Supporting Information

Ligand-Controlled Iron-Catalyzed Coupling of α-Substituted-β-Ketoesters with Phenols.

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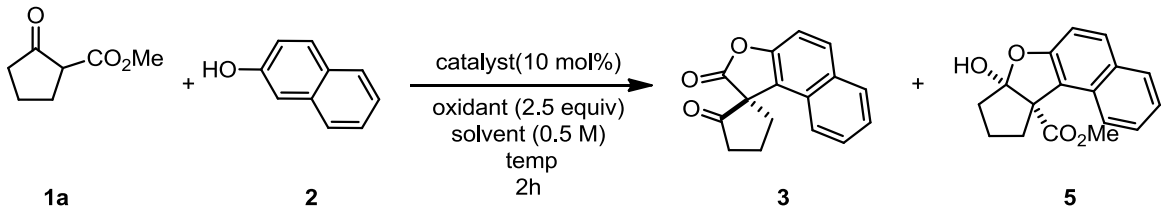
Table of Contents

General procedures. All reagents were of reagent grade quality, purchased commercially from Sigma-Aldrich, Alfa-Aesar, or Fluka, and used without further purification. Purification by column chromatography was performed on Merck chromatographic silica gel (40-60 μm). TLC analyses were performed using Merck silica gel glass plates 60 F_{254}. NMR spectra were recorded on Bruker DPX400, or DMX500 instruments; chemical shifts, given in ppm, are relative to Me_4Si as the internal standard or to the residual solvent peak. HR-MS data were obtained using a Thermoscientific LTQU XL Orbitrap HRMS equipped with APCI (atmospheric-pressure chemical ionization). Gas chromatography data were obtained using an Agilent 7820A GC equipped with FID detector working under standard conditions and an Agilent HP-5 column. HPLC analysis was carried out on a Agilent 1260 instrument equipped with a G4212-60008 photodiode array detector and a Agilent reverse phase ZORBAX Eclipse plus C18 3.5 μm column (4.6 X 100 mm). IR spectra were recorded on a Nicolet 380 FTIR spectrometer.

Table 1S. Optimization study in the coupling of ethyl 2-oxocyclopentanecarboxylate (**1a**) with β-naphthol (**2**).[a]

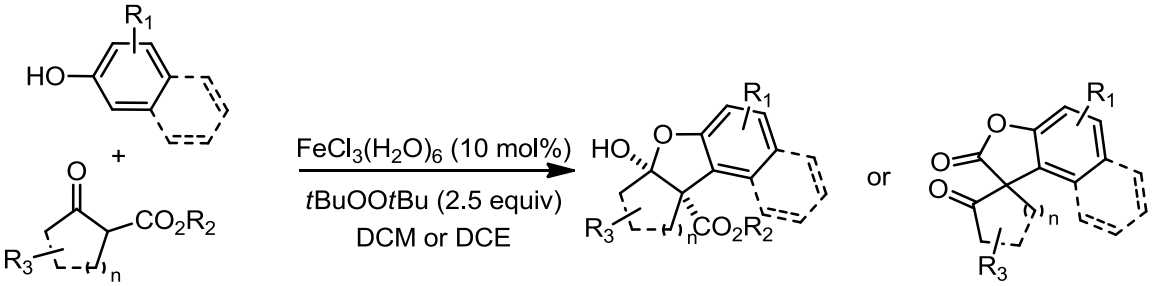


1a **2** **3** **5**

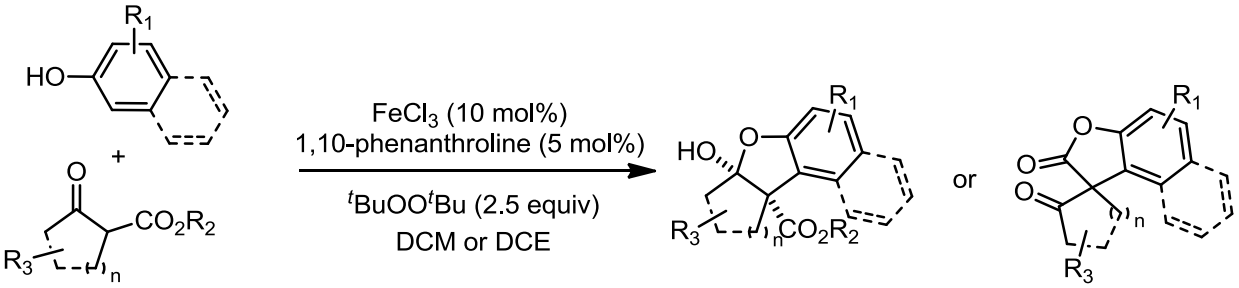
Entry	Catalyst	Oxidant	solvent	T[°C][b]	**3**, yield [%]	**5**, yield [%][c]
1	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	DCE	100	44	--
2	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	DCE	80	7	64
3	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	DCE	60	--	69
4	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	DCM[d]	60	--	90
5	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	DCM	60	--	97
6	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	toluene	60	--	26
7	$FeCl_3(H_2O)_6$	*t*BuOO*t*Bu	THF	60	--	NR[d]
8	$FeCl_3(H_2O)_6$[e]	*t*BuOO*t*Bu	DCM	60	--	71
9	$FeCl_3$	*t*BuOO*t*Bu	DCM	60	--	80
10	$FeBr_2$	*t*BuOO*t*Bu	DCM	60	--	43
11	$FeCl_2$	*t*BuOO*t*Bu	DCM	60	--	71
12	$CuCl_2$	*t*BuOO*t*Bu	DCM	60	--	7
13	Fe(acac)	*t*BuOO*t*Bu	DCM	60	--	5
14	Fe sulfate	*t*BuOO*t*Bu	DCM	60	--	10
15	$FeCl_3(H_2O)_6$	tBuOOH	DCM	60	--	48
16	$FeCl_3(H_2O)_6$	lauroyl peroxide	DCM	60	--	18
17	$FeCl_3(H_2O)_6$	DDQ	DCM	60	--	13
18[f]	$FeCl_3$	*t*BuOO*t*Bu	Neat	60	--	47

[a]Reaction conditions: To a stirred solution of **1a** (1 mmol), **2** (1.2 mmol) and catalyst (10 mol%) in solvent (0.5M) under nitrogen atmosphere was added drop-wise oxidant (2.5 mmol) and the mixture was heated for 2 h. After cooling sat. sol. of $NaHCO_3$ (10 ml) was added and extracted with diethyl ether (3 X 10 ml), the combined organic phase was washed with brine (30 ml), dried over Na_2SO_4, filtered and concentrated under reduce pressure. [b]Oil Bath temperature. [c]HPLC yield using mesitylene as internal standard. [d]DCM (0.1M). [d]NR= no reaction. [e]$FeCl_3(H_2O)_6$ (5 mol%). [f]Solvent free conditions.

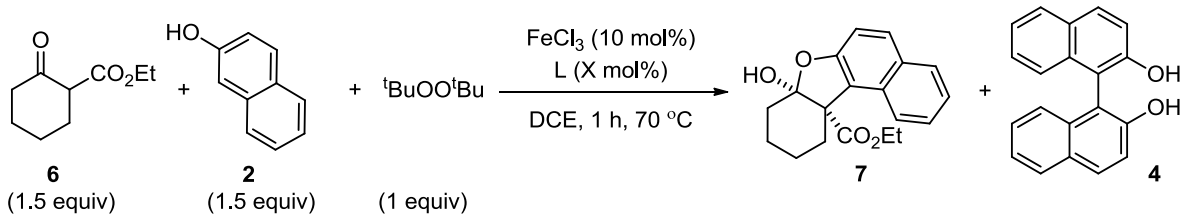
General Methods



Method A: Di-*tert*-butyl peroxide (2.5 equiv) was added drop-wise into a stirred solution of α-substituted-β-ketoester (1.0 equiv), phenol derivative (1.5 equiv) and $FeCl_3(H_2O)_6$ (0.1 equiv) in DCM or DCE (0.5M) under nitrogen atmosphere at room temperature. The reaction mixture was heated for 1-12 hours, cooled to room temperature, quenched with saturated $NaHCO_3$ (10 mL) and extracted with diethyl ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



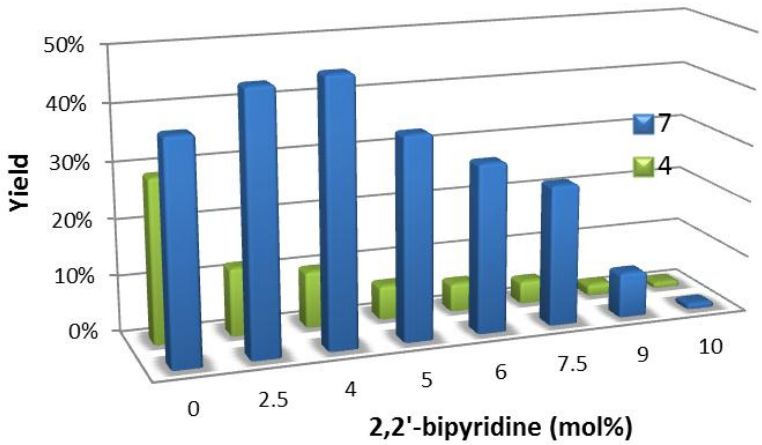
Method B**:** Di-*tert*-butyl peroxide (2.5 equiv) was added drop-wise into a stirred solution of α-substituted-β-ketoester (1.0 equiv), phenol derivative (1.5 equiv), 1,10-phenanthroline (0.05 equiv) and $FeCl_3$ (0.1 equiv) in dichloroethane (0.5M) under nitrogen atmosphere at room temperature. The reaction mixture was heated for 1-12 hours, cooled to room temperature, quenched with saturated $NaHCO_3$ (10 mL) and extracted with ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.



Procedure for comparative experiments for ligand effect of phenanthroline: Di-*tert*-butyl peroxide (1.0 equiv) was added drop-wise into a stirred solution of ethyl 2-oxocyclohexanecarboxylate (**6**) (1.5 equiv) and **2** (1.5 equiv), 1,10-phenanthroline (X mol%) and $FeCl_3$ (0.1 equiv, 10%) in dichloroethane (0.5M) under nitrogen atmosphere at room temperature. The reaction mixture was heated to 70 °C for 1 hr, cooled to room temperature, quenched with saturated $NaHCO_3$ (10 mL) and extracted with ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the yields of compound **7** and **4** were determined by HPLC using mesitylene as internal standard.

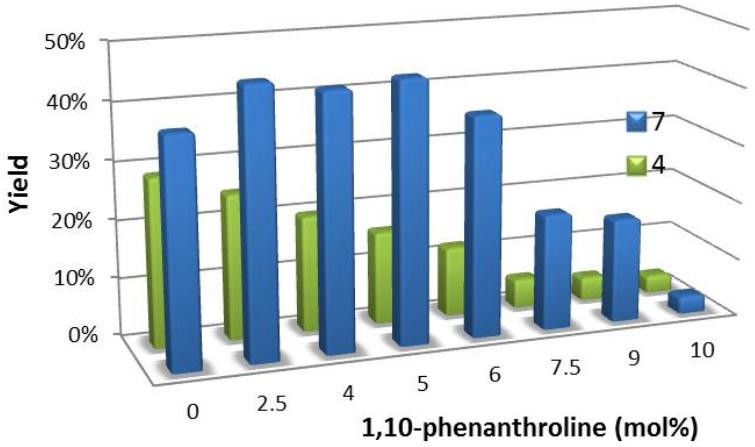
Formation of **7** and **4** as a function of 2,2'-bipyridine concentration:

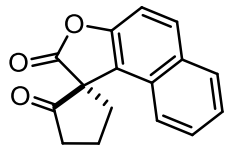
Entry	2,2'-Bipyridine (mol%)	Yield (%) 4	7
1	0	29	39
2	2.5	12	46
3	4	10	47
4	5	6	36
5	6	5	30
6	7.5	4	25
7	9	2	8
8	10	1	0



Formation of **7** and **4** as a function of 1,10-phenanthroline concentration:

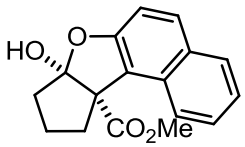
Entry	1,10-phenanthroline (mol%)	Yield (%) 4	7
1	0	29	39
2	2.5	25	46
3	4	20	44
4	5	16	45
5	6	12	38
6	7.5	5	20
7	9	4	18
8	10	3	3





3

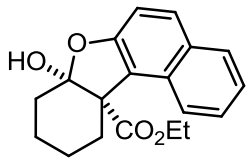
Compound 3: Di-*tert*-butyl peroxide (292 mg, 2 mmol) was added drop-wise into a stirred solution of **1a** (142 mg, 1 mmol), 2-naphthol (432 mg, 3 mmol) and $FeCl_3(H_2O)_6$ (27 mg, 0.1 mmol) in dichloroethane (5 mL) under nitrogen atmosphere at room temperature. The reaction mixture was heated to 100 °C for 1 h, cooled to room temperature, quenched with saturated $NaHCO_3$ (10 mL) and extracted with ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 9:1) affording compound **3** (118 mg, 47%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.91 (t, J = 8.9 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 11.3 Hz, 1H), 7.38 (d, J = 11.3 Hz, 1H), 2.65–2.95 (m, 5H), 2.39–2.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 210.2, 174.6, 152.3, 131.4, 131.1, 130.0, 128.3, 128.0, 124.9, 121.9, 120.2, 111.3, 61.7, 38.2, 34.3, 19.7; IR (CH_3Cl): 1674.9, 1797.4, 2919.8, 2939.1 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{12}O_3$ $[M+H]^+$ 253.0859, found 253.0856.



5

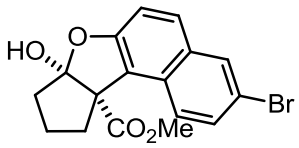
Compound 5: Methyl 2-oxocyclopentanecarboxylate (**1a)** (284 mg, 2 mmol) and 2-naphthol (432 mg, 3 mmol) were coupled according to Method A. The reaction mixture was heated to 60 °C for 2 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **5** (540 mg, 95%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.82 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.48–7.44 (m, 1H), 7.34–7.30 (m, 1H), 7.11(d, J = 8.8 Hz, 1H), 4.34 (br s, 1H), 3.76 (s, 3H) , 2.92 (ddd, J = 12.8, 11.8 & 6.3 Hz, 1H), 2.40 (ddt, J = 12.8, 6.3 & 2.0 Hz, 1H), 2.30 (ddt, J = 11.8, 6.3 & 2.0 Hz, 1H), 2.14 (ddd, J = 12.8, 11.8 & 6.3 Hz, 1H), 1.79–1.87 (m, 1H), 1.52 (tq, J = 11.8 & 6.3 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.8, 156.3, 130.6, 129.7, 129.7, 129.2, 127.4, 123.1, 121.3, 120.8, 119.5, 111.7, 64.2, 52.9, 39.9, 34.8, 22.5; IR (CH_3Cl): 1704.9, 2946.8, 2962.3, 3421.3 cm-1; HRMS (ESI): *m/z* calcd for $C_{17}H_{16}O_4$ $[M–OH]^+$ 267.1016, found 267.1011.



7

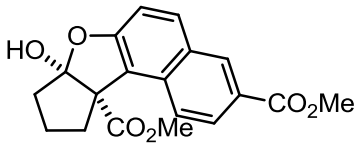
Compound 7: Ethyl 2-oxocyclohexanecarboxylate (**6)** (200 mg, 1.2 mmol) and *2*-naphthol (346 mg, 2.4 mmol) were coupled according to Method B. The reaction mixture was heated to 70 °C for 1 h then *β*-naphthol (173 mg, 1.2 mmol) was added and continued heating for further 2 hr. The crude residue was purified (hexanes-ethyl acetate, 17:3) affording compound **7** (329 mg, 93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.44 (ddd, *J* = 8.8, 6.7 & 1.2 Hz, 1H), 7.32 (ddd, *J* = 8.8, 6.7 & 1.2 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 4.76 (br s, 1H), 4.21–4.37 (m, 2H), 2.64-2.72 (m, 1H), 2.29 (dt, *J* = 14.4 & 4.3 Hz, 1H), 1.99 (ddd, *J* = 14.4, 11.4 & 5.0 Hz, 1H), 1.67–1.83 (m, 3H), 1.50-1.62 (m, 1H), 1.37–1.46 (m, 1H), 1.24 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.8, 154.9, 130.6, 130.2, 130.1, 129.3, 126.9, 123.2, 122.3, 122.2 112.8, 109.6, 61.8, 59.0, 32.6, 32.0, 20.5, 19.9, 14.1; HRMS (ESI): *m/z* calcd for $C_{19}H_{20}O_4$ $[M–OH]^+$ 295.1329, found 295.1325.



8

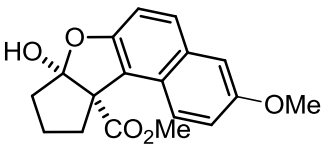
Compound 8: Methyl 2-oxocyclopentanecarboxylate (**1a)** (213 mg, 1.5 mmol) and 6-bromo-2-naphthol (502 mg, 2.25 mmol) were coupled according to Method A. The reaction mixture was heated to 60 °C for 2 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **8** (487 mg, 90%) as a bright yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.96 (d, *J* = 2.3Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.36 (br s, 1H), 3.74 (s, 3H), 2.90 (ddd, *J* = 12.9, 11.7 & 6.4 Hz, 1H), 2.38 (ddt, *J* = 13.3, 6.4 & 2.0 Hz, 1H), 2.24 (ddt, *J* = 12.9, 6.4 & 2.0 Hz,

1H), 2.13 (ddd, *J* = 13.3, 12.9 & 6.4 Hz, 1H), 1.83 (dtt, *J* = 12.9, 6.4 & 2.0 Hz, 1H), 1.49 (tq, *J* = 12.9 & 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.6, 156.6, 131.2, 131.0, 130.7, 129.8, 128.2, 122.9, 121.2, 120.0, 116.7, 112.9, 64.1, 53.0, 40.0, 35.1, 22.6; HRMS (ESI): *m/z* calcd for $C_{17}H_{15}BrO_4$ $[M–OH]^+$ 345.0121, 347.0100 found 345.0109, 347.0086.



9

Compound 9: Methyl 2-oxocyclopentanecarboxylate (**1a**) (142 mg, 1 mmol) and methyl 6-hydroxy-2-naphthoate (252 mg, 1.25 mmol) were coupled according to Method A. The reaction mixture was heated to 80 °C for 2 h. The crude residue was purified (hexane-ethyl acetate, 3:1) affording compound **9** (239 mg, 70%) as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.57 (d, *J* = 1.2Hz, 1H), 8.04 (dd, *J* = 8.7 & 1.56 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 4.36 (br s, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 2.92 (ddd, *J* = 12.7, 11.9 & 6.4 Hz, 1H), 2.41 (ddt, *J* = 13.3, 6.4 & 2.0 Hz, 1H), 2.28 (ddt, *J* = 13.3, 6.5 & 2.0 Hz, 1H), 2.15 (ddd, *J* = 13.3, 12.7 & 6.4 Hz, 1H), 1.82–1.89 (m, 1H), 1.52 (tq, *J* = 12.7 & 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.6, 167.2, 158.3, 132.4, 132.4, 132.1, 128.8, 127.0, 124.8, 121.4, 121.3, 120.0, 112.7, 64.0, 53.0, 52.2, 39.9, 35.0, 22.5; IR (CH_3Cl): 1701.0, 1735.7, 3946.8, 3405.8 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{18}O_6$ $[M+H]^+$ 343.1176, found 343.1167.

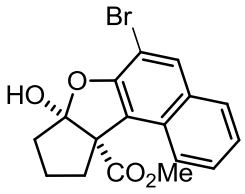


10

Compound 10:

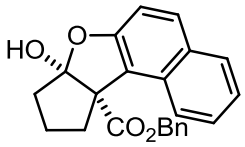
Method A: Methyl 2-oxocyclopentanecarboxylate **(1a)** (142 mg, 1 mmol) and 6-methoxy-2-naphthol (261 mg, 1.5 mmol) were coupled according to method A. The reaction mixture was heated to 60 °C for 2 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 4:1) affording compound **10** (202 mg, 64%) as a yellow solid.

Method B: **1a** (142 mg, 1 mmol) and 6-methoxy-2-naphthol (261 mg, 1.5 mmol) were coupled according to the general procedure. The reaction mixture was heated to 60 °C for 2 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 4:1) affording compound **10** (298 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (d, *J*= 8.6 Hz, 1H), 7.46 (d, *J* = 9.7 Hz, 1H), 7.14–7.17 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 3.8 (s, 3H), 3.73 (s, 3H), 2.94 (ddd, *J* = 12.8, 11.8 & 6.4 Hz, 1H), 2.38 (ddt, *J* = 12.8, 6.4 & 2.0 Hz, 1H), 2.26 (ddt, *J* = 11.8, 6.4 & 2.0 Hz, 1H), 2.13 (ddd, *J* = 12.8, 11.8 & 6.4 Hz, 1H), 1.48 (dtt, *J* = 11.8, 6.4 & 2.0 Hz, 1H), 1.51 (tq, *J* = 11.8 & 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.9, 155.7, 154.8, 130.8, 129.2, 125.1, 122.7, 120.8, 120.1, 120.0, 112.1, 107.6, 64.4, 55.4, 52.9, 40.0, 35.1, 22.6; HRMS (ESI): *m/z* calcd for $C_{18}H_{18}O_5$ $[M+H]^+$ 297.1121, found 297.1111.



11

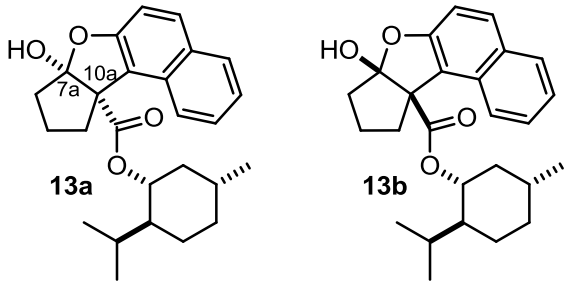
Compound 11: Methyl 2-oxocyclopentanecarboxylate **(1a)** (532 mg, 2 mmol) and 3-bromo-2-naphthol (432 mg, 3 mmol) were coupled according to Method A. The reaction mixture was heated to 60 °C for 2 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **11** (227 mg, 63%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.95 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.44–7.50 (m, 2H), 7.34 (ddd, *J* = 8.1, 6.6 & 1.4 Hz, 1H), 4.34 (br s, 1H), 3.75 (s, 3H), 2.94 (dq, *J* = 11.6 & 6.4 Hz, 1H), 2.44–2.50 (m, 1H), 2.24–2.30 (m, 1H), 2.16 (dq, *J* = 11.6 & 6.4 Hz, 1H), 1.82–1.88 (m, 1H), 1.50–1.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.2, 153.4, 132.5, 130.7, 128.7, 128.4, 127.6, 124.1, 121.4, 121.2, 121.0, 104.7, 65.4, 53.1, 40.0, 35.2, 22.6; HRMS (ESI): *m/z* calcd for $C_{17}H_{15}BrO_4$ $[M–OH]^+$ 345.0121, 347.0100 found 345.0112, 347.0090.



