



## Supporting Information

### **Regioselectivity Switch Based on the Stoichiometry: Stereoselective Synthesis of Trisubstituted Vinyl Epoxides by Cu- Catalyzed 3-*exo-trig* Cyclization of $\alpha$ -Allenols**

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## Supporting Information for the Paper

# Regioselectivity Switch Based on the Stoichiometry: Stereoselective Synthesis of Trisubstituted Vinyl Epoxides by Cu-Catalyzed 3-*exo-trig* Cyclization of $\alpha$ -Allenols

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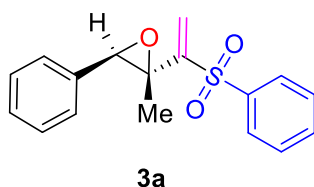
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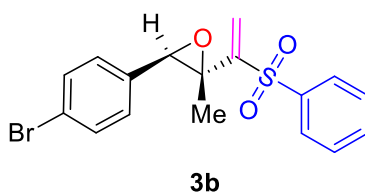
**1. General Methods:** <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra were recorded on a Bruker AVIII 700MHz, Bruker AV 500MHz or Bruker AVIII HD 300MHz BACS-60. NMR spectra were recorded in CDCl<sub>3</sub> solution, except otherwise stated. Chemical shifts are given in ppm relative to TMS (<sup>1</sup>H, 0.0 ppm), CDCl<sub>3</sub> (<sup>1</sup>H, 7.27 ppm; <sup>13</sup>C, 76.9 ppm) and CD<sub>3</sub>CN (<sup>1</sup>H, 1.94 ppm; <sup>13</sup>C, 118.7 ppm). Low- and high-resolution mass spectra were taken on an AGILENT 6520 Accurate Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. IR spectra were recorded on a Bruker Alpha II spectrometer. All commercially available compounds were used without further purification.

## 2. General procedure for the preparation of compounds **3a**–**r**, [D]-**3a**, [D]-**3m** and [D]-**3r**.

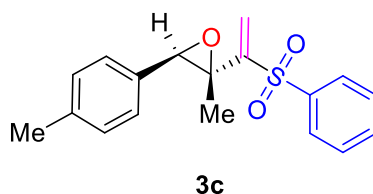
To a solution of the appropriate allenol **1** (1.0 mmol) in acetonitrile (10 mL) was added Cu(OAc)<sub>2</sub> (5 mol %), the corresponding sodium sulfinate **2** (0.5 mmol) and AgNO<sub>3</sub> (0.5 mmol). The reaction was stirred at 100 °C in a sealed tube until completion, which was monitored by TLC. The mixture was cooled to room temperature and was diluted with ethyl acetate (3 × 5 mL). The organic extract was washed with brine (3 × 3 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds **3** follow.



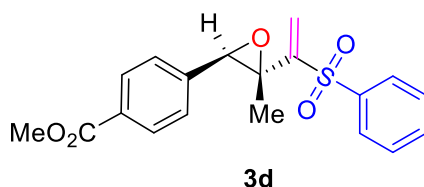
**Epoxide 3a.** From 118 mg (0.74 mmol) of  $\alpha$ -allenic alcohol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3a** (75 mg, 68%) as a yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  7.95 (m, 2H), 7.71 (m, 1H), 7.62 (m, 2H), 7.30 (m, 3H), 7.02 (m, 2H), 6.52 (s, 1H), 6.28 (s, 1H), 3.60 (s, 1H), 1.25 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, 25 °C)  $\delta$  152.7, 139.8, 133.9, 133.8, 129.4 (2C), 128.4 (2C), 128.1 (2C), 128.0, 126.5 (2C), 125.7, 65.3, 61.2, 16.7; IR (AcOEt, cm<sup>-1</sup>):  $\nu$  2942, 1307, 1130; HRMS (ESI-TOF) m/z: [M + H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>17</sub>O<sub>3</sub>S 301.08929; Found 301.08984.



**Epoxide 3b.** From 126 mg (0.53 mmol) of  $\alpha$ -allenenic alcohol **1b**, and after chromatography of the residue using toluene/ethyl acetate (8:1) as eluent, gave compound **3b** (53 mg, 51%) as a pale green oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.93 (m, 2H), 7.71 (m, 1H), 7.61 (m, 2H), 7.45 (d,  $J = 8.4$  Hz, 2H), 6.91 (d,  $J = 8.2$  Hz, 2H), 6.50 (s, 1H), 6.26 (s, 1H), 3.58 (s, 1H), 1.21 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  152.4, 139.7, 133.8, 133.0, 131.3 (2C), 129.4 (2C), 128.3 (2C), 128.1 (2C), 125.7, 122.1, 64.7, 61.1, 16.6; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1304, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{BrO}_3\text{S}$  380.00303; Found 380.00339.

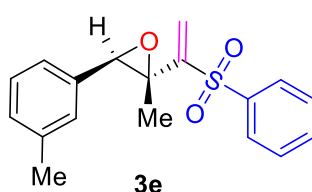


**Epoxide 3c.** From 53 mg (0.33 mmol) of  $\alpha$ -allenenic alcohol **1c**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, gave compound **3c** (44 mg, 46%) as a yellow oil;  $^1\text{H NMR}$  (700 MHz  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ )  $\delta$  7.96 (m, 2H), 7.79 (m, 1H), 7.63 (m, 2H), 7.13 (d,  $J = 7.9$  Hz, 2H), 6.84 (d,  $J = 8.0$  Hz, 2H), 6.50 (s, 1H), 6.27 (s, 1H), 3.53 (s, 1H), 2.30 (s, 3H), 1.19 (s, 3H);  $^{13}\text{C NMR}$  (175 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ )  $\delta$  153.4, 140.8, 139.1, 135.2, 132.1, 130.8 (2C), 129.8 (2C), 129.1 (2C), 127.4 (2C), 126.9, 66.0, 62.0, 21.2, 17.0; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2924, 1307, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}$  315.10494; Found 315.10443.

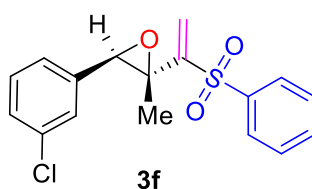


**Epoxide 3d.** From 122 mg (0.56 mmol) of  $\alpha$ -allenenic alcohol **1d**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave

compound **3d** (55 mg, 55%) as a pale brown oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.98 (d,  $J = 8.4$  Hz, 2H), 7.93 (m, 2H), 7.71 (m, 1H), 7.62 (m, 2H), 7.09 (d,  $J = 8.1$  Hz, 2H), 6.51 (s, 1H), 6.27 (s, 1H), 3.91 (s, 3H), 3.66 (s, 1H), 1.21 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  166.7, 152.4, 139.7, 139.1, 133.9, 130.0, 129.5 (2C), 129.4 (2C), 128.4 (2C), 126.6 (2C), 125.9, 64.9, 61.3, 52.2, 16.7; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1306, 1129; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_5\text{S}$  359.09477; Found 359.09514.

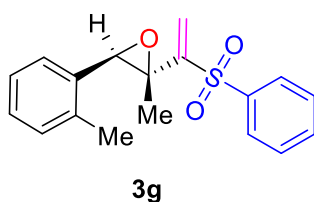


**Epoxide 3e.** From 114 mg (0.66 mmol) of  $\alpha$ -allenic alcohol **1e**, and after chromatography of the residue using toluene/ethyl acetate (4:1) as eluent, gave compound **3e** (41 mg, 40%) as a pale yellow solid; mp 54–56  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.95 (m, 2H), 7.72 (m, 1H), 7.62 (m, 2H), 7.19 (t,  $J = 7.6$  Hz, 1H), 7.09 (d,  $J = 7.6$  Hz, 1H), 6.81 (d,  $J = 7.6$  Hz, 1H), 6.76 (s, 1H), 6.52 (s, 1H), 6.27 (s, 1H), 3.54 (s, 1H), 2.33 (s, 3H), 1.26 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  152.7, 139.8, 137.8, 133.8, 133.7, 129.4 (2C), 128.8, 128.4 (2C), 127.9, 127.1, 125.5, 123.4, 65.4, 61.1, 21.3, 16.6; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2924, 1307, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}$  315.10494; Found 315.10443.

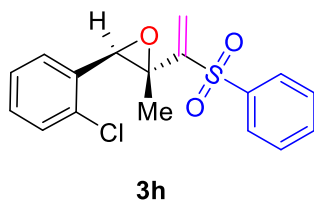


**Epoxide 3f.** From 111 mg (0.57 mmol) of  $\alpha$ -allenic alcohol **1f**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3f** (54 mg,

58%) as a brown oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.96 (m, 2H), 7.76 (m, 1H), 7.66 (m, 2H), 7.28 (m, 2H), 6.96 (m, 1H), 6.91 (m, 1H), 6.54 (s, 1H), 6.28 (s, 1H), 3.56 (s, 1H), 1.27 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  152.3, 139.6, 136.0, 134.2, 133.9, 129.5 (3C), 128.3 (2C), 128.2, 126.6, 125.6, 124.5, 64.6, 61.2, 16.6; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1310, 1132; the product did not respond successfully to the ionizations conditions in MS.

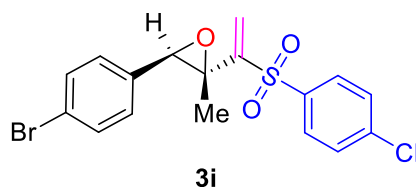


**Epoxide 3g.** From 111 mg (0.64 mmol) of  $\alpha$ -allenenic alcohol **1g**, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3g** (43 mg, 43%) as a yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.96 (m, 2H), 7.65 (m, 1H), 7.58 (m, 2H), 7.19 (m, 4H), 6.44 (s, 1H), 6.29 (s, 1H), 3.96 (s, 1H), 2.35 (s, 3H), 1.15 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  152.8, 139.9, 136.5, 133.6, 132.6, 129.8, 129.2 (2C), 128.1 (2C), 127.9, 126.3, 126.1, 125.4, 64.7, 61.2, 18.9, 17.0; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2924, 1308, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}$  315.10494; Found 315.10403.

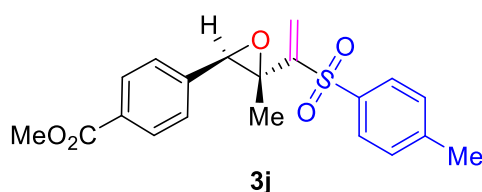


**Epoxide 3h.** From 105 mg (0.54 mmol) of  $\alpha$ -allenenic alcohol **1h**, and after chromatography of the residue using toluene as eluent, gave compound **3h** (37 mg, 41%) as a colourless oil;  $^1\text{H}$  NMR (700 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ )  $\delta$  7.94 (m, 2H), 7.71 (m, 1H), 7.62 (t,  $J = 7.9$  Hz, 2H), 7.42 (m, 1H), 7.32 (m, 2H), 7.20 (m, 1H), 6.59 (d,  $J = 0.7$  Hz,

1H), 6.41 (m, 1H), 4.04 (s, 1H), 1.18 (s, 3H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  151.9, 141.5, 134.9, 133.7, 133.7, 130.7, 130.4 (3C), 130.1, 129.3, 129.2, 128.9, 128.0, 64.0, 62.4, 18.0; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2926, 1309, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{ClO}_3\text{S}$  335.05030; Found 335.05080.

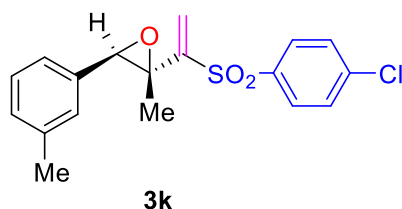


**Epoxide 3i.** From 144 mg (0.60 mmol) of  $\alpha$ -allenlic alcohol **1b**, and after chromatography of the residue using toluene as eluent, gave compound **3i** (59 mg, 48%) as a green oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  7.86 (d,  $J = 8.8$  Hz, 2H), 7.58 (d,  $J = 8.8$  Hz, 2H), 7.48 (d,  $J = 8.4$  Hz, 2H), 6.97 (d,  $J = 8.2$  Hz, 2H), 6.50 (s, 1H), 6.26 (s, 1H), 3.68 (s, 1H), 1.21 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  152.2, 140.6, 138.2, 132.9, 131.4 (2C), 129.8 (2C), 129.7 (2C), 128.1 (2C), 126.2, 122.2, 64.6, 61.0, 16.7; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1311, 1131; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{BrClO}_3\text{S}$  412.96083; Found 412.95940.

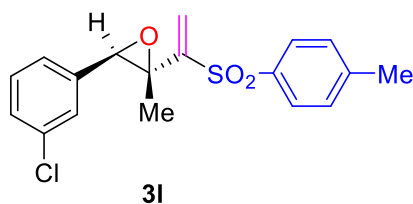


**Epoxide 3j.** From 140 mg (0.64 mmol) of  $\alpha$ -allenlic alcohol **1d**, and after chromatography of the residue using toluene/ethyl acetate (8:1) as eluent, gave compound **3j** (50 mg, 42%) as a colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  8.0 (d,  $J = 8.3$  Hz, 2H), 7.81 (d,  $J = 8.3$  Hz, 2H), 7.41 (d,  $J = 8.5$  Hz, 2H), 7.11 (d,  $J = 8.6$  Hz, 2H), 6.48 (s, 1H), 6.24 (s, 1H), 3.92 (s, 3H), 3.69 (s, 1H), 2.50 (s, 3H), 1.21 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  166.6, 152.6, 145.0, 139.1, 136.6, 130.0 (2C), 129.9, 129.3 (2C), 128.4 (2C), 126.5

(2C), 125.3, 64.8, 61.3, 52.1, 21.6, 16.7; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1306, 1132; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_5\text{S}$  373.11042; Found 373.11036.

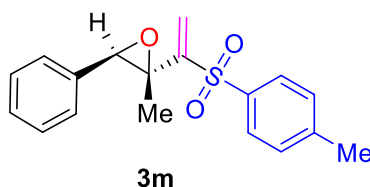


**Epoxide 3k.** From 130 mg (0.75 mmol) of  $\alpha$ -allenlic alcohol **1e**, and after chromatography of the residue using toluene/ethyl acetate (4:1) as eluent, gave compound **3k** (52 mg, 39%) as a white solid; mp 86–88 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  7.88 (m, 2H), 7.58 (m, 2H), 7.22 (t,  $J = 7.6$  Hz, 1H), 7.11 (d,  $J = 7.7$  Hz, 1H), 6.87 (d,  $J = 7.6$  Hz, 1H), 6.75 (m, 1H), 6.53 (s, 1H), 6.27 (s, 1H), 3.59 (s, 1H), 2.34 (s, 3H), 1.27 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  152.4, 140.6, 138.3, 137.9, 133.6, 129.9 (2C), 129.7 (2C), 128.9, 128.1, 127.0, 125.9, 123.4, 65.4, 61.0, 21.3, 16.6; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2926, 1321, 1132; HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{ClO}_3\text{S}$  349.06597; Found 349.06597.

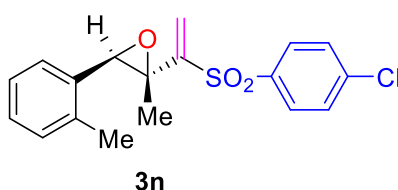


**Epoxide 3l.** From 96 mg (0.49 mmol) of  $\alpha$ -allenlic alcohol **1f**, and after chromatography of the residue using toluene as eluent, gave compound **3l** (38 mg, 44%) as a yellow oil;  $^1\text{H}$  NMR (700 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  7.79 (d,  $J = 8.3$  Hz, 2H), 7.50 (d,  $J = 8.1$  Hz, 2H), 7.31 (d,  $J = 5.2$  Hz, 2H), 6.92 (t,  $J = 3.9$  Hz, 1H), 6.75 (s, 1H), 6.47 (s, 1H), 6.24 (s, 1H), 3.54 (s, 1H), 2.50 (s, 3H), 1.20 (s, 3H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  153.4, 147.0, 137.8, 137.8, 134.9, 131.7 (2C), 131.2, 129.6 (2C), 129.4, 127.7, 126.6, 126.1,

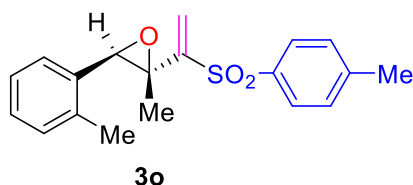
65.8, 62.4, 22.1, 17.2; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2923, 1318, 1131; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{NH}_4]^+$  Calcd for  $\text{C}_{18}\text{H}_{21}\text{ClNO}_3\text{S}$  366.09250; Found 366.09310.



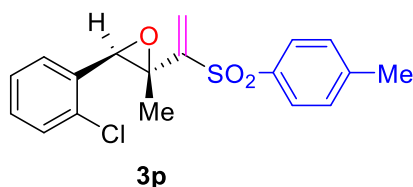
**Epoxide 3m.** From 42 mg (0.26 mmol) of  $\alpha$ -allenlic alcohol **1a**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent, gave compound **3m** (22 mg, 55%) as a yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.82 (d,  $J = 8.3$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H), 7.28 (m, 3H), 7.04 (m, 2H), 6.48 (s, 1H), 6.24 (s, 1H), 3.62 (s, 1H), 2.50 (s, 3H), 1.24 (s, 3H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ )  $\delta$  154.1, 147.1, 138.3, 135.7, 131.8 (2C), 129.8 (2C), 129.7 (2C), 129.6 (2C), 128.0, 127.0, 66.6, 62.6, 22.3, 17.6; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2924, 1306, 1130. HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{S}$  315.10490; Found 315.10480.



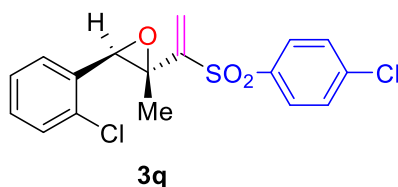
**Epoxide 3n.** From 93 mg (0.53 mmol) of  $\alpha$ -allenlic alcohol **1g**, and after chromatography of the residue using toluene/ethyl acetate (8:1) as eluent, gave compound **3n** (48 mg, 51%) as a pale yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.90 (d,  $J = 8.8$  Hz, 2H), 7.54 (d,  $J = 8.8$  Hz, 2H), 7.20 (m, 4H), 6.48 (s, 1H), 6.29 (s, 1H), 3.98 (s, 1H), 2.35 (s, 3H), 1.17 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  152.4, 140.4, 138.6, 136.3, 132.5, 129.8, 129.7 (2C), 129.5 (2C), 127.9, 126.6, 126.3, 125.5, 64.5, 61.0, 18.8, 17.1; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1312, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{ClO}_3\text{S}$  349.06597; Found 349.06595.



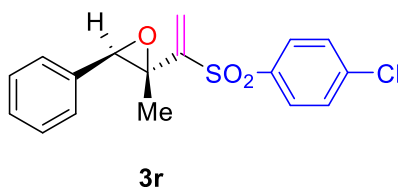
**Epoxide 3o.** From 115 mg (0.66 mmol) of  $\alpha$ -allenic alcohol **1g**, and after chromatography of the residue using hexanes/ethyl acetate (15:1) as eluent, gave compound **3o** (49 mg, 46%) as a yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.83 (d,  $J = 8.3$  Hz, 2H), 7.36 (m, 2H), 7.19 (m, 4H), 6.39 (s, 1H), 6.25 (s, 1H), 3.96 (s, 1H), 2.46 (s, 3H), 2.35 (s, 3H), 1.16 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  153.0, 144.7, 136.9, 136.6, 132.7, 129.9, 129.8 (2C), 128.2 (2C), 127.8, 126.4, 125.6, 125.4, 64.7, 61.2, 21.6, 18.9, 17.0; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2926, 1307, 1131; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{21}\text{O}_3\text{S}$  329.12059; Found 329.12177.



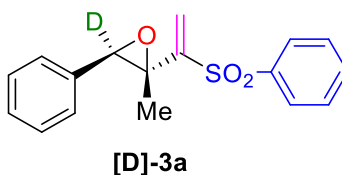
**Epoxide 3p.** From 110 mg (0.56 mmol) of  $\alpha$ -allenic alcohol **1h**, and after chromatography of the residue using toluene as eluent, gave compound **3p** (40 mg, 41%) as a yellow oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.87 (d,  $J = 8.3$  Hz, 2H), 7.36 (m, 3H), 7.26 (m, 3H), 6.56 (m, 1H), 6.31 (m, 1H), 4.02 (s, 1H), 2.46 (s, 3H), 1.27 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  151.8, 144.5, 137.3, 133.0, 132.7, 129.7 (2C), 129.2, 129.0, 128.3 (3C), 126.7, 126.5, 63.3, 61.6, 21.6, 17.6; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2926, 1310, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{ClO}_3\text{S}$  349.06597; Found 349.06679.



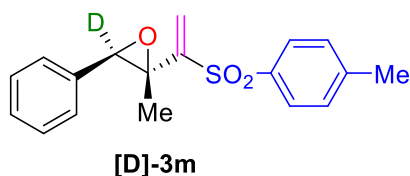
**Epoxide 3q.** From 113 mg (0.58 mmol) of  $\alpha$ -allenlic alcohol **1h**, and after chromatography of the residue using toluene as eluent, gave compound **3q** (42 mg, 40%) as a yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.93 (d,  $J = 8.8$  Hz, 2H), 7.53 (d,  $J = 8.8$  Hz, 2H), 7.36 (m, 1H), 7.27 (m, 3H), 6.62 (d,  $J = 0.6$  Hz, 1H), 6.35 (d,  $J = 0.6$  Hz, 1H), 4.01 (s, 1H), 1.28 (s, 3H);  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  151.3, 140.2, 138.9, 132.8, 132.5, 129.8 (2C), 129.3 (3C), 129.0, 128.3, 127.6, 126.6, 63.2, 61.4, 17.7; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1317, 1132; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{14}\text{Cl}_2\text{NaO}_3\text{S}$  390.99330; Found 390.99360.



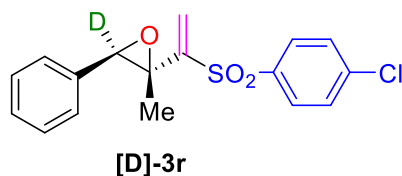
**Epoxide 3r.** From 52 mg (0.33 mmol) of  $\alpha$ -allenlic alcohol **1a**, and after chromatography of the residue using toluene as eluent, gave compound **3r** (24 mg, 42%) as a pale yellow oil;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ , 25  $^\circ\text{C}$ )  $\delta$  7.88 (d,  $J = 8.7$  Hz, 2H), 7.57 (m, 3H), 7.33 (m, 2H), 7.08 (m, 2H), 6.52 (s, 1H), 6.28 (s, 1H), 3.69 (s, 1H), 1.26 (s, 3H);  $^{13}\text{C NMR}$  (175 MHz,  $\text{CD}_3\text{CN}$ , 25  $^\circ\text{C}$ )  $\delta$  152.9, 141.2, 139.6, 135.1, 131.0 (2C), 130.8 (2C), 129.3 (2C), 129.2, 127.8, 127.5 (2C), 65.8, 62.0, 17.2; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2927, 1314, 1130 ; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{ClO}_3\text{S}$  335.05030; Found 335.05070.



**Epoxide [D]-3a.** From 92 mg (0.57 mmol) of  $\alpha$ -allenenic alcohol [D]-1a, and after chromatography of the residue using toluene as eluent, gave compound [D]-3a (32 mg, 37%) as a pale yellow solid; mp 53–55 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  7.92 (m, 2H), 7.79 (t,  $J = 7.5$  Hz, 1H), 7.68 (t,  $J = 7.8$  Hz, 2H), 7.32 (m, 3H), 6.98 (m, 2H), 6.50 (s, 1H), 6.29 (s, 1H), 1.19 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  153.4, 140.8, 135.2 (2C), 135.1, 130.8 (2C), 129.3 (2C), 129.2 (2C), 127.5 (2C), 127.1, 65.6 (t,  $J = 27.2$  Hz, CD), 62.0, 17.1; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2926, 1307, 1130 ; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{DNaO}_3\text{S}$  324.07750; Found 324.07620.



**Epoxide [D]-3m.** From 108 mg (0.67 mmol) of  $\alpha$ -allenenic alcohol [D]-1a, and after chromatography of the residue using toluene as eluent, gave compound [D]-3m (55 mg, 52%) as a yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  7.79 (d,  $J = 8.3$  Hz, 2H), 7.48 (d,  $J = 8.0$  Hz, 2H), 7.32 (m, 3H), 6.97 (m, 2H), 6.46 (s, 1H), 6.25 (s, 1H), 2.49 (s, 3H), 1.19 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  153.7, 146.6, 137.8, 135.2, 131.3 (2C), 129.3 (2C), 129.2 (2C), 129.1, 127.5 (2C), 126.5, 65.7 (t,  $J = 27.0$  Hz, CD), 62.0, 21.7, 17.1; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2925, 1306, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{17}\text{DNaO}_3\text{S}$  338.09320; Found 338.09300.

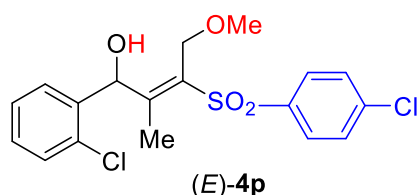


**Epoxide [D]-3r.** From 105 mg (0.65 mmol) of  $\alpha$ -allenenic alcohol [D]-1a, and after chromatography of the residue using toluene as eluent, gave compound [D]-3r (45 mg, 41%) as a yellow oil;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  7.90 (d,  $J = 8.6$  Hz, 2H),

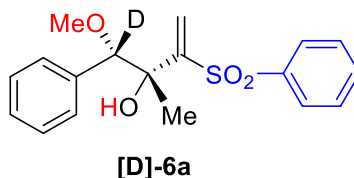
7.67 (d,  $J = 8.6$  Hz, 2H), 7.34 (m, 3H), 7.05 (m, 2H), 6.51 (s, 1H), 6.31 (s, 1H), 1.20 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  153.0, 141.2, 139.7, 135.1, 131.0 (2C), 130.9 (2C), 129.3 (2C), 129.2, 127.8, 127.5 (2C), 79.0 (t,  $J = 32.3$  Hz, CD), 62.0, 17.2; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2924, 1306, 1131; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{DClO}_3\text{S}$  336.05660; Found 336.05580.

## 2.1 General procedure for the ring opening of oxiranes **3p**, **[D]-3a** and **[D]-3m** with carbon tetrabromide.

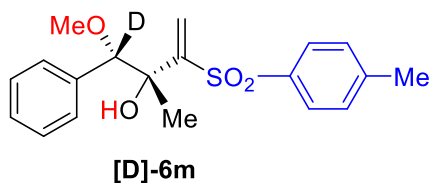
A mixture of the appropriate epoxide **3** (1 mmol) and  $\text{CBr}_4$  (0.1 mmol) was stirred at 80 °C in methanol (5 mL) for a convenient time. After complete conversion, as indicated by TLC, the solvent was removed under reduced pressure. Chromatography of the residue using toluene/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds (*E*)-**4p**, **[D]-6a** and **[D]-6m** follow.



**Allylic alcohol (*E*)-4p.** From 11 mg (0.03 mmol) of epoxide **3p**, and after chromatography of the residue using toluene/ethyl acetate (20:1) as eluent, gave compound (*E*)-**4p** (7 mg, 55%) as a white solid; mp 119–121 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  7.84 (d,  $J = 8.7$  Hz, 2H), 7.65 (m, 1H), 7.51 (d,  $J = 8.7$  Hz, 2H), 7.34 (m, 2H), 7.27 (m, 1H), 5.79 (d,  $J = 1.8$  Hz, 1H), 4.68 (d,  $J = 12.1$  Hz, 1H), 4.56 (d,  $J = 12.1$  Hz, 1H), 3.46 (s, 3H), 3.26 (m, 1H), 1.81 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  158.0, 140.3, 139.7, 136.9, 136.9, 131.7, 129.4 (2C), 129.2, 129.1, 128.6 (2C), 128.1, 127.0, 71.3, 67.6, 58.8, 16.1; IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu$  3479, 2926, 1310, 1146; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{Na}]^+$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{Cl}_2\text{NaO}_4\text{S}$  423.01950; Found 423.02040.



**Allylic alcohol [D]-6a.** From 10 mg (0.03 mmol) of epoxide **[D]-3a**, and after chromatography of the residue using toluene/ethyl acetate (20:1) as eluent, gave compound **[D]-6a** (6 mg, 58%) as a yellow oil;  $^1\text{H}$  NMR (700 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  7.89 (m, 2H), 7.66 (m, 1H), 7.58 (m, 2H), 7.33 (m, 5H), 6.48 (d,  $J = 0.9$  Hz, 1H), 6.12 (d,  $J = 1.0$  Hz, 1H), 3.60 (s, 1H), 2.96 (s, 3H), 0.99 (s, 3H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  156.8, 143.4, 138.2, 134.8, 130.6 (2C), 130.5 (2C), 129.6, 129.4, 129.3 (2C), 129.3 (2C), 87.8, 78.4, 57.8, 26.3; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2926, 1306, 1130; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{20}\text{DO}_4\text{S}$  334.12180; Found 334.12150.

