Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

[4 + 2] Cycloaddition Reactions of β-Naphtha-1-thioquinones Generated from 2-Naphthols and DAST

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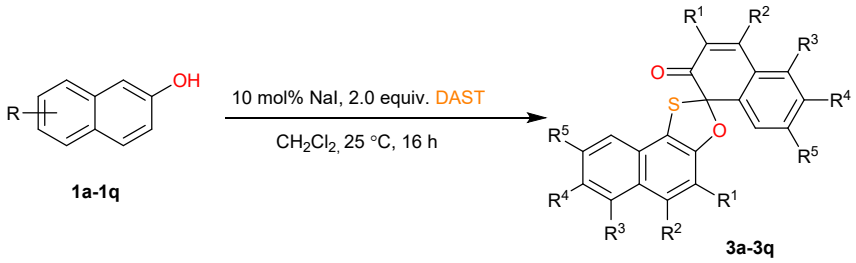
1. Experimental section

1.1 Materials and instrumentation

All manipulations were carried out in glass reaction tubes equipped with magnetic stir bars under argon atmosphere. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Melting points were recorded by XT4A micro Melting point Measurement Instruments, thermometer was unrevised. The transformation progress and Mass spectra were indicated by LC-MSD-Trap-XCT instrument. High-resolution mass spectrometry (HRMS) data were obtained on an Agilent Technologies 1290-6540 UHPLC/AccurateMass Quadrupole Time-of Flight (Q-TOF) LC/MS using ESI as the ion source. X-ray analysis was performed with a single-crystal X-ray diffractometer. Moreover, NMR spectra were obtained on Bruker AVANCE III 400 systems using $CDCl_3$ or DMSO-d_6 as solvent, TMS as internal standard substance, with proton and carbon resonances at 400 and 100 MHz, respectively.

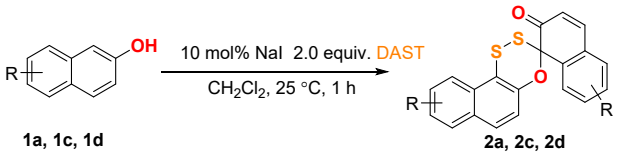
1.2 Synthetic procedures

General Procedure A: Synthesis of the products of **3a**-**3q**.



A dried glass reaction tube equipped with a magnetic stir bar was charged with 2-naphthol **1** (1.0 mmol), NaI (15 mg, 0.1 mmol) and CH_2Cl_2 (5 mL). Then DAST (0.26 mL, 2.0 mmol) was slowly injected by syringe, the mixture was stirred at room temperature for 16 h. The reaction progress was monitored by TLC. The reaction mixture was added with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (5.0 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated, and the residue was purified by flash column chromatography to give the pure product. The products were characterized by ^1H NMR, ^{13}C NMR and HRMS.

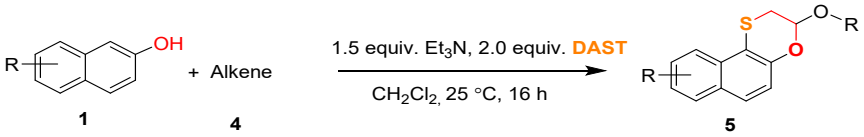
General Procedure B: Synthesis of compounds **2a**, **2c** and **2d.**



1a, 1c, 1d 2a, 2c, 2d

A dried glass reaction tube equipped with a magnetic stir bar was charged with 2-naphthol **1** (1.0 mmol), NaI (15 mg, 0.1 mmol) and CH_2Cl_2 (5 mL). Then DAST (0.26 mL, 2.0 mmol) was slowly injected by syringe, the mixture was stirred at room temperature for 1 h. Then the reaction mixture was added with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (5.0 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, concentrated, and the residue was purified by flash column chromatography to give the pure product. The products were characterized by ^1H NMR, ^{13}C NMR and HRMS.

General Procedure C: Synthesis of the compounds **5a-5ag.**



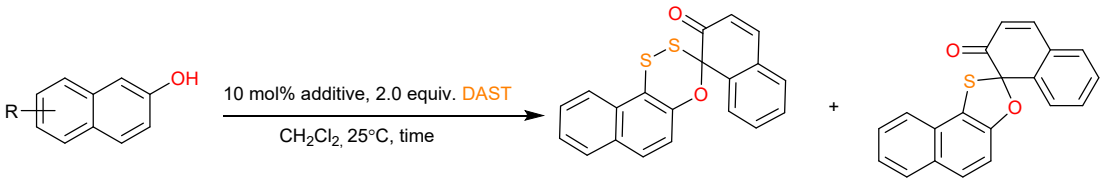
1 4 5

A dried glass reaction tube equipped with a magnetic stir bar was charged with 2-naphthol substrate **1** (1.0 mmol), **4** (3.0 mmol) and Et_3N (1.5 mmol). Then DAST (0.26 mL, 2.0 mmol) was slowly injected by syringe, the mixture was stirred at room temperature for 16 h. The reaction progress was monitored by TLC. After the reaction finished, the reaction mixture was added with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2 (5.0 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, concentrated, and the residue was purified by flash column chromatography to give the pure product. The products were characterized by ^1H NMR, ^{13}C NMR and HRMS.

2. Results and Discussion

2.1 Reaction Development and Optimization

Table S1. Additive screening[a],[b]



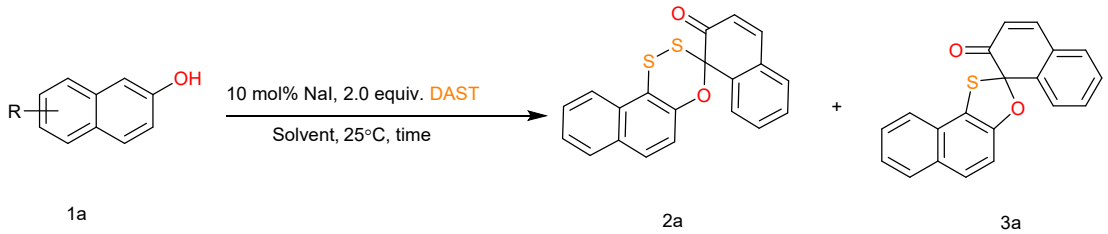
1a 2a 3a

entry	cat.	time (h)	conversion rate			yield[b]
			1a	2a	3a	

1	--	18	20%	50%	20%	9%
2	--	48	0	5%	80%	73%
3	CuI	16	0	0	85%	76%
4	ZnI_2	16	0	0	87%	73%
5	KI	16	0	0	78%	73%
6	NaI	16	0	0	87%	82%
7	CuCl	16	0	0	83%	61%
8	CuBr	16	0	0	78%	60%
9	$CuCl_2$	16	0	0	79%	68%
10	$CuBr_2$	16	0	0	74%	54%
11	NaCl	16	20%	16%	44%	10%

[a] Reaction conditions: **1a** (1.0 mmol), additive (10 mol%), DAST (2.0 mmol), 5.0 mL of CH_2Cl_2, 25 °C. [b] Yields were determined by HPLC external standard method.

Table S2. Solvent screening[a],[b]

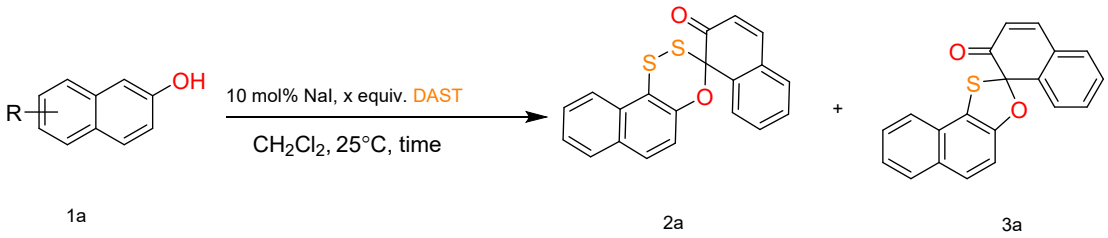


1a 2a 3a

entry	solvent	conversion rate			yield[b]
		1a	2a	3a	
1	DCE	0	0	87	79
2	THF	0	36	51	41
3	1,4-dioxane	0	28	59	38
4	CH_3CN	0	0	86	77

[a] Reaction conditions: **1a** (1.0 mmol), NaI (10 mol%), DAST (2.0 mmol), 5.0 mL of solvent, 25 °C. [b] Yields were determined by HPLC external standard method.

Table S3. Dosage of DAST screening[a],[b]

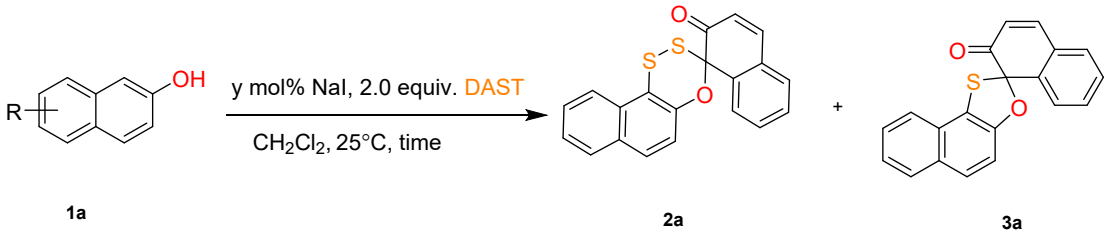


1a 2a 3a

entry	DAST (x) equiv.	conversion rate 1a	2a	3a	yield[b]
1	1.0	0	0	82	70
2	1.5	0	0	86	74
3	3.0	0	0	78	65

[a] Reaction conditions: **1a** (1.0 mmol), NaI (10 mol%), DAST (x equiv.), 5.0 mL of CH_2Cl_2, 25 °C, 16 h. [b] Yields were determined by HPLC external standard method.

Table S4. Dosage of NaI screening[a],[b]

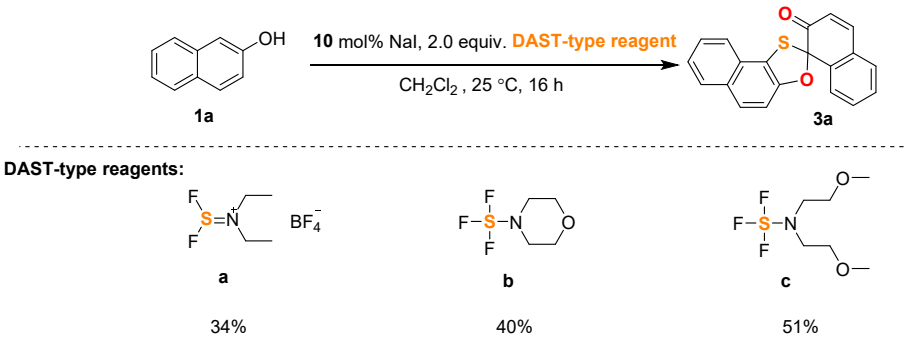


1a **2a** **3a**

entry	NaI （y）mol%	conversion rate 1a	2a	3a	Yield[b]
1	1.0	1	28	53	42
2	5.0	0	0	72	65
3	20.0	0	0	86	79
4	40.0	0	0	80	71

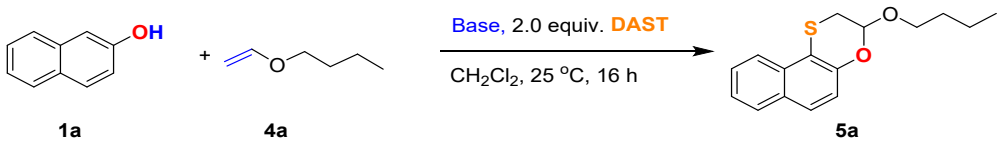
[a] Reaction conditions: **1a** (1.0 mmol), NaI (y mol%), DAST (2.0 mmol), 5 mL of solvent，25 °C, 16 h. [b] Yields were determined by HPLC external standard method.

Table S5. DAST-Type reagents screening[a],[b]



[a] Reaction conditions: **1a** (1 mmol), NaI (10 mol%), DAST-Type reagent (2.0 mmol), 5 mL of CH_2Cl_2, 25 °C, 16 h. [b] Yields were determined by HPLC external standard method.

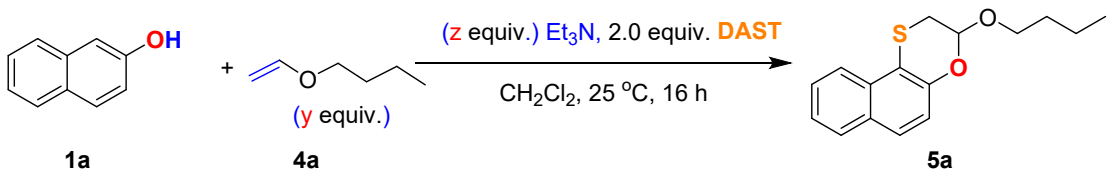
Table S6. Base and NaI screening[a],[b]



entry	NaI	Base (3.0 eq.)	Yield[b]
1	10 mol%	--	42%
2	10 mol%	Et_3N	75%
3	**--**	Et_3N	76%
4	--	DIPEA	73%
5	--	Pyridine	45%
6	--	--	15%

[a] Reaction conditions: **1a** (1 mmol), **4a** (3.0 eq.), NaI (x mol%), base (3.0 equiv.) DAST (2.0 mmol), 5 mL of CH_2Cl_2, 25 °C, 16 h. [b] Yields were determined by HPLC.

Table S7. Dosage of the olefin and Et_3N screening[a],[b]

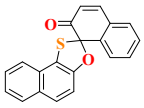


entry	4a (y equiv.)	Et_3N (z equiv.)	yield[b]
1	3.0	1.0	68%
2	**3.0**	**1.5**	**77%**
3	3.0	2.0	74%
4	3.0	3.0	76%
5	1.0	1.5	69%
6	2.0	1.5	72%
7	5.0	1.5	65%

[a] Reaction conditions: **1a** (1 mmol), **4a** (y equiv.) base (z equiv.), DAST (2.0 mmol), 5 mL of CH_2Cl_2, 25 °C, 16 h. [b] Yields were determined by HPLC.

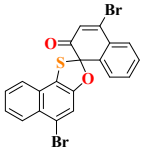
2.2 Analytical date

2.2.1 Analytical Date of 3a-3q



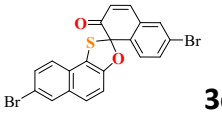
3a

2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one[1,2] (**3a**, yield 75%): Orange solid, m.p.: 160 − 162 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 7.99 - 7.96 (m, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 10.1 Hz, 1H), 7.62 - 7.43 (m, 6H), 7.36 (d, *J* = 8.1 Hz, 1H), 6.36 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 189.0, 154.0, 144.5, 138.3, 131.0, 130.5, 130.2, 130.0, 129.2, 128.8, 127.9, 127.8, 127.5, 126.4, 124.5, 123.8, 122.9, 114.6, 112.1, 95.1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.0 (dd, *J* = 1.3 Hz, 7.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.47 - 7.30 (m, 8H), 6.27 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 189.5, 154.3, 143.5, 139.4, 130.7, 130.6, 130.0, 129.6, 129.5, 128.8, 127.6, 127.0, 126.9, 124.3, 124.2, 123.8, 115.5, 111.9, 95.6. HRMS (ESI-TOF): Calcd for $C_{20}H_{13}O_2S$ $[M+H]^+$: 317.0631; Found: 317.0636.



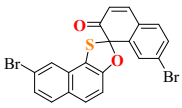
3b

4,5'-dibromo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3b**, yield 77%)**.** Orange solid, m.p.: 208 − 210 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.20 - 8.18 (m, 1H), 8.02 - 8.00 (m, 1H), 7.90 - 7.88 (m, 1H), 7.72 (s, 1H), 7.56 - 7.53 (m, 2H), 7.56 - 7.53 (m, 2H), 7.29 - 7.25 (m, 1H), 6.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 186.1, 153.4, 141.8, 137.3, 131.8, 130.4, 130.2, 129.0, 128.9, 128.8, 128.2, 127.9, 126.9, 126.6, 125.8, 124.9, 121.2, 116.1, 115.9, 95.6. HRMS (ESI-TOF): Calcd for $C_{20}H_{11}Br_2O_2S$ $[M+H]^+$: 472.8841; Found: 472.8848.



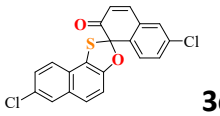
3c

6,7'-dibromo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3c**, yield 62%): Orange solid, m.p.: 153 - 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.98 (d, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.61 - 7.58 (m, 2H), 7.50 - 7.48 (m, 2H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.31 - 7.26 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 6.32 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 188.3, 154.5, 142.0, 137.6, 133.4, 132.2, 131.7, 131.2, 130.8, 130.4, 128.6, 127.2, 126.9, 125.9, 125.0, 124.3, 118.1, 115.9, 112.9, 95.4. HRMS (ESI-TOF): Calcd for $C_{20}H_{11}Br_2O_2S$ $[M+H]^+$: 472.8841; Found: 472.8841.



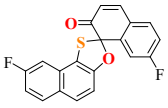
3d

7,8'-dibromo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3d**, yield 60%): Orange solid, m.p.: 215 - 216 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.14 (d, *J* = 4.8 Hz, 1H), 7.68 (dd, *J* = 4.8 Hz, 8.8 Hz, 2H), 7.57 (dd, *J* = 2.0 Hz, 8.1 Hz, 1H), 7.41 (s, 1H), 7.43 (dd, *J* = 1.8 Hz, 8.8 Hz, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 10.1 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 6.29 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 188.2, 154.9, 142.5, 140.6, 133.3, 130.8, 130.4, 130.2, 129.9, 129.1, 128.3, 127.9, 126.4, 125.3, 123.9, 121.3, 114.6, 112.3, 95.1. HRMS (ESI-TOF): Calcd for $C_{20}H_{11}Br_2O_2S$ $[M+H]^+$: 472.8841; Found: 472.8840.



3e

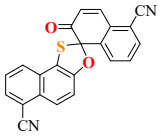
6,7'-dichloro-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3e**, yield 69%): Orange solid, m.p.: 188 - 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.93 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.42 - 7.23 (m, 6H), 6.31 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 188.4, 154.5, 142.1, 137.1, 136.2, 131.2, 131.0, 130.5, 130.1, 129.3, 128.4, 128.0, 127.5, 127.0, 126.9, 125.8, 125.0, 115.9, 112.9, 95.3. HRMS (ESI-TOF): Calcd for $C_{20}H_{11}Cl_2O_2S$ $[M+H]^+$: 384.9851; Found: 384.9848.



3f

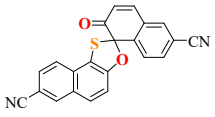
7,8'-difluoro-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one. (**3f**, yield 28%): Orange solid, m.p.: 163 - 165 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (dd, *J* = 5.6 Hz, 8.8 Hz, 1H), 7.72 - 7.68 (m, 2H), 7.36 - 7.33 (m, 3H), 7.14 - 7.30 (m, 2H), 6.92 (dd, *J* = 1.7 Hz, 9.9 Hz, 1H), 6.24 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 188.8, 165.2, 162.6 (d, *J* = 18.5 Hz), 160.1, 155.0, 142.6, 141.9 (d, *J* = 8.1 Hz), 131.5 (dd, *J* = 9.5 Hz, 17.1 Hz, 1H), 129.6 (d, *J* = 10.1 Hz), 127.9, 127.7, 125.8 (d, *J* = 3.4 Hz), 122.8 (d, *J* = 2.9 Hz), 117.3, 117.0, 114.8 (dd, *J* = 10.5 Hz, 35.97 Hz, 1H), 111.2 (d, *J* = 2.5 Hz), 107.9, 107.7, 95.1. HRMS (ESI-TOF): Calcd for $C_{20}H_{10}F_2NaO_2S$

[M+Na]$^+$: 375.0262; Found: 375.0262.



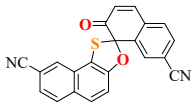
3g

2-oxo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiole]-5,6'-dicarbonitrile (**3g**, yield 66%)**:** Orange solid, m.p.: 248 - 250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.04 (d, *J* = 7.8 Hz, 1H), 7.86 - 7.80 (m, 3H), 7.58 - 7.51 (m, 3H), 7.41 - 7.36 (m, 2H), 6.42 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 187.9, 157.0, 142.7, 141.9, 136.1, 135.4, 134.7, 133.2, 131.1, 131.0, 130.5, 129.6, 128.1, 125.0, 123.3, 119.5, 116.0, 114.7, 113.9, 113.1, 106.9, 93.5. HRMS (ESI-TOF): Calcd for $C_{22}H_{10}N_2NaO_2S$ [M+Na]$^+$: 389.0355; Found: 389.0354.



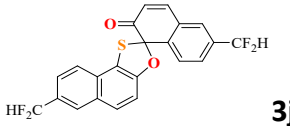
3h

2-oxo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiole]-6,7'-dicarbonitrile (**3h**, yield 71%): Orange solid, m.p.: 236 - 238 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 8.65 (s, 1H), 8.17 - 8.14 (m, 2H), 8.06 - 8.01 (m, 2H), 7.80 - 7.77 (m, 2H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 6.51 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$ and DMSO-d_6, ppm): δ = 187.4, 156.0, 142.6, 142.4, 135.1, 133.9, 133.3, 130.3, 129.2, 129.1, 129.0, 127.7, 127.4, 125.3, 124.3, 118.7, 117.4, 115.5, 113.6, 113.5, 107.1, 94.7. HRMS (ESI-TOF): Calcd for $C_{22}H_{11}N_2O_2S$ [M+H]$^+$: 367.0541; Found: 367.0538.



3i

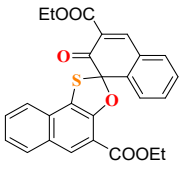
2-oxo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiole]-7,8'-dicarbonitrile (**3i**, yield 75%)**:** Orange solid, m.p.: 220 - 222 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.28 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 1H), 7.80 - 7.75 (m, 2H), 7.70 (s, 1H), 7.56 - 7.50 (m, 3H), 7.43 (d, *J* = 10.1 Hz, 1H), 6.45 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 187.2, 155.3, 141.6, 139.6, 133.8, 133.3, 132.0, 130.4, 130.2, 130.1 130.0, 128.2, 127.8, 126.4, 125.0, 118.7, 117.5, 116.4, 114.8, 114.2, 110.6, 95.0. HRMS (ESI-TOF): Calcd for $C_{22}H_{10}N_2NaO_2S$ [M+Na]$^+$: 389.0355; Found: 389.0351.



3j

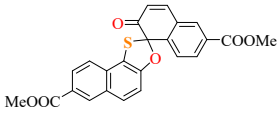
6,7'-bis(difluoromethyl)-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3j**, yield 79%): Orange solid, m.p.: 136 - 138 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.11 (d, *J* = 8.0 Hz, 1H), 7.96 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.61 - 7.52 (m, 3H), 7.47 - 7.38 (m, 3H), 6.90 - 7.52 (m, 2H), 6.36 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (100 MHz,

$CDCl_3$, ppm): δ = 188.5, 155.4, 142.6, 142.5, 141.3, 136.5, 130.3, 130.0, 129.8, 129.7, 128.6, 127.7, 127.4, 126.8, 126.4, 125.3, 124.7, 123.4, 115.9, 113.7, 112.8, 95.4. HRMS (ESI-TOF): Calcd for $C_{22}H_{13}F_4O_2S$ $[M+H]^+$: 417.0567; Found: 417.0566.



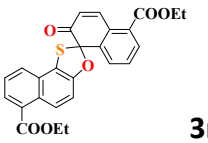
3k

diethyl 2-oxo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiole]-3,4'-dicarboxylate (**3k**, yield 31%): Orange solid, m.p.: 140 - 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.29 (s, 1H), 8.10 (s, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.51 - 7.46 (m, 1H), 7.44 - 7.39 (m, 3H), 7.33 - 7.30 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 4.41 - 4.32 (m, 2H), 4.30 - 4.20 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.24 (t, 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 184.0, 164.5, 163.7, 152.5, 148.5, 139.9, 132.7, 131.4, 130.8, 130.6, 130.4, 129.9, 129.6, 129.1, 127.9, 127.3, 125.1, 124.4, 117.9, 116.2, 96.8, 61.7, 61.3, 14.4, 14.2. HRMS (ESI-TOF): Calcd for $C_{26}H_{21}O_6S$ $[M+H]^+$: 461.1053; Found: 461.1051.



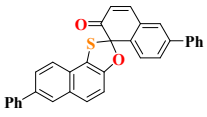
3l

dimethyl 2-oxo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiole]-6,7'-dicarboxylate (**3l**, yield 62%): Orange solid, m.p.: 228 - 229 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.59 (s, 1H), 8.13 - 8.00 (m, 4H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, *J* = 4.8 Hz, 8.8 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 1H), 6.35 (d, *J* = 10.0 Hz, 1H), 3.96 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 188.4, 166.9, 165.7, 156.0, 143.2, 142.8, 131.9, 131.5, 130.8, 130.6, 129.8, 129.7, 129.6, 127.1, 126.6, 126.1, 124.5, 124.4, 115.8, 112.7, 95.5, 52.6, 52.3. HRMS (ESI-TOF): Calcd for $C_{24}H_{17}O_6S$ $[M+H]^+$: 433.0740; Found: 433.0741.



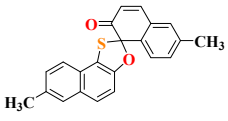
3m

diethyl 2-oxo-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiole]-5,6'-dicarboxylate (**3l**, yield 55%): Orange solid, m.p.: 140 - 142 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.82 (d, *J* = 9.3 Hz, 1H), 8.50 (d, *J* = 10.6 Hz, 1H), 8.17 (dd, *J* = 0.5 Hz, 7.8 Hz, 1H), 8.04 (dd, *J* = 2.0 Hz, 6.5 Hz, 1H), 7.98 (dd, *J* = 1.2 Hz, 7.8 Hz, 1H), 7.52 - 7.42 (m, 4H), 6.38 (d, *J* = 10.6 Hz, 1H), 4.49 - 4.41 (m, 4H), 1.47 - 1.42 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 188.4, 167.3, 166.2, 154.2, 140.7, 140.0, 132.0, 130.2, 130.1, 130.0, 129.42, 129.40, 129.3, 128.6, 128.4, 125.9, 125.8, 125.1, 116.3, 113.2, 95.7, 61.9, 61.2, 14.4, 14.3. HRMS (ESI-TOF): Calcd for $C_{26}H_{21}O_6S$ $[M+H]^+$: 461.1053; Found:. 461.1051.



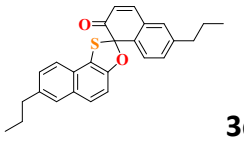
3o

6,7'-diphenyl-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3o**, yield 65%): Orange solid, m.p.: 166 - 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.08 (d, *J* = 8.0 Hz, 1H), 8.02 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.71 - 7.55 (m, 7H), 7.49 - 7.35 (m, 9H), 6.33 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 189.3, 154.5, 143.5, 143.2, 140.8, 139.5, 137.8, 137.1, 130.9, 130.0, 129.2, 129.0, 128.9, 128.3, 128.2, 128.0, 127.9, 127.5, 127.4, 127.3, 127.1, 126.8, 126.7, 124.9, 124.2, 115.6, 112.4, 95.7. HRMS (ESI-TOF): Calcd for $C_{32}H_{21}O_2S$ $[M+H]^+$: 469.1257; Found: 469.1260.



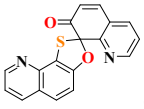
3p

6,7'-dimethyl-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3p**, yield 45%): Orange foam. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.86 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.27 - 7.18 (m, 4H), 7.09 (s, 1H), 6.23 (d, *J* = 10.0 Hz, 1H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 189.7, 153.8, 143.6, 140.1, 136.4, 133.7, 131.3, 130.8, 130.2, 129.4, 129.3, 127.7, 127.0, 126.9, 126.8, 124.1, 123.8, 115.5, 111.9, 95.7, 21.6, 21.2. HRMS (ESI-TOF): Calcd for $C_{22}H_{17}O_2S$ $[M+H]^+$: 345.0944; Found: 345.0947.



3q

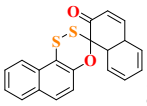
6,7'-dipropyl-2H-spiro[naphthalene-1,2'-naphtho[1,2-d][1,3]oxathiol]-2-one (**3q**, yield 48%): Orange foam. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.89 (d, *J* = 7.9 Hz, 1H), 7.61 - 7.57 (m, 2H), 7.34 - 7.23 (m, 5H), 7.12 (d, *J* = 1.4 Hz, 1H) , 6.24 (d, *J* = 10.0 Hz, 1H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H), 1.71 - 1.59 (m, 4H), 0.96 - 0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 189.7, 153.9, 144.9, 143.7, 138.5, 136.6, 130.8, 129.6, 129.4, 128.6, 127.3, 127.2, 126.9, 126.8, 124.3, 124.2, 123.7, 115.5, 111.8, 95.7, 38.0, 37.6, 24.5, 24.3, 13.8. HRMS (ESI-TOF): Calcd for $C_{26}H_{25}O_2S$ $[M+H]^+$: 401.1570; Found: 401.1577.



3r

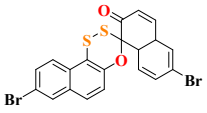
6H-spiro[quinoline-5,2'-[1,3]oxathiolo[5,4-h]quinolin]-6-one (**3r,** yield 25%): Orange foam; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.55 (dd, *J* = 1.4 Hz, 4.8 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 1H), 7.78 (dd, *J* = 1.4 Hz, 4.8 Hz, 1H), 7.51 - 7.47 (m, 2H), 7.44 - 7.40 (m, 2H), 7.10 (d, *J* = 9.3 Hz, 1H), 6.79 (t, *J* = 6.8 Hz, 1H), 6.47 (d, *J* = 10.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 186.3, 173.3, 160.0, 150.5, 142.4, 141.6, 138.8, 137.3, 136.8, 133.9, 126.4, 126.1, 125.2, 125.1, 123.5, 110.9, 102.5, 86.1. HRMS (ESI-TOF): Calcd for $C_{18}H_{11}N_2O_2S$ $[M+H]^+$: 319.0536; Found:319.0529.

2.2.2 Analytical Date of compounds of 2a, 2c and 2d.



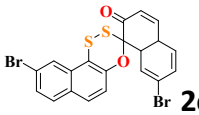
2a

4a,8a-dihydro-2H-spiro[naphthalene-1,3'-naphtho[1,2-e][1,3,4]oxadithiin]-2-one[1,2] (**2a**, yield 25%): Yellow solid, m.p.: 155-156 °C. ^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ = 8.10 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.75 - 7.72 (m, 3H), 7.67 - 7.63 (m, 3H), 7.56 - 7.52 (m, 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 6.34 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ = 186.8, 151.9, 142.3, 134.3, 130.8, 130.7, 130.5, 129.7, 128.5, 128.4, 127.4, 127.3, 124.9, 123.0, 122.1, 121.2, 109.8, 83.8. HRMS (ESI-TOF): Calcd for $C_{20}H_{13}O_2S_2$ $[M+H]^+$: 349.0351; Found:. 349.0374.



2b

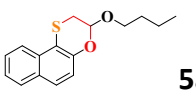
6,8'-dibromo-4a,8a-dihydro-2H-spiro[naphthalene-1,3'-naphtho[1,2-e][1,3,4]oxadithiin]-2-one[2] (**2b**, yield 30%): Yellow solid, m.p.: 152-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.00 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 0.9 Hz, 1H), 7.65 - 7.28 (m, 5H), 7.34 - 7.28 (m, 2H), 6.30 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 186.0, 152.2. 139.8. 133.9. 133.1. 132.5. 131.7. 130.3, 130.2, 130.2, 130.2, 129.3, 127.4, 125.0, 124.6, 124.5, 122.2, 118.6, 111.2, 84.4. HRMS (ESI-TOF): Calcd for $C_{20}H_{11}Br_2O_2S_2$ $[M+H]^+$: 504.8562; Found: 504.8562.



2c

7,9'-dibromo-4a,8a-dihydro-2H-spiro[naphthalene-1,3'-naphtho[1,2-e][1,3,4]oxadithiin]-2-one (**2c**, yield 22%): Yellow solid, m.p.: 200 - 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.31 (s, 1H), 7.86 (d, *J* = 1.8 Hz, 1H), 7.7 - 7.63 (m, 3H), 7.53 (dd, *J* = 1.7 Hz, 8.6 Hz, 1H), 7.37 - 7.33 (m, 3H), 6.29 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 186.0, 152.7. 140.2, 136.9, 133.5, 132.8, 131.1, 130.9, 130.0, 128.9, 128.4, 128.2, 127.6, 125.4, 125.1, 124.0, 124.7, 121.5, 110.1, 84.1. HRMS (ESI-TOF): Calcd for $C_{20}H_{11}Br_2O_2S_2$ $[M+H]^+$: 504.8562; Found: 504.8563.

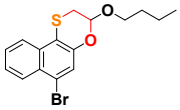
2.3.3 Analytical Date of 5a-5ag



5a

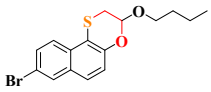
3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5a**, yield 56%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.93 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.57 - 7.50 (m, 1H), 7.42 - 7.39 (m, 1H), 7.09 (d, *J* = 8.8 Hz, 1H),

5.47 (dd, *J* = 2.0 Hz, 4.6 Hz, 1H), 3.99 - 3.93 (m, 1H), 3.75 - 3.69 (m, 1H), 3.26 - 3.14 (m, 2H), 1.65 - 1.58 (m, 2H), 1.39 - 1.33 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.2, 130.0, 128.4, 127.2, 125.3, 124.9, 123.1, 121.6, 118.8, 110.0, 93.6, 67.6, 30.35, 27.8, 18.1, 12.7. HRMS (ESI-TOF): Calcd for $C_{16}H_{18}NaO_2S$ $[M+Na]^+$: 297.0920; Found: 297.0914.



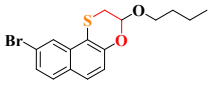
5b

3-bromo-3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5b**, yield 20%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.15 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.56 - 7.43 (m, 2H), 7.43 (S, 1H), 5.46 (d, *J* = 2.0 Hz, 4.3 Hz, 1H), 3.96 - 3.90 (m, 1H), 3.73 - 3.67 (m, 1H), 3.24 - 3.12 (m, 2H), 1.65 - 1.58 (m, 2H), 1.39 - 1.30 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.9, 131.6, 128.0, 127.6, 127.1, 125.5, 123.6, 123.0, 119.5, 111.6, 94.5, 68.8, 31.5, 28.8, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{17}BrO_2S$ $[M]^+$: 352.0127; Found: 352.0131.



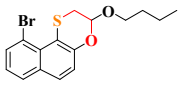
5c

8-bromo-3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5c**, yield 62%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.89 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.55 (dd, *J* =2.0 Hz, 9.0 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.07 (d, *J* = 8.9 Hz, 1H), 5.46 (dd, *J* =2.1 Hz, 4.5 Hz, 1H), 3.95 - 3.90 (m, 1H), 3.74 - 3.68 (m, 1H), 3.24 - 3.11 (m, 2H), 1.62 - 1.57 (m, 2H), 1.36 - 1.27 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.5, 130.6, 130.2, 129.6, 129.4, 125.0, 124.7, 124.4, 121.0, 118.0, 111.5, 94.5, 68.8, 31.5, 28.8, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{17}BrNaO_2S$ $[M+Na]^+$: 375.0025; Found: 375.0020.



5d

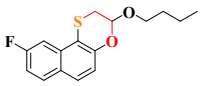
9-bromo-3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5d**, yield 48%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.05 (d, *J* = 1.7 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.44 (dd, *J* = 1.8 Hz, 8.6 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 5.45 (dd, *J* = 2.2 Hz, 4.5 Hz, 1H), 3.95 - 3.90 (m, 1H), 3.74 - 3.68 (m, 1H), 3.24 - 3.11 (m, 2H), 1.62 - 1.57 (m, 2H), 1.36 - 1.27 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.0, 132.3, 129.8, 127.9, 127.5, 125.9, 125.1, 120.9, 120.3, 110.4, 94.6, 68.8, 53.5, 31.6, 28.8, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{17}BrNaO_2S$ $[M+Na]^+$: 375.0025; Found: 375.0024.



5e

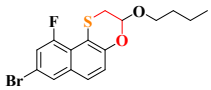
10-bromo-3-butoxy-2,3-dihydronaphtho[2,1-*b*][1,4]oxathiine (**5e**, yield 42%):

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.77 (dd, *J* = 1.1 Hz, 7.5 Hz, 1H), 7.67 (dd, *J* = 0.7 Hz, 8.0 Hz, 1H), 7.51 (d, 8.8 Hz, 1H), 7.15 - 7.09 (m, 2H), 5.53 (dd, *J* = 2.7 Hz, 6.1 Hz, 1H), 4.03 - 3.98 (m, 1H), 3.74 - 3.68 (m, 1H), 3.03 (dd, *J* = 2.7 Hz, 13.1 Hz, 1H), 2.80 (dd, *J* = 6.1 Hz, 13.1 Hz, 1H), 1.69 - 1.62 (m, 2H), 1.45 - 1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.5, 134.1, 132.4, 130.7, 128.9, 127.4, 124.5, 121.2, 118.3, 114.9, 98.3, 68.7, 31.6, 31.2, 19.3, 13.9. HRMS (ESI-TOF): Calcd for $C_{16}H_{17}BrO_2S$ $[M]^+$: 352.0127; Found: 352.0129.



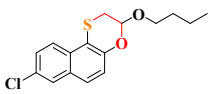
5f

3-butoxy-9-fluoro-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**3f**, yield 35%): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.72 (dd, *J* = 5.9 Hz, 8.9 Hz, 1H), 7.56 - 7.51 (m, 2H), 7.17 - 7.12 (m, 1H), 7.03 (d, *J* = 8.9 Hz, 1H), 5.47 (dd, *J* = 2.1 Hz, 4.5 Hz, 1H), 3.98 - 3.91 (m, 1H), 3.74 - 3.68 (m, 1H), 3.24 - 3.12 (m, 2H), 1.65 - 1.58 (m, 2H), 1.37 - 1.32 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 161.3 (d, *J* = 245.3 Hz), 148.2, 132.2 (d, *J* = 9.5 Hz), 130.6 (d, *J* = 9.5 Hz), 126.3, 125.9, 119.2 (d, *J* = 2.7 Hz), 114.2 (d, *J* = 2.1 Hz), 110.3 (d, *J* = 5.5 Hz), 106.9 (d, *J* = 23.0 Hz), 94.6, 68.8, 31.6, 28.8, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{18}FO_2S$ $[M+H]^+$: 293.1006; Found: 293.1004.



5g

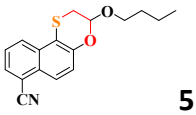
8-bromo-3-butoxy-10-fluoro-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5g**, yield 28%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.65 (s, 1H), 7.39 (dd, *J* = 1.6 Hz, 8.9 Hz, 1H), 7.22 (dd, *J* = 1.9 Hz, 14.6 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 5.46 - 5.44 (m, 1H), 3.95 - 3.90 (m, 1H), 3.73 - 3.67 (m, 1H), 3.15 (dd, *J* = 1.6 Hz, 13.0 Hz, 1H), 3.03 (dd, *J* = 4.6 Hz, 12.9 Hz, 1H), 1.65 - 1.58 (m, 2H), 1.39 - 1.30 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.1 (d, *J* = 256.2 Hz), 148.0, 132.7 (d, *J* = 5.4 Hz), 126.5 (d, *J* = 17.0 Hz), 124.7 (d, *J* = 2.9 Hz), 122.1 (d, *J* = 1.5 Hz), 120.4 (d, *J* = 11.2 Hz), 116.1 (d, *J* = 10.2 Hz), 115.3 (d, *J* = 26.1 Hz), 110.7 (d, *J* = 7.7 Hz), 94.7, 68.8, 31.6, 29.2 (d, *J* = 10.1 Hz), 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{16}BrFO_2S$ $[M]^+$: 370.0033; Found: 370.0032.



5h

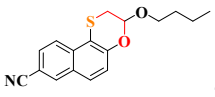
3-butoxy-8-chloro-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5h**, yield 45%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.74 (d, *J* = 8.9 Hz, 1H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.35 - 7.32 (m, 2H), 7.43 (d, *J* = 8.9 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 5.37 - 5.35 (m, 1H), 3.86 - 3.80 (m, 1H), 3.64 - 3.58 (m, 1H), 3.14 - 3.02 (m, 2H), 1.55 - 1.48 (m, 2H), 1.28 - 1.17 (m, 2H), 0.79 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.4, 130.2, 129.9, 129.4, 127.0, 126.9, 125.0, 124.3, 121.0, , 111.5, 94.5, 94.4, 68.8, 31.5, 28.8, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{18}ClO_2S$ $[M+Na]^+$:331.0530;

Found:331.0531.



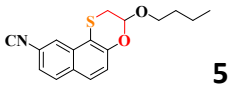
5i

3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine-7-carbonitrile (**5i**, yield 48%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.93 - 7.88 (m, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.51 (dd, *J* = 2.4 Hz, 5.3 Hz, 1H), 4.00 - 3.94 (m, 1H), 3.74 - 3.68 (m, 1H), 3.18 - 2.99 (m 2H), 1.66 - 1.59 (m, 2H), 1.41 - 1.32 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.5, 137.4, 134.2, 130.3, 130.2, 127.5, 123.1, 121.6, 120.9, 112.5, 107.0, 96.3, 68.9, 31.6, 29.7, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{17}H_{17}NO_2S$ $[M]^+$: 299.0975; Found: 299.0985.



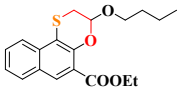
5j

3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine-8-carbonitrile (**5j**, yield 47%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.05 (d, *J* = 1.0 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.57 - 7.52 (m, 2H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.48 (dd, *J* = 2.0 Hz, 4.3 Hz, 1H), 3.95 - 3.89 (m, 1H), 3.74 - 3.68 (m, 1H), 3.24 - 3.11 (m, 2H), 1.62 - 1.57 (m, 2H), 1.36 - 1.24 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.7, 134.0, 132.7, 128.4, 126.9, 126.3, 123.9, 121.7, 119.3, 112.0, 107.4, 94.6, 68.9, 31.9, 28.6, 19.1, 13.8. HRMS (ESI-TOF): Calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1058; Found: 300.1054.



5k

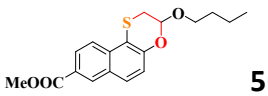
3-butoxy-9-isocyano-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5k**, yield 38%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.26 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.48 (dd, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 5.49 (dd, *J* = 2.1 Hz, 4.2 Hz, 1H), 3.97 - 3.89 (m, 1H), 3.74 - 3.68 (m, 1H), 3.25 - 3.13 (m, 2H), 1.63 - 1.56 (m, 2H), 1.37 - 1.25 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.5, 131.0, 130.3, 129.4, 128.6, 125.9, 124.8, 123.0, 119.4, 112.3, 109.6, 94.4, 68.9, 31.5, 28.7, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1053; Found: 300.1053.



5l

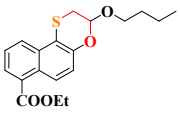
ethyl 3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine-5-carboxylate (**5l**, yield 35%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.90 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.46 - 7.42 (m, 1H), 7.32 - 7.28 (m, 1H), 5.42 (dd, *J* = 2.2 Hz, 4.5 Hz, 1H), 4.35 - 4.29 (m, 2H), 3.95 - 3.89 (m, 1H), 3.65 - 3.59 (m, 1H), 3.20 -

3.04 (m, 2H), 1.53 - 1.46 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 - 1.18 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 166.2, 144.8, 132.1, 129.2, 128.7, 128.0, 127.8, 124.9, 123.3, 122.5, 113.2, 94.3 (d, *J* = 4.3 Hz), 68.7, 61.2, 31.5, 28.6, 19.2, 14.3, 13.8. HRMS (ESI-TOF): Calcd for $C_{19}H_{22}NaO_4S$ [M+Na]$^+$: 369.1131; Found: 369.1130.



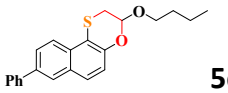
5m

methyl 3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine-8-carboxylate (**5m**, yield 42%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.48 (d, *J* = 1.6 Hz, 1H), 8.06 (dd, *J* = 1.7 Hz, 8.8 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 5.48 (dd, *J* =2.1 Hz, 4.5 Hz, 1H), 3.96 (s, 3H), 3.95 - 3.91 (m, 1H), 3.73 - 3.68 (m, 1H), 3.24 - 3.11 (m, 2H), 1.64 - 1.57 (m, 2H), 1.37 - 1.28 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 167.2, 149.2, 133.4, 131.2, 128.5, 127.3, 125.8, 125.7, 122.9, 120.7, 111.4, 94.7, 68.8, 52.1, 31.5, 28.7, 19.1, 13.8. HRMS (ESI-TOF): Calcd for $C_{18}H_{21}O_4S$ [M+H]$^+$: 333.1155; Found: 333.1155.



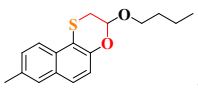
5n

ethyl 3-butoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine-7-carboxylate (**5n**, yield 52%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.00 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.57 - 7.53 (m, 1H), 7.43 - 7.39 (m, 1H), 5.53 (dd, *J* = 2.2 Hz, 4.5 Hz, 1H), 4.44 - 4.39 (m, 2H), 4.05 - 3.99 (m, 1H), 3.75 - 3.70 (m, 1H), 3.31 (m, 2H), 1.61 - 1.55 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.36 - 1.25 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 166.2, 144.7, 132.1, 129.2, 128.4, 128.0, 127.8, 124.9, 123.3, 122.5, 113.2, 94.3, 68.7, 61.2, 31.4, 28.6, 19.2, 14.4, 13.8. HRMS (ESI-TOF): Calcd for $C_{19}H_{22}NaO_4S$ [M+Na]$^+$: 369.1131; Found: 369.1124.



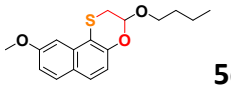
5o

3-butoxy-8-phenyl-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5o**, yield 55%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.00 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 1.7 Hz, 1H), 7.79 (dd, *J* = 1.9 Hz, 8.7 Hz, 1H), 7.74 - 7.71 (m, 2H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.52 - 7.48 (m, 2H), 7.41 - 7.38 (m, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.49 (dd, *J* = 2.1 Hz, 4.6 Hz, 1H), 4.00 - 3.95 (m, 1H), 3.76 - 3.71 (m, 1H), 3.28 - 3.15 (m, 2H), 1.68 - 1.61 (m, 2H), 1.40 - 1.30 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.4, 140.9, 136.9, 130.3, 129.8, 128.9, 127.3, 126.3, 126.2, 125.9, 123.3, 120.3, 111.1, 94.7, 68.7, 31.6, 28.9, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{22}H_{22}NaO_2S$ [M+Na]$^+$: 373.1233; Found: 373.1231.



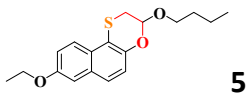
5p

3-butoxy-8-methyl-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5p**, yield 46%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.82 (d, *J* = 8.6 Hz, 1H), 7.53 (s, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.34 (dd, *J* = 1.6 Hz, 8.6 Hz, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 5.45 (dd, *J* = 2.1 Hz, 4.6 Hz, 1H), 3.97 - 3.92 (m, 1H), 3.74 - 3.68 (m, 1H), 3.25 - 3.12 (m, 2H), 2.49 (s, 3H), 1.66 - 1.57 (m, 2H), 1.40 - 1.29 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 146.7, 133.7, 129.7, 129.2, 128.5, 127.4, 125.4, 122.5, 119.8, 110.9, 94.6, 68.7, 31.6, 18.9, 21.4, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{17}H_{20}NaO_2S$ $[M+Na]^+$: 311.1076; Found: 311.1075.



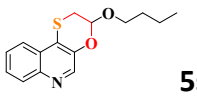
5q

3-butoxy-2,3-dihydro-8-methoxynaphtho[2,1-b][1,4]oxathiine (**5q**, yield 26%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53 (d, *J* = 8.9 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.93 (dd, *J* = 2.3 Hz, 8.9Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 5.33 (dd, *J* = 2.1 Hz, 4.6 Hz, 1H), 3.86 - 3.79 (m, 4H), 3.61 - 3.56 (m, 1H), 3.12 (dd, *J* = 2.2 Hz, 12.8 Hz, 1H), 3.03 (dd, *J* = 4.6 Hz, 12.8 Hz, 1H), 1.54 - 1.47 (m, 2H), 1.26 - 1.20 (m, 2H), 1.16 (s, 1H), 0.78 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 158.4, 148.0, 132.3, 129.8, 125.8, 124.6, 117.4, 116.5, 109.7, 101.8, 94.6 (d, *J* = 5.1 Hz), 68.7, 55.4, 55.3, 31.6, 28.9, 19.2, 13.8. HRMS (ESI-TOF): Calcd for $C_{17}H_{21}O_3S$ $[M+H]^+$: 305.1206; Found: 305.1210.