12

Compound 12: Benzyl 2-oxocyclopentanecarboxylate (**1c)**

[1] (445 mg, 2 mmol) and 2-naphthol (432 mg, 3 mmol) were coupled according to Method A. The reaction mixture was heated to 60 °C for 2 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **12** (618 mg, 85%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.80–7.82 (m, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.24–7.36 (m, 5H), 7.16 (dd, *J* = 7.9 & 1.7 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 1H), 5.27 (d, *J* = 12.3 Hz, 1H), 5.14 (d, *J* = 12.3 Hz, 1H), 4.34 (br s, 1H), 2.91 (ddd, *J* = 12.9, 11.7 & 6.4 Hz, 2H), 2.39 (ddt, *J* = 12.9, 6.4 & 1.9 Hz, 2H), 2.30 (ddt, *J* = 11.7, 6.4 & 1.9 Hz, 2H), 2.14 (ddd, *J* = 12.9, 11.7 & 6.4 Hz, 2H), 1.82 (dtt, *J* = 11.7, 6.4 & 1.9 Hz, 2H), 1.50 (tq, *J* = 11.7 & 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.2, 156.3, 135.0, 130.6, 129.7, 129.6, 129.1, 128.5, 128.4, 128.3, 127.2, 123.1, 121.3, 120.9, 119.5, 111.7, 67.5, 64.2, 40.0, 34.8, 22.5; HRMS (ESI): *m/z* calcd for $C_{23}H_{20}O_4$ $[M–OH]^+$ 343.1329, found 343.1323.

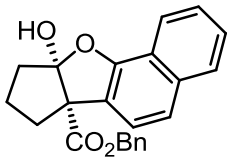


Compound 13a and **13b**: Di-*tert*-butyl peroxide (3.0 mmol, 1.5 equiv) was added drop-wise into a stirred solution of **1d**[1] (504 mg, 2 mmol), 2-naphthol (288 mg, 2 mmol) and $FeCl_3(H_2O)_6$ (0.2 mmol, 0.1 equiv) in dichloroethane (20.0 mL) under nitrogen atmosphere at room temperature. The reaction mixture was heated to 100 °C for 2 h, cooled to room temperature, quenched with saturated $NaHCO_3$ (00 mL) and extracted with ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 19:1) affording compound **13a** (302 mg, 37%) as a yellow solid and compound **13b** (351 mg, 43%) as a yellow solid.

(7a*R*,10a*S*)-**13a**: $[\alpha]_D^{25}$ = -91.4 (c = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.9 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.6 (d, *J* = 8.4 Hz, 1H), 7.43 (ddd, *J* = 8.3 Hz, *J* = 6.8 & 1.3 Hz, 1H), 7.29 (ddd, *J* = 8.1 6.7 & 1.2 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.7(td, *J* = 10.9 & 4.3 Hz, 1H), 4.42 (br s, 1H), 2.88 (ddd, *J* = 12.911.4 & 6.3 Hz, 1H), 2.28–2.42 (m, 3H), 2.07–2.18 (m, 2H), 1.86-1.78 (m, 1H), 1.64–1.59 (m, 1H), 1.56–1.41 (m, 3H), 1.19–1.11

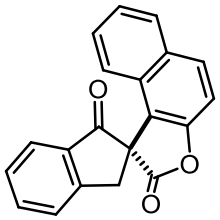
(m, 1H), 0.91–0.87 (m, 5H), 0.77–0.74 (m, 1H), 0.4 (d, *J* = 7 Hz, 3H), 0.29 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 171.4, 156.3, 130.4, 129.7, 129.6, 129, 127, 123, 121.5, 120.8, 119.7, 111.6, 76.4 64.4, 46.8, 40.8, 40.1, 34.5, 34, 31.4, 25.2, 22.9, 22.4, 21.9, 20.2, 15.5; HRMS (ESI): *m/z* calcd for $C_{26}H_{31}O_3$ $[M–OH]^+$ 391.2268, found 391.2262.

(7a*S*,10a*R*)-**13b**: $[\alpha]_D^{25}$ = +8.5 (c = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.8 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.41 (ddd, *J* = 8.3, 6.8 & 1.3 Hz, 1H), 7.3 (ddd, *J* = 8.1, 6.7 & 1.2 Hz, 1H), 7.1 (d, *J* = 8.8 Hz, 1H), 4.8(td, *J* = 10.9 Hz, *J* = 4.4 Hz, 1H), 4.47 (br s, 1H), 2.88 (ddd, *J* = 12.7, 11.5 & 6.4 Hz, 1H), 2.36–2.4 (m, 1H), 2.26–2.31 (m, 1H), 2.1–2.18 (m, 1H), 1.97–1.88 (m, 2H), 1.69–1.62 (m, 2H), 1.57–1.35 (m, 4H), 1.07–0.97 (m, 1H), 0.89 (d, *J* = 7 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.3, 156.3, 130.6, 129.8, 129.7, 129.2, 126.9, 123.1, 121.7, 120.9, 120, 111.8, 76.7, 64.7, 46.7, 40.4, 40, 34.9, 34, 31.4, 26.2, 22.8, 22.7, 21.9, 21, 15.7 ; HRMS (ESI): *m/z* calcd for $C_{26}H_{32}O_4$ $[M–OH]^+$ 391.2268, found 391.2261.



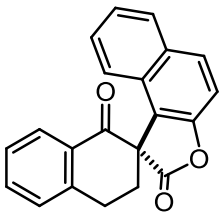
14

Compound 14: Benzyl 2-oxocyclopentanecarboxylate **(1c)**[1] (208 mg, 1 mmol) and 1-naphthol (216 mg, 1.5 mmol) were coupled according to Method B. The reaction mixture was heated to 70 °C for 6 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **14** (72 mg, 20%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00–8.02 (m, 1H), 7.78–7.80 (m, 1H), 7.46–7.48 (m, 2H), 7.31–7.38 (m, 6H), 7.16 (d, *J* = 8.3 Hz, 1H), 5.56 (br s, 1H), 5.26 (d, *J* = 12.2 Hz, 1H), 5.21 (d, *J* = 12.2 Hz, 1H), 2.61 (td, *J* = 12.5 & 6.4 Hz, 1H), 2.48 (ddt, *J* = 13.3, 6.4 & 2.0 Hz, 1H), 2.24 (ddt, *J* = 12.5, 6.4 & 2.0 Hz, 1H), 2.16 (td, *J* = 12.5 & 6.4 Hz, 1H), 1.77 (dtt, *J* = 12.5, 6.4 & 2.0 Hz, 1H), 1.41–1.48 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.2, 156.3, 135.0, 130.6, 129.7, 129.6, 129.1, 128.5, 128.4, 128.3, 127.2, 123.1, 121.3, 120.9, 119.5, 111.7, 67.5, 64.2, 40.0, 34.8, 22.5; HRMS (ESI): *m/z* calcd for $C_{23}H_{20}O_4$ $[M+H]^+$ 361.1434 found 361.1433.



15

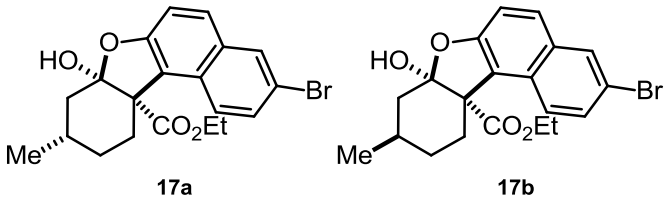
Compound 15: Benzyl 1-oxo-2-indancarboxylate[2] (532 mg, 2 mmol) and 2-naphthol (432 mg, 3 mmol) were coupled according to Method A. The reaction mixture was heated to 100 °C for 2 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **15** (230 mg, 77%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88–7.93 (m, 3H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.96 (d, *J* = 17.4 Hz, 1H), 3.88 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 198.1, 175.0, 152.8, 152.6, 136.5, 134.9, 131.3, 131.1, 129.8, 128.8, 128.3, 128.2, 126.9, 125.9, 125.0, 121.4, 120.6, 111.6, 61.5, 37.9; HRMS (ESI): *m/z* calcd for $C_{20}H_{12}O_3$ $[M+H]^+$ 301.0859, found 301.0844.



16

Compound 16: Methyl 1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate[3] (204 mg, 1 mmol) and 2-naphthol (216 mg, 1.5 mmol) were coupled according to Method A. The reaction mixture was heated to 80 °C for 1.5 h. The crude residue was purified (hexanes-ethyl acetate, 17:3) affording compound **16** (259 mg, 83%) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.14 (ddt, *J* = 7.9, 1.6 & 0.5 Hz, 1H), 7.91–7.94 (m, 2H), 7.64 (td, *J* = 7.5 & 1.3 Hz, 1H), 7.36–7.45 (m, 6H), 3.90 (ddd, *J* = 17.1, 12.8 & 4.8 Hz, 1H), 3.18 (ddd, *J* = 13.9, 13.3 & 4.8 Hz, 1H), 3.02–3.08 (m, 1H), 2.49 (dq, *J* =13.9, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 190.8, 173.1, 151.5, 144.4, 134.8, 131.4, 131.1, 130.9, 129.8, 129.1, 129.0, 128.4, 127.8, 127.4, 124.8, 122.8, 122.1, 111.4, 59.2, 32.1, 24.5; IR (CH_3Cl): 1674.0, 1797.4,

2916.0, 3051.0 cm-1; HRMS (ESI): *m/z* calcd for $C_{21}H_{14}O_3$ $[M+H]^+$ 315.1016, found 315.1007.

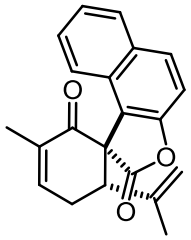


17a **17b**

Compound 17a and **17b:** Methyl 4-methyl-2-cyclohexnone-1-carboxylate (276 mg, 1.5 mmol) and 6-Bromo-2-naphthol (502 mg, 2.25 mmol) were coupled according to Method A. The reaction mixture was heated to 70 °C for 6 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **17a** (304 mg, 52%) and compound **17b** (76 mg, 13%) as a brown solid.

17a: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.95 (s, 1H), 7.79 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.36 (br s, 1H), 4.03–4.22 (m, 2H), 2.69 (dt, *J* = 14.5 & 4.0 Hz, 1H), 2.69 (dt, *J* =14.5 & 3.8 Hz, 1H), 2.24–2.32 (m, 1H), 2.13 (dd, *J* = 13.9 & 4.8 Hz, 1H), 1.74–1.90 (m, 2H), 1.54 (dd, *J* = 13.6 & 10.3 Hz, 1H), 1.24–1.32 (m, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 174.1, 156.2, 131.2, 131.1, 130.3, 130.1, 129.6, 123.8, 119.1, 116.5, 114.1, 112.1, 62.0, 57.5, 41.4, 29.0, 28.8, 27.3, 21.8, 13.9; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}BrO_4$ $[M-OH]^+$ 387.0590 and 389.0570 found 387.0577 and 389.0553.

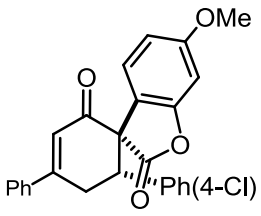
17b: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.97 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 9.0 & 1.8 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 4.34 (dq, *J* = 10.8 & 7.0 Hz, 1H), 4.28 (dq, *J* = 10.8 & 7.0 Hz, 1H), 2.76 (dt, *J* = 14.3 & 4.0 Hz, 1H), 2.38 (dd, *J* = 13.9 & 3.1 Hz, 1H), 1.35–1.75 (m, 5H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.2, 154.6, 131.4, 131.1, 130.1, 129.5, 128.4, 124.2, 124.0, 116.8, 114.0, 109.9, 61.9, 58.4, 40.5, 34.2, 29.2, 27.8, 21.9, 14.2; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}BrO_4$ $[M–OH]^+$ 387.0590 and 389.0570 found 387.0576 and 389.0556.



18

Compound 18: (*R*)-3-methyl-6-(1-methylethenyl)-2-oxo-3-Cyclohexene-1-carboxylic acid methyl ester[4] (208mg, 1 mmol) and 2-naphthol (216 mg, 1.5 mmol) were coupled according to Method B. The reaction mixture was heated to 80 °C for 4 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 9:1) affording compound **18** (124 mg, 39%) as a white solid.

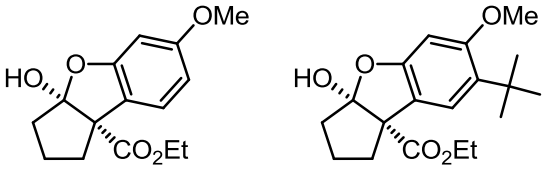
$[\alpha]_D^{25}$ = +146.0 (c = 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.88 (t, *J* = 8.2 Hz, 2H), 7.42–7.53 (m, 2H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.14 (d, *J* = 6.0 Hz, 1H), 4.66 (s, 1H), 4.60 (s, 1H), 3.85 (dd, *J* = 11.9 & 4.6 Hz, 1H), 3.38 (ddt, *J* = 19.0, 11.9 & 2.3, 1H), 2.46 (dt, *J* = 19.0 & 5.9, 1H), 1.95 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 191.1, 171.9, 151.5, 147.7, 142.3, 133.3, 131.0, 130.9, 129.6, 129.1, 127.5, 124.5, 122.7, 119.7, 114.6, 111.0, 64.1, 49.0, 27.9, 21.5, 16.5; IR (CH_3Cl): 1666.3, 1785.8, 2916.0, 2950.7 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{18}O_3$ $[M+H]^+$ 319.1329, found 319.1320.



19

Compound 19: 3-Cyclohexene-1-carboxylic acid, 6-(4-chlorophenyl)-2-oxo-4-phenyl-, ethyl ester[5] (100 mg, 0.3 mmol) and 3-methoxy phenol (53 mg, 0.4 mmol) were coupled according to Method B. The reaction mixture was heated to 70 °C for 16 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 4:1) affording compound **19** (52 mg, 40%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65–7.67 (m, 2H), 7.46–7.48 (m, 3H), 7.01–7.15 (m, 5H), 6.71 (td, *J* = 3.8 & 2.3 Hz, 2H), 6.45 (d, *J* = 2.3 Hz, 1H), 4.01 (ddd, *J* = 12.0, 17.5 & 2.3 Hz, 1H), 3.91 (dd, *J* = 12.0 & 3.8 Hz, 1H), 3.75 (s, 3H), 3.08 (dd, *J* = 17.5 & 3.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 191.2, 171.9, 160.9, 160.8, 154.4, 137.5, 136.3, 133.8, 131.0, 129.4, 129.0, 128.8, 126.4, 124.6, 122.7,

118.1, 110.6, 97.1, 63.2, 55.6, 48.5, 31.0; HRMS (ESI): *m/z* calcd for $C_{26}H_{19}ClO_4$ $[M+H]^+$ 431.1045 found 431.1043.



20a **20b**

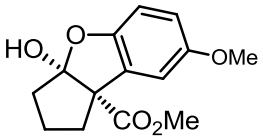
Compound 20a and **20b:**

Method A: Ethyl 2-oxocyclopentanecarboxylate **1b** (200 mg, 1.3 mmol) and 3-methoxy phenol (238 mg, 1.9 mmol) were coupled according to the general procedure. The reaction mixture was heated to 70 °C for 2 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 9:1) affording compound **20a** (152 mg, 42%) and compound **20b** (108 mg, 25%) as white solids.

Method B: Ethyl 2-oxocyclopentanecarboxylate **1b** (200 mg, 1.3 mmol) and 3-methoxy phenol (238 mg, 1.9 mmol) were coupled according to the general procedure. The mixture was heated to 70 °C for 2 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 9:1) affording compound **20a** (248 mg, 68%) and compound **20b** (51 mg, 12%).

20a: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.98 (d, J = 8.4 Hz, 1H), 6.42 (dd, J = 8.4 & 2.5 Hz, 1H), 6.36 (d, J = 2.5 Hz, 1H), 5.79 (s, 1H), 4.16–4.31 (m, 2H), 3.74 (s, 3H), 2.45 (dt, J = 12.6 & 6.3 Hz, 1H), 2.34 (ddt, J = 13.3, 6.3 & 2.0, 1H), 2.12 (ddt, J = 12.6, 6.3 & 2.0, 1H), 2.03 (ddd, J = 13.3, 12.6 & 6.3 Hz, 1H), 1.72 (dtt, J = 12.6, 6.3 & 2.0, 1H), 1.43 (tq, J = 12.6 & 6.3 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 161.2, 159.6, 124.1, 120.5 (2 carbons), 107.0, 95.5, 61.7, 60.9, 55.3, 40.3, 36.8, 21.5, 14.0; HRMS (ESI): *m/z* calcd for $C_{15}H_{18}O_5$ $[M+H]^+$ 279.1227, found 279.1221.

20b: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.97 (s, 1H), 6.36 (s, 1H), 5.90 (s, 1H), 4.28–4.36 (m, 1H), 4.19–4.25 (m, 1H), 3.78 (s, 3H), 2.43 (dt, J = 12.3 & 6.4 Hz, 1H), 2.29–2.36 (m, 1H), 2.14 (ddt, J = 12.3, 6.4 & 1.8 Hz, 1H), 2.03 (ddd, J =13.3, 12.3 & 6.4 Hz, 1H), 1.72 (dtt, J = 12.3, 6.4 & 1.8 Hz, 1H), 1.46 (tq, J = 12.3 & 6.4 Hz, 1H), 1.30 (s, 9H), 1.30 (t, J = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.6, 159.9, 157.5, 131.1, 121.1, 120.3, 118.5, 93.9, 61.5, 61.1, 55.0, 40.4, 36.7, 34.4, 29.9, 21.5, 14.1; HRMS (ESI): *m/z* calcd for $C_{19}H_{26}O_5$ $[M+H]^+$ 335.1853, found 335.1843.

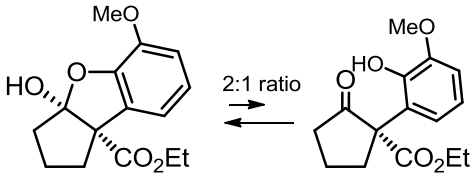


21

Compound 21:

Method A: Methyl 2-oxocyclopentanecarboxylate (**1a)** (200 mg, 1.3 mmol) and 4-methoxy phenol (238 mg, 1.9 mmol) were coupled according to the general procedure. The reaction mixture was heated to 70 °C for 2 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 17:3) affording compound **26** (185 mg, 50%).

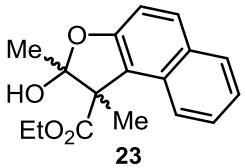
Method B: Methyl 2-oxocyclopentanecarboxylate **(1a)** (200mg, 1.4 mmol) and 4-methoxy phenol (262 mg, 2.1 mmol) were coupled according to the general procedure. The reaction mixture was heated to 70 °C for 2 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 17:3) affording compound **21** (252 mg, 68%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.64–6.70 (m, 3H), 5.24 (br s, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 2.56 (ddd, J = 13.3, 11.9 & 6.5 Hz, 1H), 2.27 (ddt, J = 13.0, 6.5 & 2.0 Hz, 1H), 1.96–2.08 (m, 2H), 1.71 (ddt, J = 11.9, 6.5 & 2.0 Hz, 1H), 1.58 (tq, J = 11.9 & 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.9, 154.3, 152.5, 129.3, 120.1, 114.5, 110.0, 109.4, 63.0, 55.8, 52.7, 40.0, 36.9, 21.9; HRMS (ESI): *m/z* calcd for $C_{14}H_{16}O_5$ $[M+H]^+$ 265.1071, found 265.1071.



22

Compound 22: Ethyl 2-oxocyclopentanecarboxylate (**1b)** (156mg, 1 mmol) and 2-methoxy phenol (186 mg, 1.5 mmol) were coupled according to Method B. The reaction mixture was heated to 70 °C for 12 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 4:1) affording compound **22** (62mg, 22%) as a yellow oil.

Compound **22** was obtained as a mixture of hemiacetal and ketone forms (2:1 ratio). The NMR data of the major isomer is given: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 6.77–6.86 (m, 2H), 6.72 (dd, *J* = 7.4 & 1.4 Hz, 1H), 5.40 (s, 1H), 4.27 (dq, *J* = 10.7 & 7.1 Hz, 1H), 4.22 (dq, *J* = 10.7 & 7.1 Hz, 1H), 3.88 (s, 3H), 2.50-2.58 (m, 1H), 1.96–2.08 (m, 1H), 2.44 (ddt, *J* = 13.5, 6.4 & 2.0 Hz, 1H), 2.14 (ddt, *J* = 13.5, 6.4 & 2.0 Hz, 1H), 2.06 (ddd, *J* = 13.5, 12.5 & 6.4 Hz, 1H), 1.74 (dtt, *J* = 12.5, 6.4 & 2.0 Hz, 1H), 1.42–1.53 (m, 1H), 1.74 (t, *J* = 7.1 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 191.0, 151.5, 144.4, 134.8, 131.1, 129.8, 129.1, 129.0, 127.8, 127.4, 124.8, 122.8, 111.4, 32.1, 24.5; HRMS (ESI): *m/z* calcd for $C_{15}H_{18}O_5$ $[M+H]^+$ 279.1227, found 279.1230.



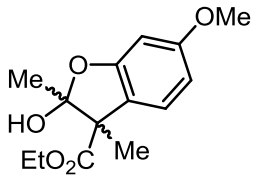
23

Compound 23:

Method A: Di-*tert*-butyl peroxide (3.5 mmol, 2.5 equiv) was added drop-wise into a stirred solution of Ethyl 2-methylacetoacetate (200 mg, 1.4 mmol), 2-naphthol (300 mg, 2 mmol) and $FeCl_3$ (0.14 mmol, 0.1 equiv) under nitrogen atmosphere at room temperature. The reaction mixture was heated to 70 °C for 2 h, cooled to room temperature, quenched with saturated $NaHCO_3$ (10 mL) and extracted with ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 17:3) affording compound **23** (212 mg, 53%, mixture of diastereoisomers) as a yellow solid.

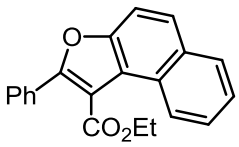
Method B: Ethyl 2-methylacetoacetate (200 mg, 1.4 mmol) and 2-naphthol (300 mg, 2 mmol) were coupled according to the general procedure. The reaction mixture was heated to 70 °C for 2.5 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 17:3) affording compound **23** (262 mg, 66%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.44–7.50 (m, 2H), 7.34 (ddd, *J* = 7.2, 6.4 & 1.7 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 4.35 (dq, *J* = 10.8 & 7.1 Hz, 1H), 4.28 (dq, *J* = 10.8 & 7.1 Hz, 1H), 1.78 (s, 3H), 1.63 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.3, 154.4, 130.8, 130.3, 129.9, 129.3, 126.9,

123.2, 122.4, 121.6, 112.6, 111.0, 61.9, 59.7, 21.2, 20.9, 14.1; HRMS (ESI): *m/z* calcd for $C_{17}H_{18}O_4$ $[M–OH]^+$ 269.1172, found 269.1163.



24

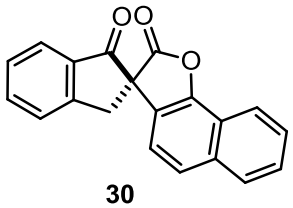
Compound 24: Ethyl 2-methylacetoacetate (200 mg, 1.4 mmol) and 4-methoxy phenol (258 mg, 2.1 mmol) were coupled according to Method B. The reaction mixture was heated to 70 °C for 1.5 h. The crude residue was purified by flash column chromatography on silica gel (hexanes-ethyl acetate, 17:3) affording compound **24** (81 mg, 22%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.14 (d, J = 8.6 Hz, 1H), 6.47 (dd, J = 8.6 & 2.3 Hz, 1H), 6.39 (d, J = 2.3 Hz, 1H), 4.39 (br s, 1H), 4.23 (dq, J = 10.8 & 7.1 Hz, 1H), 4.18 (dq, J = 10.8 & 7.1 Hz, 1H), 3.74 (s, 3H), 1.66 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.0, 161.0, 157.7, 125.7, 122.4, 111.8, 107.3, 97.0, 61.6, 57.8, 55.5, 22.4, 21.7, 14.0; HRMS (ESI): *m/z* calcd for $C_{14}H_{18}O_5$ $[M+H]^+$ 267.1227, found 249.1227.



