Temperature Controlled Di- and Monosulfonylation of Propargyl Alcohols with Sodium Sulfinates: Switchable Access to (*E*)-Allyl, Vinyldisulfones and Propargyl Sulfones

Chang-Qing Liu[†a,b], Hang Li[†a], Bo Wang[a], Zi-Yi Guo[a], Yu Wang[a], Ji-Tan Zhang[a*], Mei-Hua Xie[a*]

[a]Key Laboratory of Functional Molecular Solids (Ministry of Education), Anhui Key Laboratory of Molecular Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China

[b]Department of Pharmaceutical Synthesis, Bengbu Medical College, Bengbu, 233030, China

Supporting Information

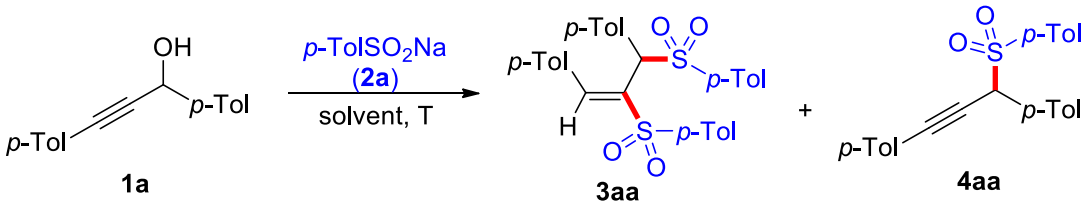
General techniques. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a BRUKER AVANCE-500 spectrometer in $CDCl_3$ with TMS as the internal standard. All the melting points are uncorrected. High-resolution mass spectra were recorded on an Agilent QTOF mass spectrometer. The crystal structure analysis was performed on a Bruker SMART Bruker Platon II area detector diffractometer. All reagents were obtained from commercial sources and used without further purification. The starting material propargyl alcohols were prepared according to previously reported procedures[1].

Reference

1. (a) Liu, C.; Wang, B.; Guo, Z.; Zhang, J.; Xie, M. Metal-Free Cascade Rearrangement/Radical Addition/Oxidative C-H Annulation of Propargyl Alcohols with Sodium Sulfinates: Access to 2-Sulfenylindenones *Org. Chem. Front.* **2019**, *6*, 2796-2800. (b) Zhu, H-T.; Ji, K-G; Yang, F.; Wang, L.-J.; Zhao, S.-C.; Ali, S.; Liu, X.-Y.; Liang, Y.-M. Electrophilic Carbocyclization of Aryl Propargylic Alcohols: A Facile Synthesis of Diiodinated Carbocycles and Heterocycles *Org. Lett.*, **2011**, *13*, 684-687.

Optimization of the Reaction Conditions

Table 1. Optimization of the Reaction Conditions[a]

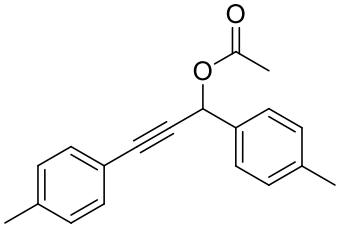


Entry	Ratio of **1a:2a**	Solvent	Temp (°C)	Yield[b] (%)	
				3aa	**4aa**
1	1:2	CH_3CN	32	n.r.	n.r.
2[c]	1:2	HOAc/CH_3CN (1:1)	32	trace	trace
3	1:2	HOAc/ H_2O (1:1)	32	trace	54
4	1:2	HOAc/ H_2O (1:1)	50	trace	57
5	1:2	HOAc/ H_2O (1:1)	80	15	63
6	1:2	HOAc/H_2O (1:1)	Reflux	92	n.d.
7	1:2	HOAc/EtOH (1:1)	Reflux	23	n.d.

8	1:2	HOAc/CH_2Cl_2 (1:1)	Reflux	64	trace
9	1:2	HOAc/DCE (1:1)	Reflux	53	trace
10	1:2	HOAc/THF (1:1)	Reflux	48	trace
11	1:1.2	HOAc/H_2O (1:1)	Reflux	40	10
12[d]	1:1.2	HOAc/H_2O (1:1)	32	n.d.	96
13[d]	1:1.2	HOAc/H_2O (1:1)	32	n.d.	91

[a] Reaction conditions: **1a** (0.2 mmol) and **2a** in 1 mL of solvent, 24 h, air; DCE = $ClCH_2CH_2Cl$; n.r.: no reaction; n.d.: not detected. [b]Isolated yield. [c]1,3-di-*p*-tolylprop-2-yn-1-yl acetate (1a-OAc) was isolated in 54%. [d]48 h.

1,3-Di-p-tolylprop-2-yn-1-yl acetate (1a-OAc)

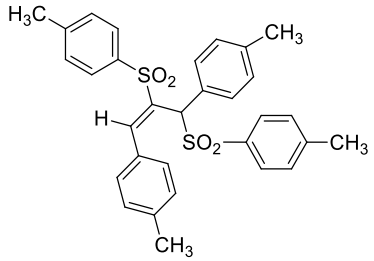


White Oil; 30 mg; yield: 54%; PE/EA = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.66 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 139.0, 138.9, 134.4, 131.9, 129.5, 129.4, 129.1, 127.9, 119.1, 87.1, 85.1, 66.1, 25.6, 25.3, 25.3; HRMS m/z (ESI) calcd for $C_{19}H_{19}O_2$ $(M+H)^+$ 279.1380, found 279.1384.

General procedure for the synthesis of 3 and spectral data for 3

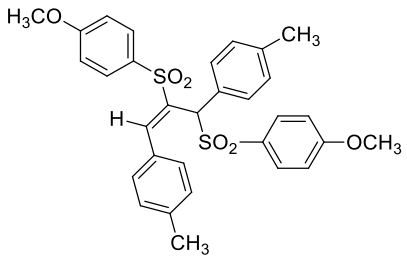
1,3-Di-*p*-tolylprop-2-yn-1-ol (**1a**, 47.2 mg, 0.2 mmol) and sodium *p*-toluenesulfinate (**2a**, 71.3 mg, 0.4 mmol) were sequentially added to the solvent of HOAc/H_2O (1 mL, v/v = 1:1) at room temperature. The reaction mixture was heated to reflux and stirred until the complete consumption of **1a** (monitored by TLC). Then the reaction mixture was cooled to room temperature, diluted with water (5 mL), and extracted with dichloromethane (3 × 10 mL). The organic extracts were dried over anhydrous Na_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to give product **3aa**.

(*E*)-4,4'-(1,3-di-*p*-tolylprop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3aa)



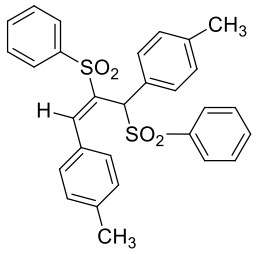
Light yellow solid; mp 189-190 °C; 98 mg, 92% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 4H), 7.20-7.17 (m, 4H), 7.13 (t, *J* = 8.5 Hz, 4H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.88 (s, 1H), 2.38 (s, 6H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 146.9, 145.0, 144.5, 141.1, 138.9, 137.5, 137.0, 135.9, 130.4, 130.2, 130.1, 129.9, 129.7, 129.5, 129.4, 129.2, 128.8, 127.7, 69.9, 22.0, 21.9, 21.8, 21.5; IR (KBr): ν (cm^{-1}) 1631, 1596, 1143, 811, 695, 593; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{31}H_{30}O_4S_2Na$: 553.1478, found: 553.1479.

(*E*)-4,4'-(2,3-bis((4-methoxyphenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ab)



White solid; mp 141-142 °C; 92 mg, 82% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 1H), 7.68-7.67 (m, 2H), 7.45-7.43 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18-7.16 (m, 4H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.85-6.84 (m, 2H), 6.79-6.78 (m, 2H), 5.89 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.38 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.1, 163.7, 146.2, 141.1, 138.8, 131.4, 131.2, 131.0, 130.5, 130.1, 130.0, 129.5, 129.4, 127.8, 114.5, 114.2, 70.1, 56.0, 55.9, 21.9, 21.5; IR (KBr): ν (cm^{-1}) 1630, 1595, 1328, 1314, 1149, 1127, 695; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{31}H_{30}O_6S_2Na$: 585.1376, found: 585.1379.

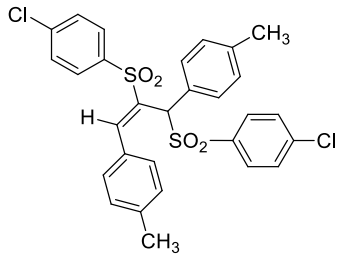
(*E*)-4,4'-(2,3-bis(phenylsulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ac)



Light yellow solid; mp 156-157 °C; 82 mg, 82% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.54-7.50 (m, 4H), 7.41-7.34 (m, 6H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 5.91 (s, 1H), 2.39 (s, 3H), 2.25 (s,

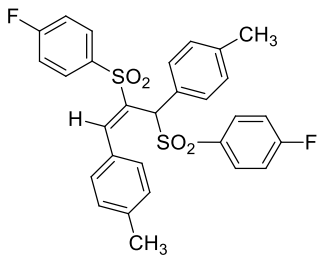
3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 147.5, 141.3, 140.4, 139.8, 139.1, 134.1, 133.5, 130.5, 130.4, 130.1, 129.9, 129.8, 129.4, 129.3, 129.2, 129.1, 128.6, 127.3, 69.9, 21.9, 21.5; IR (KBr): ν (cm^{-1}) 1630, 1598, 1307, 1154, 730, 598; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{26}O_4S_2Na$: 525.1165, found: 525.1160.

(*E*)-4,4'-(2,3-bis((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (**3ad**)



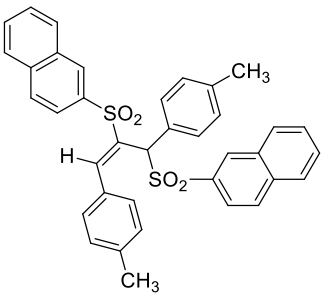
White solid; mp 223-224 °C; 104 mg, 91% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.33-7.28 (m, 6H), 7.22-7.17 (m, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 5.91 (s, 1H), 2.40 (s, 3H), 2.28 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 148.3, 141.5, 141.0, 140.2, 139.5, 139.2, 137.9, 130.6, 130.3, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 126.7, 69.8, 21.9, 21.5; IR (KBr): ν (cm^{-1}) 1631, 1601, 1330, 1158, 1145, 1084, 814, 623; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{24}O_4S_2Cl_2Na$: 593.0385, found: 593.0388.

(*E*)-4,4'-(2,3-bis((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (**3ae**)



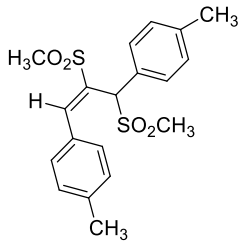
White solid; mp 190-191 °C; 97 mg, 90% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.74-7.70 (m, 2H), 7.56-7.53 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.20-7.16 (m, 4H), 7.06-6.98 (m, 4H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.91 (s, 1H), 2.39 (s, 3H), 2.26 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 166.2 (d, $^{1}J_{CF}$ = 255.0 Hz), 165.8 (d, $^{1}J_{CF}$ = 254.6 Hz), 148.0, 141.5, 139.4, 136.7, 135.7 (d, $^{4}J_{CF}$ = 3.1 Hz), 135.4 (d, $^{4}J_{CF}$ = 2.5 Hz), 132.1 (d, $^{3}J_{CF}$ = 9.6 Hz), 131.4 (d, $^{3}J_{CF}$ = 9.5 Hz), 130.2, 130.1, 129.8, 129.6, 126.9, 116.5 (d, $^{2}J_{CF}$ = 22.5 Hz), 116.4 (d, $^{2}J_{CF}$ = 22.5 Hz), 70.0, 21.9, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.01, -104.04; IR (KBr): ν (cm^{-1}) 1630, 1589, 1317, 1292, 1146, 593; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{24}O_4S_2F_2Na$: 561.0976, found: 561.0976.

(*E*)-2,2'-(1,3-di-*p*-tolylprop-2-ene-1,2-diyldisulfonyl)dinaphthalene (3af)



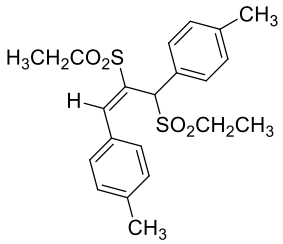
White solid; mp 187-188 °C; 86 mg, 71% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.13 (s, 1H), 7.94 (s, 1H), 7.82-7.77 (m, 4H), 7.66-7.60 (m, 5H), 7.59-7.56 (m, 1H), 7.54-7.51 (m, 1H), 7.45 (d, *J* = 9.4 Hz, 1H), 7.25-7.24 (m, 4H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.08 (s, 1H), 2.33 (s, 3H), 2.08 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.8, 141.1, 139.1, 137.3, 136.6, 135.6, 135.2, 132.2, 131.1, 130.5, 130.3, 129.9, 129.8, 129.6, 129.5, 129.4, 129.2, 128.2, 127.8, 127.7, 127.1, 123.8, 123.0, 69.4, 21.9, 21.3; IR (KBr): ν (cm^{-1}) 1631, 1597, 1511, 1146, 695, 592; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{37}H_{30}O_4S_2Na$: 625.1478, found: 625.1475.

(*E*)-4,4'-(2,3-bis(methylsulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ag)



White solid; mp 139-140 °C; 61 mg, 80% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.84 (s, 1H), 3.36 (s, 3H), 2.89 (s, 3H), 2.37 (s, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.1, 141.4, 139.8, 139.0, 130.4, 130.1, 129.8, 129.7, 129.6, 129.4, 73.3, 45.9, 40.9, 21.8, 21.6; IR (KBr): ν (cm^{-1}) 1610, 1510, 1293, 1123, 970, 817; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{19}H_{22}O_4S_2Na$: 401.0852, found: 401.0849.

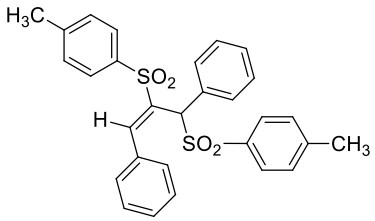
(*E*)-4,4'-(2,3-bis(ethylsulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ah)



Colorless liquid; 70 mg, 86% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 5.1 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 5.89 (s, 1H), 3.48-3.33 (m, 2H), 3.23-3.16 (m, 1H), 2.93-2.86 (m, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 1.42 (t, *J* = 7.4 Hz, 3H), 1.24 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 150.5,

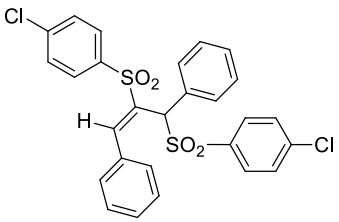
141.0, 139.6, 135.9, 130.1, 130.0, 130.0, 129.9, 129.4, 129.0, 69.4, 51.2, 47.4, 21.8, 21.5, 7.5, 6.5; IR (KBr): ν (cm^{-1}) 1630, 1604, 1314, 1135, 815; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{21}H_{26}O_4S_2Na$: 429.1165, found: 429.1161.

***(E)*-4,4'-(1,3-diphenylprop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ba)**



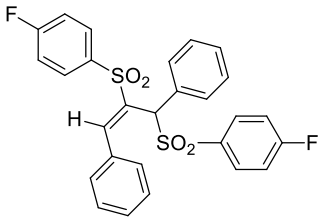
White solid; mp 165-166 °C; 68 mg, 68% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.65 (d, J = 8.3 Hz, 2H), 7.42-7.35 (m, 7H), 7.26-7.25 (m, 2H), 7.20-7.17 (m, 3H), 7.11-7.08 (m, 4H), 5.85 (s, 1H), 2.37 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.1, 145.1, 144.7, 137.5, 137.4, 136.7, 133.1, 130.7, 130.5, 130.4, 130.0, 129.8, 129.7, 129.1, 129.0, 128.9, 128.8, 128.6, 69.9, 22.0, 21.9; IR (KBr): ν (cm^{-1}) 1625, 1598, 1305, 1127, 804; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{26}O_4S_2Na$: 525.1165, found: 525.1160.

(*E*)-4,4'-(1,3-diphenylprop-2-ene-1,2-diyldisulfonyl)bis(chlorobenzene) (3bb)



Yellow solid; mp 216-217 °C; 98 mg, 90% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.65-7.62 (m, 2H), 7.44-7.41 (m, 5H), 7.38-7.36 (m, 4H), 7.31-7.23 (m, 5H), 7.15 (d, J = 7.9 Hz, 2H), 5.88 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 148.6, 141.1, 140.4, 139.1, 137.6, 137.1, 132.8, 130.7, 130.6, 130.5, 130.0, 129.8, 129.6, 129.5, 129.4, 129.3, 129.2, 128.9, 69.8; IR (KBr): ν (cm^{-1}) 1632, 1602, 1332, 1147, 814; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{27}H_{20}O_4S_2Cl_2Na$: 565.0072, found: 565.0077.

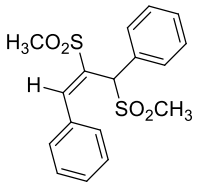
(*E*)-4,4'-(1,3-diphenylprop-2-ene-1,2-diyldisulfonyl)bis(fluorobenzene) (3bc)



Yellow solid; mp 176-177 °C; 93 mg, 91% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.76-7.73 (m, 2H), 7.53-7.50 (m, 2H), 7.42-7.39 (m, 5H), 7.29 (d, J = 7.5 Hz, 2H), 7.22 (d, J = 7.4 Hz, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 5.89 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.2 (d, $^1J_{CF}$ = 255.5 Hz), 165.8 (d, $^1J_{CF}$

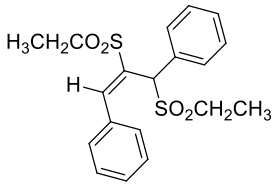
= 254.0 Hz), 148.3, 137.3, 136.6 (d, $^4J_{CF}$ = 2.4 Hz), 135.2 (d, $^4J_{CF}$ = 2.6 Hz), 132.8, 132.0 (d, $^3J_{CF}$ = 9.8 Hz), 131.5 (d, $^3J_{CF}$ = 9.6 Hz), 130.6, 130.5, 130.0, 129.5, 129.4, 129.1, 128.9, 116.6 (d, $^2J_{CF}$ = 22.6 Hz), 116.5 (d, $^2J_{CF}$ = 22.5 Hz), 69.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.81, -103.74; IR (KBr): ν (cm^{-1}) 1630, 1586, 1319, 1296, 819; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{27}H_{20}O_4S_2F_2Na$: 533.0663, found: 533.0661.

(*E*)-(2,3-bis(methylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (3bd)



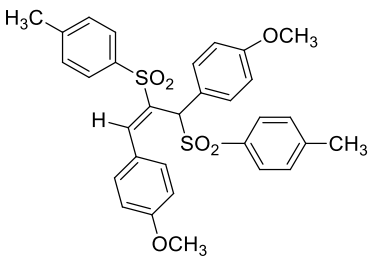
Yellow liquid; 36 mg, 52% yield; PE/EA = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.70-7.68 (m, 2H), 7.62-7.60 (m, 2H), 7.46-7.45 (m, 3H), 7.43-7.41 (m, 3H), 5.95 (s, 1H), 2.95 (s, 3H), 2.75 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.4, 136.3, 133.3, 132.6, 130.4, 130.1, 130.0, 129.8, 129.0, 66.8, 43.2, 40.6; IR (KBr): ν (cm^{-1}) 1612, 1514, 1295, 1116, 1026; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{17}H_{18}O_4S_2Na$: 373.0539, found: 373.0542.

(*E*)-(2,3-bis(ethylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (3be)



Yellow liquid; 42 mg, 55% yield; PE/EA = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.69-7.67 (m, 2H), 7.62-7.60 (m, 2H), 7.47-7.40 (m, 6H), 5.87 (s, 1H), 3.07 (q, J = 7.5 Hz, 2H), 2.87-2.80 (m, 1H), 2.70-2.63 (m, 1H), 1.42 (t, J = 7.5 Hz, 3H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.1, 135.1, 133.4, 132.3, 130.4, 130.0, 129.94, 129.9, 129.8, 128.9, 64.2, 48.9, 47.1, 6.9, 6.8; IR (KBr): ν (cm^{-1}) 1630, 1608, 1315, 1136; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{19}H_{22}O_4S_2Na$: 401.0852, found: 401.0855.

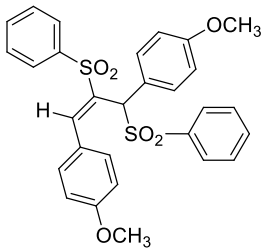
(*E*)-4,4'-(1,3-bis(4-methoxyphenyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (**3ca**)



Light yellow solid; mp 157-158 ^{o}C; 79 mg, 70% yield; PE/EA = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.66 (d, J = 8.3 Hz, 2H), 7.35-7.33 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.19-7.17 (m,

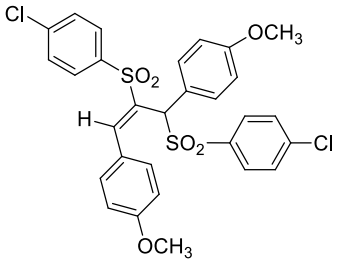
2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.90-6.84 (m, 4H), 6.72 (d, *J* = 8.8 Hz, 2H), 5.87 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 2.45 (s, 3H), 2.25 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 160.7, 160.6, 145.4, 144.1, 143.7, 137.5, 136.7, 135.5, 132.0, 131.7, 130.1, 129.7, 129.1, 128.0, 125.9, 123.2, 114.6, 113.6, 68.2, 55.7, 22.1, 21.9; IR (KBr): ν (cm^{-1}) 1630, 1594, 1141, 809, 690; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{31}H_{30}O_6S_2Na$: 585.1376, found: 585.1380.

(*E*)-4,4'-(2,3-bis(phenylsulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (3cb)



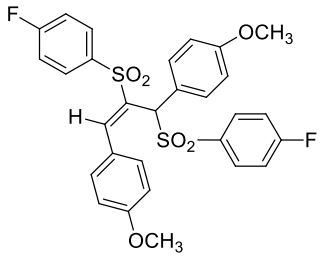
White solid; mp 160-161 °C; 58 mg, 54% yield; PE/EA = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.81-7.79 (m, 2H), 7.68-7.65 (m, 1H), 7.54-7.51 (m, 2H), 7.36-7.34 (m, 2H), 7.31-7.29 (m, 1H), 7.20-7.15 (m, 4H), 7.12-7.08 (m, 2H), 6.87-6.85 (m, 2H), 6.71-6.69 (m, 2H), 5.94 (s, 1H), 3.81 (s, 3H), 3.78 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 160.8, 144.1, 140.4, 138.3, 136.4, 134.4, 133.2, 131.9, 131.7, 129.7, 129.5, 128.5, 127.9, 125.7, 123.0, 114.7, 113.7, 68.0, 55.7; IR (KBr): ν (cm^{-1}) 1631, 1599, 1308, 1155, 731; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{26}O_6S_2Na$: 557.1063, found: 557.1059.

(*E*)-4,4'-(2,3-bis((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (3cc)



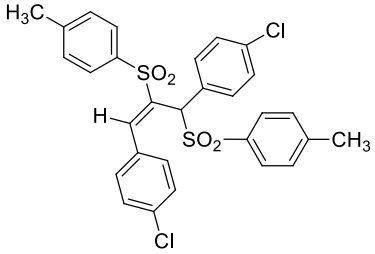
White solid; mp 155-156 °C; 75 mg, 62% yield; PE/EA = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.51-7.49 (m, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.34-7.32 (m, 4H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.9 Hz, 2H), 5.98 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 162.2, 160.4, 147.5, 147.4, 141.1, 140.1, 139.2, 137.8, 133.0, 131.5, 130.7, 129.8, 129.6, 129.4, 124.6, 121.4, 114.5, 114.4, 69.8, 55.9, 55.7; IR (KBr): ν (cm^{-1}) 1631, 1605, 1332, 1145, 1088, 812; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{24}O_6S_2Cl_2Na$: 625.0284, found: 625.0285.

(*E*)-4,4'-(2,3-bis((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (**3cd**)



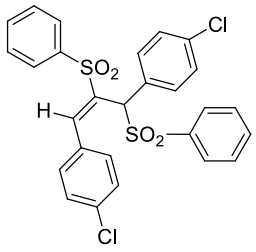
White solid; mp 171-172 °C; 57 mg, 50% yield; PE/EA = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (s, 1H), 7.78-7.76 (m, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.28-7.25 (m, 2H), 7.20-7.17 (m, 4H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.80 (t, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.91 (s, 1H), 3.82 (s, 3H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.4 (d, $^{1}J_{CF}$ = 255.8 Hz), 165.5 (d, $^{1}J_{CF}$ = 254.3 Hz), 161.0, 160.9, 144.3, 136.5, 136.3 (d, $^{4}J_{CF}$ = 2.5 Hz), 134.2 (d, $^{4}J_{CF}$ = 2.5 Hz), 132.5 (d, $^{3}J_{CF}$ = 9.5 Hz), 131.8, 131.7, 130.9 (d, $^{3}J_{CF}$ = 9.4 Hz), 125.5, 123.1, 116.8 (d, $^{2}J_{CF}$ = 22.5 Hz), 115.8 (d, $^{2}J_{CF}$ = 22.5 Hz), 114.8, 113.8, 68.1, 55.8.; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.40, -104.12; IR (KBr): ν (cm^{-1}) 1631, 1588, 1318, 1290, 1145, 812; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{24}O_6S_2F_2Na$: 593.0875, found: 593.0878.

(*E*)-4,4'-(1,3-bis(4-chlorophenyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (**3da**)



White solid; mp 222-223 °C; 97 mg, 85% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.37-7.36 (m, 6H), 7.26-7.25 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 7.09-7.06 (m, 2H), 5.74 (s, 1H), 2.42 (s, 3H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.6, 145.5, 145.2, 137.6, 136.8, 136.7, 136.4, 135.4, 131.6, 131.3, 131.2, 130.1, 130.0, 129.3, 129.1, 129.0, 128.9, 128.8, 69.1, 22.0; IR (KBr): ν (cm^{-1}) 1631, 1598, 1146, 813, 702; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{24}O_4S_2Cl_2Na$: 593.0385, found: 593.0389.

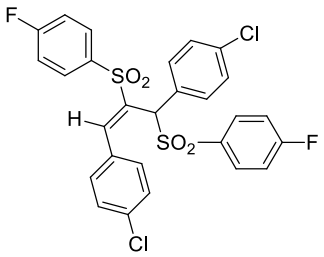
(*E*)-4,4'-(2,3-bis(phenylsulfonyl)prop-1-ene-1,3-diyl)bis(chlorobenzene) (3db)



White solid; mp 189-190 °C; 95 mg, 87% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.61-7.55 (m, 2H), 7.50-7.45 (m, 4H), 7.41-7.38 (m, 6H),

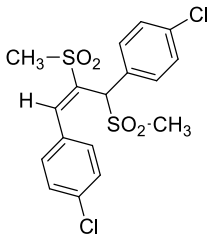
7.12 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.6 Hz, 2H), 5.76 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 146.2, 139.7, 139.2, 137.2, 136.9, 135.5, 134.5, 134.0, 131.6, 131.3, 131.0, 129.6, 129.4, 129.2, 129.0, 128.9, 128.8, 69.1; IR (KBr): ν (cm^{-1}) 1630, 1601, 1308, 1150, 732; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{27}H_{20}O_4S_2Cl_2Na$: 565.0072, found: 565.0073.

(*E*)-4,4'-(2,3-bis((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(chlorobenzene) (**3dc**)



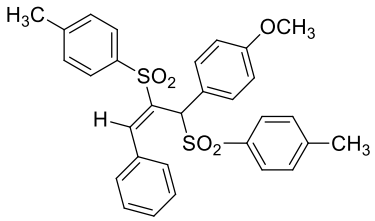
White solid; mp 217-218 °C; 98 mg, 85% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.83-7.80 (m, 2H), 7.55-7.52 (m, 2H), 7.40-7.34 (m, 4H), 7.17-7.11 (m, 6H), 7.07 (t, *J* = 8.4 Hz, 2H), 5.76 (s, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 166.4 (d, $^{1}J_{CF}$ = 256.4 Hz), 166.1 (d, $^{1}J_{CF}$ = 256.0 Hz), 146.7, 137.5, 137.1, 135.9 (d, $^{4}J_{CF}$ = 2.4 Hz), 135.8, 134.9 (d, $^{4}J_{CF}$ = 2.8 Hz), 132.0 (d, $^{3}J_{CF}$ = 9.6 Hz), 131.7 (d, $^{3}J_{CF}$ = 9.6 Hz), 131.6, 131.1, 130.9, 129.4, 129.1, 128.7, 116.9 (d, $^{2}J_{CF}$ = 22.6 Hz), 116.8 (d, $^{2}J_{CF}$ = 22.5 Hz), 69.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -101.82, -102.68; IR (KBr): ν (cm^{-1}) 1630, 1586, 1315, 1290, 1142, 596; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{27}H_{18}O_4S_2F_2Cl_2Na$: 600.9884, found: 600.9887.

(*E*)-4,4'-(2,3-bis(methylsulfonyl)prop-1-ene-1,3-diyl)bis(chlorobenzene) (3dd)



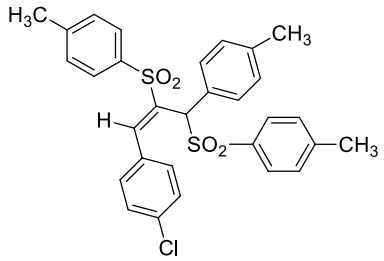
White solid; mp 155-156 °C; 35 mg, 42% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.63-7.62 (m, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.46-7.43 (m, 2H), 7.42-7.40 (m, 2H), 5.90 (s, 1H), 2.95 (s, 3H), 2.79 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 144.2, 136.9, 136.7, 136.5, 131.5, 131.3, 131.0, 130.9, 130.3, 129.3, 66.2, 43.2, 40.6; IR (KBr): ν (cm^{-1}) 1612, 1518, 1296, 1128, 819; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{17}H_{16}O_4S_2Cl_2Na$: 440.9759, found: 440.9762.

(*E*)-4,4'-(1-(4-methoxyphenyl)-3-phenylprop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ea)



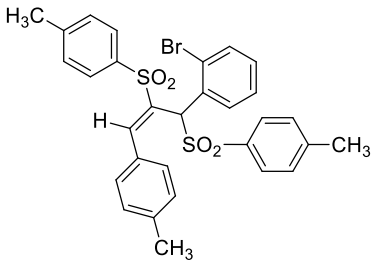
White solid; mp 134-135 °C; 64 mg, 60% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.69-7.67 (m, 2H), 7.44-7.42 (m, 2H), 7.41-7.38 (m, 3H), 7.34-7.32 (m, 2H), 7.23-7.22 (m, 2H), 7.16 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.63 (d, J = 8.9 Hz, 2H), 5.76 (s, 1H), 3.74 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.1, 146.8, 145.0, 144.6, 137.8, 137.4, 136.7, 133.2, 131.9, 130.3, 129.9, 129.8, 129.7, 129.6, 129.1, 128.9, 128.8, 122.5, 114.0, 69.5, 55.6, 22.0; IR (KBr): ν (cm^{-1}) 1630, 1601, 1145, 806; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{30}H_{28}O_5S_2Na$: 555.1270, found: 555.1270.

(*E*)-4,4'-(3-(4-chlorophenyl)-1-(p-tolyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3fa)



White solid; m.p. 221-222 °C; 86 mg, 78% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.36-7.33 (m, 4H), 7.23 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.2 Hz, 2H), 5.77 (s, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.3, 145.0, 144.9, 139.1, 136.8, 136.8, 136.6, 131.6, 131.4, 130.1, 130.0, 129.9, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 69.7, 22.0, 22.0, 21.5; IR (KBr, v, cm^{-1}): ; HRMS m/z (ESI) calcd for $C_{23}H_{20}IO_3S$ (M+Na)$^+$ 573.0931, found: 573.0935.

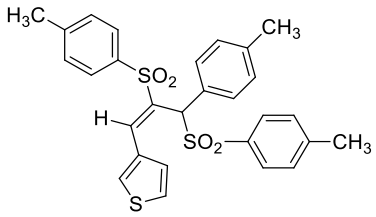
(*E*)-4,4'-(1-(2-bromophenyl)-3-(*p*-tolyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ga)



White solid; mp 188-189 °C; 77 mg, 65% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (d, J = 7.8 Hz, 1H), 8.32 (s, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.50 (t, J = 8.4 Hz, 4H), 7.27-7.23 (m, 3H), 7.11-7.06 (m, 5H), 7.01-6.98 (m, 1H), 6.26 (s, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.31 (s,

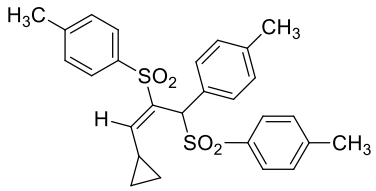
3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 149.8, 145.3, 143.9, 140.9, 138.2, 136.3, 134.6, 134.1, 132.7, 130.9, 130.5, 130.0, 129.9, 129.8, 129.7, 129.6, 129.2, 128.0, 127.4, 126.3, 68.6, 22.0, 21.93, 21.9; IR (KBr): ν (cm^{-1}) 1632, 1598, 1332, 1143, 812; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{30}H_{27}O_4S_2BrNa$: 617.0426, found: 617.0428.

(*E*)-3-(3-(*p*-tolyl)-1,2-ditosylallyl)thiophene (3ha)



White solid; mp 159-160 °C; 77 mg, 74% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.84 (s, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 4.7 Hz, 1H), 7.27-7.25 (m, 1H), 7.20-7.13 (m, 6H), 6.94 (d, *J* = 8.1 Hz, 2H), 5.98 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 145.3, 144.7, 139.4, 139.0, 136.9, 133.8, 133.4, 130.4, 130.1, 129.8, 129.5, 129.5, 129.4, 128.7, 127.2, 126.1, 70.3, 22.1, 22.0, 21.5; IR (KBr): ν (cm^{-1}) 1632, 1596, 1330, 1148, 814; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{28}H_{26}O_4S_3Na$: 545.0886, found: 545.0880.

(*E*)-4,4'-(3-cyclopropyl-1-(*p*-tolyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ia)



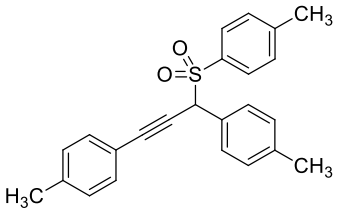
White solid; mp 191-192 °C; 55 mg, 57% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.64 (d, *J* = 11.6 Hz, 1H), 5.33 (s, 1H), 2.86-2.82 (m, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H), 1.36-1.33 (m, 1H), 1.25-1.21 (m, 1H), 0.91-0.87 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 154.1, 145.3, 144.5, 139.1, 136.3, 135.8, 131.9, 130.2, 130.0, 129.8, 129.6, 129.3, 128.6, 128.1, 70.2, 22.1, 22.0, 21.5, 14.5, 11.2, 11.1; IR (KBr): ν (cm^{-1}) 1626, 1589, 1307, 1147, 815; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{27}H_{28}O_4S_2Na$: 503.1322, found: 503.1319.

General procedure for the synthesis of 4 and spectral data for 4

1,3-Di-*p*-tolylprop-2-yn-1-ol (**1a**, 47.2 mg, 0.2 mmol) and sodium *p*-toluenesulfinate (**2a**, 42.8 mg, 0.24 mmol) were sequentially added to the solvent of HOAc/H_2O (1 mL, v/v = 1:1) at room temperature. The reaction mixture was heated to 32 °C and stirred until the complete consumption of **1a** (monitored by TLC). Then the reaction mixture was cooled to room

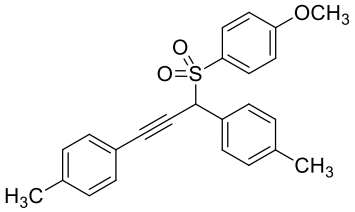
temperature, diluted with water (5 mL), and extracted with ethyl acetate (3 × 10 mL). The organic extracts were dried over anhydrous Na_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/20) to give product **4aa**.

4,4'-(3-Tosylprop-1-yne-1,3-diyl)bis(methylbenzene) (4aa)



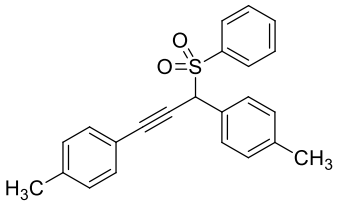
White solid; mp 140-141 °C; 72 mg, 96% yield; PE/EA = 20:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.31-7.29 (m, 4H), 7.26-7.25 (m, 2H), 7.14 (t, J = 8.3 Hz, 4H), 5.21 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4, 139.8, 139.6, 133.6, 132.1, 130.6, 130.5, 129.6, 127.7, 119.3, 89.6, 81.2, 65.9, 22.1, 21.9, 21.7; IR (KBr): ν (cm^{-1}) 2230, 1509, 1324, 1147, 1084, 817; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{24}H_{22}O_2SNa$: 397.1233, found: 397.1230.

4,4'-(3-((4-Methoxyphenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ab)



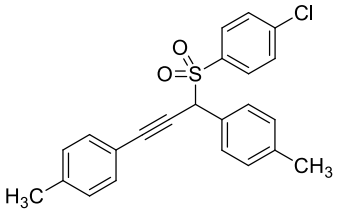
White solid; mp 120-121 °C; 70 mg, 90% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.31-7.29 (m, 4H), 7.13 (t, J = 8.1 Hz, 4H), 6.91-6.89 (m, 2H), 5.21 (s, 1H), 3.85 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.5, 139.8, 139.6, 132.7, 132.1, 130.4, 129.6, 129.5, 127.8, 127.7, 119.3, 114.1, 89.6, 81.3, 66.0, 56.1, 22.0, 21.7; IR (KBr): ν (cm^{-1}) 2225, 1631, 1593, 1508, 1321, 1302, 1145, 818; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{24}H_{22}O_3SNa$: 413.1182, found: 413.1185.

4,4'-(3-(Phenylsulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ac)



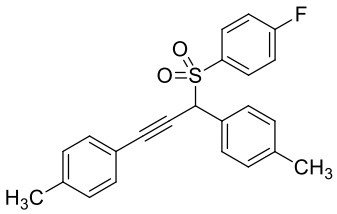
White solid; mp 126-127 °C; 61 mg, 85% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77-7.75 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.47-7.44 (m, 2H), 7.31-7.27 (m, 4H), 7.15-7.11 (m, 4H), 5.24 (s, 1H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 139.9, 139.7, 136.4, 134.4, 132.1, 130.5, 130.4, 129.6, 129.5, 128.9, 127.4, 119.2, 89.8, 81.0, 65.9, 22.0, 21.7; IR (KBr): ν (cm^{-1}) 2227, 1631, 1599, 1322, 1150, 818; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{20}O_2SNa$: 383.1076, found: 383.1079.

4,4'-(3-((4-Chlorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ad)



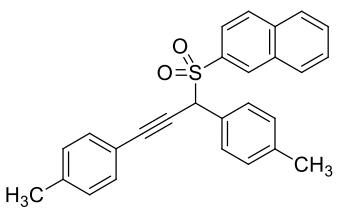
White solid; mp 157-158 °C; 77 mg, 97% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.44-7.42 (m, 2H), 7.31-7.29 (m, 4H), 7.15 (t, J = 8.4 Hz, 4H), 5.24 (s, 1H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 141.3, 140.1, 139.9, 134.8, 132.1, 132.0, 130.4, 129.7, 129.6, 129.2, 127.2, 119.0, 90.1, 80.7, 66.0, 22.0, 21.7; IR (KBr): ν (cm^{-1}) 1720, 1705, 1657, 1594, 1098, 804; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{19}O_2SClNa$: 417.0687, found: 417.0686.

4,4'-(3-((4-Fluorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ae)



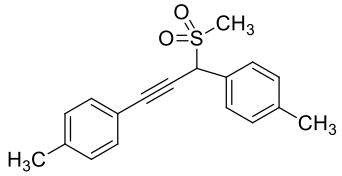
White solid; mp 141-142 °C; 73 mg, 96% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.72 (m, 2H), 7.30-7.28 (m, 4H), 7.16-7.11 (m, 6H), 5.24 (s, 1H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.5 (d, $^{1}J_{CF}$ = 255.6 Hz), 140.1, 139.9, 133.4 (d, $^{3}J_{CF}$ = 9.6 Hz), 132.3 (d, $^{4}J_{CF}$ = 2.6 Hz), 132.1, 130.4, 129.7, 129.6, 127.3, 119.0, 116.2 (d, $^{2}J_{CF}$ = 22.5 Hz), 90.0, 80.8, 66.0, 22.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.79; IR (KBr): ν (cm^{-1}) 2225, 1630, 1589, 1490, 1331, 1143, 813, 581; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{19}O_2SFNa$: 401.0983, found: 401.0979.

2-((1,3-Di-*p*-tolylprop-2-yn-1-yl)sulfonyl)naphthalene (4af)



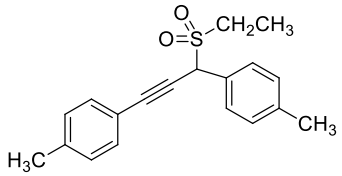
Yellow solid; mp 132-133 °C; 67 mg, 82% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.90-7.85 (m, 3H), 7.75-7.73 (m, 1H), 7.65-7.63 (m, 1H), 7.59-7.56 (m, 1H), 7.33-7.31 (m, 2H), 7.23-7.22 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.08-7.07 (m, 2H), 5.31 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.0, 139.7, 135.9, 133.5, 132.7, 132.2, 132.1, 130.5, 129.9, 129.8, 129.6, 129.5, 128.8, 128.4, 127.9, 127.4, 125.1, 119.2, 90.0, 81.1, 66.1, 22.0, 21.7; IR (KBr): ν (cm^{-1}) 2226, 1631, 1595, 1314, 1143, 1126, 817; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{27}H_{22}O_2SNa$: 433.1233, found: 433.1231.

4,4'-(3-(Methylsulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ag)



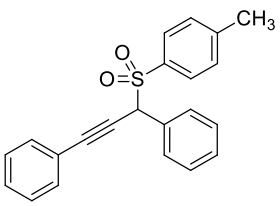
White solid; mp 110-111 °C; 51 mg, 86% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43-7.41 (m, 2H), 7.25-7.23 (m, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.16 (s, 1H), 2.98 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.2, 140.0, 132.3, 130.2, 130.0, 129.7, 126.9, 118.9, 90.0, 80.4, 64.3, 37.2, 22.0, 21.7; IR (KBr): ν (cm^{-1}) 2225, 1631, 1508, 1309, 1123, 961, 838, 541; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{18}H_{18}O_2SNa$: 321.0920, found: 321.0915.

4,4'-(3-(Ethylsulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ah)



White solid; mp 93-94 °C; 48 mg, 77% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.18 (s, 1H), 3.36-3.29 (m, 1H), 3.15-3.08 (m, 1H), 2.38 (s, 3H), 2.37 (s, 3H), 1.44 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 140.1, 139.9, 132.2, 130.3, 129.9, 129.6, 126.6, 119.0, 89.8, 80.4, 62.4, 44.5, 22.0, 21.7, 6.8; IR (KBr): ν (cm^{-1}) 2230, 1631, 1510, 1314, 1134, 821; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{19}H_{20}O_2SNa$: 335.1077, found: 335.1076.

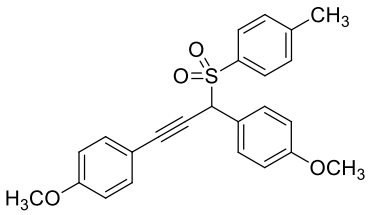
(3-Tosylprop-1-yne-1,3-diyl)dibenzene (4ba)



White solid; mp 154-155 °C; 28 mg, 41% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.43-7.41 (m, 4H), 7.39-7.33 (m, 6H), 7.26 (m, 1H), 7.24 (m, 1H), 5.27

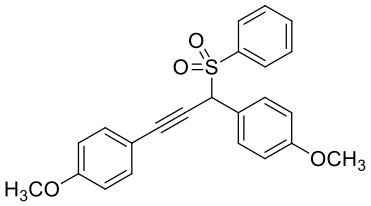
(s, 1H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 145.6, 133.3, 133.2, 132.2, 130.7, 130.6, 130.5, 129.8, 129.4, 128.8, 128.7, 122.3, 89.6, 81.6, 66.1, 22.1; IR (KBr): ν (cm^{-1}) 2230, 1508, 1322, 1148, 815; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{22}H_{18}O_2SNa$: 369.0920, found: 369.0916.

4,4'-(3-Tosylprop-1-yne-1,3-diyl)bis(methoxybenzene) (4ca)



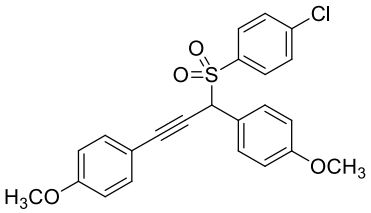
Brown solid; mp 122-123 °C; 76 mg, 93% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.2 Hz, 2H), 7.36-7.33 (m, 4H), 7.27-7.25 (m, 2H), 6.88-6.84 (m, 4H), 5.20 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 2.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 160.8, 160.5, 145.4, 133.7, 133.4, 131.8, 130.6, 129.5, 122.6, 114.4, 114.2, 89.5, 80.4, 65.6, 55.8, 22.2; IR (KBr): ν (cm^{-1}) 2229, 1510, 1324, 1255, 1085, 815; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{24}H_{22}O_4SNa$: 429.1132, found: 429.1130.

4,4'-(3-(Phenylsulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4cb)



White solid; mp 118-119 °C; 75 mg, 95% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.74 (m, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.35-7.32 (m, 4H), 6.88-6.84 (m, 4H), 5.23 (s, 1H), 3.82 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 160.9, 160.5, 136.3, 134.4, 133.7, 131.8, 130.5, 128.9, 122.3, 114.4, 114.3, 89.7, 80.2, 65.6, 55.8, 55.7; IR (KBr): ν (cm^{-1}) 2226, 1630, 1322, 1256, 1150, 816; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{20}O_4SNa$: 415.0975, found: 415.0972.

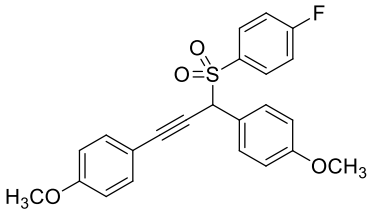
4,4'-(3-((4-Chlorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4cc)



Brown solid; mp 119-120 °C; 73 mg, 86% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66-7.64 (m, 2H), 7.44-7.42 (m, 2H), 7.35-7.32 (m, 4H), 6.88-6.85 (m, 4H), 5.23 (s, 1H), 3.82 (s, 6H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 161.0, 160.6, 141.2, 134.7, 133.7, 132.0, 131.8, 129.2,

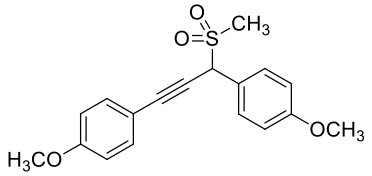
122.0, 114.5, 114.3, 114.0, 90.0, 80.0, 65.7, 55.8; IR (KBr): ν (cm^{-1}) 2225, 1629, 1585, 1331, 1255, 813; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{19}O_4SClNa$: 449.0585, found: 449.0582.

4,4'-(3-((4-Fluorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4cd)



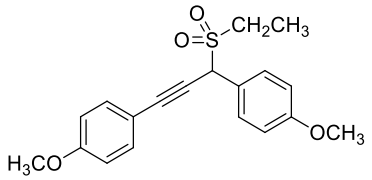
Yellow solid; mp 132-133 °C; 67 mg, 82% yield; PE/EA = 8:1; ^1H NMR (500 MHz, $CDCl_3$): δ 7.74-7.72 (m, 2H), 7.36-7.32 (m, 4H), 7.16-7.12 (m, 2H), 6.88-6.85 (m, 4H), 5.23 (s, 1H), 3.83 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 166.5 (d, $^1J_{CF}$ = 255.0 Hz), 161.0, 160.6, 133.7, 133.4 (d, $^3J_{CF}$ = 9.6 Hz), 132.2 (d, $^4J_{CF}$ = 2.5 Hz), 131.7, 122.2, 116.2 (d, $^2J_{CF}$ = 22.5 Hz), 114.5, 114.3, 114.1, 89.9, 80.1, 65.7, 55.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.86; IR (KBr): ν (cm^{-1}) 2226, 1631, 1332, 1252, 1153, 812; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{19}O_4SFNa$: 433.0881, found: 433.0877.

4,4'-(3-(Methylsulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4ce)



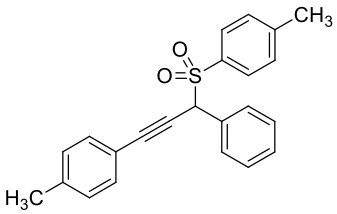
Yellow solid; mp 108-109 °C; 60 mg, 90% yield; PE/EA = 8:1; ^1H NMR (500 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.48-7.46 (m, 2H), 6.98-6.95 (m, 2H), 6.89-6.86 (m, 2H), 5.14 (s, 1H), 3.83 (s, 6H), 2.98 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 161.1, 160.7, 133.9, 131.6, 121.7, 114.7, 114.5, 114.0, 89.9, 79.8, 64.0, 55.8, 55.7, 37.1; IR (KBr): ν (cm^{-1}) 2223, 1630, 1505, 1309, 1250, 1120, 960, 828; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{18}H_{18}O_4SNa$: 353.0819, found: 353.0815.

4,4'-(3-(Ethylsulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4cf)



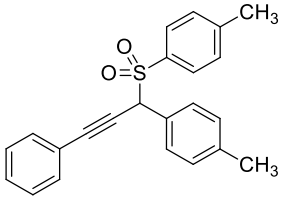
Red liquid; 59 mg, 86% yield; PE/EA = 8:1; ^1H NMR (500 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2H), 7.47-7.44 (m, 2H), 6.98-6.95 (m, 2H), 6.89-6.86 (m, 2H), 5.17 (s, 1H), 3.83 (s, 6H), 3.36-3.29 (m, 1H), 3.16-3.09 (m, 1H), 1.44 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 161.0, 160.7, 133.9, 131.7, 121.4, 114,6, 114.5, 114.0, 89.6, 79.8, 62.1, 55.8, 44.4, 6.8; IR (KBr): ν (cm^{-1}) 2231, 1630, 1512, 1316, 1134, 812; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{19}H_{20}O_4SNa$: 367.0975, found: 367.0974.

1-Methyl-4-((1-phenyl-3-(*p*-tolyl)prop-2-yn-1-yl)sulfonyl)benzene (4da)



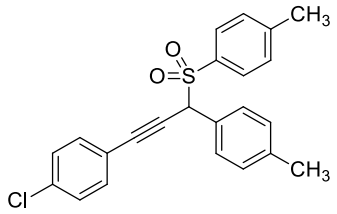
White solid; mp 162-163 °C; 56 mg, 77% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 8.2 Hz, 2H), 7.43-7.41 (m, 2H), 7.38-7.37 (m, 1H), 7.35-7.31 (m, 4H), 7.25 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.26 (s, 1H), 2.43 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.5, 139.7, 133.3, 132.1, 130.7, 130.6, 130.5, 129.8, 129.6, 129.5, 128.8, 119.2, 89.8, 80.9, 66.2, 22.1, 22.0; IR (KBr): ν (cm^{-1}) 2228, 1632, 1320, 1152, 819; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{20}O_2SNa$: 383.1076, found: 383.1072.

1-Methyl-4-((3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)sulfonyl)benzene (4ea)



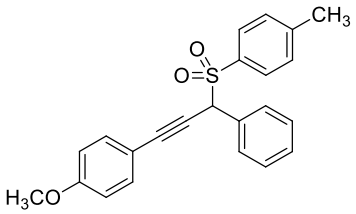
White solid; mp 107-108 °C; 58 mg, 81% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 8.3 Hz, 2H), 7.42-7.40 (m, 2H), 7.36-7.30 (m, 5H), 7.27 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 5.23 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.5, 139.9, 133.4, 132.2, 130.6, 130.4, 129.6 , 129.4, 128.8, 127.5, 122.4, 89.4, 81.9, 65.8, 22.2, 21.7; IR (KBr): ν (cm^{-1}) 2229, 1628, 1595, 1318, 1152, 798; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{20}O_2SNa$: 383.1076, found: 383.1080.

1-Chloro-4-(3-(*p*-tolyl)-3-tosylprop-1-yn-1-yl)benzene (4fa)



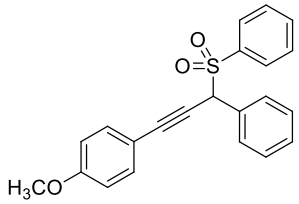
White solid; m.p. 161-162°C; 62 mg, yield: 78%; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = *8*.3 Hz, 2H), 7.34-7.31 (m, 4H), 7.30-7.25 (m, 4H), 7.15 (d, J = 8.0 Hz, 2H), 5.21 (s, 1H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.6, 140.0, 135.5, 133.4, 130.5, 130.4, 129.6, 129.5, 129.2, 127.3, 120.8, 88.2, 82.9, 65.8, 22.1, 21.7; HRMS (ESI) $(M+Na)^+$: m/z calcd for $C_{23}H_{19}ClO_2SNa$: 417.0686, found: 417.0687.

1-Methoxy-4-(3-phenyl-3-tosylprop-1-yn-1-yl)benzene (4ga)



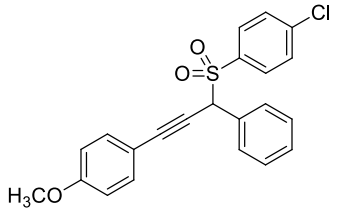
White solid; mp 155-156 °C; 64 mg, 85% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.3 Hz, 2H), 7.42-7.40 (m, 2H), 7.38-7.34 (m, 5H), 7.26-7.24 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 5.25 (s, 1H), 3.83 (s, 3H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.5, 145.5, 133.7, 133.3, 130.8, 130.6, 129.7, 129.5, 128.8, 114.4, 114.3, 89.7, 80.2, 66.2, 55.7, 22.1; IR (KBr): ν (cm^{-1}) 2228, 1622, 1578, 1310, 1245, 802; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{23}H_{20}O_3SNa$: 399.1026, found: 399.1024.

1-Methoxy-4-(3-phenyl-3-(phenylsulfonyl)prop-1-yn-1-yl)benzene (4gb)



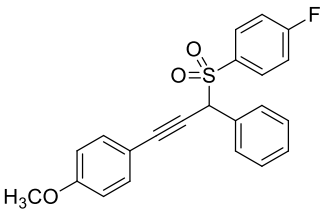
White solid; mp 111-118 °C; 58 mg, 80% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74-7.73 (m, 2H), 7.65-7.62 (t, J = 7.5 Hz, 1H), 7.48-7.45 (m, 2H), 7.43-7.37 (m, 3H), 7.35-7.32 (m, 4H), 6.86-6.83 (m, 2H), 5.28 (s, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.6, 136.3, 134.5, 133.7, 130.6, 130.5, 129.8, 128.9, 128.8, 114.4, 114.2, 89.9, 80.0, 66.2, 55.8; IR (KBr): ν (cm^{-1}) 2228, 1635, 1586, 1322, 1257, 819; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{22}H_{18}O_3SNa$: 385.0869, found: 385.0872.

1-Chloro-4-((3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl)sulfonyl)benzene (4gc)



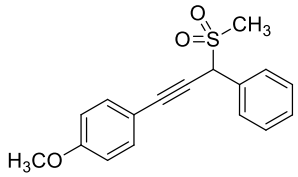
White solid; mp 129-130 °C; 71 mg, 90% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65-7.63 (m, 2H), 7.44-7.41 (m, 4H), 7.40-7.34 (m, 5H), 6.88-6.85 (m, 2H), 5.29 (s, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.7, 141.3, 134.6, 133.7, 132.0, 130.5, 130.3, 130.0, 129.2, 128.9, 114.5, 114.0, 90.2, 79.7, 66.3, 55.8; IR (KBr): ν (cm^{-1}) 2230, 1629, 1560, 1314, 1256, 802; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{22}H_{17}O_3SClNa$: 419.0480, found: 419.0479.

1-Fluoro-4-((3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl)sulfonyl)benzene (4gd)



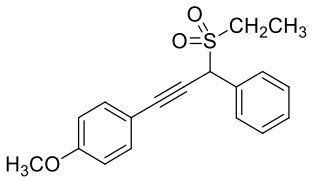
Yellow solid; mp 109-110 ºC; 67 mg, 88% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73-7.70 (m, 2H), 7.42-7.38 (m, 3H), 7.37-7.33 (m, 4H), 7.14-7.11 (m, 2H), 6.87-6.85 (m, 2H), 5.28 (s, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.6 (d, $^{1}J_{CF}$ = 255.5 Hz), 160.7, 133.7, 133.4 (d, $^{3}J_{CF}$ = 9.8 Hz), 132.1 (d, $^{4}J_{CF}$ = 3.1 Hz), 130.5, 130.4, 130.0, 128.9, 116.2 (d, $^{2}J_{CF}$ = 22.5 Hz), 114.5, 114.0, 90.1, 79.8, 66.3, 55.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.68; IR (KBr): ν (cm^{-1}) 2230, 1619, 1569, 1323, 1250, 801; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{22}H_{17}O_3SFNa$: 403.0775, found: 403.0770.

