

**Supporting Information**

**One Pot Synthesis of Substituted Imidazopyridine and Thiazoles from Styrene in Water Assisted by NBS**

Mahesh H. Shinde and Umesh A. Kshirsagar\*

Department of Chemistry, Savitribai Phule Pune University (Formerly: University of Pune), Ganeshkhind, Pune- 411007, Maharashtra, INDIA.

*uakshirsagar@chem.unipune.ac.in*

**Table of contents**

|   |               |
|---|---------------|
| General   | <b>S1</b>     |
| General procedure   | <b>S2</b>     |
| Spectral and analytical data of all the compounds                           | <b>S3-S8</b>  |
| Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of all the compounds | <b>S9-S30</b> |

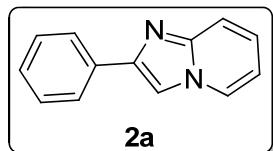
**General**

All chemicals were of reagent grade quality, purchased commercially from TCI-Chemicals, Sigma-Aldrich, or Spectrochem, and used without further purification except NBS. NBS was recrystallized from water using literature procedure. Purification by column chromatography was performed on Merck chromatographic silica gel (100-200 mesh). TLC analyses were performed using Merck silica gel 60 F<sub>254</sub> precoated aluminium plates. NMR spectra were recorded on Bruker Avance III (500MHz), or Varian Mercury (300 MHz) instruments; chemical shifts, given in ppm, are relative to Me<sub>4</sub>Si as the internal standard or to the residual solvent peak. HR-MS data were obtained using a Thermo-Scientific Bruker Daltonik GmbH, Germany Impact II UHR-ToF Mass Spectrometer ESI (Electron Spray Ionization).

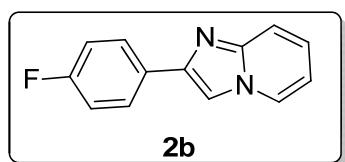
**General procedure for 2-substituted imidazo[1,2-a]pyridine (2):** *N*-Bromosuccinimide (2.0 mmole) was added to the flask containing styrene (1.0 mmole) and H<sub>2</sub>O (1.0 mL) at room temperature under nitrogen atmosphere. Reaction flask was immersed in oil bath and temperature was raised to 80 °C. Reaction mixture was stirred at 80 °C for 2 hr. The reaction mixture was then cooled to room temperature and 2-aminopyridine (2.0 mmole) was added. Reaction mixture was further heated to 80 °C for 2 hrs. After completion of reaction (checked by TLC), crude product was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vaccuo. The crude product was purified by silica gel column chromatography with hexane–ethyl acetate to give 2-substituted imidazo[1,2-a]pyridine.

**General procedure for the synthesis of 2, 4-disubstituted thiazoles (3):** *N*-Bromosuccinimide (2.0 mmole) was added to the flask containing styrene (1.0 mmole) and H<sub>2</sub>O (1.0 mL) at room temperature under nitrogen atmosphere. Reaction flask was immersed in oil bath and temperature was raised to 80 °C. Reaction mixture was stirred at 80 °C for 2 hr. The reaction mixture was then cooled to room temperature and thioamide (2.0 mmole) was added. Reaction mixture was further heated at 80 °C for 2 hrs. After completion of reaction (checked by TLC), crude product was extracted with ethyl acetate (3 x 20 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vaccuo. The crude product was purified by silica gel column chromatography with hexane to give 2, 4-disubstituted thiazoles.

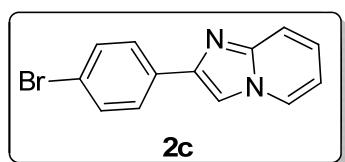
**Spectral and Analytical data:**



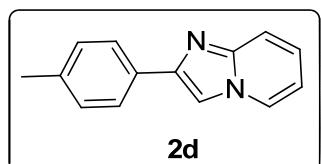
**2-phenylimidazo[1,2-a]pyridine (2a):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 6.80 (td,  $J = 0.92, 6.71$  Hz, 1H), 7.17-7.22 (m, 1H), 7.33-7.38 (m, 1H), 7.44-7.49 (m, 2H), 7.67 (d,  $J = 9.16$  Hz, 1H), 7.88 (s, 1H), 7.96-8.01 (m, 2H), 8.14 (dt,  $J = 6.71, 1.22$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  108.1, 112.5, 117.5, 124.7, 125.6, 126.1, 128.0, 128.7, 133.6, 145.6, 145.7; HRMS (ESI, m/z) calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2 = 195.0922$   $[\text{M} + \text{H}]^+$ , found 195.0920.



**2-(4-fluorophenyl)imidazo[1,2-a]pyridine (2b):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 6.79 (td,  $J = 0.92, 6.71$  Hz, 1H), 7.11-7.16 (m, 2H), 7.17-7.21 (m, 1H), 7.64 (dd,  $J = 0.92, 8.8$  Hz, 1H), 7.81 (s, 1H), 7.91-7.96 (m, 2H), 8.12 (dt,  $J = 1.22, 6.71$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  107.7, 112.5, 115.6 (d,  $J_{\text{C}-\text{F}} = 21.8$  Hz); 117.5, 124.7, 125.5, 127.7 (d,  $J_{\text{C}-\text{F}} = 8.1$  Hz), 130.0 (d,  $J_{\text{C}-\text{F}} = 3.63$  Hz), 145.4 (d,  $J_{\text{C}-\text{F}} = 90.83$  Hz), 161.7, 163.7; HRMS (ESI, m/z) calcd for  $\text{C}_{13}\text{H}_{10}\text{FN}_2 = 213.0828$   $[\text{M} + \text{H}]^+$ , found 213.0822.

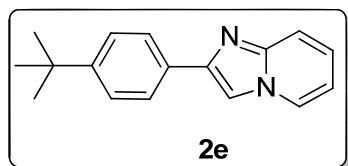


**2-(4-chlorophenyl)imidazo[1,2-a]pyridine (2c):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 6.79-6.84 (m, 1H), 7.18-7.24 (m, 1H), 7.56-7.60 (m, 2H), 7.65 (d,  $J = 9.16$  Hz, 1H), 7.81 (s, 1H), 7.91-7.96 (m, 2H), 8.10-8.14 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  108.2, 112.6, 117.6, 121.9, 124.9, 125.6, 127.6, 131.9, 132.8, 144.8, 145.8; HRMS (ESI, m/z) calcd for  $\text{C}_{13}\text{H}_{10}\text{BrN}_2 = 273.0027$   $[\text{M} + \text{H}]^+$ , found 273.0022.

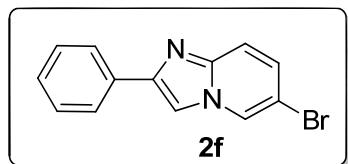


**2-(p-tolyl)imidazo[1,2-a]pyridine (2d):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 2.41 (s, 3H), 6.75 (t,  $J = 6.71$  Hz, 1H), 7.13-7.18 (m, 1H), 7.26 (d,  $J = 7.93$  Hz, 2H), 7.64 (d,  $J = 9.16$  Hz, 1H), 7.81 (s, 1H), 7.87 (d,  $J = 7.93$  Hz, 2H), 8.09 (d,  $J$

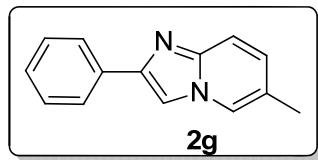
= 7.02 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.2, 107.7, 112.2, 117.4, 124.4, 125.5, 125.9, 129.4, 130.9, 137.7, 145.6, 145.9; HRMS (ESI, m/z) calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2 = 209.1079$  [ $\text{M} + \text{H}]^+$ , found 209.1079.



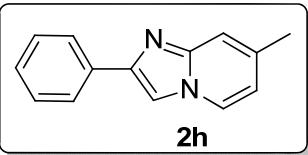
**2-(4-(tert-butyl)phenyl)imidazo[1,2-a]pyridine (2e):** white solid,  $R_f = 0.3$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 1.38 (s, 9H), 6.79 (dt,  $J = 1.22, 6.71$  Hz, 1H), 7.15-7.21 (m, 1H), 7.46-7.51 (m, 2H), 7.67 (dd,  $J = 0.92, 9.16$  Hz, 1H), 7.86 (s, 1H), 7.89-7.93 (m, 2H), 8.13 (dt,  $J = 1.22, 6.71$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.3, 34.9, 107.8, 112.3, 117.5, 124.5, 125.5, 125.6, 125.8, 130.8, 140.2, 145.6, 151.1; HRMS (ESI, m/z) calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2 = 251.1548$  [ $\text{M} + \text{H}]^+$ , found 251.1545.



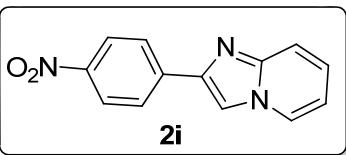
**6-bromo-2-phenylimidazo[1,2-a]pyridine (2f):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 7.23 (dd,  $J = 1.83, 9.77$  Hz, 1H), 7.35-7.39 (m, 1H), 7.43-7.48 (m, 2H), 7.54 (d,  $J = 9.77$  Hz, 1H), 7.81 (s, 1H), 7.92-7.96 (m, 2H), 8.23-8.26 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  107.1, 108.3, 118.0, 125.5, 126.1, 128.2, 128.3, 128.8, 133.0, 144.0, 146.4; HRMS (ESI, m/z) calcd for  $\text{C}_{13}\text{H}_{10}\text{BrN}_2 = 273.0027$  [ $\text{M} + \text{H}]^+$ , found 273.0023.



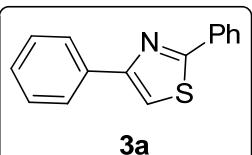
**6-methyl-2-phenylimidazo[1,2-a]pyridine (2g):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ): 2.31 (s, 3H), 7.00-7.05 (m, 1H), 7.26-7.36 (m, 1H), 7.39-7.48 (m, 2H), 7.54 (d,  $J = 8.97$  Hz, 1H), 7.77 (s, 1H), 7.88-7.97 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  18.1, 107.9, 116.5, 122.5, 123.4, 126.0, 128.0, 128.4, 128.7, 133.4, 144.3, 144.8; HRMS (ESI, m/z) calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2 = 209.1079$  [ $\text{M} + \text{H}]^+$ , found 209.1075.



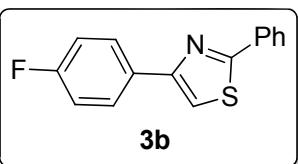
**7-methyl-2-phenylimidazo[1,2-a]pyridine (2h):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 2.4 (s, 3H), 6.61 (dd,  $J = 1.83, 6.71$  Hz, 1H), 7.31-7.36(m, 1H), 7.38-7.41 (m, 1H), 7.42-7.47 (m, 2H), 7.77 (s, 1H), 7.98-8.00 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.4, 107.5, 115.1, 115.8, 124.7, 125.9, 127.8, 128.7, 133.8, 135.7, 145.3, 14.1; HRMS (ESI, m/z) calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2 = 209.1079$   $[\text{M} + \text{H}]^+$ , found 209.1077.



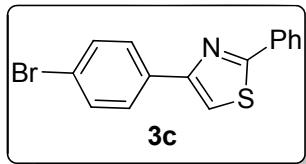
**2-(4-nitrophenyl)imidazo[1,2-a]pyridine (2i):** yellow solid,  $R_f = 0.2$  (ethyl acetate:hexane, 4:6);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$  [7:3]): 6.90 (td,  $J = 0.92, 6.87$  Hz, 1H), 7.28-7.31 (m, 1H), 7.60 (d,  $J = 9.61$  Hz, 1H), 8.07 (dt,  $J = 1.98, 9.00$  Hz, 2H), 8.12 (s, 1H), 8.25-8.30 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3 + \text{CD}_3\text{OD}$  [7:3]):  $\delta$  114.5, 117.4, 120.9, 128.1, 130.2 (2C), 130.4, 143.8, 146.9, 150.0, 151.1; HRMS (ESI, m/z) calcd for  $\text{C}_{13}\text{H}_{10}\text{N}_3\text{O}_2 = 240.0773$   $[\text{M} + \text{H}]^+$ , found 240.0772.



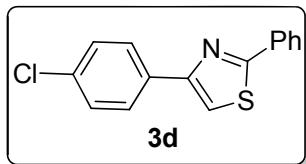
**2,4-diphenylthiazole (3a):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.23-7.39 (m, 1H), 7.43-7.49 (m, 6H), 8.00 (m, 1H), 8.02-8.03 (m, 1H), 8.05-8.08 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  112.6, 126.4, 126.6, 128.1, 128.7, 128.9, 130.0, 133.7, 134.5, 156.2, 167.8; HRMS (ESI, m/z) calcd for  $\text{C}_{15}\text{H}_{12}\text{NS} = 238.0690$   $[\text{M} + \text{H}]^+$ , found 238.0688.



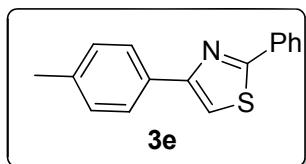
**4-(4-fluorophenyl)-2-phenylthiazole (3b):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.12 (t,  $J = 8.79$  Hz, 2H), 7.38 (s, 1H), 7.42-7.50 (m, 3H), 7.96 (dd,  $J = 5.57, 8.79$  Hz, 2H) 8.00-8.04 (m, 2H); HRMS (ESI, m/z) calcd for  $\text{C}_{15}\text{H}_{11}\text{FNS} = 256.0596$   $[\text{M} + \text{H}]^+$ , found 256.0590.



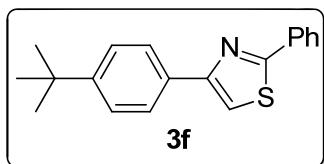
**4-(4-bromophenyl)-2-phenylthiazole (3c):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 7.43-7.46 (m, 3H), 7.51-7.57 (m, 3H), 7.84-7.87 (m, 2H), 8.01-8.06 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  113.0, 126.6, 128.0, 128.7, 128.9, 130.2, 131.8, 133.4, 133.5, 155.0, 168.1; HRMS (ESI, m/z) calcd for  $\text{C}_{15}\text{H}_{11}\text{BrNS} = 315.9796$  [ $\text{M} + 2\text{H}]^+$ , found 317.9768.



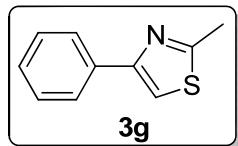
**4-(4-chlorophenyl)-2-phenylthiazole (3d):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.40-7.50 (m, 5H), 7.51-7.55 (m, 1H), 7.92 (s, 1H), 7.95 (s, 1H), 8.01-8.07 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  112.9, 126.5, 128.3, 128.8, 128.9, 130.1, 131.8, 133.5, 133.9, 155.0, 168.1; HRMS (ESI, m/z) calcd for  $\text{C}_{15}\text{H}_{11}\text{ClNS} = 272.0301$  [ $\text{M} + \text{H}]^+$ , found 272.0301.



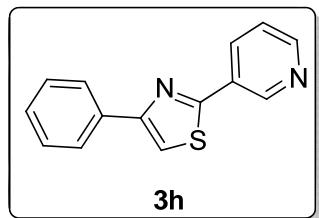
**2-phenyl-4-(p-tolyl)thiazole (3e):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 2.42 (s, 3H), 7.26-7.30 (m, 2H), 7.42 (s, 1H), 7.45-7.49 (m, 3H), 7.89-7.94 (m, 2H), 8.04-8.08 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  21.3, 111.8, 126.3, 126.6, 128.7, 128.9, 129.4, 129.9, 131.8, 133.8, 156.3, 167.7; HRMS (ESI, m/z) calcd for  $\text{C}_{16}\text{H}_{14}\text{NS} = 252.0847$  [ $\text{M} + \text{H}]^+$ , found 252.0845.



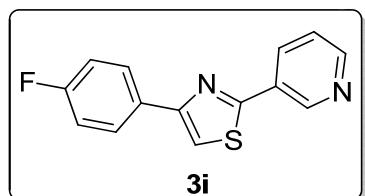
**4-(4-(tert-butyl)phenyl)-2-phenylthiazole (3f):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 1.29 (s, 9H), 7.34-7.42 (m, 6H), 7.82-7.87 (m, 2H), 7.95-8.00 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  31.3, 34.6, 112.0, 125.6, 126.2, 126.6, 128.9, 130.0, 131.8, 133.8, 151.3, 156.4, 167.7; HRMS (ESI, m/z) calcd for  $\text{C}_{19}\text{H}_{20}\text{NS} = 294.1316$  [ $\text{M} + \text{H}]^+$ , found 294.1308.



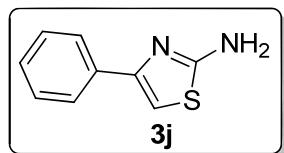
**2-methyl-4-phenylthiazole (3g):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 2.78 (s, 3H), 7.29-7.35 (m, 2H), 7.38-7.45 (m, 2H), 7.88 (d, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.3, 112.2, 126.3, 128.0, 128.7, 134.5, 155.1, 165.9; HRMS (ESI, m/z) calcd for  $\text{C}_{10}\text{H}_{10}\text{NS} = 176.0534$   $[\text{M} + \text{H}]^+$ , found 176.0530.



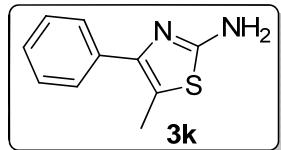
**4-phenyl-2-(pyridin-3-yl)thiazole (3h):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ): 7.35-7.51 (m, 4H), 7.55 (s, 1H), 7.98-8.03 (m, 2H), 8.31-8.37 (m, 1H), 8.68 (dd,  $J = 0.95, 4.76$  Hz, 1H), 9.26 (d,  $J = 1.43$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  113.3, 123.7, 126.4, 128.4, 128.8, 129.7, 133.7, 134.0, 147.7, 151.7, 156.7, 164.3; HRMS (ESI, m/z) calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_2\text{S} = 239.0643$   $[\text{M} + \text{H}]^+$ , found 239.0640.



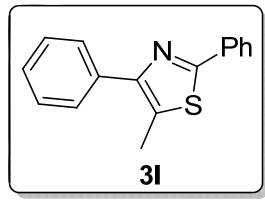
**4-(4-fluorophenyl)-2-(pyridin-3-yl)thiazole (3i):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 7.13-7.20 (m, 2H), 7.40-7.45 (m, 1H), 7.49 (s, 1H), 7.96-8.00 (m, 2H), 8.31-8.35 (m, 1H), 8.69 (dd,  $J = 1.83$  Hz, 1H), 9.24-9.27 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  128.8, 115.7 (d,  $J_{\text{C-F}} = 21.8$  Hz), 123.7, 128.2 (d,  $J_{\text{C-F}} = 8.17$  Hz), 129.7, 130.4 (d,  $J_{\text{C-F}} = 3.63$  Hz), 133.7, 147.8, 150.9, 155.8, 161.9, 164.3 (d,  $J_{\text{C-F}} = 79.2$  Hz); HRMS (ESI, m/z) calcd for  $\text{C}_{14}\text{H}_{10}\text{FN}_2\text{S} = 257.0549$   $[\text{M} + \text{H}]^+$ , found 257.0543.



