Synthesis of 1,3,5-trisubstituted pyrazoles via 1,3-dipolar cycloaddition of nitrile imines with ninhydrin-derived Morita−Baylis−Hillman carbonates

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Supporting Information

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1. General methods

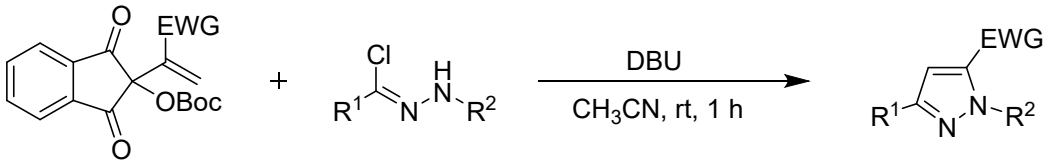
NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 100 MHz. Chemical shifts were reported in

ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. ESI HRMS was recorded on a Waters SYNAPT G2. Column chromatography was performed on silica gel (200-300 mesh) eluting with ethyl acetate/petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and ethyl acetate were distilled. THF was freshly distilled from sodium/benzophenone. Unless otherwise noted, experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes. The ninhydrin-derived Morita−Baylis−Hillman carbonates **1**[1] and hydrazonyl chloride **2**[2] were prepared according to the literature procedures.

(1) (a) Lu, Z.; Jia, Y.; Chen, X.; Li, P., Organocatalytic Regio- and Enantioselective [3 + 2]-Annulations of Ninhydrin-Derived Morita–Baylis–Hillman Carbonates with 3-Methyleneoxindoles. *J. Org. Chem.* **2022**, *87*, 3184-3194. (b) Tang, X.; Wu, Y.; Jiang, J.; Fang, H.; Zhou, W.-J.; Huang, W.; Zhan, G., Formal (3 + 1 + 1) Carboannulation of Morita–Baylis–Hillman Carbonates with Pyridinium Ylides: Access to Spiro-Cyclopentadiene Oxindoles. *Org. Lett.* **2021**, *23*, 8937-8941.

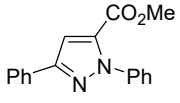
(2) (a) Wang, G.; Liu, X.; Huang, T.; Kuang, Y.; Lin, L.; Feng, X., Asymmetric Catalytic 1,3-Dipolar Cycloaddition Reaction of Nitrile Imines for the Synthesis of Chiral Spiro-Pyrazoline-Oxindoles. *Org. Lett.* **2013**, *15*, 76-79. (b) Garve, L. K. B.; Petzold, M.; Jones, P. G.; Werz, D. B., [3 + 3]-Cycloaddition of Donor–Acceptor Cyclopropanes with Nitrile Imines Generated in Situ: Access to Tetrahydropyridazines. *Org. Lett.* **2016**, *18*, 564-567.

2. General procedure for synthesis of the 1,3,5-trisubstituted pyrazoles 3.



1 **2** **3**

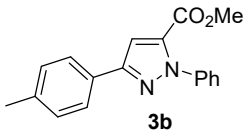
To a solution of ninhydrin-derived Morita−Baylis−Hillman carbonates **1** (0.2 mmol, 1.0 equiv), hydrazonyl chloride **2** (0.22 mmol, 1.1 equiv), and DBU (0.22 mmol, 1.1 equiv) in CH_3CN (1.0 mL) was stirred at room temperature for 1 h. After completion, product **3** was obtained by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 5:1).



3a

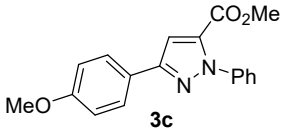
Methyl 1,3-diphenyl-1*H*-pyrazole-5-carboxylate (3a). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (50.6 mg, 91% yield); m.p. 106-107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.41 (m, 7H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 (s, 1H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 151.5, 140.3,

134.2, 132.1, 128.75, 128.73, 128.6, 128.4, 126.1, 125.8, 109.5, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{15}N_2O_2$ 279.1128, found 279.1121.



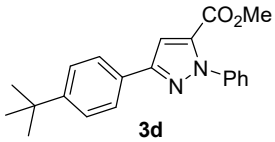
3b

Methyl 1-phenyl-3-(p-tolyl)-1*H*-pyrazole-5-carboxylate (3b) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (53.7 mg, 92% yield); m.p. 58-59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.44 (m, 5H), 7.29 (s, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 3.81 (s, 3H), 2.38 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 151.6, 140.3, 138.3, 134.1, 129.4, 129.3, 128.7, 128.6, 126.1, 125.7, 109.3, 52.0, 21.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{18}H_{17}N_2O_2$ 293.1285, found 293.1276.



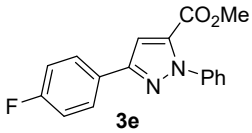
3c

Methyl 3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3c) . Purification by flash chromatography (PE/EA = 10:1) gave a white solid (55.4 mg, 90% yield); m.p. 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.44 (m, 5H), 7.25 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9, 159.6, 151.4, 140.3, 134.1, 128.63, 128.61, 127.1, 126.1, 124.9, 114.1, 109.0, 55.3, 52.0 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{18}H_{17}N_2O_3$ 309.1234, found 309.1227.



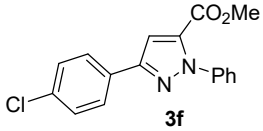
3d

Methyl 3-(4-(tert-butyl)phenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3d) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (60.1 mg, 90% yield); m.p. 53-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.55 – 7.47 (m, 7H), 7.35 (s, 1H), 3.84 (s, 3H), 1.39 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 151.60, 151,56, 140.4, 134.1, 129.4, 128.7, 128.6, 126.1, 125.7, 125.6, 109.4, 52.1, 34.7, 31.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{21}H_{23}N_2O_2$ 335.1754, found 335.1744.



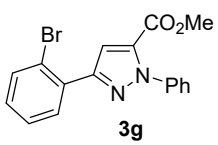
3e

Methyl 3-(4-fluorophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3e) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (62.8 mg, 94% yield); m.p. 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.2, 5.6 Hz, 2H), 7.48 (s, 5H), 7.26 (d, *J* = 5.2 Hz, 1H), 7.11 (t, *J* = 8.4 Hz, 2H), 3.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 246.1 Hz), 159.5, 150.6, 140.2, 134.3, 128.8, 128.6, 128.4 (d, *J* = 3.2 Hz), 127.5 (d, *J* = 8.2 Hz), 126.0, 115.7 (d, *J* = 21.6 Hz), 109.3, 52.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{14}FN_2O_2$ 297.1034, found 297.1030.



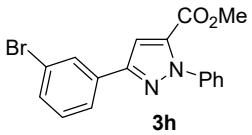
3f

Methyl 3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3f) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (57.4 mg, 92% yield); m.p. 92-93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 5H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 1H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 150.4, 140.1, 134.4, 134.2, 130.7, 129.0, 128.9, 128.7, 127.1, 126.0, 109.4, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{14}ClN_2O_2$ 313.0738, found 313.0735.



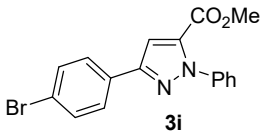
3g

Methyl 3-(2-bromophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3g) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (66.2 mg, 93% yield); m.p. 85-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.43 (m, 6H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 150.6, 140.1, 133.6, 133.23, 133.15, 131.2, 129.7, 128.8, 128.6, 127.5, 126.0, 122.0, 113.4, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{14}BrN_2O_2$ 357.0233(^{79}Br) and 359.0213(^{81}Br), found 357.0224, 359.0203.



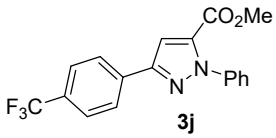
3h

Methyl 3-(3-bromophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3h) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (64.8 mg, 91% yield); m.p. 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.49 (s, 6H), 7.31 – 7.26 (m, 2H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 150.0, 140.1, 134.4, 134.2, 131.3, 130.3, 128.9, 128.8, 128.7, 126.0, 124.3, 123.0, 109.6, 52.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{14}BrN_2O_2$ 357.0233(^{79}Br) and 359.0213(^{81}Br), found 357.0223, 359.0202.



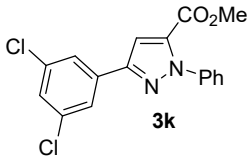
3i

Methyl 3-(4-bromophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3i) . Purification by flash chromatography (PE/EA = 15:1) gave a white solid (66.9 mg, 94% yield); m.p. 79-80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.48 (s, 5H), 7.29 (s, 1H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 150.4, 140.1, 134.4, 131.9, 131.1, 128.9, 128.7, 127.3, 126.0, 122.4, 109.4, 52.1. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{14}BrN_2O_2$ 357.0233(^{79}Br) and 359.0213(^{81}Br), found 357.0223, 359.0204.



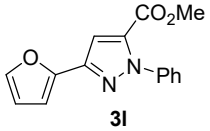
3j

Methyl 1-phenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole-5-carboxylate (3j). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (64.4 mg, 93% yield); m.p. 76-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.50 (s, 5H), 7.37 (s, 1H), 3.83 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 150.1, 140.1, 135.6, 134.6, 130.2 (q, *J* = 32.1 Hz), 129.0, 128.7, 128.23 (s), 126.0 (q, *J* = 7.5 Hz), 125.7 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 270.4 Hz), 109.8, 52.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{18}H_{14}F_3N_2O_2$ 347.1002, found 347.0997.



3k

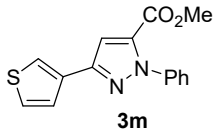
Methyl 3-(3,5-dichlorophenyl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3k). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (65.7 mg, 95% yield); m.p. 153-154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.49 (d, *J* = 4.2 Hz, 5H), 7.33 (s, 1H), 7.30 (s, 1H), 3.82 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 149.0, 140.0, 135.4, 135.0, 134.6, 129.1, 128.7, 128.2, 126.0, 124.1, 109.7, 52.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{13}Cl_2N_2O_2$ 347.0349, found 347.0341.



3l

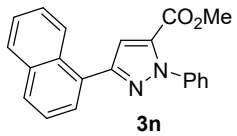
Methyl 3-(furan-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3l). Purification by flash chromatography (PE/EA = 10:1) gave a white solid (45.6 mg, 85% yield); m.p. 56-57

°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 6H), 7.23 (s, 1H), 6.78 (d, *J* = 3.2 Hz, 1H), 6.49 – 6.48 (m, 1H), 3.80 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 147.5, 144.1, 142.4, 140.0, 134.0, 128.9, 128.6, 126.1, 111.5, 109.1, 106.8, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{15}H_{13}N_2O_3$ 269.0921, found 269.0916.



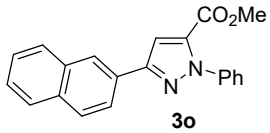
3m

Methyl 1-phenyl-3-(thiophen-3-yl)-1*H*-pyrazole-5-carboxylate (3m). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (51.2 mg, 90% yield); m.p. 66-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 1.2 Hz, 1H), 7.52 (d, *J* = 4.8 Hz, 1H), 7.47 – 7.44 (m, 5H), 7.38 – 7.36 (m, 1H), 7.20 (s, 1H), 3.80 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 147.9, 140.2, 133.94, 133.88, 128.7, 128.6, 126.2, 126.1, 125.9, 121.5, 109.8, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{15}H_{13}N_2O_2S$ 285.0692, found 285.0683.



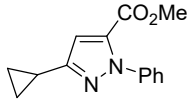
3n

Methyl 3-(naphthalen-1-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3n). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (59.7 mg, 91% yield); m.p. 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.6 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.58 – 7.45 (m, 8H), 7.34 (s, 1H), 3.84 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 151.4, 140.2, 133.9, 133.6, 131.2, 130.0, 129.0, 128.7, 128.6, 127.4, 126.6, 126.1, 125.9, 125.7, 125.3, 113.3, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{21}H_{17}N_2O_2$ 329.1285, found 329.1276.



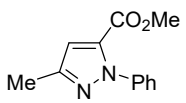
3o

Methyl 3-(naphthalen-2-yl)-1-phenyl-1*H*-pyrazole-5-carboxylate (3o). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (59.0 mg, 90% yield); m.p. 67-68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.91 – 7.83 (m, 3H), 7.55 – 7.45 (m, 8H), 3.83 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 151.5, 140.3, 134.4, 133.5, 133.4, 129.5, 128.8, 128.7, 128.5, 128.3, 127.8, 126.4, 126.2, 126.1, 124.6, 123.8, 109.8, 52.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{21}H_{17}N_2O_2$ 329.1285, found 329.1276.



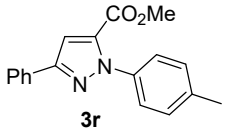
3p

Methyl 3-cyclopropyl-1-phenyl-1*H*-pyrazole-5-carboxylate (3p). Purification by flash chromatography (PE/EA = 15:1) gave a white solid **(**41.4 mg, 85% yield); m.p. 41-42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 5H), 6.66 (s, 1H), 3.75 (s, 3H), 2.04 – 1.97 (m, 1H), 0.97 (dt, *J* = 9.2, 5.2 Hz, 2H), 0.82 – 0.78 (m, 2H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 155.5, 140.3, 133.3, 128.5, 128.4, 125.9, 108.8, 51.9, 9.0, 8.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{14}H_{15}N_2O_2$ 243.1128, found 243.1125.



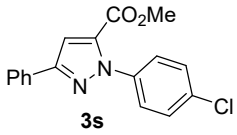
3q

Methyl 3-methyl-1-phenyl-1*H*-pyrazole-5-carboxylate (3q). Purification by flash chromatography (PE/EA = 5:1) gave colourless oil **(**37.2 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 5H), 6.80 (s, 1H), 3.77 (s, 3H), 2.36 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 148.9, 140.3, 133.4, 128.5, 128.4, 125.9, 112.1, 51.9, 13.4 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{12}H_{13}N_2O_2$ 217.0972, found 217.0968.



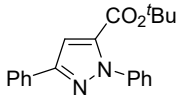
3r

Methyl 3-phenyl-1-(*p*-tolyl)-1*H*-pyrazole-5-carboxylate (3r). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (53.7 mg, 92% yield); m.p. 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.33 (m, 5H), 7.30 – 7.27 (m, 3H), 3.82 (s, 3H), 2.43 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 151.3, 138.8, 137.8, 134.1, 132.2, 129.2, 128.7, 128.3, 125.9, 125.8, 109.3, 52.0, 21.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{18}H_{17}N_2O_2$ 293.1285, found 293.1277.



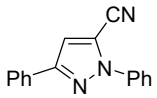
3s

Methyl 1-(4-chlorophenyl)-3-phenyl-1*H*-pyrazole-5-carboxylate (3s). Purification by flash chromatography (PE/EA = 15:1) gave a white solid (59.3 mg, 95% yield); m.p. 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.45 – 7.41 (m, 6H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.32 (s, 1H), 3.83 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 151.8, 138.7, 134.6, 134.2, 131.9, 128.8, 128.6, 127.4, 125.8, 109.8, 52.2 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{17}H_{14}ClN_2O_2$ 313.0738, found 313.0731.



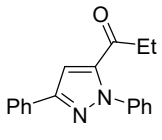
3t

***tert*-Butyl 1,3-diphenyl-1*H*-pyrazole-5-carboxylate (3t)**. Purification by flash chromatography (PE/EA = 15:1) gave a white solid (59.5 mg, 93% yield); m.p. 57-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.40 (m, 7H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.26 (s, 1H), 1.41 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 151.3, 140.8, 136.4, 132.3, 128.7, 128.6, 128.5, 128.3, 126.2, 125.8, 109.3, 82.5, 27.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{20}H_{21}N_2O_2$ 321.1598, found 321.1589.



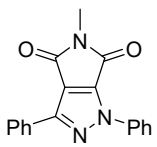
3u

1,3-Diphenyl-1*H*-pyrazole-5-carbonitrile (3u). Purification by flash chromatography (PE/EA = 15:1) gave a tawny solid (46.1 mg, 94% yield); m.p. 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.30 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.7, 138.6, 131.1, 129.6, 129.1, 128.9, 125.9, 122.8, 115.0, 113.1, 111.1 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{16}H_{12}N_3$ 246.1026, found 246.1018.



3v

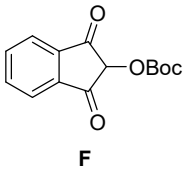
1-(1,3-Diphenyl-1*H*-pyrazol-5-yl)propan-1-one (3v). Purification by flash chromatography (PE/EA = 10:1) gave a yellow solid (52.4 mg, 95% yield); m.p. 45-46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.43 (m, 7H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.27 (s, 1H), 2.93 (q, *J* = 7.2 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.2, 151.4, 140.8, 140.7, 132.1, 128.8, 128.7, 128.6, 126.0, 125.8, 108.8, 34.1, 7.9 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{18}H_{17}N_2O$ 277.1335, found 277.1330.



3x

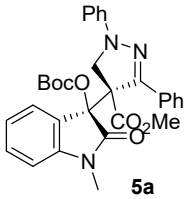
5-Methyl-1,3-diphenylpyrrolo[3,4-*c*]pyrazole-4,6(1*H*,5*H*)-dione (3x). Purification by flash chromatography (PE/EA = 5:1) gave a white solid (57.6 mg, 95% yield); m.p. 129-130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.6 Hz, 2H), 8.24 (d, *J* = 8.0 Hz, 2H), 7.54 – 7.38 (m, 6H), 3.14 (s, 3H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.2, 157.9, 147.5, 142.7, 138.1,

130.0, 129.8, 129.4, 128.8, 128.5, 127.4, 121.2, 120.2, 24.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{18}H_{14}N_3O_2$ 304.1081, found 304.1074.



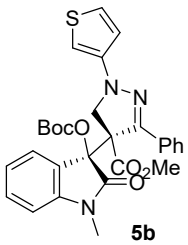
F

***tert*-Butyl (1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl) carbonate (F)**. Purification by flash chromatography (PE/EA = 2:1) gave a white solid (47.2 mg, 90% yield); m.p. 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.90 (dd, *J* = 5.2, 3.2 Hz, 2H), 5.07 (s, 1H), 1.45 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.9, 152.2, 139.7, 136.4, 123.8, 84.6, 76.1, 27.5 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{14}H_{15}O_5$ 263.0914, found 263.0910.



5a

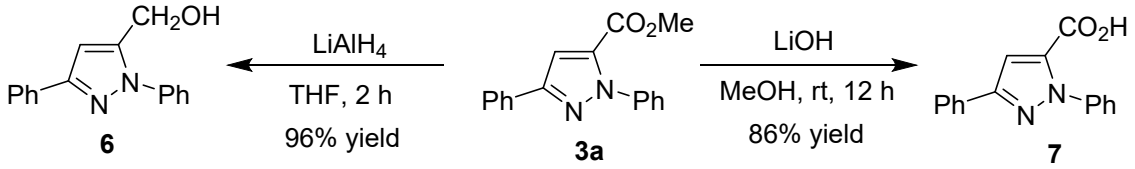
***rac*-methyl (*S*)-4-((*S*)-3-((tert-butoxycarbonyl)oxy)-1-methyl-2-oxoindolin-3-yl)-1,3-diphenyl-4,5-dihydro-1*H*-pyrazole-4-carboxylate (5a)**. Purification by flash chromatography (PE/EA = 15:1) gave a white solid (99.5 mg, 92% yield); m.p. 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.31 (m, 3H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 7.6 Hz, 1H), 4.96 (d, *J* = 16.0 Hz, 1H), 3.72 (d, *J* = 18.0 Hz, 1H), 3.64 (s, 3H), 2.94 (s, 3H), 1.33 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.5, 169.5, 150.1, 149.0, 146.0, 143.5, 131.6, 130.6, 128.9, 128.5, 127.7, 127.0, 126.2, 125.8, 122.3, 120.4, 116.6, 107.8, 83.8, 80.4, 75.8, 52.6, 44.7, 27.6, 26.3 ppm. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{31}H_{32}N_3O_6$ 542.2286, found 542.2277.



5b

***rac*-Methyl (*S*)-4-((*S*)-3-((tert-butoxycarbonyl)oxy)-1-methyl-2-oxoindolin-3-yl)-3-phenyl-1-(thiophen-3-yl)-4,5-dihydro-1*H*-pyrazole-4-carboxylate (5b)**. Purification by flash chromatography (PE/EA = 15:1) gave a white solid (99.6 mg, 91% yield); m.p. 145-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 5.2 Hz, 1H), 7.53 (s, 1H), 7.38 – 7.32 (m, 3H), 7.02 (t, *J* = 8.0 Hz, 2H), 6.84 – 6.77 (m, 5H), 4.67 (d, *J* = 16.4 Hz, 1H), 3.80 (d, *J* = 18.0 Hz, 1H), 3.38 (s, 3H), 3.21 (s, 3H), 1.20 (s, 9H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.8, 169.8, 150.1, 145.8, 145.6, 134.0, 130.8, 128.0, 127.0, 126.2, 126.1, 124.4, 124.2, 122.2, 120.7, 116.3, 108.0, 83.2, 81.7, 79.4, 52.6, 44.7, 27.4, 26.4. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for: $C_{29}H_{30}N_3O_6S$ 548.1850, found 548.1847.

3. Transformations of product 3a

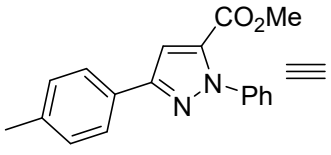


To a stirred suspension of **3a** (0.3 mmol, 83.4 mg) in 3 mL of anhydrous THF was added in portions 22.8 mg (0.6 mmol) of lithium aluminum hydride at 0°C, after stirring for 2 h from 0°C to room temperature until the

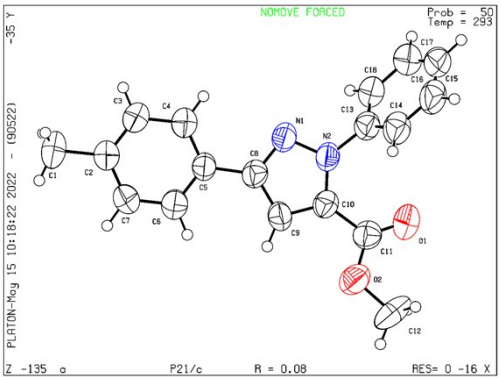
reaction was completed as monitored by TLC analysis. The reaction mixture is stirred for another 15 min, diluted with ether (5 mL), and quenched by dropwise addition of water (5 mL). It was extracted with ether (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered. The filtrate was concentrated under vacuum, and the residue was purified by a flash column chromatography on silica gel (PE /EA = 2:1) to give the product **(1,3-diphenyl-1*H*-pyrazol-5-yl)methanol (6)** (72.0 mg, 96% yield) as a white solid. m.p. 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.31 (m, 6H), 6.73 (s, 1H), 4.65 (s, 2H), 2.12 (br, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.7, 143.3, 139.5, 132.9, 129.3, 128.7, 128.03, 127.92, 125.8, 124.5, 104.9, 55.8 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for: calcd. for $C_{16}H_{15}N_2O$ 251.1179, found 251.1176.

To a solution of compound **3a** (0.3 mmol, 83.4 mg) in MeOH (2 ml) at 0°C was slowly added aqueous LiOH (1M, 2 ml) over 15 min. The reaction mixture was allowed to warm to room temperature overnight with stirring. The organic solvent was removed *in vacuo* and the residual aqueous solution was partitioned with Et_2O, then the organic phase was extracted with H_2O (two times). The combined aqueous extract was acidified to pH 2 with 1N HCl. The aqueous phase was extracted with $CHCl_3$ (three times). The combined organic extract was dried over $MgSO_4$ and concentrated to afford the desired acid **7** (68.2 mg, 86%). m.p. 137-138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.25 (br, 1H), 7.36 – 7.30 (m, 8H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.12 (s, 1H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 145.1, 143.3, 139.3, 129.3, 129.0, 128.9, 128.8, 128.6, 128.5, 125.6, 110.4 ppm. HRMS (ESI) m/z: $[M + H]^+$ calcd for: calcd. for $C_{16}H_{13}N_2O_2$ 265.0972, found 265.0970.

