

Supporting Information

Sustainable synthesis of pyrazoles using alcohols as the primary feedstock by an iron catalyzed tandem C-C and C-N coupling approach

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Experimental Section.

General Information. Toluene, xylene, 1,4-dioxane, THF, and all other solvents used in this work were distilled and dried following the standard procedures. All other chemicals were used as received from the different commercial suppliers without further purification. Merck 60 F254 silica gel plate (0.25 mm thickness), Merck silica gel-G and Merck 60 silica gel (60–120 mesh) were used for analytical TLC and column chromatography. All ESI-MS were recorded on a micro mass Q-TOF mass spectrometer, and the NMR spectra were recorded on Bruker Avance-400 spectrometer. Tetramethylsilane (TMS) was used as the internal standard.

Catalyst Synthesis. The catalysts **1** and **2** were prepared following our previously reported article.¹

General Procedure for 1,3,5-triphenyl-(1H)-pyrazole Synthesis (path-A). 3.0 mol% **1**, 1.0 mmol of aryl hydrazine, and 0.5 equiv. ^tBuOK were added to an oven-dried 35 mL ace pressure tube containing a magnetic bar under air. 2.0 mmol of the respective primary and secondary alcohols dissolved in 4.0 mL of dry toluene were added, and the tube was tightly capped with a PTFE screw cap. The sealed tube containing the reaction mixture was then placed in a preheated oil bath at 100 °C. The reaction was continued for 24 h. After completion of the reaction, the solvent and the volatiles were evaporated under vacuum, and the concentrated reaction mixture was purified by silica gel column chromatography using hexane/ethyl acetate (19:1) as the eluent.

General Procedure for 1,3,5-triphenyl-(1H)-pyrazole Synthesis (path-B). 3.0 mol% **1**, 1.0 mmol of aryl hydrzine, and 0.5 equiv. ^tBuOK were added to an oven-dried 35 mL ace pressure tube containing a magnetic bar under air. 2.0 mmol of the respective primary alcohols and aryl alkynes dissolved in 4.0 mL of dry toluene were added, and the tube was tightly capped with a PTFE screw cap. The sealed tube containing the reaction mixture was then placed in a preheated oil bath at 100 °C. The reaction was continued for 24 h. After completion of the reaction, the solvent and the volatiles were evaporated under vacuum, and the concentrated reaction mixture was purified by silica gel column chromatography using hexane/ethyl acetate (19:1) as the eluent.

Spectrophotometric Detection of Hydrogen Peroxide During the 1-Catalyzed Synthesis of pyrazoles.¹ The formation of H₂O₂ during catalytic alcohol oxidation reaction was detected spectrophotometrically by monitoring the gradual rise of the characteristic

absorption band at 350 nm for I_3^- . **1**-catalyzed dehydrogenative functionalization of alcohols to **7a** was performed in an oven-dried ace pressure tube containing a magnetic stir bar, 2.0 mmol of benzyl alcohol (**4a**), and 1-phenyl ethanol (**5a**) (**path-A**) or 1-phenyl acetylene (**6a**) (**path-B**), 1.0 mmol of phenylhydrazine (**3a**), 3.0 mol% of catalyst **1**, and 0.5 equiv. t BuOK in 4 mL of dry toluene. The reaction mixture was heated at 100 °C for 24 h. To it, 10 mL of distilled water was added. Next, the whole solution was extracted with dichloromethane, and the separated aqueous layer was further acidified using concentrated H_2SO_4 to maintain pH 2 to stop any additional oxidation. Subsequently, 1.0 mL of a 10% solution of KI and a few drops of a 3% ammonium molybdate solution were added. Then the in-situ formed hydrogen peroxide oxidizes I^- to molecular iodine (I_2), which upon reaction with excess I^- generated I_3^- following the reaction sequences below:

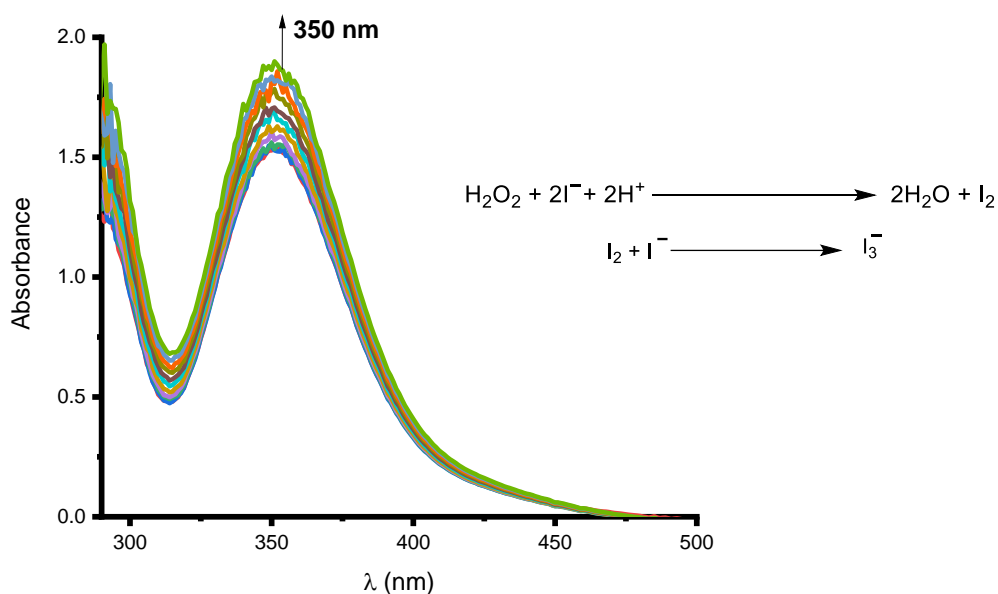
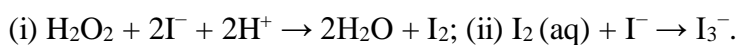


Figure S1. Detection of H_2O_2 . Absorption spectral changes during formation of I_3^- in the presence of H_2O_2 .

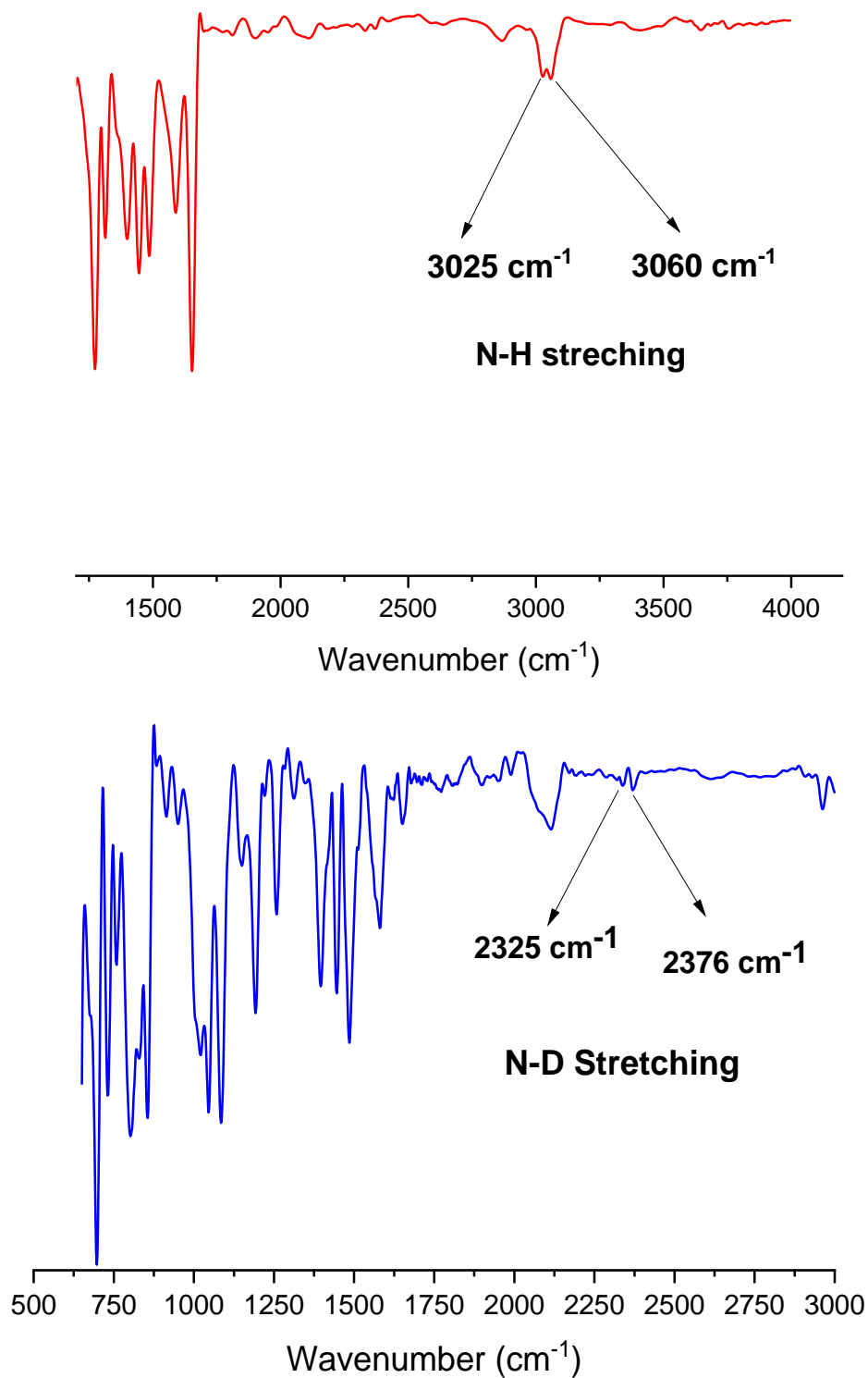


Figure S2. IR spectroscopic analysis of the reaction mixture (detection of azo/hydrazo redox couple).

Characterization Data of the Isolated Compounds.

1,3,5-triphenyl-1H-pyrazole (7a). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 243 mg, 82%; Path B: 249 mg, 84%. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.48–7.32 (m, 13H), 6.86 (s, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 152.0, 144.4, 140.1, 133.0, 130.6, 128.9, 128.7, 128.7, 128.5, 128.3, 128.0, 127.4, 125.8, 125.3, 105.2 ppm. HRMS (ESI) *m/z*: [M+H]⁺ Calcd. for [C₂₁H₁₇N₂]⁺ 297.1386; found = 297.1384.

1,3-diphenyl-5-(*o*-tolyl)-1H-pyrazole (7b). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 257 mg, 83%; Path B: 264 mg, 85%. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.39–7.33 (m, 3H), 7.29–1.24 (m, 7H), 6.91 (s, 1H), 2.07 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 152.4, 143.3, 140.0, 136.2, 132.7, 130.8, 130.6, 129.3, 128.8, 128.8, 128.5, 128.2, 127.9, 127.3, 125.8, 125.2, 108.2, 21.3 ppm. [M+H]⁺ Calcd. for [C₂₂H₁₉N₂]⁺ 311.1543; found = 311.1542.

5-(3-methoxyphenyl)-1,3-diphenyl-1H-pyrazole (7c). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 261 mg, 80%; Path B: 271 mg, 83%. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.47–7.30 (m, 8H), 7.24–7.22 (m, 1H), 6.89–6.82 (m, 4H), 3.69 (s, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 159.9, 151.8, 144.4, 140.0, 129.7, 128.9, 128.7, 128.5, 128.3, 127.5, 125.3, 118.4, 114.2, 110.8, 105.4, 55.4 ppm. [M+H]⁺ Calcd. for [C₂₂H₁₈N₂NaO]⁺ 349.1311; found = 349.1309.

1,3-diphenyl-5-(*p*-tolyl)-1H-pyrazole (7d). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 267 mg, 86%; Path B: 273 mg, 88%. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.46–7.31 (m, 8H), 7.20–7.13 (m, 4H), 6.81 (s, 1H), 2.37 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 151.9, 144.4, 140.2, 138.2, 133.1, 129.1, 128.8, 128.6, 127.9, 127.6, 127.3, 125.8, 125.3, 104.9, 21.2 ppm. [M+H]⁺ Calcd. for [C₂₂H₁₉N₂]⁺ 311.1543; found = 311.1541.

5-(4-fluorophenyl)-1,3-diphenyl-1H-pyrazole (7e). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 204 mg, 65%; Path B: 214 mg, 68%. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.47–7.43 (m, 2H), 7.38–7.32 (m, 6H), 7.28–7.25 (m, 2H), 7.05–7.00 (m, 2H), 6.81 (s, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 163.0, 160.5, 152.0, 144.6, 136.1, 132.6, 130.2, 128.7 (d, *J* = 4.0 Hz), 128.6,

128.5, 128.2, 127.1 (d, $J = 4.0$ Hz), 125.9, 115.9 (d, $J = 8.0$ Hz), 105.2 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): $\delta -112.6$ (s) ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{FN}_2]^+$ 315.1292; found = 315.1290.

5-(4-chlorophenyl)-1,3-diphenyl-1H-pyrazole (7f). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 228 mg, 69%; Path B: 234 mg, 71%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.44 (t, $J = 8.0$ Hz, 2H), 7.37–7.29 (m, 8H), 7.22–7.20 (m, 2H), 6.82 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.2, 144.4, 138.6, 132.9, 132.7, 130.4, 130.2, 129.0, 128.7, 128.6, 128.5, 128.1, 126.2, 125.7, 105.5 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{ClN}_2]^+$ 331.0997; found = 331.0996.

5-(4-bromophenyl)-1,3-diphenyl-1H-pyrazole (7g). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 263 mg, 70%; Path B: 274 mg, 73%. ^1H NMR (400 MHz, CDCl_3): δ 7.73–7.69 (m, 5H), 7.48–7.38 (m, 7H), 7.28 (s, 2H), 6.85 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.2, 144.4, 139.0, 132.0, 128.7, 128.7, 128.6, 128.6, 128.2, 126.5, 125.8, 121.0, 105.6 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{BrN}_2]^+$ 375.0491; found = 375.0490.

1,3-diphenyl-5-(4-(trifluoromethyl)phenyl)-1H-pyrazole (7h). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 240 mg, 66%; Path B: 248 mg, 68%. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.52–7.44 (m, 4H), 7.39–7.38 (m, 4H), 7.31–7.29 (m, 2H), 6.85 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.6, 144.7, 142.6, 132.3–132.2 (m, $J = 6.0$ Hz), 130.0, 129.9, 128.9–128.7 (q, $J = 4.0$ Hz), 128.5, 127.7, 126.1–125.9 (q, $J = 4.0$ Hz), 125.2, 125.9, 124.9, 124.3, 122.7, 106.2 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): $\delta -62.3$ (s) ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{N}_2\text{F}_3]^+$ 365.1260; found = 365.1258.

5-(3-nitrophenyl)-1,3-diphenyl-1H-pyrazole (7i). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 215 mg, 63%; Path B: 229 mg, 67%. ^1H NMR (400 MHz, CDCl_3): δ 8.21–8.17 (m, 2H), 7.93 (d, $J = 8.0$ Hz, 2H), 7.53–7.35 (m, 10H), 6.95 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.3, 148.3, 141.8, 139.5, 134.3, 132.5, 132.1, 129.5, 129.3, 128.7, 128.3, 128.2, 125.8, 125.4, 123.4, 123.0, 105.8 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{15}\text{N}_3\text{NaO}_2]^+$ 364.1056; found = 364.1054.

2-(1,3-diphenyl-1H-pyrazol-5-yl)pyridine (7j). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 208 mg, 70% (from **2j** and **3a**); Path B: 217 mg, 73%. ^1H NMR (400 MHz, CDCl_3): δ 8.62 (d, $J = 8.0$ Hz, 1H), 7.94 (d, J

= 8.0 Hz, 2H), 7.62–7.58 (m, 1H), 7.43–7.33 (m, 9H), 7.23–7.13 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.1, 149.8, 149.5, 143.6, 140.3, 136.2, 132.9, 129.0, 128.6, 128.0, 127.7, 125.8, 125.4, 123.5, 122.8, 106.2 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{20}\text{H}_{15}\text{N}_3\text{Na}]^+$ 320.1158; found = 320.1155.

1,3-diphenyl-5-(thiophen-2-yl)-1H-pyrazole (7k). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 218 mg, 72%; Path B: 224 mg, 74%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, $J = 8.0$ Hz, 2H), 7.48–7.42 (m, 7H), 7.37–7.29 (m, 2H), 6.96 (t, $J = 4.0$ Hz, 1H), 6.89–6.86 (m, 2H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 151.9, 139.9, 138.2, 132.8, 131.4, 129.0, 128.7, 128.3, 128.1, 127.4, 127.3, 126.5, 126.3, 125.8, 105.0 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{19}\text{H}_{15}\text{N}_2\text{S}]^+$ 303.0950; found = 303.0947.

1,5-diphenyl-3-(o-tolyl)-1H-pyrazole (8a). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 248 mg, 80%; Path B: 254 mg, 82%. ^1H NMR (400 MHz, CDCl_3): δ 7.70 (t, $J = 4.0$ Hz, 1H), 7.39–7.28 (m, 13H), 6.68 (s, 1H), 2.60 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.4, 143.3, 140.0, 136.2, 132.7, 130.8, 130.6, 129.3, 128.8, 128.8, 128.5, 128.2, 127.9, 127.3, 125.8, 125.2, 108.2, 21.3 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{22}\text{H}_{19}\text{N}_2]^+$ 311.1543; found = 311.1540.

3-(3-methoxyphenyl)-1,5-diphenyl-1H-pyrazole (8b). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 254 mg, 78%; Path B: 260 mg, 80%. ^1H NMR (400 MHz, CDCl_3): δ 7.50–7.49 (m, 2H), 7.37–7.28 (m, 11H), 6.92–6.89 (m, 1H), 6.82(s, 1H), 3.89 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 159.9, 151.8, 144.4, 139.9, 134.3, 130.4, 129.6, 128.9, 128.7, 128.5, 128.3, 127.5, 125.3, 118.4, 114.2, 110.8, 105.4, 55.4 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}]^+$ 327.1492; found = 327.1489.

3-(4-(tert-butyl)phenyl)-1,5-diphenyl-1H-pyrazole (8c). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 271 mg, 77%; Path B: 282 mg, 80%. ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.46–7.29 (m, 13H), 6.80 (s, 1H), 1.36–1.32(m, 9H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.0, 151.0, 144.2, 140.1, 130.6, 130.2, 128.9, 128.7, 128.4, 128.2, 127.3, 125.8, 125.5, 125.4, 125.3, 105.1, 34.6, 31.3, 31.2 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{25}\text{H}_{25}\text{N}_2]^+$ 353.2012; found = 353.2010.

3-(4-methoxyphenyl)-1,5-diphenyl-1H-pyrazole (8d). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 267 mg,

82%; Path B: 277 mg, 85%. ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.41–7.32 (m, 10H), 7.01–6.99 (m, 2H), 6.79 (s, 1H), 3.88 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.8, 144.3, 140.2, 131.4, 130.7, 129.3, 128.8, 128.4, 128.5, 127.3, 127.1, 125.8, 125.3, 114.0, 104.8, 55.3 ppm. [M+H]⁺ Calcd. for [C₂₂H₁₉N₂O]⁺ 327.1492; found = 327.1491.

3-(2-bromophenyl)-1,5-diphenyl-1H-pyrazole (8e). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 243 mg, 65%; Path B: 251 mg, 67%. ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.38–7.27 (m, 9H), 6.86 (s, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.6, 142.6, 140.1, 133.2, 133.0, 132.5, 132.2, 130.4, 128.8, 128.7, 128.4, 128.0, 127.3, 127.1, 125.8, 124.1, 106.7 ppm. [C₂₁H₁₆BrN₂]⁺ 375.0491; found = 375.0489.

3-(3-chlorophenyl)-1,5-diphenyl-1H-pyrazole (8f). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 234 mg, 71%; Path B: 238 mg, 72%. ¹H NMR (400 MHz, CDCl₃): δ 7.95 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.37–7.28 (m, 12H), 6.81 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 150.6, 144.6, 140.0, 134.9, 134.6, 130.3, 129.9, 128.9, 128.7, 128.5, 127.9, 127.6, 125.8, 125.3, 123.8, 113.4, 105.2 ppm. [M+H]⁺ Calcd. for [C₂₁H₁₆ClN₂]⁺ 331.0997; found = 331.0993.

3-(3-nitrophenyl)-1,5-diphenyl-1H-pyrazole (8g). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 208 mg, 61%; Path B: 215 mg, 63%. ¹H NMR (400 MHz, CDCl₃): δ 8.75 (s, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.37–7.08 (m, 10H), 6.90 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.6, 148.6, 142.1, 139.8, 134.6, 132.8, 132.4, 129.8, 129.6, 129.0, 128.6, 128.5, 126.1, 125.7, 123.7, 123.3, 106.1 ppm. [M+H]⁺ Calcd. for [C₂₁H₁₆N₃O₂]⁺ 364.1056; found = 364.1054.

1,5-diphenyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole (8h). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 233 mg, 64%; Path B: 240 mg, 66%. ¹H NMR (400 MHz, CDCl₃): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.52–7.44 (m, 4H), 7.40–7.38 (m, 4H), 7.31–7.30 (m, 2H), 6.86 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.6, 144.7, 142.6, 132.3, 130.1, 129.2, 128.8–128.7 (q, *J* = 4.0 Hz), 128.4, 127.7, 126.1–126.0 (q, *J* = 4.0 Hz), 125.9, 125.2, 124.9, 124.3, 122.5, 106.3 ppm. ¹⁹F{¹H} NMR (376 MHz, CDCl₃): δ –62.9 (s) ppm. [M+H]⁺ Calcd. for [C₂₁H₁₆N₂F₃]⁺ 365.3787; found = 365.3786.

3-cyclopropyl-1,5-diphenyl-1H-pyrazole (8i). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 151 mg, 58%; Path B: 156 mg, 60%. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.36–7.22 (m, 6H), 7.02–6.90 (m, 2H), 6.69–6.65 (m, 1H), 3.67–3.64 (m, 2H), 2.53–2.50 (m, 1H), 2.14–2.08 (m, 2H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 147.3, 142.2, 137.4, 130.0, 128.9, 128.6, 127.5, 126.4, 125.9, 120.1, 113.9, 43.2, 20.3, 18.2 ppm. [M+H]⁺ Calcd. for [C₁₈H₁₇N₂]⁺ 261.1386; found = 261.1384.

2-(1,5-diphenyl-1H-pyrazol-3-yl)pyridine (8j). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 199 mg, 67%; Path B: 211 mg, 71%. ¹H NMR (400 MHz, CDCl₃): δ 8.62 (d, *J* = 4.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.45–7.30 (m, 8H), 7.23–7.16 (m, 2H), 7.13 (s, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 152.1, 149.8, 143.6, 140.4, 136.2, 132.9, 128.9, 128.6, 128.0, 127.7, 125.8, 125.4, 123.5, 122.7, 120.3, 106.2 ppm. [M+H]⁺ Calcd. for [C₂₀H₁₅N₃Na]⁺ 320.1158; found = 320.1156.

3-(furan-2-yl)-1,5-diphenyl-1H-pyrazole (8k). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 197 mg, 69%; Path B: 203 mg, 71%. ¹H NMR (400 MHz, CDCl₃): δ 7.49 (s, 1H), 7.35–7.26 (m, 10H), 6.80–6.76 (m, 2H), 6.50 (s, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.5, 144.5, 144.1, 142.1, 139.9, 130.2, 128.9, 128.7, 128.5, 128.4, 127.6, 125.4, 111.3, 106.3, 104.8 ppm. [M+H]⁺ Calcd. for [C₁₉H₁₅N₂O]⁺ 287.1179; found = 287.1177.

1,5-diphenyl-3-(thiophen-2-yl)-1H-pyrazole (8l). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 223 mg, 74%; Path B: 226 mg, 75%. ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.49–7.29 (m, 9H), 6.97 (t, *J* = 4.0 Hz, 1H), 6.89–6.86 (m, 2H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.9, 139.9, 138.2, 132.8, 131.3, 129.0, 128.6, 128.3, 128.0, 127.3, 127.2, 126.5, 126.2, 125.8, 105.0 ppm. [M+H]⁺ Calcd. for [C₁₉H₁₅N₂S]⁺ 303.0950; found = 303.0948.

3,5-diphenyl-1-(*o*-tolyl)-1H-pyrazole (9a). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 248 mg, 80%; Path B: 254 mg, 82%. ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.48–7.44 (m, 2H), 7.39–7.33 (m, 3H), 7.29–7.24 (m, 7H), 6.91 (s, 1H), 2.07 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.6, 145.6, 139.3, 135.7, 132.8, 132.1, 131.1, 130.0, 129.1, 128.6, 128.4, 128.2,

128.1, 127.9, 126.7, 125.9, 103.2, 17.7 ppm. $[M+H]^+$ Calcd. for $[C_{22}H_{19}N_2]^+$ 311.1543; found = 311.1542.

3,5-diphenyl-1-(*m*-tolyl)-1H-pyrazole (9b). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 254 mg, 82%; Path B: 264 mg, 85%. 1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.46–7.43 (m, 2H), 7.37–7.31 (m, 7H), 7.22–7.18 (m, 1H), 7.14–7.12 (m, 1H), 7.06–7.04 (m, 1H), 6.83 (s, 1H), 2.36 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.8, 144.4, 140.0, 139.1, 133.0, 130.6, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 126.9, 125.8, 122.5, 105.0, 21.3 ppm. $[M+H]^+$ Calcd. for $[C_{22}H_{19}N_2]^+$ 311.1543; found = 311.1537.

3,5-diphenyl-1-(*p*-tolyl)-1H-pyrazole (9c). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 263 mg, 85%; Path B: 270 mg, 87%. 1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J = 8.0$ Hz, 2H), 7.46–7.42 (m, 3H), 7.36–7.25 (m, 7H), 7.16–7.14 (m, 2H), 6.82 (s, 1H), 2.37 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.6, 144.9, 144.4, 137.5, 132.9, 130.5, 129.5, 129.0, 128.6, 128.4, 128.0, 125.8, 125.2, 122.1, 104.9, 21.1 ppm. $[M+H]^+$ Calcd. for $[C_{22}H_{19}N_2]^+$ 311.1543; found = 311.1538.

1-(4-methoxyphenyl)-3,5-diphenyl-1H-pyrazole (9d). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 287 mg, 88%; Path B: 296 mg, 91%. 1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.45–7.42 (m, 2H), 7.36–7.29 (m, 8H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.82 (s, 1H), 3.82 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.9, 151.5, 144.4, 133.2, 132.9, 130.5, 128.7, 128.6, 128.4, 128.2, 128.0, 126.8, 125.8, 114.1, 104.6, 55.5 ppm. $[M+H]^+$ Calcd. for $[C_{22}H_{19}N_2O]^+$ 327.1492; found = 327.1490.

1-(3-chlorophenyl)-3,5-diphenyl-1H-pyrazole (9e). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 251 mg, 76%; Path B: 257 mg, 78%. 1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, $J = 8.0$ Hz, 2H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.56 (s, 1H), 7.50–7.46 (m, 2H), 7.41–7.38 (m, 4H), 7.36–7.30 (m, 4H), 7.19–7.18 (m, 1H), 6.86 (s, 1H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 152.2, 144.4, 138.6, 138.5, 132.9, 132.7, 130.5, 130.2, 129.0, 128.7, 128.6, 128.6, 128.5, 128.1, 126.2, 125.8, 105.5 ppm. $[M+H]^+$ Calcd. for $[C_{21}H_{16}ClN_2]^+$ 331.0997; found = 331.0995.

1-(3-bromophenyl)-3,5-diphenyl-1H-pyrazole (9f). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 303 mg, 81%; Path B: 307 mg, 82%. 1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, $J = 8.0$ Hz, 2H), 7.70 (s, 1H), 7.49–7.46

(m, 4H), 7.41–7.39 (m, 5H), 7.25–7.18 (m, 2H), 6.86 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.5, 144.7, 139.3, 130.5, 130.0, 129.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 125.9, 123.8, 105.7 ppm. $[\text{M}+\text{H}]^+$ Calcd. For $[\text{C}_{21}\text{H}_{16}\text{BrN}_2]^+$ 375.0491; found = 375.0485.

1-(4-fluorophenyl)-3,5-diphenyl-1H-pyrazole (9g). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 220 mg, 70%; Path B: 229 mg, 73%. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, J = 8.0 Hz, 2H), 7.46–7.42 (m, 2H), 7.36–7.34 (m, 6H), 7.29–7.27 (m, 2H), 7.05 (t, J = 8.0 Hz, 2H), 6.83 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 162.9, 160.5, 151.9, 144.6, 136.0, 132.6, 130.19, 128.7 (d, J = 4.0 Hz), 128.6, 128.5, 128.2, 127.1 (d, J = 4.0 Hz), 125.9, 115.5 (J = 12.0 Hz), 105.1 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -114.7 (s) ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{FN}_2]^+$ 315.1292; found = 315.1287.

1-(4-chlorophenyl)-3,5-diphenyl-1H-pyrazole (9h). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 245 mg, 74%; Path B: 255 mg, 77%. ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, J = 8.0 Hz, 2H), 7.48–7.44 (m, 2H), 7.39–7.29 (m, 10H), 6.84 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.2, 144.4, 138.7, 133.0, 132.8, 130.5, 130.3, 129.0, 128.8, 128.7, 128.6, 128.2, 126.3, 125.8, 105.6 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{ClN}_2]^+$ 331.0997; found = 331.0994.

