Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Multicomponent hydrosulfonylation of alkynes for the synthesis of vinyl sulfones

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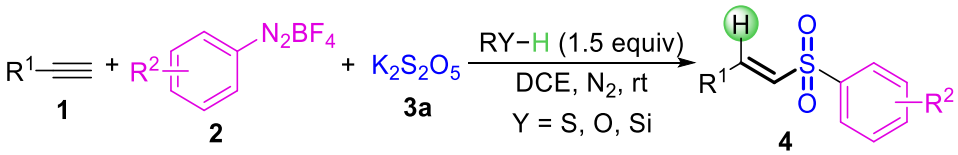
(A) General information

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. The progress of the reactions was monitored by TLC with silica gel plates and the visualization was carried out under UV light (254 nm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker 400 (400, 101, and 376 MHz) or Bruker 500 (500, 126, and 471 MHz) advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and 77.0 ppm) using TMS as internal standard. HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

(B) Typical experimental procedures

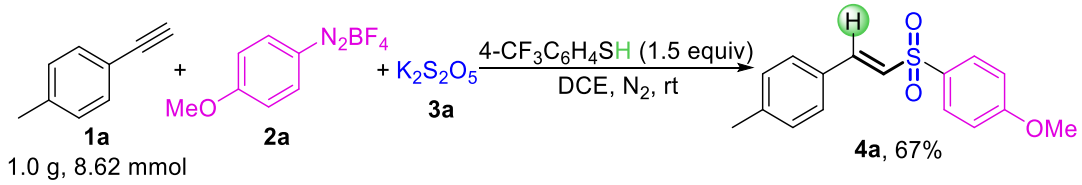
(1) General procedure for synthesis of compounds 4.



1 2 3a 4

To a dry 10 mL schlenk tube was added **1** (0.2 mmol), **2** (1.2 equiv, 0.24 mmol), **3a** (2.0 equiv, 0.6 mmol) and RY-H (1.5 equiv, 0.3 mmol). The tube was sealed, evacuated and backfilled with nitrogen three times, then 1,2-dichloroethane (DCE) (2.0 mL) was added. The resulting solution was stirred under nitrogen atmosphere at room temperature for about 10 h until complete consumption of starting material as monitored by TLC and/or gas chromatography-mass spectrometry (GC-MS) analysis. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/ ethyl acetate) to afford the desired products **4**.

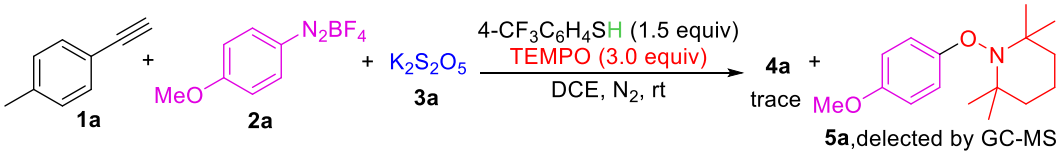
(2) Gram-scale experiment



To a dry 50 mL branched spherical flasks was added **3a** (2.0 equiv, 17.24 mmol, 3832.6 mg), **2a** (1.2 equiv, 10.34 mmol, 2295.0 mg). The tube was sealed, evacuated and backfilled with nitrogen three times, then DCE (10.0 mL), 4-$CF_3C_6H_4SH$ (1.5 equiv, 12.93 mmol, 2303.7 mg) and **1a** (8.62 mmol, 1000.0 mg) were sequentially added. The resulting solution was stirred under nitrogen atmosphere at room temperature for about 36 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to afford the desired product **4a**.

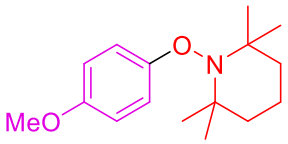
(C) Mechanistic studies

(1) Radical trapping experiment



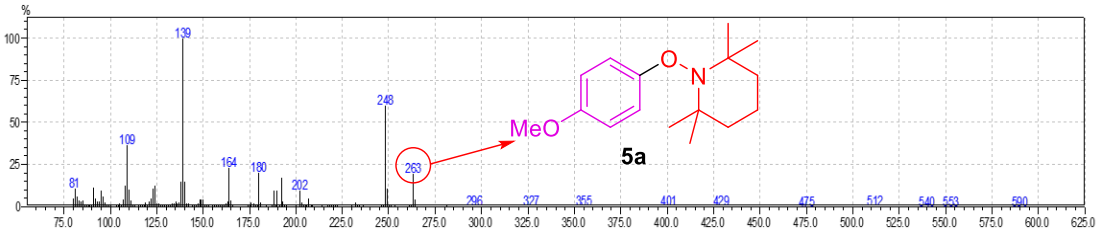
To a dry 10 mL branched spherical flasks was added **3a** (2.0 equiv, 0.4 mmol, 88.9 mg), **2a** (1.2 equiv, 0.24 mmol, 53.3 mg), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (3.0 equiv, 0.6 mmol, 93.8 mg). The tube was sealed, evacuated and backfilled with nitrogen three times, then DCE (2.0 mL), 4-$CF_3C_6H_4SH$ (1.5 equiv, 0.3 mmol, 53.5 mg) and **1a** (0.2 mmol, 23.2 mg) were sequentially added. The resulting solution was stirred under nitrogen atmosphere at room temperature for about 10 h. In

this reaction, the formation of **4a** was completely suppressed. Moreover, GC-MS analysis of this reaction mixture showed that the TEMPO-trapped product **5a** was formed.



Chemical Formula: $C_{16}H_{25}NO_2$
Molecular Weight: 263.3810

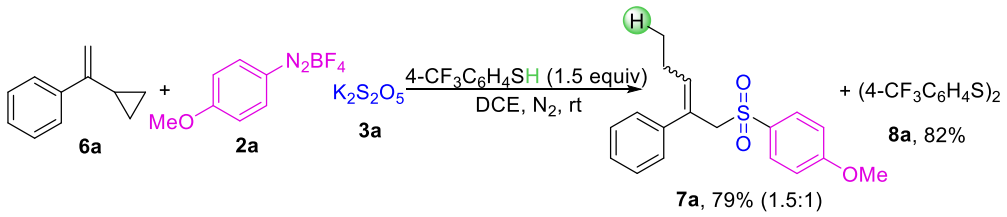
Mass spectrogram of **5a**:



80.05	1865	4.87	103.10	375	0.98	126.15	862	2.25
81.05	4220	11.01	104.10	324	0.85	127.15	502	1.31
82.05	2307	6.02	105.05	749	1.95	128.15	394	1.03
83.05	1599	4.17	106.10	642	1.68	129.10	326	0.85
84.10	1354	3.53	107.05	1675	4.37	130.15	399	1.04
85.15	1561	4.07	108.05	4918	12.83	131.10	470	1.23
86.05	283	0.74	109.05	14105	36.80	132.05	440	1.15
87.10	305	0.80	110.10	3970	10.36	133.10	823	2.15
88.10	170	0.44	111.05	1517	3.96	134.10	705	1.84
89.05	621	1.62	112.15	451	1.18	135.10	1138	2.97
90.05	455	1.19	113.20	577	1.51	136.10	708	1.85
91.10	4276	11.16	114.10	210	0.55	137.10	922	2.41
92.05	2015	5.26	115.10	641	1.67	138.10	5754	15.01
93.05	1310	3.42	116.15	403	1.05	139.10	38327	100.00
94.10	1207	3.15	117.10	522	1.36	140.10	5711	14.90
95.10	3690	9.63	118.10	506	1.32	141.10	828	2.16
96.10	2450	6.39	119.05	1028	2.68	142.20	894	2.33
97.05	1075	2.80	120.10	598	1.56	143.20	252	0.66
98.10	550	1.44	121.10	1226	3.20	144.20	326	0.85
99.10	665	1.74	122.10	1844	4.81	145.10	406	1.06
100.10	246	0.64	123.05	4143	10.81	146.05	563	1.47
101.10	142	0.37	124.05	4896	12.77	147.10	698	1.82
102.10	204	0.53	125.10	919	2.40	148.10	1604	4.19

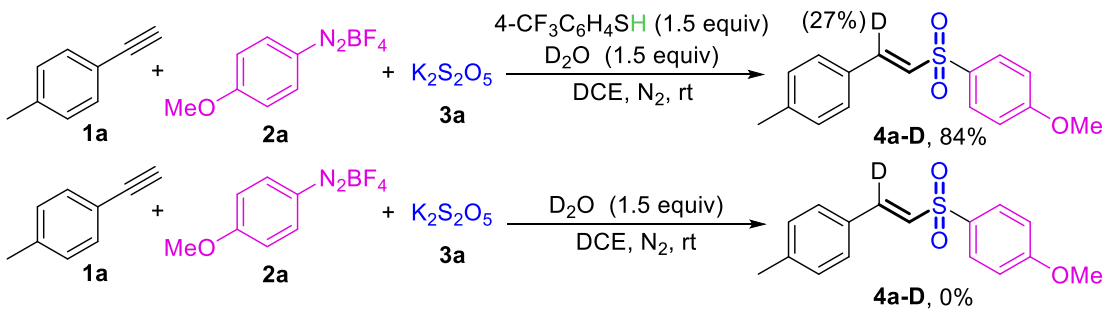
149.10	1710	4.46	189.90	3599	9.39	231.10	98	0.26
150.10	1644	4.29	191.05	622	1.62	232.10	1012	2.64
151.05	537	1.40	192.10	6524	17.02	233.10	289	0.75
152.10	401	1.05	193.10	1158	3.02	234.10	289	0.75
153.10	230	0.60	194.05	341	0.89	235.10	188	0.49
154.00	226	0.59	195.10	178	0.46	236.10	268	0.70
155.05	692	1.81	196.10	103	0.27	237.10	110	0.29
156.00	492	1.28	197.10	134	0.35	238.10	114	0.30
157.00	591	1.54	198.10	167	0.44	239.10	121	0.32
158.00	538	1.40	199.10	140	0.37	240.10	113	0.29
159.00	284	0.74	200.10	298	0.78	241.10	71	0.19
160.10	583	1.52	201.10	234	0.61	242.10	100	0.26
161.05	479	1.25	202.10	3807	9.93	243.10	110	0.29
162.10	770	2.01	203.00	1092	2.85	244.10	73	0.19
163.10	1094	2.85	204.10	636	1.66	245.10	158	0.41
164.05	8935	23.31	205.05	513	1.34	246.10	394	1.03
165.10	1369	3.57	206.00	204	0.53	247.15	429	1.12
166.10	326	0.85	207.00	1956	5.10	248.15	23058	60.16
167.10	169	0.44	208.05	483	1.26	249.15	4148	10.82
168.10	116	0.30	209.00	286	0.75	250.10	644	1.68
169.10	190	0.50	210.00	95	0.25	251.10	223	0.58
170.10	143	0.37	211.00	143	0.37	252.10	114	0.30
171.10	186	0.49	212.00	78	0.20	253.10	223	0.58
172.10	218	0.57	213.00	106	0.28	254.10	134	0.35
173.10	210	0.55	214.00	313	0.82	255.10	47	0.12
174.05	430	1.12	215.00	140	0.37	256.10	113	0.29
175.05	575	1.50	216.00	166	0.43	257.10	57	0.15
176.00	966	2.52	217.10	647	1.69	258.10	63	0.16
177.05	859	2.24	218.10	279	0.73	259.10	52	0.14
178.10	506	1.32	219.10	329	0.86	260.10	84	0.22
179.10	606	1.58	220.05	588	1.53	261.10	577	1.51
180.10	7783	20.31	221.10	302	0.79	262.15	362	0.94
181.10	1022	2.67	222.10	226	0.59	**263.20**	**7478**	**19.51**
182.10	204	0.53	223.10	98	0.26	264.20	1602	4.18
183.10	159	0.41	224.10	79	0.21	265.20	236	0.62
184.10	233	0.61	225.10	130	0.34	266.20	105	0.27
185.10	114	0.30	226.10	81	0.21	267.20	129	0.34
186.10	194	0.51	227.10	95	0.25	268.20	86	0.22
186.95	390	1.02	228.10	100	0.26	269.20	70	0.18
187.95	3618	9.44	229.10	62	0.16			
188.95	607	1.58	230.10	329	0.86			

(2) Radical clock experiment



To a dry 10 mL branched spherical flasks was added **3a** (2.0 equiv, 0.4 mmol, 88.9 mg), **2a** (1.2 equiv, 0.24 mmol, 53.3 mg). The tube was sealed, evacuated and backfilled with nitrogen three times, then DCE (2.0 mL), 4-$CF_3C_6H_4SH$ (1.5 equiv, 0.3 mmol, 53.5 mg) and **6a** (0.2 mmol, 28.8 mg) were sequentially added. The resulting solution was stirred under nitrogen atmosphere at room temperature for about 10 h until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography to afford the ring-opening product **7a** (49.9 mg, 79%, petroleum ether/ethyl acetate = 6:1) and the coupling product **8a** (58.1 mg, 82%, petroleum ether/ethyl acetate = 30:1).

(3) Deuterium-labelling experiments

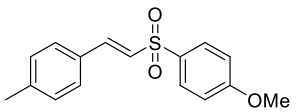


To a dry 10 mL branched spherical flasks was added **3a** (2.0 equiv, 0.4 mmol, 88.9 mg), **2a** (1.2 equiv, 0.24 mmol, 53.3 mg). The tube was sealed, evacuated and backfilled with nitrogen three times, then DCE (2.0 mL), 4-$CF_3C_6H_4SH$ (1.5 equiv, 0.3 mmol,

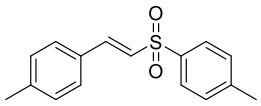
53.5 mg), D_2O (1.5 equiv, 0.3 mmol, 6.0 mg) and **1a** (0.2 mmol, 23.2 mg) were sequentially added. The resulting solution was stirred under nitrogen atmosphere at room temperature for about 10 h until complete consumption of starting material as monitored by TLC and/or gas chromatography-mass spectrometry (GC-MS) analysis. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/ ethyl acetate =3:1) to afford the desired product in 84% yield (27% of D).

To a dry 10 mL branched spherical flasks was added **3a** (2.0 equiv, 0.4 mmol, 88.9 mg), **2a** (1.2 equiv, 0.24 mmol, 53.3 mg). The tube was sealed, evacuated and backfilled with nitrogen three times, then DCE (2.0 mL), D_2O (1.5 equiv, 0.3 mmol, 6.0 mg) and **1a** (0.2 mmol, 23.2 mg) were sequentially added. The resulting solution was stirred under nitrogen atmosphere at room temperature for about 10 h until complete consumption of starting material as monitored by TLC and/or gas chromatography-mass spectrometry (GC-MS) analysis.

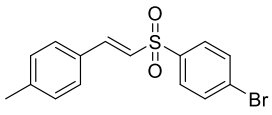
(D) Analytical data



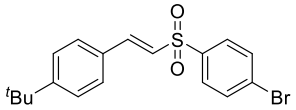
(*E*)-1-Methoxy-4-((4-methylstyryl)sulfonyl)benzene (4a).[1] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (49.0 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 15.6 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 15.6 Hz, 1H), 3.87 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.5, 141.6, 141.4, 132.4, 129.8, 129.7, 128.5, 126.7, 114.5, 55.7, 21.5.



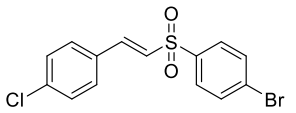
(*E*)-1-Methyl-4-((4-methylstyryl)sulfonyl)benzene (4b).[2] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (44.1 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.82 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 15.2 Hz, 1H), 7.37-7.31 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 15.2 Hz, 1H), 2.42 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.1, 141.9, 141.6, 137.8, 129.8, 129.7, 129.4, 128.4, 127.5, 126.3, 21.5, 21.4.



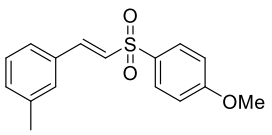
(*E*)-1-Bromo-4-((4-methylstyryl)sulfonyl)benzene (4c).[3] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (50.4 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 7.6 Hz, 3H), 7.37 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 15.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.1, 142.0, 139.9, 132.5, 129.8, 129.3, 129.1, 128.6, 128.4, 125.4, 21.5.



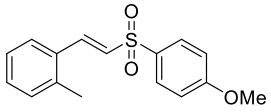
(*E*)-1-Bromo-4-((4-(*tert*-butyl)styryl)sulfonyl)benzene (4d). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (59.0 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.4 Hz, 2H), 7.68 (t, J = 8.0 Hz, 3H), 7.44-7.40 (m, 4H), 6.81 (d, J = 15.2 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 155.1, 143.0, 139.9, 132.5, 129.3, 129.0, 128.5, 128.4, 126.0, 125.6, 34.9, 31.0; HRMS *m/z* (ESI) calcd for $C_{18}H_{20}BrO_2S$ ($[M+H]^+$) 379.0362, found 379.0368.



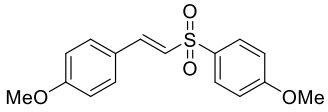
(*E*)-1-Bromo-4-((4-chlorostyryl)sulfonyl)benzene (4e).[4] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (51.3 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 15.2 Hz, 1H), 7.43-7.36 (m, 4H), 6.81 (d, J = 15.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 141.5, 139.5, 137.5, 132.7, 130.6, 129.8, 129.4, 129.2, 128.8, 127.4.



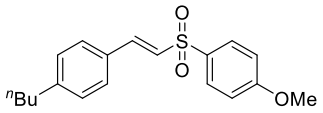
(*E*)-1-(2-((4-Methoxyphenyl)sulfonyl)vinyl)-3-methylbenzene (4f). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (48.4 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 15.6 Hz, 1H), 7.18 (d, J = 4.8 Hz, 3H), 7.12 (d, J = 4.4 Hz, 1H), 6.91 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 15.6 Hz, 1H), 3.77 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.4, 141.4, 138.7, 132.3, 132.2, 131.7, 129.7, 128.9, 128.8, 127.6, 125.6, 114.4, 55.6, 21.1; HRMS *m/z* (ESI) calcd for $C_{16}H_{17}O_3S$ ($[M+H]^+$) 289.0893, found 289.0889.



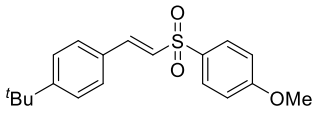
(*E*)-1-(2-((4-Methoxyphenyl)sulfonyl)vinyl)-2-methylbenzene (4g). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (47.8 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (t, J = 12.4 Hz, 3H), 7.32 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.11-7.06 (m, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 15.2 Hz, 1H), 3.76 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.4, 138.8, 137.9, 132.0, 131.2, 130.8, 130.6, 129.7, 128.7, 126.6, 126.3, 114.4, 55.6, 19.6; HRMS *m/z* (ESI) calcd for $C_{16}H_{17}O_3S$ ([M+H]$^+$) 289.0893, found 289.0889.



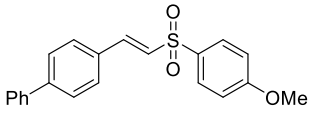
(*E*)-1-Methoxy-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4h).[1] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (52.9 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 15.2 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.69 (d, J = 15.6 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.3, 161.9, 141.1, 132.6, 130.2, 129.7, 125.1 (2), 114.4 (2), 55.6, 55.4.



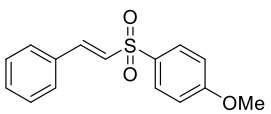
(*E*)-1-Butyl-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4i). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (55.5 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 15.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 15.6 Hz, 1H), 3.86 (s, 3H), 2.61 (t, J = 8.0 Hz, 2H), 1.63-1.56 (m, 2H), 1.36-1.30 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.4, 146.6, 141.5, 132.4, 129.9, 129.8, 129.1, 128.5, 126.7, 114.5, 55.6, 35.5, 33.3 22.2, 13.9; HRMS *m/z* (ESI) calcd for $C_{19}H_{23}O_3S$ ([M+H]$^+$) 331.1362, found: 331.1360.



(*E*)-1-(*tert*-Butyl)-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4j).[5] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (54.8 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 15.6 Hz, 1H), 7.42-7.39 (m, 4H), 7.00 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 15.2 Hz, 1H), 3.87 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.4, 154.7, 141.4, 132.4, 129.8, 129.7, 128.3, 126.9, 126.0, 114.5, 55.7, 34.9, 31.1.

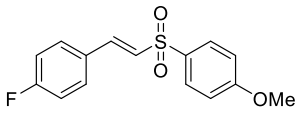


(*E*)-4-(2-((4-Methoxyphenyl)sulfonyl)vinyl)-1,1'-biphenyl (4k). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (56.7 mg, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 15.5 Hz, 1H), 7.62-7.58 (m, 4H), 7.54 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 15.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.5, 143.7, 140.9, 139.8, 132.2, 131.4, 129.9, 129.0, 128.9, 128.0, 127.6 (2), 127.0, 114.5, 55.7.; HRMS *m/z* (ESI) calcd for $C_{21}H_{19}O_3S$ ([M+H]$^+$) 351.1049, found: 351.1045.

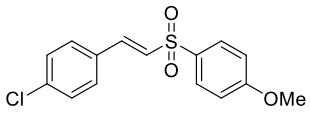


(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene (4l).[1] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (43.9 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 15.6 Hz, 1H), 7.45 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 6.4 Hz, 3H), 6.99 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 15.2 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz,

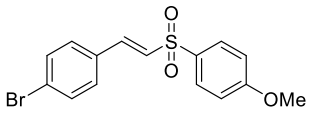
$CDCl_3$) δ: 163.4, 141.2, 132.3, 132.0, 130.9, 129.7, 128.9, 128.3, 127.8, 114.5, 55.6.



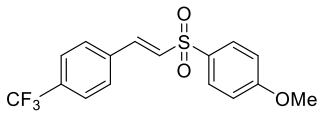
(*E*)-1-Fluoro-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4m).[6] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (44.4 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 15.2 Hz, 1H), 7.44 (t, J = 6.8 Hz, 2H), 7.04 (t, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 15.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0 (d, $J_{C\text{-}F}$ = 253.5 Hz), 163.4, 139.9, 131.9, 130.4 (d, $J_{C\text{-}F}$ = 8.8 Hz), 129.7, 128.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 127.6 (d, $J_{C\text{-}F}$ = 2.3 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.1 Hz), 114.5, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -108.1.



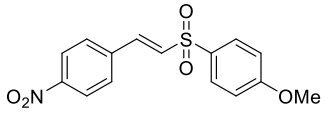
(*E*)-1-Chloro-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4n).[6] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (45.0 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 15.6 Hz, 1H), 7.41-7.34 (m, 4H), 7.01 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 15.6 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.7, 139.8, 137.0, 131.9, 131.0, 129.9, 129.6, 129.3, 128.5, 114.6, 55.7.



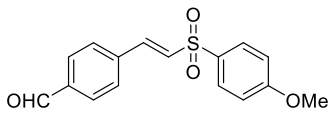
(*E*)-1-Bromo-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4o). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (50.7 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (d, J = 8.8 Hz, 2H), 7.57-7.50 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 15.2 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.6, 139.9, 132.3, 131.8, 131.4, 129.9, 129.8, 128.6, 125.4, 114.6, 55.7; HRMS *m/z* (ESI) calcd for $C_{15}H_{14}BrO_3S$ ([M+H]$^+$) 352.9842, found: 352.9846.



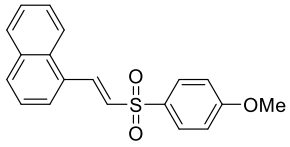
(*E*)-1-Methoxy-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene (4p).[1] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (47.9 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88 (d, J = 9.0 Hz, 2H), 7.66-7.63 (m, 3H), 7.58 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 15.5 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.8, 139.3, 135.9, 132.4 (q, $J_{C\text{-}F}$ = 32.9 Hz), 131.5, 130.6, 130.0, 126.0 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.9 Hz),122.5, 114.7, 55.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ: -63.0.



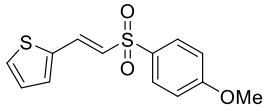
(*E*)-1-Methoxy-4-((4-nitrostyryl)sulfonyl)benzene (4q).[4] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). Yellow solid (35.7 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (t, J = 7.6 Hz, 2H), 7.89 (t, J = 8.4 Hz, 2H), 7.67-7.52 (m, 4H), 7.03 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 164.0, 147.9, 140.2, 138.1, 133.0, 132.3, 130.2, 129.1, 124.2, 114.8, 55.7.



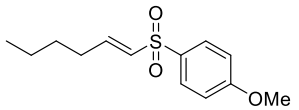
(*E*)-4-(2-((4-Methoxyphenyl)sulfonyl)vinyl)benzaldehyde (4r). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (36.9 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.02 (s, 1H), 7.88-7.85 (m, 4H), 7.67-7.58 (m, 3H), 7.03-6.95 (m, 3H), 3.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.2, 163.8, 139.4, 138.0, 137.5, 131.4, 131.1, 130.2, 130.1, 128.9, 114.7, 55.7; HRMS *m/z* (ESI) calcd for $C_{16}H_{15}O_4S$ ([M+H]$^+$) 303.0686, found: 303.0680.



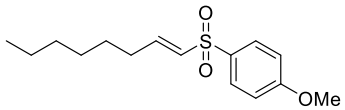
(*E*)-1-(2-((4-Methoxyphenyl)sulfonyl)vinyl)naphthalene (4s). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). white solid (48.0 mg, 74% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.46 (d, J = 15.0 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 9.0 Hz, 2H), 7.90-7.85 (m, 2H), 7.65- 7.52 (m, 3H), 7.43 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 15.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.6, 138.3, 133.6, 132.0, 131.2, 130.2, 129.9, 129.6, 128.8, 127.2, 126.4, 125.5, 125.3, 123.0, 114.6, 55.7; HRMS *m/z* (ESI) calcd for $C_{19}H_{17}O_3S$ ($[M+H]^+$) 325.0893, found: 325.0897.



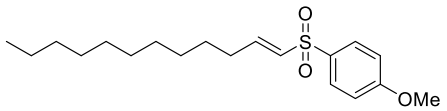
(*E*)-2-(2-((4-Methoxyphenyl)sulfonyl)vinyl)thiophene (4t). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Yellow solid (36.4 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (t, J = 7.0 Hz, 2H), 7.74 (d, J = 15.0 Hz, 1H), 7.42 (d, J = 5.0 Hz, 1H), 7.29 (d, J = 3.5 Hz, 1H), 7.06 (t, J = 4.5 Hz, 1H), 7.01 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 15.5 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.5, 137.0, 134.0, 132.2, 132.1, 129.8, 129.7, 128.2, 126.1, 114.5, 55.7; HRMS *m/z* (ESI) calcd for $C_{13}H_{13}O_3S_2$ ($[M+H]^+$) 281.0301, found: 281.0307.