25

Compound 25[6]**:** Di-*tert*-butyl peroxide (0.46 mL, 2.5 mmol) was added drop-wise into a stirred solution of ethyl 3-oxo-3-phenylpropanoate (192 mg, 1.0 mmol), *β*-naphthol (288 mg, 2 mmol), 1,10-phenanthroline (9 mg, 0.05 equiv.) and $FeCl_3$ (16 mg, 0.1 equiv.) in dichloroethane (1 mL) under nitrogen atmosphere at room temperature. The reaction mixture was heated to 70 ^{o}C for 5 h, cooled to room temperature, quenched with saturated $NaHCO_3$ (10 mL) and extracted with ether (3 X 10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (10 mL), water (10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexanes-diethyl-ether, 96:4) affording compound **25** (215 mg, 68%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.64 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 8.5 Hz, 1H), 7.81 (d, J

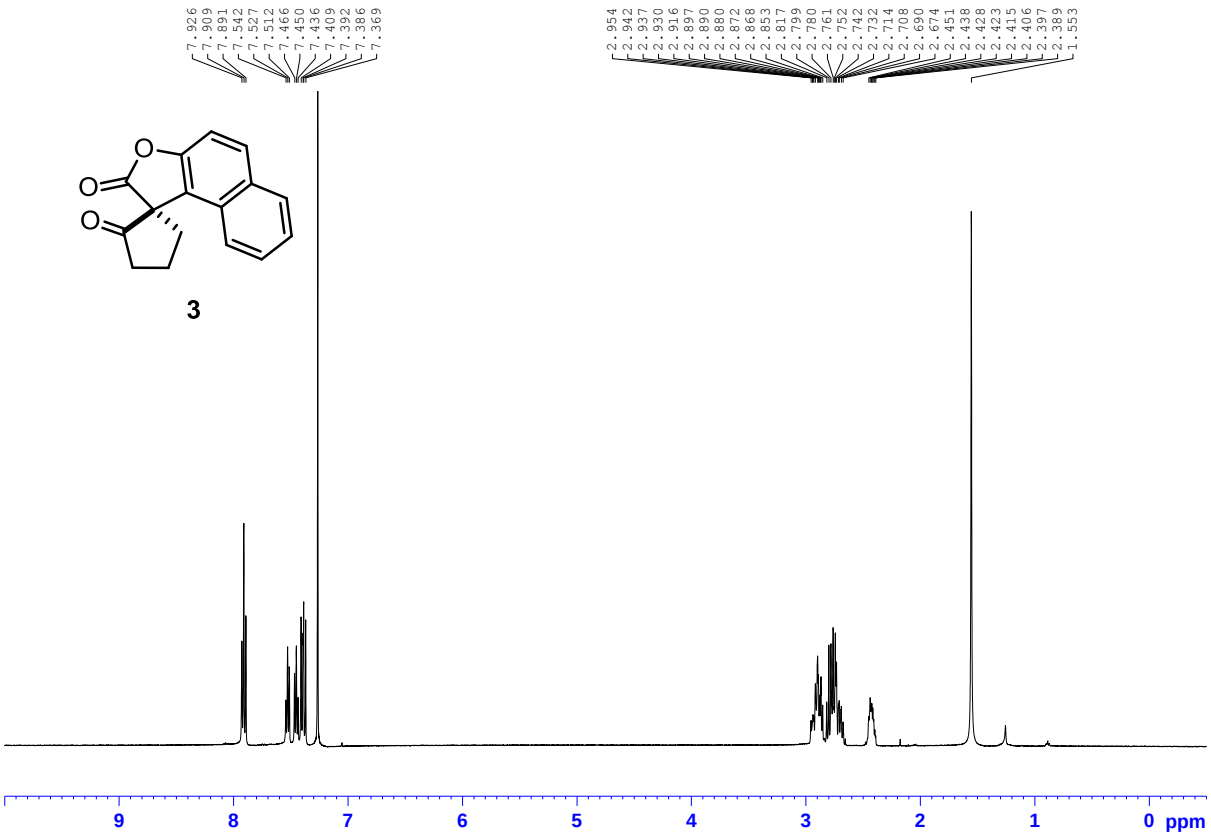
= 7.5 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.54–7.64 (m, 2H), 7.32–7.52 (m, 4H), 4.47 (q, *J* = 6.9 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 166.1, 155.9, 151.6, 130.9, 129.8, 129.3, 128.9, 128.2, 127.8, 127.4, 126.9, 126.4, 124.7, 124.2, 120.9, 111.8, 111.5, 61.4, 13.7; GCMS: *m/z* 316 $[M]^+$.



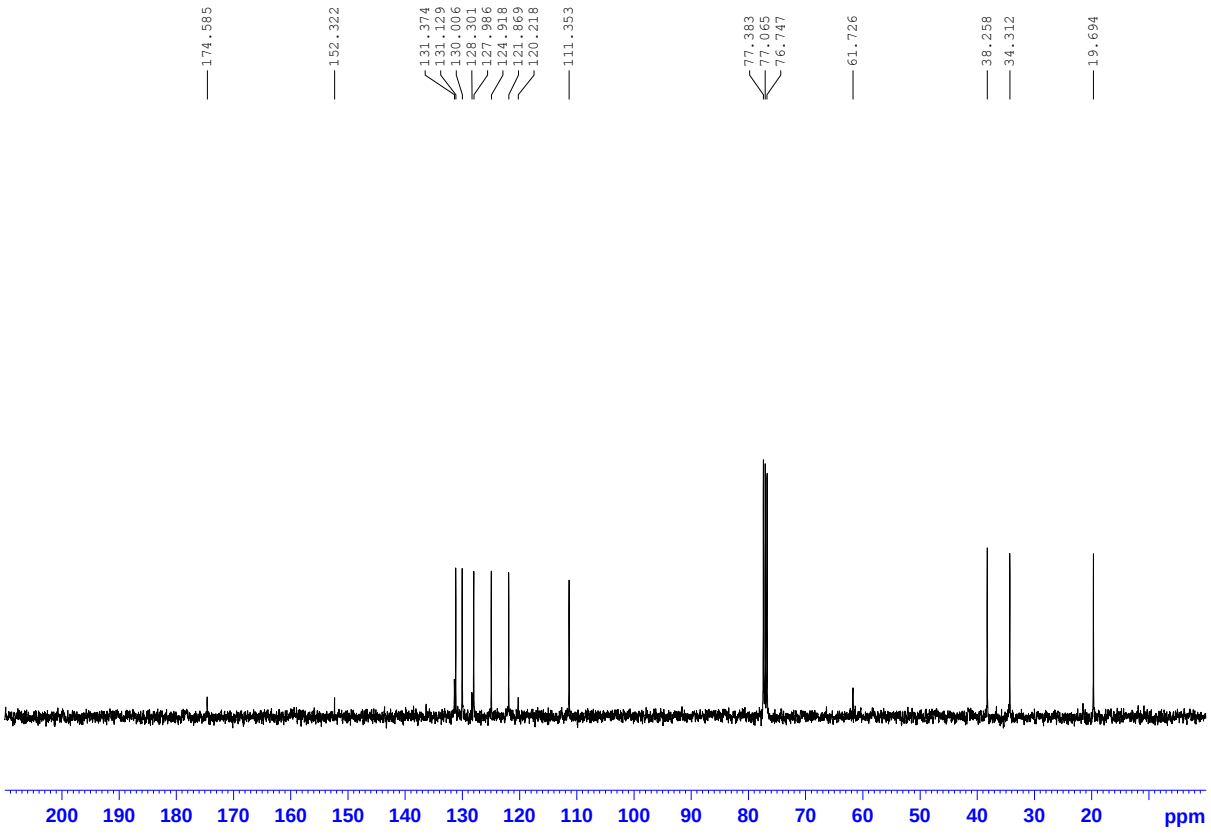
30

Compound 30: Methyl 1-oxo-2-indancarboxylate **29**[2] (200 mg, 1 mmol) and 1-naphthol (182 mg, 1.3 mmol) were coupled according to Method B. The reaction mixture was heated to 70 °C for 6 h. The crude residue was purified (hexanes-ethyl acetate, 9:1) affording compound **30** (130 mg, 43%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.48–7.67 (m, 5H), 7.03 (d, *J* = 8.1 Hz, 1H), 3.96 (d, *J* = 17.4 Hz, 1H), 3.62 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 197.9, 174.8, 153.0, 150.4, 136.3, 134.4, 134.2, 128.7, 128.3, 127.2 (2 carbons), 126.6, 125.9, 124.9, 122.5, 121.2, 119.9, 118.7, 62.2, 38.3; HRMS (ESI): *m/z* calcd for $C_{20}H_{12}O_3$ $[M+H]^+$ 301.0859, found 301.0846.

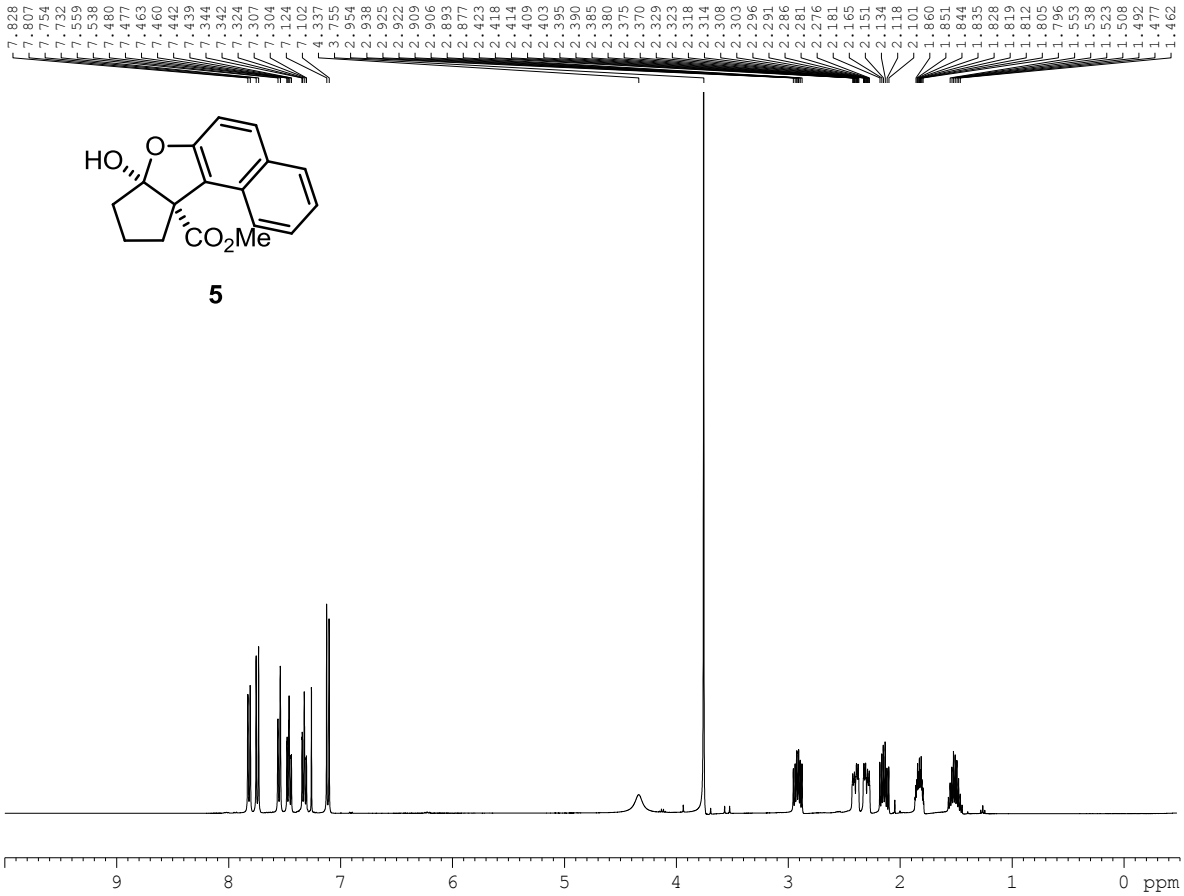
^{1}H- NMR spectrum for compound **3** ($CDCl_3$, 500 MHz)



^{13}C- NMR spectrum for compound **3** ($CDCl_3$, 100 MHz)

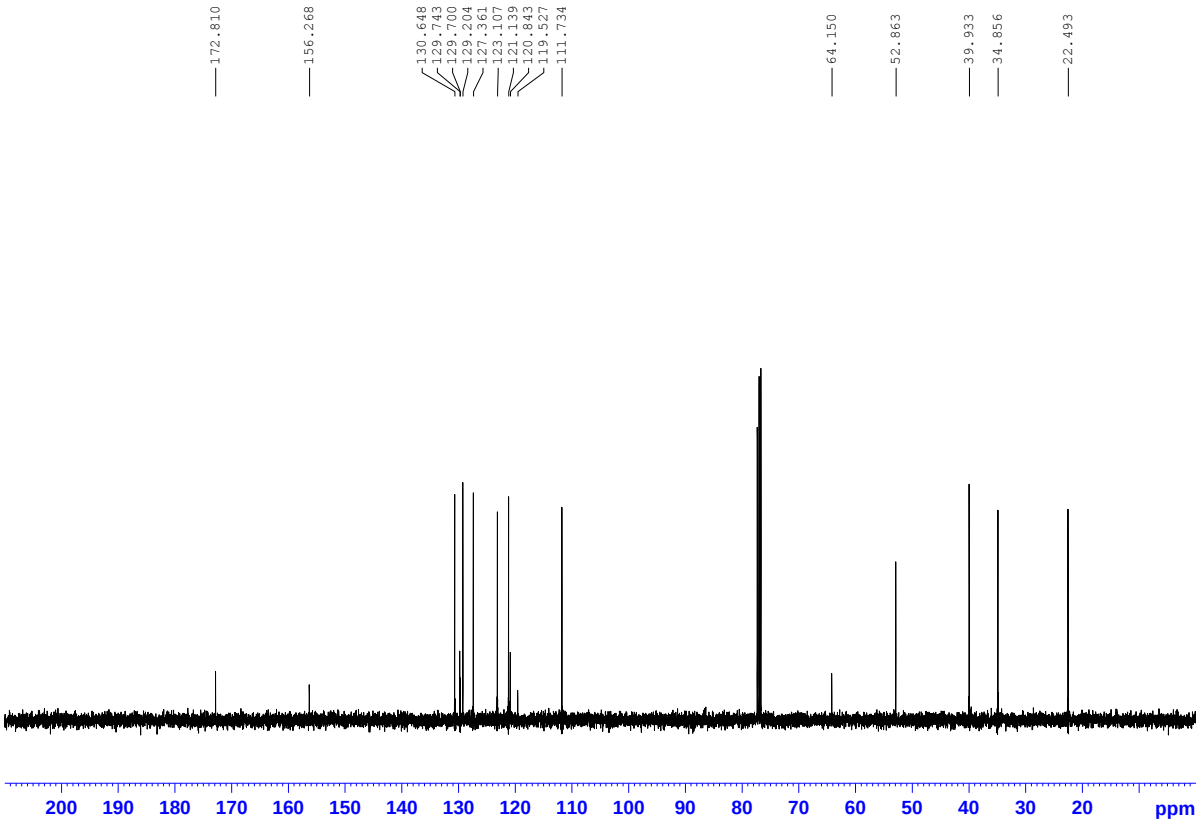


^{1}H- NMR spectrum for compound **5** ($CDCl_3$, 400 MHz)

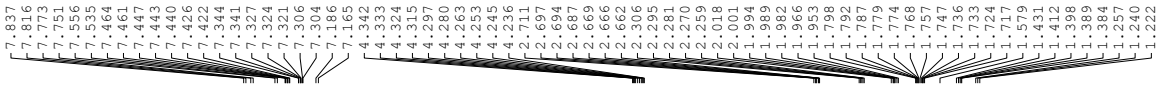


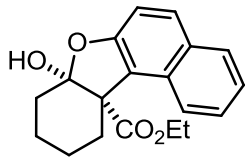
5

^{13}C- NMR spectrum for compound **5** ($CDCl_3$, 100 MHz)

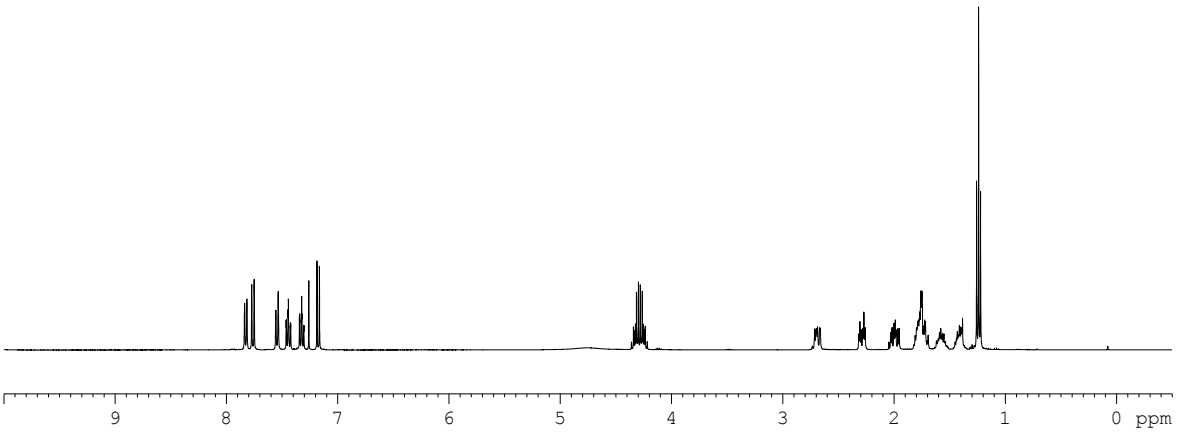


^{1}H- NMR spectrum for compound **7** ($CDCl_3$, 400 MHz)

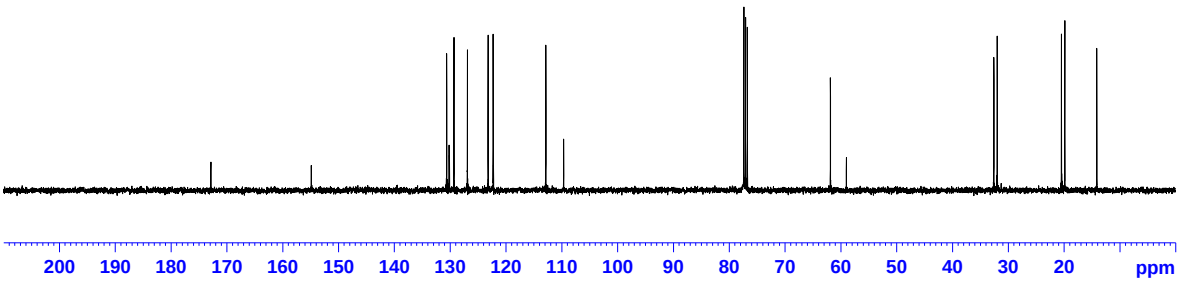




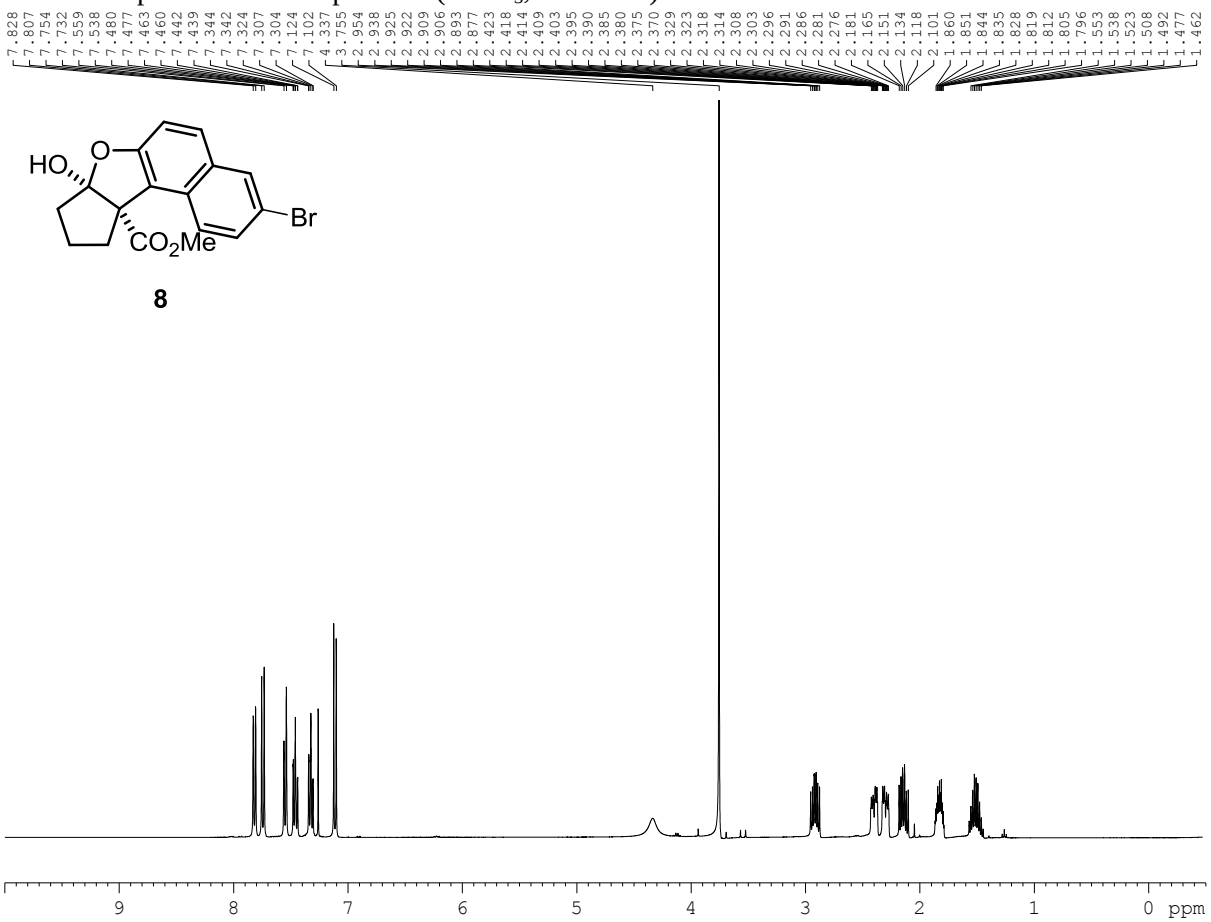
7



^{13}C - NMR spectrum for compound **7** ($CDCl_3$, 100 MHz)

