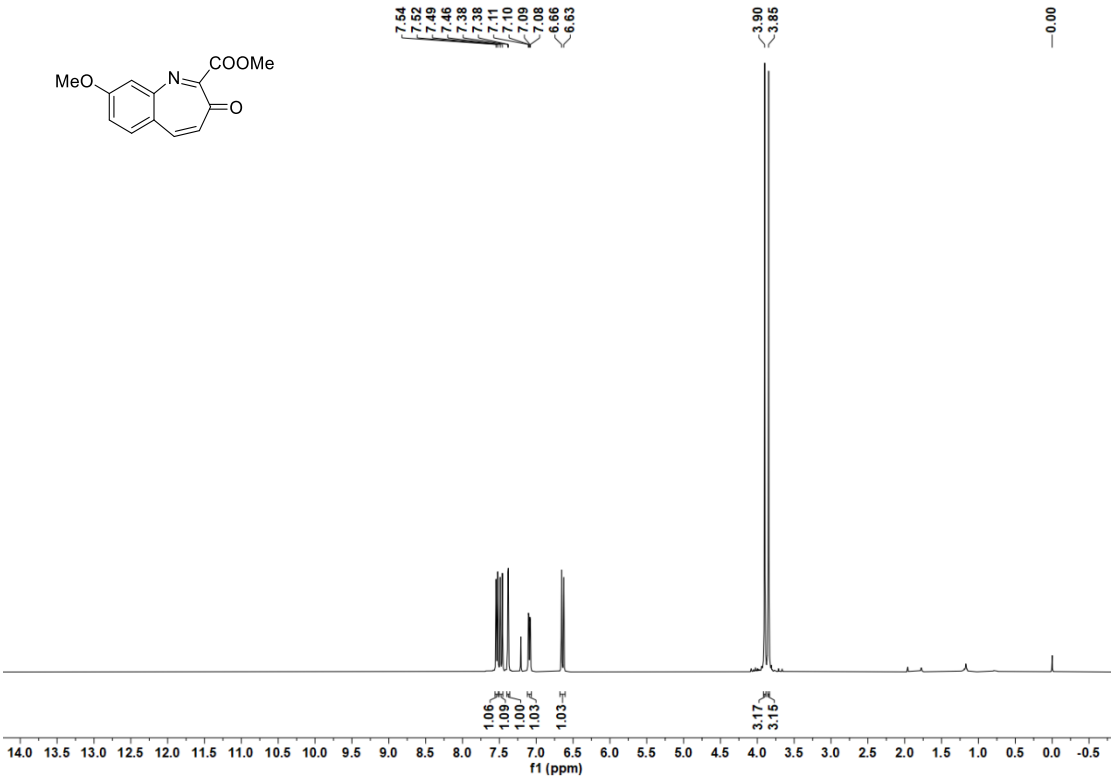
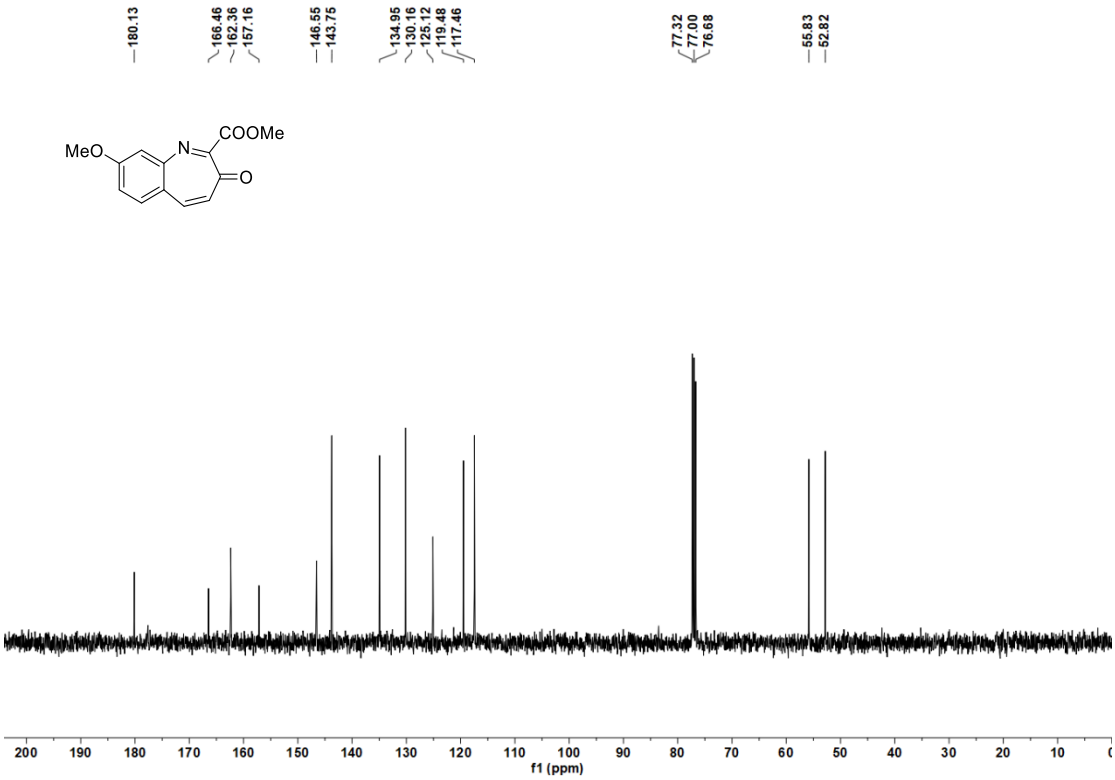
143.44
142.31
142.02
136.19
133.43
131.98
131.85
130.82
130.61
130.50
127.64
126.16
126.12
126.08
126.04
77.32
77.00
76.68
52.96
COOMe
N
O
F3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

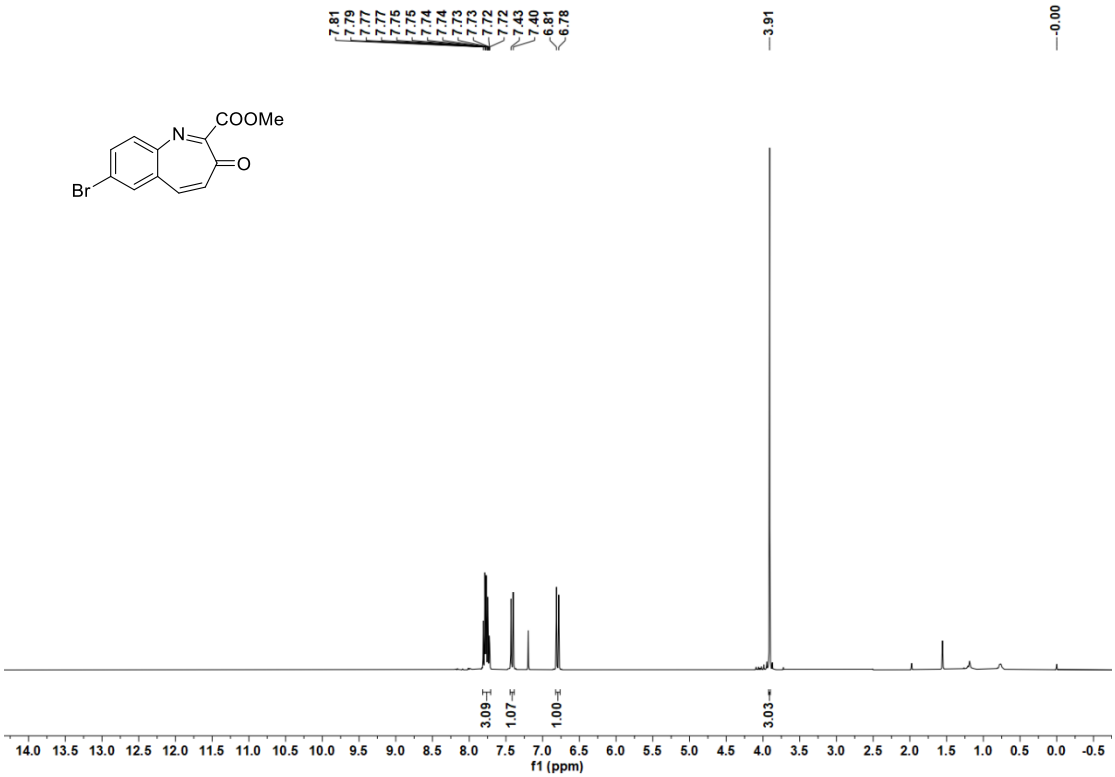


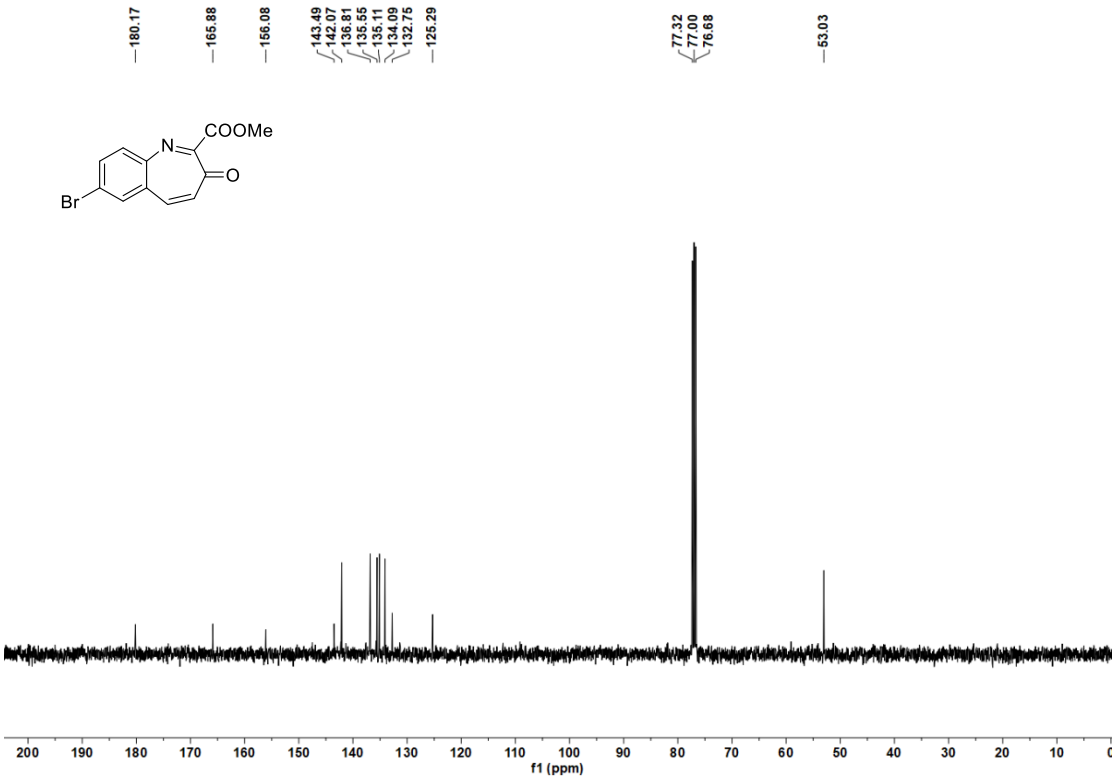
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **17**



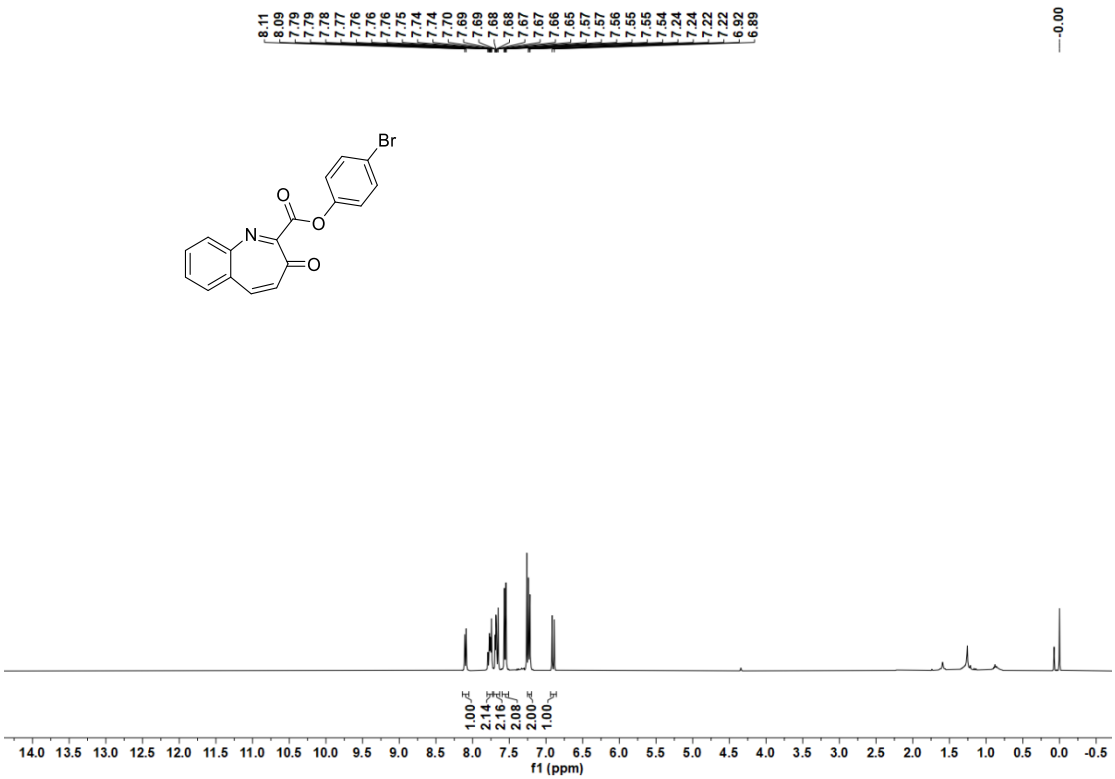


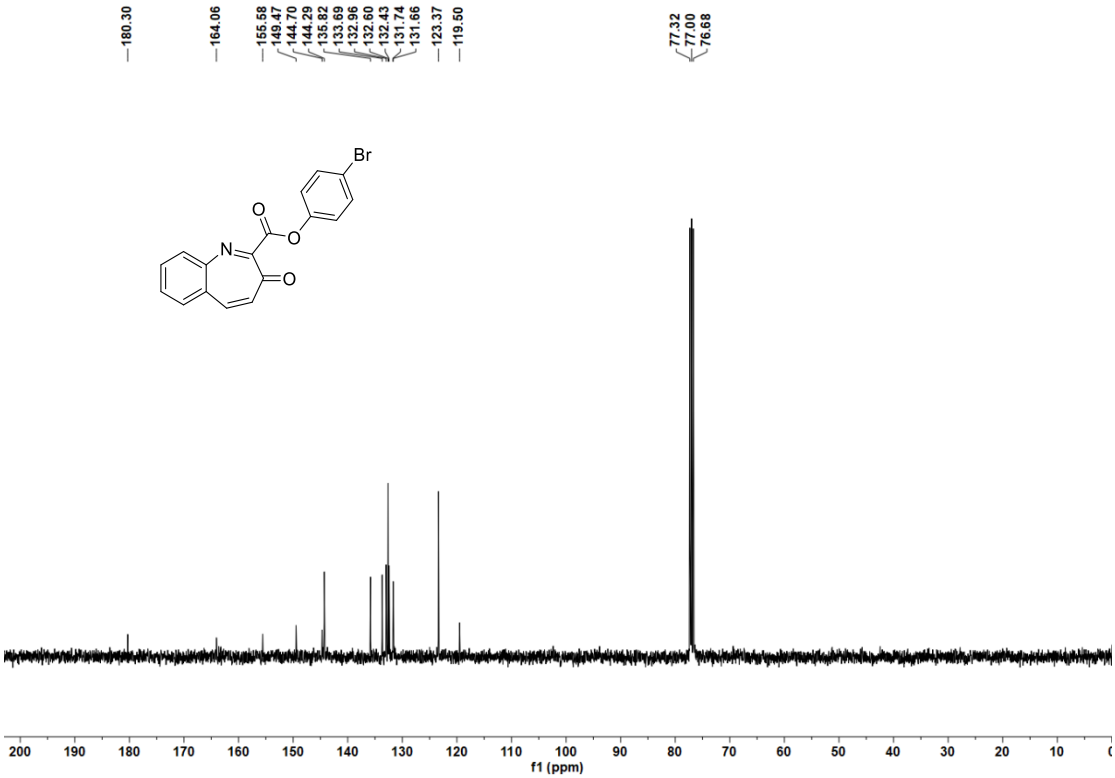
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **18**



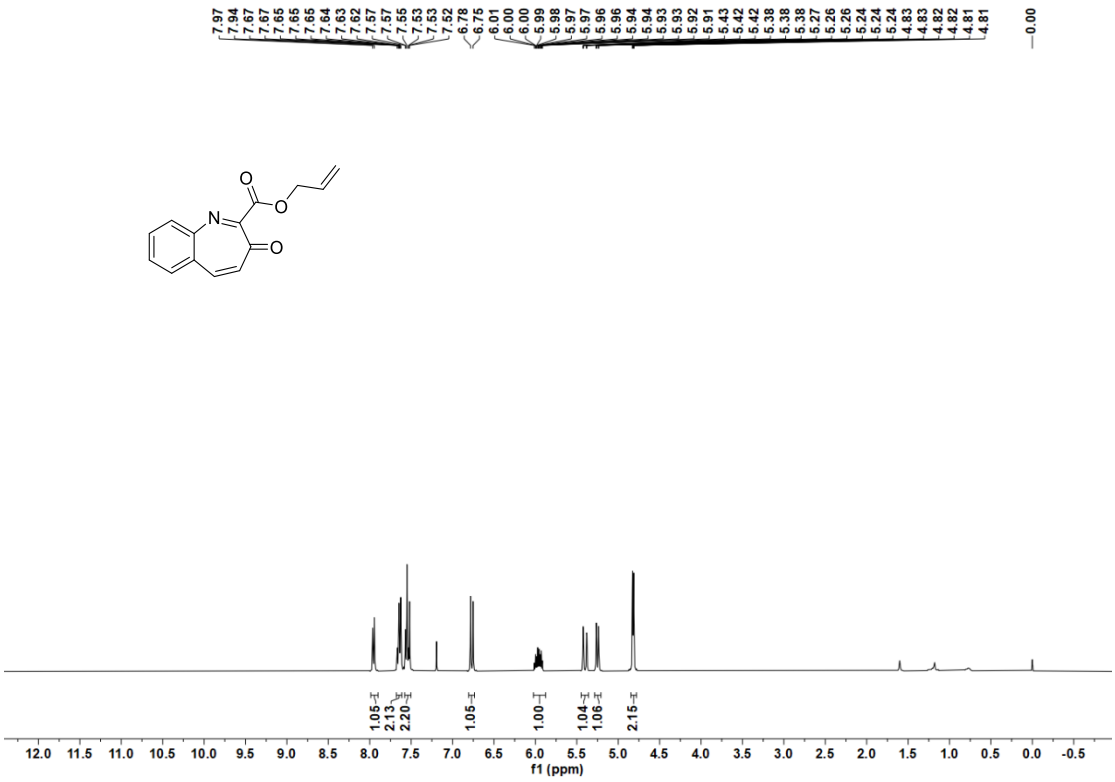


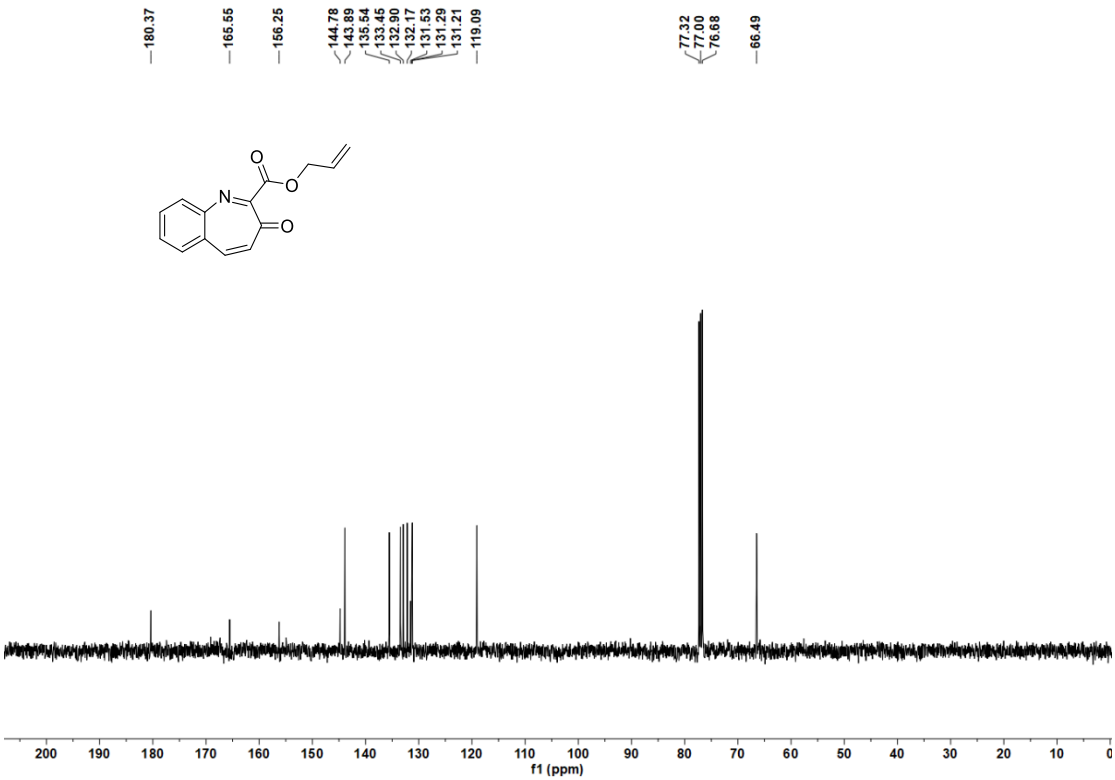
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **19**



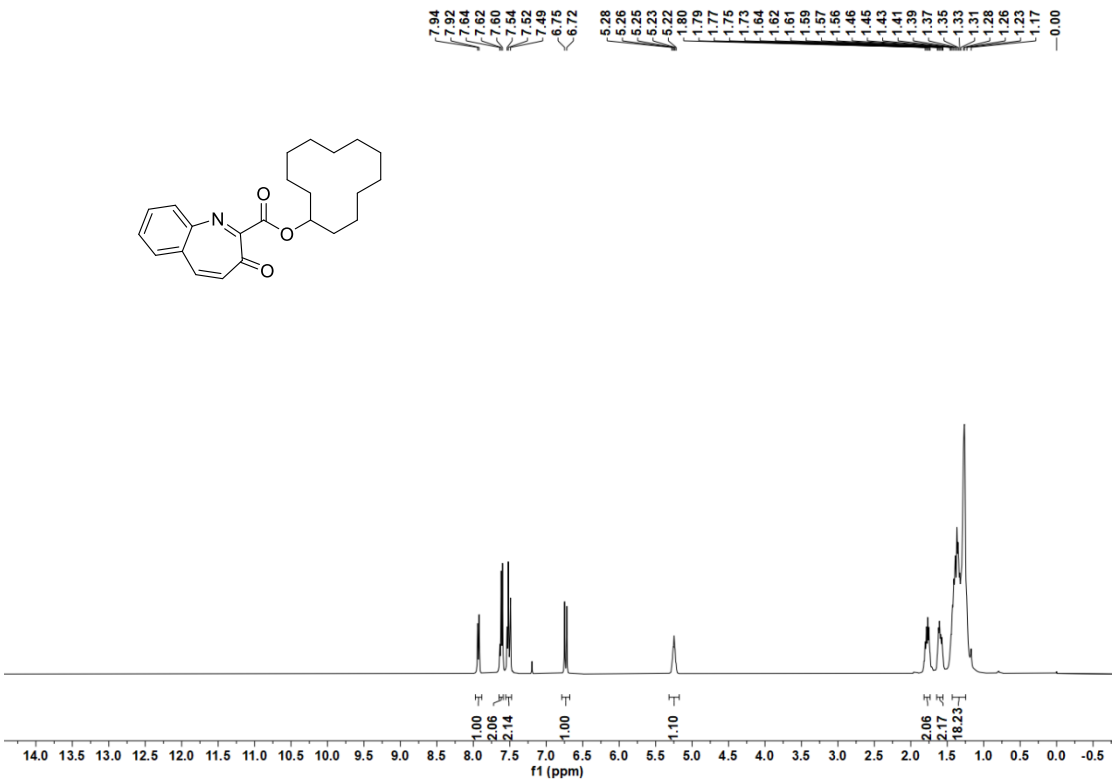


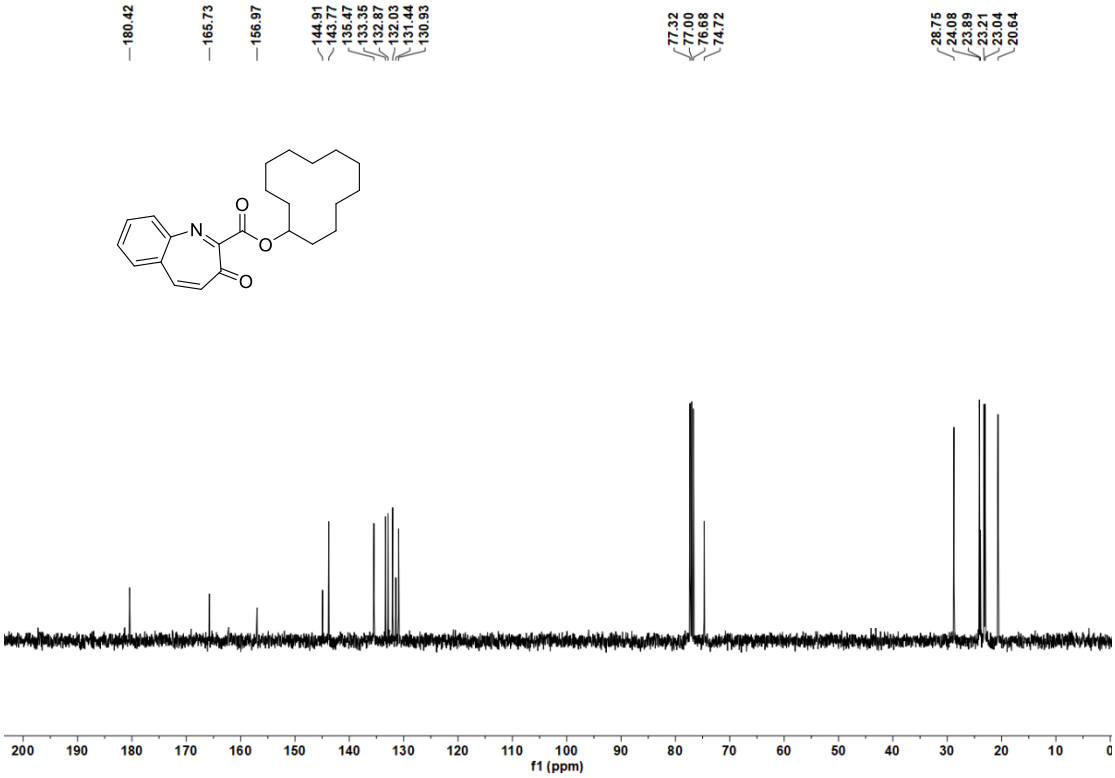
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **20**