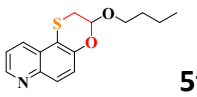
5r

3-butoxy-8-ethoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5r**, yield 45%): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.64 (d, *J* = 8.9 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.2 (d, *J* = 2.0 Hz, 1H), 7.04 (dd, *J* = 2.3 Hz, 8.9 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 1H), 5.47 (dd, *J* = 2.0 Hz, 4.5 Hz, 1H), 4.20 - 4.14 (m, 2H), 3.97 - 3.92 (m, 1H), 3.73 - 3.68 (m, 1H), 3.25 - 3.12 (m, 2H), 1.66 - 1.58 (m, 2H), 1.49 (t, *J* = 7.0 Hz, 3H), 1.39 - 1.30 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.7, 147.9, 132.3, 129.8, 125.8, 124.5, 117.3, 116.7, 109.5, 102.6, 94.6, 68.7, 63.5, 31.6, 28.9, 19.2, 14.8, 13.8. HRMS (ESI-TOF): Calcd for $C_{18}H_{23}O_3S$ $[M+H]^+$: 319.1362; Found: 319.1356.



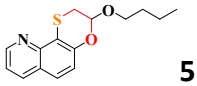
5s

3-butoxy-2,3-dihydro-[1,4]oxathiino[3,2-f]quinoline (**5s**, yield 43%): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.40 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.75 (dd, *J* = 0.7 Hz, 8.1 Hz, 1H), 7.53 - 7.42 (m, 2H), 5.40 (dd, *J* = 2.0 Hz, 3.7 Hz, 1H), 3.85 - 3.79 (m, 1H), 3.65 - 3.59 (m, 1H), 3.19 - 3.06 (m, 2H), 1.53 - 1.46 (m, 2H), 1.27 - 1.17 (m, 2H), 0.78 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.4, 143.2, 142.6, 129.7, 127.3, 126.6, 125.7, 122.5, 122.4, 93.1, 68.8, 31.4, 28.7, 19.1, 13.7. HRMS (ESI-TOF): Calcd for $C_{15}H_{18}NO_2S$ $[M+H]^+$: 276.1053; Found: 276.1059.



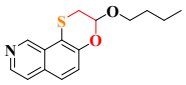
5t

3-butoxy-2,3-dihydro-[1,4]oxathiino[3,2-f]quinoline (**5t**, yield 33%): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.74 (dd, *J* = 1.3 Hz, 4.2 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 9.1 Hz, 1H), 7.32 (dd, *J* = 2.8 Hz, 4.2 Hz, 1H), 7.24 (d, *J* = 9.1 Hz, 1H), 5.43 (dd, *J* = 2.0 Hz, 4.2 Hz, 1H), 3.91 - 3.85 (m, 1H), 3.69 - 3.63 (m, 1H), 3.19 - 3.07 (m, 2H), 1.59 - 1.51 (m, 2H), 1.32 - 1.21 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.2, 147.2, 144.6, 130.9, 127.2, 126.2, 123.4, 120.8, 110.9, 94.3, 68.7, 31.5, 28.5, 19.1, 13.8. HRMS (ESI-TOF): Calcd for $C_{15}H_{18}NO_2S$ $[M+H]^+$: 276.1053; Found: 276.1056.



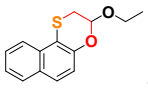
5u

3-butoxy-2,3-dihydro-[1,4]oxathiino[2,3-h]quinoline (**5u**, yield 29%): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.82 (dd, *J* = 1.6 Hz, 4.3 Hz, 1H), 7.98 (dd, *J* = 1.6 Hz, 8.2 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.24 (dd, *J* = 4.3 Hz, 8.2 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 5.42 (dd, *J* = 2.0 Hz, 4.6 Hz, 1H), 3.92 - 3.86 (m, 1H), 3.69 - 3.63 (m, 1H), 3.20 - 3.09 (m, 2H), 1.59 - 1.52 (m, 2H), 1.33 - 1.24 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 149.9, 149.4, 145.7, 135.9, 124.3, 124.0, 120.6, 119.6, 114.8, 94.9, 68.8, 31.5, 28.6, 19.1, 13.8. HRMS (ESI-TOF): Calcd for $C_{15}H_{18}NO_2S$ $[M+H]^+$: 276.1053; Found: 276.1062.



5v

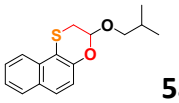
3-**butoxy-2,3-dihydro-[1,4]oxathiino[2,3-h]isoquinoline** (**5v,** yield 36%): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 9.01 (s, 1H), 8.43 (d, *J* = 5.9 Hz, 1H), 7.60 - 7.55 (m, 2H), 7.08 (d, *J* = 8.8 Hz, 1H), 5.42 (dd, *J* = 2.0 Hz, 4.2 Hz, 1H), 3.89 - 3.83 (m, 1H), 3.67 - 3.62 (m, 1H), 3.17 - 3.05 (m, 2H), 1.57 - 1.50 (m, 2H), 1.30 - 1.19 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 151.9, 150.3, 143.3, 134.3 125.5, 124.7, 121.3, 115.9, 110.4, 94.6, 68.9, 31.4, 28.3, 19.1, 13.7. HRMS (ESI-TOF): Calcd for $C_{15}H_{18}NO_2S$ $[M+H]^+$: 276.1053; Found: 276.1060.



5ab

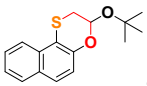
3-ethoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine [3-5] (**5ab**, yield 57%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.81 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.45 - 7.38 (m, 2H), 7.30 - 7.26 (m, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 5.36 (dd, *J* = 2.1 Hz, 4.7 Hz, 1H), 3.93 - 3.85 (m, 1H), 3.70 - 3.63 (m, 1H), 3.12 (dd, *J* = 2.2 Hz, 12.9 Hz, 1H), 3.03 (dd, *J* = 4.7 Hz, 12.9 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =147.3, 131.1, 129.5, 128.3, 126.4, 126.1, 124.2, 122.7, 119.9, 111.0, 94.4 (d, *J* = 4.3 Hz) , 64.5, 28.9, 12.2. HRMS (ESI-TOF): Calcd for $C_{14}H_{14}NaO_2S$ $[M+Na]^+$:

269.0607; Found: 269.0607.



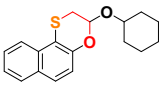
5ac

3-isobutoxy-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5ac**, yield 52%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.02 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.61 - 7.55 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 5.47 (dd, *J* = 1.9 Hz, 6.4 Hz, 1H), 3.78 (dd, *J* = 6.8 Hz, 12.3 Hz, 1H), 3.50 (dd, *J* = 9.3 Hz, 6.4 Hz, 1H), 3.28 - 3.17 (m, 2H), 2.03 - 1.94 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.4, 131.1, 129.5, 128.4, 126.4, 126.0, 124.3, 122.8, 120.0, 111.2, 94.8, 75.5, 28.9, 28.5, 19.4, 19.3. HRMS (ESI-TOF): Calcd for $C_{16}H_{19}O_2S$ $[M+H]^+$: 275.1100; Found: 275.1100.



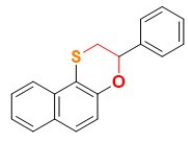
5ad

3-(tert-butoxy)-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5ad**, yield 39%): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.94 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.57 - 7.51 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 5.69 (dd, *J* = 2.5 Hz, 5.0 Hz, 1H), 3.20 - 3.11 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 148.2, 131.1, 129.4, 128.3, 126.3, 125.9, 124.1, 122.7, 120.2, 110.6, 90.5, 76.4, 30.1, 28.8. HRMS (ESI-TOF): Calcd for $C_{16}H_{19}O_2S$ $[M+H]^+$: 275.1100; Found: 275.1094.



5ae

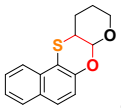
3-(cyclohexyloxy)-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5ae**, yield 33%): Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.93 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.57 - 7.50 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 5.60 (dd, *J* = 2.0 Hz, 4.8 Hz, 1H), 3.92 - 3.80 (m, 1H), 3.25 - 3.13 (m, 2H), 2.0 (dd, *J* = 2.7 Hz, 9.8 Hz, 1H), 1.91 (dd, *J* = 3.8 Hz, 11.1 Hz, 1H), 1.81 - 1.72 (m, 2H), 1.57 - 1.54 (m, 1H), 1.48 - 1.16 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 147.6, 131.1, 129.4, 128.3, 126.3, 126.0, 124.2, 122.7, 120.0, 110.9, 93.2, 33.5, 32.1, 29.3, 25.6, 24.3, 24.2. HRMS (ESI-TOF): Calcd for $C_{18}H_{21}O_2S$ $[M+H]^+$: 301.1257; Found: 301.1258.



5af

3-phenyl-2,3-dihydronaphtho[2,1-b][1,4]oxathiine (**5af**, yield 12%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.90 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.55 - 7.36 (m, 8H), 7.14 (d, *J* = 8.9 Hz, 1H), 5.30 (dd, *J* = 2.3 Hz, 8.9 Hz, 1H), 3.36 - 3.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 150.0, 140.3, 131.2, 129.4, 128.7, 128.5,

128.3, 126.4, 126.0, 125.9, 124.2, 122.6, 120.0, 110.3, 31.5, 29.7. HRMS (ESI-TOF): Calcd for $C_{18}H_{15}OS$ $[M+H]^+$: 279.0838; Found: 279.0843.



5ag

7a,10,11,11a-tetrahydro-9H-naphtho[2,1-b]pyrano[3,2-e][1,4]oxathiine[6] (**5ag**, yield 15%): Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.77 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.43 - 7.38 (m, 1H), 7.31 - 7.27 (m, 1H), 7.04 (d, *J* = 8.9 Hz, 1H), 5.57 (d, *J* =2.2 Hz, 1H), 4.04 - 3.97 (m, 1H), 3.70 - 3.66 (m, 1H), 3.29 - 3.25 (m, 1H), 1.94 - 1.66 (m, 4H). HRMS (ESI-TOF): Calcd for $C_{15}H_{15}O_2S$ $[M+H]^+$:259.0793; Found: 259.0788.

2.3 ^{1}H NMR and ^{13}C NMR spectra

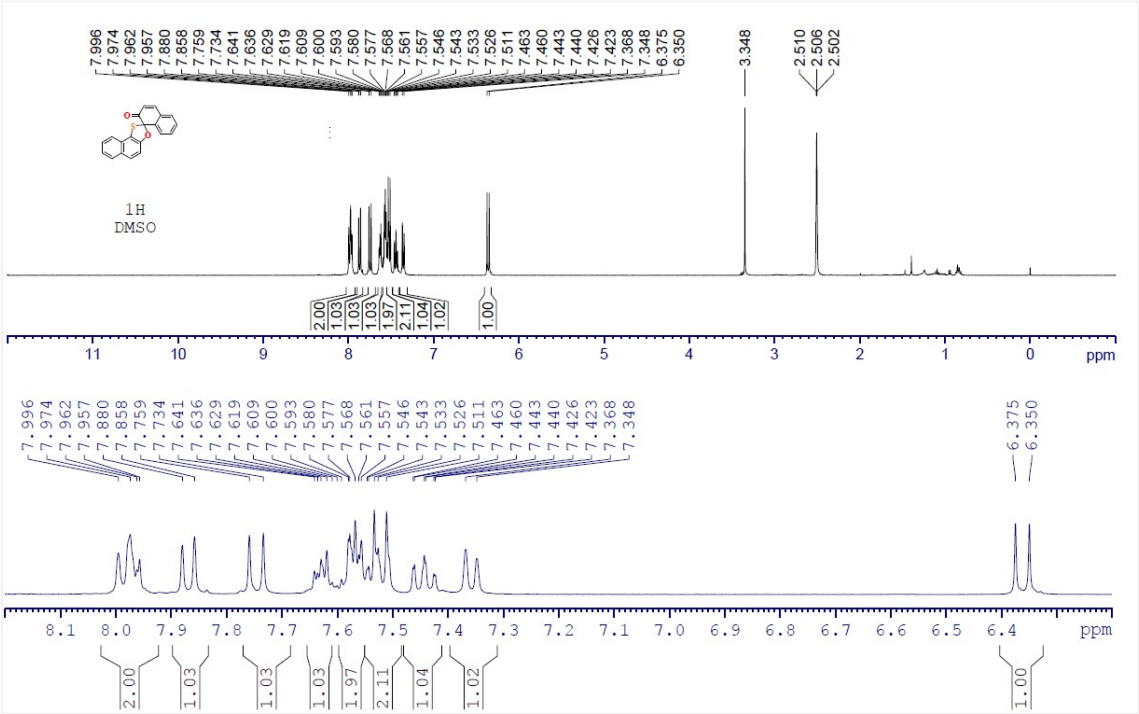


Figure S1. ^{1}H NMR (400 MHz, DMSO-d_6) Spectrum of Compound **3a**

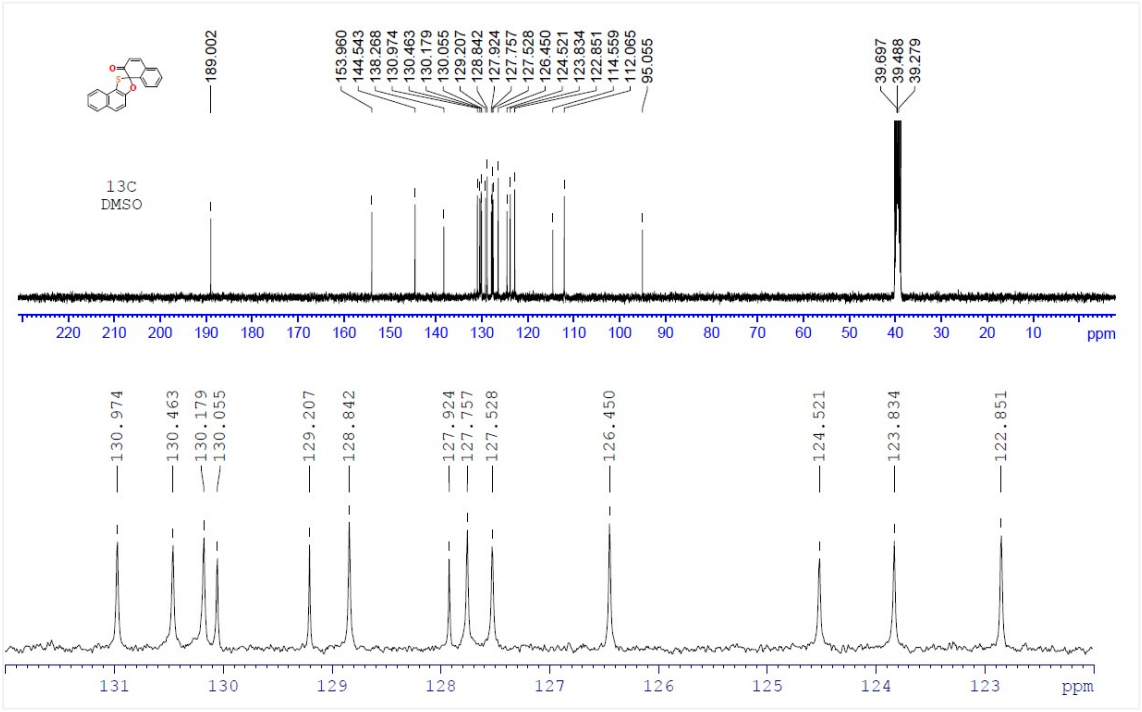


Figure S2. ^{13}C NMR (100 MHz, DMSO-d_6) Spectrum of Compound **3a**

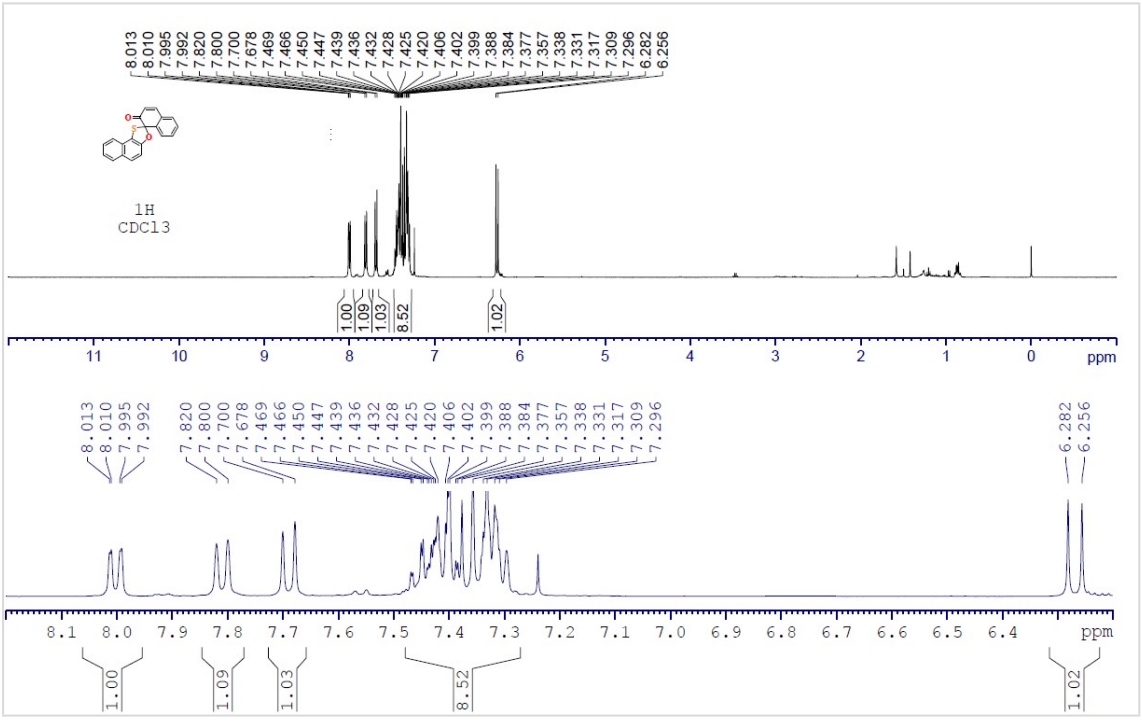


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3a**

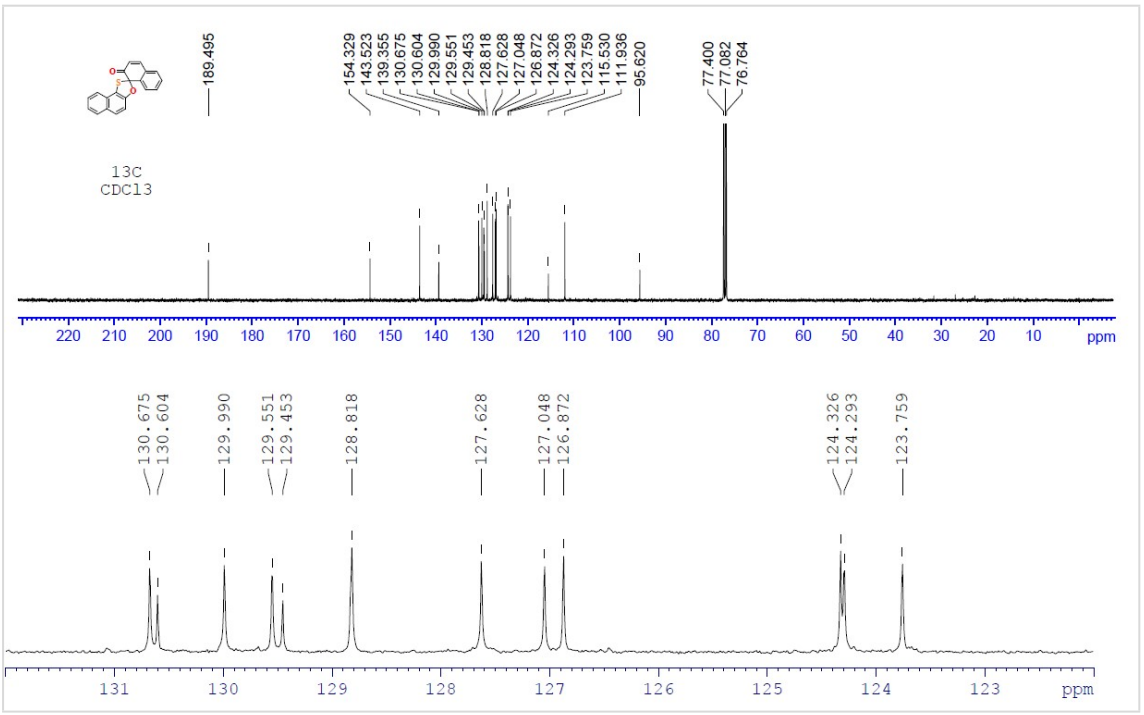


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3a**

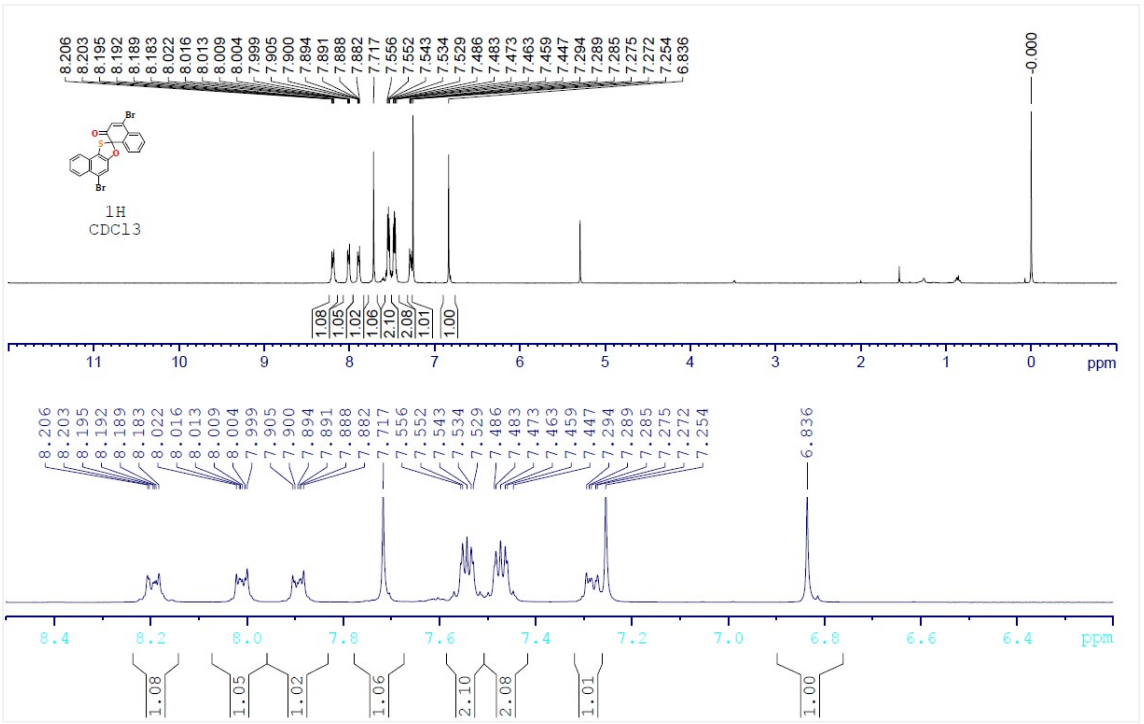


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3b**

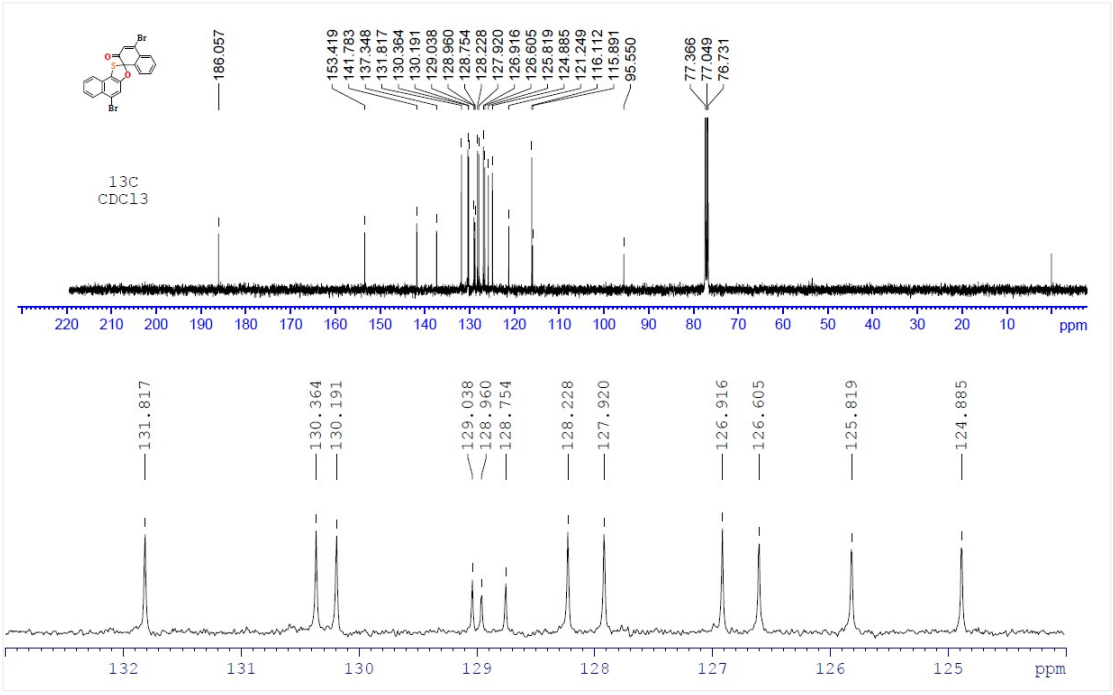


Figure S6. ^{13}C NMR (100 MHz, CDCl3) Spectrum of Compound **3b**

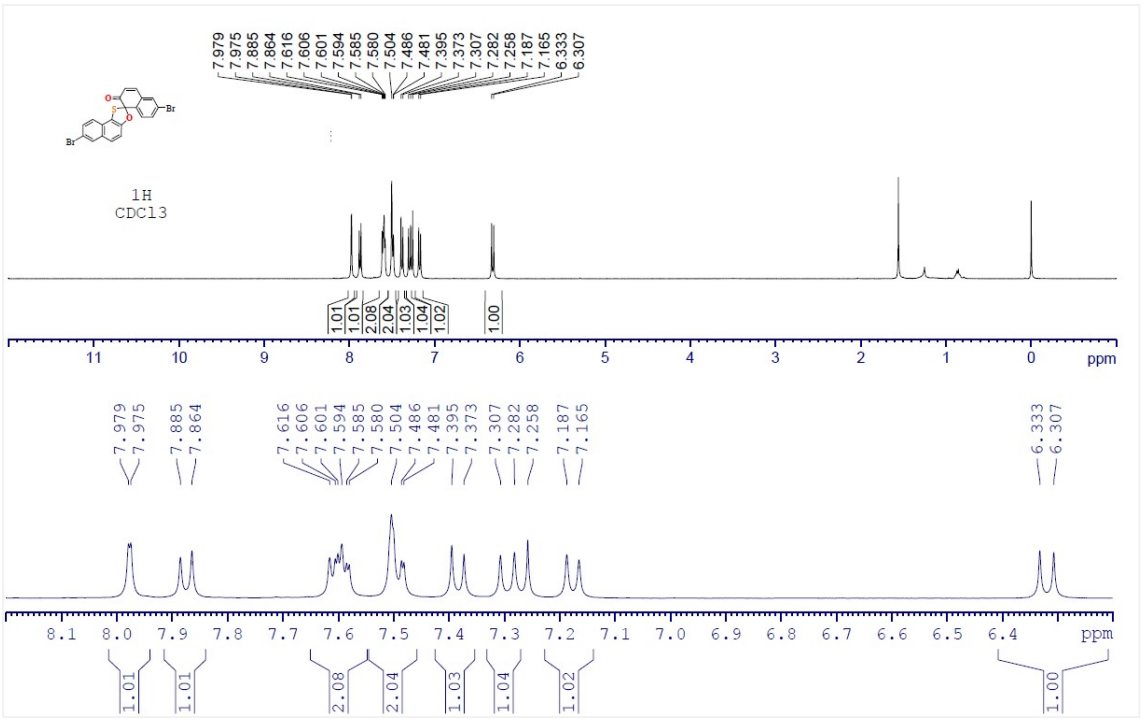


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3c**

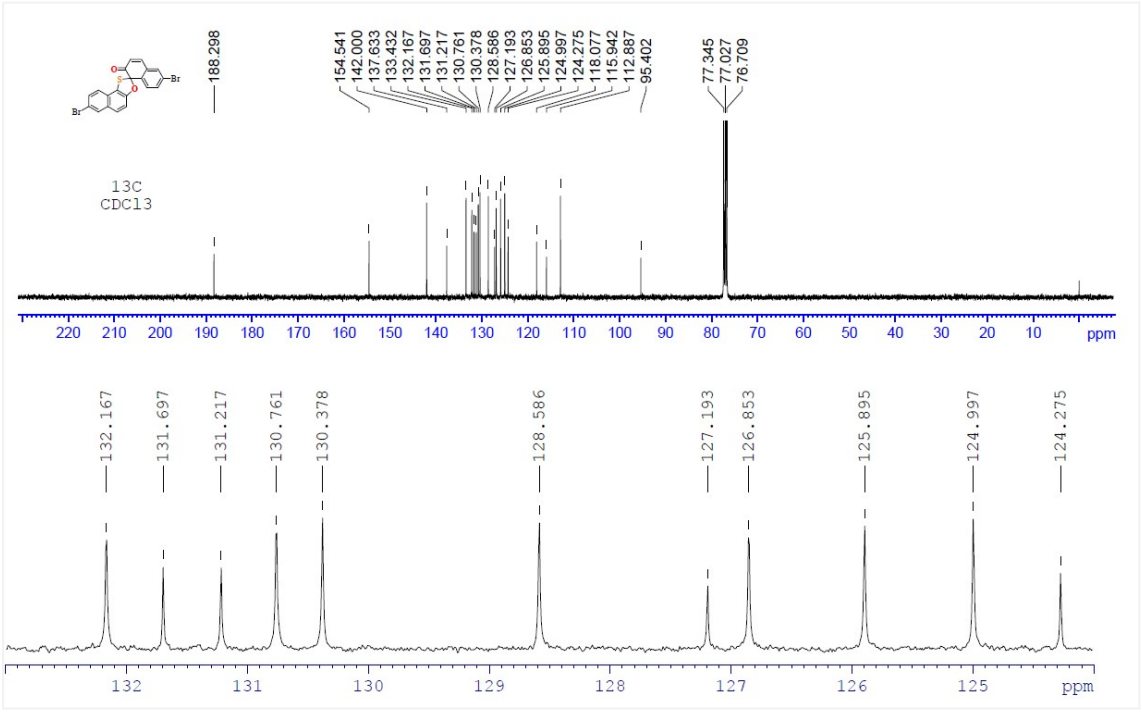


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3c**

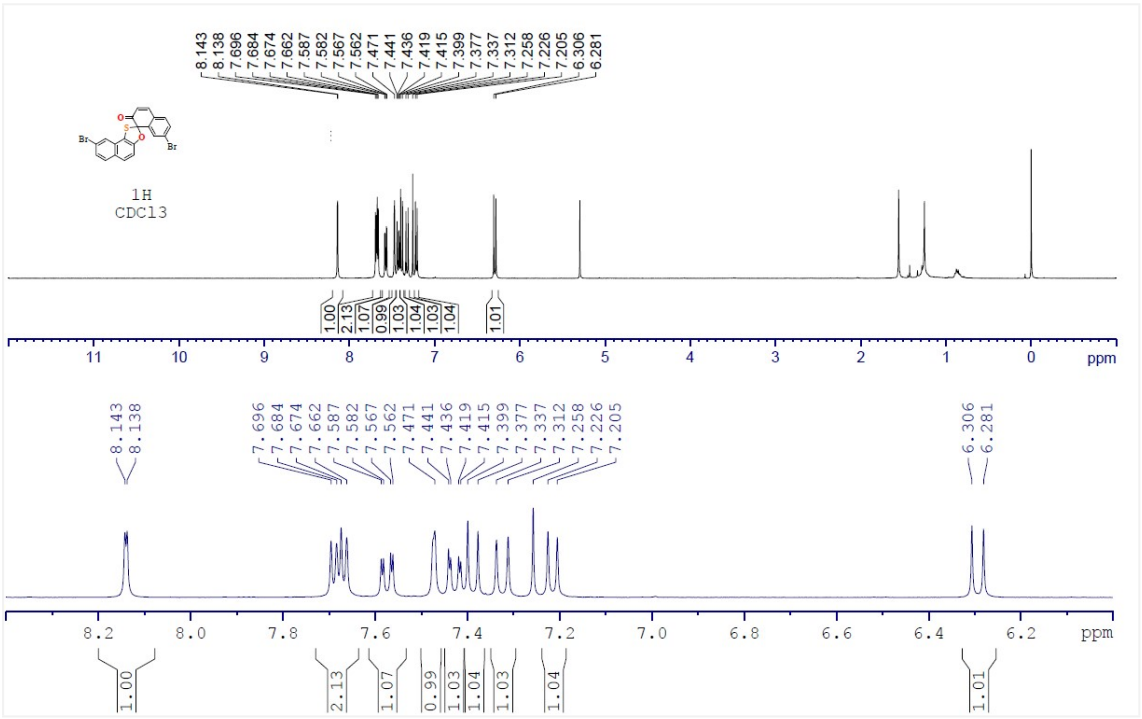


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3d**

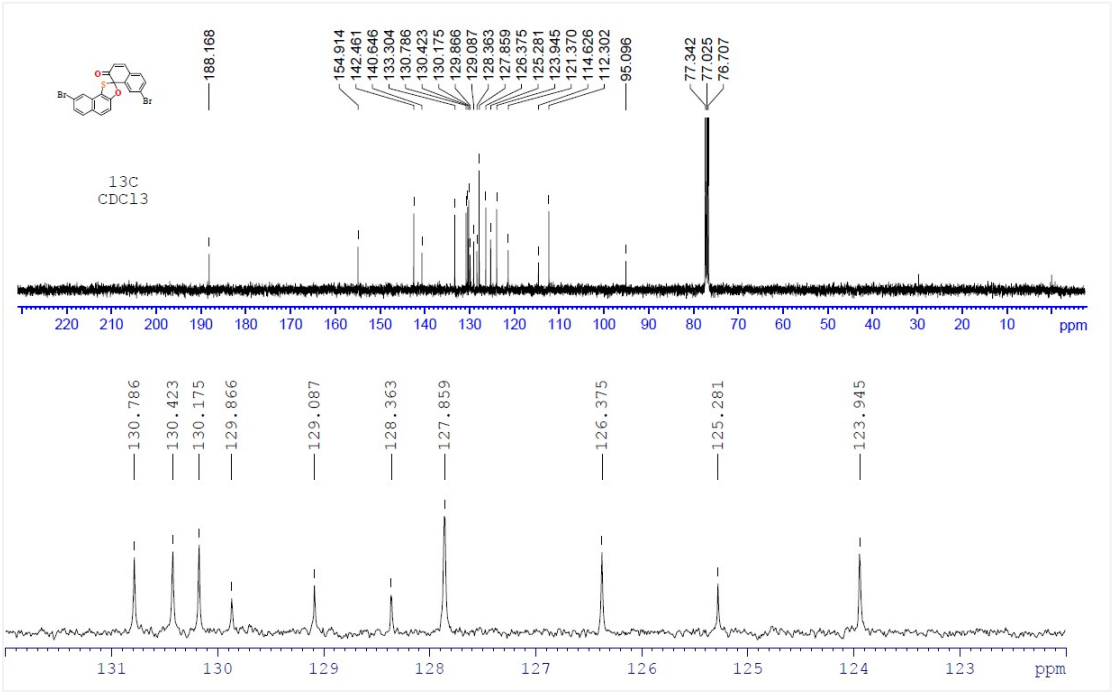


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3d**

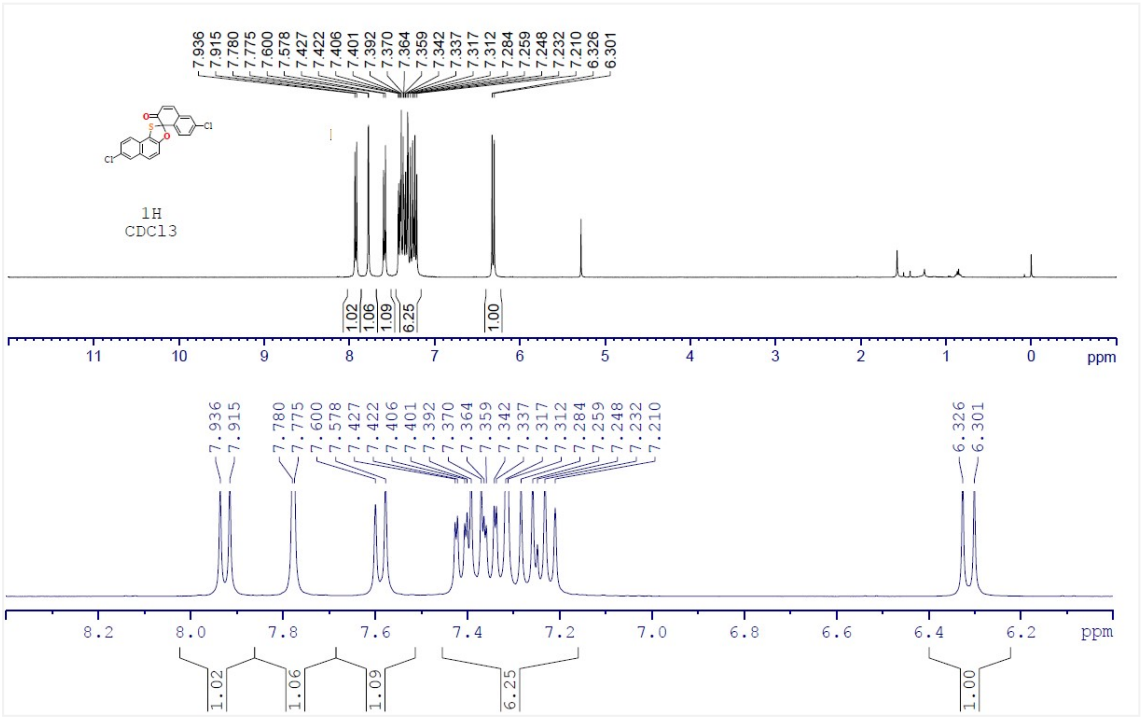


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3e**

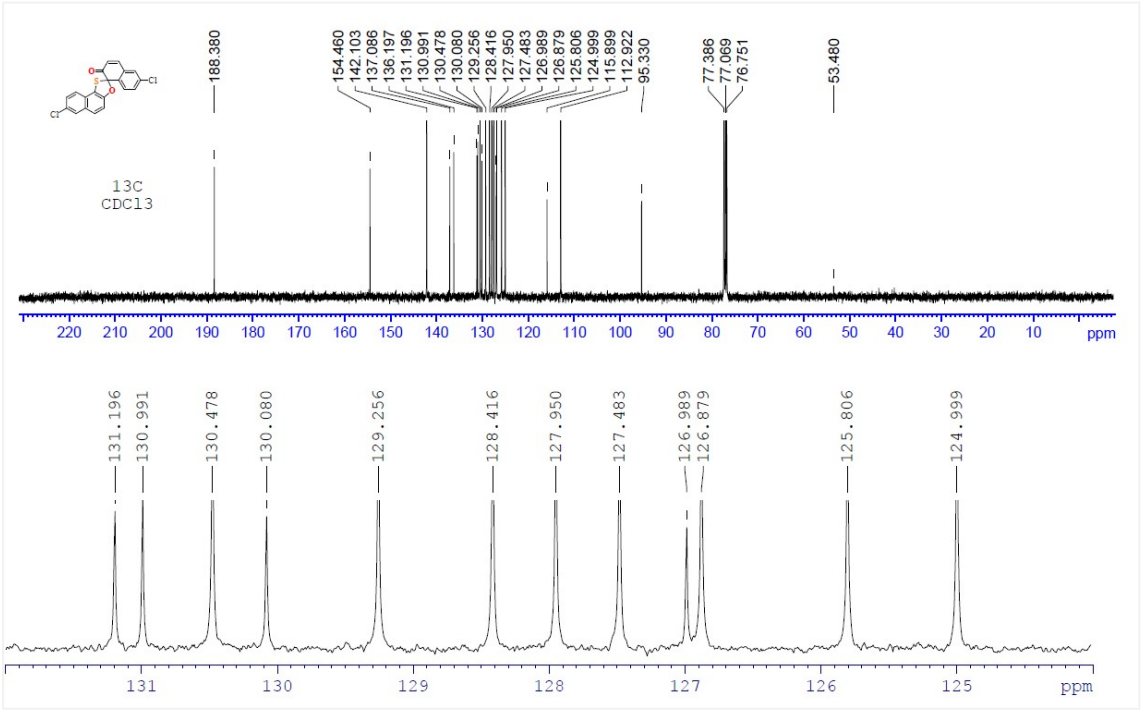


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3e**

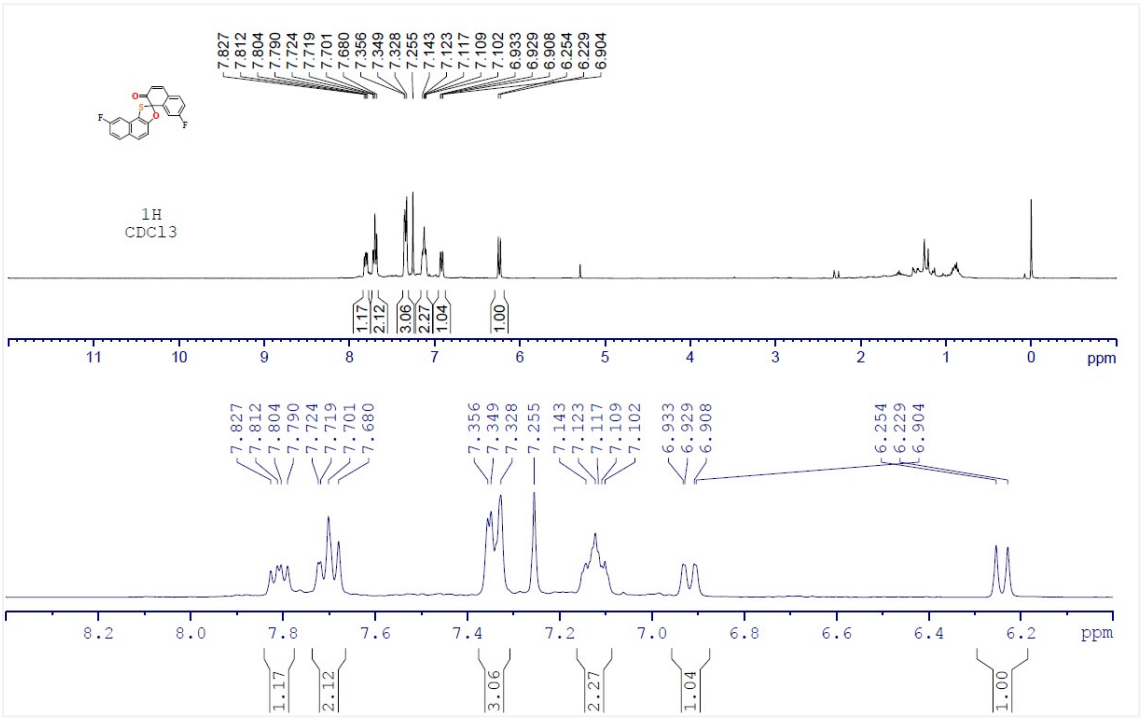


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3f**

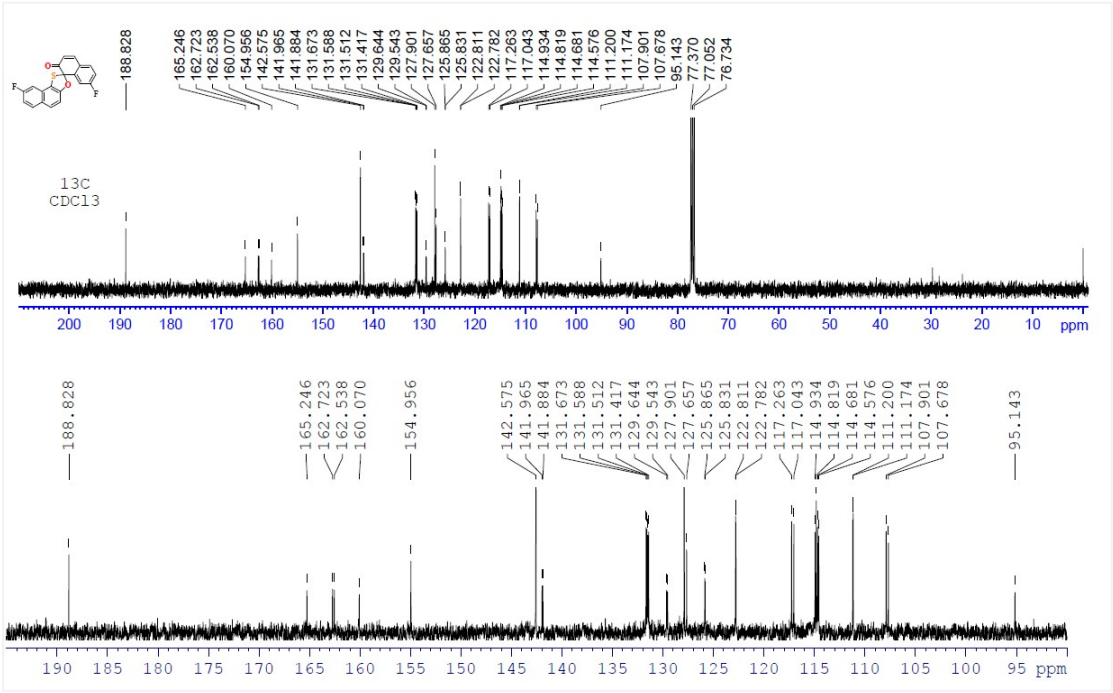


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3f**

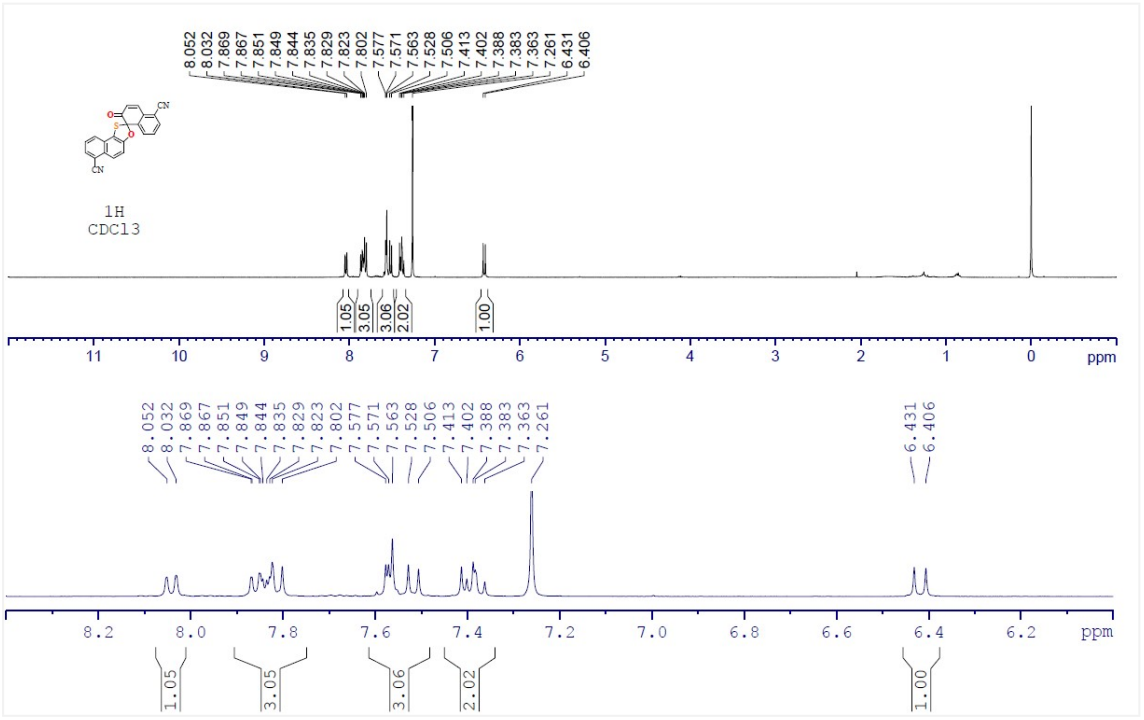


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3g**

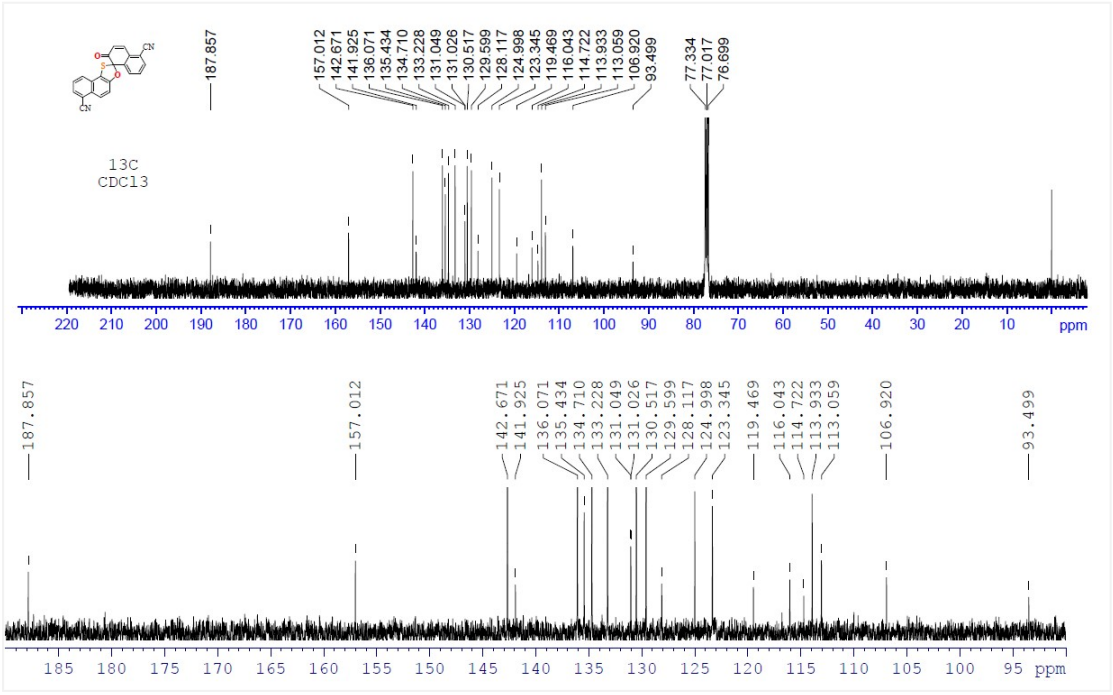


Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3g**

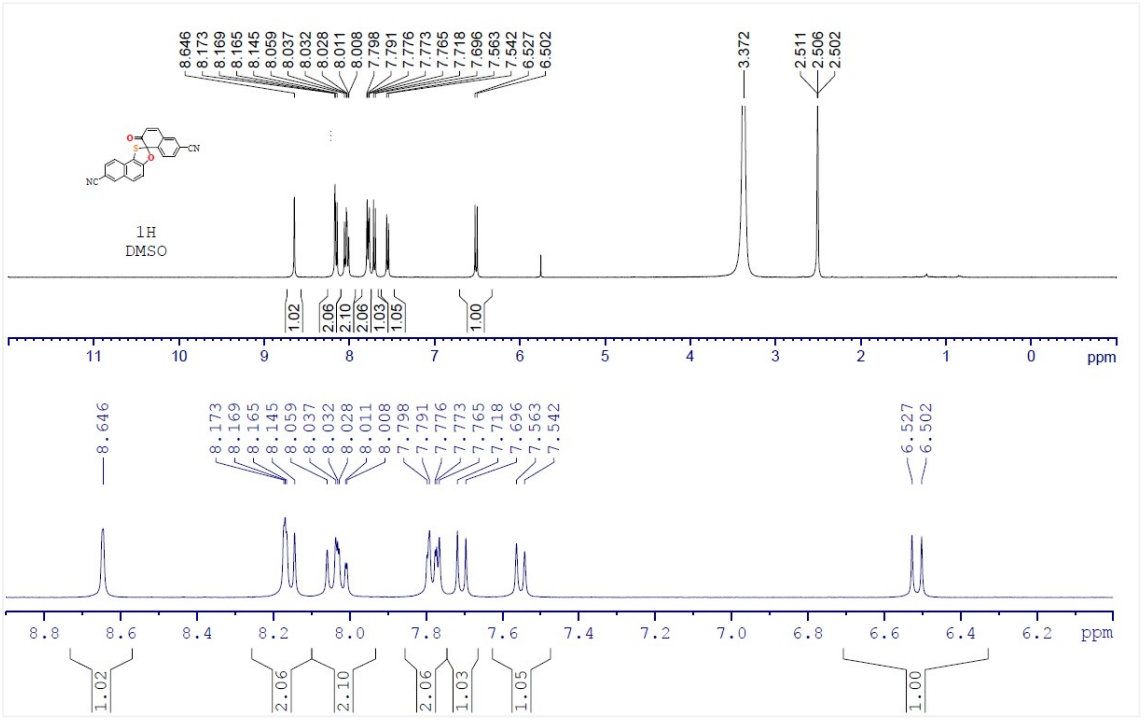


Figure S17. ^{1}H NMR (400 MHz, DMSO-d_6 Spectrum of Compound **3h**

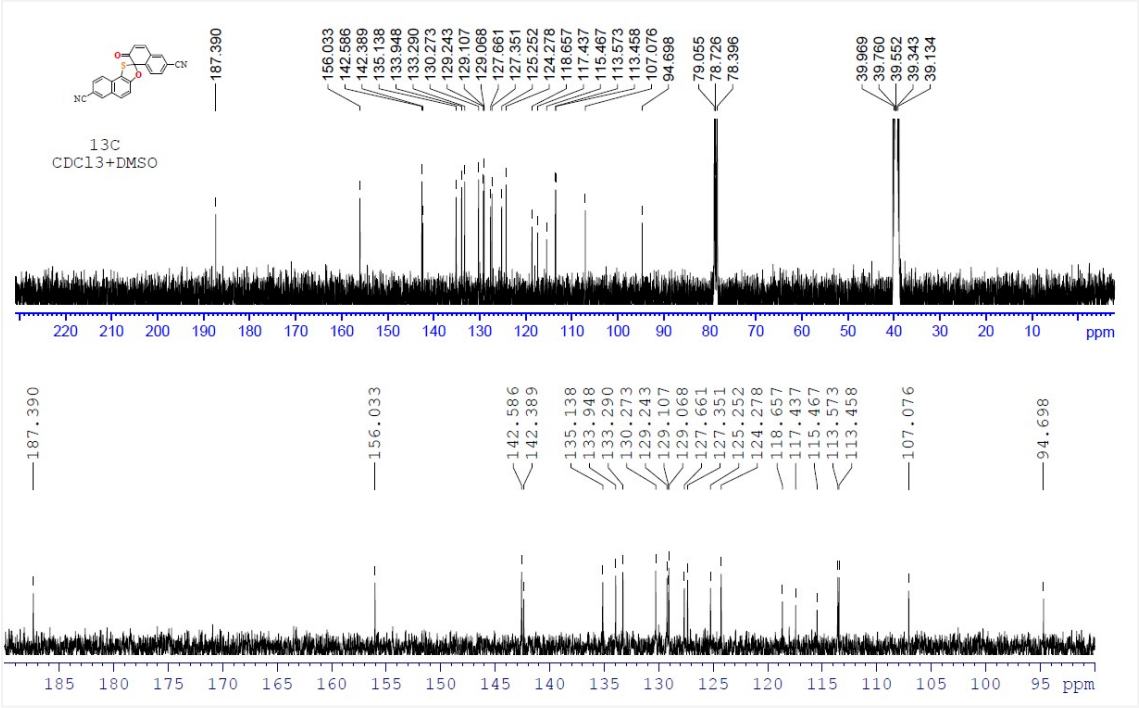


Figure S18. ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO-d_6) Spectrum of Compound **3h**

