

Supporting Information

NH₄I-Mediated Three-Component Coupling Reaction: Metal-Free Synthesis of β -Alkoxy Methylsulfides from DMSO, Alcohols and Styrenes

Xiaofang Gao, Xiaojun Pan, Jian Gao, Huanfeng Jiang, Gaoqing Yuan* and Yingwei Li*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

E-mail: gqyuan@scut.edu.cn, liyw@scut.edu.cn

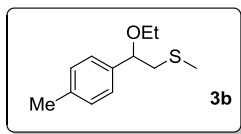
1. General information

Unless otherwise stated, analytical grade commercial reagents and solvents were used as the received. Styrenes 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 ¹³C NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer (400 MHz for ¹H, 100 MHz for ¹³C). CDCl₃ 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.

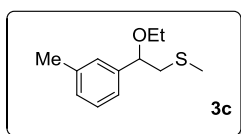
2. General procedure for the synthesis of β -alkoxy methylsulfides

In a typical experiment, NH₄I (3.0 equiv.), olefin (1.0 mmol), ROH (or H₂O for **3aa**) (2.0 equiv.), and DMSO (2.5 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 125 °C for 26 h. After cooled to room temperature, the reaction mixture was decolorized with Na₂S₂O₃, and then washed with distilled water (50 mL) and extracted with ethyl acetate (4 mL × 3). The organic layer was dried over MgSO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate (100:1) to give desired product.

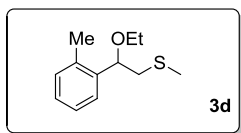
3. Characterization data of products



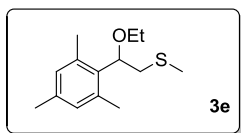
(2-ethoxy-2-(p-tolyl)ethyl)(methyl)sulfane (3b); 161 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.25–7.21 (m, 2H), 7.17–7.15 (m, 2H), 4.36 (t, $J=6.4$ Hz, 1H), 3.42–3.34 (m, 2H), 2.90 (dd, $J=13.2$, 7.6 Hz, 1H), 2.66 (dd, $J=13.2$, 4.8 Hz, 1H), 2.34 (s, 3H), 2.08 (s, 3H), 1.18 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.5, 137.5, 129.1, 126.55, 81.9, 64.29, 41.9, 21.1, 16.6, 15.3 ppm; IR (KBr): 2972, 2918, 2359, 2342, 1094 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 233.0976, found 233.0971.



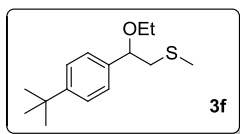
(2-ethoxy-2-(m-tolyl)ethyl)(methyl)sulfane (3c); 168 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.25–7.21 (m, 1H), 7.13–7.08 (m, 3H), 4.36 (t, $J=6.4$ Hz, 1H), 3.43–3.35 (m, 2H), 2.89 (dd, $J=13.6$, 8.0 Hz, 1H), 2.67 (dd, $J=13.2$, 4.0 Hz, 1H), 2.35 (s, 3H), 2.08 (s, 3H), 1.19 (t, $J=7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 137.9, 128.50, 128.2, 127.2, 123.6, 82.2, 64.4, 41.9, 21.4, 16.6, 15.2 ppm; IR (KBr): 2972, 2919, 2357, 2343, 1096 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 233.0976, found 233.0971.



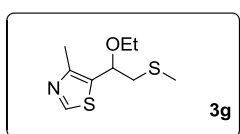
(2-ethoxy-2-(o-tolyl)ethyl)(methyl)sulfane (3d); 172 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, $J=7.6$ Hz, 1H), 7.24–7.11 (m, 3H), 4.68 (dd, $J=8.0$, 4.4 Hz, 1H), 3.41–3.45 (m, 2H), 2.85 (dd, $J=13.6$, 8.4 Hz, 1H), 2.66 (dd, $J=13.6$, 4.0 Hz, 1H), 2.35 (s, 3H), 2.12 (s, 3H), 1.19 (t, $J=7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 135.2, 130.3, 127.3, 126.2, 125.9, 78.7, 64.4, 40.9, 19.1, 16.7, 15.3 ppm; IR (KBr): 2972, 2919, 2359, 2342, 1085, 744 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 233.0976, found 233.0971.



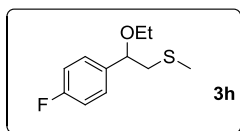
(2-ethoxy-2-mesitylethyl)(methyl)sulfane (3e); 178 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 6.80 (s, 2H), 4.91 (t, $J=7.0$ Hz, 1H), 3.36–3.31 (m, 2H), 3.08 (dd, $J=13.6$, 8.8 Hz, 1H), 2.71 (dd, $J=13.6$, 5.2 Hz, 1H), 2.39 (s, 6H), 2.24 (s, 3H), 2.10 (s, 3H), 1.17 (t, $J=7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 136.6, 136.5, 133.5, 78.7, 63.9, 38.6, 20.6, 20.4, 16.5, 15.2 ppm; IR (KBr): 2972, 2921, 2359, 1054, 1032, 1012 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{14}\text{H}_{22}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 261.1289, found 261.1284.



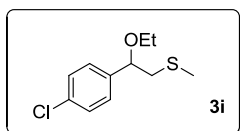
(2-(4-(tert-butyl)phenyl)-2-ethoxyethyl)(methyl)sulfane (3f); 196 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.24 (dd, $J=45.0$, 7.4 Hz, 4H), 4.31 (t, $J=6.4$ Hz, 1H), 3.40–3.27 (m, 2H), 2.83 (dd, $J=13.2$, 8.0 Hz, 1H), 2.60 (dd, $J=13.2$, 4.4 Hz, 1H), 2.02 (s, 3H), 1.25 (s, 9H), 1.12 (t, $J=6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 150.7, 138.5, 126.2, 125.2, 81.9, 64.4, 42.0, 34.5, 31.3, 16.6, 15.3 ppm; IR (KBr): 2359, 2342, 1117, 1261, 800 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{15}\text{H}_{24}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 275.1445, found 275.1440.



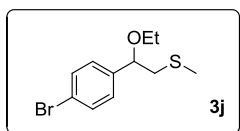
5-(1-ethoxy-2-(methylthio)ethyl)-4-methylthiazole (3g); 168 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.69 (s, 1H), 4.75 (t, $J=6.6$ Hz, 1H), 3.46–3.41 (m, 2H), 2.96 (dd, $J=13.6$, 6.8 Hz, 1H), 2.73 (dd, $J=13.6$, 6.0 Hz, 1H), 2.47 (s, 3H), 2.12 (s, 3H), 1.19 (t, $J=6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 151.4, 150.1, 133.1, 75.3, 64.6, 41.8, 16.8, 15.5, 15.1 ppm; IR (KBr): 2359, 2342, 1653, 1647, 1008, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_9\text{H}_{16}\text{NOS}_2$ [$\text{M}+\text{H}$] $^+$ 218.0671, found 218.0668.



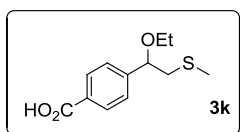
(2-ethoxy-2-(4-fluorophenyl)ethyl)(methyl)sulfane (3h); 177 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.31 (t, $J=6.2$ Hz, 2H), 7.04 (t, $J=8.2$ Hz, 2H), 4.38 (t, $J=6.4$ Hz, 1H), 3.38 (dd, $J=13.6$, 6.8 Hz, 2H), 2.92–2.87 (m, 1H), 2.67–2.63 (m, 1H), 2.07 (s, 3H), 1.19 (t, $J=6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 161.1, 137.3, 137.3, 128.3, 128.2, 115.4, 115.2, 81.5, 64.4, 41.9, 16.7, 15.2 ppm; IR (KBr): 2973, 2922, 2360, 2342, 1508, 1033 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{11}\text{H}_{15}\text{FNaOS}$ [$\text{M}+\text{Na}$] $^+$ 237.0719, found 237.0720.



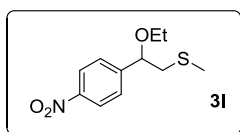
(2-(4-chlorophenyl)-2-ethoxyethyl)(methyl)sulfane (3i); 165 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.30 (dd, $J=20.4$, 7.6 Hz, 4H), 4.37 (t, $J=6.4$ Hz, 1H), 3.38 (dd, $J=13.6$, 6.8 Hz, 2H), 2.91–2.85 (m, 1H), 2.66–2.64 (m, 1H), 2.08 (s, 3H), 1.19 (t, $J=6.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 140.1, 133.5, 128.6, 128.0, 81.5, 64.6, 41.8, 16.7, 15.3 ppm; IR (KBr): 2360, 2342, 1489, 1088, 667 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{11}\text{H}_{15}\text{ClNaOS}$ [$\text{M}+\text{Na}$] $^+$ 253.0429, found 253.0424.



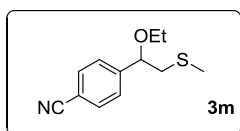
(2-(4-bromophenyl)-2-ethoxyethyl)(methyl)sulfane (3j); 186 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J=7.6$ Hz, 2H), 7.22 (d, $J=7.6$ Hz, 2H), 4.36 (t, $J=6.4$ Hz, 1H), 3.38 (dd, $J=13.8, 7.0$ Hz, 2H), 2.90–2.85 (m, 1H), 2.67–2.62 (m, 1H), 2.08 (s, 3H), 1.18 (t, $J=7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 131.5, 128.4, 121.6, 81.5, 64.6, 41.7, 16.7, 15.2 ppm; IR (KBr): 2359, 2342, 1636, 1105, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{11}\text{H}_{15}\text{BrNaOS}$ [$\text{M}+\text{Na}$] $^+$ 296.9918, found 296.9919.



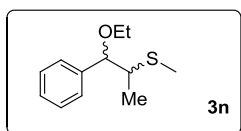
4-(1-ethoxy-2-(methylthio)ethyl)benzoic acid (3k); 148 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.11 (d, $J=7.6$ Hz, 2H), 7.46 (d, $J=8.0$ Hz, 2H), 4.48 (t, $J=6.4$ Hz, 1H), 3.45–3.40 (m, 2H), 2.91 (dd, $J=13.6, 7.6$ Hz, 1H), 2.69 (dd, $J=13.6, 5.6$ Hz, 1H), 2.09 (s, 3H), 1.21 (t, $J=6.8$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 171.7, 147.9, 130.4, 126.8, 81.8, 64.9, 41.7, 16.8, 15.3 ppm; IR (KBr): 2359, 2342, 1688, 1652, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{16}\text{NaO}_3\text{S}$ [$\text{M}+\text{Na}$] $^+$ 263.0711, found 263.0712.



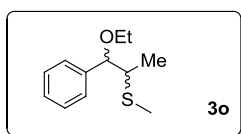
(2-ethoxy-2-(4-nitrophenyl)ethyl)(methyl)sulfane (3l); 192 mg isolated as a brown oil; ^1H NMR (400 MHz, CDCl_3): δ 8.22 (d, $J=8.0$ Hz, 2H), 7.53 (d, $J=8.0$ Hz, 2H), 4.51 (t, $J=6.4$ Hz, 1H), 3.49–3.36 (m, 2H), 2.92–2.87 (m, 1H), 2.72–2.67 (m, 1H), 2.10 (s, 3H), 1.24 (t, $J=7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 147.6, 127.5, 123.7, 81.3, 65.2, 41.6, 16.8, 15.3 ppm; IR (KBr): 2359, 2342, 1521, 1094, 680 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{11}\text{H}_{15}\text{NNaO}_3\text{S}$ [$\text{M}+\text{Na}$] $^+$ 264.0665, found 264.0665.



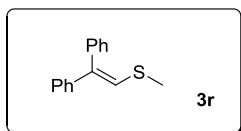
4-(1-ethoxy-2-(methylthio)ethyl)benzonitrile (3m); 174 mg isolated as a brown oil; ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J=8.0$ Hz, 2H), 7.47 (d, $J=7.6$ Hz, 2H), 4.46 (t, $J=6.4$ Hz, 1H), 3.45–3.37 (m, 2H), 2.88 (dd, $J=13.4, 7.0$ Hz, 1H), 2.67 (dd, $J=13.2, 5.2$ Hz, 1H), 2.09 (s, 3H), 1.21 (t, $J=7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 147.1, 132.3, 127.3, 118.7, 111.6, 81.4, 65.0, 41.5, 16.7, 15.2 ppm; IR (KBr): 2359, 2342, 1646, 1094, 1021, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{15}\text{NNaOS}$ [$\text{M}+\text{Na}$] $^+$ 244.0767, found 244.0767.



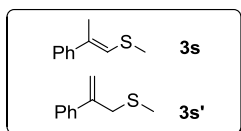
(1-ethoxy-1-phenylpropan-2-yl)(methyl)sulfane (3n); (1:1.2 mixture of syn and anti); 57 mg isolated as a brown oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.26 (m, 5H), 4.27 (d, $J=6.0$ Hz, 0.45 H), 4.19 (d, $J=7.2$ Hz, 0.55H), 3.45–3.30 (m, 2H), 2.99–2.92 (m, 0.55H), 2.86–2.80 (m, 0.45H), 2.14 (s, 1.65H), 1.91 (s, 1.35H), 1.30 (d, $J=6.8$ Hz, 1.35H), 1.18 (t, $J=7.0$ Hz, 3H), 1.07 (d, $J=7.2$ Hz, 1.65H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 140.2, 128.0, 128.0, 127.7, 127.5, 127.4, 127.2, 86.4, 85.4, 64.7, 64.4, 47.6, 47.1, 17.2, 16.3, 15.2, 14.8, 14.4 ppm; IR (KBr): 2359, 2340, 1644, 1066, 1021, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 233.0971, found 233.0971.



(1-ethoxy-1-phenylpropan-2-yl)(methyl)sulfane (3o); (1:5 mixture of syn and anti); 55 mg isolated as a brown oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.26 (m, 5H), 4.27 (d, $J=6.0$ Hz, 0.84H), 4.19 (d, $J=7.2$ Hz, 0.16H), 3.43–3.33 (m, 2H), 2.88–2.85 (m, 0.16H), 2.84–2.80 (m, 0.84H), 2.14 (s, 0.46H), 1.91 (s, 2.54H), 1.30 (d, $J=6.8$ Hz, 2.50H), 1.18 (t, $J=7.0$ Hz, 3H), 1.07 (d, $J=6.8$ Hz, 0.50H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 140.7, 128.0, 127.6, 127.3, 85.5, 64.8, 47.7, 16.4, 15.2, 14.5 ppm; IR (KBr): 2359, 2339, 1644, 1068, 1021, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 233.0971, found 233.0969.

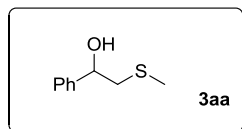


(2,2-diphenylvinyl)(methyl)sulfane (3r)^[1]; 176 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38–7.34 (m, 2H), 7.29–7.26 (m, 3H), 7.22–7.17 (m, 5H), 6.53 (s, 1H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 139.4, 138.3, 128.2, 128.1, 127.6, 127.4, 126.9, 126.8, 17.9 ppm; MS (EI) m/z : 226, 211, 178, 152.

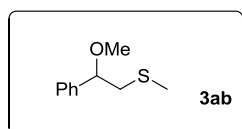


A mixture of methyl(2-phenylprop-1-enyl) sulfane (3s) and (*E*)-methyl(2-phenylprop-1-enyl) sulfane (3s')^[1]; 134 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.48–7.46 (m, 2H), 7.35–7.28 (m, 11H), 7.23–7.18 (m, 2H), 6.26 (s, 2H), 5.44 (s, 1H), 5.18 (s, 1H), 3.56 (s, 2H), 2.38 (s, 6H), 2.11 (s, 6H), 2.02 (s,

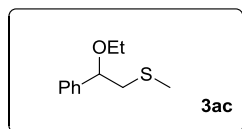
3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 139.3, 132.9, 127.5, 126.6, 125.0, 114.8, 38.6, 17.5, 17.3, 14.9 ppm; MS (EI) m/z: 164, 149, 133, 115.



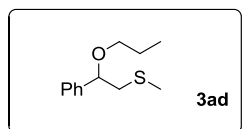
2-(Methylthio)-1-phenylethanol (3aa)^[3]; 92 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38–7.25 (m, 5H), 4.76 (dd, $J=9.2$, 3.6 Hz, 1H), 2.88–2.85 (m, 1H), 2.75–2.70 (m, 1H), 2.12 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 128.5, 127.8, 125.8, 71.1, 44.0, 15.4 ppm; MS (EI) m/z: 168, 107, 79, 62.



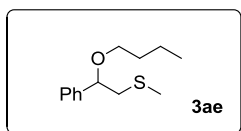
(2-Methoxy-2-phenylethyl)(methyl)sulfane (3ab)^[2]; 156 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.38–7.28 (m, 5H), 4.29 (dd, $J=7.2$, 5.2 Hz, 1H), 3.25 (s, 3H), 2.91 (dd, $J=14.6$, 7.6 Hz, 1H), 2.69 (dd, $J=13.2$, 4.4 Hz, 1H), 2.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 128.4, 127.9, 126.6, 83.7, 56.8, 41.7, 16.5 ppm; MS (EI) m/z: 182, 121, 105, 77, 61.