1-(4-bromophenyl)-3,5-diphenyl-1H-pyrazole (9i). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 295 mg, 79%; Path B: 303 mg, 81%. ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, J = 8.0 Hz, 2H), 7.50–7.44 (m, 4H), 7.39–7.34 (m, 5H), 7.31–7.29 (m, 3H), 6.84 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.2, 144.5, 139.0, 132.7, 132.0, 130.2, 128.8, 128.7, 128.7, 128.6, 128.2, 126.6, 125.8, 121.0, 105.7 ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{BrN}_2]^+$ 375.0491; found = 375.0487.

3,5-diphenyl-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole (9j). Purification by column chromatography (silica gel, hexane/ethyl acetate, 19:1). White solid, Yield: Path A: 237 mg, 65%; Path B: 251 mg, 69%. ^1H NMR (400 MHz, CDCl_3): δ 7.93 (d, J = 8.0 Hz, 2H), 7.62–7.59 (m, 2H), 7.52–7.50 (m, 2H), 7.47–7.43 (m, 2H), 7.39–7.35 (m, 4H), 7.31–7.29 (m, 2H), 6.85 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.6, 144.7, 142.6, 132.3, 130.1, 129.2, 128.8–128.7 (q, J = 4.0 Hz), 128.4, 127.7, 126.1–126.0 (q, J = 4.0 Hz), 125.9, 125.2, 124.9, 124.3, 122.5, 106.2 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CDCl_3): δ -62.3 (s) ppm. $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{21}\text{H}_{16}\text{N}_2\text{F}_3]^+$ 365.1260; found = 365.3785.

(E)-chalcone (10).^{28a,d} Purification by column chromatography (silica gel, hexane/diethyl ether (30:1)). Light yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.80 (s, 2H), 7.72 (d, *J* = 8.0 Hz, 4H), 7.49 (t, *J* = 8.0 Hz, 4H), 7.42–7.38 (m, 2H) ppm.

1-((E)-1,3-diphenylallylidene)-2-phenylhydrazine (11). Purification by column chromatography (silica gel, hexane/diethyl ether (30:1)). Brown solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.51–7.33 (m, 14H), 7.21 (s, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.4, 144.6, 140.2, 133.1, 130.4, 129.5, 129.2, 129.1, 128.9, 128.9, 128.5, 128.2, 125.8, 125.7, 105.8 ppm. [M+H]⁺ Calcd. for [C₂₁H₁₈N₂Na]⁺ 321.1362; found = 321.1360.

(E)-1-benzylidene-2-phenylhydrazine (12).² Purification by column chromatography (silica gel, hexane/diethyl ether (30:1)). Yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.68–7.66 (m, 3H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.32–7.27 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.88 (t, *J* = 8.0 Hz, 1H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 144.6, 137.2, 135.3, 129.3, 128.6, 128.4, 126.2, 120.1, 112.7 ppm.

NMR Spectra of the Isolated Compounds

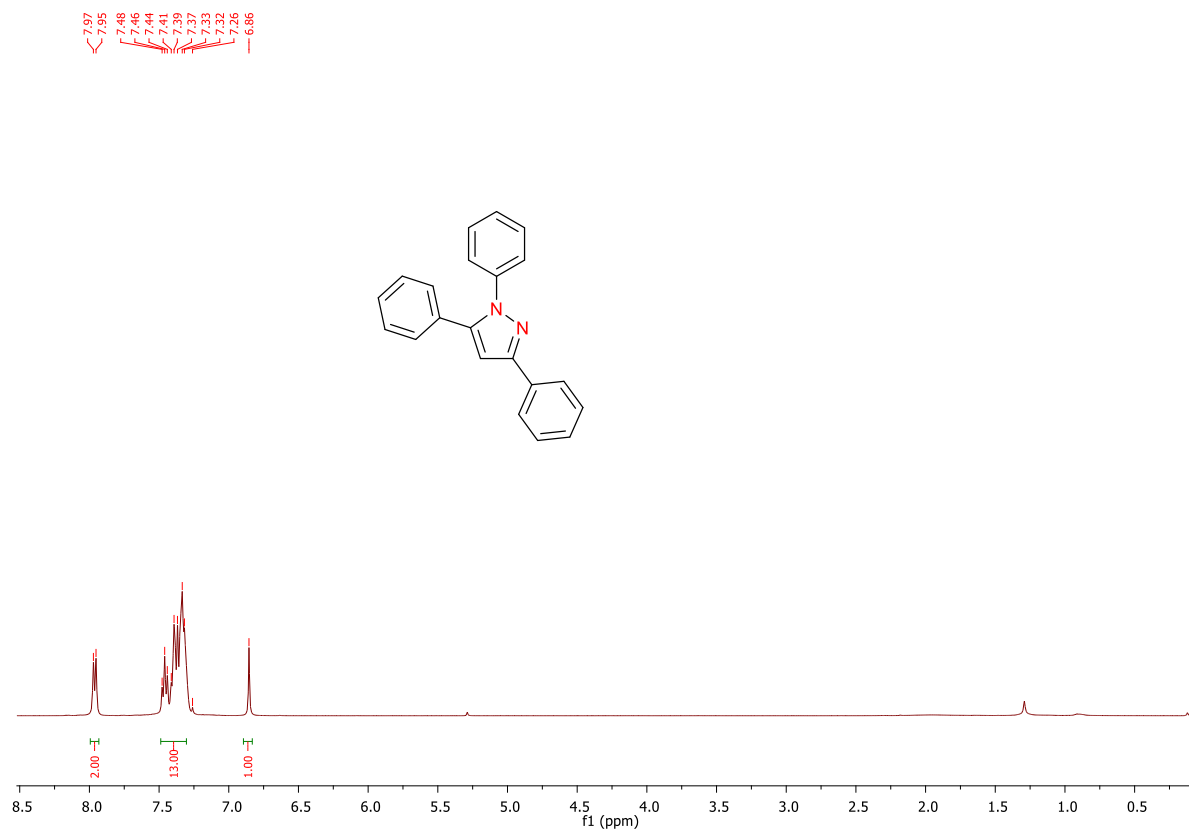


Figure S3. ¹H NMR spectrum of **7a** (400 MHz in CDCl₃).

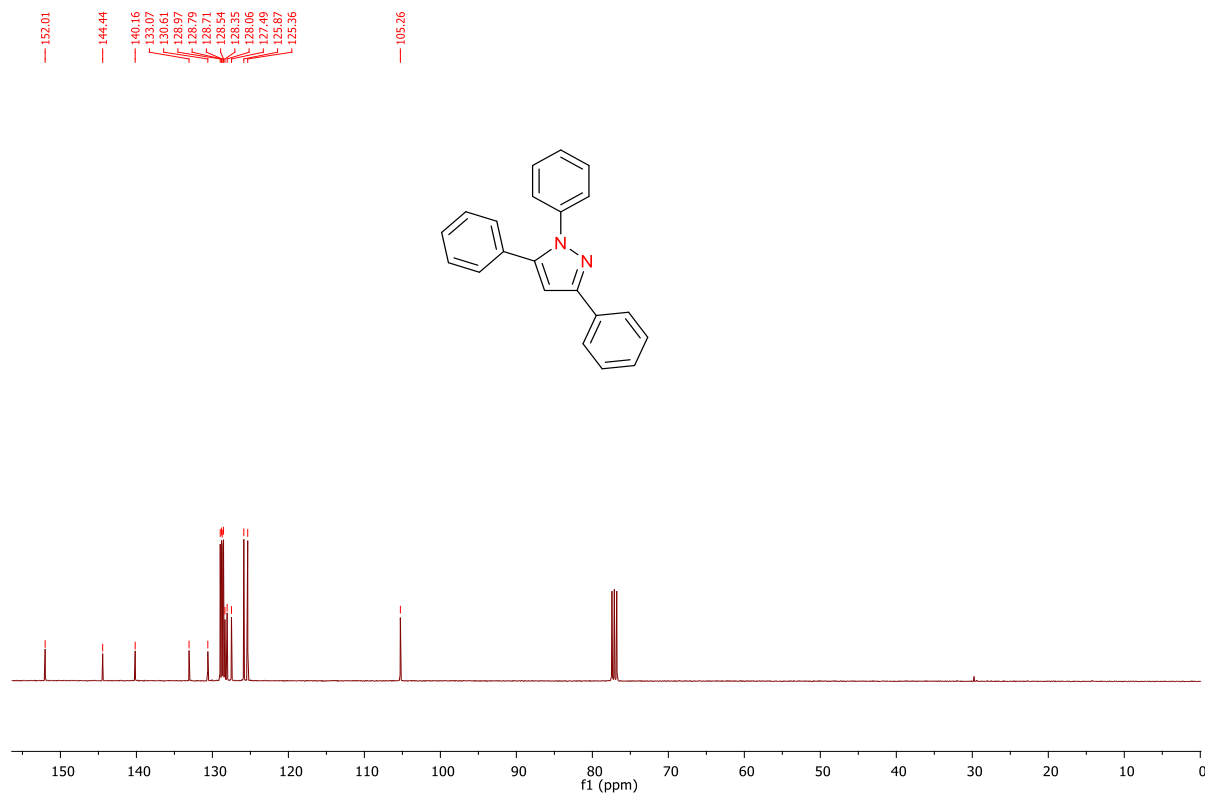


Figure S4. ¹³C NMR spectrum of **7a** (100 MHz in CDCl₃).

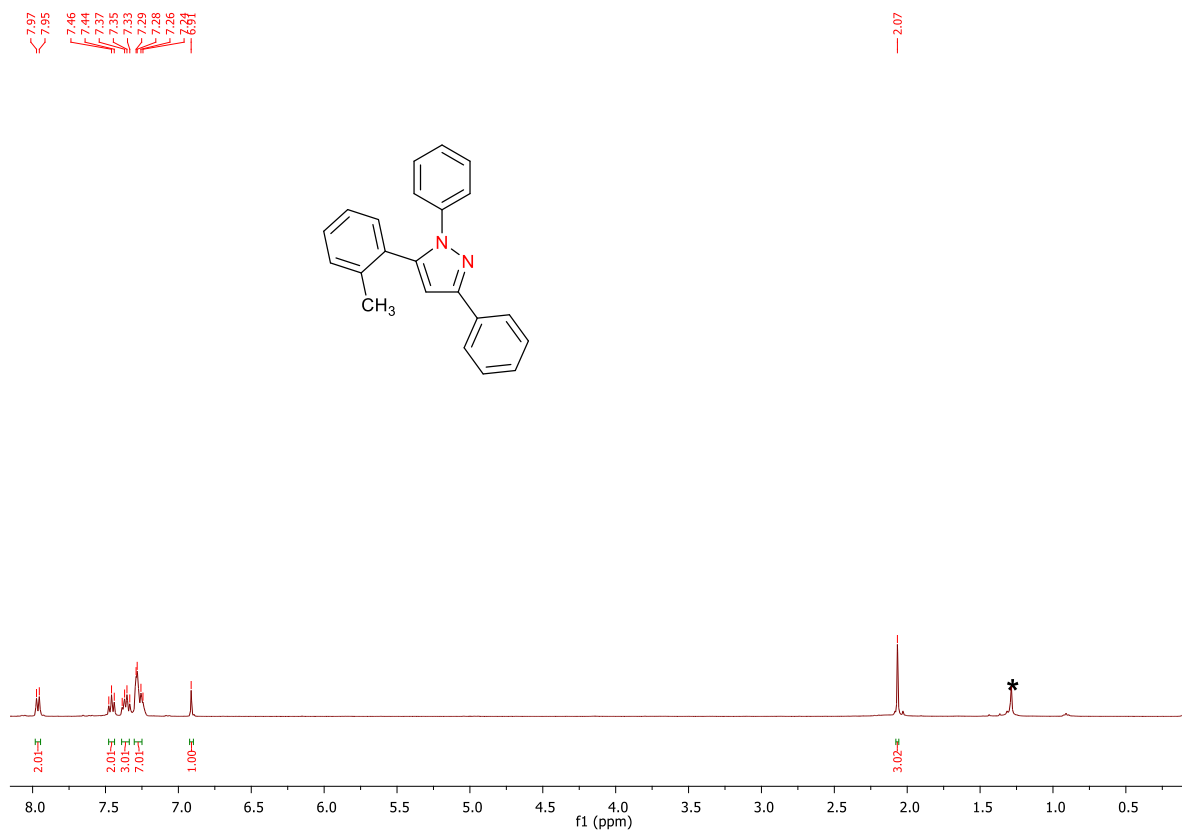


Figure S5. ¹H NMR spectrum of **7b** (400 MHz in CDCl₃). (*hexane)

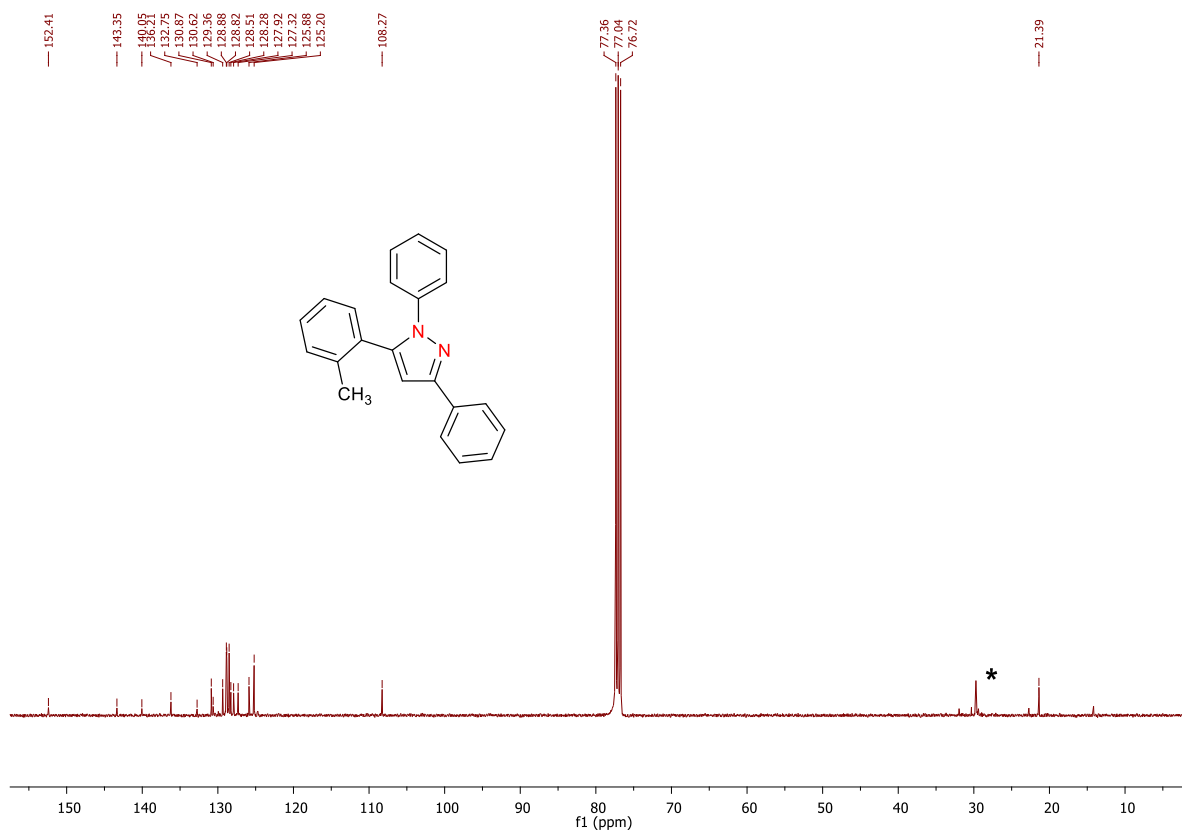


Figure S6. ¹³C NMR spectrum of **7b** (100 MHz in CDCl₃). (*hexane)

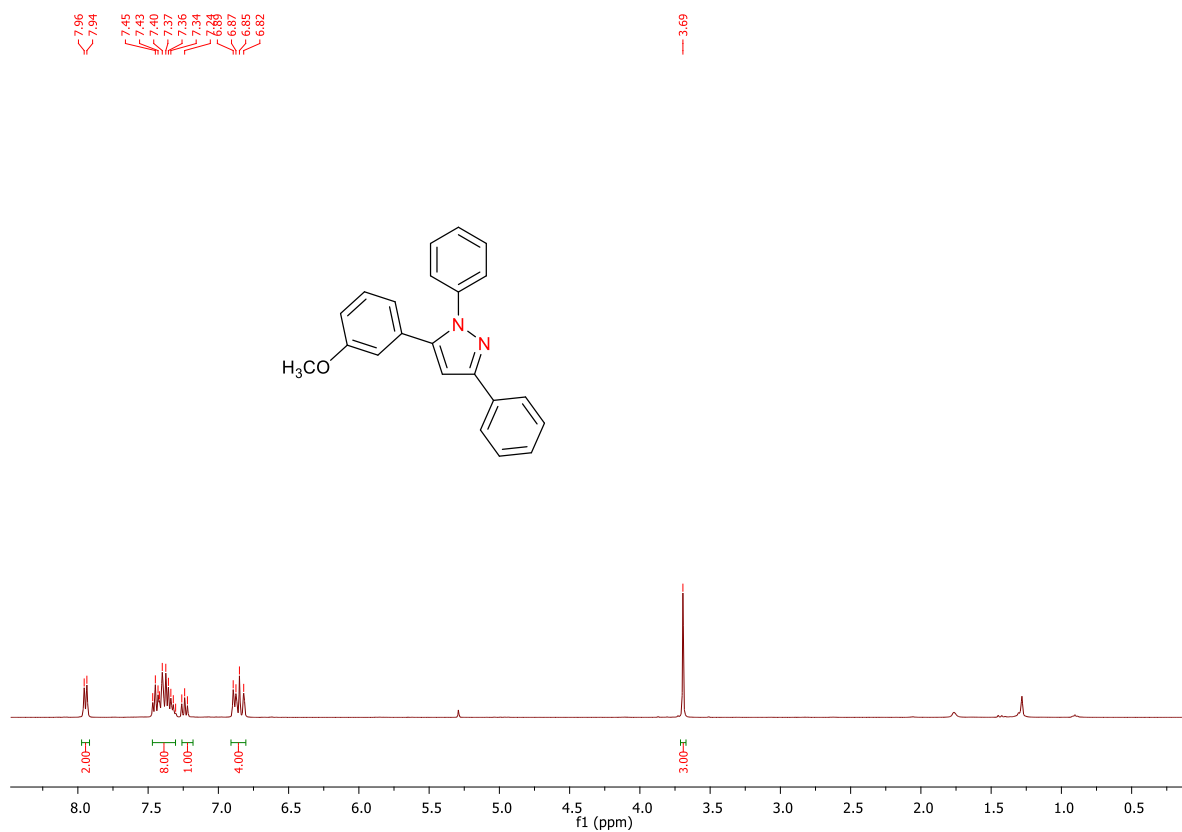


Figure S7. ¹H NMR spectrum of **7c** (400 MHz in CDCl₃).

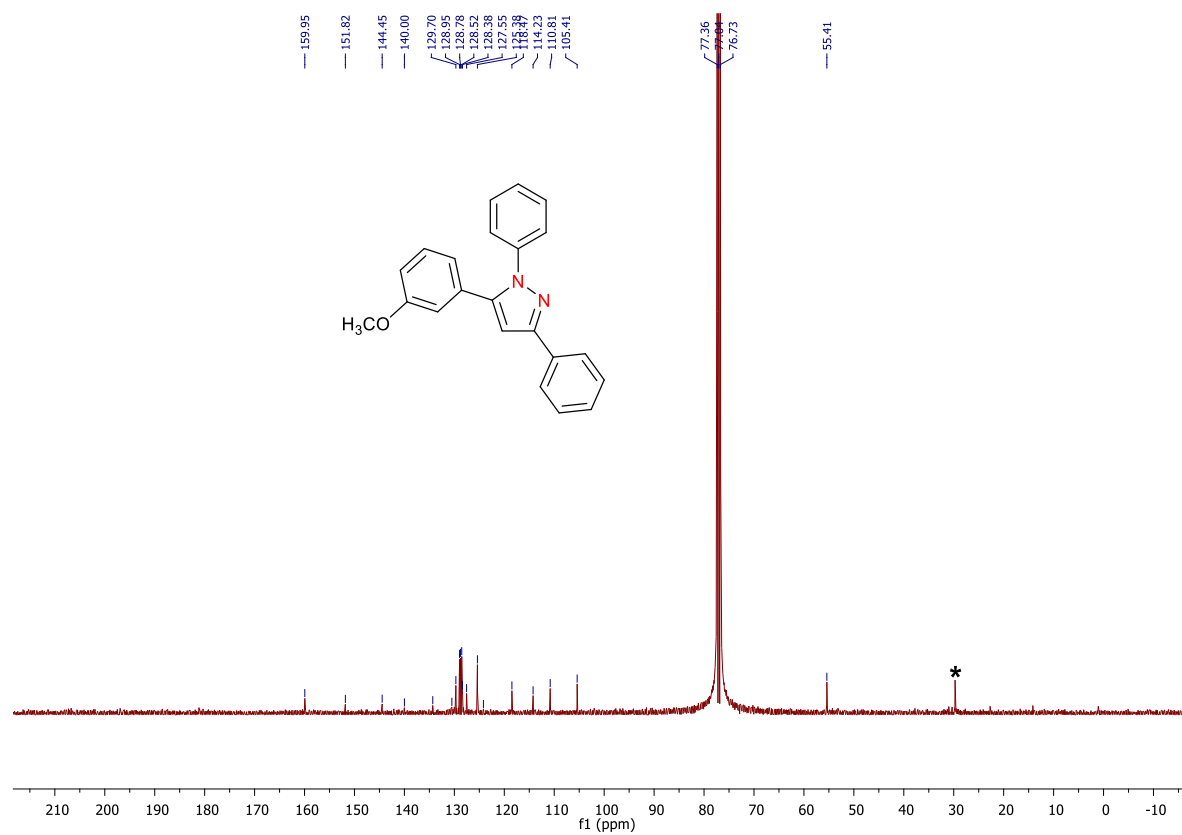


Figure S8. ¹³C NMR spectrum of **7c** (100 MHz in CDCl₃). (*hexane)

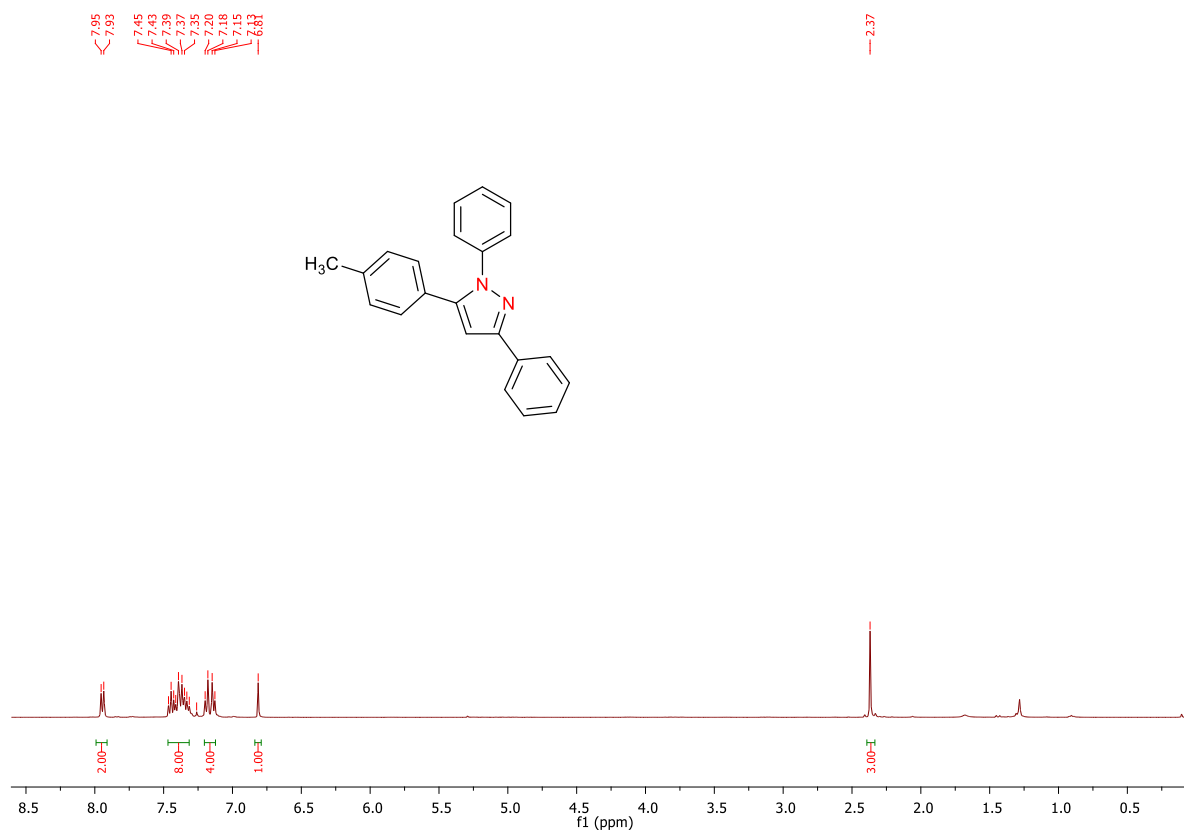


Figure S9. ¹H NMR spectrum of **7d** (400 MHz in CDCl₃).

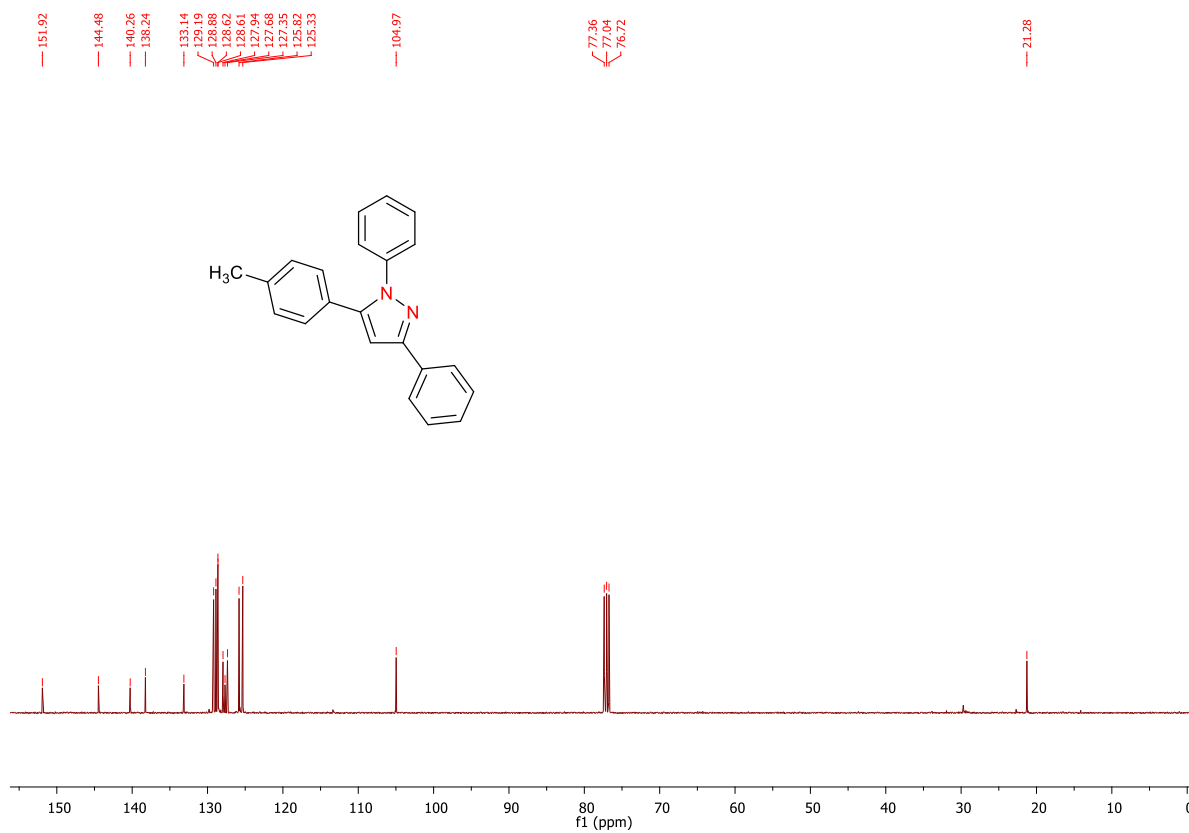


Figure S10. ¹³C NMR spectrum of **7d** (100 MHz in CDCl₃).