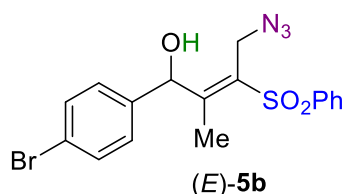


**Allylic alcohol [D]-6m.** From 9 mg (0.03 mmol) of epoxide **[D]-3m**, and after chromatography of the residue using toluene/ethyl acetate (20:1) as eluent, gave compound **[D]-6m** (6 mg, 55%) as a pale orange oil;  $^1\text{H}$  NMR (700 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  7.77 (d,  $J = 8.3$  Hz, 2H), 7.38 (d,  $J = 8.1$  Hz, 2H), 7.32 (m, 5H), 6.43 (s, 1H), 6.09 (s, 1H), 3.58 (s, 1H), 2.99 (s, 3H), 2.42 (s, 3H), 1.00 (s, 3H);  $^{13}\text{C}$  NMR (175 MHz,  $\text{CD}_3\text{CN}$ , 25 °C)  $\delta$  156.7, 145.5, 139.9, 137.8, 130.6 (2C), 130.1 (2C), 129.1, 129.0 (2C), 128.8 (2C), 128.3, 87.3, 77.9, 57.3, 25.9, 21.7; IR (AcOEt,  $\text{cm}^{-1}$ ):  $\nu$  2924, 1306, 1132; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{Na}]^+$  Calcd for  $\text{C}_{19}\text{H}_{21}\text{DNaO}_4\text{S}$  370.11940; Found 370.11950.

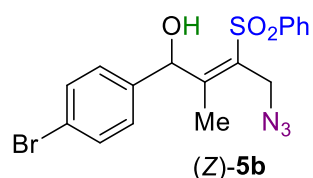
## 2.2 Procedure for the ring opening of oxirane 3b with sodium azide

A mixture of epoxide **3b** (1 mmol) in H<sub>2</sub>O–MeCN (1:9, v/v), and Oxone (0.5 mmol) was stirred for 5 min at room temperature. Then, NaN<sub>3</sub> (1 mmol) was added, and the reaction mixture was stirred at room temperature for additional 3.5 h. After completion, as indicated by TLC, the solvent was removed under reduced pressure and the residue was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub> and concentrated under reduced pressure. Chromatography of the residue using toluene/ethyl acetate mixtures gave the corresponding azido alcohols **5** as analytically pure isomers.

From 11 mg (0.03 mmol) of epoxide **3b**, and after chromatography of the residue using toluene/ethyl acetate (10:1) as eluent, gave compound (*E*)-**5b** (5 mg, 37%) as a yellow oil and compound (*Z*)-**5b** (5 mg, 37%) as a yellow oil. Spectroscopic and analytical data for pure forms of isomers (*E*)-**5b** and (*Z*)-**5b** follow.



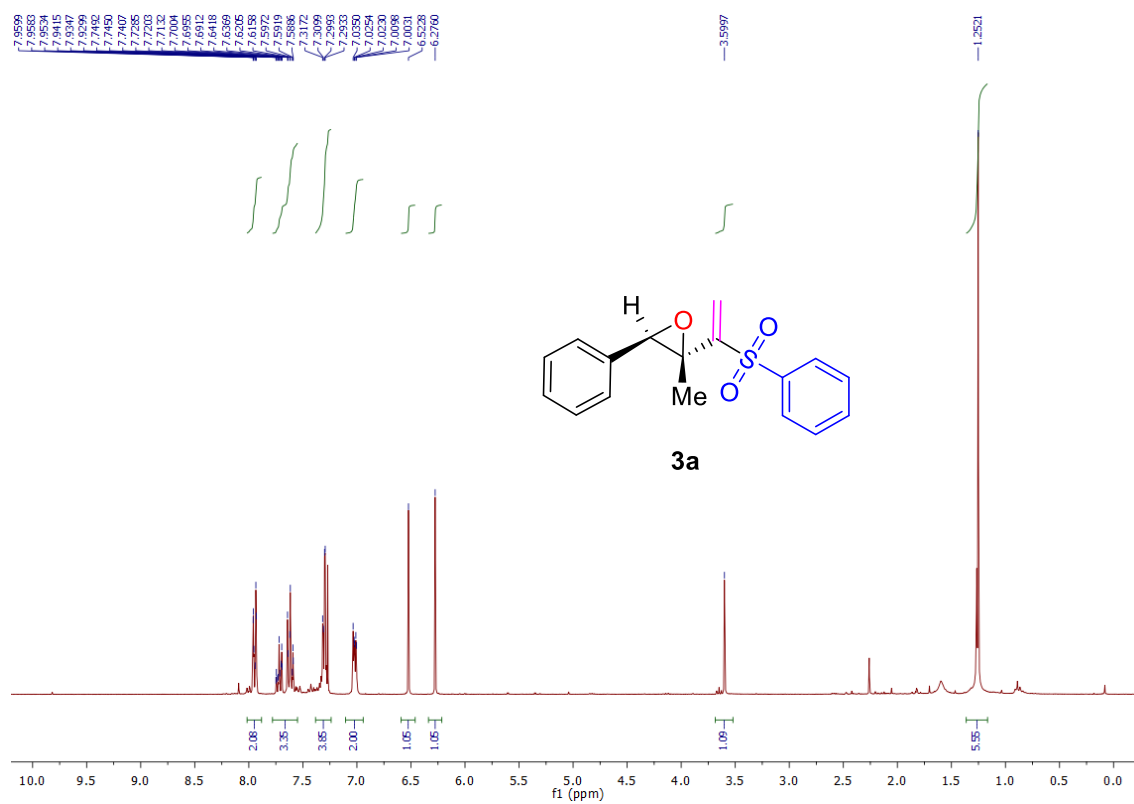
**Azido alcohol (*E*)-5b.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) δ 7.94 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.69 (s, 1H), 4.58 (m, 2H), 2.29 (br s, 1H), 1.91 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C) δ 156.1, 141.1, 138.0, 135.2, 133.6, 131.8 (2C), 129.2 (2C), 127.4 (2C), 127.3 (2C), 122.1, 72.6, 47.3, 14.9; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): ν 3482, 2925, 2100, 1303, 1144; HRMS (ESI-TOF) *m/z*: [*M* + Na]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>16</sub>BrN<sub>3</sub>NaO<sub>3</sub>S 443.99880; Found 443.99910.



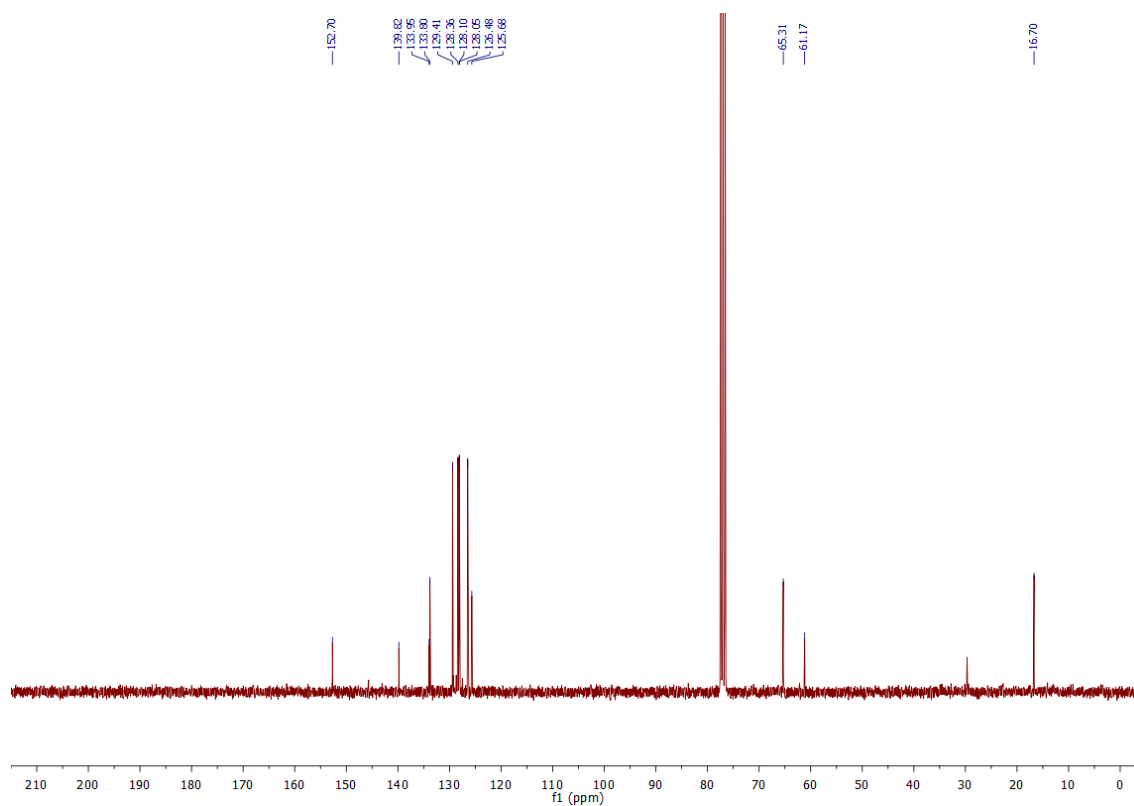
**Azido alcohol-(Z)-5b.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  8.01 (m, 2H), 7.69 (t,  $J = 7.4$  Hz, 1H), 7.61 (t,  $J = 7.7$  Hz, 2H), 7.41 (d,  $J = 8.5$  Hz, 2H), 7.05 (d,  $J = 8.4$  Hz, 2H), 6.63 (s, 1H), 4.39 (d,  $J = 14.2$  Hz, 1H), 4.33 (d,  $J = 14.2$  Hz, 1H), 2.32 (br s, 1H), 1.77 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C)  $\delta$  157.5, 141.6, 138.2, 135.2, 133.8, 131.5 (2C), 129.6 (2C), 127.2 (2C), 127.1 (2C), 121.6, 69.2, 48.1, 15.8; IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ):  $\nu$  3484, 2924, 2096, 1301, 1144; HRMS (ESI-TOF)  $m/z$ :  $[M + \text{Na}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{BrN}_3\text{NaO}_3\text{S}$  443.99880; Found 443.99890.

### 3. NMR Spectra

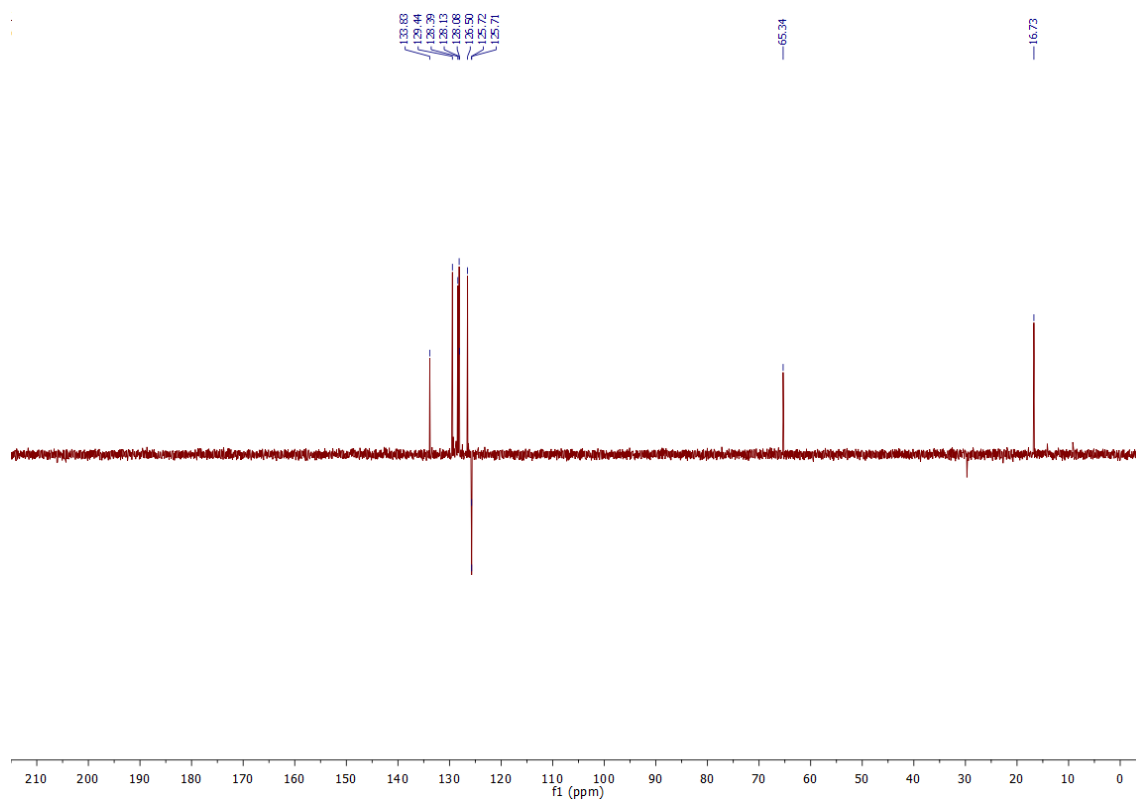
$^1\text{H}$  NMR spectrum of **3a** in  $\text{CDCl}_3$  at 300 MHz



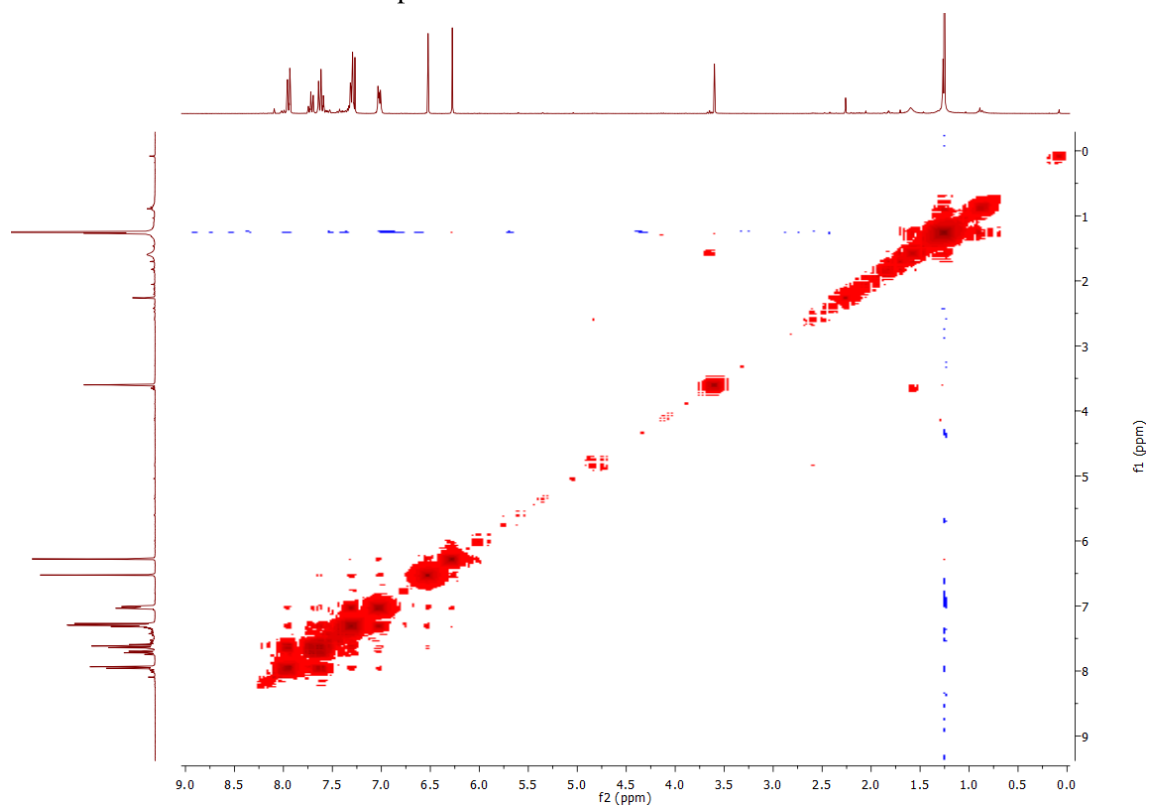
$^{13}\text{C}$  NMR spectrum of **3a** in  $\text{CDCl}_3$  at 75 MHz

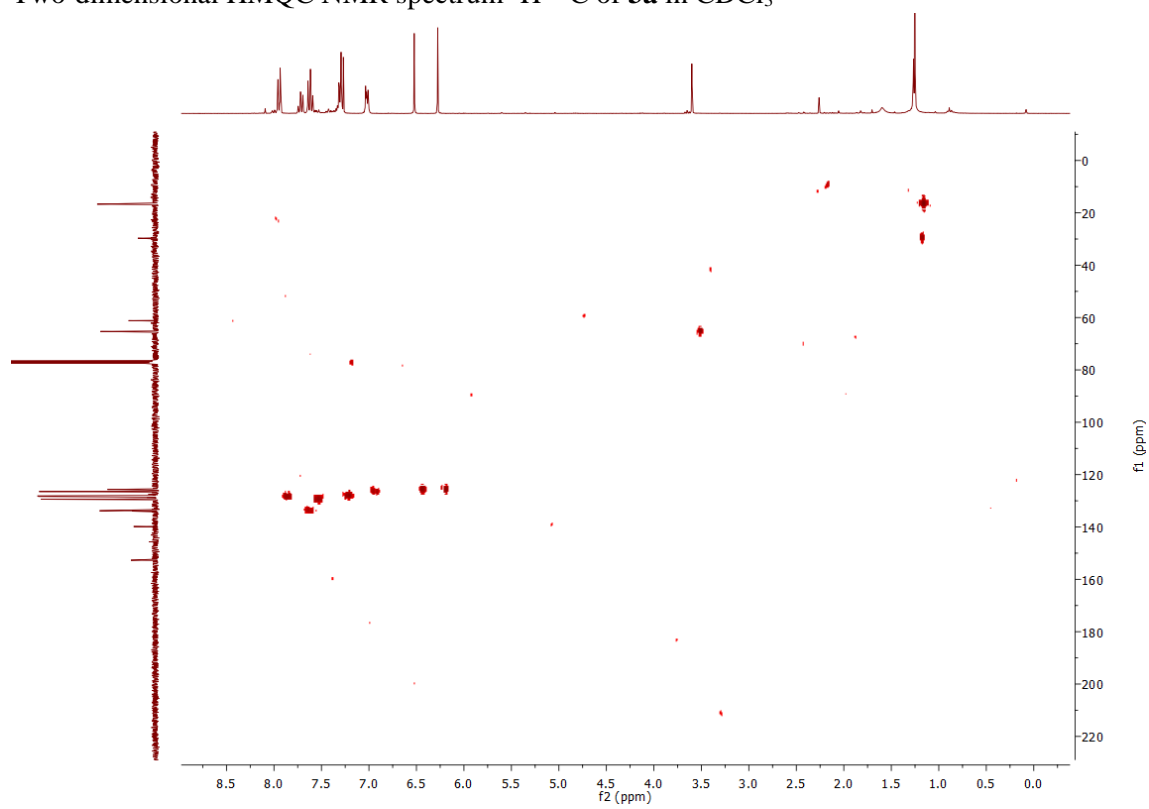
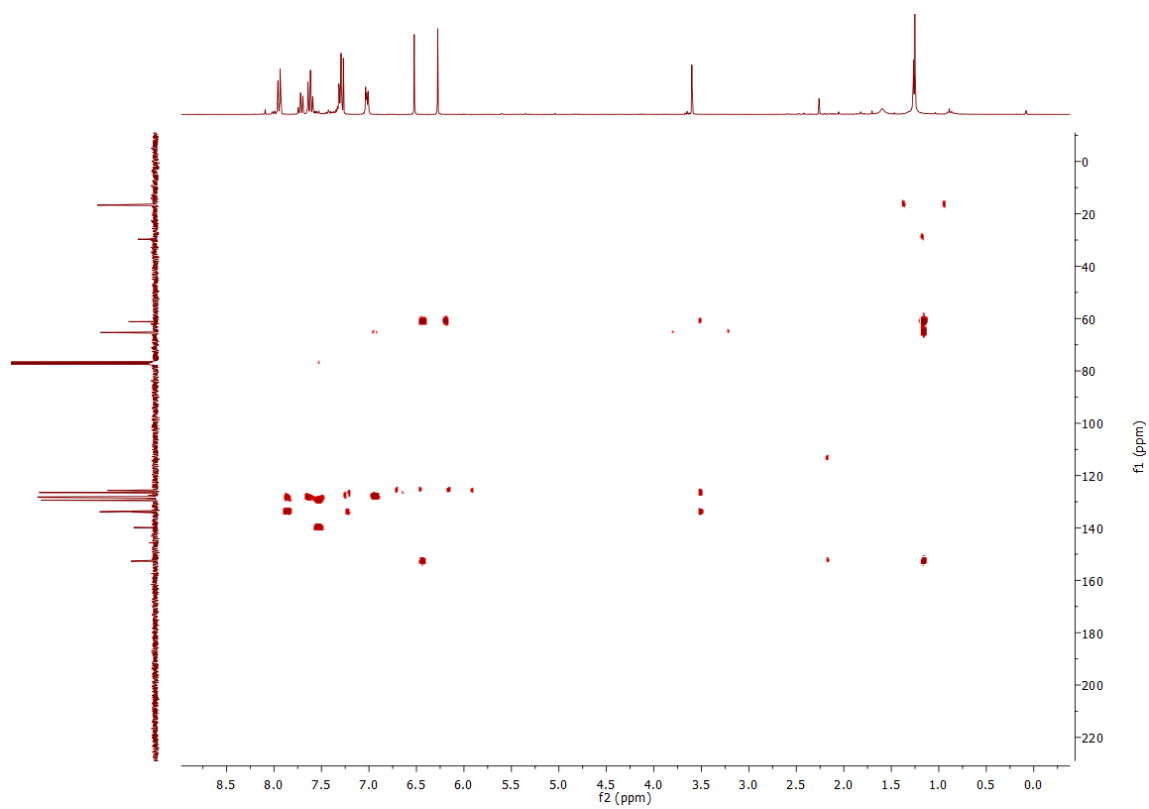


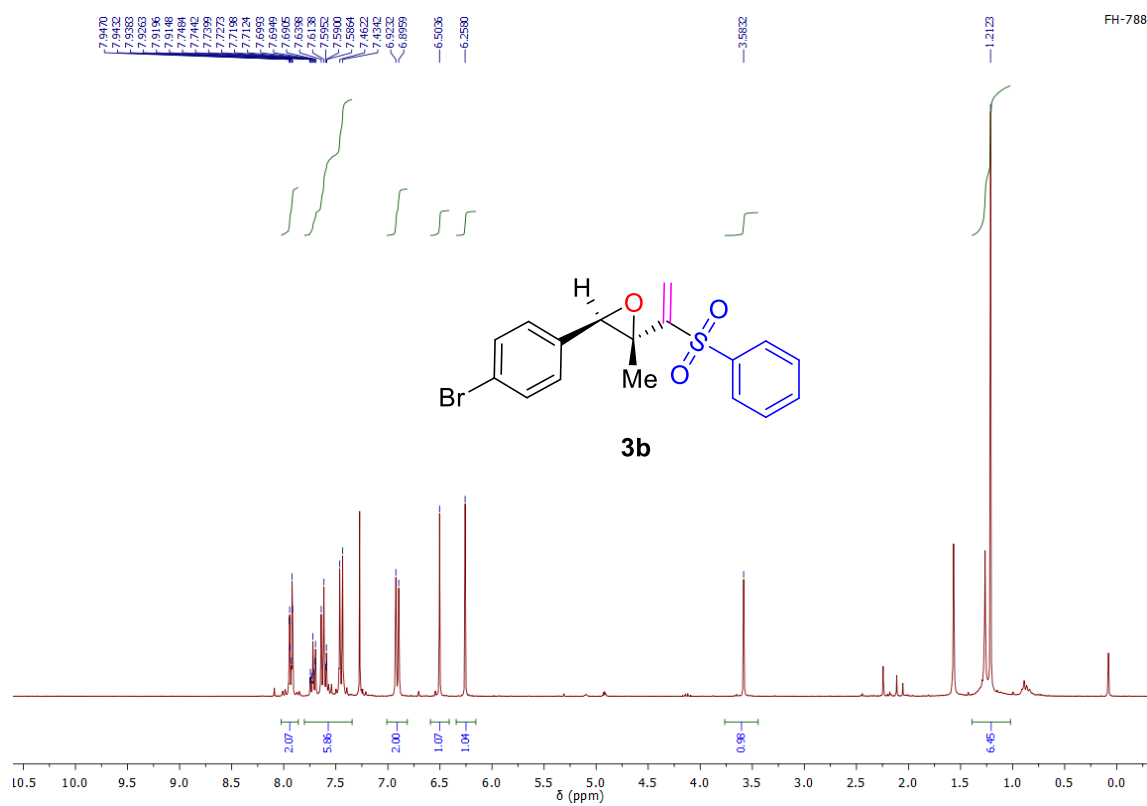
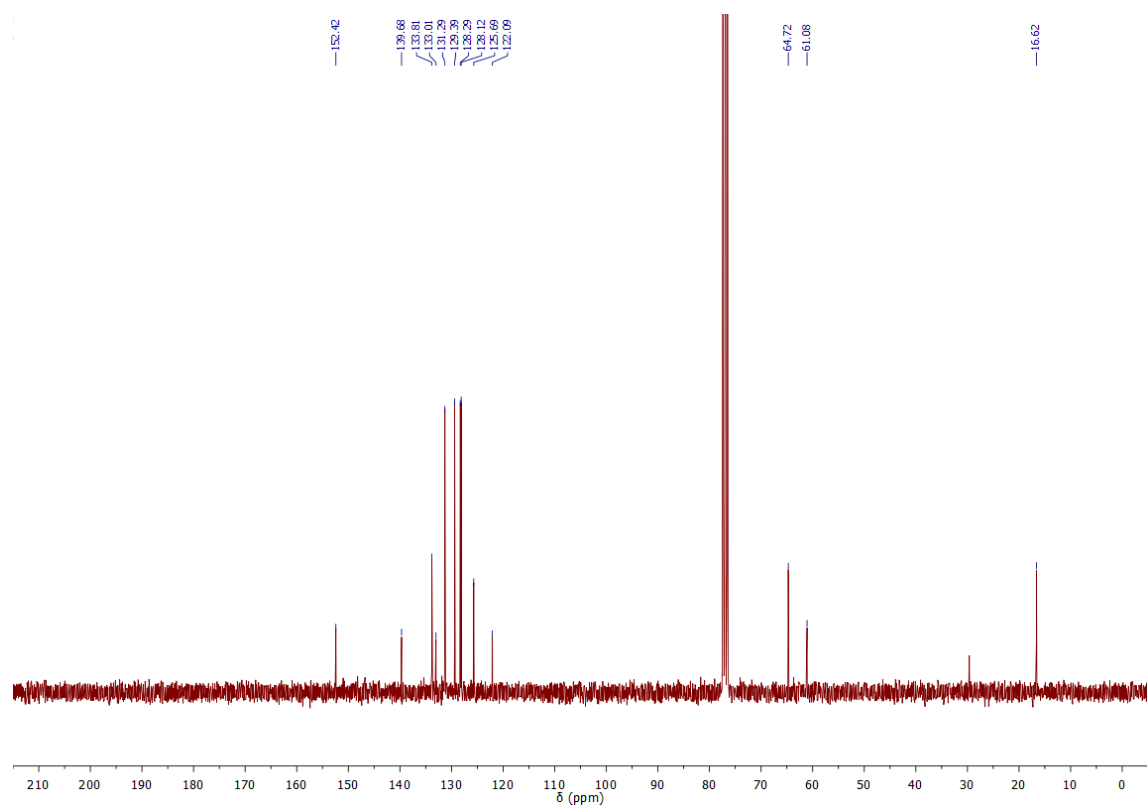
DEPT NMR spectrum of **3a** in CDCl<sub>3</sub> at 75 MHz