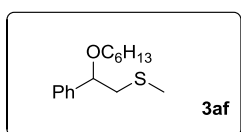
(2-ethoxy-2-phenylethyl)(methyl)sulfane (3ac)^[3]; 174 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.25 (m, 5H), 4.40 (dd, $J=7.6$, 5.6 Hz, 1H), 3.43–3.36 (m, 2H), 2.91 (dd, $J=13.4$, 7.8 Hz, 1H), 2.68 (dd, $J=13.4$, 5.4 Hz, 1H), 2.07 (s, 3H), 1.19 (t, $J=7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 128.4, 127.8, 126.6, 82.1, 64.4, 41.9, 16.6, 15.2 ppm; MS (EI) m/z: 196, 151, 135, 79, 61.



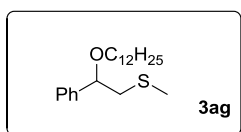
methyl(2-phenyl-2-propoxyethyl)sulfane (3ad); 178 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36–7.27 (m, 5H), 4.38 (t, $J=6.6$ Hz, 1H), 3.30–3.24 (m, 2H), 2.90 (dd, $J=13.6$, 8.0 Hz, 1H), 2.67 (dd, $J=13.6$, 5.0 Hz, 1H), 2.07 (s, 3H), 1.59 (dd, $J=14.2$, 7.0 Hz, 2H), 0.90 (t, $J=7.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 127.7, 126.5, 82.3, 70.7, 41.9, 23.0, 16.6, 10.5 ppm; IR (KBr): 2978, 2360, 2342, 1098, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 233.1106, found 233.1104.



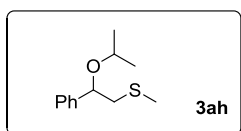
(2-(butoxy)-2-phenylethyl)(methyl)sulfane (3ae); 186 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36–7.28 (m, 5H), 4.38 (t, $J=6.6$ Hz, 1H), 3.38–3.28 (m, 2H), 2.90 (dd, $J=13.0$, 8.2 Hz, 1H), 2.96–2.66 (m, 1H), 2.07 (s, 3H), 1.59–1.52 (m, 2H), 1.38–1.32 (m, 2H), 0.88 (t, $J=7.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 128.3, 127.7, 126.6, 82.4, 68.89, 42.01, 31.9, 19.3, 16.7, 13.8 ppm; IR (KBr): 2957, 2360, 2342, 1095, 1032, 699 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{13}\text{H}_{20}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 247.1131, found 247.1127.



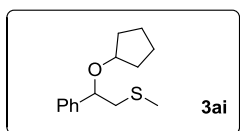
(2-(hexyloxy)-2-phenylethyl)(methyl)sulfane (3af); 196 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36–7.25 (m, 5H), 4.37 (t, $J=6.6$ Hz, 1H), 3.37–3.27 (m, 2H), 2.90 (dd, $J=13.2$, 8.0 Hz, 1H), 2.67 (dd, $J=13.2$, 4.8 Hz, 1H), 2.07 (s, 3H), 1.60–1.51 (m, 2H), 1.34–1.24 (m, 6H), 0.87 (t, $J=6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.6, 127.7, 126.6, 69.2, 42.0, 31.6, 29.8, 25.7, 22.5, 16.7, 14.0 ppm; IR (KBr): 2360, 2342, 1636, 698, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{15}\text{H}_{24}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 275.1444, found 275.1440.



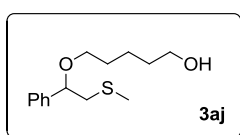
(2-(dodecyloxy)-2-phenylethyl)(methyl)sulfane (3ag); 221 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.36–7.25 (m, 5H), 4.37 (t, $J=6.4$ Hz, 1H), 3.34–3.29 (m, 2H), 2.90 (dd, $J=13.6$, 8.0 Hz, 1H), 2.67 (dd, $J=13.6$, 5.2 Hz, 1H), 2.07 (s, 3H), 1.59–1.53 (m, 2H), 1.30–1.25 (m, 18H), 0.88 (t, $J=6.4$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 128.4, 127.8, 126.6, 82.4, 69.2, 42.0, 31.9, 29.8, 29.6, 29.6, 29.6, 29.4, 29.3, 26.1, 22.6, 16.7, 14.1 ppm; IR (KBr): 2922, 2852, 2359, 2342, 1095, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{21}\text{H}_{36}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 359.2385, found 359.2379.



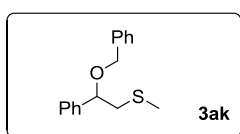
(2-isopropoxy-2-phenylethyl)(methyl)sulfane (3ah); 170 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.34–7.27 (m, 5H), 4.51 (t, $J=6.4$ Hz, 1H), 3.56–3.47 (m, 1H), 2.86 (dd, $J=13.6$, 8.0 Hz, 1H), 2.65 (dd, $J=13.6$, 5.0 Hz, 1H), 2.06 (s, 3H), 1.19 (d, $J=6.0$ Hz, 3H), 1.09 (d, $J=6.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 128.2, 127.6, 126.5, 79.3, 69.3, 42.5, 23.3, 21.1, 16.6 ppm; IR (KBr): 2922, 2850, 2342, 1010, 680 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{12}\text{H}_{18}\text{NaOS}$ $[\text{M}+\text{Na}]^+$ 233.1106, found 233.1103.



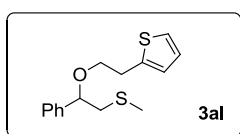
(2-(cyclopentyloxy)-2-phenylethyl)(methyl)sulfane (3ai); 179 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.28 (m, 5H), 4.45 (dd, $J=7.0, 5.4$ Hz, 1H), 3.87–3.80 (m, 1H), 2.87–2.82 (m, 1H), 2.66 (d, $J=0.8$ Hz, 1H), 2.10 (s, 3H), 1.80–1.60 (m, 6H), 1.51–1.41 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 142.2, 128.3, 127.6, 126.7, 80.2, 79.2, 42.4, 33.1, 31.6, 23.4, 16.7 ppm; IR (KBr): 2360, 2342, 1636, 684, 667 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{14}\text{H}_{20}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 259.1126, found 259.1127.



5-(2-(methylthio)-1-phenylethoxy)pentan-1-ol (3aj); 185 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.29 (m, 5H), 4.38 (t, $J=6.6$ Hz, 1H), 3.62 (t, $J=6.4$ Hz, 2H), 3.39–3.29 (m, 2H), 2.91 (dd, $J=13.0, 7.8$ Hz, 1H), 2.69–2.66 (m, 1H), 2.07 (s, 3H), 1.78 (s, 1H), 1.63–1.52 (m, 4H), 1.46–1.39 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 128.4, 127.8, 126.6, 82.3, 68.97, 62.7, 42.0, 32.4, 29.4, 22.3, 16.6 ppm; IR (KBr): 2935, 2862, 2359, 2342, 1095, 1073, 701 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{14}\text{H}_{22}\text{NaO}_2\text{S}$ [$\text{M}+\text{Na}$] $^+$ 277.1236, found 277.1233.



(2-(benzyloxy)-2-phenylethyl)(methyl)sulfane (3ak); 152 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.37–7.33 (m, 10H), 4.56–4.46 (m, 2H), 4.34–4.27 (m, 1H), 3.00–2.94 (m, 1H), 2.74–2.71 (m, 1H), 2.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 138.2, 128.5, 128.3, 128.1, 127.7, 127.5, 126.9, 81.3, 70.6, 42.0, 16.7 ppm; IR (KBr): 2360, 2342, 1653, 696, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{16}\text{H}_{18}\text{NaOS}$ [$\text{M}+\text{Na}$] $^+$ 281.0975, found 281.0971.

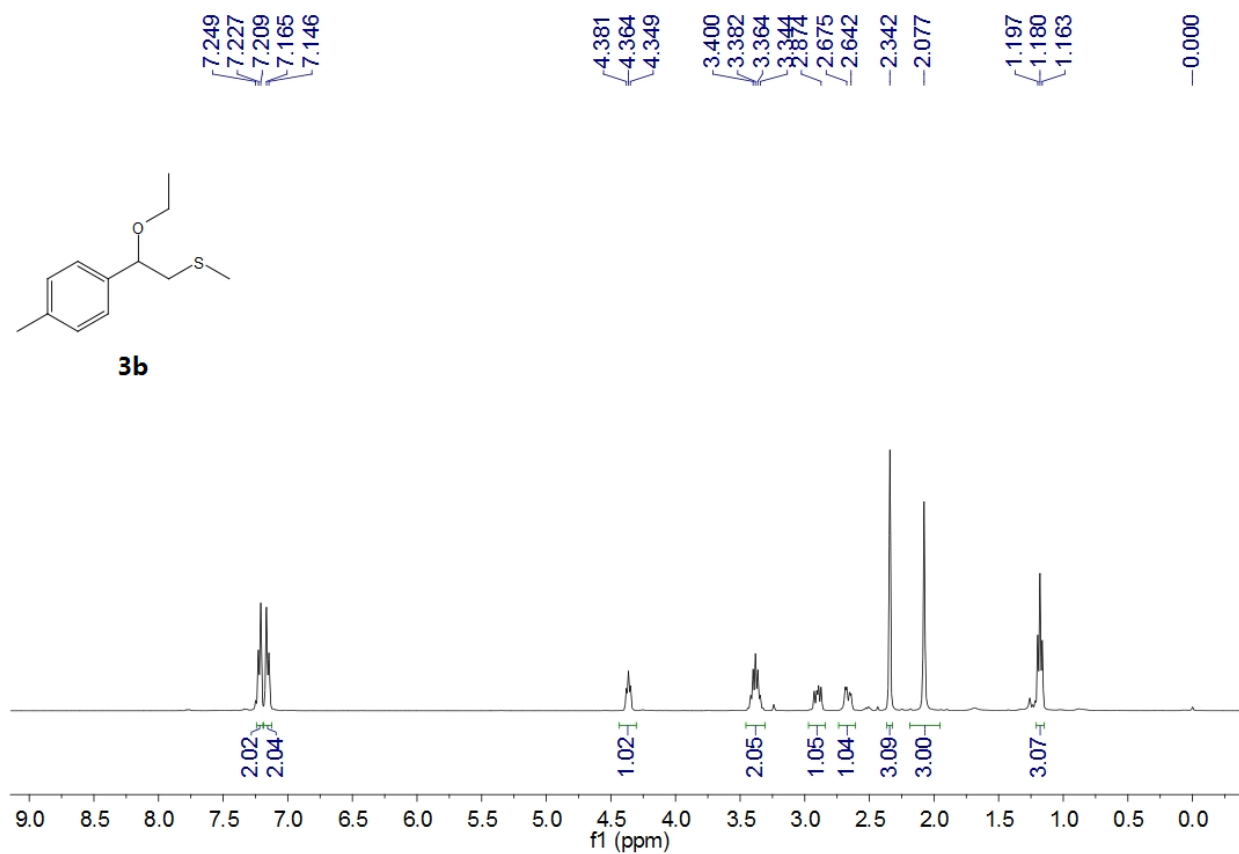


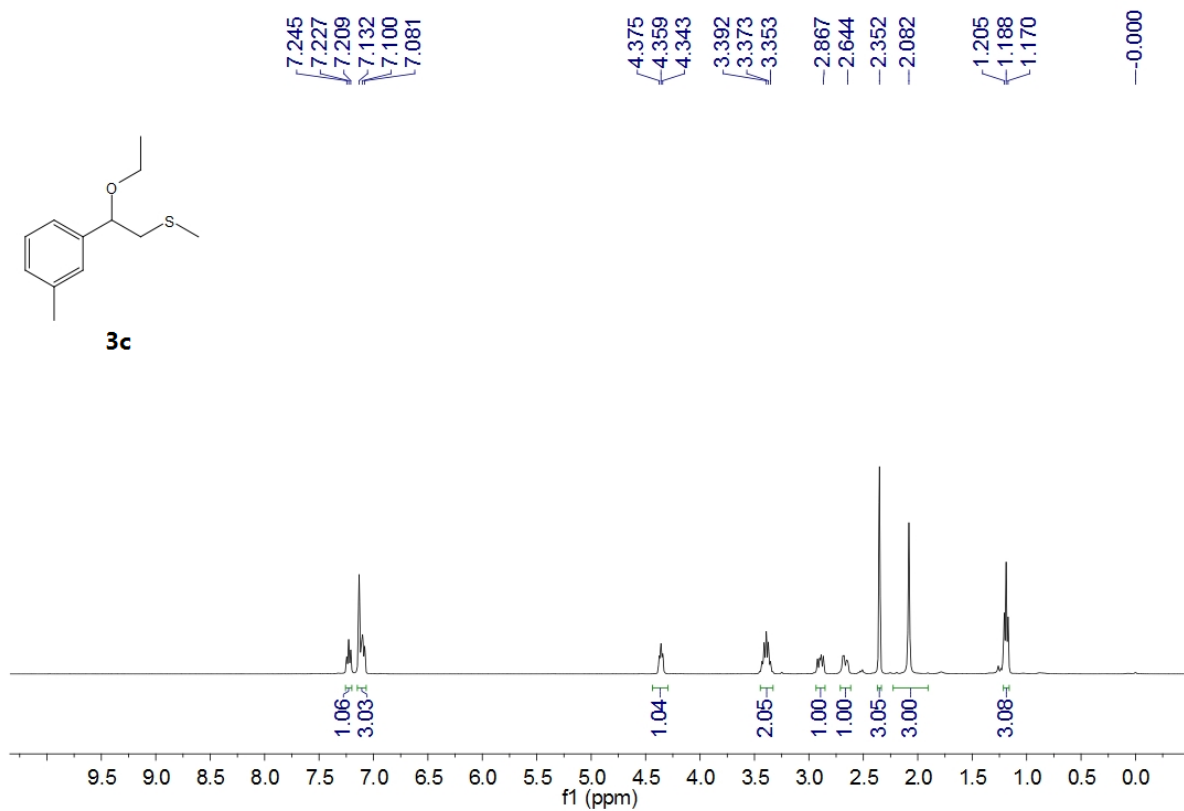
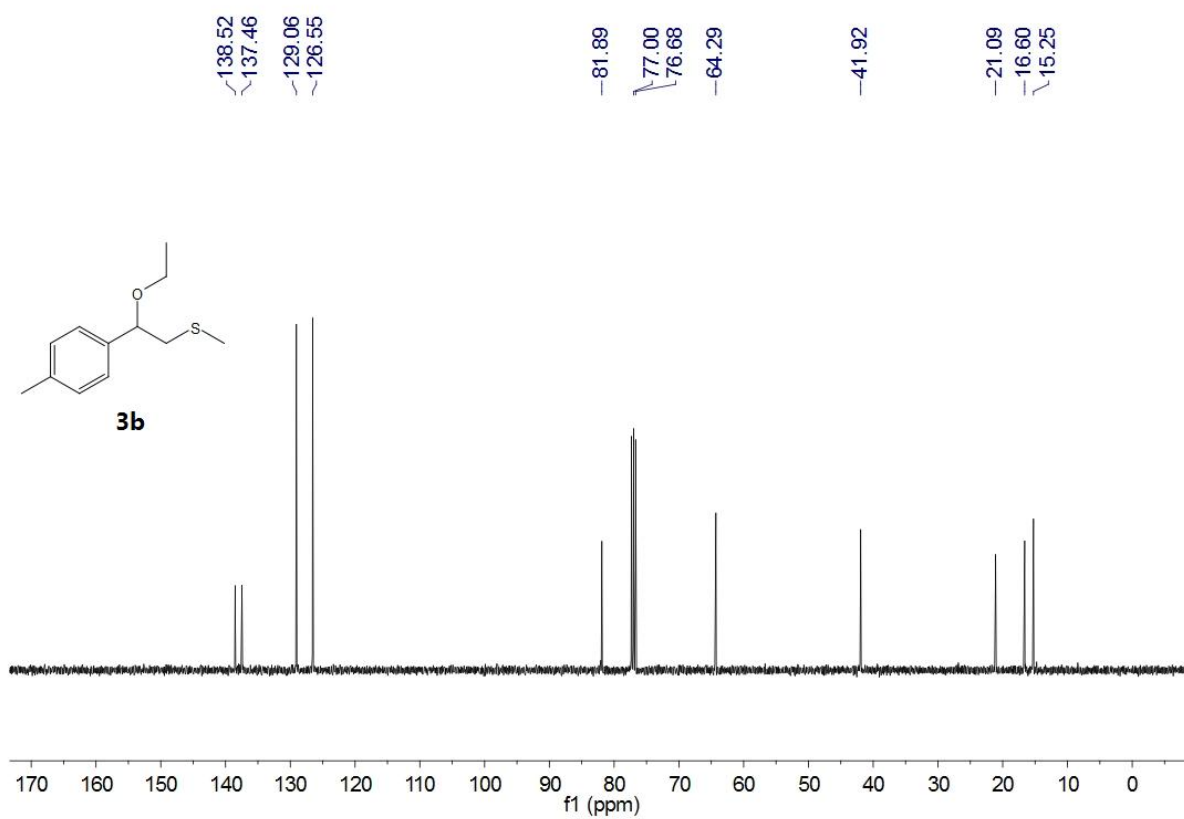
2-(2-(2-(methylthio)-1-phenylethoxy)ethyl)thiophene (3al); 133 mg isolated as a light yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.35–7.25 (m, 5H), 7.11 (d, $J=5.2$ Hz, 1H), 6.90 (t, $J=4.0$ Hz, 1H), 6.82 (s, 1H), 4.43 (t, $J=6.6$ Hz, 1H), 3.62–3.52 (m, 2H), 3.11–3.08 (m, 2H), 2.92 (dd, $J=13.2, 7.6$ Hz, 1H), 2.71–2.68 (m, 1H), 2.05 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 141.2, 141.1, 128.4, 128.0, 126.7, 126.6, 125.2, 123.5, 82.9, 69.7, 41.9, 30.6, 16.8 ppm; IR (KBr): 2360, 2342, 1652, 1095, 668 cm^{-1} ; HRMS-ESI (m/z): calcd. for $\text{C}_{15}\text{H}_{18}\text{NaOS}_2$ [$\text{M}+\text{Na}$] $^+$ 301.0697, found 301.0691.