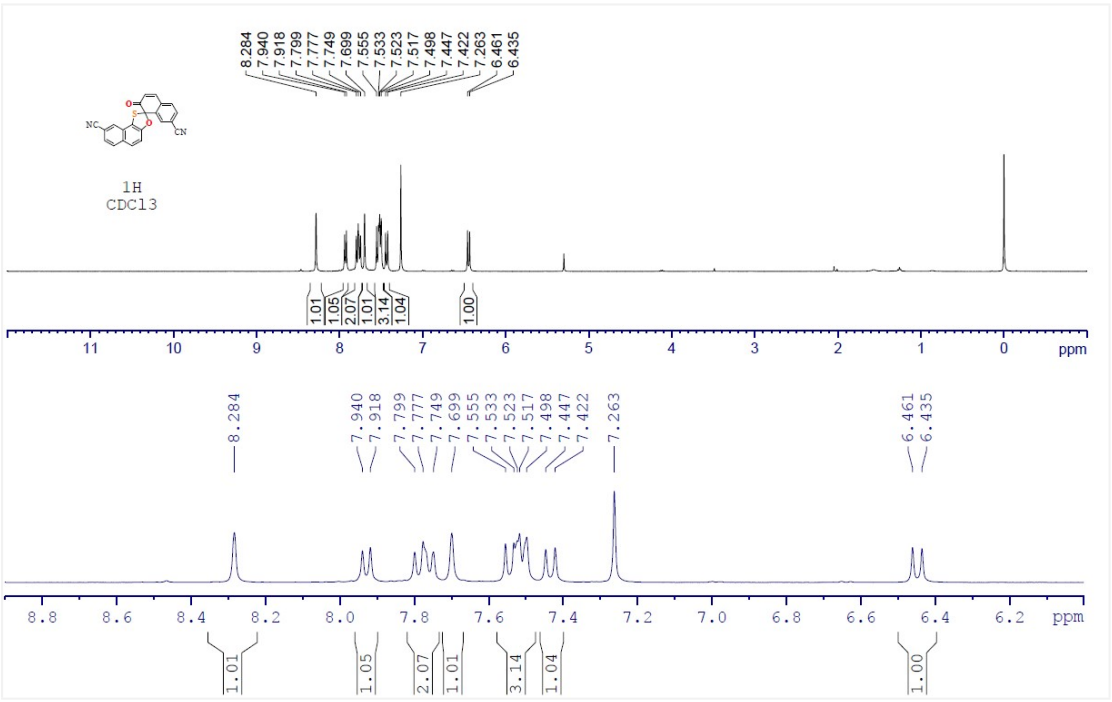


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3i**

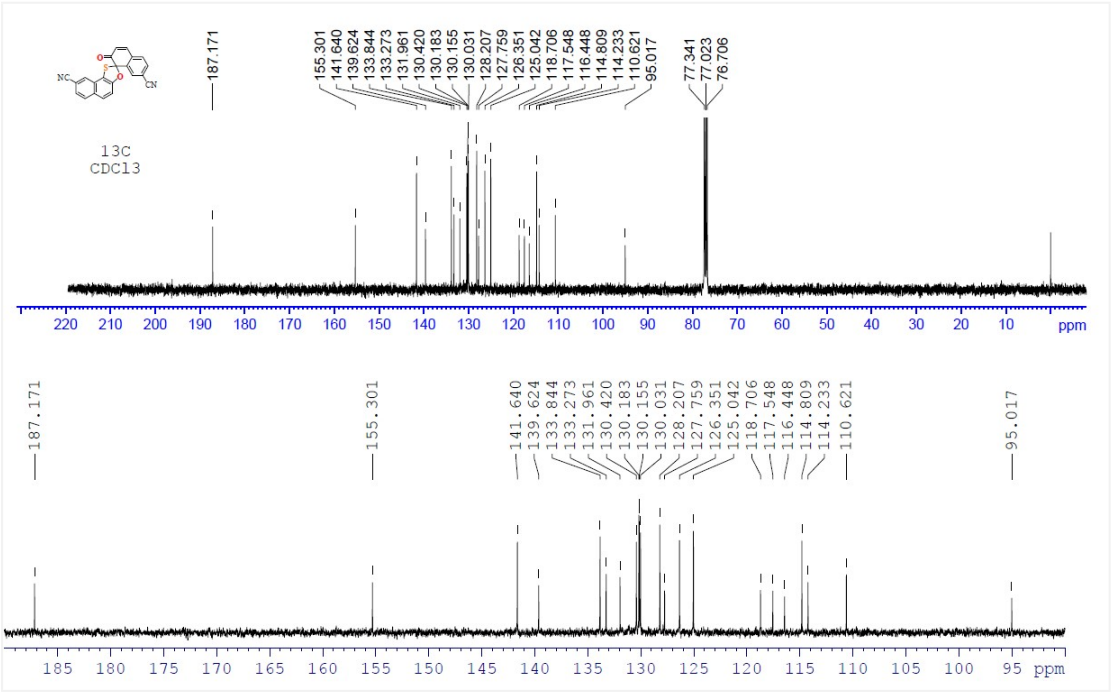


Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3i**

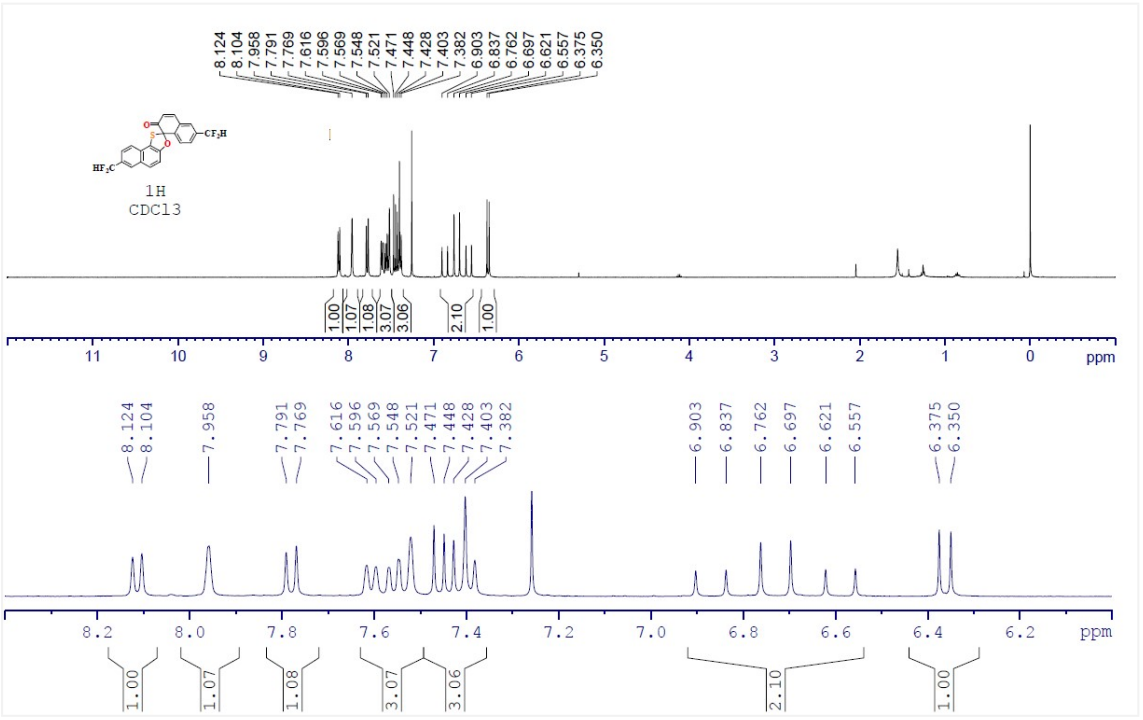


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3j**

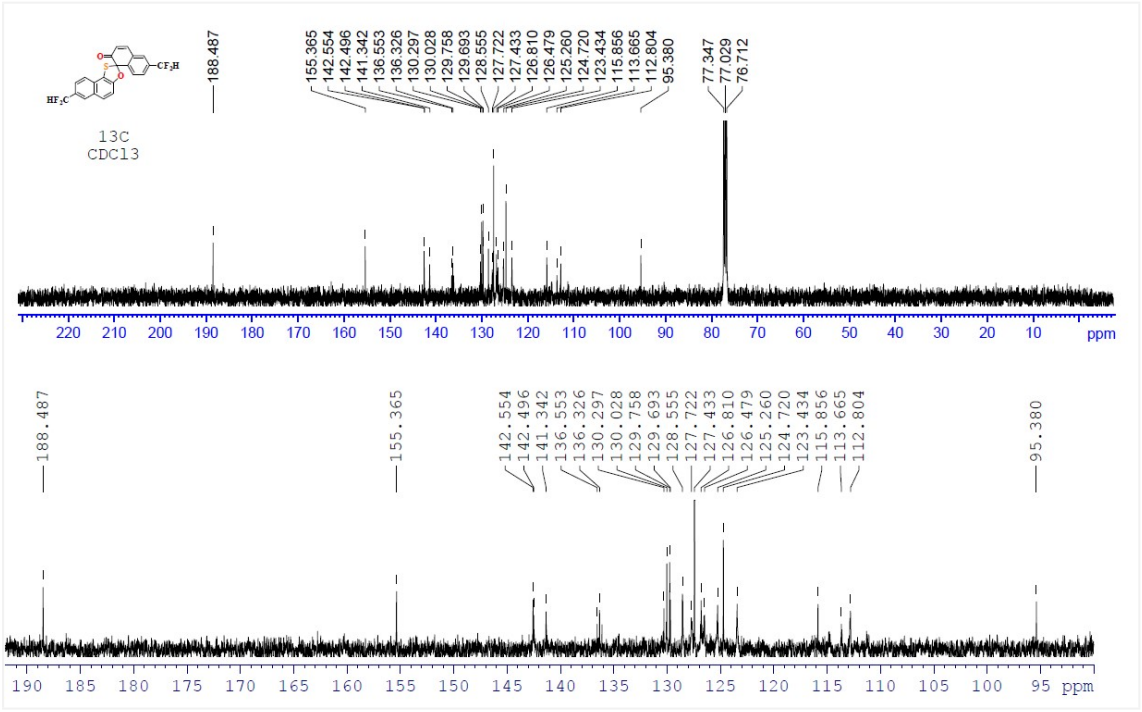


Figure S22 ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3j**

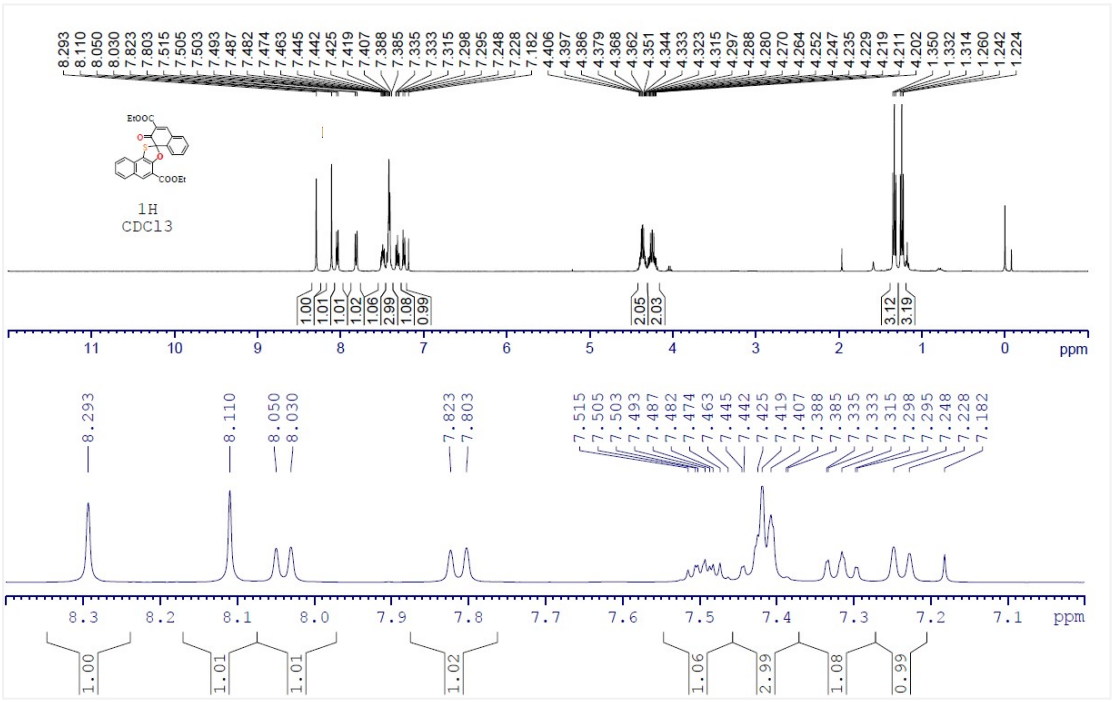


Figure S23 ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3k**

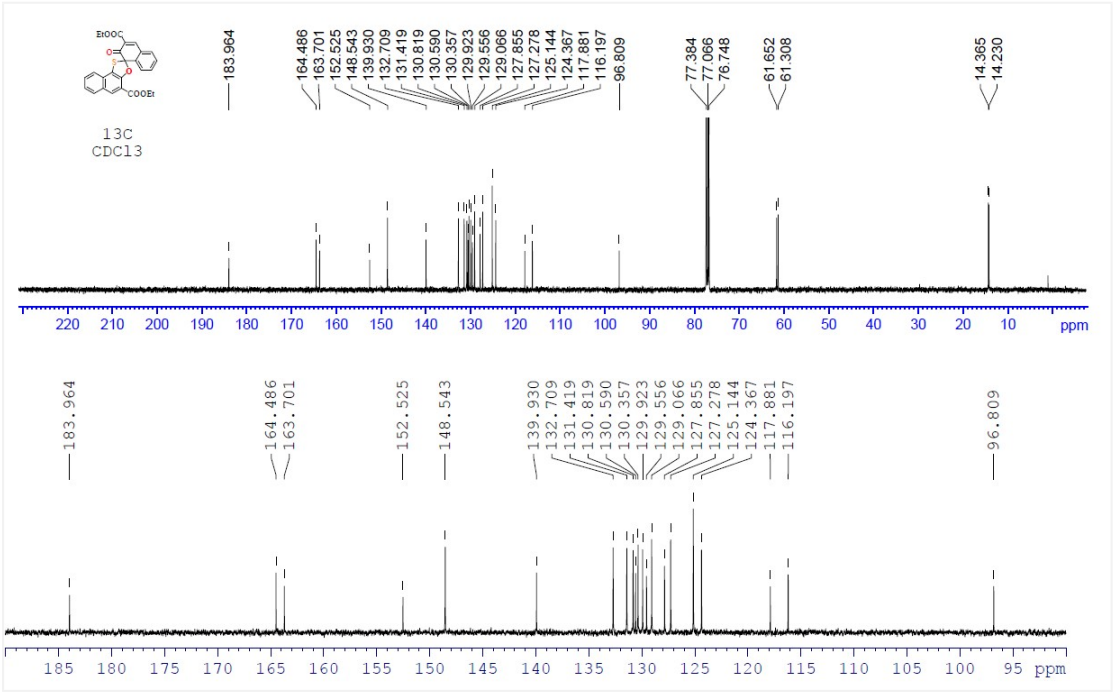


Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3k**

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3l**

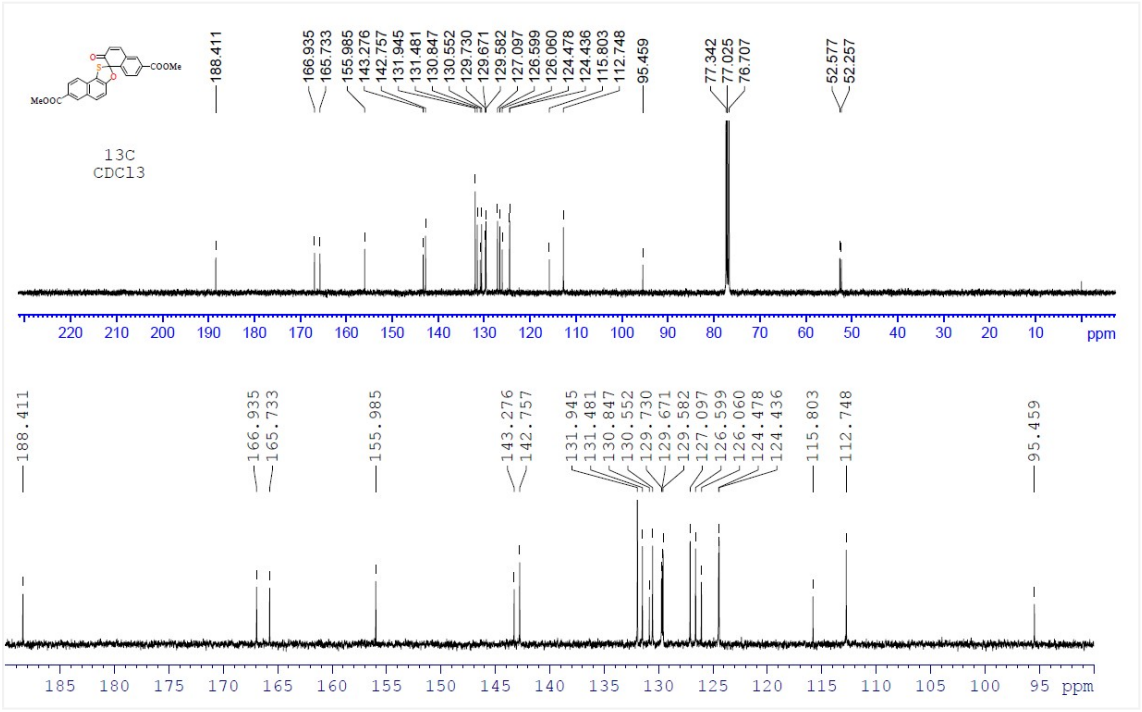


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3l**

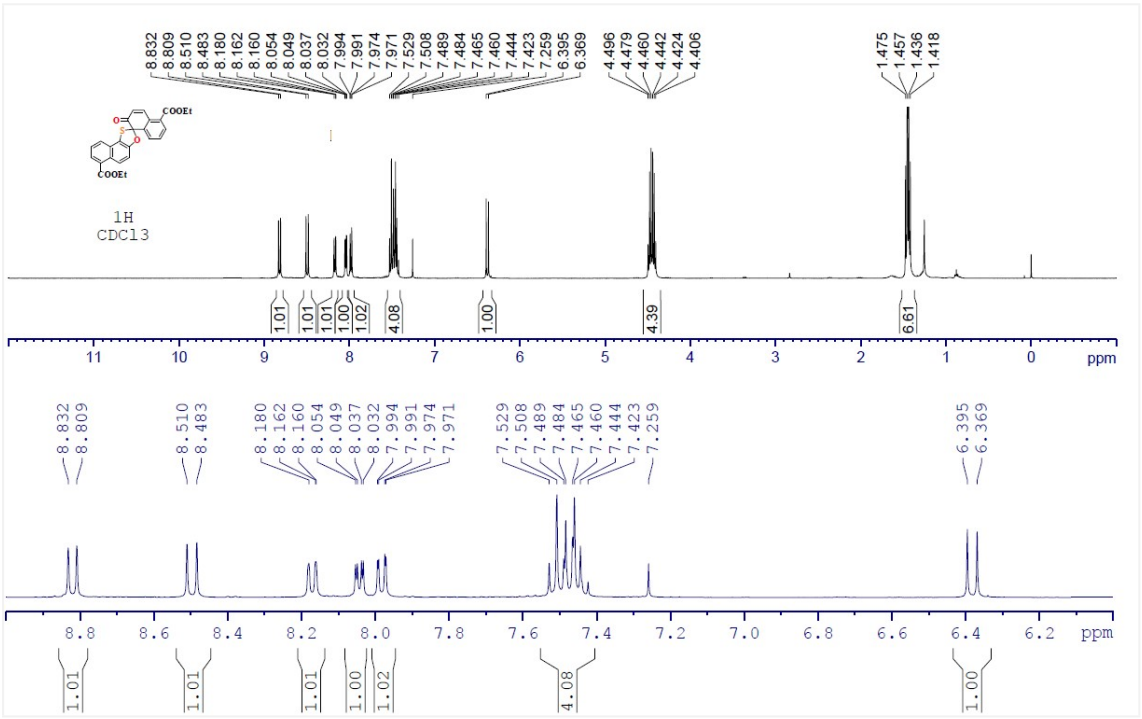


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3m**

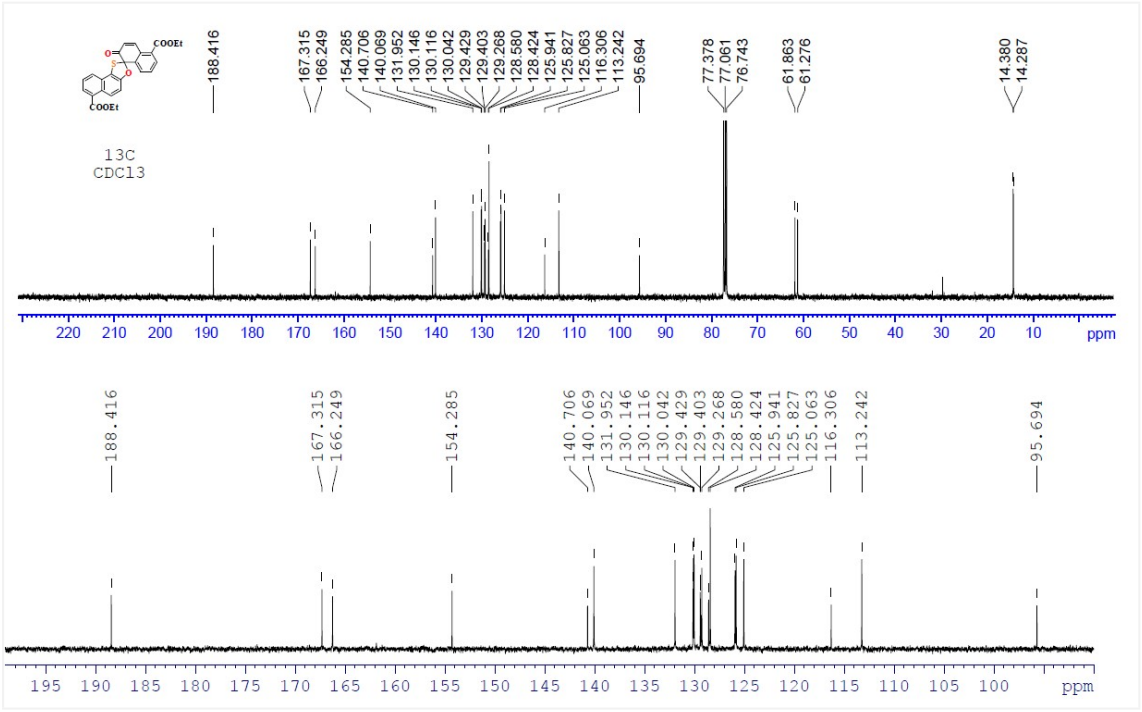


Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3m**

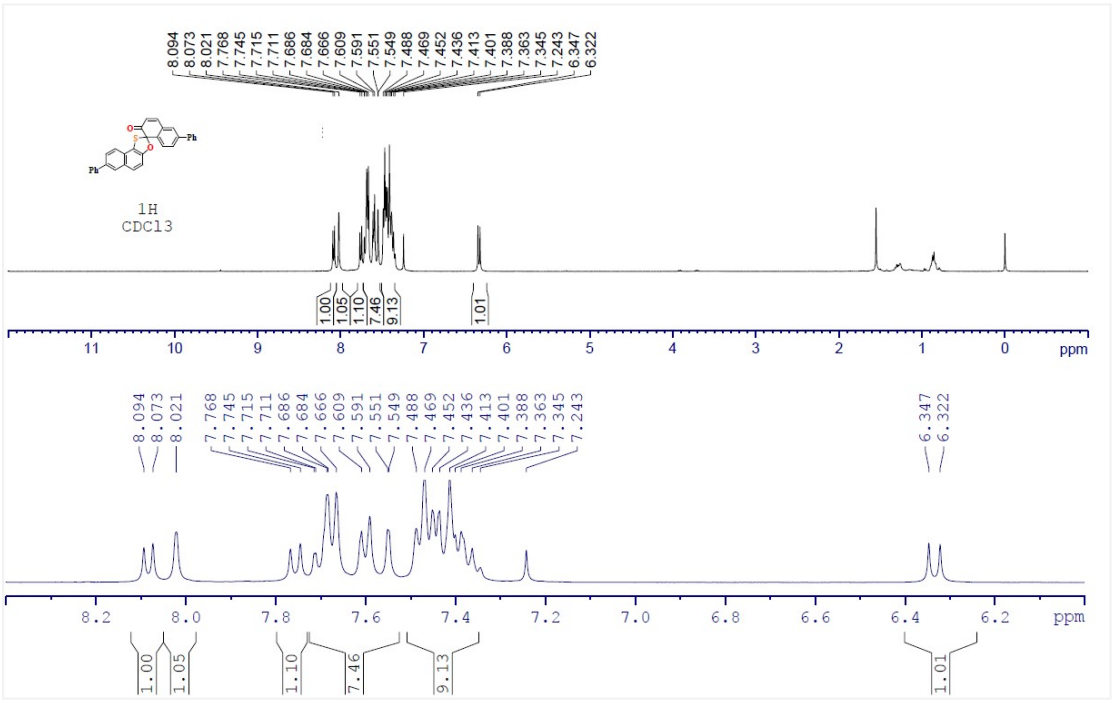


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3o**

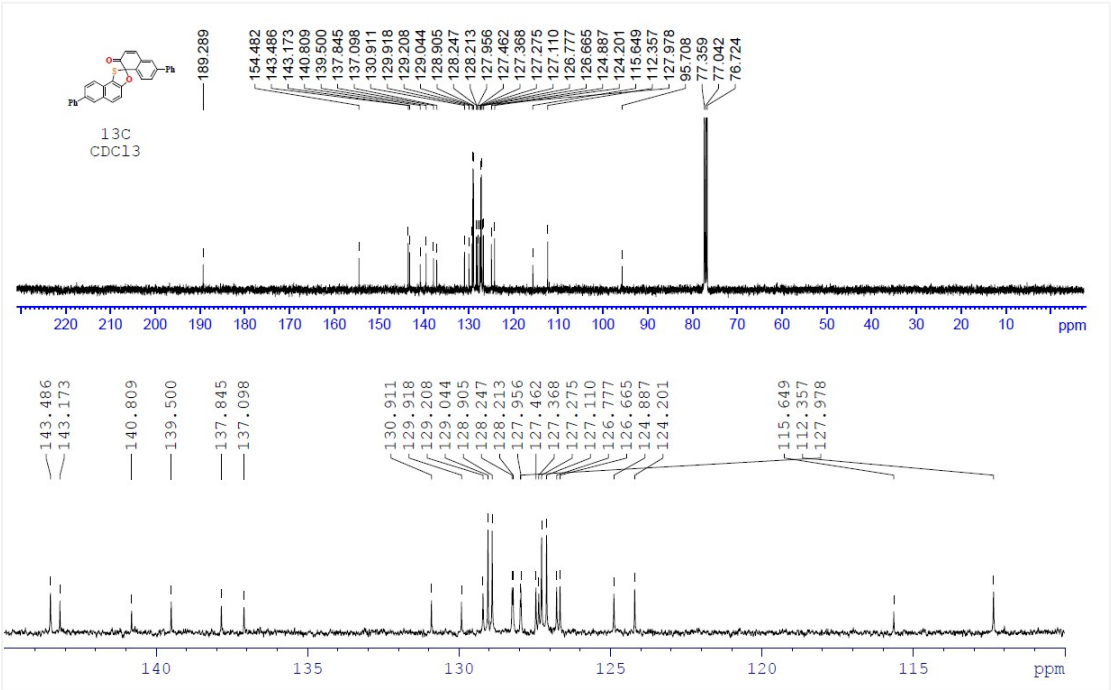


Figure S30. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3o**

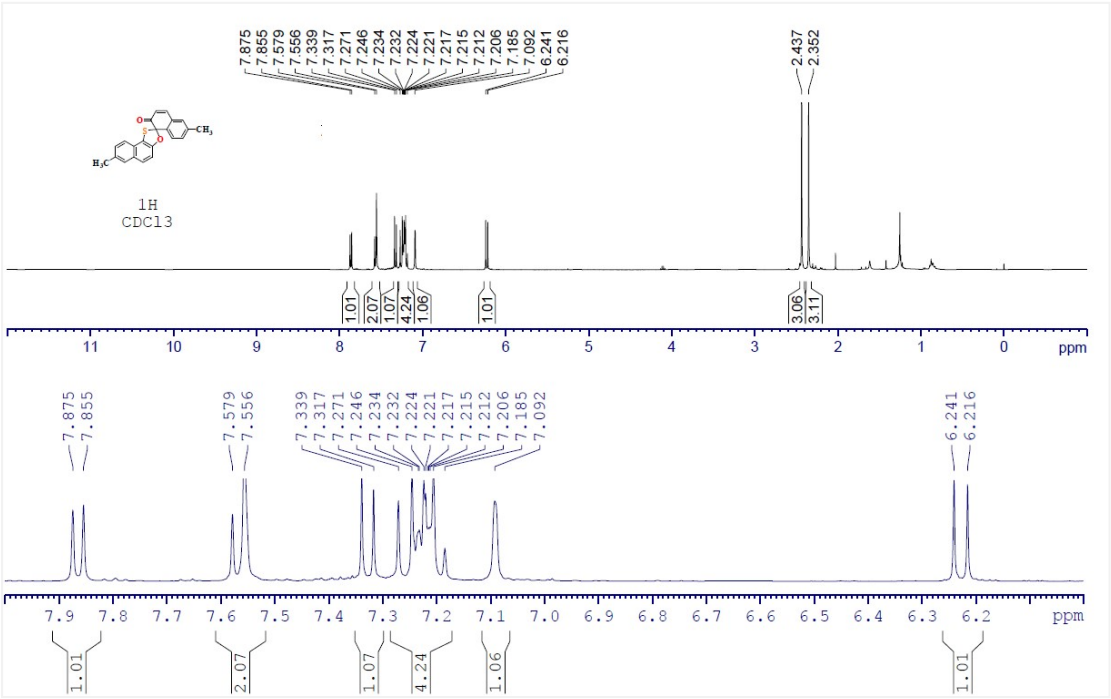


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3p**

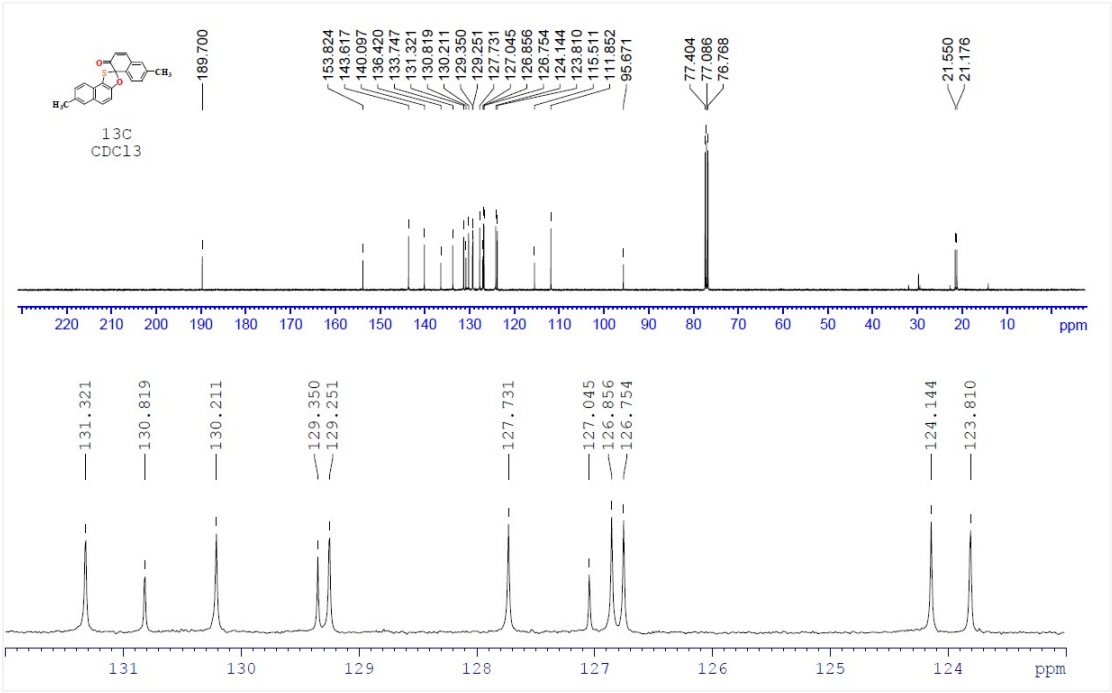


Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3p**

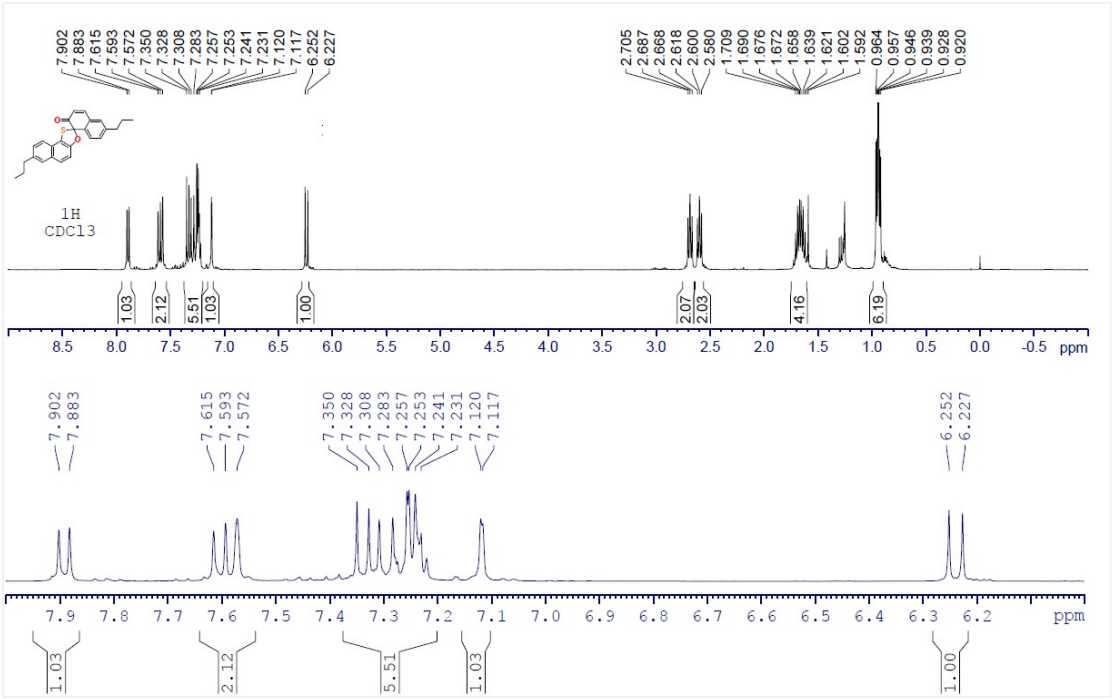


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3q**

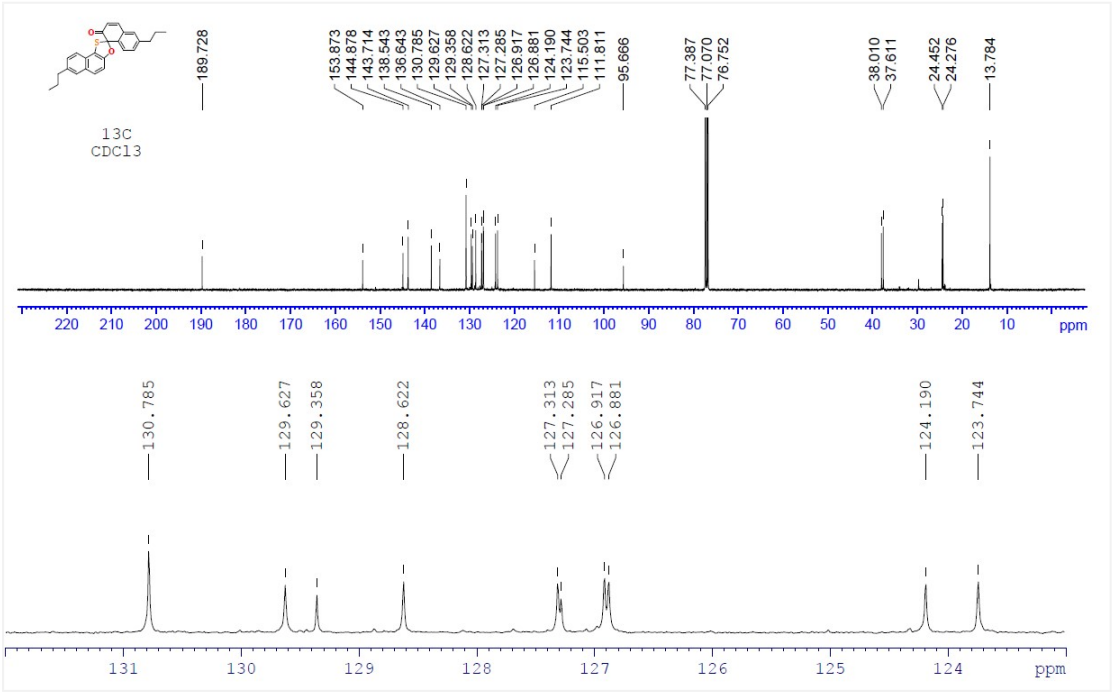


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3q**

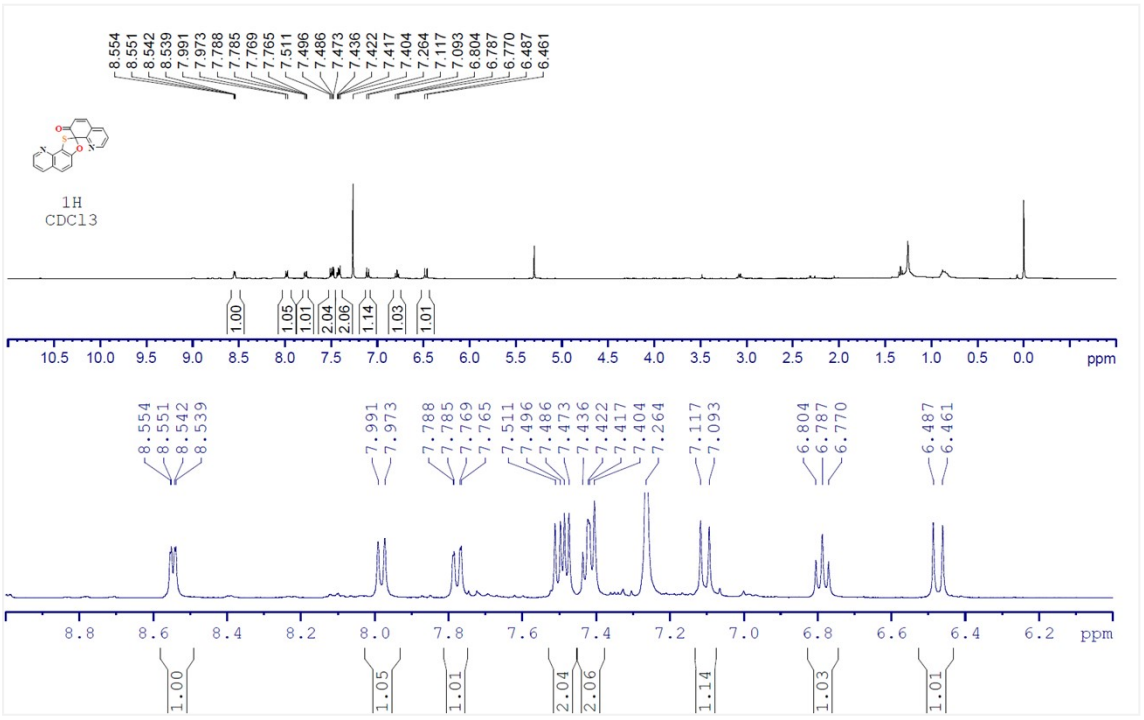


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **3r**

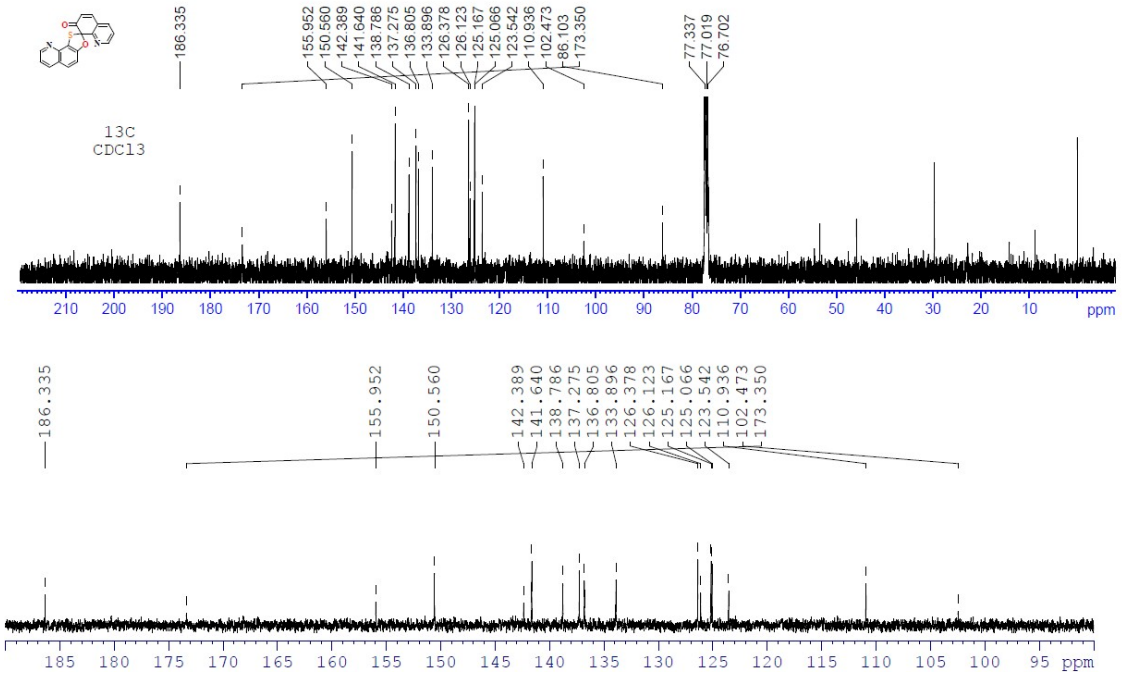


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **3r**

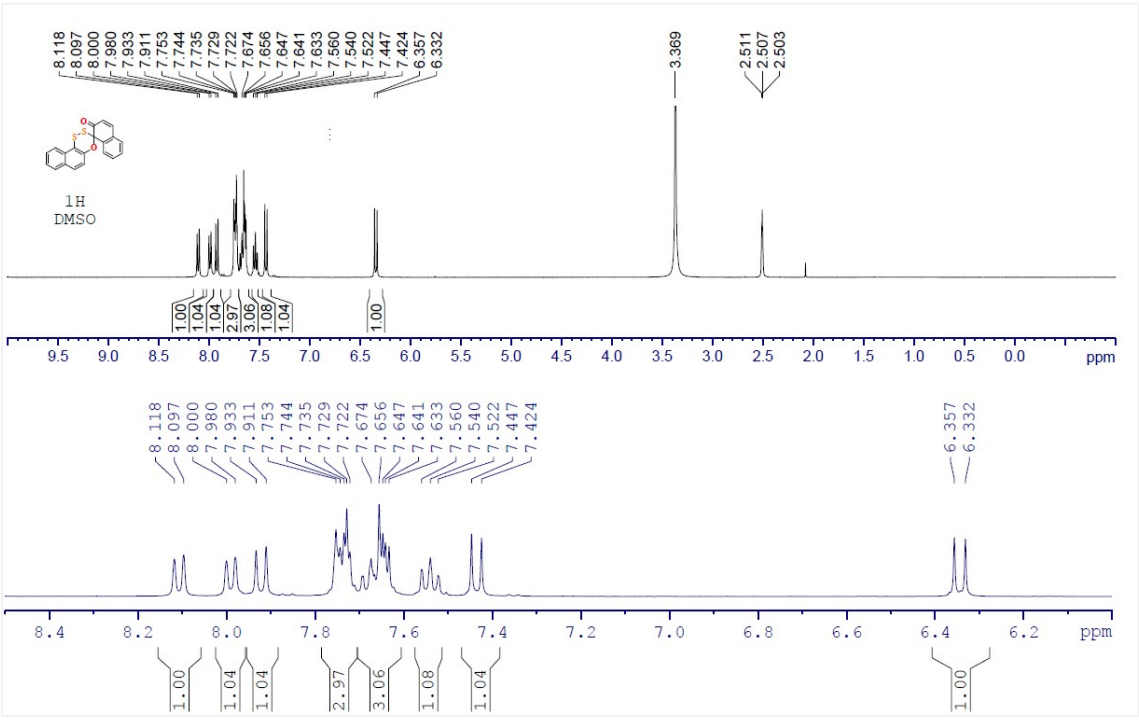


Figure S37. ^{1}H NMR (400 MHz, DMSO-d6) Spectrum of Compound **2a**

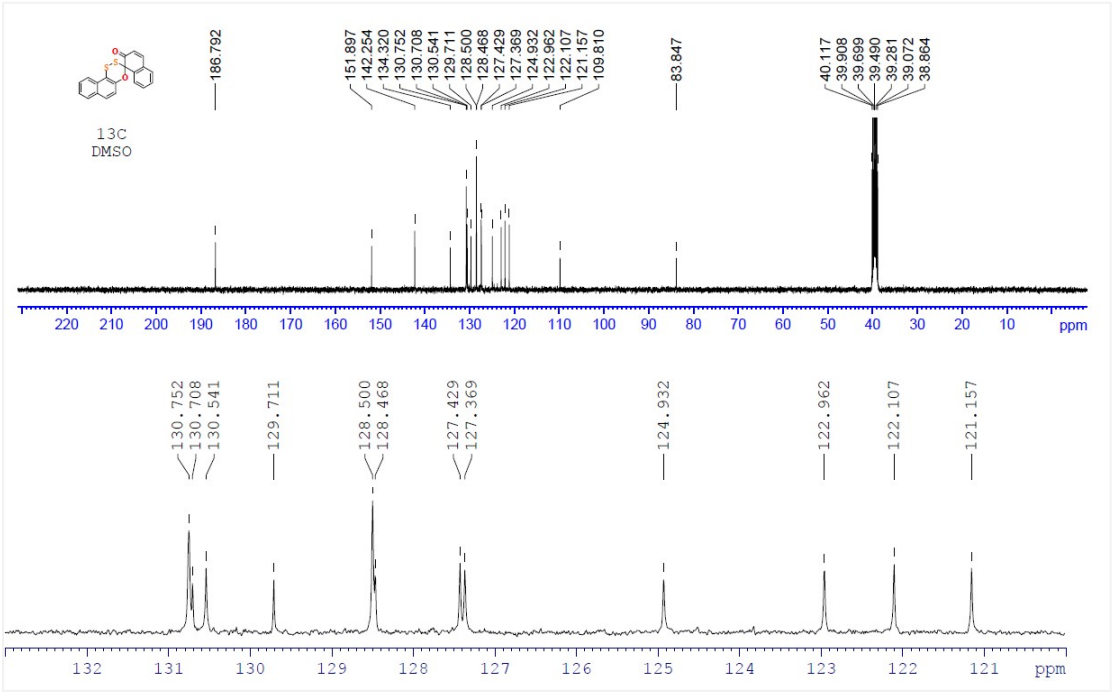


Figure S38. ^{13}C NMR (100 MHz, DMSO-d6) Spectrum of Compound **2a**

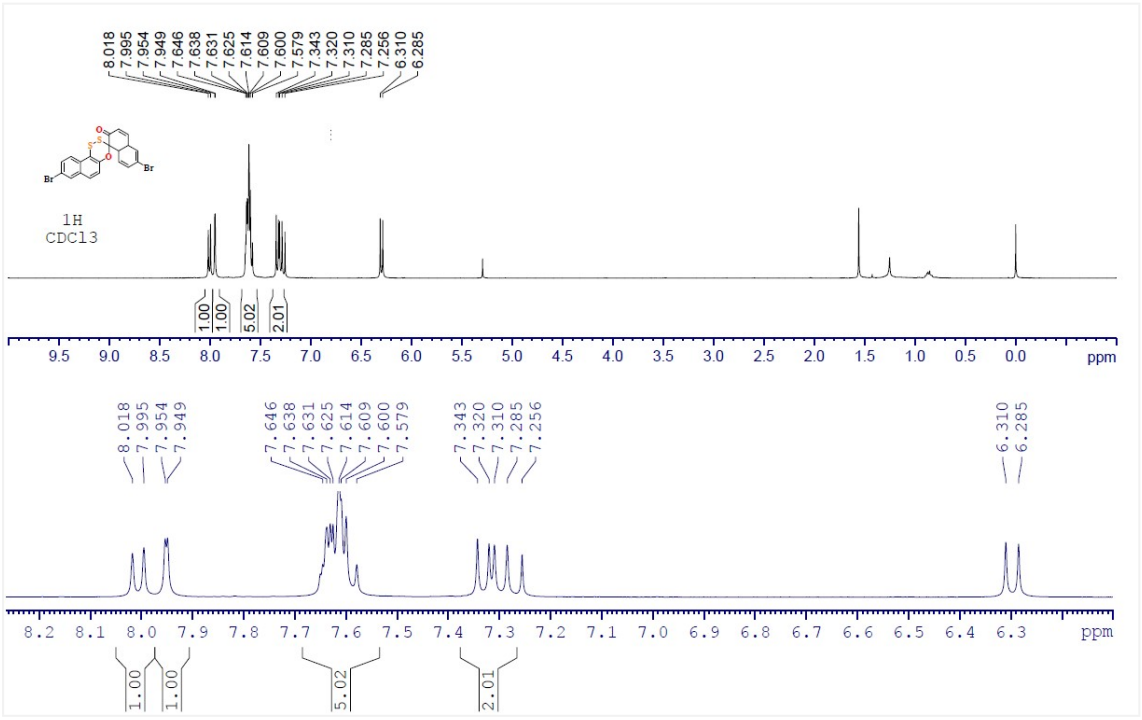