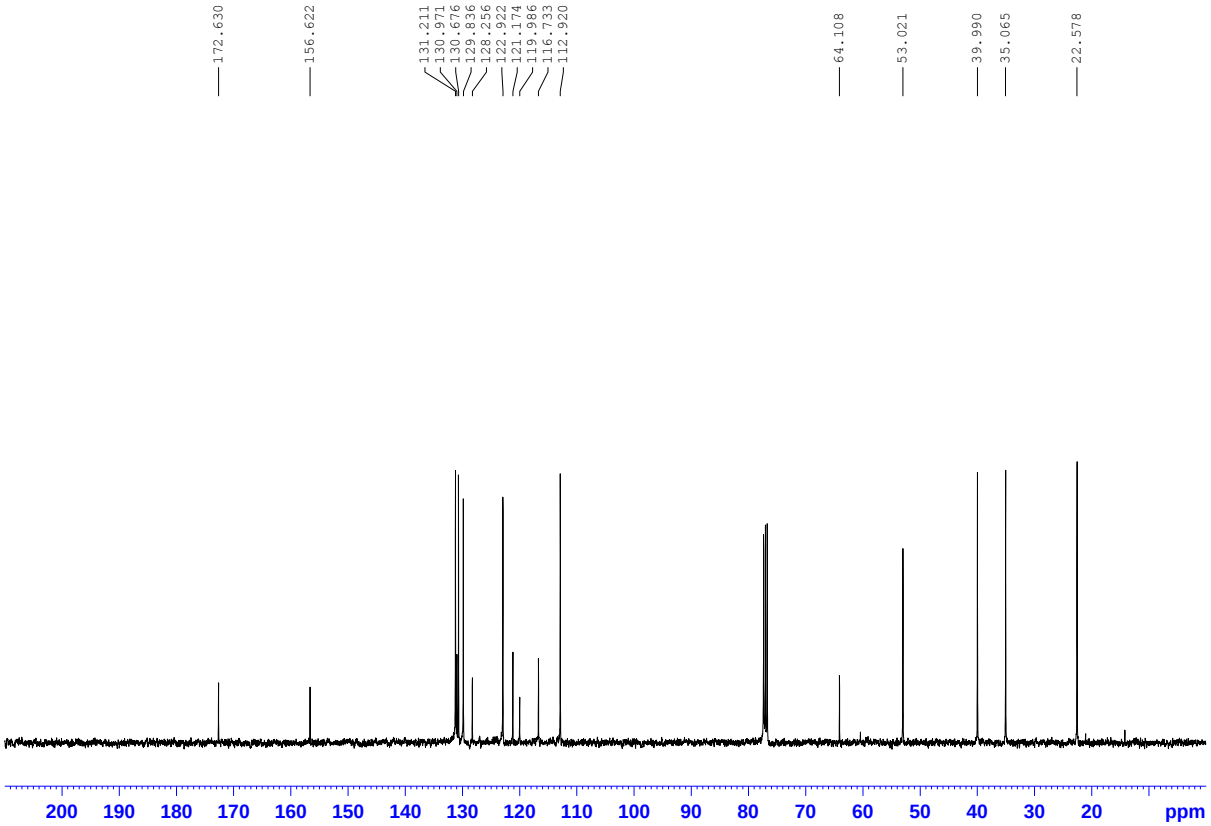


^{1}H- NMR spectrum for compound **8** ($CDCl_3$, 400 MHz)

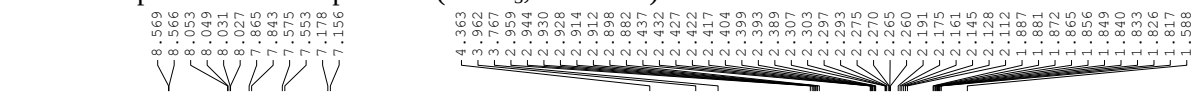


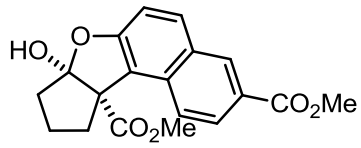
8

^{13}C - NMR spectrum for compound **8** ($CDCl_3$, 100 MHz)

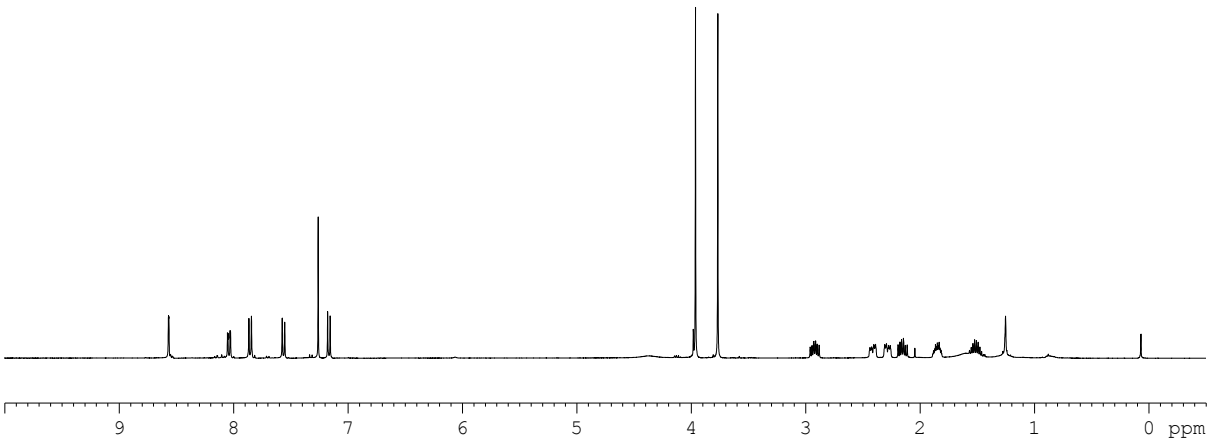


^{1}H- NMR spectrum for compound **9** ($CDCl_3$, 400 MHz)

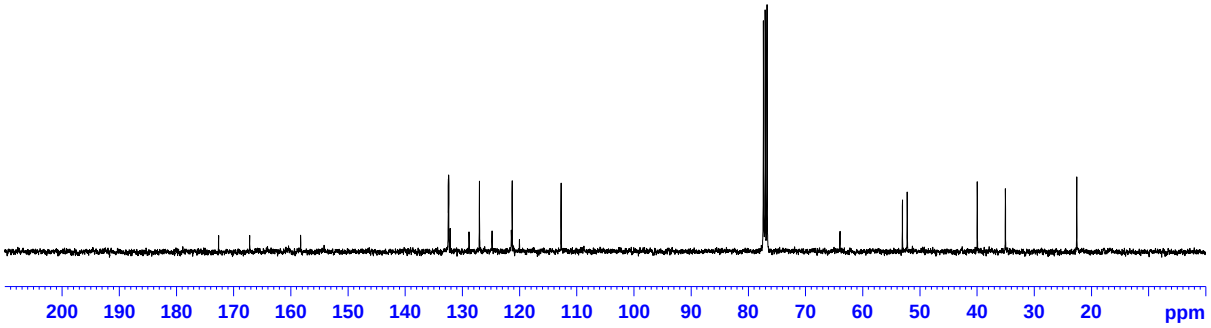




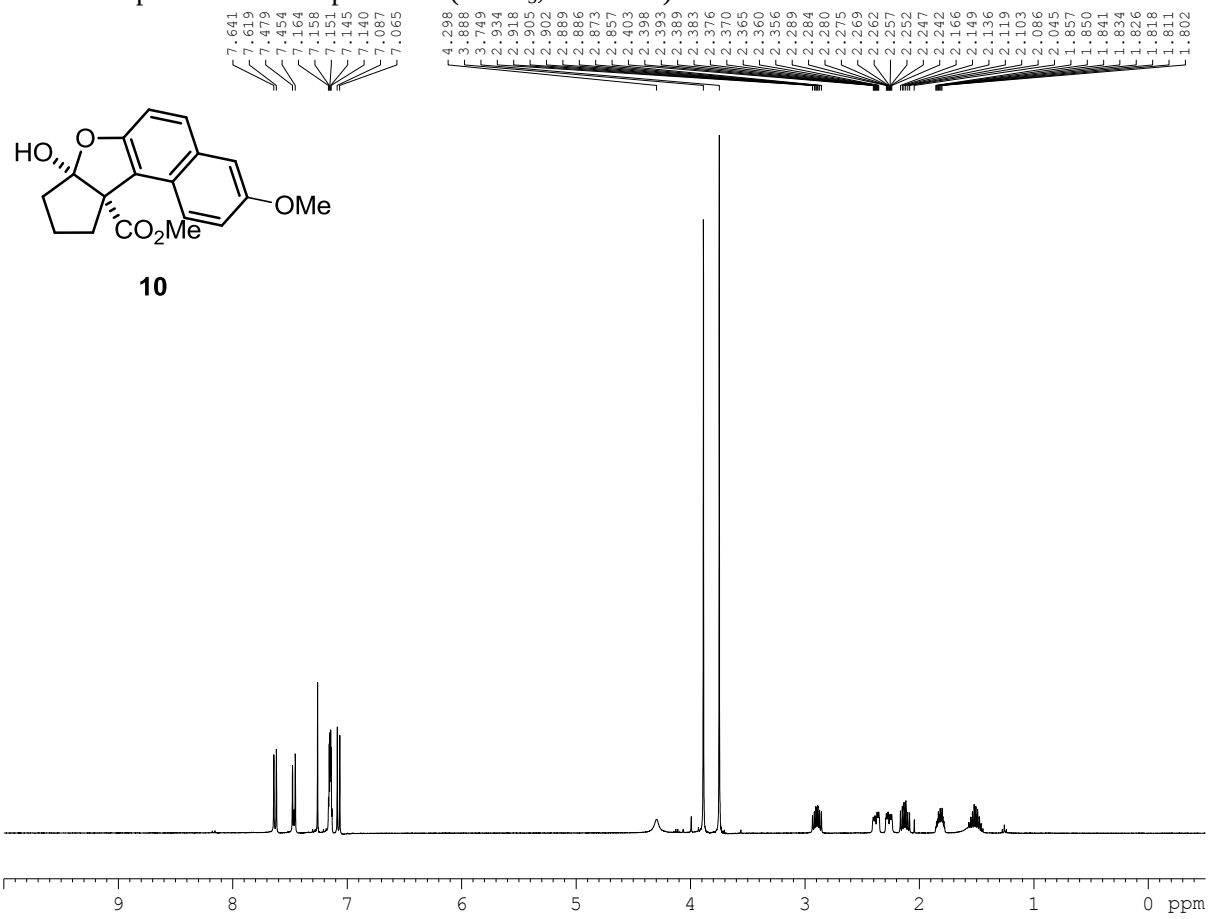
9



^{13}C - NMR spectrum for compound **9** ($CDCl_3$, 100 MHz)

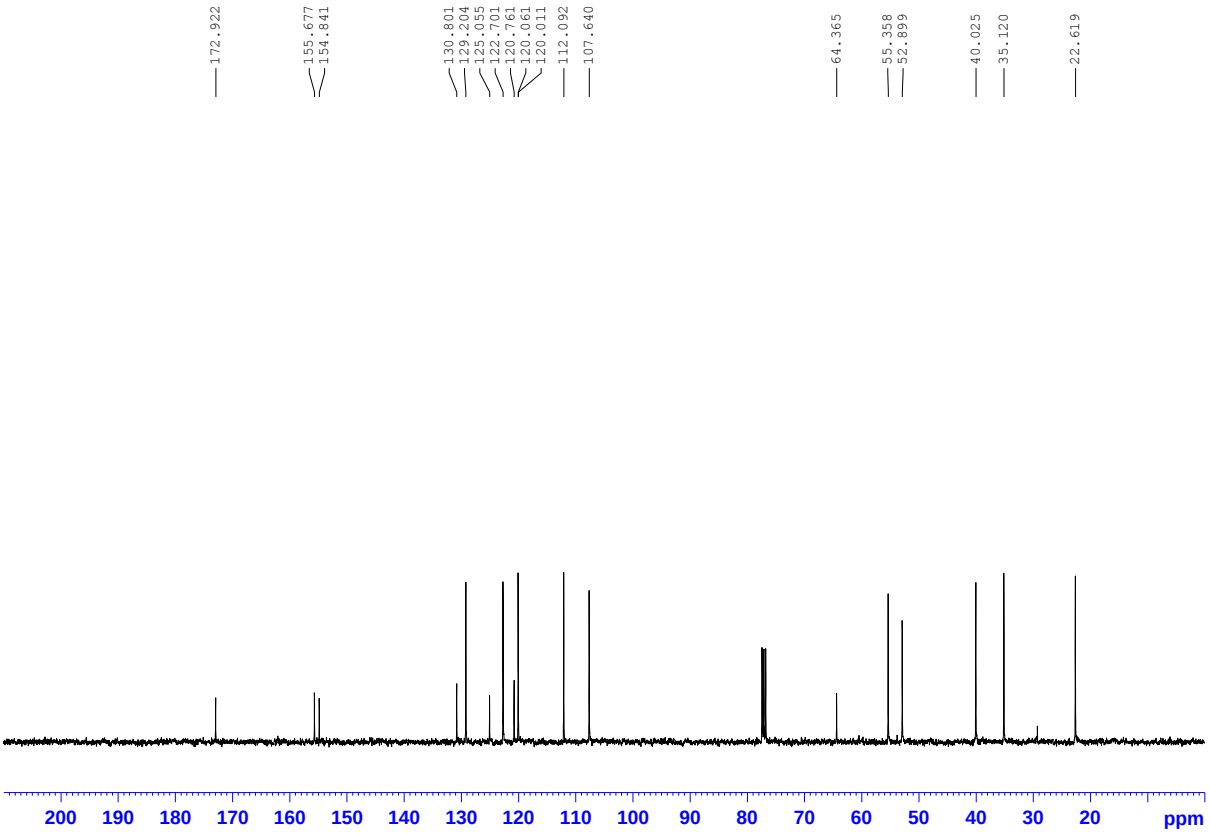


^{1}H- NMR spectrum for compound **10** ($CDCl_3$, 400 MHz)

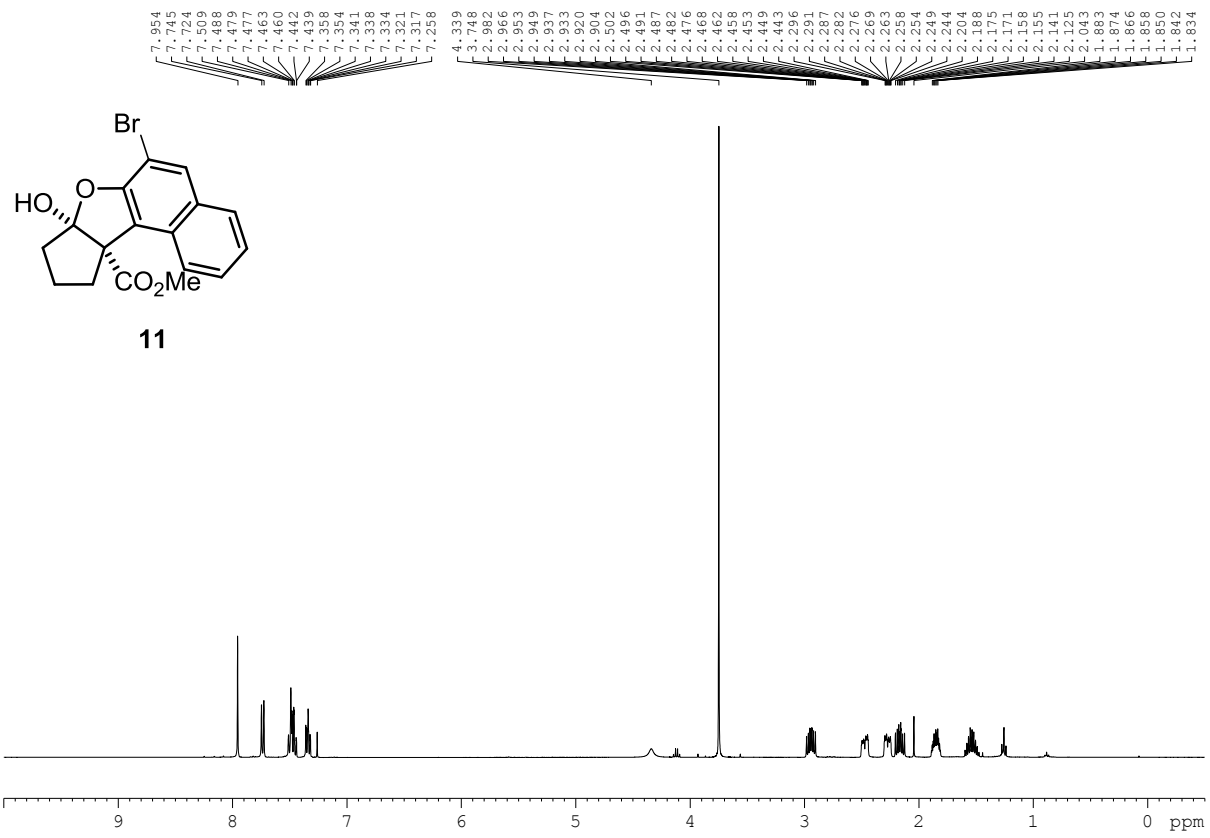


10

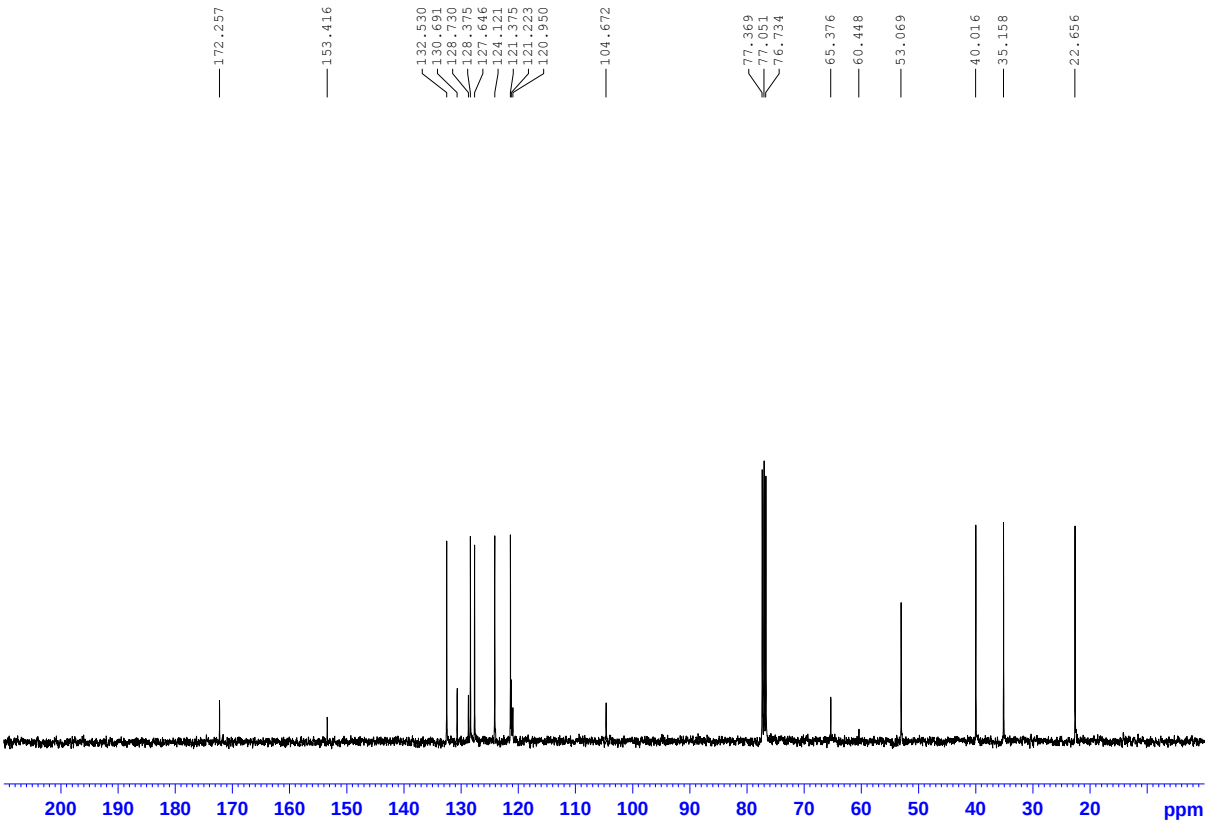
^{13}C - NMR spectrum for compound **10** ($CDCl_3$, 100 MHz)



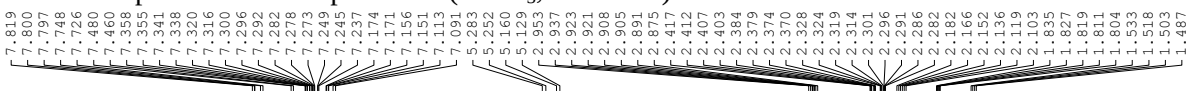
^{1}H- NMR spectrum for compound **11** ($CDCl_3$, 400 MHz)

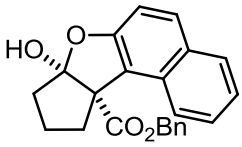


^{13}C- NMR spectrum for compound **11** ($CDCl_3$, 100 MHz)

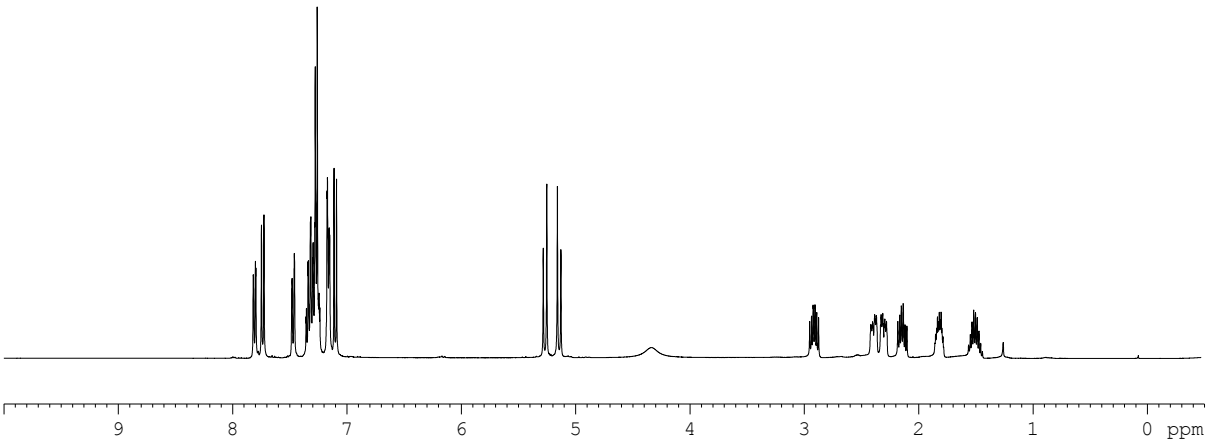


^{1}H- NMR spectrum for compound **12** ($CDCl_3$, 400 MHz)