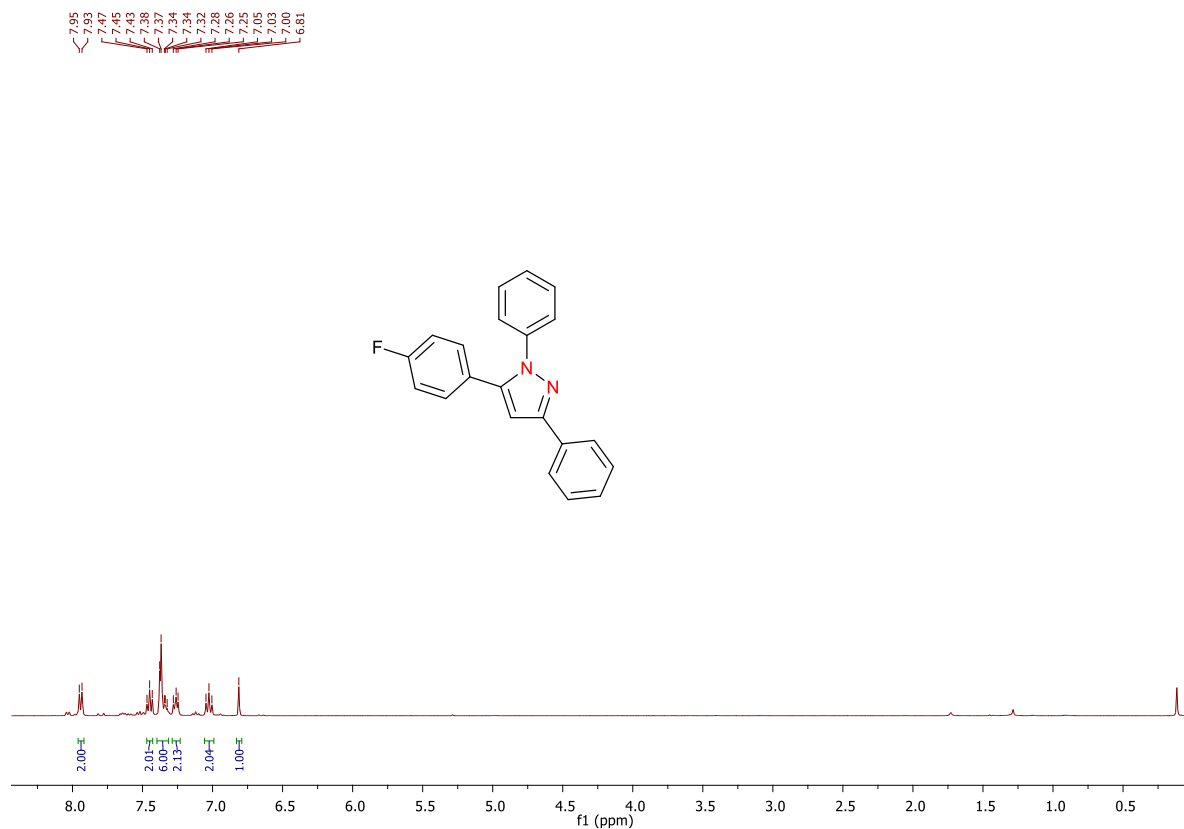


Figure S11. ¹H NMR spectrum of **7e** (400 MHz in CDCl₃).

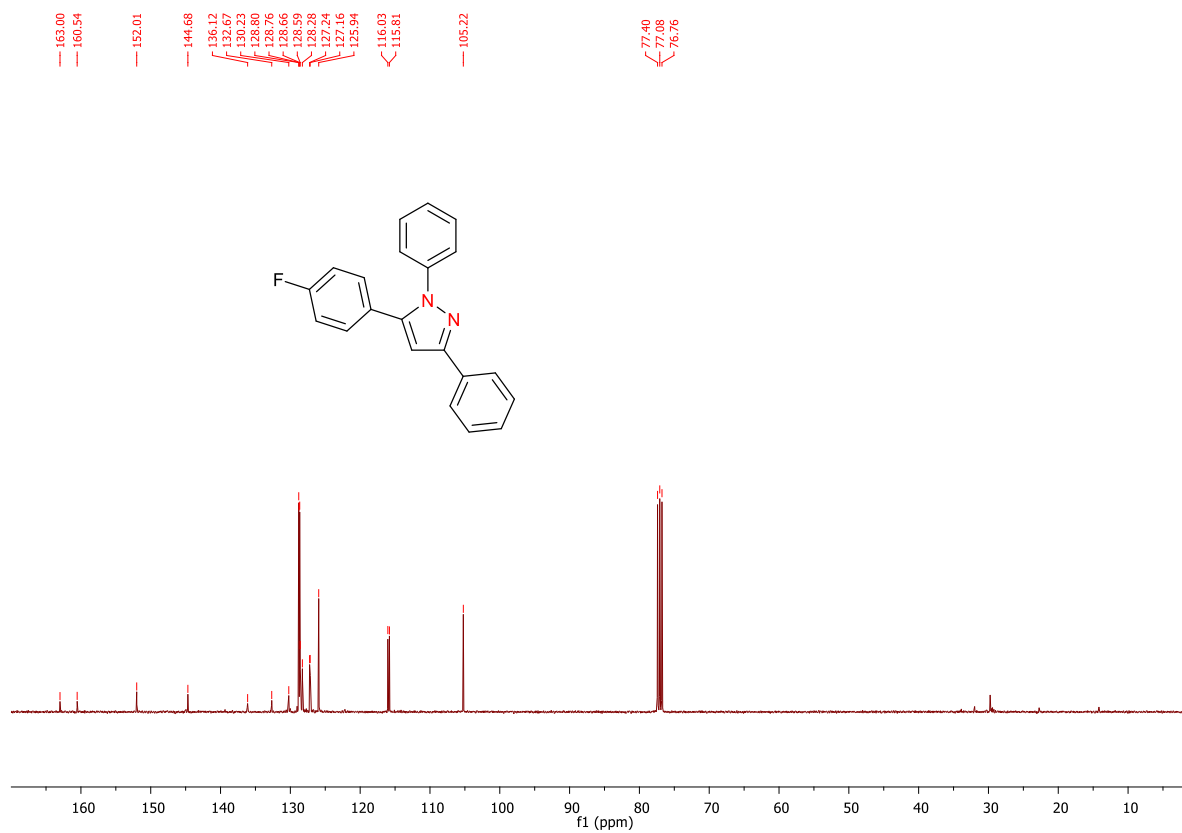


Figure S12. ¹³C NMR spectrum of **7e** (100 MHz in CDCl₃).

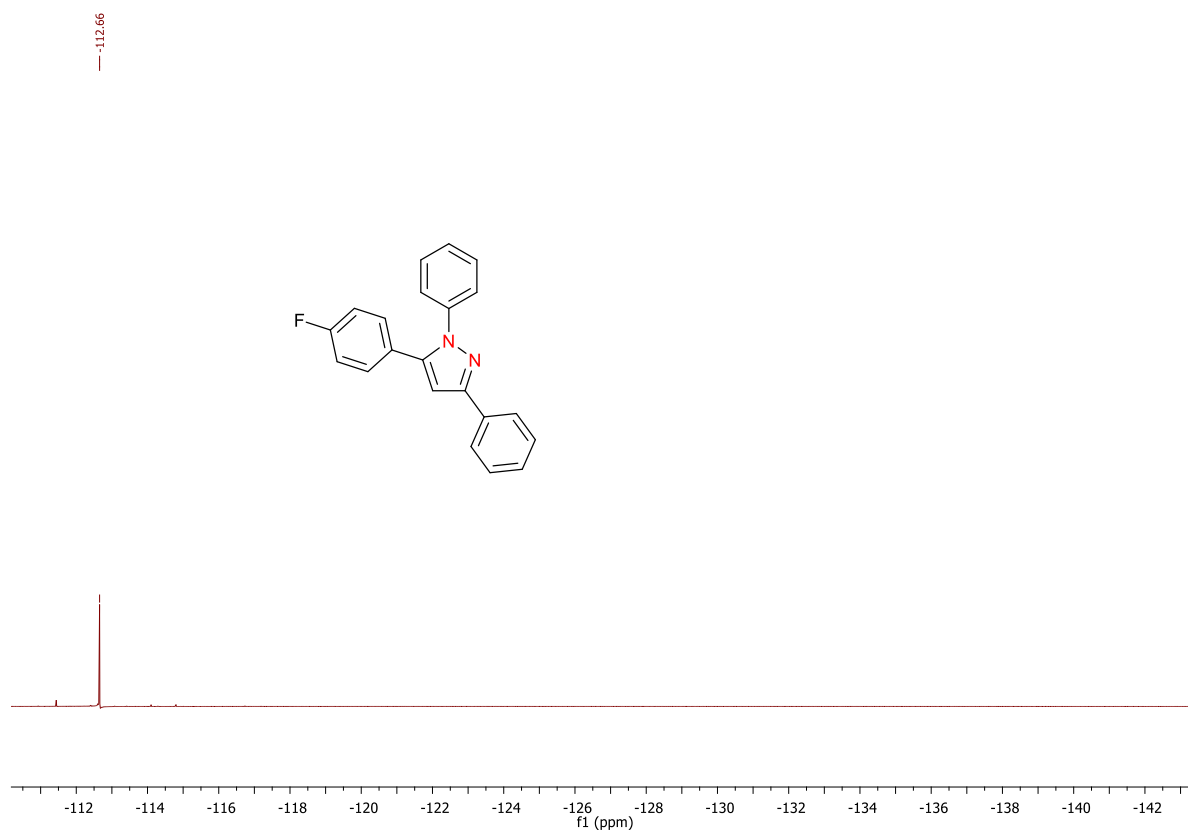


Figure S13. ^{19}F NMR spectrum of **7e** (376 MHz in CDCl_3).

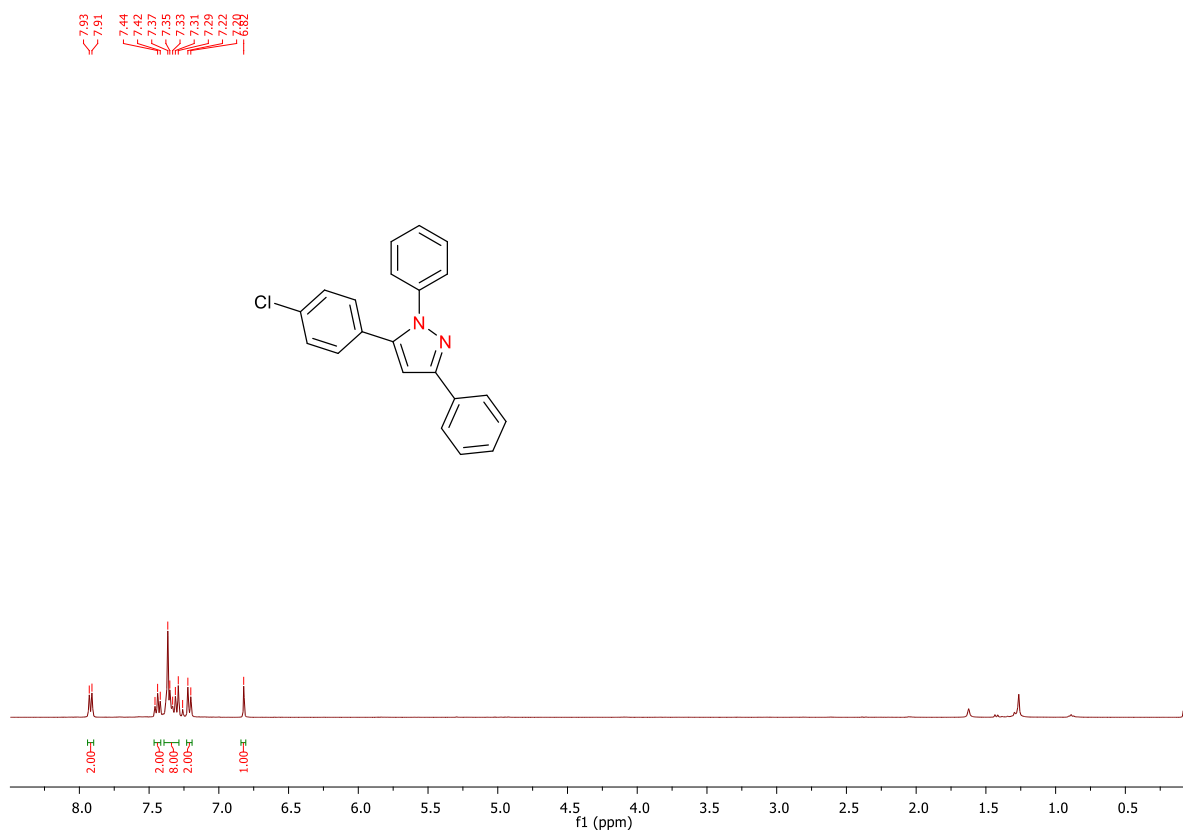


Figure S14. ¹H NMR spectrum of **7f** (400 MHz in CDCl₃).

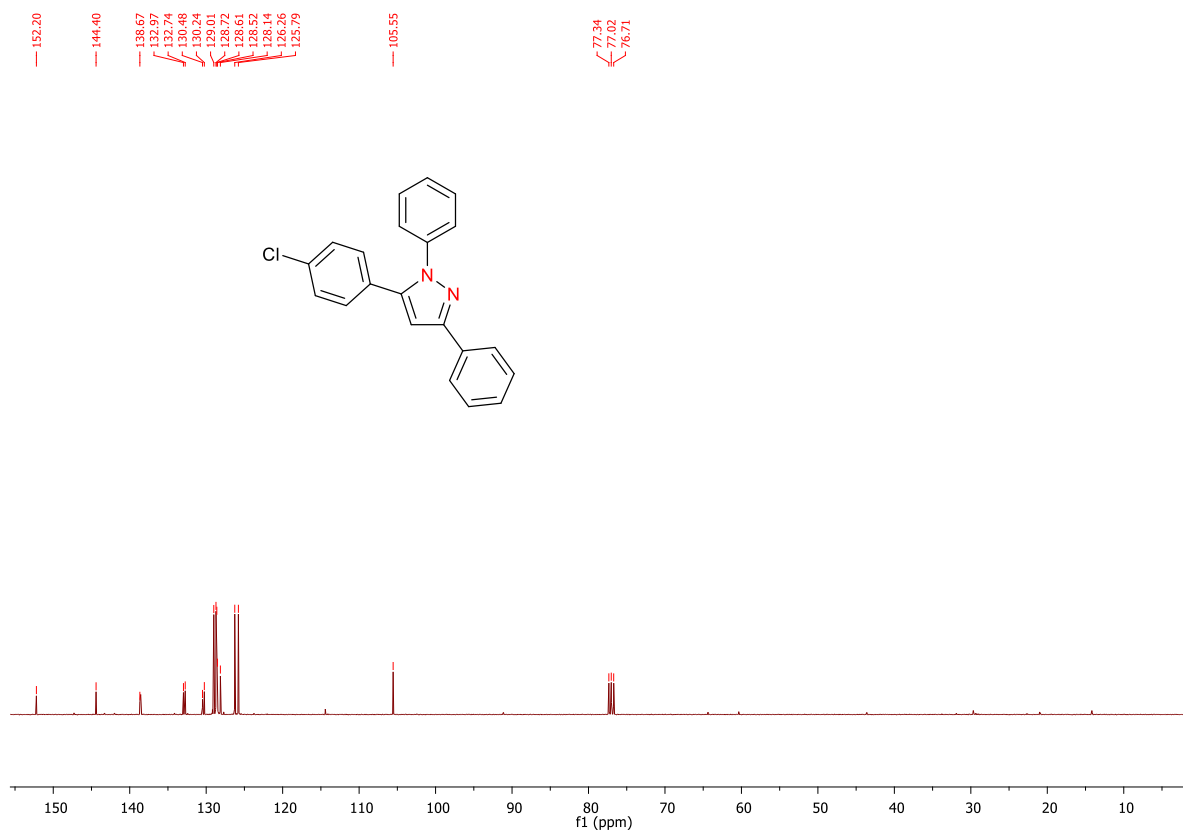


Figure S15. ¹³C NMR spectrum of **7f** (100 MHz in CDCl₃).

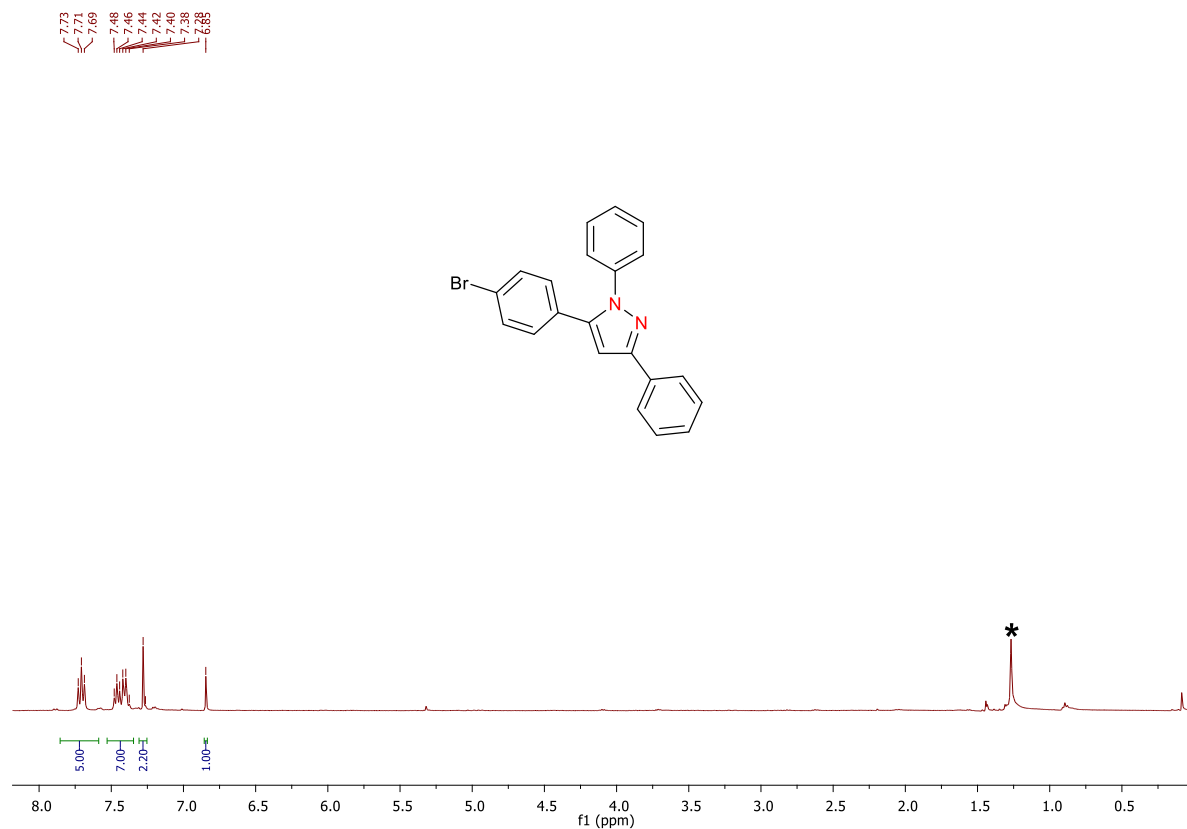


Figure S16. ¹H NMR spectrum of **7g** (400 MHz in CDCl₃). (*hexane)

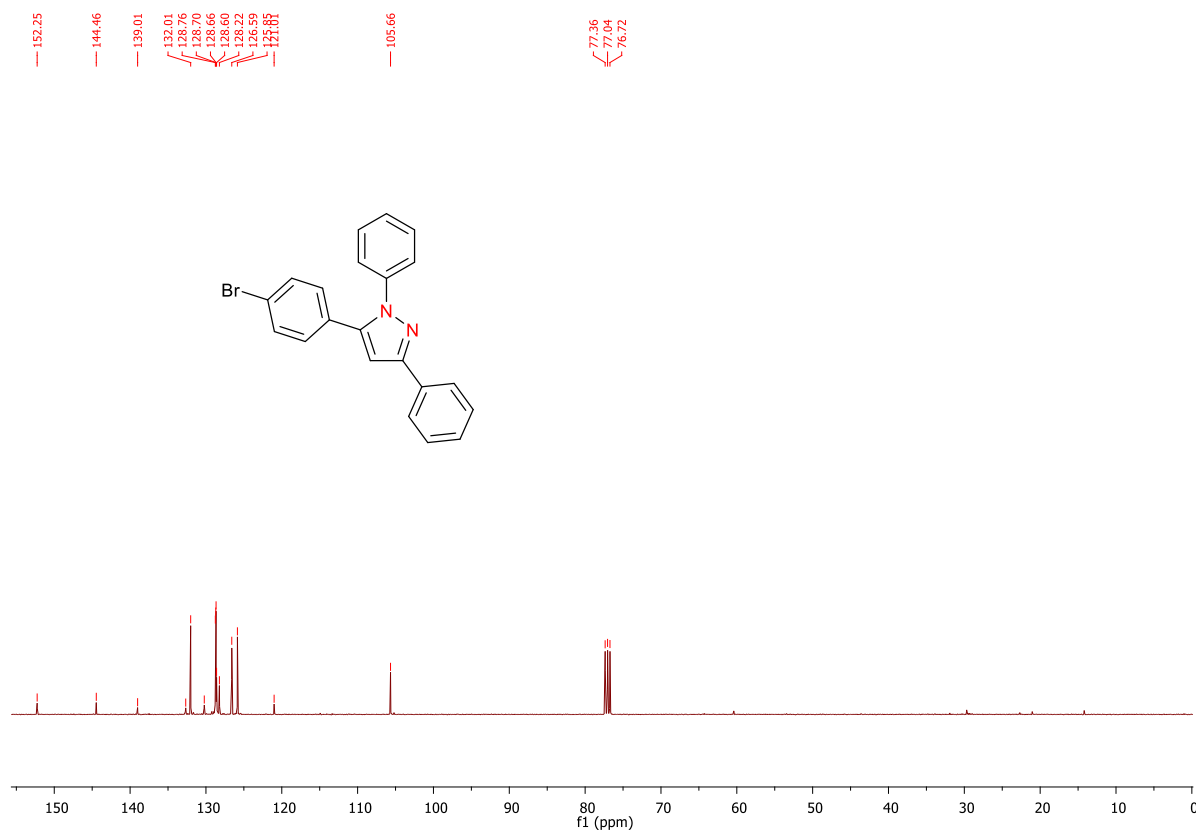


Figure S17. ¹³C NMR spectrum of **7g** (100 MHz in CDCl₃).

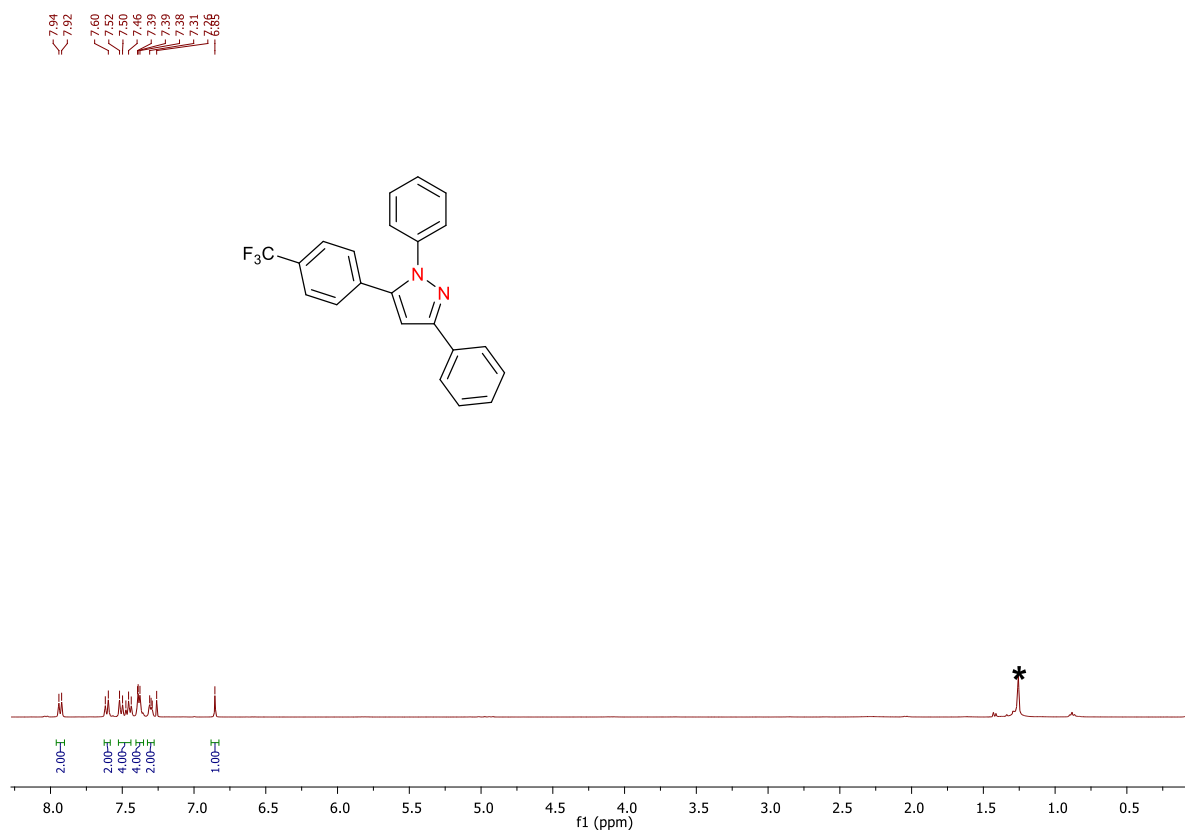


Figure S18. ¹H NMR spectrum of **7h** (400 MHz in CDCl₃). (*hexane)

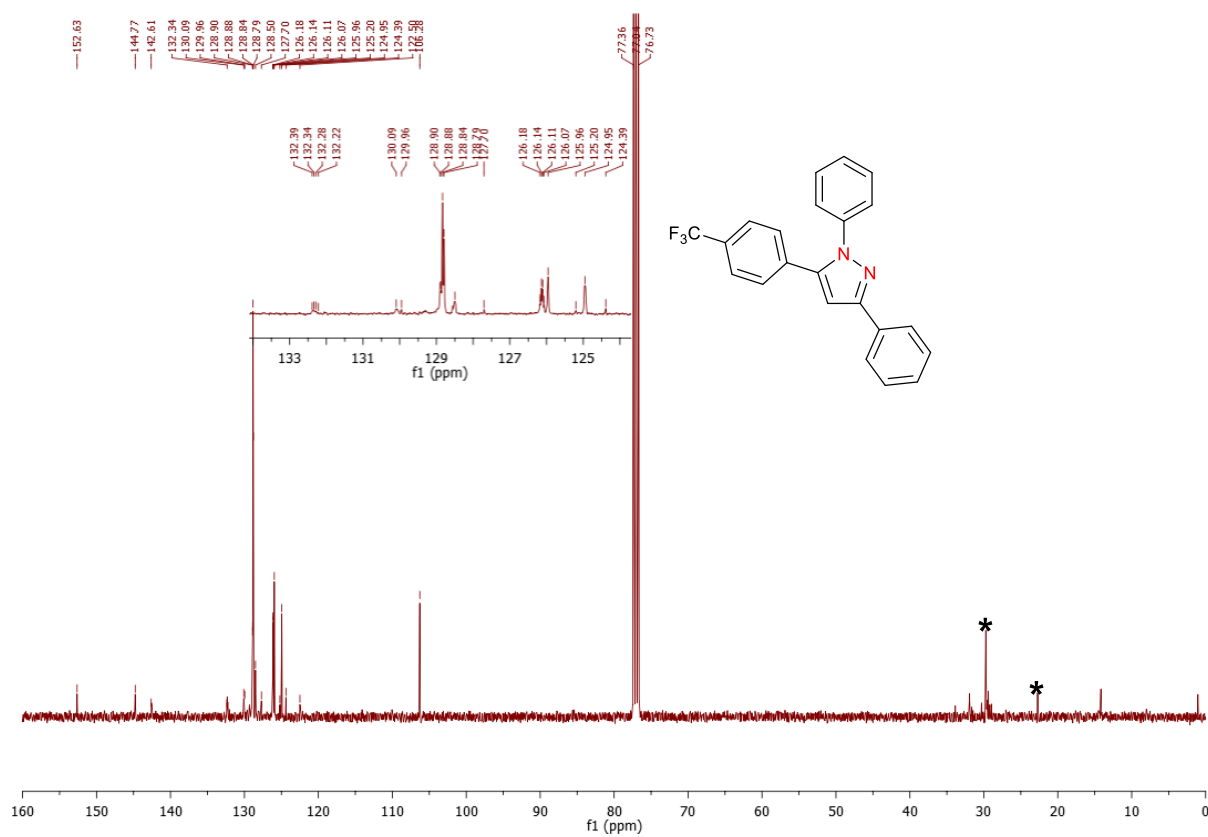


Figure S19. ¹³C NMR spectrum of **7h** (100 MHz in CDCl₃). (*hexane)

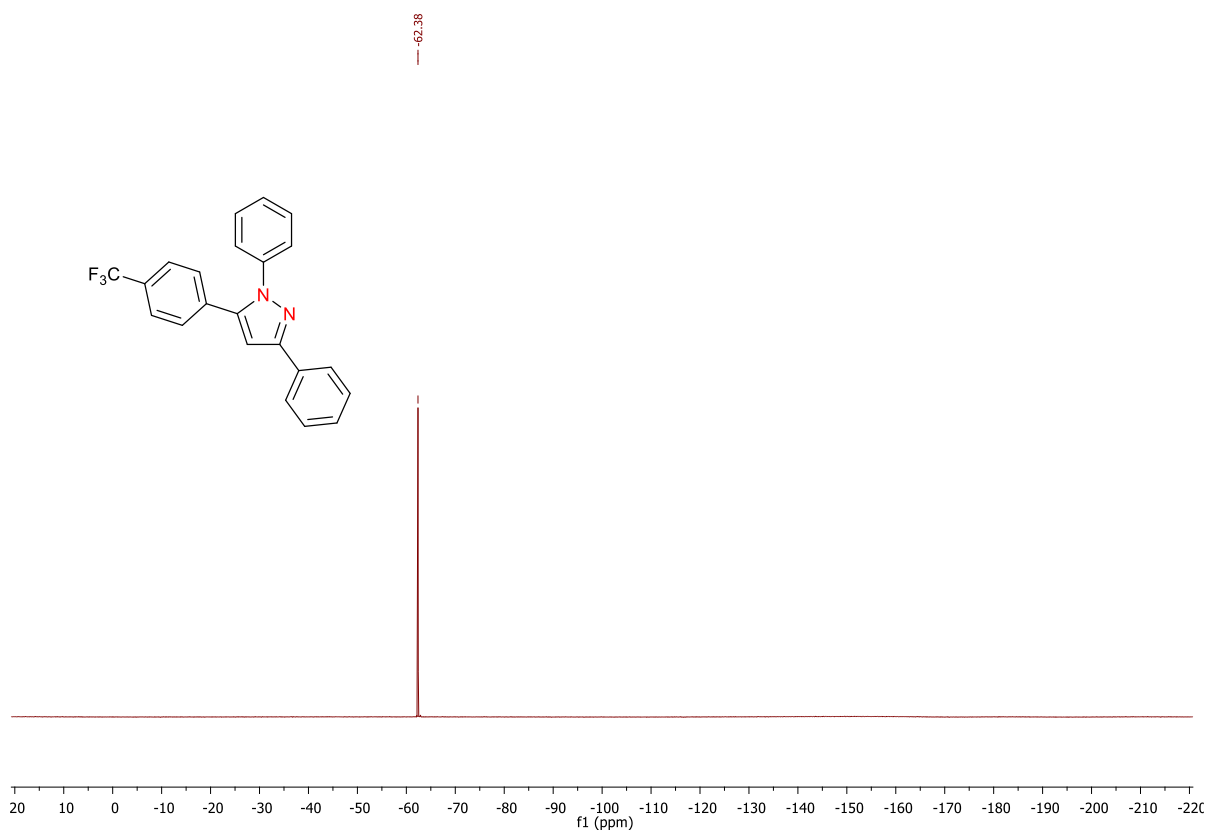


Figure S20. ^{19}F NMR spectrum of **7h** (376 MHz in CDCl_3).

