

Supplementary Information

Metal-Free Chemoselective Oxidation of Sulfides to Sulfoxides Catalyzed by Immobilized L-Aspartic Acid and L-Glutamic Acid in Aqueous Phase at Room Temperature

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1 Experimental Section

1.1 General

The FT-IR spectra were measured on a Nicolet 6700 spectrometer as KBr pellets. The XPS spectra were measured on a Kratos AXIS Ultra DLD photoelectron spectrometer. Contact angle measurement were measured employing the KRÜSS DSA100 Drop Shape Analysis System. The SEM images were obtained employing the S-4700 (II) SEM instrument. The TGA were carried out on a STA 449 F3 Jupiter® spectrometer. The XRD patterns were recorded on a X' Pert PRO X-ray diffractometer. ¹H NMR and ¹³C NMR spectra were measured on a AVANCE III NMR spectrometer at 500MHz in CDCl₃. Tetramethylsilane was used as the internal standard (0.00 ppm) in CDCl₃. The ESI-MS spectra were measured on an Agilent 6210 TOF LC/MS mass spectrometer. GC analyses were performed on a Shimadzu GC-14B instrument using a SPB-5 column (0.25 mm × 30 m). In the GC experiments, *p*-xylene was employed as an internal standard. All the catalytic reaction were carried out in the Wattecs parallel synthesis system.

1.2 Materials

Tetraethyl orthosilicate (TEOS) in 98% purity, (3-chloropropyl)triethoxysilane (CPTES) in 98% purity, and tetrabutylammonium fluoride (1 M solution in anhydrous THF) were purchased from Shanghai Energy Chemical Co. Ltd., China. L-Aspartic acid in 98% purity and L-glutamic acid in 98% purity were purchased from Aladdin Chemistry Co. Ltd., China. Potassium iodide (KI) in 99% purity were purchased from Xilong Chemical Co. Ltd., China. 30% H₂O₂ were purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd., China. Ethanol in 99% purity was purchased from Anhui Ante Food Co. Ltd., China. Triethanolamine in 98% purity were purchased from Wuxi Haishuo Biological Co. Ltd., China. Methyl phenyl sulfide, methyl 4-methylphenyl sulfide, methyl 4-methoxyphenyl sulfide, ethyl phenyl sulfide, 2-chloroethyl phenyl sulfide, diphenyl sulfide, dibutyl sulfide and other sulfides were purchased from Shanghai Energy Chemical Co. Ltd., China, Aladdin Chemistry Co. Ltd., China,

TCI Co. Ltd., or Aldrich Co. Ltd. Methyl phenyl sulfoxide was purchased from Aldrich Co. Ltd. All the other common reagents were analytical grade. All of the reagents were used as received without further purification unless otherwise noted.

1.3 Preparation of hybrid silica Si@Cl

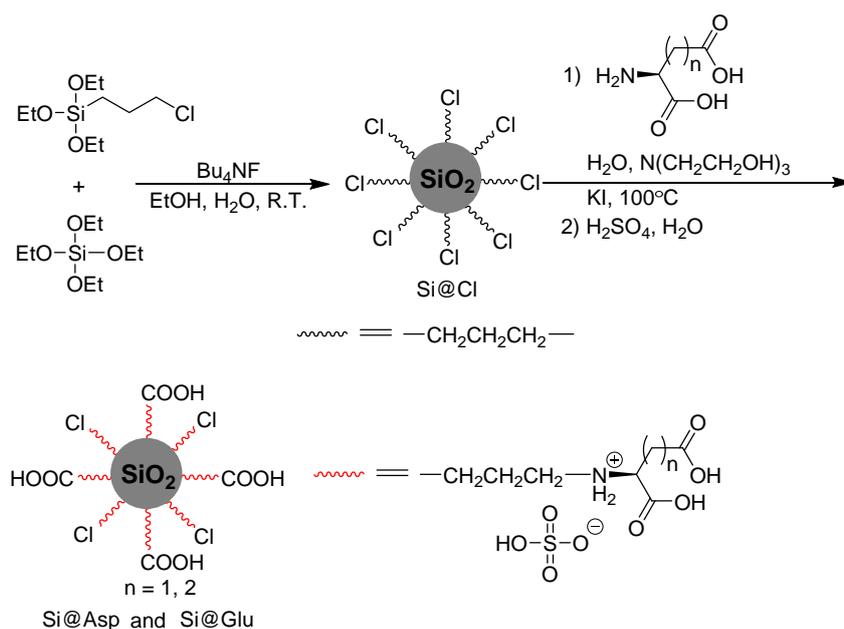
Si@Cl was prepared through the procedure reported in the previous literature.^[1-3] (3-Chloropropyl)triethoxysilane (CPTES) (2.4080 g, 10.0 mmol) and tetraethyl orthosilicate (TEOS) (10.4165 g, 50 mmol) were dissolved in anhydrous ethanol (10 mL). Then, a solution of distilled water (3.6040 g, 200.0 mmol) and tetrabutylammonium fluoride (3.0 mL, 1 M solution in anhydrous THF) in anhydrous EtOH (20.0 mL) was added to the first solution. The obtained mixture was shaken vigorously for 10 s to obtain a clear solution. After 5.0 min, a gel formed that was then aged at room temperature for a week. Then, the obtained gel was pulverized, collected by suction filtration, and washed with EtOH (3 × 50 mL) and acetone (2 × 50 mL) successively. The final solid was dried under vacuum at 60 °C for 8.0 h to afford Si@Cl as a white solid powder (4.4802 g).

1.4 Preparation of immobilized L-aspartic acid Si@Asp

Hybrid silica (Si@Cl) (3.0000 g) and KI (0.1500 g) were dispersed in a mixture of water (30 mL) and triethanolamine (30 mL), and L-aspartic acid (7.5000 g) was added to the stirring mixture. Then the reaction mixture was heated to 100°C and vigorously stirred under a nitrogen atmosphere at 100°C for 96 h. At the end of the reaction, a light yellow solid was collected by suction filtration, and washed with EtOH (3 × 50 mL) and water (2 × 50 mL) successively. Then the obtained solid was dispersed in ethanol (30 mL), and 20% H₂SO₄ aqueous solution (30 mL, V/V) was added dropwise at room temperature. The reaction mixture was refluxed for 24.0 h, and filtered, washed successively with EtOH (2 × 50 mL) and water (2 × 50 mL). The final white solid was dried under vacuum at 60 °C for 12.0 h to afford Si@Asp as a white solid powder (1.8962g).

1.5 Preparation of immobilized L-glutamic acid Si@Glu

Hybrid silica (Si@Cl) (3.0000 g) and KI (0.1500 g) were dispersed in a mixture of water (30 mL) and triethanolamine (30 mL), and L-glutamic acid (7.5000 g) was added to the stirring mixture. Then the reaction mixture was heated to 100°C and vigorously stirred under a nitrogen atmosphere at 100°C for 96 h. At the end of the reaction, a light yellow solid was collected by suction filtration, and washed with EtOH (3 × 50 mL) and water (2 × 50 mL) successively. Then the obtained solid was dispersed in ethanol (30 mL), and 20% H₂SO₄ aqueous solution (30 mL, V/V) was added dropwise at room temperature. The reaction mixture was refluxed for 24.0 h, and filtered, washed successively with EtOH (2 × 50 mL) and water (2 × 50 mL). The final white solid was dried under vacuum at 60 °C for 12.0 h to afford Si@Glu as a white solid powder (2.0251 g).



Scheme S1. Schematic immobilization of L-aspartic acid and L-glutamic acid on the hybrid silica.

1.6 General procedure for oxidation of sulfides catalyzed by Si@Asp

Sulfide (1.0 mmol) was added to a solution of water (1.0 mL) and Si@Asp (86.9 mg), after stirring at 25°C for 15 min, 30% H₂O₂ (1.15 mmol) was added. Then, the

resultant mixture was kept stirring at 25°C for 24.0 h or 48.0 h. At the end of the reaction, saturated aqueous Na₂SO₃ (2.0 mL) was added to stop deep oxidation. The obtained solution was extracted with ethyl acetate (3 × 2.0 mL), and the combined organic phase was washed with brine (2.0 mL) and dried over anhydrous Na₂SO₄. The obtained solution was analyzed by GC (p-xylene as internal standard) or subjected to column chromatography (Silica, eluent V_{cyclohexane} / V_{ethyl acetate} = 6 : 4) to determine the conversion and yield. For some solid sulfides, 0.5 mL acetonitrile was added to enhance their dispersion in water.

1.7 Recyclability of Si@Asp

Methyl phenyl sulfide (3.0 mmol) was added to a solution of water (3.0 mL) and Si@Asp (260.7 mg), after stirring at 25°C for 15 min, 30% H₂O₂ (3.45 mmol) was added. Then, the resultant mixture was kept stirring at 25°C for 24.0 h. At the end of the reaction, saturated aqueous Na₂SO₃ (6.0 mL) was added to stop deep oxidation. The obtained solution was extracted with ethyl acetate (3 × 3.0 mL), and the combined organic phase was washed with brine (6.0 mL) and dried over anhydrous Na₂SO₄. The obtained solution was analyzed by GC to determine the conversion and yield with p-xylene as internal standard. The remaining aqueous phase from extraction was centrifuged at 4500 rpm for 10.0 min. The obtained solid was washed successively with ethyl acetate (3 × 3.0 mL) and water (2 × 3.0 mL) under ultrasonic condition, and then dried at 50°C under vacuum. Then the obtained Si@Asp was subjected to the second run under the same reaction conditions, and for the loss of catalyst in the reusability experiment, the substrate added should be decreased proportionally in each run.

2 Characterization spectra of Si@Cl, Si@Asp, and Si@Glu

Fig. S1. FT-IR spectra of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

Fig. S2. SEM images of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

Fig. S3. TGA curves of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

Fig. S4. XRD patterns of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

Fig. S5. Contract angles of water on (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

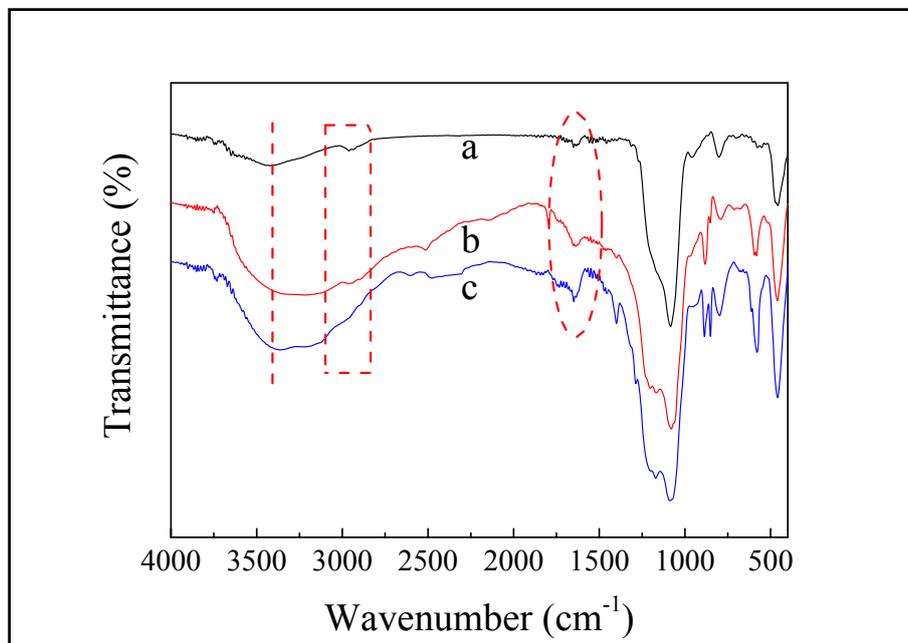
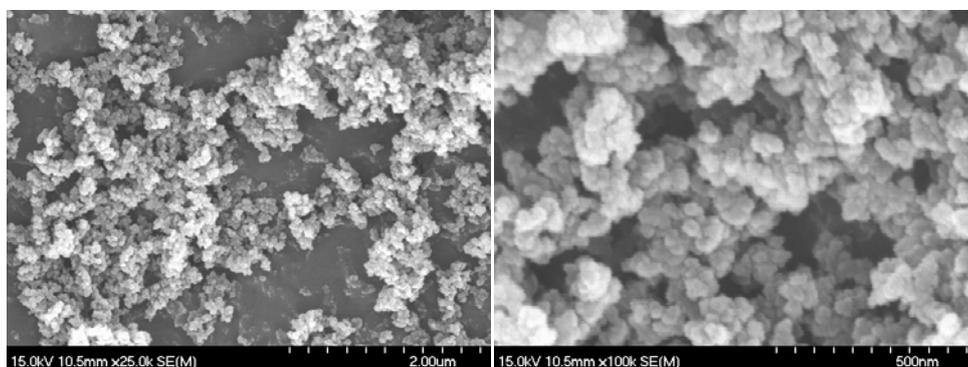
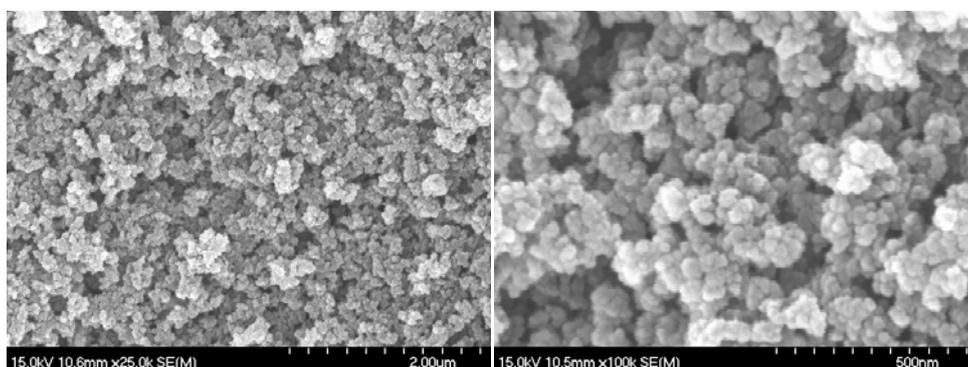


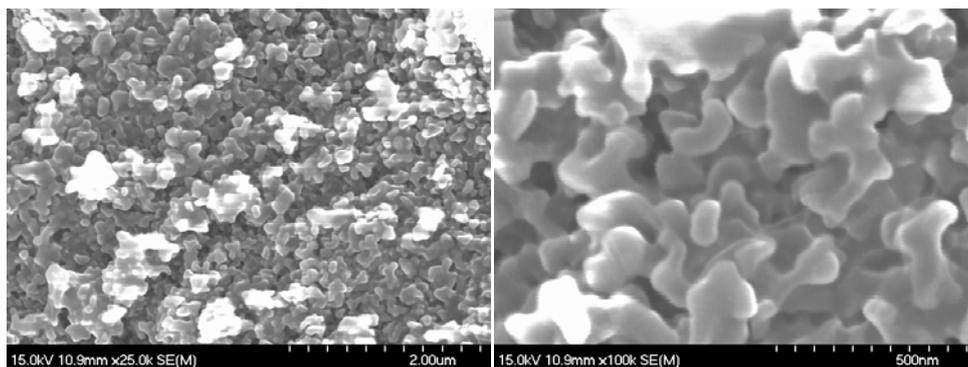
Fig. S1. FT-IR spectra of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.



a



b



c

Fig. S2. SEM images of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

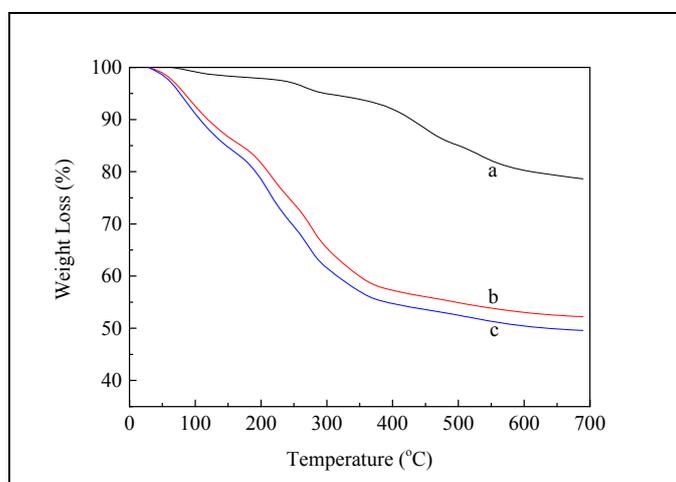


Fig. S3. TGA curves of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

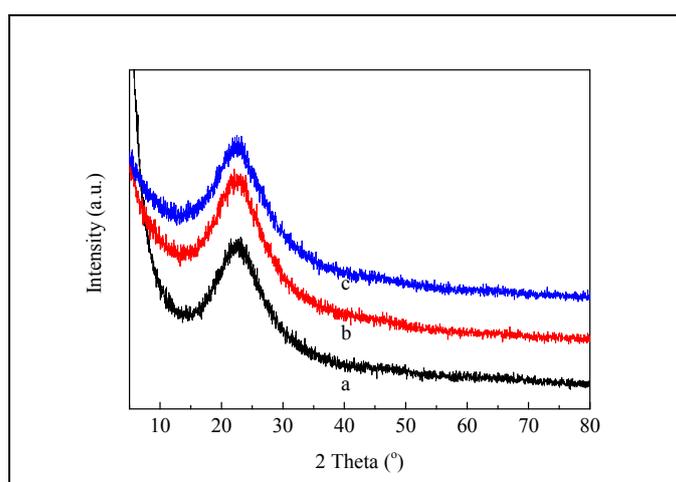


Fig. S4. XRD patterns of (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

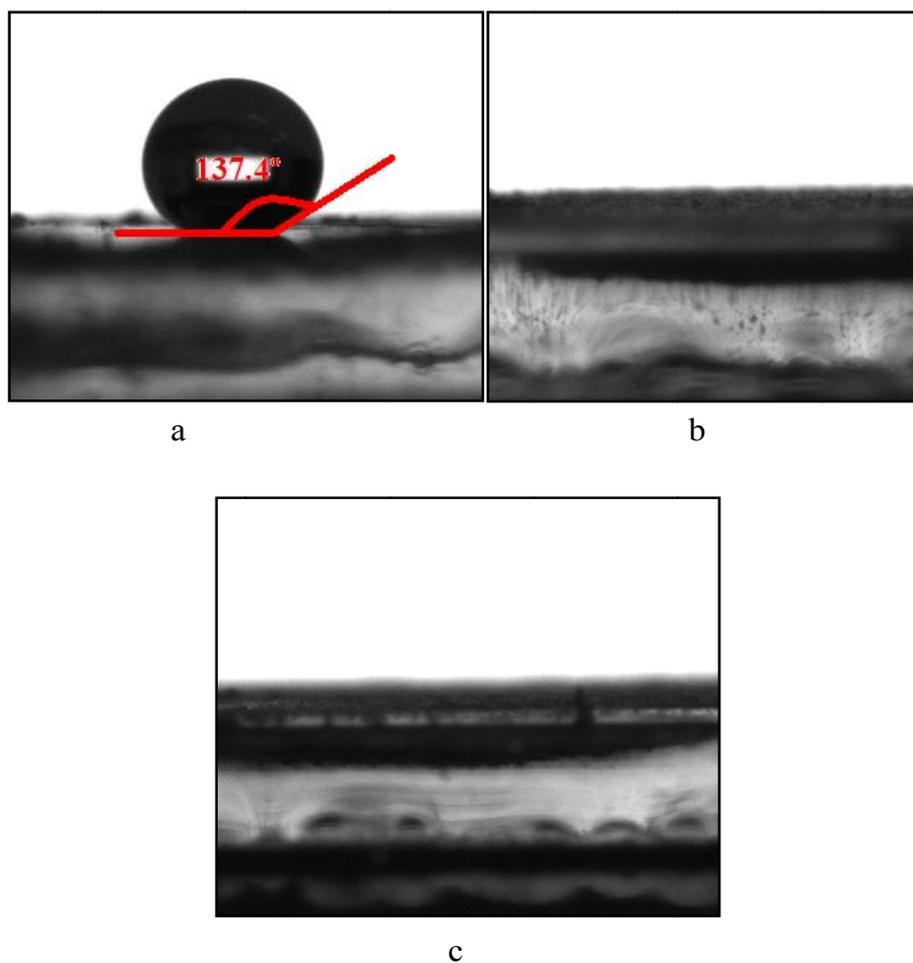
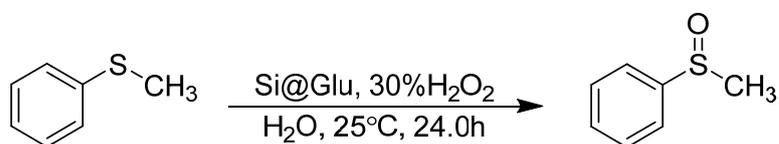


Fig. S5. Contact angles of water on (a) Si@Cl, (b) Si@Asp, and (c) Si@Glu.