4. Crystal data and structural refinement for 3b and 5b

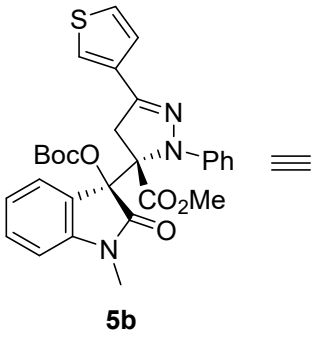


3b CCDC 2173121

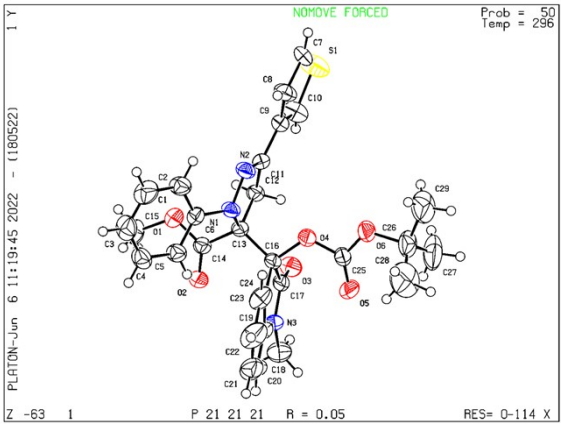


Identification code	**3b**
Empirical formula	$C_{18}H_{16}N_2O_2$
Formula weight	292.33
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	P21/c

a/Å	5.8340(10)
b/Å	18.3400(9)
c/Å	14.5000(11)
α/°	90
β/°	97.21(3)
γ/°	90
Volume/Å^3	1539.2(3)
Z	4
ρ_{calc}g/cm^3	1.262
μ/mm^{-1}	0.083
F(000)	616
Crystal size/mm^3	0.32 × 0.25 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.80 to 24.99
Index ranges	$-6 \le h \le 6$, $-21 \le k \le 13$, $-17 \le l \le 17$
Reflections collected	7344
Independent reflections	948 [R_{int} = 0.0786]
Data/restraints/parameters	2694 / 0 / 200
Goodness-of-fit on F^2	0.825
Final R indexes [I>=2σ (I)]	R_1 = 0.0786, wR_2 = 0.1681
R indices (all data)	R_1 = 0.2123, wR_2 = 0.2139
Largest diff. peak and hole/ 1-sigma level	0.202 / −0.187 / 0.053



5b

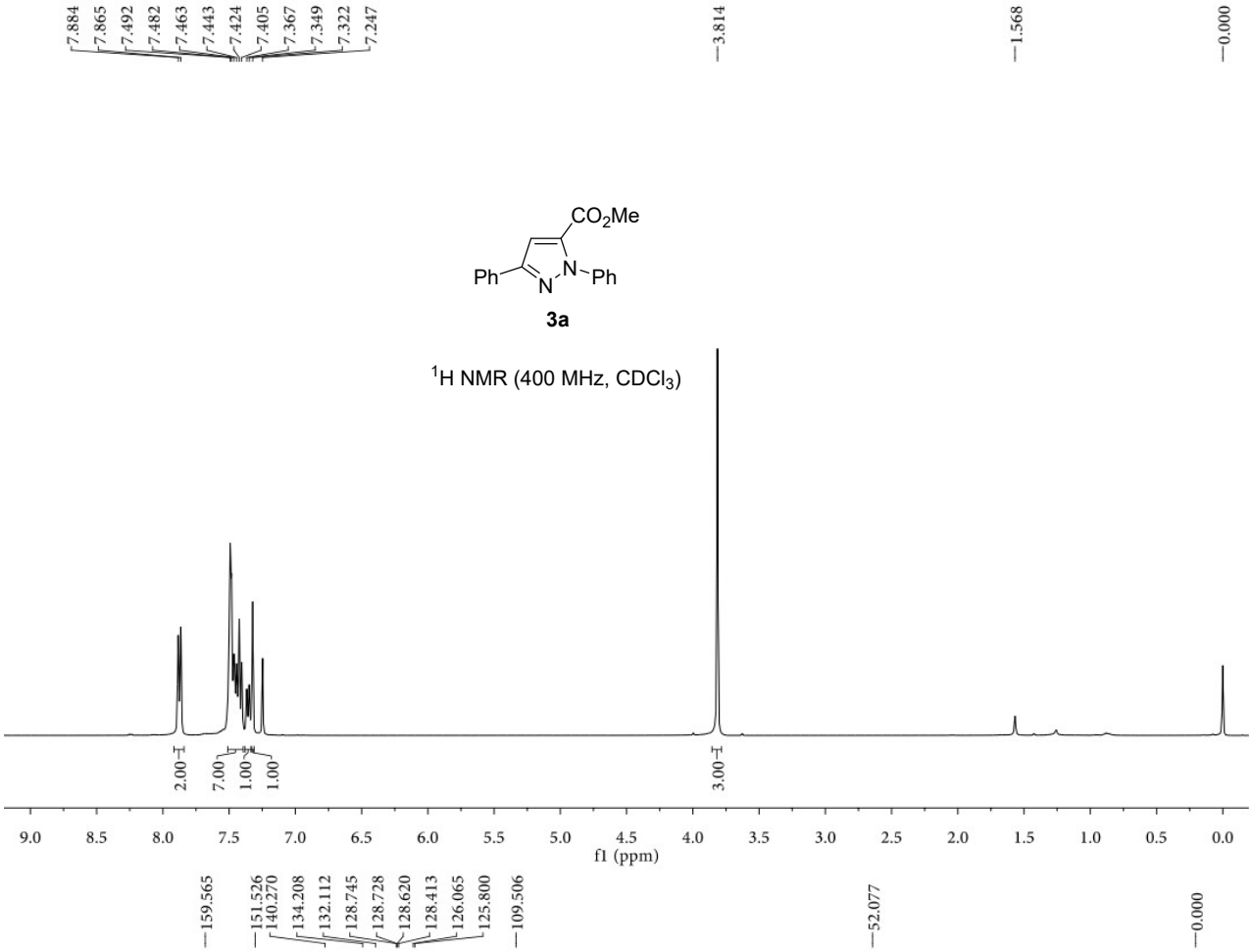


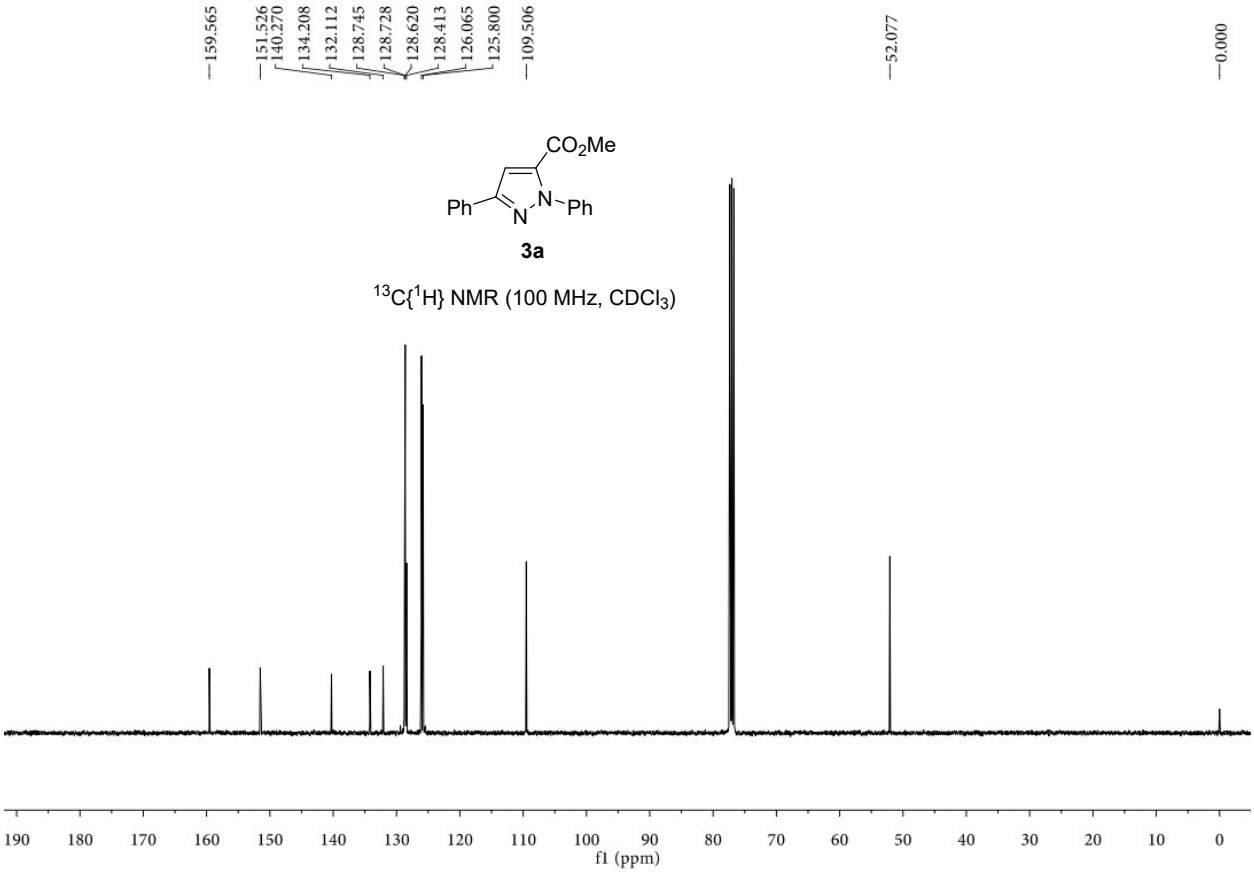
CCDC 2177446

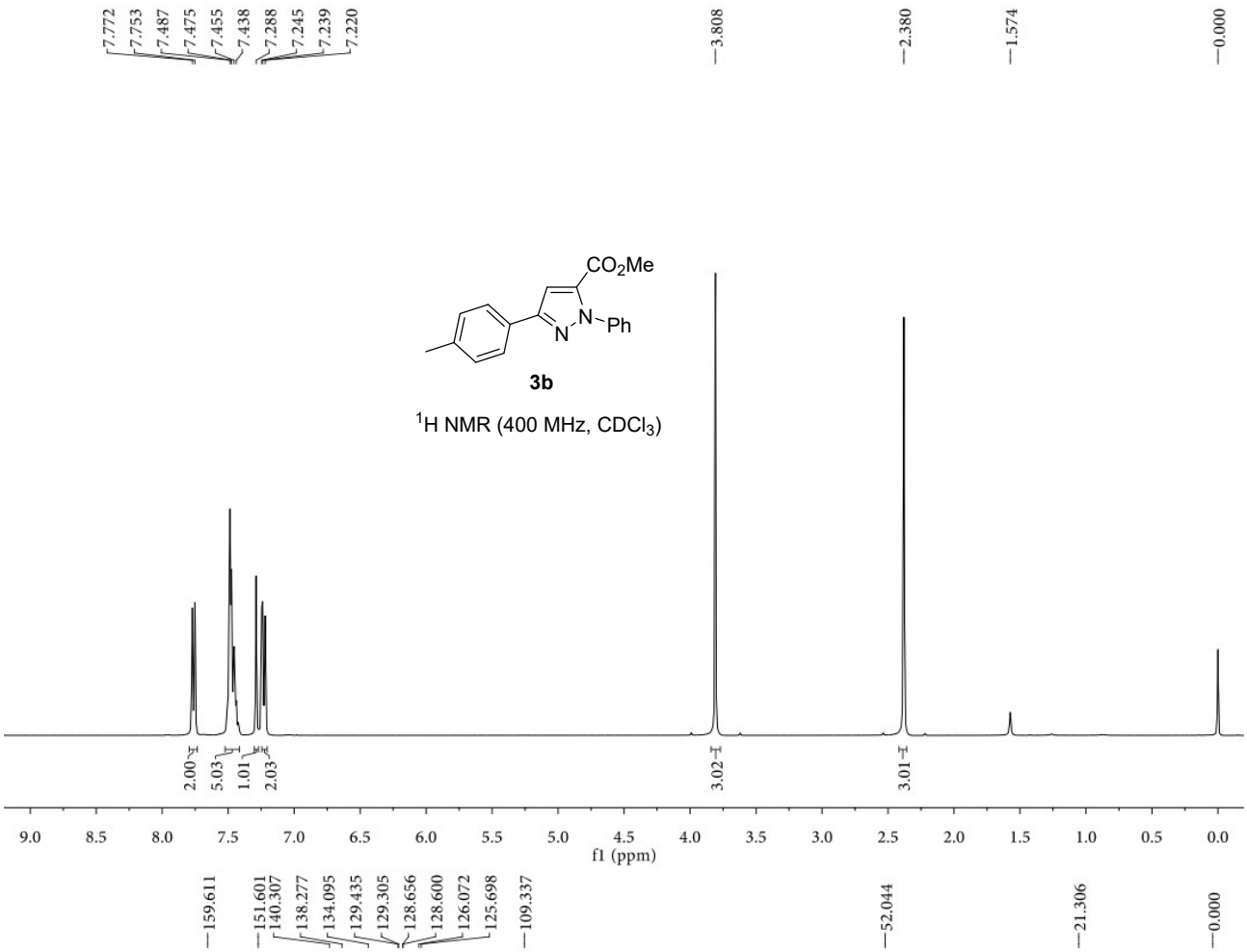
Identification code	**5b**
Empirical formula	$C_{29}H_{29}N_3O_6S$
Formula weight	547.61
Temperature/K	293
Crystal system	orthorhombic
Space group	P 21 21 21
a/Å	11.1944(15)
b/Å	12.3535(17)
c/Å	20.244(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2799.5(7)
Z	4
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	0.163
F(000)	1152.0
Crystal size/mm^3	0.26 × 0.25 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.46 to 22.67

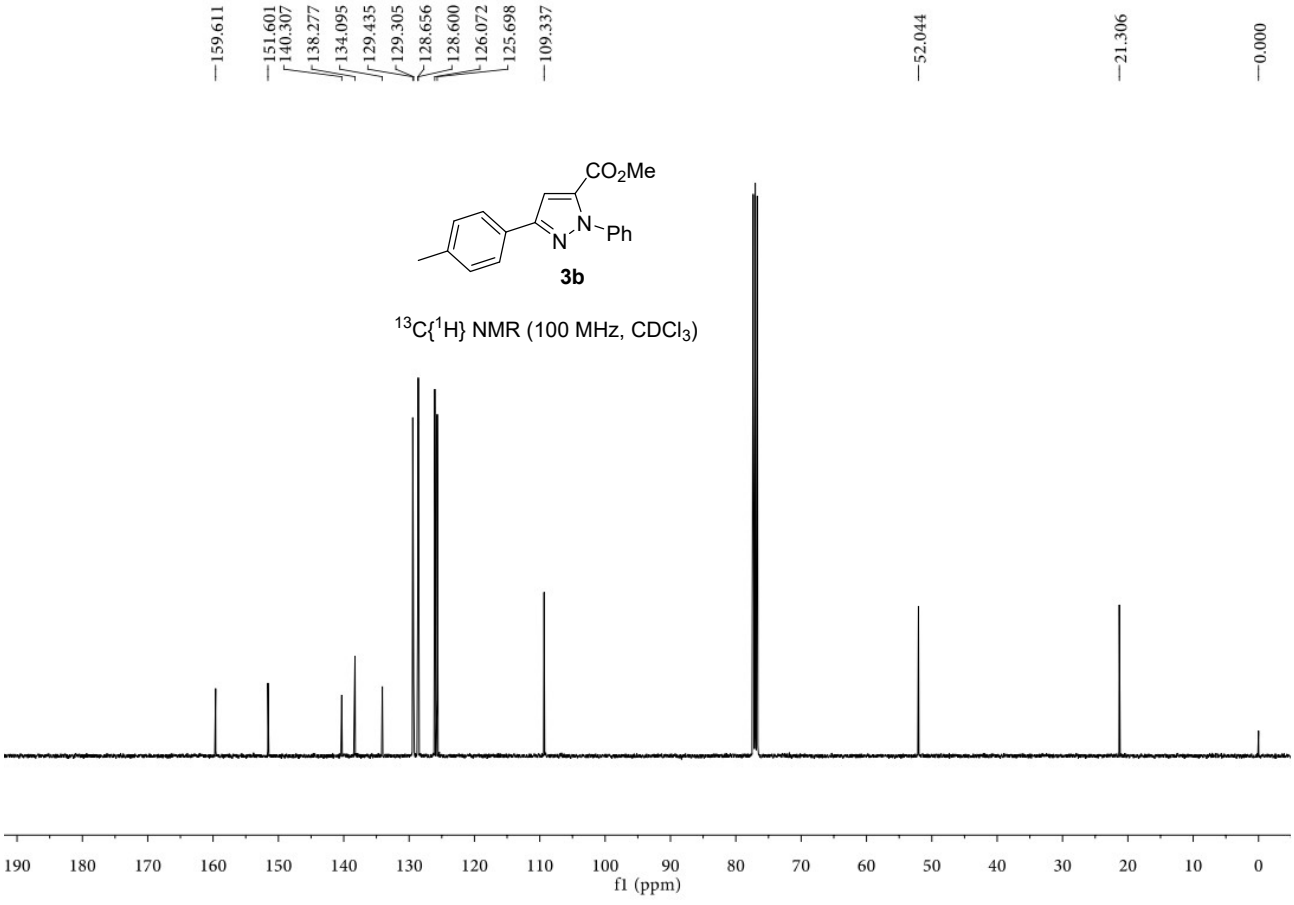
Index ranges	$-8 \leq h \leq 13, -14 \leq k \leq 14, -22 \leq l \leq 24$
Reflections collected	14358
Independent reflections	4004 [$R_{int} = 0.0339$]
Data/restraints/parameters	4918 / 2 / 357
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	$R_1 = 0.0622$, $wR_2 = 0.1327$
R indices (all data)	$R_1 = 0.0472$, $wR_2 = 0.1252$
Largest diff. peak and hole/ 1-sigma level	0.431 / − 0.373 / 0.050

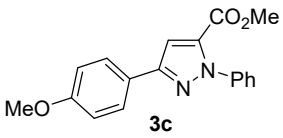
5. NMR spectra





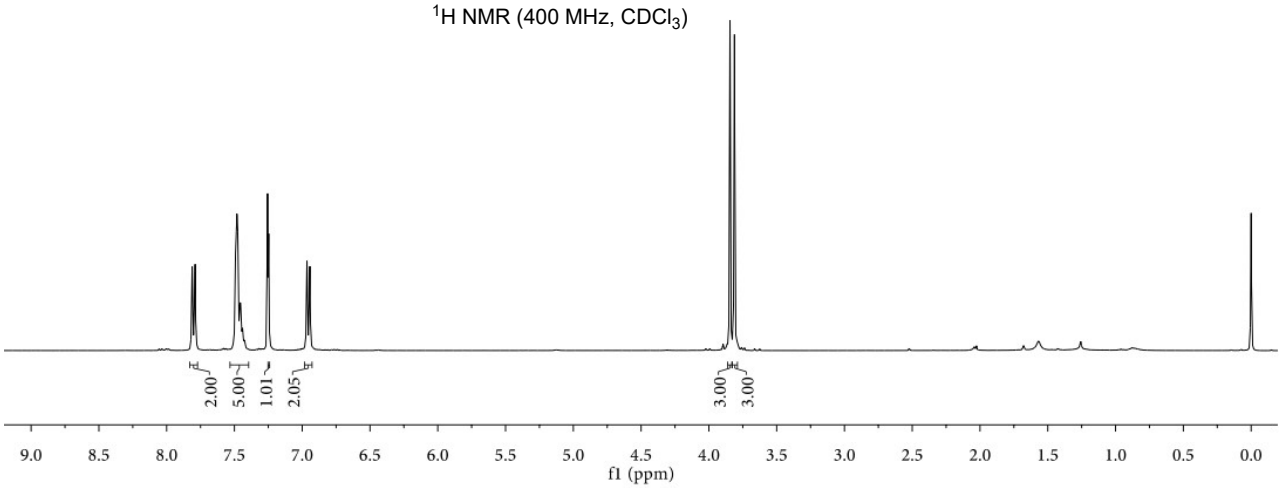

7.772
7.753
7.487
7.475
7.455
7.438
7.288
7.245
7.239
7.220
3.808
2.380
1.574
0.000
CO2Me
N
N
Ph
3b
1H NMR (400 MHz, CDCl3)
2.00
5.03
1.01
2.03
3.02
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

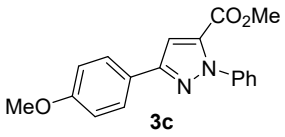

159.611
151.601
140.307
138.277
134.095
129.435
129.305
128.656
128.600
126.072
125.698
109.337
52.044
21.306
0.000
CO2Me
N
N
Ph
3b
13C{1H} NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3c

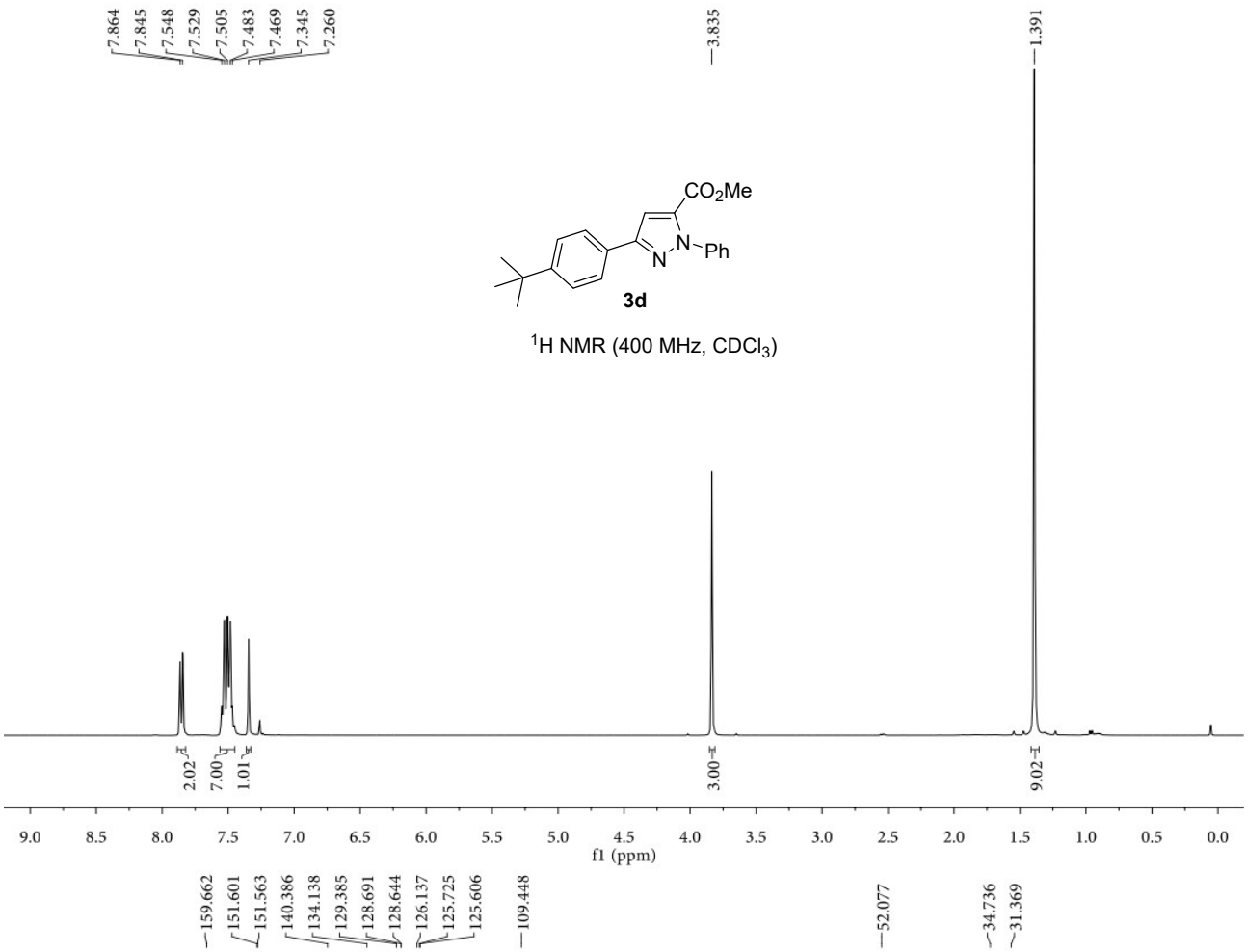
^{1}H NMR (400 MHz, $CDCl_3$)