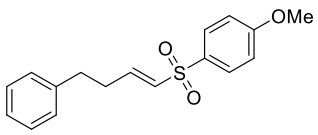
(*E*)-1-(Hex-1-en-1-ylsulfonyl)-4-methoxybenzene (4u). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v). Yellow oil (27.4 mg, 54% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 6.28-6.17 (m, 2H), 3.88 (s, 3H), 2.68-2.63 (m, 2H), 1.41-1.33 (m, 4H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.4, 146.4, 133.5, 130.8, 129.5, 114.4, 55.7, 30.8, 27.4, 22.3, 13.8; HRMS *m/z* (ESI) calcd for $C_{13}H_{19}O_3S$ ($[M+H]^+$) 255.1049, found: 255.1045.



(*E*)-1-Methoxy-4-(oct-1-en-1-ylsulfonyl)benzene (4v). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (28.8 mg, 51% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, J = 8.5 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.5 Hz, 1H), 7.00 (d, J = 8.5 Hz, 1H), 6.27 (d, J = 11.0 Hz, 1H), 6.22-6.18 (m, 1H), 3.88 (s, 3H), 2.64 (t, J = 7.5 Hz, 1H), 2.22 (t, J = 7.0 Hz, 1H), 1.31-1.25 (m, 4H), 0.88 (t, J = 6.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.4, 146.5, 132.5, 129.5, 126.0, 114.4, 55.6, 32.1, 31.5, 28.7, 27.7, 22.5, 14.0; HRMS *m/z* (ESI) calcd for $C_{15}H_{23}O_3S$ ($[M+H]^+$) 283.1362, found: 283.1364.

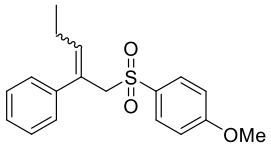


(*E*)-1-(Dodec-1-en-1-ylsulfonyl)-4-methoxybenzene (4w). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (8:1, v/v). Yellow oil (33.8 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 6.30-6.15 (m, 2H), 3.87 (s, 3H), 2.67-2.61 (m, 2H), 1.29-1.22 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 163.4, 146.5, 133.5, 130.8, 129.4, 114.3, 55.6, 31.9, 29.7, 29.5 (2), 29.3 (2), 28.7, 27.7, 22.7, 14.1; HRMS *m/z* (ESI) calcd for $C_{19}H_{31}O_3S$ ($[M+H]^+$) 339.1988, found: 339.1984.

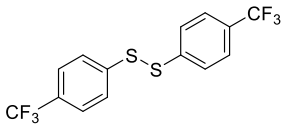


(*E*)-1-Methoxy-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (4x).[7] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v). Colorless oil (39.3 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76-7.73 (m, 2H), 7.30-7.27 (m, 2H), 7.22-7.17 (m, 3H), 6.97-6.94 (m, 2H), 6.29-6.17 (m, 2H), 3.87 (s, 3H), 3.04-2.99 (m, 2H), 2.76 (t, J = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.4,

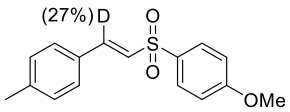
144.8, 140.3, 133.2, 131.3, 129.5, 128.5 (2), 126.2, 114.4, 55.6, 34.8, 29.7.



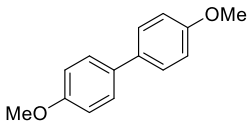
1-Methoxy-4-((2-phenylpent-2-en-1-yl)sulfonyl)benzene (7a). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (6:1, v/v). Yellow oil (49.9 mg, 79% yield, 1.5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.68-7.62 (m, 2H), 7.24-7.15 (m, 4H), 7.04 (d, J = 7.0 Hz, 1H), 6.88 (d, J = 8.5 Hz, 0.8H), 6.81 (d, J = 9.0 Hz, 1.2H), 5.95 (t, J = 7.5 Hz, 0.6H), 5.60 (t, J = 7.5 Hz, 0.4H), 4.33 (s, 1.2H), 4.09 (s, 0.8H), 3.83 (s, 1.2H), 3.80 (s, 1.8H), 2.12-2.08 (m, 1.2H), 2.03-1.97 (m, 0.8H), 0,98 (t, J = 7.5 Hz, 1.8H), 0.88 (t, J = 7.5 Hz, 1.2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.5, 163.4, 140.8, 140.0 (2), 138.4, 130.6, 130.5, 128.4, 128.1, 128.0, 127.7, 127.5, 127.0, 126.9, 126.3, 114.0, 113.9, 65.2, 57.7, 55.6, 55.5, 22.7, 22.6, 13.9, 13.5; HRMS m/z (ESI) calcd for $C_{18}H_{21}O_3S$ ($[M+H]^+$) 317.1206, found: 317.1202.



1,2-Bis(4-(trifluoromethyl)phenyl)disulfane (8a).[8] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v). Yellow solid (58.1 mg, 82% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.58-7.54 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.8 (q, J = 1.3 Hz), 129.4 (q, J = 32.9 Hz), 126.6, 126.1 (q, J = 3.8 Hz), 123.9 (q, J = 272.4 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ: -62.6.



(*E*)-1-Methoxy-4-((2-(*p*-tolyl)vinyl-2-d)sulfonyl)benzene (4a-D). The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v). White solid (48.6 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86 (d, J = 9.0 Hz, 2H), 7.59 (d, J = 15.5 Hz, 0.73H), 7.36 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 9.5 Hz, 2H), 6.80 (d, J = 15.5 Hz, 1H), 3.86 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.4, 141.5, 141.4, 132.4, 129.7, 129.7, 128.4, 126.7, 114.5, 55.6, 21.4.



4,4'-Dimethoxybiphenyl (9a).[9] The product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v). White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (d, J = 9.0 Hz, 4H), 6.94 (d, J = 9.0 Hz, 4H), 3.82 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.7, 133.4, 127.7, 114.1, 55.3.

(E) References

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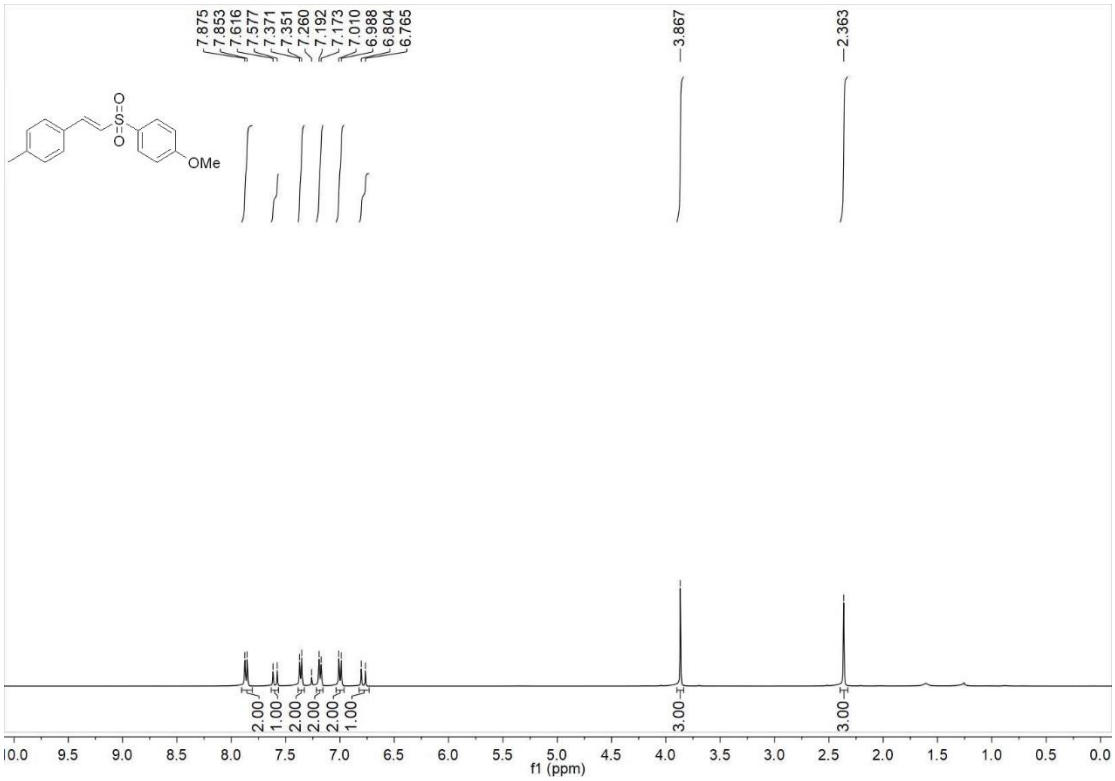
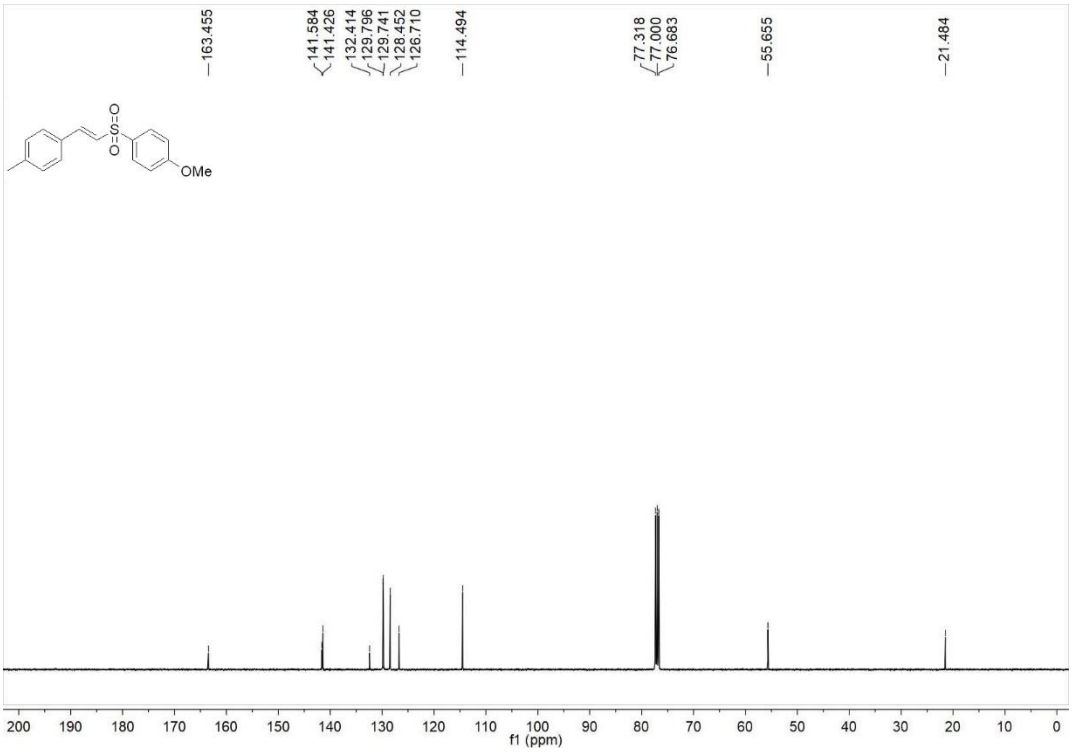
(F) Spectra

(*E*)-1-Methoxy-4-((4-methylstyryl)sulfonyl)benzene (4a)

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

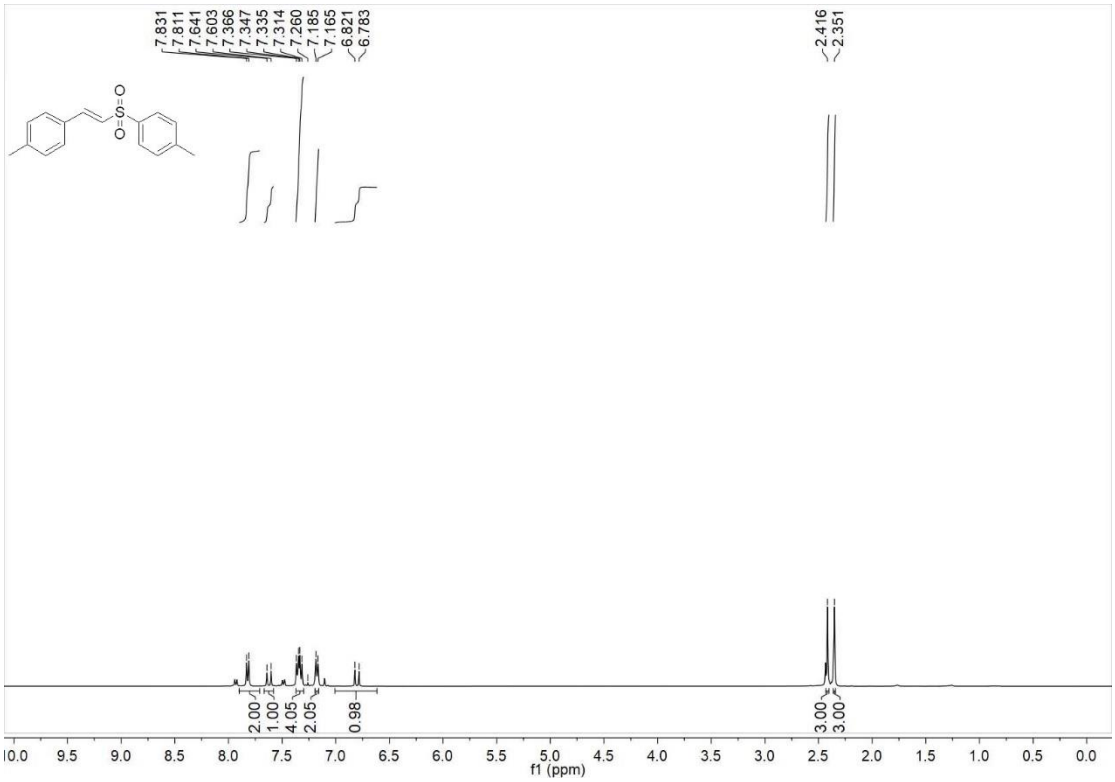


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4a**

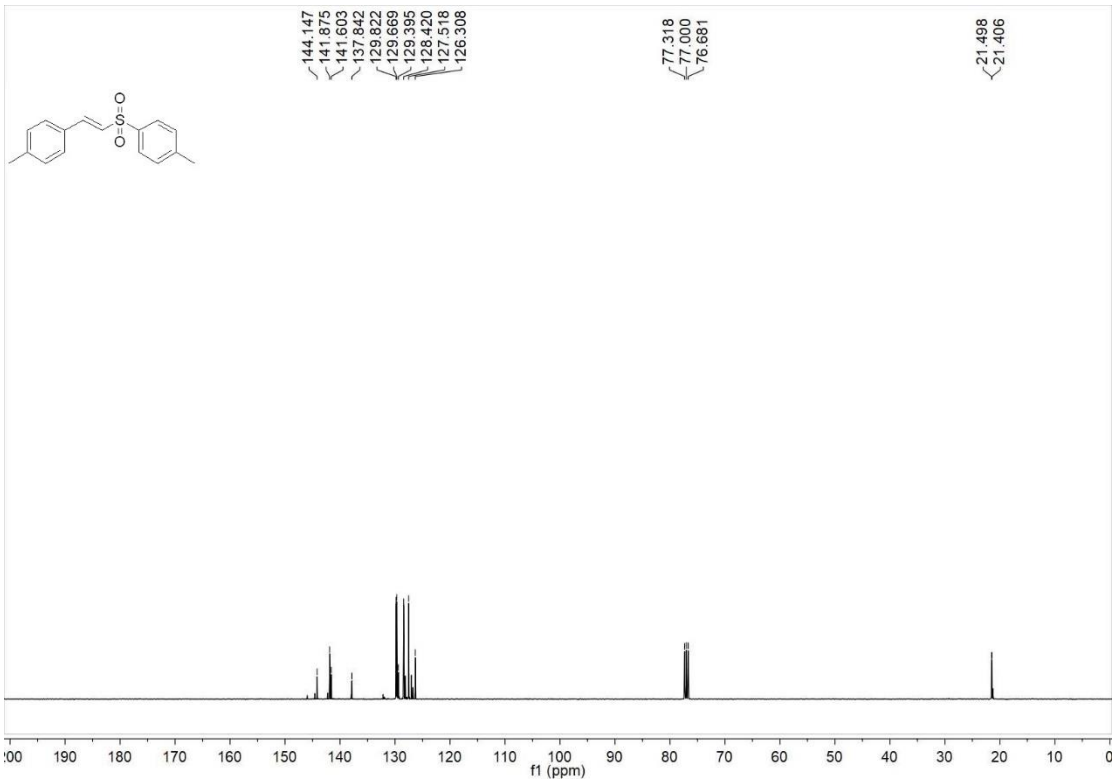


(*E*)-1-Methyl-4-((4-methylstyryl)sulfonyl)benzene (4b)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4b**

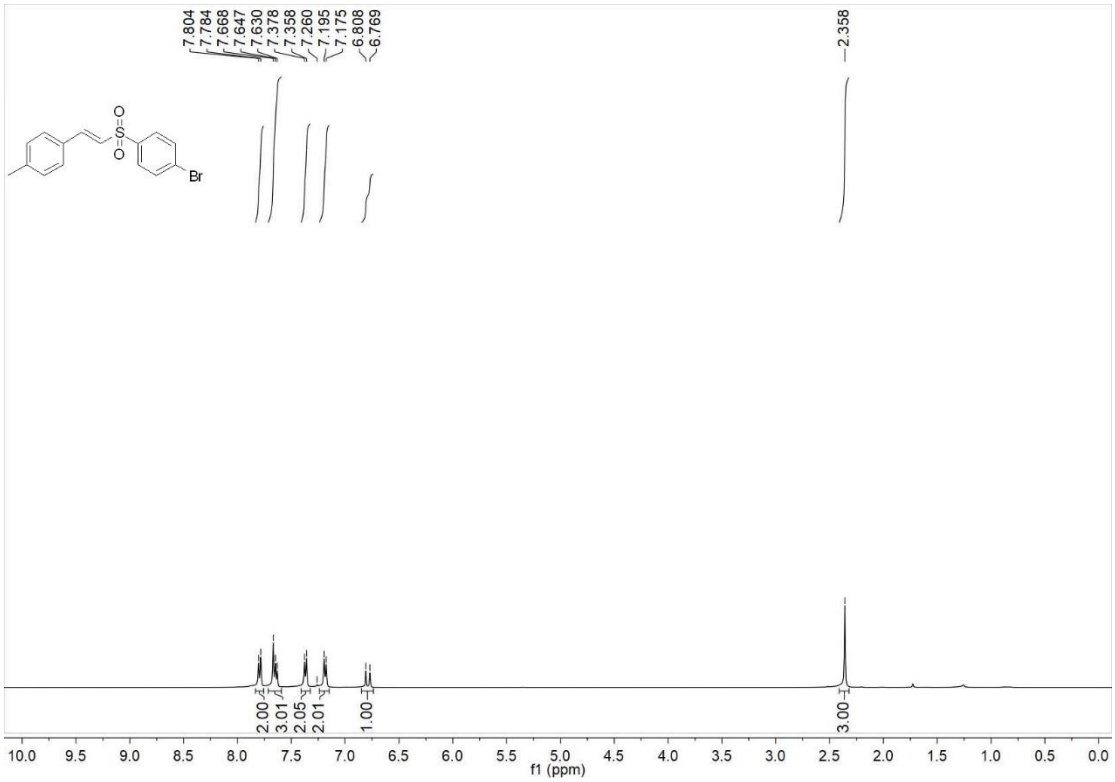


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4b**

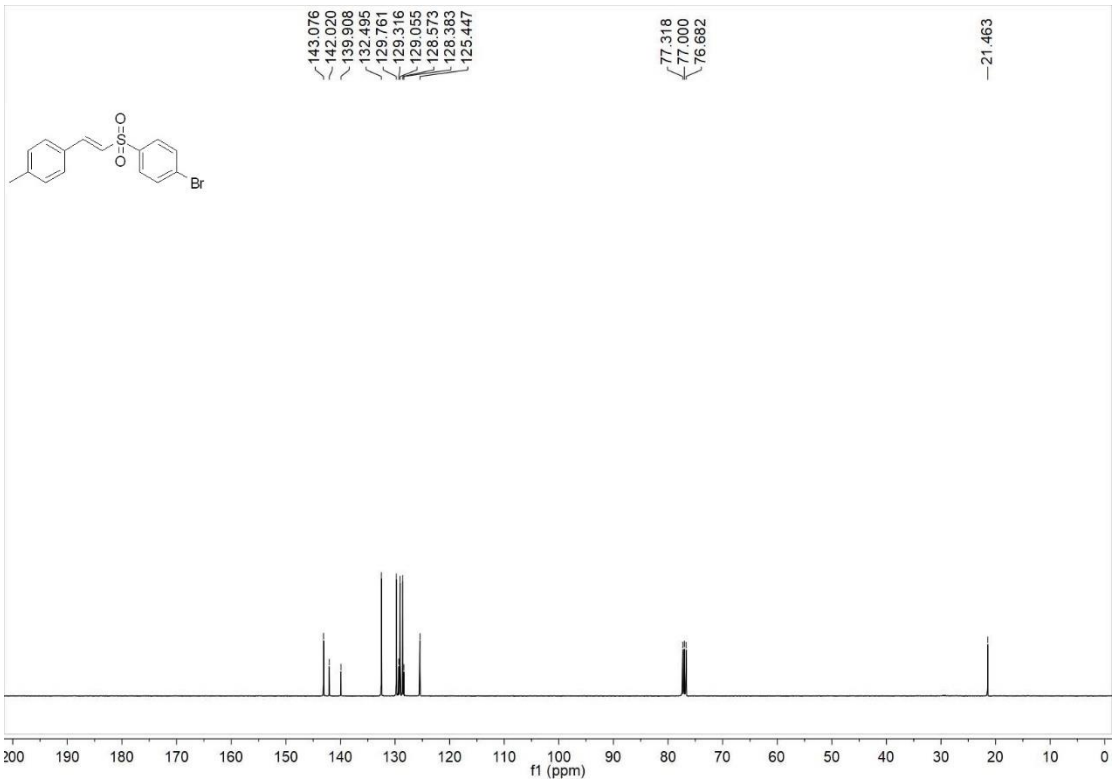


(*E*)-1-Bromo-4-((4-methylstyryl)sulfonyl)benzene (4c)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4c**

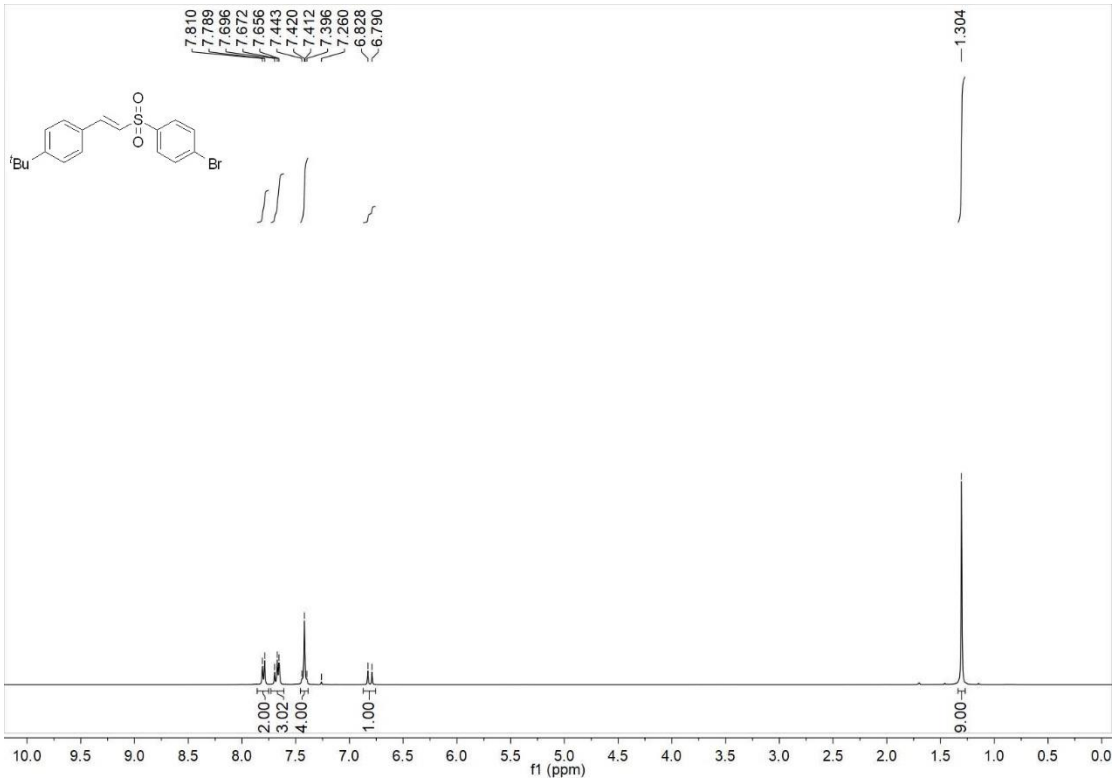


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4c**

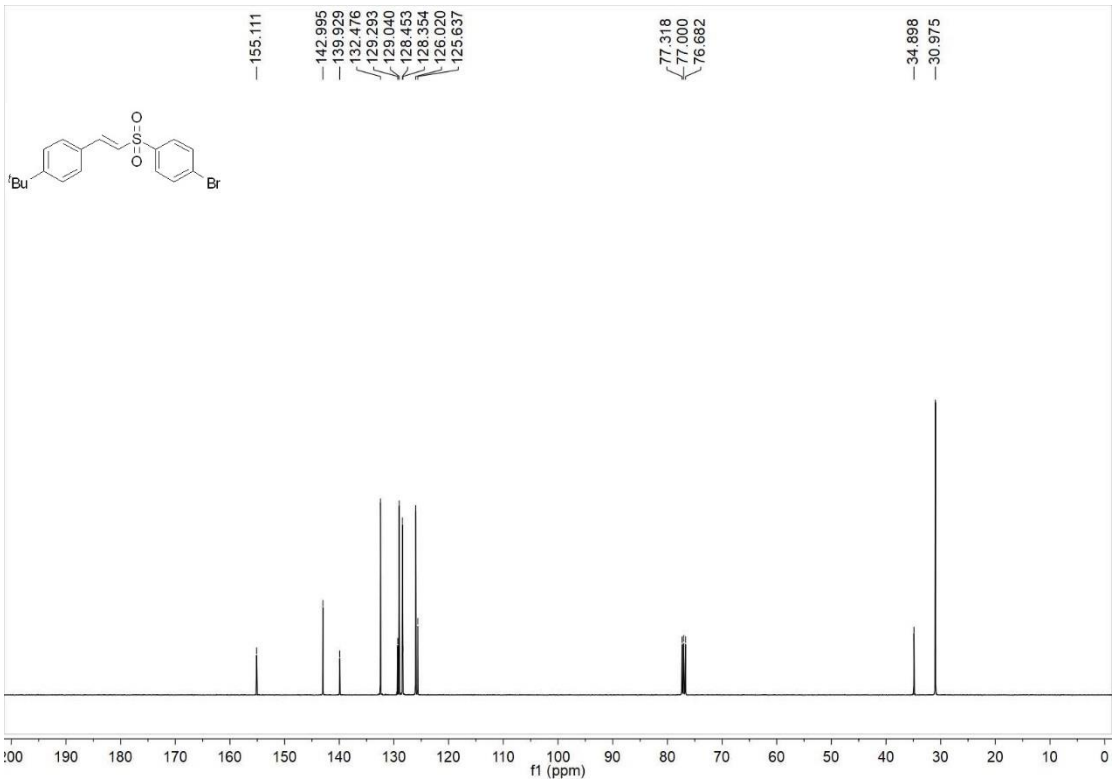


(*E*)-1-Bromo-4-((4-(*tert*-butyl)styryl)sulfonyl)benzene (4d)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4d**