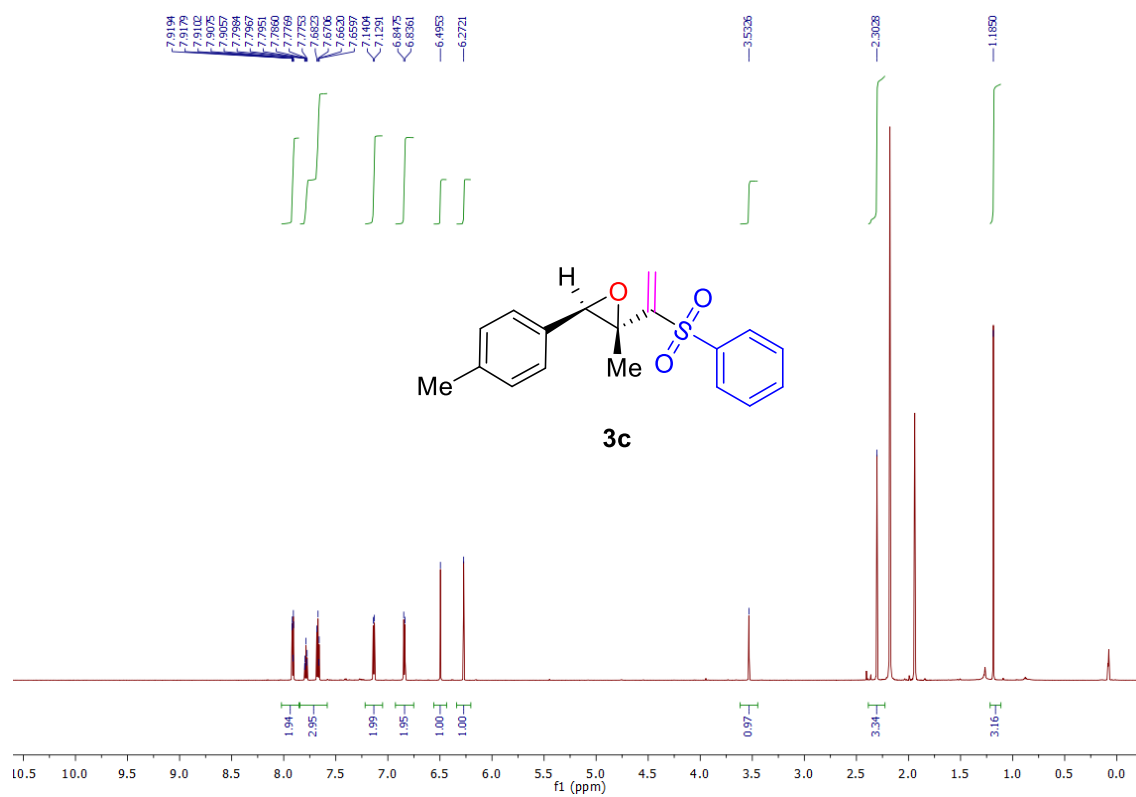
Two-dimensional COSY NMR spectrum <sup>1</sup>H-<sup>1</sup>H of **3a** in CDCl<sub>3</sub> at 300 MHz



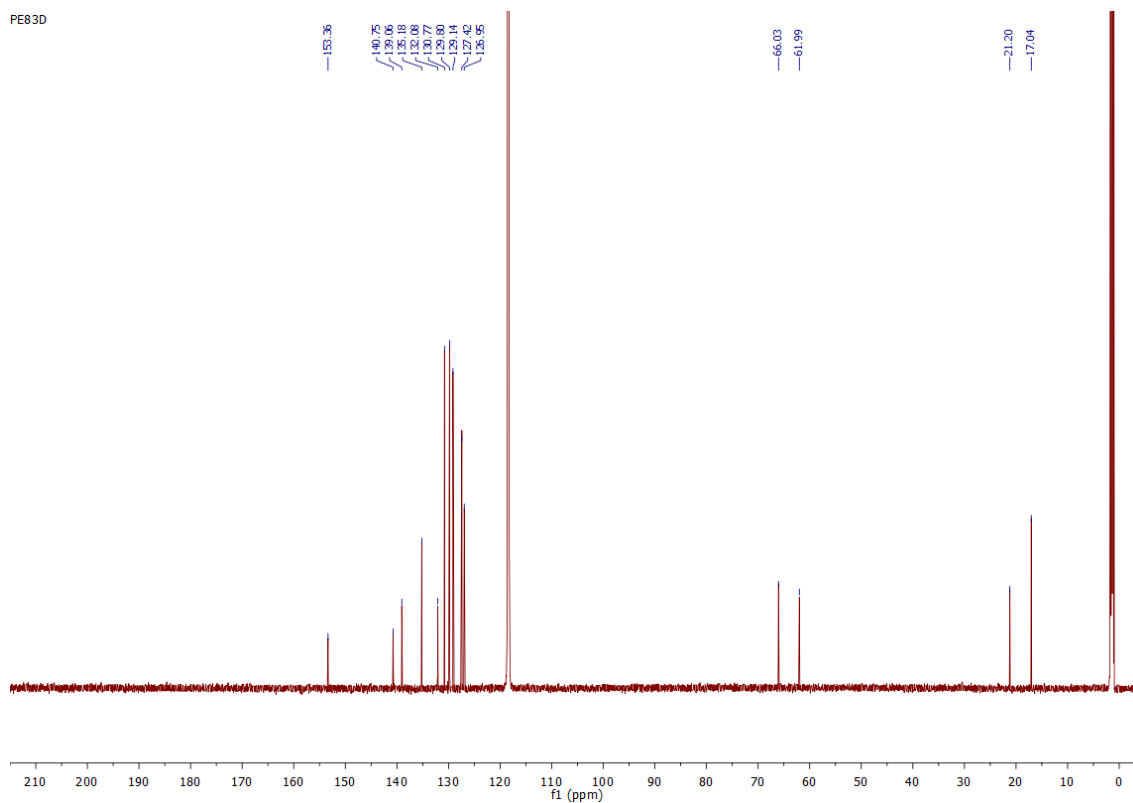
Two-dimensional HMQC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of **3a** in  $\text{CDCl}_3$ Two-dimensional HMBC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of **3a** in  $\text{CDCl}_3$ 

$^1\text{H}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3b** in  $\text{CDCl}_3$  at 75 MHz

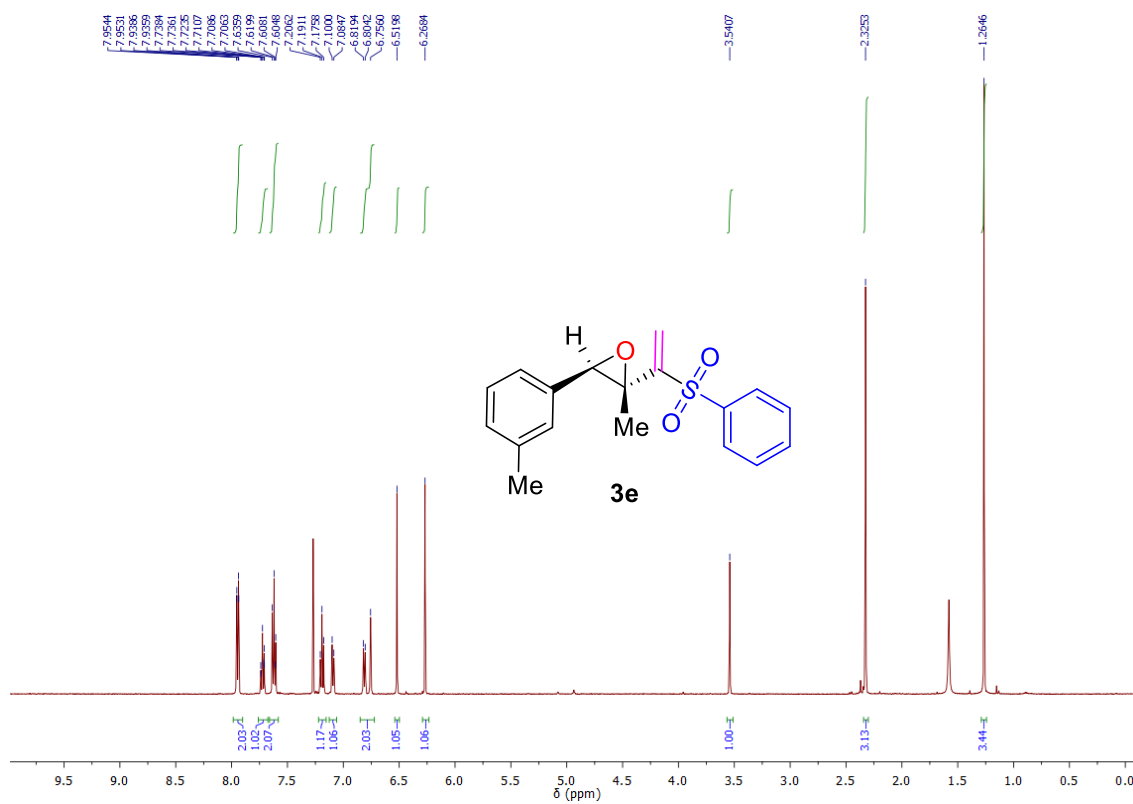
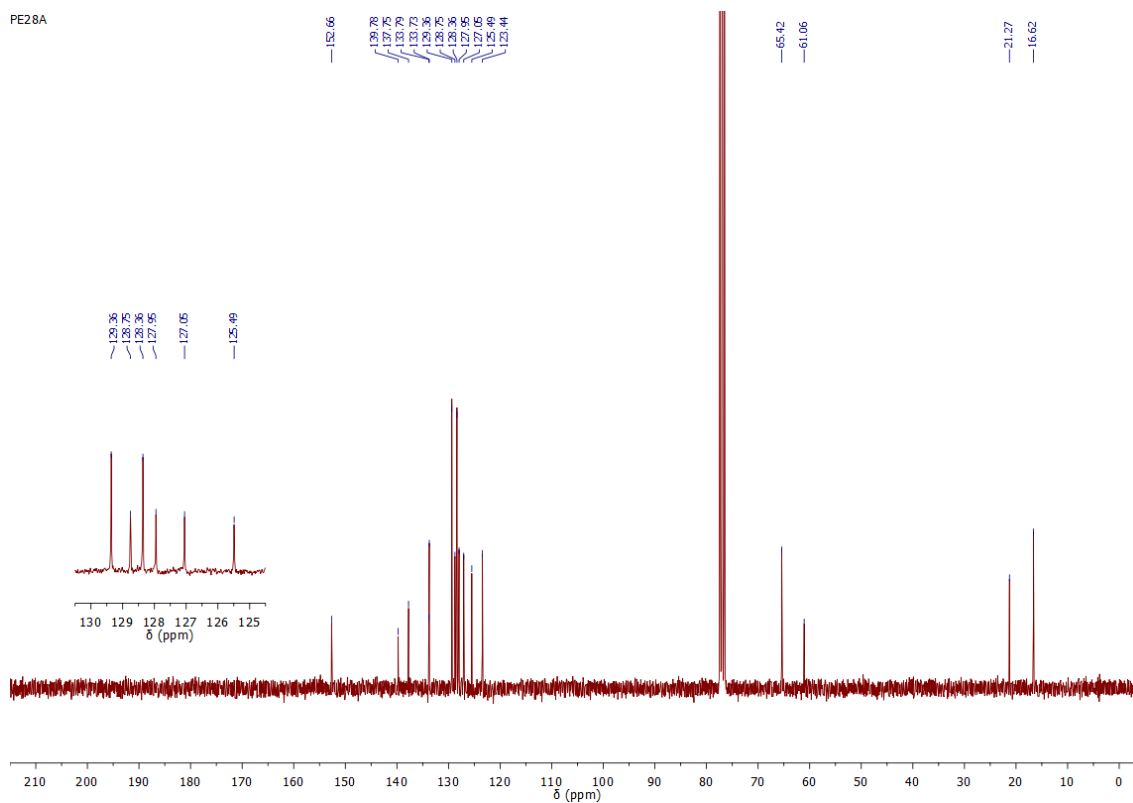
$^1\text{H}$  NMR spectrum of **3c** in  $\text{CD}_3\text{CN}$  at 700 MHz



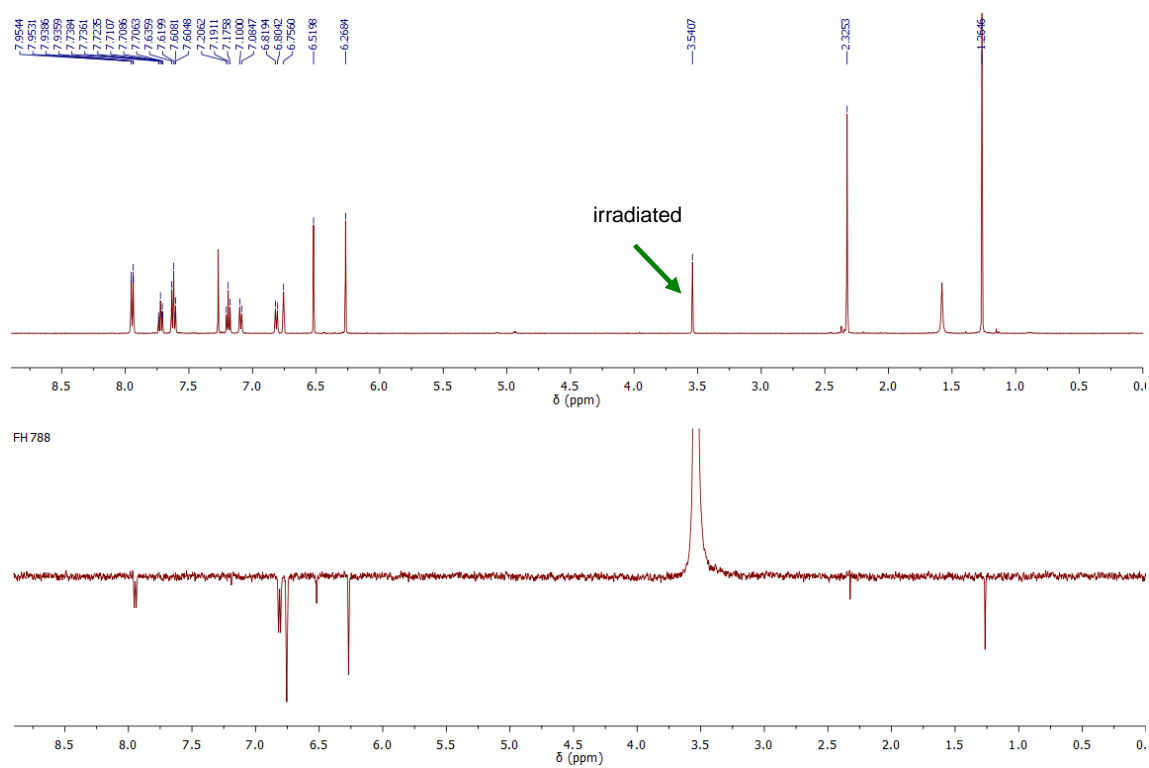
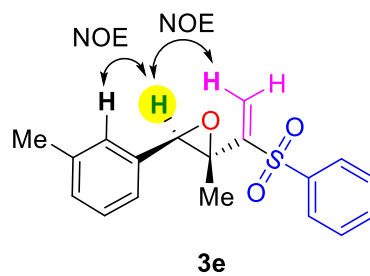
$^{13}\text{C}$  NMR spectrum of **3c** in  $\text{CD}_3\text{CN}$  at 175 MHz

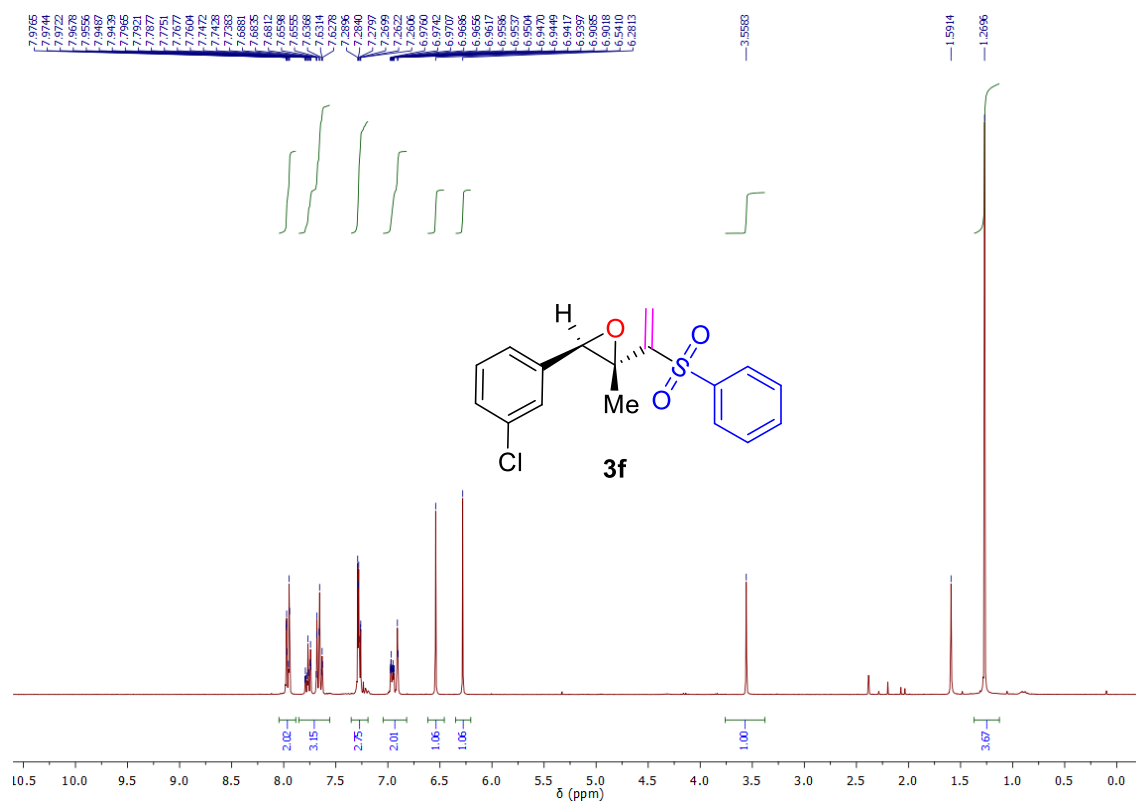
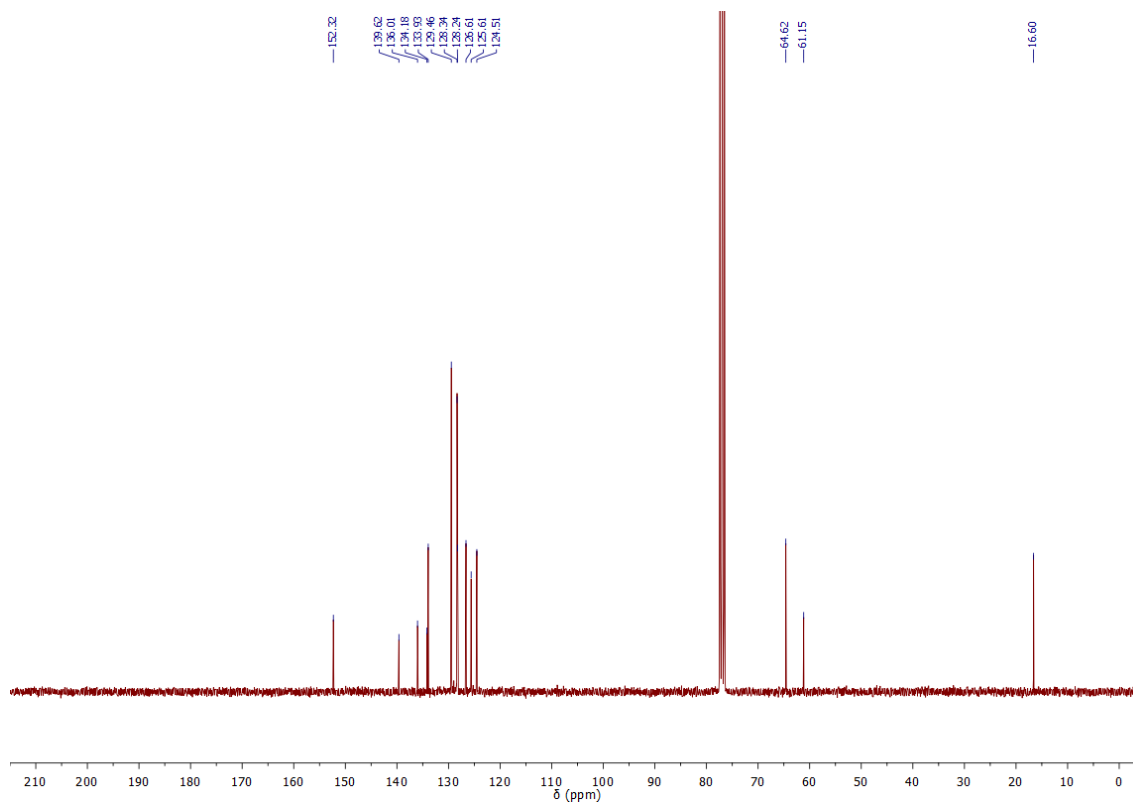




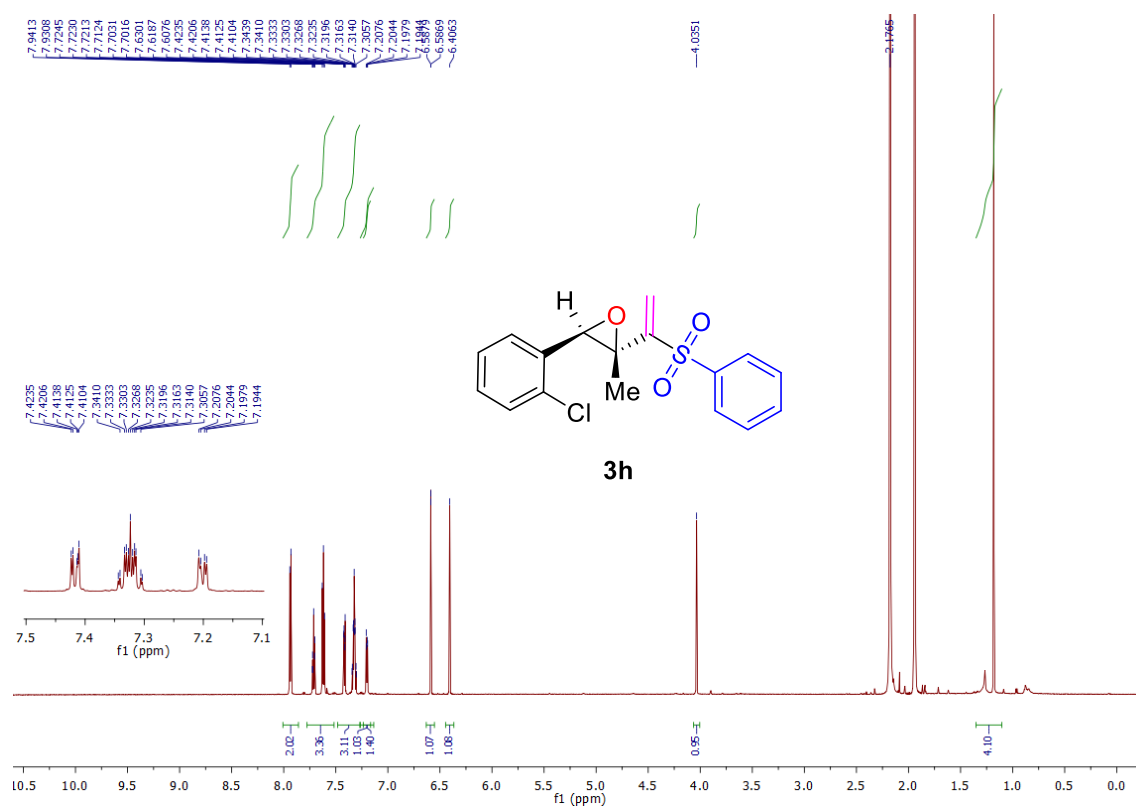
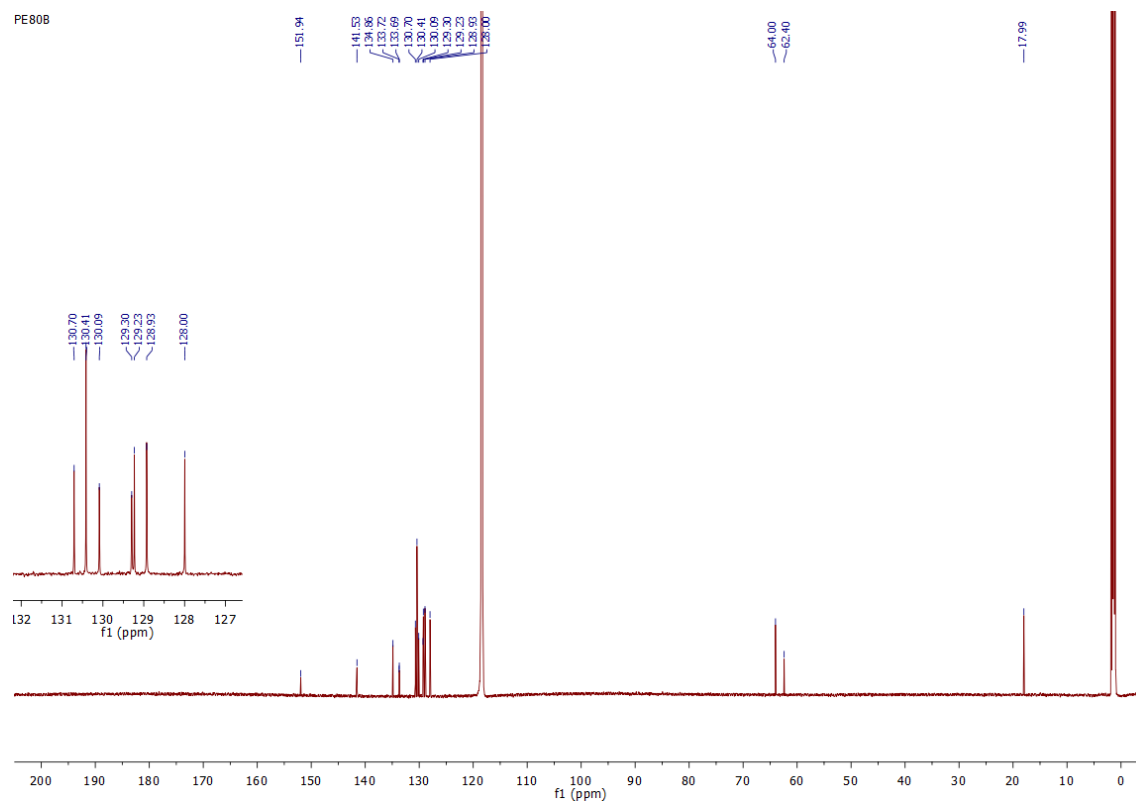
$^1\text{H}$  NMR spectrum of **3e** in  $\text{CDCl}_3$  at 500 MHz $^{13}\text{C}$  NMR spectrum of **3e** in  $\text{CDCl}_3$  at 75 MHz

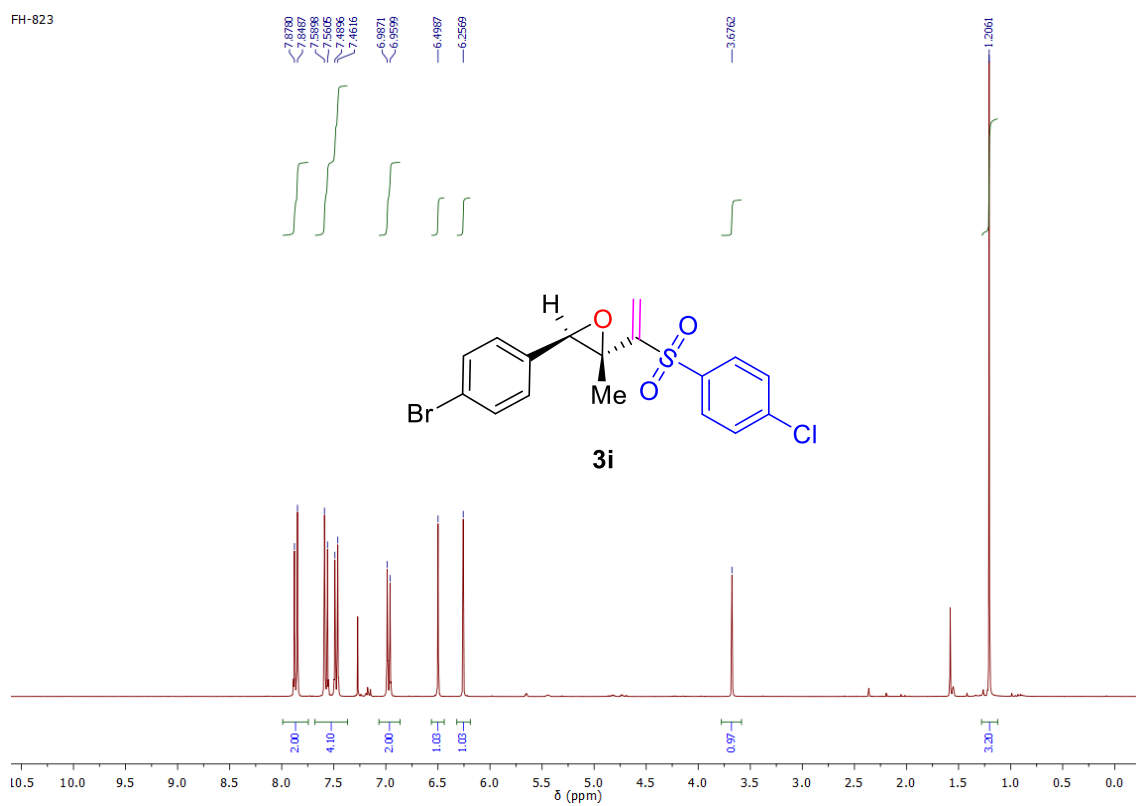
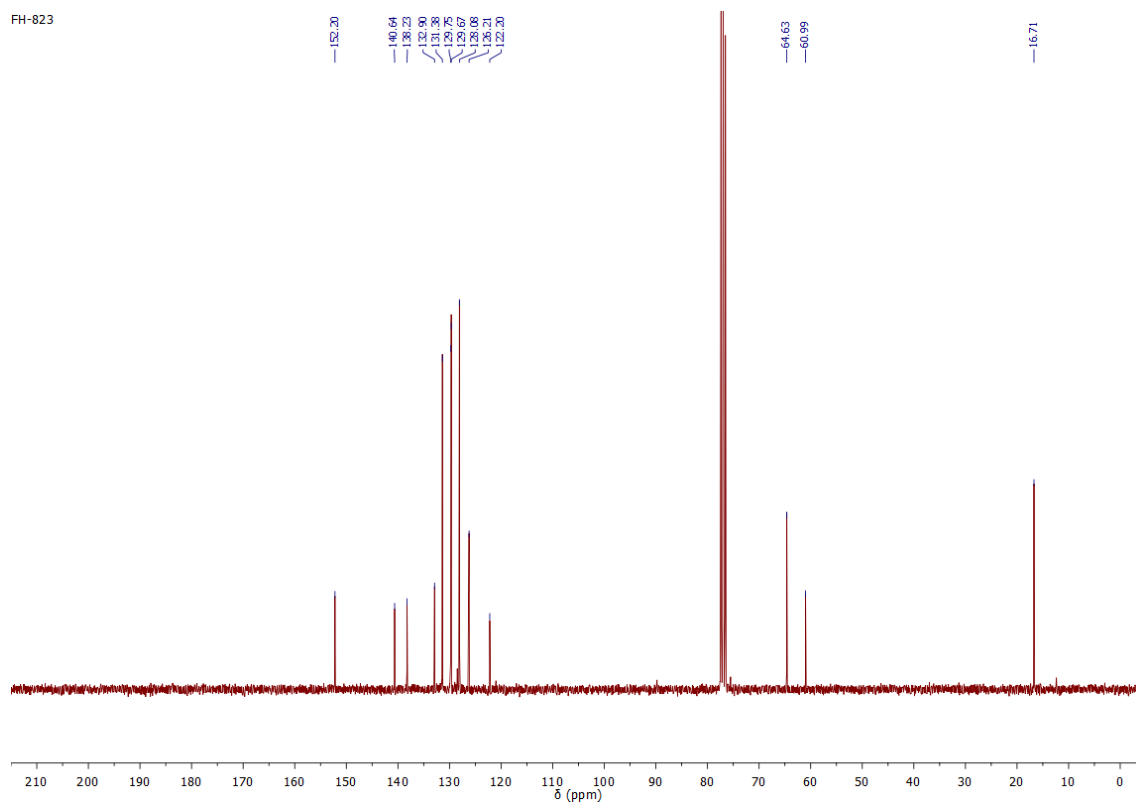
One-dimensional NOE NMR spectrum of **3e** in CDCl<sub>3</sub> at 500 MHz, showing selected NOE correlations highlighted in the structure