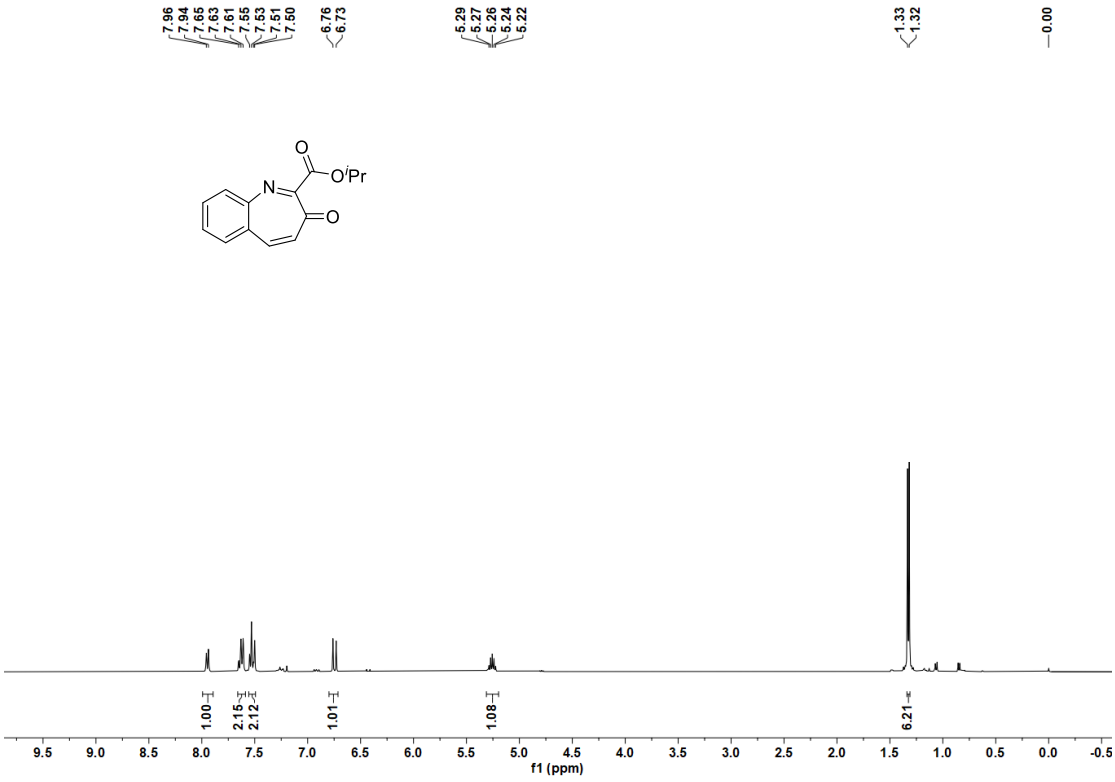


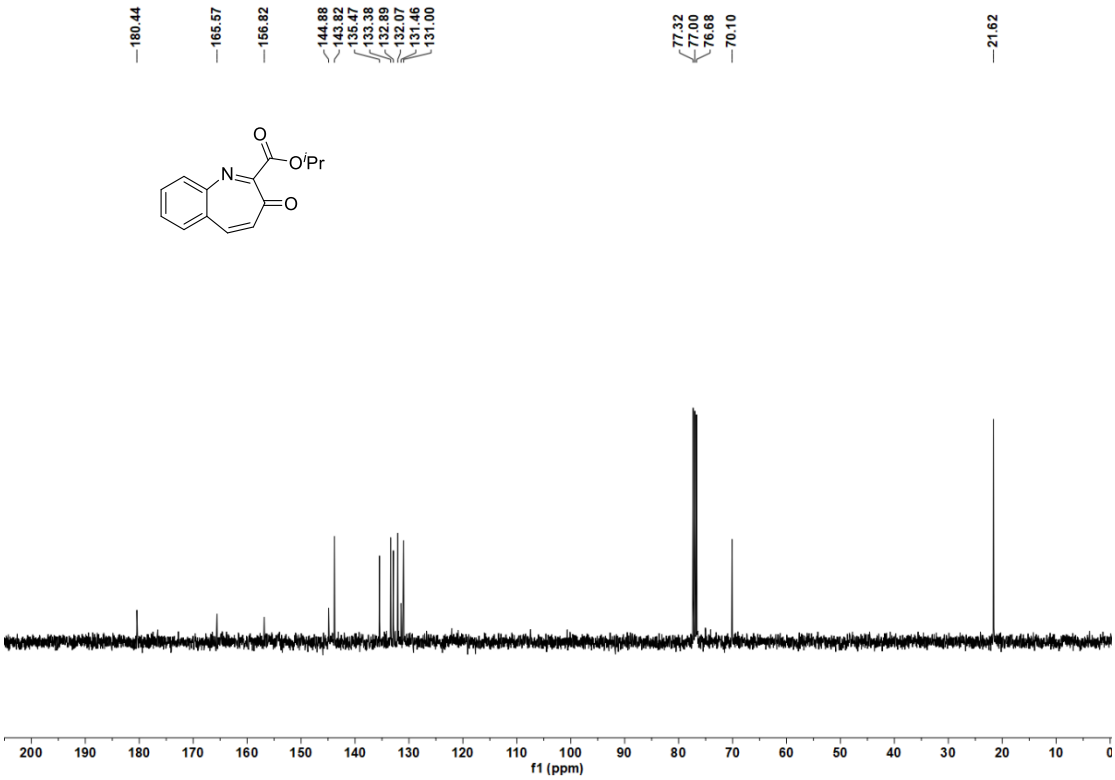
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **21**



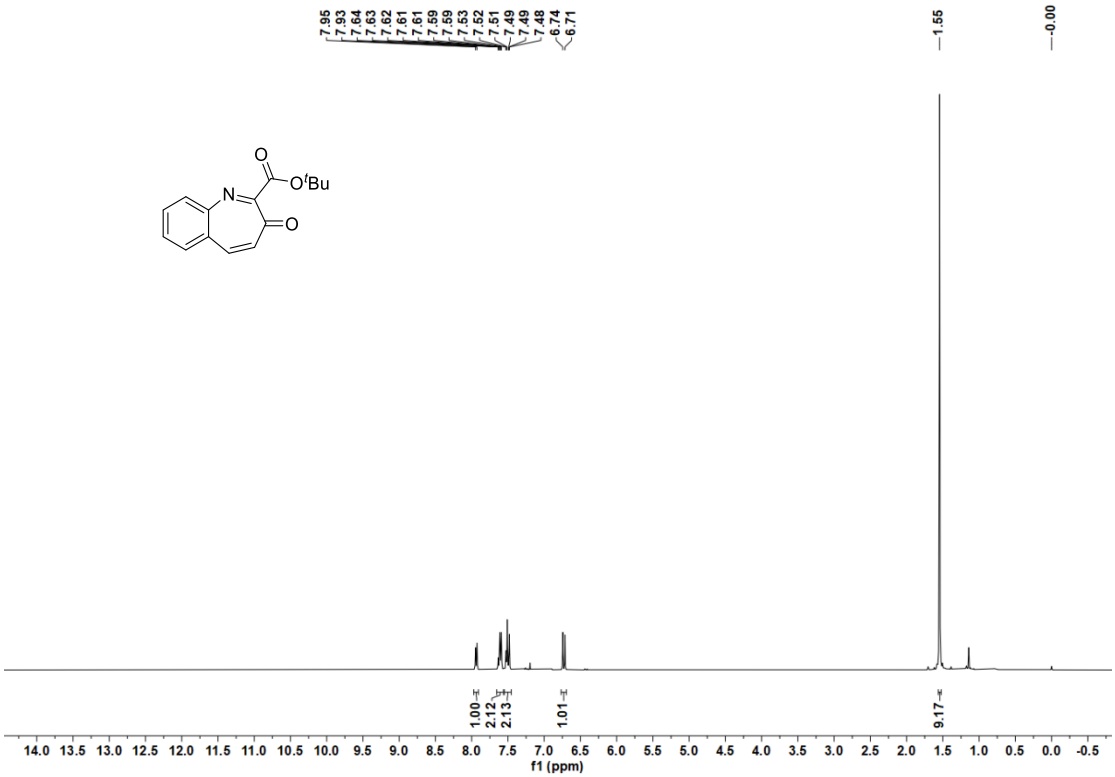


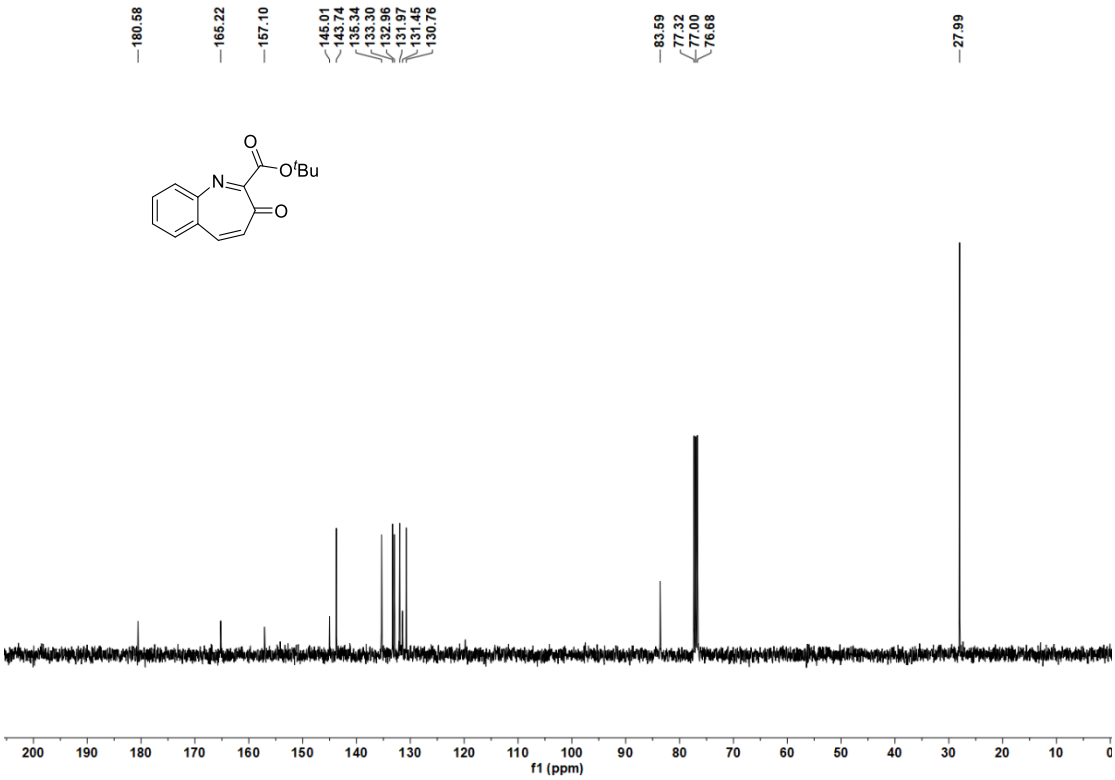
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **22**



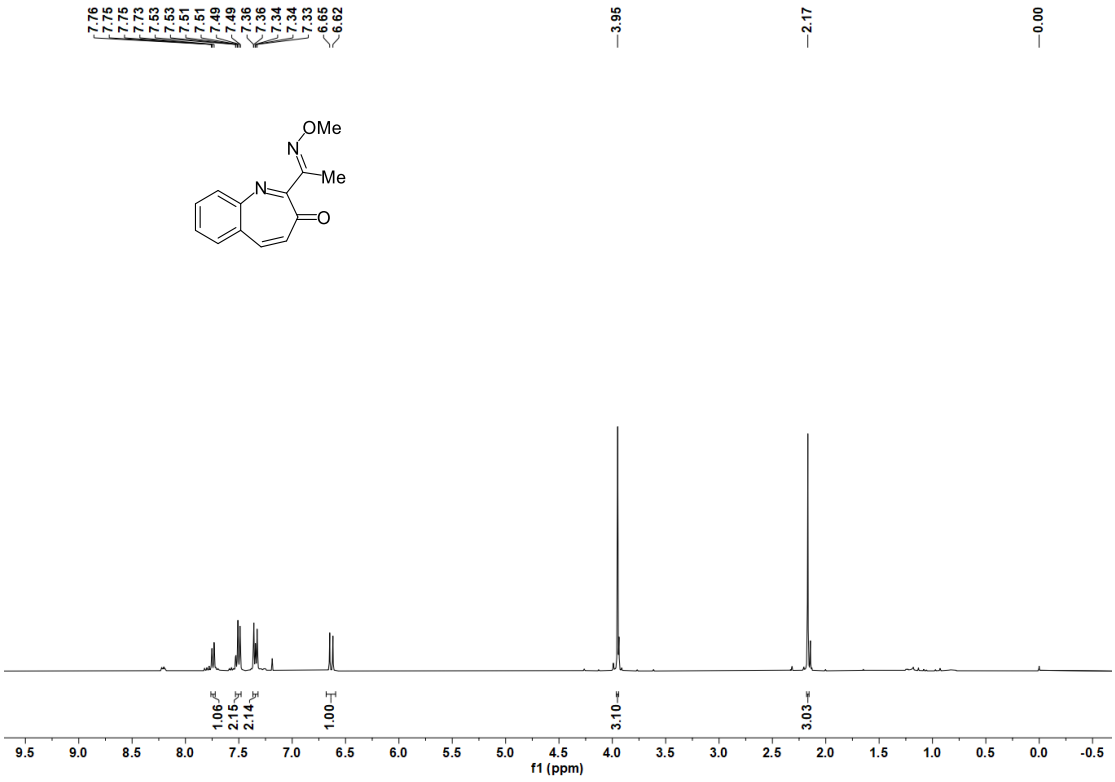


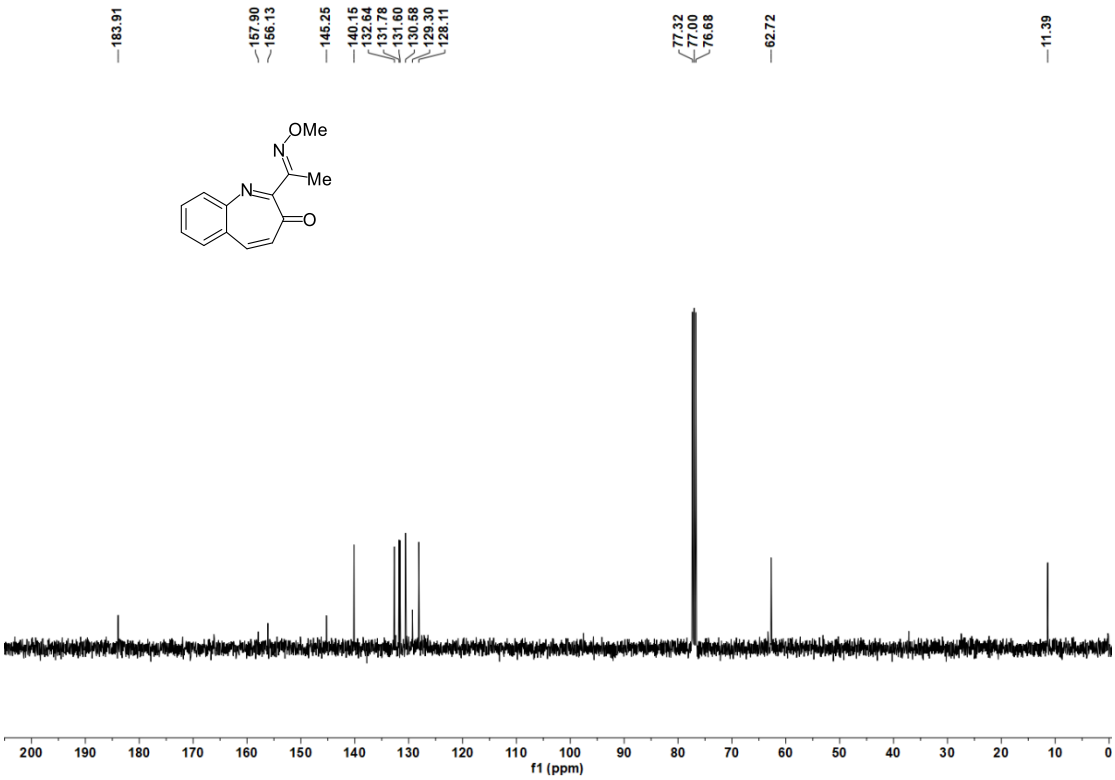
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **23**



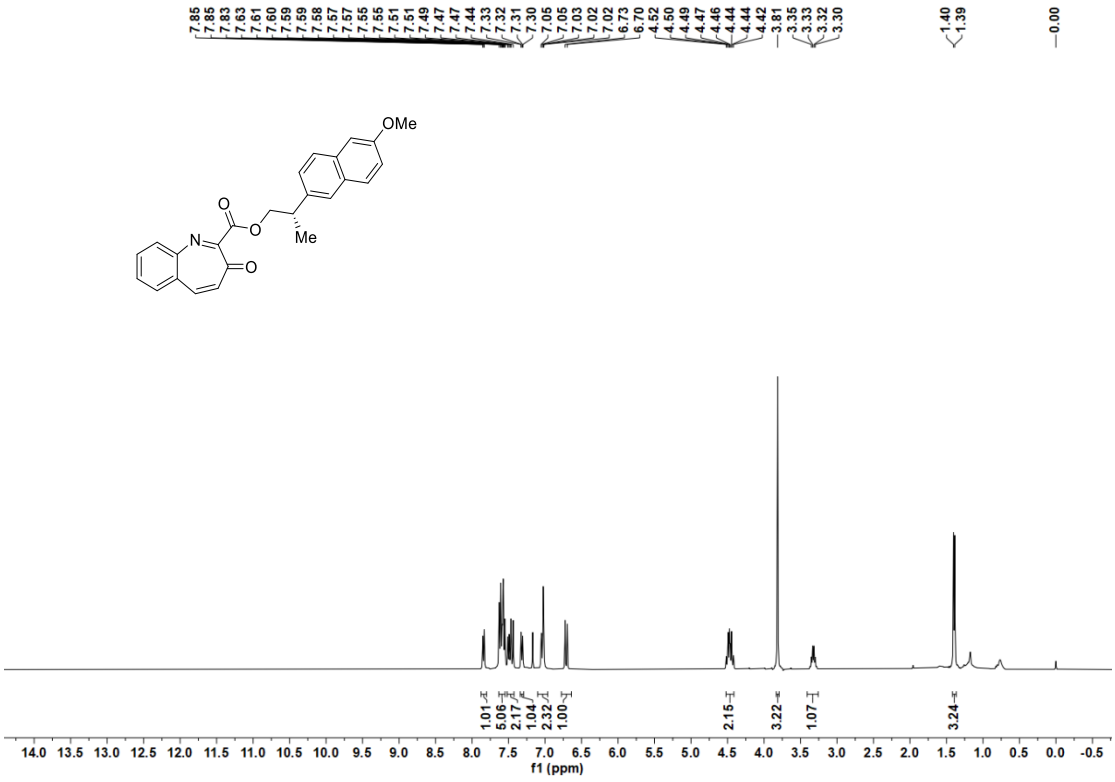


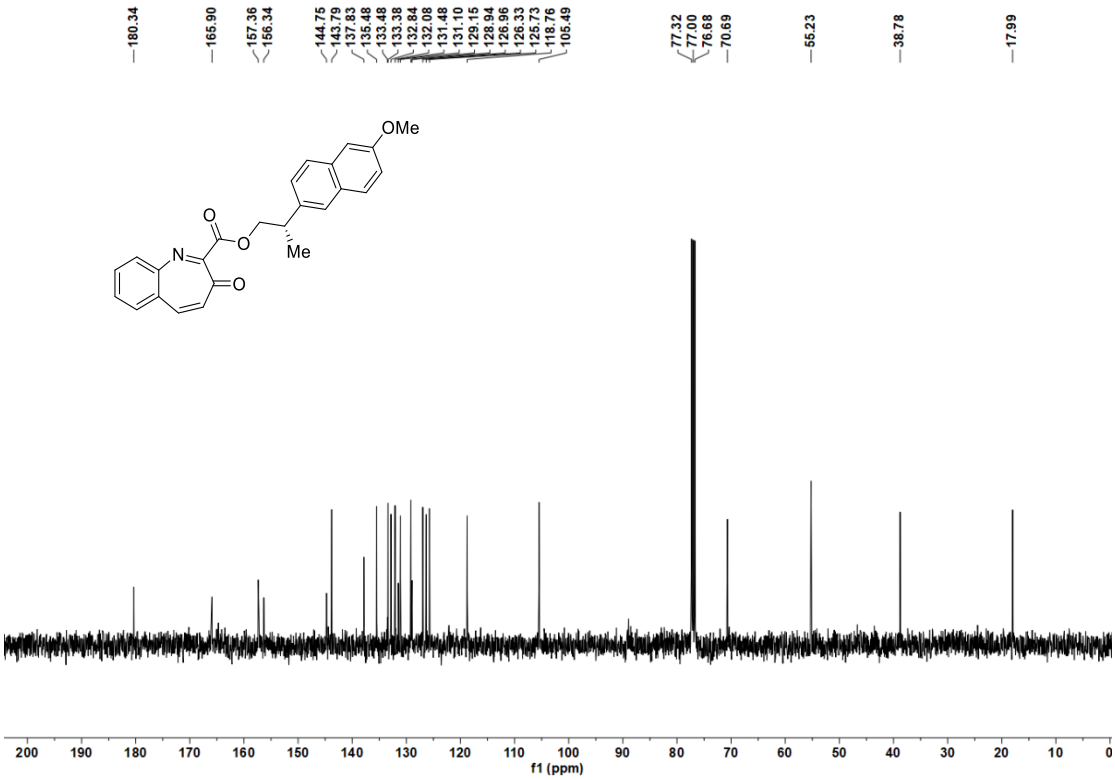
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **24**



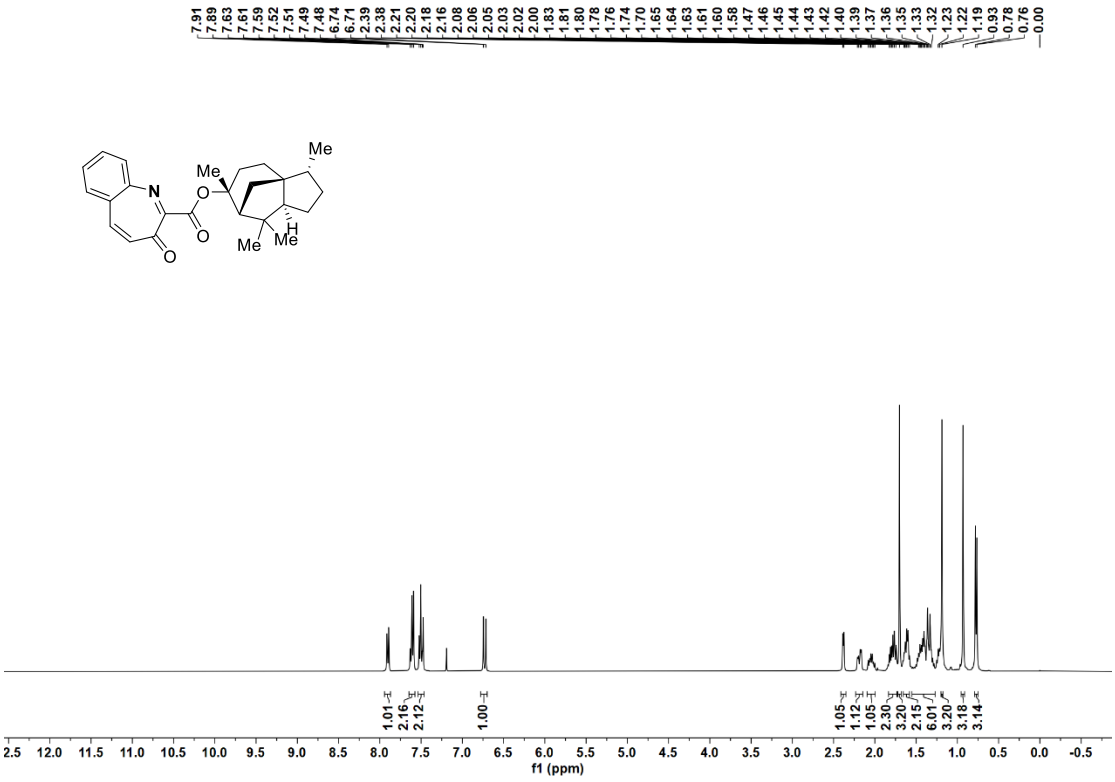


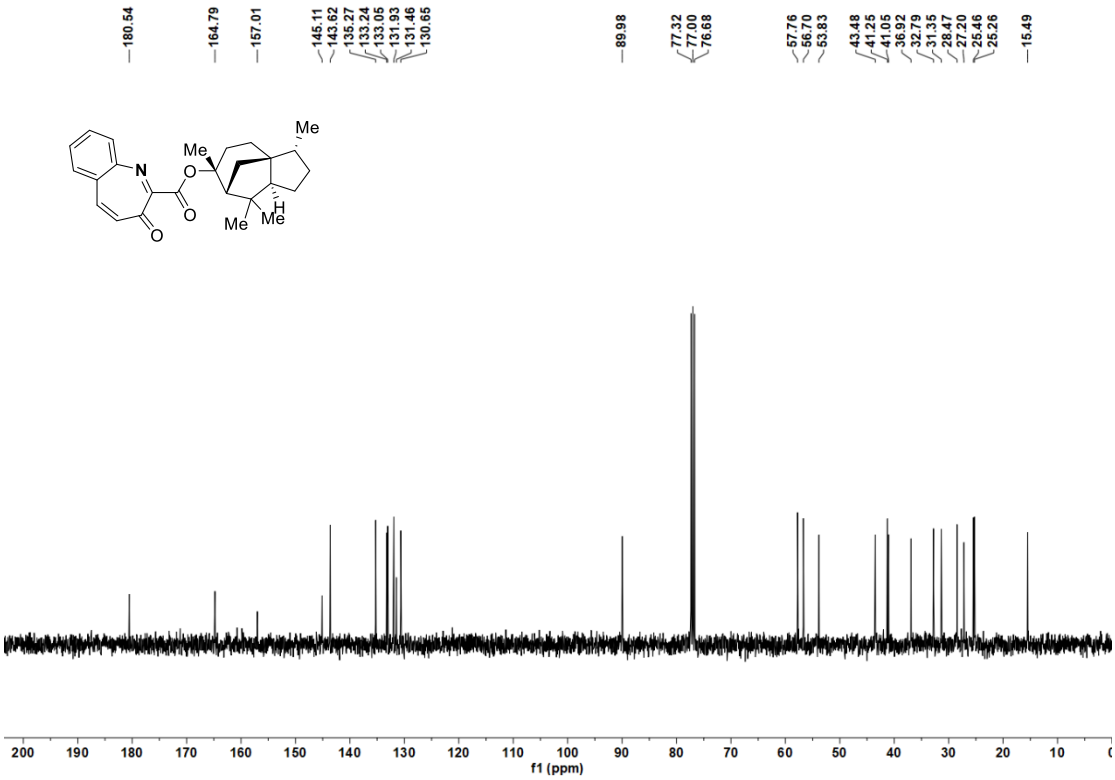
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **25**