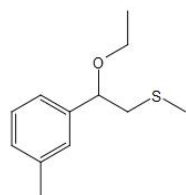
4. References

- [1] Benati, L.; Capella, L.; Montecvecchi, P. C.; Spagnolo, P. *J. Org. Chem.* **1994**, 59, 2818.
[2] Tiecco, M.; Chianelli, D.; Tingoli, M.; Testaferri, L.; Bartoli, D. *Tetrahedron* **1986**, 42, 4897.
[3] Reisner, D. B. *J. Am. Chem. Soc.* **1956**, 78, 2132.

5. NMR spectra of products







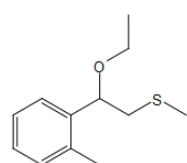
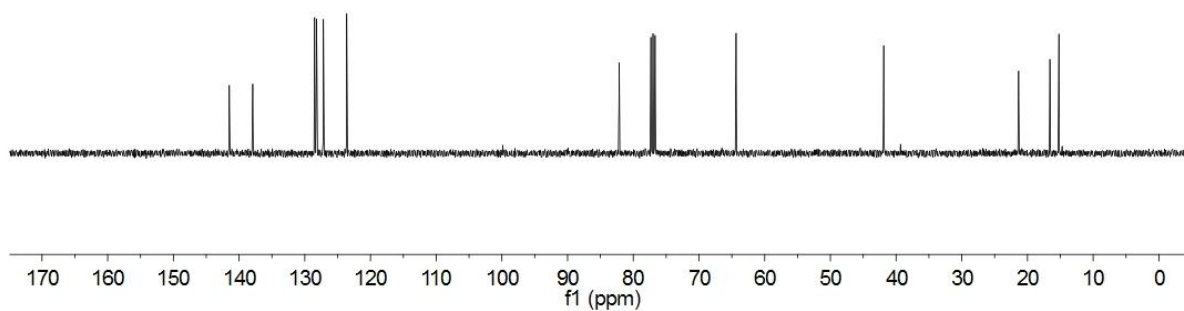
3c

141.49
137.92
128.50
128.21
127.17
123.62

82.15
77.00
76.68
64.35

41.88

21.35
16.58
15.21



3d

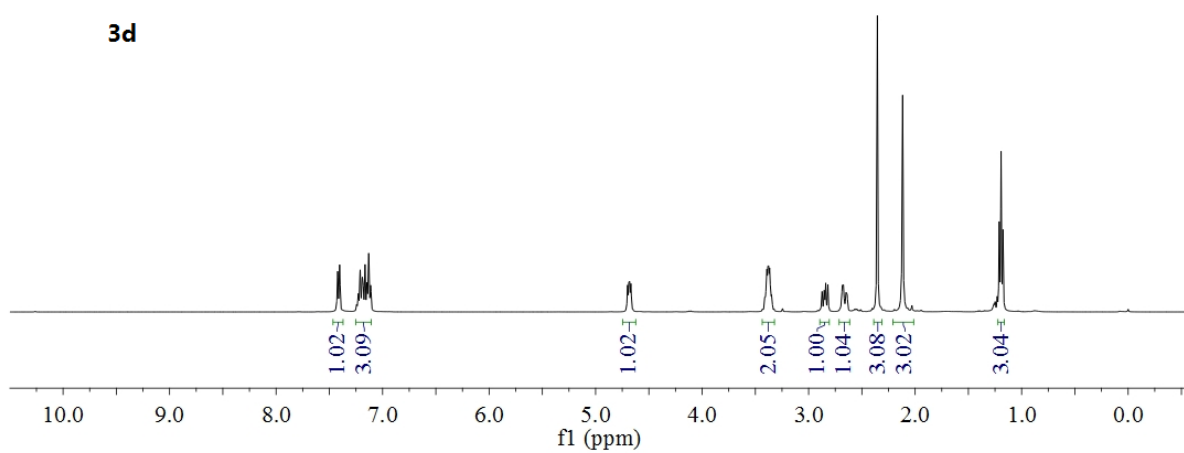
7.422
7.403
7.243
7.228
7.210
7.190
7.165
7.147
7.130
7.112

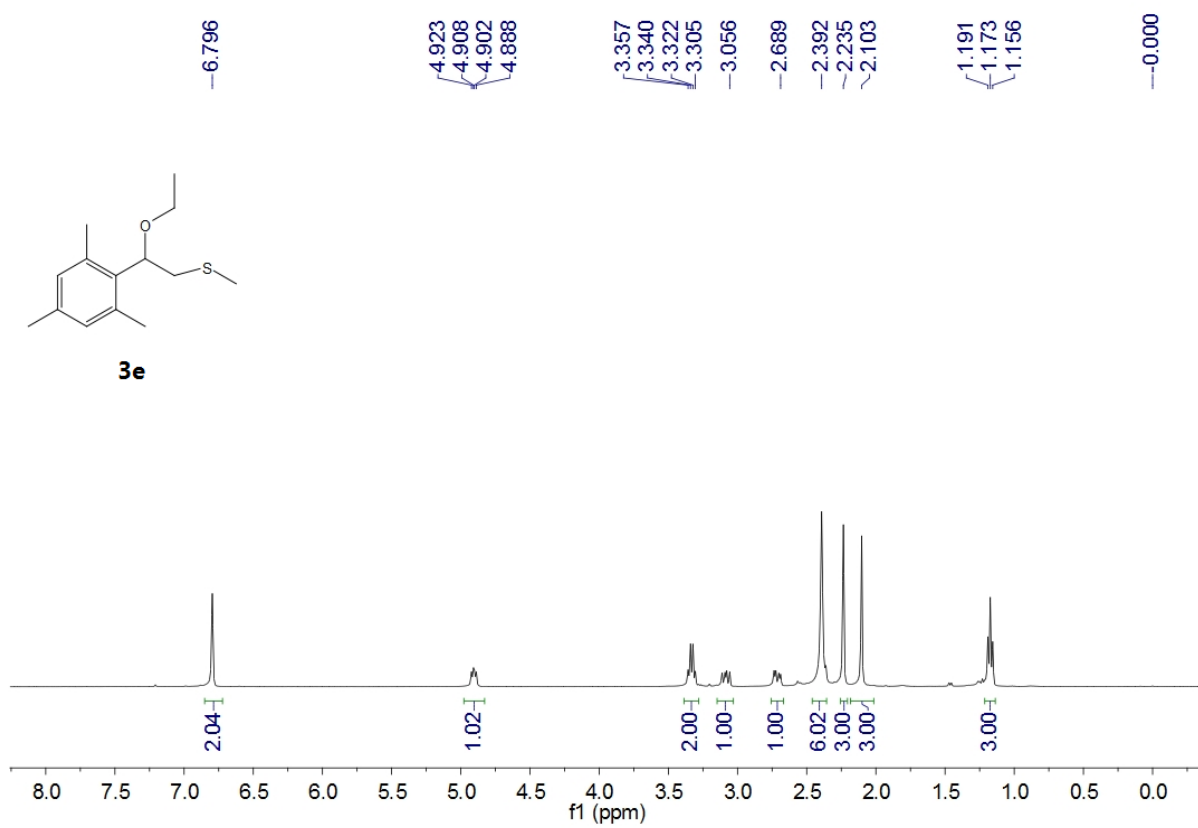
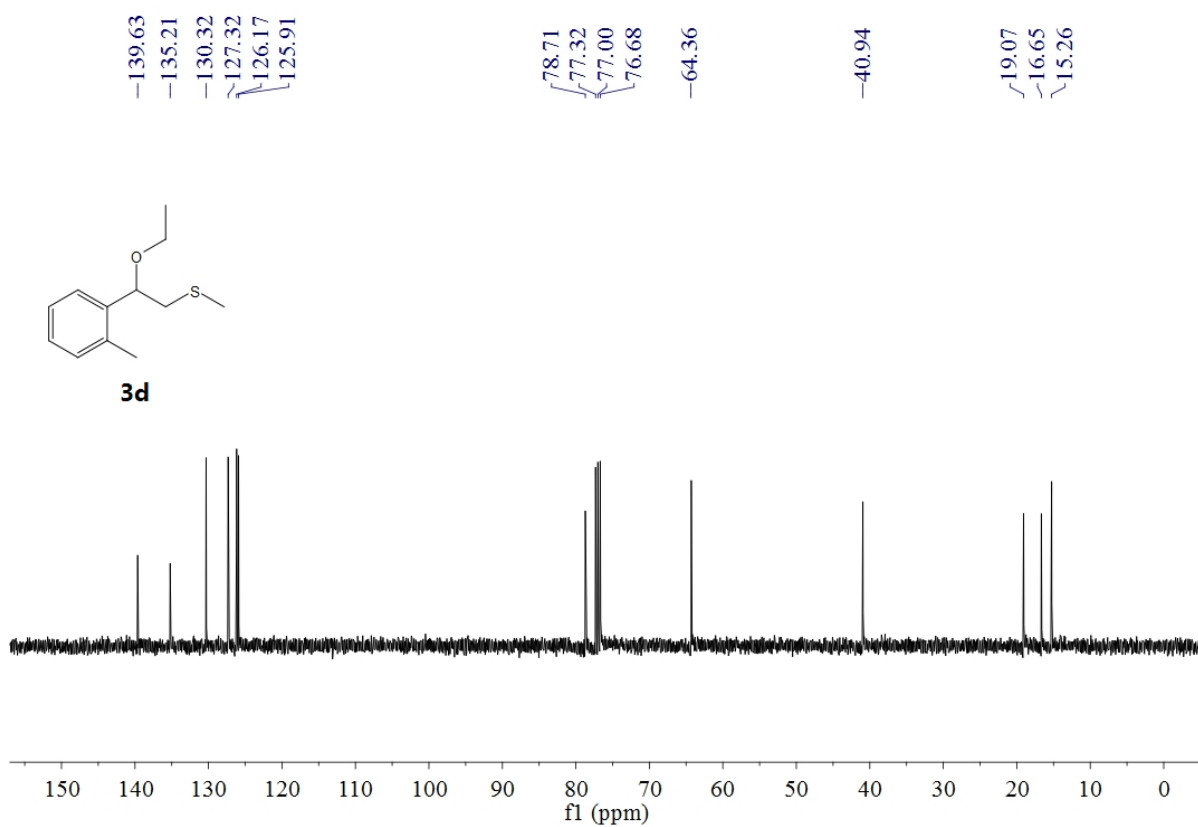
4.700
4.689
4.680
4.669
3.392
3.375
3.348

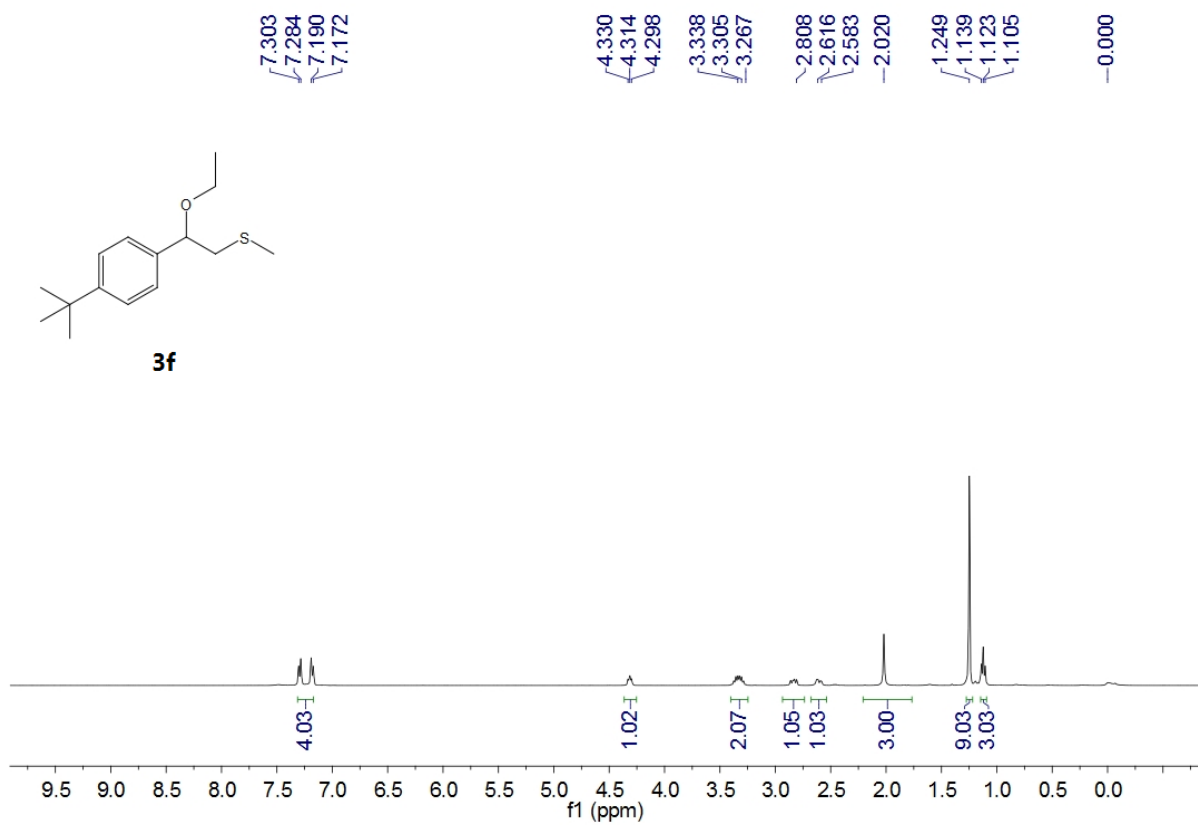
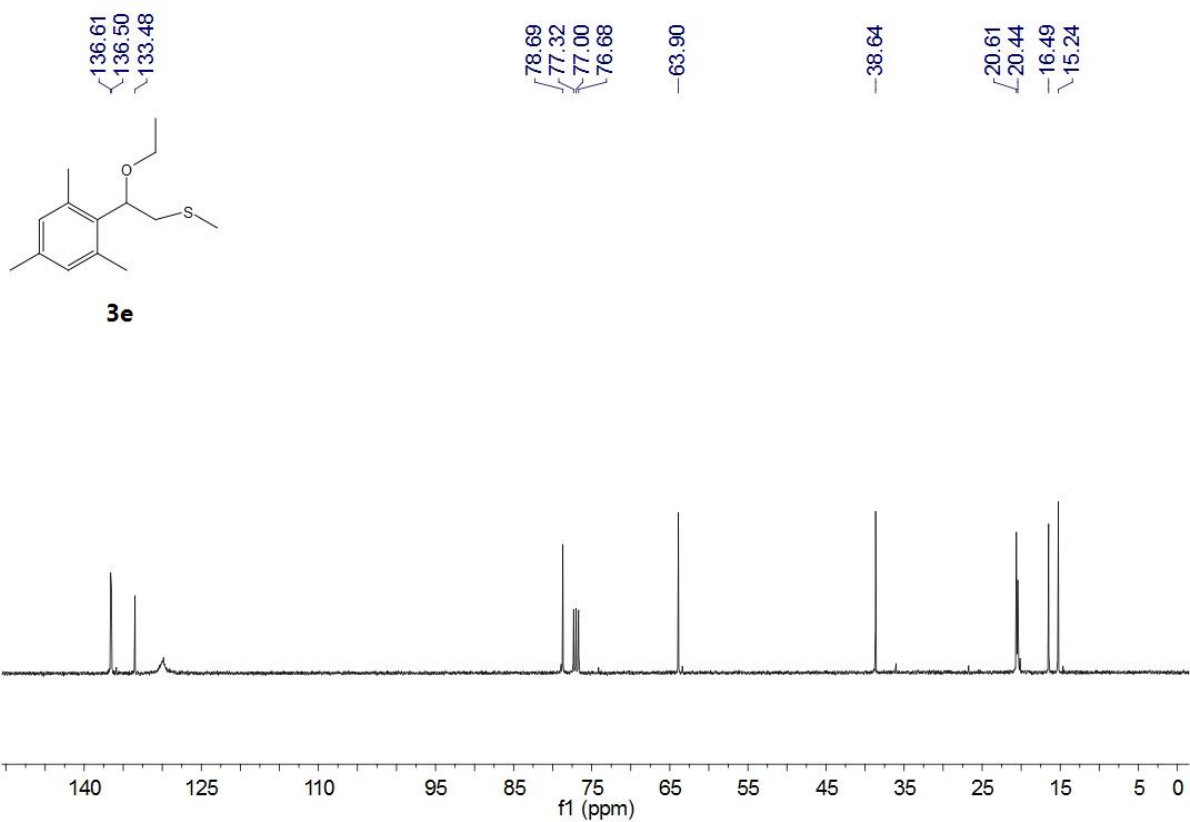
2.649
2.354
2.117