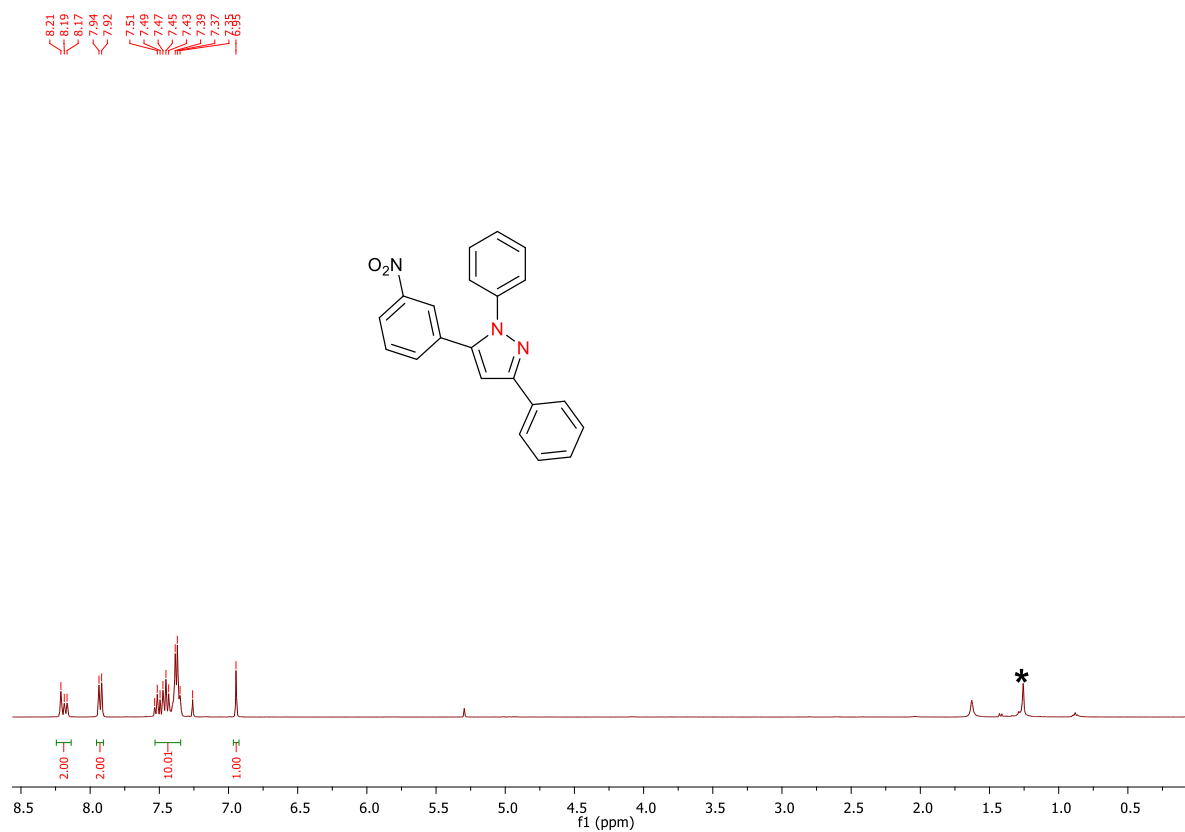


Figure S21. ^1H NMR spectrum of **7i** (400 MHz in CDCl_3). (*hexane)

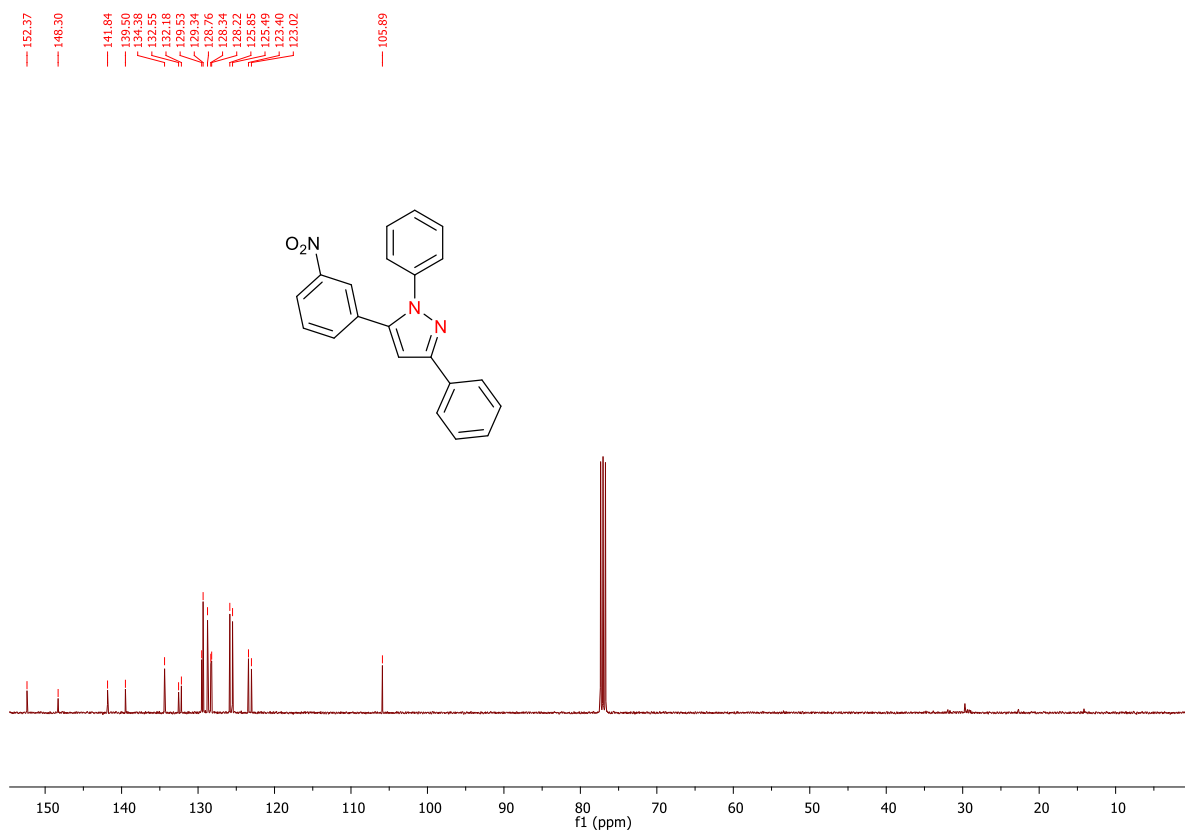


Figure S22. ^{13}C NMR spectrum of **7i** (100 MHz in CDCl_3).

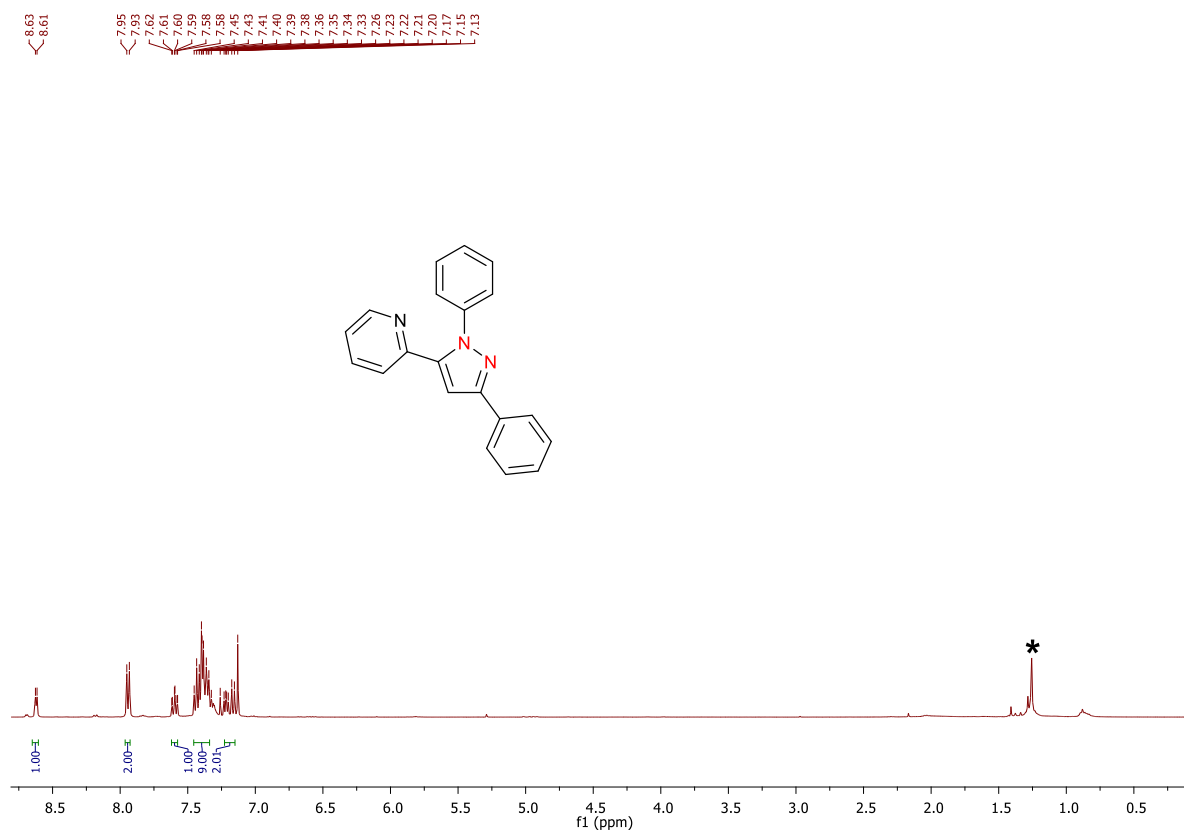


Figure S23. ¹H NMR spectrum of **7j** (400 MHz in CDCl₃). (*hexane)

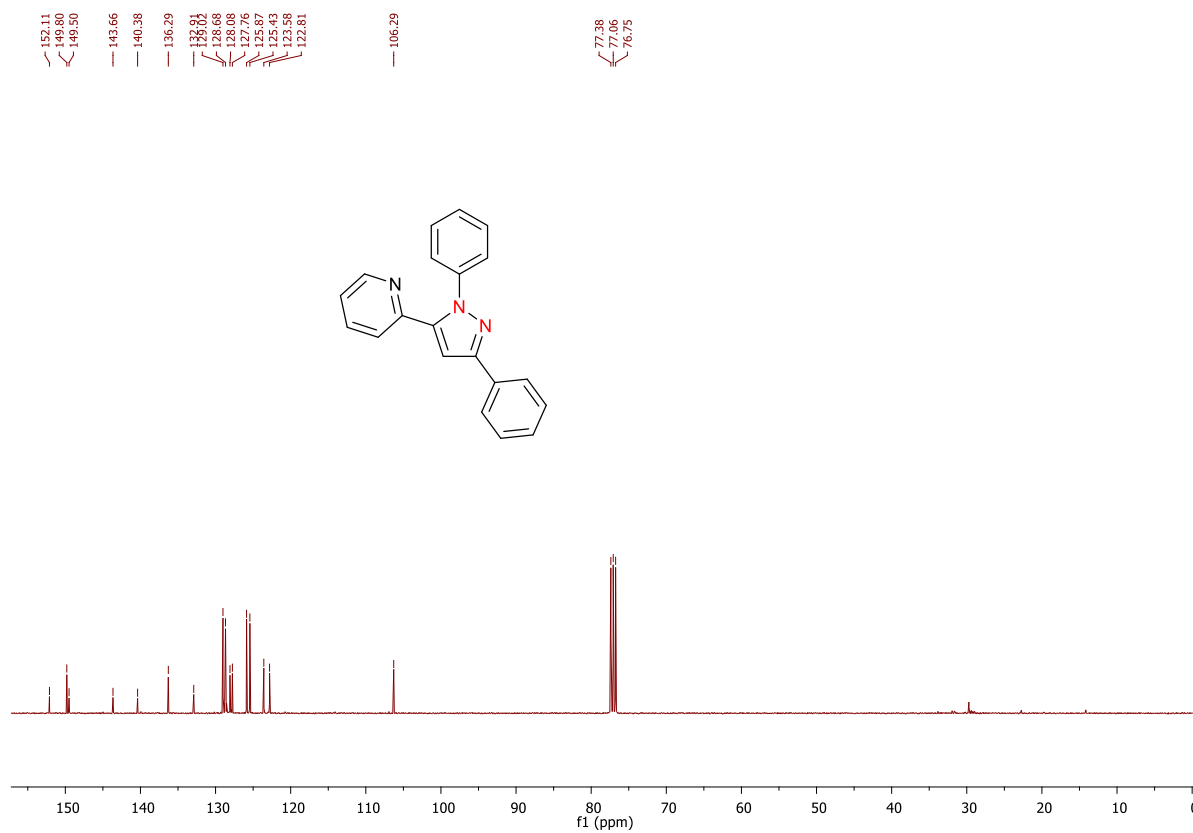


Figure S24. ¹³C NMR spectrum of **7j** (100 MHz in CDCl₃).

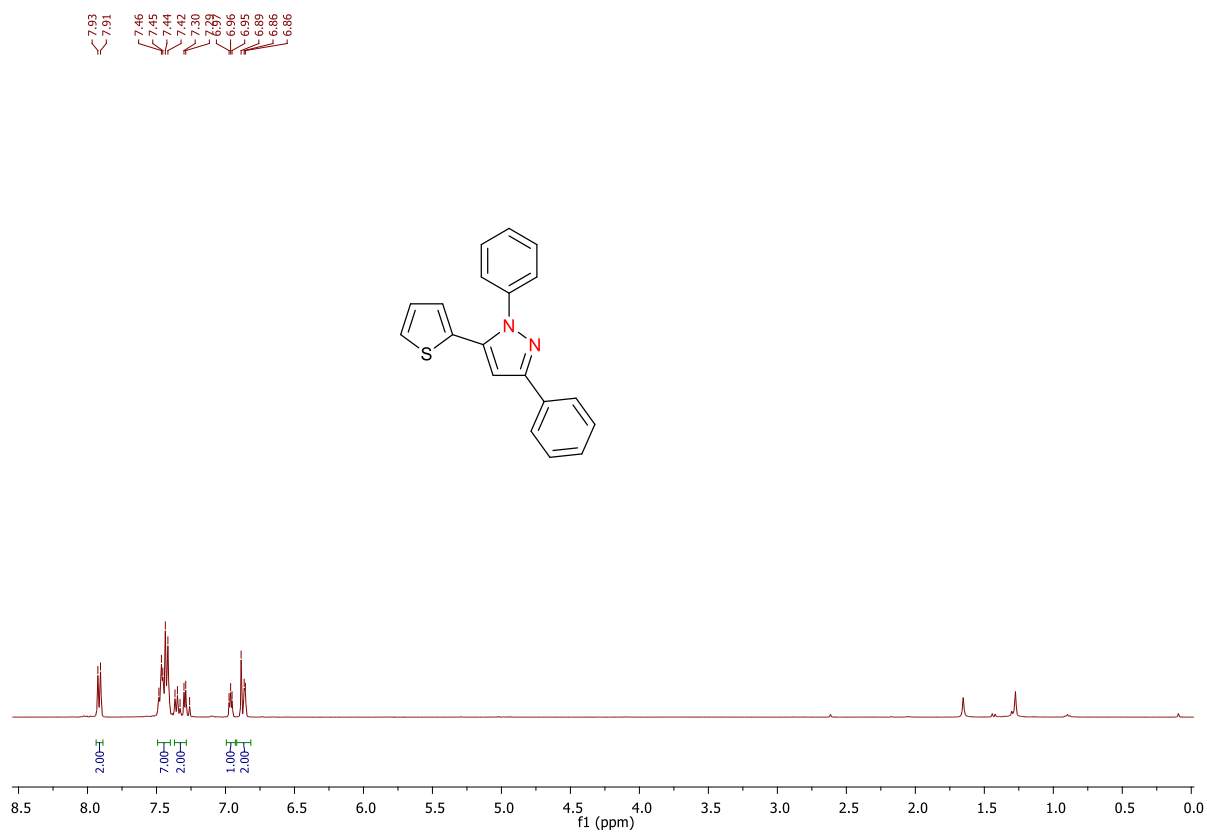


Figure S25. ¹H NMR spectrum of **7k** (400 MHz in CDCl₃).

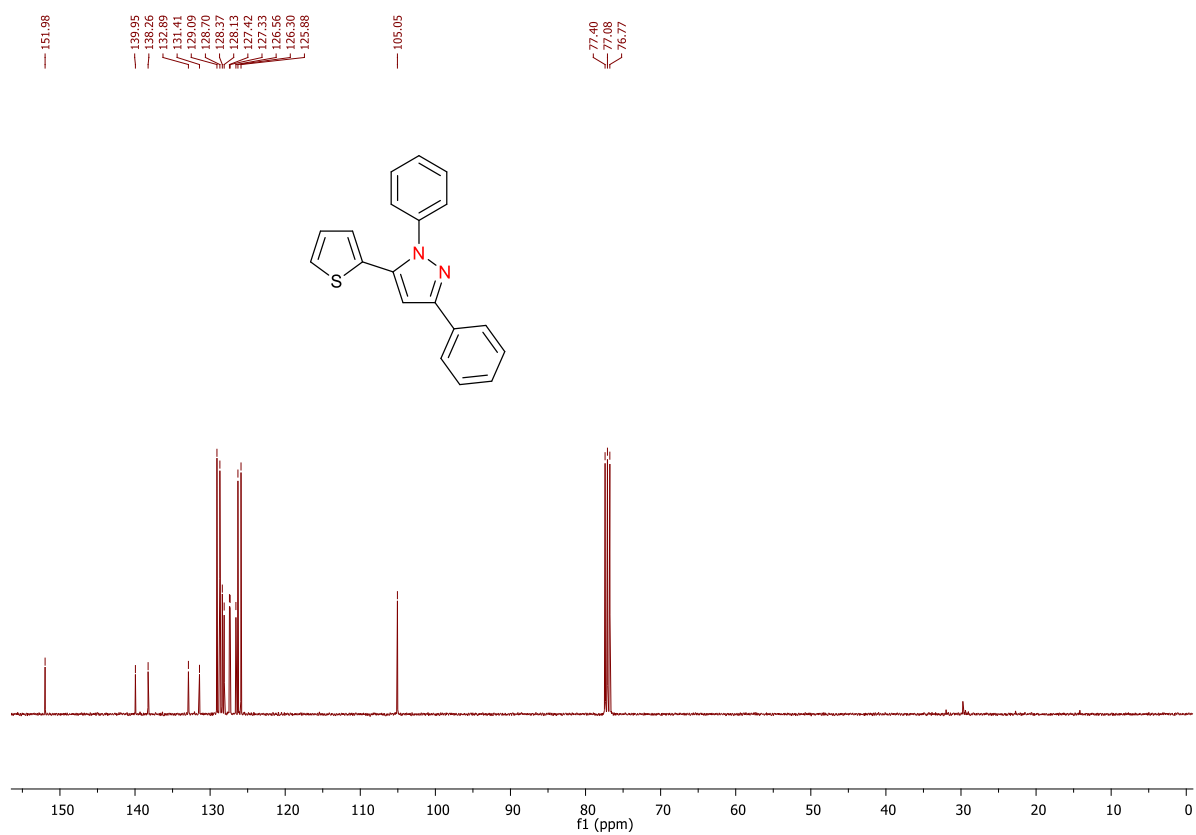


Figure S26. ¹³C NMR spectrum of **7k** (100 MHz in CDCl₃).

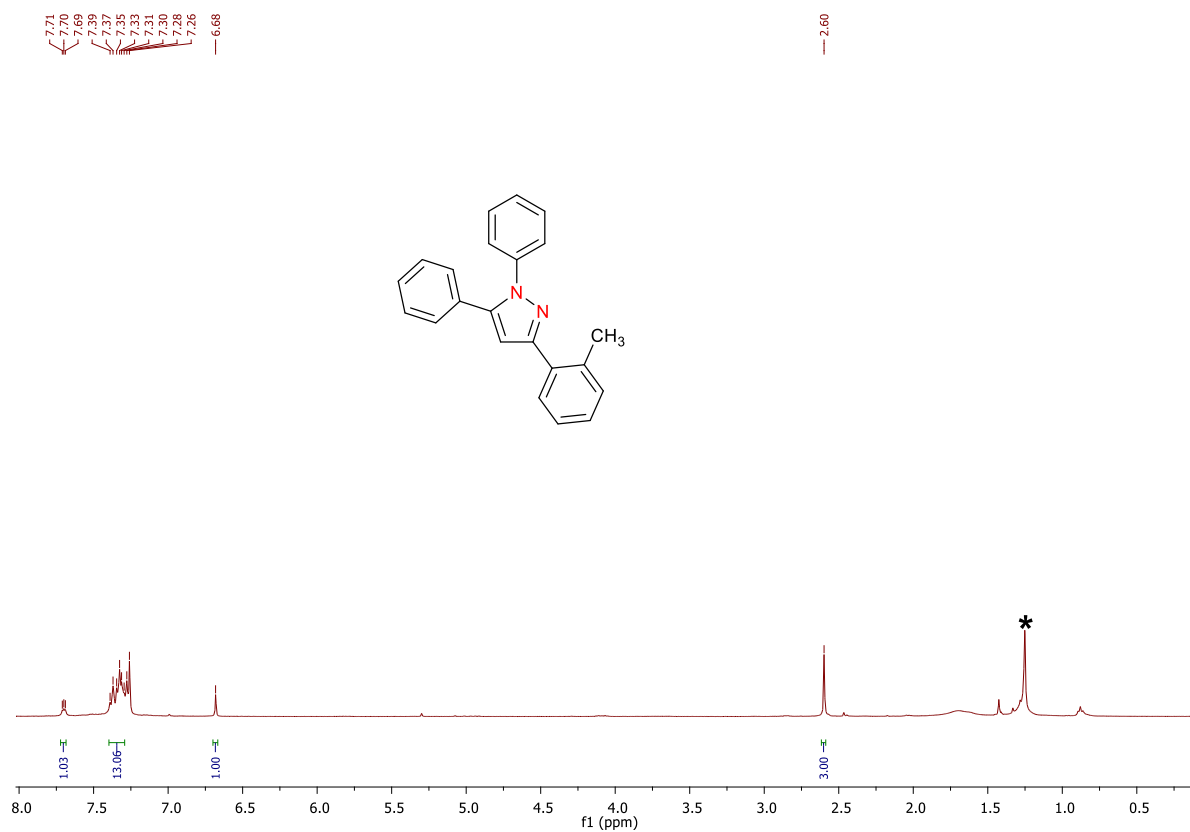


Figure S27. ¹H NMR spectrum of **8a** (400 MHz in CDCl₃). (*hexane)

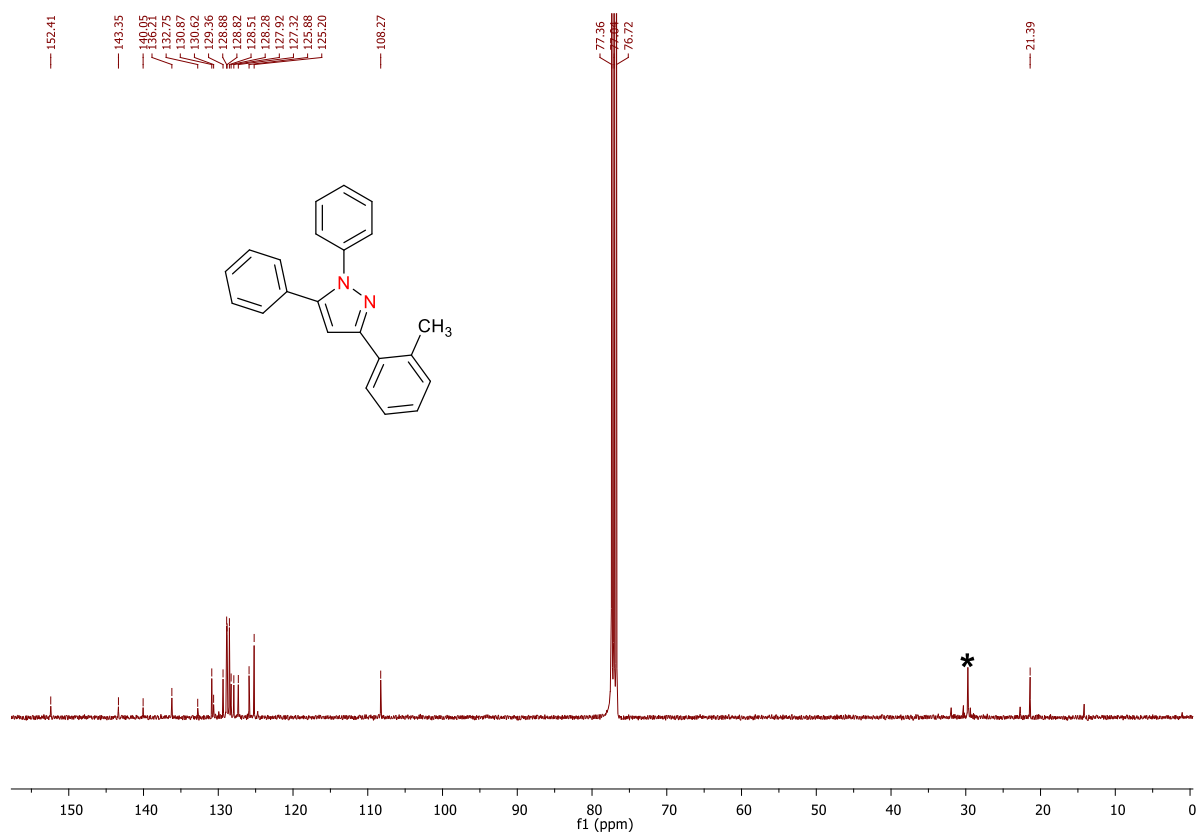


Figure S28. ¹³C NMR spectrum of **8a** (100 MHz in CDCl₃). (*hexane)

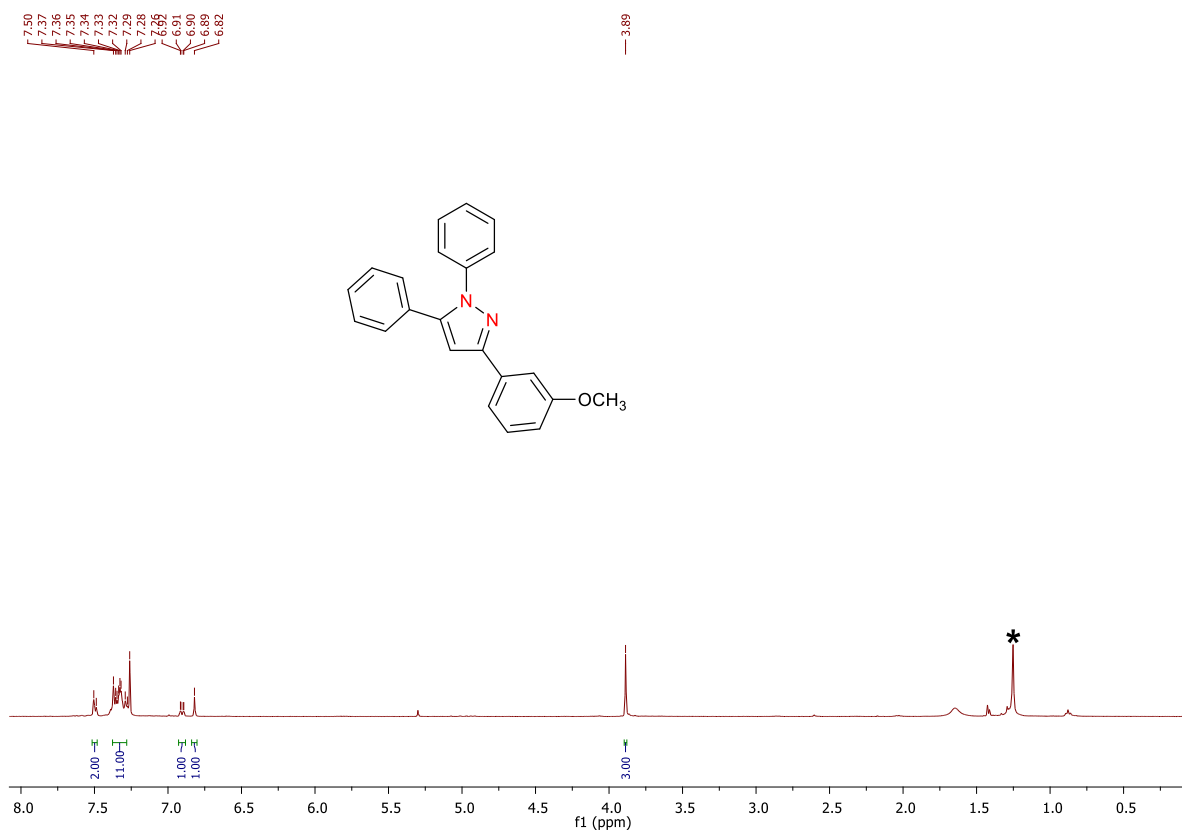


Figure S29. ¹H NMR spectrum of **8b** (400 MHz in CDCl₃). (*hexane)

