Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Ammonium iodide-induced sulfonylation of alkenes with DMSO and water toward the synthesis of vinyl methyl sulfones

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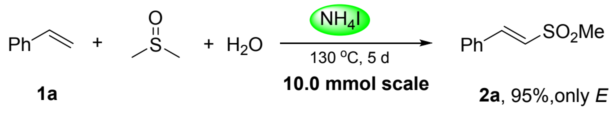
1. General information

Unless otherwise stated, analytical grade commercial reagents and solvents were used as the received. $H_2{}^{18}O$ (97%) and DMSO-d_6 were purchased from Alfa Aesar Chemical Company. DMSO (99.8%) was purchased from Aldrich. 2,2-Difluoro-5-vinylbenzo[d][1,3]dioxole, and but-1-en-2-ylbenzene were synthesized from commercially available compounds by Witting reaction following literature procedures. [1] Other alkenes were bought from Alfa Aesar, Acros and Aldrich. Analytical thin layer chromatography (TLC) was performed by using commercially prepared 100–400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). $CDCl_3$ was used as the solvent with TMS as the internal standard, and the chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Shimadzu GCMS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). HRMS analysis was performed in a MAT95XP high resolution mass spectrometer. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Melting points were measured with a Buchi B-545 melting point instrument.

2. General procedure for NH_4I-induced sulphonylation of alkenes

In a typical experiment, NH_4I (4 equiv), olefin (1 mmol), H_2O (0.5 g), and DMSO (1 mL) were added to a 10 mL seal tube in sequence. The seal tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 130 °C for the desired reaction time. After cooled to room temperature, the reaction mixture was decolorized with $Na_2S_2O_3$, and then washed with distilled water (50 mL) and extracted with ethyl acetate (4 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give desired product.

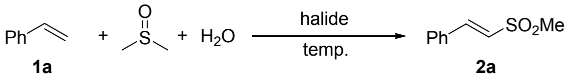
3. Procedure for the scale up experiment in 10 mmol



NH_4I (30 equiv), olefin (10 mmol), H_2O (5 g), and DMSO (15 mL) were added to a 50 mL round bottom flask in sequence. A condenser was connected to the flask, and the reaction mixture was stirred at 130 °C for 5 days. After cooled to room temperature, the reaction mixture was decolorized with $Na_2S_2O_3$, and then washed with distilled water (150 mL) and extracted with ethyl acetate (15 mL × 3). The organic layer was dried over

$MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give desired product.

4. Optimization of the sulphonylation of styrene[a]

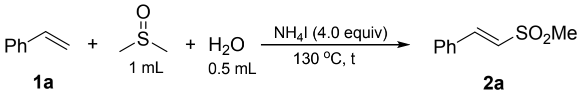


Entry	Halide (equiv)	Solvent	Temp/°C	Yield/%[b]
1	KI (4)	$DMSO/H_2O$ (2:1)	130	0
2	*n*-Bu_4NI (4)	$DMSO/H_2O$ (2:1)	130	0
3	NaI (4)	$DMSO/H_2O$ (2:1)	130	0
4	NH_4Br (4)	$DMSO/H_2O$ (2:1)	130	0
5	NH_4Cl (4)	$DMSO/H_2O$ (2:1)	130	0
6	**NH_4I (4)**	**$DMSO/H_2O$ (2:1)**	**130**	**98**
7	NH_4I (3)	DMSO	130	12
8	NH_4I (4)	$DMSO/H_2O$ (2:0.1)	130	35
9	NH_4I (4)	$DMSO/H_2O$ (2:0.5)	130	88
10	NH_4I (4)	$DMSO/H_2O$ (1:1)	130	75
11	NH_4I (4)	$DMSO/H_2O$ (2:3)	130	45
12	NH_4I (4)	$DMSO/H_2O$ (1:2)	130	0
13	NH_4I (1)	$DMSO/H_2O$ (2:1)	130	0
14	NH_4I (2)	$DMSO/H_2O$ (2:1)	130	56
15	NH_4I (5)	$DMSO/H_2O$ (2:1)	130	99
16	NH_4I (4)	$DMSO/H_2O$ (2:1)	100	0
17	NH_4I (4)	$DMSO/H_2O$ (2:1)	110	0
18	NH_4I (4)	$DMSO/H_2O$ (2:1)	115	5
19	NH_4I (4)	$DMSO/H_2O$ (2:1)	120	39
20	NH_4I (4)	$DMSO/H_2O$ (2:1)	135	94

[a] Reaction conditions: all of the reactions were performed with **1a** (1 mmol), DMSO (1 mL) in a 10 mL seal tube for 24 h. [b] Yield determined by ^1H NMR (internal standard: 1,3,5-trimethyl benzene).

5. Preliminary mechanistic studies

5.1 Reaction profiles of styrene and DMSO



A single factor parallel experimental method was adopted to obtain the reaction profile. NH_4I (4 equiv), olefin (1 mmol), H_2O (0.5 g), and DMSO (1 mL) were added to a 10 mL seal tube in sequence. The seal tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 130 °C for the different reaction times. An aliquot was taken from the reaction mixture at 4 h, 8 h, 10 h, 12 h, 16 h, 20 h and 24 h in the seven tubes in sequence and the product distributions of the corresponding reaction were analyzed by ^{1}H NMR (internal standard: 1,3,5-trimethyl benzene).

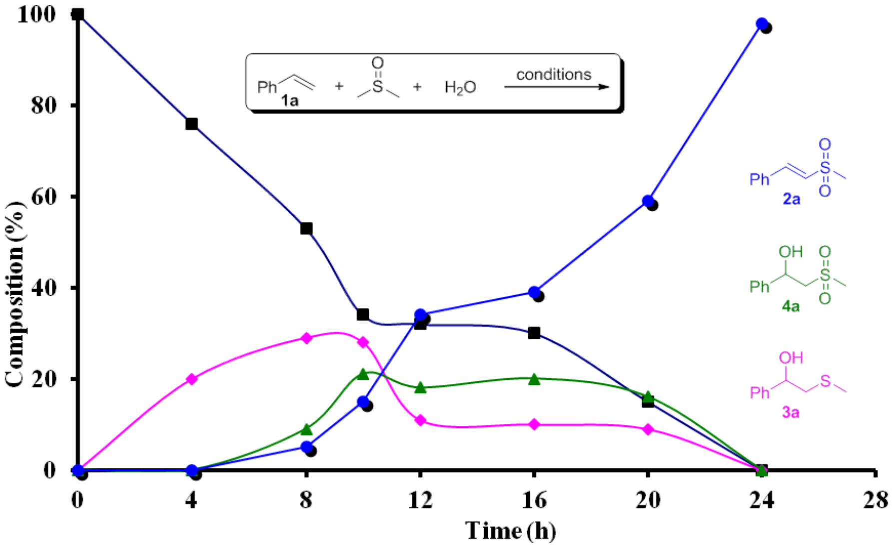
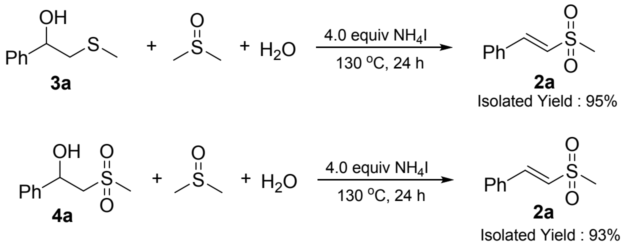
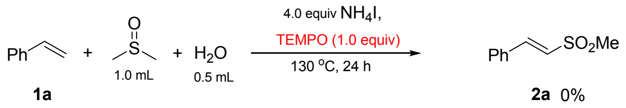


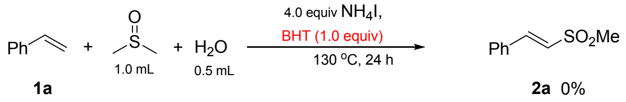
Figure S1. Reaction profile of the sulphonylation of styrene



In a typical experiment, NH_4I (4 equiv), **3a** or **4a** (1 mmol, isolated from the reaction mixture), H_2O (0.5 g), and DMSO (1 mL) were added to a 10 mL seal tube in sequence. The seal tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 130 °C for the desired reaction time. After cooled to room temperature, the reaction mixture was decolorized with $Na_2S_2O_3$, and then washed with distilled water (50 mL) and extracted with ethyl acetate (4 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give desired product.

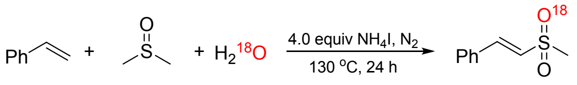
5.2 Radical trapping experiments





In a typical radical trapping experiment, NH_4I (4 equiv), TEMPO or BHT (1 mmol), olefin (1 mmol), H_2O (0.5 g), and DMSO (1 mL) were added to a 10 mL seal tube in sequence. The seal tube was sealed with a Teflon lined cap, and the reaction mixture was stirred at 130 °C for 24 h. After cooled to room temperature, the reaction mixture was decolorized with $Na_2S_2O_3$, and then washed with distilled water (50 mL) and extracted with ethyl acetate (4 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was analyzed by ^{1}H NMR (internal standard: 1, 3, 5-trimethyl benzene).

5.3 Isotope labeling experiments



Isolated Yield : 96%

Generic Display Report

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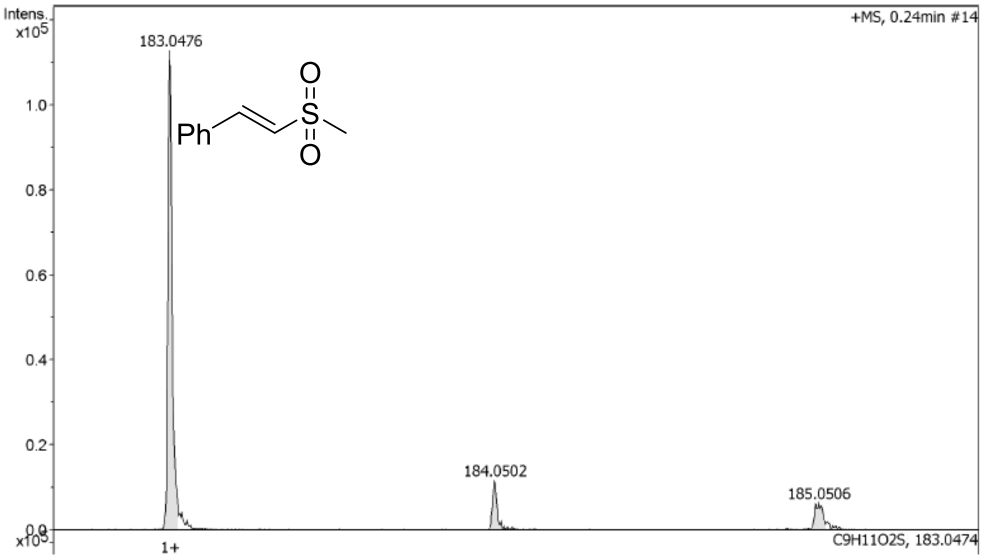
Instrument maXis impact



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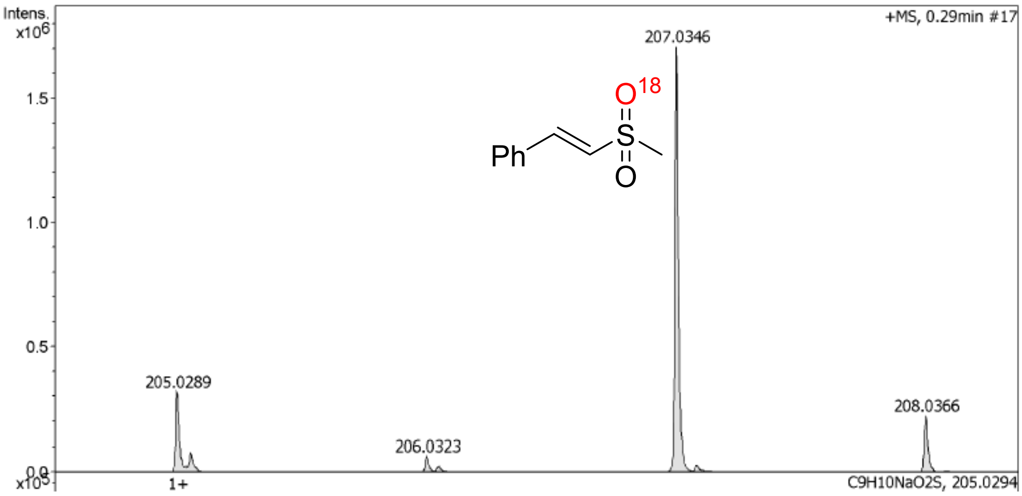
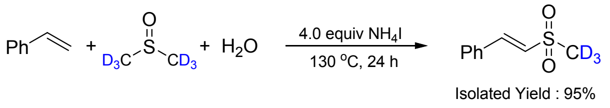
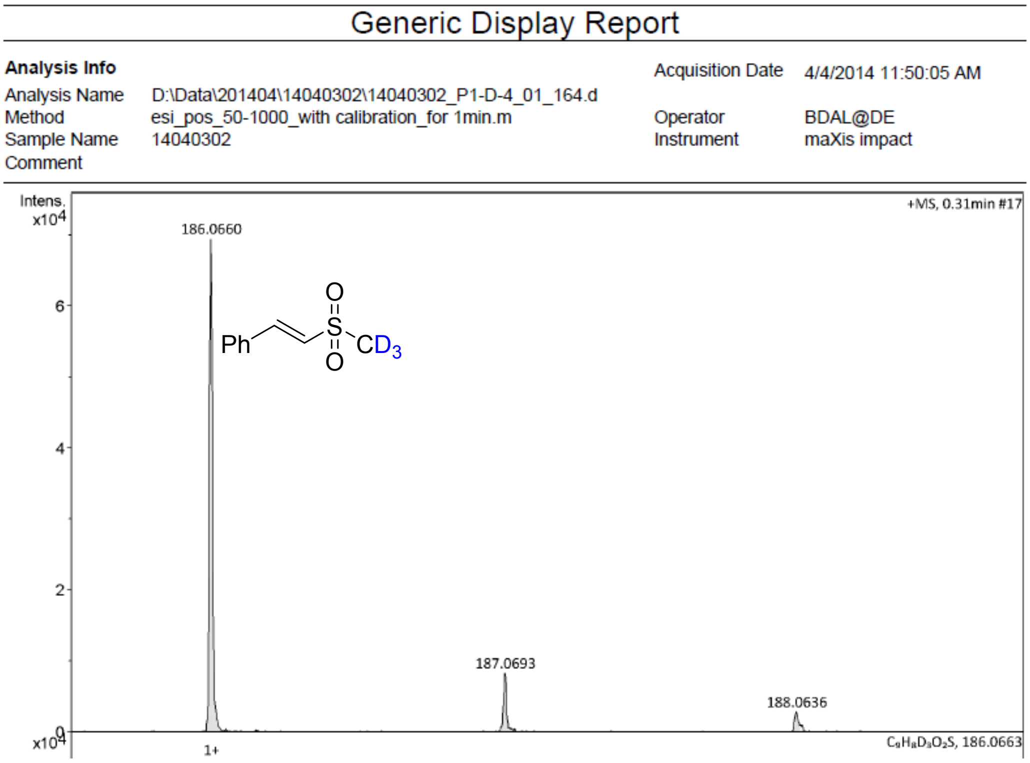


In a typical $H_2{}^{18}O$ labeling experiment, NH_4I (4 equiv, dehydration *via* dried at 100 °C), olefin (1 mmol), $H_2{}^{18}O$ (0.5 g), and DMSO (1 mL, 99.8%) were added to an oven-dried 10 mL seal tube in sequence in the glovebox. The seal tube was sealed with a Teflon lined cap, and then the tube was put into an oil bath at 130 °C under magnetic stirring for 24 h. After cooled to room temperature, the reaction mixture was decolorized with $Na_2S_2O_3$, and then washed with distilled water (50 mL) and extracted with ethyl acetate (4 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give desired product.



In a typical DMSO-d_6 labeling experiment, NH_4I (4 equiv, dehydration via dried at 100 °C), olefin (1 mmol), H_2O (0.5 g), and DMSO-d_6 (1 mL) were added to an oven-dried 10 mL seal tube in sequence in the glovebox. The seal tube was sealed with a Teflon lined cap, and then the tube was put into an oil bath at 130 °C under magnetic stirring for 24 h. After cooled to room temperature, the reaction mixture was decolorized with $Na_2S_2O_3$, and then washed with distilled water (50 mL) and extracted with ethyl acetate (4 mL × 3). The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (5:1) to give desired product.



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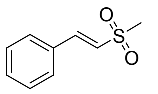
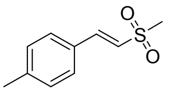
Comment			

6. Characterization data of products



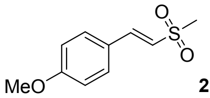
2a

(*E*)-(2-Methanesulfonyl-vinyl)-benzene (2a); white solid; m.p. 81–82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J*=15.6 Hz, 1H), 7.42–7.40 (m, 2H), 7.35–7.28 (m, 3H), 6.88 (d, *J*=15.6 Hz, 1H), 2.94 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 131.9, 131.1, 128.9, 128.4, 126.1, 43.0 ppm; IR (KBr): 1622, 1298, 1128, 966, 748, 500 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_9H_{11}O_2S$ $[M+H]^+$ 183.0474, found 183.0476.



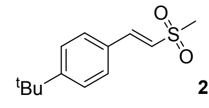
2b

(*E*)-1-(2-Methanesulfonyl-vinyl)-4-methyl-benzene (2b); white solid; m.p. 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J*=15.2 Hz, 1H), 7.41 (d, *J*=8.0 Hz, 2H), 7.23 (d, *J*=7.6 Hz, 2H), 6.86 (d, *J*=15.6 Hz, 1H), 3.03 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 142.1, 129.9, 129.4, 128.7, 125.1, 43.4, 21.8 ppm; IR (KBr): 2943, 2830, 1453, 1299, 1130, 1030 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{12}NaO_2S$ $[M+Na]^+$ 219.0450, found 219.0451.



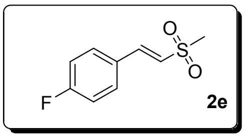
2c

(*E*)-1-(2-Methanesulfonyl-vinyl)-4-methoxy-benzene (2c); brown solid; m.p. 138–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=15.2 Hz, 1H), 7.46 (d, *J*=8.8 Hz, 2H), 6.93 (d, *J*=8.8 Hz, 2H), 6.77 (d, *J*=15.2 Hz, 1H), 3.85 (s, 3H), 3.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 144.0, 130.5, 124.6, 123.6, 114.7, 55.6, 43.7 ppm; IR (KBr): 2943, 2828, 1425, 1290, 1133, 1029 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{12}NaO_3S$ $[M+Na]^+$ 235.0399, found 235.0401.



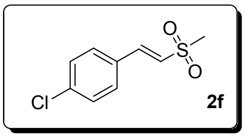
2d

(*E*)-1-tert-Butyl-4-(2-methanesulfonyl-vinyl)-benzene (2d); light yellow solid; m.p. 88–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J*=15.2 Hz, 1H), 7.47–7.43 (m, 4H), 6.88 (d, *J*=15.6 Hz, 1H), 3.03 (s, 3H), 1.33 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 143.9, 129.3, 128.4, 126.1, 125.2, 43.4, 35.0, 31.1 ppm; IR (KBr): 3082, 3008, 1430, 1106, 621, 546 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{13}H_{18}NaO_2S$ $[M+Na]^+$ 261.0920, found 261.0919.



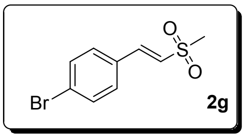
2e

(*E*)-1-Fluoro-4-(2-methanesulfonyl-vinyl)-benzene (2e); white solid; m.p. 128–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J*=15.2 Hz, 1H), 7.52 (dd, *J*=8.6, 5.4 Hz, 2H), 7.13 (t, *J*=8.6 Hz, 2H), 6.85 (d, *J*=15.6 Hz, 1H), 3.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 163.3, 142.7, 130.7, 130.6, 128.4, 128.3, 125.9, 125.9, 116.5, 116.3, 43.28 ppm; IR (KBr): 2946, 2834, 1640, 1302, 1132, 1028 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_9H_9FNaO_2S$ $[M+Na]^+$ 223.0199, found 223.0199.



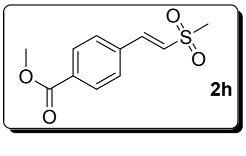
2f

(*E*)-1-Chloro-4-(2-methanesulfonyl-vinyl)-benzene (2f); light yellow solid; m.p. 129–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 15.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 16.0 Hz, 2H), 6.94 (d, *J* = 15.6 Hz, 1H), 3.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.3, 130.5, 129.7, 129.3, 126.7, 43.1 ppm; IR (KBr): 2939, 2832, 1638, 1298, 1128, 1028 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_9H_9ClNaO_2S$ $[M+Na]^+$ 238.9904, found 238.9907.



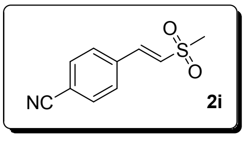
2g

(*E*)-1-Bromo-4-(2-methanesulfonyl-vinyl)-benzene (2g); light yellow solid; m.p. 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J*=12.0, 3.2 Hz, 3H), 7.38 (d, *J*=8.4, 2H), 6.93 (d, *J*=15.6 Hz, 1H), 3.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 132.3, 130.9, 129.9, 126.9, 125.7, 43.12 ppm; IR (KBr): 2941, 2831, 1638, 1404, 1129, 1027 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_9H_9BrNaO_2S$ $[M+Na]^+$ 282.9399, found 282.9399.



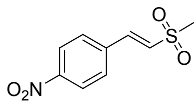
2h

(*E*)- 4-(2-Methanesulfonyl-vinyl)-benzoic acid methyl ester (2h); white solid; m.p. 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 15.5 Hz, 1H), 3.94 (s, 3H), 3.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 142.6, 136.2, 132.4, 130.3, 129.3, 128.4, 52.4, 43.1 ppm; IR (KBr): 2941, 2830, 1573, 1409, 1120, 1029 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{11}H_{12}NaO_4S$ $[M+Na]^+$ 263.0349, found 263.0348.



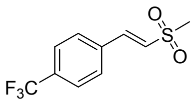
2i

(*E*)-4-(2-Methanesulfonyl-vinyl)-benzonitrile (2i); light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.66–7.62(m, 3H), 7.05 (d, *J* = 15.6 Hz, 1H), 3.07 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 136.3, 132.8, 129.8, 128.9, 117.9, 114.5, 43.0 ppm; IR (KBr): 2939, 2831, 1647, 1404, 1122, 1029 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_9NNaO_2S$ $[M+Na]^+$ 230.0246, found 230.0237.



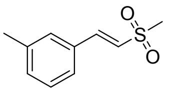
2j

(E)-1-(2-(Methylsulfonyl)vinyl)-4-nitrobenzene (2j); light yellow solid; m.p. 181–182 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.69 (dd, *J* = 12.0, 3.2 Hz, 3H), 7.07 (d, *J* = 14.2 Hz, 1H), 3.08 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.1, 130.5, 129.3, 124.4, 43.1 ppm; IR (KBr): 2942, 2831, 2356, 1647, 1405, 1028 cm^{-1}; MS (EI) m/z: 89, 102, 118, 148, 164, 227.



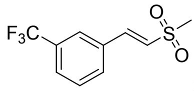
2k

(*E*)-1-(2-Methanesulfonyl-vinyl)-4-trifluoromethyl-benzene (2k); light yellow solid; m.p. 143–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.64 (m, 5H), 7.07 (d, *J* = 15.2 Hz, 1H), 3.07 (s, 3H) ppm; ^{13}C NMR (100MHz, $CDCl_3$) δ 142.0, 135.4, 133.2, 132.8, 132.5, 132.2, 128.8, 128.7, 128.3, 127.6, 127.6, 126.1, 126.1, 126.0, 126.0, 124.9, 122.2, 43.0 ppm; IR (KBr): 2934, 2831, 2356, 1530, 1303, 1127 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_9F_3NaO_2S$ $[M+Na]^+$ 273.0168, found 273.0161.



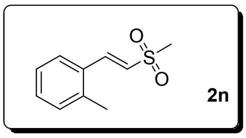
2l

(*E*)-1-(2-Methanesulfonyl-vinyl)-3-methyl-benzene (2l); light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J*=15.2 Hz, 1H), 7.32–7.31 (m, 3H), 7.29–7.26 (m, 1H), 6.90 (d, *J*=15.2 Hz, 1H), 3.03 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 138.9, 132.2, 132.0, 129.2, 129.0, 125.9, 125.8, 43.4, 21.3 ppm; IR (KBr): 2942, 2831, 1644, 1395, 1123, 1028 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{12}NaO_2S$ $[M+Na]^+$ 219.0450, found 219.0446.

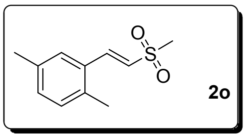


2m

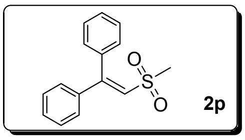
(*E*)-1-(2-Methanesulfonyl-vinyl)-3-trifluoromethyl-benzene (2m); brown solid; m.p. 142–143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.72–7.65(m, 3H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 15.6 Hz, 1H), 3.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 132.9, 131.9, 131.7, 131.6, 129.8, 128.3, 127.8, 127.8, 127.7, 127.7, 125.1, 125.0, 125.0, 124.9, 124.9, 122.2, 43.1 ppm; IR (KBr): 2968, 1629, 1425, 989, 1101, 622 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_9F_3NaO_2S$ [M+Na]$^+$ 273.0168, found 273.0173.



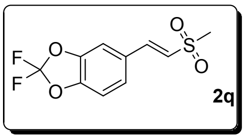
(*E*)-1-(2-Methanesulfonyl-vinyl)-2-methyl-benzene (2n); light yellow solid; m.p. 112–113 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (d, *J*=15.2 Hz, 1H), 7.51 (d, *J*=8.4 Hz, 1H), 7.34 (t, *J*=7.4 Hz, 1H), 7.62–7.24 (m, 2H), 6.85 (d, *J*=15.6 Hz, 1H), 3.04 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.8, 138.3, 131.1, 131.0, 127.1, 126.9, 126.6, 43.4, 19.8 ppm; IR (KBr): 3008, 1628, 1425, 1171, 1102, 621 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{12}NaO_2S$ [M+Na]$^+$ 219.0450, found 219.0453.



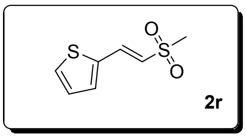
(*E*)-2-(2-Methanesulfonyl-vinyl)-1,4-dimethyl-benzene (2o); light yellow solid; m.p. 80–81 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.88 (d, *J* = 15.2 Hz, 1H), 7.32 (s, 1H), 7.16–7.11 (m, 2H), 6.83 (d, *J* = 15.2 Hz, 1H), 3.04 (s, 3H), 2.40 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.8, 136.0, 135.3, 132.0, 131.0, 130.7, 127.3, 126.7, 43.3, 20.8, 19.2 ppm; IR (KBr): 3002, 1629, 1425, 1174, 621, 545 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{11}H_{14}NaO_2S$ [M+Na]$^+$ 233.0607, found 233.0603.



(2-(Methylsulfonyl)ethene-1,1-diyl)dibenzene (2p); white solid; m.p. 101–102 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49–7.26 (m, 10H), 6.86 (s, 1H), 2.68 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.8, 139.0, 135.6, 130.4, 129.8, 129.5, 128.7, 128.3, 128.0, 43.2 ppm; IR (KBr): 2943, 2832, 1648, 1567, 1405, 1027 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{15}H_{14}NaO_2S$ [M+Na]$^+$ 281.0607, found 281.0603.

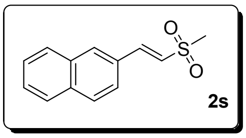


(*E*)-2,2-Difluoro-5-(2-methanesulfonyl-vinyl)-benzo[1,3]dioxole (2q); light yellow solid; m.p. 142–143 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.58 (d, *J* = 15.6 Hz, 1H), 7.27 (d, *J* = 9.2 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 15.6 Hz, 1H), 3.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 145.8, 144.4, 142.5, 134.1, 131.6, 129.0, 128.5, 126.5, 125.9, 110.0, 108.3, 43.21 ppm; IR (KBr): 3114, 2978, 1624, 1377, 1098, 619 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_8F_2NaO_4S$ [M+Na]$^+$ 285.0004, found 285.0004.