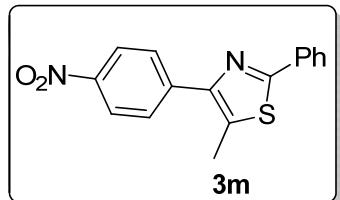
**4-phenylthiazol-2-amine (3j):** white solid,  $R_f = 0.2$  (ethyl acetate:hexane, 2:8);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ): 5.10 (brs. s, 2H), 6.72 (s, 1H), 7.27-7.32 (m, 1H), 7.35-7.40 (m, 2H), 7.75-7.80 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  102.8, 126.0, 127.7, 128.6, 134.7, 151.3, 167.4; HRMS (ESI, m/z) calcd for  $\text{C}_9\text{H}_9\text{N}_2\text{S} = 177.0486$   $[\text{M} + \text{H}]^+$ , found 177.0481



**5-methyl-4-phenylthiazol-2-amine (3k):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.37 (s, 3H), 7.29 (dt,  $J = 2.29, 7.78$  Hz, 1H), 7.35-7.41 (m, 2H), 7.51-7.55 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.3, 117.6, 127.2, 128.2, 128.3, 135.0, 146.0, 163.9; HRMS (ESI, m/z) calcd for  $\text{C}_{10}\text{H}_{11}\text{N}_2\text{S} = 191.0643$   $[\text{M} + \text{H}]^+$ , found 191.0635.



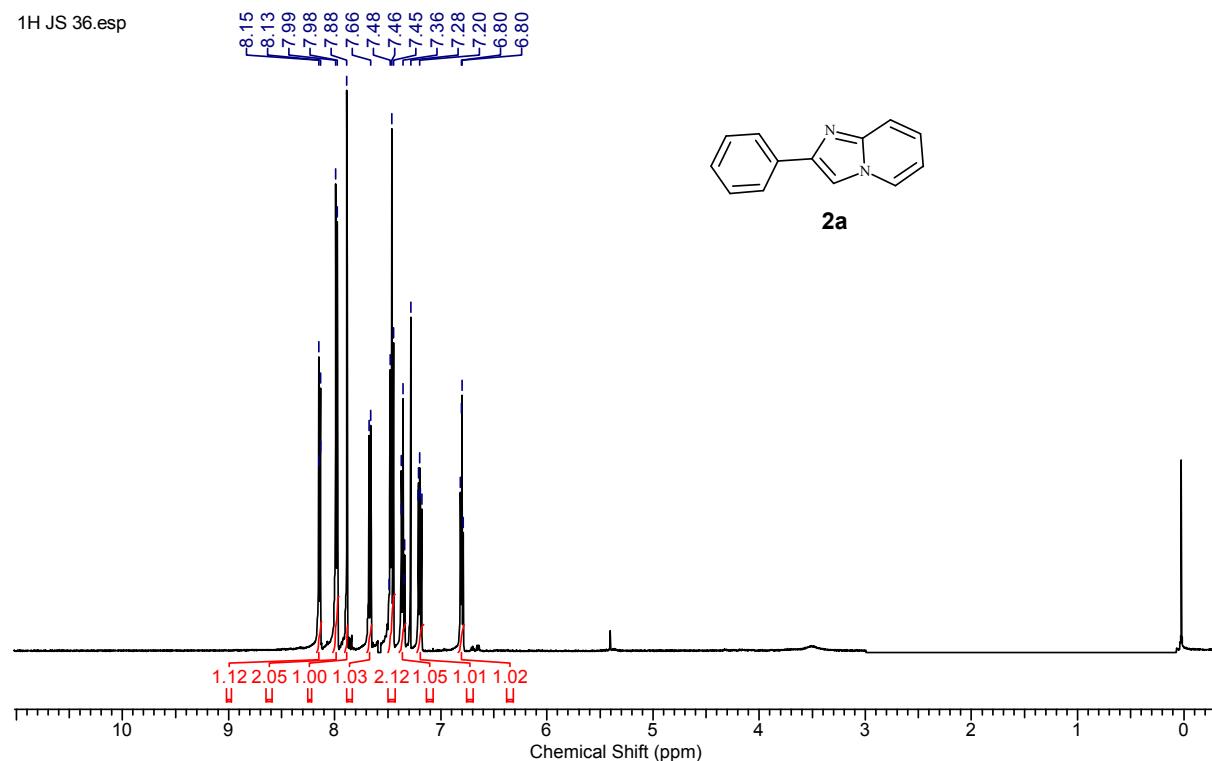
**5-methyl-2,4-diphenylthiazole (3l):** white solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.60 (s, 3H), 7.36-7.48 (m, 6H), 7.73 (dd,  $J = 1.37, 8.24$  Hz, 2H), 7.96 (dd,  $J = 1.83, 8.24$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.8, 126.3, 127.6, 128.4, 128.6, 128.8, 129.6, 133.8, 135.1, 151.9, 163.6; HRMS (ESI, m/z) calcd for  $\text{C}_{16}\text{H}_{14}\text{NS} = 252.0847$   $[\text{M} + \text{H}]^+$ , found 252.0841.



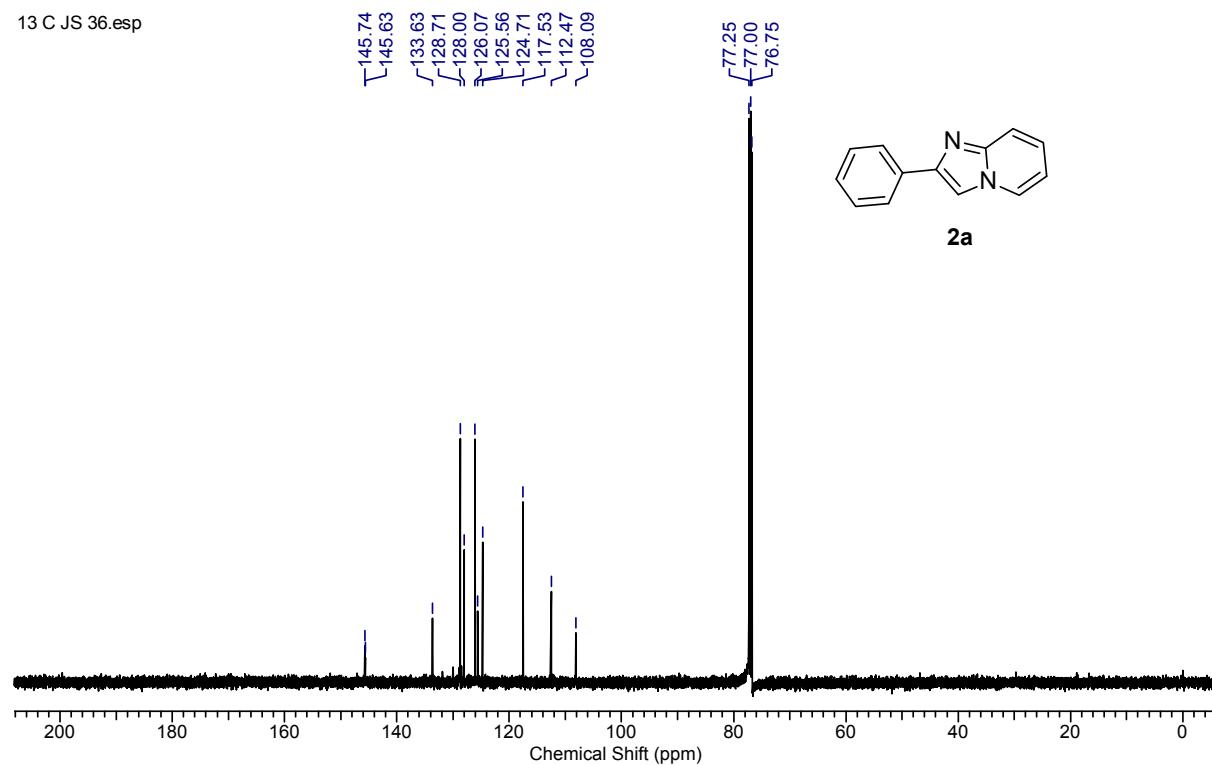
**5-methyl-4-(4-nitrophenyl)-2-phenylthiazole (3m):** Yellow solid,  $R_f = 0.6$  (ethyl acetate:hexane, 1:9);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.69 (s, 3H), 7.46-7.48 (m, 3H), 7.95-8.00 (m, 4H), 8.34 (dt,  $J = 1.98, 8.85$  Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.1, 123.7, 126.3, 129.0, 129.1, 130.1, 131.4, 132.3, 141.4, 146.8, 149.4, 164.4; HRMS (ESI, m/z) calcd for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_2\text{S} = 297.0698$   $[\text{M} + \text{H}]^+$ , found 297.0692.

**Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra:**

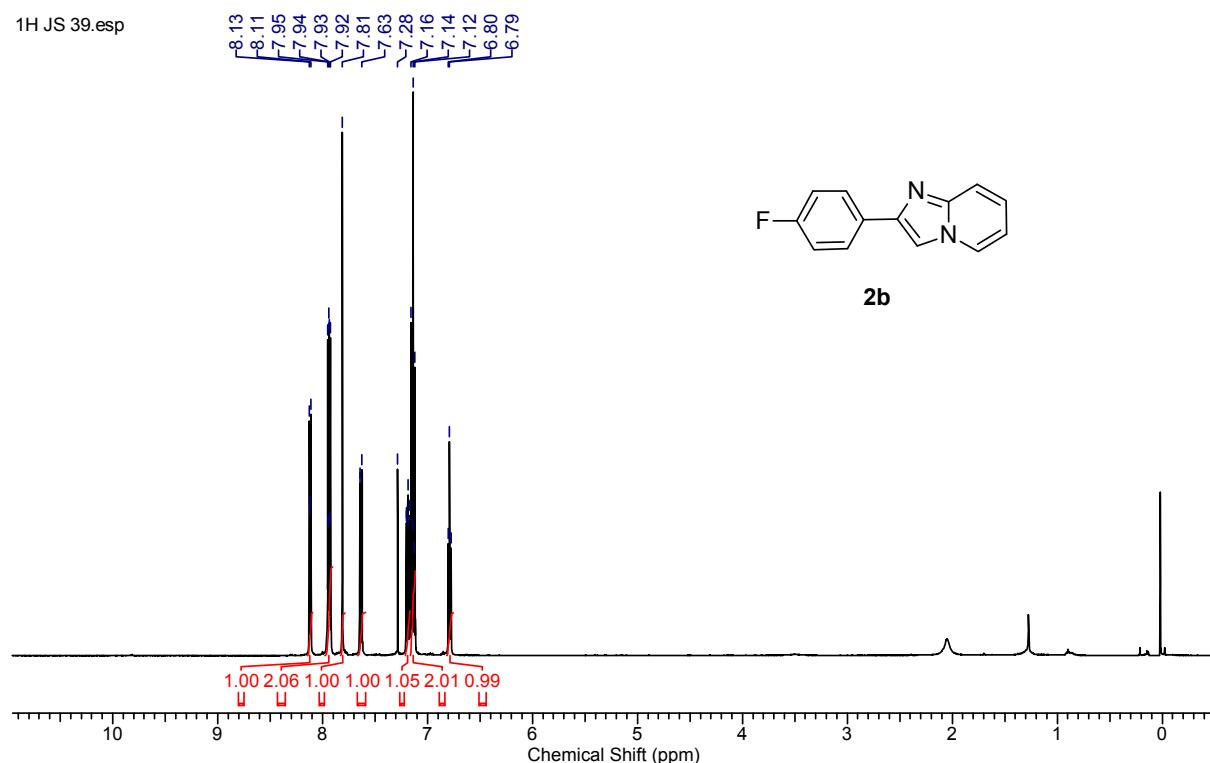
$^1\text{H}$  NMR spectrum for compound **2a** ( $\text{CDCl}_3$ , 500 MHz)



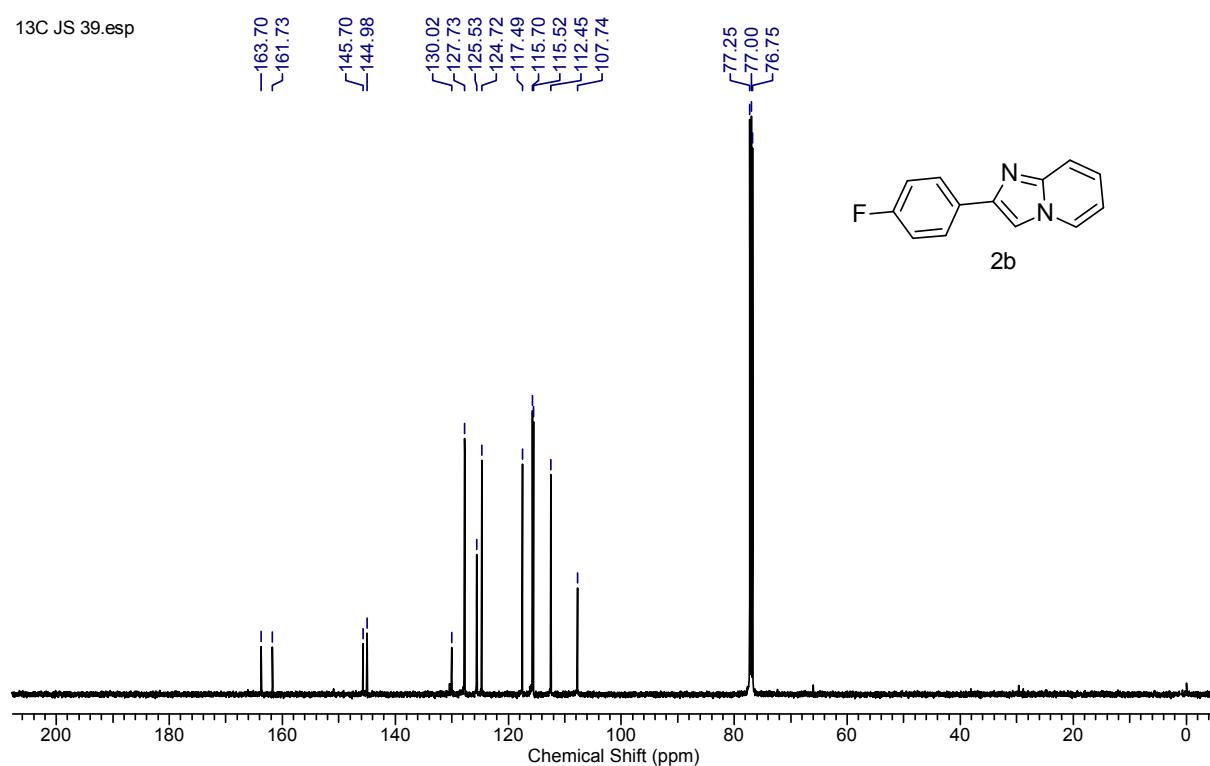
$^{13}\text{C}$  NMR spectrum for compound **2a** ( $\text{CDCl}_3$ , 125 MHz)



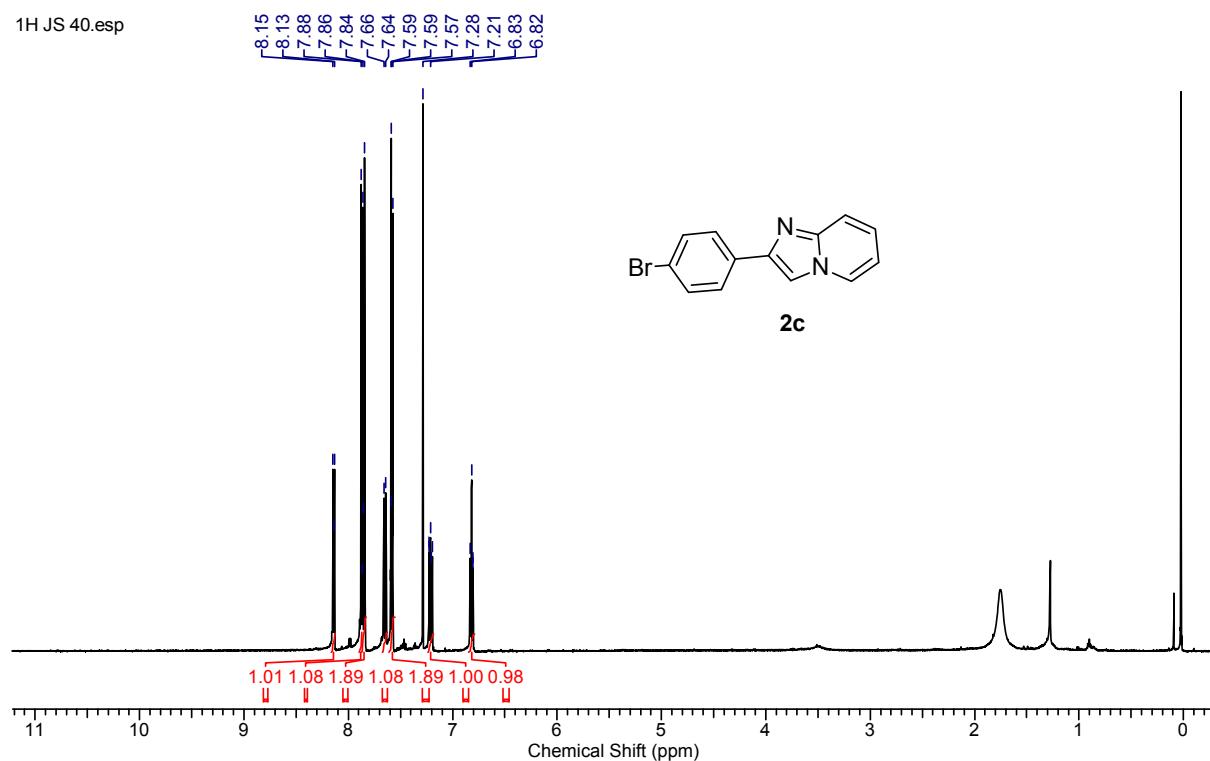
<sup>1</sup>H NMR spectrum for compound **2b** (CDCl<sub>3</sub>, 500 MHz)