Methoxy-4-(3-(methylsulfonyl)-3-phenylprop-1-yn-1-yl)benzene (4ge)



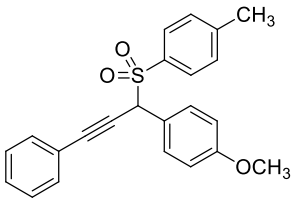
Yellow liquid; 48 mg, 80% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.48-7.47 (m, 2H), 7.45-7.44 (m, 3H), 6.88-6.87 (m, 2H), 5.19 (s, 1H), 3.83 (s, 3H), 3.00 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.8, 133.9, 130.4, 130.1, 130.0, 129.3, 114.5, 113.9, 90.1, 79.5, 64.6, 55.8, 37.3; IR (KBr): ν (cm^{-1}) 2227, 1631, 1558, 1309, 961, 838; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{17}H_{16}O_3SNa$: 323.0713, found: 323.0716.

1-(3-(Ethylsulfonyl)-3-phenylprop-1-yn-1-yl)-4-methoxybenzene (4gf)



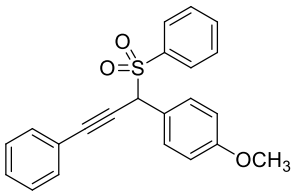
Yellow liquid; 52 mg, 82% yield; PE/EA = 8:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.47-7.43 (m, 5H), 6.88-6.86 (m, 2H), 5.21 (s, 1H), 3.82 (s, 3H), 3.38-3.30 (m, 1H), 3.17-3.10 (m, 1H), 1.44 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.7, 133.9, 130.5, 130.0, 129.7, 129.2, 114.5, 114.0, 89.8, 79.6, 62.7, 55.8, 44.6, 6.8; IR (KBr): ν (cm^{-1}) 2229, 1630, 1512, 1316, 818; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{18}H_{18}O_3SNa$: 337.0869, found: 337.0872.

Methoxy-4-(3-phenyl-1-tosylprop-2-yn-1-yl)benzene (4ha)



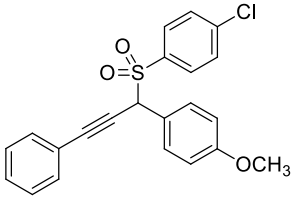
Yellow solid; mp 112-113 °C; 64 mg, 85% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.42-7.40 (m, 2H), 7.35-7.30 (m, 5H), 7.26-7.25 (m, 2H), 6.87-6.86 (m, 2H), 5.22 (s, 1H), 3.81 (s, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.9, 145.6, 133.3, 132.2, 131.8, 130.5, 129.6, 129.4, 128.8, 122.4, 122.3, 114.3, 89.4, 81.9, 65.5, 55.8, 22.2; IR (KBr): ν (cm^{-1}) 2227, 1632, 1588, 1320, 1255, 812; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{23}H_{20}O_3SNa$: 399.1026, found: 399.1023.

1-Methoxy-4-(3-phenyl-1-(phenylsulfonyl)prop-2-yn-1-yl)benzene (4hb)



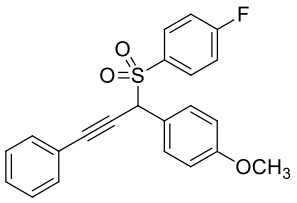
Yellow solid; mp 120-121 °C; 69 mg, 95% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76-7.75 (m, 2H), 7.63 (t, J =7.5 Hz, 1H), 7.47 (t, J =7.7 Hz, 2H), 7.40-7.38 (m, 2H), 7.35-7.30 (m, 5H), 6.87-6.86 (m, 2H), 5.24 (s, 1H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.0, 136.3, 134.5, 132.2, 131.8, 130.5, 129.5, 129.0, 128.9, 122.2, 122.1, 114.3, 89.6, 81.7, 65.5, 55.8; IR (KBr): ν (cm^{-1}) 2229, 1639, 1578, 1322, 1258, 815; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{22}H_{18}O_3SNa$: 385.0869, found: 385.0870.

1-Chloro-4-((1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)sulfonyl)benzene (4hc)



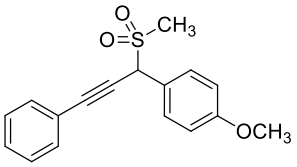
White solid; mp 104-1105 °C; 76 mg, 96% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J =8.6 Hz, 2H), 7.44-7.40 (m, 4H), 7.37-7.33 (m, 5H), 6.87 (d, J =8.8 Hz, 2H), 5.25 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.1, 141.3, 134.7, 132.2, 132.0, 131.8, 129.6, 129.3, 128.9, 122.0, 121.9, 114.4, 89.9, 81.4, 65.6, 55.8; IR (KBr): ν (cm^{-1}) 2229, 1629 1586, 1314, 1259, 809; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{22}H_{17}O_3SClNa$: 419.0480, found: 419.0483.

1-Fluoro-4-((1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)sulfonyl)benzene (4hd)



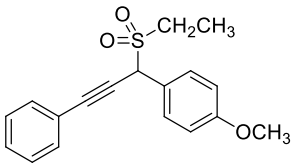
Yellow solid; mp 101-102 °C; 72 mg, 95% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75-7.72 (m, 2H), 7.42-7.40 (m, 2H), 7.36-7.31 (m, 5H), 7.14 (t, J = 8.7 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.25 (s, 1H), 3.81 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.6 (d, $^{1}J_{CF}$ = 255.3 Hz), 161.0, 133.4 (d, $^{3}J_{CF}$ = 9.7 Hz), 132.2, 131.8, 129.6, 128.9, 122.1, 122.0, 116.3 (d, $^{2}J_{CF}$ = 22.4 Hz), 114.4, 89.8, 81.5, 65.6, 55.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -102.64; IR (KBr): ν (cm^{-1}) 2230, 1630, 1599, 1326, 1265, 802; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{22}H_{17}O_3SFNa$: 403.0775, found: 403.0772.

1-Methoxy-4-(1-(methylsulfonyl)-3-phenylprop-2-yn-1-yl)benzene (4he)



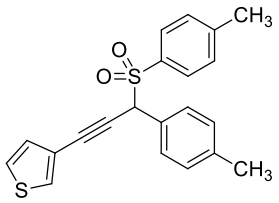
White solid; mp 124-125 °C; 58 mg, 96% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.57 (m, 2H), 7.55-7.53 (m, 2H), 7.41-7.34 (m, 3H), 6.98-6.96 (m, 2H), 5.16 (s, 1H), 3.83 (s, 3H), 2.99 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.1, 132.4, 131.6, 129.7, 128.9, 121.9, 121.5, 114.7, 89.8, 81.1, 63.9, 55.8, 37.2; IR (KBr): ν (cm^{-1}) 2225, 1630, 1510, 1308, 1123, 838; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{17}H_{16}O_3SNa$: 323.0713, found: 323.0709.

1-(1-(Ethylsulfonyl)-3-phenylprop-2-yn-1-yl)-4-methoxybenzene (4hf)



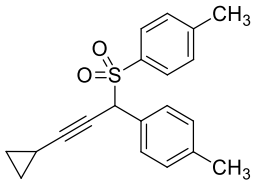
White solid; mp 79-80 °C; 55 mg, 88% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58-7.57 (m, 2H), 7.53-7.51 (m, 2H), 7.39-7.33 (m, 3H), 6.97-6.96 (m, 2H), 5.18 (s, 1H), 3.83 (s, 3H), 3.36-3.29 (m, 1H), 3.17-3.10 (m, 1H), 1.45 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.0, 132.4, 131.7, 129.7, 128.9, 122.0, 121.2, 114.7, 89.6, 81.2, 62.0, 55.8, 44.5, 6.9; IR (KBr): ν (cm^{-1}) 2230, 1631, 1512, 1316, 1130, 823; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{18}H_{18}O_3SNa$: 337.0869, found: 337.0865.

3-(3-(*p*-Tolyl)-3-tosylprop-1-yn-1-yl)thiophene (4ia)



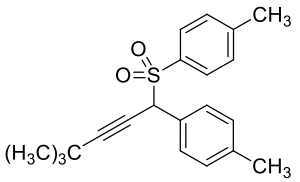
White solid; mp 100-101 °C; 59 mg, 80% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.3 Hz, 2H), 7.46-7.45 (m, 1H), 7.30-7.25 (m, 5H), 7.14 (d, J = 7.9 Hz, 2H), 7.09-7.07 (m, 1H), 5.21 (s, 1H), 2.44 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.5, 139.9, 133.4, 130.6, 130.4, 130.2, 130.1, 129.6, 129.5, 127.5, 126.0, 121.4, 84.7, 81.4, 65.9, 22.2, 21.7; IR (KBr): ν (cm^{-1}) 2229, 1631, 1332, 1154, 811; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{21}H_{18}O_2S_2Na$: 389.0640, found: 389.0644.

1-((3-Cyclopropyl-1-(*p*-tolyl)prop-2-yn-1-yl)sulfonyl)-4-methylbenzene (4ja)



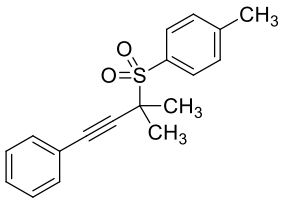
White solid; mp 114-115 °C; 27 mg, 42% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.3 Hz, 2H), 7.26-7.24 (m, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.94 (d, J = 1.9 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 3H), 1.31-1.26 (m, 1H), 0.81-0.77 (m, 2H), 0.68-0.65 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.2, 139.6, 133.4, 130.4, 130.3, 129.3, 129.3, 127.8, 93.5, 67.6, 65.4, 22.1, 21.6, 8.6, 8.5; IR (KBr): ν (cm^{-1}) 2223, 1628, 1598, 1314, 786; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{20}H_{20}O_2SNa$: 347.1076, found: 347.1075.

1-((4,4-Dimethyl-1-(*p*-tolyl)pent-2-yn-1-yl)sulfonyl)-4-methylbenzene (4ka)



White solid; m.p. 120-121 °C; 56 mg, 82% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.1 Hz, 2H), 7.27-7.23 (m, 4H), 7.13 (d, J = 7.9 Hz, 2H), 4.98 (s, 1H), 2.44 (s, 3H), 2.35 (s, 3H), 1.20 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.2, 139.6, 133.4, 130.7, 130.4, 129.4, 129.3, 127.9, 98.5, 71.4, 65.2, 30.9, 28.1, 22.1, 21.7; IR (KBr): ν (cm^{-1}) 2221, 1620, 1322, 1142, 812; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{21}H_{24}O_2SNa$: 363.1389, found: 363.1385.

1-Methyl-4-((2-methyl-4-phenylbut-3-yn-2-yl)sulfonyl)benzene (4la)

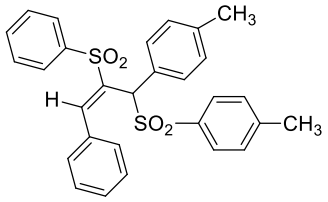


White solid; mp 133-134 °C; 36 mg, 60% yield; PE/EA = 15:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91-7.89 (m, 2H), 7.36-7.30 (m, 7H), 2.46 (s, 3H), 1.69 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 145.4, 132.4, 132.1, 131.3, 129.6, 129.1, 128.7, 122.5, 87.9, 86.7, 59.8, 23.8, 22.1; IR (KBr): ν (cm^{-1}) 2230, 1630, 1601, 1335, 818; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{18}H_{18}O_2SNa$: 321.0920, found: 321.0918.

General procedure for the synthesis of 5 and spectral data for 5

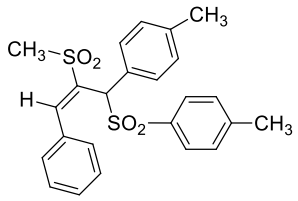
Propargyl sulfone **4ea** (72 mg, 0.2 mmol) and sodium sulfinate **2b** (33 mg, 0.2 mmol) were added to the solvent of HOAc/H_2O (1 mL, v/v = 1:1) at room temperature. The reaction mixture was heated to reflux and stirred until the complete consumption of **4ea** (monitored by TLC). Then the reaction mixture was cooled to room temperature, diluted with water (5 mL), and extracted with dichloromethane (3 × 10 mL). The organic extracts were dried over anhydrous Na_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/8) to give product **5a**.

(*E*)-1-methyl-4-((3-phenyl-2-(phenylsulfonyl)-1-(*p*-tolyl)allyl)sulfonyl)benzene (5a)



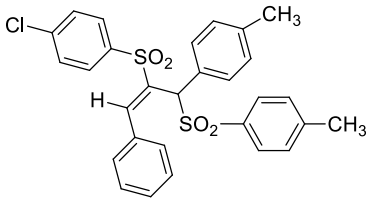
White solid; mp 165-166 °C; 82 mg, 82% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45-7.39 (m, 7H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.12 (t, *J* = 8.4 Hz, 4H), 6.90 (d, *J* = 8.1 Hz, 2H), 5.81 (s, 1H), 2.36 (s, 3H), 2.24 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 147.4, 145.1, 140.3, 139.0, 137.1, 136.7, 133.5, 133.0, 130.4, 130.3, 129.8, 129.4, 129.3, 129.1, 128.9, 128.7, 127.4, 69.6, 22.0, 21.5; IR (KBr): ν (cm^{-1}) 1630, 1596, 1351, 1146, 768, 596; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{26}O_4S_2Na$: 525.1165, found: 525.1168.

(*E*)-1-methyl-4-((2-(methylsulfonyl)-3-phenyl-1-(*p*-tolyl)allyl)sulfonyl)benzene (5b)



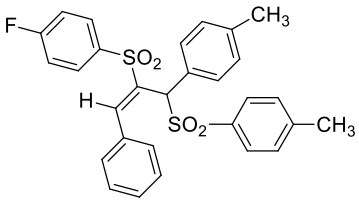
White solid; mp 118-119 °C; 63 mg, 72% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.42 (s, 5H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 2H), 5.91 (s, 1H), 3.16 (s, 3H), 2.34 (s, 3H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 149.0, 145.3, 139.3, 138.6, 136.2, 133.3, 130.5, 130.1, 129.9, 129.4, 129.1, 129.0, 128.9, 127.7, 69.8, 45.0, 22.0, 21.5; IR (KBr): ν (cm^{-1}) 1594, 1313, 1150, 1084, 956, 816; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{24}H_{24}O_4S_2Na$: 463.1008, found: 463.1005.

(*E*)-1-chloro-4-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)benzene (5c)



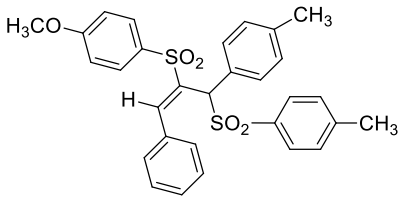
White solid; mp 201-202 °C; 103 mg, 96% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.43-7.41 (m, 5H), 7.35 (t, *J* = 8.7 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 5.80 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 148.1, 145.2, 140.2, 139.2, 139.1, 137.2, 136.5, 133.0, 130.5, 130.3, 130.1, 129.9, 129.5, 129.4, 129.0, 127.2, 69.4, 22.0, 21.5; IR (KBr): ν (cm^{-1}) 1600, 1327, 1313, 1151, 1085, 755, 685; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{25}O_4S_2ClNa$: 559.0775, found: 559.0779.

(*E*)-1-fluoro-4-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)benzene (5d)



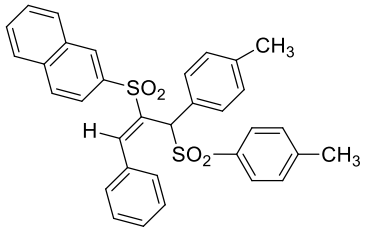
White solid; mp 168-169 °C; 83 mg, 80% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.78-7.76 (m, 2H), 7.44-7.39 (m, 5H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 5.81 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.8 (d, $^1J_{CF}$ = 254.4 Hz), 147.8, 145.2, 139.2, 137.4, 136.6, 136.5, 133.0, 131.6 (d, $^3J_{CF}$ = 9.5 Hz), 130.5, 130.3, 129.9, 129.6, 129.4, 129.0, 128.9, 127.3, 116.5 (d, $^2J_{CF}$ = 22.6 Hz), 69.2, 22.0, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.12; IR (KBr): ν (cm^{-1}) 1588, 1490, 1317, 1230, 1147, 833; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{29}H_{25}O_4S_2FNa$: 543.1070, found: 543.1069.

(*E*)-1-methoxy-4-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)benzene (5e)



White solid; mp 147-148 °C; 43 mg, 40% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.71 (d, J = 9.0 Hz, 2H), 7.43-7.34 (m, 7H), 7.15-7.10 (m, 4H), 6.93 (d, J = 8.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 5.81 (s, 1H), 3.84 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.8, 146.4, 145.0, 138.9, 136.8, 133.1, 131.7, 131.4, 131.1, 130.3, 129.8, 129.7, 129.4, 129.1, 128.8, 127.7, 114.5, 69.7, 56.0, 22.0, 21.5; IR (KBr): ν (cm^{-1}) 1592, 1320, 1262, 1144, 692, 592; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{30}H_{28}O_5S_2Na$: 555.1270, found: 555.1275.

(*E*)-2-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)naphthalene (5f)

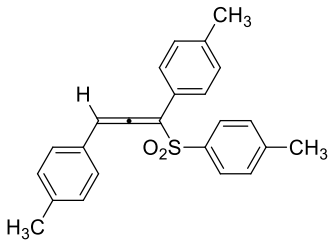


White solid; mp 181-182 °C; 91 mg, 82% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 1H), 8.17 (s, 1H), 7.83-7.79 (m, 3H), 7.67-7.65 (m, 1H), 7.61-7.55 (m, 2H), 7.45-7.43 (m, 2H), 7.39-7.37 (m, 3H), 7.29 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.7 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 8.1 Hz, 2H), 5.86 (s, 1H), 2.28 (s, 3H), 2.03 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 147.7, 145.1, 139.1, 137.2, 136.7, 135.2, 133.1, 132.2, 130.6, 130.4, 130.3, 129.8, 129.7, 129.6, 129.5, 129.3, 129.0, 128.9, 128.3, 127.8, 127.2, 123.1, 69.4, 22.0, 21.3; IR (KBr): ν (cm^{-1}) 1593, 1327, 1314, 1147, 1128, 697, 651; HRMS (ESI) [M+Na]$^+$: m/z calcd for $C_{33}H_{28}O_4S_2Na$: 575.1321, found: 575.1315.

Procedure for the synthesis of allene sulfone 6 and spectral data for 6

Propargyl sulfone **4aa** (0.2 mmol) and NaOAc (0.4 mmol) were added to the solvent of HOAc/H_2O (1 mL, v/v = 1:1) at room temperature. The reaction mixture was heated to reflux and stirred until the complete consumption of **4aa** (monitored by TLC). Then the reaction mixture was cooled to room temperature, diluted with water (5 mL), and extracted with dichloromethane (3 × 10 mL). The organic extracts were dried over anhydrous Na_2SO_4. After filtration and removal of the solvent in vacuo, the crude product was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to give allene sulfone **6**.

4,4'-(1-Tosylpropa-1,2-diene-1,3-diyl)bis(methylbenzene)



Yellow oil; 22 mg, 30% yield; PE/EA = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.17-7.12 (m, 6H), 6.80 (s, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 2.323 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 207.8, 144.8, 139.5, 139.3, 138.0, 130.1, 129.9, 129.8, 129.1, 128.7, 128.4, 128.0, 126.6, 119.3, 103.5, 22.0, 21.8, 21.7; IR (KBr): ν (cm^{-1}) 2025, 1631, 1596, 1351, 1145, 812, 575; HRMS (ESI) $[M+Na]^+$: m/z calcd for $C_{24}H_{22}O_2SNa$: 397.1233, found: 397.1230.

X-ray crystal structures of 3ag, 3ha, 4ea and 5a

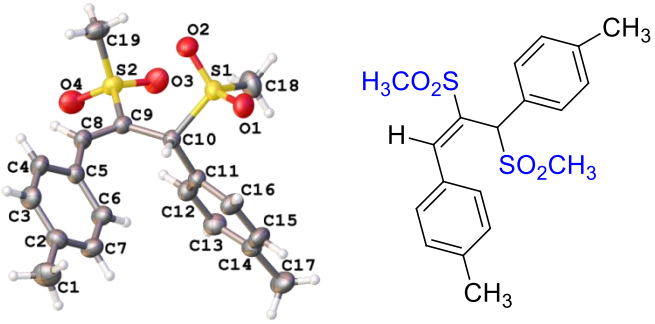


Figure 1 Molecular structure of compound 3ag (CCDC 1935864**)**

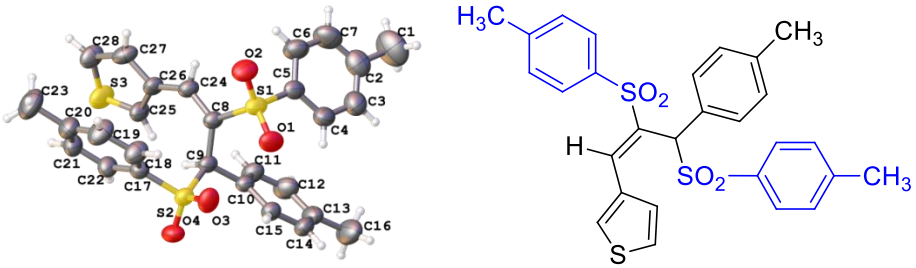


Figure 2 Molecular structure of compound 3ha (CCDC 1935877**)**

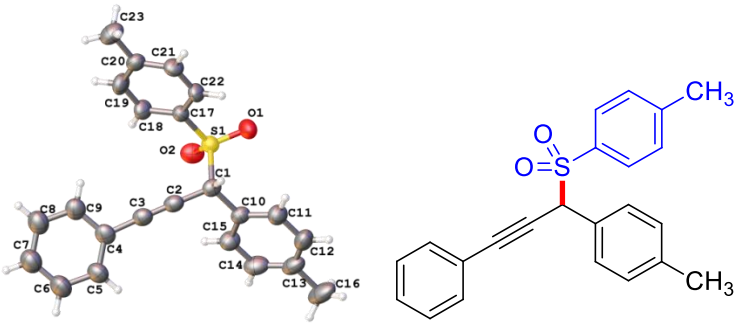


Figure 1 Molecular structure of compound 4ea (CCDC 2117640**)**

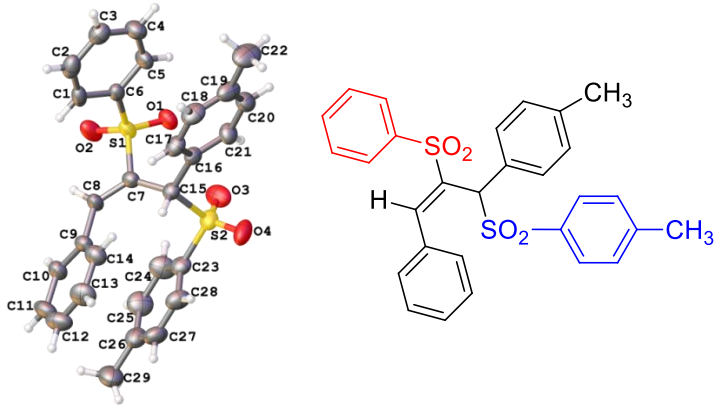
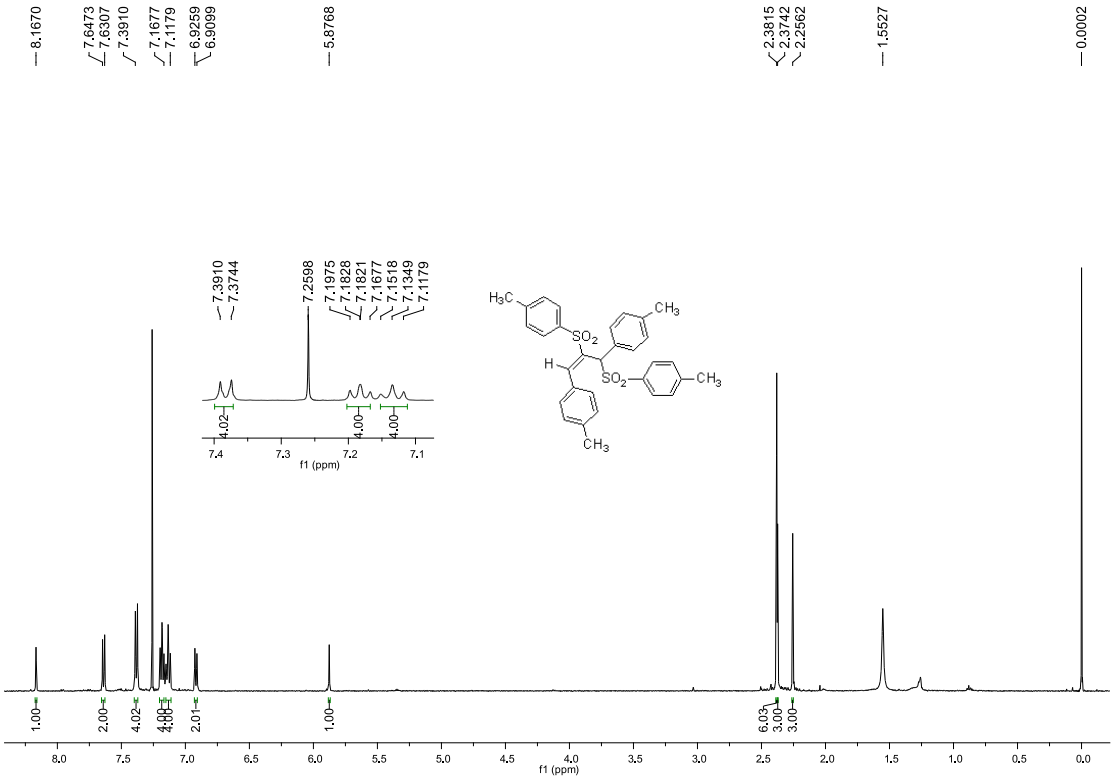
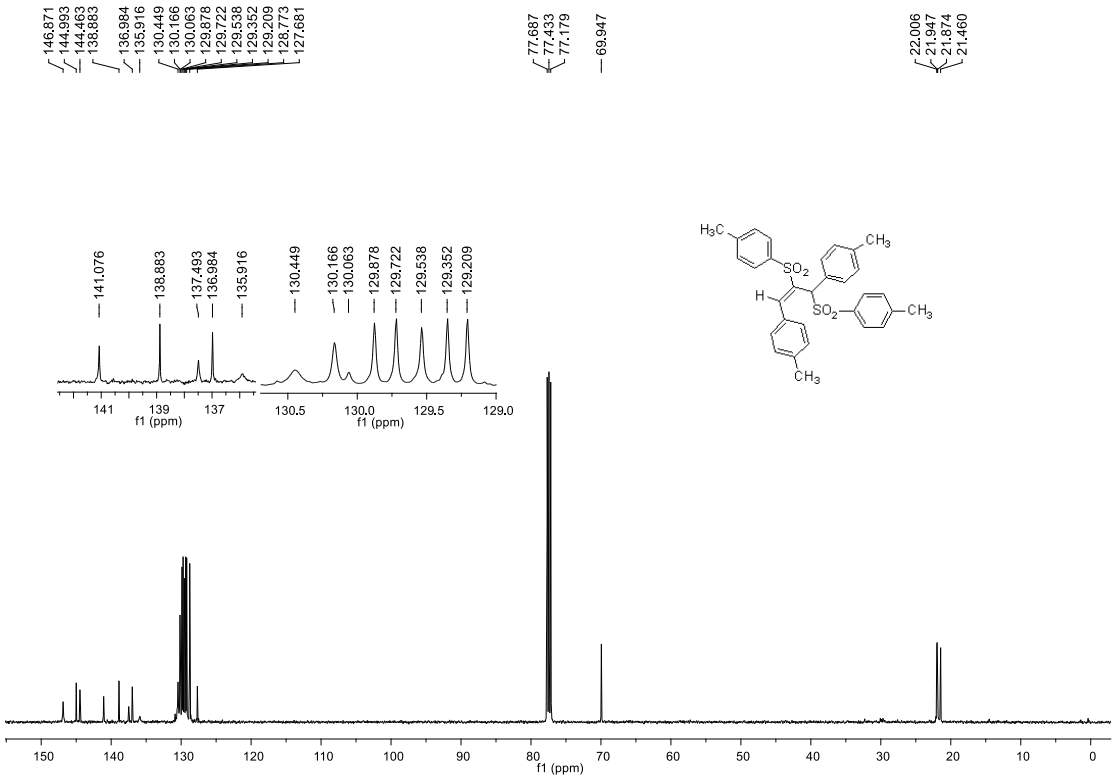


Figure 3 Molecular structure of compound 5a (CCDC 1935875**)**

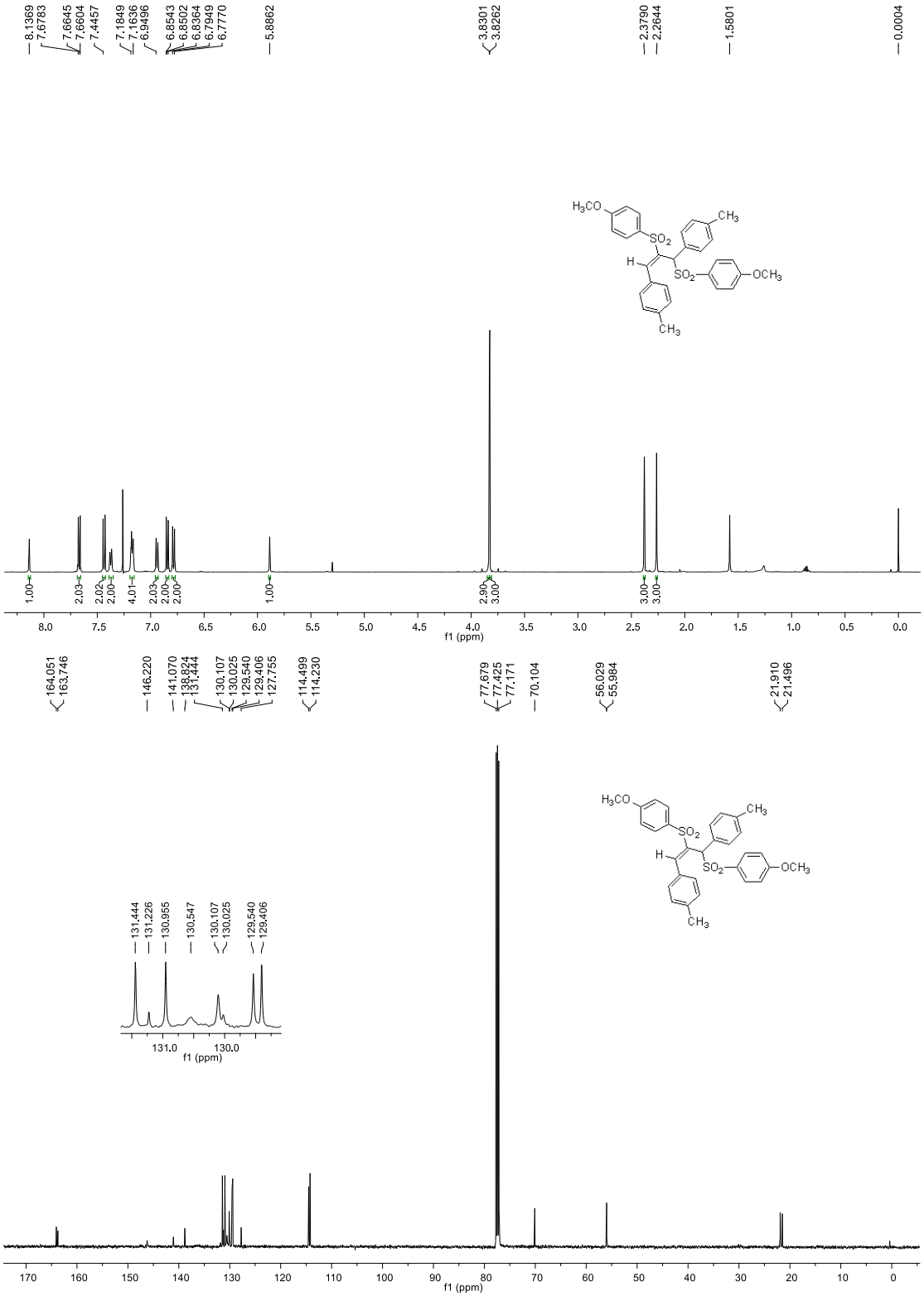
Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 3

(*E*)-4,4'-(1,3-di-*p*-tolylprop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3aa)

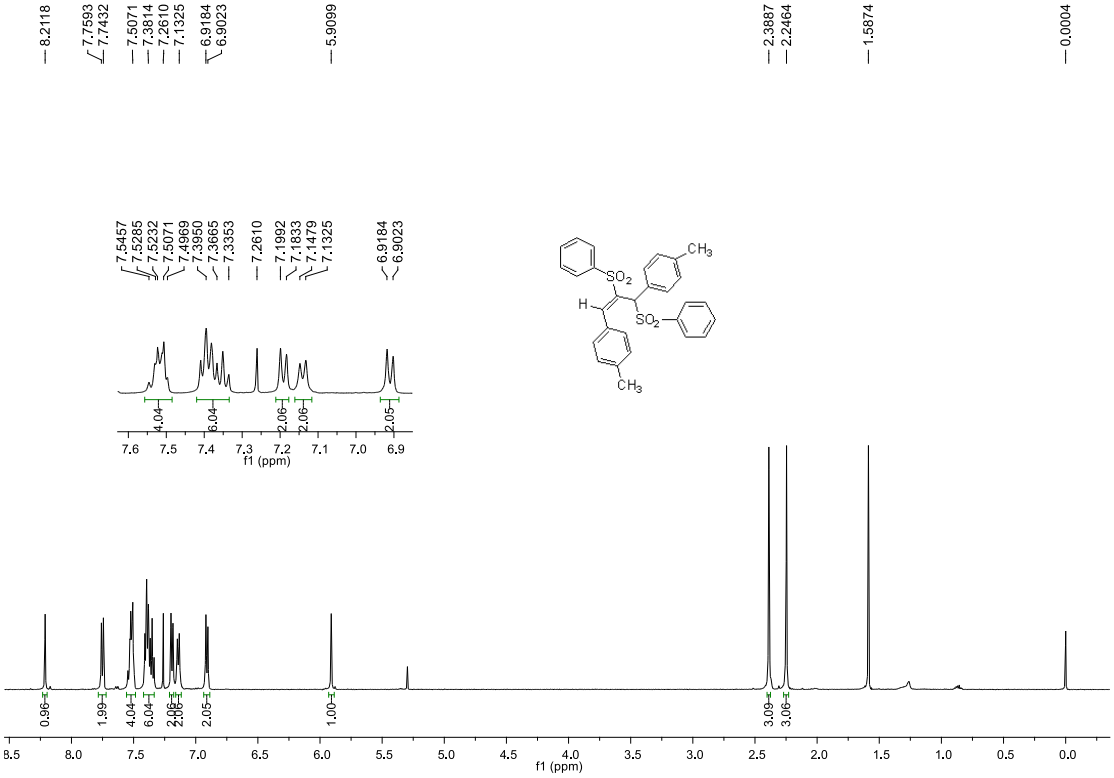


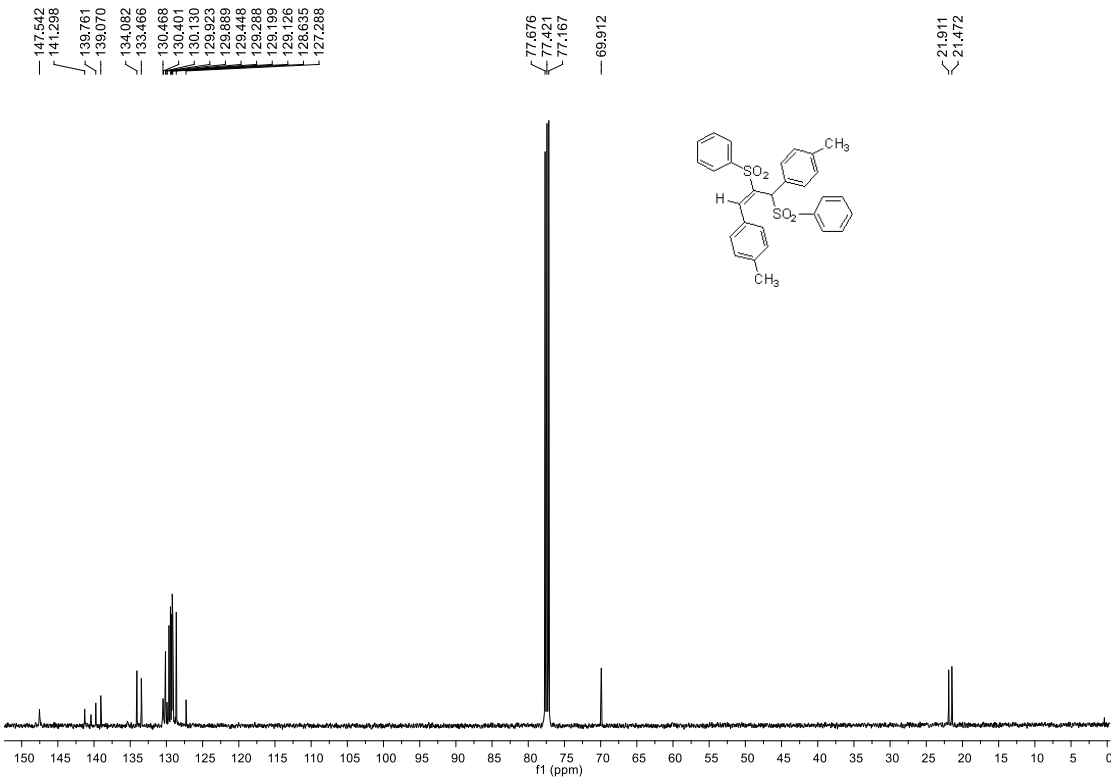


(*E*)-4,4'-(2,3-bis((4-methoxyphenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ab)

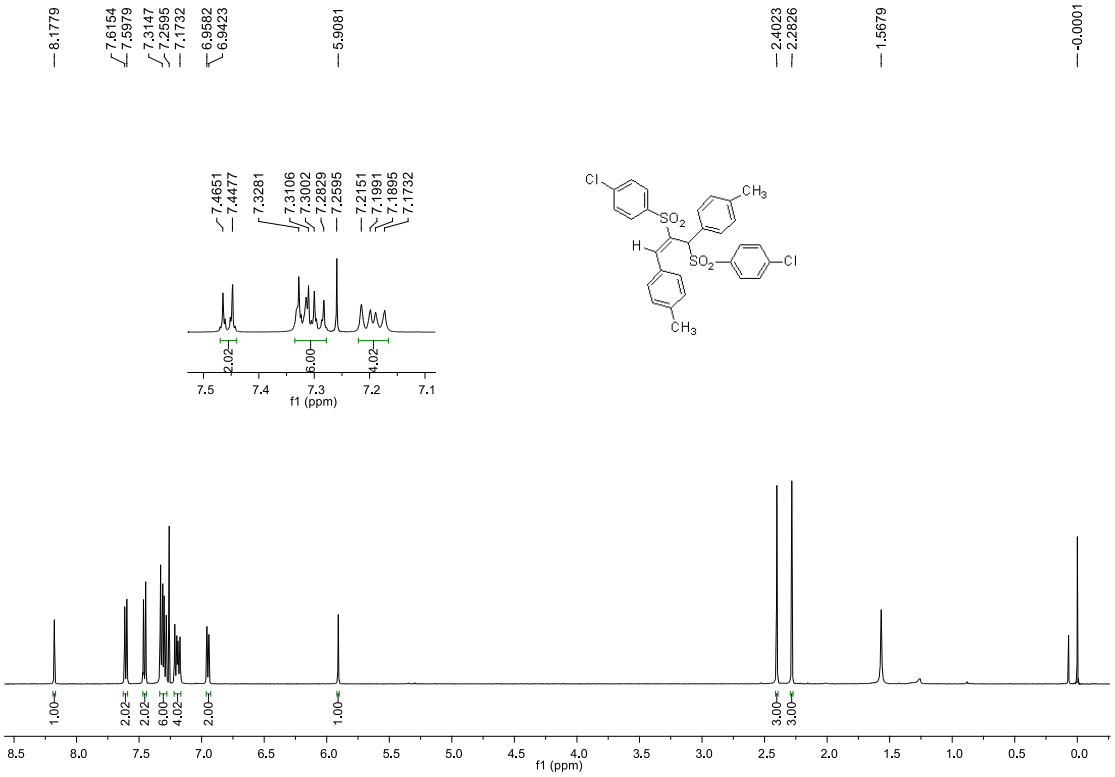


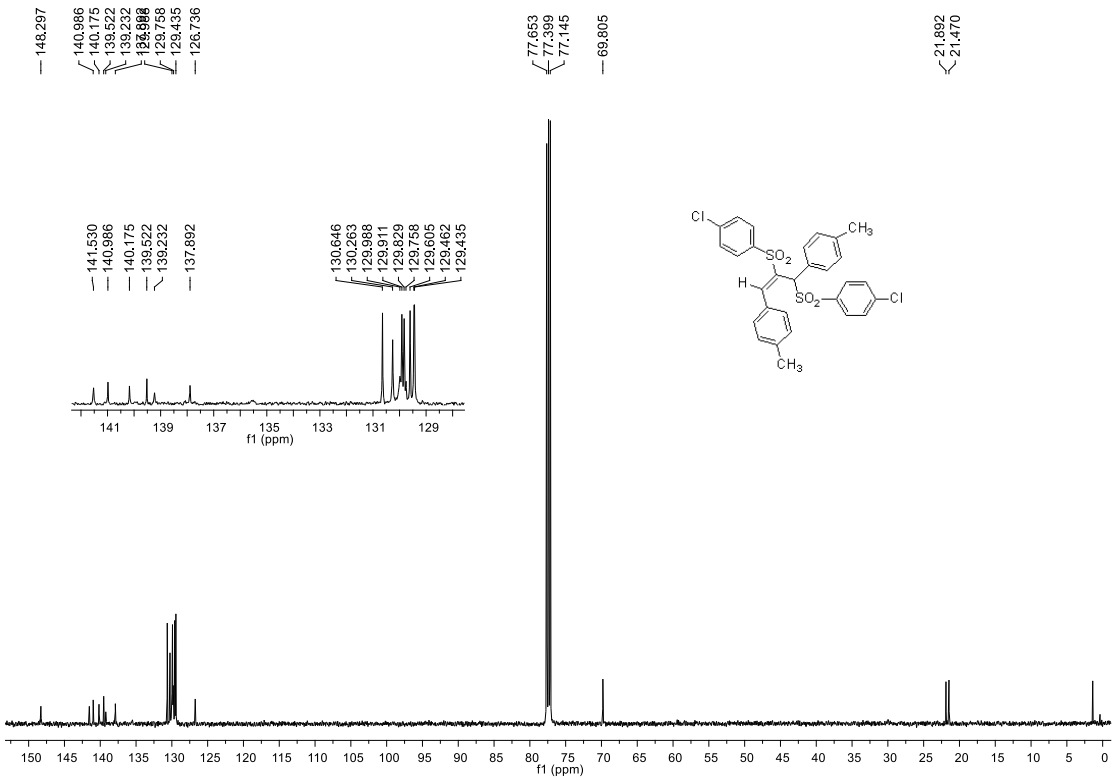
(*E*)-4,4'-(2,3-bis(phenylsulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ac)



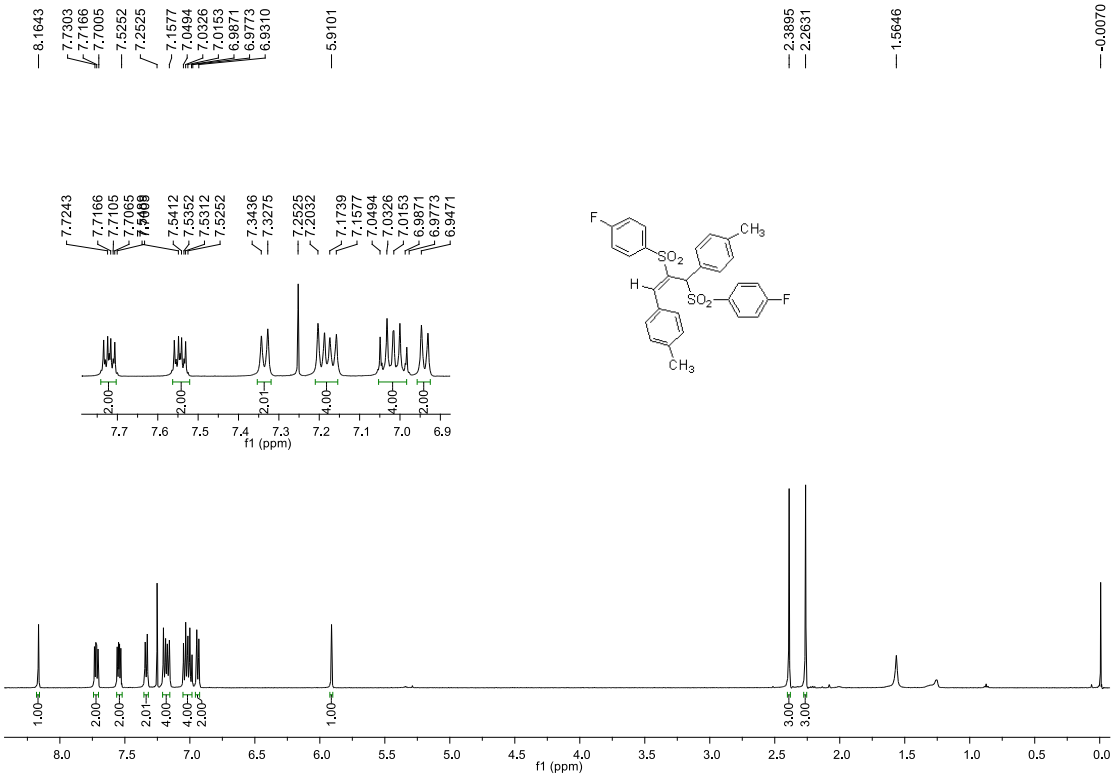


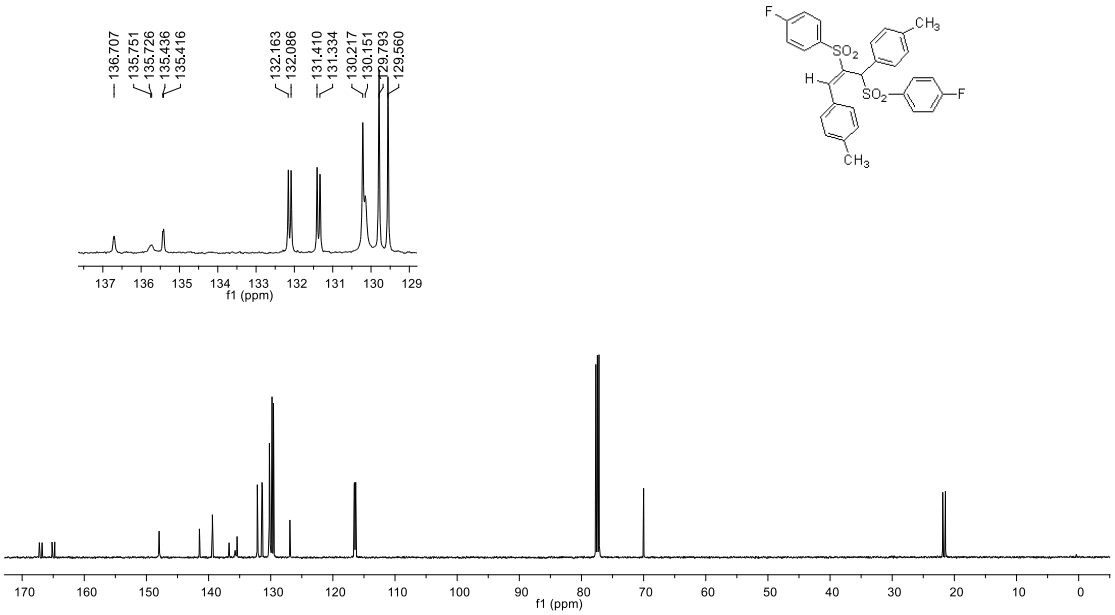
(*E*)-4,4'-(2,3-bis((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (**3ad**)

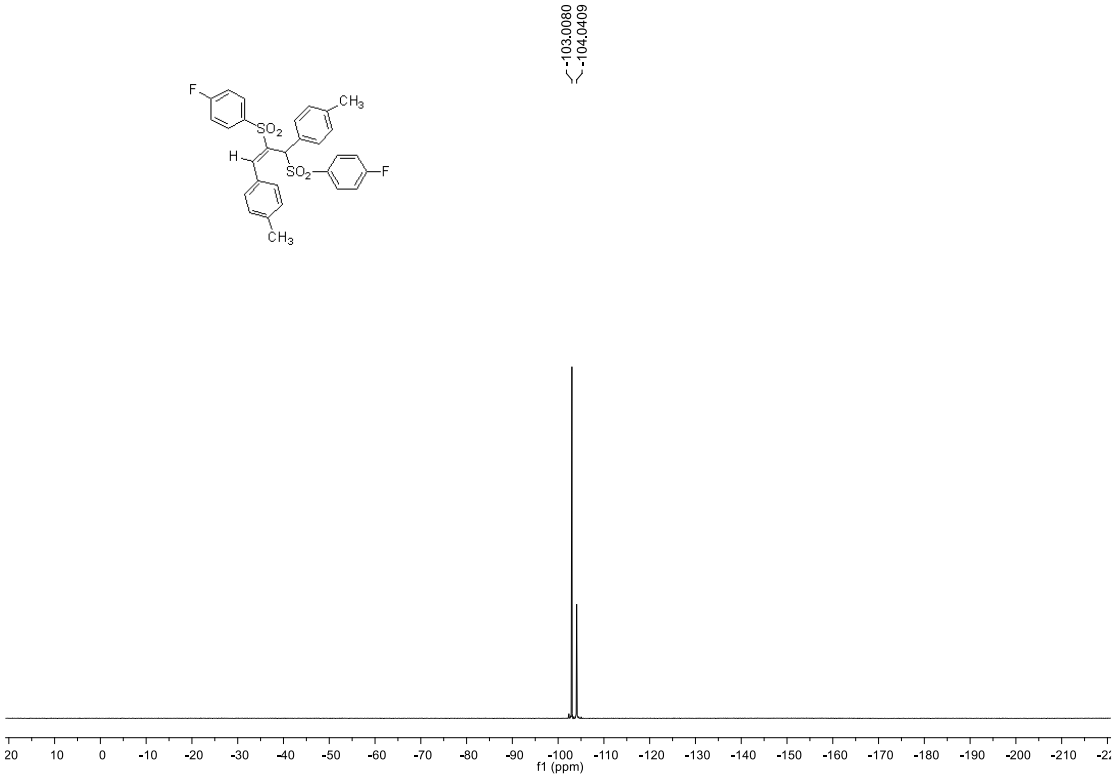




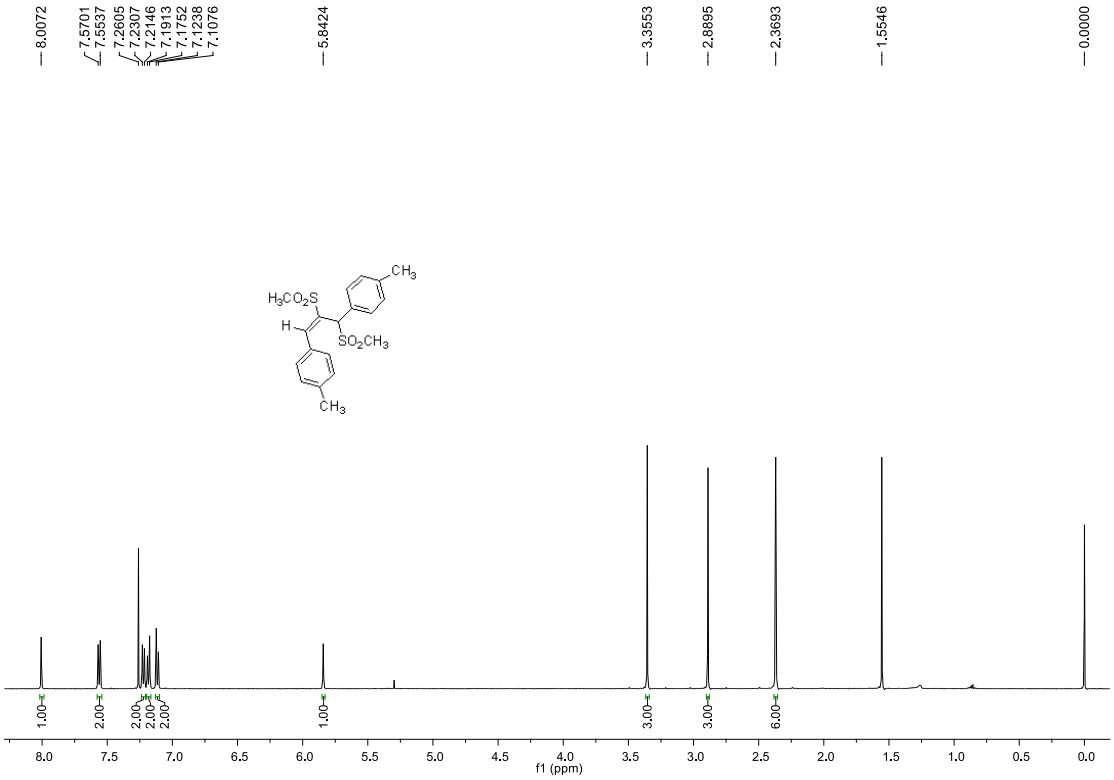
(*E*)-4,4'-(2,3-bis((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ae)

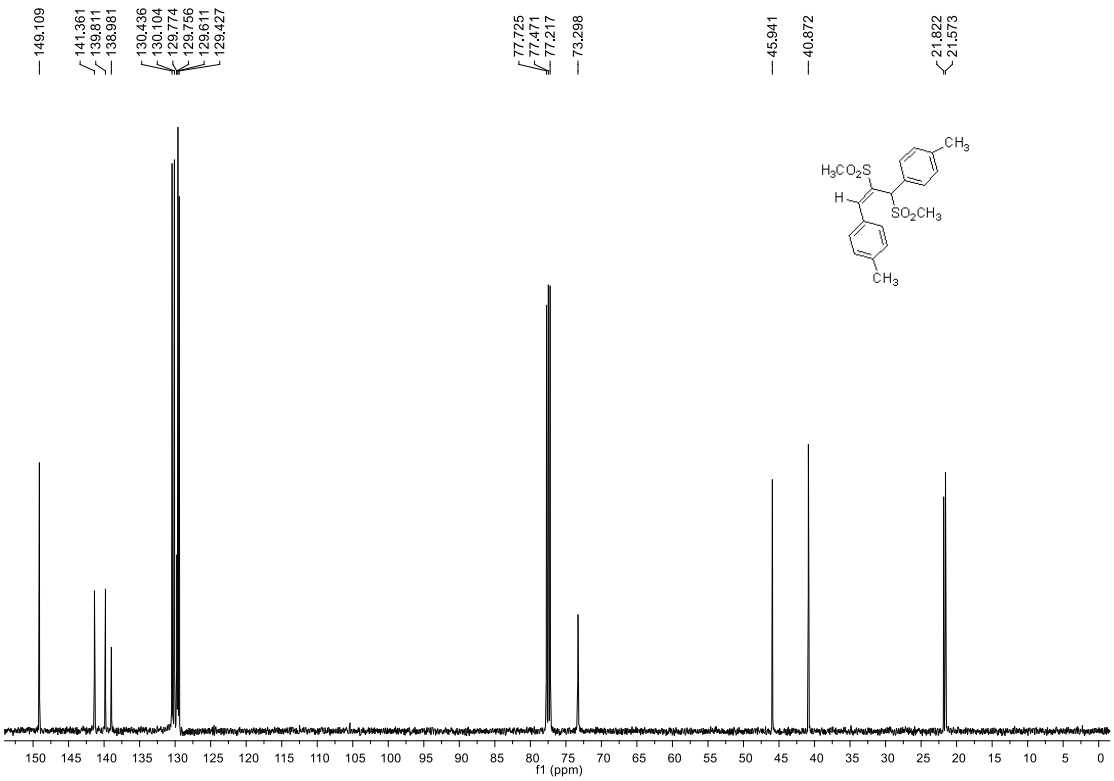




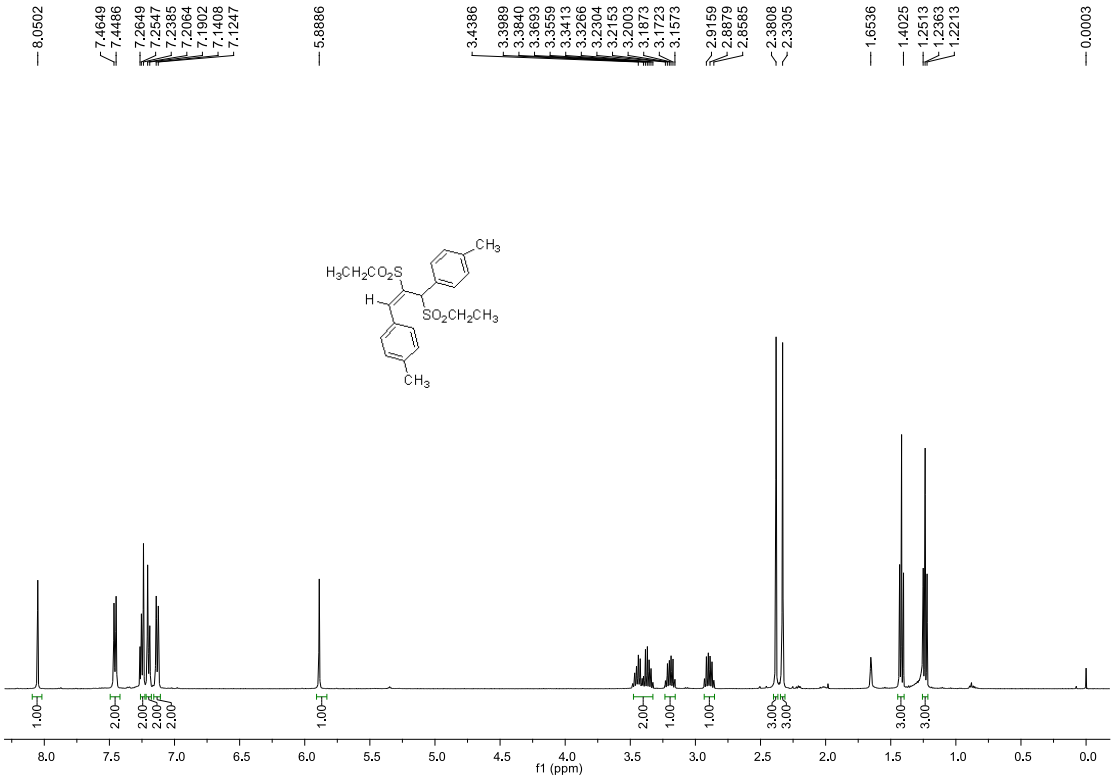

-103.0080
-104.0409
F
CH3
SO2
H
SO2
F
CH3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