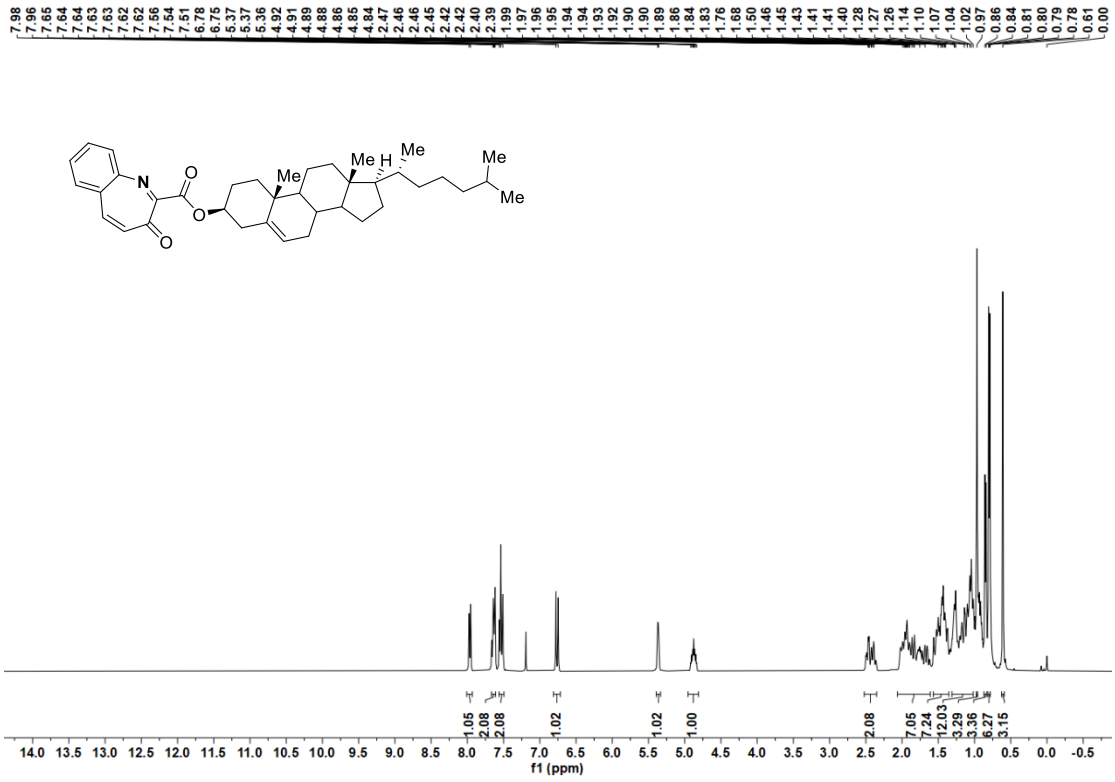


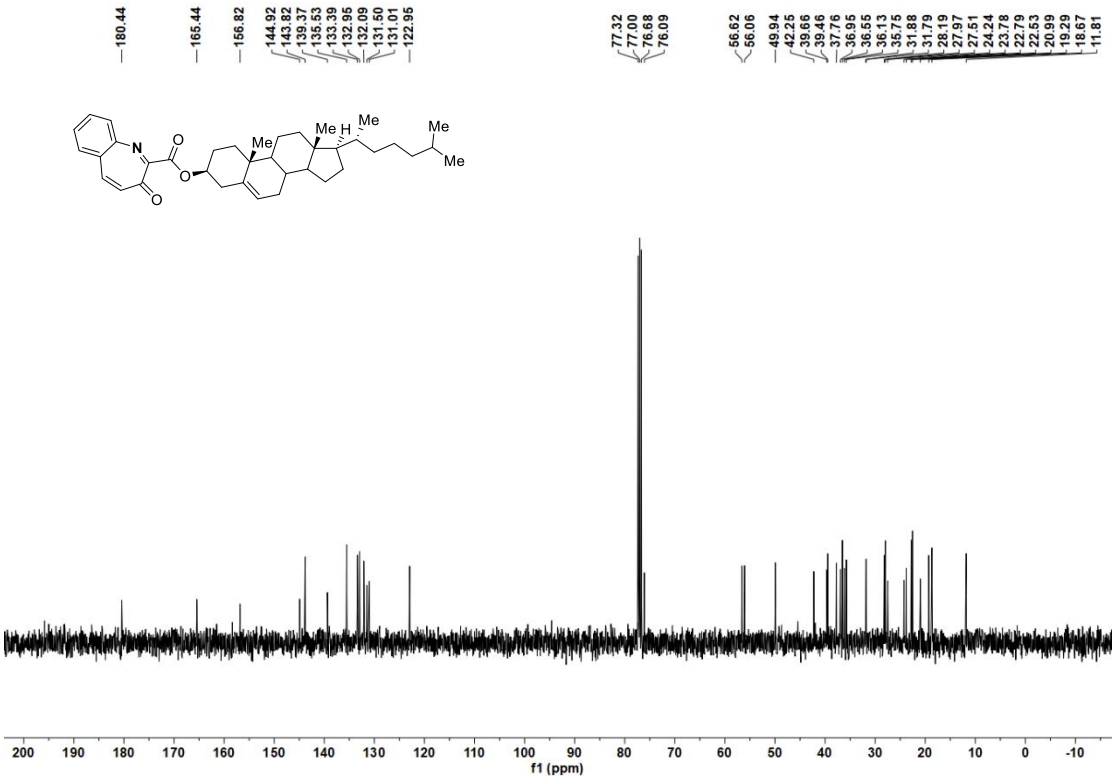
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **26**



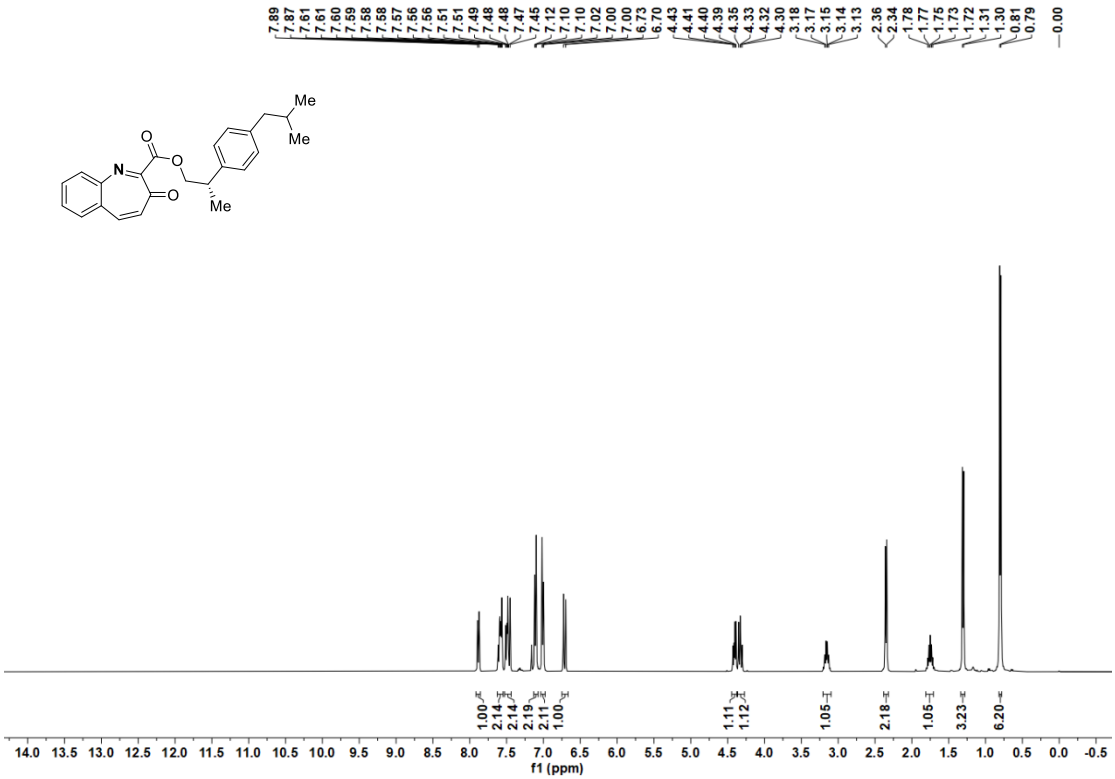


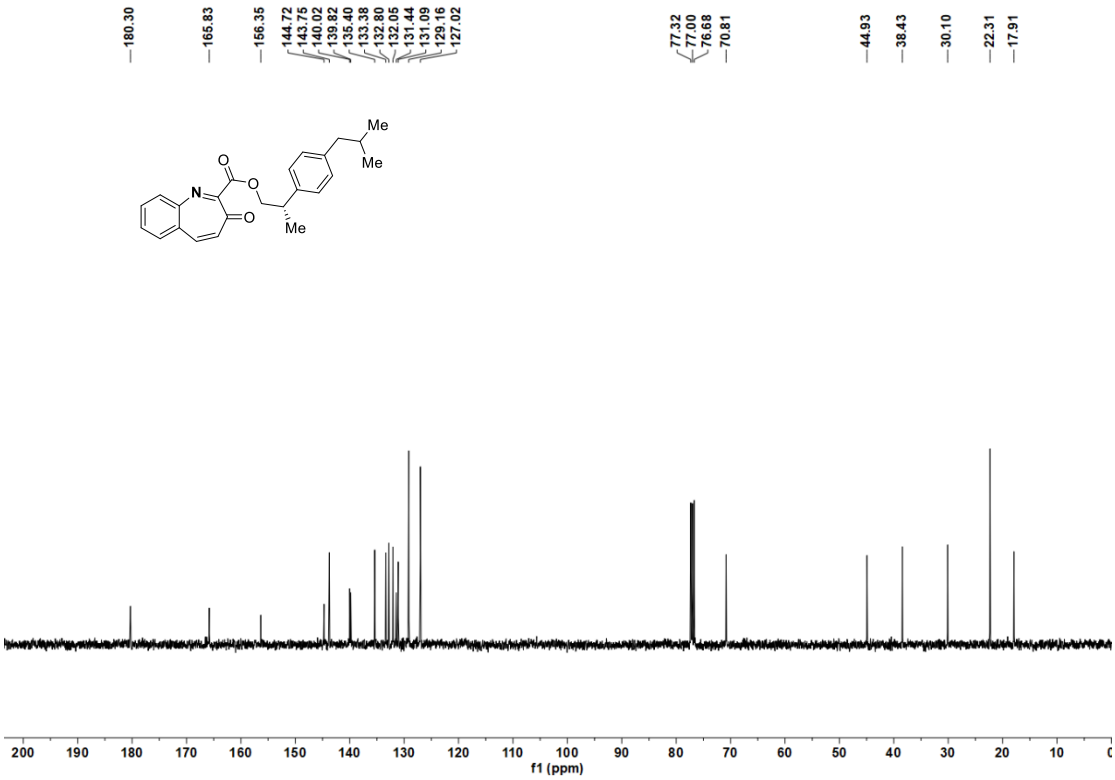
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **27**



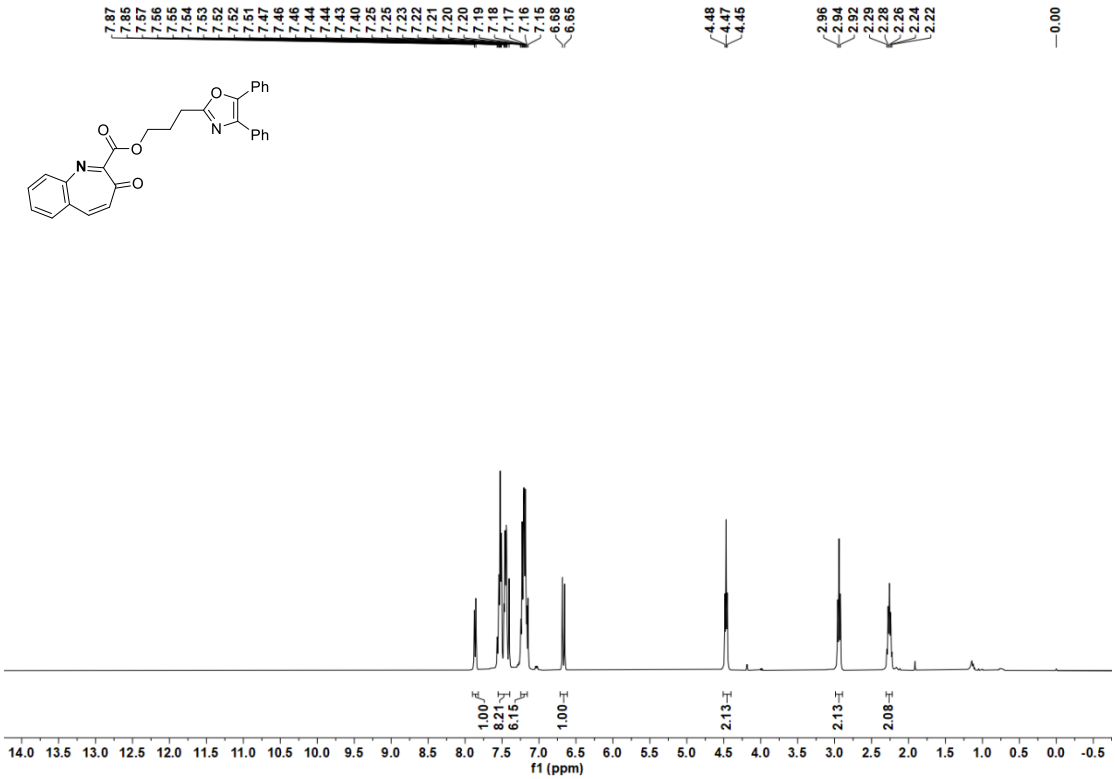


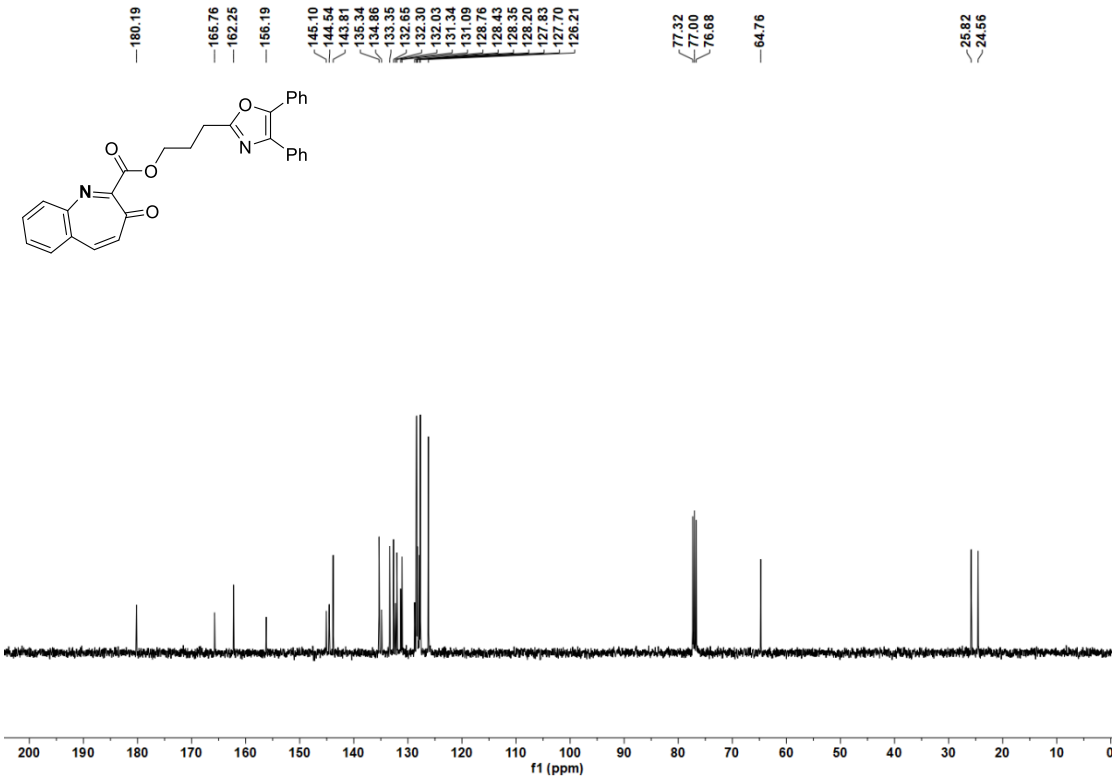
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **28**



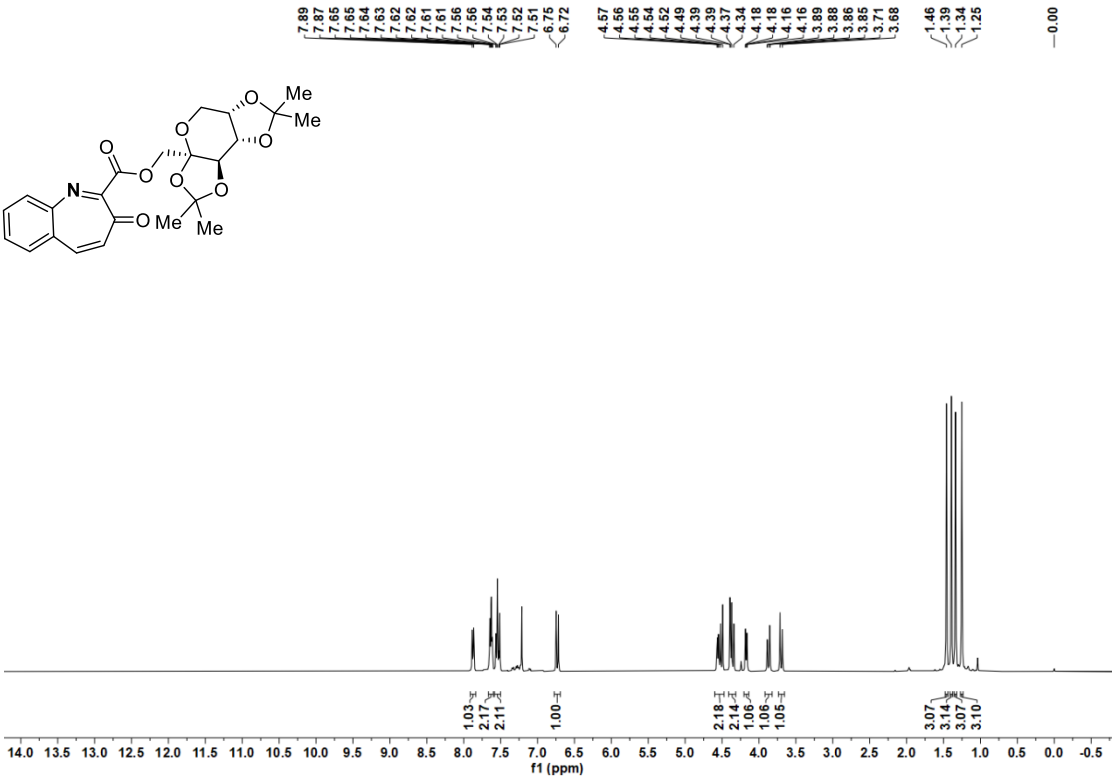


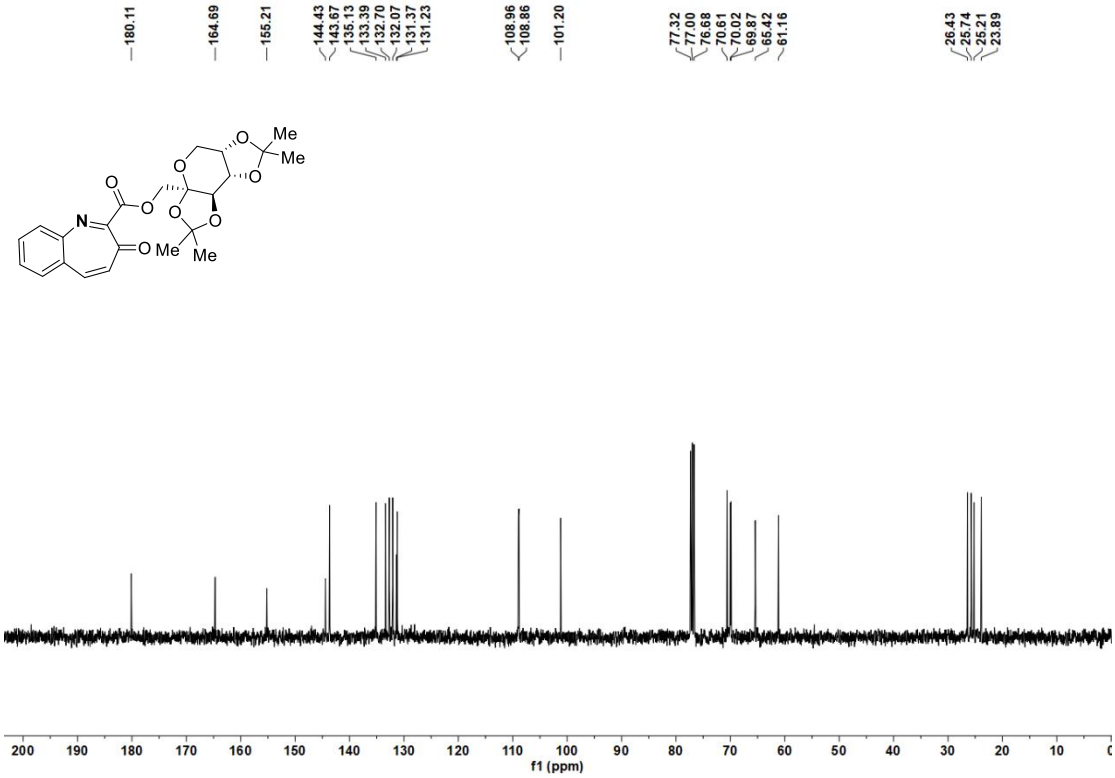
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **29**



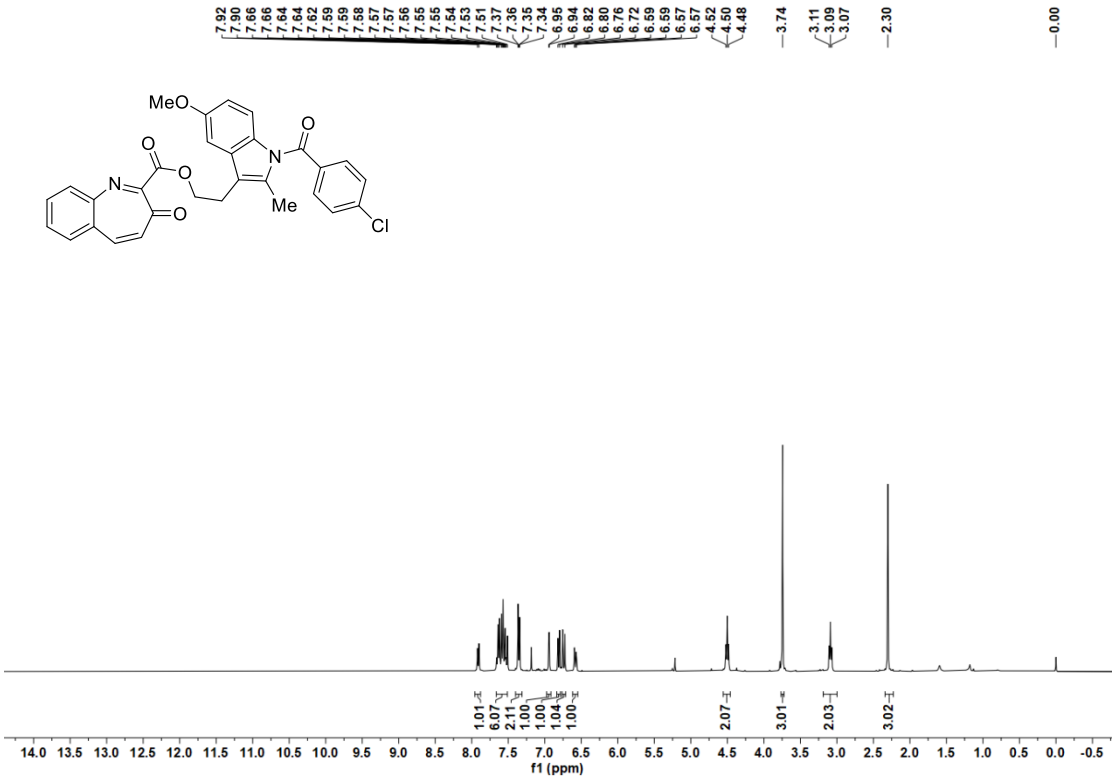


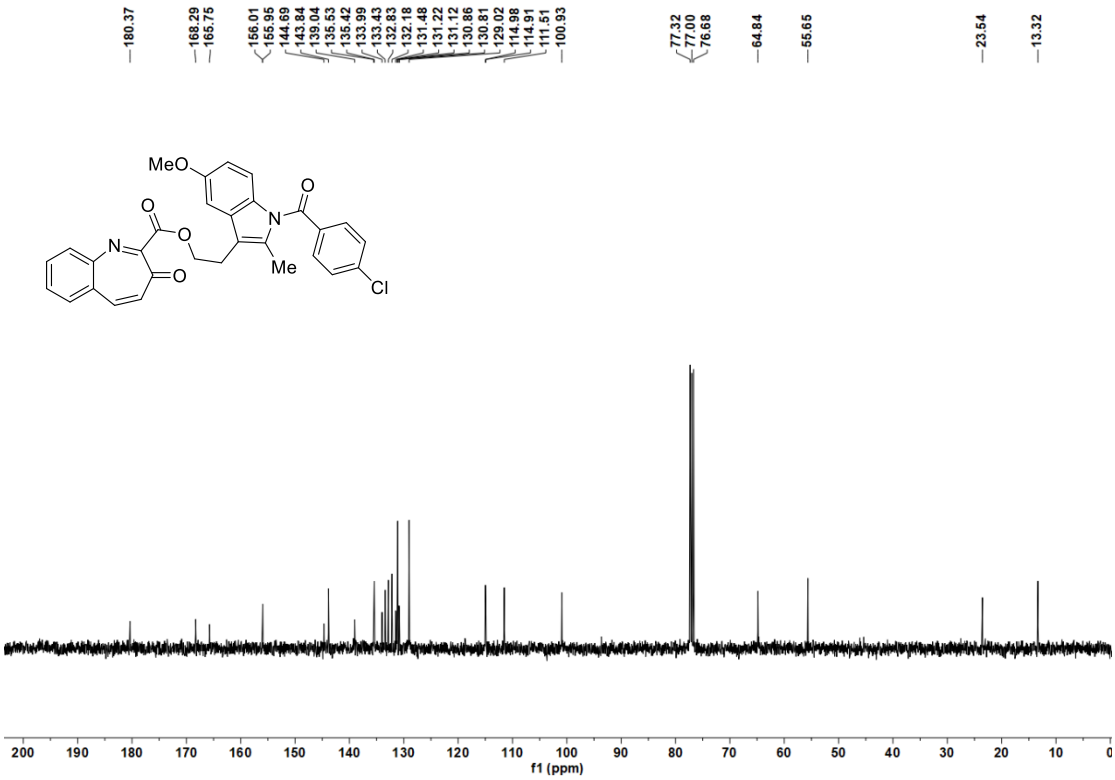
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **30**



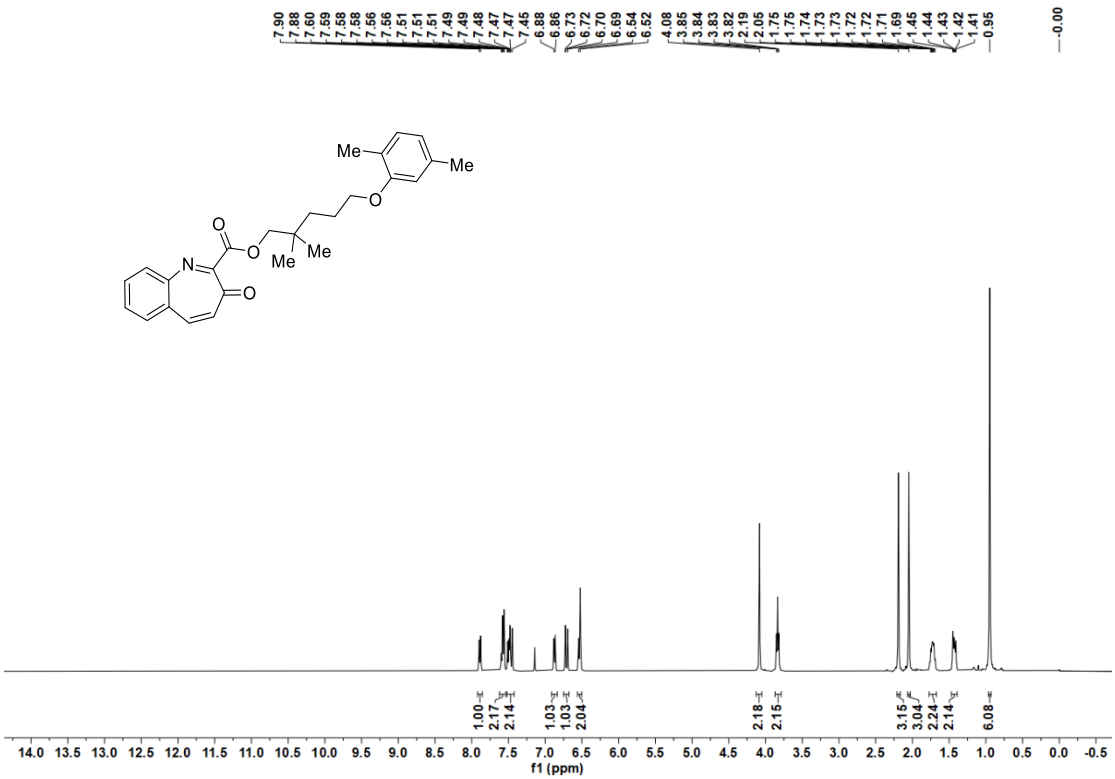


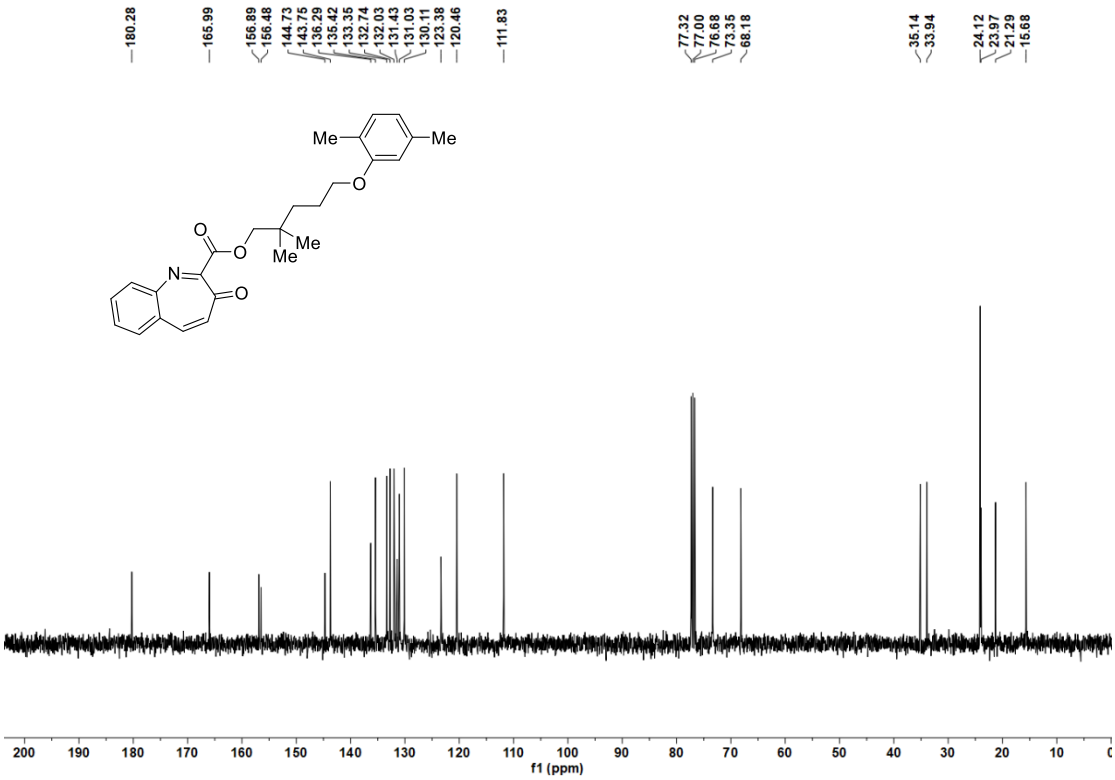
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **31**