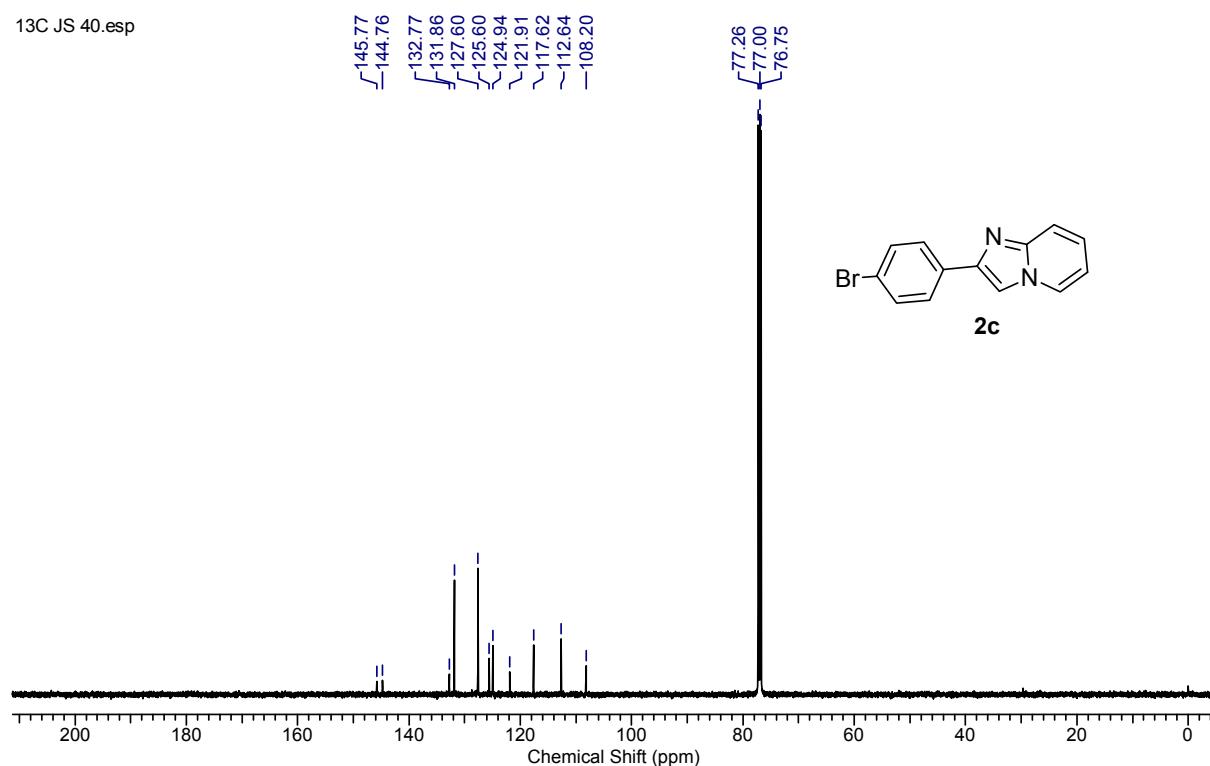
<sup>13</sup>C NMR spectrum for compound **2b** (CDCl<sub>3</sub>, 125 MHz)



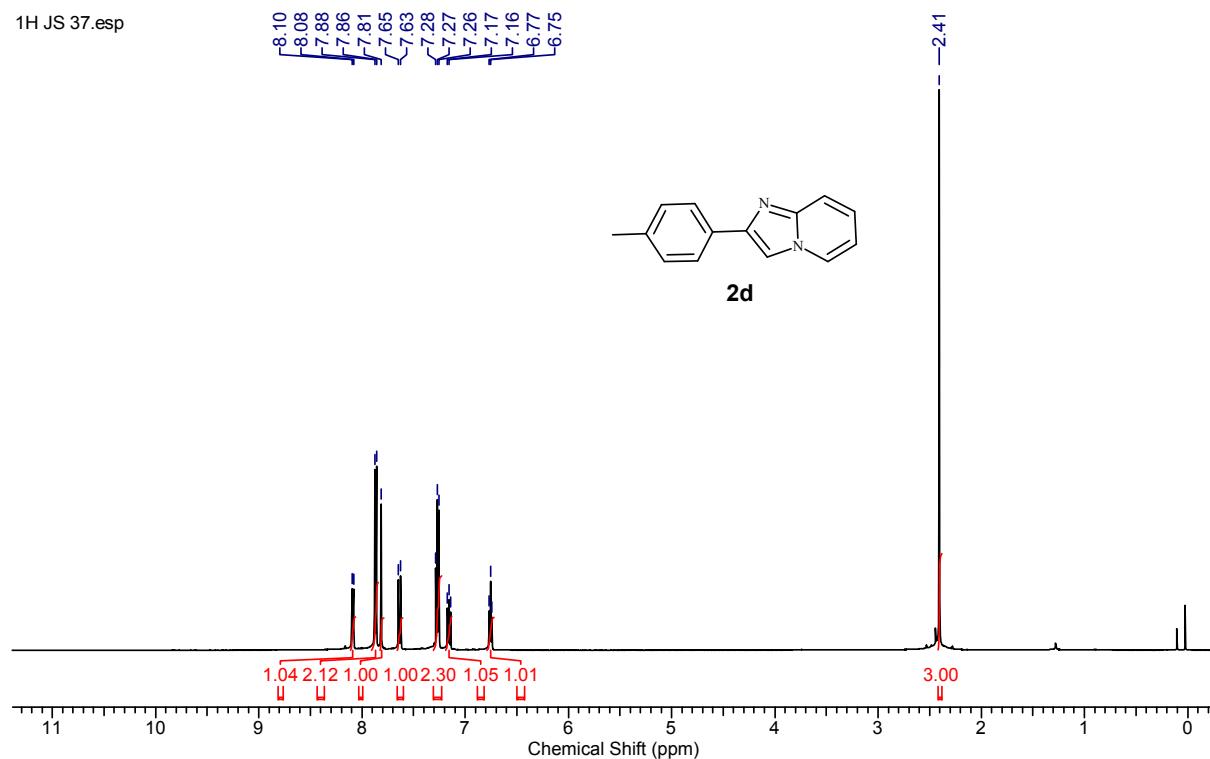
<sup>1</sup>H NMR spectrum for compound **2c** (CDCl<sub>3</sub>, 500 MHz)



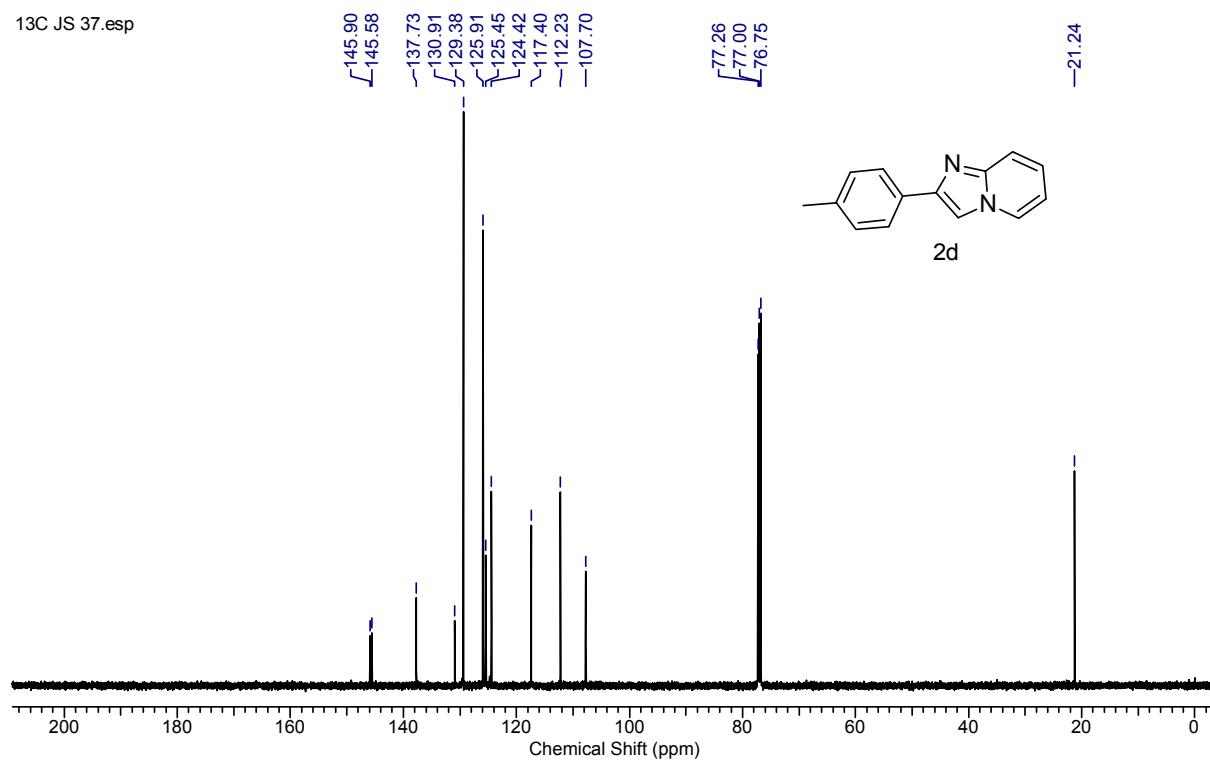
<sup>13</sup>C NMR spectrum for compound **2c** (CDCl<sub>3</sub>, 125 MHz)



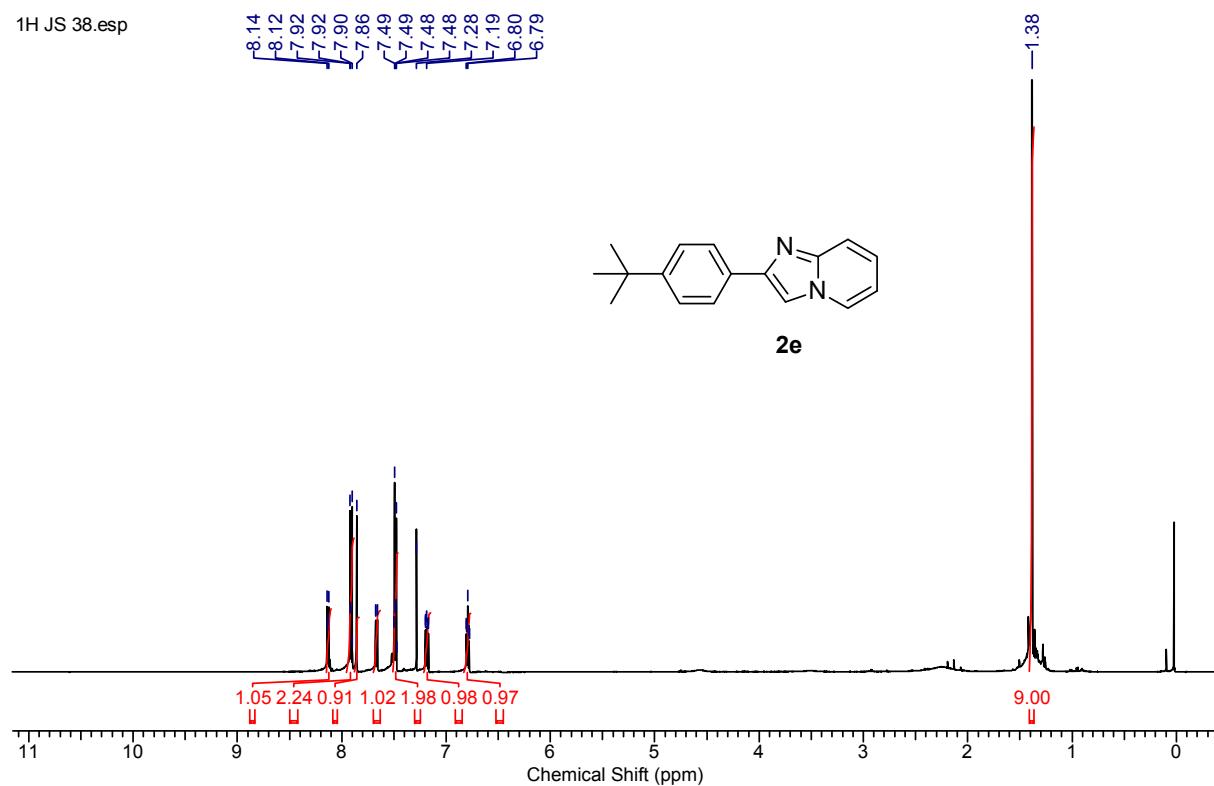
<sup>1</sup>H NMR spectrum for compound **2d** (CDCl<sub>3</sub>, 500 MHz)



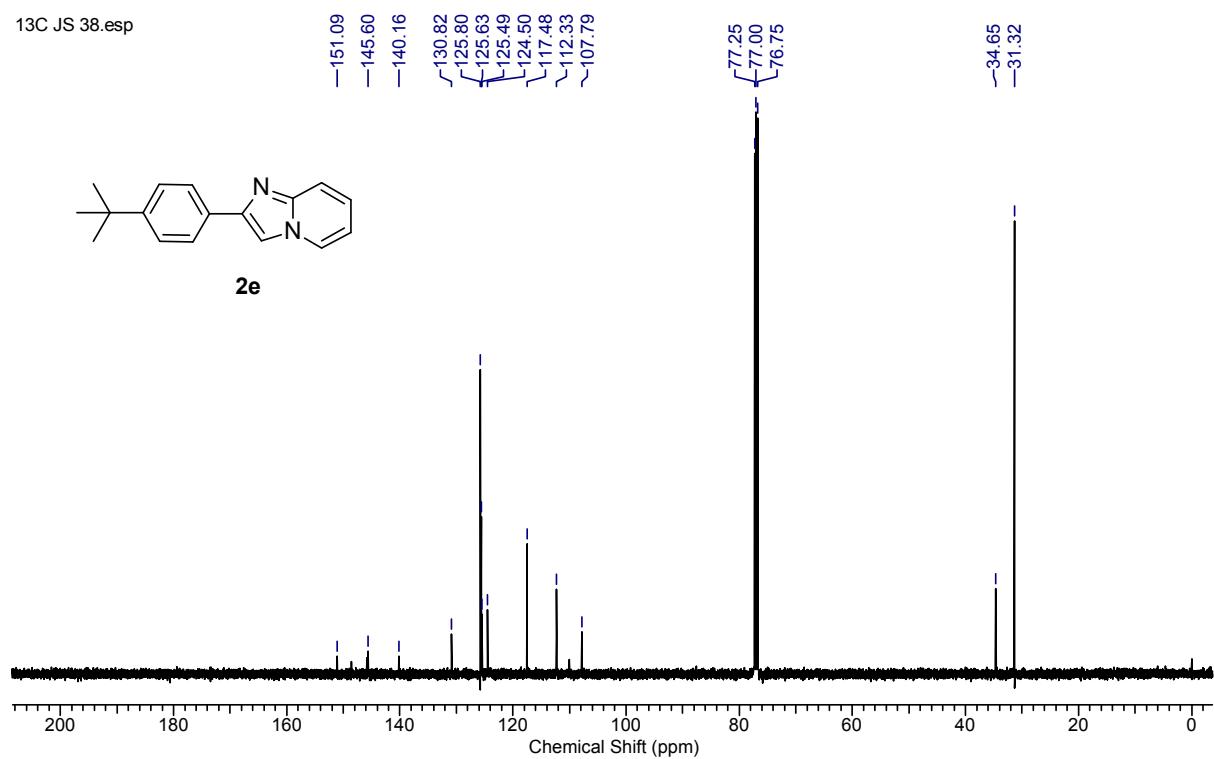
<sup>13</sup>C NMR spectrum for compound **2d** (CDCl<sub>3</sub>, 125 MHz)



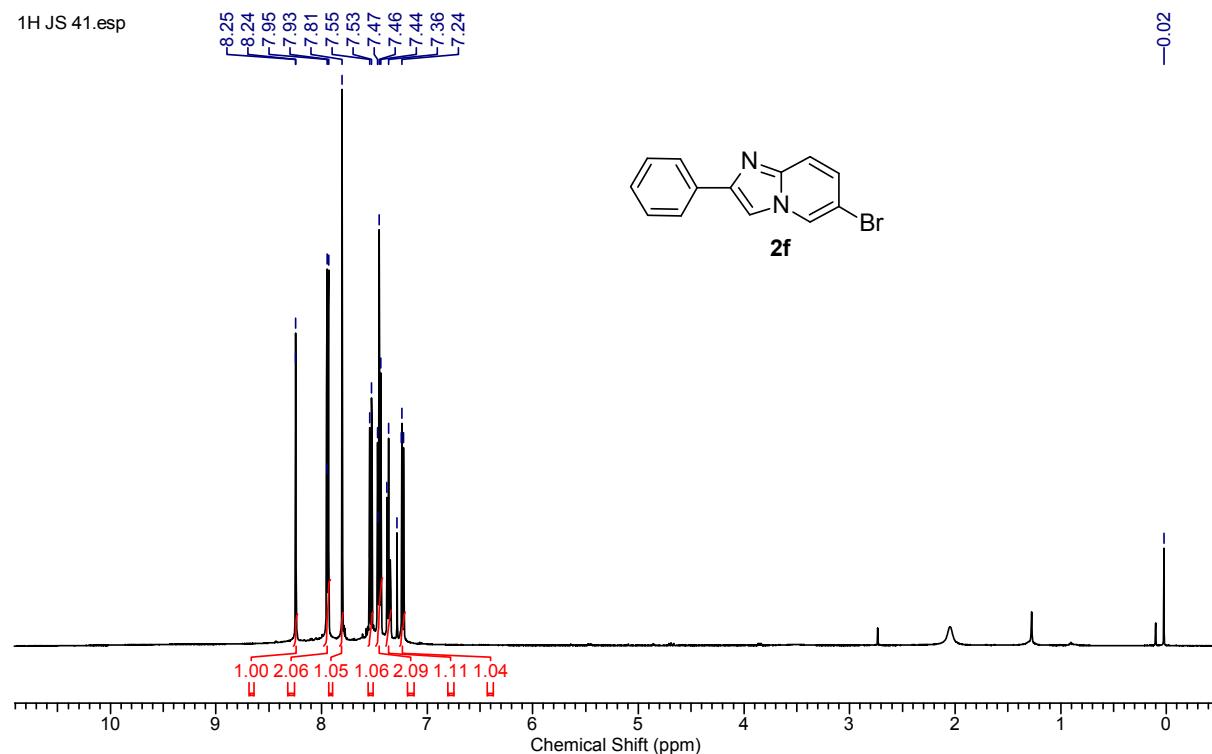
<sup>1</sup>H NMR spectrum for compound **2e** (CDCl<sub>3</sub>, 500 MHz)



