

***tert*-Butyl nitrite-mediated vicinal sulfoximation of alkenes  
with sulfinic acids: a highly efficient approach toward  
 $\alpha$ -sulfonyl ketoximes**

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## General:

All reagents were purchased from commercial suppliers and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Melting points were determined without correction on a digital melting-point apparatus.  $^1\text{H}$  NMR (400 MHz) and  $^{13}\text{C}$  NMR (100.6 MHz) spectra were recorded in  $\text{CDCl}_3$ ,  $\text{DMSO}-d_6$  and  $\text{Acetone}-d_6$ . Chemical shifts ( $\delta$ ) are reported in ppm using TMS as internal standard and spin-spin coupling constants ( $J$ ) are given in Hz. EI-MS spectra were measured on a TRACE DSQ spectrometer by direct inlet at 70 eV. The high-resolution mass spectra (HRMS) were measured on a Bruker Daltonics APEX II 47e spectrometer by ESI. Data collections for crystal structure were performed at room temperature (293 K) using  $\text{MoK}\alpha$  radiation on a Bruker APEXII diffractometer. Integration of the frames and data reduction was carried out using SAINT. The structure was solved by direct methods using SHELXS-97.

## General experimental procedure:

### Typical experimental procedure for TBN-mediated vicinal sulfoximation of alkenes:

A 25 mL oven-dried round-bottom flask were charged with sulfinic acids **2** (0.3 mmol, 1.0 equiv.),  $\text{CHCl}_3$  (2 ml), pyridine (0.3 mmol, 1.0 equiv.), alkenes **1** (0.6 mmol, 2.0 equiv.) and TBN (0.6 mmol, 2.0 equiv.) under Argon (1 atm). The round-bottom flask was then sealed and the mixture was stirred at room temperature for 5 h. Upon completion of the reaction, the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/20 to 1/1) to give the corresponding products **4** or **5** in yields listed in Table 2 and Table 3. The identity and purity of the product was confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic analysis.

### Follow-up transformations of $\alpha$ -sulfonyl ketoxime:

#### Acetylation of **4a** to synthesize product **6**

The mixture of **4a** (0.5 mmol), acetic anhydride (1.0 mmol, 2.0 equiv.), was stirred at

room temperature to 100 °C for 3h. The reaction mixture was cooled to room temperature, diluted with EtOAc (20 mL) and washed with H<sub>2</sub>O (10 mL) and brine (10 mL). The organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the product **6** with hexane/ethyl acetate as the eluent.<sup>1</sup>

#### **Deoxygenation of 4a to synthesize product 7**

To a stirred solution of **4a** (0.2 mmol) in DCM saturated with water prior to use (1 mL, DCM was saturated by shaking with equal amount of water and allowed to settle for 30 minutes before draining the aqueous layer) was added Dess-Martin periodinane (0.22 mmol) at room temperature. As soon as the reaction was complete (as indicated by TLC), the reaction mixture was diluted with 5% aqueous sodium hydroxide solution (5 mL) and DCM (20 mL) followed by water (10 mL). The organic layer was washed with water (10 mL), dried over sodium sulphate and evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the product **7** with hexane/ethyl acetate as the eluent.<sup>2</sup>

#### **Beckman rearrangement of 4a to synthesize product 8**

To a solution of **4a** (0.2 mmol) in anhydrous CH<sub>3</sub>CN (1 mL), 0.1 mL of BF<sub>3</sub>•OEt<sub>2</sub> in CH<sub>3</sub>CN (borontrifluoride etherate in CH<sub>3</sub>CN solvent, 0.2 mol/L) was added. The mixture was refluxed for 3 h under an Argon atmosphere. After the reaction had been completed, the organic layer was diluted with 10 mL of ethyl acetate, washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting crude product was purified by silica gel column chromatography with hexane/ethyl acetate as the eluent.<sup>3</sup>

#### **Synthesis of (3-phenyl-2-(phenylsulfonyl)-2H-azirine) 9 from 4a**

To a solution of **4a** (1 mmol) in methylene chloride (5 mL) was added triethylamine (0.56 mL, 4 mmol). The solution was cooled to 0 °C under an Argon atmosphere, and trifluoroacetic anhydride (0.17 mL, 1.2 mmol) was added dropwise. The reaction was stirred for 0.5 h then quenched with water. The organic layer was separated and dried (MgSO<sub>4</sub>). The drying agent was removed by filtration and the solvent was evaporated. The resulting crude product was purified by silica gel column chromatography with

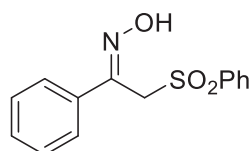
hexane/ethyl acetate as the eluent.<sup>4</sup>

## References:

- [1] L.-F. Ran, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *Green Chem.*, 2014, **16**, 112.  
[2] S. S. Chaudhari and K. G. Akamanchi, *Tetrahedron Lett.*, 1998, **39**, 3209.  
[3] N. An, H.-J. Pi, L.-F. Liu, W.-T. Du and W.-P. Deng, *Chin. J. Chem.*, 2011, **29**, 947.  
[4] K. L. Stevens, D. K. Jung, M. J. Alberti, J. G. Badiang, G. E. Peckham, J. M. Veal, M. Cheung, P. A. Harris, S. D. Chamberlain and M. R. Peel, *Org. Lett.*, 2005, **7**, 4753.

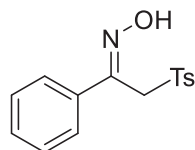
## Analytical Data for Products:

### **1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (4a)**



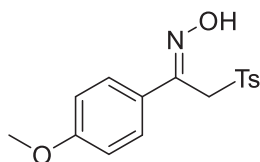
White solid; (72 mg, 87%); mp: 123–124 °C;  $R_f$  = 0.17 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.13 (brs, 1H), 7.84 (d,  $J$  = 7.6 Hz, 2H), 7.61 (m, 2H), 7.56 (d,  $J$  = 7.6 Hz, 1H), 7.41–7.47 (m, 2H), 7.34–7.40 (m, 3H), 4.75 (s, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.0, 139.5, 133.8, 133.5, 133.0, 128.8, 128.6, 128.5, 122.6, 52.7; MS  $m/z$  (relative intensity, %): 275 (8.12), 211 (40.7), 196 (40.9), 143 (58.0), 105 (88.5), 103 (69.1), 77 (100); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}+\text{Na}]^+$ : 298.0508, found 298.0509.

### **1-phenyl-2-tosylethan-1-one oxime (4b)**



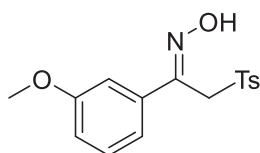
White solid; (74 mg, 86%); mp: 139–141 °C;  $R_f$  = 0.21 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  11.77 (s, 1H), 7.61–7.65 (m, 4H), 7.35–7.37 (m, 5H), 4.90 (s, 2H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  145.6, 144.3, 136.9, 134.5, 129.4, 128.9, 128.2, 127.8, 126.4, 51.5, 21.0; MS  $m/z$  (relative intensity, %): 289 (0.1), 227 (27.2), 134 (23.3), 121 (30.8), 103 (100), 77 (29.6); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}+\text{Na}]^+$ : 312.0665, found 312.0667.

### **1-(4-methoxyphenyl)-2-tosylethan-1-one oxime (4c)**



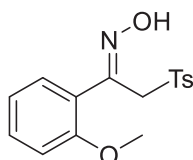
White solid; (83 mg, 87%); mp: 140–141 °C;  $R_f$  = 0.06 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.27 (brs, 1H), 7.71 (d,  $J$  = 8.4 Hz, 2H), 7.57 (d,  $J$  = 8.8 Hz, 2H), 7.23 (d,  $J$  = 8.4 Hz, 2H), 6.87 (d,  $J$  = 8.8 Hz, 2H), 4.70 (s, 2H), 3.83 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.0, 147.5, 144.8, 136.6, 129.4, 128.5, 128.1, 126.1, 114.0, 55.3, 52.7, 21.6; MS  $m/z$  (relative intensity, %): 319 (0.1), 240 (11.2), 135 (100), 133 (21.9), 91 (7.4), 77 (6.7); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{16}\text{H}_{17}\text{NO}_4\text{S}+\text{Na}]^+$ :342.0770, found 342.0772.

**1-(3-methoxyphenyl)-2-tosylethan-1-one oxime (4d)**



White solid; (79 mg, 83%); mp: 104–105 °C;  $R_f$  = 0.21 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.54 (brs, 1H), 7.71 (d,  $J$  = 8.4 Hz, 2H), 7.16–7.28 (m, 5H), 6.92–6.95(m, 1H), 4.71 (s, 2H), 3.80 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.6, 147.8, 144.9, 136.5, 135.0, 129.6, 129.4, 128.4, 119.2, 115.8, 111.2, 55.3, 52.9, 21.6; MS  $m/z$  (relative intensity, %): 319 (39.4), 255 (20.8), 238 (19.3), 157 (32.8), 147 (16.2), 139(41.6), 133(100), 91 (23.0); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{16}\text{H}_{17}\text{NO}_4\text{S}+\text{Na}]^+$ : 342.0770, found 342.0768.

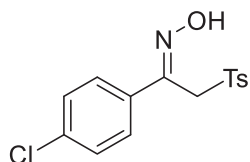
**1-(2-methoxyphenyl)-2-tosylethan-1-one oxime (4e)**



White solid; (75 mg, 78%); mp: 112–114 °C;  $R_f$  = 0.27 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.19 (brs, 1H), 7.59 (d,  $J$  = 8.0 Hz, 2H), 7.30–7.34 (m, 1H), 7.23–7.26 (m, 1H), 7.16 (d,  $J$  = 8.0 Hz, 2H), 6.91–6.95 (m, 1H), 6.74 (d,  $J$  = 8.0 Hz, 1H), 4.93 (s, 2H), 3.73 (s, 3H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.0, 148.7, 144.3,

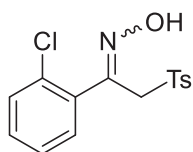
136.7, 131.1, 130.8, 129.2, 128.2, 122.9, 120.8, 110.8, 55.3, 53.3, 21.6; MS  $m/z$  (relative intensity, %): 319(1.6), 304 (9.0), 240 (3.6), 135 (100), 91(12.2); ESI–HRMS:  $m/z$  Calcd for  $[C_{16}H_{17}NO_4S+Na]^+$ : 342.0770, found 342.0773.

**1-(4-chlorophenyl)-2-tosylethan-1-one oxime (4f)**



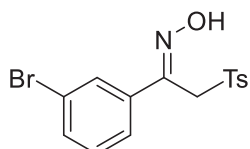
White solid; (79 mg, 82%); mp: 144–145 °C;  $R_f$  = 0.30 (hexanes/ethyl acetate 3:1);  $^1H$  NMR (400 MHz, Acetone- $d_6$ ):  $\delta$  11.03 (brs, 1H), 7.67–7.73 (m, 4H), 7.34–7.39 (m, 4H), 4.86 (s, 2H), 2.41 (s, 3H);  $^{13}C$  NMR (100.6 MHz, Acetone- $d_6$ ):  $\delta$  146.7, 145.7, 138.3, 135.4, 134.6, 130.3, 129.24, 129.17, 52.5, 21.6; MS  $m/z$  (relative intensity, %): 323 (7.4), 261(11.6), 259 (12.4), 157 (69.9), 139 (100), 91 (55.3); ESI–HRMS:  $m/z$  Calcd for  $[C_{15}H_{14}ClNO_3S+Na]^+$ : 346.0275, found 346.0276.

**1-(2-chlorophenyl)-2-tosylethan-1-one oxime (4g)**



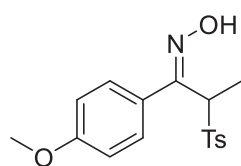
Colourless oil; (74 mg, 76%); (Z/E mixture; 1:0.7);  $R_f$  = 0.21 (hexanes/ethyl acetate 3:1); Major:  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  8.95 (brs, 1H), 7.67 (d,  $J$  = 8.0 Hz, 2H), 7.33–7.36 (m, 2H), 7.27–7.32 (m, 2H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 4.83 (s, 2H), 2.38 (s, 3H); Minor:  $^1H$  NMR (400 MHz,  $CDCl_3$ ): 8.67 (brs, 1H), 7.71 (d,  $J$  = 8.0 Hz, 2H), 7.27–7.32 (m, 6H), 4.36 (s, 2H), 2.40 (s, 3H);  $^{13}C$  NMR (100.6 MHz,  $CDCl_3$ ):  $\delta$  147.9, 146.8, 145.0, 144.8, 136.8, 135.8, 133.2, 132.3, 131.8, 131.1, 130.9, 130.7, 130.6, 130.5, 129.7, 129.8, 129.7, 129.4, 128.2, 128.0, 126.9, 126.5, 60.5, 54.0, 21.58, 21.55; MS  $m/z$  (relative intensity, %): 323 (1.4), 288 (100), 259 (34.7), 242 (34.2), 157 (79.5), 139 (97.3), 137 (86.1), 91 (54.8); ESI–HRMS:  $m/z$  Calcd for  $[C_{15}H_{14}ClNO_3S+Na]^+$ : 346.0275, found 346.0276.

**1-(3-bromophenyl)-2-tosylethan-1-one oxime (4h)**



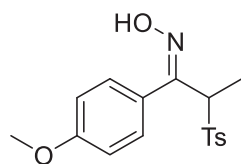
White solid; (82 mg, 75%); mp: 107–108 °C;  $R_f$  = 0.38 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.37 (brs, 1H), 7.66–7.71 (m, 3H), 7.57 (d,  $J$  = 7.6 Hz, 1H), 7.49 (d,  $J$  = 8.0 Hz, 1H), 7.20–7.26 (m, 3H), 4.69 (s, 2H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.7, 145.1, 136.3, 135.6, 132.6, 130.0, 129.6, 129.4, 128.4, 125.4, 122.7, 52.5, 21.6; MS  $m/z$  (relative intensity, %): 368(1.8), 304 (9.9), 303 (35.8), 197 (26.6), 183 (33.7), 157 (100), 155 (37.9), 139 (96.4), 102 (26.4), 77 (71.9); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{15}\text{H}_{14}\text{BrNO}_3\text{S}+\text{Na}]^+$ : 389.9770, found 389.9771.

**(Z)-1-(4-methoxyphenyl)-2-tosylpropan-1-one oxime (4i)**



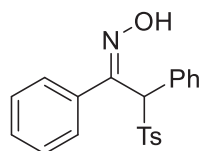
White solid; (43 mg, 43%); mp: 133–134 °C;  $R_f$  = 0.29 (hexanes/ethyl acetate 2:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.85 (brs, 1H), 7.70 (d,  $J$  = 8.4 Hz, 2H), 7.36 (d,  $J$  = 8.8 Hz, 2H), 7.27 (d,  $J$  = 8.0 Hz, 2H), 6.86 (d,  $J$  = 8.8 Hz, 2H), 4.30 (q,  $J$  = 7.2 Hz, 1H), 3.81 (s, 3H), 2.40 (s, 3H), 1.59 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.1, 151.6, 144.8, 134.3, 129.8, 129.5, 129.3, 124.2, 113.5, 65.2, 55.2, 21.6, 14.0; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{17}\text{H}_{19}\text{NO}_4\text{S}+\text{H}]^+$ : 334.1108, found 334.1110.

**(E)-1-(4-methoxyphenyl)-2-tosylpropan-1-one oxime (4i')**



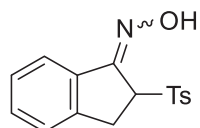
White solid; (35 mg, 35%); mp: 113–114 °C;  $R_f$  = 0.35 (hexanes/ethyl acetate 2:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94 (brs, 1H), 7.81 (d,  $J$  = 8.0 Hz, 2H), 7.67 (d,  $J$  = 8.8 Hz, 2H), 7.28 (d,  $J$  = 8.0 Hz, 2H), 6.92 (d,  $J$  = 8.8 Hz, 2H), 5.32 (q,  $J$  = 7.2 Hz, 1H), 3.84 (s, 3H), 2.40 (s, 3H), 1.51 (d,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.6, 152.9, 144.8, 136.0, 129.9, 129.5, 128.8, 125.5, 113.8, 57.5, 55.3, 21.6, 12.2; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{17}\text{H}_{19}\text{NO}_4\text{S}+\text{H}]^+$ : 334.1108, found 334.1109.

**1,2-diphenyl-2-tosylethan-1-one oxime (4j)**



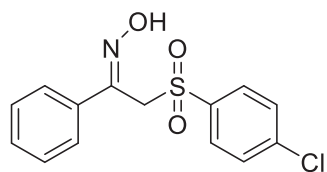
White solid; (83 mg, 76%); mp: 132–133 °C;  $R_f$  = 0.25 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.32 (s, 1H), 7.55 (d,  $J$  = 8.0 Hz, 2H), 7.41 (d,  $J$  = 7.2 Hz, 2H), 7.27–7.32 (m, 6H), 7.18–7.22 (m, 4H), 5.19 (s, 1H), 2.40 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.0, 144.7, 135.1, 133.0, 130.9, 129.9, 129.6, 129.28, 129.25, 129.2, 128.5, 128.3, 127.6, 75.3, 21.6; MS  $m/z$  (relative intensity, %): 365 (0.2), 210 (100), 193 (20.0), 179 (25.2), 132 (27.5), 91 (13.8), 77 (11.2); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{19}\text{NO}_3\text{S}+\text{Na}]^+$ : 388.0978, found 388.0979.

**2-tosyl-2,3-dihydro-1H-inden-1-one oxime (4k)**



White solid; (78 mg, 86%); (Z/E mixture; 1:0.62);  $R_f$  = 0.12 (hexanes/ethyl acetate 3:1); Major:  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ):  $\delta$  10.81 (brs, 1H), 8.29 (d,  $J$  = 7.6 Hz, 1H), 7.70–7.73 (m, 2H), 7.30–7.39 (m, 4H), 7.22–7.28 (m, 1H), 4.59 (dd,  $J$  = 2.4 Hz,  $J$  = 8.4 Hz, 1H), 3.53–3.69 (m, 2H), 2.39 (s, 3H); Minor:  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ): 10.30 (s, 1H), 7.70–7.73 (m, 2H), 7.50 (d,  $J$  = 7.6 Hz, 1H), 7.30–7.39 (m, 4H), 7.22–7.28 (m, 1H), 5.17 (dd,  $J$  = 1.2 Hz,  $J$  = 8.0 Hz, 1H), 3.41–3.51 (m, 2H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz, Acetone- $d_6$ ):  $\delta$  154.2, 153.3, 146.0, 145.4, 145.33, 145.27, 137.9, 137.0, 136.0, 134.3, 131.8, 131.0, 130.2, 130.1, 129.8, 129.7, 128.1, 127.8, 126.01, 125.98, 122.0, 66.2, 64.6, 32.3, 31.6, 21.6, 21.5; MS  $m/z$  (relative intensity, %): 301 (1.9), 237 (67.2), 220 (41.5), 157 (24.1), 145 (81.2), 128 (100), 105 (32.3), 91 (22.4), 77 (19.0); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{16}\text{H}_{15}\text{NO}_3\text{S}+\text{Na}]^+$ : 324.0665, found 324.0668.

**2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one oxime (4l)**

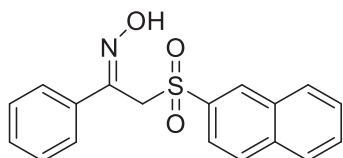


White solid; (82 mg, 88%); mp: 101–102 °C;  $R_f$  = 0.34 (hexanes/ethyl acetate 3:1);  $^1\text{H}$



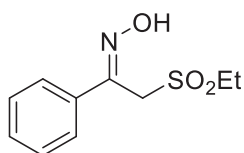
NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.70 (brs, 1H), 7.74 (d,  $J$  = 8.4 Hz, 2H), 7.57 (m,  $J$  = 6.8 Hz, 2H), 7.34–7.43 (m, 5H), 4.74 (s, 2H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  147.6, 140.6, 137.7, 133.3, 130.1, 130.0, 129.1, 128.7, 126.5, 52.8; MS  $m/z$  (relative intensity, %): 309 (0.6), 230 (31.0), 128 (22.5), 111 (18.6), 105 (100), 77 (33.4); ESI–HRMS:  $m/z$  Calcd for [C<sub>14</sub>H<sub>12</sub>ClNO<sub>3</sub>S+Na]<sup>+</sup>: 332.0119, found 332.0117.

**2-(naphthalen-2-ylsulfonyl)-1-phenylethan-1-one oxime (4m)**



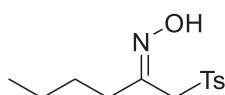
White solid; (82 mg, 84%); mp: 126–127 °C;  $R_f$  = 0.21 (hexanes/ethyl acetate 3:1); <sup>1</sup>H NMR (400 MHz, Acetone-*d*<sub>6</sub>):  $\delta$  10.81 (s, 1H), 8.40 (s, 1H), 8.01–8.40 (m, 3H), 7.84–7.87 (dd,  $J$  = 1.6,  $J$  = 8.4 Hz, 1H), 7.69–7.75 (m, 3H), 7.65–7.68 (m, 1H), 7.30–7.33 (m, 3H), 4.98 (s, 2H); <sup>13</sup>C NMR (100.6 MHz, Acetone-*d*<sub>6</sub>):  $\delta$  147.1, 138.1, 135.9, 135.4, 132.6, 130.5, 130.1, 129.7, 129.6, 129.5, 128.7, 128.4, 128.0, 127.2, 123.8, 52.3; MS  $m/z$  (relative intensity, %): 325 (19.1), 261 (28.1), 244 (74.0), 210 (43.9), 193 (43.8), 127(100), 103(42.3), 77 (30.2); ESI–HRMS:  $m/z$  Calcd for [C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>S+Na]<sup>+</sup>: 348.0665, found 348.0666.

**2-(ethylsulfonyl)-1-phenylethan-1-one oxime (4n)**



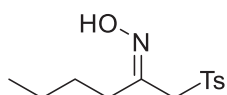
White solid; (59 mg, 87%); mp: 106–108 °C;  $R_f$  = 0.15 (hexanes/ethyl acetate 3:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.26 (brs, 1H), 7.74–7.76 (m, 2H), 7.38–7.44 (m, 3H), 4.60 (s, 2H), 3.15 (q,  $J$  = 7.6, 2H), 1.40 (t,  $J$  = 7.2, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  148.5, 133.7, 130.2, 128.7, 126.7, 49.5, 49.4, 6.3; MS  $m/z$  (relative intensity, %): 227 (5.3), 212 (9.6), 105 (100), 103 (23.1), 91 (13.2), 77 (30.1); ESI–HRMS:  $m/z$  Calcd for [C<sub>10</sub>H<sub>13</sub>NO<sub>3</sub>S+Na]<sup>+</sup>: 250.0508, found 250.0510.

**(Z)-1-tosylhexan-2-one oxime (4o)**



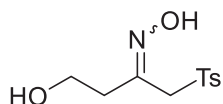
Pale yellow solid; (20 mg, 25%); mp: 109–110 °C;  $R_f$  = 0.30 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (brs, 1H), 7.73 (d,  $J$  = 8.4 Hz, 2H), 7.34 (d,  $J$  = 8.0 Hz, 2H), 3.90 (s, 2H), 2.51 (t,  $J$  = 8.0 Hz, 2H), 2.44 (s, 3H), 1.44–1.51 (m, 2H), 1.28–1.38 (m, 2H), 0.91 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.4, 145.0, 135.4, 129.8, 128.4, 60.0, 27.4, 27.3, 22.7, 21.6, 13.7; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{13}\text{H}_{19}\text{NO}_3\text{S}+\text{Na}]^+$ : 292.0978, found 292.0980.

**(E)-1-tosylhexan-2-one oxime (4o')**



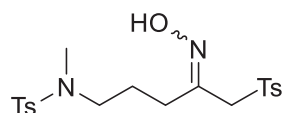
Pale yellow solid; (41 mg, 51%); mp: 105–106 °C;  $R_f$  = 0.43 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (d,  $J$  = 8.4 Hz, 2H), 7.48 (s, 1H), 7.32 (d,  $J$  = 8.0 Hz, 2H), 4.23 (s, 2H), 2.43–2.48 (m, 5H), 1.46–1.53 (m, 2H), 1.28–1.37 (m, 2H), 0.91 (t,  $J$  = 7.6 Hz, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.9, 144.9, 136.5, 129.6, 128.3, 53.2, 33.5, 28.0, 22.2, 21.7, 13.7; MS  $m/z$  (relative intensity, %): 269 (0.2), 227 (12.8), 163 (100), 157 (20.8), 146 (29.4), 139 (43.6), 105 (24.8), 91 (33.9), 77 (11.6); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{13}\text{H}_{19}\text{NO}_3\text{S}+\text{Na}]^+$ : 292.0978, found 292.0976.

**4-hydroxy-1-tosylbutan-2-one oxime (4p)**



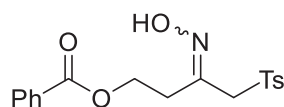
Colourless oil; (56 mg, 73%); (Z/E mixture; 0.74:1);  $R_f$  = 0.10 (hexanes/ethyl acetate 2:1); Major:  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  10.29 (s, 1H), 7.72–7.79 (m, 2H), 7.40–7.44 (m, 2H), 4.11 (s, 2H), 3.79–3.82 (m, 2H), 3.75–3.78 (m, 1H), 2.75–2.78 (m, 2H), 2.44 (s, 3H); Minor:  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ): 10.05 (s, 1H), 7.72–7.79 (m, 2H), 7.40–7.44 (m, 2H), 4.40 (s, 2H), 3.79–3.82 (m, 2H), 3.64–3.67 (m, 1H), 2.61–2.64 (m, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz, Acetone- $d_6$ ):  $\delta$  150.1, 147.5, 145.5, 138.4, 137.5, 130.6, 130.4, 129.2, 129.1, 61.6, 60.0, 59.0, 54.2, 37.5, 31.9, 21.6; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{11}\text{H}_{15}\text{NO}_4\text{S}+\text{Na}]^+$ : 280.0614, found 280.0615.

**N-(4-(hydroxyimino)-5-tosylpentyl)-N,4-dimethylbenzenesulfonamide (4q)**



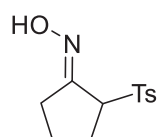
White solid; (79 mg, 60%); (Z/E mixture; 0.82:1);  $R_f = 0.28$  (hexanes/ethyl acetate 1:1); Major:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.83 (brs, 1H), 7.78 (d,  $J = 8.0$  Hz, 2H), 7.65 (d,  $J = 8.0$  Hz, 2H), 7.31–7.36 (m, 4H), 4.24 (s, 2H), 2.97–3.02 (m, 2H), 2.70 (s, 3H), 2.48–2.56 (m, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 1.80–1.86 (m, 2H); Minor:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.16 (brs, 1H), 7.74 (d,  $J = 8.0$  Hz, 2H), 7.65 (d,  $J = 8.0$  Hz, 2H), 7.31–7.36 (m, 4H), 3.97 (s, 2H), 2.97–3.02 (m, 2H), 2.69 (s, 3H), 2.48–2.56 (m, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 1.80–1.86 (m, 2H);  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.3, 148.5, 145.1, 145.0, 143.38, 143.35, 136.5, 135.5, 134.3, 134.1, 129.9, 129.72, 129.66, 128.3, 128.1, 127.40, 127.37, 60.7, 53.9, 49.8, 49.4, 34.8, 34.5, 31.0, 25.6, 23.8, 22.9, 21.6, 21.4; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_5\text{S}_2+\text{H}]^+$ : 439.1356, found 439.1358.

