Supporting information

Synthesis of Acyloxy-2*H*-Azirine and Sulfonyloxy-2*H*-Azirine Derivatives via the One-Pot Reaction of *β*-Enamino Esters, PIDA and Carboxylic Acid or Sulfonic Acid

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General information

All starting materials were of the highest commercially available grade and used without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography (FC) was performed using the silica gel of particle size 200-300 mesh. ^{1}H NMR spectra were recorded on 600 MHz in $CDCl_3$ or DMSO-d_6 and ^{13}C NMR spectra were recorded on 151 MHz in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ = 7.26 ppm or DMSO-d_6, δ = 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.16 ppm or DMSO-d_6, δ = 39.52 ppm). ESI HRMS spectra were recorded on Bio TOF Q.

General Procedure for the PIDA Mediated Reaction of Unsubstituted β-Enamino Esters to Acetoxy 2*H*-Azirines 2

β-enamino esters **1** (0.2 mmol) and PIDA (0.4 mmol, 128.8 mg) were added in 2 mL CH_2Cl_2. The reaction mixture was stirred at room temperature for 12 h. Then the resulting mixture was directly purified by column chromatography (silica gel, hexane/EtOAc = 7/1) to afforded the desired compounds **2**.

General Procedure for the PIDA Mediated Reaction of Unsubstituted β-Enamino Esters with Sulfonic Acids to Sulfonyloxy-2*H*-Azirines 3

To the powder mixture of 4Å MS (50 mg), PIDA (0.4 mmol, 128.8 mg), sulfonic acids (0.2 mmol) and β-enamino esters **1** (0.2 mmol), 2 mL CH_2Cl_2 was added at room temperature. The reaction was stirred at room temperature for 12 h. Then the resulting mixture was directly purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 5/1) to afforded the desired compounds **3**.

General Procedure for the PIDA Mediated Reaction of Unsubstituted β-Enamino Esters with Other Carboxylic Acid to Acyloxy 2*H*-Azirines 4

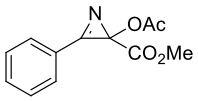
(A) To the powder mixture of 4Å MS (50 mg), PIDA (0.4 mmol, 128.8 mg), other carboxylic acid (0.2 mmol) and β-enamino esters **1** (0.2 mmol), 2 mL CH_2Cl_2 was added at room temperature. The reaction was stirred at room temperature for 12 h. Then the resulting mixture was directly purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 5/1) to afforded the desired compounds **4**.

(B) To the powder mixture of 4Å MS (50 mg), PIDA (0.4 mmol, 128.8 mg), other carboxylic acid (0.4 mmol) and β-enamino esters **1** (0.2 mmol), 2 mL CH_2Cl_2 was added at room temperature. The reaction was stirred at room temperature for 12 h. Then the reaction was filtered through celite, washed with aqueous potassium carbonate solution and brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting mixture was purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to afforded the desired compounds **4**.

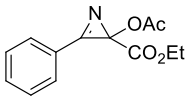
The Procedure for the PIDA and TsOH Mediated Oxidative Sulfonyloxylation of Unsubstituted β-Enamino Ester 1a to compound 5

To the powder mixture of PIDA (0.24 mmol, 77.3 mg), TsOH (0.2 mmol, 34.4 mg) and β-enamino esters **1a** (0.2 mmol, 35.4 mg), 2 mL CH_2Cl_2 was added at room temperature. The reaction was stirred at room temperature for 12 h. Then the resulting mixture was directly purified by column chromatography (silica gel, hexane/EtOAc = 5/1) to afforded the desired compounds **5** with 65% yield.

Experiment Data for the Acetoxy 2*H*-Azirines 2

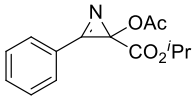


Methyl 2-acetoxy-3-phenyl-2*H*-azirine-2-carboxylate (2a): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11-8.09 (m, 2H), 7.67-7.70 (m, 1H), 7.58-7.61 (m, 2H), 3.77 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (151 MHz, CDCl3) δ 170.50, 168.05, 165.38, 134.83, 131.33, 129.51, 120.88, 63.34, 53.39, 20.69; ESI HRMS exact mass calcd. for $(C_{12}H_{11}NO_4+Na)^+$ requires *m/z* 256.0580, found *m/z* 256.0583.

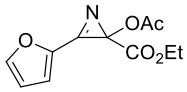


Ethyl 2-acetoxy-3-phenyl-2*H*-azirine-2-carboxylate (2b): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.07 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J*

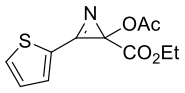
= 7.7 Hz, 1H), 4.24 (qd, *J* = 7.1, 0.9 Hz, 1H), 2.15 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.48, 167.55, 165.46, 134.75, 131.29, 129.48, 120.95, 63.45, 62.61, 20.67, 14.17; ESI HRMS exact mass calcd. for $(C_{13}H_{13}NO_4+Na)^+$ requires *m/z* 270.0737, found *m/z* 270.0740.



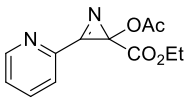
Isopropyl 2-acetoxy-3-phenyl-2*H*-azirine-2-carboxylate (2c): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 1H), 5.08 (dt, *J* = 12.5, 6.2 Hz, 1H), 2.14 (s, 2H), 1.24 (d, *J* = 6.2 Hz, 2H), 1.22 (d, *J* = 6.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.48, 167.07, 165.63, 134.69, 131.25, 129.47, 121.03, 70.57, 63.63, 21.74, 21.73, 20.66; ESI HRMS exact mass calcd. for $(C_{14}H_{15}NO_4+Na)^+$ requires *m/z* 284.0893, found *m/z* 284.0896.



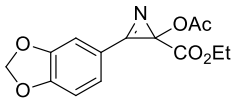
Ethyl 2-acetoxy-3-(furan-2-yl)-2*H*-azirine-2-carboxylate (2d): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.5 Hz, 1H), 7.49 (d, *J* = 3.6 Hz, 1H), 6.69 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.23 (qd, *J* = 7.1, 2.8 Hz, 2H), 2.14 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.44, 167.03, 155.03, 150.65, 138.05, 124.70, 113.27, 62.78, 62.21, 20.63, 14.16; ESI HRMS exact mass calcd. for $(C_{11}H_{11}NO_5+Na)^+$ requires *m/z* 260.0529, found *m/z* 260.0535.



Ethyl 2-acetoxy-3-(thiophen-2-yl)-2*H*-azirine-2-carboxylate (2e): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 3.7, 0.9 Hz, 1H), 7.94 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.28 (dd, *J* = 4.8, 4.0 Hz, 1H), 4.24 (tt, *J* = 7.6, 3.9 Hz, 2H), 2.15 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.56, 167.28, 158.91, 137.80, 137.15, 128.93, 122.60, 63.41, 62.69, 20.63, 14.17; ESI HRMS exact mass calcd. for $(C_{11}H_{11}NO_4S+Na)^+$ requires *m/z* 276.0301, found *m/z* 276.0306.

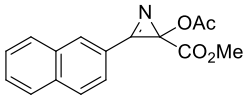


Ethyl 2-acetoxy-3-(pyridin-2-yl)-2*H*-azirine-2-carboxylate (2f): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.96-8.90 (m, 1H), 8.17 (d, *J* = 7.7 Hz, 1H), 7.95 (td, *J* = 7.7, 1.7 Hz, 1H), 7.56 (ddd, *J* = 7.7, 4.7, 1.1 Hz, 1H), 4.24 (qd, *J* = 7.1, 1.2 Hz, 2H), 2.16 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.34, 166.96, 166.32, 151.72, 142.02, 137.47, 128.51, 127.83, 63.97, 62.78, 20.71, 14.16; ESI HRMS exact mass calcd. for $(C_{12}H_{12}N_2O_4+Na)^+$ requires *m/z* 271.0689, found *m/z* 271.0692.

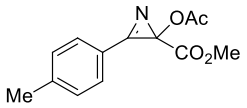


Ethyl 2-acetoxy-3-(benzo[d][1,3]dioxol-5-yl)-2*H*-azirine-2-carboxylate (2g): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.51 (d, *J* = 1.5 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.10 (dd, *J* = 2.7, 1.2 Hz, 2H),

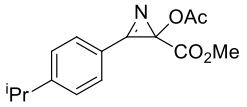
4.27-4.19 (m, 2H), 2.14 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.61, 167.66, 164.30, 153.33, 148.72, 128.36, 114.55, 110.04, 109.34, 102.42, 63.80, 62.55, 20.67, 14.18; ESI HRMS exact mass calcd. for $(C_{14}H_{13}NO_6+Na)^+$ requires *m/z* 314.0635, found *m/z* 314.0635.



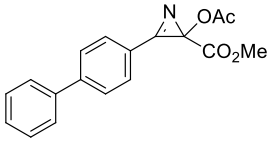
Methyl 2-acetoxy-3-(naphthalen-2-yl)-2*H*-azirine-2-carboxylate (2h): white solid, mp 121.6-122.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.10 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 3.79 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.63, 168.14, 165.42, 136.31, 134.39, 132.79, 129.79, 129.66, 129.58, 128.23, 127.54, 125.10, 118.01, 63.53, 53.42, 20.73; ESI HRMS exact mass calcd. for $(C_{16}H_{13}NO_4+Na)^+$ requires *m/z* 306.0737, found *m/z* 306.0741.



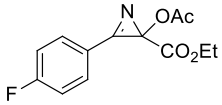
Methyl 2-acetoxy-3-(p-tolyl)-2*H*-azirine-2-carboxylate (2i): white solid, mp 50-51 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 3.69 (s, 3H), 2.44 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 170.19, 167.60, 164.09, 146.43, 130.86, 130.55, 117.08, 62.55, 53.33, 21.59, 20.27; ESI HRMS exact mass calcd. for $(C_{13}H_{13}NO_4+Na)^+$ requires *m/z* 270.0737, found *m/z* 270.0739.



Methyl 2-acetoxy-3-(4-isopropylphenyl)-2*H*-azirine-2-carboxylate (2j): colorless viscous oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 3.70 (s, 3H), 3.01 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.11 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 170.09, 167.56, 164.12, 156.72, 131.03, 127.96, 117.47, 62.52, 53.24, 33.87, 23.33, 23.31, 20.19; ESI HRMS exact mass calcd. for $(C_{15}H_{17}NO_4+Na)^+$ requires *m/z* 298.1050, found *m/z* 298.1056.

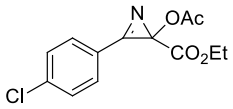


Methyl 3-([1,1'-biphenyl]-4-yl)-2-acetoxy-2*H*-azirine-2-carboxylate (2k): white solid, mp 96-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 7.82-7.80 (m, 2H), 7.65-7.63 (m, 2H), 7.50 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.46-7.42 (m, 1H), 3.78 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.58, 168.11, 164.93, 147.68, 139.58, 131.83, 129.23, 128.84, 128.15, 127.48, 119.42, 63.29, 53.42, 20.72; ESI HRMS exact mass calcd. for $(C_{18}H_{15}NO_4+H)^+$ requires *m/z* 310.1074, found *m/z* 310.1075.

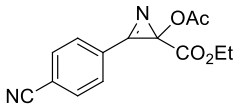


Ethyl 2-acetoxy-3-(4-fluorophenyl)-2*H*-azirine-2-carboxylate (2l): yellow viscous oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.20-8.13 (m, 2H), 7.59 (d, J = 8.8 Hz, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.12 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz,

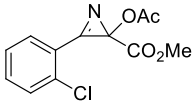
DMSO-d_6) δ 170.24, 166.85, 166.10 (d, J = 249.2 Hz), 163.94, 133.92 (d, J = 10.6 Hz), 117.53 (d, J = 22.7 Hz), 116.69 (d, J = 3.0 Hz), 62.65, 62.34, 20.25, 13.91; ESI HRMS exact mass calcd. for $(C_{13}H_{12}FNO_4+H)^+$ requires *m/z* 266.0823, found *m/z* 266.0824.



Ethyl 2-acetoxy-3-(4-chlorophenyl)-2*H*-azirine-2-carboxylate (2m): white solid, mp 75-76 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07-8.03 (m, 2H), 7.59-7.56 (m, 2H), 4.23 (qd, J = 7.1, 1.0 Hz, 2H), 2.15 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.58, 167.33, 164.98, 141.46, 132.50, 130.02, 119.43, 63.30, 62.76, 20.68, 14.18; ESI HRMS exact mass calcd. for $(C_{13}H_{12}ClNO_4+H)^+$ requires *m/z* 282.0528, found *m/z* 282.0532.

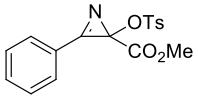


Ethyl 2-acetoxy-3-(4-cyanophenyl)-2*H*-azirine-2-carboxylate (2n): white solid, mp 135-136 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24-8.21 (m, 2H), 7.90 -7.87 (m, 2H), 4.24 (qd, J = 7.1, 2.1 Hz, 2H), 2.16 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.49, 168.83, 165.76, 133.10, 131.54, 124.98, 117.93, 117.63, 63.20, 62.98, 20.63, 14.15; ESI HRMS exact mass calcd. for $(C_{14}H_{12}N_2O_4+H)^+$ requires *m/z* 273.0870, found *m/z* 273.0875.

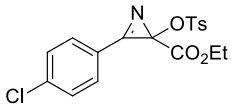


Methyl 2-acetoxy-3-(2-chlorophenyl)-2*H*-azirine-2-carboxylate (2o): white solid, mp 106-107 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.10-8.07 (m, 1H), 7.85-7.82 (m, 2H), 7.70-7.67 (m, 1H), 3.72 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 170.01, 167.20, 162.84, 136.76, 135.68, 134.16, 131.16, 128.54, 118.72, 61.39, 53.44, 20.32; ESI HRMS exact mass calcd. for $(C_{12}H_{10}ClNO_4+Na)^+$ requires *m/z* 290.0191, found *m/z* 290.0190.

Experiment Data for the Sulfonyloxy-2*H*-Azirines 3

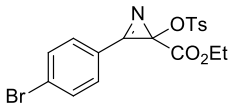


Methyl 3-phenyl-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3a): white solid, mp 127.6-128.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06-8.00 (m, 2H), 7.77 (d, J = 8.3 Hz, 2H), 7.70 (t, J = 7.5 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 3.80 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.44, 163.81, 145.32, 135.12, 134.00, 131.31, 129.71, 129.52, 128.21, 120.49, 66.74, 53.72, 21.78; ESI HRMS exact mass calcd. for $(C_{17}H_{15}NO_5S+H)^+$ requires *m/z* 346.0744, found *m/z* 346.0750.

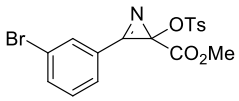


Ethyl 3-(4-chlorophenyl)-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3b): white solid, mp 119.3-120.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H),

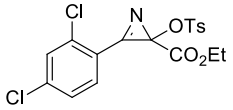
4.26 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.71, 163.41, 145.47, 141.78, 133.86, 132.45, 130.06, 129.77, 128.18, 119.10, 66.59, 63.20, 21.80, 14.14; ESI HRMS exact mass calcd. for $(C_{18}H_{16}ClNO_5S+Na)^+$ requires *m/z* 416.0330, found *m/z* 416.0336.



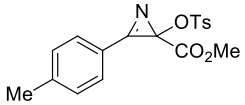
Ethyl 3-(4-bromophenyl)-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3c): white solid, mp 112.5-113.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.0 Hz, 2H), 7.78 (d, *J* = 6.0 Hz, 2H), 7.76 (d, *J* = 12.0 Hz, 2H), 7.28 (d, *J* = 12.0 Hz, 2H), 4.27 (q, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.27 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.68, 163.59, 145.48, 133.78, 133.02, 132.44, 130.53, 129.76, 128.16, 119.47, 66.51, 63.20, 21.80, 14.13; ESI HRMS exact mass calcd. for $(C_{18}H_{16}BrNO_5S+H)^+$ requires *m/z* 438.0005, found *m/z* 438.0009.



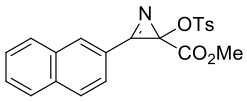
Methyl 3-(3-bromophenyl)-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3d): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (t, *J* = 1.6 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.81 (ddd, *J* = 8.0, 1.7, 0.9 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.02, 163.51, 145.55, 137.91, 133.73, 133.63, 131.01, 129.77, 129.73, 128.22, 123.42, 122.47, 66.47, 53.82, 21.80; ESI HRMS exact mass calcd. for $(C_{18}H_{16}BrNO_5S+H)^+$ requires *m/z* 438.0005, found *m/z* 438.0009.



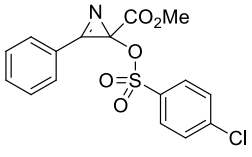
Ethyl 3-(2,4-dichlorophenyl)-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3e): white solid, mp 63.5-64.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.82-7.77 (m, 2H), 7.60 (d, *J* = 1.9 Hz, 1H), 7.49 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.28 (qd, *J* = 7.1, 1.0 Hz, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.50, 162.14, 145.46, 141.99, 138.16, 134.52, 134.00, 131.06, 129.77, 128.24, 128.22, 118.42, 65.67, 63.25, 21.82, 14.19; ESI HRMS exact mass calcd. for $(C_{18}H_{15}Cl_2NO_5S+H)^+$ requires *m/z* 428.0121, found *m/z* 428.0125.



Methyl 3-(p-tolyl)-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3f): white solid, mp 101.1-102.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 2.48 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.61, 163.20, 146.55, 145.26, 134.10, 131.39, 130.30, 129.70, 128.21, 117.62, 66.80, 53.67, 21.25, 21.80; ESI HRMS exact mass calcd. for $(C_{18}H_{17}NO_5S+Na)^+$ requires *m/z* 382.0720, found *m/z* 382.0725.

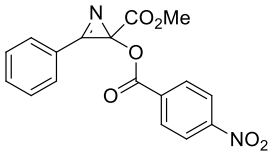


Methyl 3-(naphthalen-2-yl)-2-(tosyloxy)-2*H*-azirine-2-carboxylate (3g): white solid, mp 144.0-145.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.01 (t, J = 3.4 Hz, 3H), 7.93 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.72-7.66 (m, 1H), 7.66-7.60 (m, 1H), 7.20 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.55, 163.75, 145.31, 136.35, 134.34, 134.00, 132.62, 129.89, 129.75, 129.69, 129.60, 128.24, 128.19, 127.67, 125.03, 117.56, 66.93, 53.77, 21.73; ESI HRMS exact mass calcd. for $(C_{21}H_{17}NO_5S+H)^+$ requires *m/z* 396.0900, found *m/z* 396.0906.

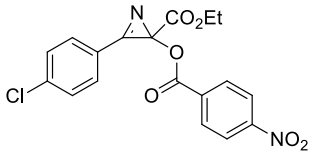


Methyl 2-(((4-chlorophenyl)sulfonyl)oxy)-3-phenyl-2*H*-azirine-2-carboxylate (3h): white solid, mp 96.5-97.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05-7.99 (m, 2H), 7.88-7.82 (m, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.61 (t, J = 7.8 Hz, 2H), 7.47-7.41 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.21, 163.69, 140.96, 135.53, 135.35, 131.33, 129.66, 129.65, 129.47, 120.24, 67.20, 53.80; ESI HRMS exact mass calcd. for $(C_{16}H_{12}ClNO_5S+Na)^+$ requires *m/z* 388.0017, found *m/z* 388.0023.

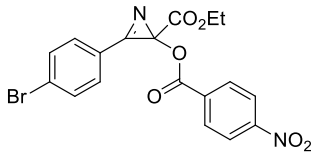
Experiment Data for the Acyloxy 2*H*-Azirines 4



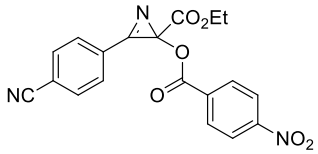
Methyl 2-((4-nitrobenzoyl)oxy)-3-phenyl-2*H*-azirine-2-carboxylate (4a): white solid, mp 120.4-121.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 9.0 Hz, 2H), 8.27 (d, J = 9.0 Hz, 2H), 8.22-8.15 (m, 2H), 7.72 (ddd, J = 8.8, 2.5, 1.2 Hz, 1H), 7.63 (dd, J = 10.7, 4.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.64, 165.16, 164.32, 151.11, 135.16, 134.17, 131.49, 131.44, 129.66, 123.78, 120.57, 64.55, 53.65; ESI HRMS exact mass calcd. for $(C_{17}H_{12}N_2O_6+H)^+$ requires *m/z* 341.0768, found *m/z* 341.0777.



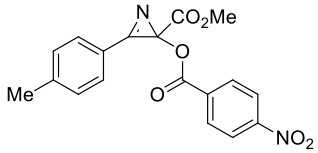
Ethyl 3-(4-chlorophenyl)-2-((4-nitrobenzoyl)oxy)-2*H*-azirine-2-carboxylate (4b): white solid, mp 121.2-122.3 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.36 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.9 Hz, 2H), 8.19 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 166.38, 164.11, 163.94, 150.81, 140.52, 133.24, 132.72, 131.21, 130.27, 124.11, 118.71, 63.87, 62.66, 13.88; ESI HRMS exact mass calcd. for $(C_{18}H_{13}ClN_2O_6+H)^+$ requires *m/z* 389.0535, found *m/z* 389.0544.



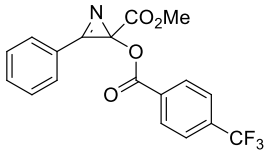
Ethyl 3-(4-bromophenyl)-2-((4-nitrobenzoyl)oxy)-2*H*-azirine-2-carboxylate (4c): white solid, mp 122.1-123.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 8.9 Hz, 2H), 8.26 (d, J = 8.9 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H), 4.26 (qd, J = 7.1, 1.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.87, 164.98, 164.37, 151.15, 134.06, 133.17, 132.64, 131.42, 130.59, 123.82, 119.56, 64.48, 63.05, 14.19; ESI HRMS exact mass calcd. for $(C_{18}H_{13}BrN_2O_6+H)^+$ requires *m/z* 433.0030, found *m/z* 433.0038.



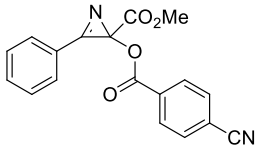
Ethyl 3-(4-cyanophenyl)-2-((4-nitrobenzoyl)oxy)-2*H*-azirine-2-carboxylate (4d): white solid, mp 144.2-145.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37-8.29 (m, 4H), 8.26 (d, J = 9.0 Hz, 2H), 7.93 (d, J = 8.5 Hz, 2H), 4.28 (qd, J = 7.1, 2.8 Hz, 2H), 1.24 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.42, 165.59, 164.32, 151.25, 133.78, 133.23, 131.71, 131.46, 124.72, 123.88, 118.28, 117.55, 64.39, 63.28, 14.18; ESI HRMS exact mass calcd. for $(C_{19}H_{13}N_3O_6+H)^+$ requires *m/z* 380.0877, found *m/z* 380.0881.



Methyl 2-((4-nitrobenzoyl)oxy)-3-(p-tolyl)-2*H*-azirine-2-carboxylate (4e): white solid, mp 131.3-132.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (d, J = 9.0 Hz, 2H), 8.27 (d, J = 9.1 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 7.9 Hz, 2H), 3.80 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.82, 164.52, 164.35, 151.07, 146.56, 134.25, 131.53, 131.43, 130.42, 123.76, 117.67, 64.53, 53.59, 22.26; ESI HRMS exact mass calcd. for $(C_{18}H_{14}N_2O_6+Na)^+$ requires *m/z* 377.0744, found *m/z* 377.0752.

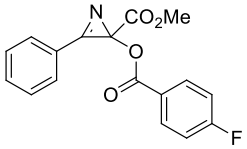


Methyl 3-phenyl-2-((4-(trifluoromethyl)benzoyl)oxy)-2*H*-azirine-2-carboxylate (4f): white solid, mp 62.5-63.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28-8.12 (m, 4H), 7.72 (dd, J = 10.2, 8.1 Hz, 3H), 7.63 (t, J = 7.7 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.82, 165.32, 164.97, 135.30 (q, J = 33.2 Hz), 135.04, 132.03, 131.47, 130.69, 129.62, 125.69 (q, J = 4.5 Hz), 123.62 (q, J = 273.3 Hz), 120.70, 64.31, 53.57; ESI HRMS exact mass calcd. for $(C_{18}H_{12}F_3NO_4+Na)^+$ requires *m/z* 386.0611, found *m/z* 386.0617.

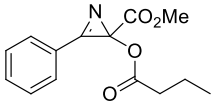


Methyl 2-((4-cyanobenzoyl)oxy)-3-phenyl-2*H*-azirine-2-carboxylate (4g): white solid, mp 90.6-91.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25-8.12 (m,

2H), 7.79-7.74 (m, 2H), 7.74-7.68 (m, 1H), 7.63 (dd, *J* = 10.7, 4.7 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.68, 165.18, 164.56, 135.12, 132.60, 132.44, 131.47, 130.74, 129.64, 120.57, 117.91, 117.28, 64.43, 53.61; ESI HRMS exact mass calcd. for $(C_{18}H_{12}N_2O_4+H)^+$ requires *m/z* 321.0870, found *m/z* 321.0876.