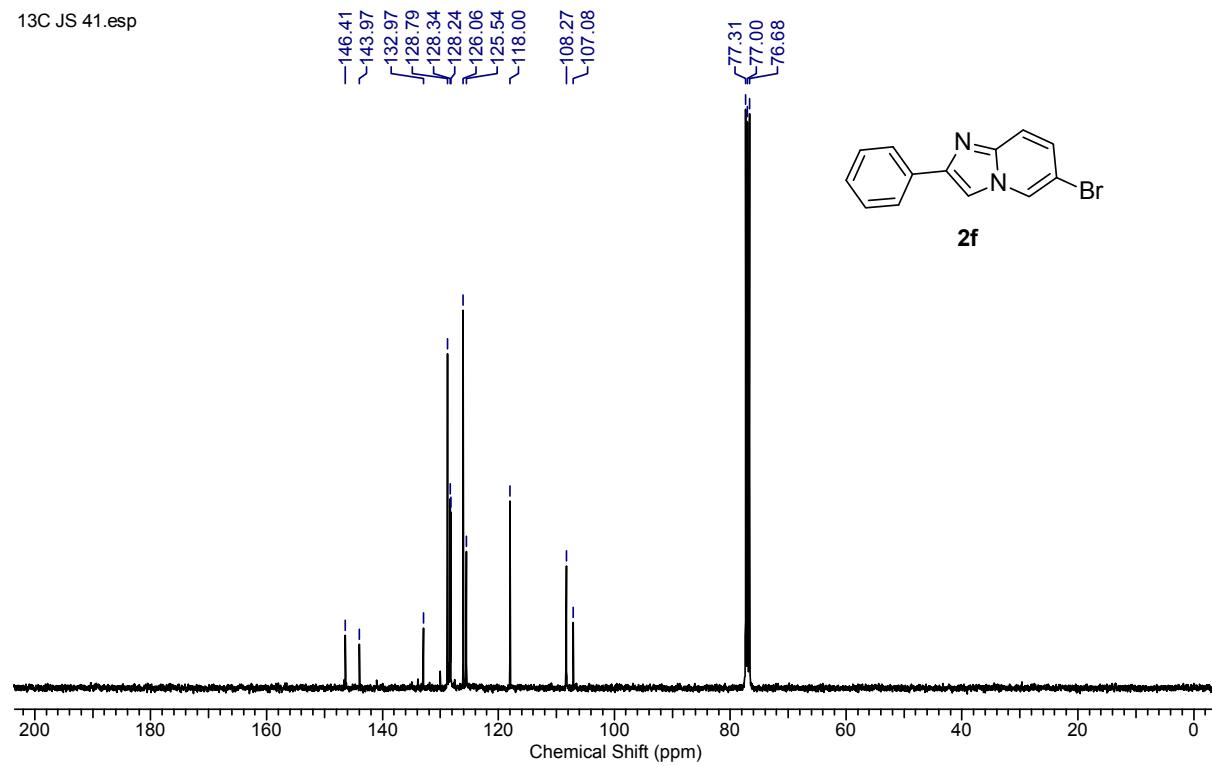
<sup>13</sup>C NMR spectrum for compound **2e** (CDCl<sub>3</sub>, 125 MHz)



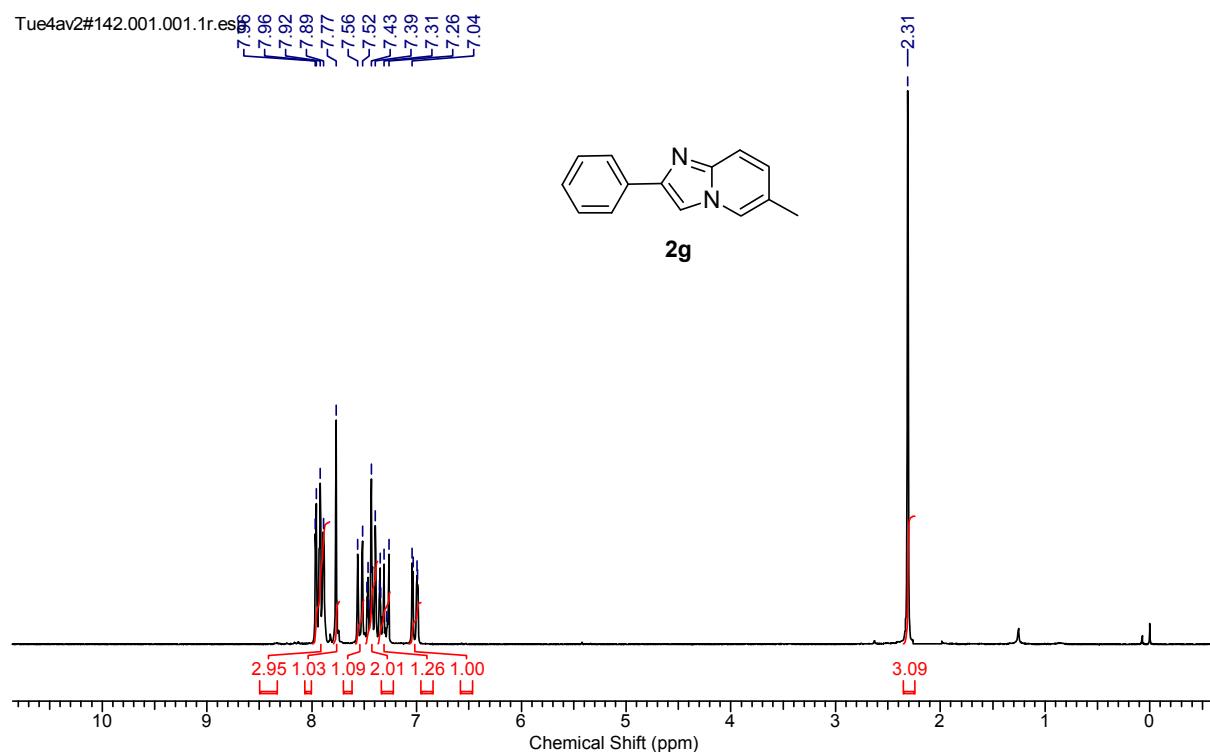
<sup>1</sup>H NMR spectrum for compound **2f** (CDCl<sub>3</sub>, 500 MHz)



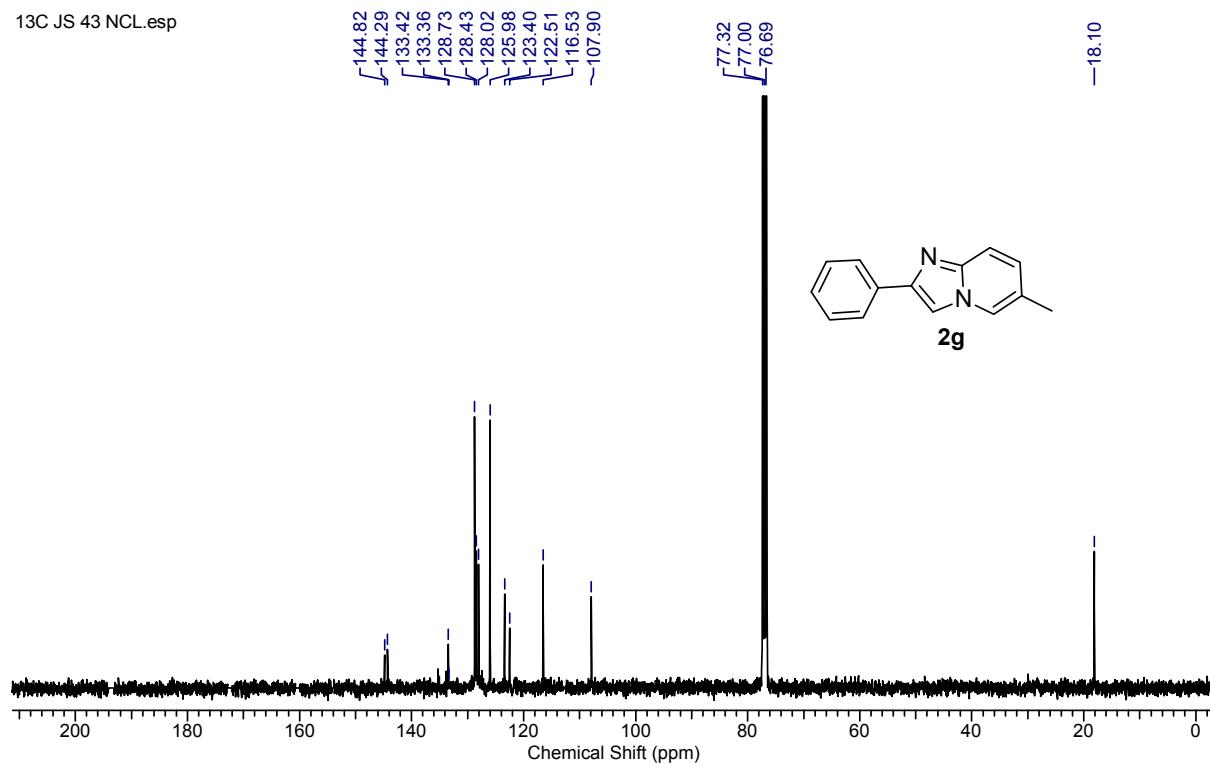
<sup>13</sup>C NMR spectrum for compound **2f** (CDCl<sub>3</sub>, 100 MHz)



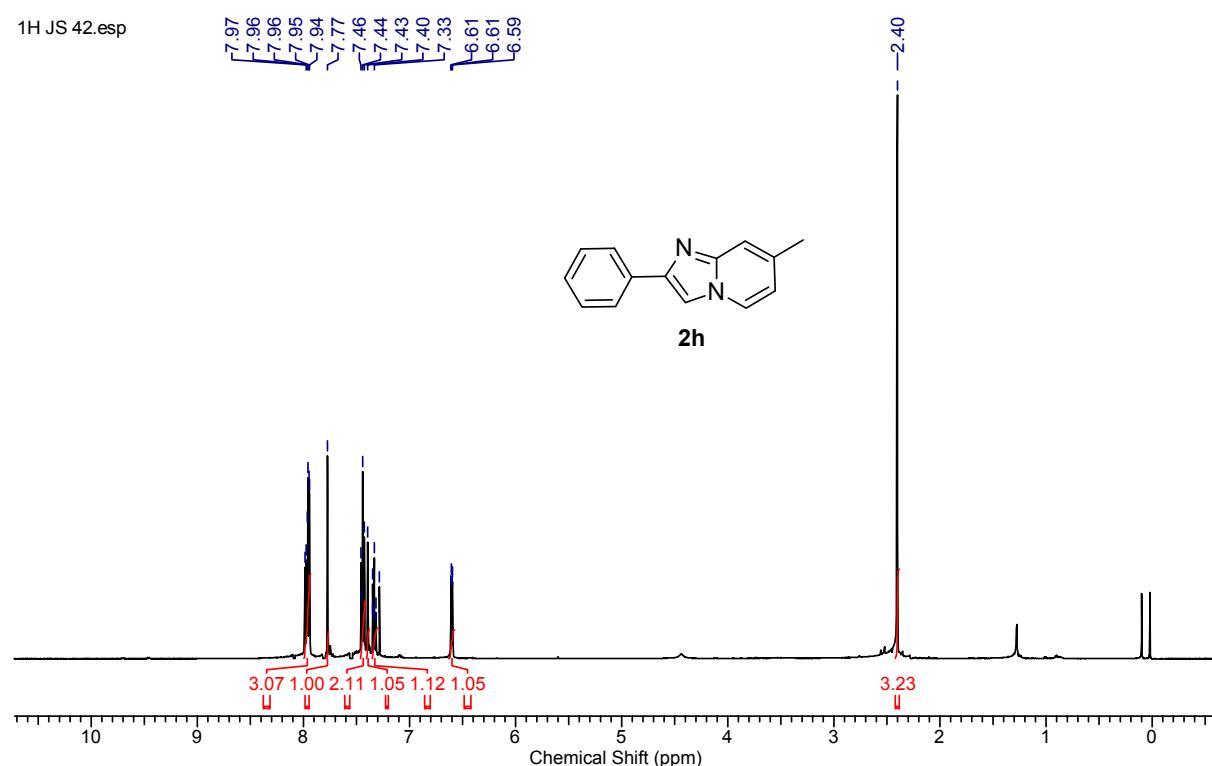
<sup>1</sup>H NMR spectrum for compound **2g** (CDCl<sub>3</sub>, 200 MHz)



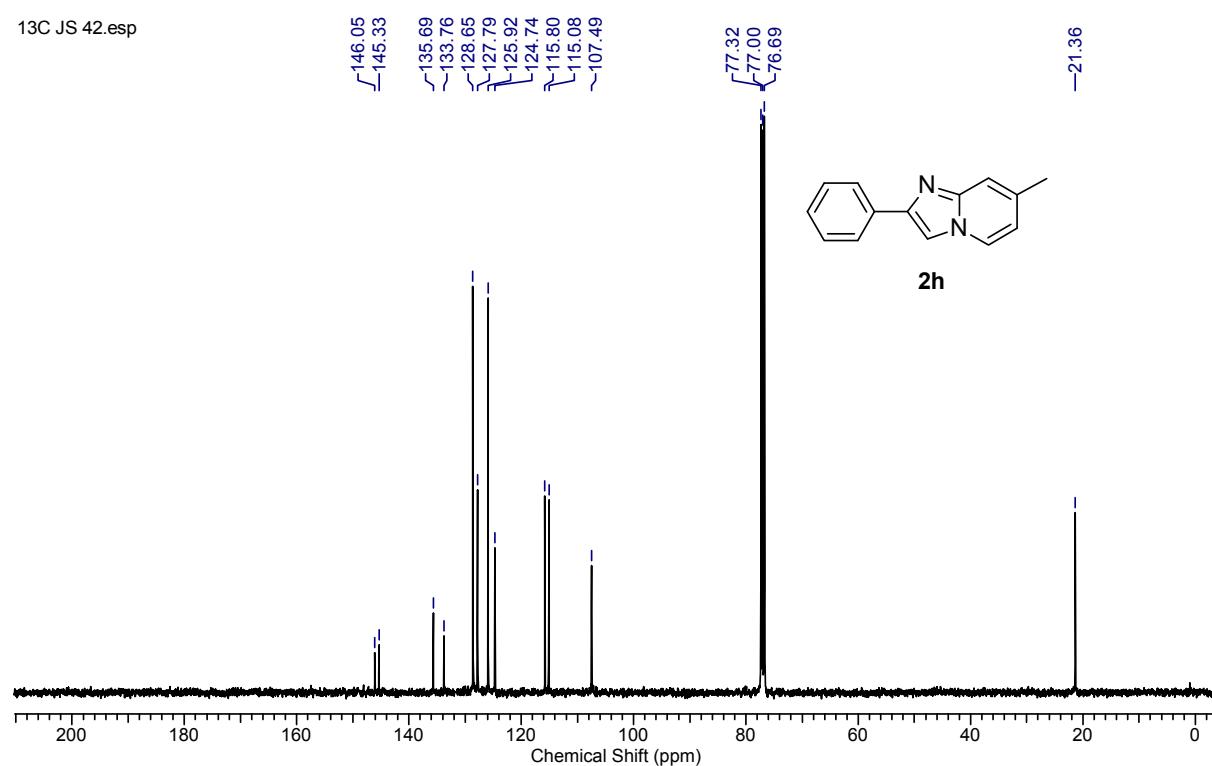
<sup>13</sup>C NMR spectrum for compound **2g** (CDCl<sub>3</sub>, 100 MHz)



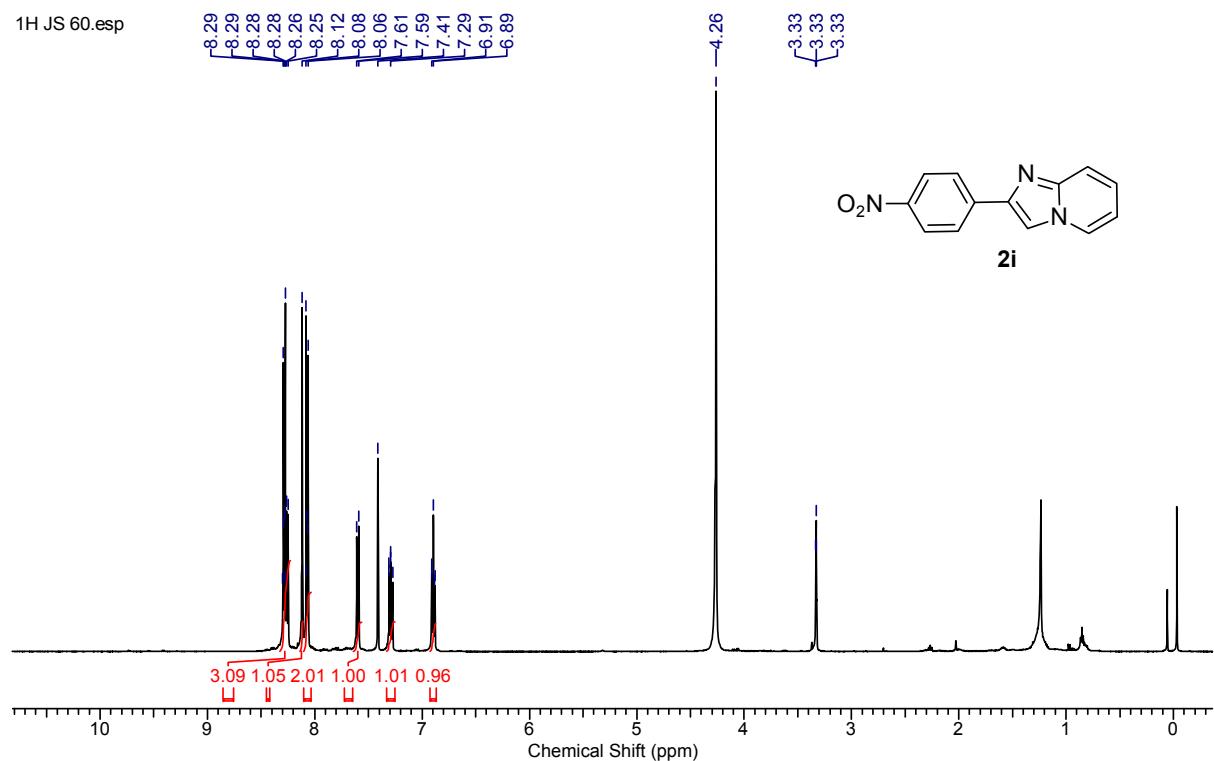
<sup>1</sup>H NMR spectrum for compound **2h** (CDCl<sub>3</sub>, 500 MHz)



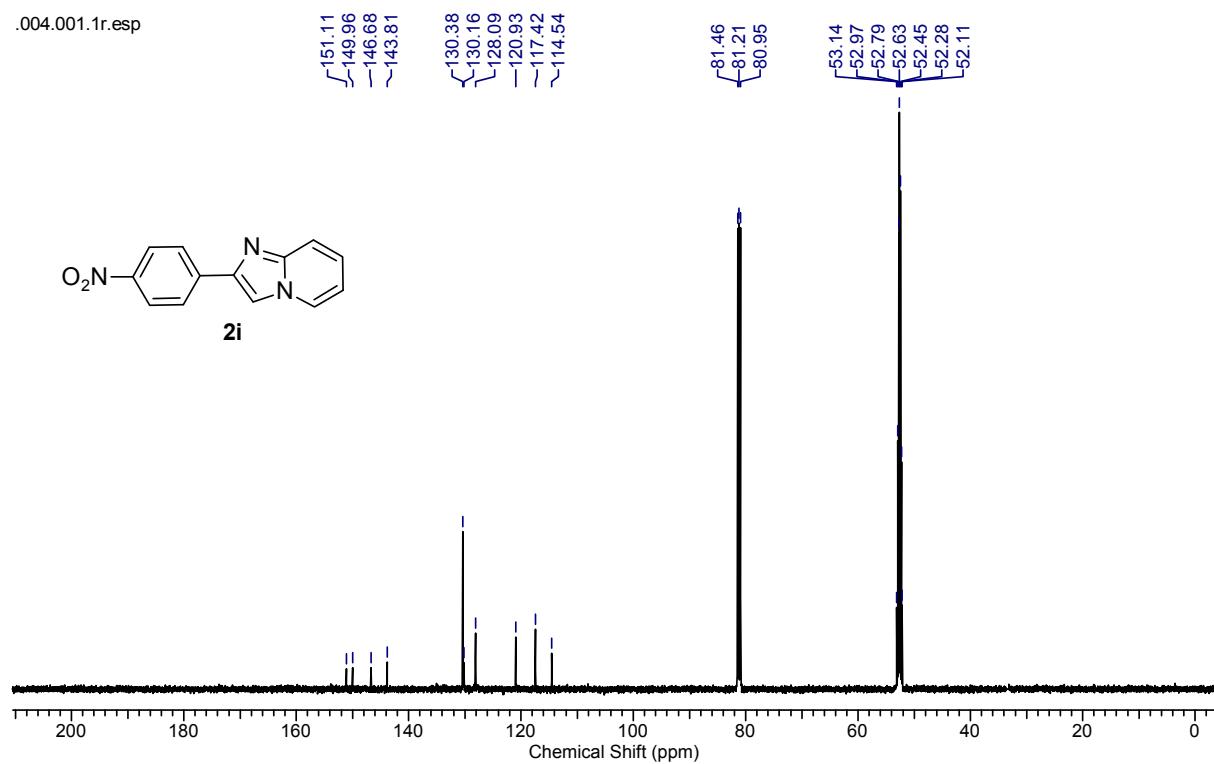
<sup>13</sup>C NMR spectrum for compound **2h** (CDCl<sub>3</sub>, 100 MHz)



