Supporting Information

Catalyst-free Electrosynthesis of Benzothiophenes from 2-Alkenylaryl Disulfides

Juyeong Lee,‡[a] Eunsoo Yu‡[a] and Cheol-Min Park[a*]

[a] Department of Chemistry, UNIST (Ulsan National Institute of Science & Technology), Ulsan 44919, Korea

‡ These authors contributed equally to this work.

1. General Information

All reactions were conducted under a nitrogen atmosphere with oven-dried glassware and standard Schlenk or vacuum line techniques. All solutions were handled under nitrogen and transferred via syringe. Anhydrous solvents were purchased and stored over activated 4 Å molecular sieves. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar or TCI. Progress of reactions was monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plate and visualized by short-wave ultraviolet light as well as by treatment with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash chromatography was performed with Silica Flash P60 silica gel (230 – 400 mesh). ^{1}H and ^{13}C NMR spectra were obtained using an Agilent 400-MR DD2 Fourier-transform NMR spectrometer. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The residual solvent signals were taken as the reference ($CDCl_3$, 7.26 ppm ^{1}H NMR spectra and $CDCl_3$, 77.0 ppm for ^{13}C NMR spectra). The signals observed are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). Mass analysis were carried out using Advion Expression CMS mass spectrometer or Agilent 6130 Quadrupole LC/MS. High resolution mass analysis was performed with JOEL AccuTOF 4G+ DART-HRMS and on Bruker, 1200 Series & HCT Basic System.

2. Procedure for the electrolysis

Electrode materials/dimensions:

Graphite, nickel electrodes with dimensions of 0.8 cm x 0.2 cm x 5.2 cm were employed.

Photographed images of ElectraSyn 2.0

(From left to right) ElectraSyn 2.0; ElectraSyn vial (5 mL); ElectraSyn 2.0 vial cap, electrode holders with nickel, graphite electrodes; The electrode holders were plugged into the vial cap.

General Procedure (A) for benzothiophene synthesis in 0.1 mmol scale

The reaction was carried out in an undivided cell, under inert atmosphere. A 5 mL vial was charged with the alkenyl disulfide **1** (0.1 mmol, 1 equiv.), Et_4NOTs (0.3 mmol, 0.1 M), 1,2-dichloroethane (3 mL), and a stir bar, and was closed with a cap attached with a graphite anode and a nickel cathode. The solution was stirred at 900 rpm for 1 minute at room temperature before current was turned on. The electrolysis was performed at a constant current of 2.0 mA. Upon full consumption of the disulfide starting material as determined by thin-layer chromatography analysis, electrolysis was terminated. The reaction mixture was transferred into the round bottom flask and the electrodes were washed several times with ethyl acetate which was combined into the same round bottom flask. The combined solution was concentrated under reduced pressure and purified by flash chromatography.

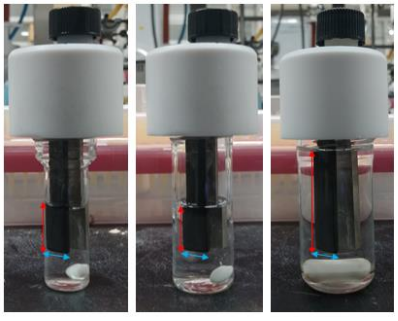
General Procedure (B) for benzothiophene synthesis in 0.3 mmol scale

The reaction was carried out in an undivided cell, under inert atmosphere. A 10 mL vial was charged with the alkenyl disulfide **1** (0.3 mmol, 1 equiv.), Et_4NOTs (0.6 mmol, 0.1 M), 1,2-dichloroethane (6 mL), and a stir bar, and was closed with a cap attached with a graphite anode and a nickel cathode. The solution was stirred at 900 rpm for 1 minute at room temperature before current was turned on. The electrolysis was performed at a constant current of 4.0 mA. Upon full consumption of the disulfide starting material as determined by thin-layer chromatography analysis, electrolysis was terminated. The reaction mixture was transferred into the round bottom flask and the electrodes were washed several times with ethyl acetate which was combined into the same round bottom flask. The combined solution was concentrated under reduced pressure and purified by flash chromatography.

Procedure for benzothiophene synthesis in 1.05 mmol scale

The reaction was carried out in an undivided cell, under inert atmosphere. A 20 mL vial was charged with the alkenyl disulfide **1a** (406 mg, 1.05 mmol, 1 equiv.), Et_4NOTs (603 mg, 2.0 mmol, 0.105 M), 1,2-dichloroethane (19 mL), and a stir bar, and was closed with a cap attached with a graphite anode and a nickel cathode. The solution was stirred at 900 rpm for 1 minute at room temperature before current was turned on. The electrolysis was performed at a constant current of 10.0 mA. Upon full consumption of the disulfide starting material as determined by thin-layer chromatography analysis (13 h), electrolysis was terminated. The reaction mixture was transferred into the round bottom flask and the electrodes were washed several times with ethyl acetate which was combined into the same round bottom flask. The combined solution was concentrated under reduced pressure and purified by flash chromatography to yield desired product as a white solid (272 mg, 1.41 mmol, 67% yield).

Surface area of the electrodes dipped into the solution



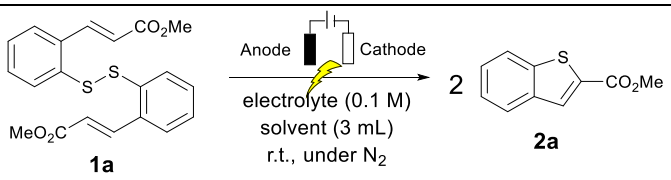
(From left to right)

0.1 mmol scale (5 ml vial) : 1.6 cm x 0.8 cm

0.3 mmol scale (10 ml vial) : 1.7 cm x 0.8 cm

1.05 mmol scale (20 ml vial) : 3.6 cm x 0.8 cm

3. Reaction optimizations



Entry	Additive	Electrolyte	Solvent	I (mA)/t (h)	Anode/Cathode	Yield[b]
1	-	Bu_4NPF_6	DCM	2 mA/10.5 h	Graphite/Graphite	31%
2	-	Bu_4NPF_6	DCE	2 mA/9 h	Graphite/Graphite	36%
3	-	Bu_4NPF_6	DMF	2 mA/8 h	Graphite/Graphite	trace
4	-	Bu_4NPF_6	DMA	2 mA/10 h	Graphite/Graphite	38%
5	-	Bu_4NPF_6	HFIP	2 mA/10 h	Graphite/Graphite	15%
6	-	Bu_4NPF_6	MeOH	2 mA/8 h	Graphite/Graphite	40%
7	-	Bu_4NBF_4	DCE	2 mA/13 h	Graphite/Graphite	40%
8	-	Bu_4NClO_4	DCE	2 mA/12 h	Graphite/Graphite	30%
9	-	Et_4NOTs	DCE	2 mA/10.5 h	Graphite/Graphite	43%
10	-	Bu_4NBF_4	MeOH	2 mA/12 h	Graphite/Graphite	27%
11	-	Bu_4NClO_4	MeOH	2 mA/12 h	Graphite/Graphite	28%
12	-	Et_4NOTs	MeOH	2 mA/10 h	Graphite/Graphite	26%
13	-	Et_4NOTs	DCE	2 mA/7 h	Graphite/Glassy-C	42%
14	-	Et_4NOTs	DCE	2 mA/8 h	Graphite/Ni	70%
15	-	Et_4NOTs	DCE	2 mA/8 h	Graphite/Fe	38%
16	-	Et_4NOTs	DCE	2 mA/18 h	Graphite/Ni-foam	43%
17	-	Et_4NOTs	DCE	2 mA/15 h	RVC/Ni	57%
18	-	Bu_4NPF_6	DCE	2 mA/13 h	Graphite/Ni	47%
19	-	Bu_4NBF_4	DCE	2 mA/12 h	Graphite/Ni	22%
20	-	Bu_4NClO_4	DCE	2 mA/13 h	Graphite/Ni	23%
21[c]	-	Et_4NOTs	DCE	2 mA/8 h	Graphite/Ni	n.d.
22[d]	-	Et_4NOTs	DCE	2 mA/15 h	Graphite/Ni	46%
23	-	Et_4NOTs	DCE	3 mA/8 h	Graphite/Ni	60%
24	-	Et_4NOTs	DCE	1 mA/34 h	Graphite/Ni	50%
25	1 eq. 2,4,6-collidine	Et_4NOTs	DCE	2 mA/13 h	Graphite/Ni	45%
26	1 eq. TEA	Et_4NOTs	DCE	2 mA/13 h	Graphite/Ni	34%
27	1 eq. AcOH	Et_4NOTs	DCE	2 mA/19 h	Graphite/Ni	43%
28	1 eq. TFA	Et_4NOTs	DCE	2 mA/15 h	Graphite/Ni	43%
29	1 eq. H_2SO_4	Et_4NOTs	DCE	2 mA/13 h	Graphite/Ni	32%
30	1 eq. TsOH	Et_4NOTs	DCE	2 mA/13 h	Graphite/Ni	29%
31[e]	-	Et_4NOTs	DCE	-- /8 h	Graphite/Ni	n.d.

[a] Reaction conditions: Undivided cell, **1a** (0.1 mmol), electrolyte (0.1 M), solvent (3 mL), room temperature, under N_2. [b] Isolated yields. [c] Under air. [d] 2 mL solvent instead of 3 mL. [e] No electric current. [f] DCE = 1,2-dichloroethane; Glassy-C = glassy carbon electrode; Ni-foam = nickel foam electrode; TEA = triethylamine; AcOH = acetic acid; TFA = trifluoroacetic acid; TsOH = p-toluenesulfonic acid; n.d. = not detected.

Table S1. Optimization for benzothiophene synthesis with model substrate **1a**

4. Mechanism Study

4.1. Cyclic voltammetry studies

The cyclic voltammograms were recorded in an electrolyte solution of Et_4NOTs (0.1 M) in anhydrous 1,2-dichloroethane (3 mL) with 0.1 mmol of substrate using a glassy carbon working electrode, a Pt wire counter electrode, and a 3 M KCl Ag/AgCl reference electrode with scan rate of 100 mV/s. The obtained value was converted to SCE by subtracting 0.04 V.

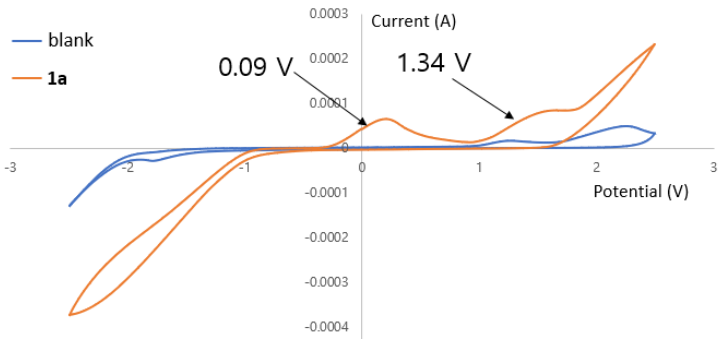
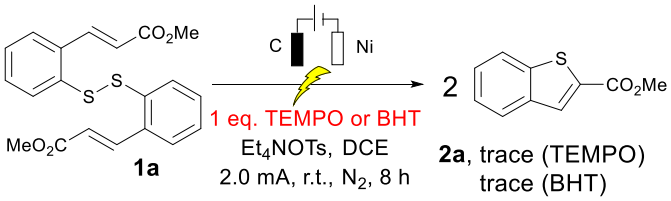


Figure S1. Electrochemical measurements of **1a** with cyclic voltammogram.

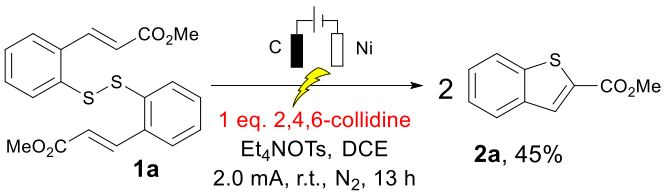
4.2. Control experiments

Exp. 1. Radical scavenger experiments



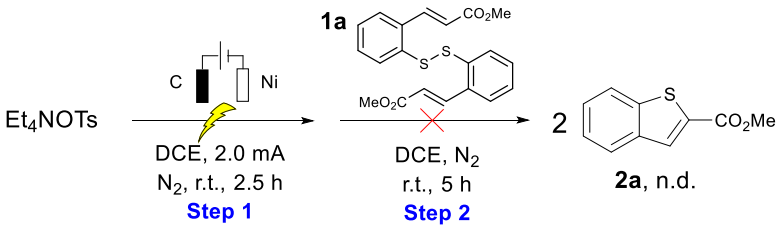
Experiments were carried out with the General Procedure (A) with 1 equiv. TEMPO or BHT as additives.

Exp. 2. Base additive experiment



Experiment was carried out with the General Procedure (A) with 1 equiv. 2,4,6-collidine as additive.

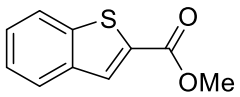
Exp. 3. Pre-electrolysis of solvent-electrolyte system



Experiment was carried out with the General Procedure (A) without disulfide **1a** for 2.5 h. Then, electrolysis was stopped and **1a** was added and stirred for 5 h.

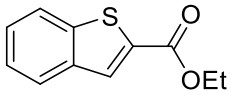
5. Characterization of products

Methyl benzo[b]thiophene-2-carboxylate (2a)



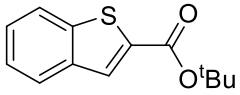
General procedure (A), 8 h, 26.9 mg, 70% yield; General procedure (B), 14 h, 76mg, 66% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.88 (t, J = 5.2 Hz, 2H), 7.51 – 7.35 (m, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 142.1, 138.6, 133.3, 130.6, 126.9, 125.5, 124.8, 122.7, 52.4; HRMS (DART) calcd for $C_{10}H_9O_2S^+$ 193.0318, observed 193.0316; Spectral data were consistent with data reported in the literature.[1]

Ethyl benzo[b]thiophene-2-carboxylate (2b)



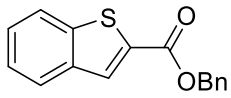
General procedure (A), 11 h, 22.2 mg, 54% yield; Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.90 – 7.80 (m, 2H), 7.48 – 7.34 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 142.2, 138.7, 133.9, 130.3, 126.8, 125.5, 124.8, 122.7, 61.5, 14.3; HRMS (DART) calcd for $C_{11}H_{11}O_2S^+$ 207.0475, observed 207.0479; Spectral data were consistent with data reported in the literature.[2]

tert-butyl benzo[b]thiophene-2-carboxylate (2c)



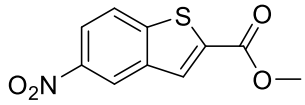
General procedure (A), 8 h, 23 mg, 49% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.89 – 7.77 (m, 2H), 7.47 – 7.29 (m, 2H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 142.1, 138.8, 135.8, 129.6, 126.6, 125.3, 124.7, 122.6, 82.3, 28.2; HRMS (DART) calcd for $C_{13}H_{15}O_2S^+$ 235.0788, observed 235.0788; Spectral data were consistent with data reported in the literature.[3]

Benzyl benzo[b]thiophene-2-carboxylate (2d)



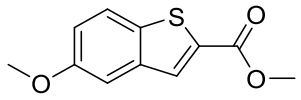
General procedure (A), 8 h, 32.2 mg, 60% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.93 – 7.77 (m, 2H), 7.52 – 7.32 (m, 7H), 5.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 142.3, 138.7, 135.6, 133.4, 130.7, 128.6, 128.4, 128.2, 127.0, 125.5, 124.9, 122.7, 67.1; HRMS (ESI) calcd for $C_{16}H_{12}NaO_2S^+$ 291.0451, observed 291.0452; Spectral data were consistent with data reported in the literature.[4]

Methyl 5-nitrobenzo[b]thiophene-2-carboxylate (2e)



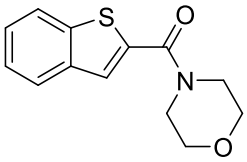
General procedure (A), 8 h, 33.8 mg, 71% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.31 (d, *J* = 8.6 Hz, 1H), 8.19 (s, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 147.3, 145.9, 138.3, 137.2, 130.7, 123.6, 121.2, 120.9, 52.9; HRMS (DART) calcd for $C_{10}H_8NO_4S^+$ 238.0169, observed 238.0171; Spectral data were consistent with data reported in the literature.[5]

Methyl 5-methoxybenzo[b]thiophene-2-carboxylate (2f)



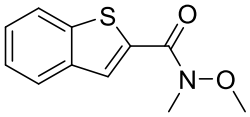
General procedure (A), 8 h, 29 mg, 65% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.29 – 7.27 (m, 1H), 7.12 (dd, J = 8.9, 2.4 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 159.0, 143.2, 135.1, 134.0, 120.7, 117.6, 116.0, 112.6, 55.6, 51.9; HRMS (DART) calcd for $C_{11}H_{11}O_3S^+$ 223.0424, observed 223.0428; Spectral data were consistent with data reported in the literature.[1]

Benzo[b]thiophen-2-yl(morpholino)methanone (2g)



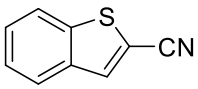
General procedure (A), 8 h, 33.6 mg, 68% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.77 (m, 2H), 7.48 (s, 1H), 7.42 – 7.34 (m, 2H), 3.81 – 3.70 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 140.1, 138.5, 136.1, 125.8, 125.3, 124.8, 124.6, 122.3, 66.8, 45.1; HRMS (DART) calcd for $C_{13}H_{14}NO_2S^+$ 248.0740, observed 248.0738; Spectral data were consistent with data reported in the literature.[6]

N-methoxy-N-methylbenzo[b]thiophene-2-carboxamide (2h)



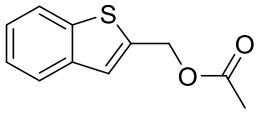
General procedure (A), 6 h, 25.3 mg, 57% yield; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.89 – 7.84 (m, 2H), 7.46 – 7.36 (m, 2H), 3.82 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 142.5, 138.1, 133.4, 131.1, 126.5, 125.3, 124.6, 122.3, 61.8, 33.2; HRMS (DART) calcd for $C_{11}H_{12}NO_2S^+$ 222.0583, observed 222.0582; Spectral data were consistent with data reported in the literature.[7]

Benzo[b]thiophene-2-carbonitrile (2i)



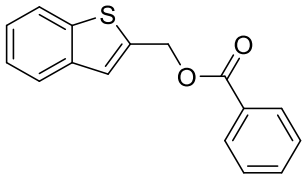
General procedure (A), 12 h, 19.8 mg, 62% yield; General procedure (B), 21 h, 50.2 mg, 53% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 3H), 7.53 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 137.5, 135.0, 127.9, 125.7, 125.3, 122.4, 114.4, 109.7; HRMS (ESI) calcd for $C_9H_5NNaS^+$ 182.0035, observed 182.0035; Spectral data were consistent with data reported in the literature.[8]

Benzo[b]thiophen-2-ylmethyl acetate (2j)



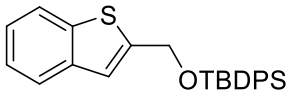
General procedure (A), 10 h, 22.4 mg, 54% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 1H), 7.77 – 7.73 (m, 1H), 7.37 – 7.31 (m, 2H), 7.29 (s, 1H), 5.34 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 140.4, 139.2, 138.8, 124.7, 124.4, 124.3, 123.8, 122.4, 61.3, 20.9; HRMS (DART) calcd for $C_{11}H_{11}O_2S^+$ 207.0475, observed 207.0478; Spectral data were consistent with data reported in the literature.[9]

Benzo[b]thiophen-2-ylmethyl benzoate (2k)



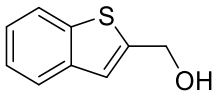
General procedure (A), 10 h, 24.6 mg, 46% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.2 Hz, 2H), 7.86 – 7.70 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.38 (s, 1H), 7.36 – 7.29 (m, 2H), 5.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 140.4, 139.2, 138.9, 133.2, 129.8, 128.5, 128.4, 124.7, 124.4, 124.3, 123.8, 122.4, 61.9; HRMS (DART) calcd for $C_{16}H_{13}O_2S^+$ 269.0631, observed 269.0632;

(benzo[b]thiophen-2-ylmethoxy)(tert-butyl)diphenylsilane (2l)



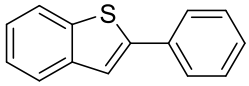
General procedure (A), 6 h, 17.5 mg, 22% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.64 (m, 6H), 7.52 – 7.21 (m, 8H), 7.05 (s, 1H), 4.97 (s, 2H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 137.1, 136.9, 135.6, 132.9, 129.9, 127.8, 124.9, 124.7, 122.6, 121.3, 115.4, 60.3, 26.8, 19.4; HRMS (DART) calcd for $C_{25}H_{27}OSSi^+$ 403.1547, observed 403.1549;

Benzo[b]thiophen-2-ylmethanol (2m)



General procedure (A), 7 h, 11 mg, 33% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.37 – 7.26 (m, 2H), 7.19 (s, 1H), 4.91 (s, 2H), 2.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.9, 139.5, 124.3, 124.3, 123.5, 122.5, 121.5, 60.8; HRMS (DART) calcd for $C_9H_9OS^+$ 165.0369, observed 165.0372; Spectral data were consistent with data reported in the literature.[10]

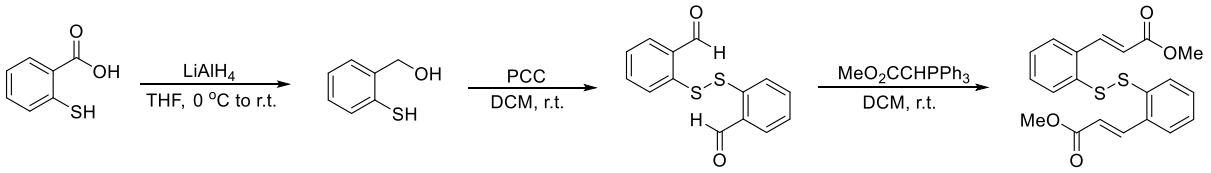
2-Phenylbenzo[b]thiophene (2o)



General procedure (A), 5 h, 19.2 mg, 46% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.58 (s, 1H), 7.46 (t, J = 7.3 Hz, 2H), 7.42 – 7.30 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 140.7, 139.5, 134.3, 128.9, 128.2, 126.5, 124.5, 124.3, 123.5, 122.2, 119.4; HRMS (DART) calcd for $C_{14}H_{11}S^+$ 211.0576, observed 211.0570; Spectral data were consistent with data reported in the literature.[11]

6. Synthesis of substrates

General Procedure (C) for alkenyl disulfide synthesis



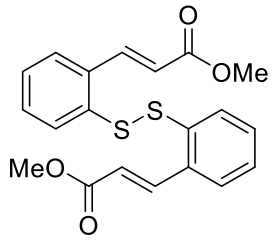
Substrates were prepared according to the reported procedure.[12]

To a stirred suspension of $LiAlH_4$ (100 mg, 2.6 mmol, 1.2 equiv.) in anhydrous THF (2.4 mL) at 0 ℃ was added a solution of thiosalicylic acid (335 mg, 2.2 mmol, 1 equiv.) in anhydrous THF (3 mL). Once the reaction was determined to be completed by TLC, the mixture was cooled to 0 ℃ and was carefully added water (0.1 mL), 15% aqueous NaOH (0.1 mL) and then water (0.3 mL). The resulting aqueous phase was acidified with 1 N HCl solution until pH 2-3 and extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The resulting yellow liquid was used without further purification.

To a mixture of (2-mercaptophenyl)methanol (294 mg, 2.1 mmol, 1 equiv.) in dry CH_2Cl_2 (5.3 mL, 0.4 M) was added PCC (924 mg, 4.2 mmol, 2 equiv.). After stirring at room temperature, the mixture was passed through a plug of silica gel, rinsing with CH_2Cl_2, to yield the dialdehyde as a colorless solid (156 mg, 54% yield for 2 steps).

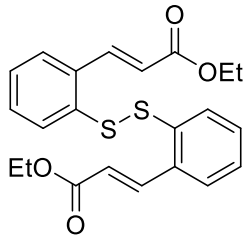
To a solution of dialdehyde (156 mg, 0.57 mmol, 1 equiv.) in dry CH_2Cl_2 (1.4 mL, 0.4 M) was added PPh_3=$CHCO_2Me$ (419 mg, 1.25 mmol, 2.2 equiv.). After stirring at room temperature, the solution was concentrated under reduced pressure. The crude material was purified through the flash chromatography to yield **1a** as a colorless solid (137 mg, 62% yield).