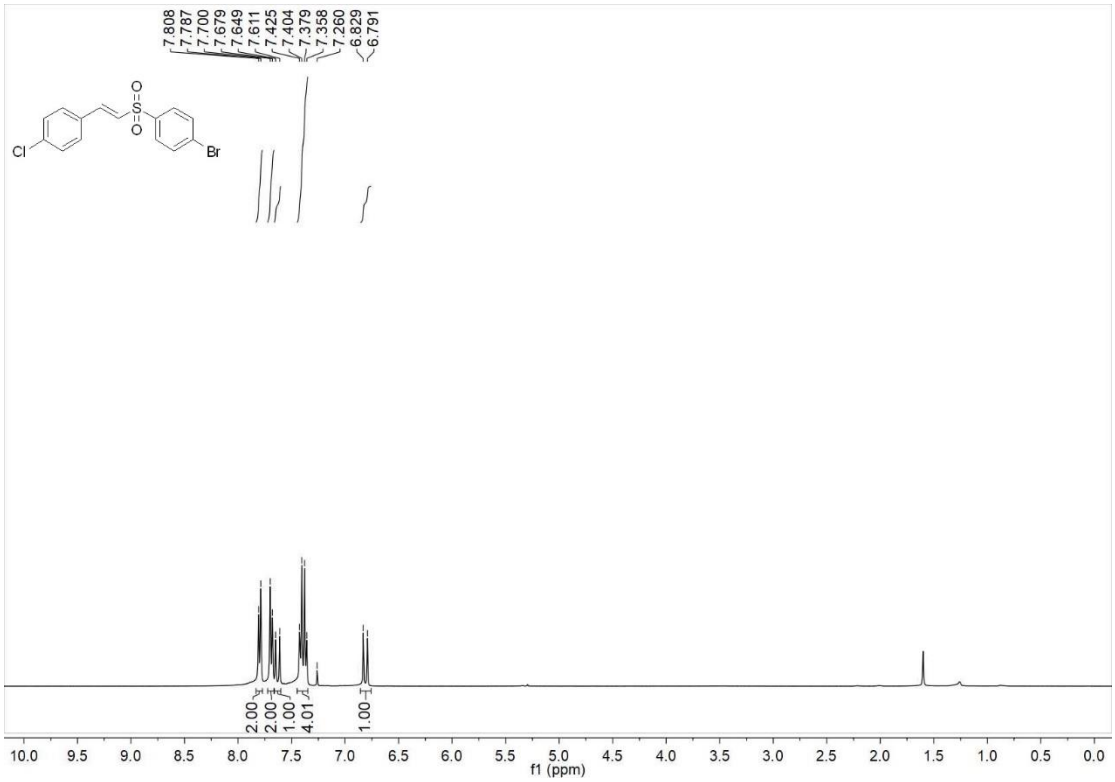


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4d**

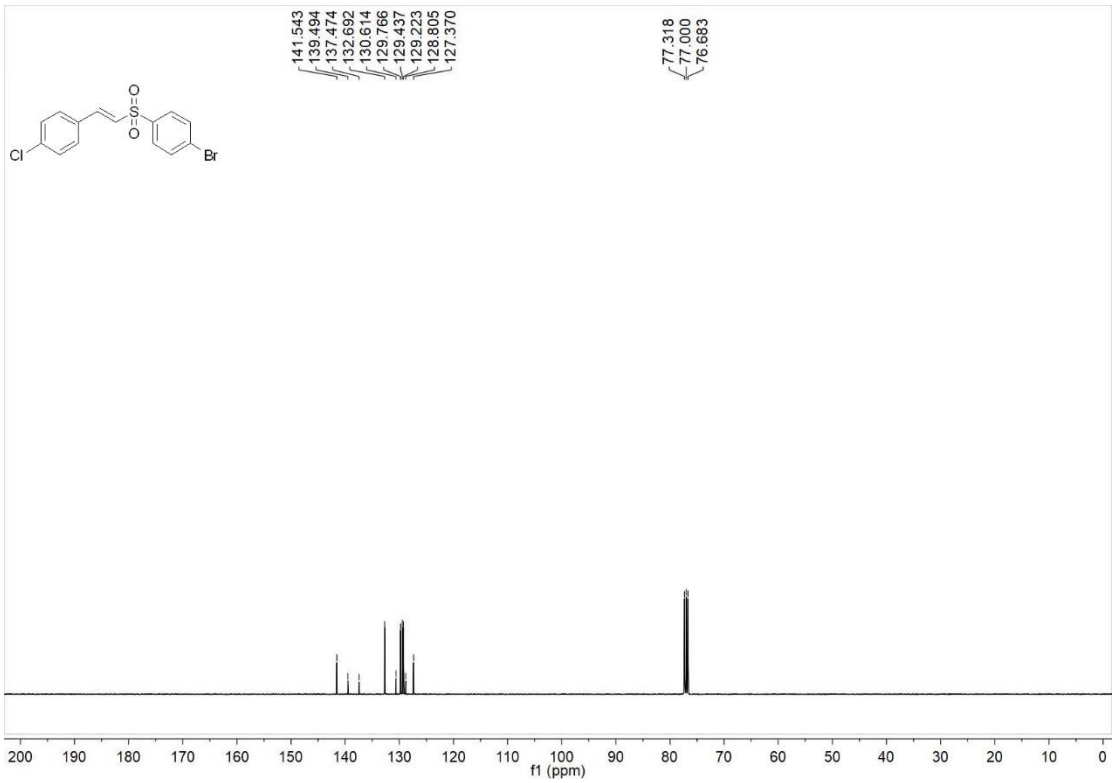


(E)-1-Bromo-4-((4-chlorostyryl)sulfonyl)benzene (4e)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4e**

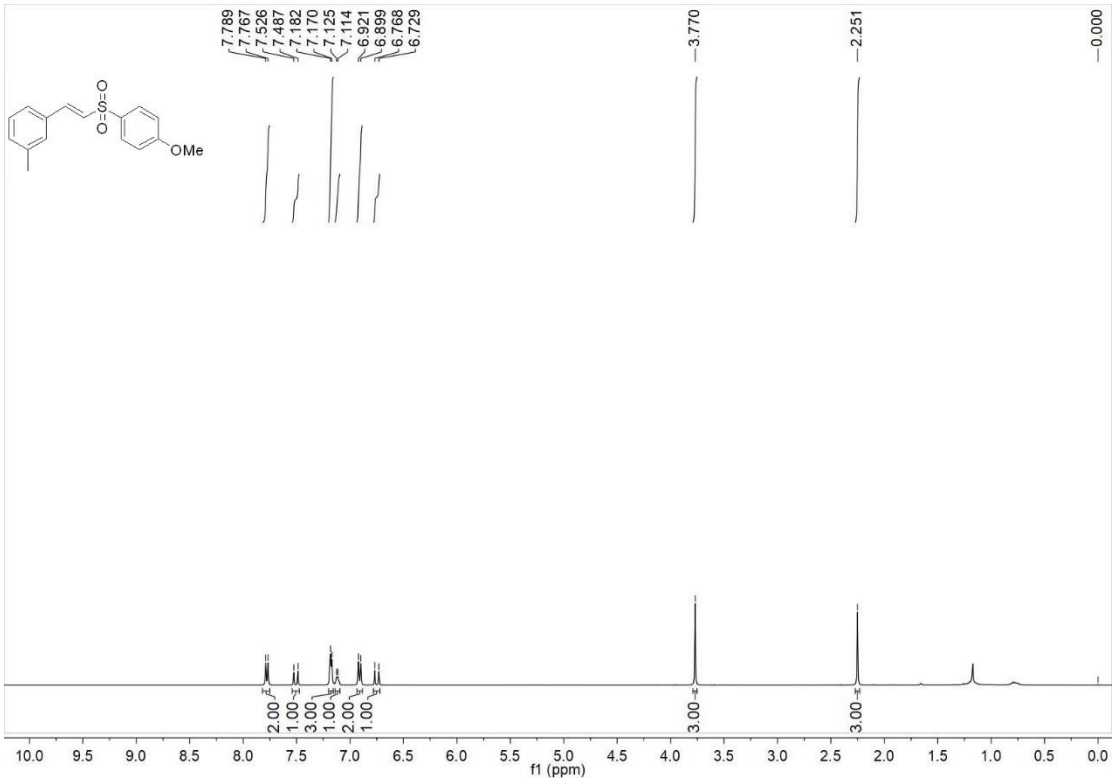


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4e**

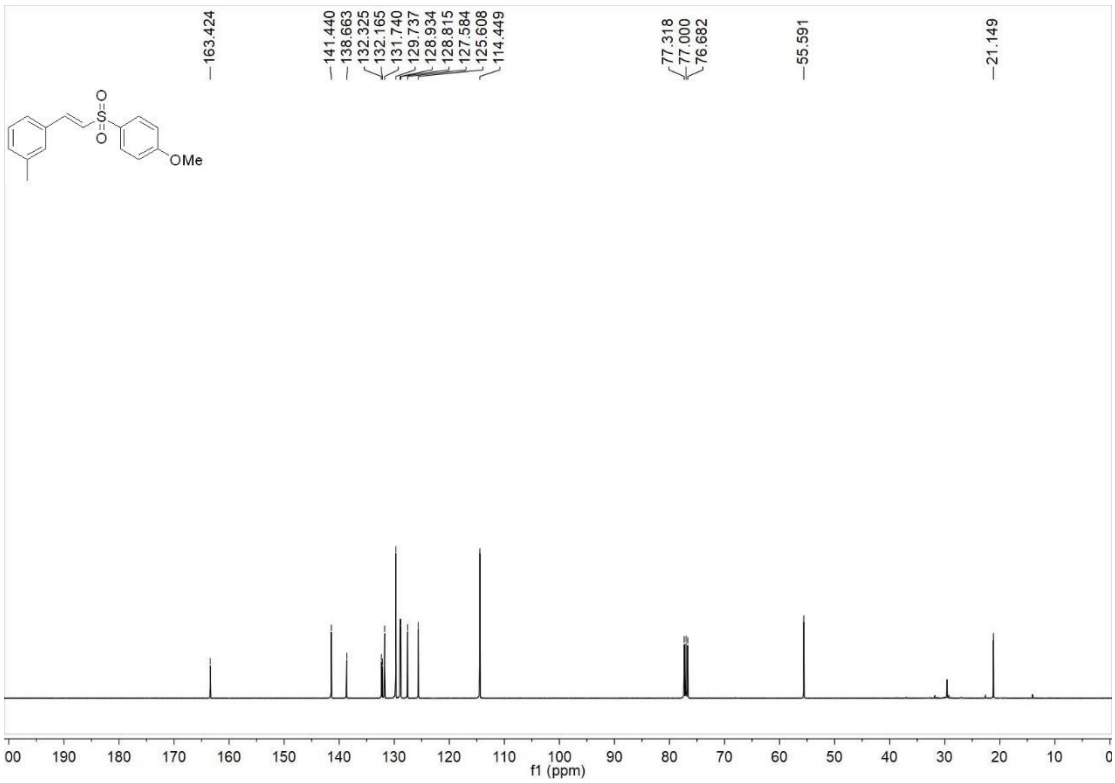


(*E*)-1-(2-((4-Methoxyphenyl)sulfonyl)vinyl)-3-methylbenzene (4f)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4f**

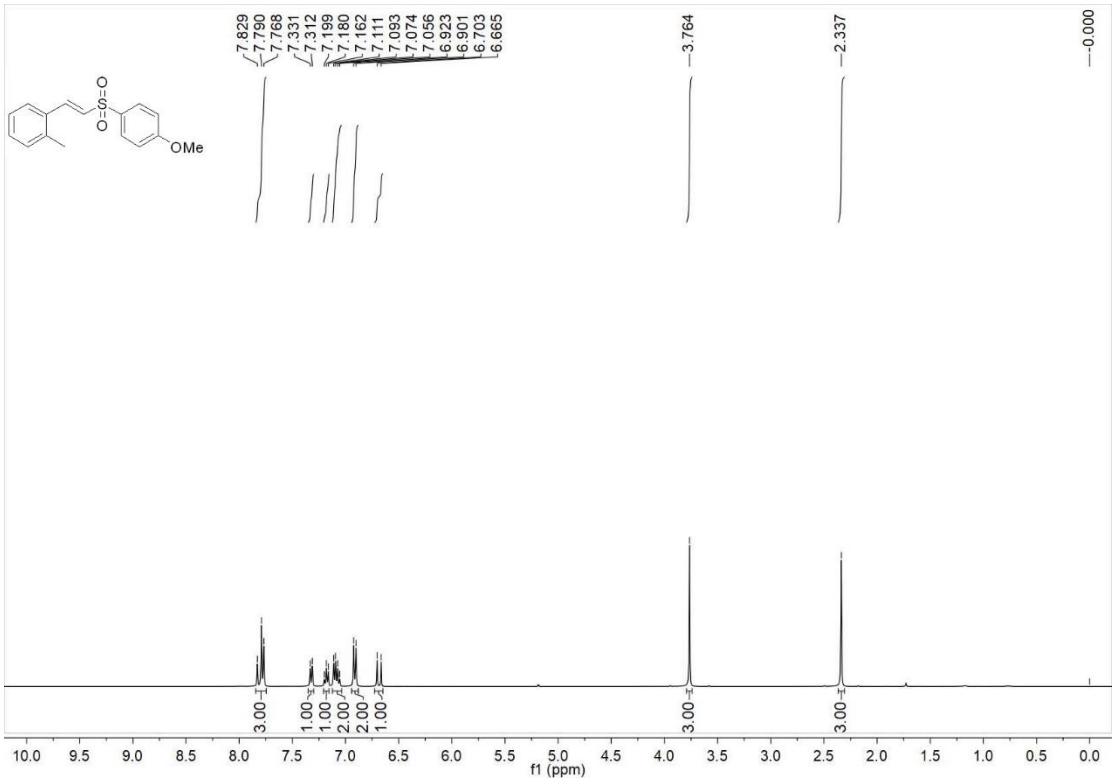


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4f**

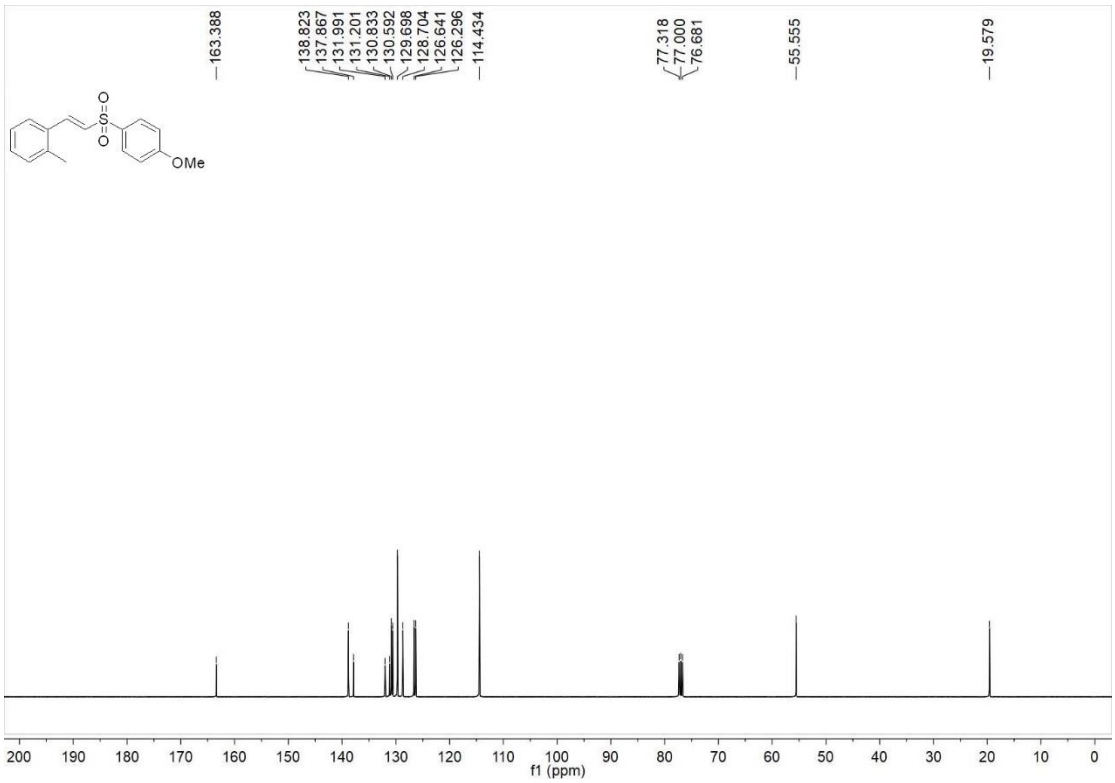


(*E*)-1-(2-((4-Methoxyphenyl)sulfonyl)vinyl)-2-methylbenzene (4g)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4g**

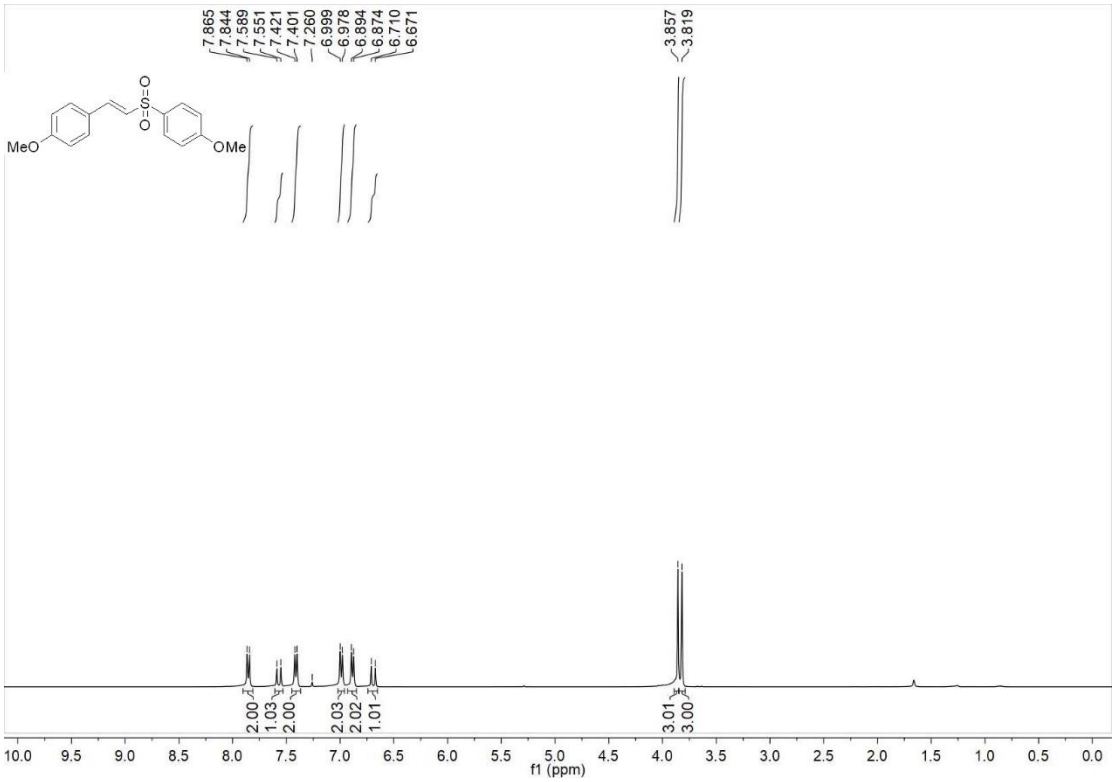


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4g**

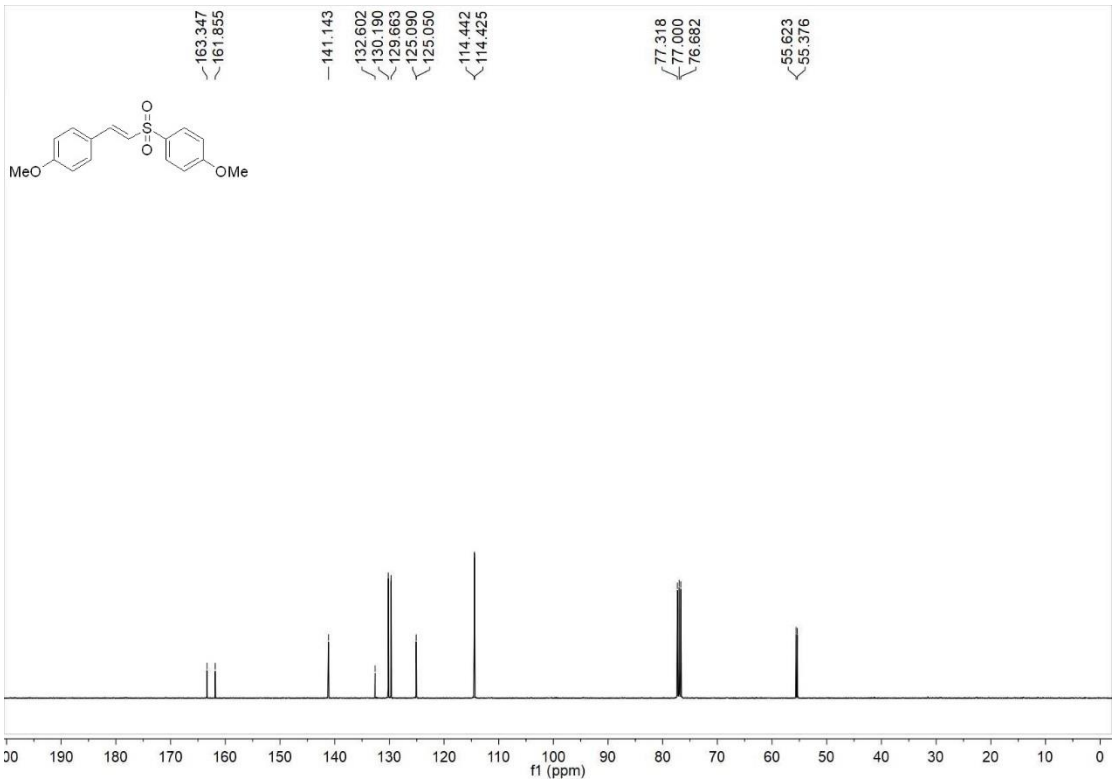


(*E*)-1-Methoxy-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4h)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4h**