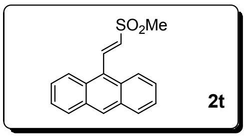
2r

(*E*)-2-(2-Methanesulfonyl-vinyl)-thiophene (2r); brown liquid; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.73 (d, *J* = 15.2 Hz, 1H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 3.6 Hz, 1H), 7.11–7.09 (m, 1H), 6.70 (d, *J* = 15.2 Hz, 1H), 3.03 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.6, 130.1, 128.4, 124.3, 43.5 ppm; IR (KBr): 2940, 2831, 1640, 1552, 1390, 1028 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_7H_8NaO_2S_2$ [M+Na]$^+$ 210.9858, found 210.9857.



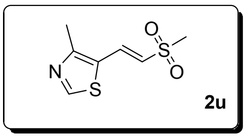
2s

(*E*)-2-(2-Methanesulfonyl-vinyl)-naphthalene (2s); tawny solid; m.p. 145–146 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95–7.77 (m, 5H), 7.61–7.52 (m, 3H), 7.02 (d, *J*=15.6 Hz, 1H), 3.07 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.1, 134.6, 133.1, 131.0, 129.5, 129.1, 128.7, 127.9, 127.8, 127.0, 126.2, 123.3, 43.5 ppm; IR (KBr): 2944, 2832, 1644, 1552, 1119, 1022 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{13}H_{12}NaO_2S$ [M+Na]$^+$ 255.0450, found 255.0454.



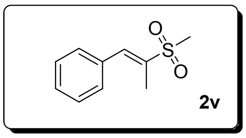
2t

(*E*)-9-(2-Methanesulfonyl-vinyl)-anthracene (2t); brown solid; m.p. 165–166 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.60 (d, *J* = 15.6 Hz, 1H), 8.49 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.57–7.46 (m, 4H), 6.98 (d, *J* = 15.6 Hz, 1H), 3.19 (s, 3H) ppm； ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.1, 134.5, 131.1, 129.3, 129.3, 129.0, 127.0, 126.0, 125.5, 124.4, 43.2 ppm; IR (KBr): 2930, 2839, 1640, 1550, 1309, 1022 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{17}H_{14}NaO_2S$ [M+Na]$^+$ 305.0607, found 305.0610.



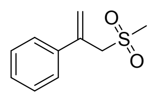
2u

(*E*)-5-(2-Methanesulfonyl-vinyl)-4-methyl-thiazole (2u); brown solid; m.p. 125–126 ^{o}C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.79 (s, 1H), 7.77 (d, *J* = 15.2 Hz, 1H), 6.66 (d, *J* = 15.2 Hz, 1H), 3.05 (s, 3H), 2.59 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.8, 154.0, 133.2, 126.9, 125.7, 43.3, 15.7 ppm; IR (KBr): 2926, 1747, 1555, 1385, 1129, 1026 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_7H_9NaO_2S_2$ [M+Na]$^+$ 225.9967, found 225.9965.



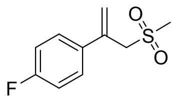
2v

(E)-(2-(Methylsulfonyl)prop-1-enyl)benzene (2v); light yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (s, 1H), 7.46–7.38 (m, 5H), 2.97 (s, 3H), 2.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.0, 136.7, 133.5, 129.6, 129.4, 128.7, 40.4, 13.4 ppm; IR (KBr): 3106, 2975, 1624, 1425, 1098, 619 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{12}NaO_2S$ [M+Na]$^+$ 219.0450, found 219.0453.



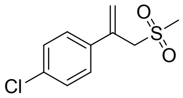
2w

(1-Methanesulfonylmethyl-vinyl)-benzene (2w); light yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.48–7.45 (m, 2H), 7.41–7.32 (m, 3H), 5.76 (s, 1H), 5.57 (s, 1H), 4.19 (s, 2H), 2.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.6, 136.7, 128.8, 128.5, 126.3, 122.1, 60.7, 40.2 ppm; IR (KBr): 3005, 1628, 1425, 1174, 1100, 620 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{12}NaO_2S$ [M+Na]$^+$ 219.0450, found 219.0451.



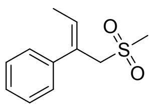
2x

1-Fluoro-4-(1-methanesulfonylmethyl-vinyl)-benzene (2x); light yellow solid; m.p. 80–81 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46 (dd, *J* = 8.0, 5.1 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.73 (s, 1H), 5.54 (s, 1H), 4.17 (s, 2H), 2.78 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.1, 161.6, 135.7, 134.8, 134.7, 128.2, 128.1, 122.0, 115.9, 115.6, 60.9, 40.2 ppm; IR (KBr): 3105, 2787, 1625, 1425, 1099, 620 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{11}FNaO_2S$ [M+Na]$^+$ 237.0356, found 237.0362.



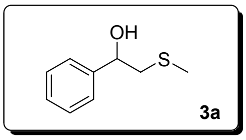
2y

1-Chloro-4-(1-methanesulfonylmethyl-vinyl)-benzene (2y); light yellow solid; m.p. 85–86 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43–7.34 (m, 4H), 5.77 (s, 1H), 5.56 (s, 1H), 4.16 (s, 2H), 2.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.0, 135.6, 134.5, 127.6, 122.5, 60.5, 40.2 ppm; IR (KBr): 3002, 2847, 1595, 1425, 1106, 621 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{10}H_{11}ClNaO_2S$ [M+Na]$^+$ 253.0060, found 253.0062.

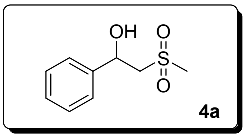


2z

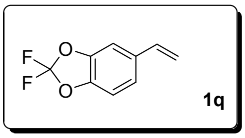
(1-Methanesulfonylmethyl-propenyl)-benzene (2z); light yellow liquid; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41–7.33 (m, 5H), 6.25 (q, *J* = 7.0, 14.2 Hz, 1H), 4.27 (s, 2H), 2.56 (s, 3H), 1.99 (d, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.0, 133.6, 128.9, 127.7, 126.4, 125.5, 56.2, 41.1, 15.5 ppm; IR (KBr): 2943, 2831, 1574, 1410, 1119,1029 cm^{-1}; HRMS-ESI (m/z): calcd. for $C_{11}H_{14}NaO_2S$ [M+Na]$^+$ 233.0607, found 233.0615.



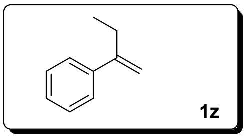
2-(Methylthio)-1-phenylethanol (3a)[2]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.27 (m, 5H), 4.77 (dd, *J* = 9.2, 3.2 Hz, 1H), 2.89–2.69 (m, 3H), 2.13 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.5, 127.8, 125.8, 71.2, 44.0, 15.4 ppm; MS (EI) m/z: 168, 107, 79, 62.



2-(Methylsulfonyl)-1-phenylethanol (4a)[2]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.29 (m, 5H), 5.35 (d, *J* = 10.4 Hz, 1H), 3.46 (dd, *J* = 14.8, 10.2 Hz, 1H), 3.17 (d, *J* = 14.8 Hz, 1H), 3.05 (s, 4H), 3.02 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 129.0, 128.7, 125.6, 69.3, 62.5, 42.8 ppm; MS (EI) m/z: 200, 120, 107, 94, 78.



2,2-Difluoro-5-vinyl-benzo[1,3]dioxole (1q); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.61 (d, *J* = 17.6 Hz, 1H), 5.21 (d, *J* = 11.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 143.3, 135.6, 134.3, 131.7, 129.2, 122.3, 114.0, 109.2, 106.4 ppm.



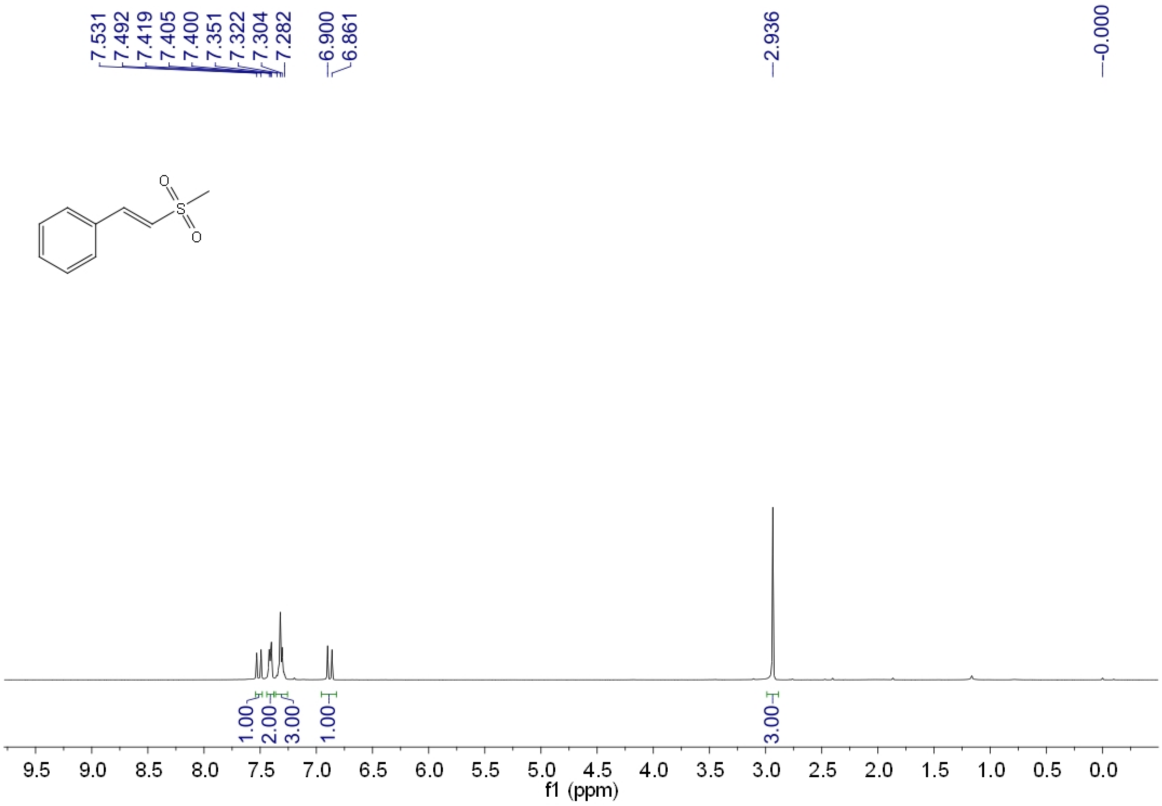
But-1-en-2-ylbenzene (1z); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.37 (m, 2H), 7.30–7.26 (m, 2H), 7.23–7.21 (m, 1H), 5.26 (s, 1H), 5.04 (s, 1H), 2.52 – 2.46 (m, 2H), 1.11–1.06 (m, 3H) ppm;^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 141.5, 128.2, 127.2, 126.0, 110.9, 28.1, 13.0 ppm.

7. References

[1] Taber, D. F.; Nelson, C. G. *J. Org. Chem.*, **2006**, *71*, 8973.

[2] Truce, W. E.; Buser, K.R. *J. Am. Chem. Soc.*, **1954**, *76*, 3577.

8. NMR spectra of products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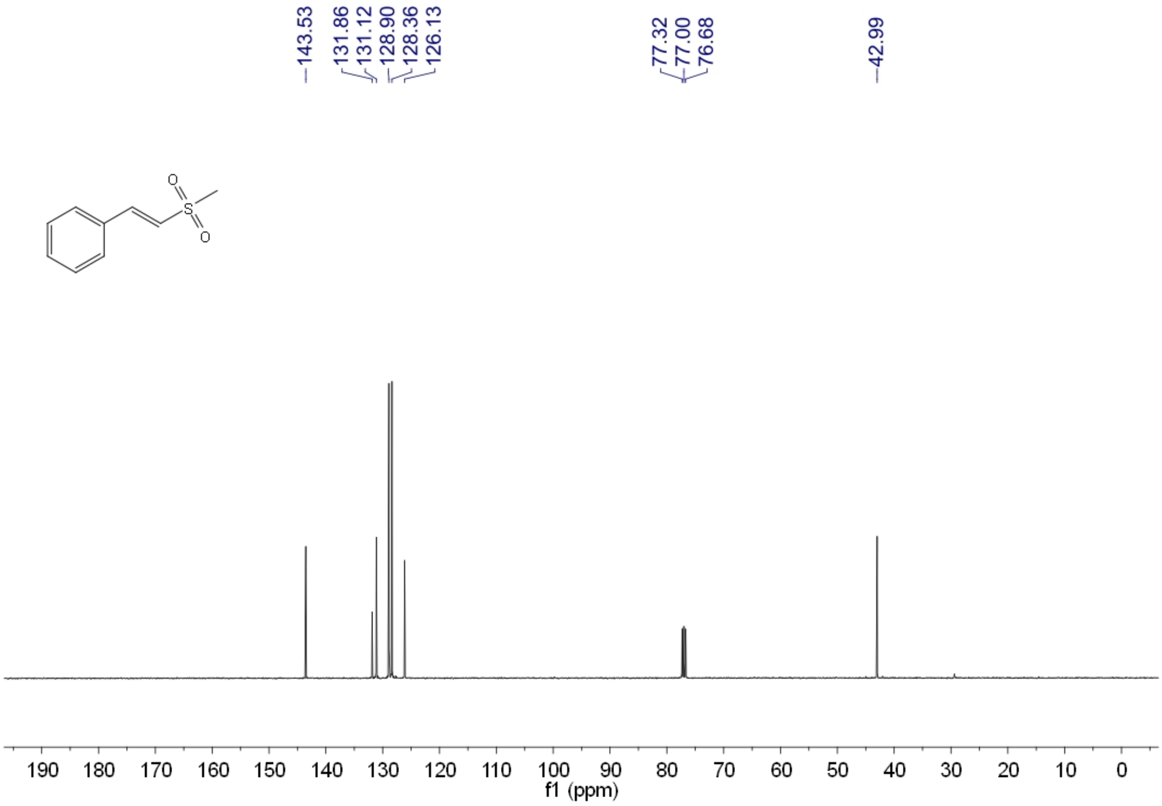
7.419
7.405
7.400
7.351
7.322
7.304
7.282
6.900
6.861
2.936
-0.000
O
S
O
1.00
2.00
3.00
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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77.00
76.68
42.99
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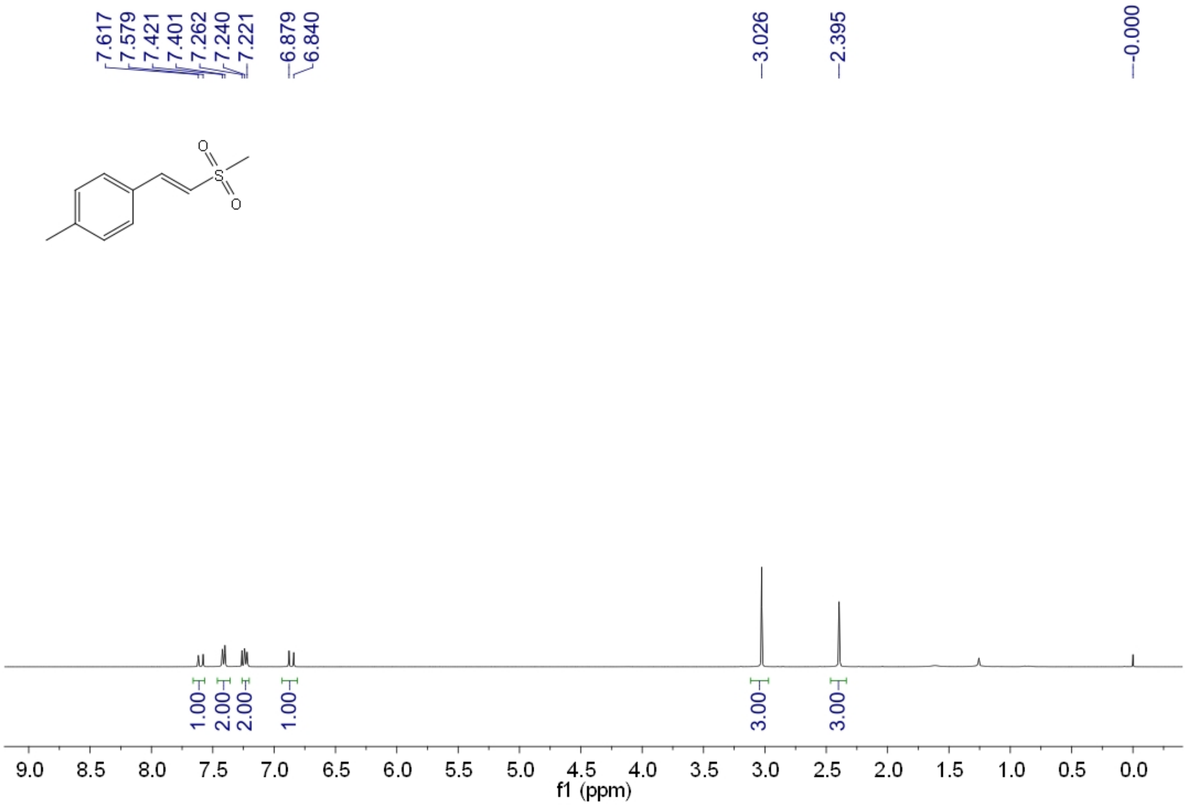
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.401
7.262
7.240
7.221
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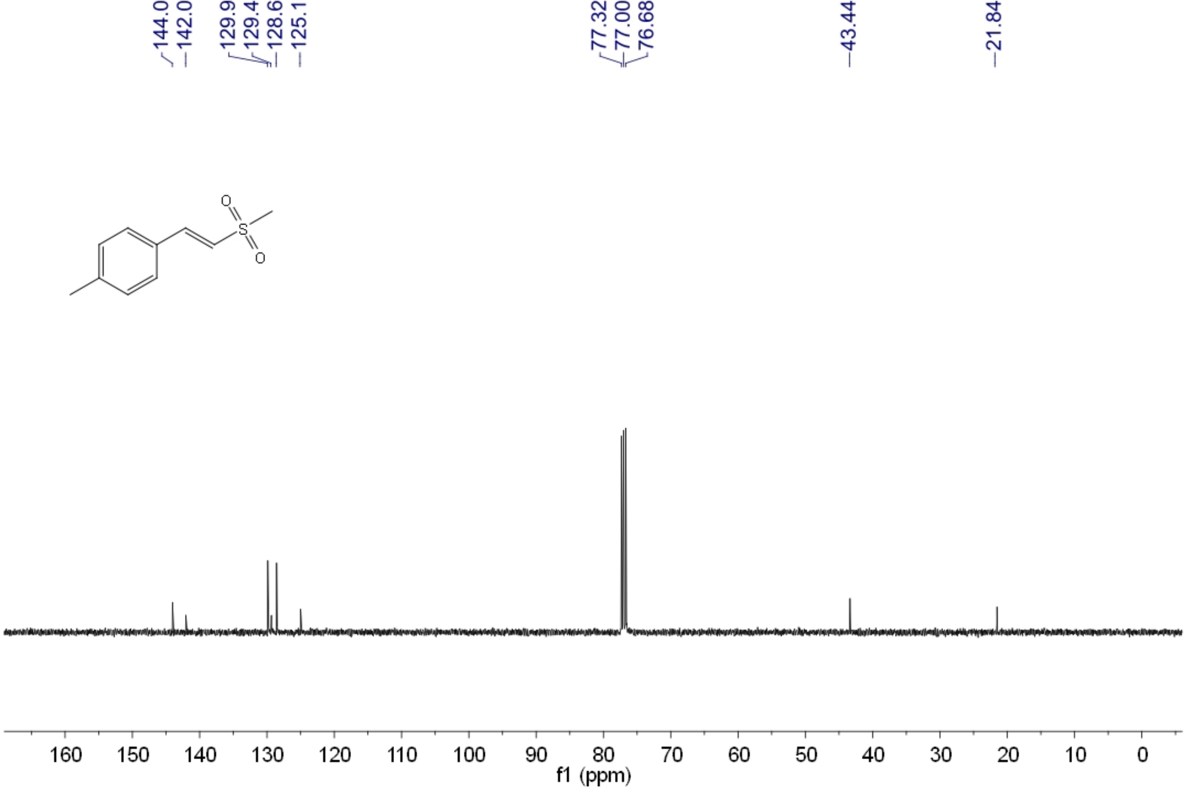
O
S
O
1.00
2.00
2.00
1.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


144.07
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129.42
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125.10
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77.00
76.68
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O
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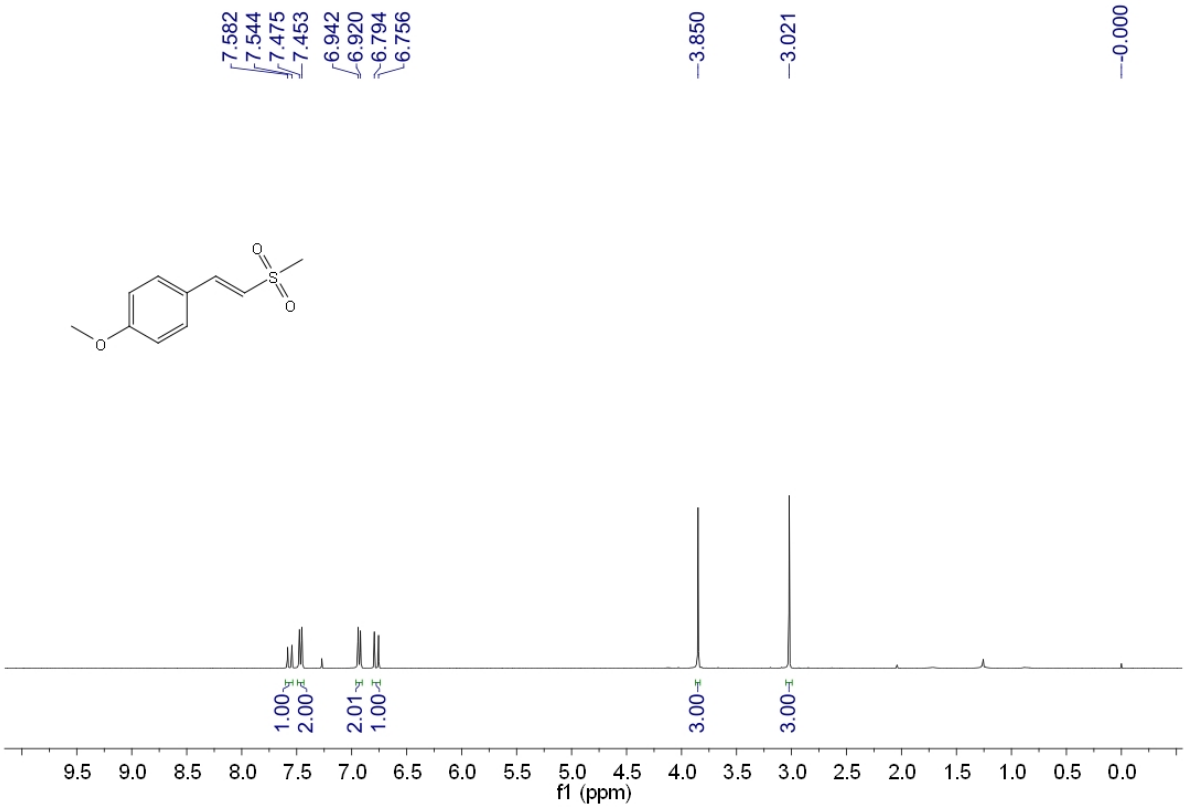
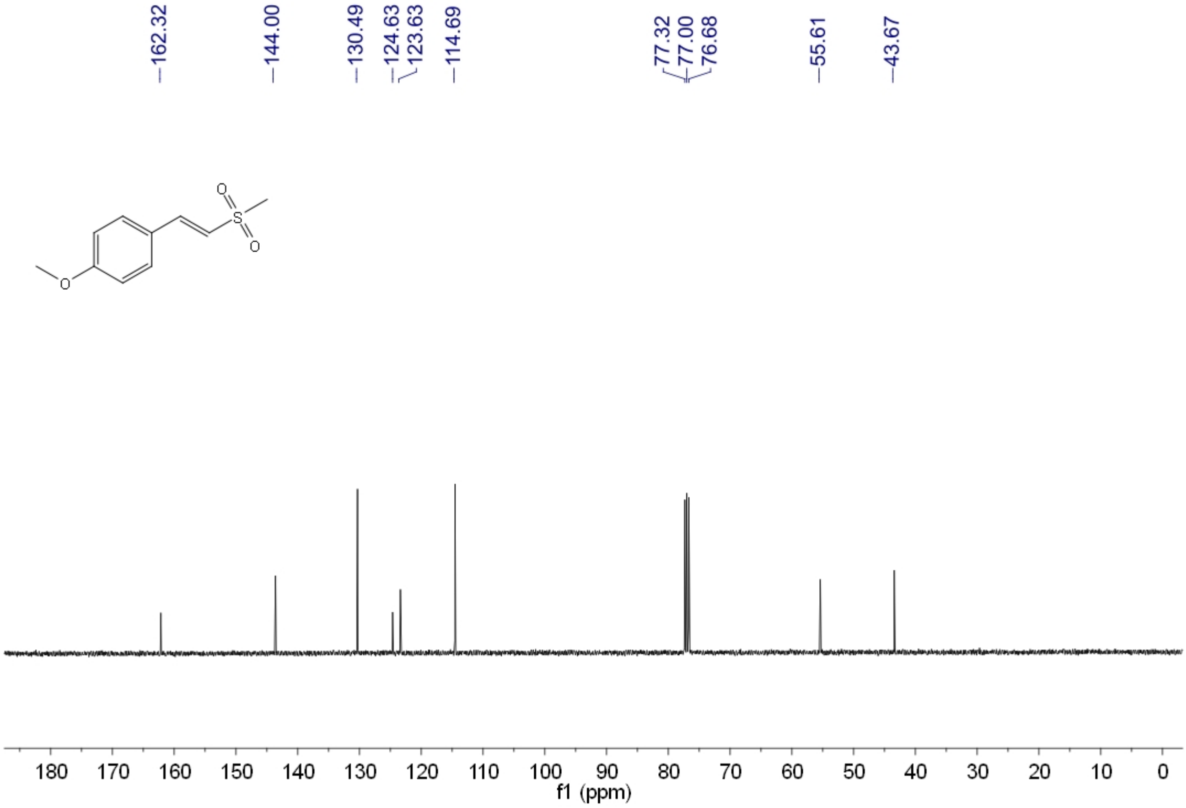
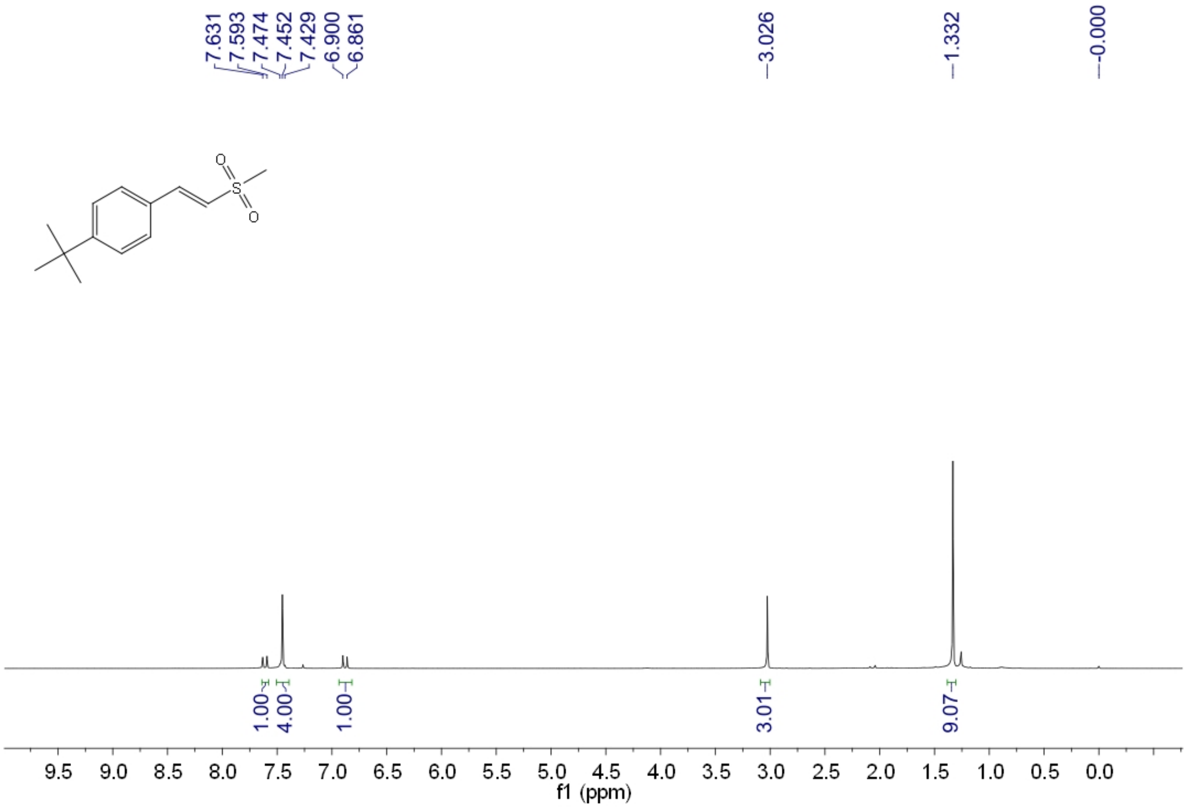
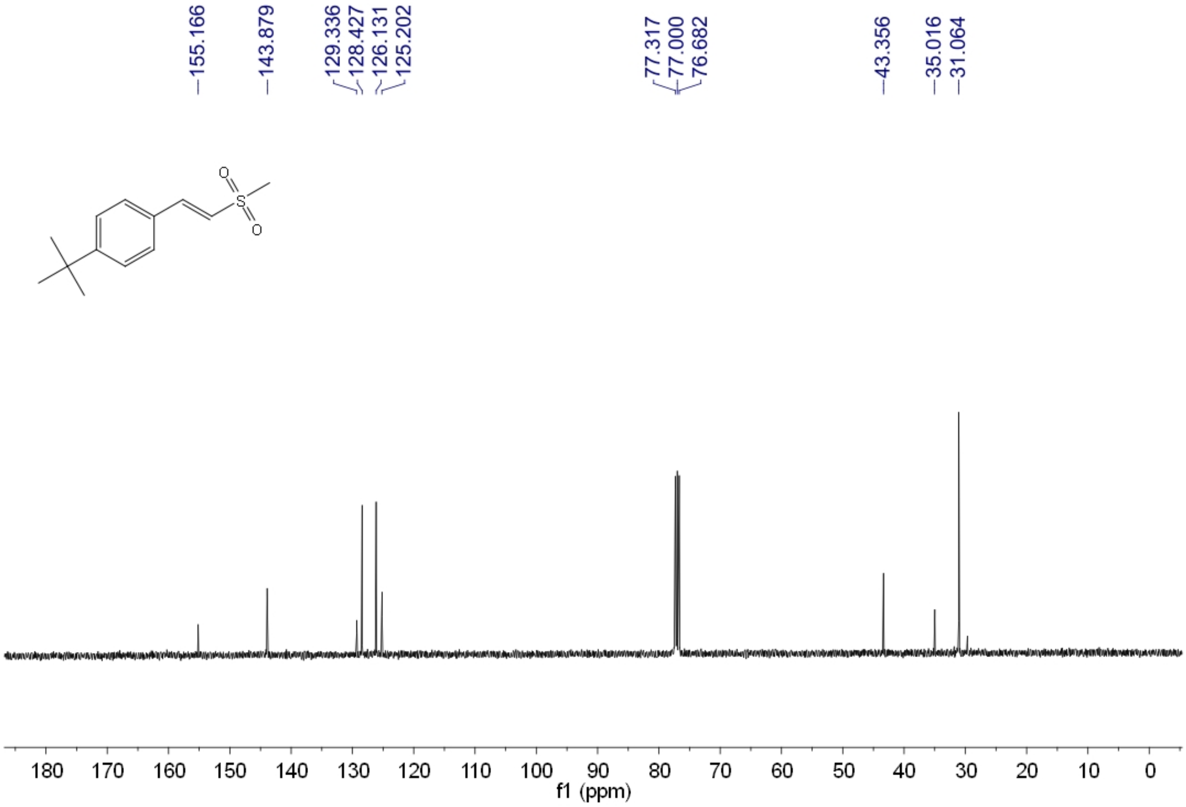
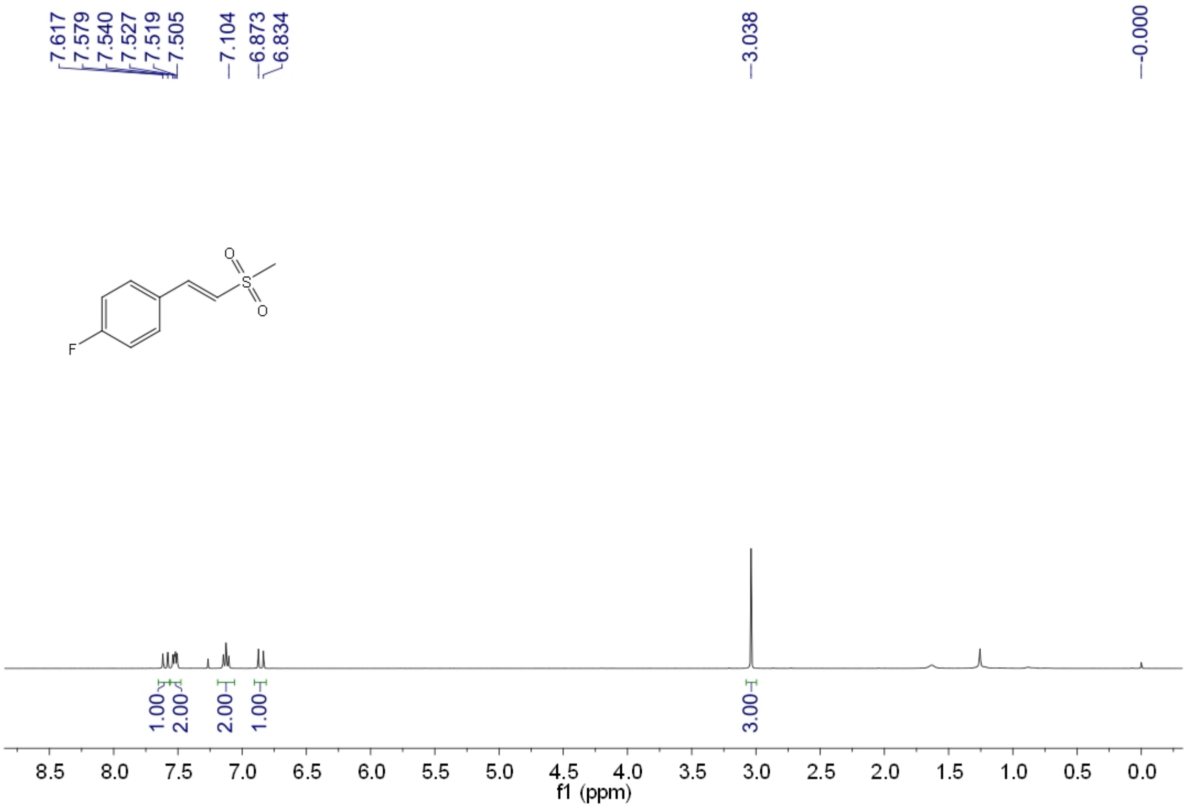
f1 (ppm)