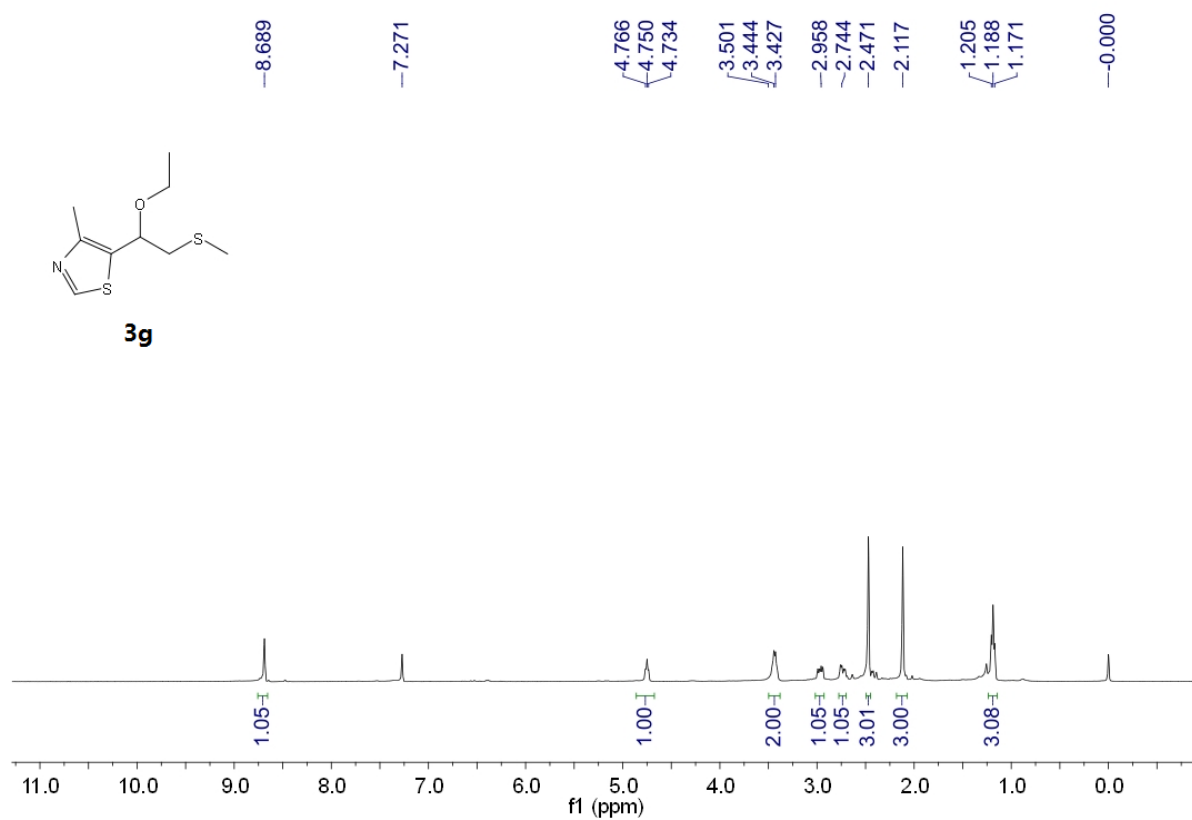
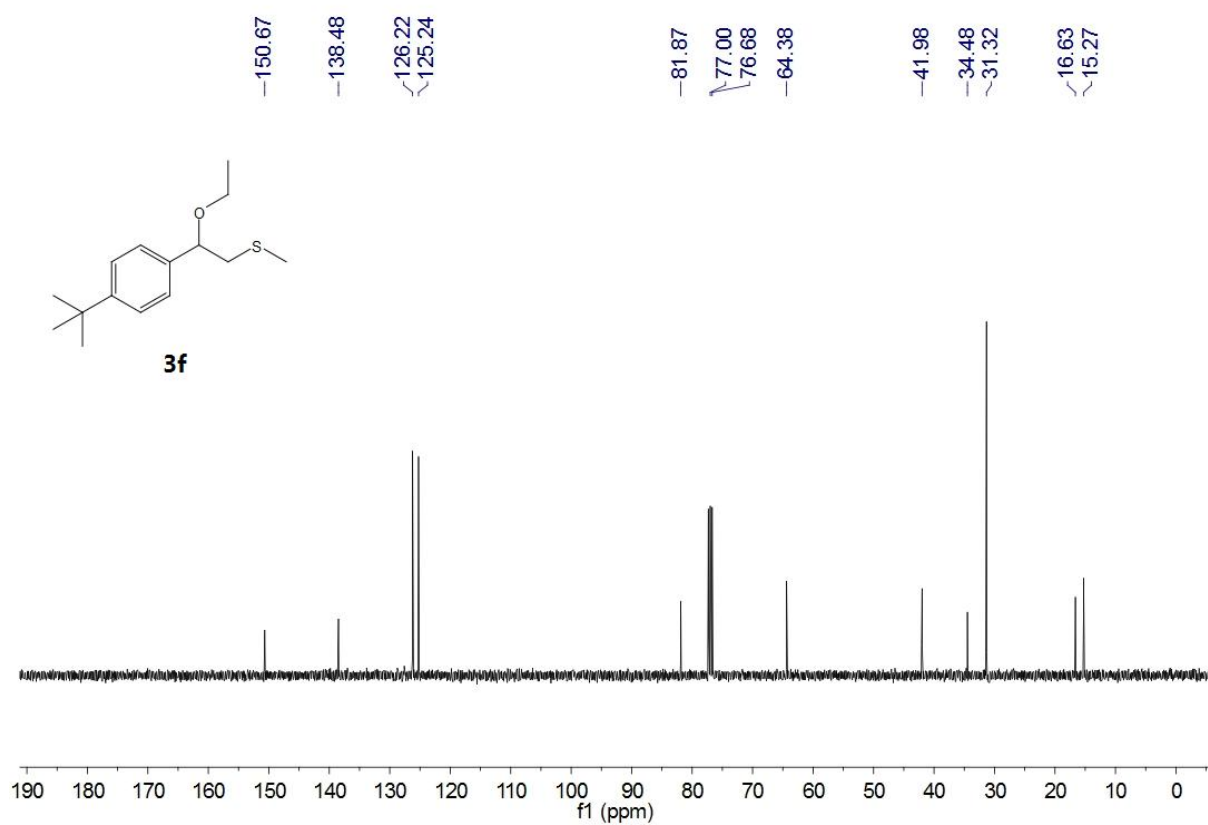
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1.193
1.175

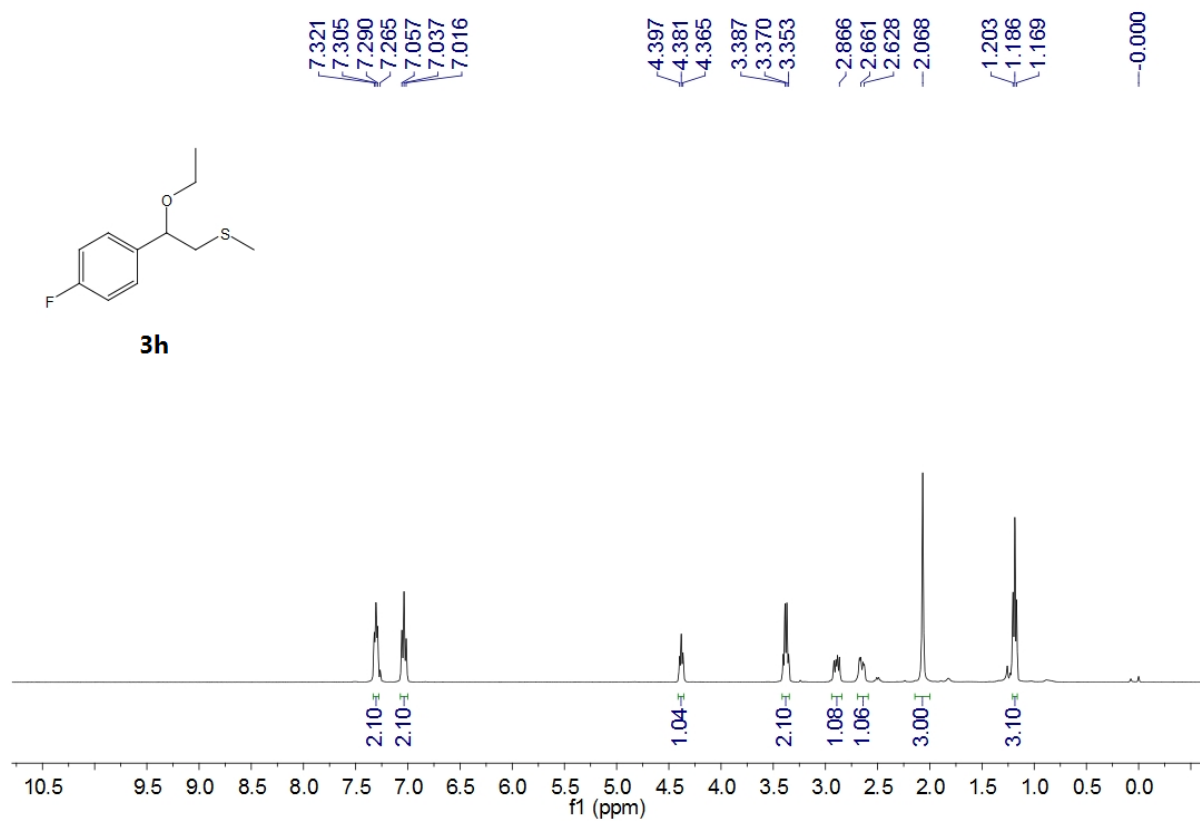
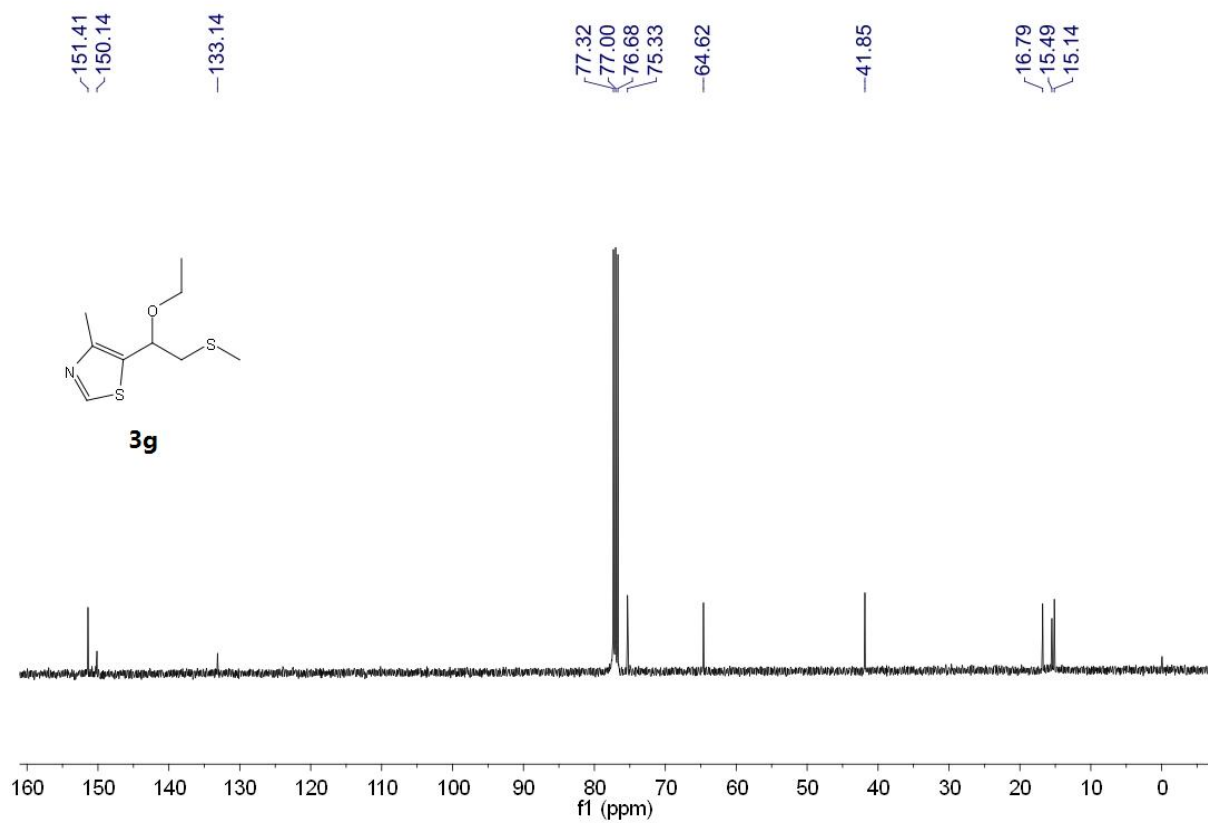
0.000

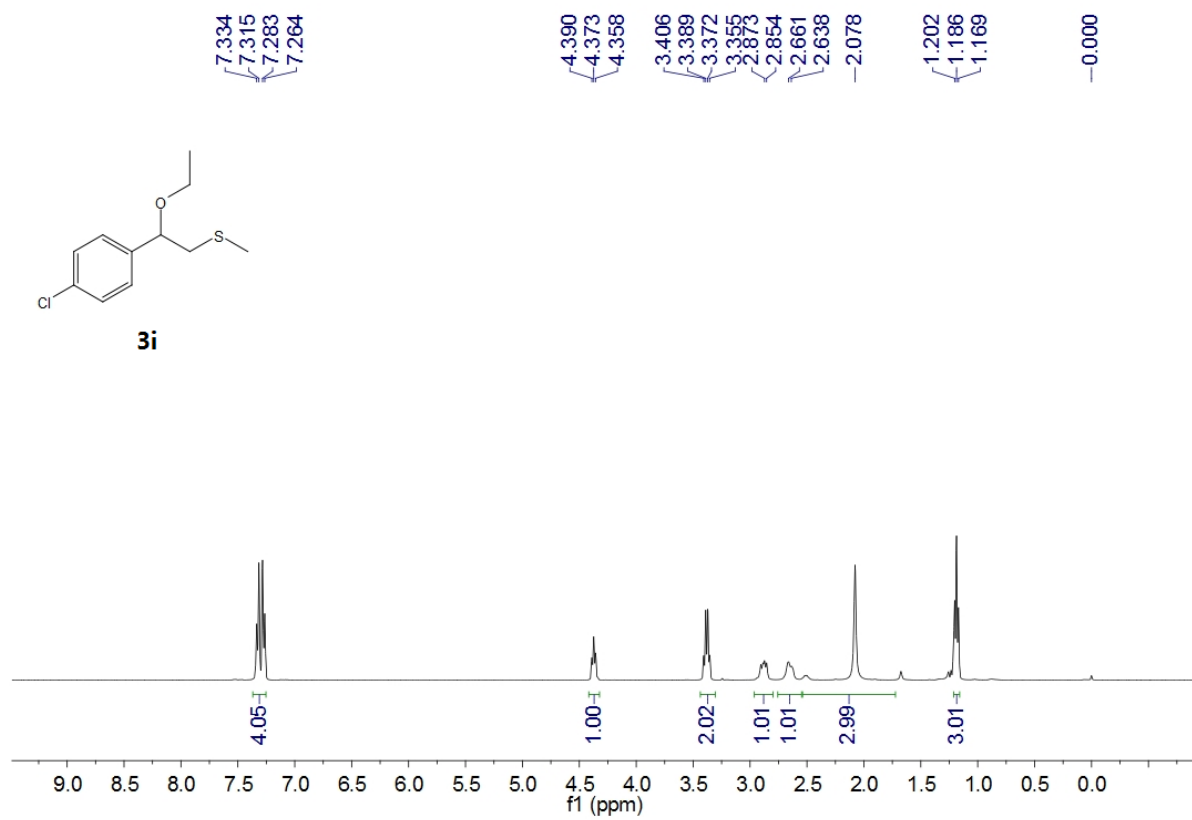
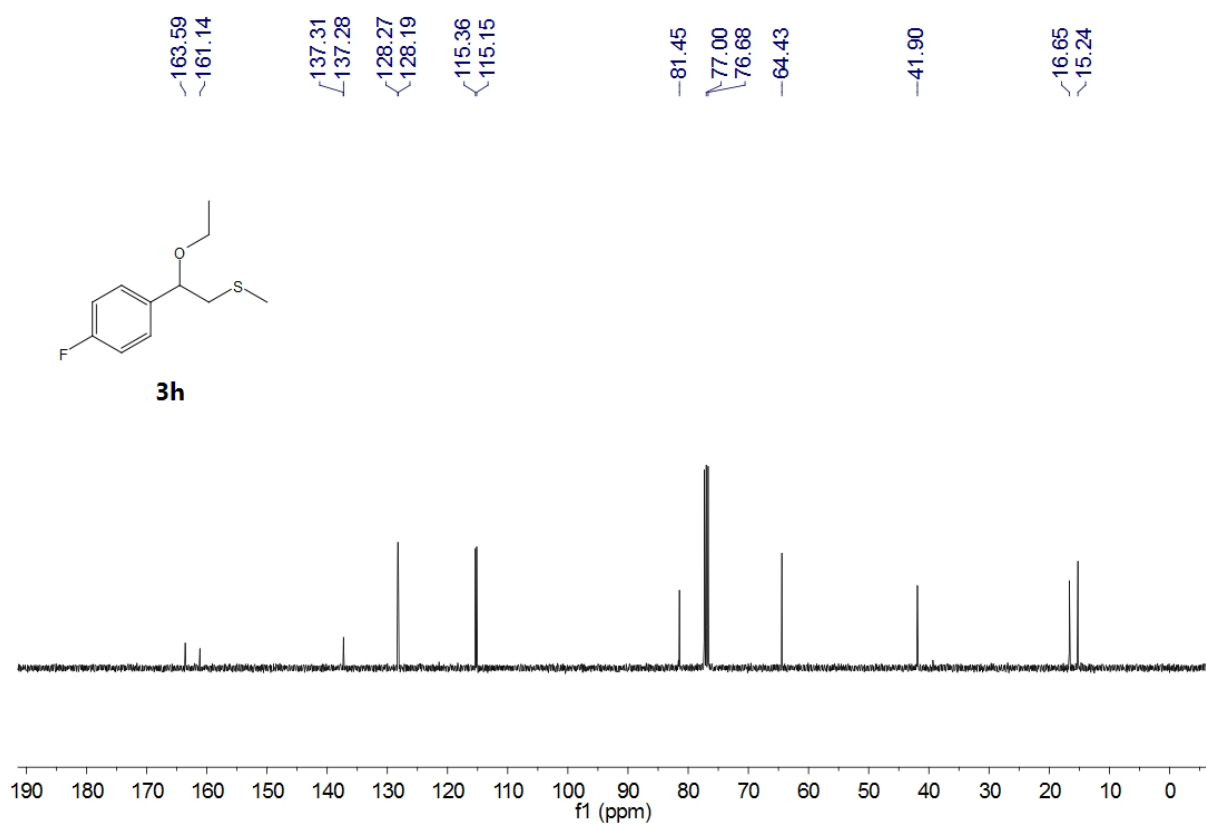