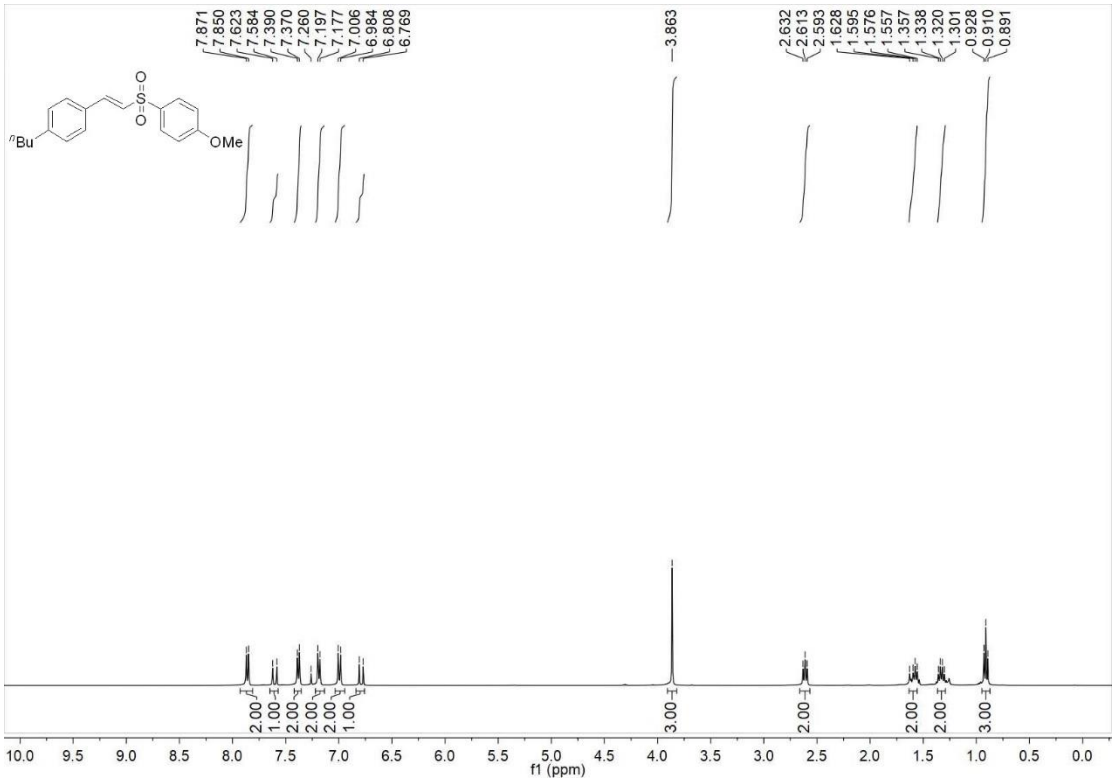


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4h**

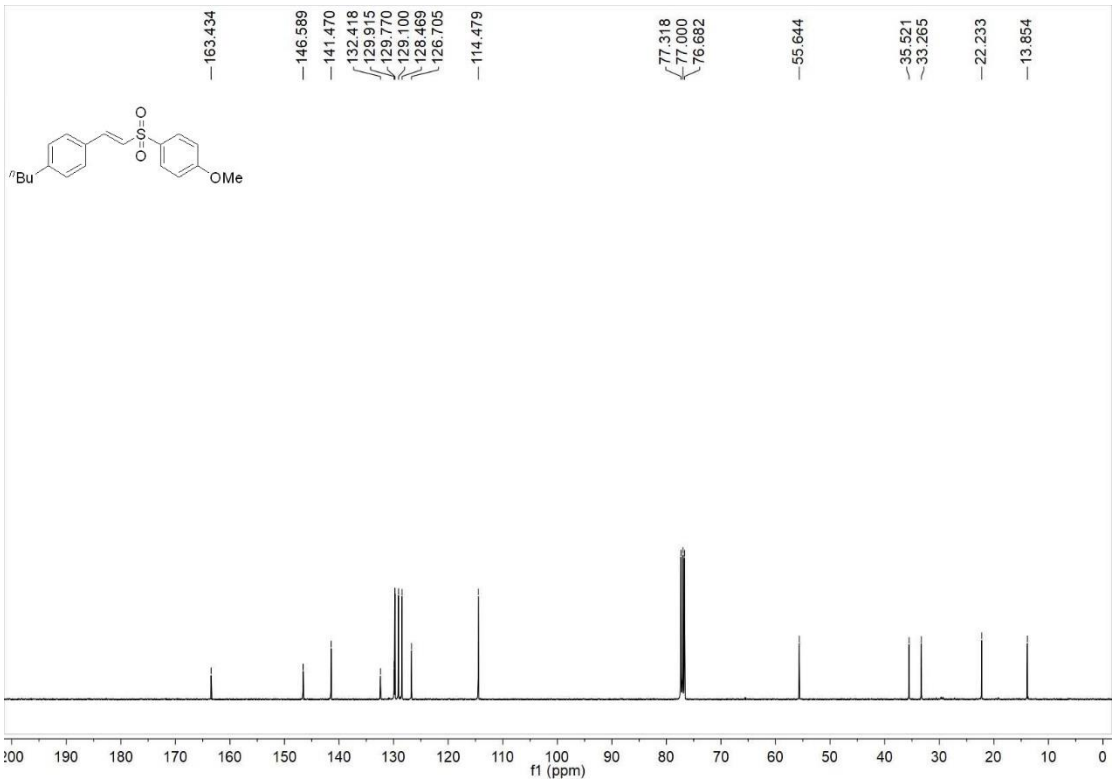


(*E*)-1-Butyl-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4i)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4i**

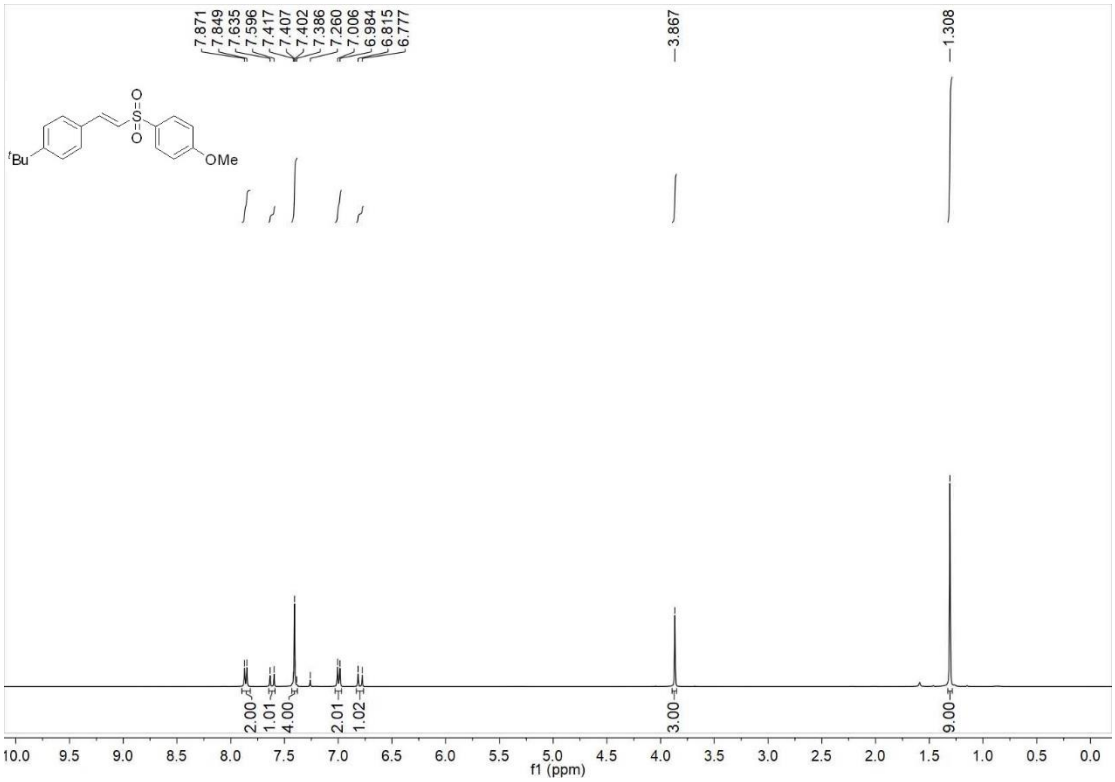


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4i**

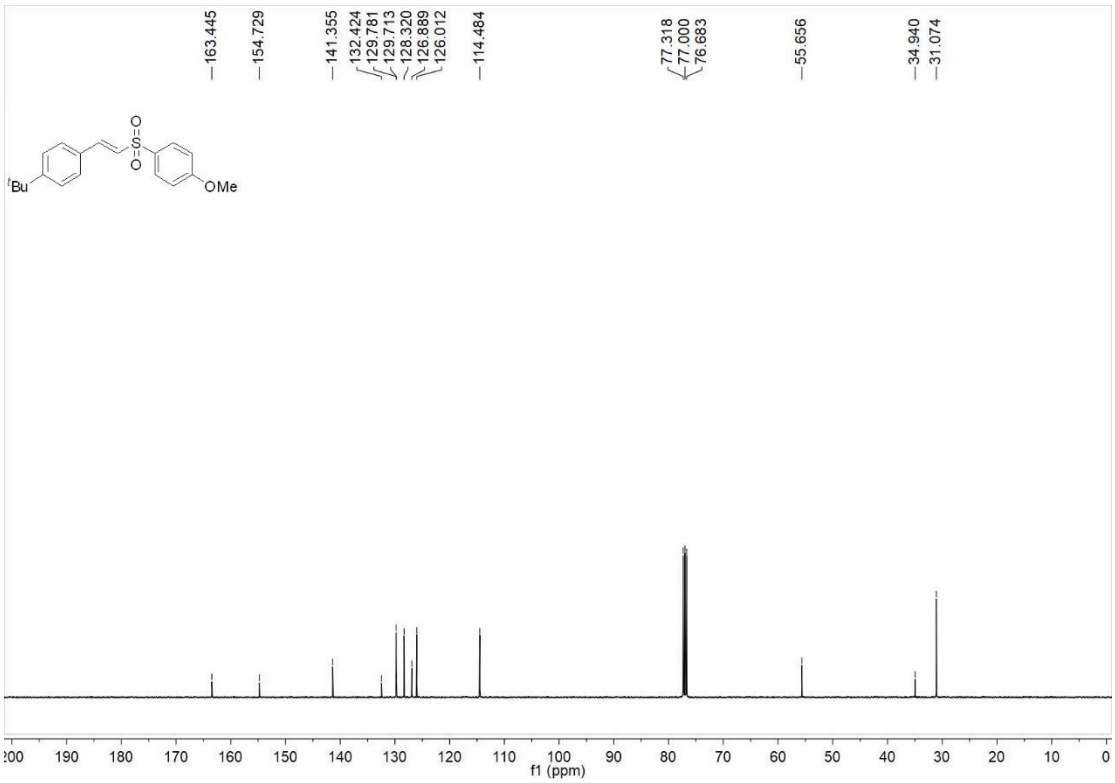


(*E*)-1-(*tert*-Butyl)-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4j)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4j**

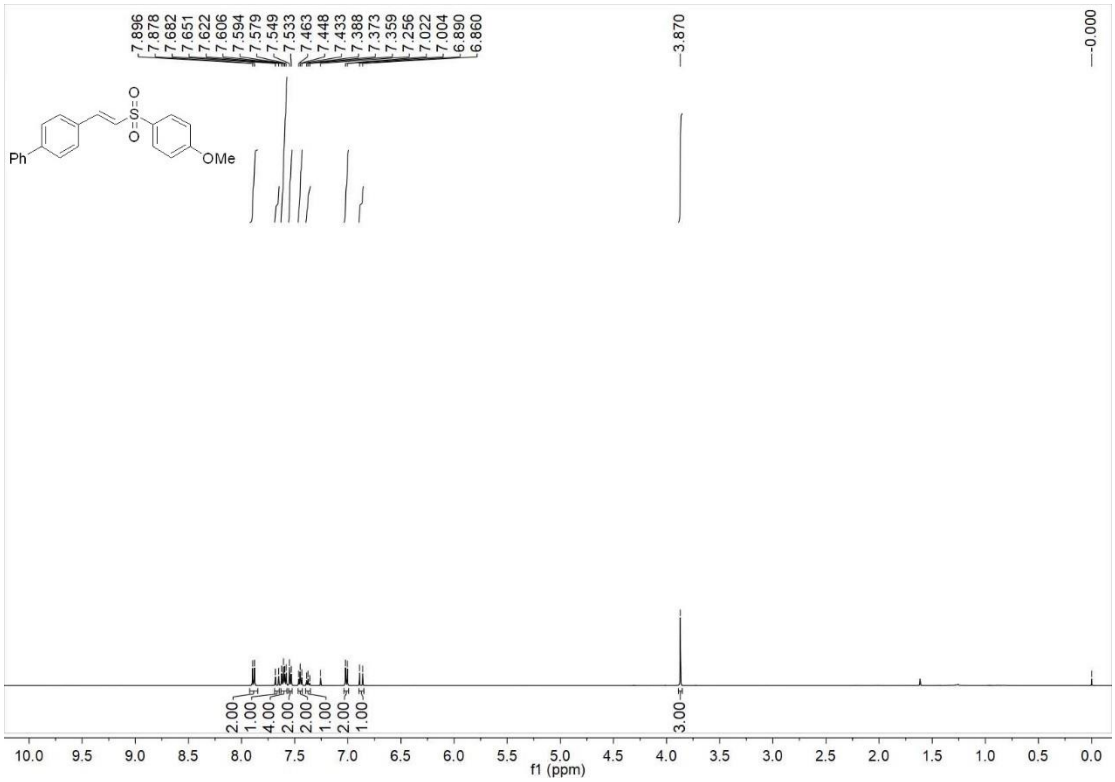


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4j**

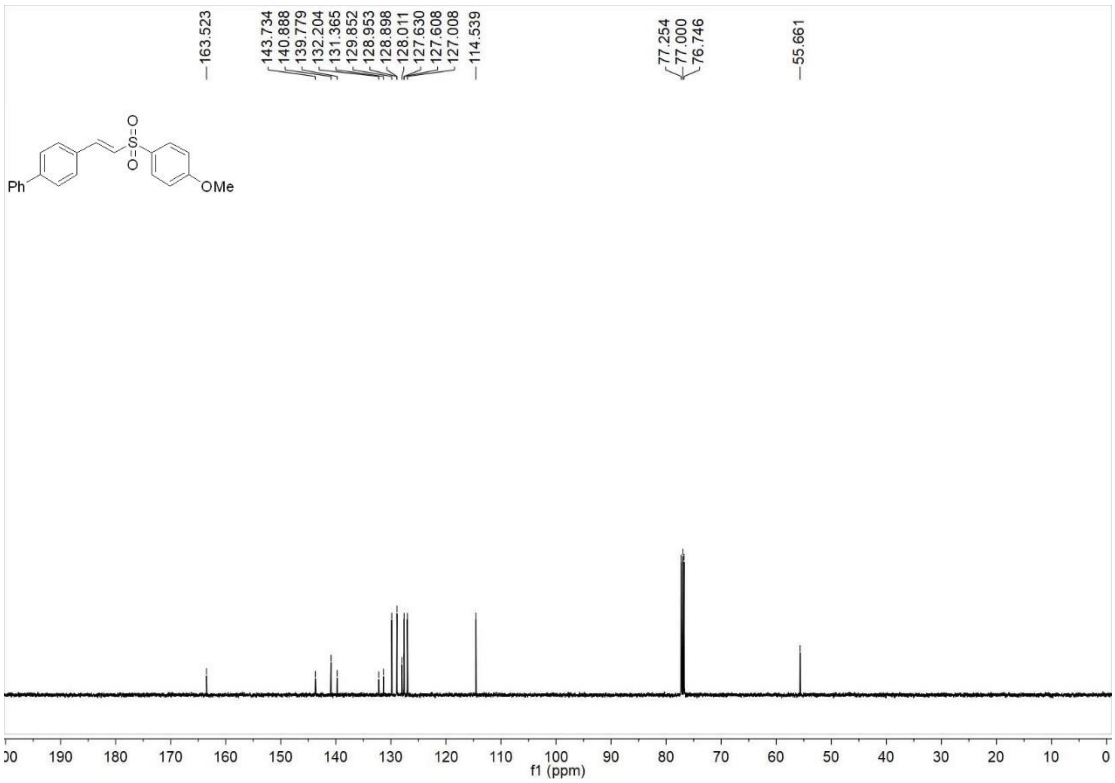


(*E*)-4-(2-((4-Methoxyphenyl)sulfonyl)vinyl)-1,1'-biphenyl (4k)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4k**

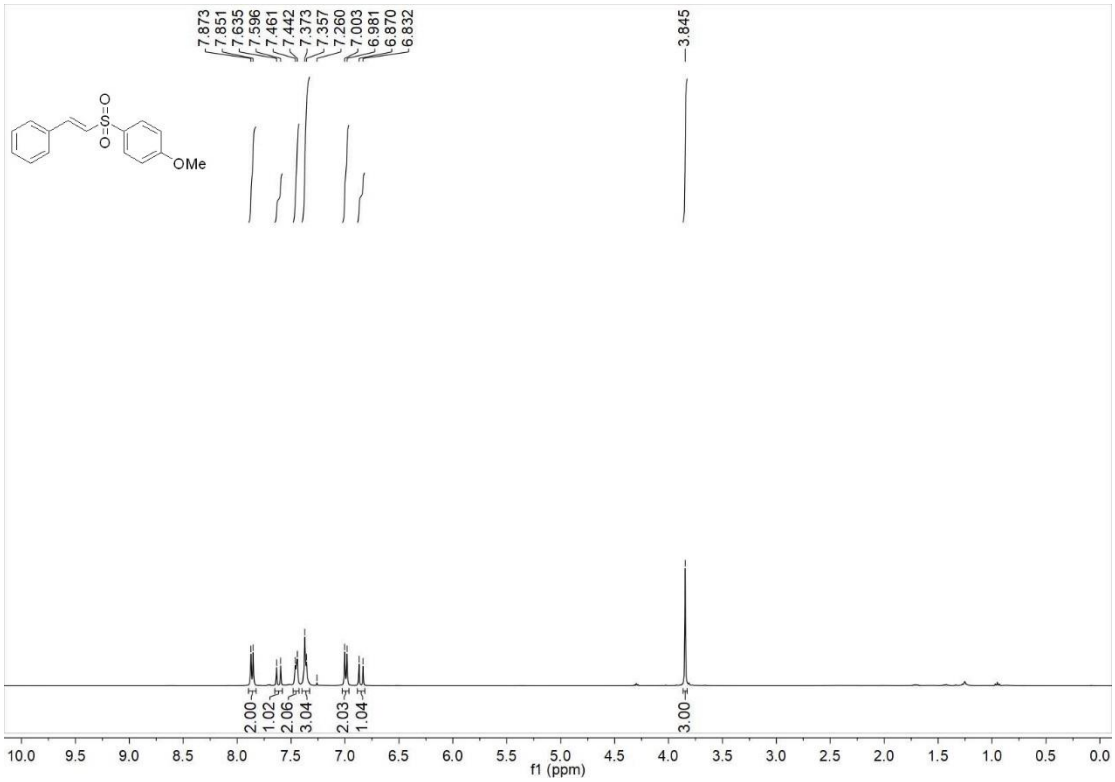


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4k**

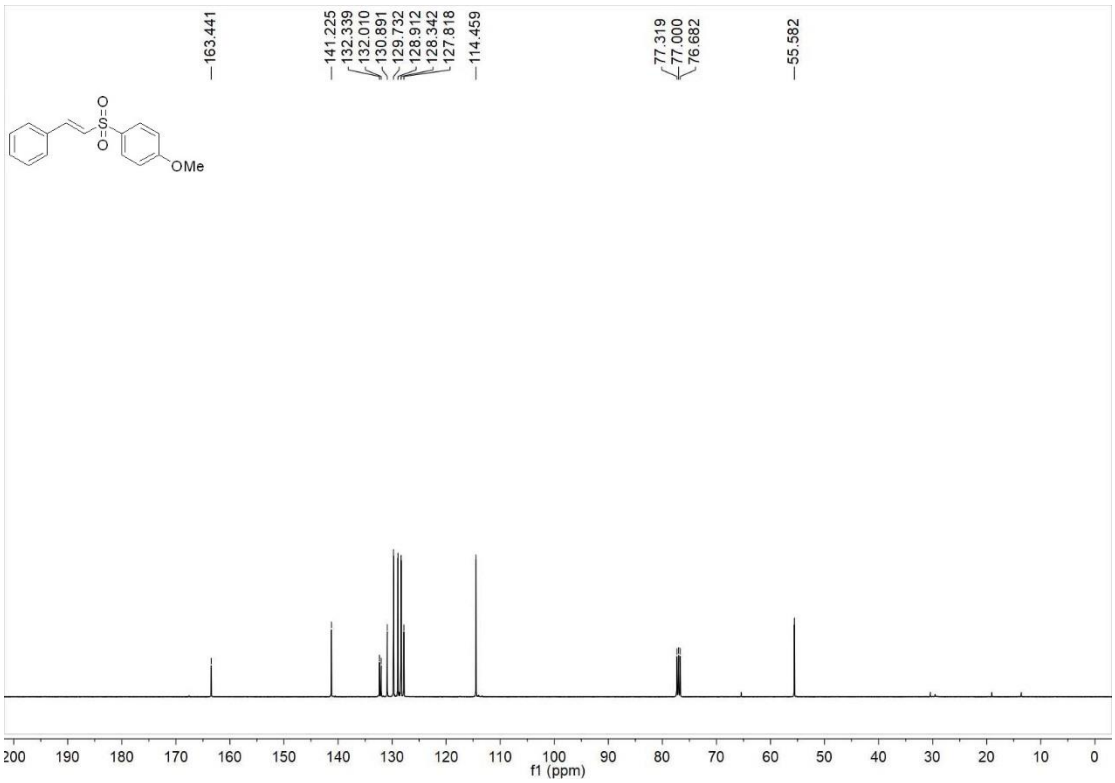


(*E*)-1-Methoxy-4-(styrylsulfonyl)benzene (4l)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4l**

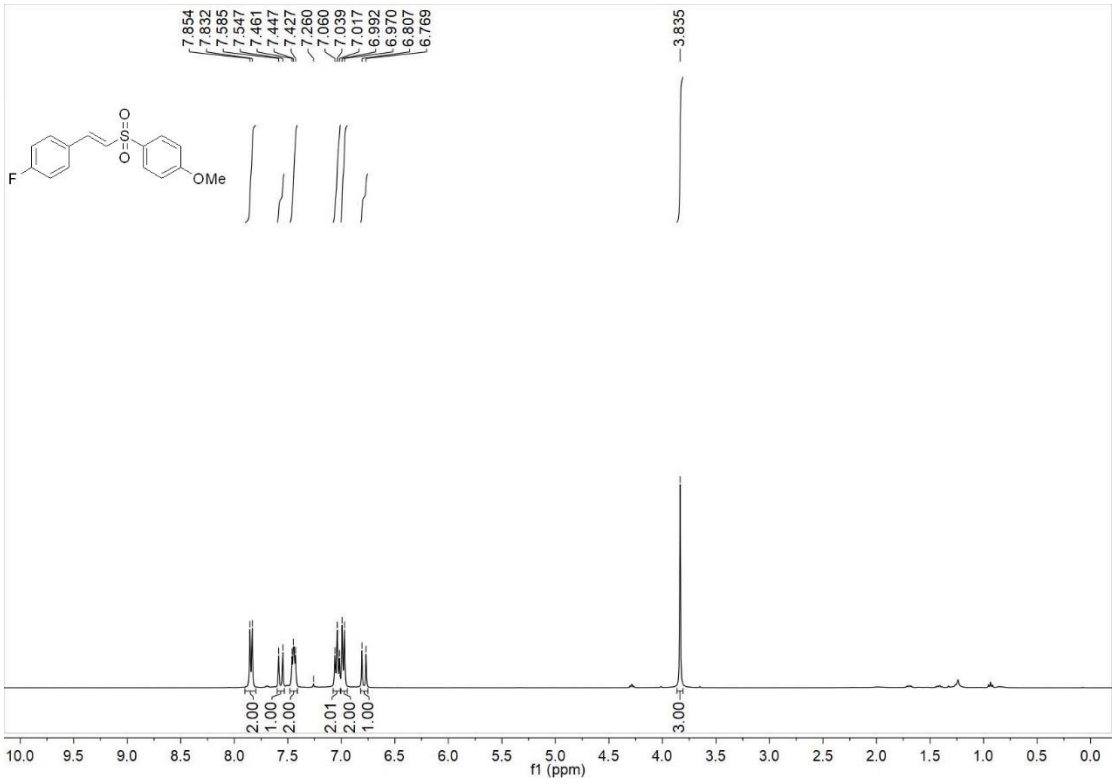


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4l**

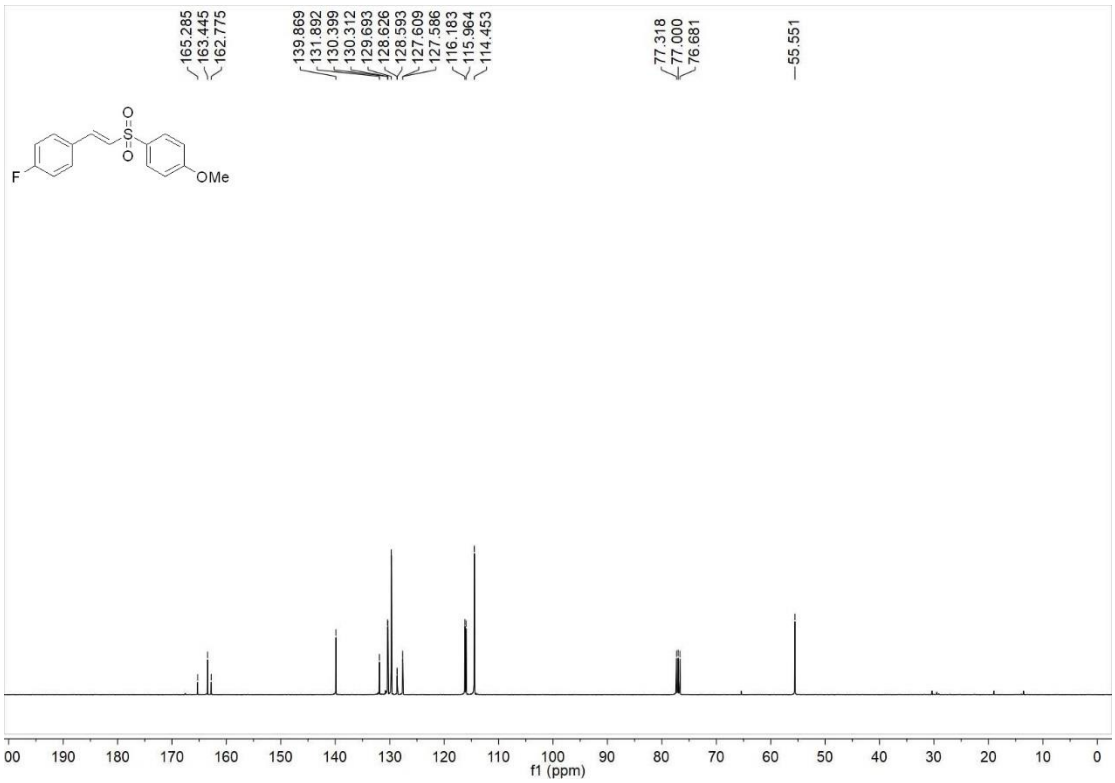


(*E*)-1-Fluoro-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4m)