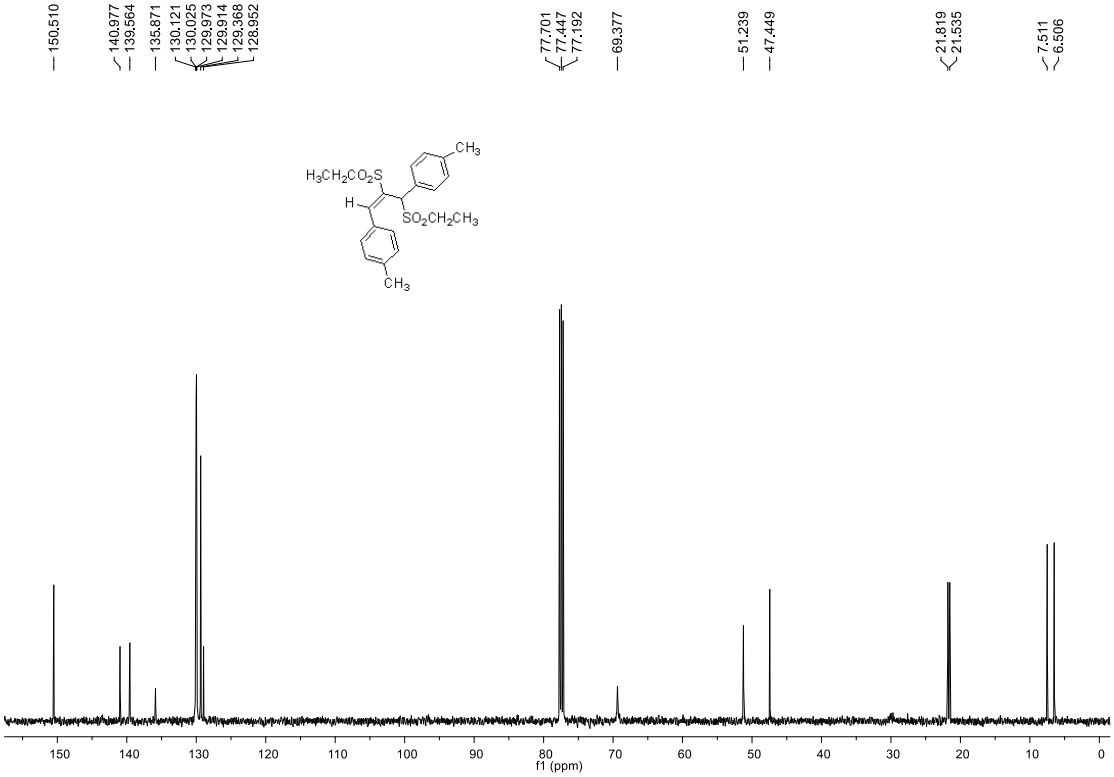
(*E*)-4,4'-(2,3-bis(methylsulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3af)



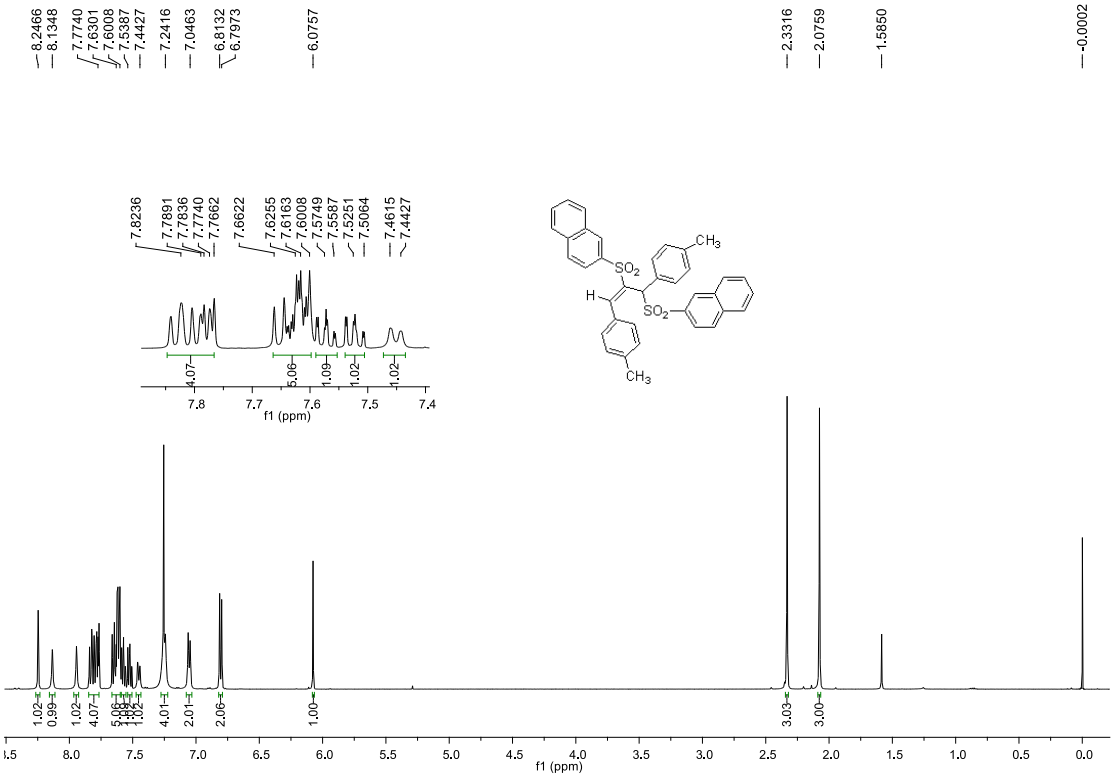


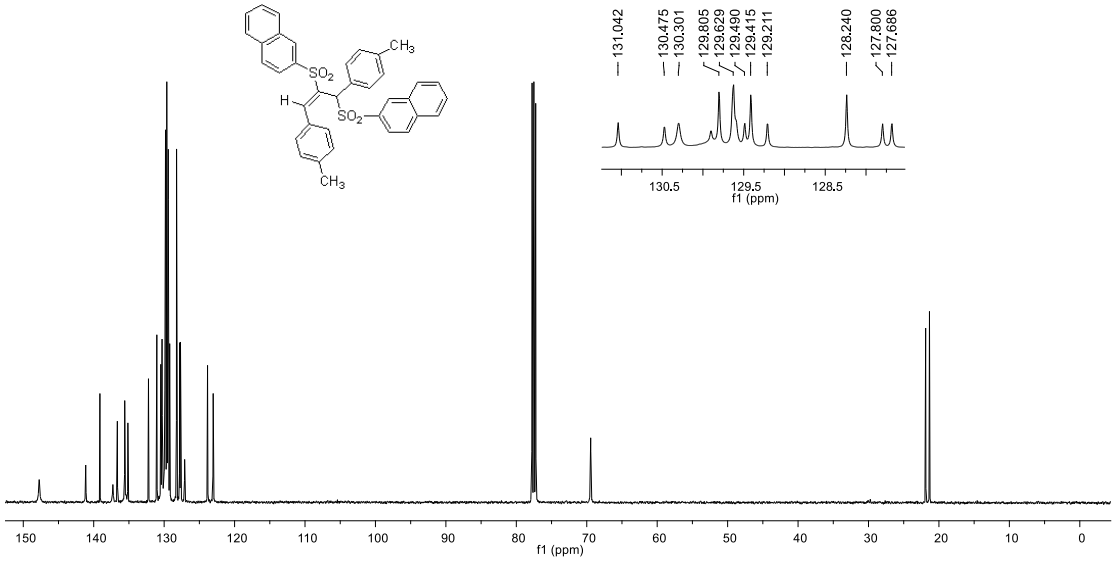
(*E*)-4,4'-(2,3-bis(ethylsulfonyl)prop-1-ene-1,3-diyl)bis(methylbenzene) (3ag)



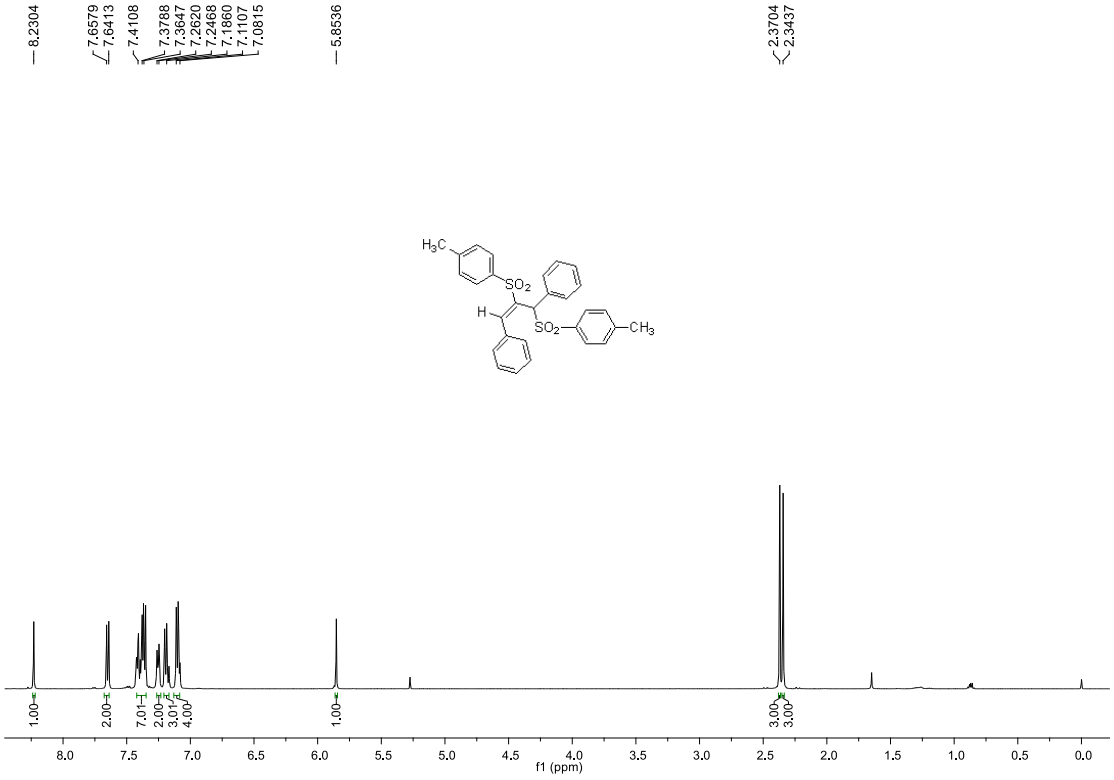


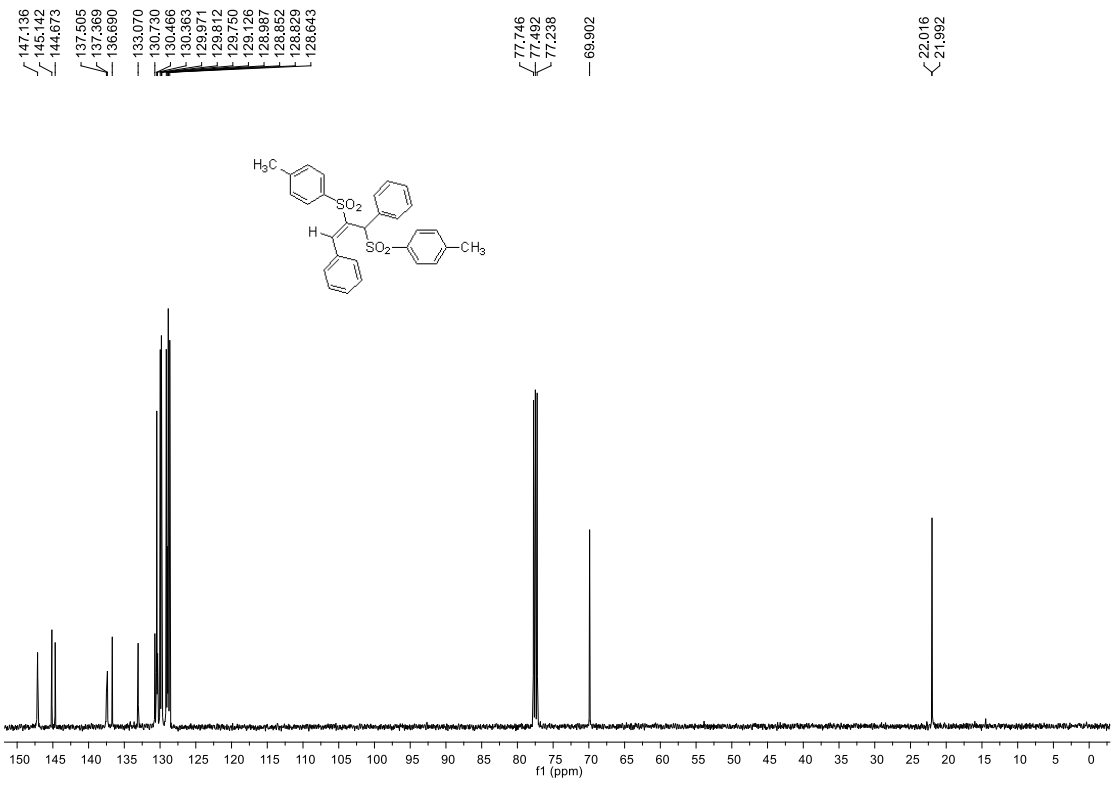
(*E*)-2,2'-(1,3-di-*p*-tolylprop-2-ene-1,2-diyldisulfonyl)dinaphthalene (3ah)



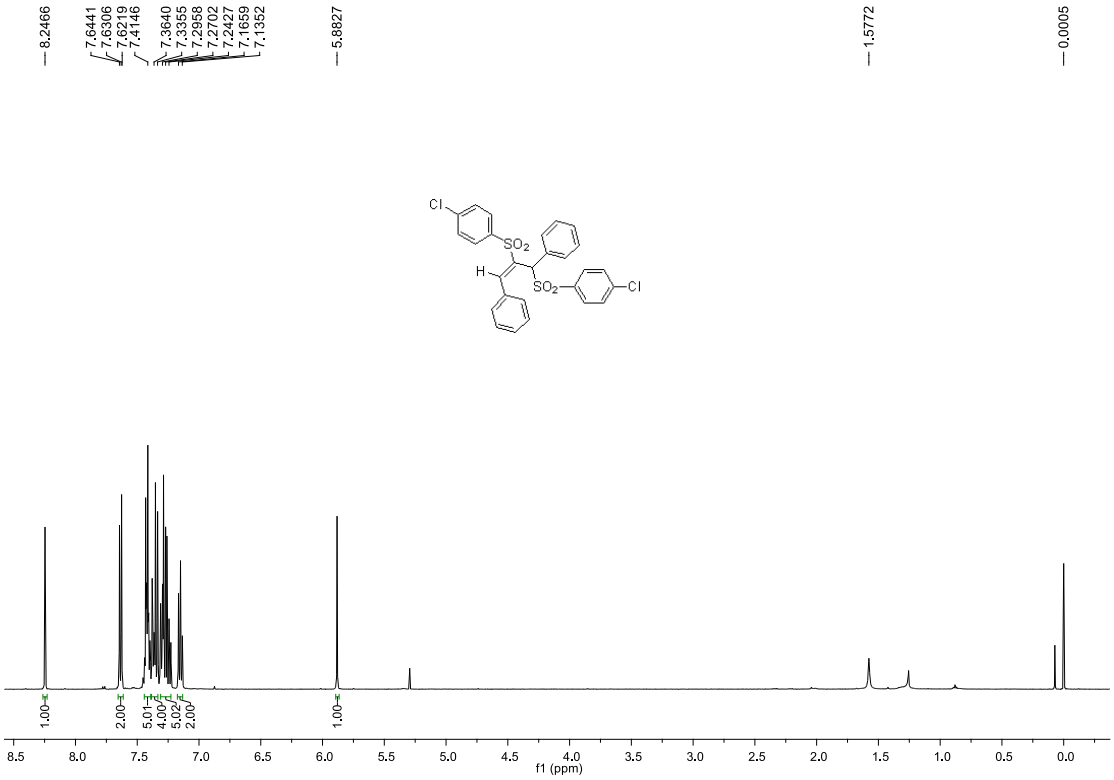


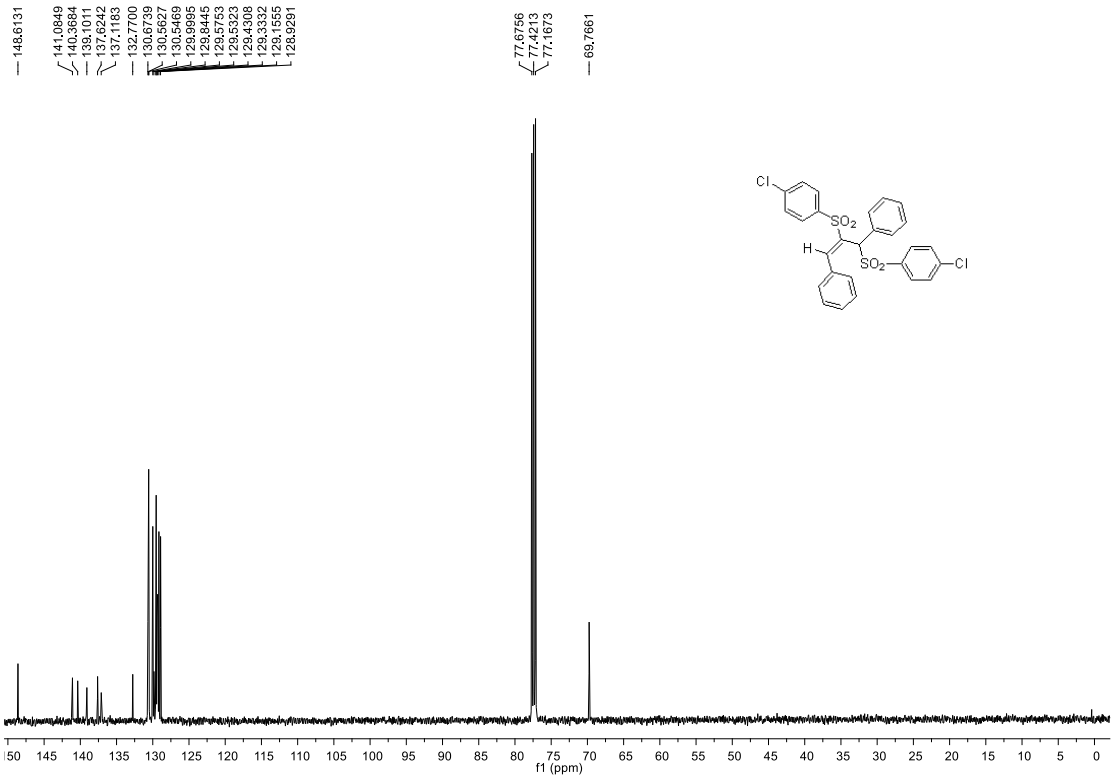
***(E)*-4,4'-(1,3-diphenylprop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ba)**



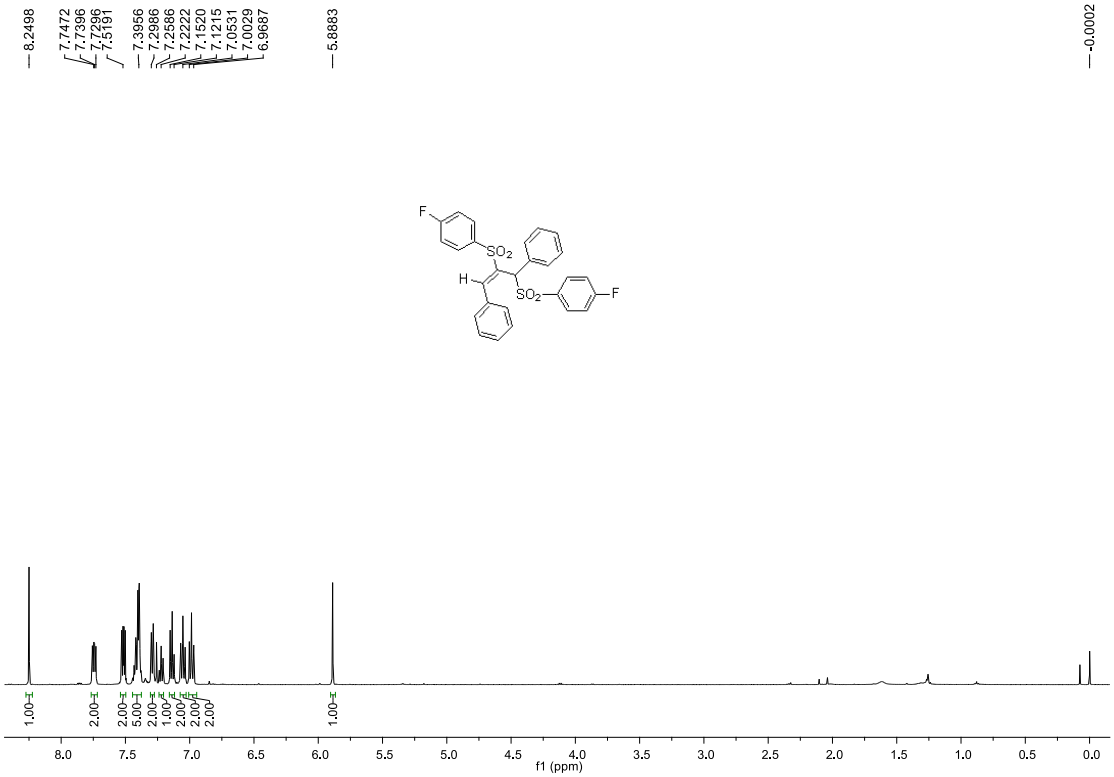


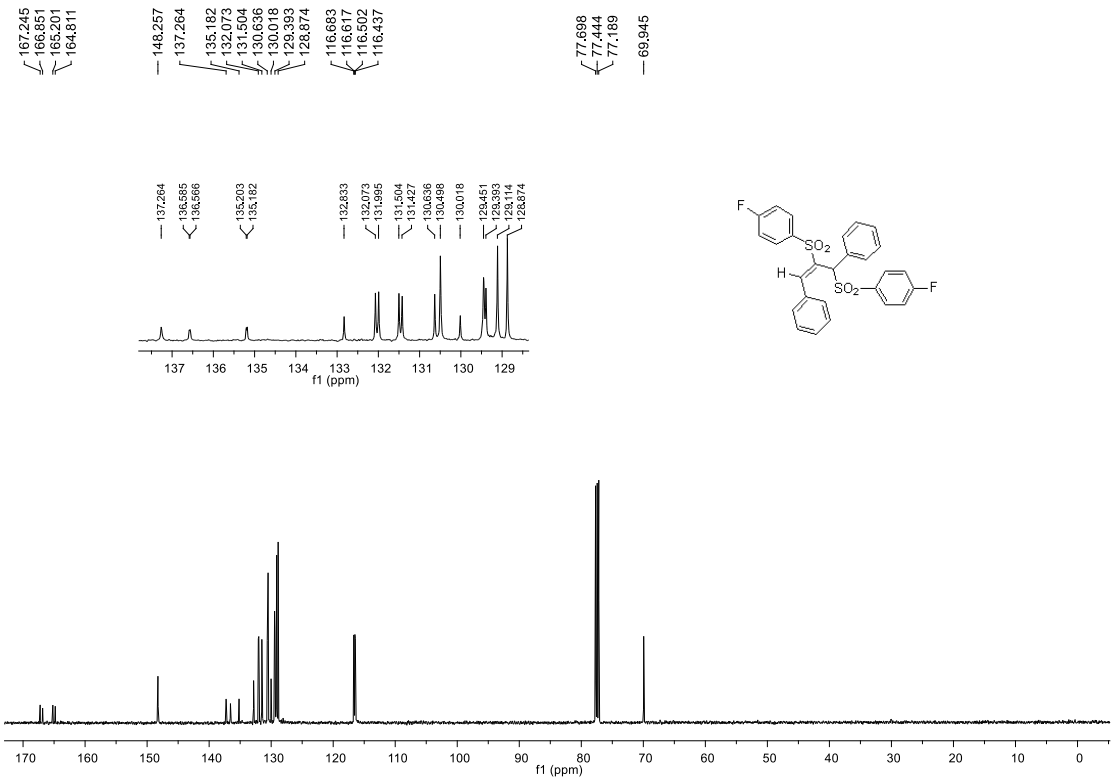
(*E*)-4,4'-(1,3-diphenylprop-2-ene-1,2-diyldisulfonyl)bis(chlorobenzene) (3bb)

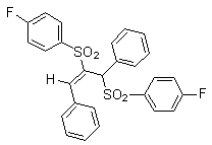




(*E*)-4,4'-(1,3-diphenylprop-2-ene-1,2-diyldisulfonyl)bis(fluorobenzene) (3bc)

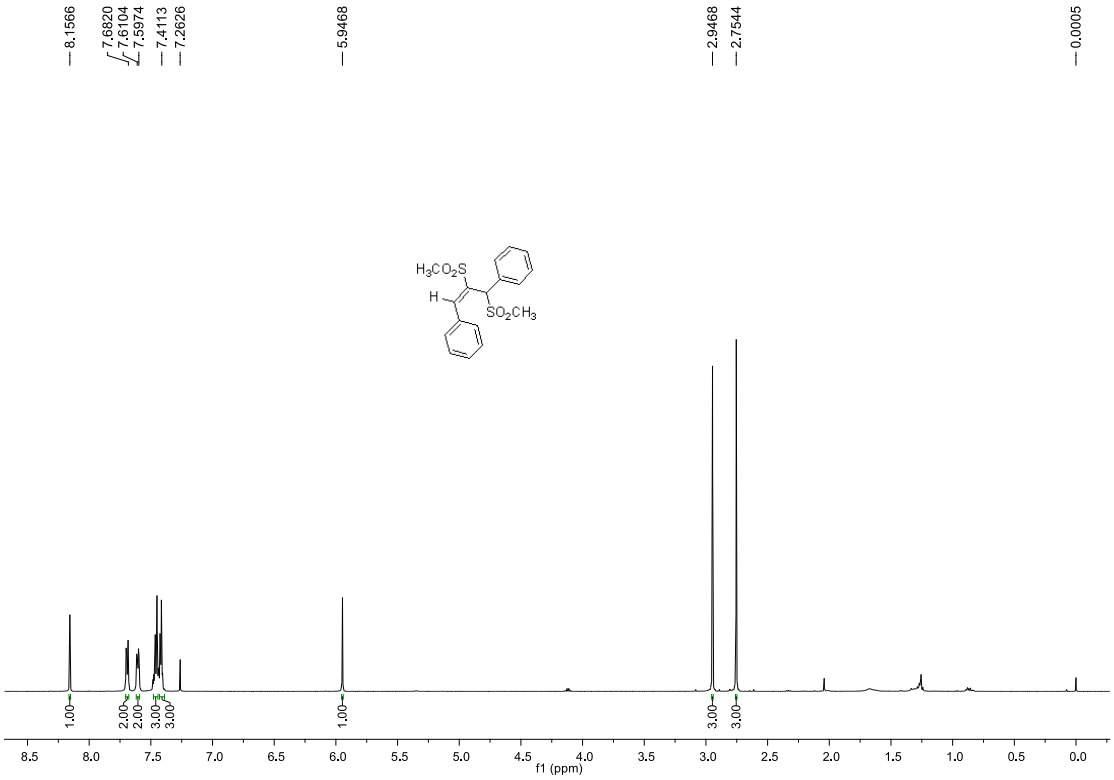


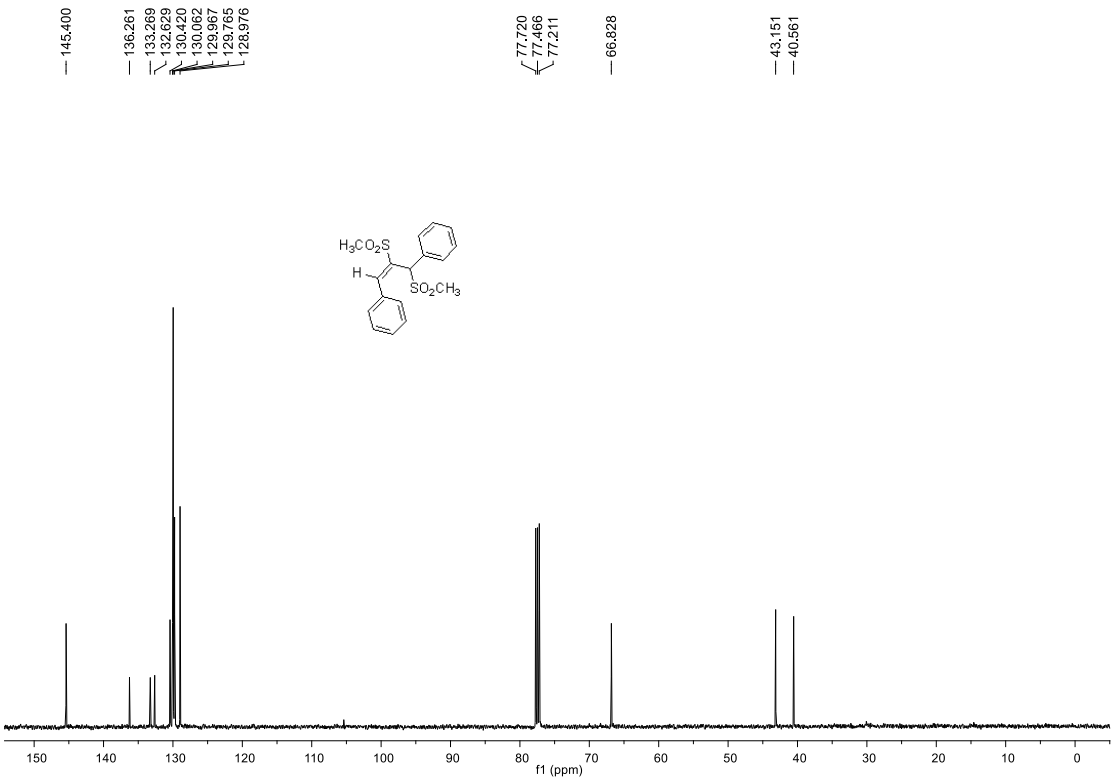



F
SO2
H
SO2
F

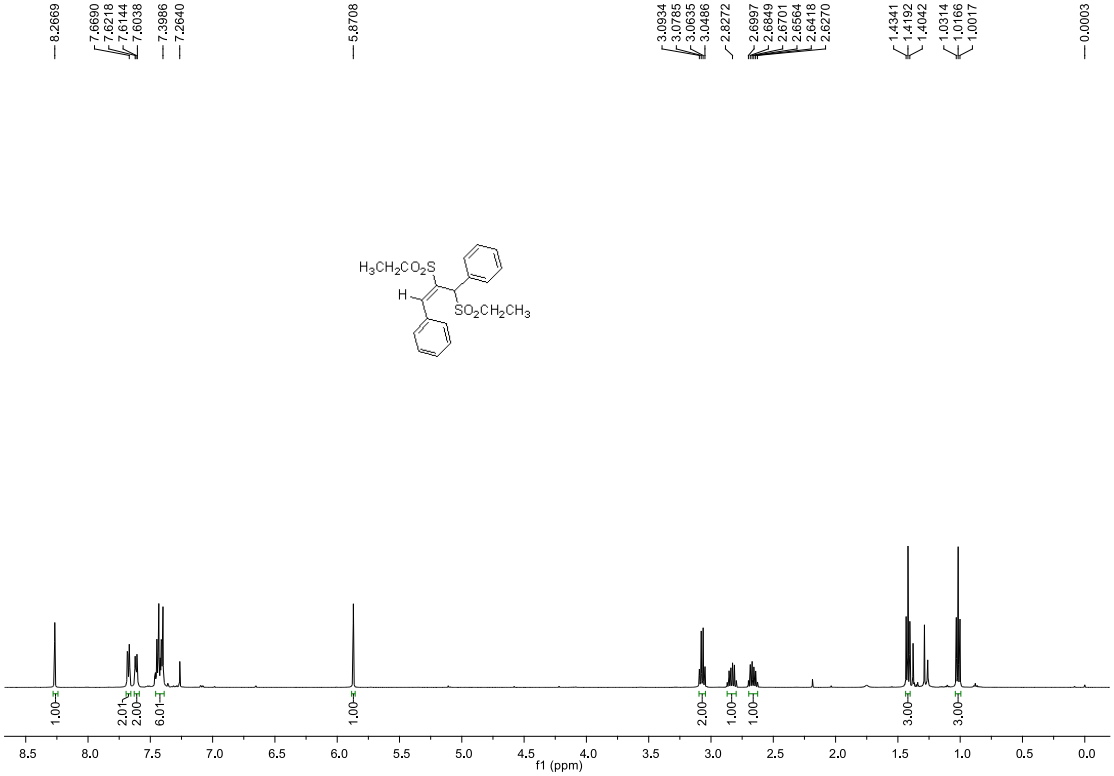
-102.8083
-103.7387
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

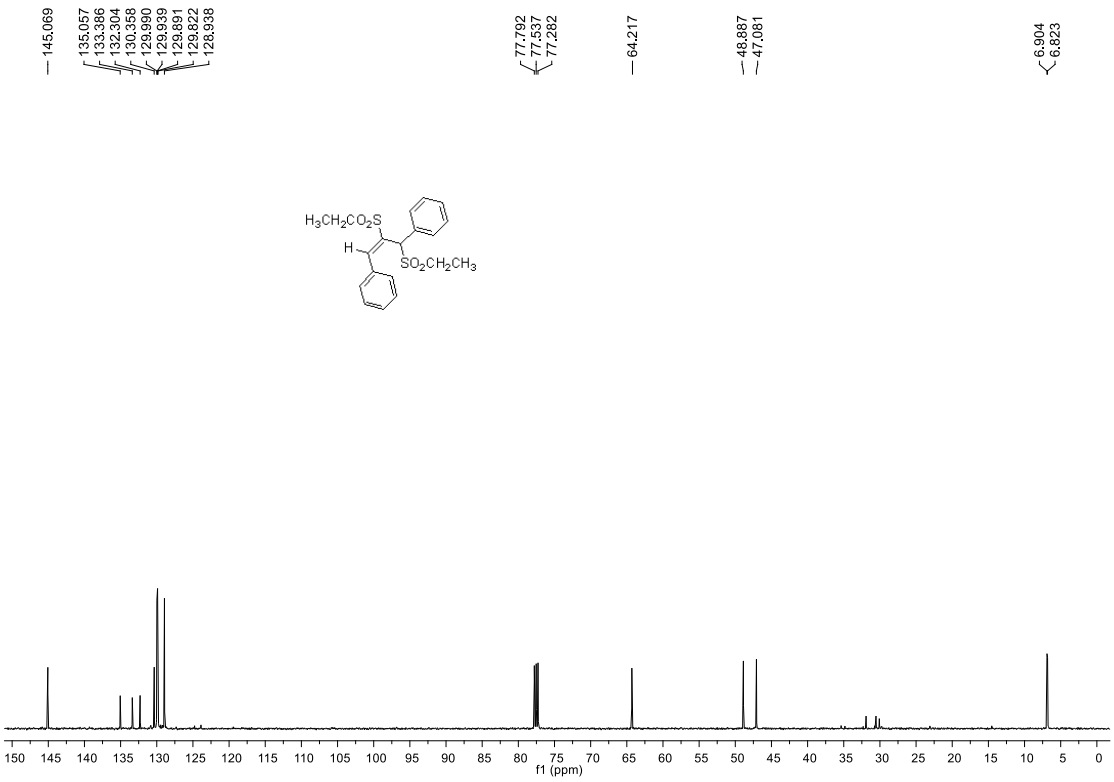
(*E*)-(2,3-bis(methylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (3bd)



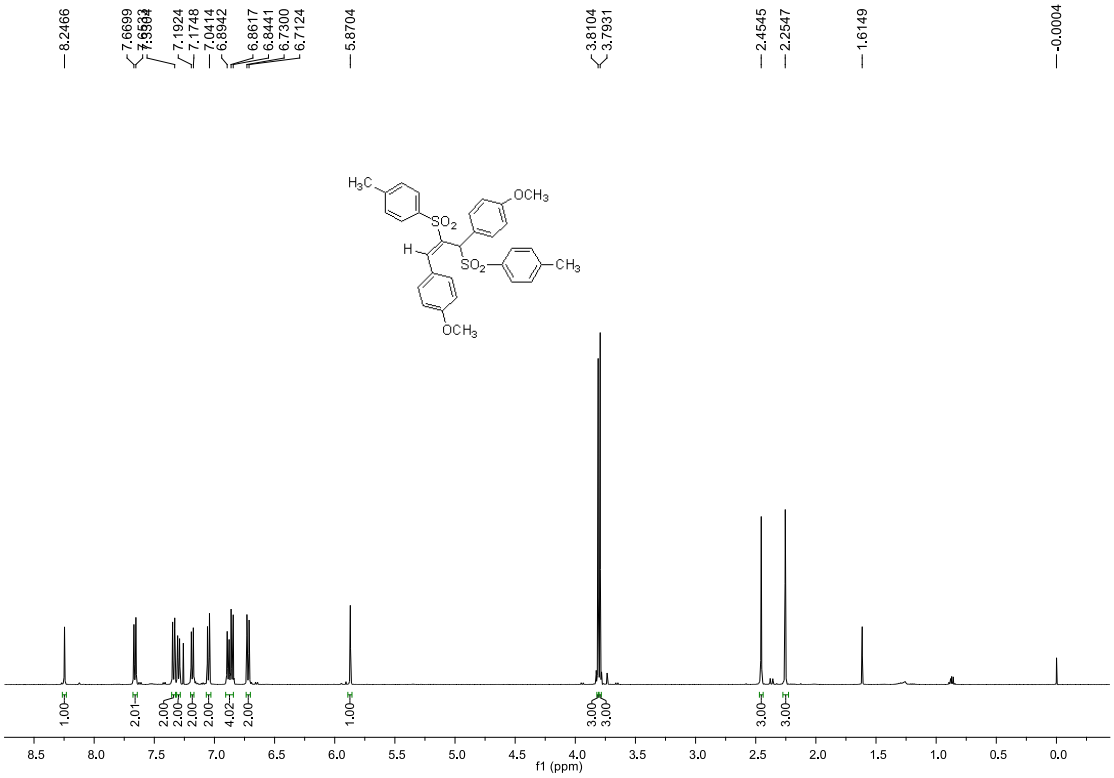


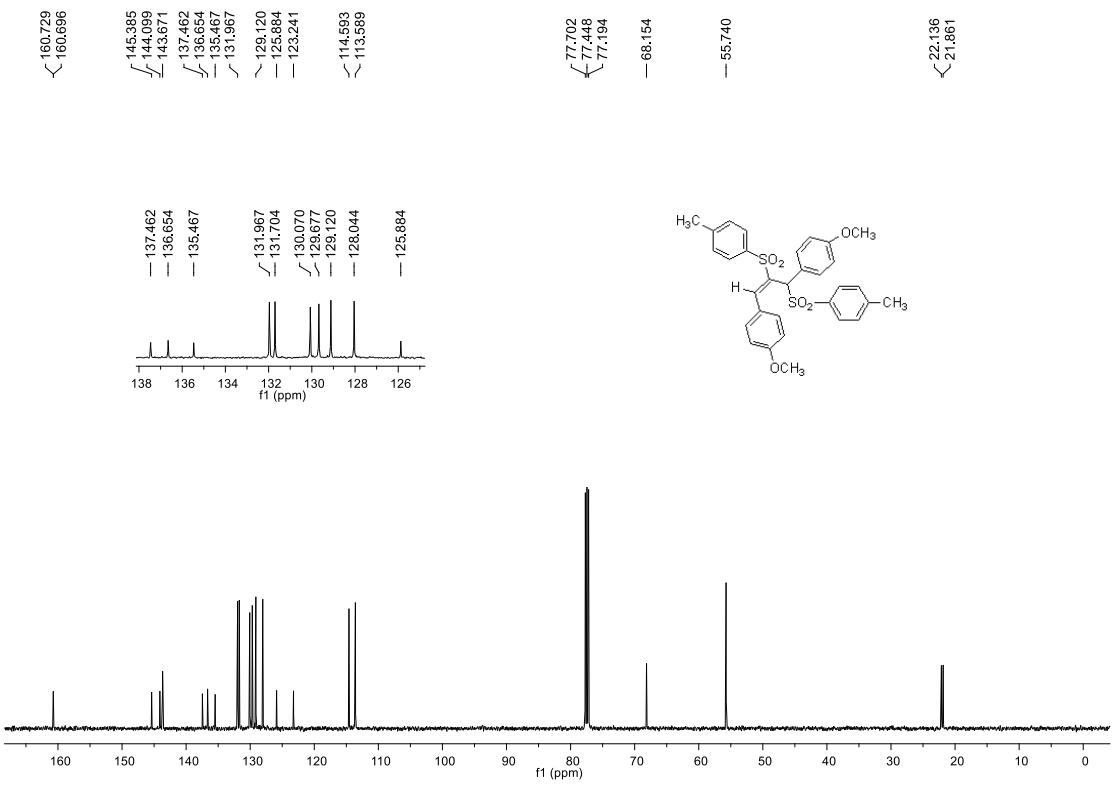
(*E*)-(2,3-bis(ethylsulfonyl)prop-1-ene-1,3-diyl)dibenzene (3be)



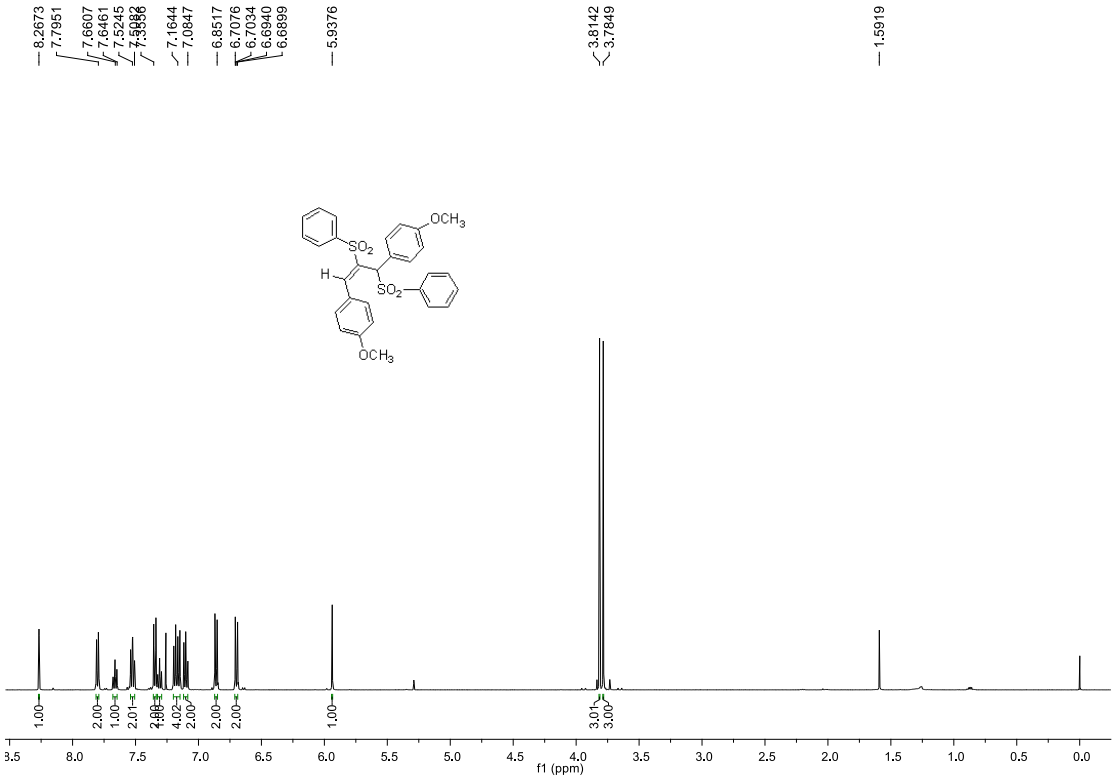


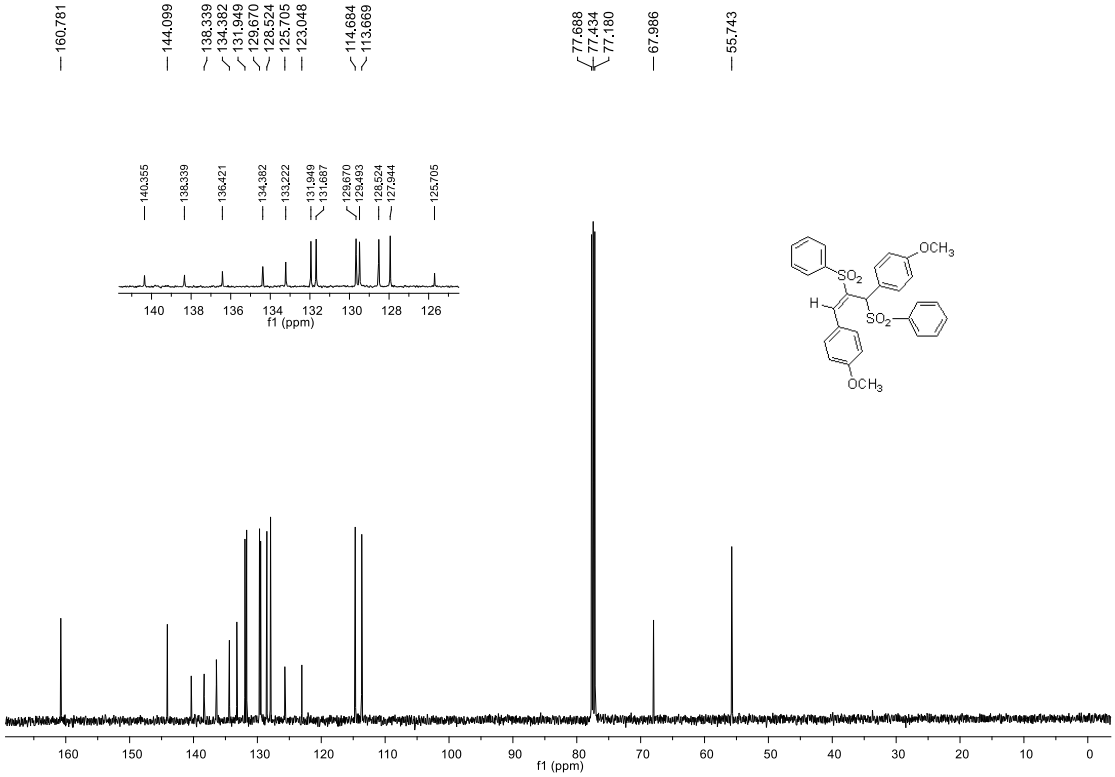
(*E*)-4,4'-(1,3-bis(4-methoxyphenyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ca)



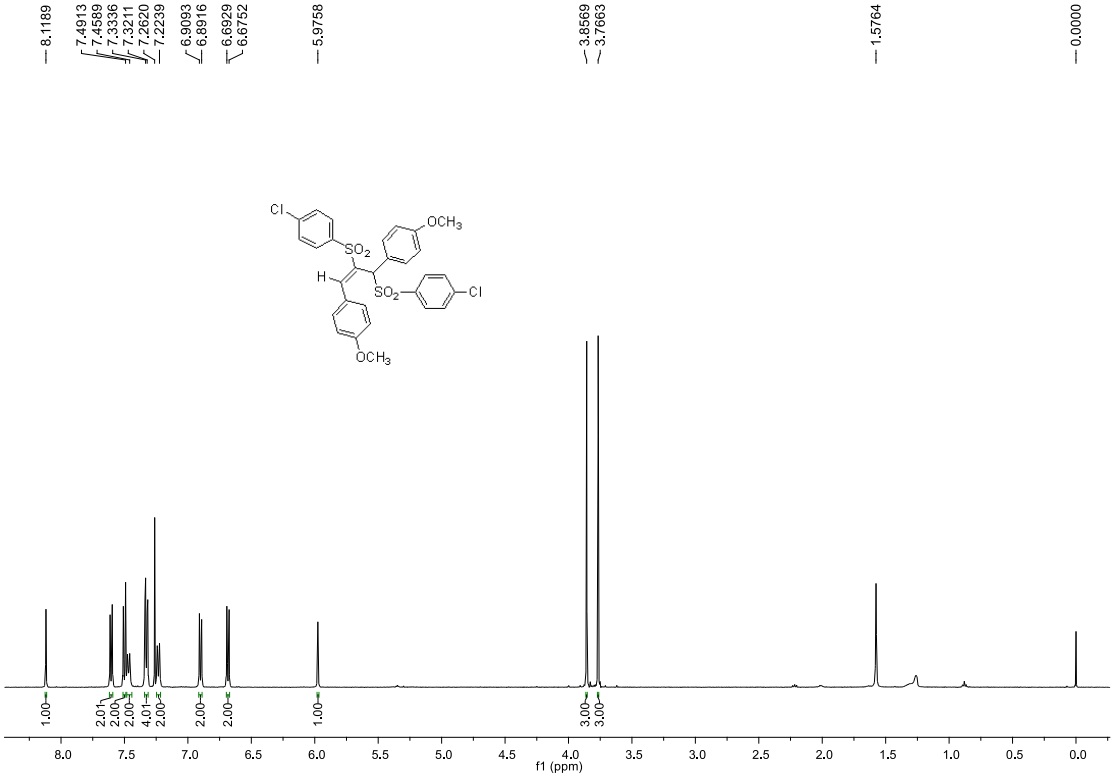


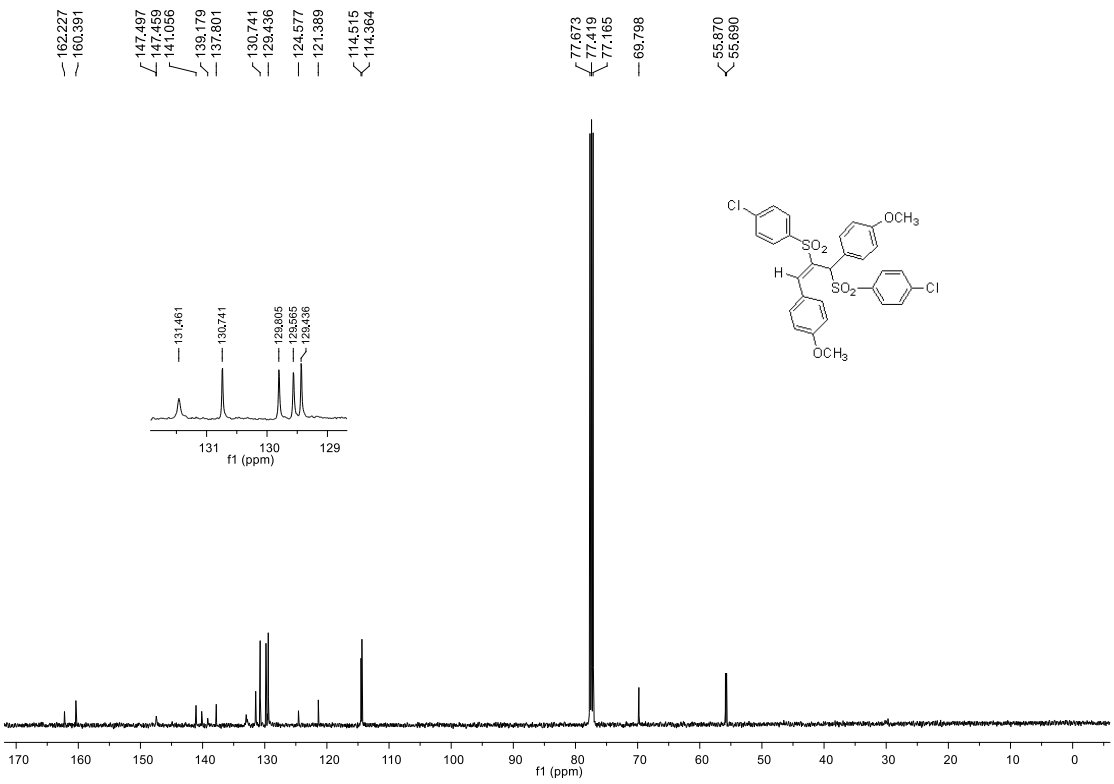
(*E*)-4,4'-(2,3-bis(phenylsulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (3cb)



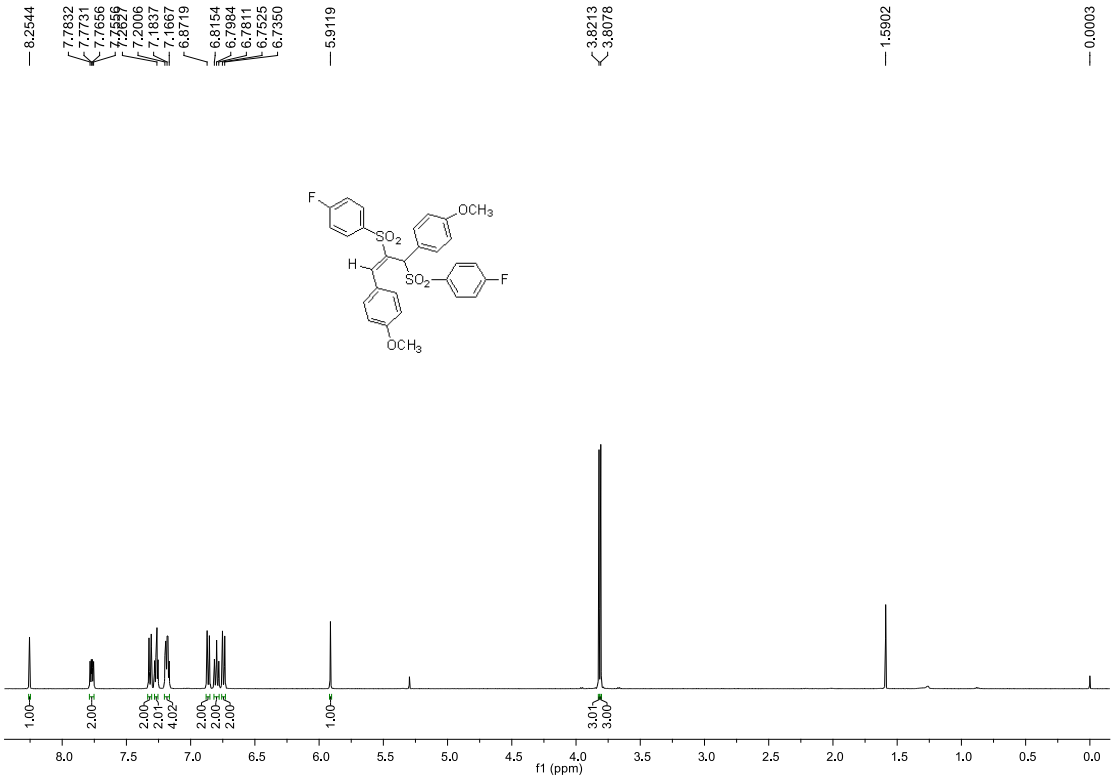


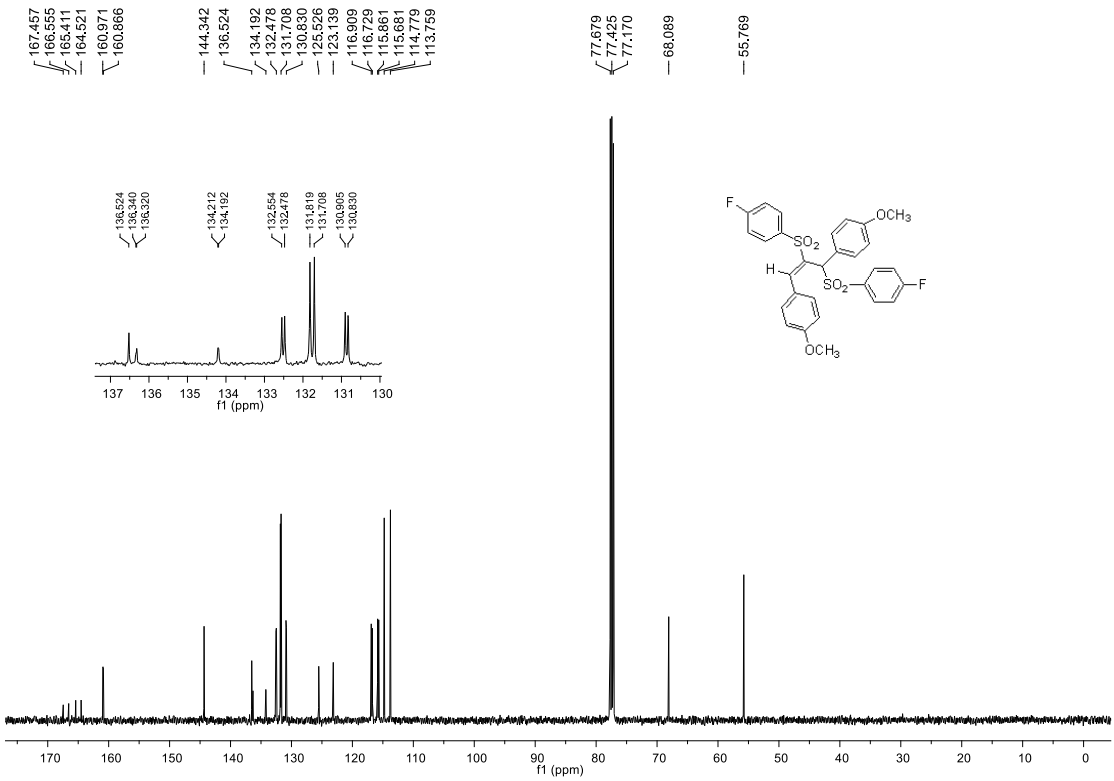
(*E*)-4,4'-(2,3-bis((4-chlorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (3cc)

