Supporting Information

Copper-Catalyzed One-Pot Three-Component Thioamination of 1,4-Naphthoquinone

Fan-Lin Zeng,[a] Xiao-Lan Chen,*[a,d] Shuai-Qi He,[a] Kai Sun,[a] Yan Liu,[a,c] Rui Fu,[a] Ling-Bo Qu,[a] Yu-Fen Zhao,[a,d] and Bing Yu*[a,b]

[a] *College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, China. E-mail: chenxl@zzu.edu.cn; bingyu@zzu.edu.cn*

[b] *Henan Nonferrous Metals Geological Exploration Institute, Zhengzhou 450052, Henan Province, China.*

[c] *College of biological and pharmaceutical engineering, Xinyang Agriculture & Forestry University, Xinyang 464000, China*

[d] *The Key Laboratory for Chemical Biology of Fujian Province, Xiamen University, Xiamen 361005, China*

Table of Contents

1. General information 2
2. Experimental procedure for synthesis of **4a-4z** 2
3. Experimental procedure for synthesis of **6a-6c** 2
4. Optimization of the reaction conditions 3
5. Control experiments 4
6. Characterization data 6
7. ^{1}H, ^{13}C and ^{19}F NMR spectra 16

1. General information

Solvents and all the naphthoquinone, thiols and amines were purchased from commercial suppliers and used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry. The ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra data were recorded on Bruker advance 400 MHz spectrometer using $CDCl_3$ as solvent. ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra being recorded with broad band proton decoupled. ^{1}H NMR and ^{13}C NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference. High resolution mass spectra (HRMS) were obtained with a Waters Micromass Q-Tof Micro instrument using the ESI technique.

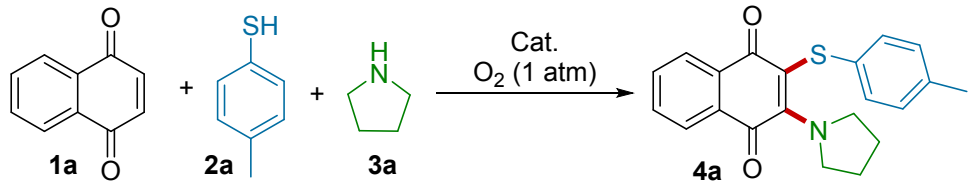
2. Experimental procedure for synthesis of 4a-4z

To a 25 mL Schlenk tube, naphthoquinone **1** (0.5 mmol), thiols **2** (0.5 mmol), amines **3** (1.75 mmol) and CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 ^{o}C for 10 h under O_2 balloon. After reaction, the mixture was diluted with saturated saline (15 mL×2) and extracted with ethyl acetate (25 mL×3). The combined organic layers were collected and dried by anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel to afford the desired products (eluent: ethyl acetate/PE, 1/10-1/20). (For the synthesis of **4y**, a condenser was necessary due to the low boil point of n-propylamine)

3. Experimental procedure for synthesis of 6a-6c

To a 25 mL Schlenk tube, naphthoquinone **1** (0.5 mmol), **5** (0.75 mmol), and CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 ^{o}C for 10 h under O_2 balloon. After reaction, the mixture was diluted with saturated saline (15 mL×2) and extracted with ethyl acetate (25 mL×3). The combined organic layers were collected and dried by anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel to afford the desired products.

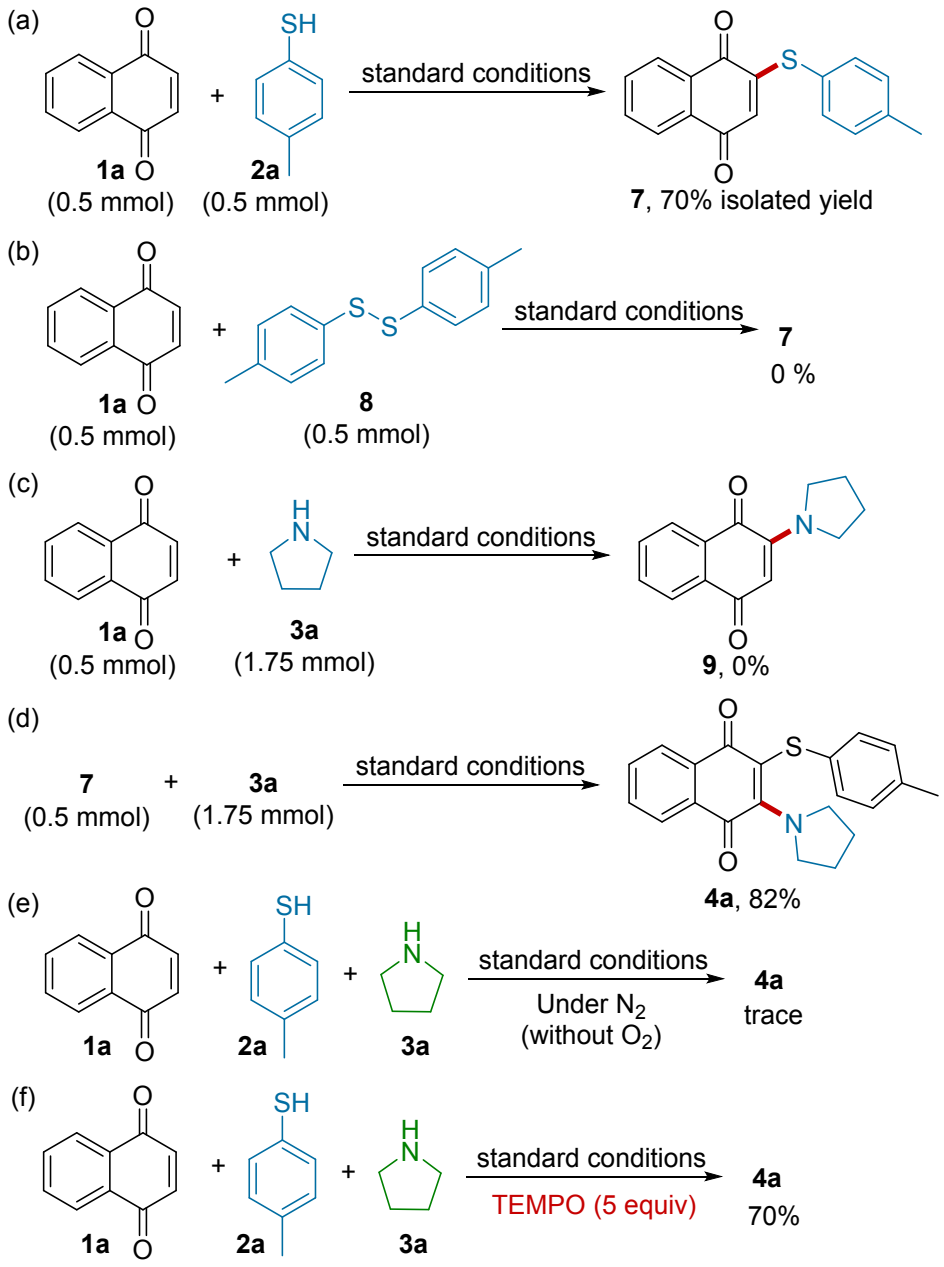
4. Optimization of the reaction conditions [a]



Entry	Cat.	Solvent	Temp.(℃)	Yield(%)[b]
1	$FeSO_4·7H_2O$	DMA	100	20
2	CuCl	DMA	100	35
3	I_2	DMA	100	12
4	$Cu(OAc)_2$	DMA	100	15
5	CuBr	DMA	100	55
6	CuCN	DMA	100	54
7	$CuCl_2$	DMA	100	40
8	Cu_2O	DMA	100	40
9	CuI	DMA	100	74
10	CuI	DMSO	100	50
11	CuI	MeCN	100	30
12	CuI	DMF	100	82
13	CuI	H_2O	100	trace
14	CuI	THF	100	30
15	CuI	toluene	100	20
16	CuI	DMF:H_2O=1:1	100	15
17	CuI	DMF:H_2O=2:1	100	25
18	CuI	DMF	120	78
19	CuI	DMF	90	70
20	CuI	DMF	80	58
21	-	DMF	100	15
22[c]	CuI	DMF	100	35
23[d]	CuI	DMF	100	76
24[e]	CuI	DMF	100	64
25[f]	CuI	DMF	100	80

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), **3a** (0.75 mmol), catalyst (20 mol%), solvent (1 mL), O_2 balloon, 10 h. [b] Yields were given by ^1H NMR using 1,1,2,2-tetrachloroethane as internal standard. [c] Air condition. [d]Reaction for 8 h. [e] CuI (10 mol%). [f] Reaction for 12 h. DMA = *N, N*-dimethylacetamide.

5. Control experiments



Experimental procedure for synthesis of Scheme (a): To a 25 mL Schlenk tube, **1a** (0.5 mmol), **2a** (0.5 mmol), and CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 °C for 10 h under O_2 balloon. After reaction, the mixture was diluted with saturated saline (15ml×2) and extracted with ethyl acetate (25 mL×3). The combined organic layers were collected and dried by anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel to afford the desired products.

Experimental procedure for synthesis of Scheme (b): To a 25 mL Schlenk tube, **1a** (0.5 mmol), **8** (0.5 mmol), CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 °C for 10 h under O_2 balloon.

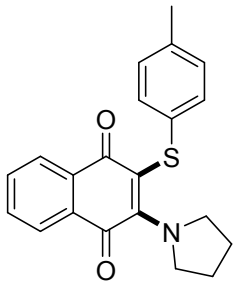
Experimental procedure for synthesis of Scheme (c): To a 25 mL Schlenk tube, **1a** (0.5 mmol), **3a** (1.75 mmol), CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 °C for 10 h under O_2 balloon.

Experimental procedure for synthesis of Scheme (d): To a 25 mL Schlenk tube, **7** (0.5 mmol), **3a** (0.75 mmol), and CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 °C for 10 h under O_2 balloon. After reaction, the mixture was diluted with saturated saline (15ml×2) and extracted with ethyl acetate (25 mL×3). The combined organic layers were collected and dried by anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel to afford the desired products.

Experimental procedure for synthesis of Scheme (e): To a 25 mL Schlenk tube, **1a** (0.5 mmol), **2a** (0.5 mmol), **3a** (0.75 mmol) and CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 °C for 10 h under N_2 balloon.

Experimental procedure for synthesis of Scheme (f): To a 25 mL Schlenk tube, **1a** (0.5 mmol), **2a** (0.5 mmol), **3a** (0.75 mmol), TEMPO (5equiv) and CuI (0.1 mmol) were dissolved in DMF (2 mL), and then the tube was covered and stirred at 100 °C for 10 h under O_2 balloon. After reaction, the mixture was diluted with saturated saline (15ml×2) and extracted with ethyl acetate (25 mL×3). The combined organic layers were collected and dried by anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel to afford the desired products.

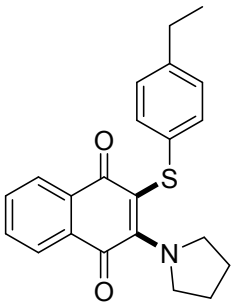
6. Characterization data



2-(pyrrolidin-1-ylmethyl)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4a**)

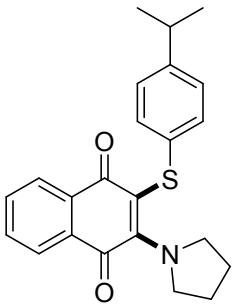
Red solid, 80% yield (145 mg), mp 56.3-57.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.69 (td, *J* = 7.5, 1.4 Hz, 1H), 7.60 (td, *J* = 7.5, 1.3 Hz, 1H), 7.05 (q, *J* = 8.3 Hz, 5H), 3.94 – 3.85 (m, 4H), 2.28 (s, 3H), 1.85 – 1.77 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.38, 180.28, 155.60, 135.05, 134.77, 134.08, 133.46, 131.95,

131.89, 129.58, 126.38, 126.23, 125.89, 105.65, 53.81, 25.50, 20.93; HRMS Calcd for $C_{21}H_{20}NO_2S$ $[M + H]^+$: m/z 350.1209, found: 350.1196.



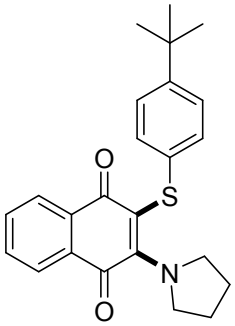
2-((4-ethylphenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4b**)

Red solid, 65% yield (117 mg), mp 62.5-63.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.94 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.70 (td, *J* = 7.5, 1.4 Hz, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 – 7.04 (m, 4H), 3.97 – 3.85 (m, 4H), 2.58 (q, *J* = 7.6 Hz, 2H), 1.87 – 1.75 (m, 4H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.43, 180.30, 155.63, 141.19, 135.23, 134.10, 133.46, 131.94, 131.91, 128.40, 126.41, 126.23, 125.90, 105.59, 53.83, 28.32, 25.51, 15.57. HRMS Calcd for $C_{22}H_{22}NO_2S$ $[M + H]^+$: m/z 364.1366, found: 364.1365.



2-((4-isopropylphenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4c**)

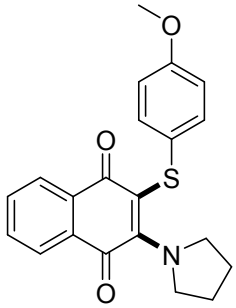
Red solid, 70% yield (131 mg), mp 62.4-63.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.92 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.68 (td, *J* = 7.5, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.3 Hz, 1H), 7.07 (m, 4H), 3.94 – 3.82 (m, 4H), 2.81 (m, *J* = 6.9 Hz, 1H), 1.83 – 1.74 (m, 4H), 1.19 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.42, 180.31, 155.60, 145.80, 135.26, 134.09, 133.46, 131.94, 131.90, 126.97, 126.41, 126.19, 125.90, 105.66, 53.83, 33.59, 25.50, 23.98. HRMS Calcd for $C_{23}H_{24}NO_2S$ $[M + H]^+$: m/z 378.1522, found: 378.1525.



2-((4-(tert-butyl)phenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4d**)

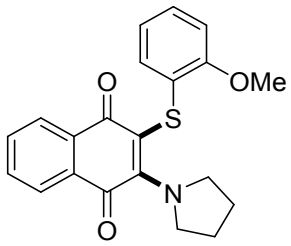
Red solid, 77% yield (150 mg), mp 62.6-64.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.67 (td, *J* = 7.5, 1.4 Hz, 1H), 7.58 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 3.94 – 3.82 (m, 4H), 1.85 – 1.70

(m, 4H), 1.26 (s, 10H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.42, 180.30, 155.66, 148.05, 135.02, 134.08, 133.48, 131.97, 131.89, 126.39, 125.90, 125.85, 105.62, 53.84, 34.34, 31.33, 25.49. HRMS Calcd for $C_{24}H_{25}NO_2SNa$ $[M + Na]^+$: m/z 414.1498, found: 414.1505.



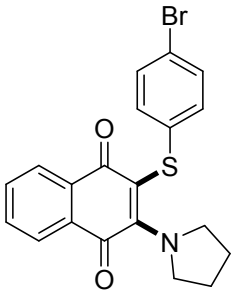
2-((4-methoxyphenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4e**)

Red solid, 60% yield (110 mg), mp 53.5-55.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.66 (td, *J* = 7.5, 1.4 Hz, 1H), 7.58 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 – 7.08 (m, 2H), 6.80 – 6.73 (m, 2H), 3.90 – 3.83 (m, 4H), 3.74 (s, 3H), 1.85 – 1.74 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.35, 180.43, 157.80, 155.15, 134.05, 133.43, 131.90, 129.11, 128.42, 126.34, 125.88, 114.58, 107.21, 55.35, 53.83, 25.52. HRMS Calcd for $C_{21}H_{20}NO_3S$ $[M + H]^+$: m/z 366.1158, found: 366.1150.



2-((2-methoxyphenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4f**)

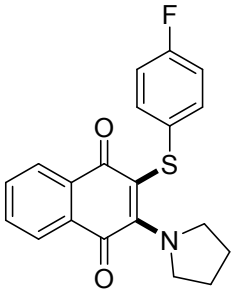
Red solid, 71% yield (129 mg), mp 64.5-66.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.68 (td, *J* = 7.6, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.4 Hz, 1H), 7.06 (ddd, *J* = 8.5, 7.1, 1.8 Hz, 1H), 6.90 – 6.77 (m, 3H), 3.90 (d, *J* = 3.7 Hz, 7H), 1.85 – 1.75 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 184.50, 180.09, 156.73, 155.51, 134.11, 133.59, 132.03, 131.85, 127.10, 126.42, 126.37, 125.90, 125.61, 121.16, 110.36, 103.00, 55.87, 53.80, 25.50. HRMS Calcd for $C_{21}H_{20}NO_3S$ $[M + H]^+$: m/z 366.1158, found: 366.1157.



2-((4-bromophenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4g**)

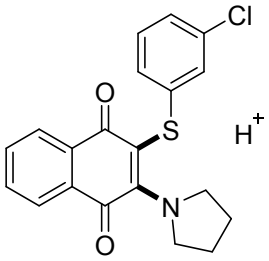
Red solid, 70% yield (144 mg), mp 66.8-68.7 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.68 (td, *J* = 7.5, 1.4 Hz, 1H), 7.60 (td, *J* = 7.6, 1.4 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.04 – 6.99 (m, 2H), 3.94 – 3.85 (m, 4H), 1.88 – 1.79 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.29, 180.00, 156.44, 138.39, 134.27, 133.32, 132.06, 131.92, 131.78, 127.41, 126.42, 126.03, 118.34, 103.34, 54.08, 25.50. HRMS Calcd for $C_{20}H_{16}BrNO_2SNa$ $[M + Na]^+$: m/z 435.9977, found: 435.9980.



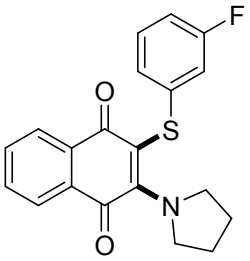
2-((4-fluorophenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4h**)

Red solid, 70% yield (123 mg), mp 62.2-63.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.91 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.68 (td, *J* = 7.5, 1.4 Hz, 1H), 7.59 (td, *J* = 7.5, 1.3 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 3.94 – 3.84 (m, 4H), 1.86 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.33, 180.21, 162.03, 159.60, 156.04, 134.20, 133.86 (d, *J* = 3.2 Hz), 133.35, 131.95 (d, *J* = 12.8 Hz), 127.89 (d, *J* = 7.6 Hz), 126.38, 125.97, 115.91 (d, *J* = 22.0 Hz), 105.03, 54.03, 25.50. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.67. HRMS Calcd for $C_{20}H_{17}FNO_2S$ $[M + H]^+$: m/z 354.0959, found: 354.0959.



2-((3-chlorophenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4i**)

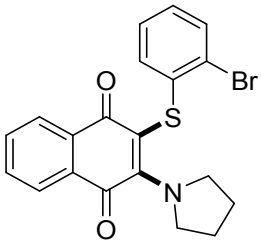
Red solid, 60% yield (110 mg), mp 62.5-63.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.93 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.70 (td, *J* = 7.5, 1.4 Hz, 1H), 7.61 (td, *J* = 7.6, 1.4 Hz, 1H), 7.17 – 7.08 (m, 2H), 7.03 (m, *J* = 7.6, 4.4, 1.4 Hz, 2H), 3.96 – 3.87 (m, 4H), 1.89 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.30, 180.00, 156.51, 141.31, 134.72, 134.30, 133.34, 132.07, 131.95, 129.86, 126.49, 126.06, 125.39, 124.99, 123.81, 102.91, 54.12, 25.50. HRMS Calcd for $C_{20}H_{17}ClNO_2S$ $[M + H]^+$: m/z 370.0663, found: 370.0661.



2-((3-fluorophenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4j**)

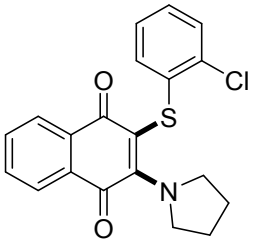
Red solid, 60% yield (106 mg), mp 117.0-118.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.70 (td, *J* = 7.6, 1.4 Hz, 1H), 7.61 (td, *J* = 7.5, 1.4 Hz, 1H), 7.17 (td, *J* = 8.0, 5.9 Hz, 1H), 6.98 – 6.90 (m, 1H), 6.83 (dt, *J* = 9.6, 2.2 Hz,

1H), 6.76 (td, *J* = 8.4, 2.5 Hz, 1H), 3.96 – 3.88 (m, 4H), 1.90 – 1.80 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.34, 180.02, 164.30, 161.84, 156.57, 141.72 (d, *J* = 7.4 Hz), 134.29, 133.35, 132.01 (d, *J* = 9.7 Hz), 130.09 (d, *J* = 8.7 Hz), 126.49, 126.05, 121.30, 112.62 (d, *J* = 24.2 Hz), 111.80 (d, *J* = 21.4 Hz), 102.99, 54.11, 25.49. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -112.39. HRMS Calcd for $C_{20}H_{17}FNO_2S$ [M + H]$^+$: m/z 354.0959, found: 354.0962.