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **2b**

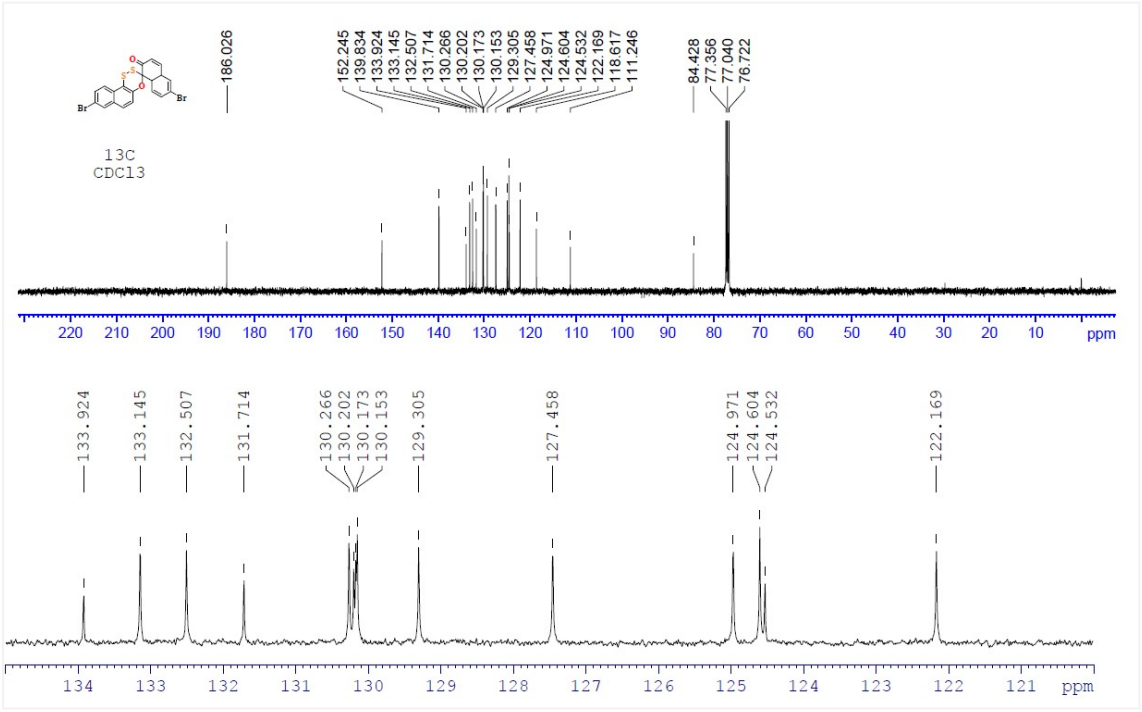


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **2b**

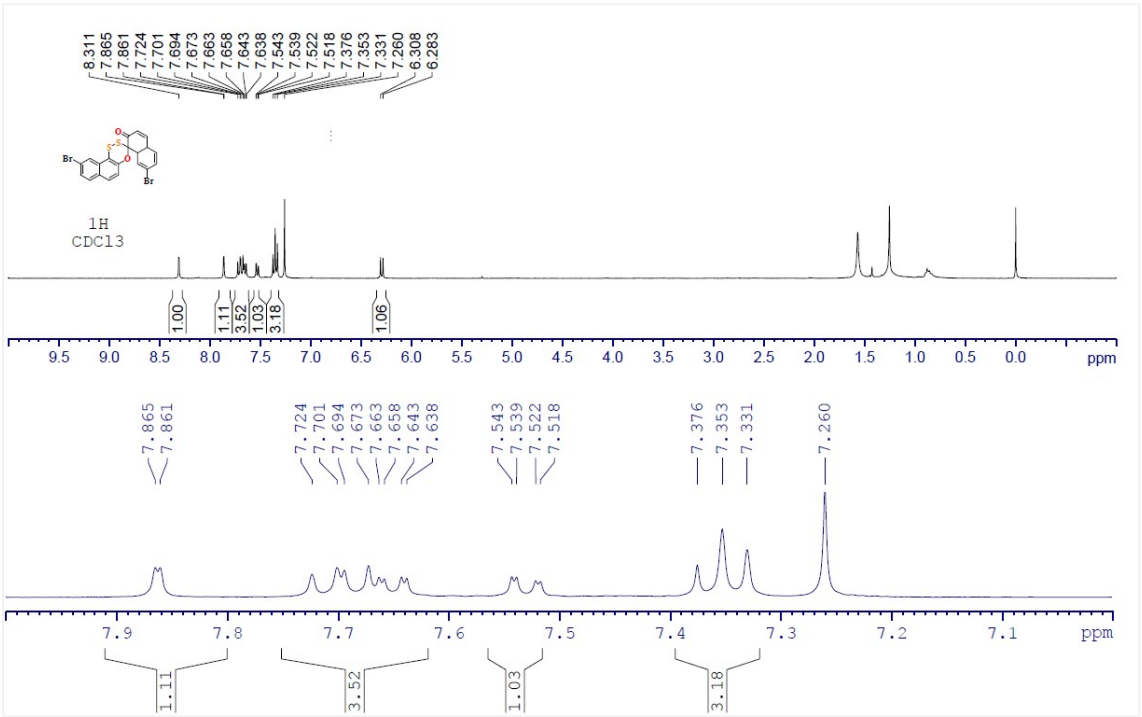


Figure 41 ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **2c**

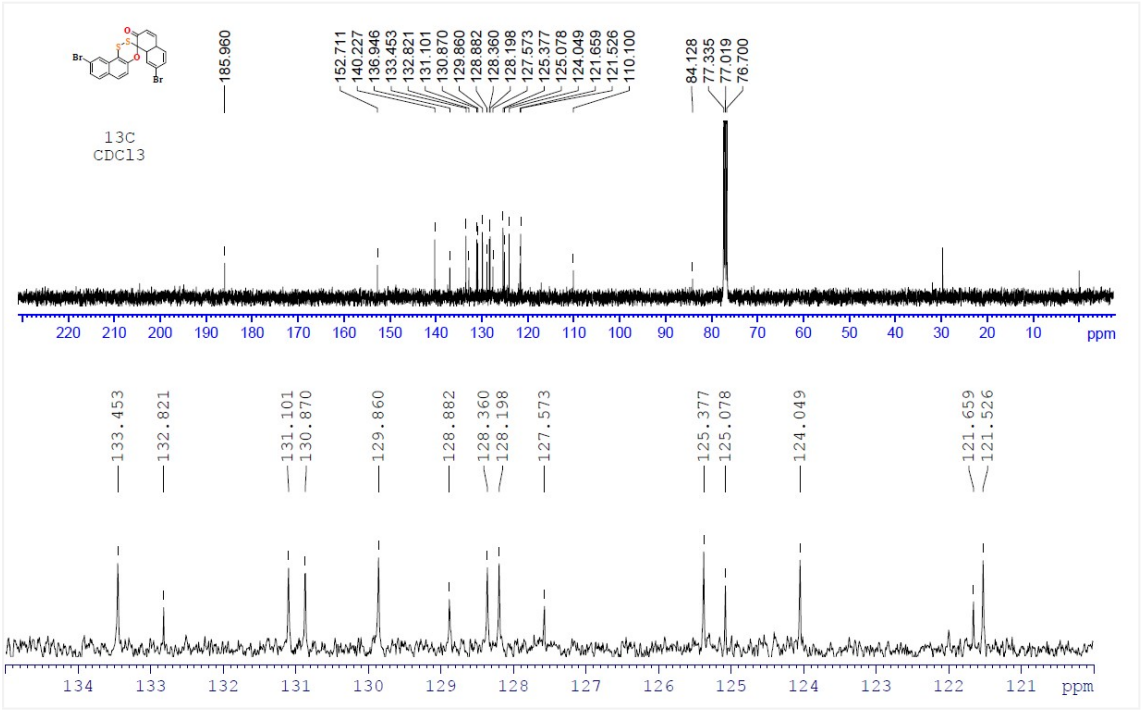


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **2c**

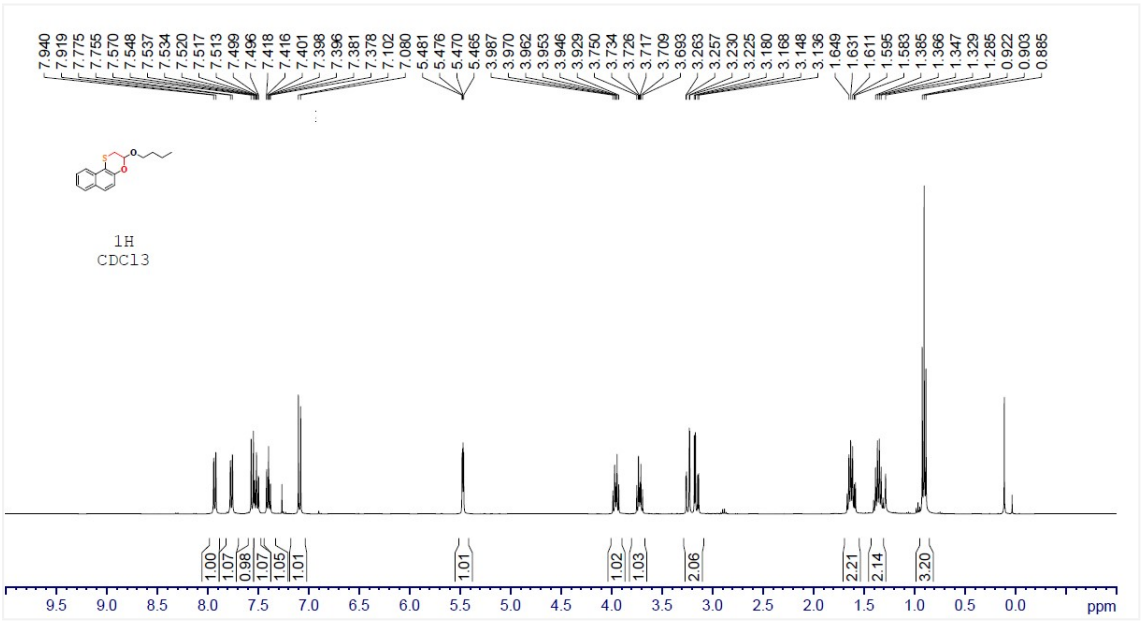


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5a**

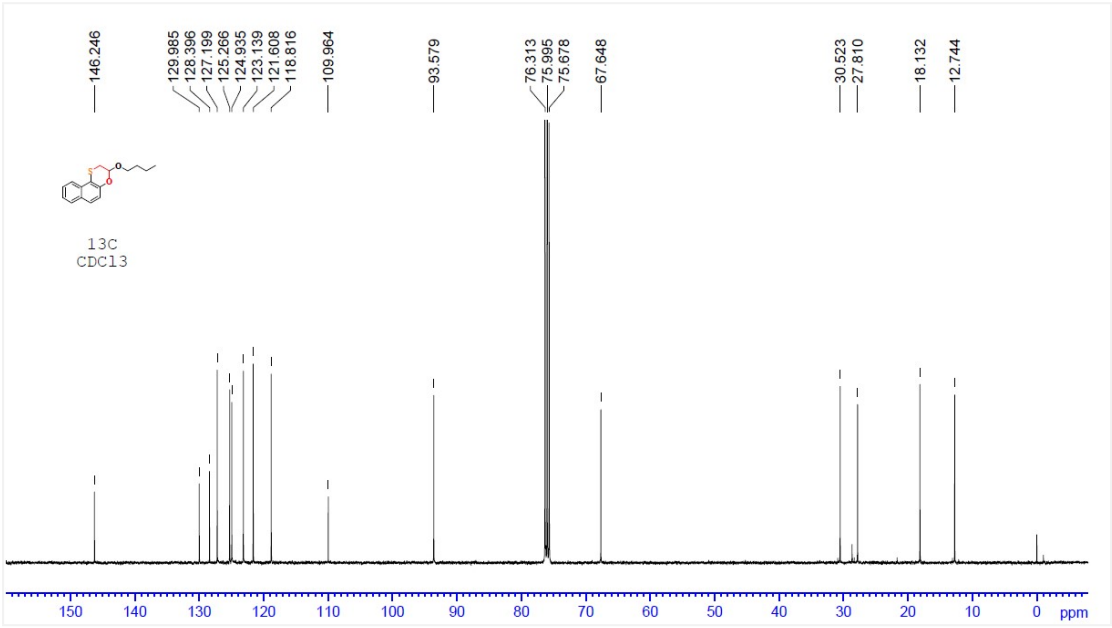


Figure S44. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5a**

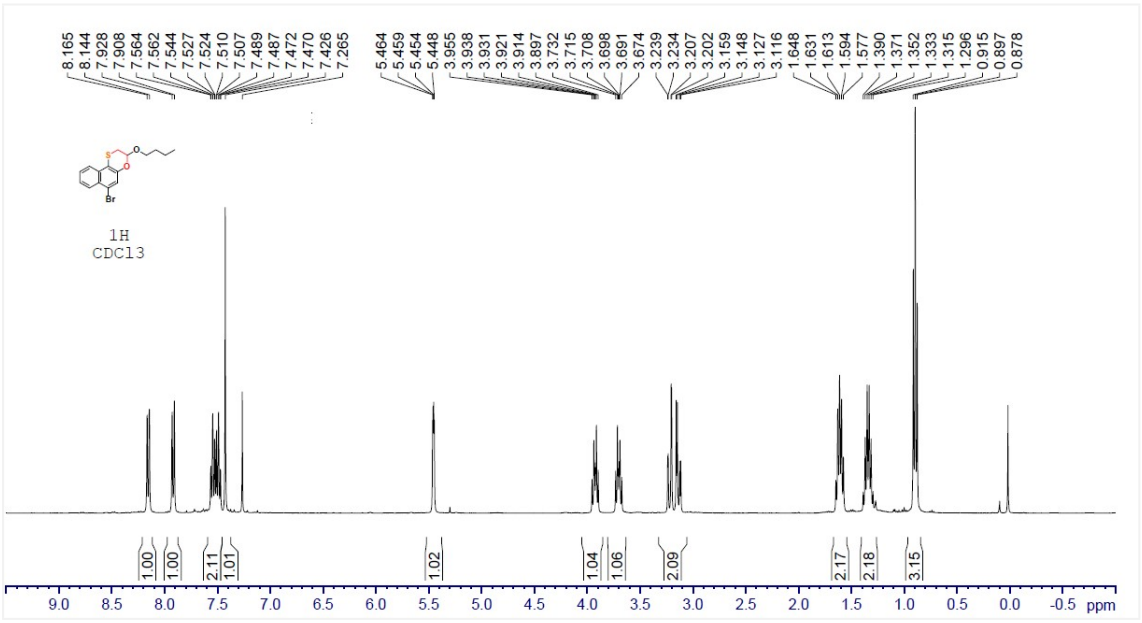


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5b**

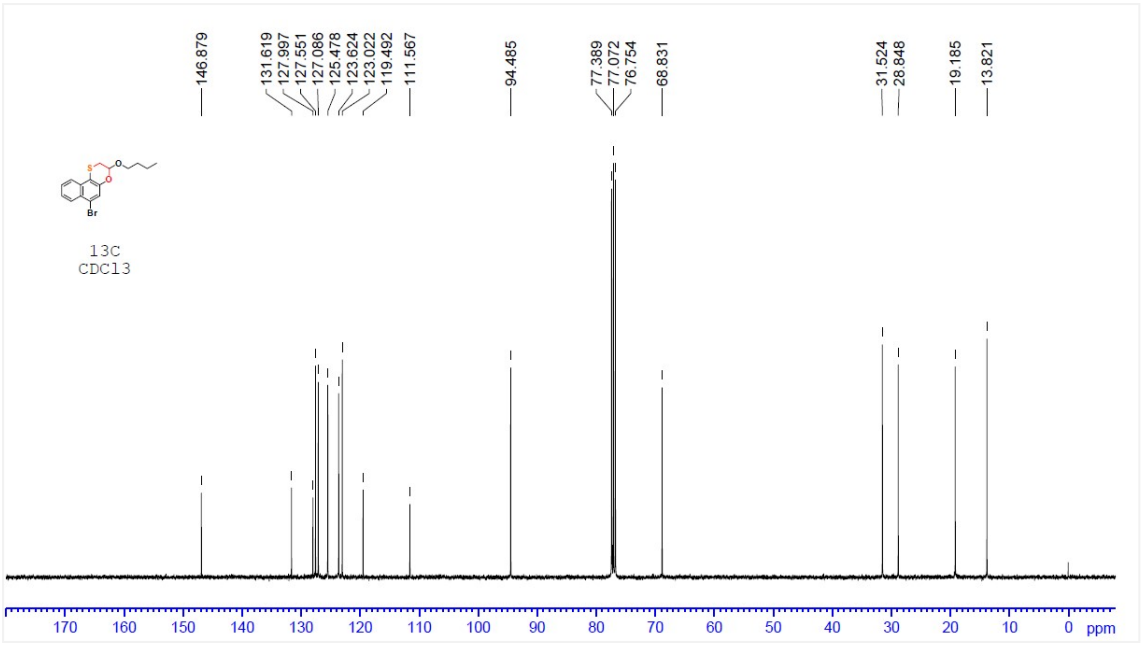


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5b**

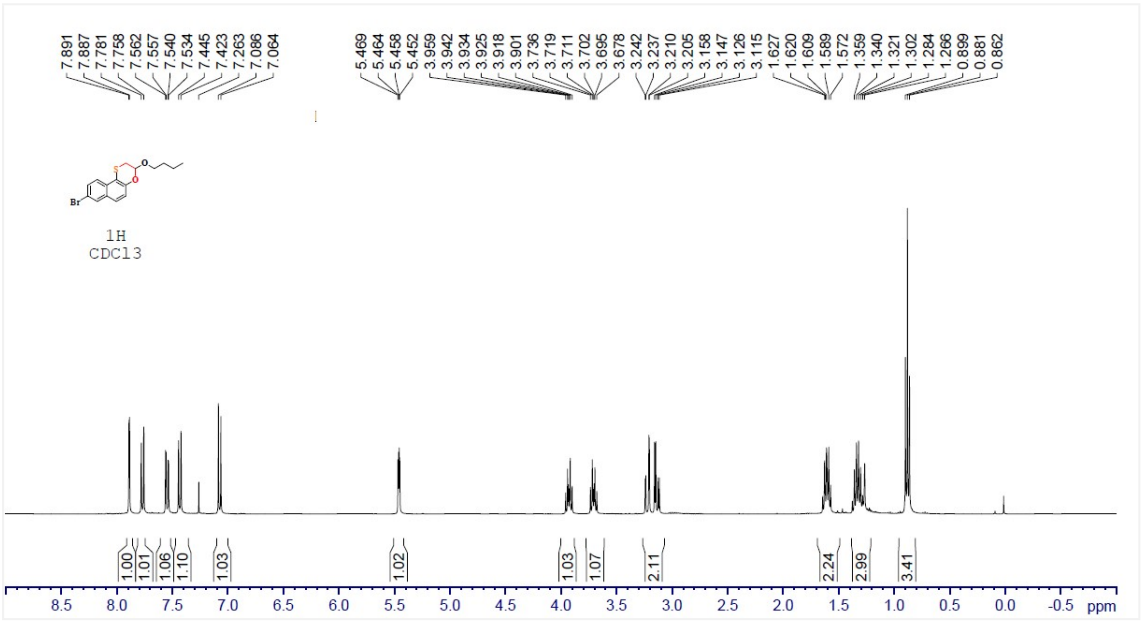


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5c**

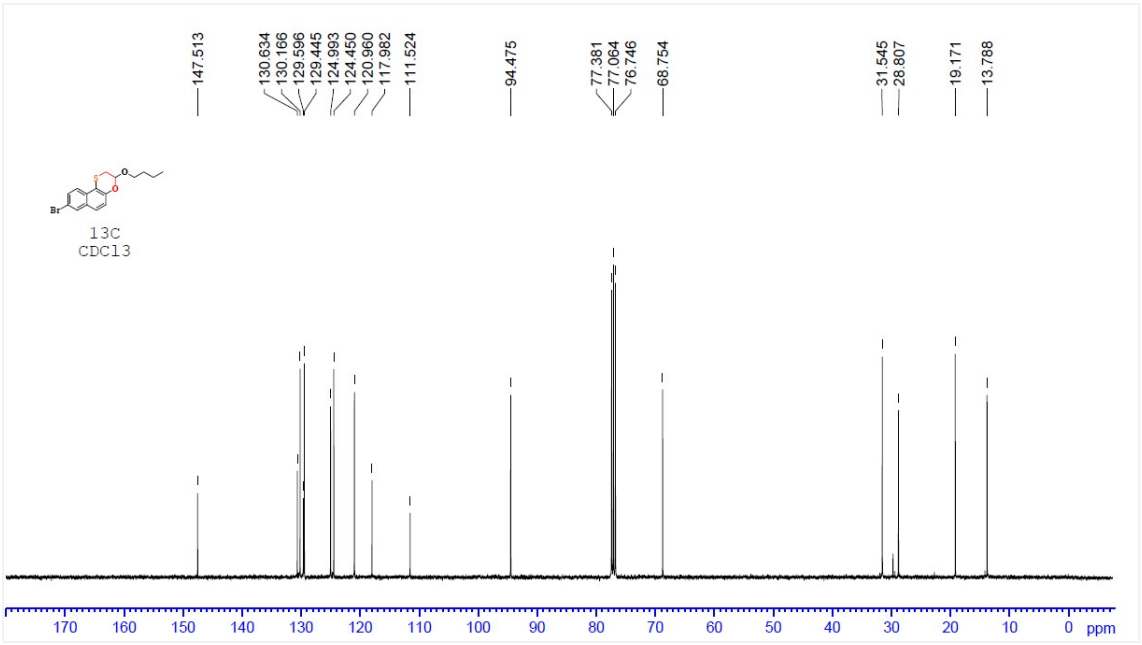


Figure S48. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5c**

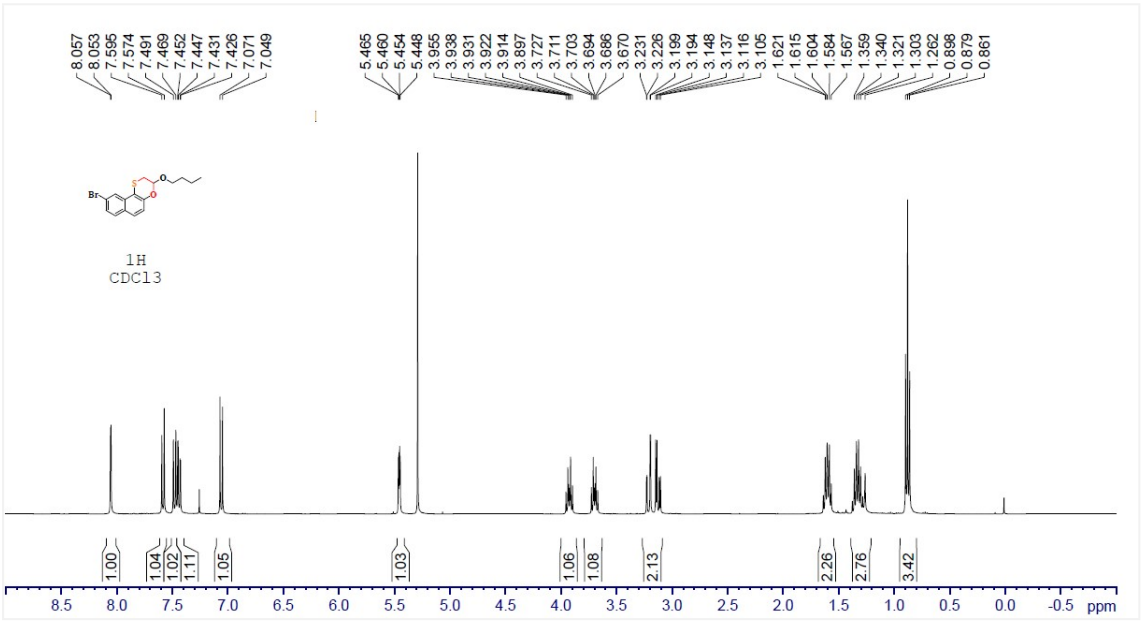


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5d**

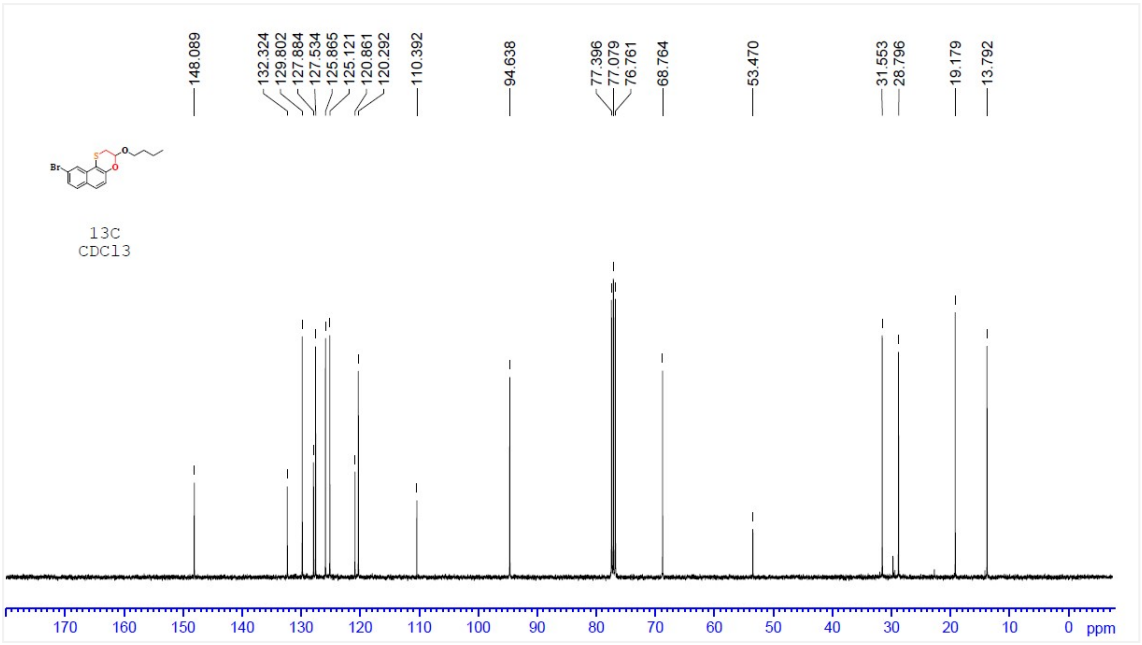


Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5d**

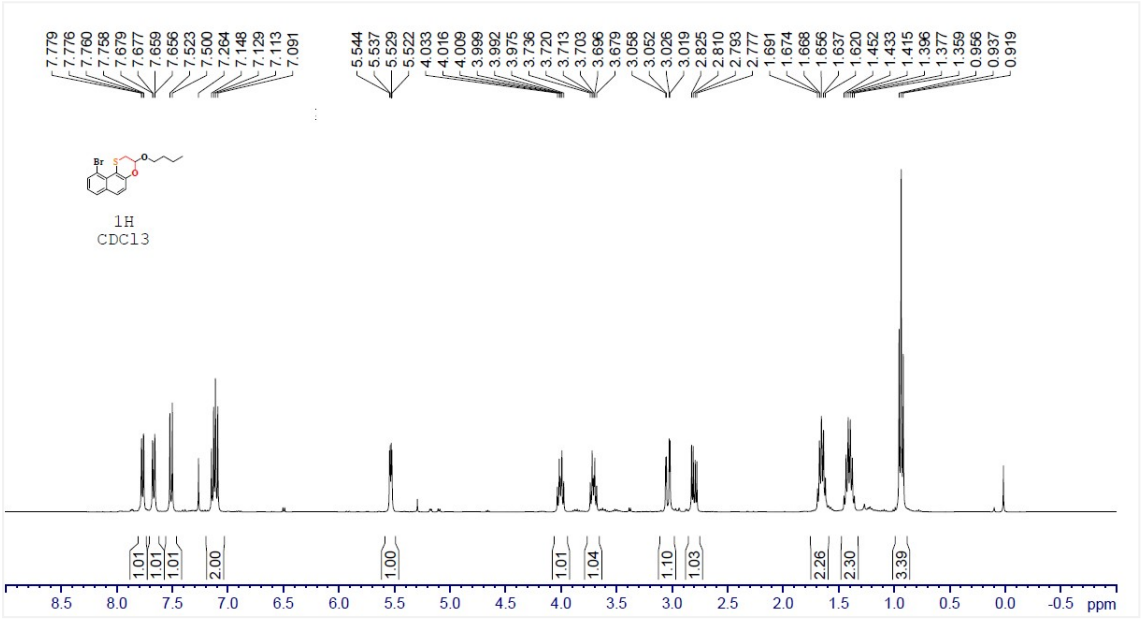


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5e**

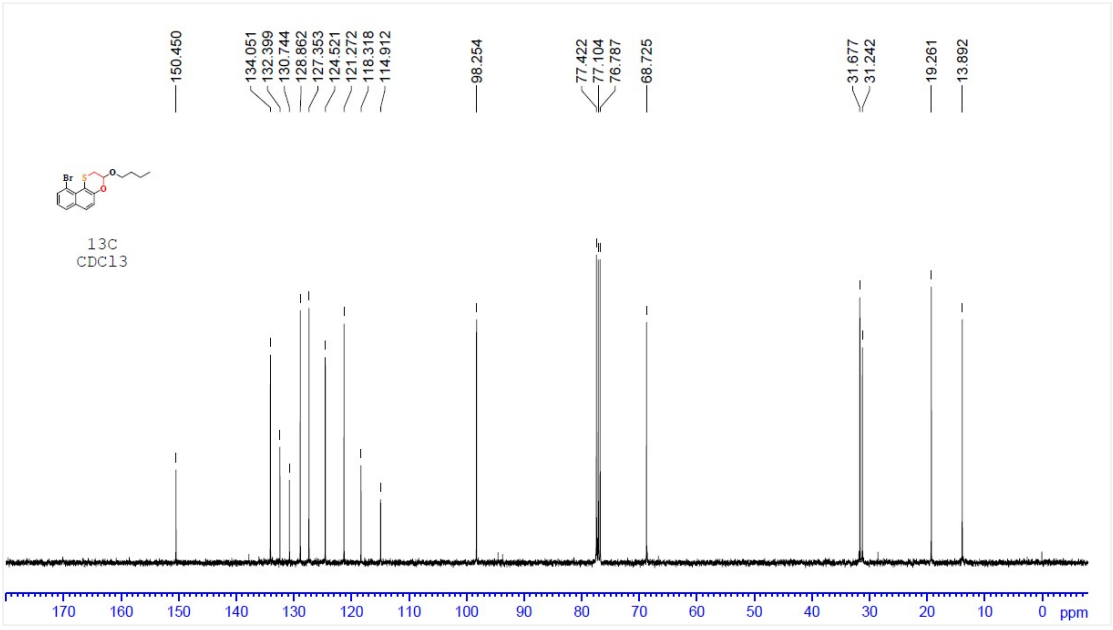


Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5e**

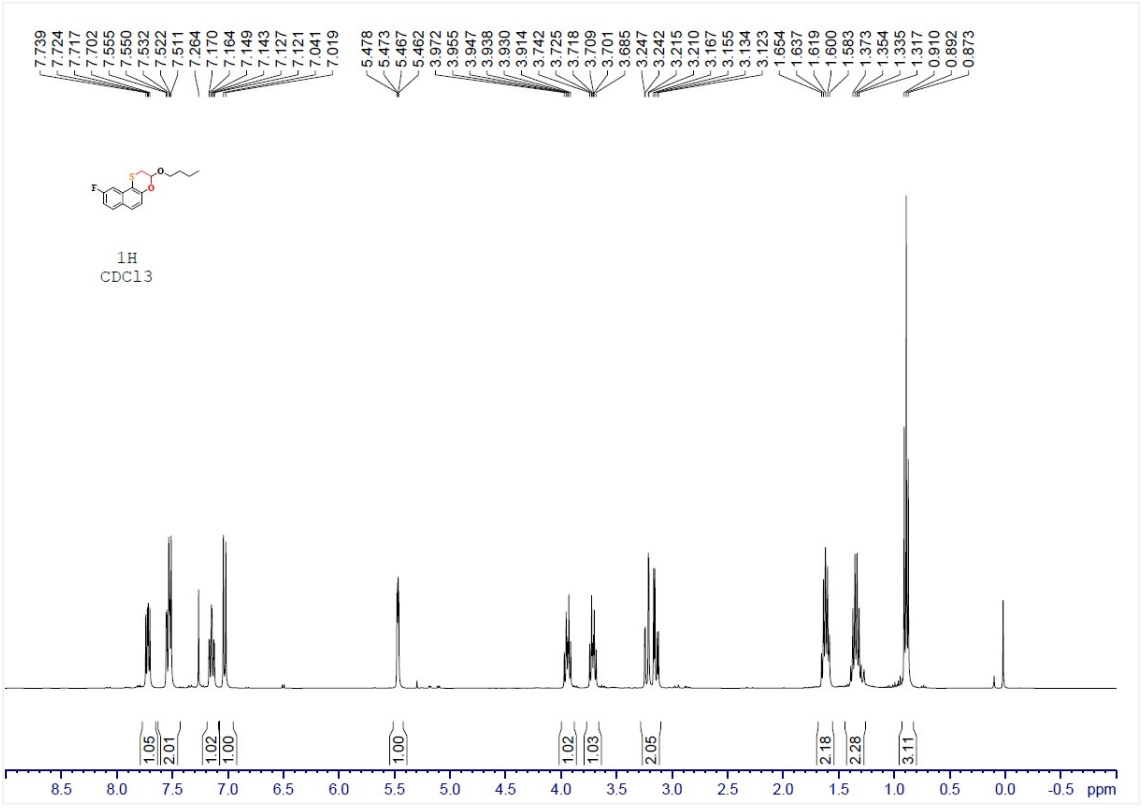


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5f**

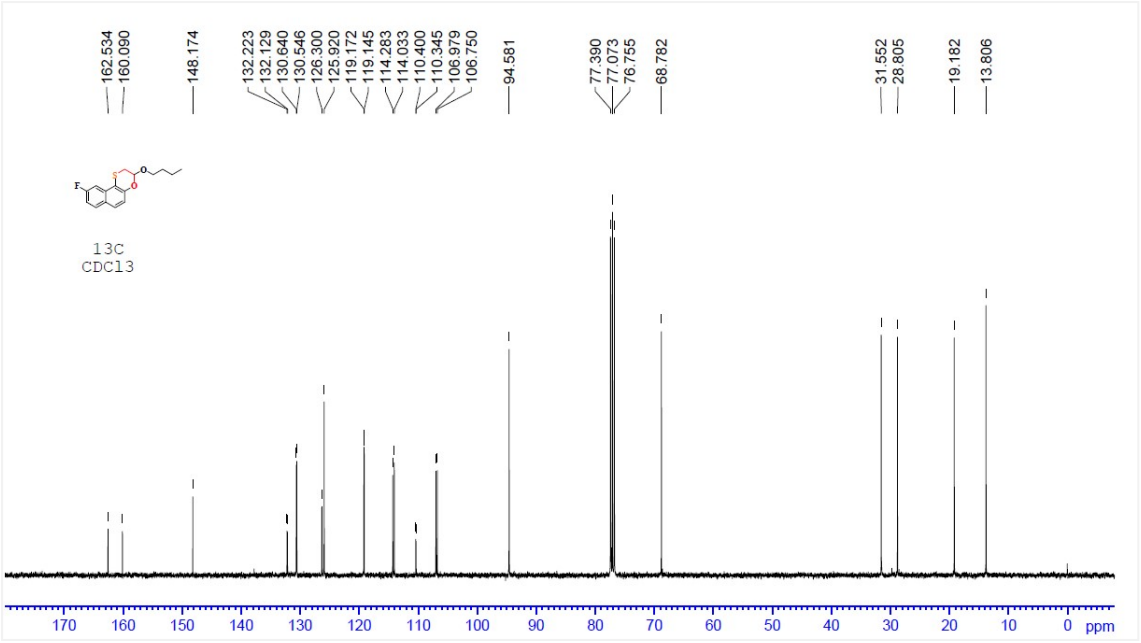


Figure S54. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5f**

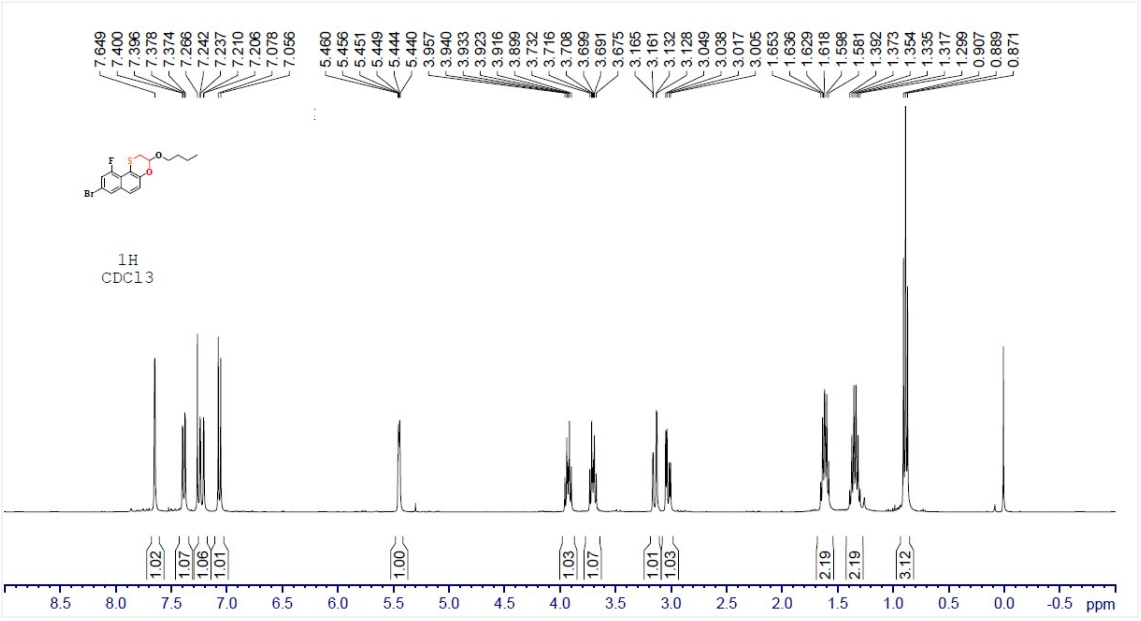


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5g**

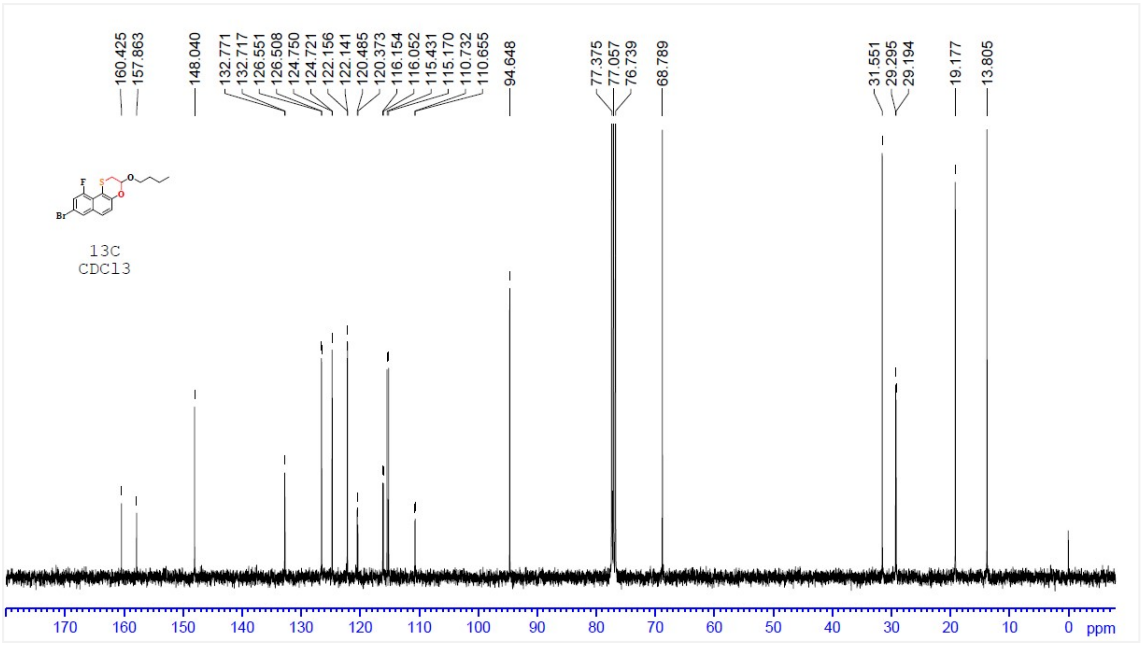


Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5g**

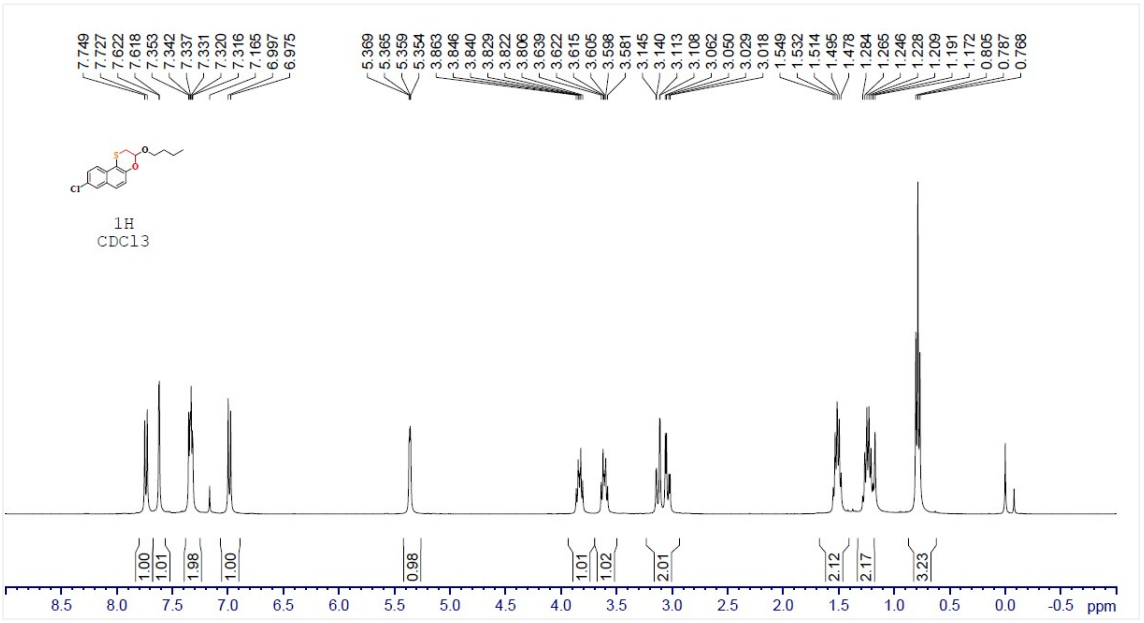


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5h**

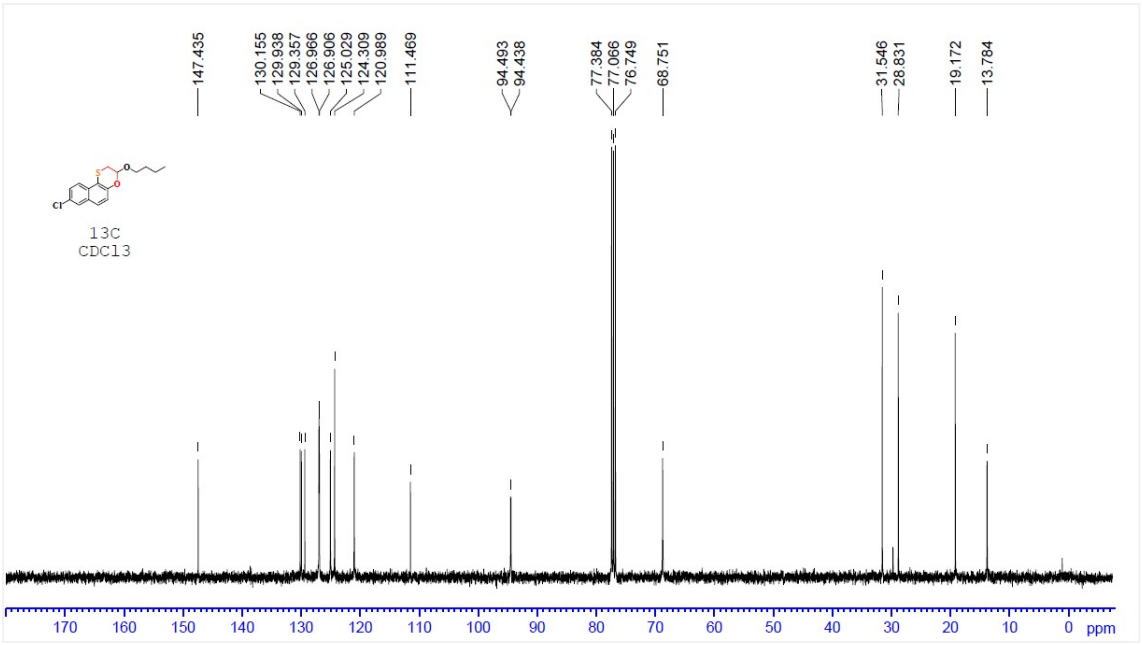


Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5h**

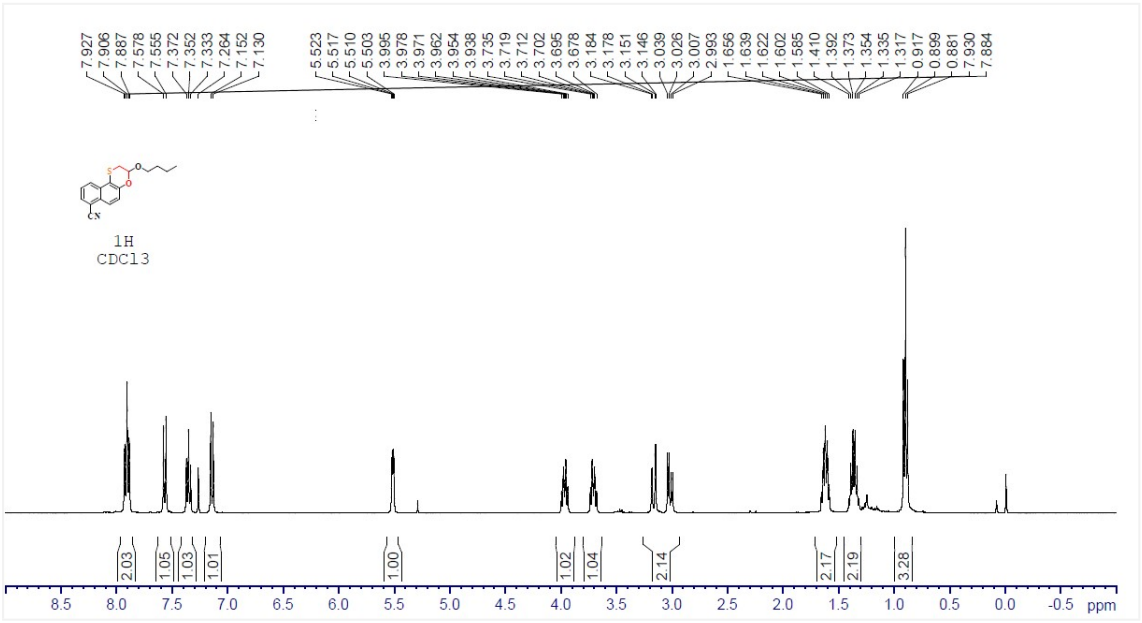


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5i**