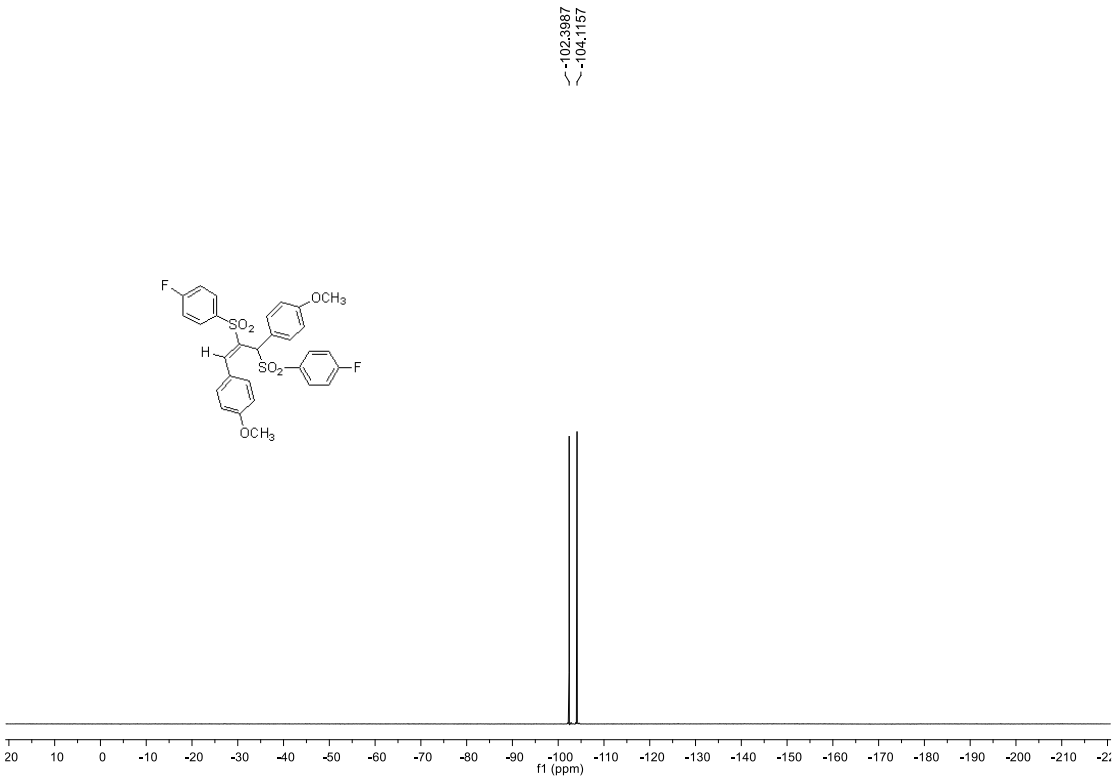




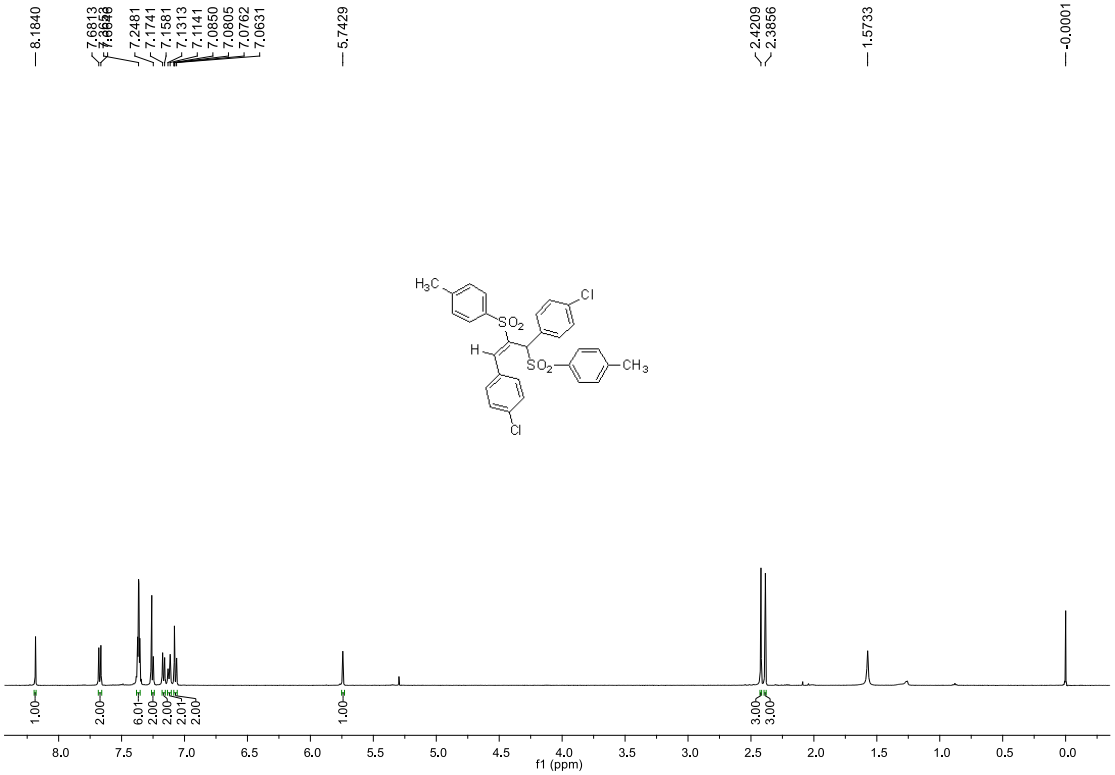
(*E*)-4,4'-(2,3-bis((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(methoxybenzene) (3cd)

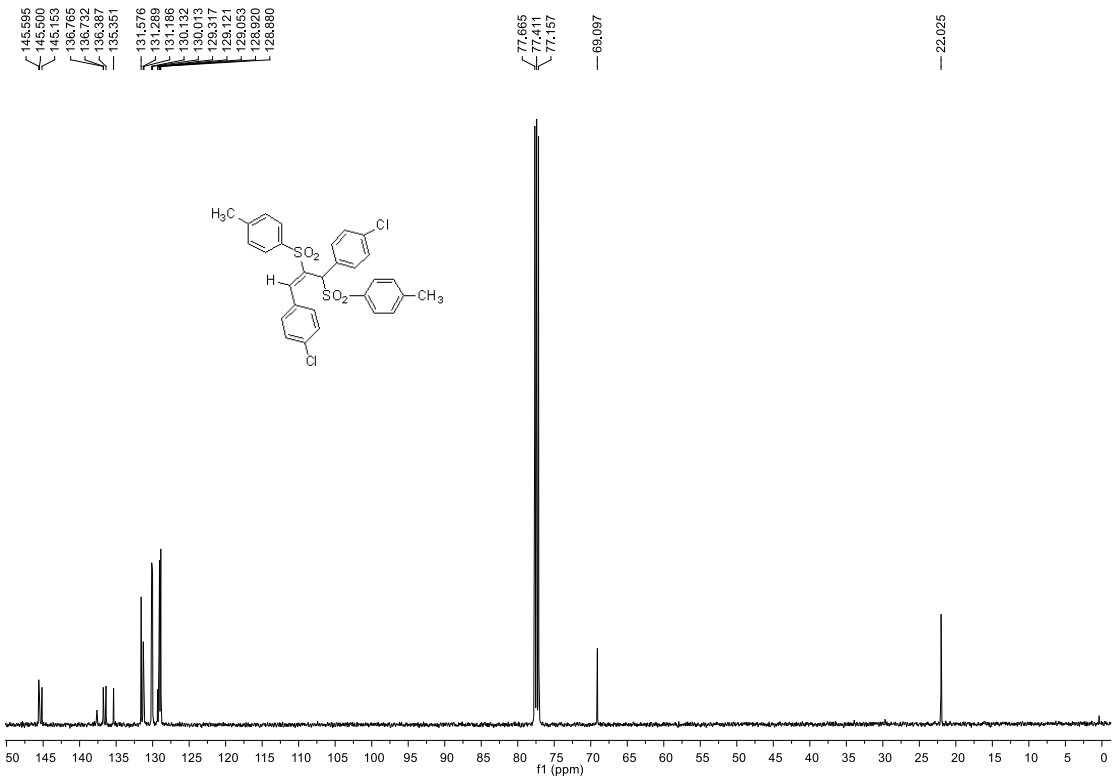




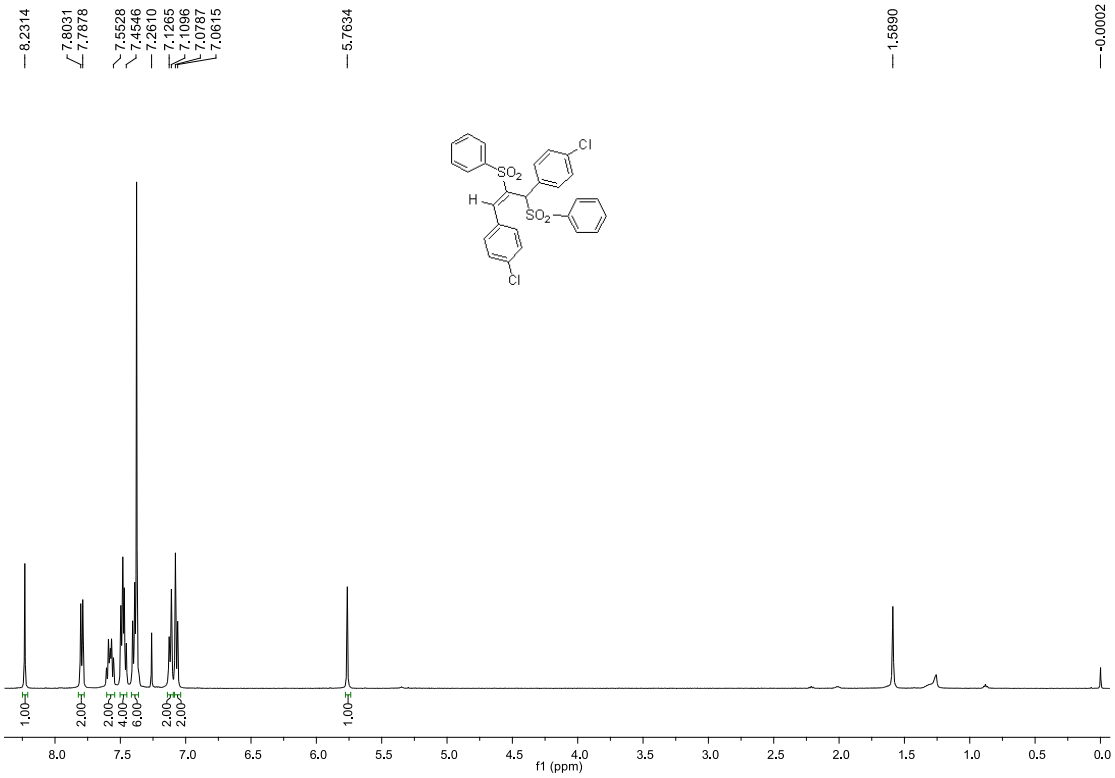

-102.3987
-104.1157
F
OCH3
SO2
H
SO2
F
OCH3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

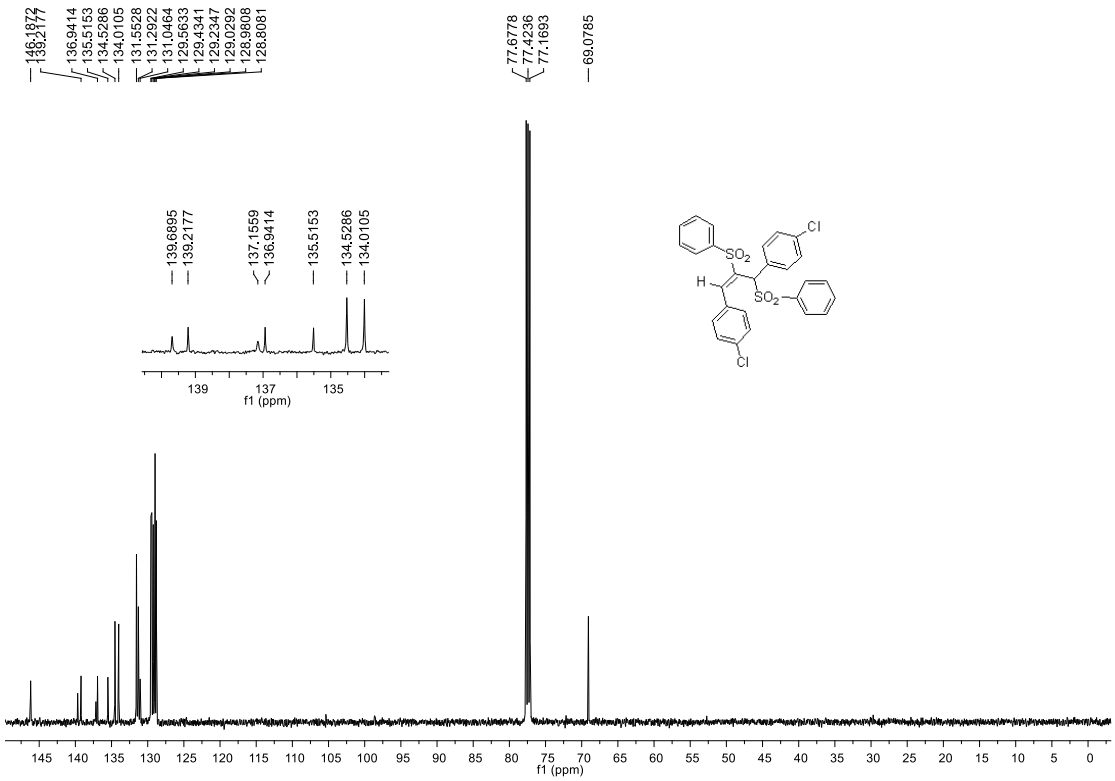
(*E*)-4,4'-(1,3-bis(4-chlorophenyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (**3da**)



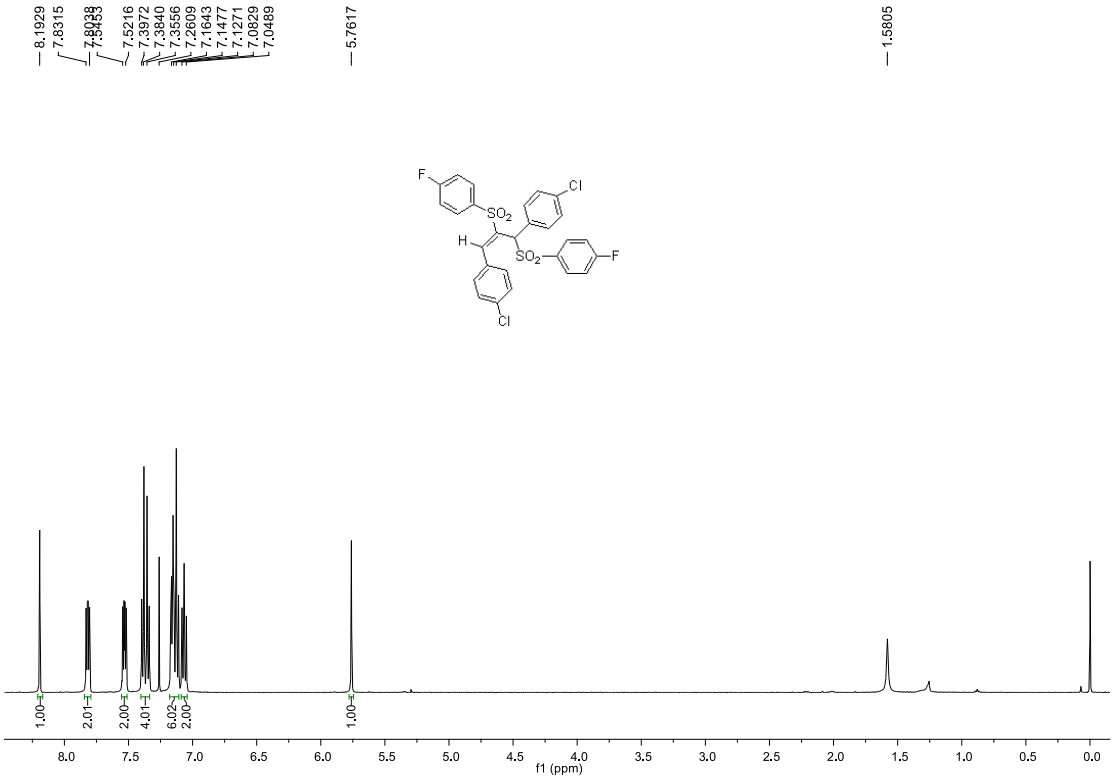


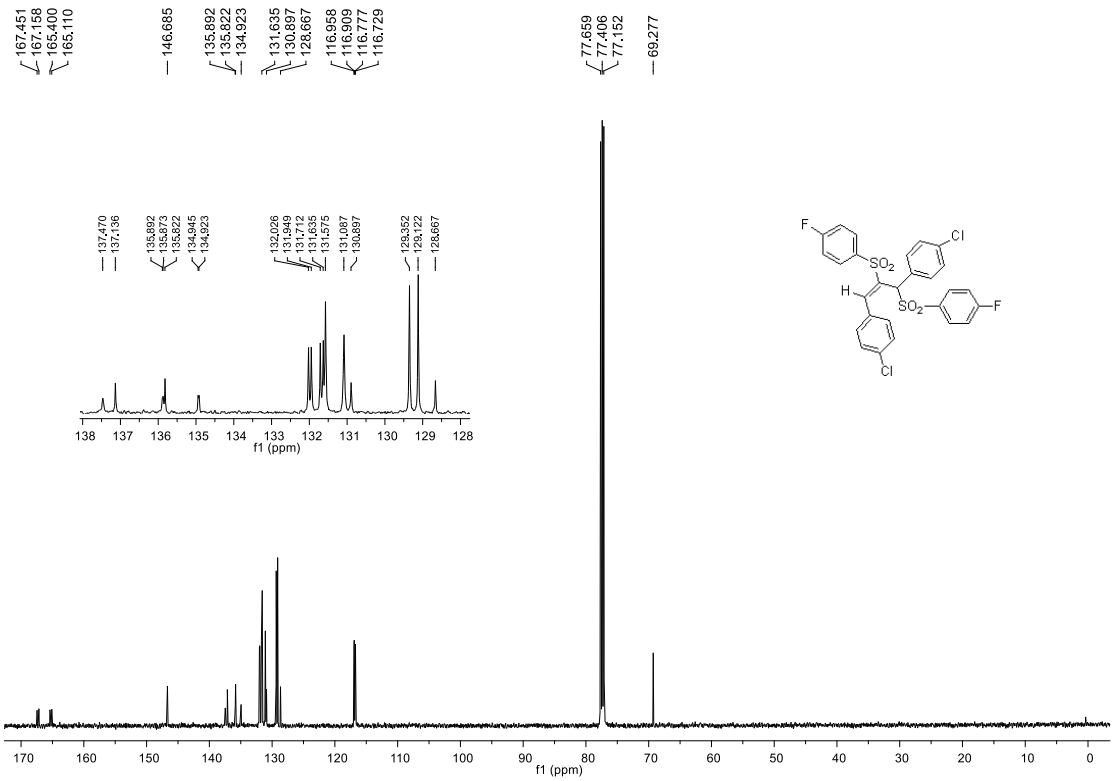
(*E*)-4,4'-(2,3-bis(phenylsulfonyl)prop-1-ene-1,3-diyl)bis(chlorobenzene) (3db)

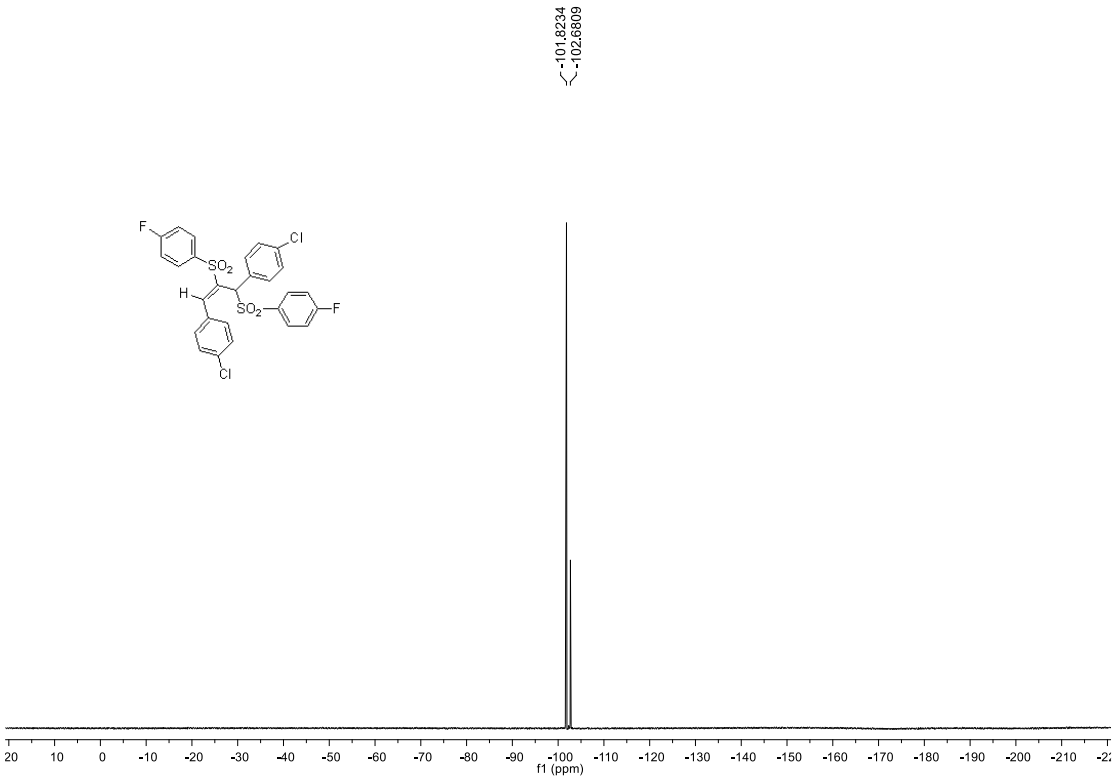




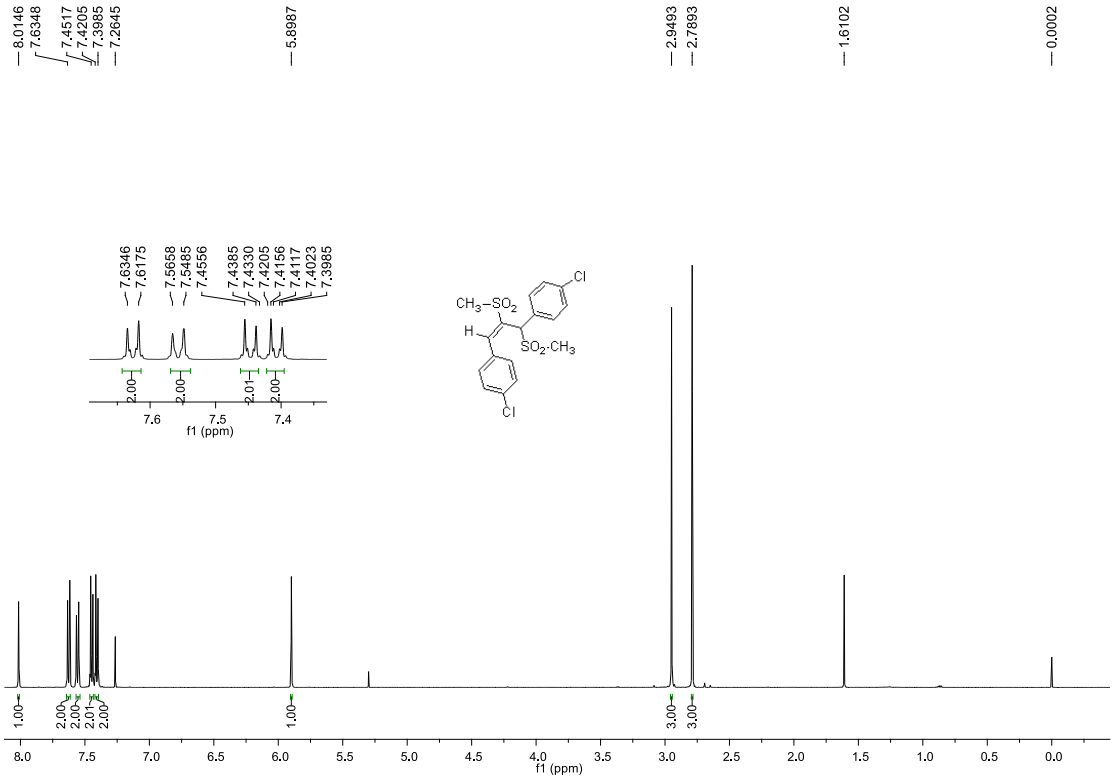
(*E*)-4,4'-(2,3-bis((4-fluorophenyl)sulfonyl)prop-1-ene-1,3-diyl)bis(chlorobenzene) (**3dc**)

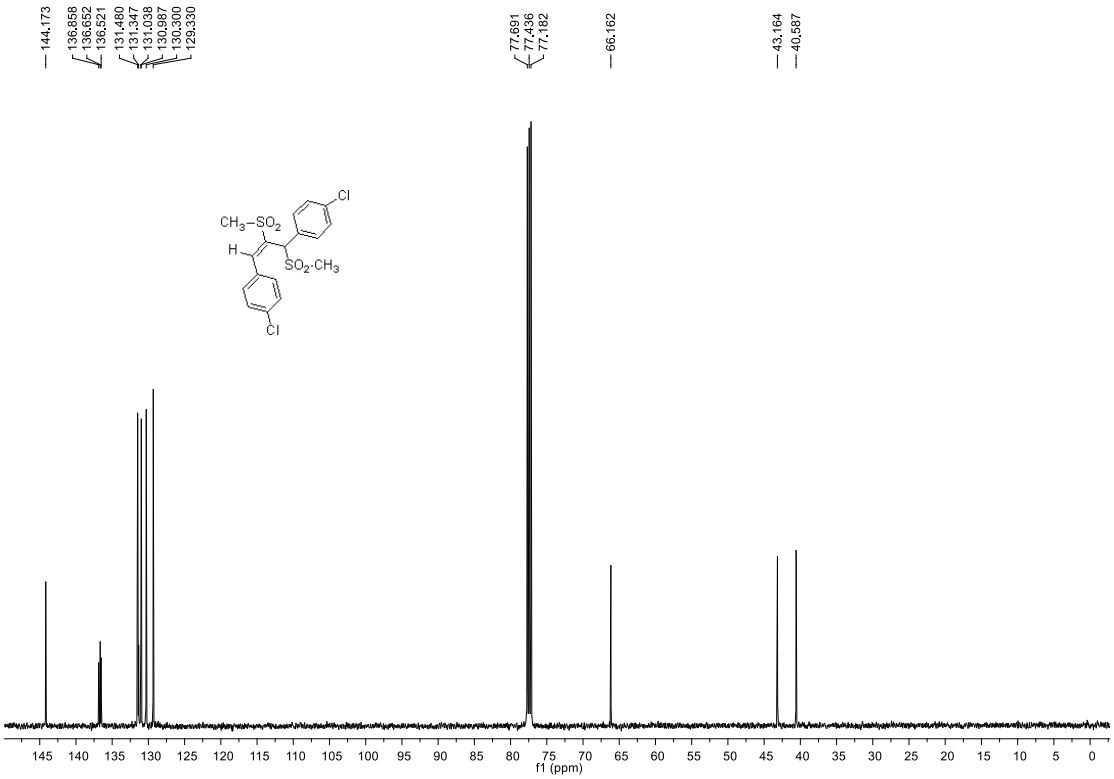




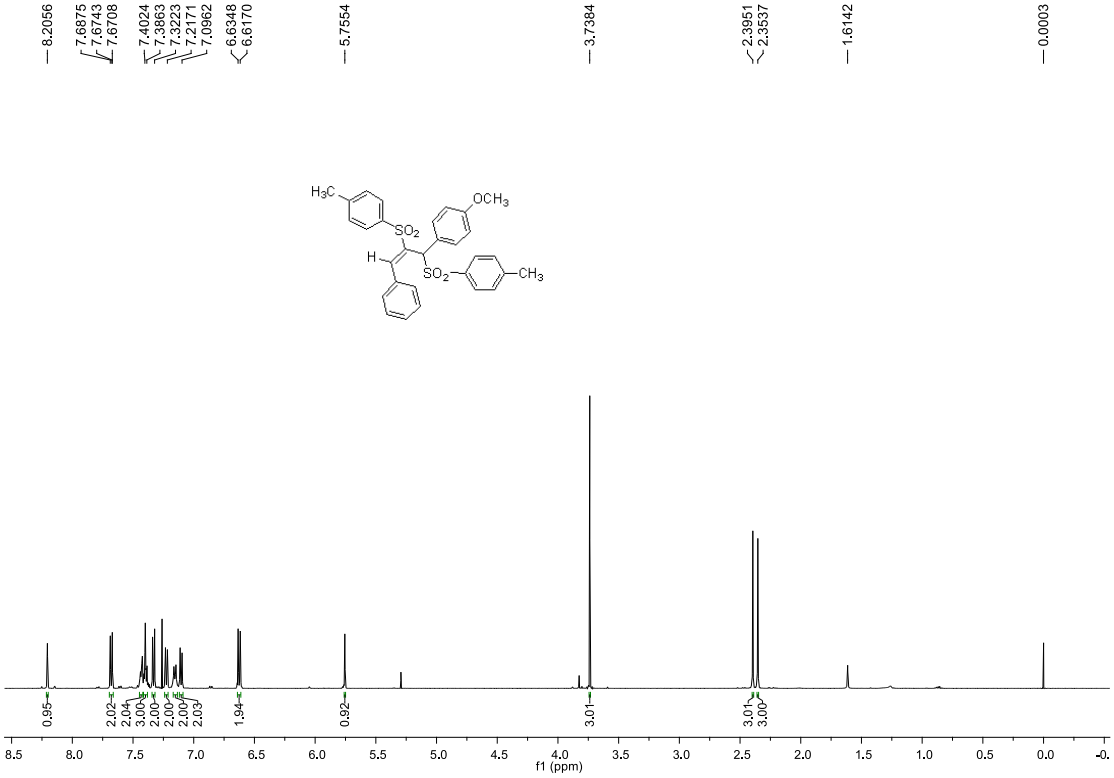

-101.8234
-102.6809
F
SO2
Cl
H
SO2
F
Cl
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

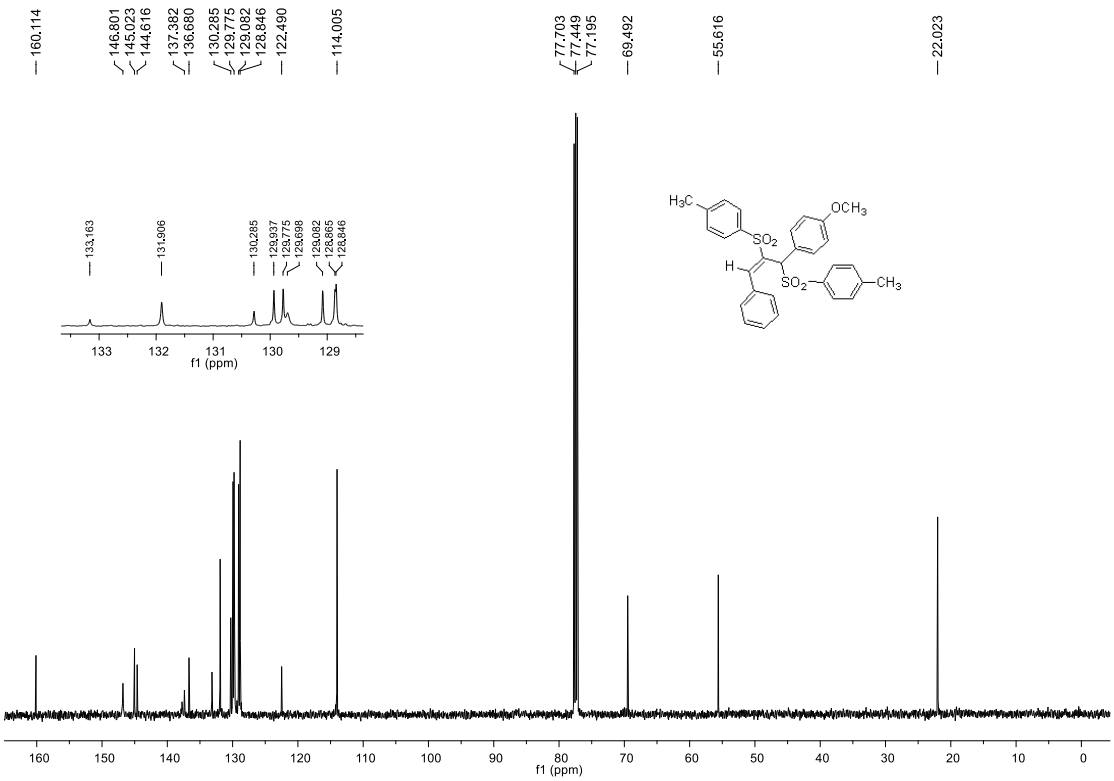
(*E*)-4,4'-(2,3-bis(methylsulfonyl)prop-1-ene-1,3-diyl)bis(chlorobenzene) (3dd)



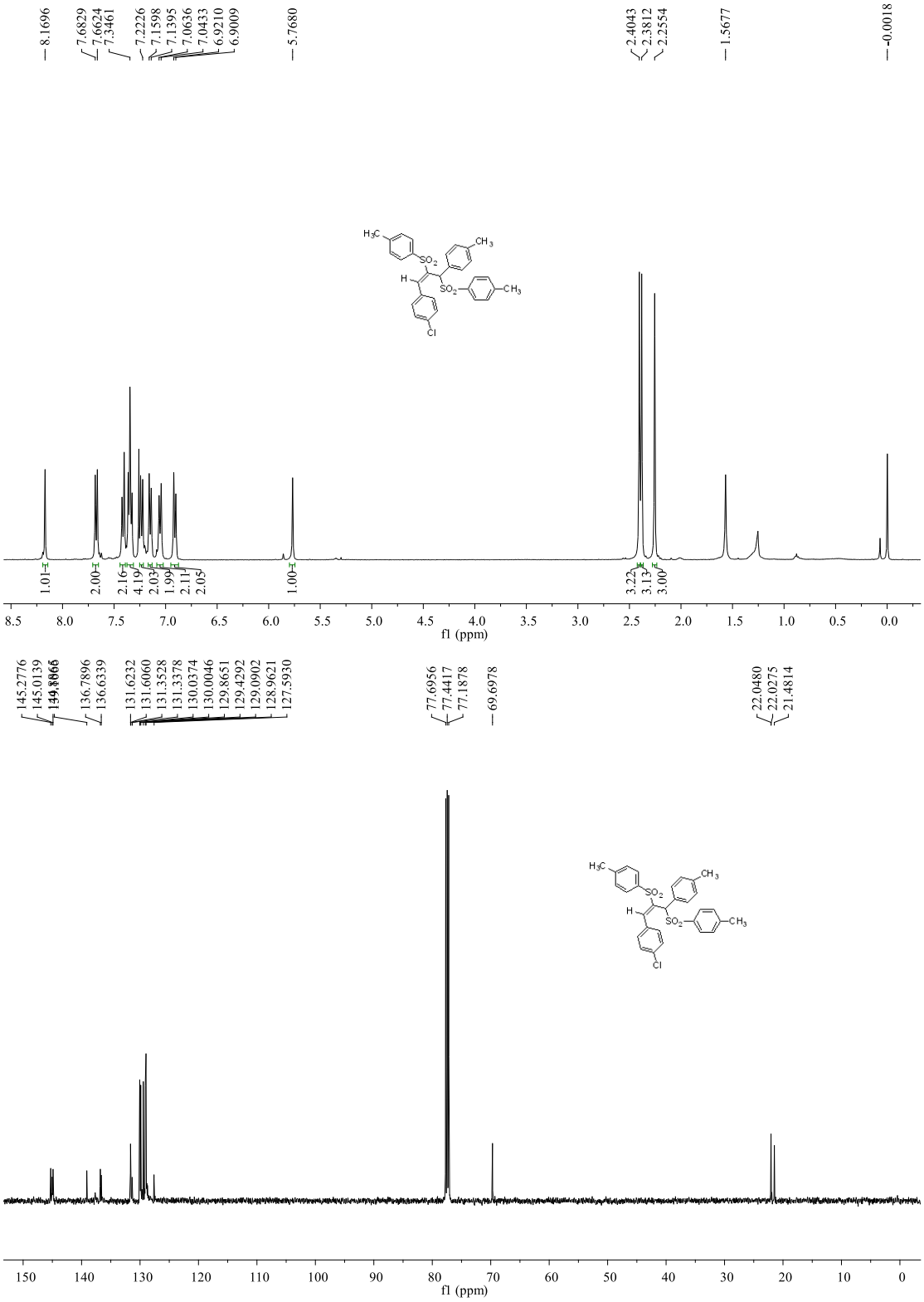


(*E*)-4,4'-(1-(4-methoxyphenyl)-3-phenylprop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ea)

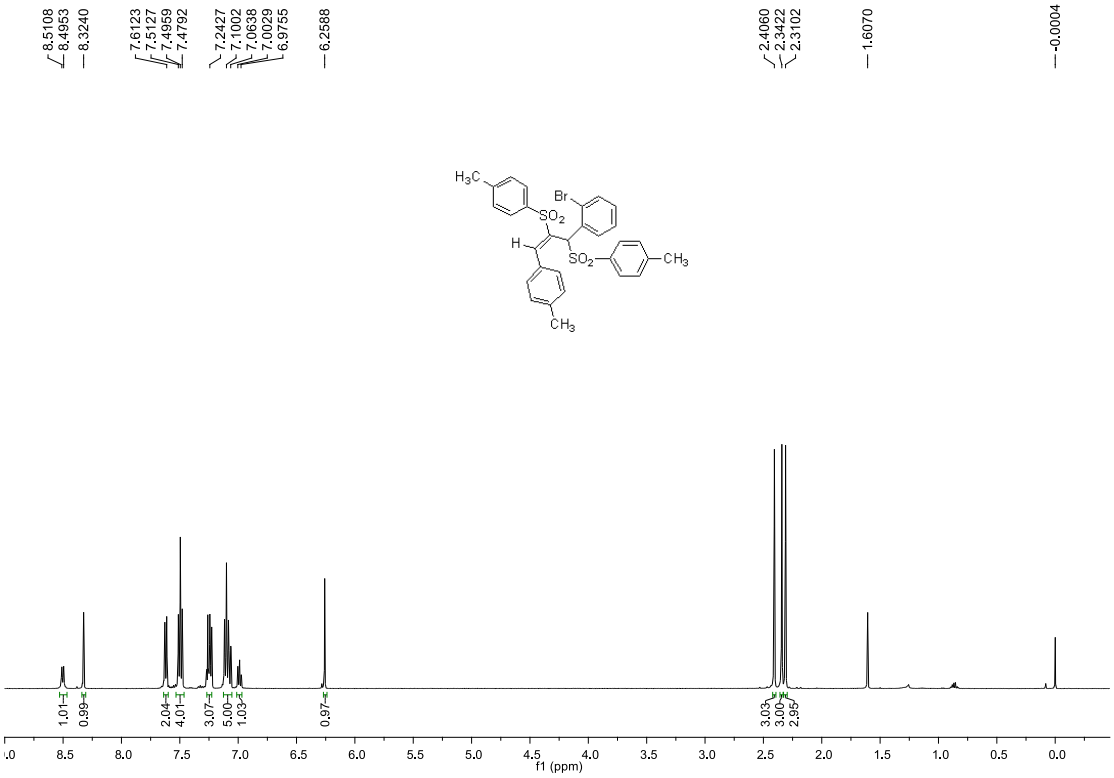


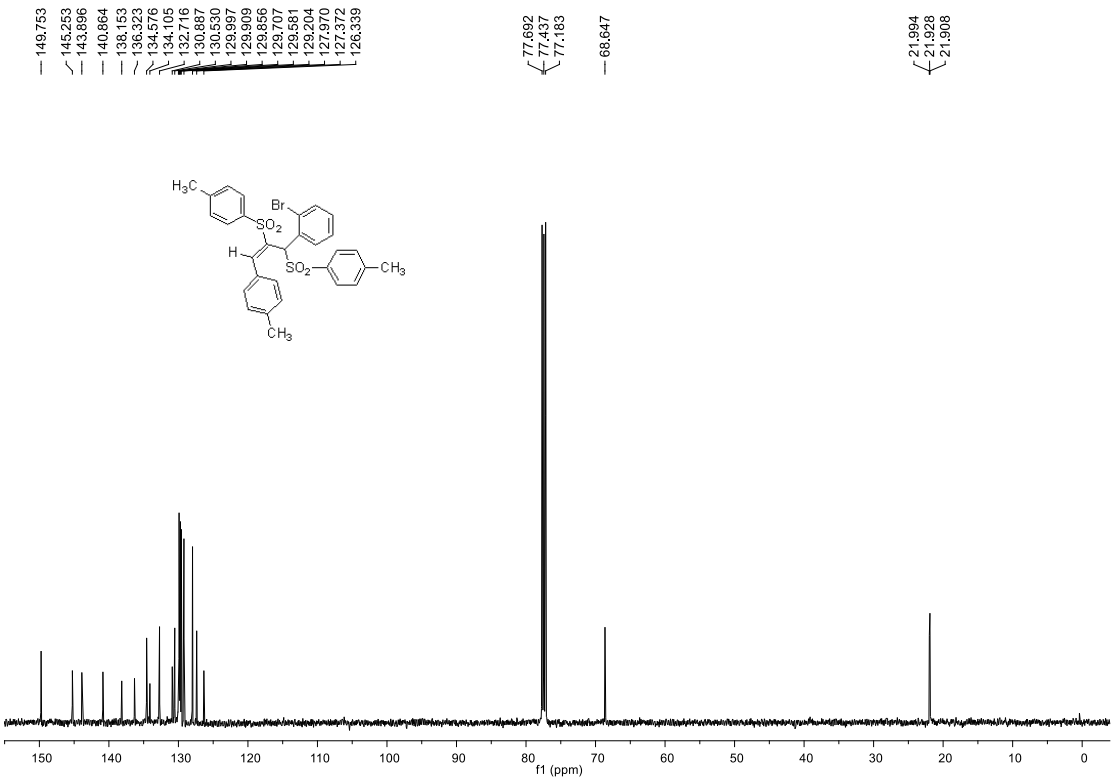


(*E*)-4,4'-(3-(4-chlorophenyl)-1-(p-tolyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3fa)

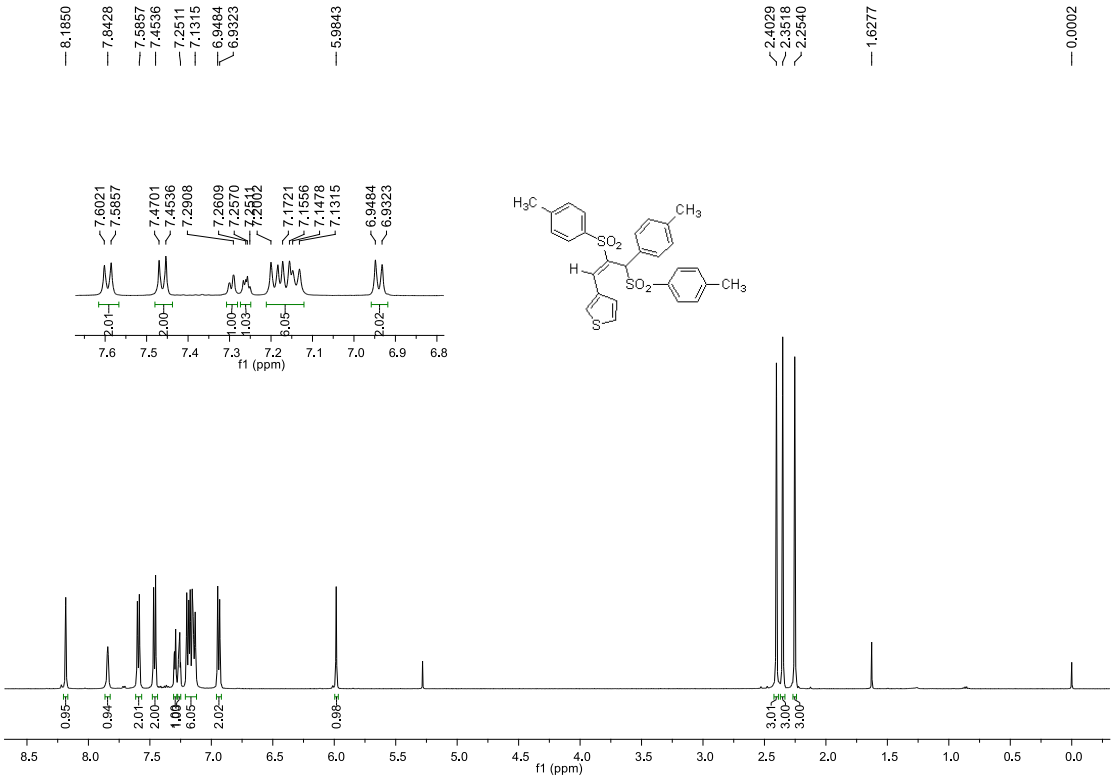


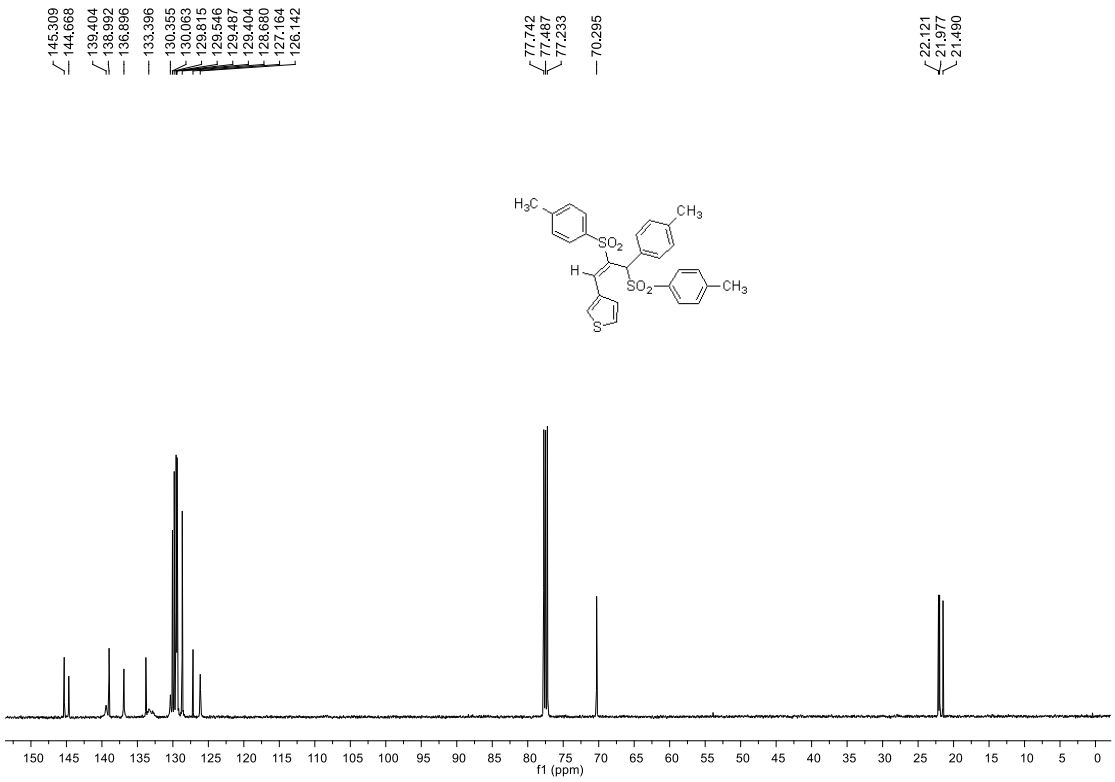
(*E*)-4,4'-(1-(2-bromophenyl)-3-(*p*-tolyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ga)



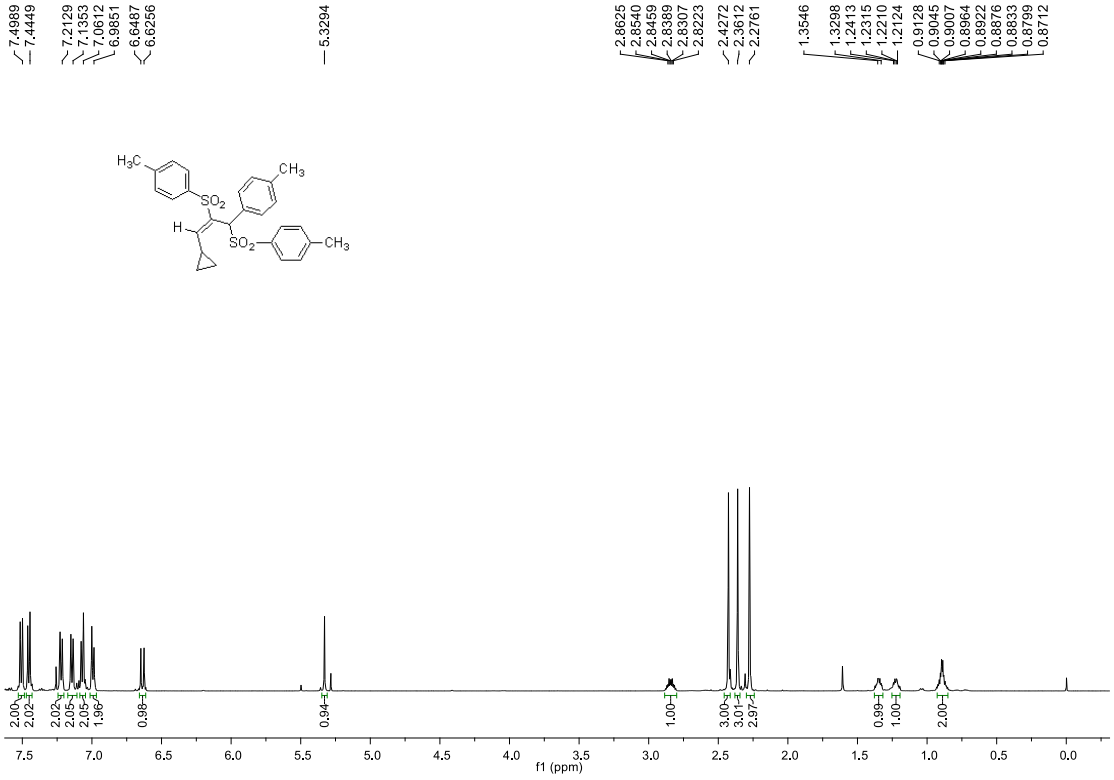


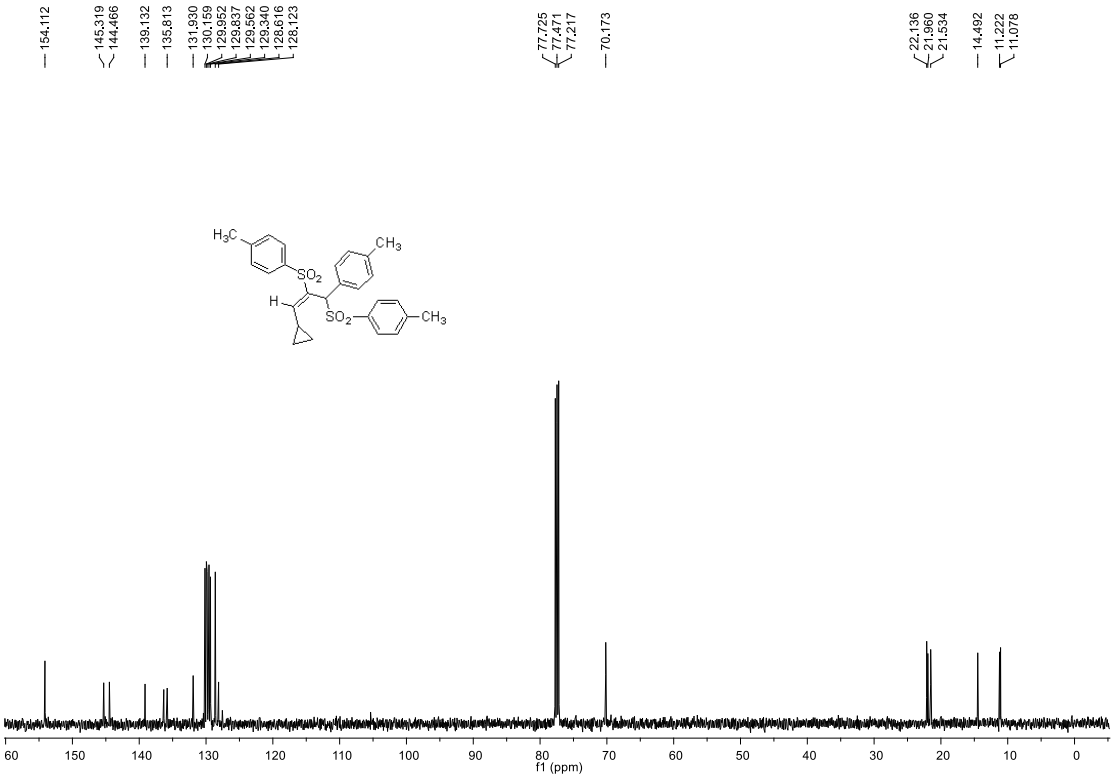
(*E*)-3-(3-(*p*-tolyl)-1,2-ditosylallyl)thiophene (3ha)





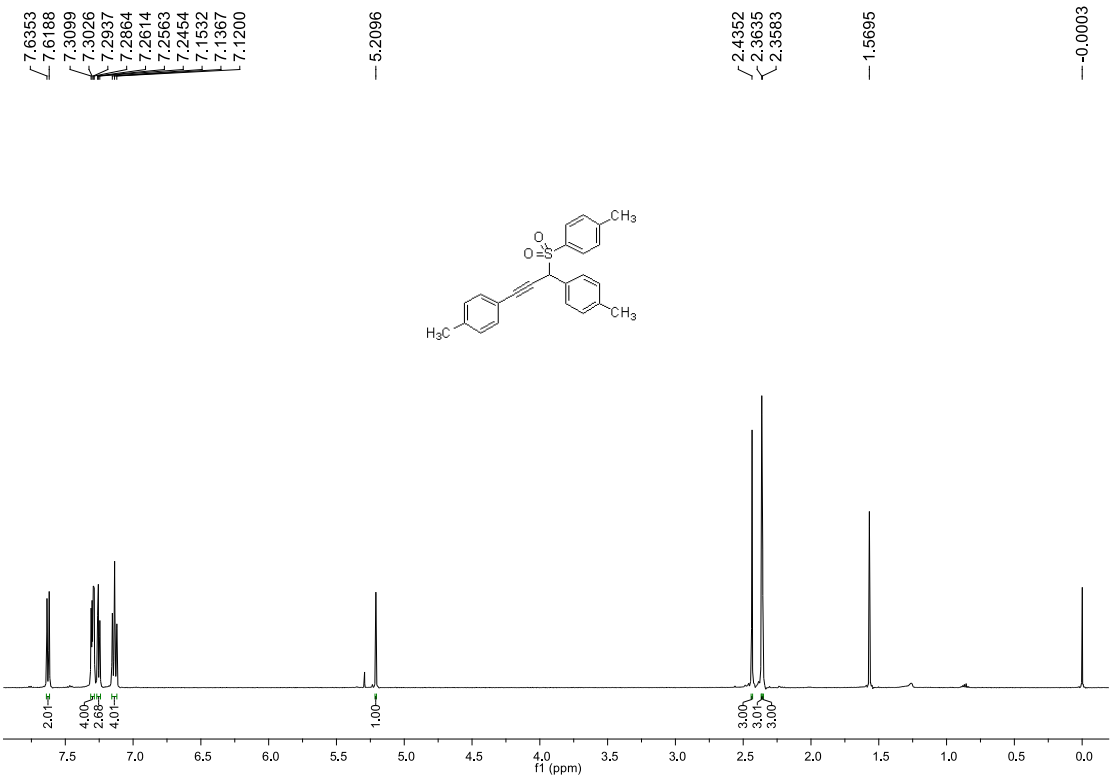
(*E*)-4,4'-(3-cyclopropyl-1-(*p*-tolyl)prop-2-ene-1,2-diyldisulfonyl)bis(methylbenzene) (3ia)