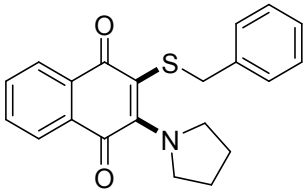
2-((2-bromophenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4k**)

Red solid, 63% yield (130 mg), mp 136.2-138.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.70 (td, *J* = 7.5, 1.4 Hz, 1H), 7.61 (td, *J* = 7.6, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.14 (td, *J* = 7.7, 1.4 Hz, 1H), 6.97 – 6.89 (m, 2H), 3.95 – 3.88 (m, 4H), 1.89 – 1.79 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-d) δ 184.41, 179.90, 157.05, 139.95, 134.31, 133.43, 132.72, 132.03, 127.67, 126.92, 126.49, 126.05, 125.82, 120.24, 102.74, 54.06, 25.49. HRMS Calcd for $C_{20}H_{17}BrNO_2S$ [M + H]$^+$: m/z 414.0158, found: 414.0162.



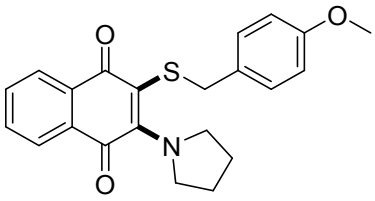
2-((2-chlorophenyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4l**)

Red solid, 62% yield (114 mg), mp 148.5-149.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.93 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.69 (td, *J* = 7.6, 1.4 Hz, 1H), 7.61 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.09 (td, *J* = 7.6, 1.5 Hz, 1H), 7.01 (td, *J* = 7.6, 1.7 Hz, 1H), 6.93 (dd, *J* = 7.8, 1.6 Hz, 1H), 3.96 – 3.87 (m, 4H), 1.90 – 1.79 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.37, 179.93, 157.12, 138.02, 134.28, 133.43, 132.02, 132.00, 130.59, 129.46, 127.08, 126.88, 126.46, 126.05, 125.58, 102.09, 54.07, 25.48. HRMS Calcd for $C_{20}H_{17}ClNO_2S$ [M + H]$^+$: m/z 370.0663, found: 370.0676.



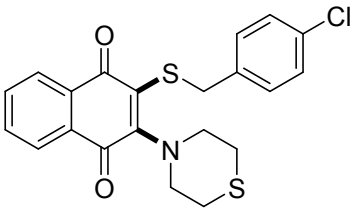
2-(benzylthio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4m**)

Red solid, 50% yield (87 mg), mp 72.0-73.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.82 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.66 (td, *J* = 7.5, 1.4 Hz, 1H), 7.55 (td, *J* = 7.6, 1.3 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.14 (td, *J* = 6.2, 1.6 Hz, 4H), 3.83 (s, 2H), 3.68 – 3.63 (m, 4H), 1.81 – 1.73 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.21, 180.65, 156.55, 138.25, 133.91, 133.72, 131.78, 131.64, 128.98, 128.18, 126.90, 126.06, 125.69, 106.69, 54.32, 40.13, 25.46. HRMS Calcd for $C_{21}H_{20}NO_2S$ [M + H]$^+$: m/z 350.1209, found: 350.1205.



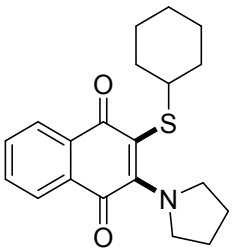
2-((4-methoxybenzyl)thio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4n**)

Red solid, 35% yield (65 mg), mp 58.5-60.3 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.67 (td, *J* = 7.6, 1.3 Hz, 1H), 7.56 (td, *J* = 7.5, 1.3 Hz, 1H), 7.12 – 7.04 (m, 2H), 6.79 – 6.71 (m, 2H), 3.79 (s, 2H), 3.75 (s, 3H), 3.73 – 3.67 (m, 4H), 1.84 – 1.78 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.24, 180.73, 158.54, 156.45, 133.92, 133.72, 131.80, 131.65, 130.22, 130.11, 126.08, 125.68, 113.62, 107.06, 55.33, 54.31, 39.51, 25.50. HRMS Calcd for $C_{22}H_{22}NO_3S$ $[M + H]^+$: m/z 380.1315, found: 380.1315.



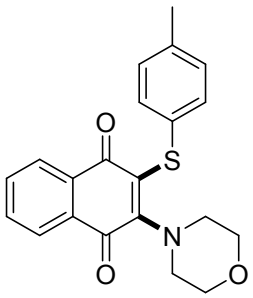
2-((4-chlorobenzyl)thio)-3-thiomorpholinonaphthalene-1,4-dione (**4o**)

Red solid, 35% yield (73 mg), mp 37.8-39.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.2, 1.7 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.67 (dtd, *J* = 16.8, 7.4, 1.6 Hz, 2H), 7.19 – 7.14 (m, 2H), 7.13 – 7.08 (m, 2H), 4.09 (s, 2H), 3.56 – 3.51 (m, 4H), 2.75 – 2.70 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.80, 181.66, 156.45, 136.56, 133.83, 133.06, 132.92, 132.74, 131.93, 130.25, 128.49, 126.70, 126.34, 125.28, 55.06, 38.27, 28.04. HRMS calcd for $C_{21}H_{19}NO_2S_2$ $[M + H]^+$: m/z 416.0540, found: 416.0542.



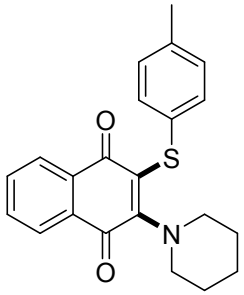
2-(cyclohexylthio)-3-(pyrrolidin-1-yl)naphthalene-1,4-dione (**4p**)

Red solid, 71% yield (121 mg), mp 48.6-49.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.66 (td, *J* = 7.5, 1.4 Hz, 1H), 7.56 (td, *J* = 7.5, 1.3 Hz, 1H), 3.98 – 3.84 (m, 4H), 2.87 (m, *J* = 10.4, 3.7 Hz, 1H), 2.00 – 1.90 (m, 4H), 1.88 – 1.82 (m, 2H), 1.71 (m, *J* = 6.3, 3.8 Hz, 2H), 1.56 (m, *J* = 9.4, 3.9 Hz, 1H), 1.31 – 1.16 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.56, 180.98, 156.27, 133.84, 133.54, 131.89, 131.68, 126.13, 125.59, 108.35, 54.36, 46.05, 32.85, 26.10, 25.90, 25.65. HRMS calcd for $C_{20}H_{24}NO_2S$ $[M + H]^+$: m/z 342.1522, found: 342.1521.



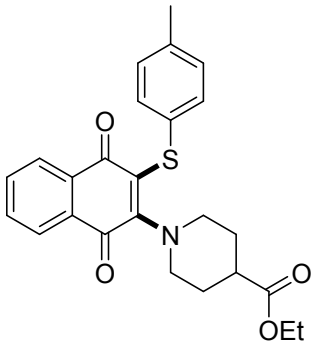
2-morpholino-3-(*p*-tolylthio)naphthalene-1,4-dione (**4q**)

Red solid, 55% yield (100 mg), mp 139.0-140.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.97 (m, 2H), 7.67 (dt, *J* = 5.9, 2.3 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 3.75 (t, *J* = 4.6 Hz, 4H), 3.44 (t, *J* = 4.5 Hz, 4H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.07, 181.91, 153.09, 136.49, 133.97, 132.98, 132.57, 132.19, 132.05, 129.79, 128.17, 126.75, 126.56, 122.11, 67.45, 51.81, 21.07. HRMS Calcd for $C_{21}H_{20}NO_3S$ $[M + H]^+$: m/z 366.1158, found: 366.1166.



2-(piperidin-1-yl)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4r**)

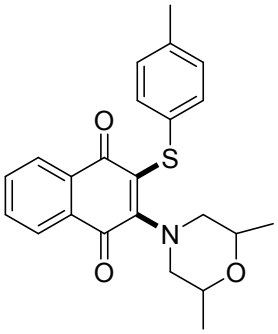
Red solid, 75% yield (136 mg), mp 69.0-71.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 7.97 (m, 2H), 7.70 – 7.61 (m, 2H), 7.19 – 7.12 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.40 (t, *J* = 5.4 Hz, 2H), 2.29 (s, 3H), 1.70 (m, *J* = 5.7 Hz, 4H), 1.61 (q, *J* = 6.6, 6.2 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.37, 181.69, 155.01, 135.92, 133.78, 133.19, 132.72 (d, *J* = 15.6 Hz), 132.24, 129.63, 127.93, 126.63, 126.44, 120.00, 53.38, 26.87, 24.10, 21.06. HRMS calcd for $C_{22}H_{22}NO_2S$ $[M + H]^+$: m/z 364.1366, found: 364.1360.



Ethyl 1-(1,4-dioxo-3-(*p*-tolylthio)-1,4-dihydronaphthalen-2-yl)piperidine-4-carboxylate (**4s**)

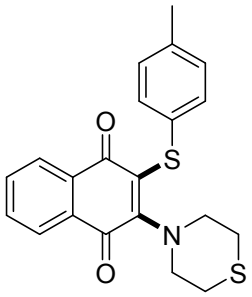
Red solid, 44% yield (95 mg), mp 73.1-75.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.98 (m, 2H), 7.71 – 7.61 (m, 2H), 7.20 – 7.12 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 4.13 (m, *J* = 7.1 Hz, 2H), 3.76 (dt, *J* = 14.1, 4.1 Hz, 2H), 3.04 (ddd, *J* = 13.7, 9.7, 4.3 Hz, 2H), 2.45 (m, *J* = 9.9, 5.2 Hz, 1H), 2.29 (s, 3H), 1.93 (m, *J* = 7.2, 3.8 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

Chloroform-*d*) δ 182.08, 181.85, 174.36, 154.23, 136.31, 133.85, 132.86, 132.67, 132.13, 129.69, 128.25, 126.71, 126.51, 122.23, 60.54, 51.33, 40.70, 28.89, 21.06, 14.24. HRMS Calcd for $C_{25}H_{26}NO_4S$ $[M + H]^+$: m/z 436.1577, found: 436.1581.



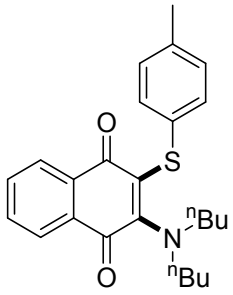
2-(2,6-dimethylmorpholino)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4t**)

Red solid, 82% yield (161 mg), mp 79.2-80.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.03 (m, 1H), 8.04 – 7.99 (m, 1H), 7.71 – 7.62 (m, 2H), 7.18 – 7.13 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.79 (m, *J* = 10.2, 6.3, 2.0 Hz, 2H), 3.72 – 3.65 (m, 2H), 2.72 (dd, *J* = 13.1, 10.2 Hz, 2H), 2.30 (s, 3H), 1.14 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.18, 181.86, 152.95, 136.42, 133.95, 132.92, 132.62, 132.23, 132.07, 129.75, 128.21, 126.70, 126.53, 121.64, 72.37, 56.93, 21.07, 18.60. HRMS calcd for $C_{23}H_{24}NO_3S$ $[M + H]^+$: m/z 394.1471, found: 394.1474.



2-thiomorpholino-3-(*p*-tolylthio)naphthalene-1,4-dione (**4u**)

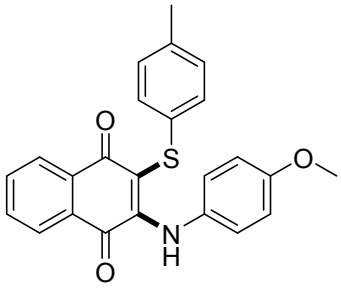
Red solid, 45% yield (86 mg), mp 149.0-150.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 7.99 (m, 2H), 7.71 – 7.64 (m, 2H), 7.21 – 7.16 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.60 – 3.47 (m, 4H), 2.79 – 2.69 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.17, 182.01, 153.56, 136.85, 133.90, 133.10, 132.49, 132.02, 131.85, 129.80, 128.70, 126.77, 126.54, 124.75, 53.66, 28.10, 21.12. HRMS Calcd for $C_{21}H_{19}NO_2S_2Na$ $[M + Na]^+$: m/z 404.0749, found: 404.0756.



2-(dibutylamino)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4v**)

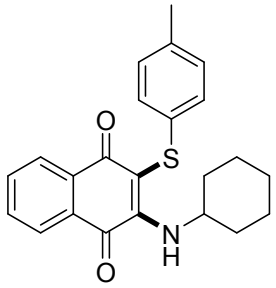
Red solid, 40% yield (82 mg), mp 50.2-51.6 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.02

(m, 1H), 8.01 – 7.96 (m, 1H), 7.65 (m, *J* = 7.4, 5.7 Hz, 2H), 7.19 – 7.12 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 3.50 – 3.41 (m, 4H), 2.28 (s, 3H), 1.46 – 1.31 (m, 4H), 1.24 (dt, *J* = 15.0, 7.4 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 183.18, 181.44, 154.96, 136.17, 133.67, 132.99, 132.89, 132.57, 132.44, 129.67, 128.68, 126.49, 126.40, 120.91, 53.14, 30.75, 21.02, 20.03, 13.86. HRMS calcd for $C_{25}H_{30}NO_2S$ [M + H]$^+$: m/z 408.1992, found: 408.1991.



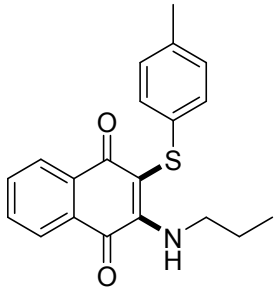
2-((4-methoxyphenyl)amino)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4w**)

Red solid, 40% yield (80 mg), mp 51.6-52.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.10 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.89 (s, 1H), 7.74 (td, *J* = 7.6, 1.4 Hz, 1H), 7.67 (td, *J* = 7.5, 1.3 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.75 – 6.66 (m, 6H), 3.81 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.96, 157.17, 143.75, 135.70, 134.84, 133.62, 132.66, 130.60, 130.49, 130.03, 129.19, 128.20, 127.09, 126.72, 124.79, 113.13, 111.91, 55.56, 21.02. HRMS calcd for $C_{24}H_{20}NO_3S$ [M + H]$^+$: m/z 402.1158, found: 402.1158.



2-(cyclohexylamino)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4x**)

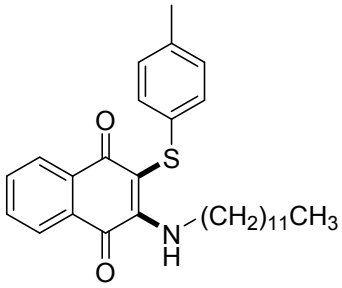
Red solid, 55% yield (103 mg), mp 93.5-95.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.70 (td, *J* = 7.5, 1.4 Hz, 1H), 7.60 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 1H), 4.60 (s, 1H), 2.26 (s, 3H), 1.98 – 1.88 (m, 2H), 1.70 (m, *J* = 12.7, 3.8 Hz, 2H), 1.60 (m, *J* = 12.6, 3.7 Hz, 1H), 1.36 – 1.13 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.60, 179.87, 149.11, 135.30, 134.88, 133.81, 132.08, 130.45, 129.76, 129.54, 127.55, 127.05, 126.57, 126.34, 52.88, 34.13, 25.29, 24.48, 20.93. HRMS calcd for $C_{23}H_{24}NO_2S$ [M + H]$^+$: m/z 378.1522, found: 378.1525.



2-(propylamino)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4y**)

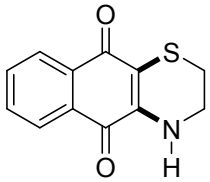
Red solid, 55% yield (93 mg), mp 133.0-134.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (dd,

J = 7.6, 1.2 Hz, 1H), 8.07 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72 (td, *J* = 7.6, 1.4 Hz, 1H), 7.63 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 2H), 7.06 – 6.99 (m, 2H), 6.59 (s, 1H), 3.88 – 3.79 (m, 2H), 2.26 (s, 3H), 1.70 – 1.57 (m, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.60, 180.00, 150.41, 135.31, 134.98, 133.82, 132.16, 130.44, 129.83, 129.55, 127.15, 126.83, 126.61, 47.03, 23.79, 20.95, 11.15. HRMS calcd for $C_{20}H_{20}NO_2S$ $[M + H]^+$: m/z 338.1209, found:338.1209.



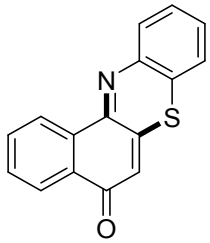
2-(dodecylamino)-3-(*p*-tolylthio)naphthalene-1,4-dione (**4z**)

Red solid, 65% yield (151 mg), mp 61.9-62.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.07 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.73 (td, *J* = 7.6, 1.4 Hz, 1H), 7.63 (td, *J* = 7.6, 1.3 Hz, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 1H), 3.86 (q, *J* = 6.8 Hz, 2H), 2.26 (s, 3H), 1.60 (m, *J* = 7.1 Hz, 2H), 1.36 – 1.17 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 181.60, 179.99, 150.24, 135.23, 134.96, 133.83, 132.12, 130.41, 130.10, 129.81, 127.14, 126.77, 126.59, 45.64, 31.91, 30.46, 29.62, 29.54, 29.50, 29.46, 29.34, 29.18, 26.62, 22.85, 22.69, 20.92, 14.13. HRMS calcd for $C_{29}H_{38}NO_2S$ $[M + H]^+$: m/z 464.2618, found: 464.2618.



3,4-dihydro-2*H*-naphtho[2,3-*b*][1,4]thiazine-5,10-dione (**6a**)

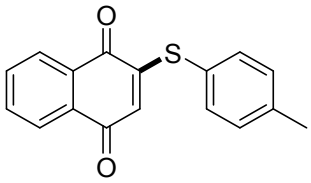
Purple solid, 85% yield (98 mg), mp 236.1-237.9 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.66 (td, *J* = 7.6, 1.4 Hz, 1H), 7.58 (td, *J* = 7.6, 1.4 Hz, 1H), 6.02 (s, 1H), 3.81 – 3.75 (m, 2H), 3.05 – 2.98 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.32, 177.93, 140.93, 134.25, 133.14, 132.33, 130.30, 126.32, 126.20, 111.40, 41.72, 23.93. HRMS calcd for $C_{12}H_{10}NO_2S$ $[M + H]^+$: m/z 232.0427, found: 232.0437.



5*H*-benzo[*a*]phenothiazin-5-one (**6b**)

Yellow solid, 64% yield (84 mg), mp 176.0-177.5 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 – 8.73 (m, 1H), 8.27 – 8.20 (m, 1H), 7.84 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.70 (ddd, *J* = 6.8, 4.5, 1.9 Hz, 2H), 7.46 – 7.35 (m, 1H), 7.39 – 7.29 (m, 2H), 6.76 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 180.23, 144.73, 138.58, 137.82, 134.21, 133.38, 132.59, 131.65, 131.33, 129.98, 127.75, 125.77,

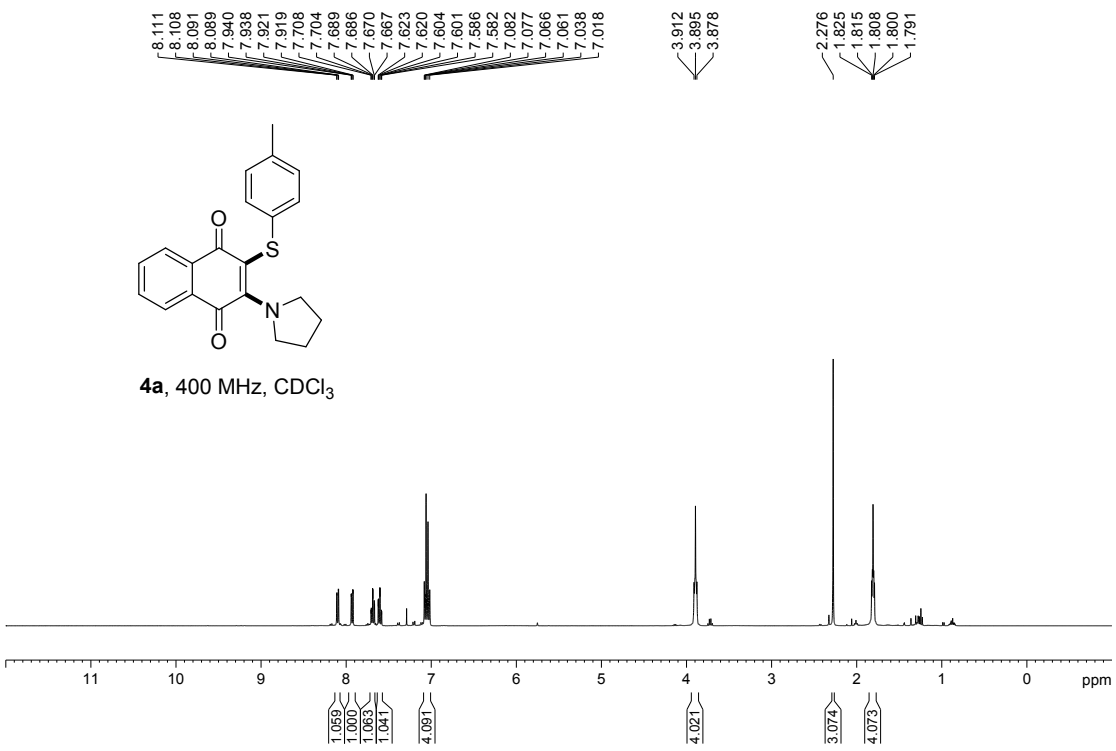
125.60, 124.68, 122.91, 120.25. HRMS calcd for $C_{16}H_{10}NOS$ $[M + H]^+$: m/z 264.0478, found: 264.0477.