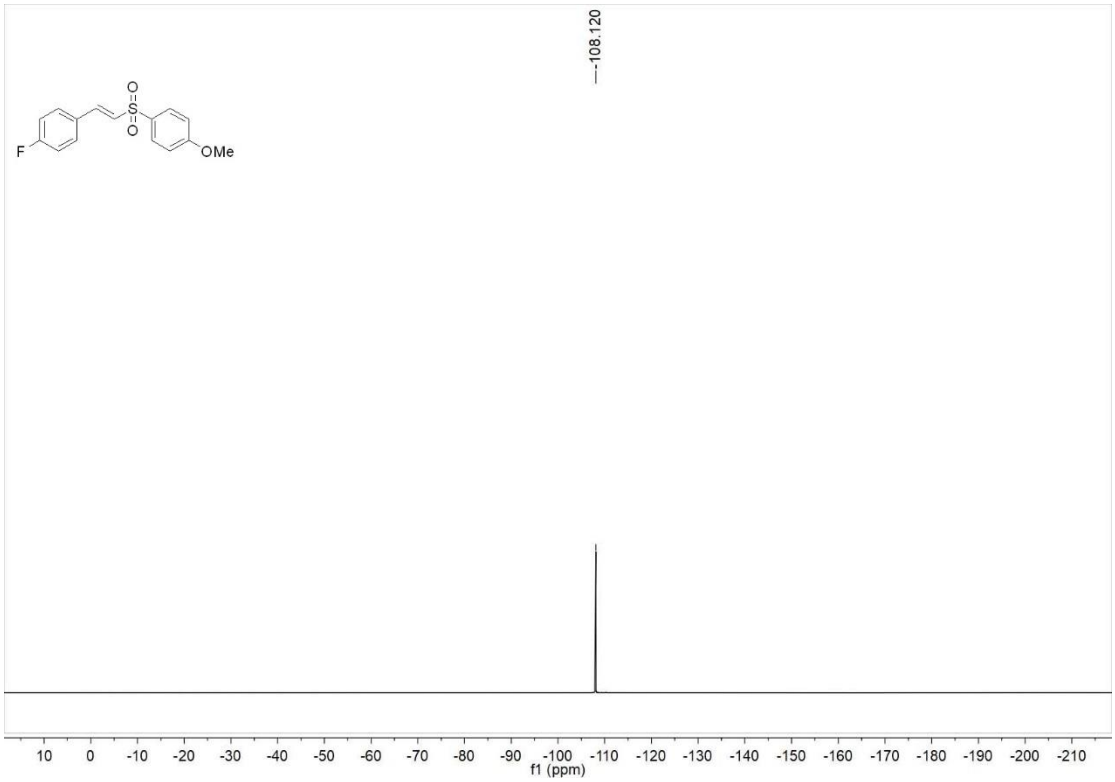
^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4m**



^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4m**

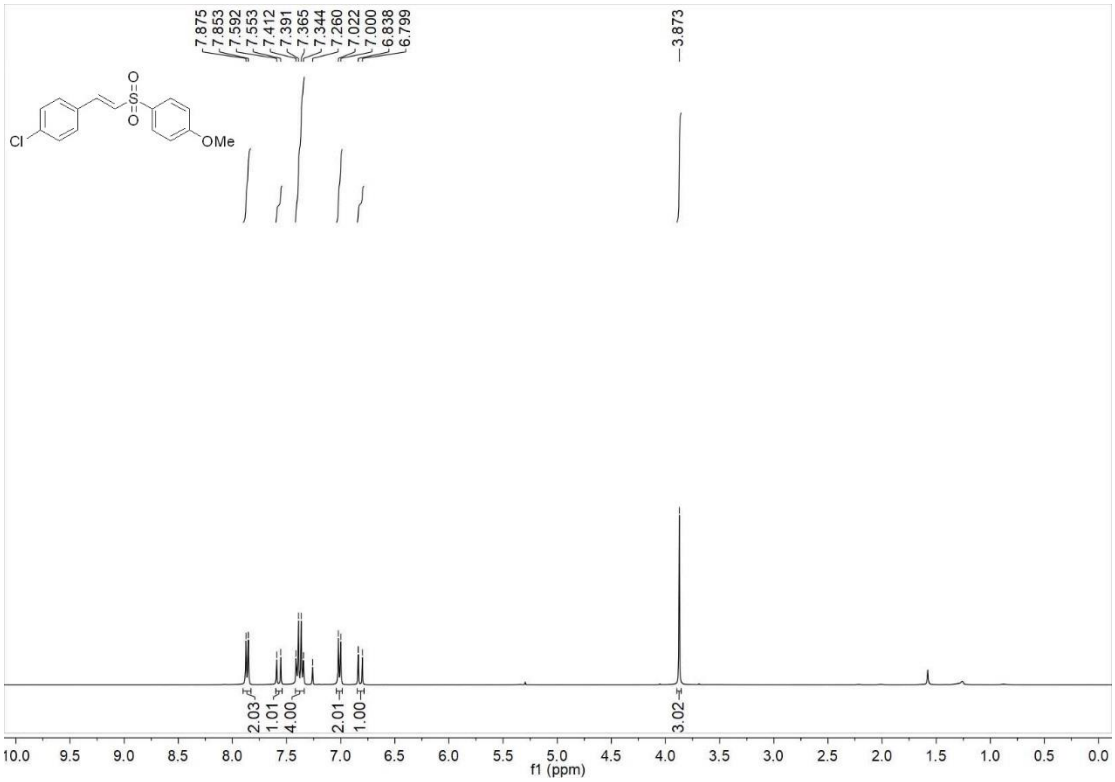


^{19}F NMR-spectrum (376 MHz, $CDCl_3$) of **4m**

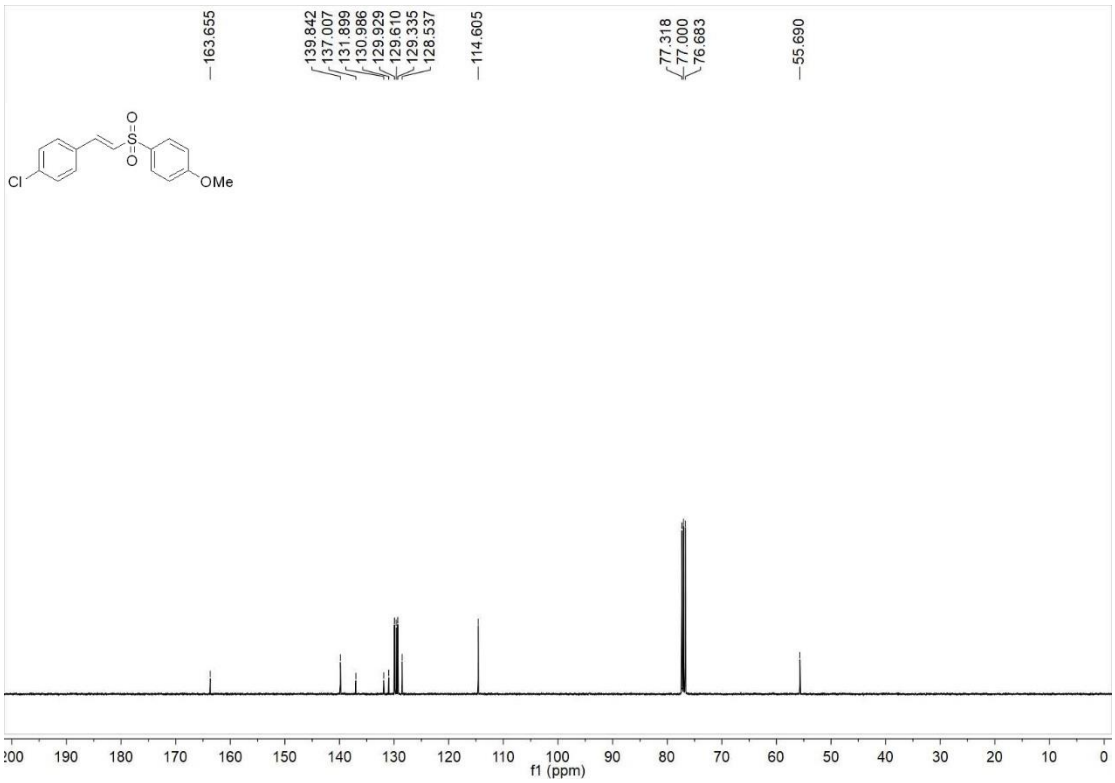


(*E*)-1-Chloro-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4n)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4n**

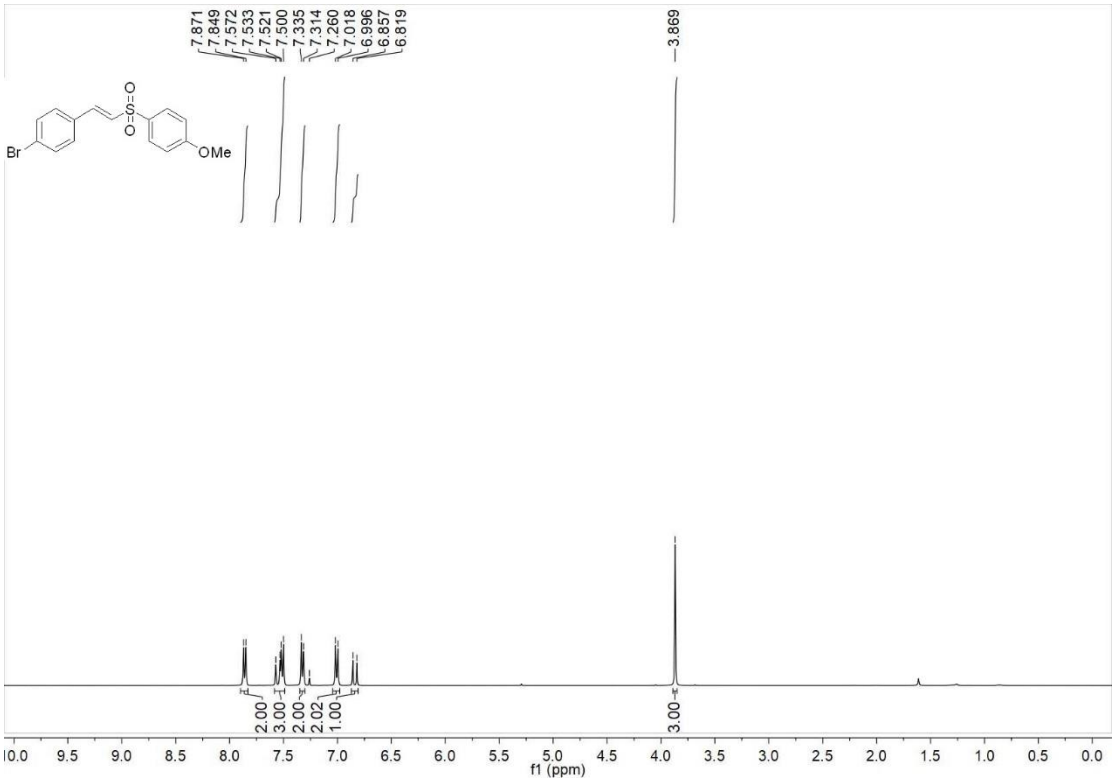


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4n**

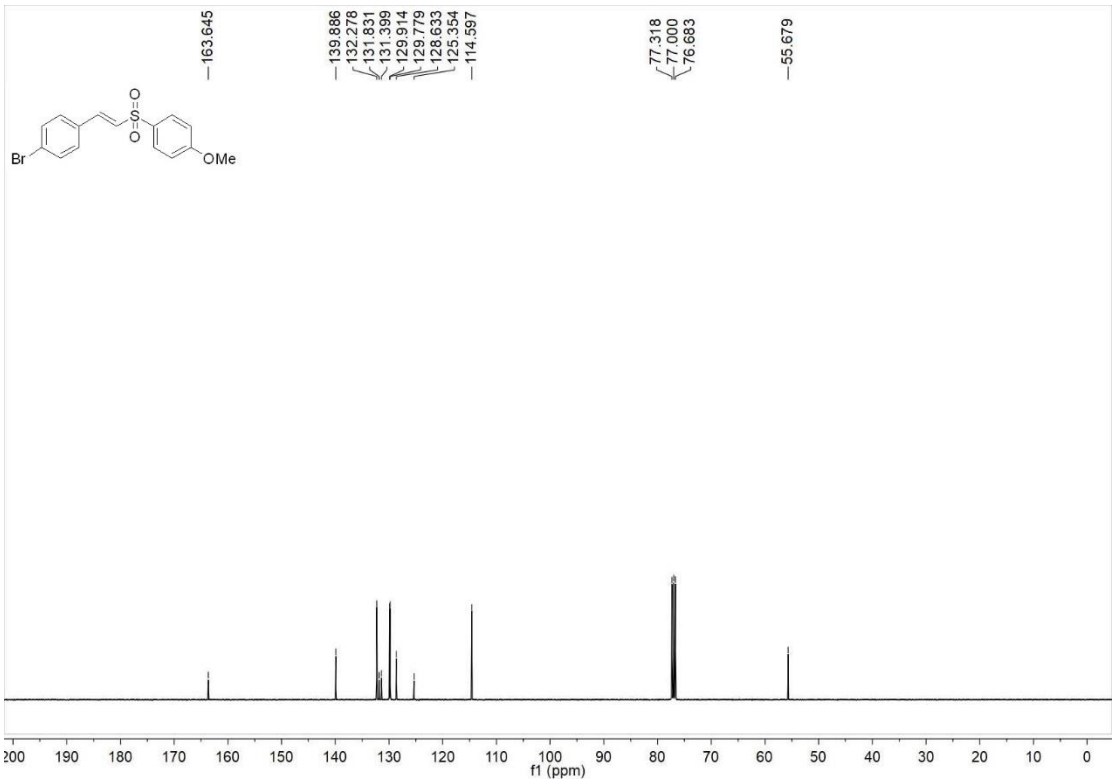


(*E*)-1-Bromo-4-(2-((4-methoxyphenyl)sulfonyl)vinyl)benzene (4o)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4o**

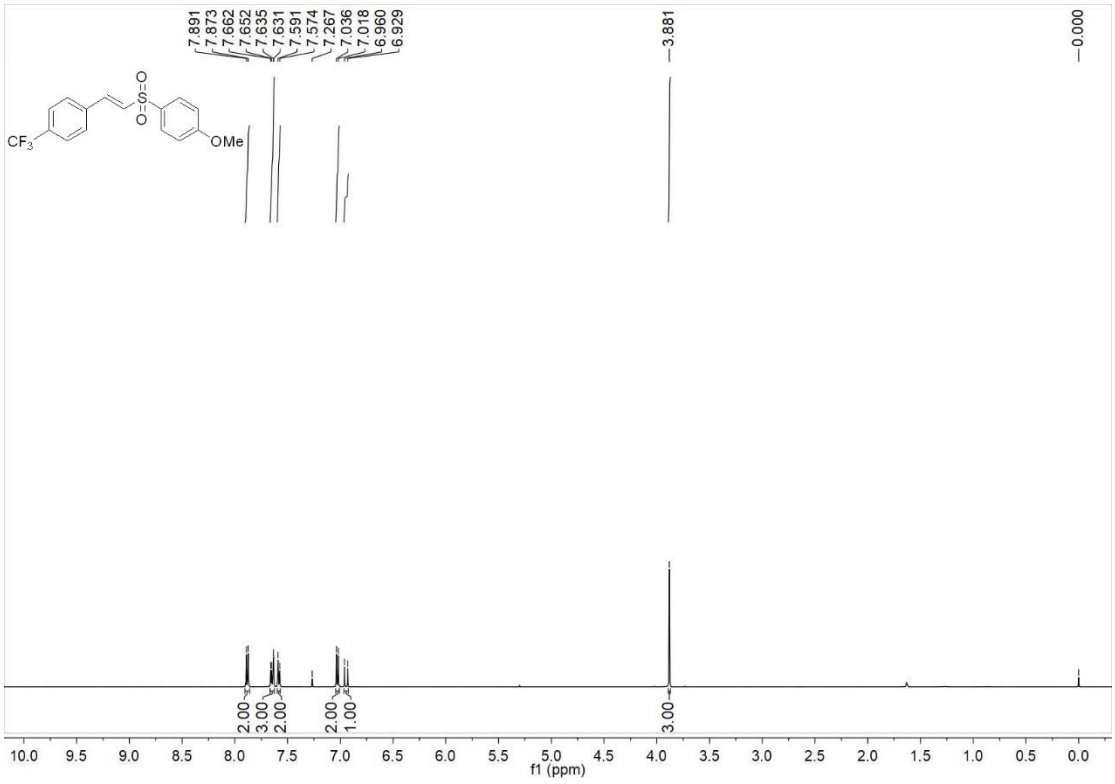


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4o**

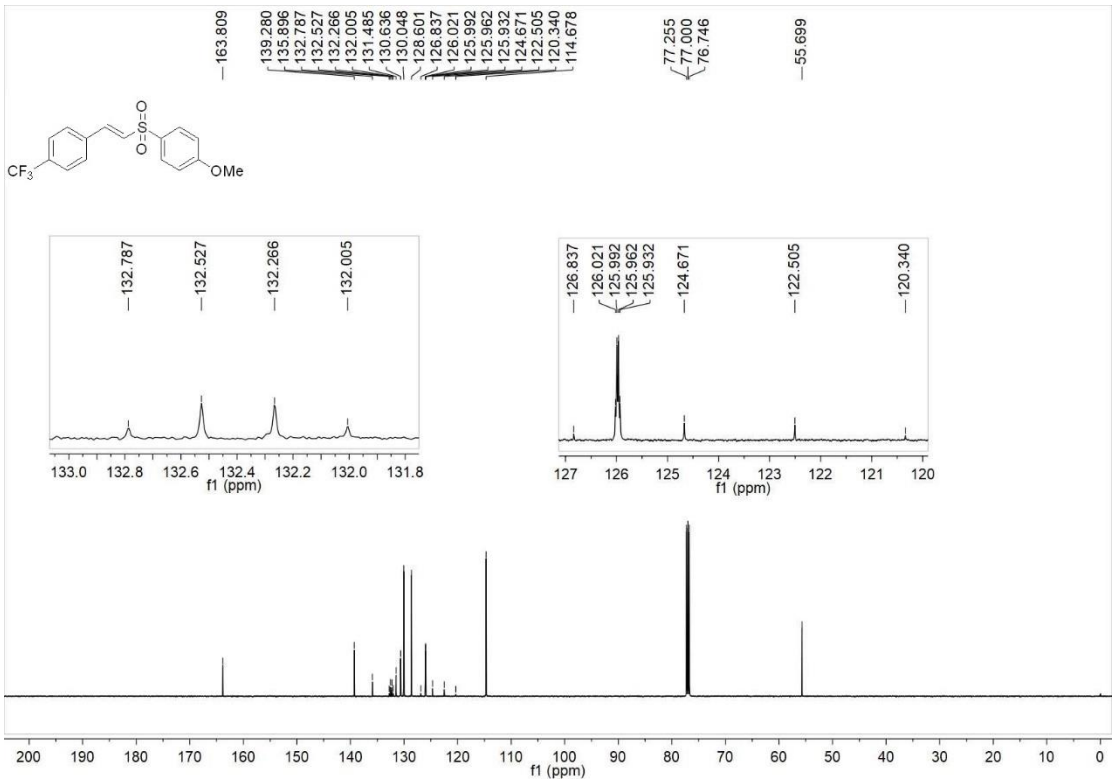


(*E*)-1-Methoxy-4-((4-(trifluoromethyl)styryl)sulfonyl)benzene (4p)

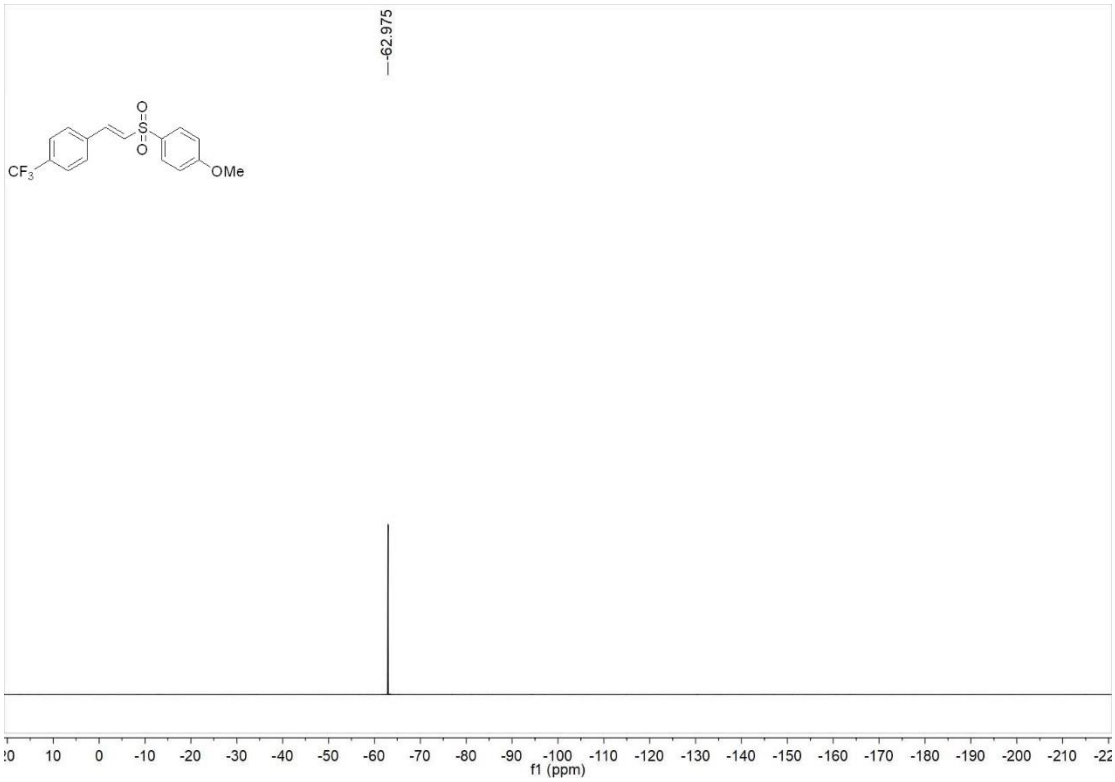
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4p**



^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4p**

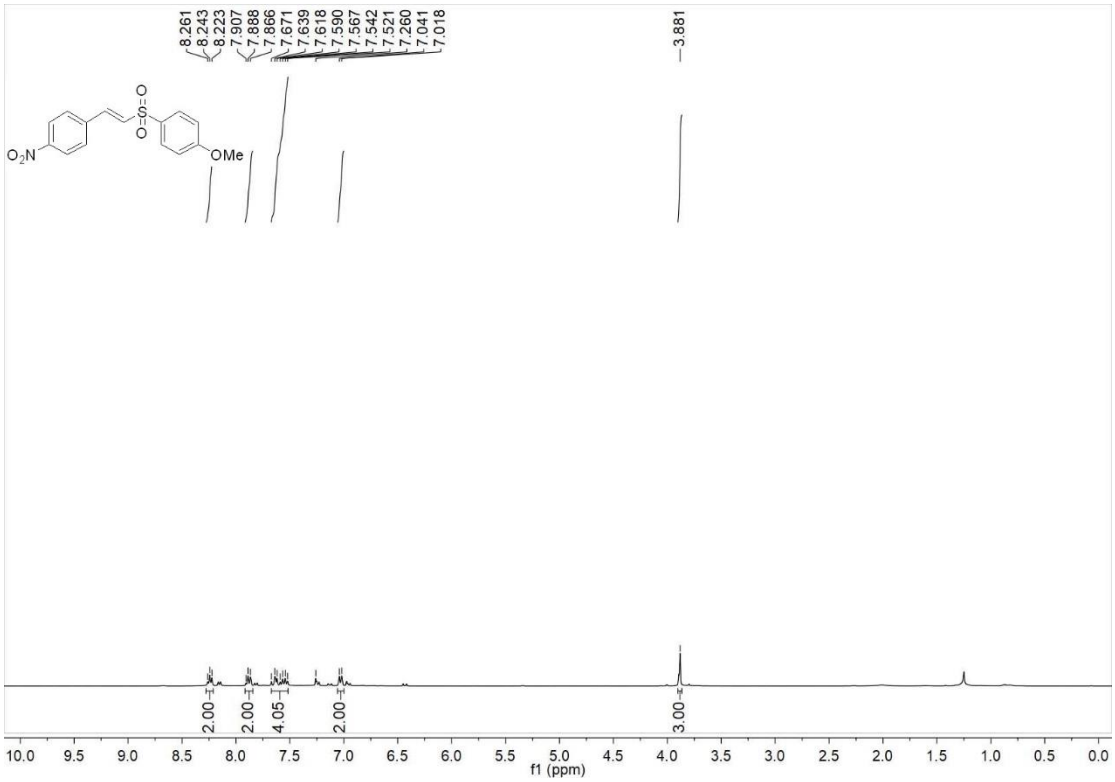


^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **4p**

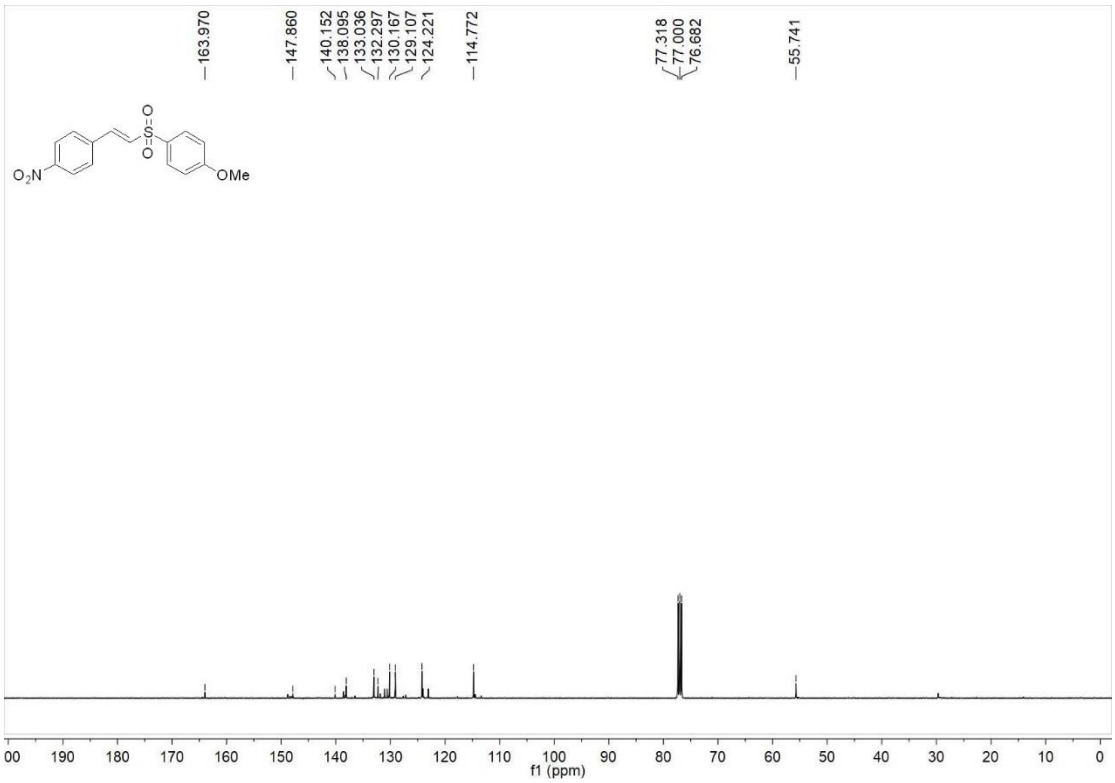


(*E*)-1-Methoxy-4-((4-nitrostyryl)sulfonyl)benzene (4q)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4q**