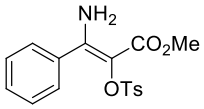


Methyl 2-((4-fluorobenzoyl)oxy)-3-phenyl-2*H*-azirine-2-carboxylate (4h): colorless viscous oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.17 (dd, *J* = 8.1, 1.2 Hz, 2H), 8.14-8.07 (m, 2H), 7.88-7.83 (m, 1H), 7.76 (t, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 8.8 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 167.33, 165.74 (d, *J* = 253.7 Hz), 164.68, 164.31, 135.51, 132.77 (d, *J* = 10.6 Hz), 130.96, 129.97, 124.45, 119.82, 116.30 (d, *J* = 22.7 Hz), 63.41, 53.52; ESI HRMS exact mass calcd. for $(C_{17}H_{12}FNO_4+Na)^+$ requires *m/z* 336.0643, found *m/z* 336.0646.



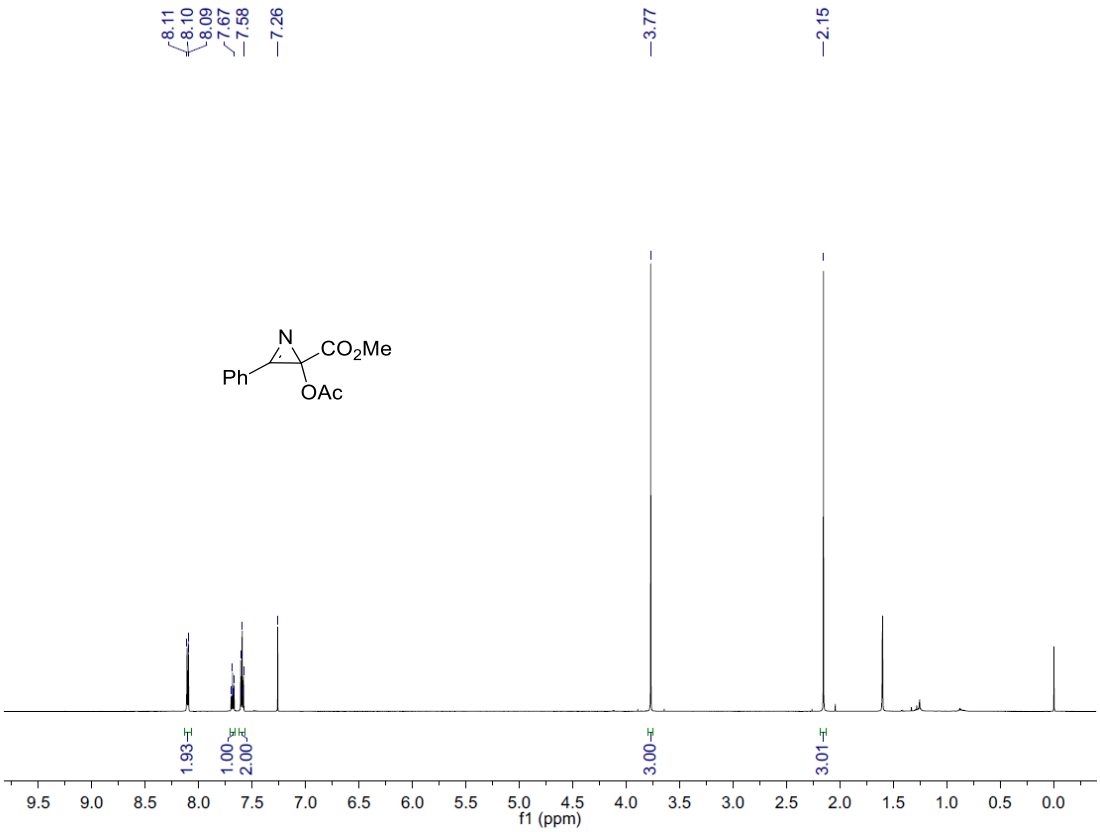
Methyl 2-(butyryloxy)-3-phenyl-2*H*-azirine-2-carboxylate (4i): colorless viscous oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 2H), 7.71-7.65 (m, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 3.76 (d, *J* = 1.0 Hz, 3H), 2.39 (ddd, *J* = 23.4, 15.9, 8.0 Hz, 2H), 1.70 (dd, *J* = 14.8, 7.4 Hz, 2H), 0.97 (dd, *J* = 7.8, 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 173.22, 168.14, 165.52, 134.80, 131.34, 129.52, 120.93, 63.21, 53.37, 35.75, 18.29, 13.61; ESI HRMS exact mass calcd. for $(C_{14}H_{15}NO_4+Na)^+$ requires *m/z* 284.0893, found *m/z* 284.0909.

Experiment Data for the compound 5

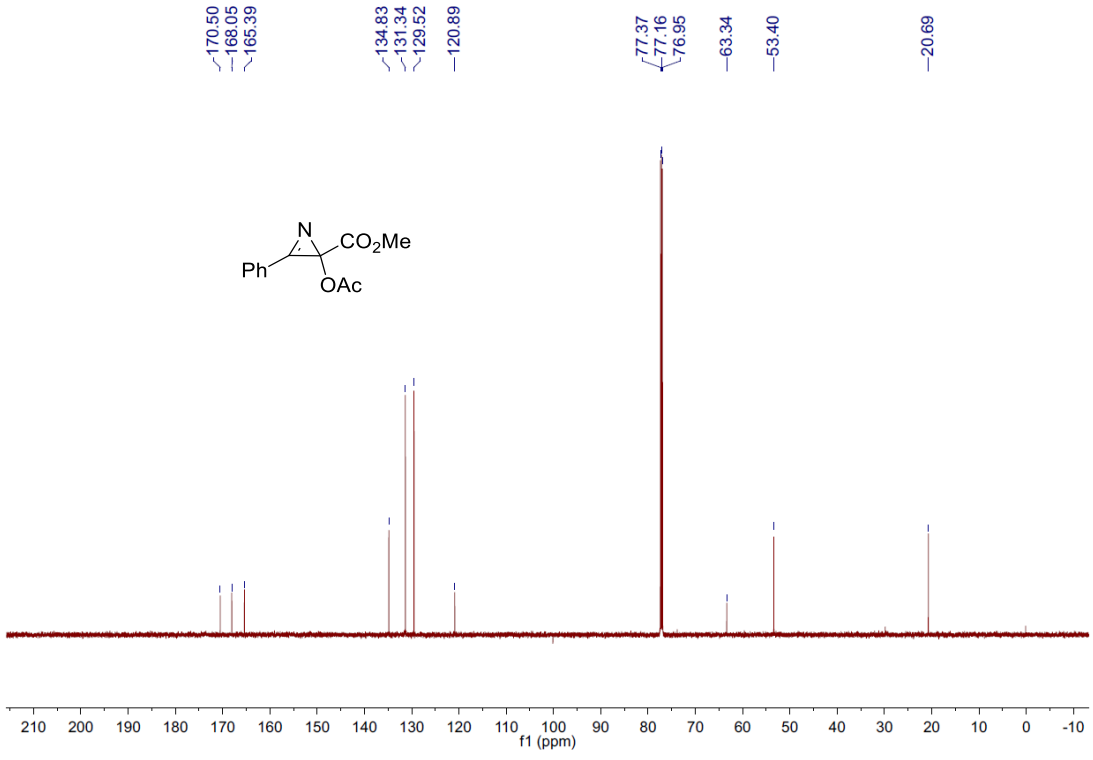


Methyl 3-amino-3-phenyl-2-(tosyloxy)acrylate (5): colorless viscous oil; ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.75 (br s, 1H), 7.38-7.32 (m, 1H), 7.30-7.26 (m, 5H), 7.20-7.14 (m, 4H), 3.48 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.93, 156.75, 144.44, 133.66, 132.59, 129.66, 129.51, 128.45, 127.90, 127.60, 110.48, 50.64, 21.11; ESI HRMS exact mass calcd. for $(C_{17}H_{17}NO_5S+H)^+$ requires *m/z* 348.0900, found *m/z* 348.0907.

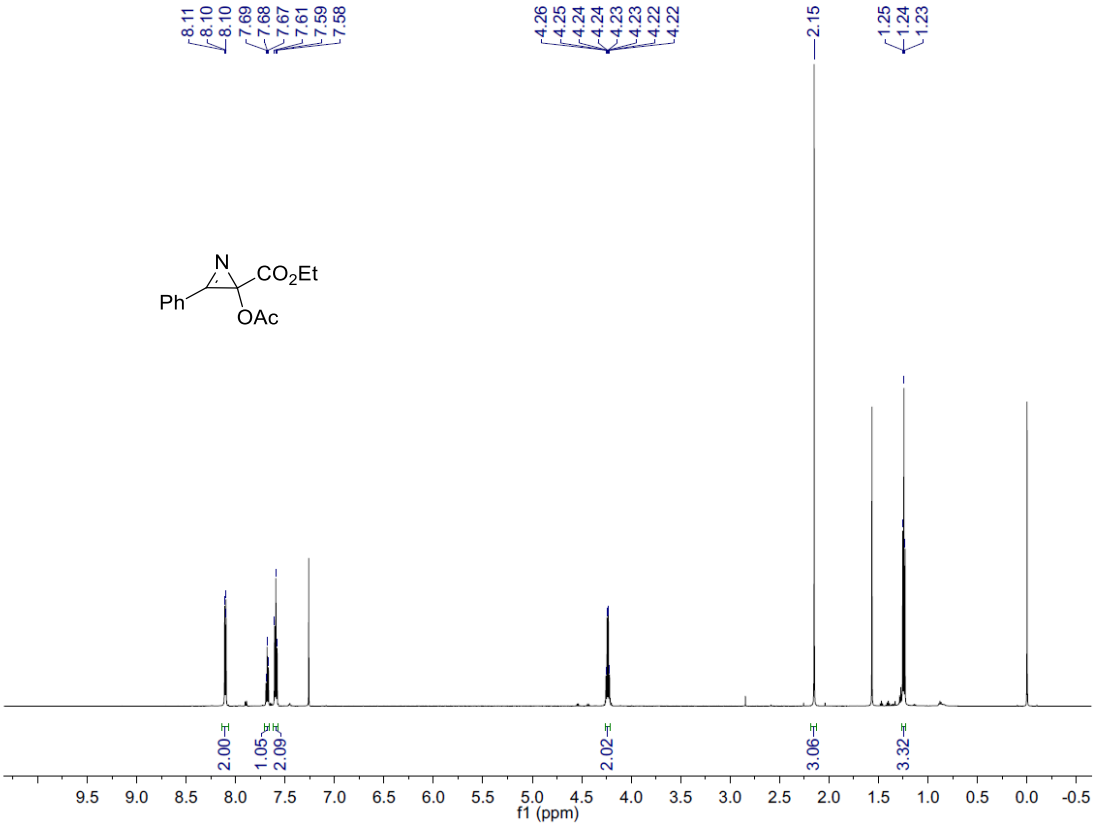
^{1}H and ^{13}C NMR Spectra



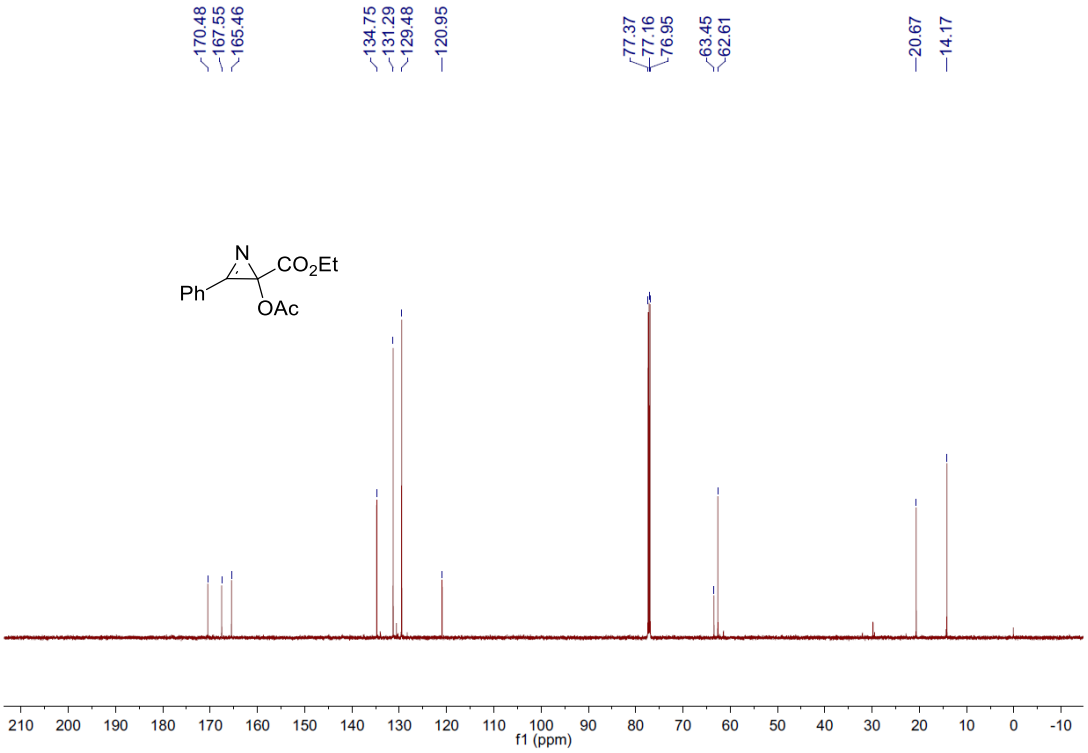
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2a**



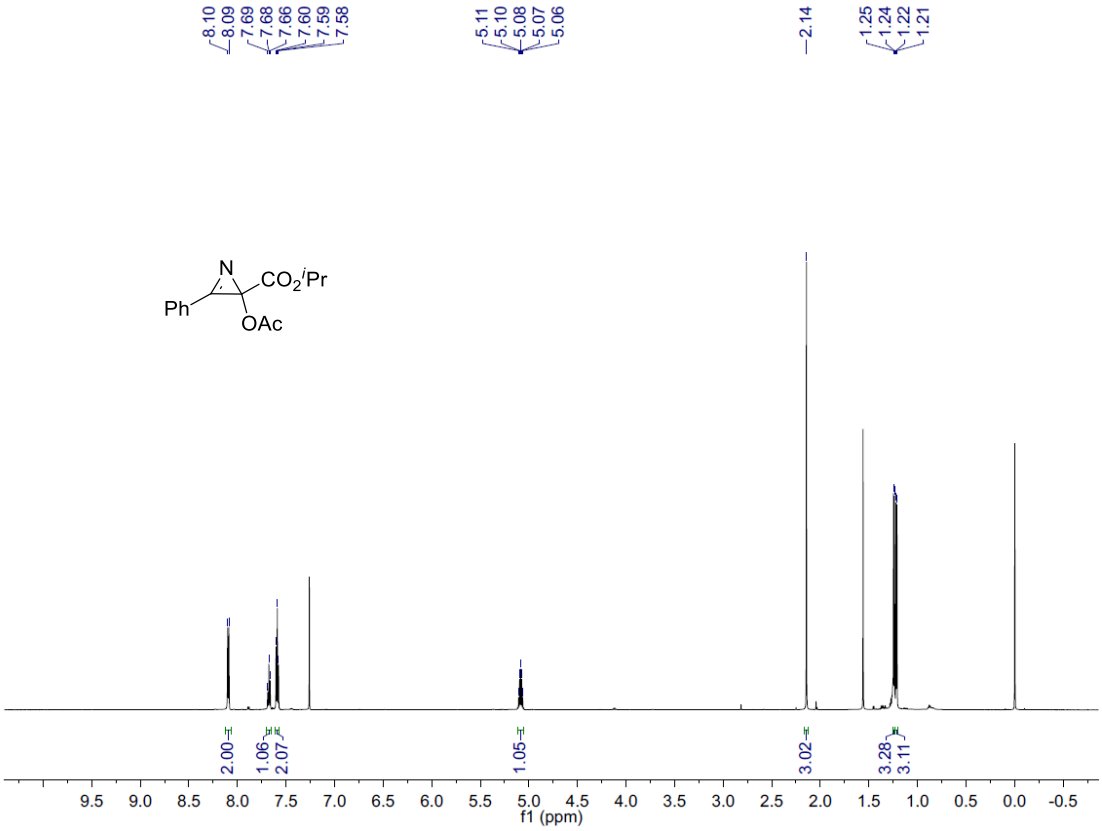
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2a**



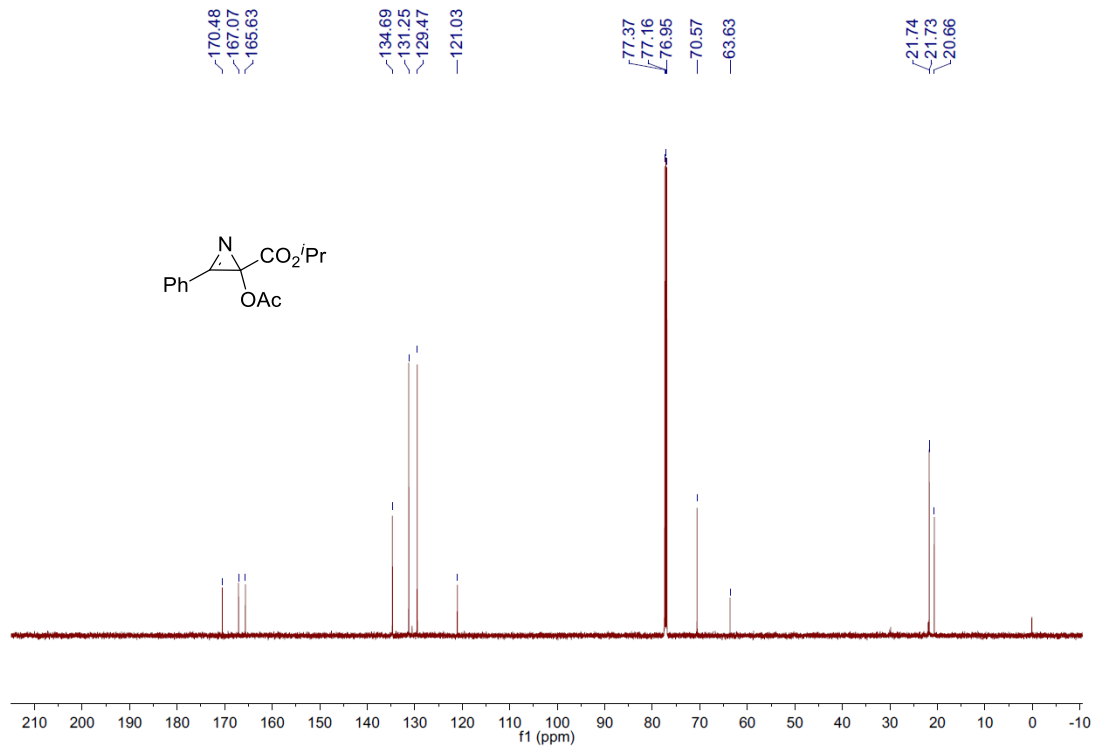
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2b**



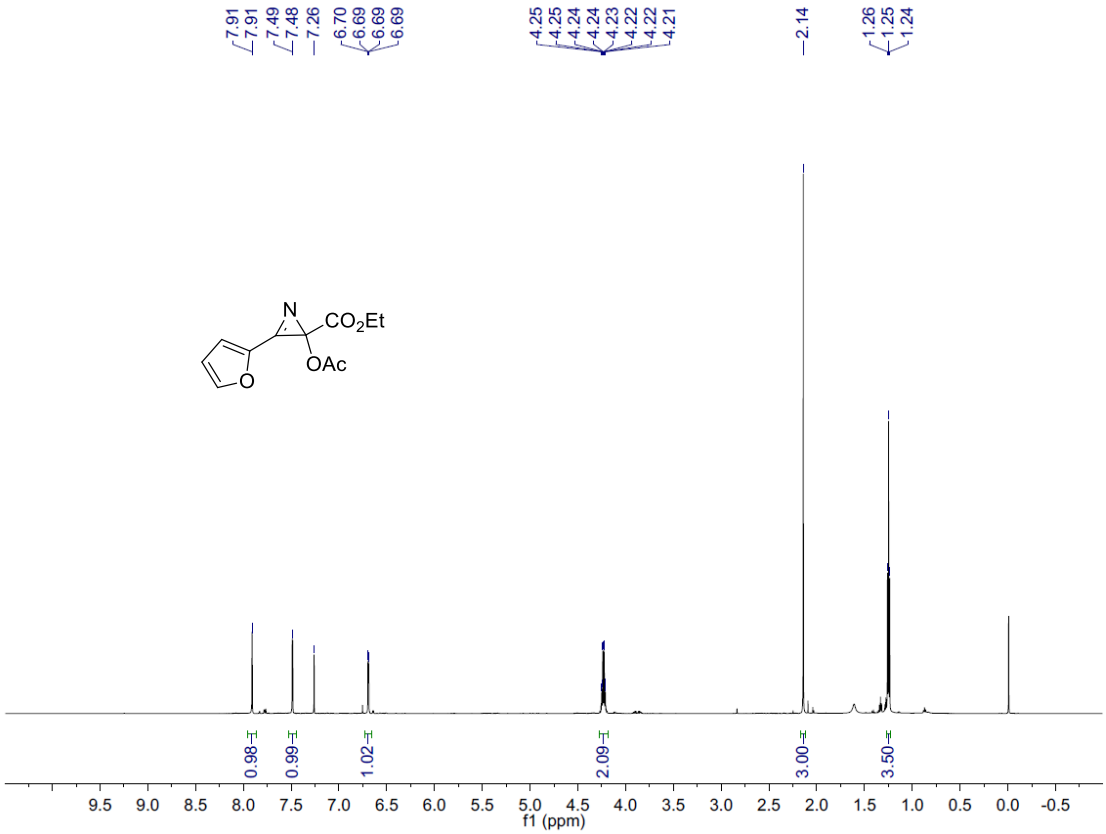
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2b**



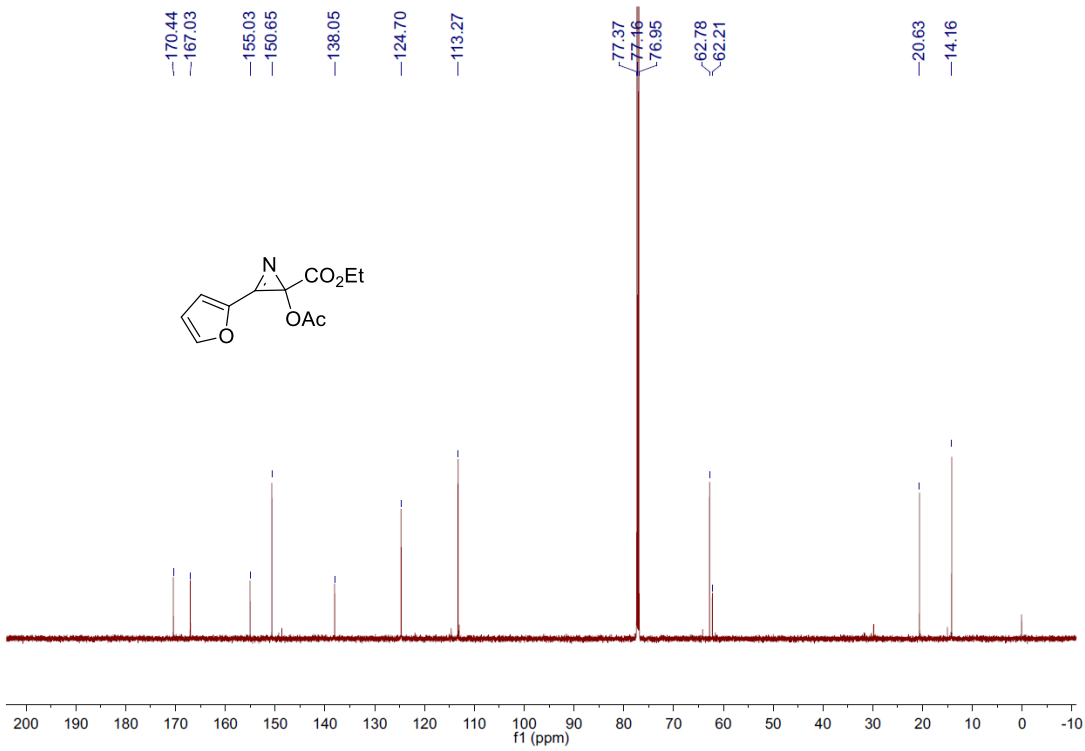
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2c**