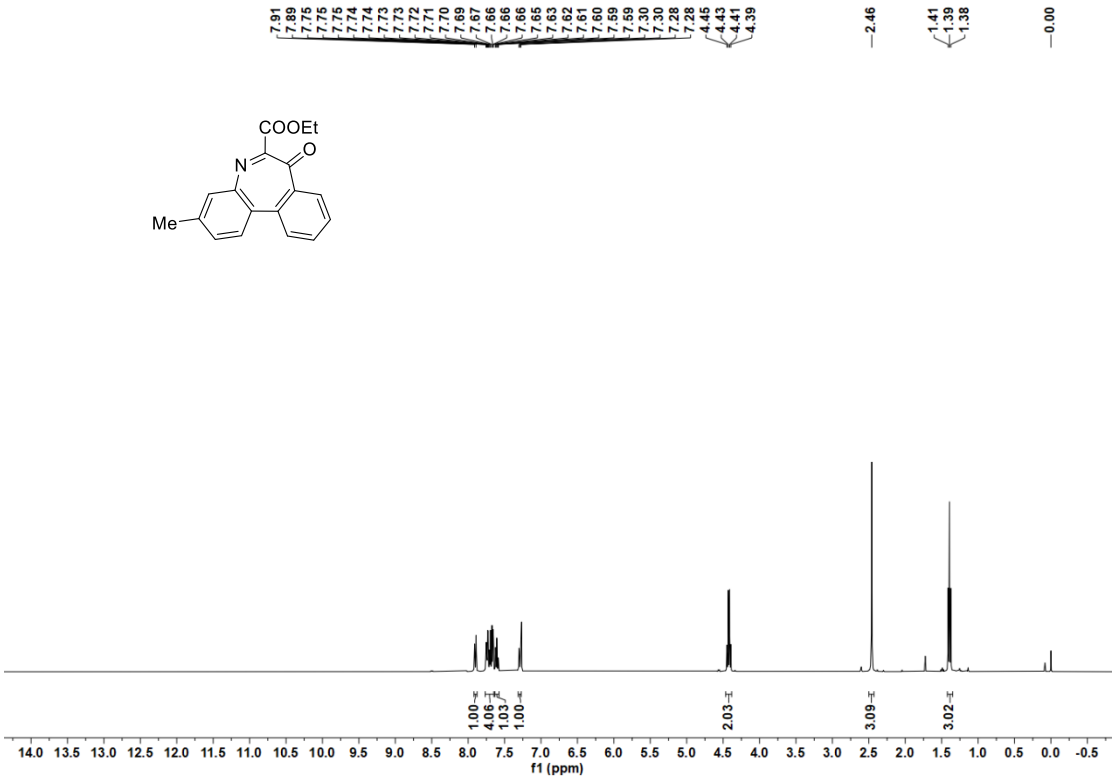


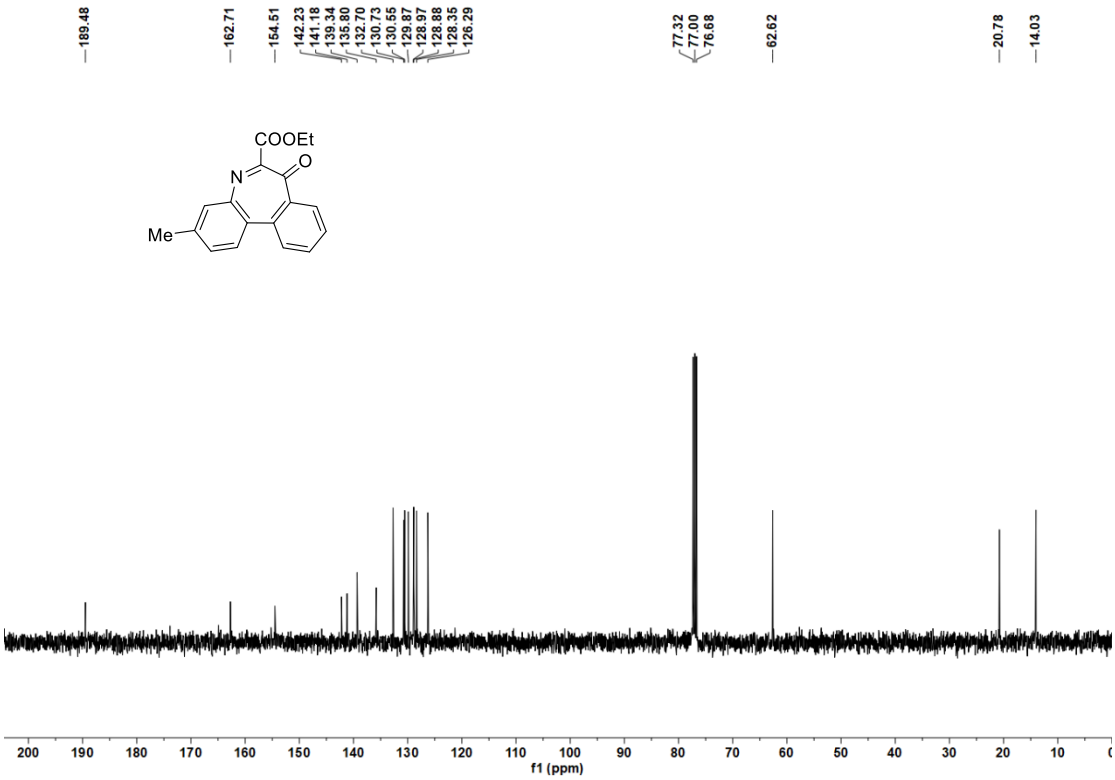
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **32**



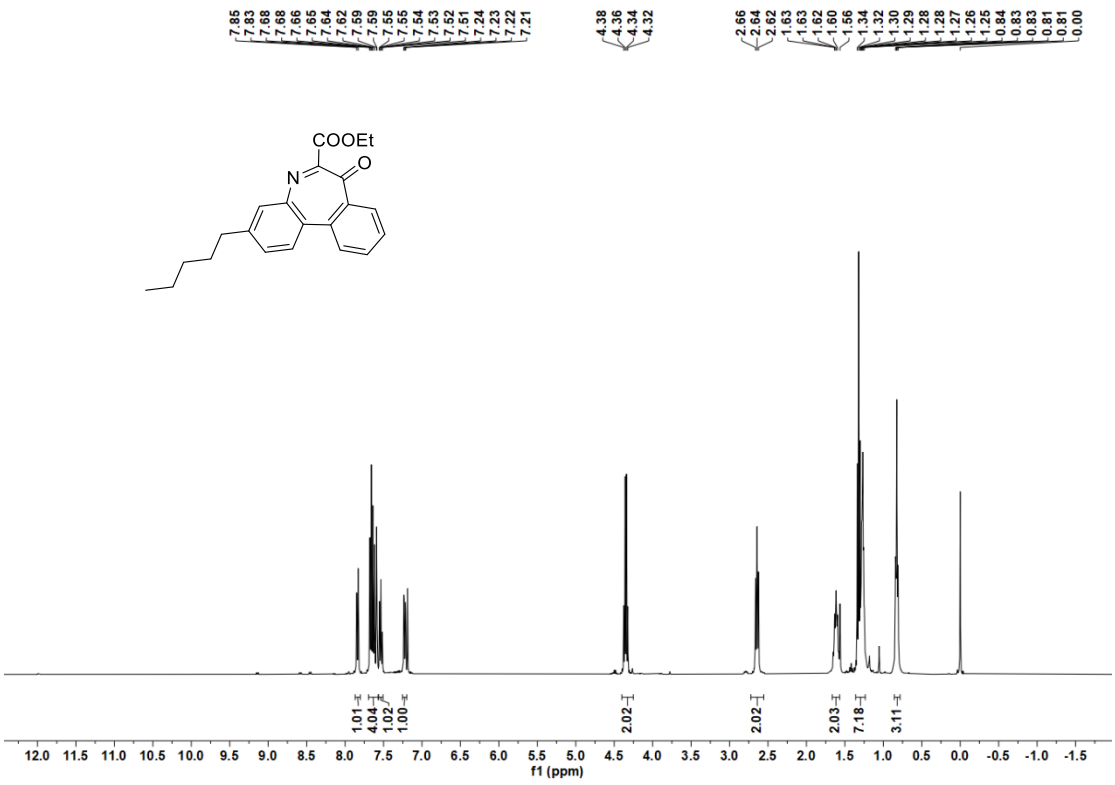


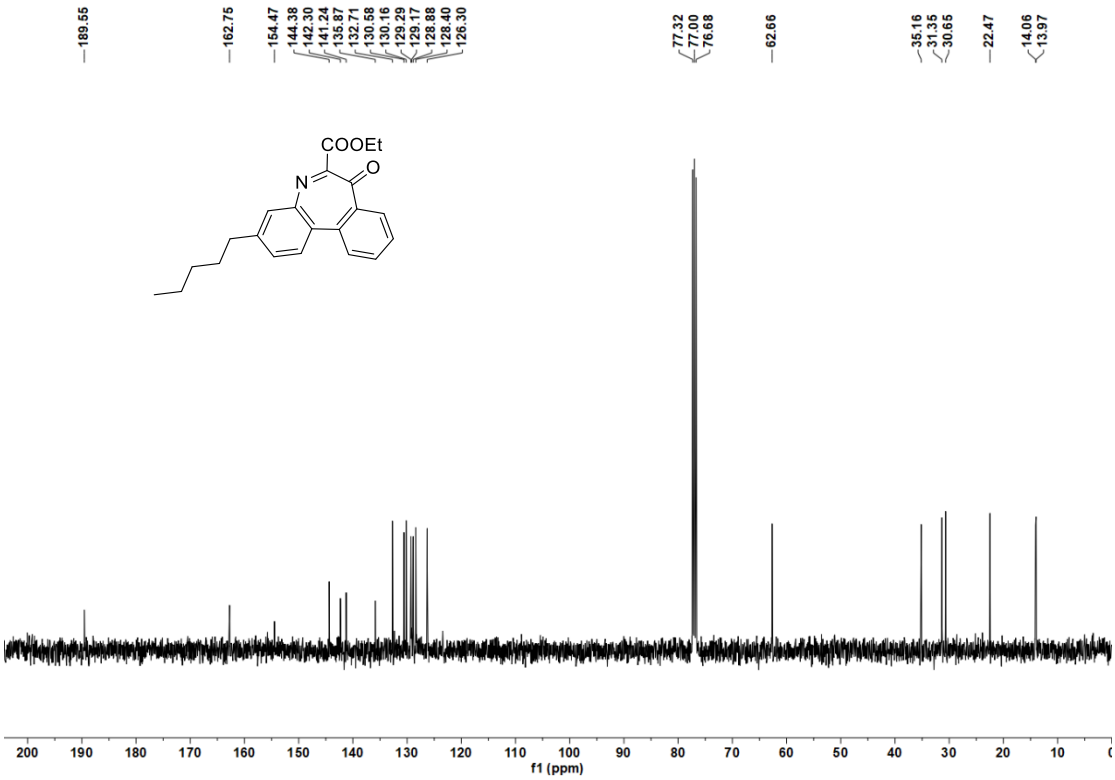
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **33**



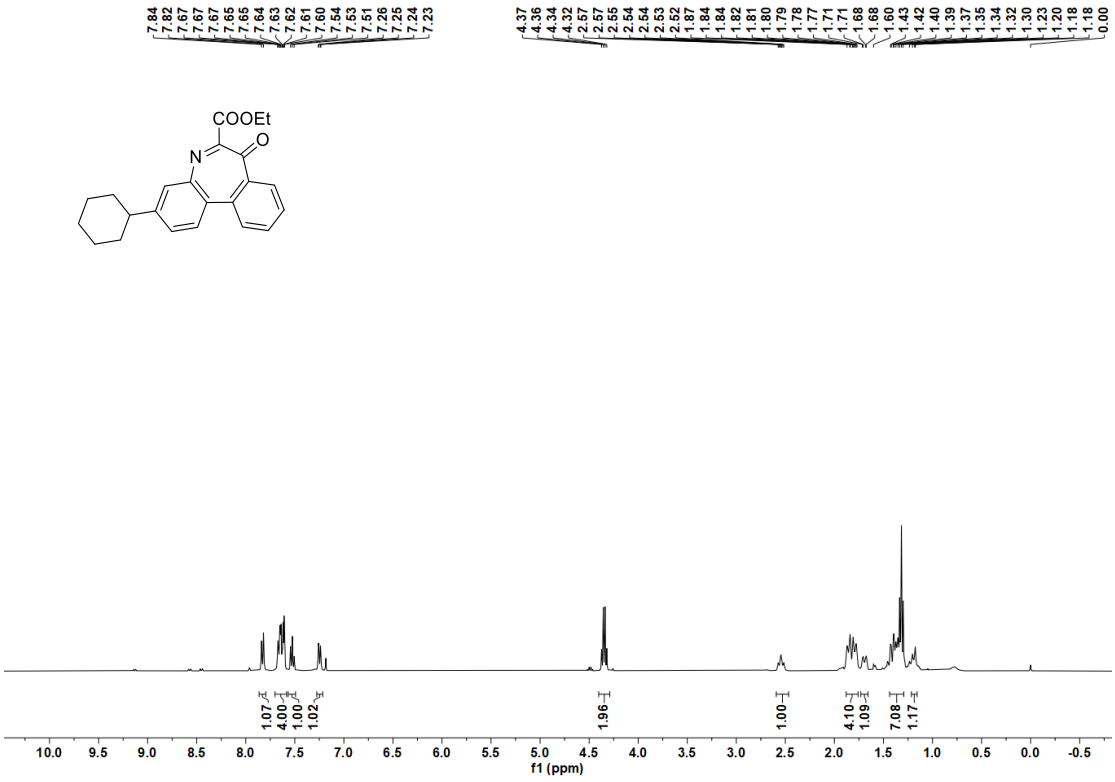


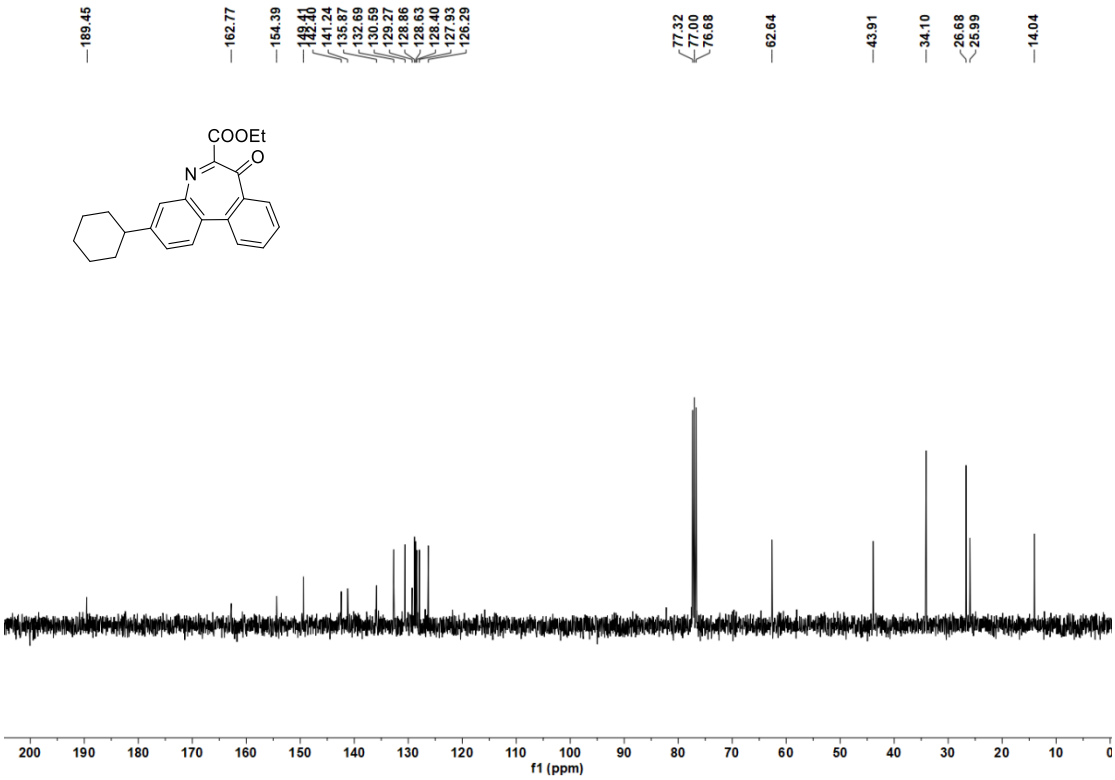
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **34**



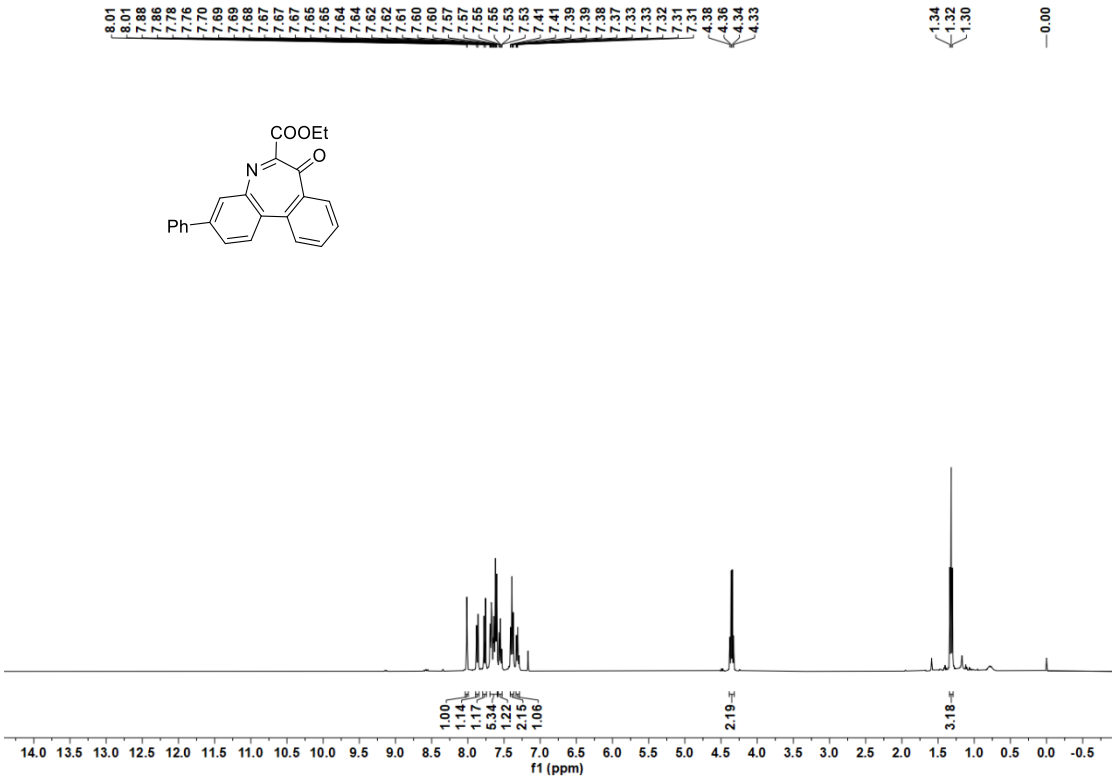


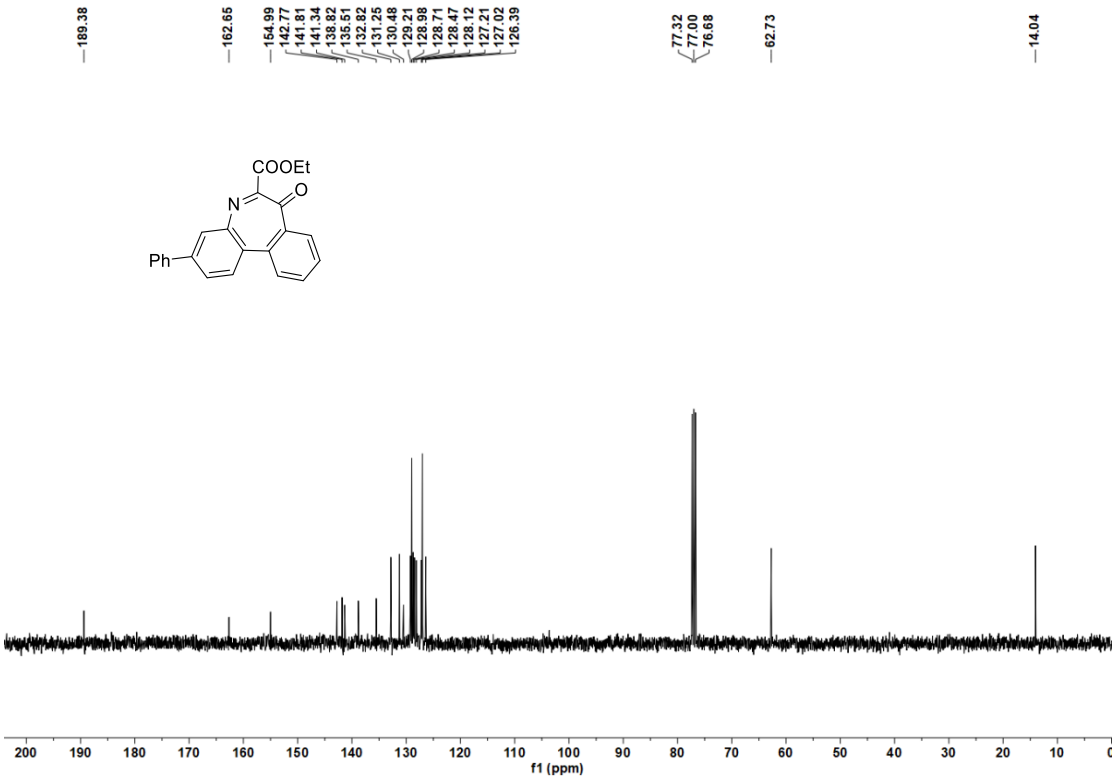
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **35**



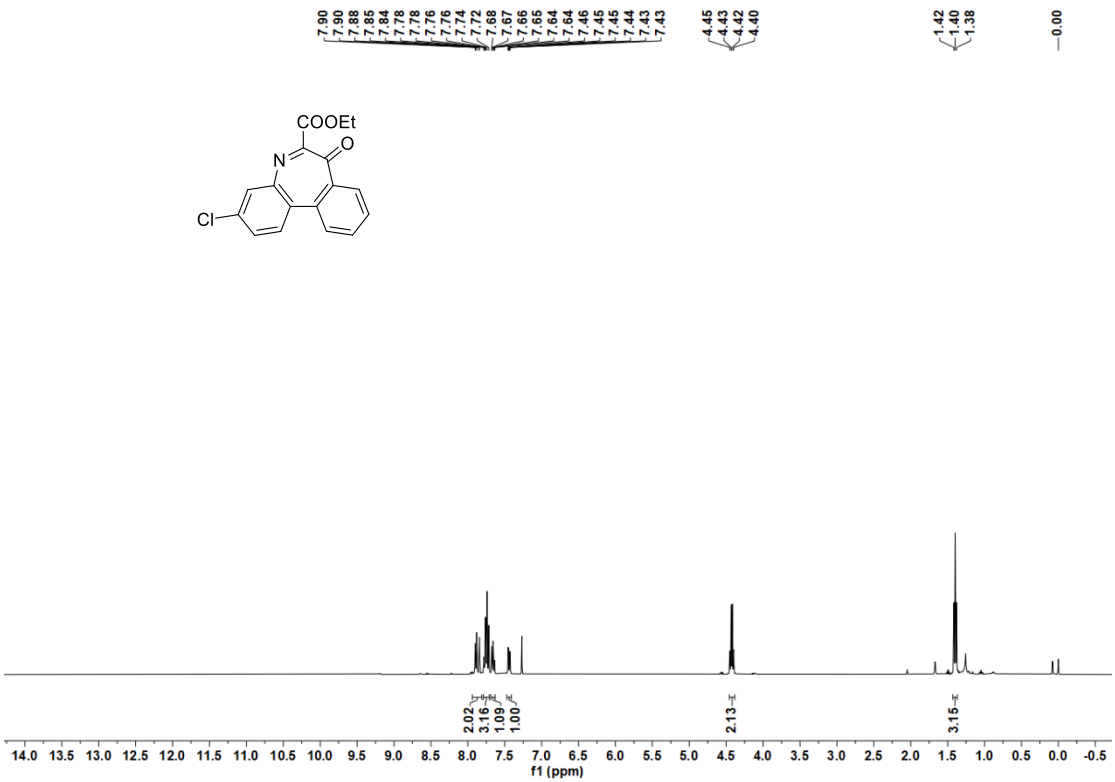


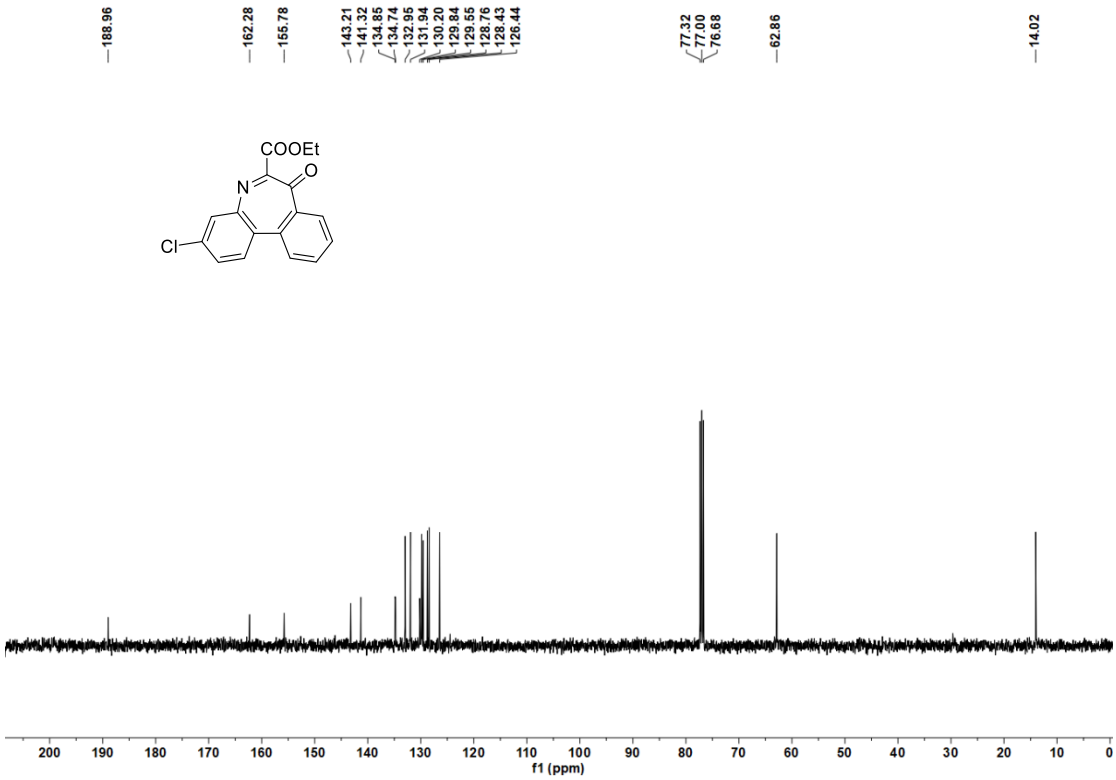
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **36**