3 Experimental Data

Table S1 Effect of Si@Glu amount on the oxidation of methyl phenyl sulfide with H₂O₂^a



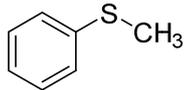
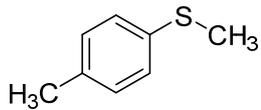
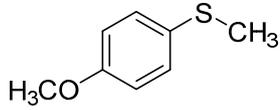
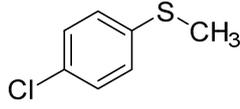
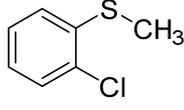
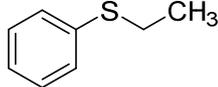
Entry	Si@Glu amount (mg)	Conversion (%) ^b	Yield (%) ^b	Selectivity (%)
1	0.0	34.3	34.3	100.0
2	12.4	53.5	53.2	99.4
3	24.8	59.6	59.0	99.0

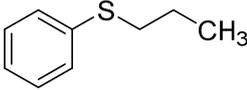
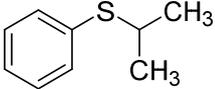
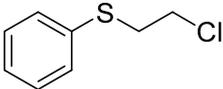
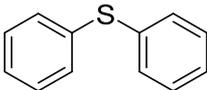
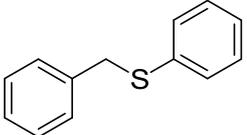
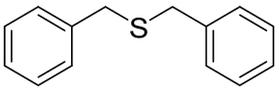
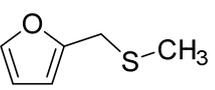
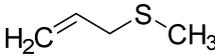
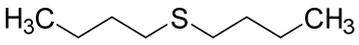
4	37.3	75.9	75.3	99.2
5	49.7	93.5	92.6	99.0
6	62.1	95.8	94.7	98.9
7	74.5	97.3	95.8	98.5
8	86.9	99.5	97.4	97.9
9	99.4	99.6	97.4	97.8
10	111.8	99.7	96.8	97.1
11	124.2	99.7	97.1	97.4

^a Reaction conditions: substrate (1.0 mmol, 124.2 mg), 30% H₂O₂ (1.15 mmol, 130 μL), solvent (1.0 mL H₂O), 25°C, 24.0h.

^b Conversion and selectivity were determined by GC with p-xylene as internal standard, product was determined by comparison with the authentic sample.

Table S2 Chemoselective oxidation of various sulfides to sulfoxides with 30% H₂O₂ catalyzed by Si@Asp^a

No	Sulfide	Time (h)	Conversion (%)	Yield (%)	Selectivity (%)
1		24	99.8	97.4	97.6
2		48	99.3	97.0	97.7
3		24	100.0	98.6	98.6
4		48	97.2	90.7	93.3
5		48	94.5	90.3	95.6
6		48	97.1	95.2	98.0

7 ^b		48	95.2	86.3	90.7
8 ^b		48	90.6	83.4	92.1
9 ^b		48	88.6	84.2	95.0
10 ^b		48	85.1	80.3	94.4
11 ^b		48	84.6	80.5	95.2
12 ^b		48	97.1	91.1	93.8
13		24	95.5	93.1	97.5
14		24	100.0	96.5	96.5
15		48	98.5	90.6	92.0

^a Reaction conditions: substrate (1.0 mmol), **Si@Asp** 86.9 mg, 30% H₂O₂ (1.15 mmol, 130 μ L), solvent (1.0 mL H₂O), 25°C. Conversion and selectivity were determined by GC with p-xylene as internal standard, product was determined by ¹H NMR, ¹³C NMR and ESI-MS.

^b Acetonitrile (0.5 mL) was added. Isolated yield, column chromatography (Silica, eluent V_{cyclohexane} / V_{ethyl acetate} = 6 : 4), product was determined by ¹H NMR, ¹³C NMR and ESI-MS.

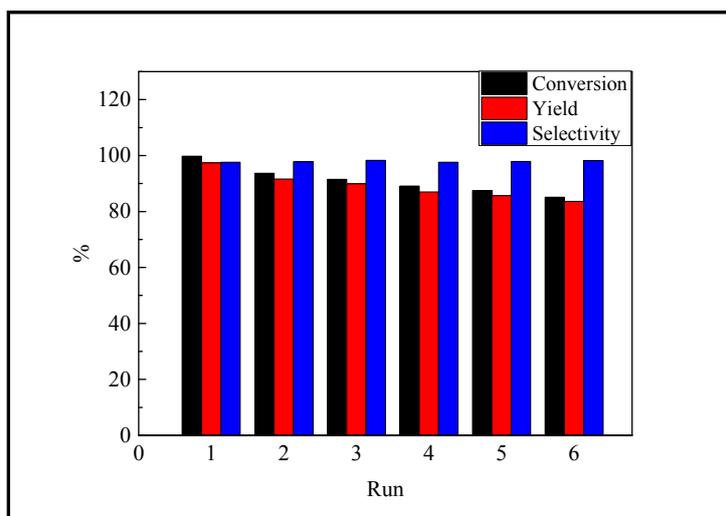
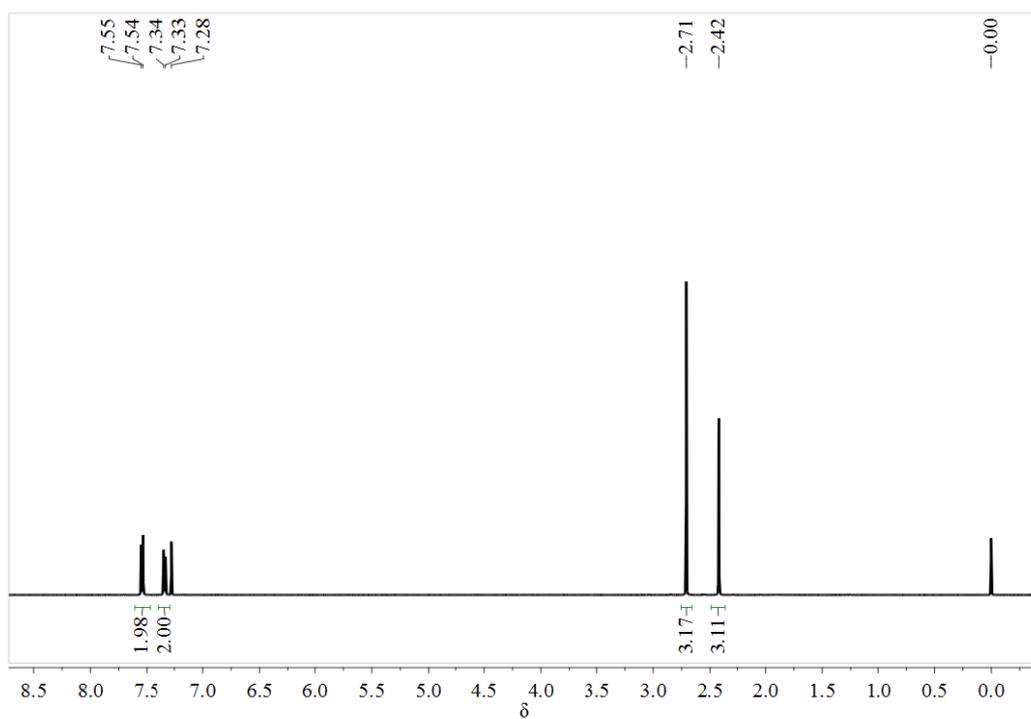
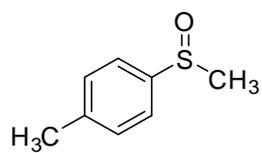
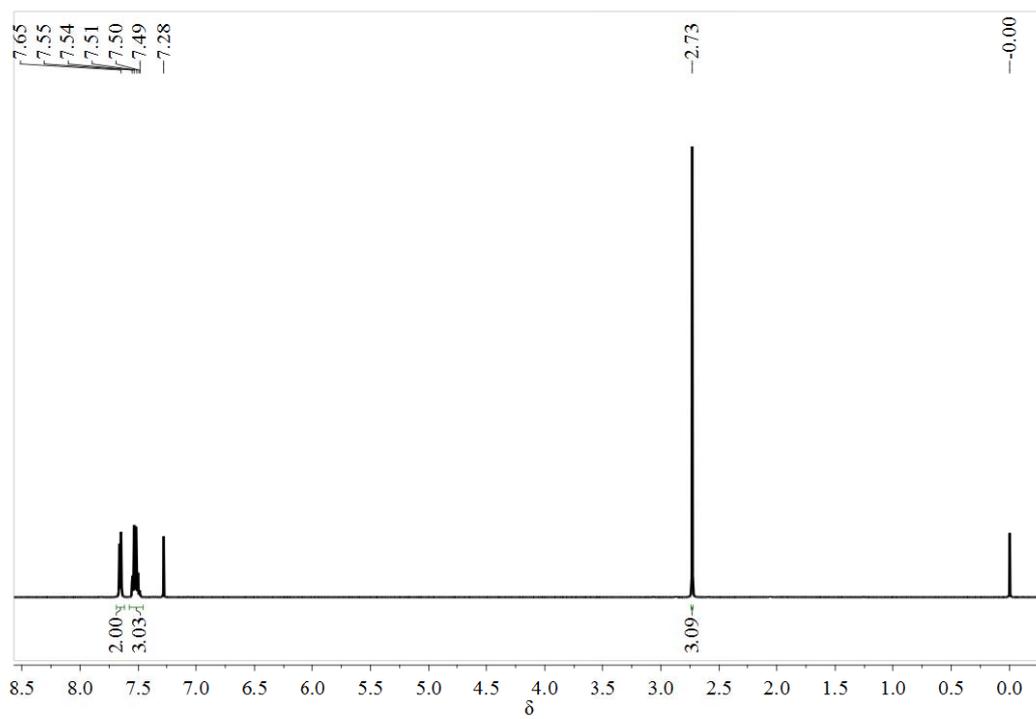
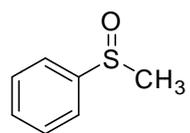
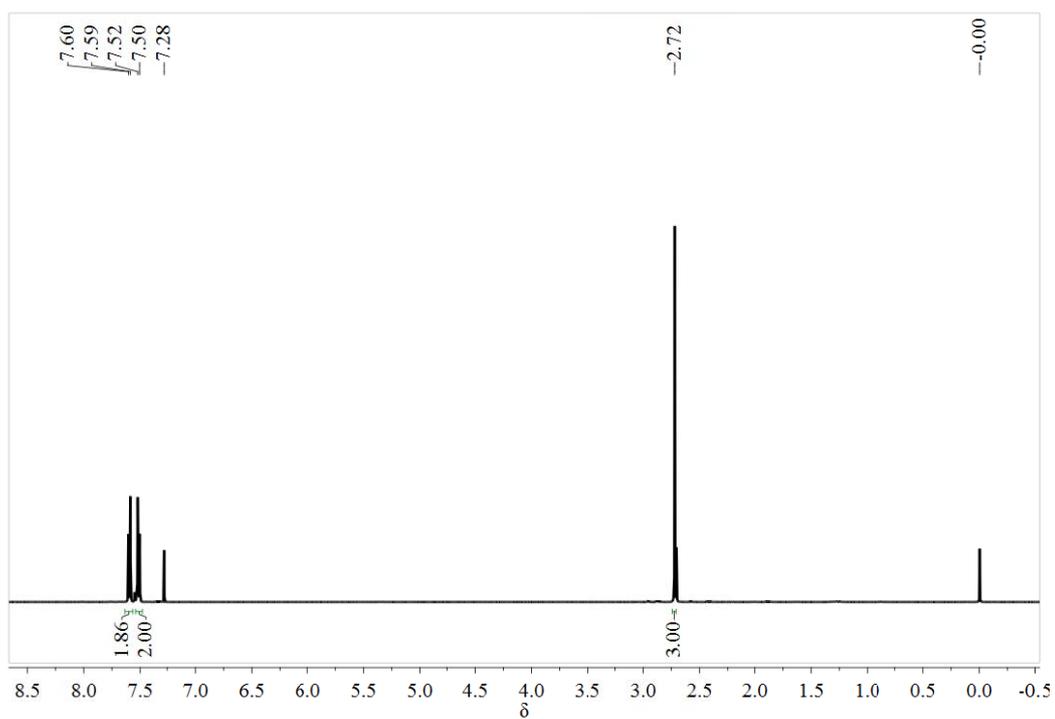
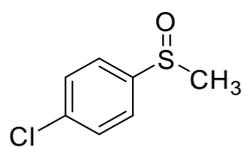
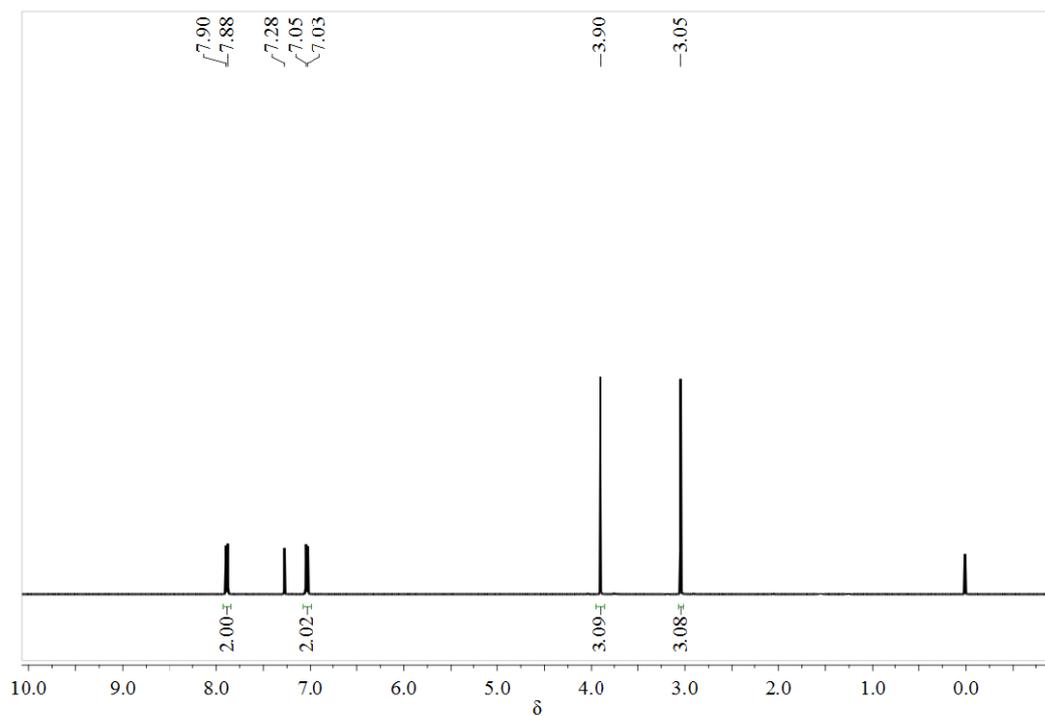
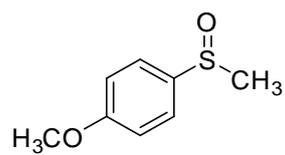
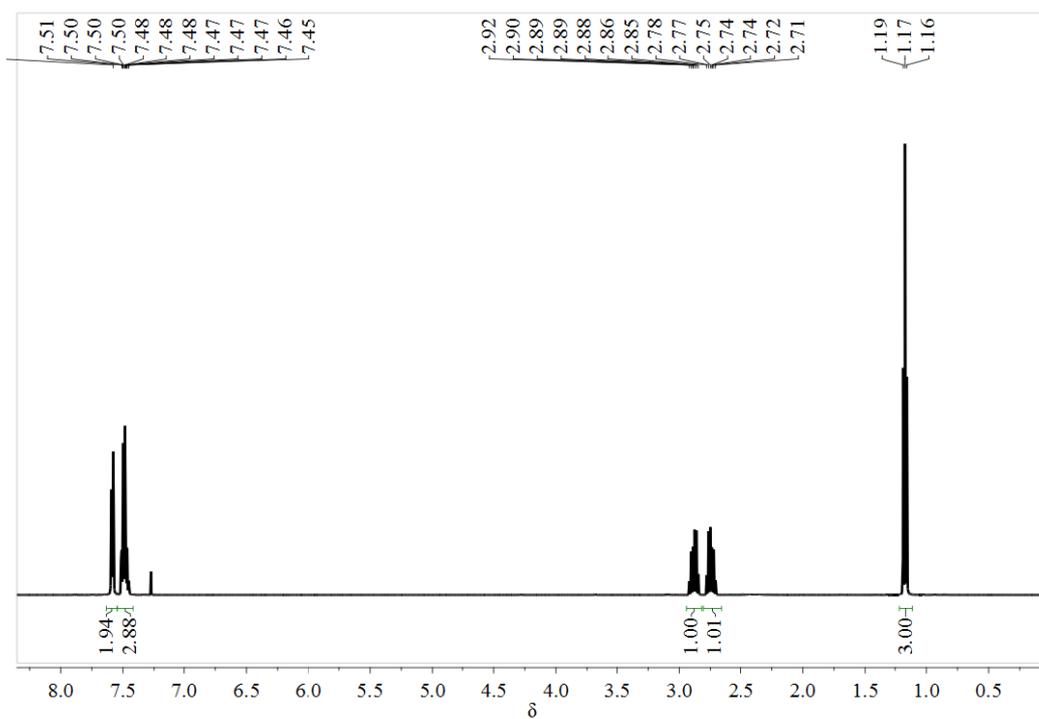
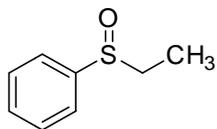
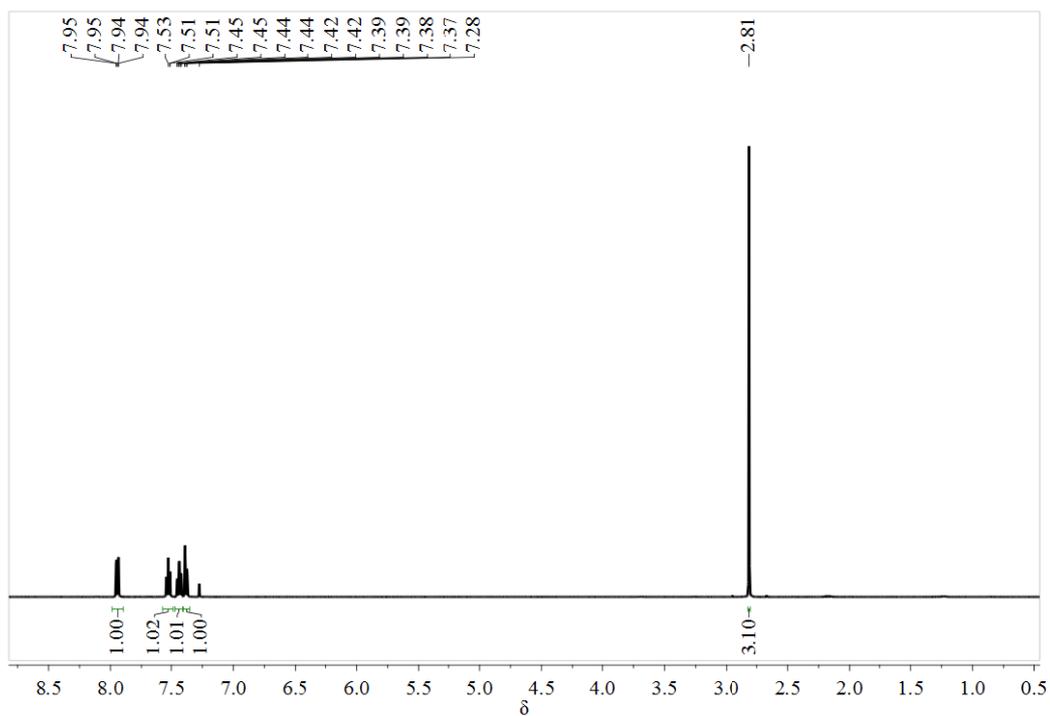
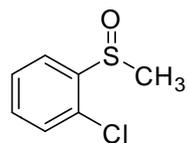