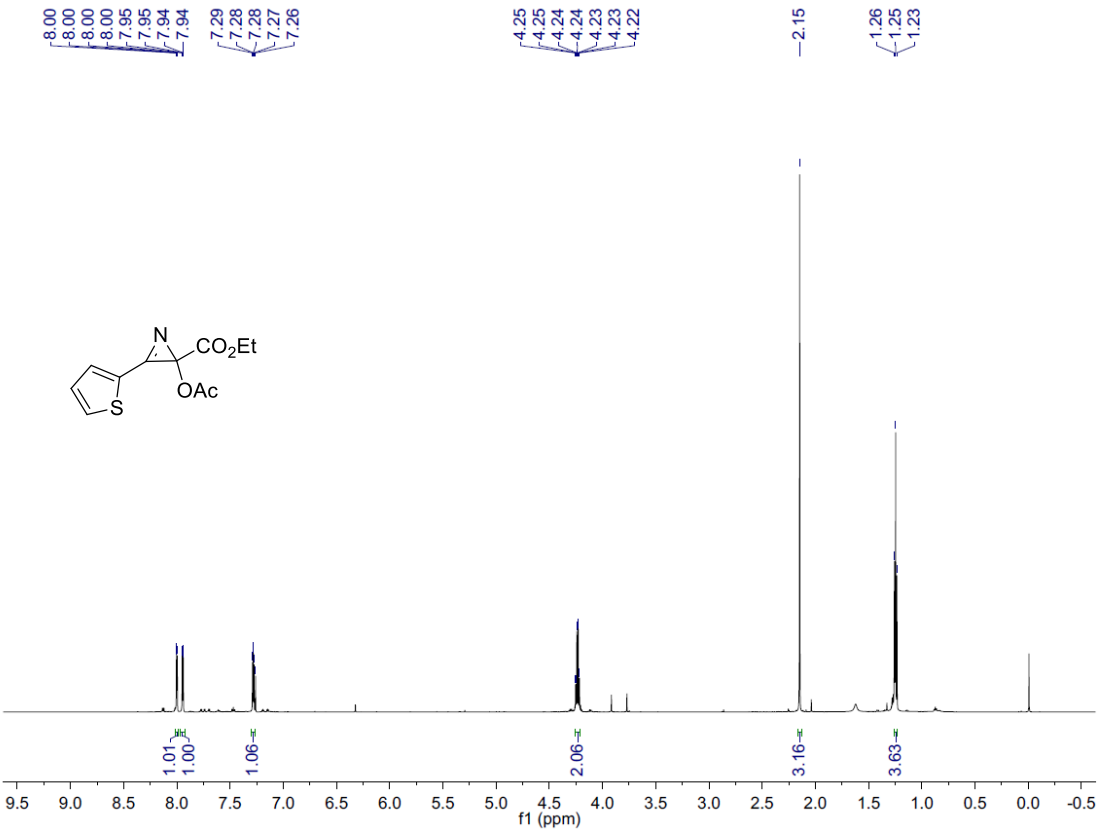
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2c**



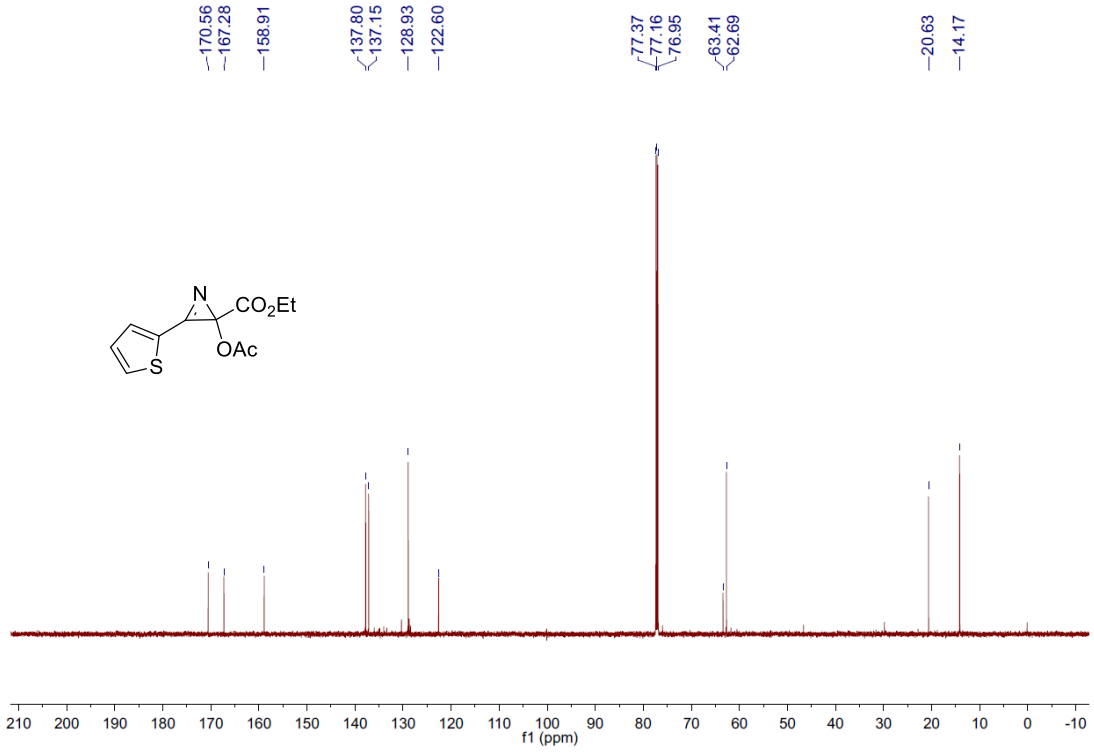
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2d**



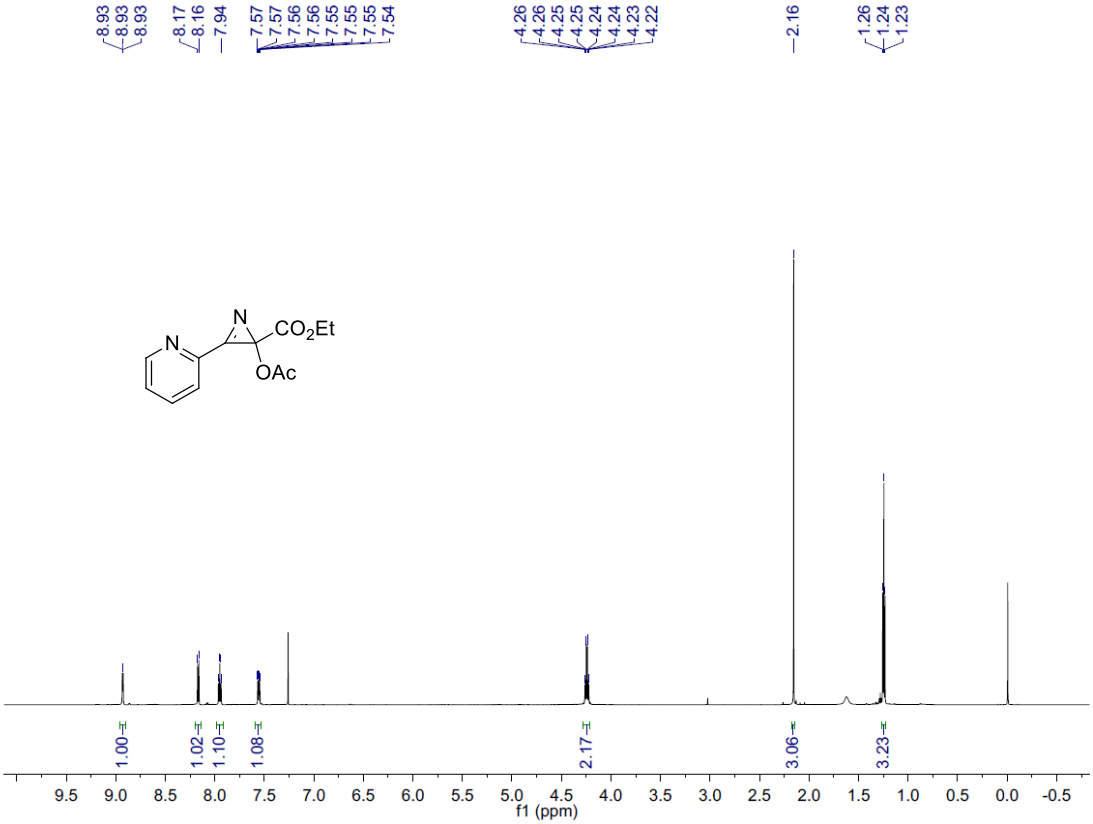
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2d**



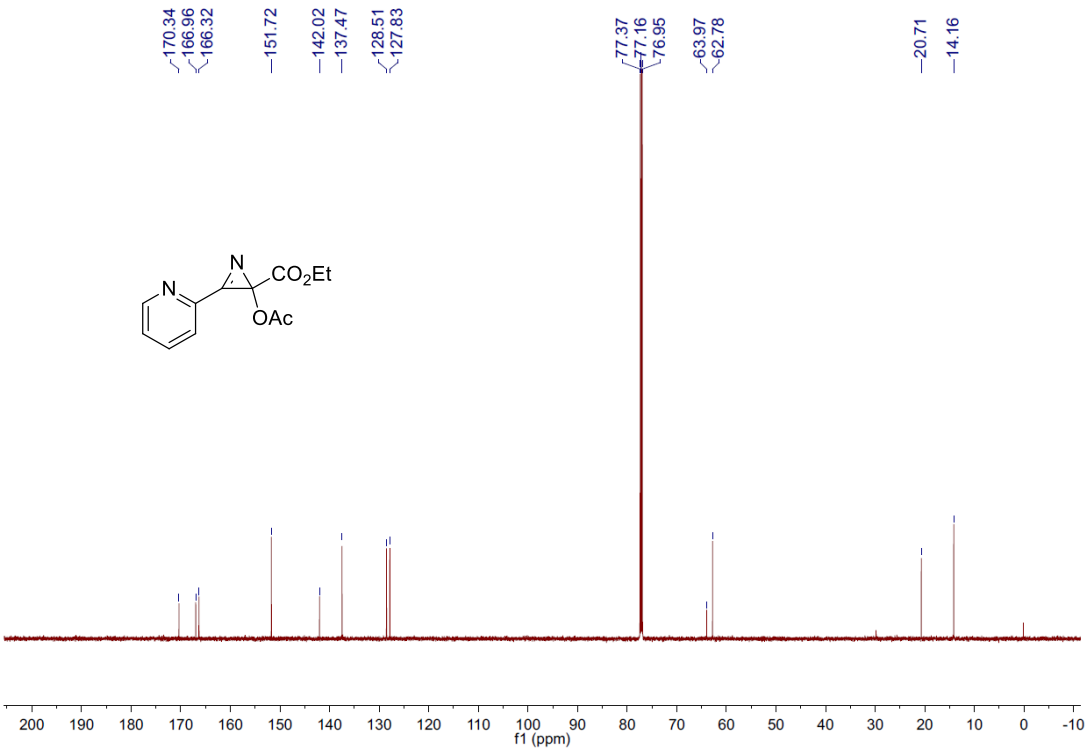
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2e**



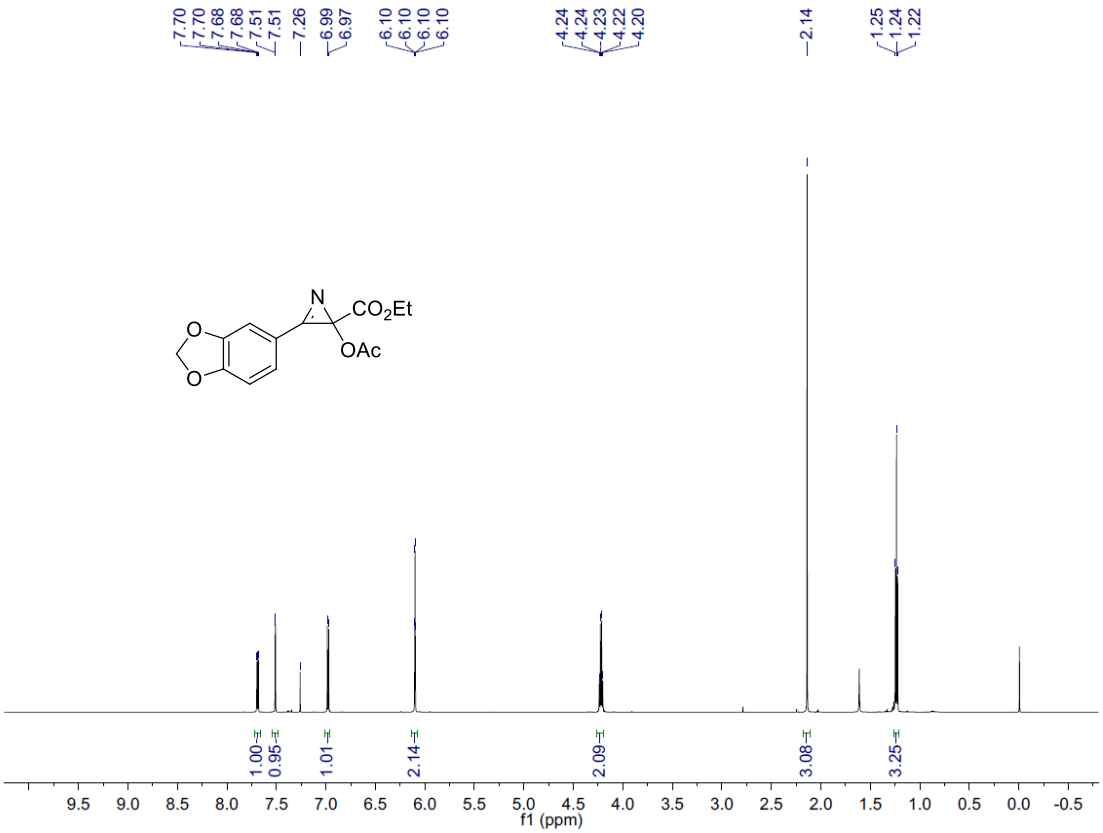
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2e**



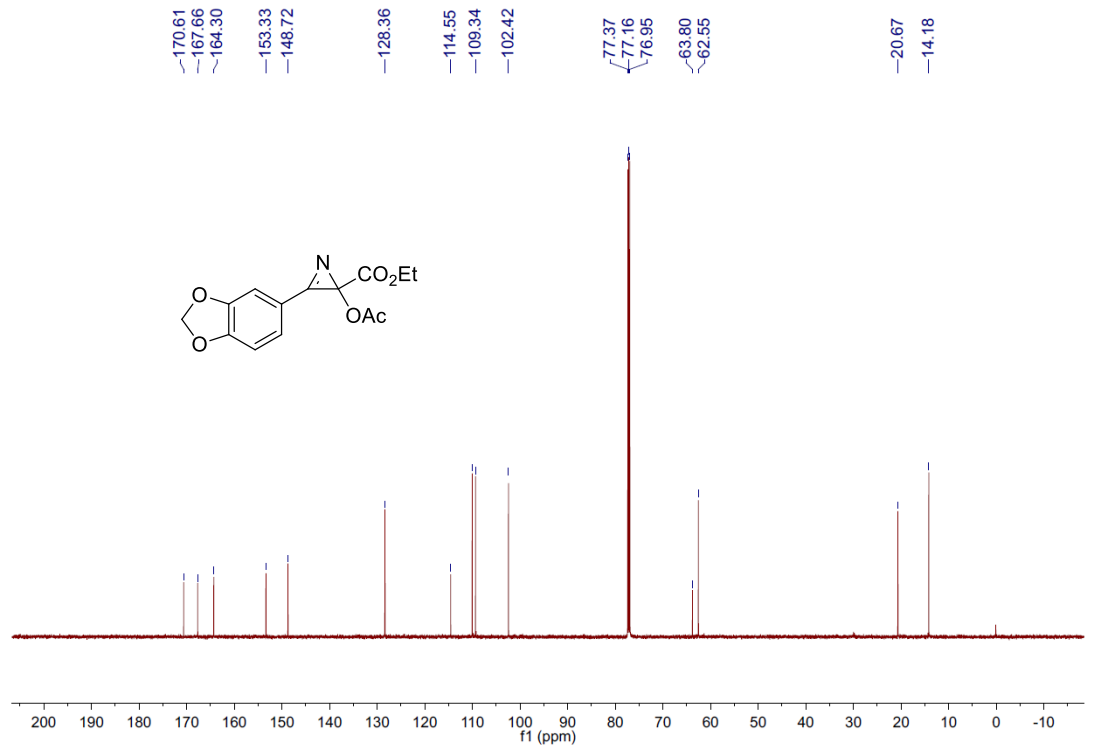
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2f**



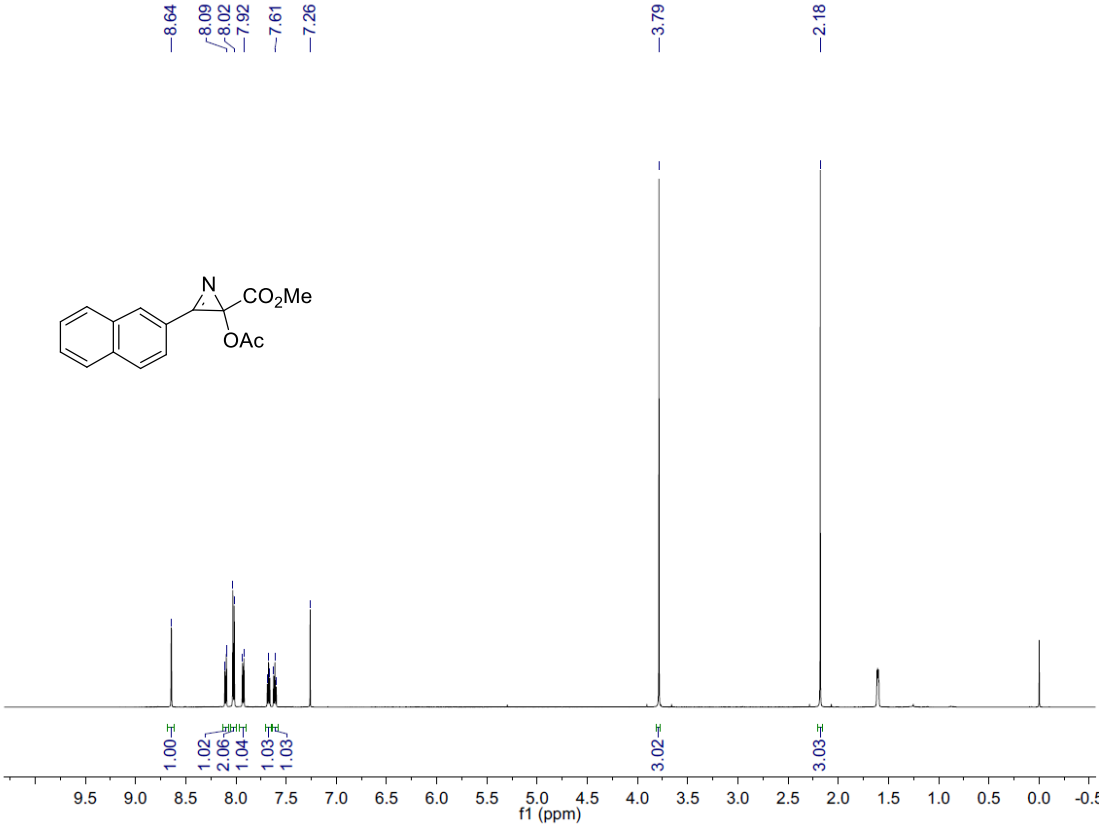
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2f**



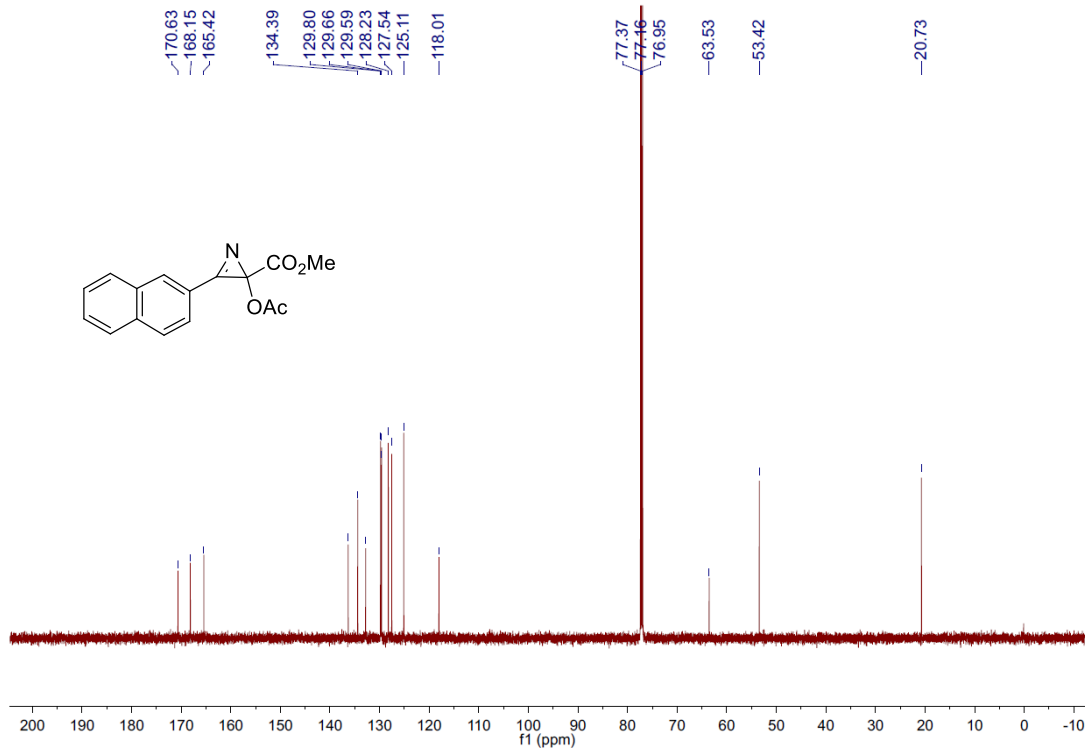
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2g**



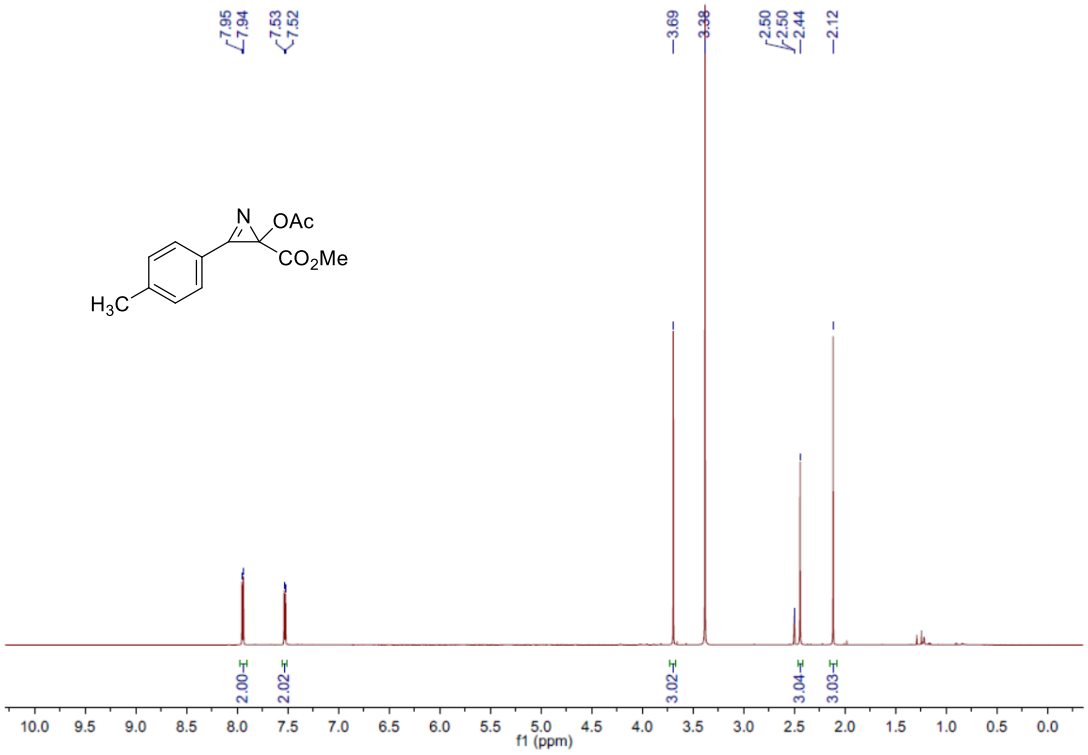
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2g**