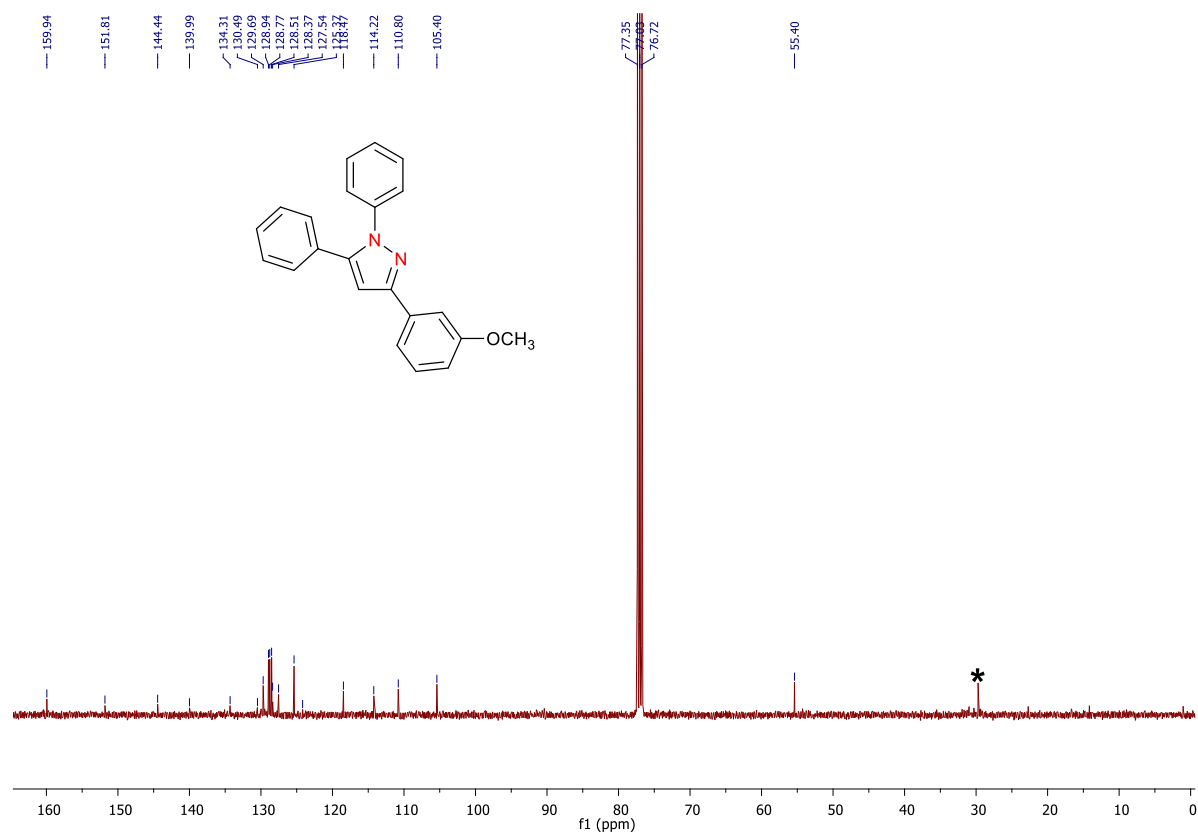


Figure S30. ¹³C NMR spectrum of **8b** (100 MHz in CDCl₃). (*hexane)

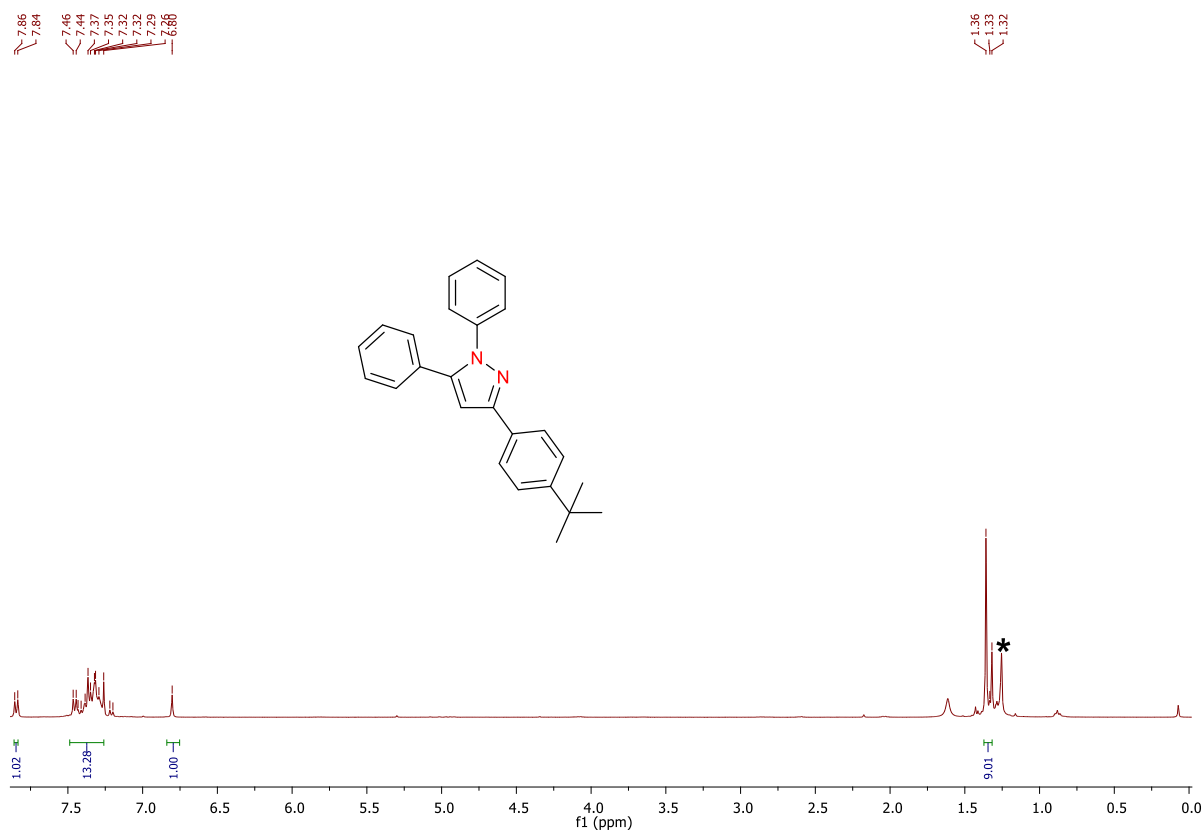


Figure S31. ¹H NMR spectrum of **8c** (400 MHz in CDCl₃). (*hexane)

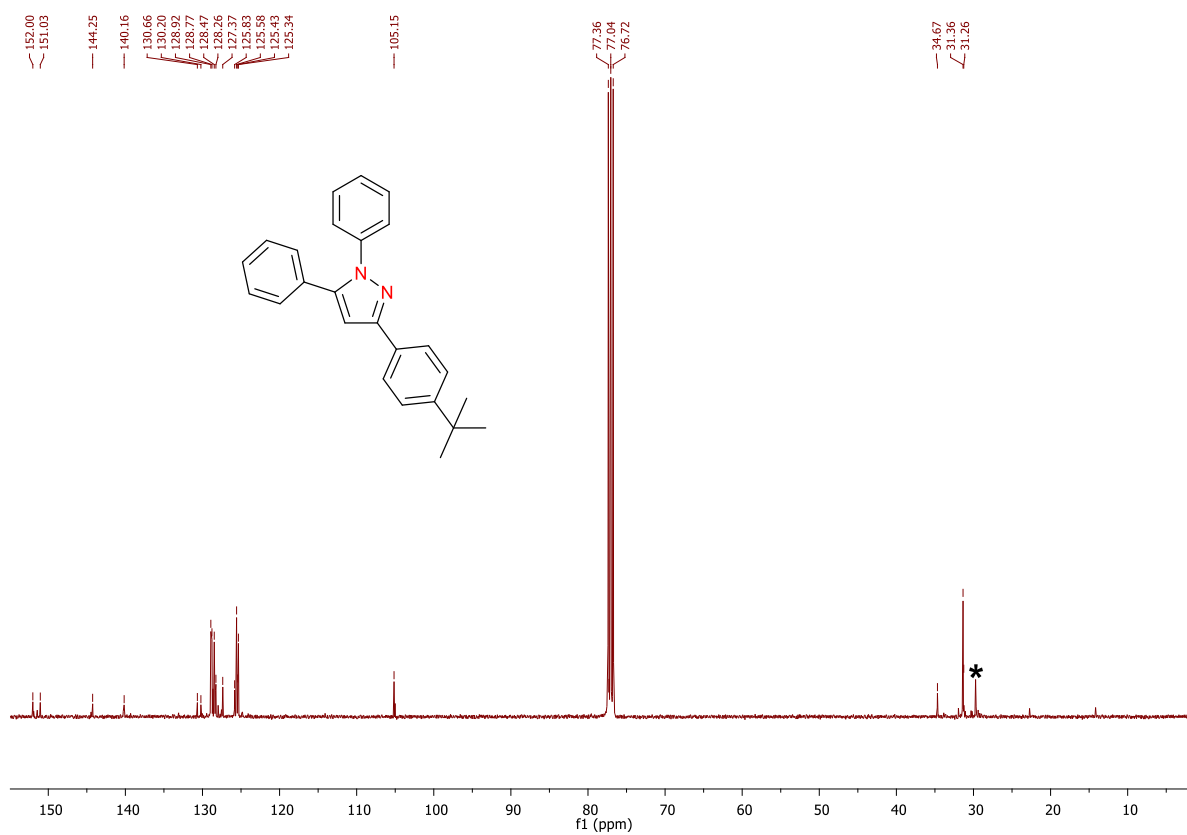


Figure S32. ¹³C NMR spectrum of **8c** (100 MHz in CDCl₃). (*hexane)

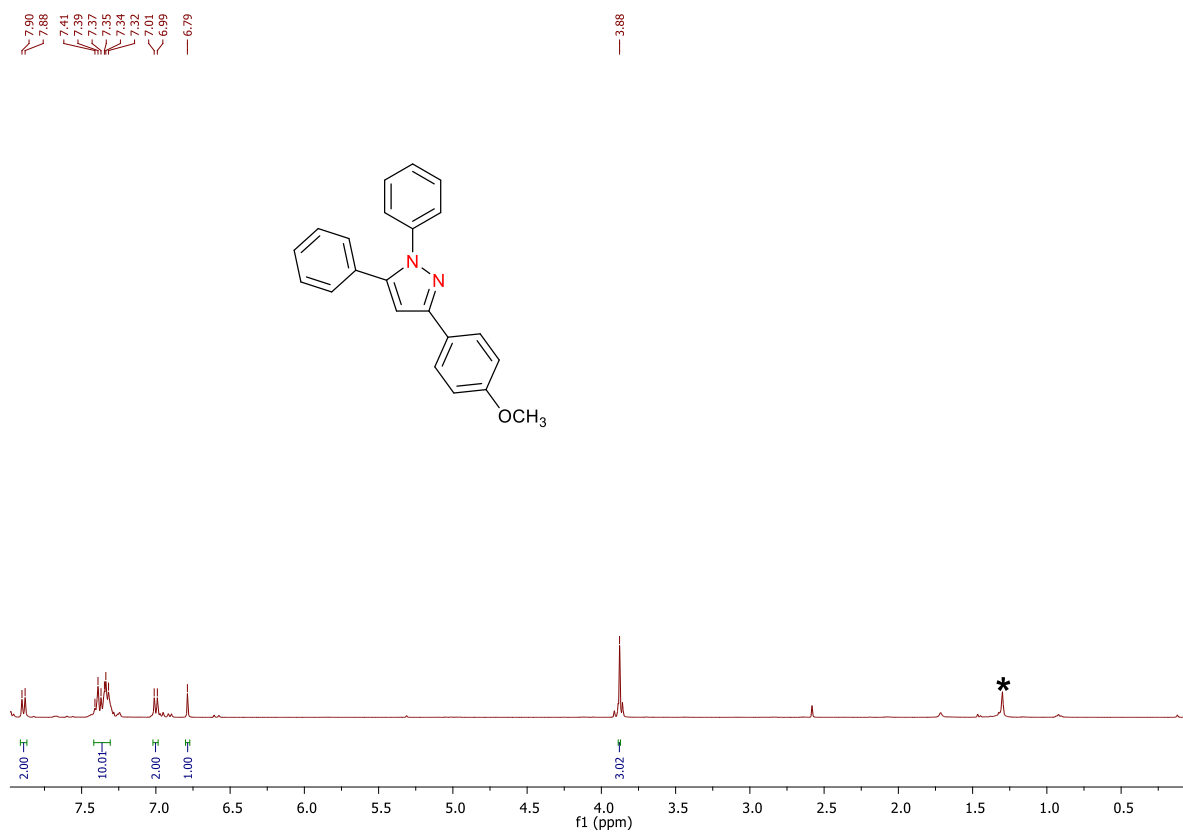


Figure S33. ¹H NMR spectrum of **8d** (400 MHz in CDCl₃). (*hexane)

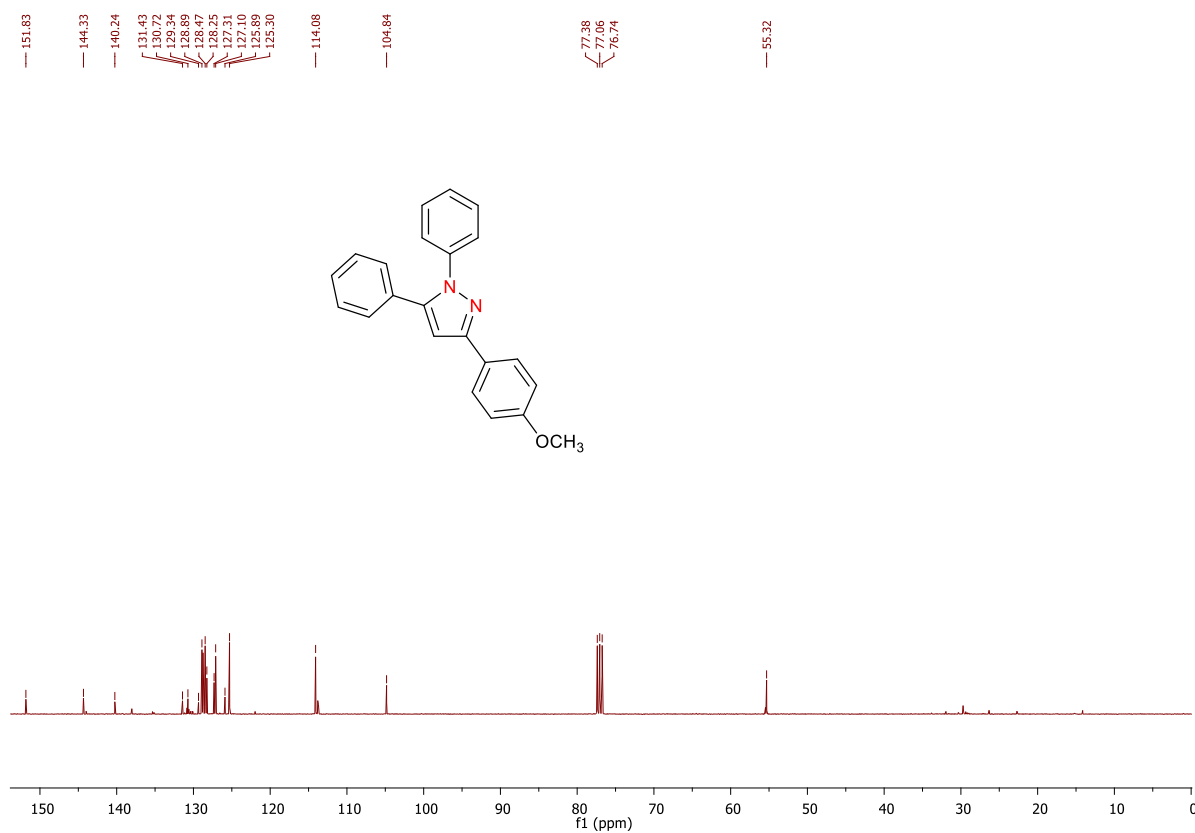


Figure S34. ¹³C NMR spectrum of **8d** (100 MHz in CDCl₃).

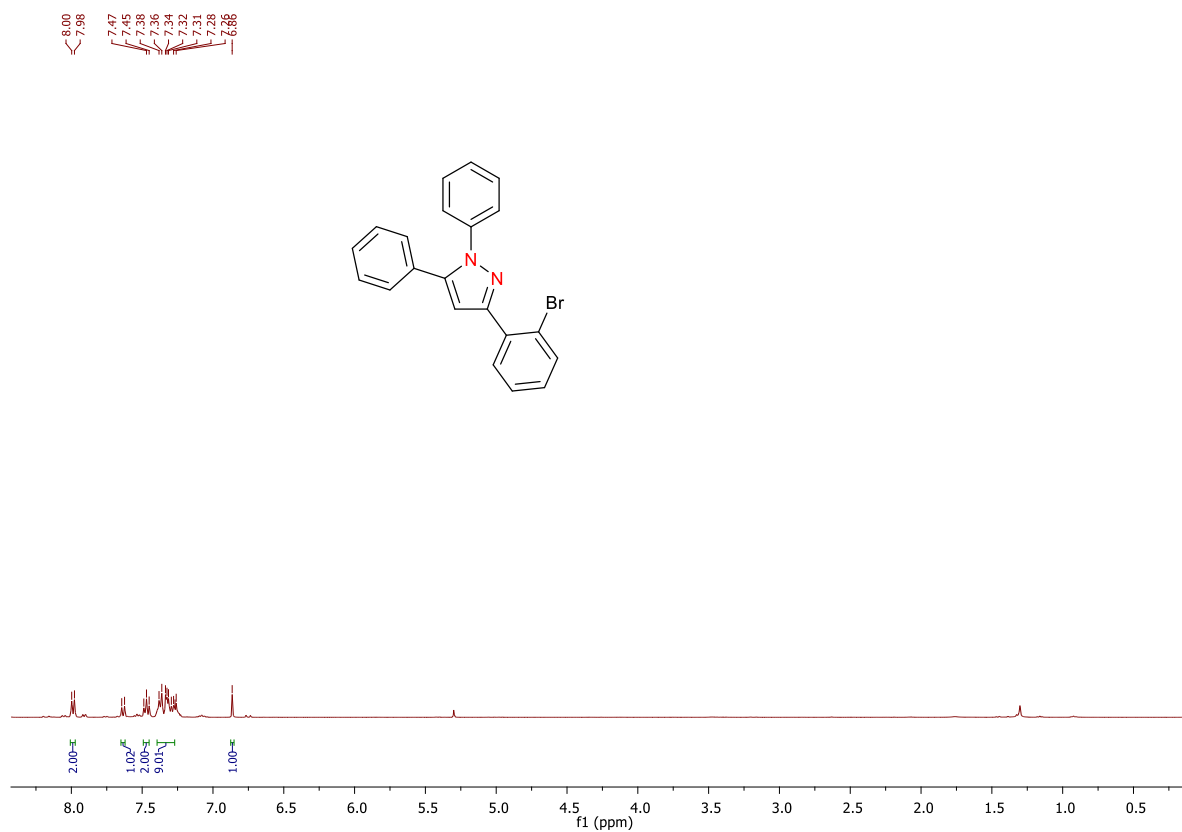


Figure S35. ¹H NMR spectrum of **8e** (400 MHz in CDCl₃).

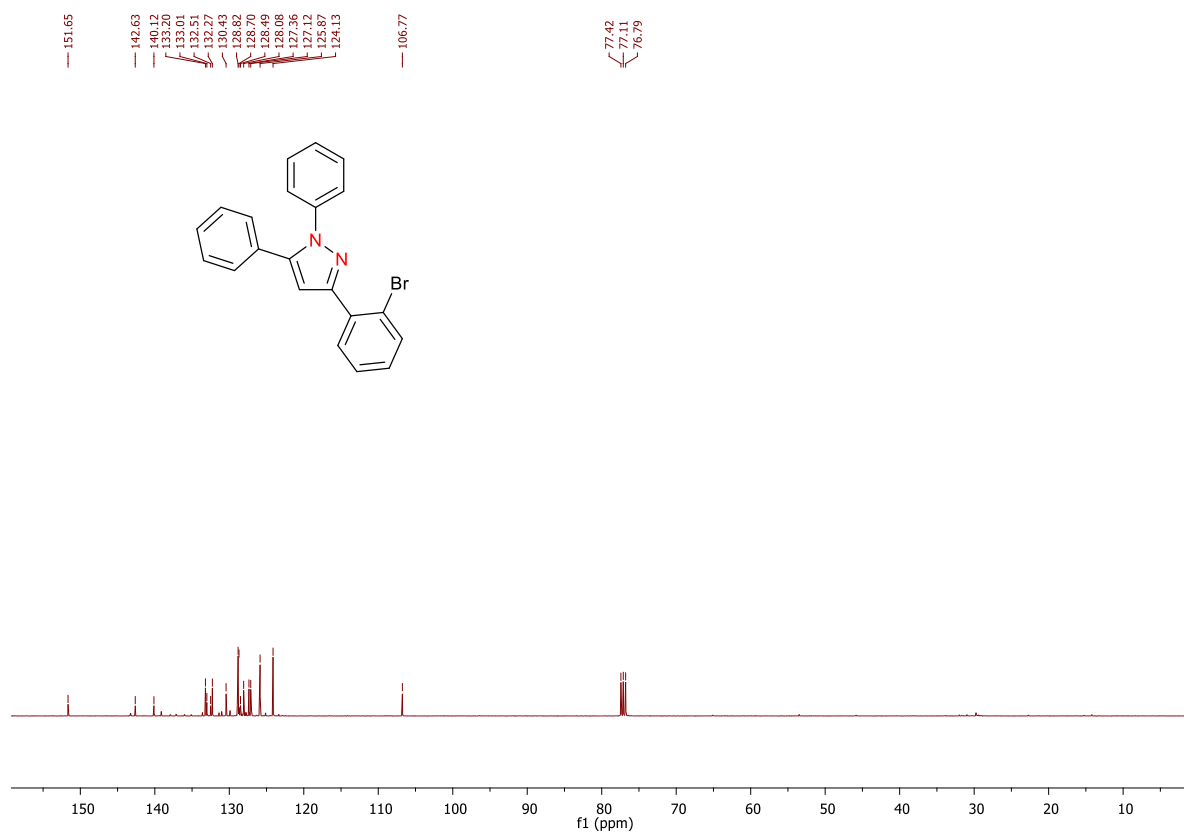


Figure S36. ¹³C NMR spectrum of **8e** (100 MHz in CDCl₃).

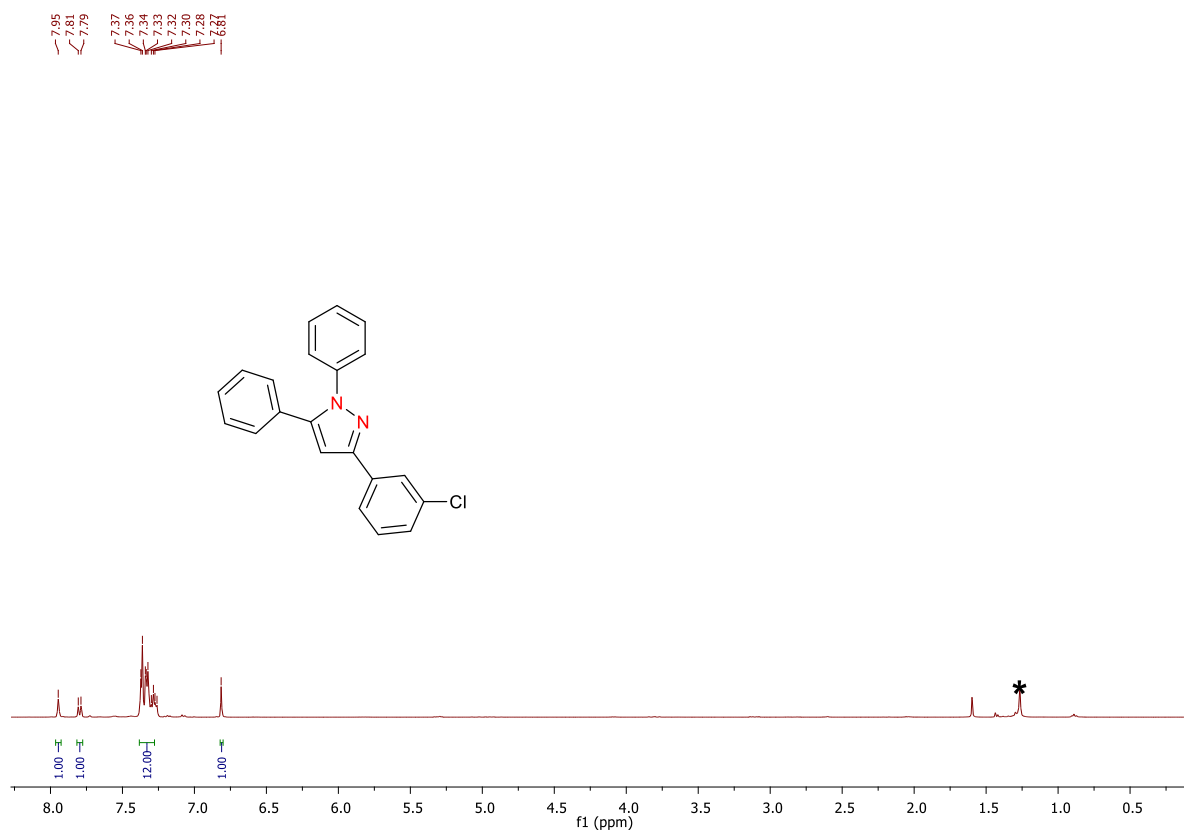


Figure S37. ¹H NMR spectrum of **8f** (400 MHz in CDCl₃). (*hexane)

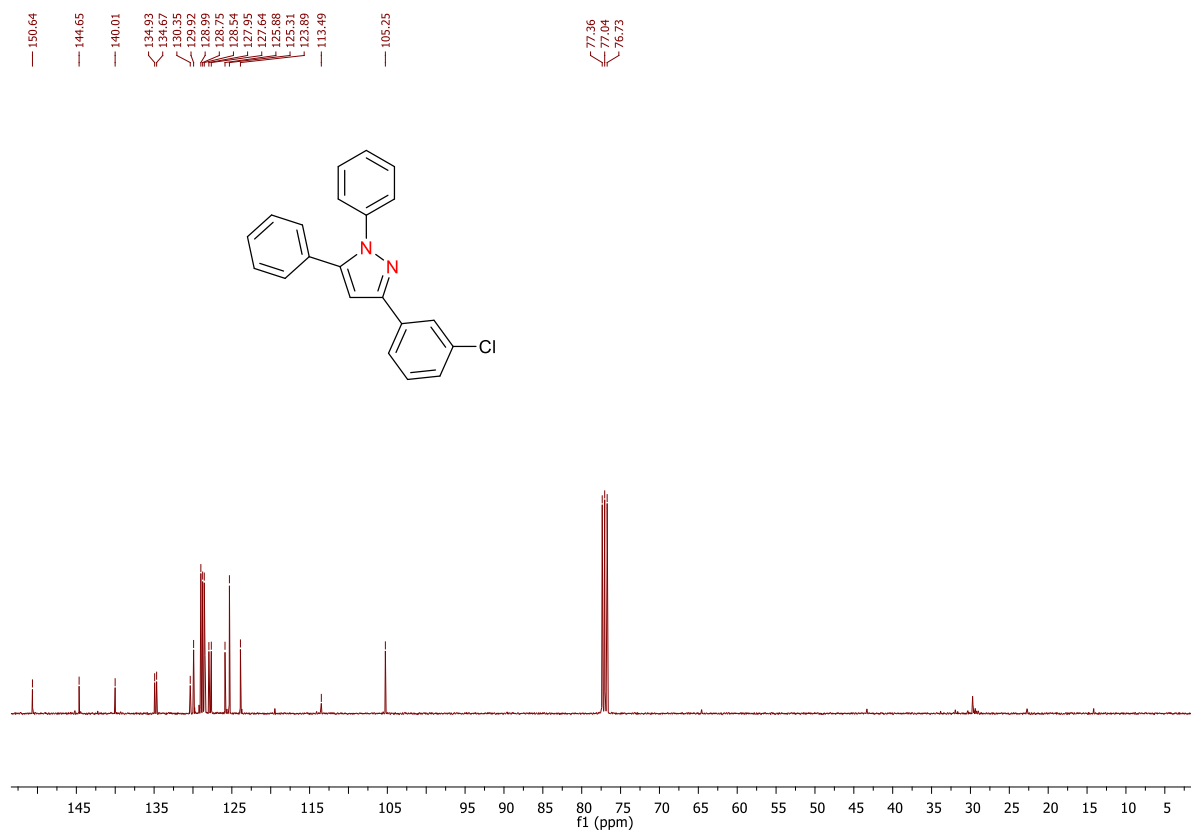


Figure S38. ¹³C NMR spectrum of **8f** (100 MHz in CDCl₃).