$^1\text{H}$  NMR spectrum of **3f** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3f** in  $\text{CDCl}_3$  at 75 MHz

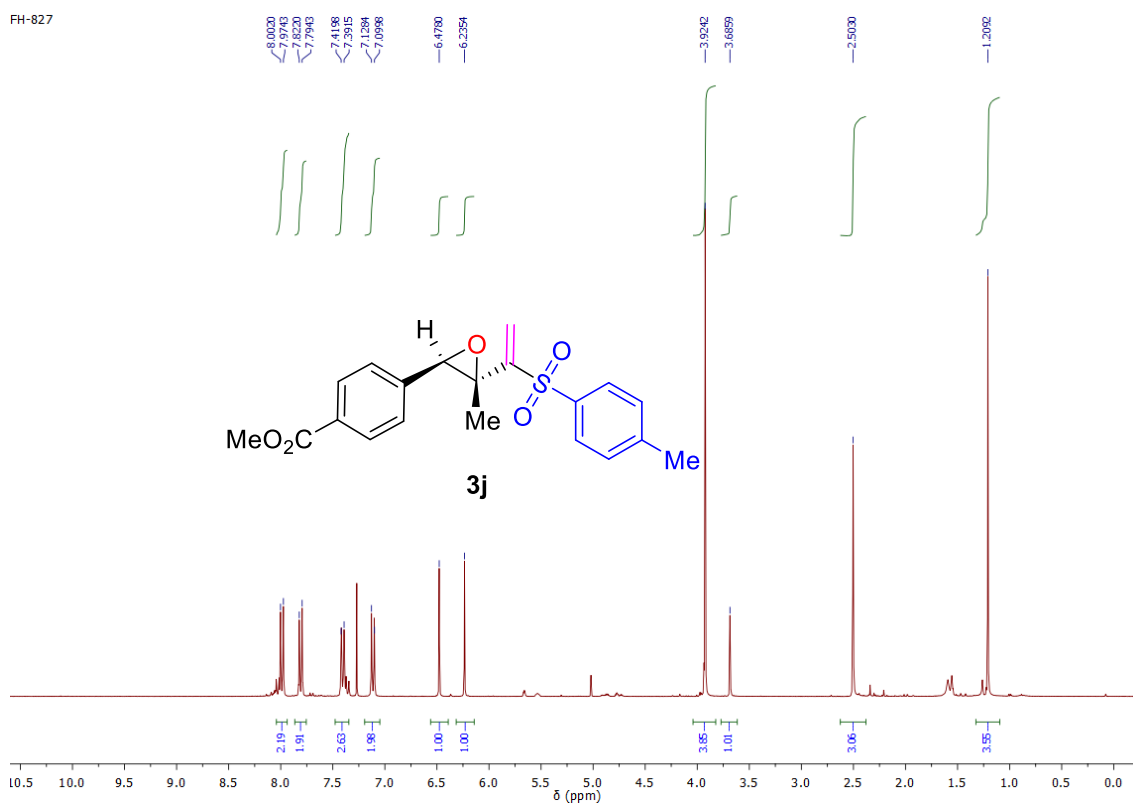
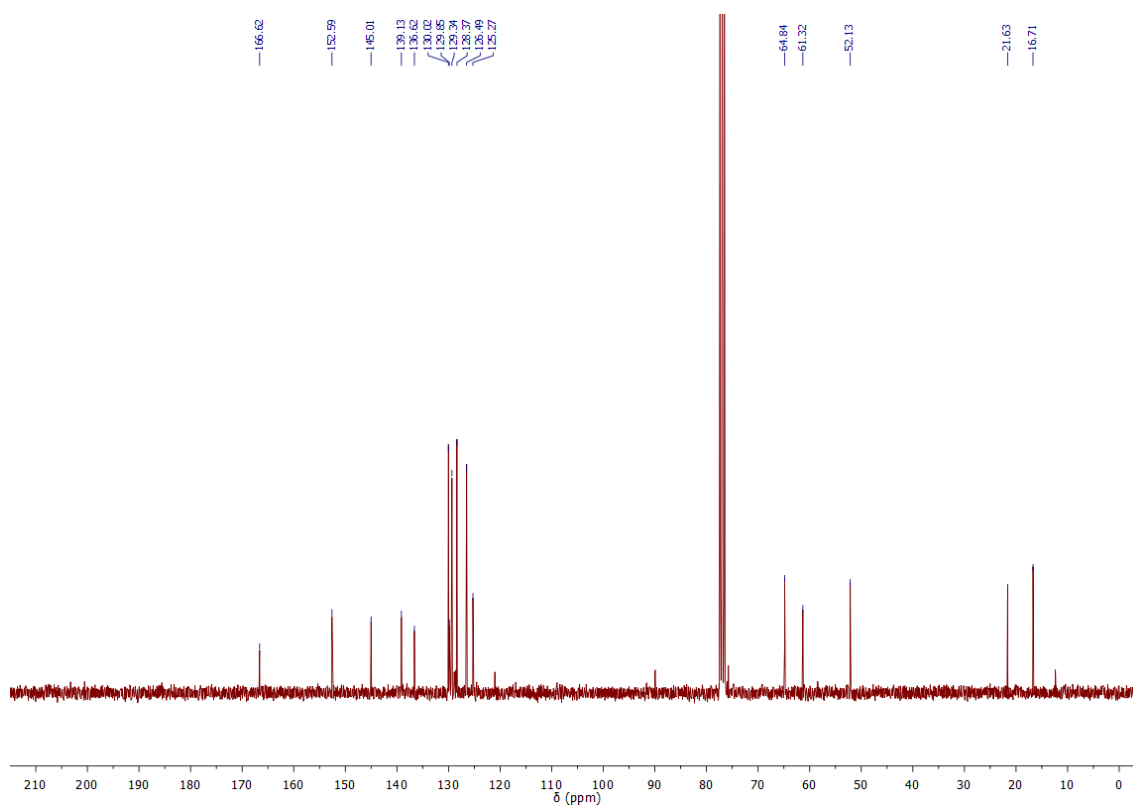


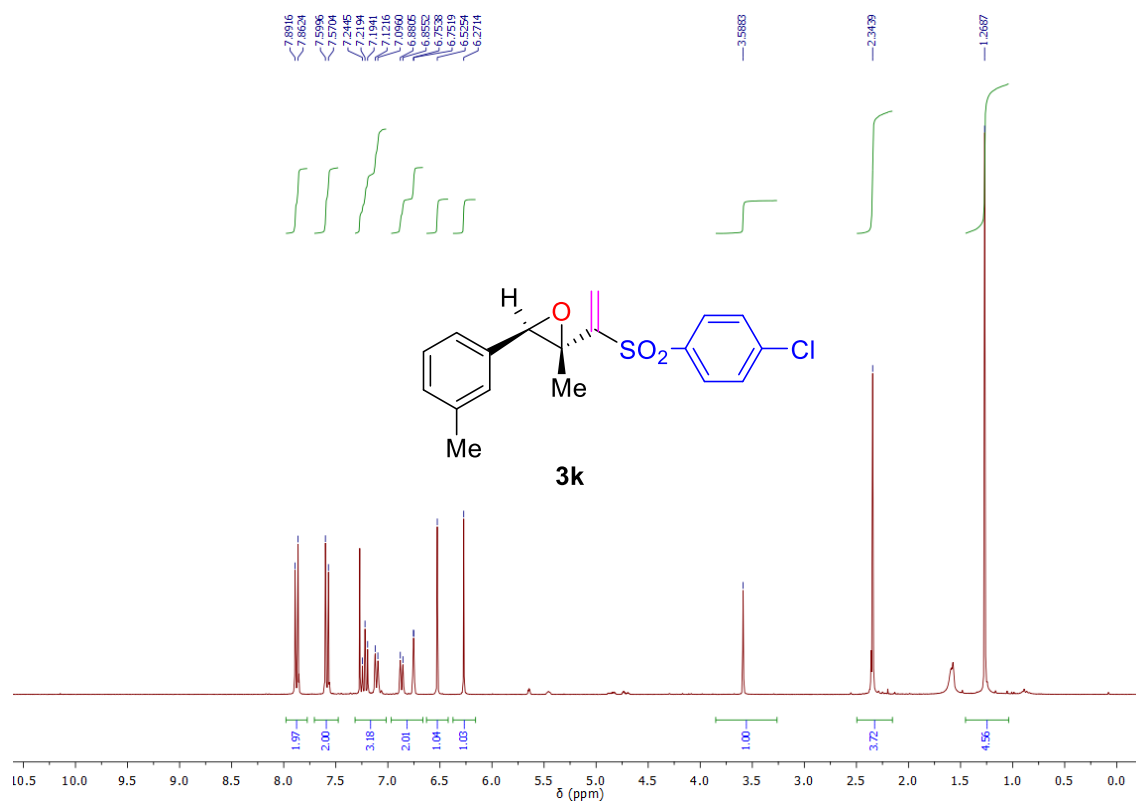
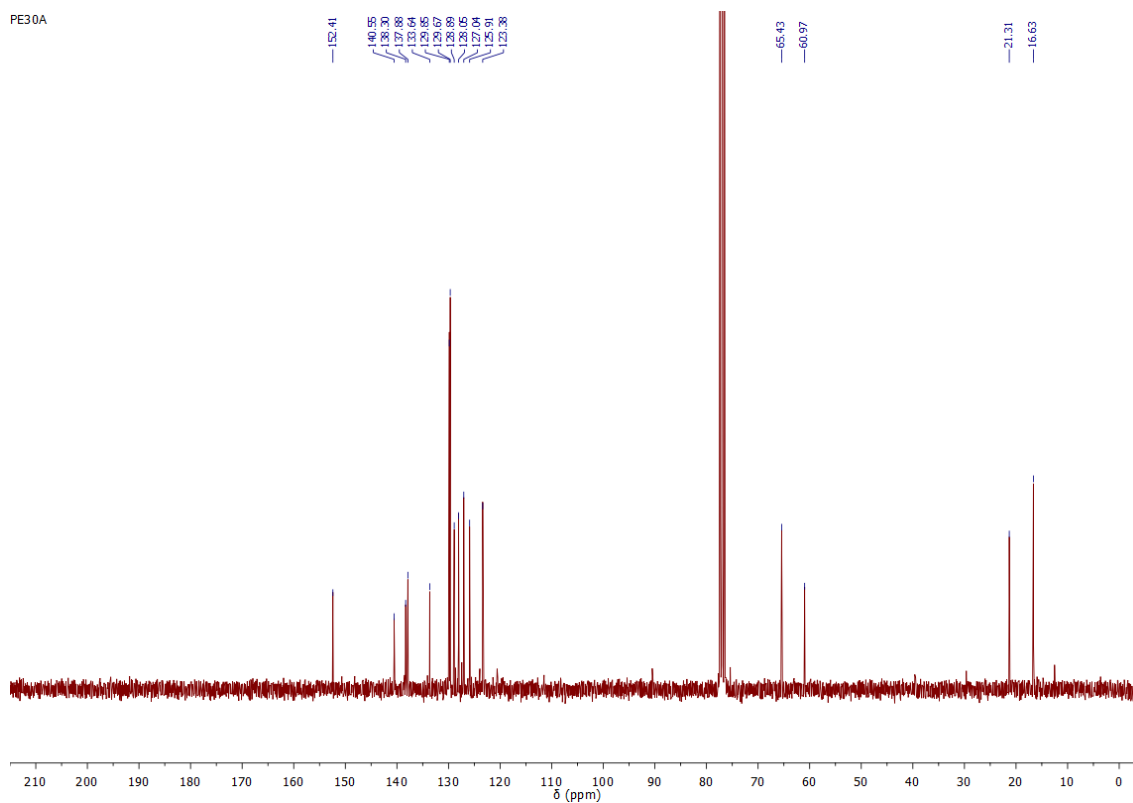
$^1\text{H}$  NMR spectrum of **3h** in  $\text{CD}_3\text{CN}$  at 700 MHz $^{13}\text{C}$  NMR spectrum of **3h** in  $\text{CD}_3\text{CN}$  at 175 MHz

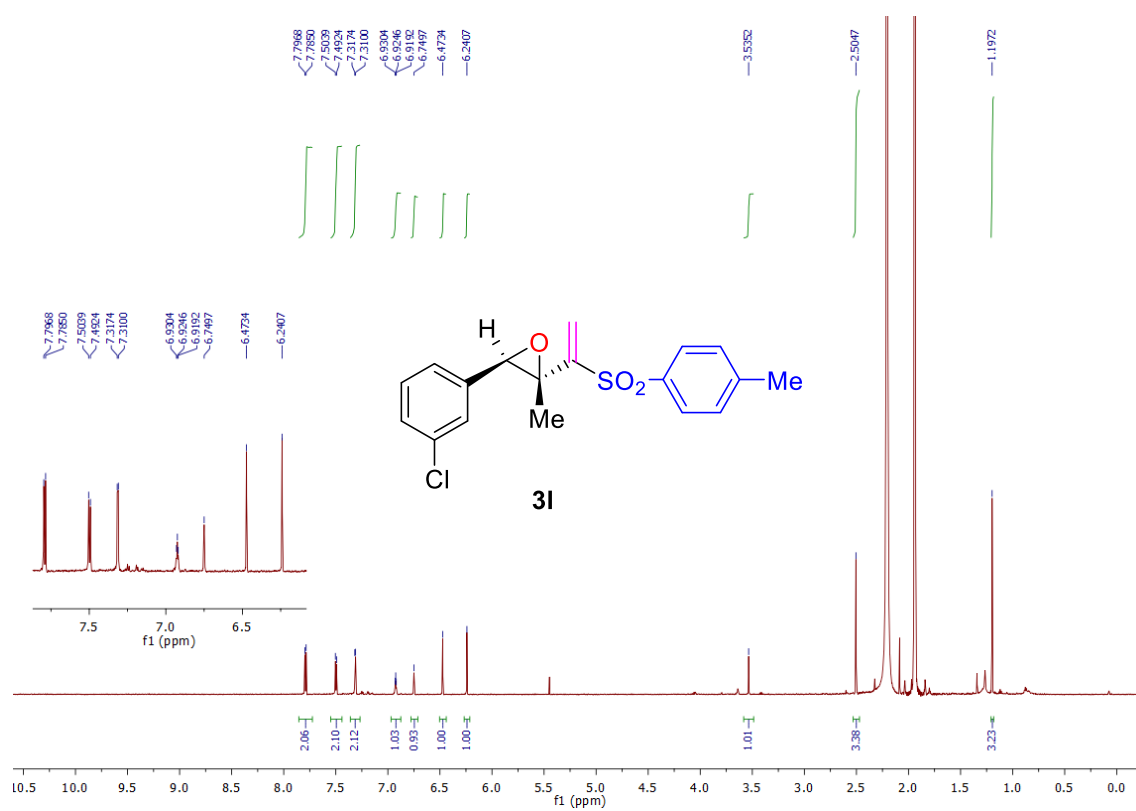
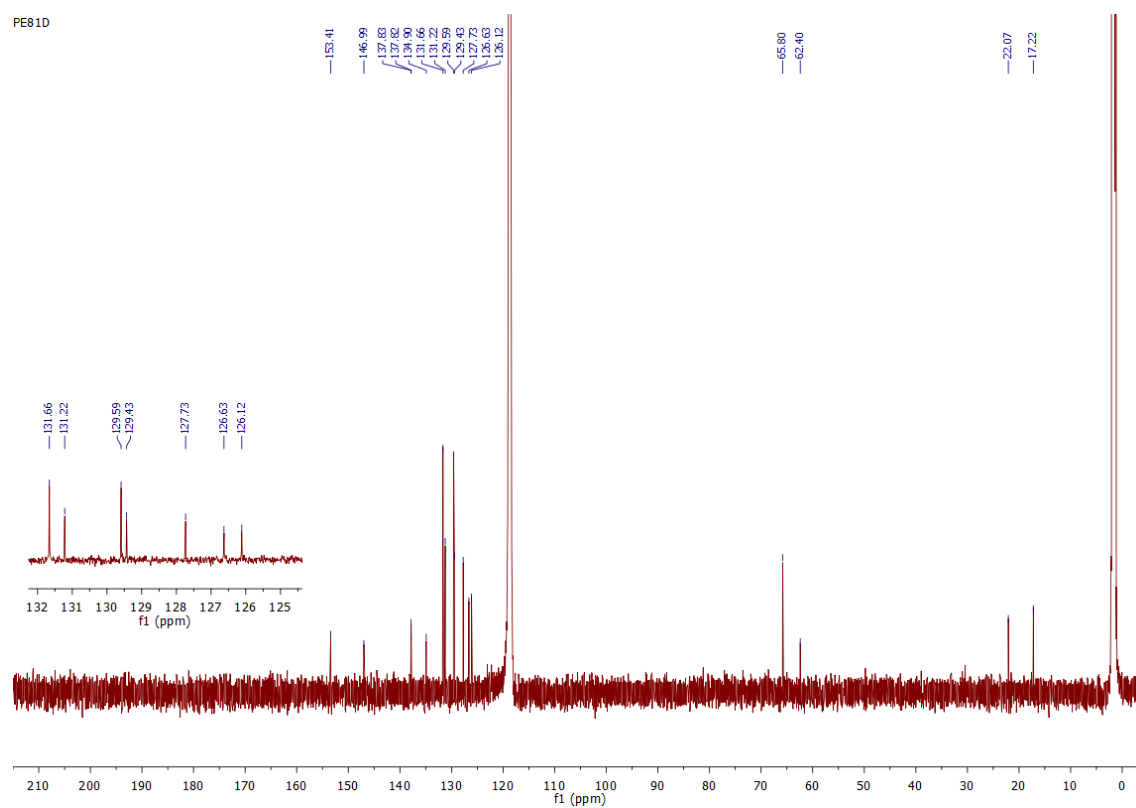
$^1\text{H}$  NMR spectrum of **3i** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3i** in  $\text{CDCl}_3$  at 75 MHz

$^1\text{H}$  NMR spectrum of **3j** in  $\text{CDCl}_3$  at 300 MHz

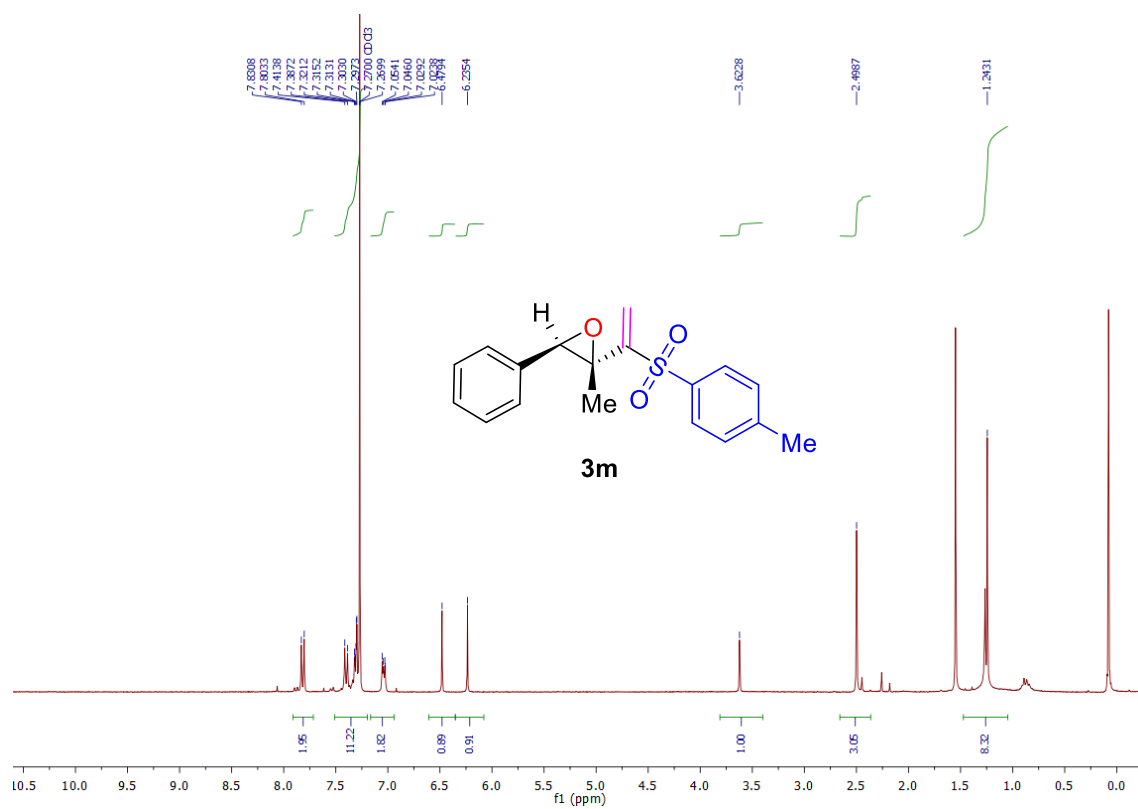
FH-827

 $^{13}\text{C}$  NMR spectrum of **3j** in  $\text{CDCl}_3$  at 75 MHz

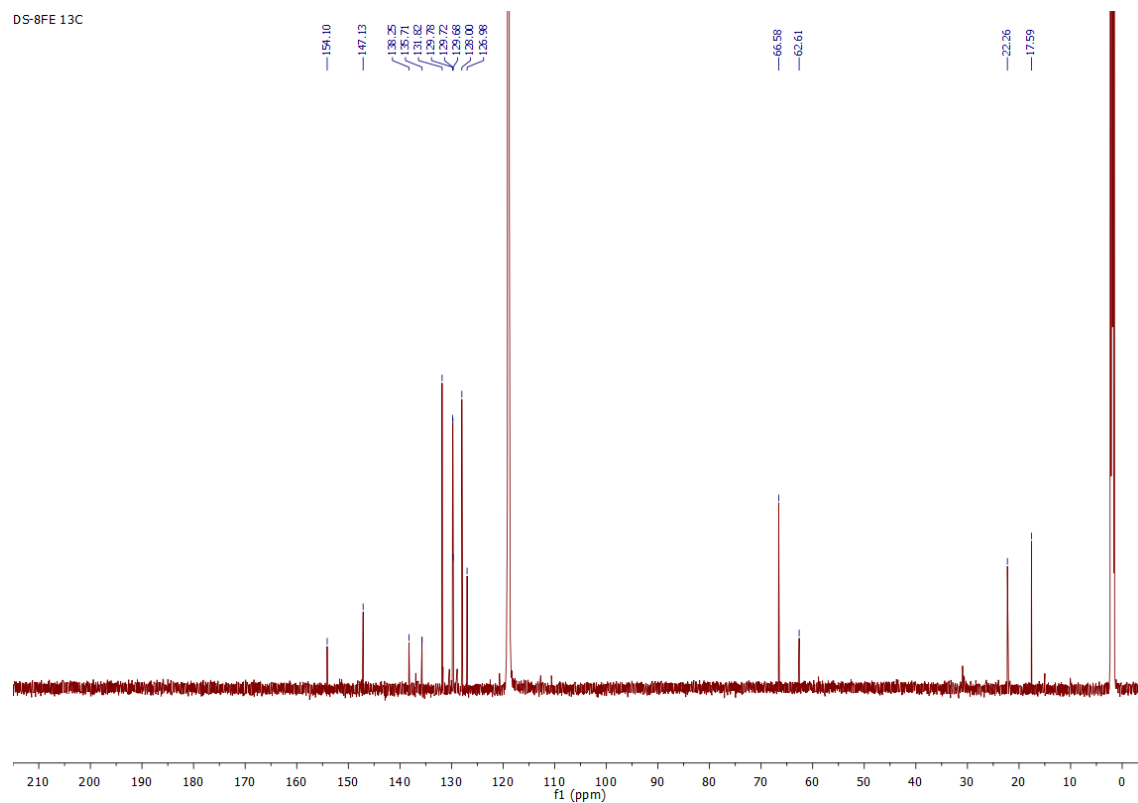
$^1\text{H}$  NMR spectrum of **3k** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3k** in  $\text{CDCl}_3$  at 75 MHz

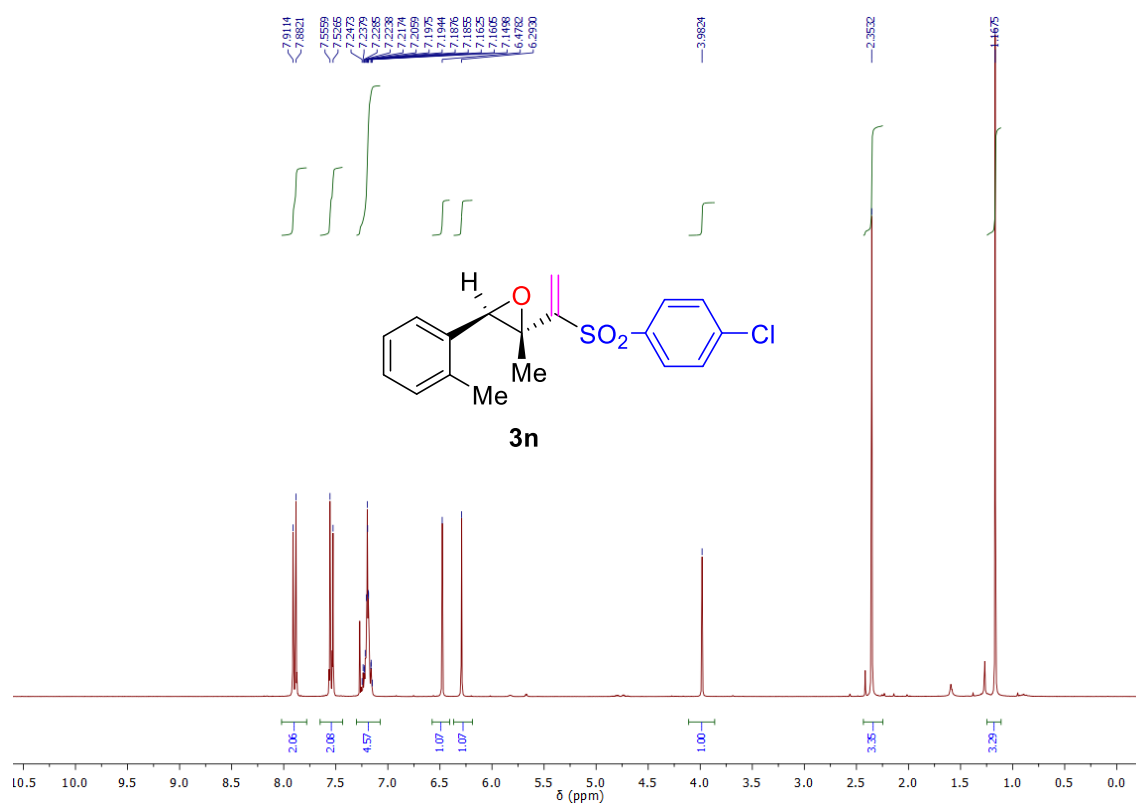
$^1\text{H}$  NMR spectrum of **31** in  $\text{CD}_3\text{CN}$  at 700 MHz $^{13}\text{C}$  NMR spectrum of **31** in  $\text{CD}_3\text{CN}$  at 175 MHz