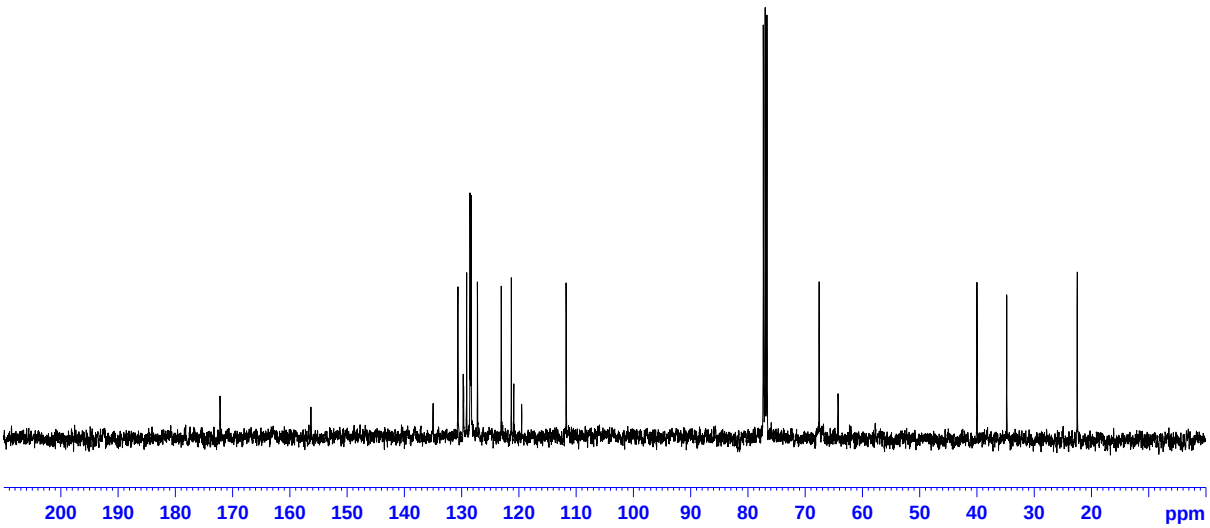




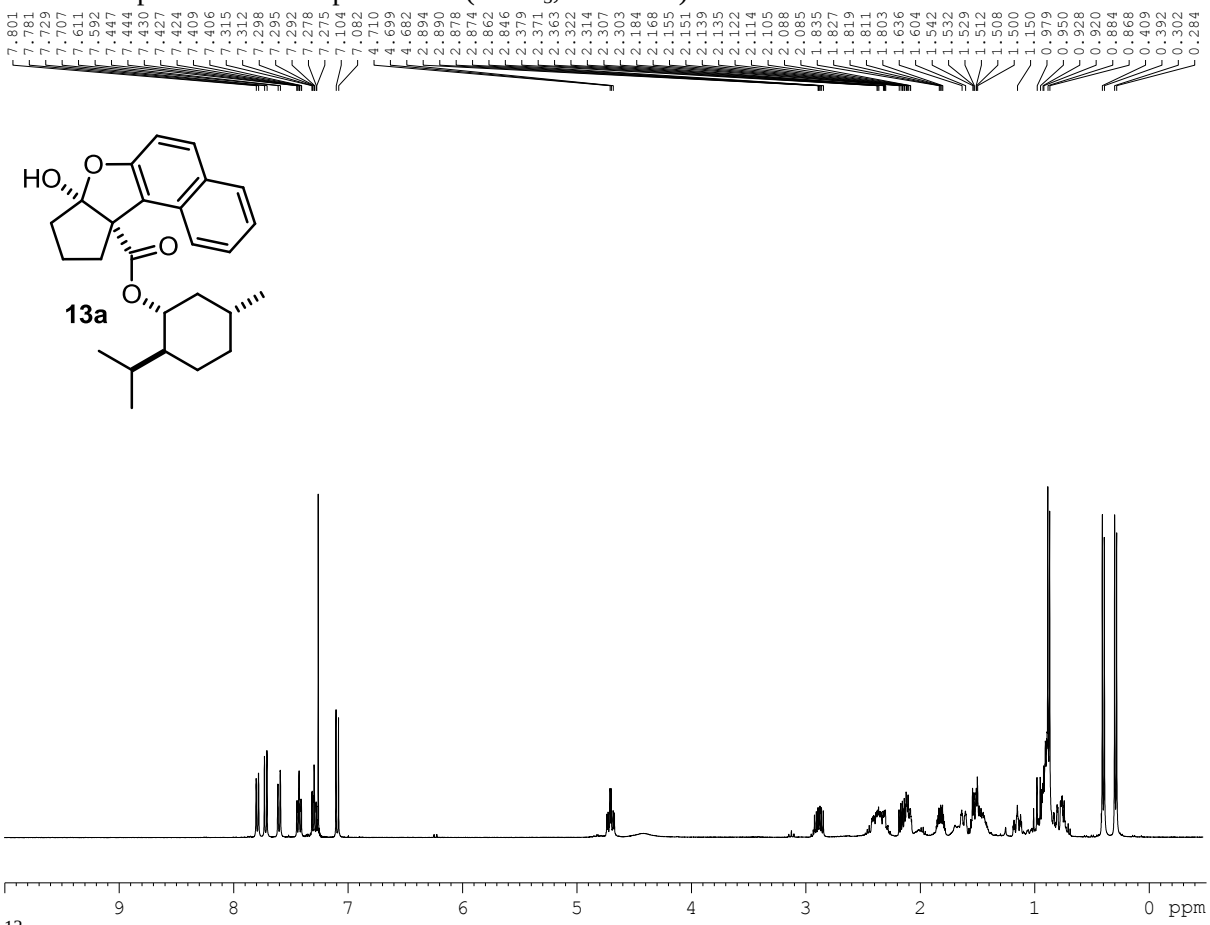
12



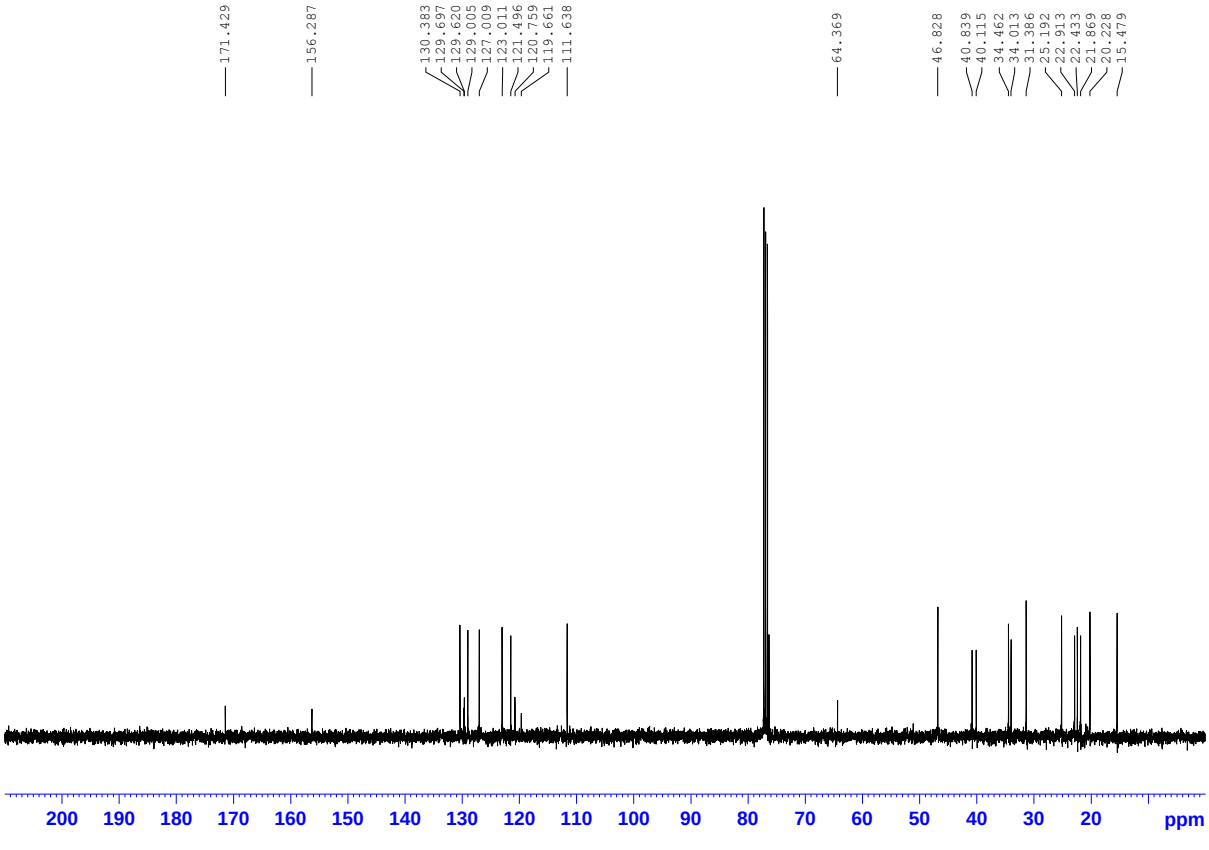
^{13}C - NMR spectrum for compound **12** ($CDCl_3$, 100 MHz)



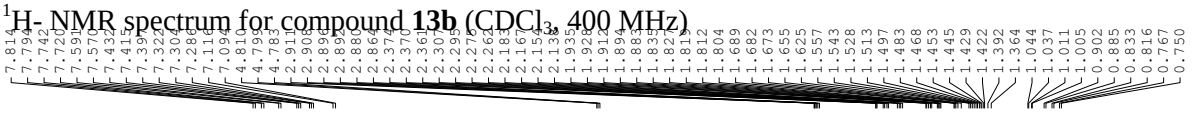
^{1}H- NMR spectrum for compound **13a** ($CDCl_3$, 400 MHz)

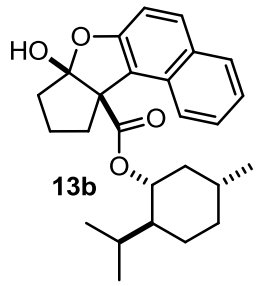


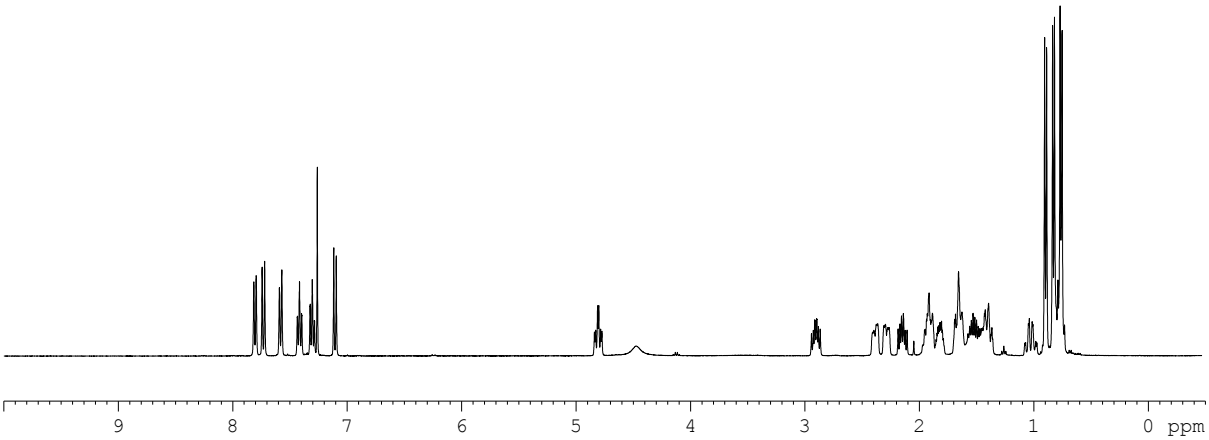
^{13}C - NMR spectrum for compound **13a** ($CDCl_3$, 100 MHz)



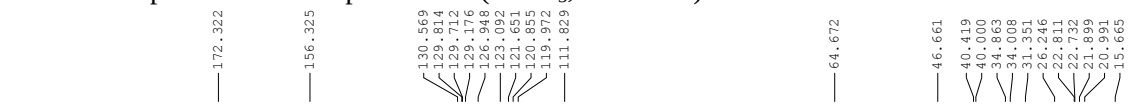
^{1}H- NMR spectrum for compound **13b** ($CDCl_3$, 400 MHz)

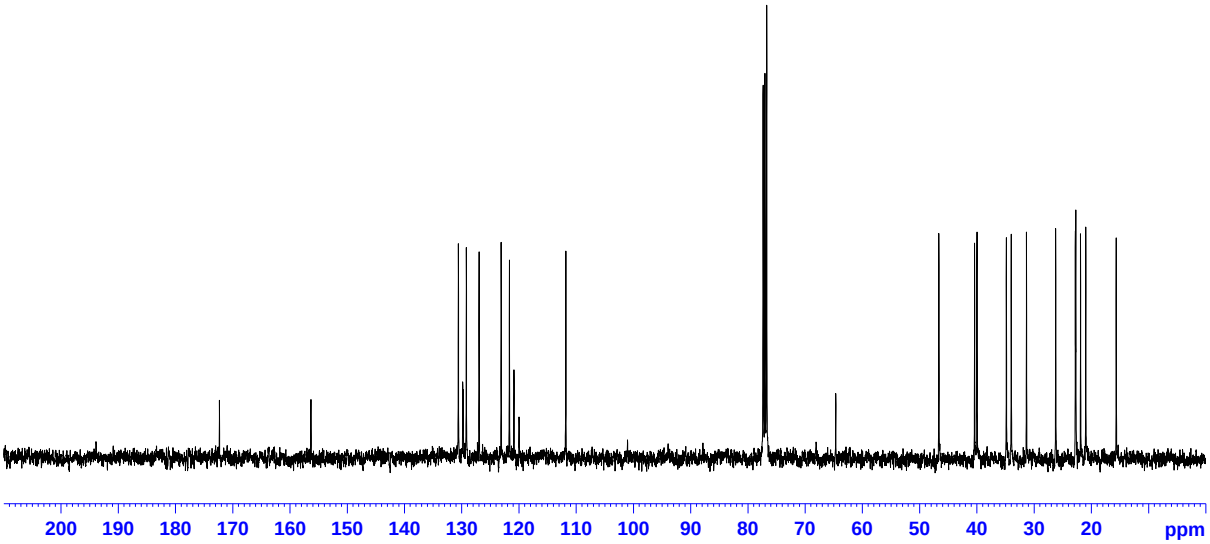




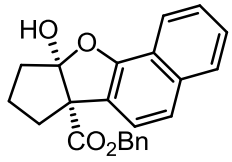


^{13}C - NMR spectrum for compound **13b** ($CDCl_3$, 100 MHz)

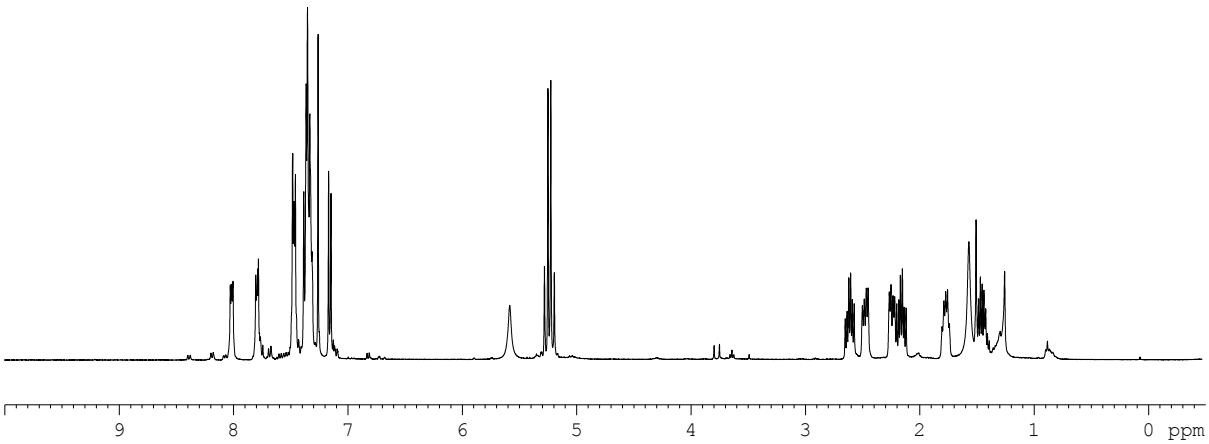




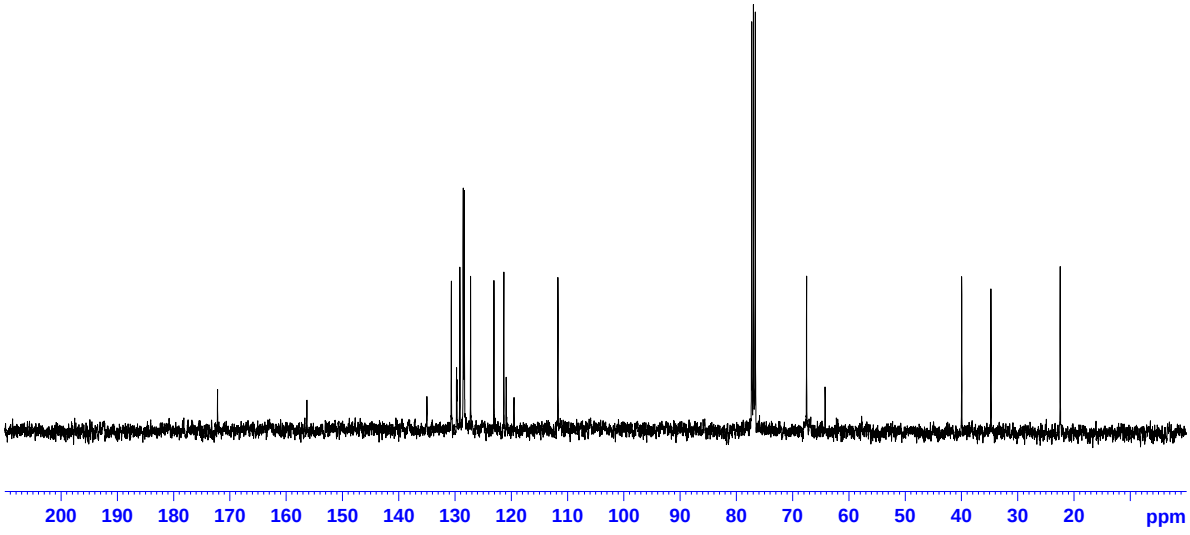
^{1}H- NMR spectrum for compound **14** ($CDCl_3$, 400 MHz)



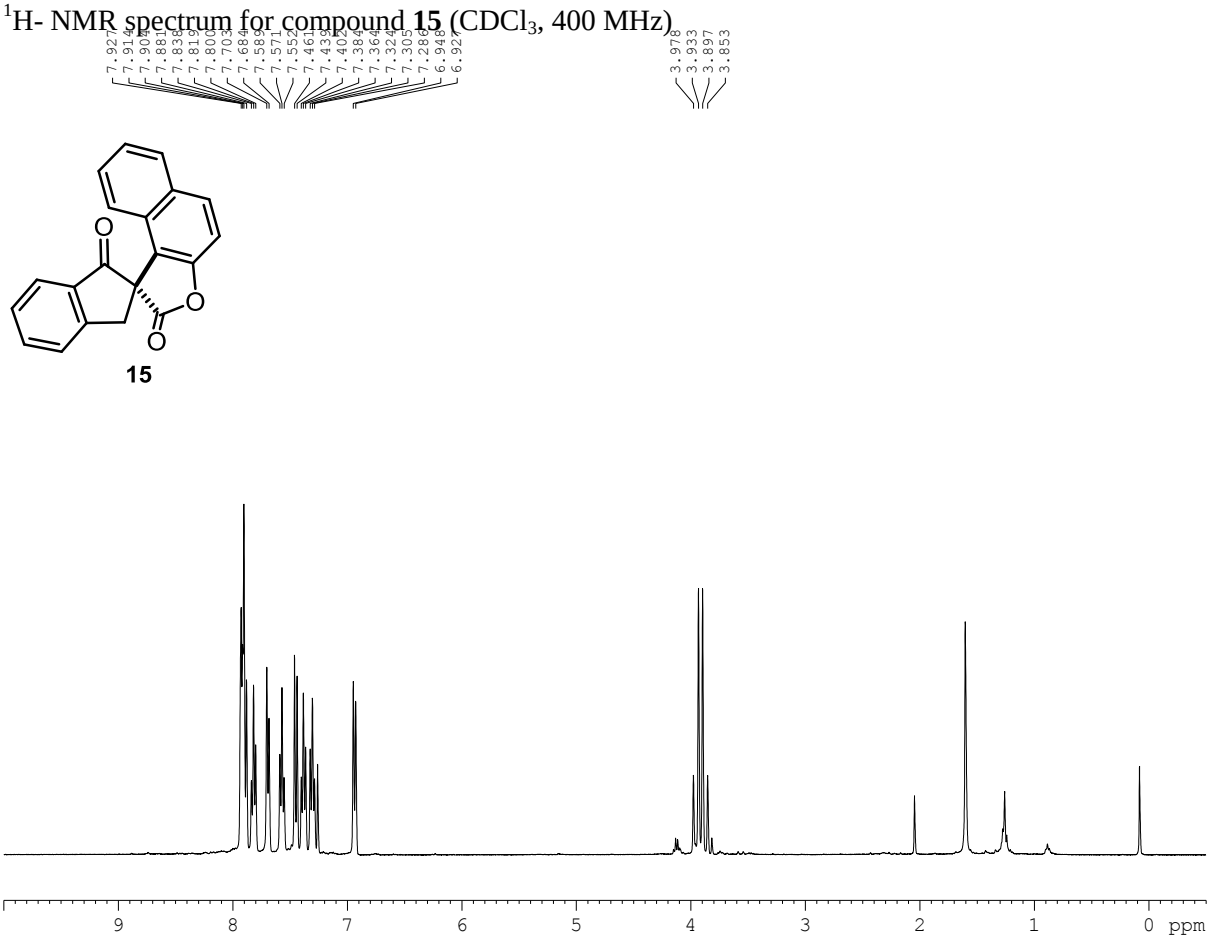
14



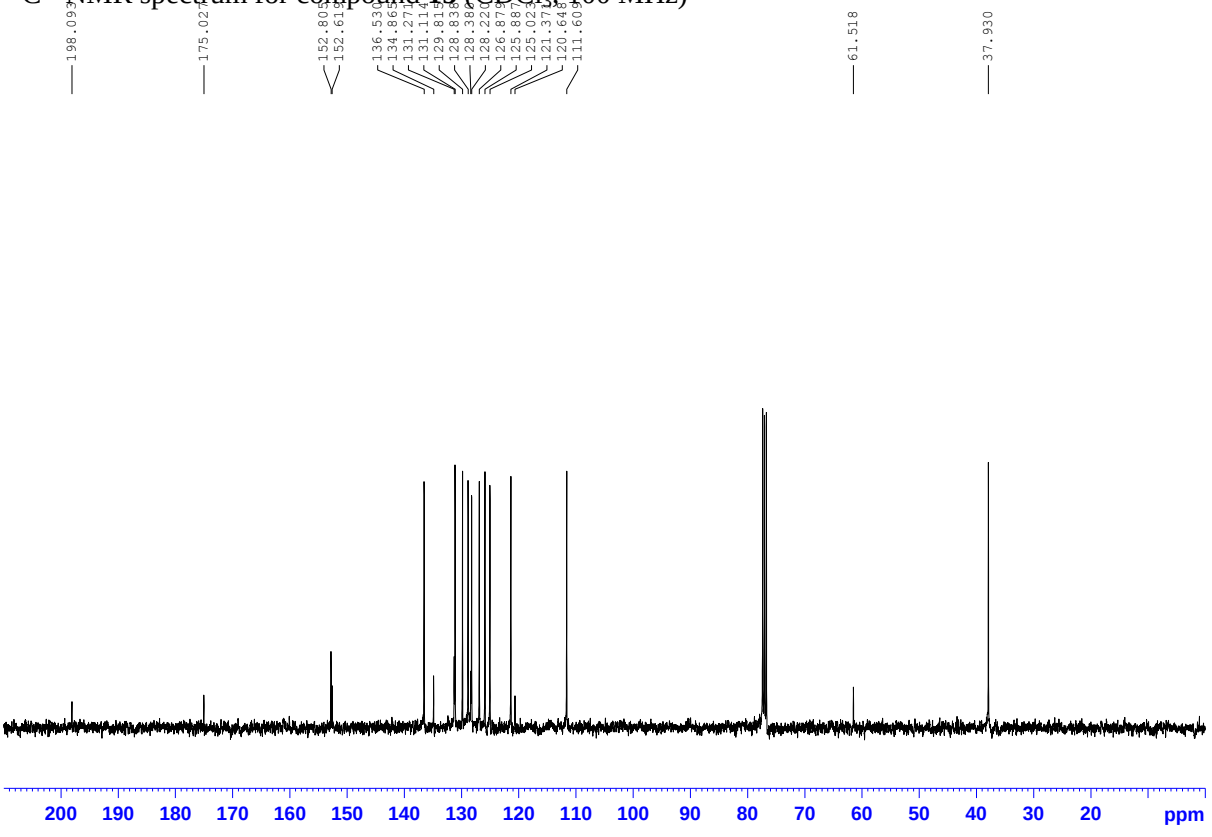
^{13}C - NMR spectrum for compound **14** ($CDCl_3$, 100 MHz)