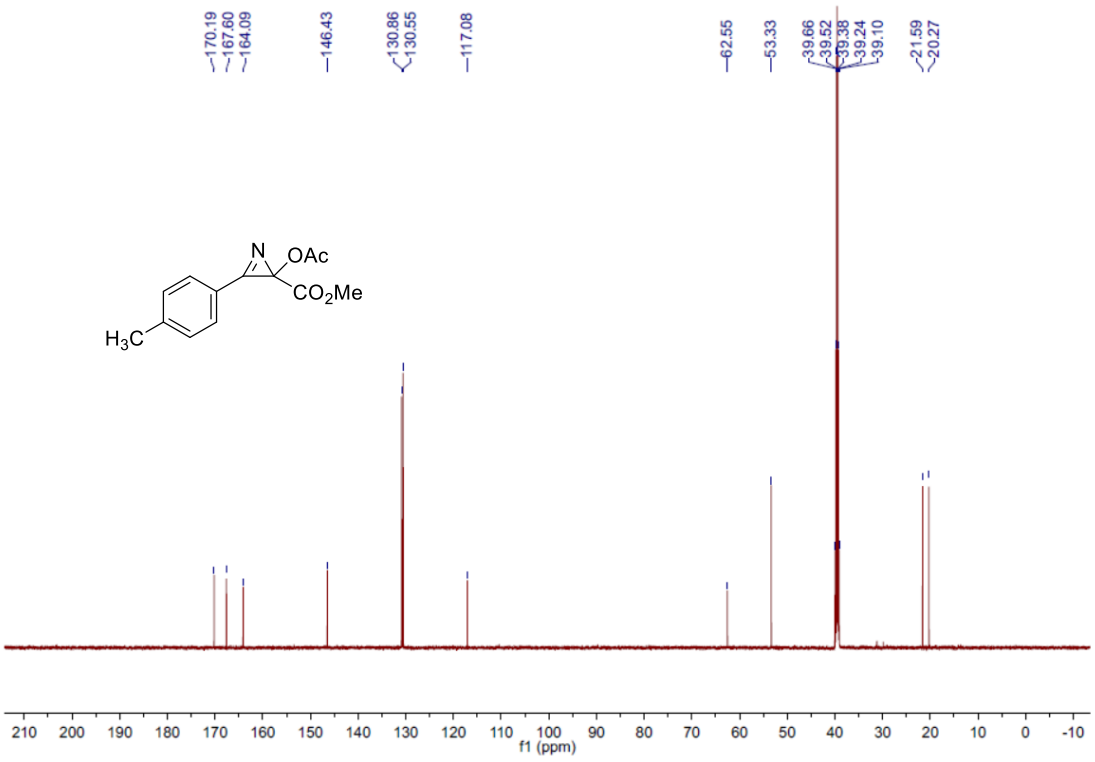
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2h**



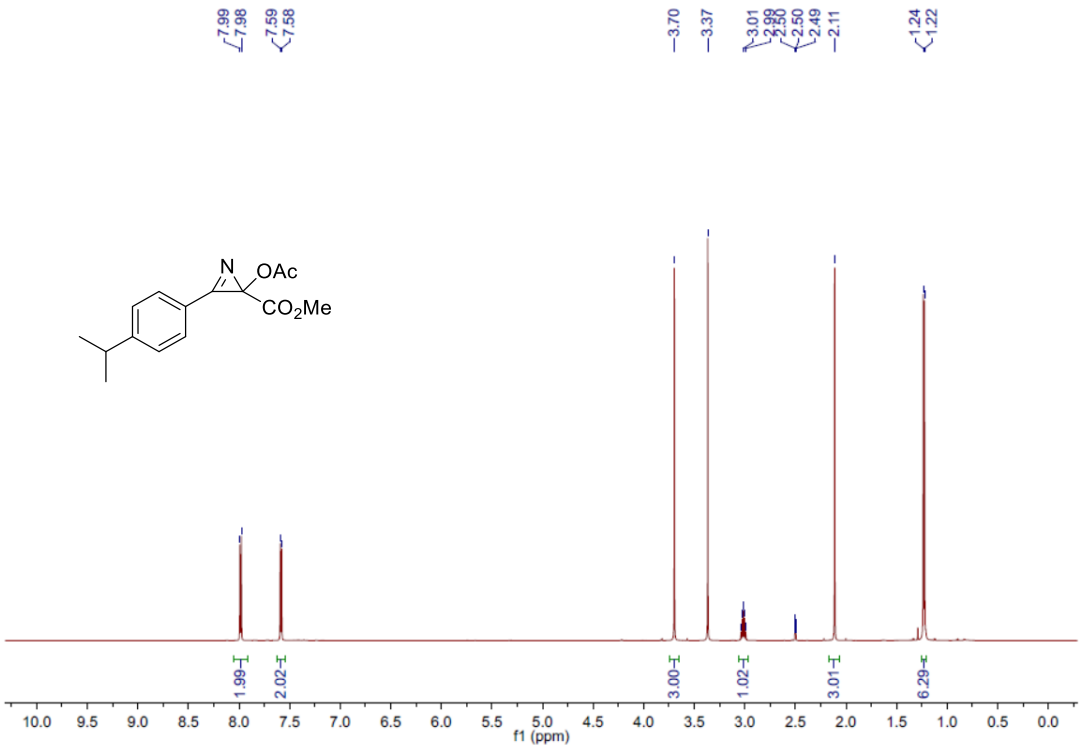
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2h**



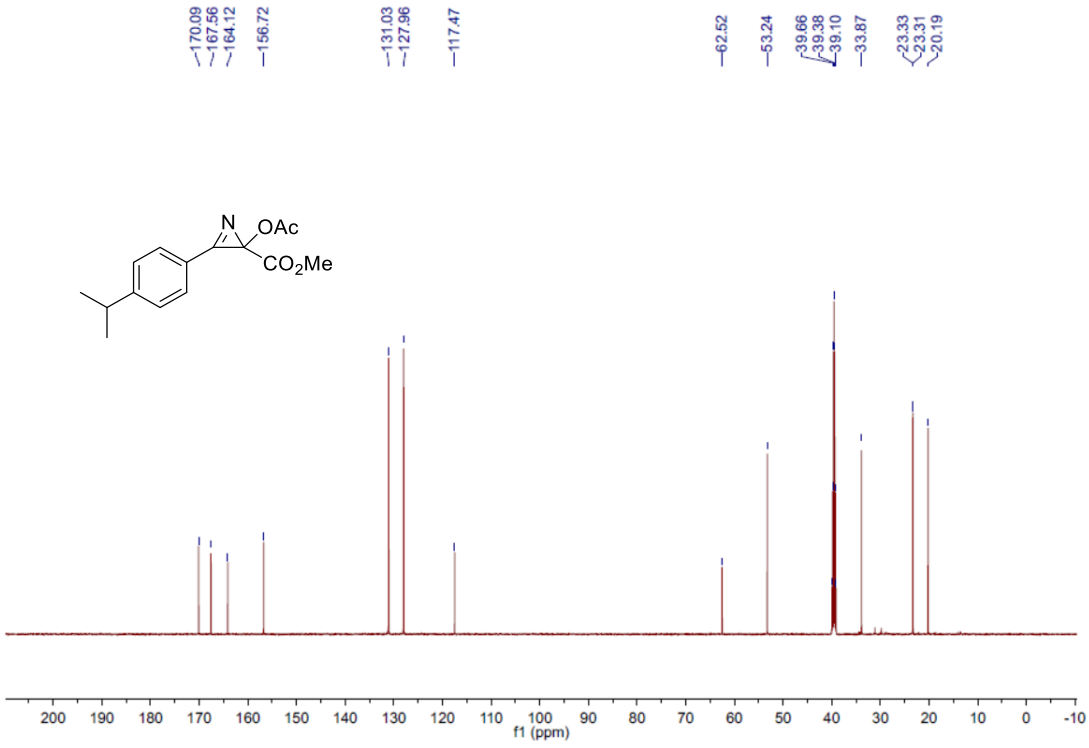
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **2i**



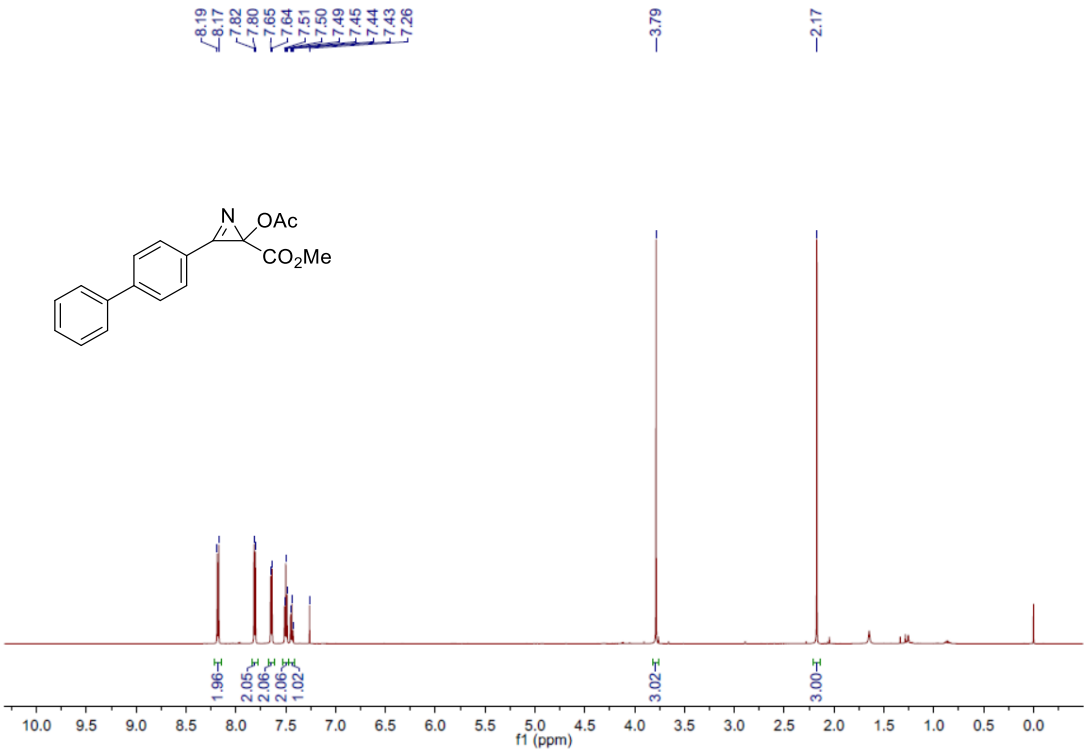
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **2i**



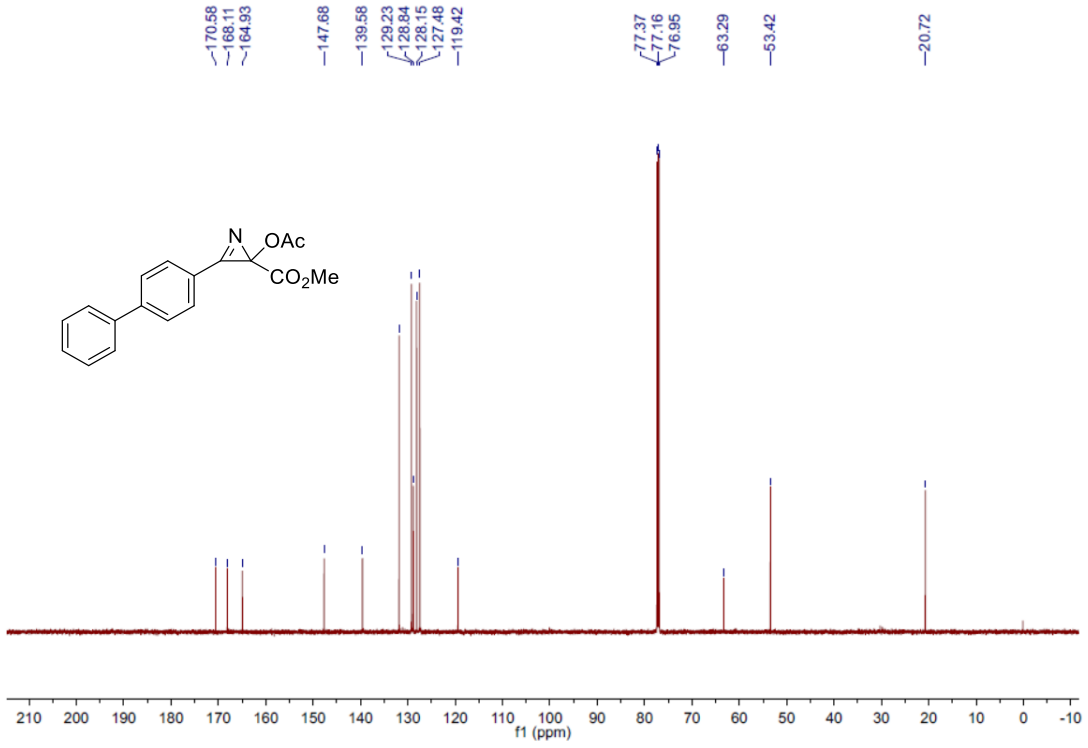
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **2j**



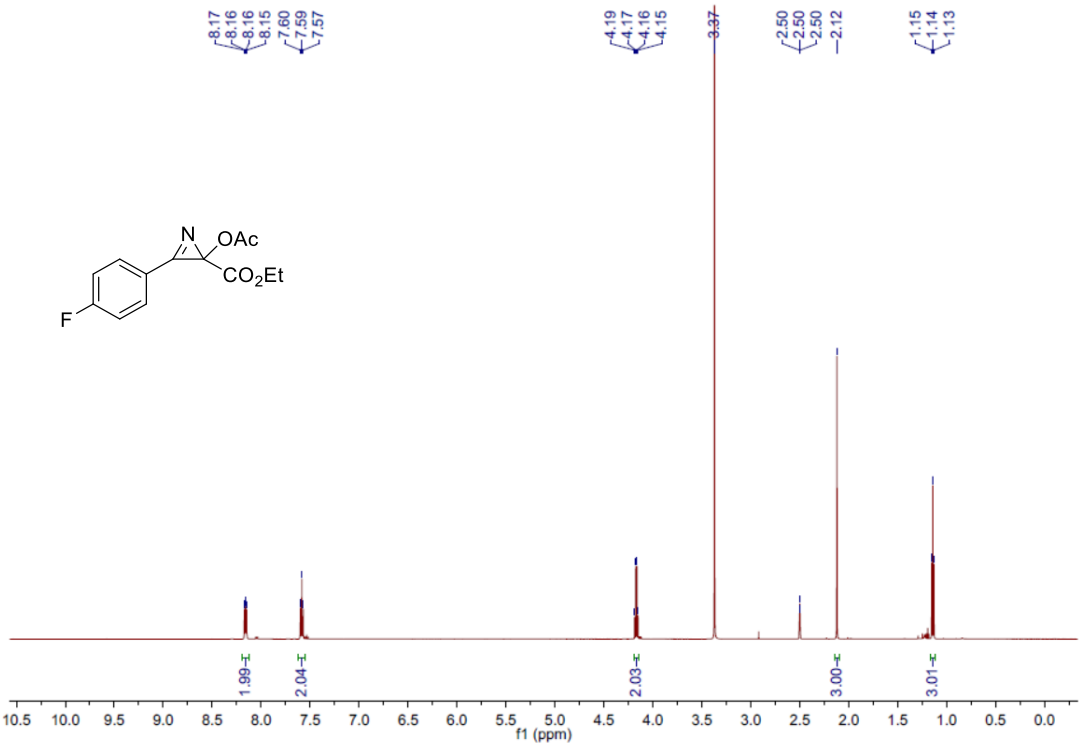
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **2j**



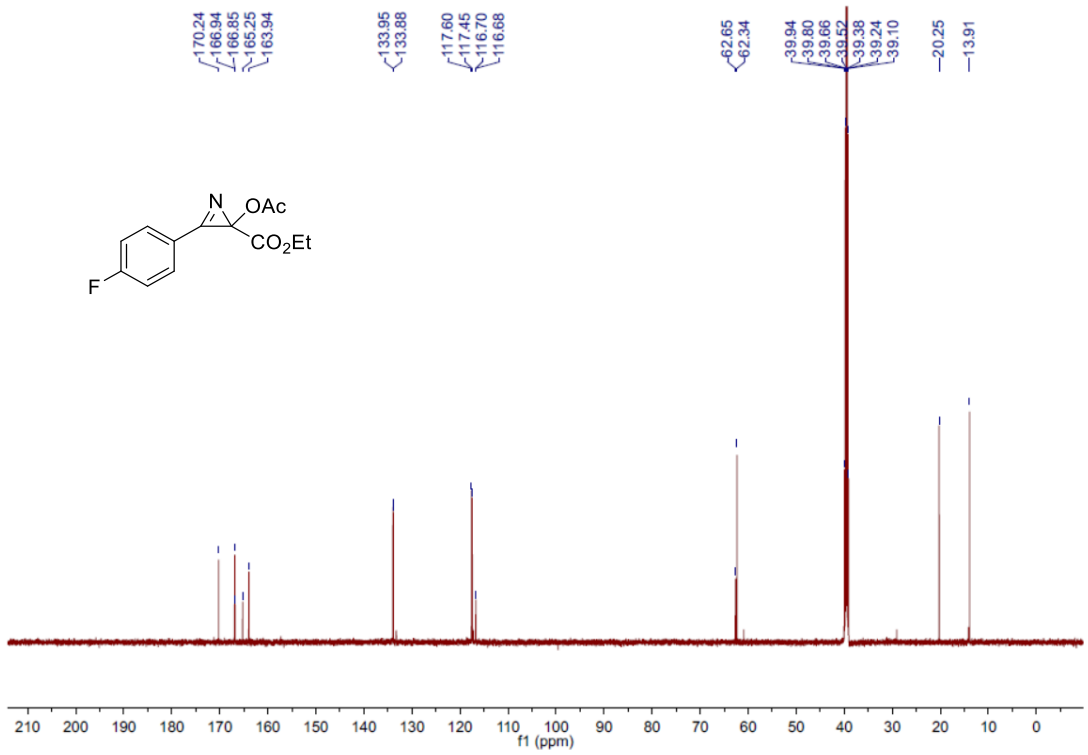
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2k**



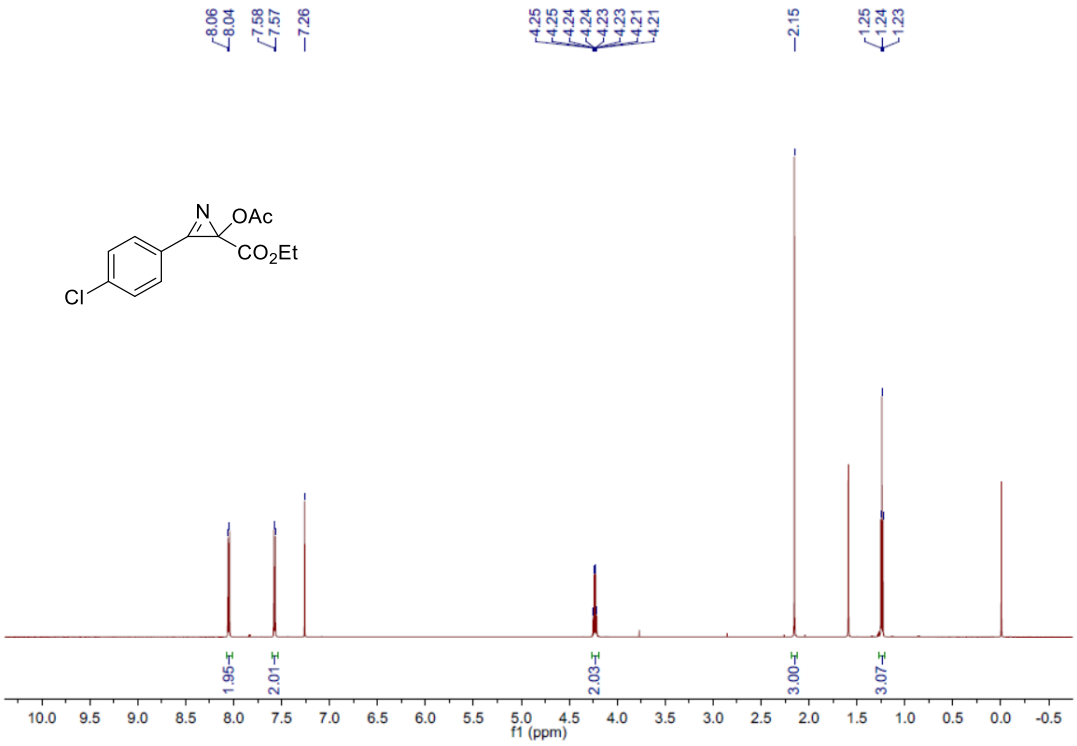
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2k**



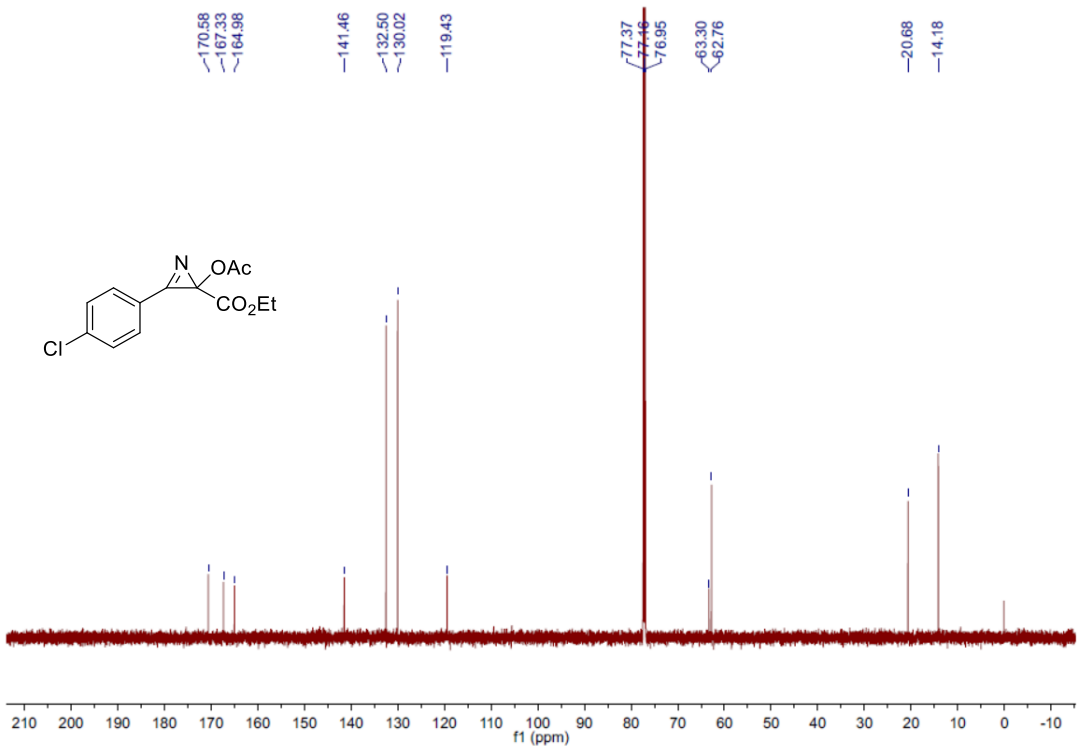
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **2l**



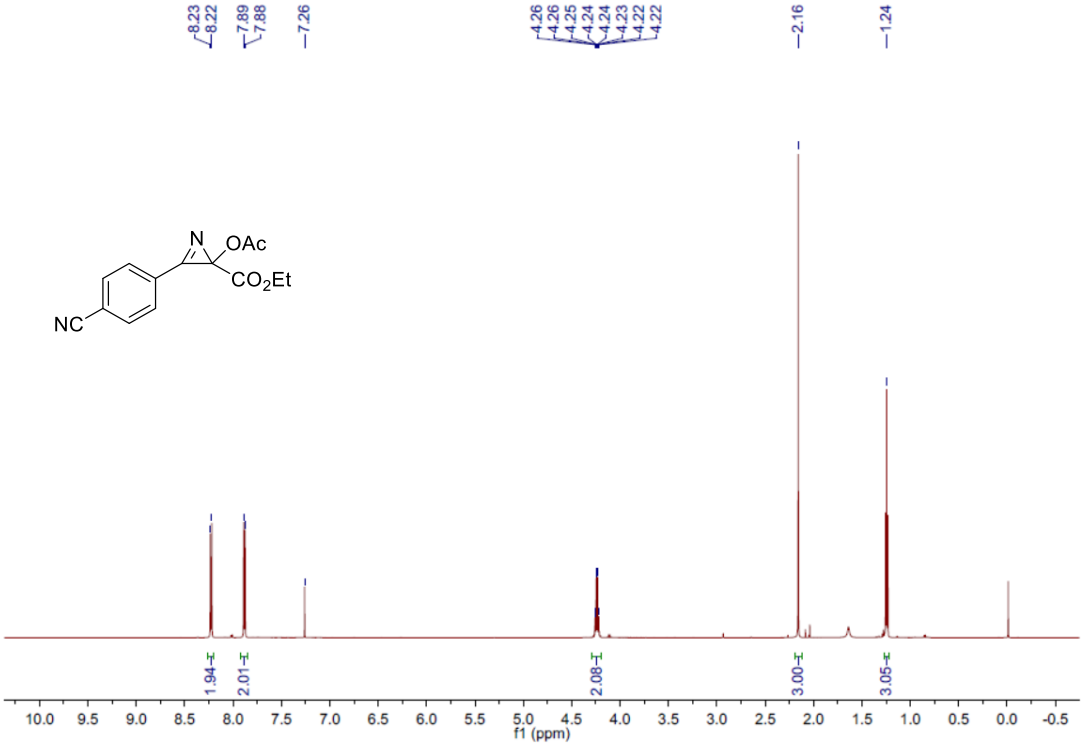
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **2l**