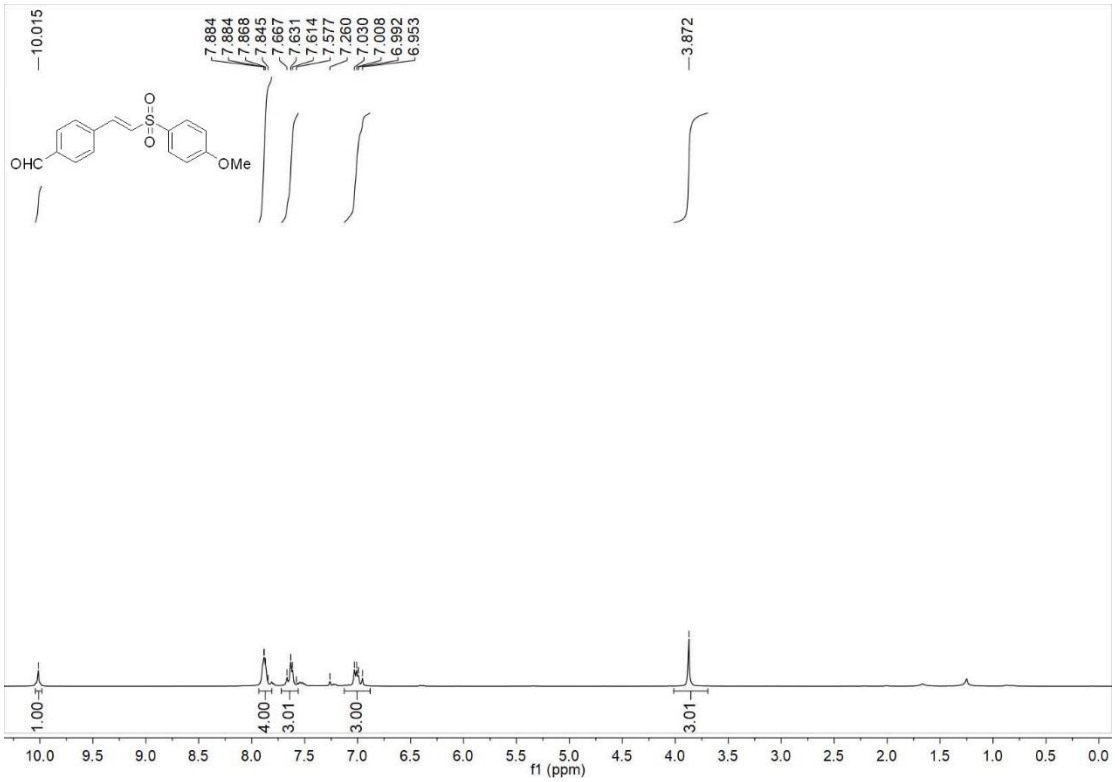


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4q**

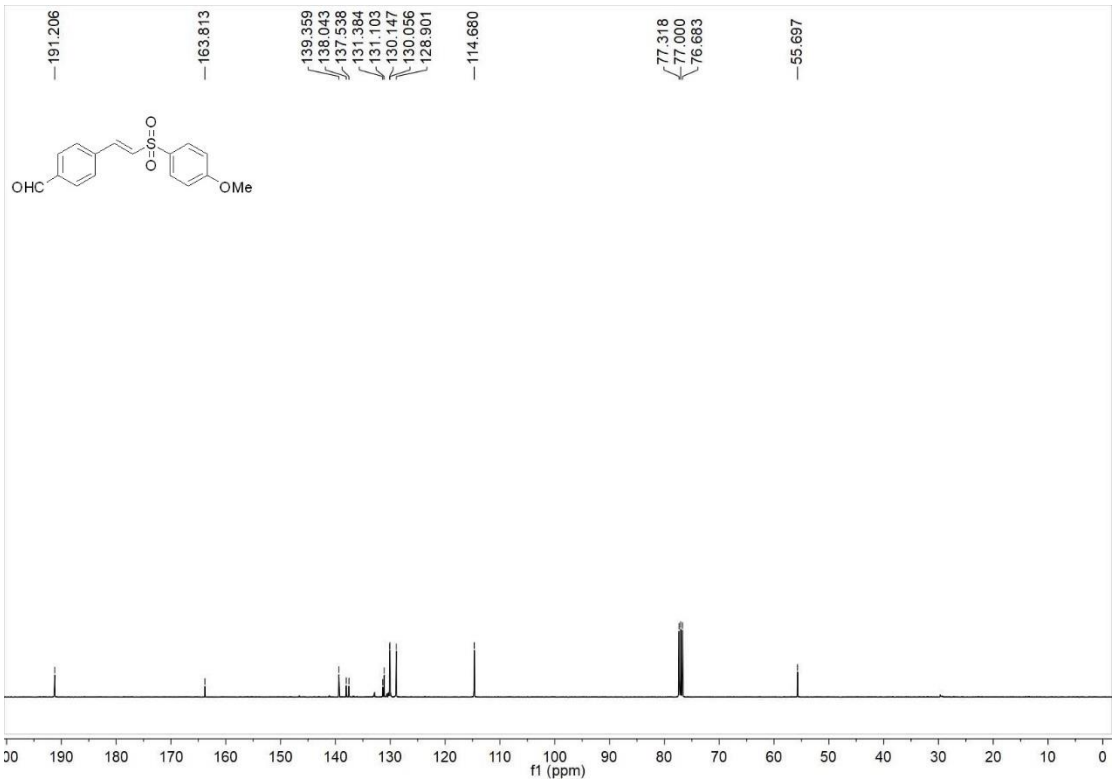


(*E*)-4-(2-((4-Methoxyphenyl)sulfonyl)vinyl)benzaldehyde (4r)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4r**

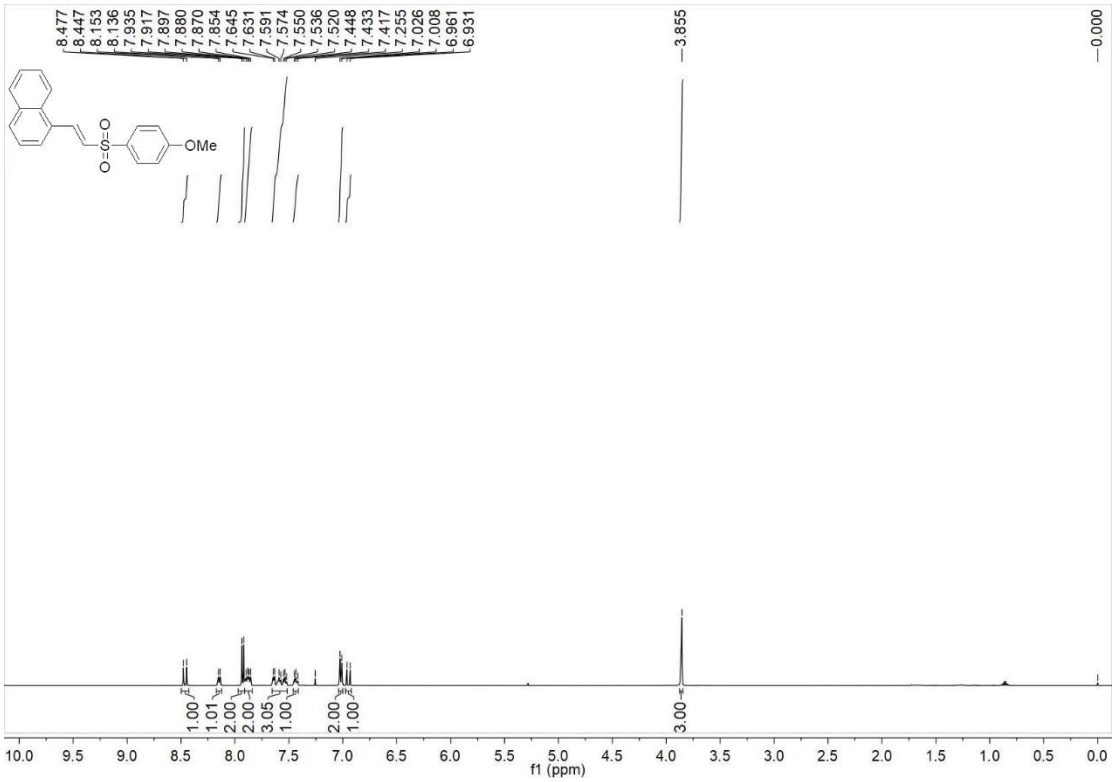


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4r**

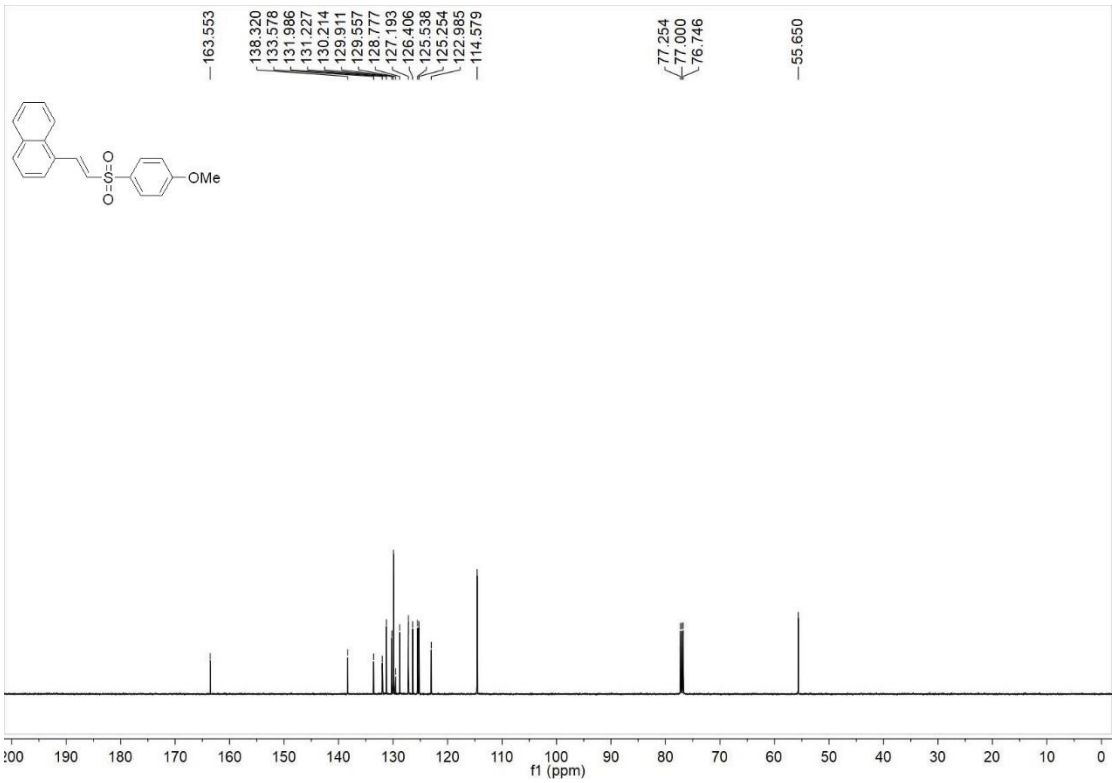


(*E*)-1-(2-((4-Methoxyphenyl)sulfonyl)vinyl)naphthalene (4s)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4s**

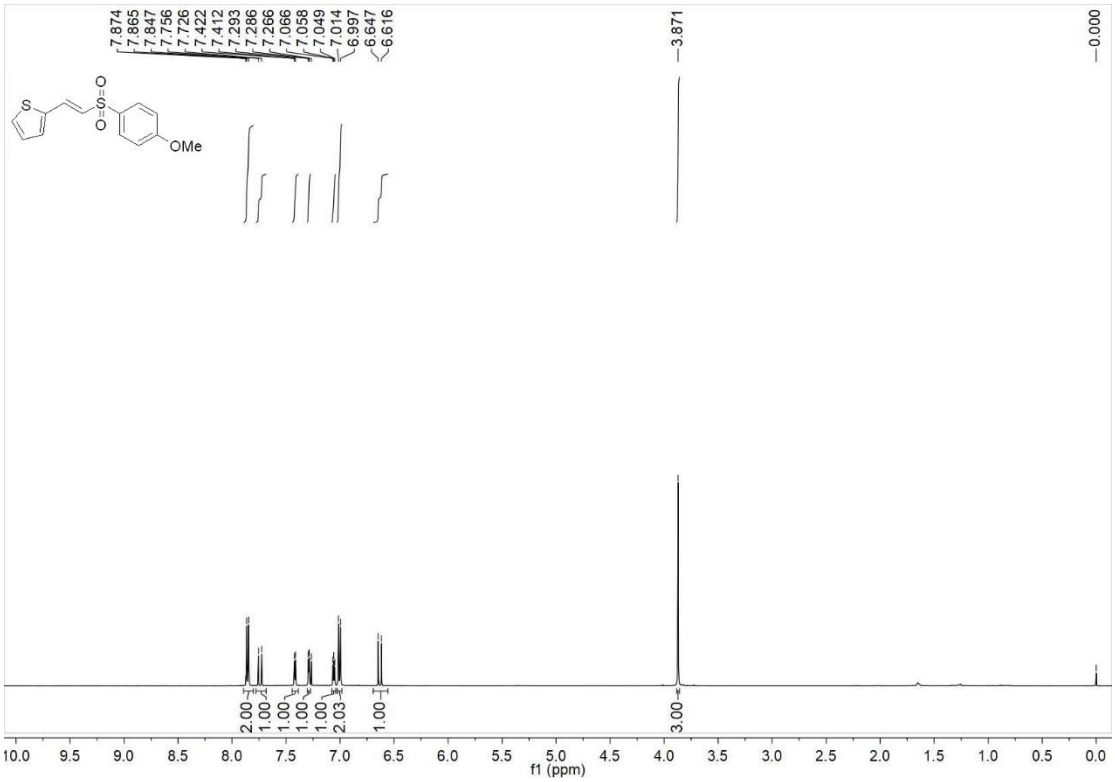


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4s**

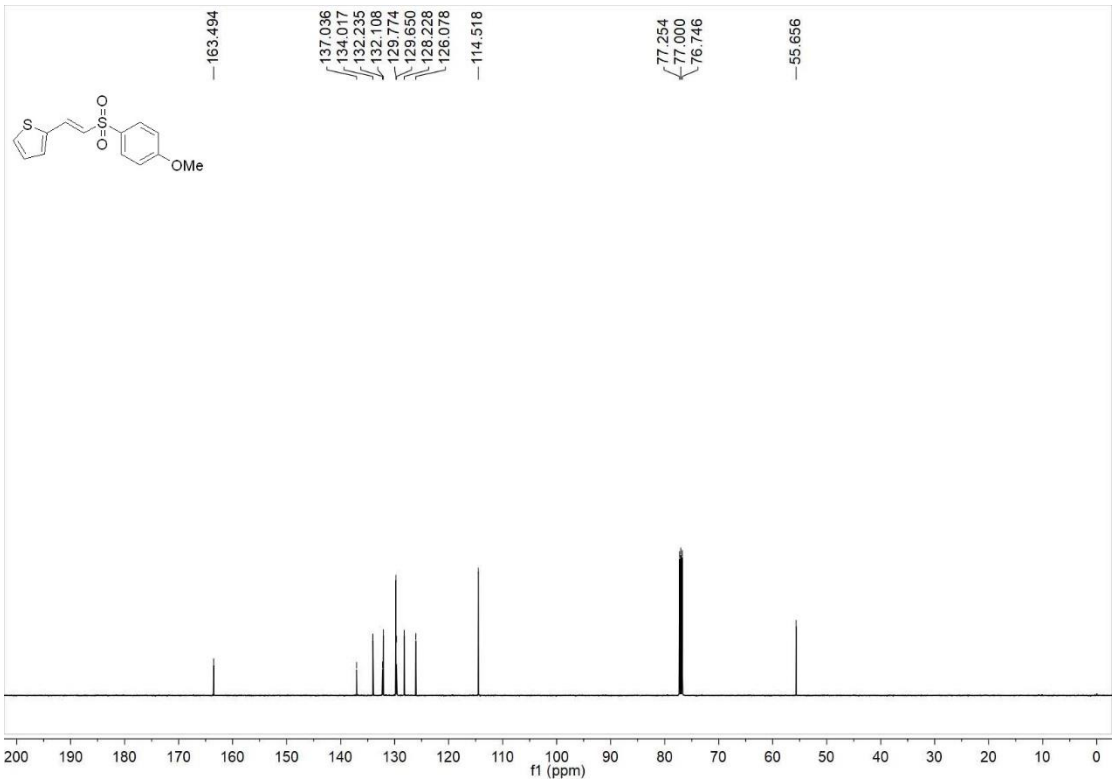


(*E*)-2-(2-((4-Methoxyphenyl)sulfonyl)vinyl)thiophene (4t)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4t**

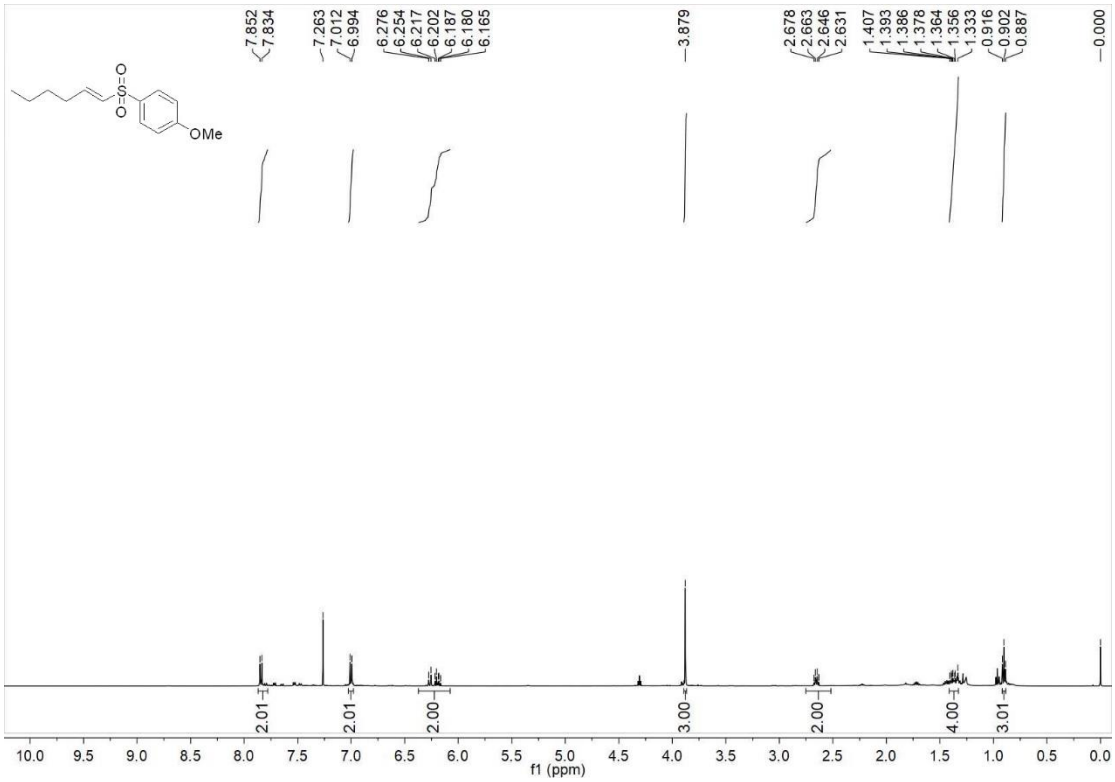


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4t**

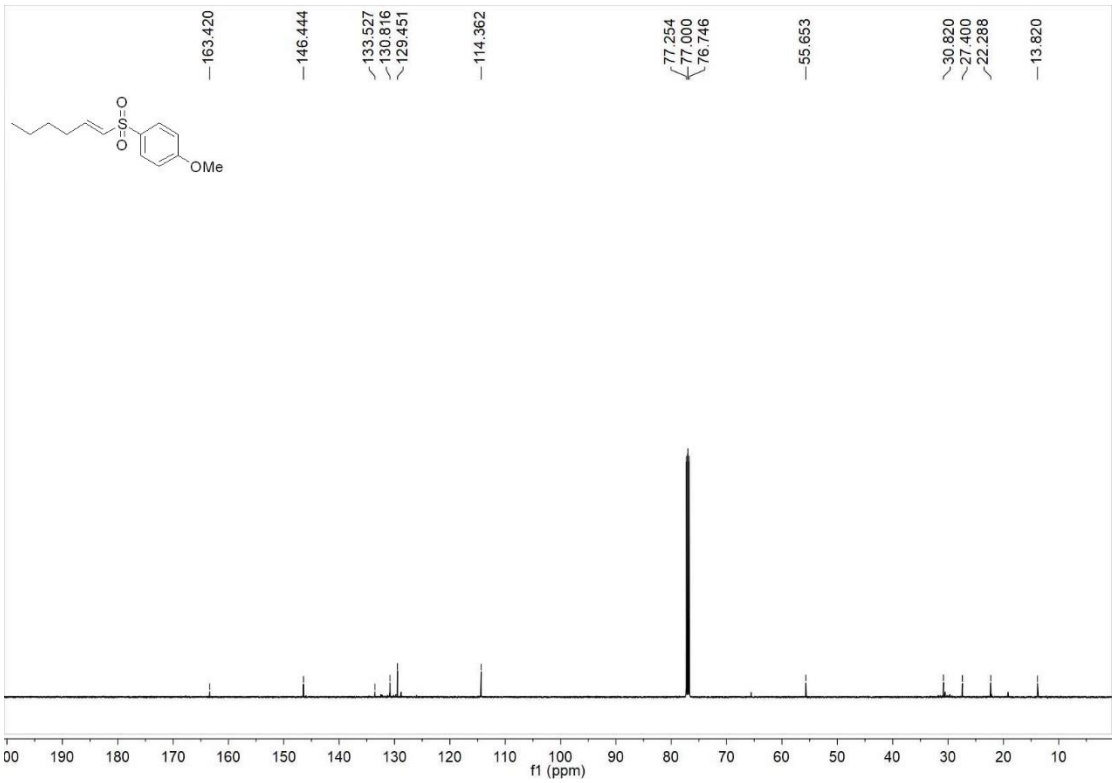


(*E*)-1-(Hex-1-en-1-ylsulfonyl)-4-methoxybenzene (4u)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4u**

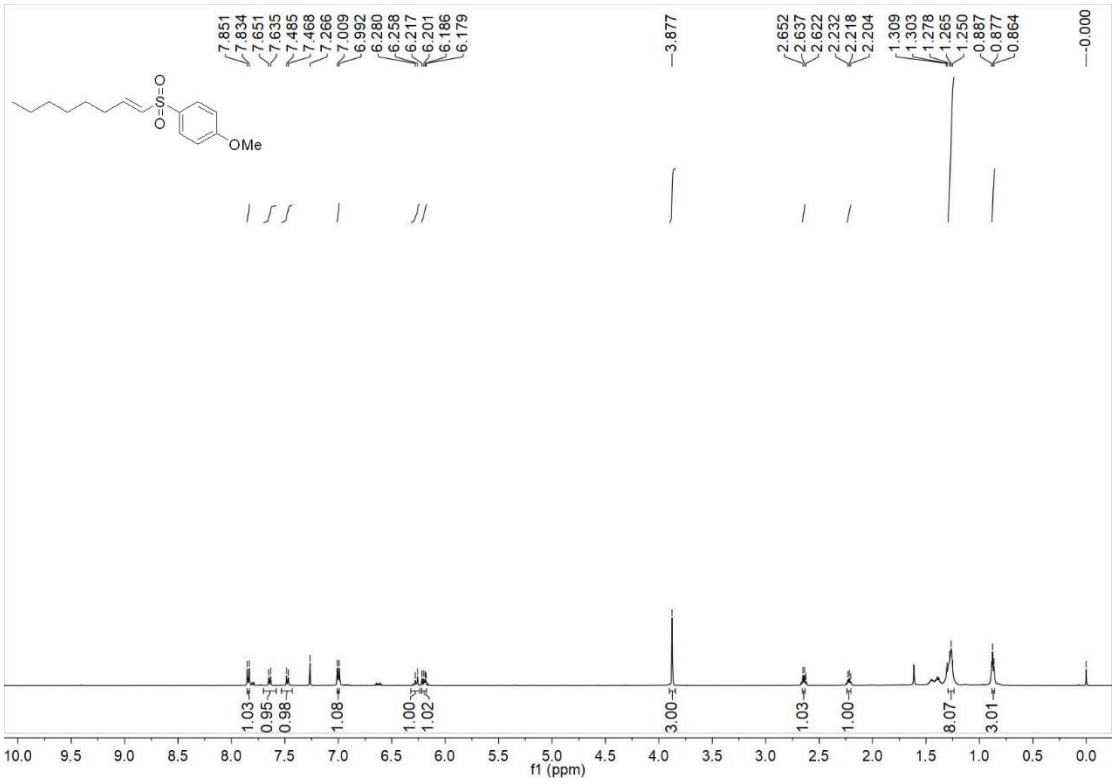


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4u**

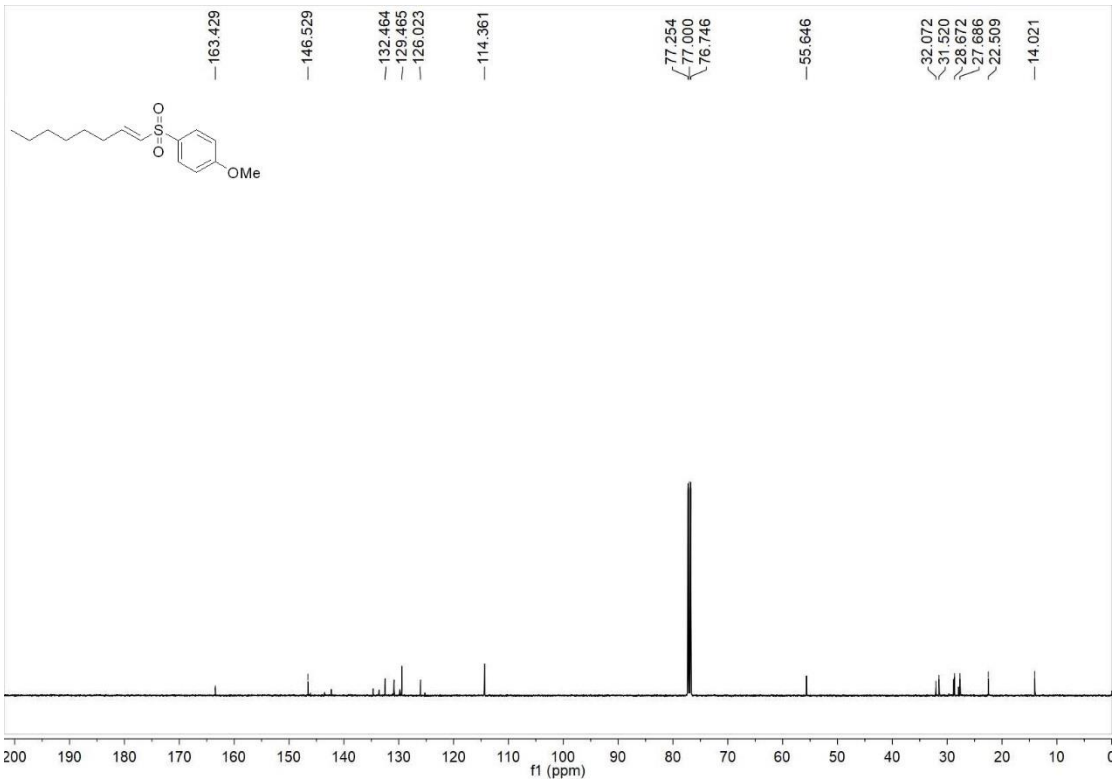


(*E*)-1-Methoxy-4-(oct-1-en-1-ylsulfonyl)benzene (4v)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4v**