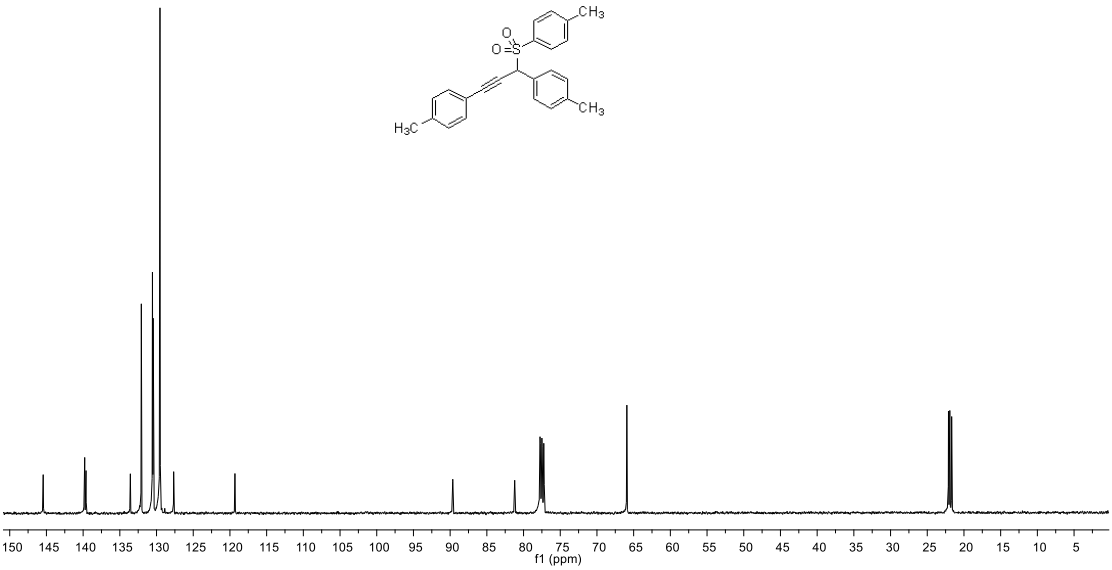




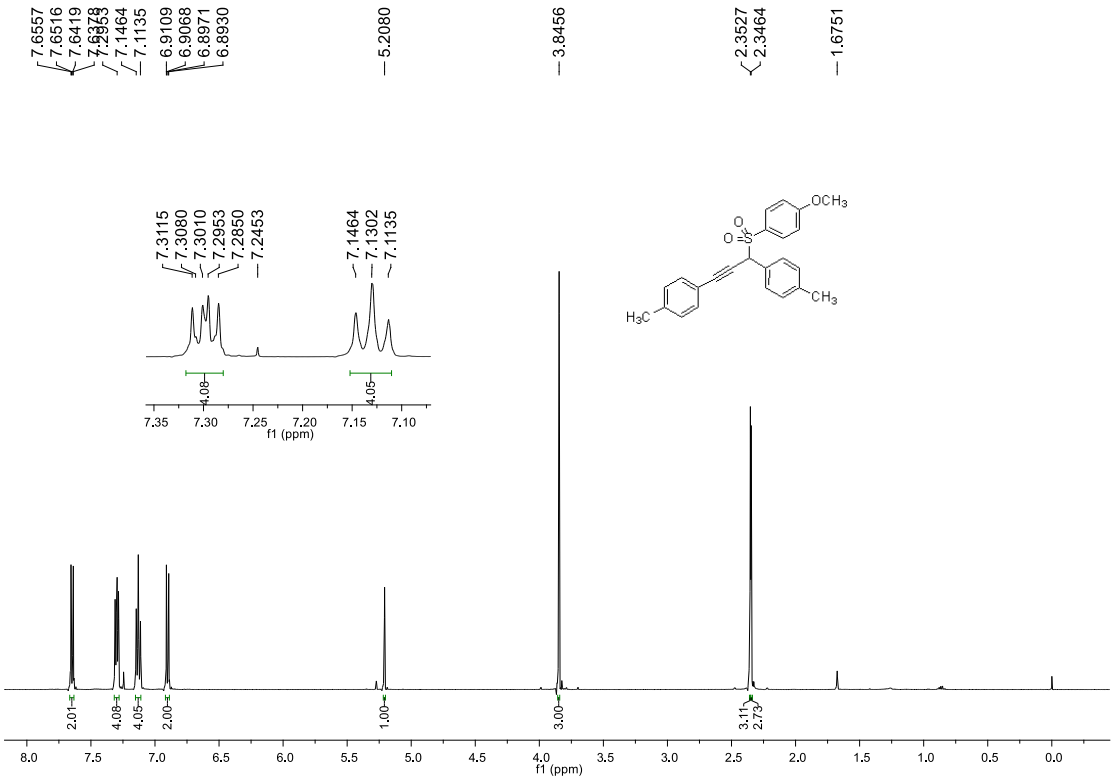
Copies of ^{1}H NMR and ^{13}C NMR spectra of compounds 4

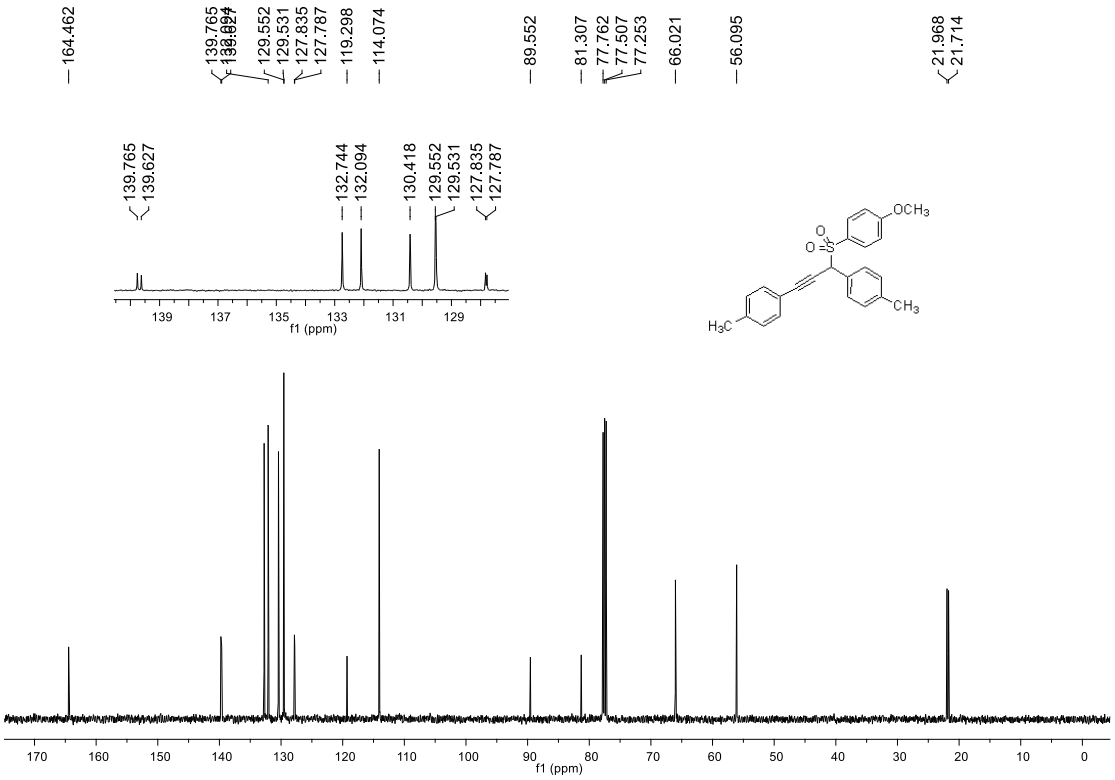
4,4'-(3-Tosylprop-1-yne-1,3-diyl)bis(methylbenzene) (4aa)



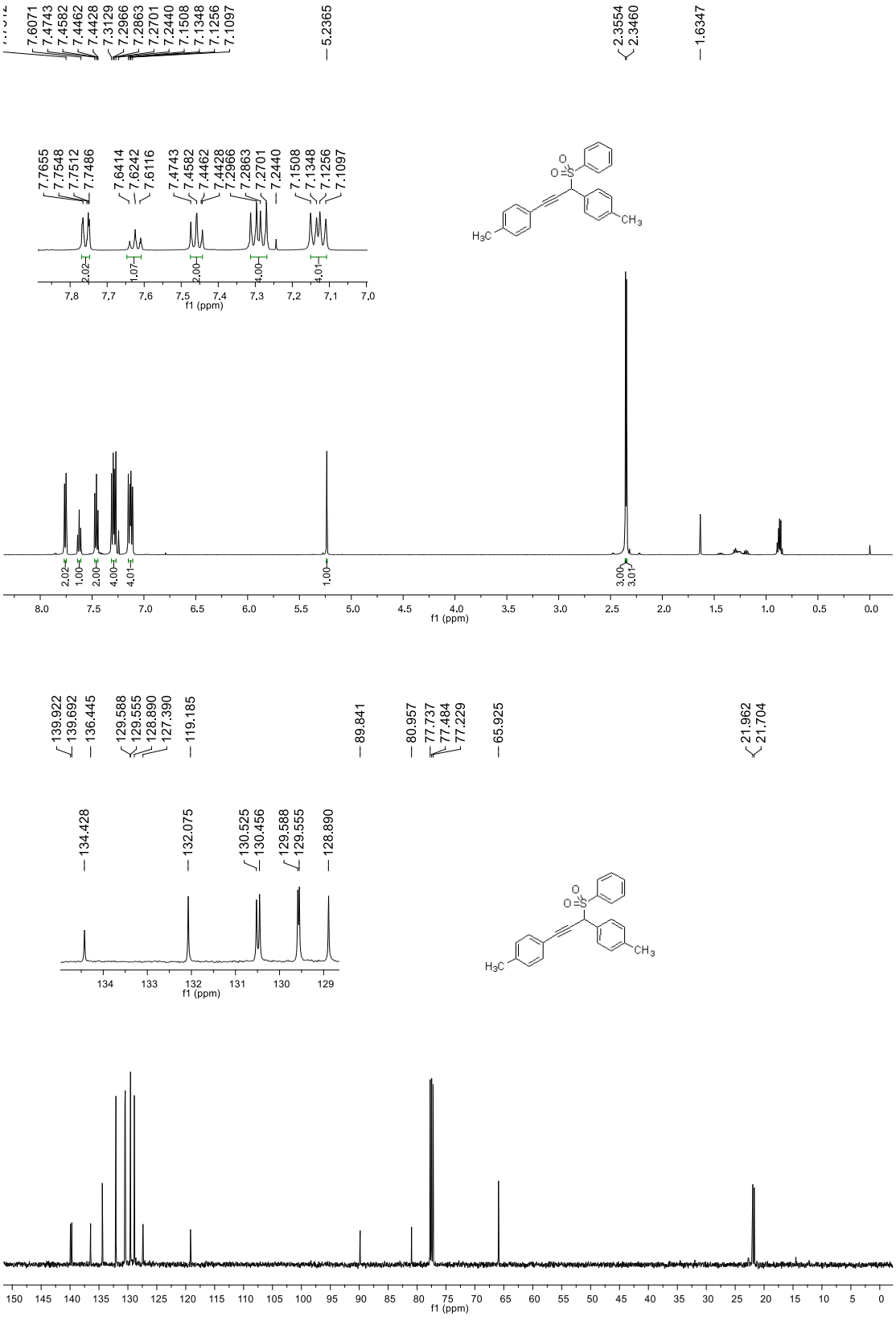


4,4'-(3-((4-Methoxyphenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ab)

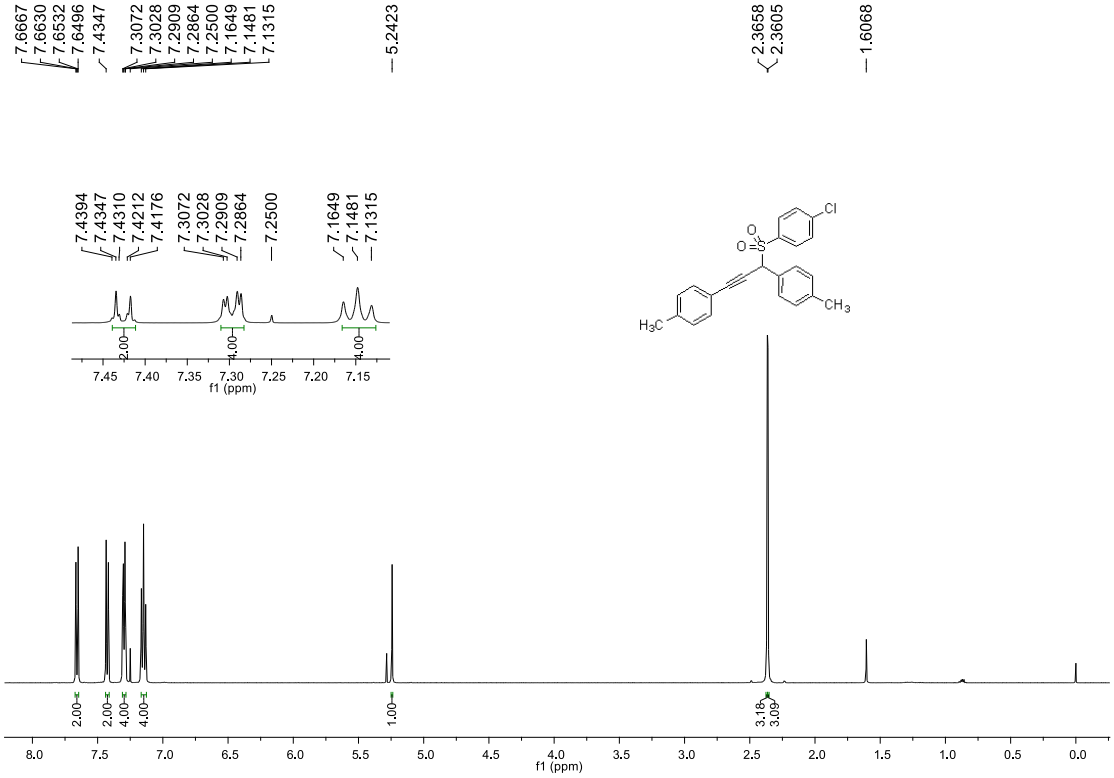


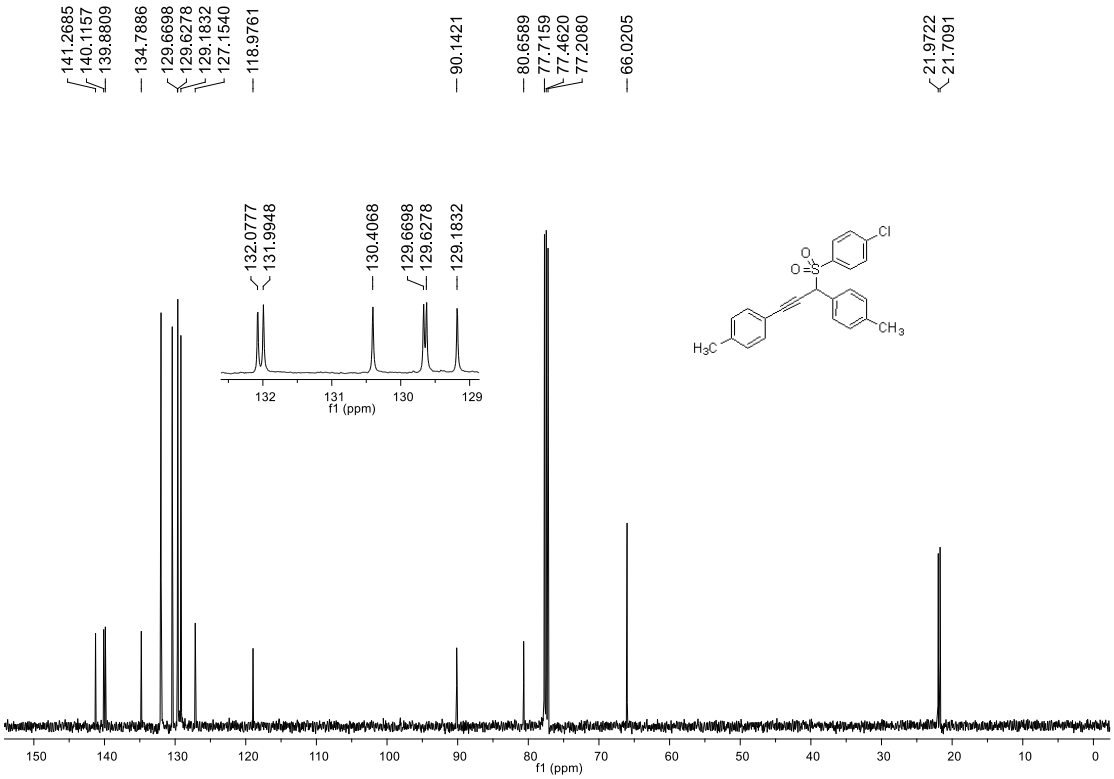


4,4'-(3-(Phenylsulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ac)

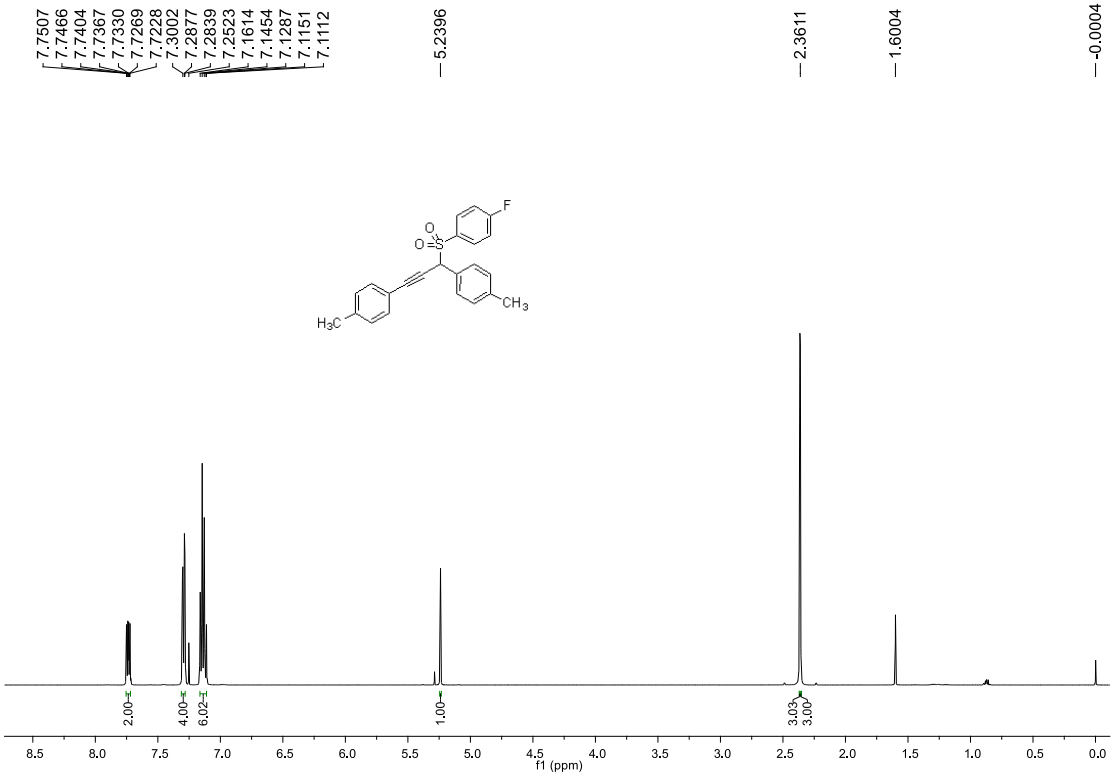


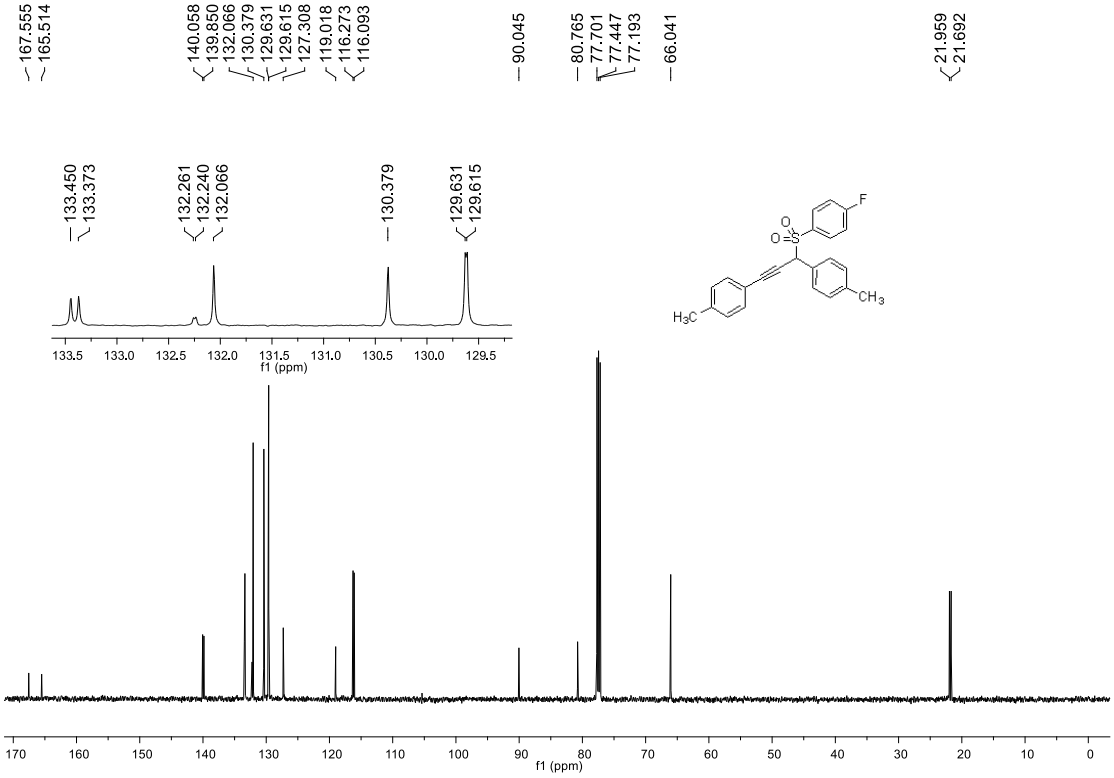
4,4'-(3-((4-Chlorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ad)

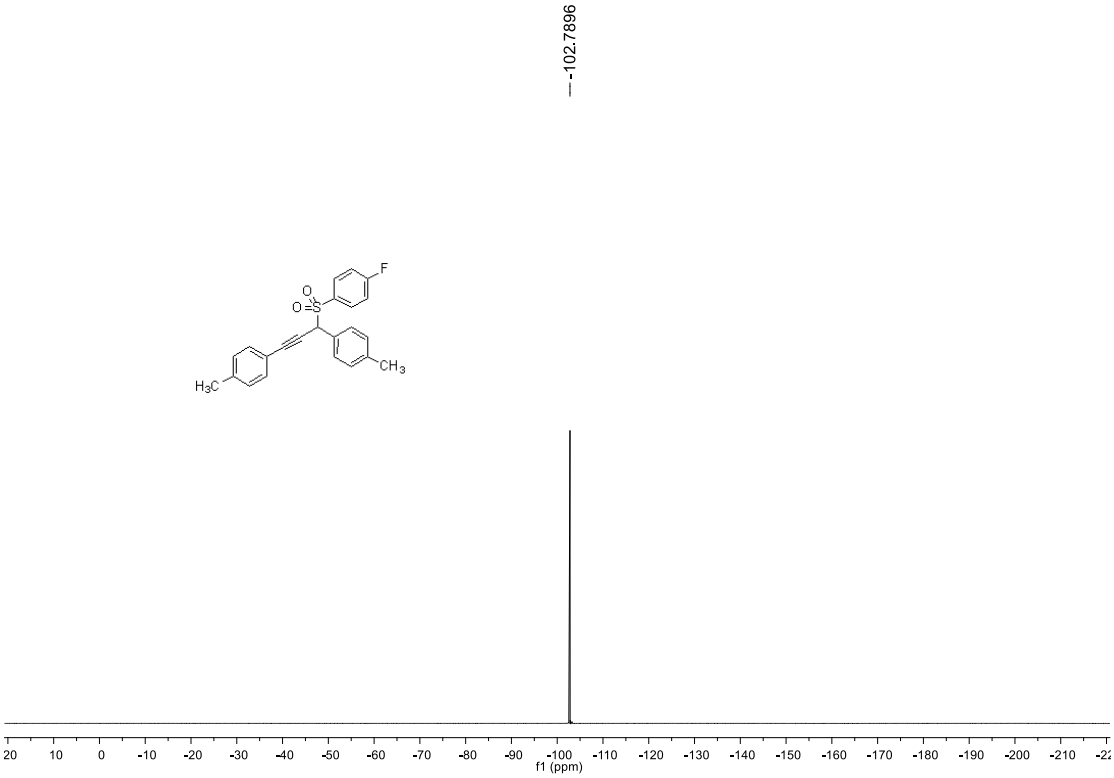




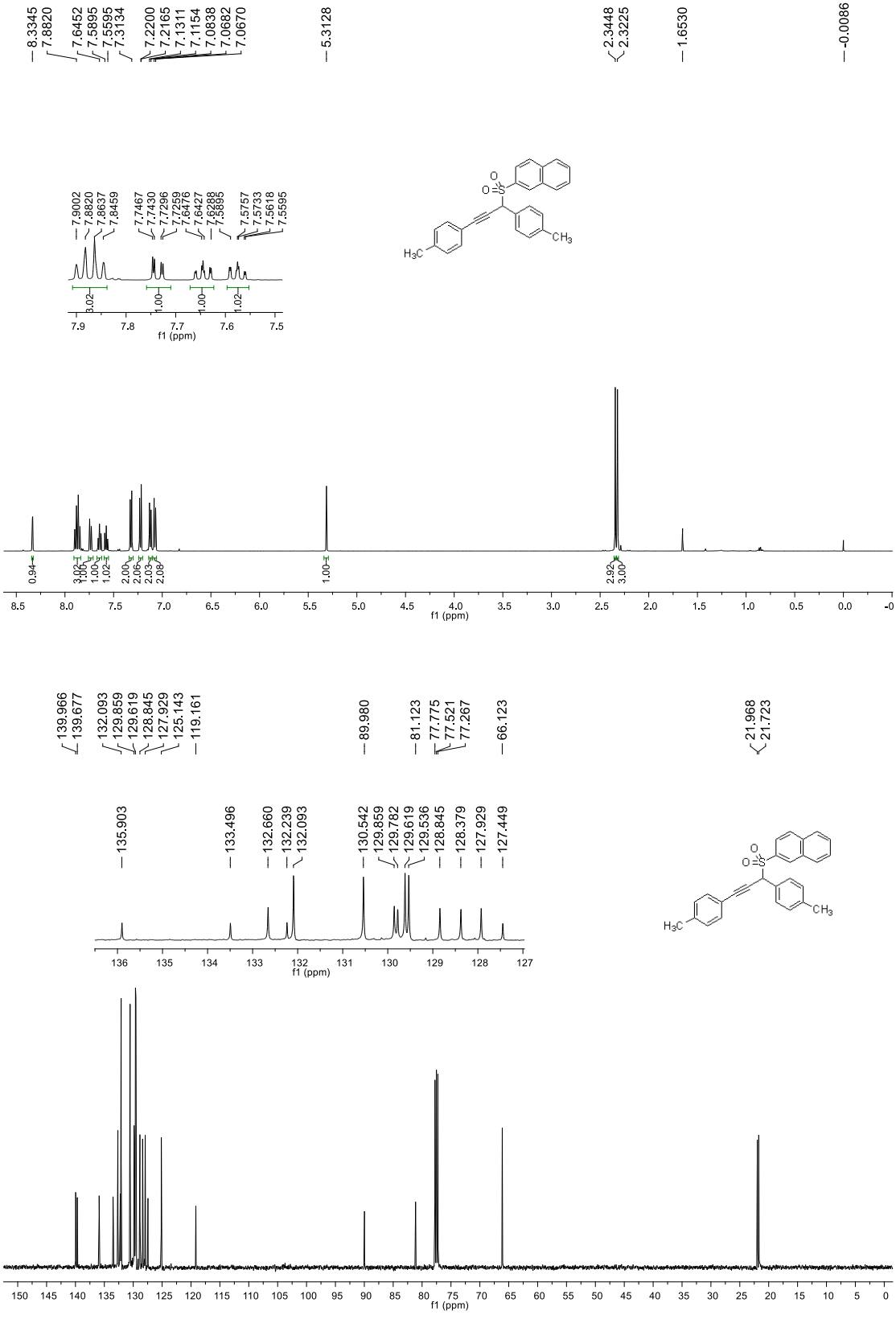
4,4'-(3-((4-Fluorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ae)



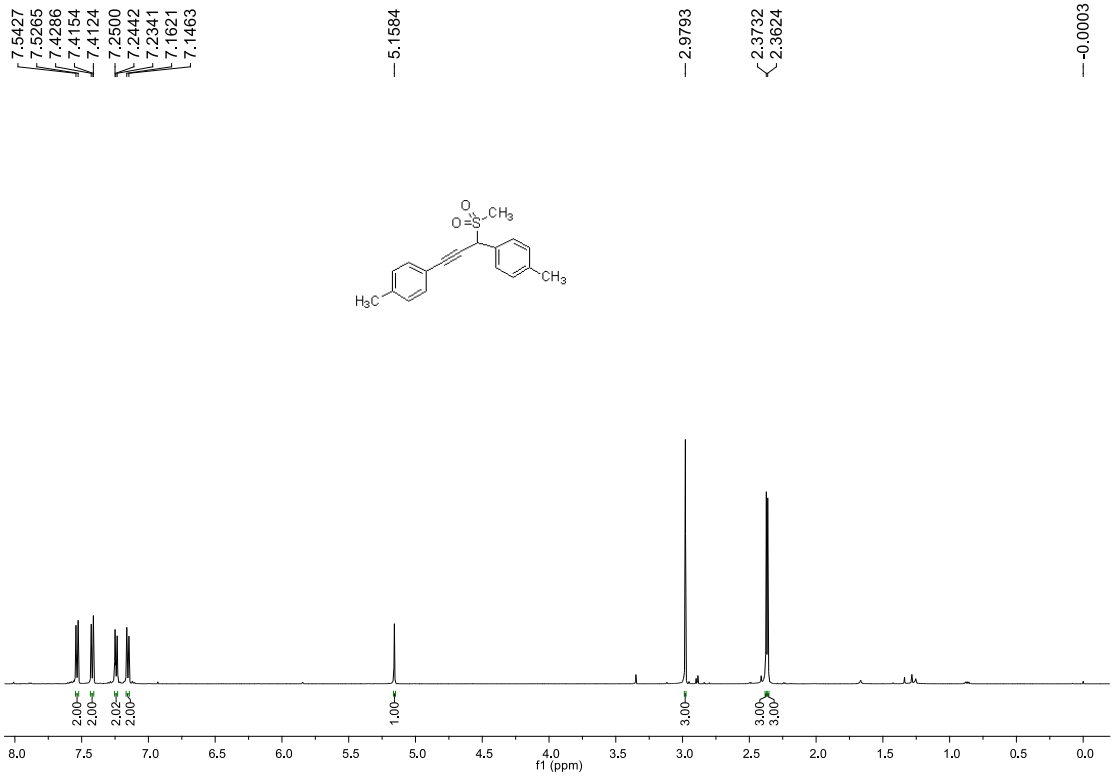


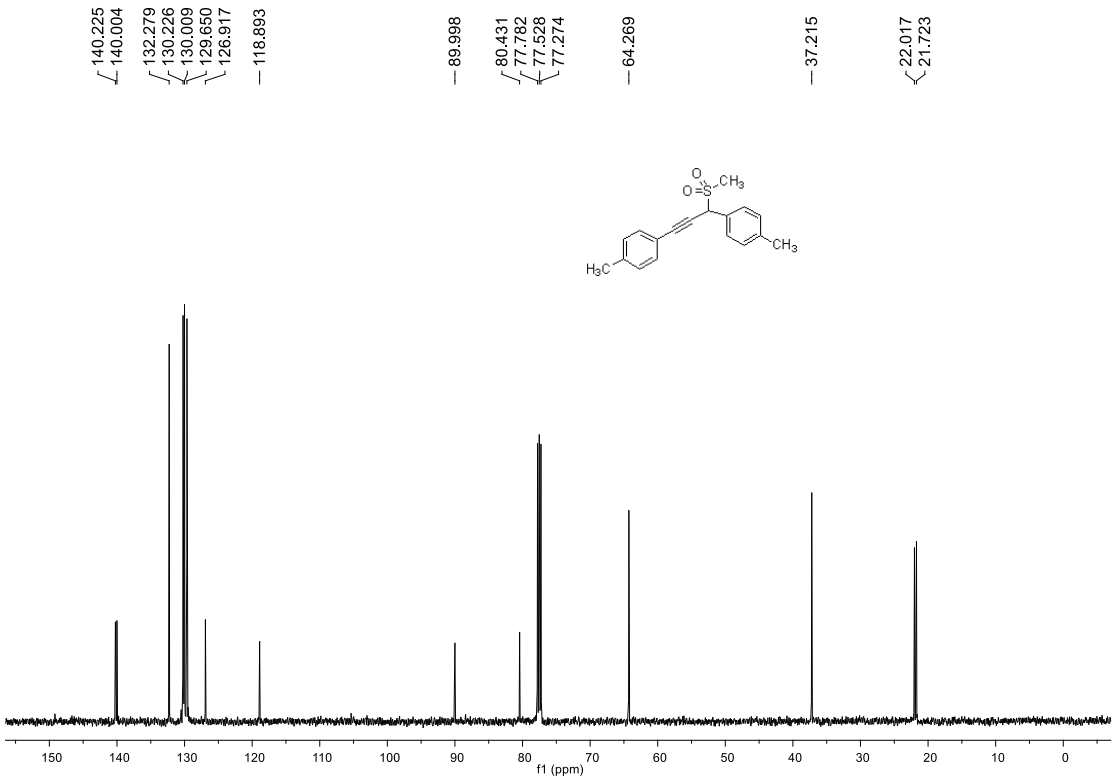

-102.7896
F
O
O=S
CH3
H3C
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

2-((1,3-Di-*p*-tolylprop-2-yn-1-yl)sulfonyl)naphthalene (4af)

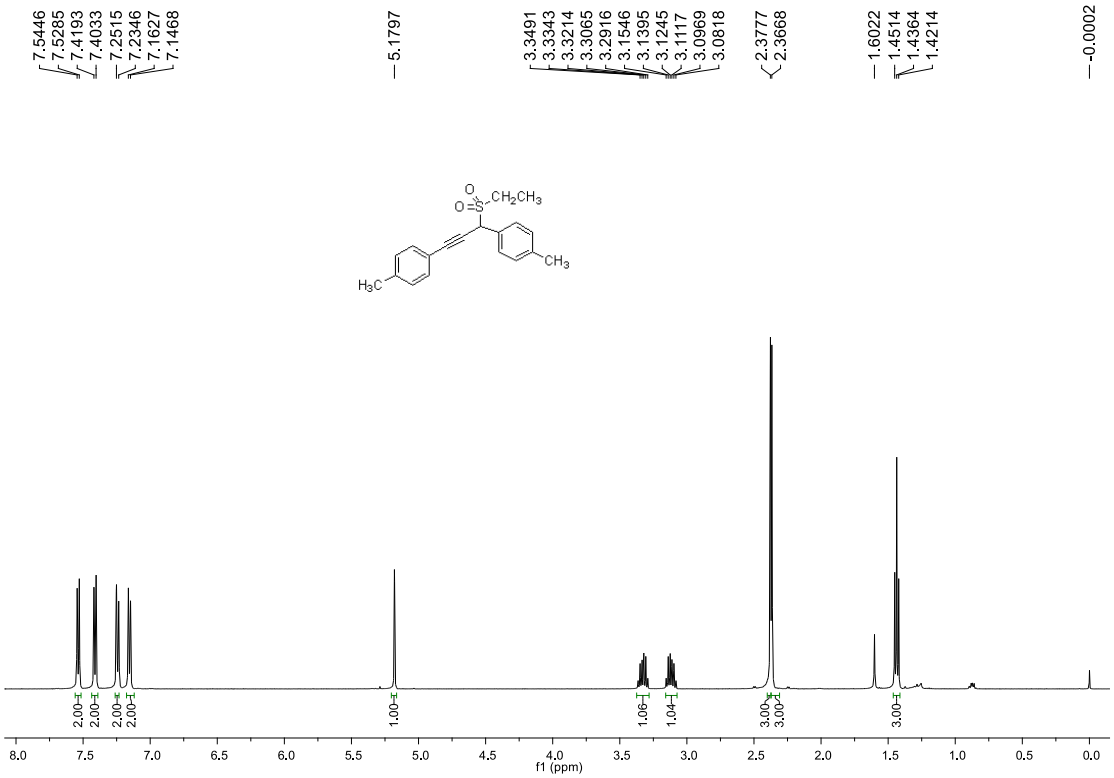


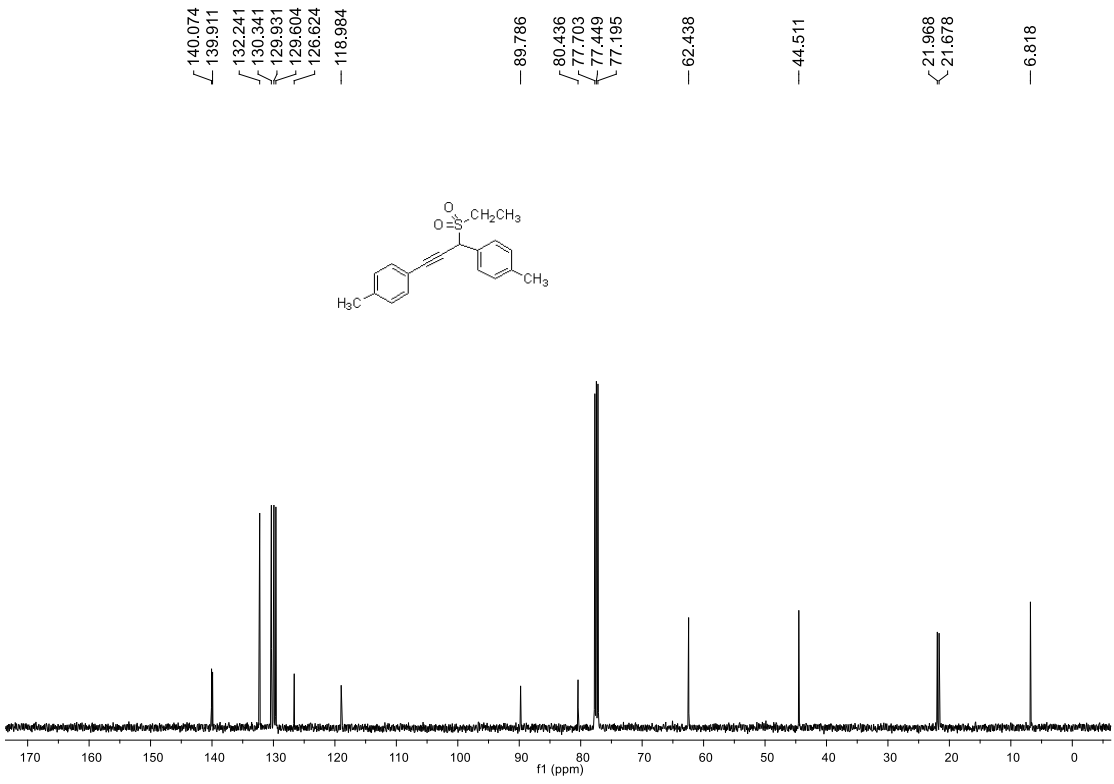
4,4'-(3-(Methylsulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ag)



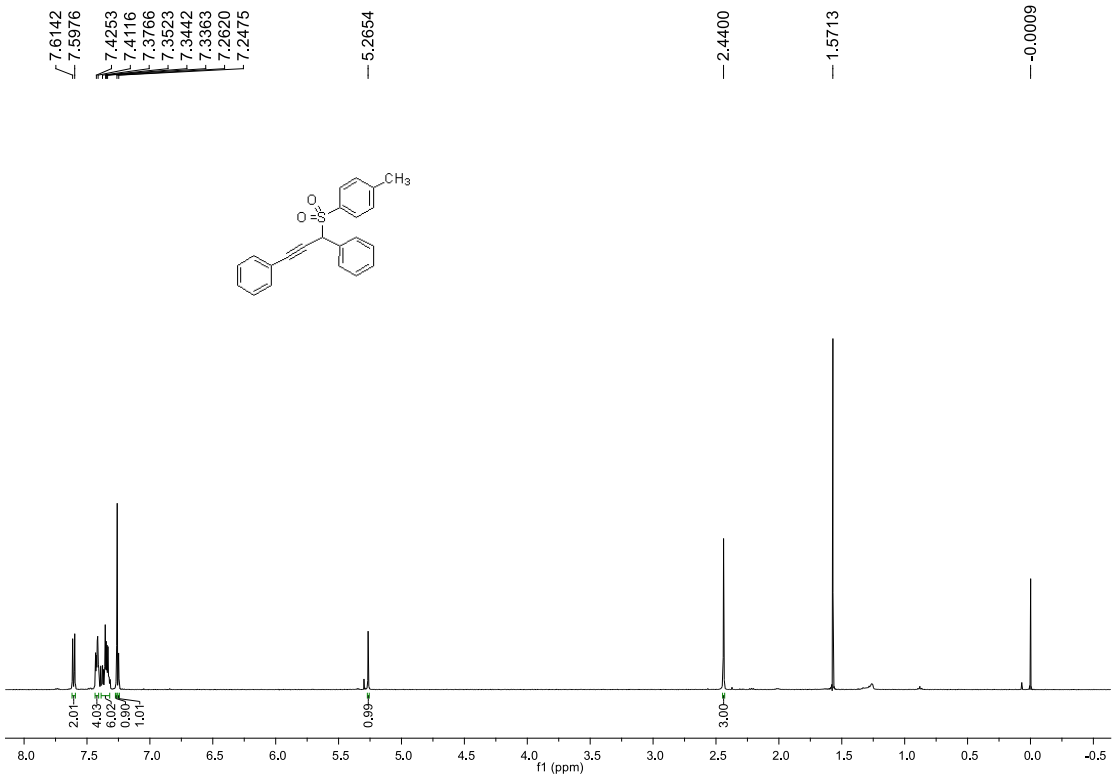


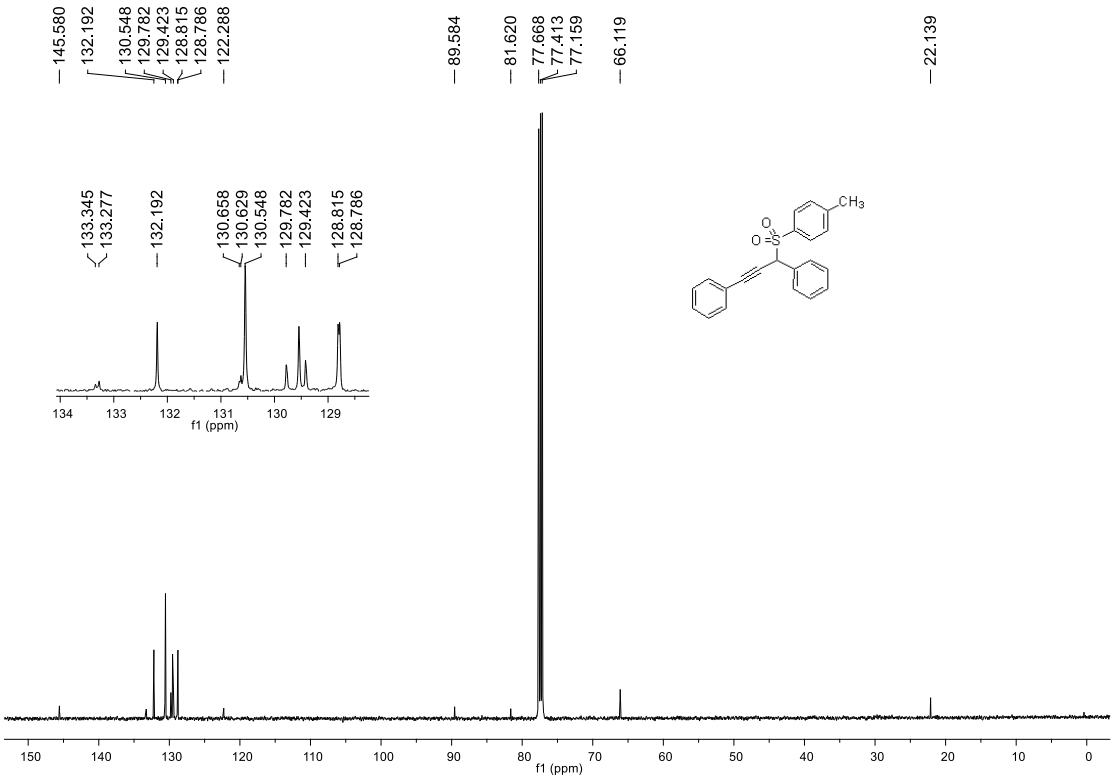
4,4'-(3-(Ethylsulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4ah)



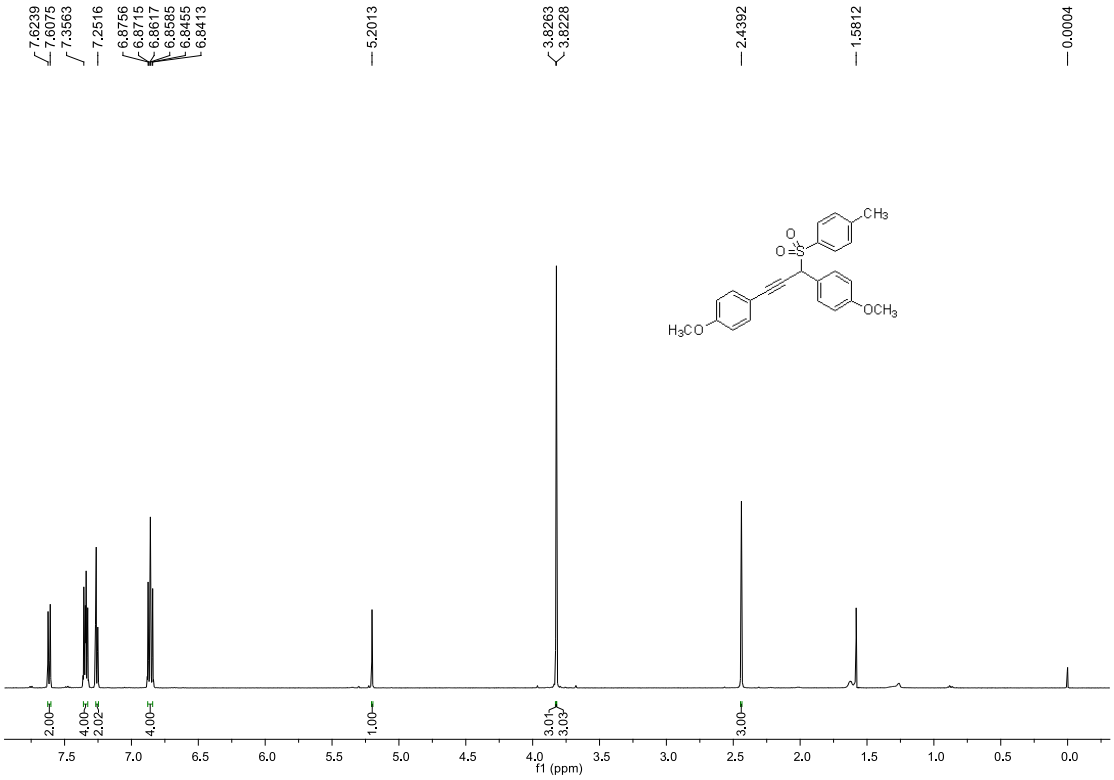


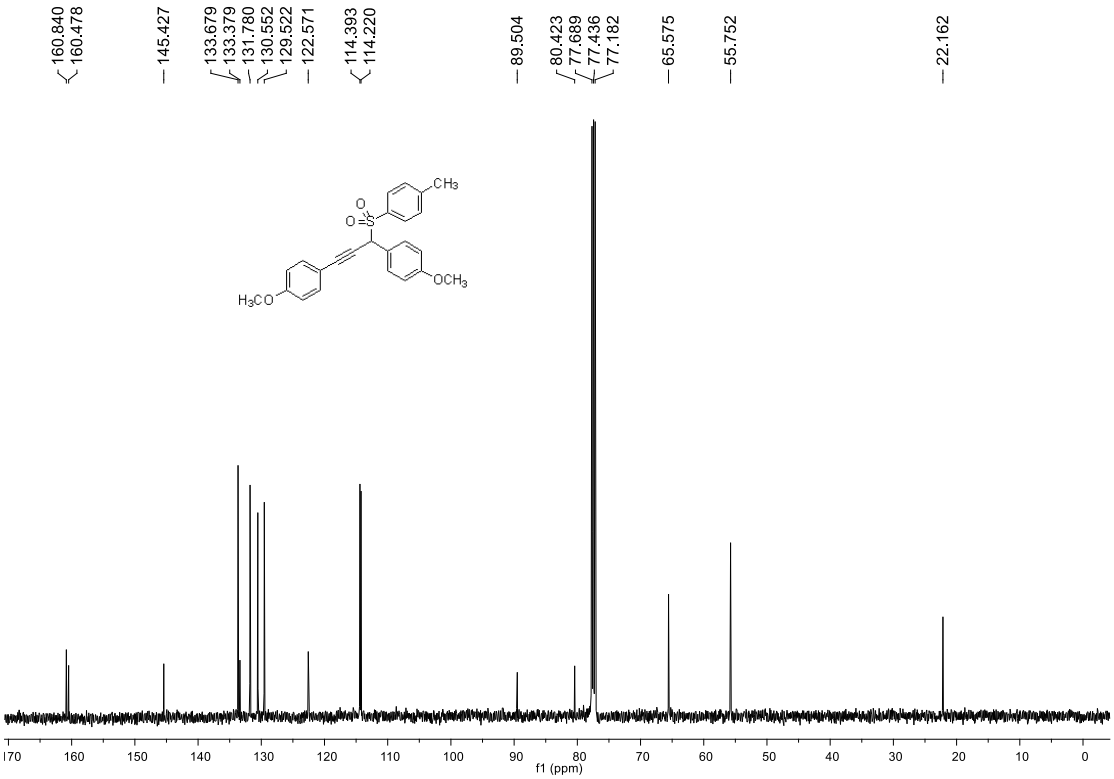
(3-Tosylprop-1-yne-1,3-diyl)dibenzene (4ba)



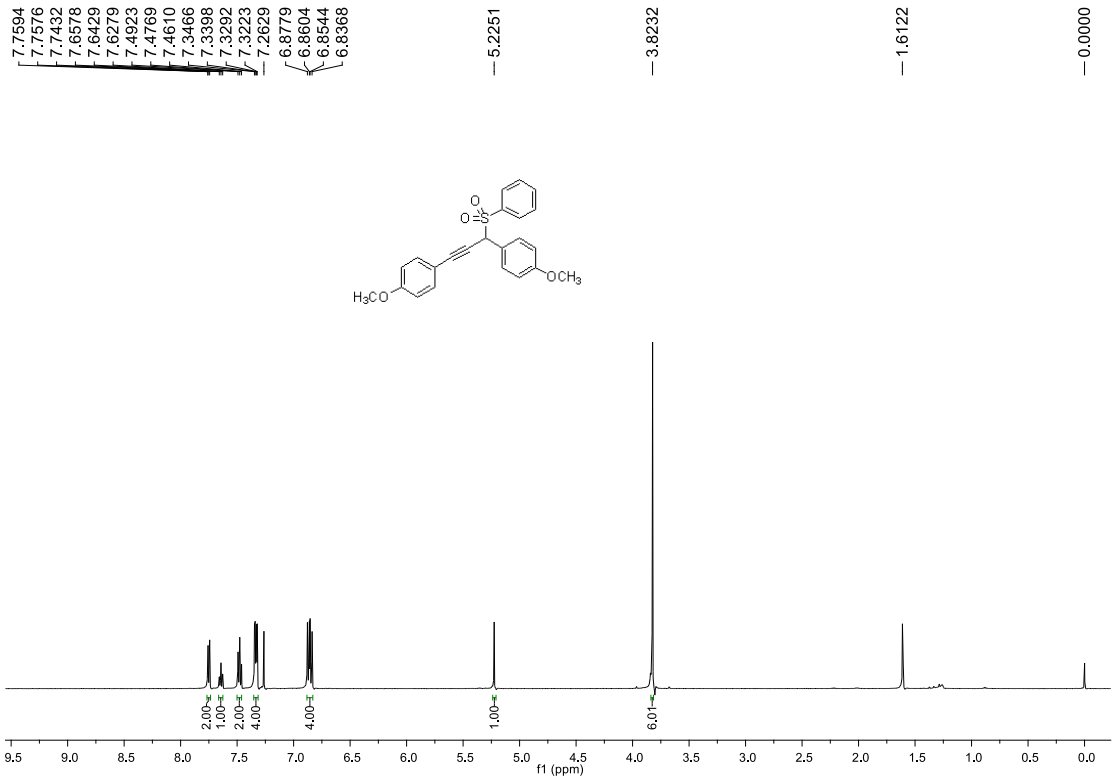


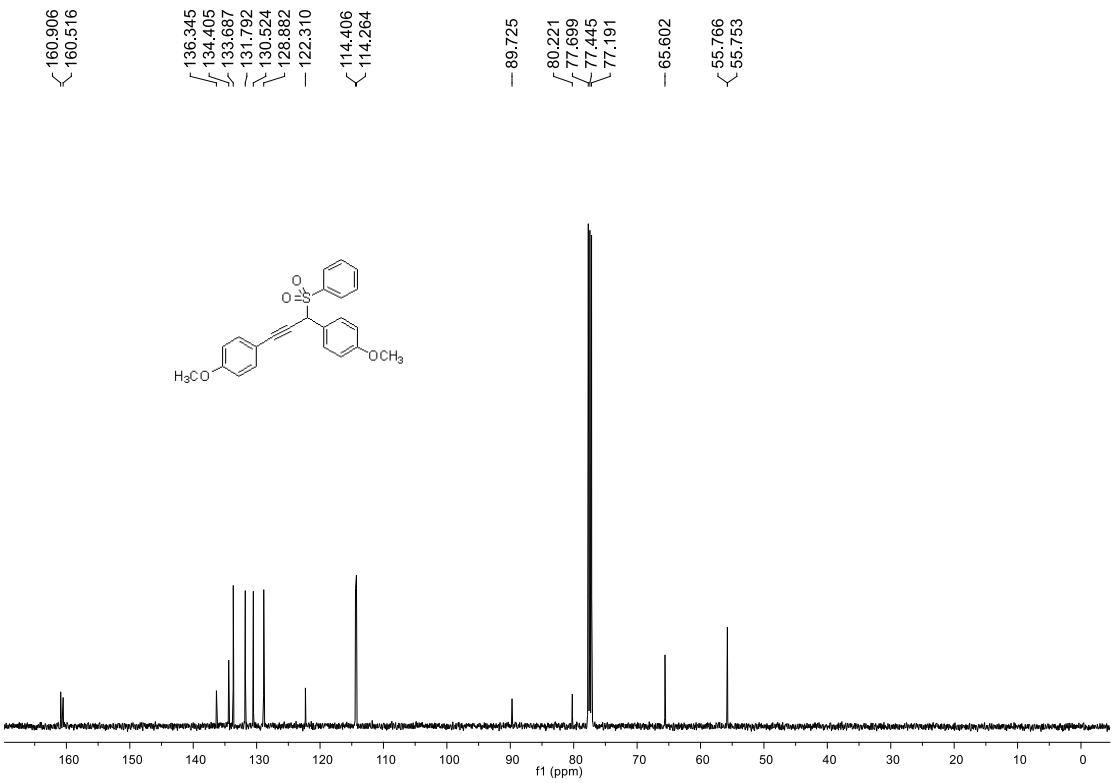
4,4'-(3-Tosylprop-1-yne-1,3-diyl)bis(methoxybenzene) (4ca)