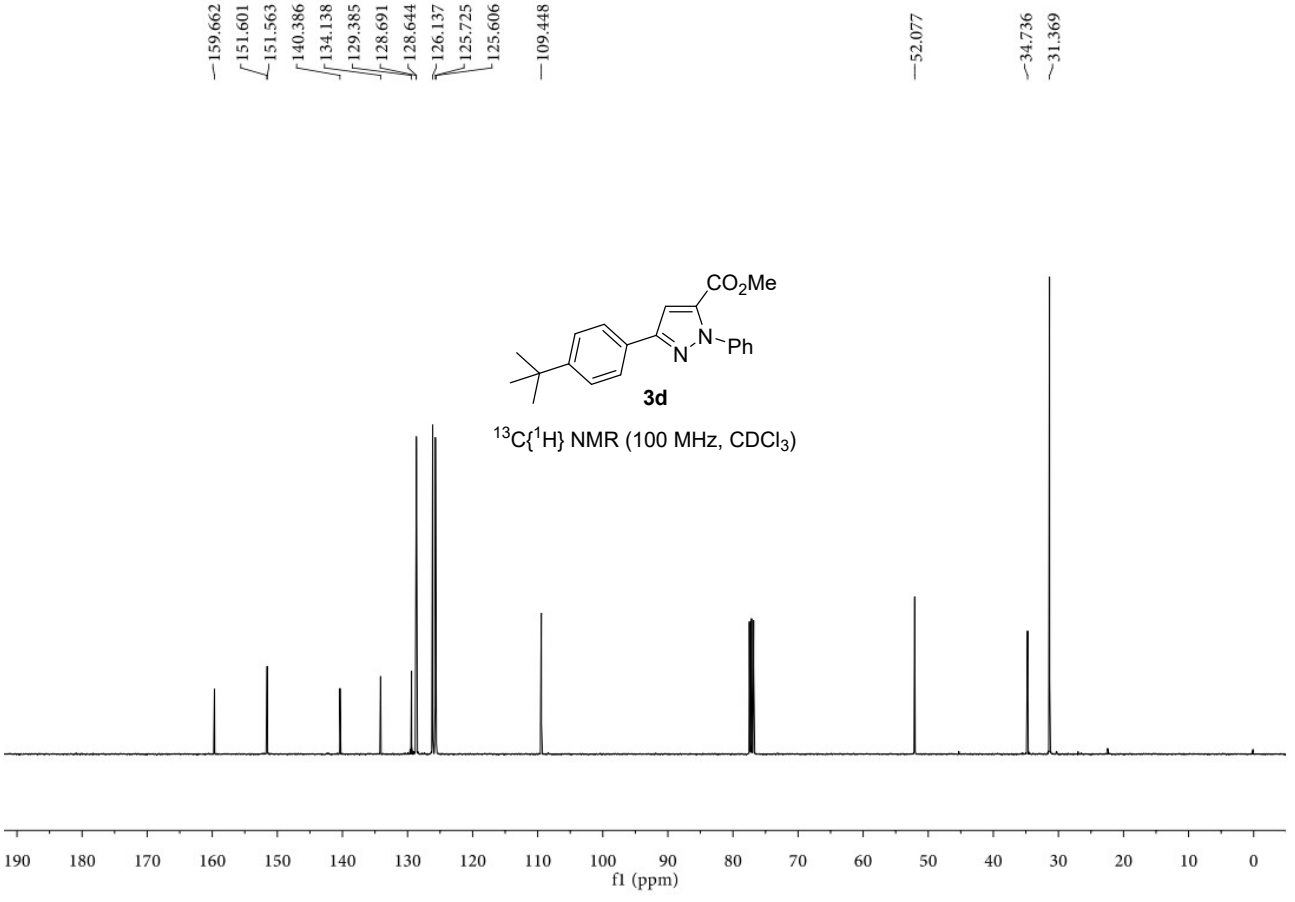
3c

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



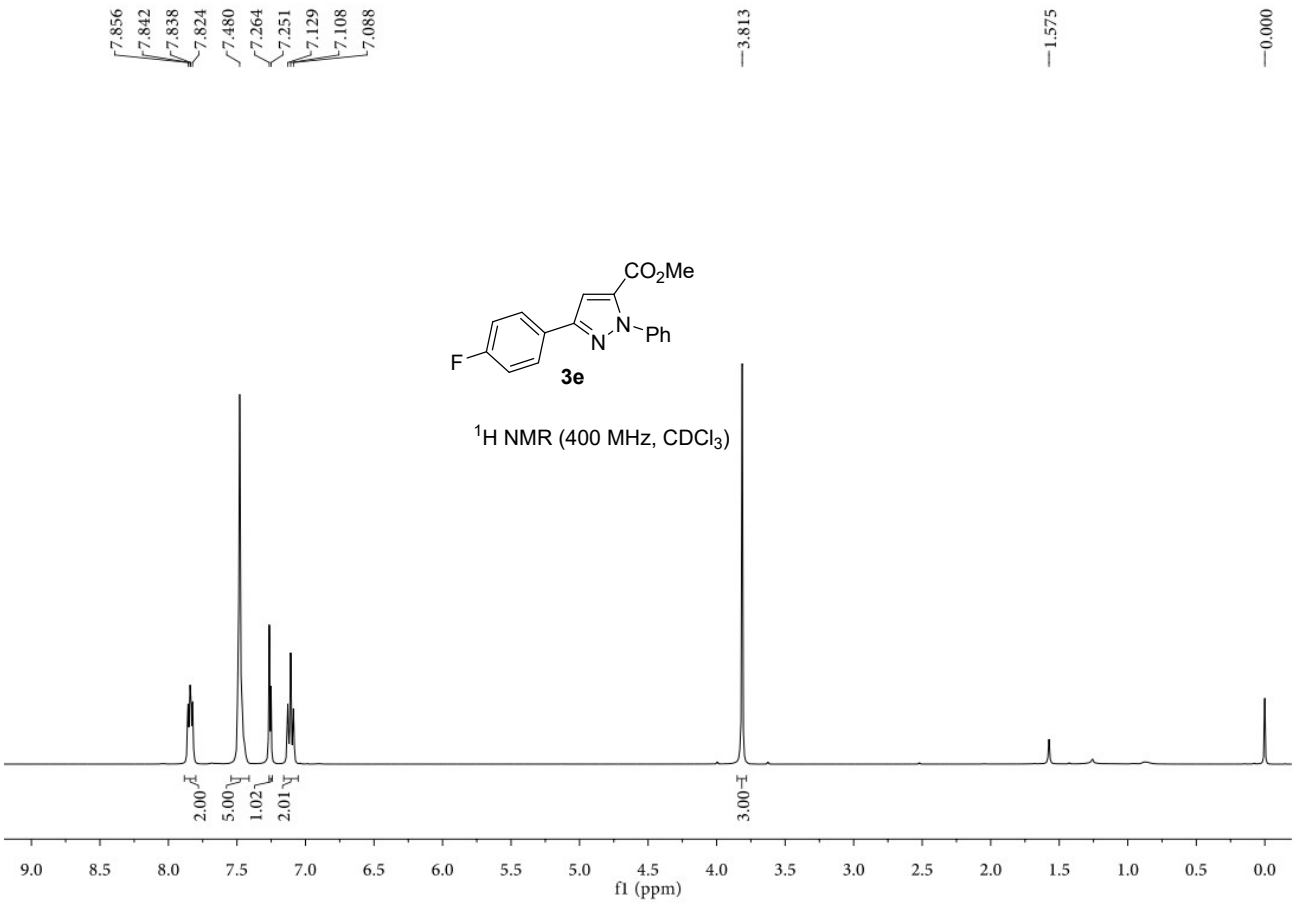
3d

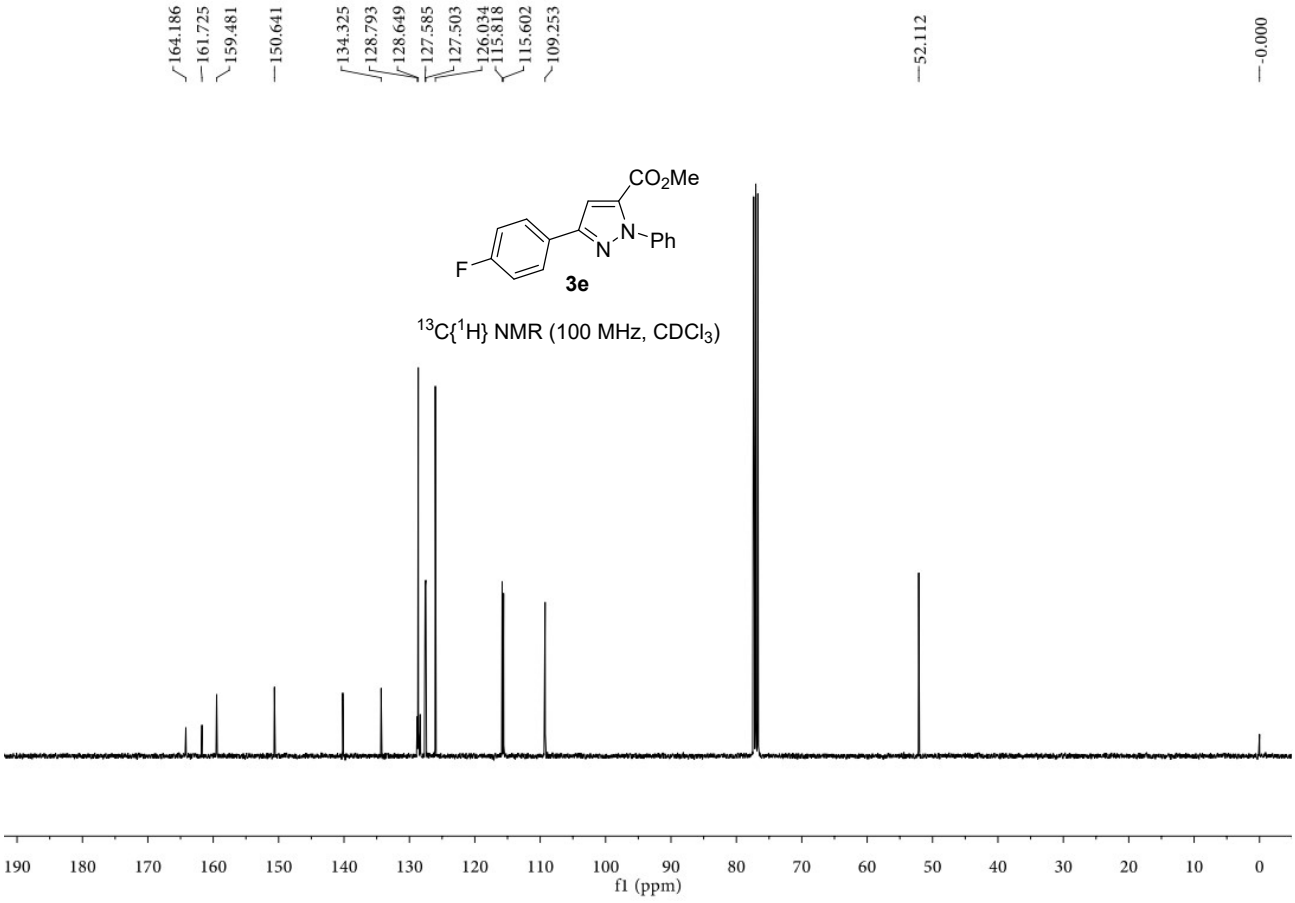
^{1}H NMR (400 MHz, $CDCl_3$)

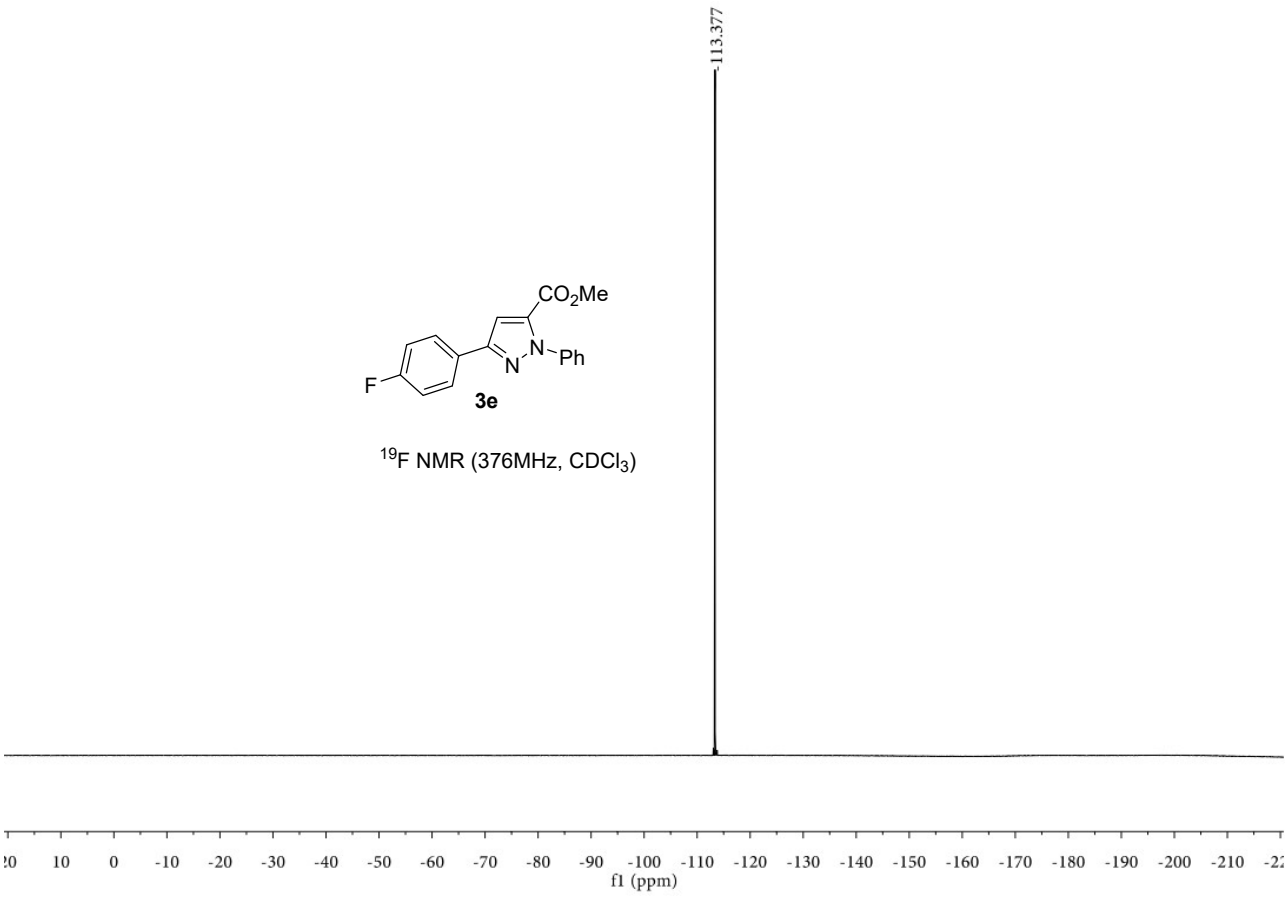


3d

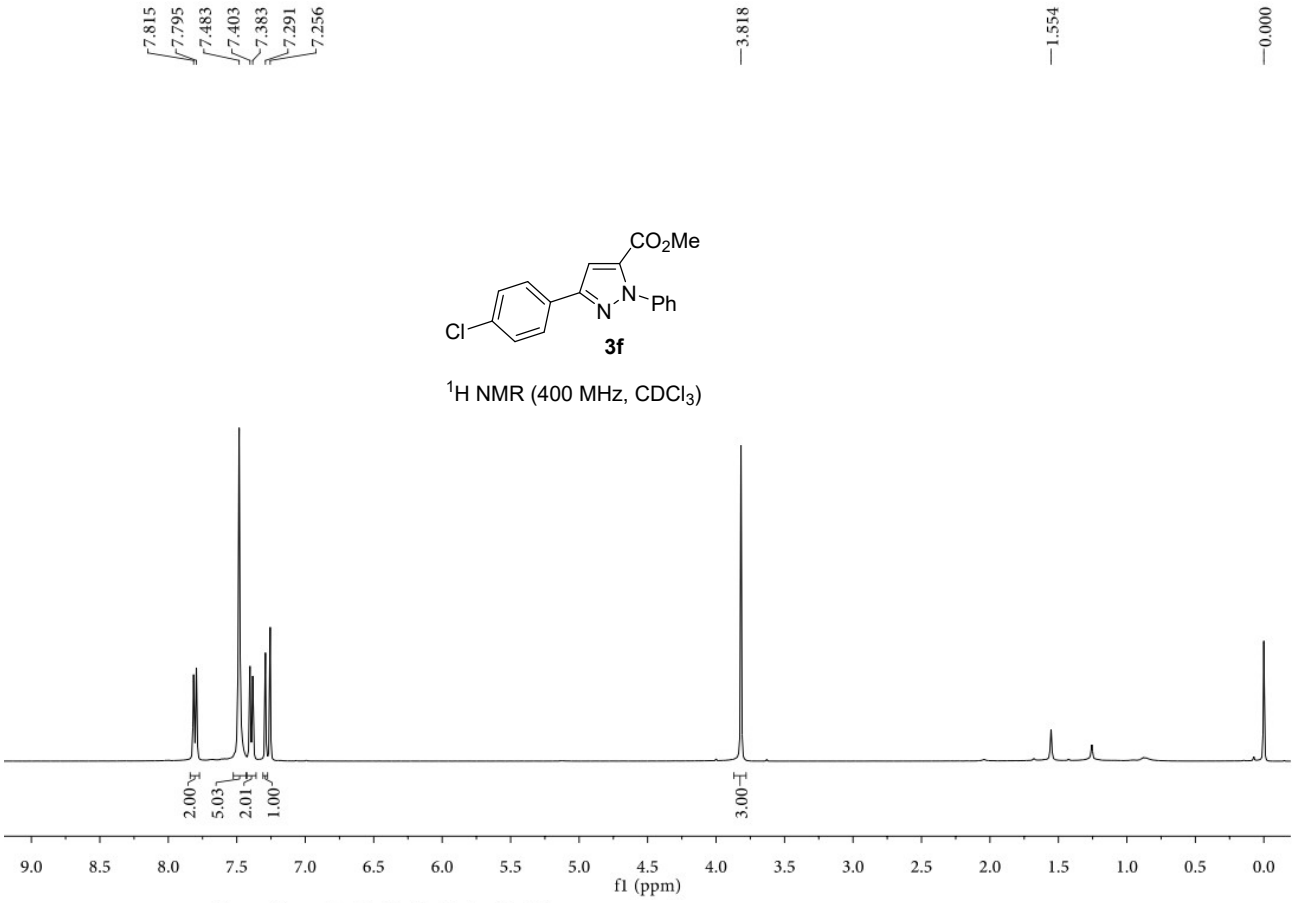
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)


7.856
7.842
7.838
7.824
7.480
7.264
7.251
7.129
7.108
7.088
3.813
1.575
0.000
CO2Me
N
N
Ph
F
3e
1H NMR (400 MHz, CDCl3)
2.00
5.00
1.02
2.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

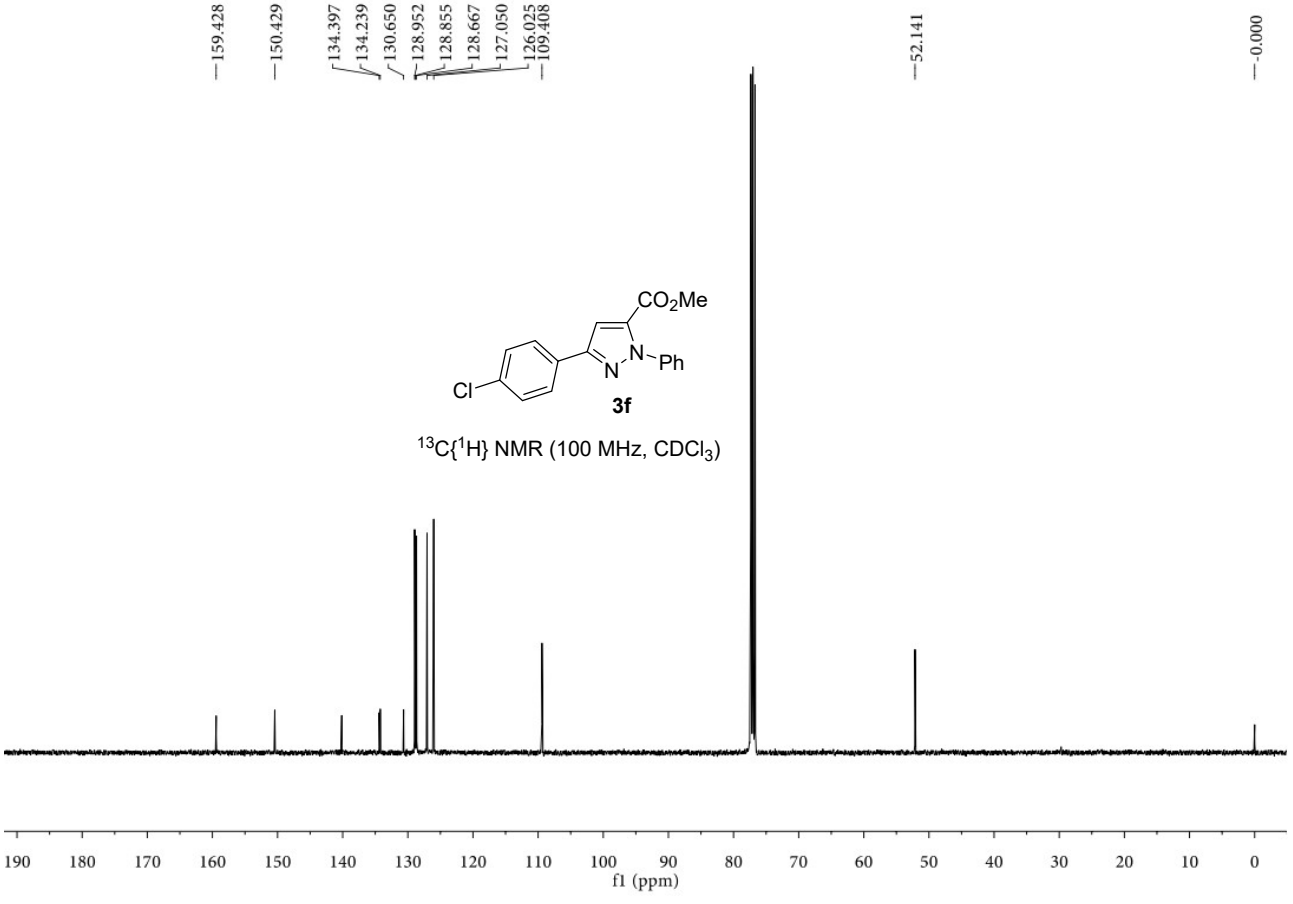

164.186
161.725
159.481
150.641
134.325
128.793
128.649
127.585
127.503
126.034
115.818
115.602
109.253
52.112
-0.000
CO2Me
N
N
Ph
F
3e
13C{1H} NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



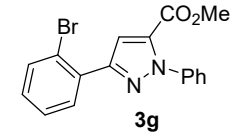
^{19}F NMR (376MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

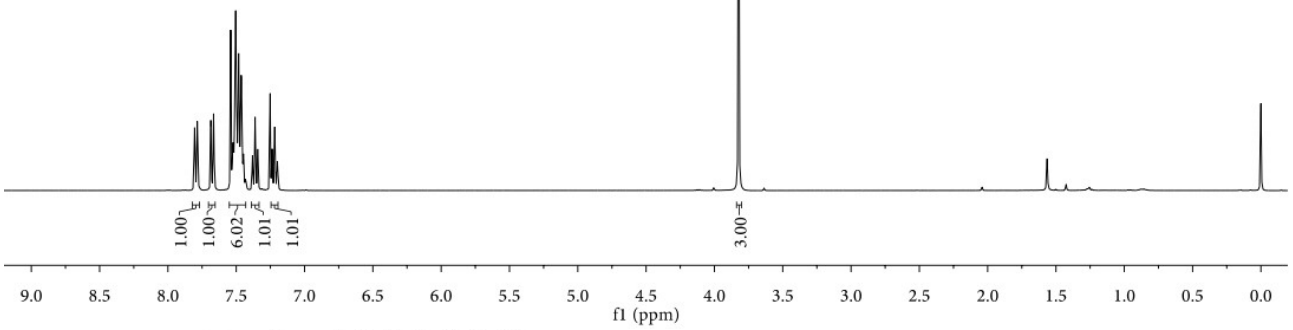


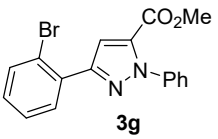
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



3g

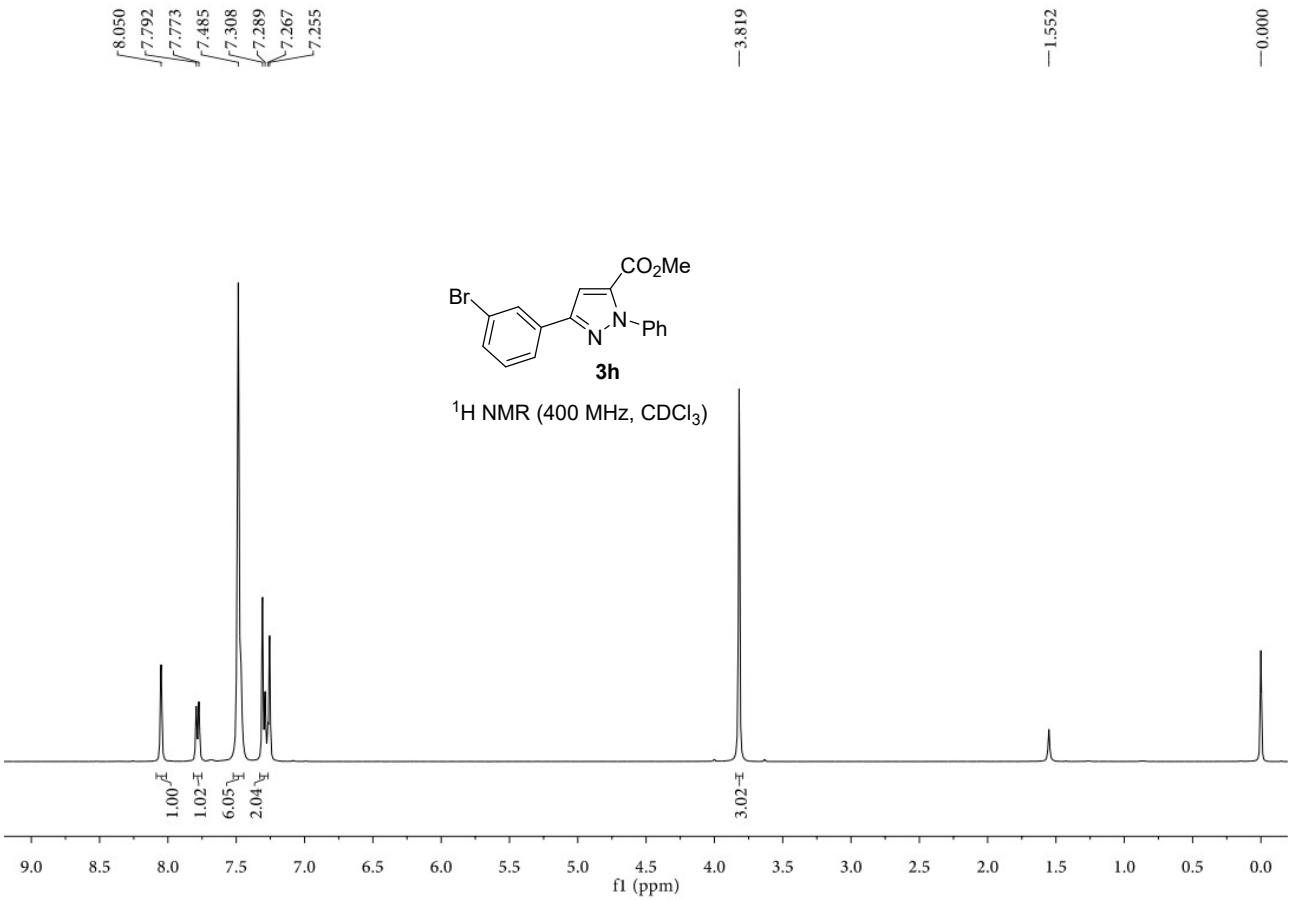
^{1}H NMR (400 MHz, $CDCl_3$)