Dimethyl 3,3'-(disulfanediylbis(2,1-phenylene))(2E,2'E)-diacrylate (1a)



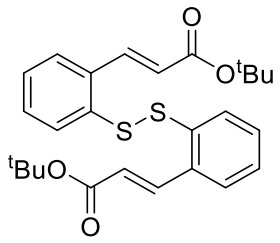
Prepared according to the general procedure (C), PPh_3=$CHCO_2Me$ (1.25 mmol, 2.2 equiv.) was used, 137 mg, 62% yield; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 15.9 Hz, 2H), 7.63 – 7.27 (m, 8H), 6.31 (d, J = 15.9 Hz, 2H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 141.3, 136.7, 136.0, 132.6, 130.5, 128.9, 127.1, 120.3, 51.7; MS (APCI): m/z 387.3 $[M+H]^+$; Spectral data were consistent with data reported in the literature.[12]

Diethyl 3,3'-(disulfanediylbis(2,1-phenylene))(2E,2'E)-diacrylate (1b)



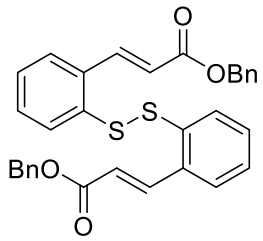
Prepared according to the general procedure (C), PPh_3=$CHCO_2Et$ (2.2 mmol, 2.2 equiv.) was used, 253 mg, 61% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 15.8 Hz, 2H), 7.63 – 7.44 (m, 4H), 7.35 – 7.23 (m, 4H), 6.31 (d, J = 15.8 Hz, 2H), 4.26 (q, J = 5.8 Hz, 4H), 1.34 (t, J = 5.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 140.9, 136.7, 136.0, 132.3, 130.4, 128.7, 127.1, 120.8, 60.5, 14.3; MS (APCI): m/z 415.5 $[M+H]^+$

Di-tert-butyl 3,3'-(disulfanediylbis(2,1-phenylene))(2E,2'E)-diacrylate (1c)



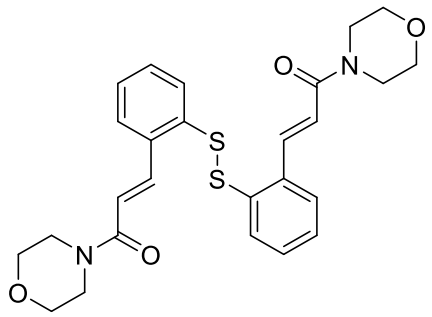
Prepared according to the general procedure (C), $PPh_3{=}CHCO_2{}^tBu$ (2.2 mmol, 2.2 equiv.) was used, 198 mg, 42% yield; Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 15.8 Hz, 2H), 7.67 – 7.56 (m, 2H), 7.55 – 7.45 (m, 2H), 7.30 – 7.23 (m, 4H), 6.25 (d, J = 15.8 Hz, 2H), 1.54 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 139.9, 136.6, 135.8, 131.7, 130.3, 128.5, 127.1, 122.6, 80.6, 28.2; MS (APCI): m/z 471.6 $[M+H]^+$

Dibenzyl 3,3'-(disulfanediylbis(2,1-phenylene))(2E,2'E)-diacrylate (1d)



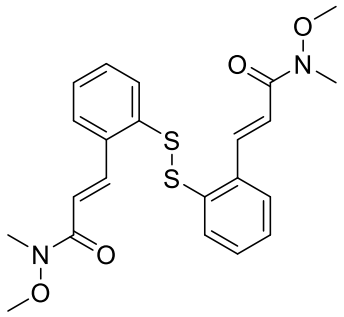
Prepared according to the general procedure (C), $PPh_3{=}CHCO_2Bn$ (2.2 mmol, 2.2 equiv.) was used, 366 mg, 68% yield; Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 15.9 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.49 – 7.31 (m, 12H), 7.25 – 7.21 (m, 4H), 6.31 (d, J = 15.9 Hz, 2H), 5.24 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 141.5, 136.6, 136.0, 132.7, 130.5, 128.8, 128.5, 128.5, 128.2, 128.2, 127.0, 120.2, 66.2; MS (APCI): m/z 539.5 $[M+H]^+$

(2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(1-morpholinoprop-2-en-1-one) (1g)



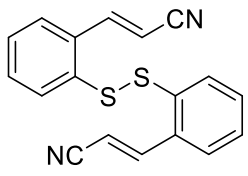
Prepared according to the general procedure (C), 1-Morpholin-4-yl-2-(triphenyl-phosphanylidene)-ethanone (2.2 mmol, 2.2 equiv.) was used, 442 mg, 89% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 15.3 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.54 – 7.41 (m, 2H), 7.30 – 7.16 (m, 4H), 6.75 (d, J = 15.3 Hz, 2H), 3.88 – 3.51 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 139.3, 136.3, 136.2, 131.0, 129.7, 128.1, 127.2, 120.1, 66.7, 46.2, 42.3; MS (APCI): m/z 492.3 $[M+H]^+$

(2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(N-methoxy-N-methylacrylamide) (1h)



Prepared according to the general procedure (C), N-methoxy-N-methyl-2-(triphenylphosphoranylidene)acetamide (2.2 mmol, 2.2 equiv.) was used, 325 mg, 73% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 15.6 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.58 – 7.51 (m, 2H), 7.32 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 6.95 (d, J = 15.6 Hz, 2H), 3.76 (s, 6H), 3.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 139.7, 136.7, 135.8, 130.4, 130.0, 127.9, 127.3, 119.0, 61.9, 32.4; MS (APCI): m/z 445.6 $[M+H]^+$

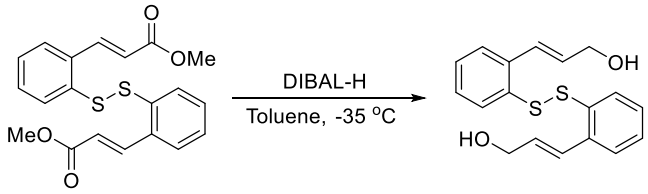
(2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))diacrylonitrile (1i)



Prepared according to the general procedure (C), PPh_3=CHCN (2.2 mmol, 2.2 equiv.) was used, 215 mg, 67% yield; Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 16.6 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.53 – 7.48 (m, 2H), 7.45 – 7.36 (m, 4H), 5.74 (d, J = 16.6 Hz, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 136.1, 135.8, 134.7, 131.6, 130.1, 126.3, 117.6, 98.3; MS (APCI): m/z 321.4 $[M+H]^+$

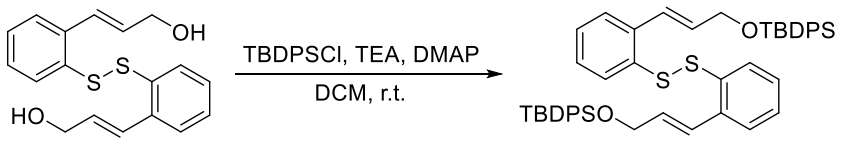
Synthesis of (2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(prop-2-en-1-ol) (1m)



Substrate was prepared according to the reported procedure.[12]

To a solution of dimethyl 3,3'-(disulfanediylbis(2,1-phenylene))(2E,2'E)-diacrylate (386 mg, 1 mmol, 1 equiv.) in dry toluene (5 ml, 0.2 M) at -35 °C was added dropwise DIBAL-H (1.0 M solution in toluene, 6 ml, 6 mmol, 6 equiv.). After stirring at -35 °C for 30 min, 0.04 mL of water, 0.04 mL of 15% aqueous NaOH and 0.1 mL of water was added slowly at -78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The resulting aqueous phase was extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography to yield **1m** as a colorless oil (245 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.4 Hz, 2H), 7.45 (d, J = 7.3 Hz, 2H), 7.32 – 7.14 (m, 4H), 6.97 (d, J = 15.7 Hz, 2H), 6.25 (dt, J = 15.6, 5.4 Hz, 2H), 4.24 (d, J = 4.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 134.6, 131.5, 131.2, 128.2, 128.0, 127.6, 126.3, 63.3; MS (APCI): m/z 331.3 $[M+H]^+$; Spectral data were consistent with data reported in the literature.[12]

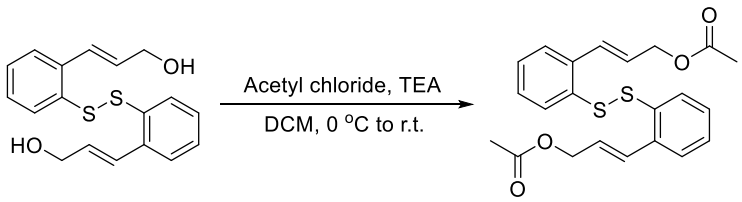
Synthesis of 1,2-bis(2-((E)-3-((tert-butyldiphenylsilyl)oxy)prop-1-en-1-yl)phenyl)disulfane (1l)



Substrate was prepared according to the reported procedure.[12]

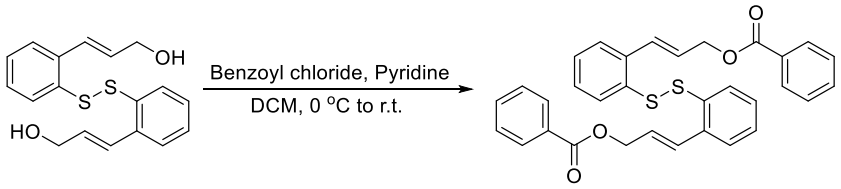
To a solution of (2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(prop-2-en-1-ol) (66 mg, 0.2 mmol, 1 equiv.) in dry CH_2Cl_2 (1 ml, 0.2 M) was added NEt_3 (0.11 mL, 0.8 mmol, 4 equiv.), DMAP (5 mg, 0.04 mmol, 0.2 equiv.) and TBDPSCl (0.21 mL, 0.8 mmol, 4 equiv.). After stirring at room temperature, the reaction mixture was quenched by addition of water. The aqueous phase was extracted with ethyl acetate with three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography to yield **1l** as a colorless oil (129 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 8H), 7.57 – 7.51 (m, 2H), 7.45 – 7.33 (m, 14H), 7.25 – 7.06 (m, 6H), 6.19 (dt, J = 16.1, 4.4 Hz, 2H), 4.60 – 4.19 (m, 4H), 1.11 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.6, 134.8, 133.6, 131.8, 129.7, 129.7, 127.9, 127.7, 127.6, 126.4, 126.2, 64.4, 26.9, 19.3; MS (APCI): m/z 807.5 $[M+H]^+$; Spectral data were consistent with data reported in the literature.[12]

Synthesis of (2E,2'E)-(disulfanediylbis(2,1-phenylene))bis(prop-2-ene-3,1-diyl) diacetate (1j)



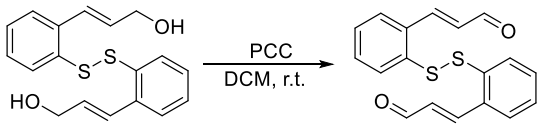
To a solution of (2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(prop-2-en-1-ol) (66 mg, 0.2 mmol, 1 equiv.) in dry CH_2Cl_2 (1.3 ml, 0.15 M) at 0 °C was added NEt_3 (0.11 mL, 0.8 mmol, 4 equiv.) and acetyl chloride (0.04 ml, 0.6 mmol, 3 equiv.). The reaction mixture was stirred at room temperature. After completion of the reaction, water was added and the aqueous phase was extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography to yield **1j** as a colorless oil (73.8 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 7.32 – 7.14 (m, 4H), 7.04 (d, J = 15.8 Hz, 2H), 6.19 (dt, J = 15.6, 6.2 Hz, 2H), 4.67 (d, J = 6.1 Hz, 4H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 137.3, 135.0, 131.4, 130.6, 128.5, 128.4, 126.4, 126.0, 64.8, 20.9; MS (APCI): m/z 415.2 $[M+H]^+$

Synthesis of (2E,2'E)-(disulfanediylbis(2,1-phenylene))bis(prop-2-ene-3,1-diyl) dibenzoate (1k)



To a solution of (2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(prop-2-en-1-ol) (66 mg, 0.2 mmol, 1 equiv.) and pyridine (0.05 mL, 0.6 mmol, 3equiv.) in dry CH_2Cl_2 (1 ml, 0.2 M) at 0 ℃ was added benzoyl chloride (0.07 mL, 0.6 mmol, 3 equiv.) via syringe. The reaction mixture was stirred at room temperature and quenched by the addition of water. The aqueous phase was extracted with ethyl acetate with three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography to yield **1k** as a colorless oil (99 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.5 Hz, 4H), 7.56 (t, J = 6.0 Hz, 4H), 7.46 (dt, J = 15.5, 8.3 Hz, 6H), 7.28 – 7.08 (m, 6H), 6.30 (dt, J = 15.6, 6.1 Hz, 2H), 4.90 (d, J = 6.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 137.5, 135.1, 133.0, 131.8, 130.8, 130.1, 129.6, 128.5, 128.5, 128.4, 126.5, 126.0, 65.3; MS (APCI): m/z 539.2 $[M+H]^+$

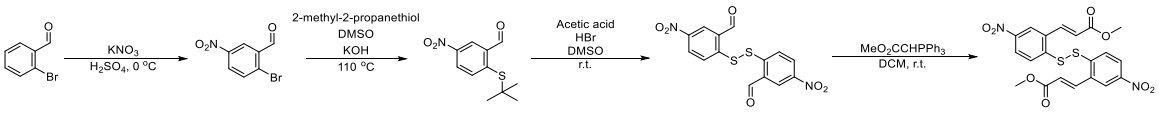
Synthesis of (2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))diacrylaldehyde (1n)



To a solution of (2E,2'E)-3,3'-(disulfanediylbis(2,1-phenylene))bis(prop-2-en-1-ol) (66 mg, 0.2 mmol, 1 equiv.) in dry CH_2Cl_2 (0.5 mL, 0.4 M) was added PCC (132 mg, 0.6 mmol, 3 equiv.). After stirring at room temperature, the mixture was passed through a plug of silica gel, rinsing with CH_2Cl_2, to yield **1n** as a colorless oil (32.6 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 7.6 Hz, 2H), 7.75 (d, *J* = 15.9 Hz, 2H), 7.70 – 7.65 (m, 2H), 7.64 – 7.53 (m, 2H), 7.45 – 7.33 (m, 4H), 6.53 (dd, *J* = 15.9, 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

193.29, 148.71, 137.05, 136.50, 134.96, 131.54, 130.19, 130.14, 127.36; MS (APCI): m/z 327.2 $[M+H]^+$

Synthesis of dimethyl 3,3'-(disulfanediylbis(5-nitro-2,1-phenylene))(2E,2'E)-diacrylate (1e)



Substrates were prepared according to reported procedures.[12-13]

KNO_3 (109 mg, 1.08 mmol, 1.15 equiv.) was added slowly to a stirred solution of 2-bromobenzaldehyde (174 mg, 0.94 mmol, 1 equiv.) in H_2SO_4 (0.94 mL, 1 M) at 0 °C. The reaction mixture was poured over ice water, extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude was purified by flash chromatography to yield 2-bromo-5-nitrobenzaldehyde as a yellow solid (201 mg, 93% yield).

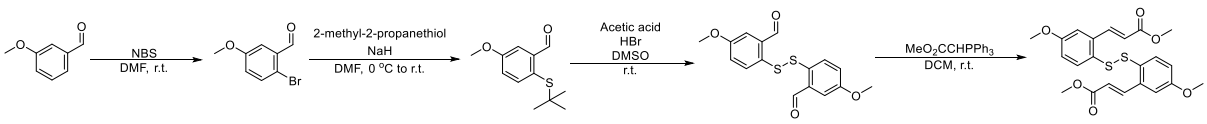
DMSO (0.25 mL, 3.48 mmol, 4 equiv.) and powdered KOH (53.7 mg, 0.96 mmol, 1.1 equiv.) were stirred at room temperature. After 5 min, 2-methyl-2-propanethiol (0.15 mL, 1.3 mmol, 1.5 equiv.) was added, and the mixture was stirred for 20 min. 2-bromo-5-nitrobenzaldehyde (200 mg, 0.87 mmol, 1 equiv.) was added, and the reaction was heated to 110 °C. After completion of the reaction, it was diluted with water and extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to yield 2-(tert-butylthio)-5-nitrobenzaldehyde as a yellow oil (162 mg, 78% yield).

2-(tert-butylthio)-5-nitrobenzaldehyde (162 mg, 0.68 mmol, 1 equiv.) was dissolved in acetic acid (0.23 mL, 4.08 mmol, 6 equiv.) and HBr (0.34 mL, 2.04 mmol, 3 equiv.) with DMSO (0.05 ml, 0.68 mmol, 1 equiv.) was added. The reaction mixture was stirred at room temperature. Once the reaction was determined to be completed by TLC, the mixture was poured into water and precipitate was collected and washed with water. The crude material was dried and purified by flash chromatography to yield 6,6'-disulfanediylbis(3-nitrobenzaldehyde) as a yellow solid.

(78 mg, 63% yield).

To a solution of 6,6'-disulfanediylbis(3-nitrobenzaldehyde) (78 mg, 0.21 mmol, 1 equiv.) in dry CH_2Cl_2 (0.53 mL) was added PPh_3=$CHCO_2Me$ (154 mg, 0.46 mmol, 2.2 equiv.). After stirring at room temperature, the solution was concentrated under reduced pressure. The crude material was purified through the flash chromatography to yield **1e** as a yellow oil (58 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 2.0 Hz, 2H), 8.15 (dd, J = 8.7, 2.2 Hz, 2H), 8.03 (d, J = 15.7 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 6.53 (d, J = 15.7 Hz, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 147.6, 142.9, 138.0, 135.7, 129.8, 124.7, 124.0, 122.3, 52.2; MS (APCI): m/z 477.8 $[M+H]^+$

Synthesis of dimethyl 3,3'-(disulfanediylbis(5-methoxy-2,1-phenylene))(2E,2'E)-diacrylate (1f)



Substrates were prepared according to reported procedures.[12, 13b, 14]

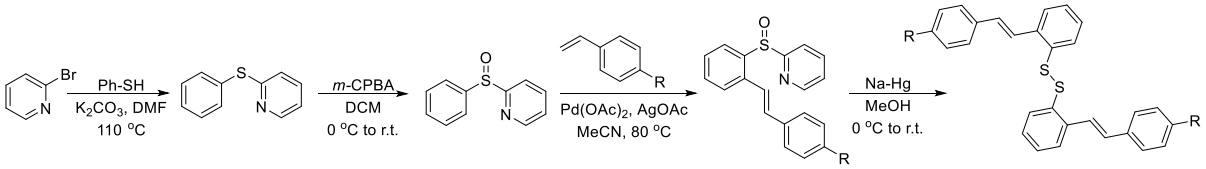
To a solution of 3-methoxybenzaldehyde (127 mg, 0.93 mmol, 1 equiv.) in DMF (1.2 mL, 0.8 M) was added NBS (196 mg, 1.1 mmol, 1.2 equiv.) at room temperature under N_2. To the reaction mixture was added H_2O at 0 ℃. The precipitate was collected by filtration, washed with water, and dried under vacuum to give 2-bromo-5-methoxybenzaldehyde as a colorless solid (156 mg, 78% yield).

To a stirred suspension of NaH (60% in mineral oil; 32 mg, 0.8 mmol, 1.1 equiv.) in DMF (1.5 mL, 0.5 M) at 0 ℃ was added 2-methyl-2-propanethiol (0.09 ml, 0.8 mmol, 1.1 equiv.) dropwise. After evolution of H_2 gas had ceased, 2-bromo-5-methoxybenzaldehyde (156 mg, 0.73 mmol, 1 equiv.) was added dropwise and the mixture was stirred at the room temperature. Saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate three times. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to yield 2-(tert-butylthio)-5-methoxybenzaldehyde as a yellow oil (73.7 mg, 45% yield).

2-(tert-butylthio)-5-methoxybenzaldehyde (74 mg, 0.33 mmol, 1 equiv.) was dissolved in acetic acid (0.11 mL, 1.98 mmol, 6 equiv.) and HBr (0.16 mL, 0.99 mmol, 3 equiv.) with DMSO (23.4 ml, 0.33 mmol, 1 equiv.) was added. The reaction mixture was then vigorously stirred at room temperature. Once the reaction was determined to be completed by TLC, the mixture was poured into water and precipitate was collected and washed with water. The crude material was dried and purified by flash chromatography to yield 6,6'-disulfanediylbis(3-methoxybenzaldehyde) as a yellow oil (33.7 mg, 61% yield).

To a solution of 6,6'-disulfanediylbis(3-methoxybenzaldehyde) (33 mg, 0.1 mmol, 1 equiv.) in dry CH_2Cl_2 (0.25 mL) was added PPh_3=$CHCO_2Me$ (73.6 mg, 0.22 mmol, 2.2 equiv.). After stirring at room temperature, the solution was concentrated under reduced pressure. The crude material was purified through the flash chromatography to yield **1f** as a colorless oil (32.6 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 16.0 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 2.5 Hz, 2H), 6.84 (dd, J = 8.6, 2.7 Hz, 2H), 6.17 (d, J = 15.9 Hz, 2H), 3.82 (s, 6H), 3.76 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 161.0, 142.1, 139.5, 138.1, 128.0, 119.6, 116.8, 111.6, 55.4, 51.6; MS (APCI): m/z 447.7 $[M+H]^+$

General Procedure (D) for alkenyl disulfide synthesis



Substrates were prepared according to the reported procedure.[15]

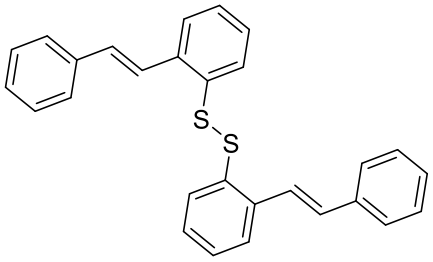
A solution of 2-bromopyridine (1.58 g, 10 mmol, 1 equiv.), thiophenol (1.32 g, 12 mmol, 1.2 equiv.), K_2CO_3 (1.84 g, 13.3 mmol, 1.33 equiv.) in anhydrous DMF (8 mL) was stirred for 24 h at 110 °C and was cooled to room temperature. The reaction mixture was filtered through celite and was added a saturated solution of $NaHCO_3$(aq) and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to yield 2-(phenylthio)pyridine as a clear oil (1.57 g, 84% yield).

To a solution of 2-(phenylthio)pyridine (1.57 g, 8.39 mmol, 1 equiv.) in anhydrous DCM (84 mL) at 0 °C was added *m*-CPBA (70 wt%, 2.17 g, 8.81 mmol, 1.05 equiv.) and the reaction was slowly warmed to room temperature and stirred overnight. To the solution, was added a saturated solution of Na_2CO_3(aq) and extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to yield 2-(phenylsulfinyl)pyridine as a white solid (1.52 g, 89% yield).

A solution of 2-(phenylsulfinyl)pyridine (407 mg, 2 mmol, 1 equiv.), styrene (458 uL, 4 mmol, 2 equiv.), $Pd(OAc)_2$ (45 mg, 0.2 mmol, 0.1 equiv.), AgOAc (835 mg, 5 mmol, 2.5 equiv.) in anhydrous MeCN (6.7 mL) was stirred for 12 h at 80 °C, and cooled to room temperature. The solution was concentrated in vacuo and purified by flash chromatography to yield (E)-2-((2-styrylphenyl)sulfinyl)pyridine as a white solid (273 mg, 45% yield).

To a solution of 1.5 wt% Na-Hg (19.9 g, 13 mmol, 14.6 equiv.) in anhydrous MeOH (2 mL) at 0 °C was added a solution of (E)-2-((2-styrylphenyl)sulfinyl)pyridine (271 mg, 0.89 mmol, 1 equiv.) in anhydrous MeOH (3.8 mL) and the solution was warmed to room temperature and stirred for 20 minutes. The reaction was diluted with ethyl acetate and filtered through celite, and was added water and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography to yield 1,2-bis(2-((E)-styryl)phenyl)disulfane as a white semi-solid (76.5 mg, 41% yield).