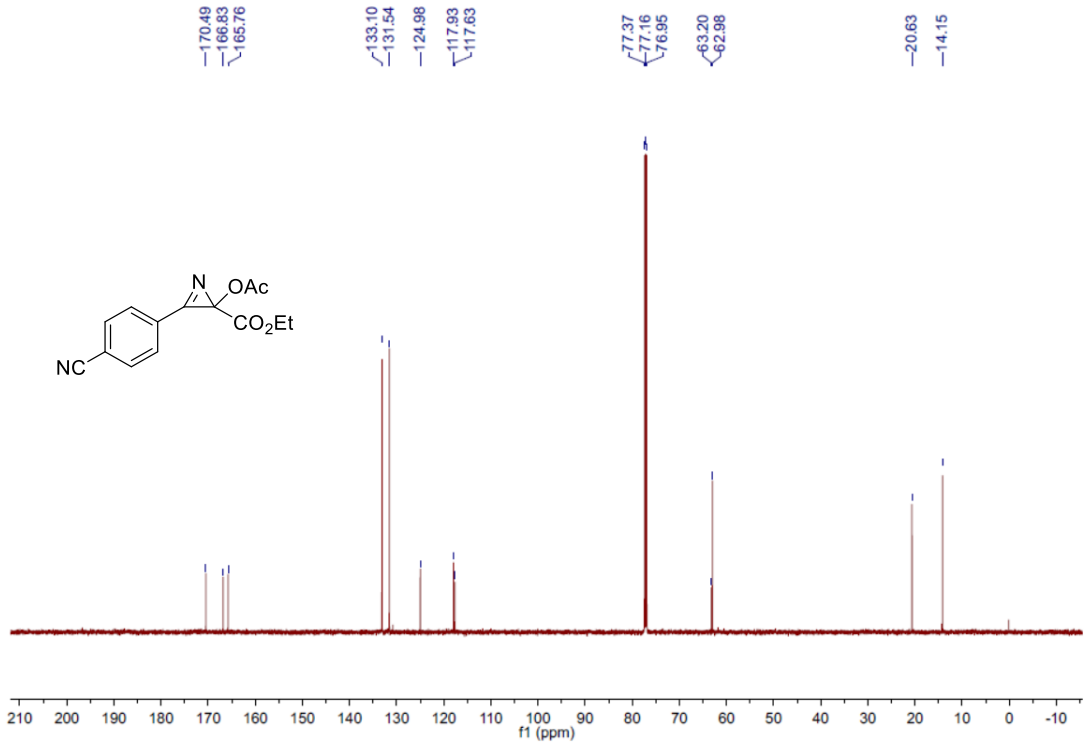
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2m**



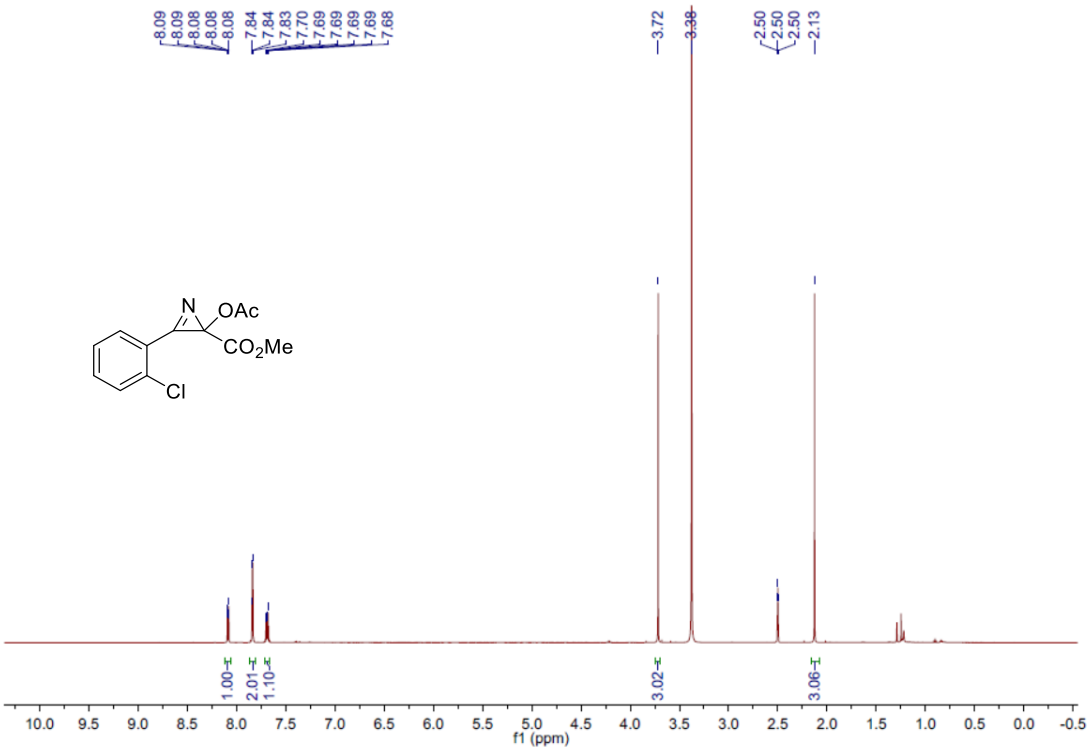
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2m**



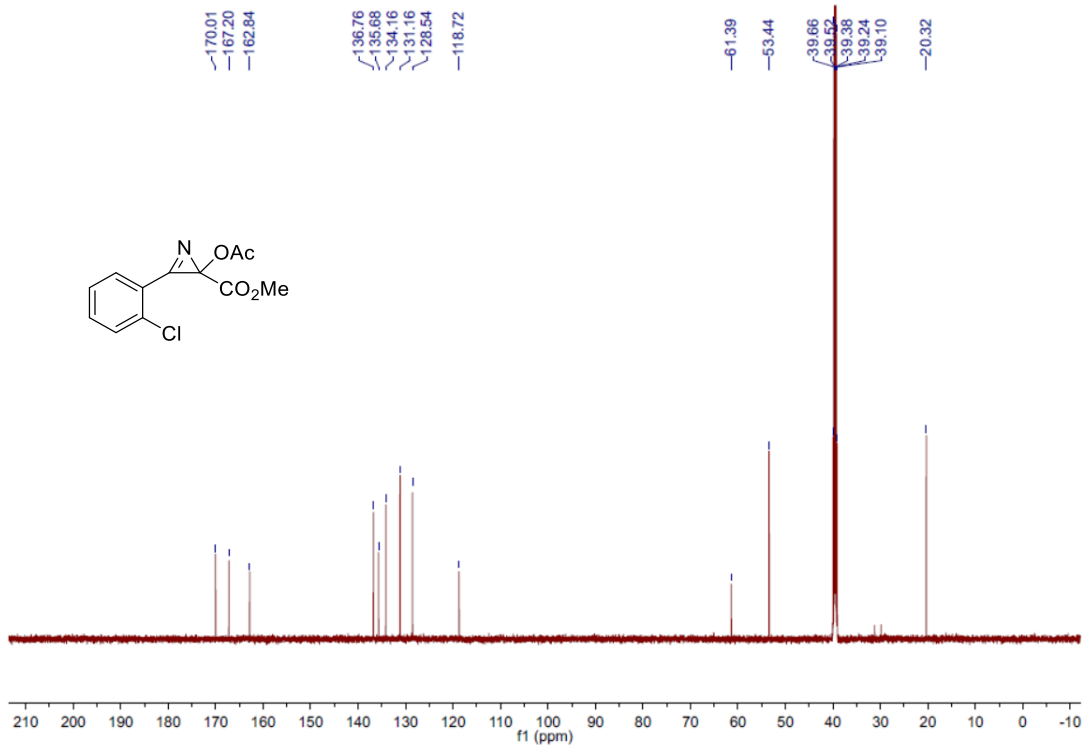
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **2n**



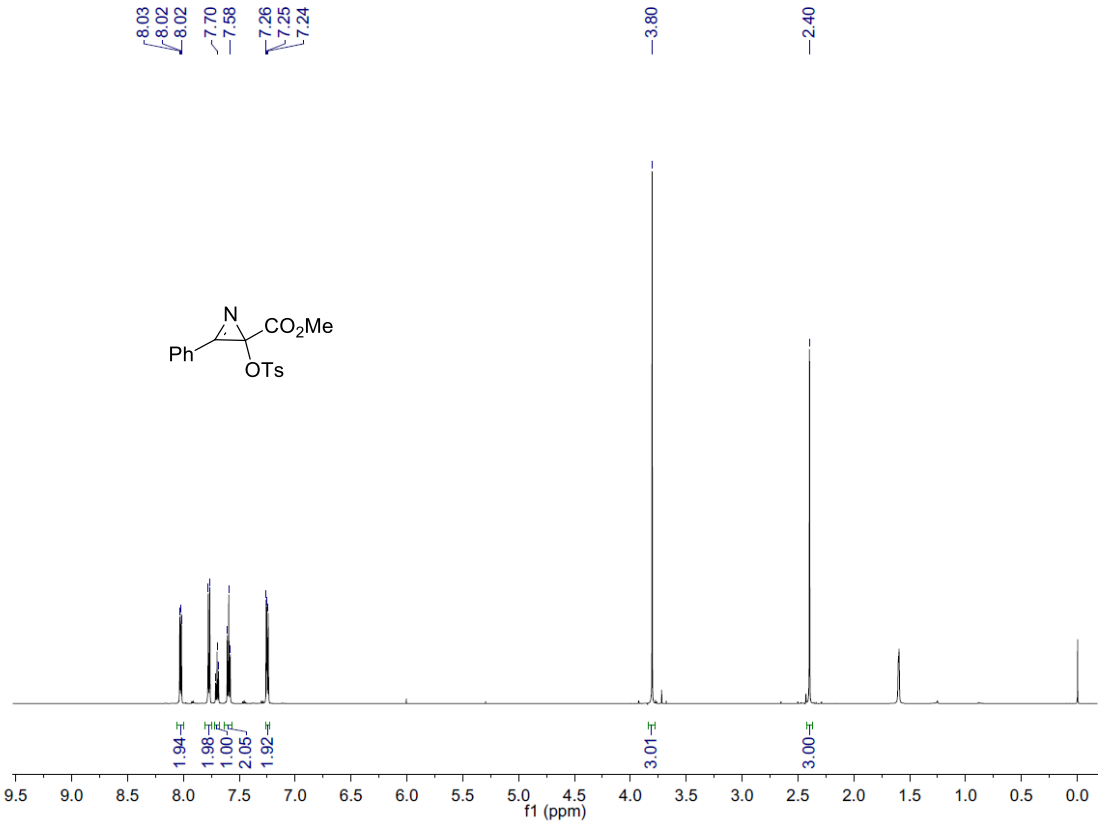
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **2n**



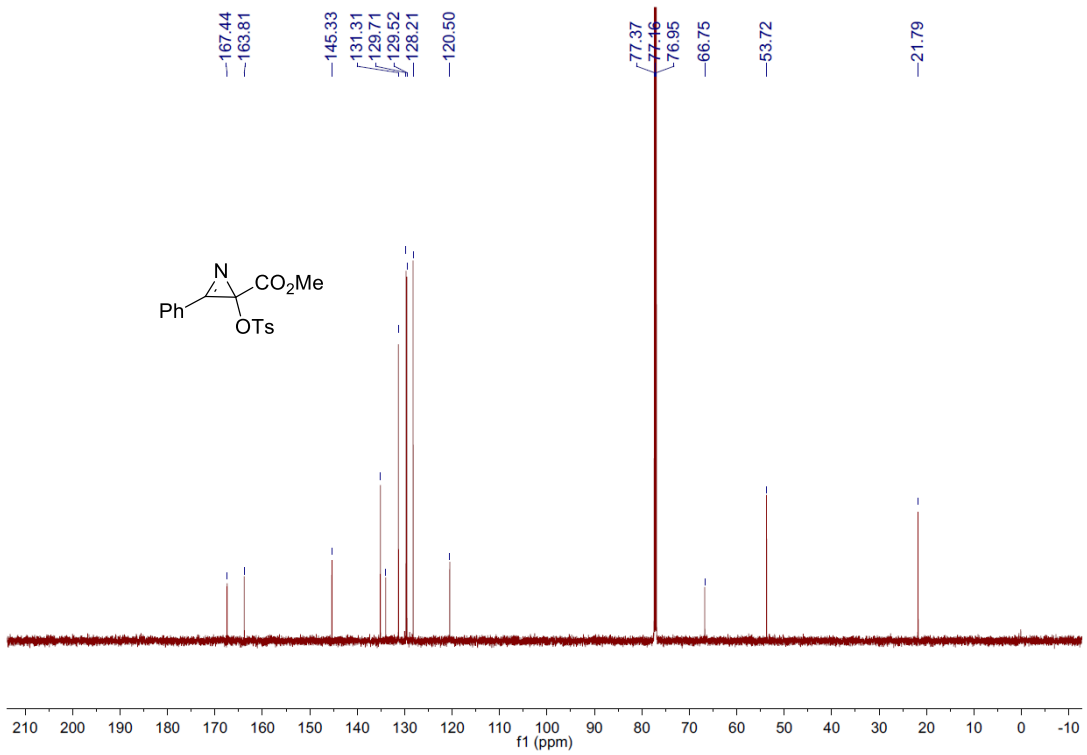
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **2o**



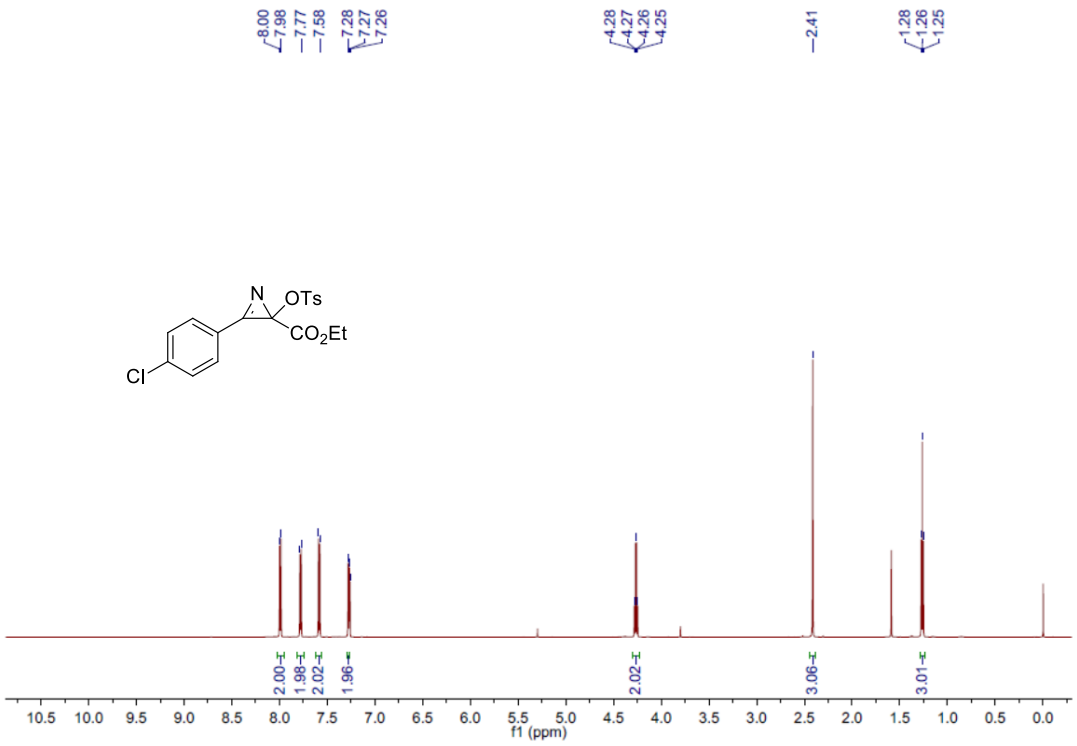
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **2o**



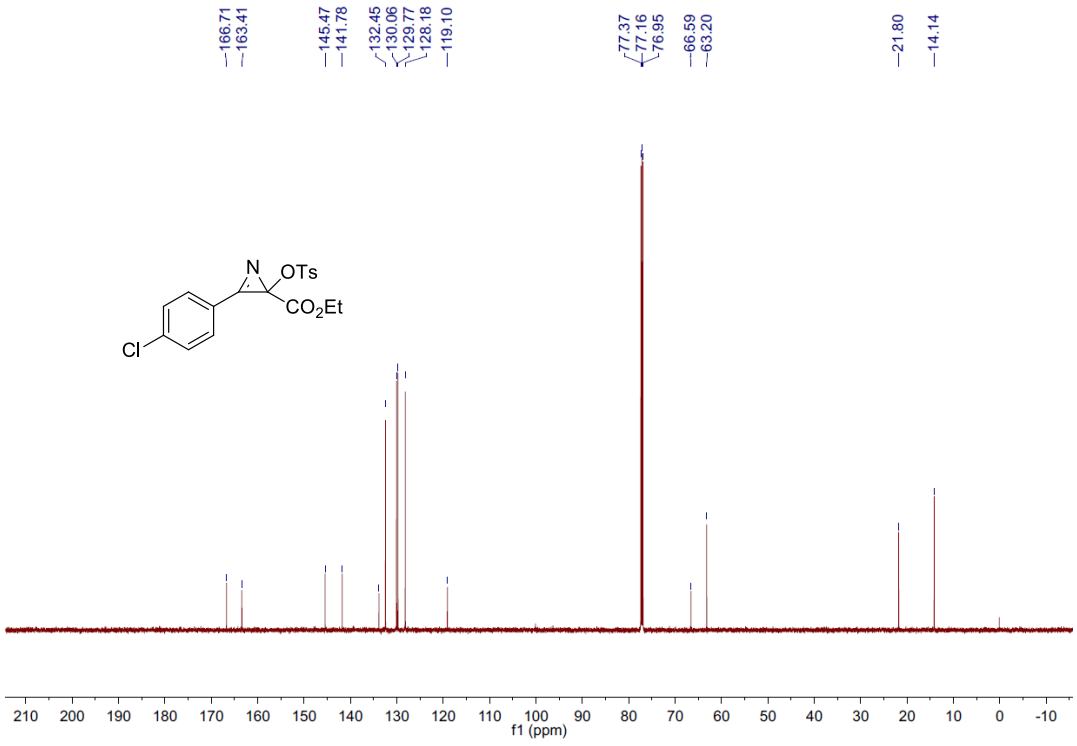
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3a**



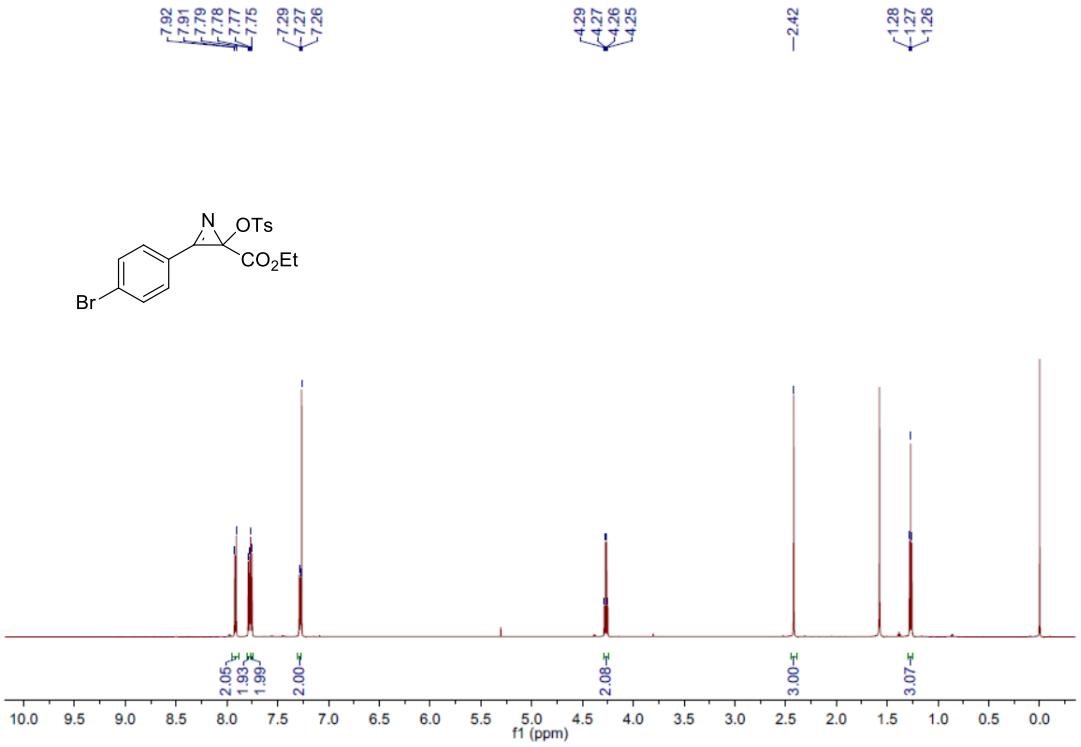
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3a**



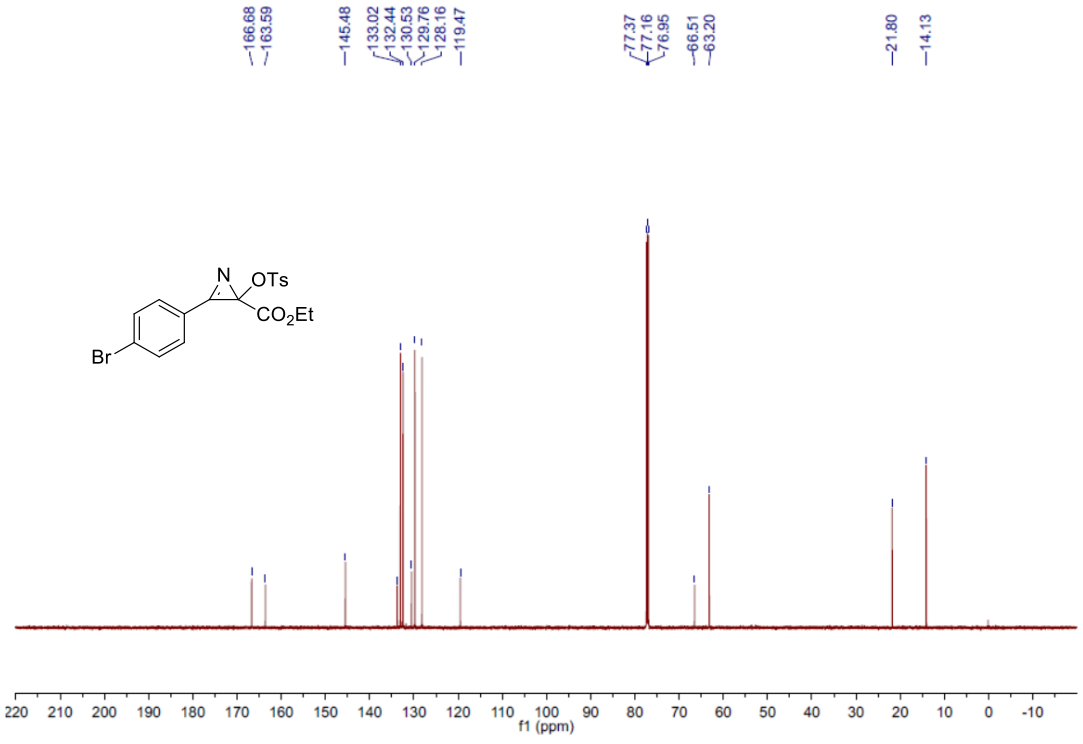
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3b**



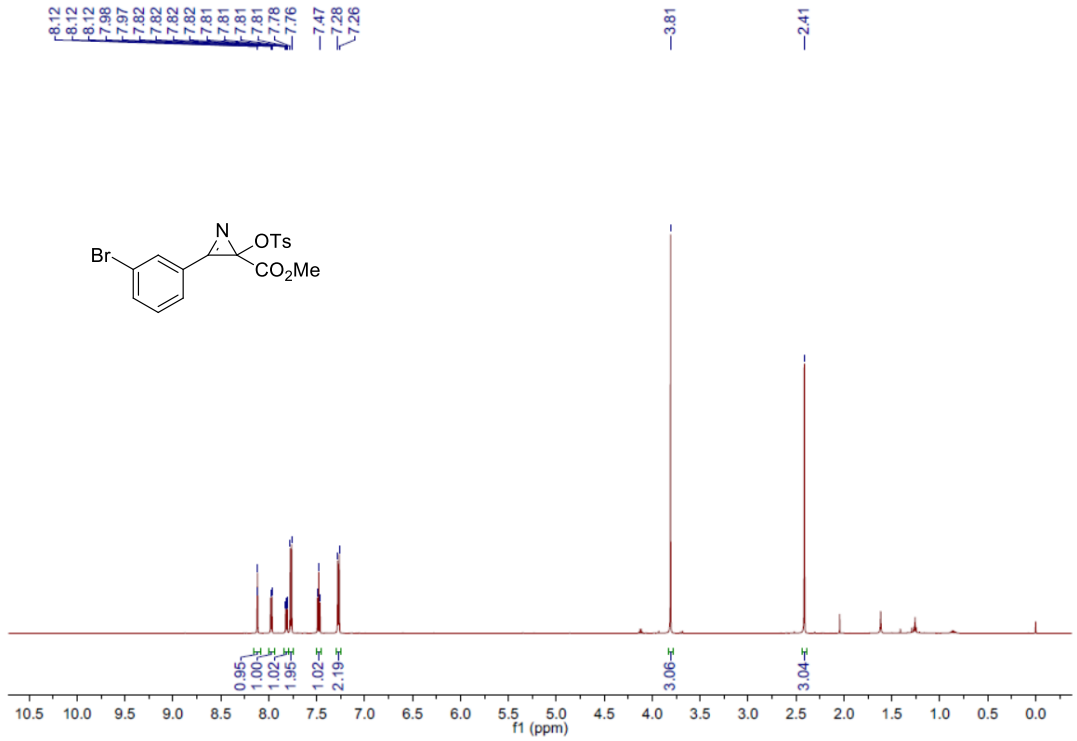
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3b**