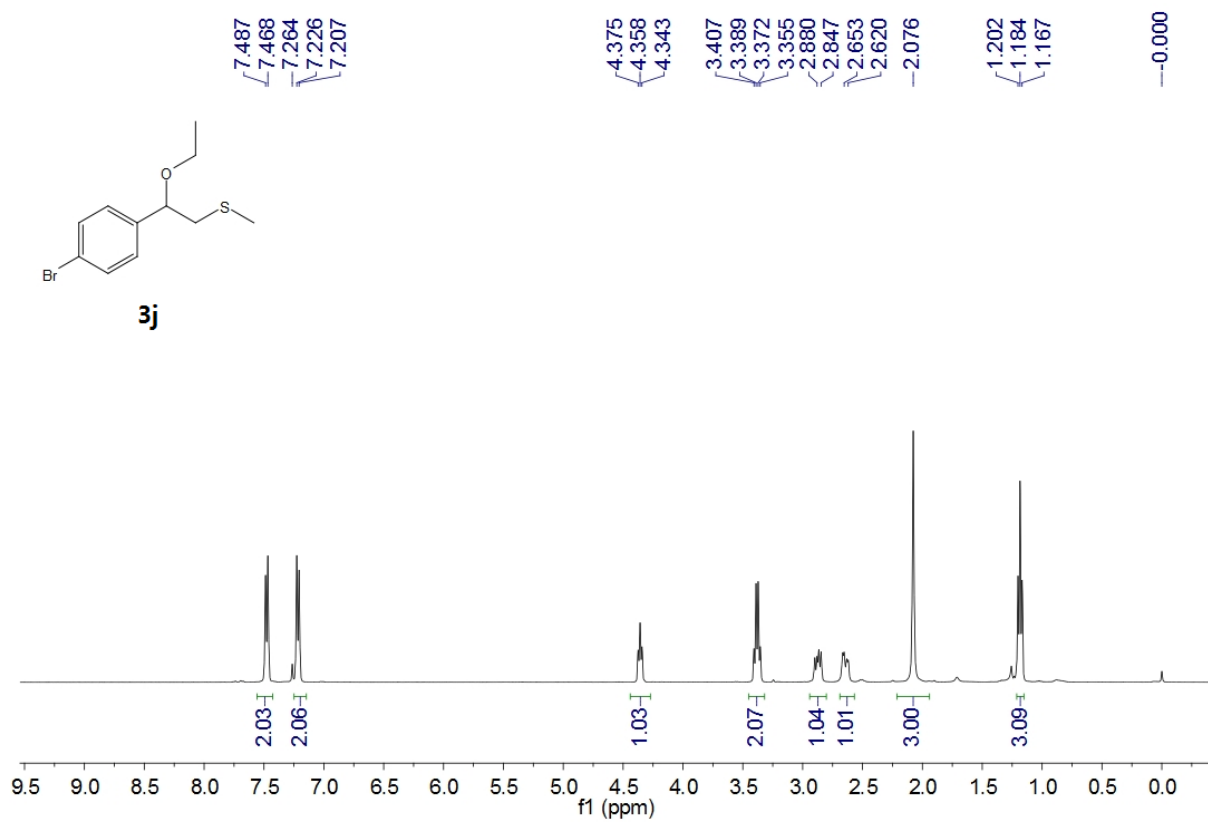
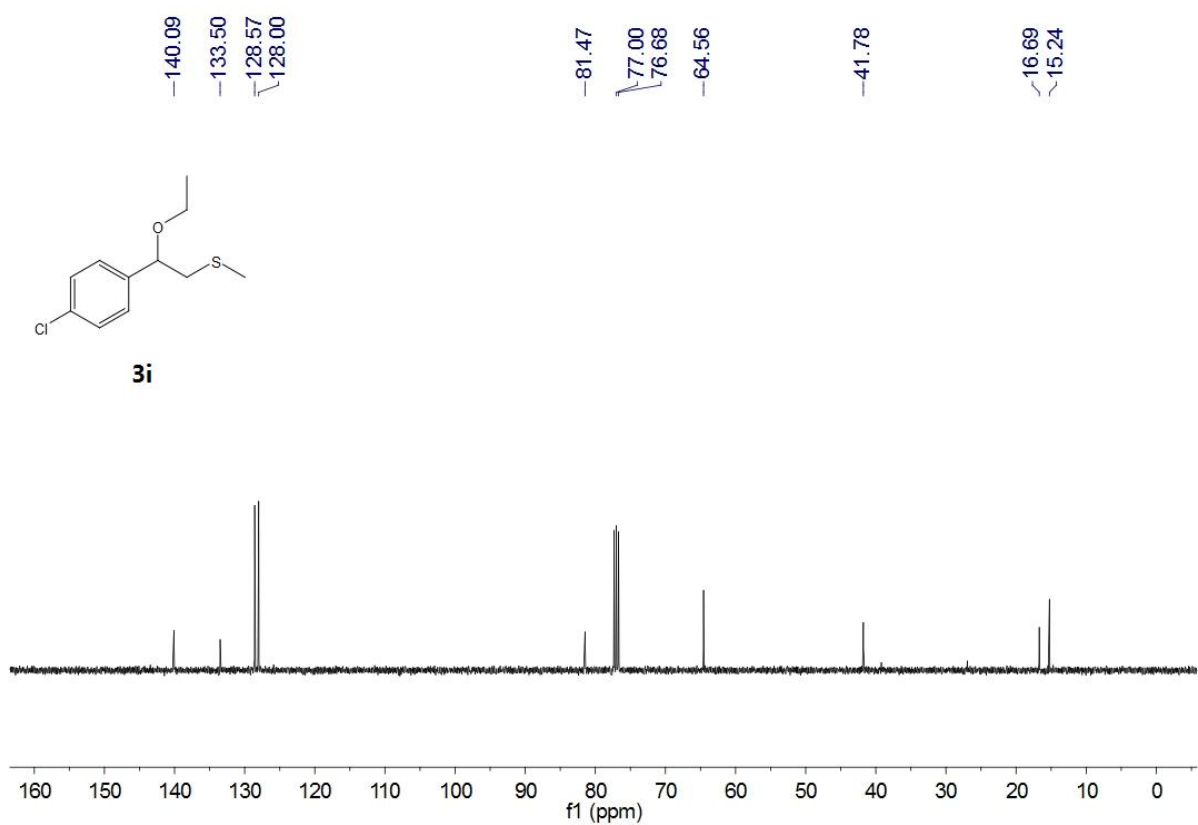


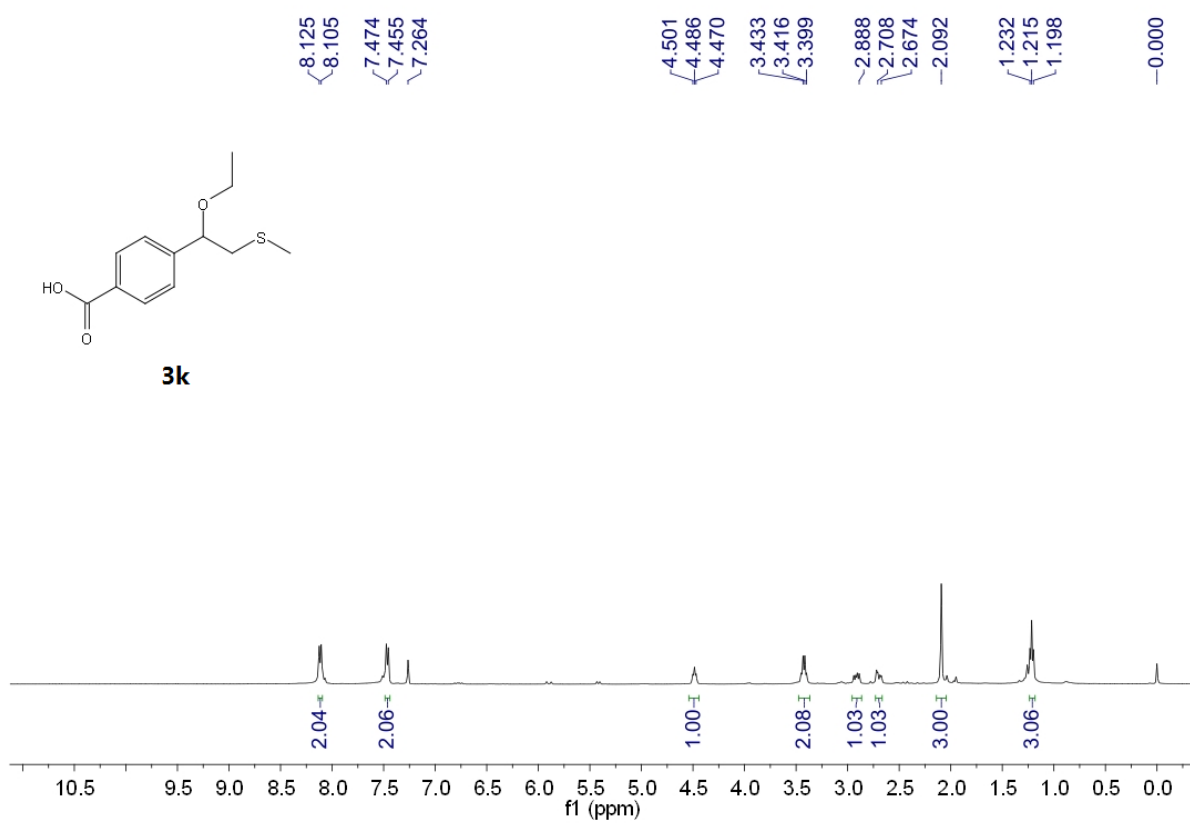
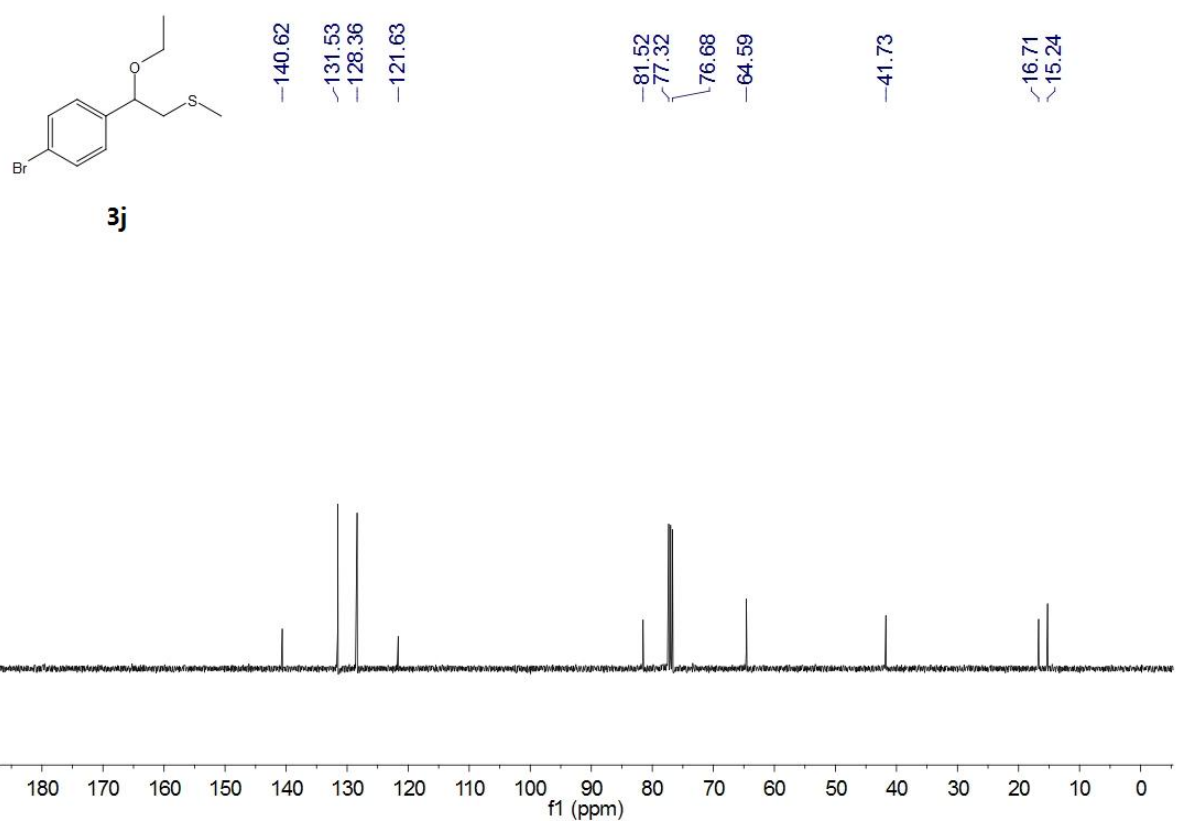