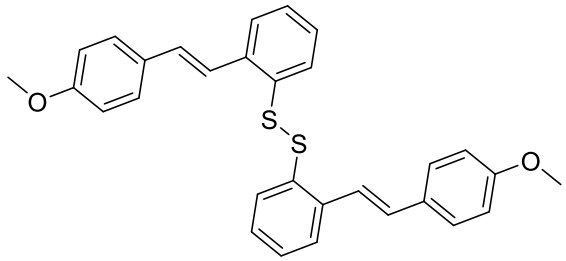
1,2-bis(2-((E)-styryl)phenyl)disulfane (1o)



Prepared according to the general procedure (D), 0.89 mmol scale, 76.5 mg, 41% yield; White semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.4 Hz, 2H), 7.58 – 7.52 (m, 3H), 7.46 – 7.41 (m, 3H), 7.37 – 7.32 (m, 3H), 7.30 – 7.25 (m, 3H), 7.24 – 7.12 (m, 6H), 6.96 (d, J = 16.2

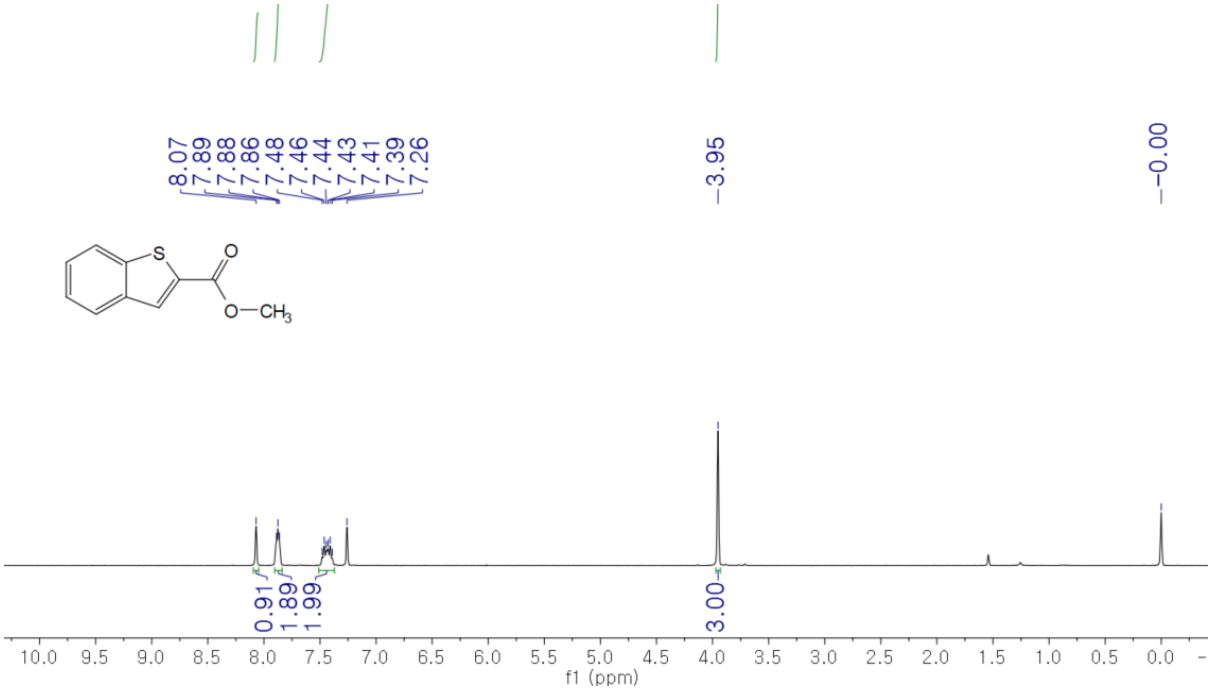
Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 137.2, 135.1, 132.2, 131.0, 128.6, 128.6, 128.1, 127.9, 126.8, 125.9, 125.8; MS (APCI): m/z 211.5 [$C_{14}H_{11}S^+$]

1,2-bis(2-((E)-4-methoxystyryl)phenyl)disulfane (1p)

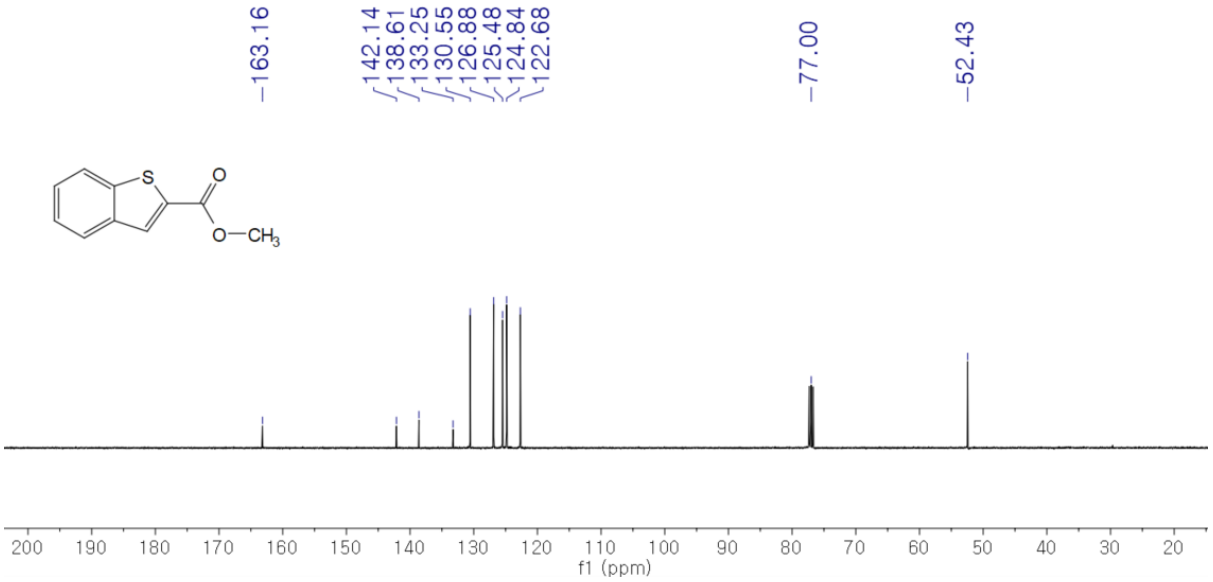


Prepared according to the general procedure (D), 0.46 mmol scale, 50.8 mg, 46% yield; White semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.7 Hz, 2H), 7.55 (d, J = 7.7 Hz, 2H), 7.45 – 7.34 (m, 6H), 7.22 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 7.5 Hz, 2H), 6.92 (d, J = 16.2 Hz, 2H), 6.88 (d, J = 8.4 Hz, 4H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 138.9, 134.8, 132.0, 130.5, 130.0, 128.5, 128.1, 127.7, 125.7, 123.6, 114.0, 55.3; Spectral data were consistent with data reported in the literature.[15]

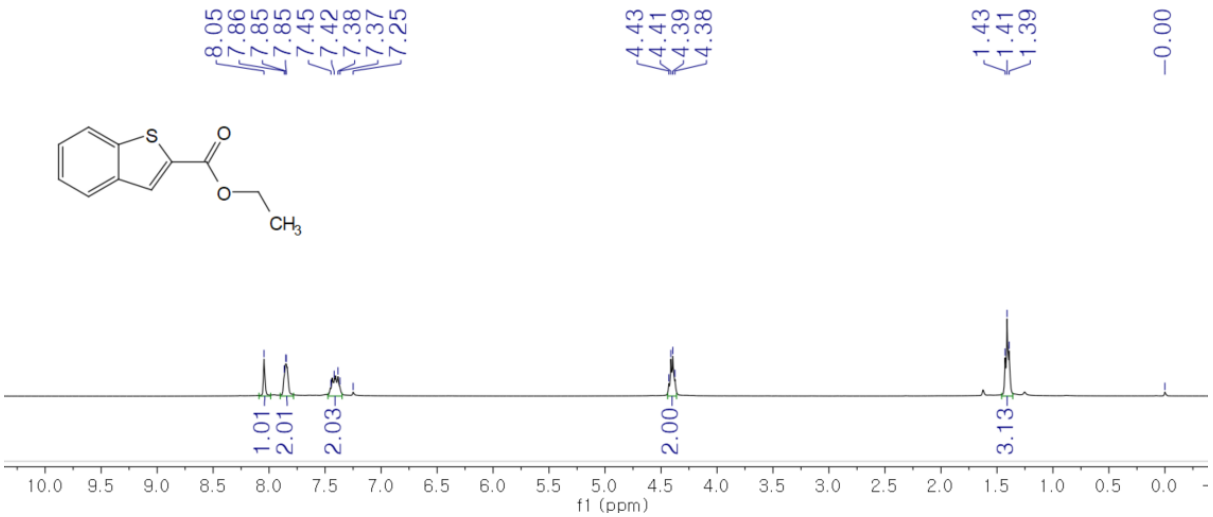
7. NMR Spectra



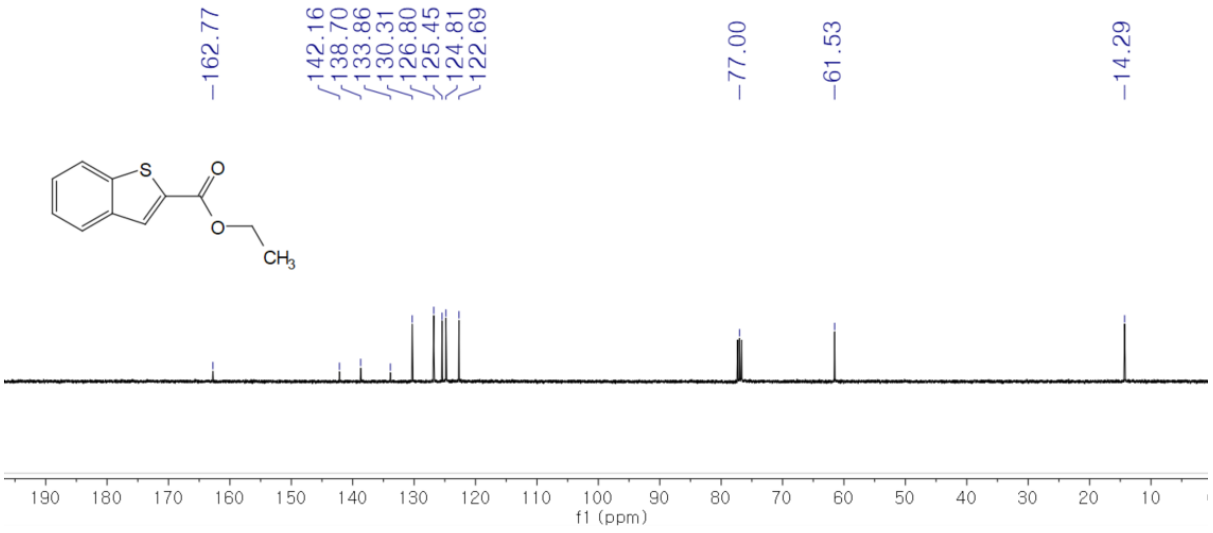
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2a**



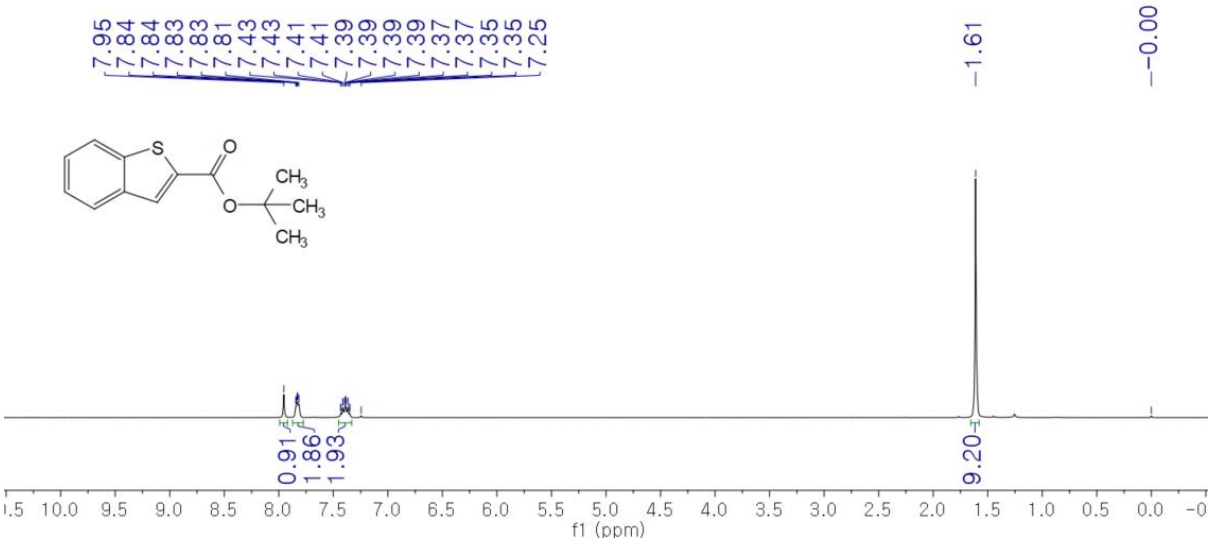
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2a**



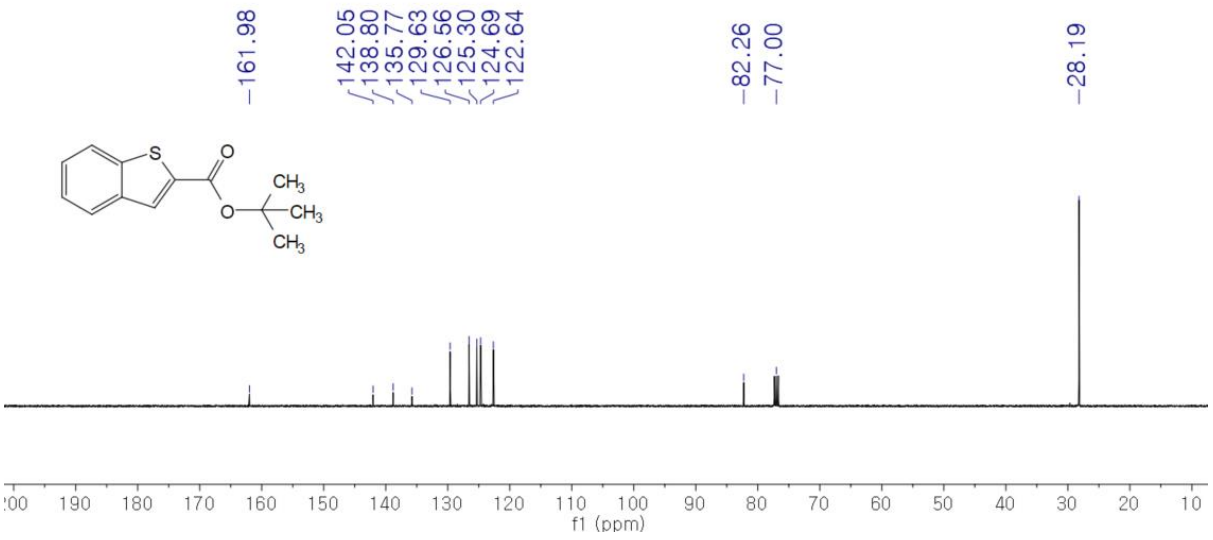
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2b**



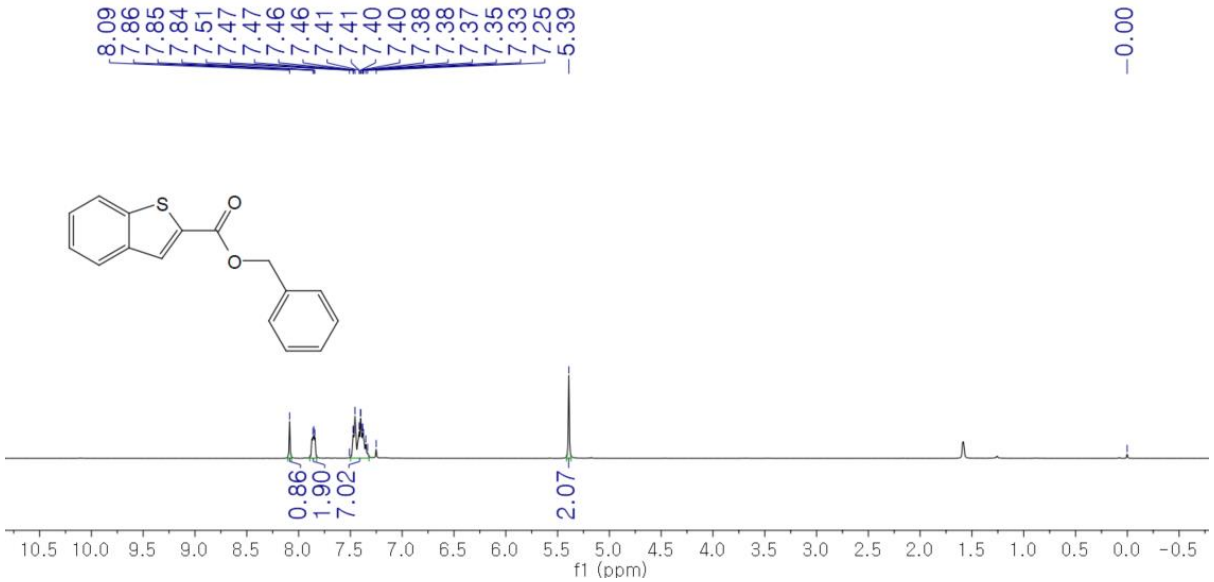
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2b**



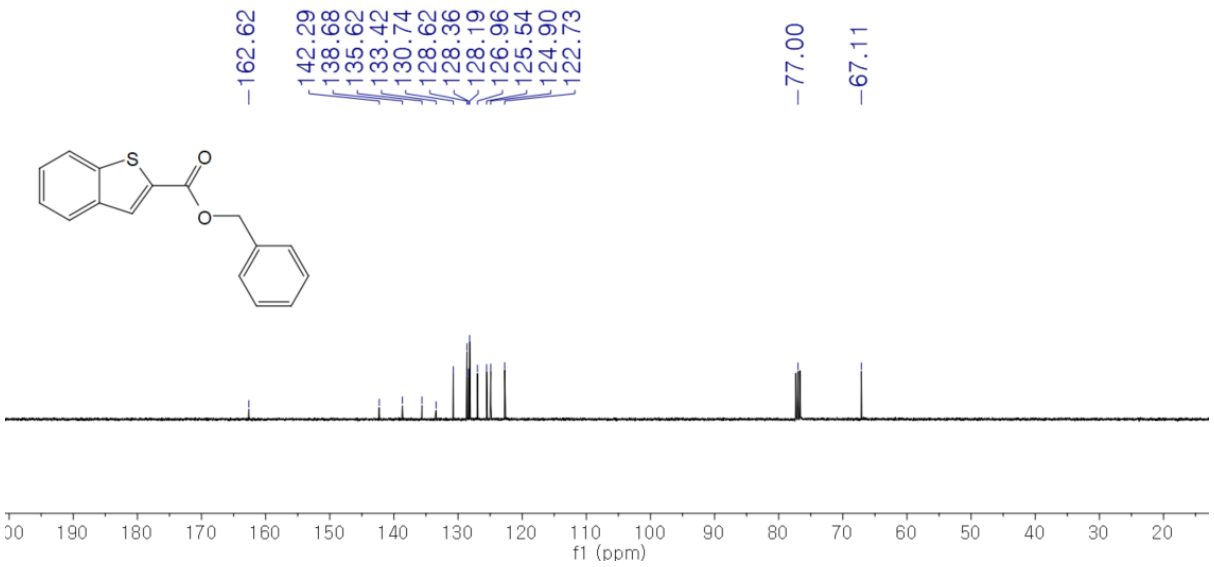
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2c**



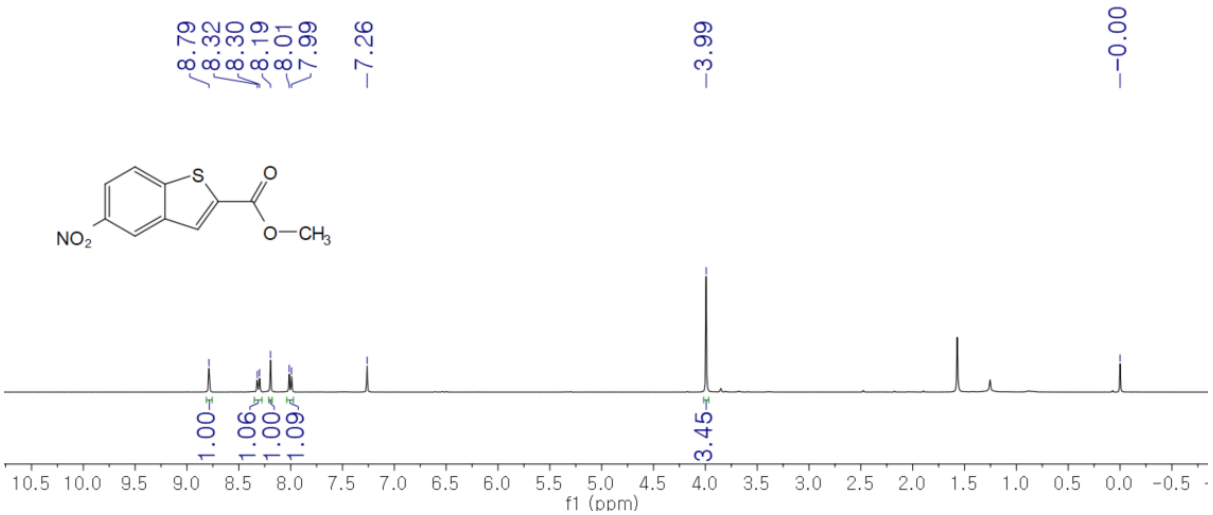
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2c**



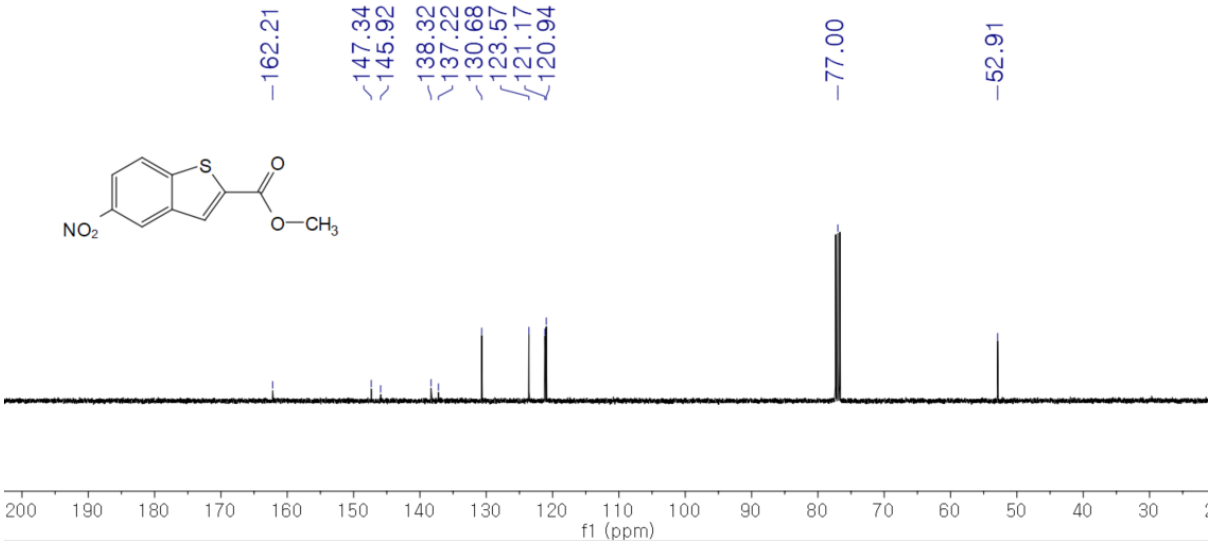
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2d**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2d**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2e**