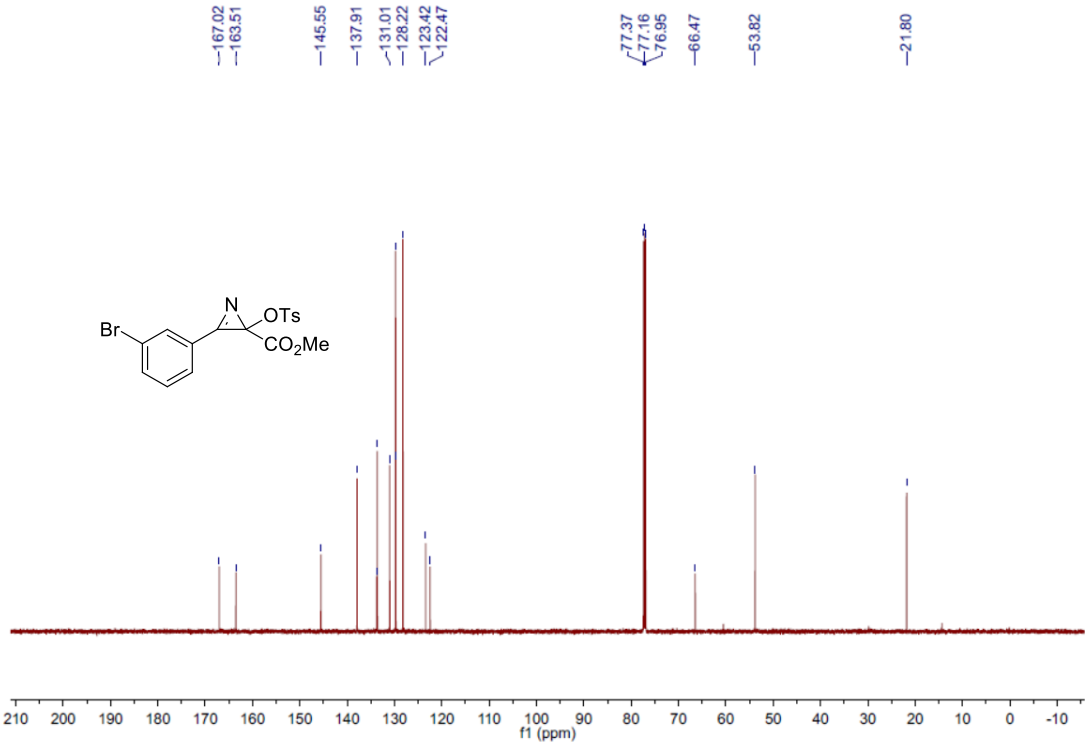
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3c**



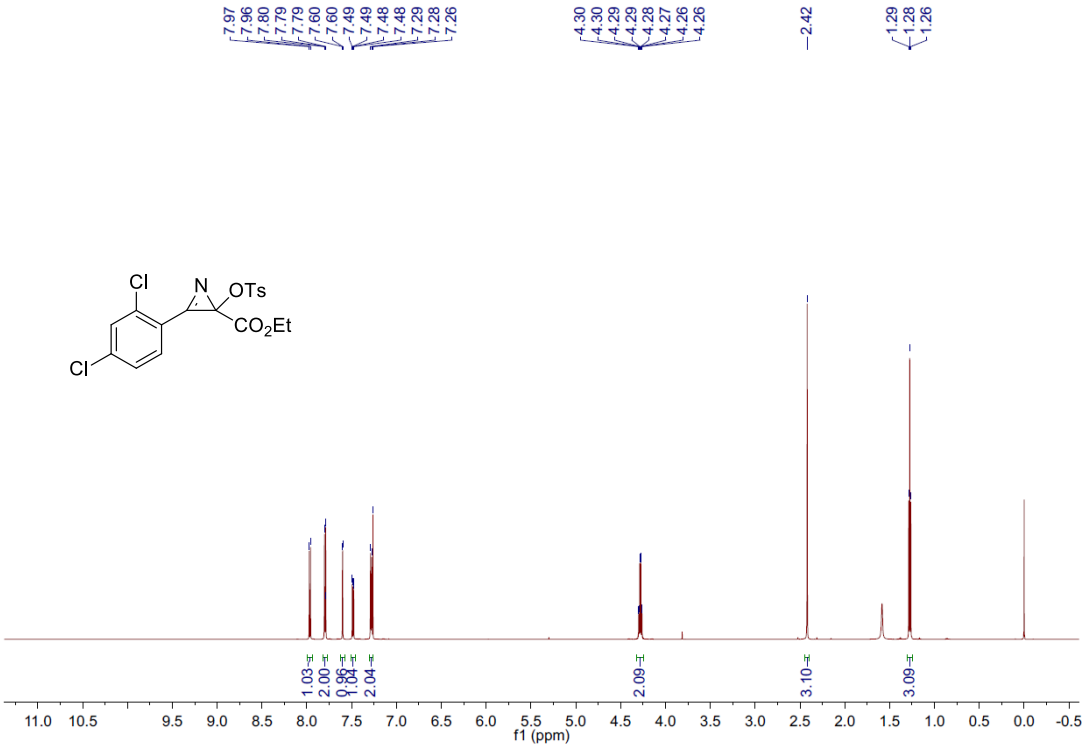
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3c**



^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3d**



^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3d**



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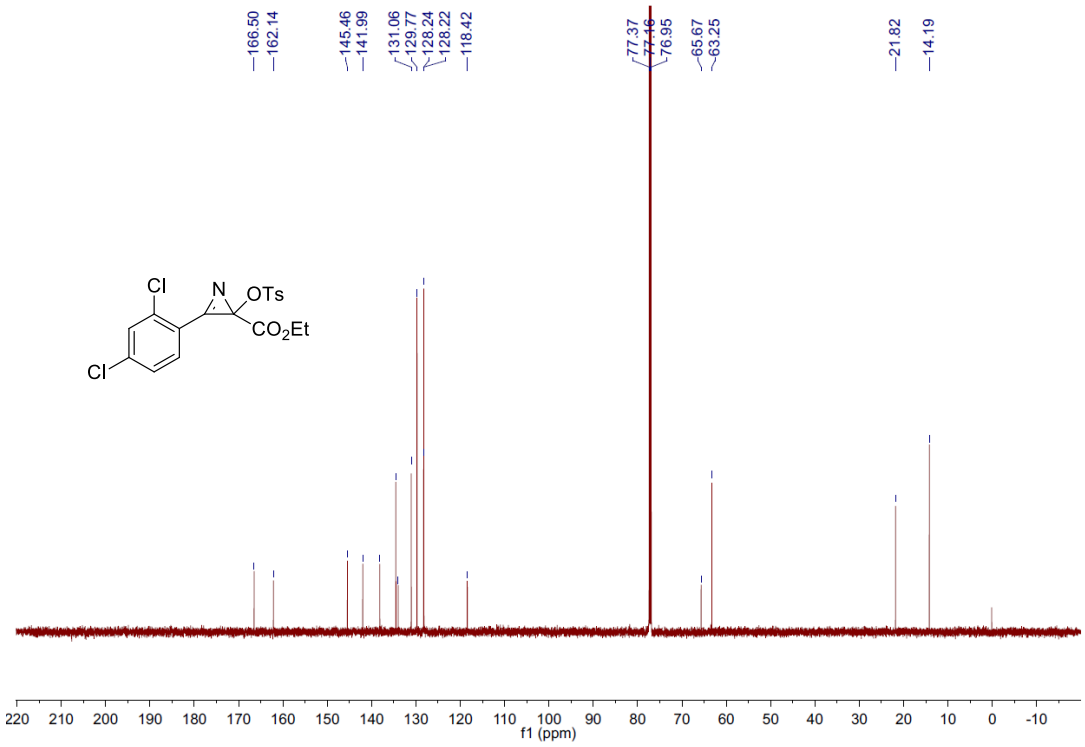
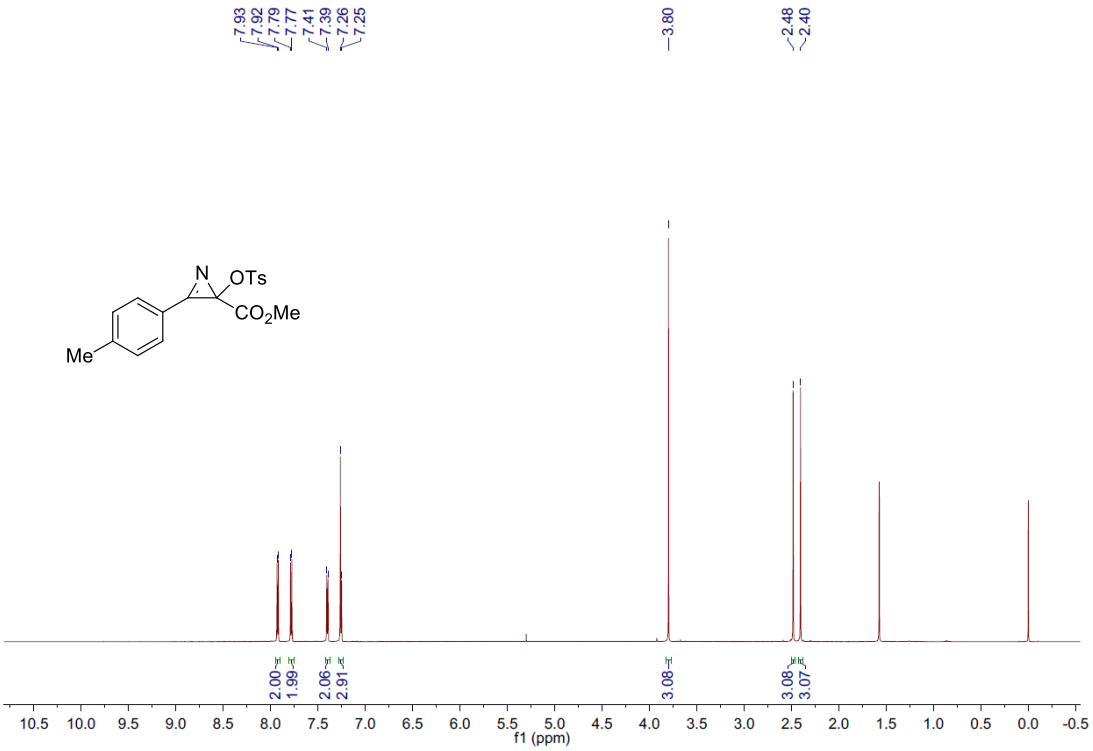
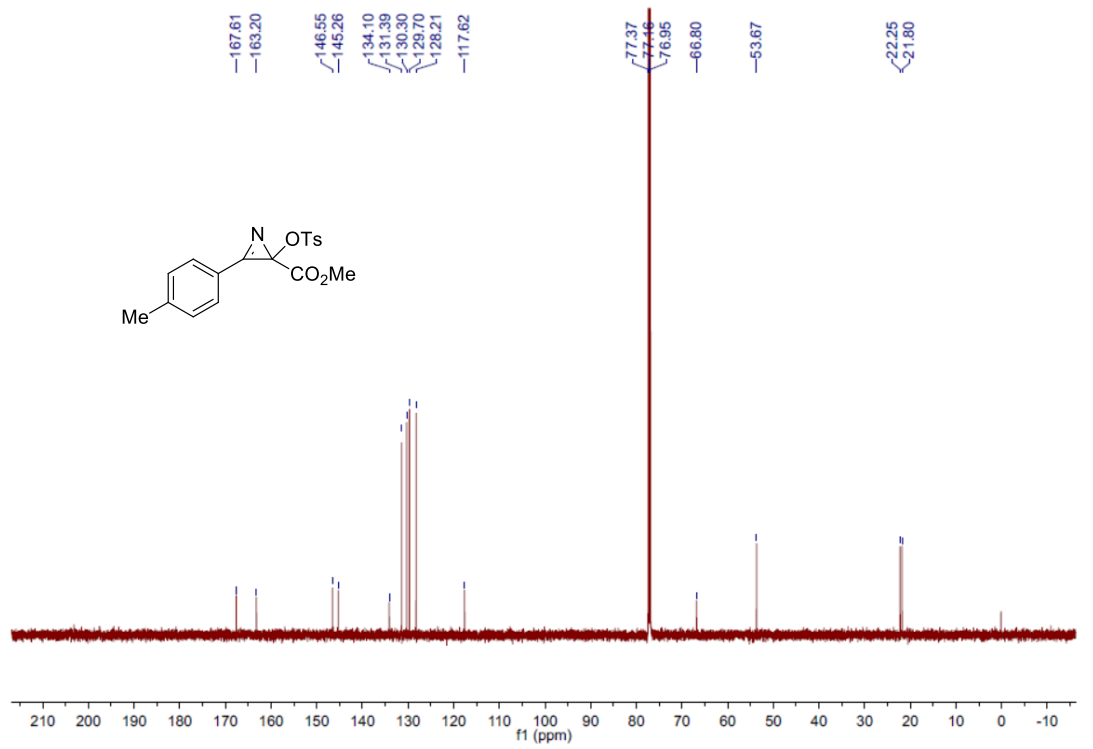


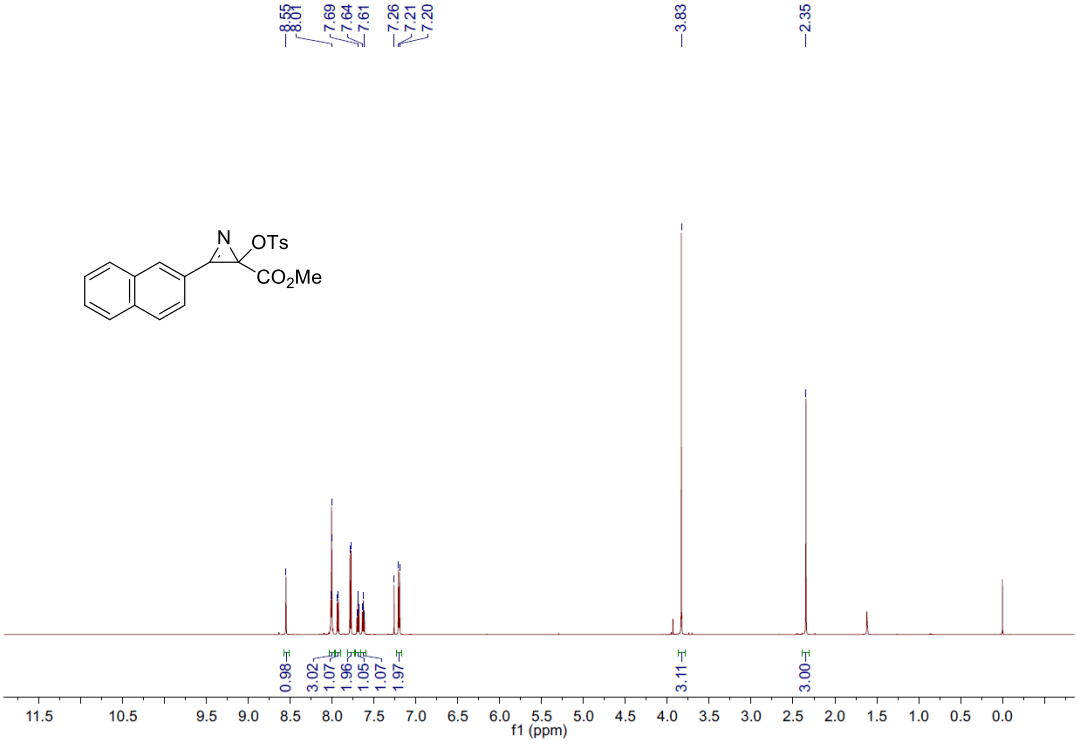
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3e**



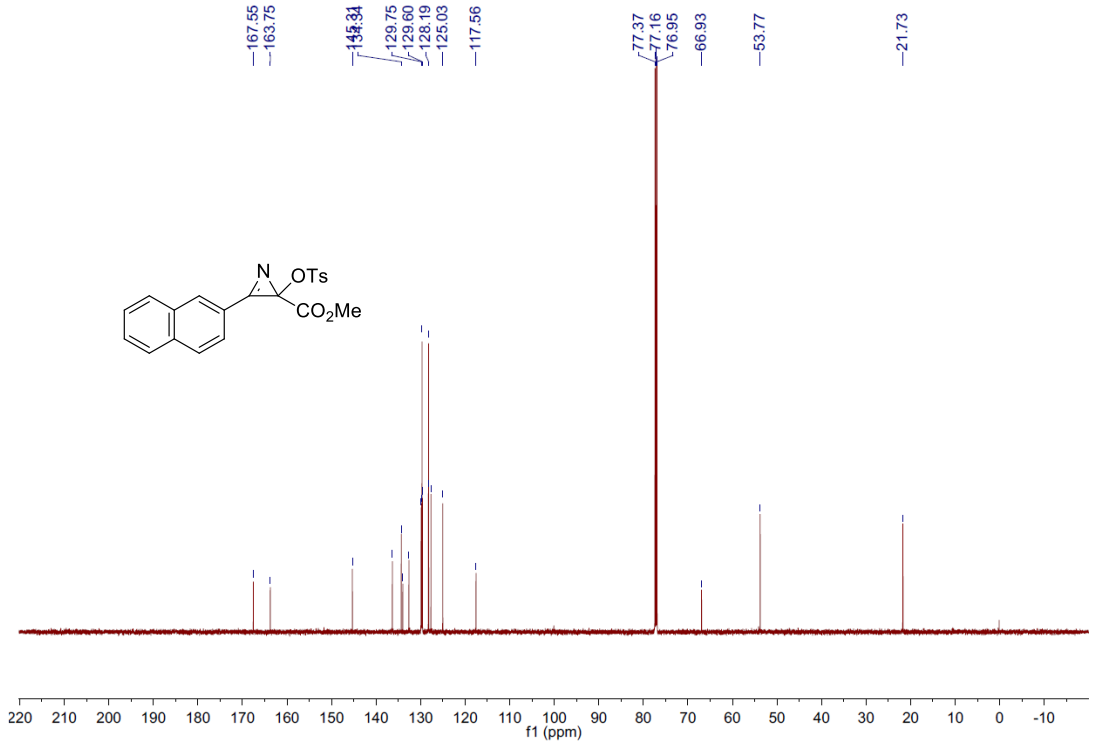
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3f**



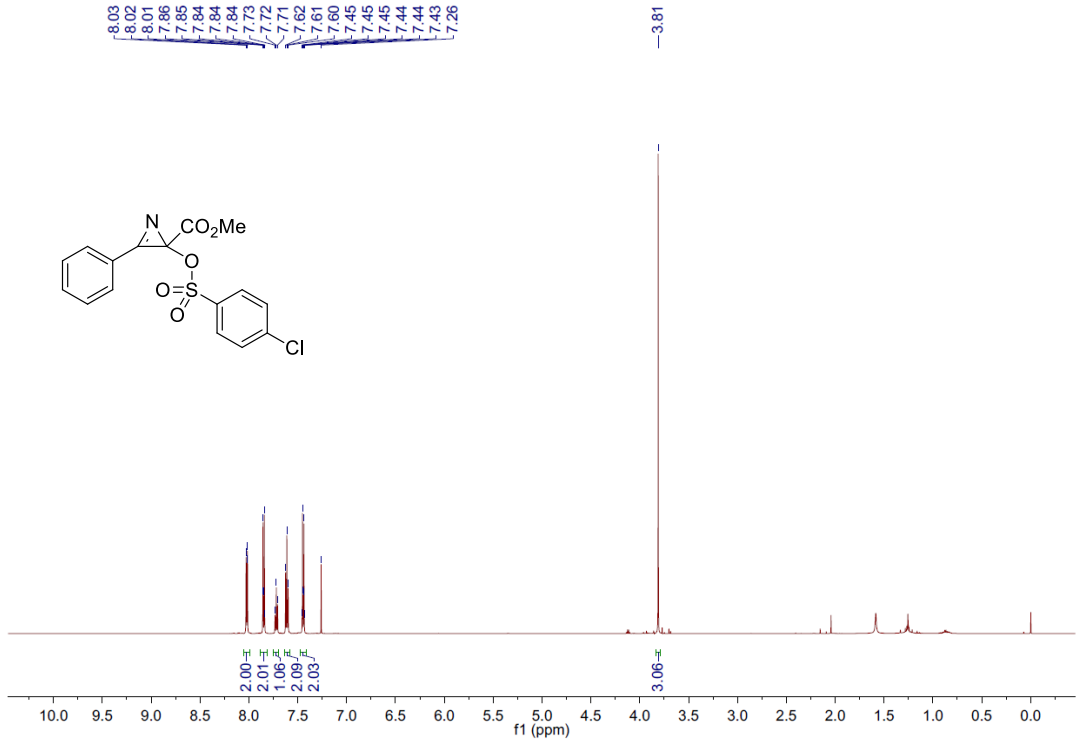
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3f**



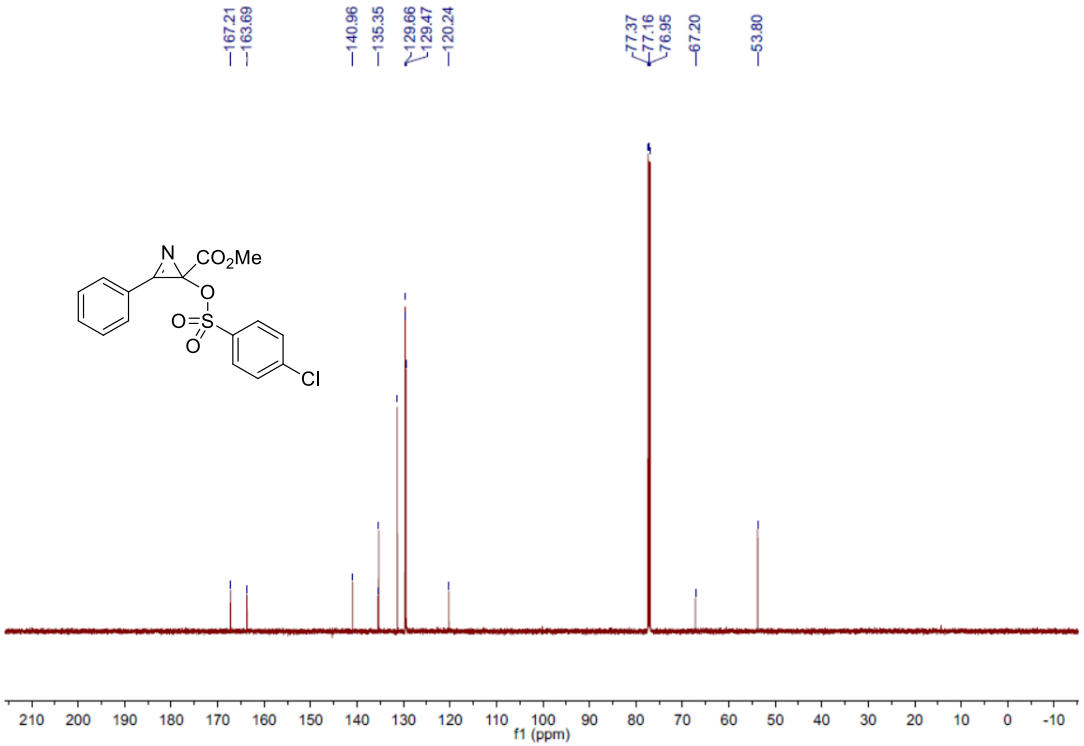
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3g**



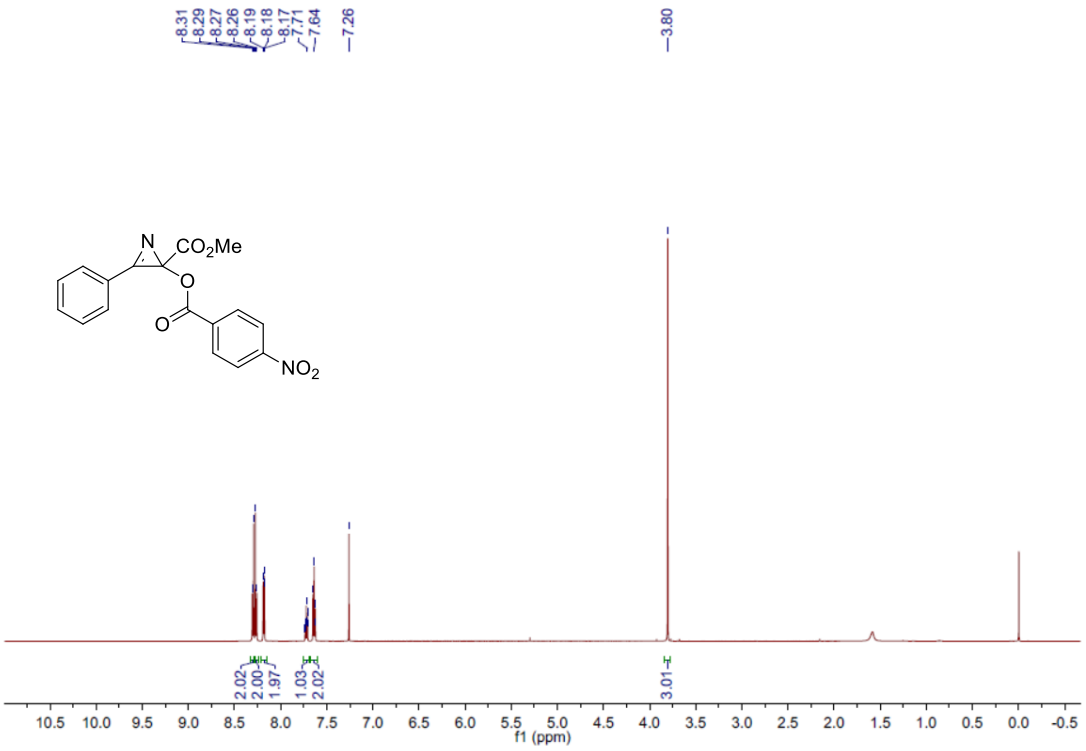
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3g**