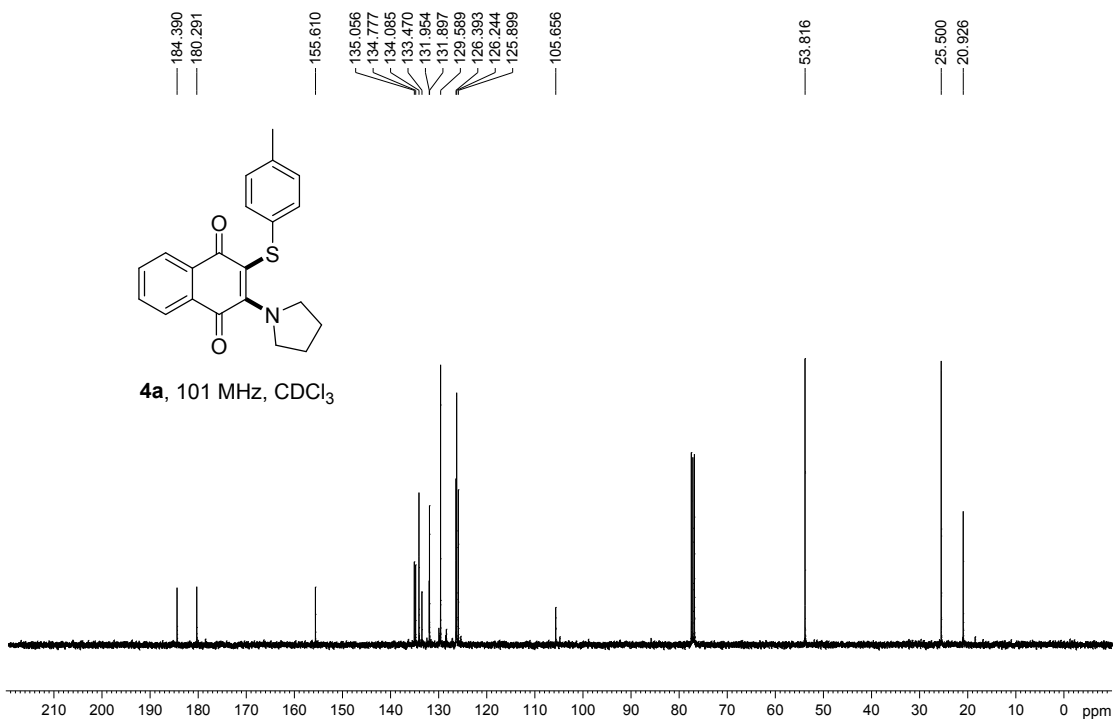
2-(*p*-tolylthio)naphthalene-1,4-dione (**7**)

Yellow solid, 70% yield (98 mg), mp 115.0-117.0 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.06 (m, 1H), 7.99 (m, *J* = 6.7, 2.2 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.41 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.33 – 7.25 (m, 2H), 6.09 (d, *J* = 1.8 Hz, 1H), 2.42 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 182.12, 181.90, 157.03, 140.95, 135.56, 134.30, 133.28, 132.20, 131.72, 131.17, 128.06, 126.77, 126.46, 123.71, 21.40. HRMS calcd for $C_{17}H_{12}NaO_2S$ $[M + Na]^+$: m/z 303.0450, found: 303.0448.

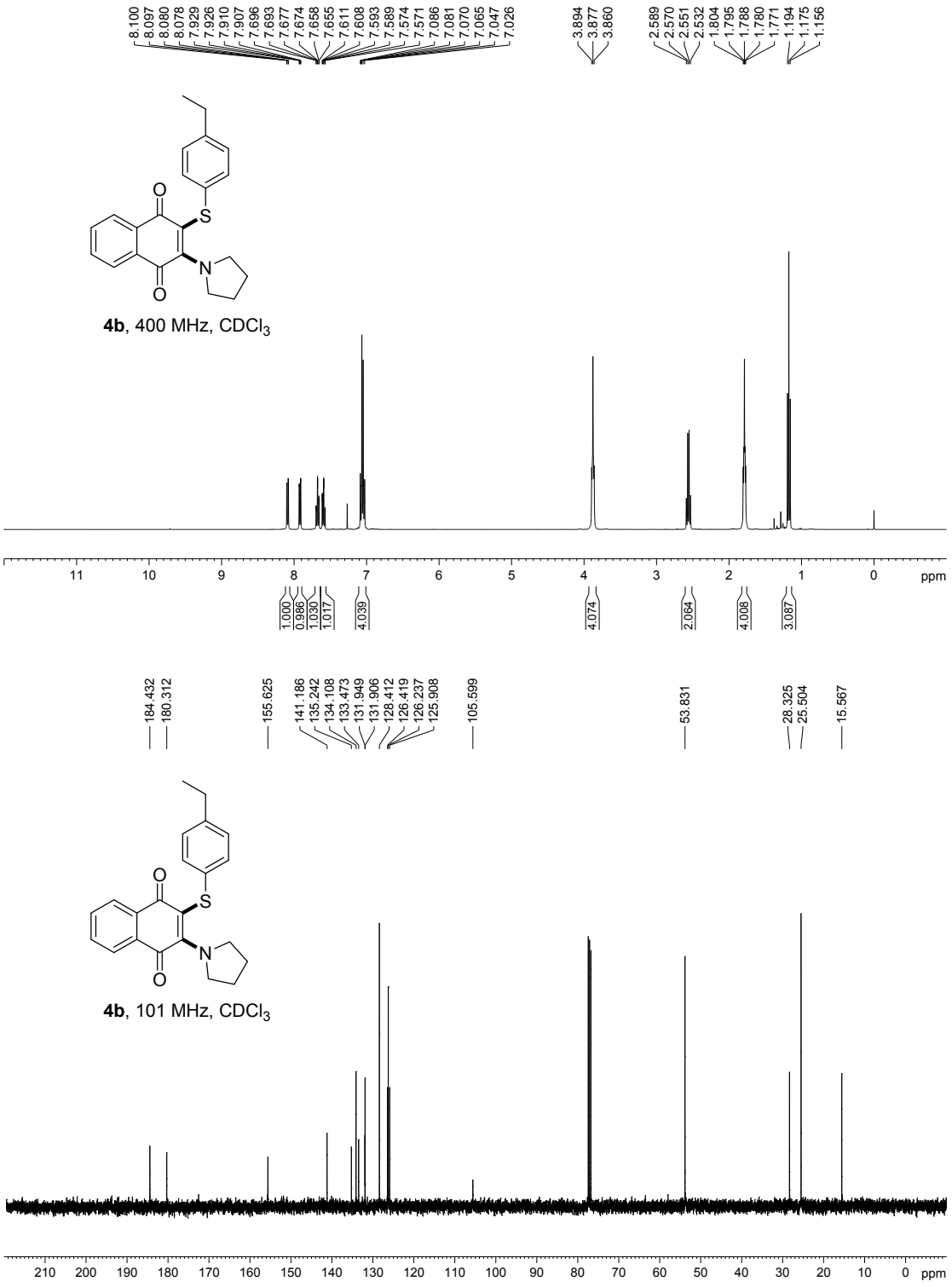
7. ^{1}H, ^{13}C and ^{19}F NMR spectra

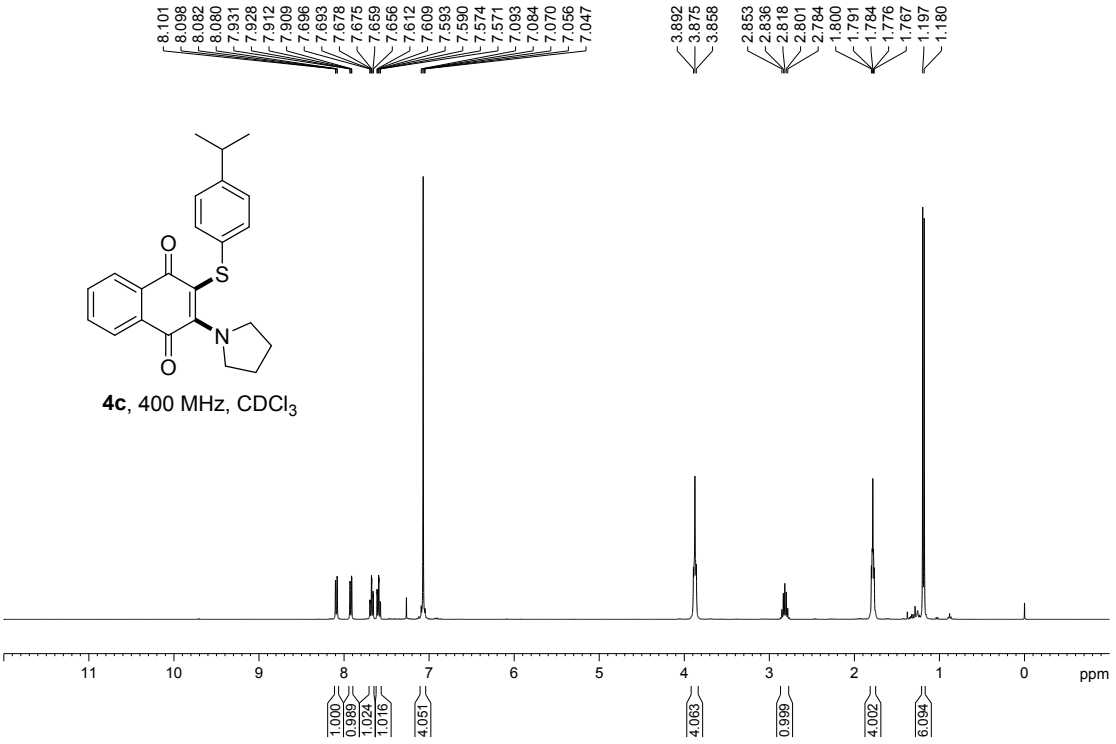


4a, 400 MHz, $CDCl_3$

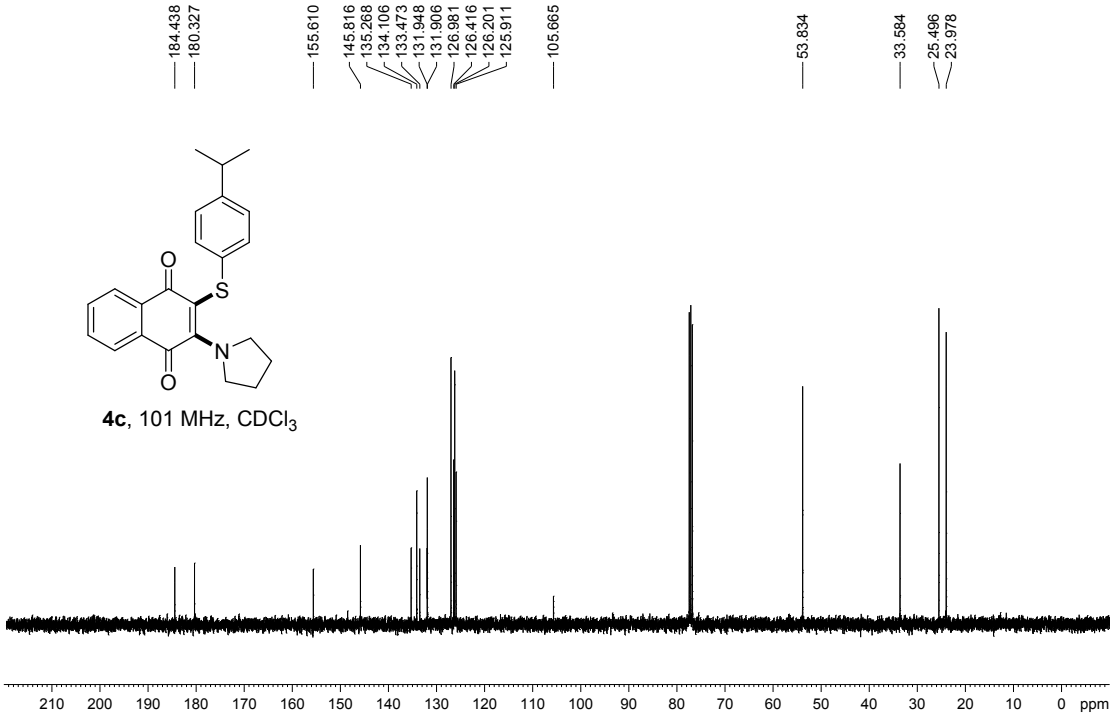


4a, 101 MHz, $CDCl_3$

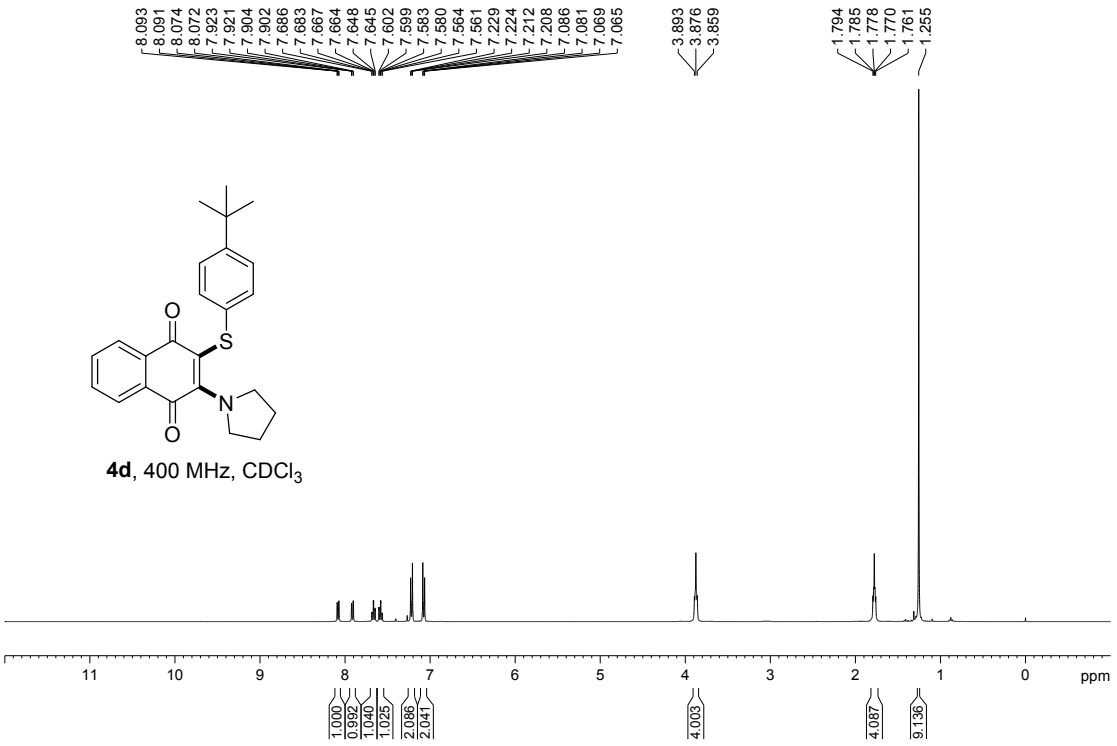

8.100
8.097
8.080
8.078
7.929
7.926
7.910
7.907
7.696
7.693
7.677
7.674
7.658
7.655
7.611
7.608
7.593
7.589
7.574
7.571
7.086
7.081
7.070
7.065
7.047
7.026
3.894
3.877
3.860
2.589
2.570
2.551
2.532
1.804
1.795
1.788
1.780
1.771
1.194
1.175
1.156
O
S
N
O
4b, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.986
1.030
1.017
4.039
4.074
2.064
4.008
3.087
184.432
180.312
155.625
141.186
135.242
134.108
133.473
131.949
131.906
128.412
126.419
126.237
125.908
105.599
53.831
28.325
25.504
15.567
O
S
N
O
4b, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