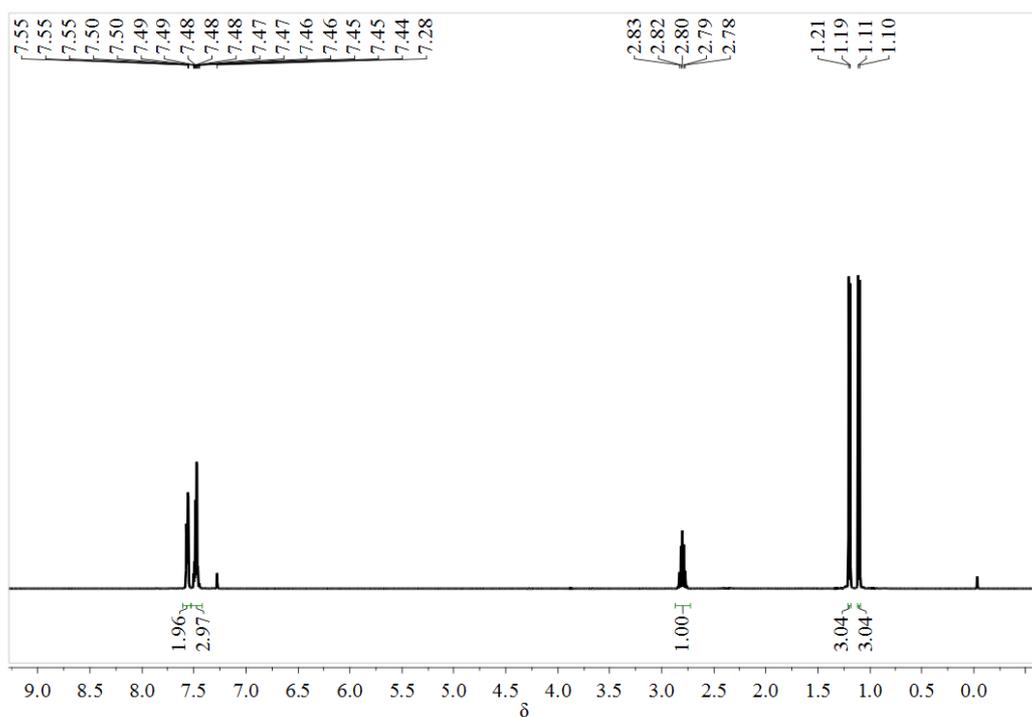
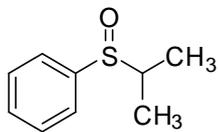
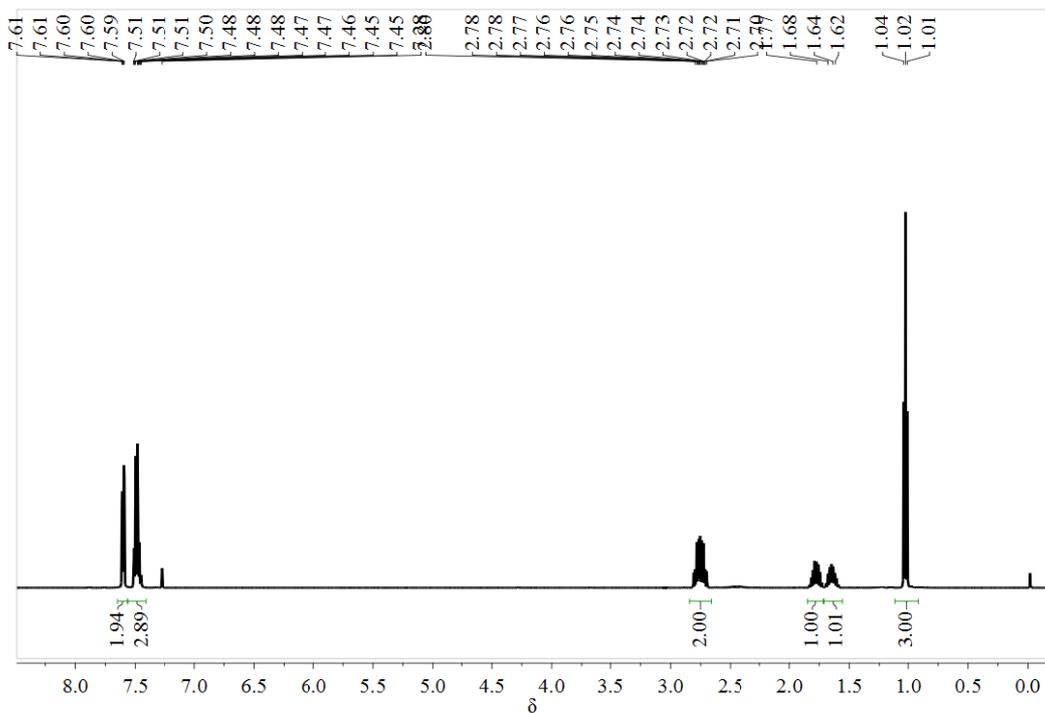
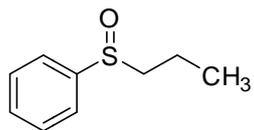
Fig. S6. Recyclability of Si@Asp in the catalytic oxidation of methyl phenyl sulfide to the corresponding sulfoxide with H₂O₂. Reaction conditions: Initially, substrate (3.0 mmol, 372.6 mg), 30% H₂O₂ (3.45 mmol, 390 μL), solvent (3.0 mL H₂O), 25°C, 24.0 h. Conversion and selectivity were determined by GC with p-xylene as internal standard, product was determined by comparison with the authentic sample. For the loss of catalyst in each reusability experiment, the substrate added should be decreased proportionally in each run.

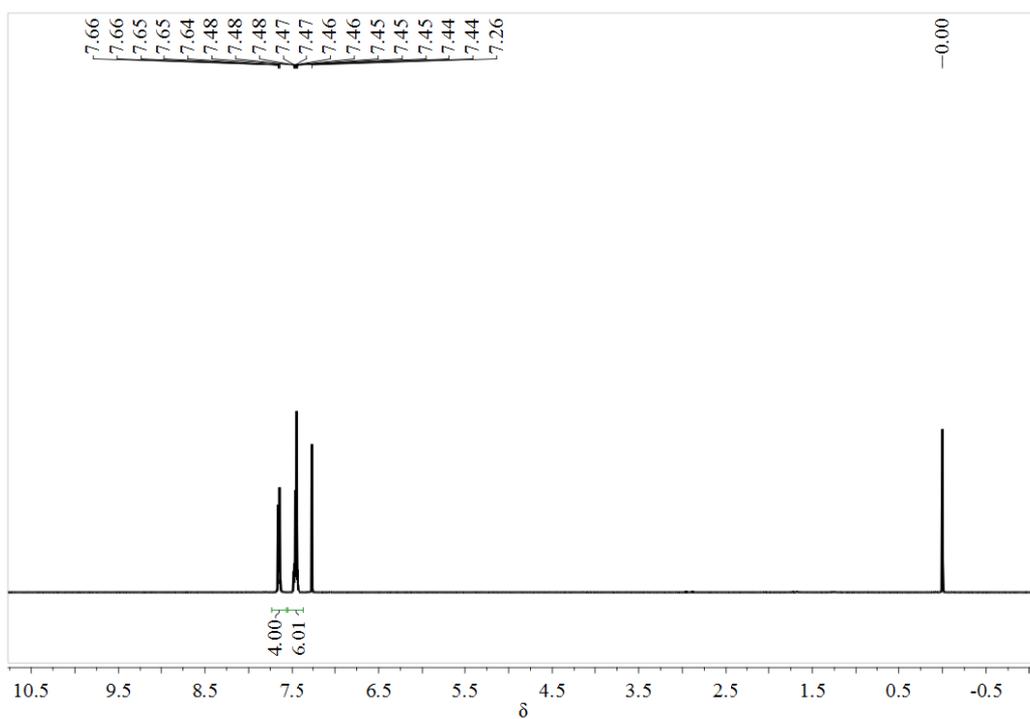
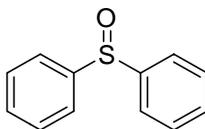
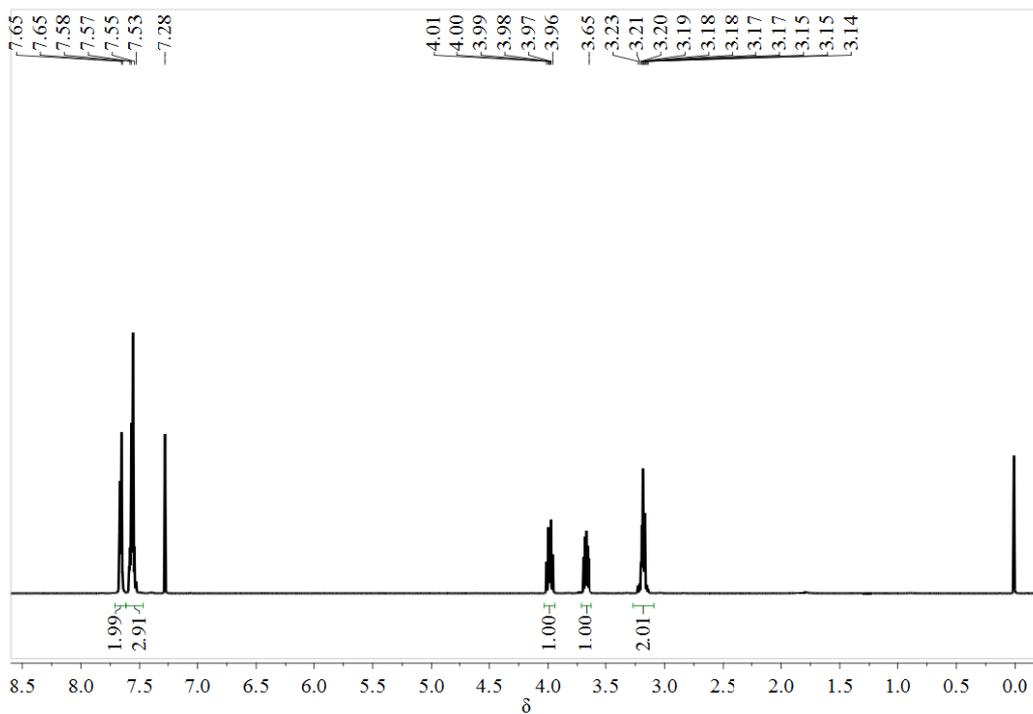
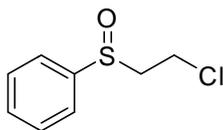
4 ¹H NMR spectra of product sulfoxides

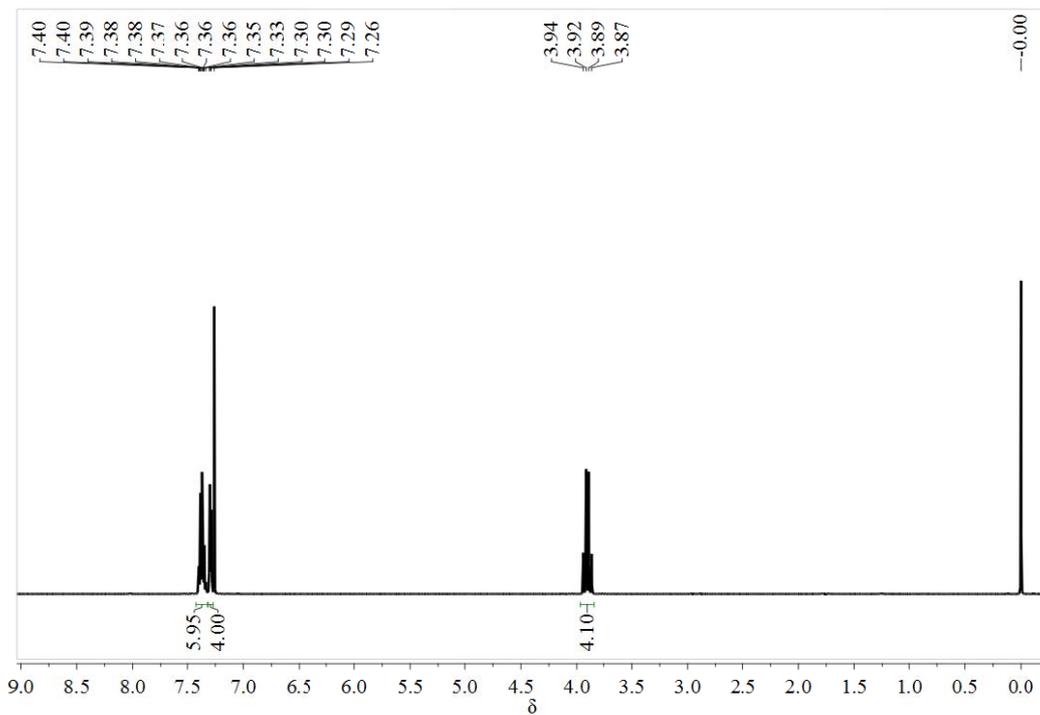
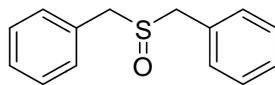
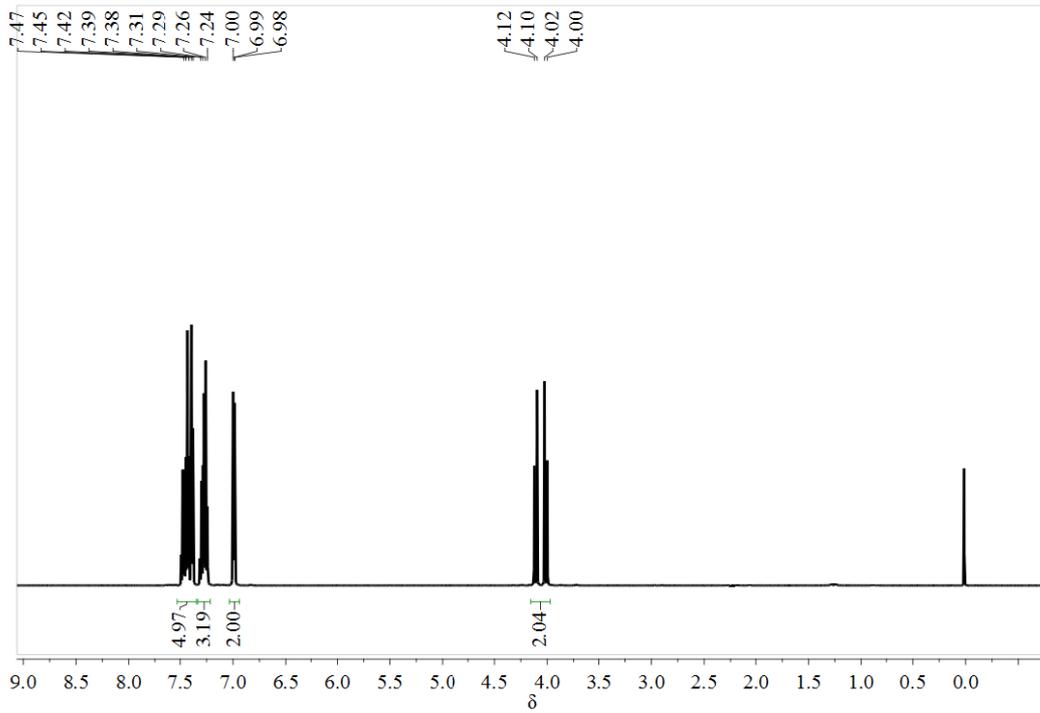
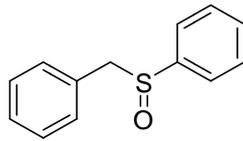