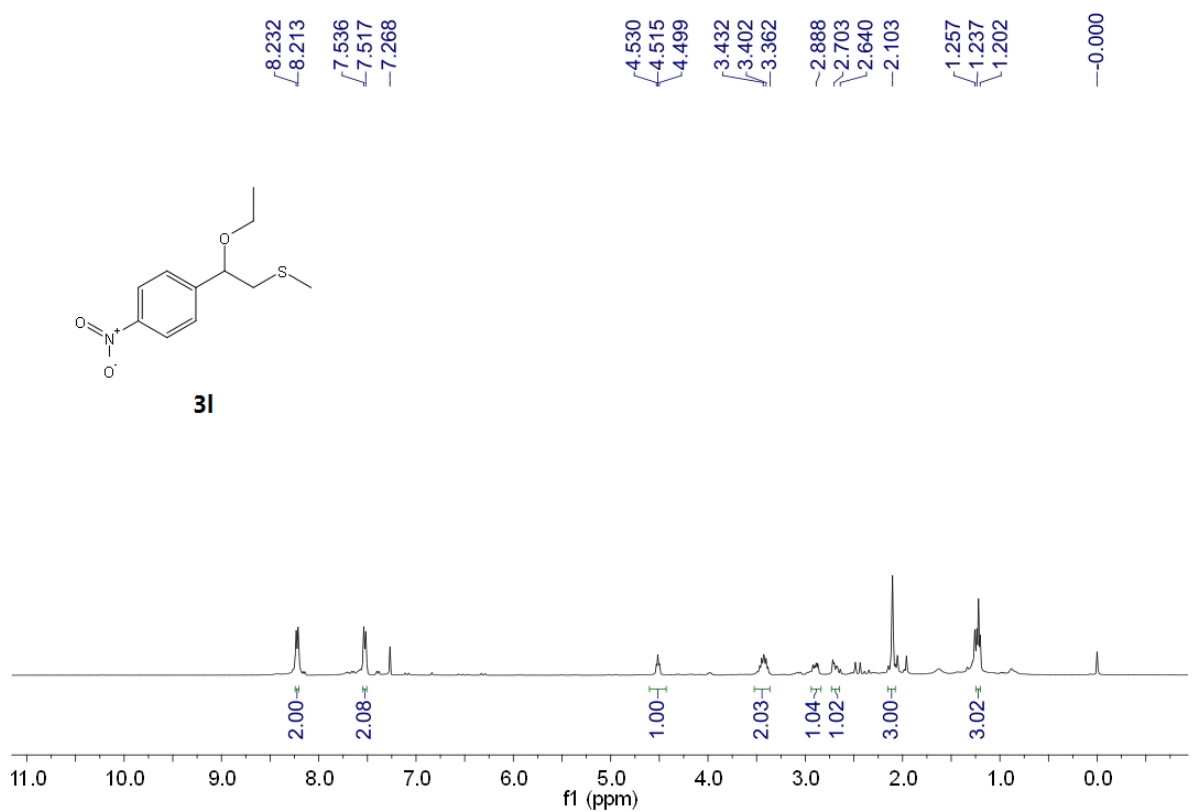
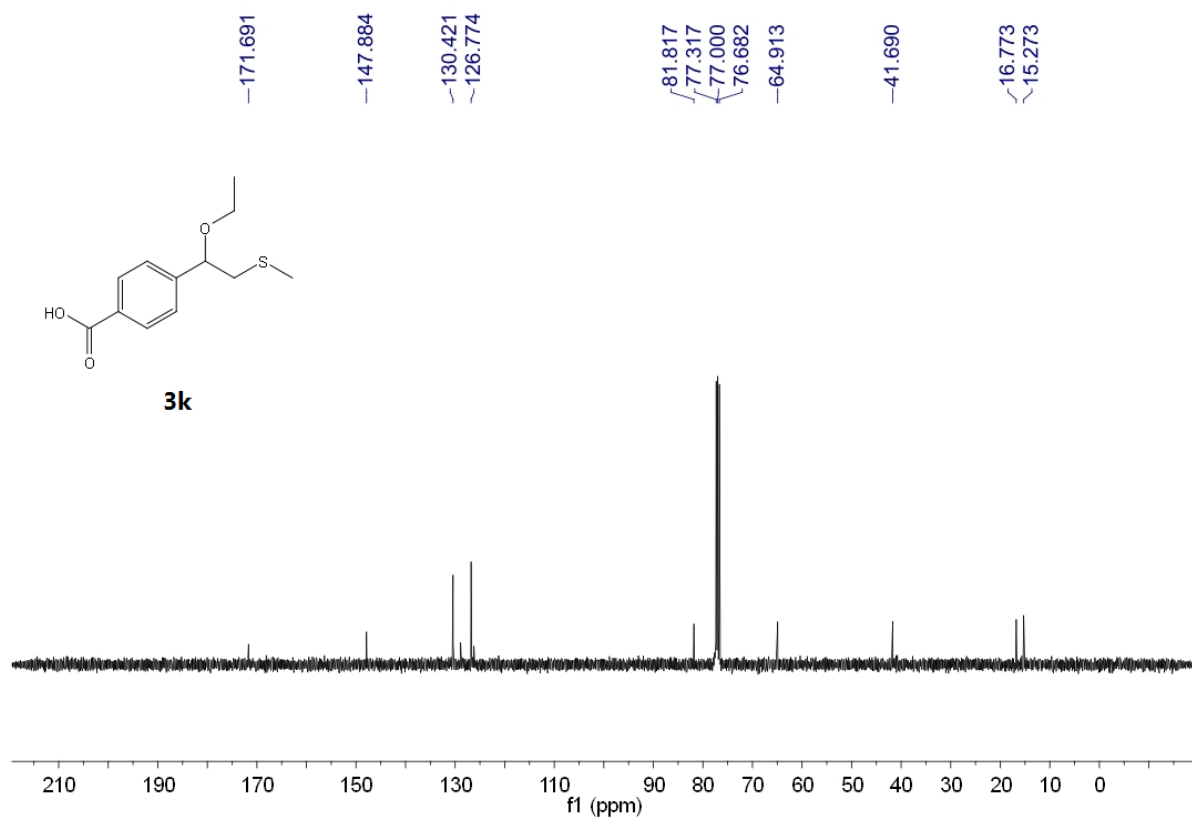


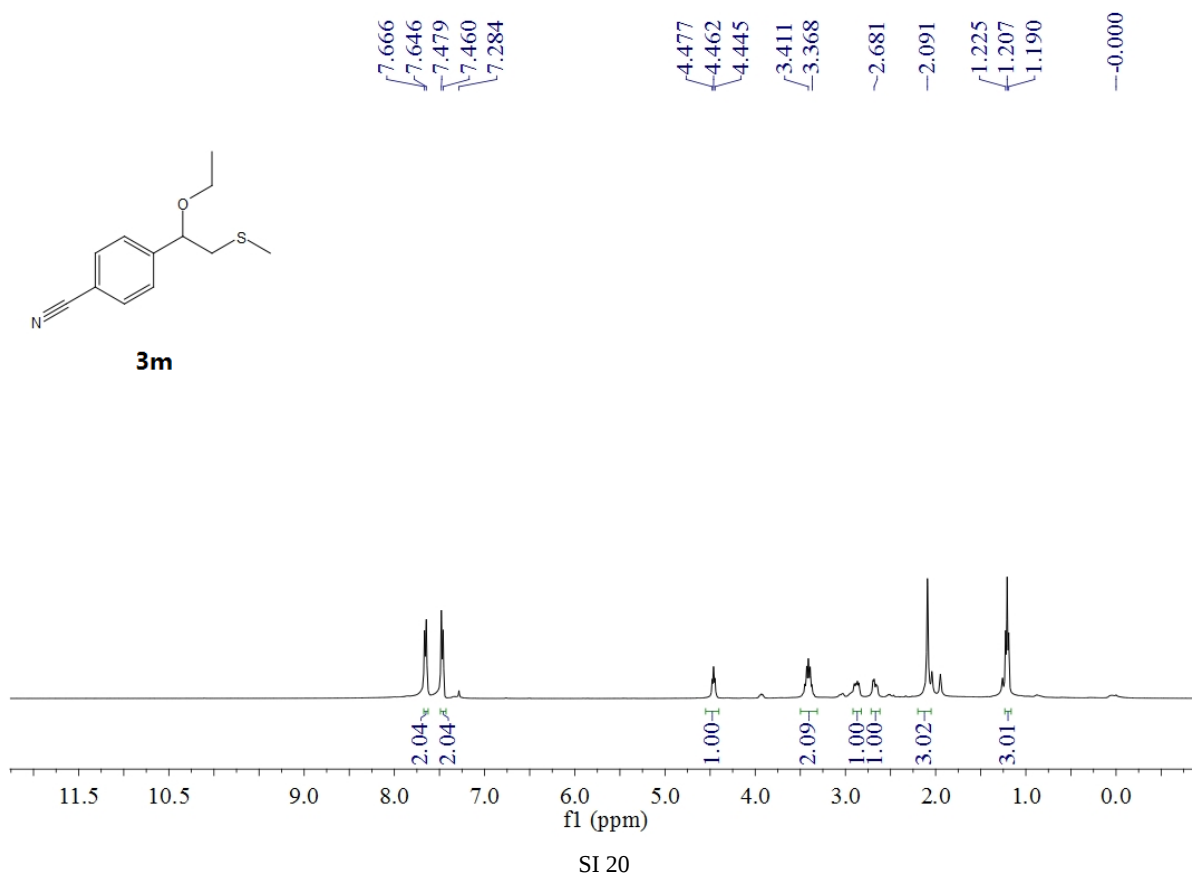
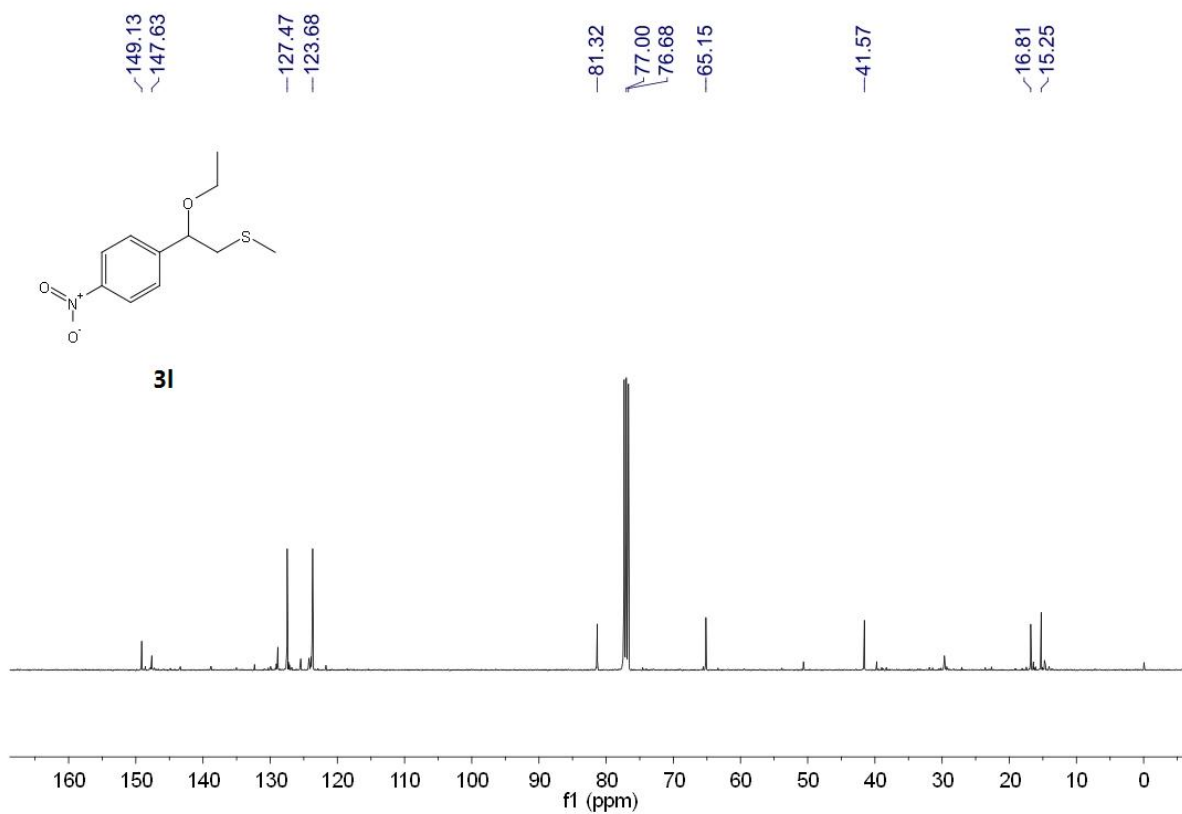


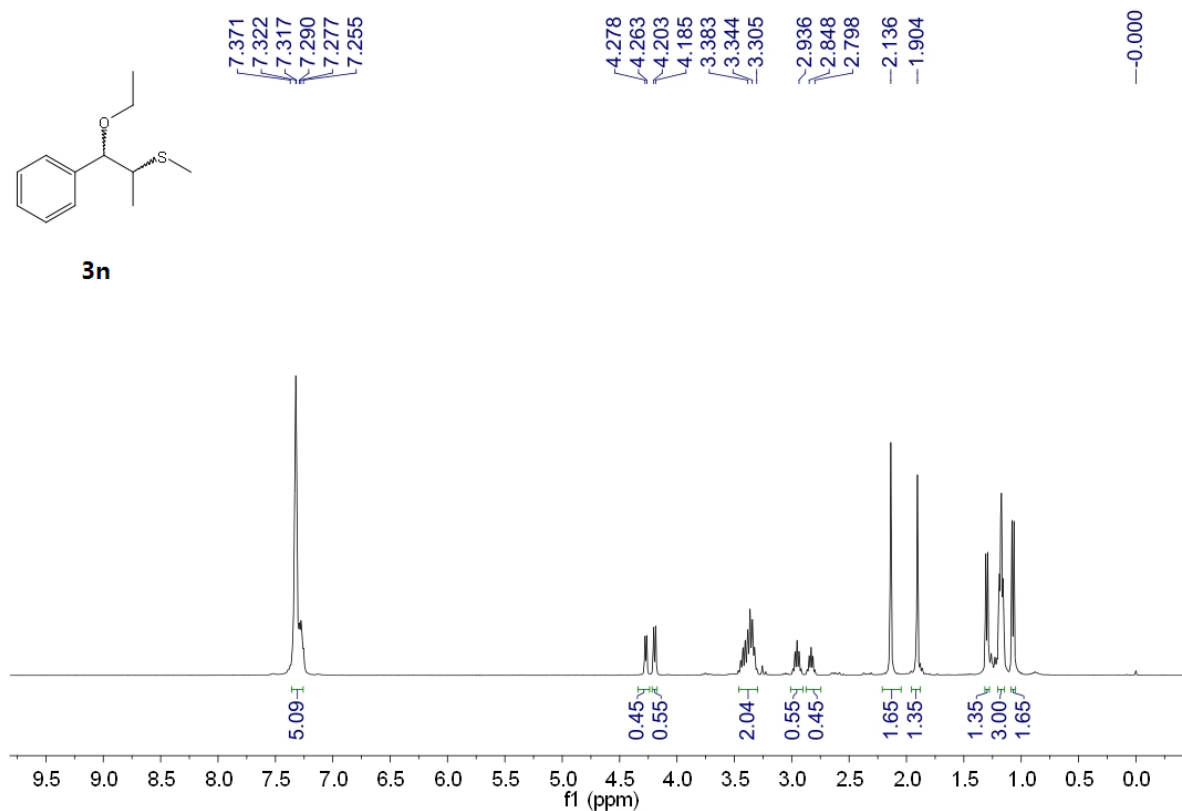
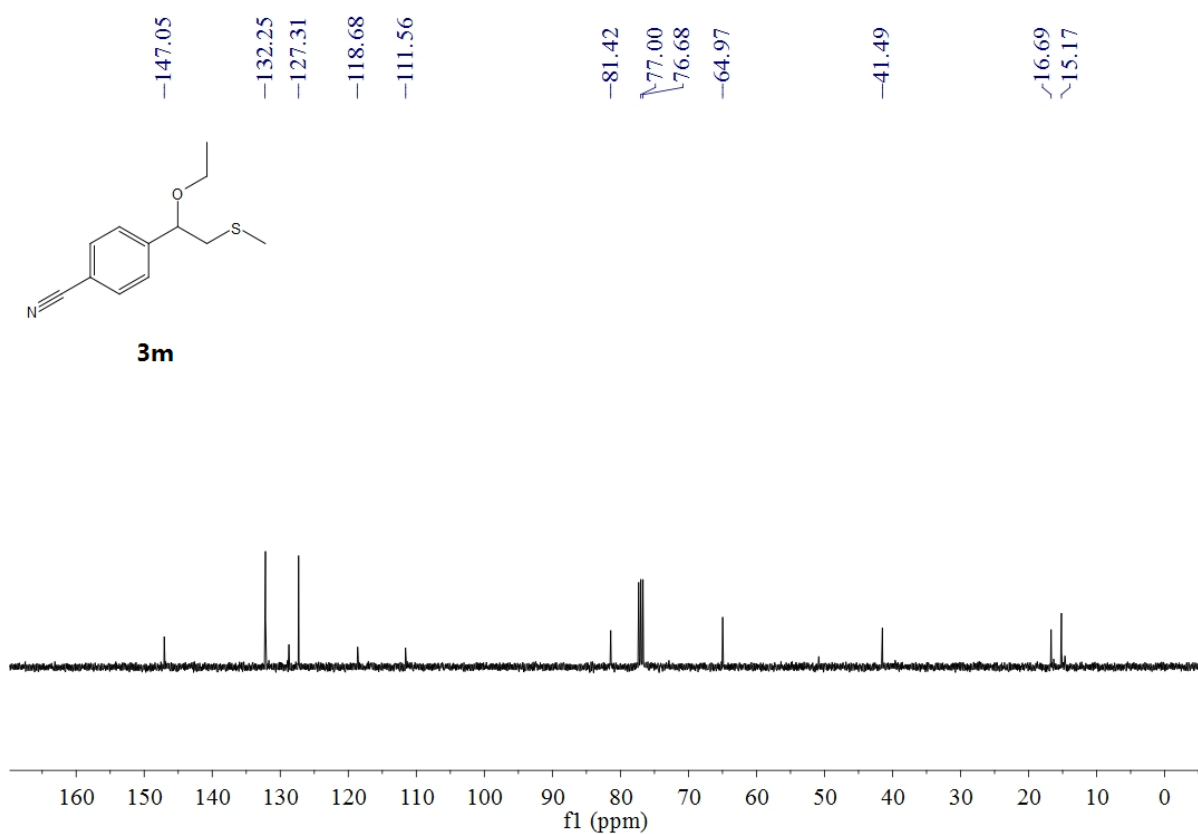