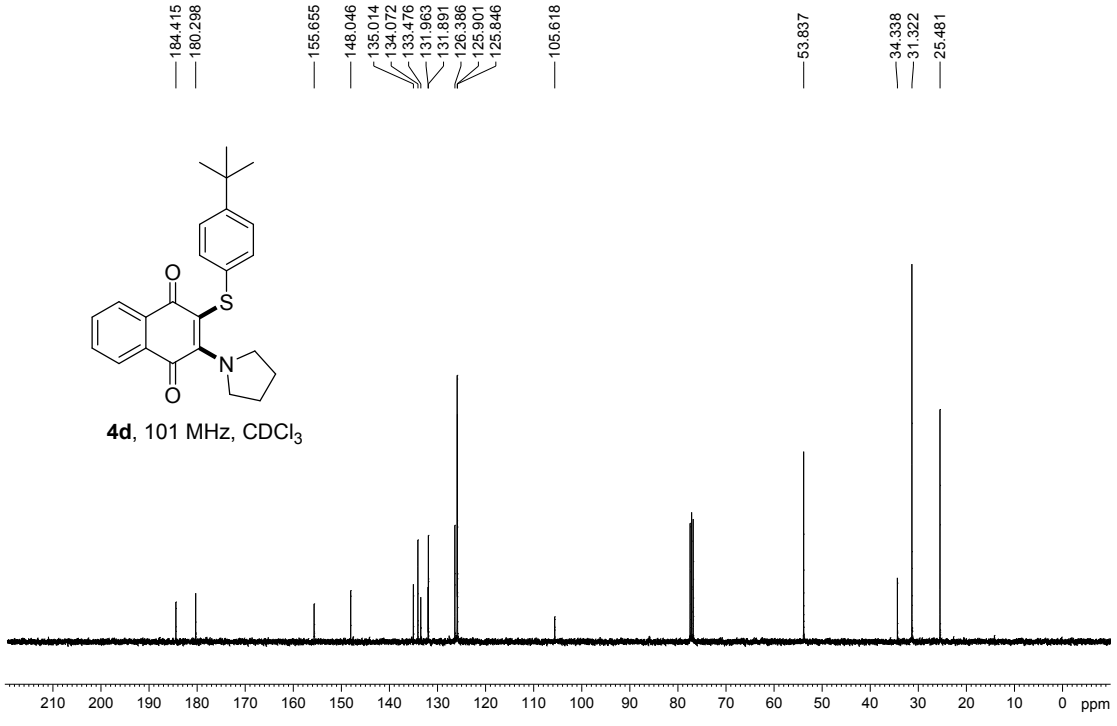
4c, 400 MHz, $CDCl_3$



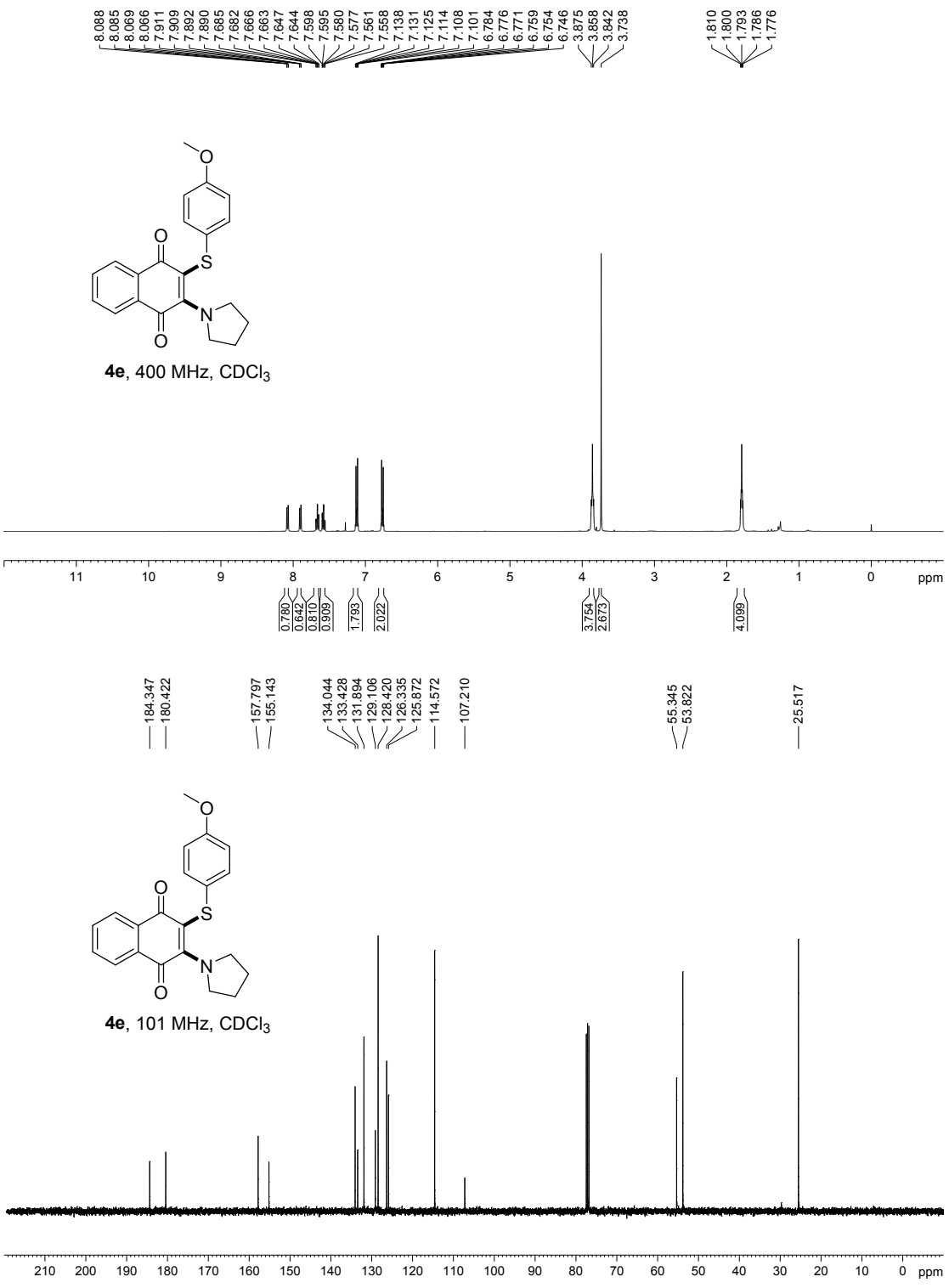
4c, 101 MHz, $CDCl_3$

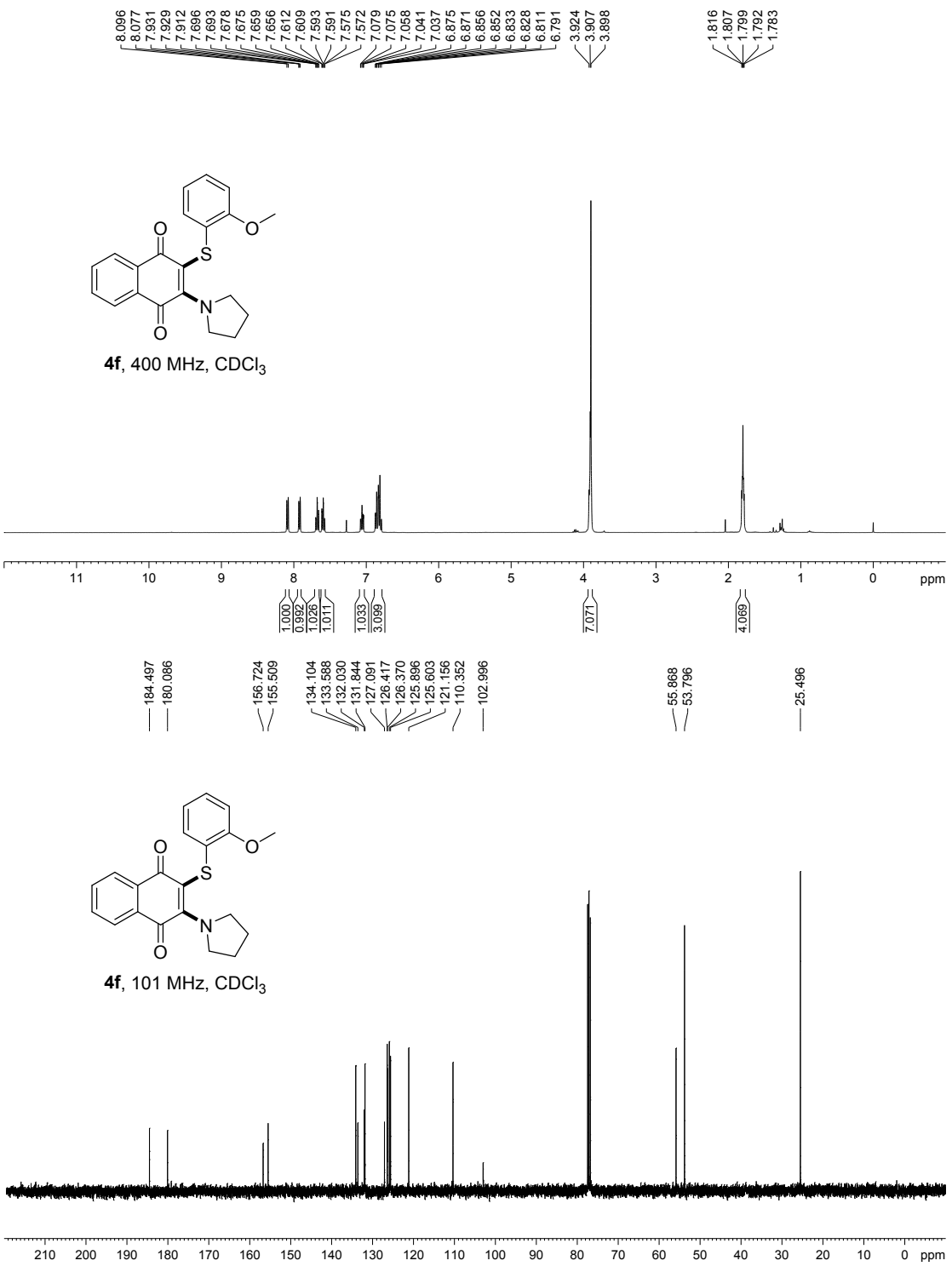


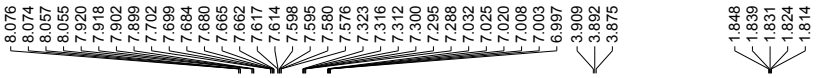
4d, 400 MHz, $CDCl_3$

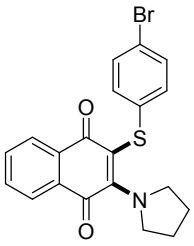


4d, 101 MHz, $CDCl_3$

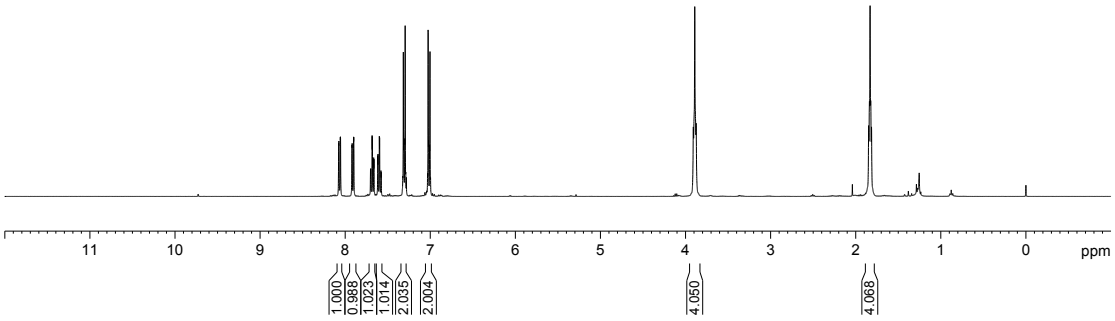

8.088
8.085
8.069
8.066
7.911
7.909
7.892
7.890
7.685
7.682
7.666
7.663
7.647
7.644
7.598
7.595
7.580
7.577
7.561
7.558
7.138
7.131
7.125
7.114
7.108
7.101
6.784
6.776
6.771
6.759
6.754
6.746
3.875
3.858
3.842
3.738
1.810
1.800
1.793
1.786
1.776
O
O
S
N
O
4e, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.780
0.642
0.810
0.909
1.793
2.022
3.754
2.673
4.099
184.347
180.422
157.797
155.143
134.044
133.428
131.894
129.106
128.420
126.335
125.872
114.572
107.210
55.345
53.822
25.517
O
O
S
N
O
4e, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

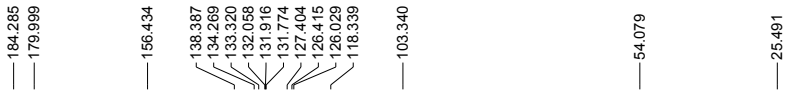

8.096
8.077
7.931
7.929
7.912
7.696
7.693
7.678
7.675
7.659
7.656
7.612
7.609
7.593
7.591
7.575
7.572
7.079
7.075
7.058
7.041
7.037
6.875
6.871
6.856
6.852
6.833
6.828
6.811
6.791
3.924
3.907
3.898
1.816
1.807
1.799
1.792
1.783
O
O
S
N
O
4f, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.992
1.026
1.011
1.033
3.099
7.071
4.069
184.497
180.086
156.724
155.509
134.104
133.588
132.030
131.844
127.091
126.417
126.370
125.896
125.603
121.156
110.352
102.996
55.868
53.796
25.496
O
O
S
N
O
4f, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