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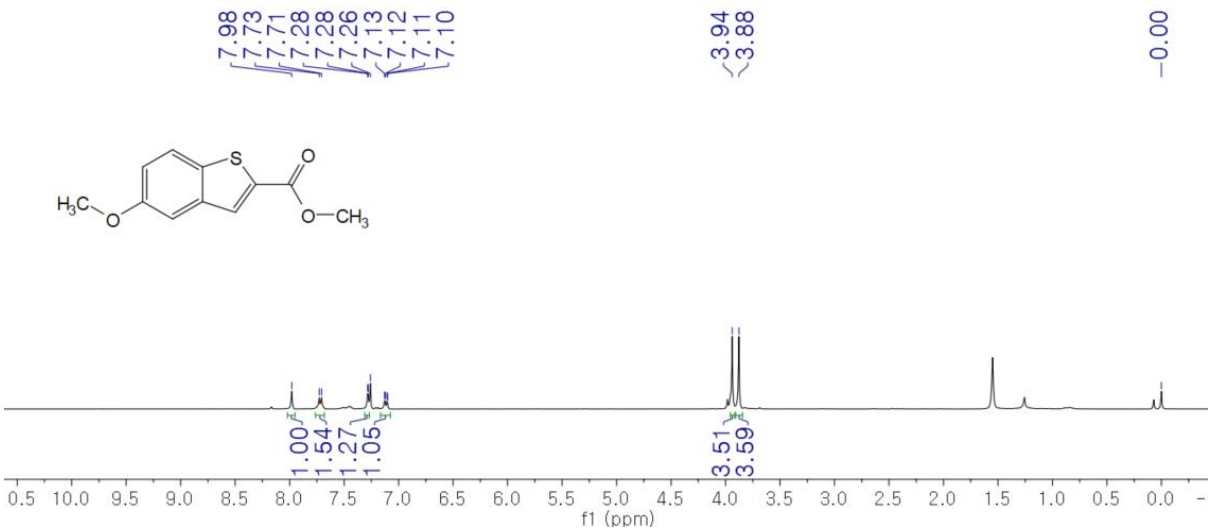
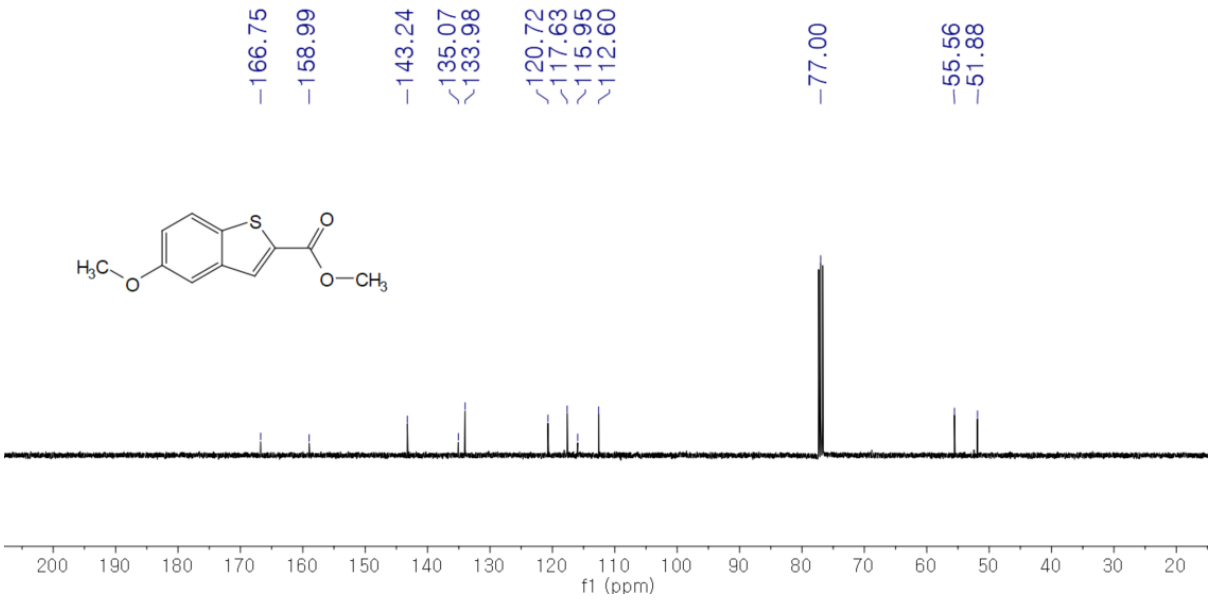
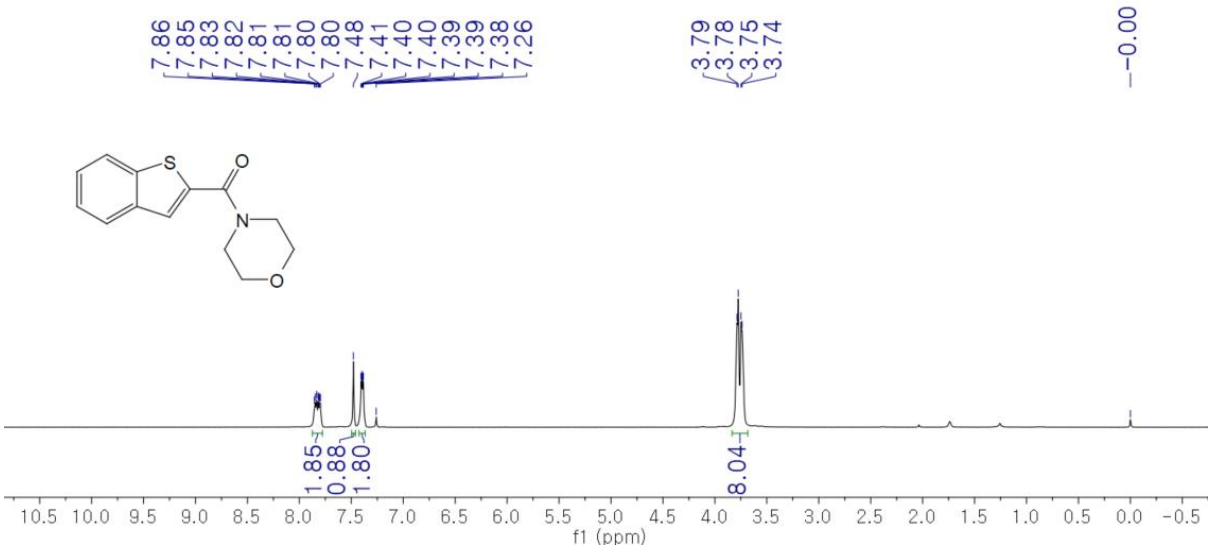


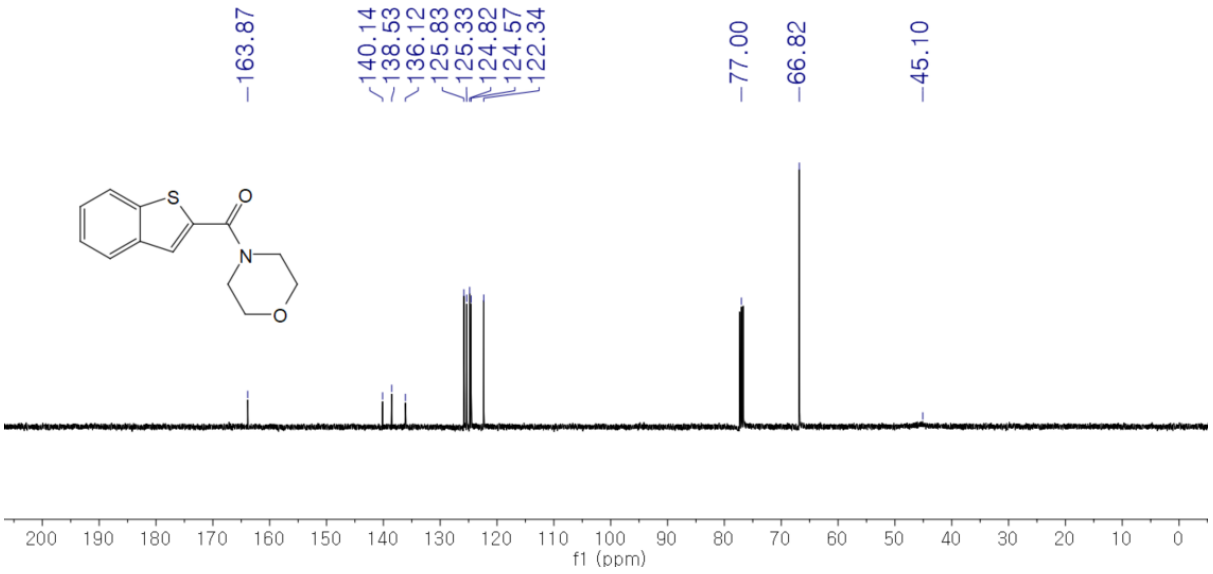
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2f**



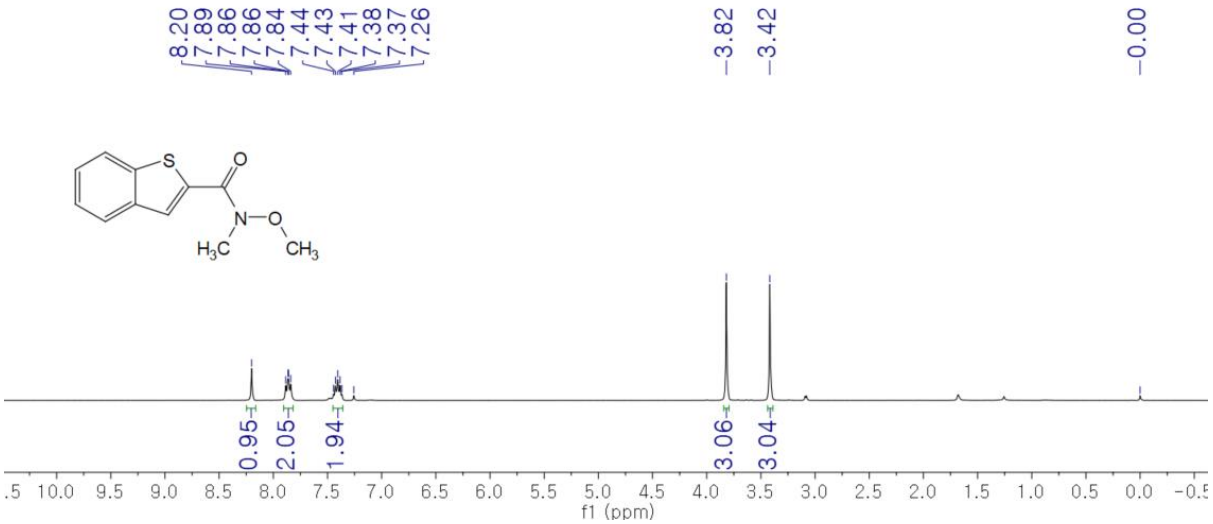
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2f**



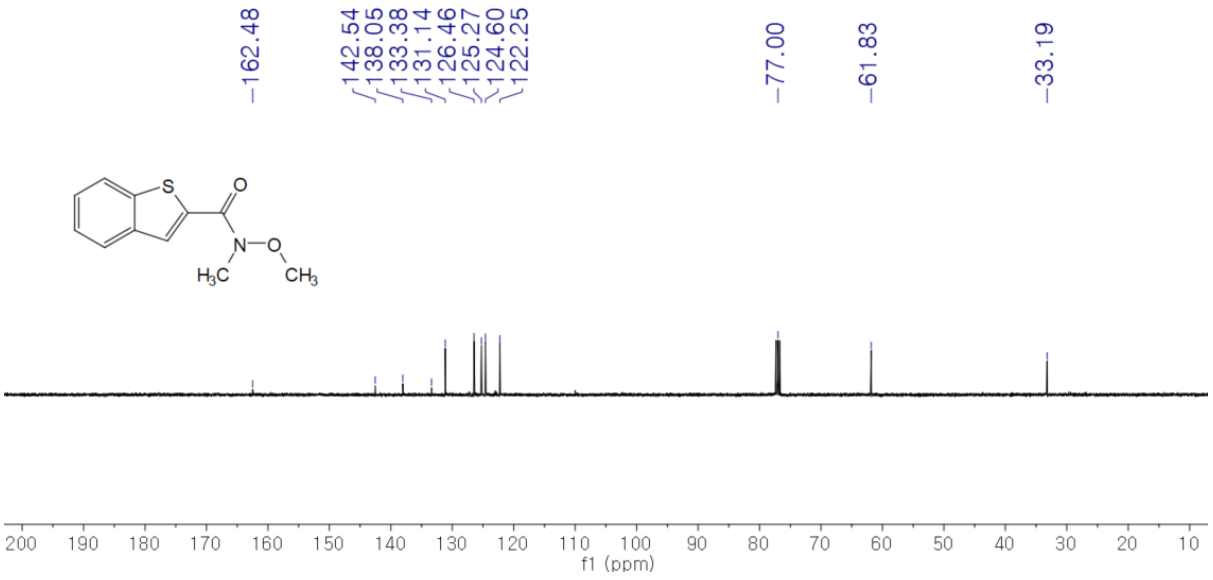
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2g**



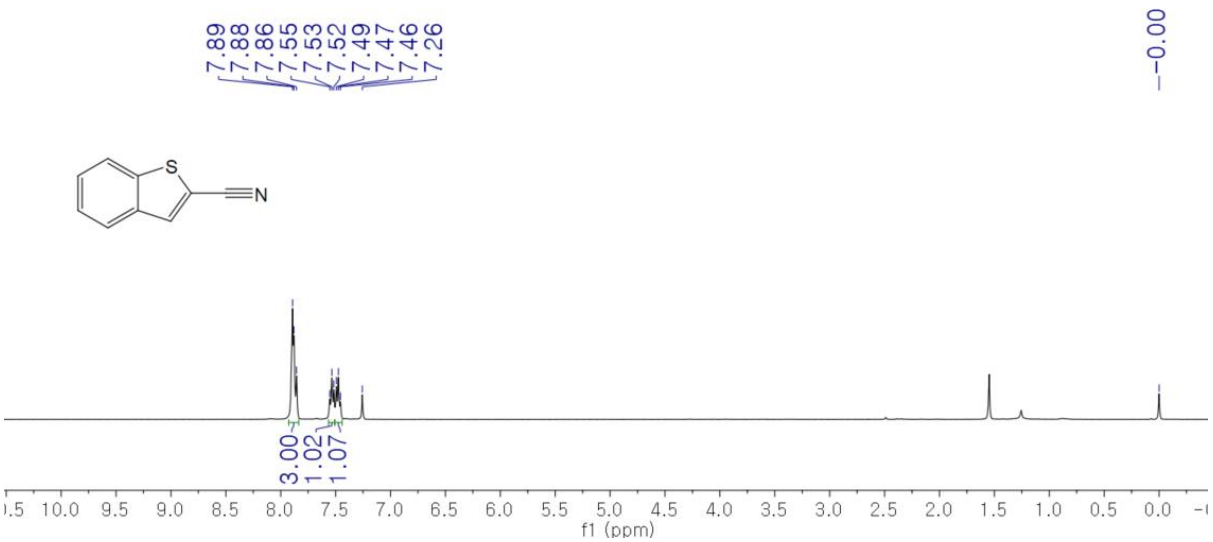
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2g**



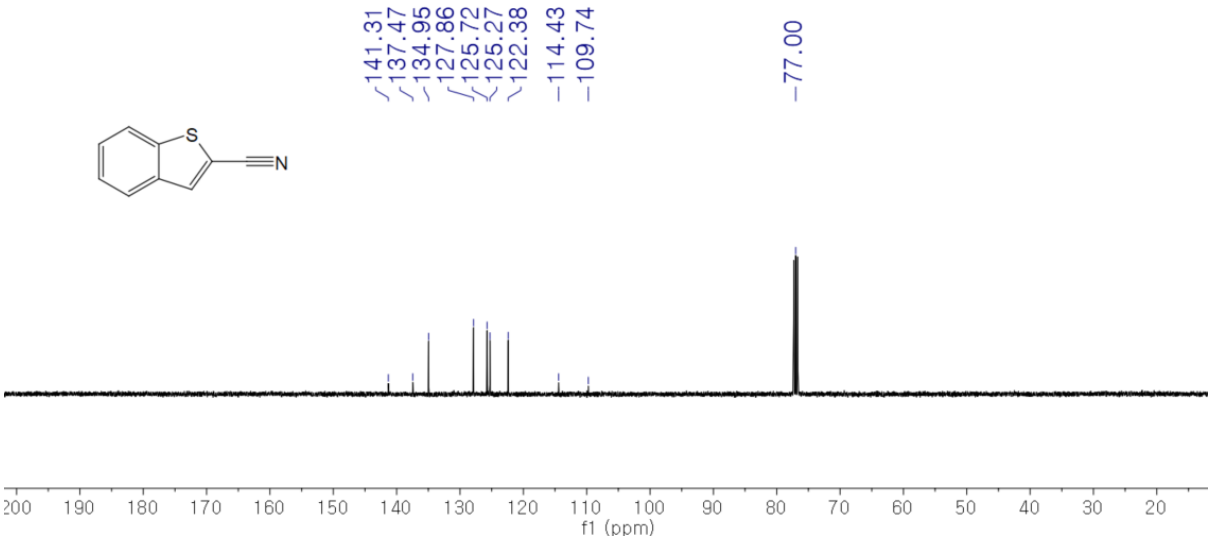
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2h**



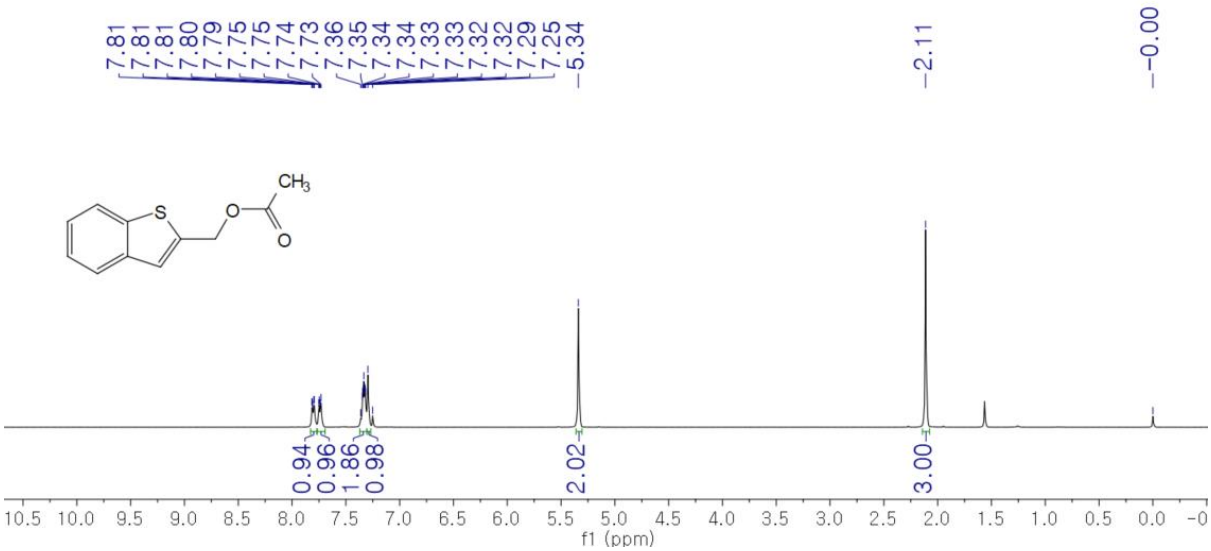
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2h**



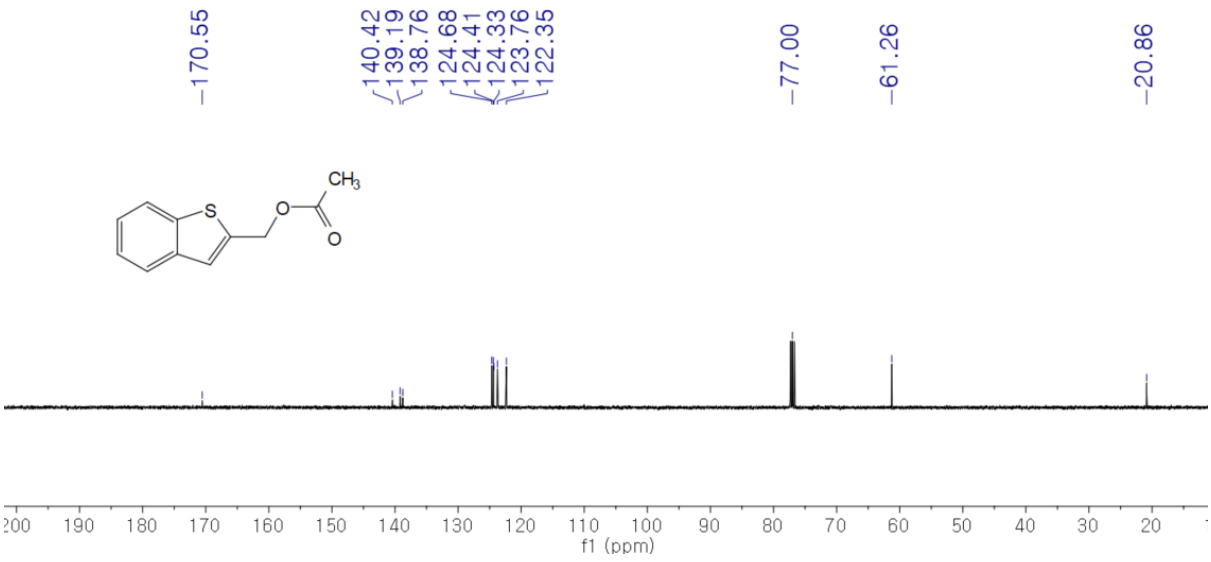
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2i**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2i**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2j**



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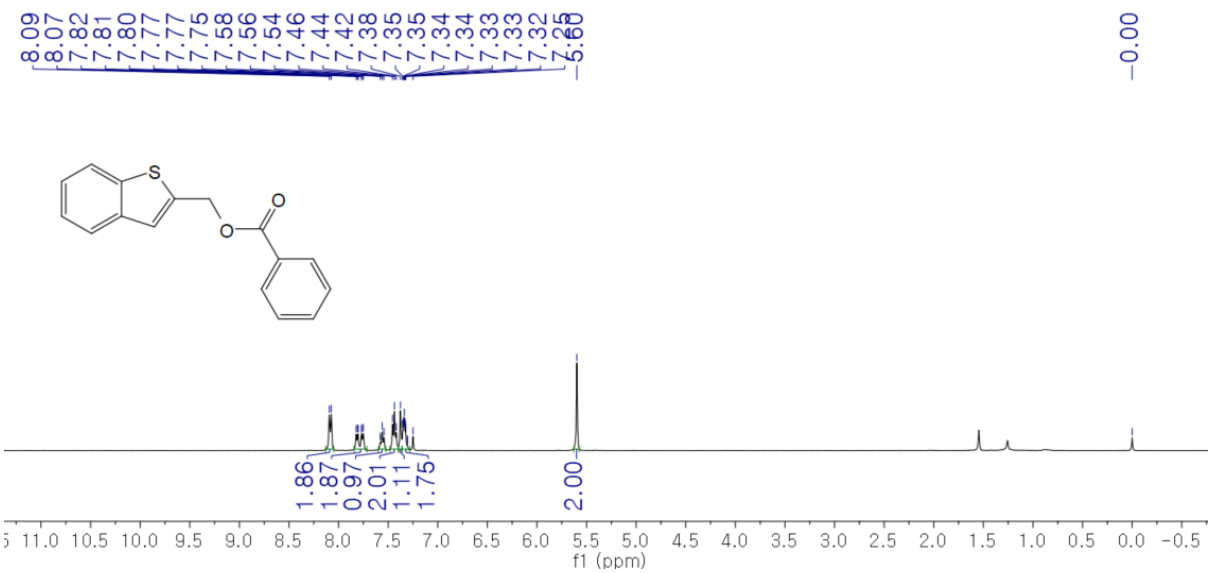
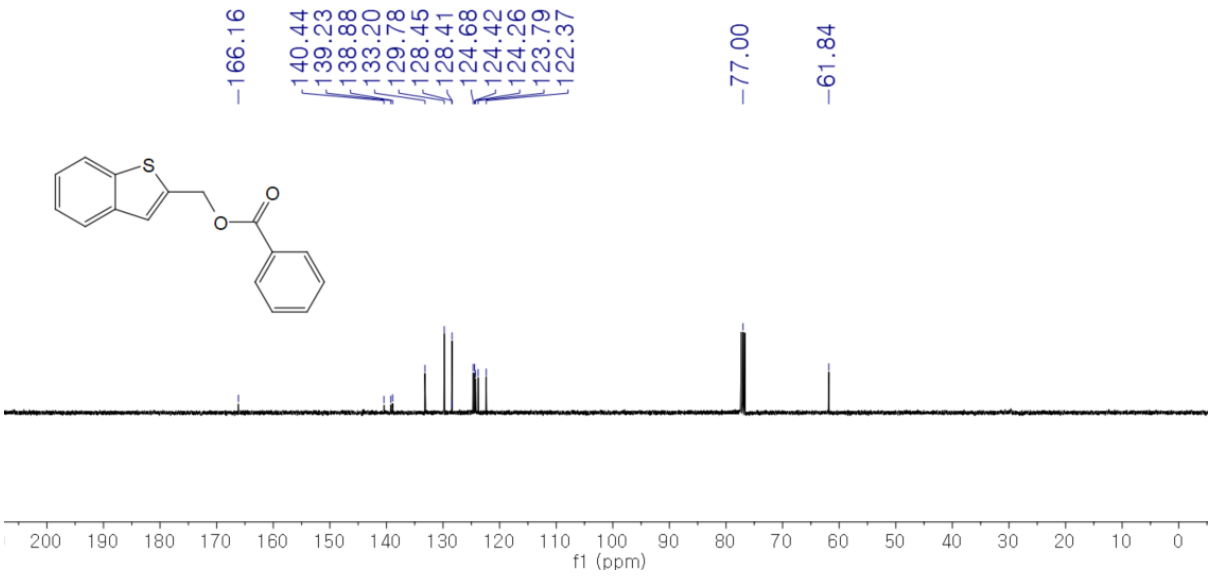


^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2k**



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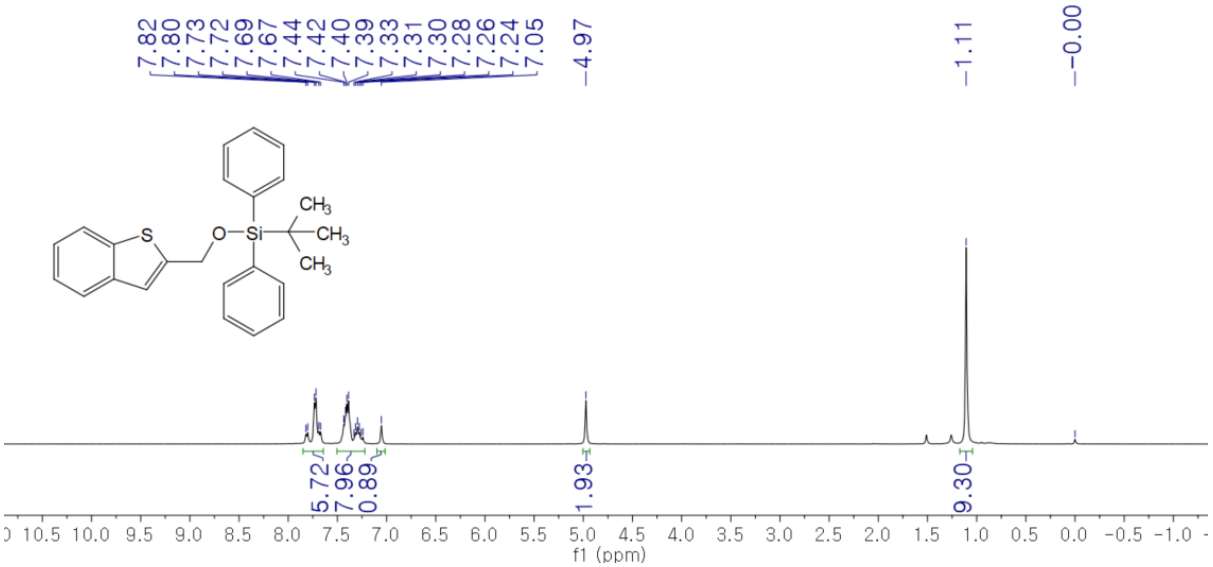