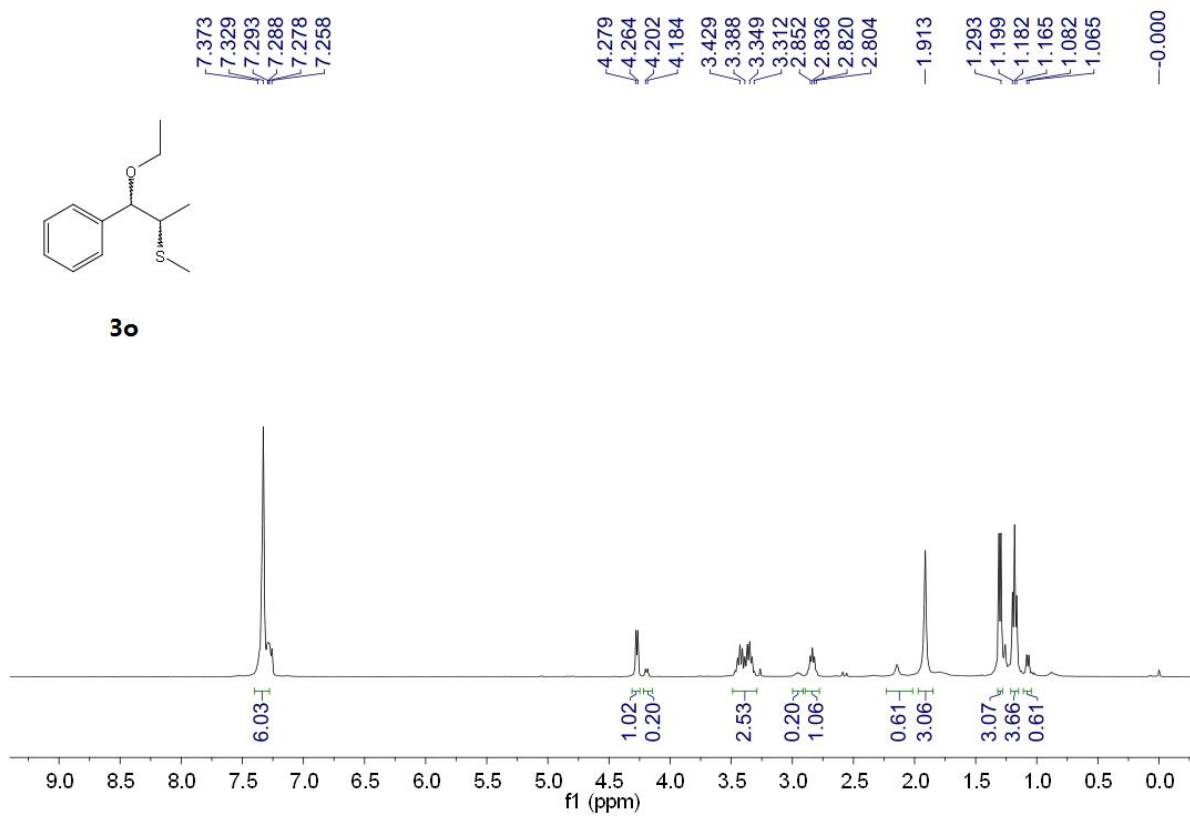
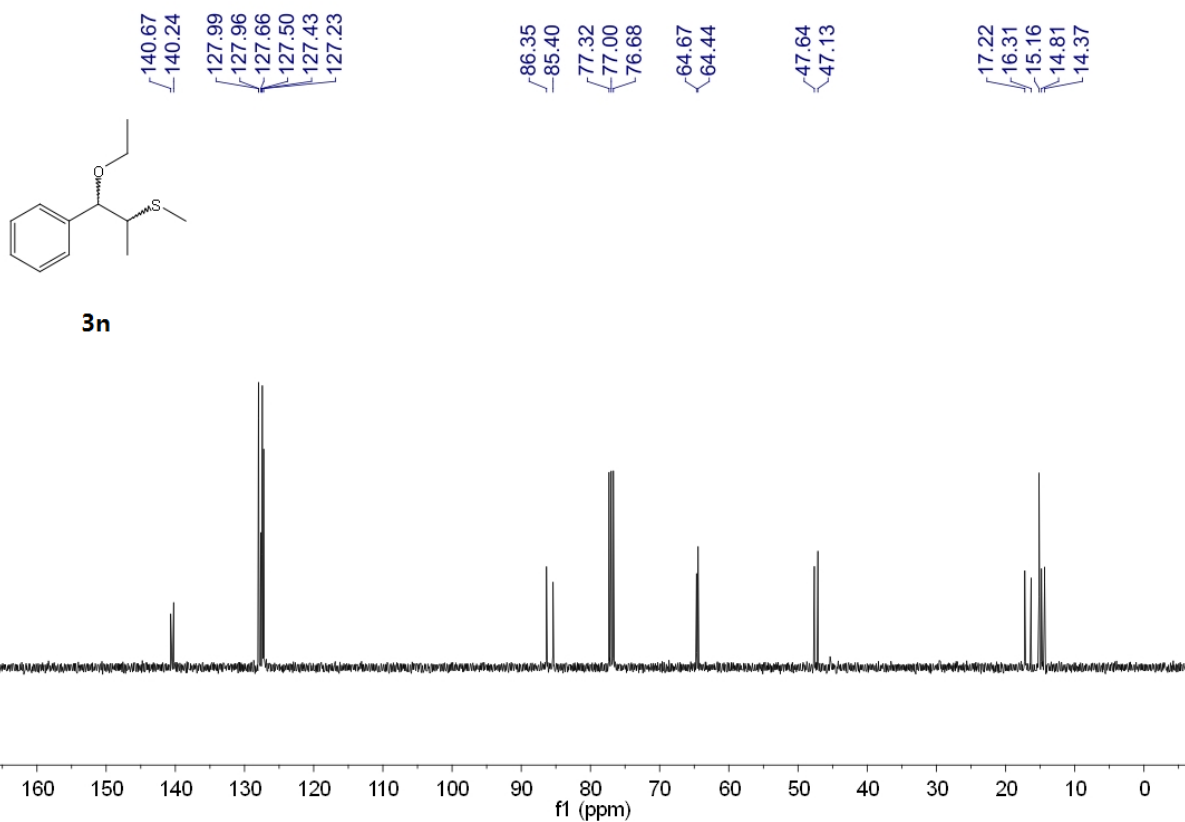


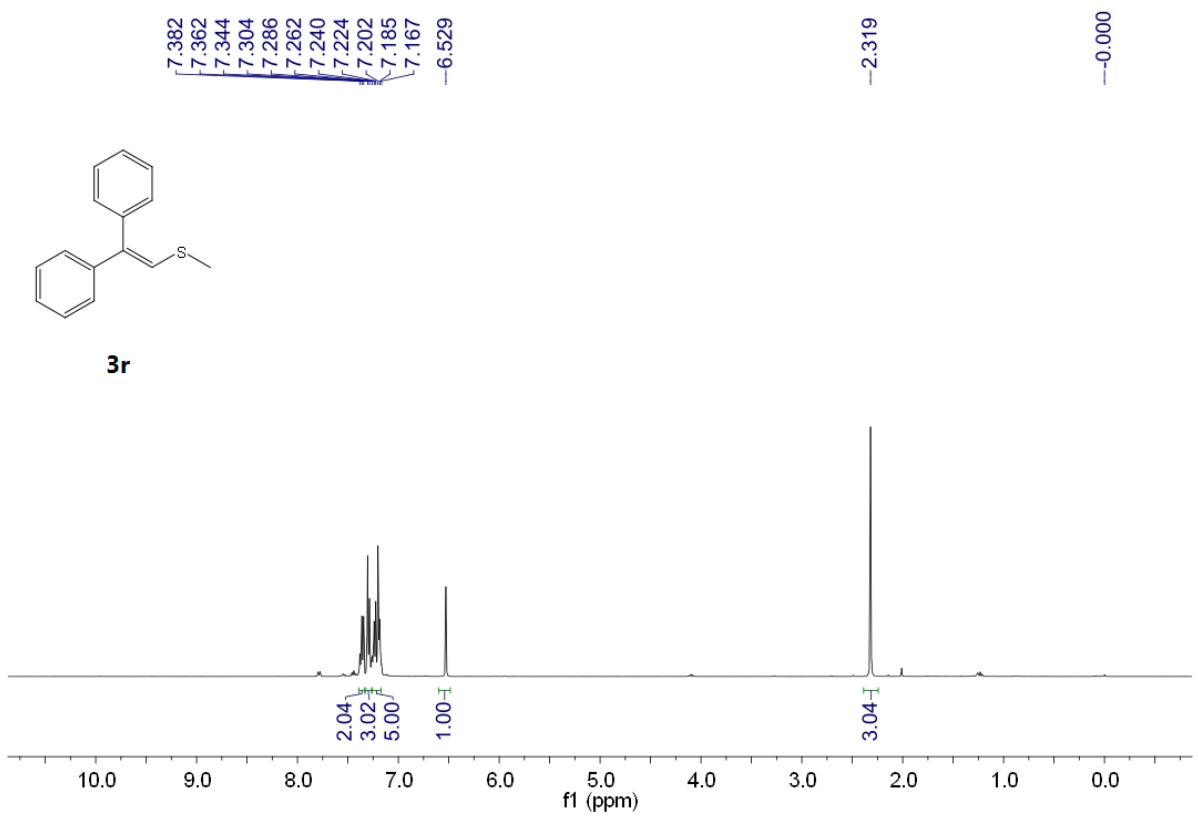
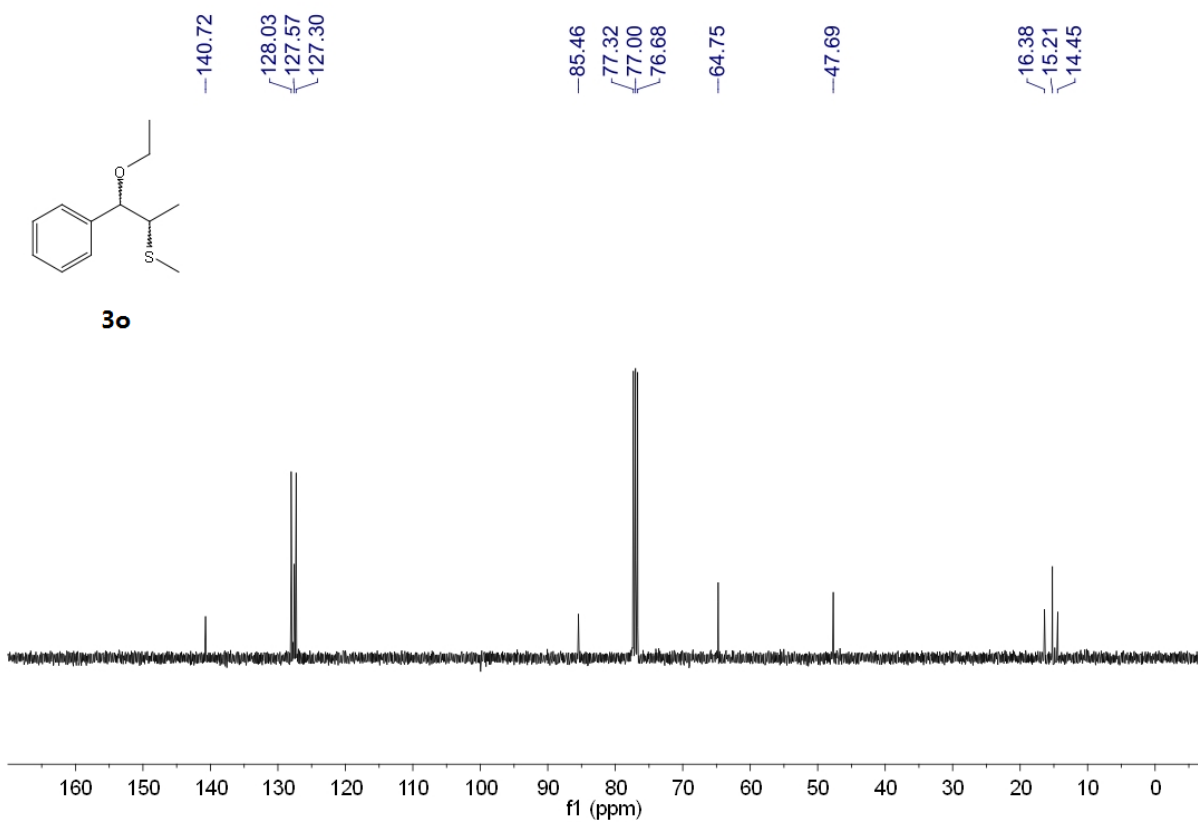


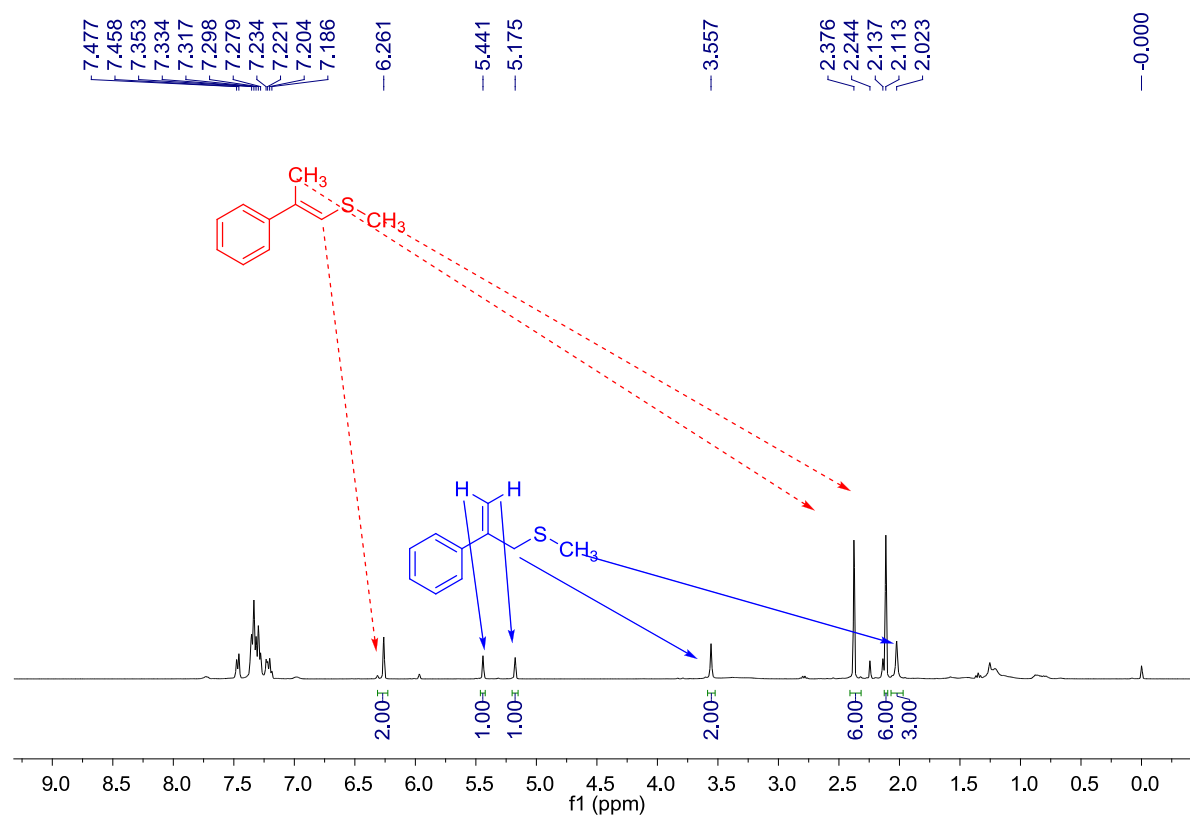
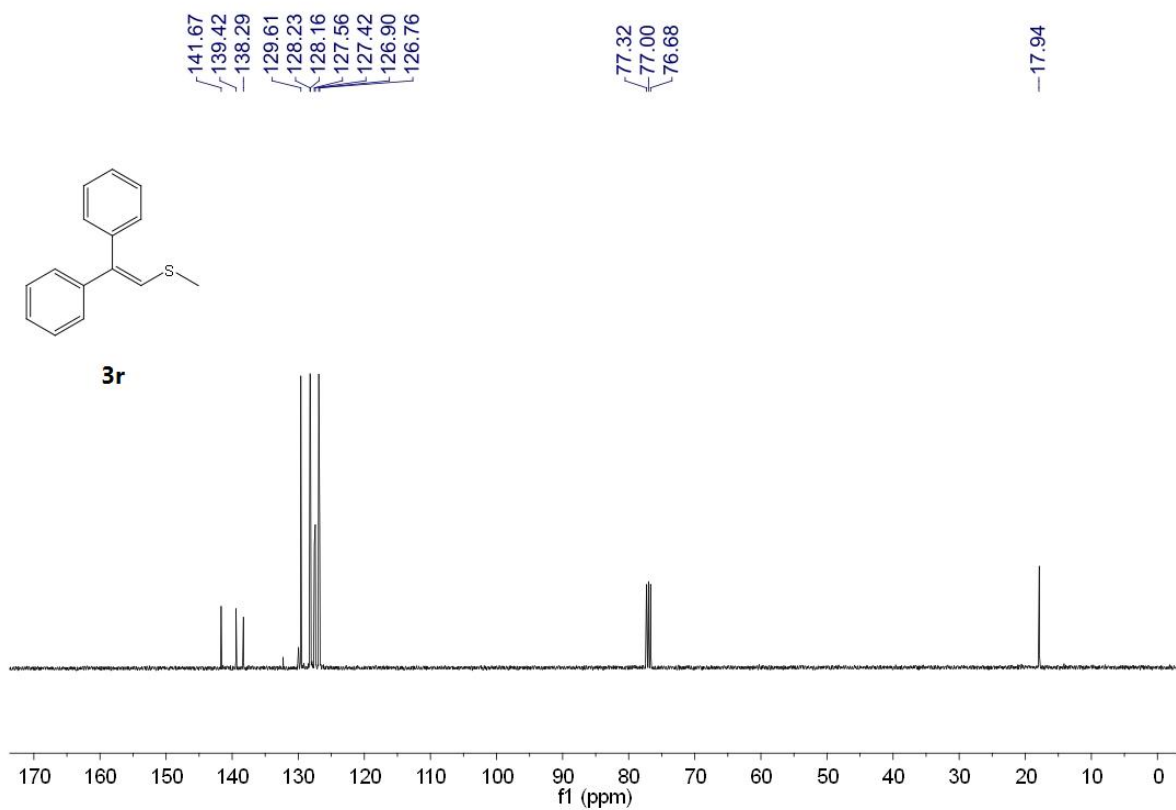