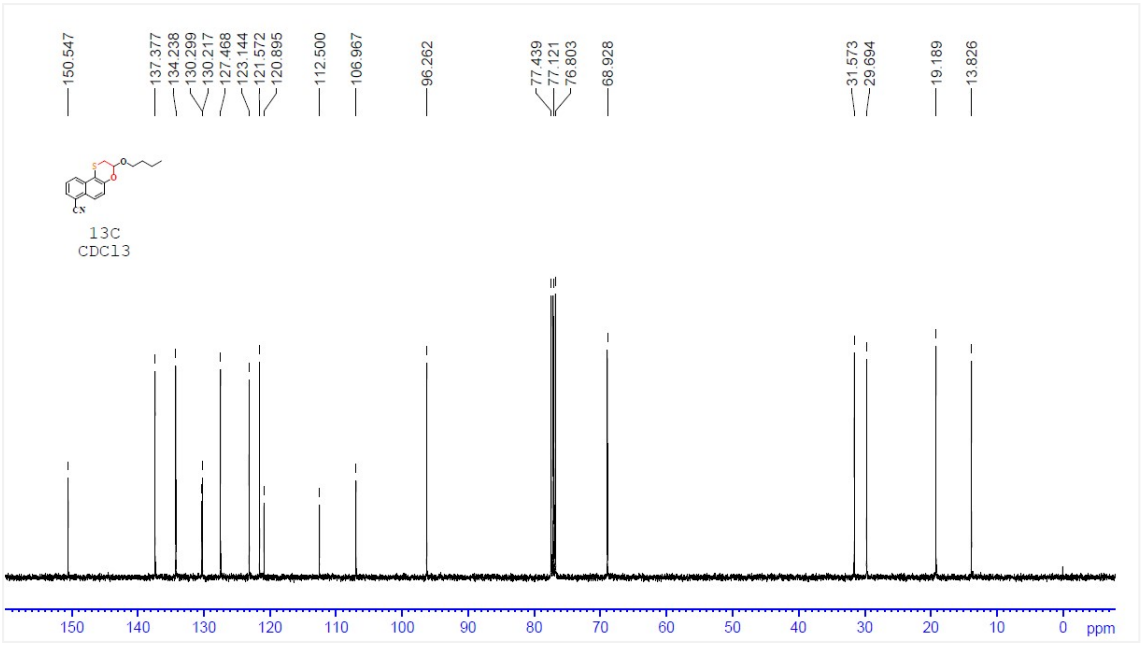


Figure S60. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5i**

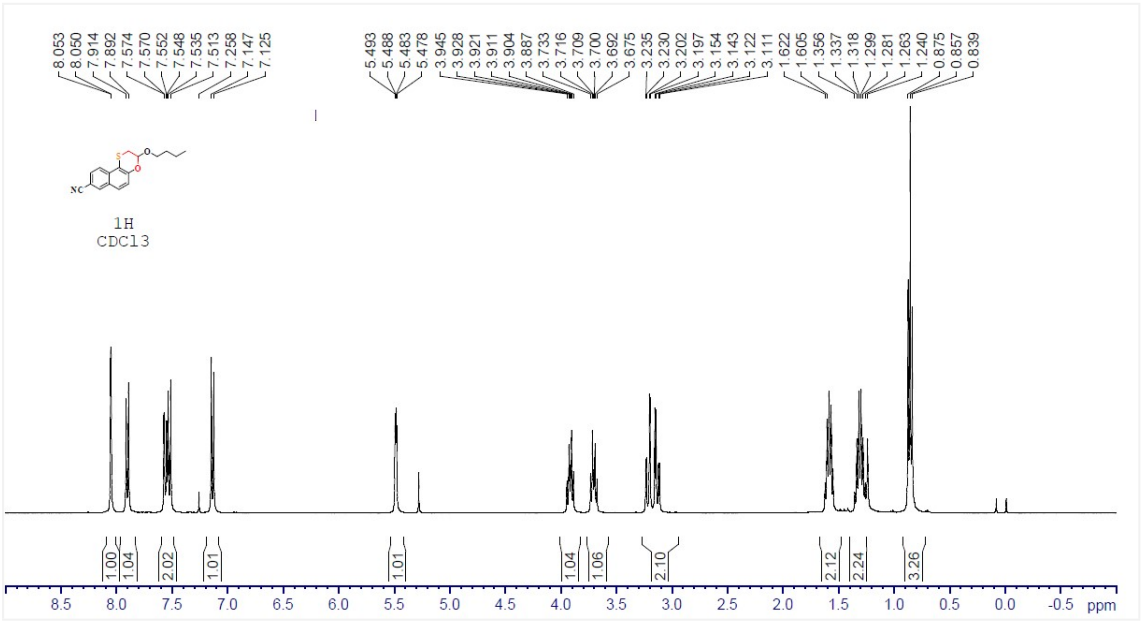


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5j**

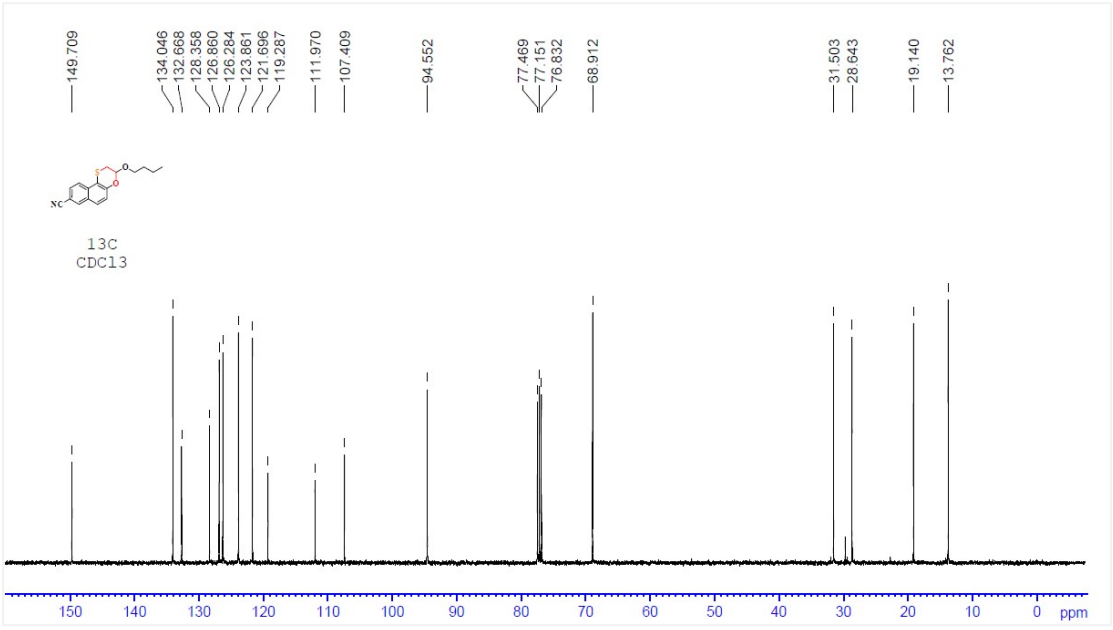


Figure S62. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5j**

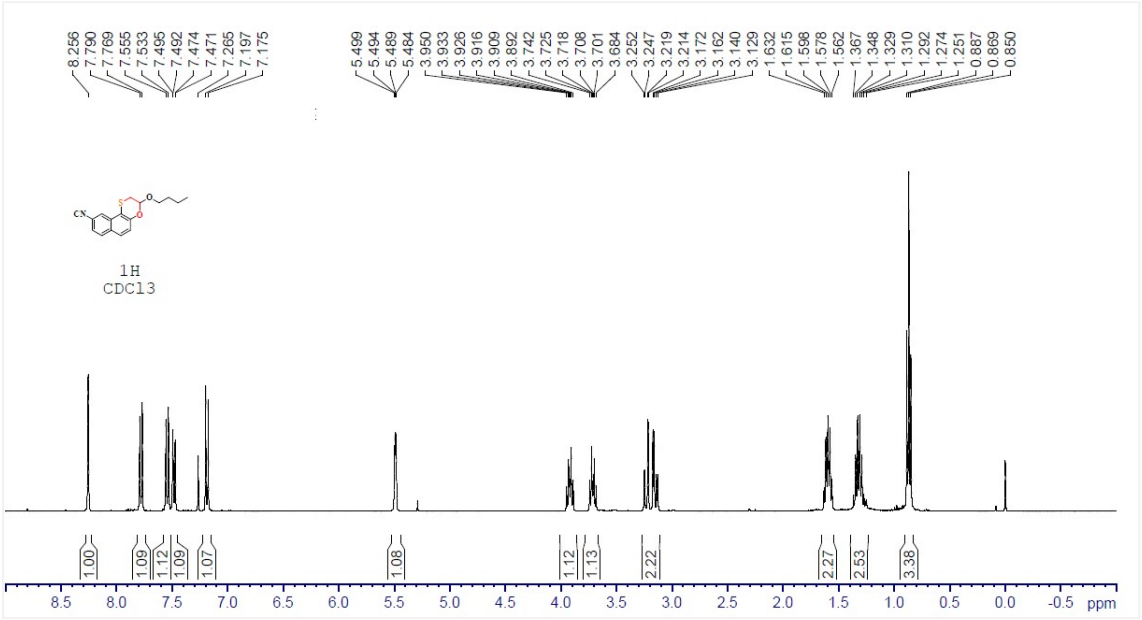


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5k**

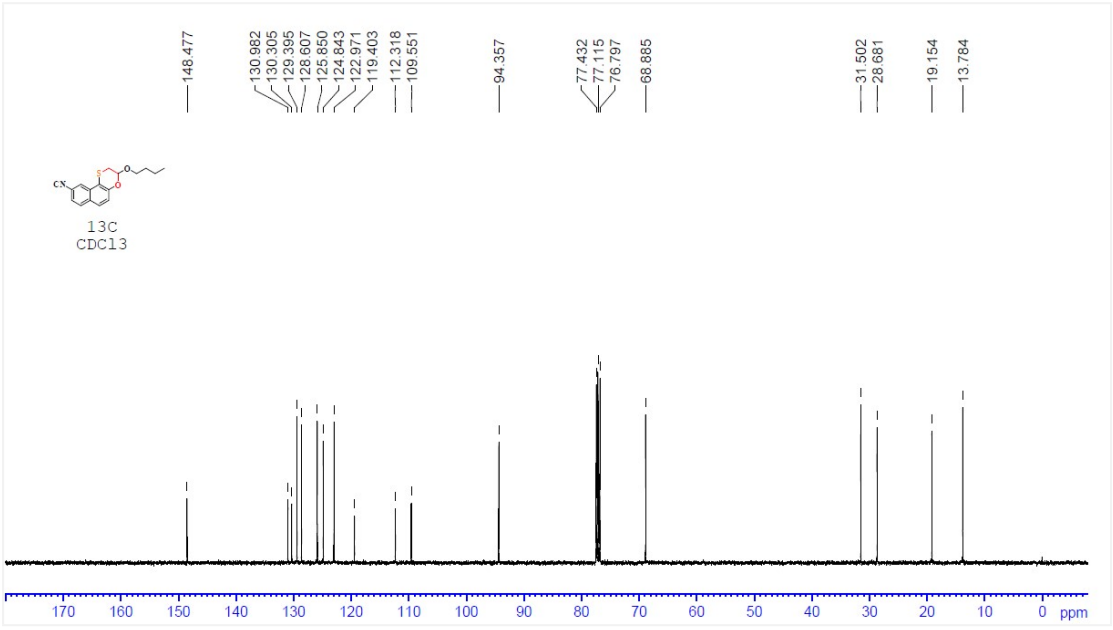


Figure S64. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5k**

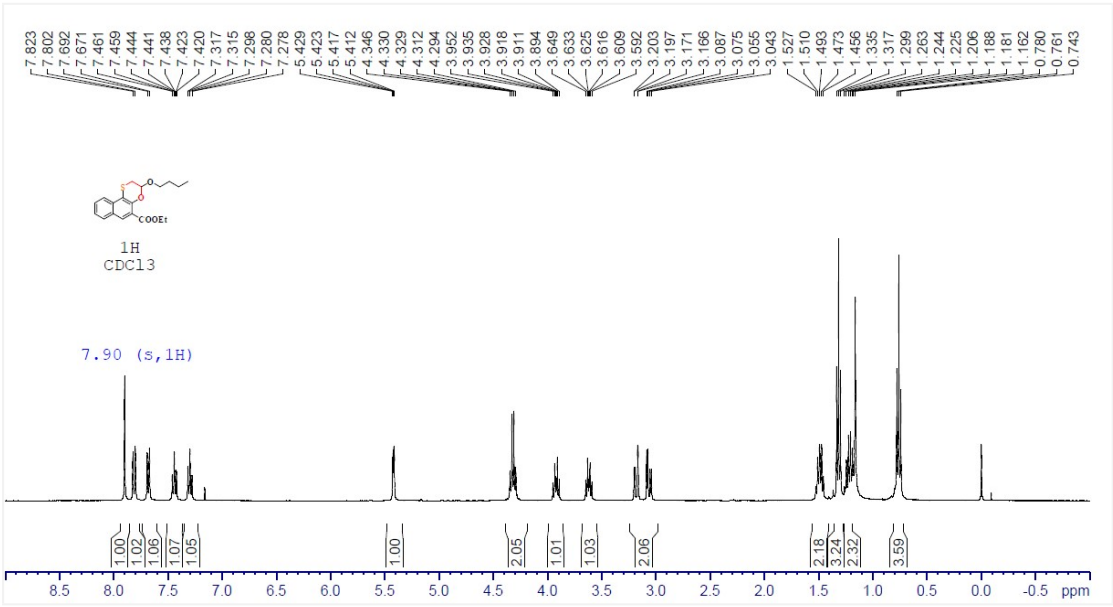


Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5l**

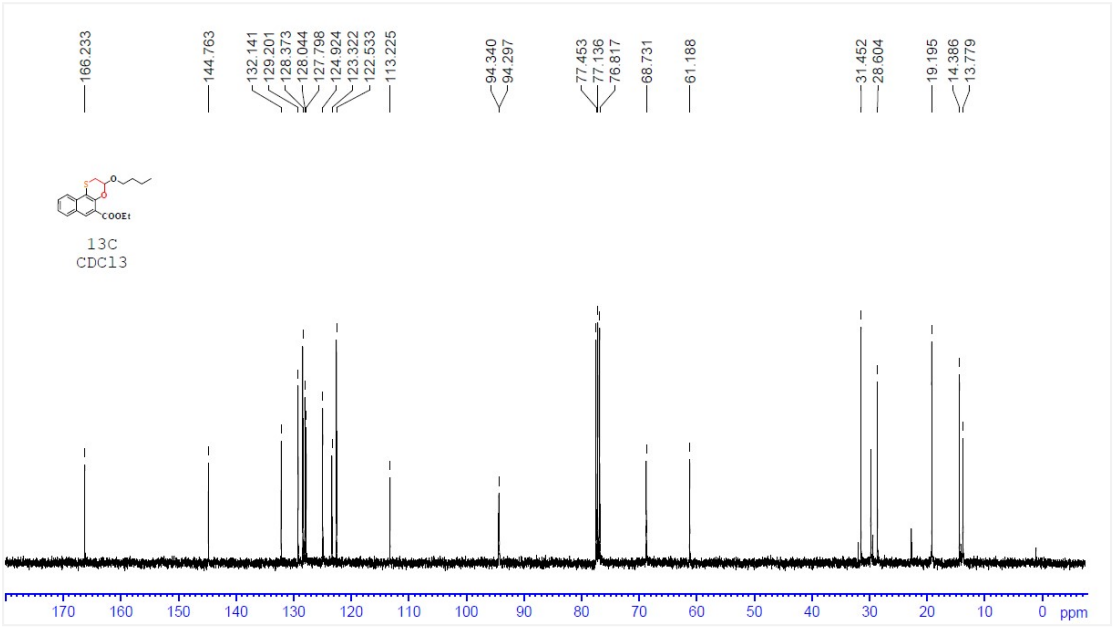


Figure S66. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5l**

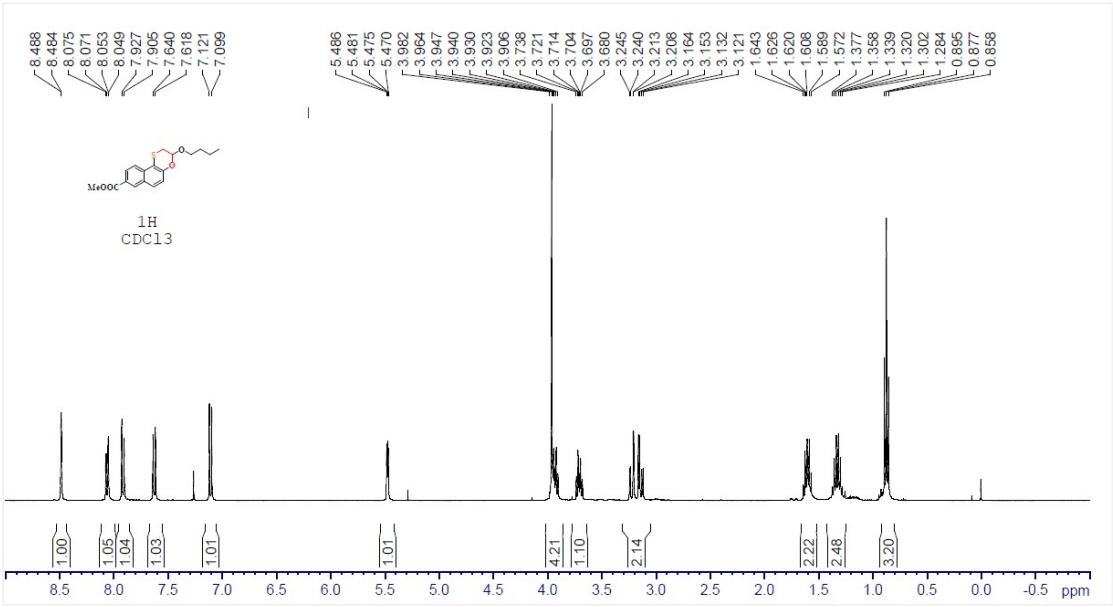


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5m**

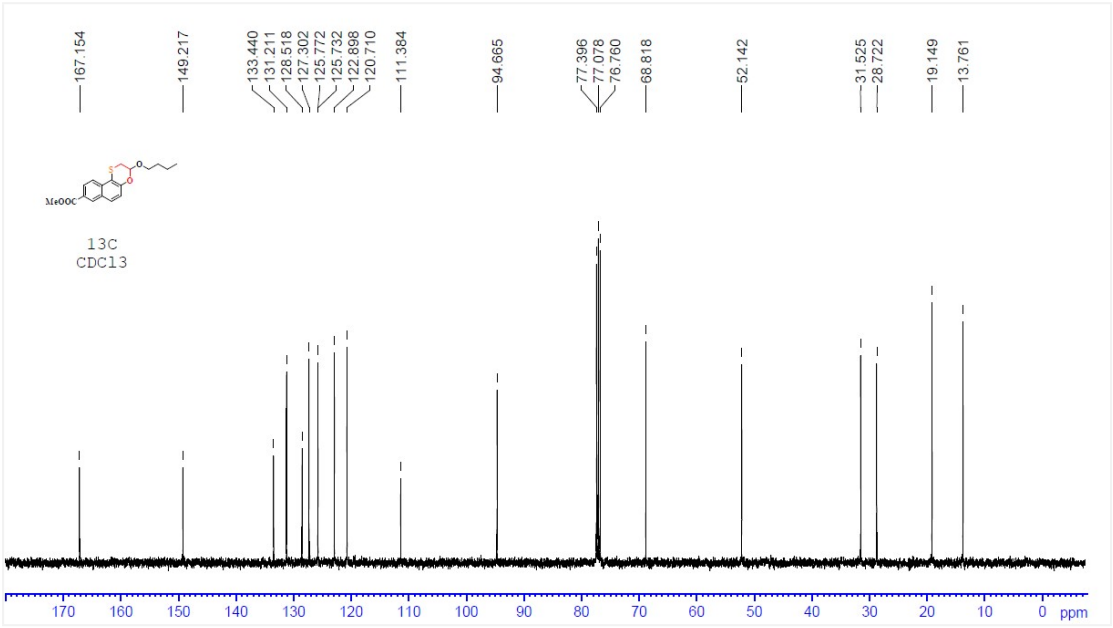


Figure S68. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5m**

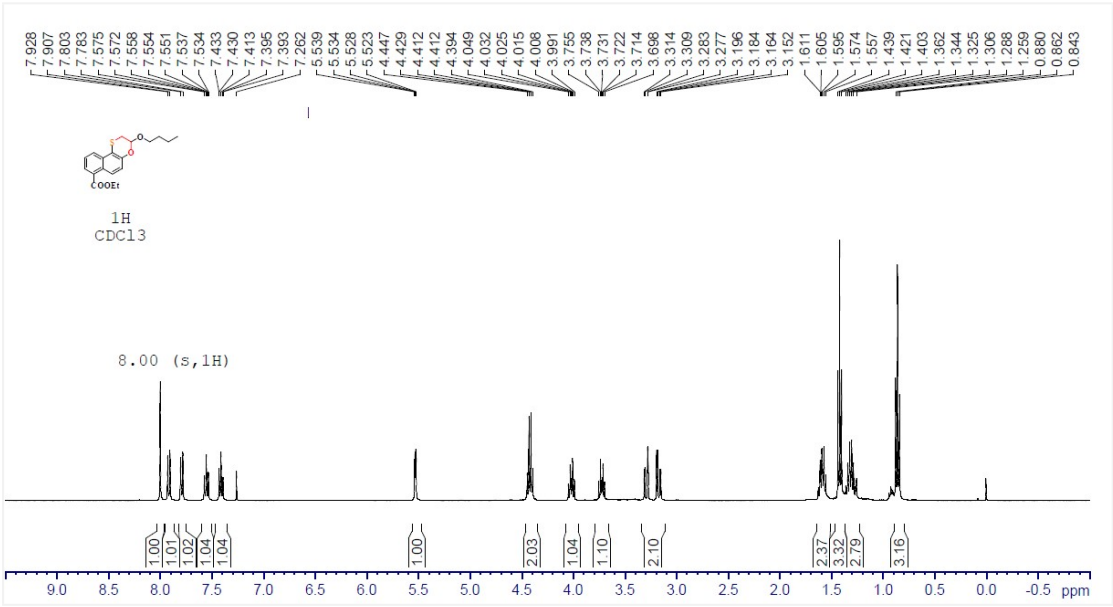


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5n**

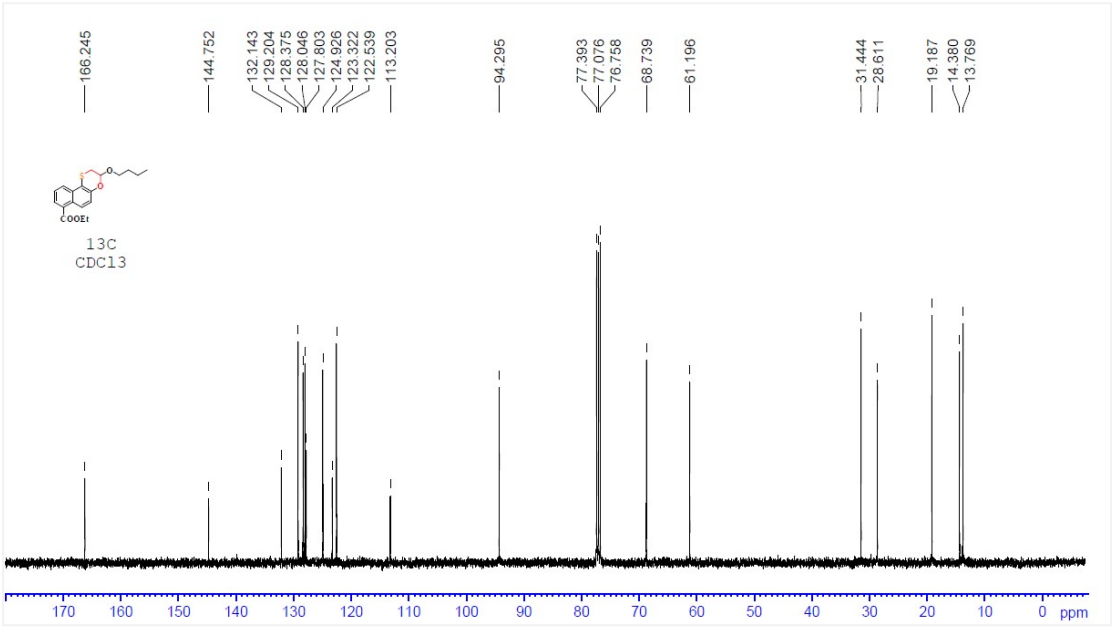


Figure S70. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5n**

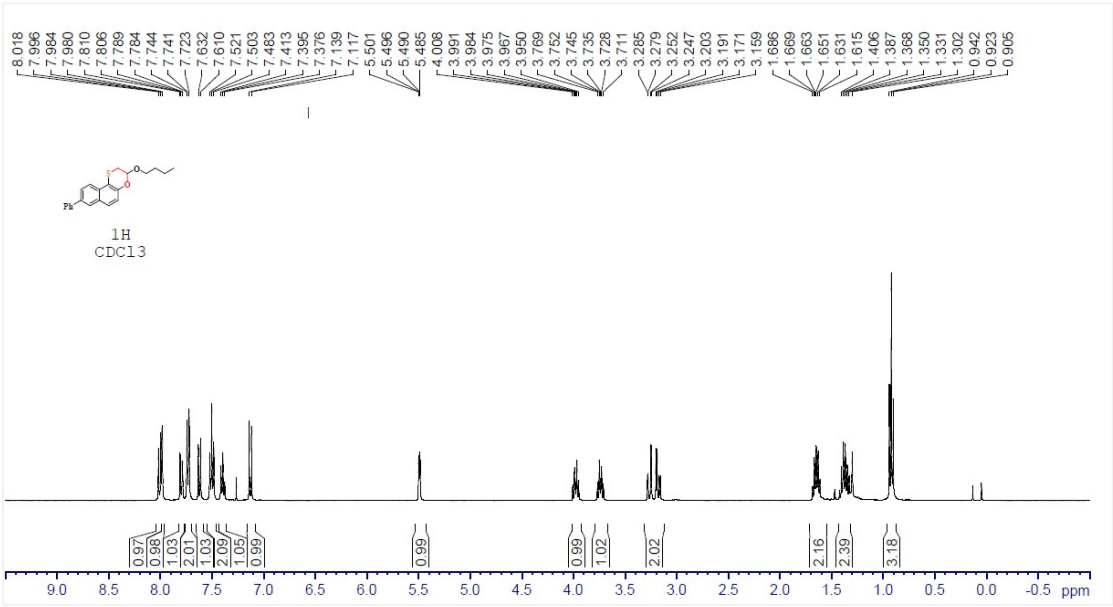


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5o**

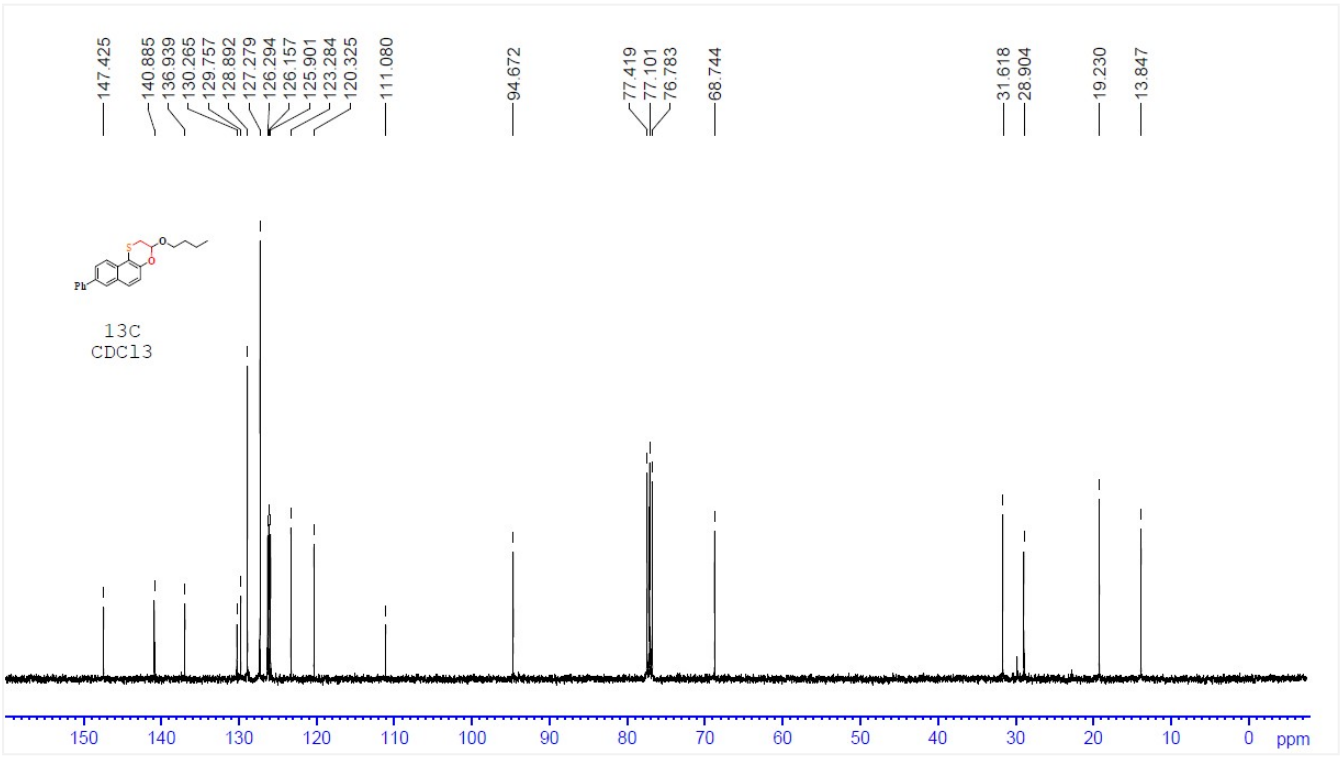


Figure S72. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5o**

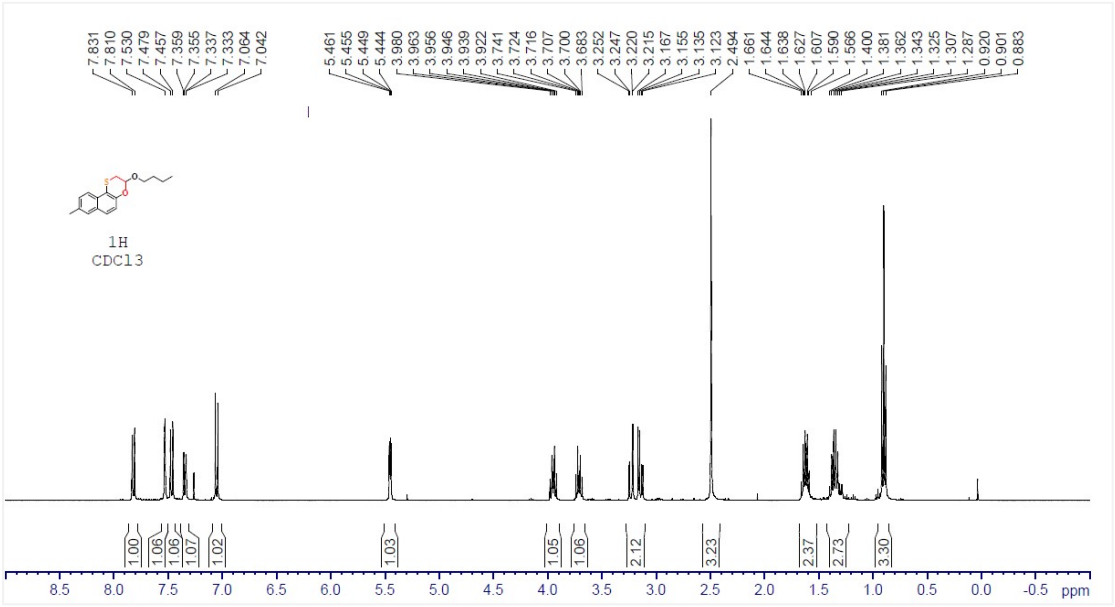


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5p**

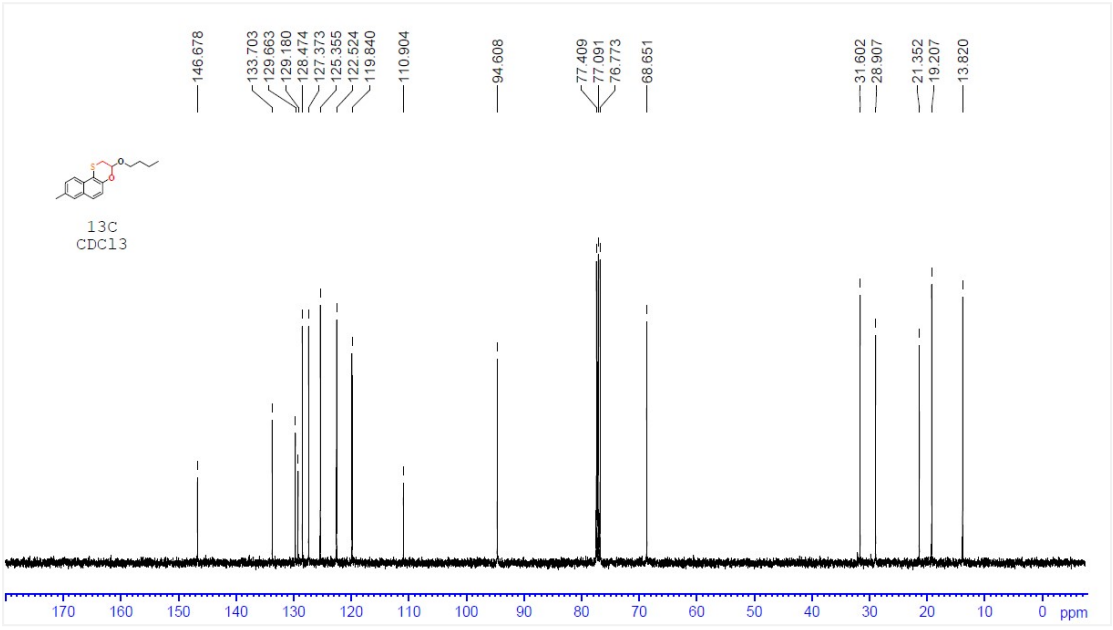


Figure S74. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5p**

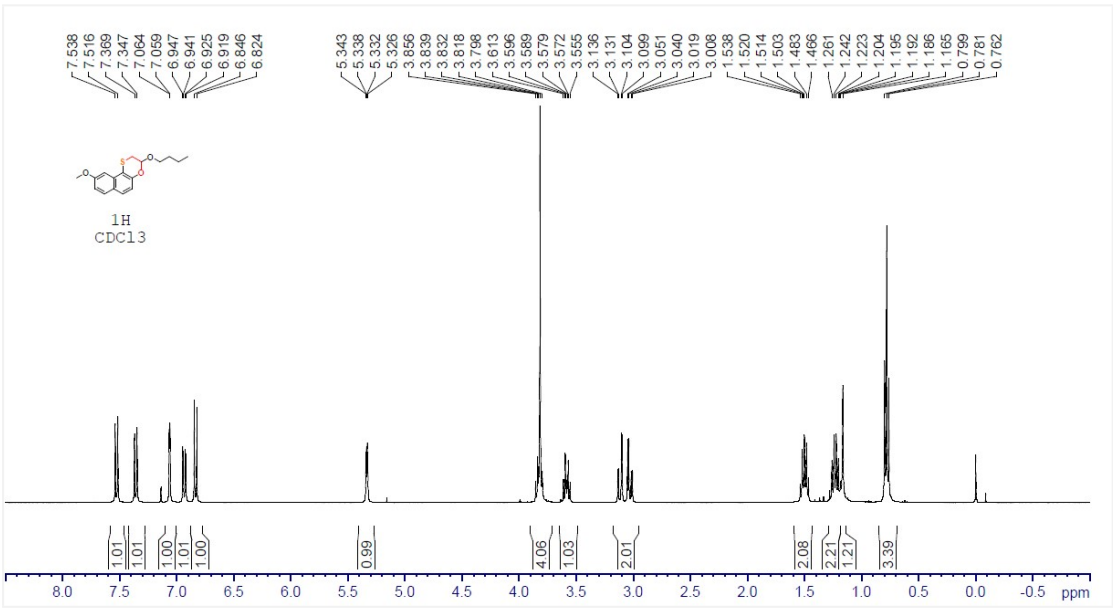


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5q**

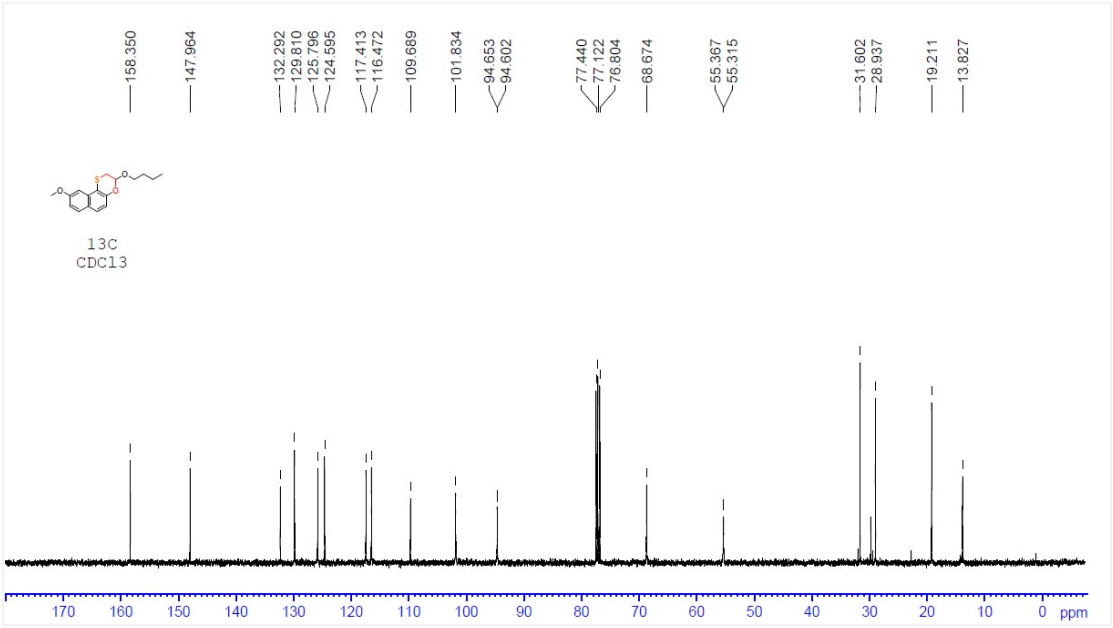


Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5q**

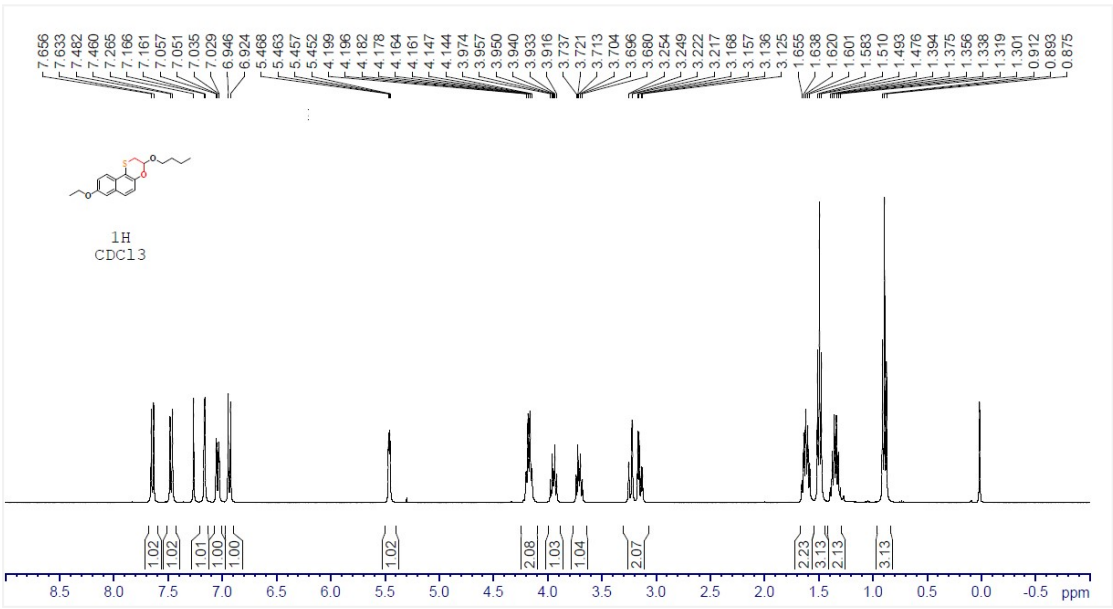


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5r**

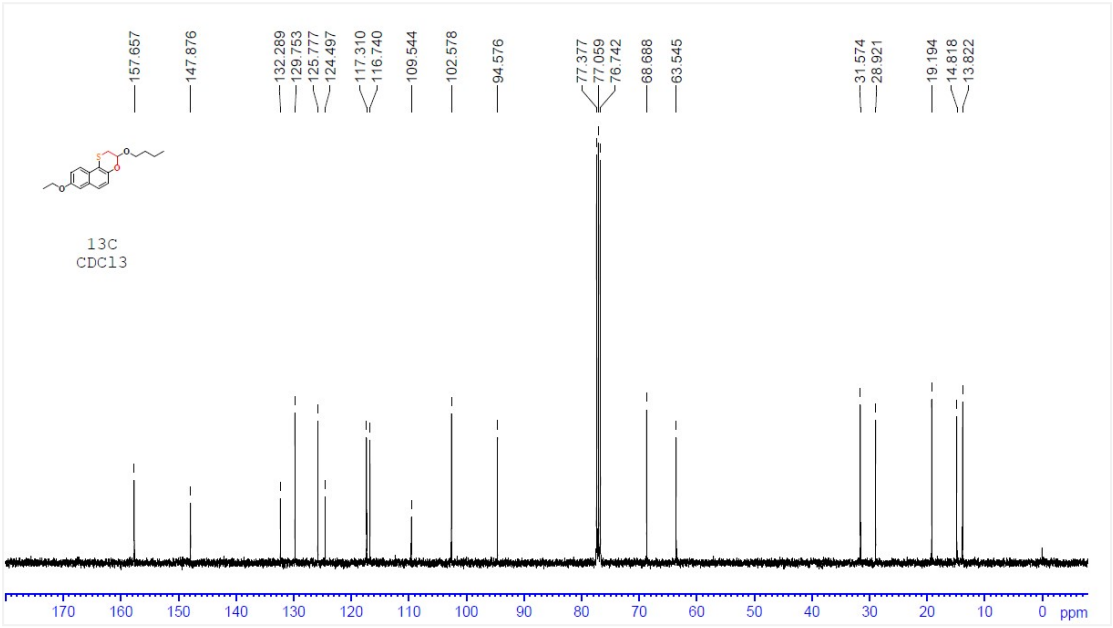


Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5r**

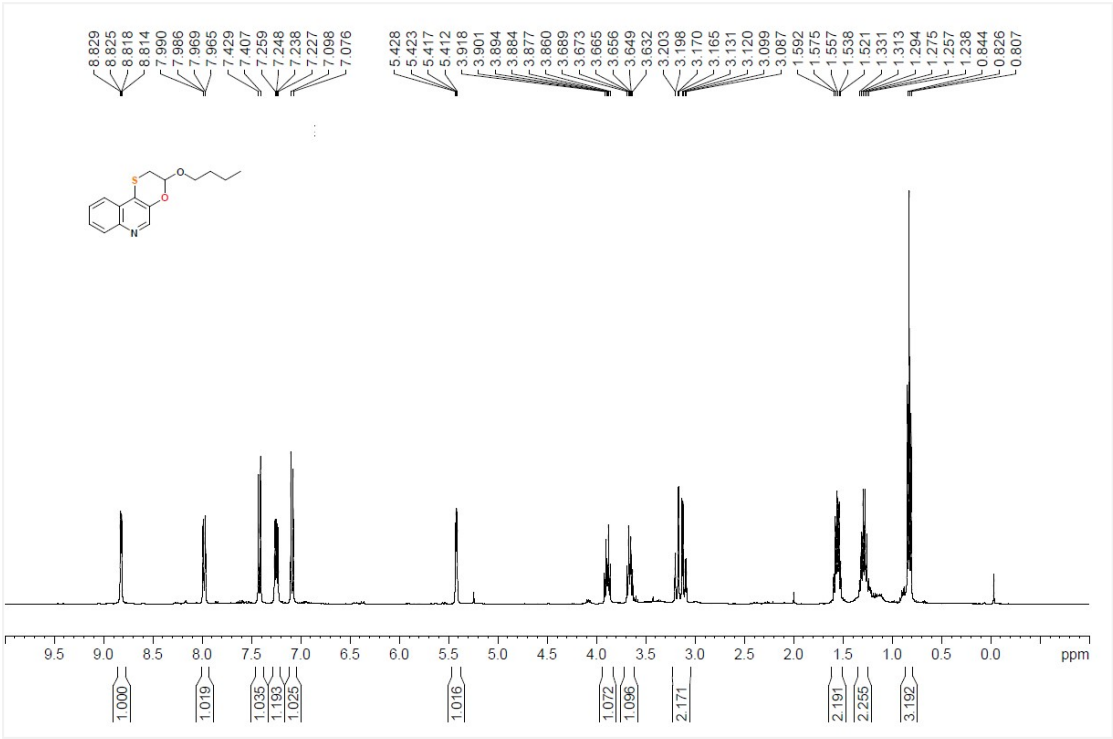


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5s**