$^1\text{H}$  NMR spectrum of **3m** in  $\text{CDCl}_3$  at 300 MHz

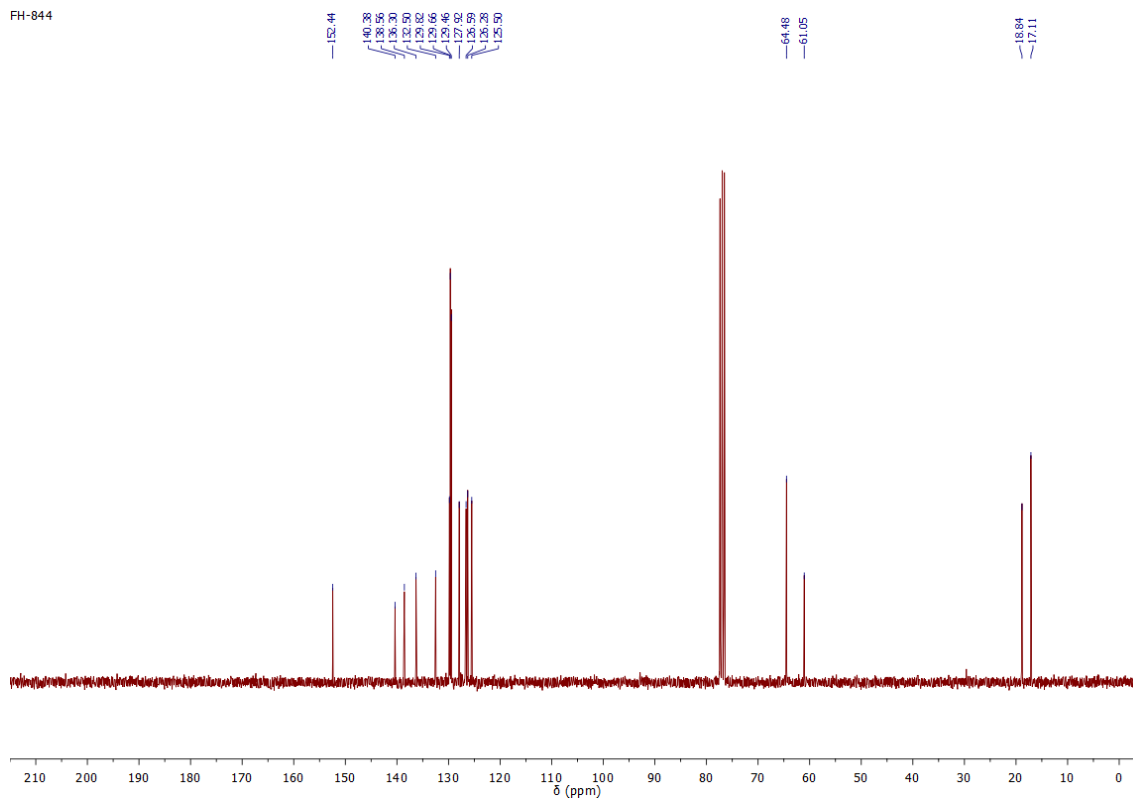


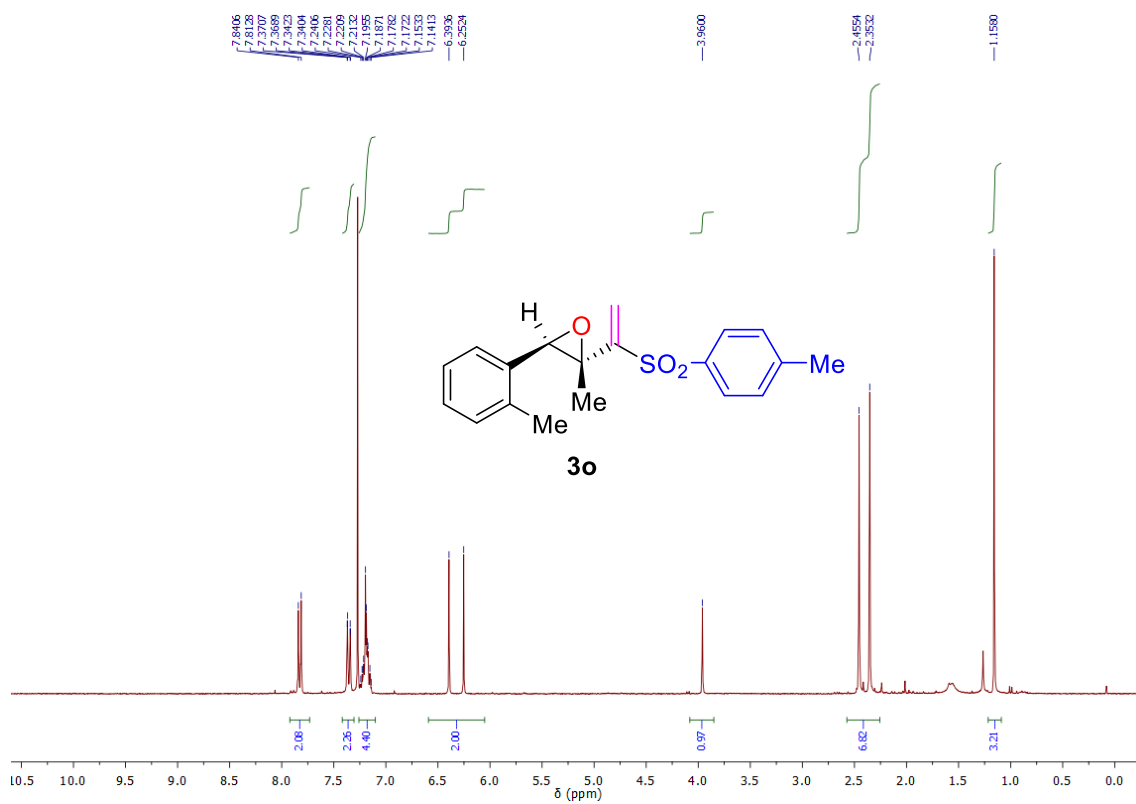
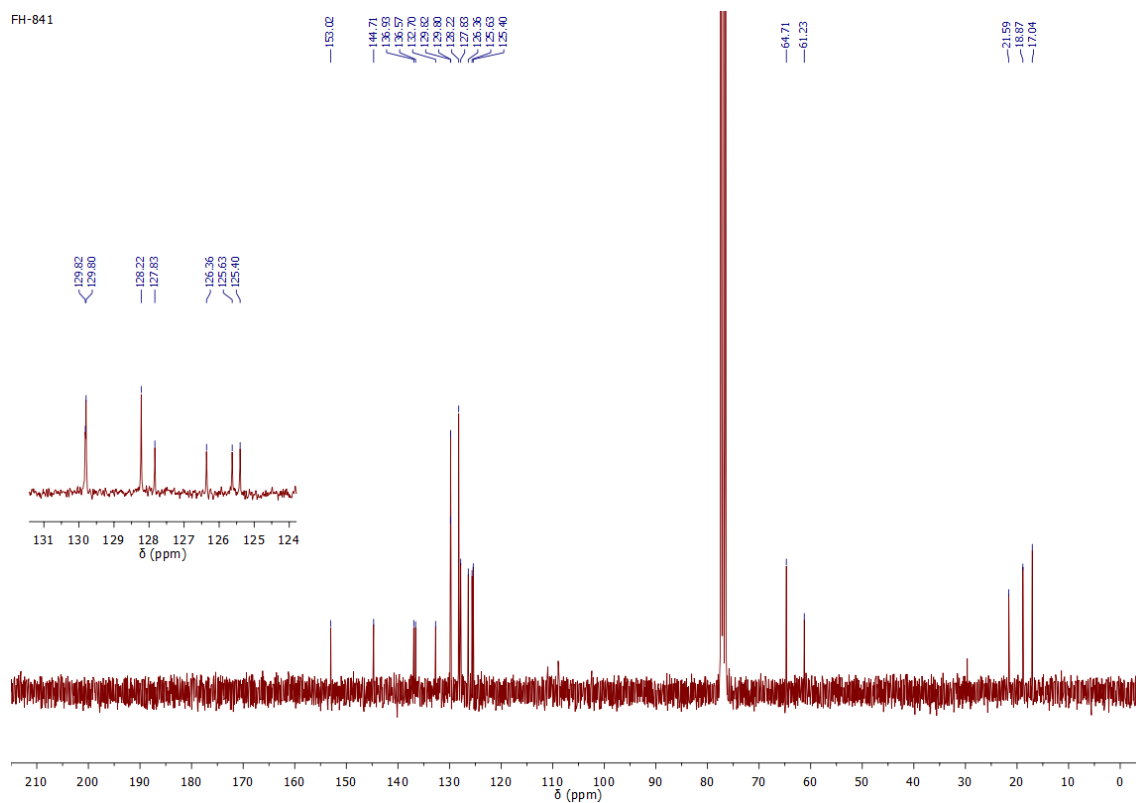
$^{13}\text{C}$  NMR spectrum of **3m** in  $\text{CD}_3\text{CN}$  at 175 MHz

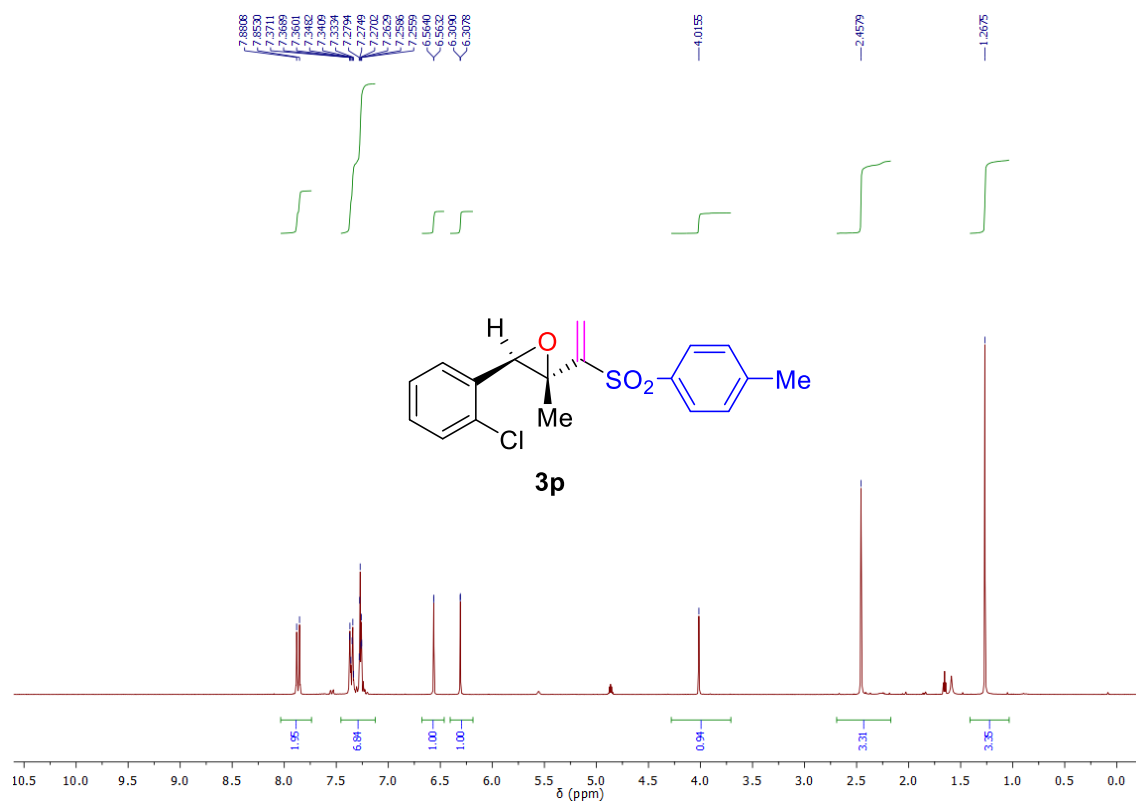


$^1\text{H}$  NMR spectrum of **3n** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3n** in  $\text{CDCl}_3$  at 75 MHz

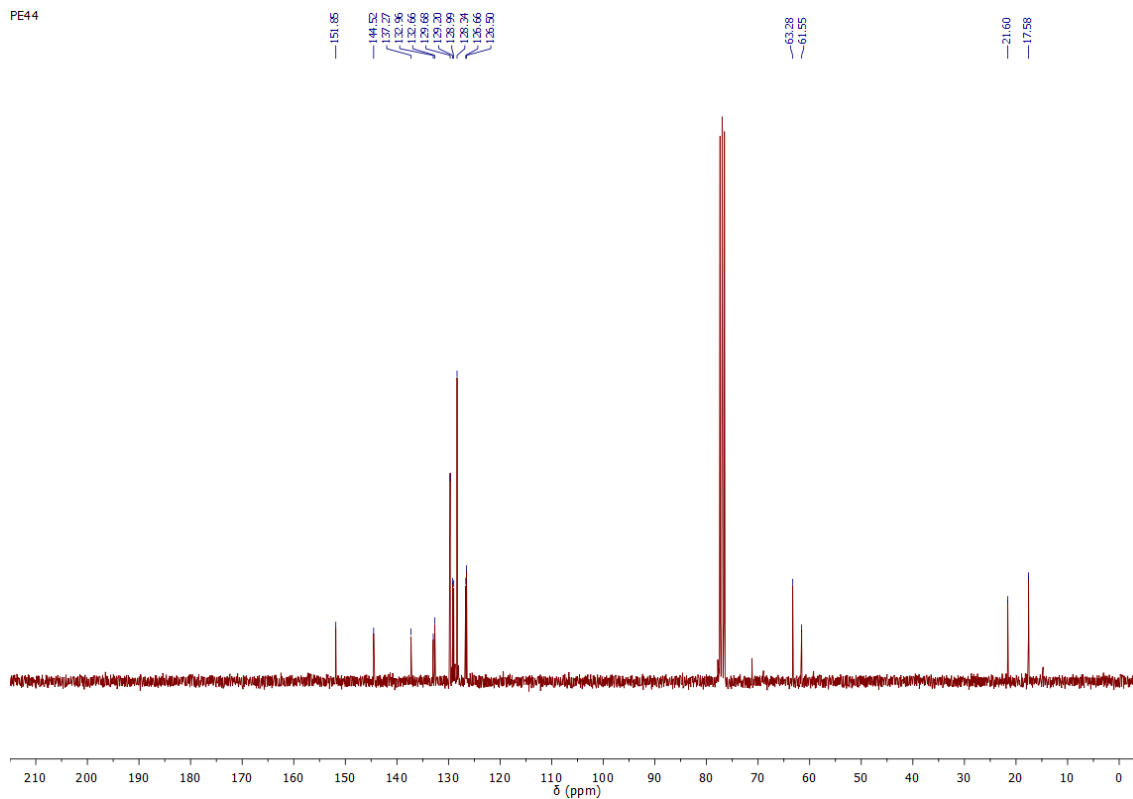
FH-844

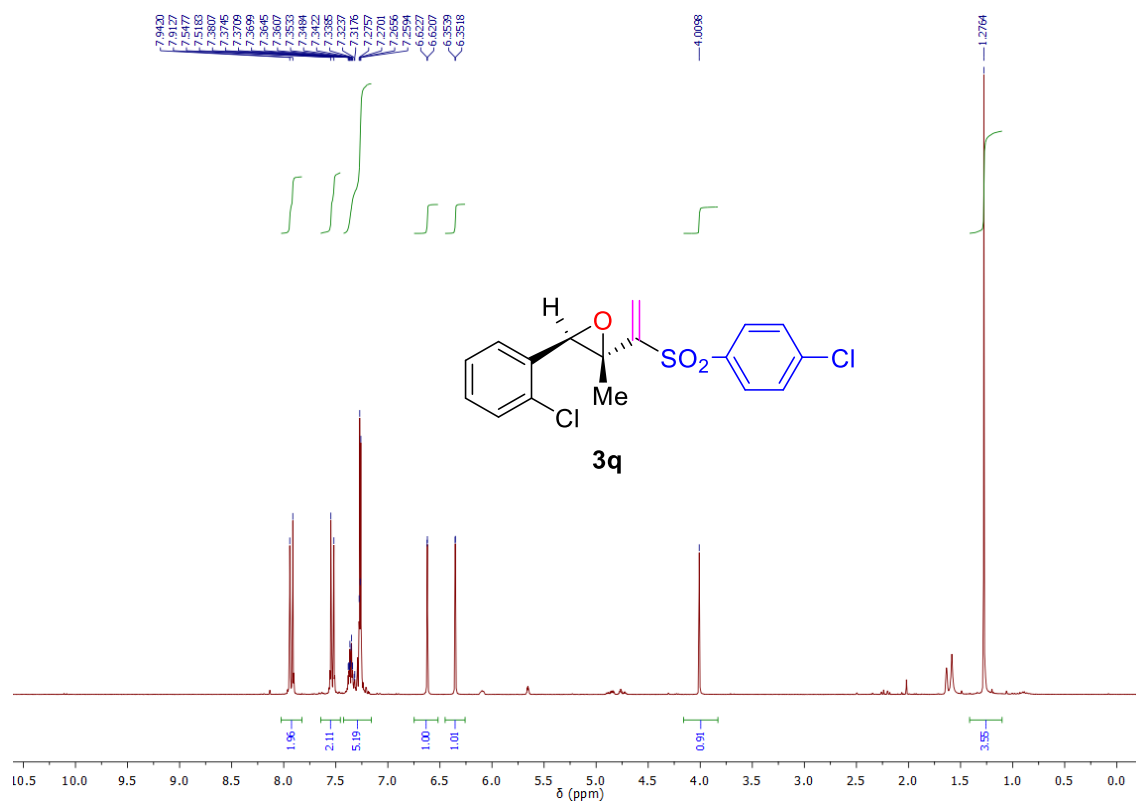
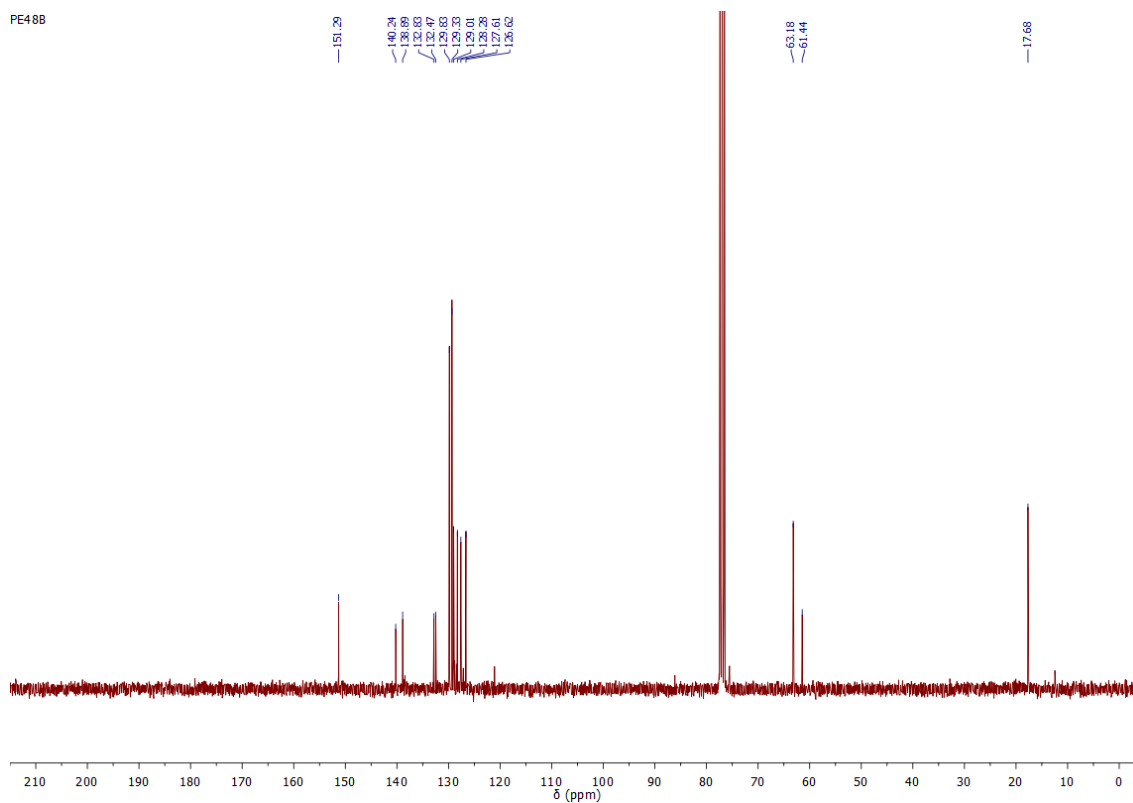


$^1\text{H}$  NMR spectrum of **3o** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3o** in  $\text{CDCl}_3$  at 75 MHz

$^1\text{H}$  NMR spectrum of **3p** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3p** in  $\text{CDCl}_3$  at 75 MHz

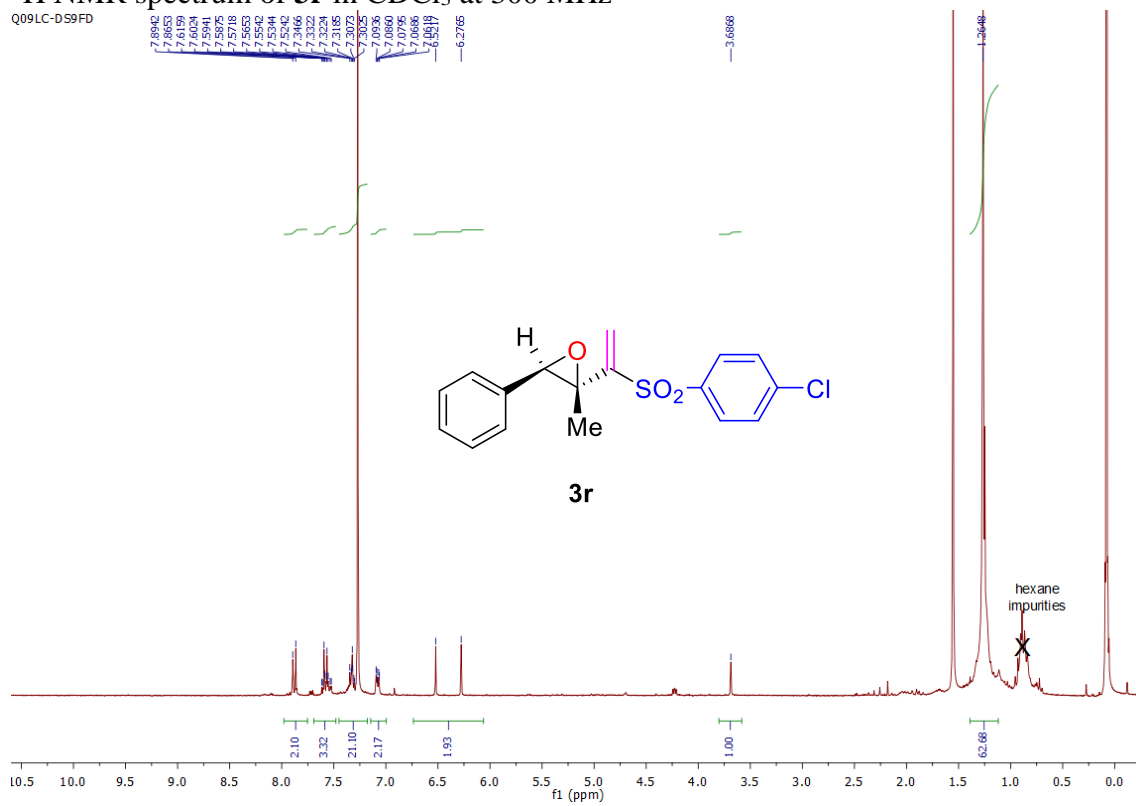
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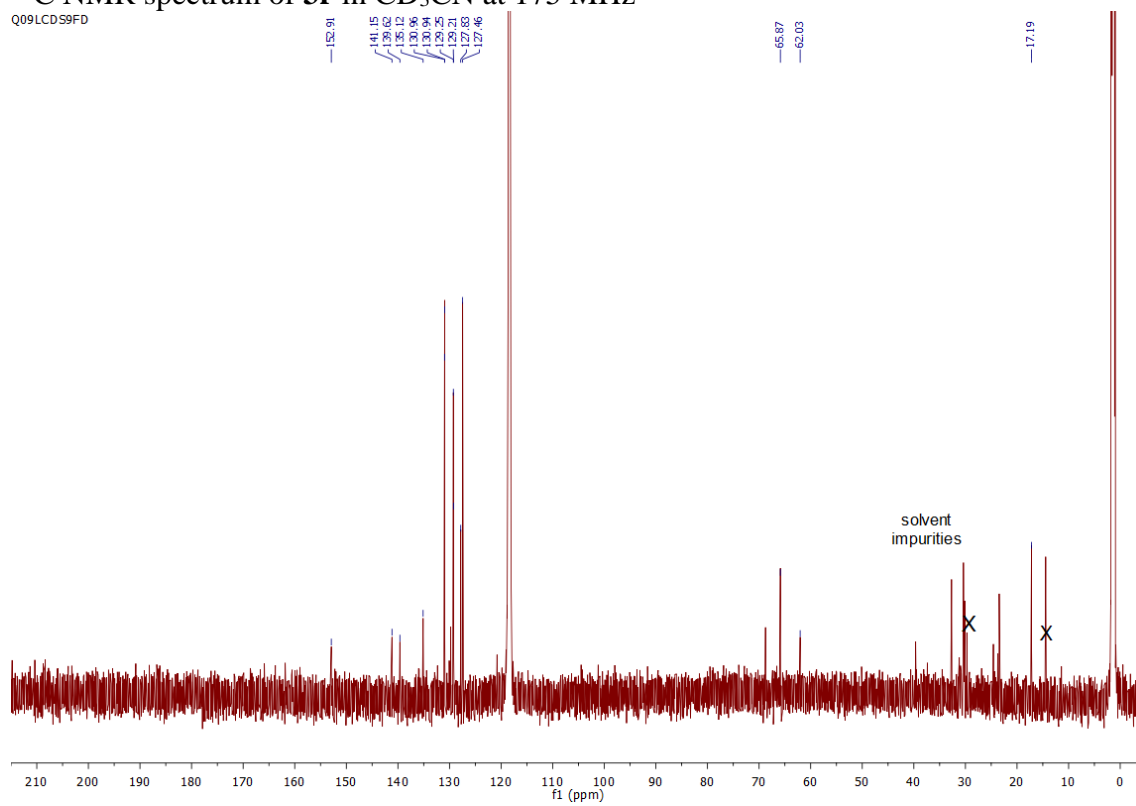
$^1\text{H}$  NMR spectrum of **3q** in  $\text{CDCl}_3$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **3q** in  $\text{CDCl}_3$  at 75 MHz