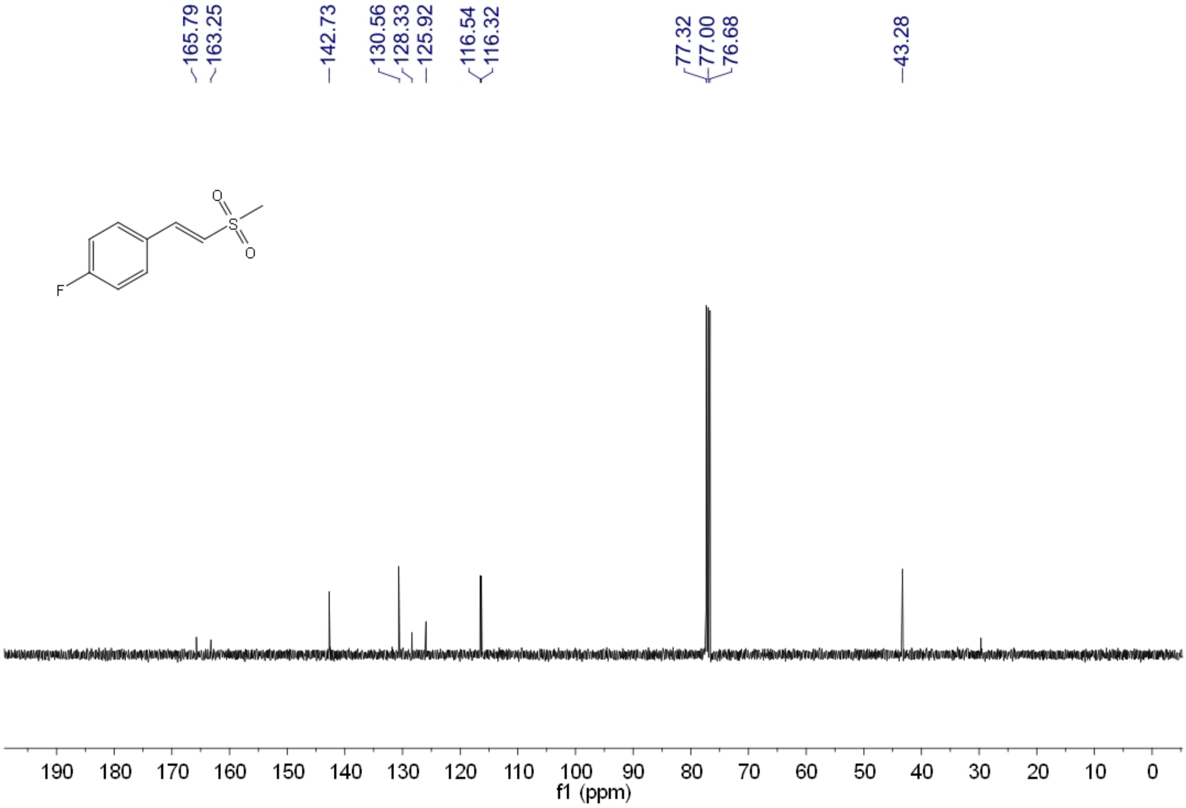

7.582
7.544
7.475
7.453
6.942
6.920
6.794
6.756
3.850
3.021
0.000
O
S
O
O
1.00
2.00
2.01
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

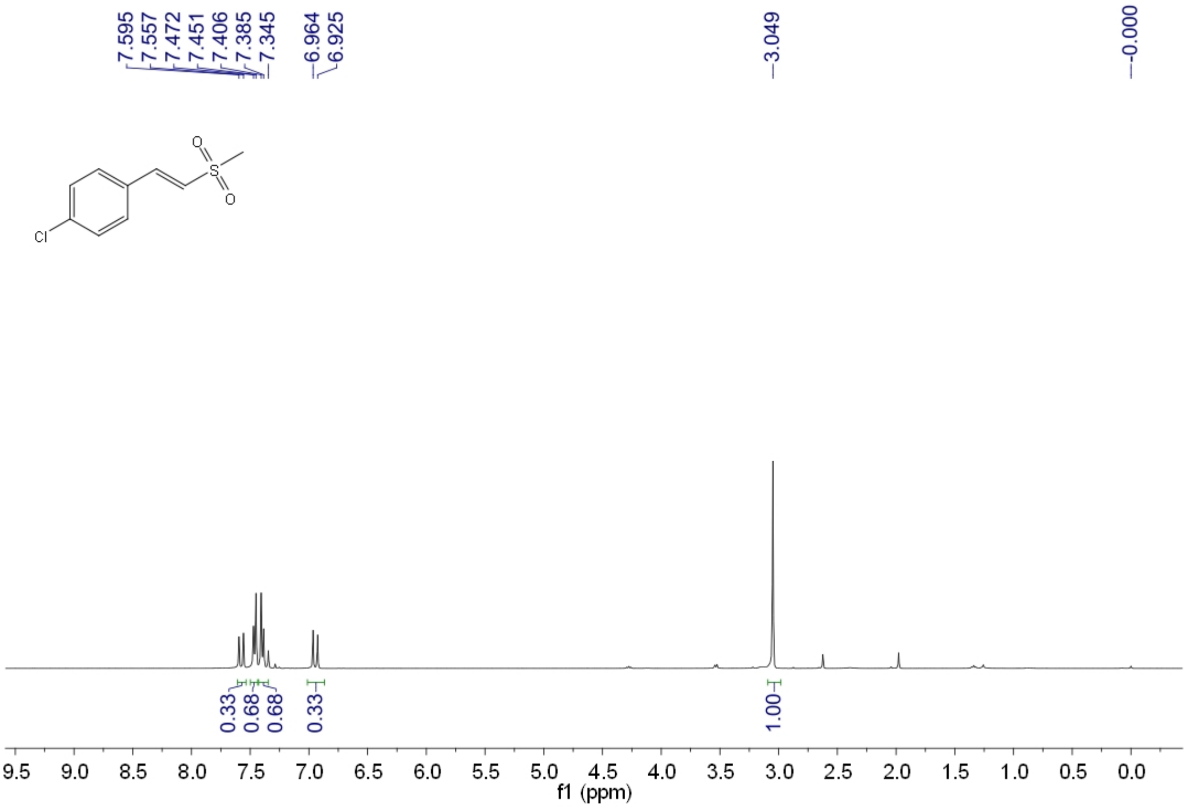

162.32
144.00
130.49
124.63
123.63
114.69
77.32
77.00
76.68
55.61
43.67
O
S
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

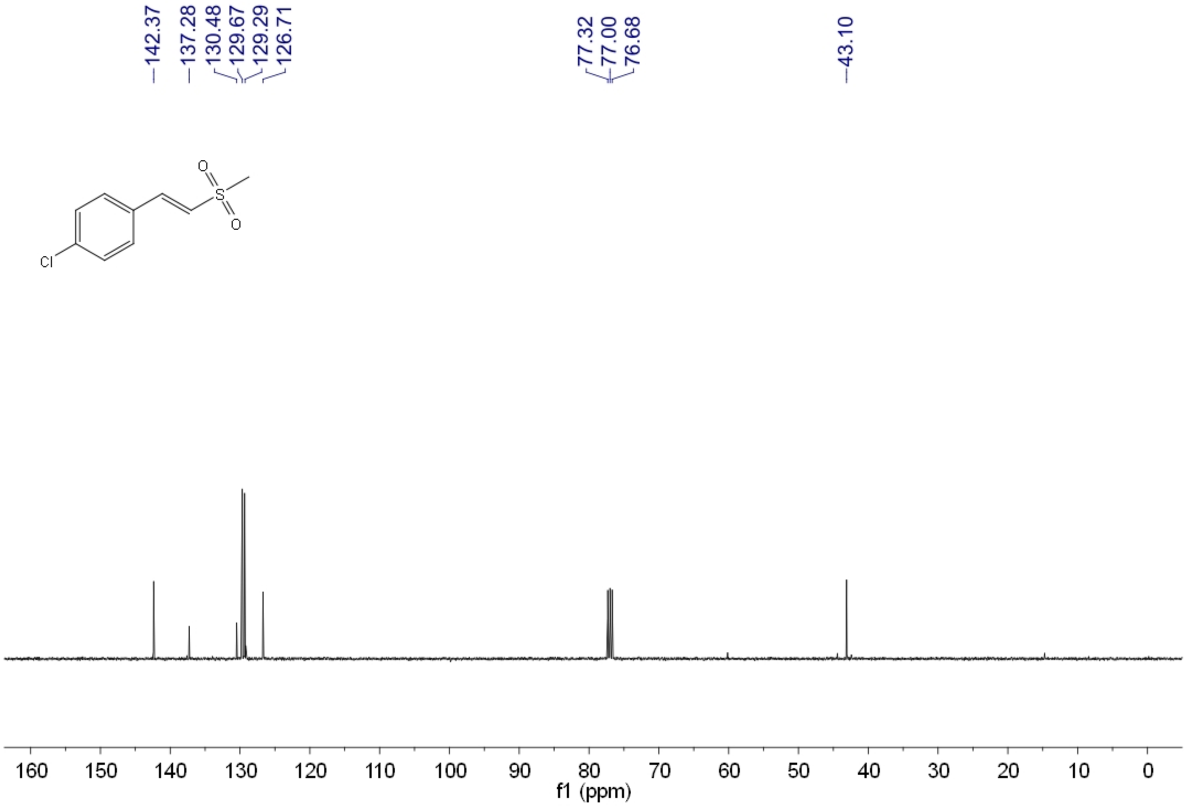

7.631
7.593
7.474
7.452
7.429
6.900
6.861
3.026
1.332
-0.000
O
S
O
1.00
4.00
1.00
3.01
9.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

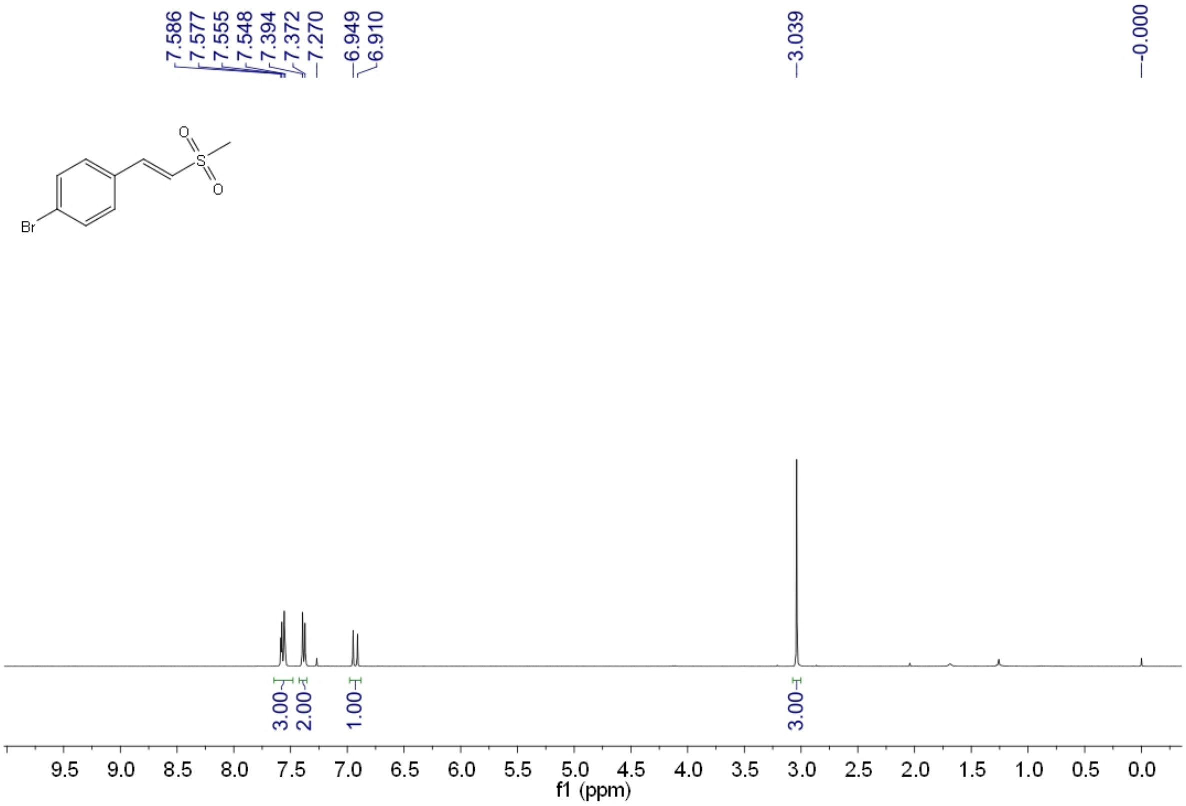

155.166
143.879
129.336
128.427
126.131
125.202
77.317
77.000
76.682
43.356
35.016
31.064
O
S
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