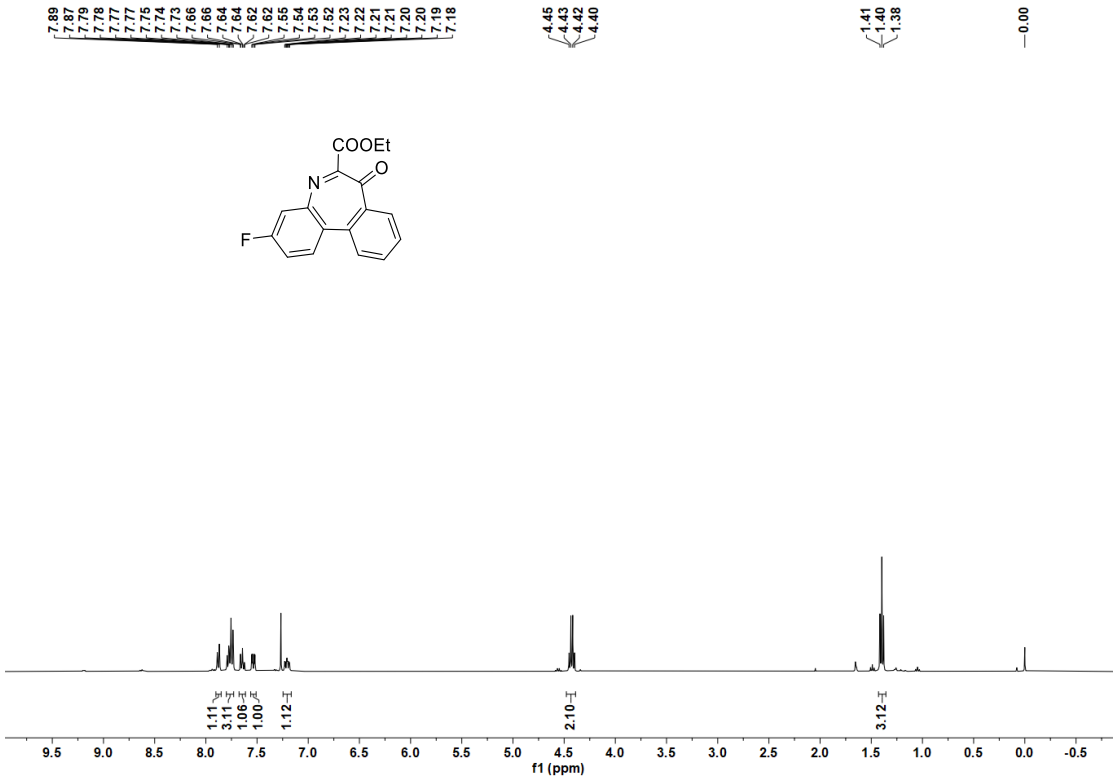


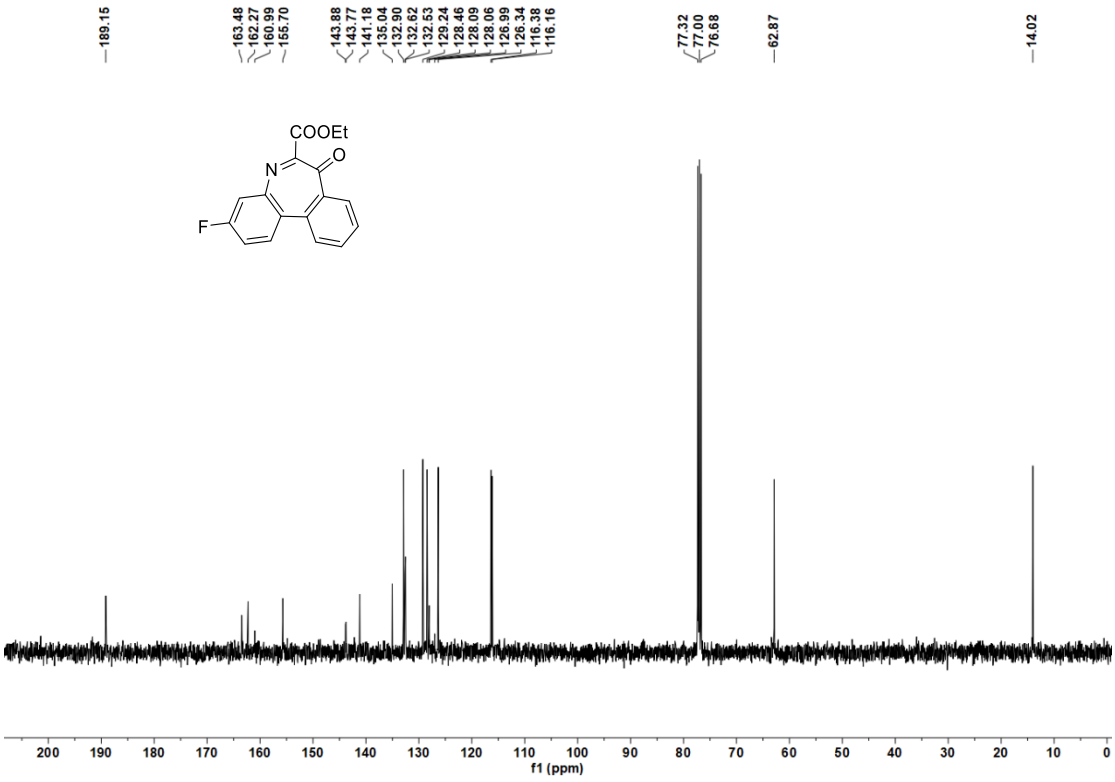
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **37**



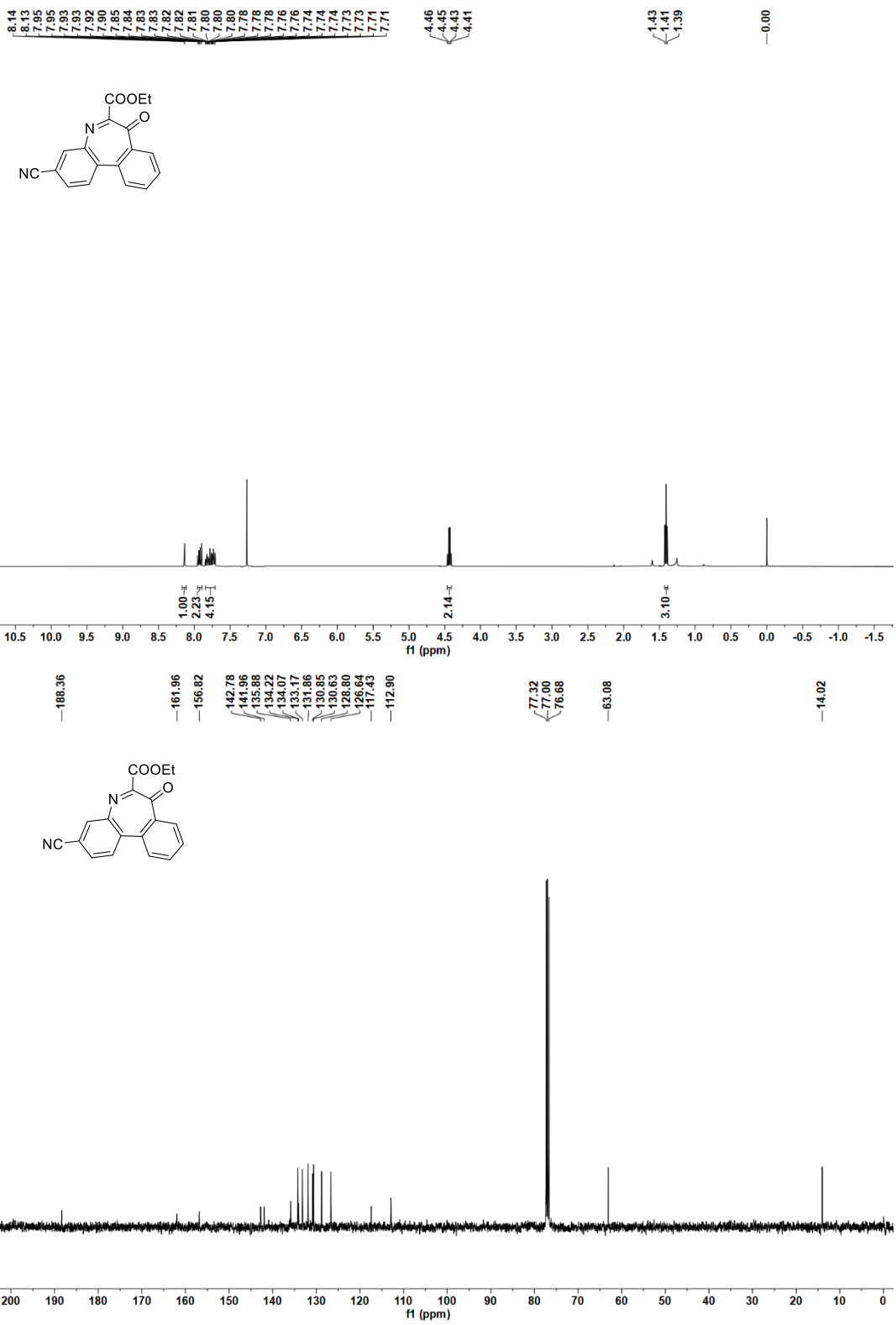


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **38**

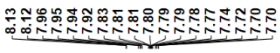




^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **39**



^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **40**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8.12
7.96
7.95
7.94
7.92
7.83
7.81
7.81
7.80
7.79
7.79
7.78
7.77
7.74
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7.70
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4.42
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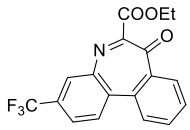
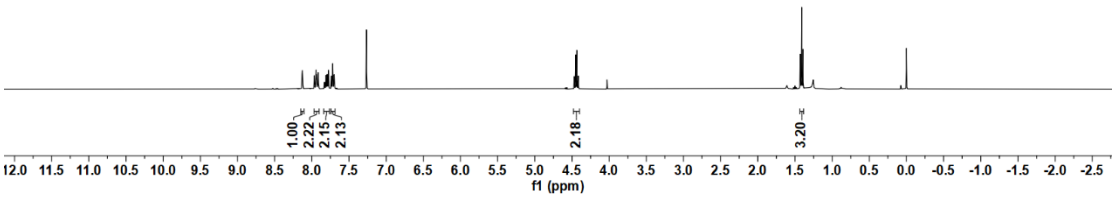
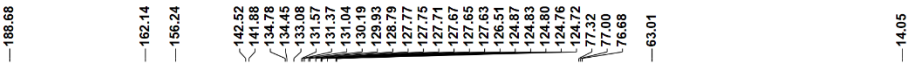
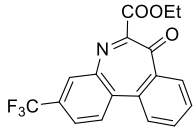
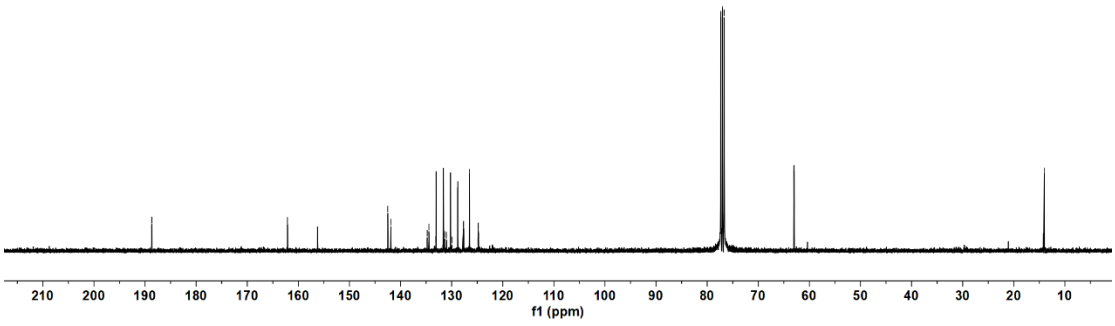
1.41
1.39
0.00


COOEt
N
O
F3C


1.00
2.22
2.15
2.13
2.18
3.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f1 (ppm)


188.68
162.14
156.24
142.52
141.88
134.78
134.45
133.08
131.57
131.37
131.04
130.19
129.93
128.79
127.77
127.75
127.71
127.67
127.65
127.63
126.51
124.87
124.83
124.80
124.76
124.72
77.32
77.00
76.68
63.01
14.05


COOEt
N
O
F3C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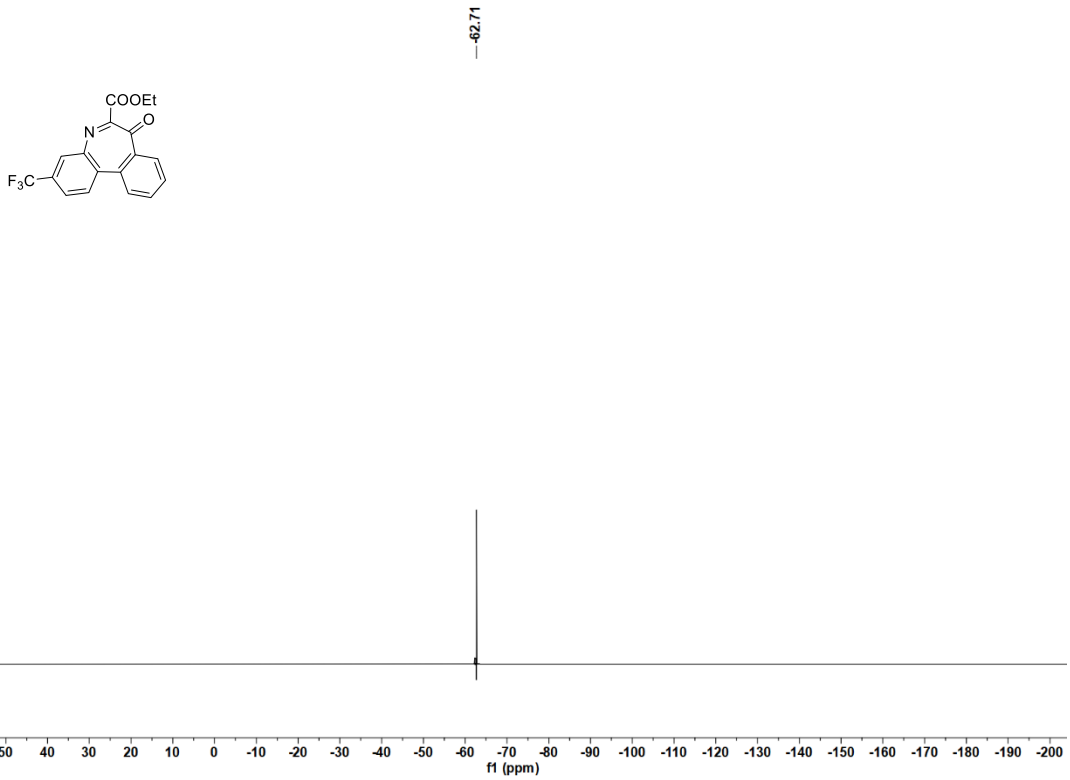
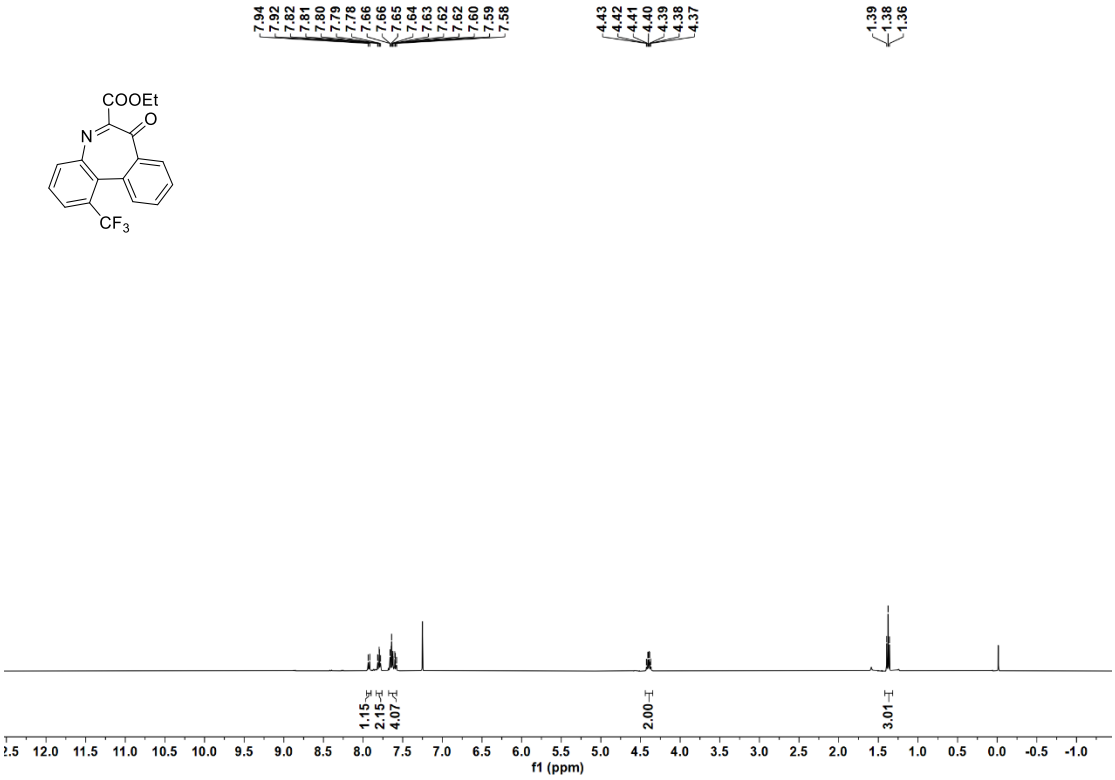
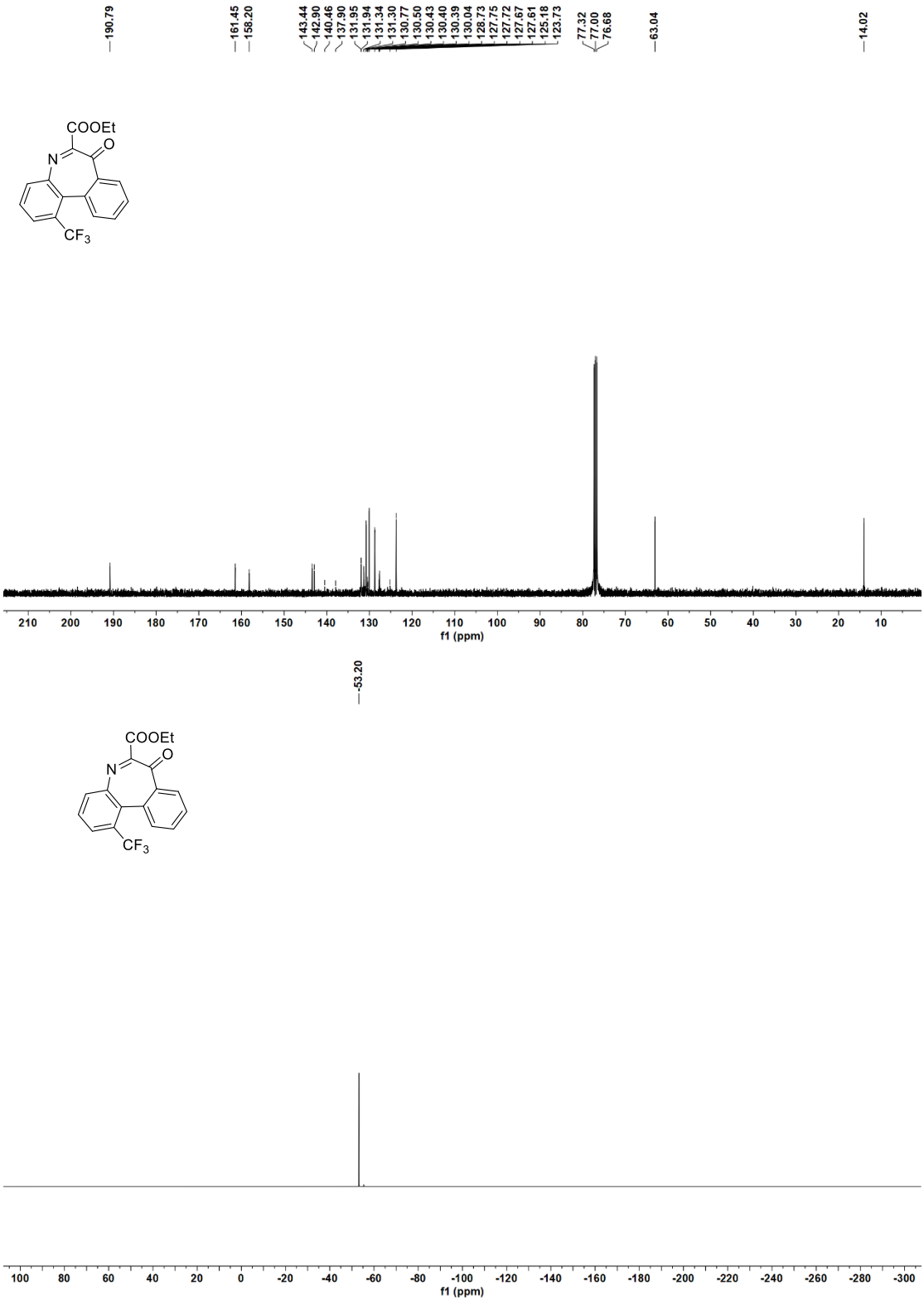
f1 (ppm)

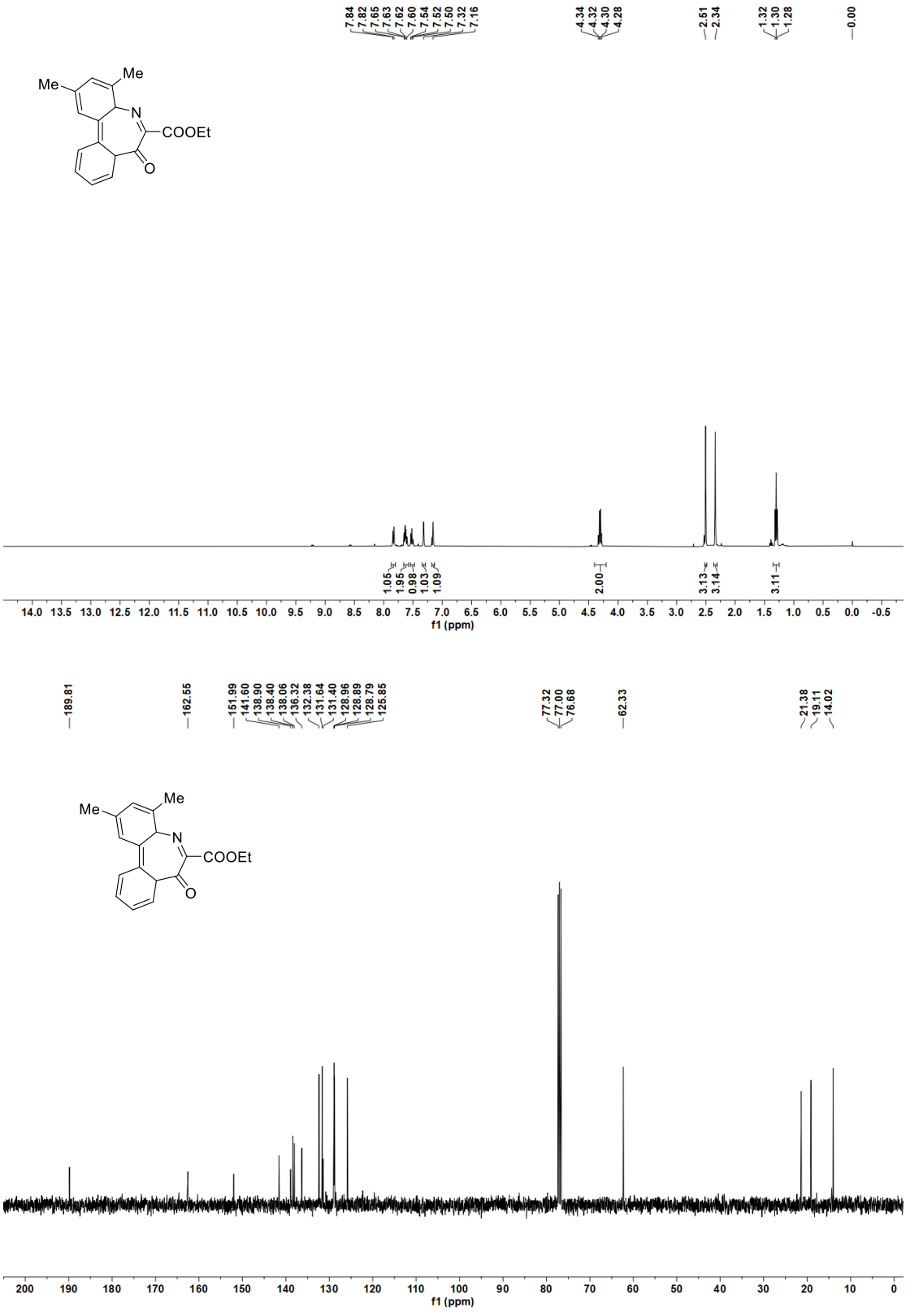


^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **41**

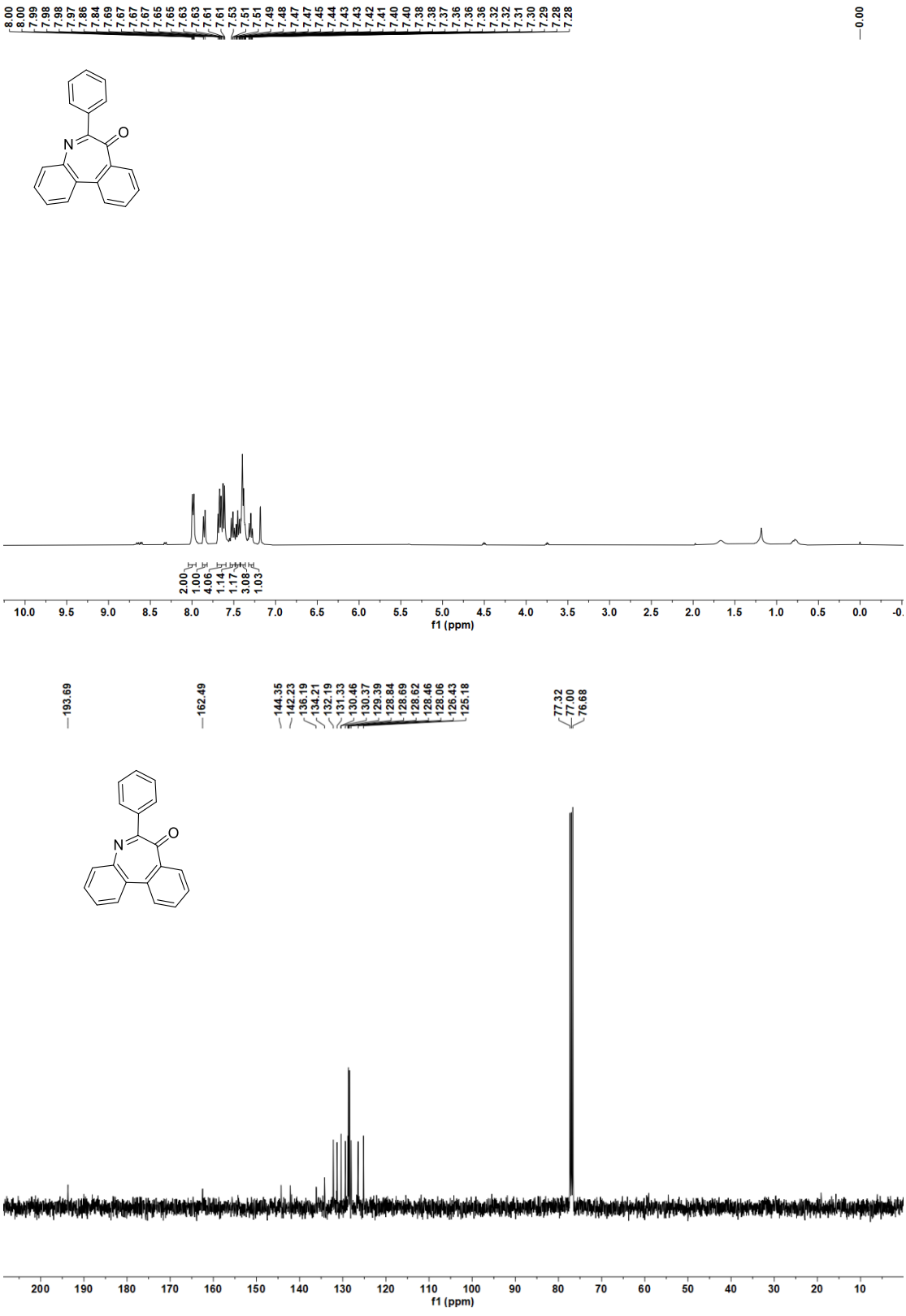




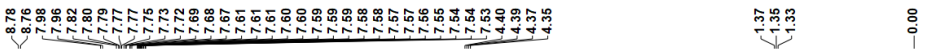
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **42**