### **3-(hydroxyimino)-4-tosylbutyl benzoate (4r)**



White solid; (93 mg, 86%); (Z/E mixture; 0.8:1);  $R_f = 0.15$  (hexanes/ethyl acetate 3:1); Major:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.03 (brs, 1H), 7.98–8.02 (m, 2H), 7.77–7.79 (m, 1H), 7.72–7.74 (m, 1H), 7.54–7.58 (m, 1H), 7.41–7.45 (m, 2H), 7.28–7.34 (m, 2H), 4.53–4.56 (m, 2H), 4.04 (s, 2H), 3.03 (t,  $J = 6.4$  Hz, 2H), 2.42 (s, 3H); Minor:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 7.98–8.02 (m, 2H), 7.77–7.79 (m, 1H), 7.72–7.74 (m, 1H), 7.67 (brs, 1H), 7.54–7.58 (m, 1H), 7.41–7.45 (m, 2H), 7.28–7.34 (m, 2H), 4.53–4.56 (m, 2H), 4.32 (s, 2H), 2.96 (t,  $J = 6.4$  Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C NMR}$  (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.4, 166.3, 149.1, 146.5, 145.2, 145.1, 136.2, 135.2, 133.14, 133.08, 129.9, 129.8, 129.7, 129.60, 129.55, 128.43, 128.38, 128.35, 128.2, 61.1, 60.8, 60.6, 53.5, 33.3, 27.6, 21.6; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{18}\text{H}_{19}\text{NO}_5\text{S}+\text{Na}]^+$ : 384.0876, found 384.0879.

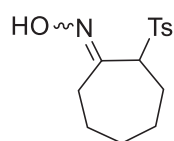
### **2-tosylcyclopentan-1-one oxime (4s)**



White solid; (55 mg, 73%); mp: 119–120 °C;  $R_f = 0.17$  (hexanes/ethyl acetate 3:1);  $^1\text{H}$

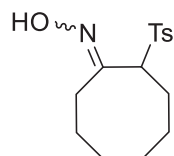
NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (brs, 1H), 7.76 (d,  $J$  = 8.0 Hz, 2H), 7.35 (d,  $J$  = 8.0 Hz, 2H), 4.07 (dd,  $J$  = 3.2 Hz,  $J$  = 8.0 Hz, 1H), 2.54–2.63 (m, 1H), 2.46–2.51 (m, 1H), 2.44 (s, 3H), 2.37–2.42 (m, 1H), 2.06–2.14 (m, 1H), 1.90–1.97 (m, 1H), 1.72–1.80 (m, 1H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  159.2, 145.0, 134.6, 129.7, 129.2, 67.0, 27.4, 27.2, 22.1, 21.7; MS  $m/z$  (relative intensity, %): 253 (0.6), 189 (100), 172 (43.3), 139 (49.9), 103 (49.5), 91 (71.2); ESI–HRMS:  $m/z$  Calcd for [C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>S+Na]<sup>+</sup>: 276.0665, found 276.0666.

**2-tosylcycloheptan-1-one oxime (4t)**



White solid; (64 mg, 76%); (Z/E mixture; 0.42:1);  $R_f$  = 0.27 (hexanes/ethyl acetate 3:1); Major: <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  9.98 (s, 1H), 7.53 (d,  $J$  = 8.4 Hz, 2H), 7.24–7.28 (m, 2H), 3.81 (dd,  $J$  = 6.8 Hz,  $J$  = 12 Hz, 1H), 2.92–2.97 (m, 1H), 2.30 (s, 3H), 2.14–2.21 (m, 1H), 1.77–1.87 (m, 3H), 1.65–1.73 (m, 2H), 1.16–1.24 (m, 3H); Minor: <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>): 9.68 (s, 1H), 7.58 (d,  $J$  = 8.0 Hz, 2H), 7.24–7.28 (m, 2H), 4.92 (dd,  $J$  = 6.8 Hz,  $J$  = 12 Hz, 1H), 2.28 (s, 3H), 2.25–2.27 (m, 1H), 2.14–2.21 (m, 1H), 1.91–1.93 (m, 1H), 1.77–1.87 (m, 4H), 0.89–1.00 (m, 3H); <sup>13</sup>C NMR (100.6 MHz, acetone-*d*<sub>6</sub>):  $\delta$  155.7, 153.7, 145.3, 137.5, 136.8, 130.4, 130.2, 129.8, 69.7, 61.4, 31.8, 31.7, 31.5, 31.0, 27.1, 26.1, 26.0, 25.8, 25.6, 25.4, 21.60, 21.58; ESI–HRMS:  $m/z$  Calcd for [C<sub>14</sub>H<sub>19</sub>NO<sub>3</sub>S+Na]<sup>+</sup>: 304.0978, found 304.0981.

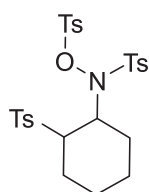
**2-tosylcyclooctan-1-one oxime (4u)**



White solid; (71 mg, 75%); (Z/E mixture; 0.09:1);  $R_f$  = 0.30 (hexanes/ethyl acetate 3:1); Major: <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>):  $\delta$  10.01 (s, 1H), 7.50 (d,  $J$  = 8.4 Hz, 2H), 7.26 (d,  $J$  = 8.0 Hz, 2H), 3.62 (dd,  $J$  = 3.6 Hz,  $J$  = 12.4 Hz, 1H), 2.65–2.70 (m, 1H), 2.30 (s, 3H), 2.11–2.17 (m, 1H), 2.05–2.09 (m, 1H), 1.96–2.03 (m, 1H), 1.91–1.93 (m, 1H), 1.62–1.68 (m, 1H), 1.47–1.57 (m, 3H), 1.35–1.42 (m, 1H), 1.16–1.23 (m, 1H), 1.01–1.09 (m, 1H); Minor: <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>): 9.81 (s, 1H), 7.58 (d,  $J$  = 8.0 Hz, 2H), 7.23 (d,  $J$  =

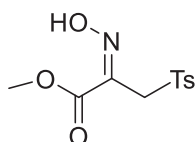
8.0 Hz, 2H), 4.78 (dd,  $J = 6.0$  Hz,  $J = 10.8$  Hz, 1H), 2.39–2.42 (m, 1H), 2.29 (s, 3H), 2.05–2.09 (m, 2H), 1.96–2.03 (m, 2H), 1.62–1.68 (m, 1H), 1.47–1.57 (m, 3H), 1.35–1.42 (m, 1H), 1.16–1.23 (m, 1H), 1.01–1.09 (m, 1H);  $^{13}\text{C}$  NMR (100.6 MHz):  $\delta$  155.7, 145.3, 136.4, 130.3, 129.9, 70.4, 27.2, 26.3, 26.0, 25.8, 25.6, 21.6, 21.2; MS  $m/z$  (relative intensity, %): 295 (0.1), 231 (15.3), 203 (48.8), 140 (100), 139 (32.8), 91 (21.2); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{15}\text{H}_{21}\text{NO}_3\text{S}+\text{Na}]^+$ : 318.1134, found 318.1135.

**4-methyl-N-(2-tosylcyclohexyl)-N-(tosyloxy)benzenesulfonamide (5v)**



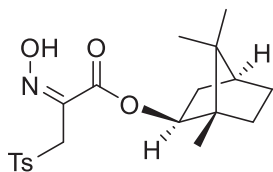
White solid; (111 mg, 64%); mp: 143–144 °C;  $R_f = 0.26$  (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76 (s, 2H), 7.89 (d,  $J = 7.6$  Hz, 2H), 7.70 (d,  $J = 8.4$  Hz, 2H), 7.37 (d,  $J = 8.0$  Hz, 2H), 7.27 (s, 2H), 7.20 (s, 2H), 4.52 (t,  $J = 8.0$  Hz, 1H), 4.02 (t,  $J = 8.0$  Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H), 1.50–1.72 (m, 6H), 1.05–1.54 (m, 2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.9, 145.4, 144.3, 136.0, 132.5, 132.4, 130.4, 130.3, 129.63, 129.58, 129.54, 129.45, 128.9, 63.7, 27.9, 27.5, 24.3, 23.8, 21.9, 21.8, 21.6; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{27}\text{H}_{31}\text{NO}_7\text{S}_3+\text{Na}]^+$ : 600.1155, found 600.1154.

**methyl-2-(hydroxyimino)-3-tosylpropanoate (4w)**



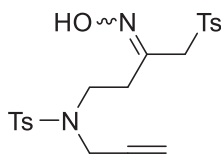
White solid; (74 mg, 91%); mp: 109–110 °C;  $R_f = 0.09$  (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.03 (brs, 1H), 7.79 (d,  $J = 8.4$  Hz, 2H), 7.42 (d,  $J = 8.0$  Hz, 2H), 4.59 (s, 2H), 3.77 (s, 3H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.4, 145.2, 141.4, 136.5, 129.8, 128.3, 53.1, 51.4, 21.6; MS  $m/z$  (relative intensity, %): 271 (3.3), 240 (7.7), 235 (100), 207 (42.5), 155 (74.6), 139 (50.8), 91 (100), 65 (17.3); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{11}\text{H}_{13}\text{NO}_5\text{S}+\text{Na}]^+$ : 294.0407, found 294.0408.

**(1S\*,2S\*,4S\*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl-2-(hydroxyimino)-3-tosylpropanoate (4x)**



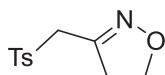
White solid; (92 mg, 78%); mp: 116–117 °C;  $R_f$  = 0.26 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.30 (brs, 1H), 7.76 (d,  $J$  = 8.4 Hz, 2H), 7.32 (d,  $J$  = 8.0 Hz, 2H), 4.72–4.74 (m, 1H), 4.55 (dd,  $J$  = 12.8 Hz,  $J$  = 25.2 Hz, 2H), 2.43 (s, 3H), 1.69–1.81 (m, 4H), 1.56–1.62 (m, 1H), 1.07–1.18 (m, 2H), 0.98 (s, 3H), 0.862 (s, 3H), 0.856 (s, 3H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.5, 145.0, 141.8, 136.5, 129.7, 128.2, 83.7, 51.4, 48.9, 46.9, 44.9, 38.4, 33.6, 26.9, 21.6, 20.0, 19.8, 11.4; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{20}\text{H}_{27}\text{NO}_5\text{S}+\text{H}]^+$ : 394.1683, found 394.1685.

***N*-(3-(hydroxyimino)-4-tosylbutyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (4z)**



White solid; (60 mg, 45%); (Z/E mixture; 0.75:1);  $R_f$  = 0.10 (hexanes/ethyl acetate 3:1); Major:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.46 (brs, 1H), 7.70–7.81 (m, 4H), 7.27–7.36 (m, 4H), 4.14 (dd,  $J$  = 2.4 Hz,  $J$  = 8.0 Hz, 2H), 4.09 (s, 2H), 3.49 (q,  $J$  = 6.8 Hz, 2H), 2.91 (t,  $J$  = 6.4 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 2.04 (dd,  $J$  = 2.4 Hz,  $J$  = 4.4 Hz, 1H); Minor:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.01 (brs, 1H), 7.70–7.81 (m, 4H), 7.27–7.36 (m, 4H), 4.37 (s, 2H), 4.14 (dd,  $J$  = 2.4 Hz,  $J$  = 8.0 Hz, 2H), 3.49 (q,  $J$  = 6.8 Hz, 2H), 2.77 (t,  $J$  = 6.4 Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H), 2.04 (dd,  $J$  = 2.4 Hz,  $J$  = 4.4 Hz, 1H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.2, 146.9, 145.1, 145.0, 143.8, 143.8, 136.3, 135.6, 135.3, 135.2, 129.9, 129.7, 129.53, 129.51, 128.2, 128.1, 127.74, 127.69, 76.1, 76.0, 74.3, 59.8, 52.6, 42.6, 42.1, 36.2, 36.0, 31.6, 25.4, 21.6, 21.5; MS  $m/z$  (relative intensity, %): 448 (0.09), 293 (22.1), 278 (7.7), 223 (15.6), 222 (100), 211 (3.2), 156 (11.7), 155 (96.1); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_5\text{S}_2+\text{H}]^+$ : 449.1199, found 449.1202.

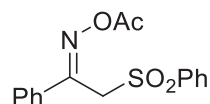
***3*-(tosylmethyl)-4,5-dihydroisoxazole (4aa)**



White solid; (32 mg, 44%); mp: 57–58 °C;  $R_f$  = 0.22 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR

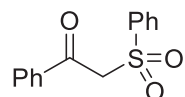
(400 MHz, CDCl<sub>3</sub>):  $\delta$  7.75 (d,  $J$  = 8.0 Hz, 2H), 7.37 (d,  $J$  = 8.0 Hz, 2H), 4.38 (t,  $J$  = 10.0 Hz, 2H), 4.18 (s, 2H), 3.19 (t,  $J$  = 10.0 Hz, 2H), 2.45 (s, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  149.3, 145.5, 134.8, 130.0, 128.2, 69.8, 55.0, 36.5, 21.6; MS  $m/z$  (relative intensity, %): 239 (4.5), 238 (5.8), 177 (1.1), 176 (12.0), 175 (100), 157 (9.0), 155 (25.5), 145 (15.9), 139 (16.8); ESI–HRMS:  $m/z$  Calcd for [C<sub>11</sub>H<sub>13</sub>NO<sub>3</sub>S+H]<sup>+</sup>: 240.0689, found 240.0687.

**1-phenyl-2-(phenylsulfonyl)ethan-1-one O-acetyl oxime (6)**



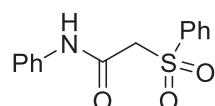
White solid; (147 mg, 93%); mp: 117–118 °C;  $R_f$  = 0.28 (hexanes/ethyl acetate 3:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.84 (d,  $J$  = 7.6 Hz, 2H), 7.77 (d,  $J$  = 7.6 Hz, 2H), 7.63 (t, 1H), 7.47–7.52 (m, 3H), 7.37–7.45 (d, 2H), 4.76 (s, 2H), 1.97 (s, 3H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  167.2, 153.5, 139.1, 134.2, 132.2, 131.4, 129.2, 128.8, 128.5, 127.7, 54.4, 19.3; MS  $m/z$  (relative intensity, %): 317 (0.1), 259 (6.2), 211 (67.4), 194 (31.3), 143 (49.1), 125 (54.3), 103 (100), 77 (89.6); ESI–HRMS:  $m/z$  Calcd for [C<sub>16</sub>H<sub>15</sub>NO<sub>4</sub>S+Na]<sup>+</sup>: 340.0614, found 340.0616.

**1-phenyl-2-(phenylsulfonyl)ethan-1-one (7)**



White solid; (32 mg, 61%); mp: 94–95 °C;  $R_f$  = 0.39 (hexanes/ethyl acetate 3:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.88–7.94 (m, 4H), 7.54–7.68 (m, 2H), 7.49–7.53 (m, 2H), 7.45–7.46 (m, 2H), 4.74 (s, 2H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  188.0, 138.7, 135.7, 134.3, 134.2, 129.24, 129.17, 128.8, 128.5, 63.4; MS  $m/z$  (relative intensity, %): 260 (0.5), 196 (21.7), 105 (100), 77 (52.3); ESI–HRMS:  $m/z$  Calcd for [C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>S+Na]<sup>+</sup>: 283.0399, found 283.0397.

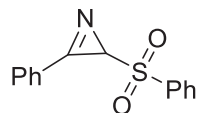
**N-phenyl-2-(phenylsulfonyl)acetamide (8)**



White solid; (51 mg, 92%); mp: 115–116 °C;  $R_f$  = 0.18 (hexanes/ethyl acetate 3:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.54 (brs, 1H), 7.93 (d,  $J$  = 7.6 Hz, 2H), 7.68–7.72 (m, 1H), 7.56–7.60 (m, 2H), 7.49 (d,  $J$  = 7.6 Hz, 2H), 7.32–7.36 (m, 2H), 7.14–7.18 (m, 1H), 4.19 (s,

2H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 137.8, 136.9, 134.7, 129.6, 129.1, 128.1, 125.2, 120.2, 62.9; MS  $m/z$  (relative intensity, %): 275 (47.7), 210 (13.6), 141 (16.1), 93 (100), 77 (33.4); ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{14}\text{H}_{13}\text{NO}_3\text{S}+\text{Na}]^+$ : 298.0508, found 298.0510.

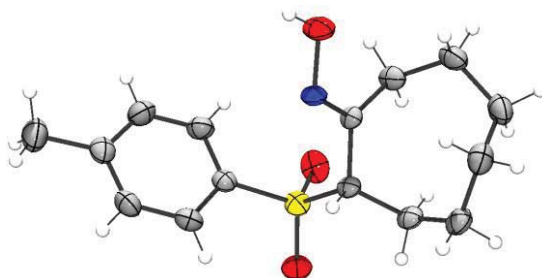
### **3-phenyl-2-(phenylsulfonyl)-2H-azirine (9)**



White solid; (172 mg, 67%); mp: 108–109 °C;  $R_f$  = 0.52 (hexanes/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94–8.00 (m, 4H), 7.68–7.72 (m, 2H), 7.58–7.63 (m, 4H), 3.63 (s, 1H);  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.1, 138.5, 134.9, 133.9, 131.1, 129.5, 129.3, 128.3, 121.4, 48.2; ESI–HRMS:  $m/z$  Calcd for  $[\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}+\text{Na}]^+$ : 280.0403, found 280.0405.

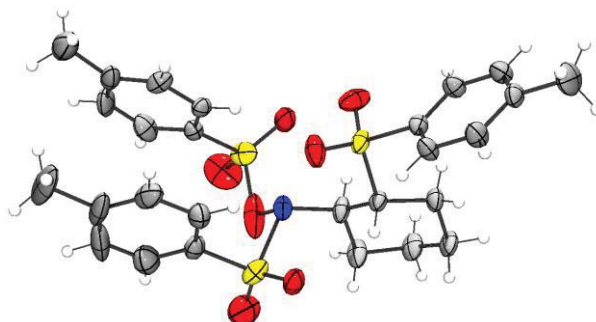
## **ORTEP Plot, Crystal Data and Refinement Results for Compounds 4u and 5v:**

### **ORTEP plot for compound 4u:**



**Figure S1.** Compound **4u**, thermal ellipsoids are drawn at 30% probability level.

### **ORTEP plot for compound 5v:**



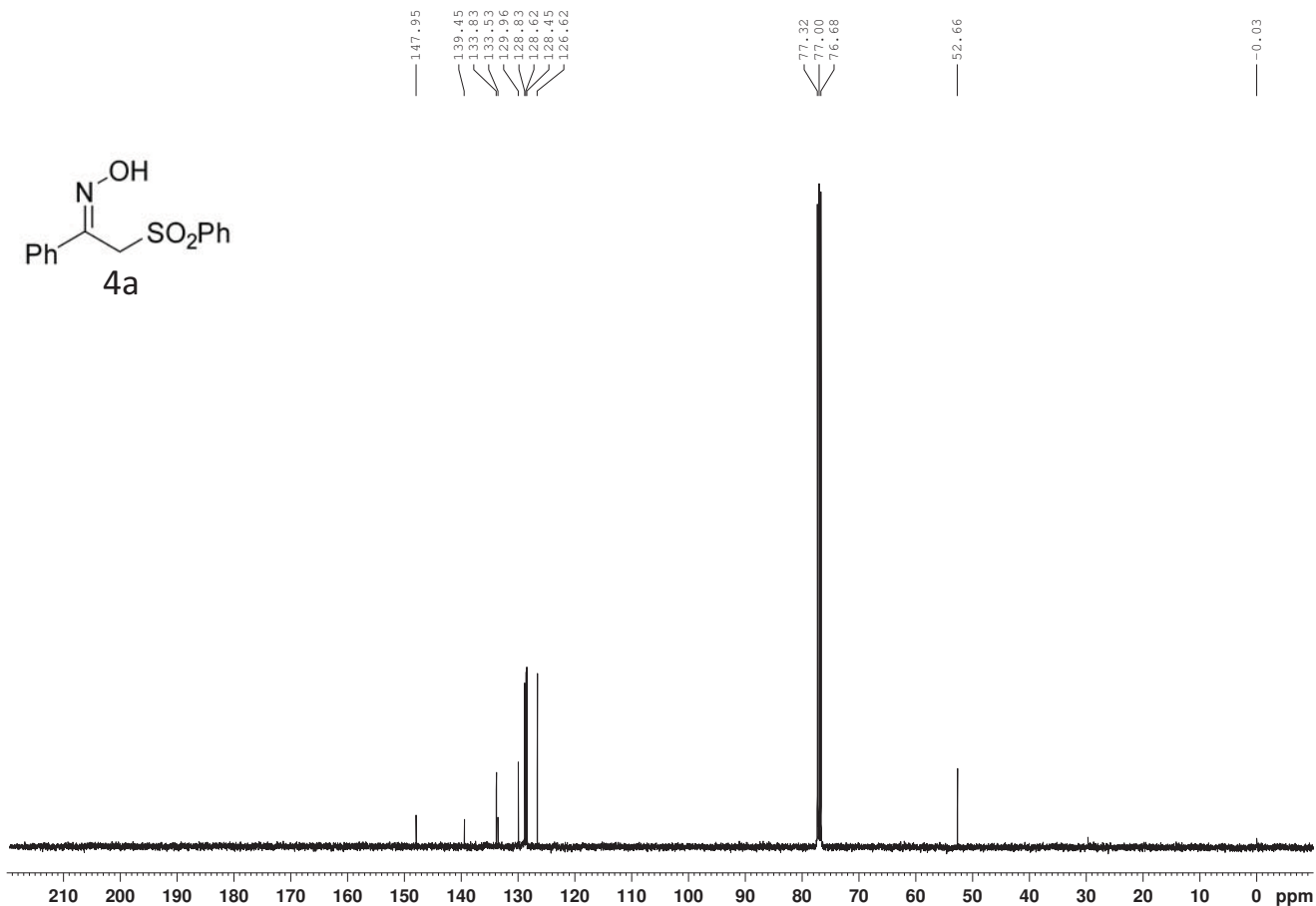
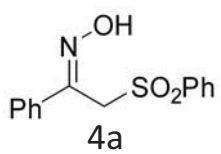
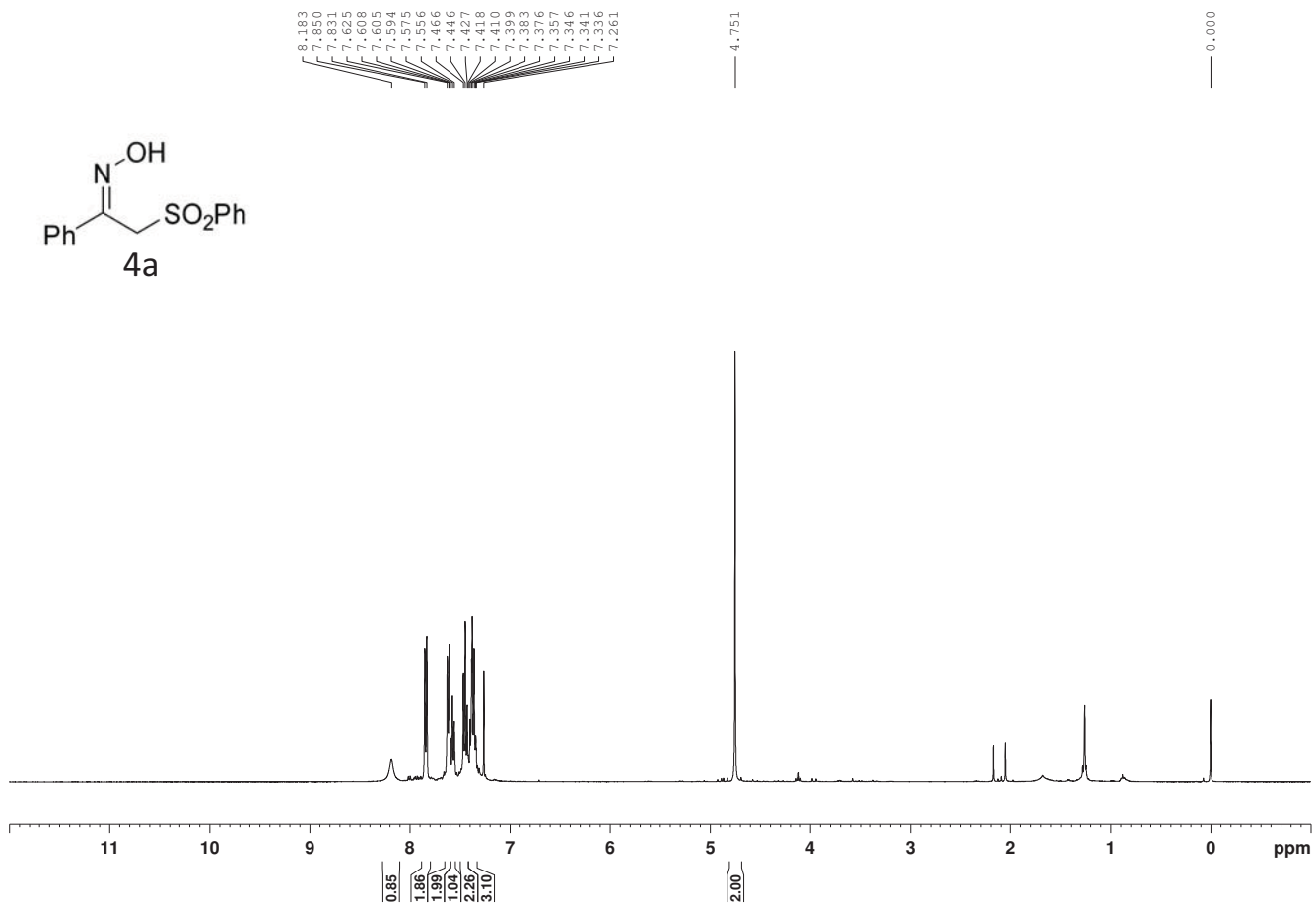
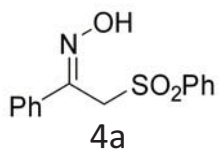
**Figure S2.** Compound **5v**, thermal ellipsoids are drawn at 30% probability level.