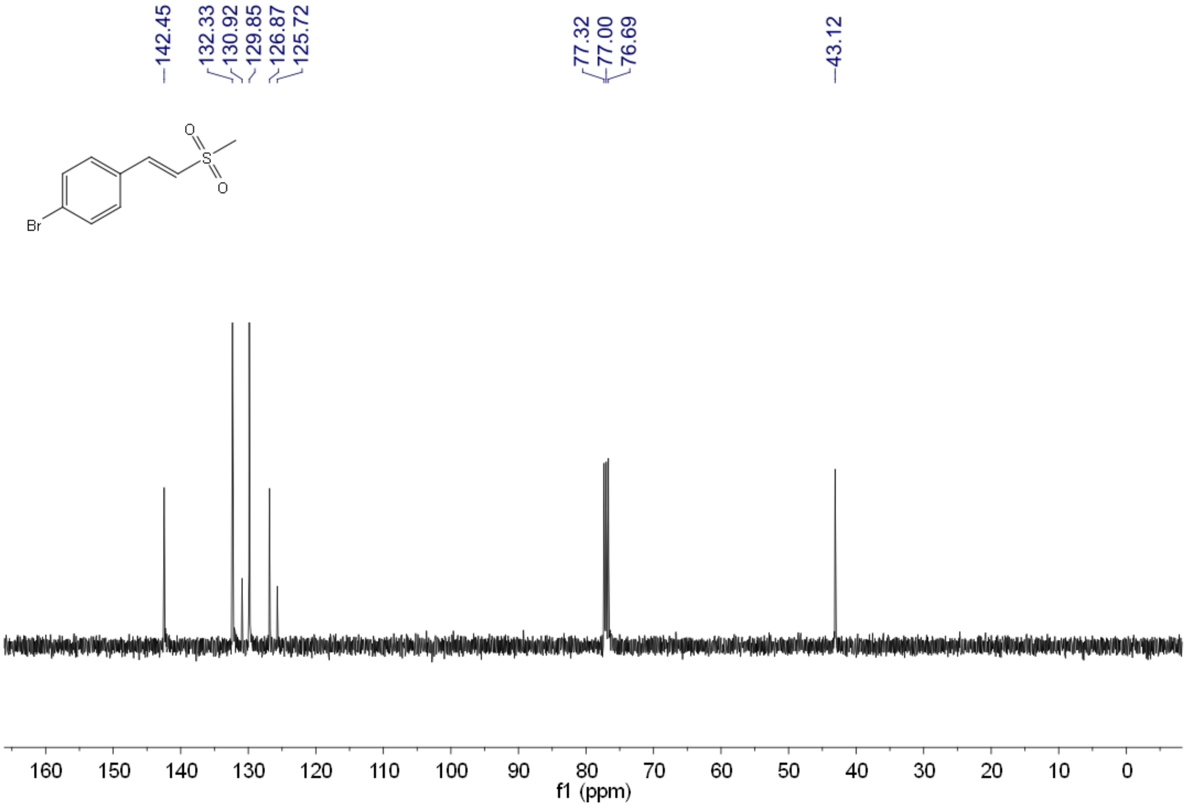

7.617
7.579
7.540
7.527
7.519
7.505
7.104
6.873
6.834
3.038
-0.000
O
S
O
F
1.00
2.00
2.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.79
163.25
142.73
130.56
128.33
125.92
116.54
116.32
77.32
77.00
76.68
43.28
O
S
O
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.595
7.557
7.472
7.451
7.406
7.385
7.345
6.964
6.925
3.049
0.000
O
S
O
Cl
0.33
0.68
0.68
0.33
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.37
137.28
130.48
129.67
129.29
126.71
77.32
77.00
76.68
43.10
O
S
O
Cl
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.586
7.577
7.555
7.548
7.394
7.372
7.270
6.949
6.910
3.039
0.000
O
S
O
Br
3.00
2.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.45
132.33
130.92
129.85
126.87
125.72
77.32
77.00
76.69
43.12
O
S
O
Br
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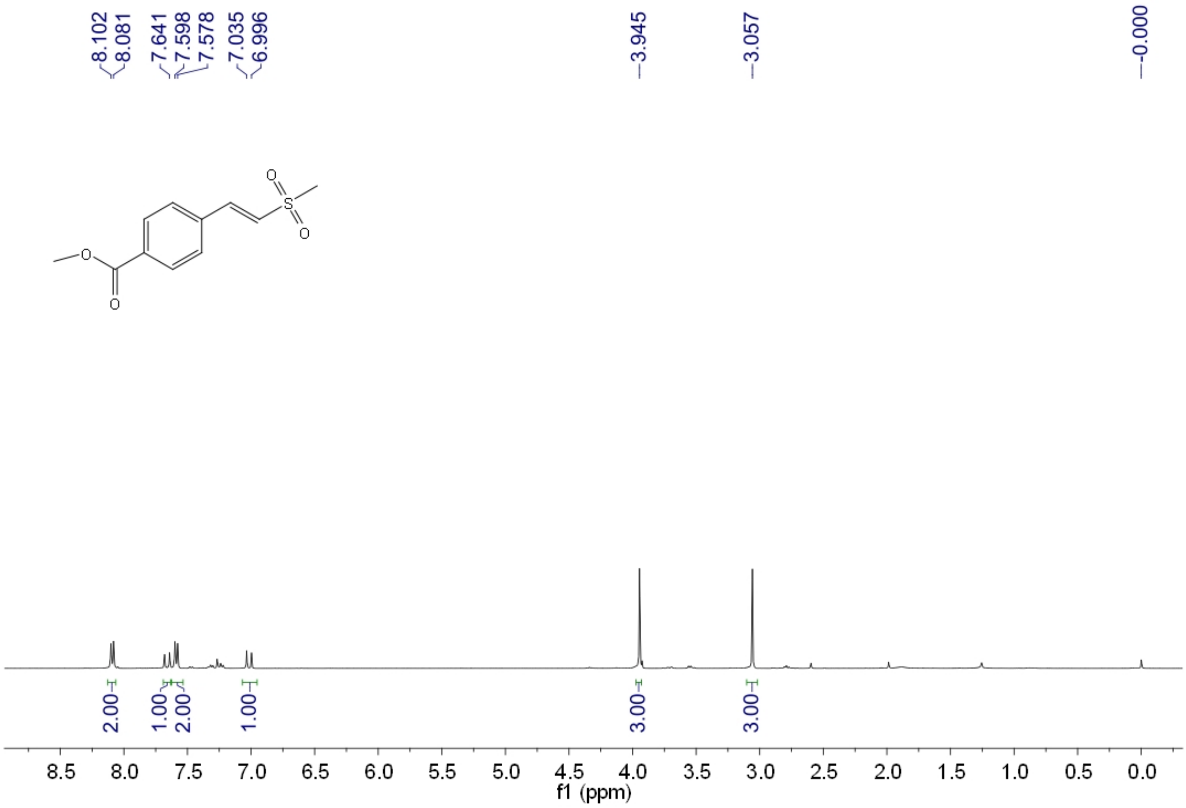
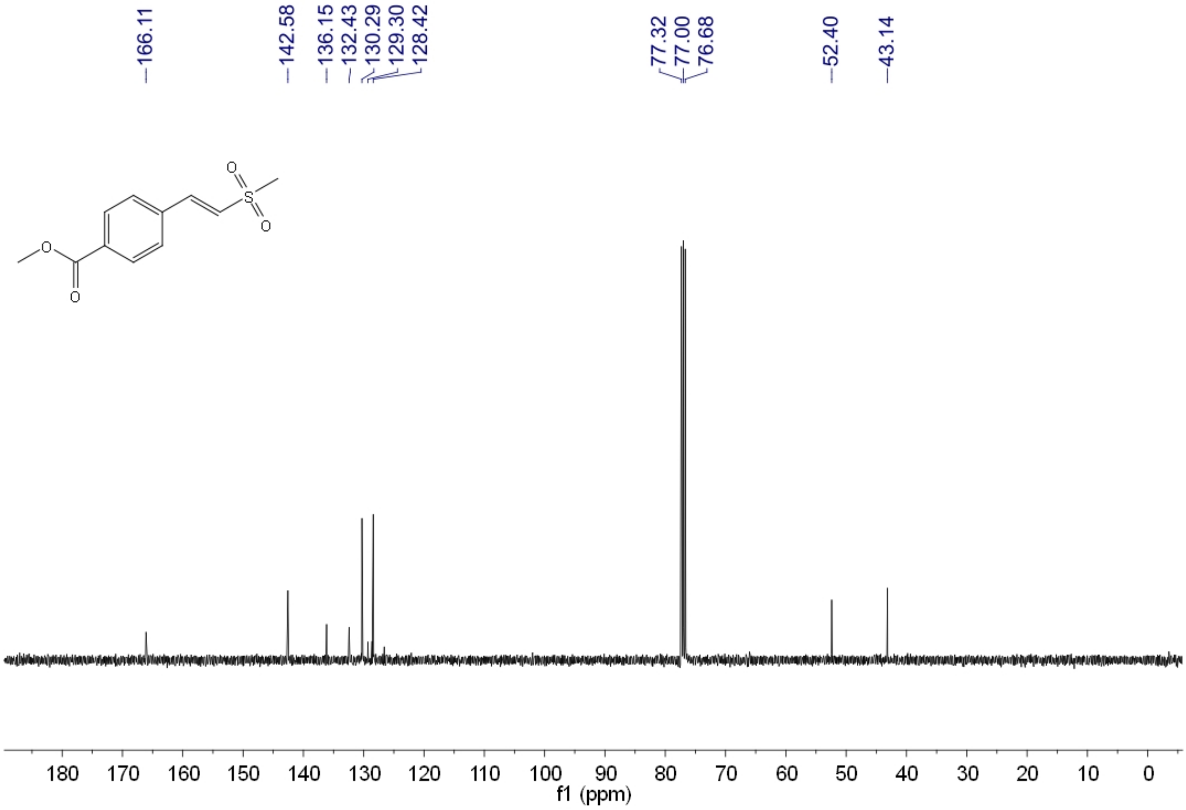
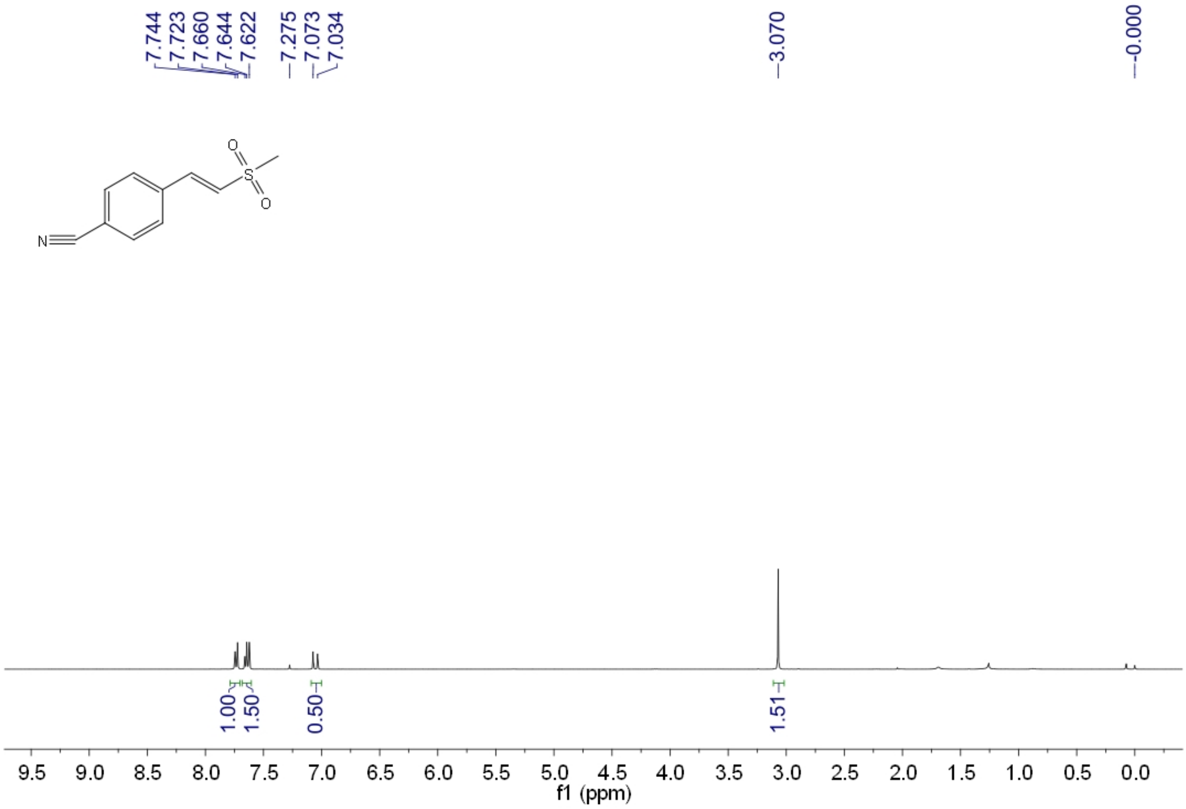
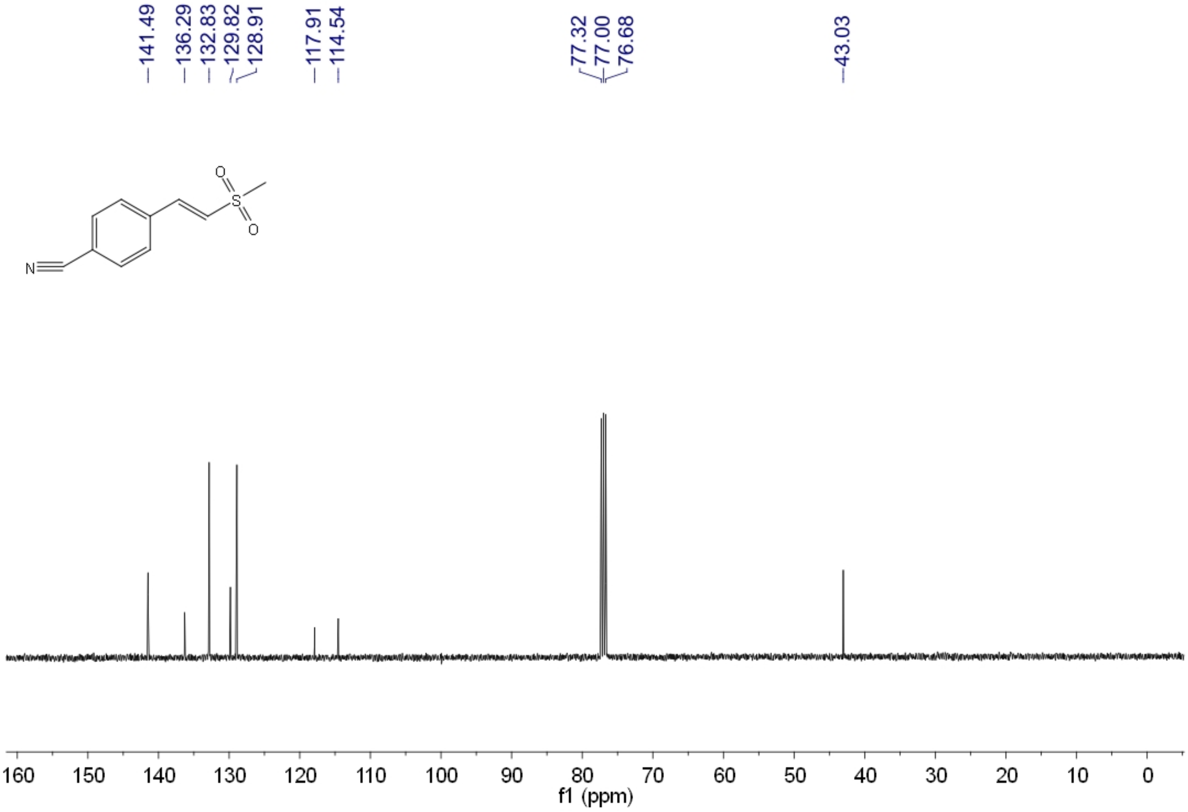
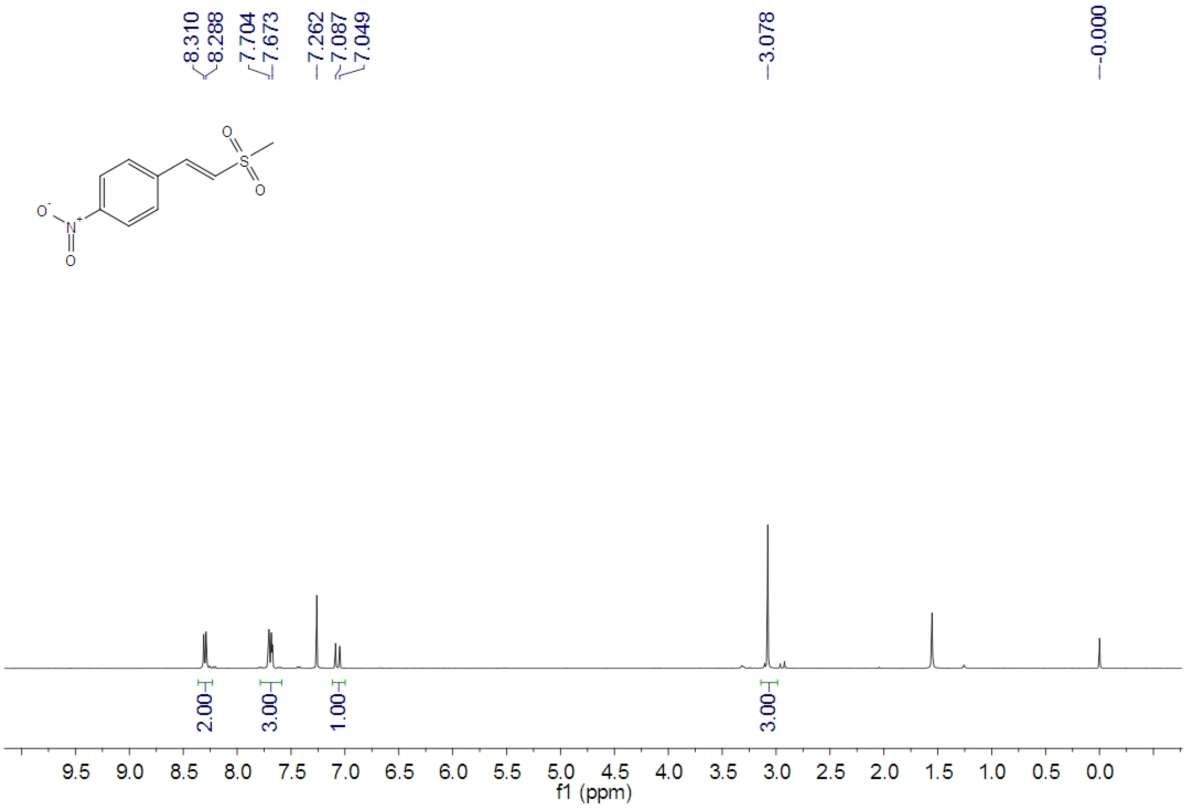
f1 (ppm)

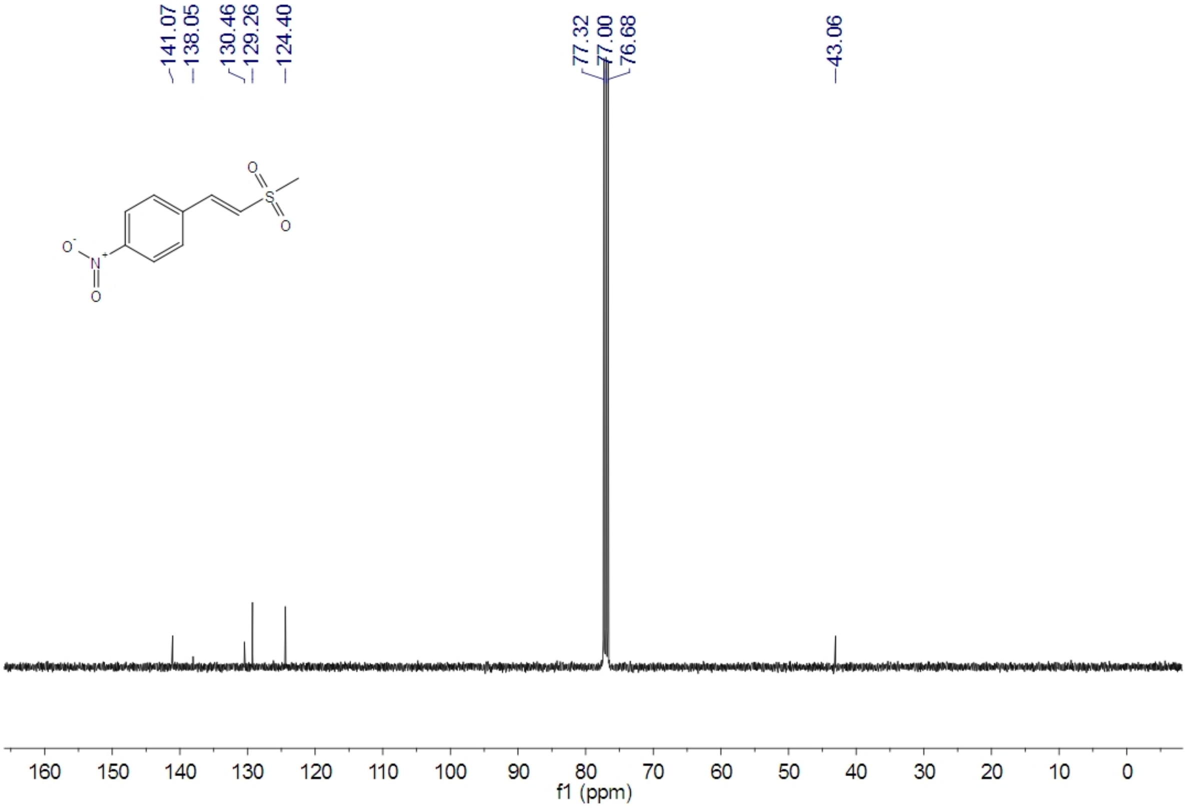

8.102
8.081
7.641
7.598
7.578
7.035
6.996
3.945
3.057
0.000
O
S
O
O
O
2.00
1.00
2.00
1.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

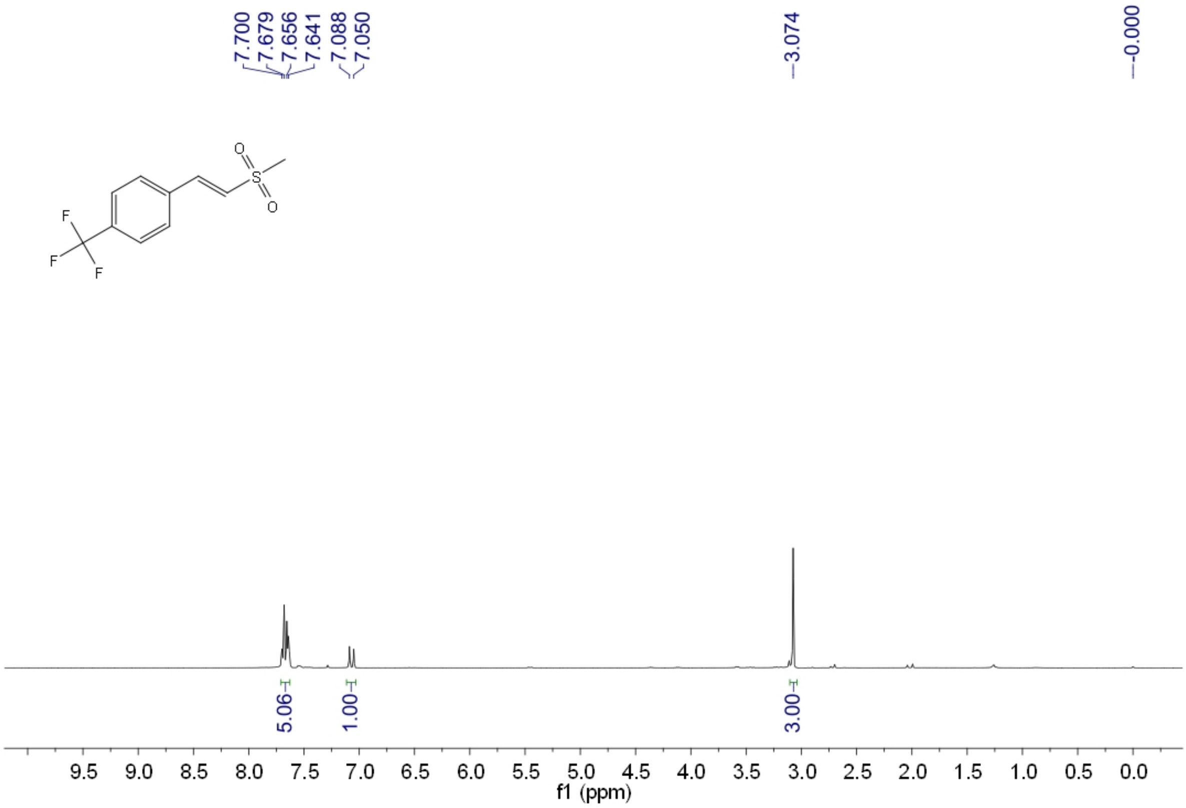

166.11
142.58
136.15
132.43
130.29
129.30
128.42
77.32
77.00
76.68
52.40
43.14
O
S
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

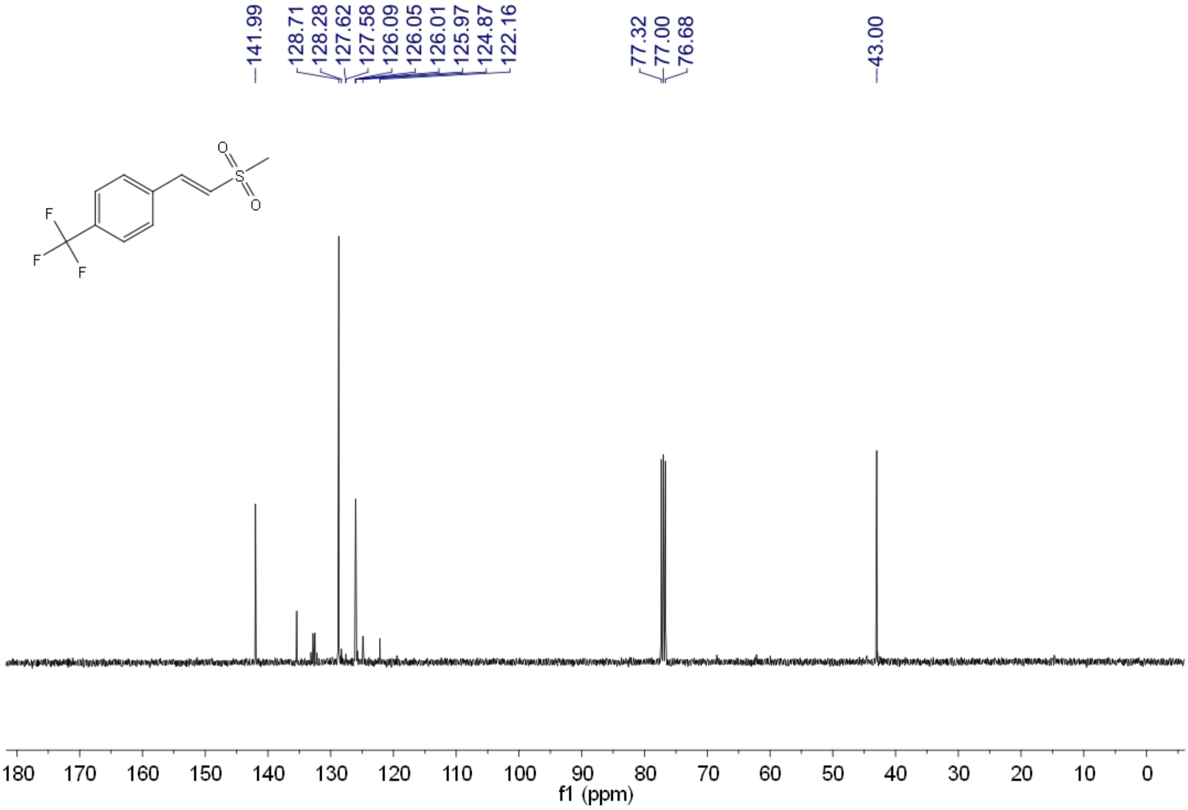

7.744
7.723
7.660
7.644
7.622
7.275
7.073
7.034
3.070
0.000
O
S
O
N
1.00
1.50
0.50
1.51
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

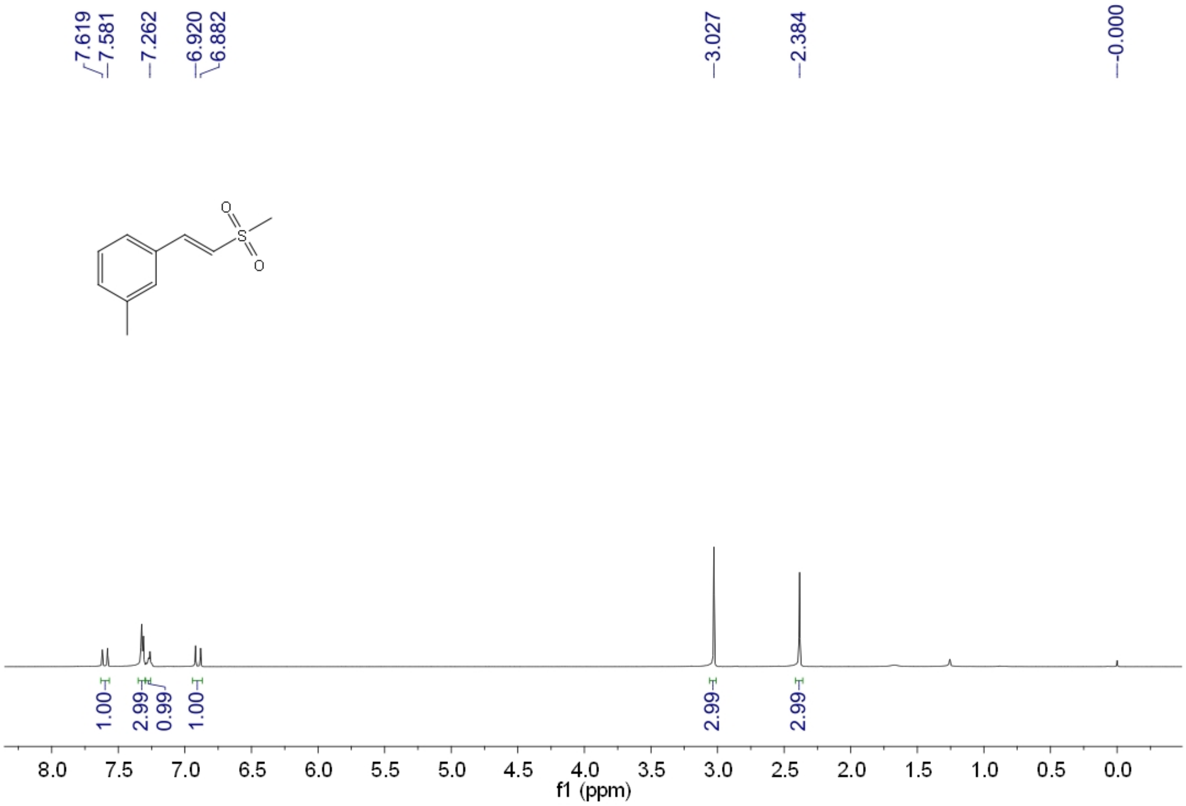

141.49
136.29
132.83
129.82
128.91
117.91
114.54
77.32
77.00
76.68
43.03
O
S
O
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

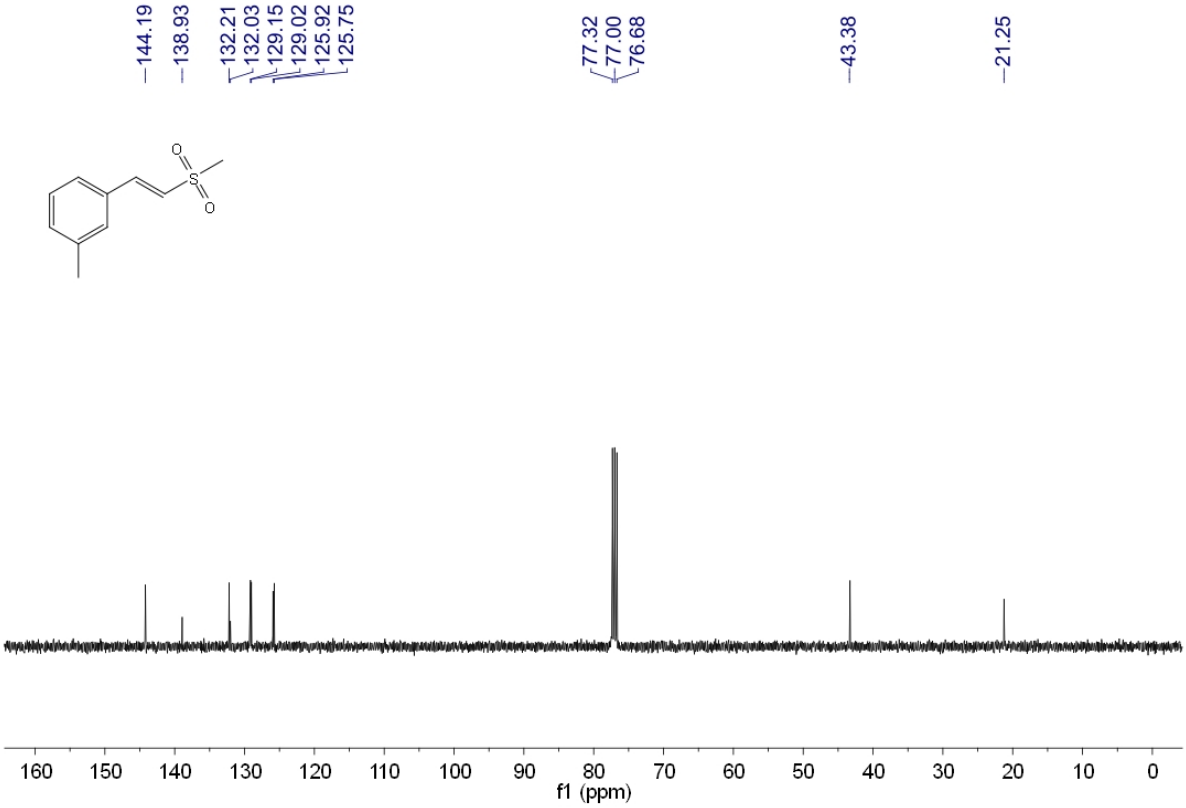

8.310
8.288
7.704
7.673
7.262
7.087
7.049
3.078
0.000
O
S
O
O
N
O
2.00
3.00
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

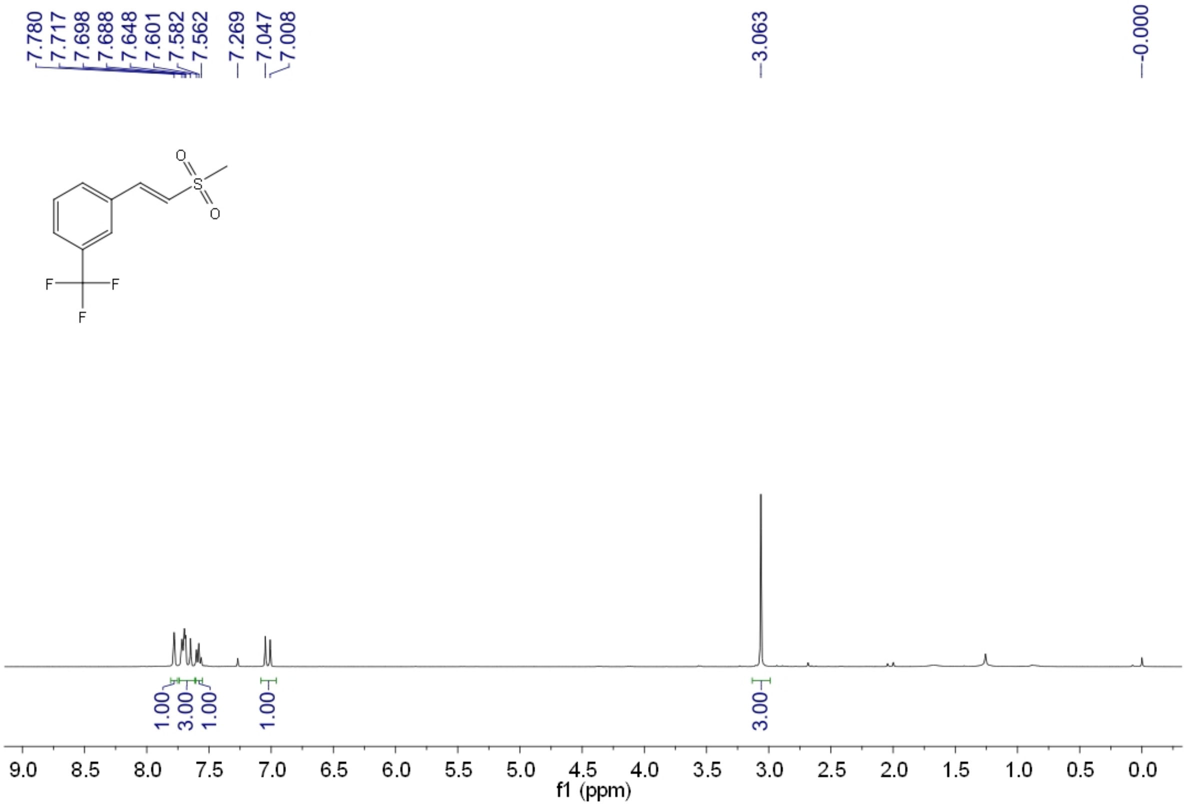

141.07
138.05
130.46
129.26
124.40
77.32
77.00
76.68
43.06
O
S
O
O
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