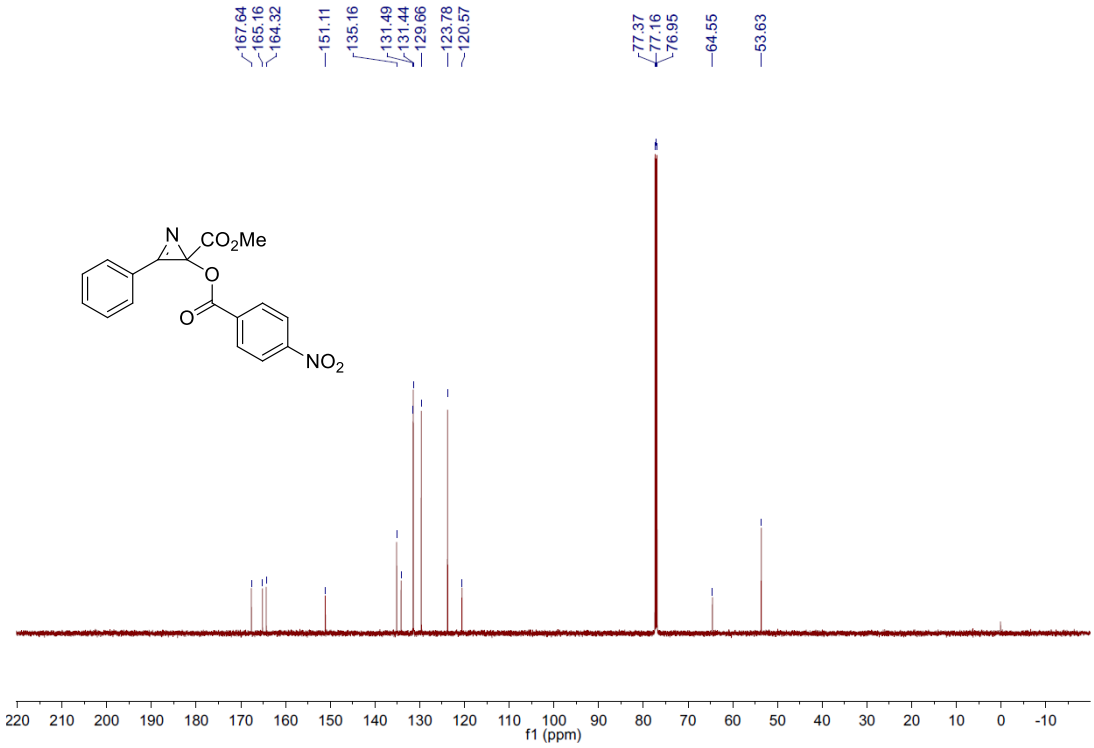
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3h**



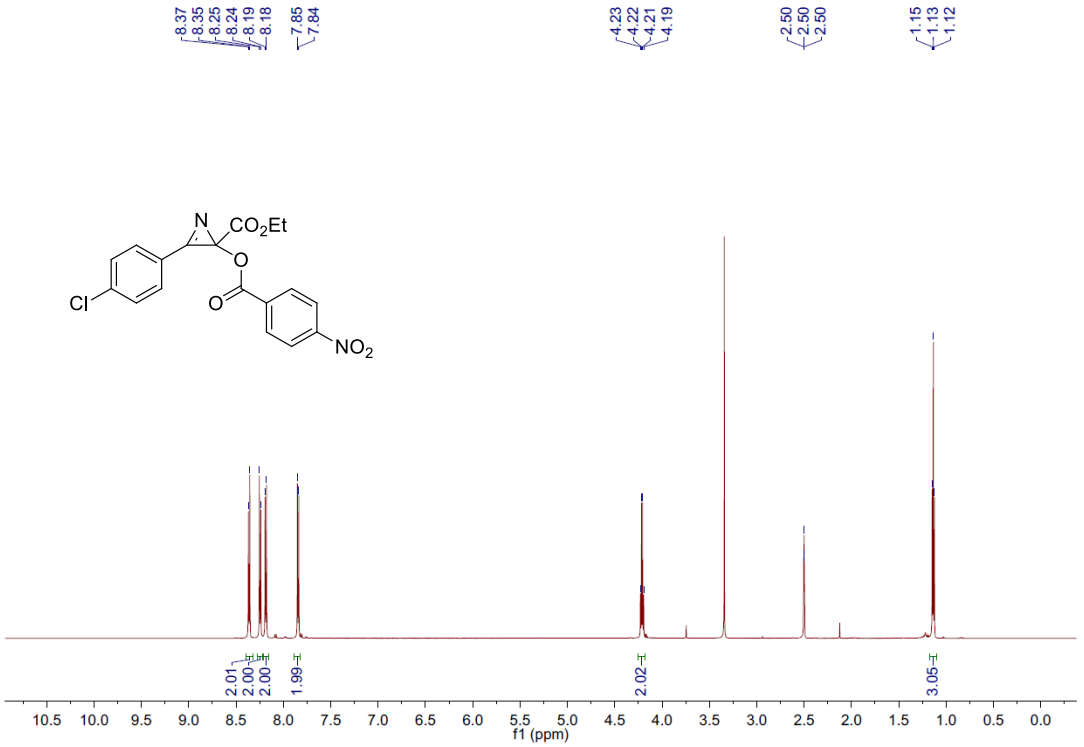
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **3h**



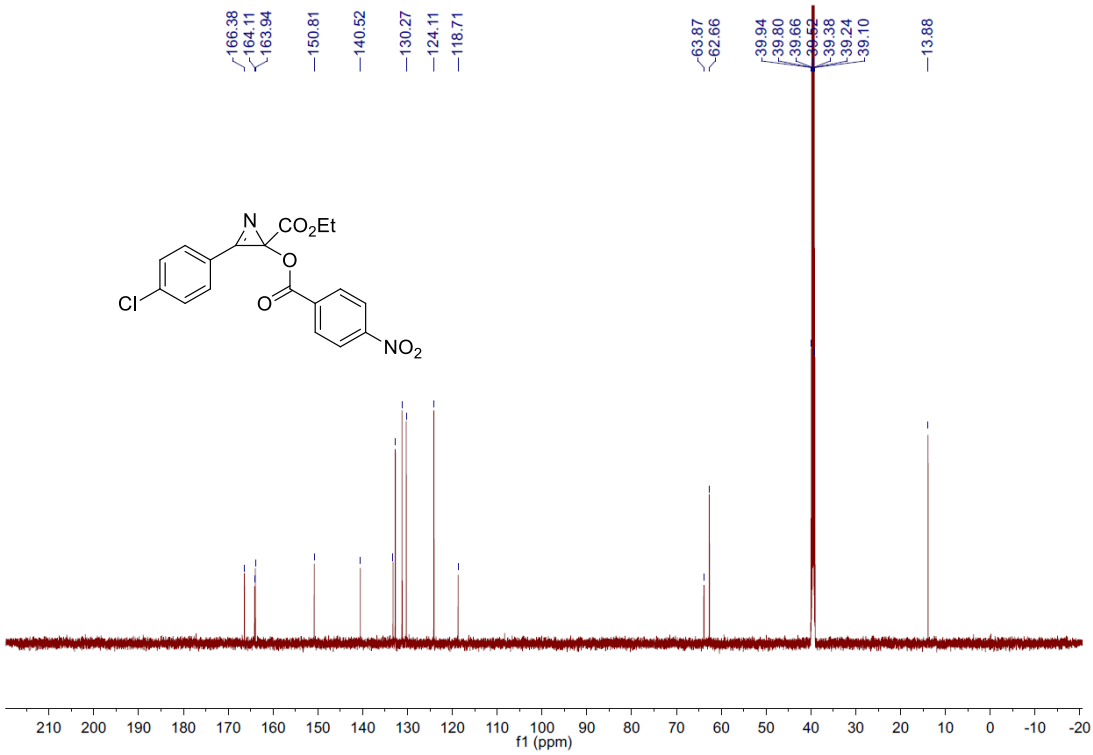
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4a**



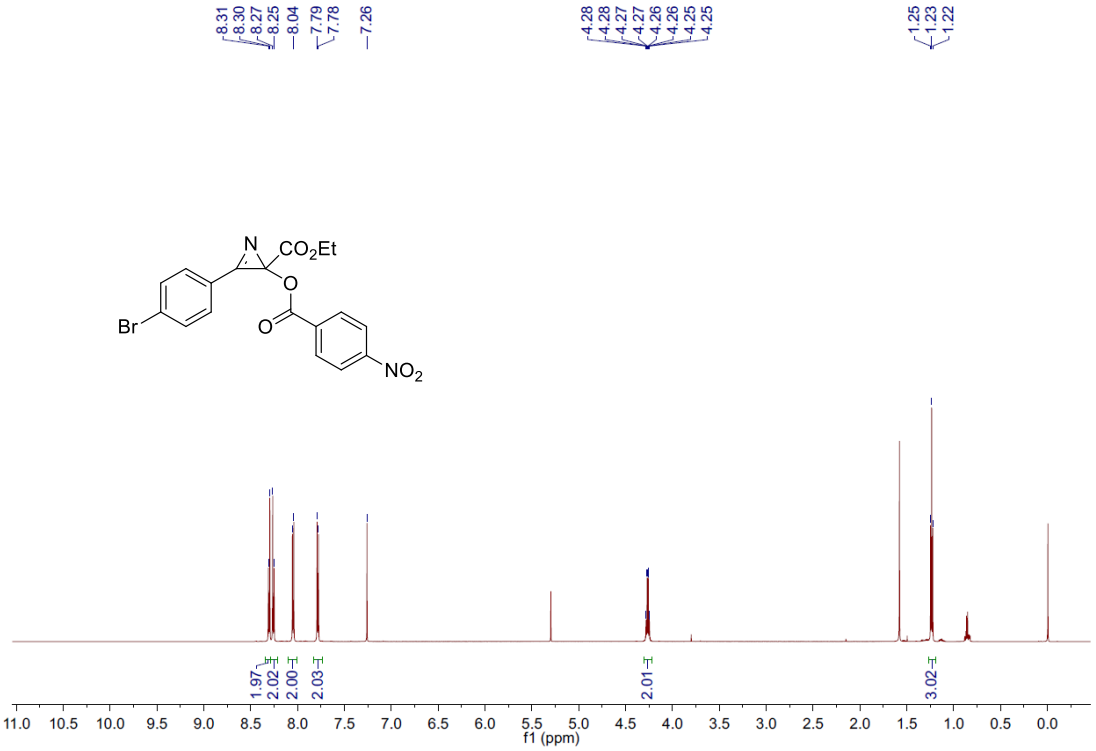
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4a**



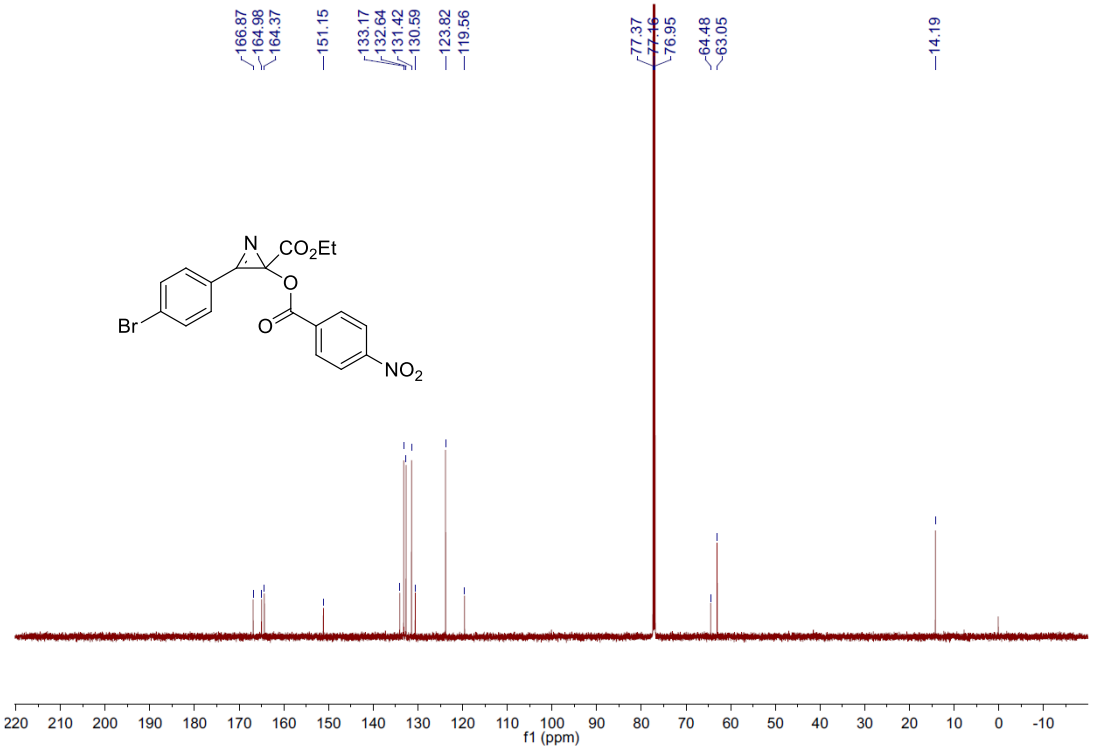
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4b**



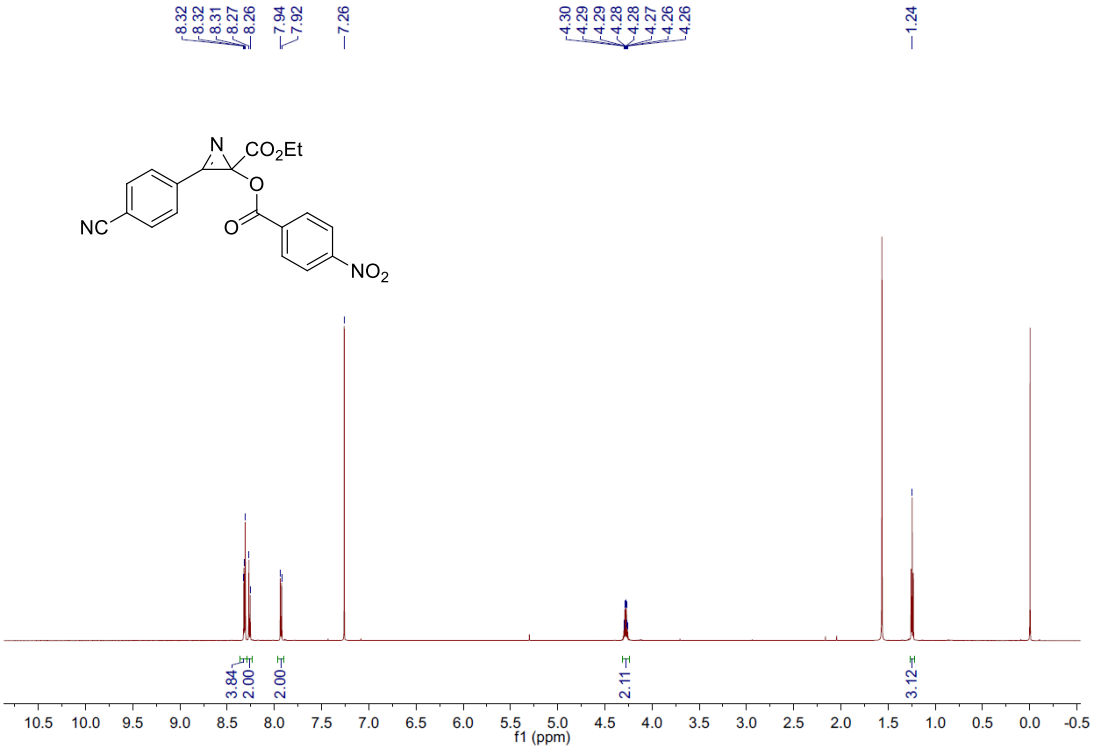
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **4b**



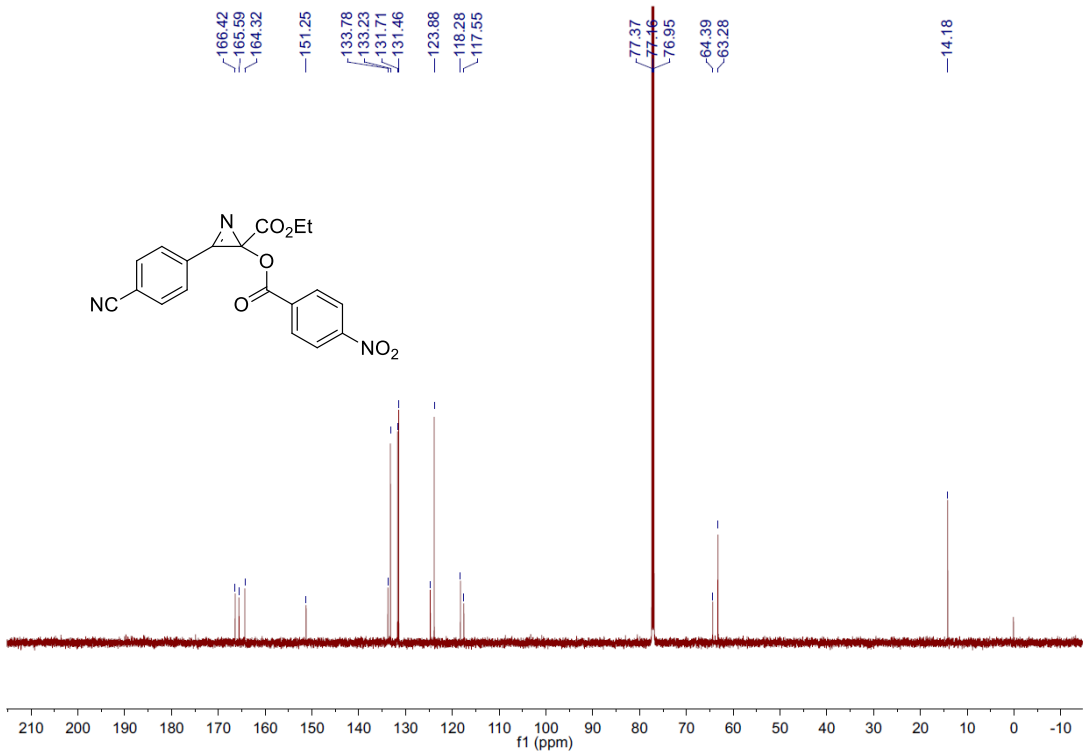
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4c**



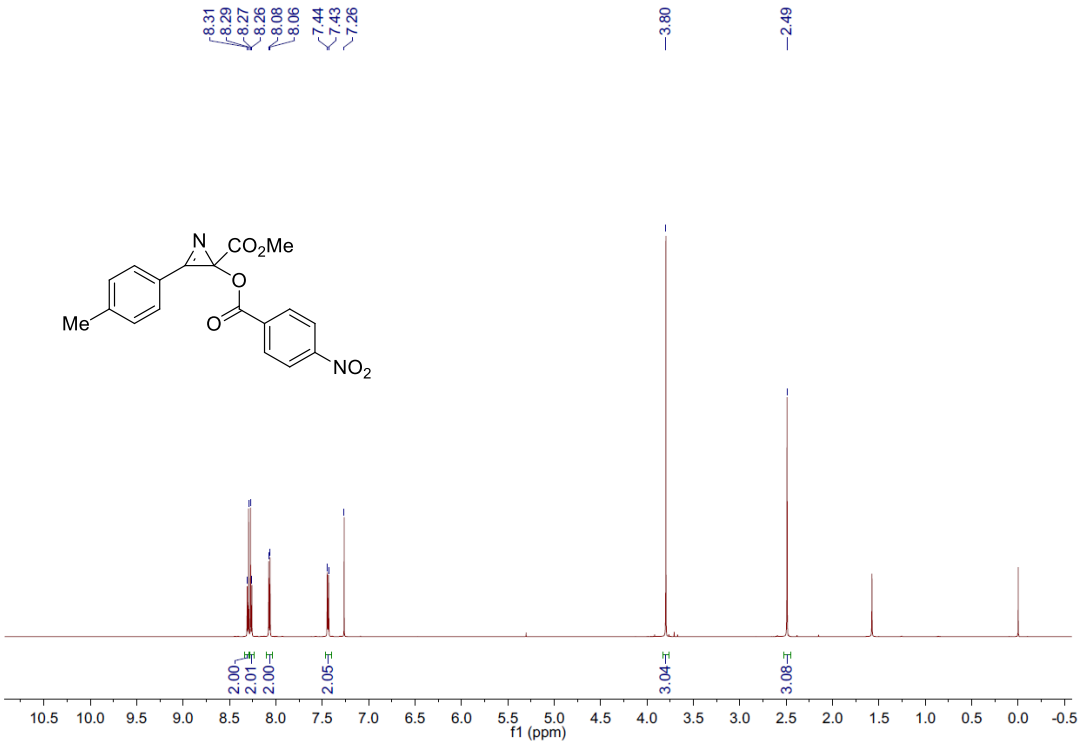
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4c**



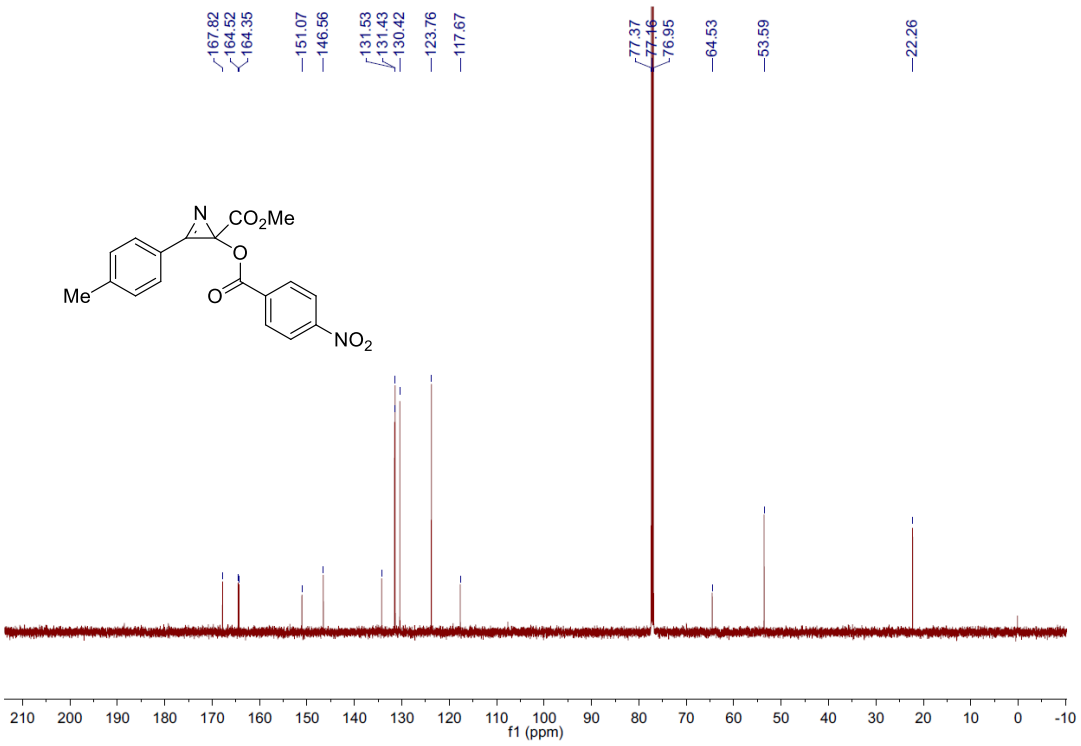
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4d**