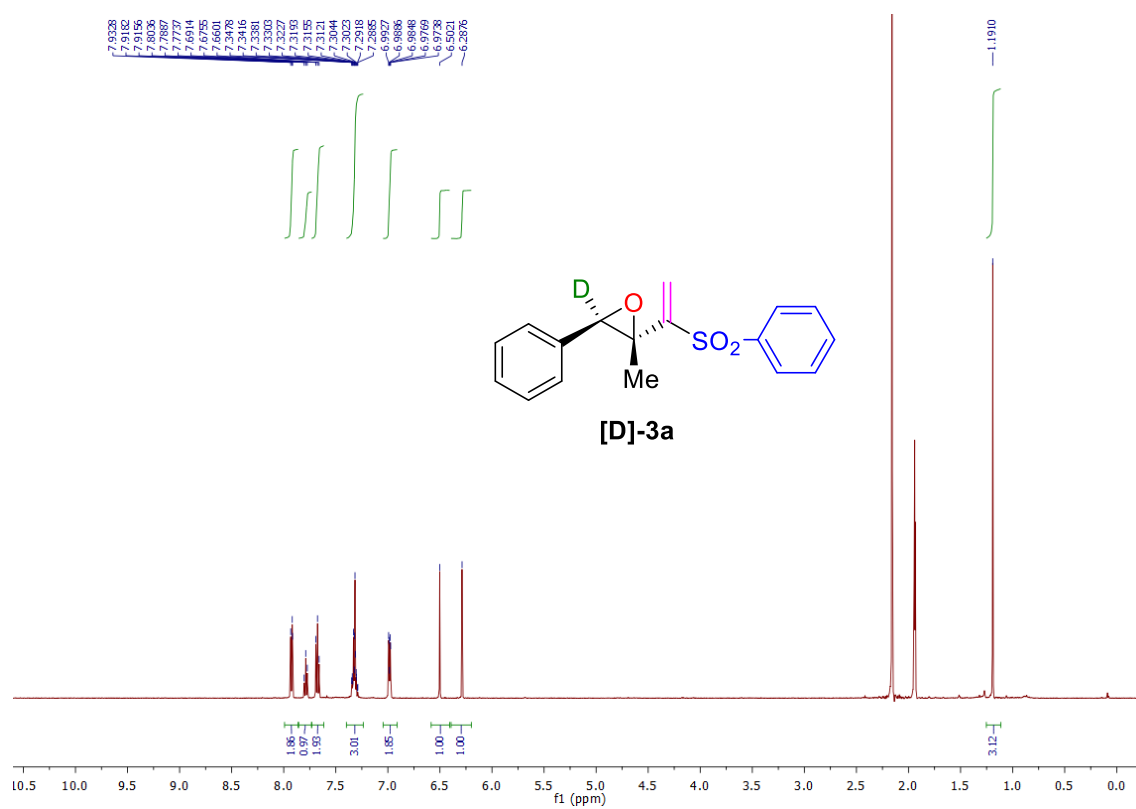
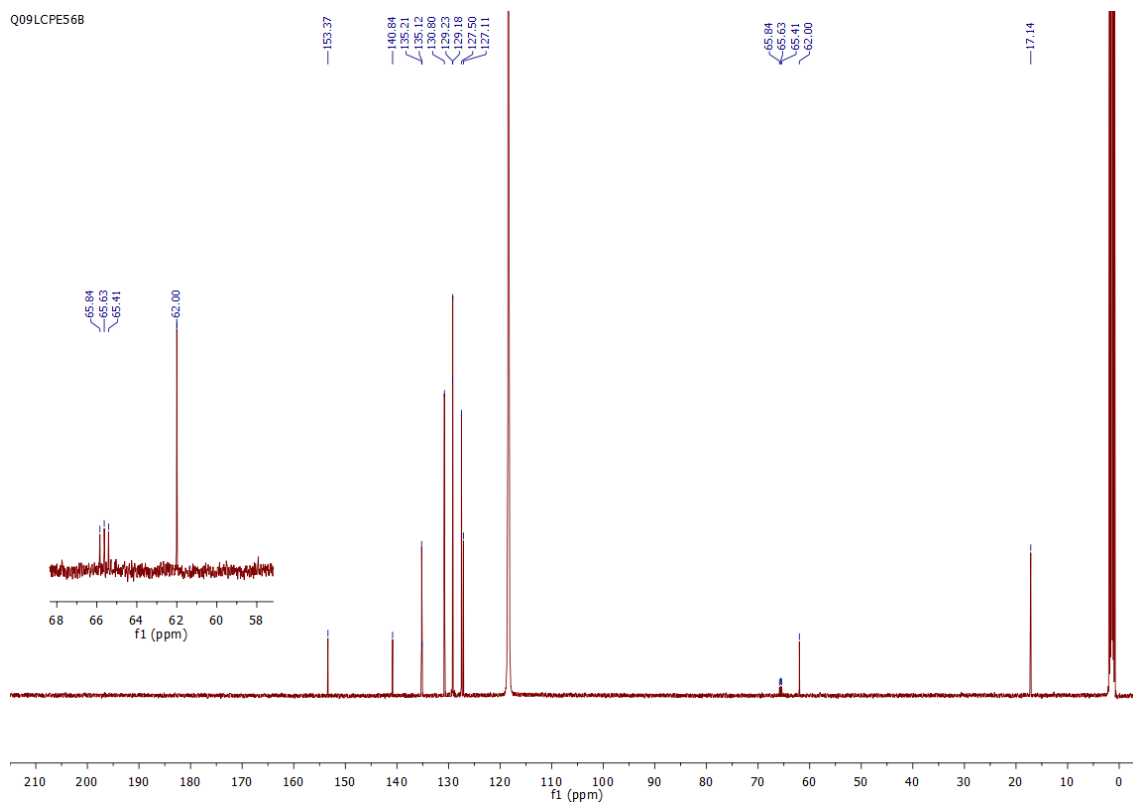
<sup>1</sup>H NMR spectrum of **3r** in CDCl<sub>3</sub> at 300 MHz

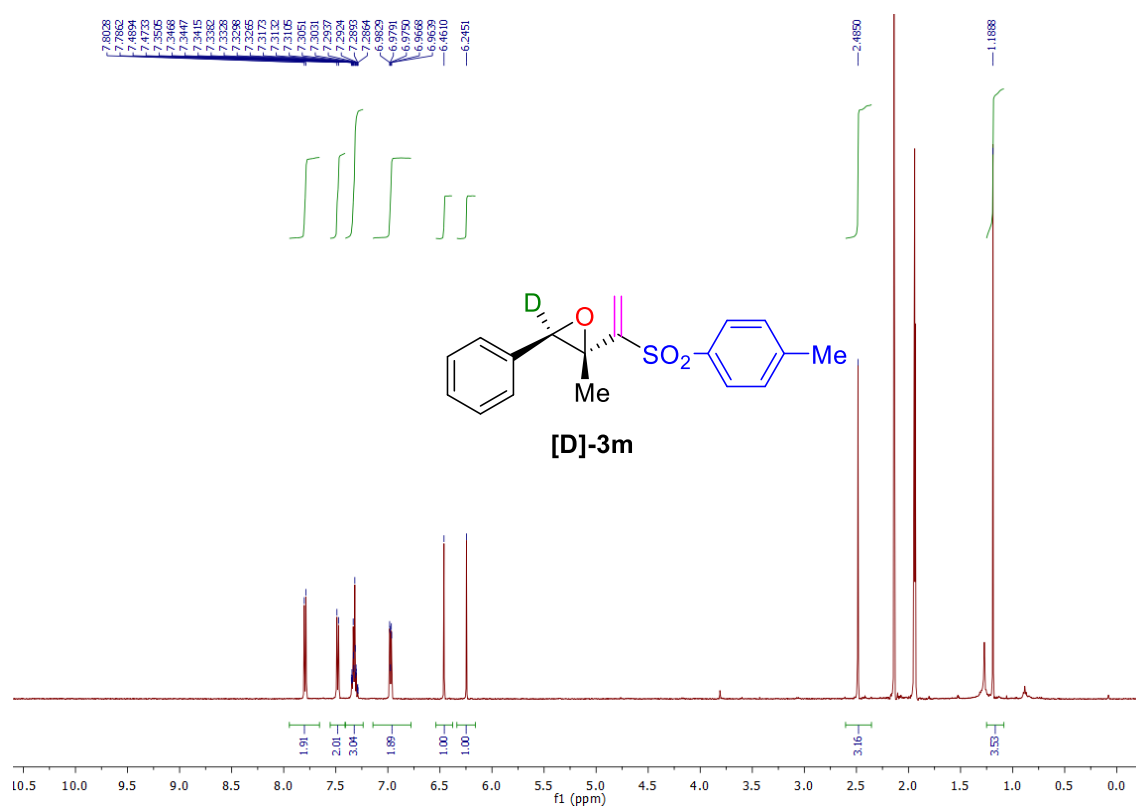
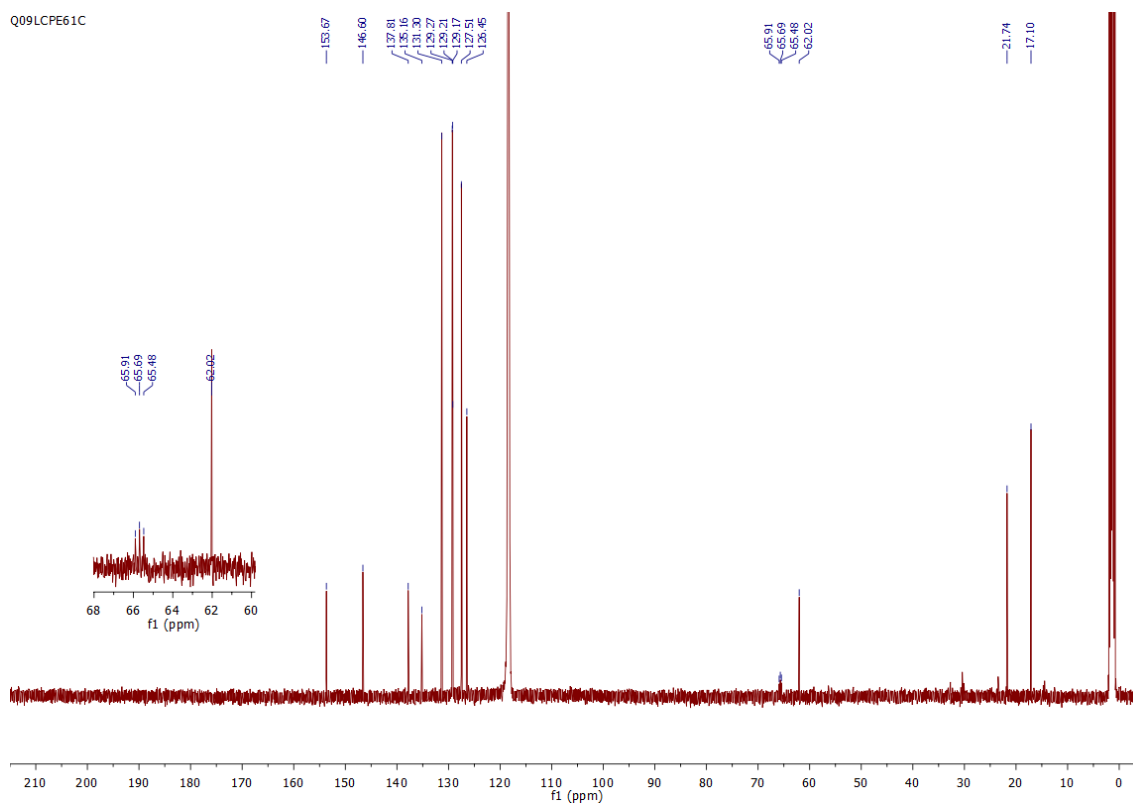
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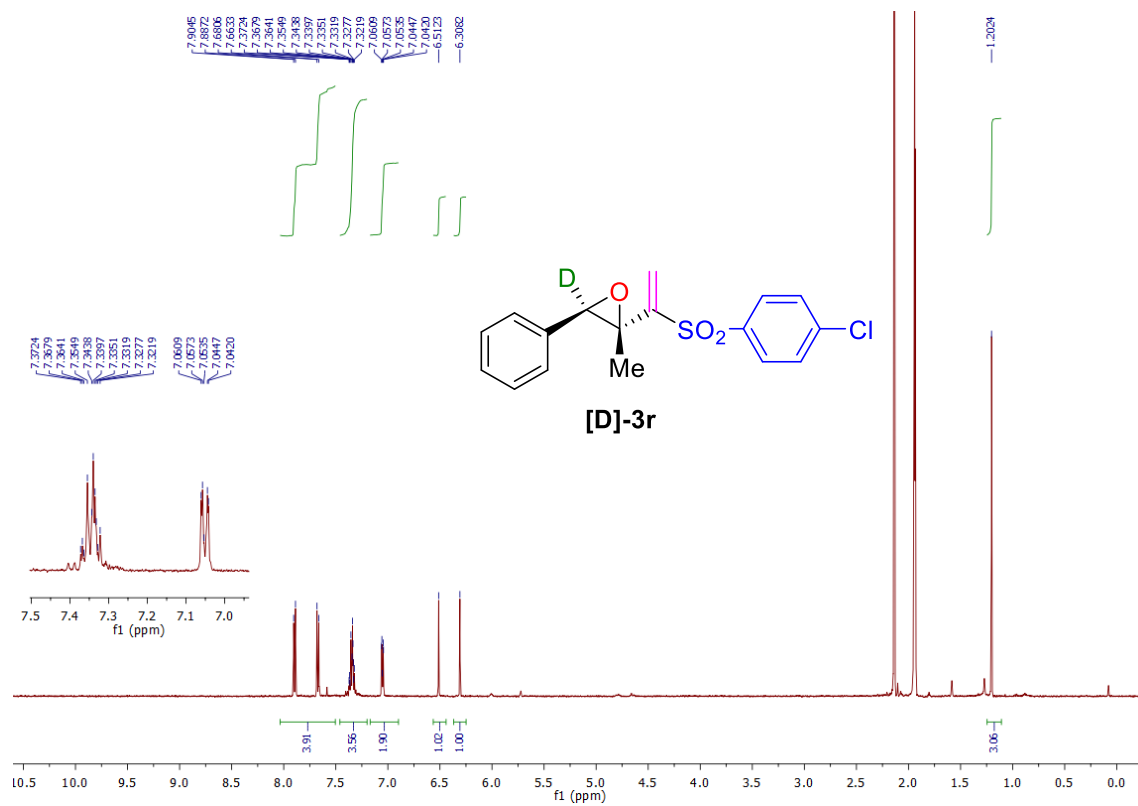
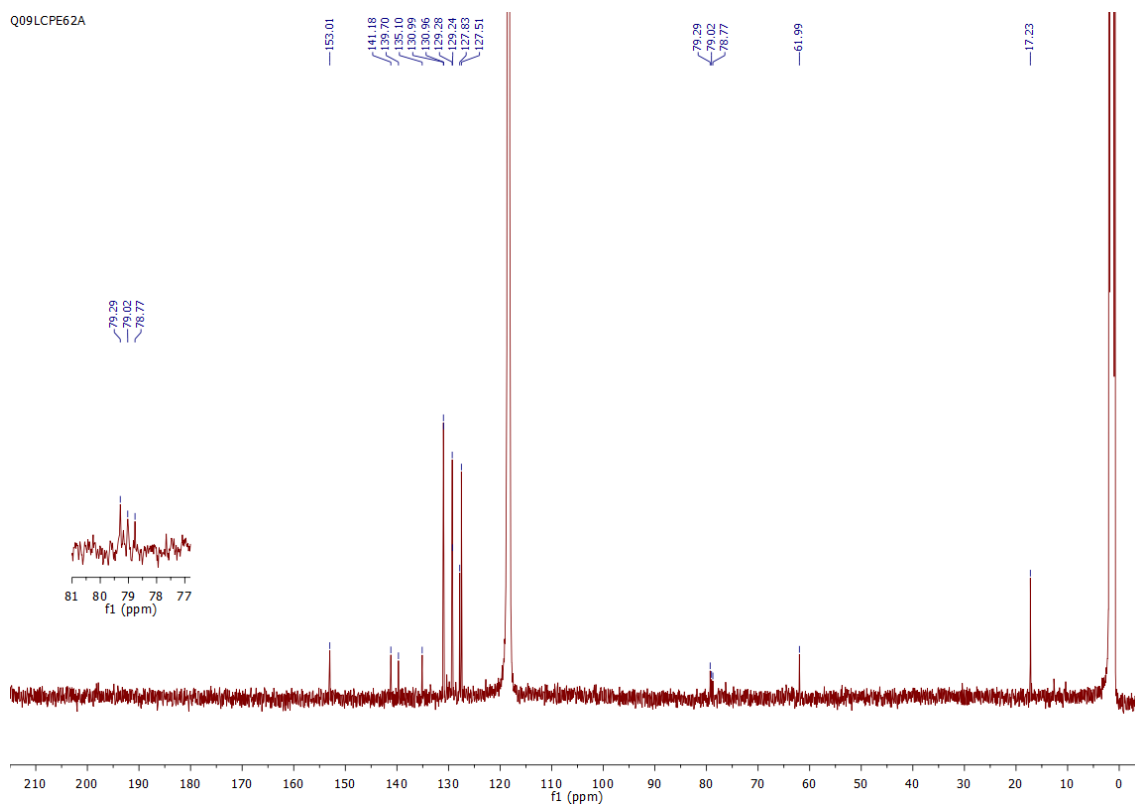
<sup>13</sup>C NMR spectrum of **3r** in CD<sub>3</sub>CN at 175 MHz

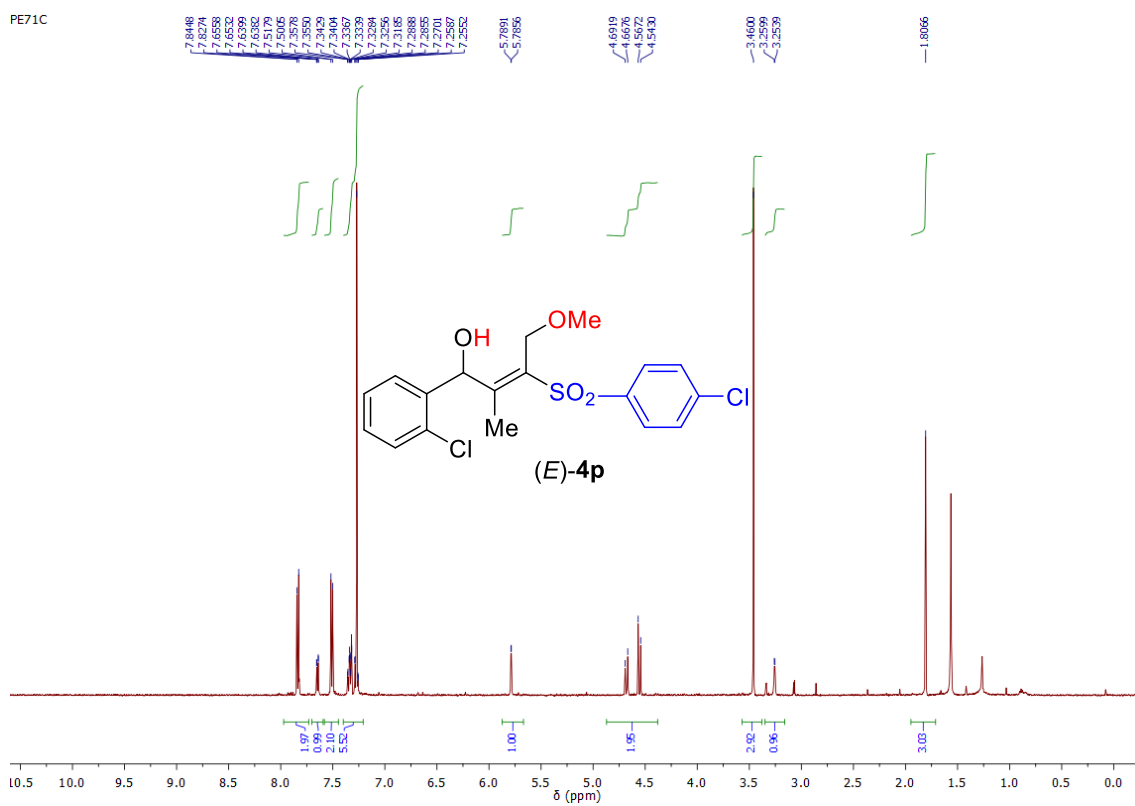
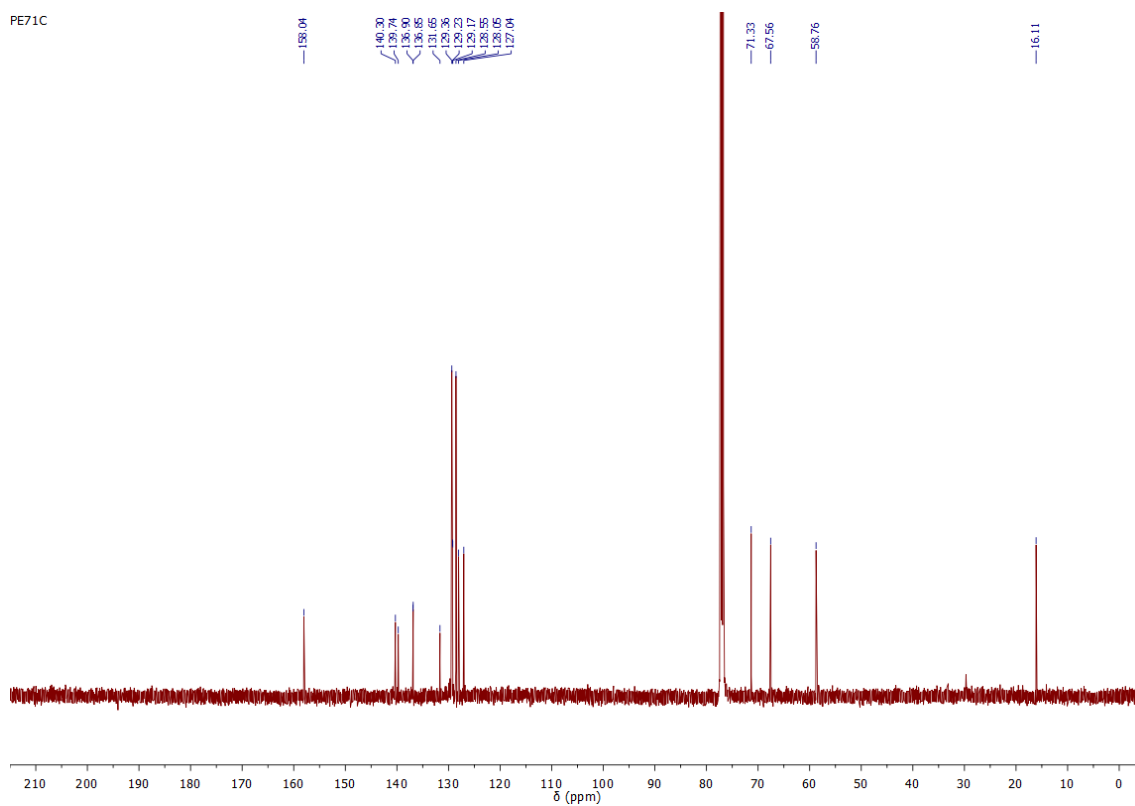
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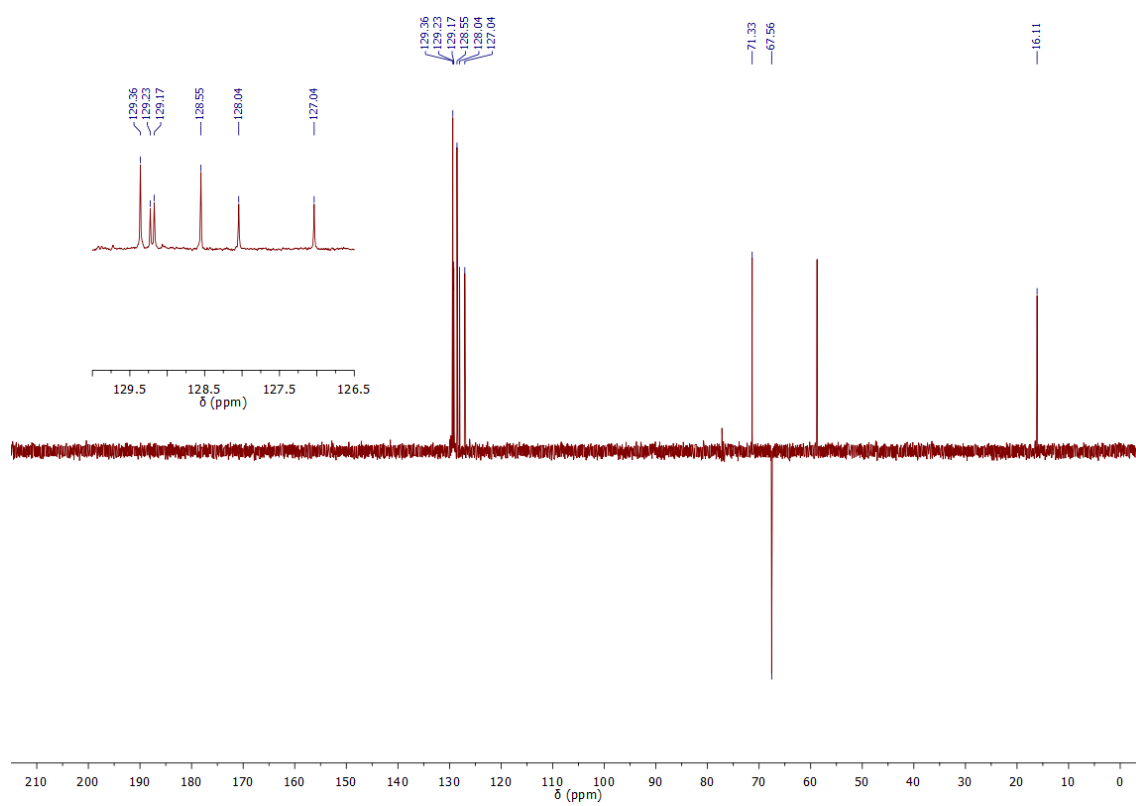
$^1\text{H}$  NMR spectrum of **[D]-3a** in  $\text{CD}_3\text{CN}$  at 500 MHz $^{13}\text{C}$  NMR spectrum of **[D]-3a** in  $\text{CD}_3\text{CN}$  at 125 MHz

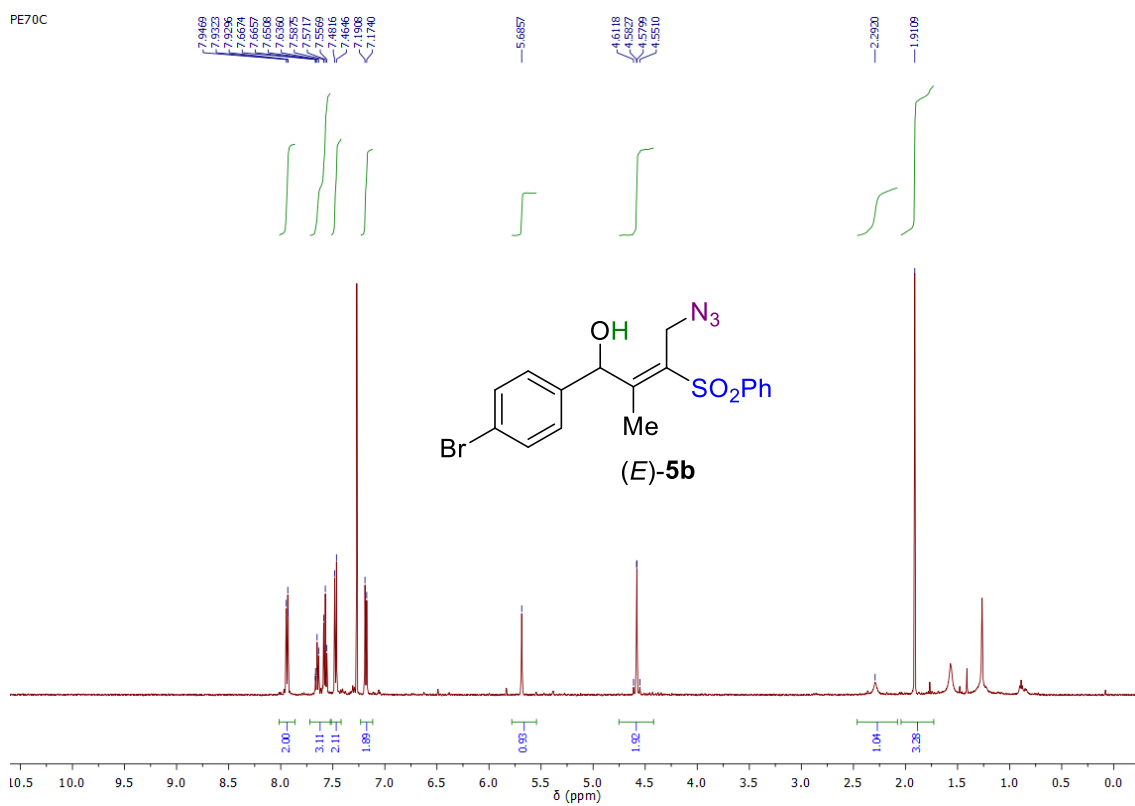
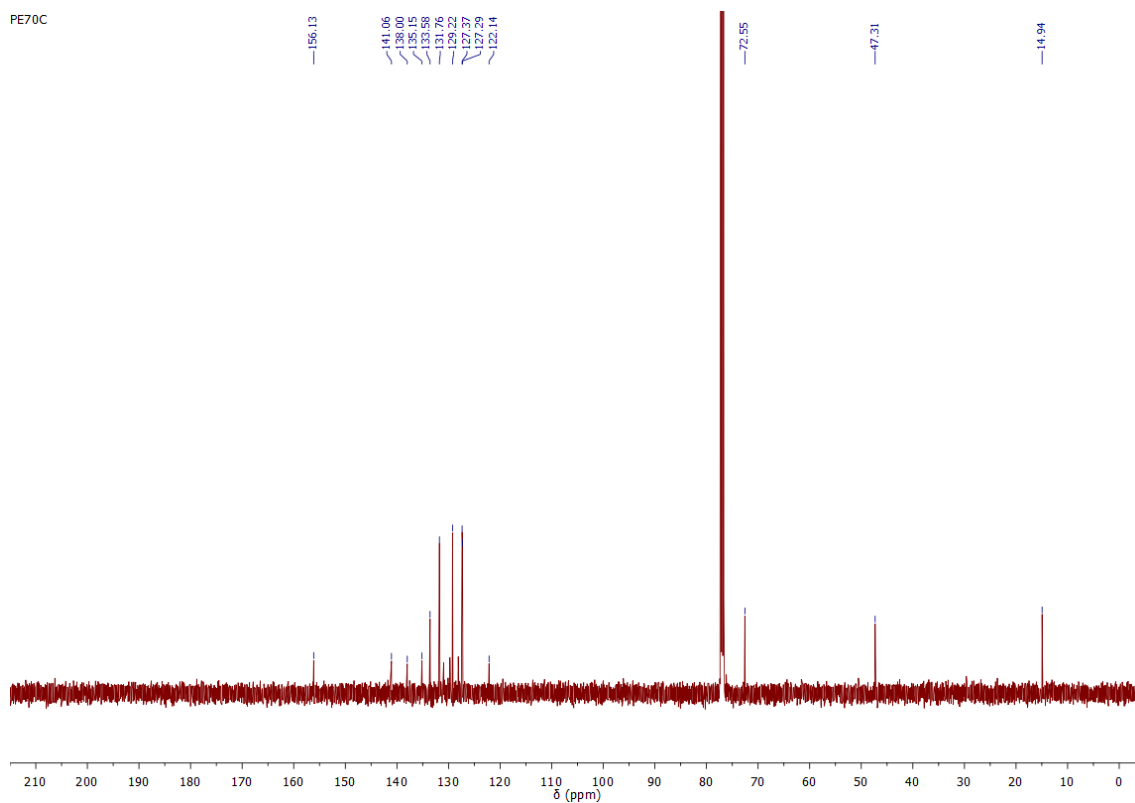
$^1\text{H}$  NMR spectrum of **[D]-3m** in  $\text{CD}_3\text{CN}$  at 500 MHz $^{13}\text{C}$  NMR spectrum of **[D]-3m** in  $\text{CD}_3\text{CN}$  at 125 MHz