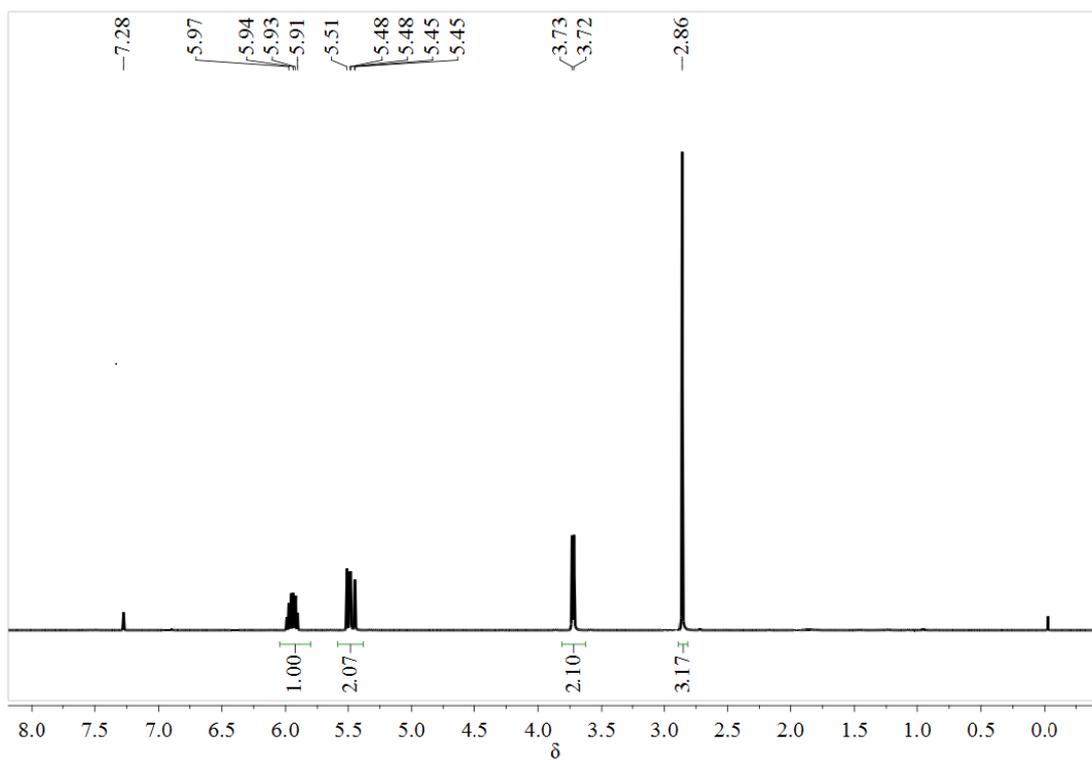
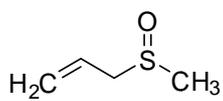
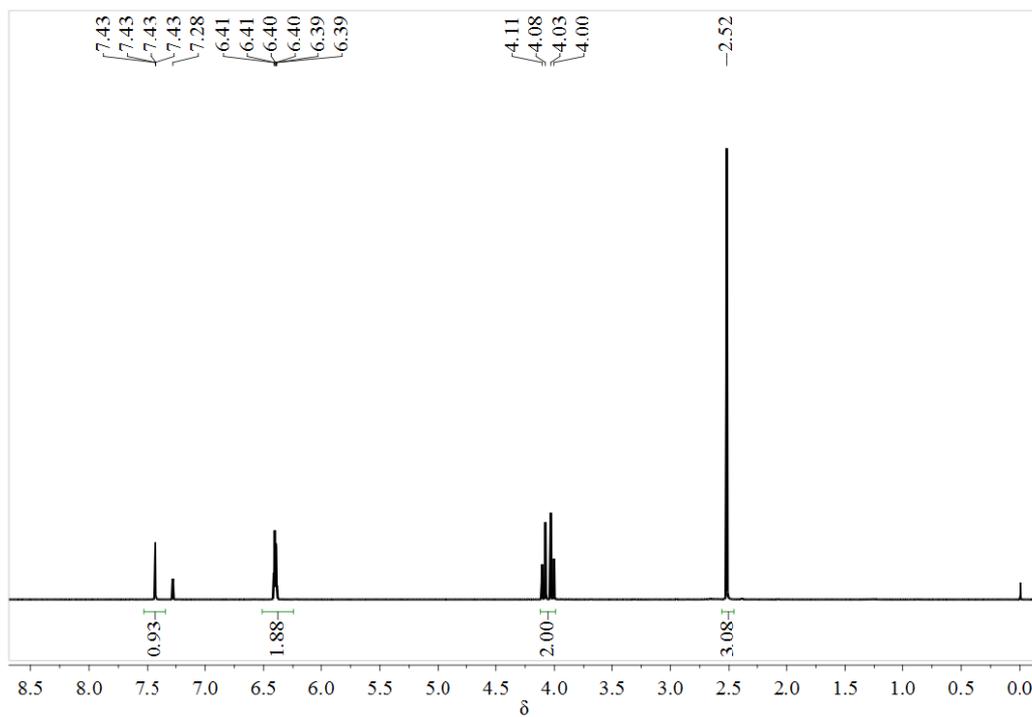
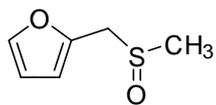


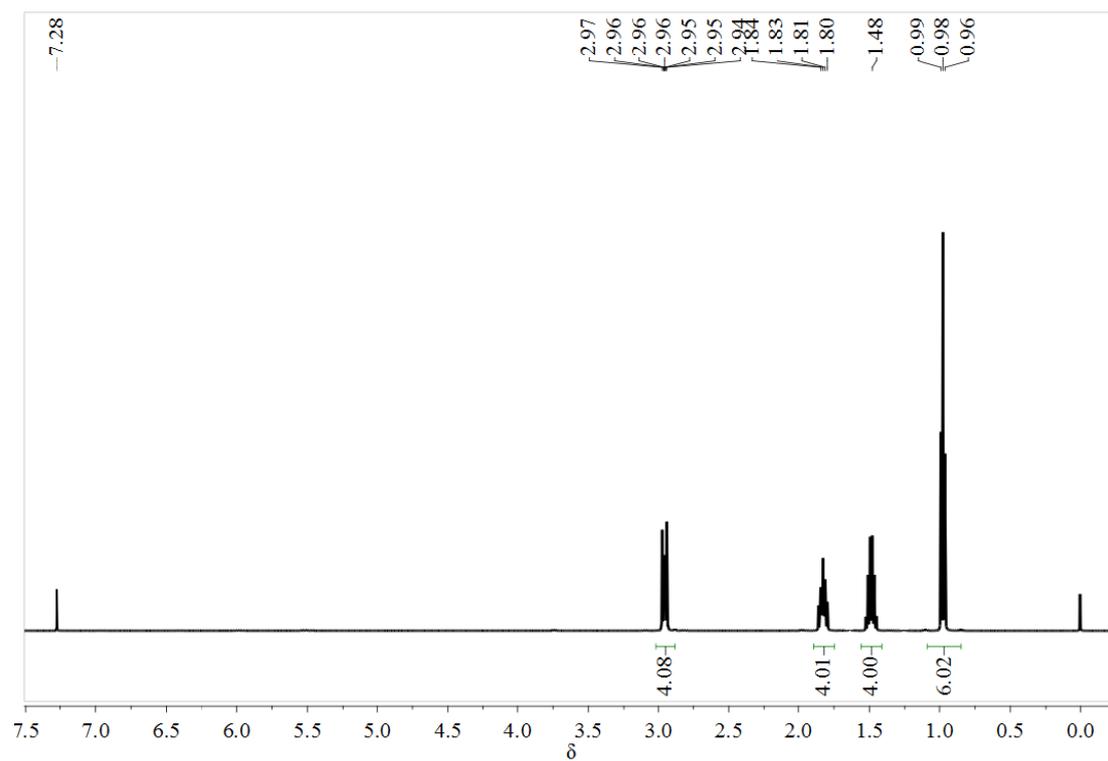
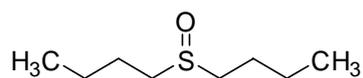




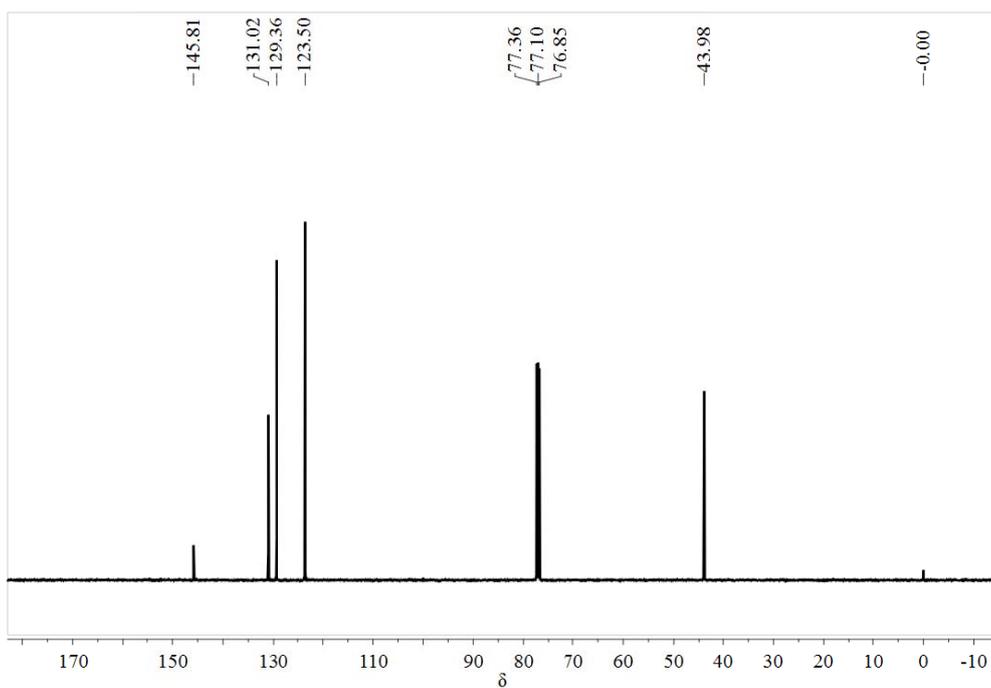
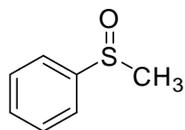


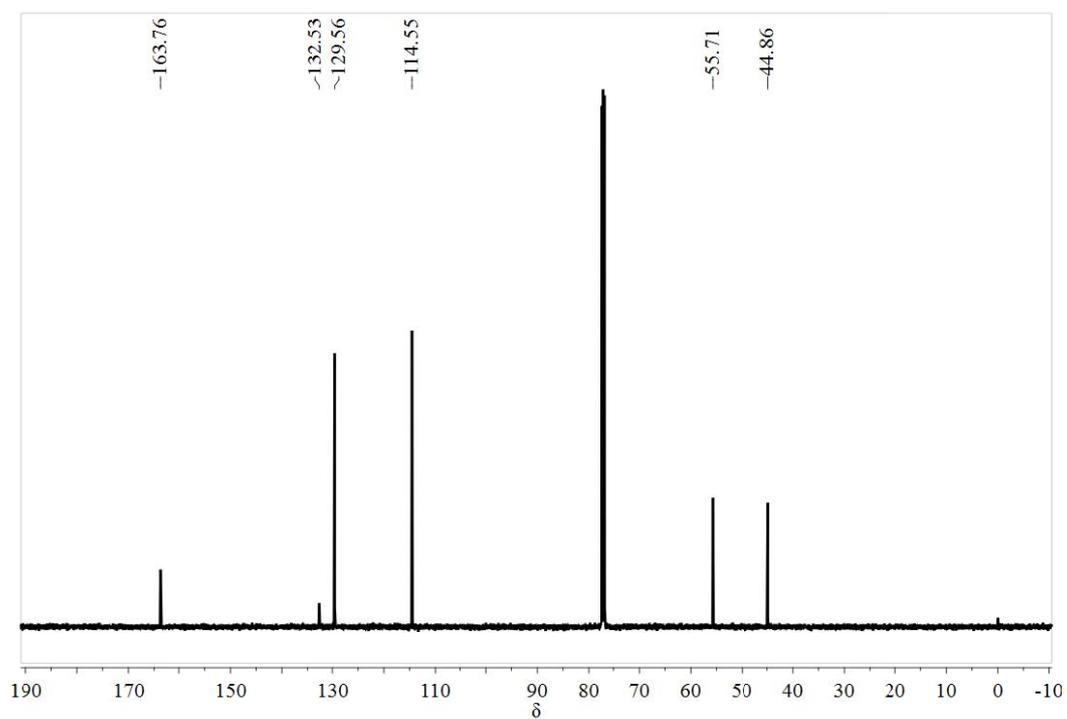
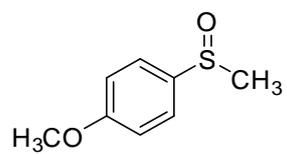
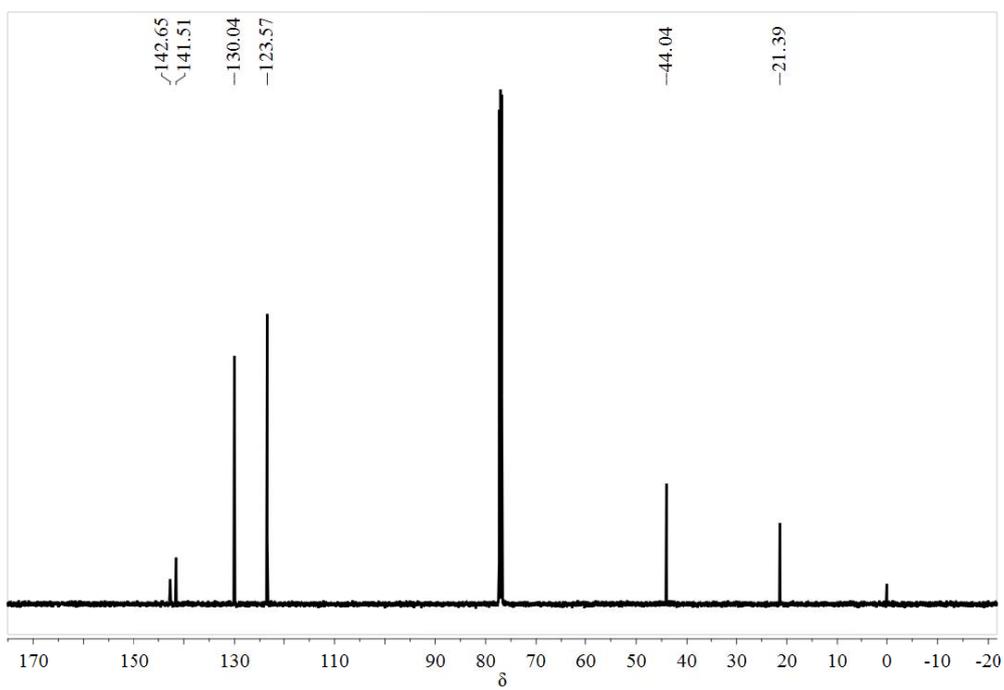
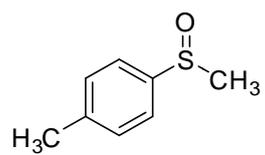


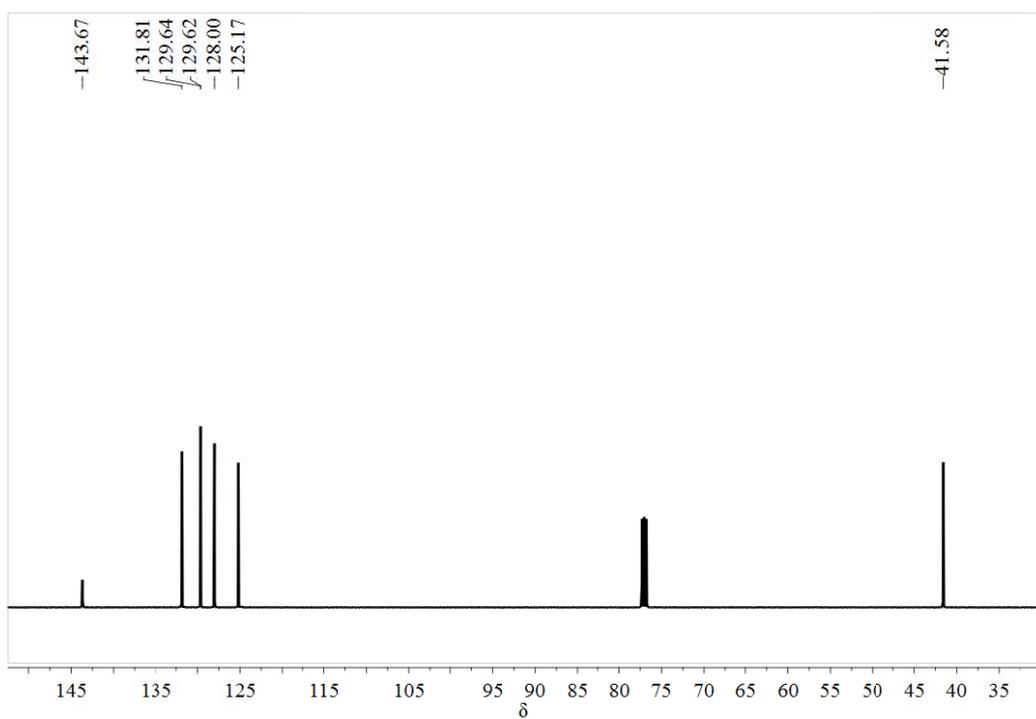
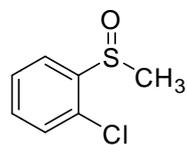
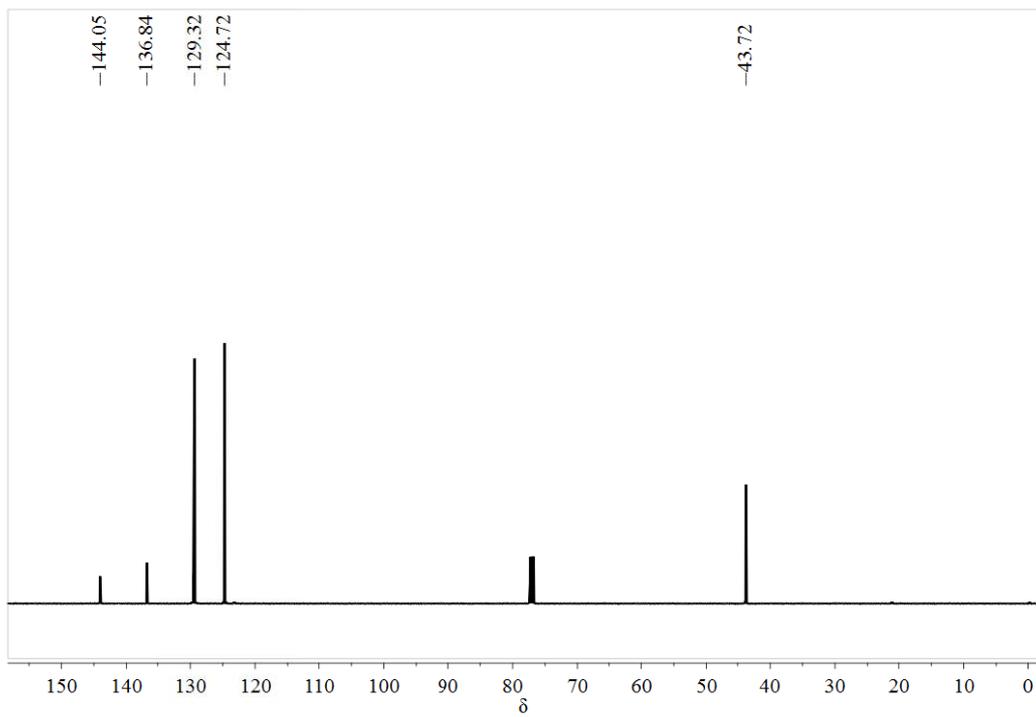
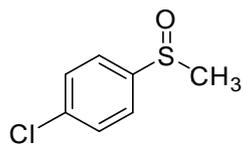