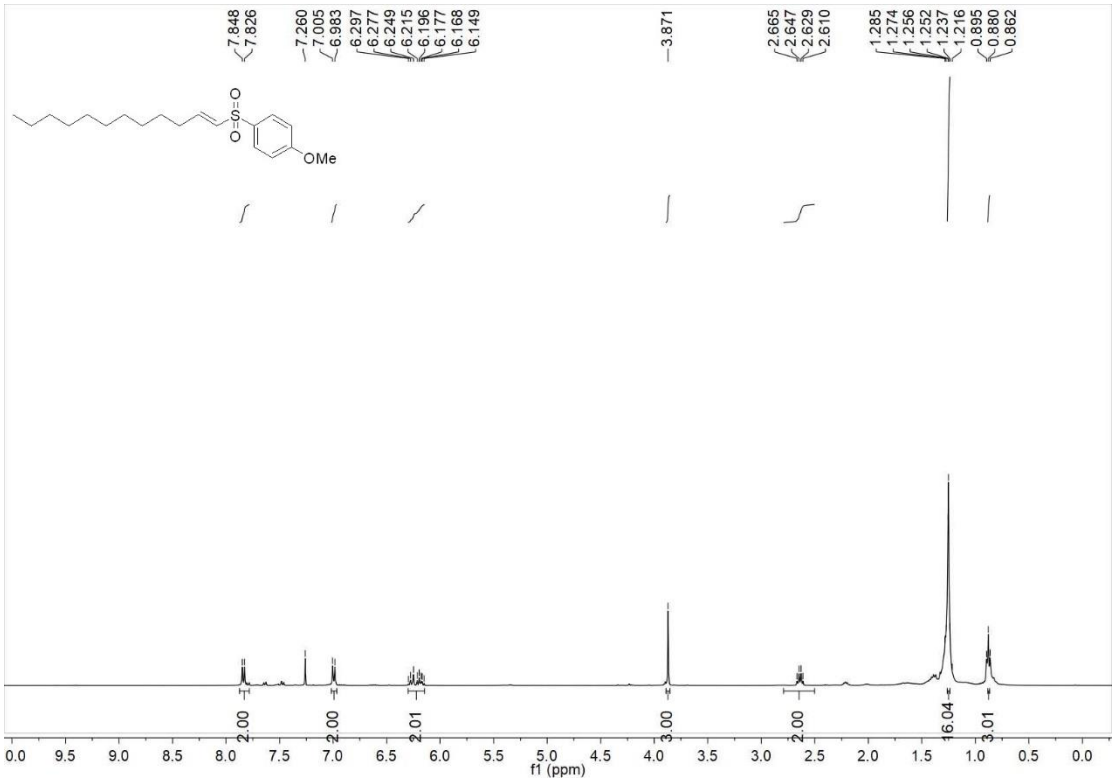


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4v**

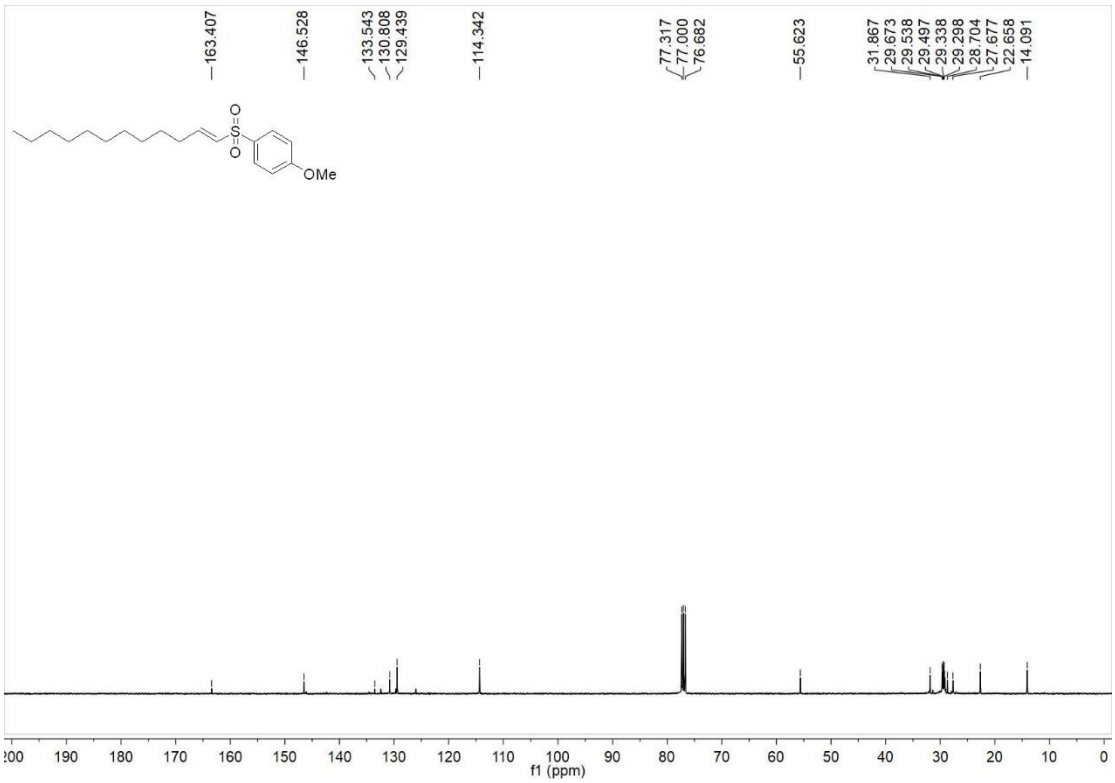


(*E*)-1-(Dodec-1-en-1-ylsulfonyl)-4-methoxybenzene (4w)

^{1}H NMR-spectrum (400 MHz, $CDCl_3$) of **4w**

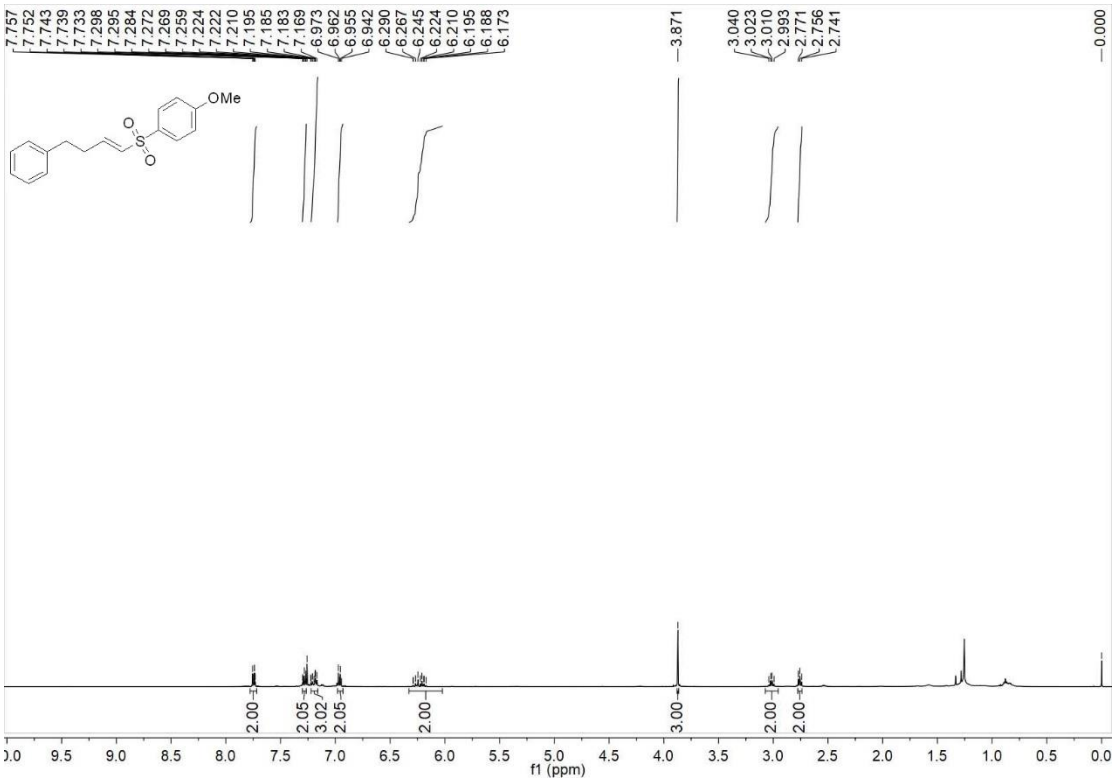


^{13}C NMR-spectrum (101 MHz, $CDCl_3$) of **4w**

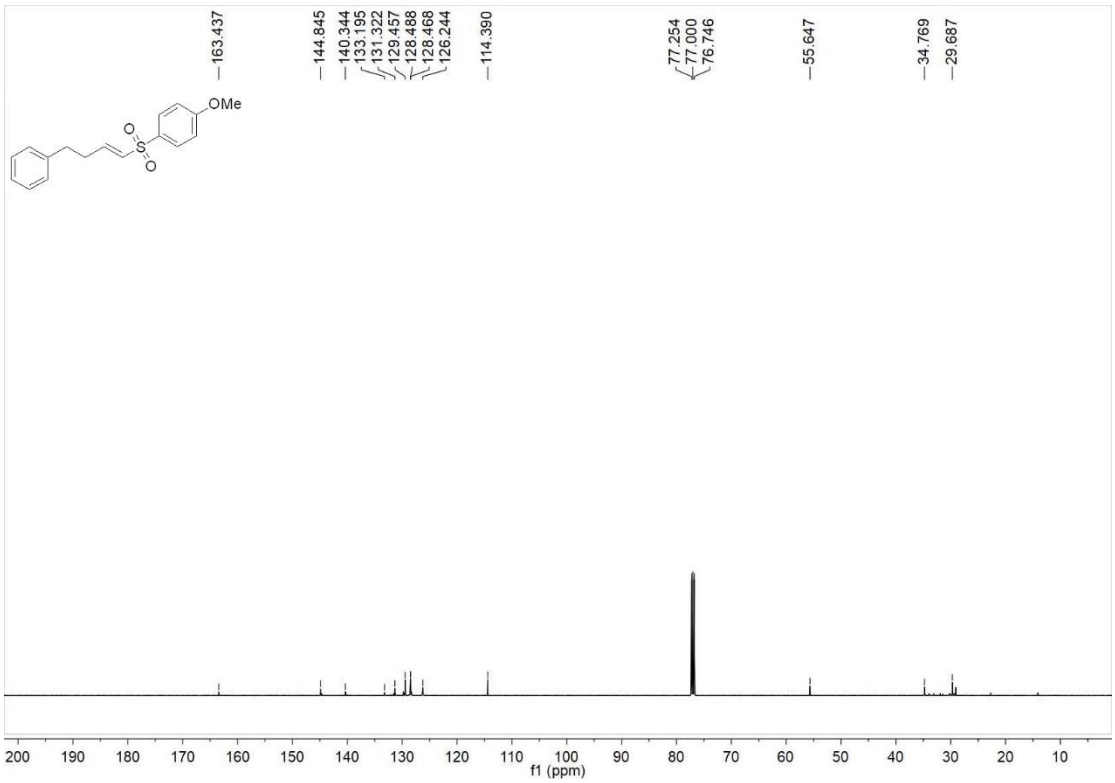


(*E*)-1-Methoxy-4-((4-phenylbut-1-en-1-yl)sulfonyl)benzene (4x)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4x**

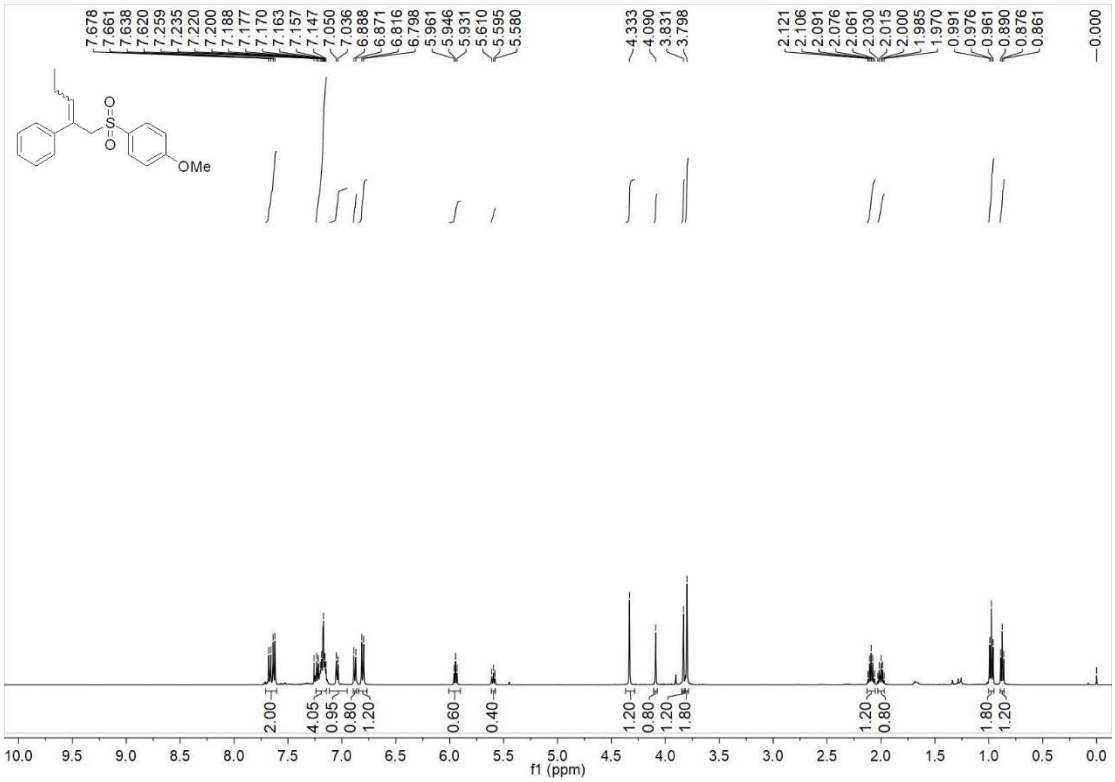


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4x**

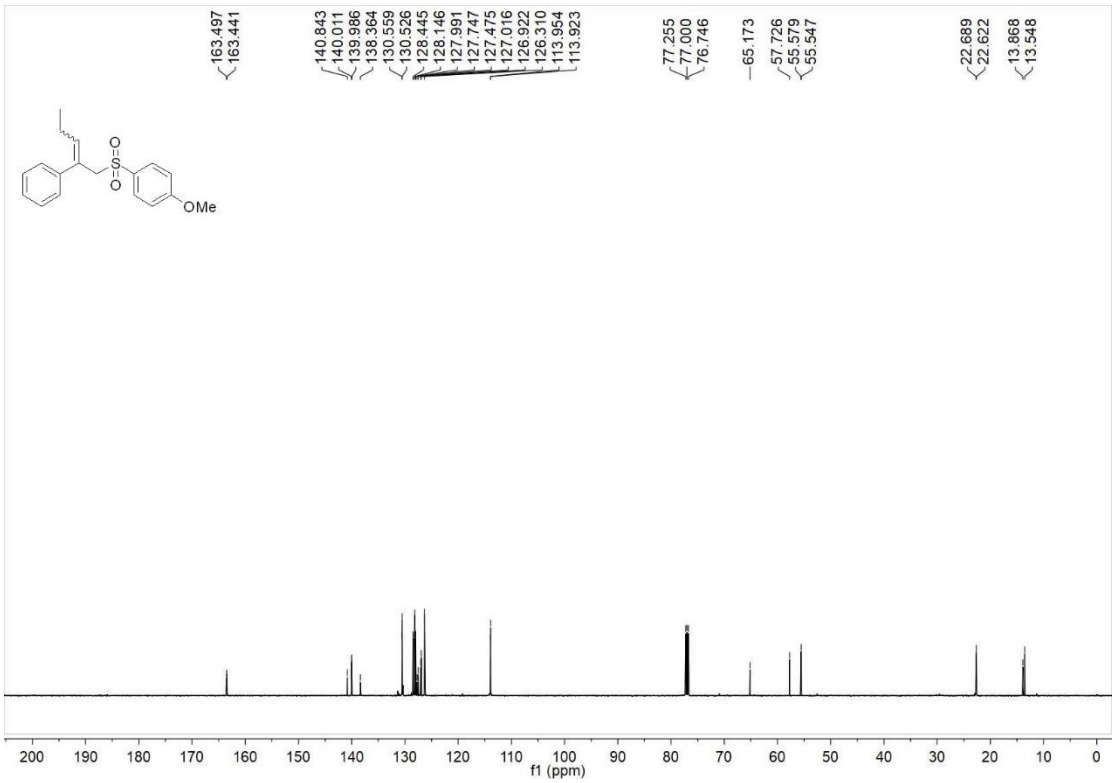


1-Methoxy-4-((2-phenylpent-2-en-1-yl)sulfonyl)benzene (7a)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **7a**

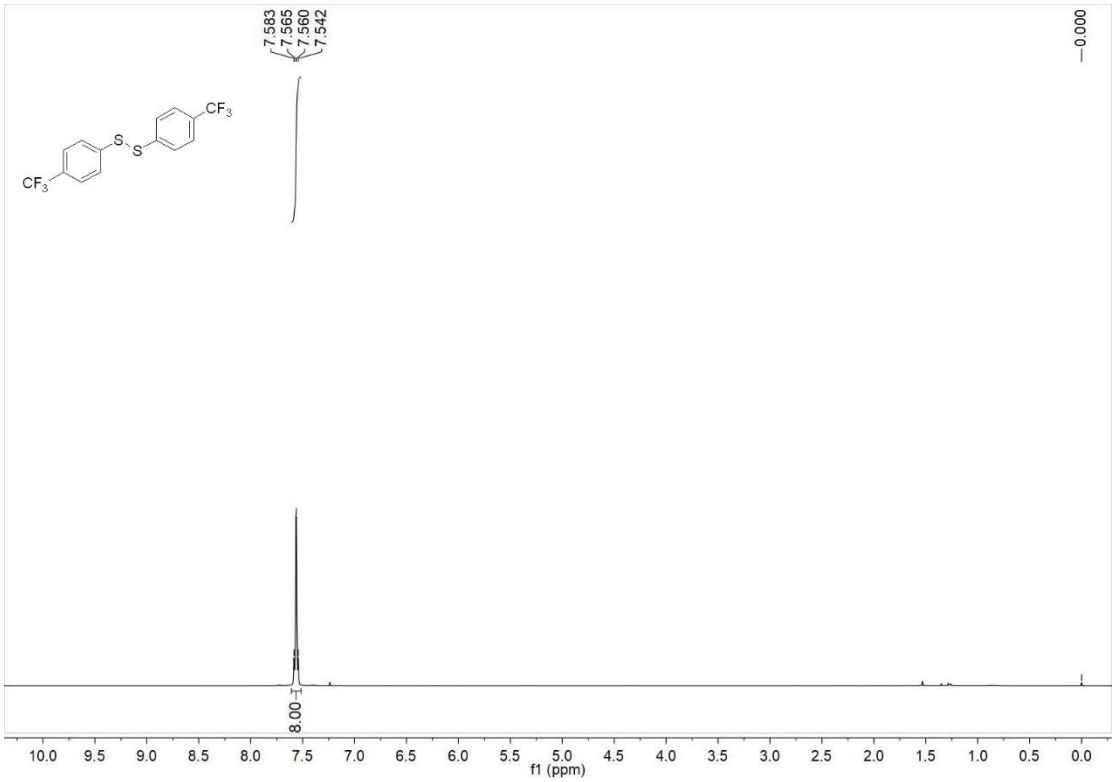


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **7a**

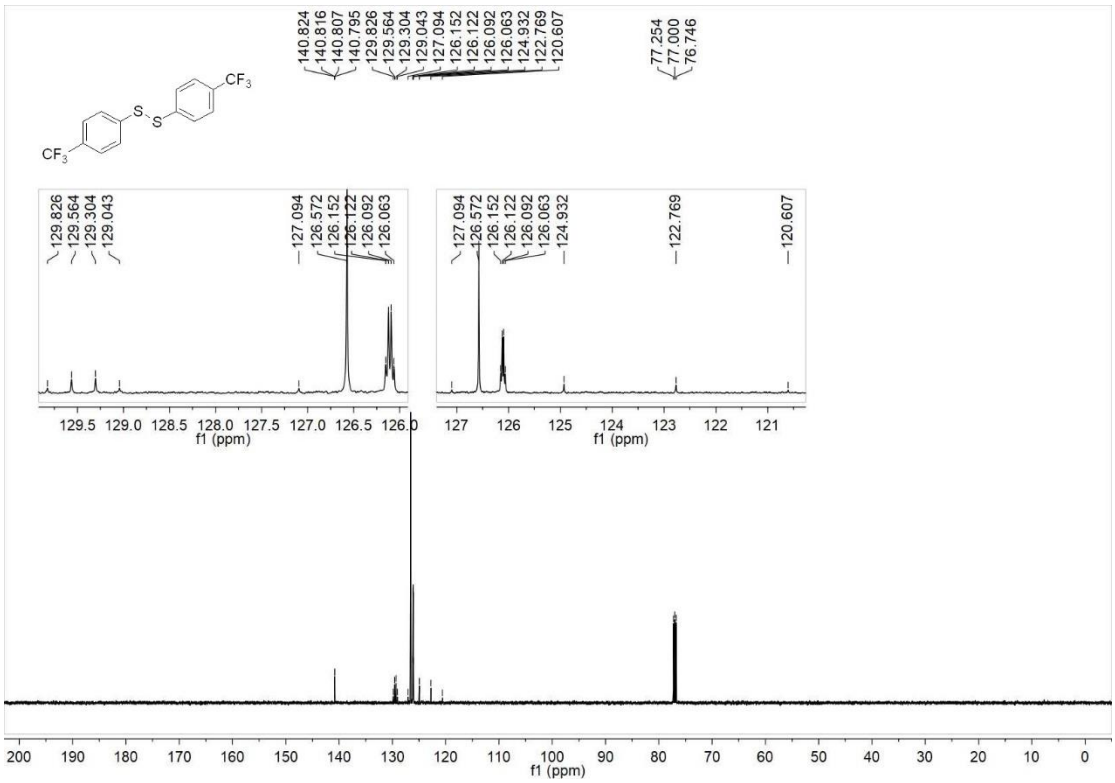


1,2-Bis(4-(trifluoromethyl)phenyl)disulfane (8a)

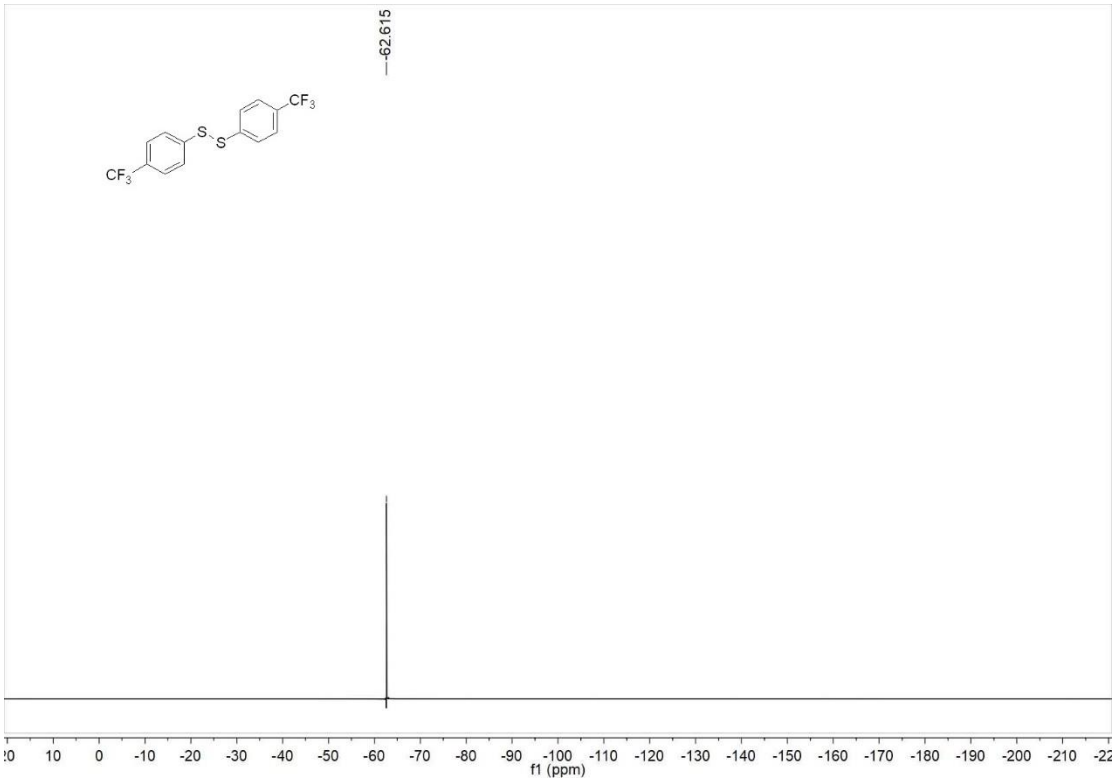
^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **8a**