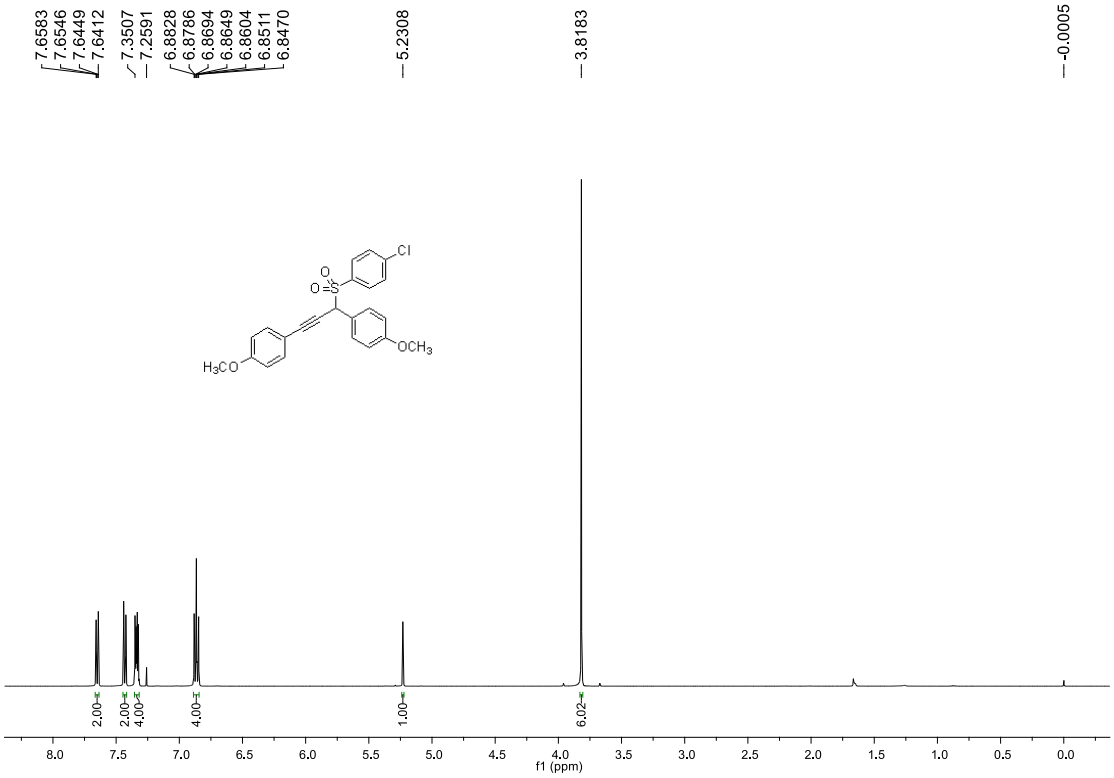


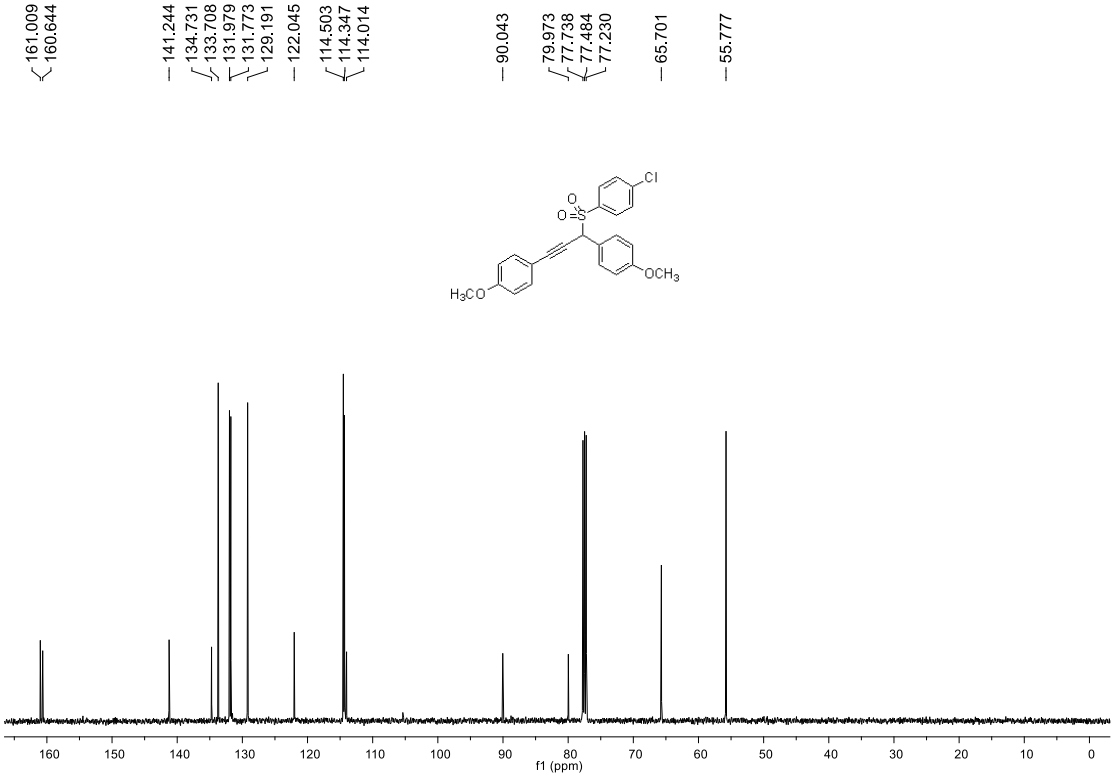
4,4'-(3-(Phenylsulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4cb)



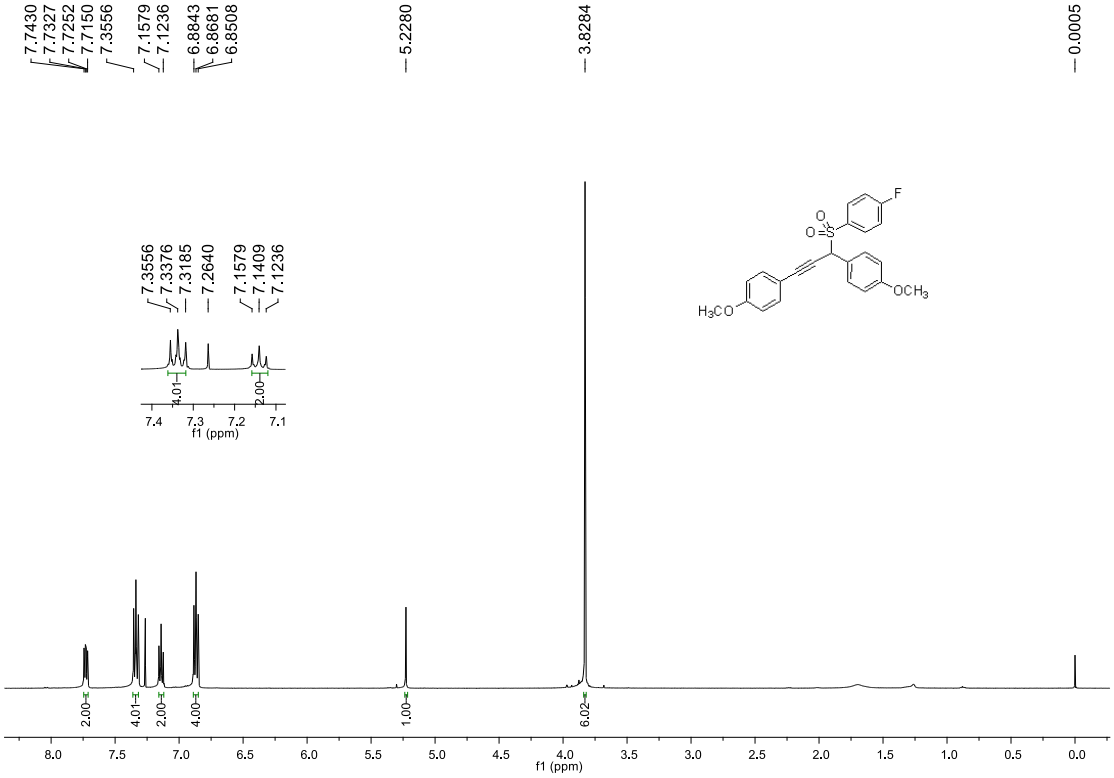


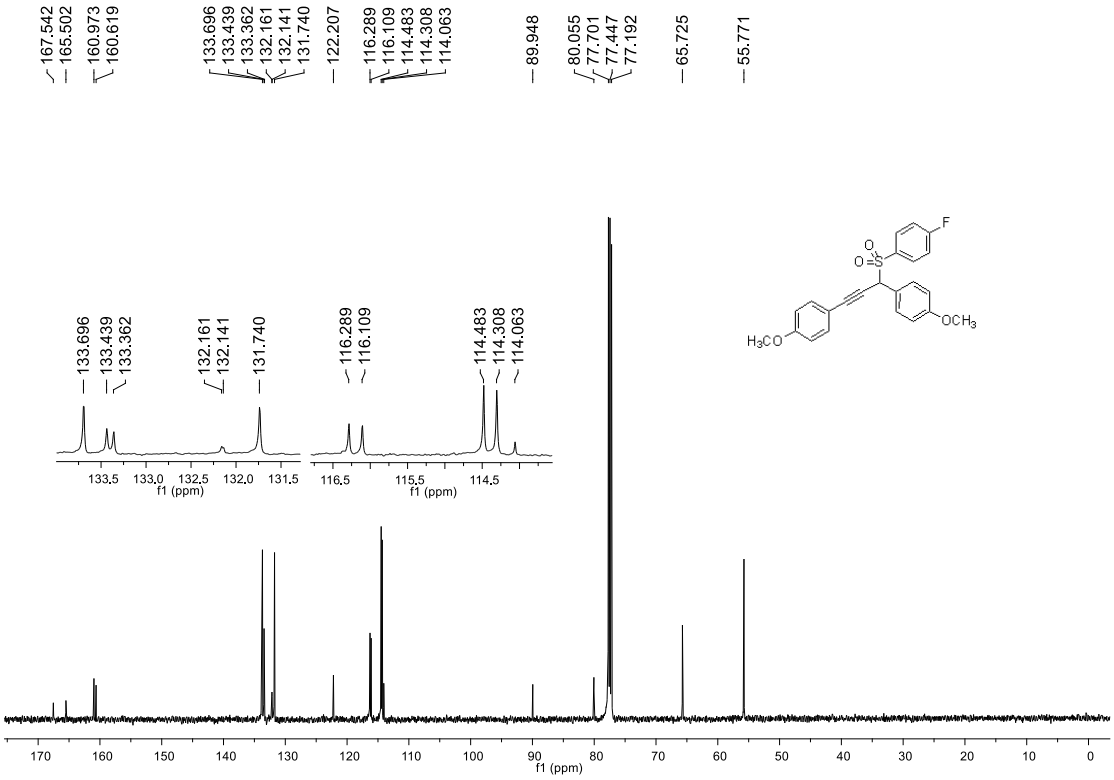
4,4'-(3-((4-Chlorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4cc)

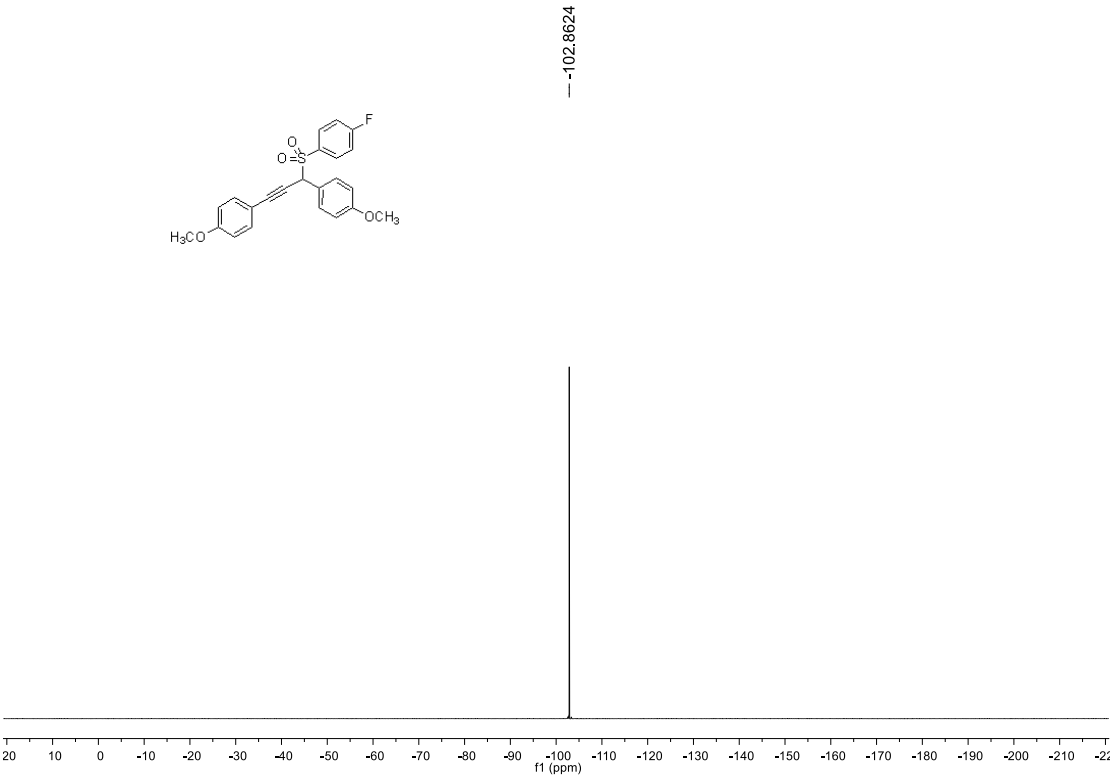




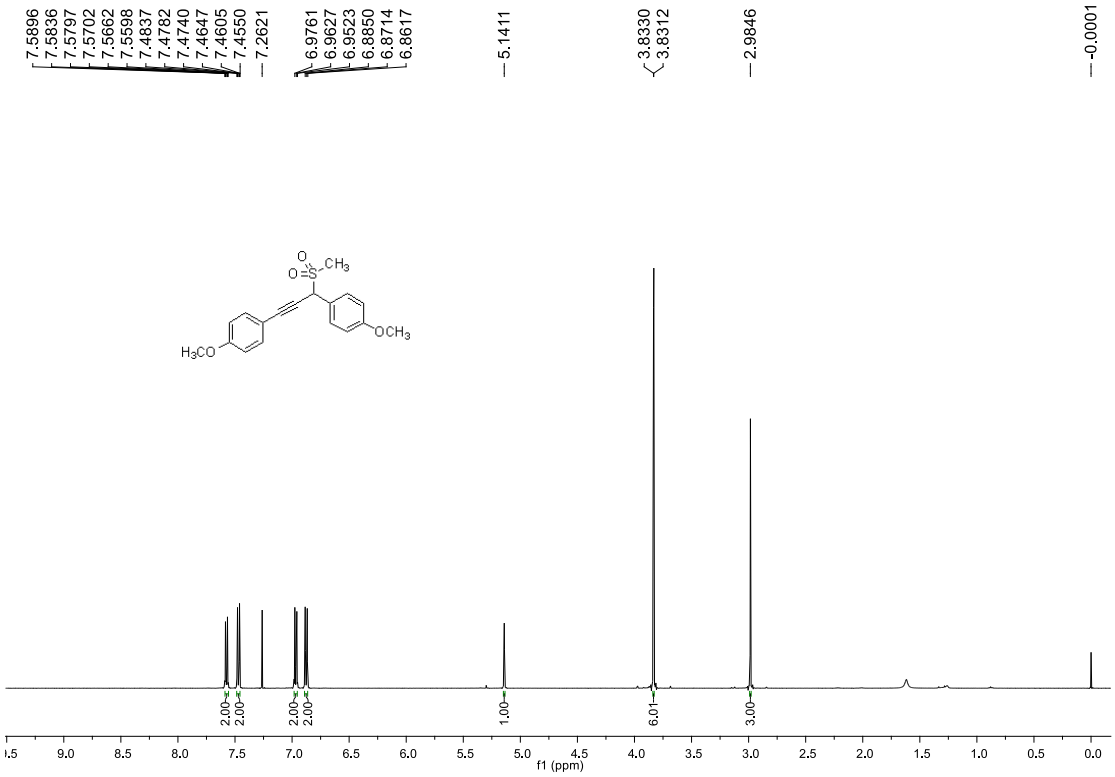
4,4'-(3-((4-Fluorophenyl)sulfonyl)prop-1-yne-1,3-diyl)bis(methylbenzene) (4cd)

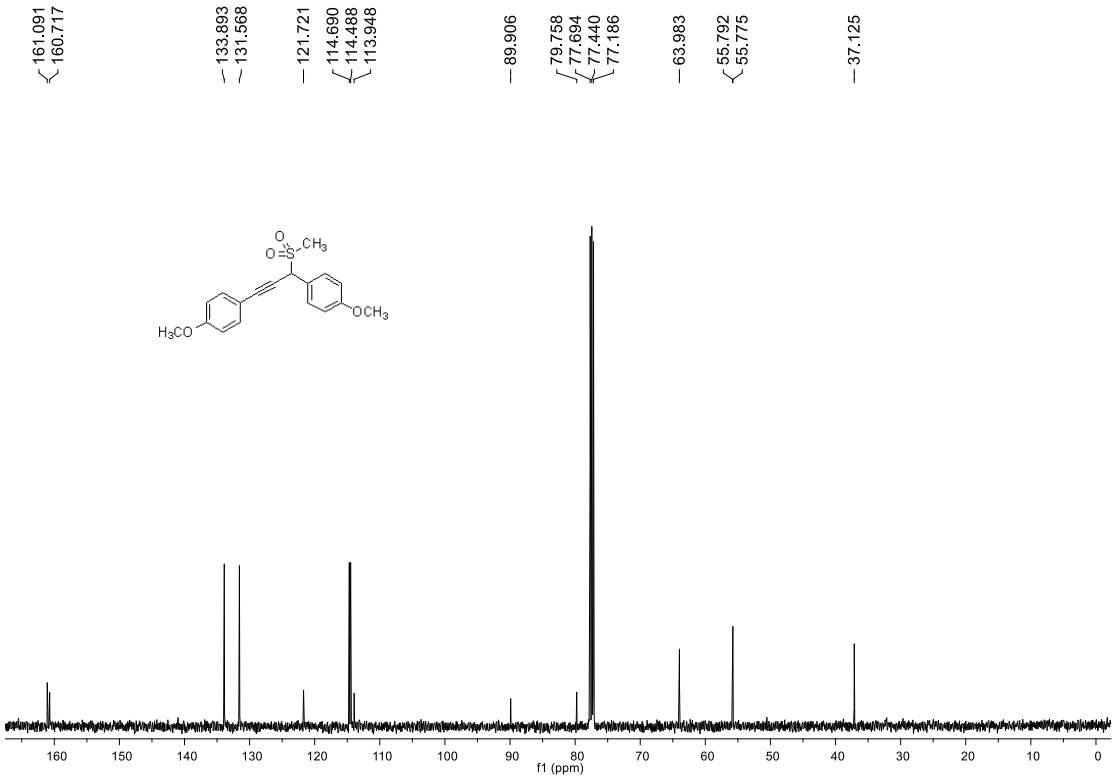




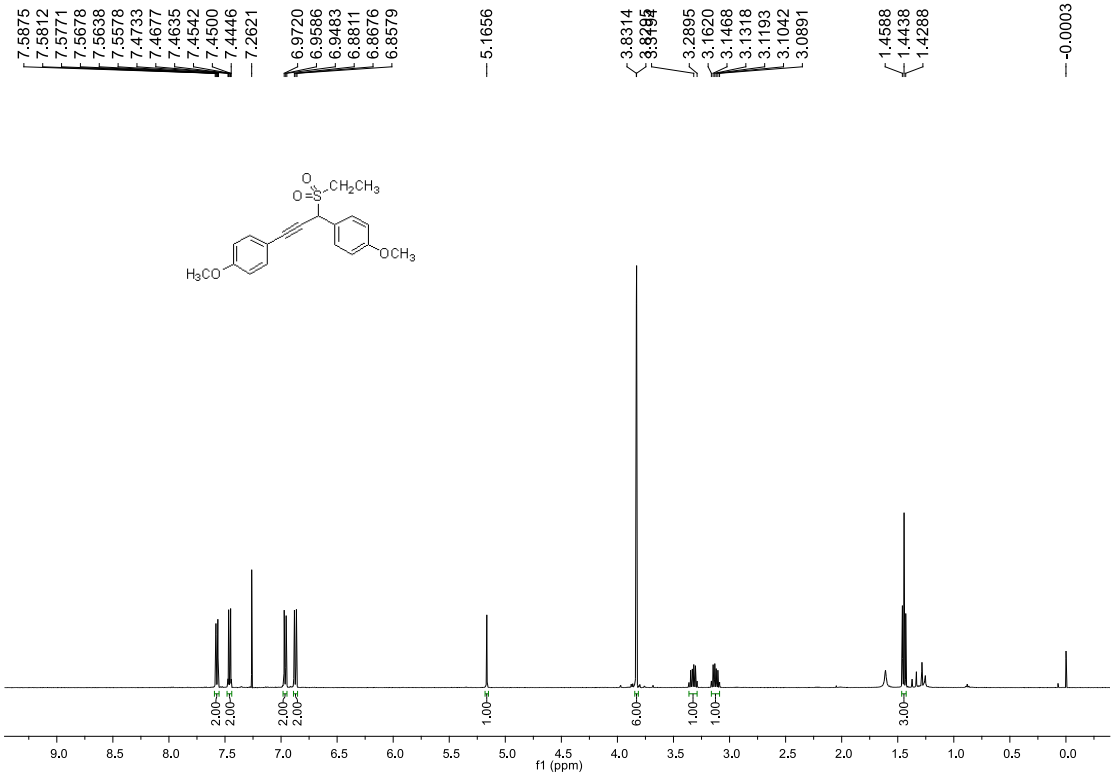

-102.8624
F
O
O=S
OCH3
H3CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

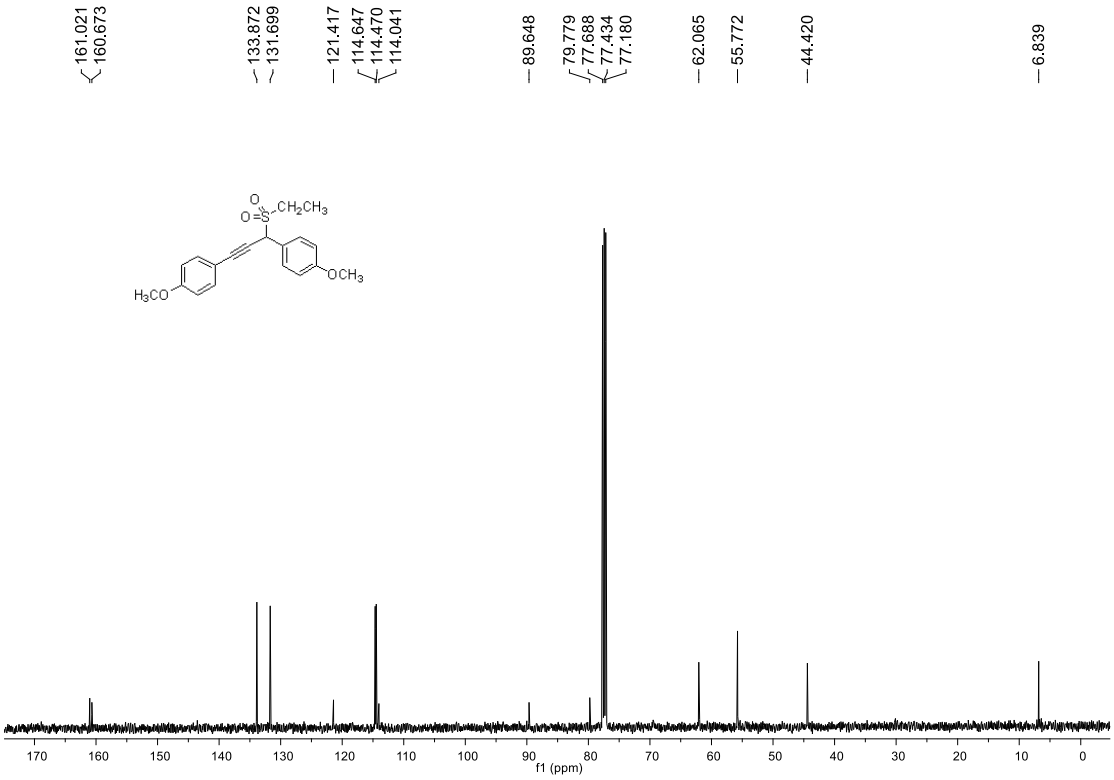
4,4'-(3-(Methylsulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4ce)



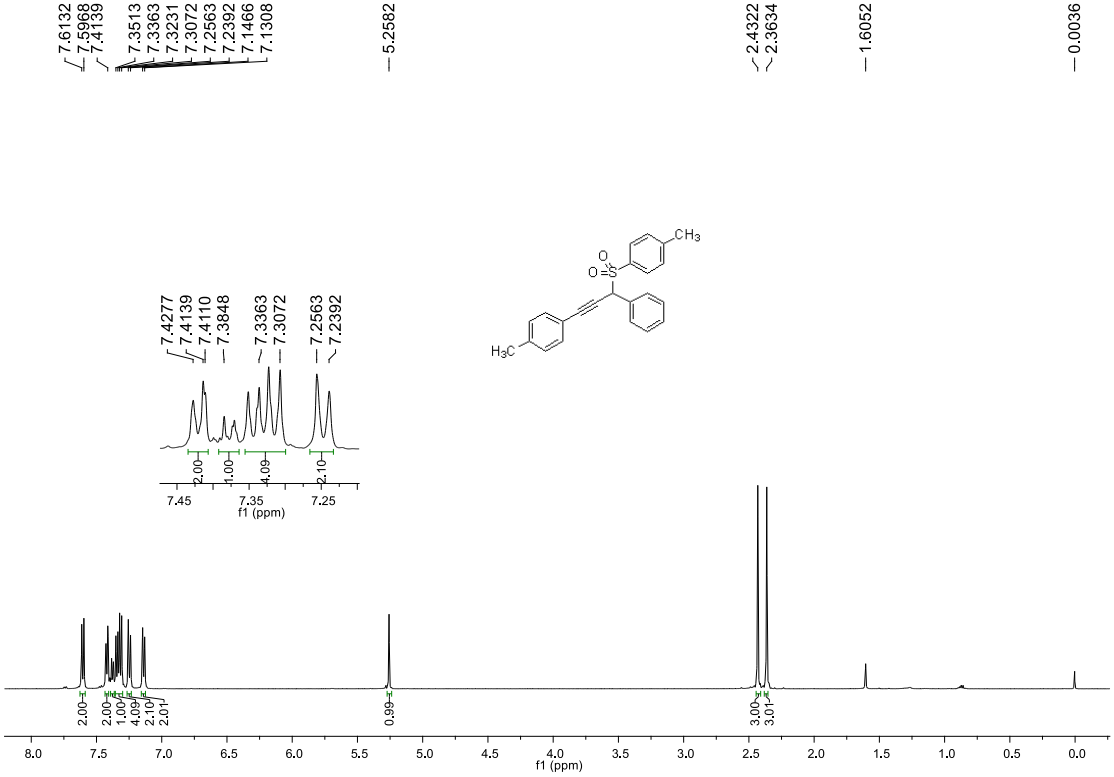


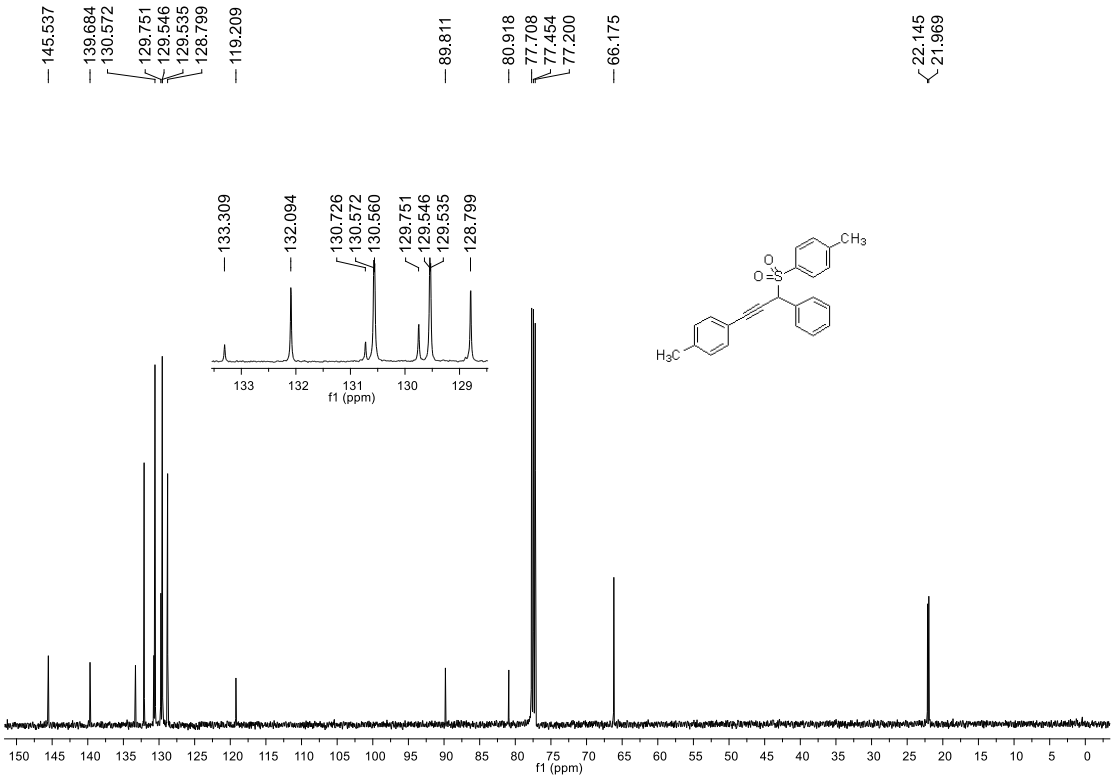
4,4'-(3-(Ethylsulfonyl)prop-1-yne-1,3-diyl)bis(methoxybenzene) (4cf)



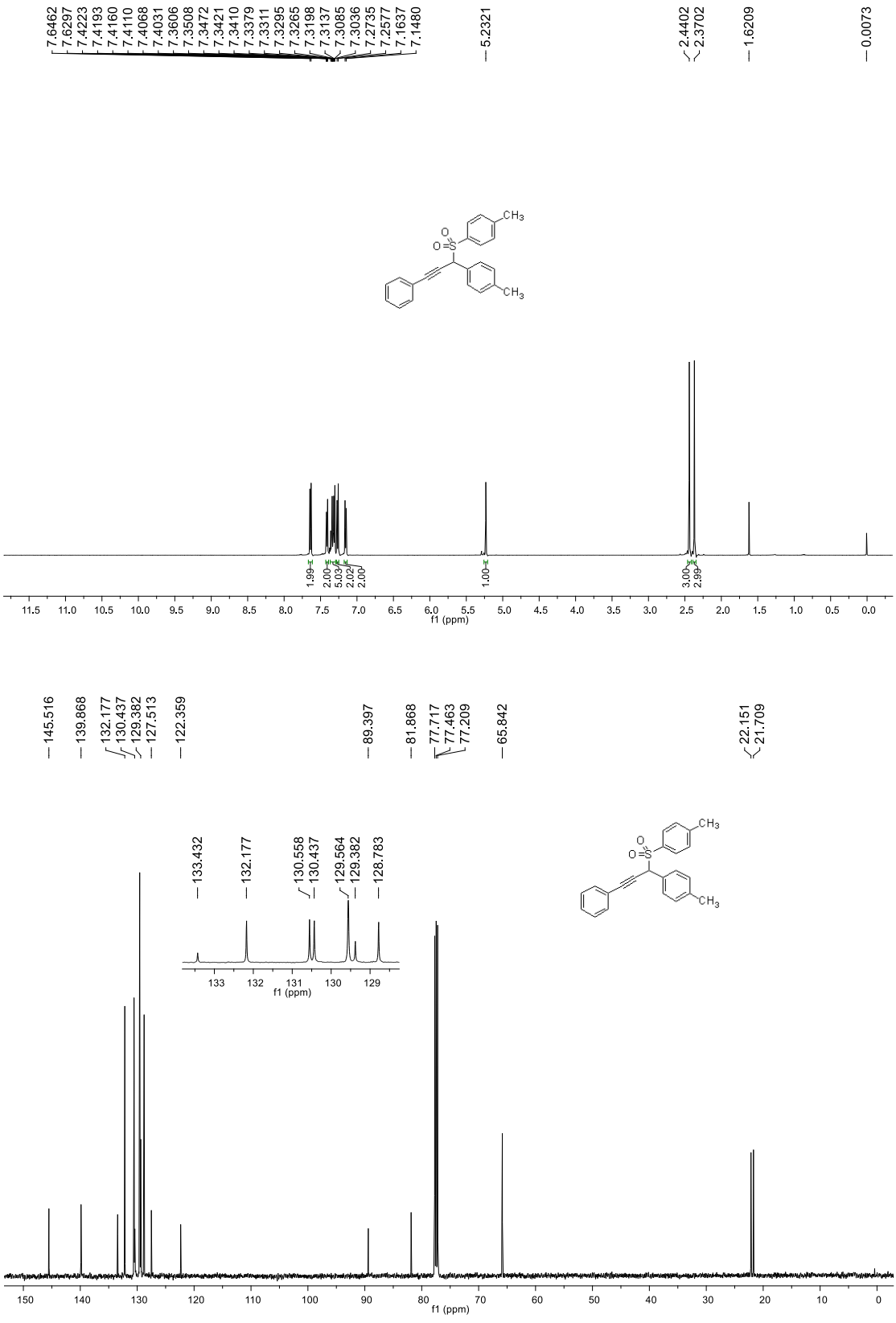


1-Methyl-4-((1-phenyl-3-(*p*-tolyl)prop-2-yn-1-yl)sulfonyl)benzene (4da)

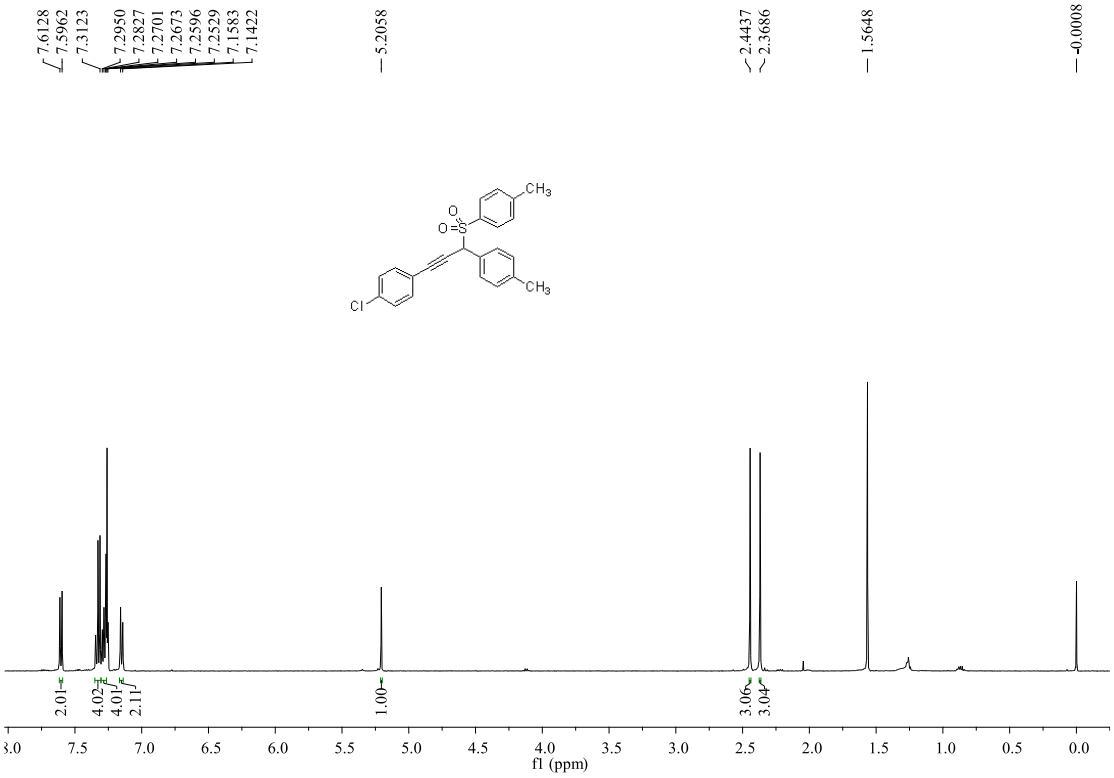


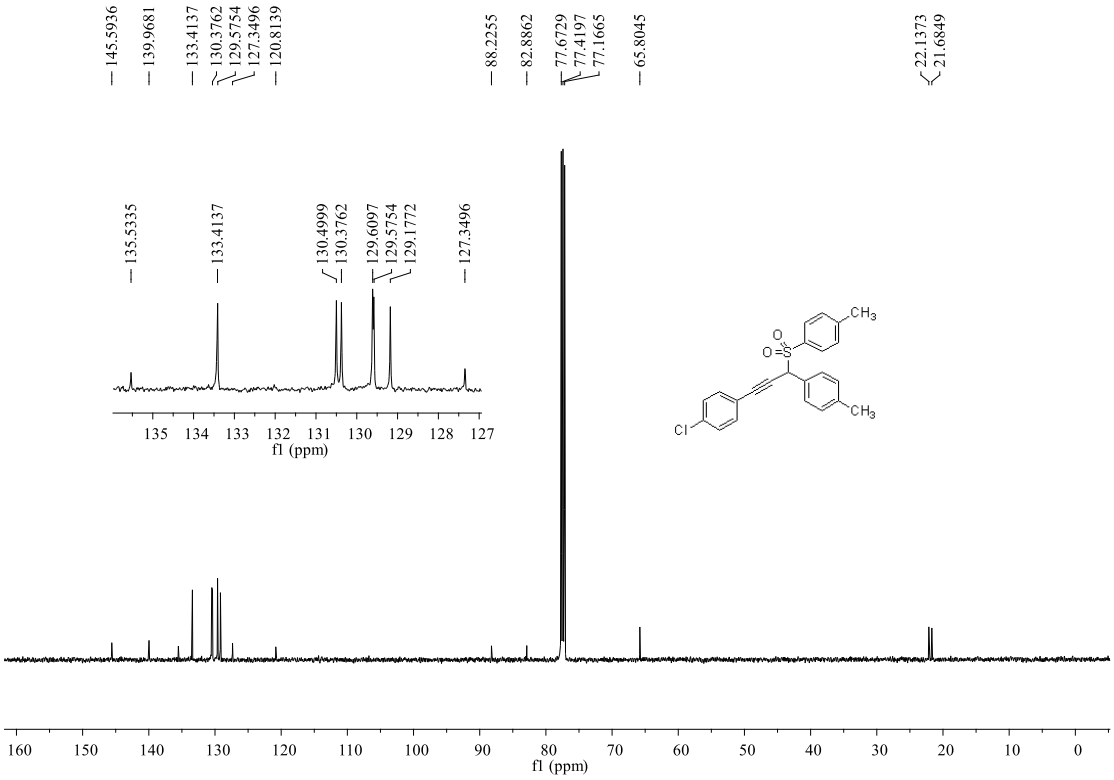


1-Methyl-4-((3-phenyl-1-(*p*-tolyl)prop-2-yn-1-yl)sulfonyl)benzene (4ea)

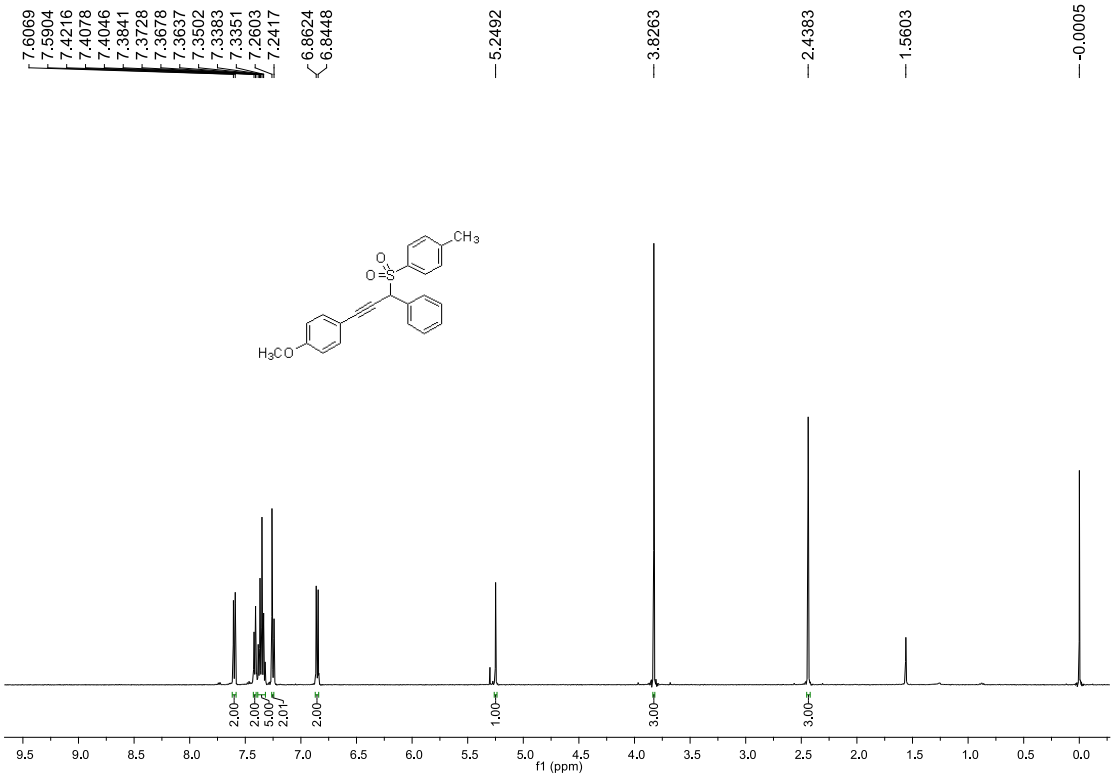


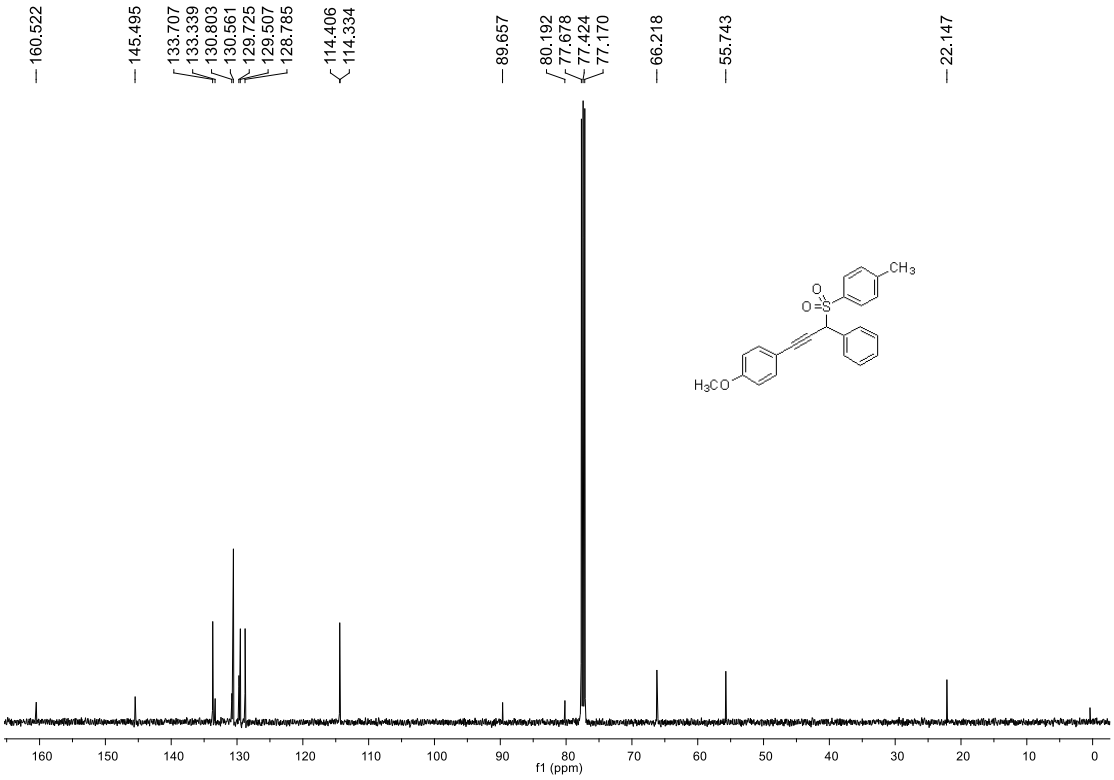
1-Chloro-4-(3-(*p*-tolyl)-3-tosylprop-1-yn-1-yl)benzene (4fa)



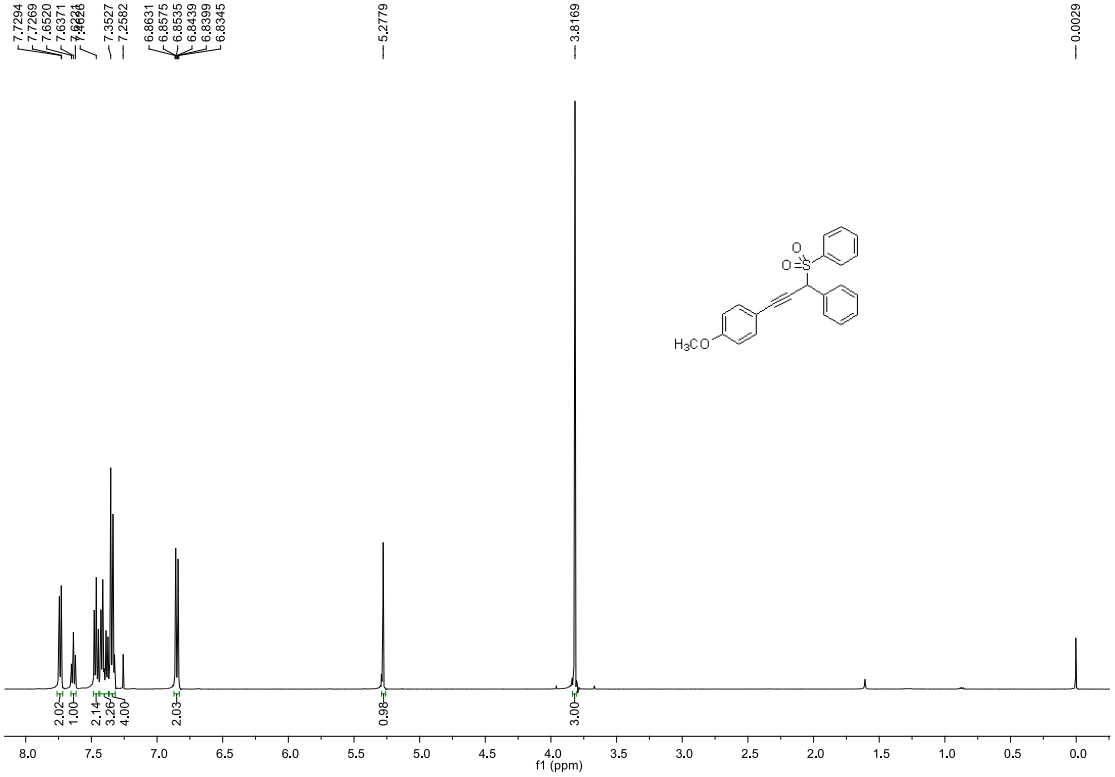


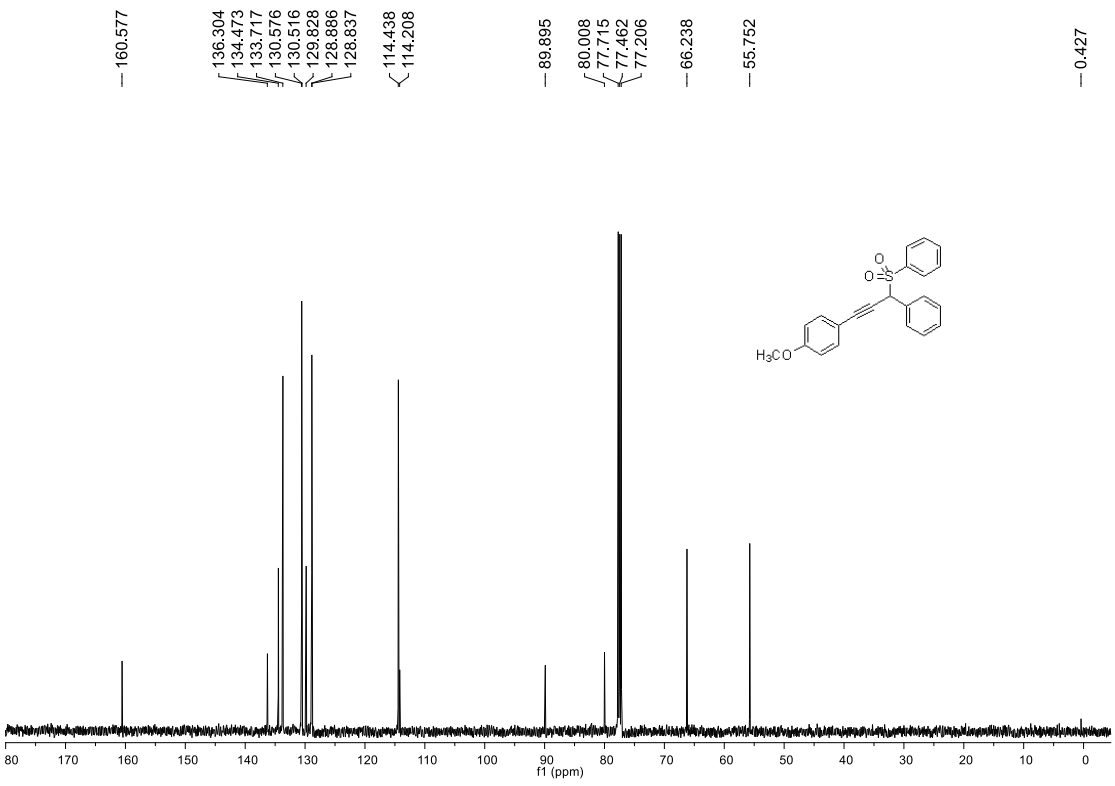
1-Methoxy-4-(3-phenyl-3-tosylprop-1-yn-1-yl)benzene (4ga)



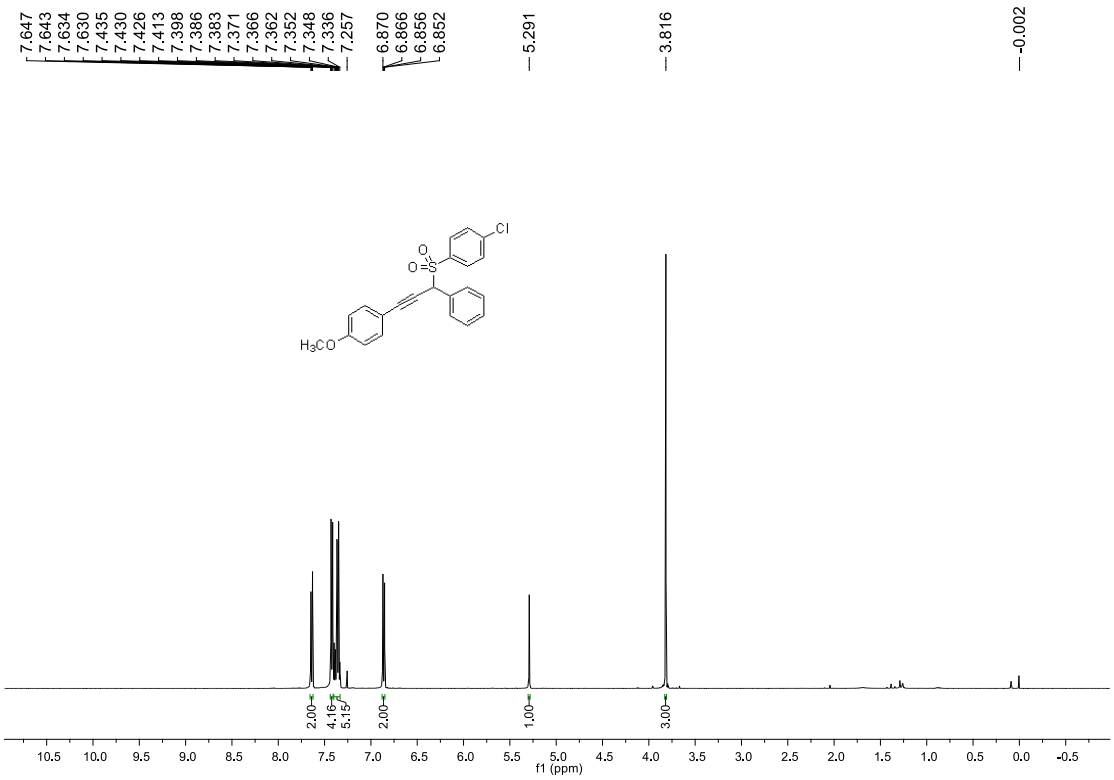


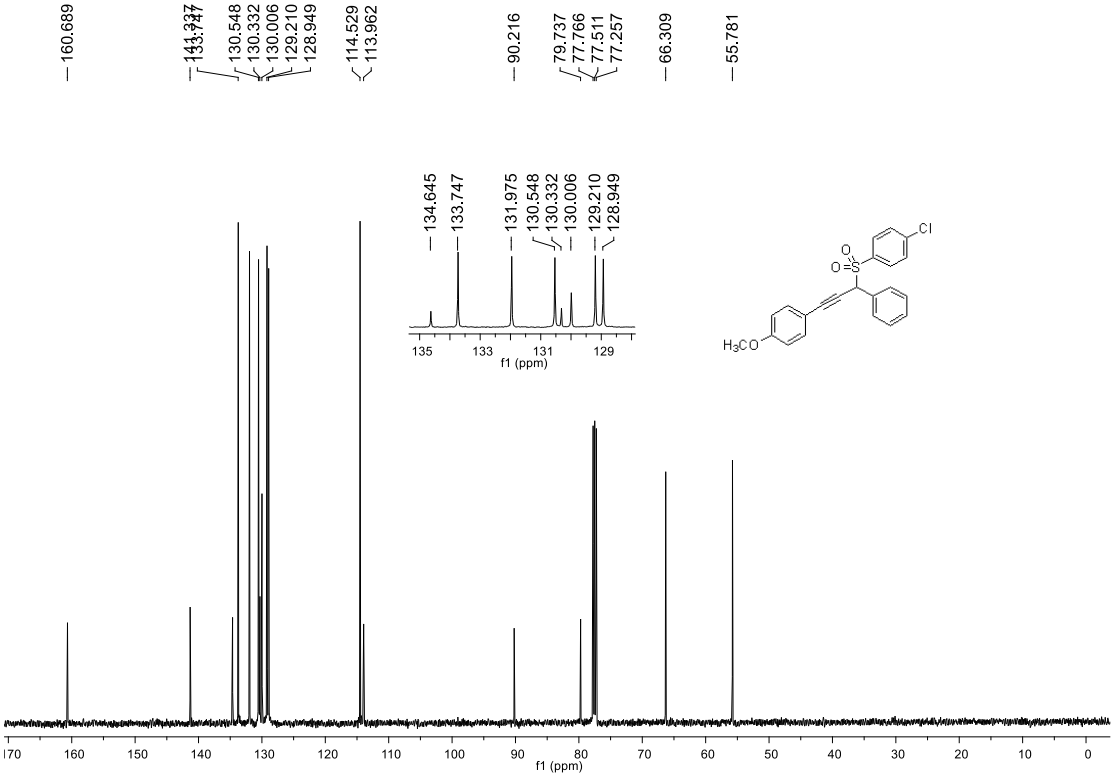
1-Methoxy-4-(3-phenyl-3-(phenylsulfonyl)prop-1-yn-1-yl)benzene (4gb)