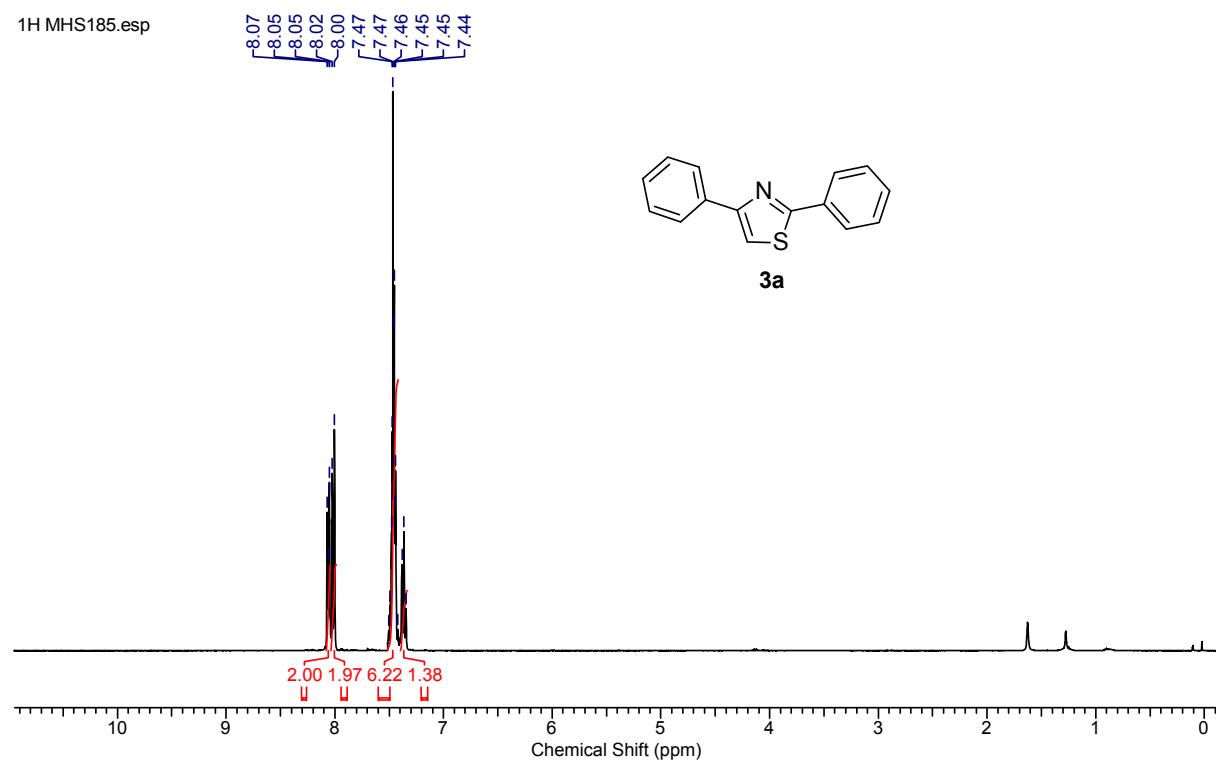
<sup>1</sup>H NMR spectrum for compound **2i** (CD<sub>3</sub>OD + CDCl<sub>3</sub>, 500 MHz)



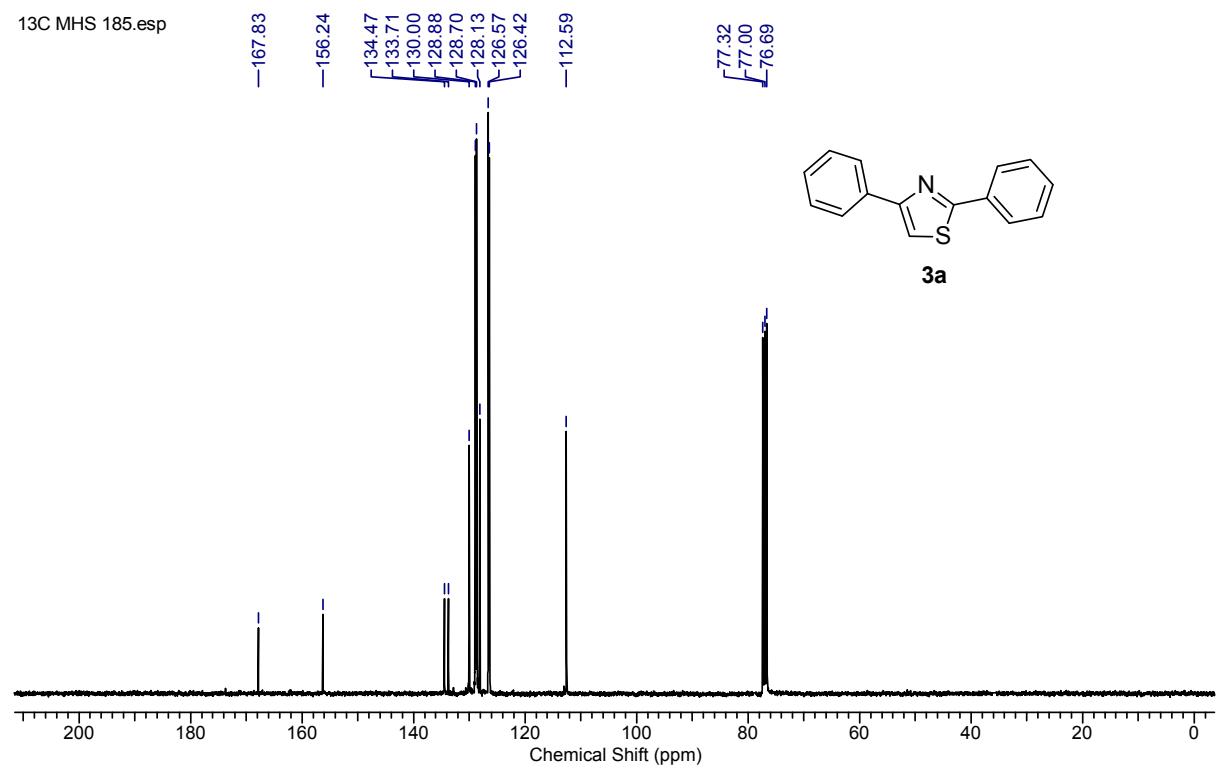
<sup>13</sup>C NMR spectrum for compound **2i** (CD<sub>3</sub>OD + CDCl<sub>3</sub>, 100 MHz)



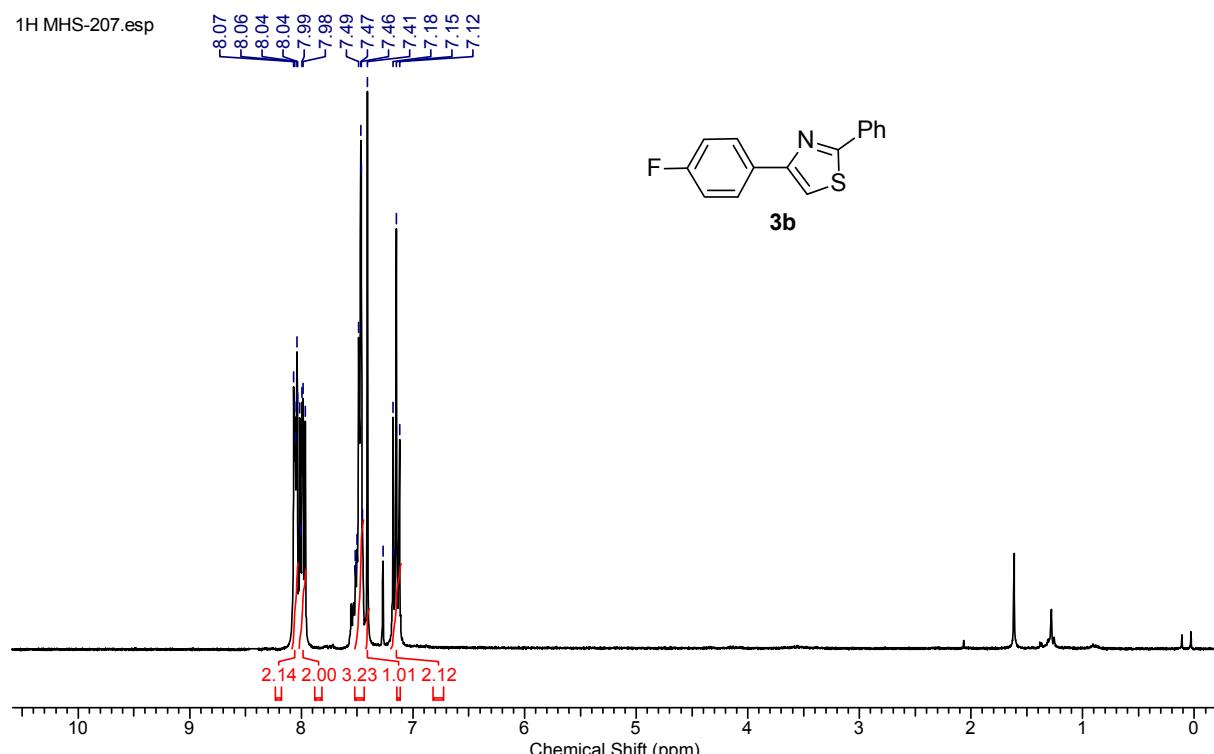
<sup>1</sup>H NMR spectrum for compound **3a** (CDCl<sub>3</sub>, 400 MHz)



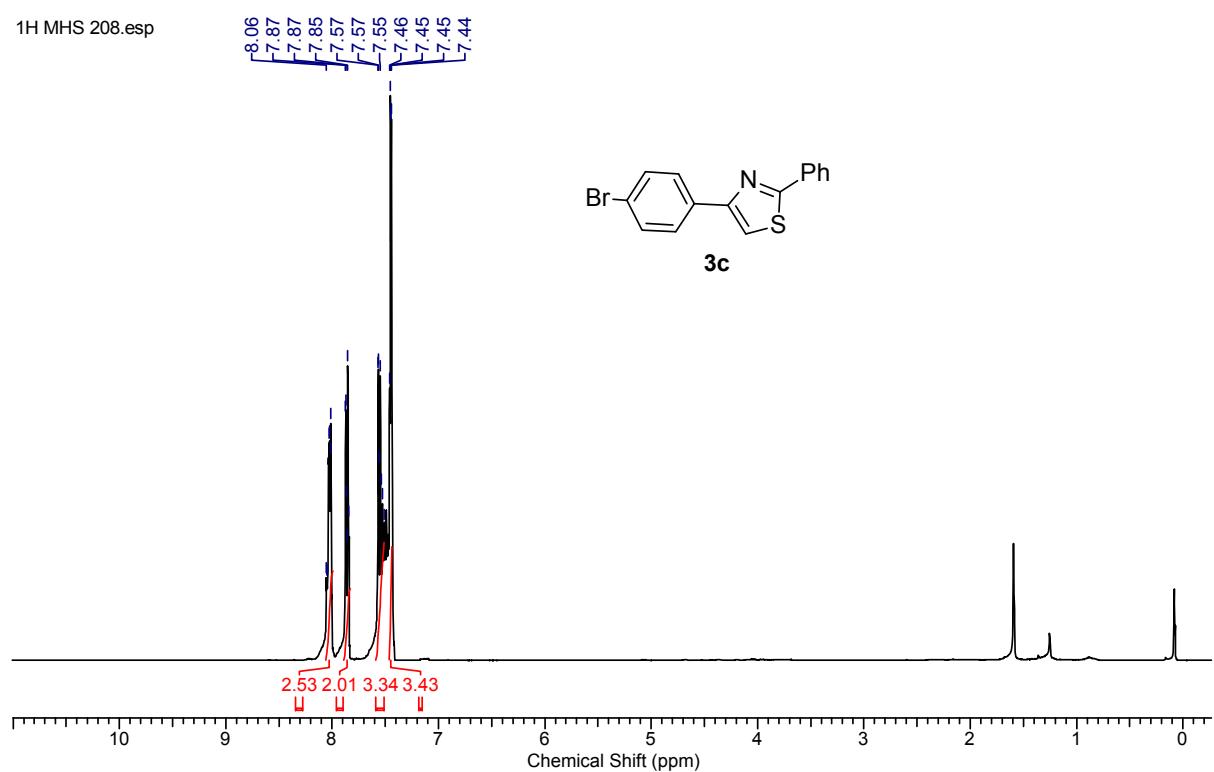
<sup>13</sup>C NMR spectrum for compound **3a** (CDCl<sub>3</sub>, 100 MHz)



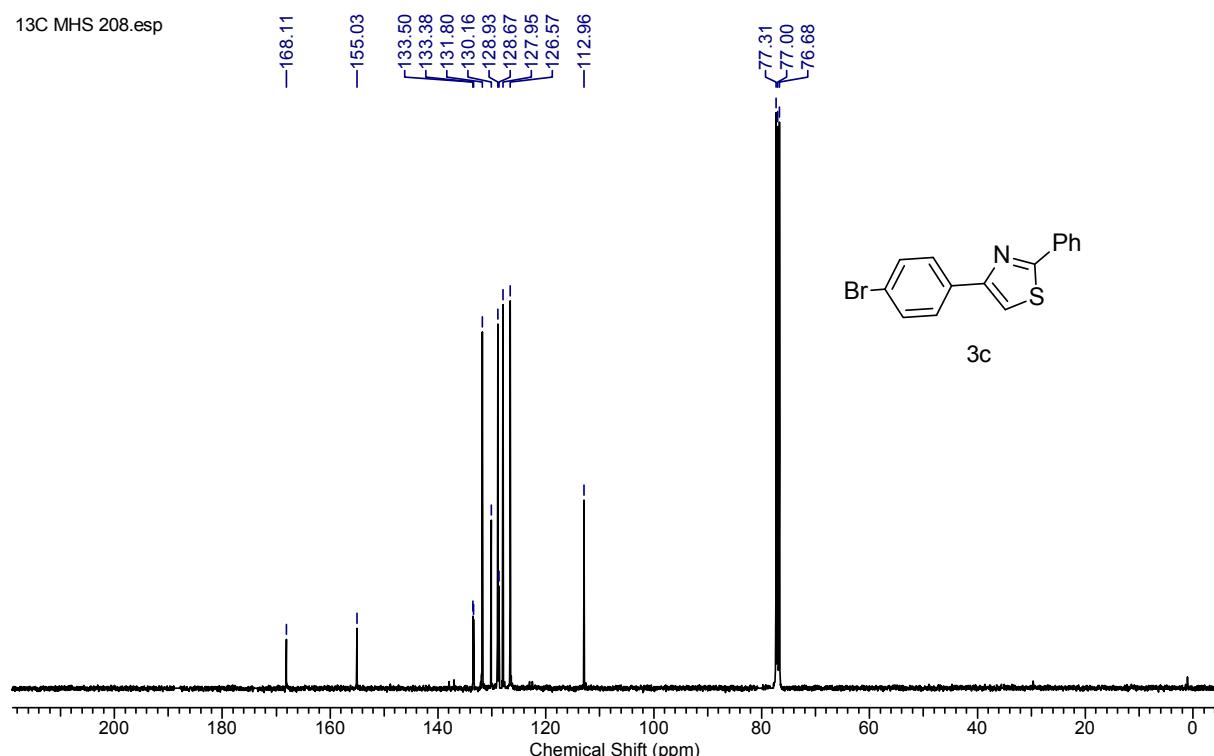
<sup>1</sup>H NMR spectrum for compound **3b** (CDCl<sub>3</sub>, 300 MHz)



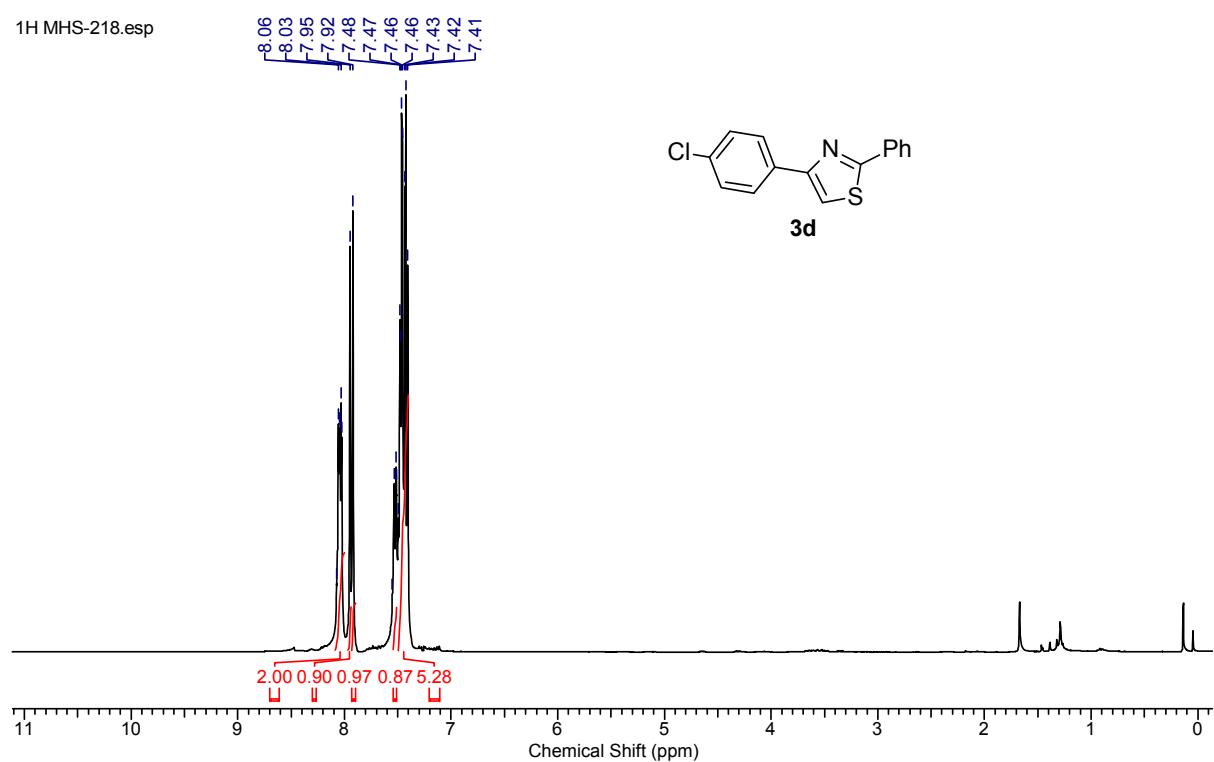
<sup>1</sup>H NMR spectrum for compound **3c** (CDCl<sub>3</sub>, 400 MHz)