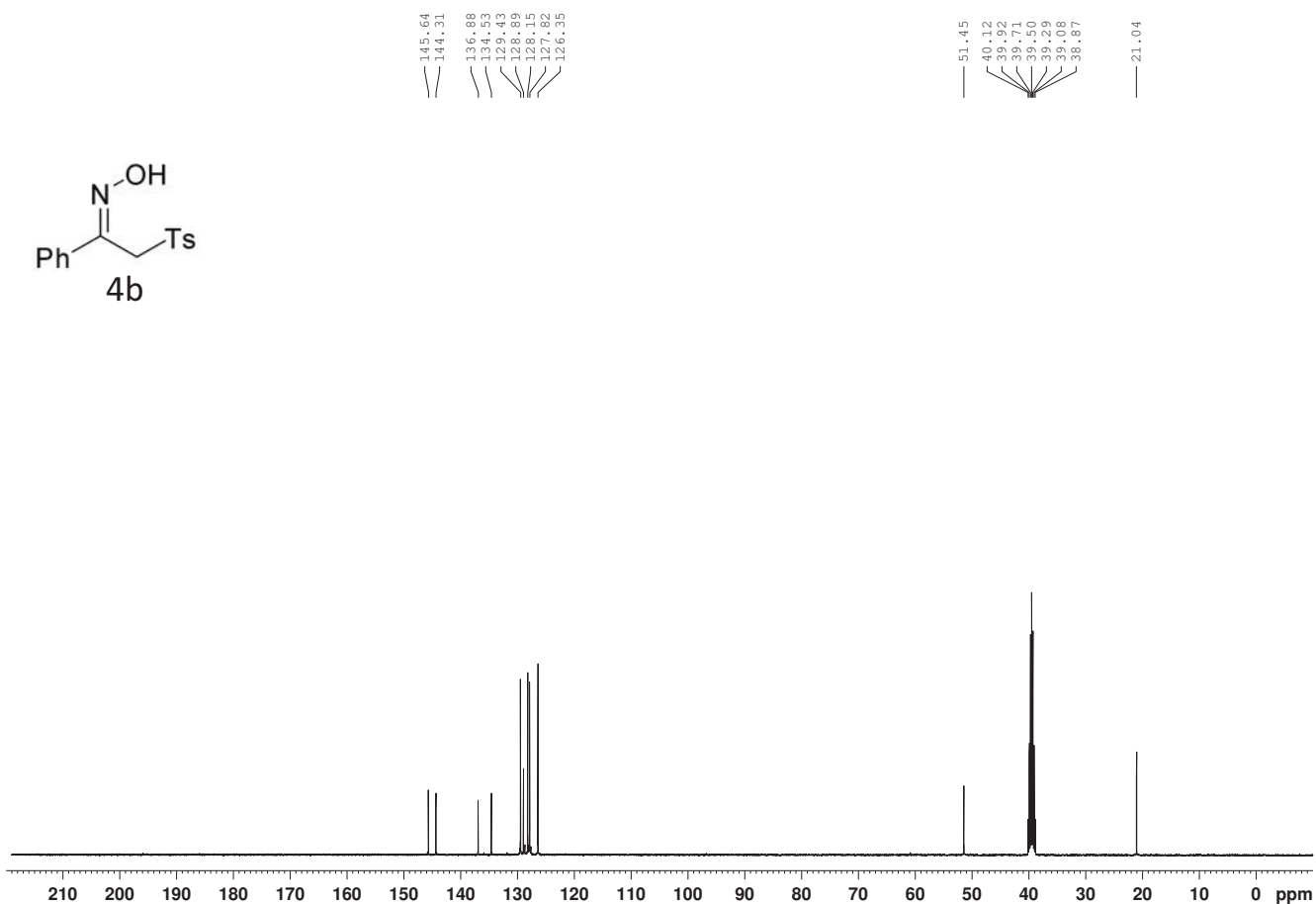
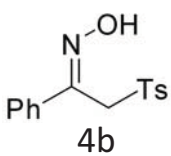
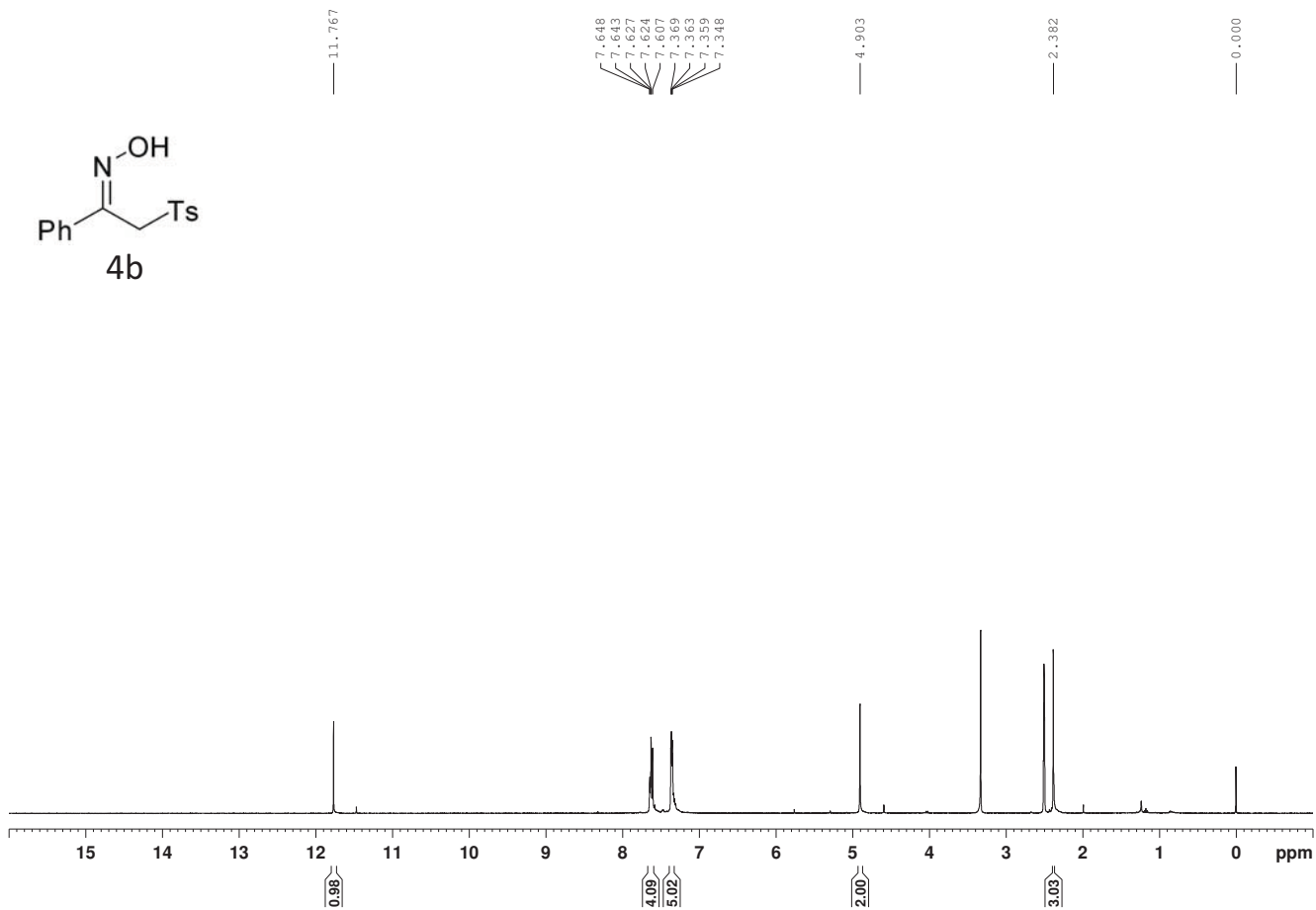
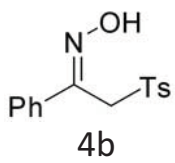
## **Crystal Data and Refinement Results for Compounds 4u and 5v:**

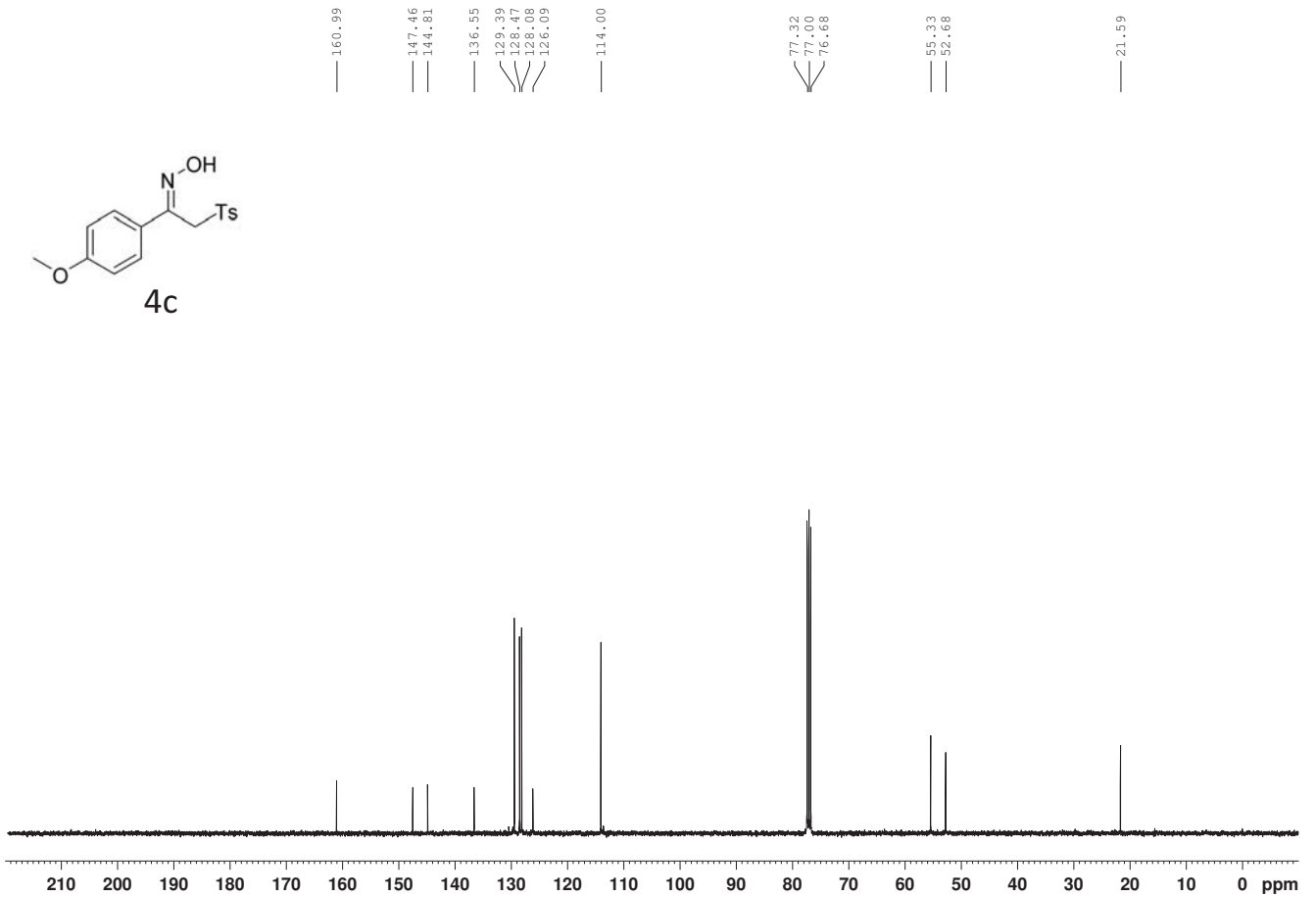
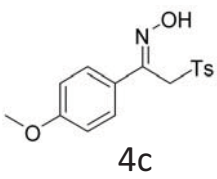
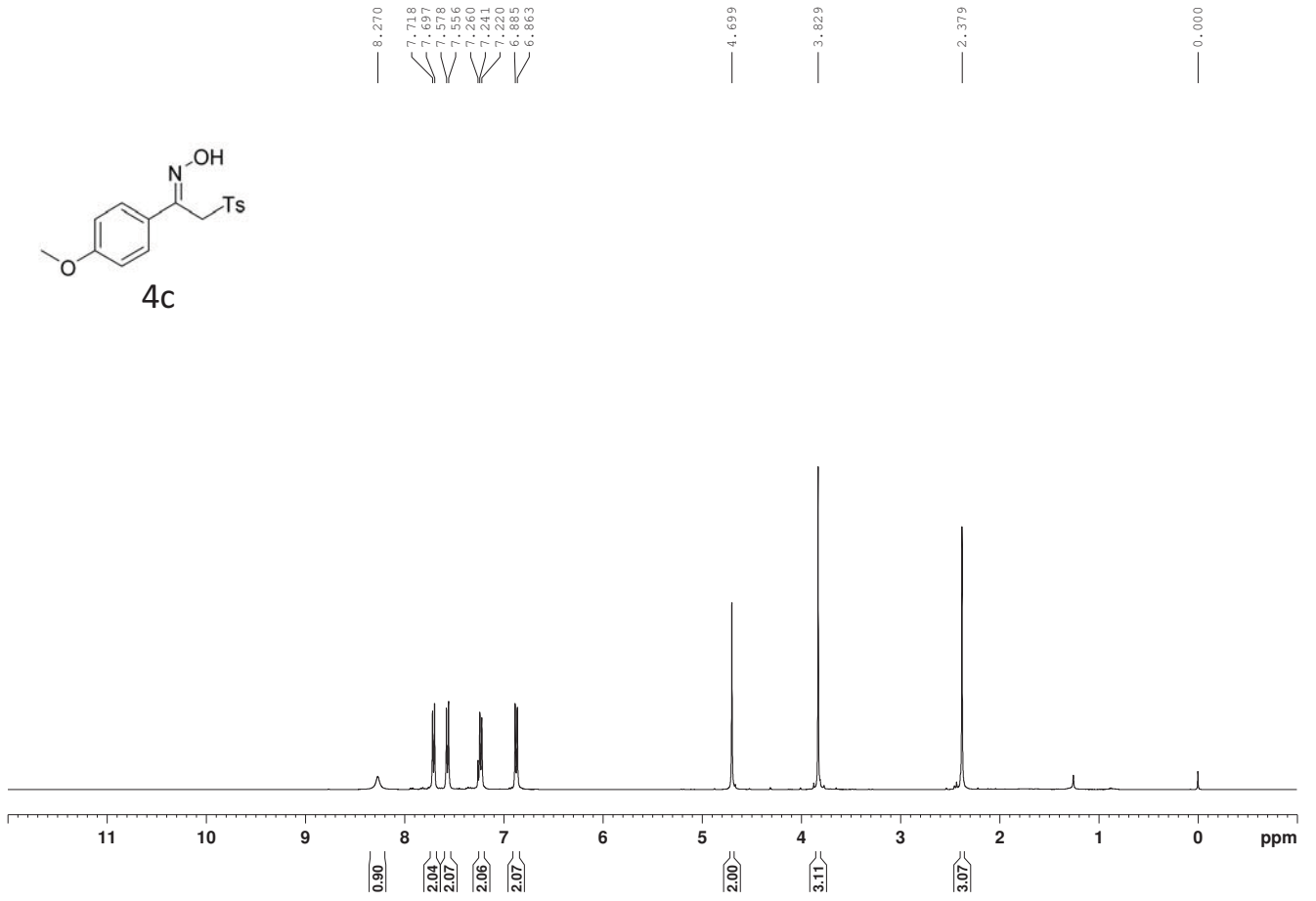
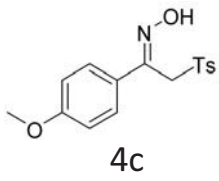


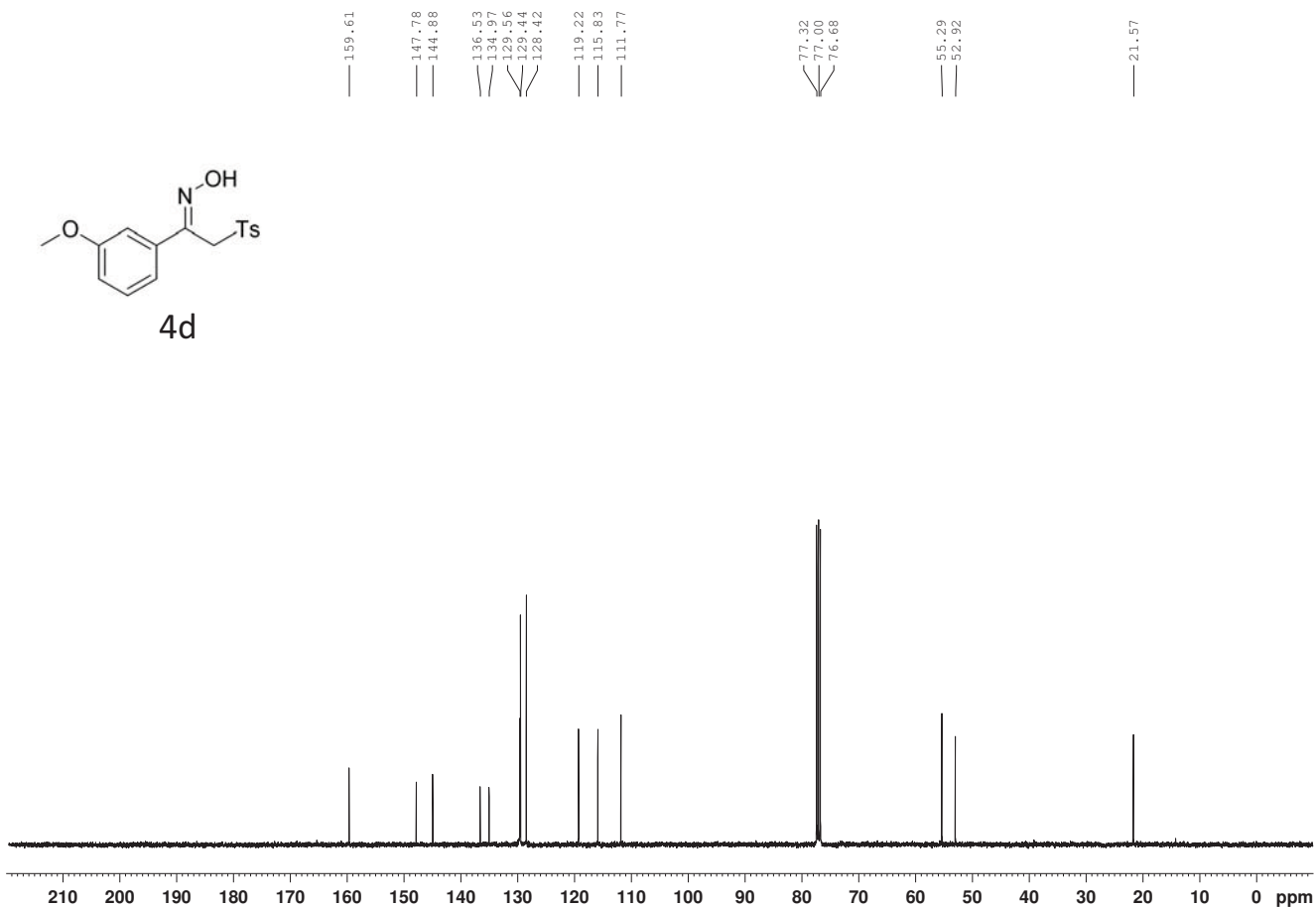
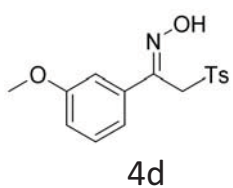
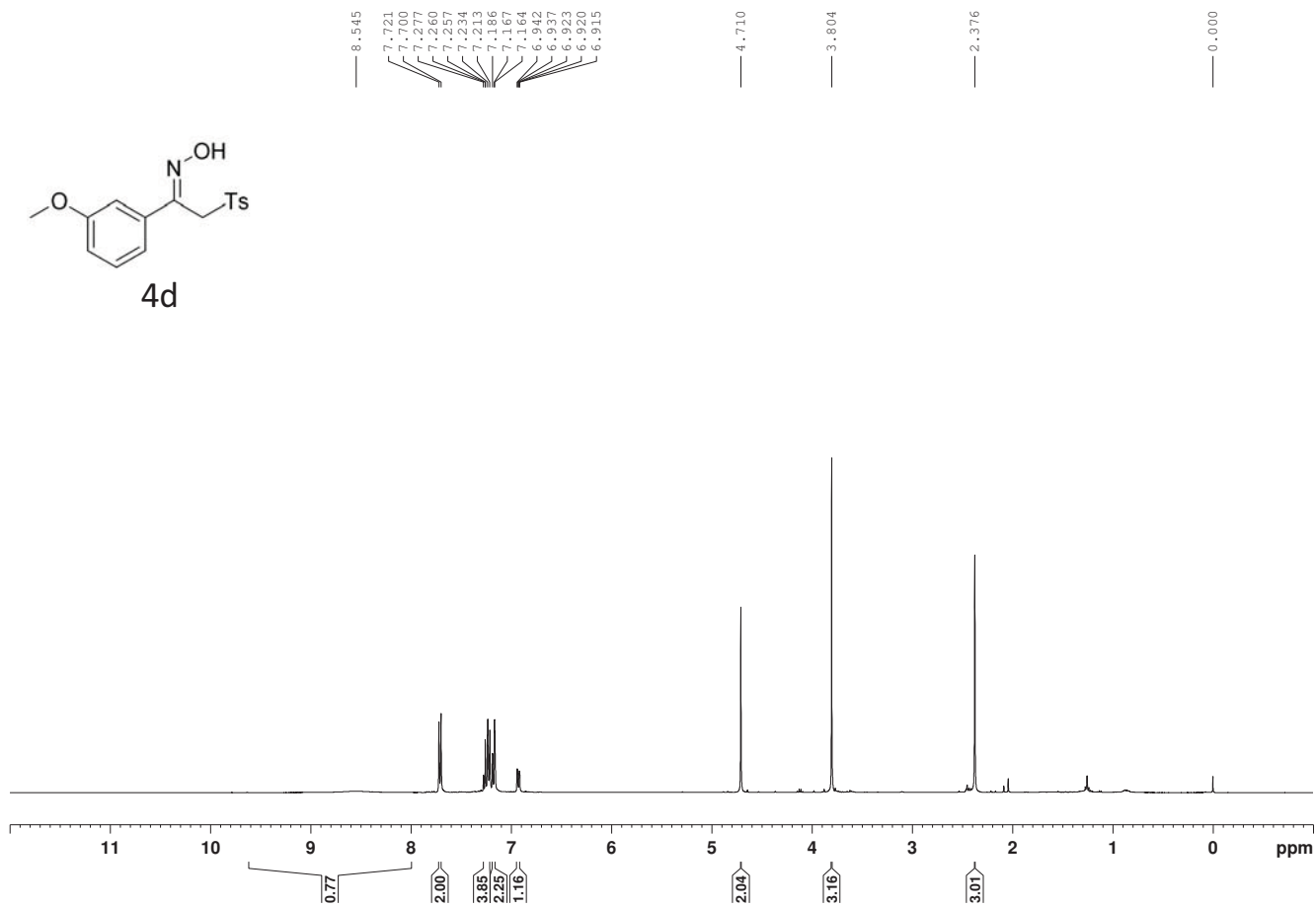
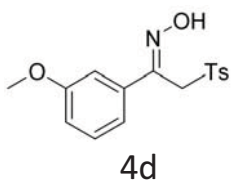
**Table S1.** The crystal data and refinement results of compounds **4u** and **5v**.

Compound number	<b>4u</b>	<b>5v</b>
Formula	C <sub>15</sub> H <sub>21</sub> NO <sub>3</sub> S	C <sub>27</sub> H <sub>31</sub> NO <sub>7</sub> S <sub>3</sub>
Fw	295.39	577.71
Temp	293.64 (10)	294.74 (10)
Crystal system	Monoclinic	Monoclinic
Space group	C 1 2/c 1	P 1 21/c 1
a Å	25.9610 (17)	21.226 (3)
b Å	5.7930 (3)	8.2493 (7)
c Å	22.2512 (17)	16.985 (2)
α°	90.00	90.00
β°	114.088(9)	109.610(14)
γ°	90.00	90.00
V Å <sup>3</sup>	3055.0 (3)	2801.5 (6)
Z	8	4
Density(calcd) g·cm <sup>-3</sup>	1.284	1.370
Absorb.coeff. mm <sup>-1</sup>	0.219	0.310
F(000)	1264	1216
Index ranges	-32 ≤ h ≤ 19 -6 ≤ k ≤ 7 -27 ≤ l ≤ 26	-27 ≤ h ≤ 28 -10 ≤ k ≤ 10 -22 ≤ l ≤ 22
refln./restr./param.	2998/0/183	6637/0/347
GOF	1.032	1.073
[I > 2σ(I)]	R <sub>1</sub> =0.0626 wR <sub>2</sub> =0.1744	R <sub>1</sub> = 0.0909 wR <sub>2</sub> = 0.2645
CCDC numbers	1481286	1481285

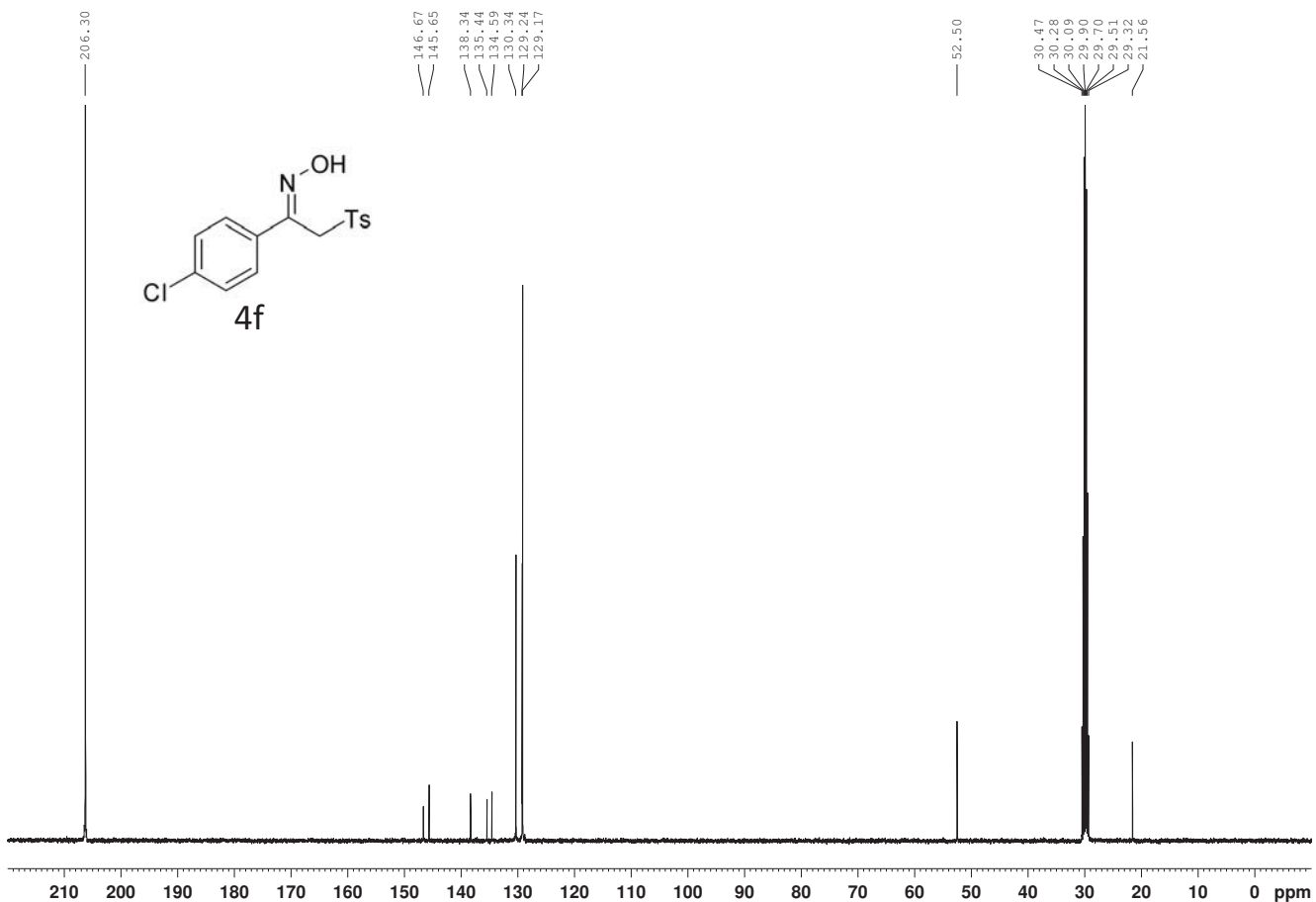
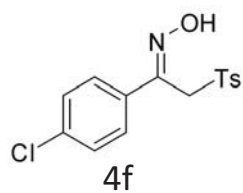
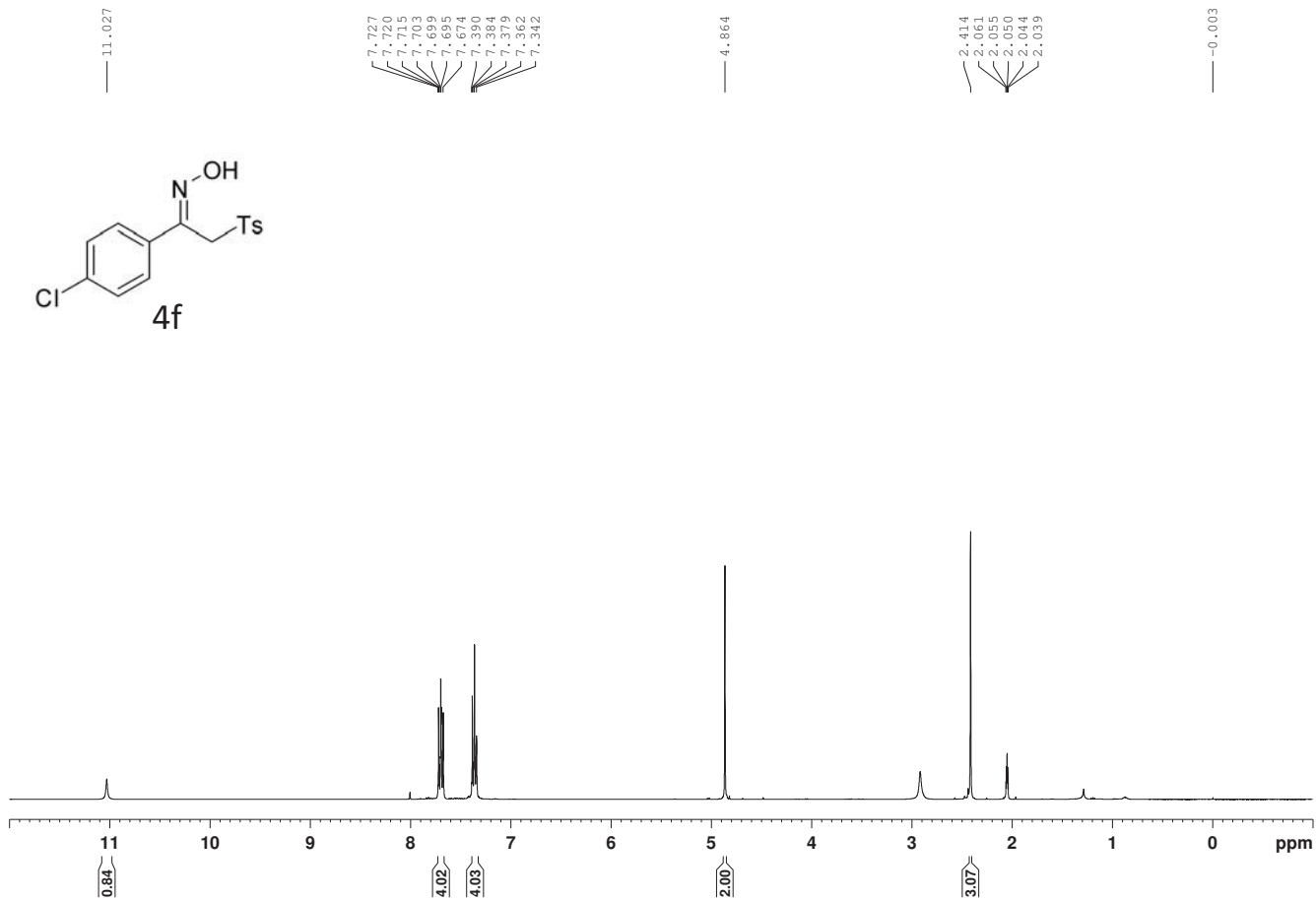
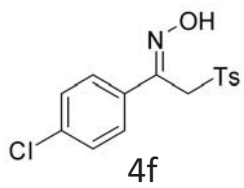