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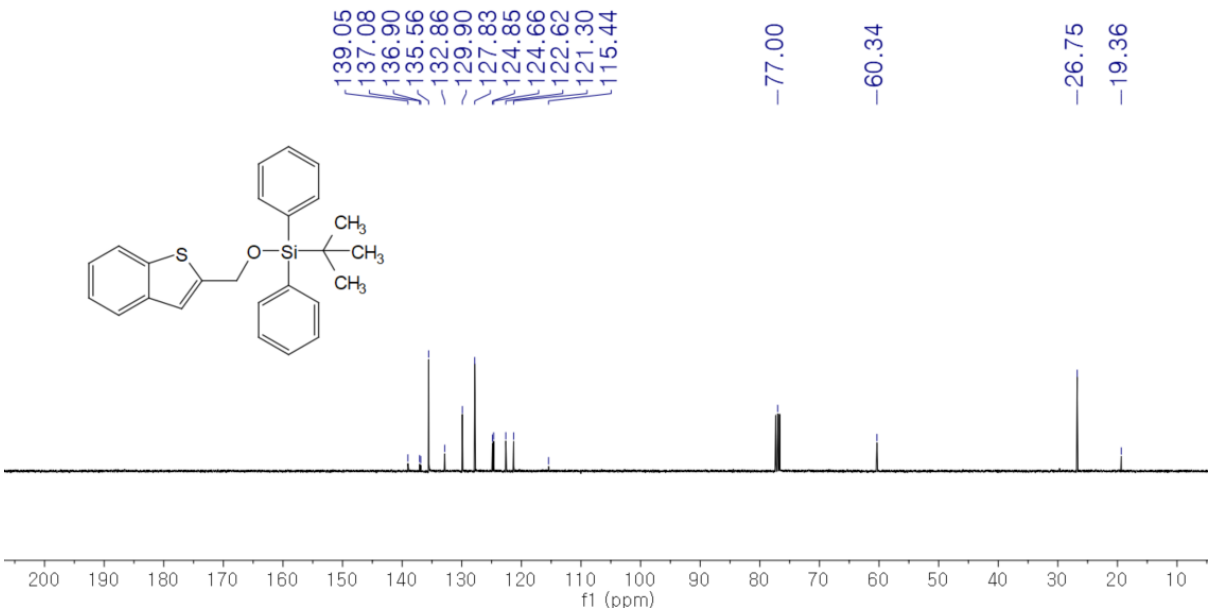

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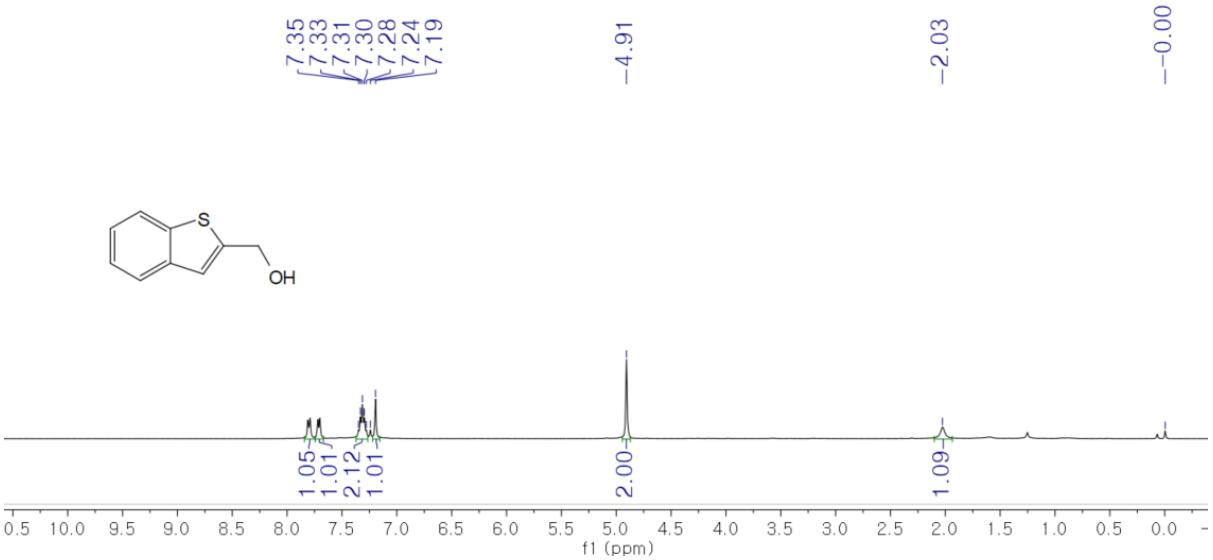
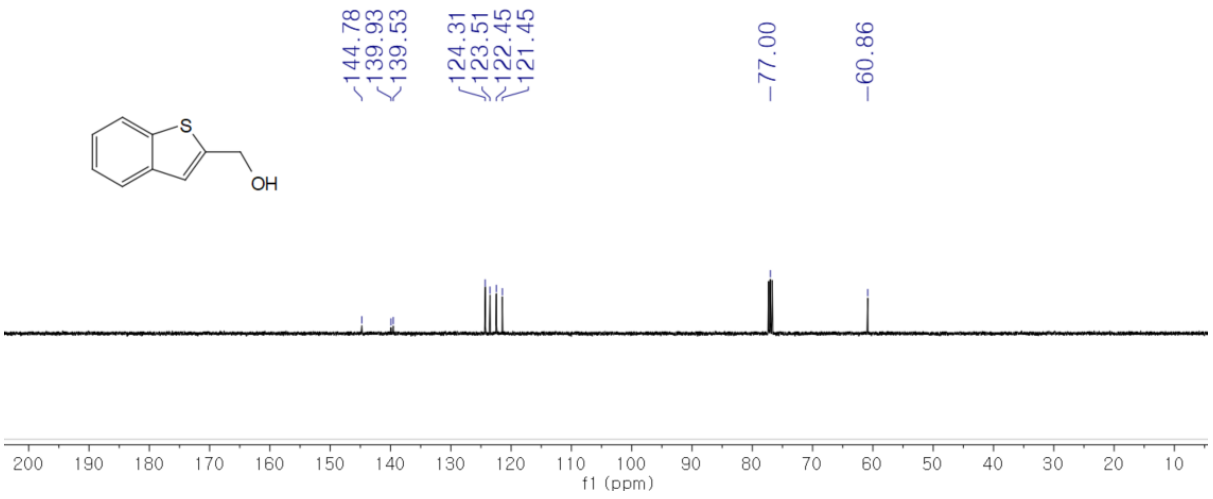
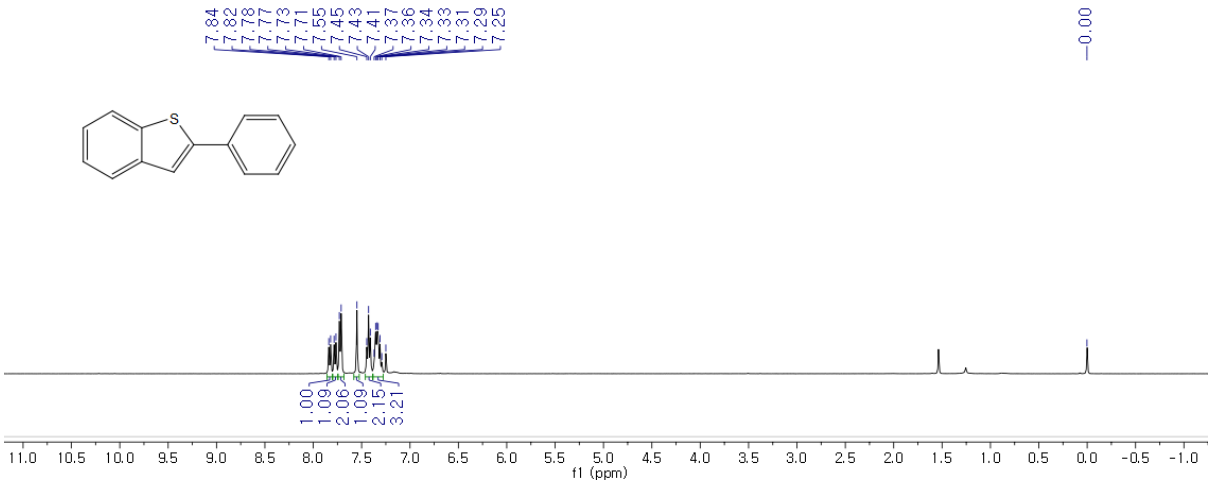


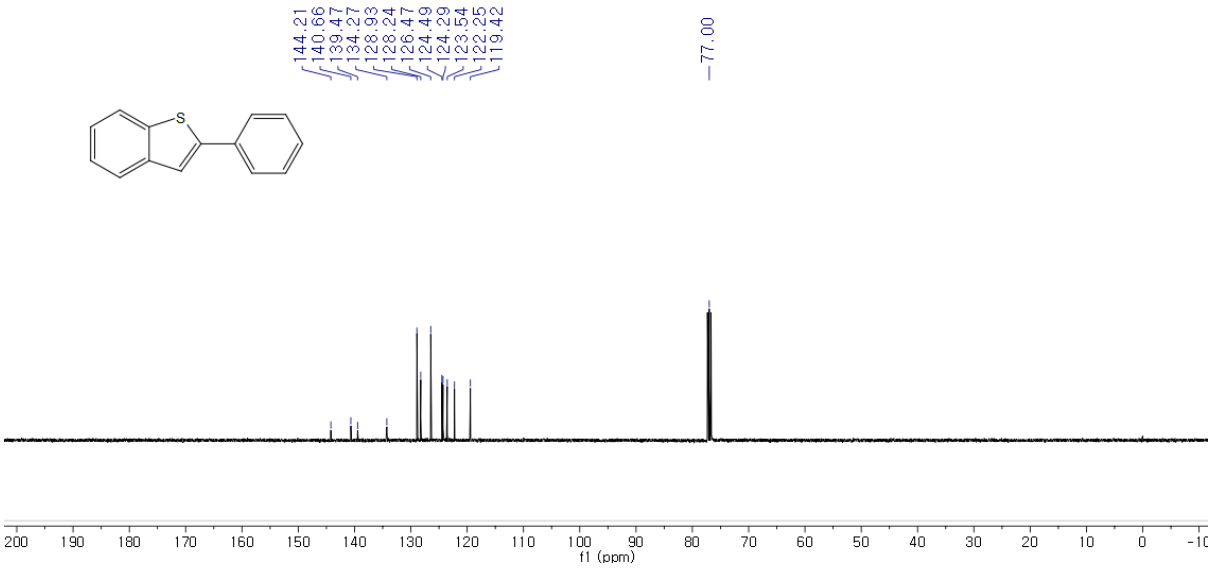
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2m**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2m**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **2o**



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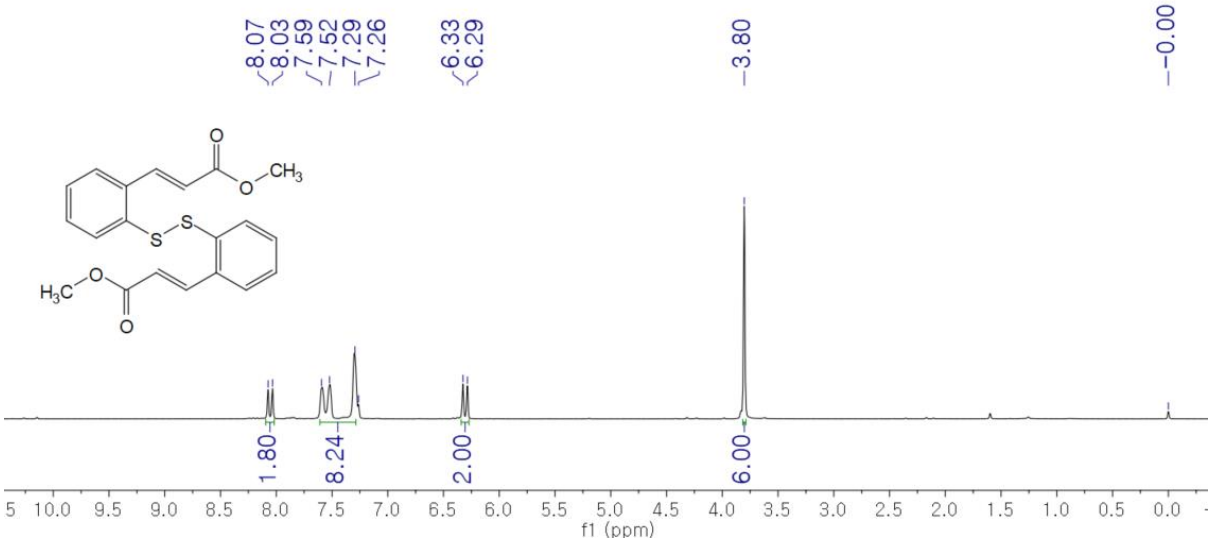
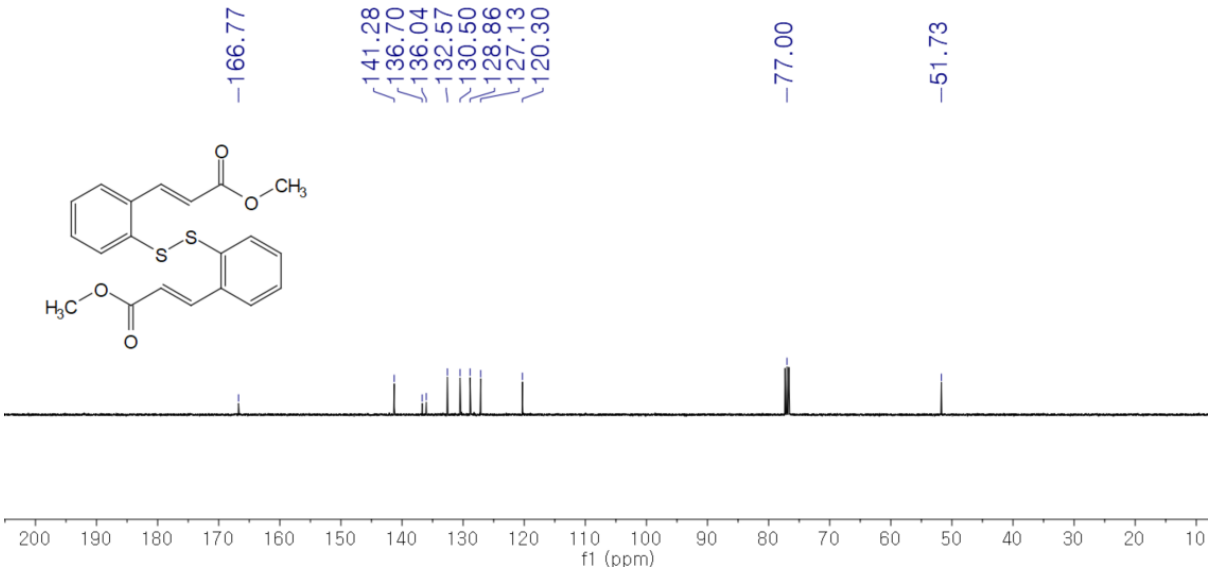
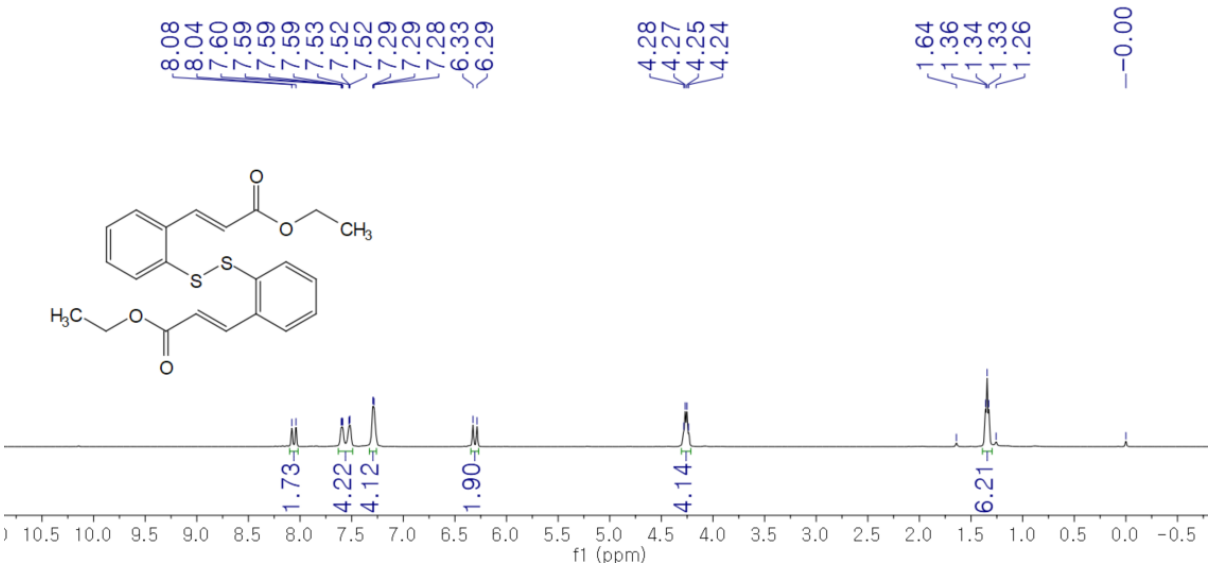


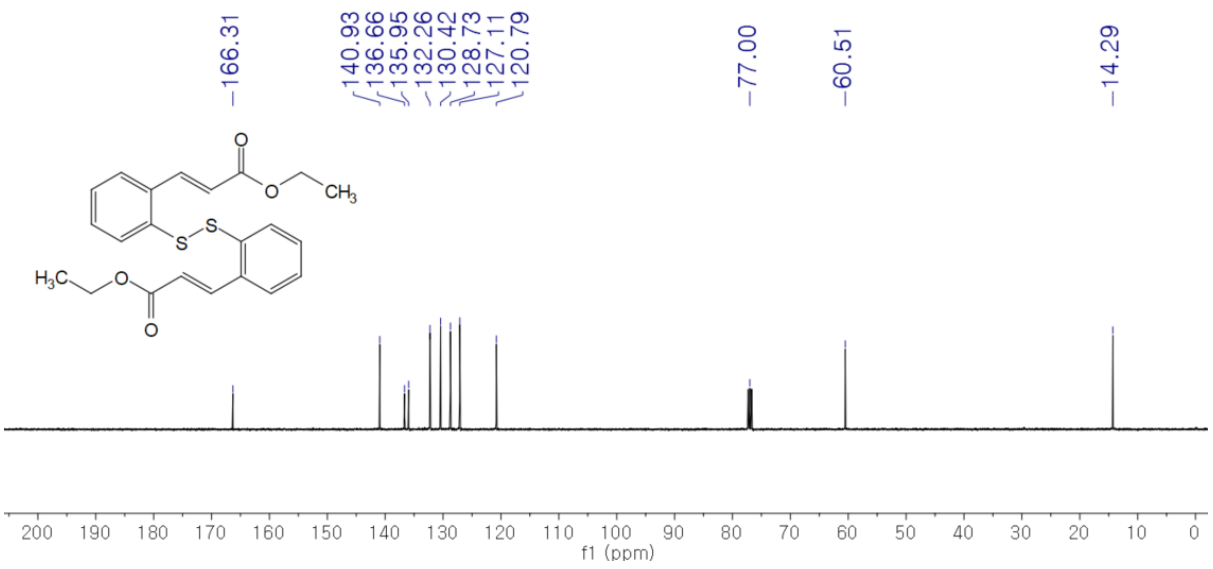
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1a**



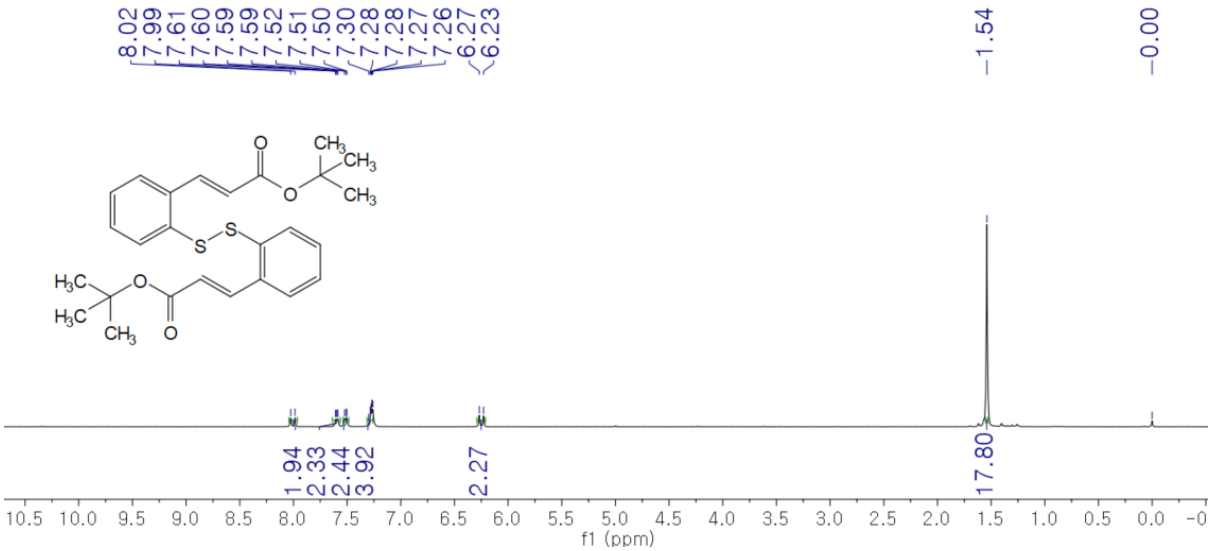
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1a**



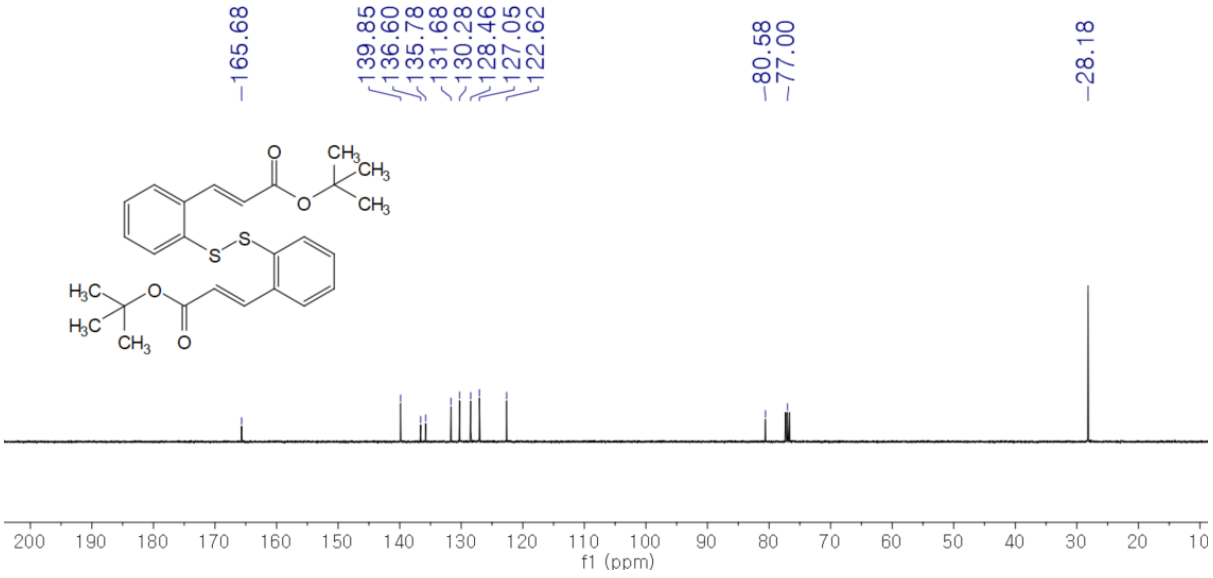
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1b**