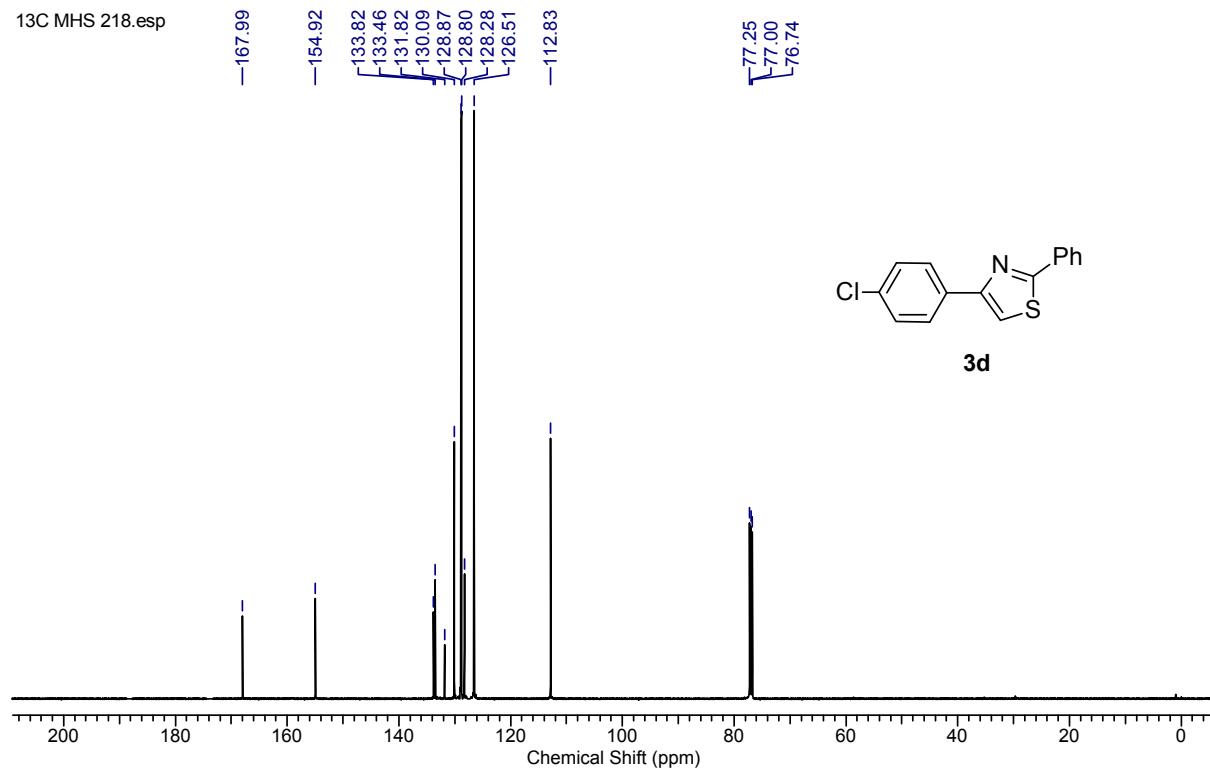
$^{13}\text{C}$  NMR spectrum for compound **3c** ( $\text{CDCl}_3$ , 100 MHz)



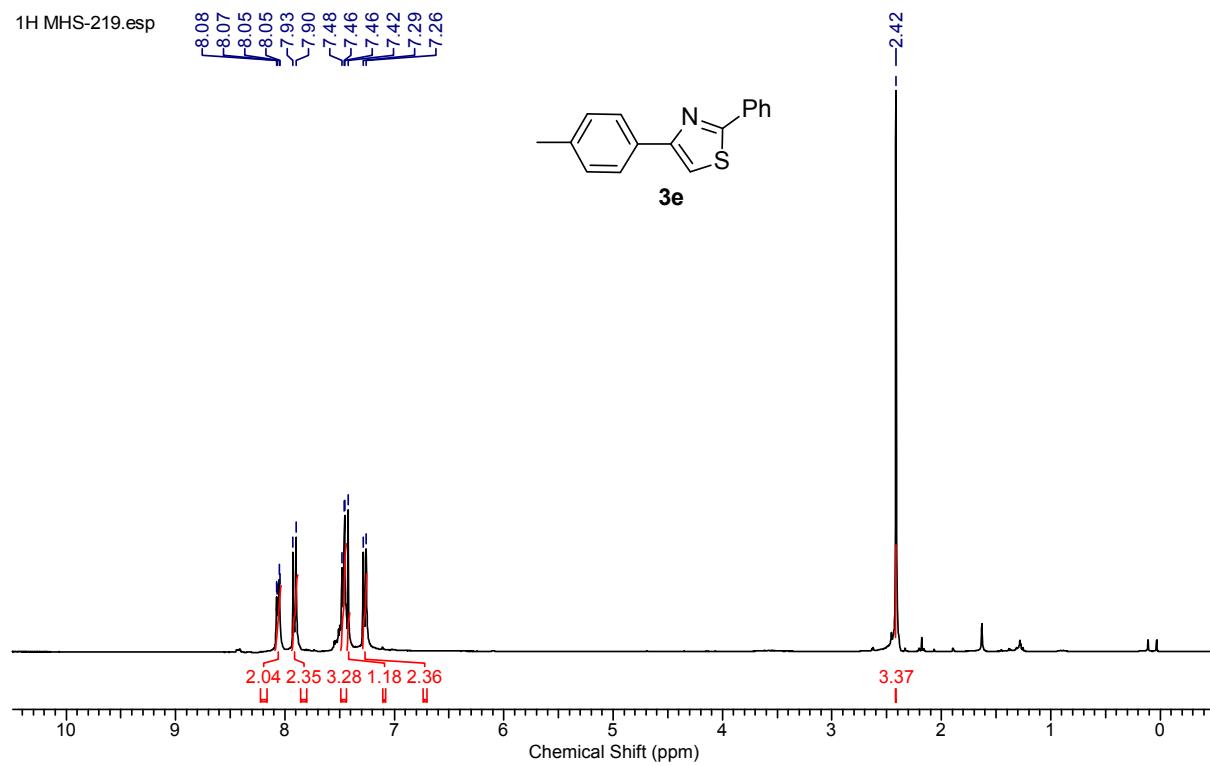
$^1\text{H}$  NMR spectrum for compound **3d** ( $\text{CDCl}_3$ , 300 MHz)



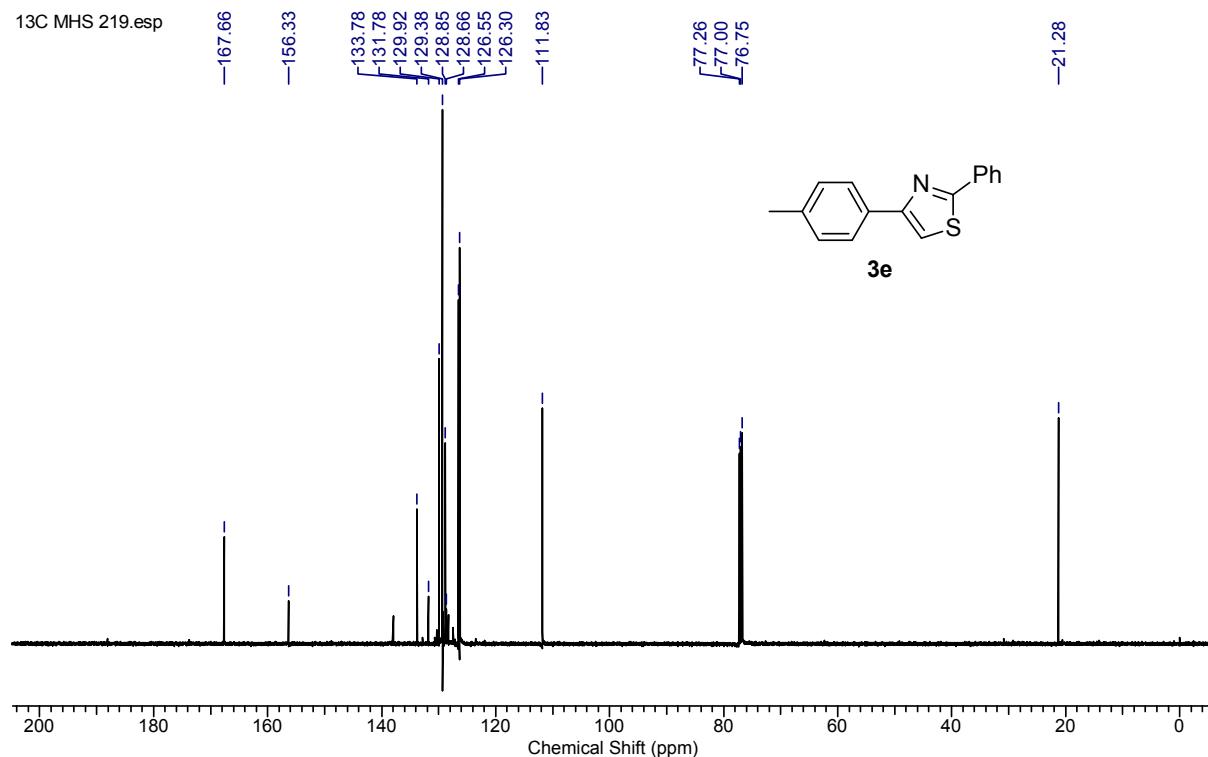
$^{13}\text{C}$  NMR spectrum for compound **3d** ( $\text{CDCl}_3$ , 100 MHz)



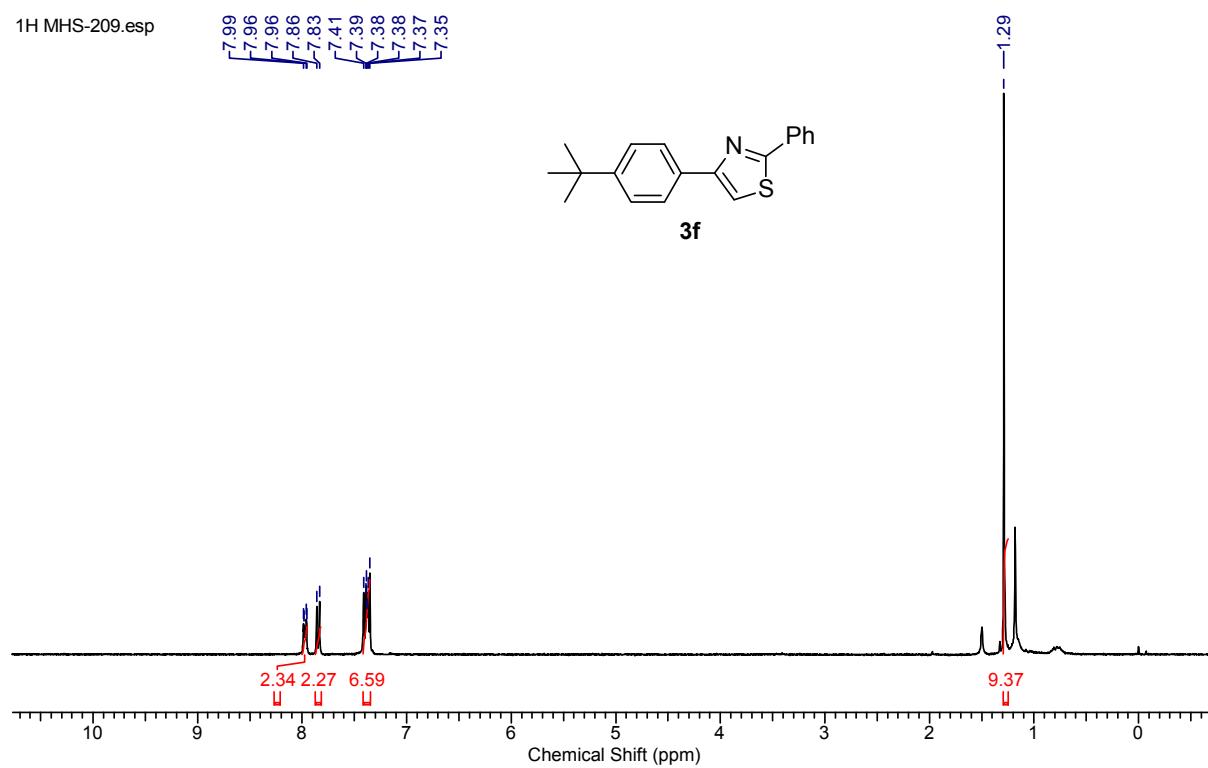
$^1\text{H}$  NMR spectrum for compound **3e** ( $\text{CDCl}_3$ , 300 MHz)



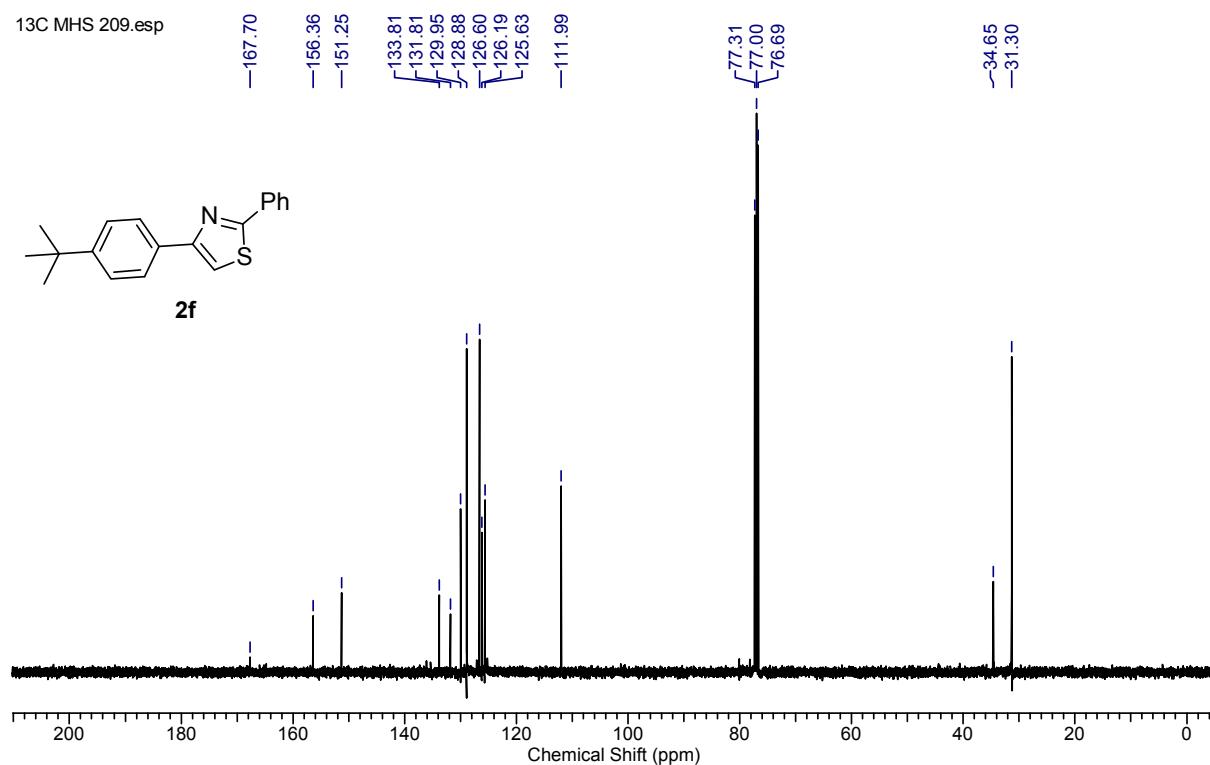
<sup>13</sup>C NMR spectrum for compound **3e** (CDCl<sub>3</sub>, 125 MHz)



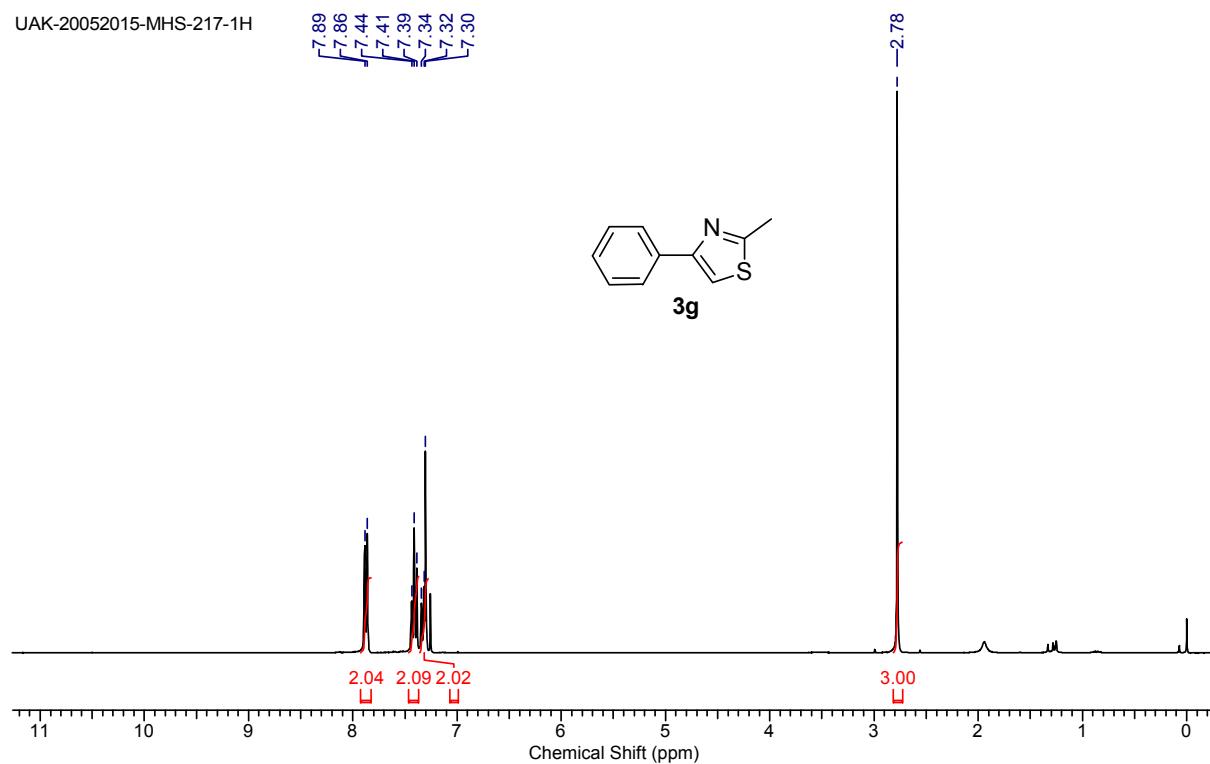
<sup>1</sup>H NMR spectrum for compound **3f** (CDCl<sub>3</sub>, 300 MHz)