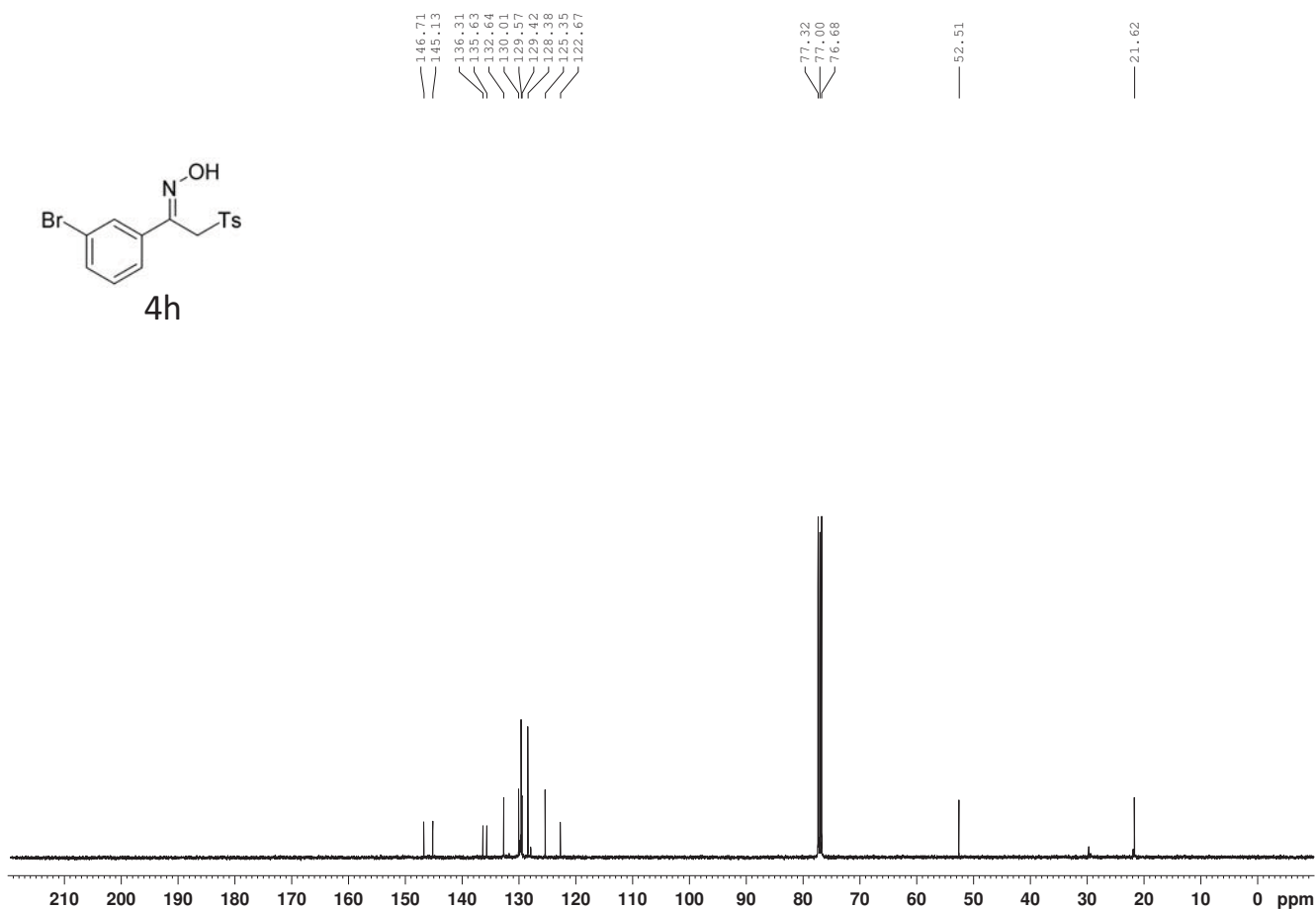
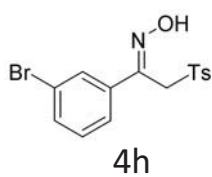
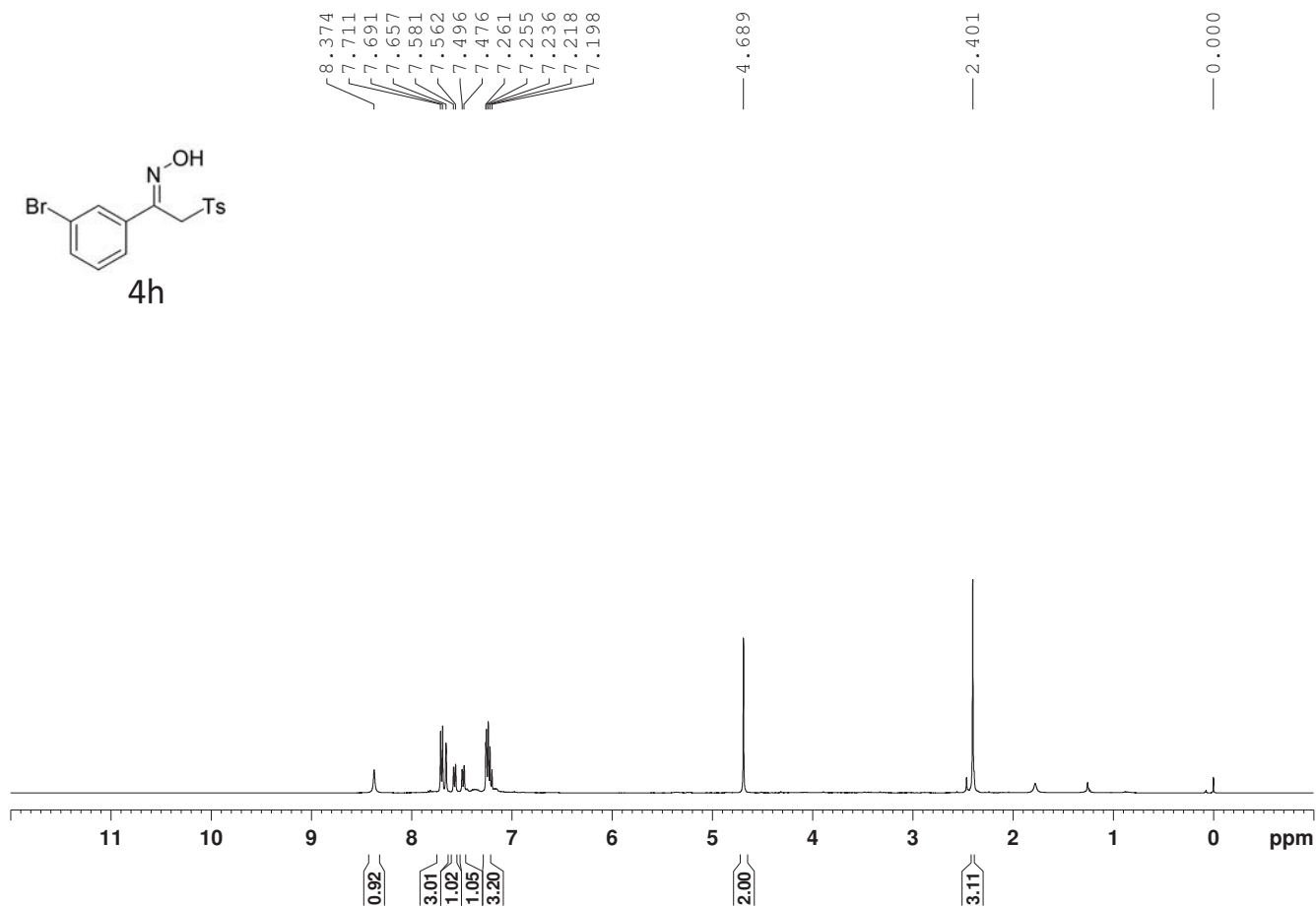
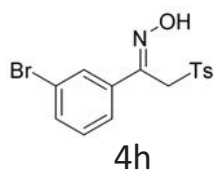


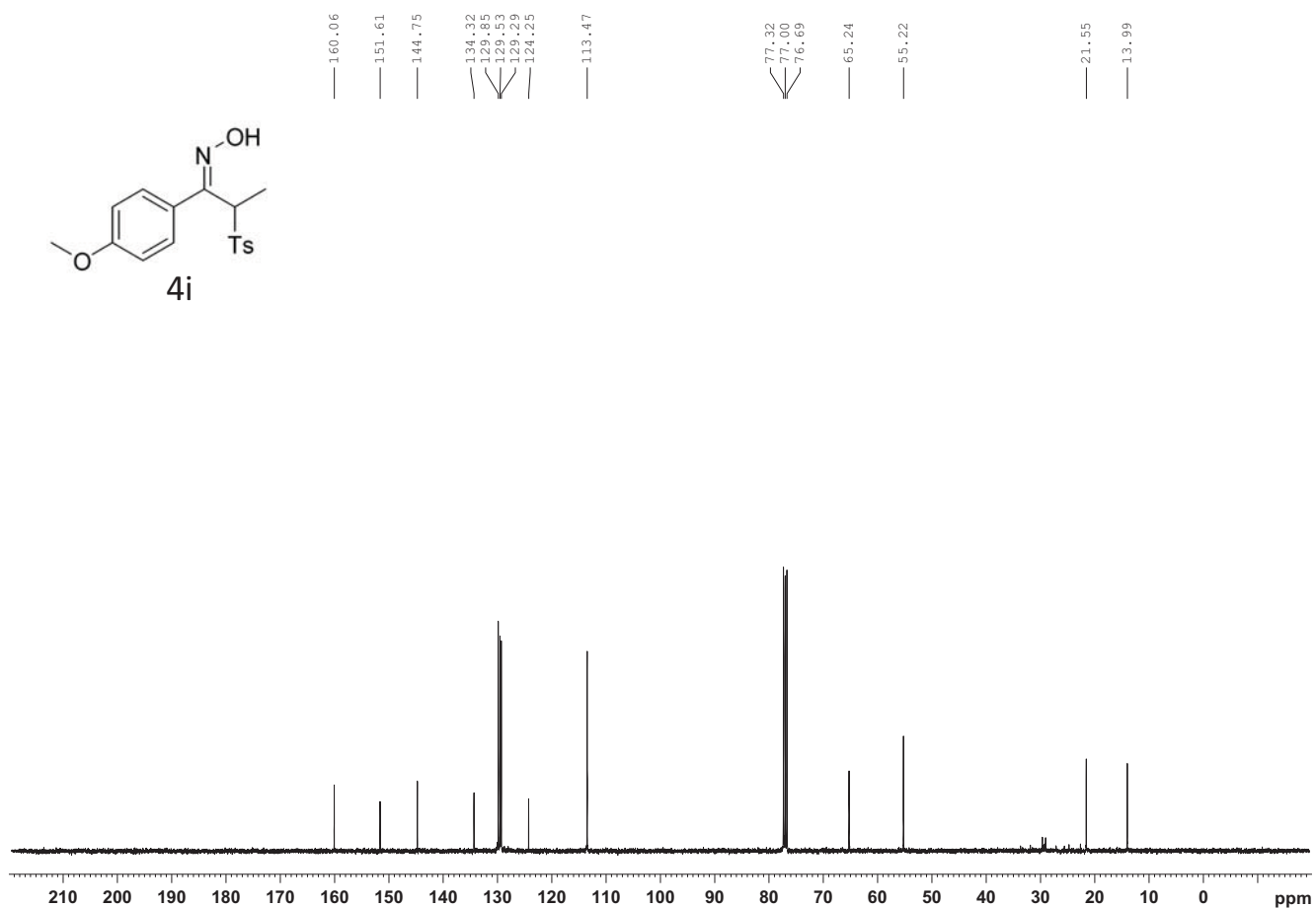
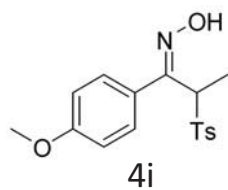
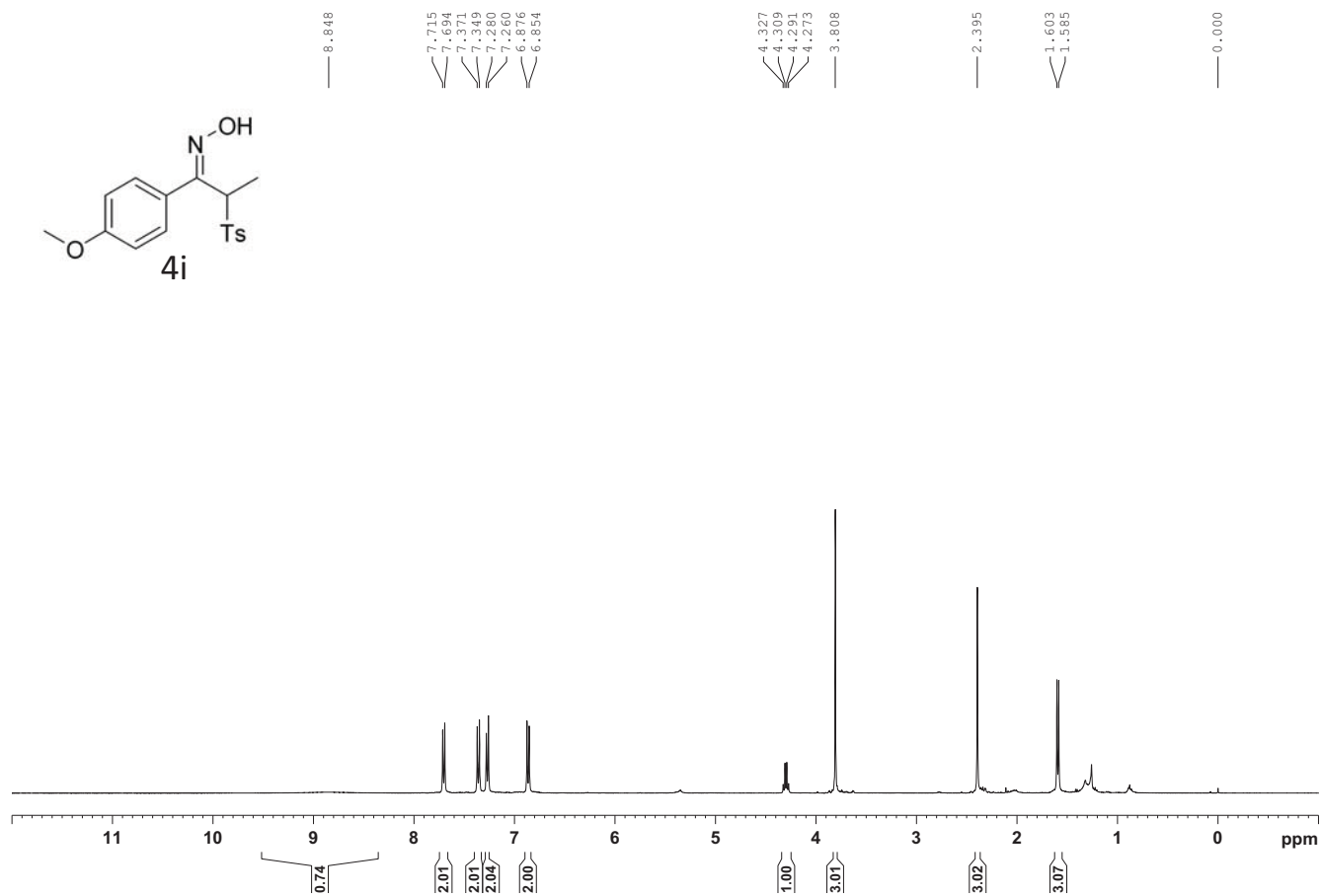
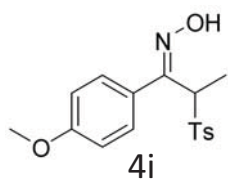


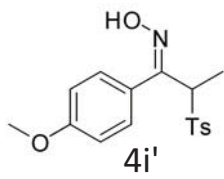




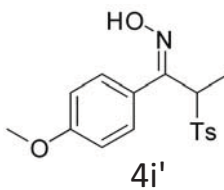
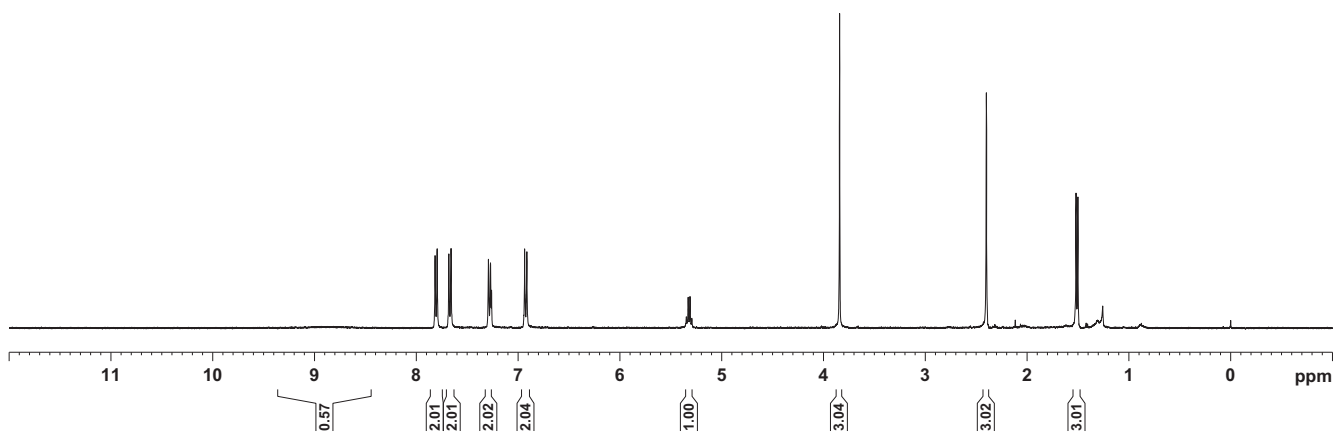




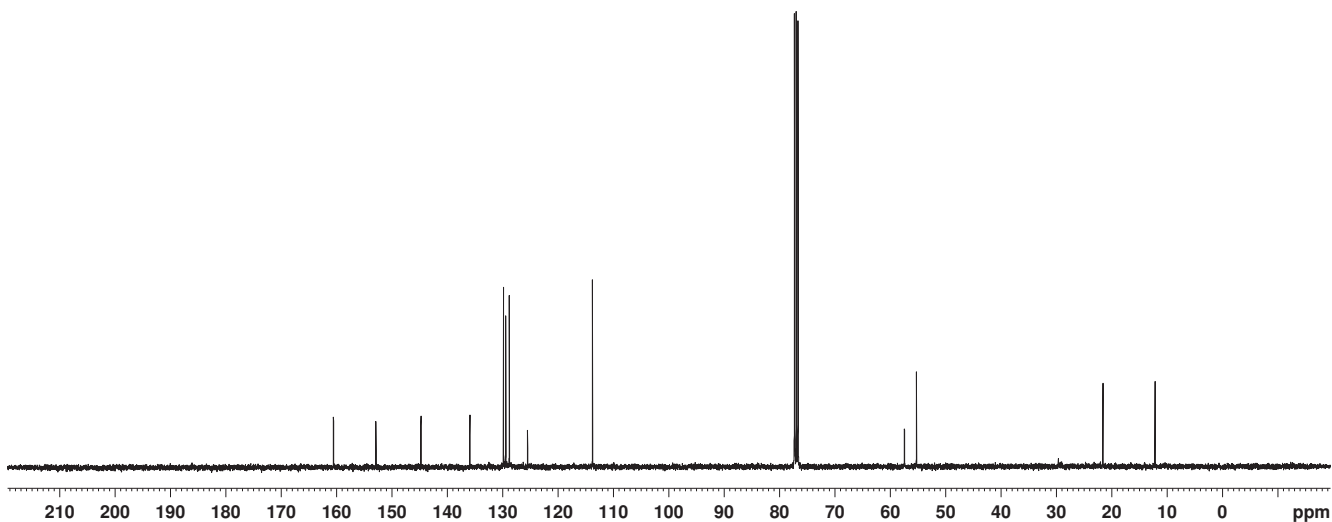




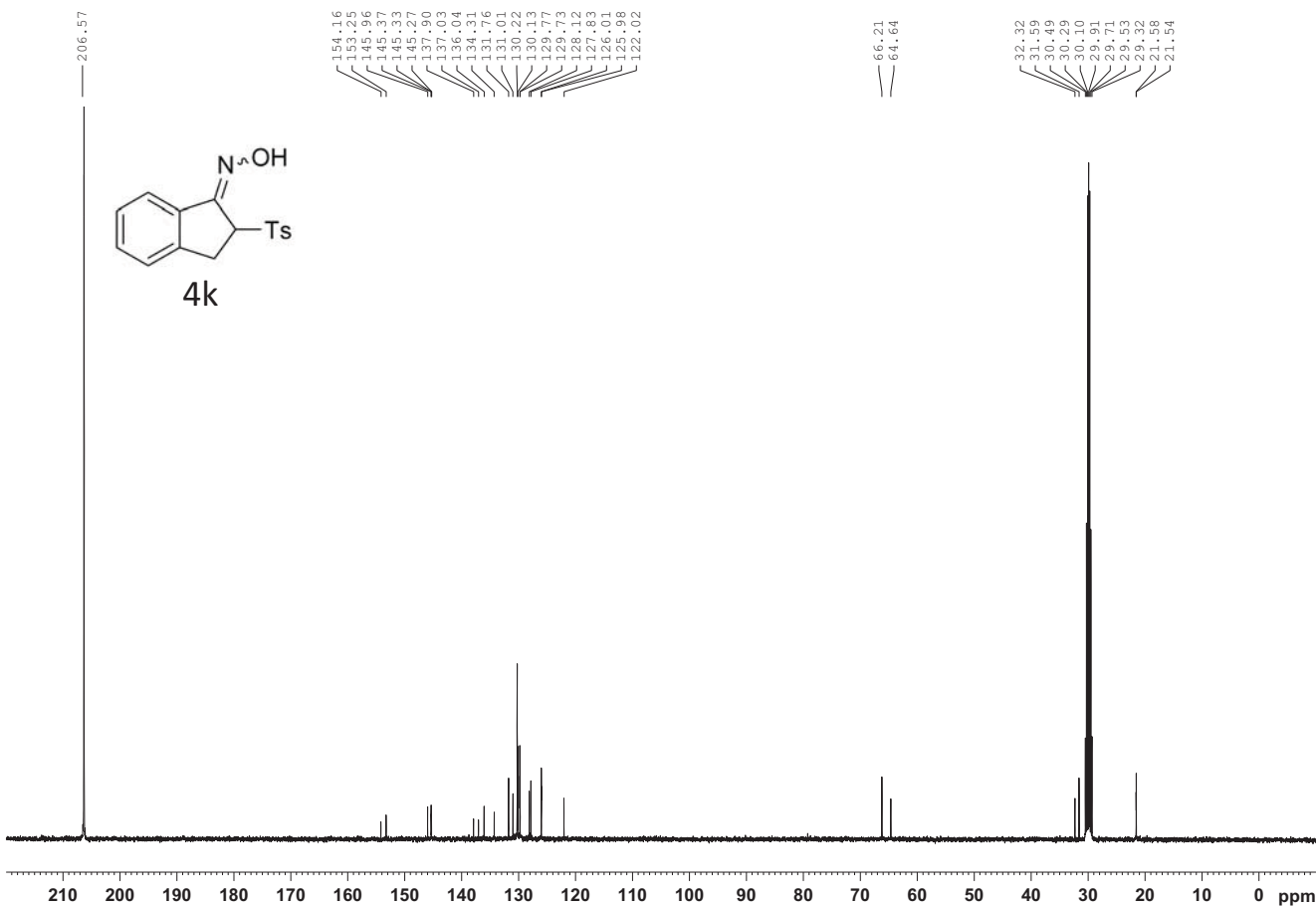
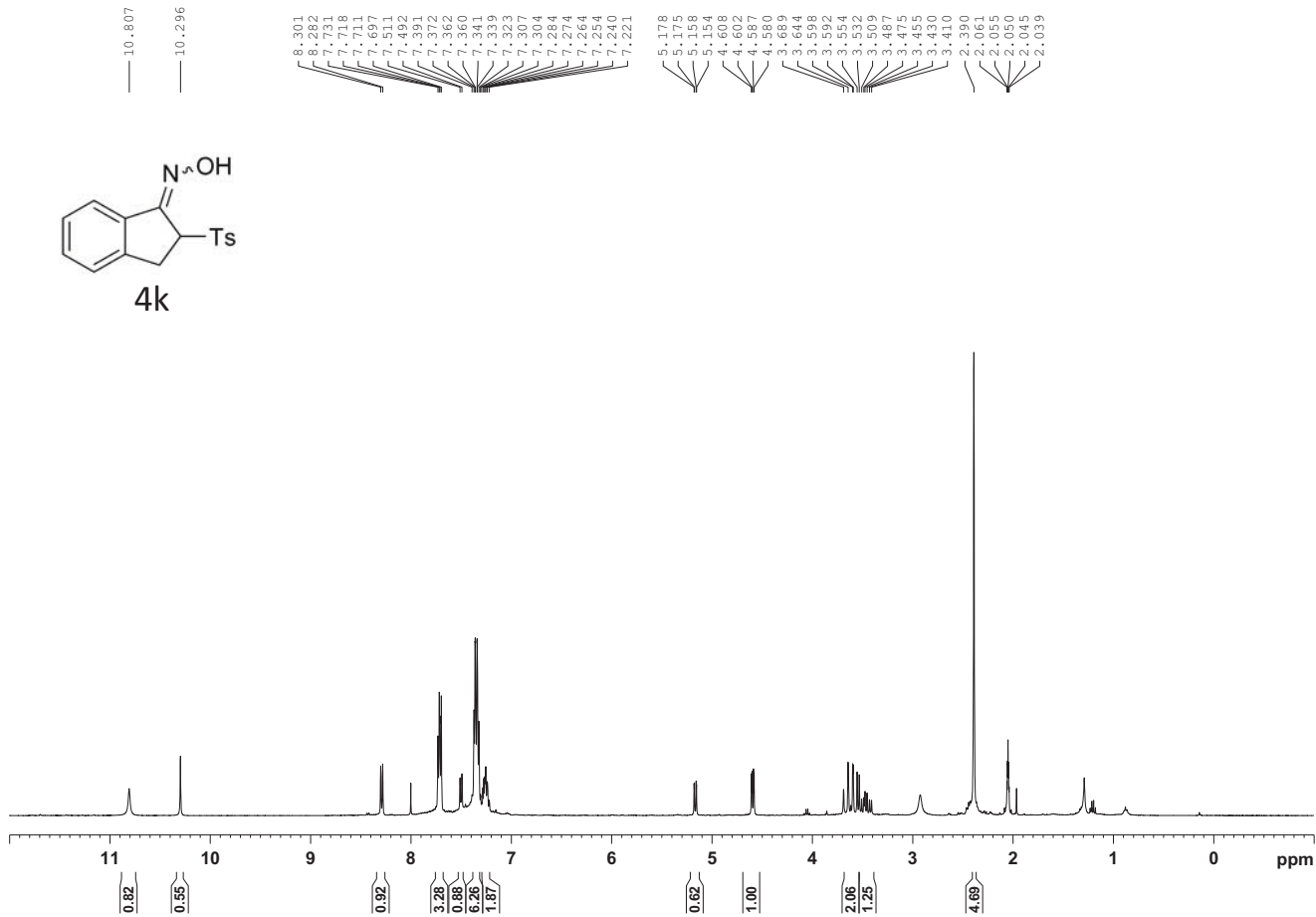
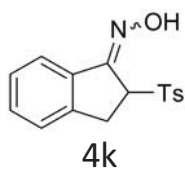
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 1.519, 1.501  
 0.000