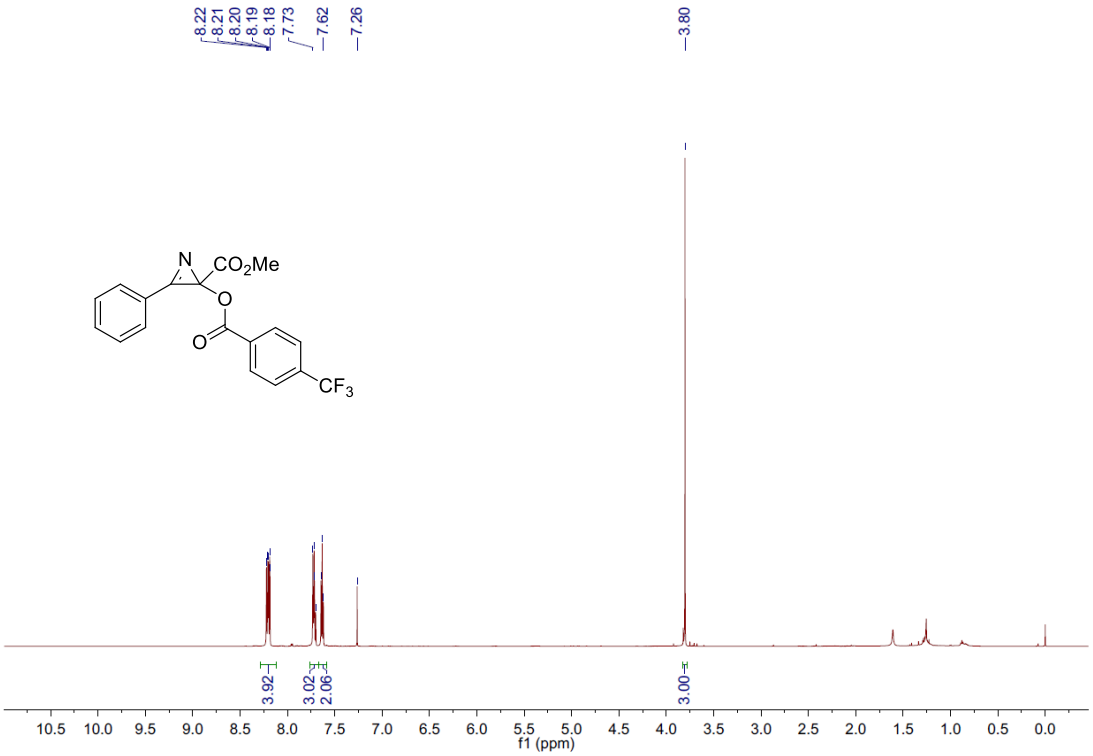
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4d**



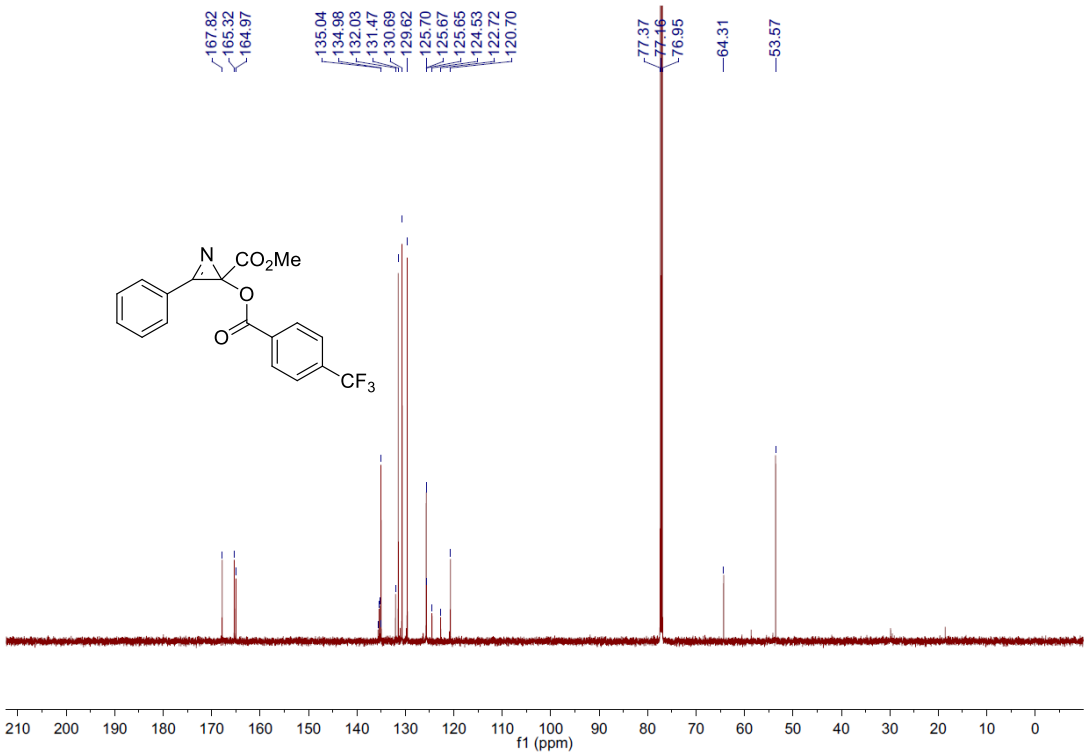
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4e**



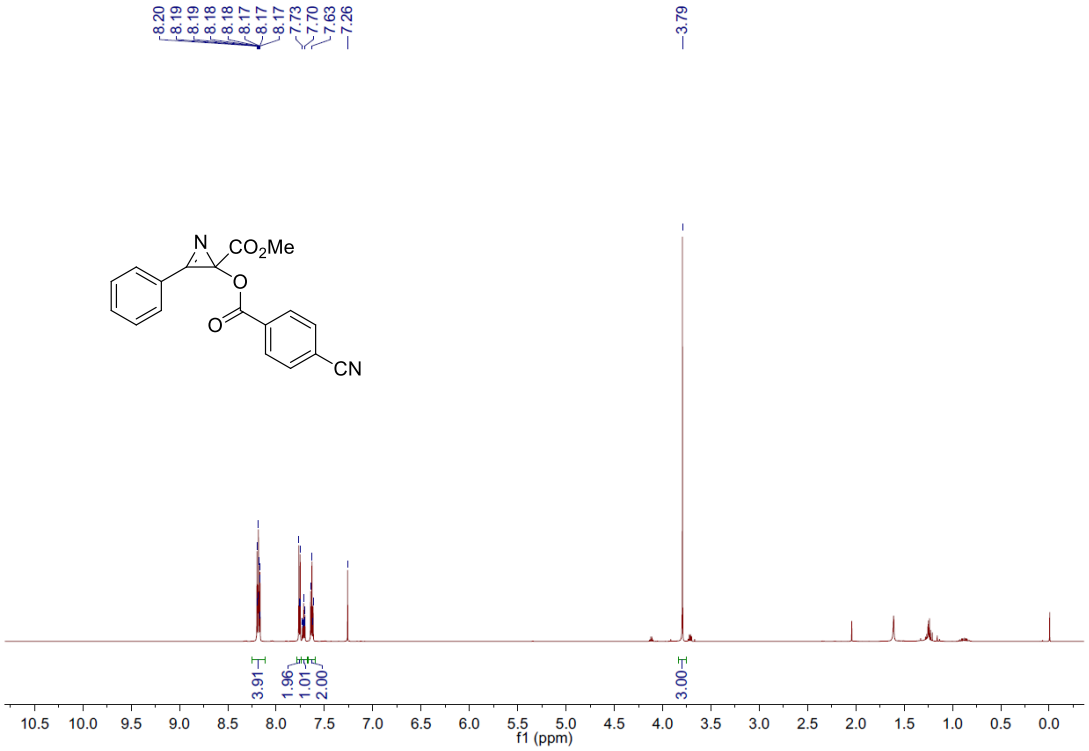
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4e**



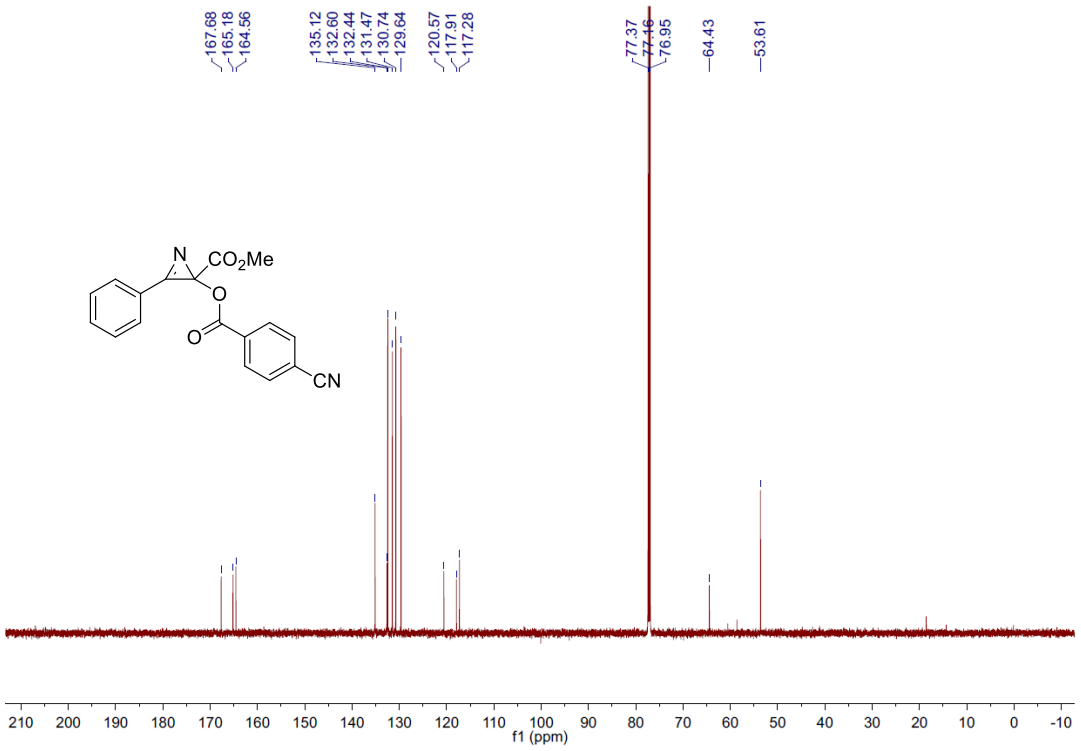
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4f**



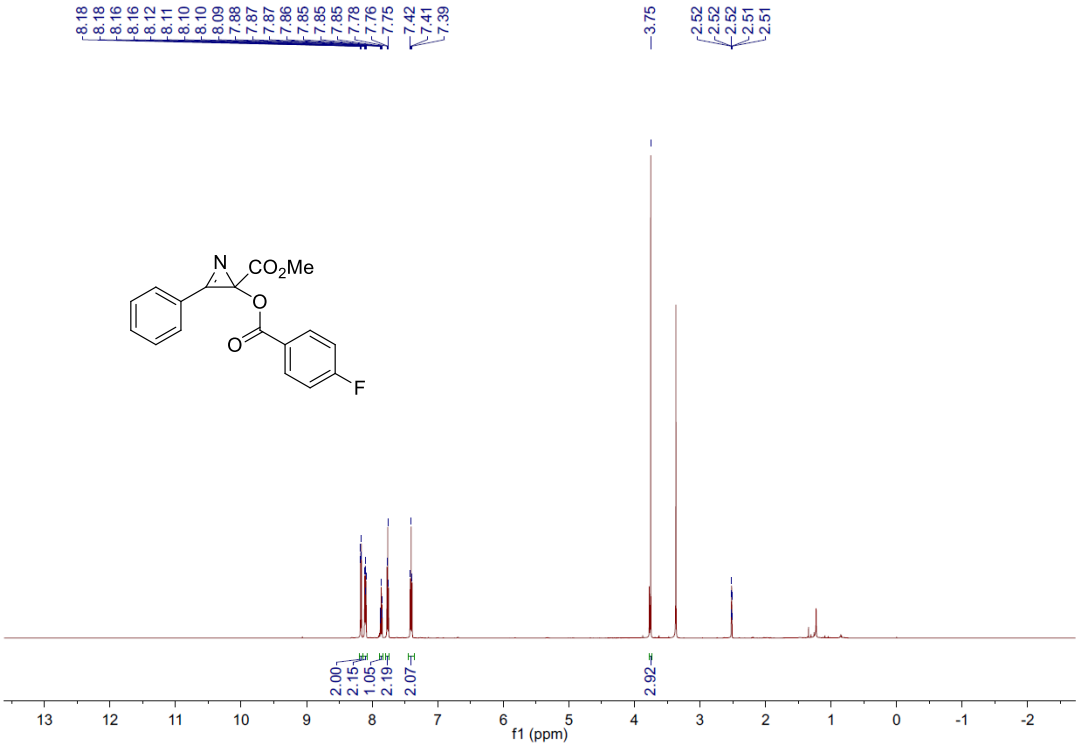
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4f**



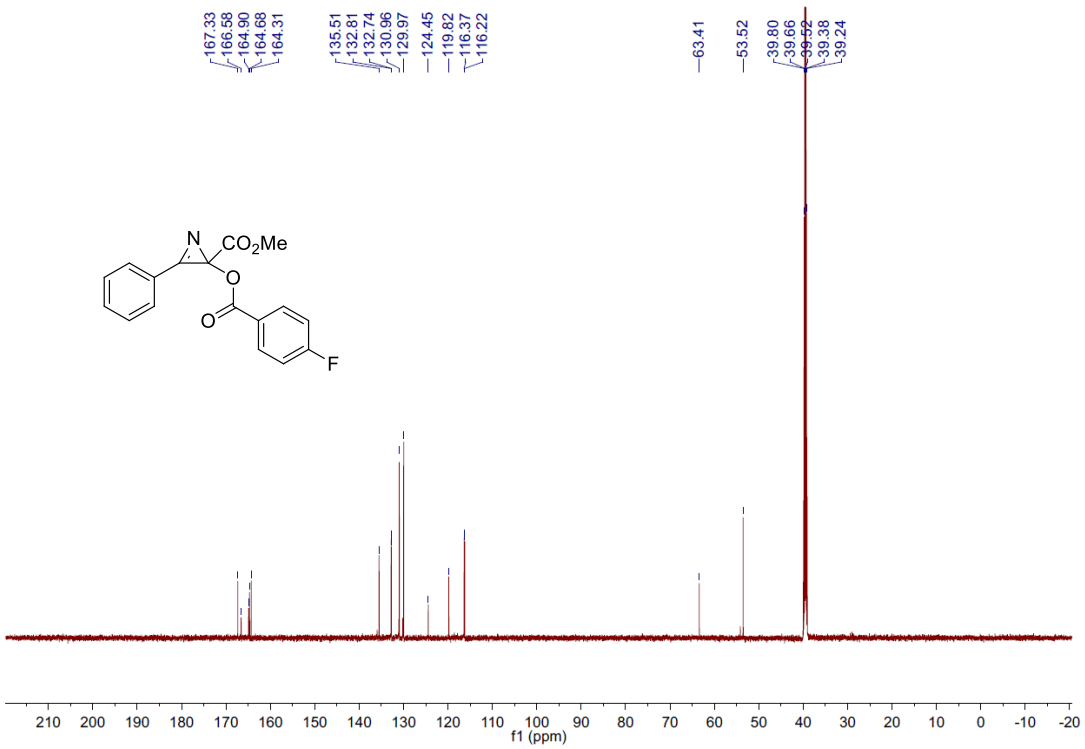
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4g**



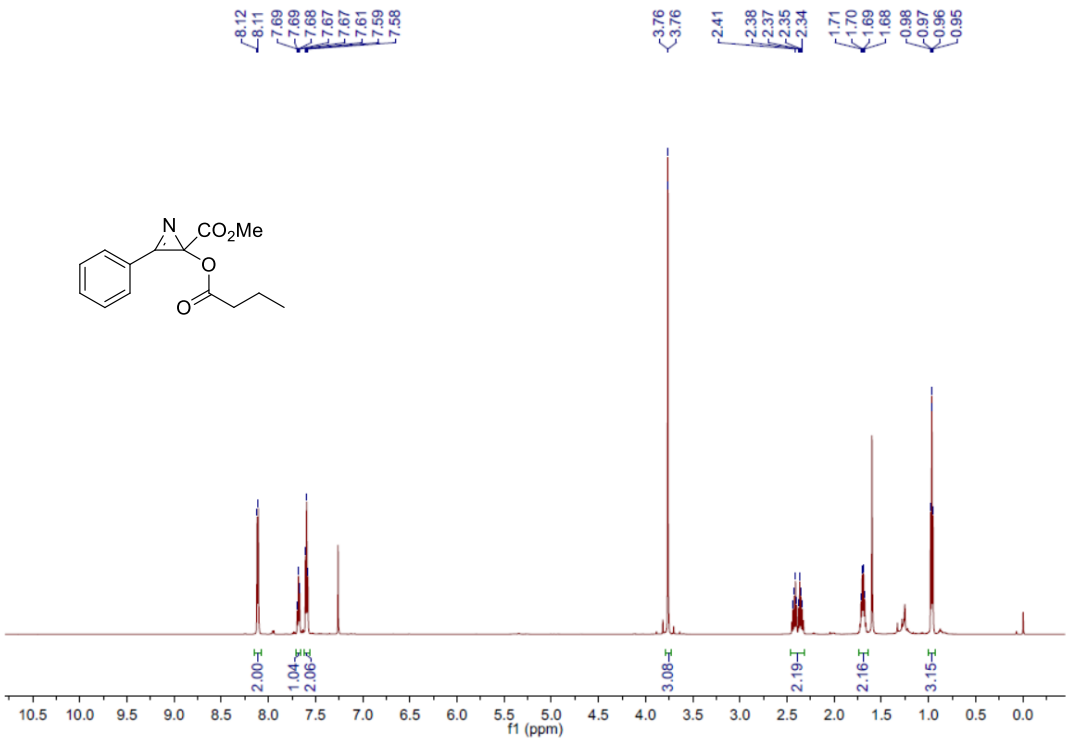
^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4g**



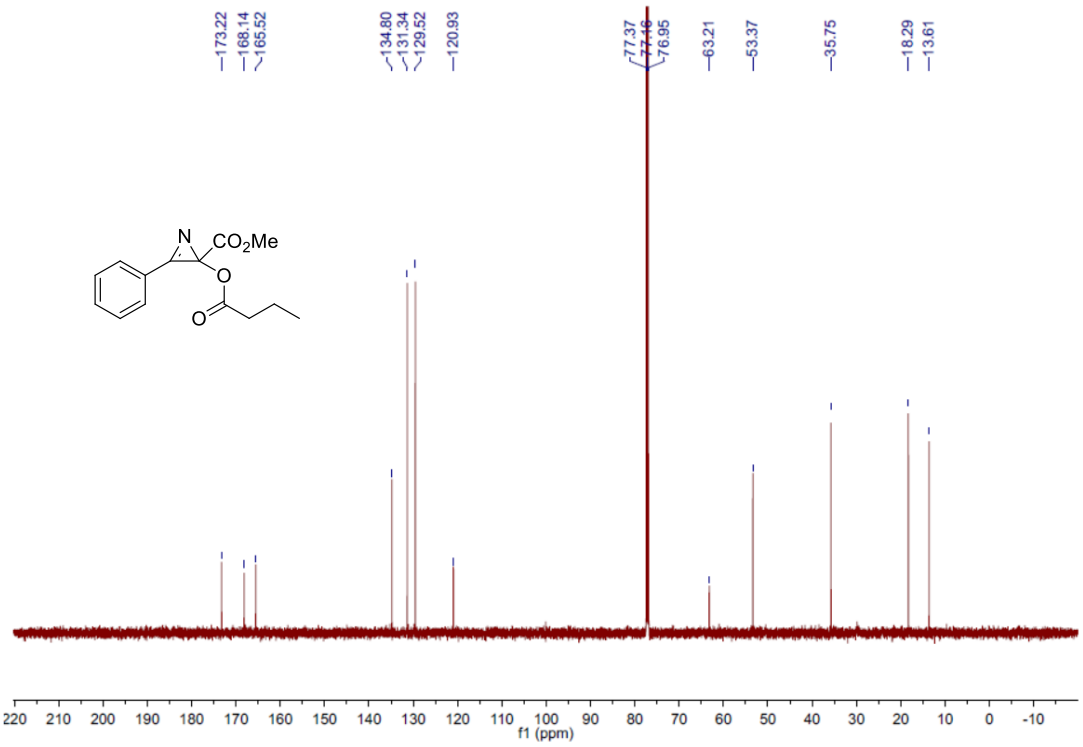
^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4h**



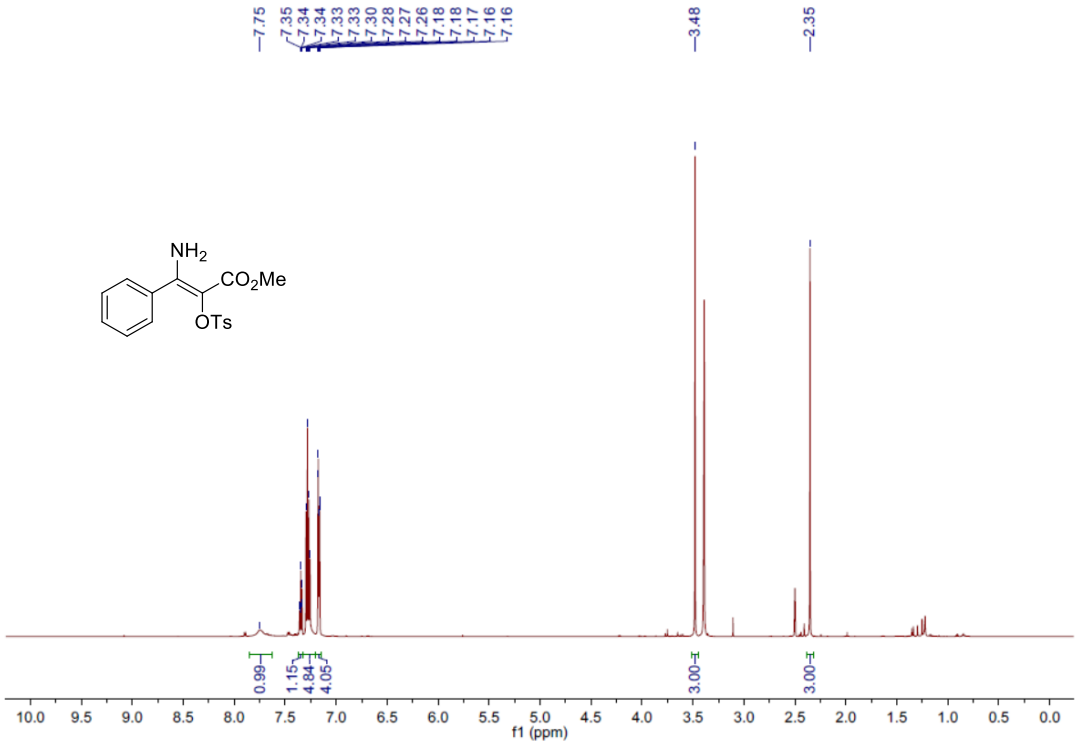
^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **4h**



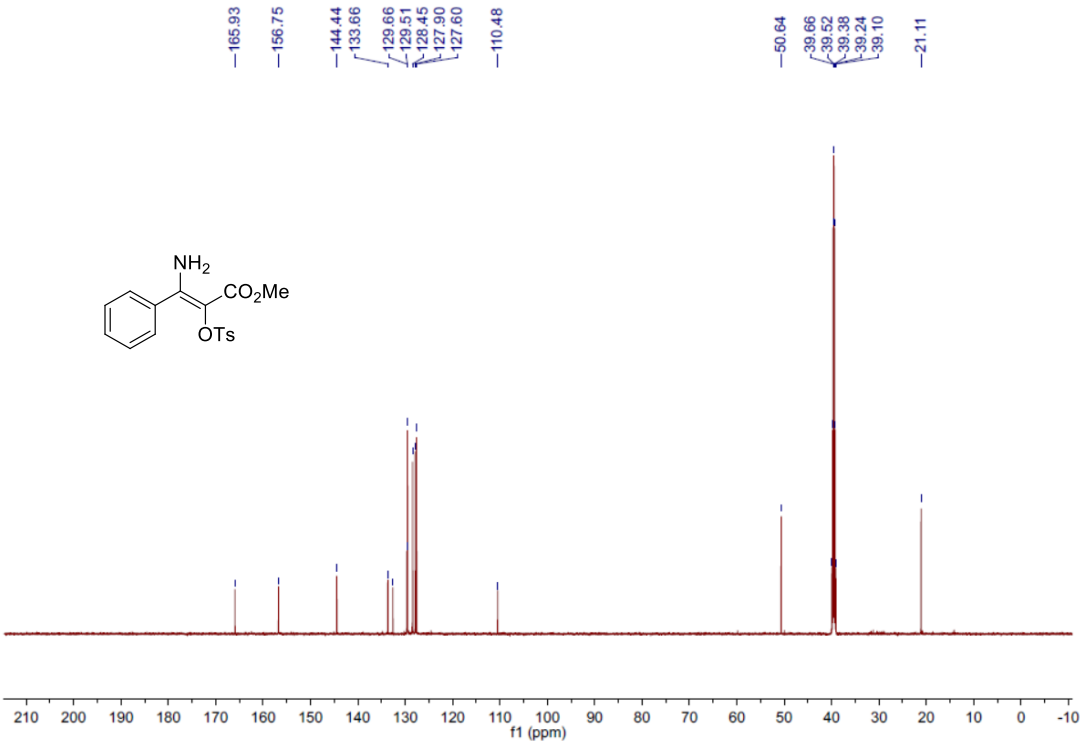
^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **4i**



^{13}C NMR (151 MHz, $CDCl_3$) spectra of compound **4i**



^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **5**



^{13}C NMR (151 MHz, DMSO-d_6) spectra of compound **5**