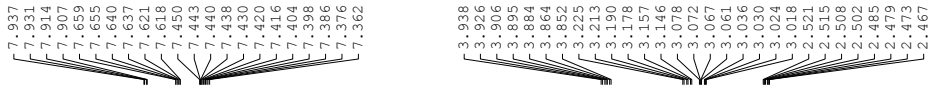
^{1}H- NMR spectrum for compound **15** ($CDCl_3$, 400 MHz)

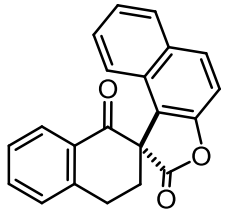


^{13}C - NMR spectrum for compound **15** ($CDCl_3$, 100 MHz)

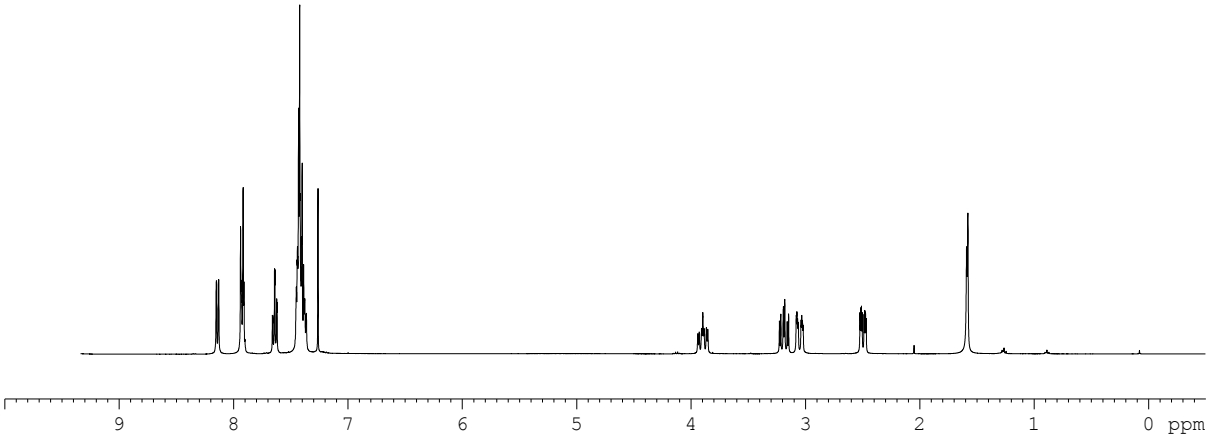


^{1}H- NMR spectrum for compound **16** ($CDCl_3$, 400 MHz)

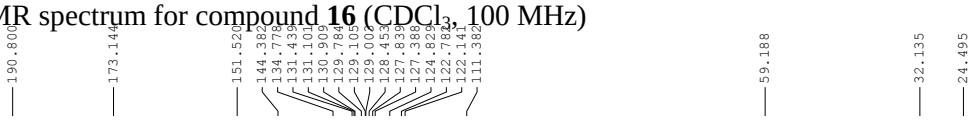


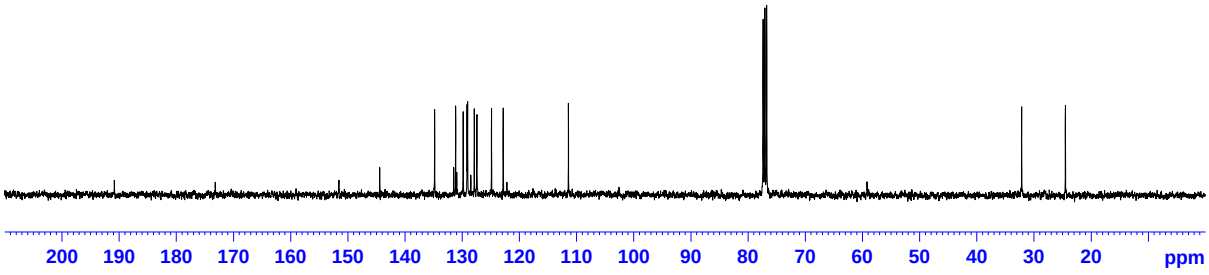


16

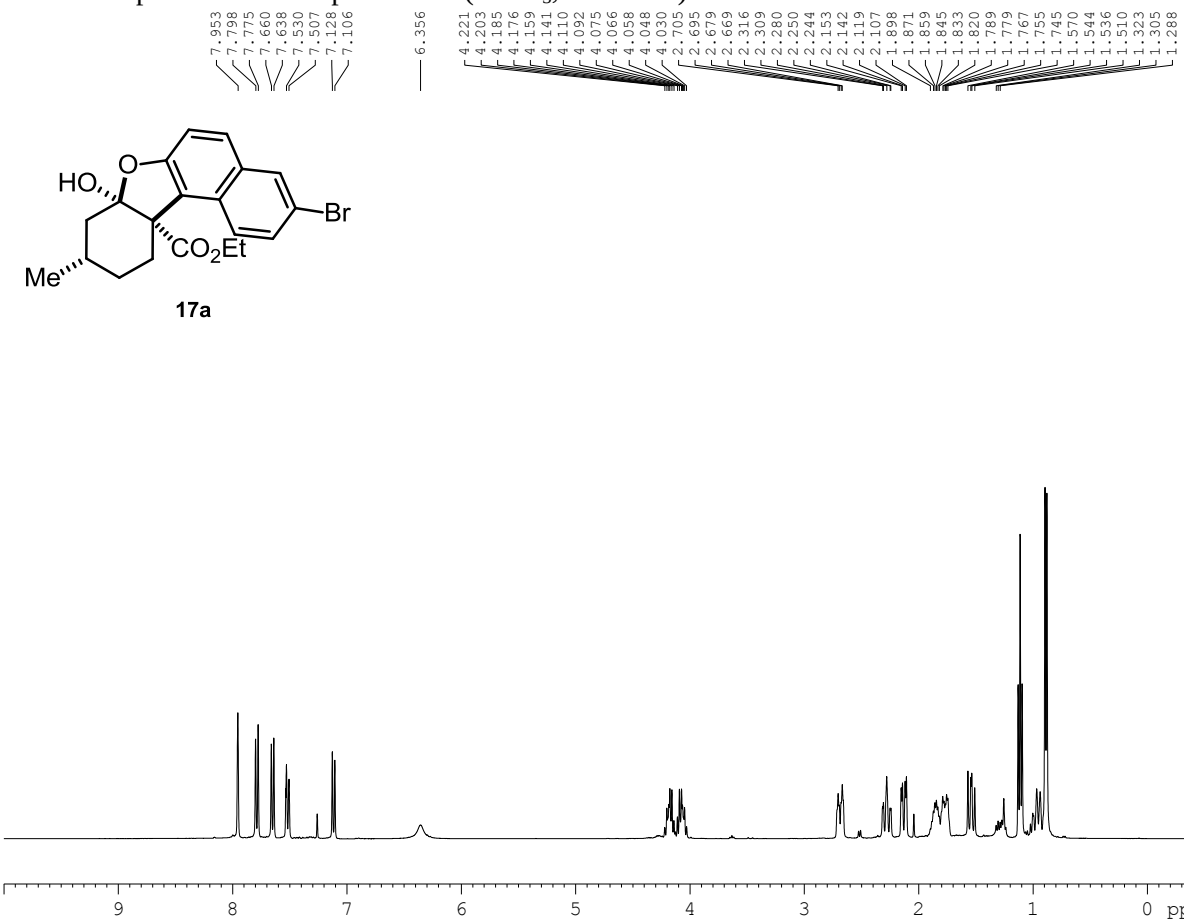


^{13}C - NMR spectrum for compound **16** ($CDCl_3$, 100 MHz)



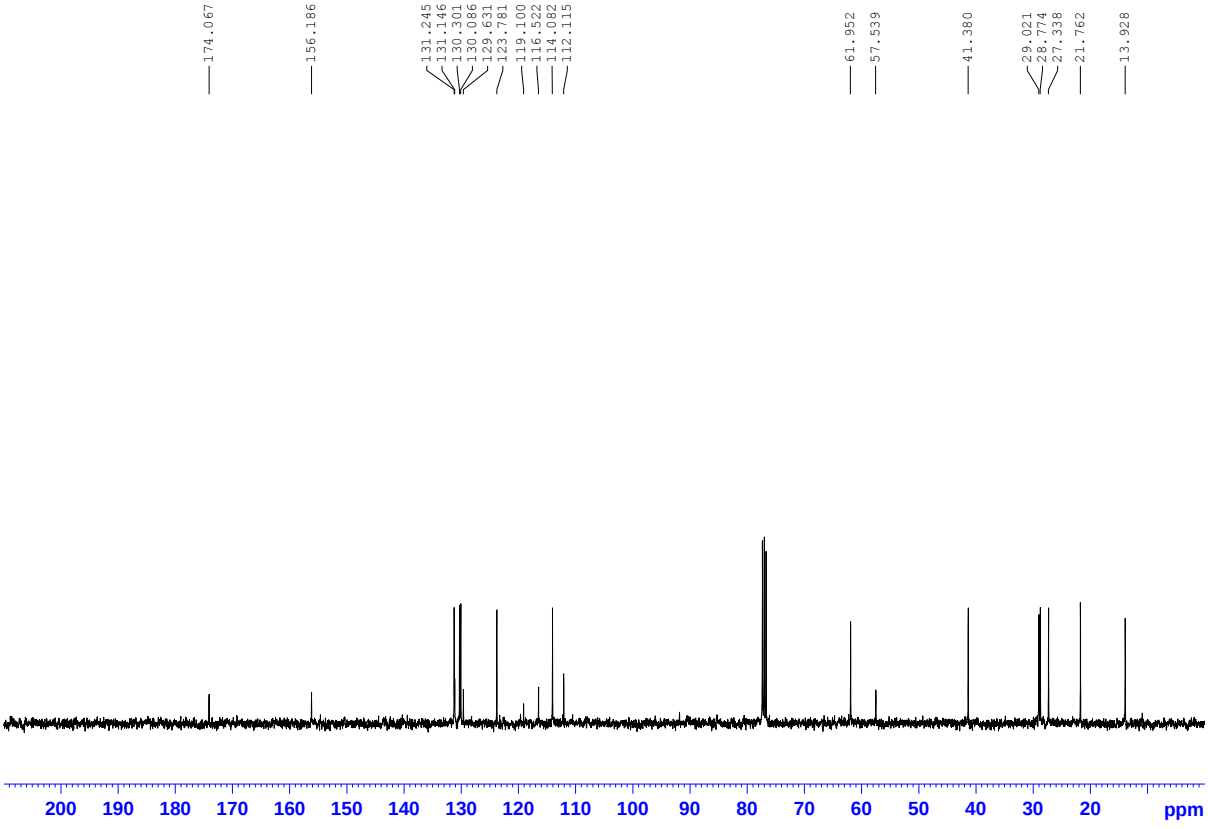


^{1}H- NMR spectrum for compound **17a** ($CDCl_3$, 400 MHz)

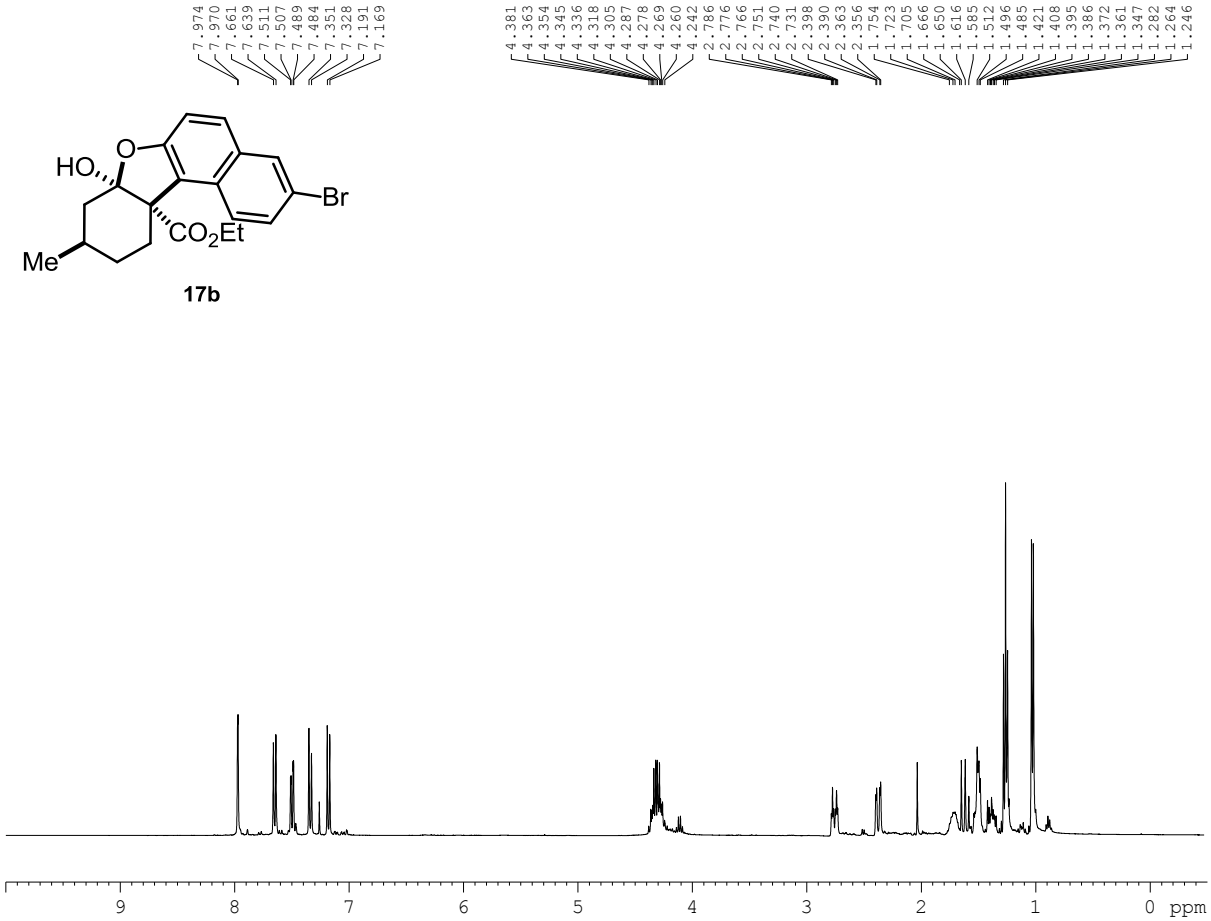


17a

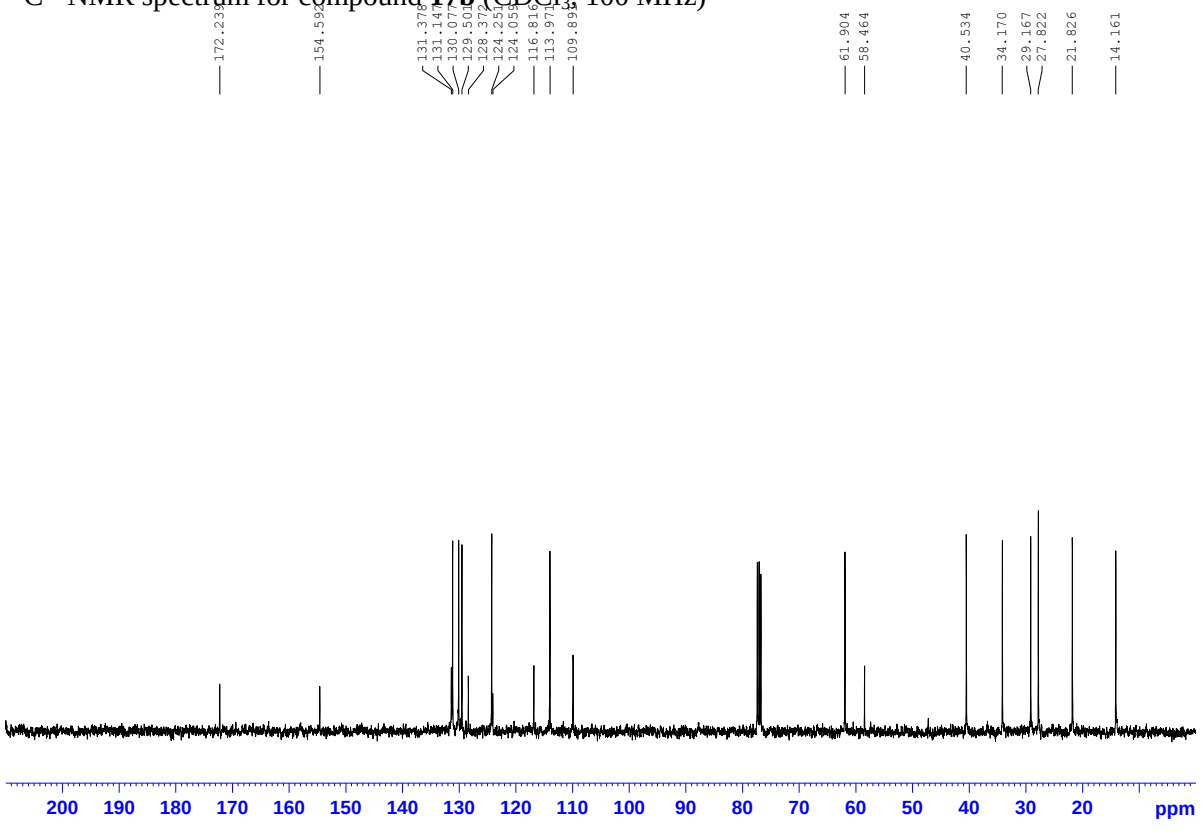
^{13}C - NMR spectrum for compound **17a** ($CDCl_3$, 100 MHz)



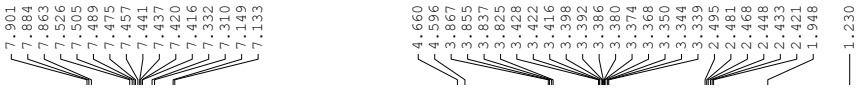
^{1}H- NMR spectrum for compound **17b** ($CDCl_3$, 400 MHz)

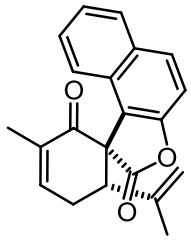


^{13}C - NMR spectrum for compound **17b** ($CDCl_3$, 100 MHz)

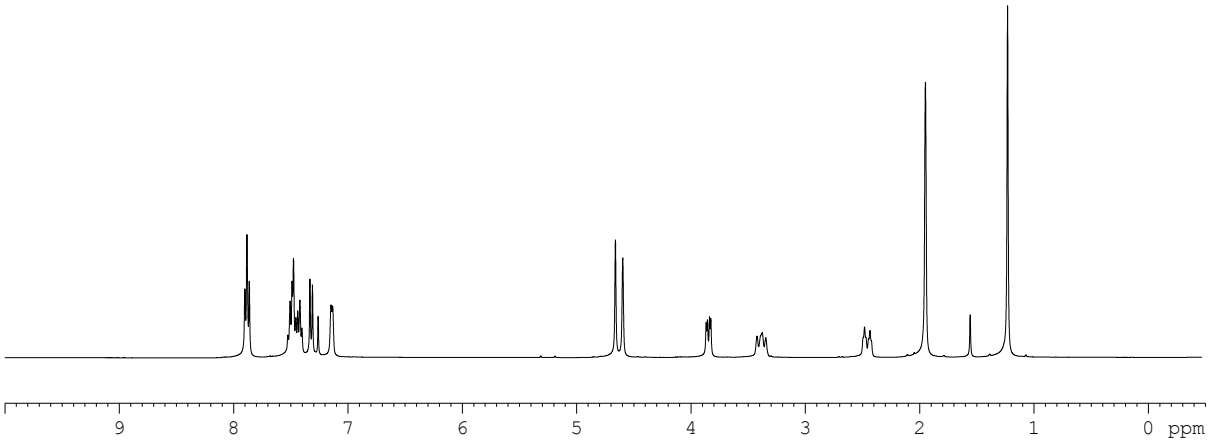


^{1}H- NMR spectrum for compound **18** ($CDCl_3$, 400 MHz)

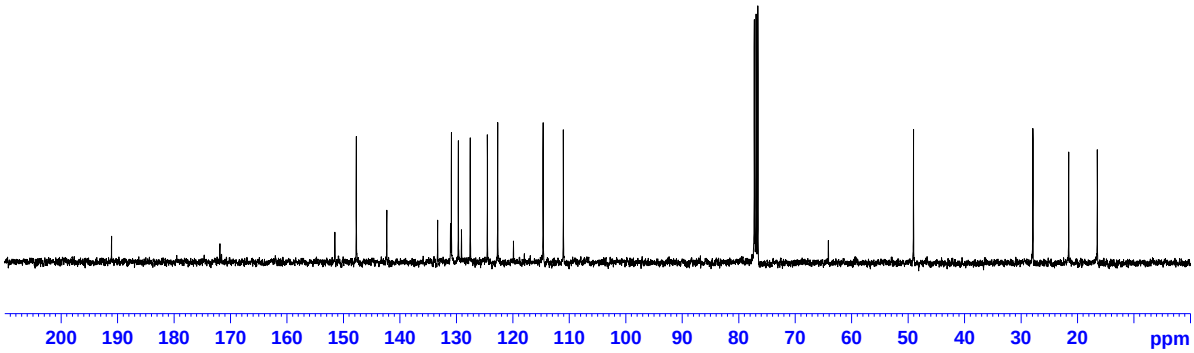




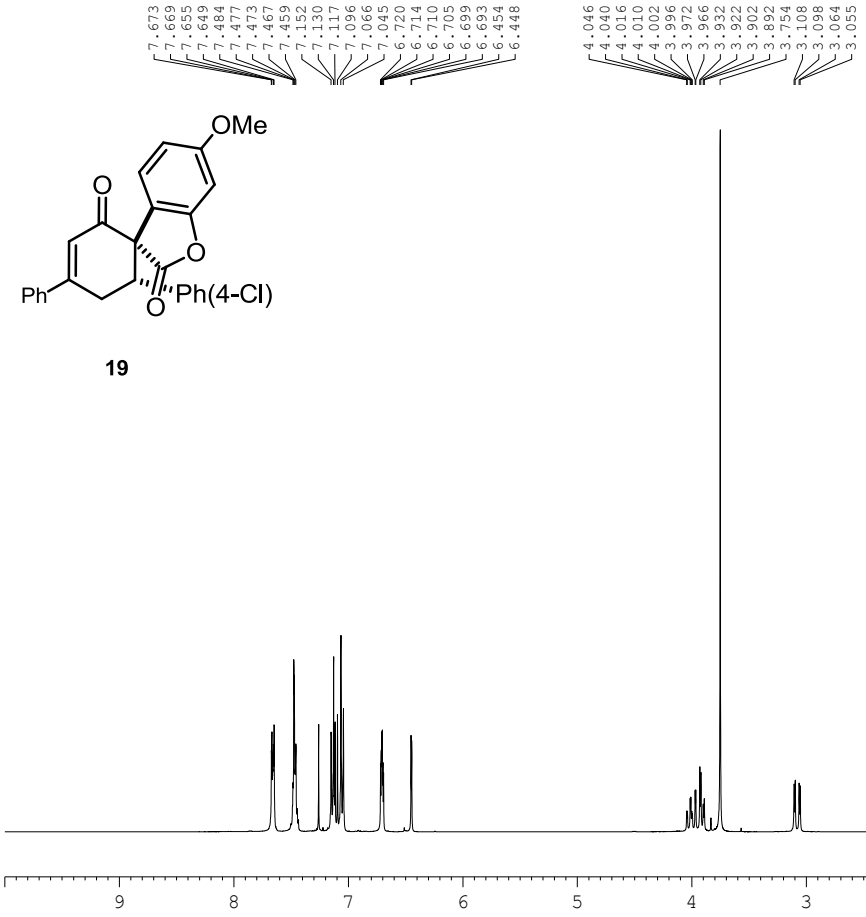
18



^{13}C - NMR spectrum for compound **18** ($CDCl_3$, 100 MHz)