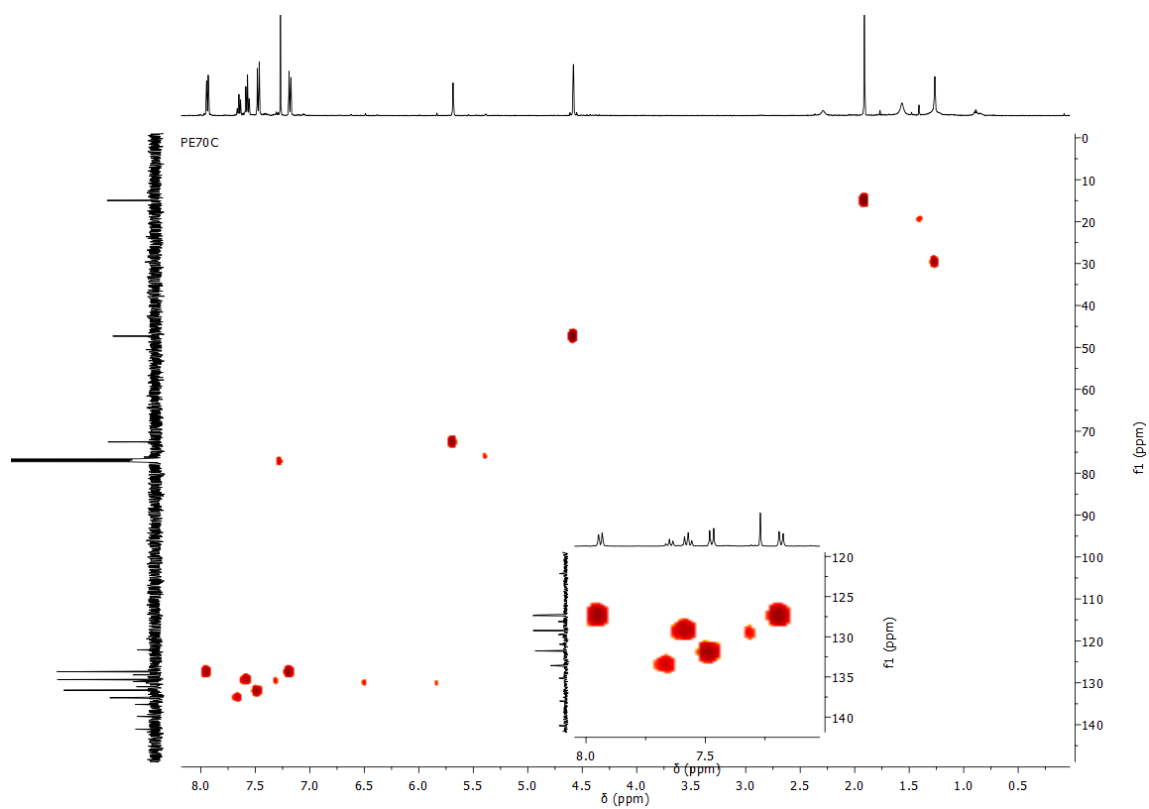
$^1\text{H}$  NMR spectrum of **[D]-3r** in  $\text{CD}_3\text{CN}$  at 500 MHz $^{13}\text{C}$  NMR spectrum of **[D]-3r** in  $\text{CD}_3\text{CN}$  at 125 MHz

$^1\text{H}$  NMR spectrum of (*E*)-**4p** in  $\text{CDCl}_3$  at 500 MHz $^{13}\text{C}$  NMR spectrum of (*E*)-**4p** in  $\text{CDCl}_3$  at 125 MHz

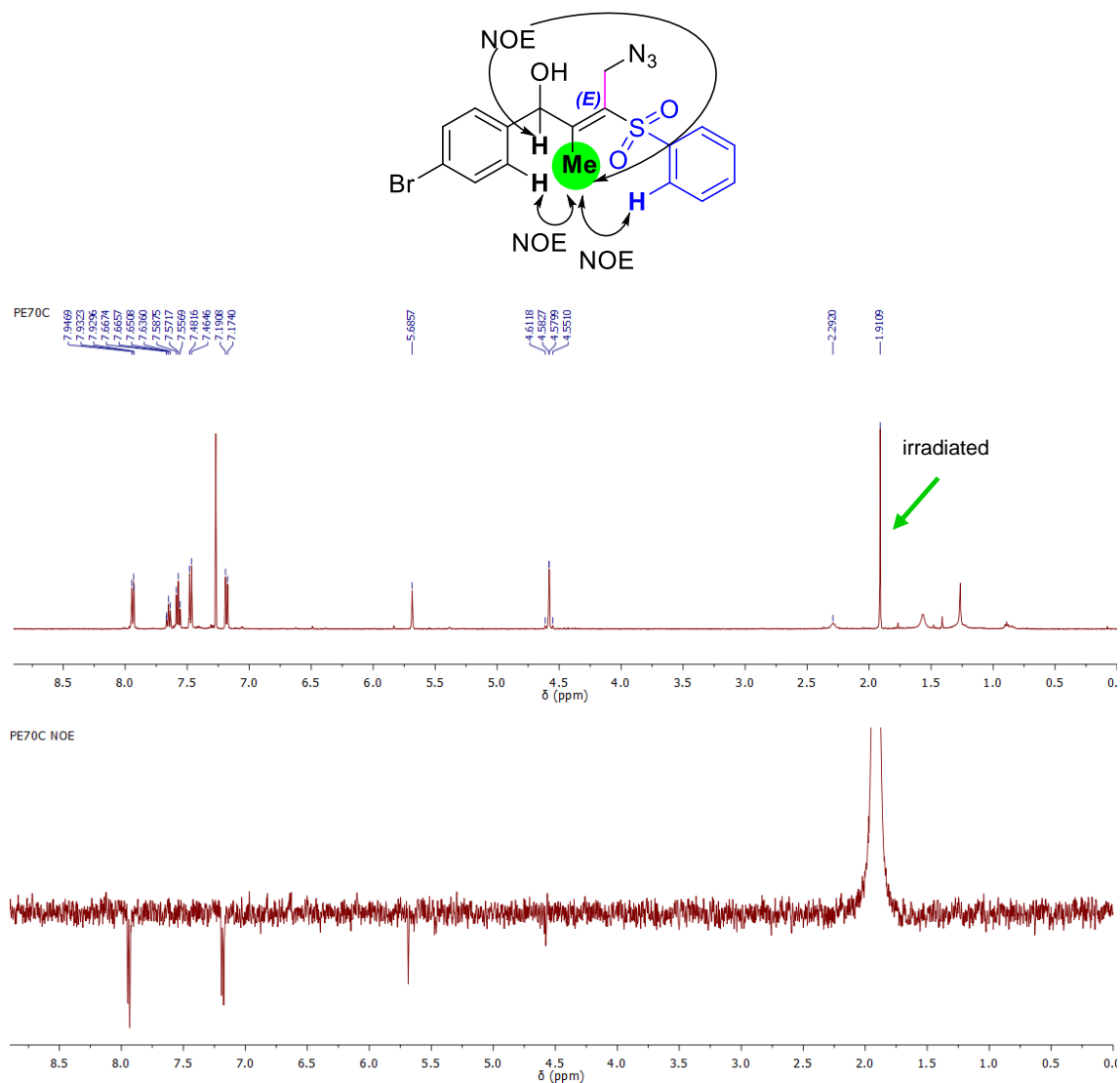
DEPT NMR spectrum of (*E*)-**4p** in CDCl<sub>3</sub> at 125 MHz



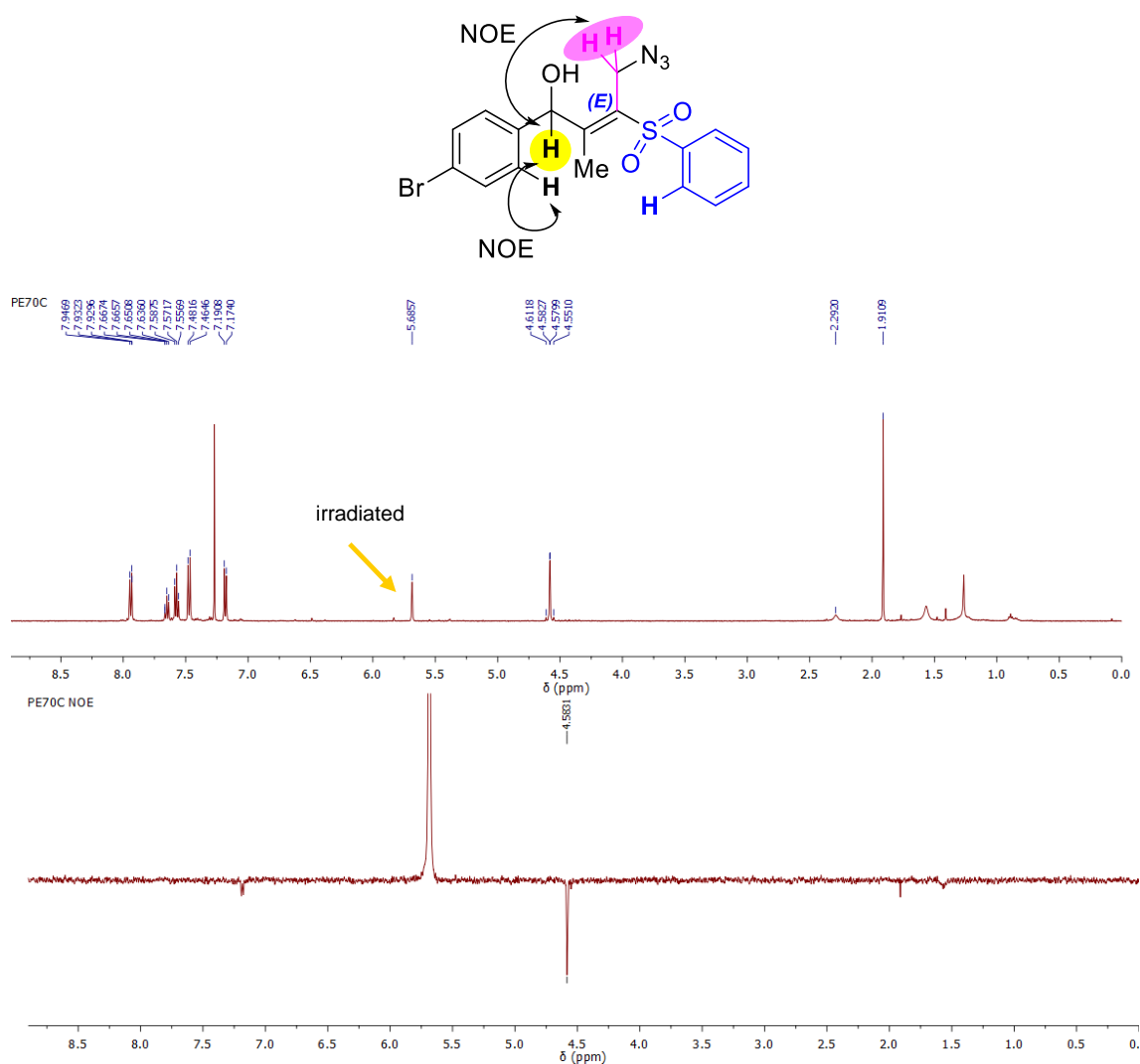
$^1\text{H}$  NMR spectrum of (*E*)-**5b** in  $\text{CDCl}_3$  at 500 MHz $^{13}\text{C}$  NMR spectrum of (*E*)-**5b** in  $\text{CDCl}_3$  at 125 MHz

Two-dimensional HMQC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of (*E*)-**5b** in  $\text{CDCl}_3$ 

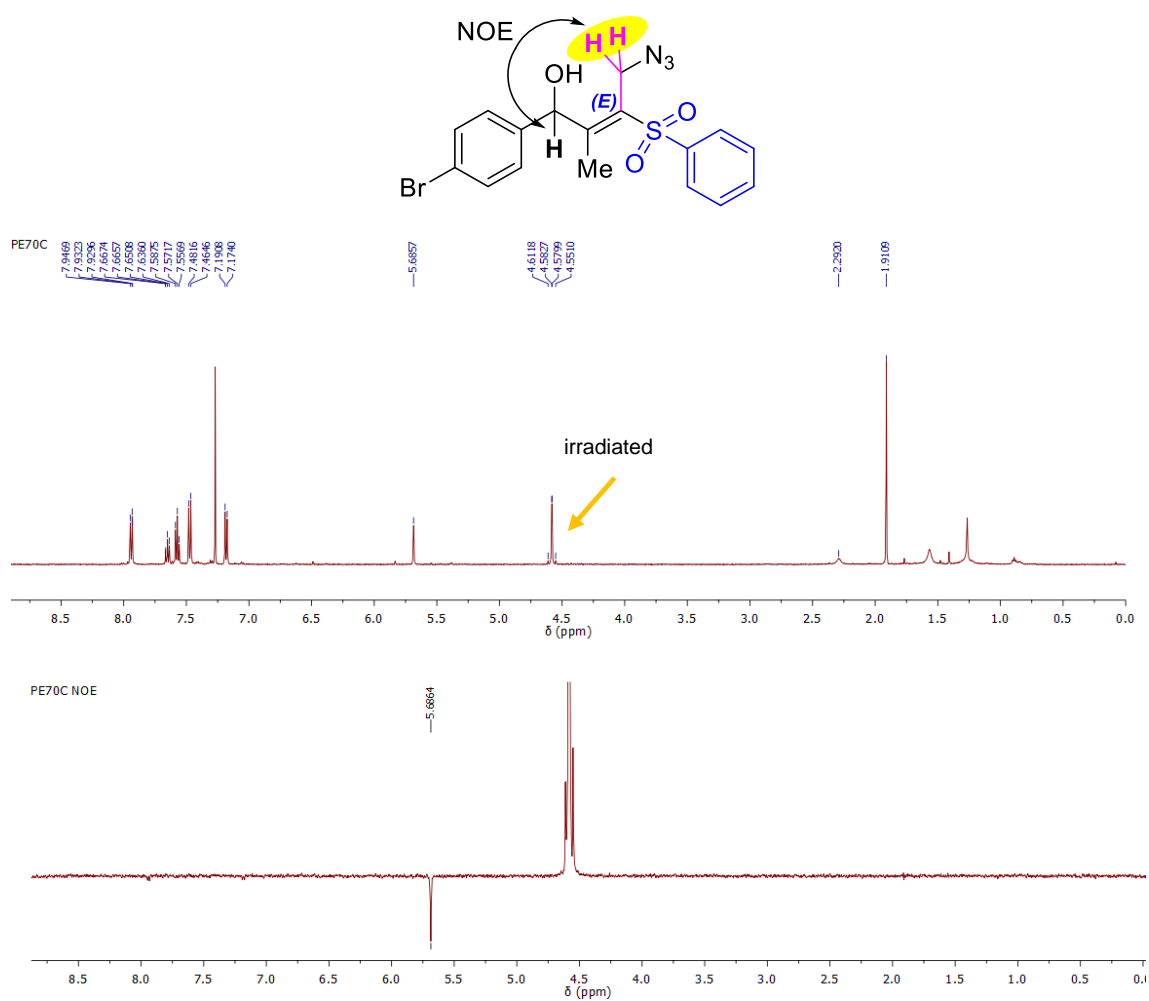
One-dimensional NOE NMR spectrum of (*E*)-**5b** in CDCl<sub>3</sub> at 500 MHz, showing selected NOE correlations highlighted in the structure

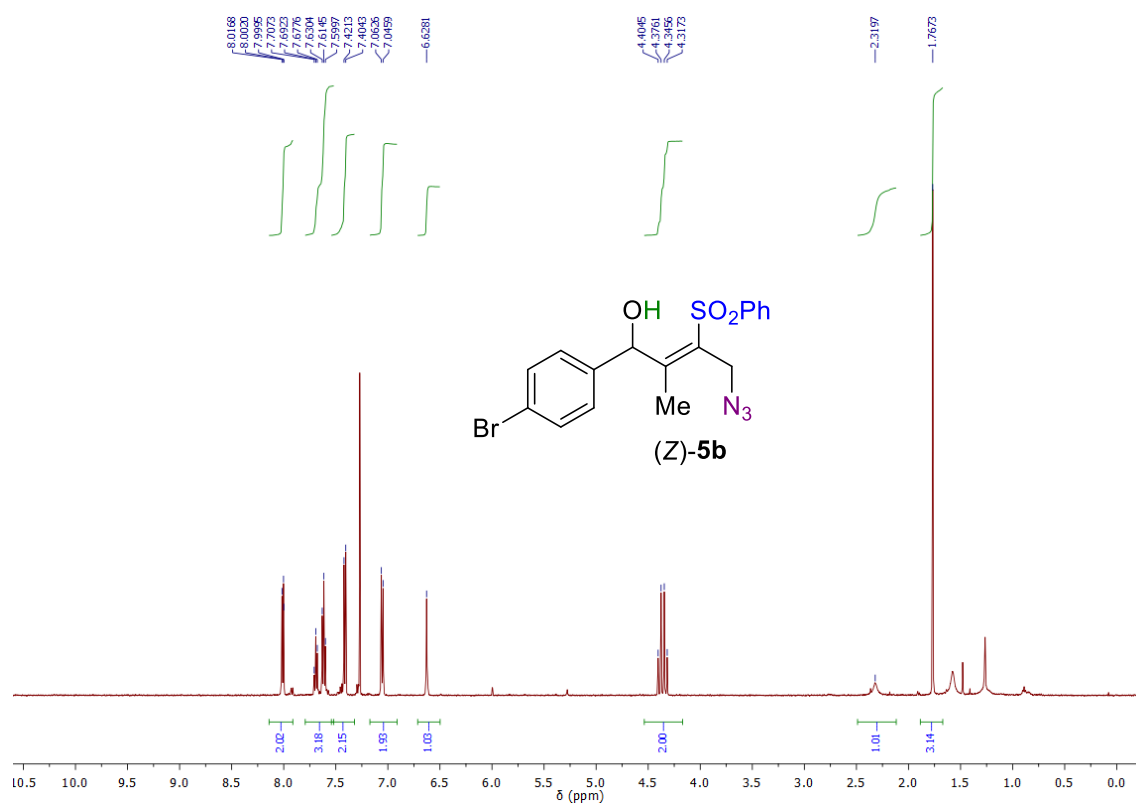
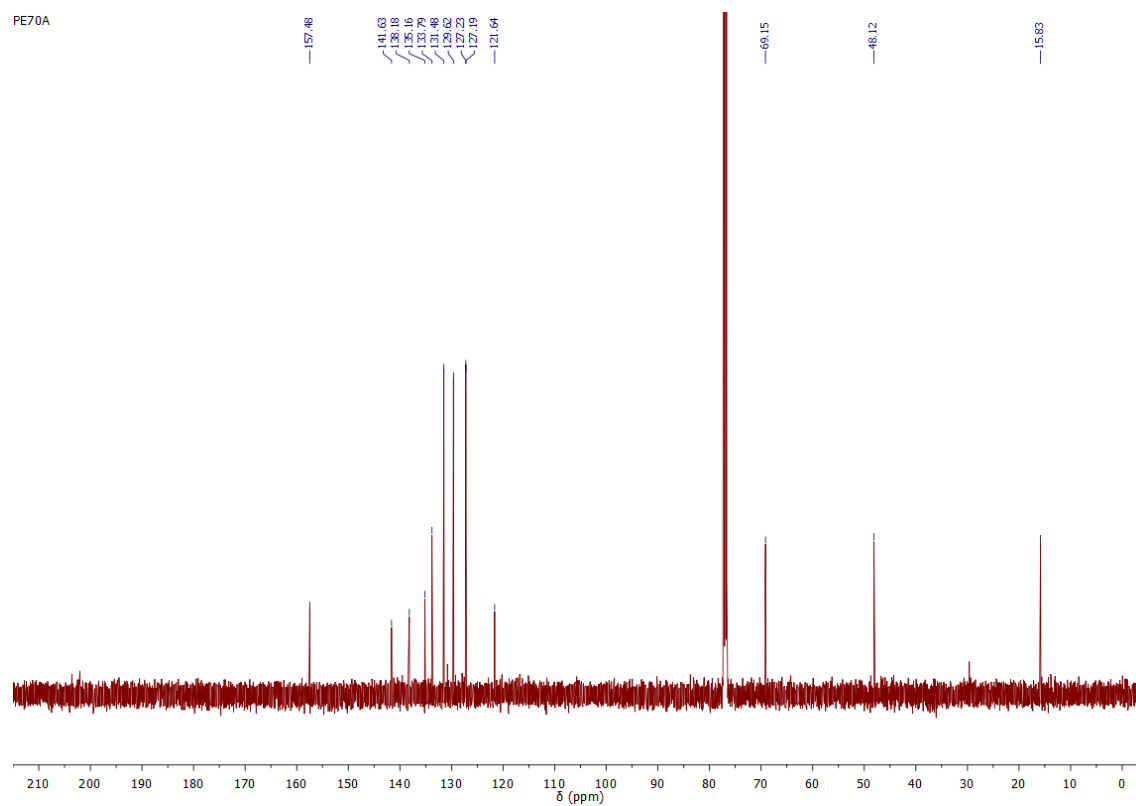


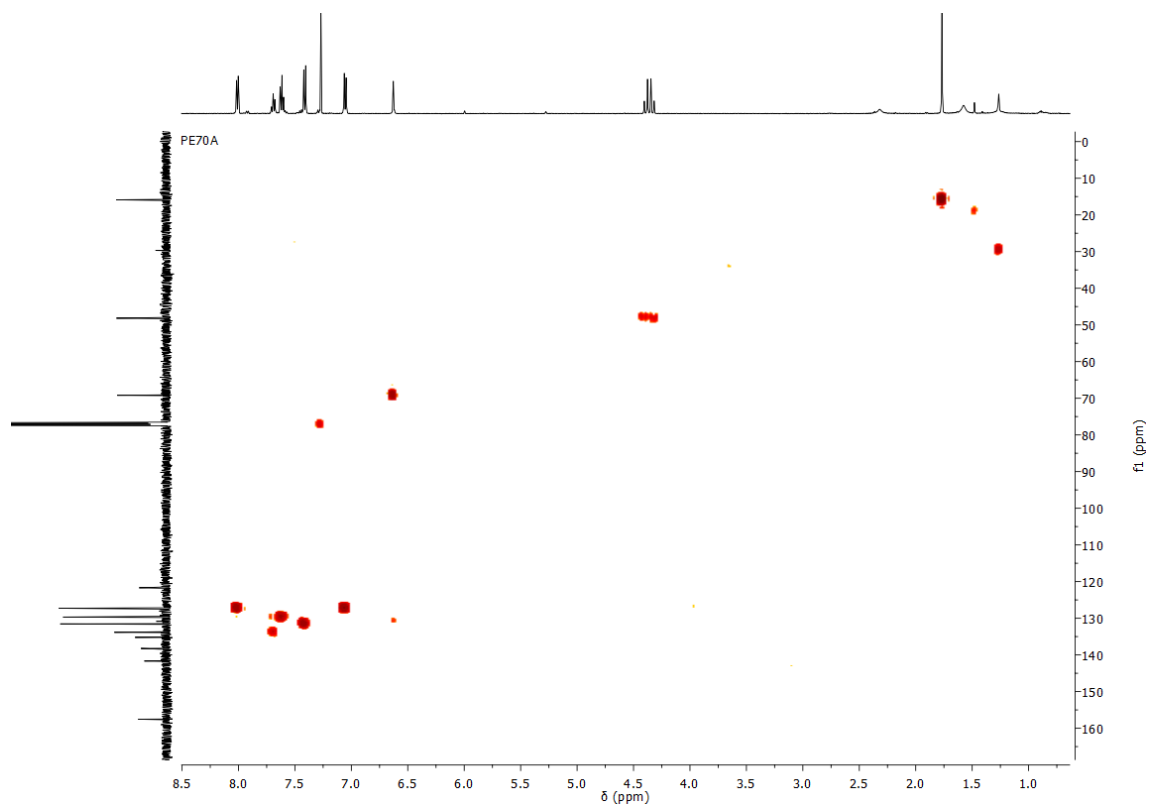
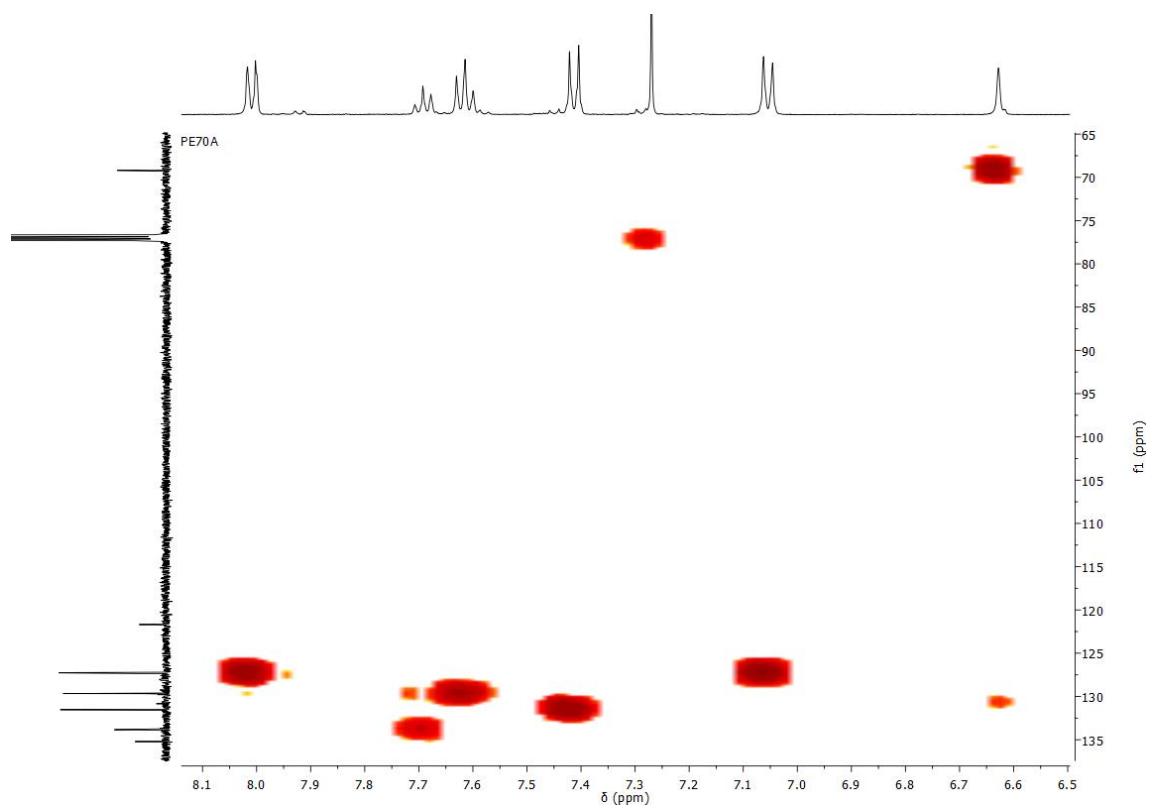
One-dimensional NOE NMR spectrum of (*E*)-**5b** in CDCl<sub>3</sub> at 500 MHz, showing selected NOE correlations highlighted in the structure