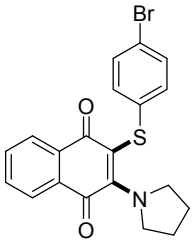




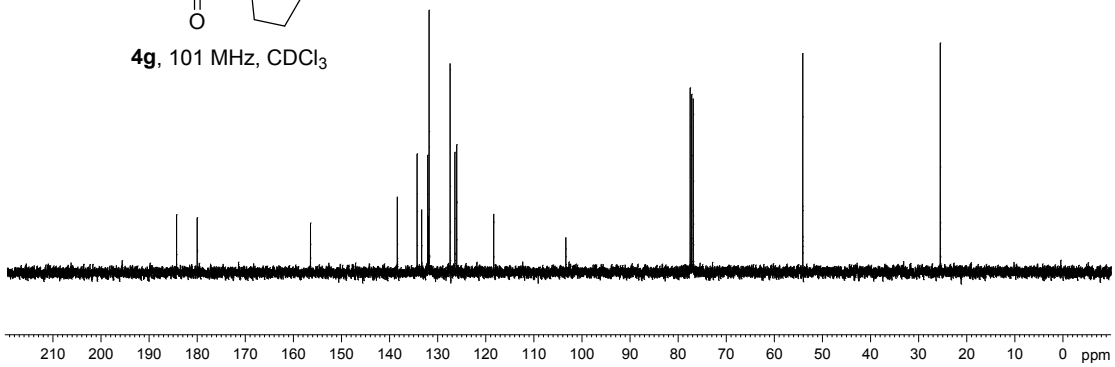
4g, 400 MHz, $CDCl_3$

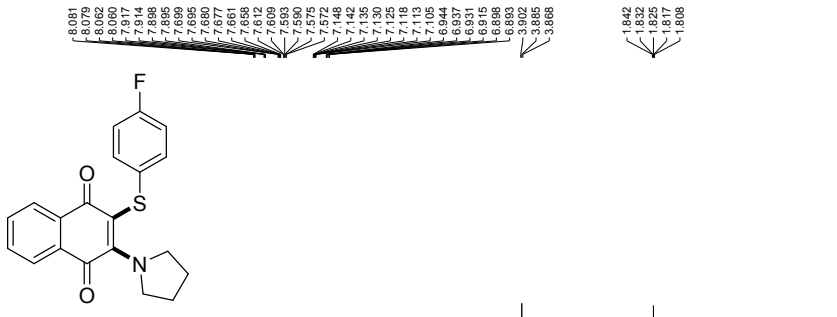




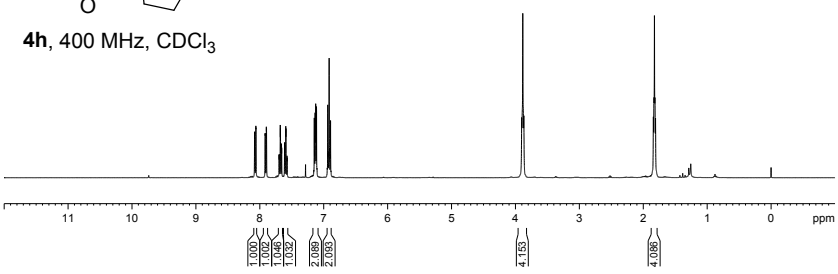


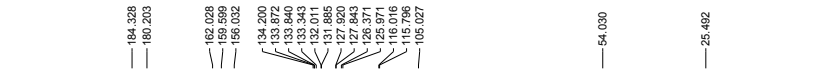
4g, 101 MHz, $CDCl_3$

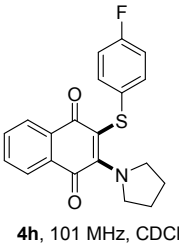




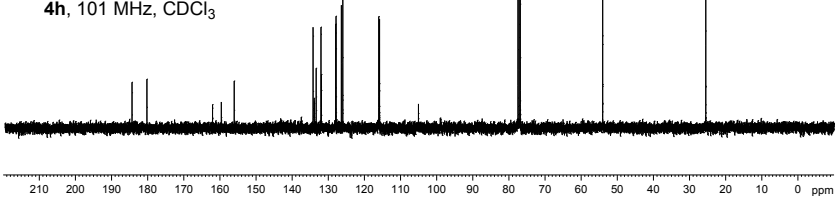
4h, 400 MHz, $CDCl_3$

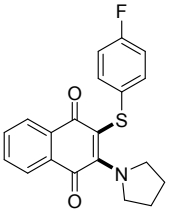




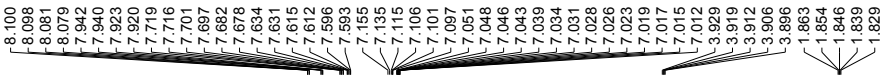


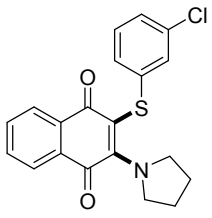
4h, 101 MHz, $CDCl_3$



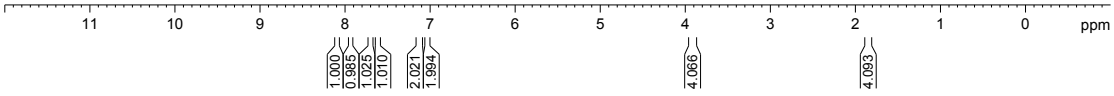


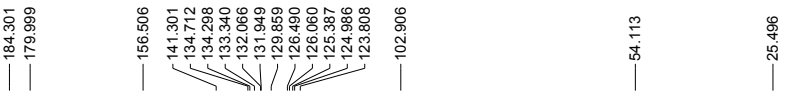
4h, 376 MHz, $CDCl_3$

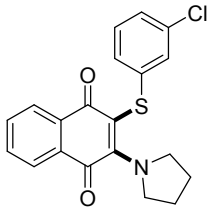




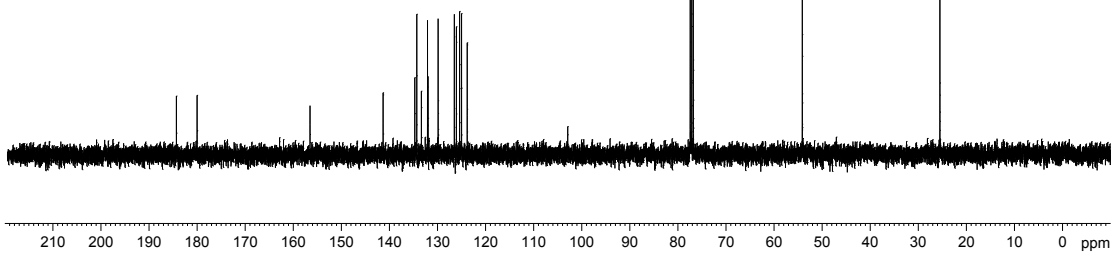
4i, 400 MHz, $CDCl_3$

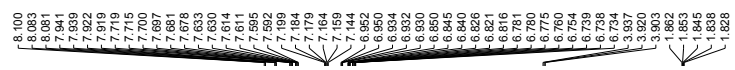


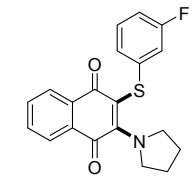




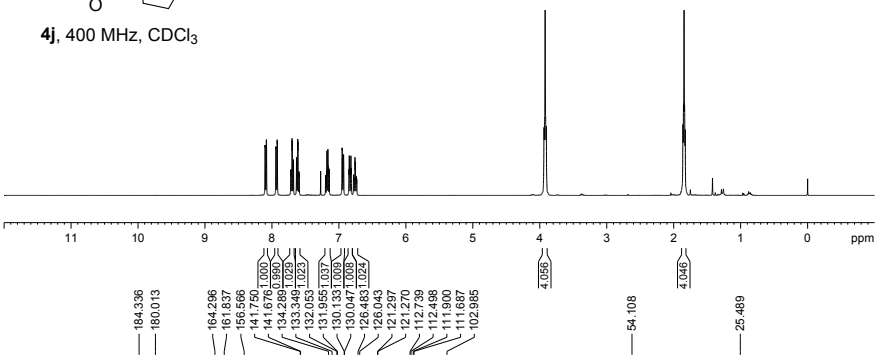
4i, 101 MHz, $CDCl_3$

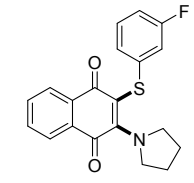




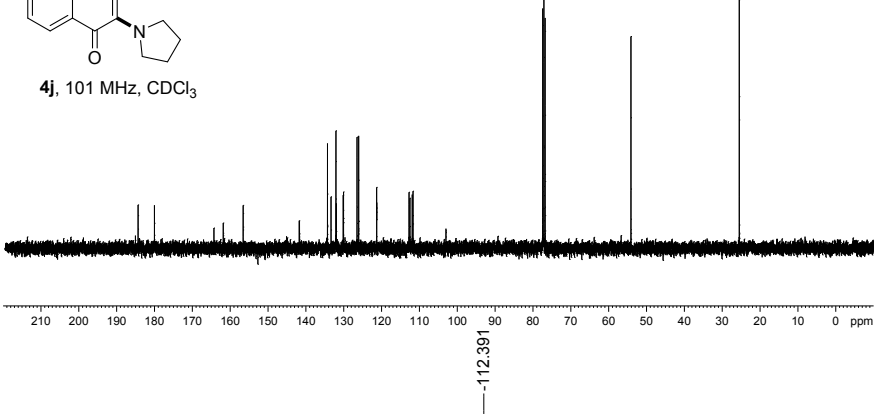


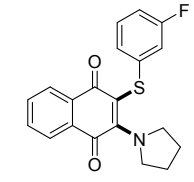
4j, 400 MHz, $CDCl_3$



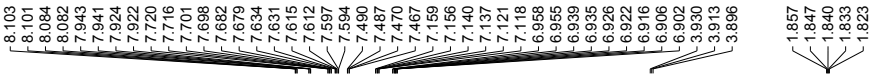


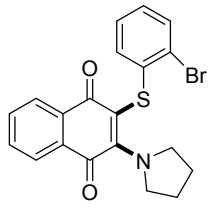
4j, 101 MHz, $CDCl_3$



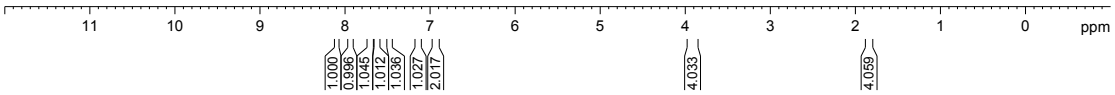


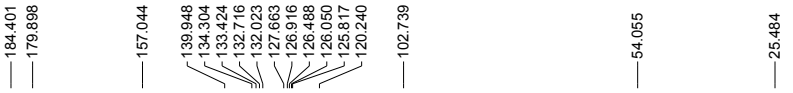
4j, 376 MHz, $CDCl_3$

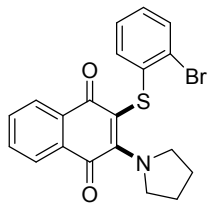




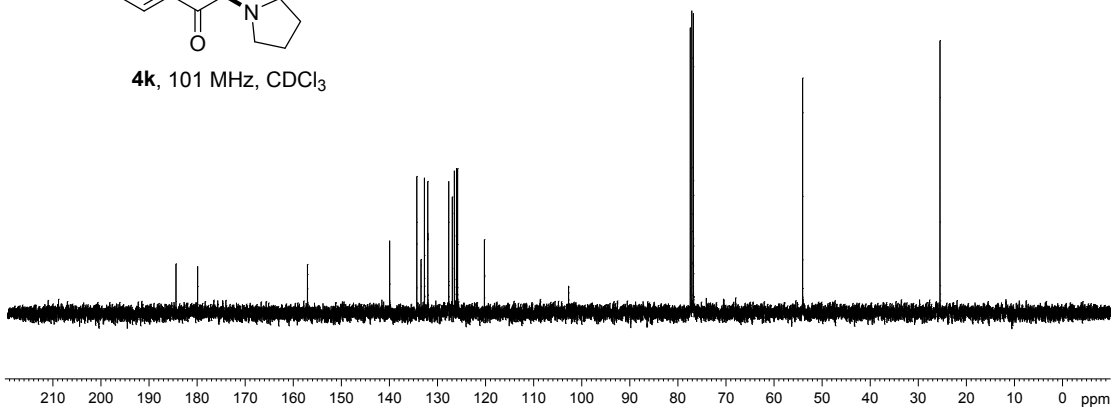
4k, 400 MHz, $CDCl_3$

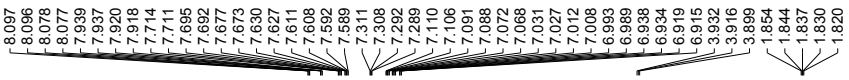


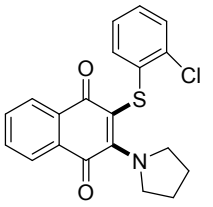




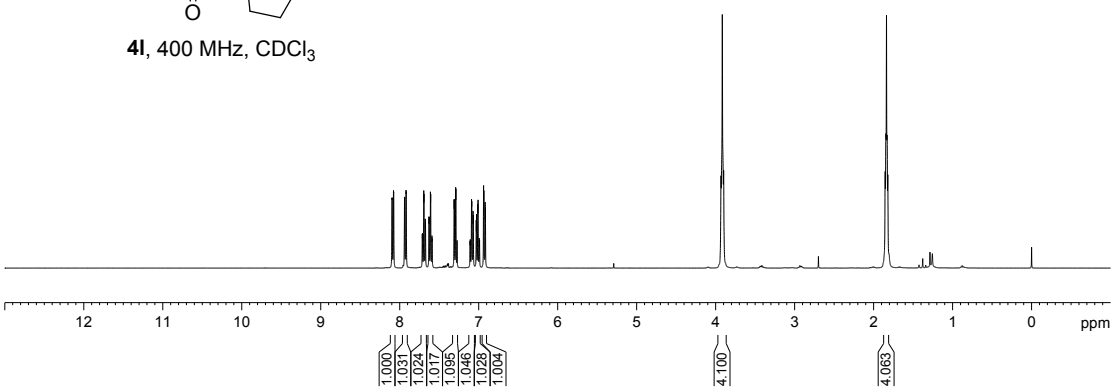
4k, 101 MHz, $CDCl_3$

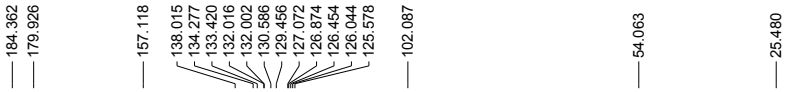


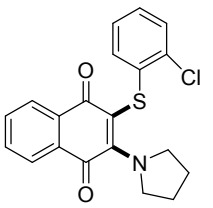




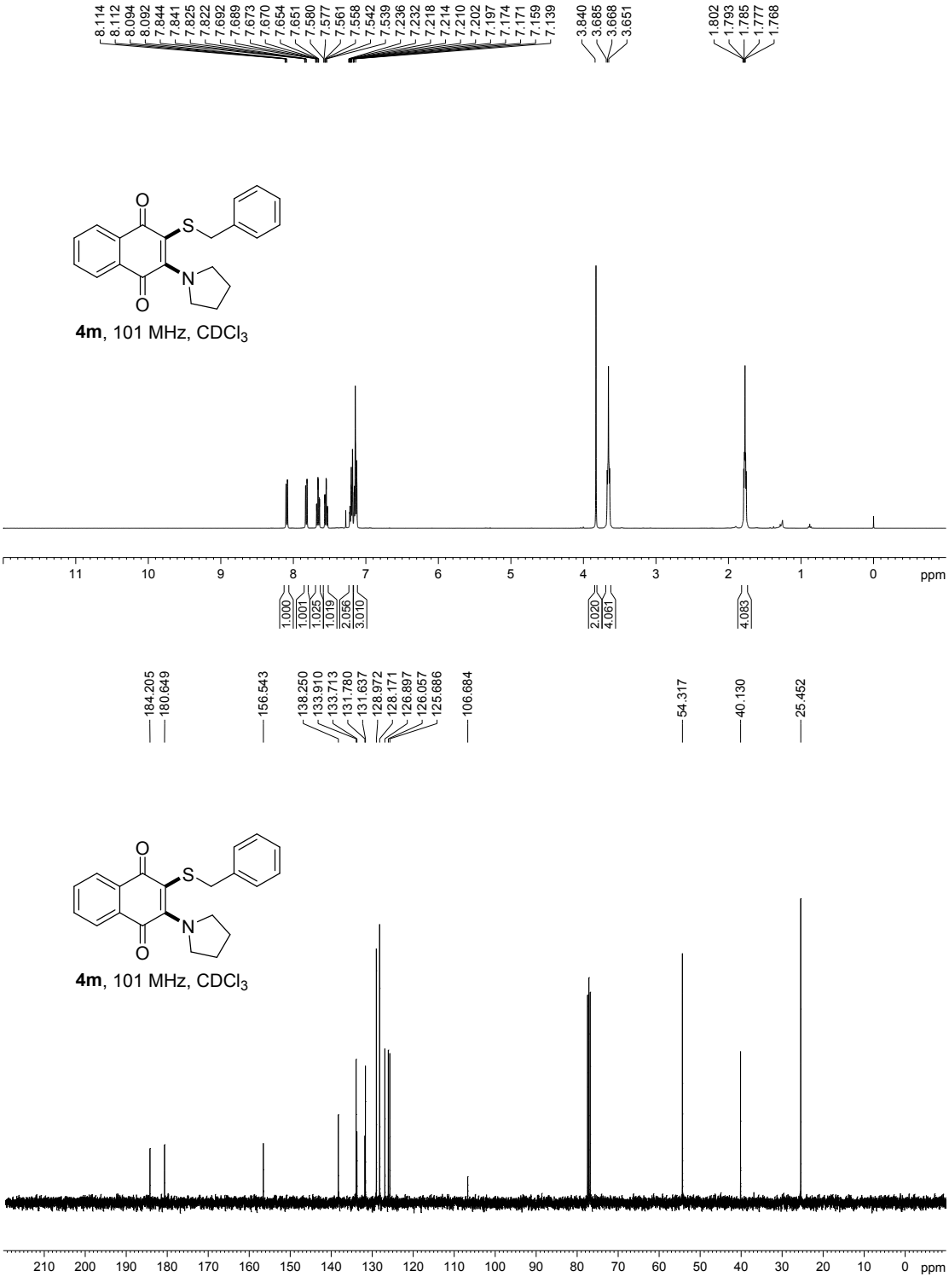
4l, 400 MHz, $CDCl_3$

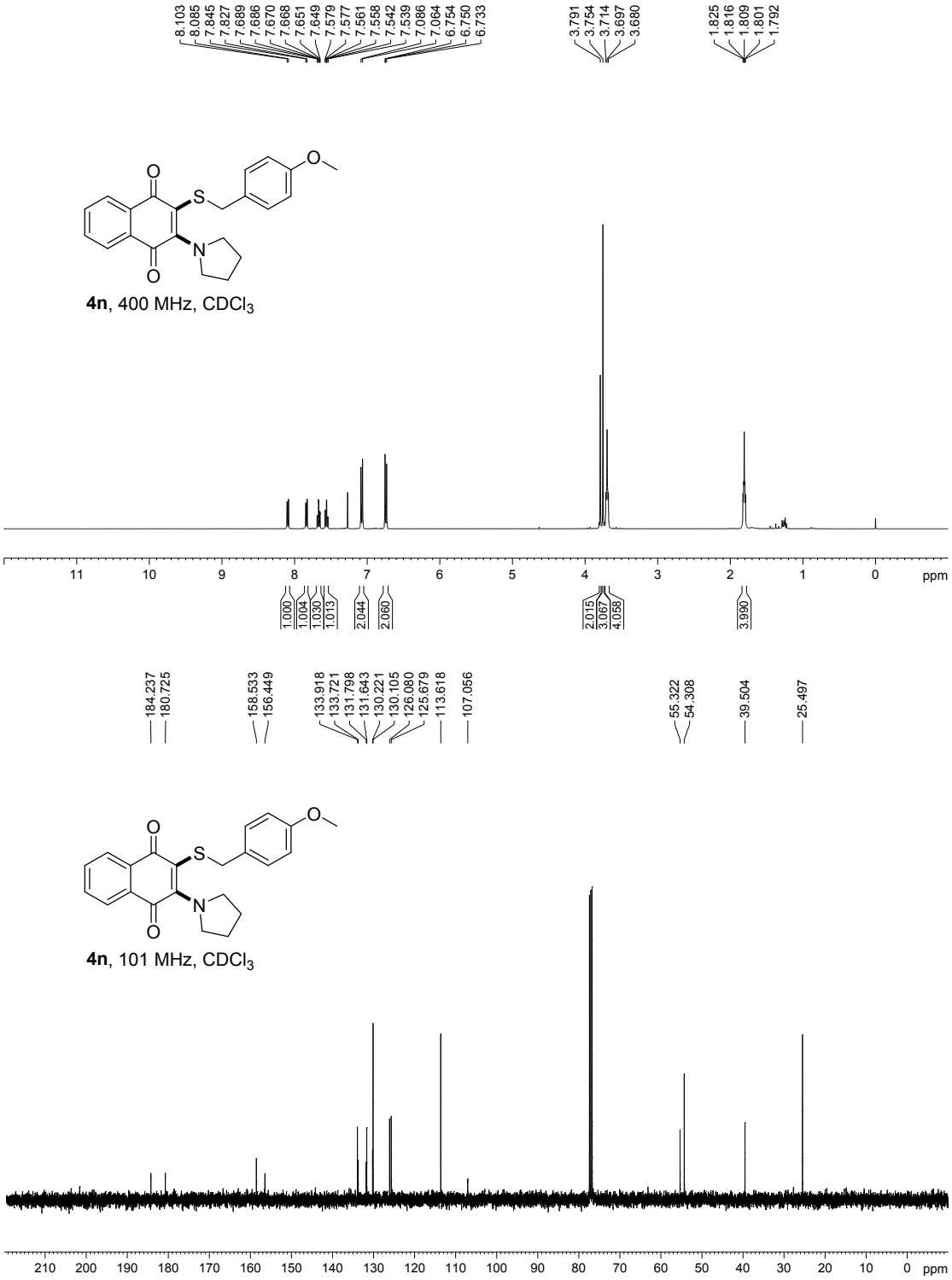


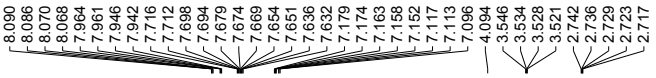


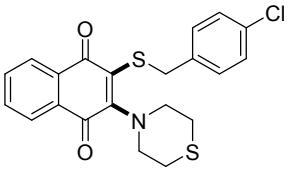


4l, 101 MHz, $CDCl_3$

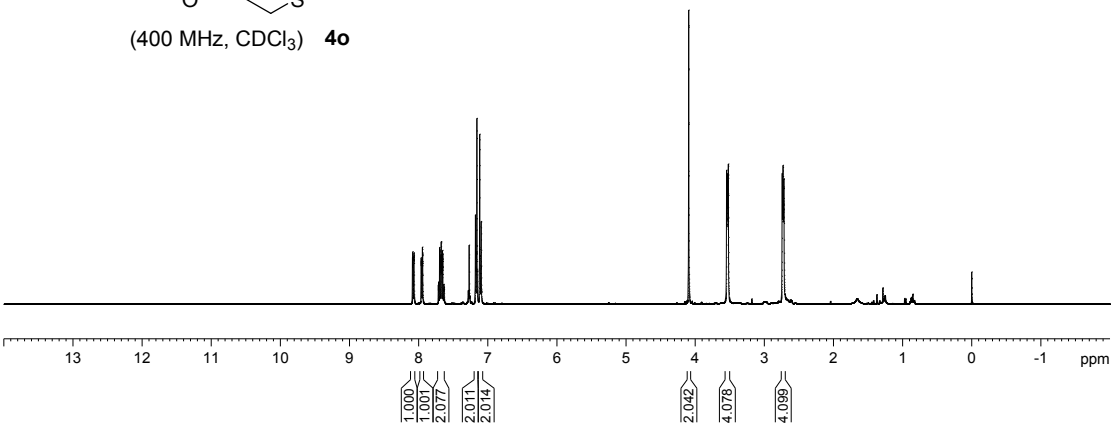

8.114
8.112
8.094
8.092
7.844
7.841
7.825
7.822
7.692
7.689
7.673
7.670
7.654
7.651
7.580
7.577
7.561
7.558
7.542
7.539
7.236
7.232
7.218
7.214
7.210
7.202
7.197
7.174
7.171
7.159
7.139
3.840
3.685
3.668
3.651
1.802
1.793
1.785
1.777
1.768
O
S
N
O
4m, 101 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.001
1.025
1.019
2.056
3.010
2.020
4.061
4.083
184.205
180.649
156.543
138.250
133.910
133.713
131.780
131.637
128.972
128.171
126.897
126.057
125.686
106.684
54.317
40.130
25.452
O
S
N
O
4m, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

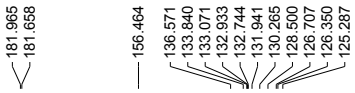

8.103
8.085
7.845
7.827
7.689
7.686
7.670
7.668
7.651
7.649
7.579
7.577
7.561
7.558
7.542
7.539
7.086
7.064
6.754
6.750
6.733
3.791
3.754
3.714
3.697
3.680
1.825
1.816
1.809
1.801
1.792
O
S
N
O
O
4n, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.004
1.030
1.013
2.044
2.060
2.015
3.067
4.058
3.990
184.237
180.725
158.533
156.449
133.918
133.721
131.798
131.643
130.221
130.105
126.080
125.679
113.618
107.056
55.322
54.308
39.504
25.497
O
S
N
O
O
4n, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