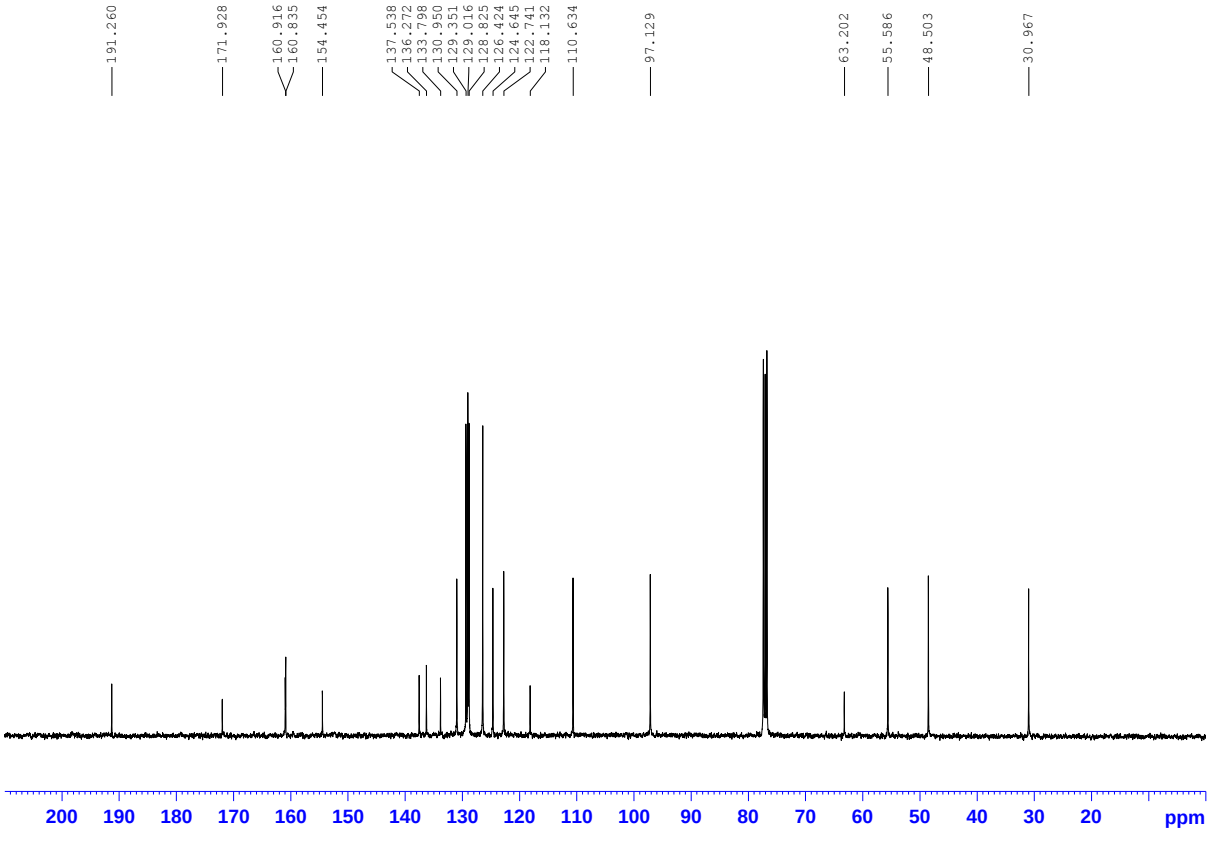


^{1}H- NMR spectrum for compound **19** ($CDCl_3$, 400 MHz)

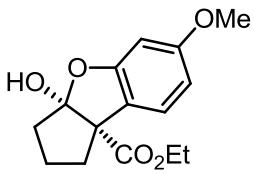


19

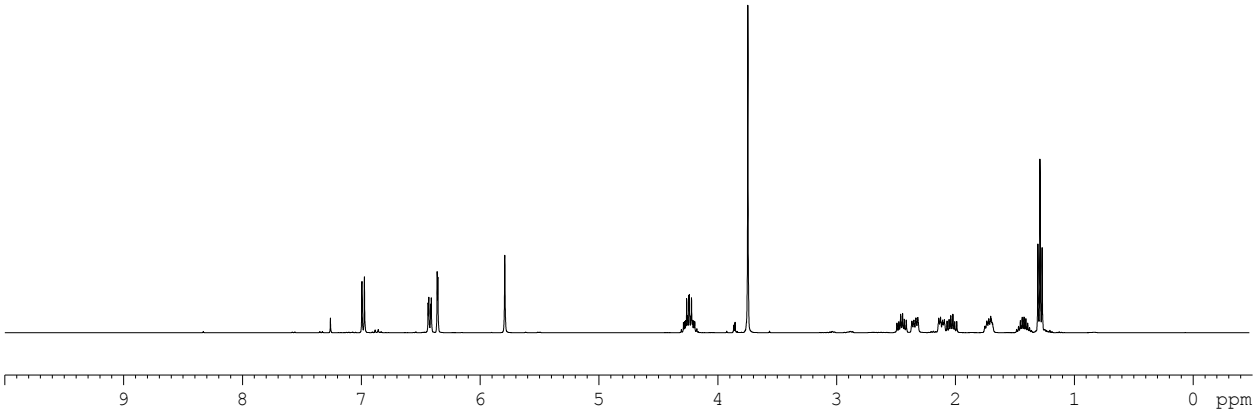
^{13}C - NMR spectrum for compound **19** ($CDCl_3$, 100 MHz)



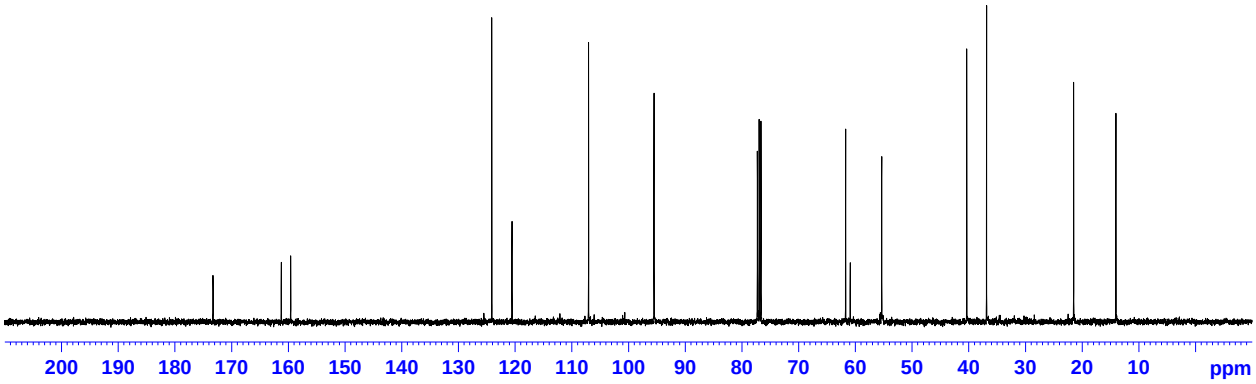
^{1}H- NMR spectrum for compound **20a** ($CDCl_3$, 400 MHz)



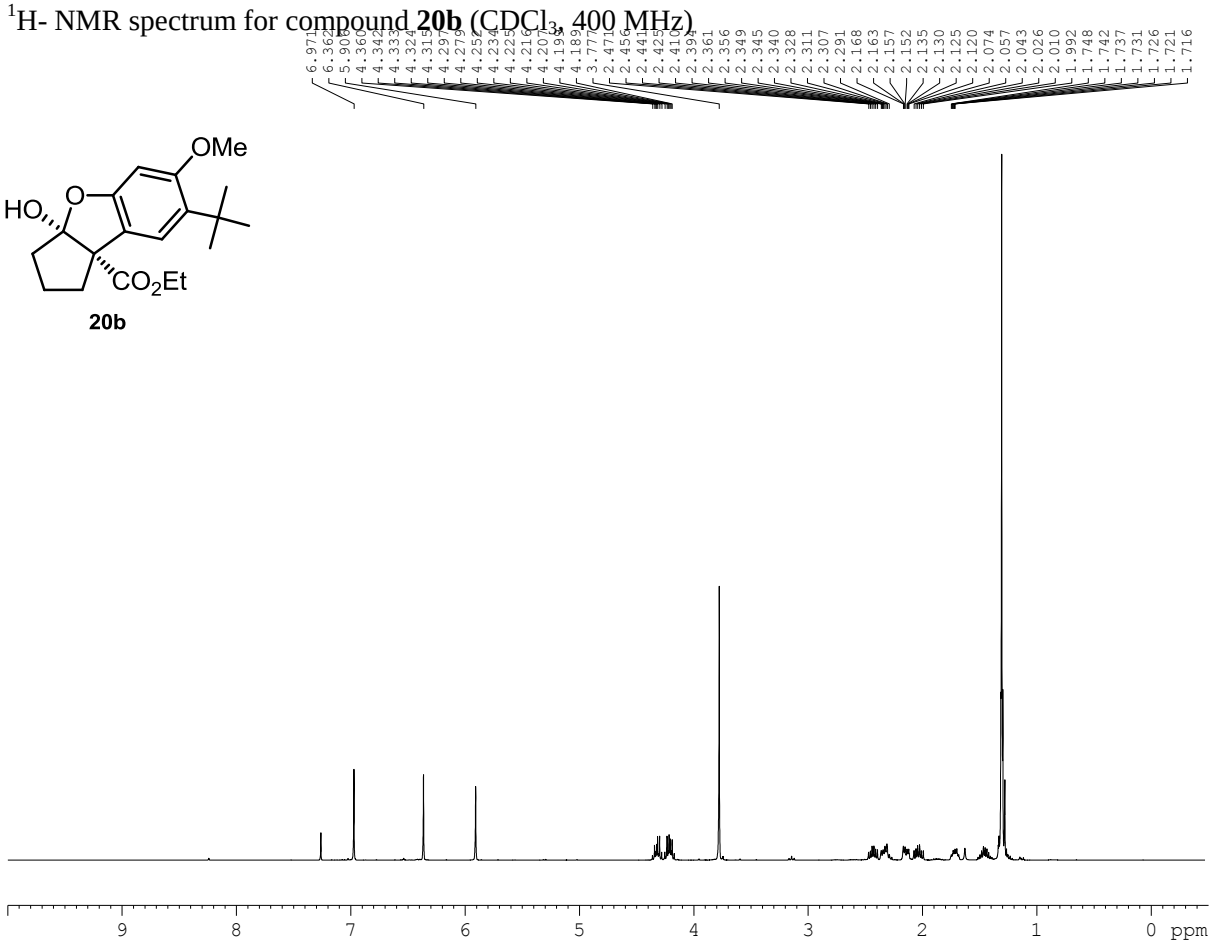
20a



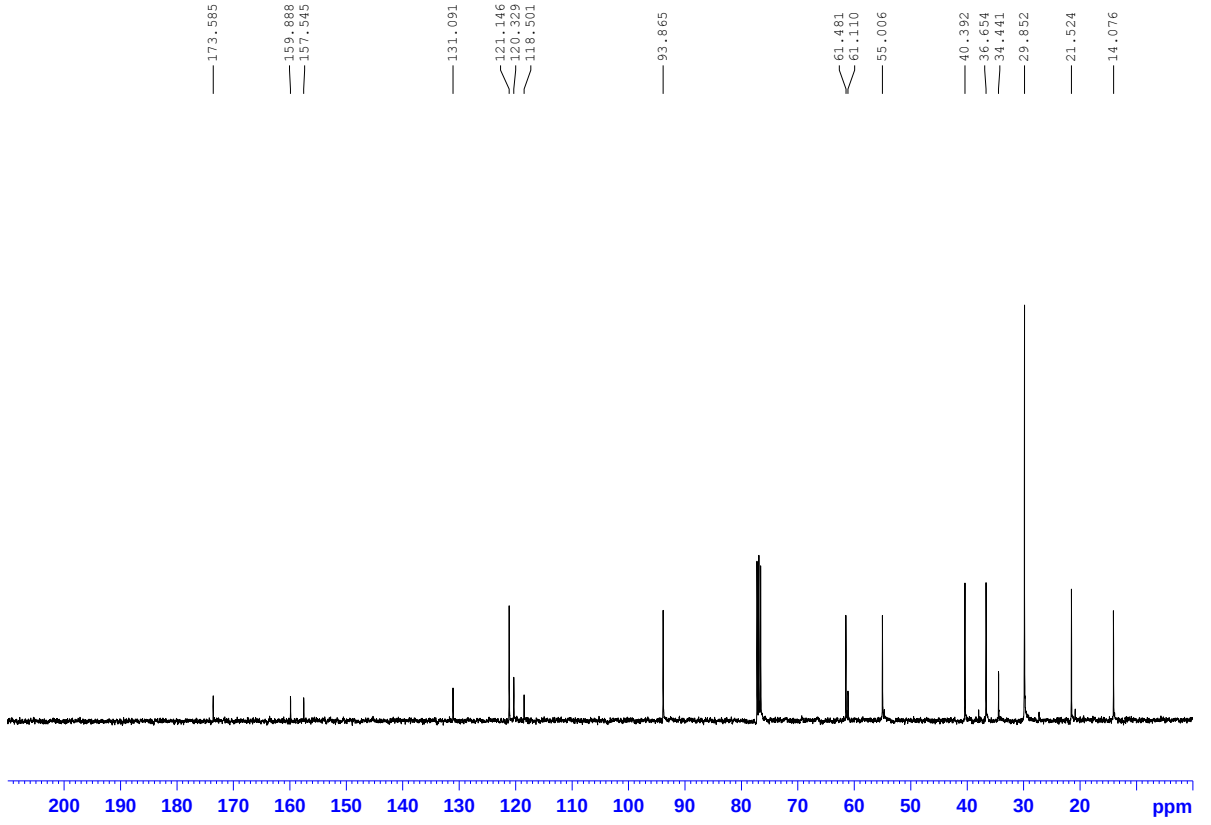
^{13}C- NMR spectrum for compound **20a** ($CDCl_3$, 100 MHz)



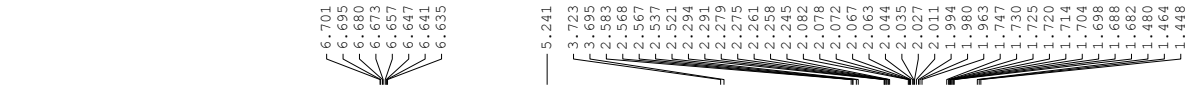
^{1}H- NMR spectrum for compound **20b** ($CDCl_3$, 400 MHz)

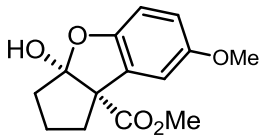


^{13}C- NMR spectrum for compound **20b** ($CDCl_3$, 100 MHz)

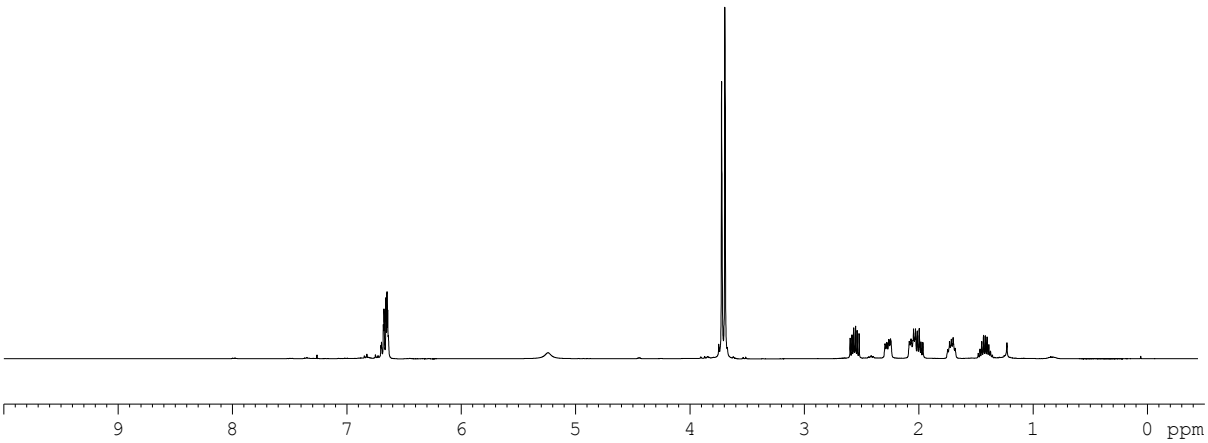


^{1}H- NMR spectrum for compound **21** ($CDCl_3$, 400 MHz)

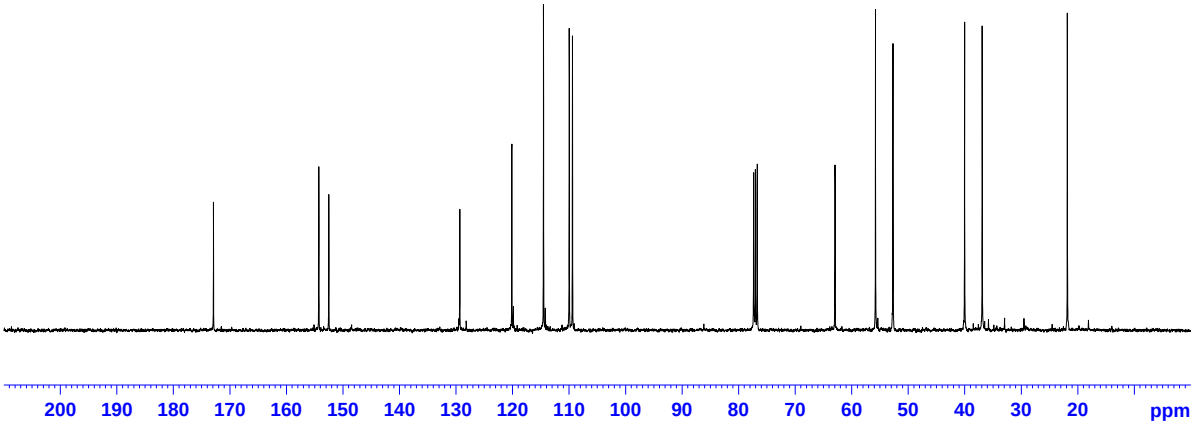




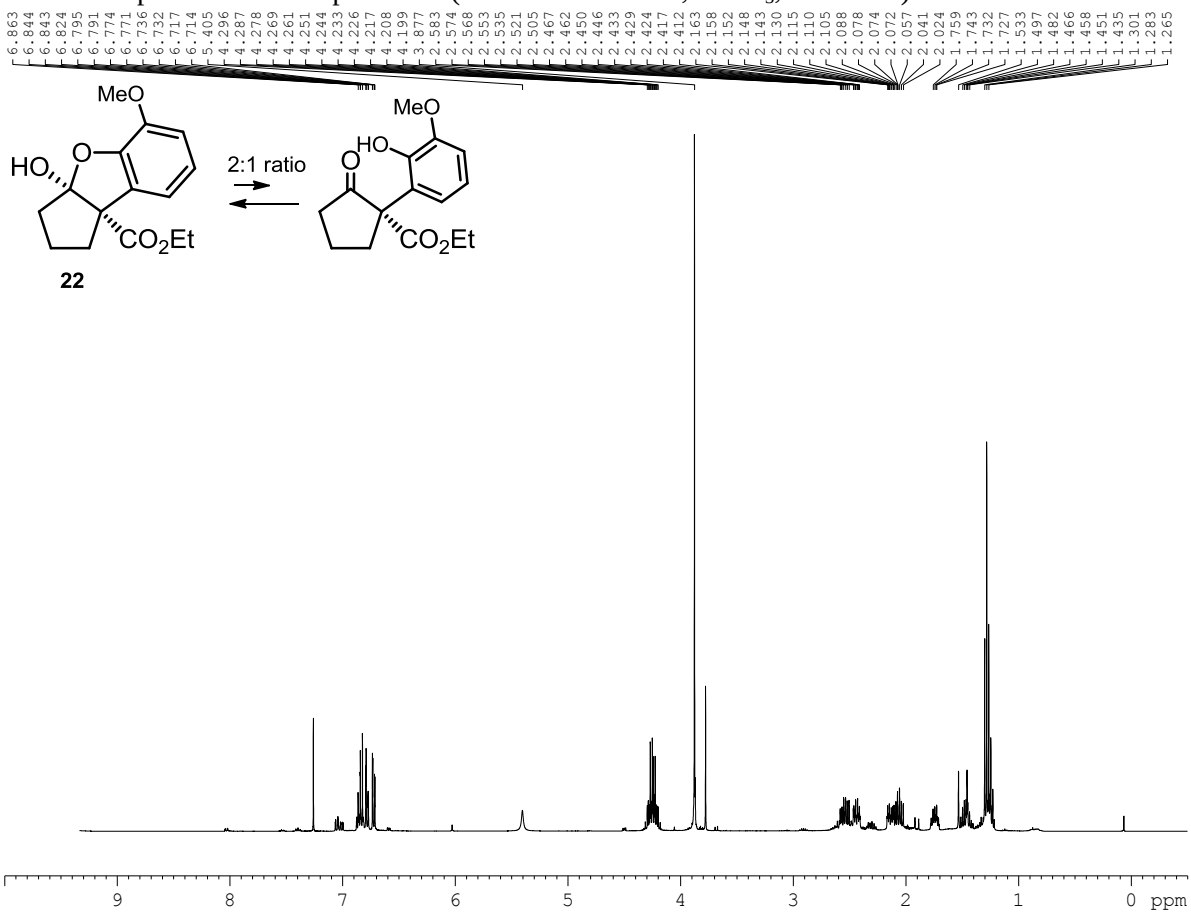
21



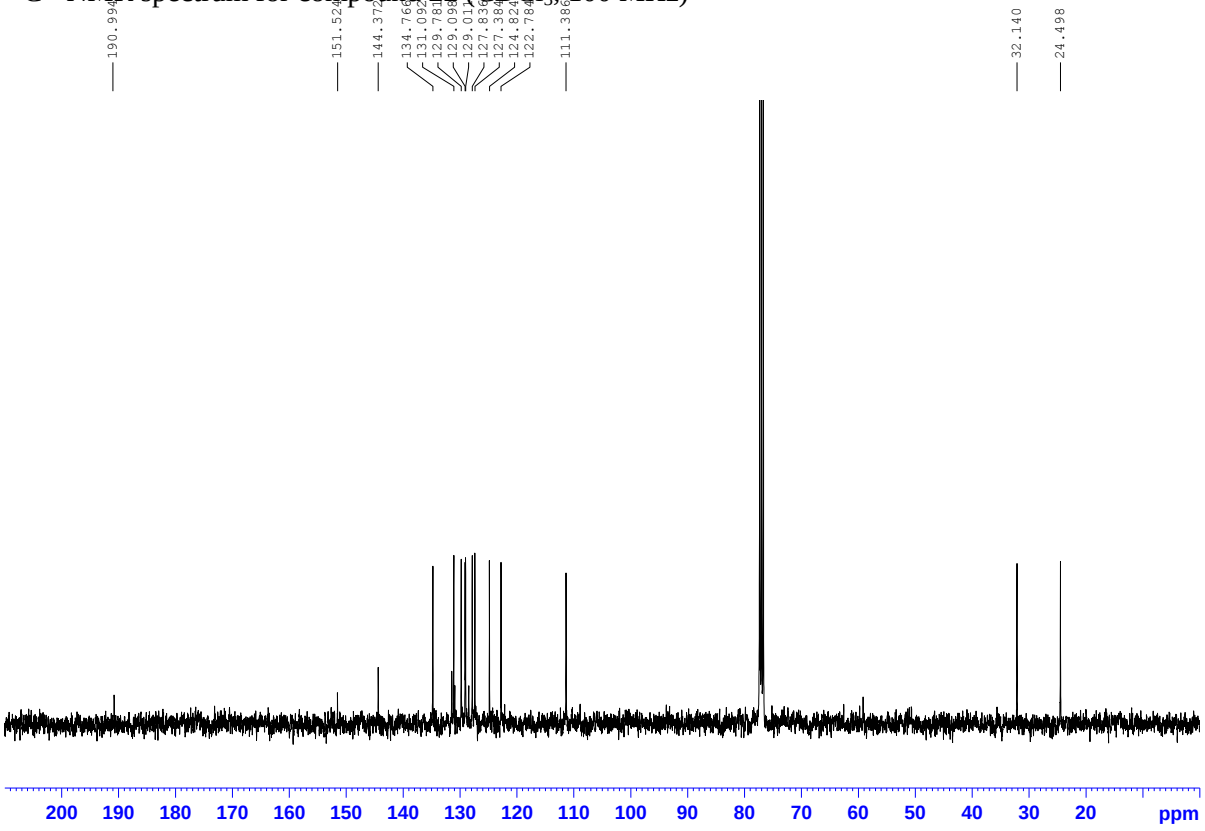
^{13}C - NMR spectrum for compound **21** ($CDCl_3$, 100 MHz)