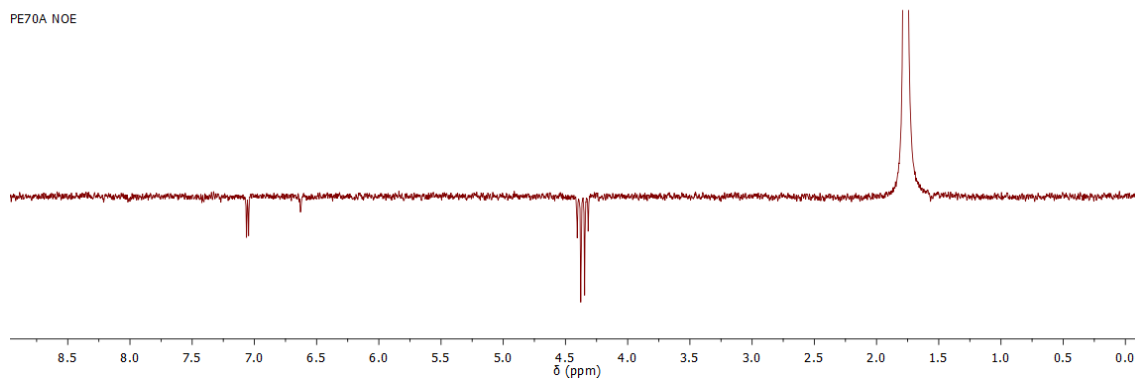
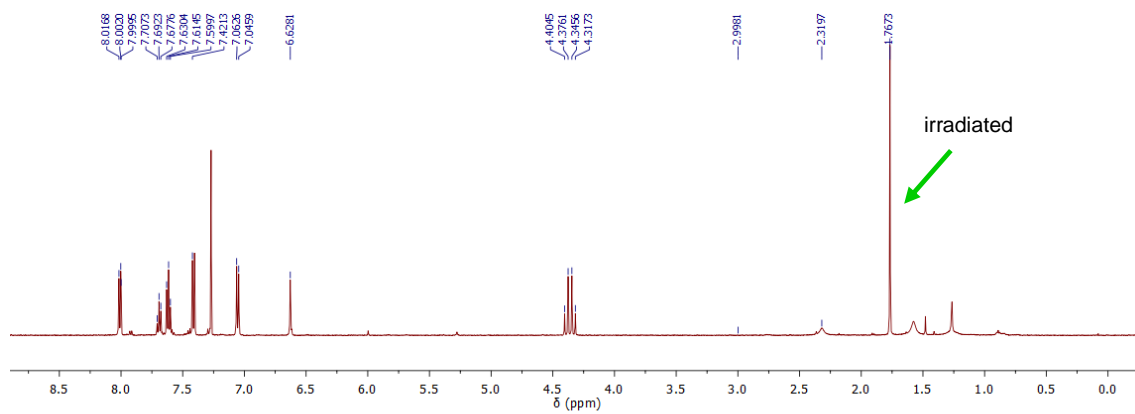
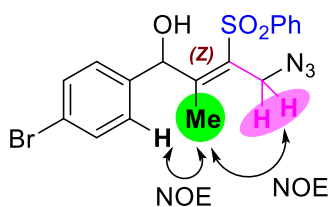
One-dimensional NOE NMR spectrum of (*E*)-**5b** in CDCl<sub>3</sub> at 500 MHz, showing selected NOE correlations highlighted in the structure

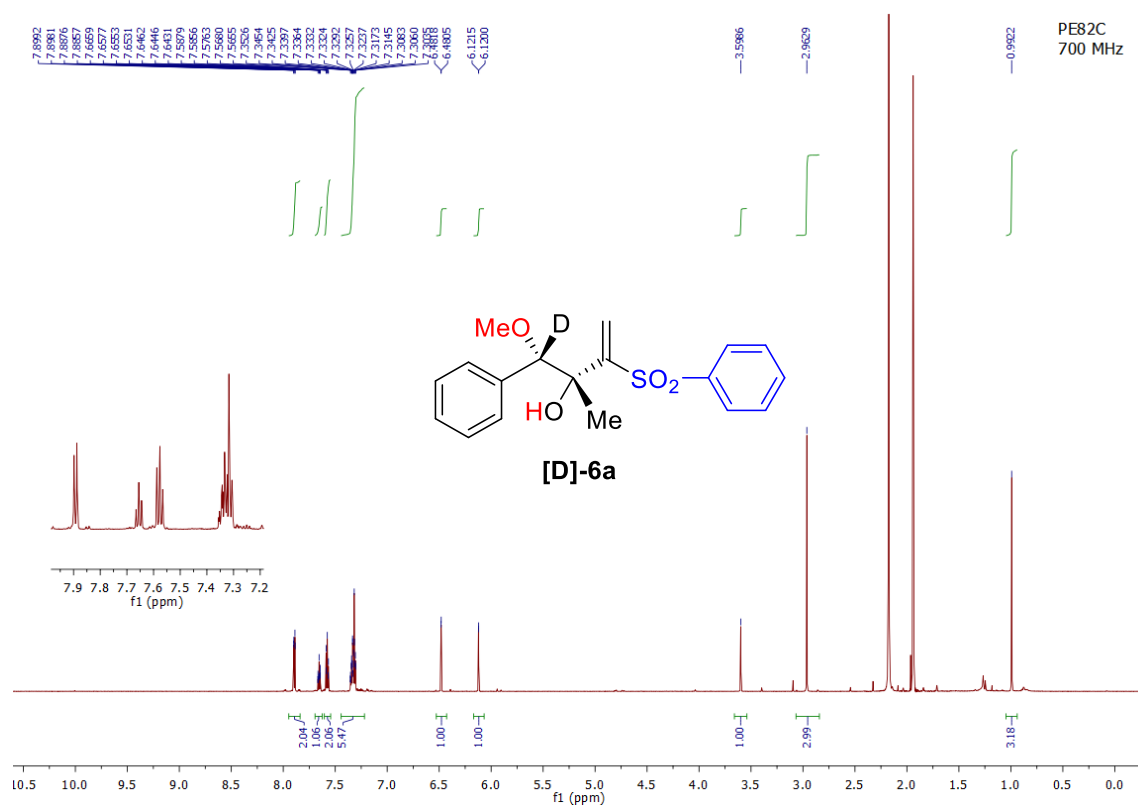
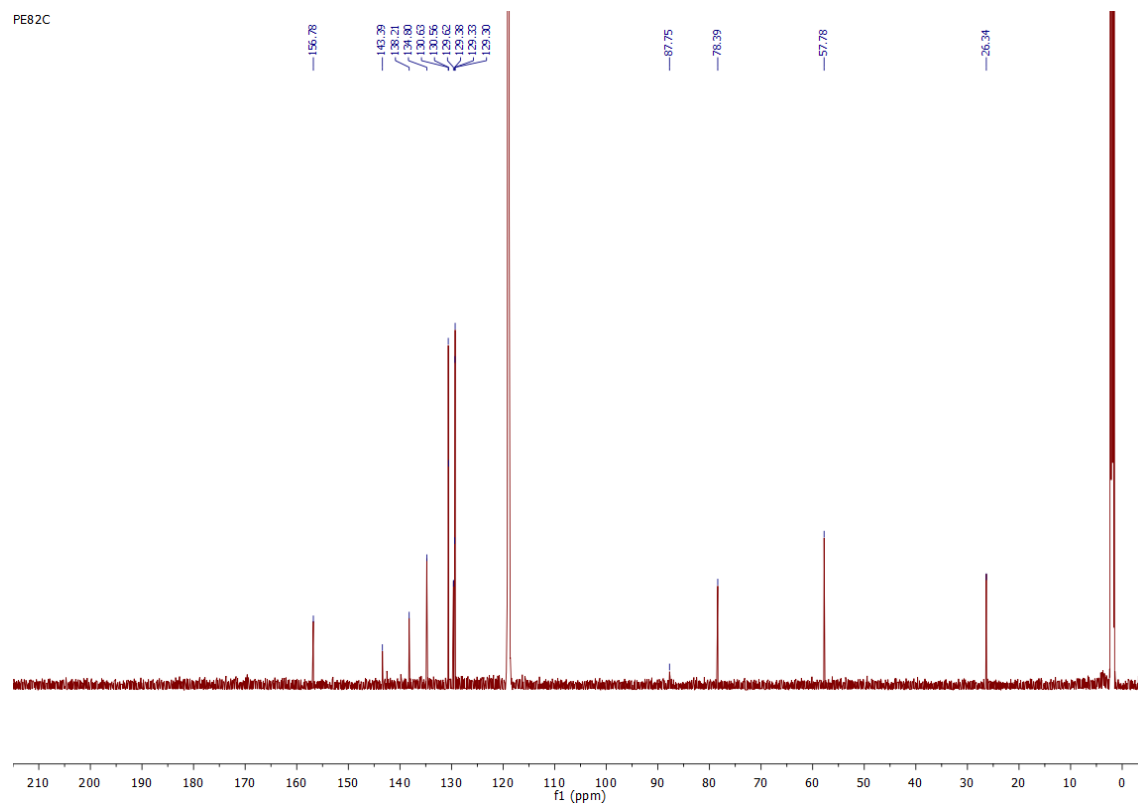


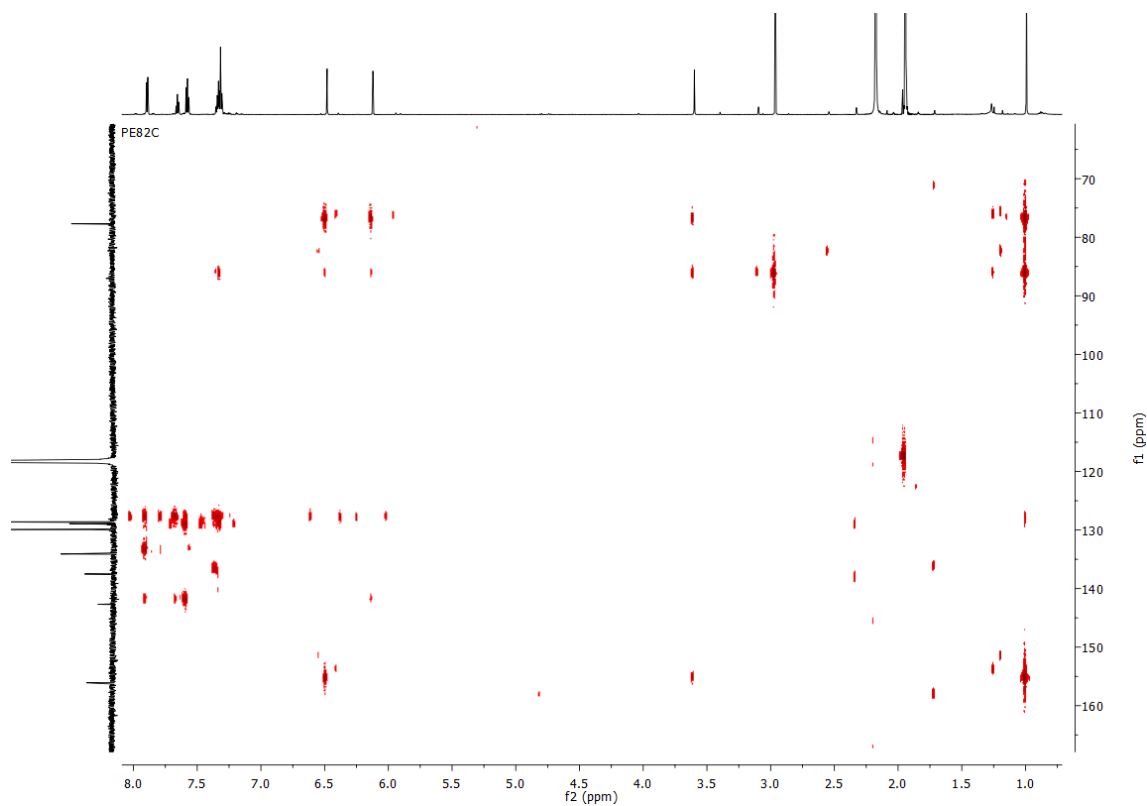
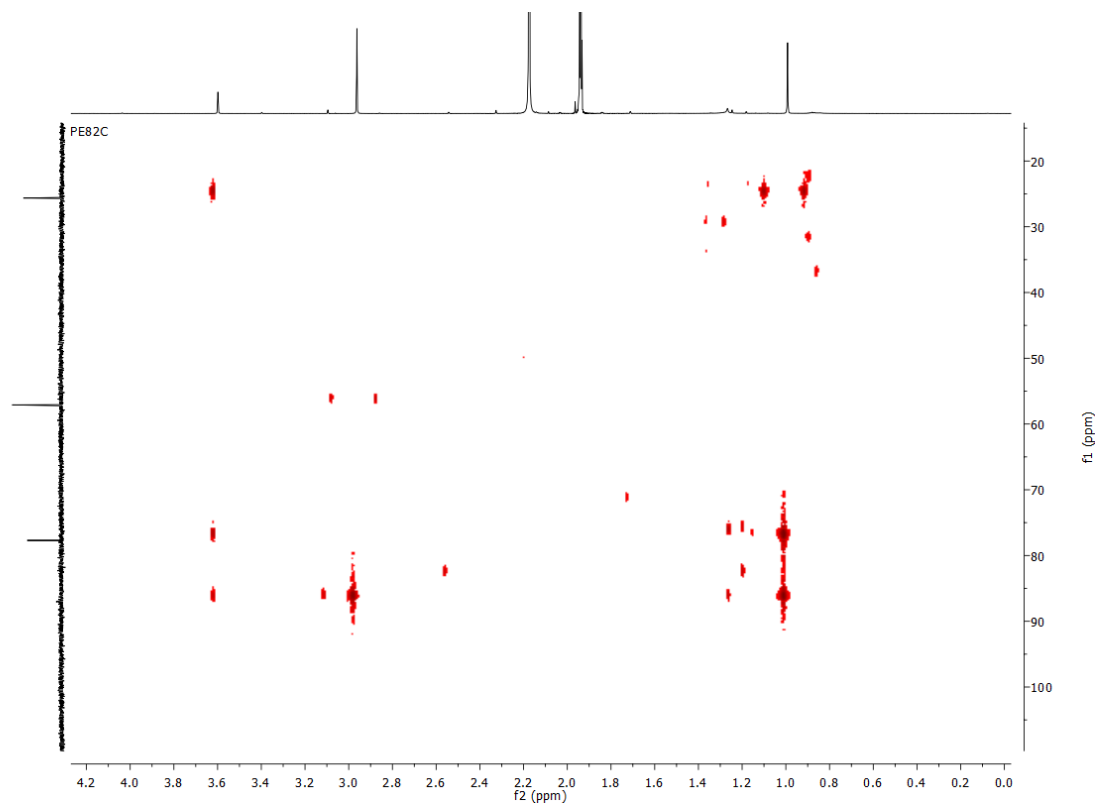
$^1\text{H}$  NMR spectrum of (Z)-**5b** in  $\text{CDCl}_3$  at 500 MHz $^{13}\text{C}$  NMR spectrum of (Z)-**5b** in  $\text{CDCl}_3$  at 125 MHz

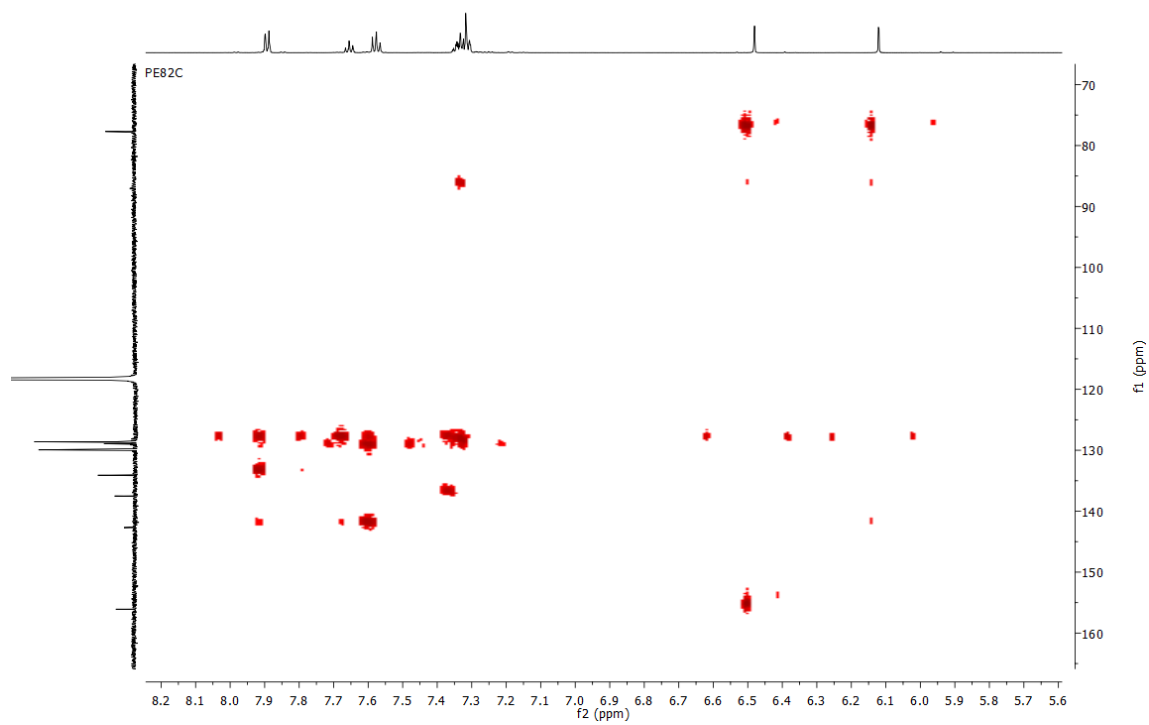
Two-dimensional HMQC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of (Z)-**5b** in  $\text{CDCl}_3$ Expansion of HMQC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of (Z)-**5b**

One-dimensional NOE NMR spectrum of (Z)-**5b** in CDCl<sub>3</sub> at 500 MHz, showing selected NOE correlations highlighted in the structure

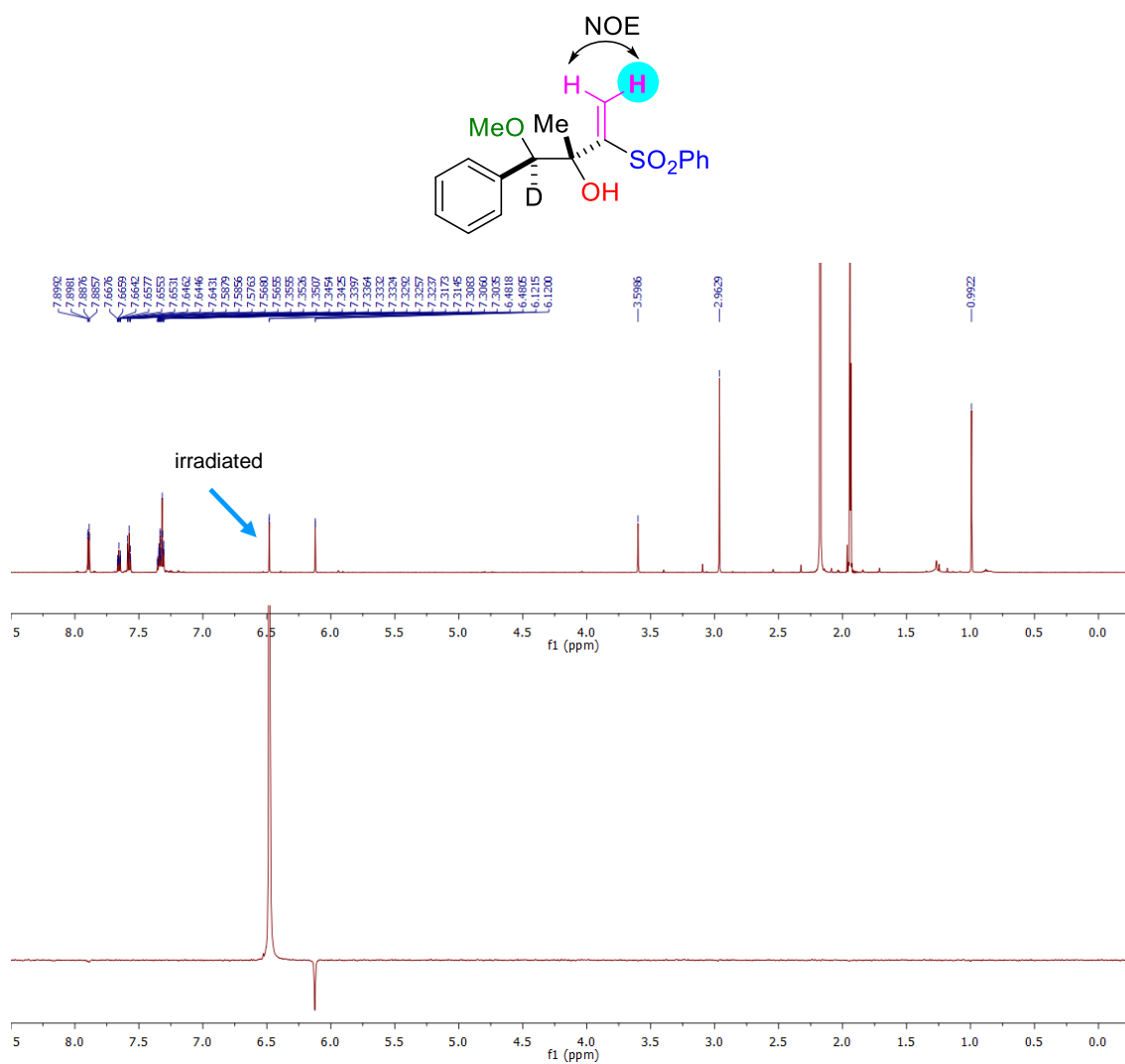


$^1\text{H}$  NMR spectrum of [D]-6a in  $\text{CD}_3\text{CN}$  at 700 MHz $^{13}\text{C}$  NMR spectrum of [D]-6a in  $\text{CD}_3\text{CN}$  at 175 MHz

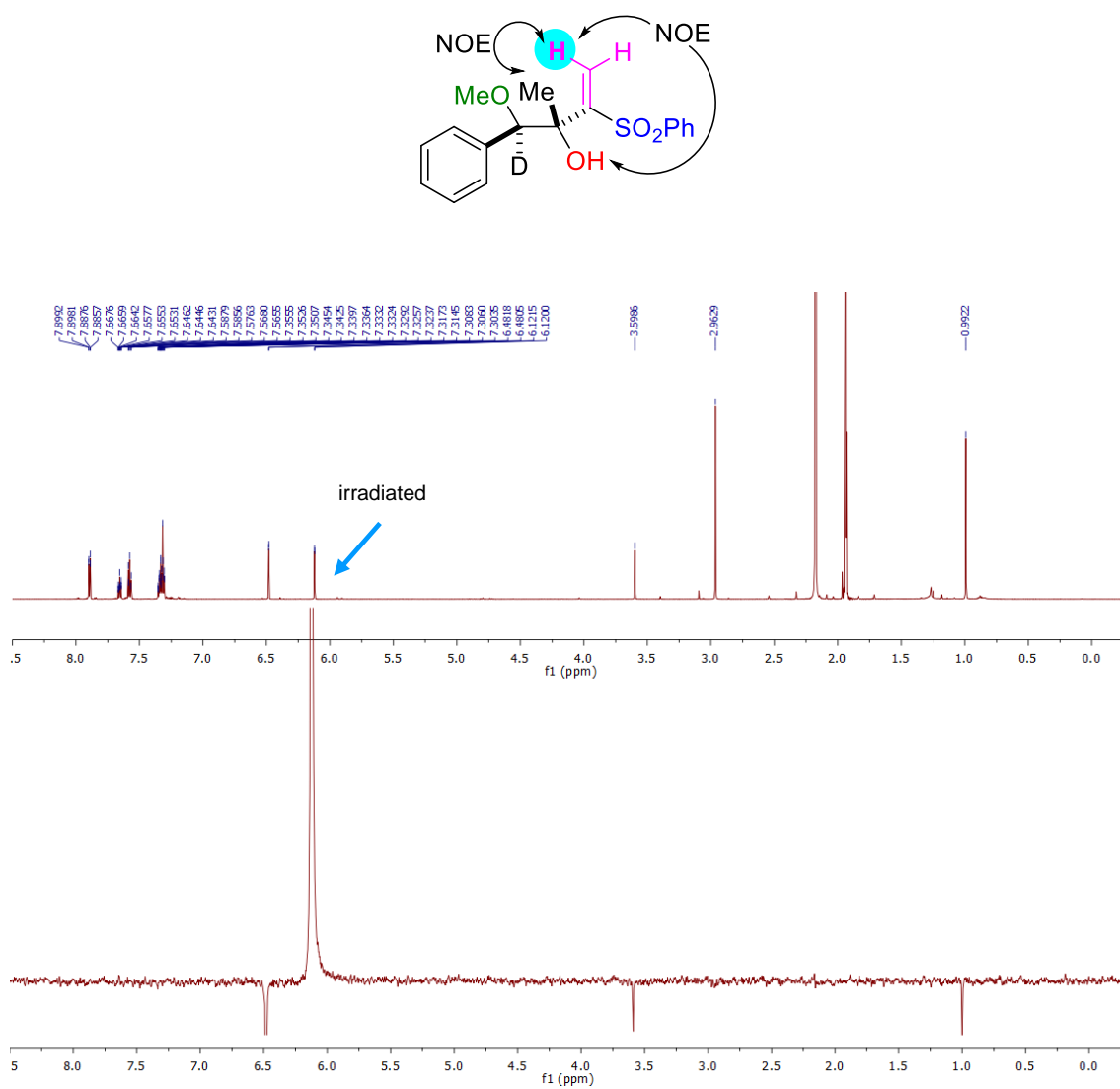
Two-dimensional HMBC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of [D]-**6a** in  $\text{CD}_3\text{CN}$ Expansion of HMBC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of [D]-**6a**

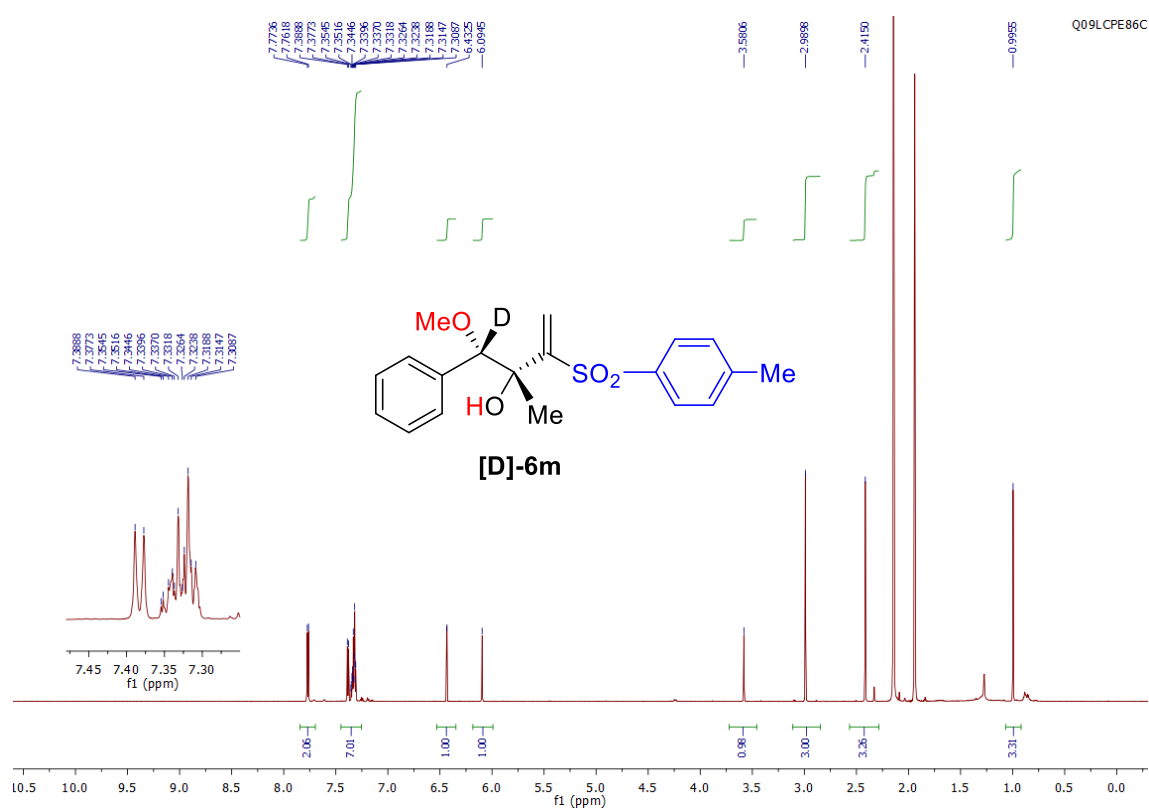
Expansion of HMBC NMR spectrum  $^1\text{H}$ - $^{13}\text{C}$  of **[D]-6a**

One-dimensional NOE NMR spectrum of **[D]-6a** in  $\text{CDCl}_3$  at 700 MHz, showing selected NOE correlations highlighted in the structure



One-dimensional NOE NMR spectrum of **[D]-6a** in CDCl<sub>3</sub> at 700 MHz, showing selected NOE correlations highlighted in the structure



$^1\text{H}$  NMR spectrum of **[D]-6m** in  $\text{CD}_3\text{CN}$  at 300 MHz $^{13}\text{C}$  NMR spectrum of **[D]-6m** in  $\text{CD}_3\text{CN}$  at 75 MHz