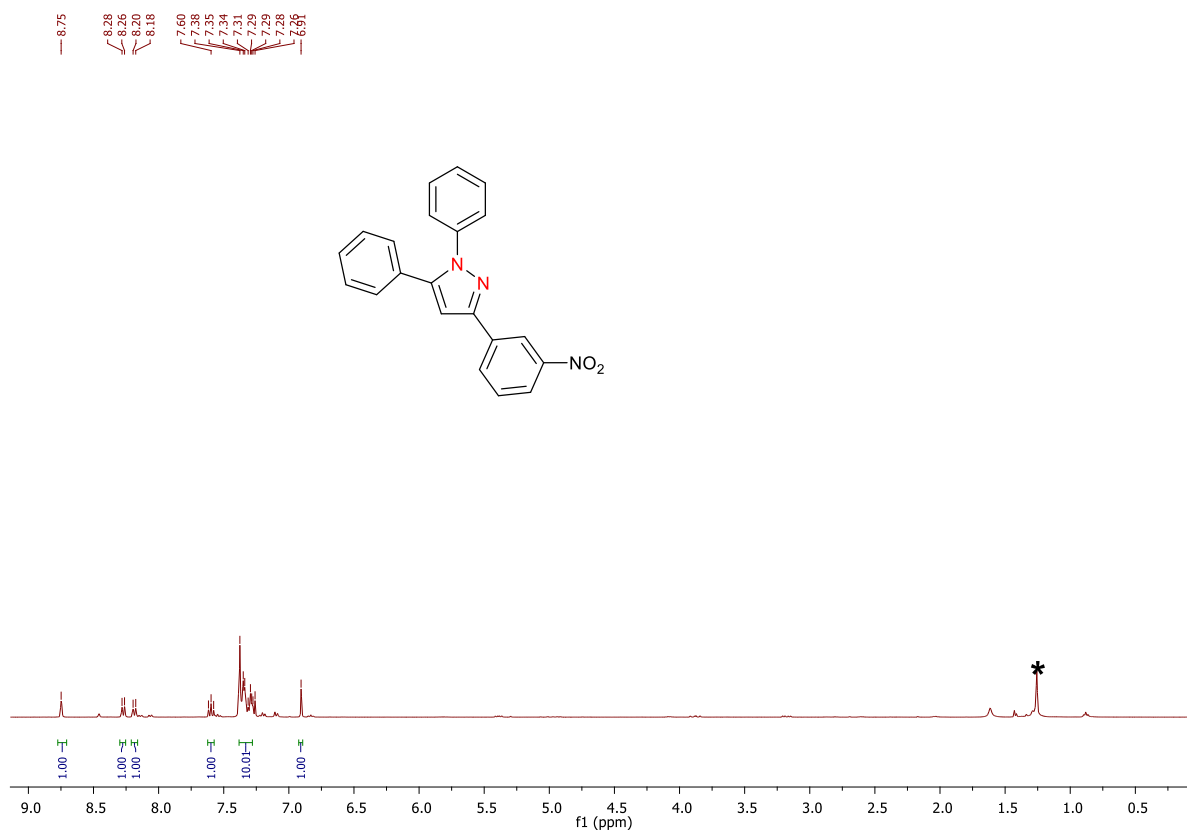


Figure S39. ¹H NMR spectrum of **8g** (400 MHz in CDCl₃). (*hexane)

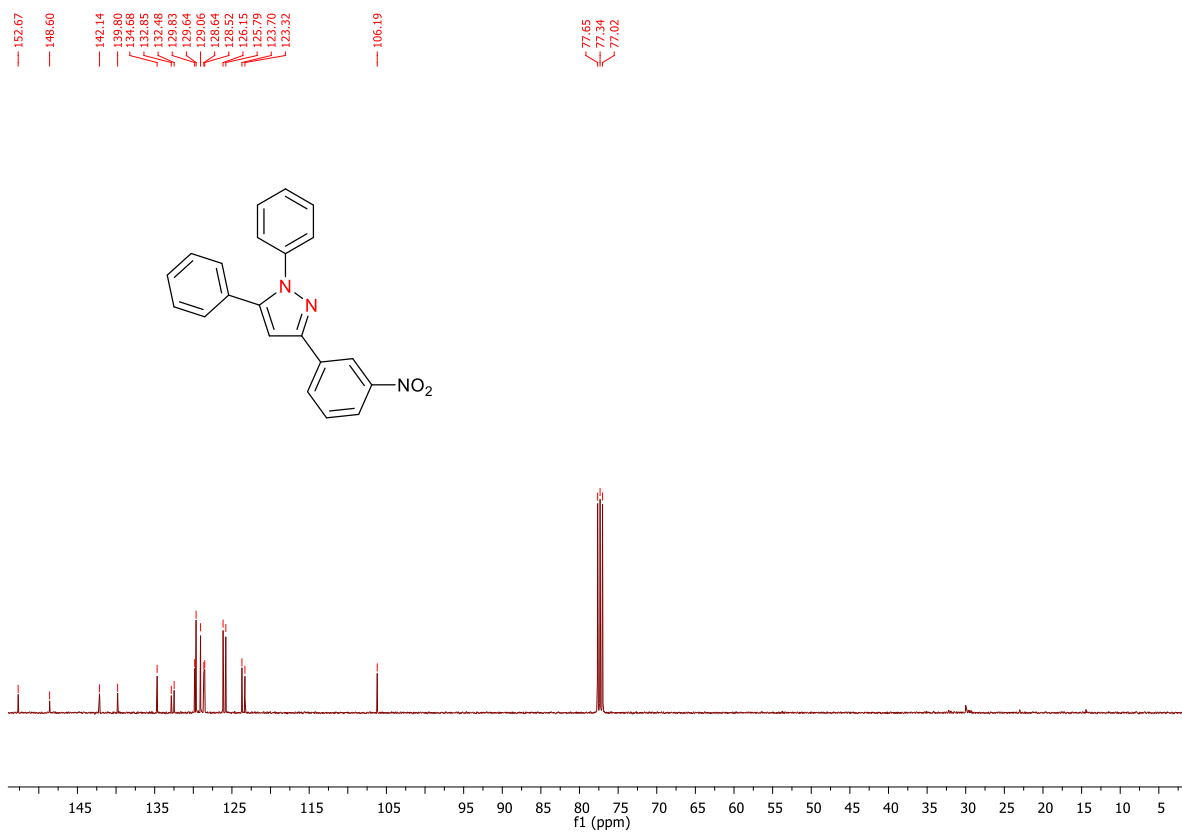


Figure S40. ¹³C NMR spectrum of **8g** (100 MHz in CDCl₃).

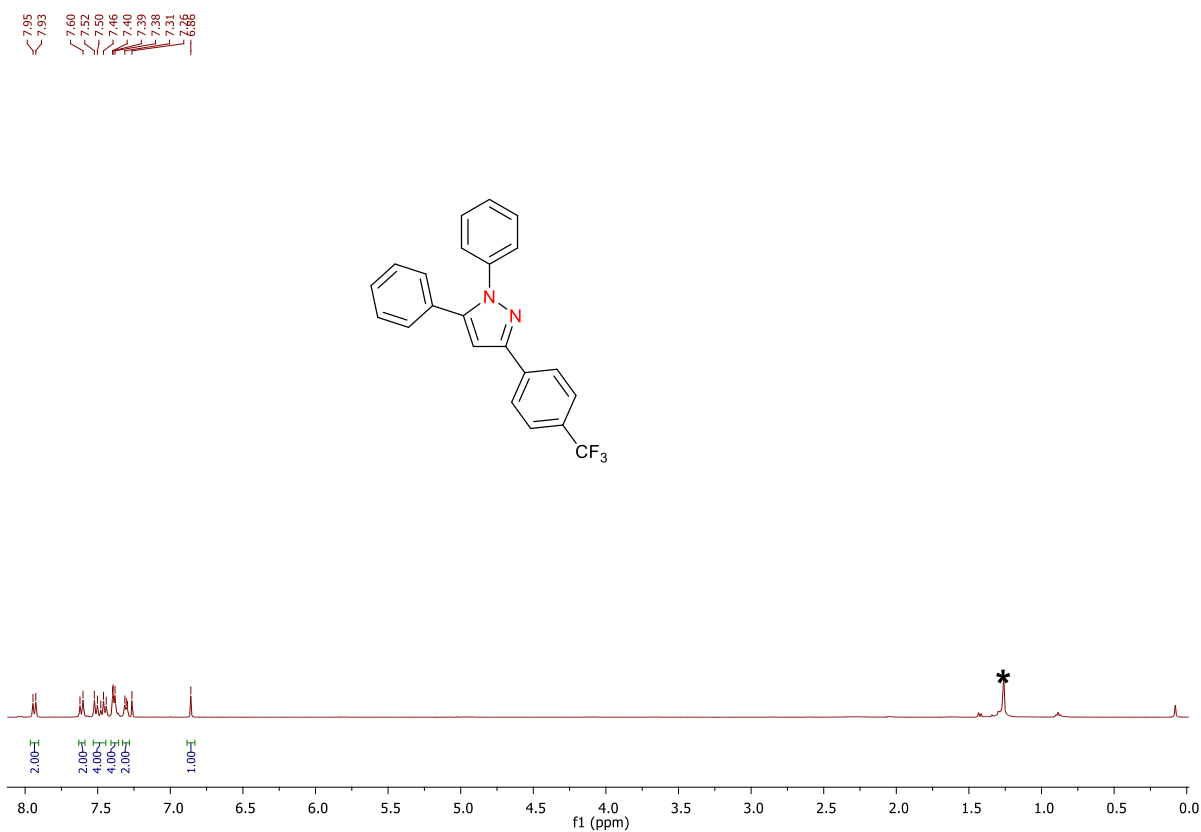


Figure S41. ¹H NMR spectrum of **8h** (400 MHz in CDCl₃). (*hexane)

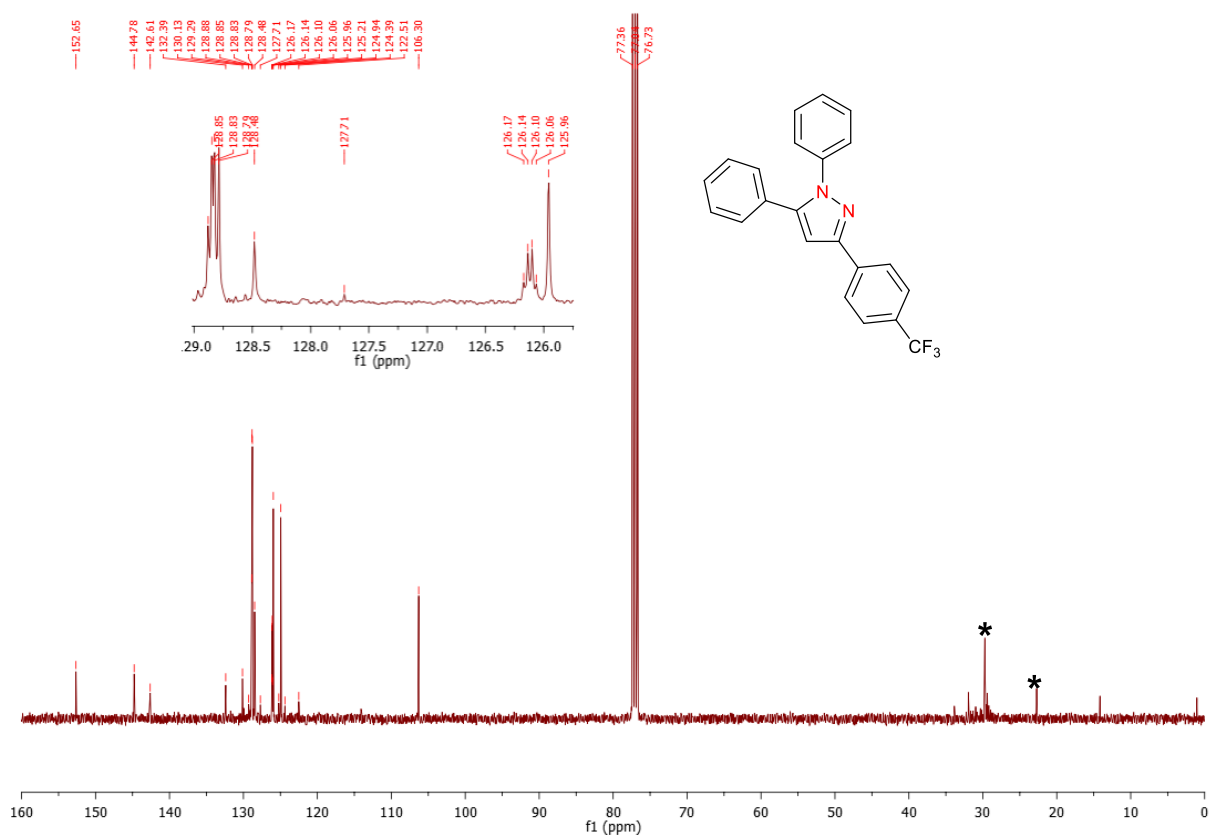


Figure S42. ¹³C NMR spectrum of **8h** (100 MHz in CDCl₃). (*hexane)

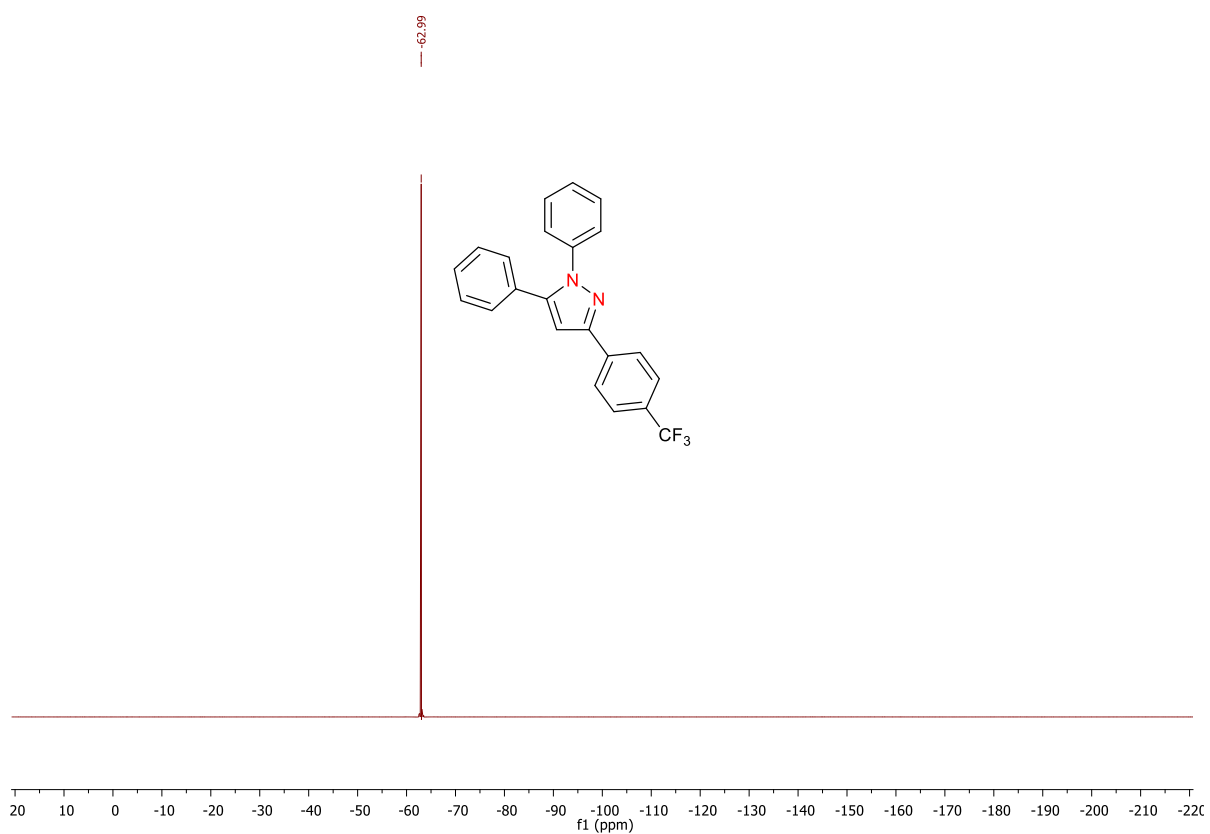


Figure S43. ^{19}F NMR spectrum of **8h** (376 MHz in CDCl_3).

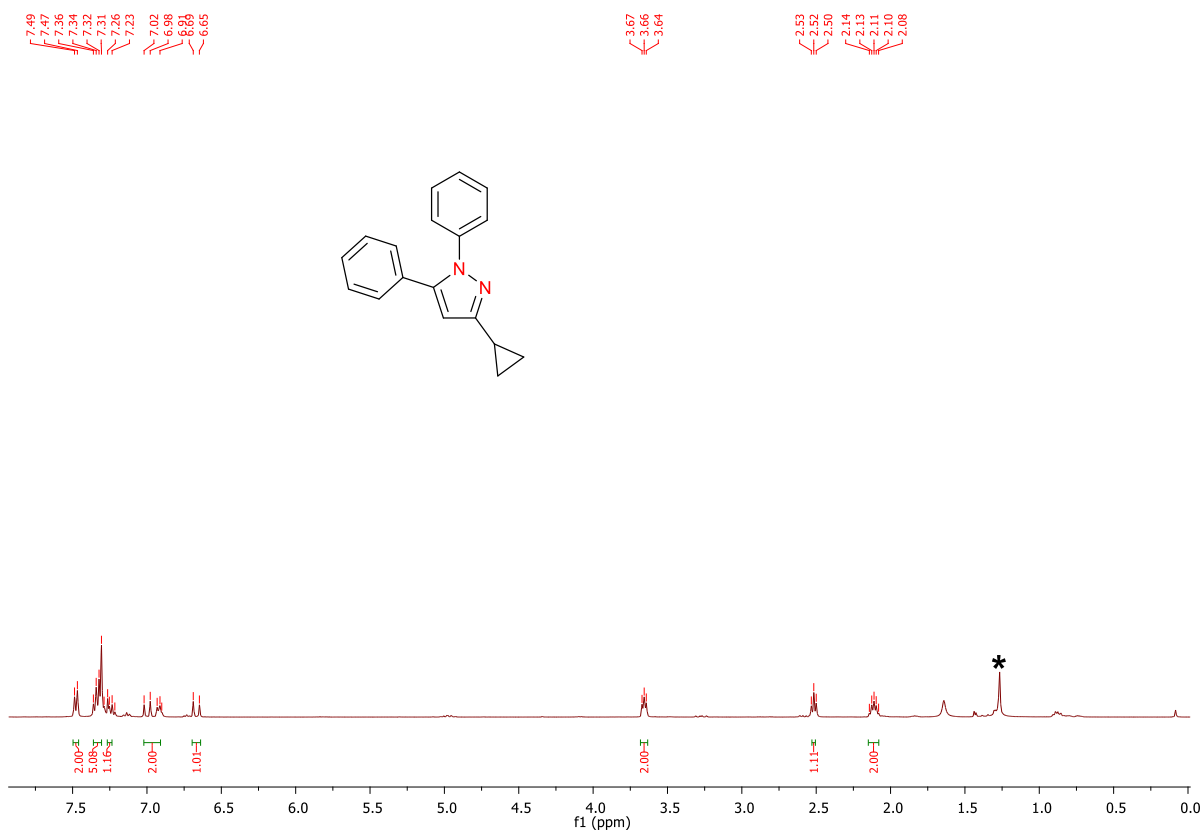


Figure S44. ¹H NMR spectrum of **8i** (400 MHz in CDCl₃). (*hexane)

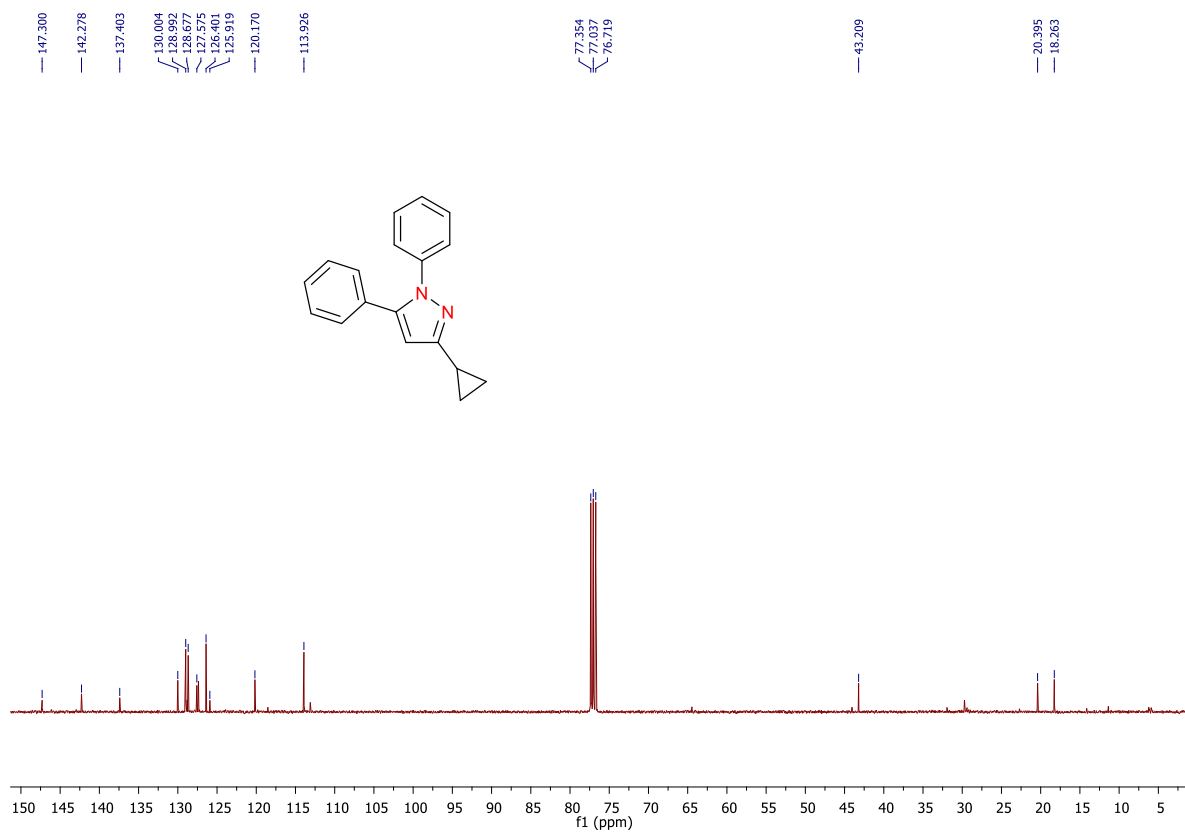


Figure S45. ¹³C NMR spectrum of **8i** (100 MHz in CDCl₃).

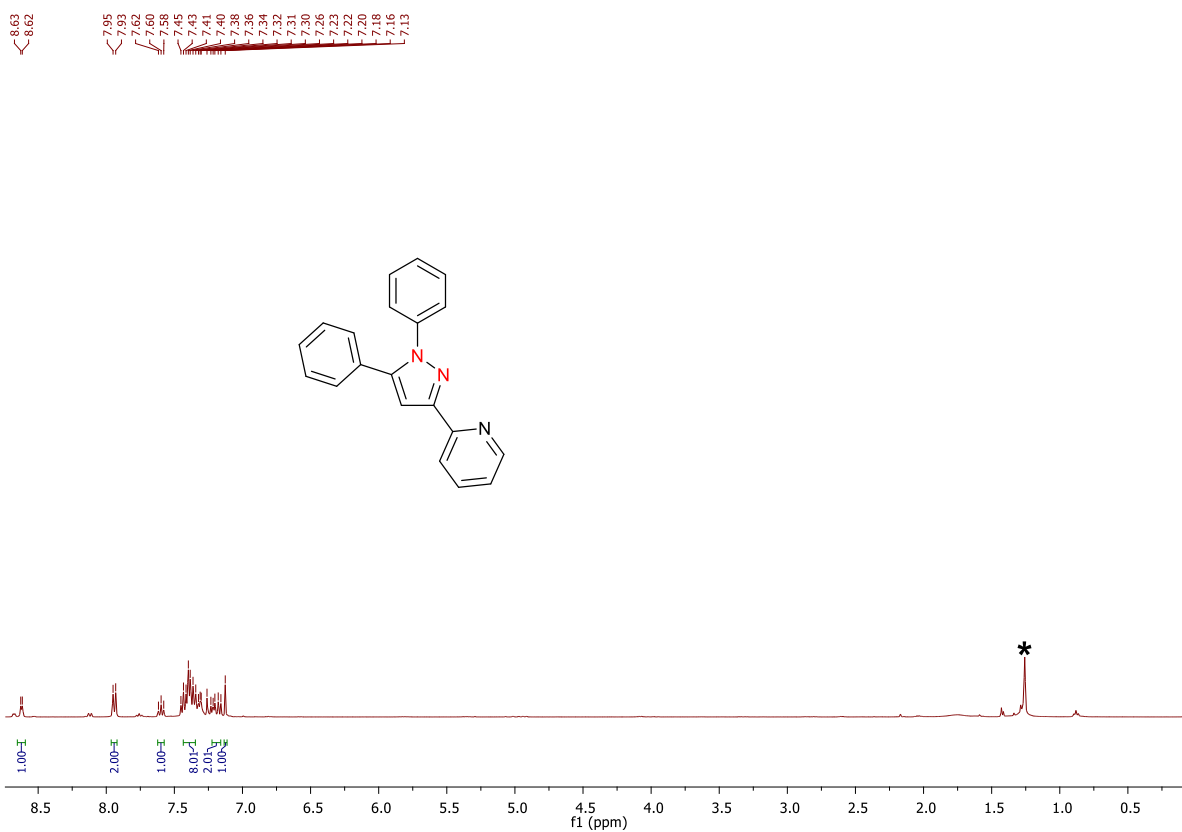


Figure S46. ¹H NMR spectrum of **8j** (400 MHz in CDCl₃). (*hexane)

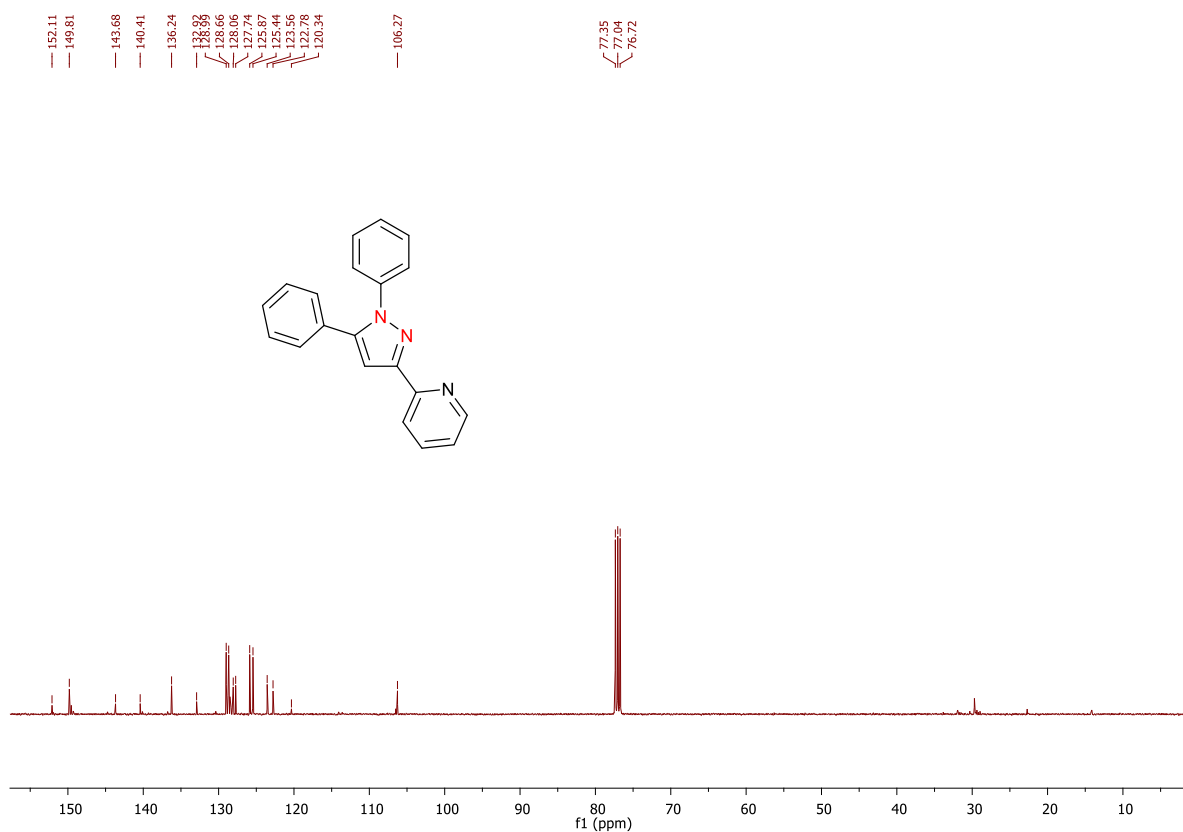


Figure S47. ¹³C NMR spectrum of **8j** (100 MHz in CDCl₃).