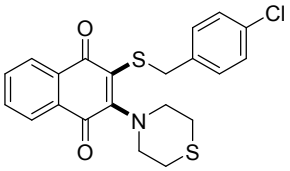




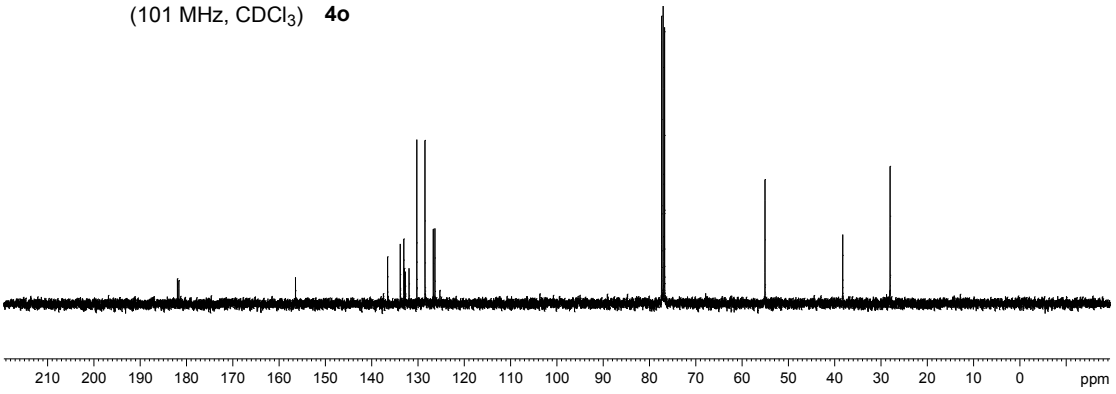
(400 MHz, $CDCl_3$) **4o**

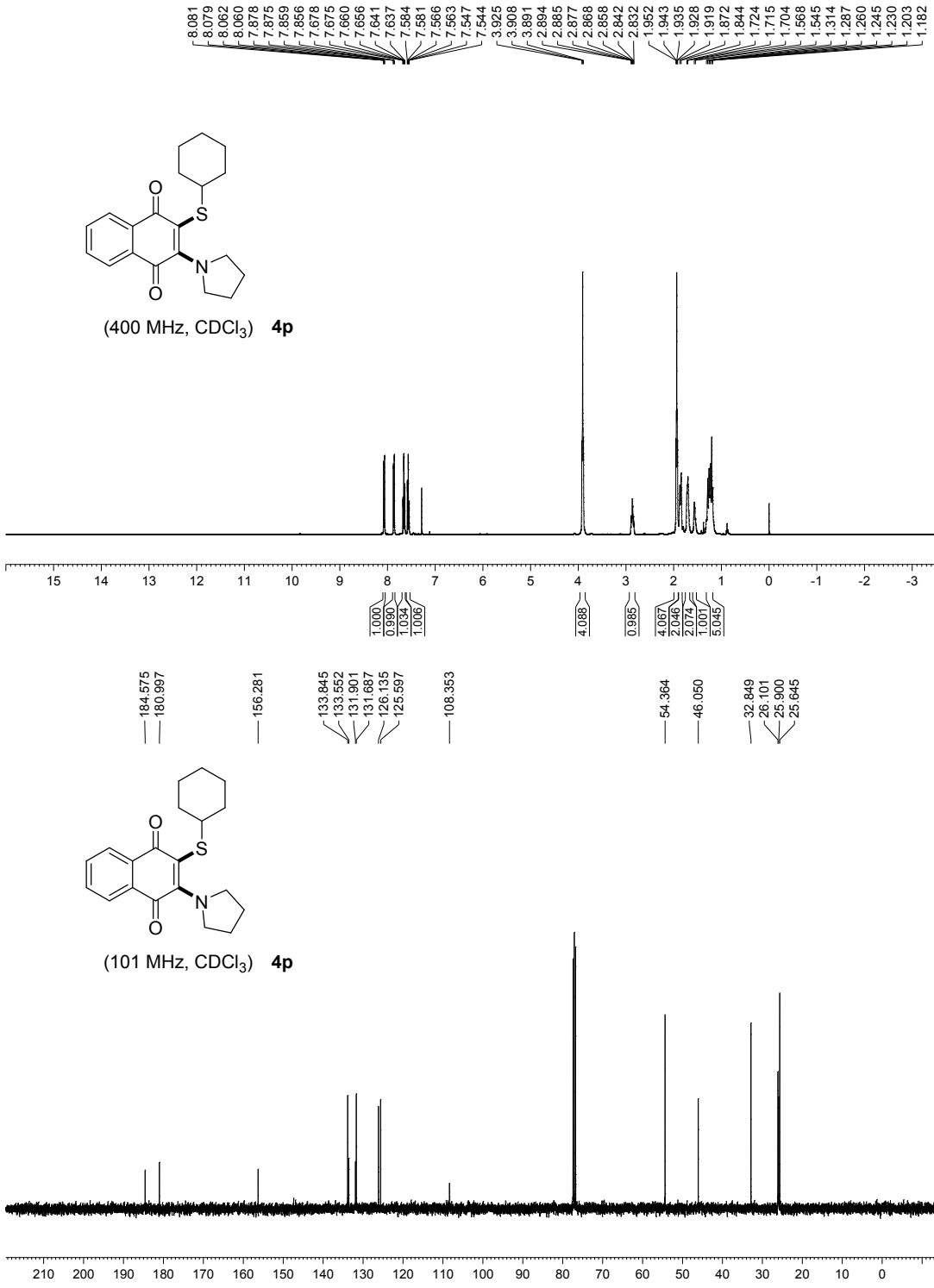


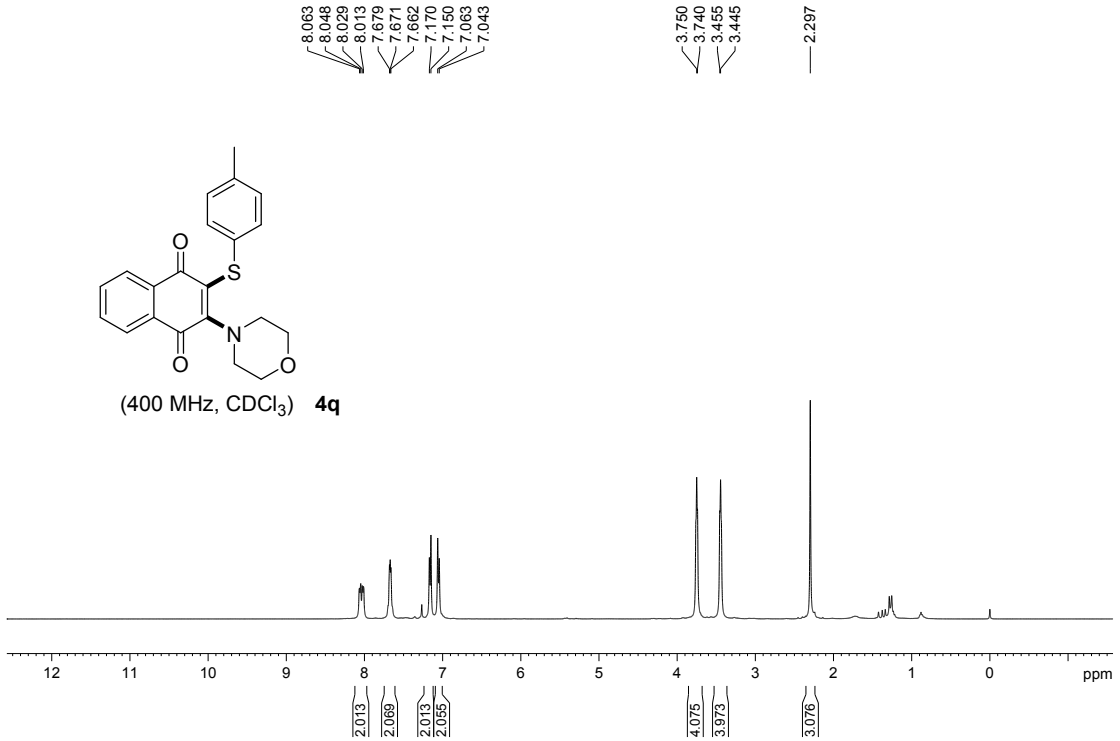




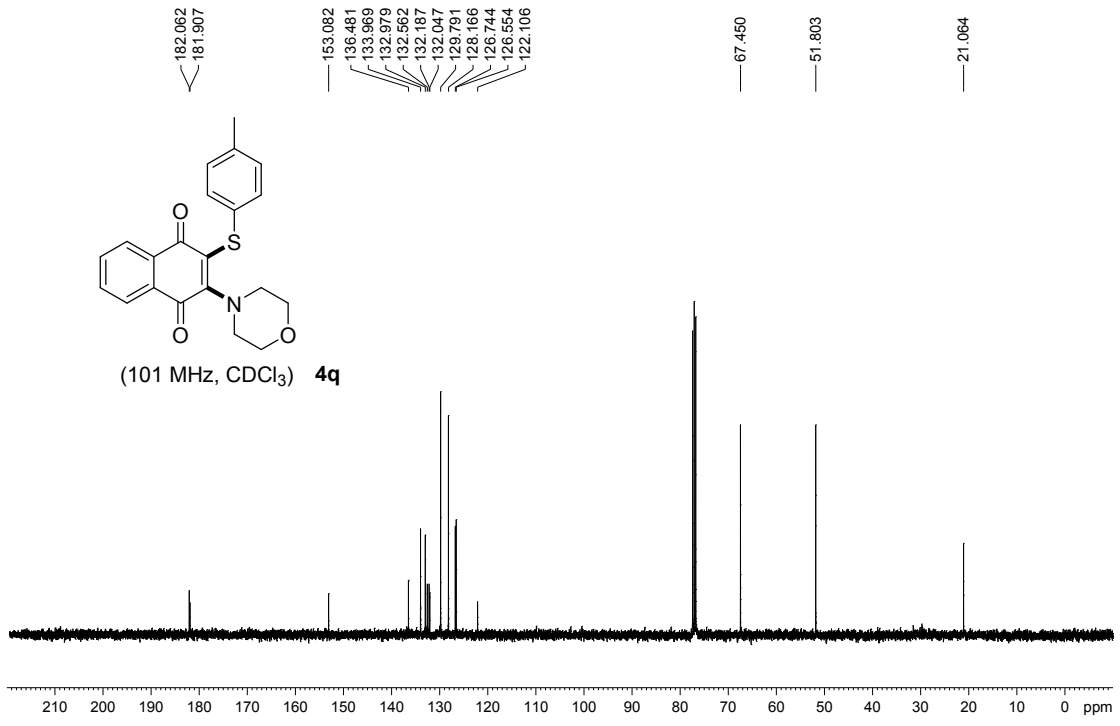
(101 MHz, $CDCl_3$) **4o**



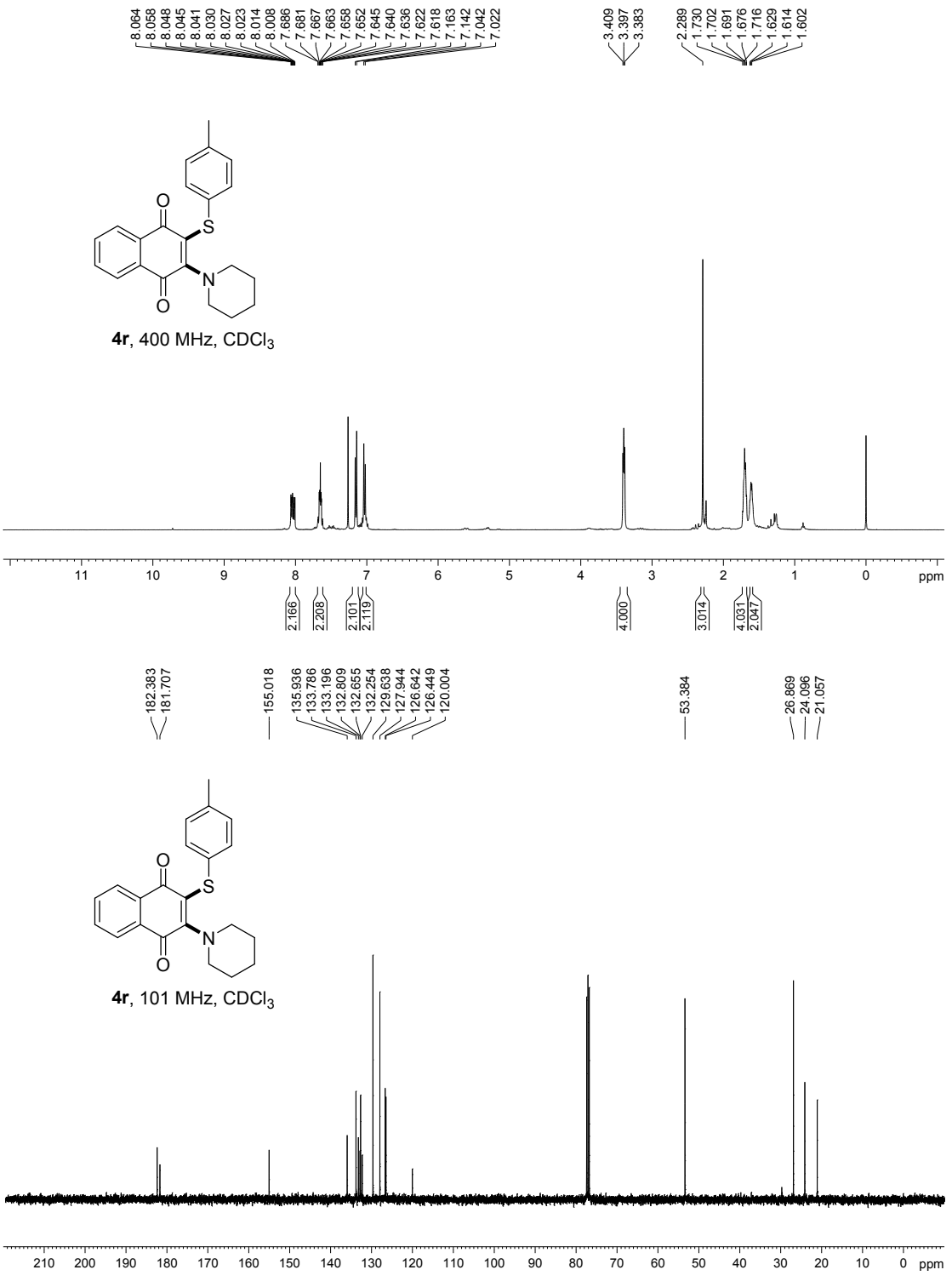

8.081
8.079
8.062
8.060
7.878
7.875
7.859
7.856
7.678
7.675
7.660
7.656
7.641
7.637
7.584
7.581
7.566
7.563
7.547
7.544
3.925
3.908
3.891
2.894
2.885
2.877
2.868
2.858
2.842
2.832
1.952
1.943
1.935
1.928
1.919
1.872
1.844
1.724
1.715
1.704
1.568
1.545
1.314
1.287
1.260
1.245
1.230
1.203
1.182
O
S
N
O
(400 MHz, CDCl3) 4p
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
1.000
0.990
1.034
1.006
4.088
0.985
4.067
2.046
2.074
1.001
5.045
184.575
180.997
156.281
133.845
133.552
131.901
131.687
126.135
125.597
108.353
54.364
46.050
32.849
26.101
25.900
25.645
O
S
N
O
(101 MHz, CDCl3) 4p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

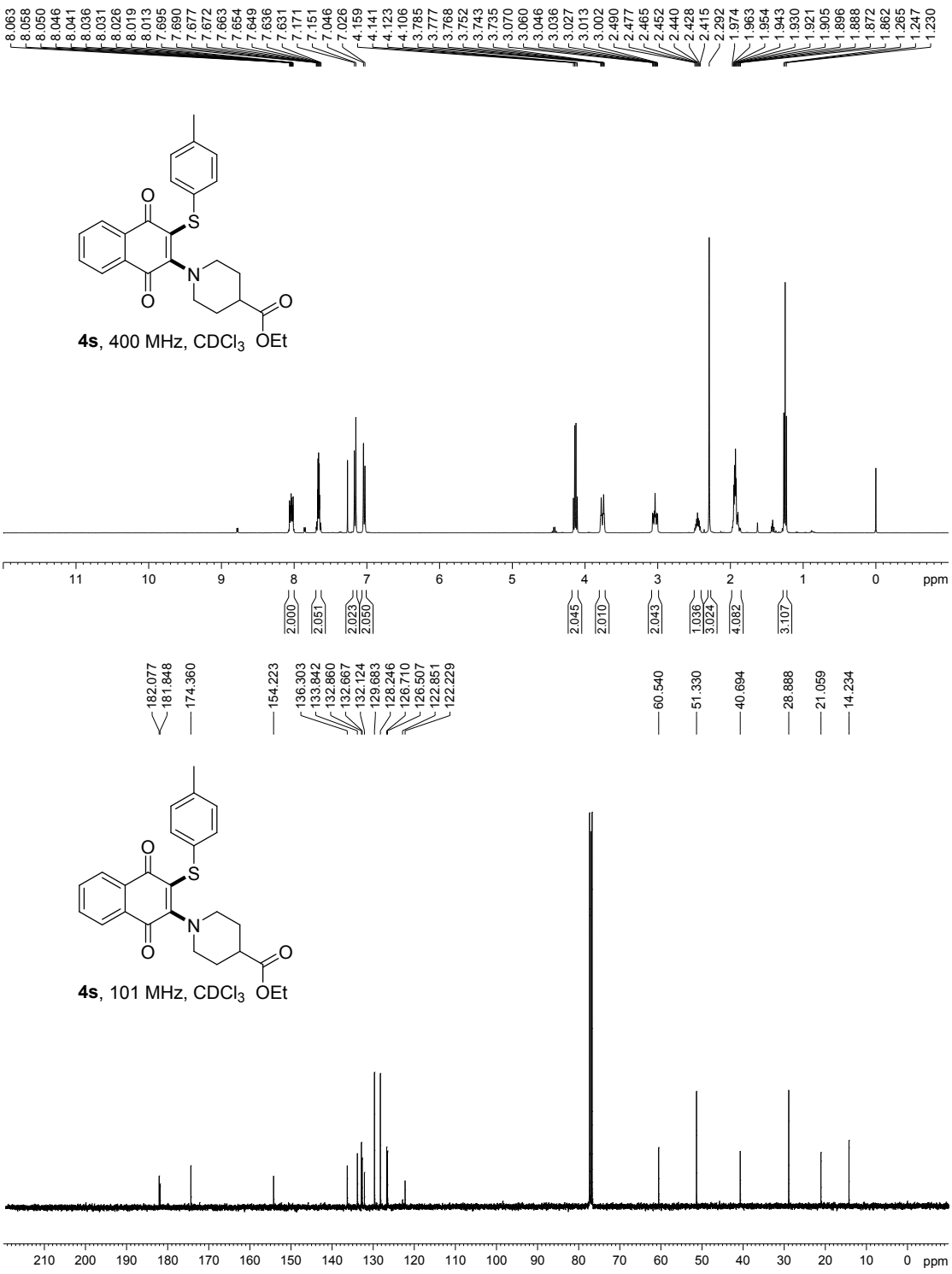


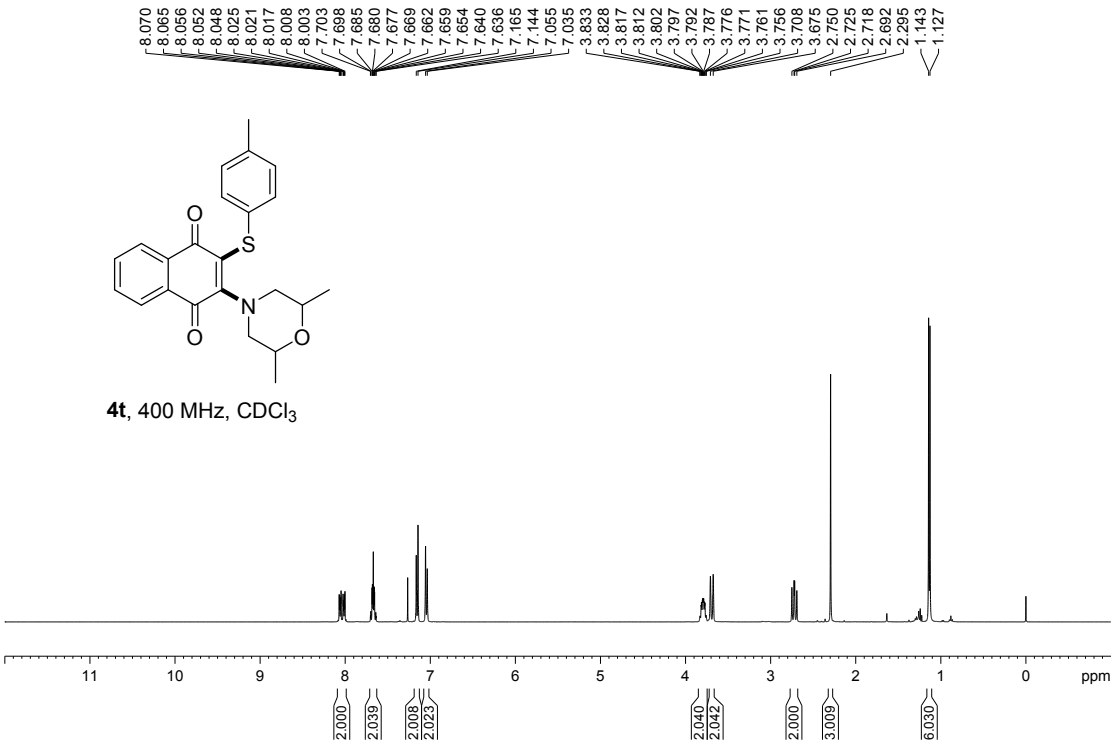
(400 MHz, $CDCl_3$) **4q**



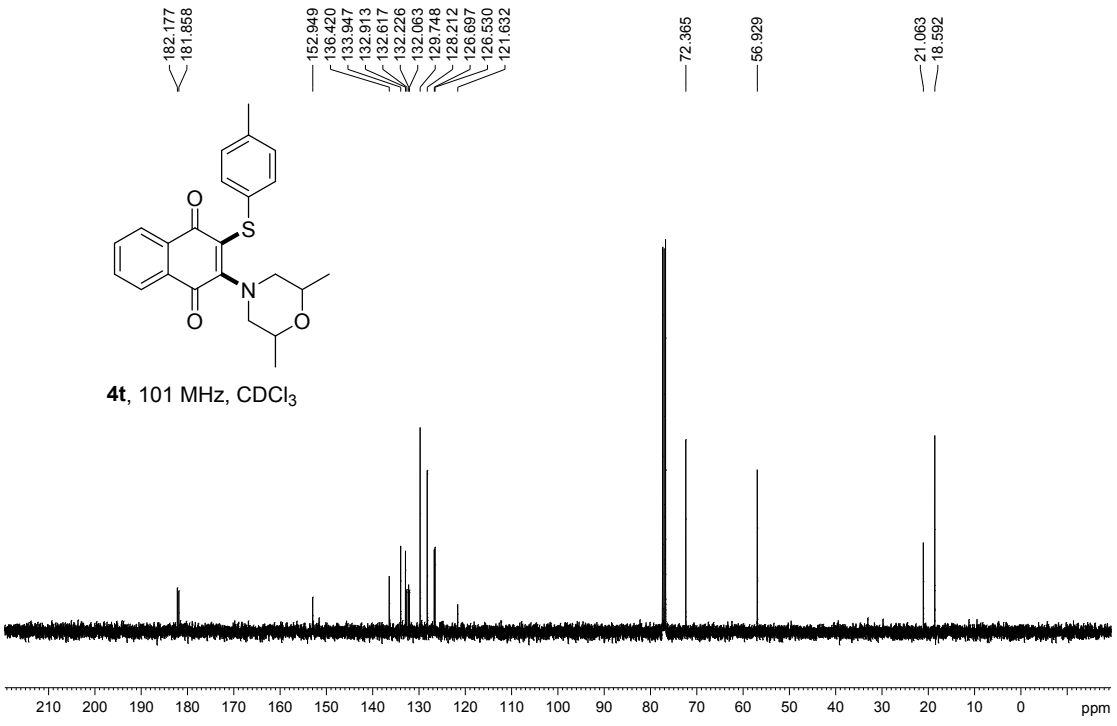
(101 MHz, $CDCl_3$) **4q**


8.064
8.058
8.048
8.045
8.041
8.030
8.027
8.023
8.014
8.008
7.686
7.681
7.667
7.663
7.658
7.652
7.645
7.640
7.636
7.622
7.618
7.163
7.142
7.042
7.022
3.409
3.397
3.383
2.289
1.730
1.702
1.691
1.676
1.716
1.629
1.614
1.602
O
S
N
O
4r, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.166
2.208
2.101
2.119
4.000
3.014
4.031
2.047
182.383
181.707
155.018
135.936
133.786
133.196
132.809
132.655
132.254
129.638
127.944
126.642
126.449
120.004
53.384
26.869
24.096
21.057
O
S
N
O
4r, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

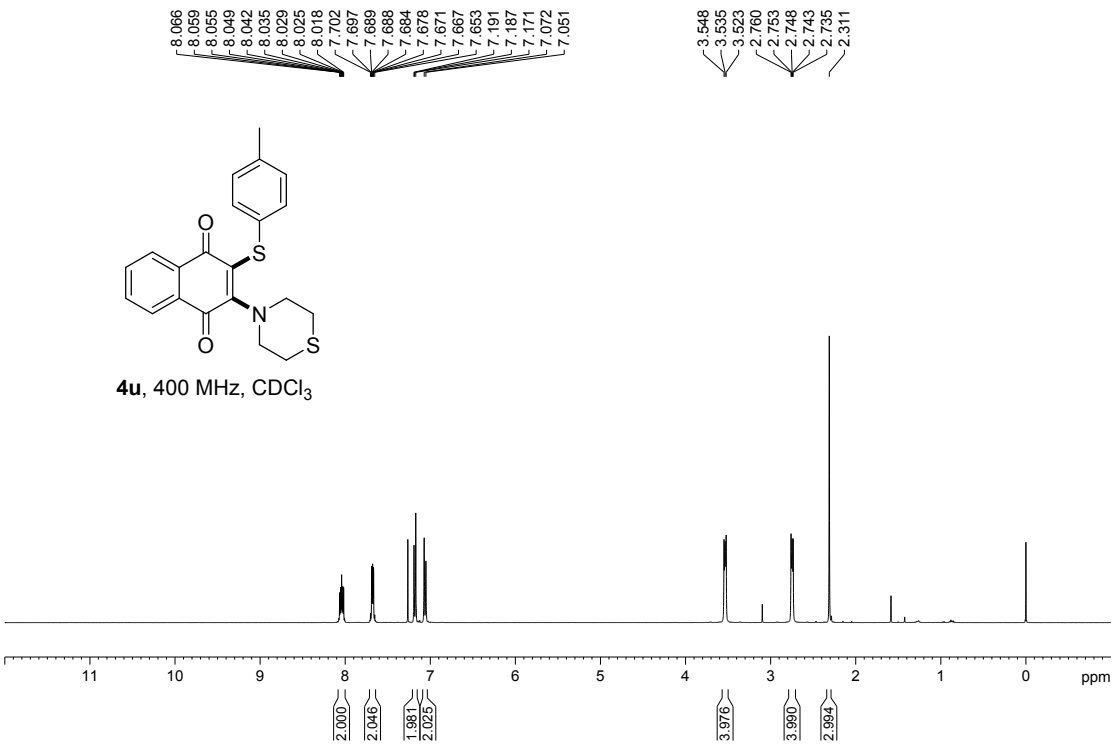

8.063
8.058
8.050
8.046
8.041
8.036
8.031
8.026
8.019
8.013
7.695
7.690
7.677
7.672
7.663
7.654
7.649
7.636
7.631
7.171
7.151
7.046
7.026
4.159
4.141
4.123
4.106
3.785
3.777
3.768
3.752
3.743
3.735
3.070
3.060
3.046
3.036
3.027
3.013
3.002
2.490
2.477
2.465
2.452
2.440
2.428
2.415
2.292
1.974
1.963
1.954
1.943
1.930
1.921
1.905
1.896
1.888
1.872
1.862
1.265
1.247
1.230
O
S
N
O
O
O
OEt
4s, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.051
2.023
2.050
2.045
2.010
2.043
1.036
3.024
4.082
3.107
182.077
181.848
174.360
154.223
136.303
133.842
132.860
132.667
132.124
129.683
128.246
126.710
126.507
122.851
122.229
60.540
51.330
40.694
28.888
21.059
14.234
O
S
N
O
O
O
OEt
4s, 101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