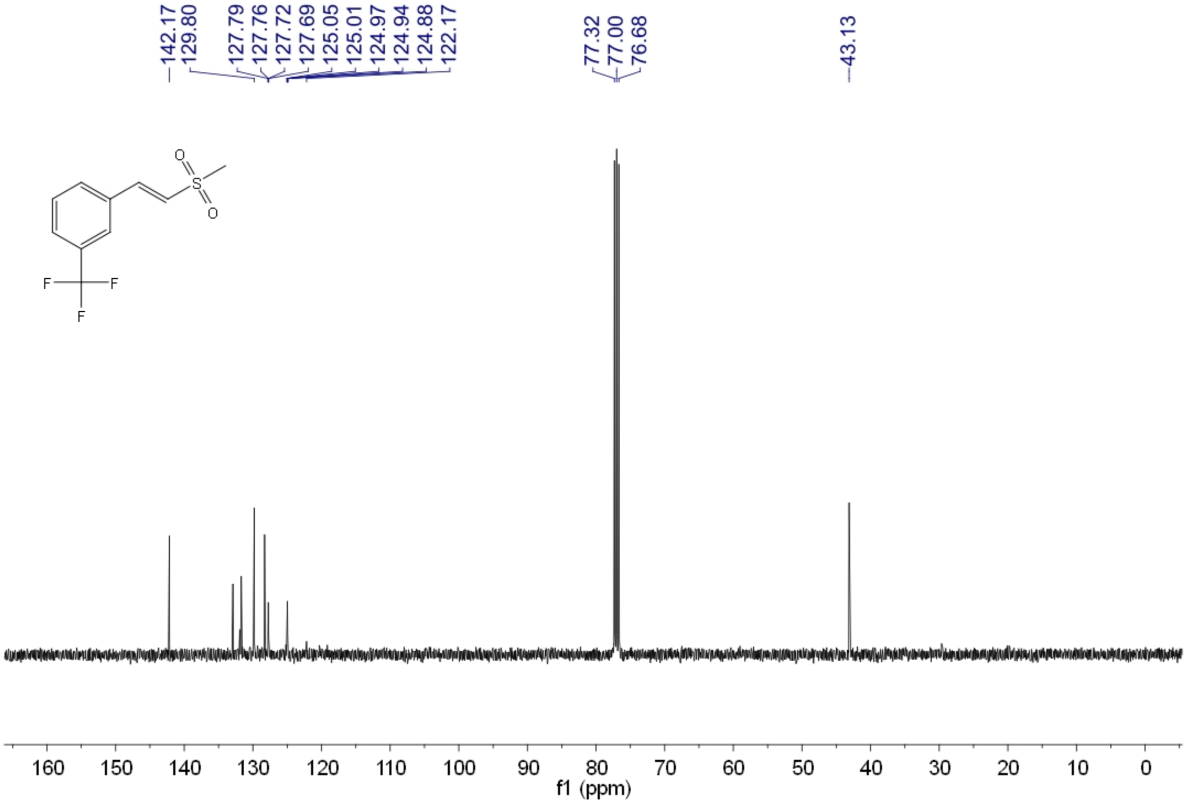

7.700
7.679
7.656
7.641
7.088
7.050
3.074
-0.000
O
S
O
F
F
F
5.06
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


141.99
128.71
128.28
127.62
127.58
126.09
126.05
126.01
125.97
124.87
122.16
77.32
77.00
76.68
43.00
O
S
O
F
F
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.619
7.581
7.262
6.920
6.882
3.027
2.384
0.000
O
S
O
1.00
2.99
0.99
1.00
2.99
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.19
138.93
132.21
132.03
129.15
129.02
125.92
125.75
77.32
77.00
76.68
43.38
21.25
O
S
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.780
7.717
7.698
7.688
7.648
7.601
7.582
7.562
7.269
7.047
7.008
3.063
0.000
O
S
O
F
F
F
1.00
3.00
1.00
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


142.17
129.80
127.79
127.76
127.72
127.69
125.05
125.01
124.97
124.94
124.88
122.17
77.32
77.00
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O
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F
F
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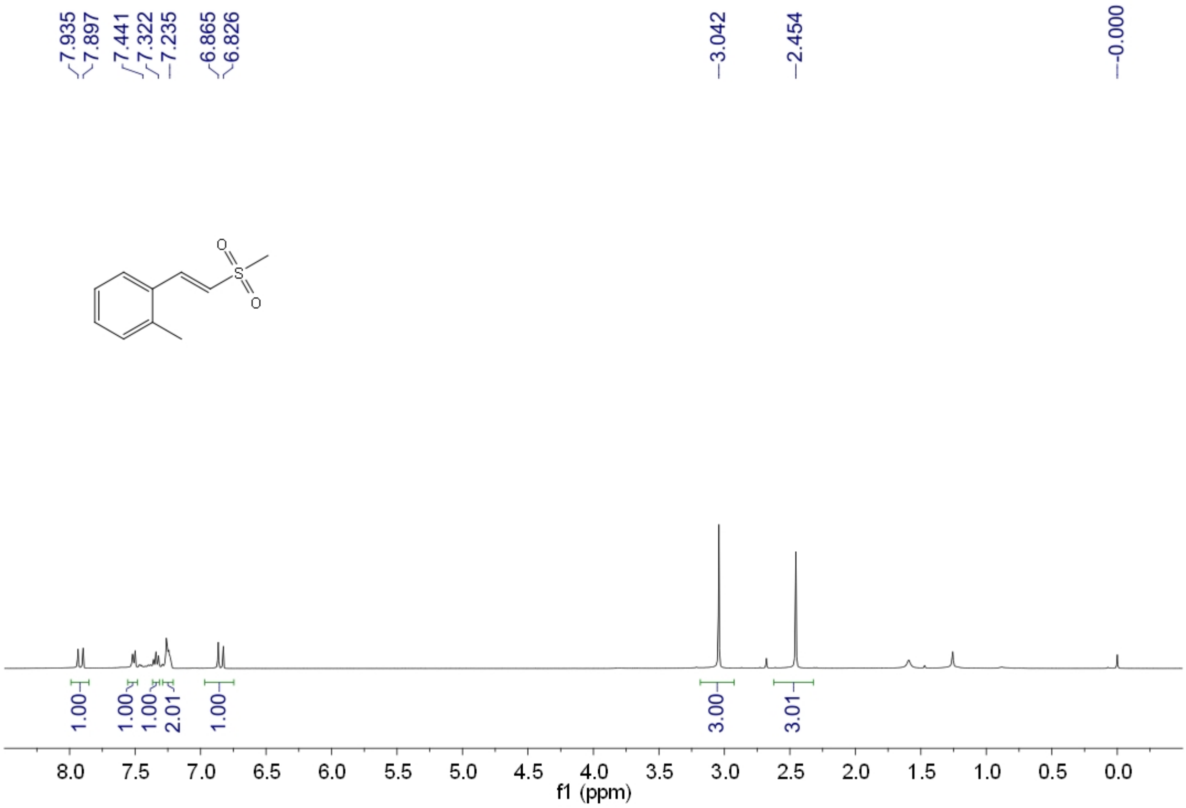
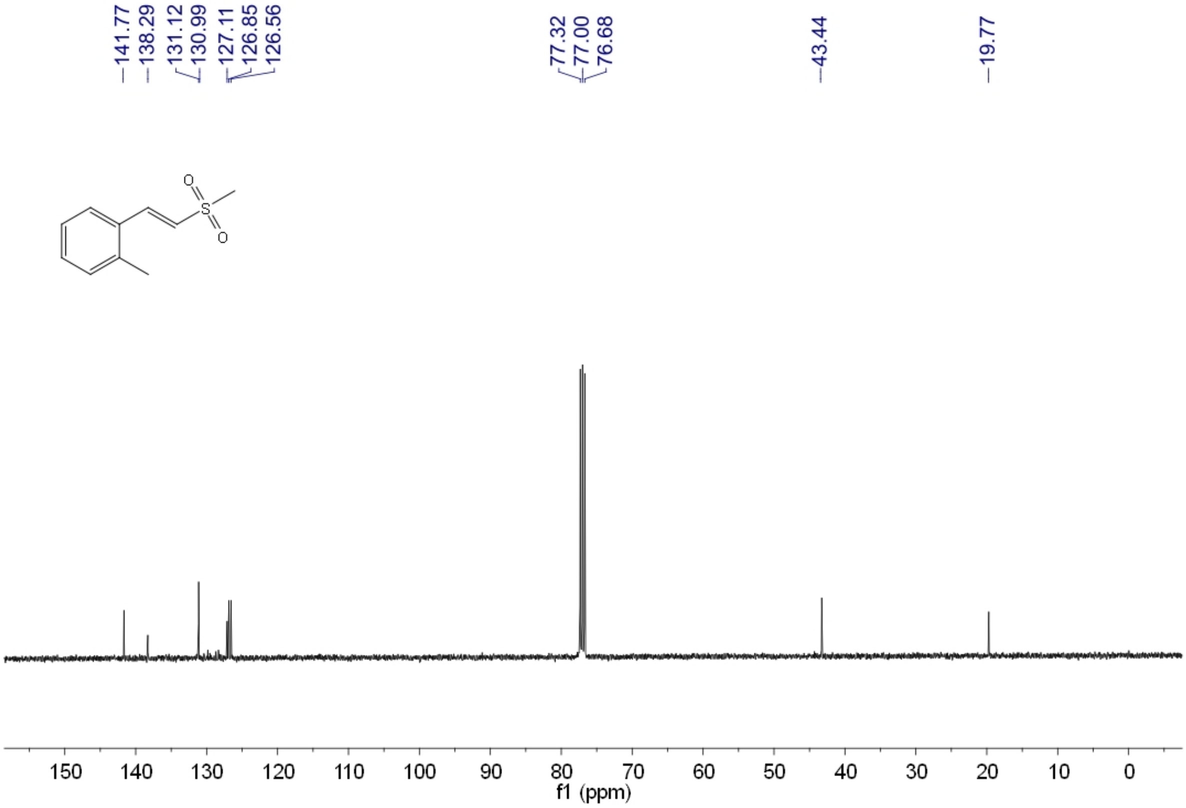
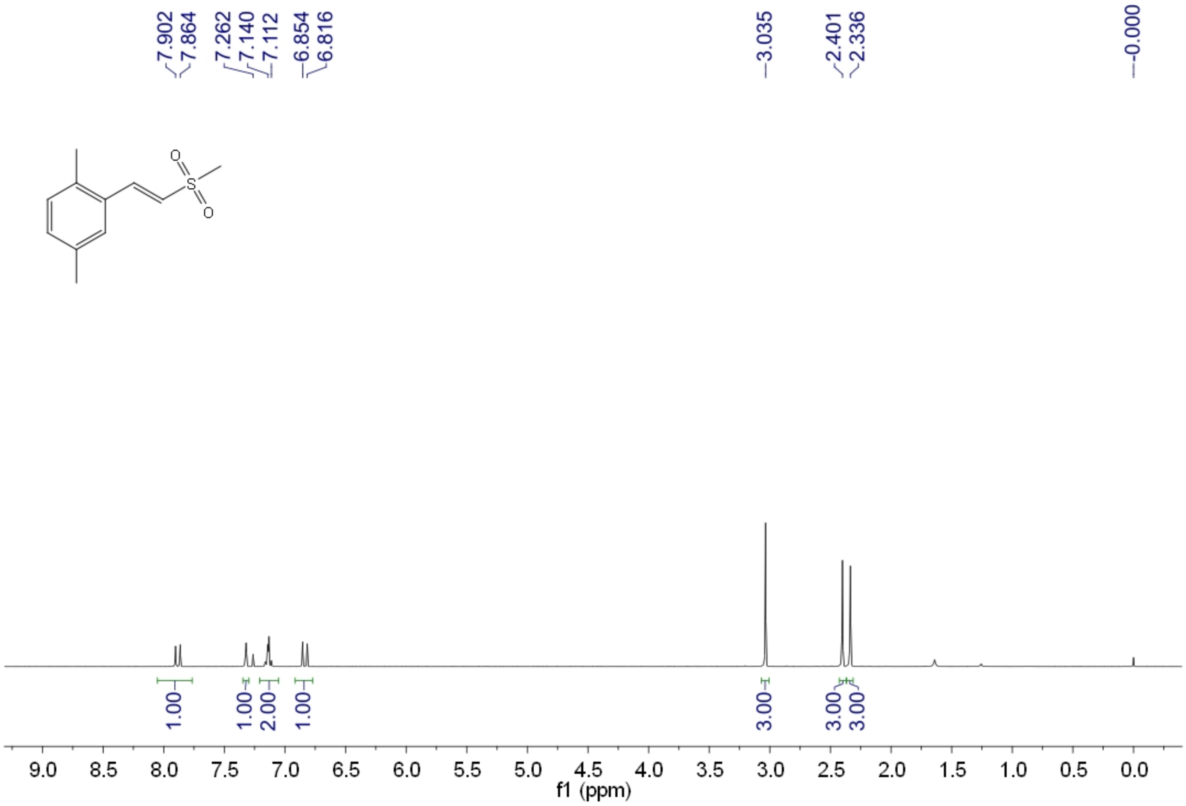
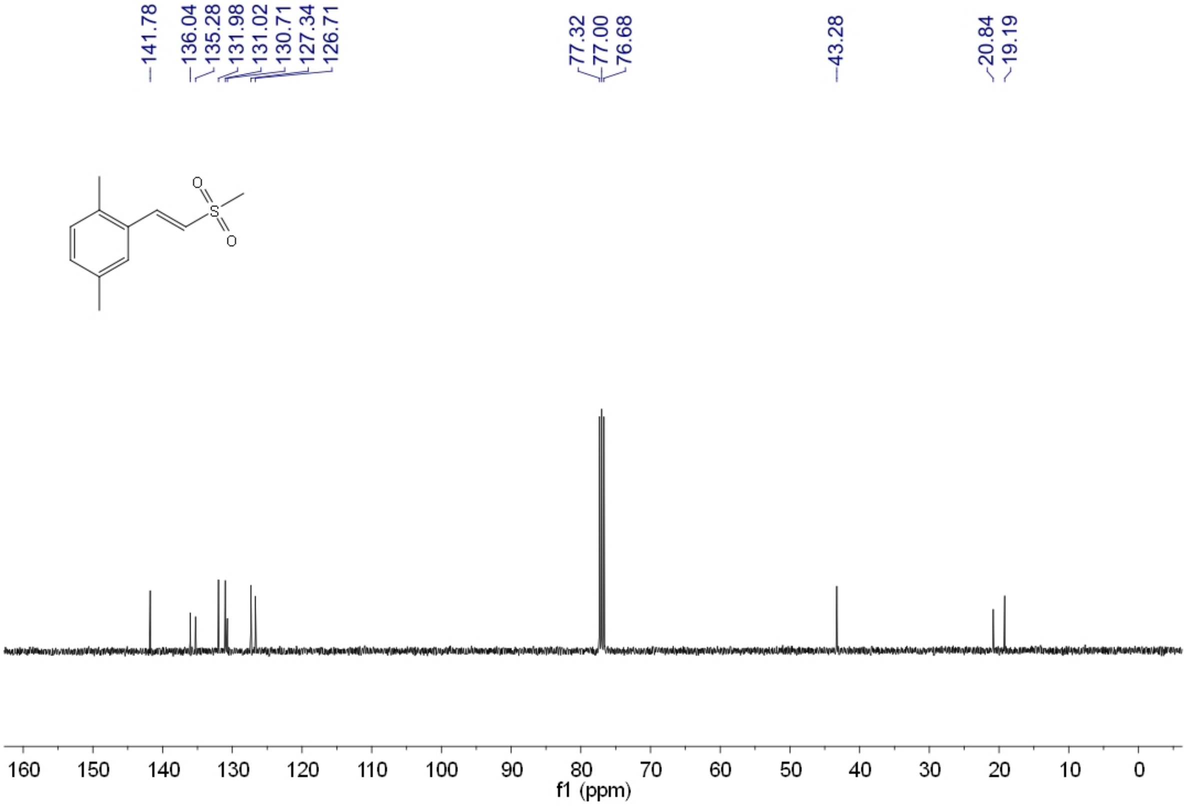
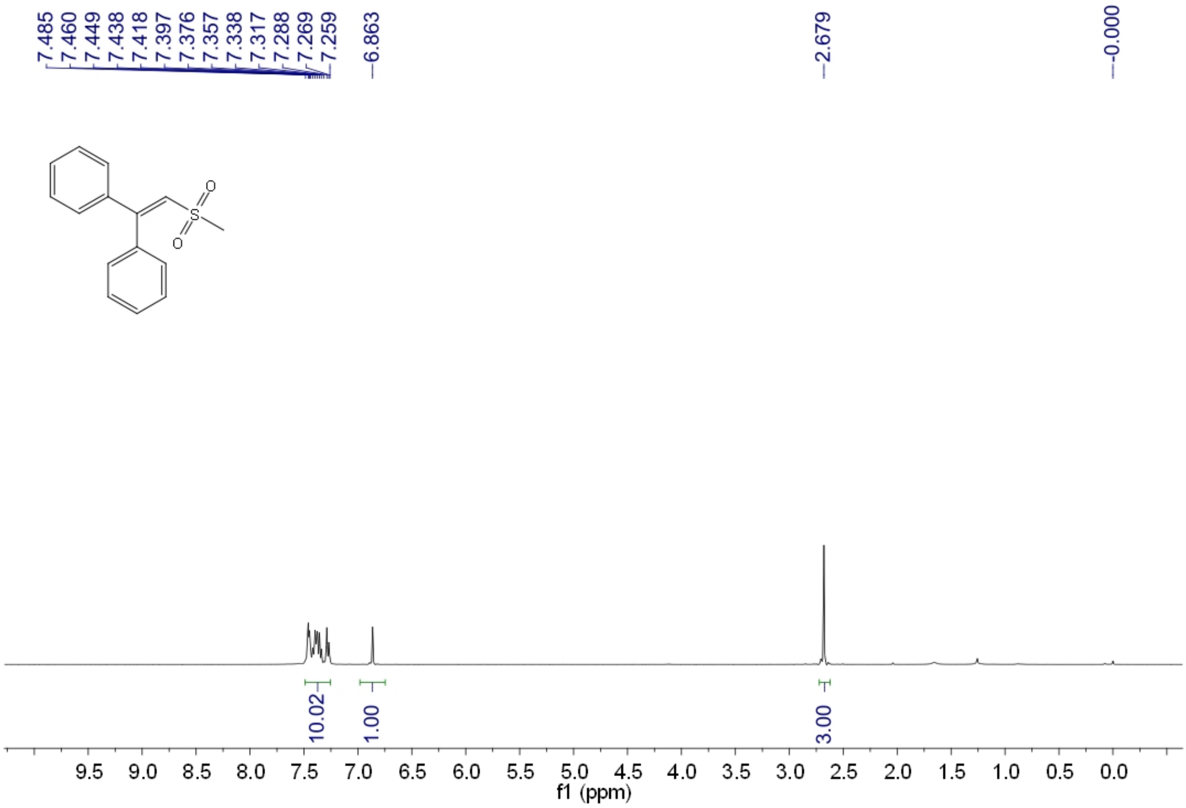
f1 (ppm)