^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **8a**

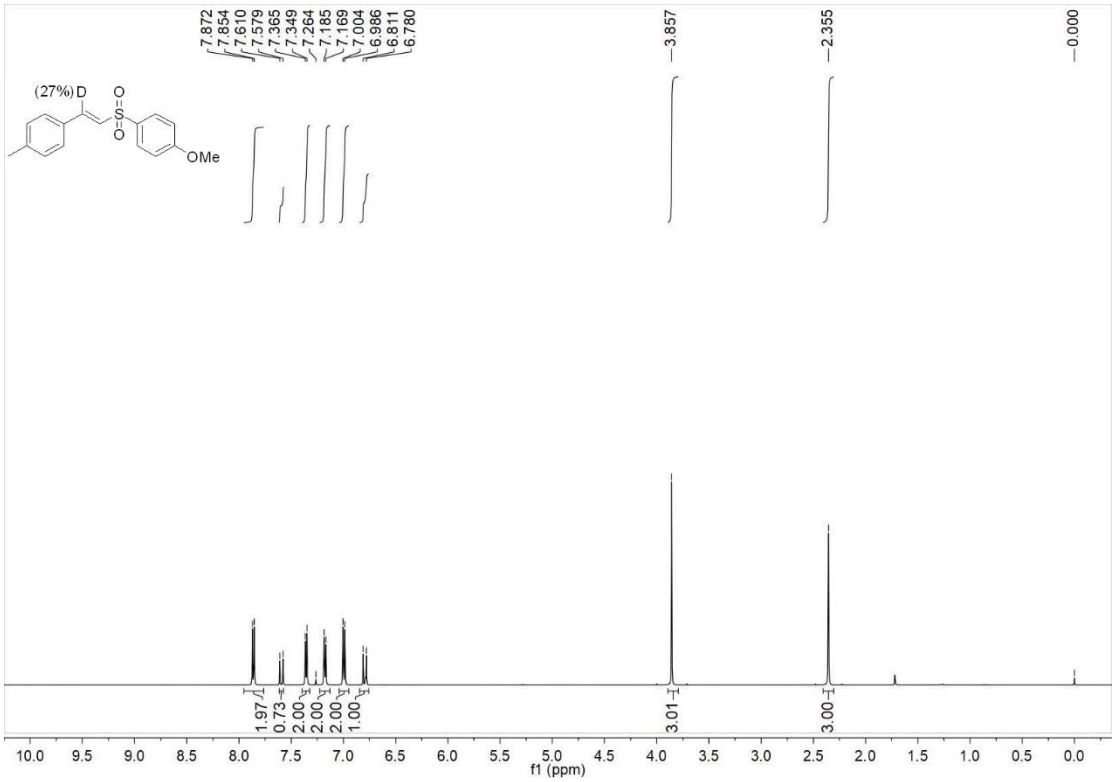


^{19}F NMR-spectrum (471 MHz, $CDCl_3$) of **8a**

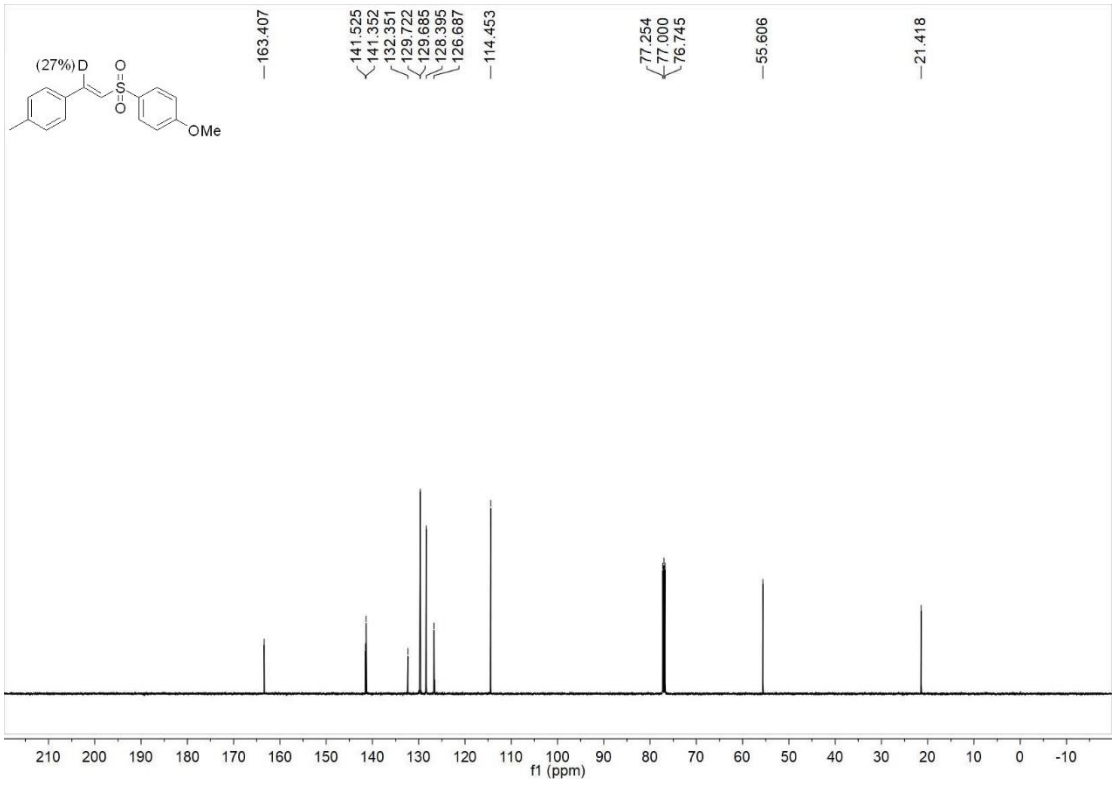


(*E*)-1-Methoxy-4-((2-(*p*-tolyl)vinyl-2-d)sulfonyl)benzene (4a-D)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **4a-D**

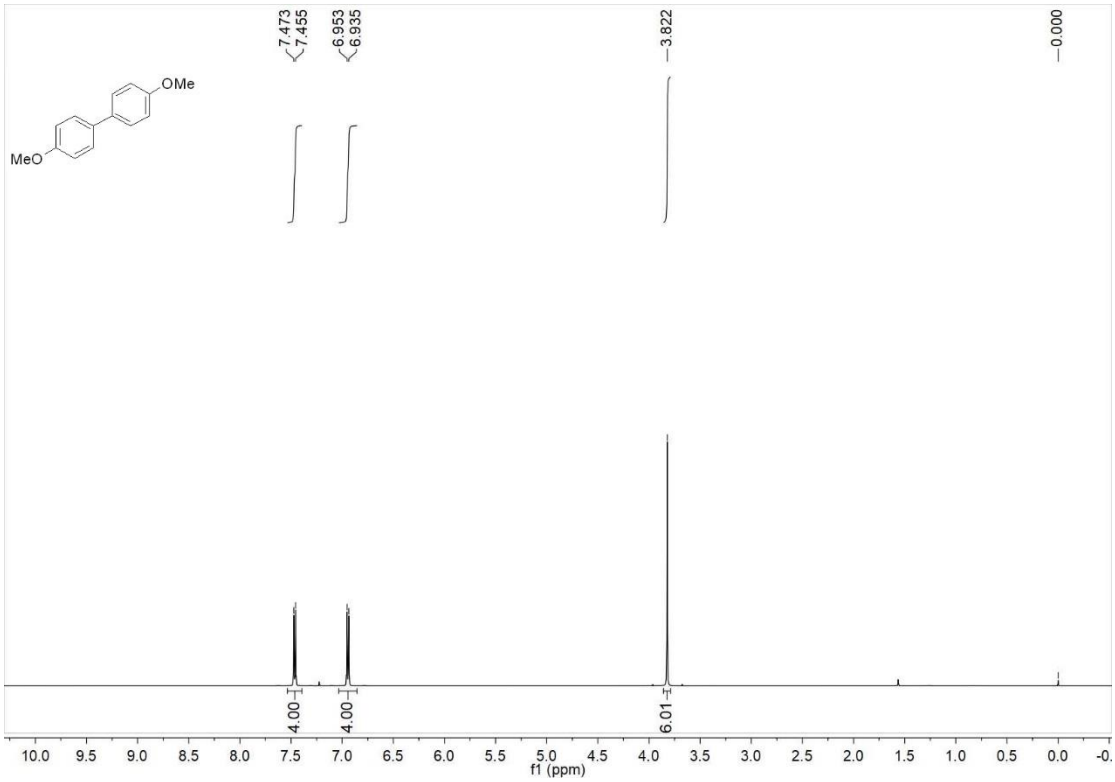


^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **4a-D**

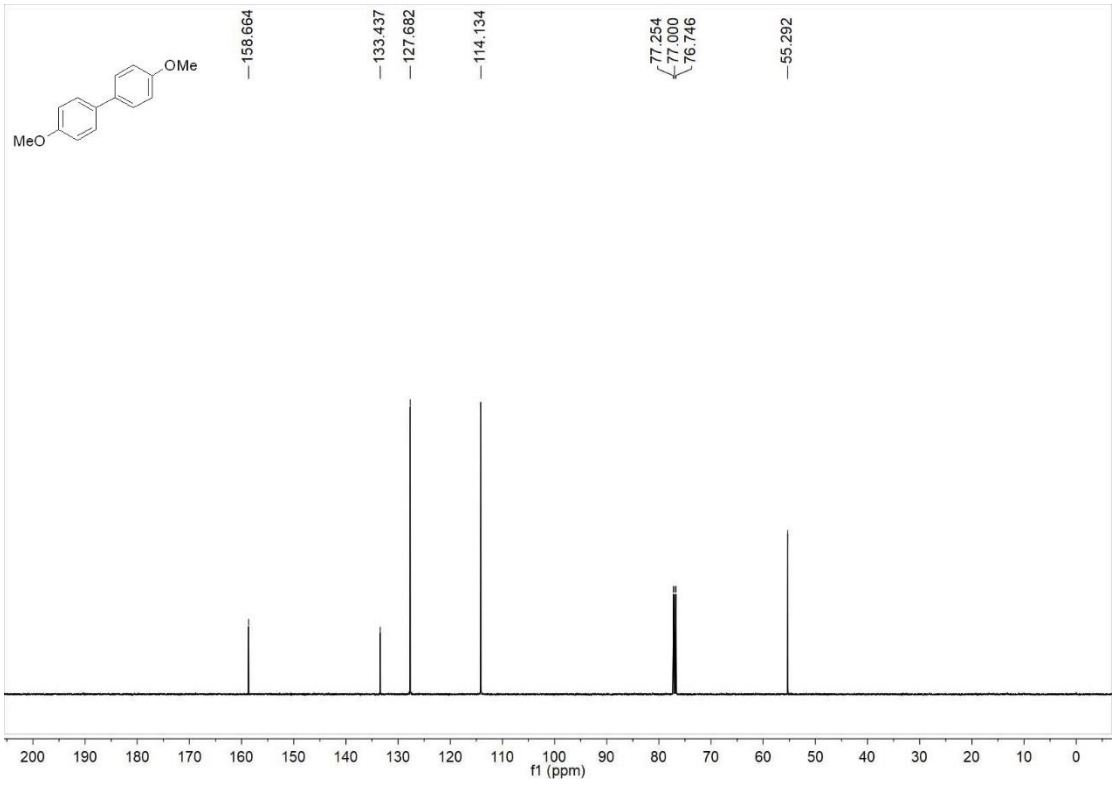


4,4'-Dimethoxybiphenyl (9a)

^{1}H NMR-spectrum (500 MHz, $CDCl_3$) of **9a**



^{13}C NMR-spectrum (126 MHz, $CDCl_3$) of **9a**



(G) The *X*-ray single-crystal diffraction analysis of product 4a

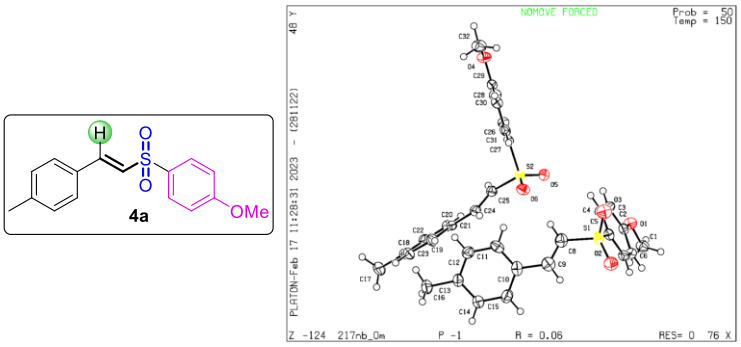


Table 1 Crystal data and structure refinement for **4a**.

Identification code	**4a**
Empirical formula	$C_{16}H_{16}O_3S$
Formula weight	288.35
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	8.1900(3)
b/Å	10.9737(3)
c/Å	16.0251(5)
α/°	92.8410(10)
β/°	98.8500(10)
γ/°	91.3280(10)
Volume/Å^3	1420.66(8)
Z	4
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	0.232
F (000)	608.0
Crystal size/mm^3	0.12 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.718 to 58.434
Index ranges	-10 ≤ h ≤ 11, -13 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	18935
Independent reflections	7246 [R_{int} = 0.0557, R_{sigma} = 0.0745]
Data/restraints/parameters	7246/7/365
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0571, wR_2 = 0.1096
Final R indexes [all data]	R_1 = 0.0973, wR_2 = 0.1341
Largest diff. peak/hole / e Å^{-3}	0.92/-0.53

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4a**.

U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S2	7201.0(8)	3875.1(5)	2174.0(4)	25.96(15)
S1	6051.0(8)	-1200.2(6)	2144.7(4)	30.46(16)
O6	7910(2)	2787.0(15)	2523.8(11)	34.5(4)
O1	364(2)	1514.8(16)	611.8(12)	33.3(4)
O4	12085(2)	6502.5(16)	548.5(11)	34.1(4)
O5	5701(2)	3754.8(17)	1567.0(11)	34.9(4)
O2	5499(2)	-2301.9(17)	2467.2(12)	40.6(5)
O3	7212(2)	-1280.2(17)	1553.4(13)	42.3(5)
C27	8702(3)	4649(2)	1708.1(14)	23.8(5)
C29	11042(3)	5846(2)	945.8(15)	25.7(5)
C21	6971(3)	5416(2)	4530.1(15)	26.4(5)
C5	4314(3)	-435(2)	1679.8(15)	26.9(5)
C26	8329(3)	5755(2)	1336.5(15)	25.6(5)
C31	10247(3)	4159(2)	1704.9(15)	26.6(5)
C2	1603(3)	834(2)	990.6(15)	26.4(5)
C30	11427(3)	4756(2)	1323.0(15)	27.3(5)
C24	7271(3)	4645(2)	3794.5(16)	28.1(5)
C13	9049(3)	1867(2)	5941.4(16)	30.4(6)
C20	5823(3)	6332(2)	4479.0(16)	29.3(5)
C18	6542(3)	6871(2)	5976.0(16)	30.3(6)
C28	9493(3)	6348(2)	957.4(16)	27.7(5)
C6	2738(3)	-857(2)	1744.4(15)	28.7(5)
C19	5597(3)	7036(2)	5194.5(16)	31.1(6)
C7	1366(3)	-224(2)	1403.2(15)	27.4(5)
C23	7680(3)	5950(2)	6022.9(16)	34.0(6)
C22	7877(3)	5224(2)	5319.2(16)	32.3(6)
C25	6796(3)	4881(2)	2991.7(15)	27.2(5)
C12	9550(3)	2054(2)	5167.6(17)	34.2(6)
C3	3192(3)	1262(2)	928.6(18)	33.6(6)
C10	7745(3)	407(2)	4486.7(17)	32.5(6)
C1	-1279(3)	1212(2)	747.3(17)	33.3(6)
C14	7907(4)	921(2)	5970.9(18)	38.9(6)
C11	8893(3)	1344(2)	4446.1(17)	35.2(6)
C4	4541(3)	637(2)	1269.3(18)	35.1(6)

C15	7286(3)	196(2)	5263.1(18)	39.1(6)
C32	13722(3)	6072(3)	555.1(18)	40.1(7)
C8	6985(3)	-165(2)	2959.9(18)	37.5(6)
C9	6986(4)	-396(3)	3746.2(18)	39.0(6)
C17	6324(4)	7660(3)	6749.0(18)	42.6(7)
C16	9724(4)	2640(3)	6725.0(18)	42.1(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for **4a**.

The Anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S2	33.5(3)	22.5(3)	22.5(3)	-1.3(2)	7.7(2)	-2.3(2)
S1	35.1(4)	25.8(3)	28.6(3)	-2.9(3)	-0.2(3)	5.5(2)
O6	51.9(12)	22.8(9)	31.9(10)	4.5(8)	15.3(8)	5.1(8)
O1	28.1(9)	34.0(10)	38.5(10)	8.2(8)	5.3(8)	4.6(7)
O4	27.3(9)	40.0(10)	38.0(10)	10.4(9)	11.6(8)	2.4(8)
O5	33.4(10)	41.4(10)	28.8(10)	-1.5(8)	3.8(8)	-10.3(8)
O2	47.3(12)	34.0(10)	40.3(11)	9.3(9)	3.3(9)	4.6(8)
O3	38.2(11)	40.0(11)	50.7(12)	4.2(10)	11.9(9)	10.3(9)
C27	26.9(12)	24.9(11)	19.7(11)	-1.0(9)	4.2(9)	0.1(9)
C29	25.8(12)	29.1(12)	22.3(12)	-0.9(10)	4.7(9)	-1.5(9)
C21	33.7(13)	22.6(11)	24.1(12)	0.3(10)	9.8(10)	-4.6(10)
C5	30.9(13)	26.2(12)	23.1(12)	-2.8(10)	3.5(10)	3.1(10)
C26	23.4(12)	25.6(12)	28.3(13)	1.8(10)	5.5(9)	2.9(9)
C31	34.5(13)	23.0(11)	21.7(12)	1.5(10)	2.3(10)	3.3(10)
C2	30.5(13)	26.1(12)	21.9(12)	-2.4(10)	3.1(9)	1.0(10)
C30	25.2(12)	30.3(12)	26.7(13)	-0.2(10)	4.4(10)	6.9(10)
C24	32.7(13)	23.1(12)	29.3(13)	1.2(10)	7.5(10)	-0.4(10)
C13	35.3(14)	25.3(12)	28.5(13)	0.0(11)	-1.7(10)	1.5(10)
C20	34.3(14)	27.2(12)	26.3(13)	1.6(10)	5.1(10)	-3.4(10)
C18	38.4(14)	25.1(12)	28.6(13)	-3.9(11)	11.3(11)	-5.4(10)
C28	27.3(13)	25.3(12)	31.3(13)	5.2(10)	4.8(10)	5.0(9)
C6	37.1(14)	25.2(12)	24.5(12)	3.5(10)	6.4(10)	-0.1(10)
C19	34.5(14)	25.9(12)	34.1(14)	-0.2(11)	9.8(11)	-0.1(10)
C7	28.9(13)	29.1(12)	24.5(12)	-0.7(10)	6.3(10)	-3.8(10)
C23	42.9(15)	36.7(14)	21.6(13)	-0.4(11)	3.5(11)	-1.9(12)
C22	38.5(15)	29.5(13)	29.3(14)	-0.5(11)	6.3(11)	4.0(11)
C25	31.2(13)	23.2(11)	28.0(13)	-0.3(10)	8.2(10)	-1.2(10)
C12	37.6(15)	28.1(13)	37.2(15)	2.8(11)	7.0(12)	-1.0(11)
C3	32.8(14)	26.8(13)	42.2(16)	9.0(12)	6.9(11)	0.0(10)
C10	33.3(14)	25.8(12)	35.0(15)	-2.5(11)	-5.2(11)	8.6(10)
C1	28.7(13)	40.3(15)	32.1(14)	3.2(12)	7.6(11)	4.0(11)
C14	48.2(17)	36.4(15)	32.1(15)	-4.7(12)	9.6(12)	-7.0(12)
C11	45.1(16)	35.3(14)	26.7(13)	5.4(11)	8.2(11)	11.5(12)
C4	29.8(14)	29.6(13)	46.6(17)	4.0(12)	8.3(12)	-3.7(10)

C15	40.8(16)	32.3(14)	43.3(17)	-4.2(13)	6.8(13)	-6.3(12)
C32	25.9(14)	55.3(18)	41.1(16)	6.8(14)	10.0(11)	2.5(12)
C8	40.4(15)	30.9(13)	39.7(15)	0.8(12)	1.6(12)	3.9(11)
C9	44.6(16)	32.1(14)	40.3(16)	3.0(12)	5.2(13)	8.6(12)
C17	56.1(19)	39.9(16)	32.8(15)	-9.9(13)	14.0(13)	-1.9(13)
C16	53.7(18)	37.2(15)	32.8(15)	-6.3(13)	2.5(13)	-6.5(13)

Table 4 Bond Lengths for **4a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S2	O6	1.4407(18)	C26	C28	1.374(3)
S2	O5	1.4439(18)	C31	C30	1.389(3)
S2	C27	1.757(2)	C2	C7	1.389(3)
S2	C25	1.747(2)	C2	C3	1.393(3)
S1	O2	1.4288(19)	C24	C25	1.326(3)
S1	O3	1.443(2)	C13	C12	1.388(4)
S1	C5	1.754(2)	C13	C14	1.388(4)
S1	C8	1.757(3)	C13	C16	1.504(3)
O1	C2	1.359(3)	C20	C19	1.389(3)
O1	C1	1.430(3)	C18	C19	1.390(4)
O4	C29	1.356(3)	C18	C23	1.388(4)
O4	C32	1.430(3)	C18	C17	1.511(3)
C27	C26	1.398(3)	C6	C7	1.388(3)
C27	C31	1.387(3)	C23	C22	1.380(3)
C29	C30	1.389(3)	C12	C11	1.391(4)
C29	C28	1.396(3)	C3	C4	1.369(4)
C21	C24	1.472(3)	C10	C11	1.387(4)
C21	C20	1.388(3)	C10	C15	1.382(4)
C21	C22	1.393(3)	C10	C9	1.489(4)
C5	C6	1.381(3)	C14	C15	1.376(4)
C5	C4	1.399(4)	C8	C9	1.297(4)

Table 5 Bond Angles for **4a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O6	S2	O5	118.56(11)	O1	C2	C3	114.9(2)
O6	S2	C27	108.49(11)	C7	C2	C3	120.6(2)
O6	S2	C25	109.54(11)	C29	C30	C31	119.3(2)
O5	S2	C27	108.13(11)	C25	C24	C21	125.5(2)
O5	S2	C25	106.65(11)	C12	C13	C14	117.4(2)
C25	S2	C27	104.59(11)	C12	C13	C16	121.9(2)
O2	S1	O3	118.50(12)	C14	C13	C16	120.7(2)
O2	S1	C5	108.44(12)	C21	C20	C19	120.8(2)
O2	S1	C8	111.78(13)	C19	C18	C17	121.1(2)
O3	S1	C5	108.54(12)	C23	C18	C19	117.7(2)
O3	S1	C8	104.94(13)	C23	C18	C17	121.2(2)
C5	S1	C8	103.60(12)	C26	C28	C29	120.1(2)
C2	O1	C1	117.31(19)	C5	C6	C7	120.5(2)
C29	O4	C32	117.7(2)	C20	C19	C18	121.2(2)
C26	C27	S2	119.76(18)	C6	C7	C2	118.9(2)
C31	C27	S2	120.05(18)	C22	C23	C18	121.4(2)
C31	C27	C26	120.2(2)	C23	C22	C21	120.9(2)
O4	C29	C30	124.5(2)	C24	C25	S2	121.0(2)
O4	C29	C28	115.0(2)	C13	C12	C11	121.1(2)
C30	C29	C28	120.5(2)	C4	C3	C2	120.2(2)
C20	C21	C24	123.3(2)	C11	C10	C9	124.0(3)
C20	C21	C22	118.0(2)	C15	C10	C11	118.2(2)
C22	C21	C24	118.8(2)	C15	C10	C9	117.8(2)
C6	C5	S1	120.62(19)	C15	C14	C13	121.7(3)
C6	C5	C4	120.1(2)	C10	C11	C12	120.7(3)
C4	C5	S1	119.21(19)	C3	C4	C5	119.6(2)
C28	C26	C27	119.7(2)	C14	C15	C10	120.9(3)
C27	C31	C30	120.2(2)	C9	C8	S1	120.6(2)
O1	C2	C7	124.5(2)	C8	C9	C10	125.3(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4a**.

Atom	***x***	***y***	***z***	**U(eq)**
H26	7275.95	6096.36	1346.05	31
H31	10499.79	3412.41	1964.86	32
H30	12485.81	4421.29	1319.89	33
H24	7852.97	3917.11	3904.28	34
H20	5184.73	6478.52	3948.47	35
H28	9243.88	7098.52	702.92	33
H6	2592.21	-1585.03	2024.5	34
H19	4781.17	7641	5148.55	37
H7	282.53	-511.22	1451.05	33
H23	8338.24	5816.55	6550.54	41
H22	8641.79	4584.21	5373.95	39
H25	6228.06	5608.61	2858.93	33
H12	10356.3	2676.79	5130.24	41
H3	3341.31	1990.5	648.77	40
H1A	-2050.96	1779.19	456.22	50
H1B	-1332.3	1273.36	1354.66	50
H1C	-1581.34	376.22	523.73	50
H14	7546.49	769.84	6493.09	47
H11	9232.73	1501.4	3920.1	42
H4	5623.85	930.09	1227.11	42
H15	6531.37	-459.05	5308.38	47
H32A	14338.72	6617.55	241.27	60
H32B	13664.54	5246.1	288.26	60
H32C	14283.41	6058.21	1140.33	60
H8	7494.62	570.12	2823.76	45
H9	6459.53	-1137.76	3858.27	47
H17A	7243.37	8261.55	6877.78	64
H17B	6310.23	7146.18	7231.02	64
H17C	5279.07	8083.75	6639.46	64
H16A	10682.09	3127.62	6620.14	63
H16B	10062.06	2111.25	7192.34	63
H16C	8868.76	3183.79	6873.27	63