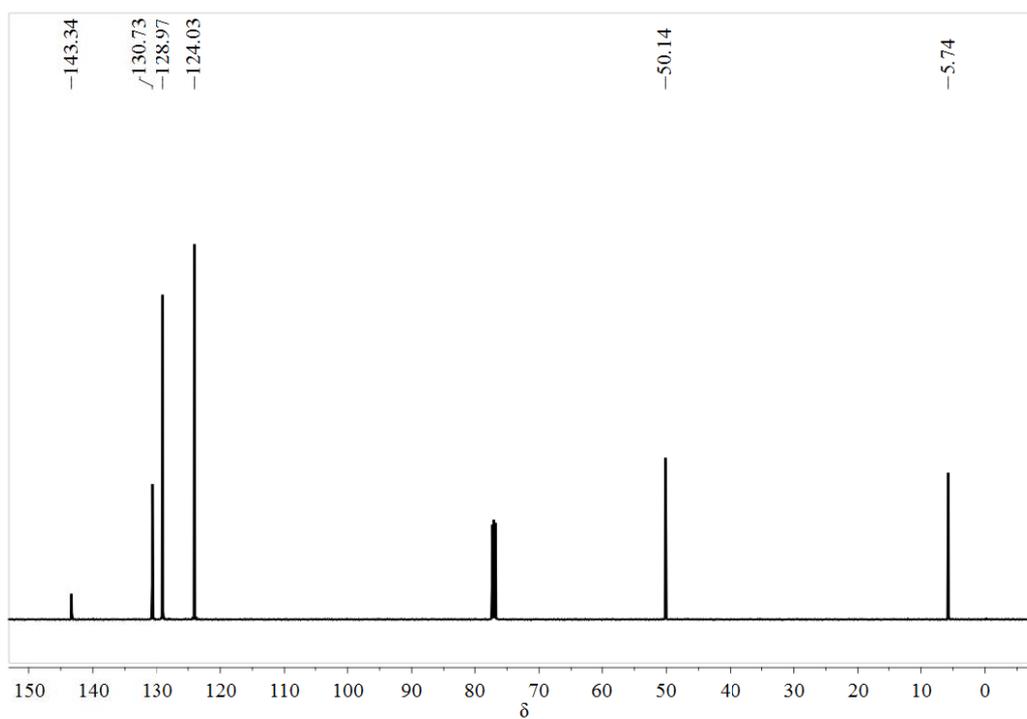
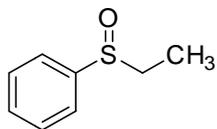
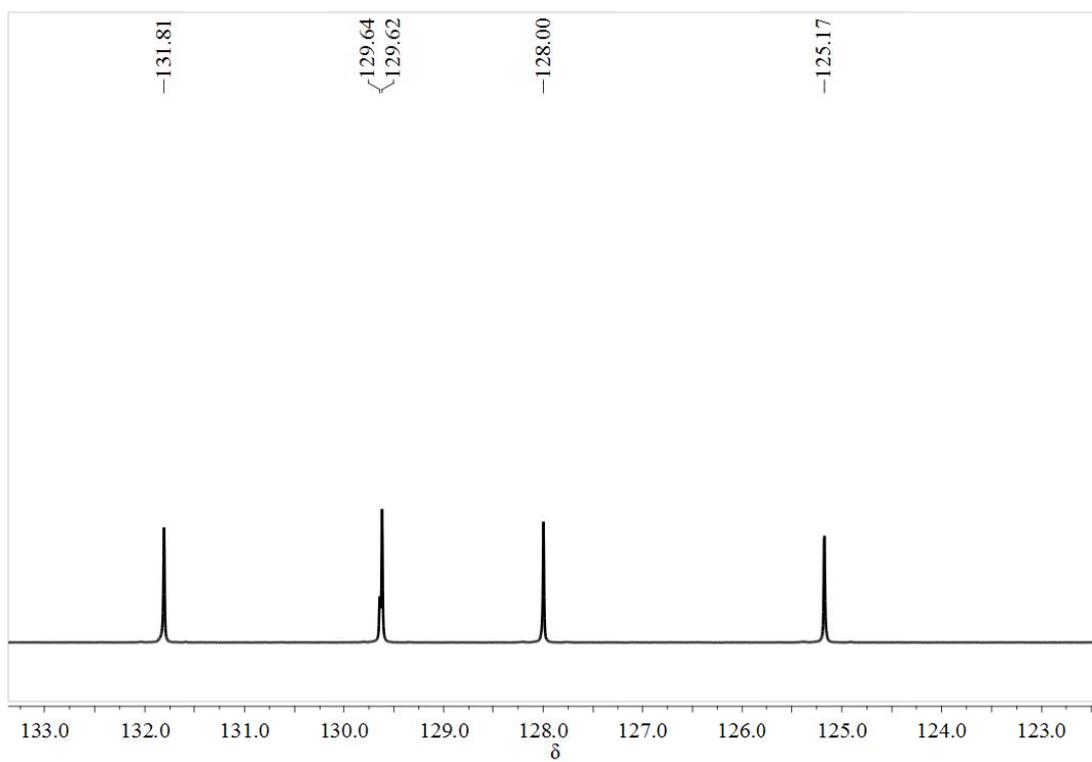
^{13}C NMR spectra of product sulfoxides

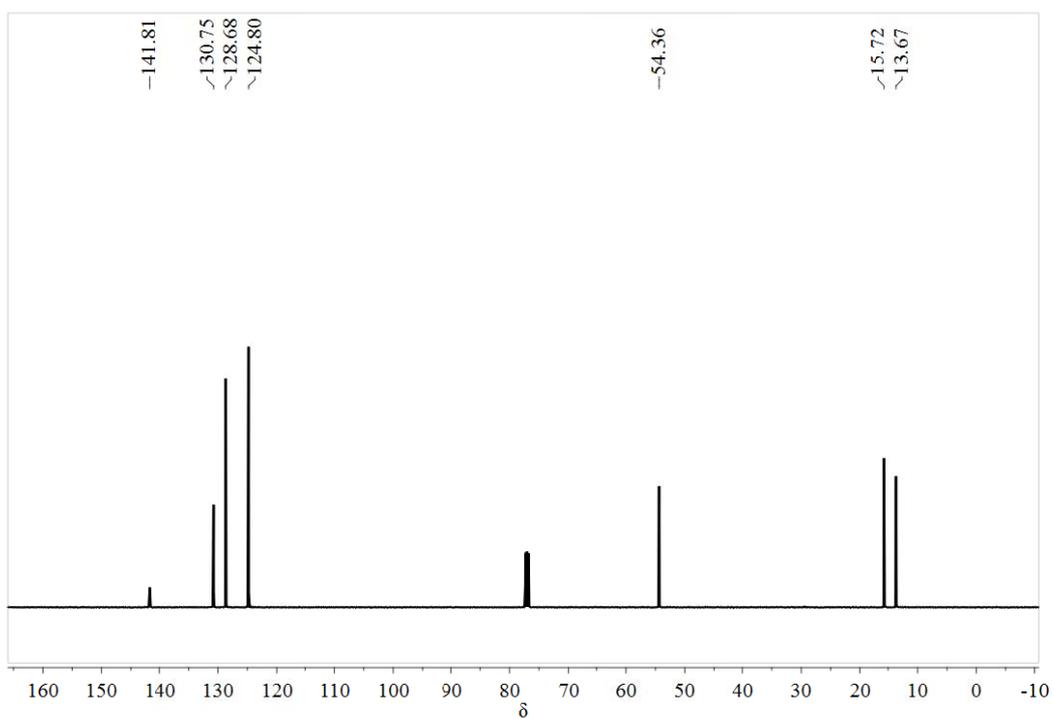
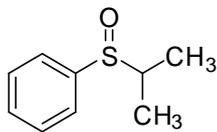
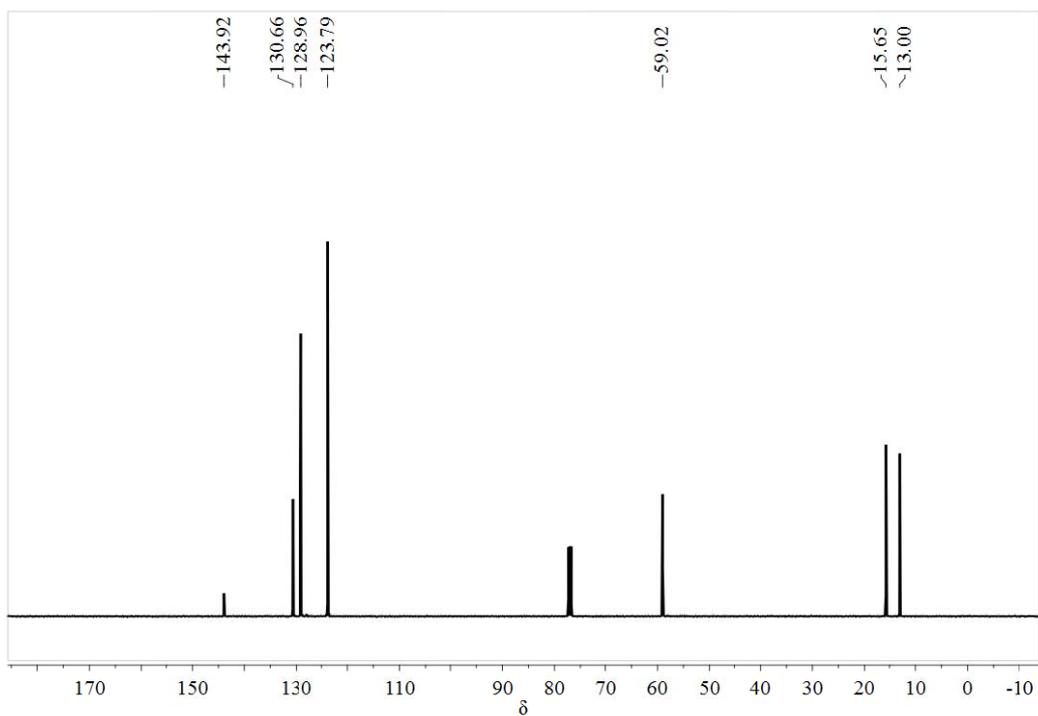
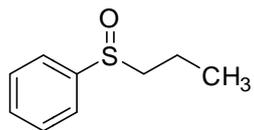


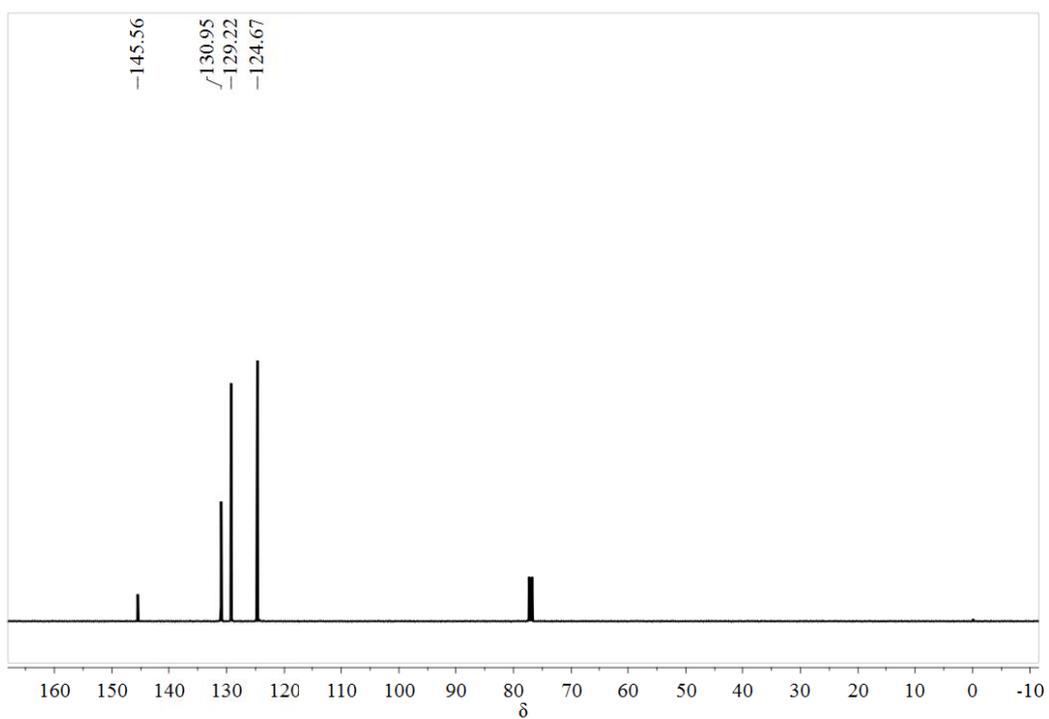
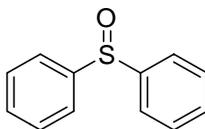
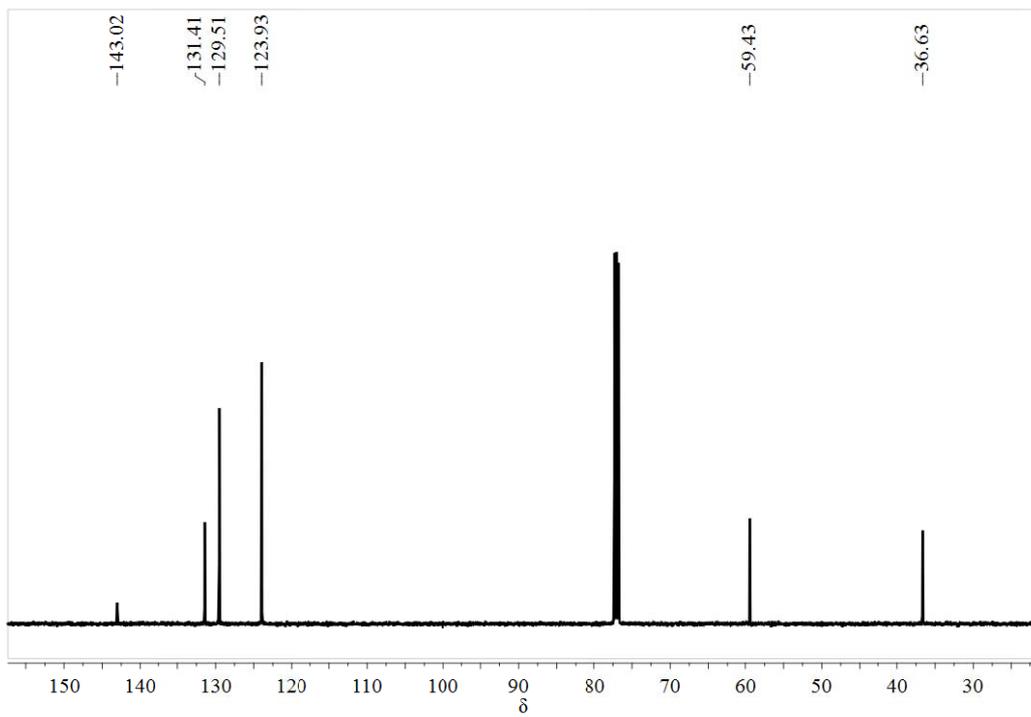
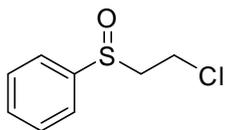


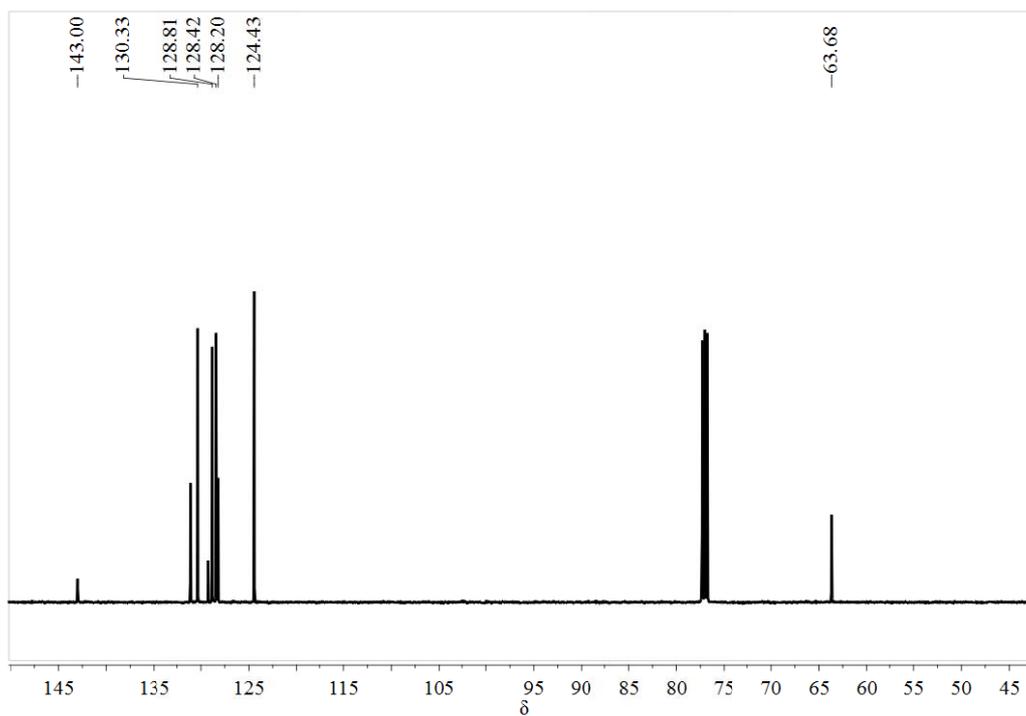
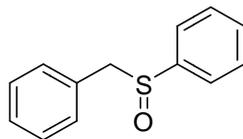


Zoom in 131.81-125.17:

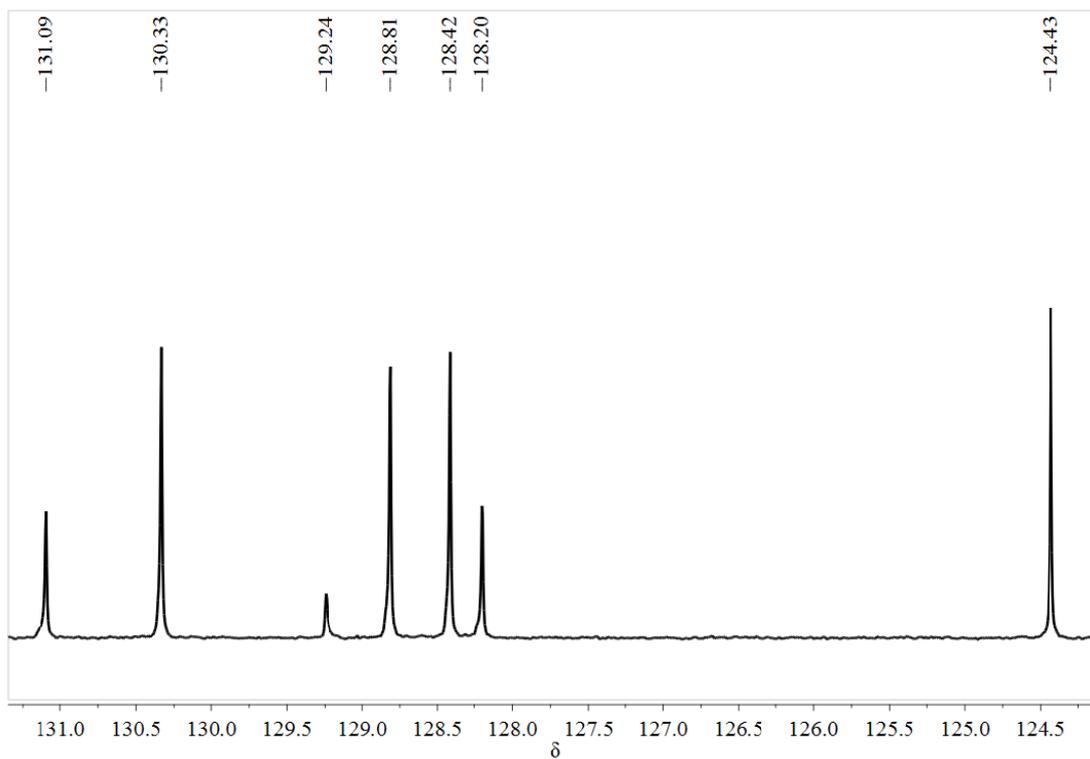


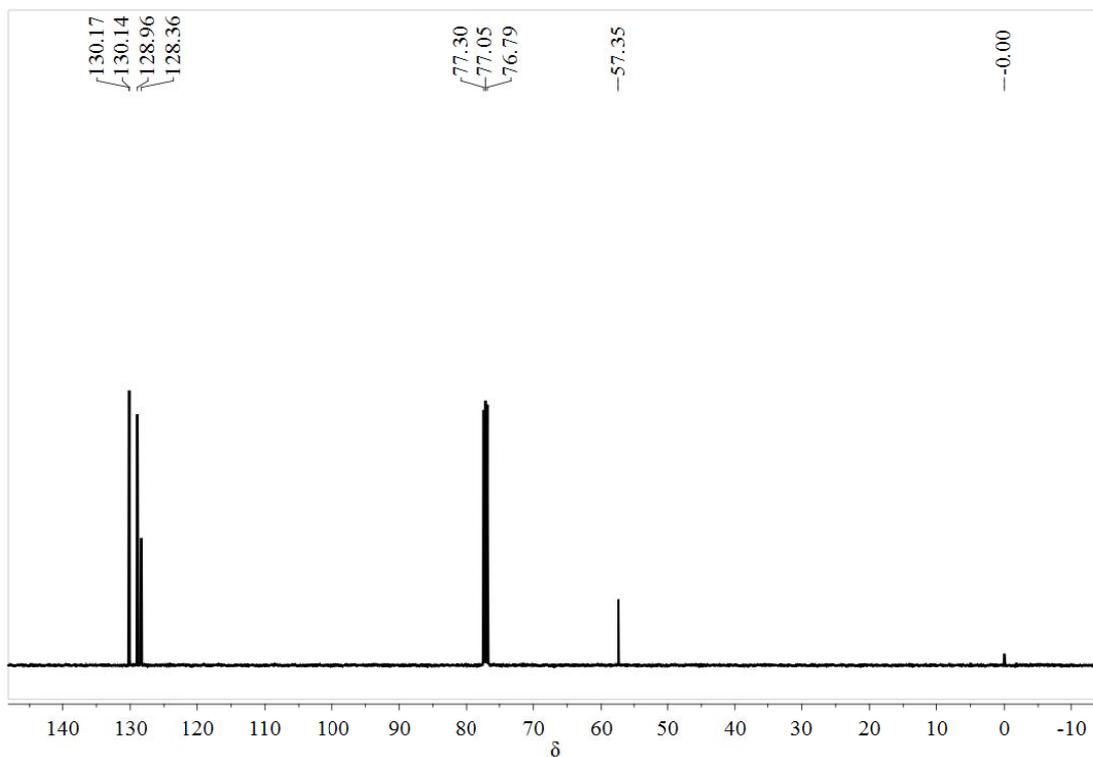
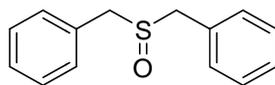