7.935
7.897
7.441
7.322
7.235
6.865
6.826
3.042
2.454
-0.000
O
S
O
1.00
1.00
1.00
2.01
1.00
3.00
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.77
138.29
131.12
130.99
127.11
126.85
126.56
77.32
77.00
76.68
43.44
19.77
O
S
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.902
7.864
7.262
7.140
7.112
6.854
6.816
3.035
2.401
2.336
0.000
O
S
O
1.00
1.00
2.00
1.00
3.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.78
136.04
135.28
131.98
131.02
130.71
127.34
126.71
77.32
77.00
76.68
43.28
20.84
19.19
O
S
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.485
7.460
7.449
7.438
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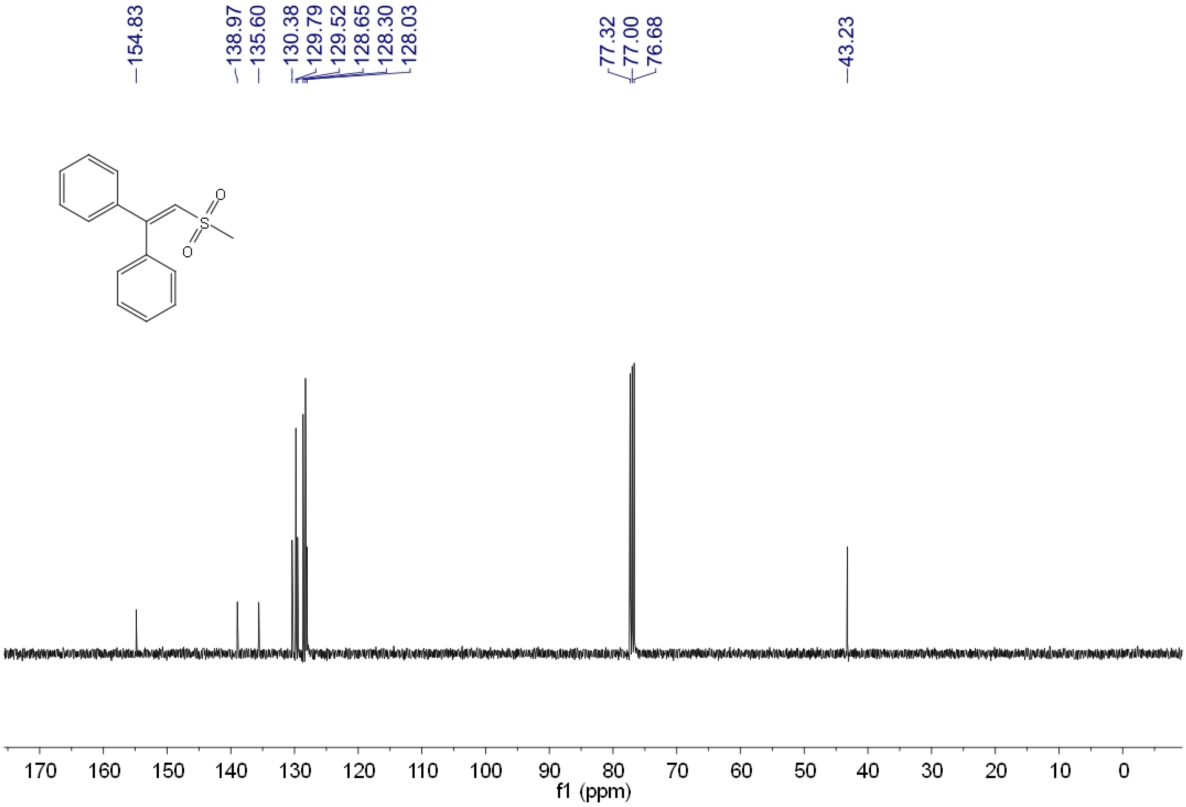
7.397
7.376
7.357
7.338
7.317
7.288
7.269
7.259
6.863
2.679
0.000
O
S
O
10.02
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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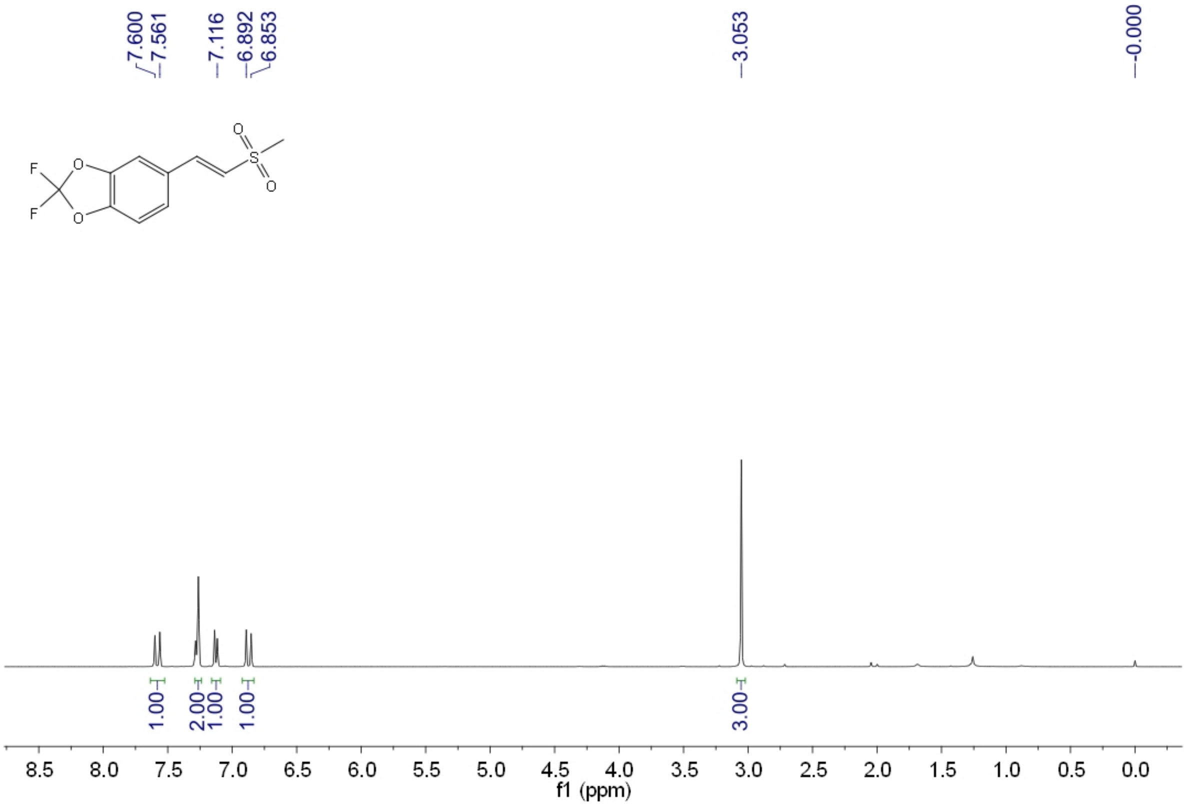
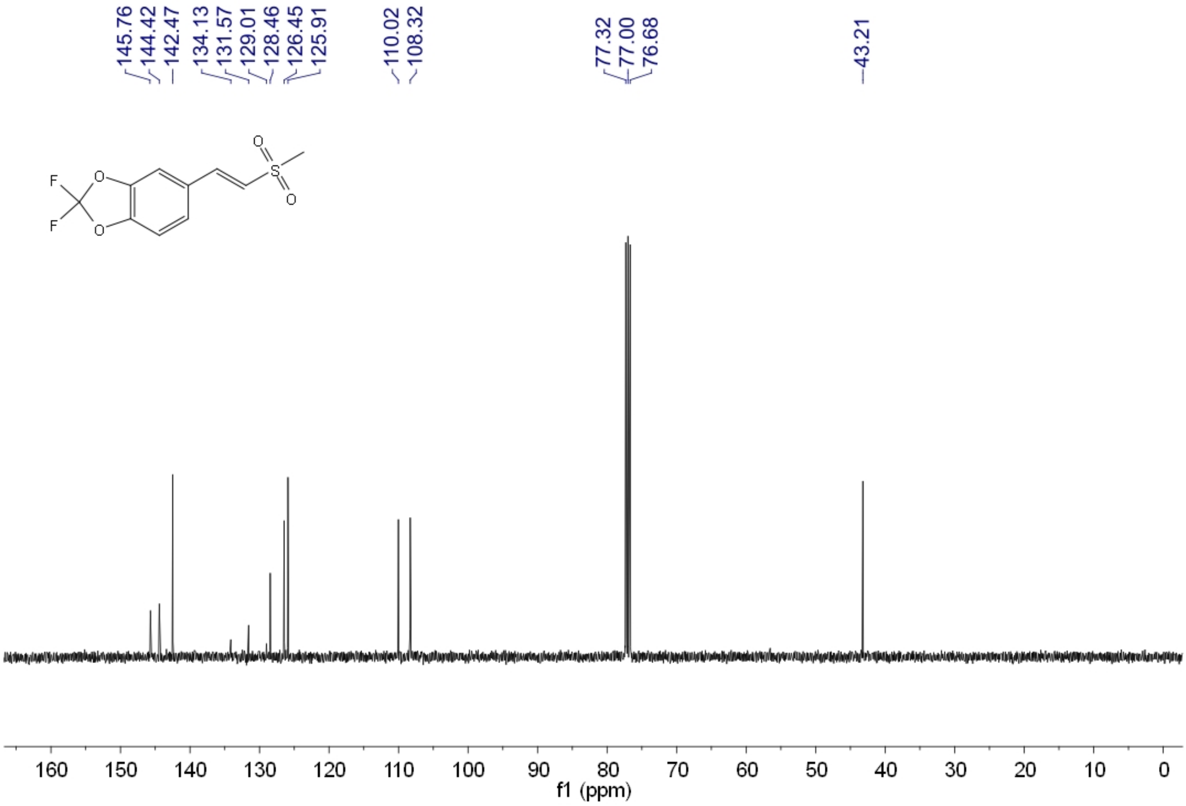
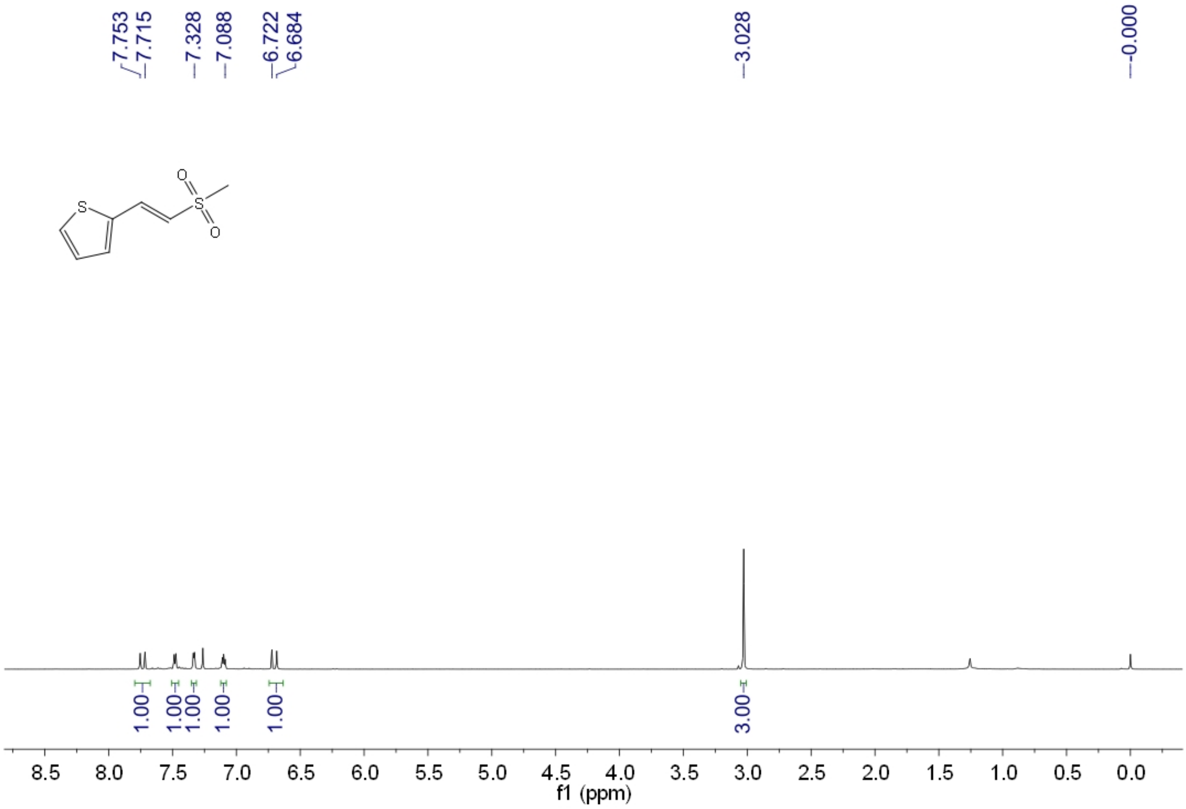
129.79
129.52
128.65
128.30
128.03
77.32
77.00
76.68
43.23
O
S
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.600
7.561
7.116
6.892
6.853
3.053
0.000
F
F
O
O
S
O
O
1.00
2.00
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.76
144.42
142.47
134.13
131.57
129.01
128.46
126.45
125.91
110.02
108.32
77.32
77.00
76.68
43.21
F
F
O
O
S
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.753
7.715
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7.088
6.722
6.684
3.028
0.000
S
O
O
1.00
1.00
1.00
1.00
1.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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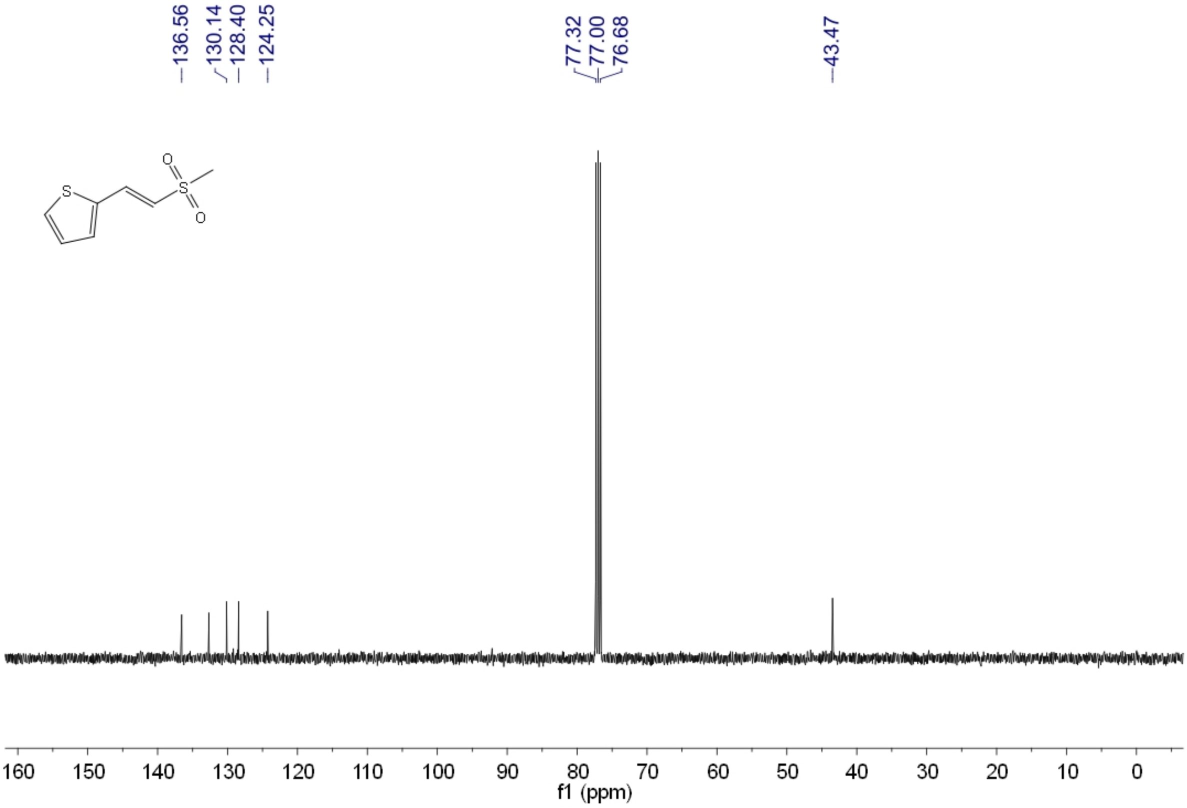
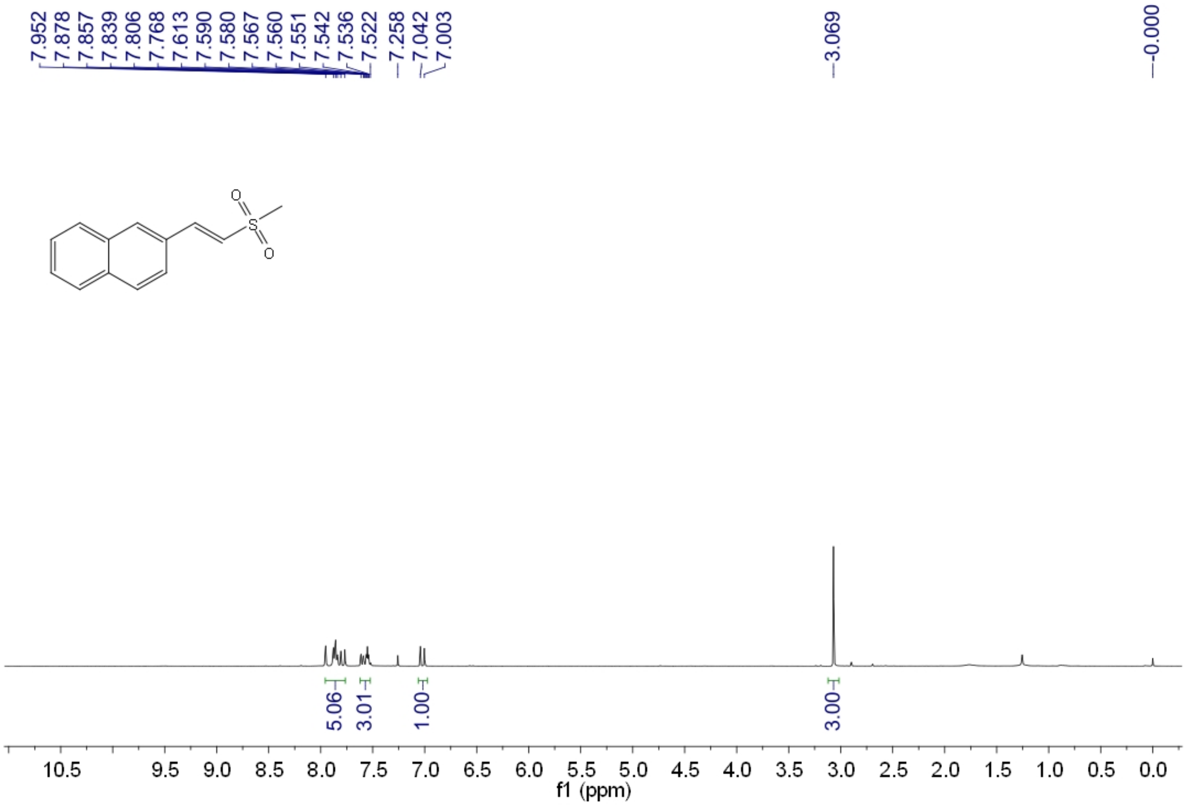
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.56
130.14
128.40
124.25
77.32
77.00
76.68
43.47
S
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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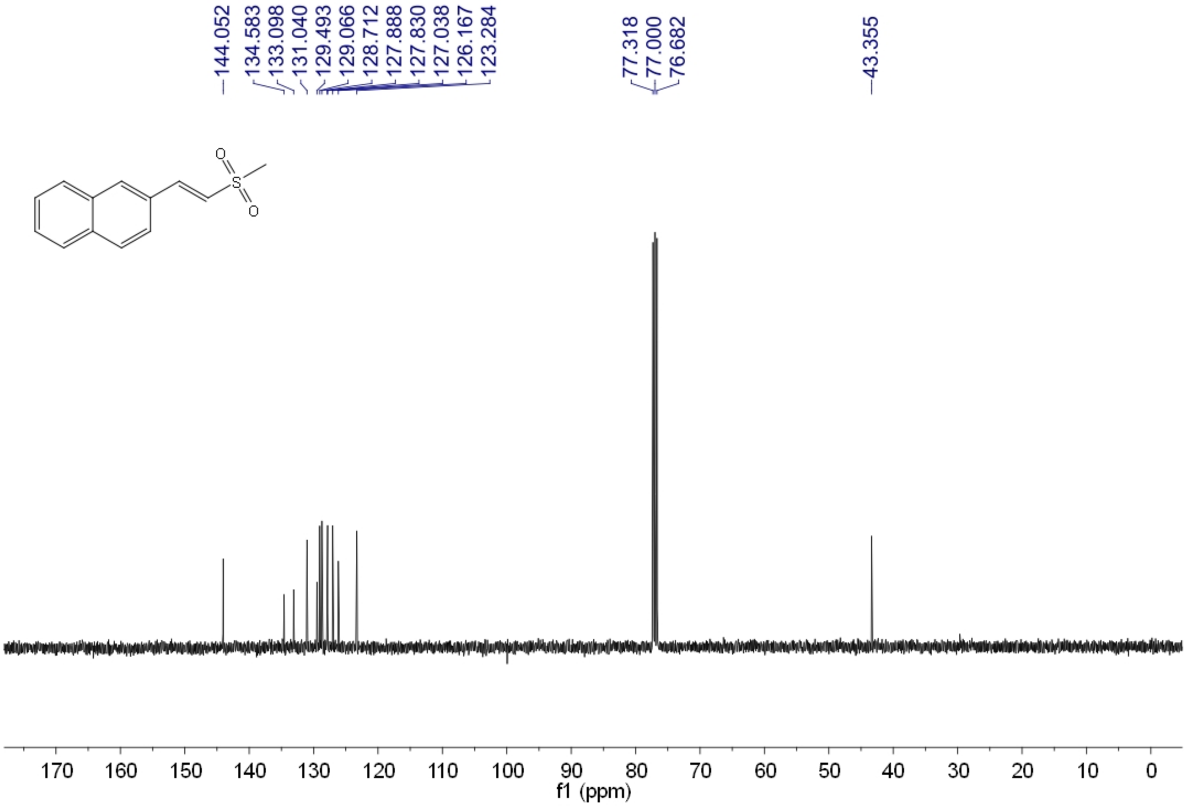
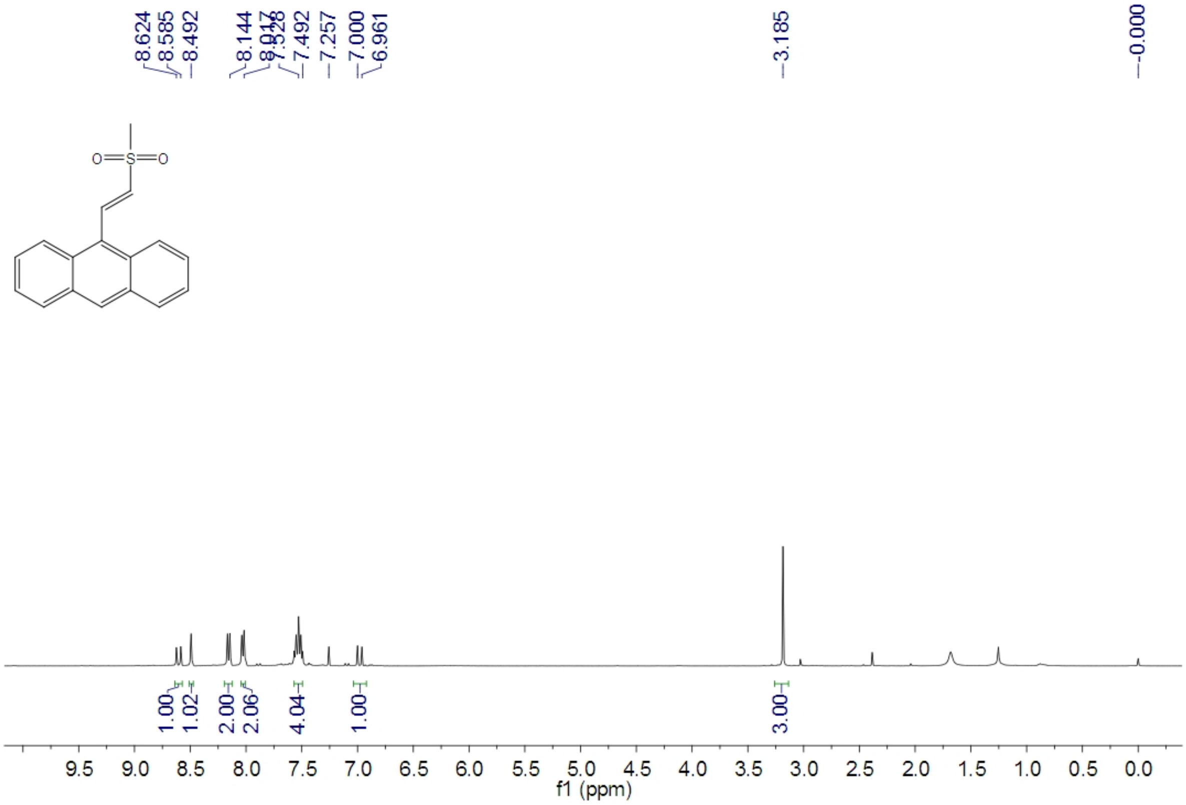
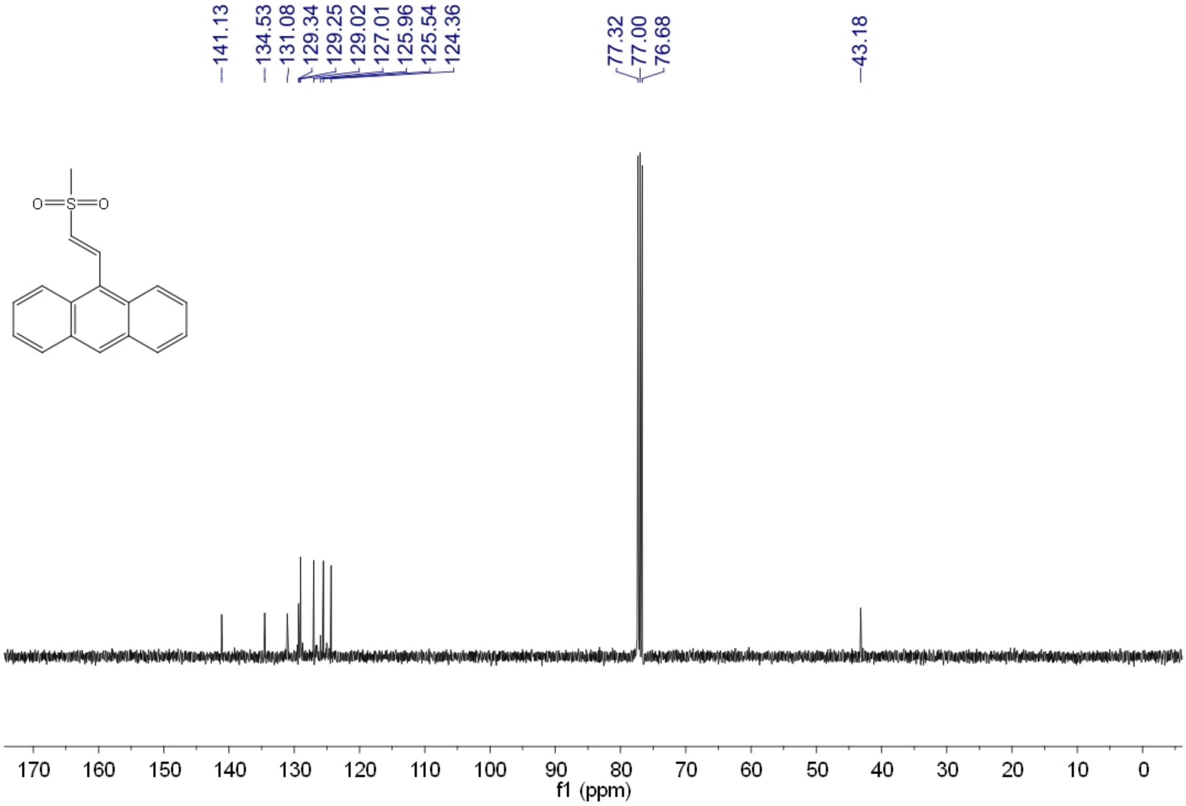
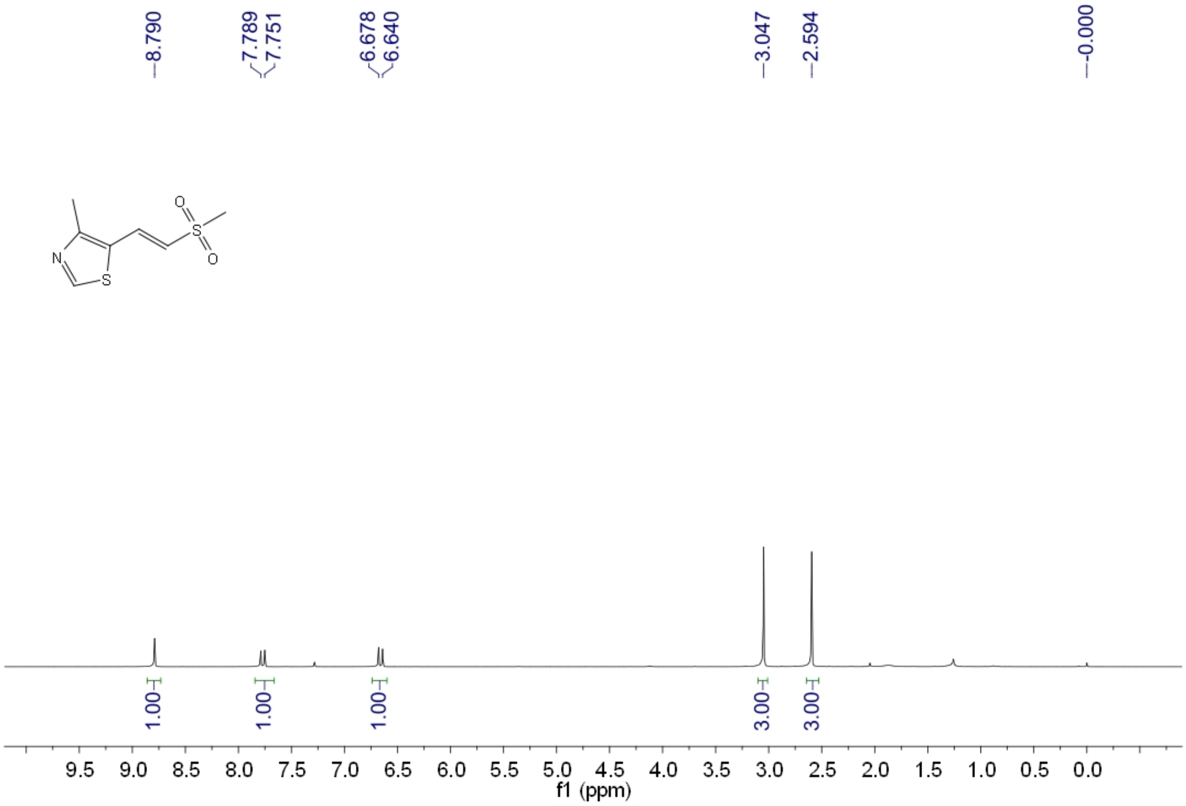
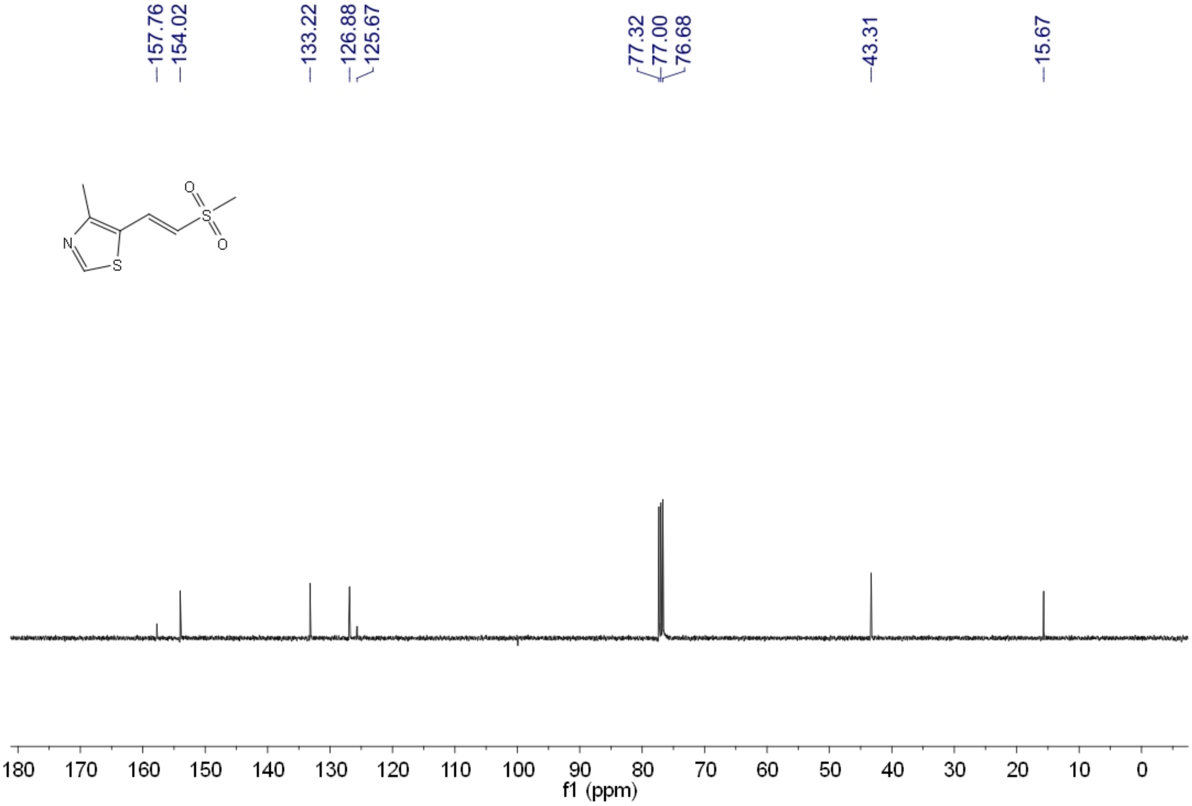
7.878
7.857
7.839
7.806
7.768
7.613
7.590
7.580
7.567
7.560
7.551
7.542
7.536
7.522
7.258
7.042
7.003
3.069
0.000
O
S
O
5.06
3.01
1.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

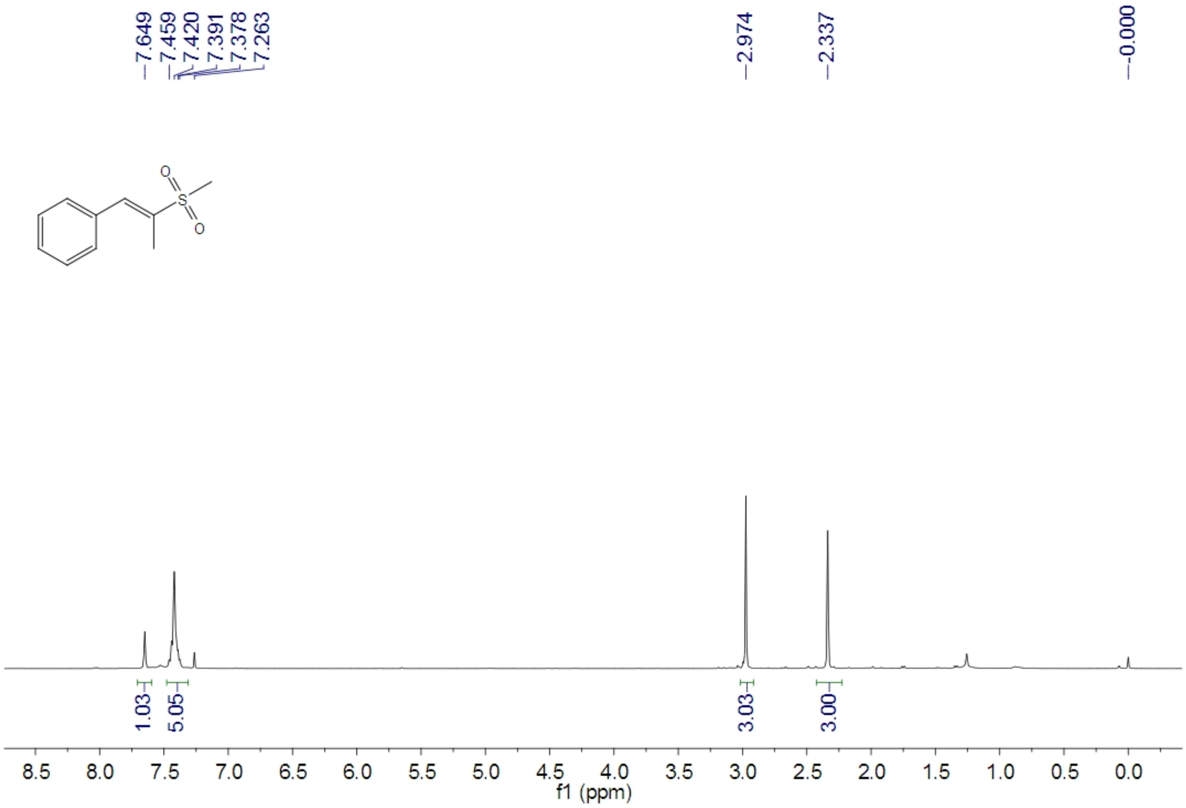

144.052
134.583
133.098
131.040
129.493
129.066
128.712
127.888
127.830
127.038
126.167
123.284
77.318
77.000
76.682
43.355
O
S
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