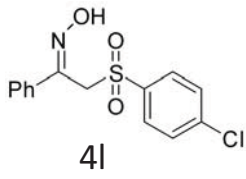


160.58, 152.92, 144.79, 135.96, 129.88, 129.48, 128.83, 125.52, 113.81  
 77.32, 77.00, 76.68  
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 21.60, 12.18





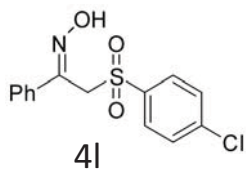
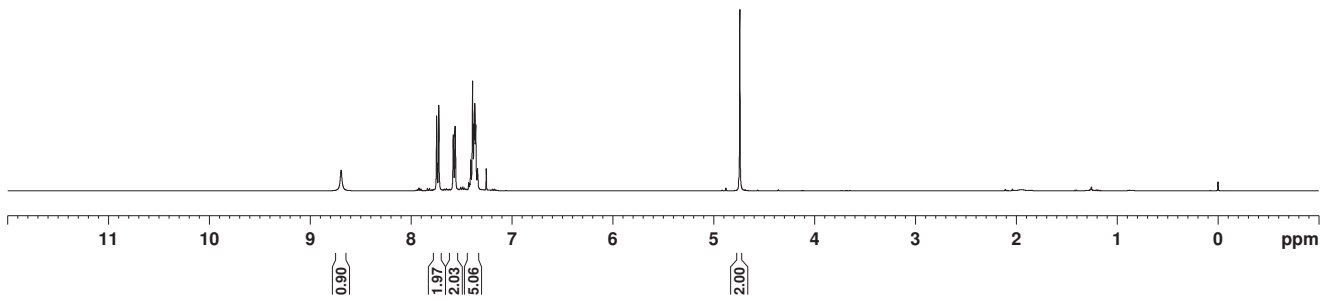




8.696  
7.748  
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7.566  
7.563  
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7.237

4.742

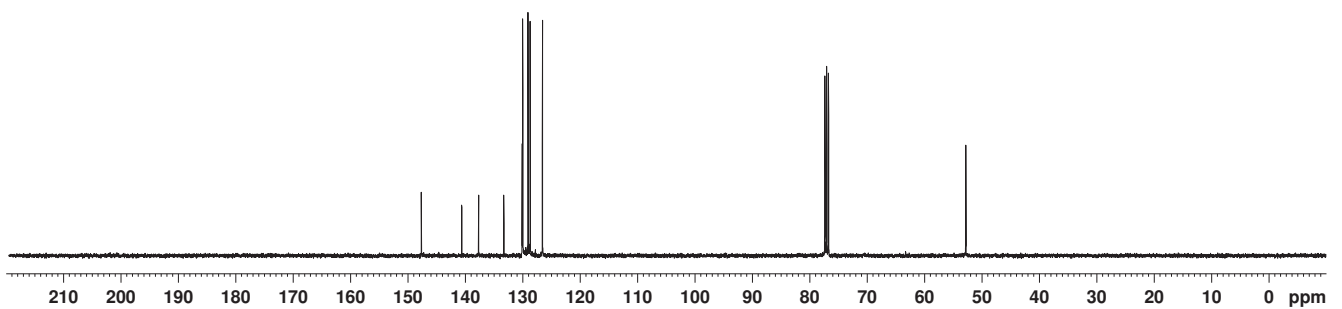
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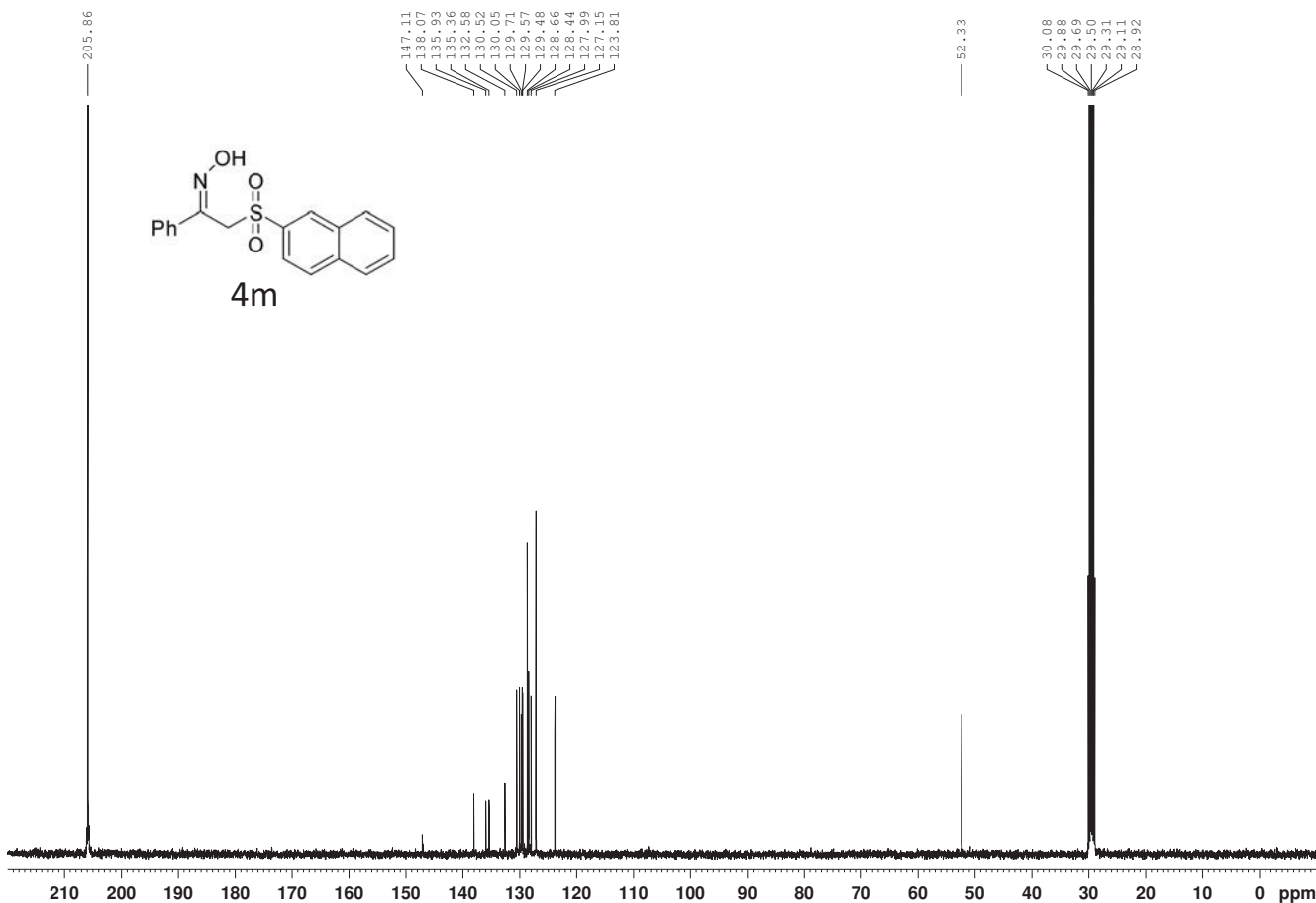
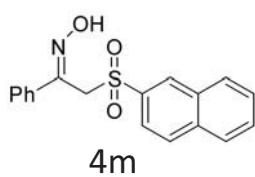
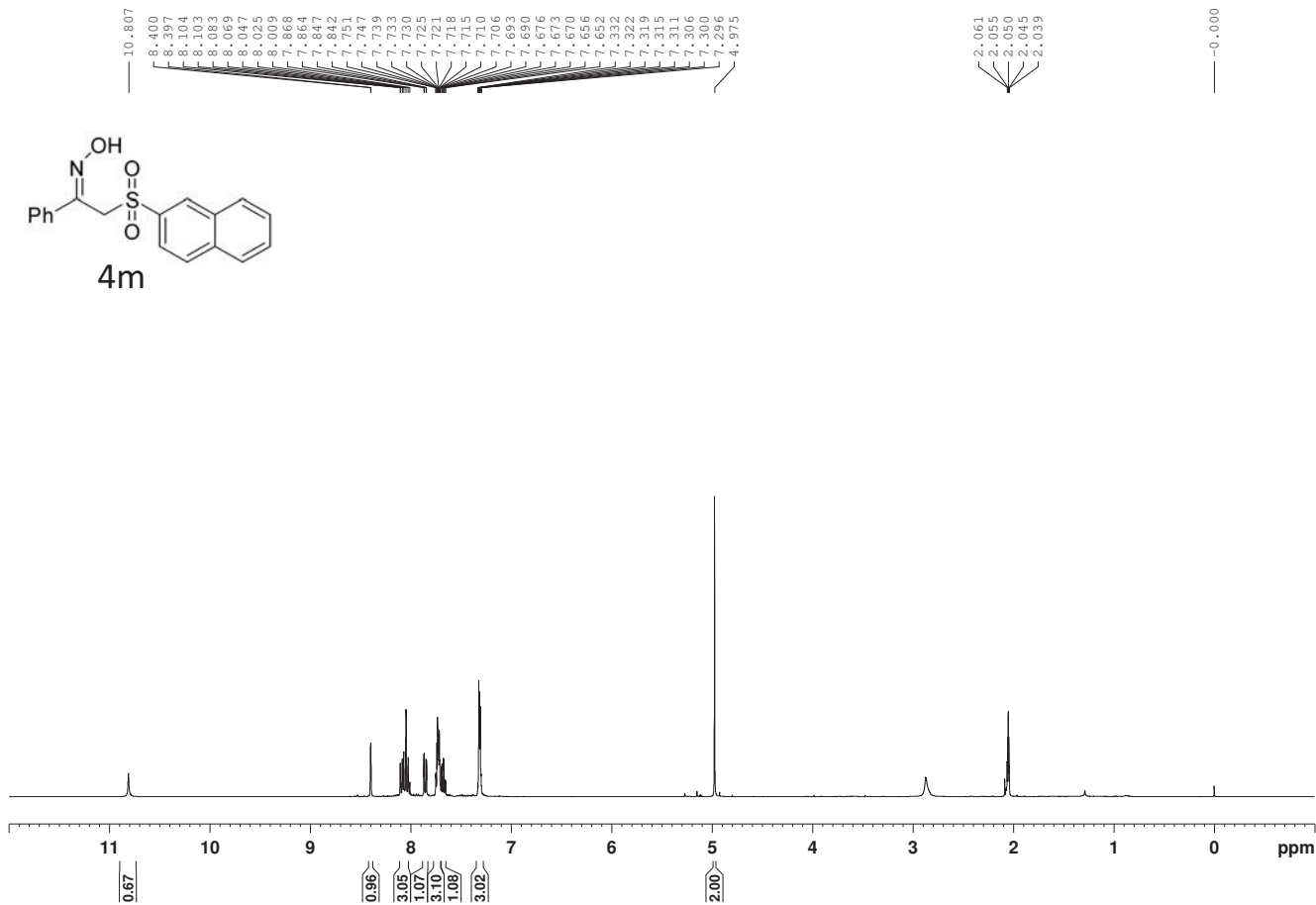
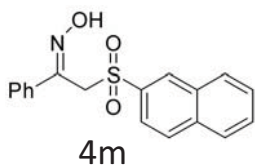


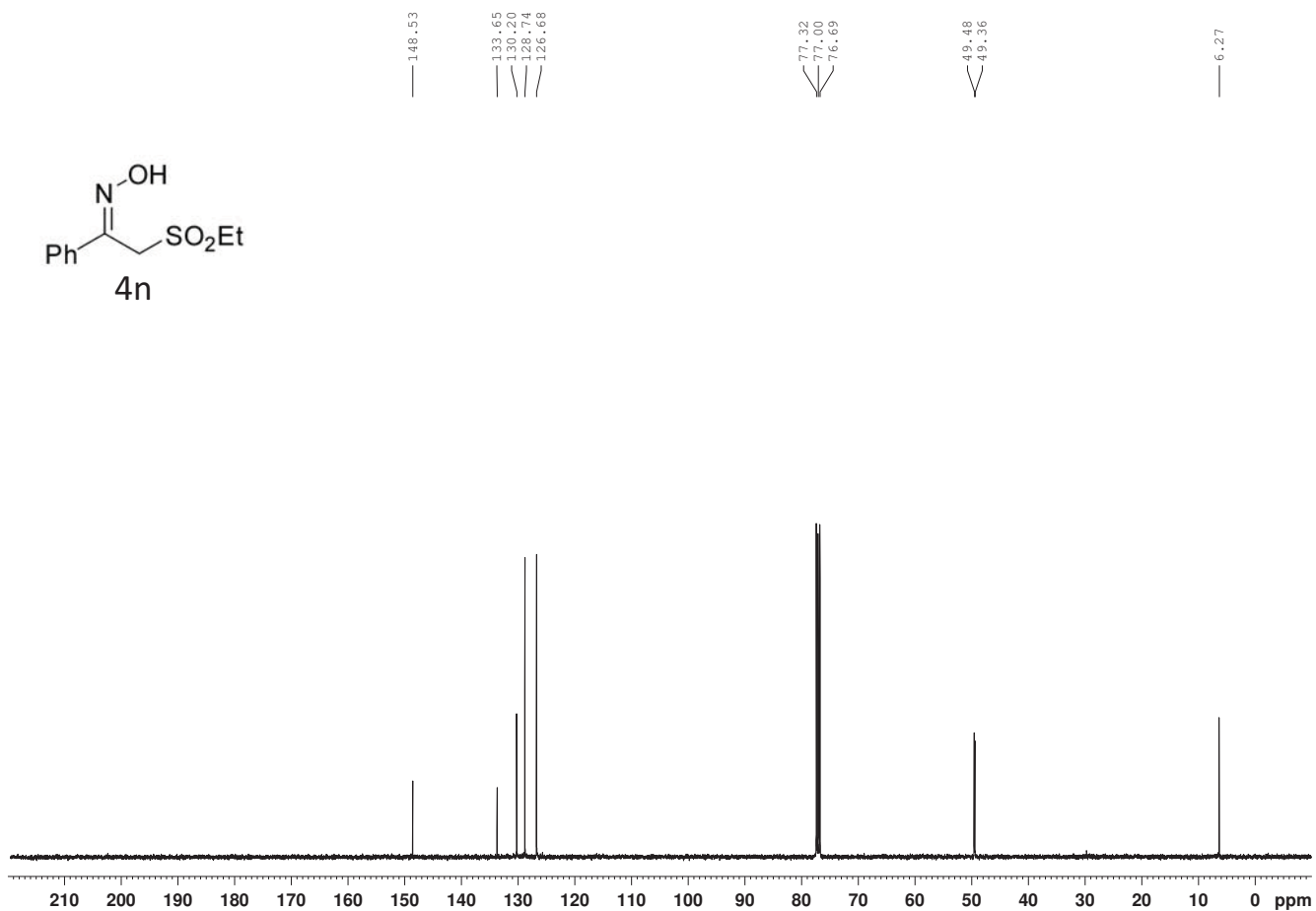
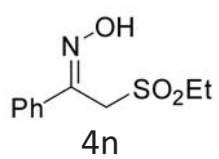
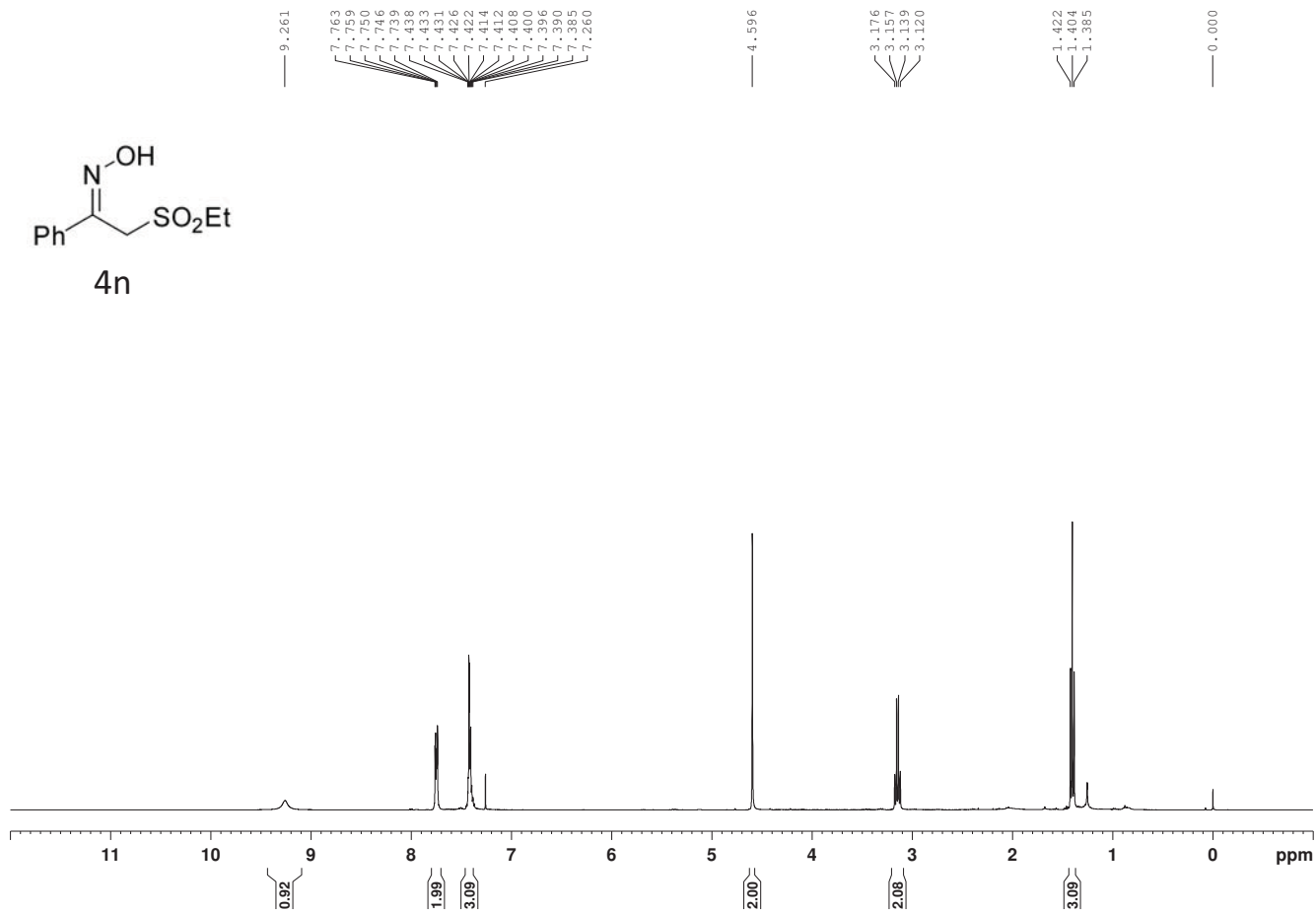
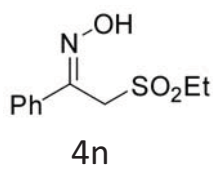
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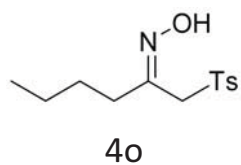
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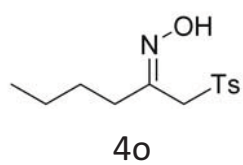
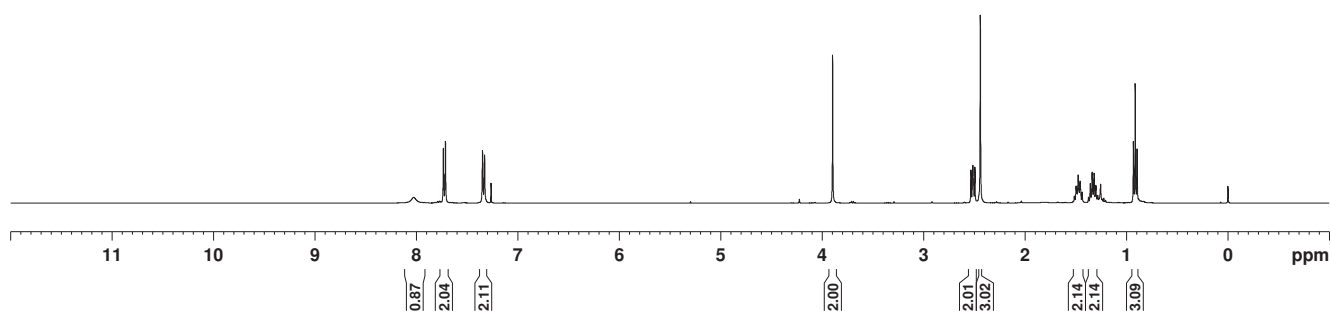




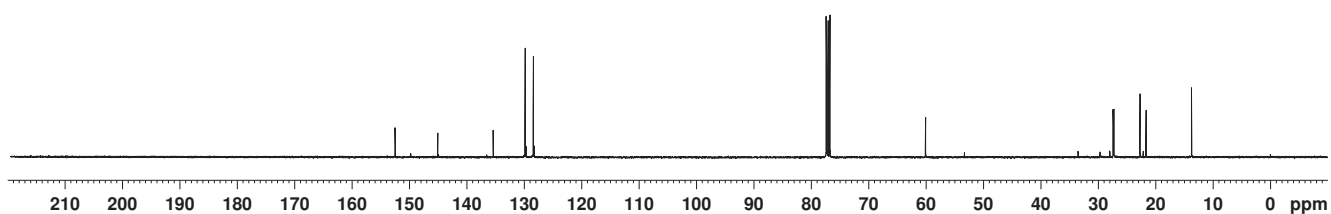


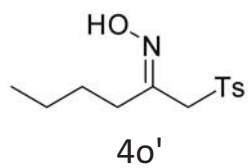


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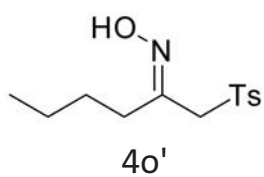
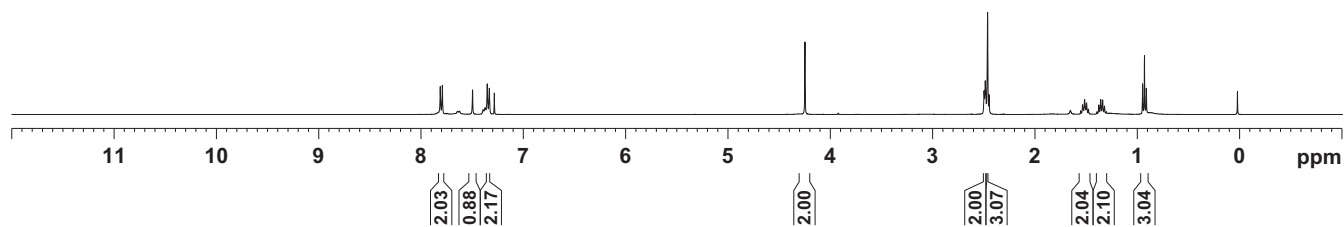




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7.263

4.227

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1.514  
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53.24