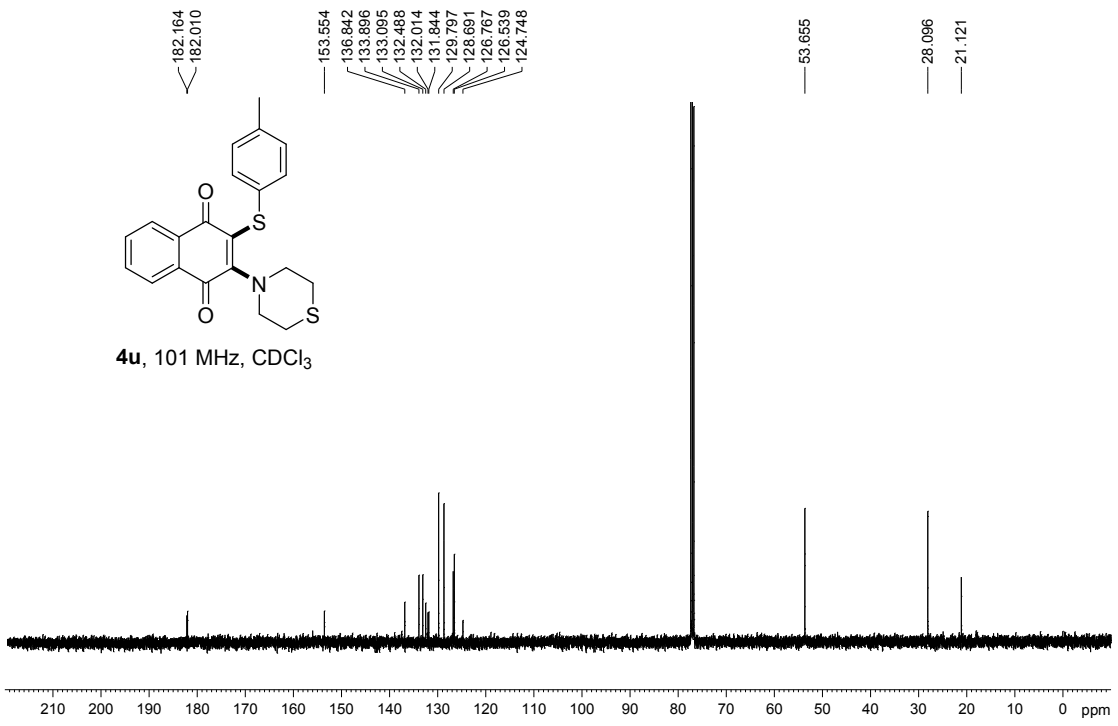
4t, 400 MHz, $CDCl_3$



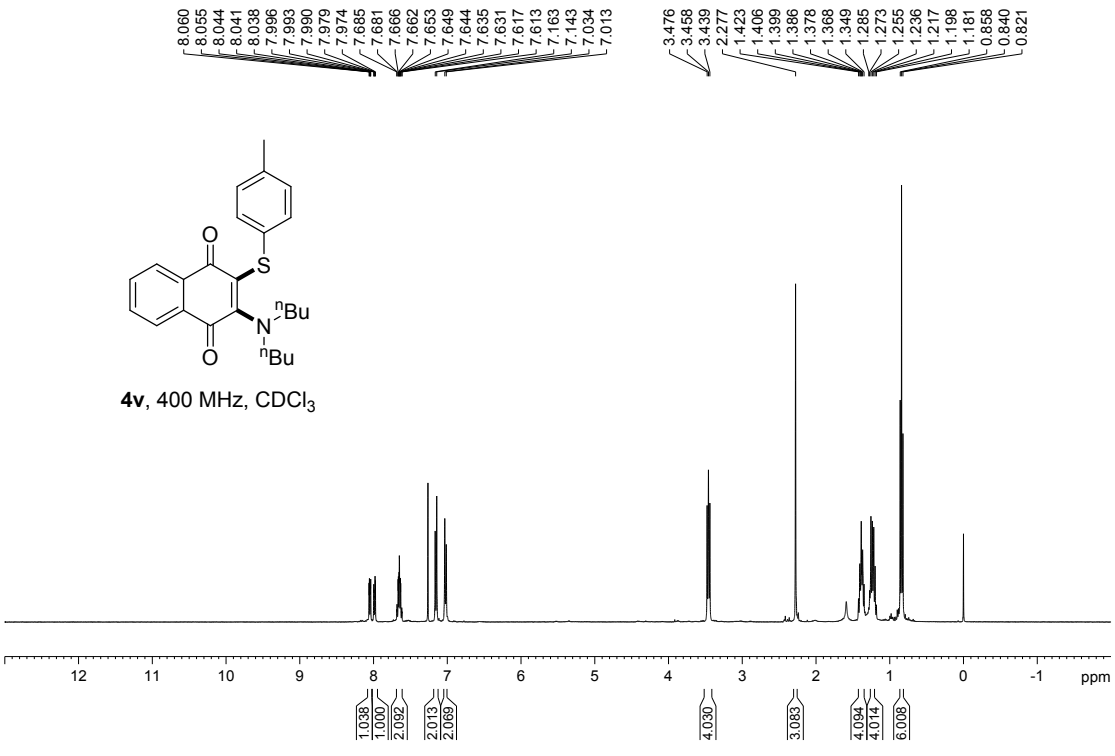
4t, 101 MHz, $CDCl_3$



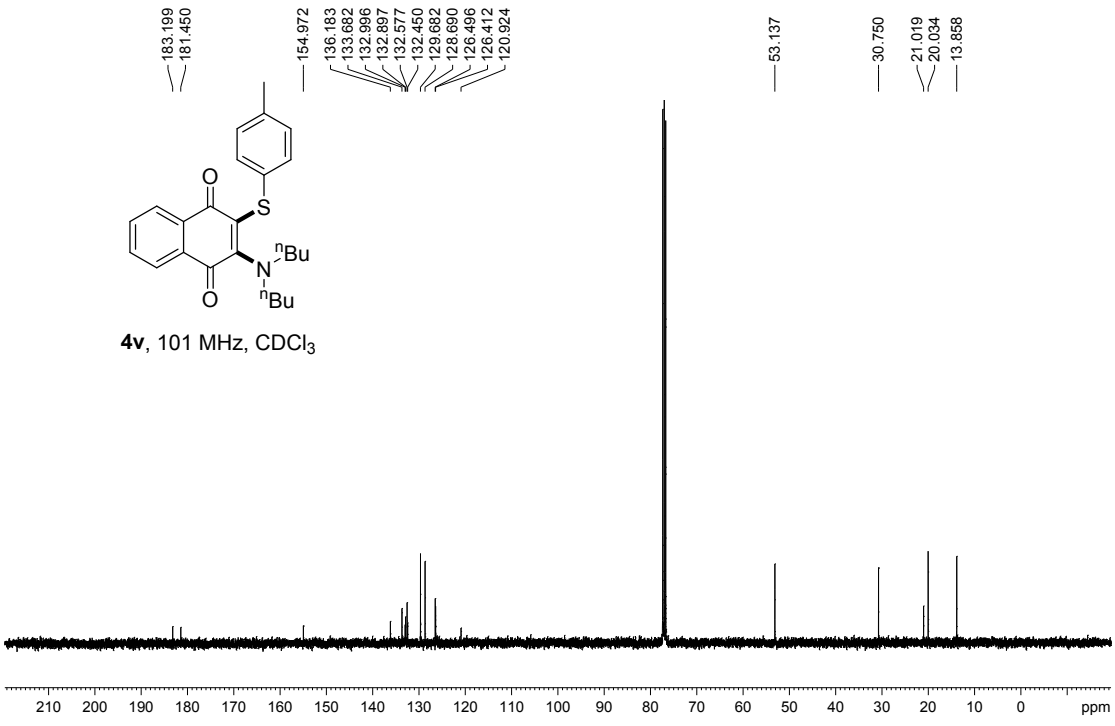
4u, 400 MHz, $CDCl_3$



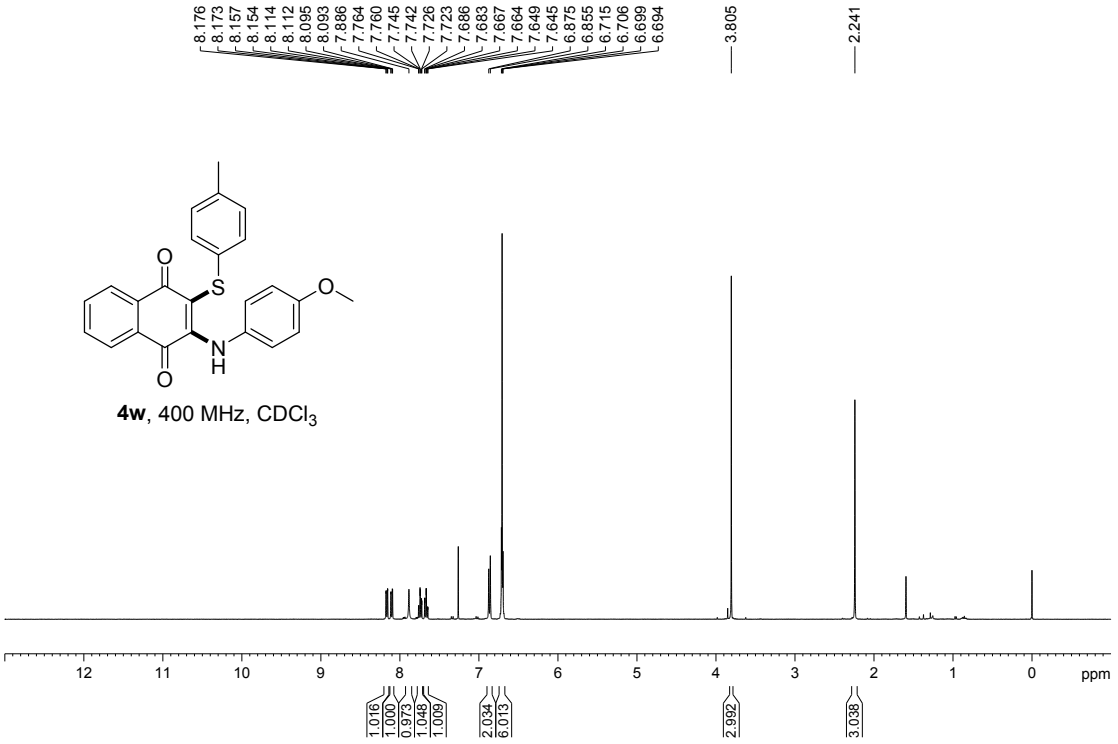
4u, 101 MHz, $CDCl_3$



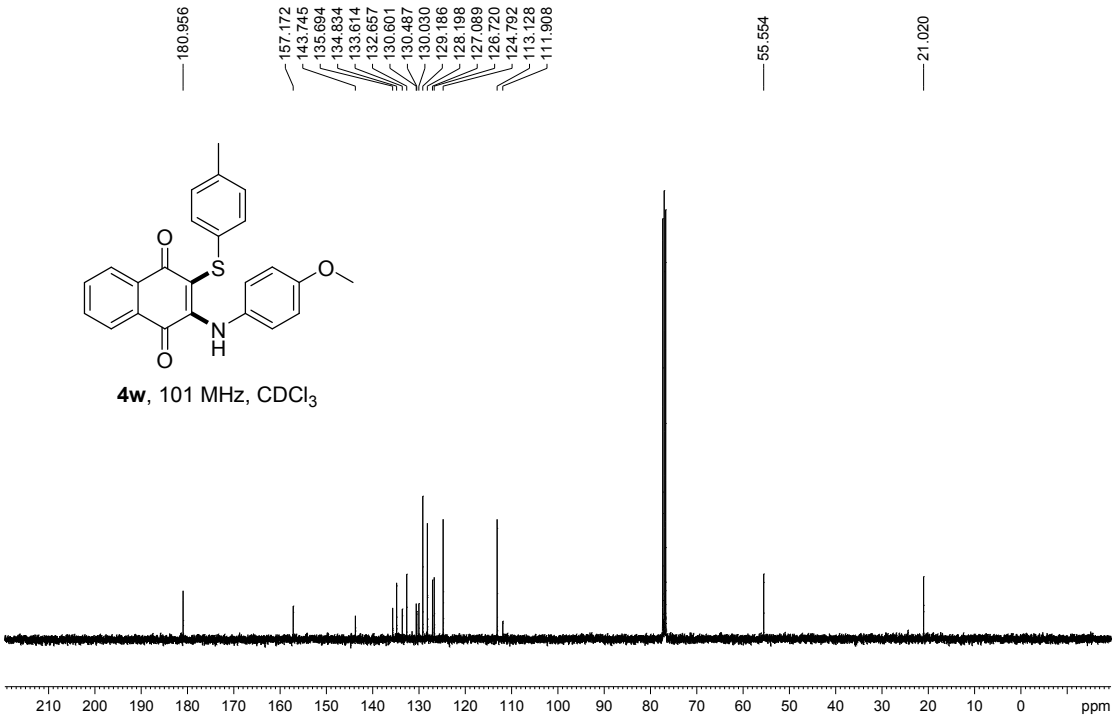
4v, 400 MHz, $CDCl_3$



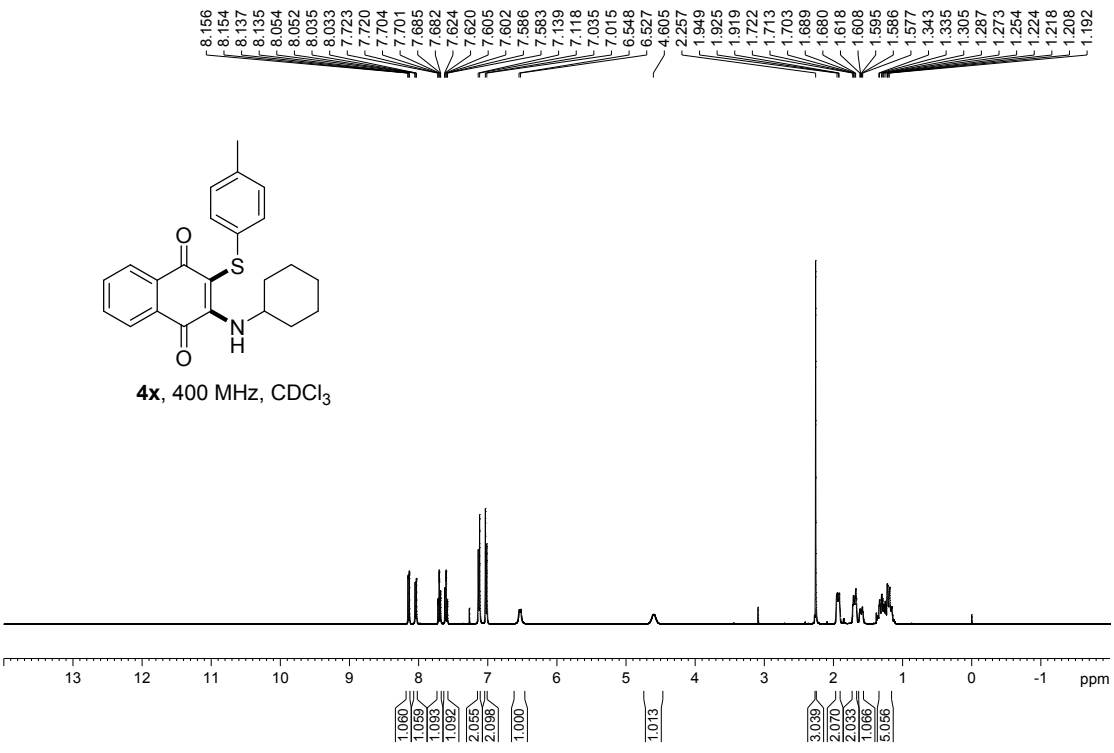
4v, 101 MHz, $CDCl_3$



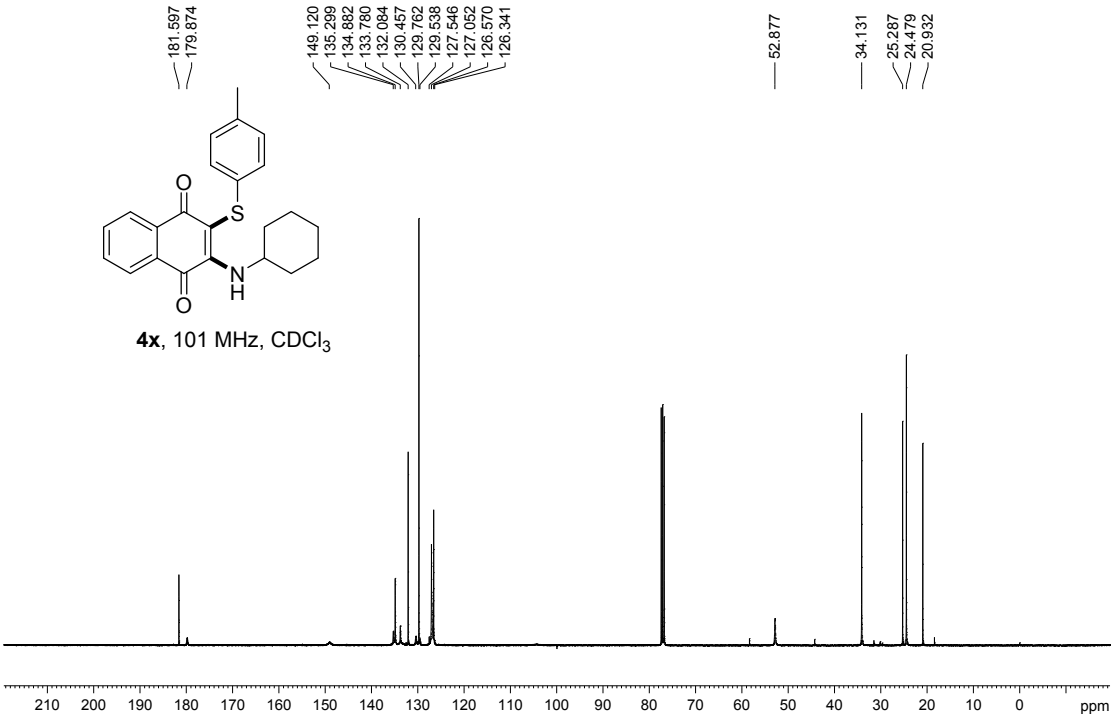
4w, 400 MHz, $CDCl_3$



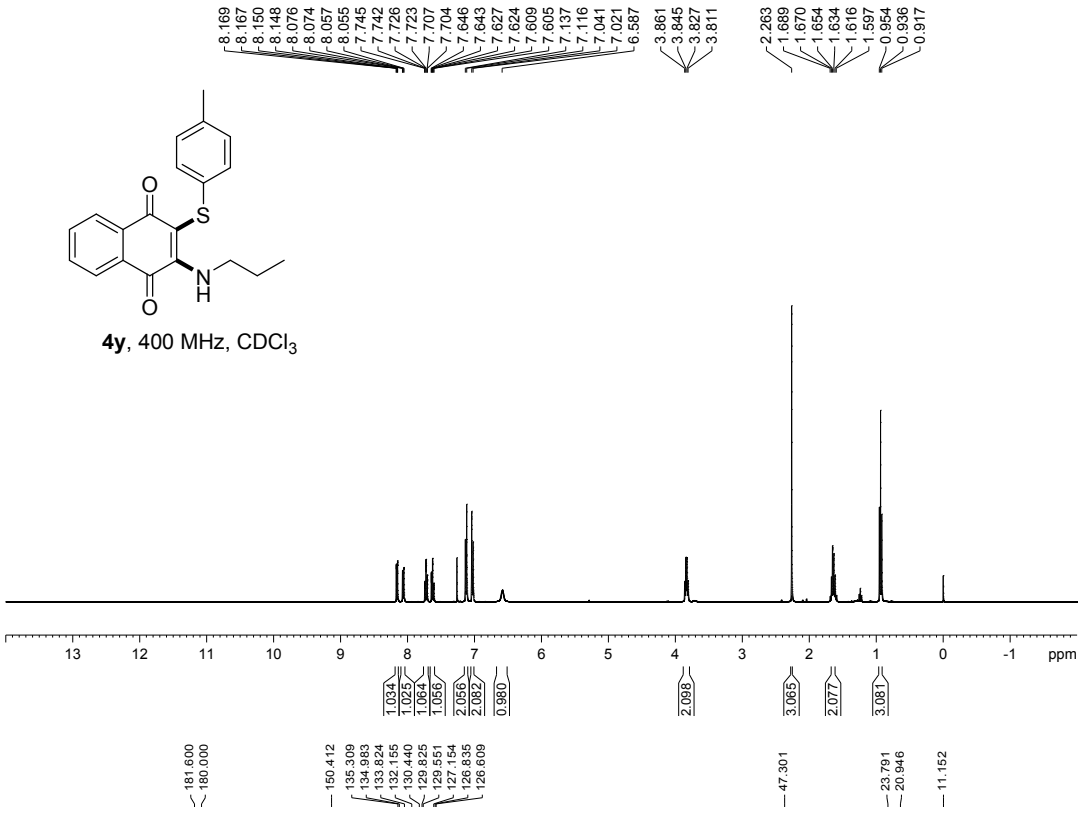
4w, 101 MHz, $CDCl_3$



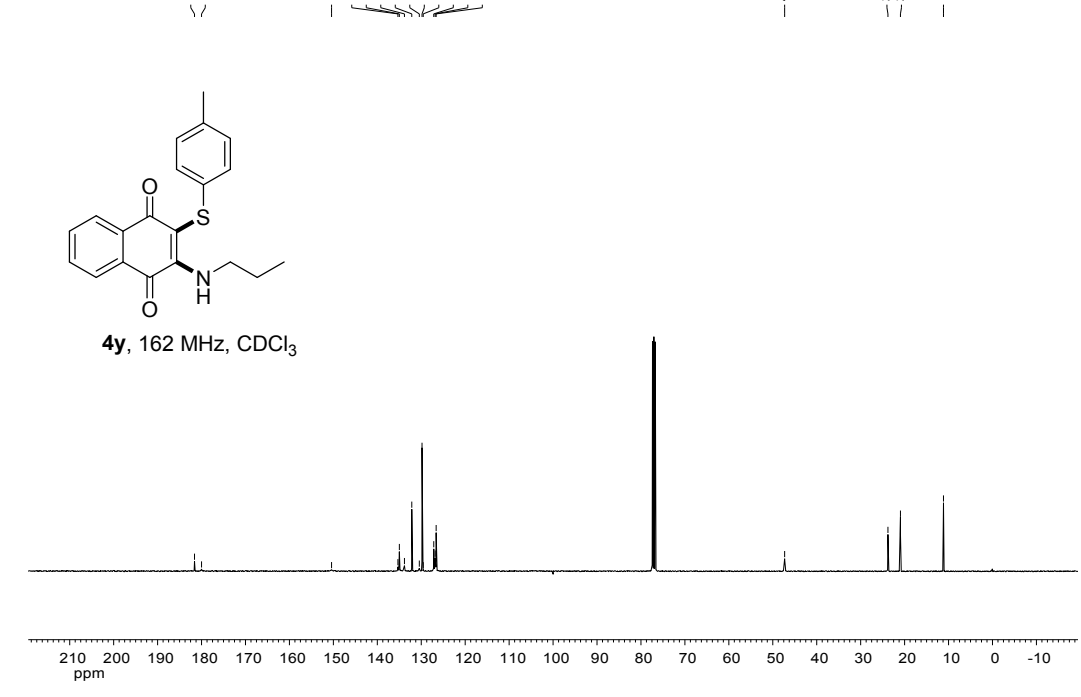
4x, 400 MHz, $CDCl_3$



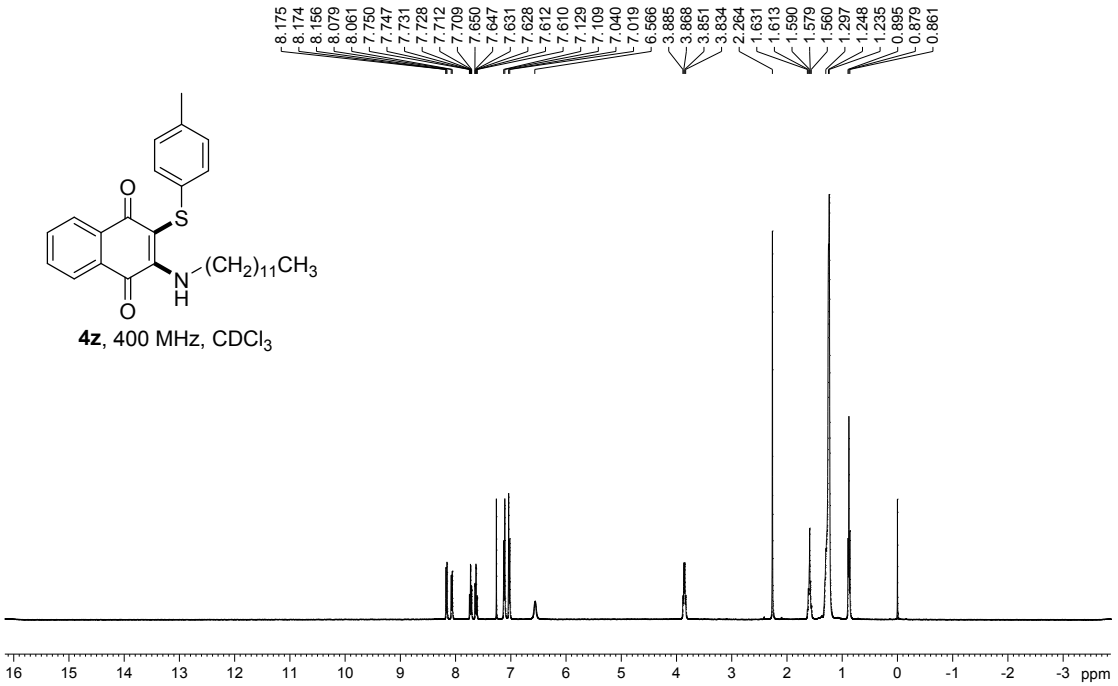
4x, 101 MHz, $CDCl_3$



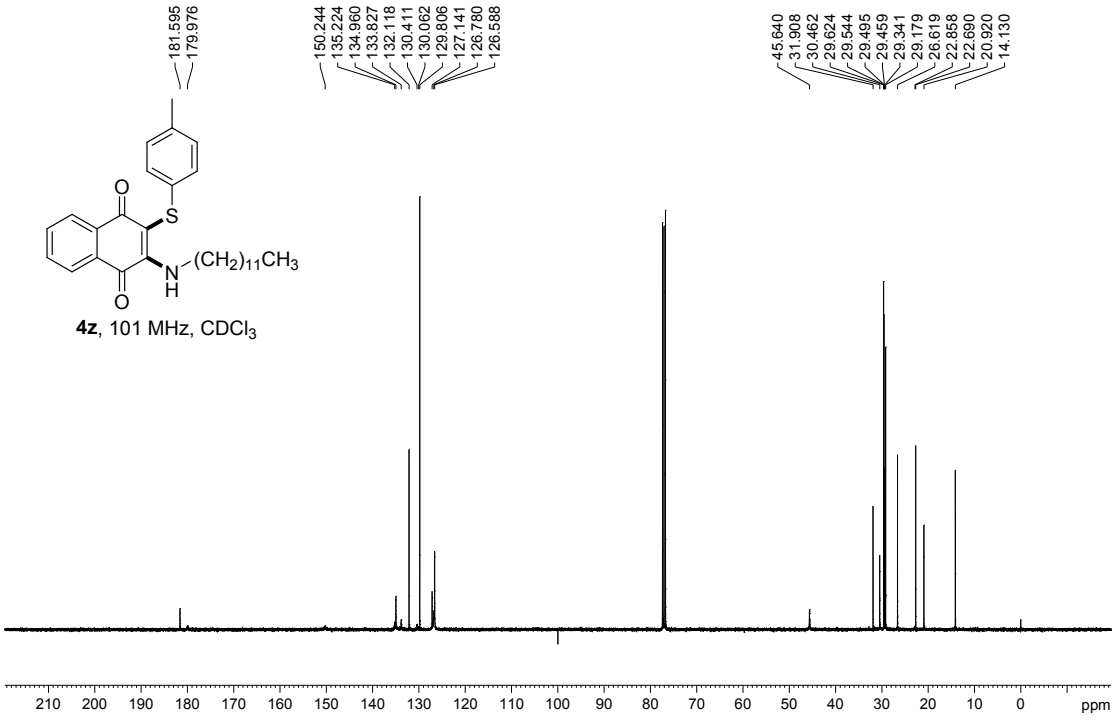
4y, 400 MHz, $CDCl_3$