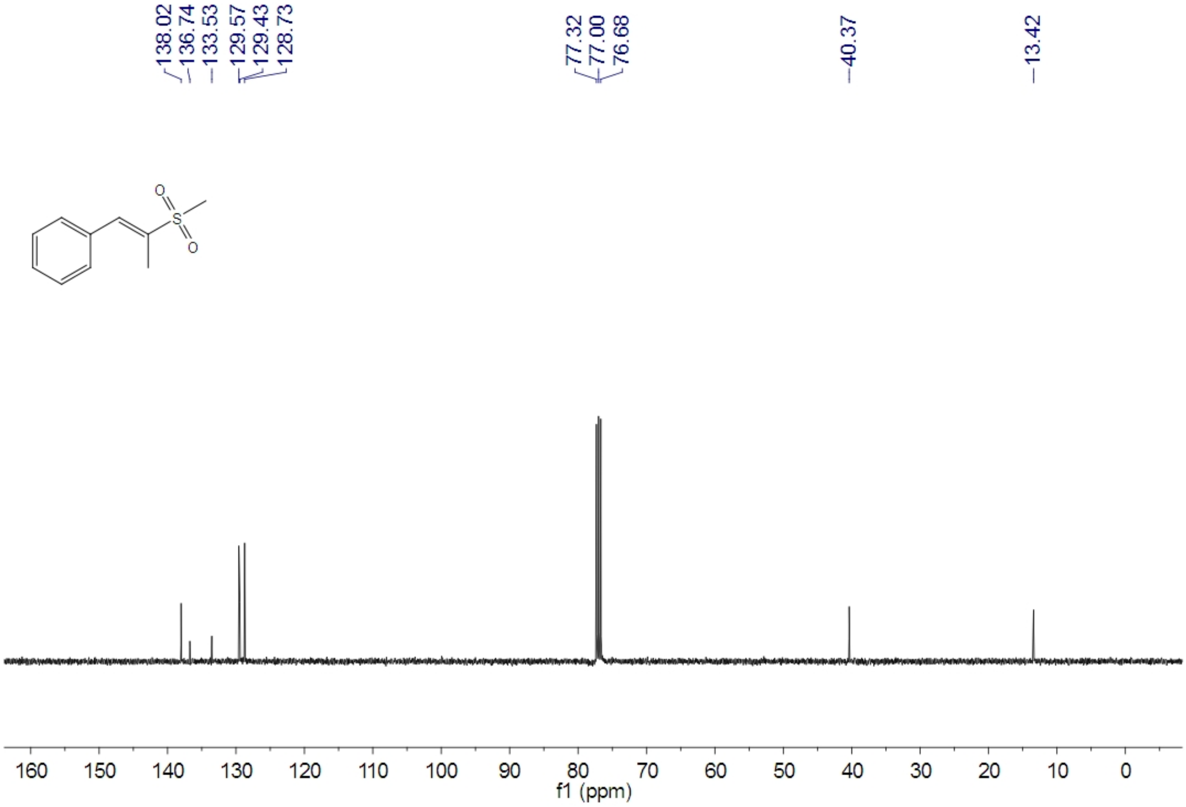

8.624
8.585
8.492
8.144
8.017
7.528
7.492
7.257
7.000
6.961
3.185
-0.000
1.00
1.02
2.00
2.06
4.04
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
S
O

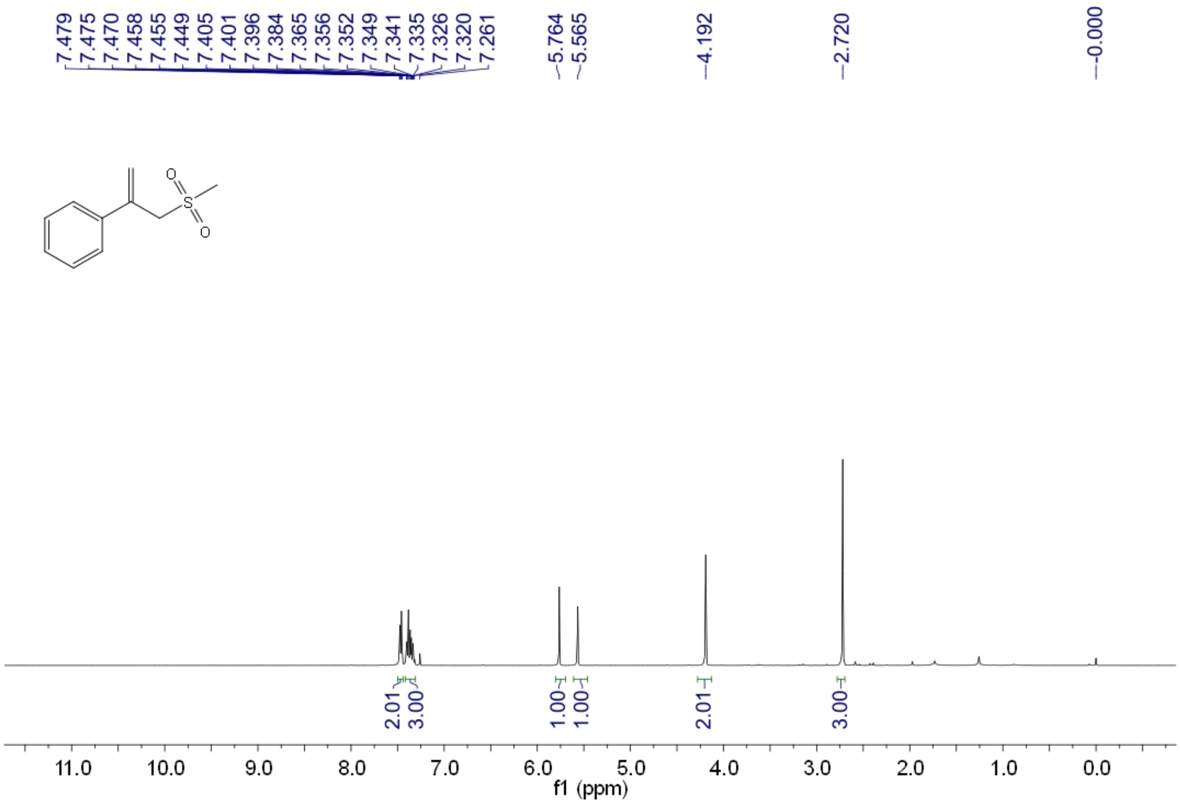

141.13
134.53
131.08
129.34
129.25
129.02
127.01
125.96
125.54
124.36
77.32
77.00
76.68
43.18
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
S
O

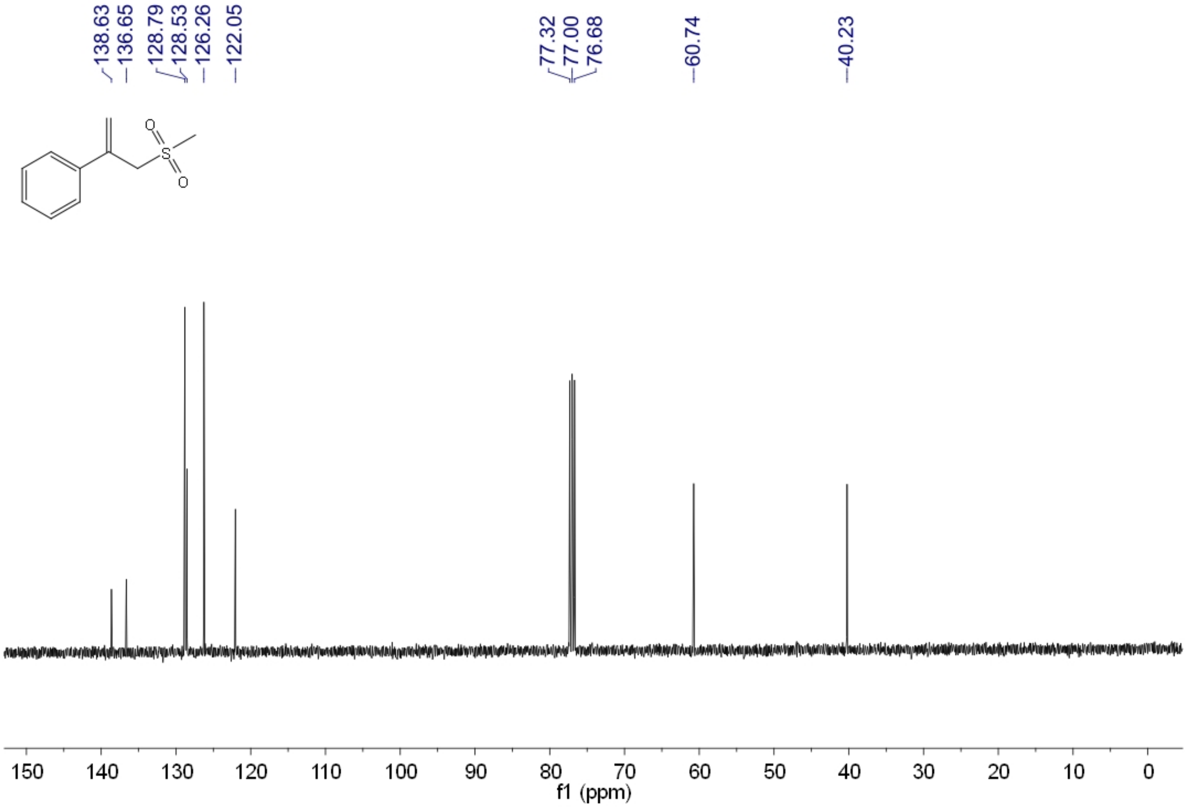

8.790
7.789
7.751
6.678
6.640
3.047
2.594
0.000
O
S
O
N
S
1.00
1.00
1.00
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

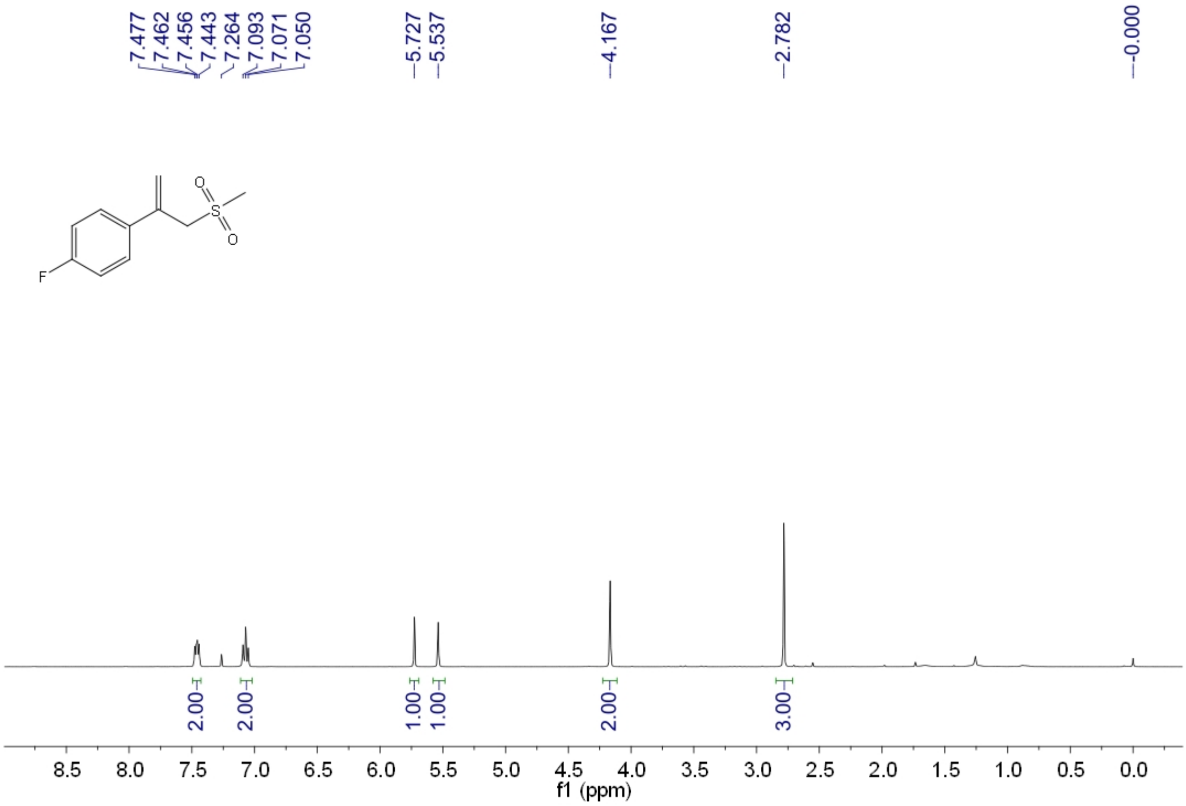

157.76
154.02
133.22
126.88
125.67
77.32
77.00
76.68
43.31
15.67
O
S
O
N
S
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

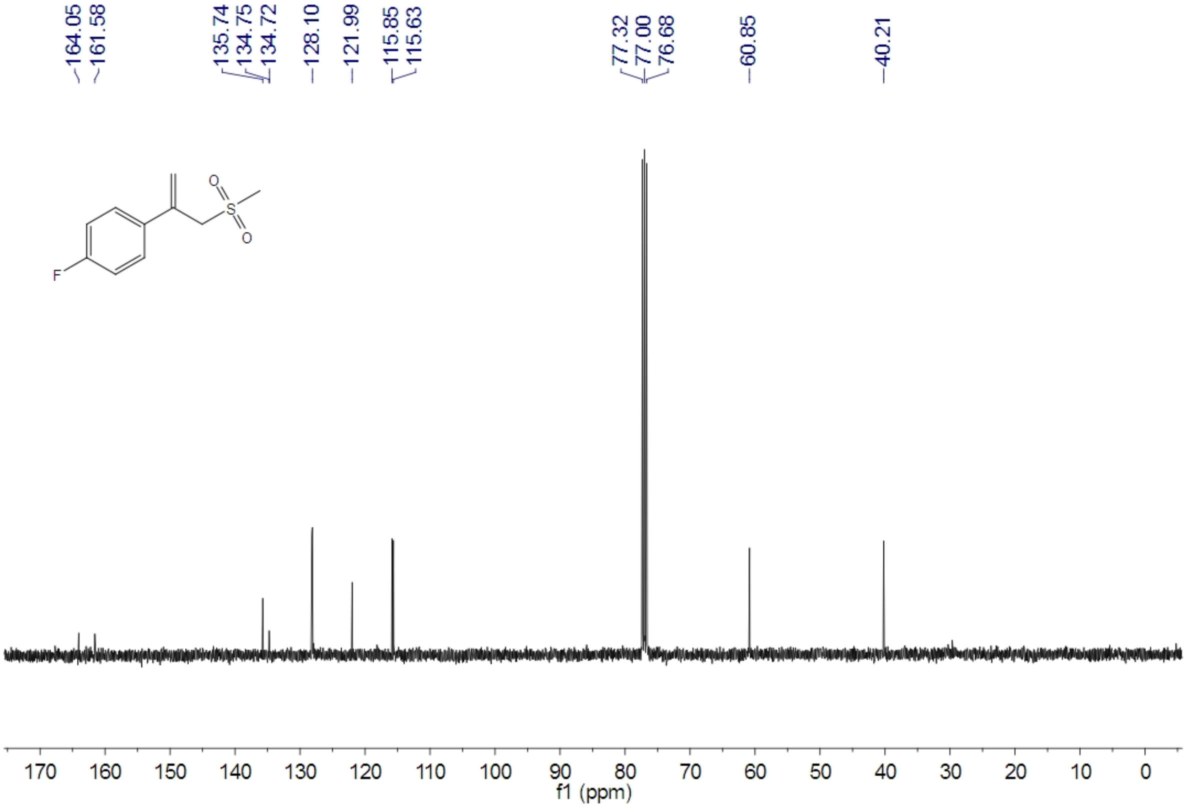

7.649
7.459
7.420
7.391
7.378
7.263
2.974
2.337
0.000
O
S
O
1.03
5.05
3.03
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

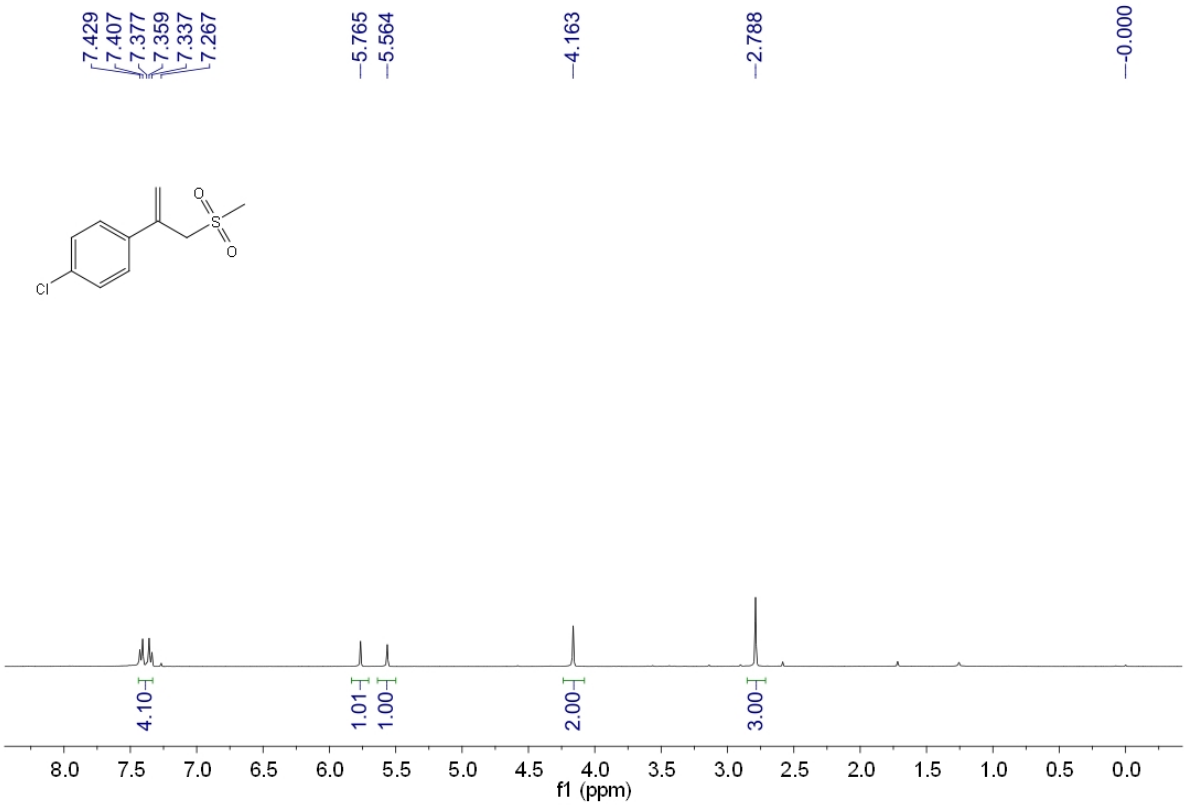

138.02
136.74
133.53
129.57
129.43
128.73
77.32
77.00
76.68
40.37
13.42
O
S
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

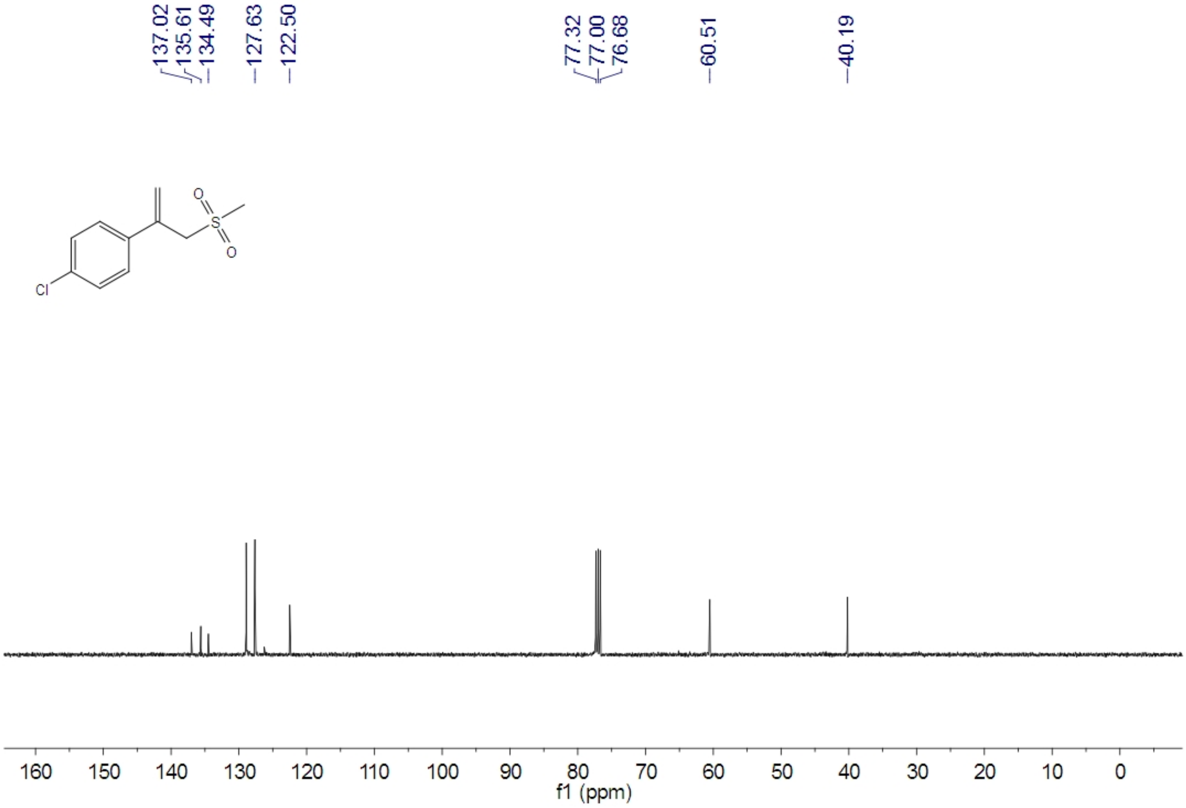

7.479
7.475
7.470
7.458
7.455
7.449
7.405
7.401
7.396
7.384
7.365
7.356
7.352
7.349
7.341
7.335
7.326
7.320
7.261
5.764
5.565
4.192
2.720
-0.000
O
S
O
2.01
3.00
1.00
1.00
2.01
3.00
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

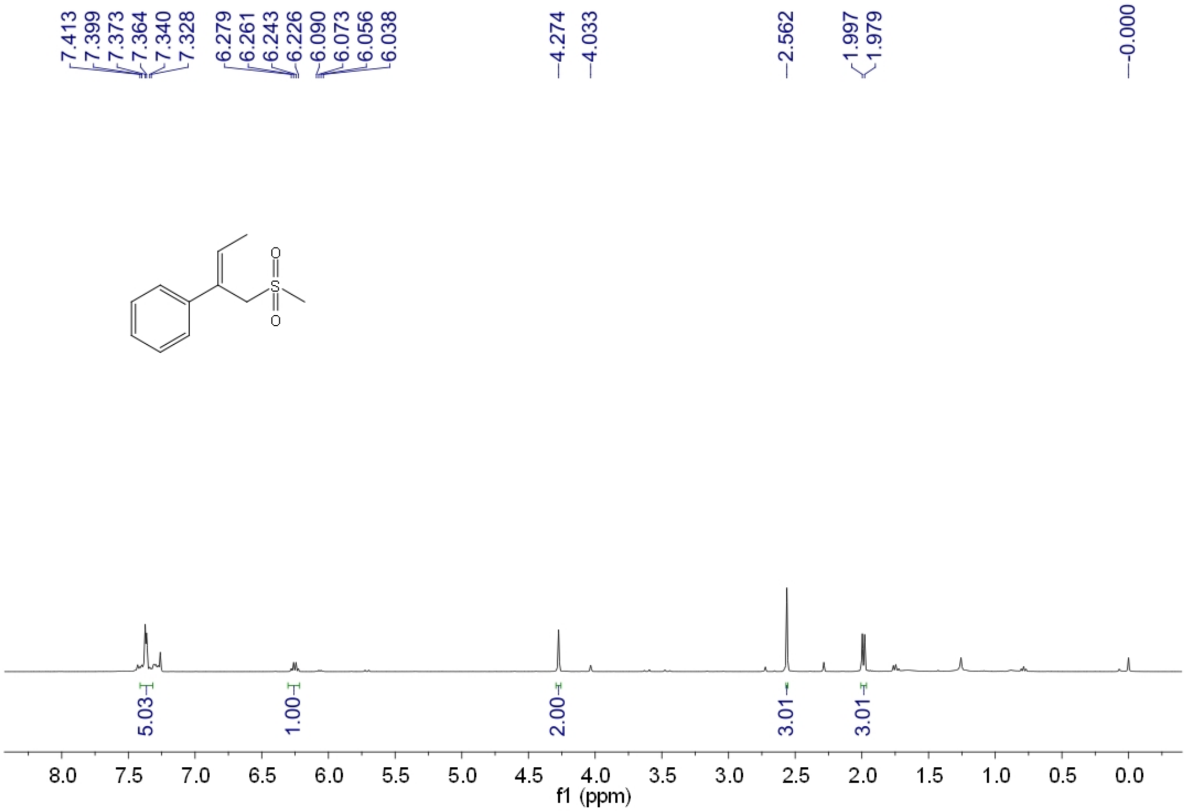

138.63
136.65
128.79
128.53
126.26
122.05
77.32
77.00
76.68
60.74
40.23
O
S
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

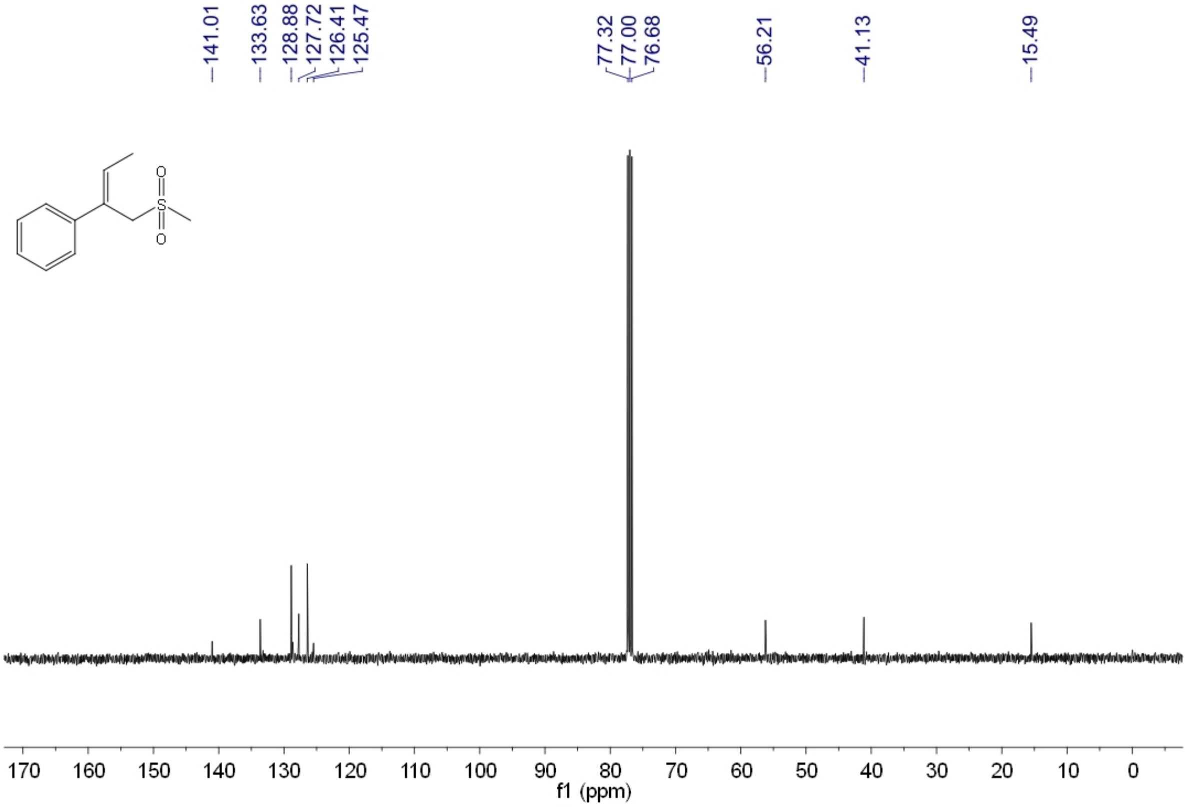

7.477
7.462
7.456
7.443
7.264
7.093
7.071
7.050
5.727
5.537
4.167
2.782
0.000
F
O
S
O
2.00
2.00
1.00
1.00
2.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