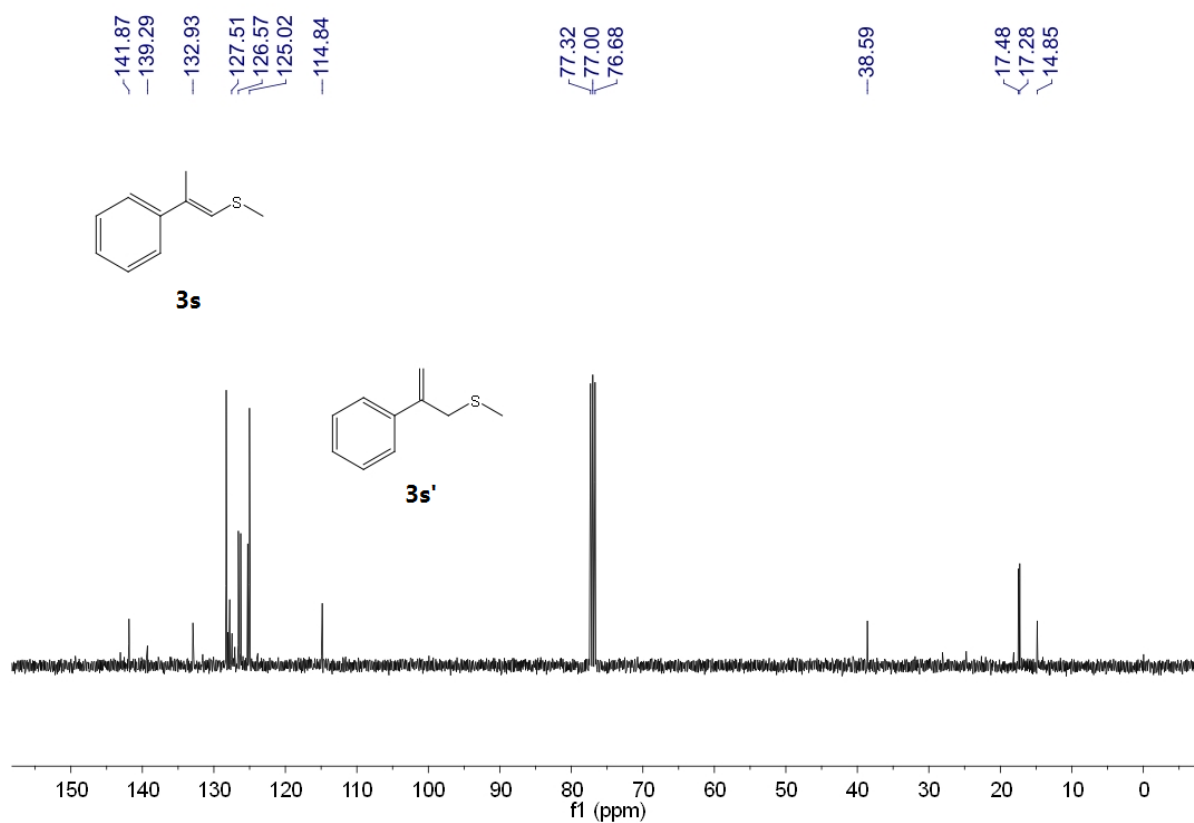
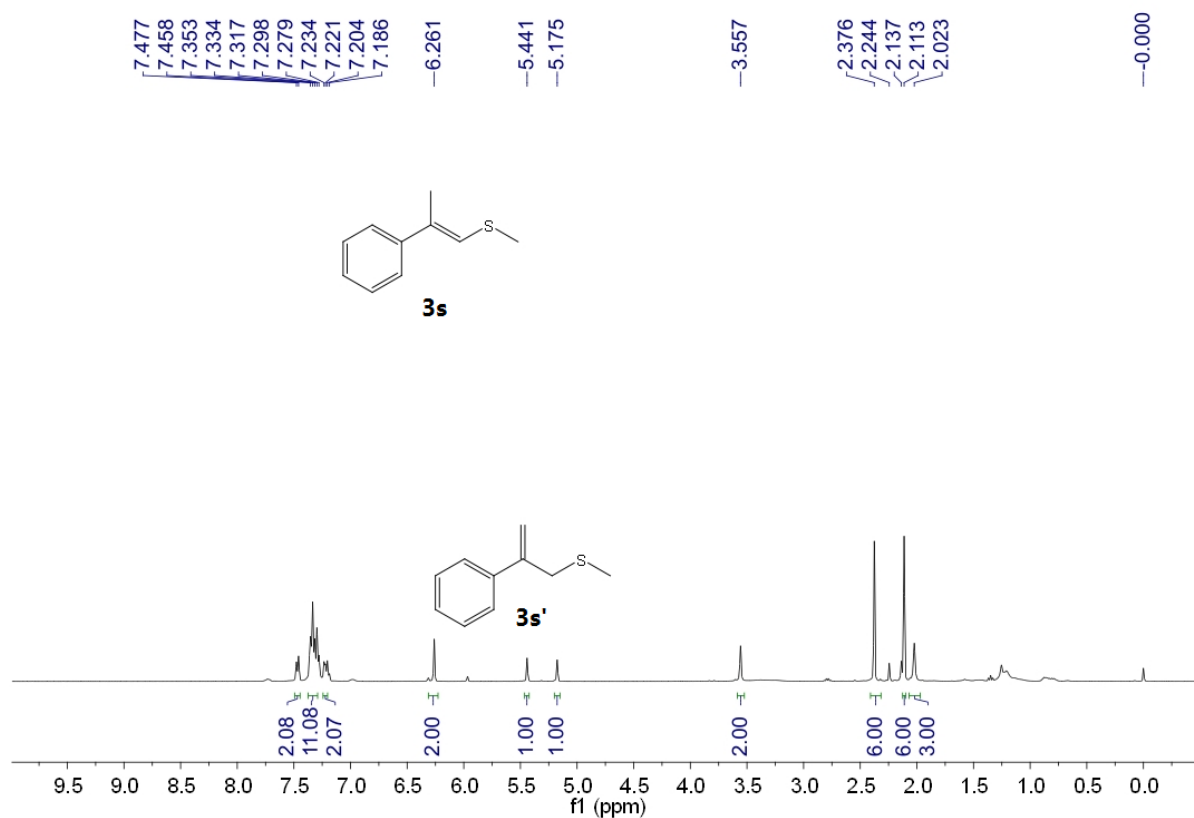


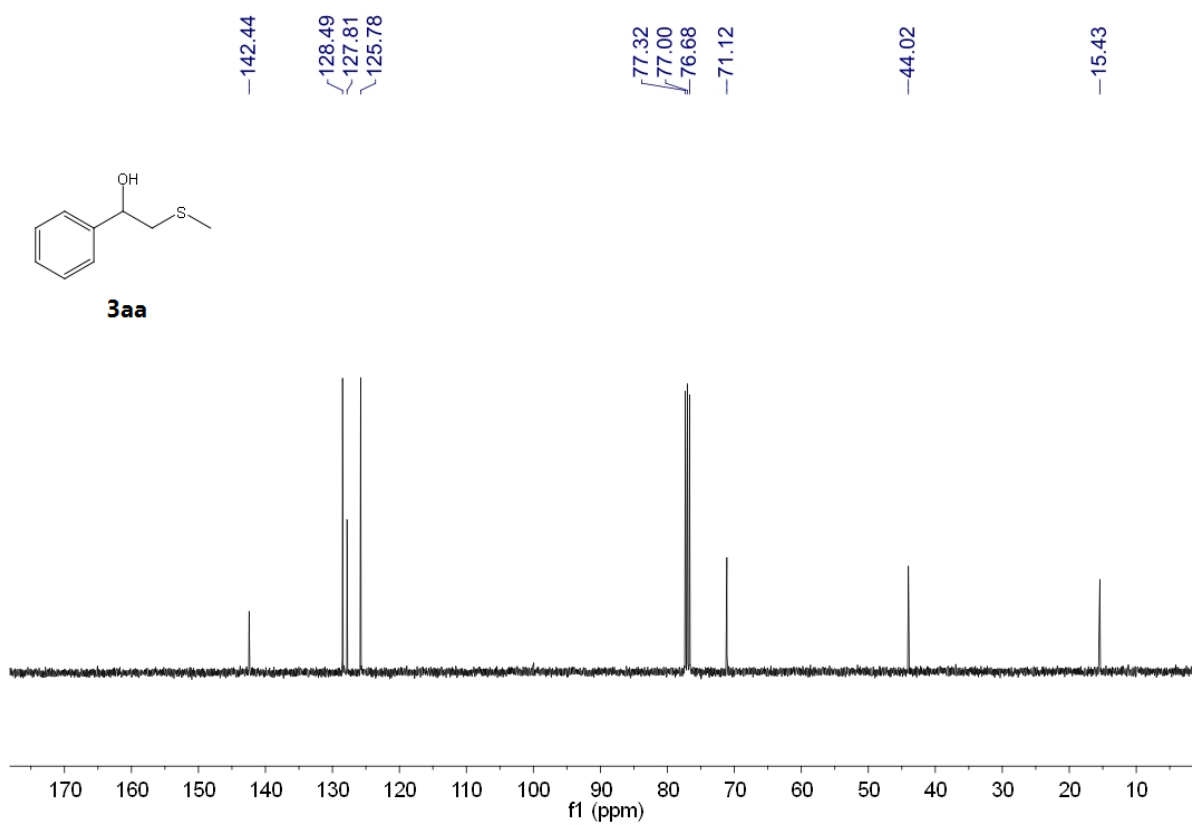
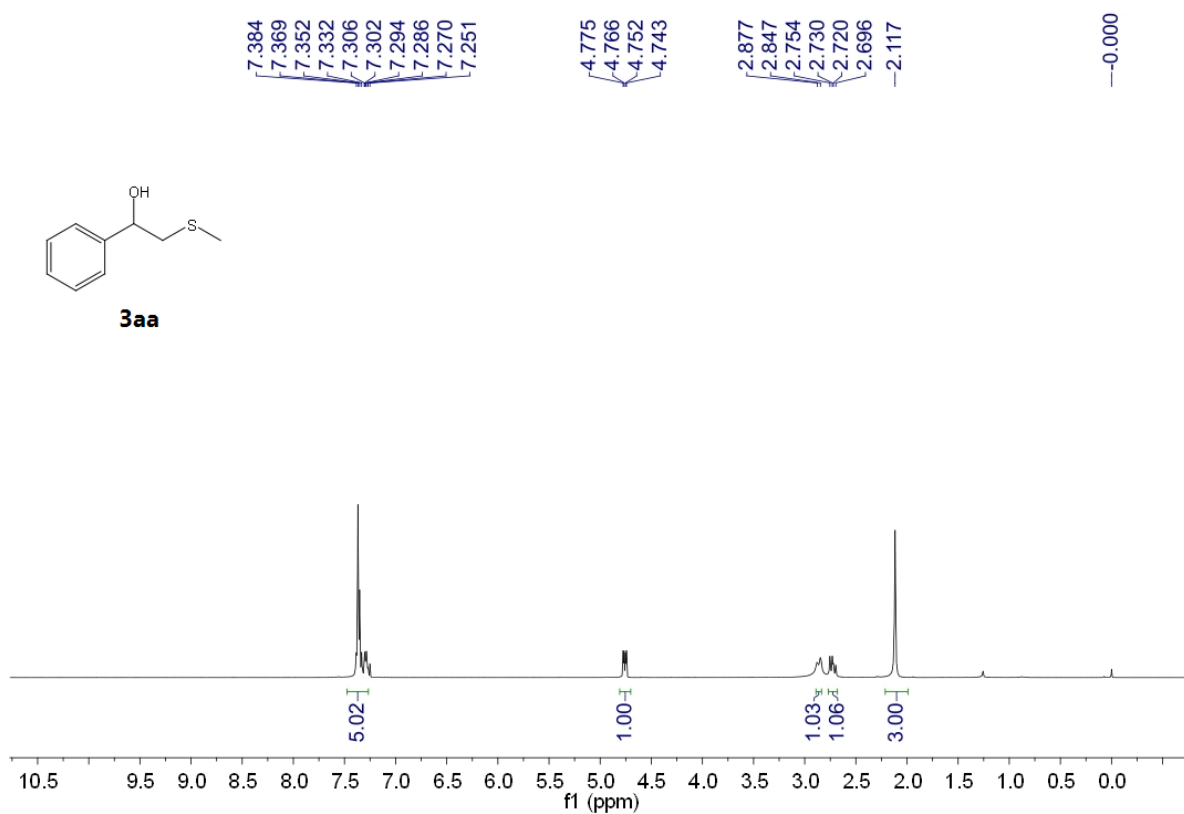


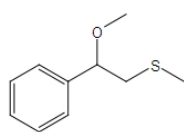




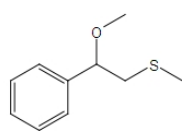
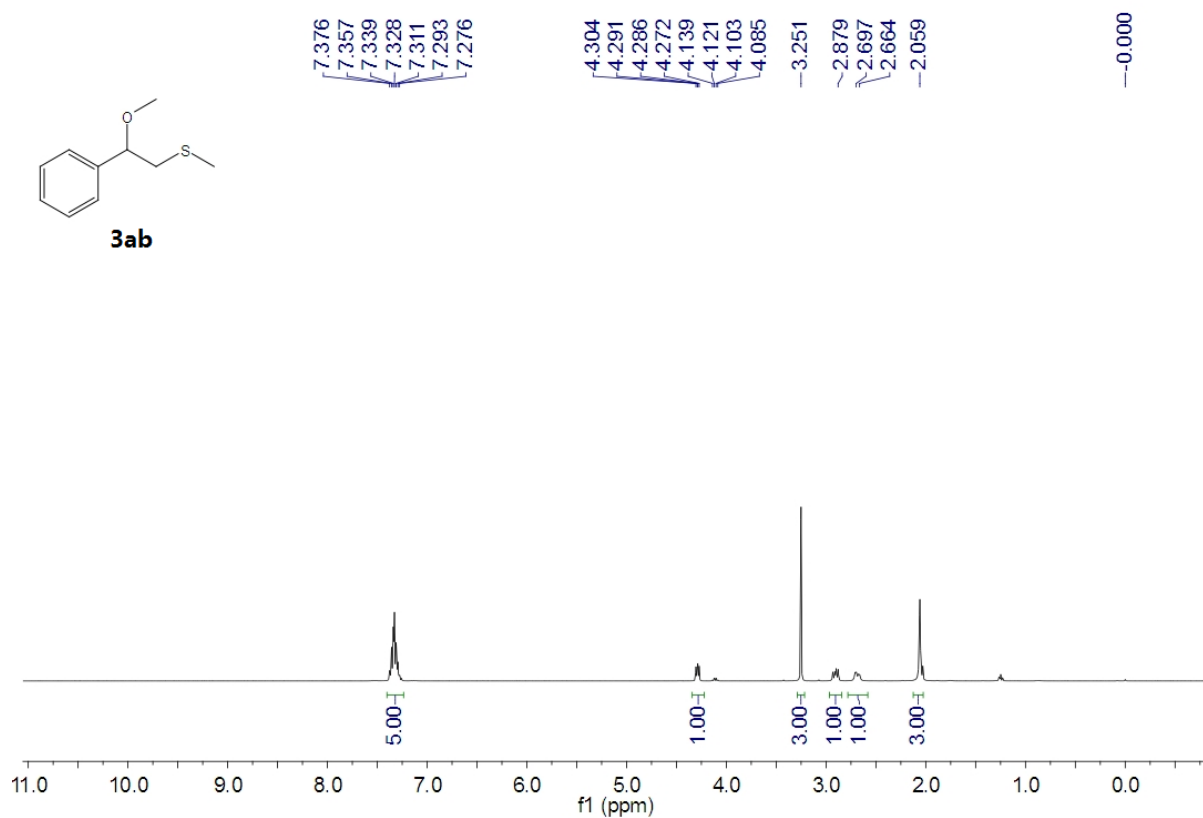








3ab



3ab