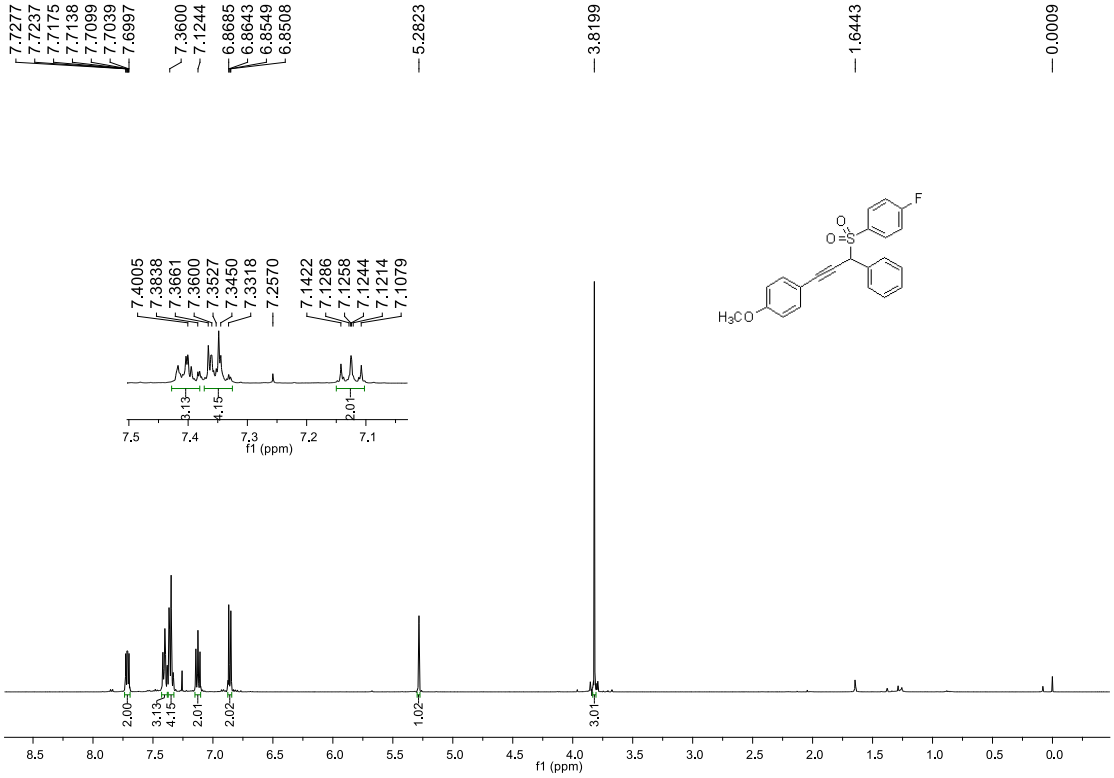


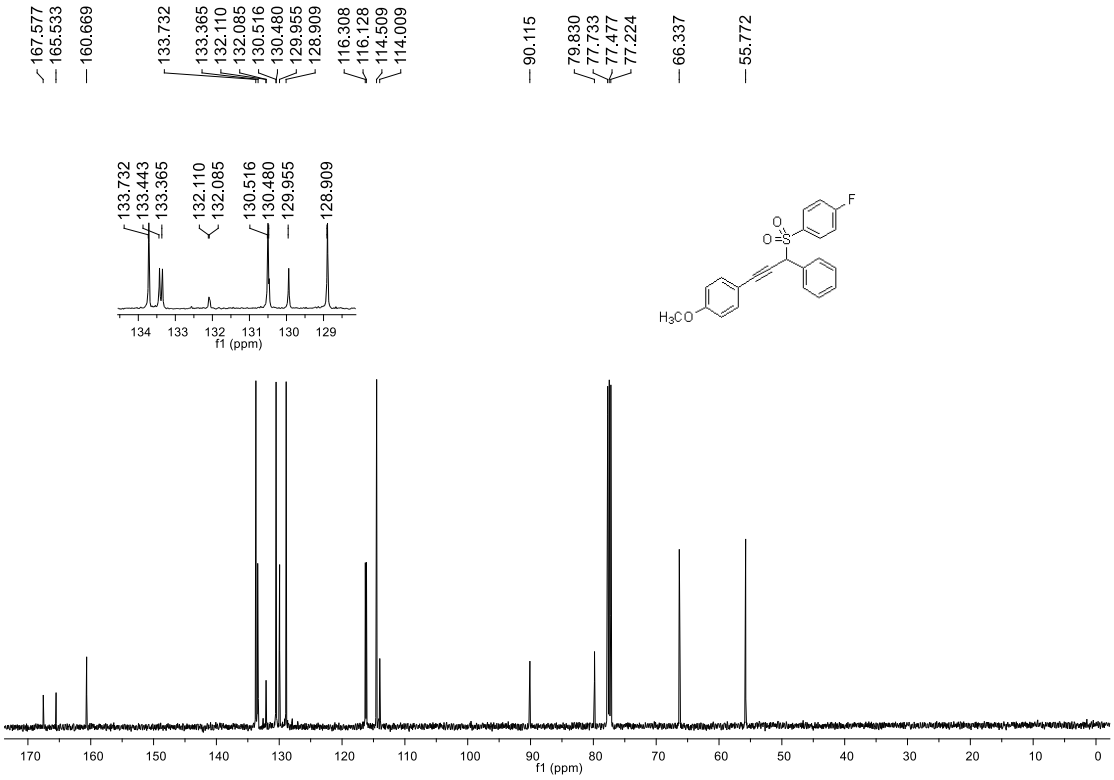
1-Chloro-4-((3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl)sulfonyl)benzene (4gc)

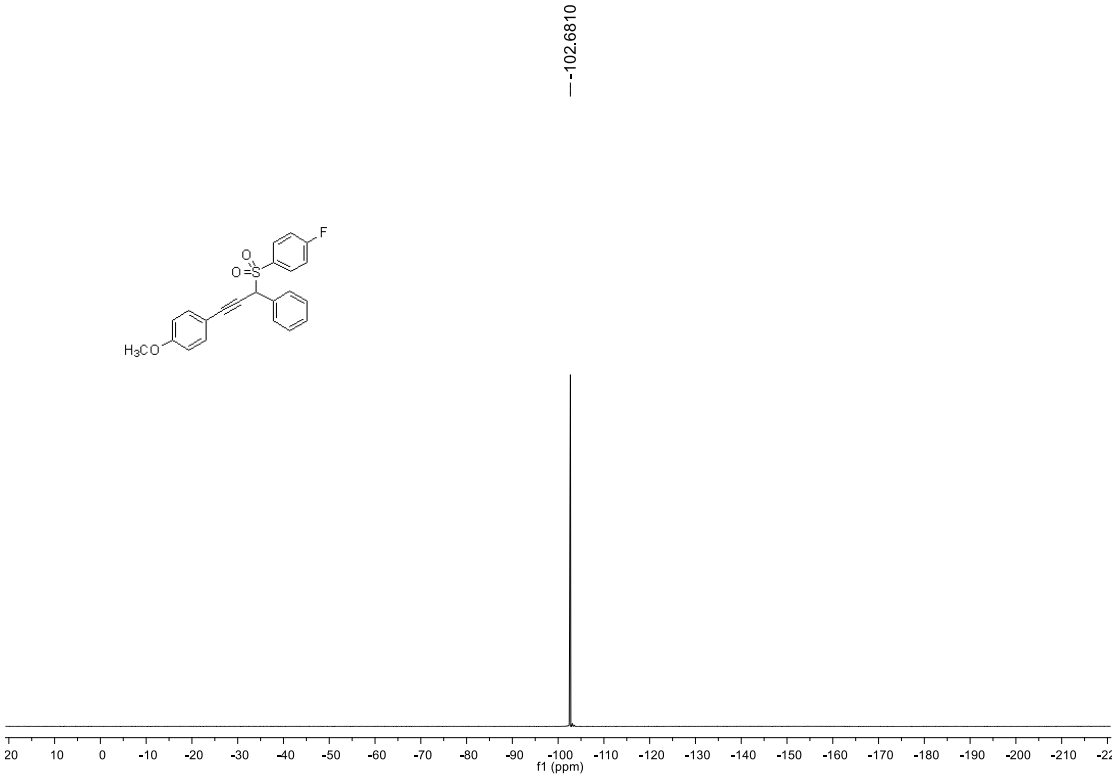




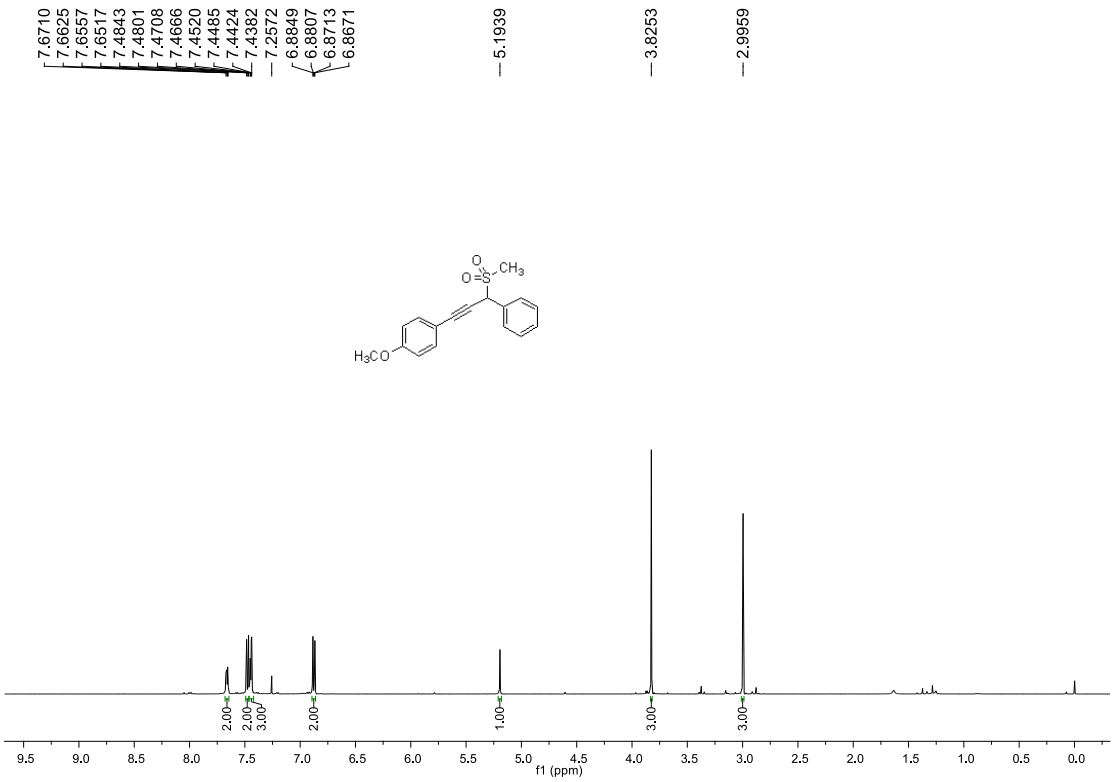
1-Fluoro-4-((3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl)sulfonyl)benzene (4gd)

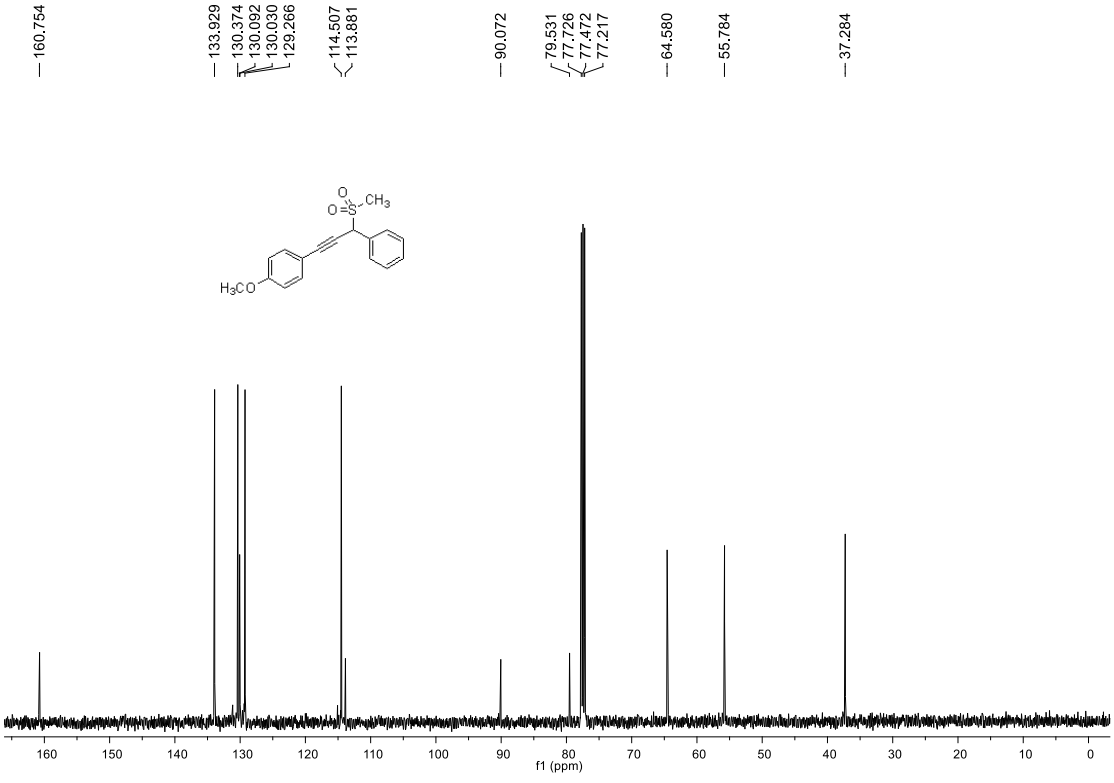




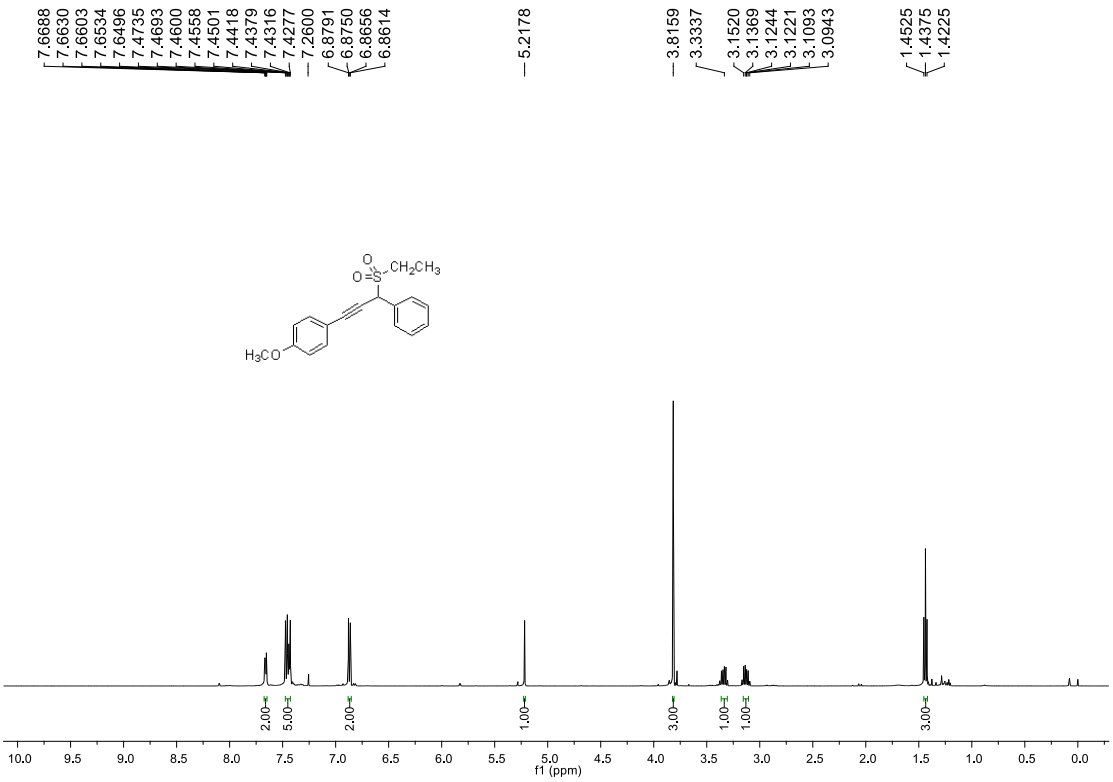

-102.6810
F
O
O=S
H3CO
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

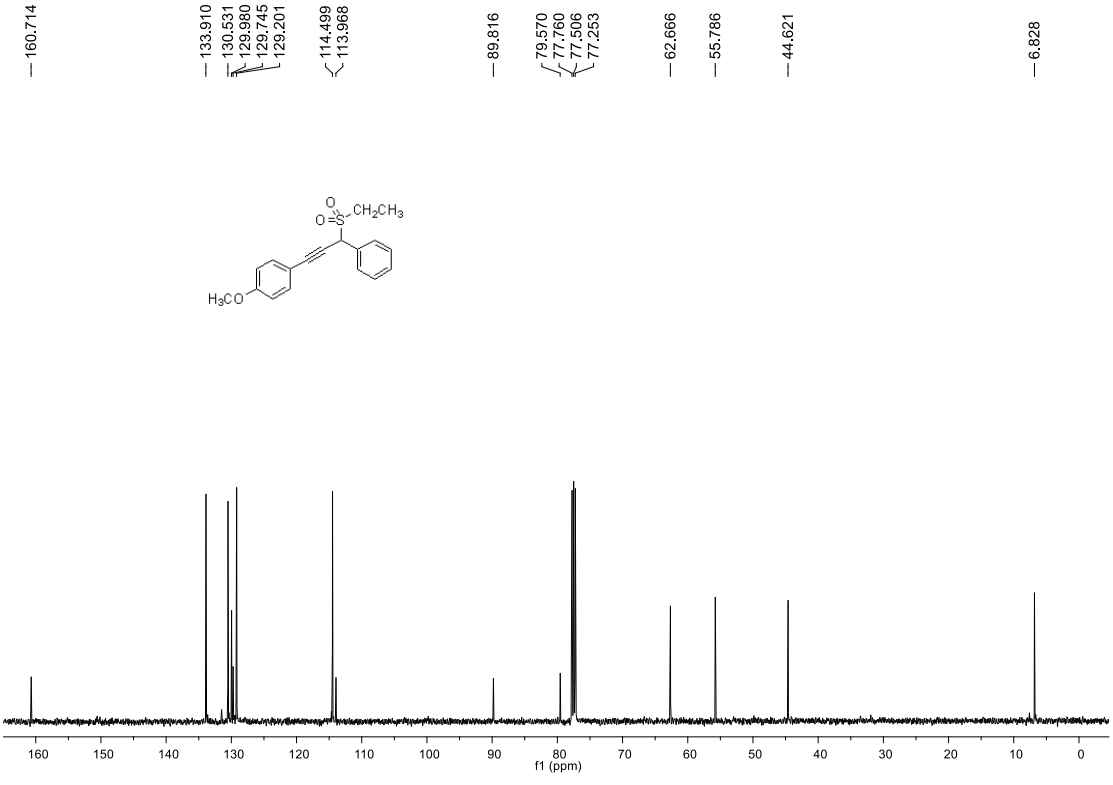
Methoxy-4-(3-(methylsulfonyl)-3-phenylprop-1-yn-1-yl)benzene (4ge)



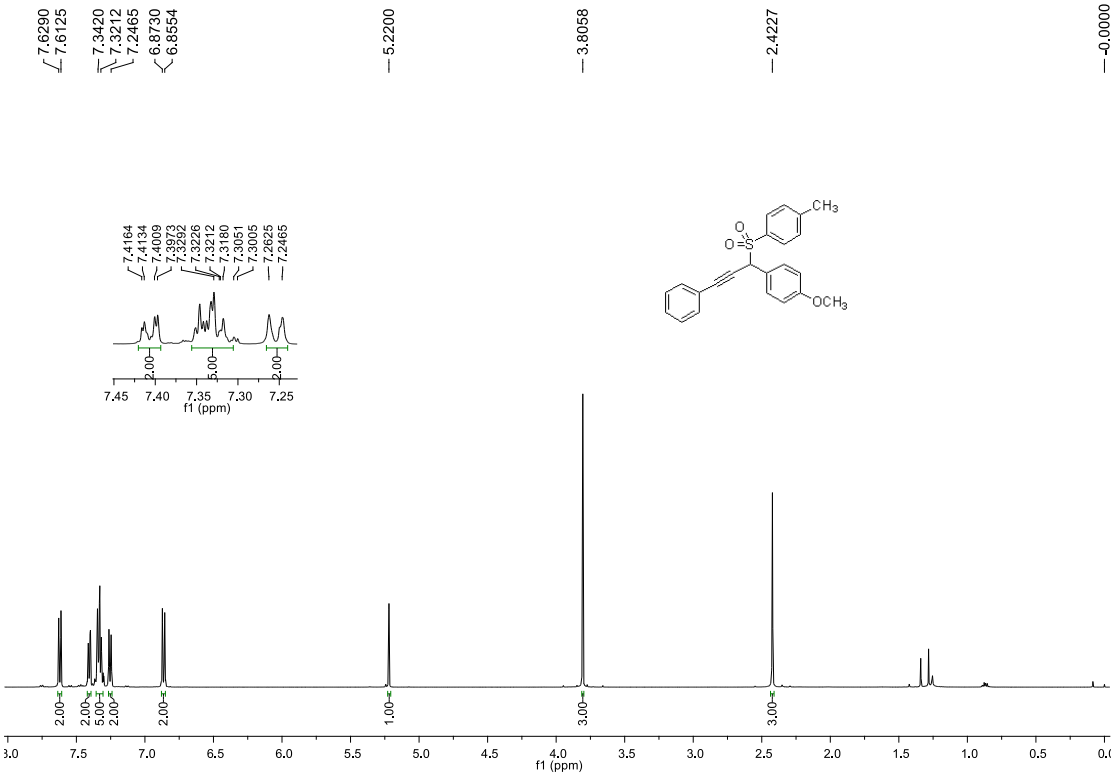


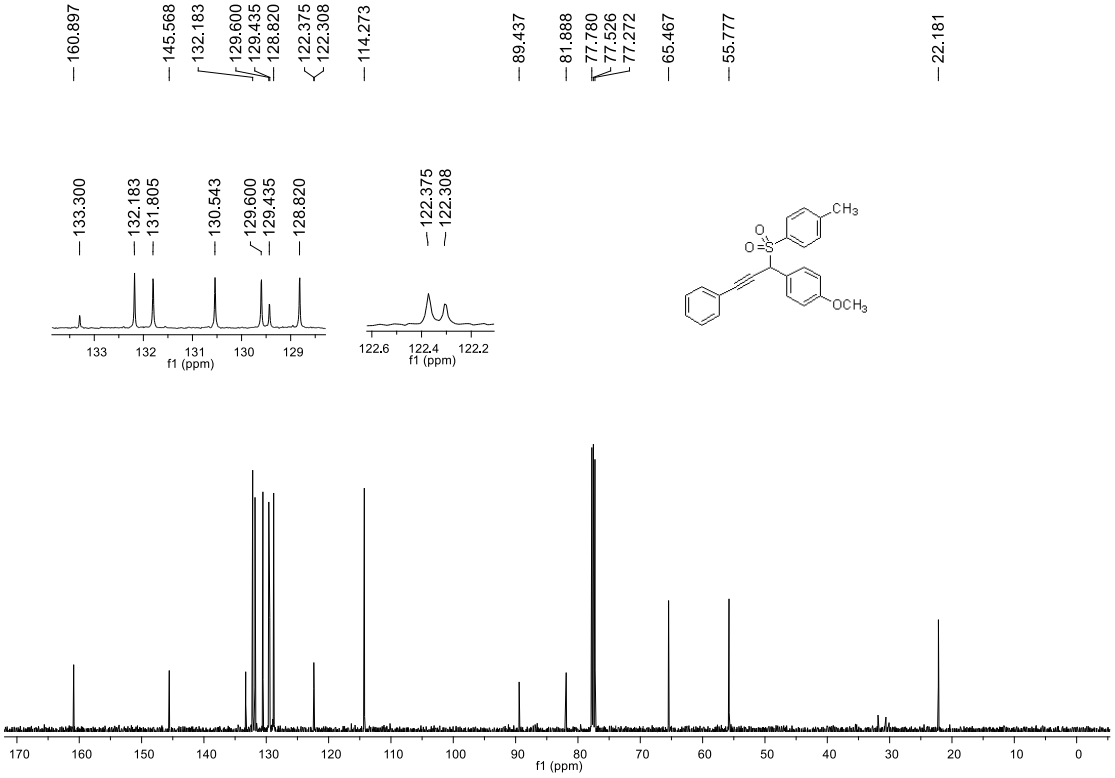
1-(3-(Ethylsulfonyl)-3-phenylprop-1-yn-1-yl)-4-methoxybenzene (4gf)



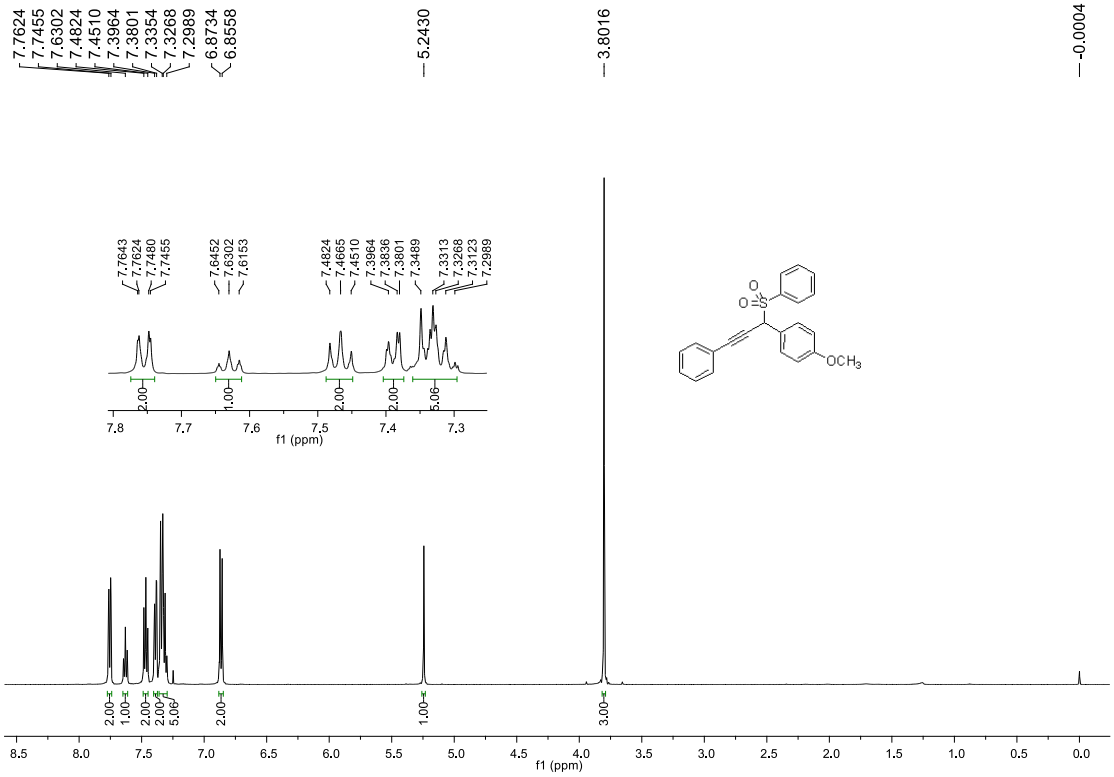


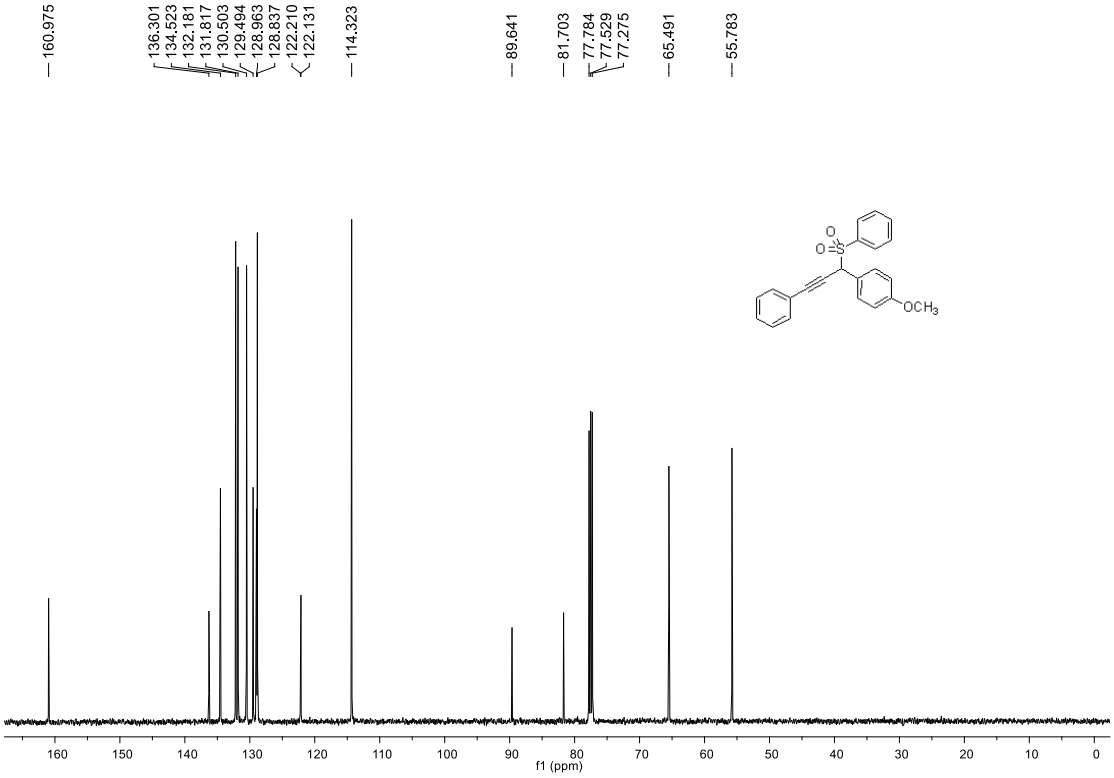
Methoxy-4-(3-phenyl-1-tosylprop-2-yn-1-yl)benzene (4ha)



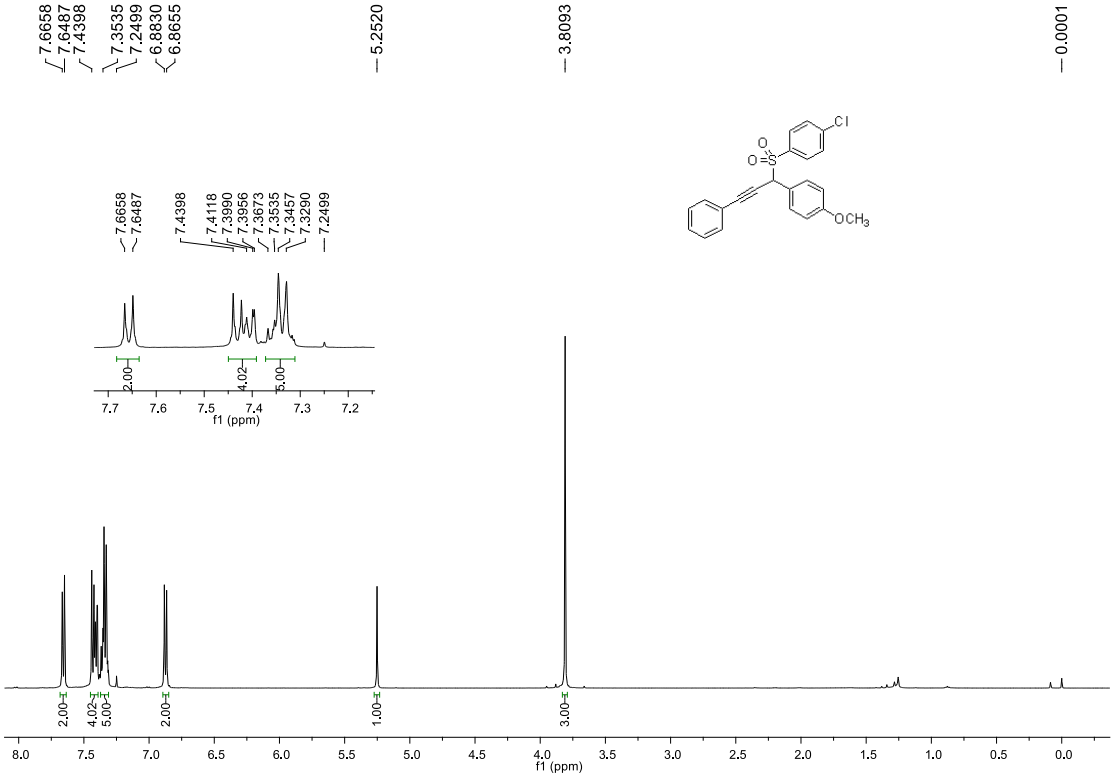


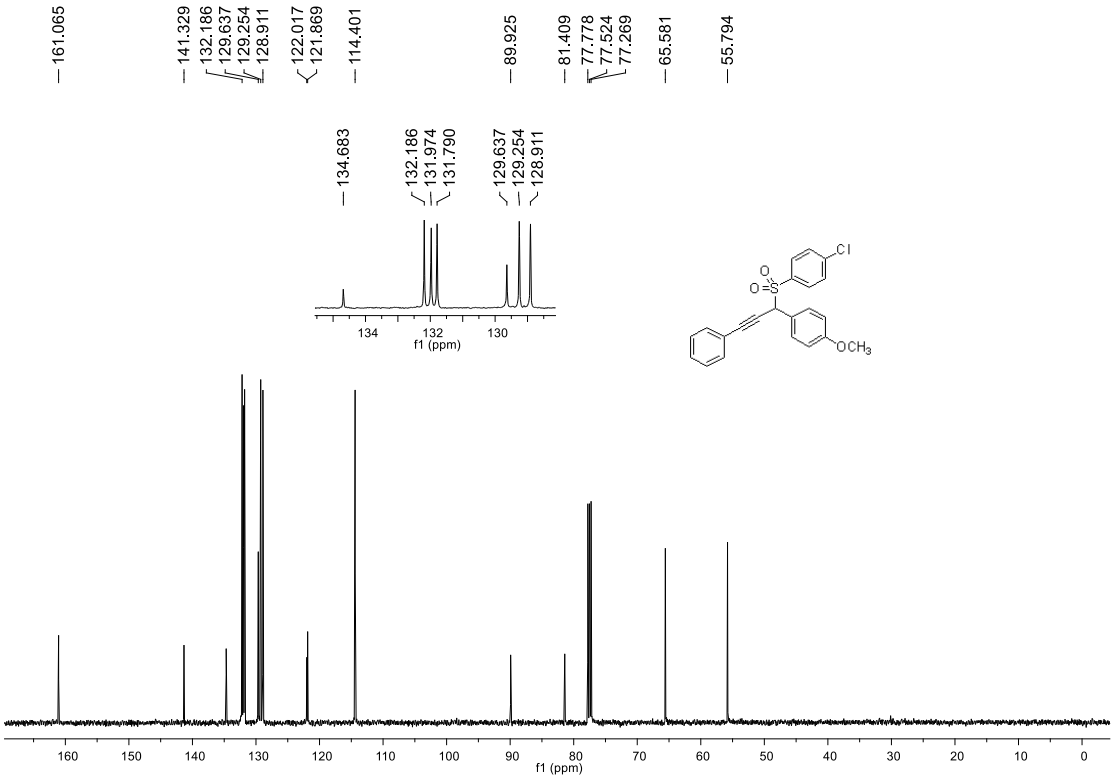
1-Methoxy-4-(3-phenyl-1-(phenylsulfonyl)prop-2-yn-1-yl)benzene (4hb)



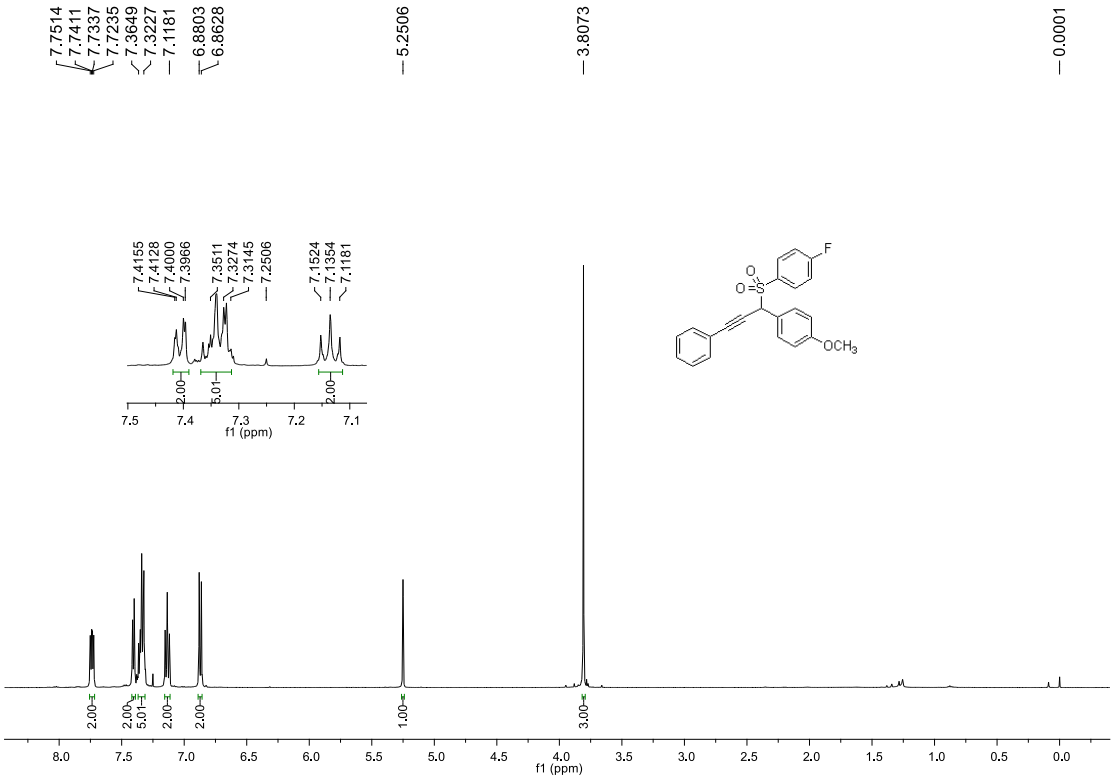


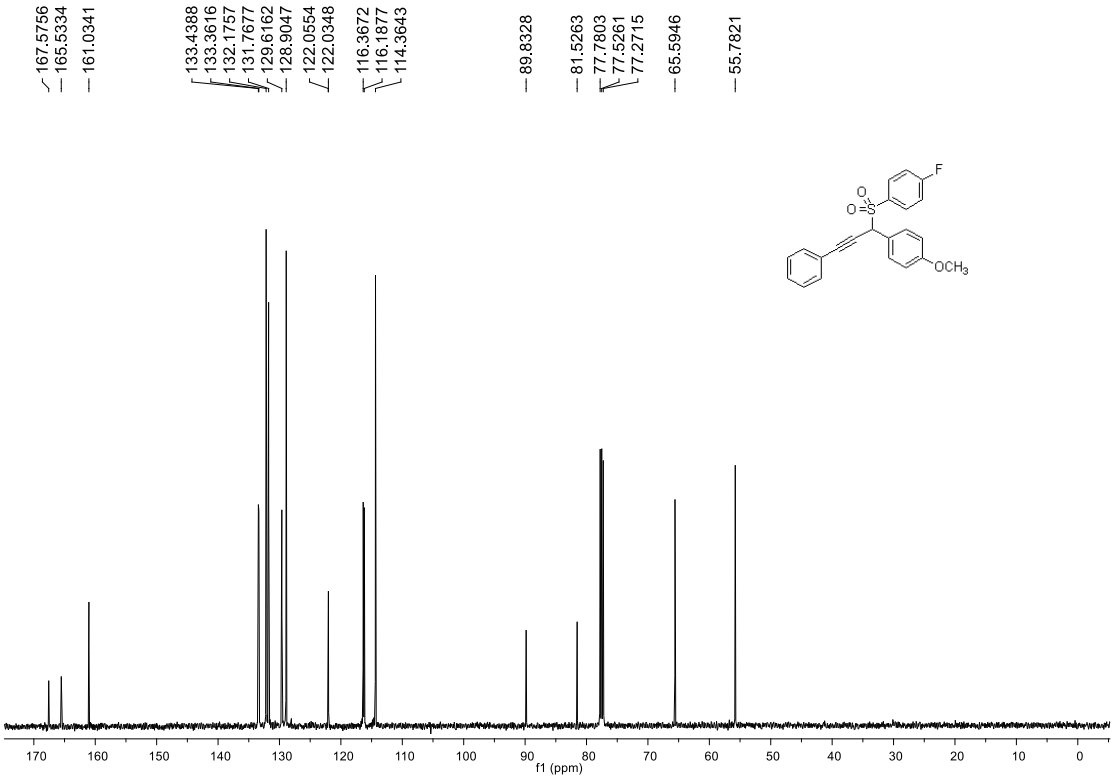
1-Chloro-4-((1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)sulfonyl)benzene (4hc)

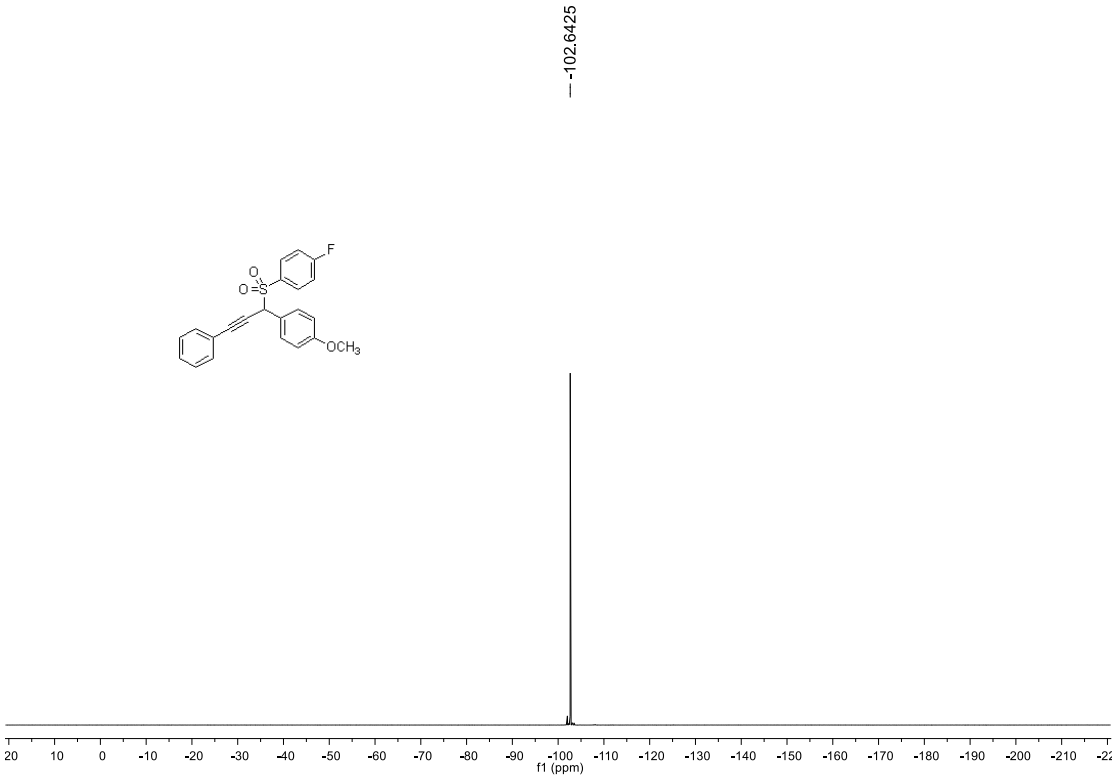




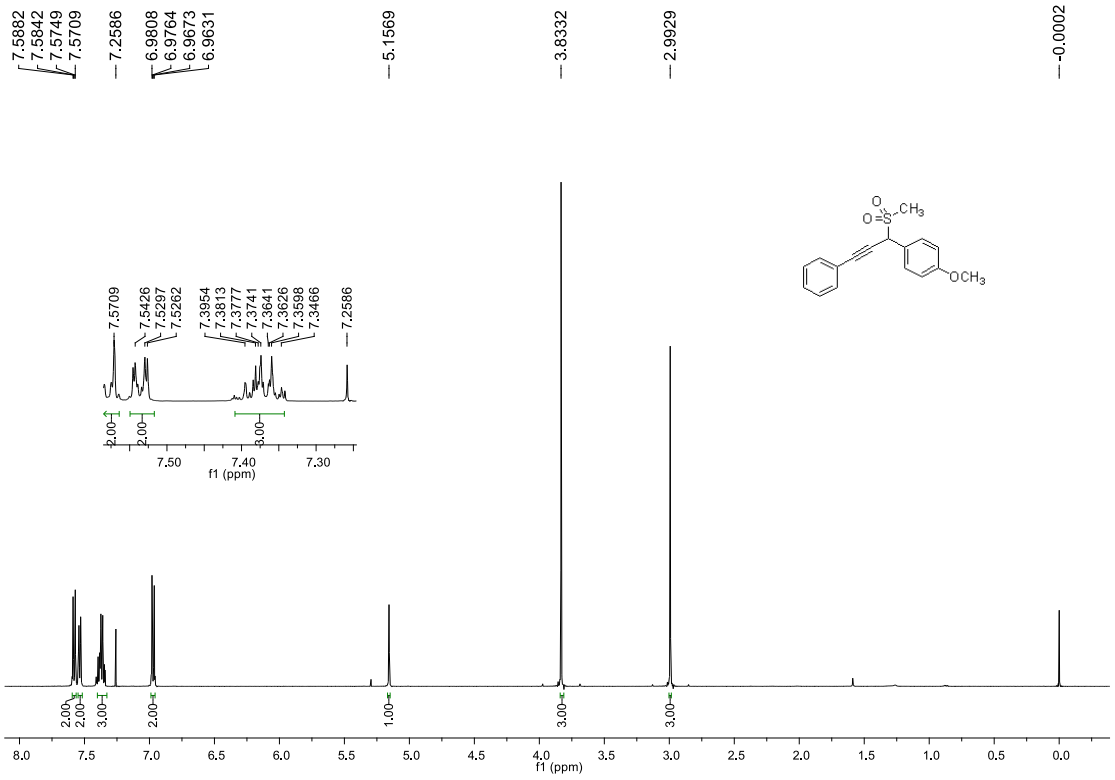
1-Fluoro-4-((1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl)sulfonyl)benzene (4hd)

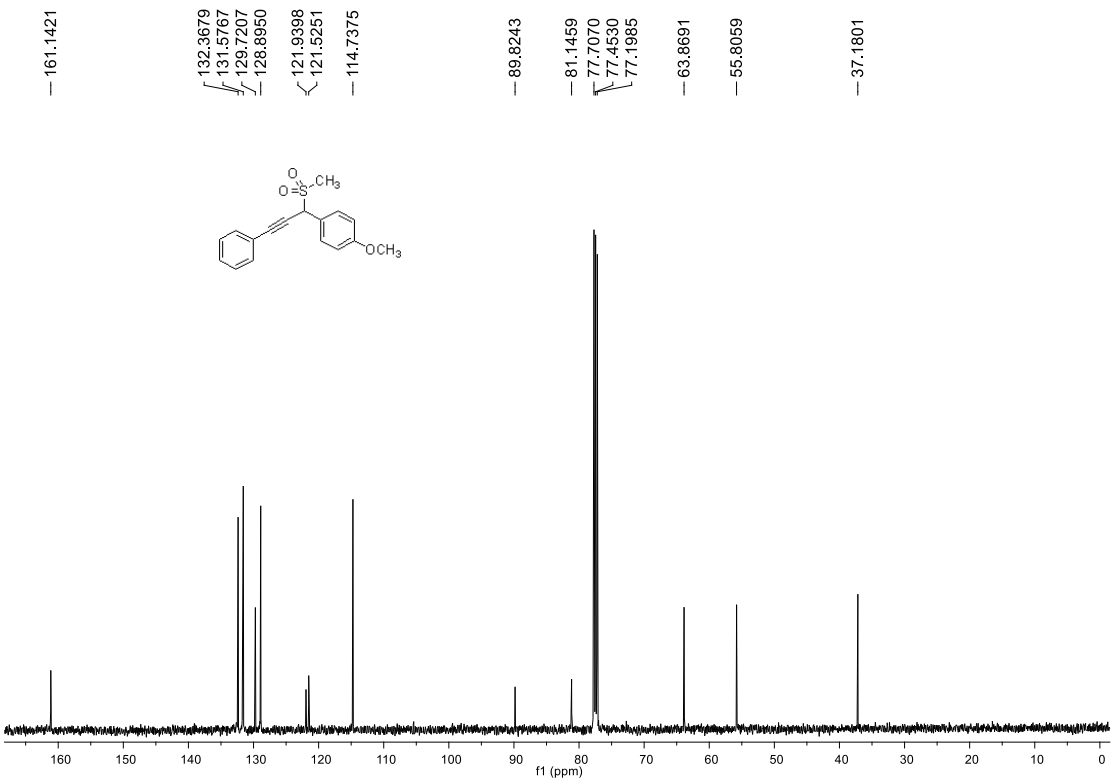




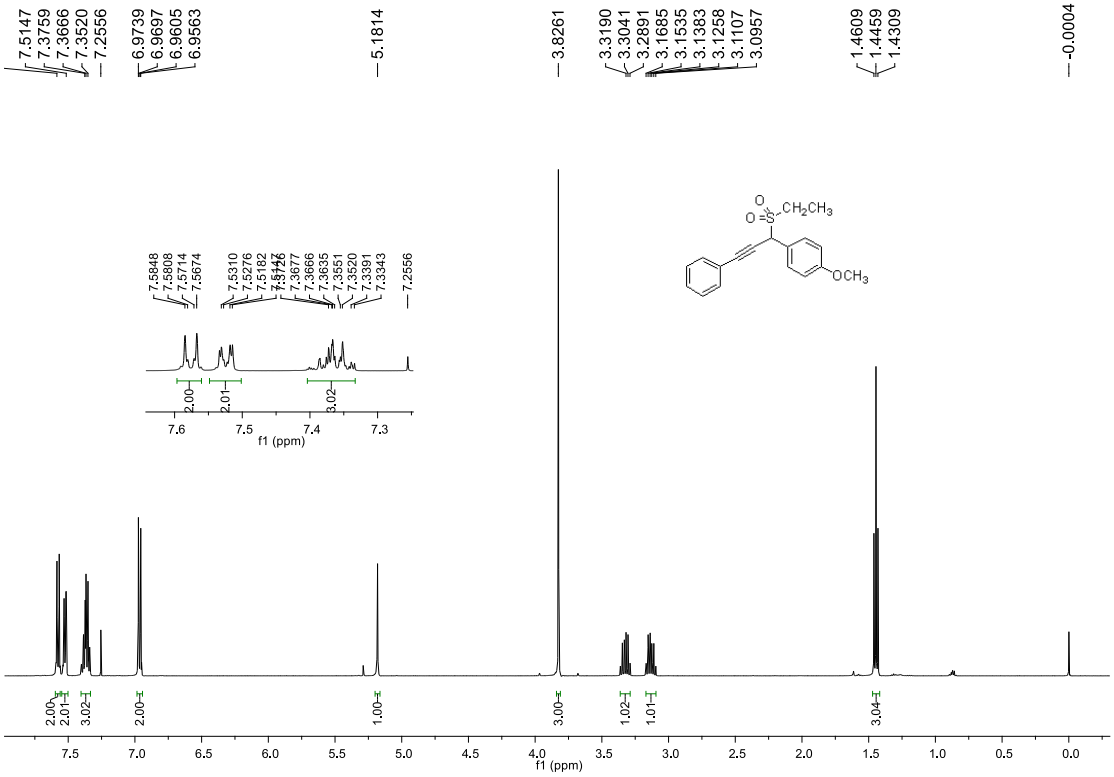

-102.6425
F
O
O
S
OCH3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

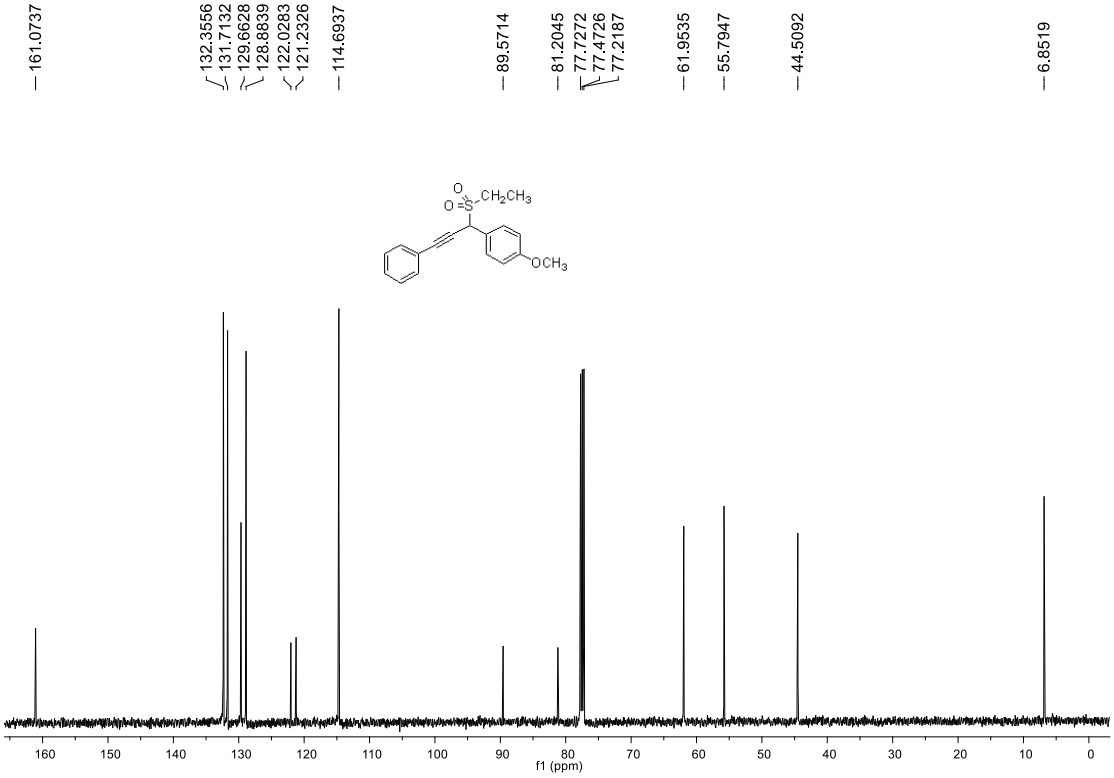
1-Methoxy-4-(1-(methylsulfonyl)-3-phenylprop-2-yn-1-yl)benzene (4he)



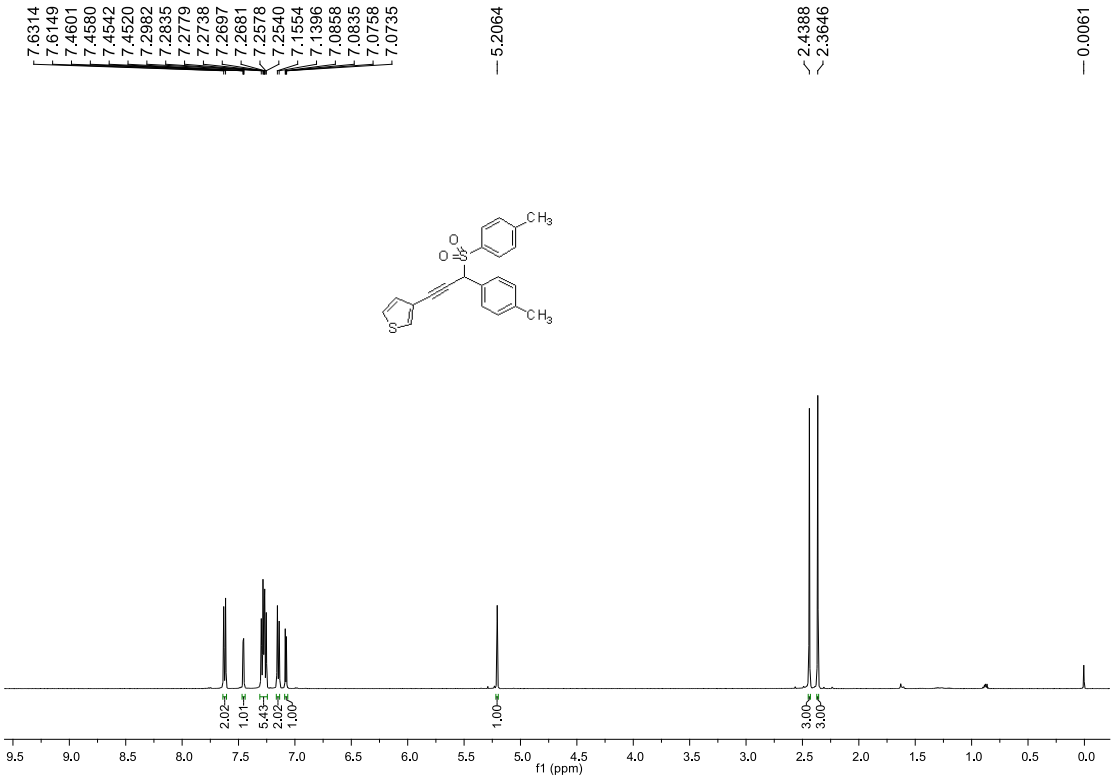


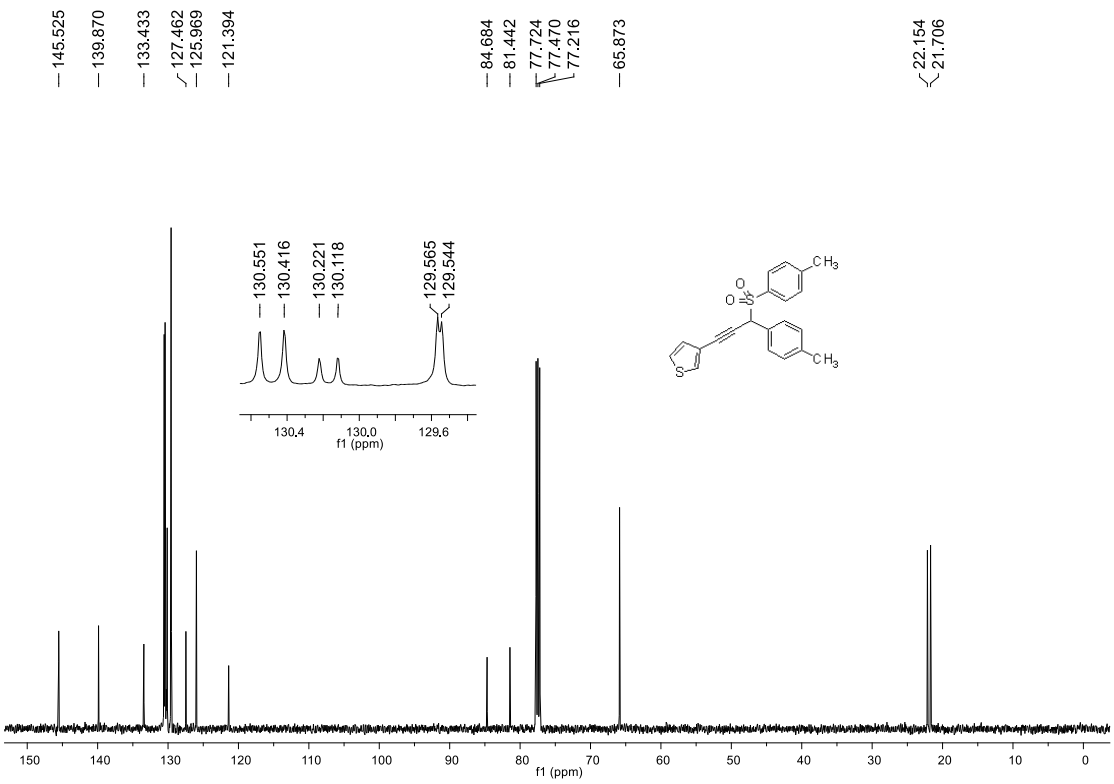
1-(1-(Ethylsulfonyl)-3-phenylprop-2-yn-1-yl)-4-methoxybenzene (4hf)