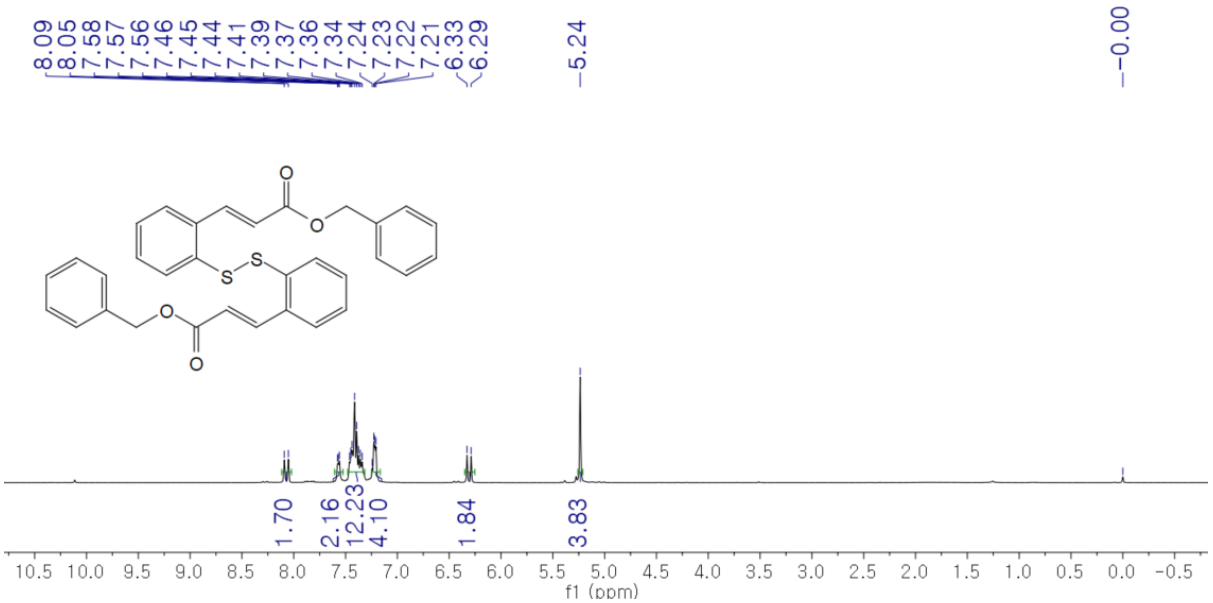
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1b**



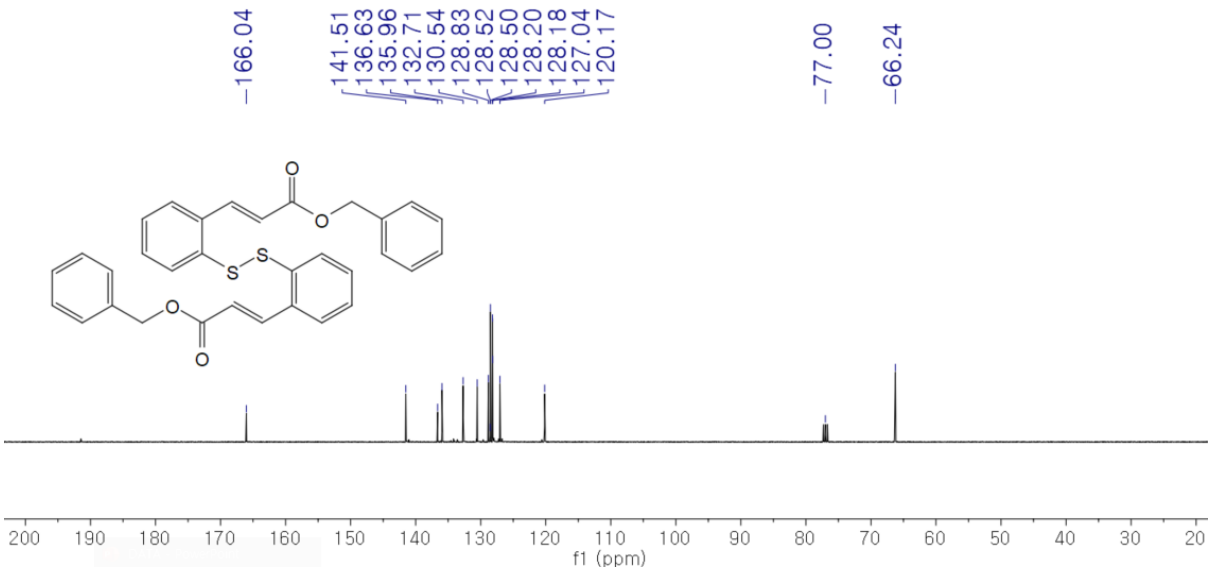
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1c**



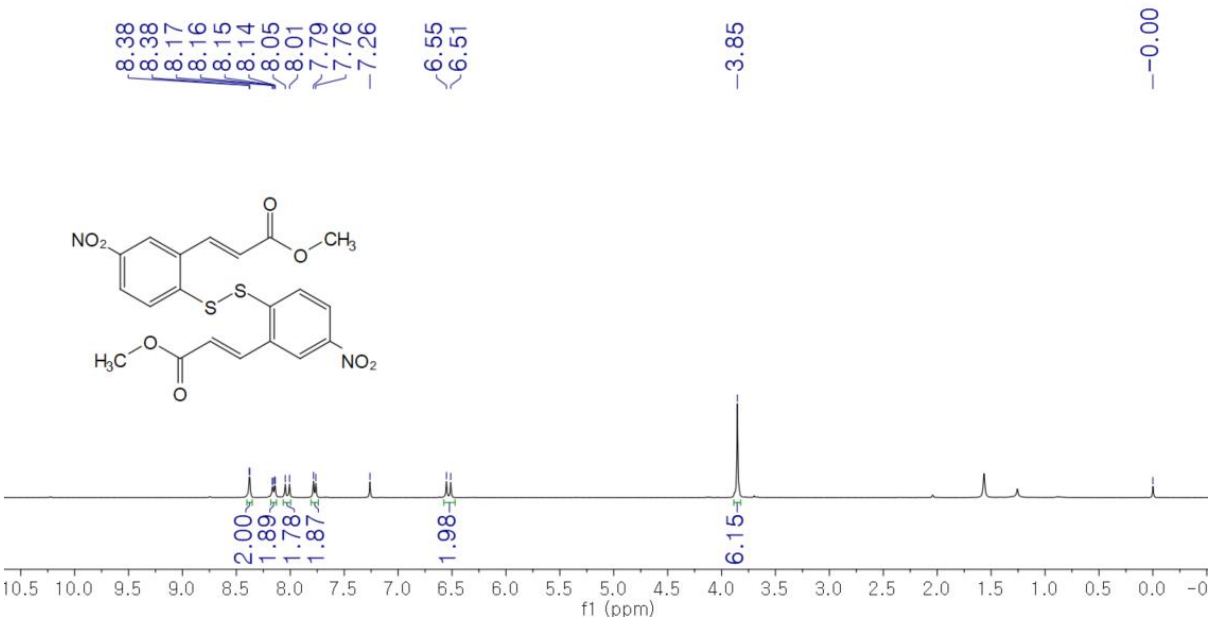
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1c**



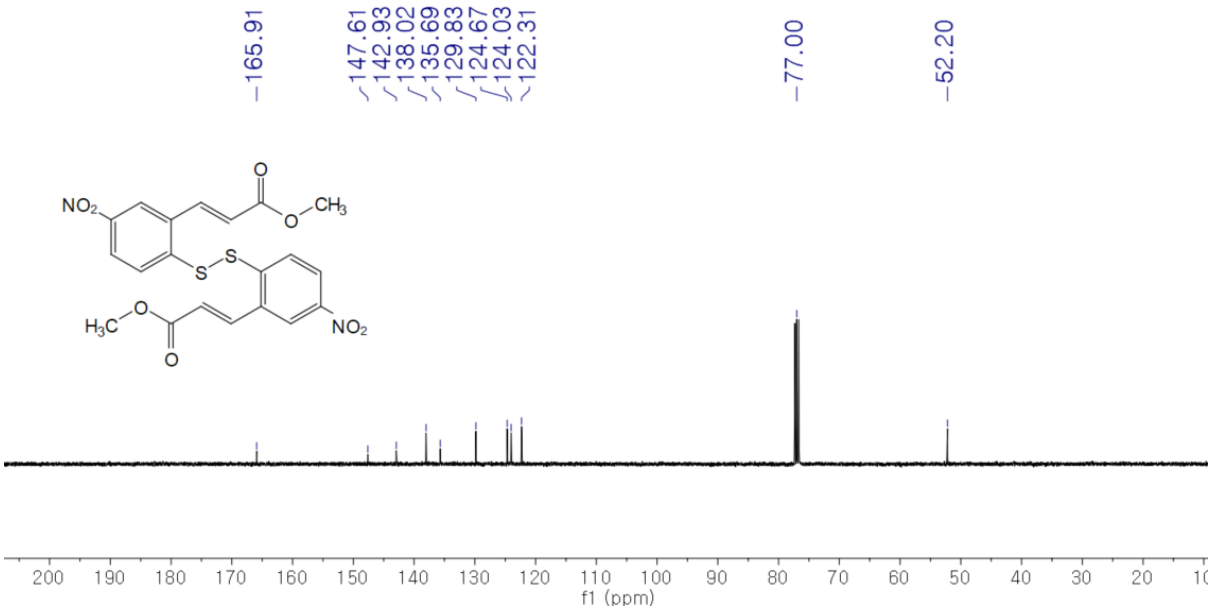
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1d**



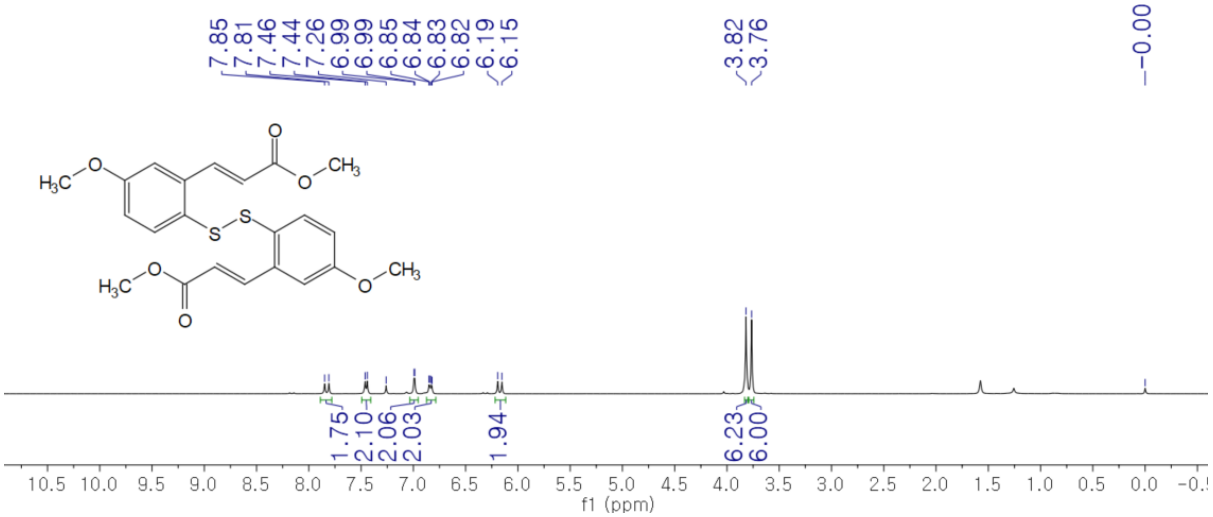
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1d**



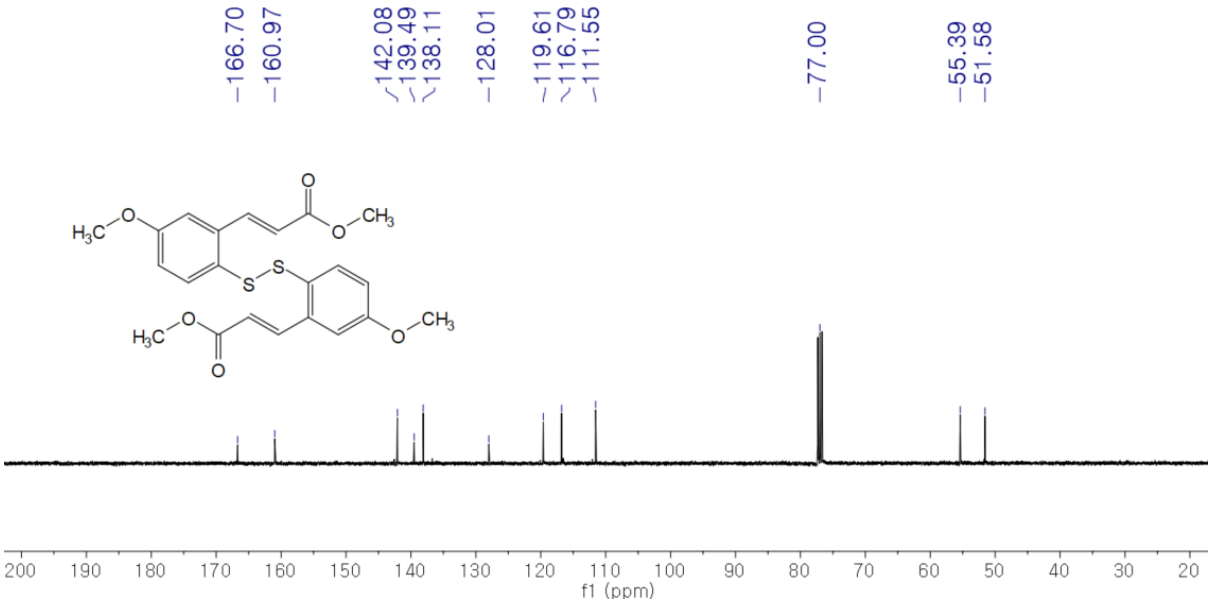
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1e**



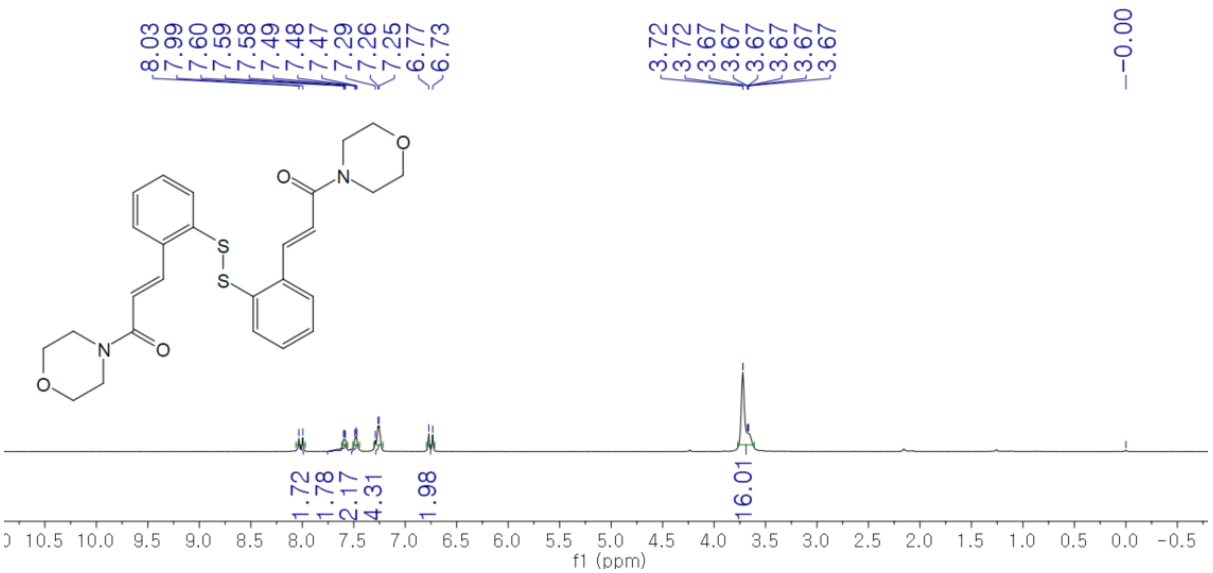
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1e**



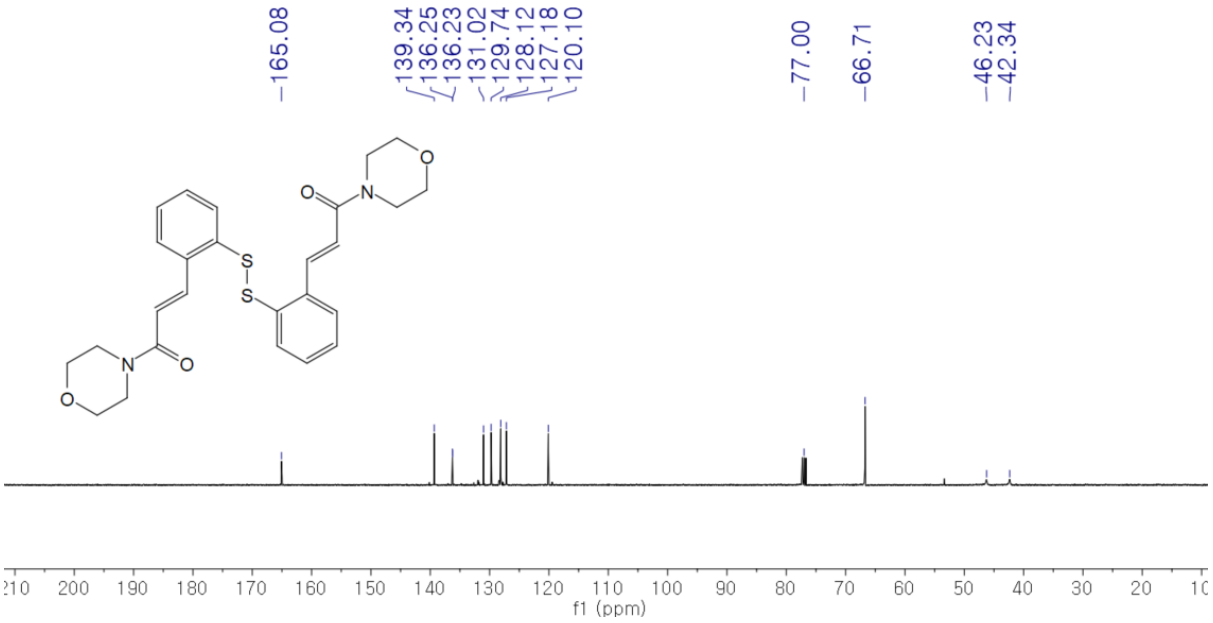
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1f**



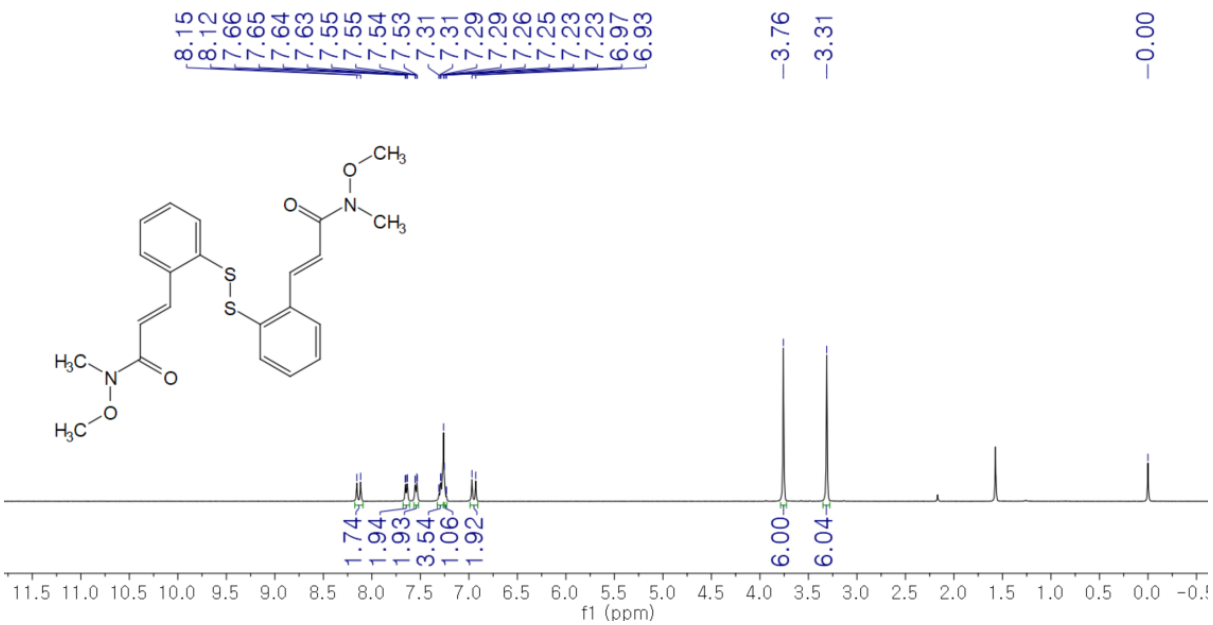
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1f**



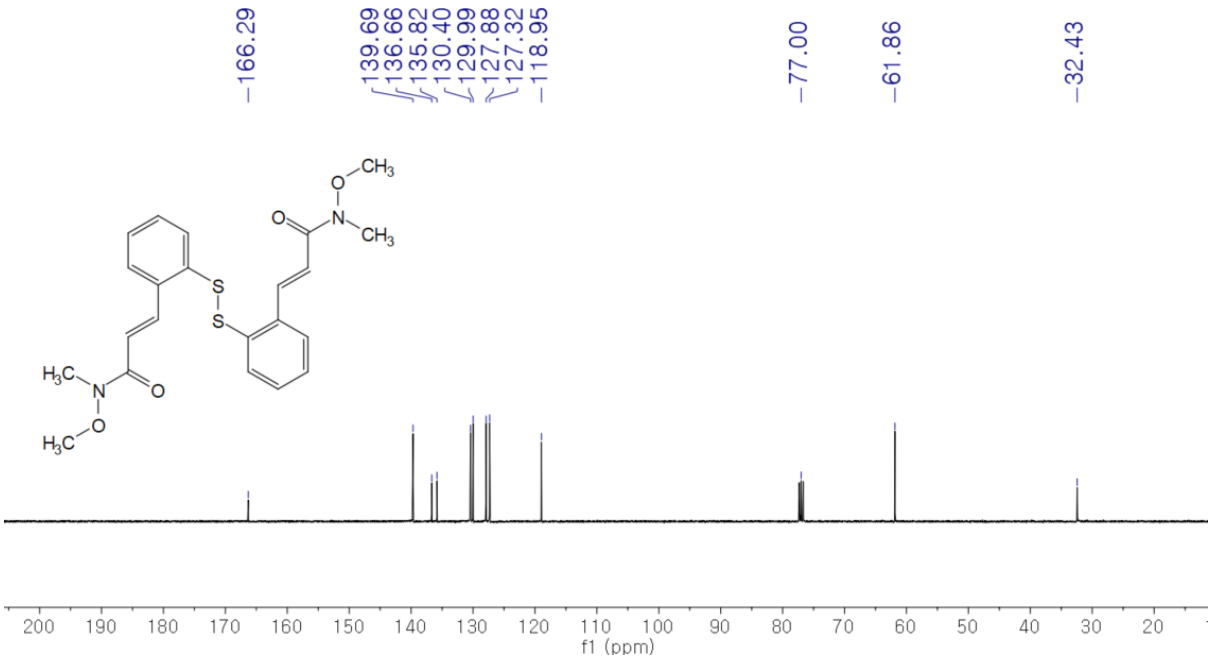
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1g**



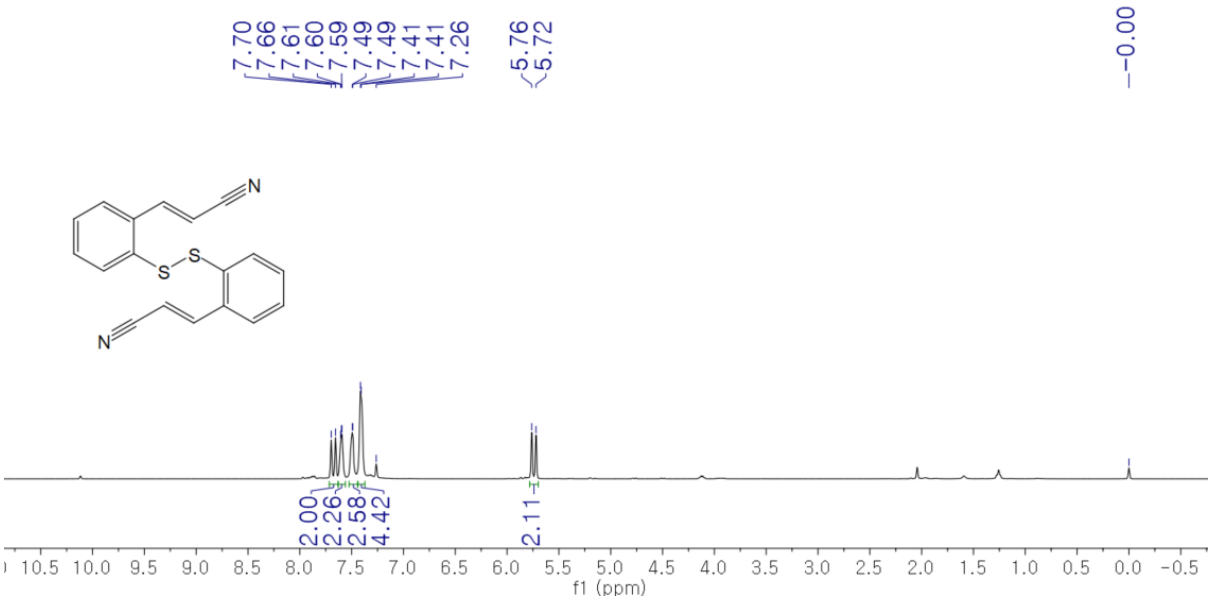
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1g**