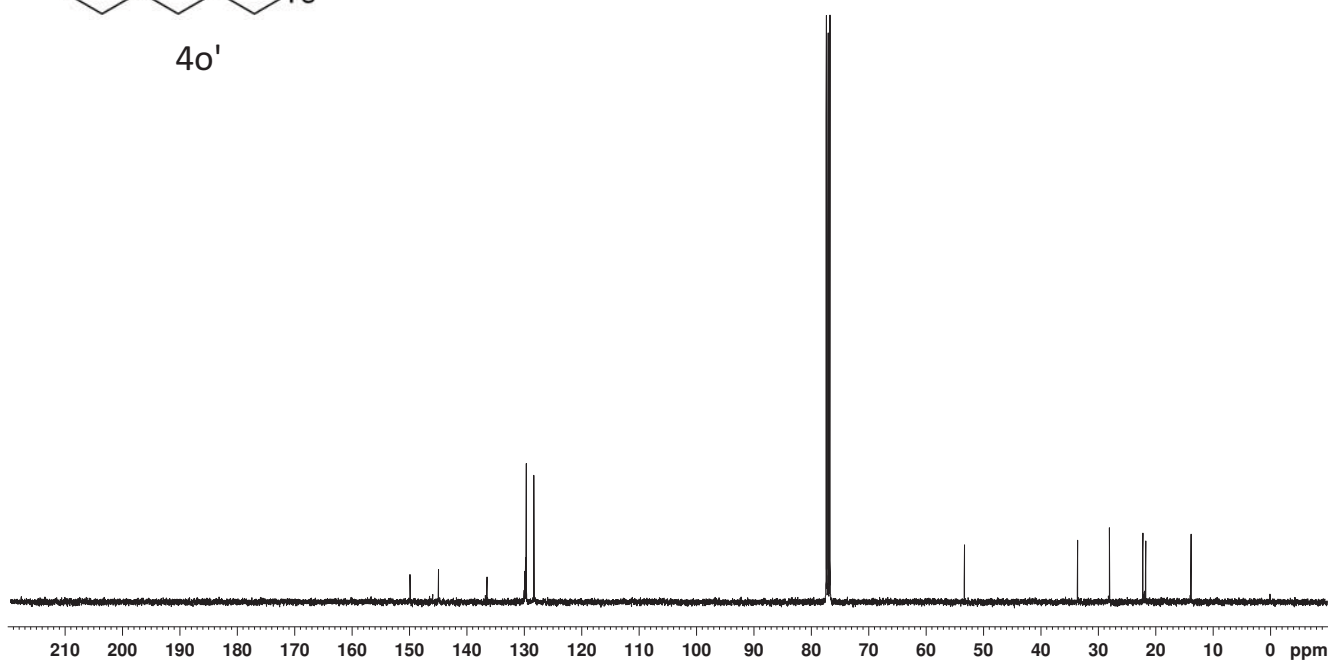
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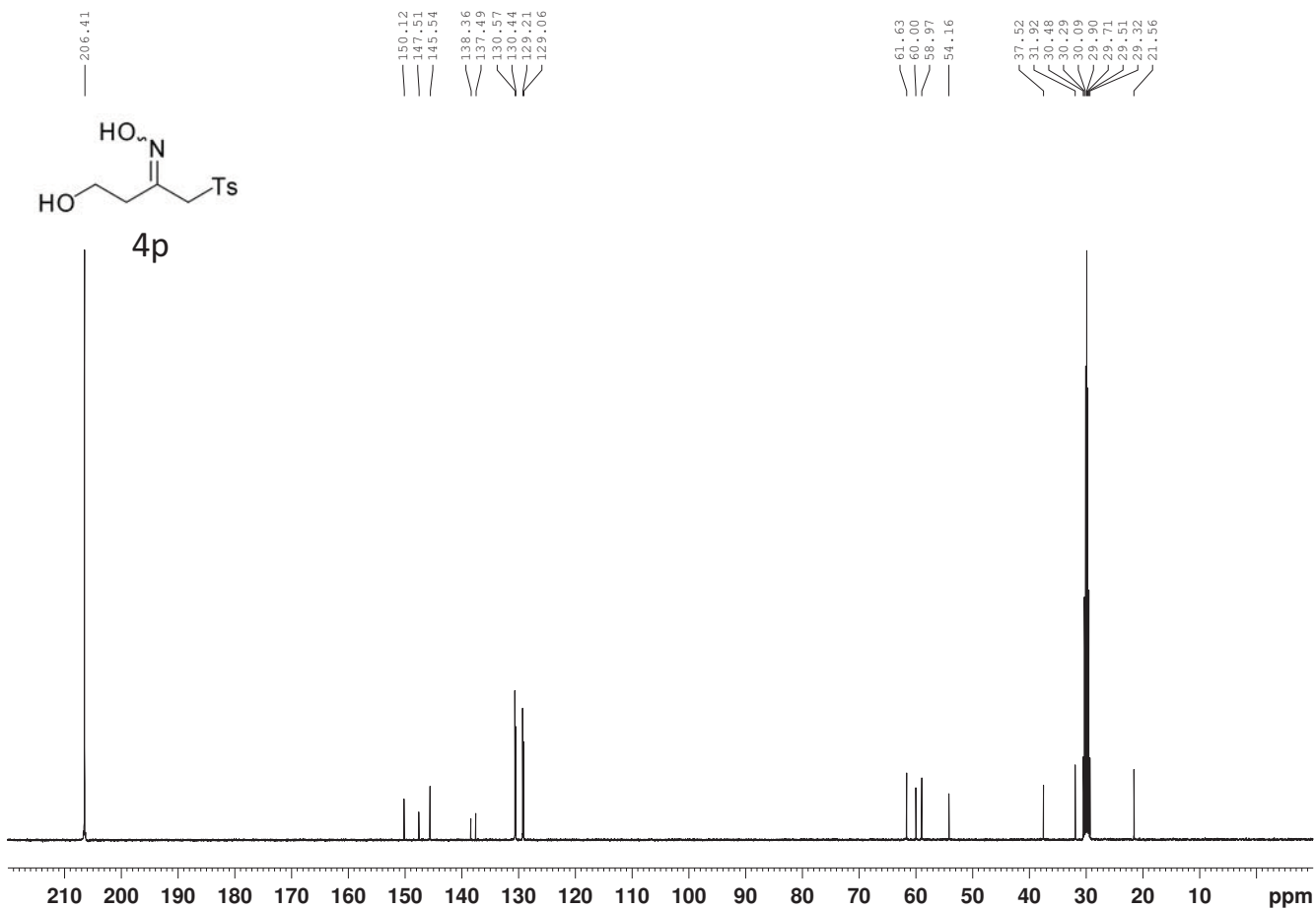
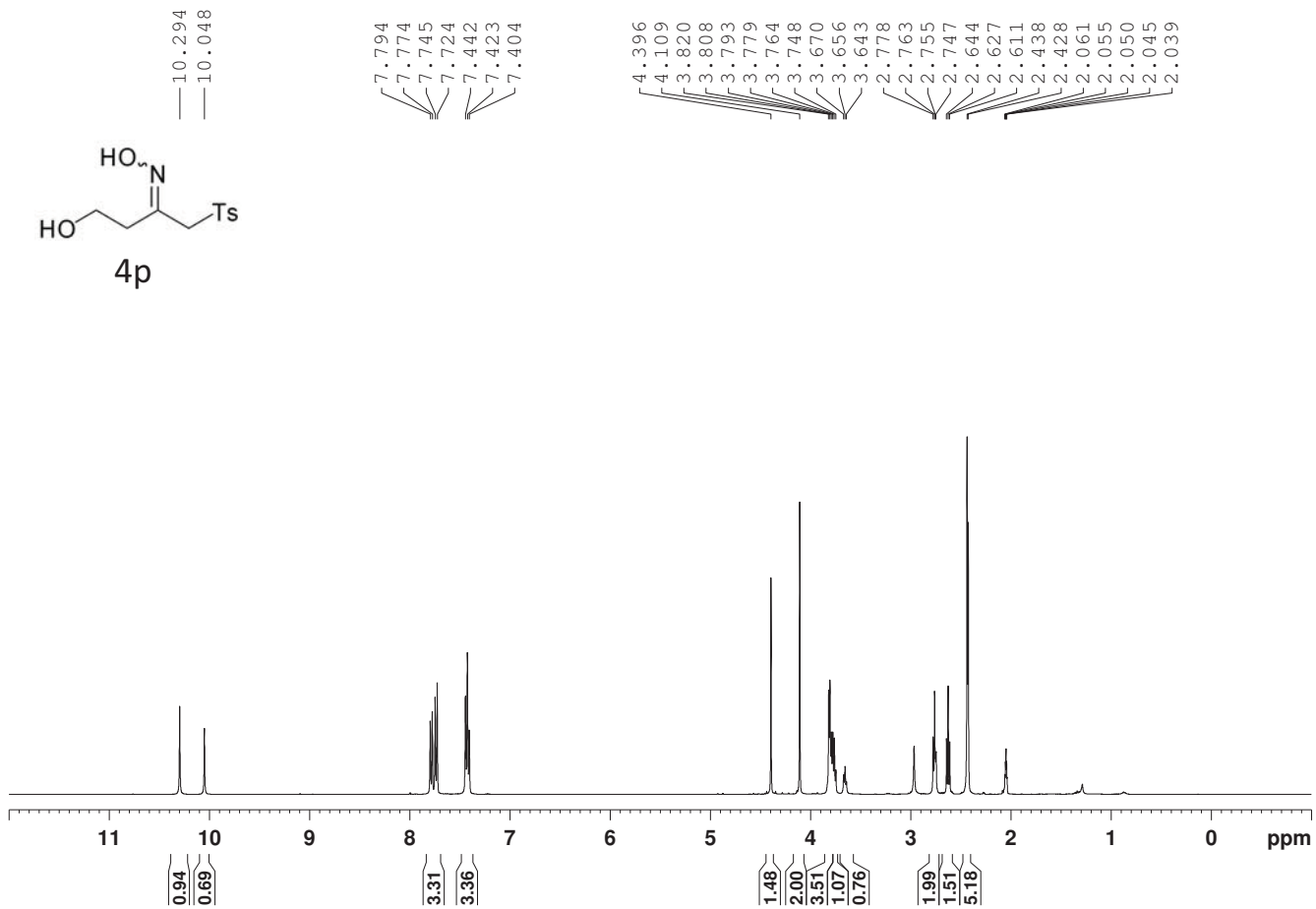
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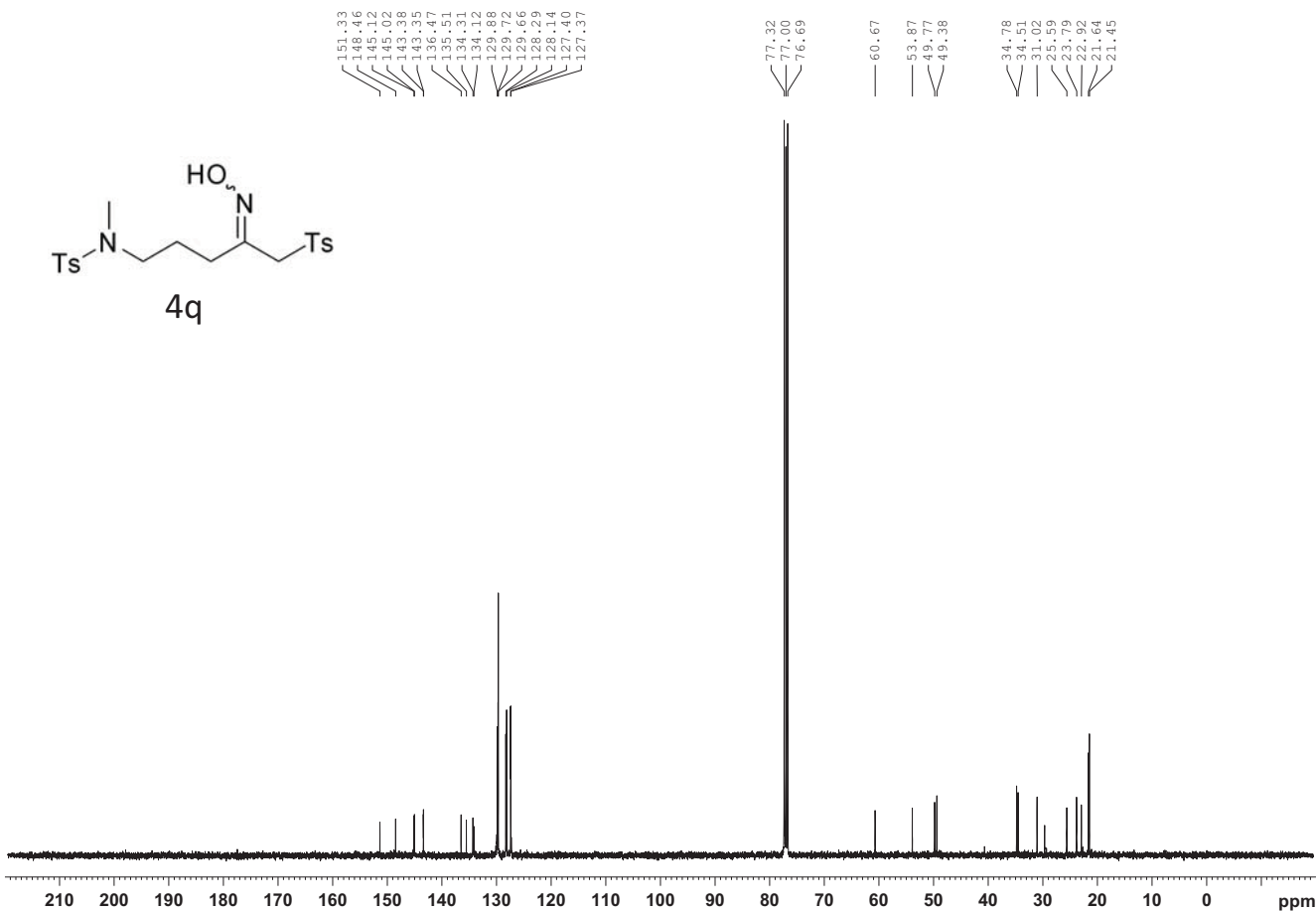
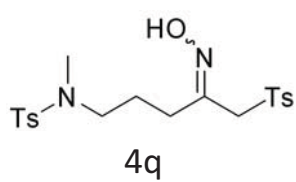
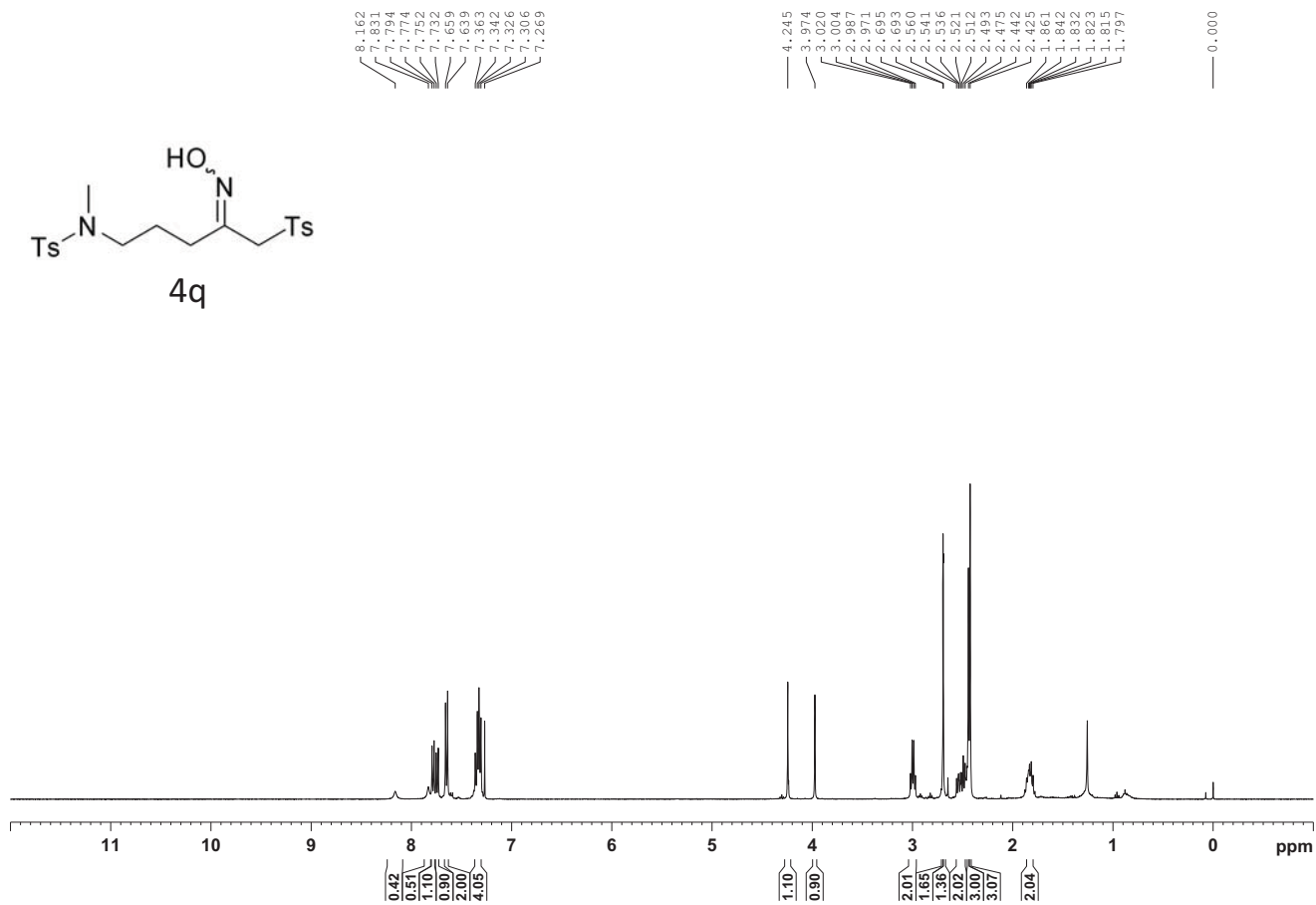
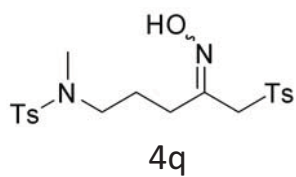
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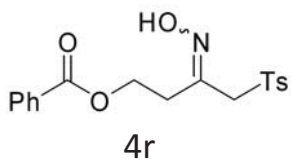
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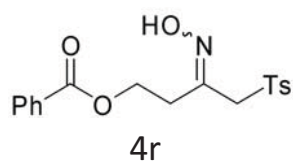
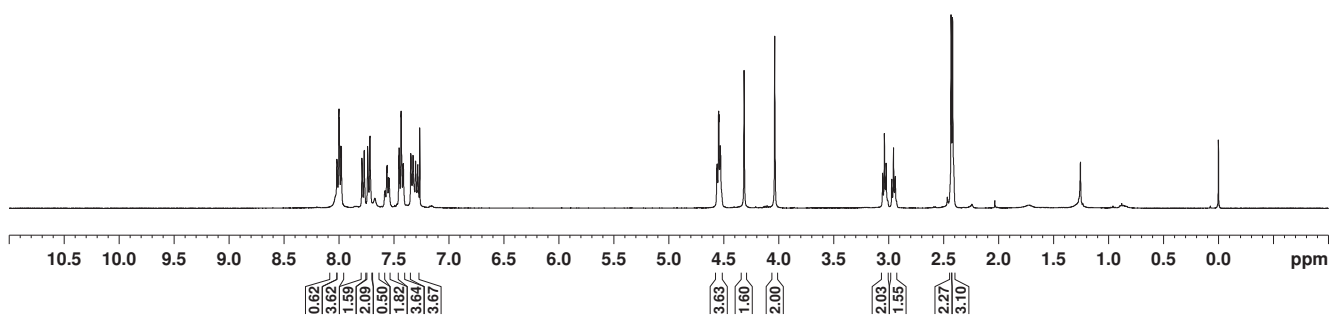


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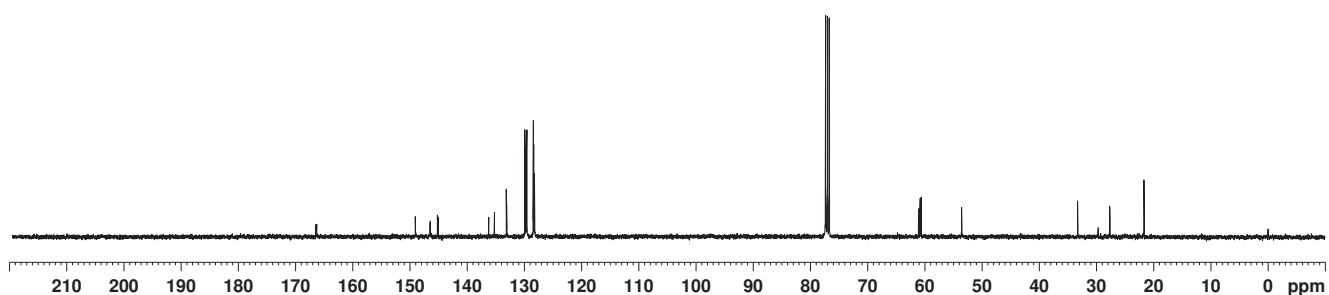
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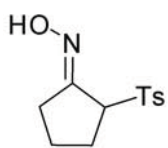
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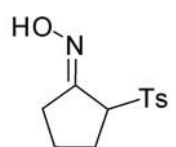
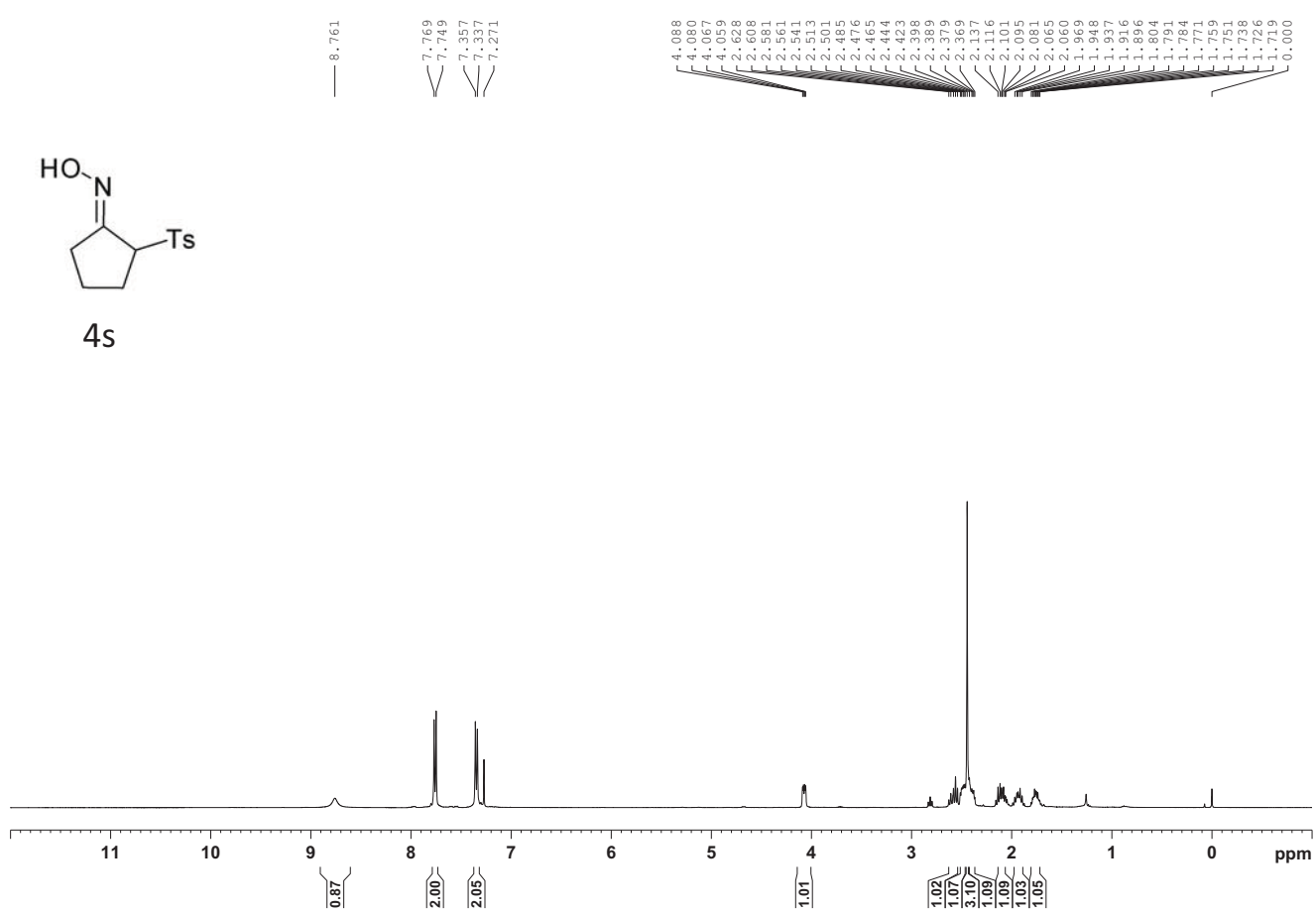
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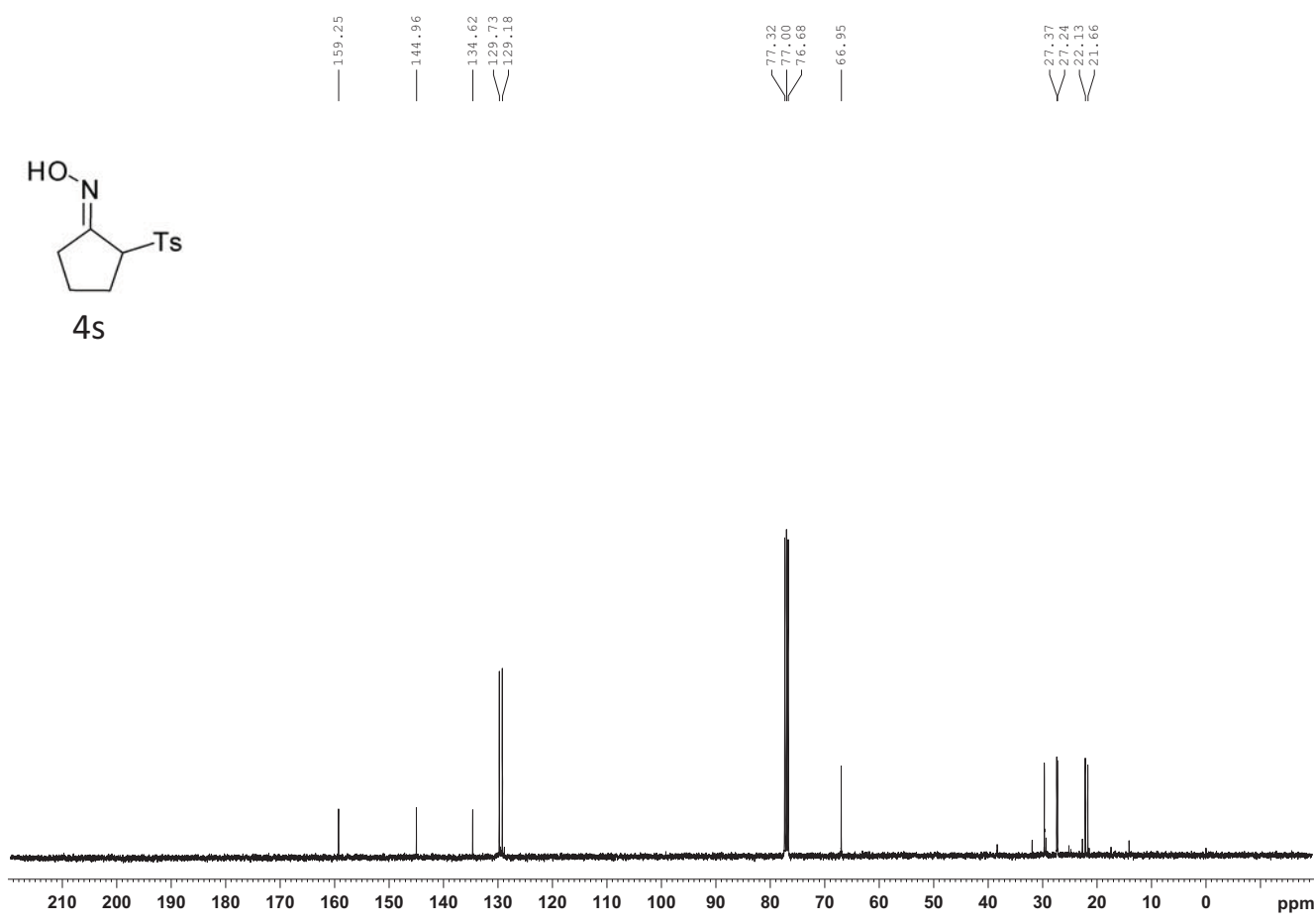