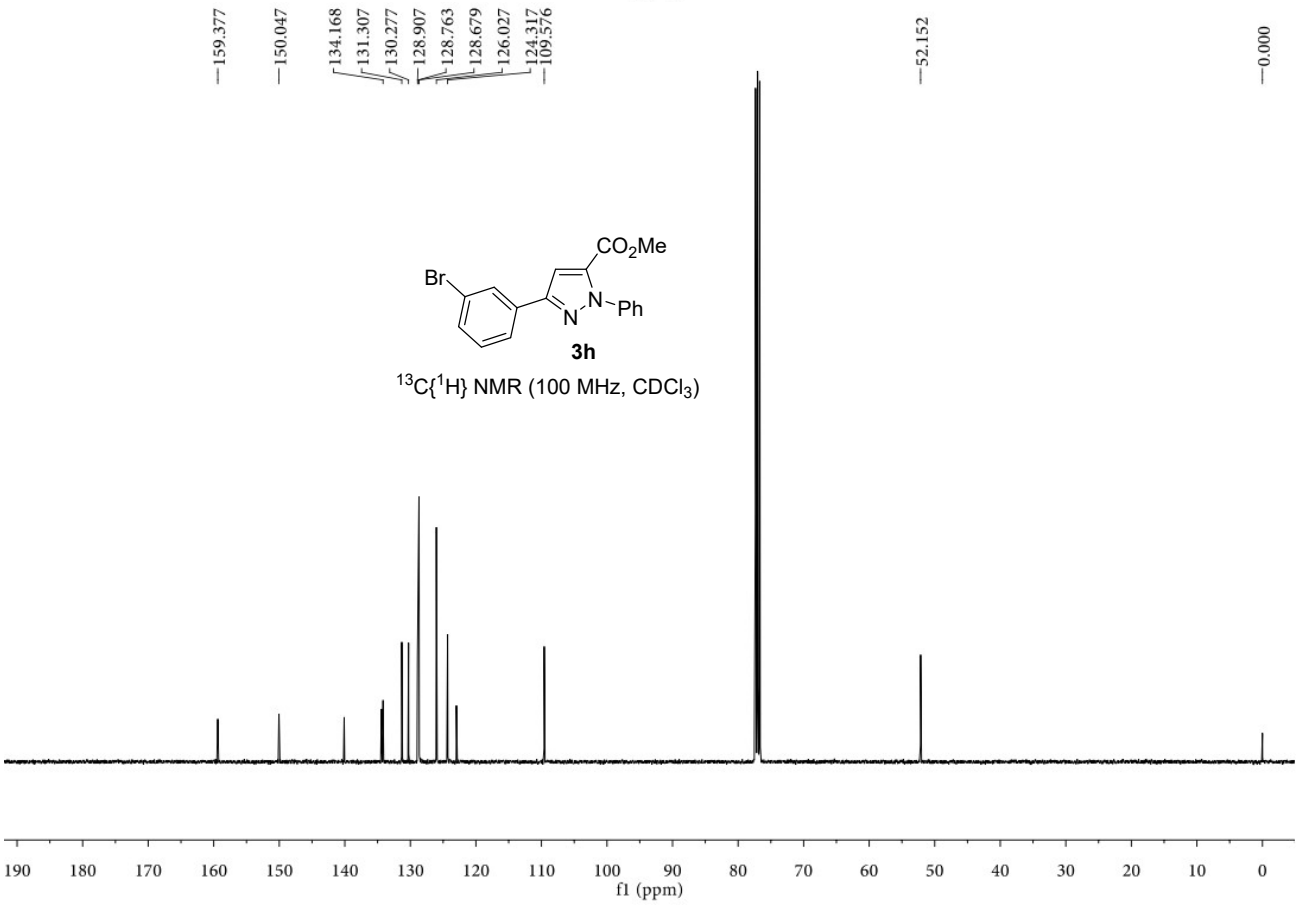


3g

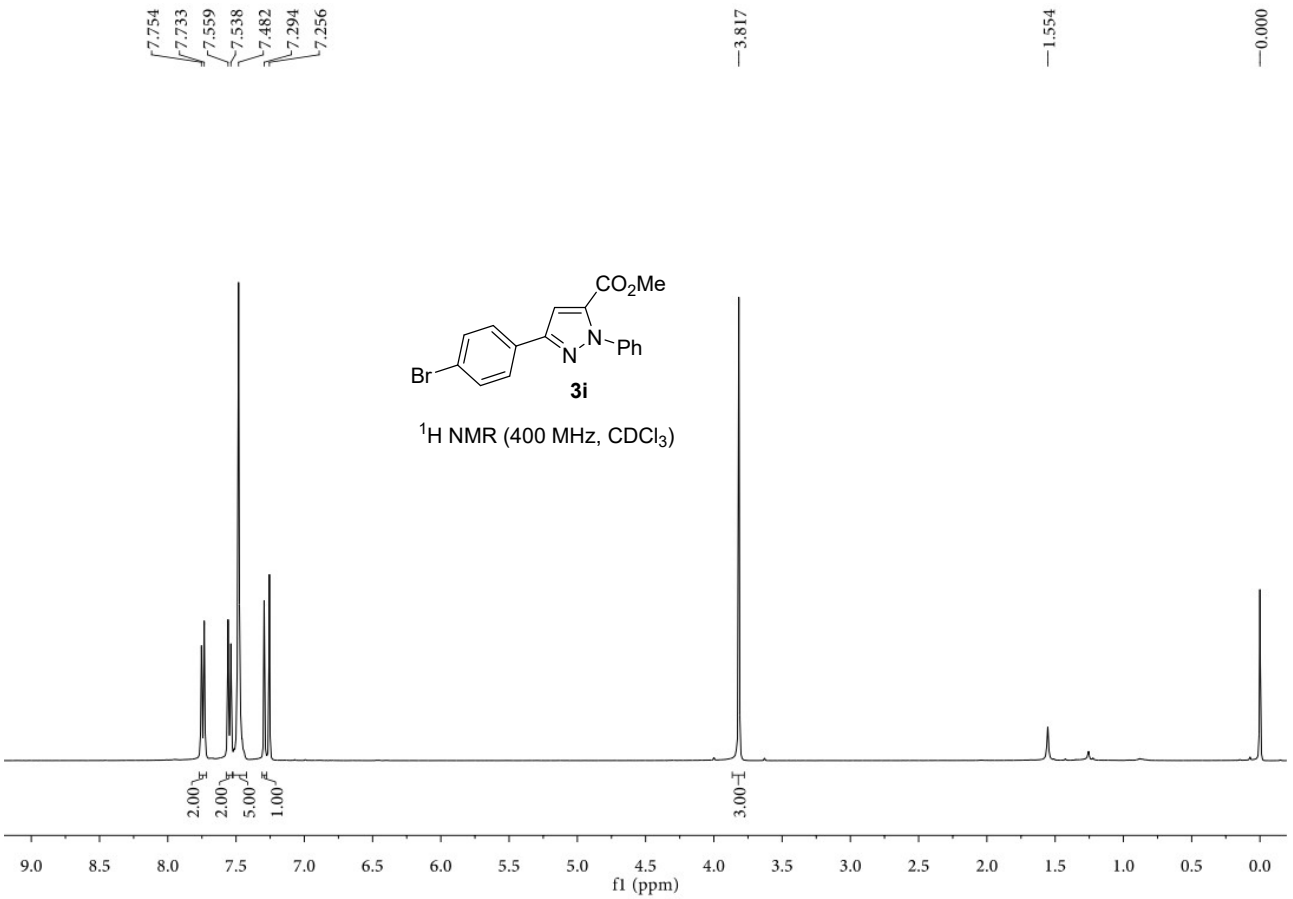
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



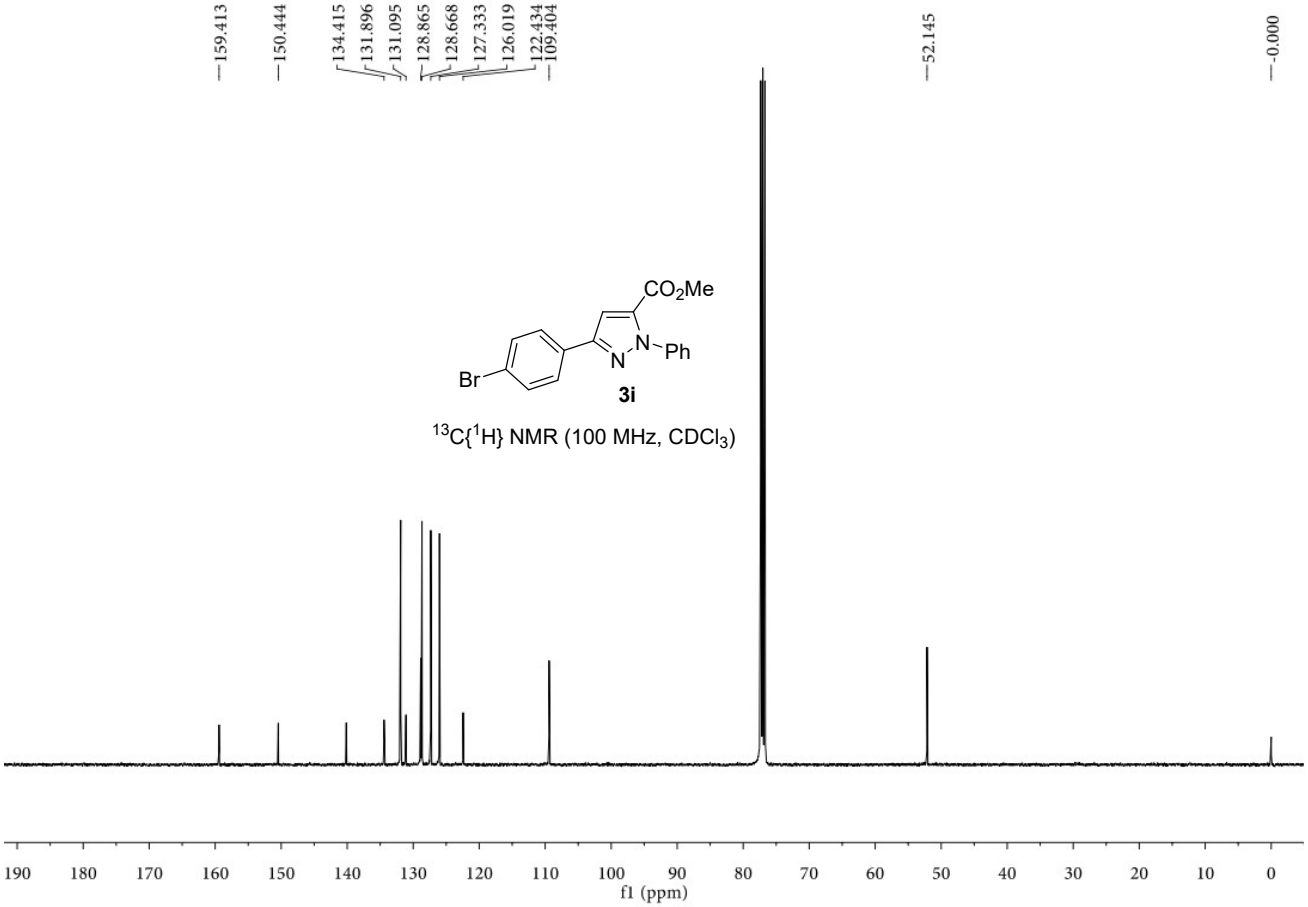
^{1}H NMR (400 MHz, $CDCl_3$)



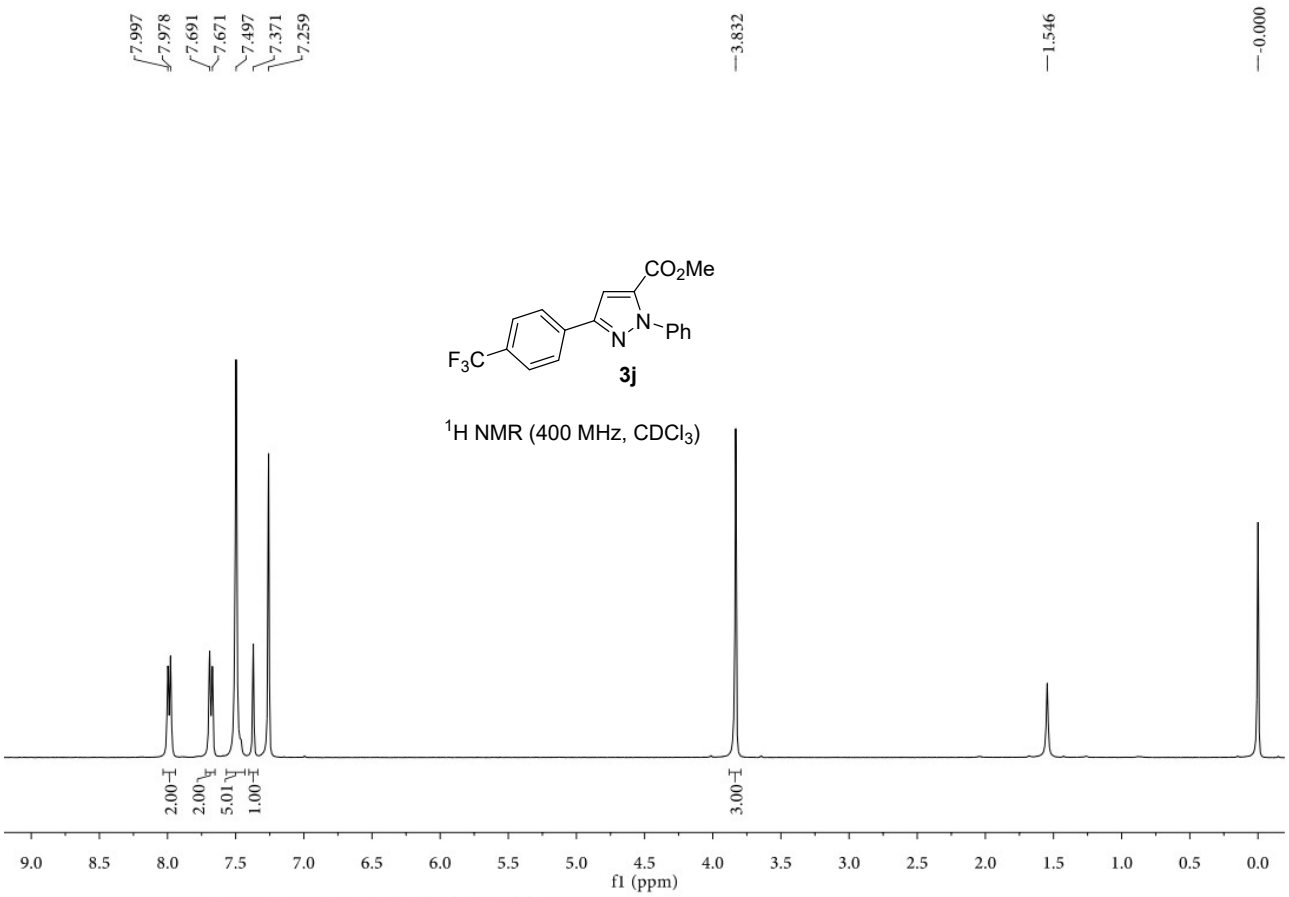
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

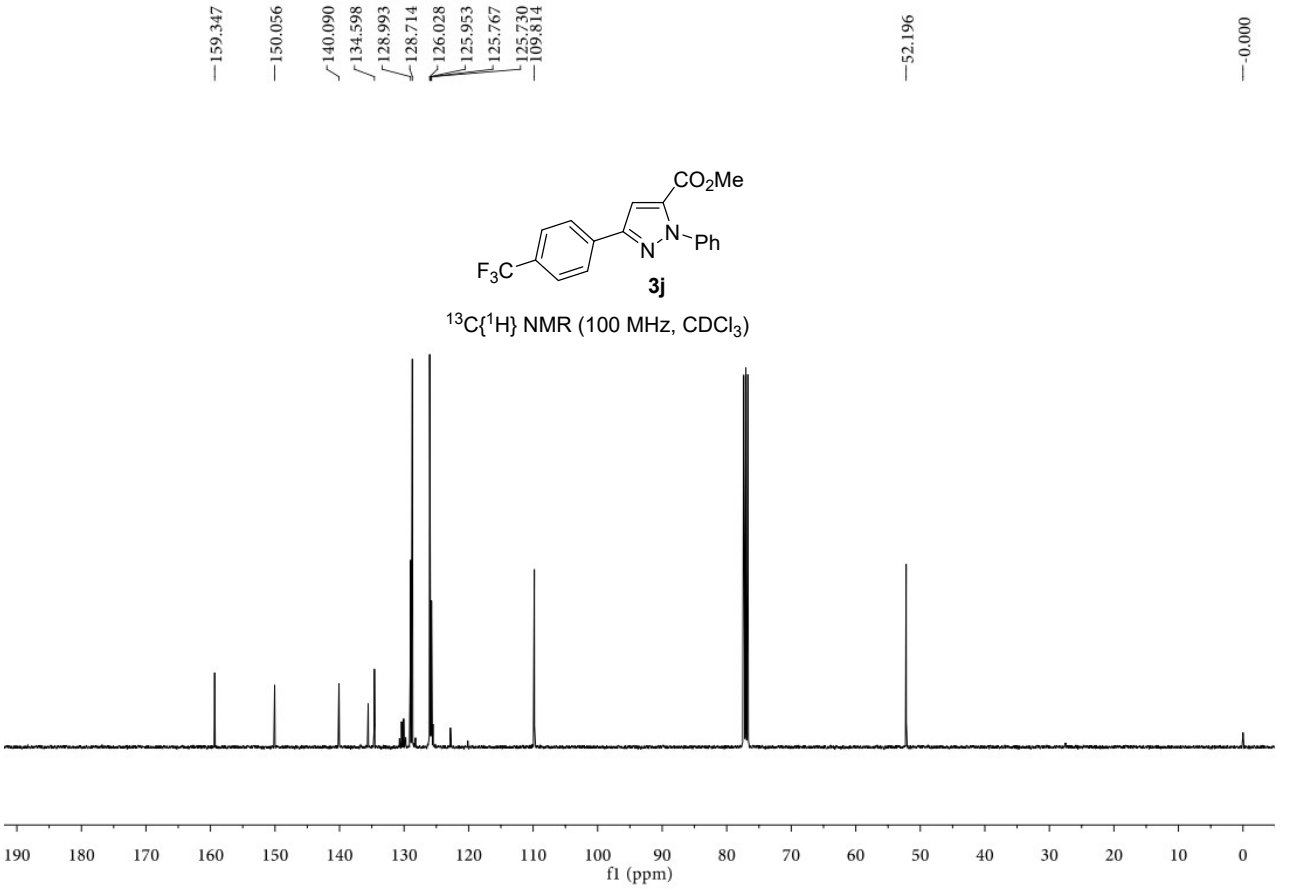


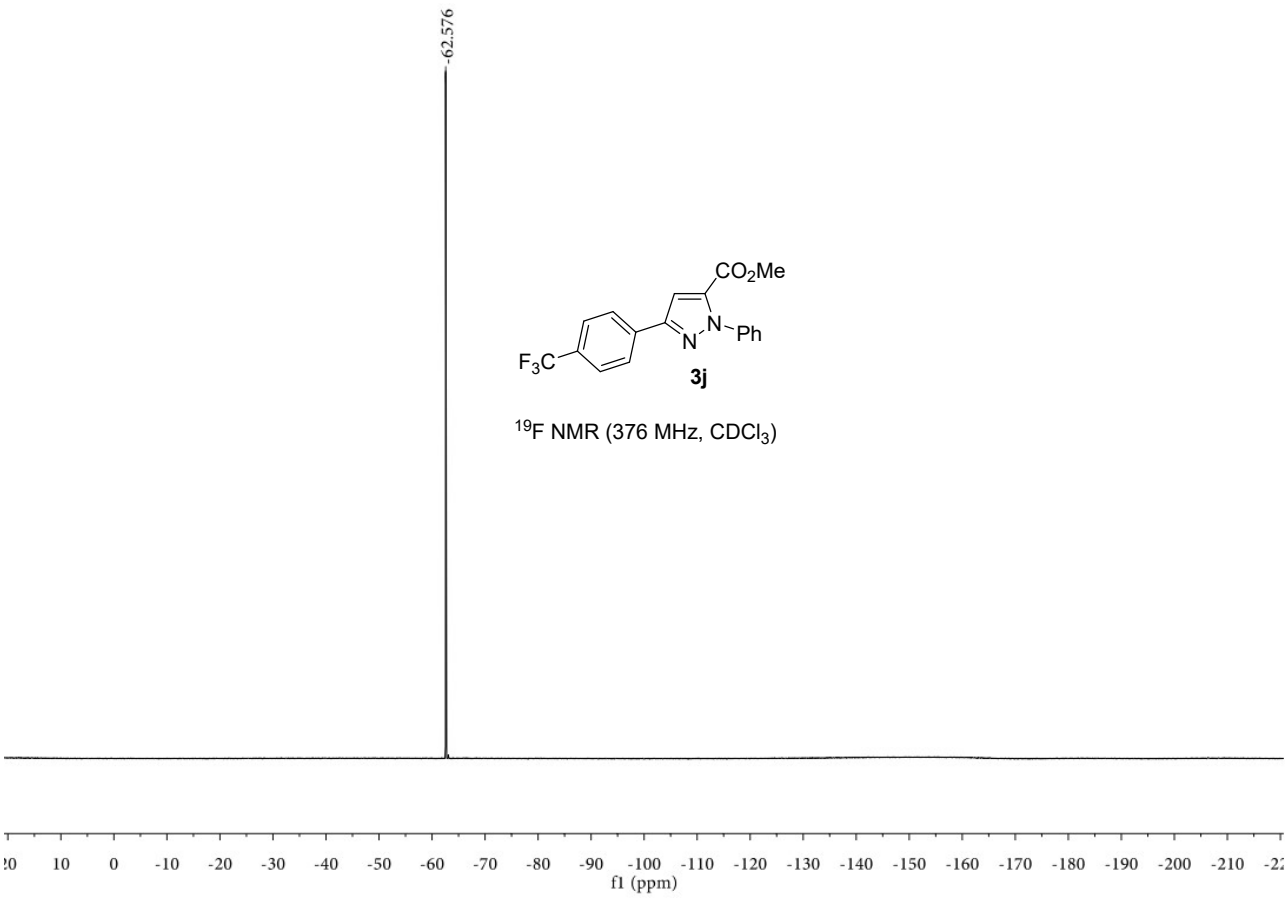
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

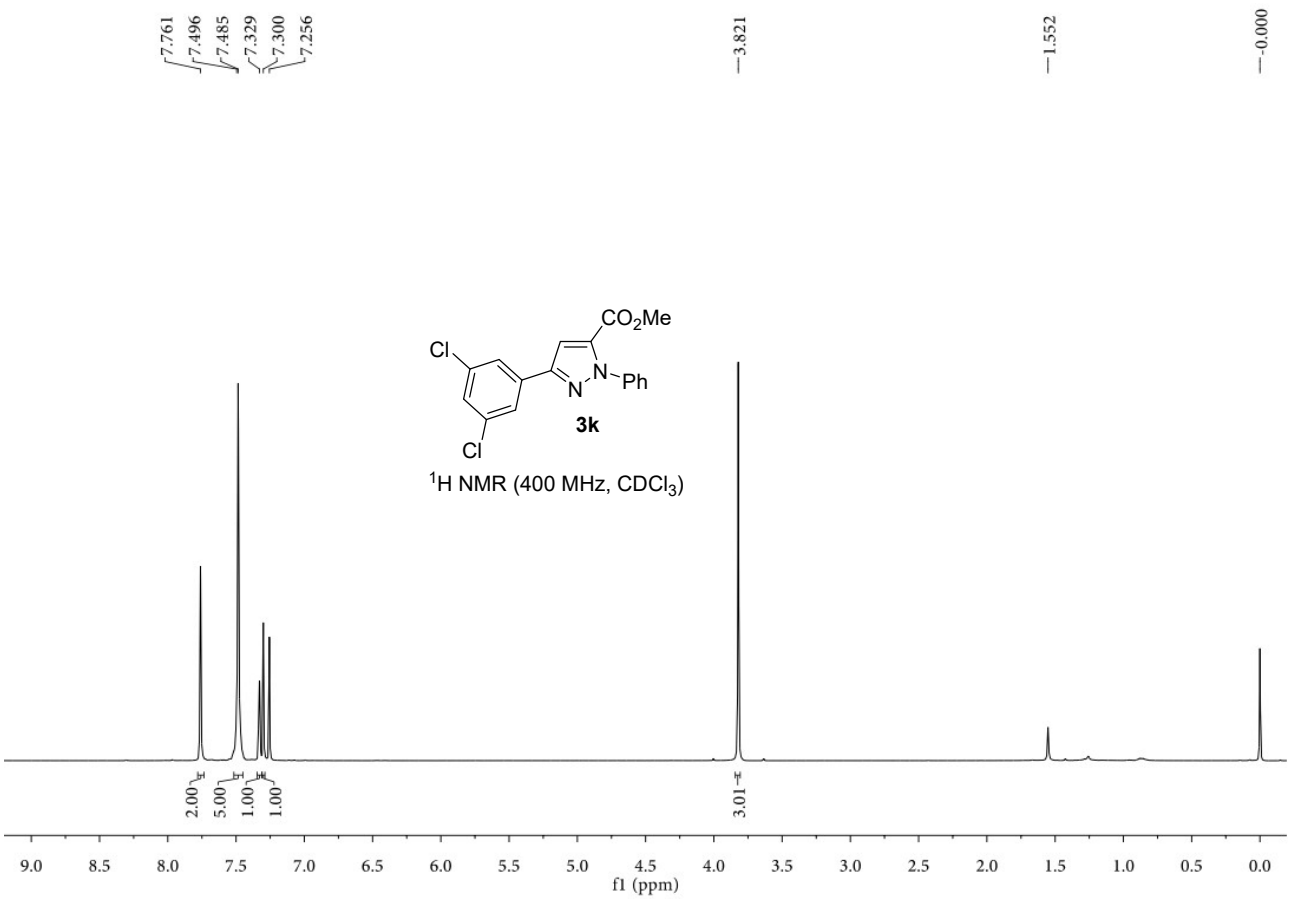

7.997
7.978
7.691
7.671
7.497
7.371
7.259
3.832
1.546
0.000
CO2Me
N
N
Ph
F3C
3j
1H NMR (400 MHz, CDCl3)
2.00
2.00
5.01
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.347
150.056
140.090
134.598
128.993
128.714
126.028
125.953
125.767
125.730
109.814
52.196
0.000
CO2Me
N
N
Ph
F3C
3j
13C{1H} NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

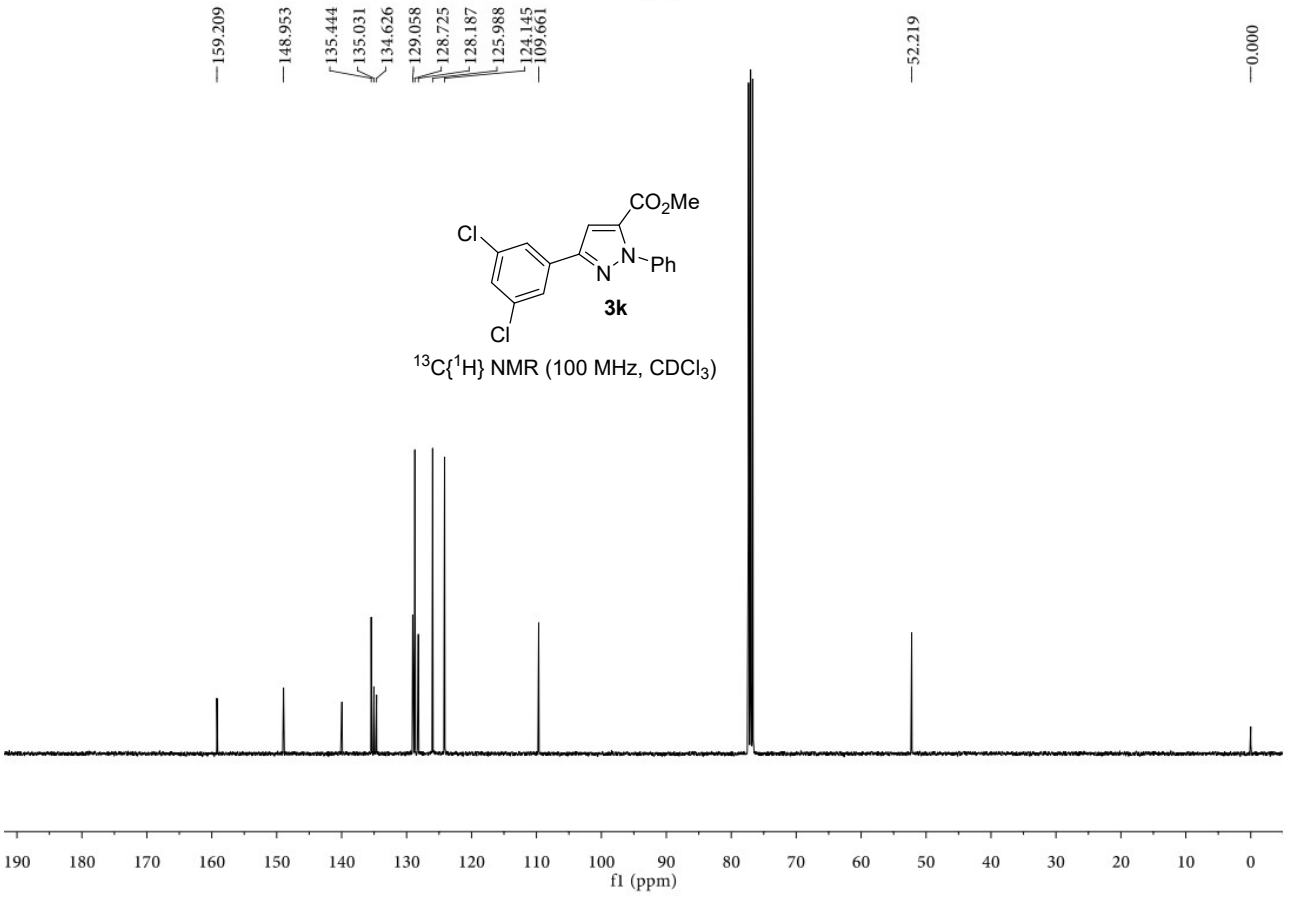


3j

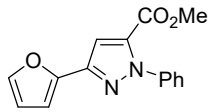
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