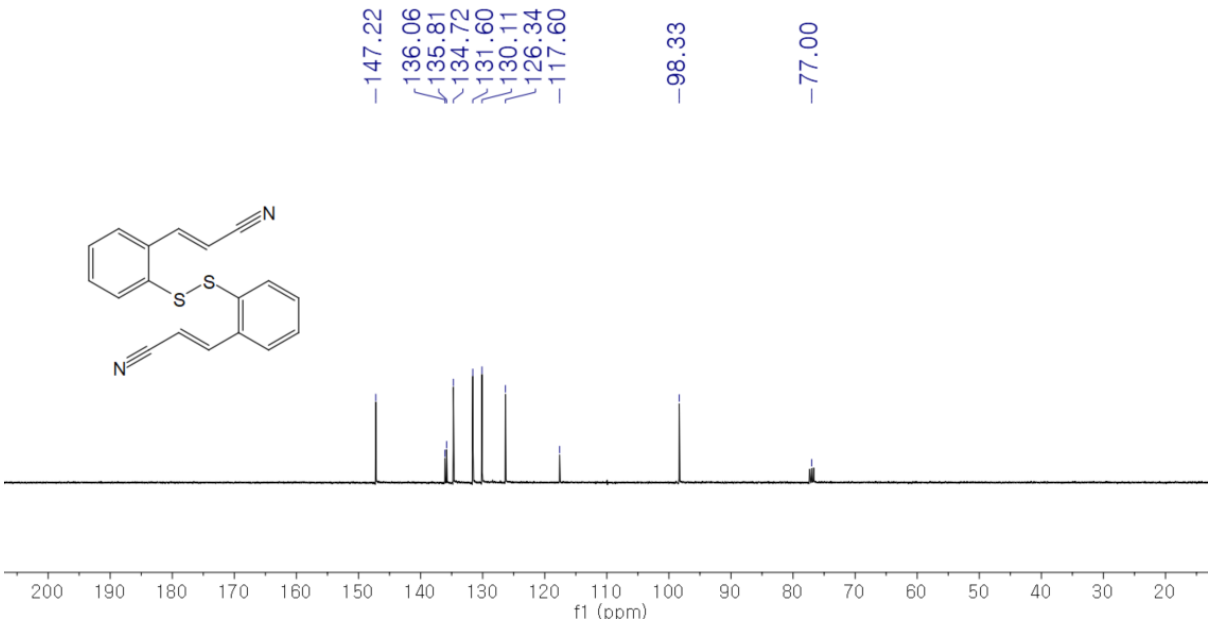
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1h**



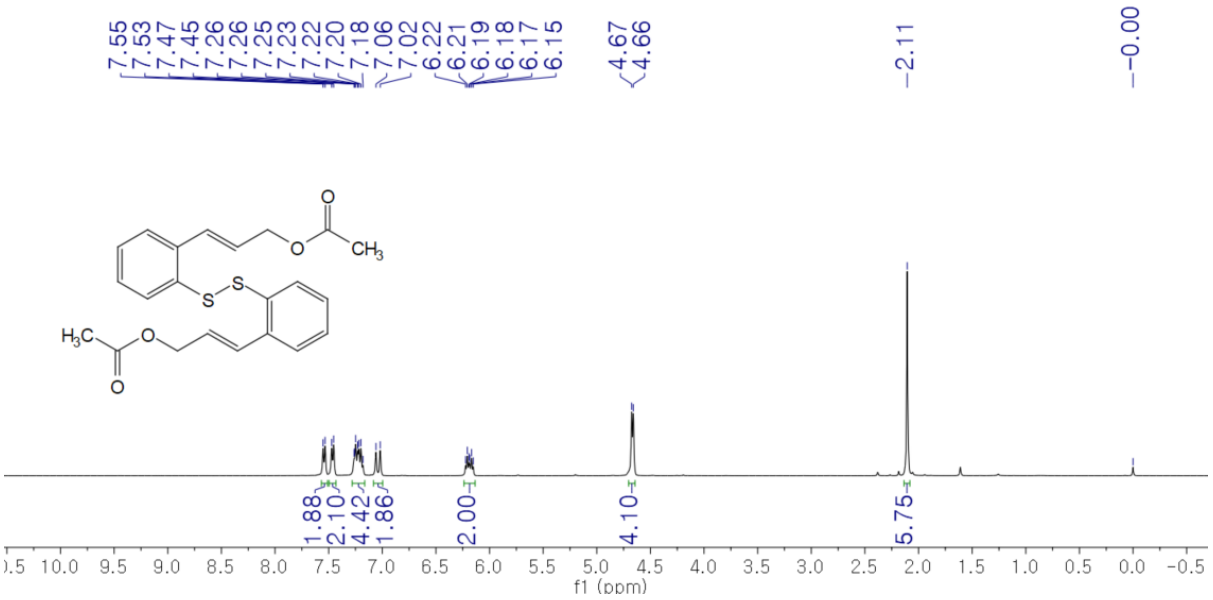
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1h**



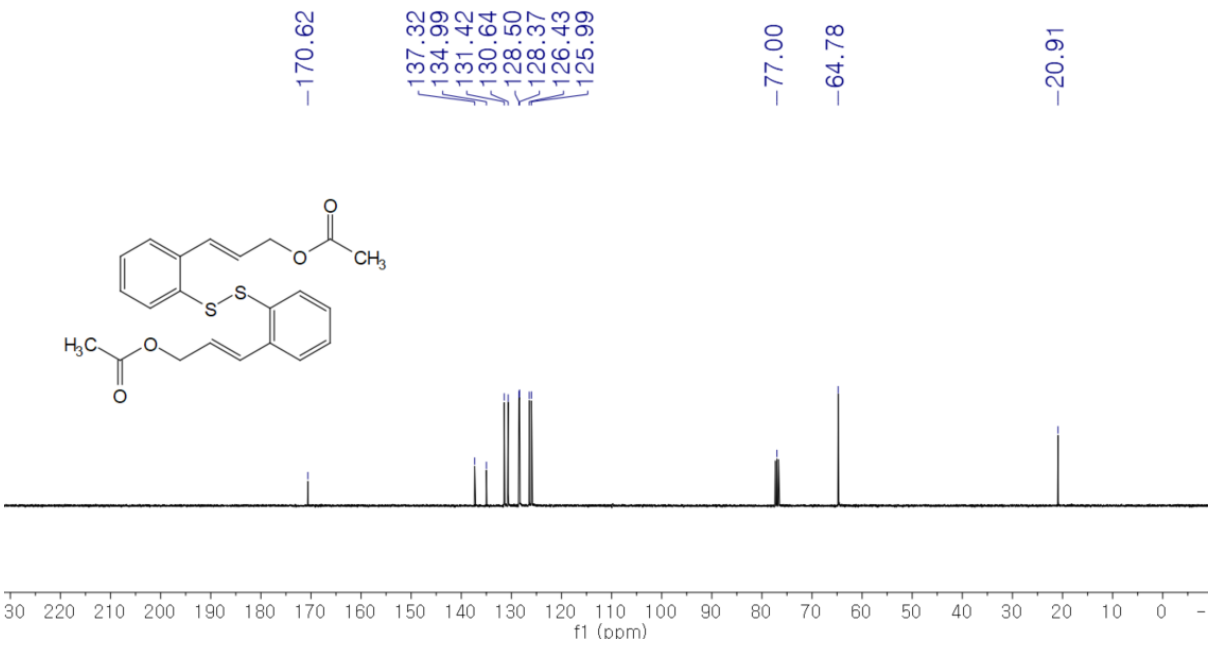
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1i**



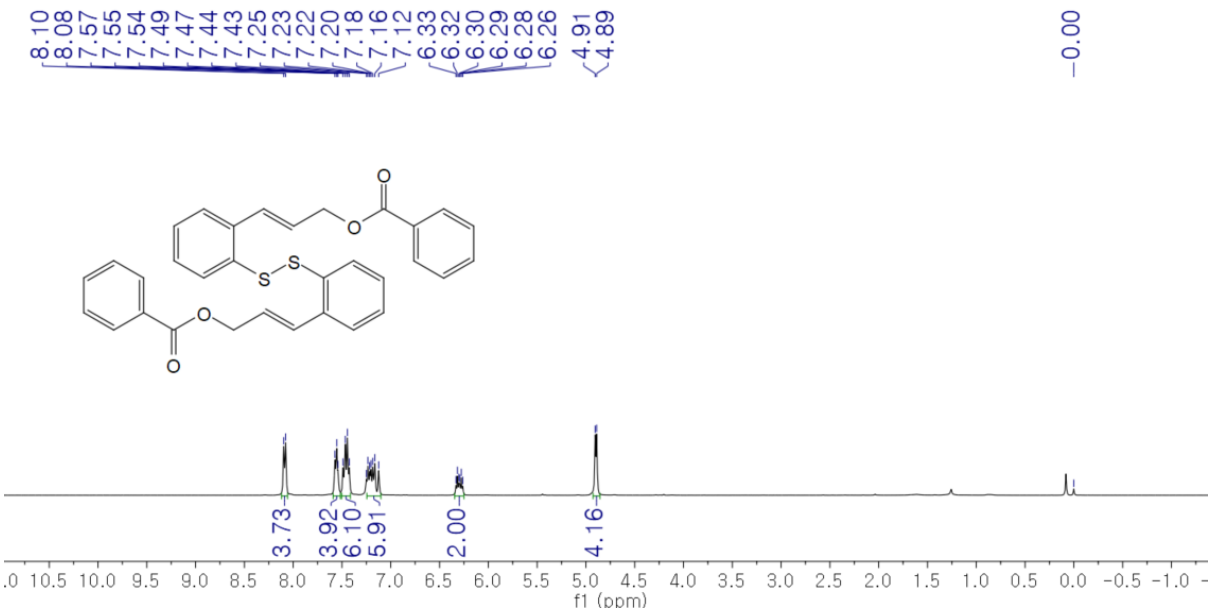
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1i**



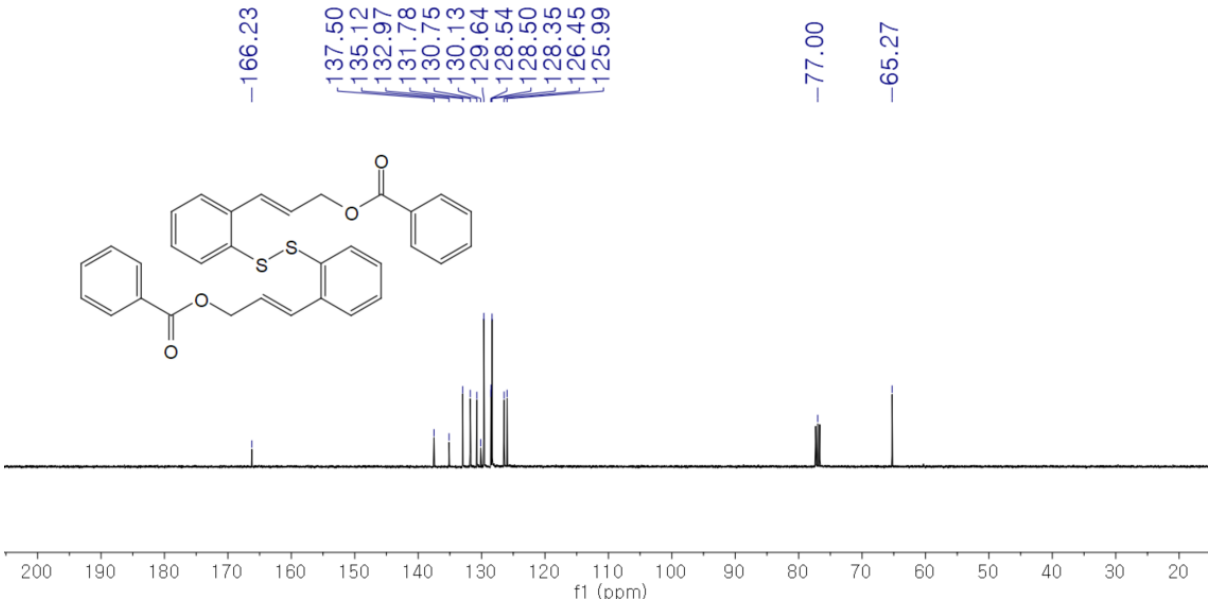
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1j**



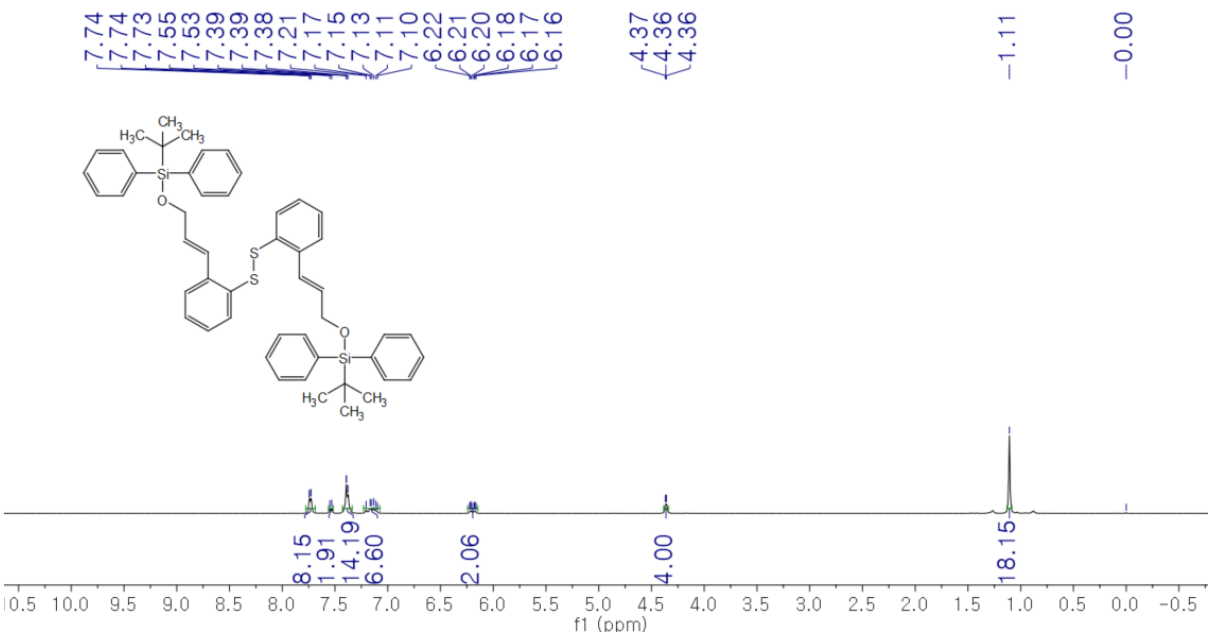
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1j**



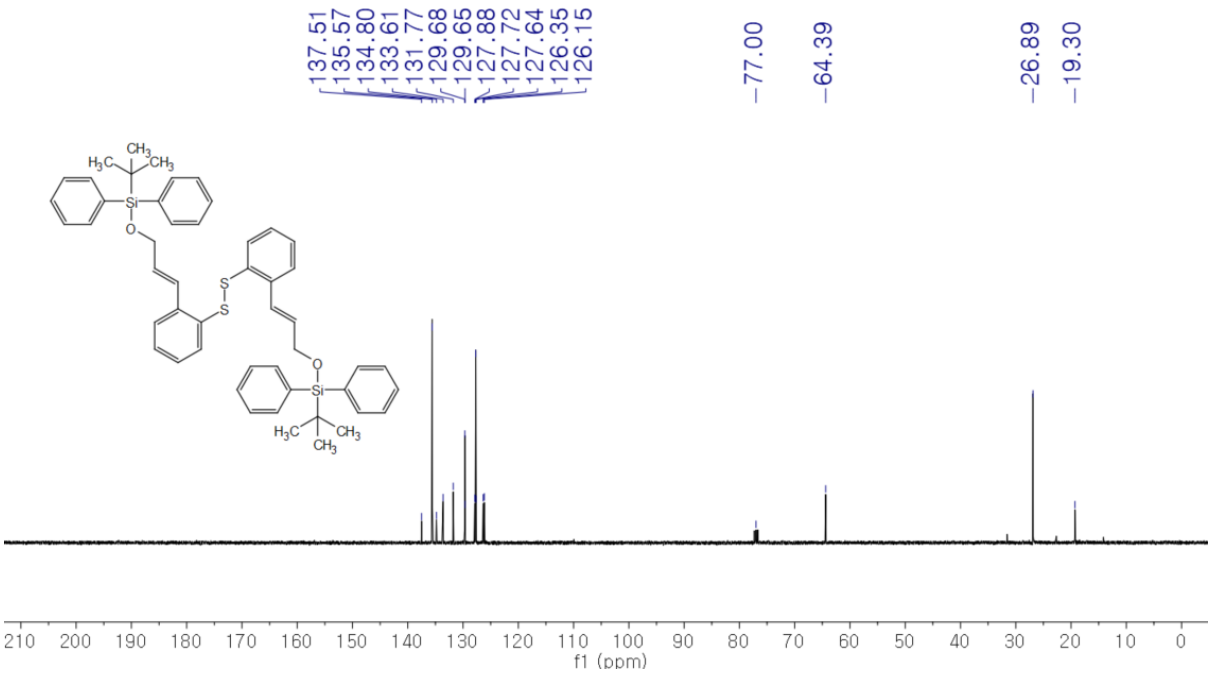
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1k**



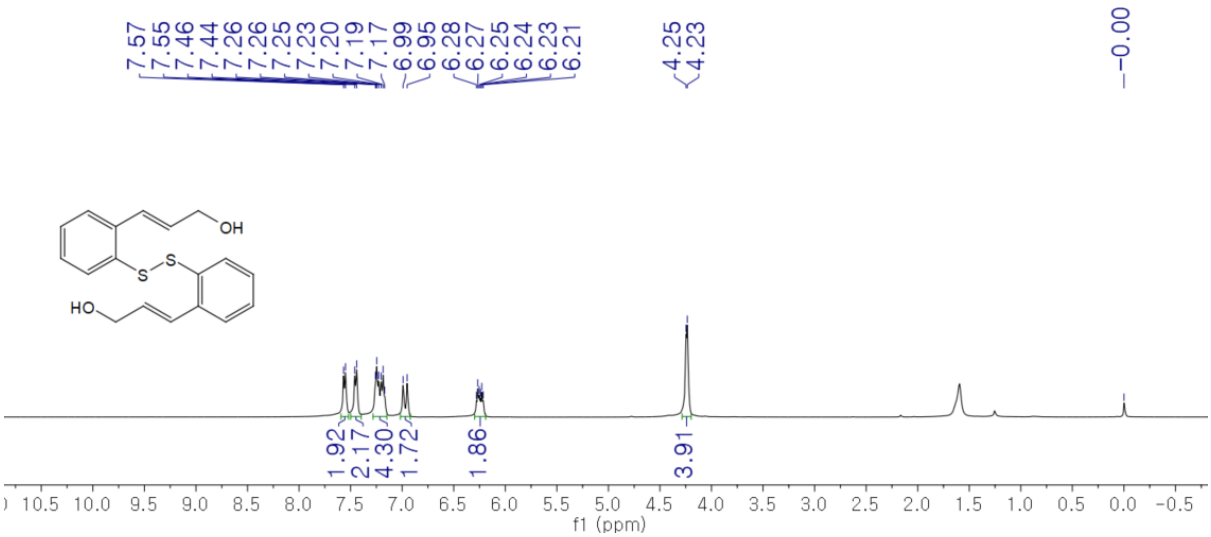
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1k**



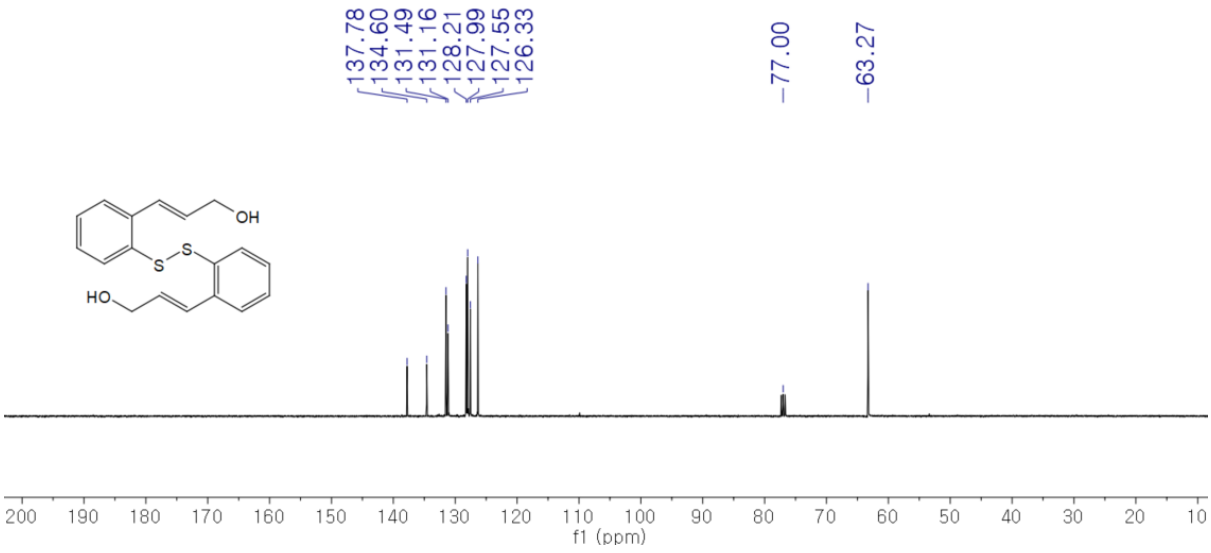
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1l**



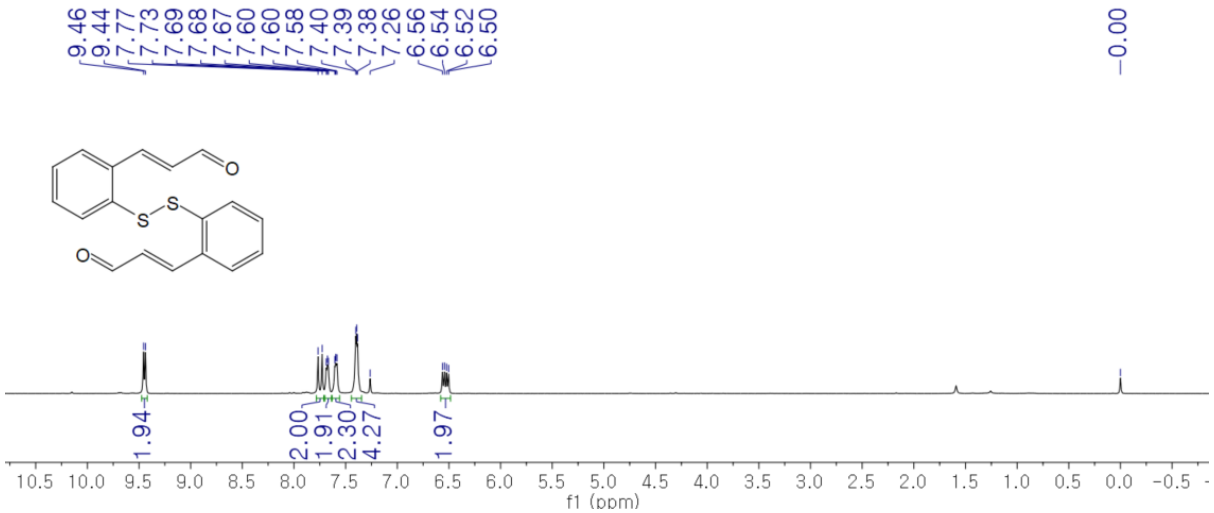
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1l**



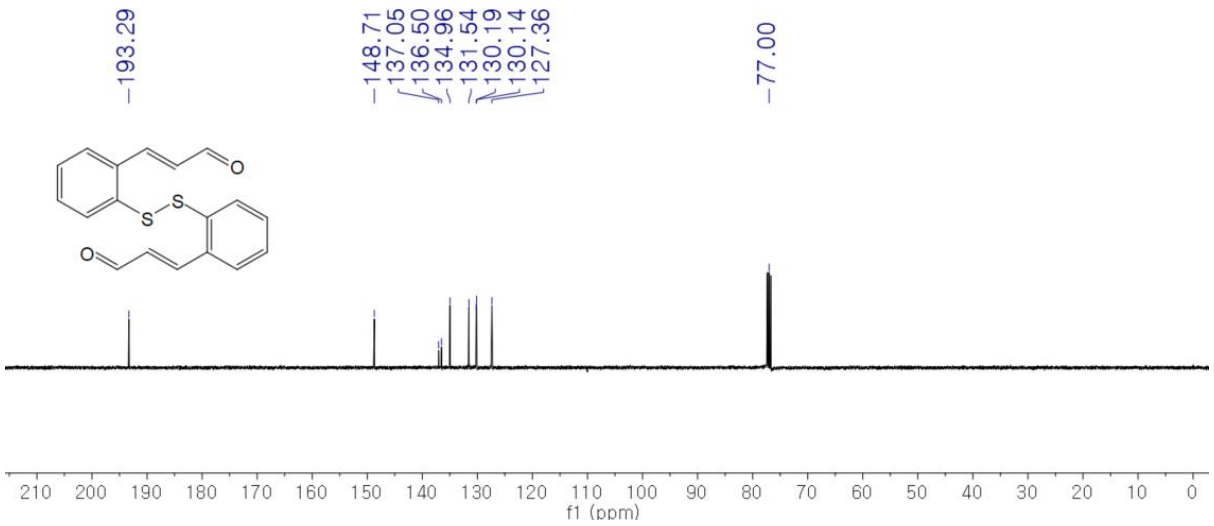
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1m**