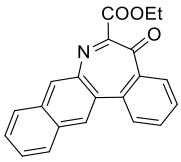


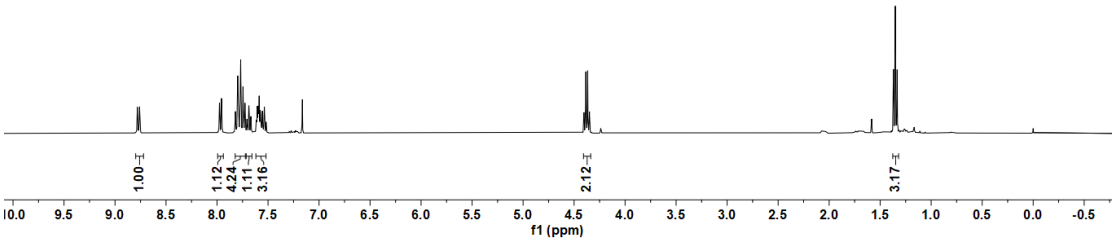
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **43**

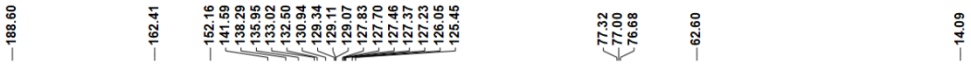


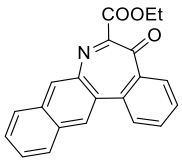
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **44**

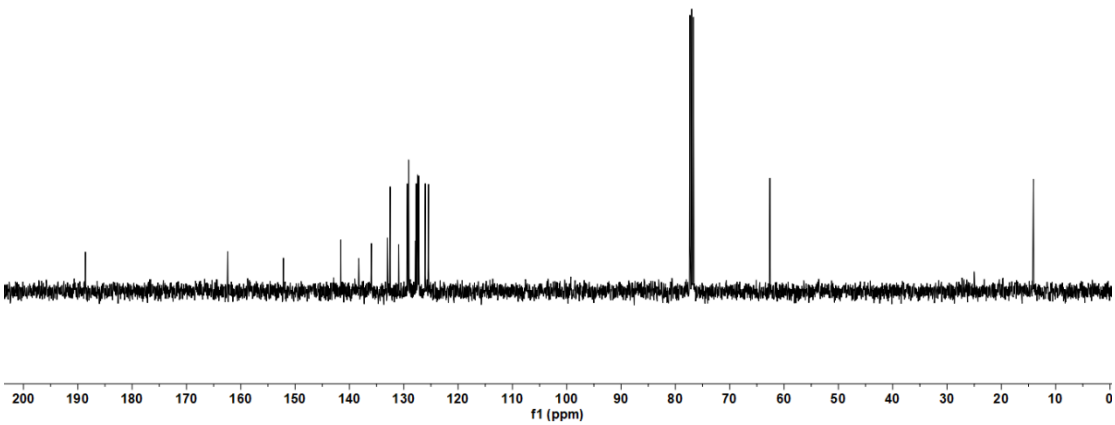




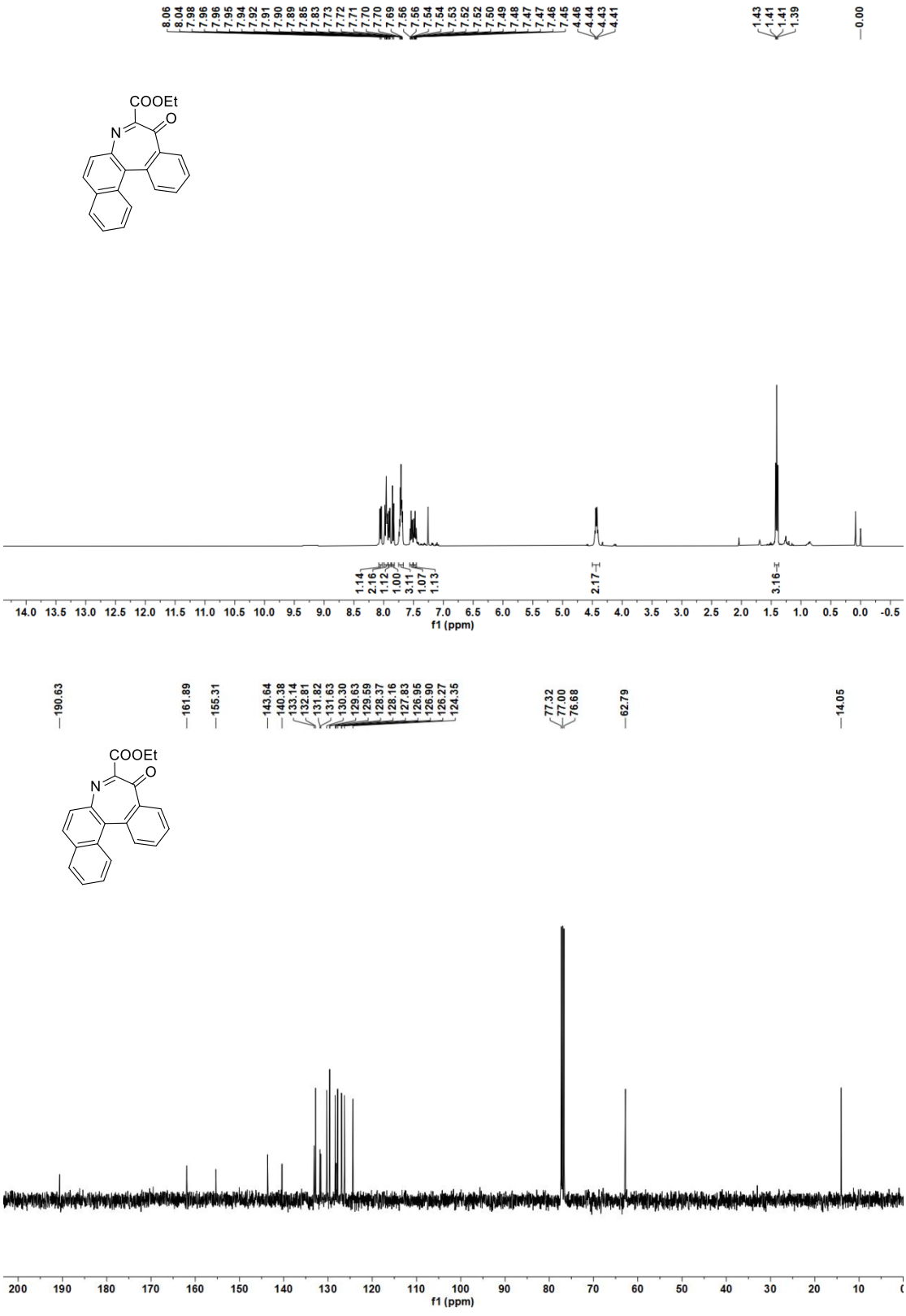




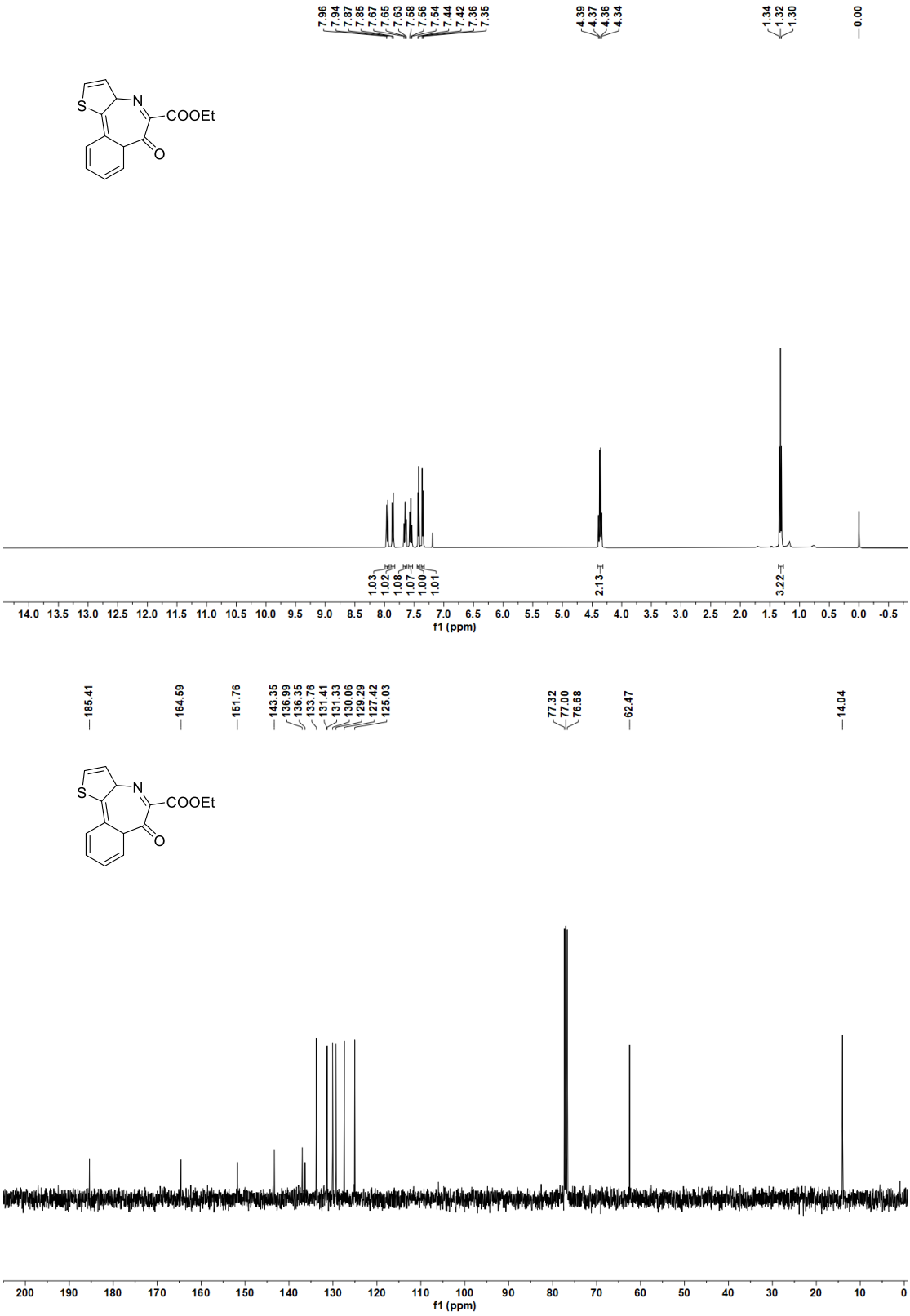




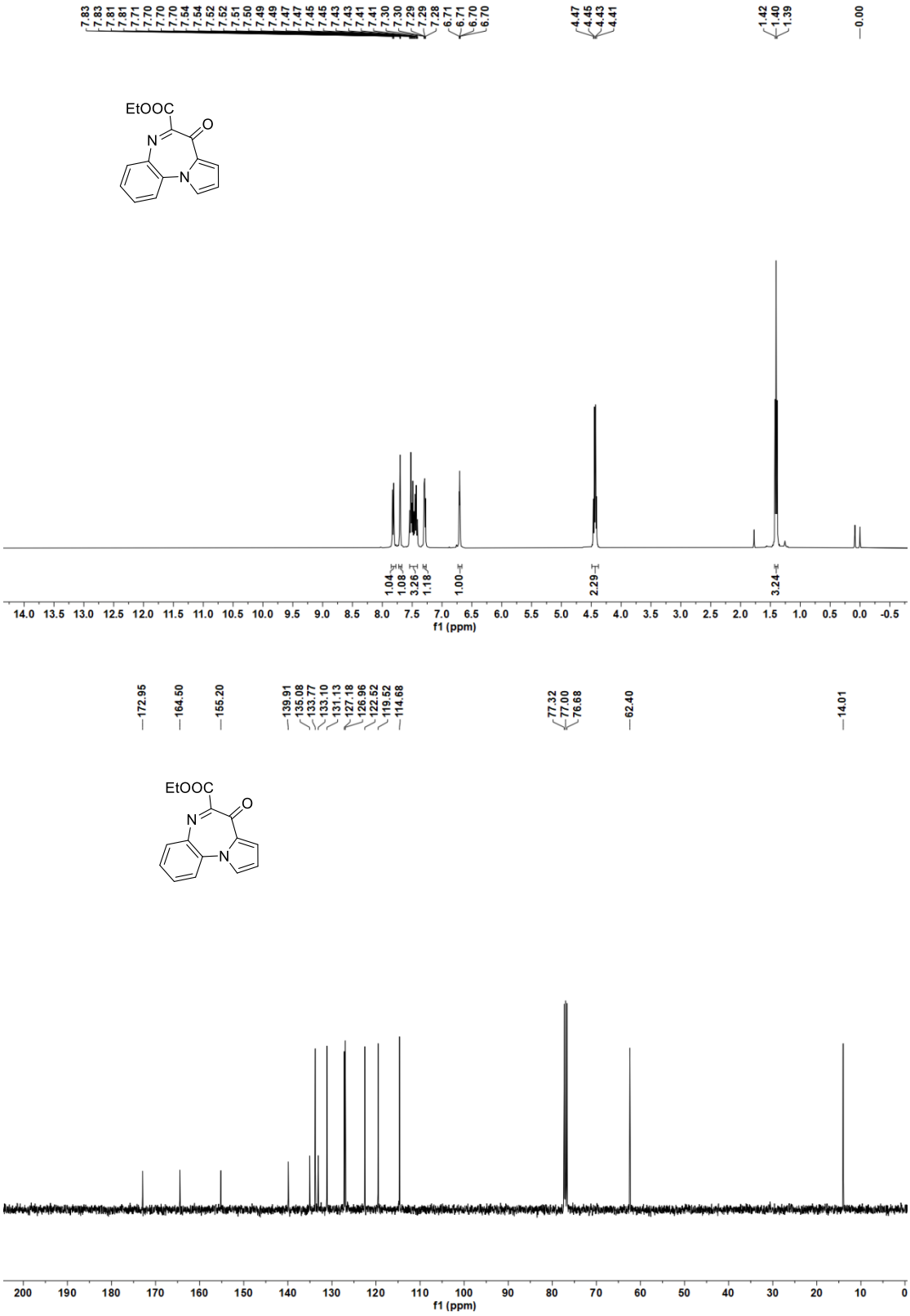
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **45**



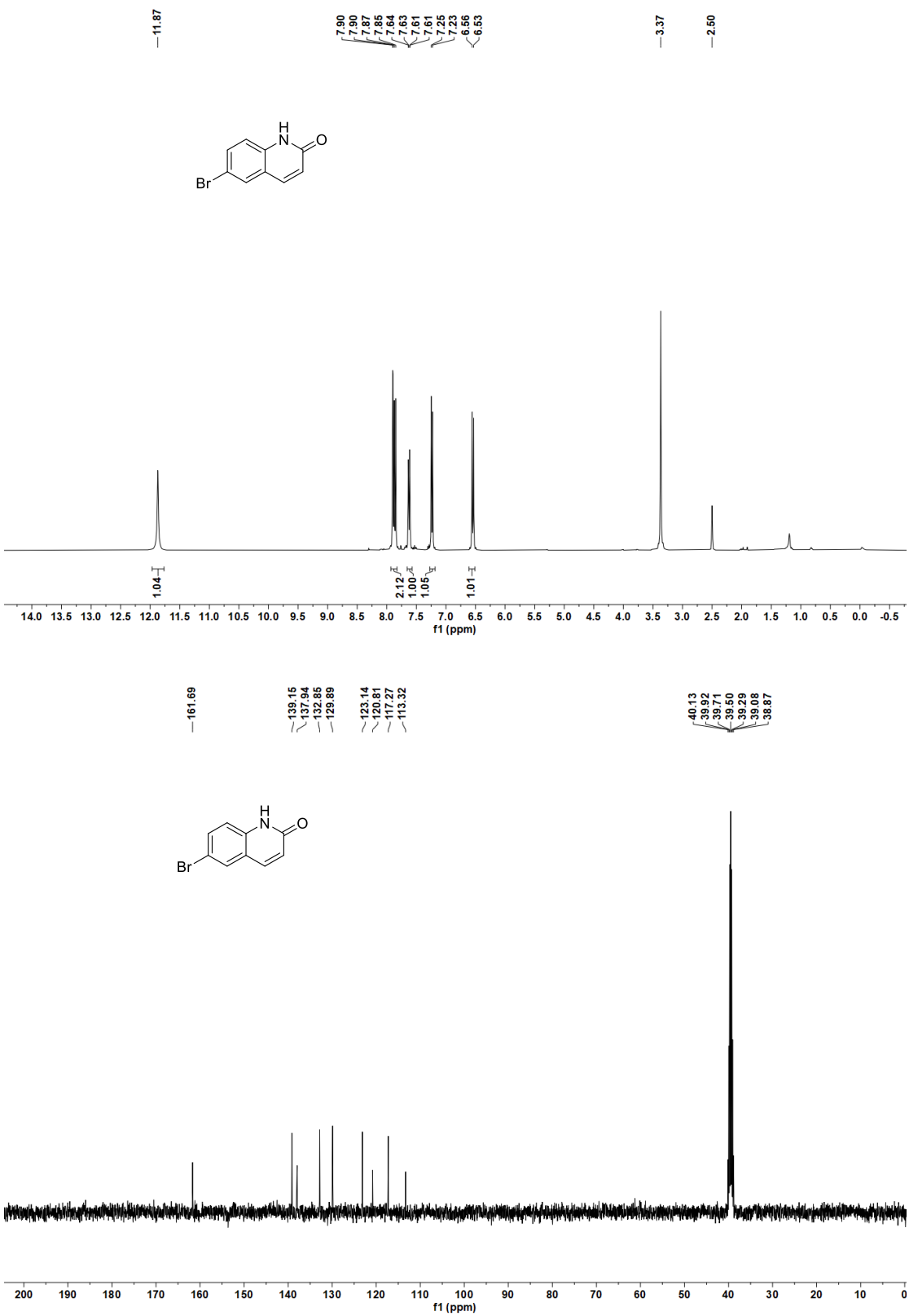
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **46**



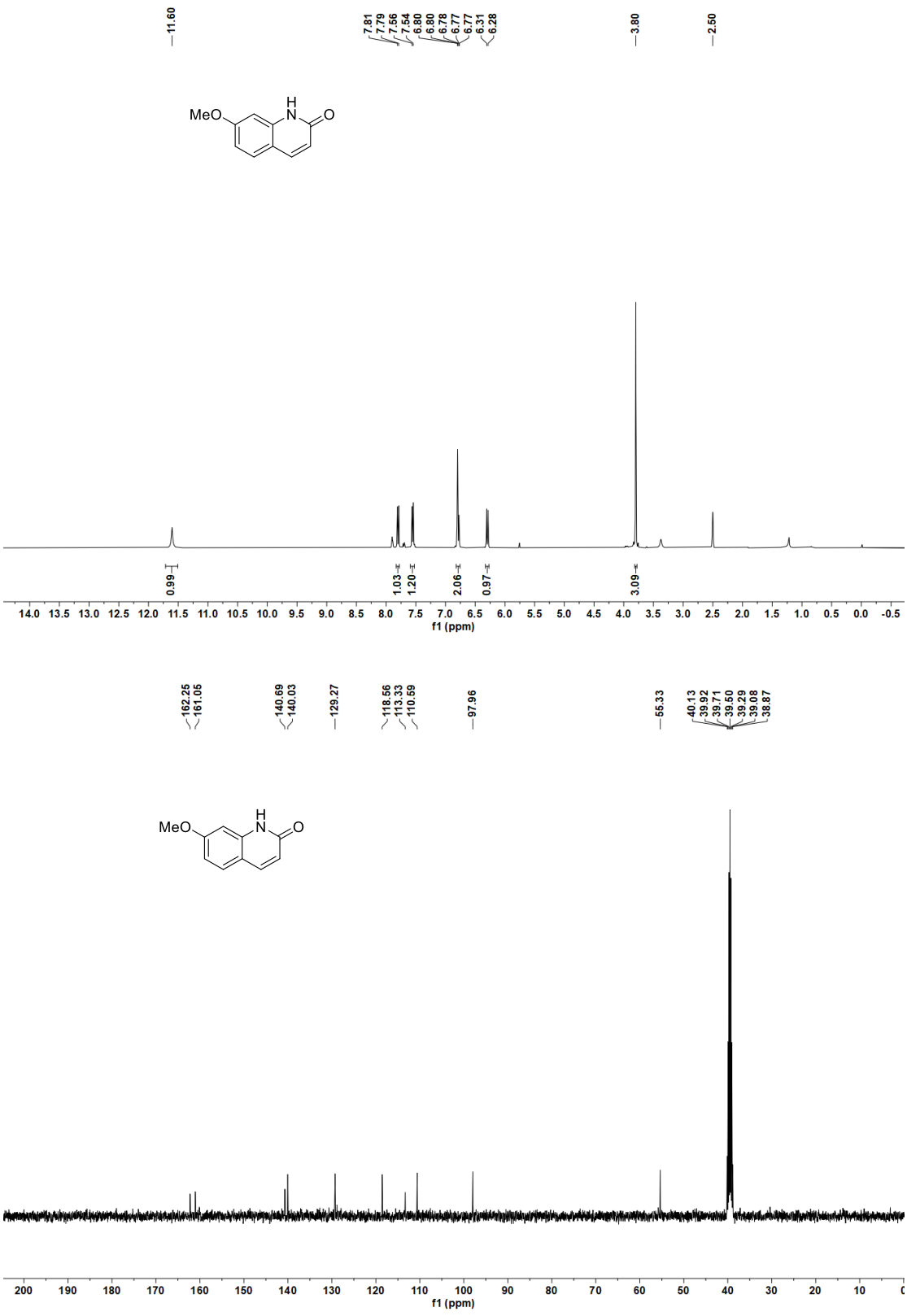
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **47**



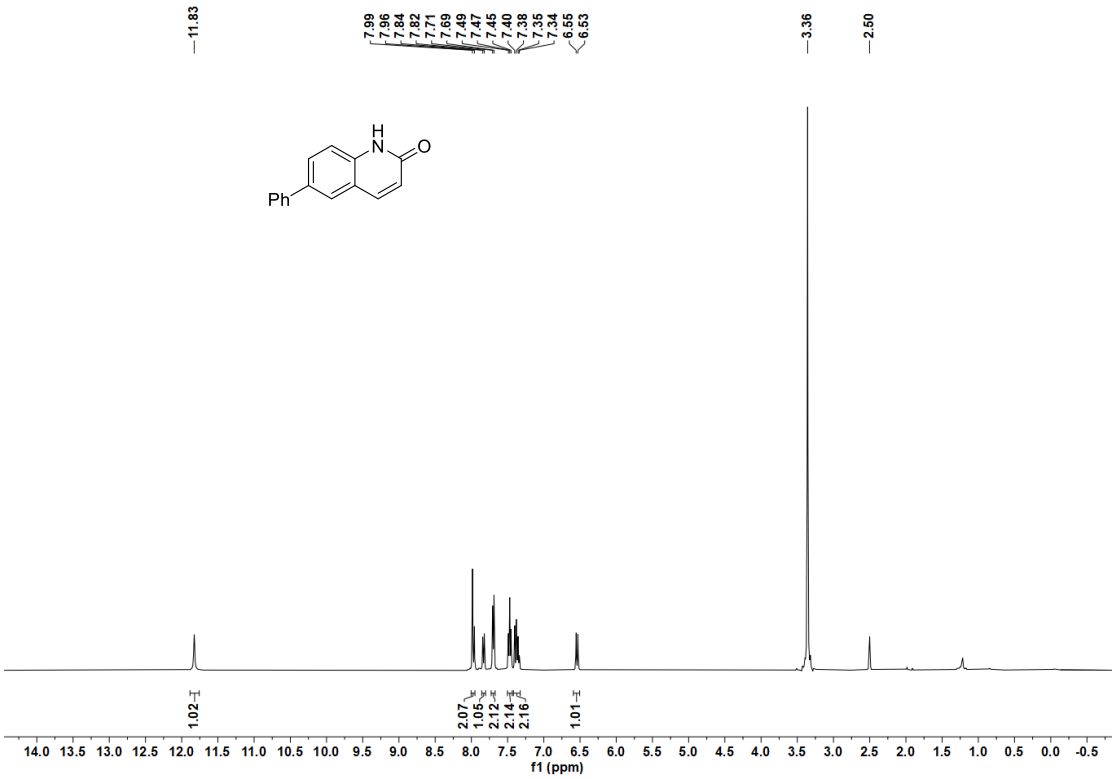
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **48**