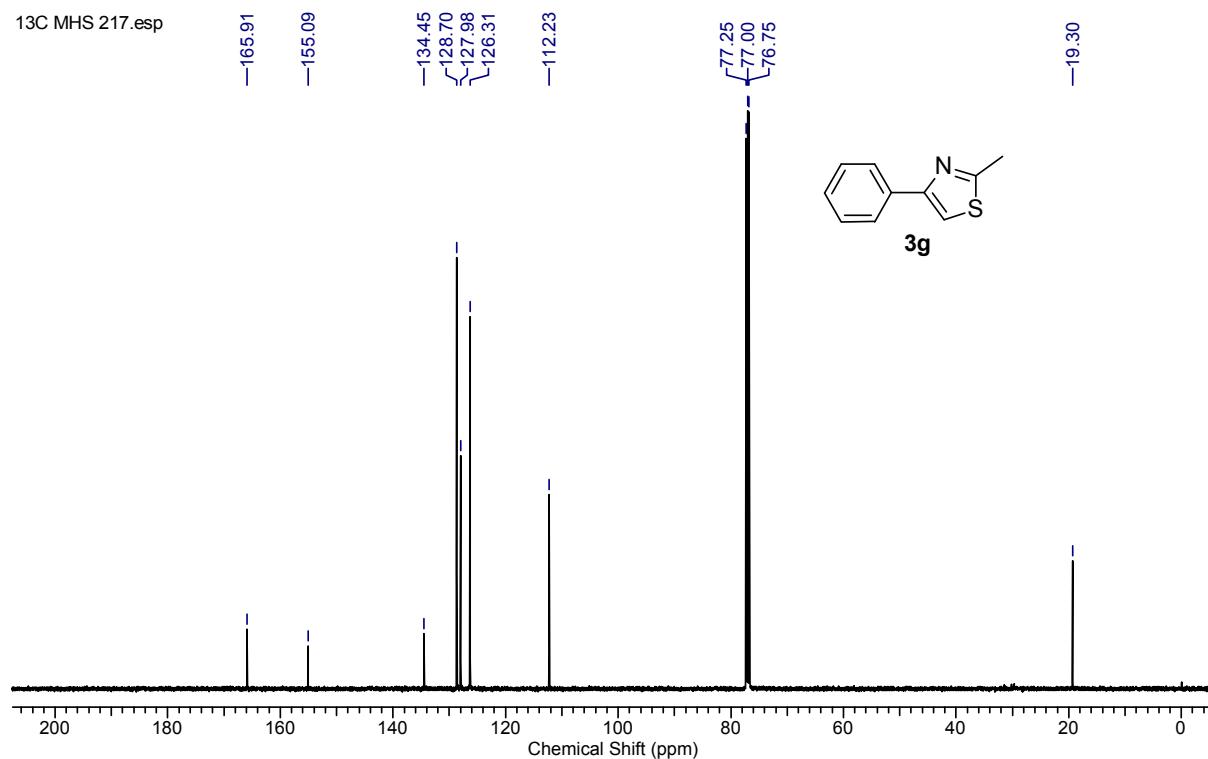
$^{13}\text{C}$  NMR spectrum for compound **3f** ( $\text{CDCl}_3$ , 125 MHz)



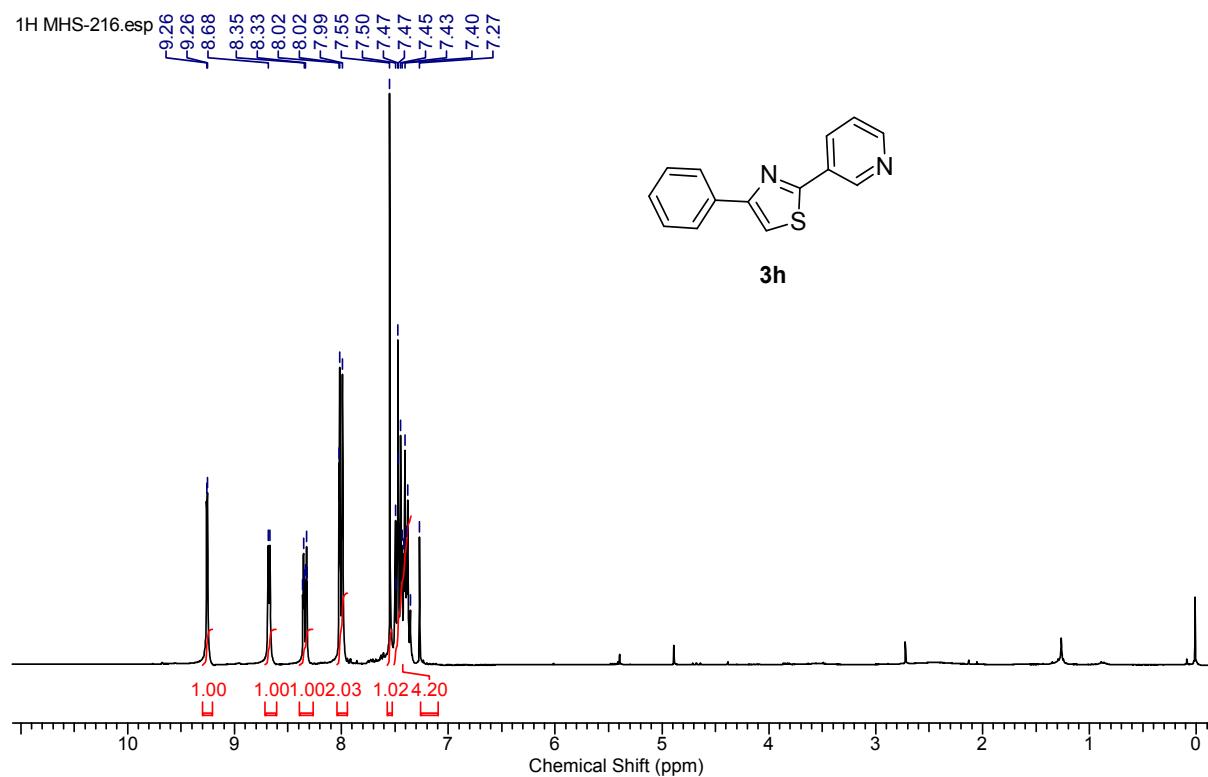
$^1\text{H}$  NMR spectrum for compound **3g** ( $\text{CDCl}_3$ , 300 MHz)



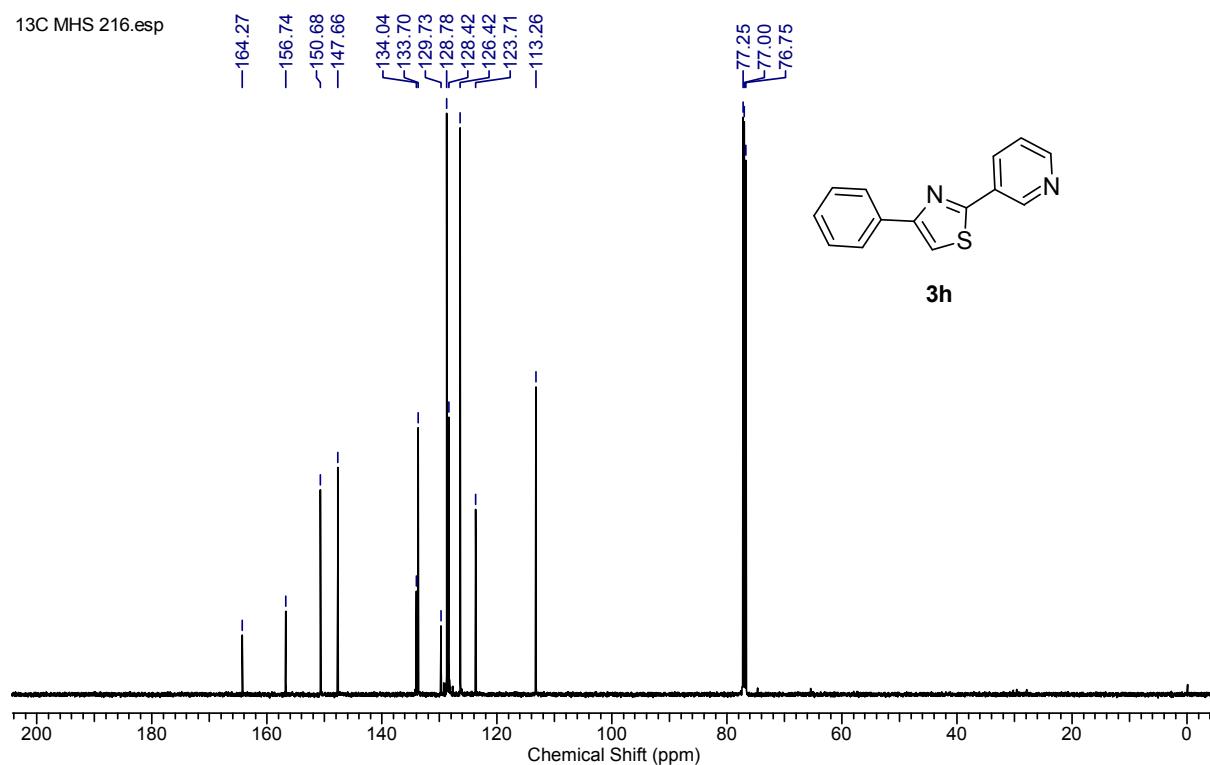
$^{13}\text{C}$  NMR spectrum for compound **3g** ( $\text{CDCl}_3$ , 125 MHz)



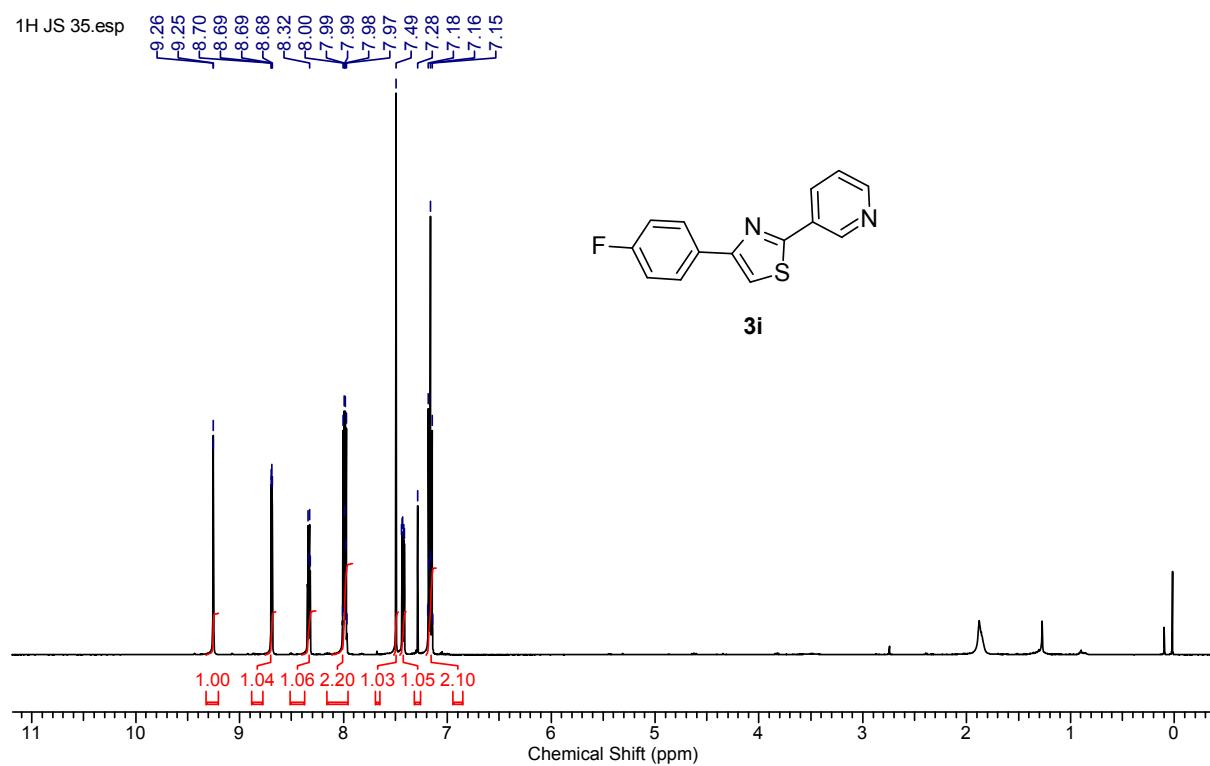
$^1\text{H}$  NMR spectrum for compound **3h** ( $\text{CDCl}_3$ , 300 MHz)



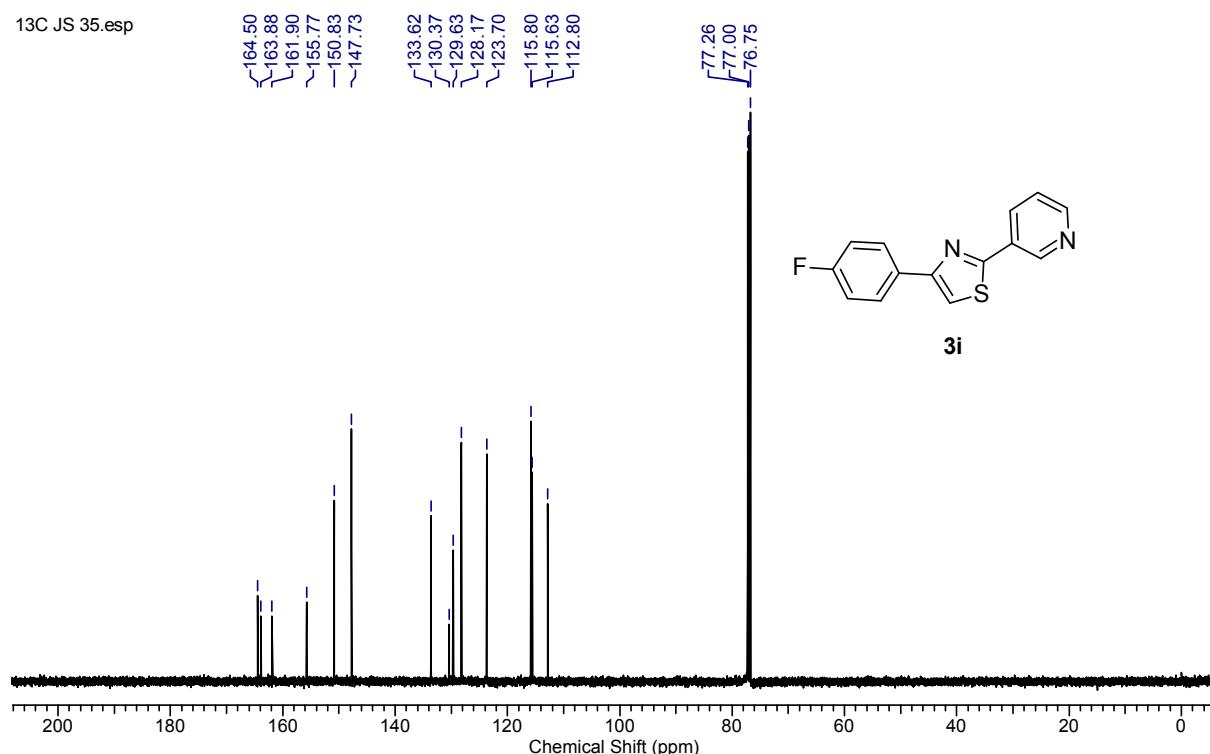
$^{13}\text{C}$  NMR spectrum for compound **3h** ( $\text{CDCl}_3$ , 125 MHz)



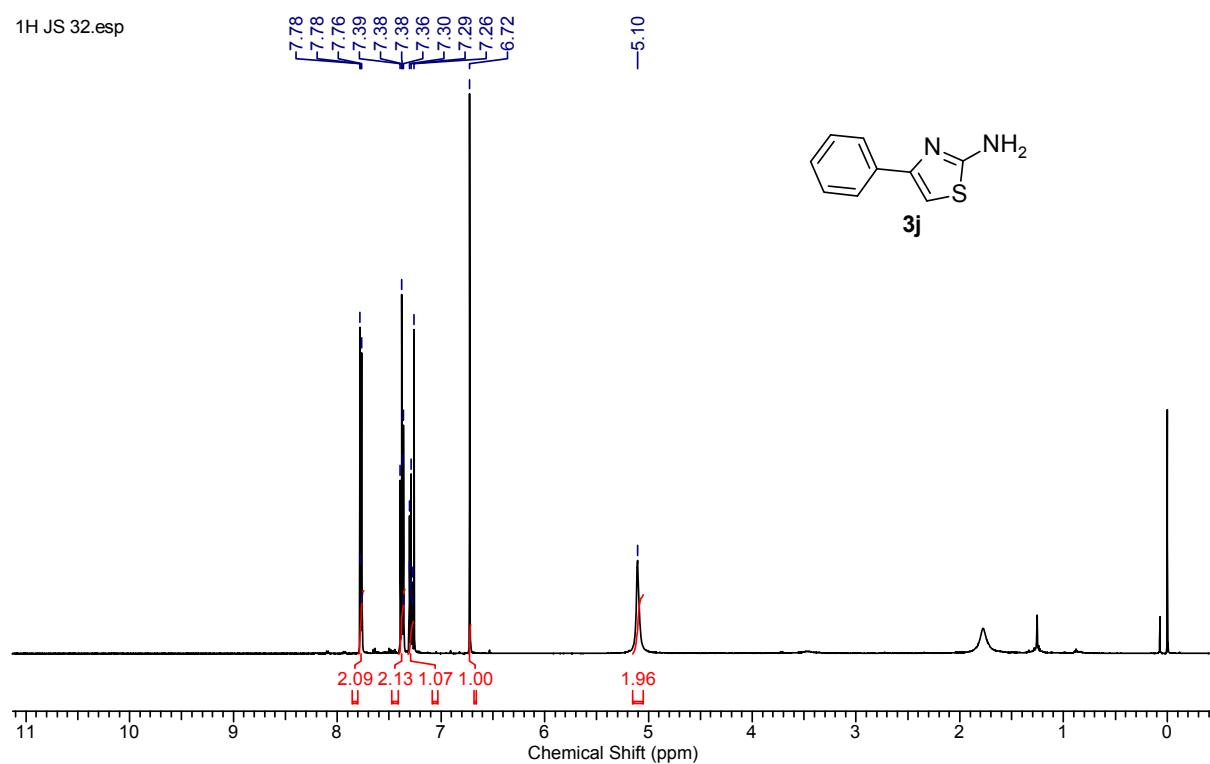
$^1\text{H}$  NMR spectrum for compound **3i** ( $\text{CDCl}_3$ , 500 MHz)