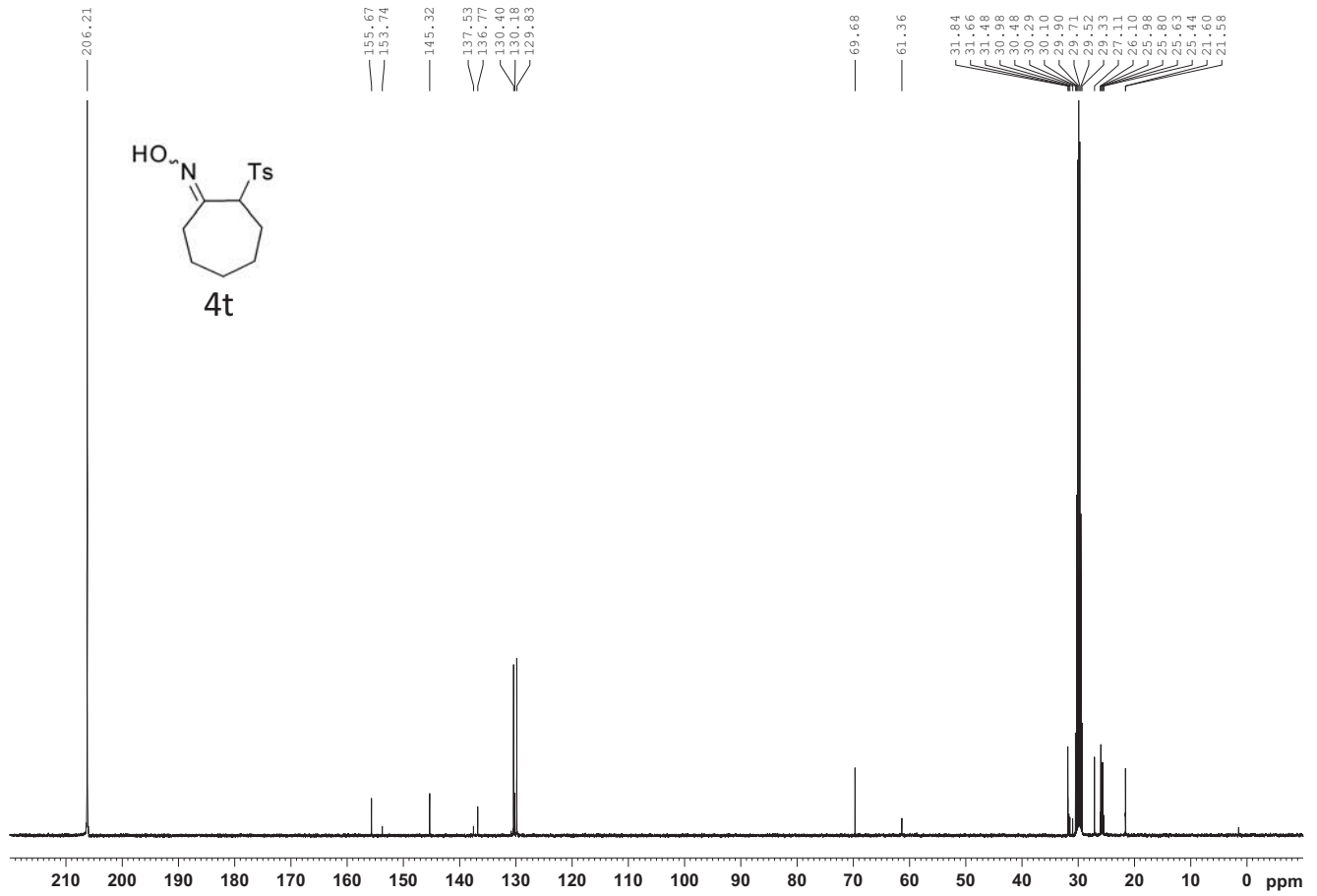
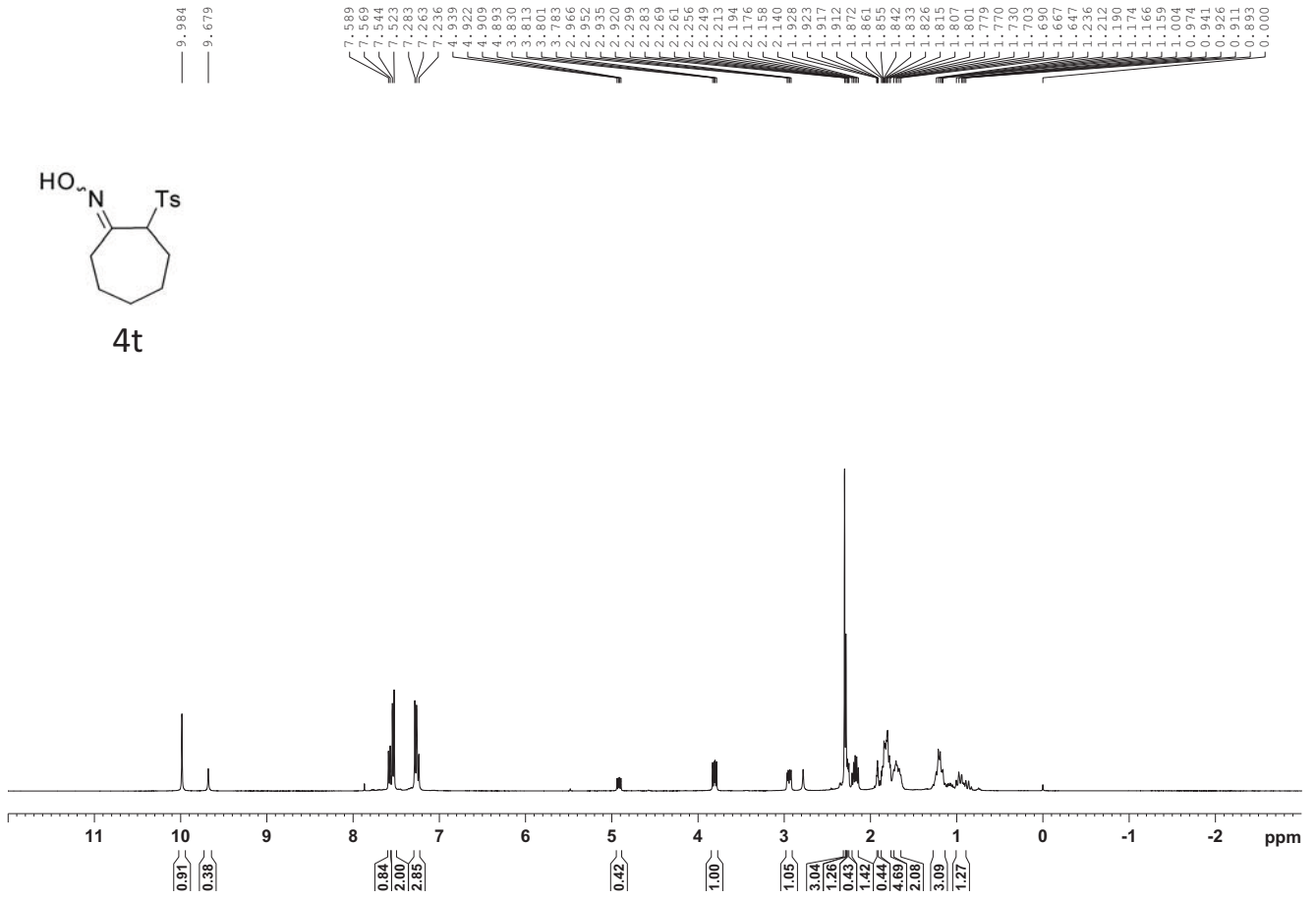
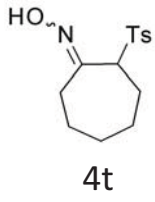


4s



4s

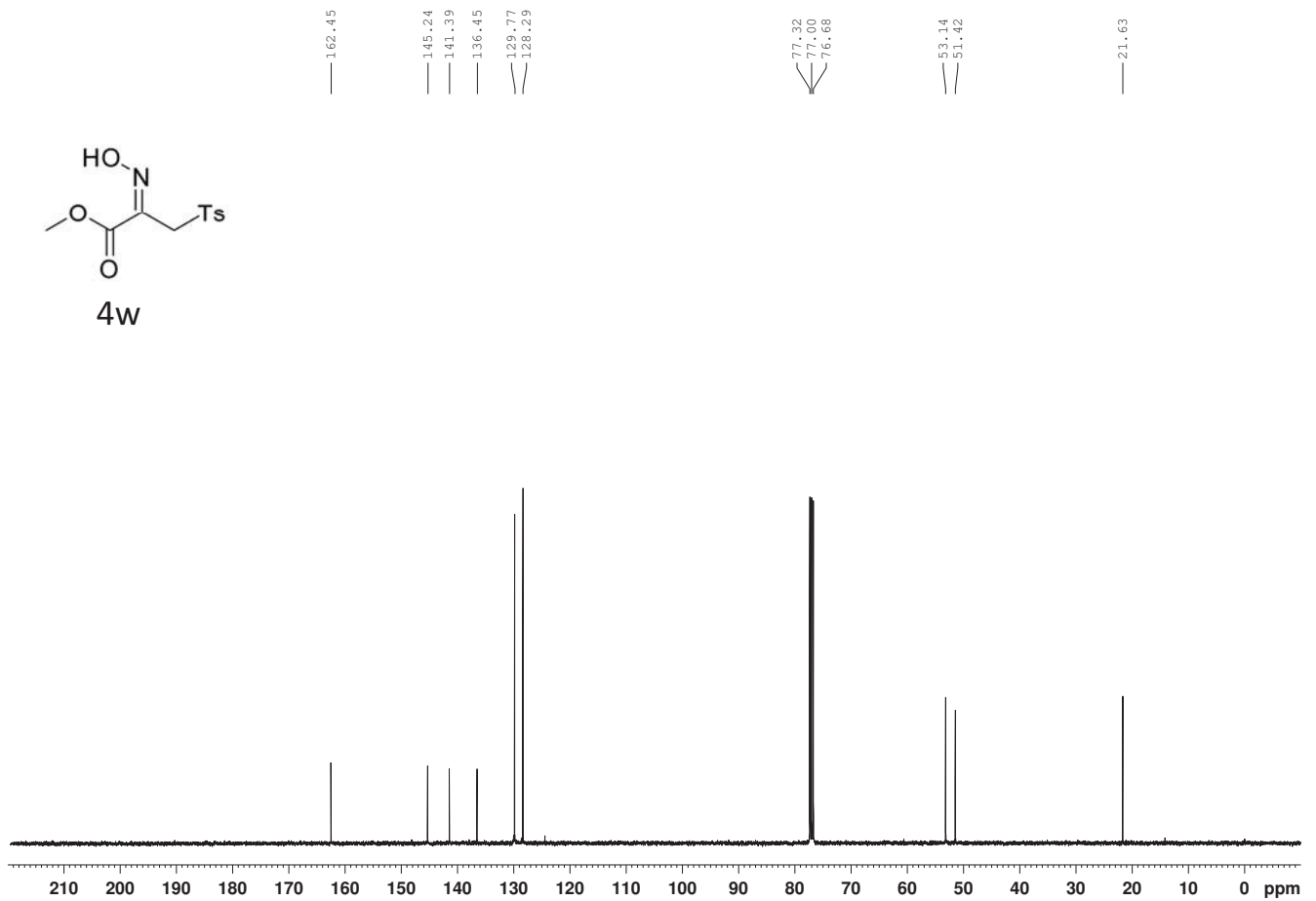
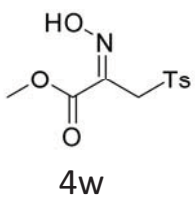
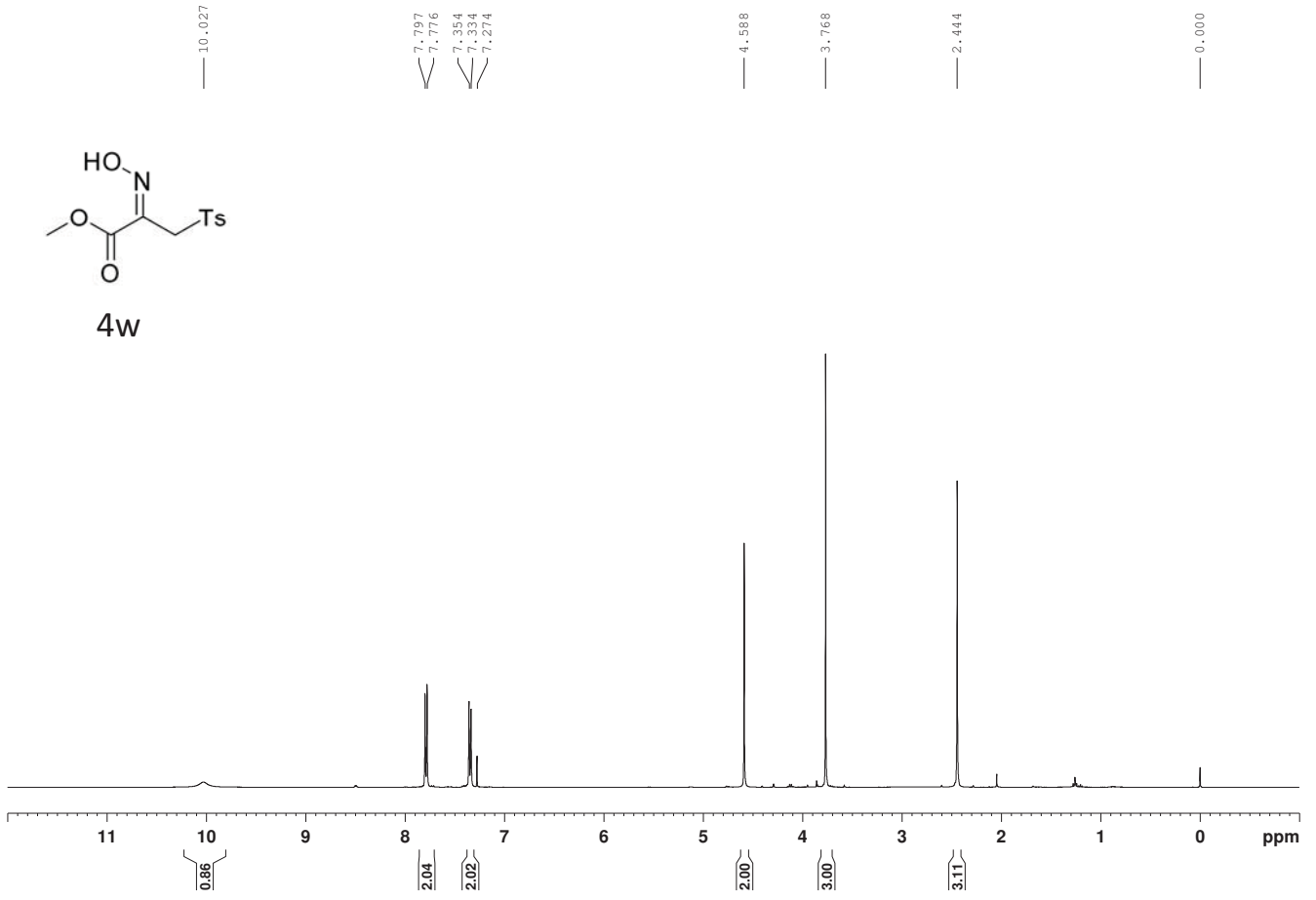
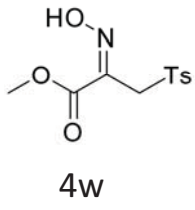


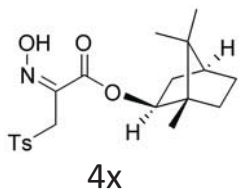










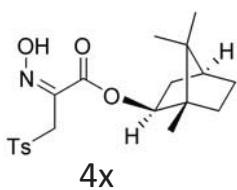
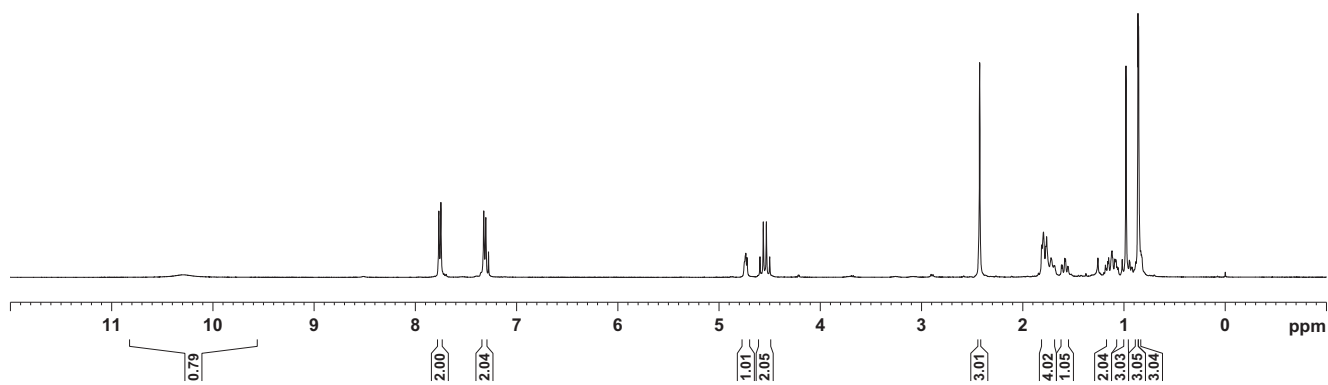


— 10.296

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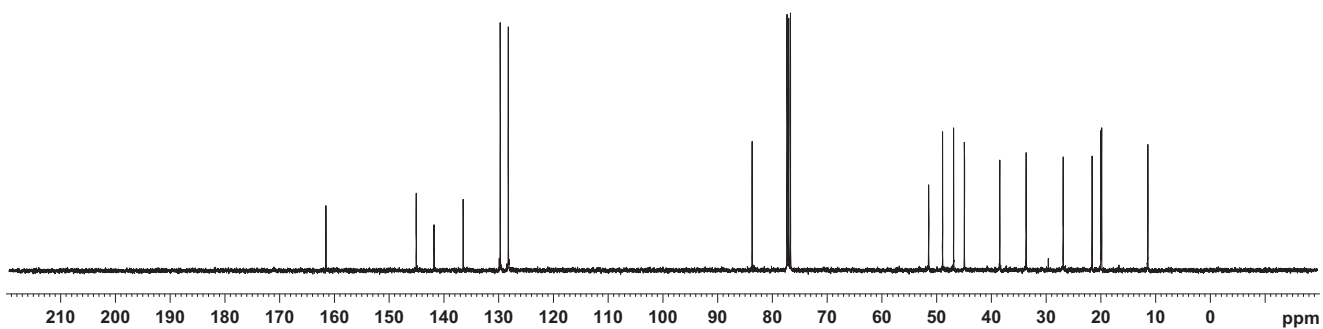