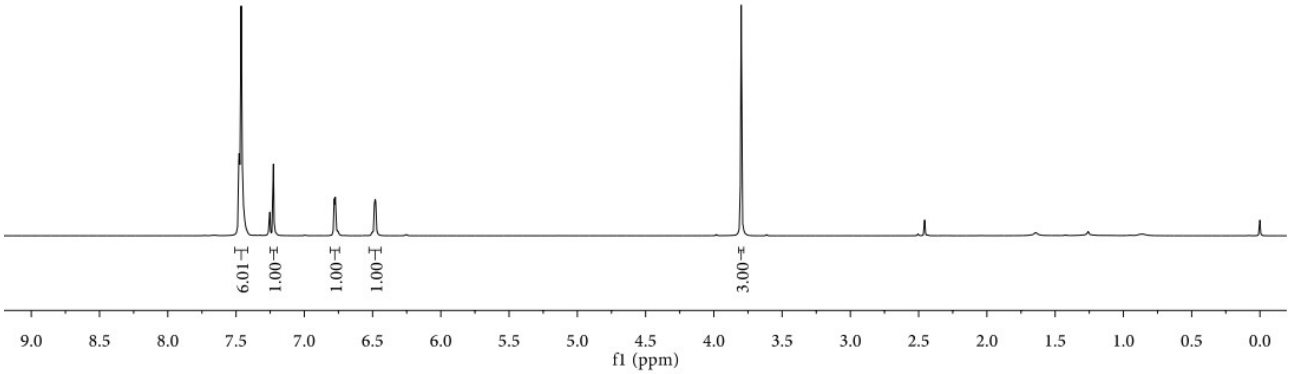


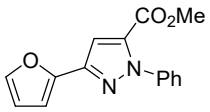
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



3l

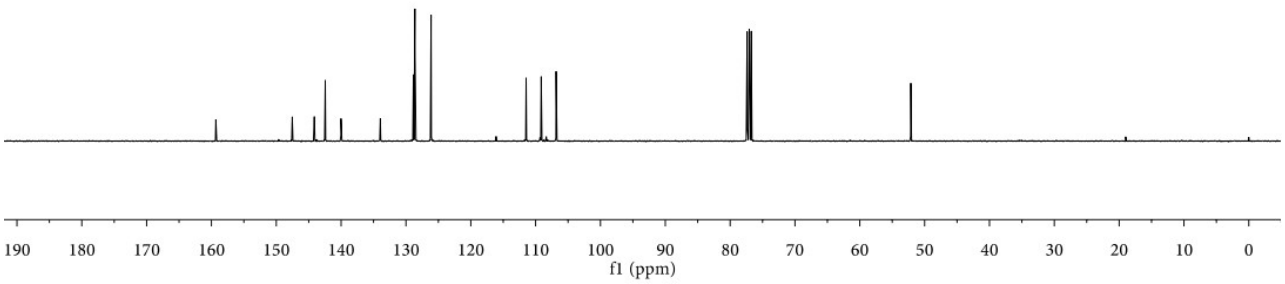
^{1}H NMR (400 MHz, $CDCl_3$)

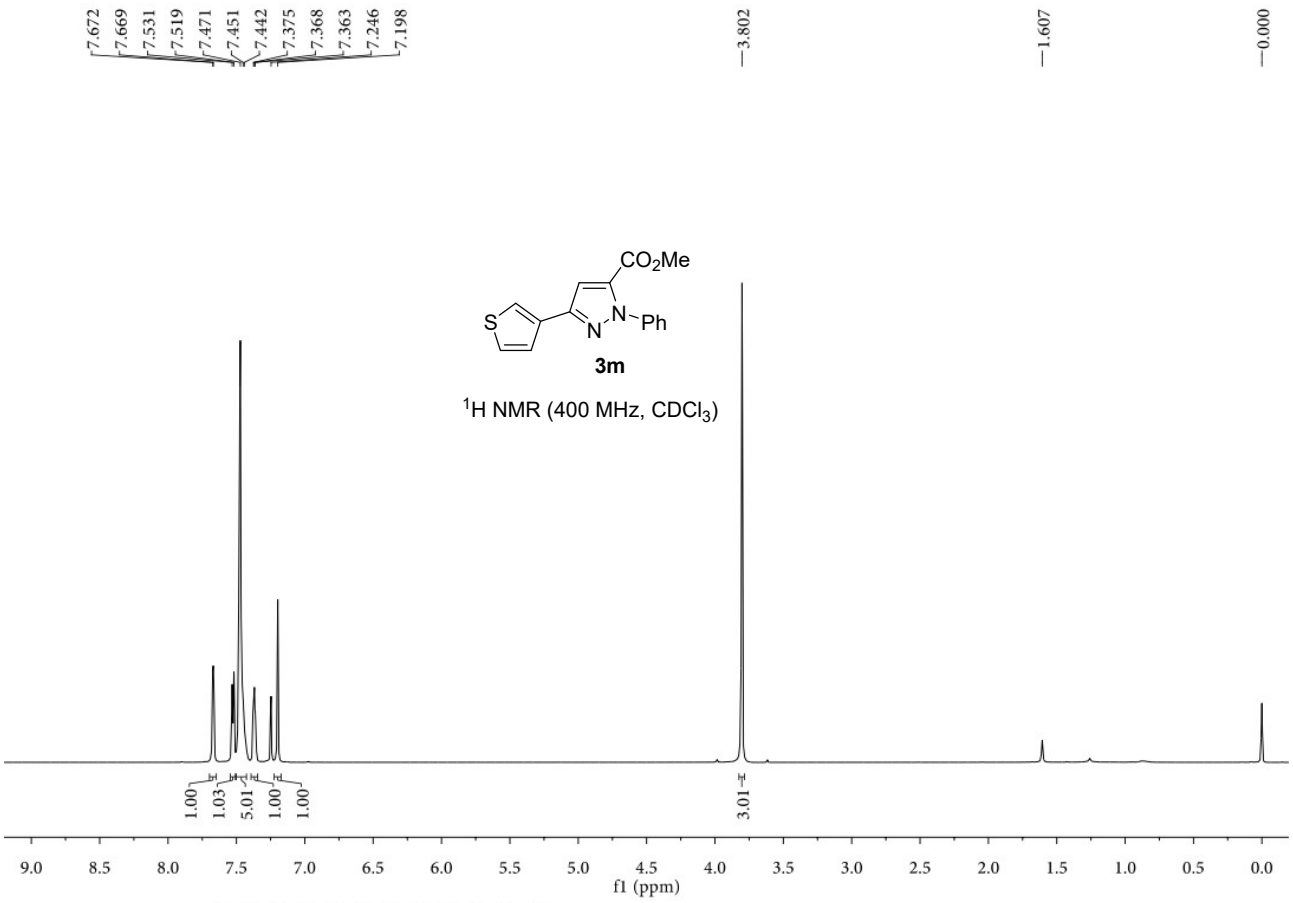


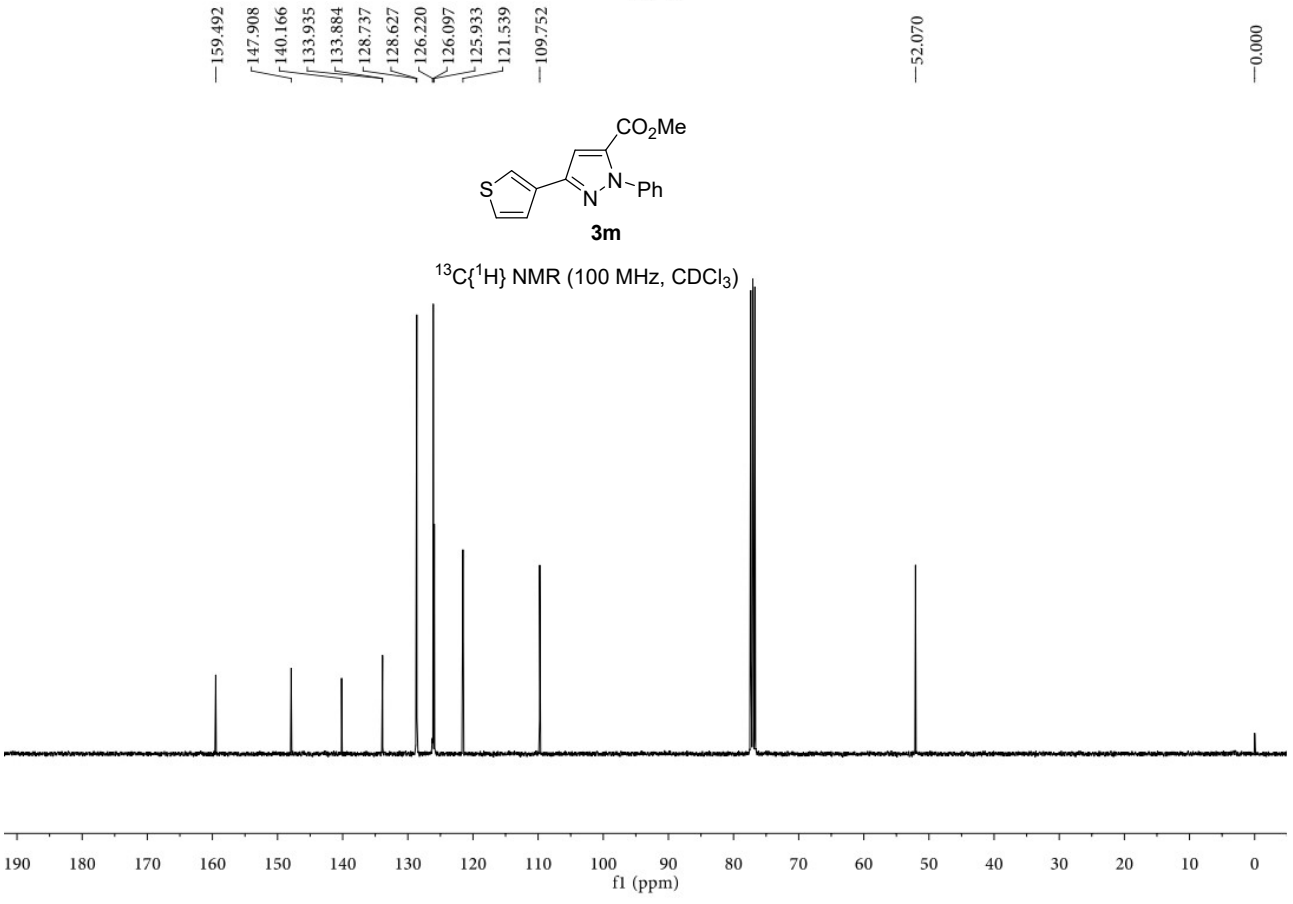


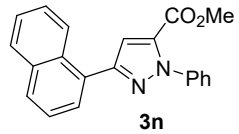
3l

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



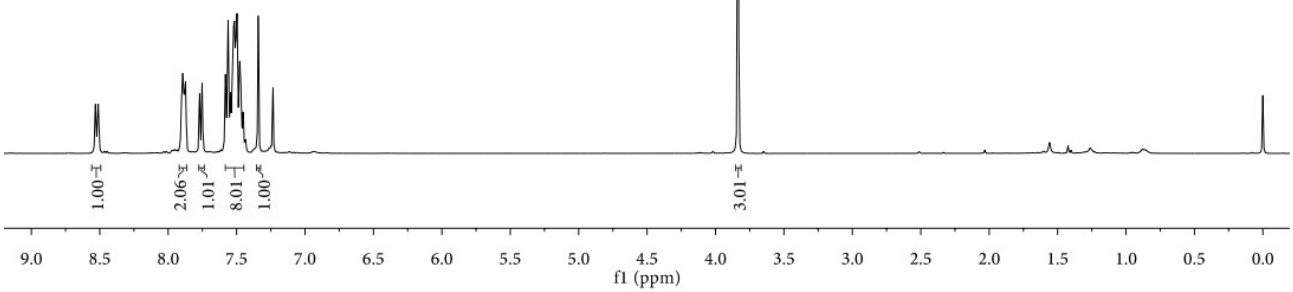

7.672
7.669
7.531
7.519
7.471
7.451
7.442
7.375
7.368
7.363
7.246
7.198
3.802
1.607
0.000
CO2Me
S
N
N
Ph
3m
1H NMR (400 MHz, CDCl3)
1.00
1.03
5.01
1.00
1.00
3.01
f1 (ppm)

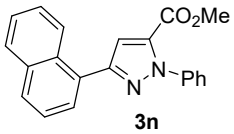

159.492
147.908
140.166
133.935
133.884
128.737
128.627
126.220
126.097
125.933
121.539
109.752
52.070
0.000
CO2Me
S
N
N
Ph
3m
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



3n

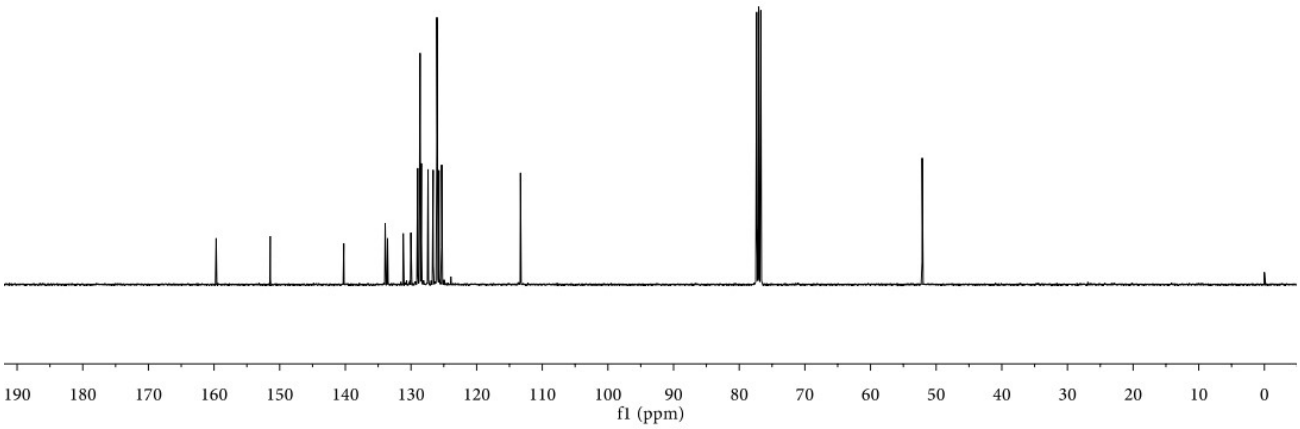
^{1}H NMR (400 MHz, $CDCl_3$)