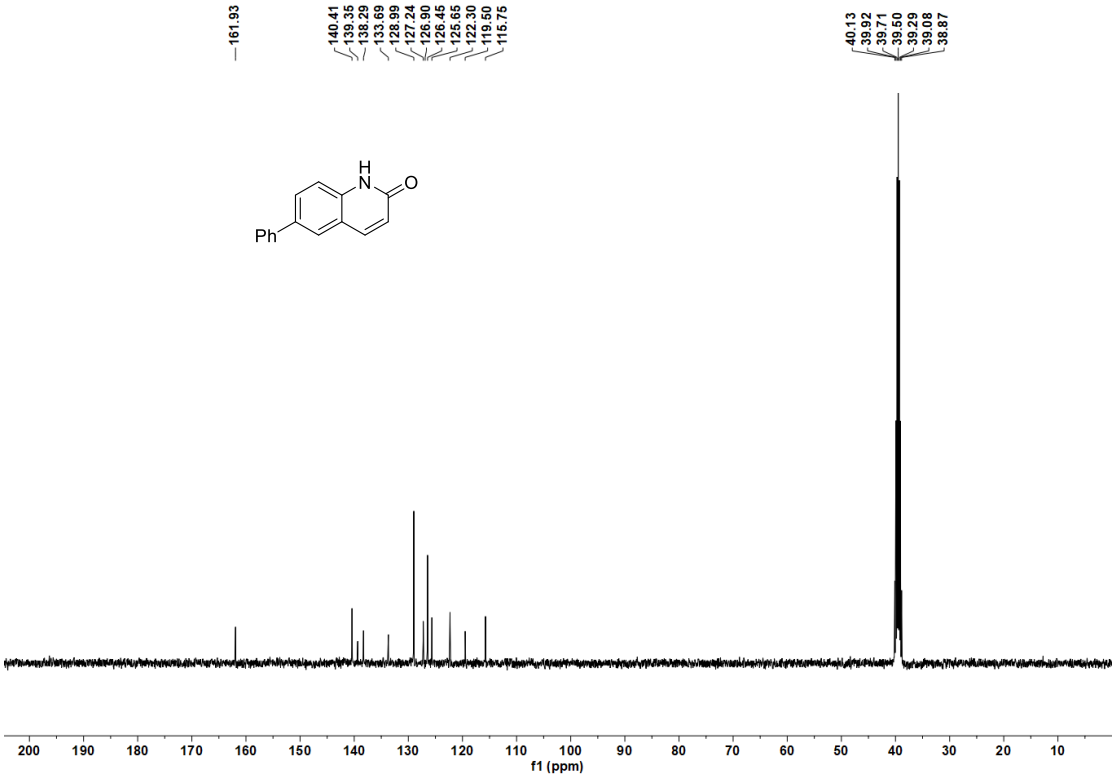


^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **49**

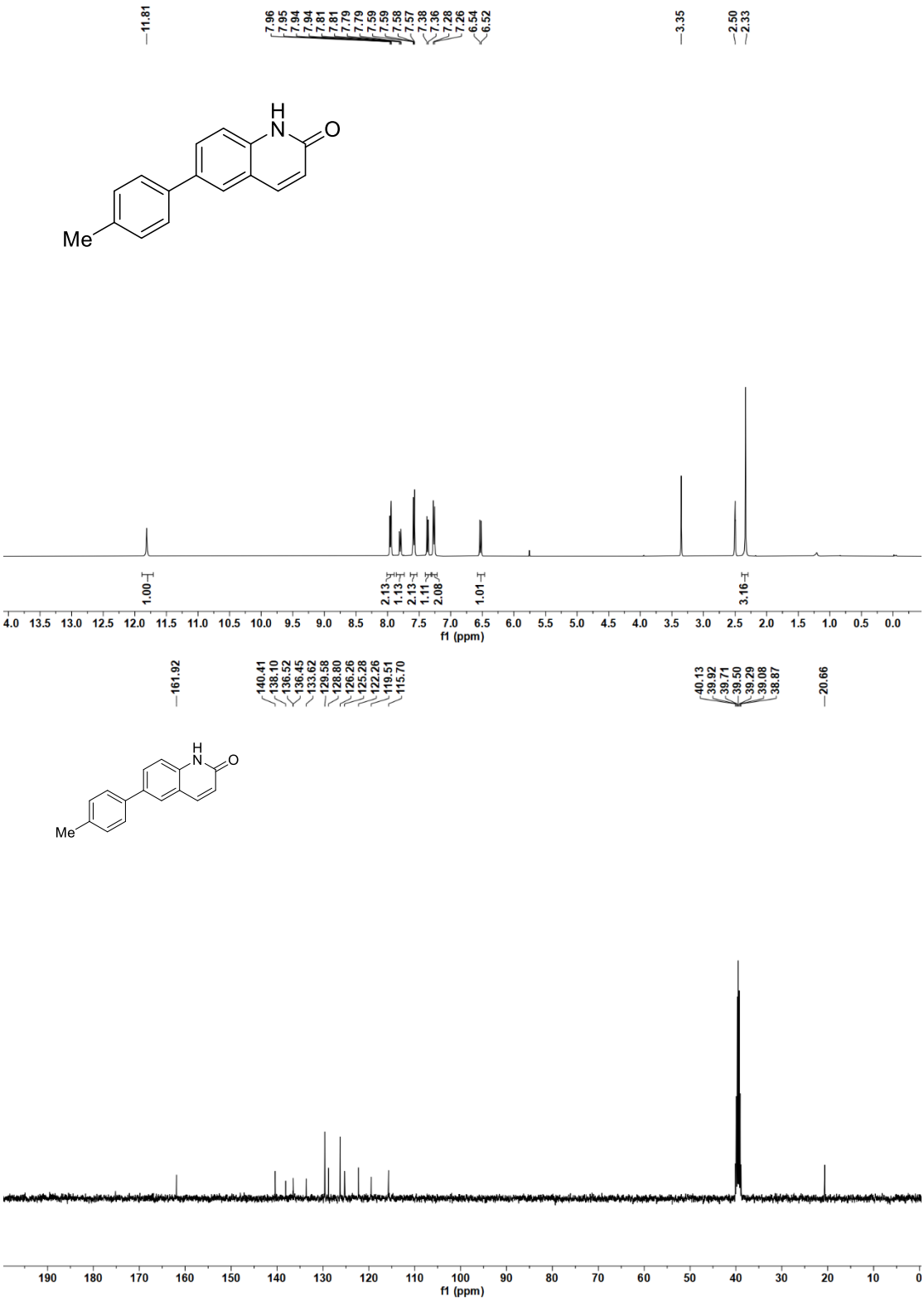


^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **50**

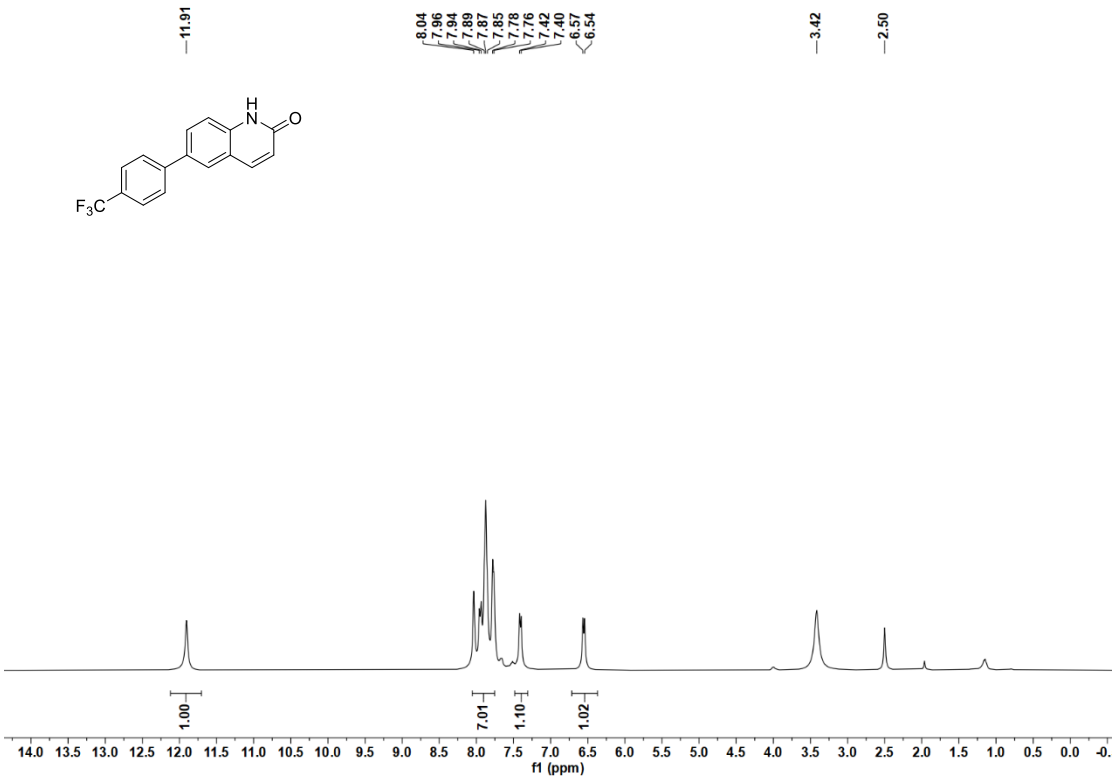


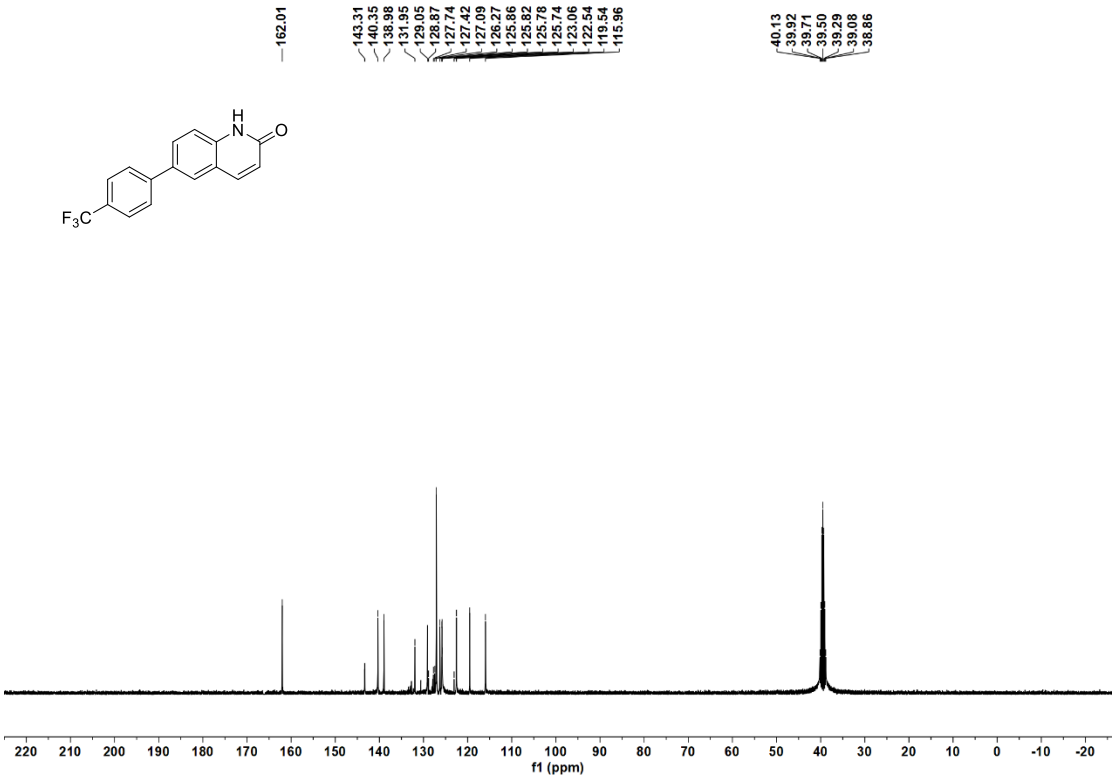


^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **51**



^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **52**


11.91
8.04
7.96
7.94
7.89
7.87
7.85
7.78
7.76
7.42
7.40
6.57
6.54
3.42
2.50
H
N
O
F3C
1.00
7.01
1.10
1.02
f1 (ppm)


162.01
143.31
140.35
138.98
131.95
129.05
128.87
127.74
127.42
127.09
126.27
125.86
125.82
125.78
125.74
123.06
122.54
119.54
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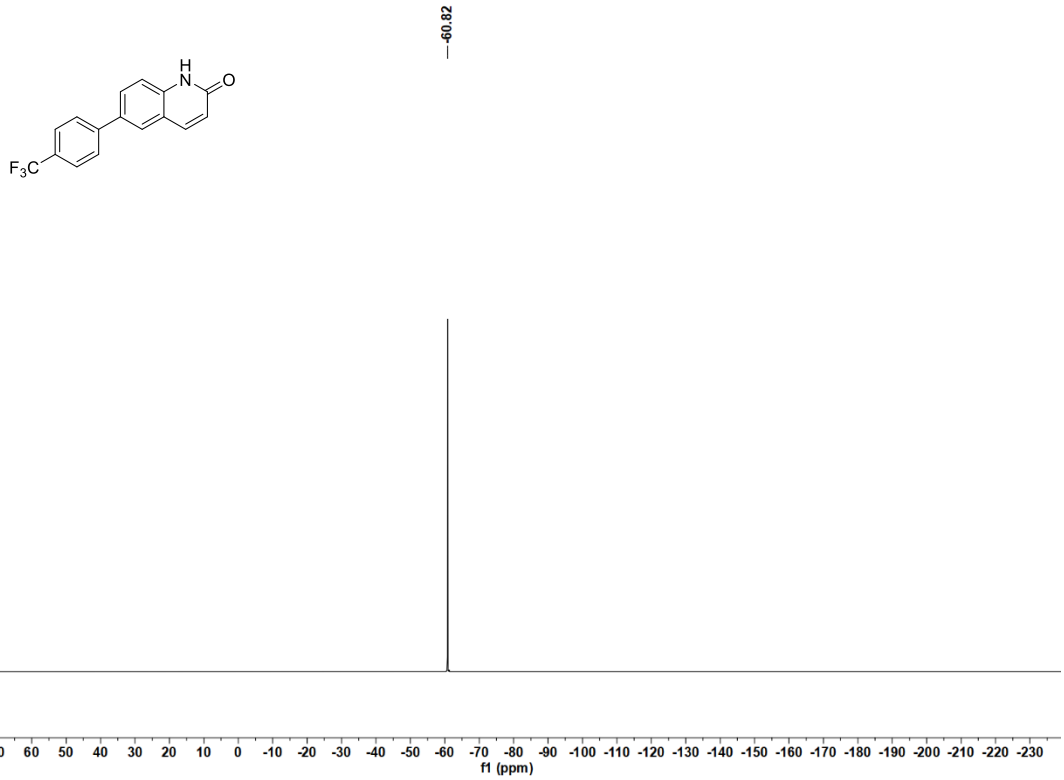
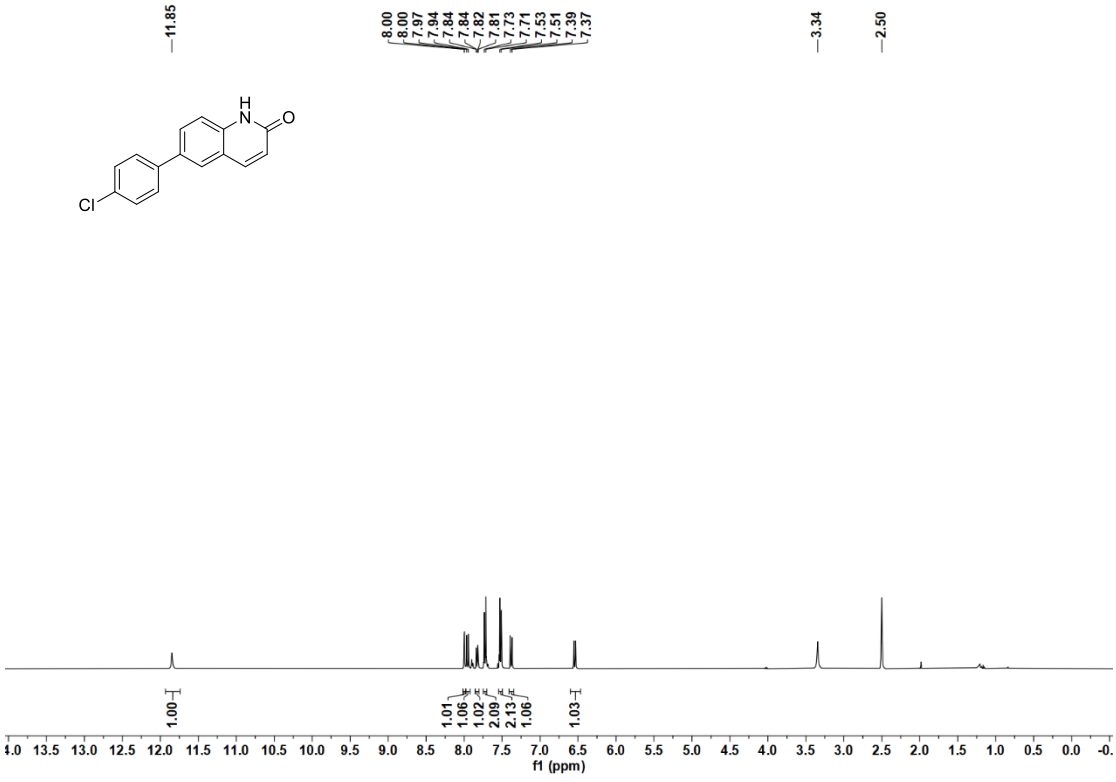
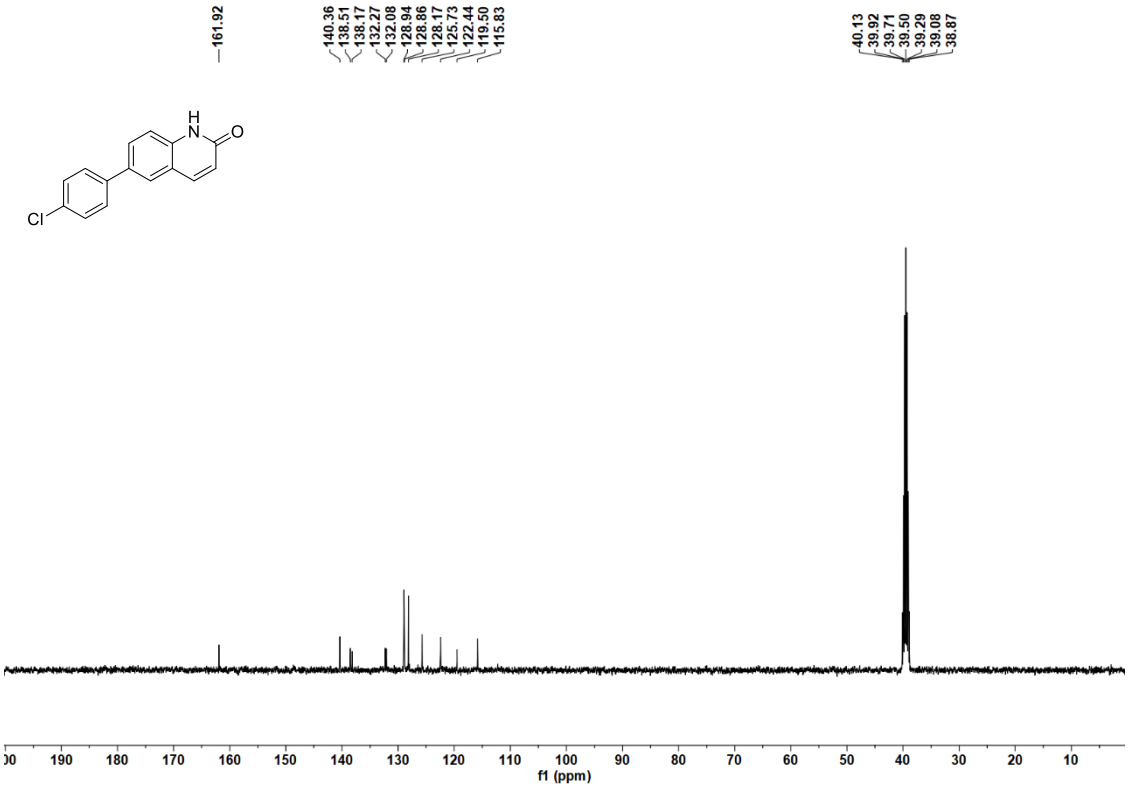
39.50
39.29
39.08
38.86
H
N
O
F3C
f1 (ppm)

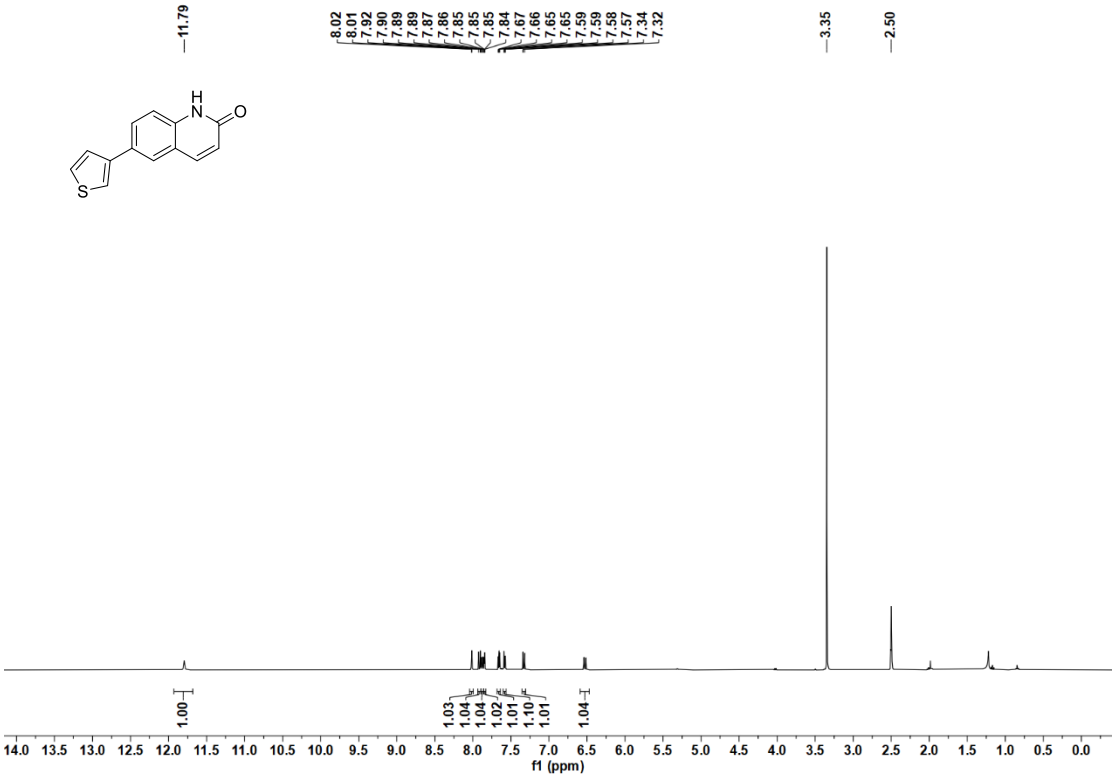


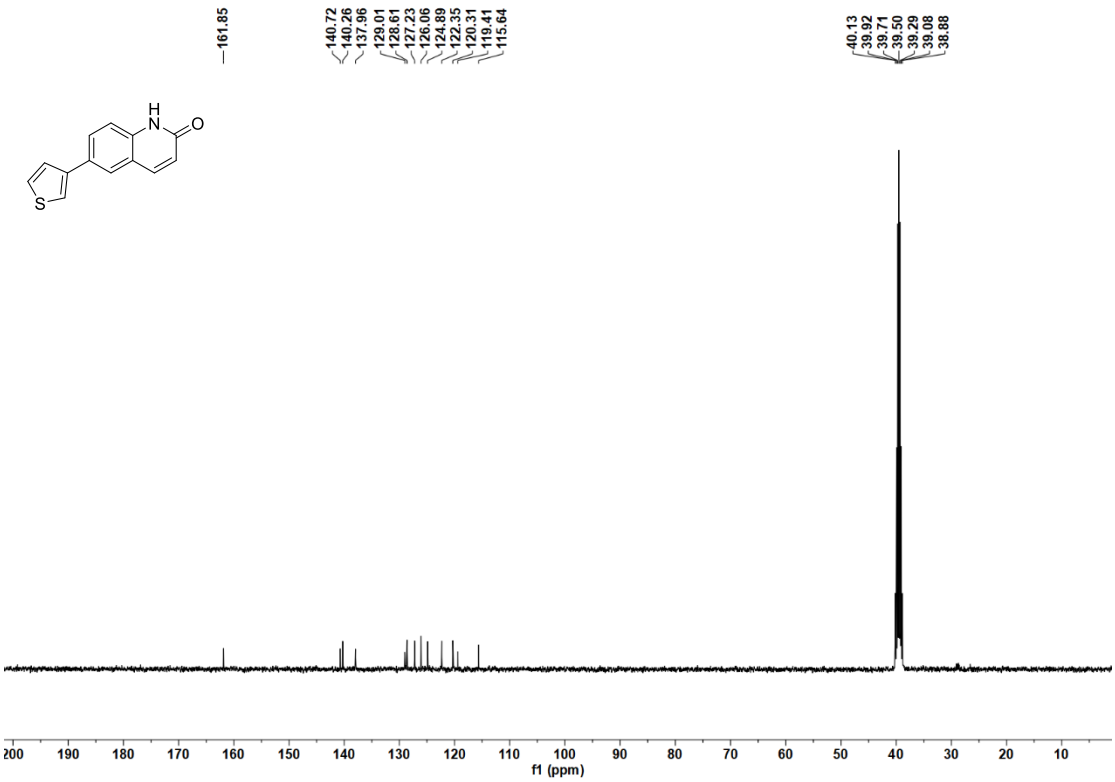
^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$), **^{19}F-NMR** (376 MHz, $CDCl_3$) of **53**



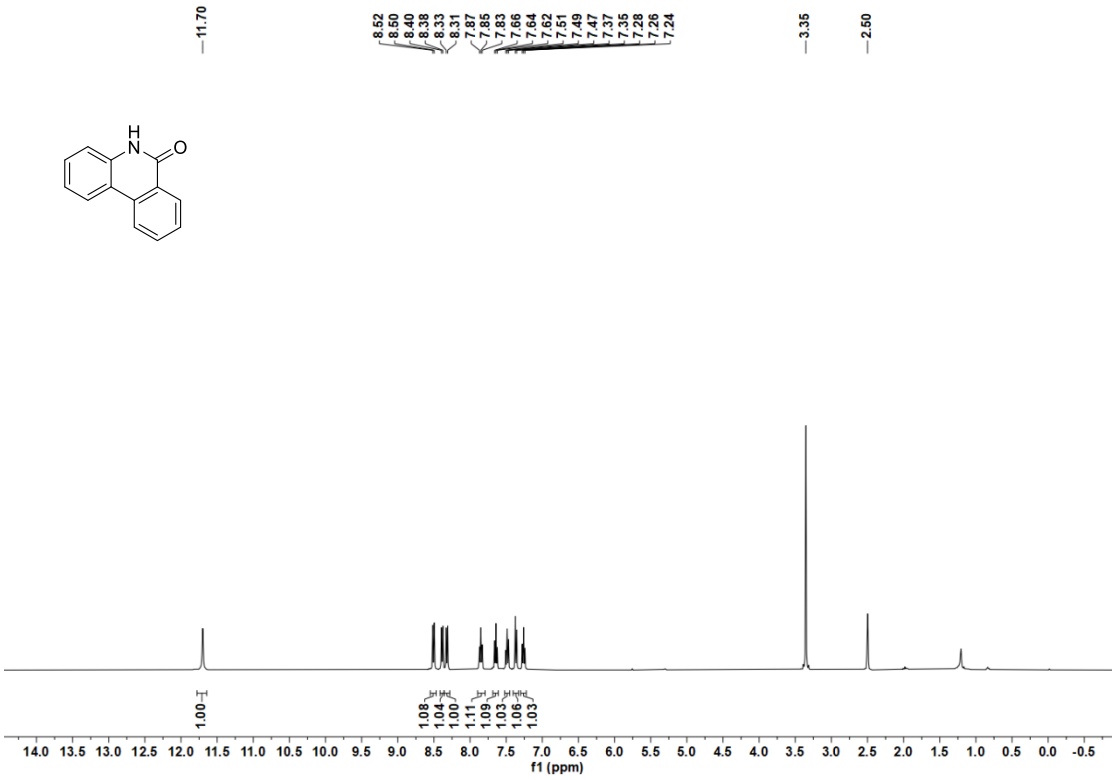


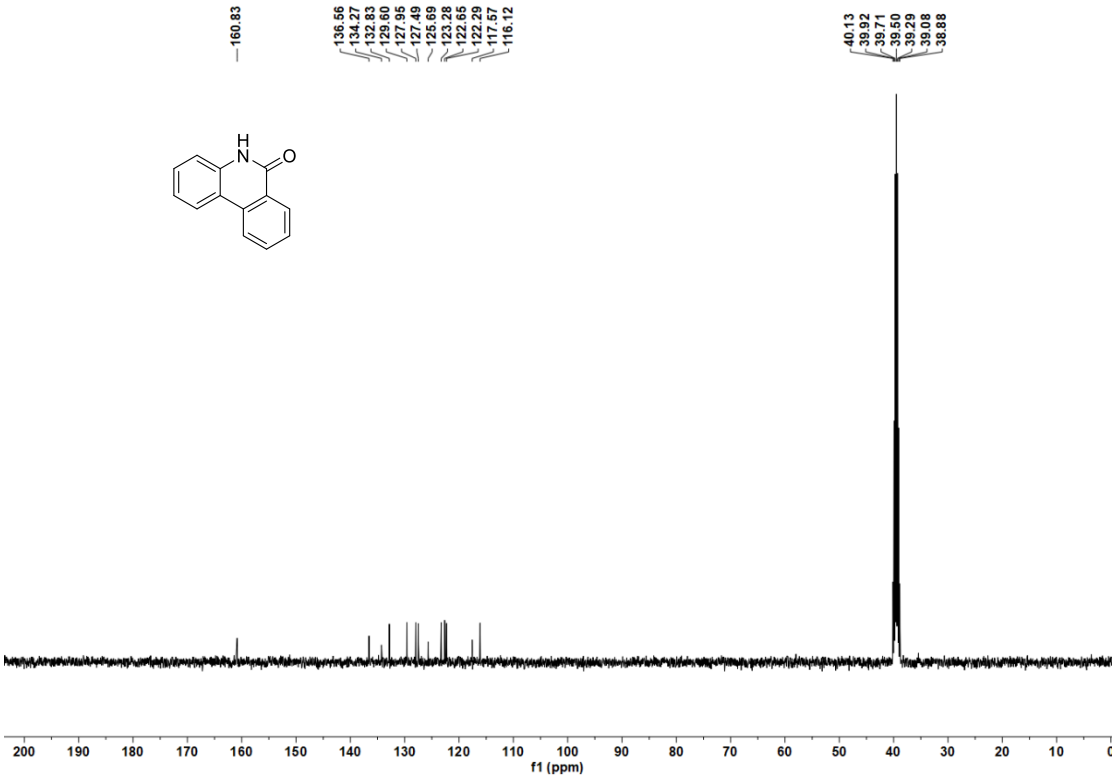
^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **54**