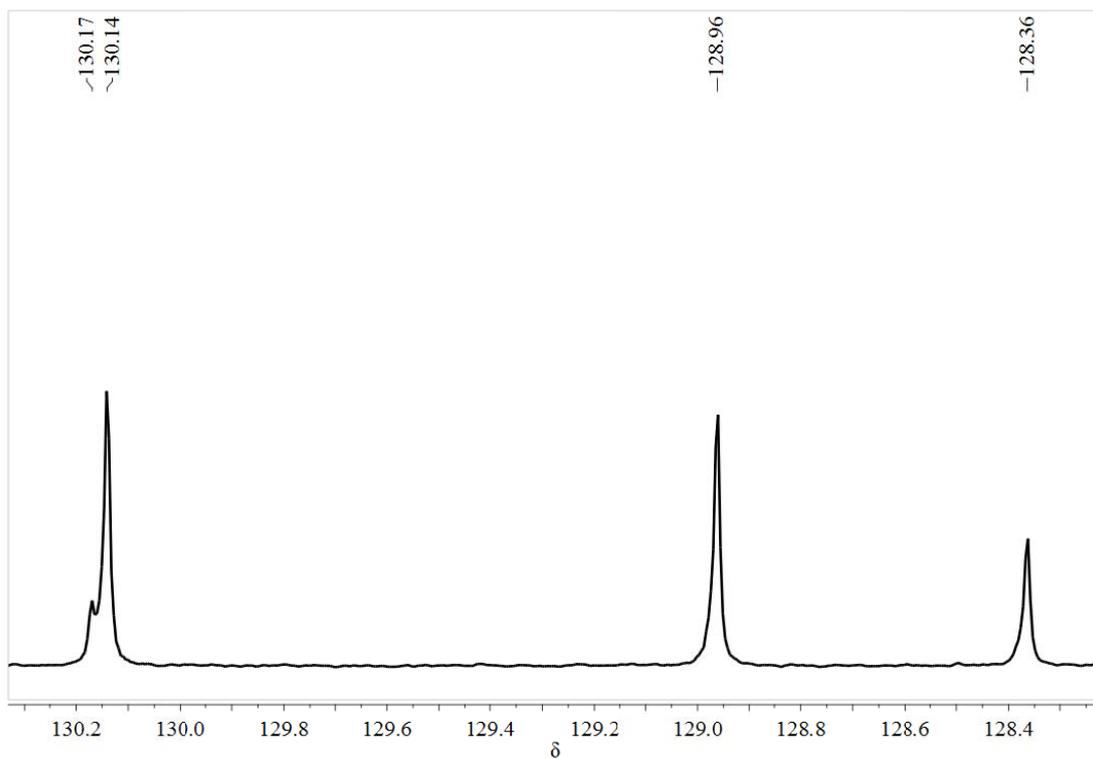


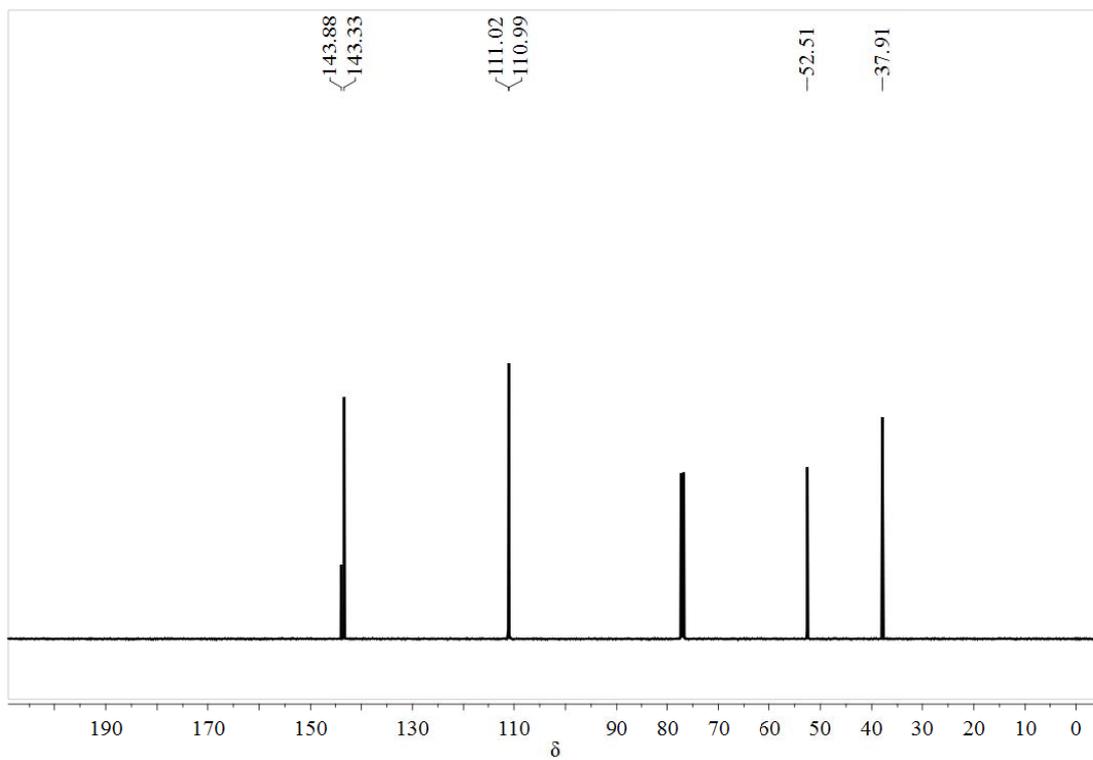
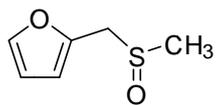
Zoom in 131.09-124.43:



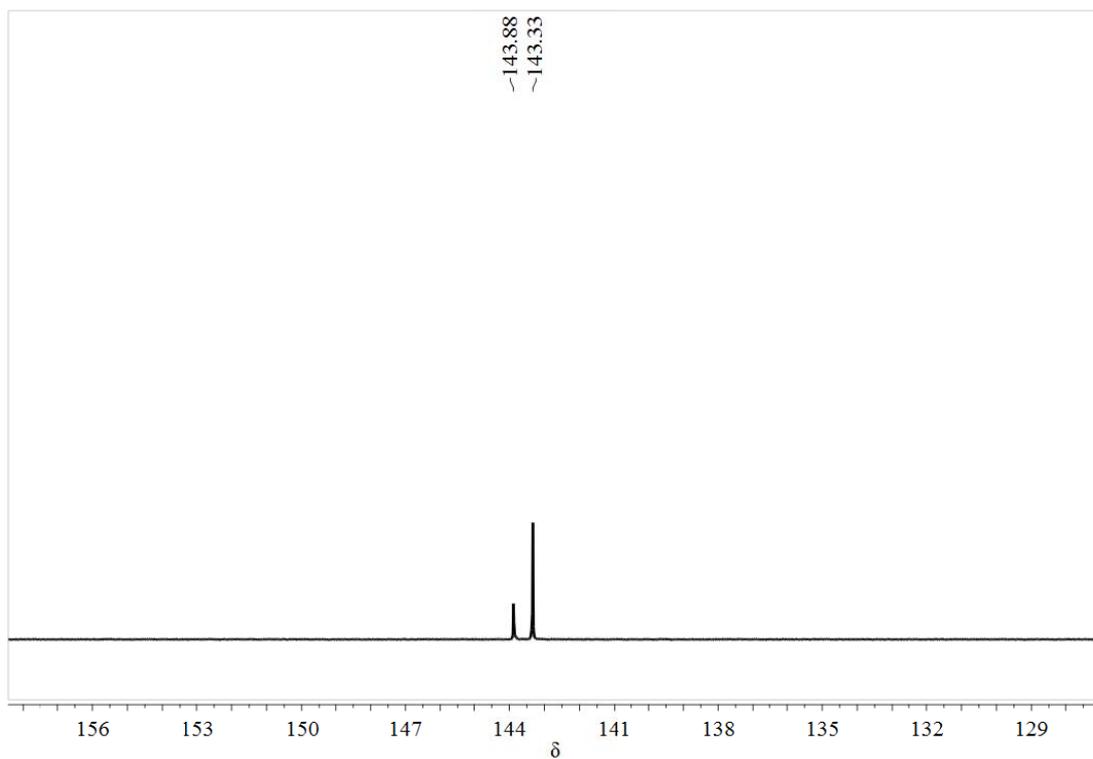


Zoom in 130.17-128.36:

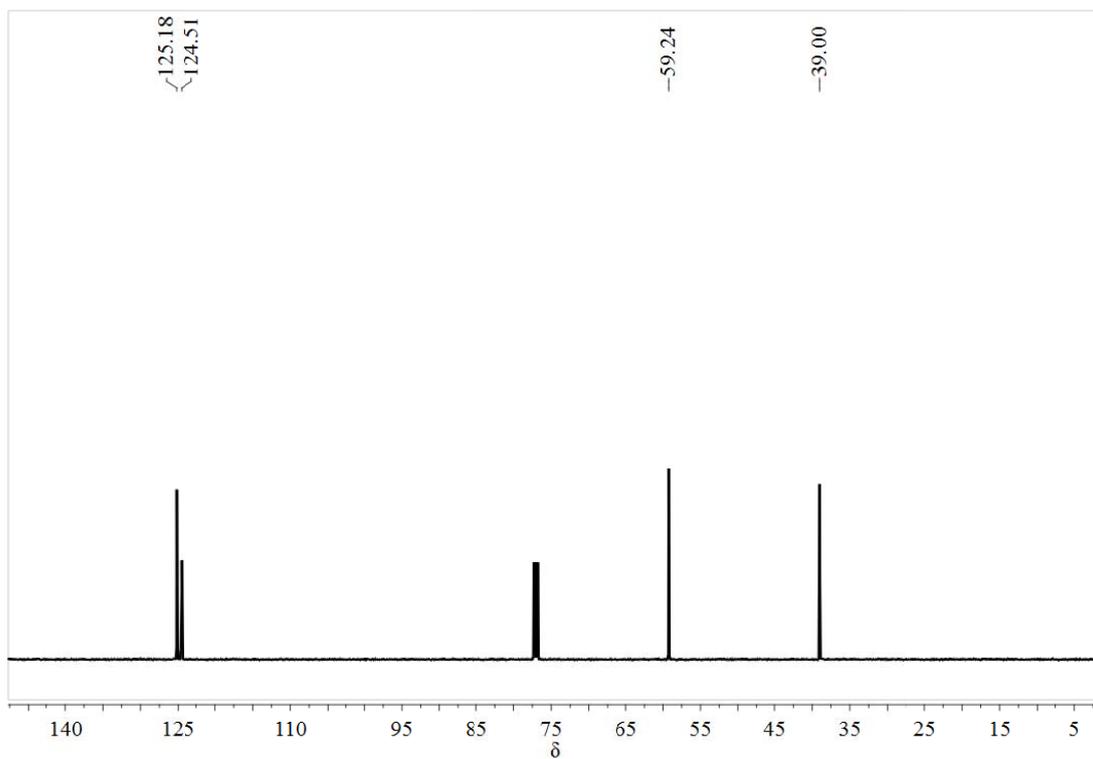
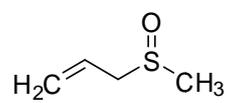
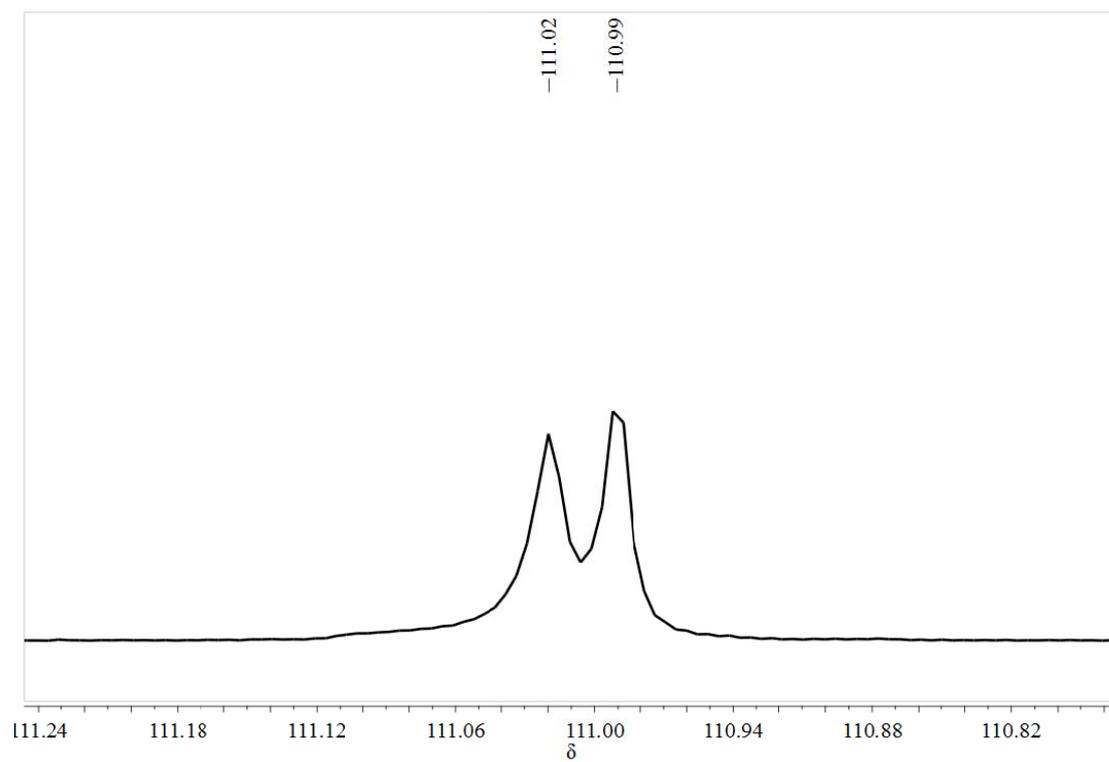


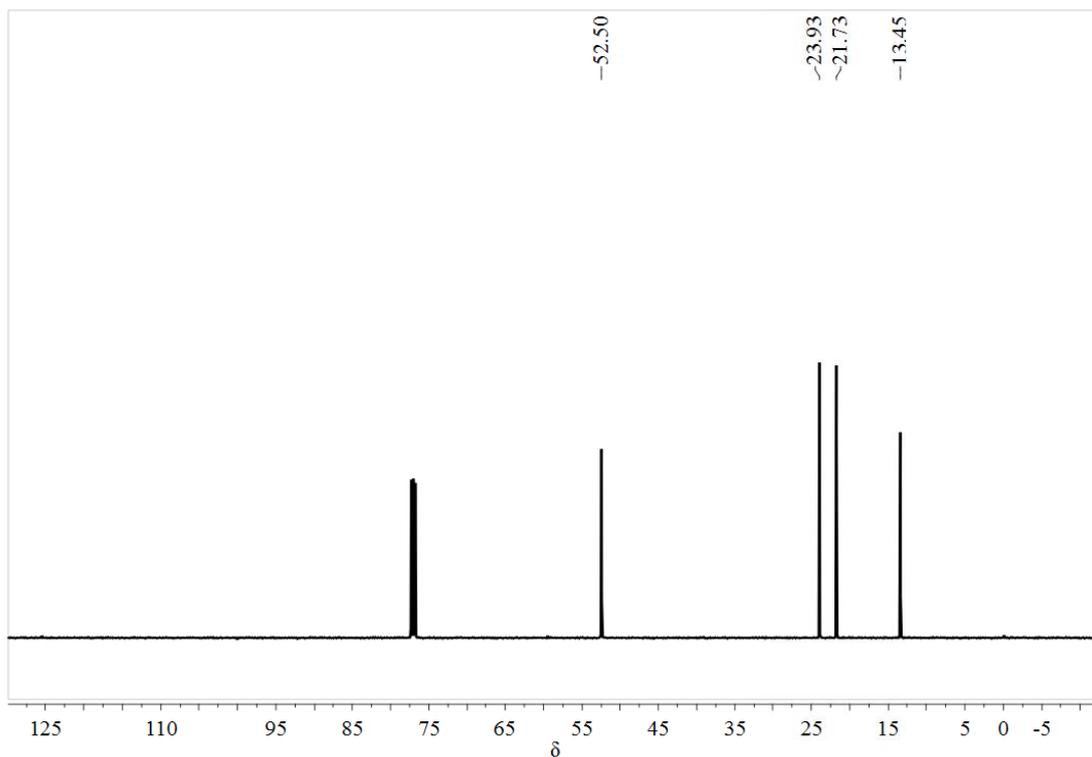
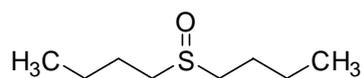


Zoom in 143.88-143.33:

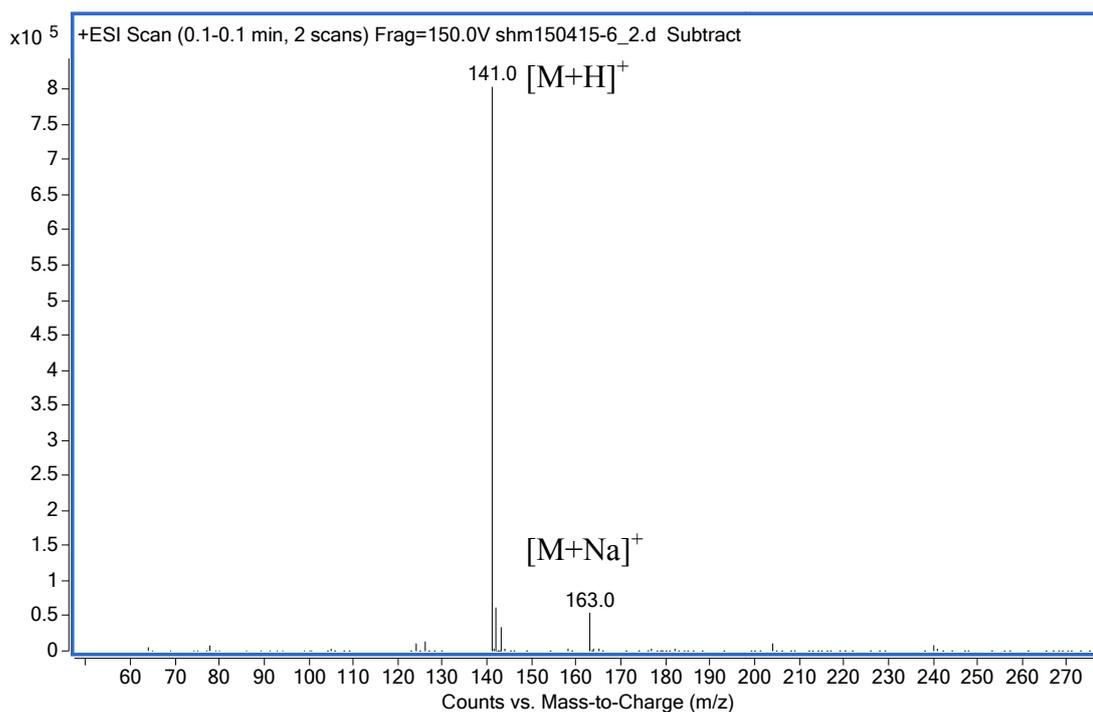
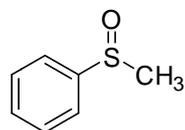


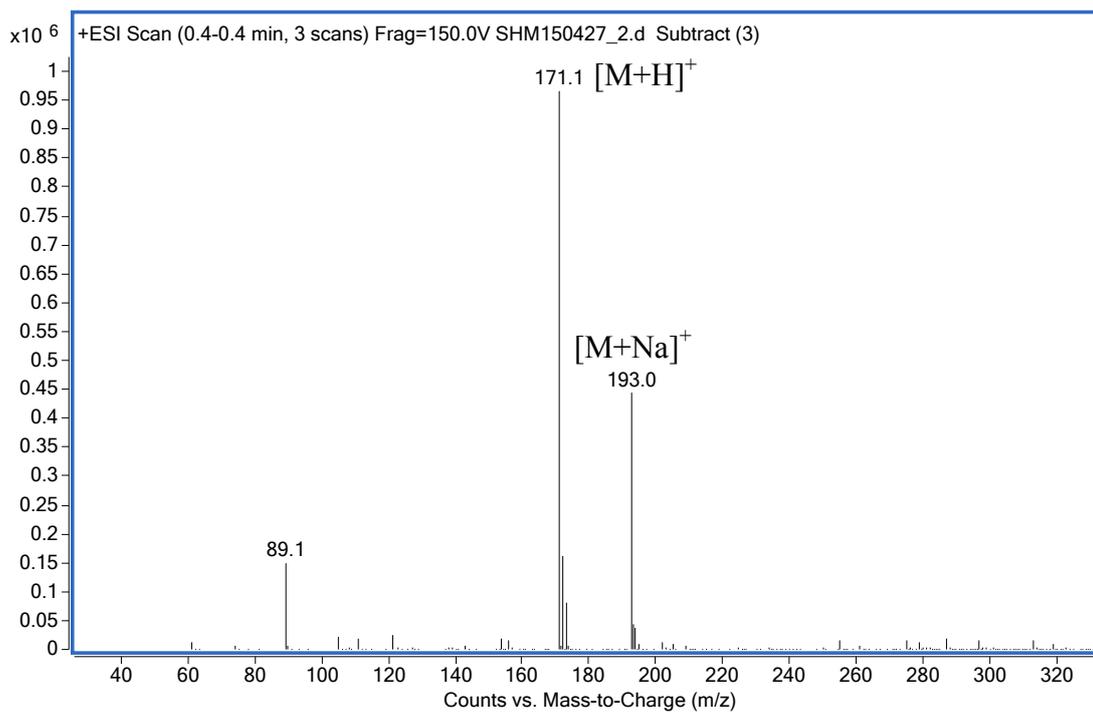
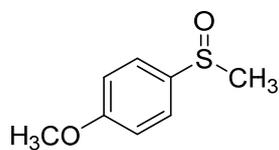
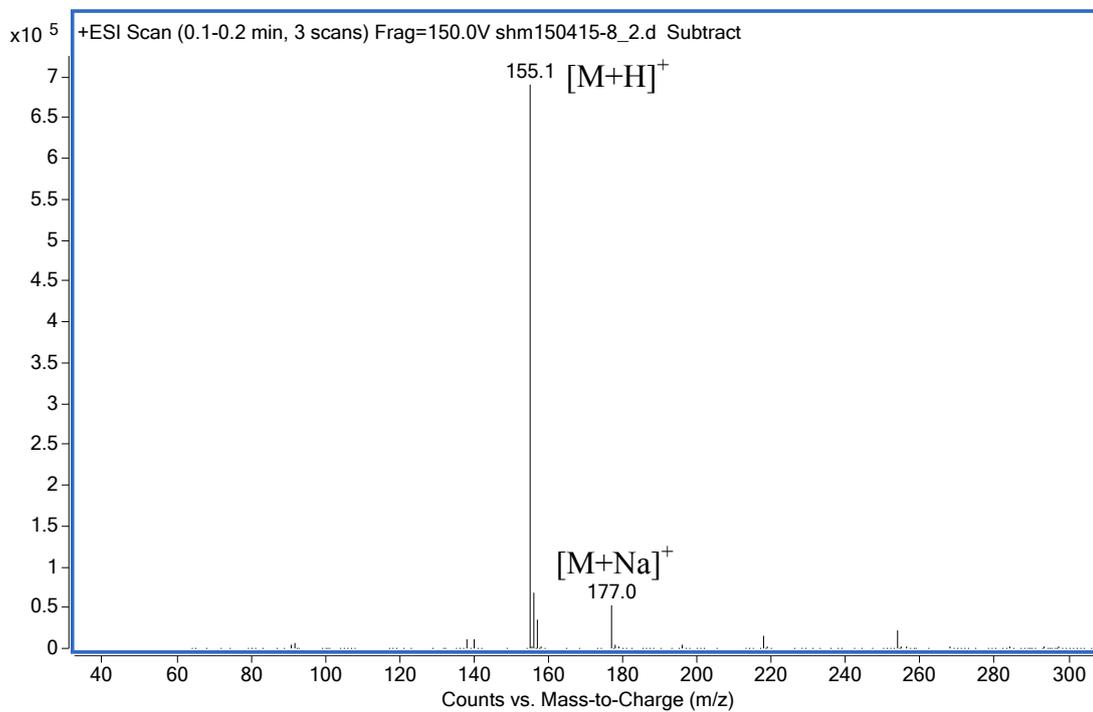
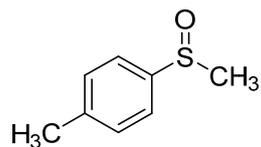
Zoom in 111.02-110.99

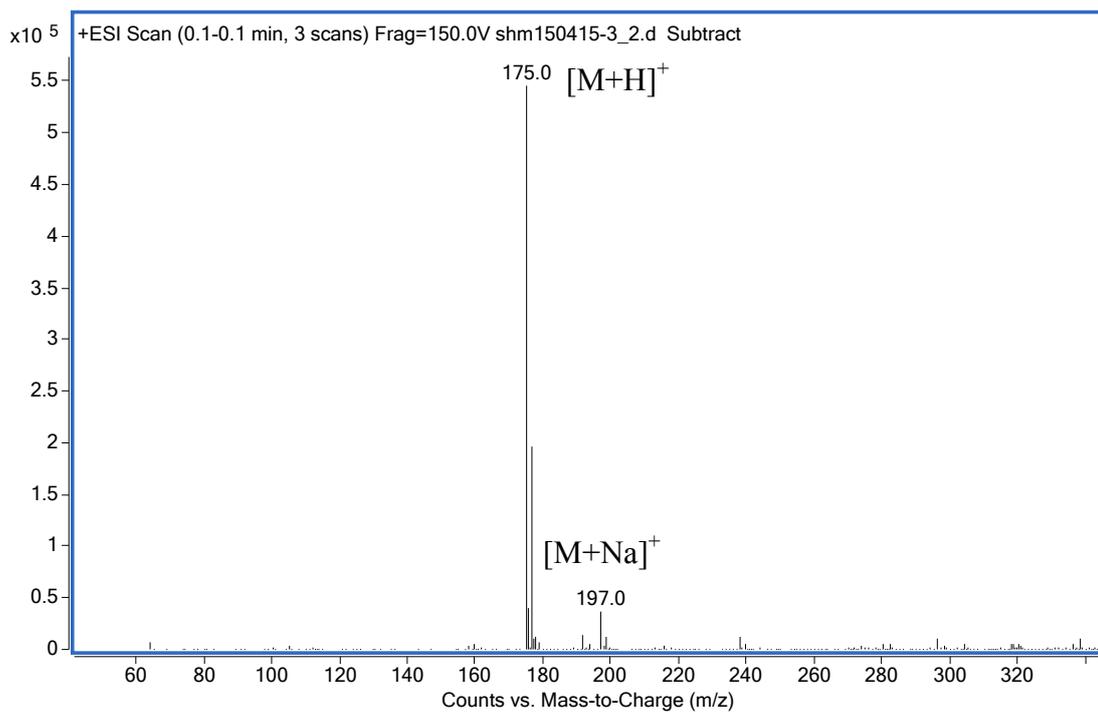
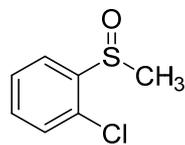
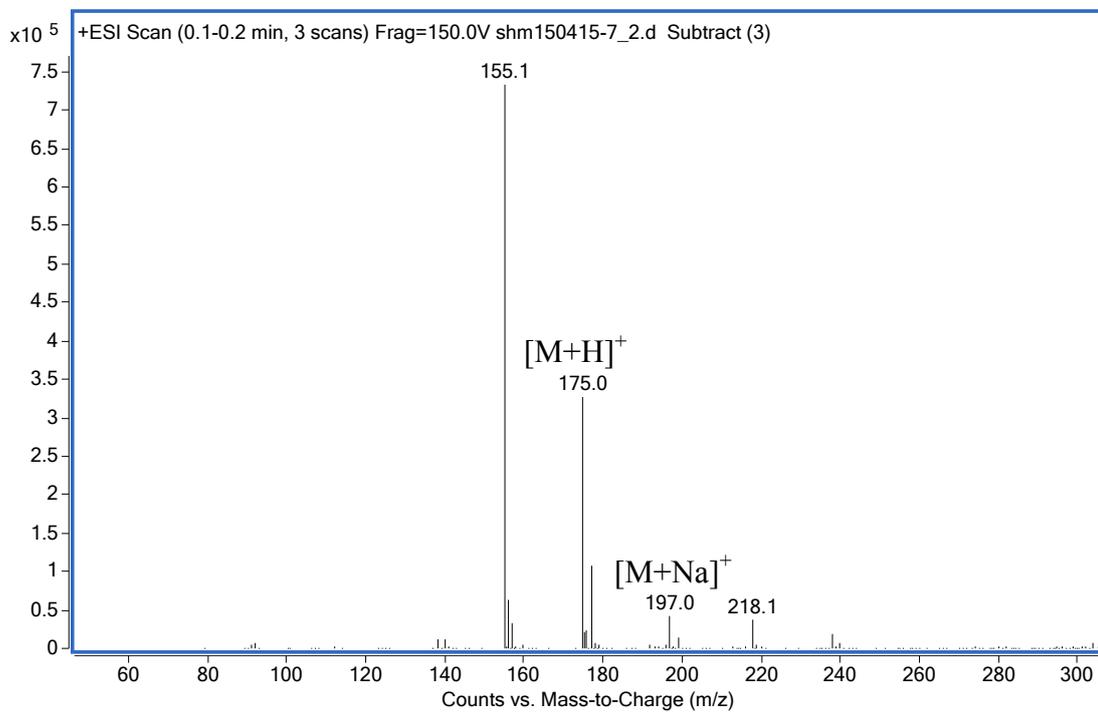
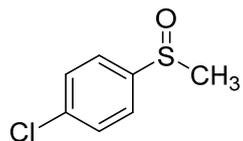


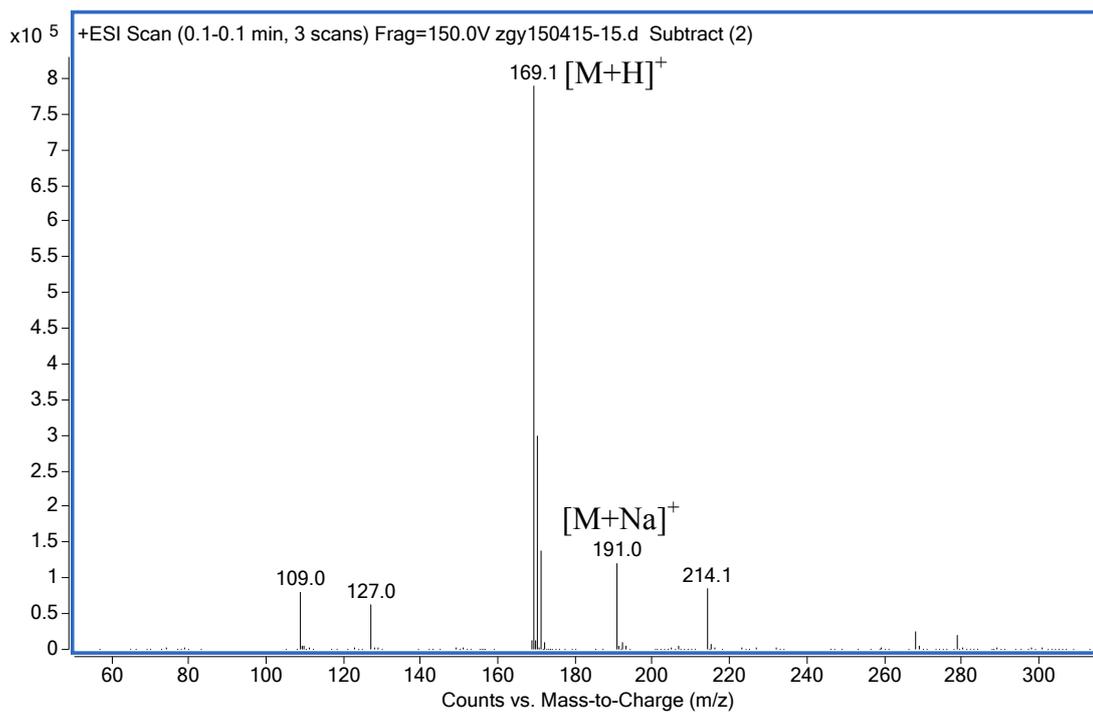
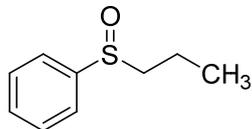
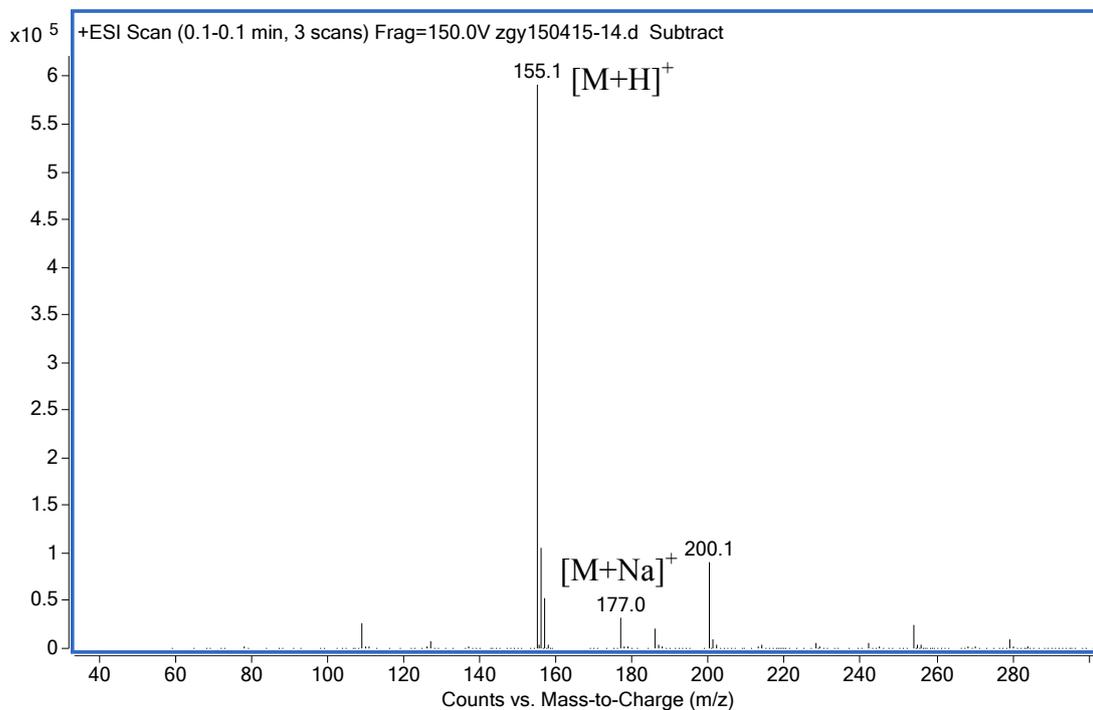
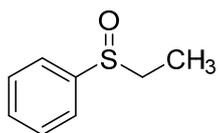