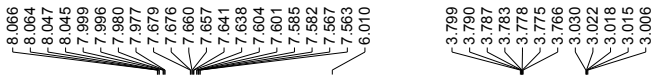
4y, 162 MHz, $CDCl_3$

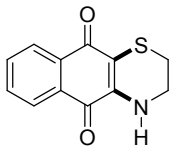


4z, 400 MHz, $CDCl_3$

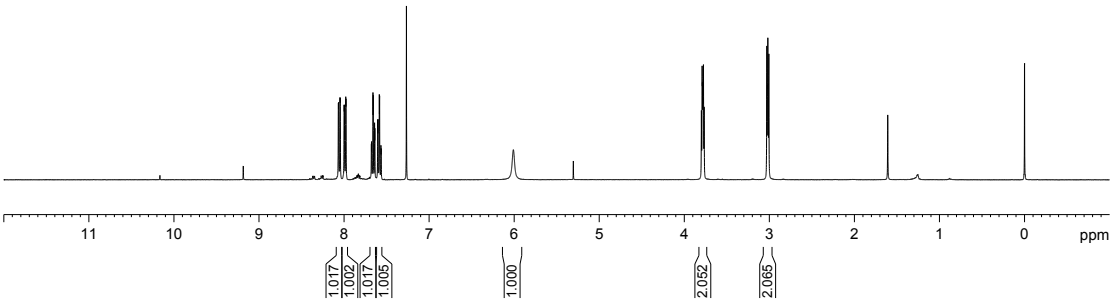


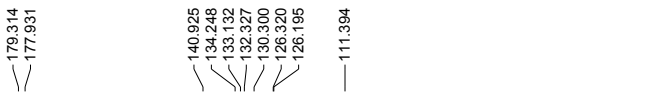
4z, 101 MHz, $CDCl_3$

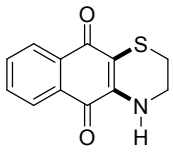




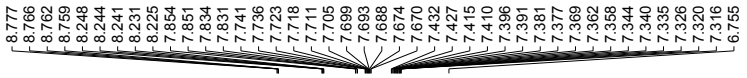
6a, 400 MHz, $CDCl_3$

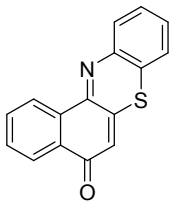




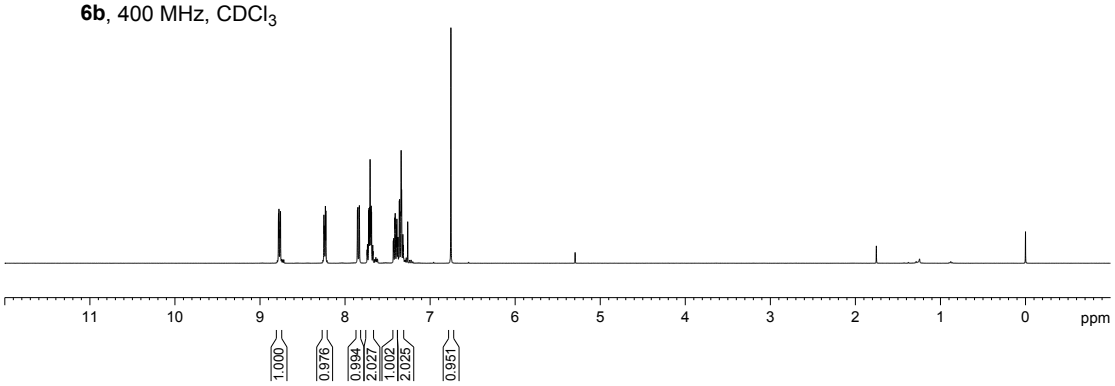


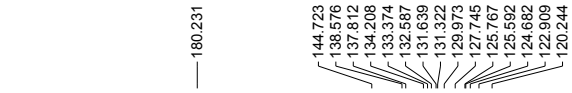
6a, 101 MHz, $CDCl_3$

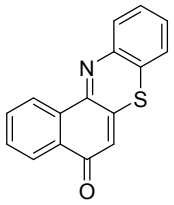




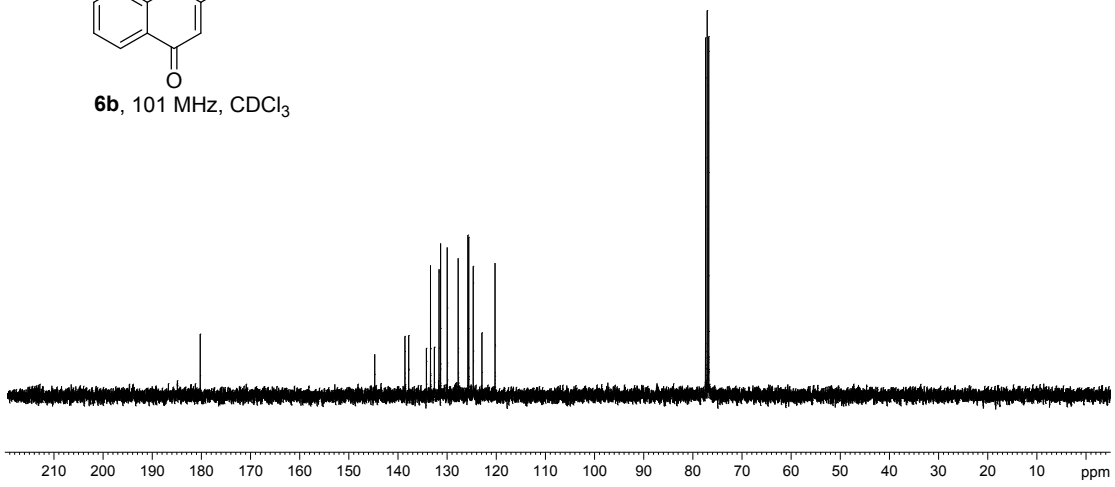
6b, 400 MHz, $CDCl_3$

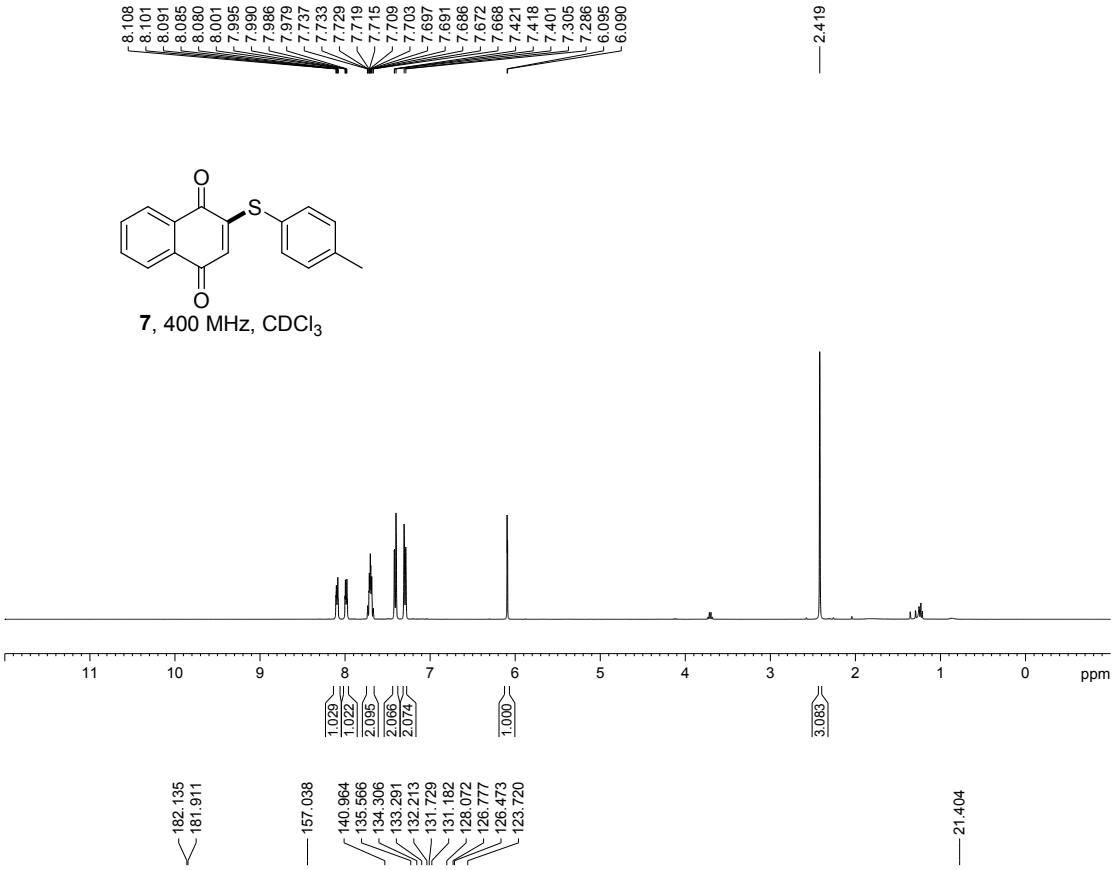




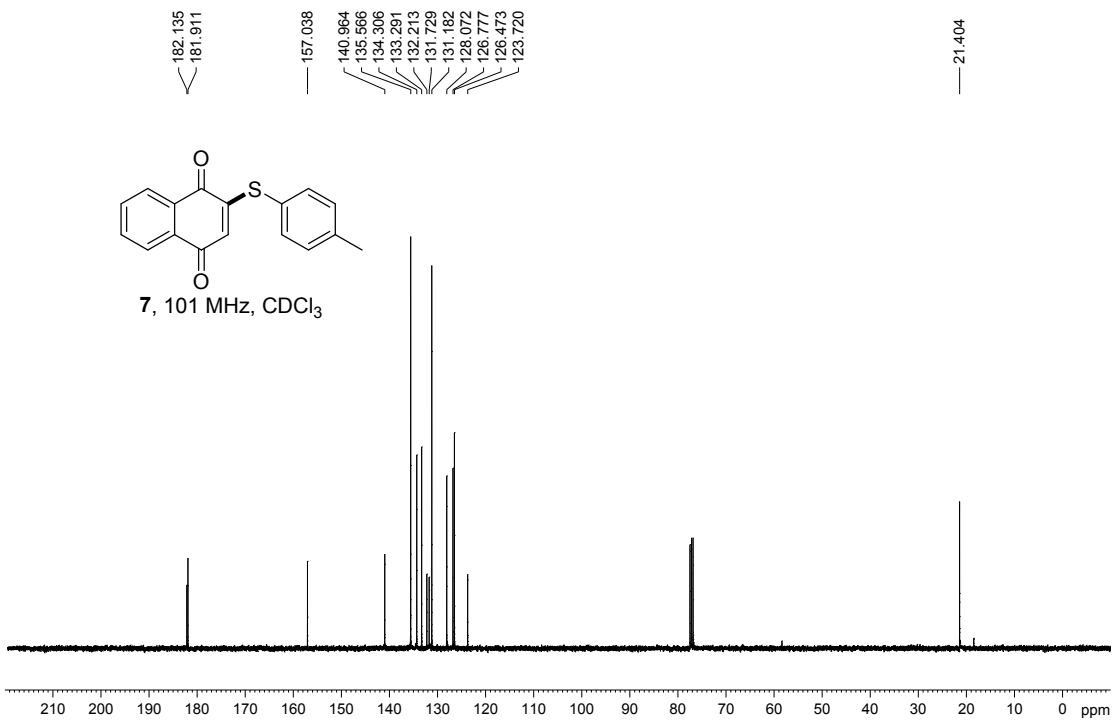


6b, 101 MHz, $CDCl_3$





7, 400 MHz, $CDCl_3$



7, 101 MHz, $CDCl_3$