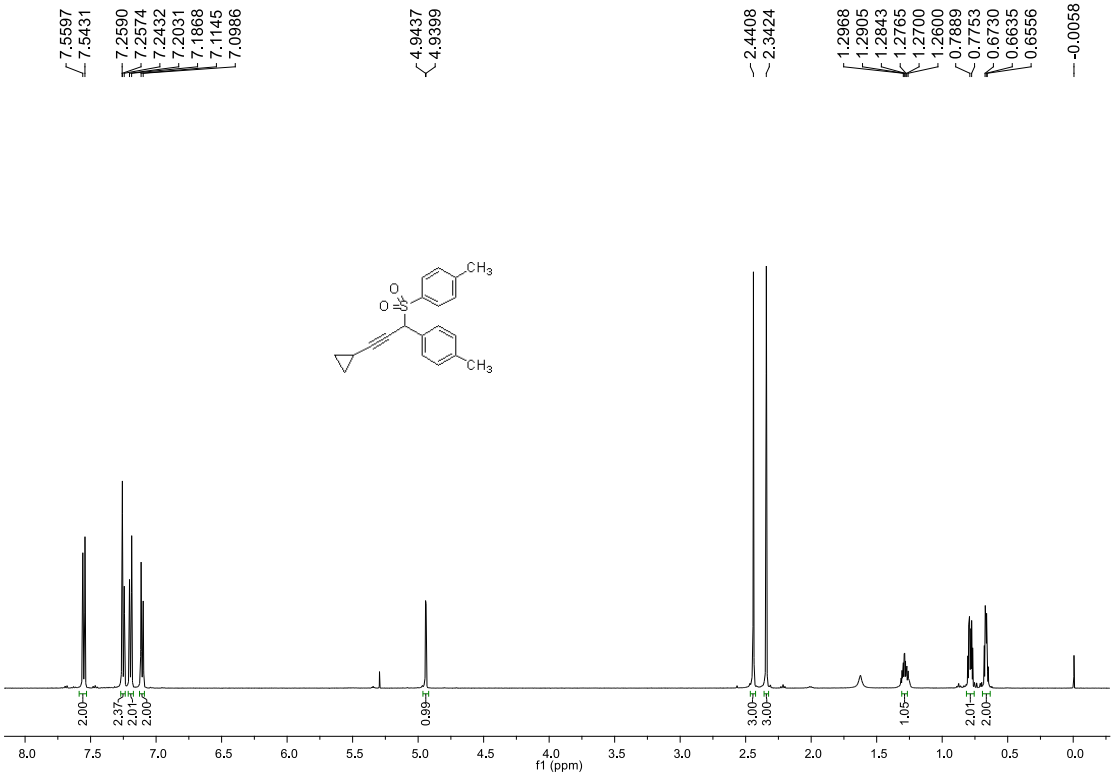


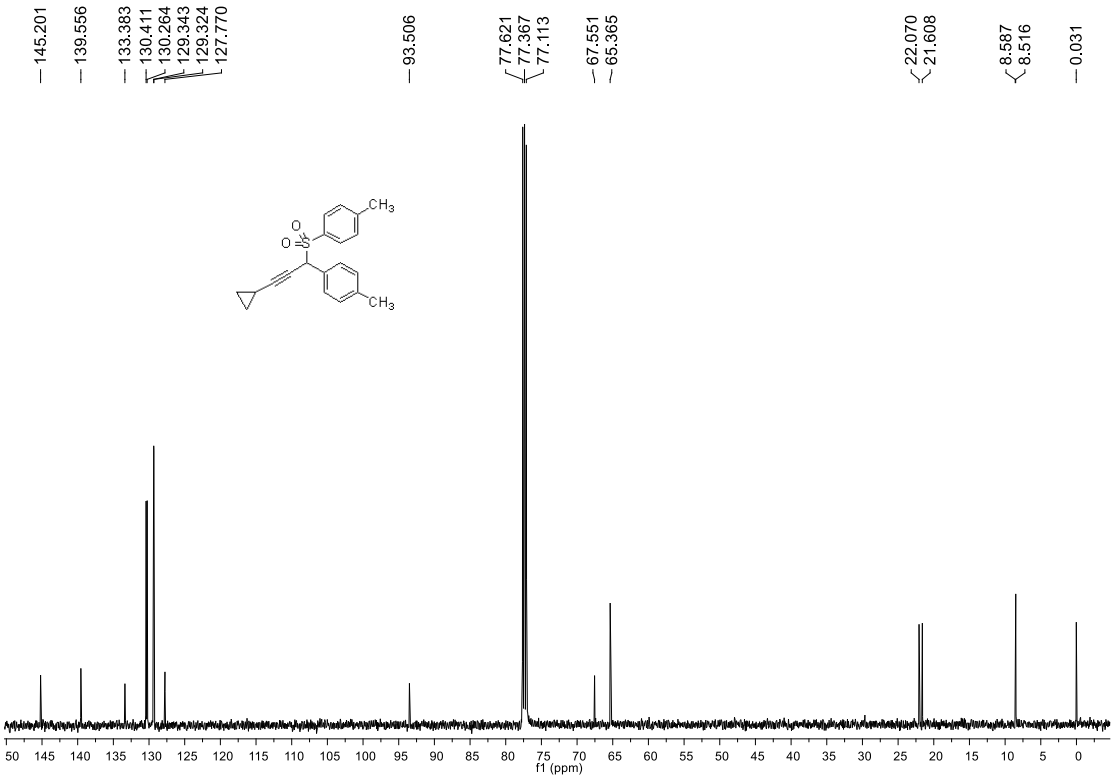
3-(3-(*p*-Tolyl)-3-tosylprop-1-yn-1-yl)thiophene (4ia)



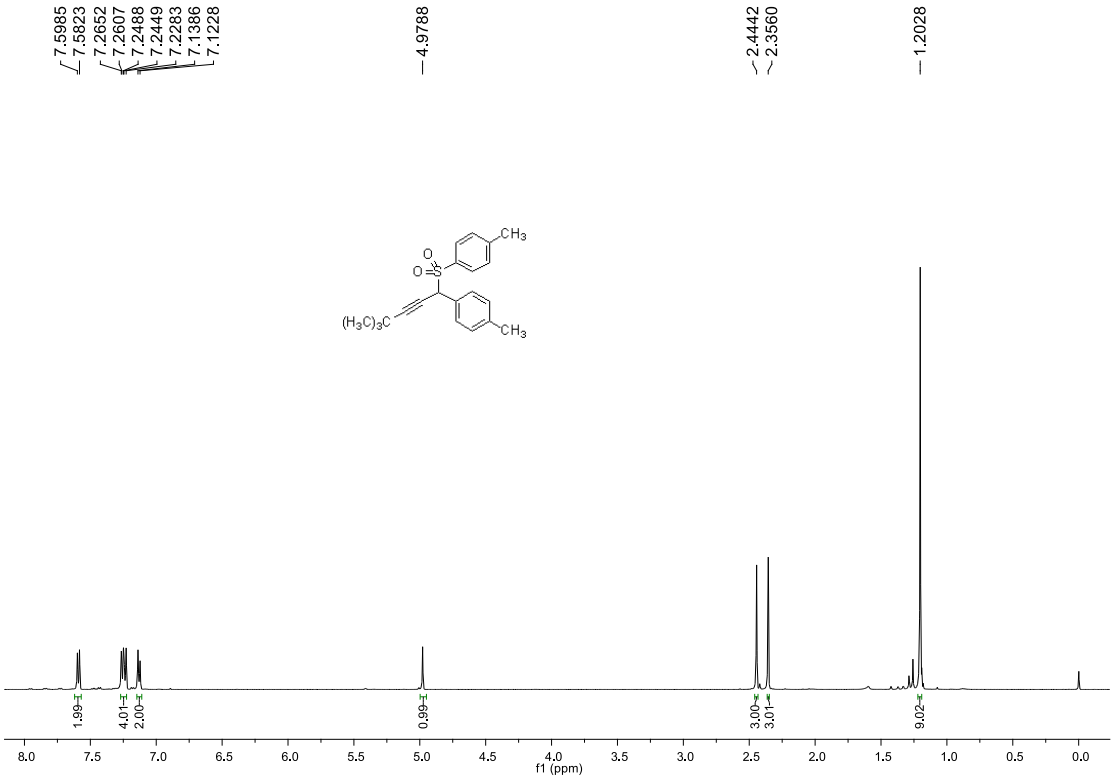


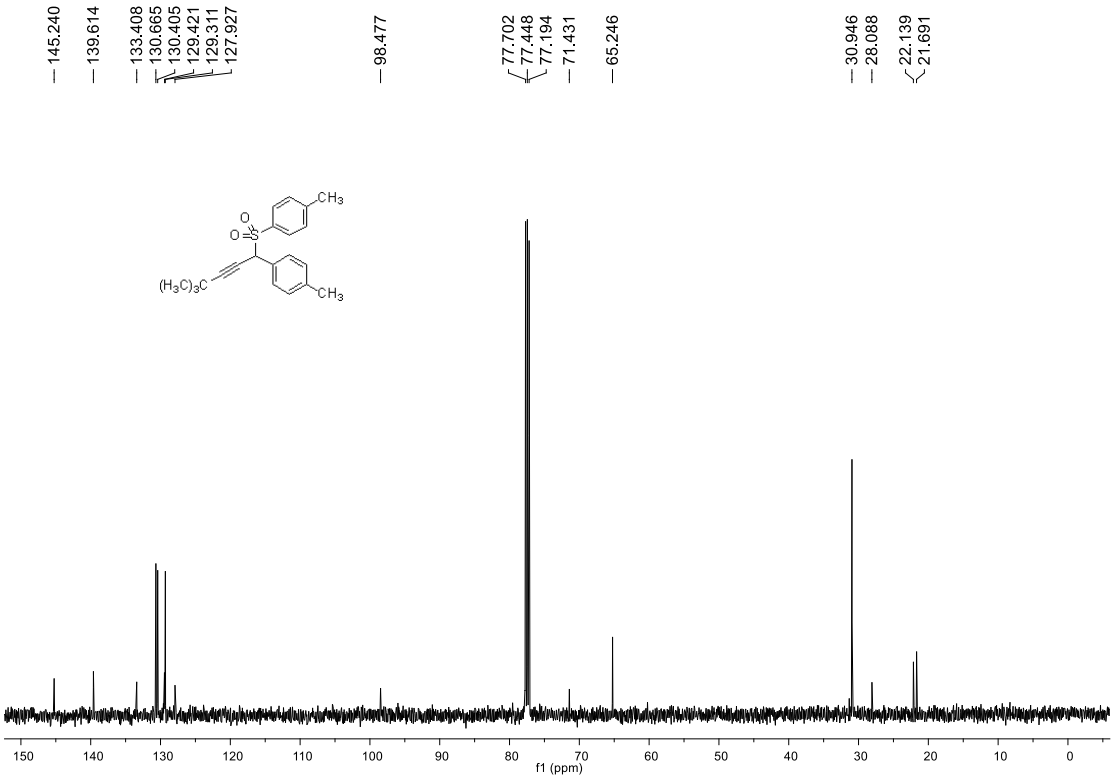
1-((3-Cyclopropyl-1-(*p*-tolyl)prop-2-yn-1-yl)sulfonyl)-4-methylbenzene (4ja)



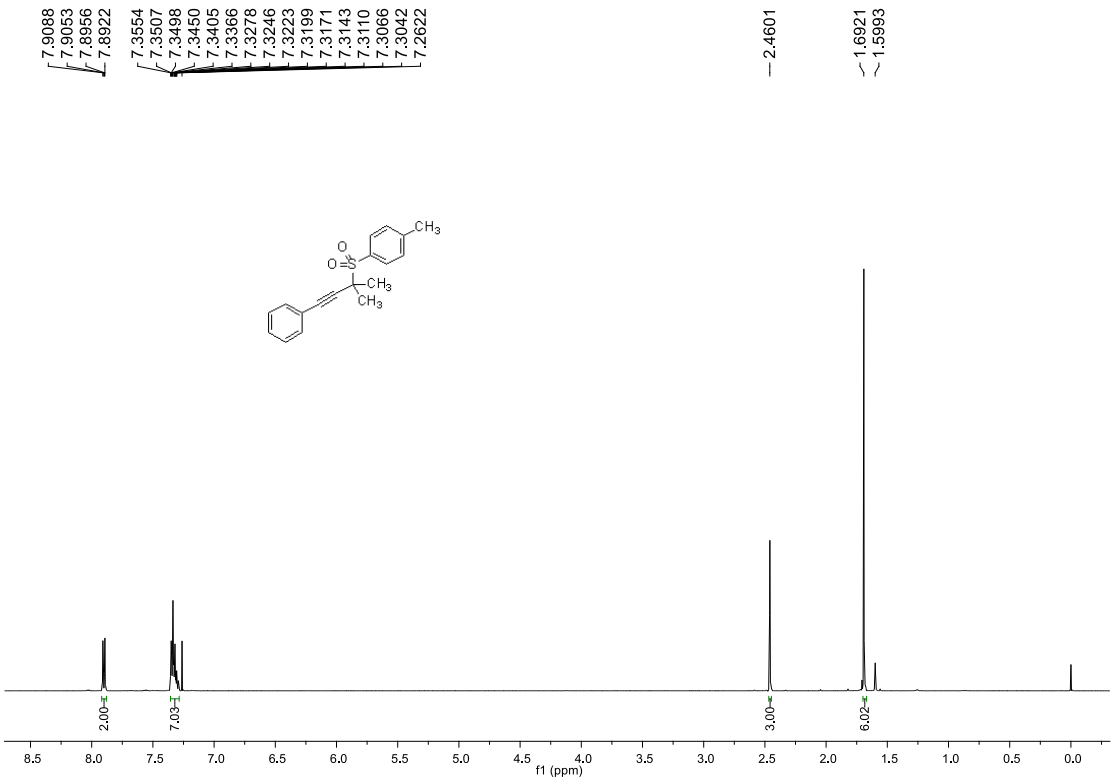


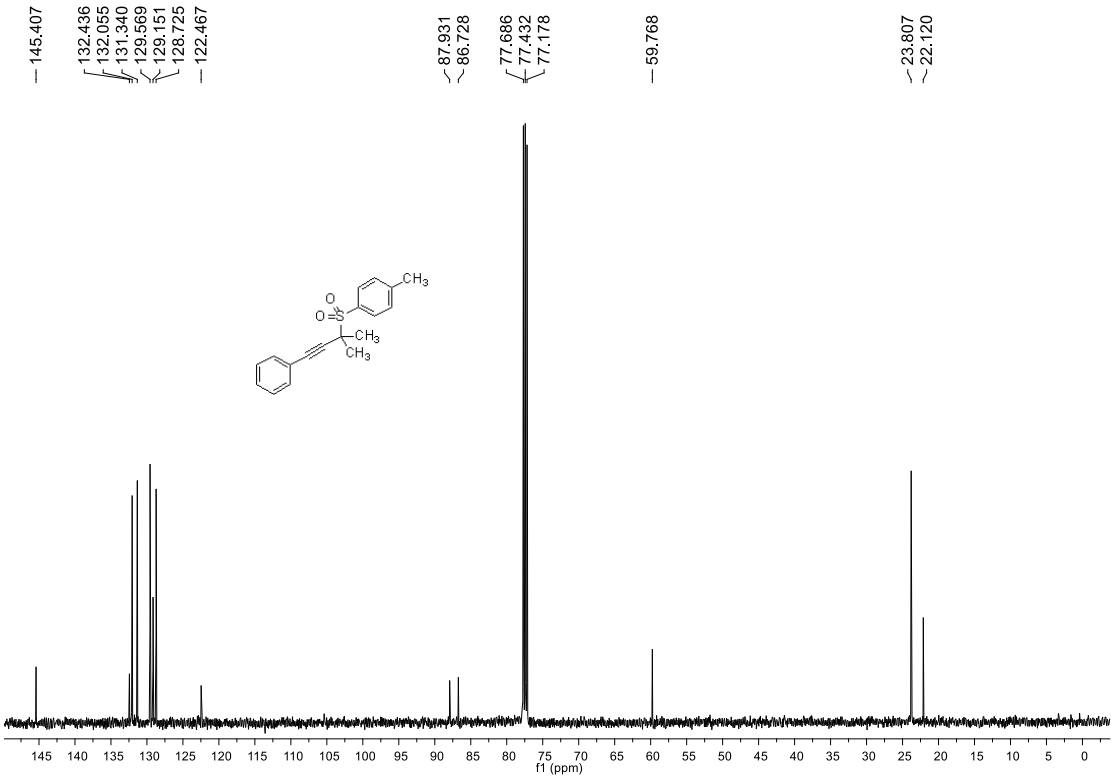
1-((4,4-Dimethyl-1-(*p*-tolyl)pent-2-yn-1-yl)sulfonyl)-4-methylbenzene (4ka)





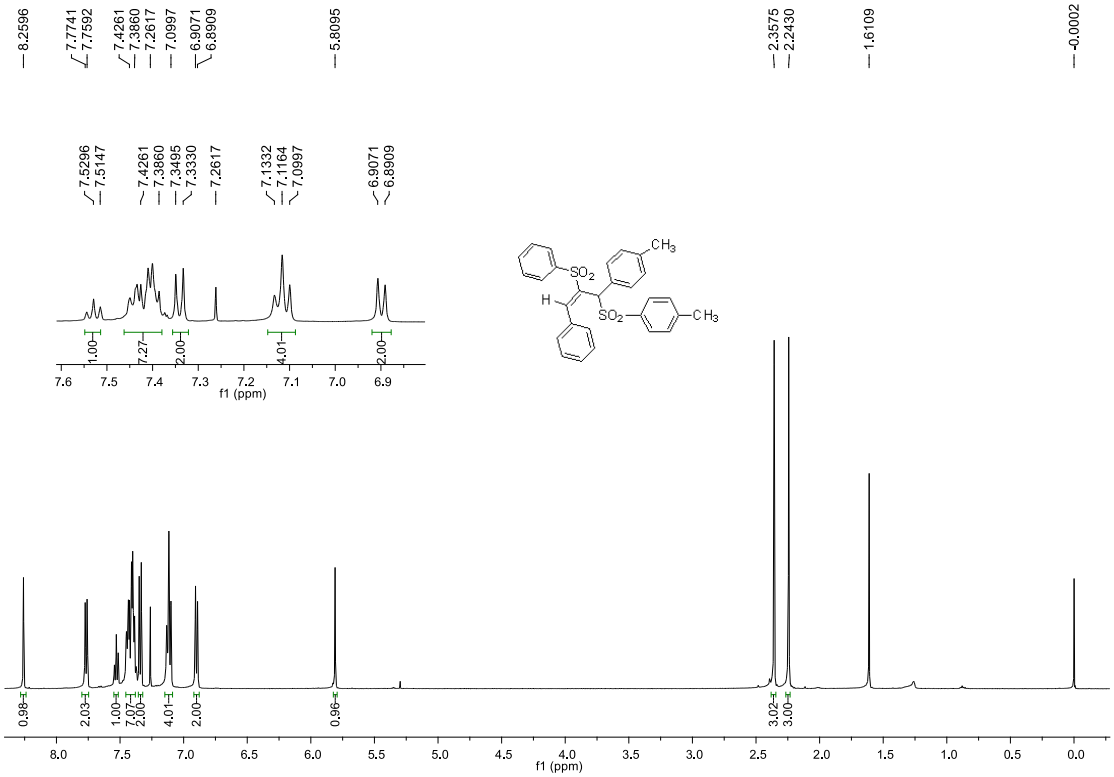
1-Methyl-4-((2-methyl-4-phenylbut-3-yn-2-yl)sulfonyl)benzene (4la)

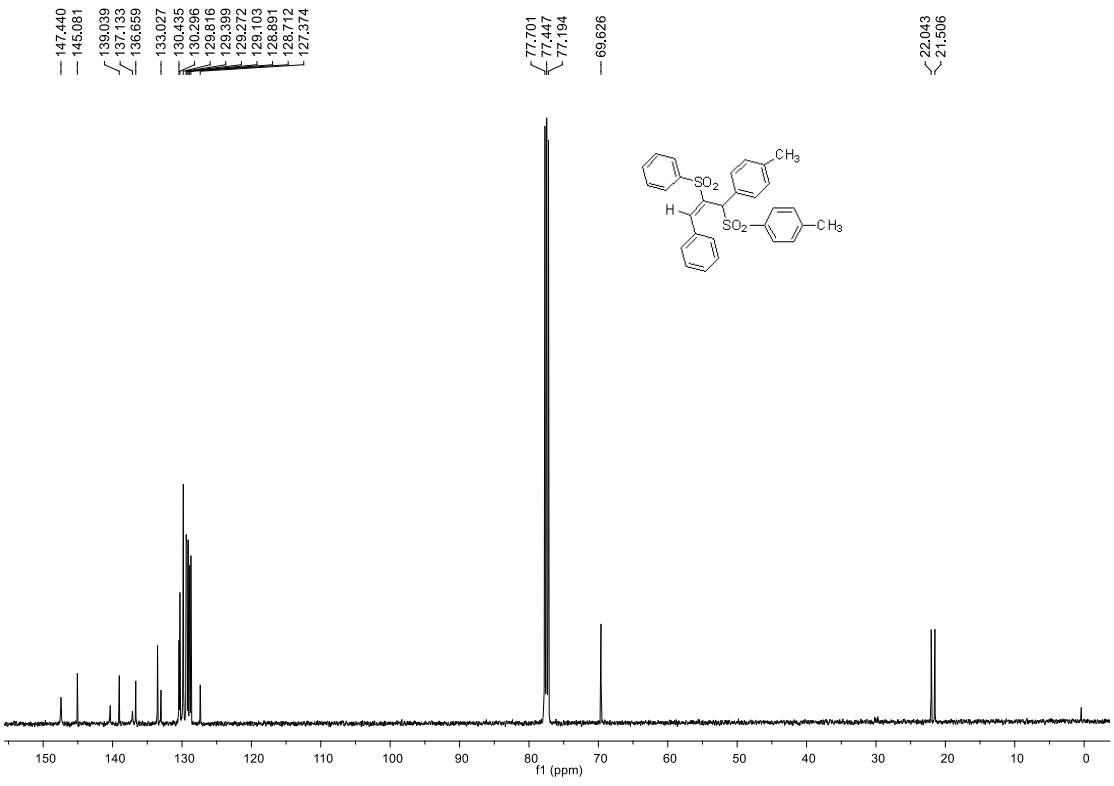




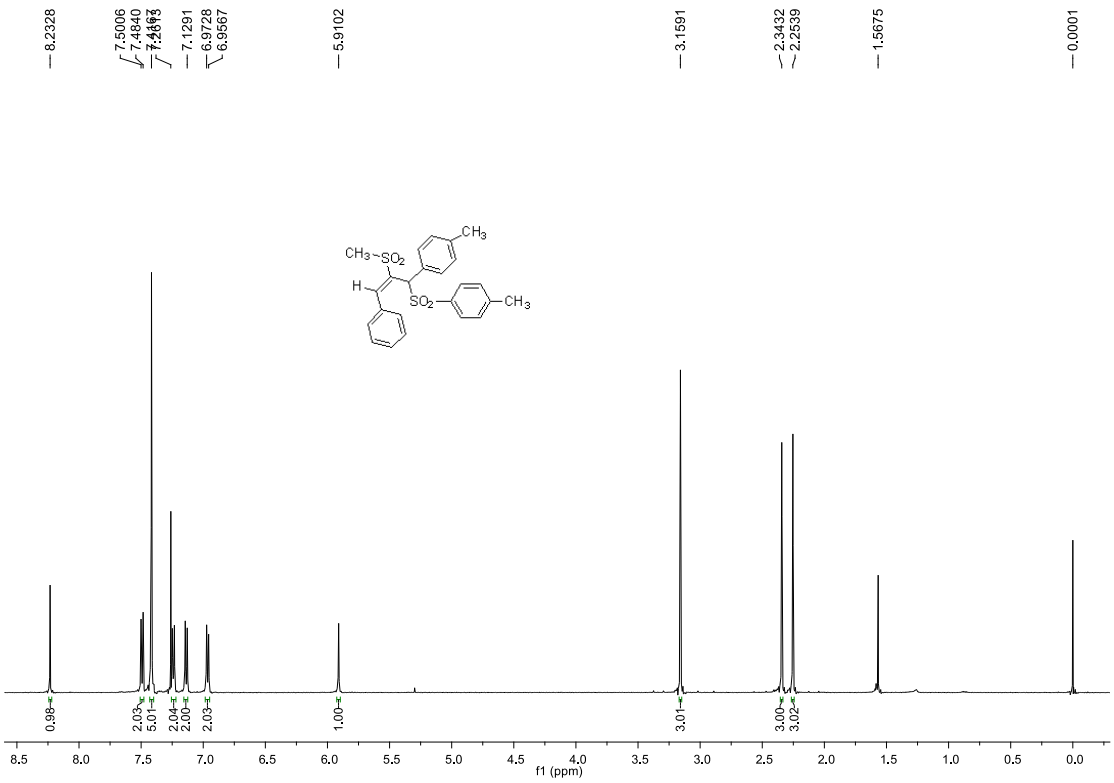
Copies of ^{1}H NMR, ^{13}C NMR spectra of compounds 5

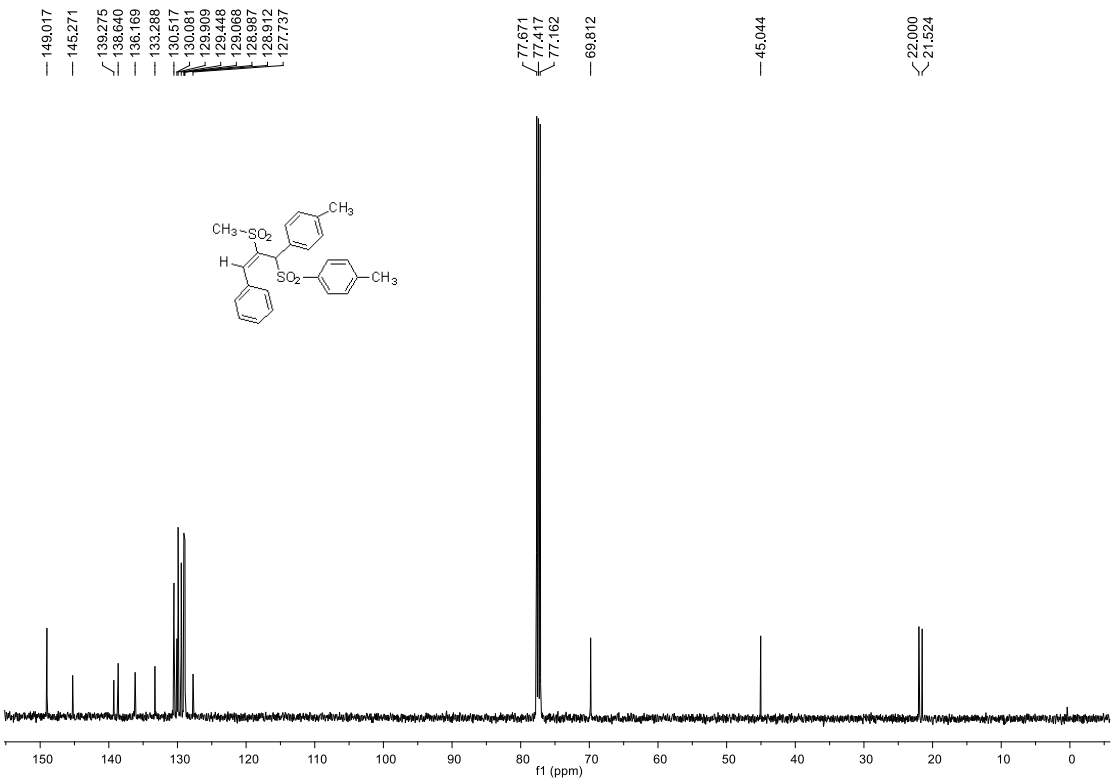
(*E*)-1-methyl-4-((3-phenyl-2-(phenylsulfonyl)-1-(*p*-tolyl)allyl)sulfonyl)benzene (5a)



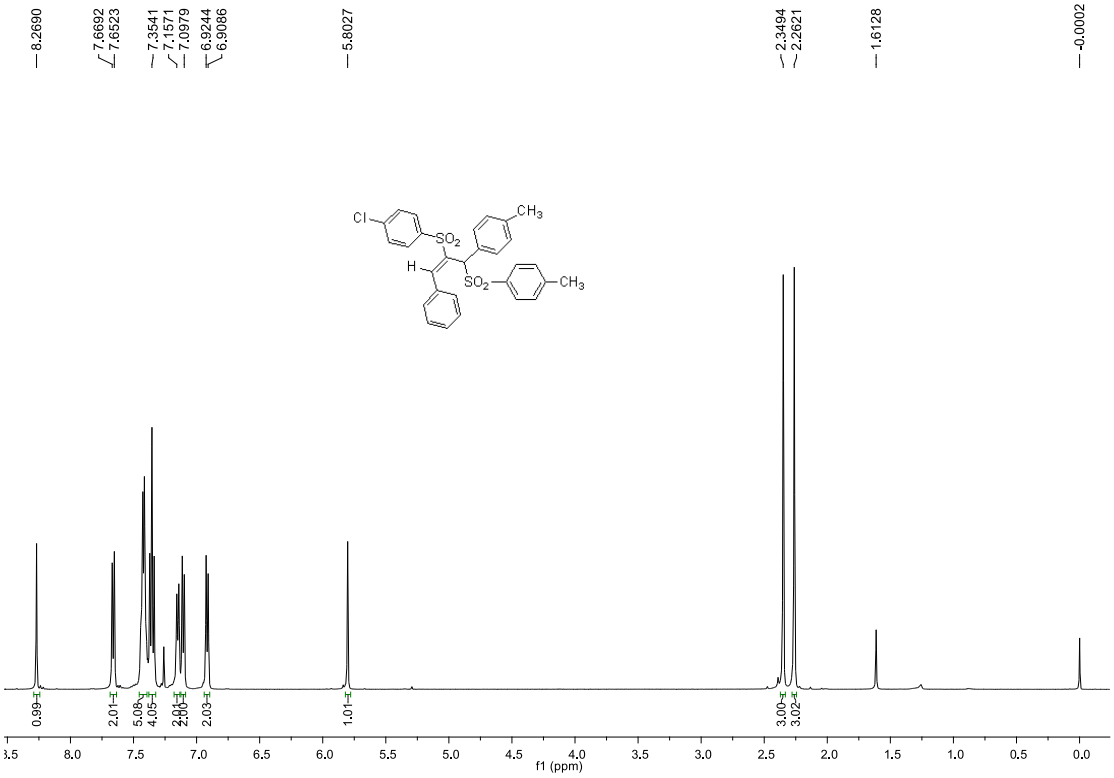


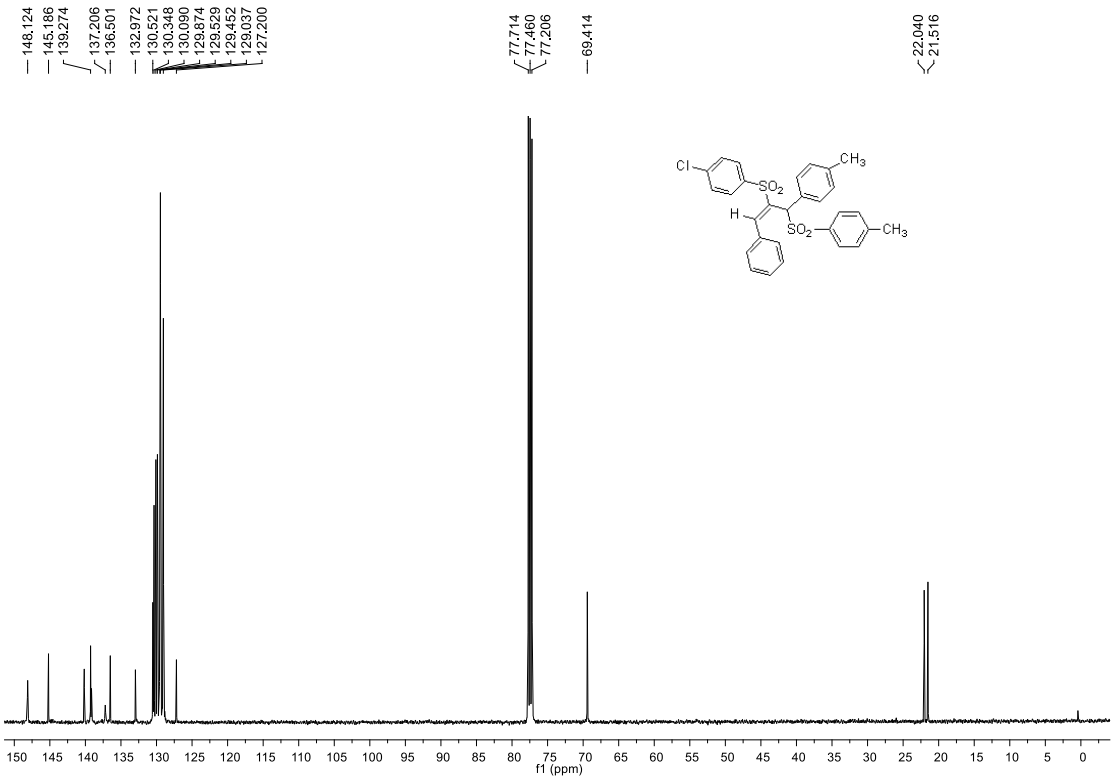
1-methyl-4-((2-(methylsulfonyl)-3-phenyl-1-(*p*-tolyl)allyl)sulfonyl)benzene (5b)



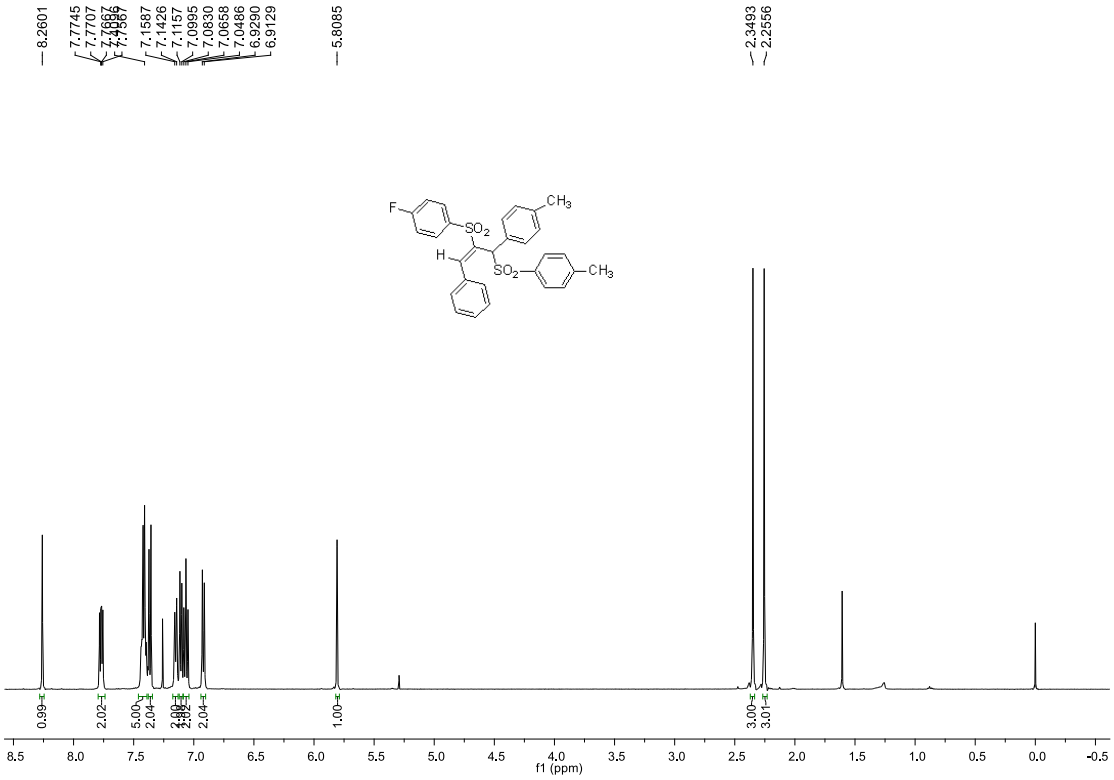


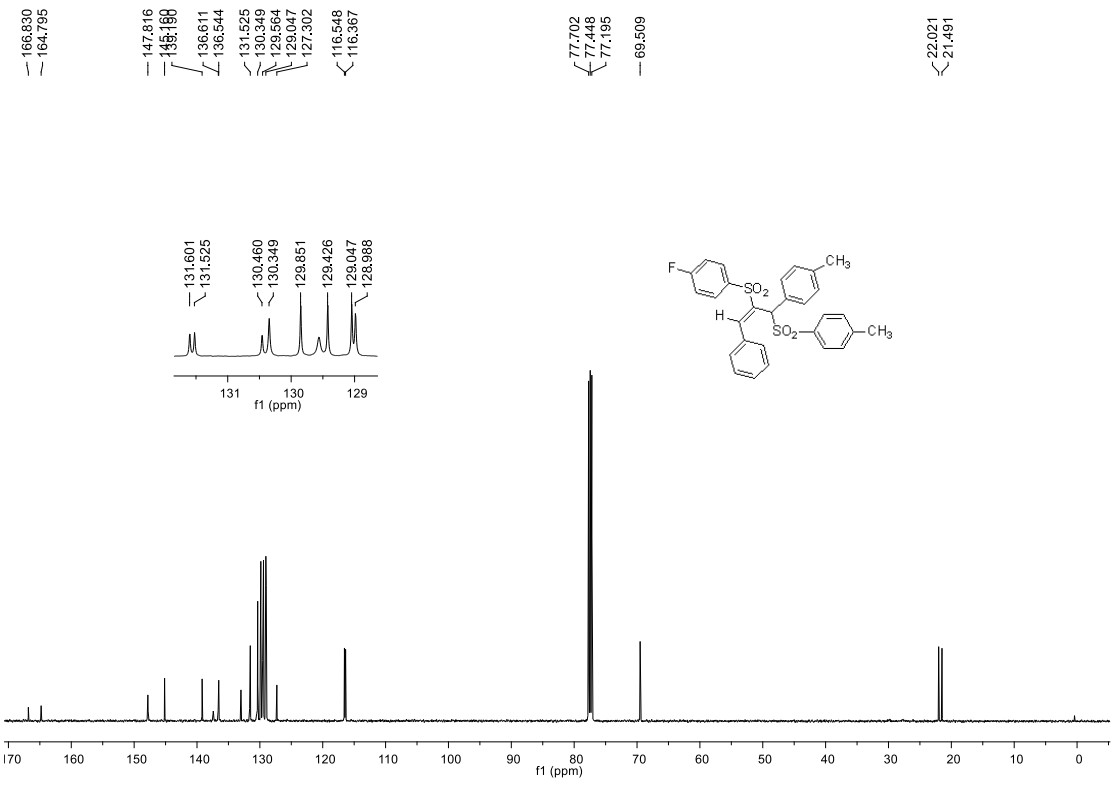
(*E*)-1-chloro-4-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)benzene (5c)

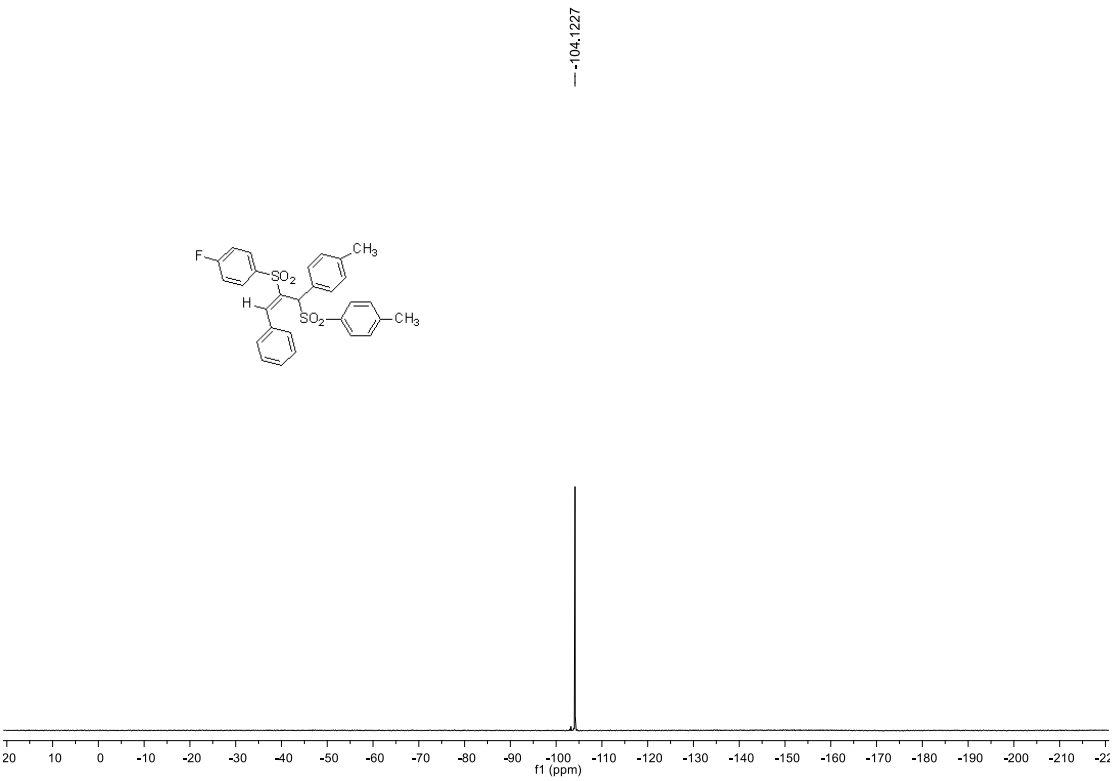




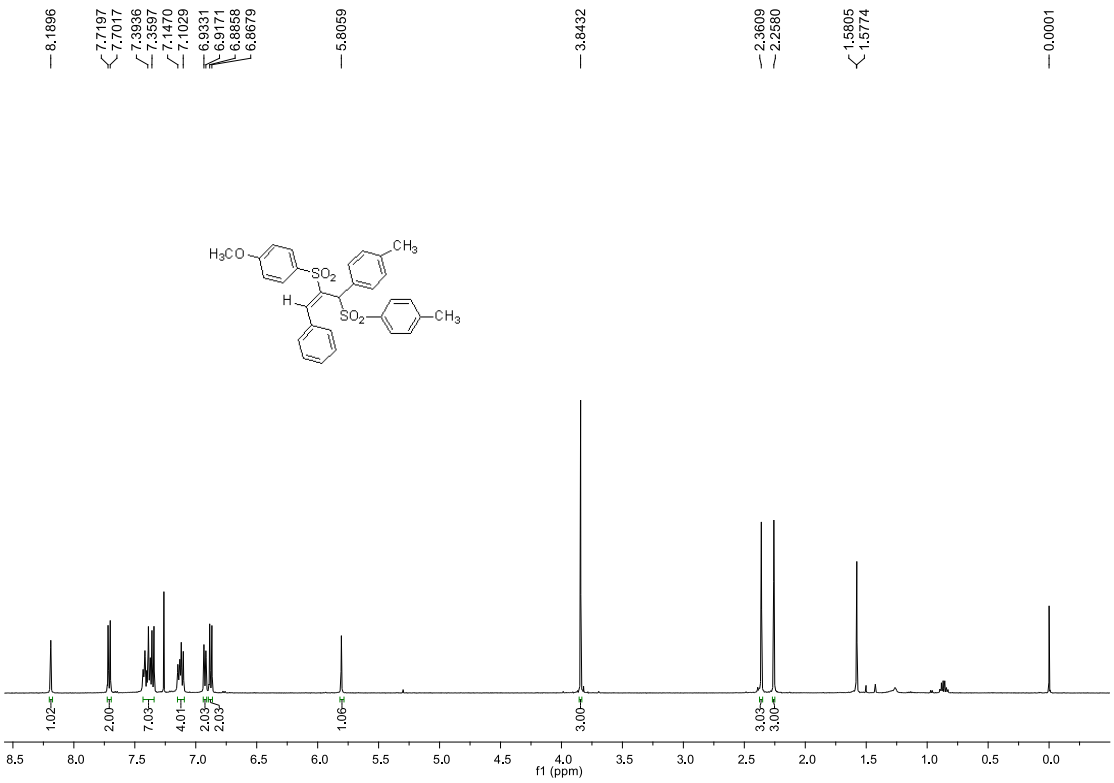
(*E*)-1-fluoro-4-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)benzene (5d)

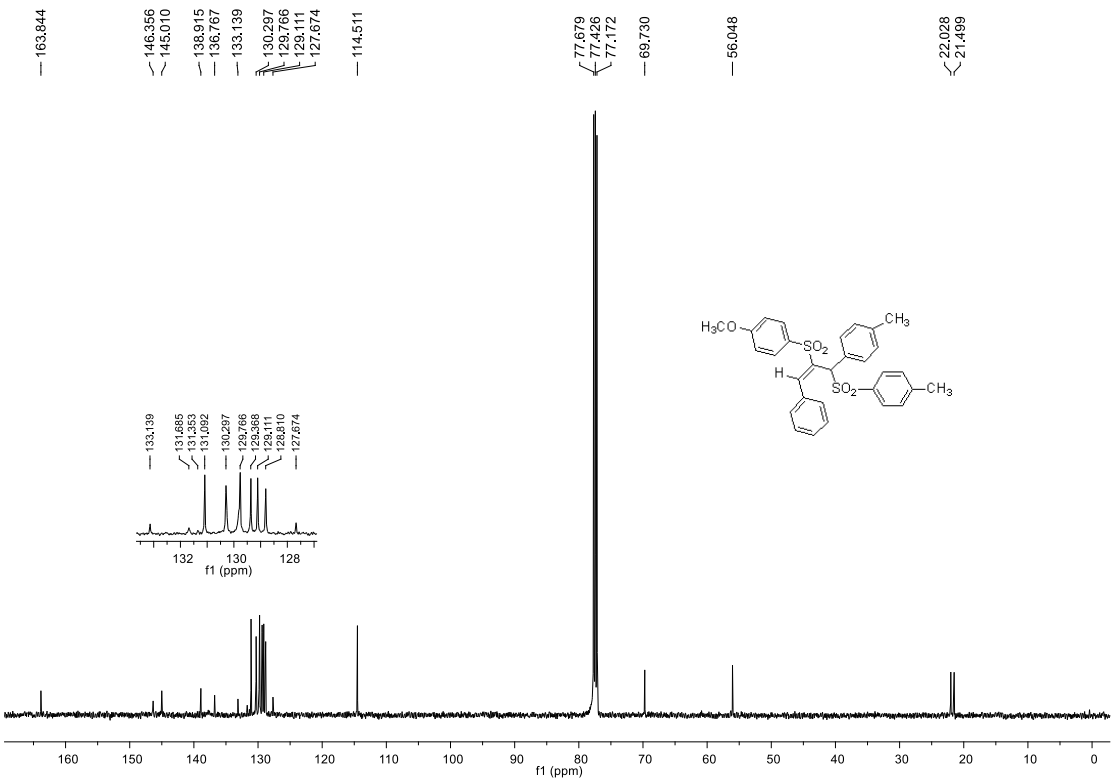




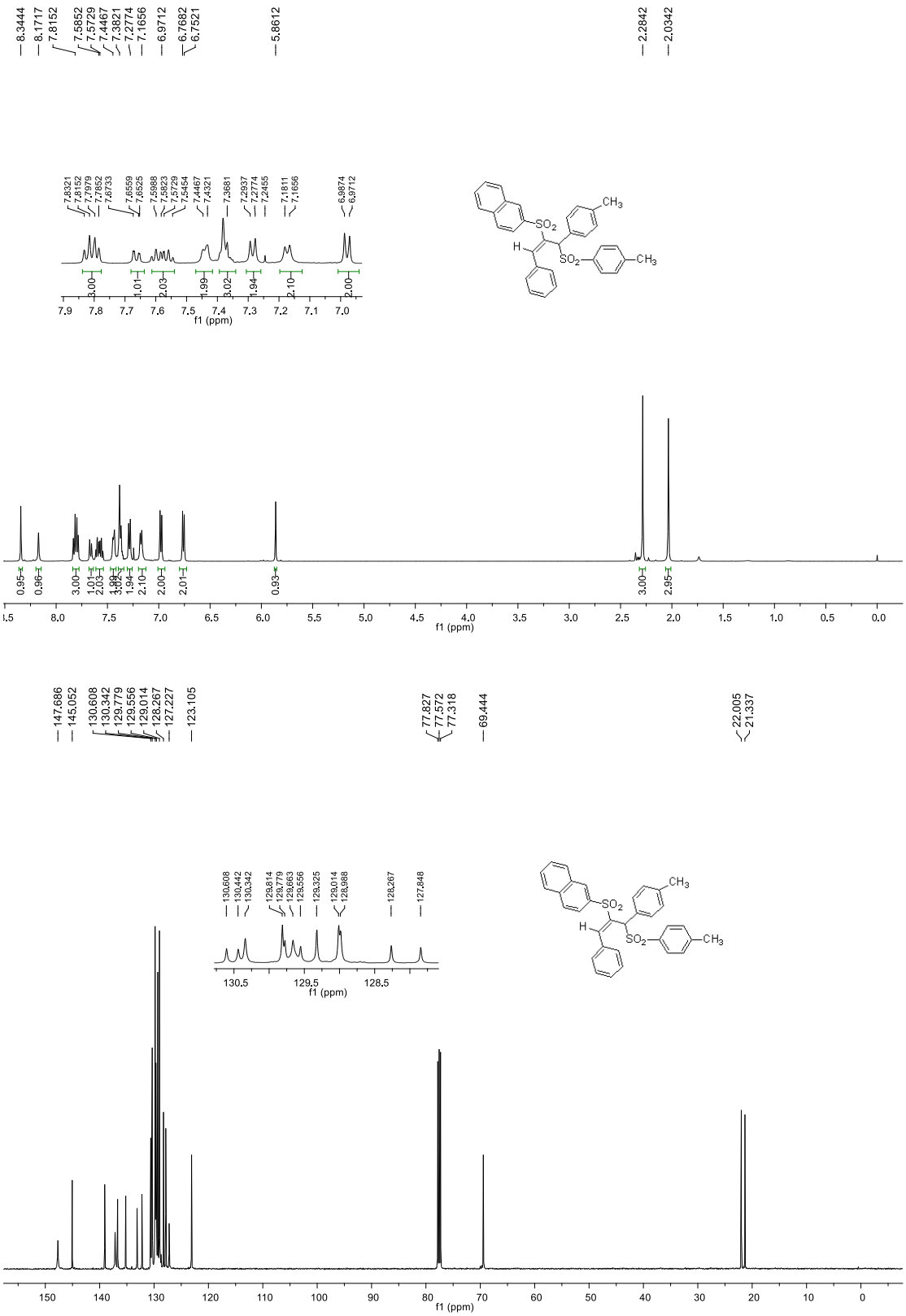

-104.1227
F
SO2
H
SO2
CH3
CH3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

(*E*)-1-methoxy-4-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)benzene (5e)

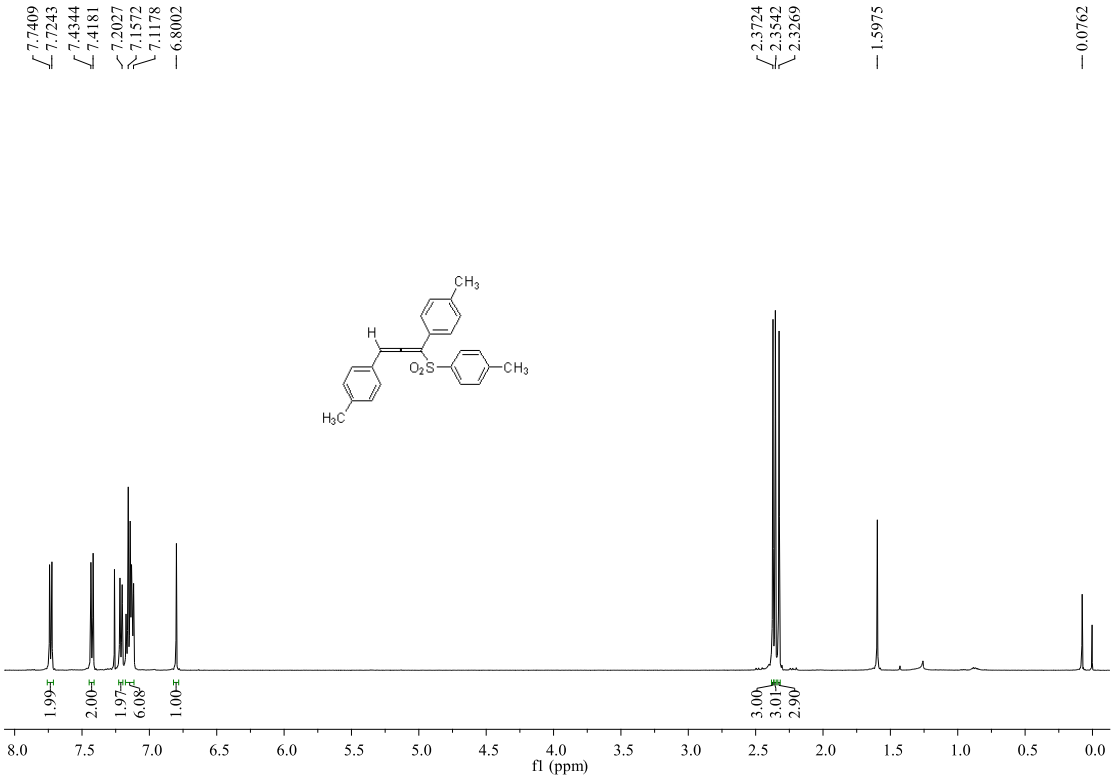


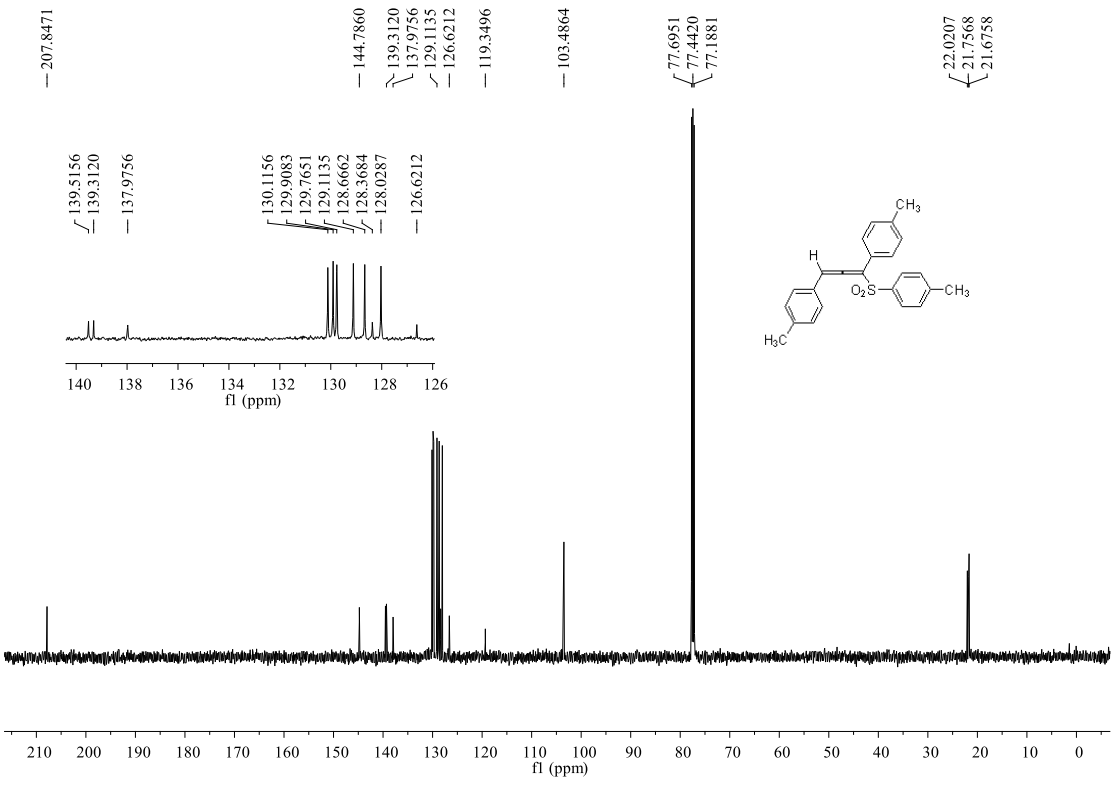


(*E*)-2-((1-phenyl-3-(*p*-tolyl)-3-tosylprop-1-en-2-yl)sulfonyl)naphthalene (5f)



Copy of ^{1}H NMR and ^{13}C NMR spectra of compound 6 and 1a-OAc





1,3-Di-p-tolylprop-2-yn-1-yl acetate (1a-OAc)