<sup>13</sup>C NMR spectrum for compound **3i** (CDCl<sub>3</sub>, 125 MHz)

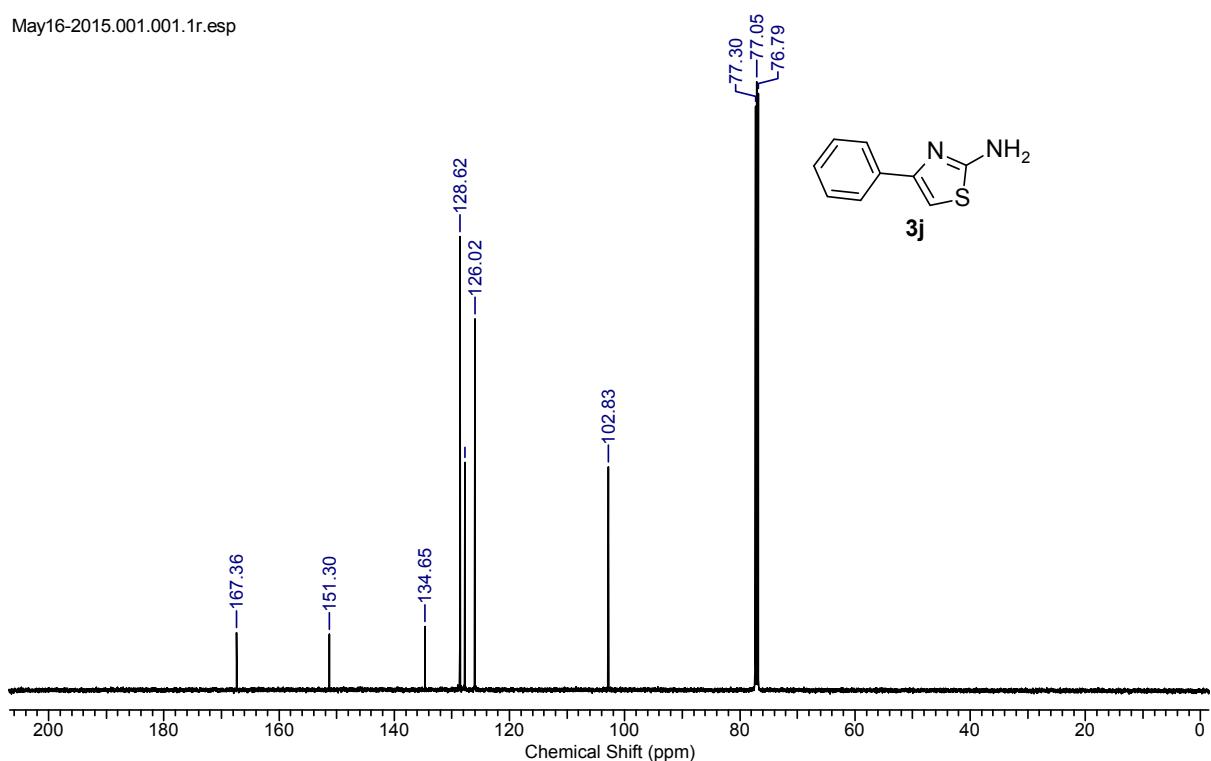


<sup>1</sup>H NMR spectrum for compound **3j** (CDCl<sub>3</sub>, 500 MHz)



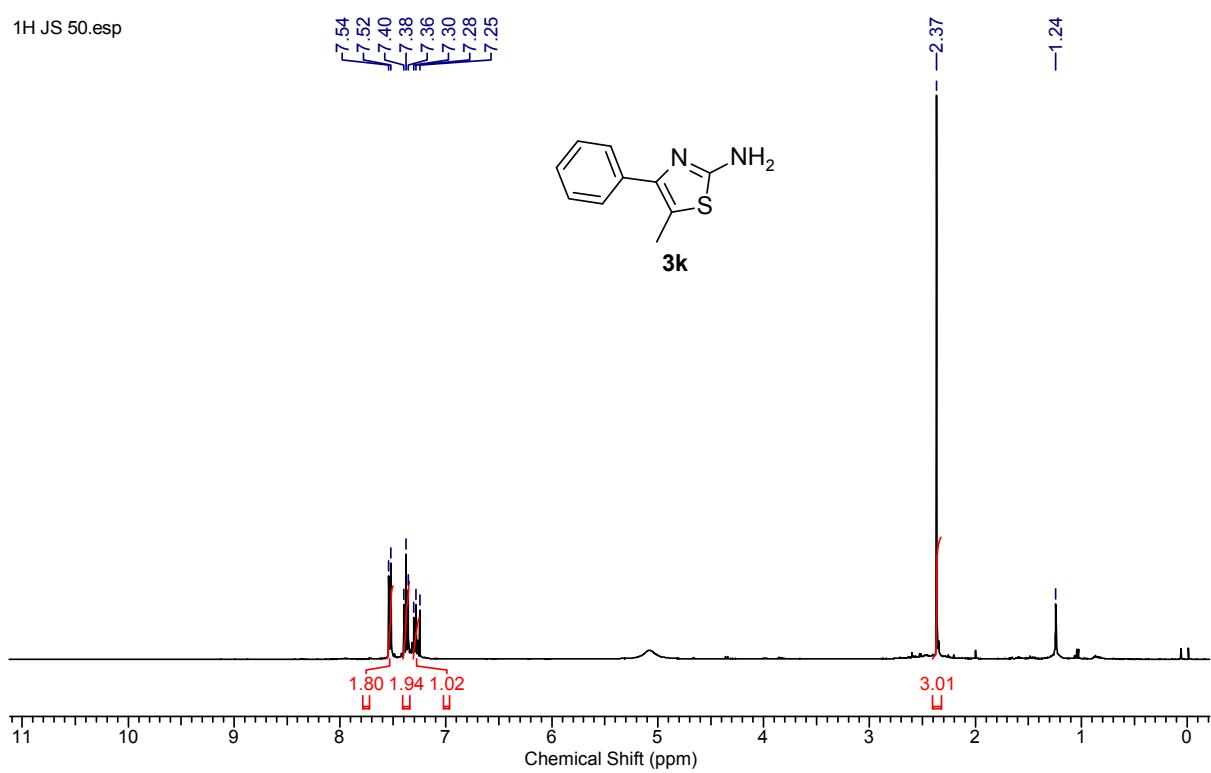
<sup>13</sup>C NMR spectrum for compound **3j** (CDCl<sub>3</sub>, 125 MHz)

May16-2015.001.001.1r.esp

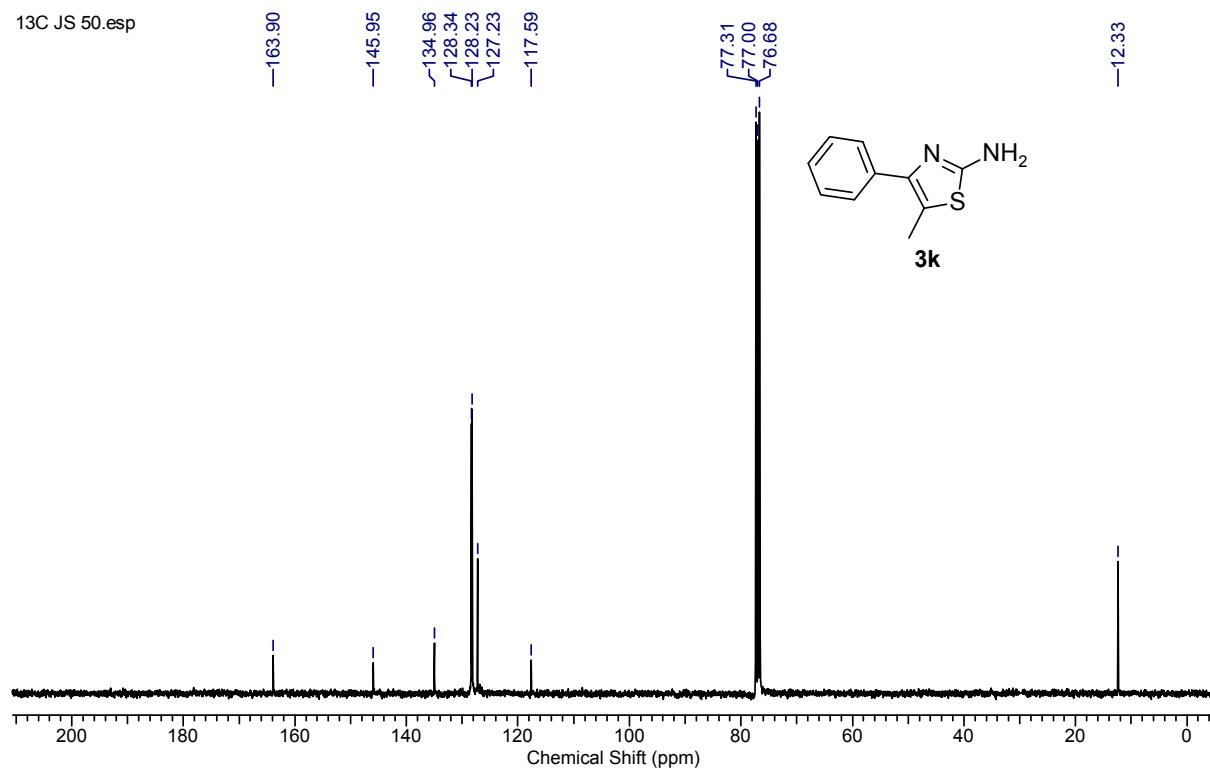


<sup>1</sup>H NMR spectrum for compound **3k** (CDCl<sub>3</sub>, 400 MHz)

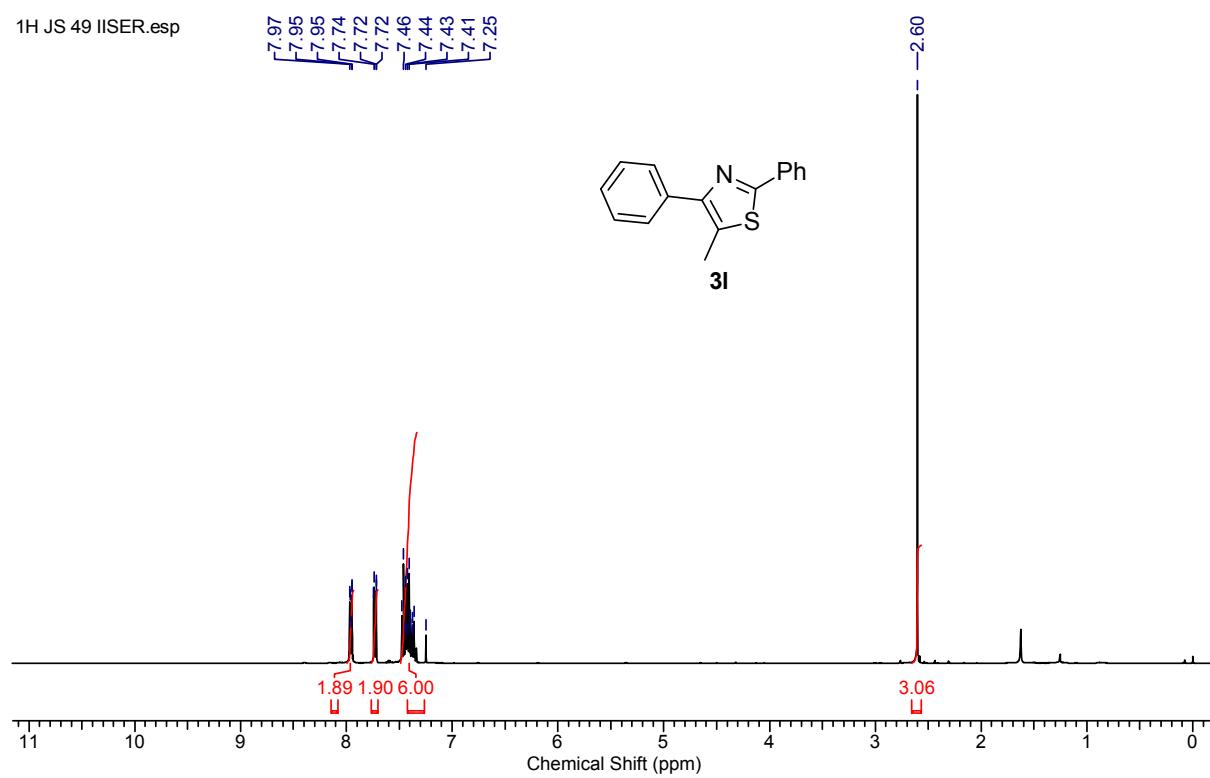
1H JS 50.esp



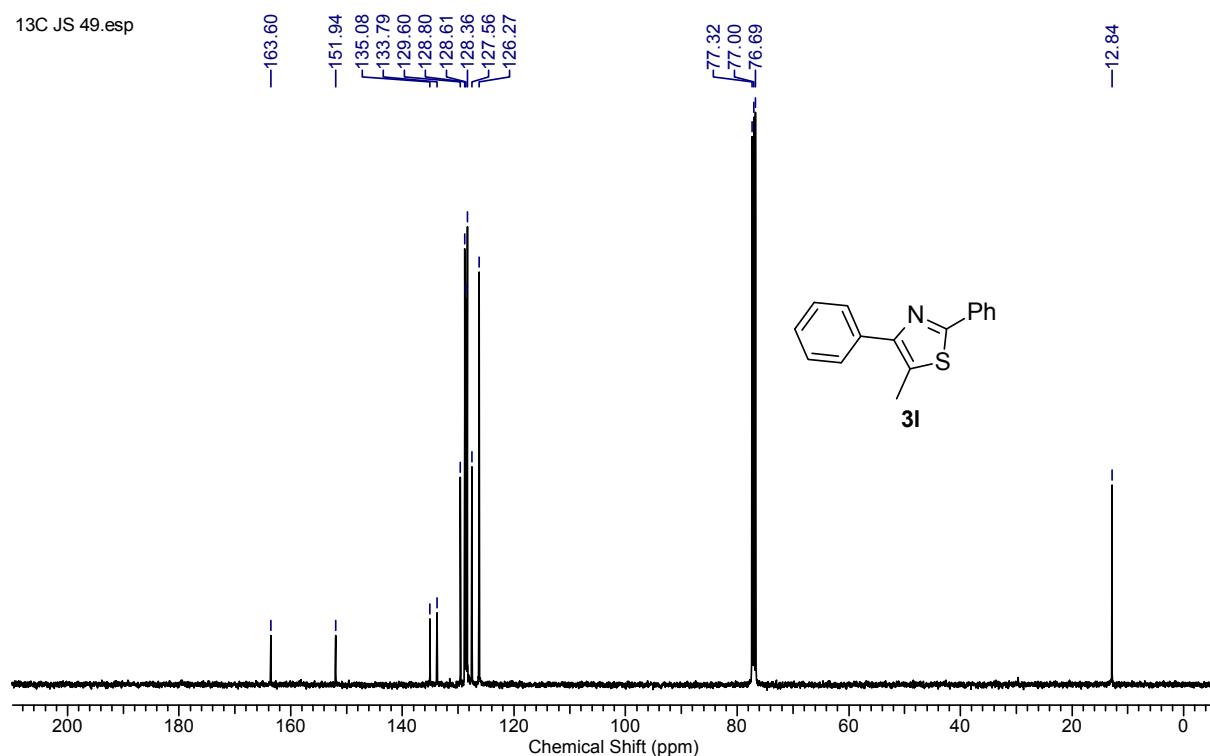
$^{13}\text{C}$  NMR spectrum for compound **3k** ( $\text{CDCl}_3$ , 100 MHz)



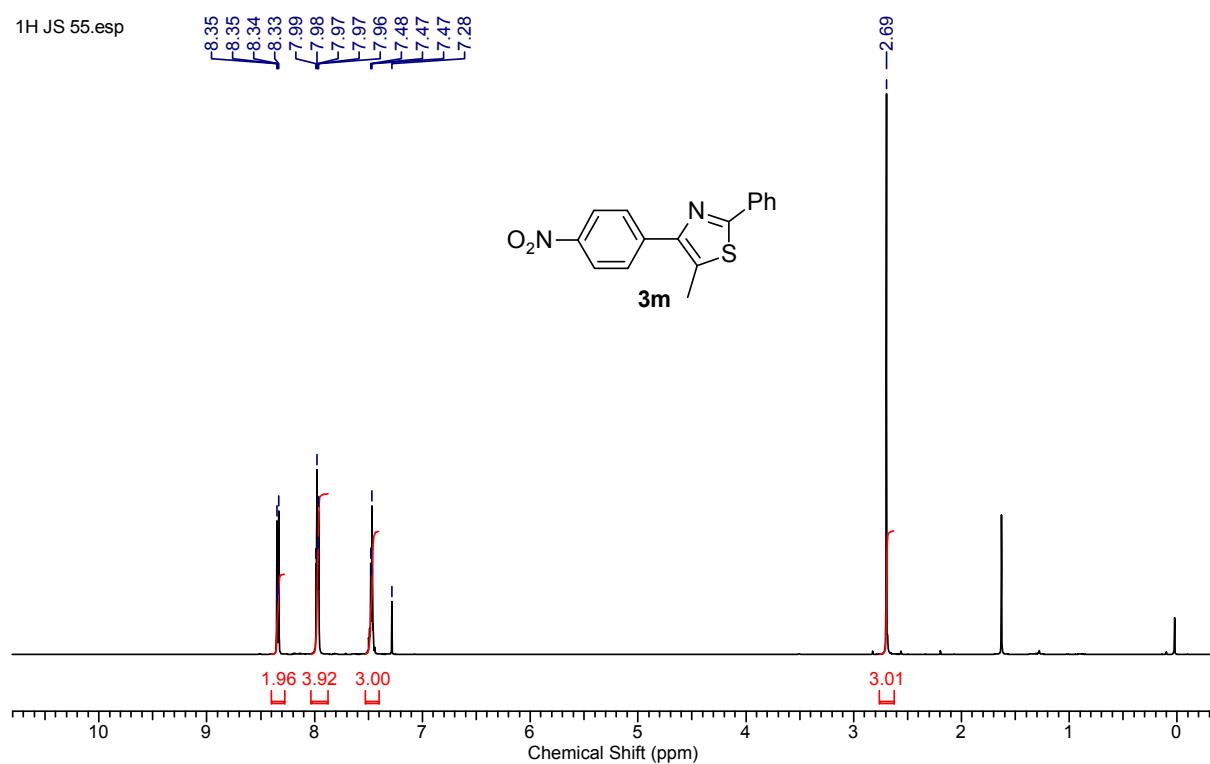
$^1\text{H}$  NMR spectrum for compound **3l** ( $\text{CDCl}_3$ , 400 MHz)



$^{13}\text{C}$  NMR spectrum for compound **3l** ( $\text{CDCl}_3$ , 100 MHz)



$^1\text{H}$  NMR spectrum for compound **3m** ( $\text{CDCl}_3$ , 500 MHz)



<sup>13</sup>C NMR spectrum for compound **3m** (CDCl<sub>3</sub>, 125 MHz)