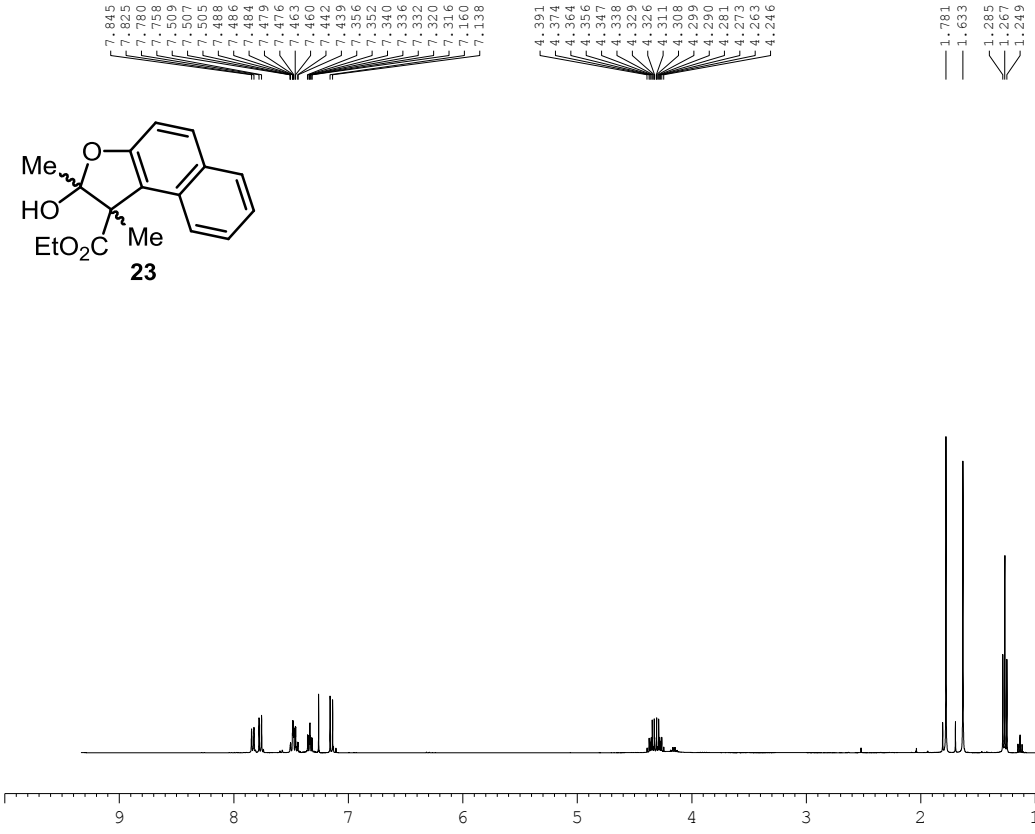
^{1}H- NMR spectrum for compound **22** (mixture of isomers, $CDCl_3$, 400 MHz)



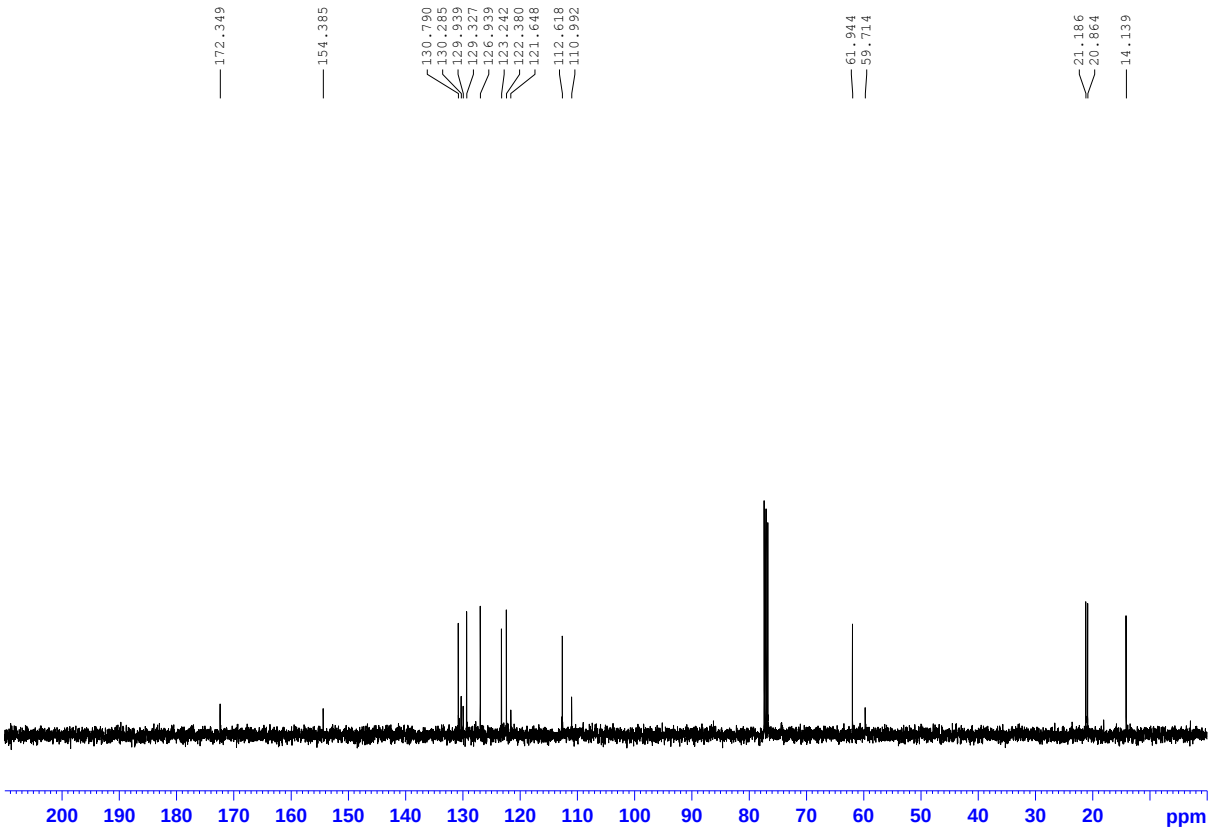
^{13}C - NMR spectrum for compound **22** ($CDCl_3$, 100 MHz)



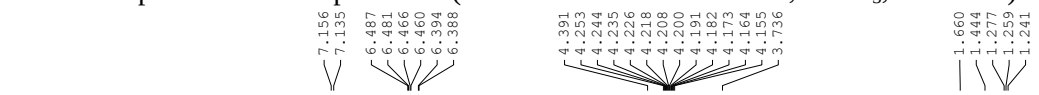
^{1}H- NMR spectrum for compound **23** (mixture of diastereoisomers, $CDCl_3$, 400 MHz)

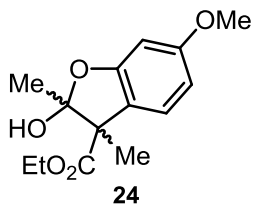


^{13}C- NMR spectrum for compound **23** ($CDCl_3$, 100 MHz)

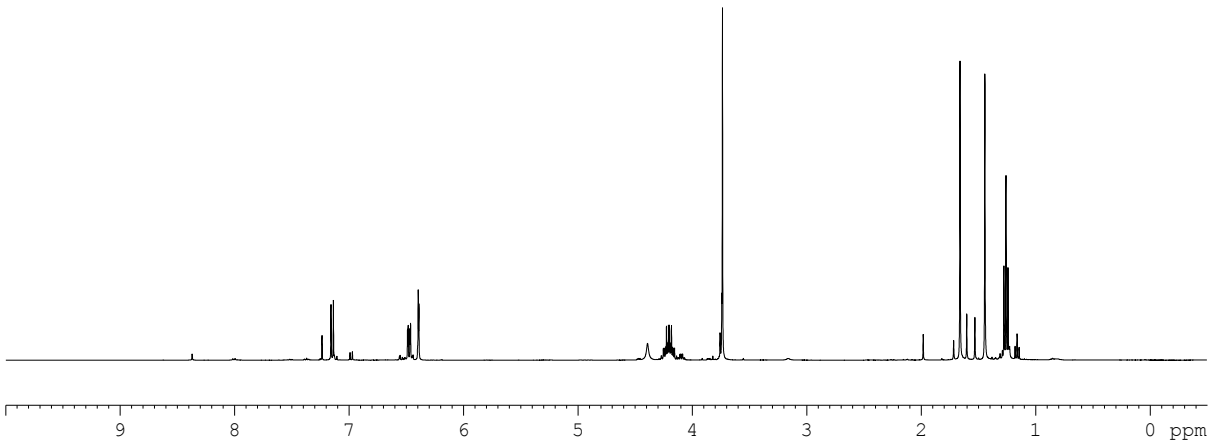


^{1}H- NMR spectrum for compound **24** (mixture of diastereoisomers, $CDCl_3$, 400 MHz)

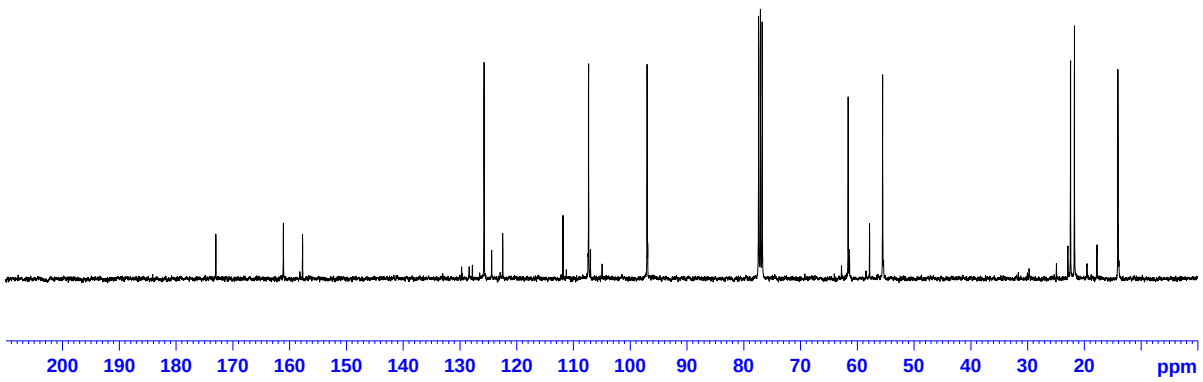




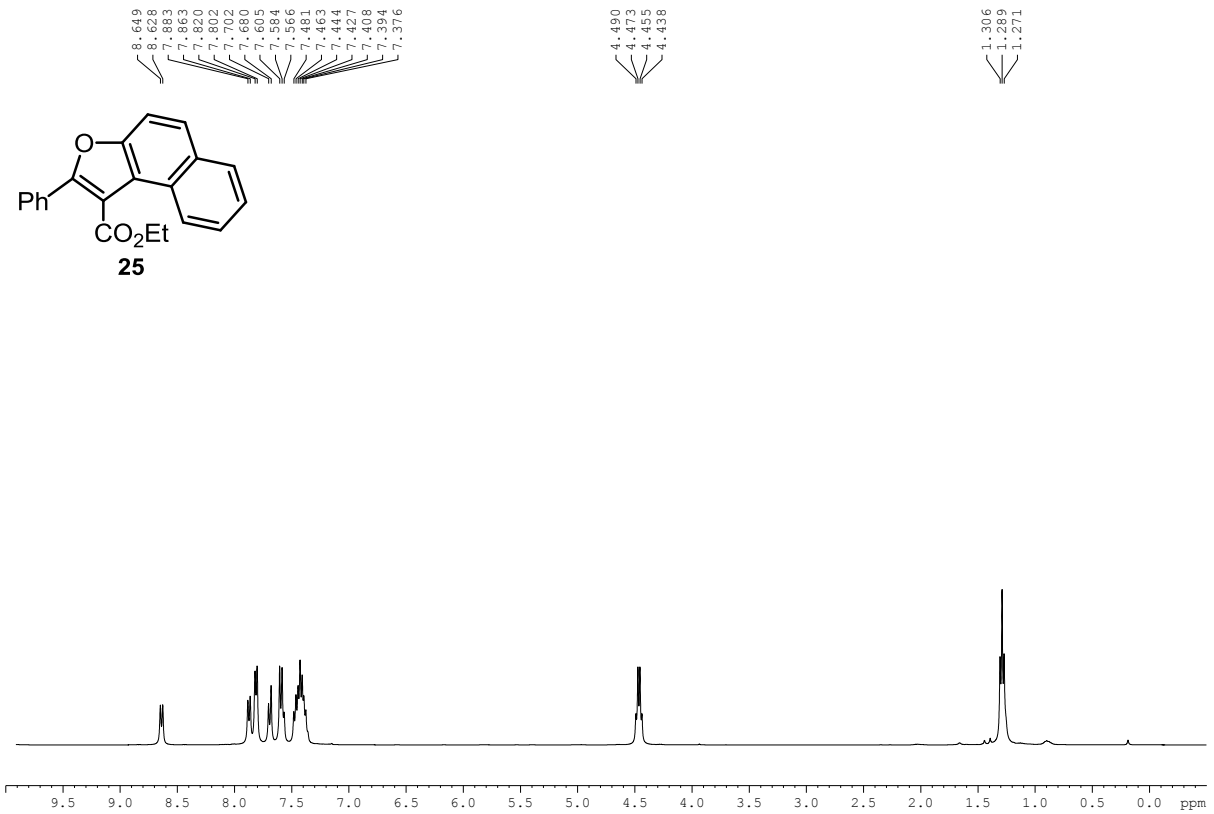
24



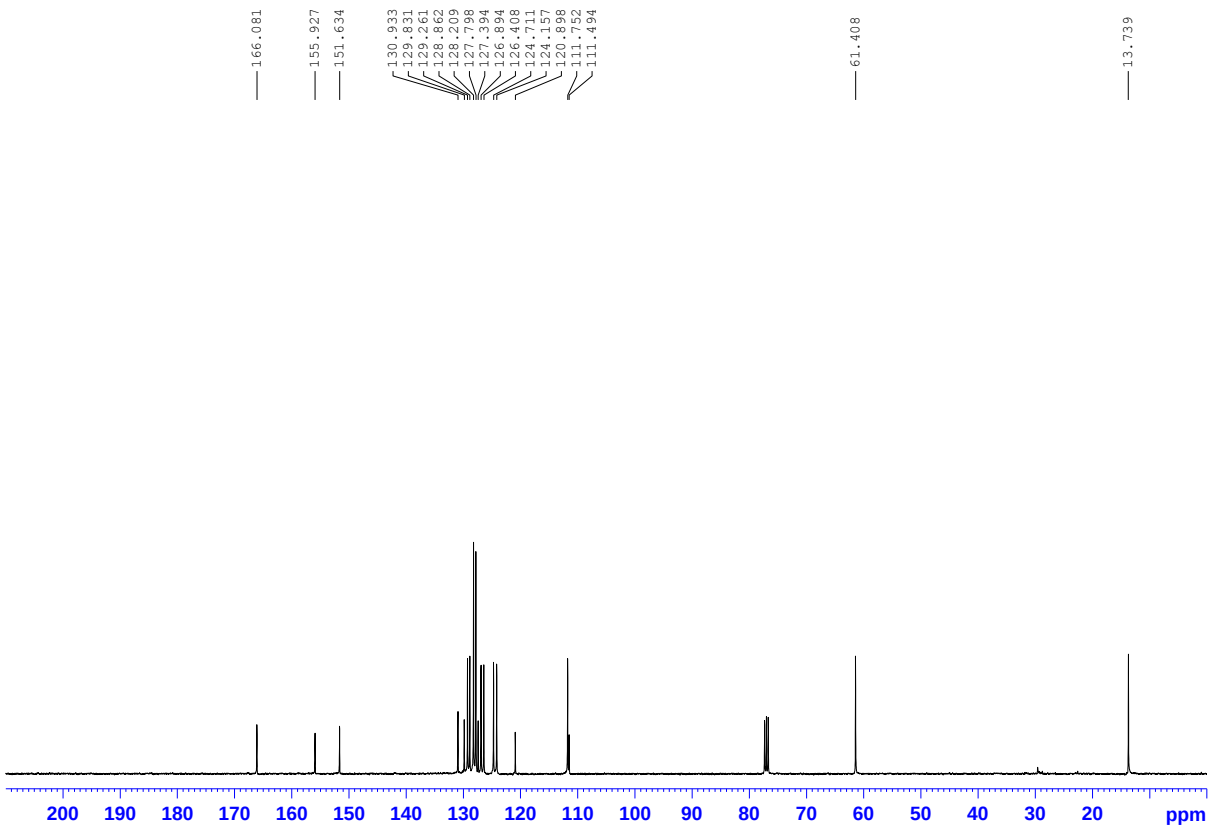
^{13}C - NMR spectrum for compound **24** ($CDCl_3$, 100 MHz)



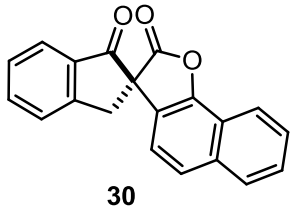
^{1}H- NMR spectrum for compound **25** ($CDCl_3$, 400 MHz)



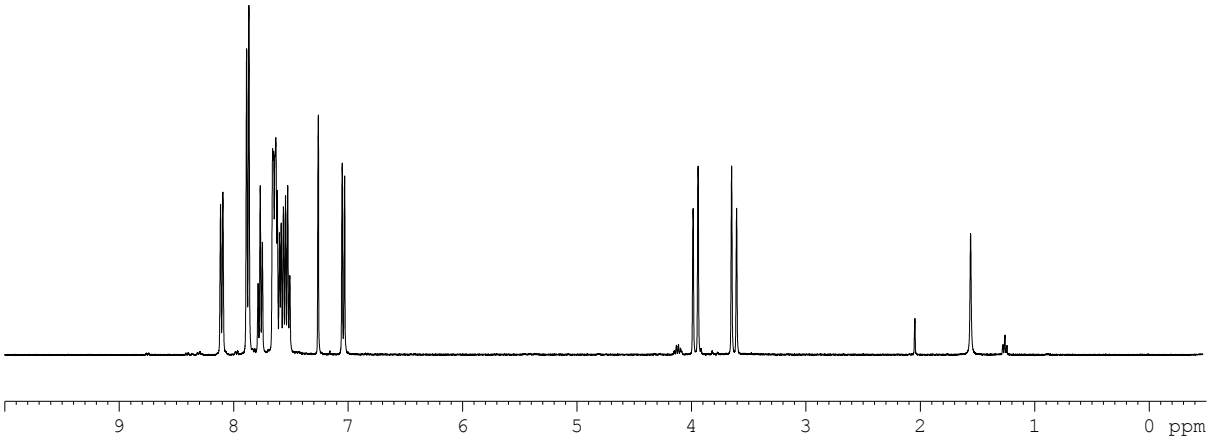
^{13}C - NMR spectrum for compound **25** ($CDCl_3$, 100 MHz)



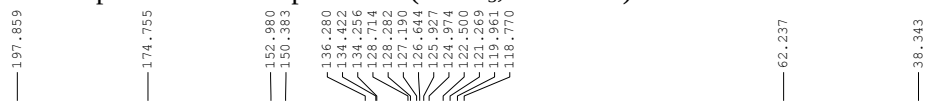
^{1}H- NMR spectrum for compound **30** ($CDCl_3$, 400 MHz)

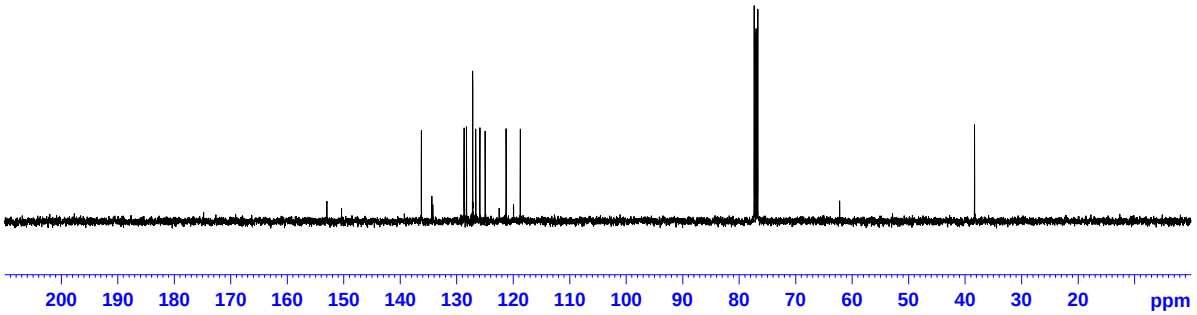


30



^{13}C - NMR spectrum for compound **30** ($CDCl_3$, 100 MHz)





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