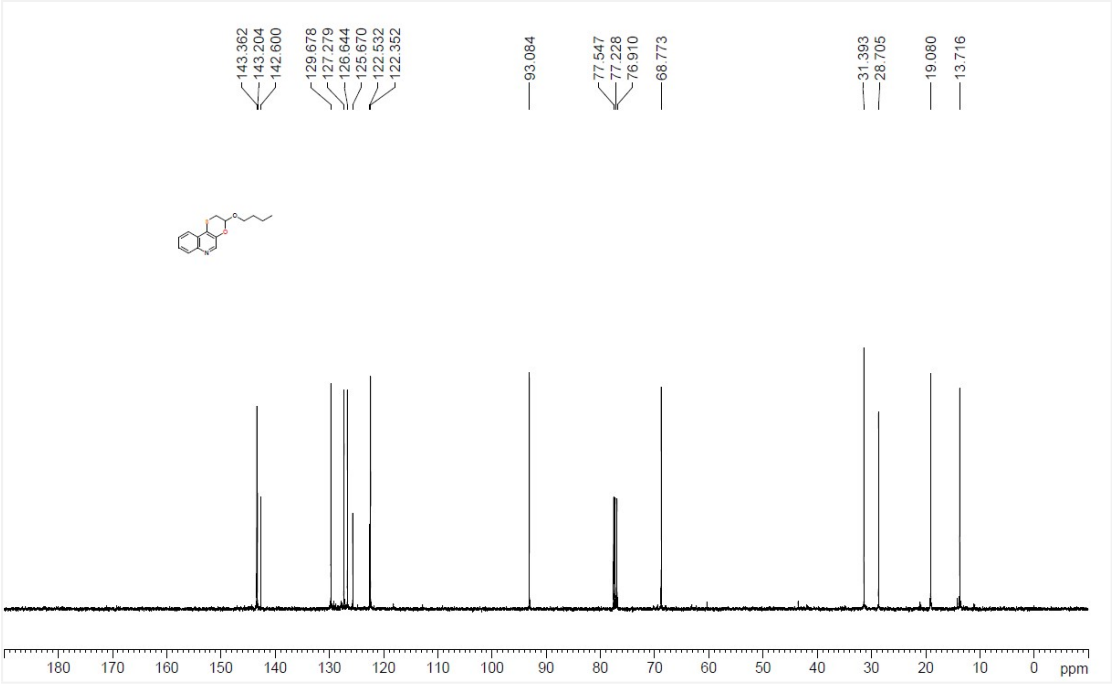


Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5s**

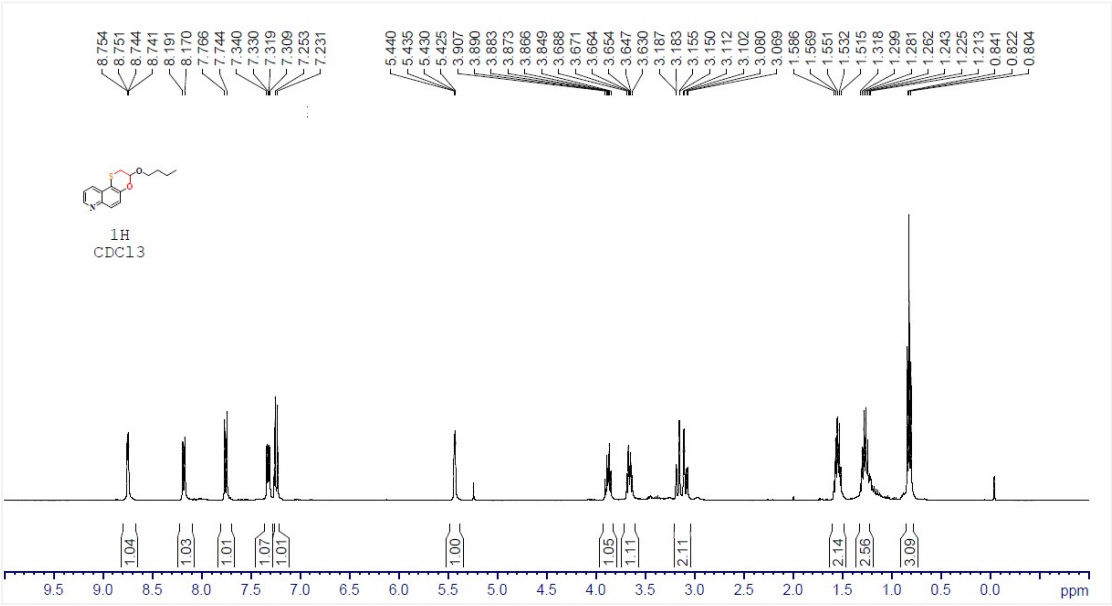


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5t**

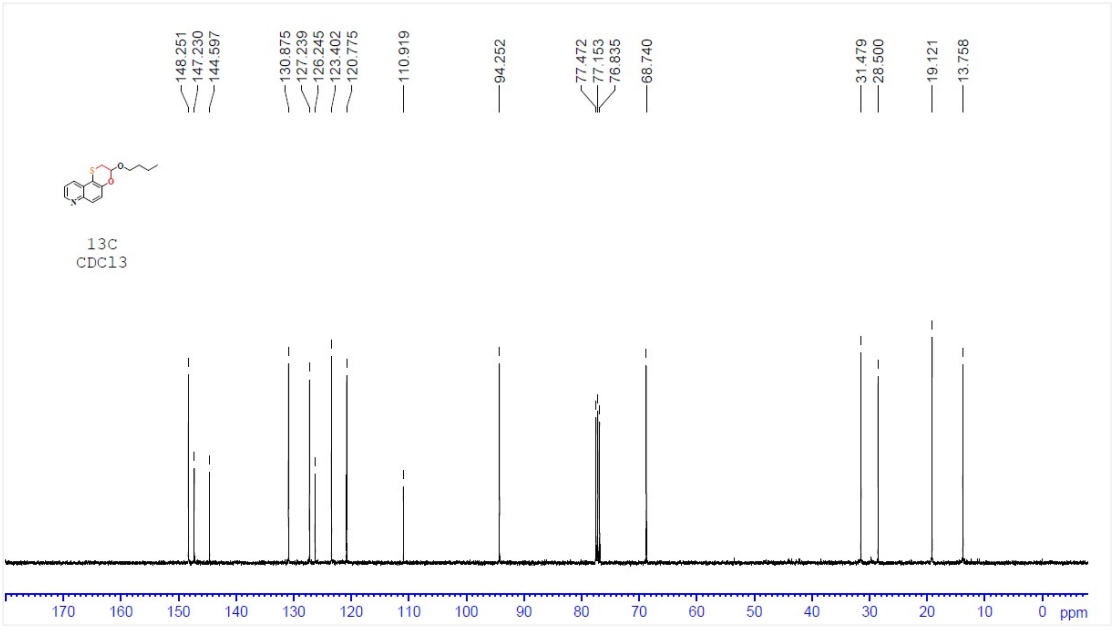


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5t**

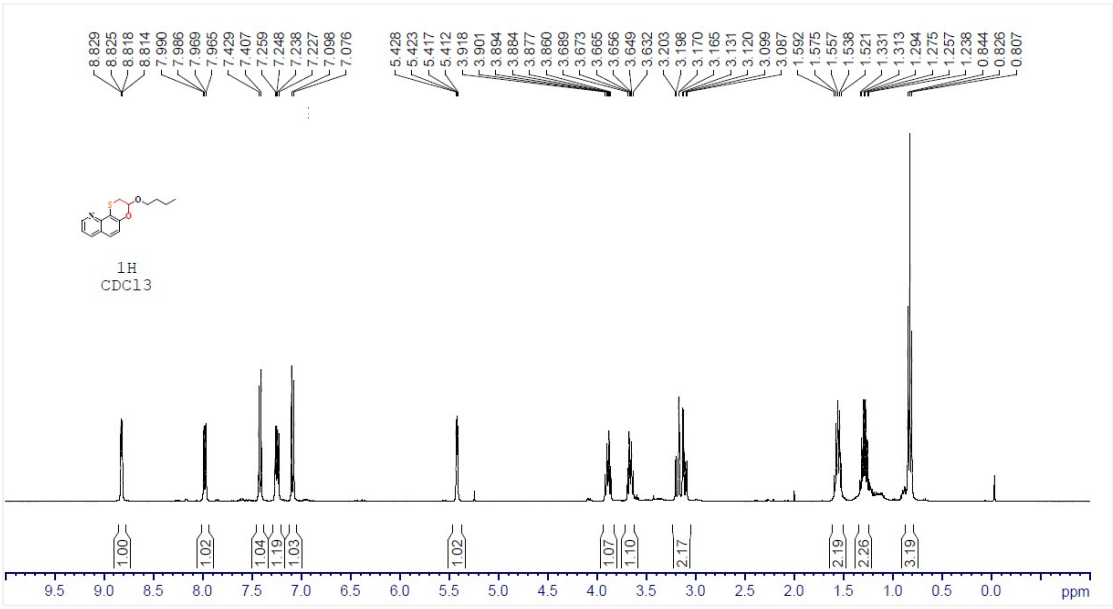


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5u**

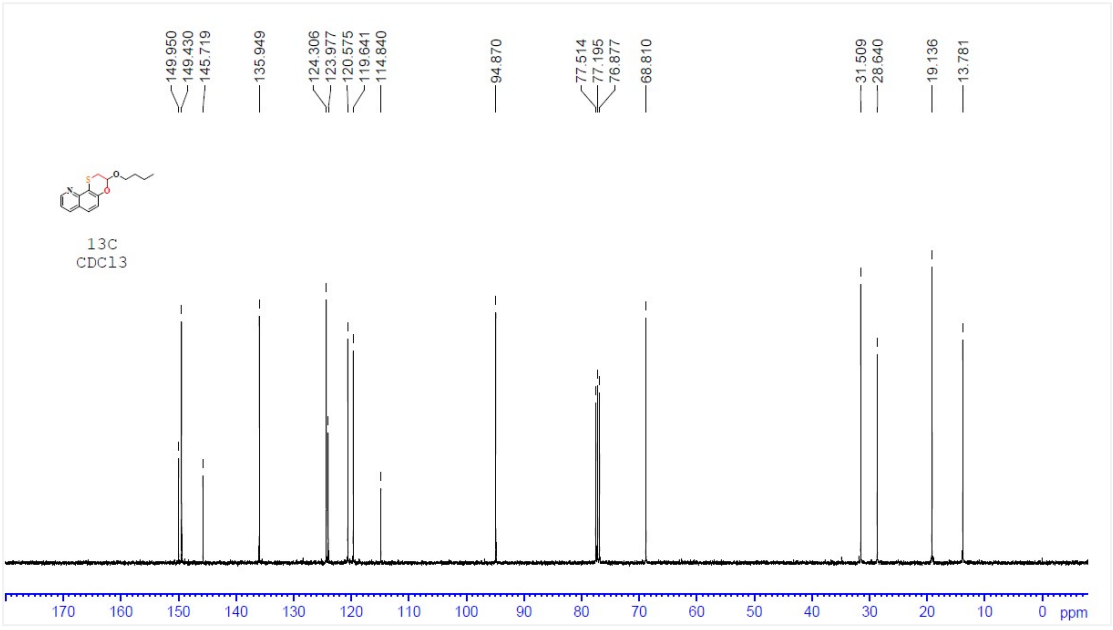


Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5u**

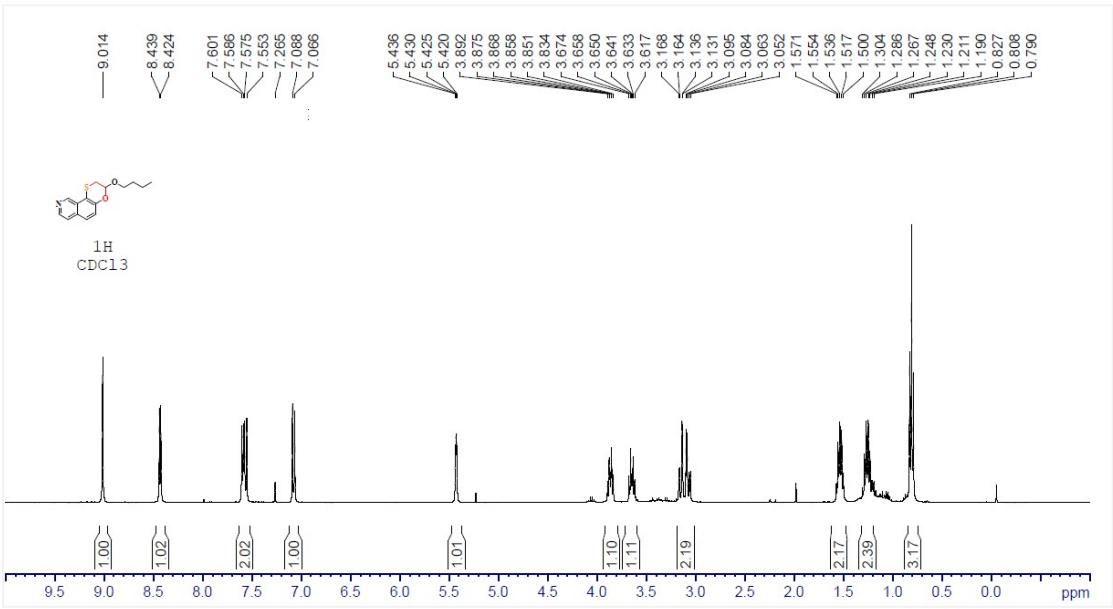


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5v**

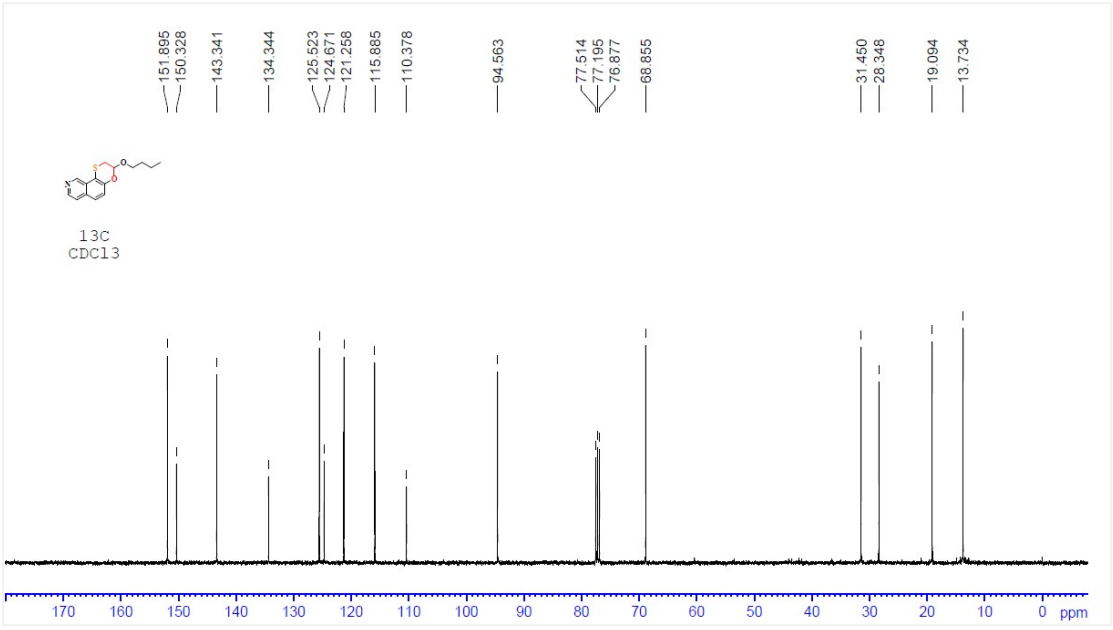


Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5v**

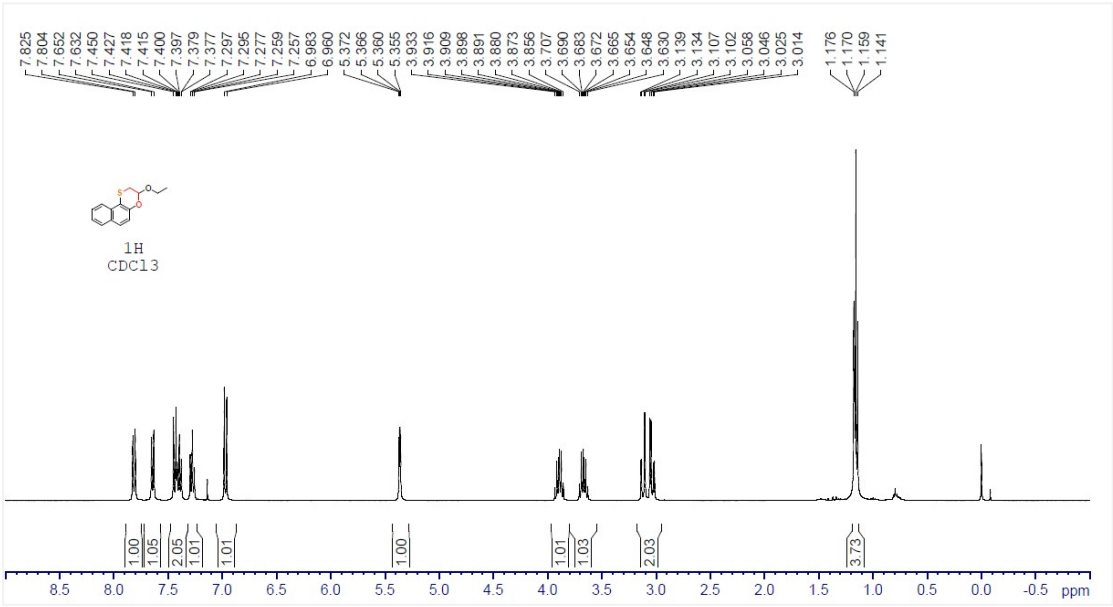


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ab**

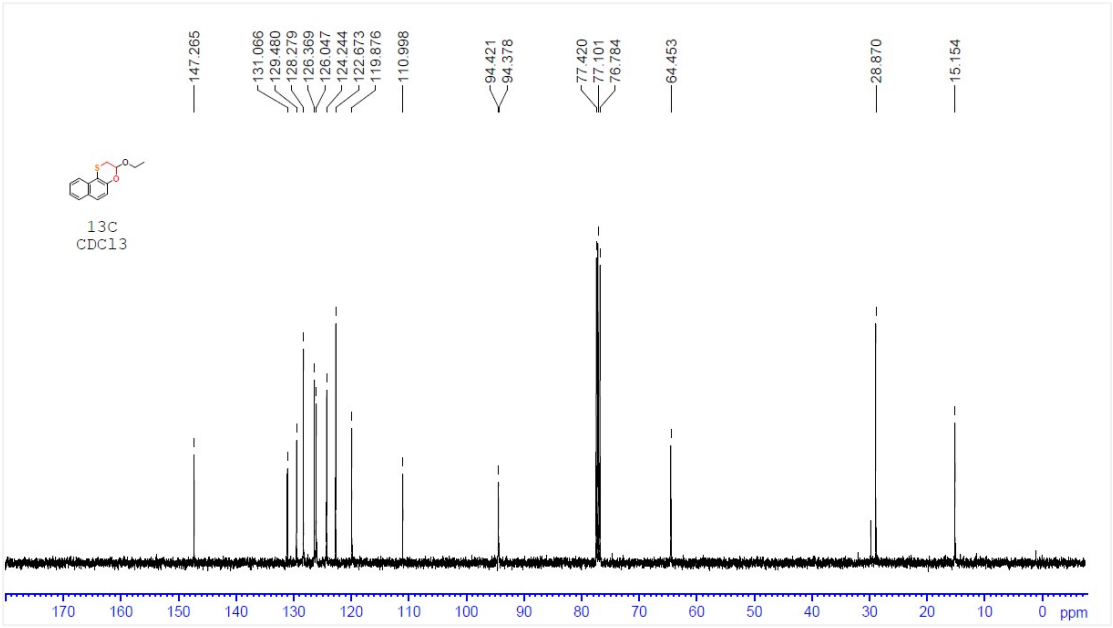


Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5ab**

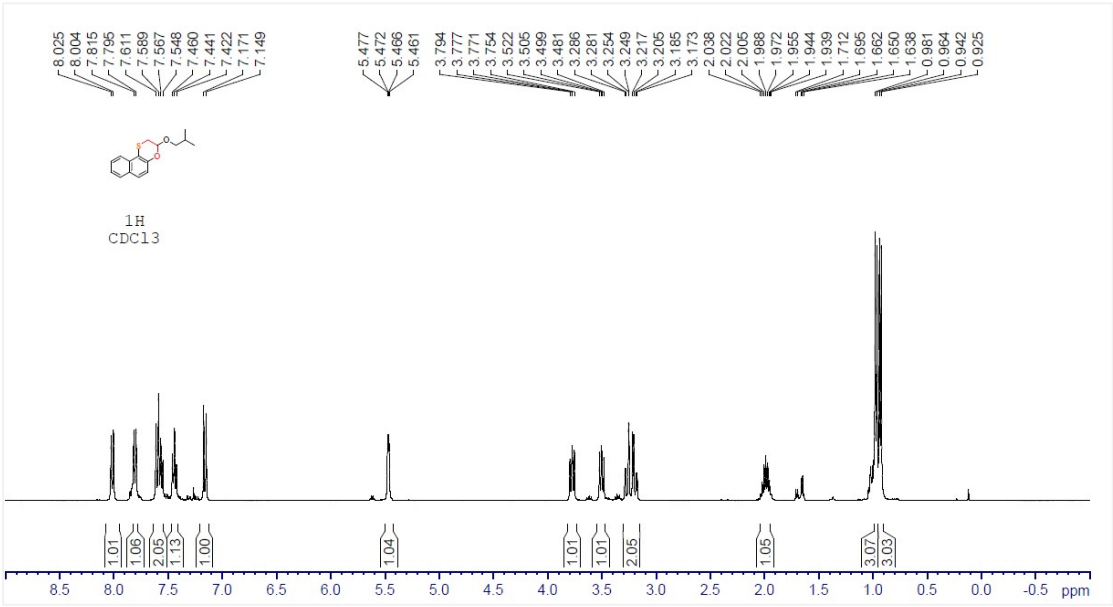


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ac**

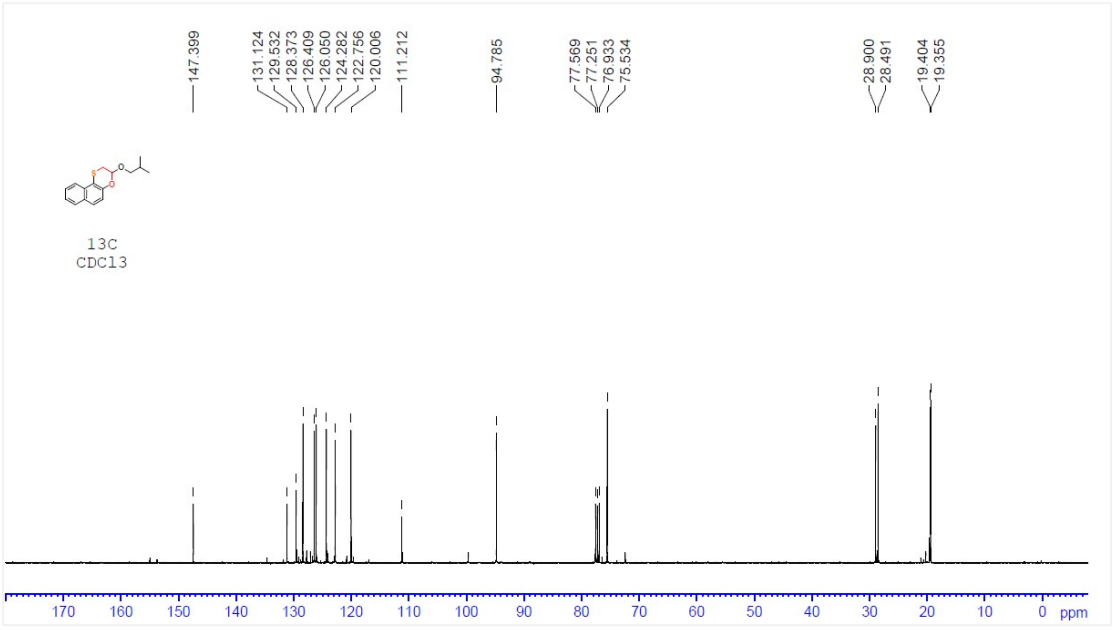


Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5ac**

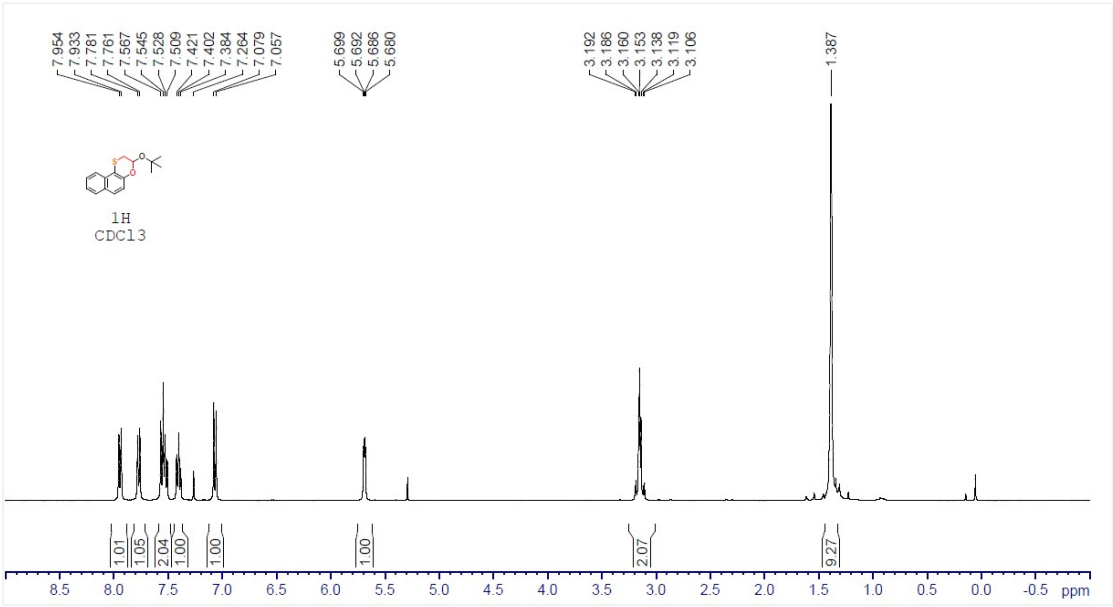


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ad**

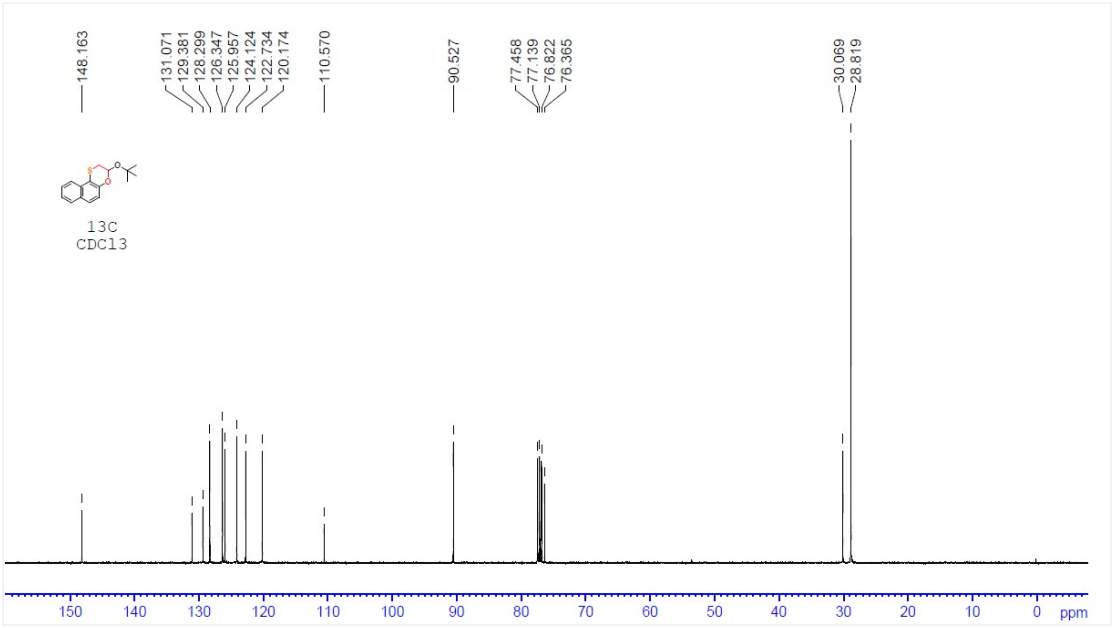


Figure S92. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5ad**

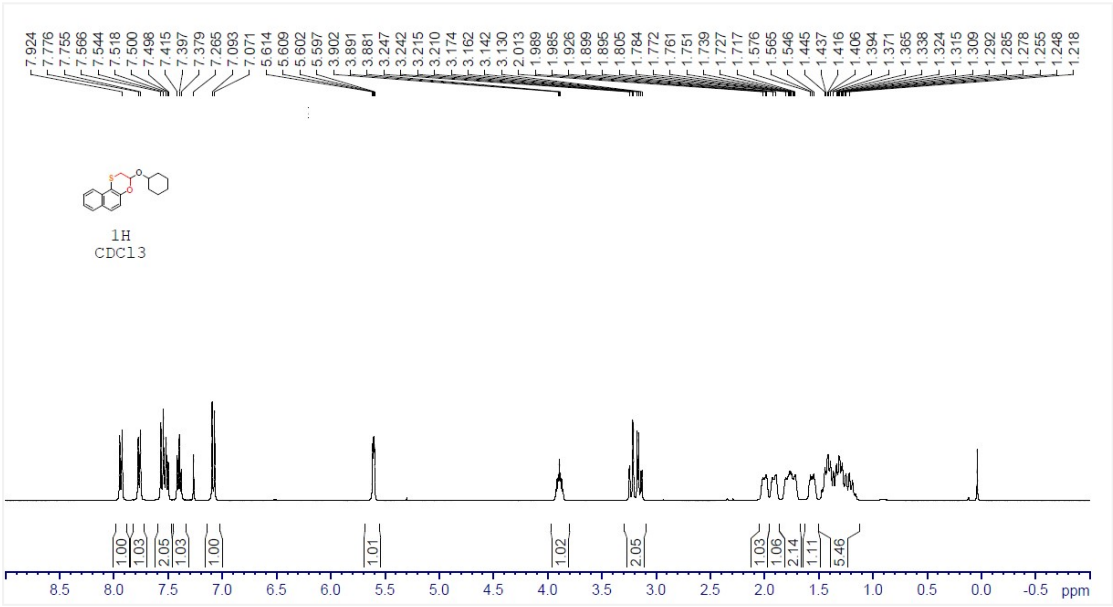


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ae**

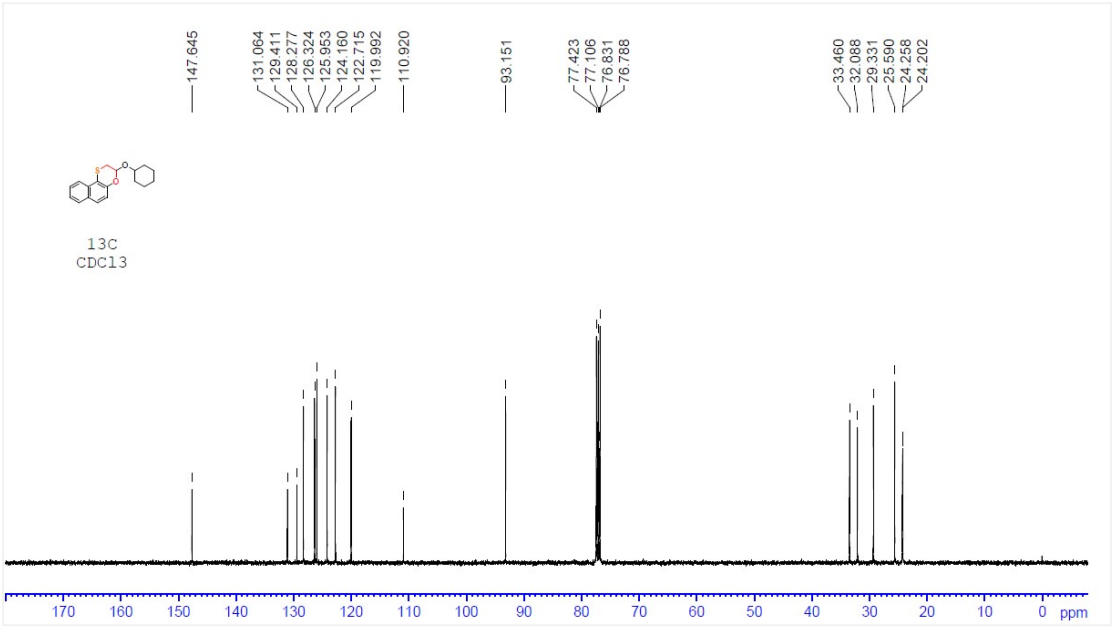


Figure S94. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5ae**

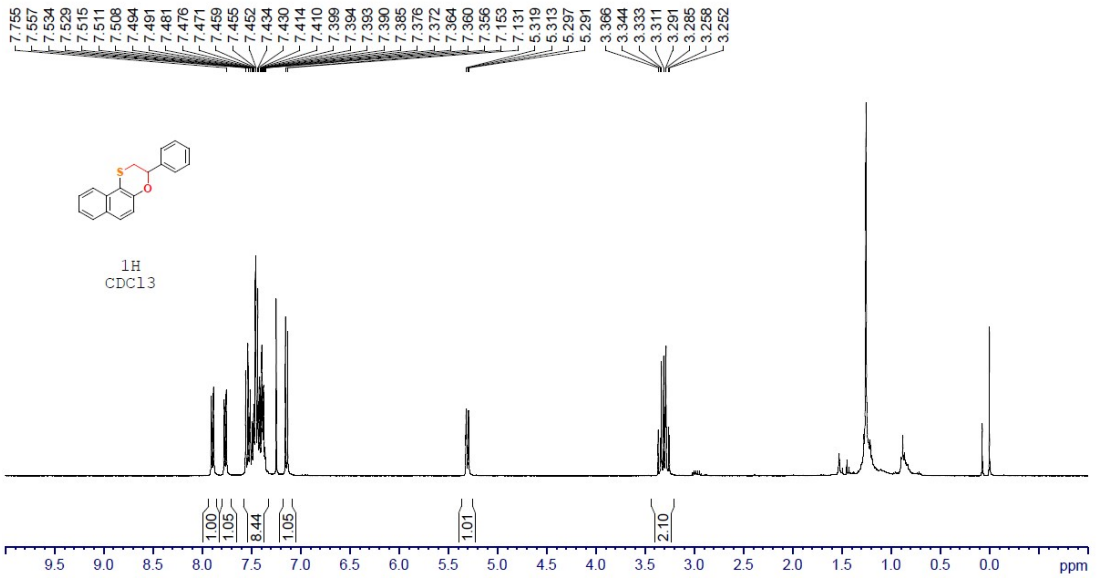


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5af**

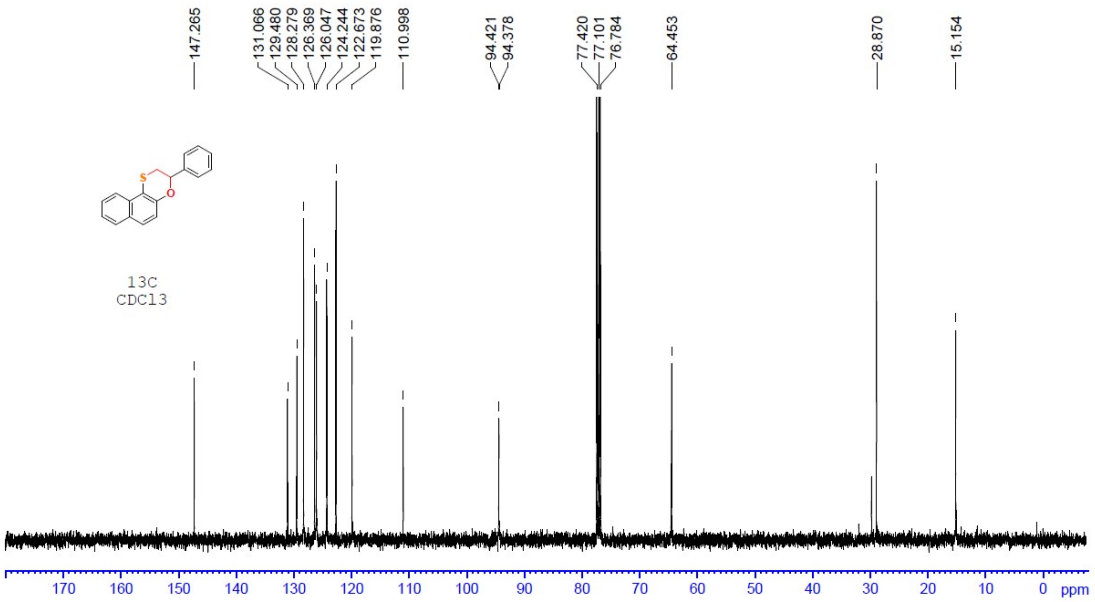


Figure S96. ^{13}C NMR (100 MHz, $CDCl_3$) Spectrum of Compound **5af**

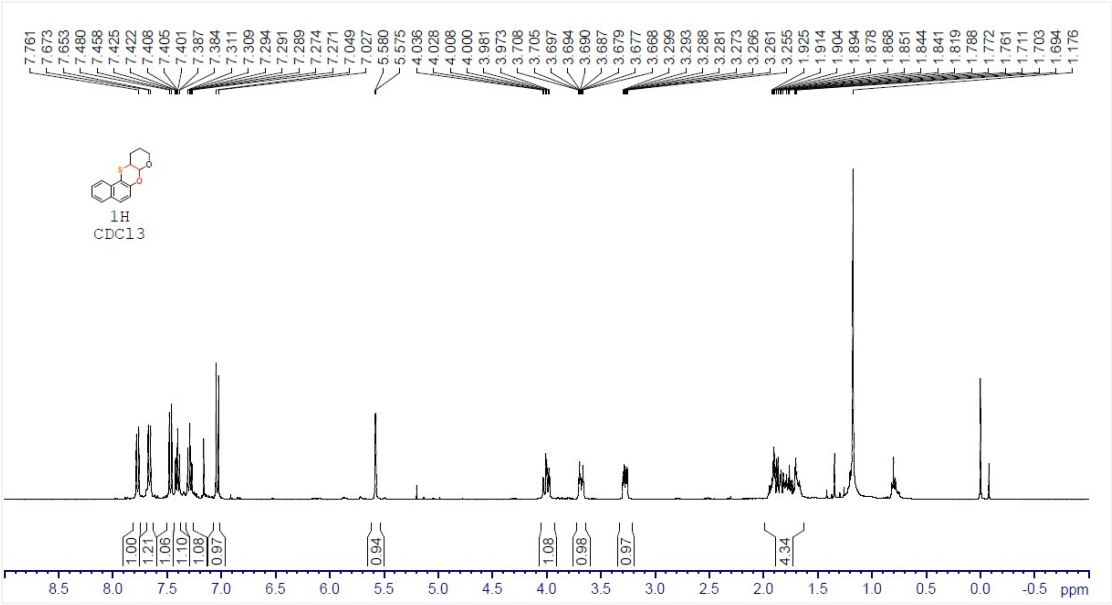


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **5ag**

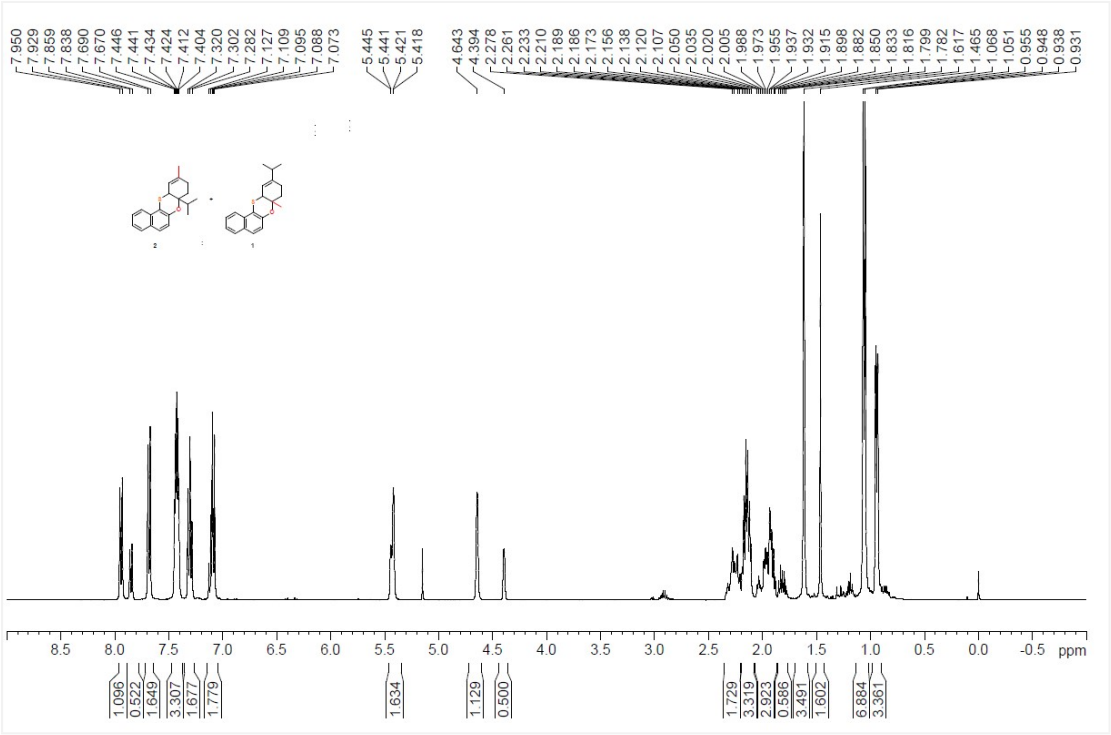


Figure S98. ^{1}H NMR (400 MHz, $CDCl_3$) Spectra of Compounds **5ah1 and 5ah2**

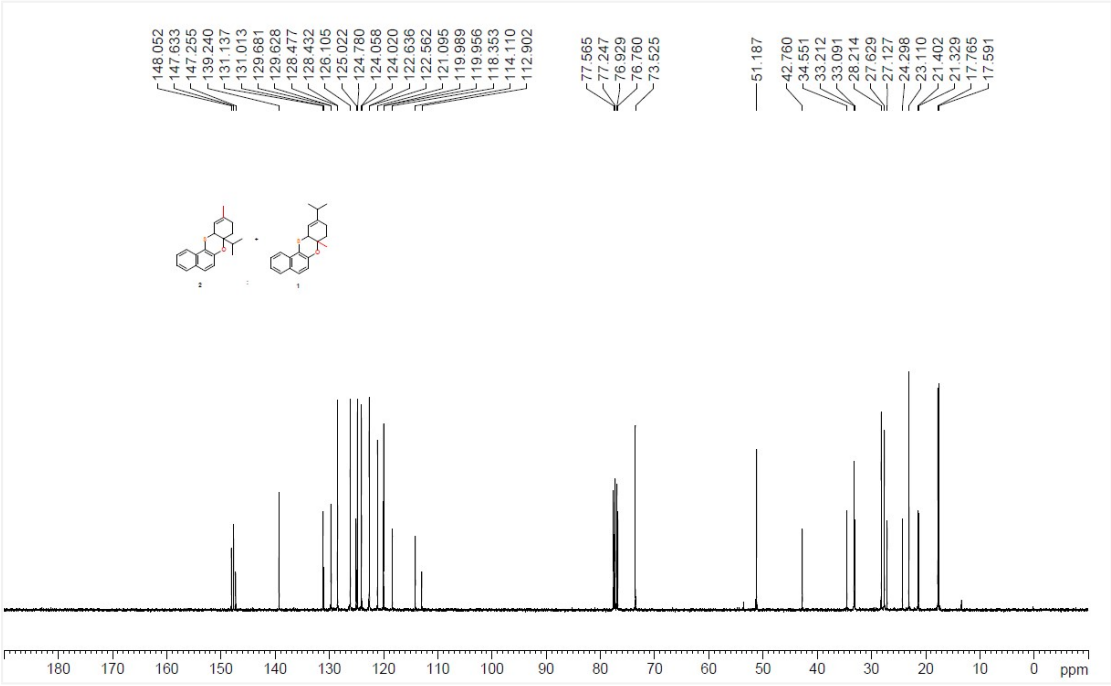


Figure S99. ^{13}C NMR (100 MHz, $CDCl_3$) Spectra of the Compounds **5ah1 and 5ah2**