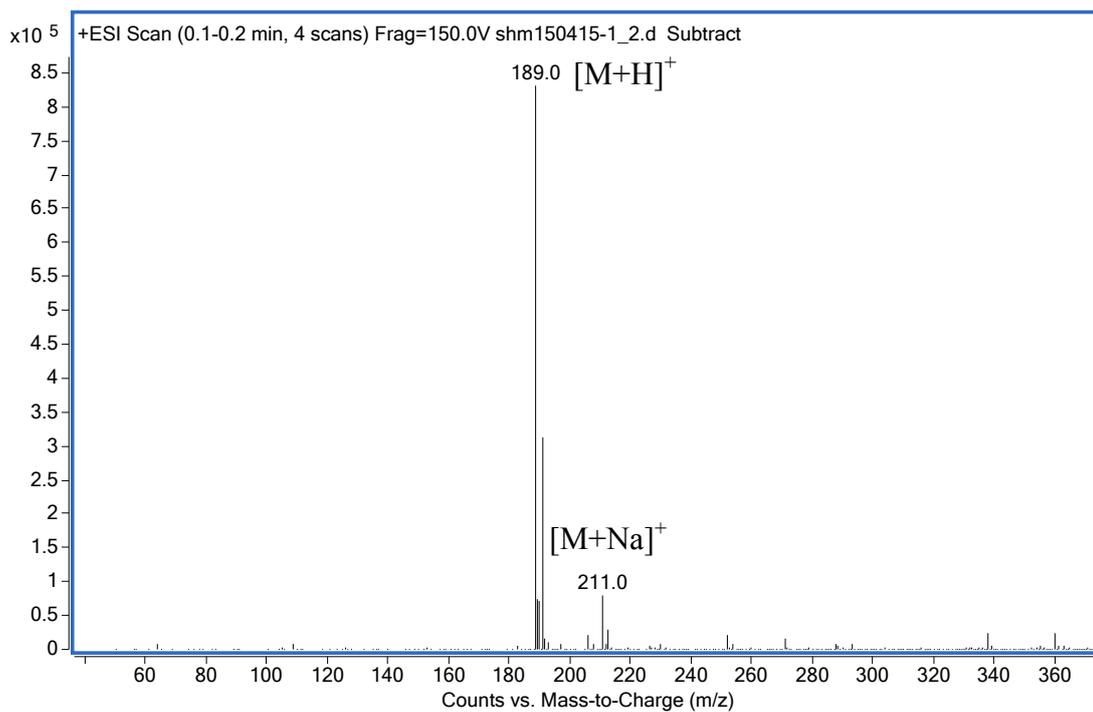
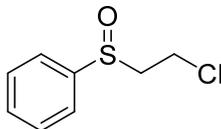
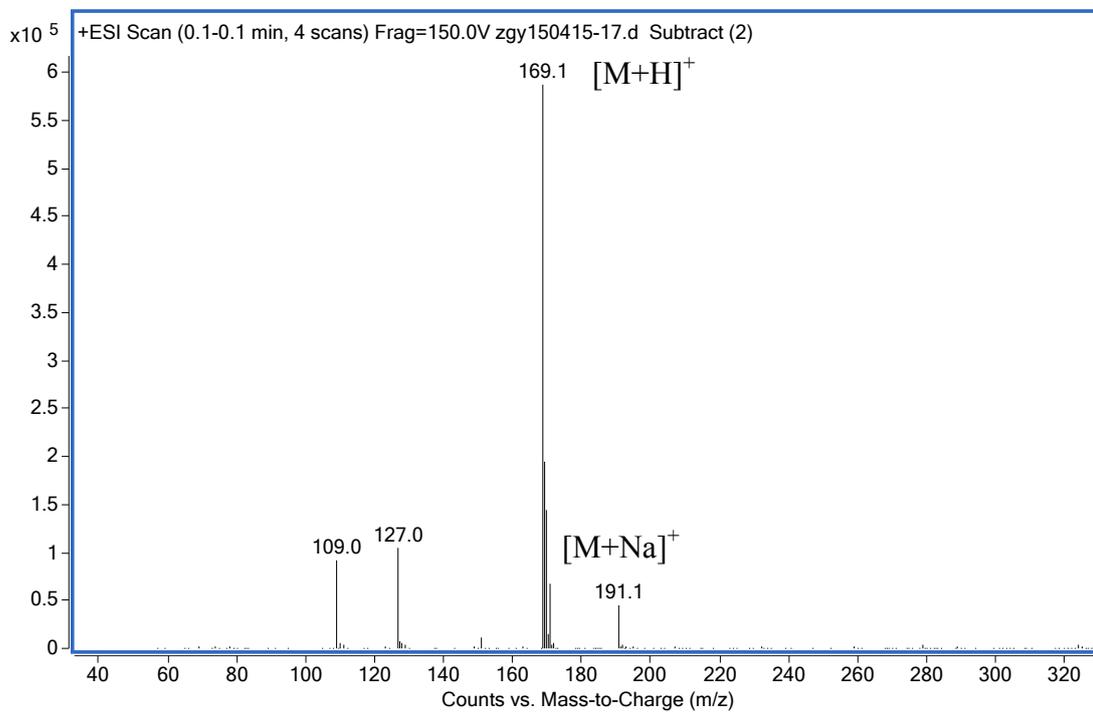
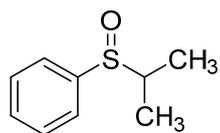
6 ESI-MS spectra of product sulfoxides

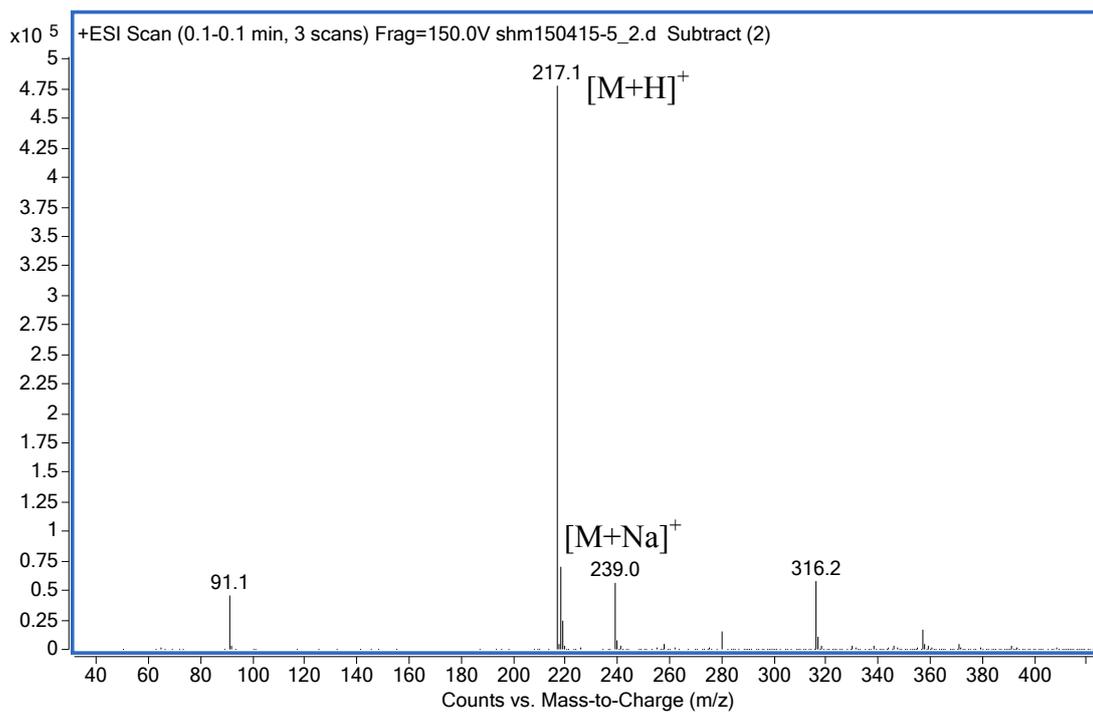
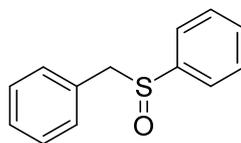
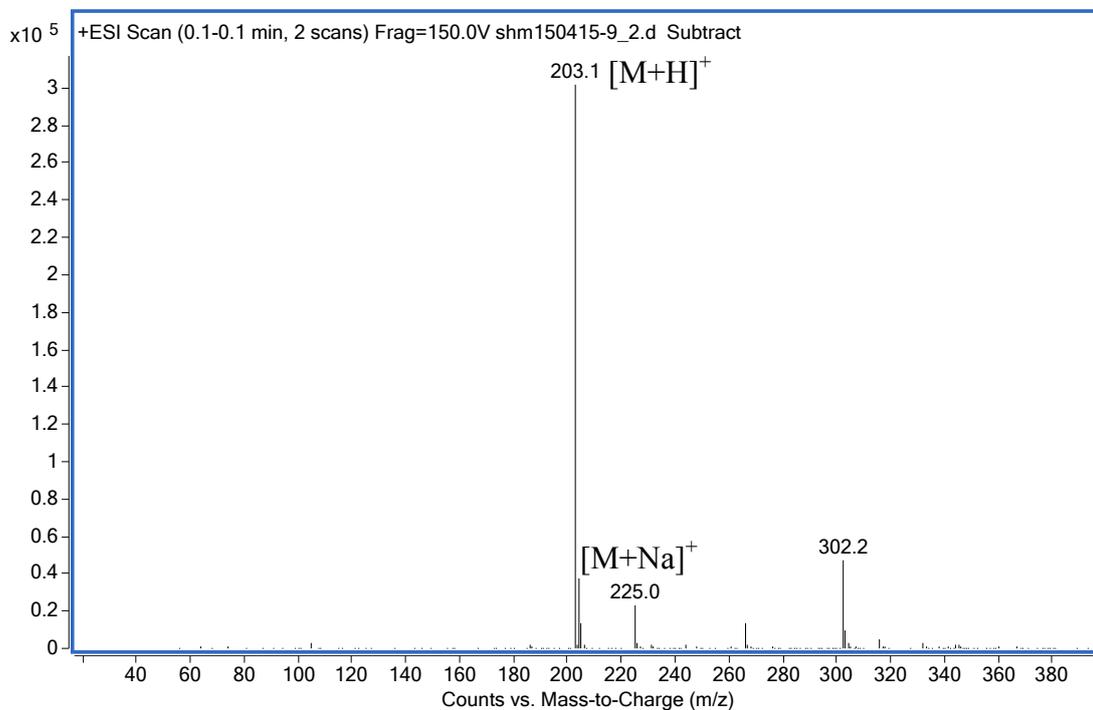
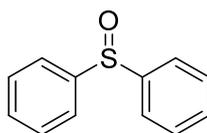


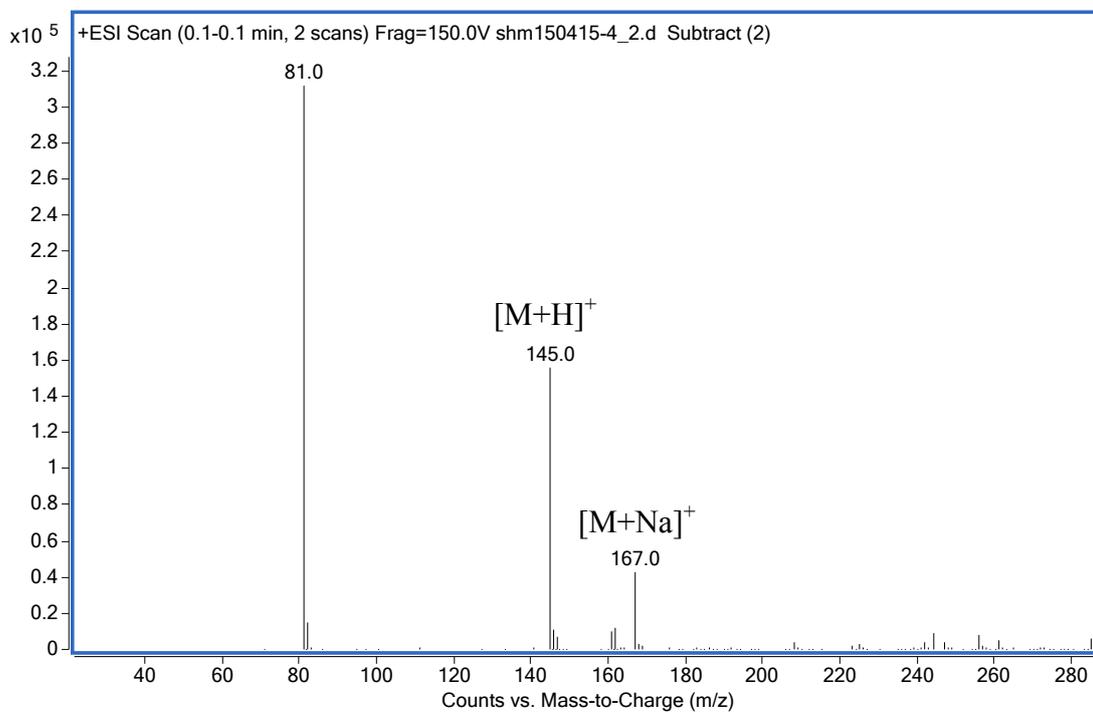
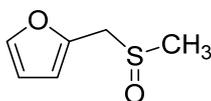
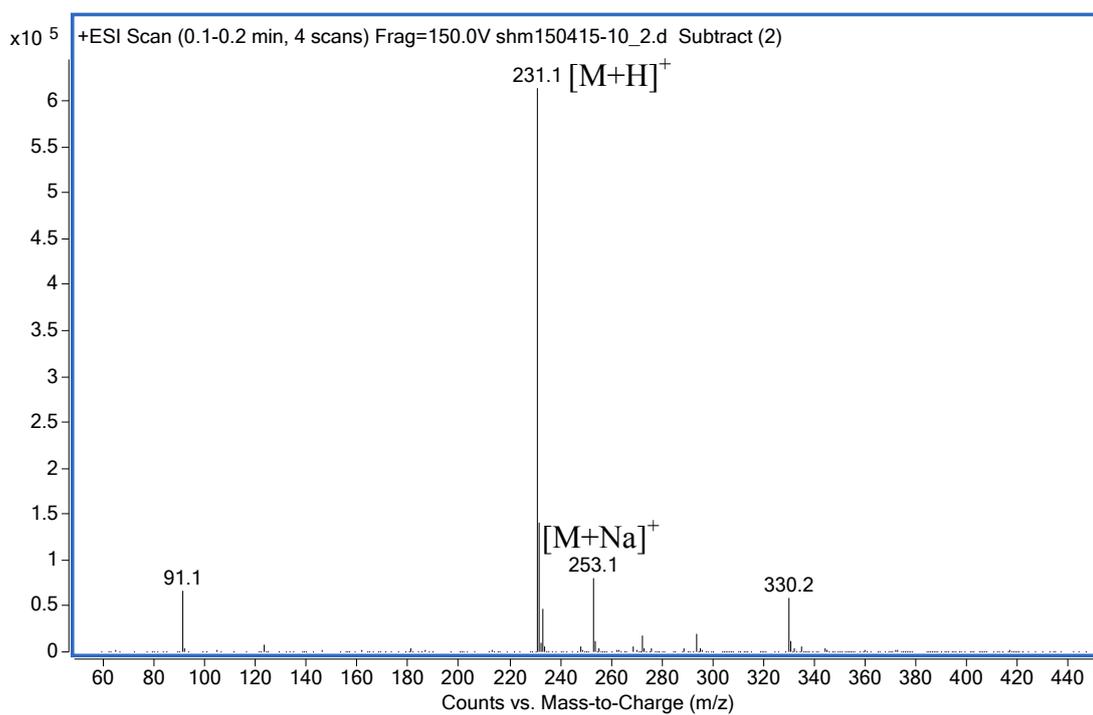
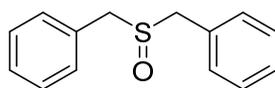


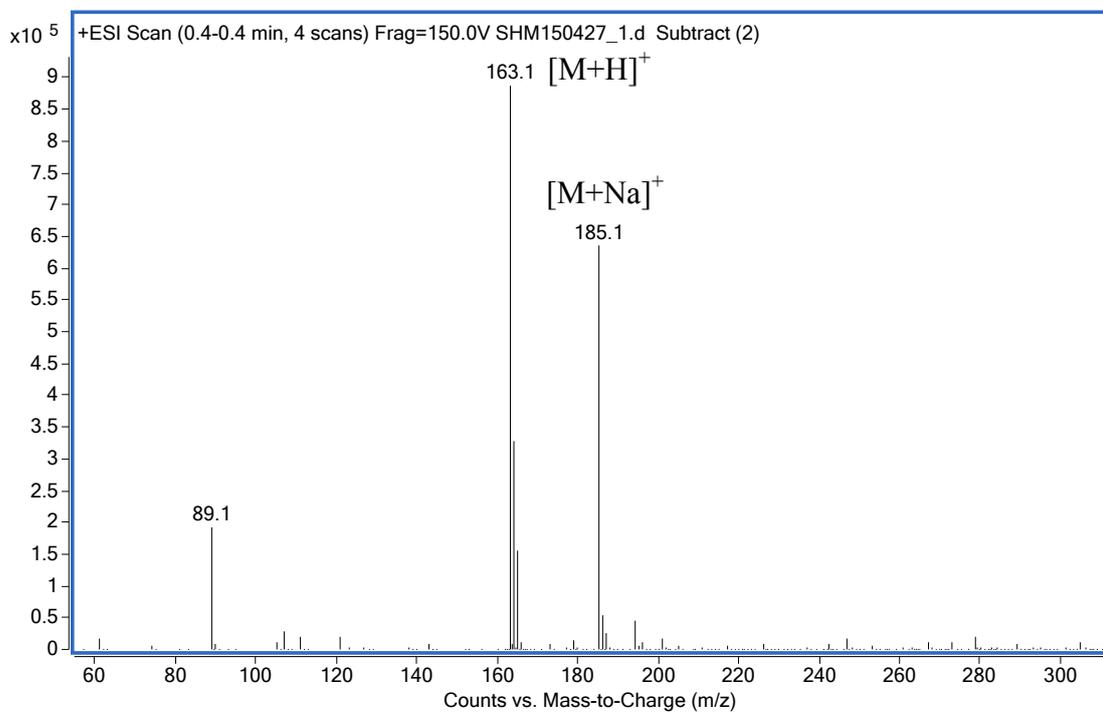
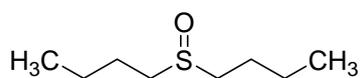
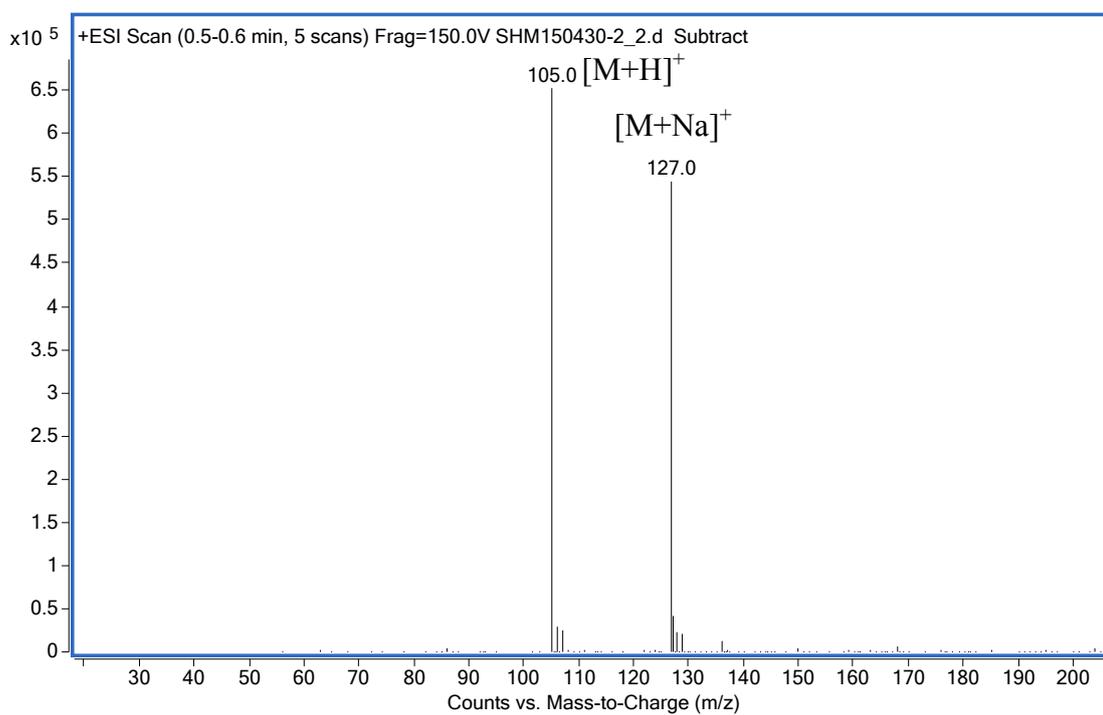
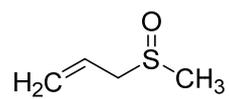












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- [3] Guo, W. S.; Monge-Marcet, A.; Cattoen, X.; Shafir, A.; Pleixats, R. *React. Funct. Polym.* **2013**, *73*, 192.