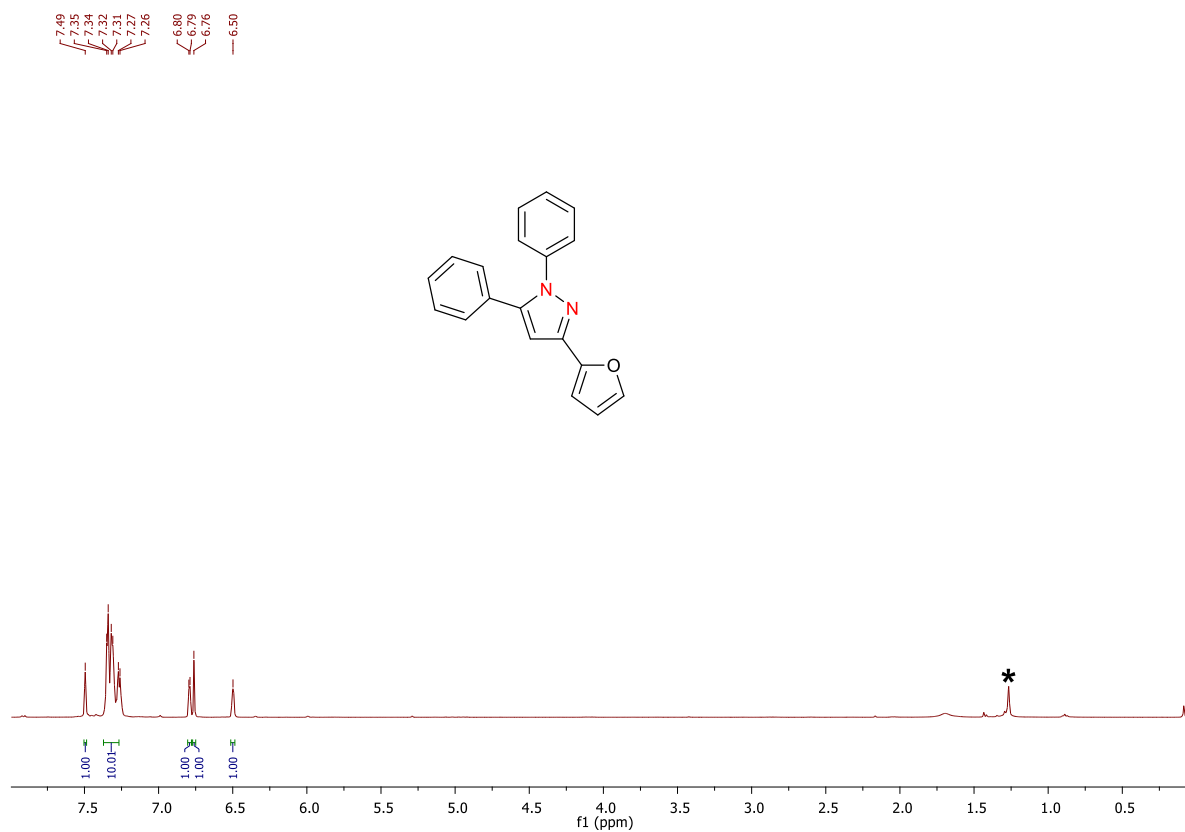


Figure S48. ^1H NMR spectrum of **8k** (400 MHz in CDCl_3). (*hexane)

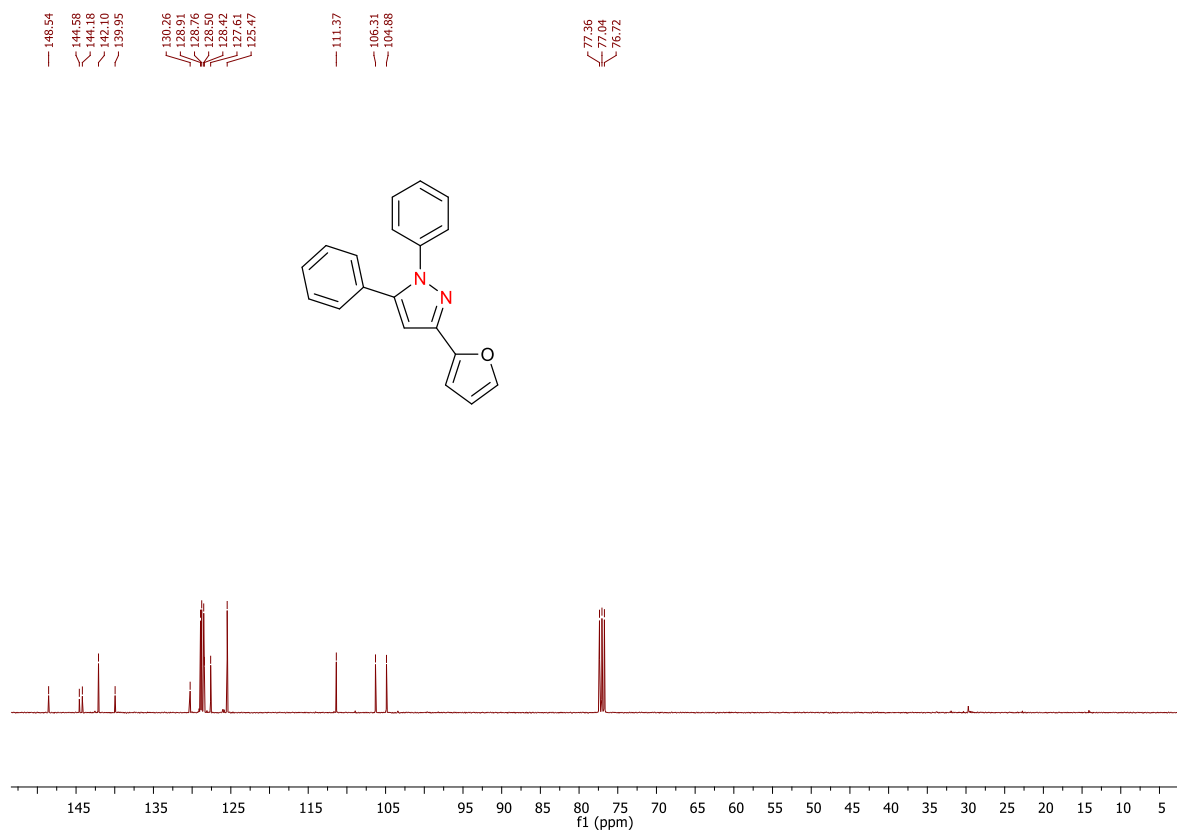


Figure S49. ^{13}C NMR spectrum of **8k** (100 MHz in CDCl_3).

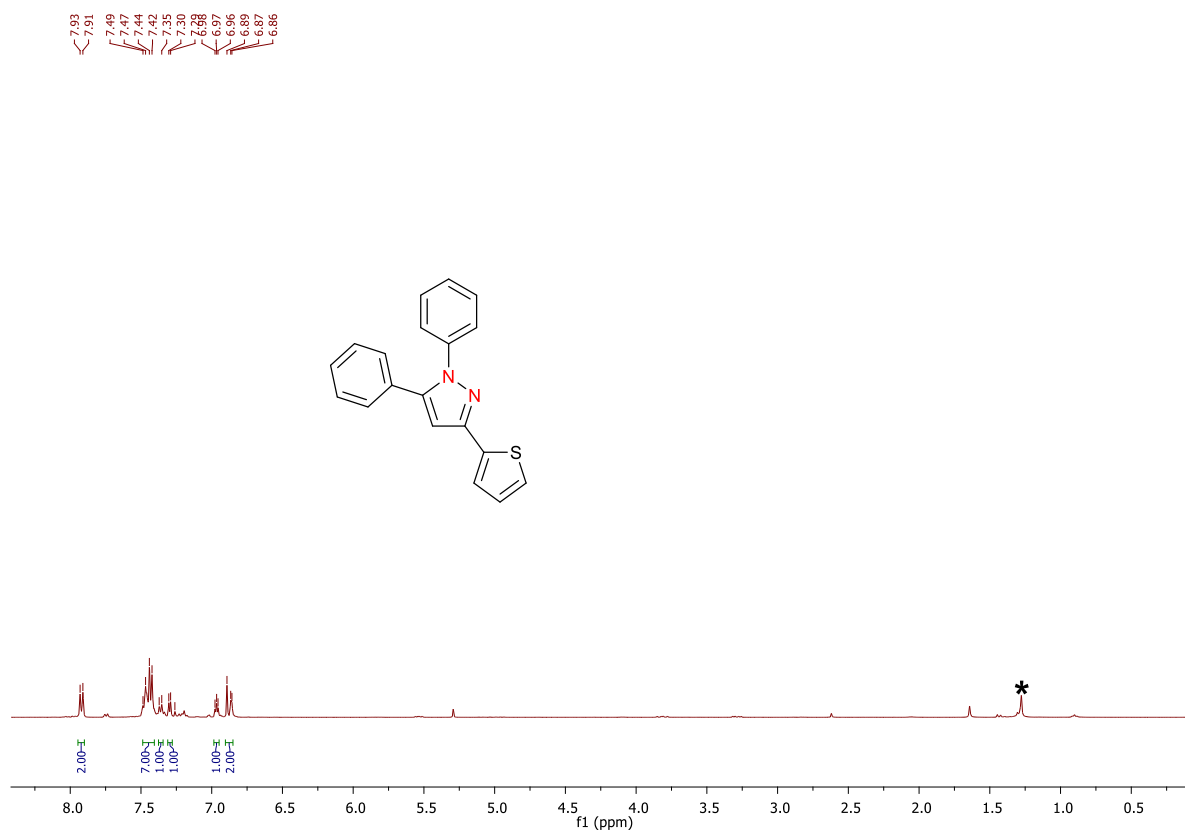


Figure S50. ^1H NMR spectrum of **8l** (400 MHz in CDCl_3). (*hexane)

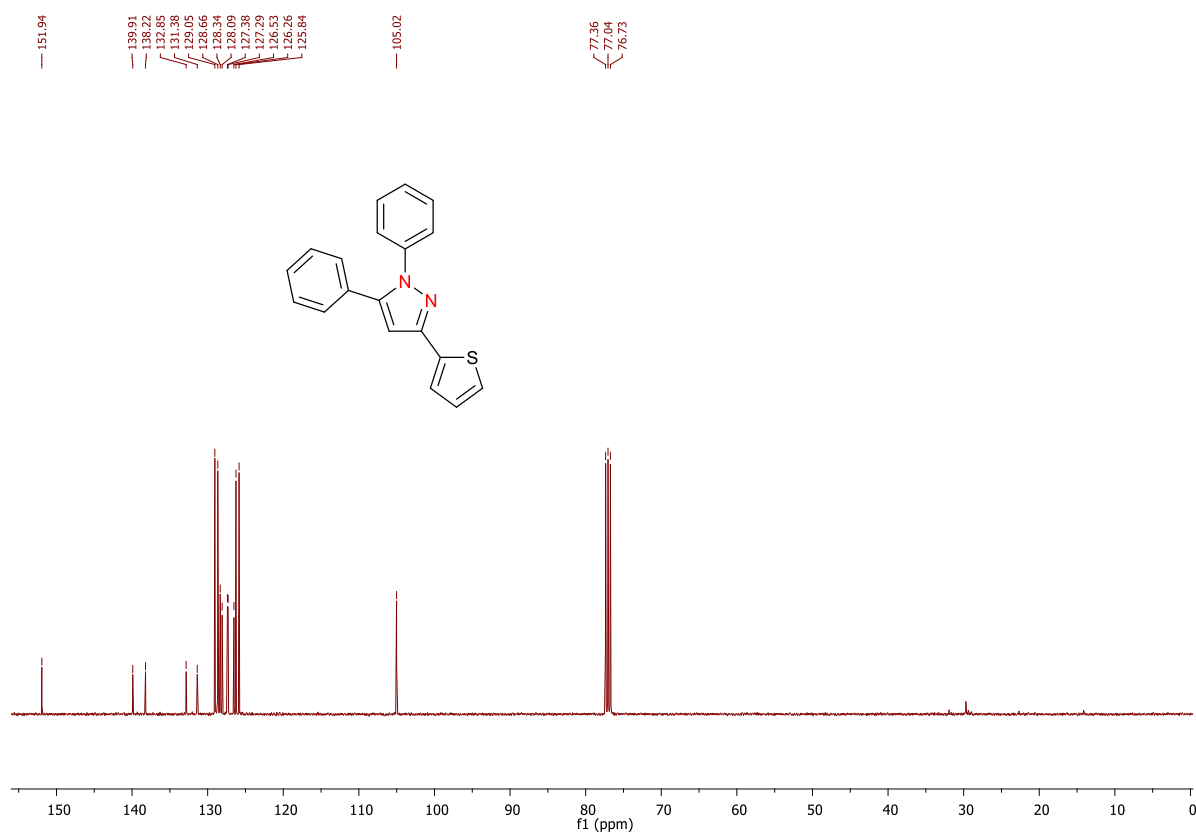


Figure S51. ^{13}C NMR spectrum of **8l** (100 MHz in CDCl_3).

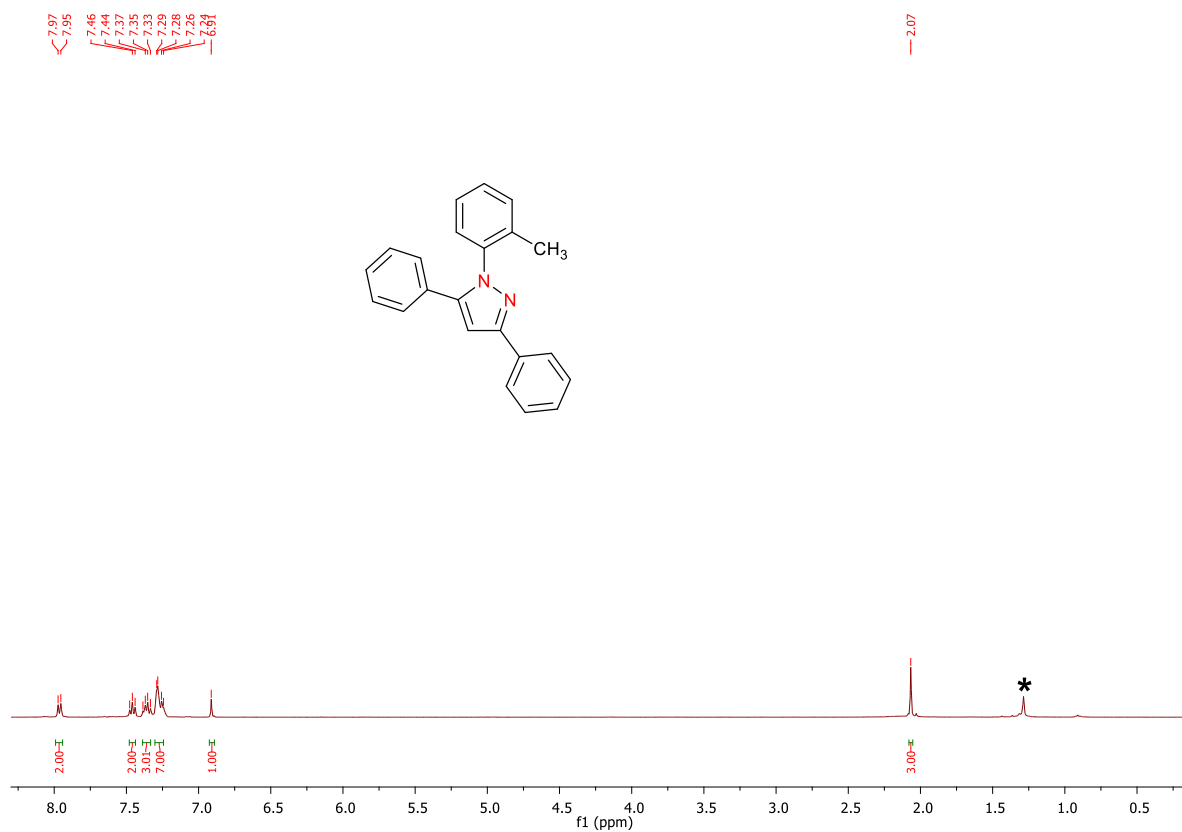


Figure S52. ¹H NMR spectrum of **9a** (400 MHz in CDCl₃). (* hexane)

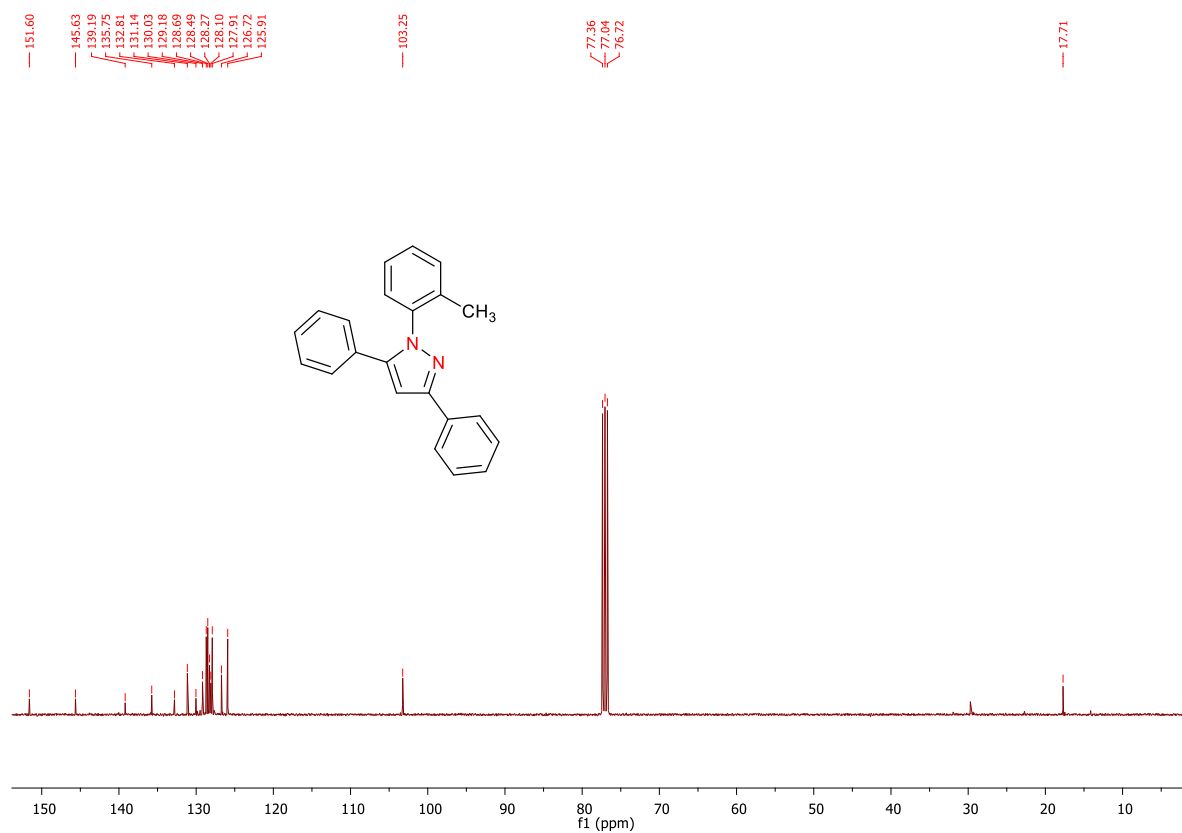


Figure S53. ¹³C NMR spectrum of **9a** (100 MHz in CDCl₃).

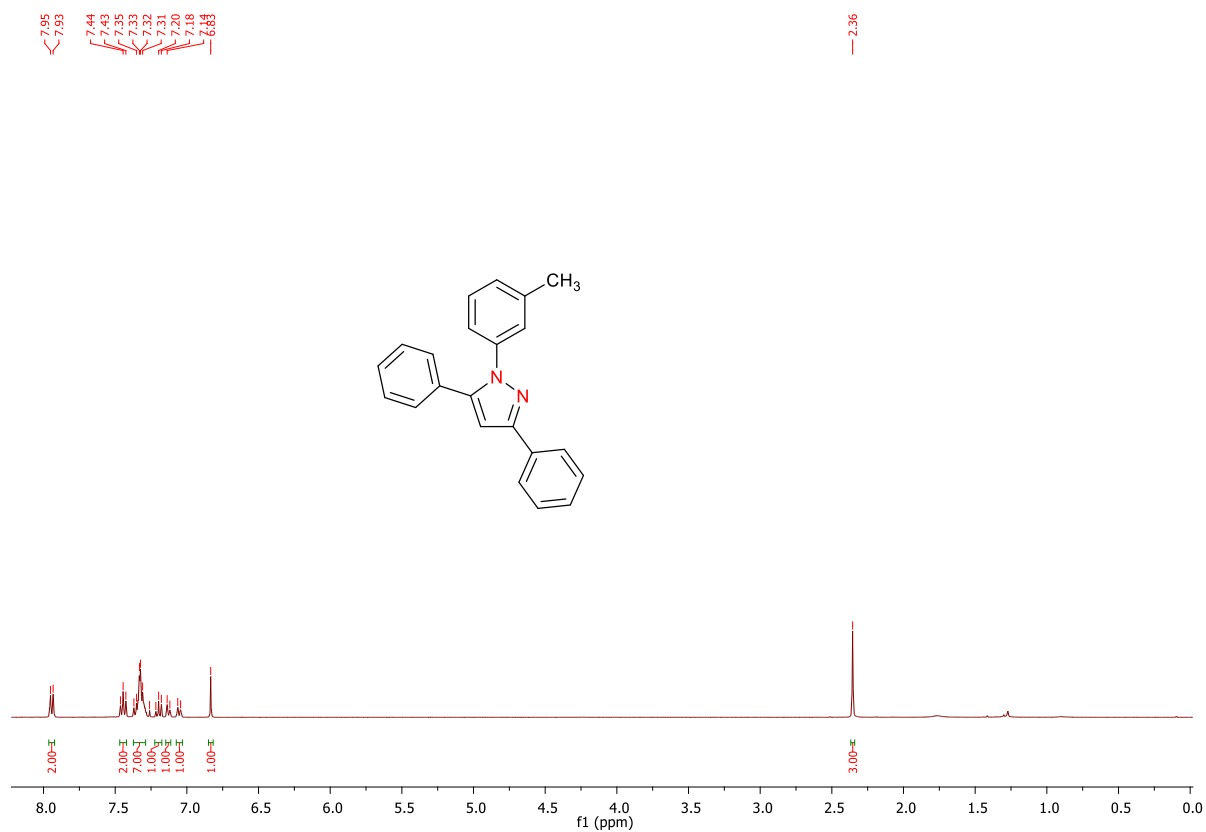


Figure S54. ¹H NMR spectrum of **9b** (400 MHz in CDCl₃).

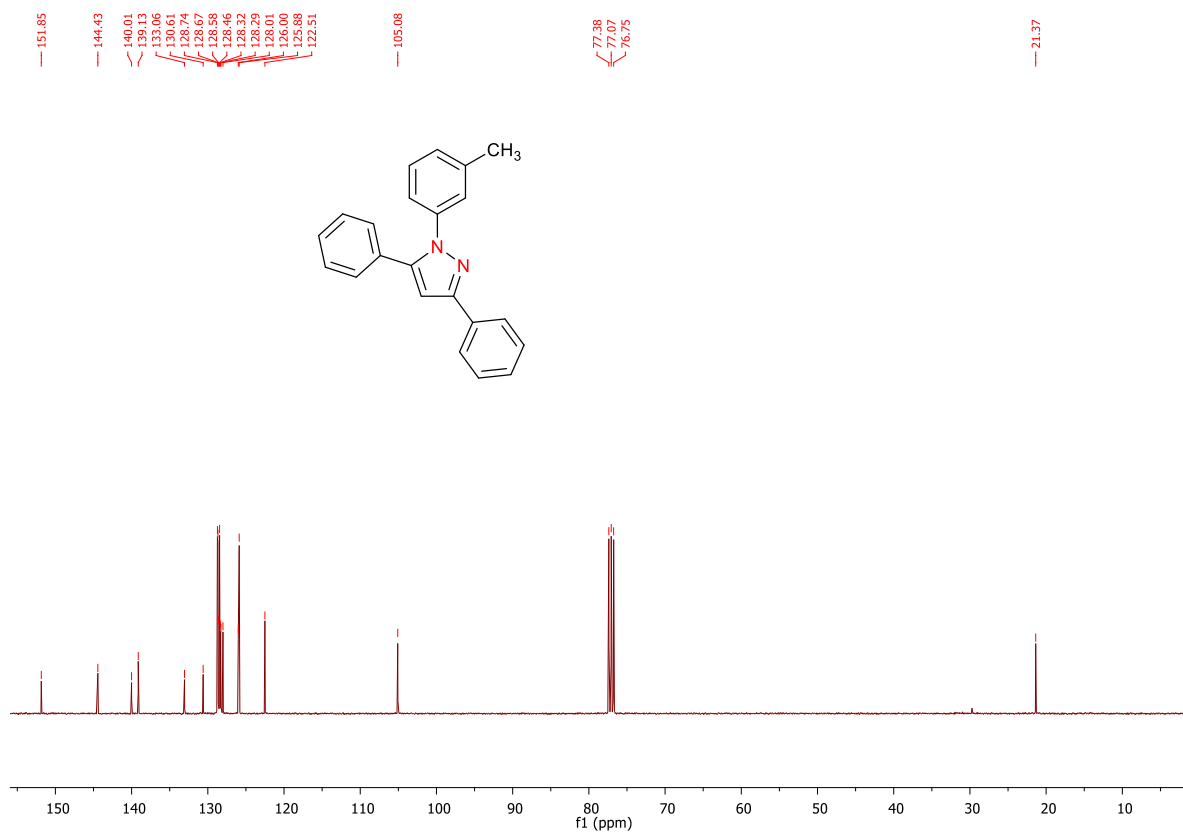


Figure S55. ¹³C NMR spectrum of **9b** (100 MHz in CDCl₃).

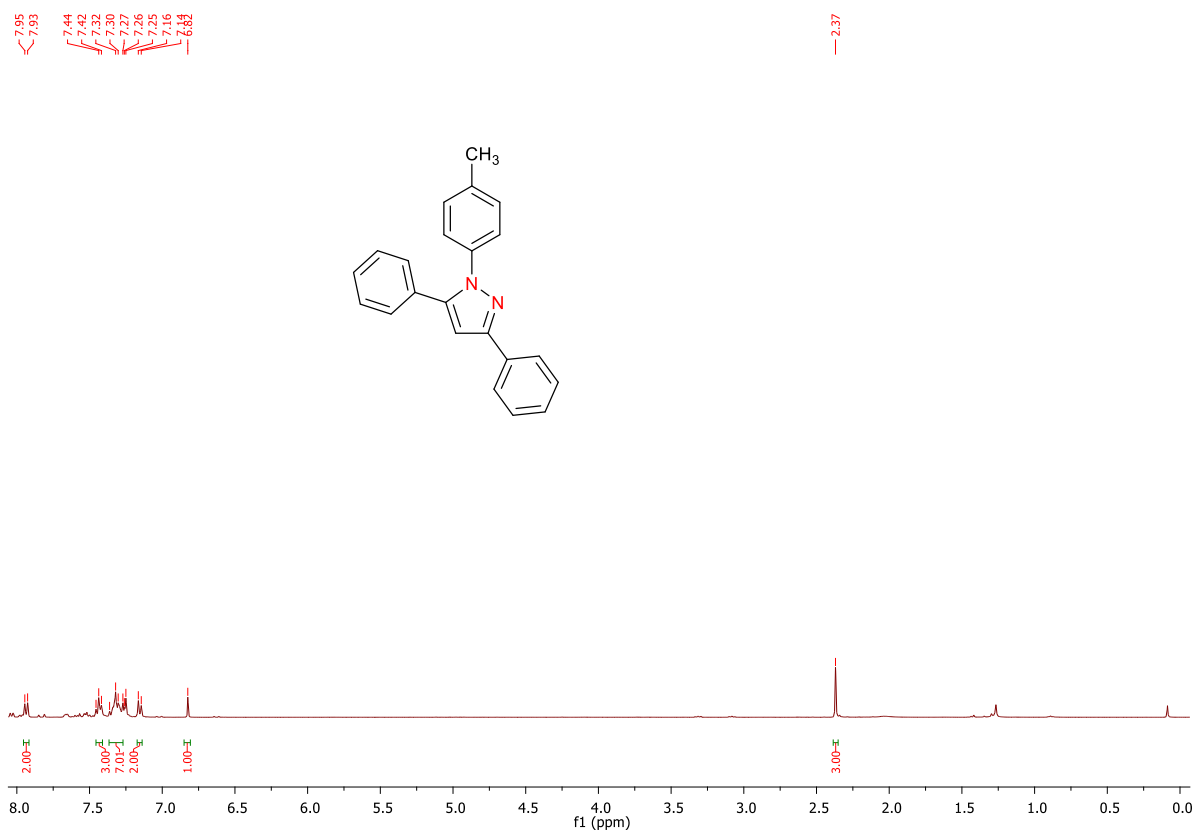


Figure S56. ¹H NMR spectrum of **9c** (400 MHz in CDCl₃).