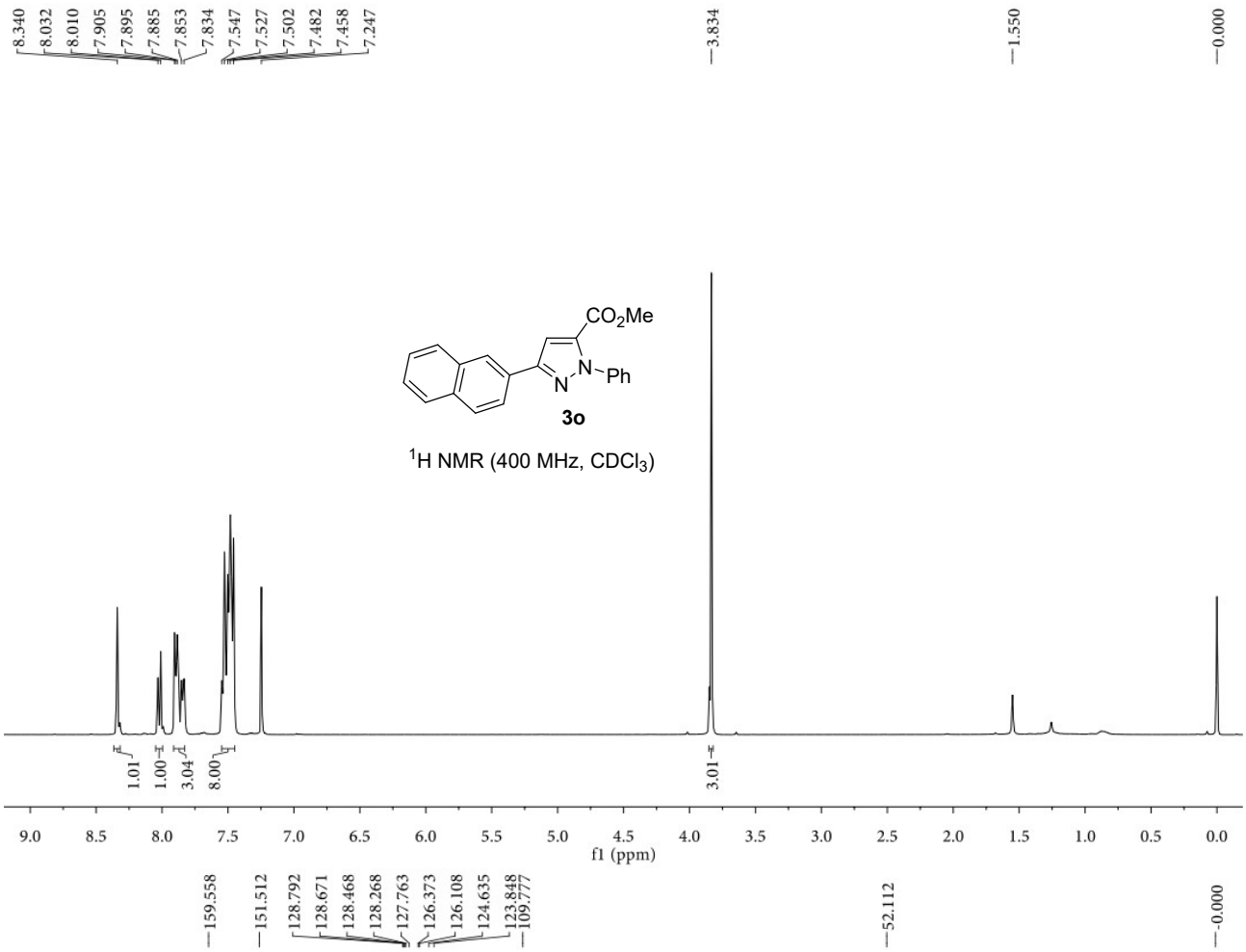


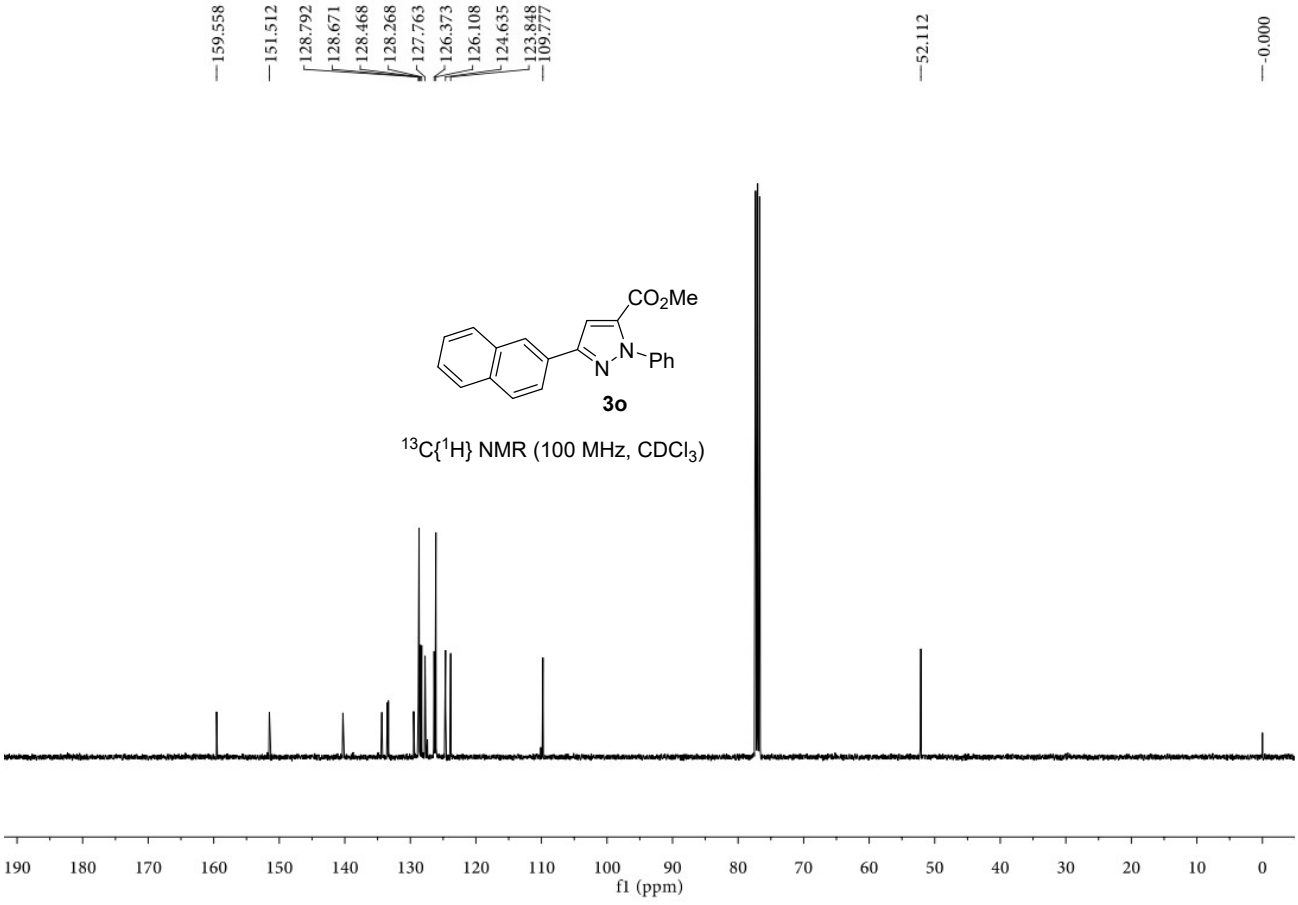


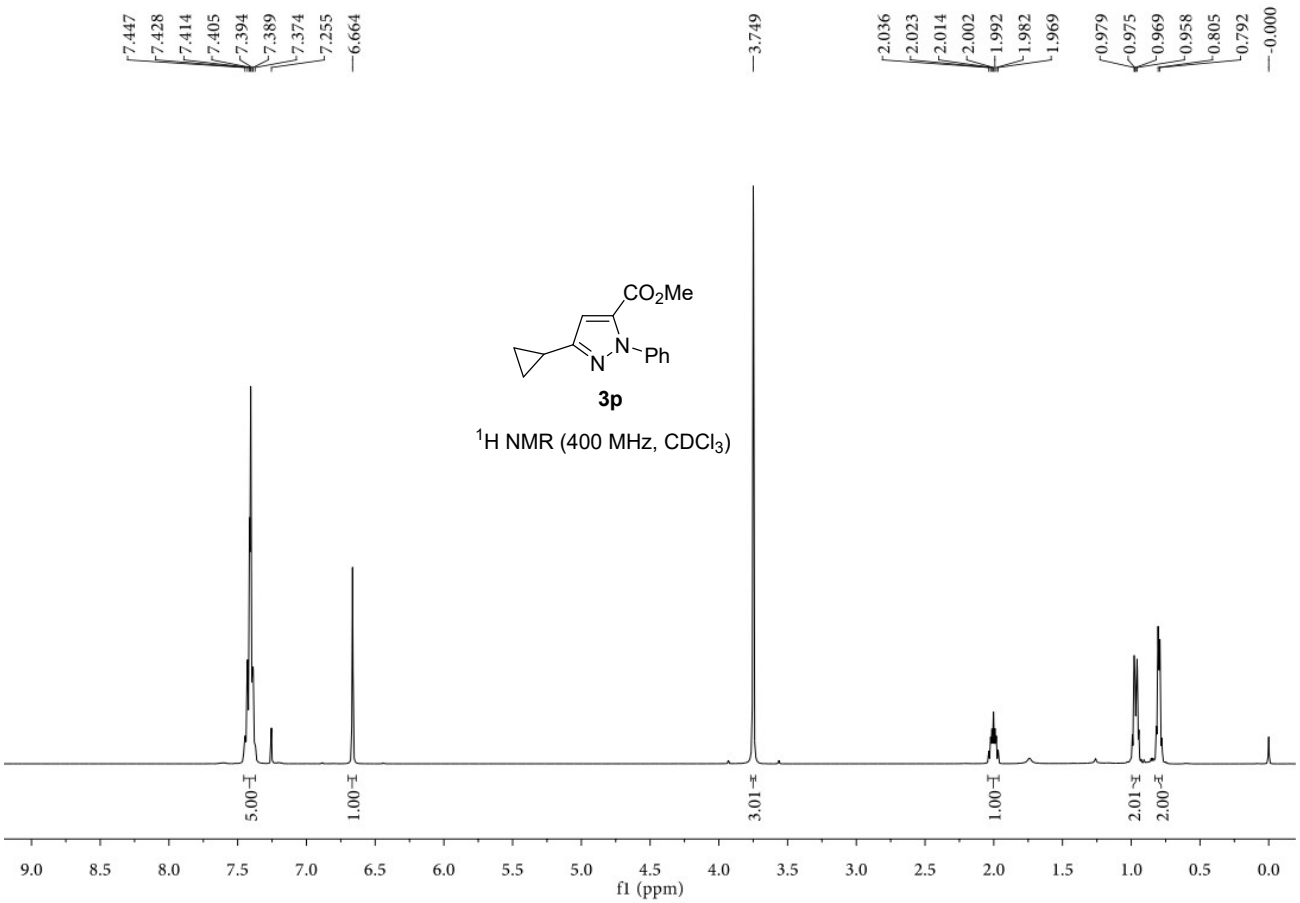
3n

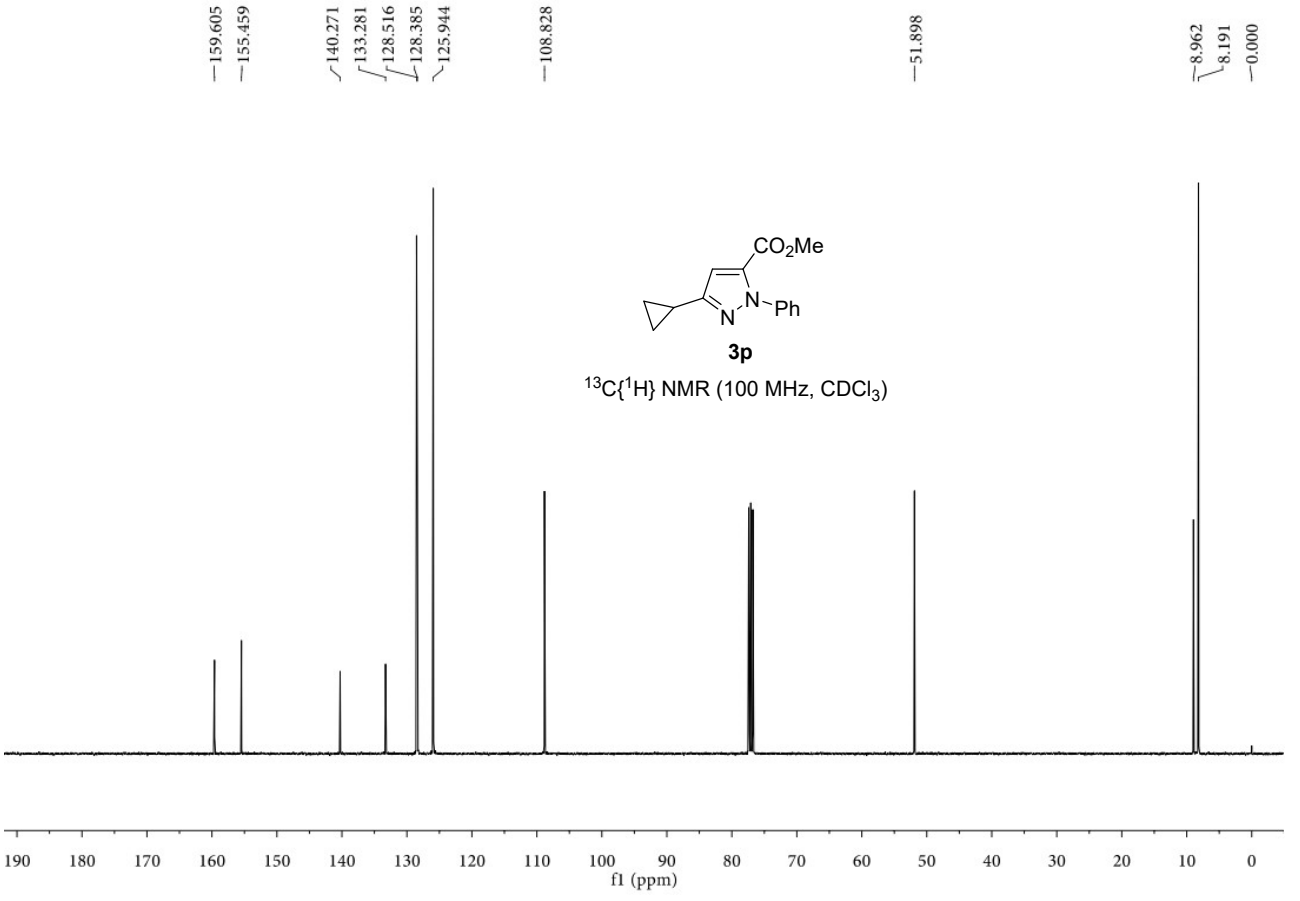
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

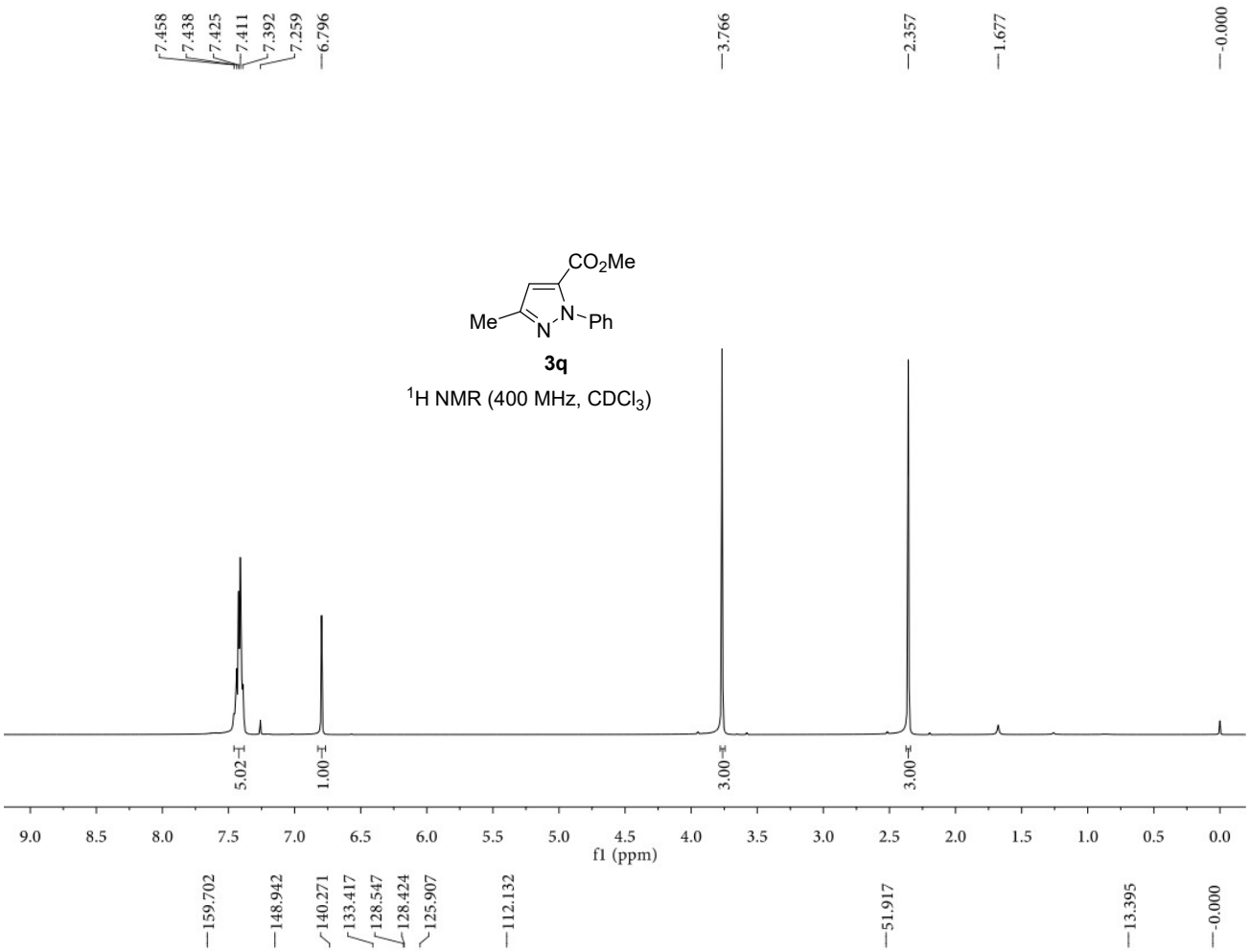



8.340
8.032
8.010
7.905
7.895
7.885
7.853
7.834
7.547
7.527
7.502
7.482
7.458
7.247
3.834
1.550
0.000
CO2Me
N
N
Ph
3o
1H NMR (400 MHz, CDCl3)
1.01
1.00
3.04
8.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


159.558
151.512
128.792
128.671
128.468
128.268
127.763
126.373
126.108
124.635
123.848
109.777
52.112
-0.000
CO2Me
N
N
Ph
3o
13C{1H} NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

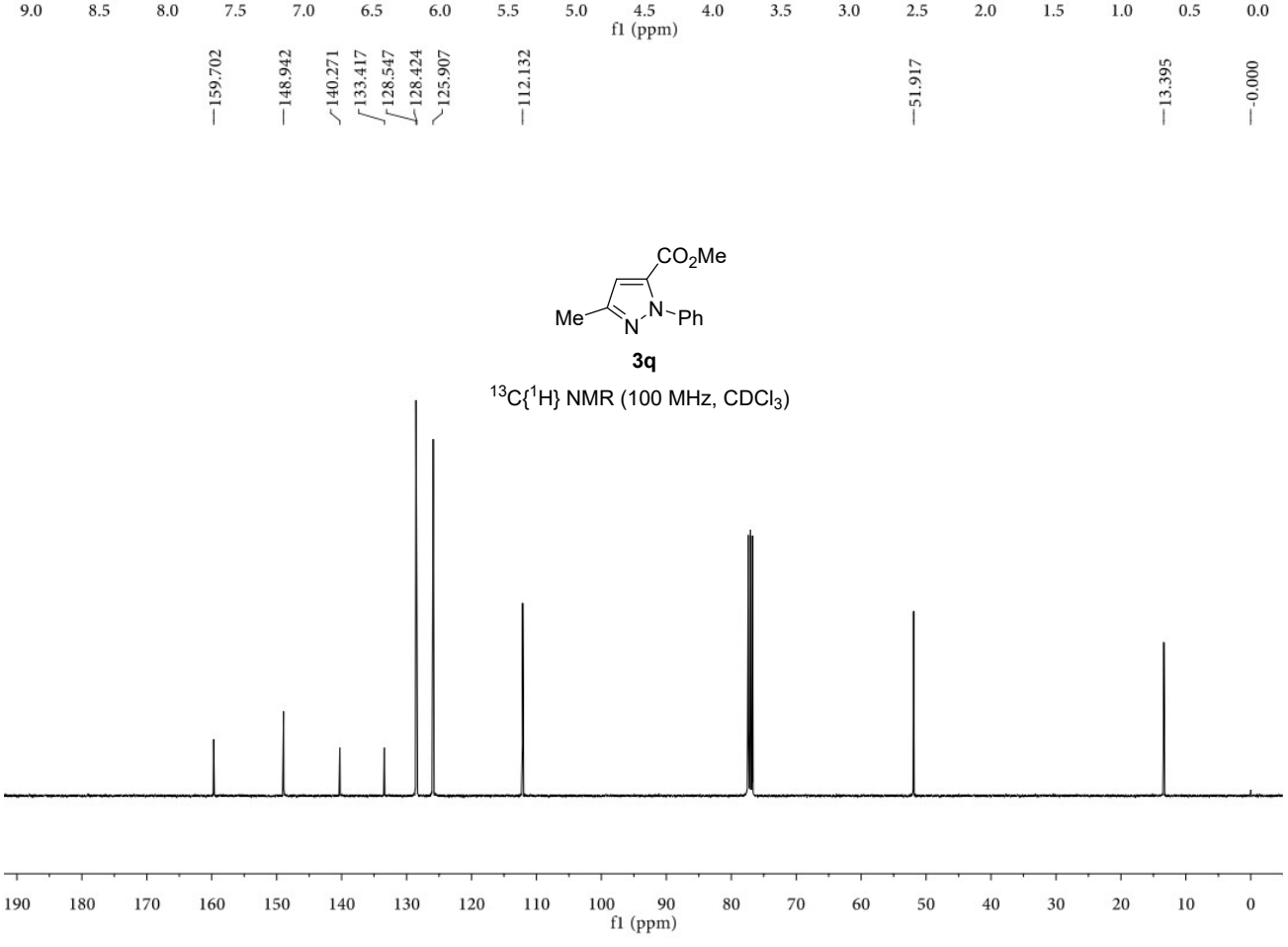

7.447
7.428
7.414
7.405
7.394
7.389
7.374
7.255
6.664
3.749
2.036
2.023
2.014
2.002
1.992
1.982
1.969
0.979
0.975
0.969
0.958
0.805
0.792
0.000
CO2Me
N
N
Ph
3p
1H NMR (400 MHz, CDCl3)
5.00
1.00
3.01
1.00
2.01
2.00
f1 (ppm)


159.605
155.459
140.271
133.281
128.516
128.385
125.944
108.828
51.898
8.962
8.191
0.000
CO2Me
N
N
Ph
3p
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



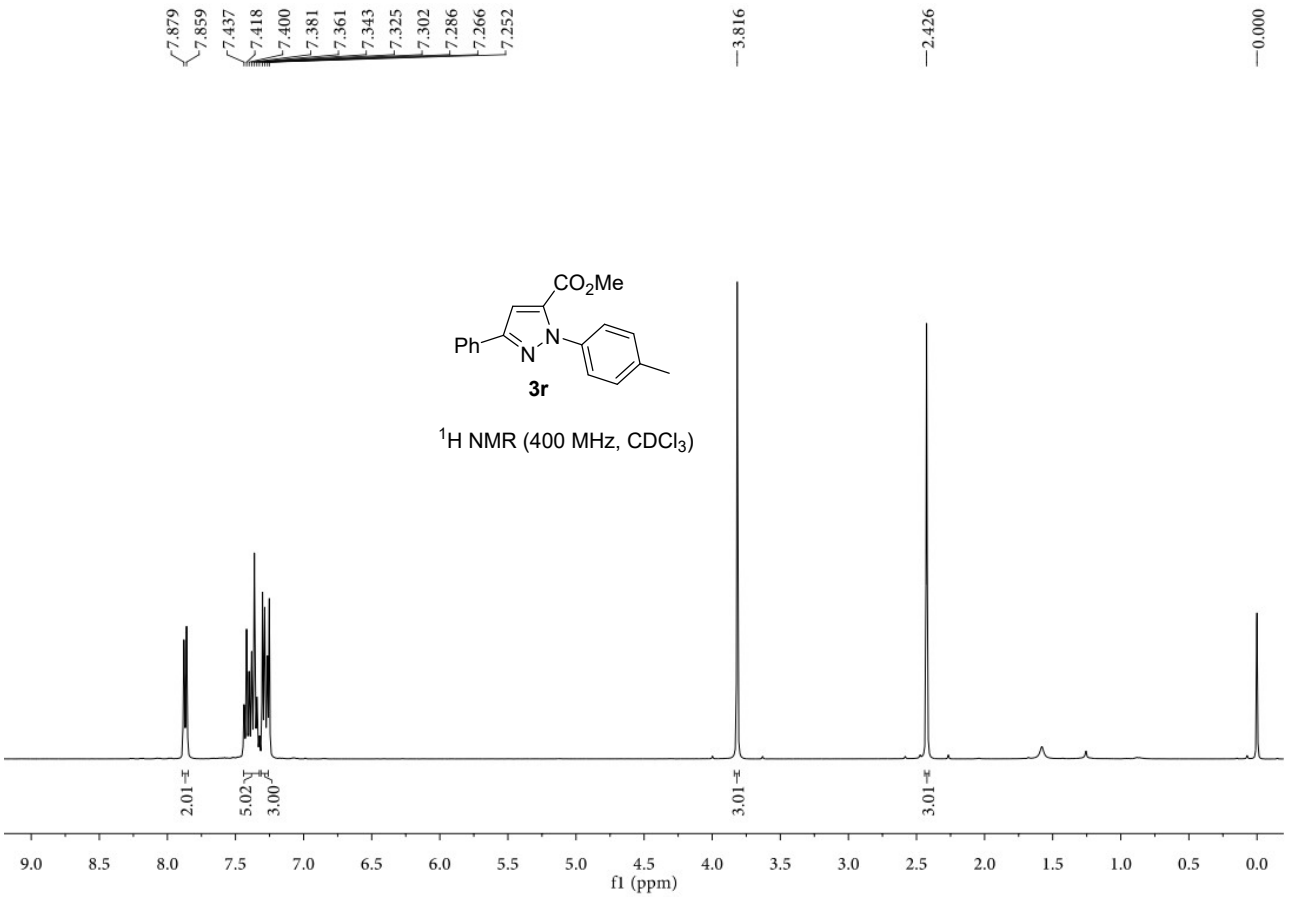
3q

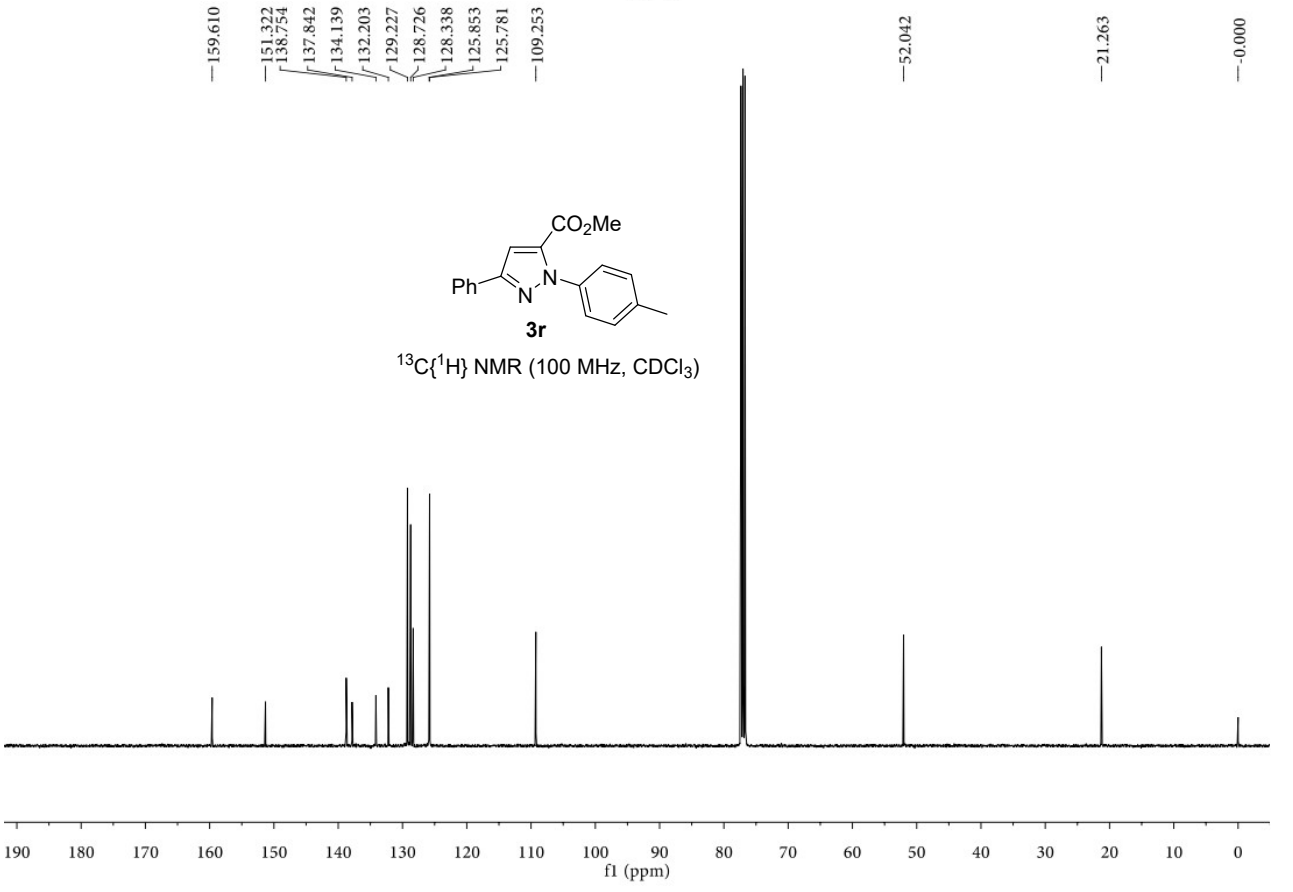
^{1}H NMR (400 MHz, $CDCl_3$)