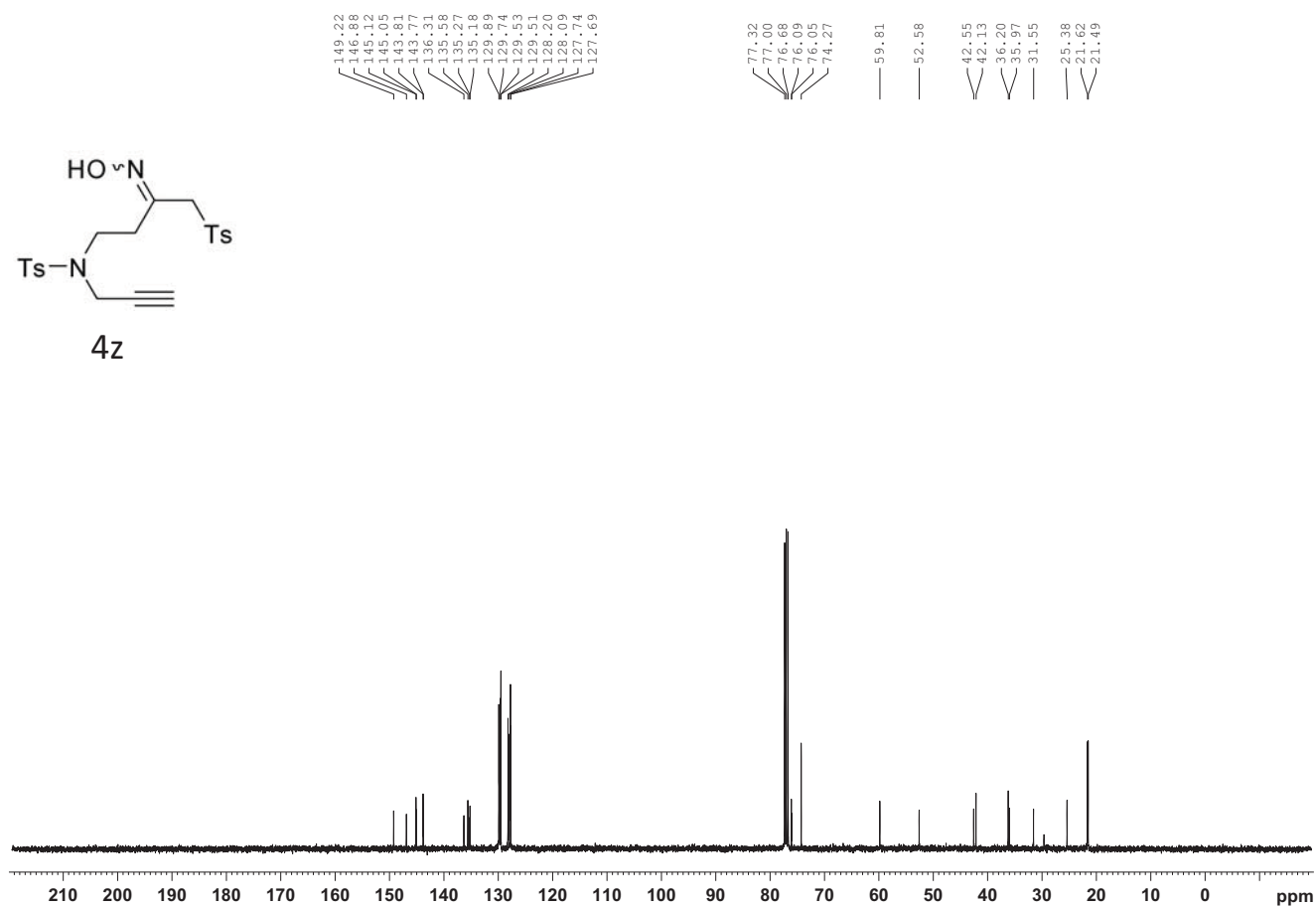
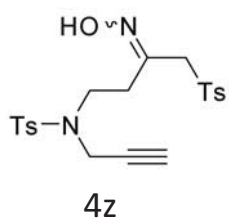
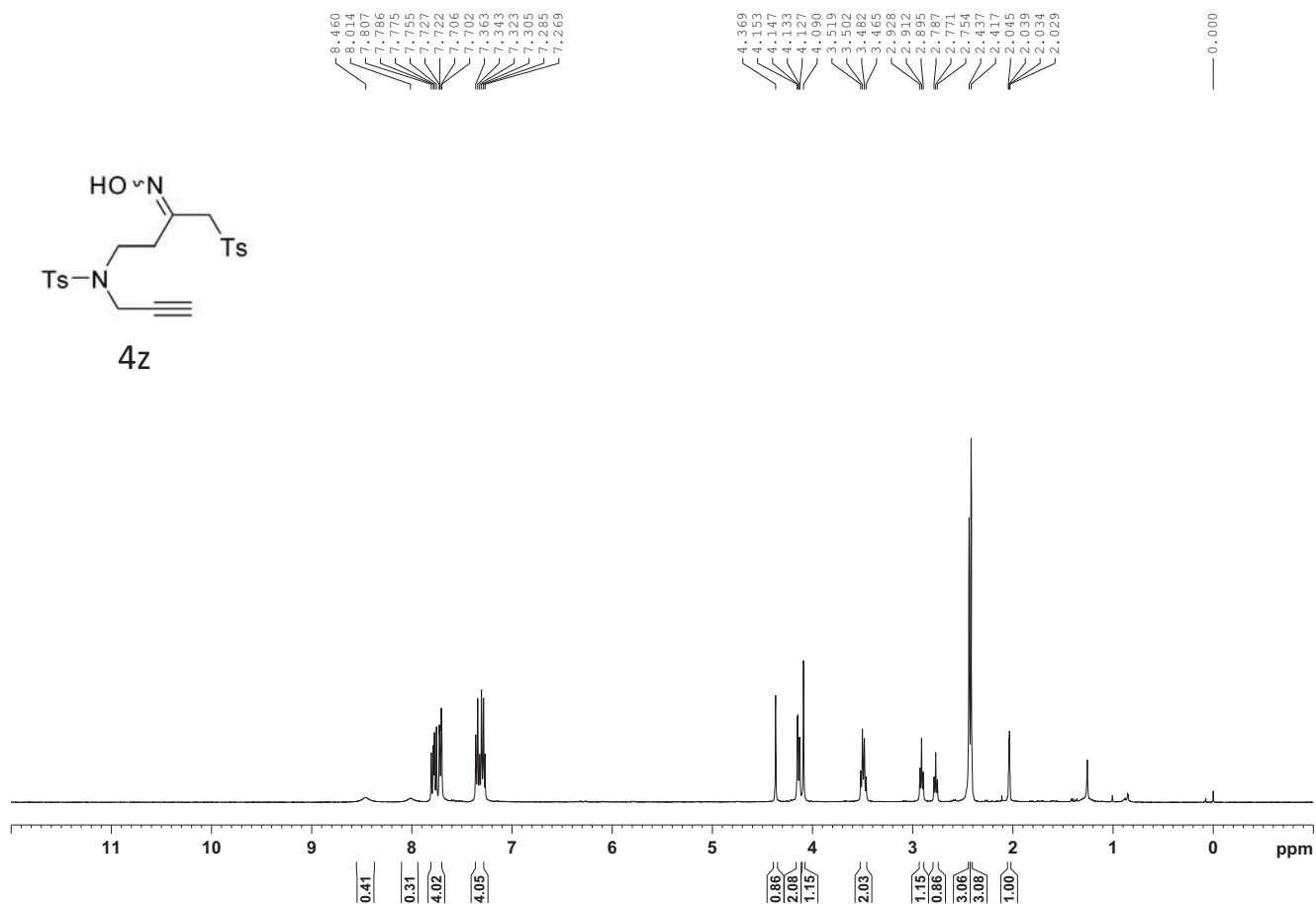
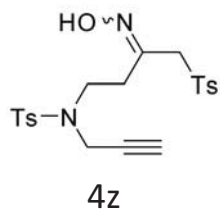
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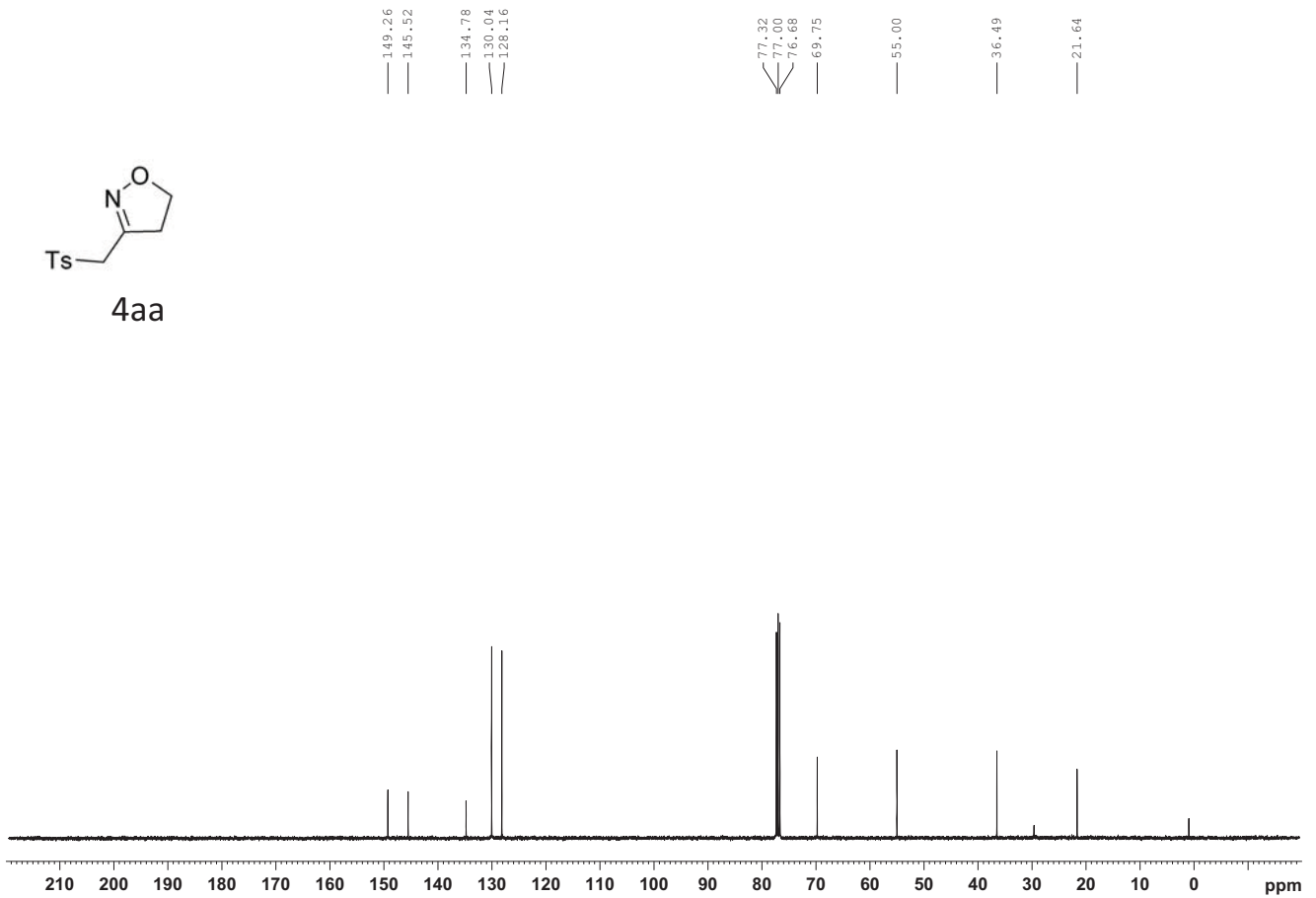
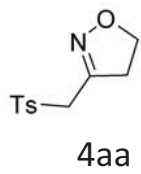
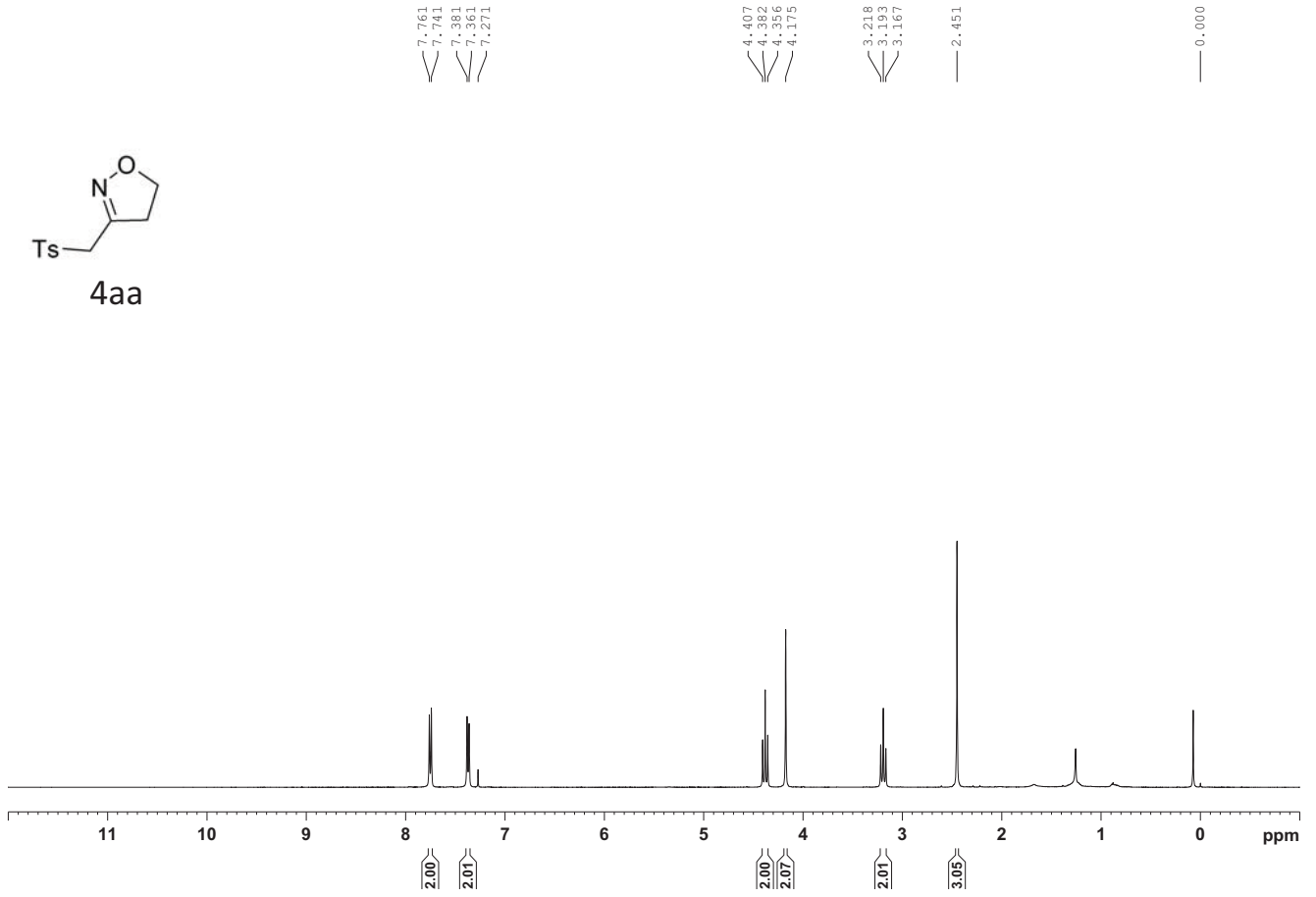
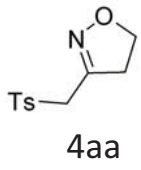
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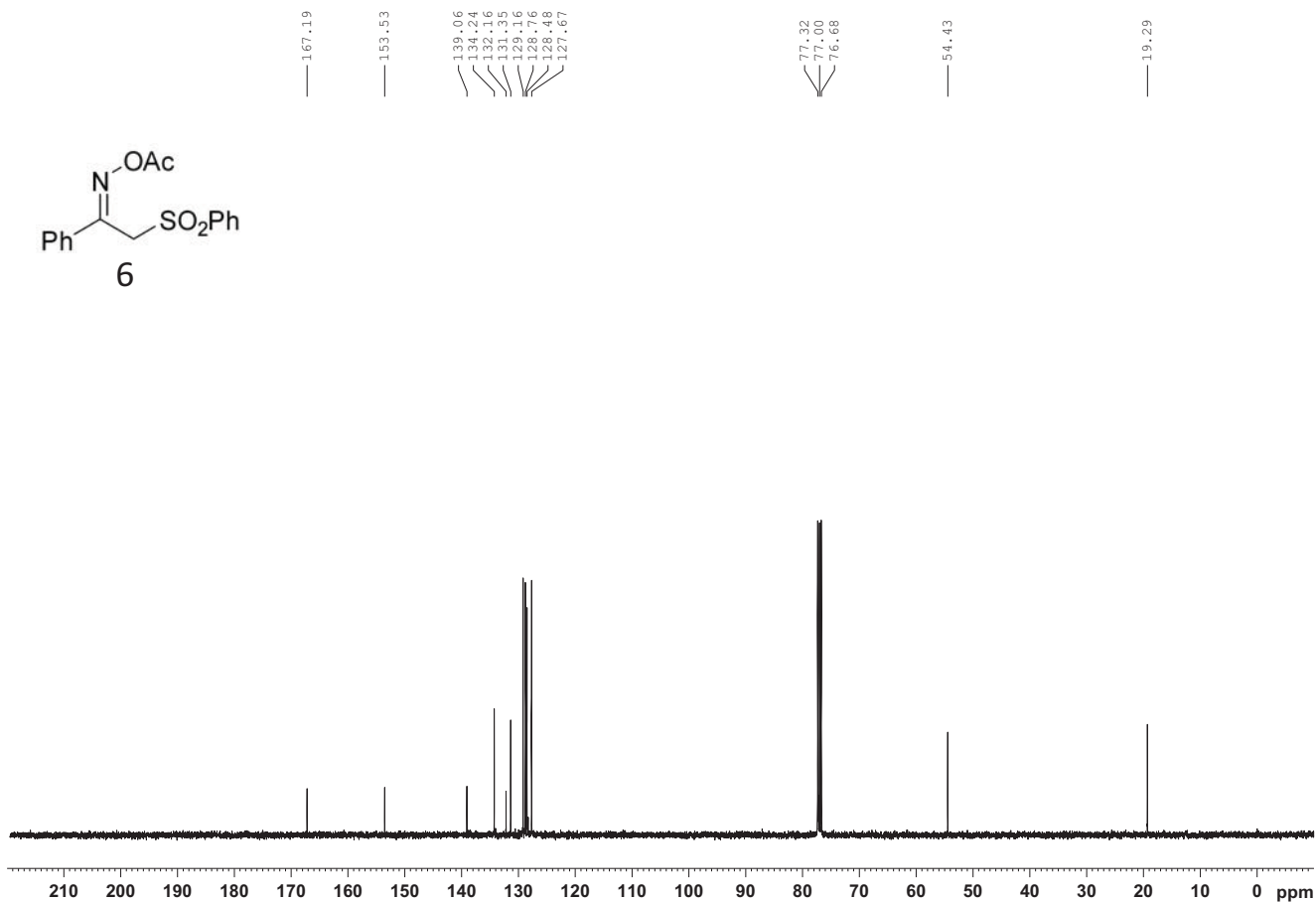
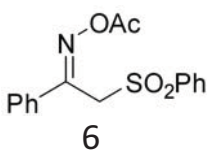
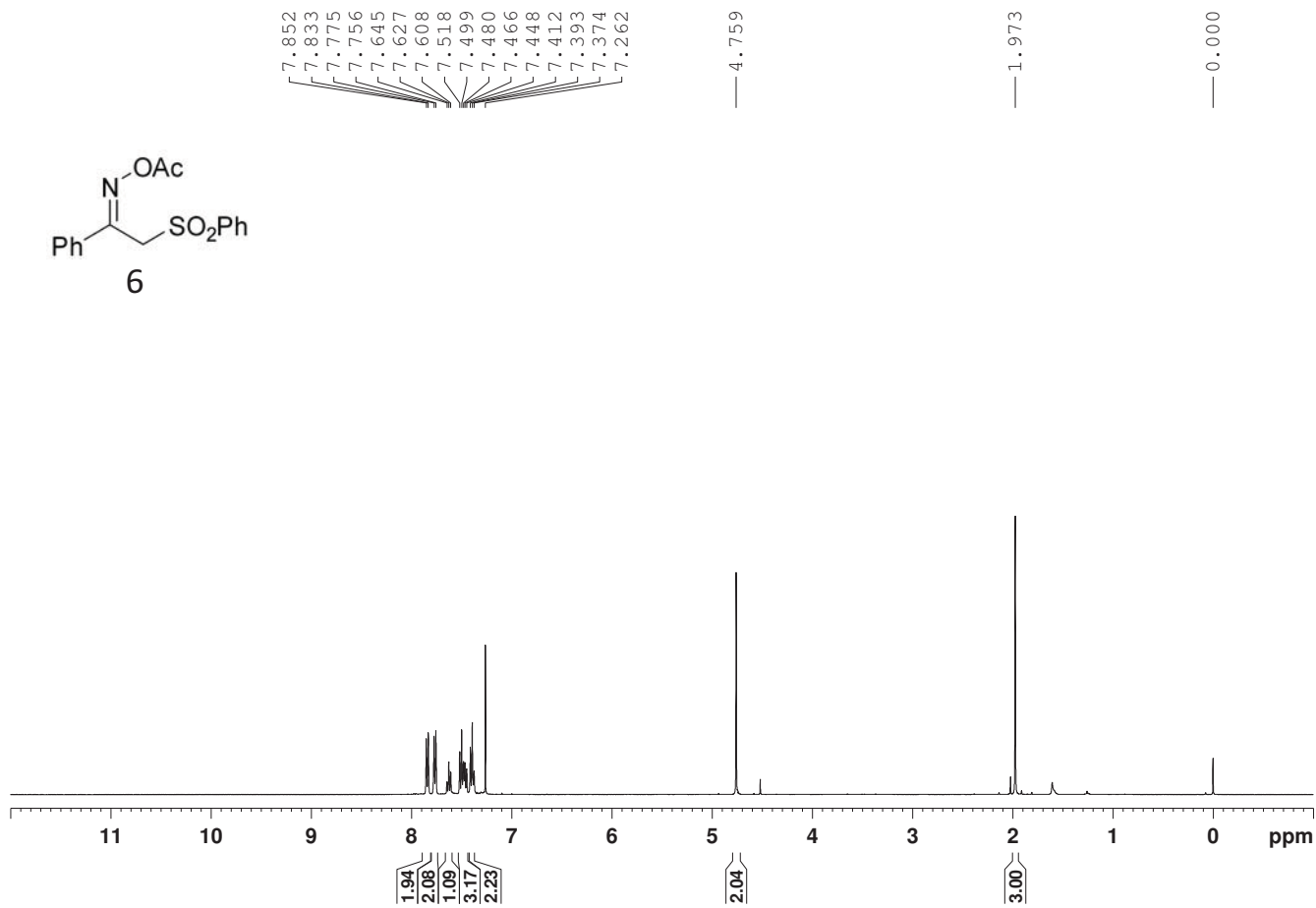
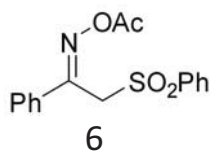
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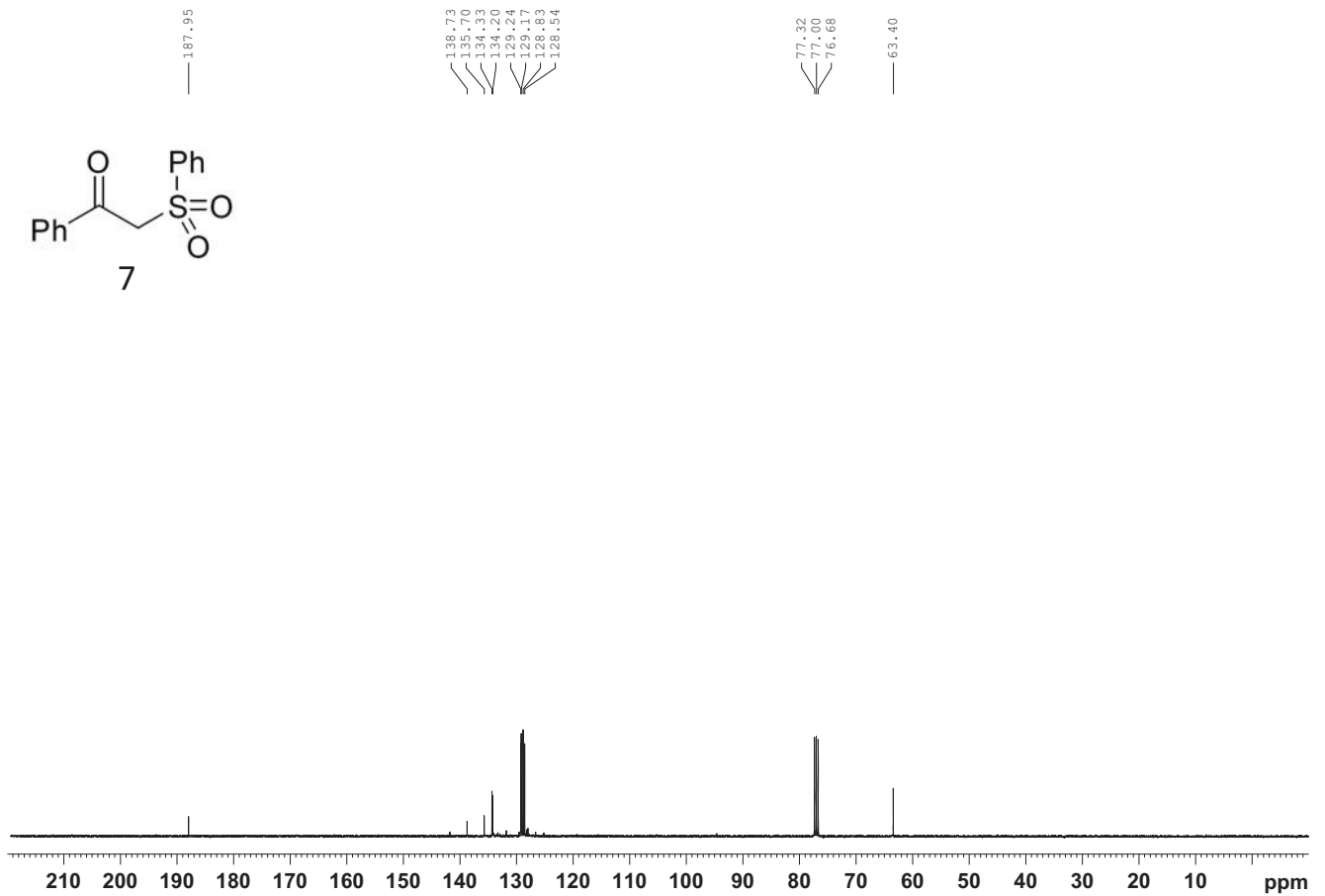
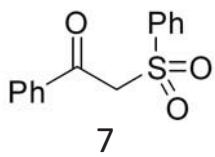
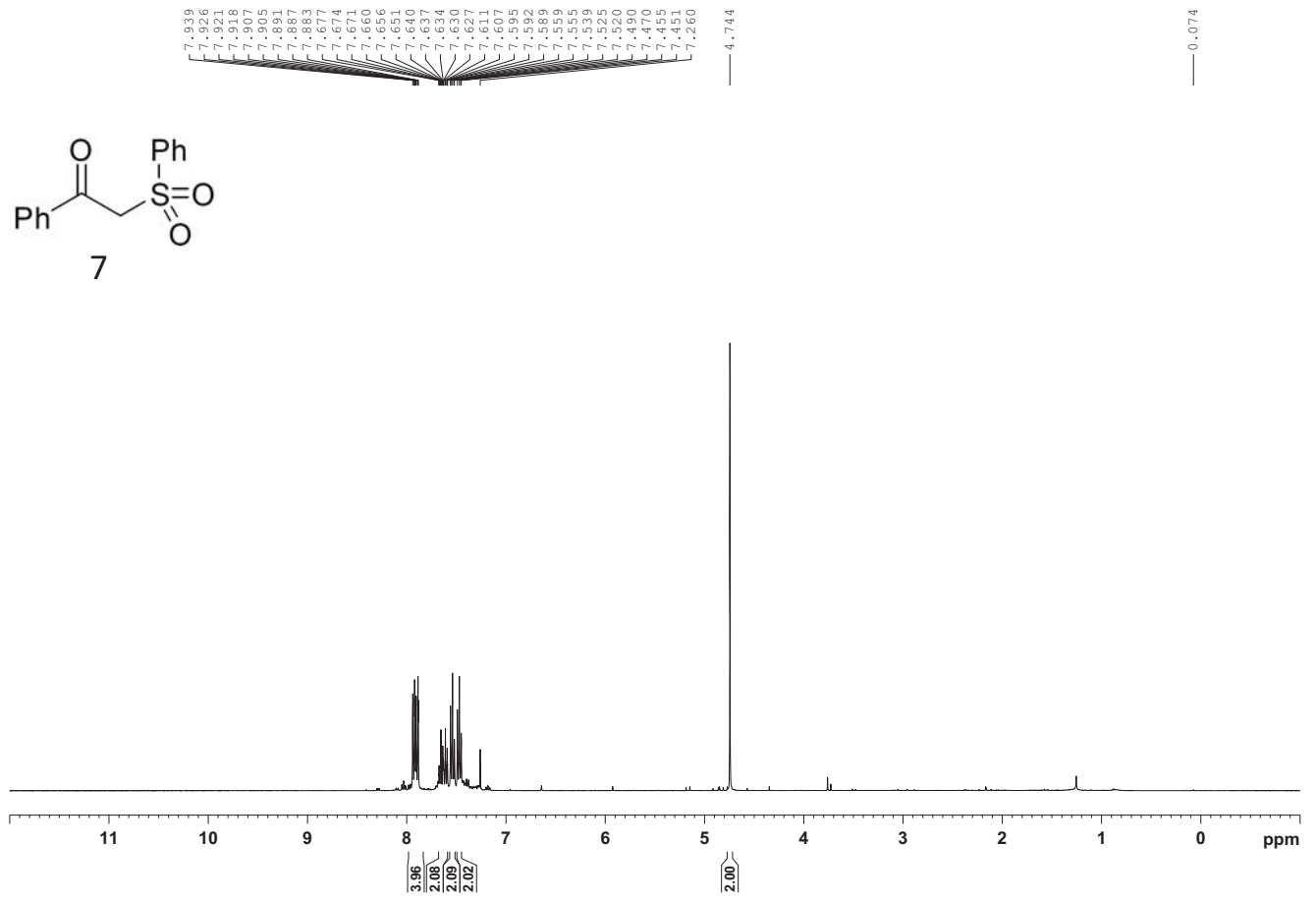
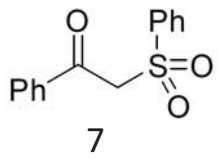
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11.40

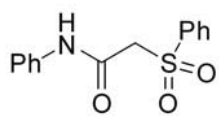




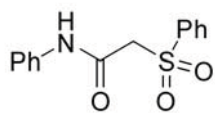
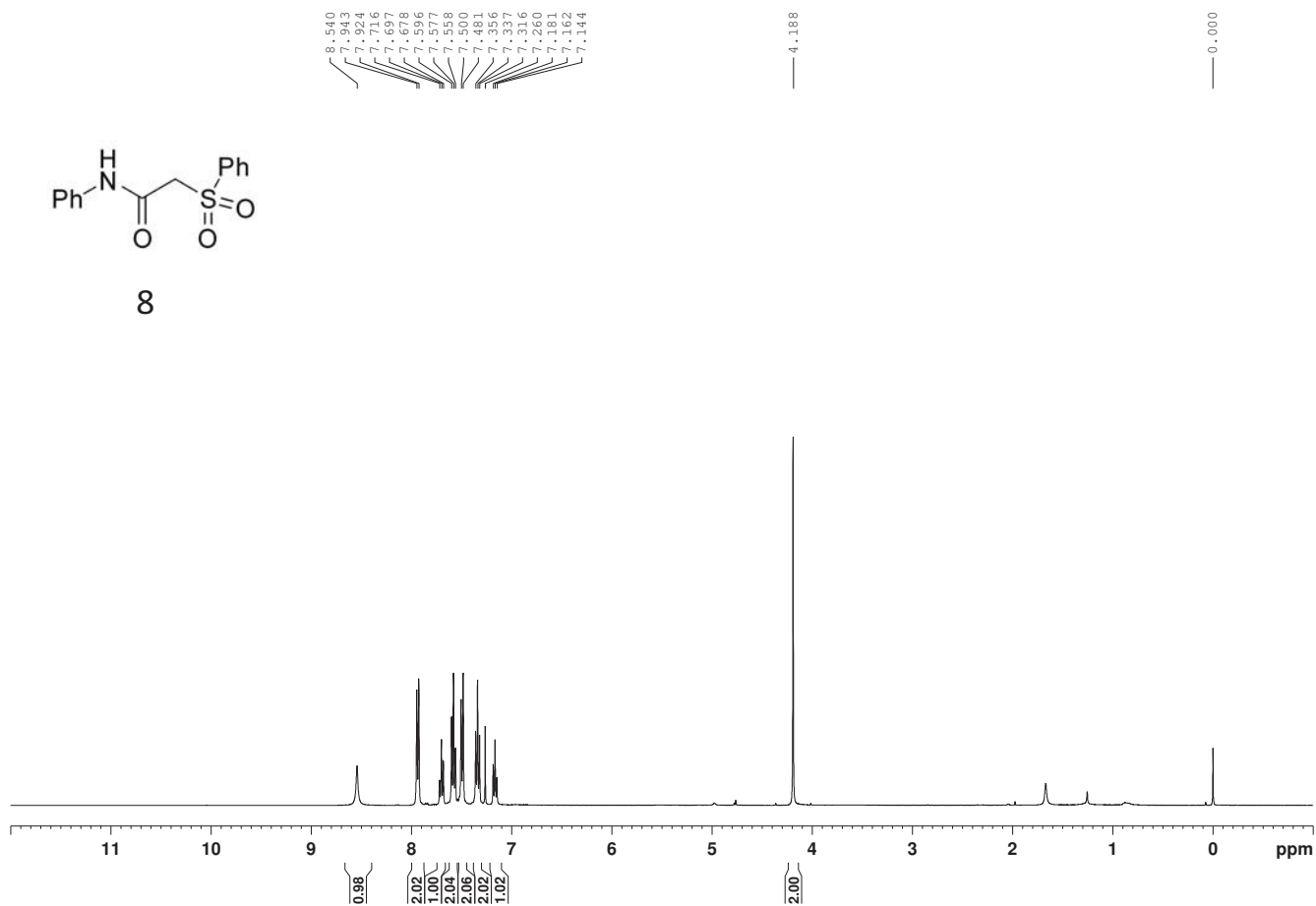




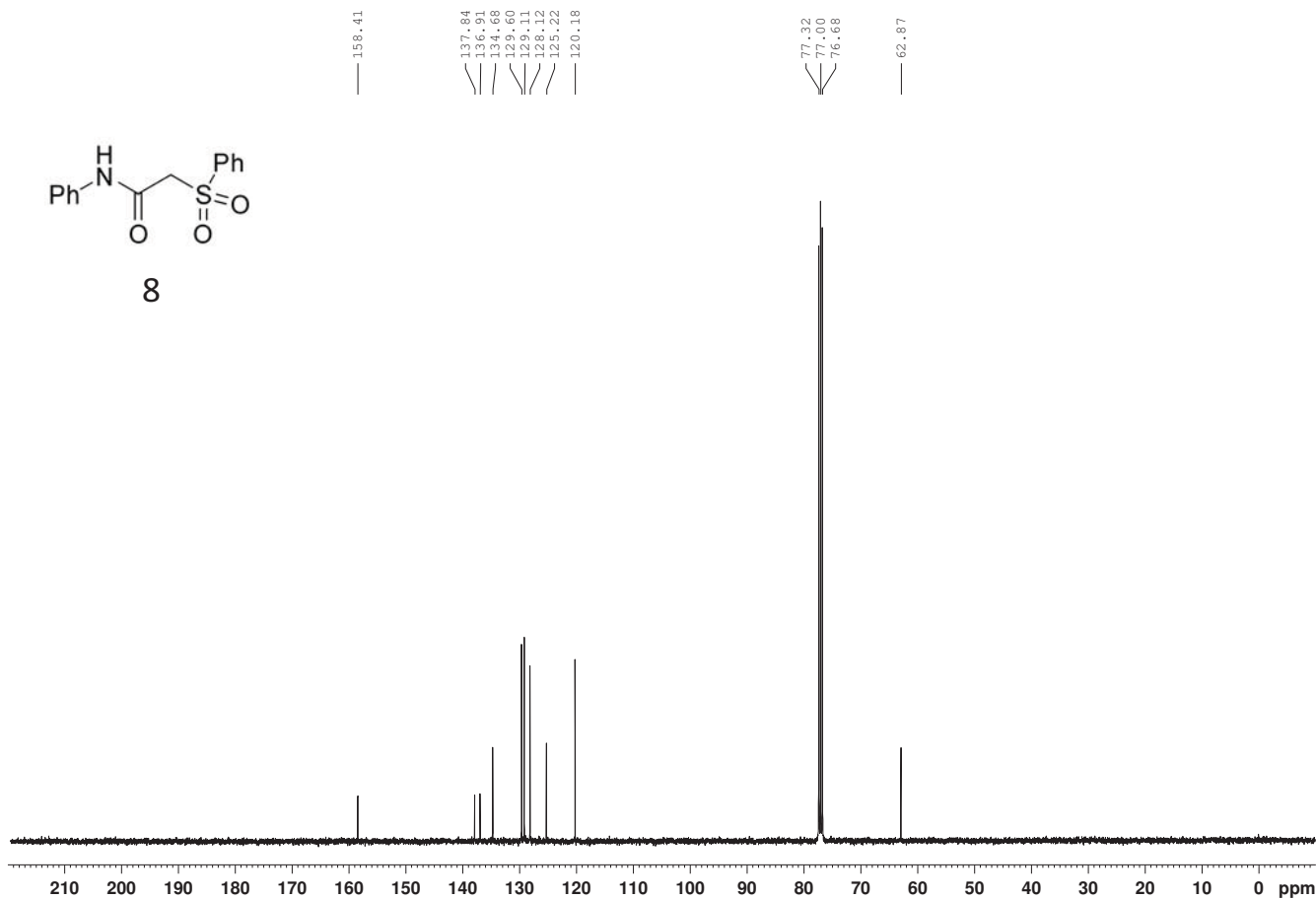




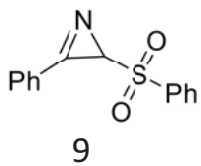
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8



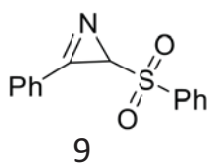
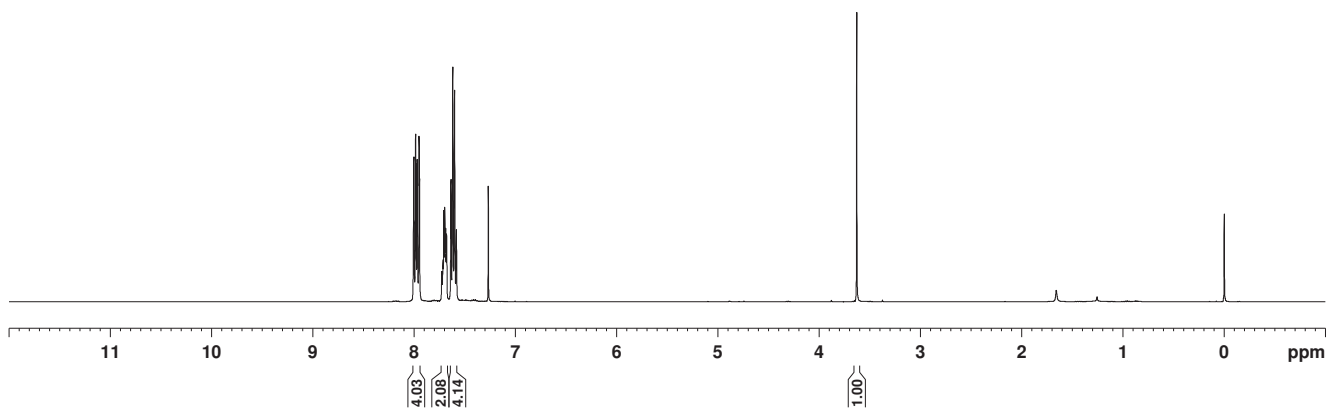




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0.000



161.11

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48.16