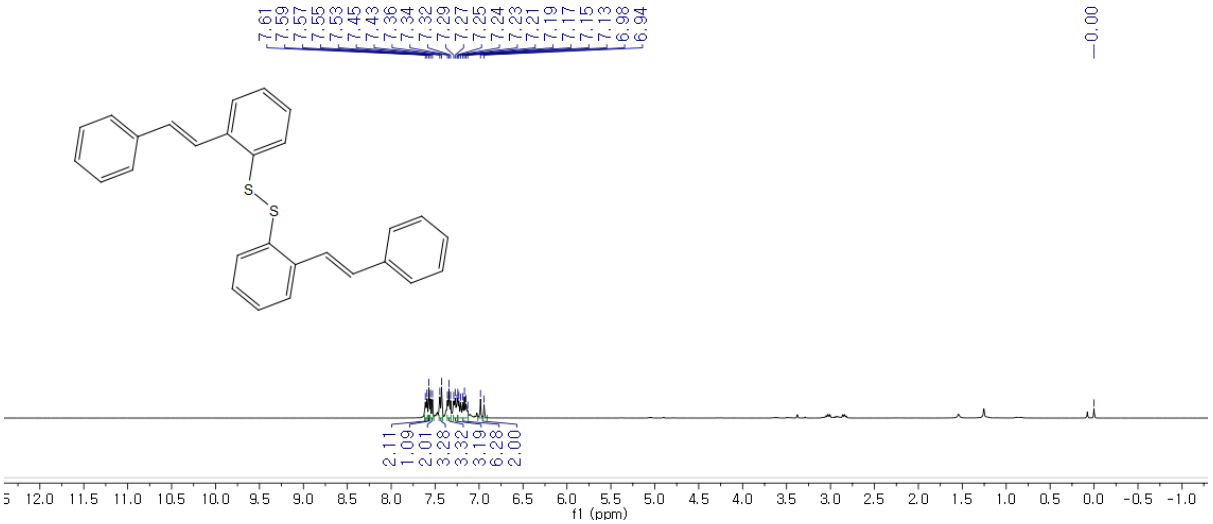
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1m**



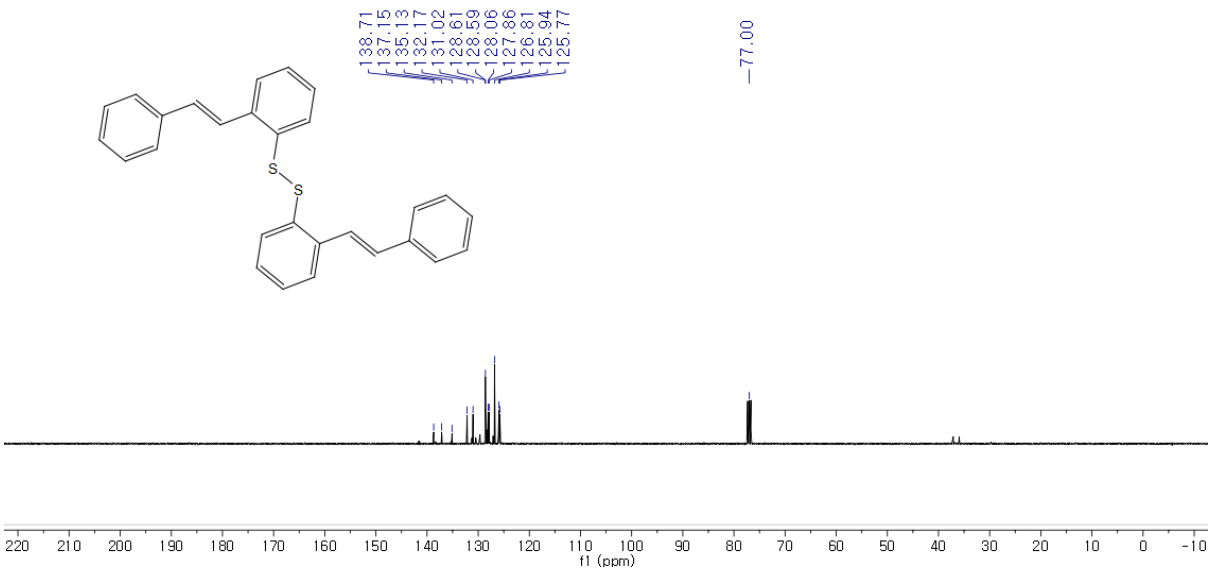
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1n**



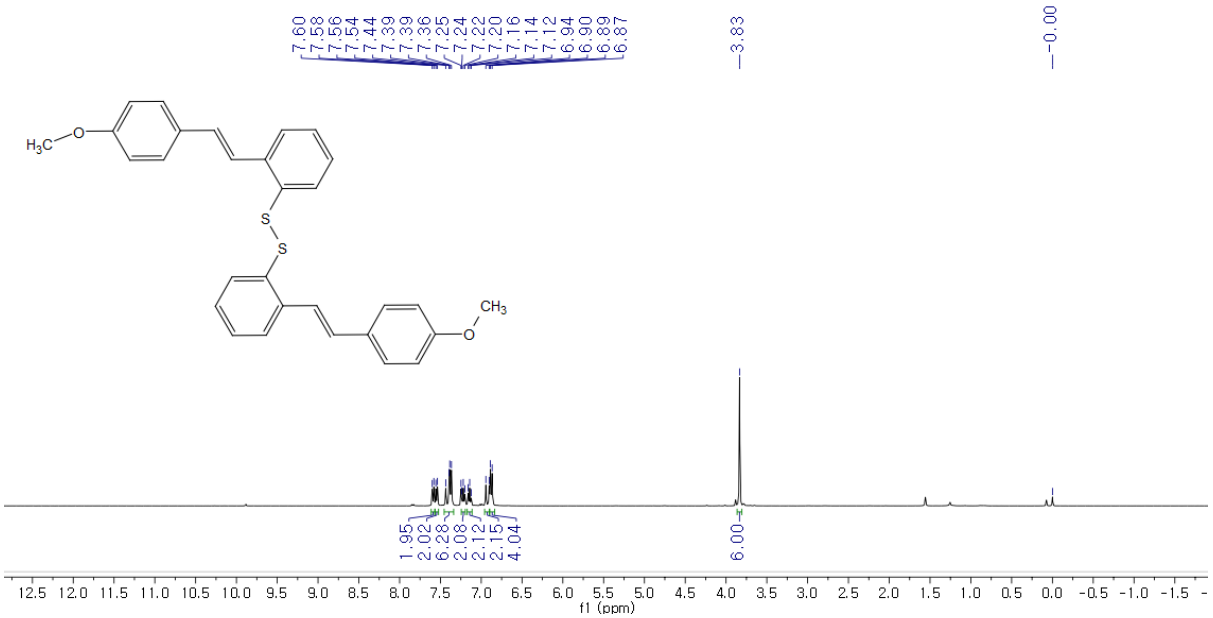
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1n**



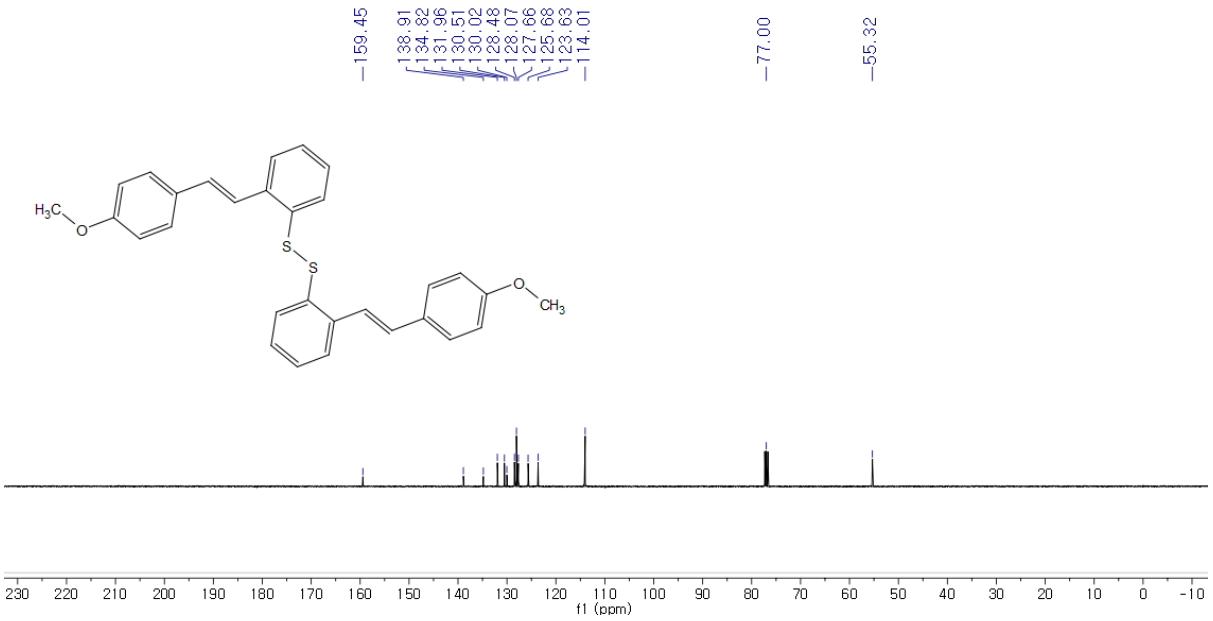
^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1o**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1o**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of **1p**



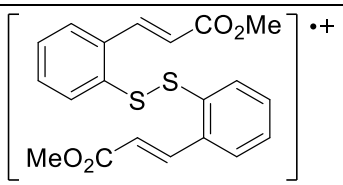
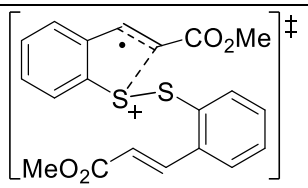
^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1p**

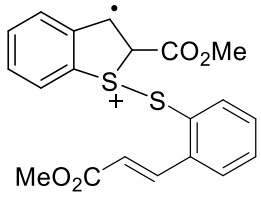
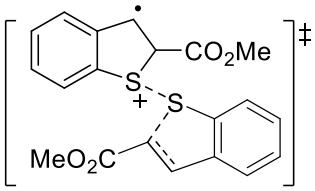
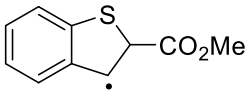
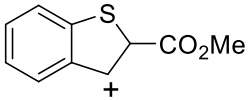
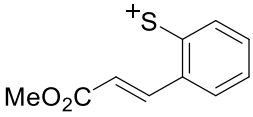
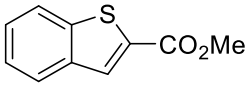
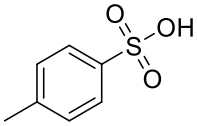
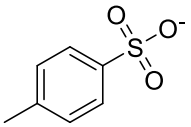
8. DFT calculations

Computational details

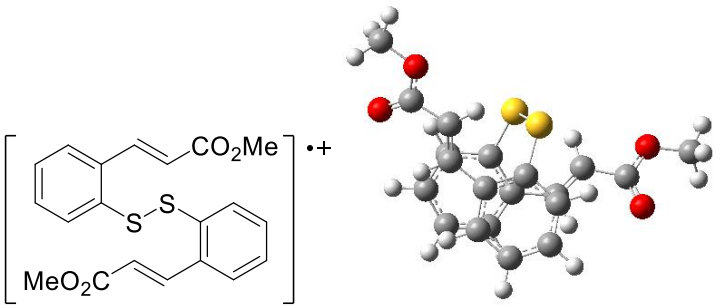
All DFT calculations were carried out in the Gaussian 09 software (Rev D.01)[16] using the M06-2X functional.[17] Geometry optimization was performed with the 6-311+g(d,p) basis set for H, C, O, S atoms,[18] which were obtained from the EMSL Basis Set Exchange.[19] Frequency calculations were performed for every optimized geometry with the same level of theory to obtain vibrational frequencies and thermochemical data at 298.15K. The SMD solvation model[20] with the solvent of dichloroethane (ε=10.125) was used for all calculations. The transition states were identified by having one imaginary frequency, and intrinsic reaction coordinate (IRC)[21] calculations were performed to connect transition states with corresponding intermediates. Each intermediate was verified as minima by having no imaginary frequency, and the geometries of intermediates with possibility of multiple conformations were optimized with several different starting geometries to find the lowest energy conformation.

Tables of energies in Hartree

Structure	E	H_{298}	G_{298}
	-1869.873193	-1869.508514	-1869.593819
	-1,869.859109	-1869.495860	-1869.577418

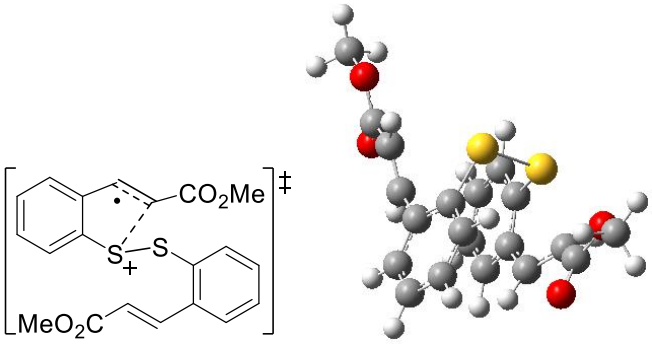
	-1,869.873625	-1869.509673	-1869.592401
	-1,869.847982	-1869.486236	-1869.568081
	-935.025716	-934.845755	-934.897292
	-934.847447	-934.665789	-934.715927
	-934.778944	-934.597733	-934.650653
	-934.470104	-934.300031	-934.349363
	-895.311612	-895.157061	-895.206654
	-894.865941	-894.723543	-894.771131

Structures and coordinates of optimized geometries



C	0.095425	2.869833	-2.197074
C	1.127528	2.000383	-2.531362
C	1.036406	0.658722	-2.182332
C	-0.103960	0.201052	-1.520277
C	-1.188076	1.052084	-1.220416
C	-1.043278	2.399966	-1.548912
C	-2.452172	0.628312	-0.598129
C	-3.107425	-0.508930	-0.837623
S	-0.055295	-1.495126	-1.026017
S	0.054949	-1.495349	1.025760
C	0.103802	0.200739	1.520321
C	1.188041	1.051668	1.220645
C	1.043413	2.399520	1.549299
C	-0.095237	2.869439	2.197512
C	-1.127490	2.000080	2.531600
C	-1.036541	0.658465	2.182370
C	2.452025	0.627839	0.598112
C	3.107627	-0.509145	0.837844
C	-4.383209	-0.778004	-0.126655
O	-4.857300	-0.080334	0.736816
O	-4.943496	-1.904724	-0.563356
C	-6.185362	-2.273966	0.053595
C	4.383271	-0.778077	0.126537
O	4.856822	-0.080572	-0.737369
O	4.944017	-1.904481	0.563425
C	6.185790	-2.273602	-0.053802
H	0.170916	3.921525	-2.446955
H	2.012907	2.361746	-3.039887
H	1.855740	-0.019683	-2.393483

H	-1.850859	3.080982	-1.304487
H	-2.906604	1.351609	0.074782
H	-2.782262	-1.251632	-1.557093
H	1.851074	3.080480	1.304983
H	-0.170581	3.921103	2.447554
H	-2.012877	2.361496	3.040071
H	-1.855993	-0.019862	2.393316
H	2.906108	1.350950	-0.075239
H	2.782930	-1.251685	1.557687
H	-6.495146	-3.191722	-0.439345
H	-6.038929	-2.445830	1.120463
H	-6.929340	-1.491466	-0.096705
H	6.495851	-3.191241	0.439182
H	6.039130	-2.445606	-1.120614
H	6.929653	-1.490945	0.096244



C	1.186460	2.571957	2.285756
C	2.128032	2.602858	1.261349
C	1.802726	2.077484	0.019099
C	0.533316	1.537612	-0.207277
C	-0.446654	1.543530	0.804769
C	-0.077997	2.043246	2.058700
C	-1.819833	1.029533	0.658217
C	-2.632055	1.233014	-0.378922
S	0.263836	0.787261	-1.800671
S	0.818672	-1.214601	-1.452995
C	-0.178906	-1.730306	-0.069750
C	0.390292	-1.571487	1.213322
C	-0.395390	-1.839461	2.340468

C	-1.684917	-2.323177	2.171977
C	-2.218750	-2.504955	0.894451
C	-1.474465	-2.193869	-0.241612
C	1.740628	-1.080140	1.239154
C	2.532970	-1.383159	0.133470
C	-3.988832	0.634738	-0.371695
O	-4.442080	-0.060894	0.505588
O	-4.659589	0.955367	-1.480388
C	-5.989563	0.429981	-1.586276
C	3.766000	-0.576308	-0.151778
O	4.311453	0.109660	0.670736
O	4.152019	-0.732586	-1.406410
C	5.323645	0.006641	-1.802323
H	1.436135	2.962155	3.265544
H	3.115515	3.014813	1.429800
H	2.534084	2.068982	-0.781693
H	-0.809677	2.025042	2.859433
H	-2.203692	0.467826	1.508386
H	-2.357993	1.823743	-1.244182
H	0.024577	-1.696486	3.329463
H	-2.287064	-2.557635	3.041564
H	-3.232932	-2.867262	0.781233
H	-1.906659	-2.290676	-1.230917
H	2.081516	-0.386037	2.003795
H	2.552233	-2.406779	-0.239239
H	-6.373165	0.788088	-2.538359
H	-5.968075	-0.660312	-1.572113
H	-6.606906	0.797528	-0.765987
H	5.480219	-0.234595	-2.849841
H	5.147520	1.075142	-1.677026
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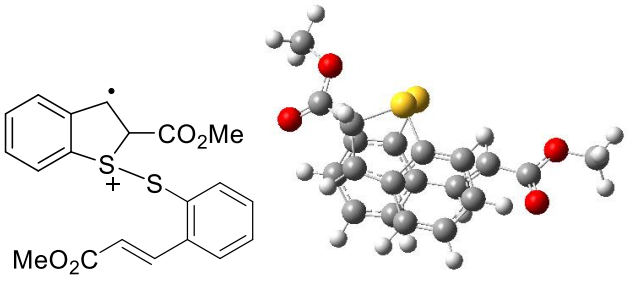

C	-1.123995	-0.813872	3.399927
C	-2.123974	-1.371946	2.608258
C	-1.879478	-1.596440	1.262088
C	-0.633432	-1.282909	0.706621
C	0.411226	-0.785176	1.513767
C	0.122044	-0.525777	2.857274
C	1.783086	-0.508929	1.054446
C	2.520890	-1.293087	0.268913
S	-0.483673	-1.473851	-1.050697
S	-0.941729	0.508448	-1.768465
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C	1.475778	1.808922	-1.253357
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H	-0.062378	3.332887	2.017432
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H	5.883378	-0.627094	-1.833131
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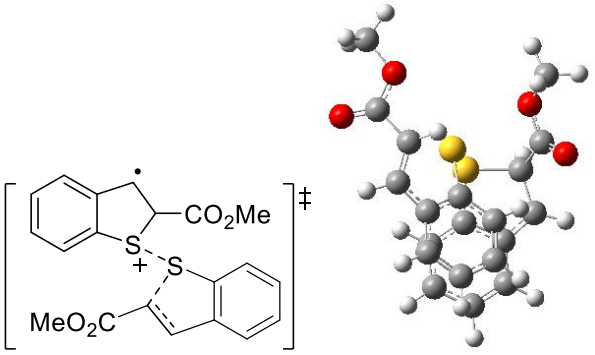

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C	1.965204	2.334800	-0.598368
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O	-4.612727	0.436364	-0.082027
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C	-0.641192	4.277826	1.149848
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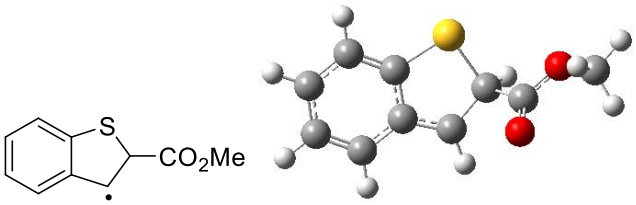

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C	-0.127984	1.211963	0.806355
C	0.965624	0.200532	0.887707
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O	3.178614	-0.264372	0.251478
C	4.308640	-0.162415	-0.628416
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H	5.054514	-0.844090	-0.227745
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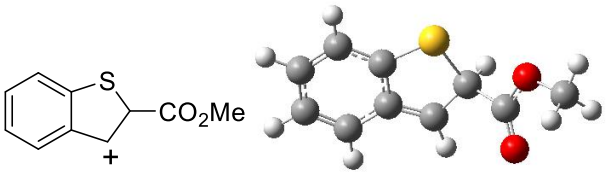

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C	-3.662510	-0.636779	-0.464106
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C	-0.148087	1.265072	0.519789
C	0.900659	0.255643	0.738313
C	2.222519	0.537474	0.018385
O	2.510020	1.608981	-0.431812
O	2.980691	-0.541004	0.015061
C	4.278062	-0.403295	-0.602907
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H	-4.644499	1.294342	-0.525476
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H	0.068924	2.322120	0.636360
H	1.134328	0.251883	1.817748
H	4.756439	-1.371395	-0.487493
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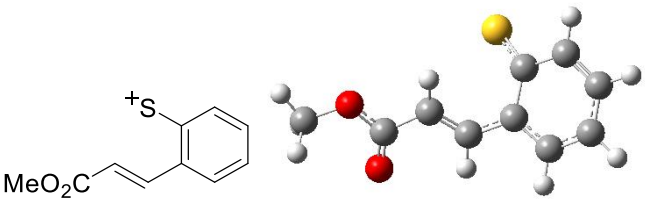

S	-1.017418	2.034682	0.609769
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C	-3.072561	0.826826	-0.562031
C	0.246546	-0.852787	0.362560
C	1.189097	-0.076327	-0.202699
C	2.631017	-0.398322	0.015405
O	3.025403	-1.326556	0.673497
O	3.407792	0.474986	-0.609337
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H	0.963208	0.742660	-0.875224
H	5.293017	1.088254	-1.010827
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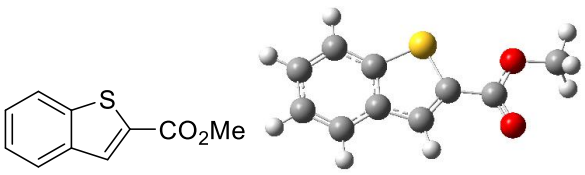

C	-3.817865	-0.640179	-0.000056
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C	0.860725	0.299059	-0.000002
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O	3.001593	-0.617902	0.000101
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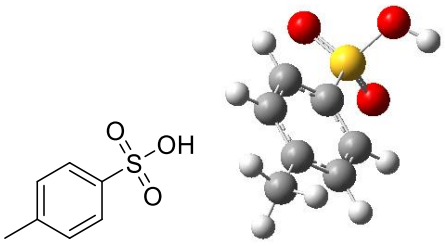

O	2.301114	-0.028236	1.438534
C	0.120956	0.013616	-0.089187
C	-0.556057	1.225561	-0.041112
C	-1.944756	1.208709	0.010974
C	-2.650845	0.003802	0.017812
C	-1.936266	-1.198904	-0.030030
C	-0.550923	-1.205864	-0.085283
C	-4.152986	-0.013970	0.061319
S	1.887629	0.017001	-0.119335
O	2.363746	1.299904	-0.576017
O	2.356642	-1.207099	-0.734429
H	2.248170	-0.936241	1.786438

H	-0.011002	2.161877	-0.051265
H	-2.487604	2.146773	0.043649
H	-2.475338	-2.140289	-0.030094
H	-0.001775	-2.139002	-0.134302
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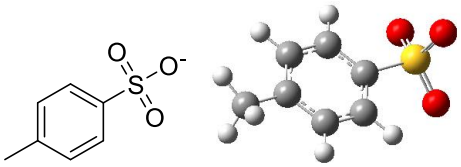

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C	-1.923589	1.203243	-0.001888
C	-2.638641	0.004578	0.011873
C	-1.922920	-1.197285	-0.001708
C	-0.533716	-1.203623	-0.029265
C	-4.144132	-0.004088	0.015020
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O	2.367301	-1.212405	-0.733327
H	0.017759	2.142995	-0.047323
H	-2.461985	2.145501	0.006968
H	-2.462994	-2.139065	0.006572
H	0.014466	-2.138800	-0.047914
H	-4.543020	0.983905	0.249377
H	-4.529227	-0.299866	-0.965174
H	-4.531406	-0.716544	0.746833

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