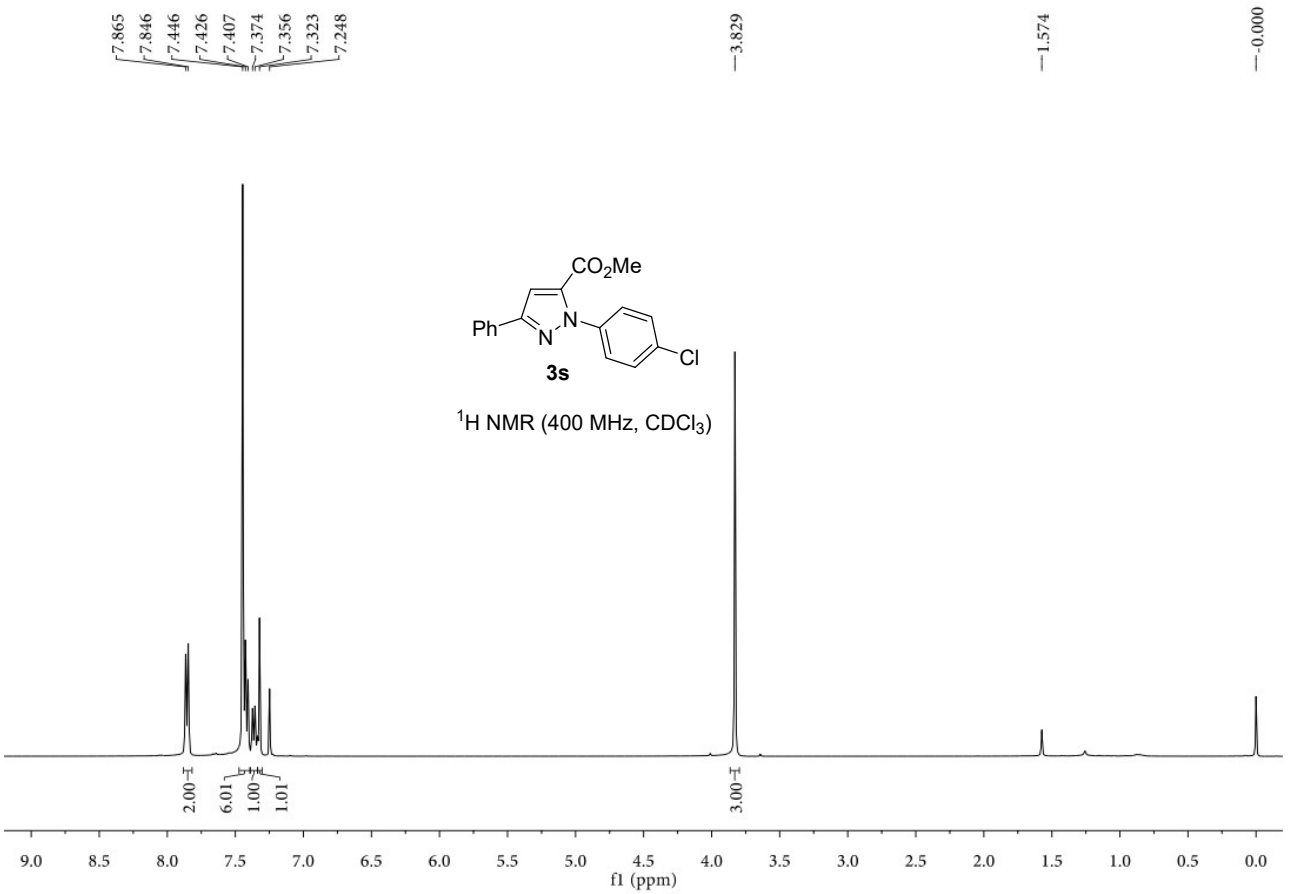


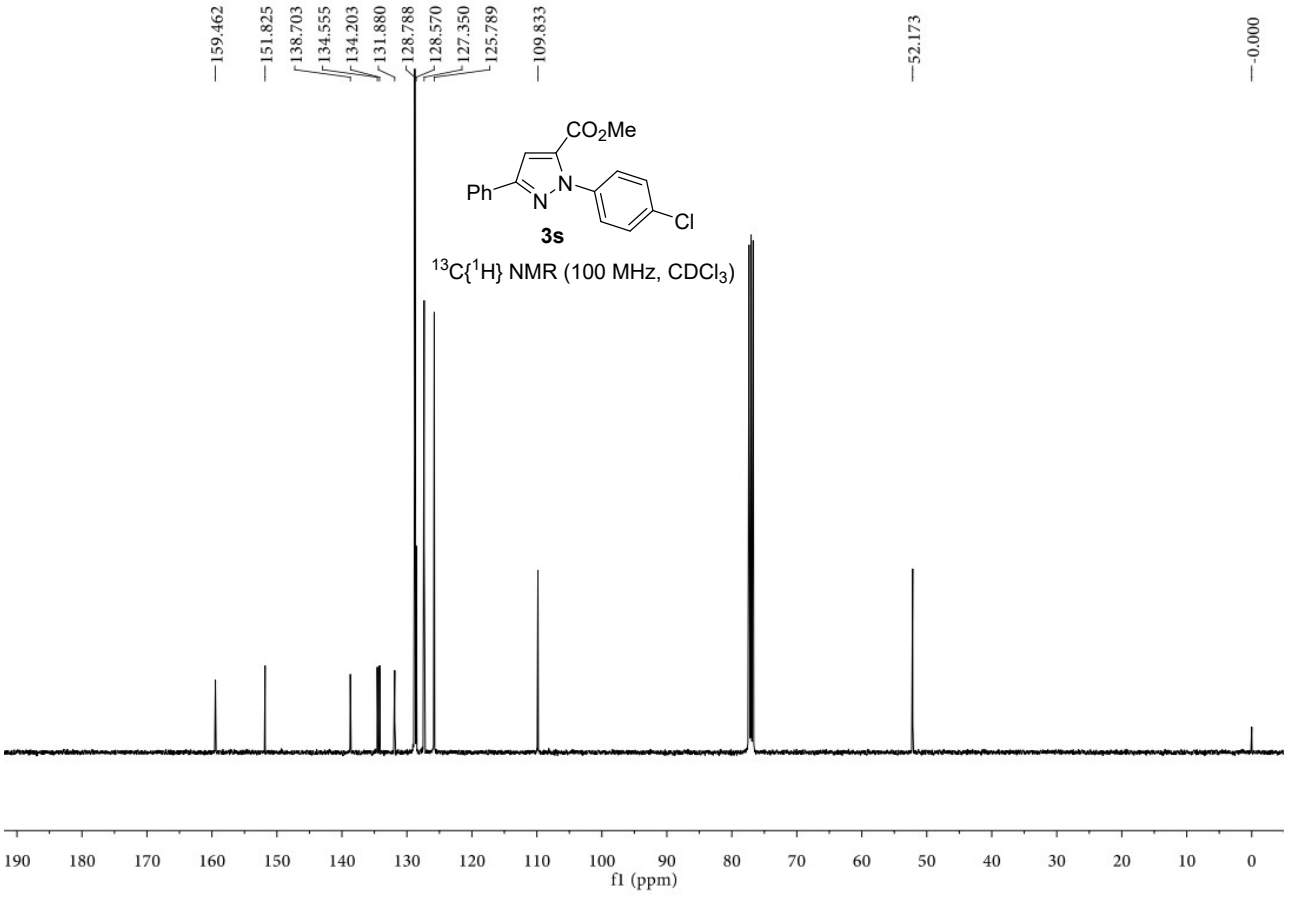
3q

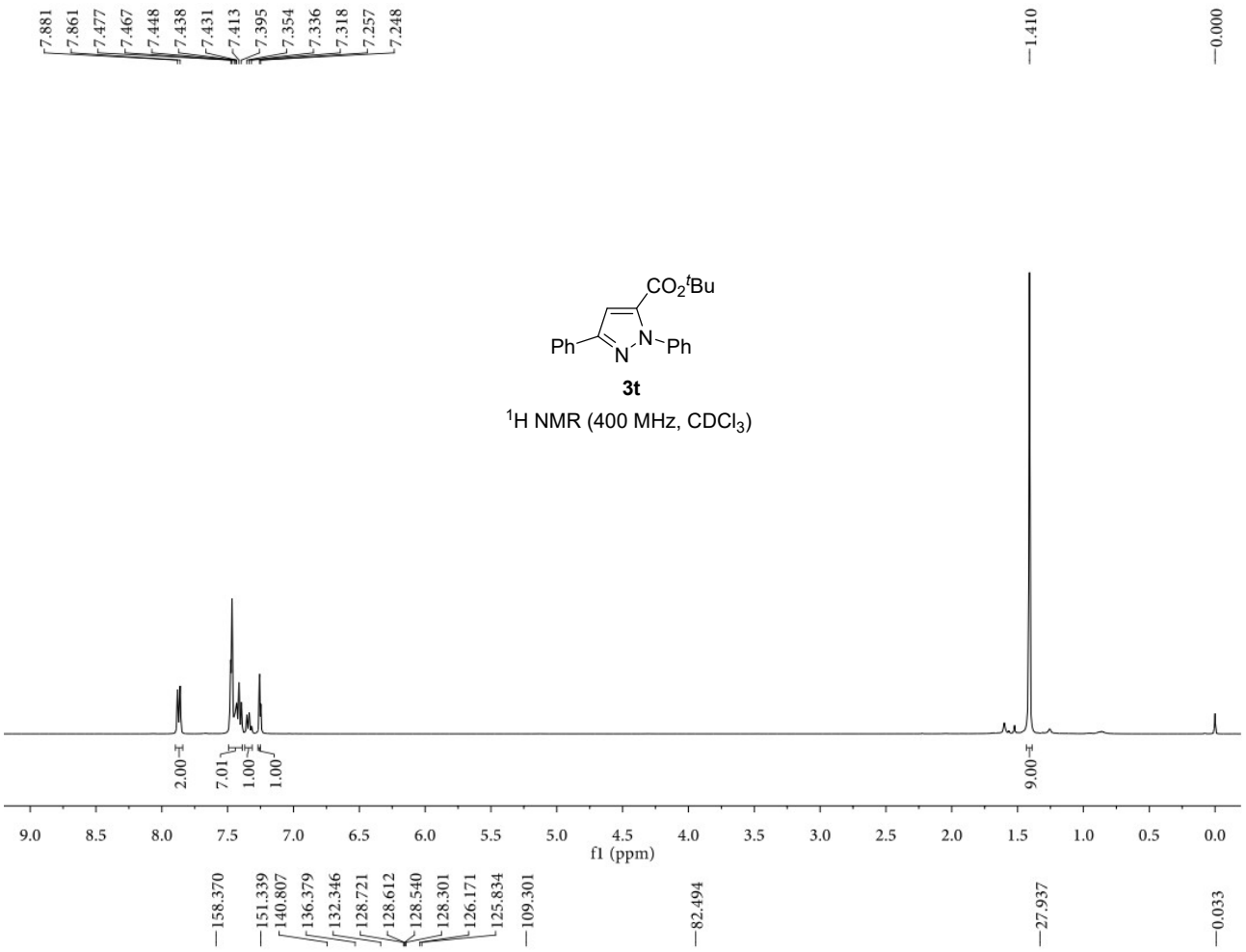
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

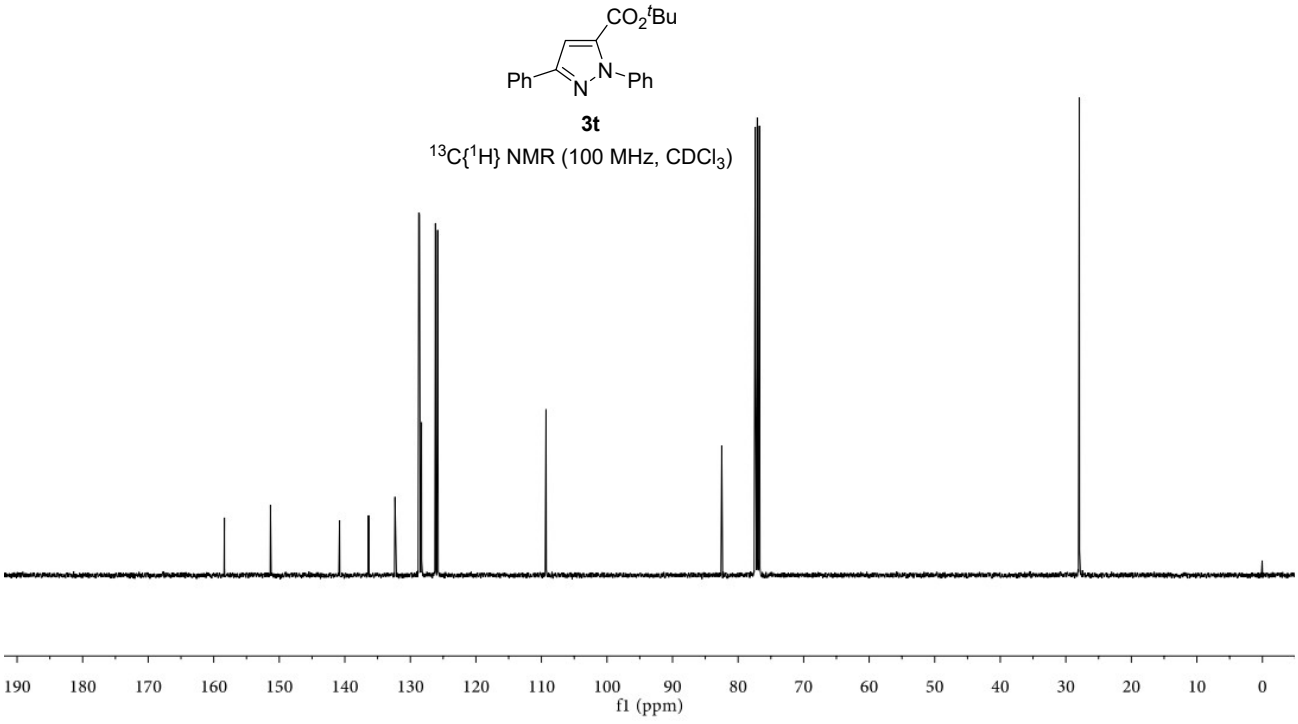

7.879
7.859
7.437
7.418
7.400
7.381
7.361
7.343
7.325
7.302
7.286
7.266
7.252
3.816
2.426
0.000
CO2Me
Ph
N
N
3r
1H NMR (400 MHz, CDCl3)
2.01
5.02
3.00
3.01
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

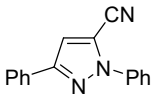

159.610
151.322
138.754
137.842
134.139
132.203
129.227
128.726
128.338
125.853
125.781
109.253
52.042
21.263
-0.000
CO2Me
Ph
N
N
3r
13C{1H} NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.865
7.846
7.446
7.426
7.407
7.374
7.356
7.323
7.248
3.829
1.574
-0.000
CO2Me
Ph
N
N
Cl
3s
1H NMR (400 MHz, CDCl3)
2.00
6.01
1.00
1.01
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.462
151.825
138.703
134.555
134.203
131.880
128.788
128.570
127.350
125.789
109.833
52.173
-0.000
CO2Me
Ph
N
N
Cl
3s
13C{1H} NMR (100 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

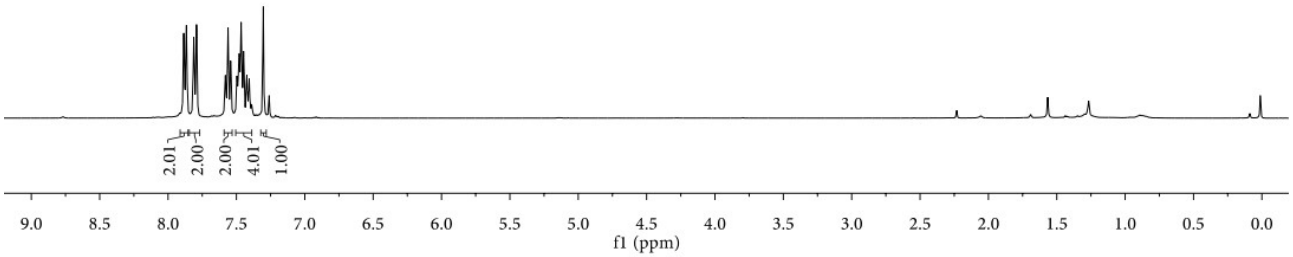

7.881
7.861
7.477
7.467
7.448
7.438
7.431
7.413
7.395
7.354
7.336
7.318
7.257
7.248
1.410
0.000
CO2tBu
Ph
N
N
Ph
3t
1H NMR (400 MHz, CDCl3)
2.00
7.01
1.00
1.00
9.00
f1 (ppm)

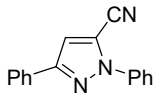

158.370
151.339
140.807
136.379
132.346
128.721
128.612
128.540
128.301
126.171
125.834
109.301
82.494
27.937
0.033
CO2tBu
Ph
N
N
Ph
3t
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



3u

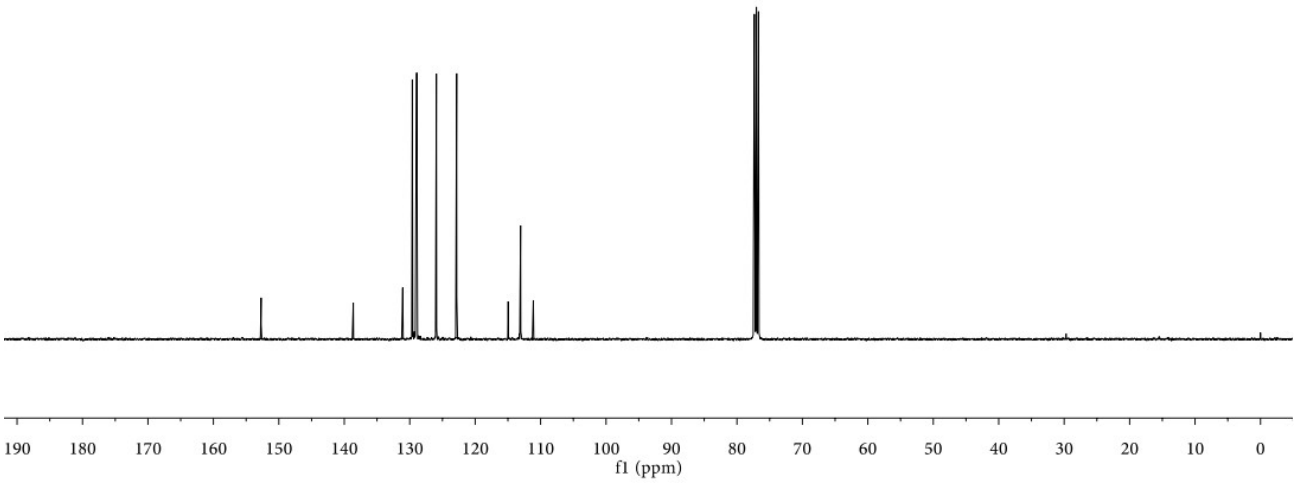
^{1}H NMR (400 MHz, $CDCl_3$)

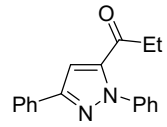




3u

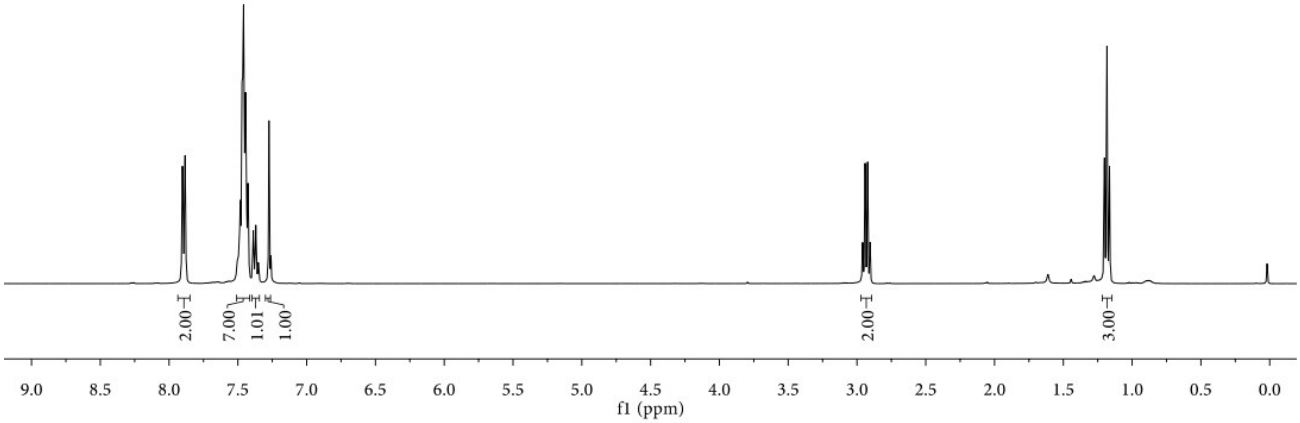
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

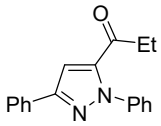




3v

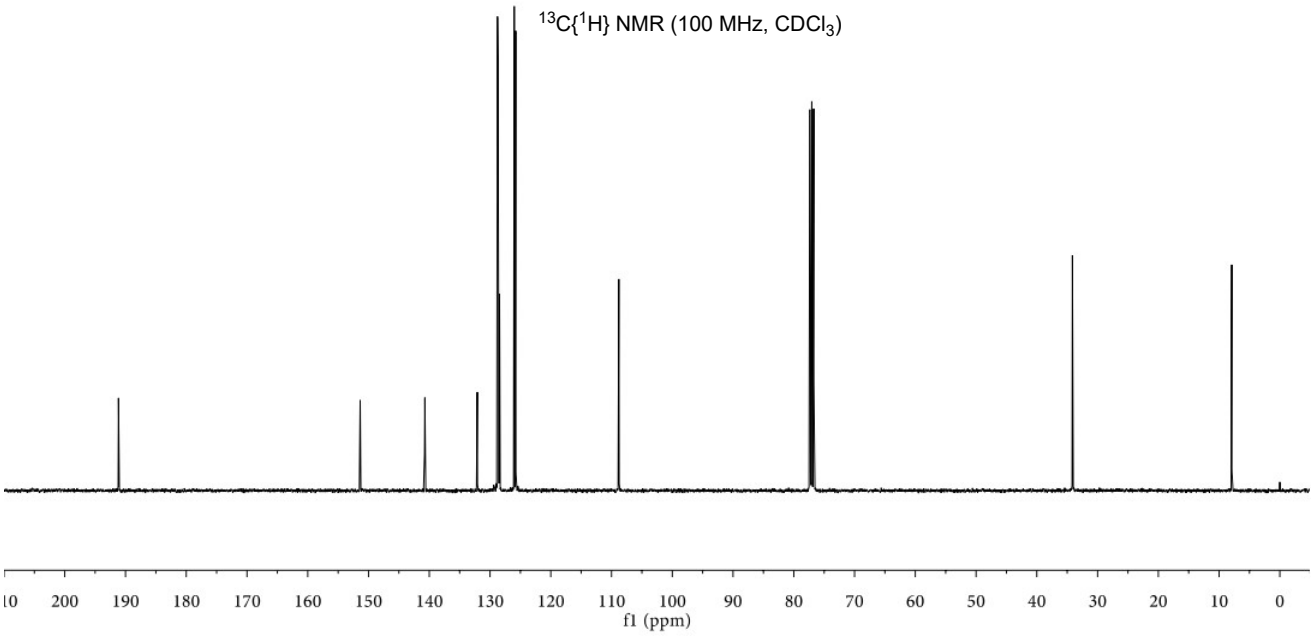
^{1}H NMR (400 MHz, $CDCl_3$)

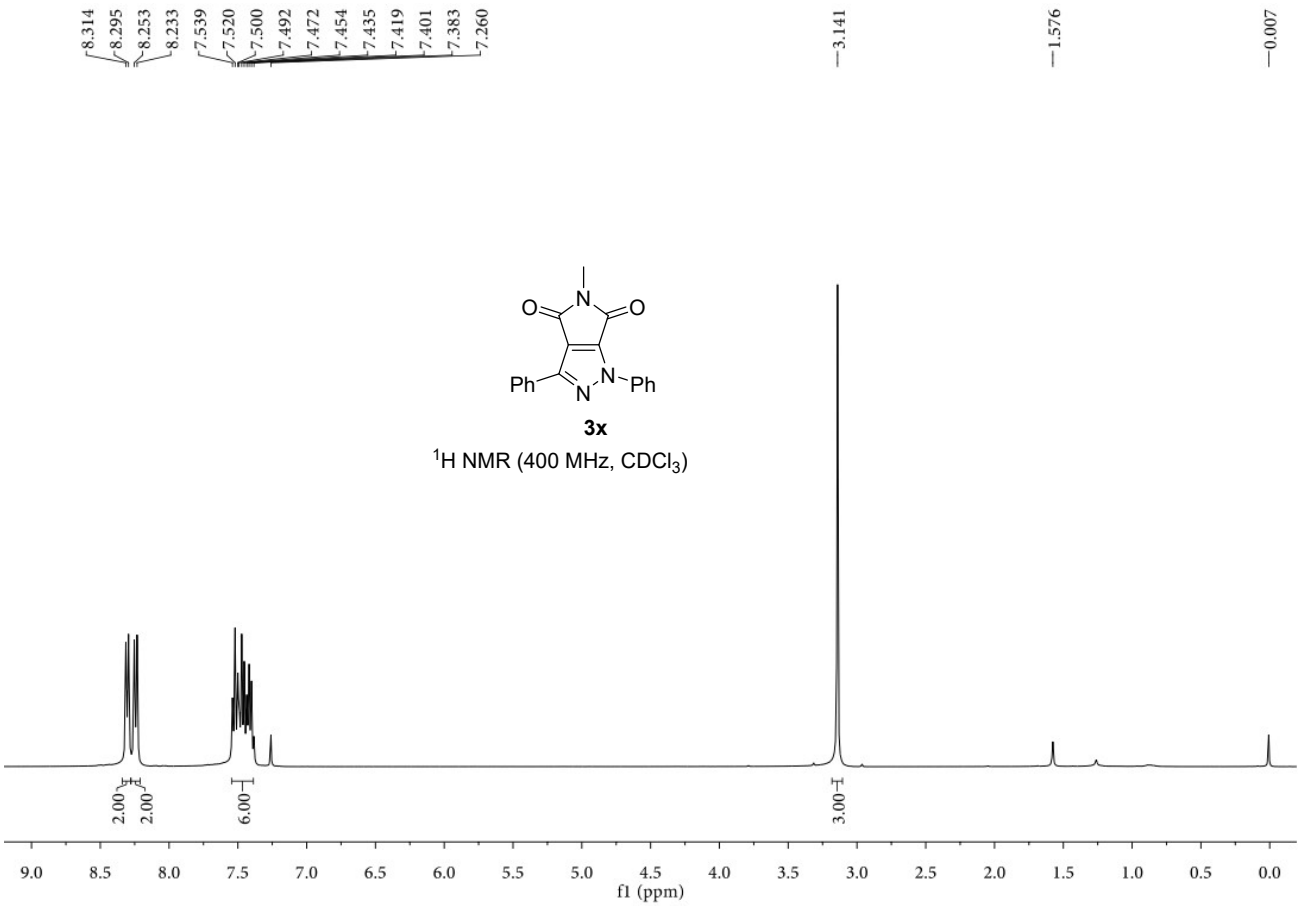


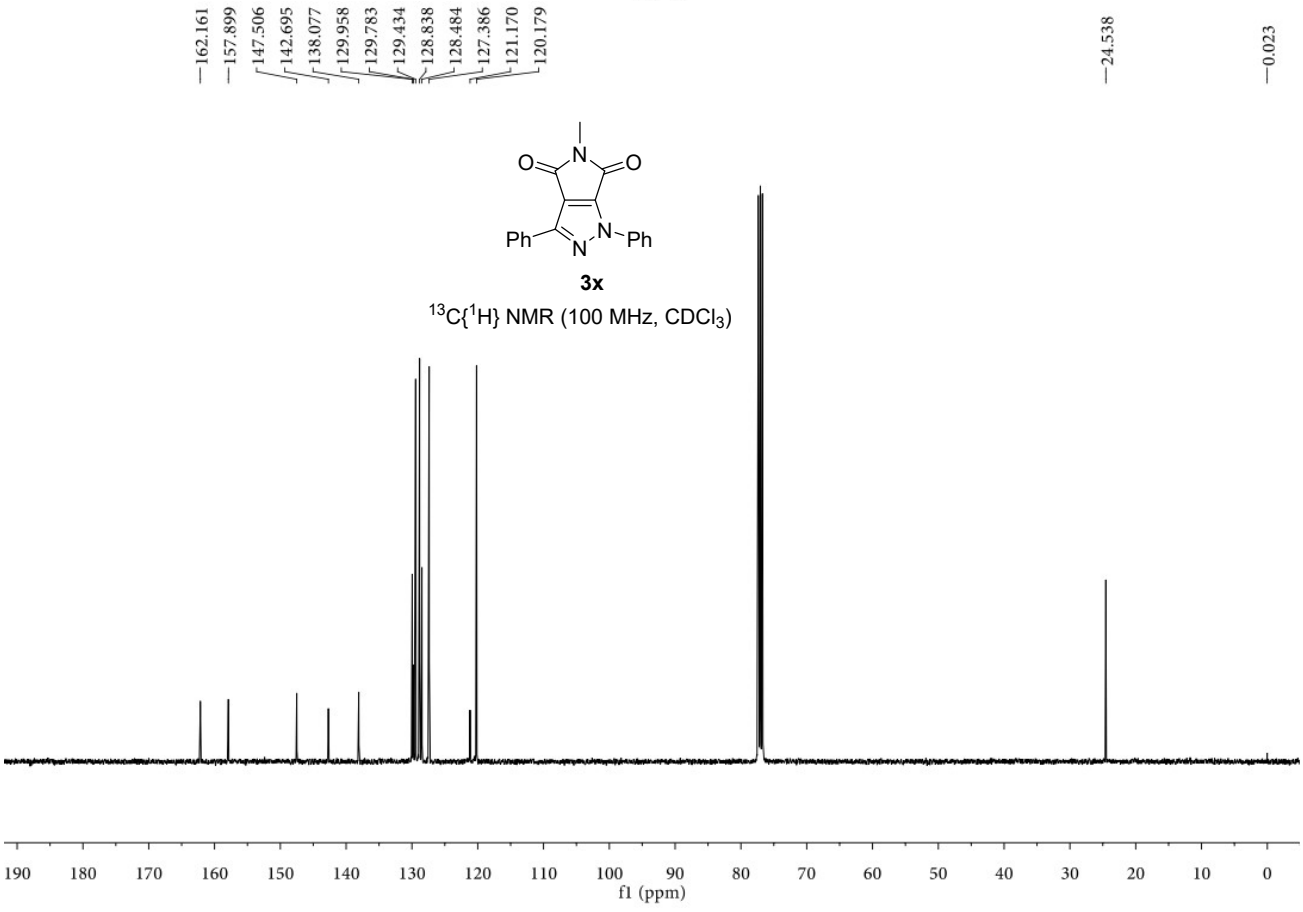


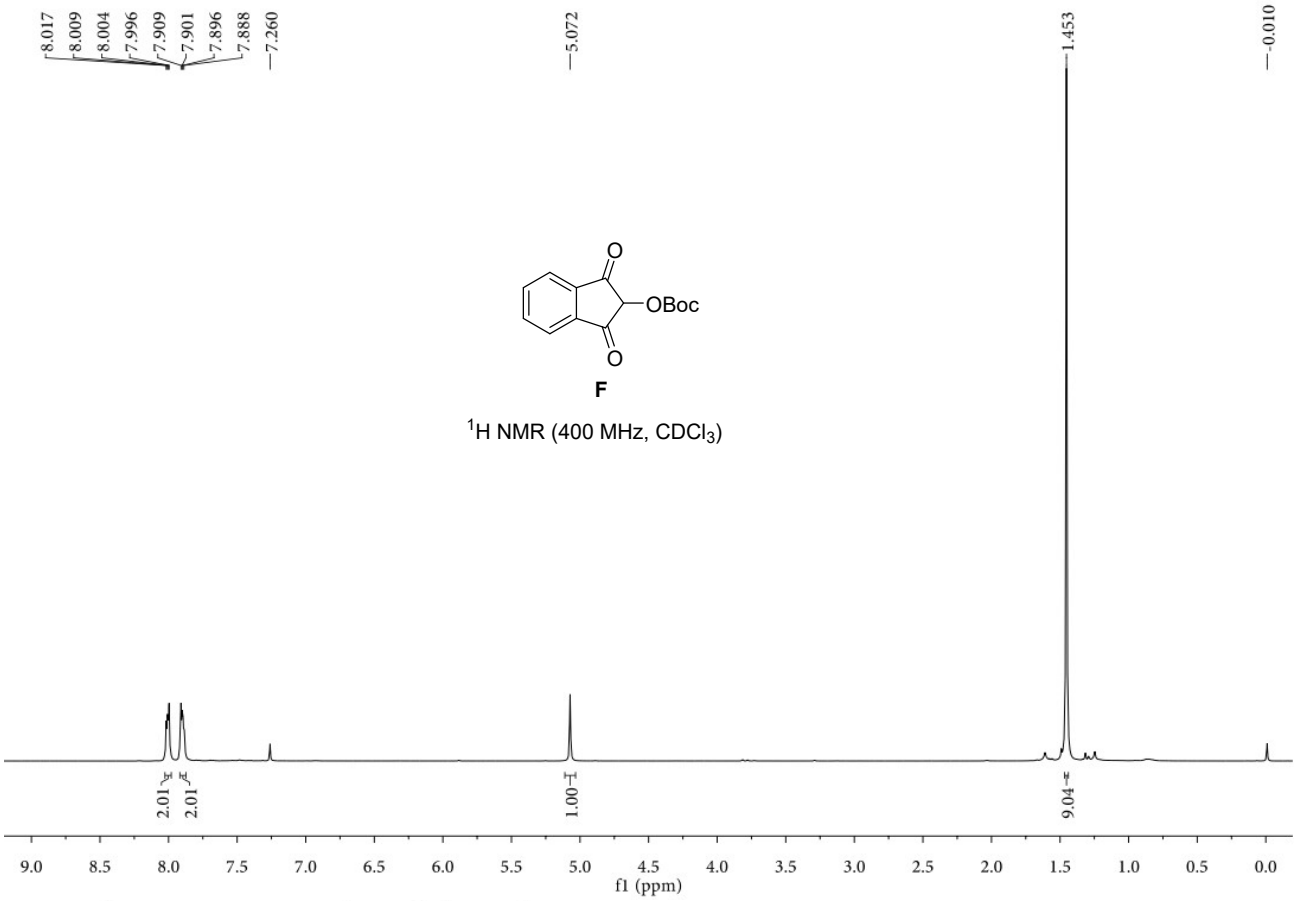
3v

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)