2.4 HRMS spectra

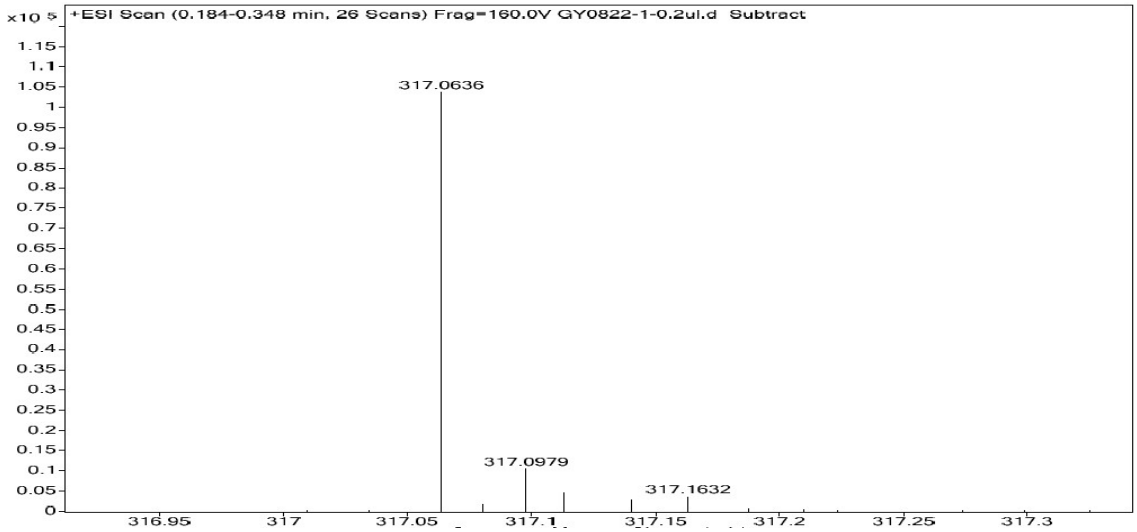


Figure S100. HRMS (ESI-TOF) Spectrum of Compound **3a**

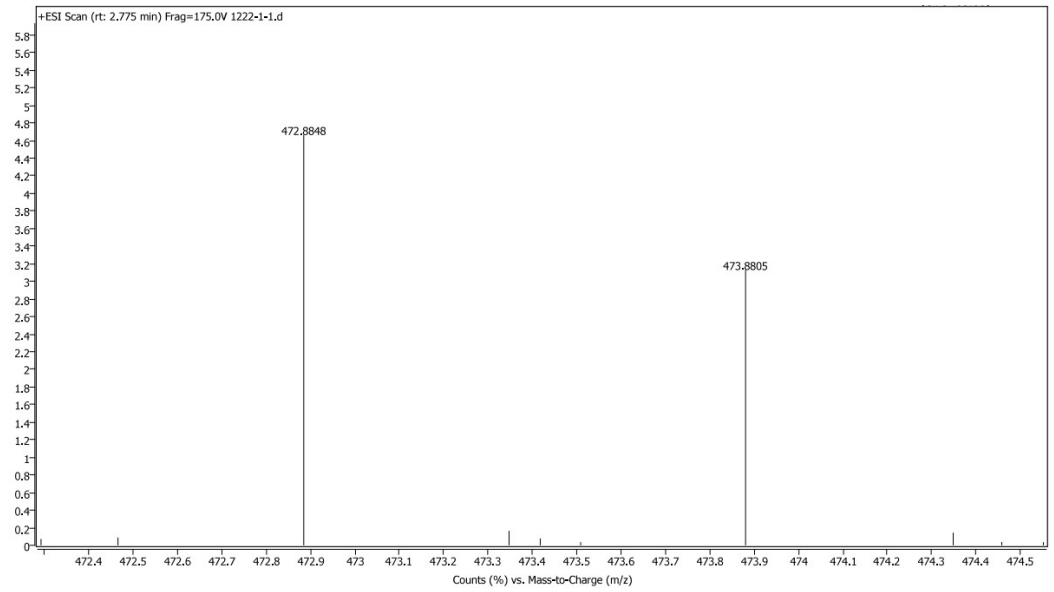


Figure S101. HRMS (ESI-TOF) Spectrum of Compound **3b**

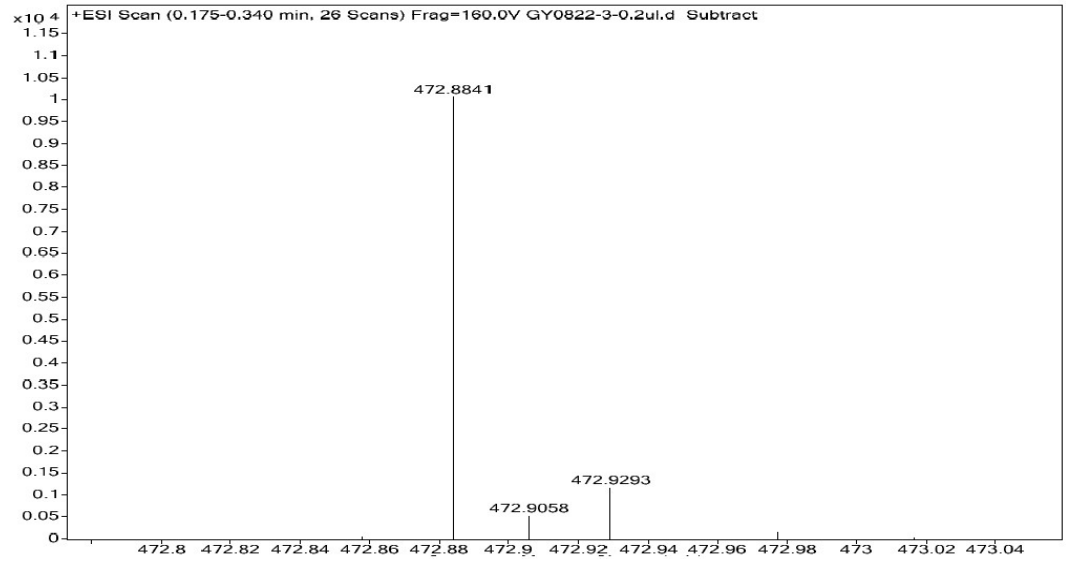


Figure S102. HRMS (ESI-TOF) Spectrum of Compound **3c**

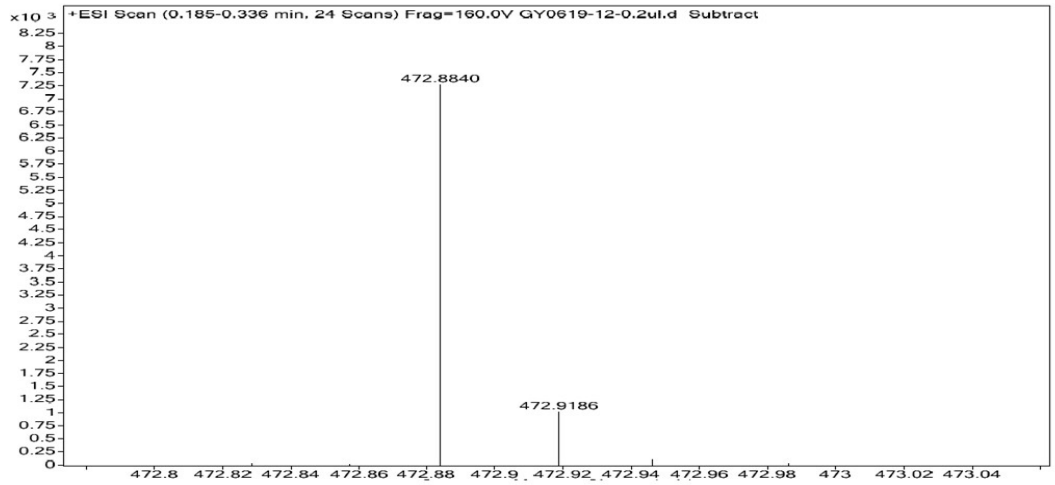


Figure S103. HRMS (ESI-TOF) Spectrum of Compound **3d**

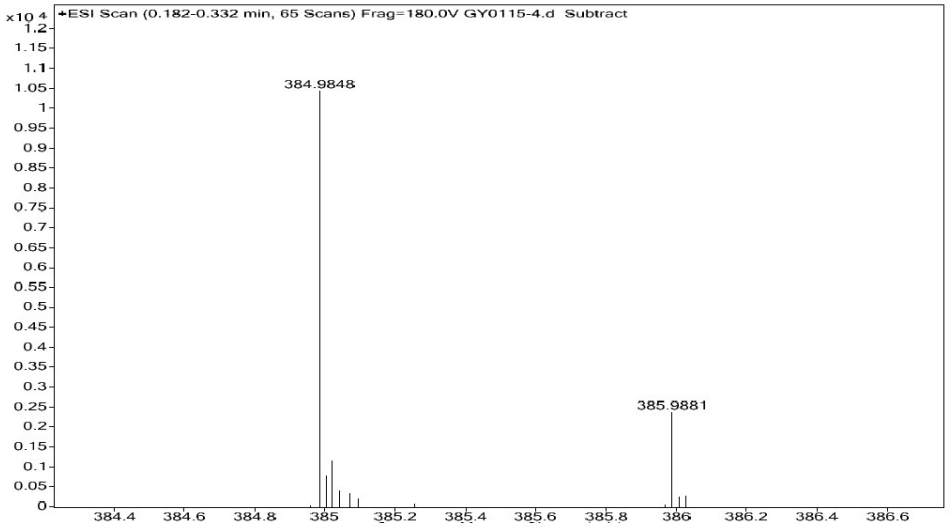


Figure S104. HRMS (ESI-TOF) Spectrum of Compound **3e**

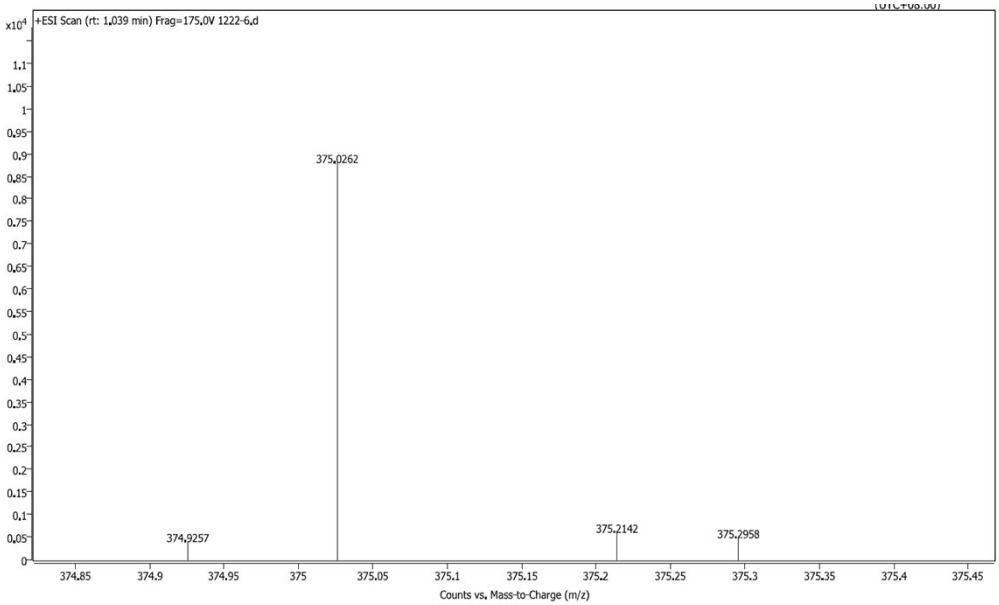


Figure S105. HRMS (ESI-TOF) Spectrum of Compound **3f**

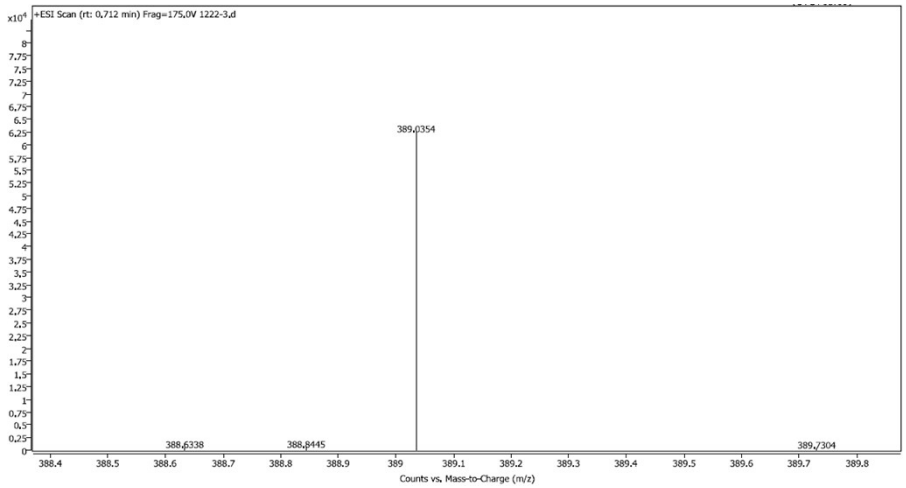


Figure S106. HRMS (ESI-TOF) Spectrum of Compound **3g**

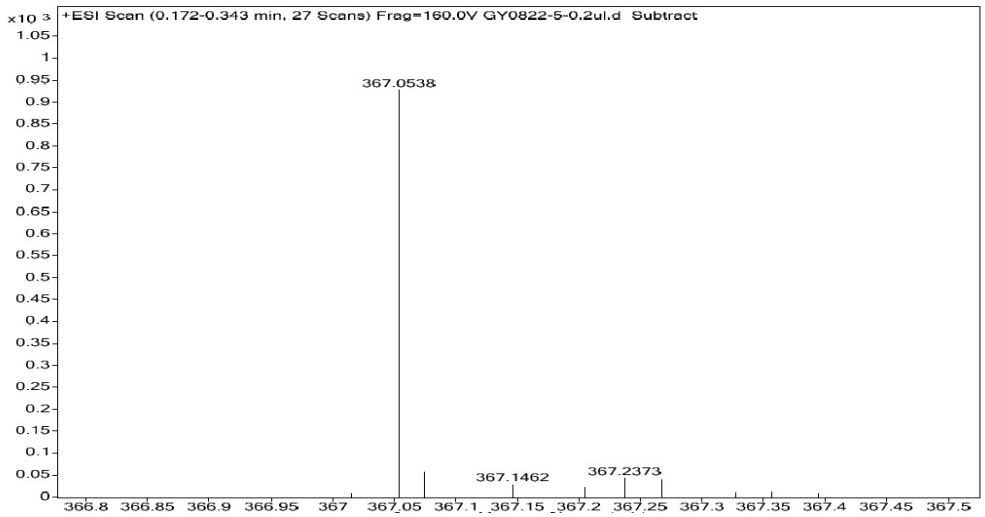


Figure S107. HRMS (ESI-TOF) Spectrum of Compound **3h**

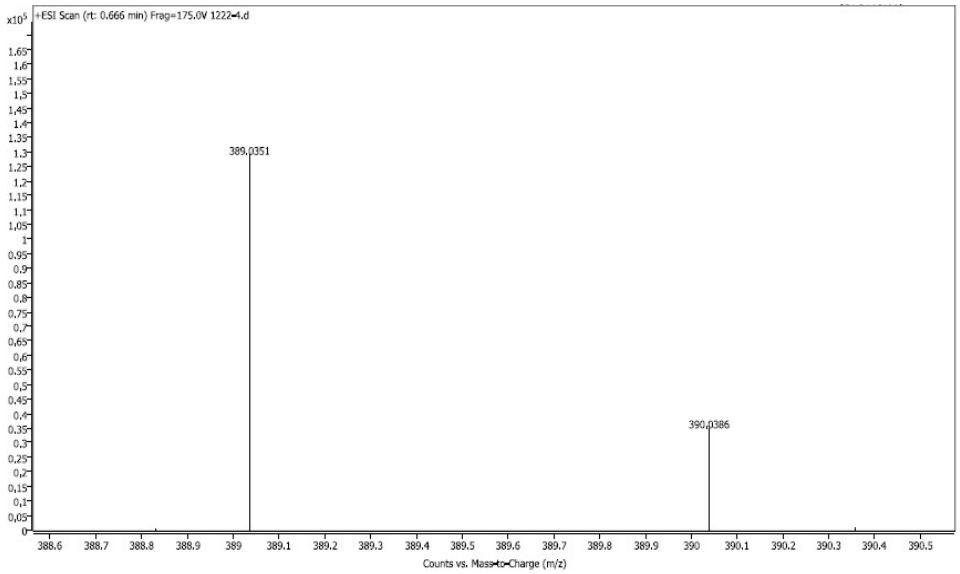


Figure S108. HRMS (ESI-TOF) Spectrum of Compound **3i**

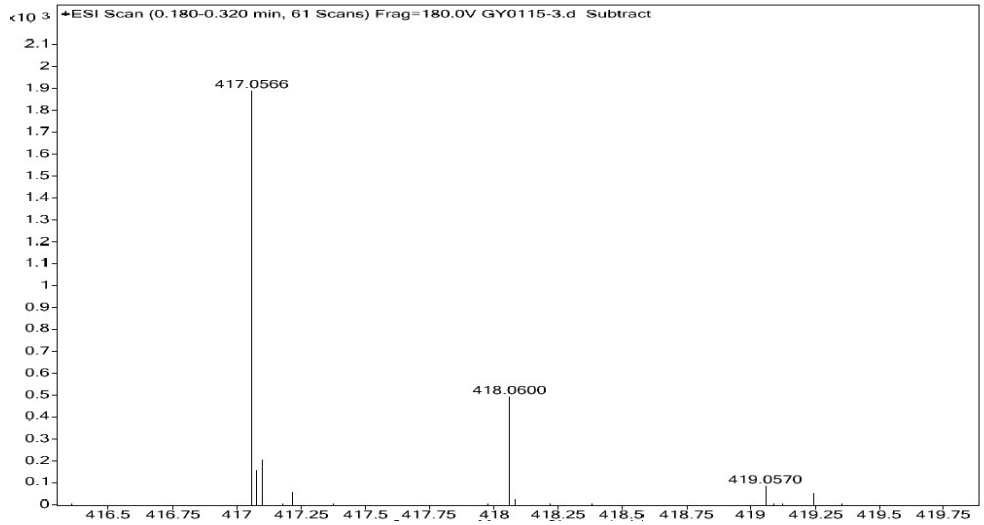


Figure S109. HRMS (ESI-TOF) Spectrum of Compound **3j**

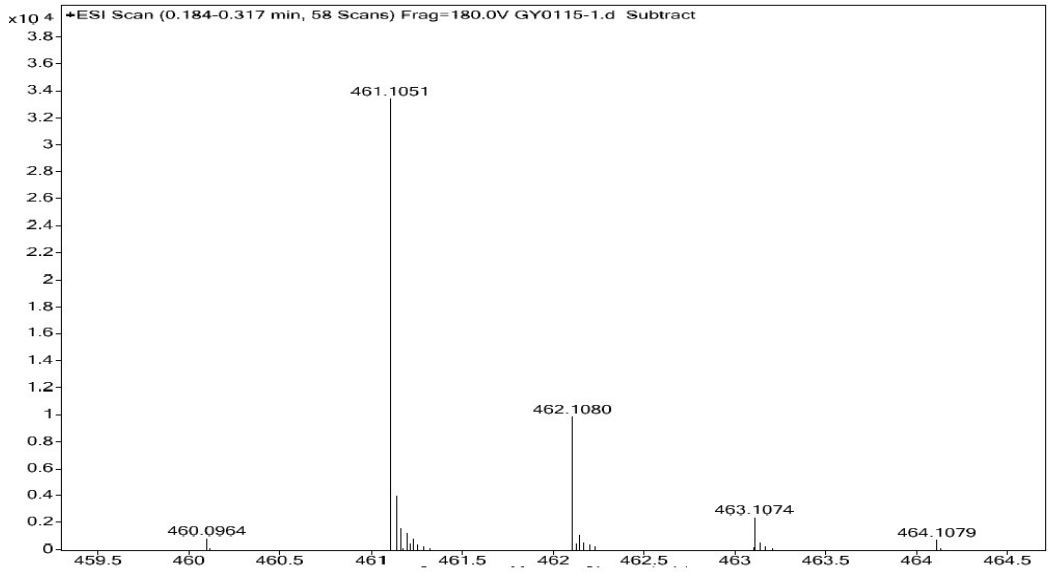


Figure S110. HRMS (ESI-TOF) Spectrum of Compound **3k**

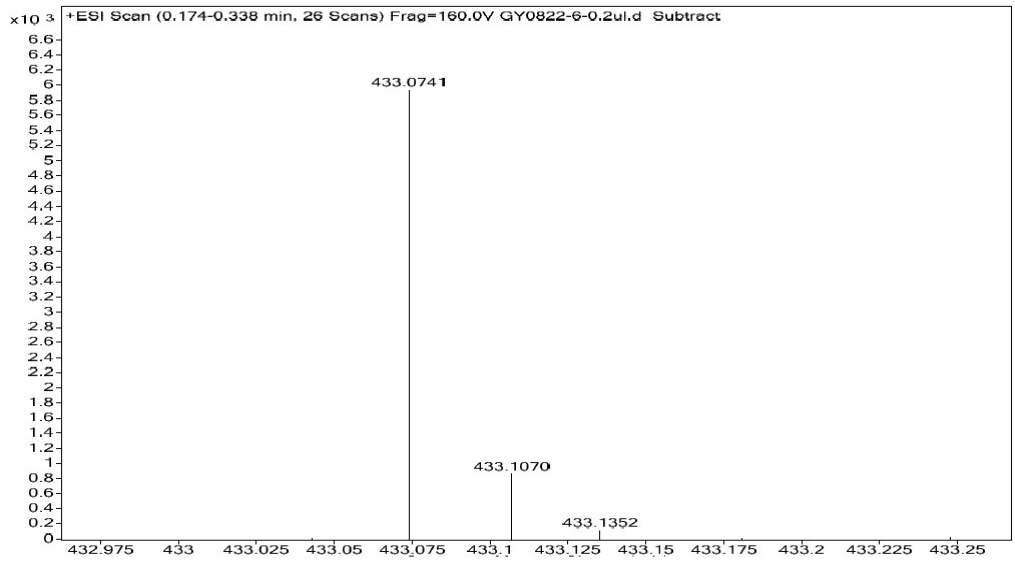


Figure S111. HRMS (ESI-TOF) Spectrum of Compound **3l**

Figure S112. HRMS (ESI-TOF) Spectrum of Compound **3m**

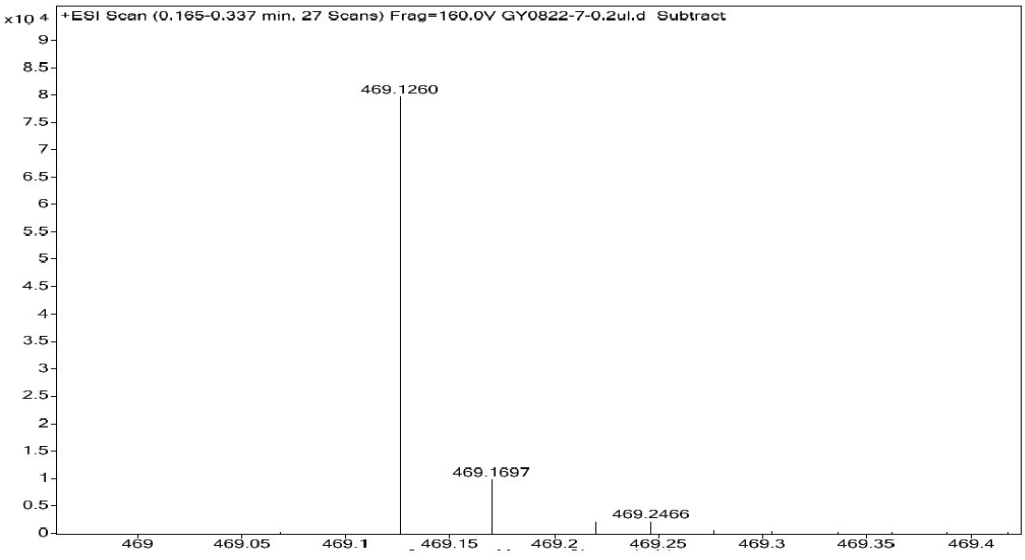


Figure S113. HRMS (ESI-TOF) Spectrum of Compound **3o**

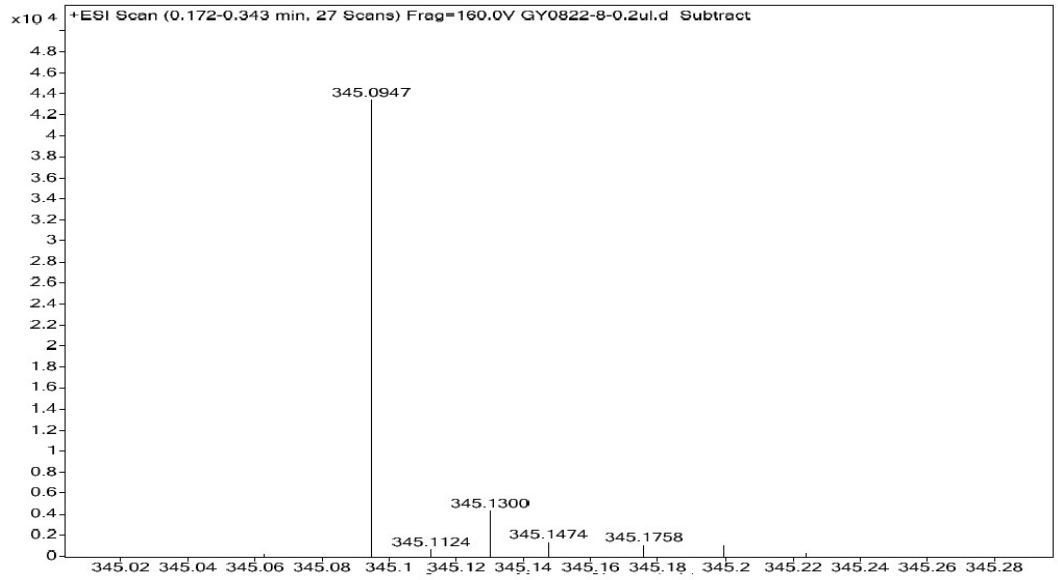


Figure S114. HRMS (ESI-TOF) Spectrum of Compound **3p**

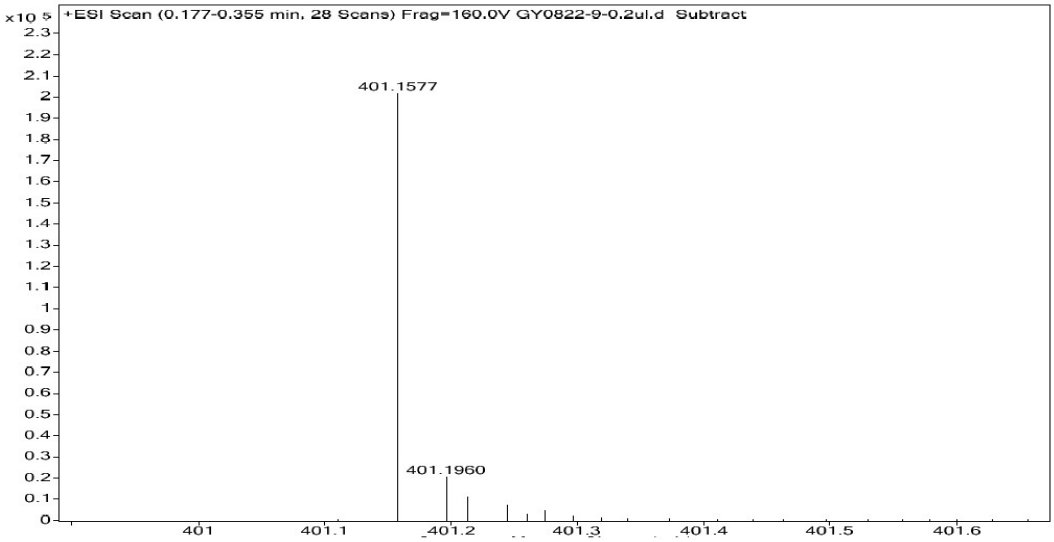


Figure S115. HRMS (ESI-TOF) Spectrum of Compound **3q**

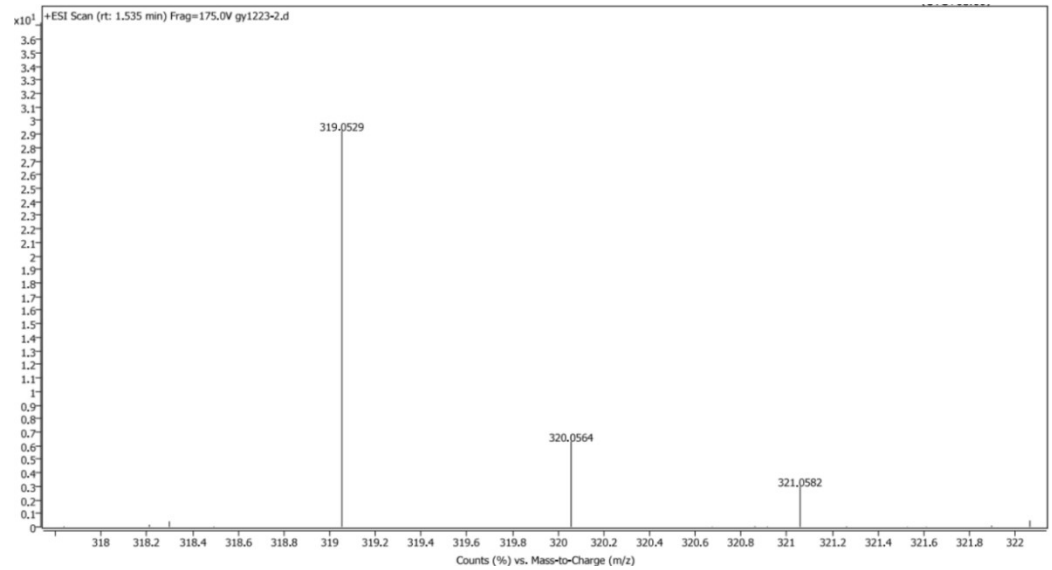


Figure S116. HRMS (ESI-TOF) Spectrum of Compound **3r**

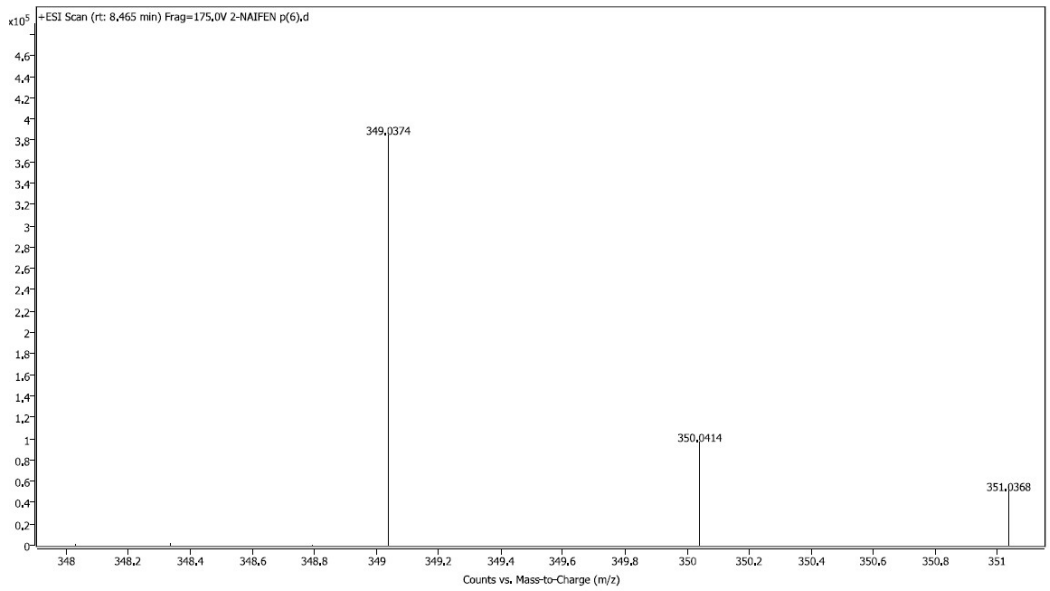


Figure S117. HRMS (ESI-TOF) Spectrum of Compound **2a**

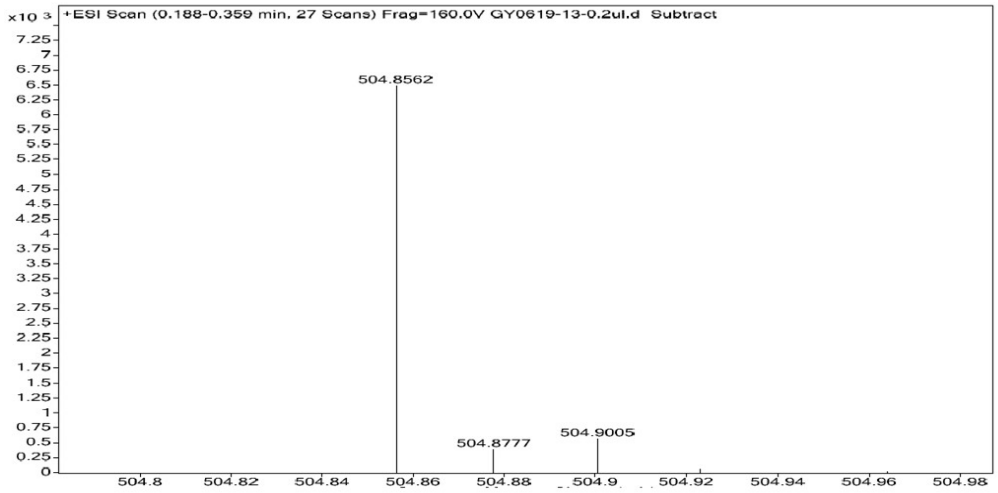


Figure S118. HRMS (ESI-TOF) Spectrum of Compound **2b**

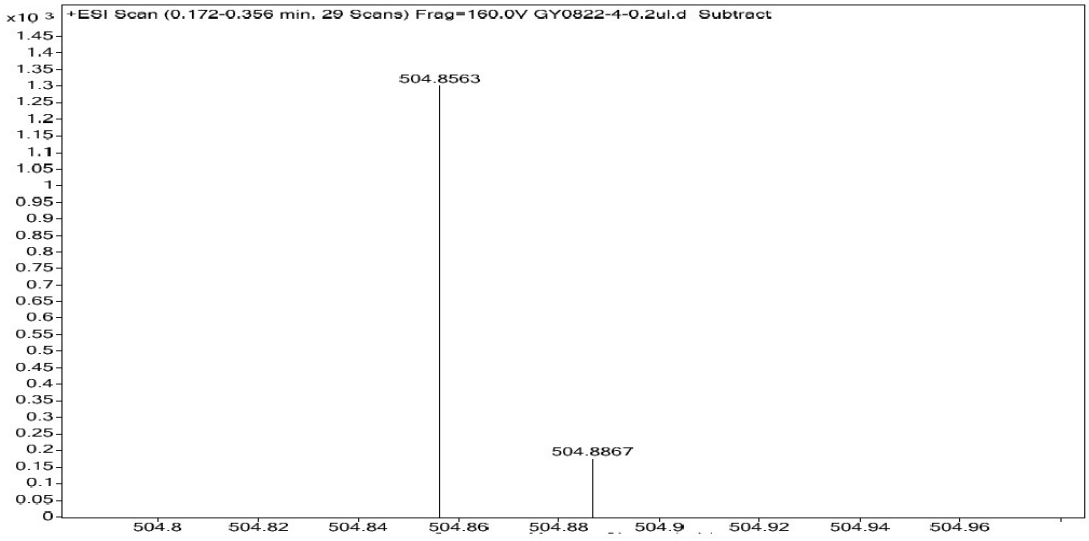


Figure S119. HRMS (ESI-TOF) Spectrum of Compound **2c**

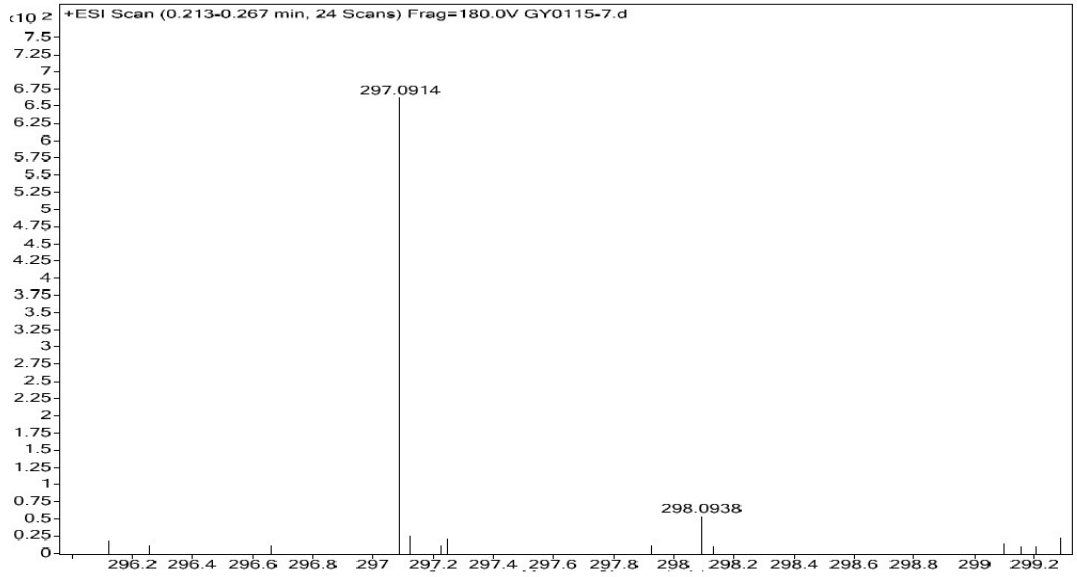


Figure S120. HRMS (ESI-TOF) Spectrum of Compound **5a**

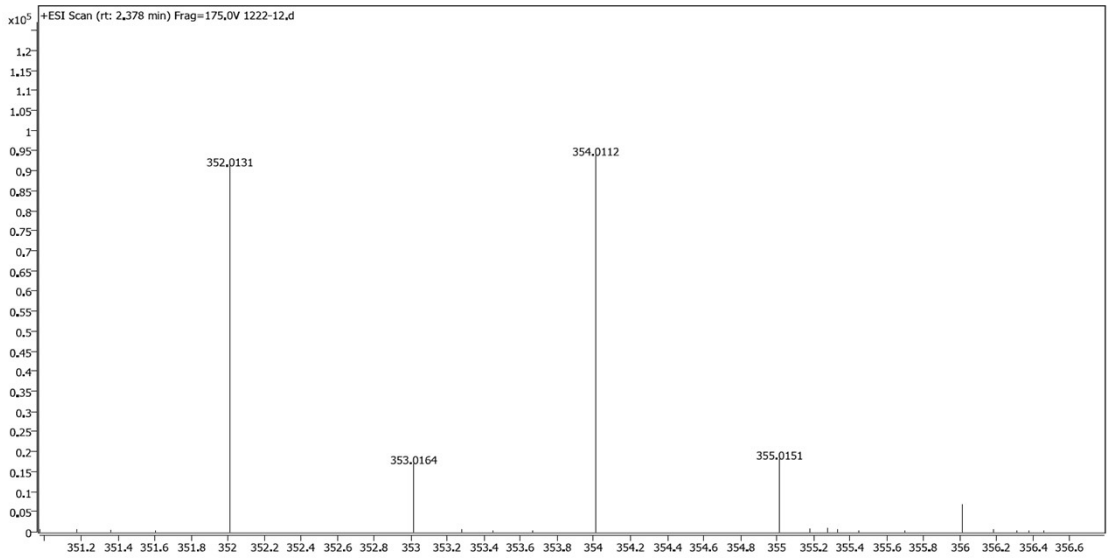


Figure S121. HRMS (ESI-TOF) Spectrum of Compound **5b**

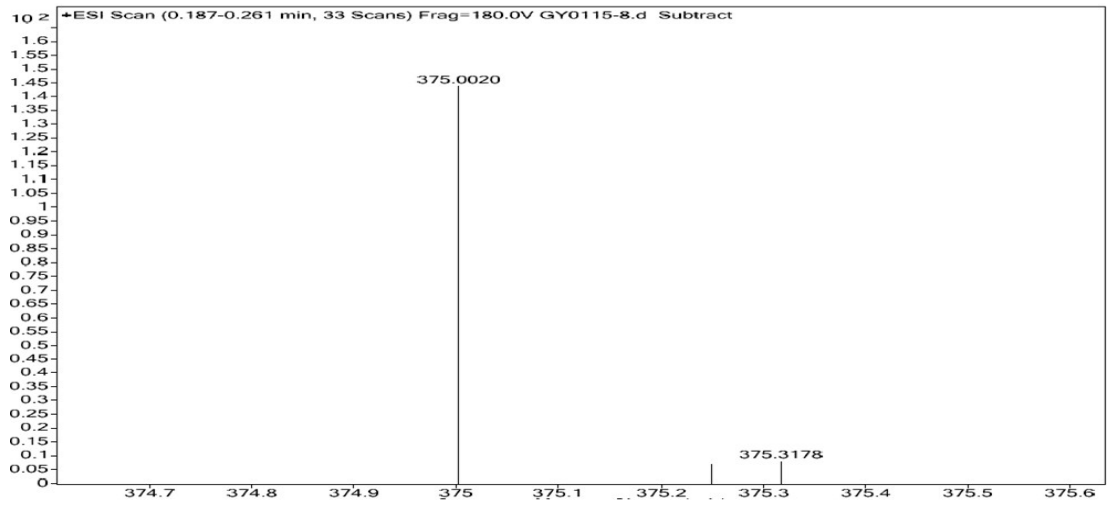


Figure S122. HRMS (ESI-TOF) Spectrum of Compound **5c**

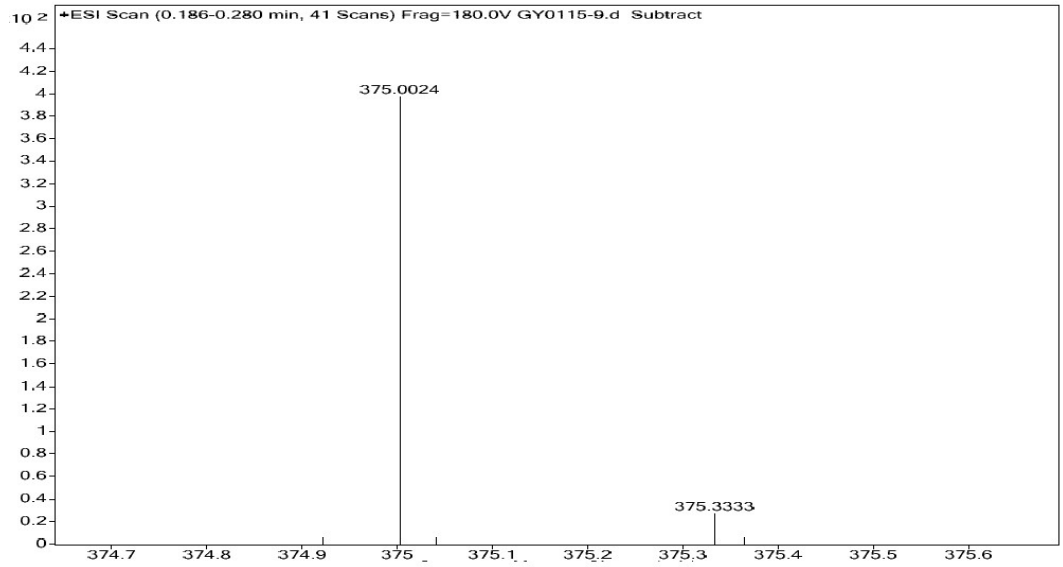


Figure S123. HRMS (ESI-TOF) Spectrum of Compound **5d**

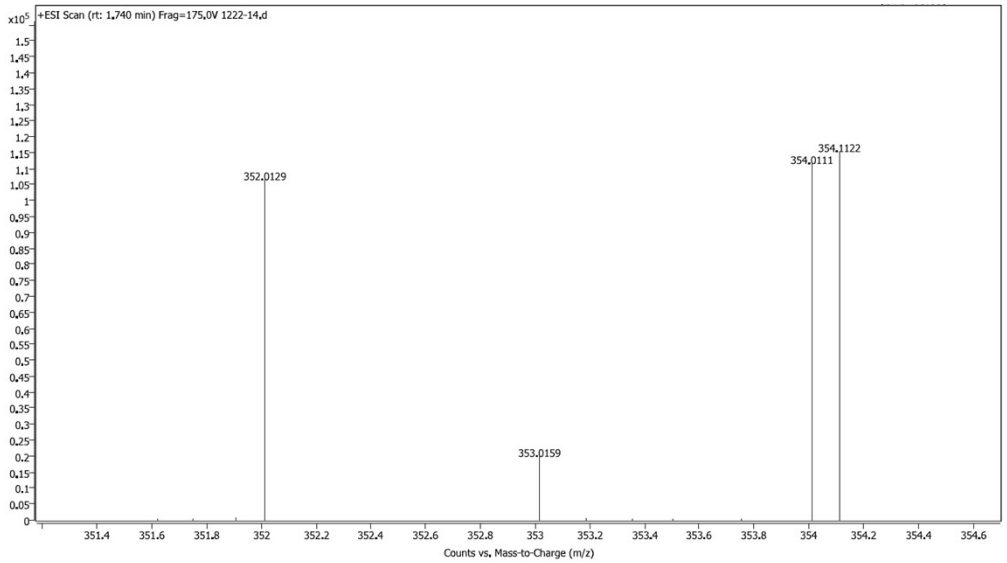


Figure S124. HRMS (ESI-TOF) Spectrum of Compound **5e**

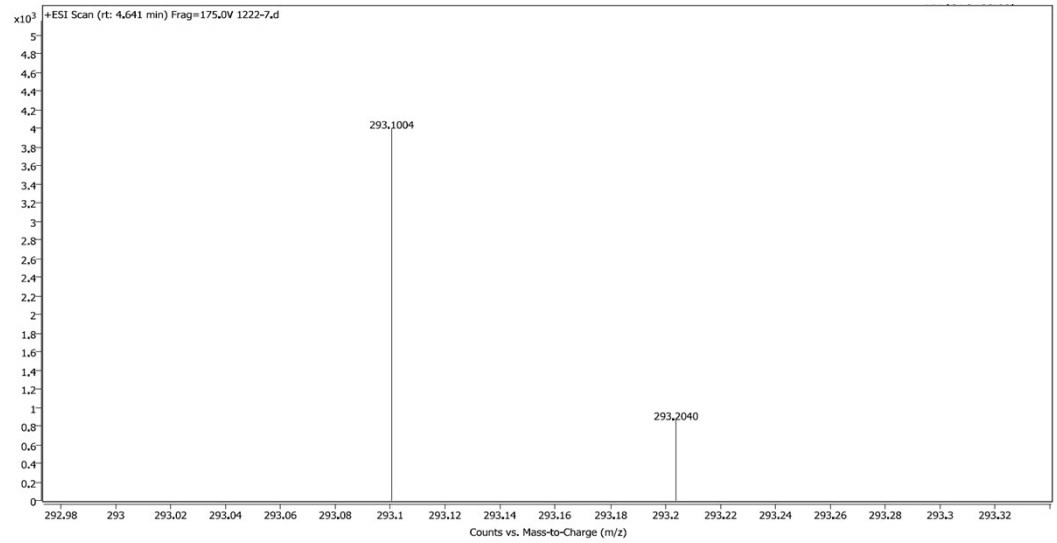


Figure S125. HRMS (ESI-TOF) Spectrum of Compound **5f**

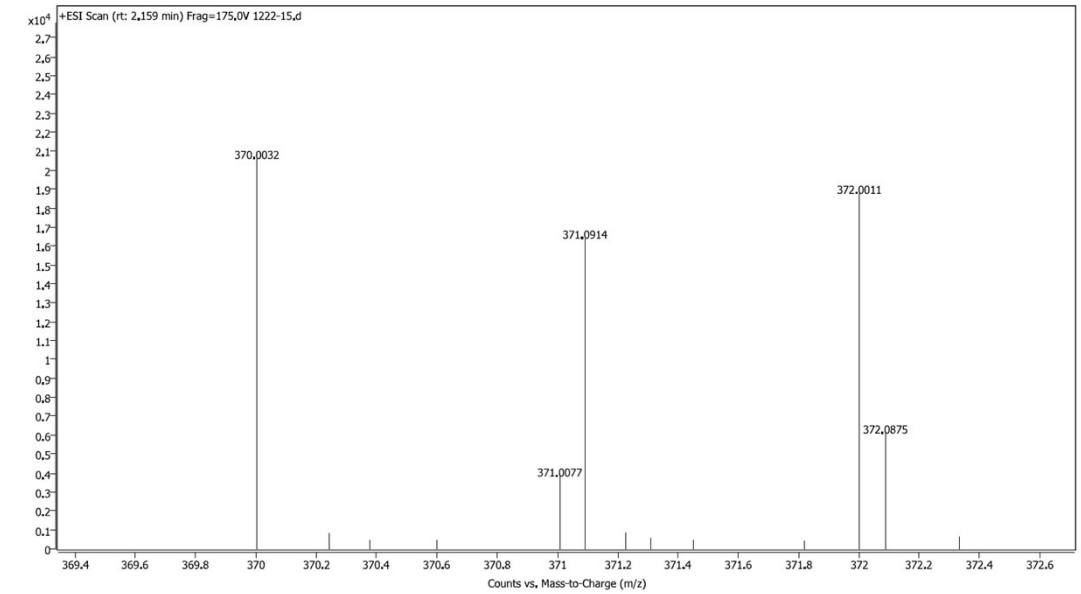


Figure S126. HRMS (ESI-TOF) Spectrum of Compound **5g**

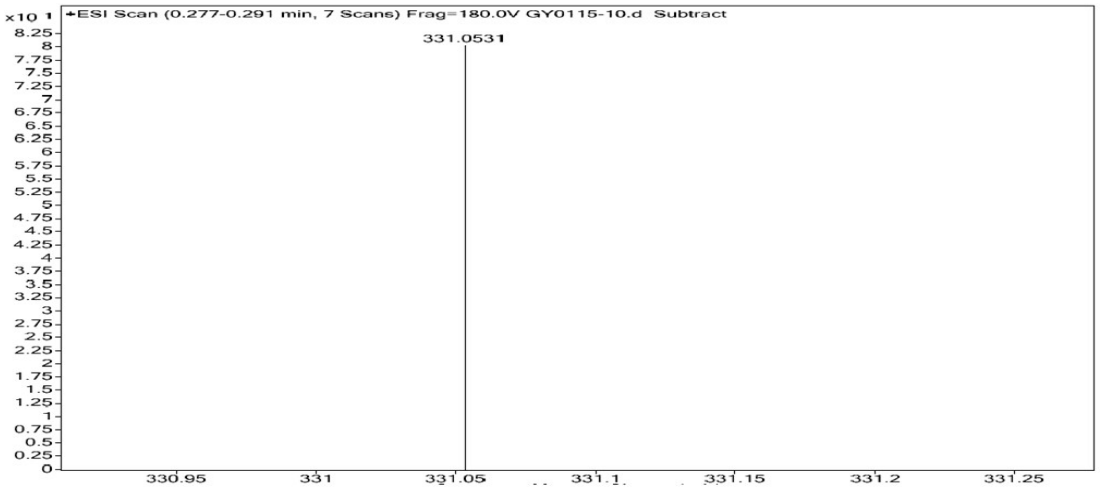


Figure S127. HRMS (ESI-TOF) Spectrum of Compound **5h**

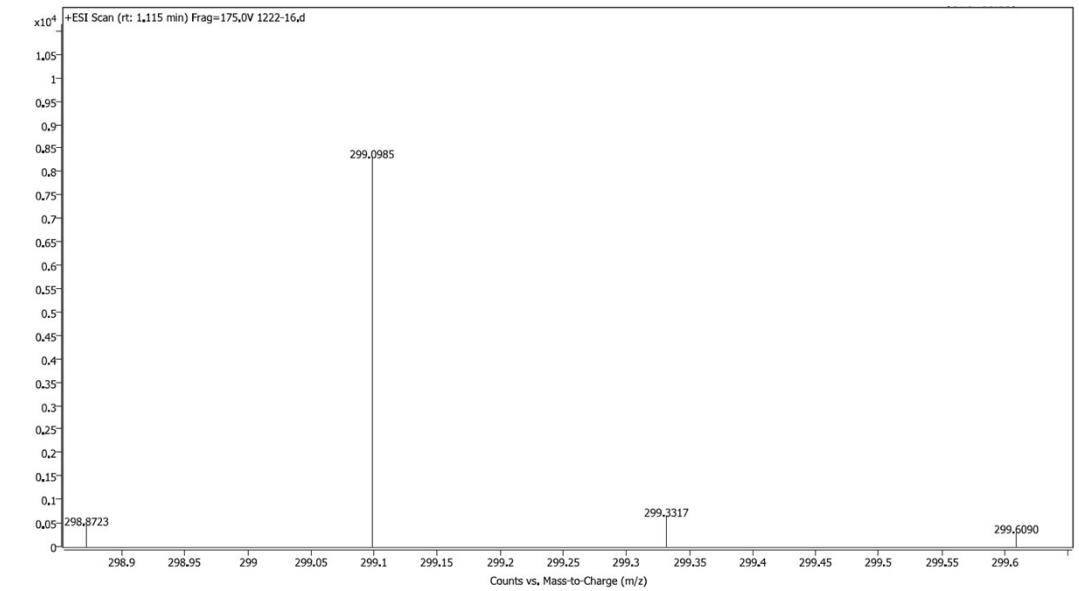


Figure S128. HRMS (ESI-TOF) Spectrum of Compound **5i**

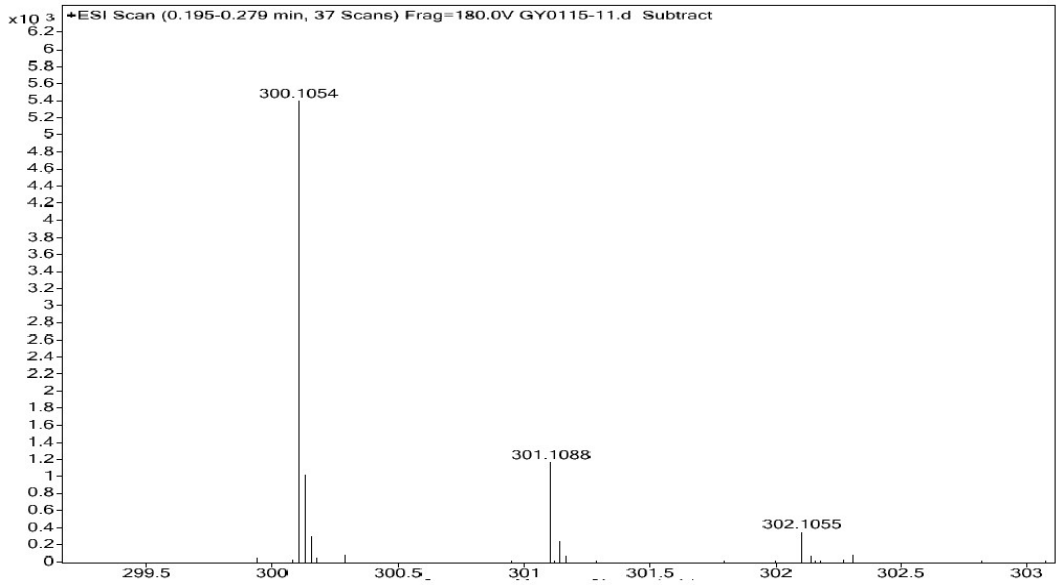


Figure S129. HRMS (ESI-TOF) Spectrum of Compound **5j**

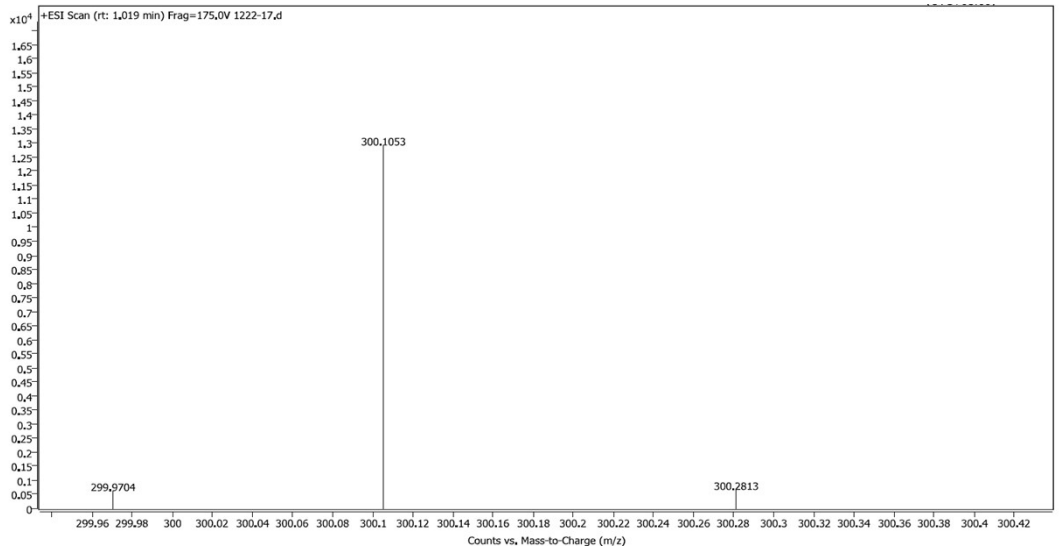


Figure S130. HRMS (ESI-TOF) Spectrum of Compound **5k**

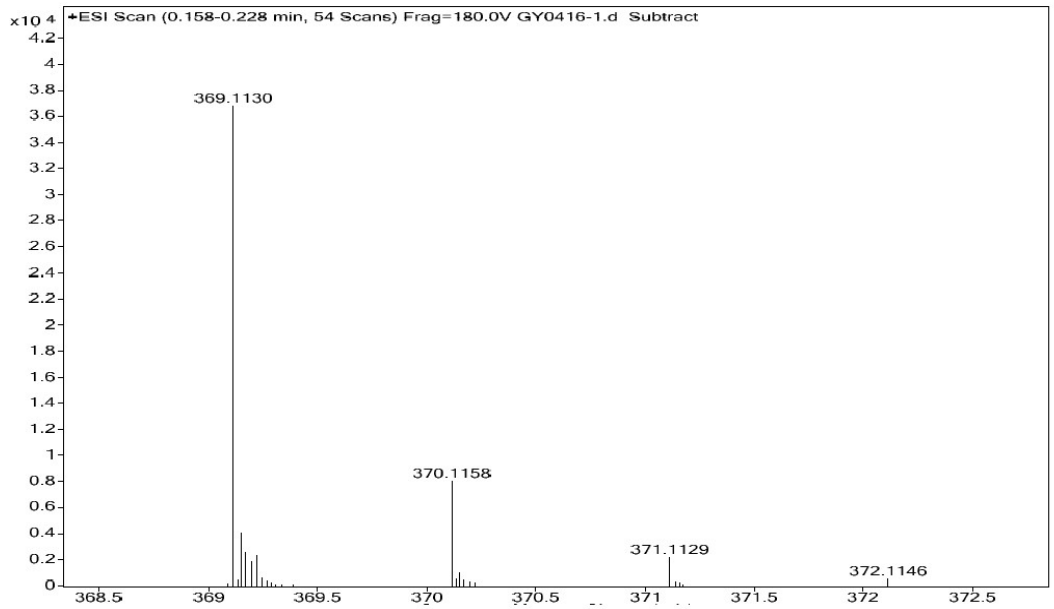


Figure S131. HRMS (ESI-TOF) Spectrum of Compound **5l**

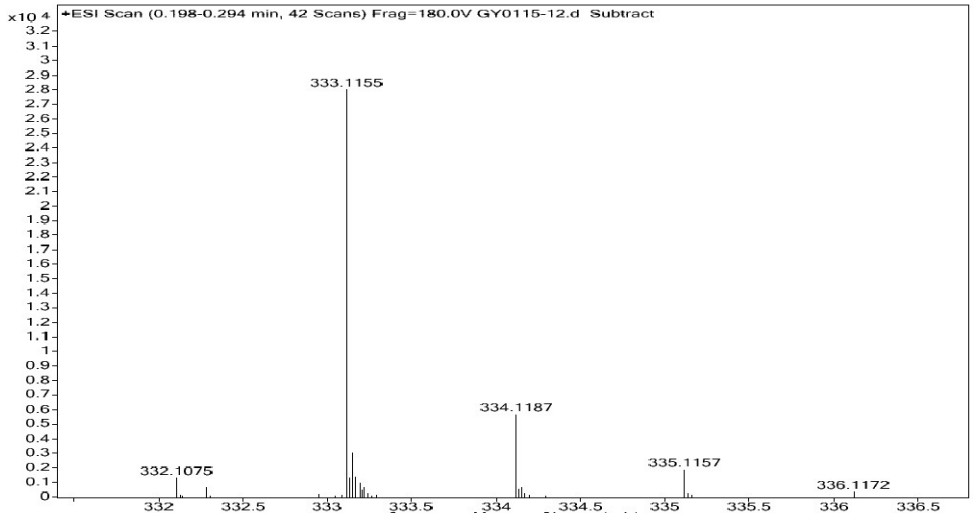


Figure S132. HRMS (ESI-TOF) Spectrum of Compound **5m**

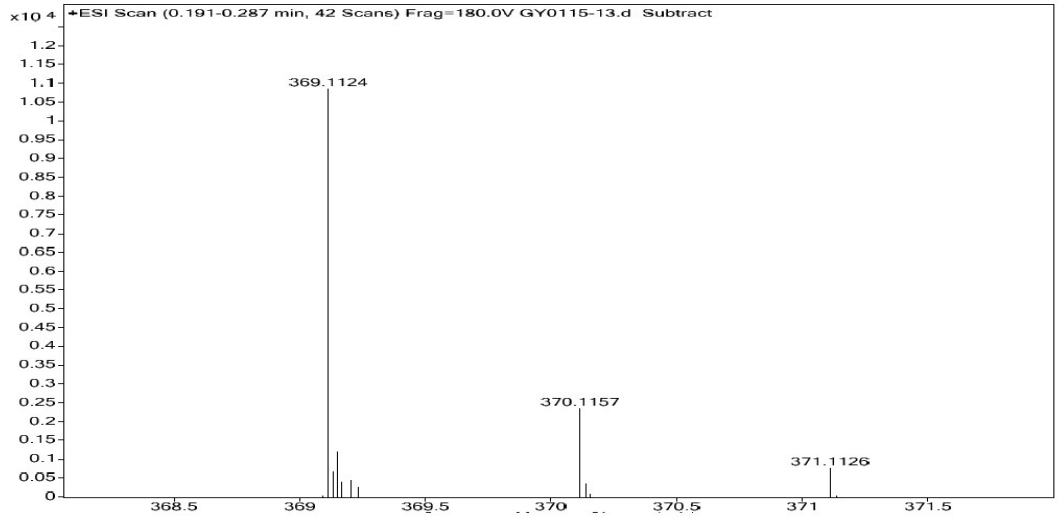


Figure S133. HRMS (ESI-TOF) Spectrum of Compound **5n**

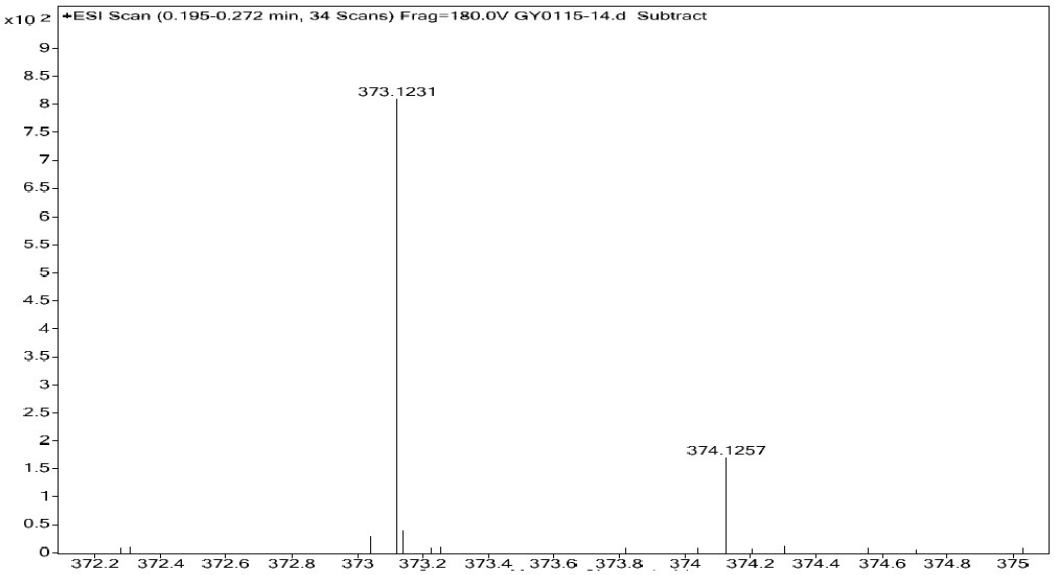


Figure S134 HRMS (ESI-TOF) Spectrum of Compound **5o**

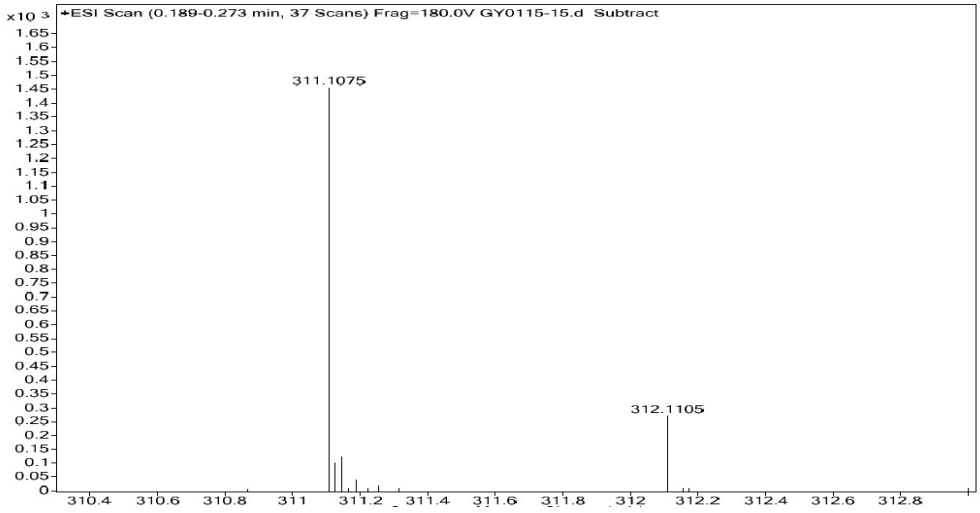


Figure S135. HRMS (ESI-TOF) Spectrum of Compound **5p**

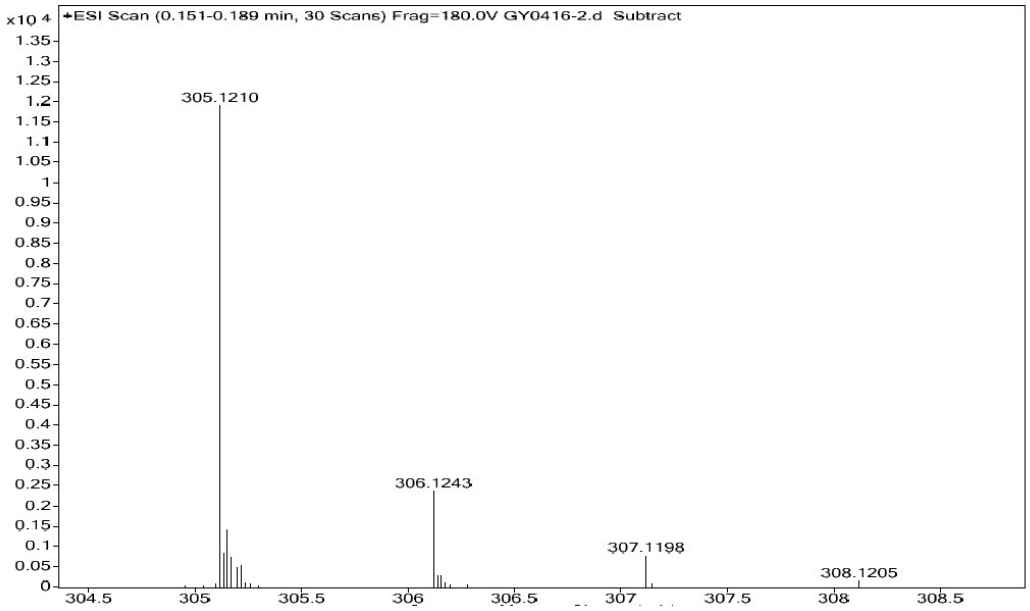


Figure S136. HRMS (ESI-TOF) Spectrum of Compound **5q**

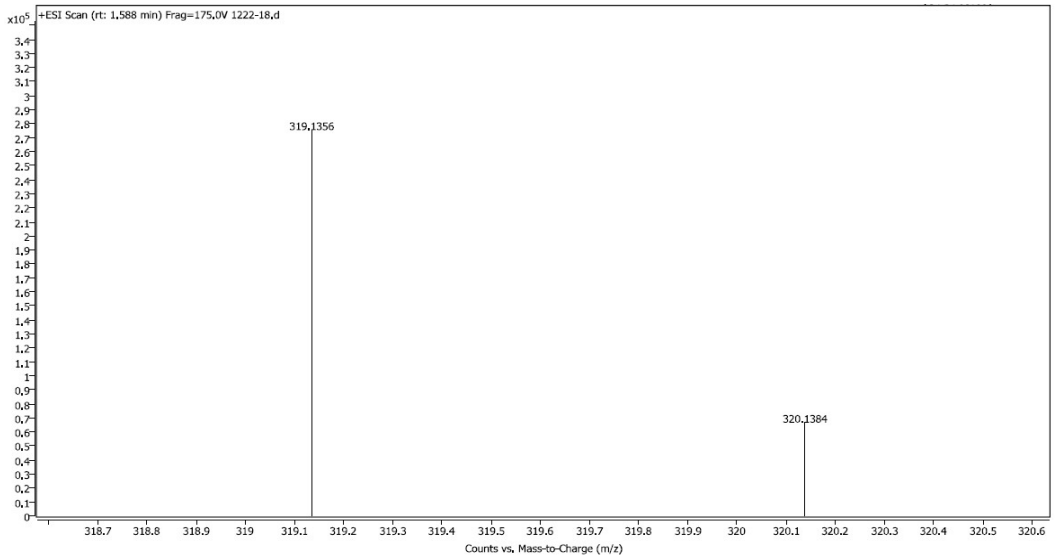


Figure S137. HRMS (ESI-TOF) Spectrum of Compound **5r**

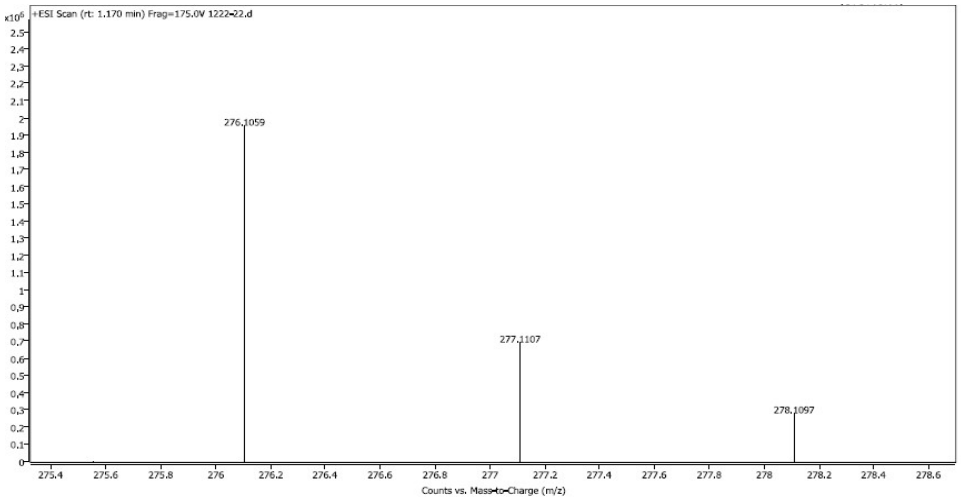


Figure S138. HRMS (ESI-TOF) Spectrum of Compound **5s**

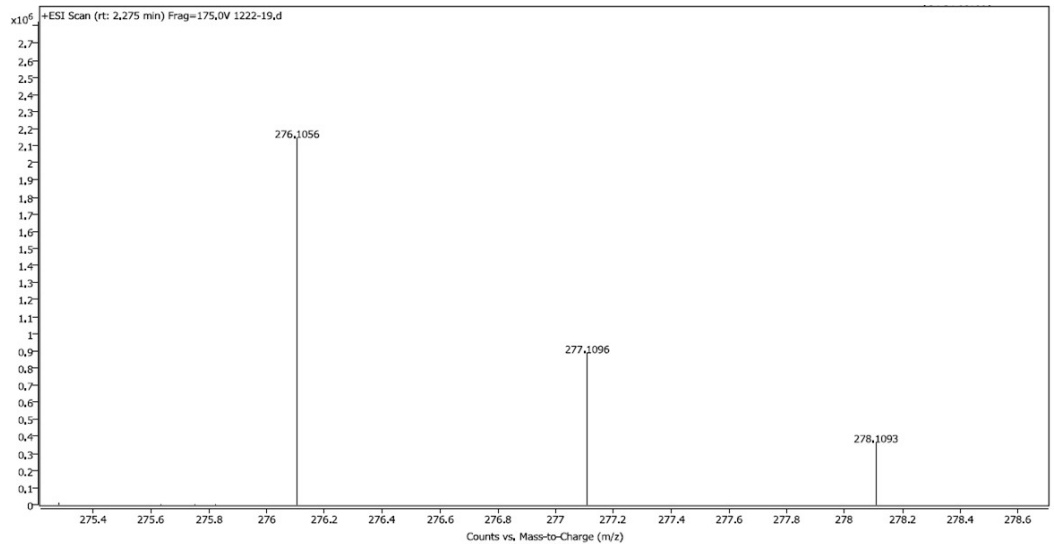


Figure S139. HRMS (ESI-TOF) Spectrum of Compound **5t**

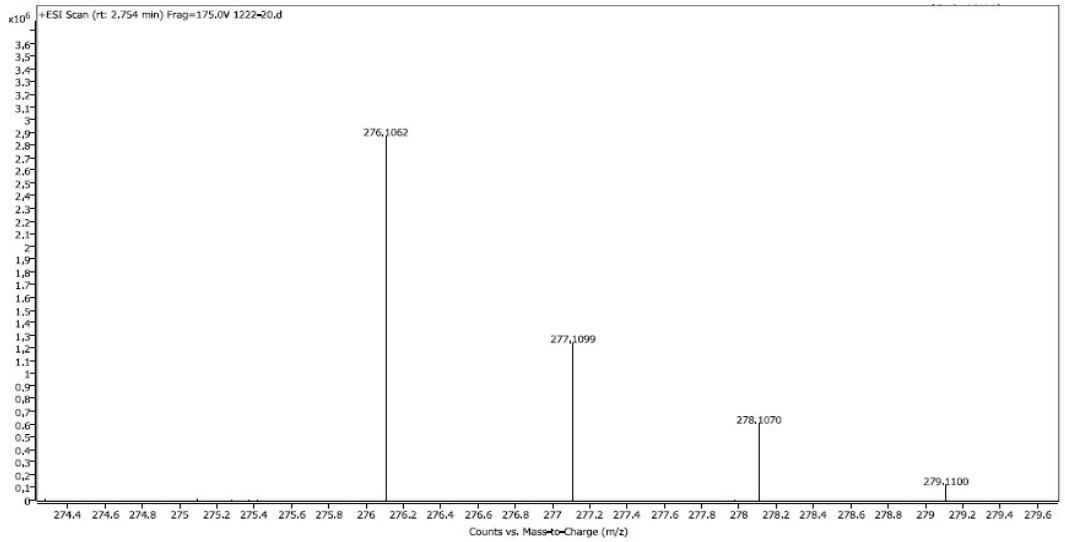


Figure S140. HRMS (ESI-TOF) Spectrum of Compound **5u**

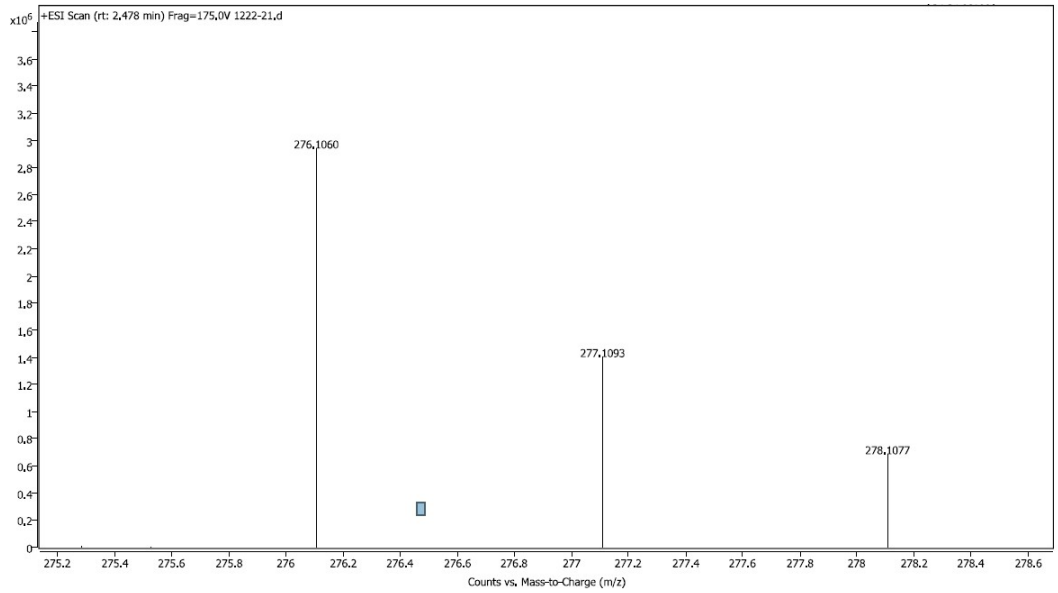


Figure S141. HRMS (ESI-TOF) Spectrum of Compound **5v**

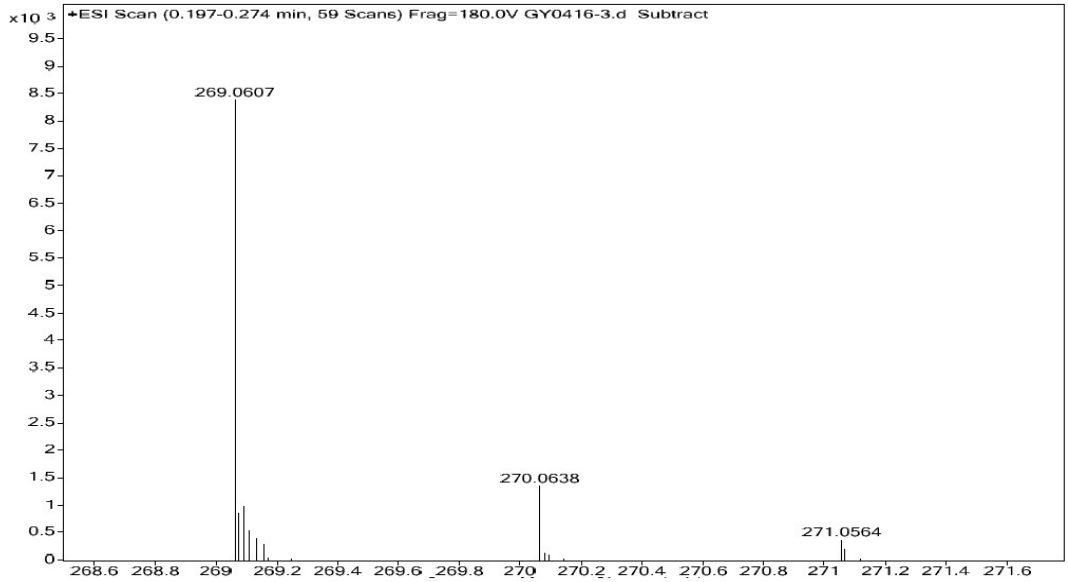


Figure S142. HRMS (ESI-TOF) Spectrum of Compound **5ab**