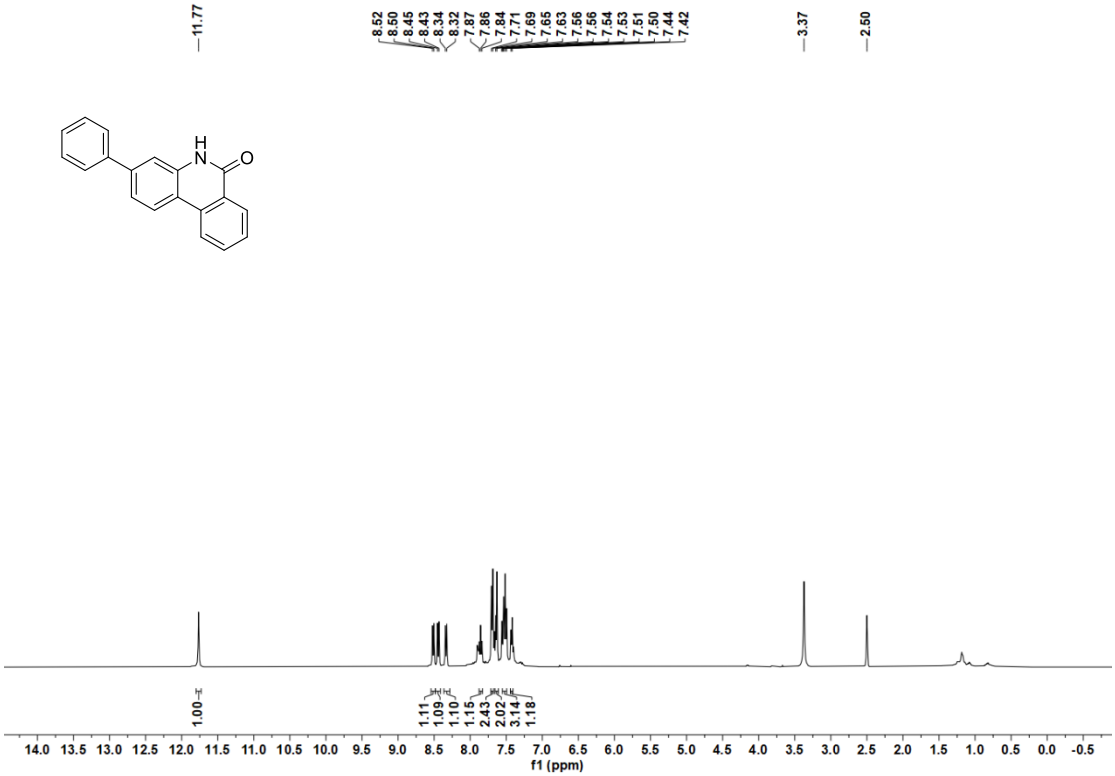


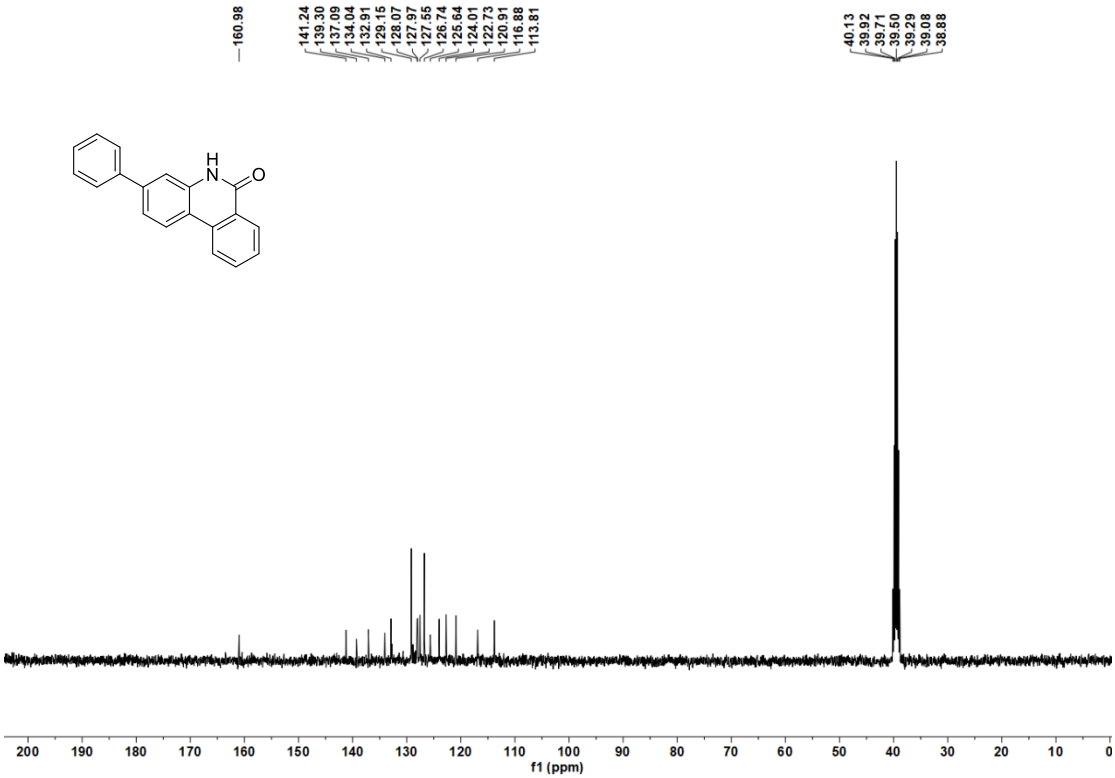
^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **55**



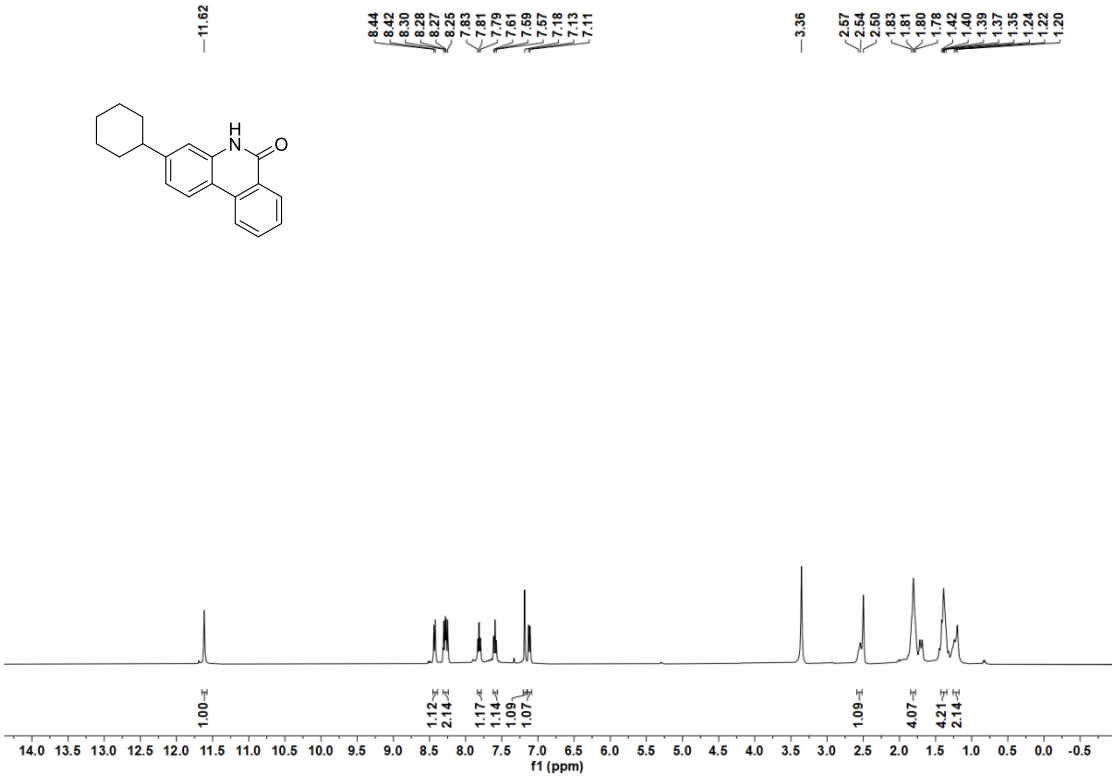


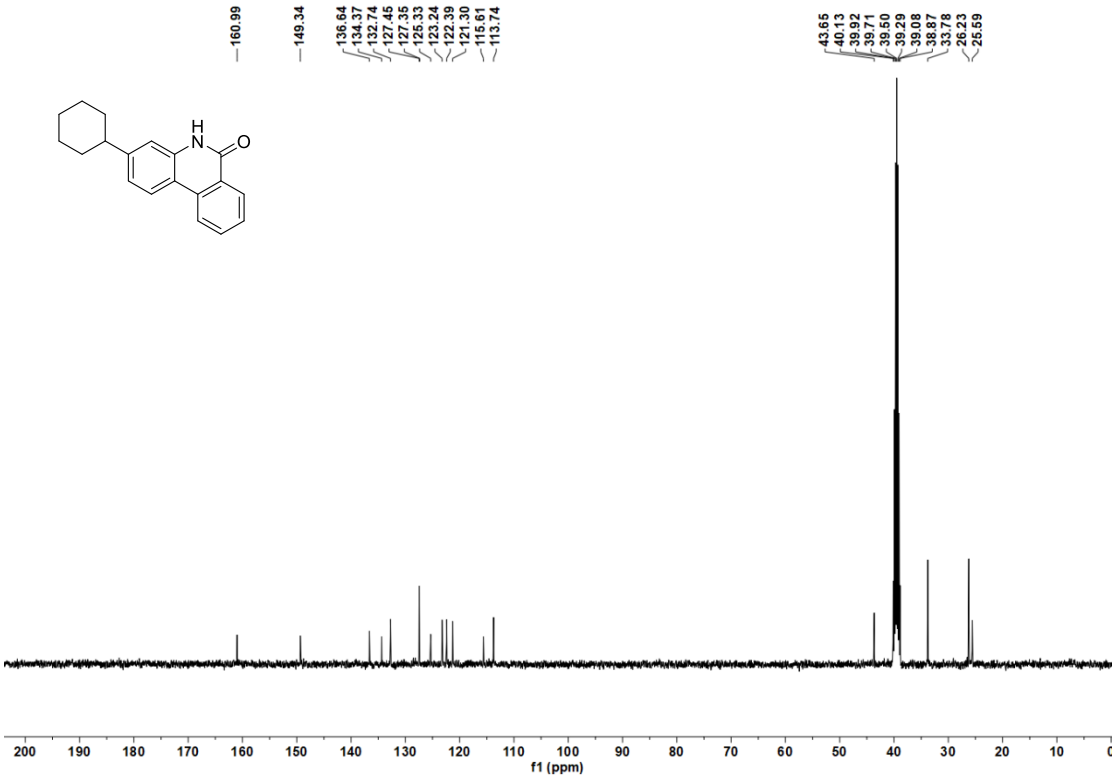
^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **56**



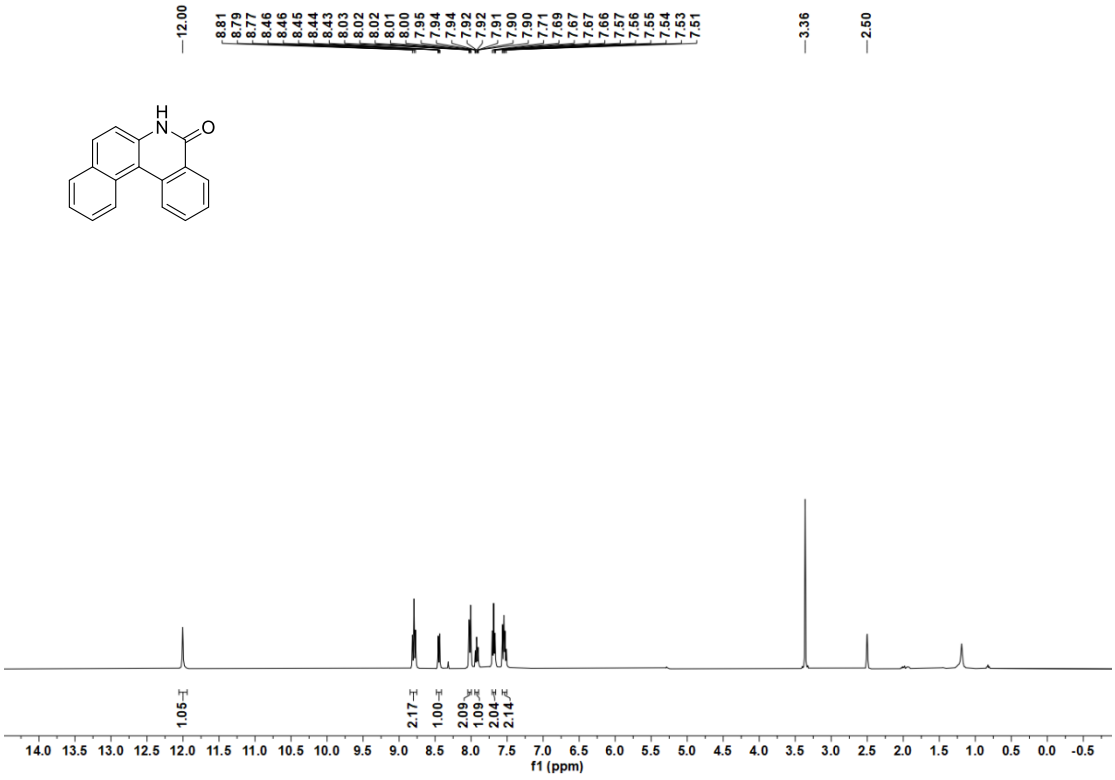


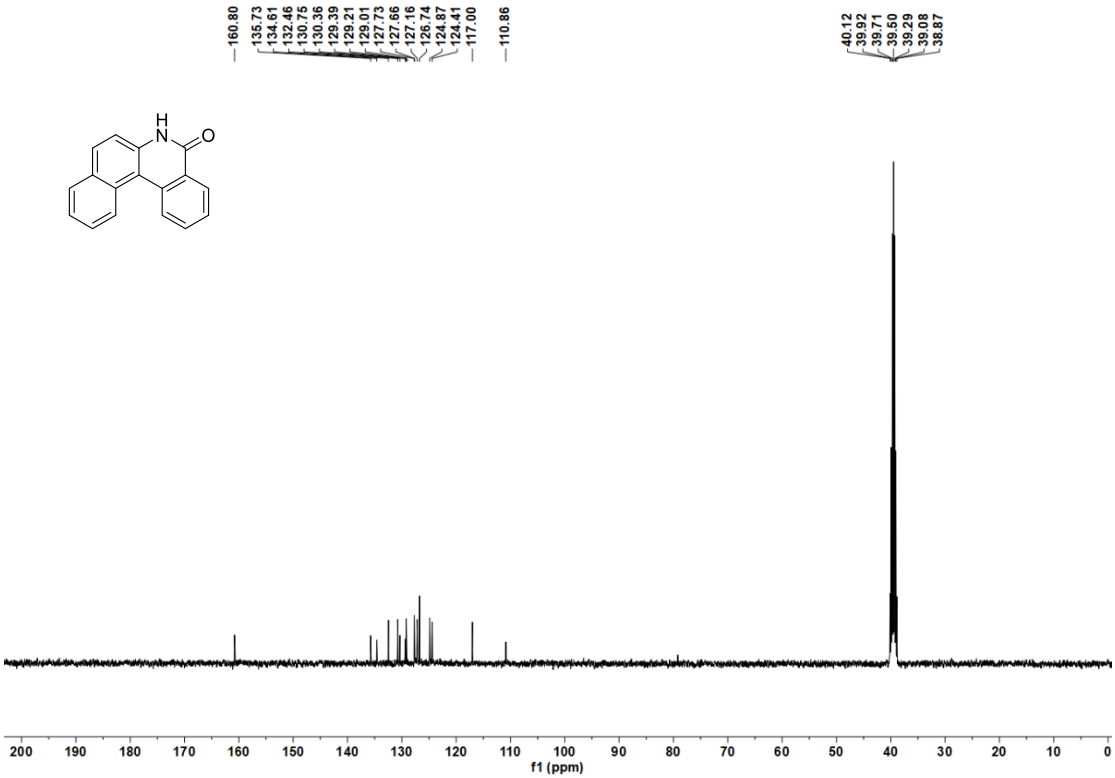
^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **57**



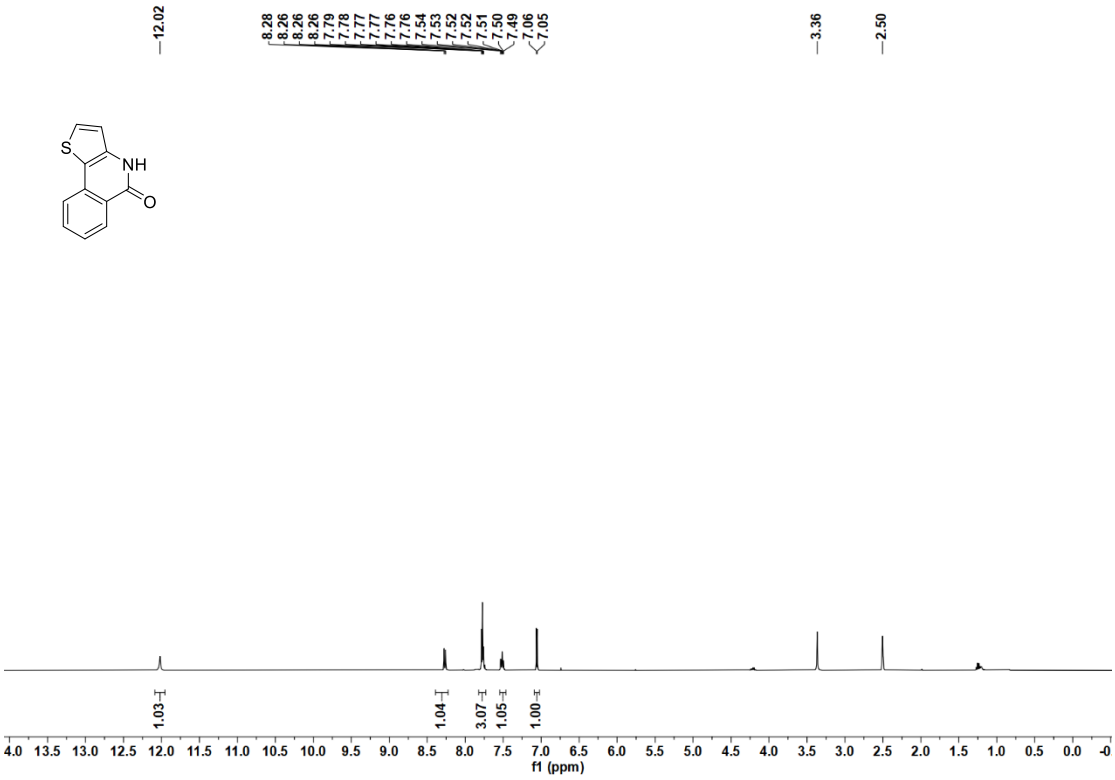


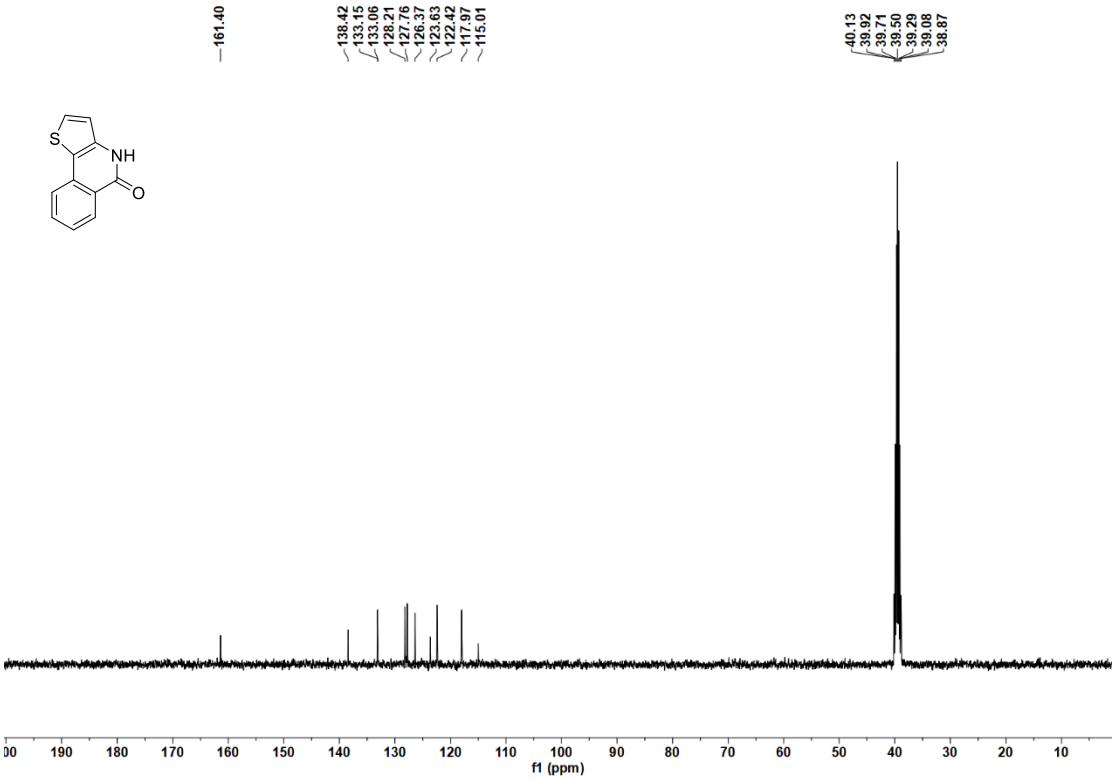
^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **58**



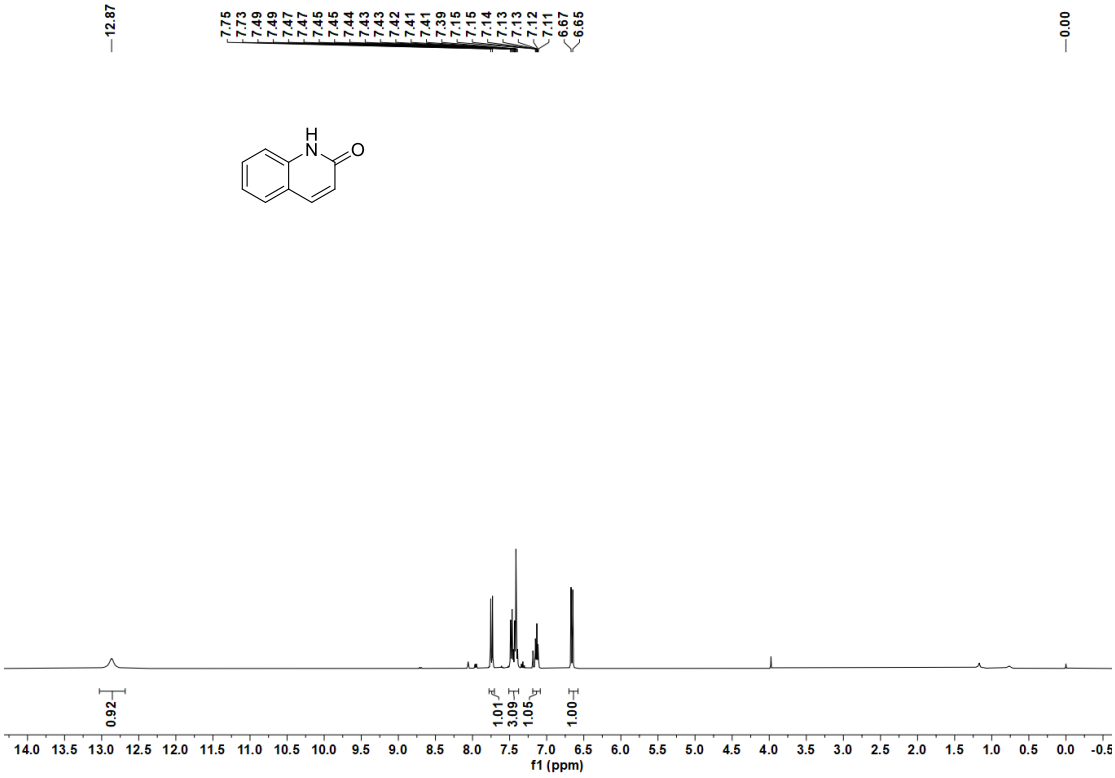


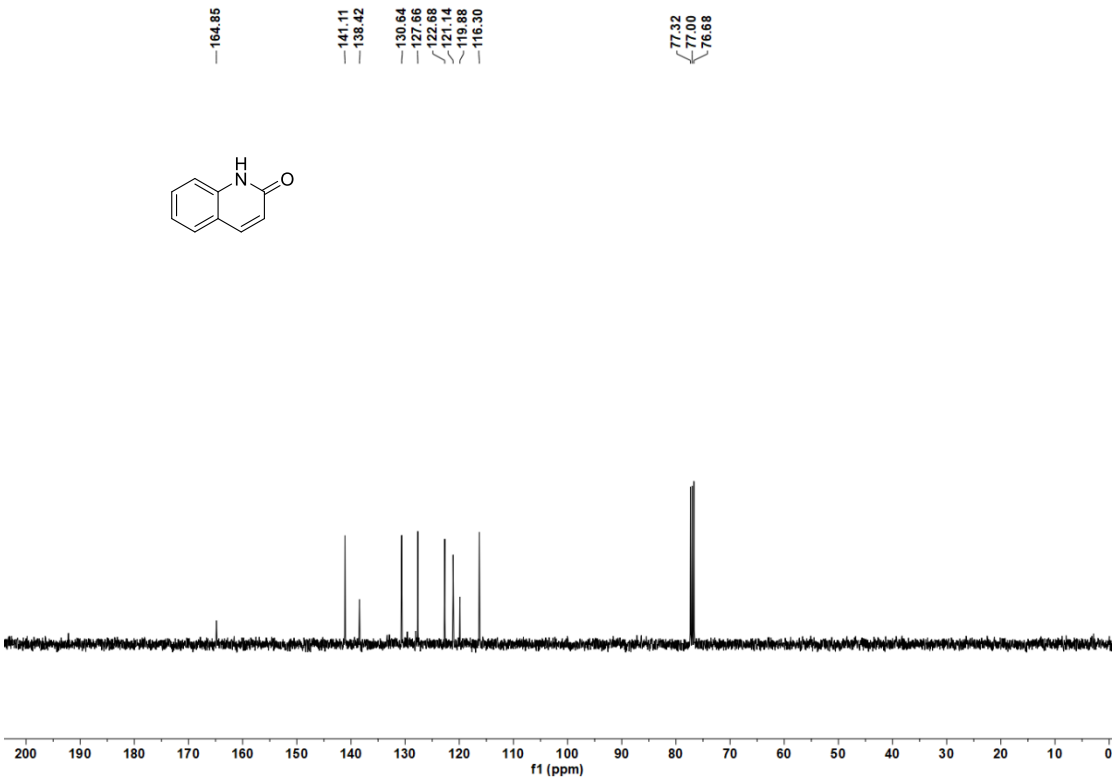
^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **59**





^{1}H-NMR (400 MHz, DMSO-d_6), **^{13}C NMR** (101 MHz, DMSO-d_6) of **60**





^{1}H-NMR (400 MHz, $CDCl_3$), **^{13}C NMR** (101 MHz, $CDCl_3$) of **61**