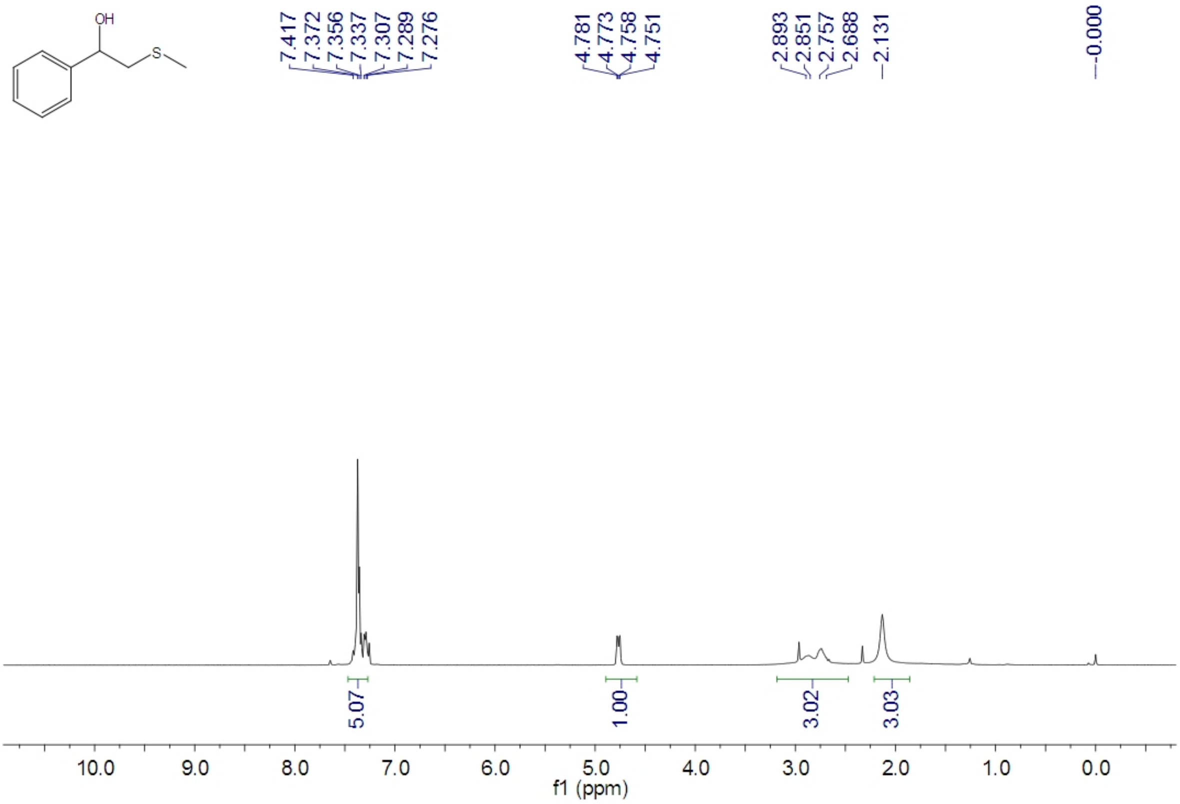

164.05
161.58
135.74
134.75
134.72
128.10
121.99
115.85
115.63
77.32
77.00
76.68
60.85
40.21
F
O
S
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

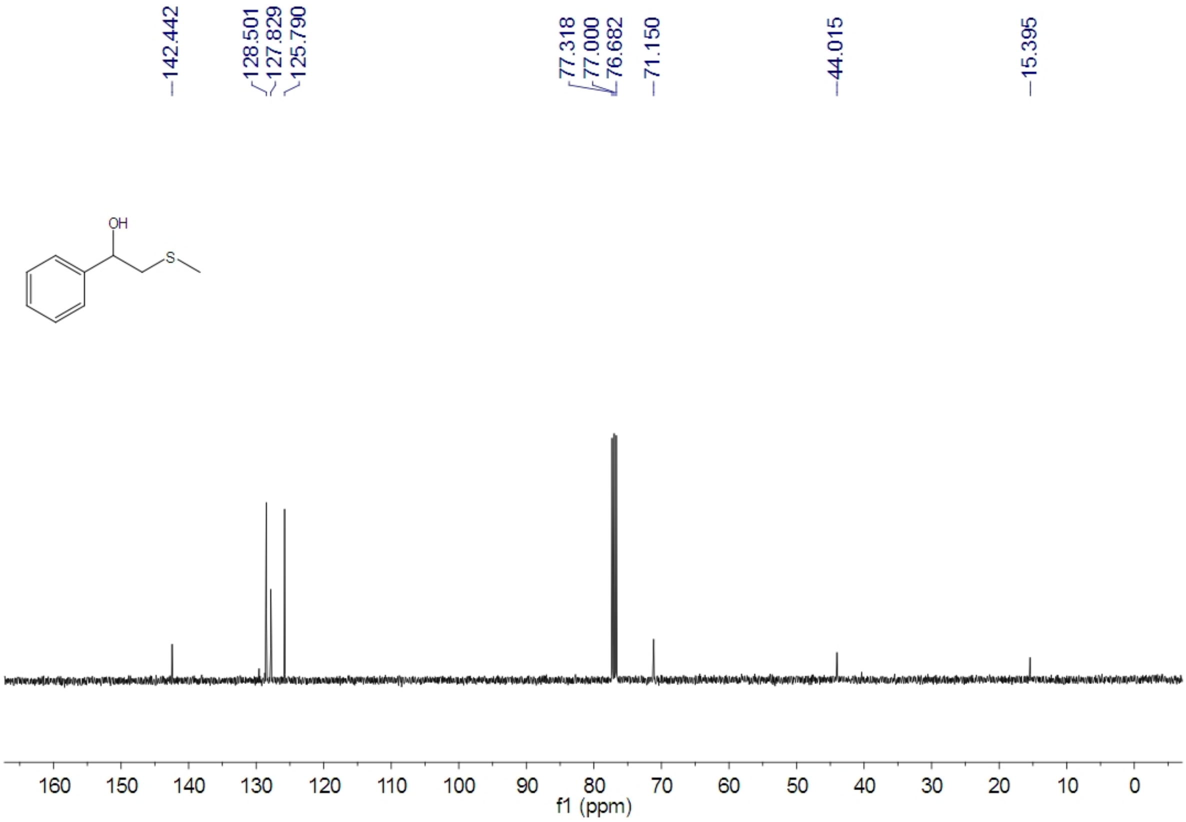

7.429
7.407
7.377
7.359
7.337
7.267
5.765
5.564
4.163
2.788
0.000
O
S
O
Cl
4.10
1.01
1.00
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

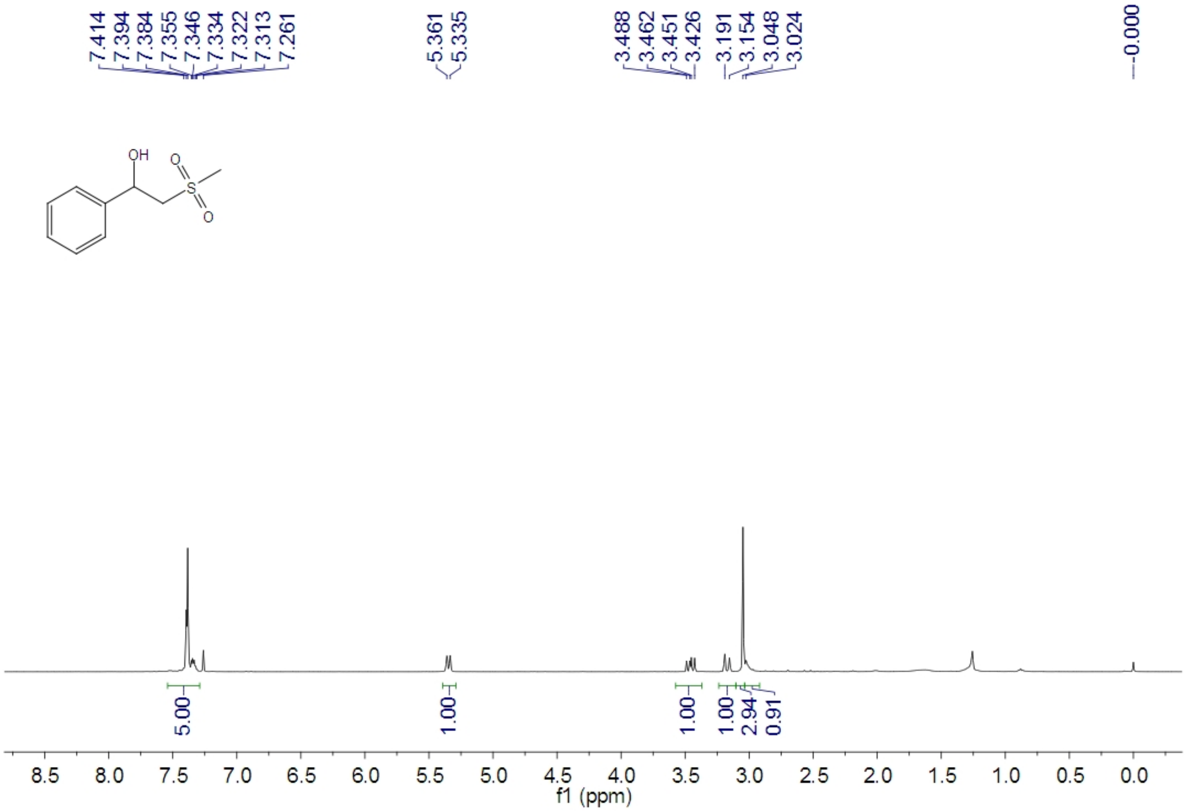

137.02
135.61
134.49
127.63
122.50
77.32
77.00
76.68
60.51
40.19
O
S
O
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

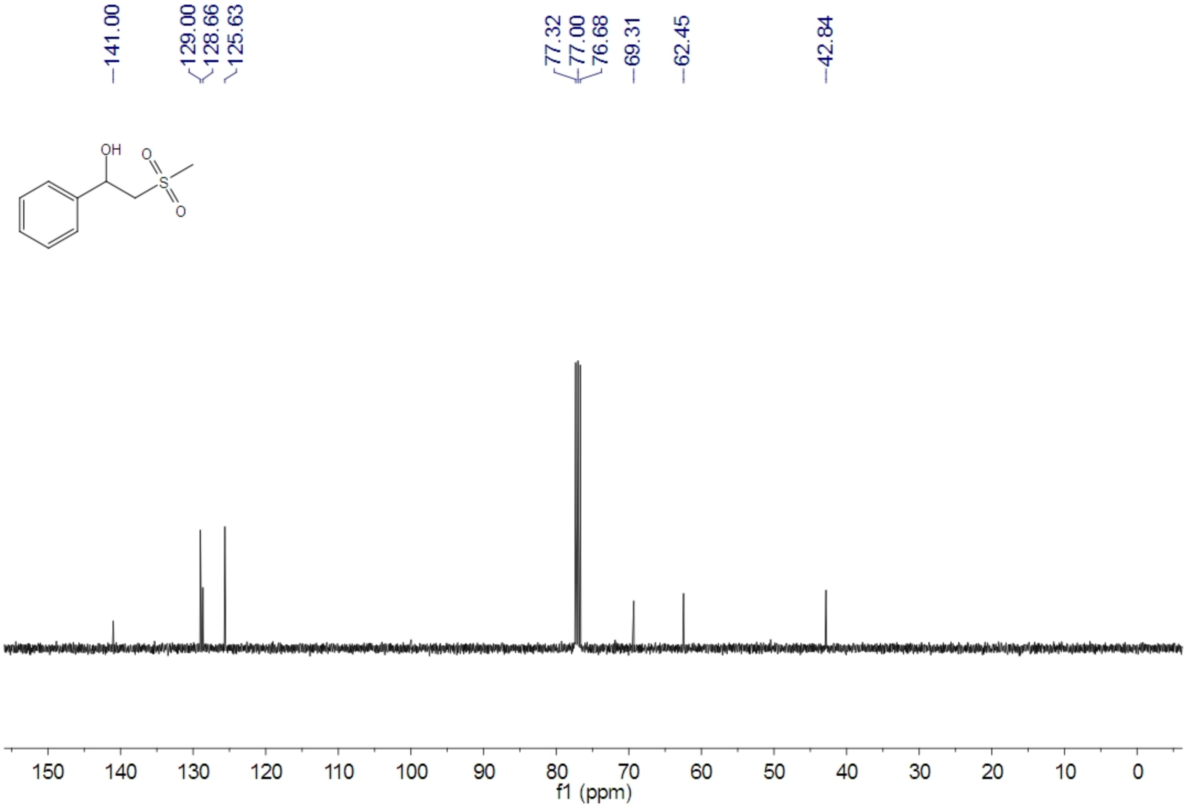

7.413
7.399
7.373
7.364
7.340
7.328
6.279
6.261
6.243
6.226
6.090
6.073
6.056
6.038
4.274
4.033
2.562
1.997
1.979
0.000
O
S
O
5.03
1.00
2.00
3.01
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


141.01
133.63
128.88
127.72
126.41
125.47
77.32
77.00
76.68
56.21
41.13
15.49
O
S
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
S
7.417
7.372
7.356
7.337
7.307
7.289
7.276
4.781
4.773
4.758
4.751
2.893
2.851
2.757
2.688
2.131
0.000
5.07
1.00
3.02
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


142.442
128.501
127.829
125.790
77.318
77.000
76.682
71.150
44.015
15.395
OH
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.414
7.394
7.384
7.355
7.346
7.334
7.322
7.313
7.261
5.361
5.335
3.488
3.462
3.451
3.426
3.191
3.154
3.048
3.024
0.000
OH
O
S
O
5.00
1.00
1.00
1.00
2.94
0.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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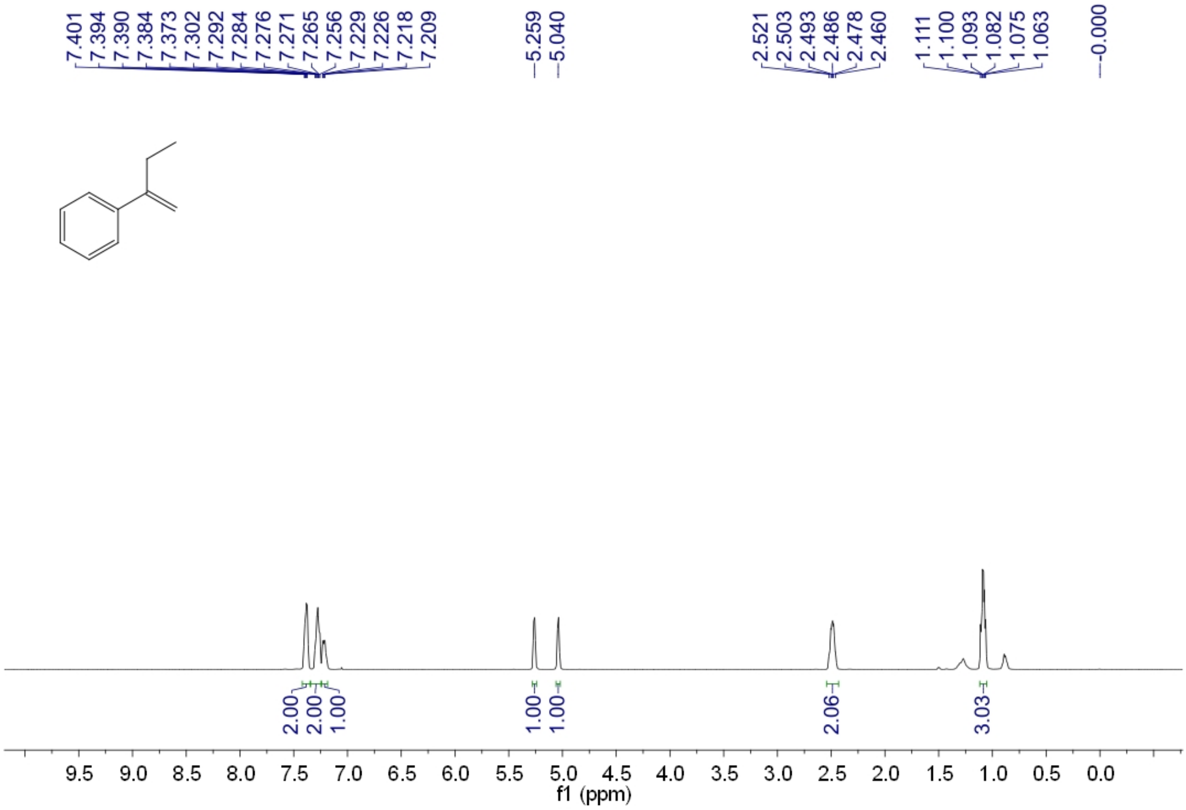
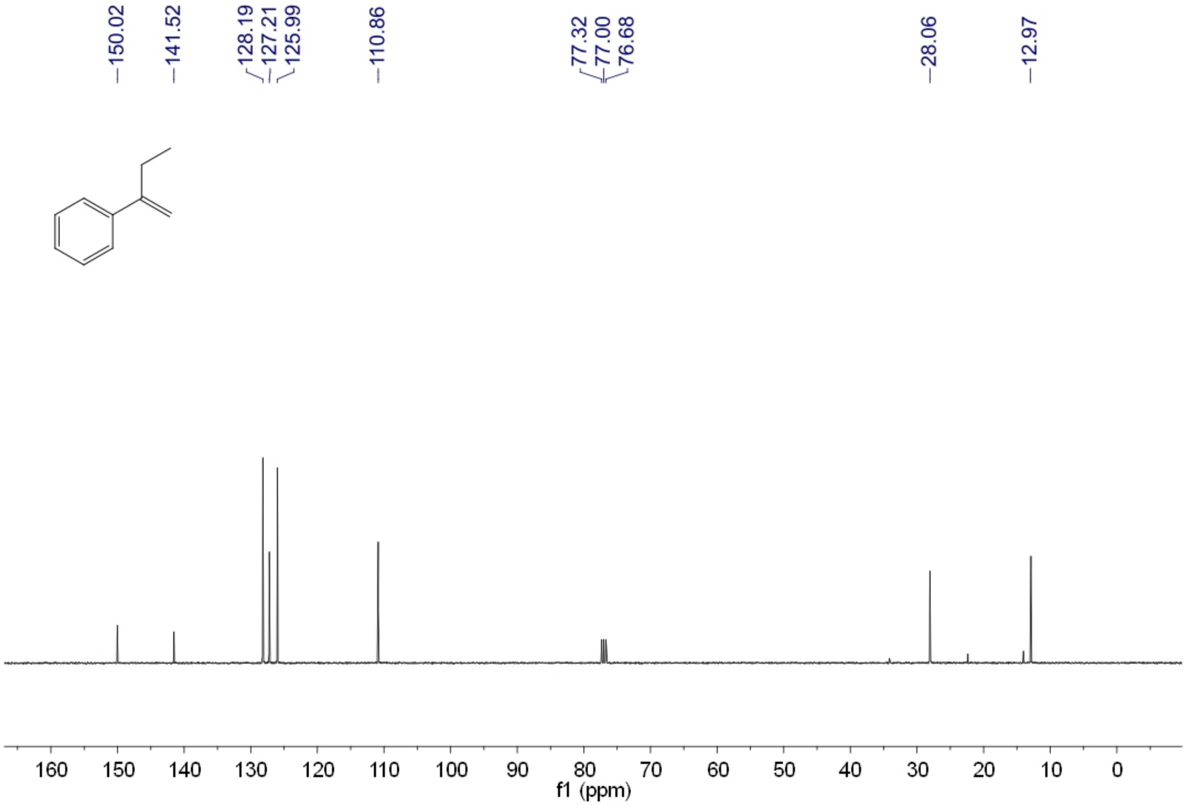
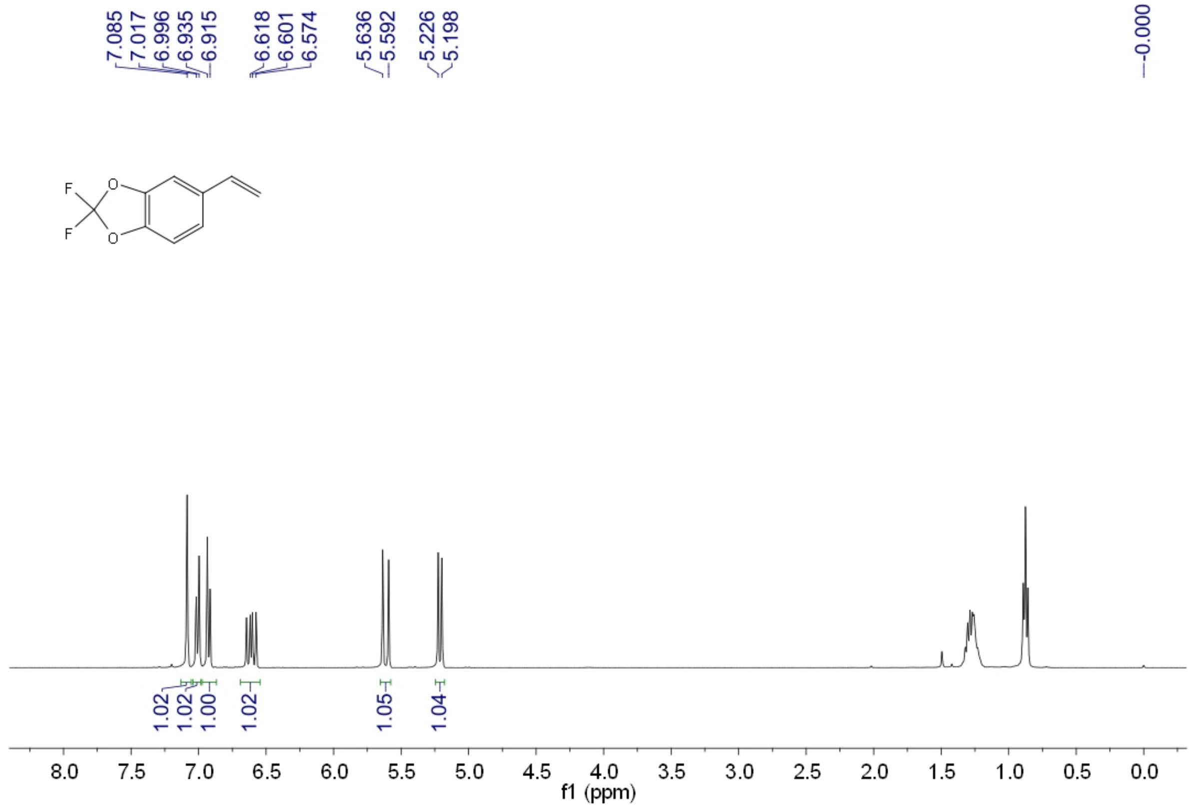
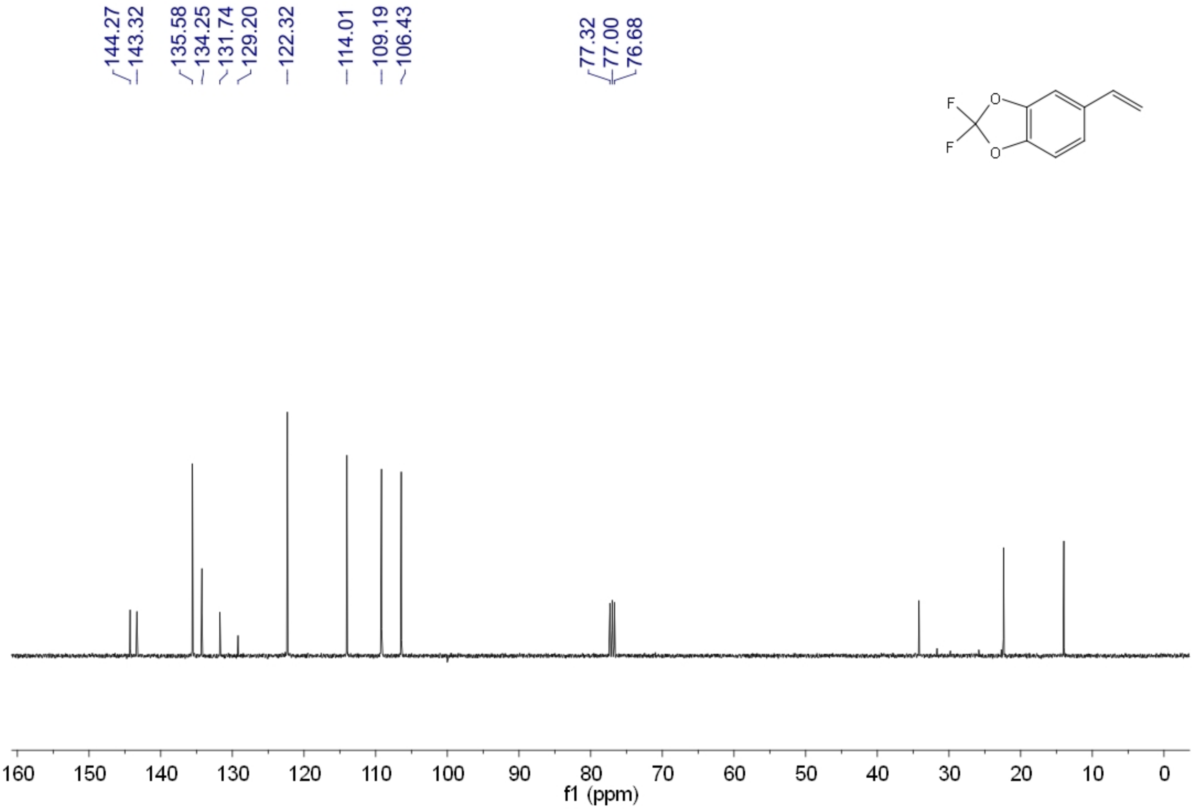
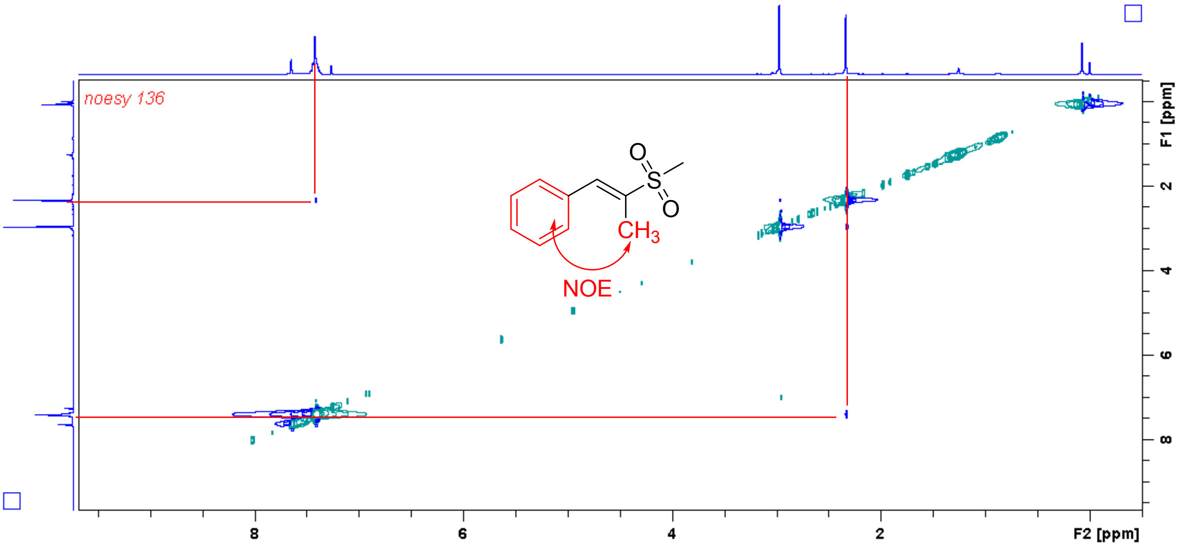
129.00
128.66
125.63
77.32
77.00
76.68
69.31
62.45
42.84
OH
O
S
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.401
7.394
7.390
7.384
7.373
7.302
7.292
7.284
7.276
7.271
7.265
7.256
7.229
7.226
7.218
7.209
5.259
5.040
2.521
2.503
2.493
2.486
2.478
2.460
1.111
1.100
1.093
1.082
1.075
1.063
-0.000
2.00
2.00
1.00
1.00
1.00
2.06
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.02
141.52
128.19
127.21
125.99
110.86
77.32
77.00
76.68
28.06
12.97
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.085
7.017
6.996
6.935
6.915
6.618
6.601
6.574
5.636
5.592
5.226
5.198
0.000
F
F
O
O
1.02
1.02
1.00
1.02
1.05
1.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.27
143.32
135.58
134.25
131.74
129.20
122.32
114.01
109.19
106.43
77.32
77.00
76.68
F
F
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


noesy 136
O
S
O
CH3
NOE
F1 [ppm]
2
4
6
8
8
6
4
2
F2 [ppm]