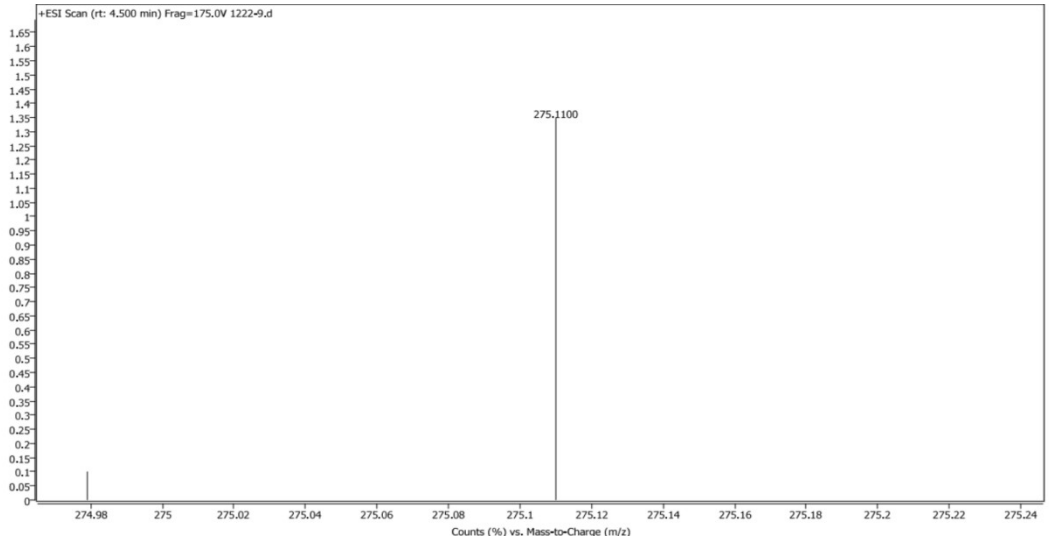


Figure S143. HRMS (ESI-TOF) Spectrum of Compound **5ac**

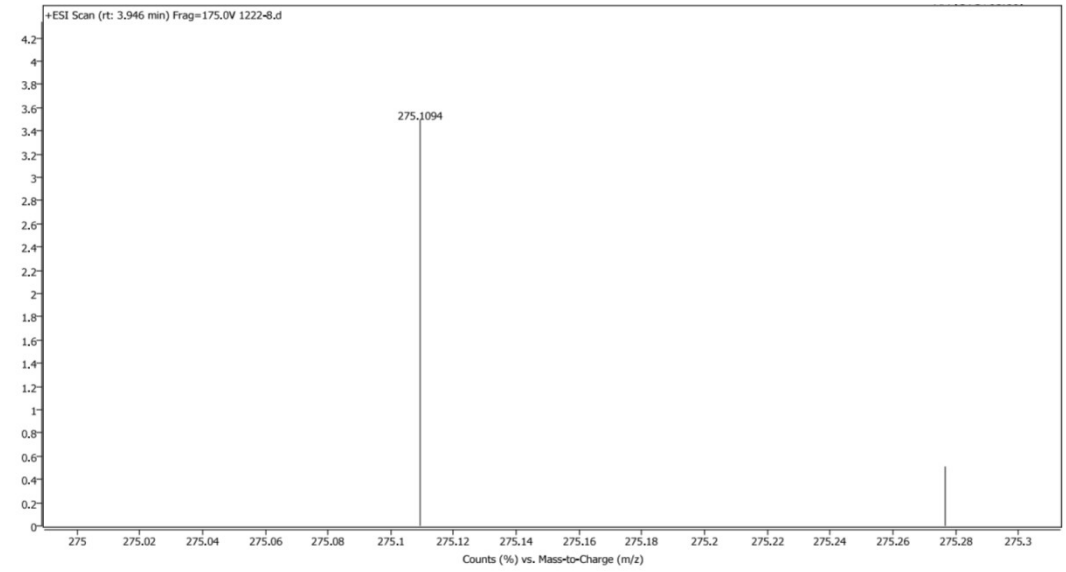


Figure S144. HRMS (ESI-TOF) Spectrum of Compound **5ad**

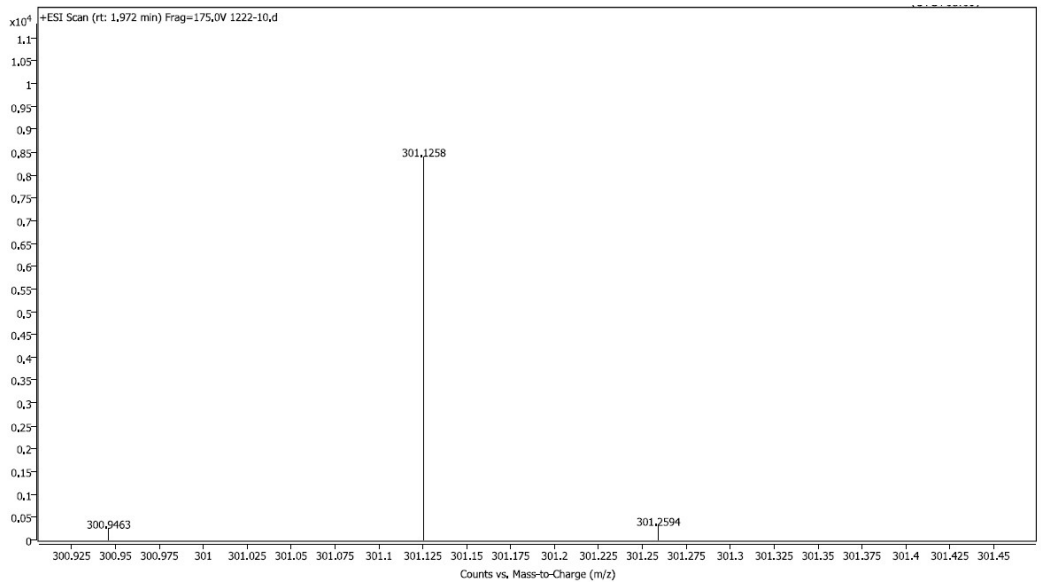


Figure S145. HRMS (ESI-TOF) Spectrum of Compound **5ae**

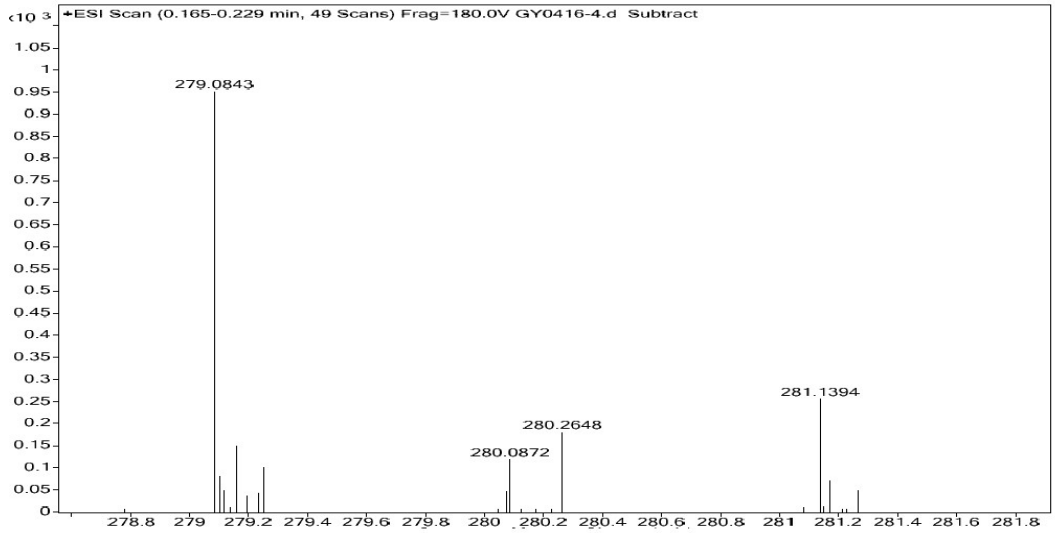


Figure S146. HRMS (ESI-TOF) Spectrum of Compound **5af**

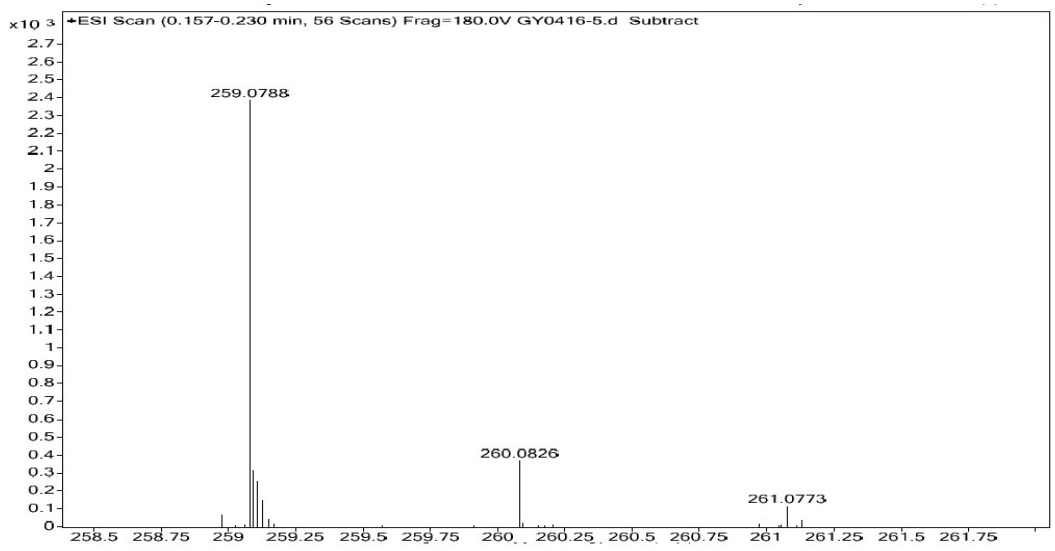


Figure S147. HRMS (ESI-TOF) Spectrum of Compound **5ag**

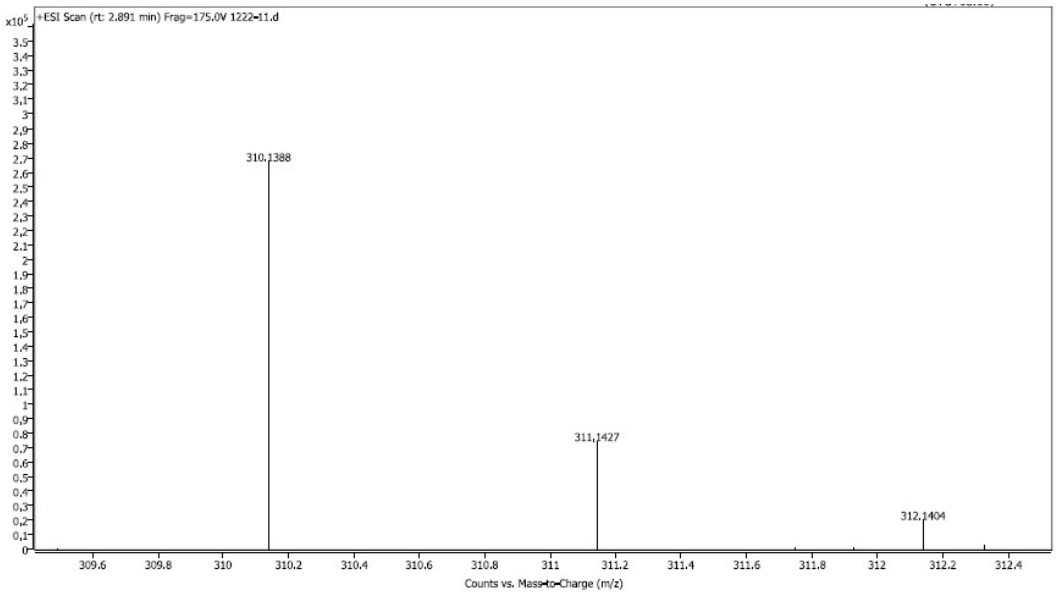


Figure S148. HRMS (ESI-TOF) Spectrum of Compounds **5ah1 and 5ah2**

2.5 Details for Single Crystal X-ray Analysis

The structure of **3a** and **2a** were determined by the X ray diffraction. Recrystallized from acetone. Further information can be found in the CIF file. There crystals were deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2113590 and CCDC 2113591. The checkCIF reports were obtained via the International Union of Crystallography's (IUCr)

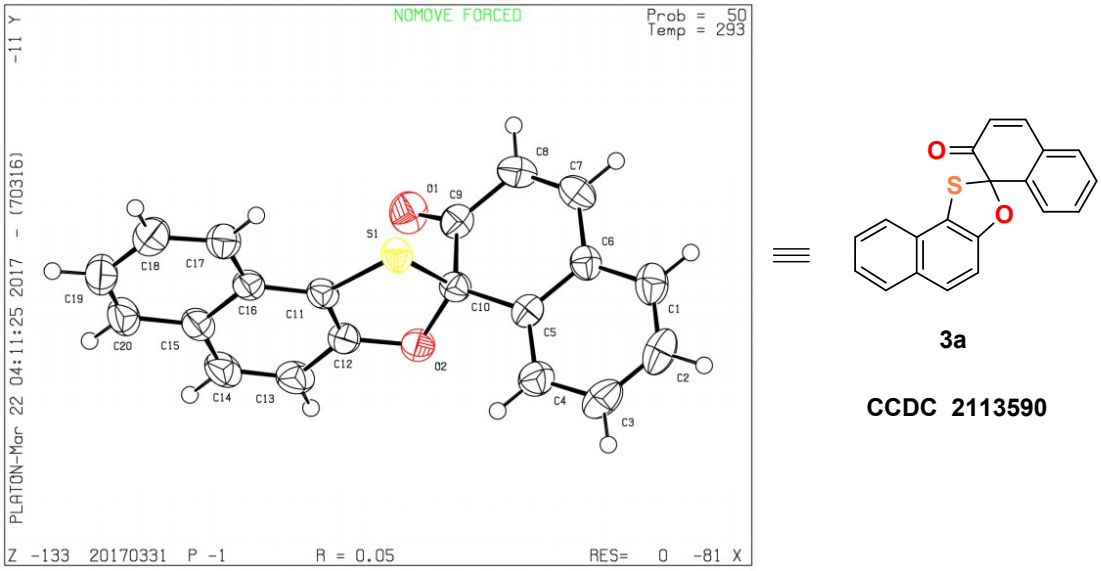


Figure S149. X-ray crystal structure of **3a** with the ellipsoid contour at 50% probability levels.8

Table S8. Crystal data and structure refinement for 20170331 (**3a**).

Datablock: 20170331

Bond precision: C-C = 0.0030 A Wavelength=0.71073

Cell: a=8.3023(5) b=9.0644(7) c=10.6356(10)
alpha=99.420(7) beta=93.883(6) gamma=108.503(7)
Temperature: 293 K

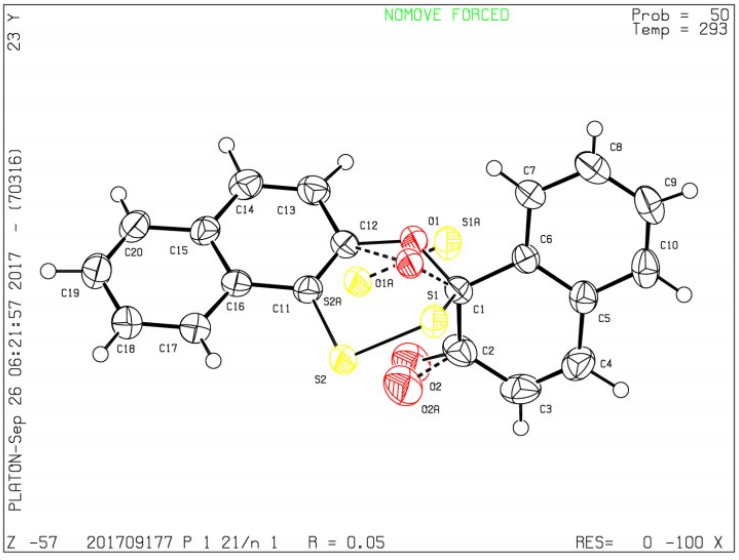
	Calculated	Reported
Volume	742.63(11)	742.63(11)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C20 H12 O2 S	C20 H12 O2 S
Sum formula	C20 H12 O2 S	C20 H12 O2 S
Mr	316.36	316.36
Dx,g cm-3	1.415	1.415
Z	2	2
Mu (mm-1)	0.225	0.225
F000	328.0	328.0
F000'	328.39	
h,k,lmax	11,12,14	11,12,14
Nref	4053	3428
Tmin,Tmax	0.955,0.965	0.950,1.000
Tmin'	0.954	

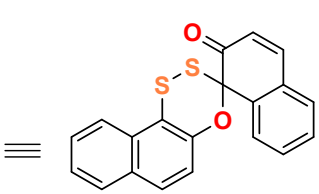
Correction method= # Reported T Limits: Tmin=0.950 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.846 Theta(max)= 29.264

R(reflections)= 0.0467(2603) wR2(reflections)= 0.1144(3428)

S = 1.040 Npar= 208





2a

CCDC 2113591

Figure S150. X-ray crystal structure of **2a** with the ellipsoid contour at 50% probability levels

Table S9. Crystal data and structure refinement for 201709117 (2a).

Datablock: 201709177

```
Bond precision:   C-C = 0.0048 A          Wavelength=1.54184

Cell:             a=9.1135(4)     b=6.4959(3)         c=26.5272(12)
                  alpha=90        beta=92.726(4)      gamma=90
Temperature:      293 K

                 Calculated                  Reported
Volume           1568.64(12)                 1568.65(13)
Space group      P 21/n                      P 1 21/n 1
Hall group       -P 2yn                      -P 2yn
Moiety formula   C20 H12 O2 S1.91, 0.044(S2) C20 H12 O2 S2
Sum formula      C20 H12 O2 S2               C20 H12 O2 S2
Mr               348.42                      348.42
Dx,g cm-3        1.475                       1.475
Z                4                           4
Mu (mm-1)        3.150                       3.150
F000             720.0                       720.0
F000'            724.45
h,k,lmax         10,7,31                     10,7,31
Nref             2797                        2786
Tmin,Tmax        0.596,0.664                 0.857,1.000
Tmin'            0.540

Correction method= # Reported T Limits: Tmin=0.857 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996           Theta(max)= 67.076

R(reflections)= 0.0520( 2327)                    wR2(reflections)=
                                                 0.1427( 2786)
S = 1.097                Npar= 266
```

3.References

[1] H. A. Stevenson and S. Smiles, *J. Chem. Soc*. 1930, 1740.

[2] J. A. C. McClell and S. Smiles, *J. Chem. Soc.* 1933, 786.

[3] G. Capozzi, C. Falciani, S. Menichetti and C. Nativi*, J. Org. Chem*. 1997, ***62***, 2611

[4] C. Viglianisi, A. Sinni and S. Menichetti*, Heteroatom Chem*. 2014, ***25***, 361.

[5] G. Capozzi, S. Menichetti, C. Nativi, M. C. Simonti, *Tetrahedron Lett*. 1994, ***35***,9451.

[6] G. Capozzi, A. Corti, S. Menichetti, and C. Nativi. *Tetrahedron* 1996, ***52***, 12233.

[7] (a) W. K. Wong-Ng, S. C. Nyburg, *Acta Cryst.* 1978, ***B34***, 2910. (b) P.-T. Cheng and S. C. Nyburg, Acta Cryst. 1978. ***B34***, 2907.