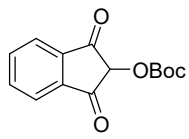

8.314
8.295
8.253
8.233
7.539
7.520
7.500
7.492
7.472
7.454
7.435
7.419
7.401
7.383
7.260
3.141
1.576
0.007
O
N
O
Ph
N
N
Ph
3x
1H NMR (400 MHz, CDCl3)
2.00
2.00
6.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.161
157.899
147.506
142.695
138.077
129.958
129.783
129.434
128.838
128.484
127.386
121.170
120.179
24.538
0.023
O
N
O
Ph
N
N
Ph
3x
13C{1H} NMR (100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



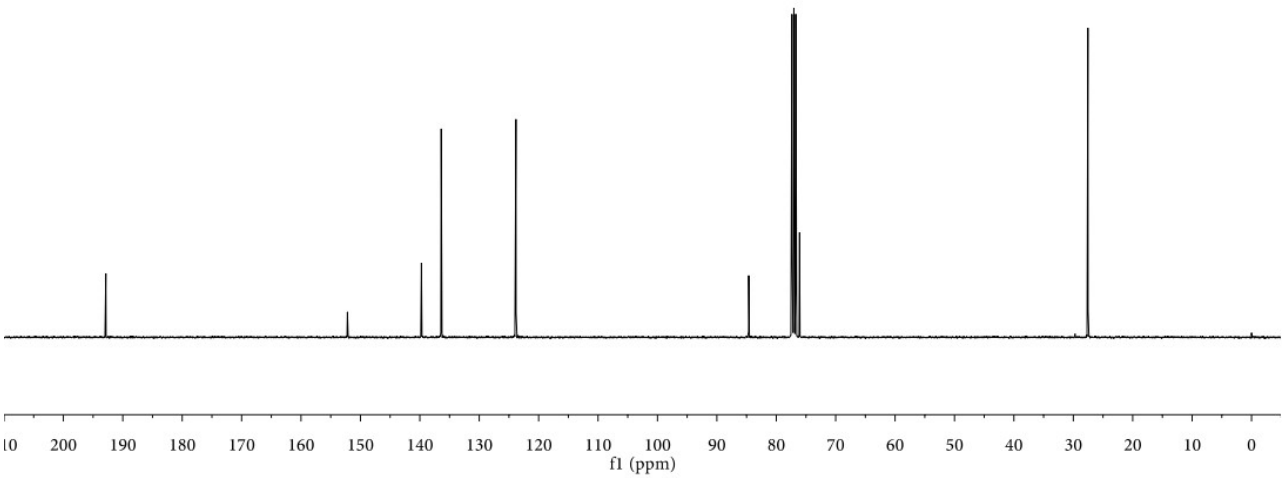
F

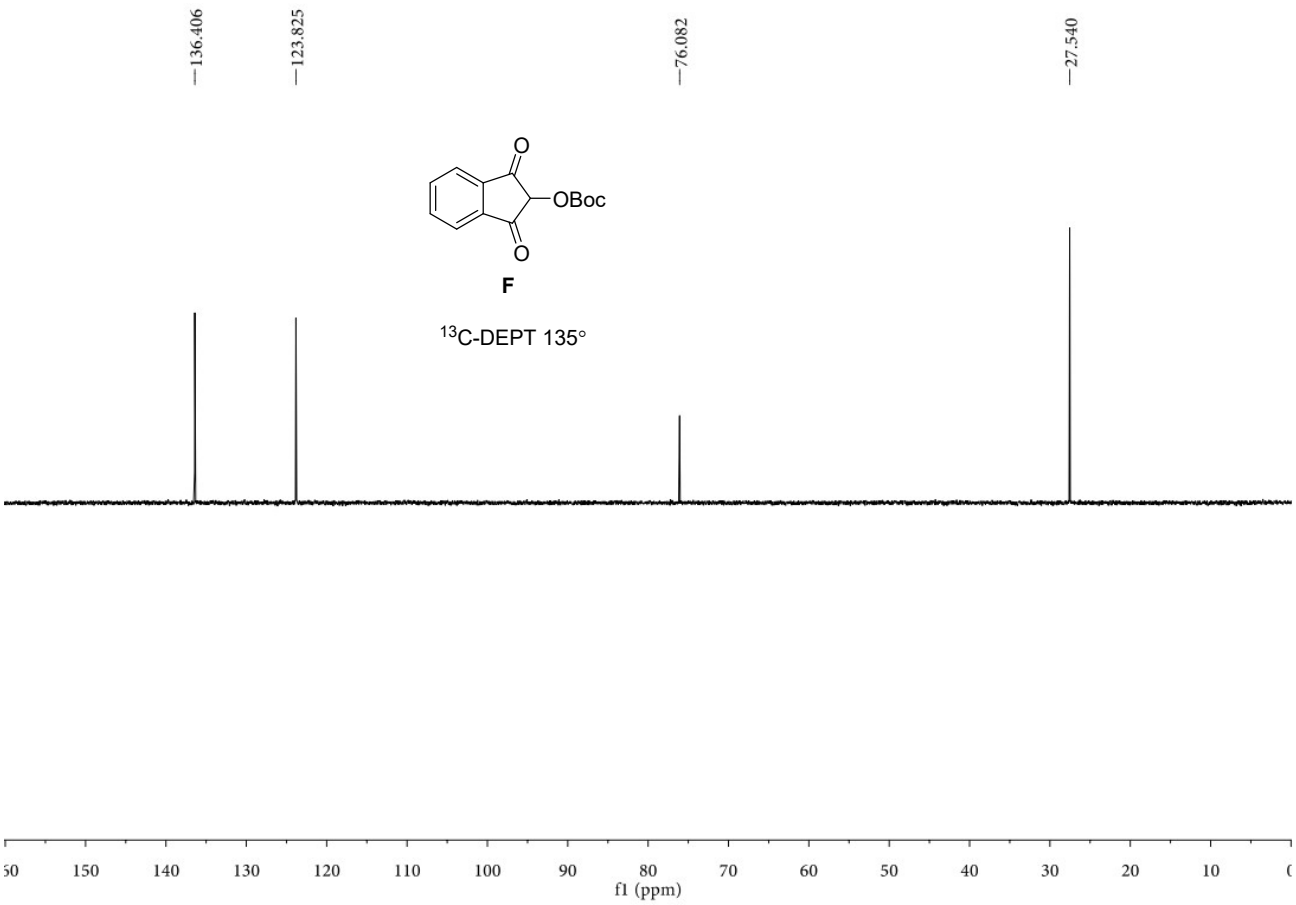
^{1}H NMR (400 MHz, $CDCl_3$)

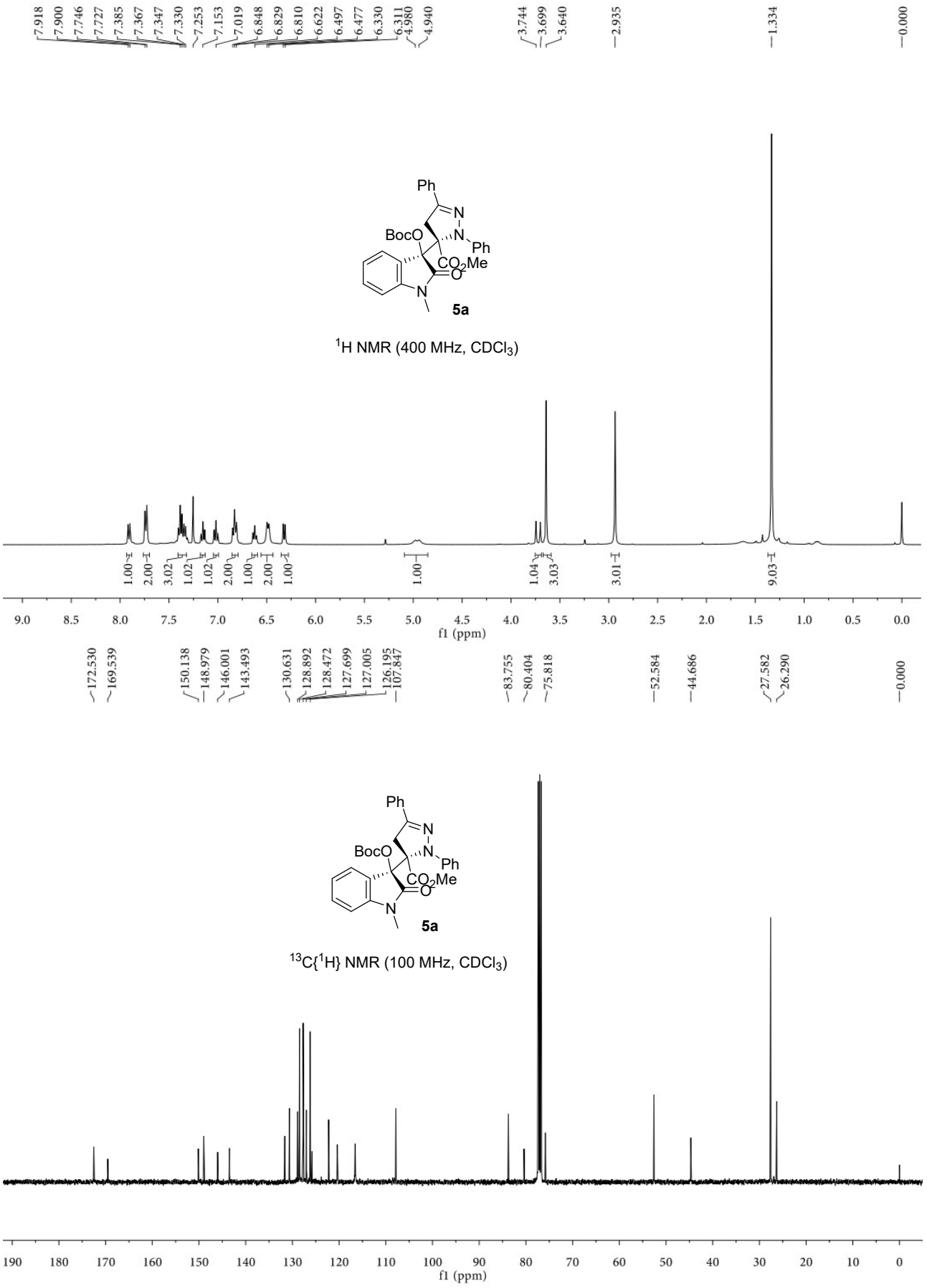


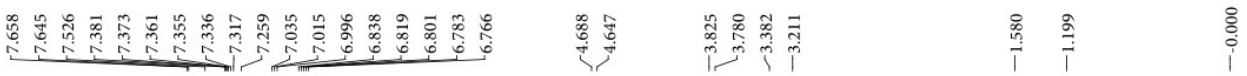
F

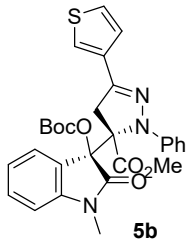
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)




136.406
123.825
76.082
27.540
O
OBoc
O
F
13C-DEPT 135°
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

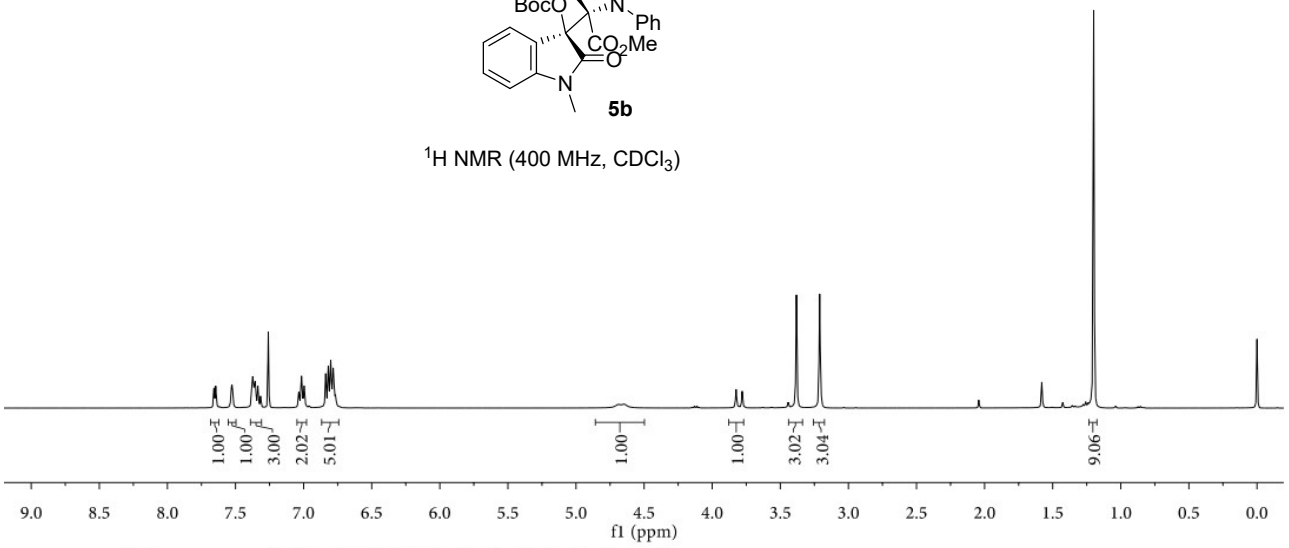

7.918
7.900
7.746
7.727
7.385
7.367
7.347
7.330
7.253
7.153
7.019
6.848
6.829
6.810
6.622
6.497
6.477
6.330
6.311
4.980
4.940
3.744
3.699
3.640
2.935
1.334
0.000
Ph
N
N
Ph
BocO
CO2Me
O
N
5a
1H NMR (400 MHz, CDCl3)
1.00
2.00
3.02
1.02
1.02
2.00
1.00
2.00
1.00
1.00
1.04
3.03
3.01
9.03
f1 (ppm)
172.530
169.539
150.138
148.979
146.001
143.493
130.631
128.892
128.472
127.699
127.005
126.195
107.847
83.755
80.404
75.818
52.584
44.686
27.582
26.290
0.000
5a
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

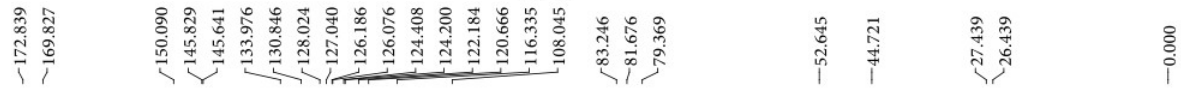


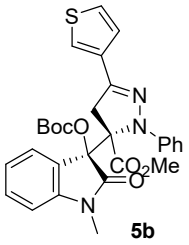


5b

^{1}H NMR (400 MHz, $CDCl_3$)

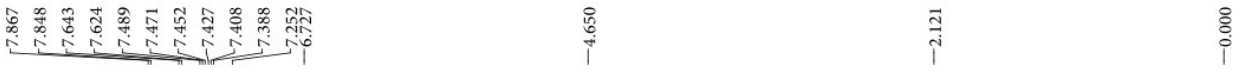


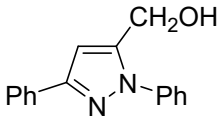




5b

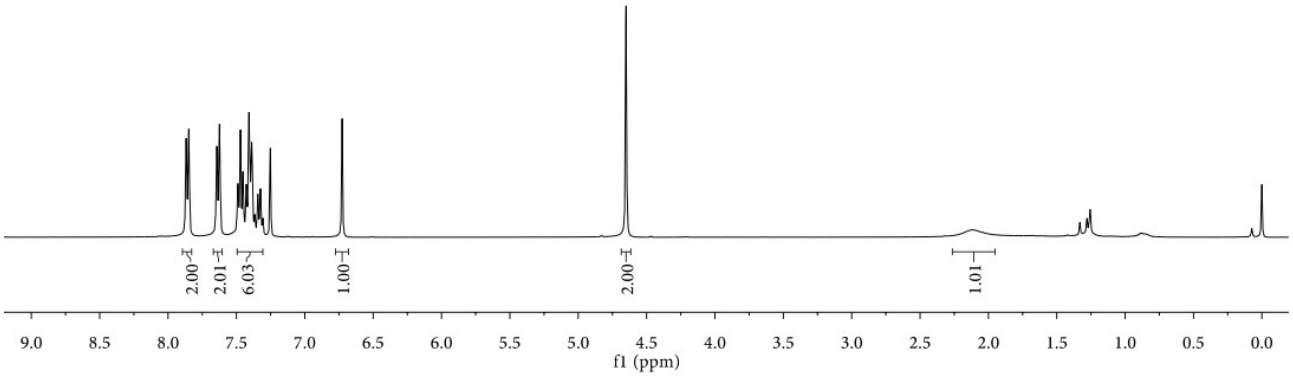
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

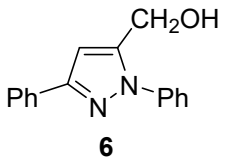




6

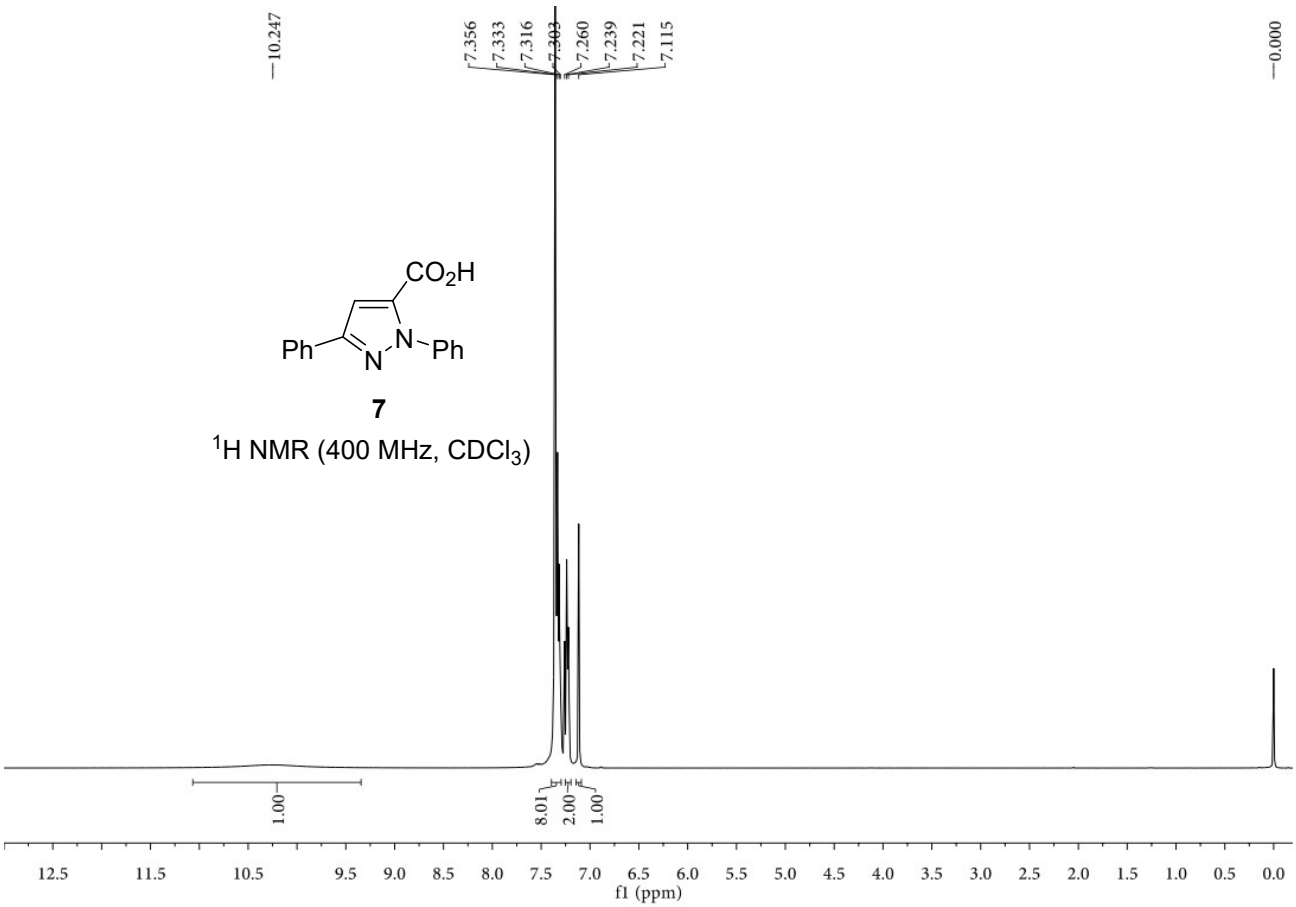
^{1}H NMR (400 MHz, $CDCl_3$)





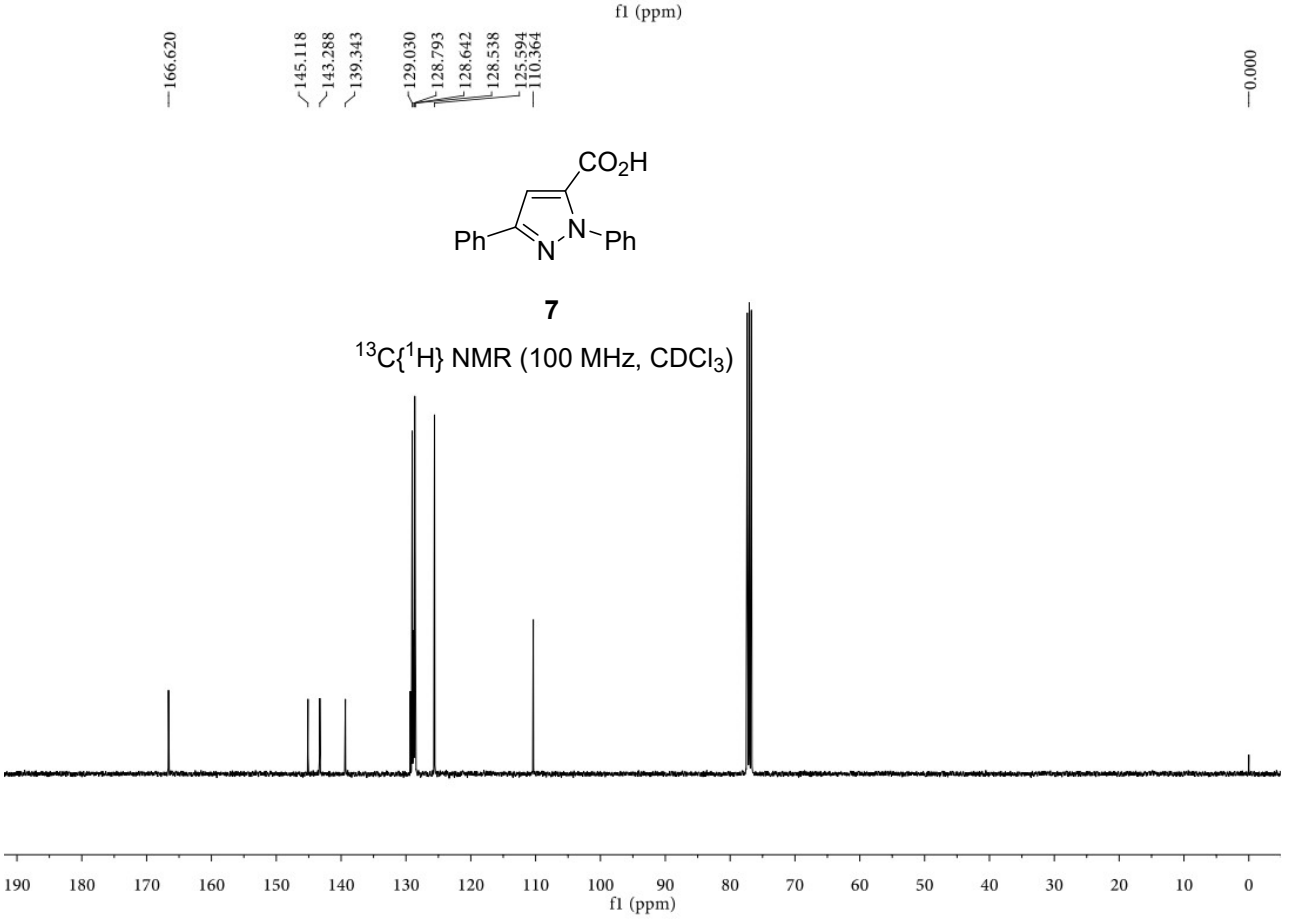
6

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



7

^{1}H NMR (400 MHz, $CDCl_3$)



7

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)