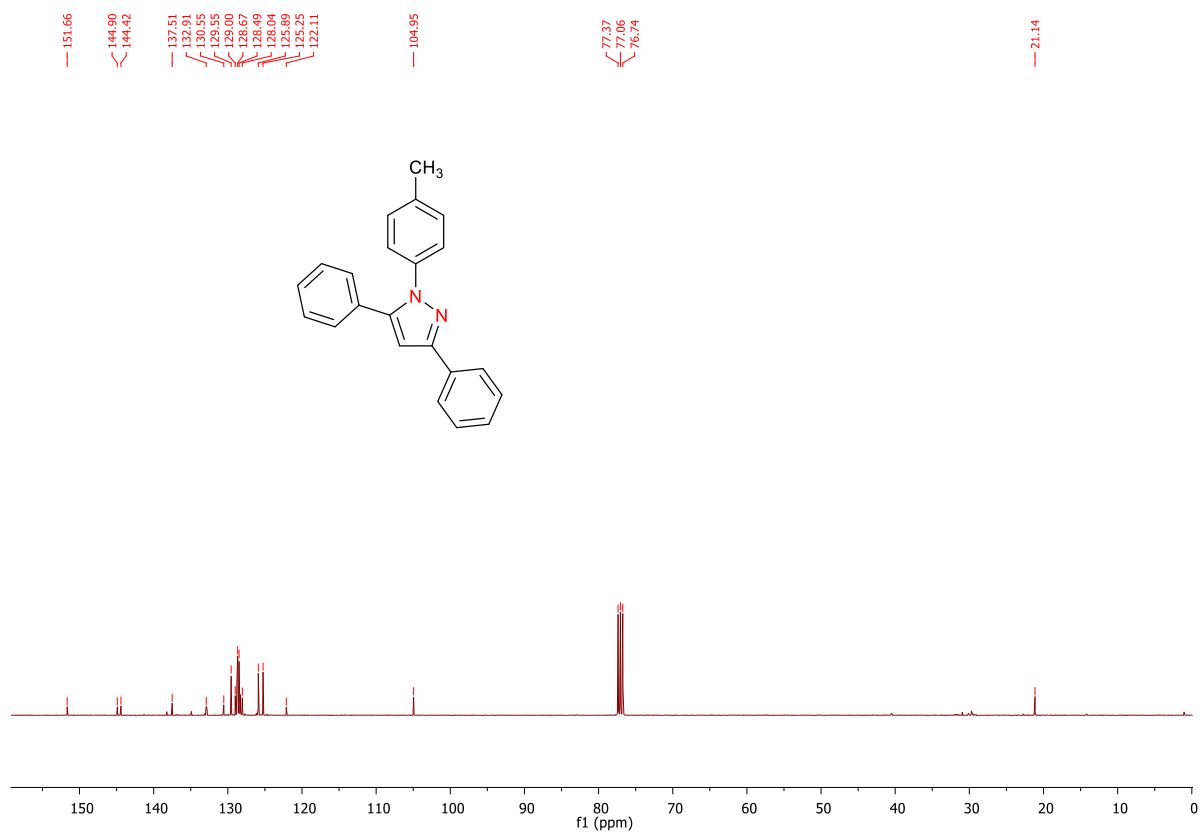


Figure S57. ¹³C NMR spectrum of **9c** (100 MHz in CDCl₃).

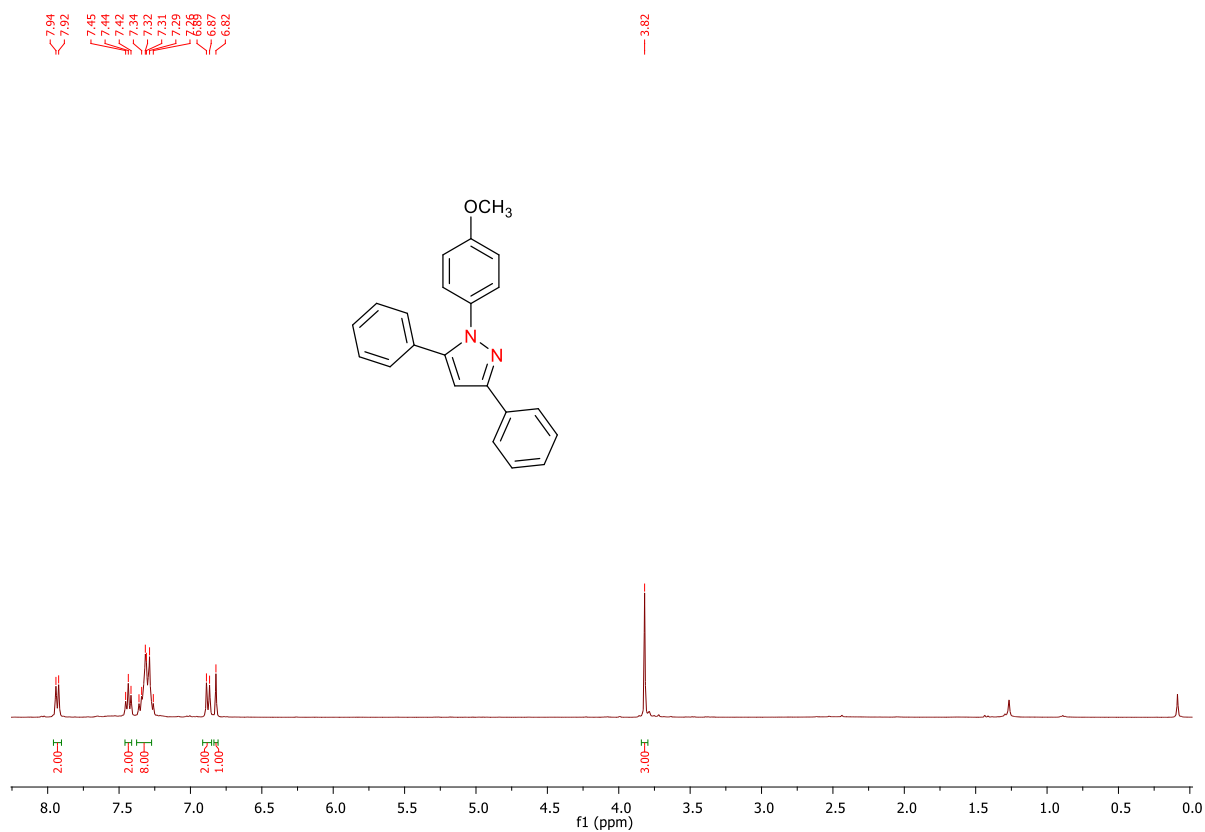


Figure S58. ¹H NMR spectrum of **9d** (400 MHz in CDCl₃).

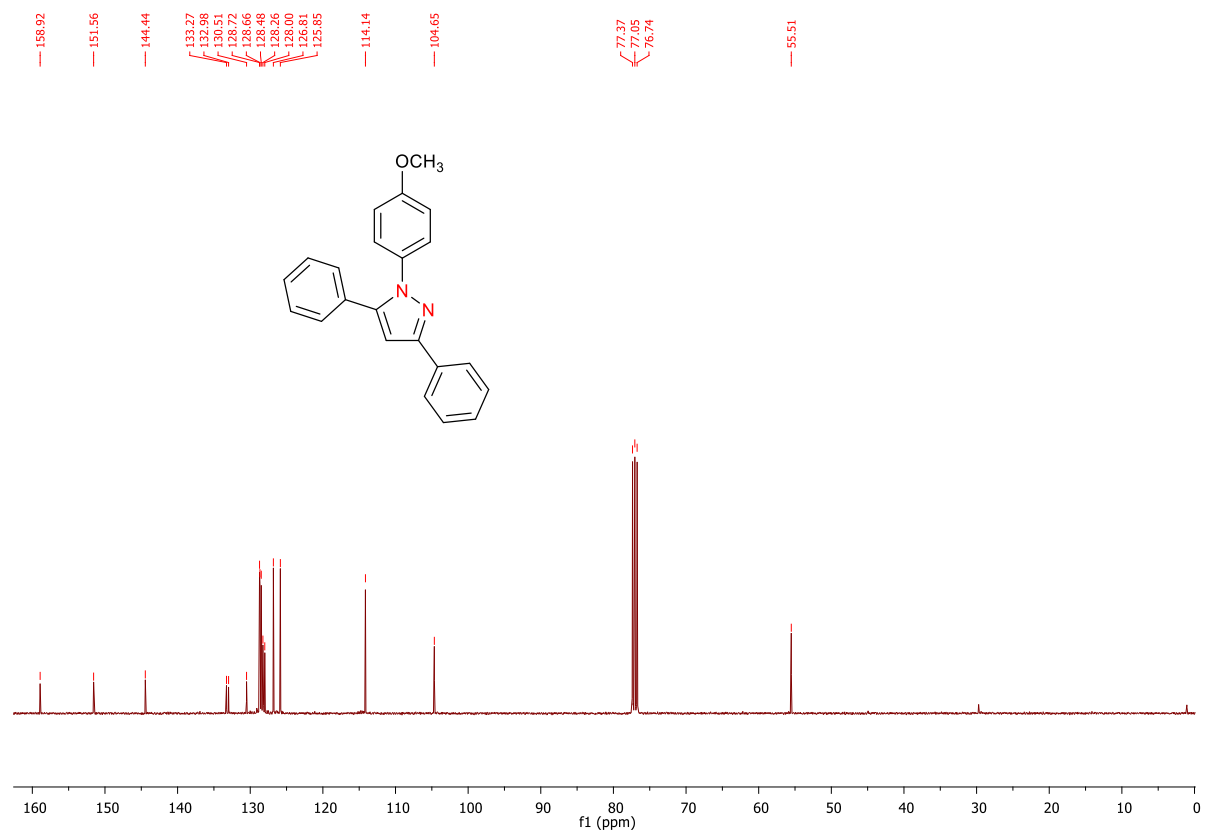


Figure S59. ¹³C NMR spectrum of **9d** (100 MHz in CDCl₃).

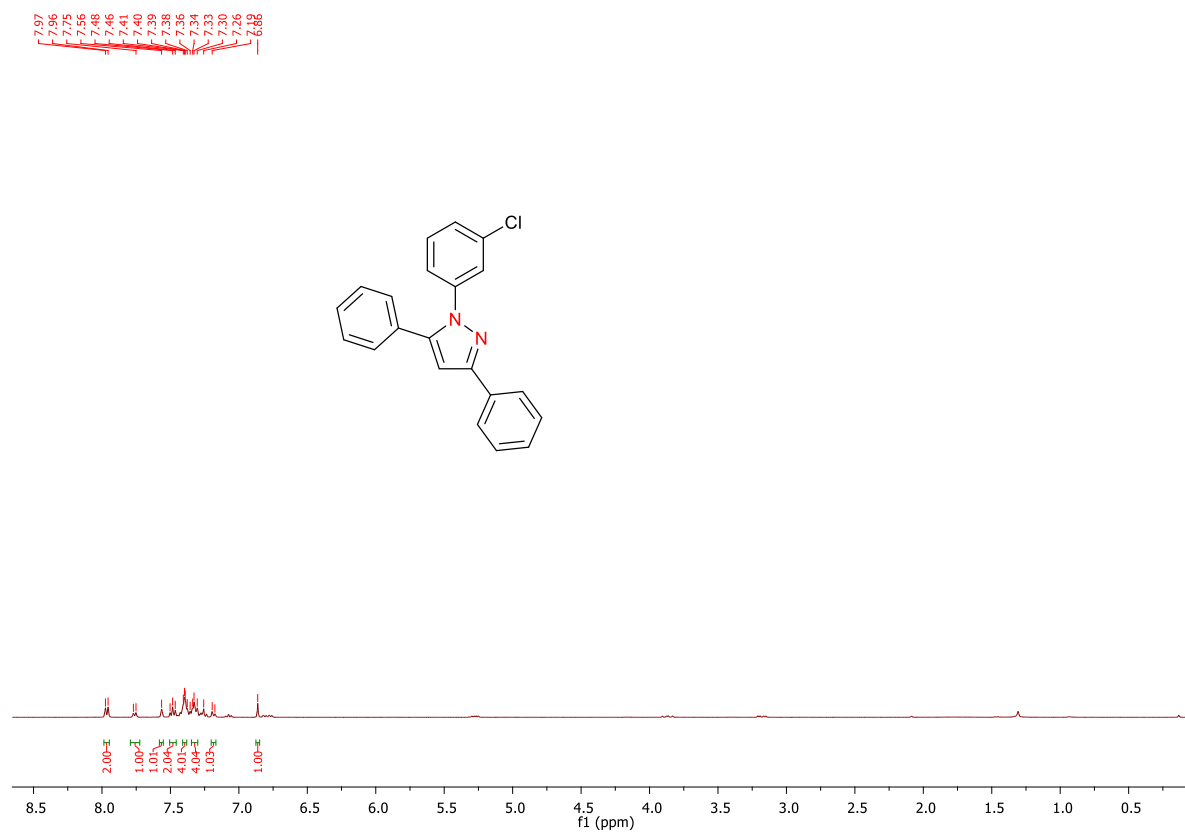


Figure S60. ¹H NMR spectrum of **9e** (400 MHz in CDCl₃).

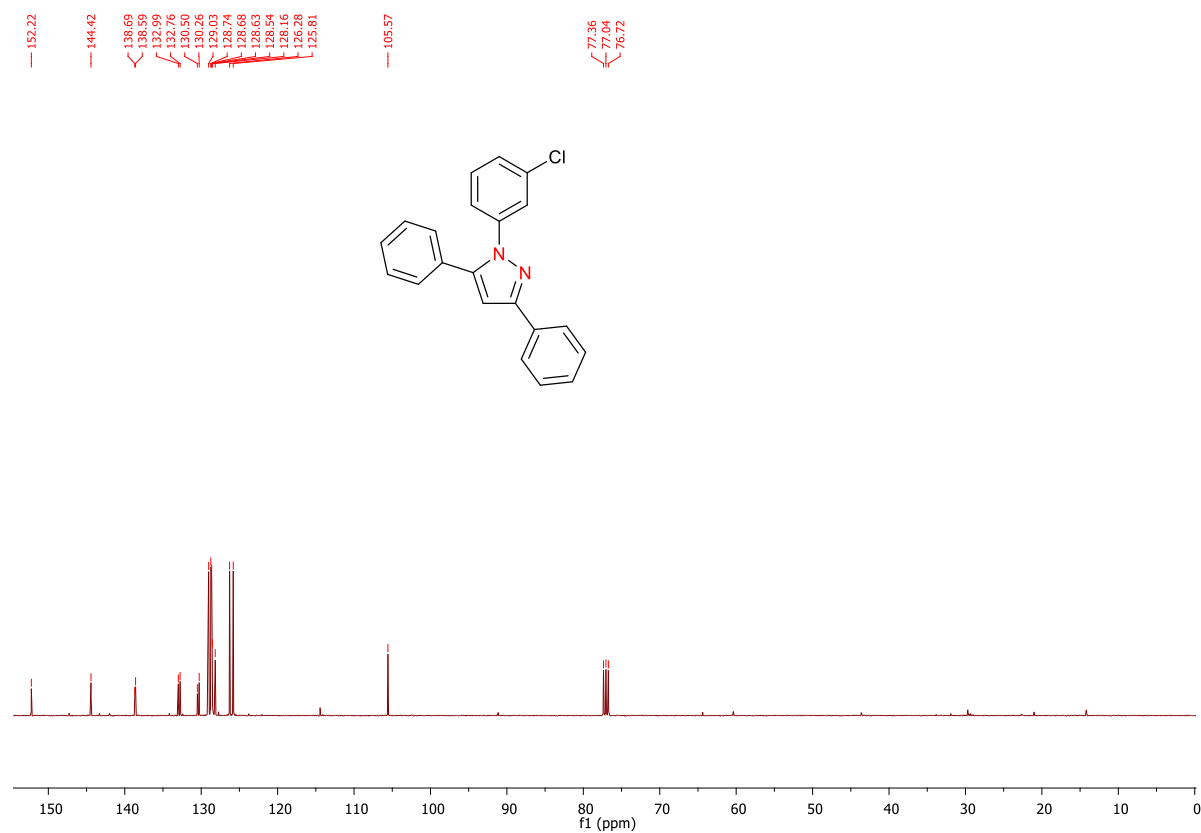


Figure S61. ¹³C NMR spectrum of **9e** (100 MHz in CDCl₃).

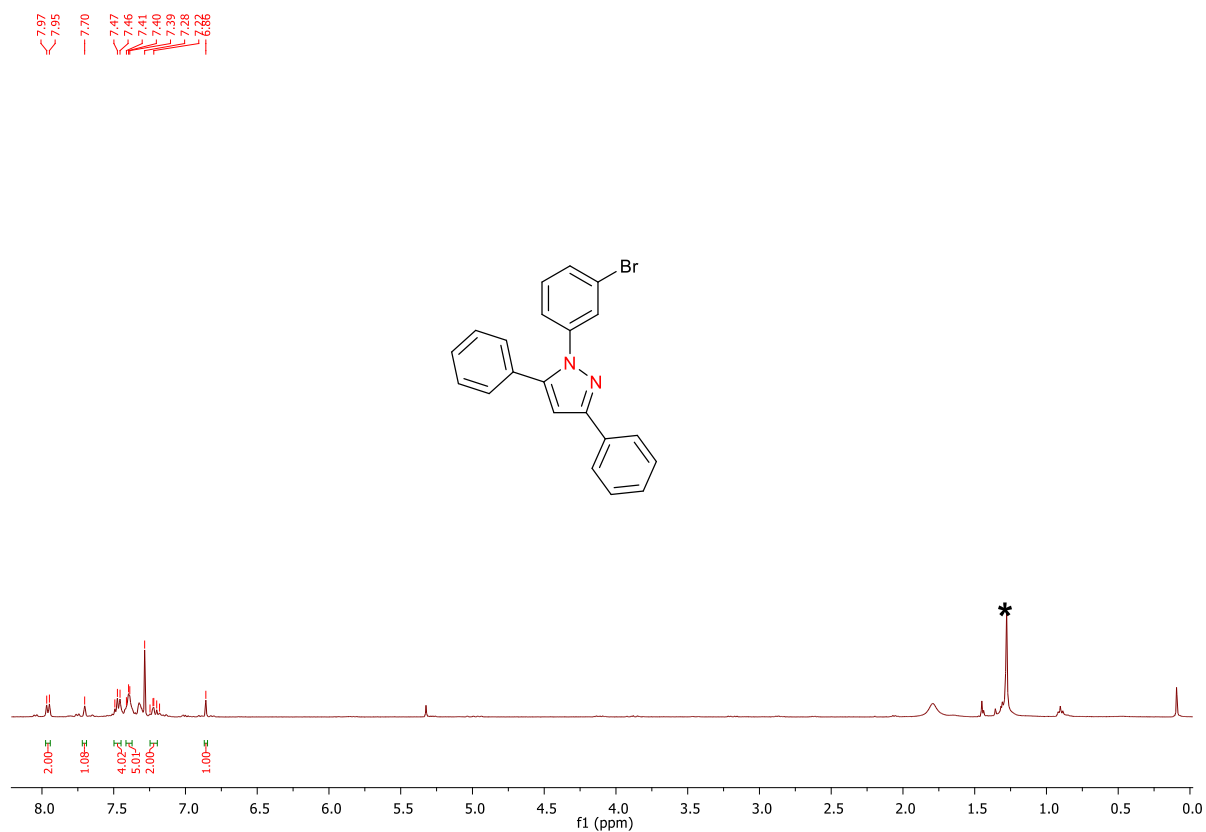


Figure 62. ¹H NMR spectrum of **9f** (400 MHz in CDCl₃). (* hexane)

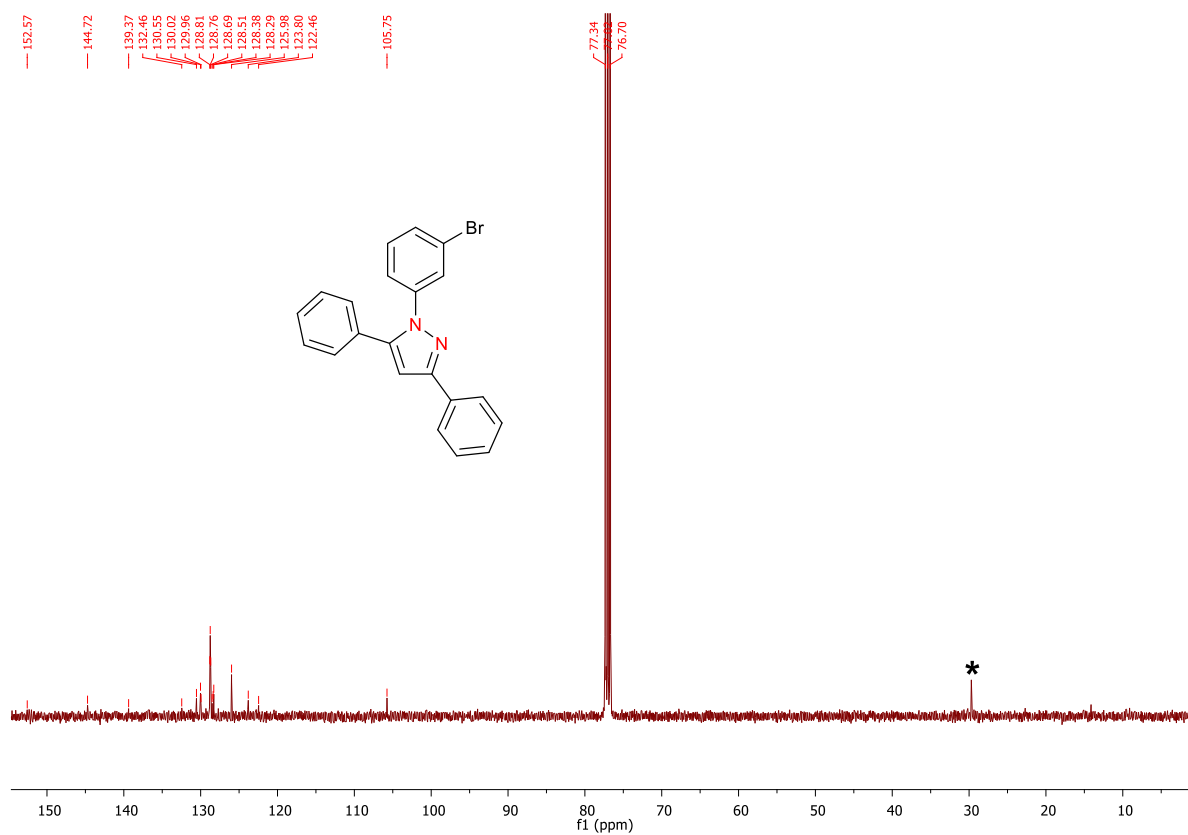


Figure S63. ¹³C NMR spectrum of **9f** (100 MHz in CDCl₃). (* hexane)

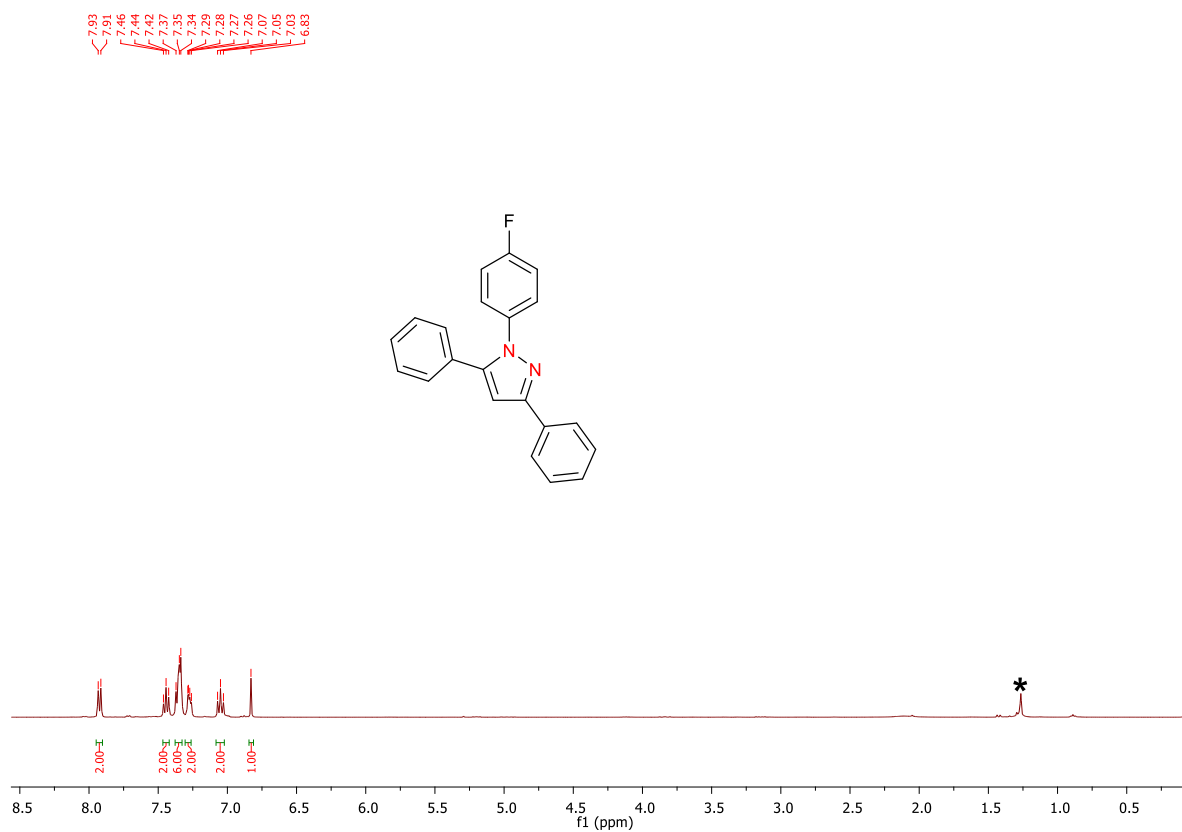


Figure S64. ¹H NMR spectrum of **9g** (400 MHz in CDCl₃). (* hexane)

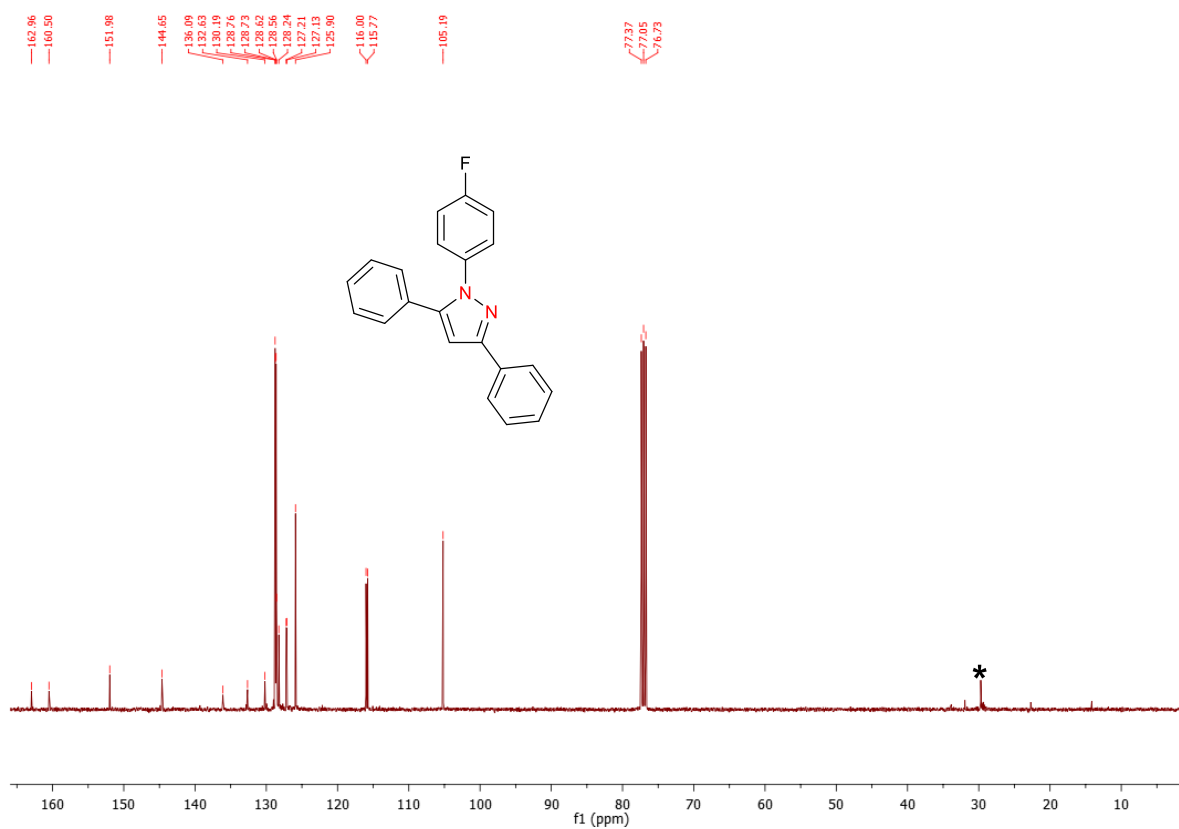


Figure S65. ¹³C NMR spectrum of **9g** (100 MHz in CDCl₃). (* hexane)

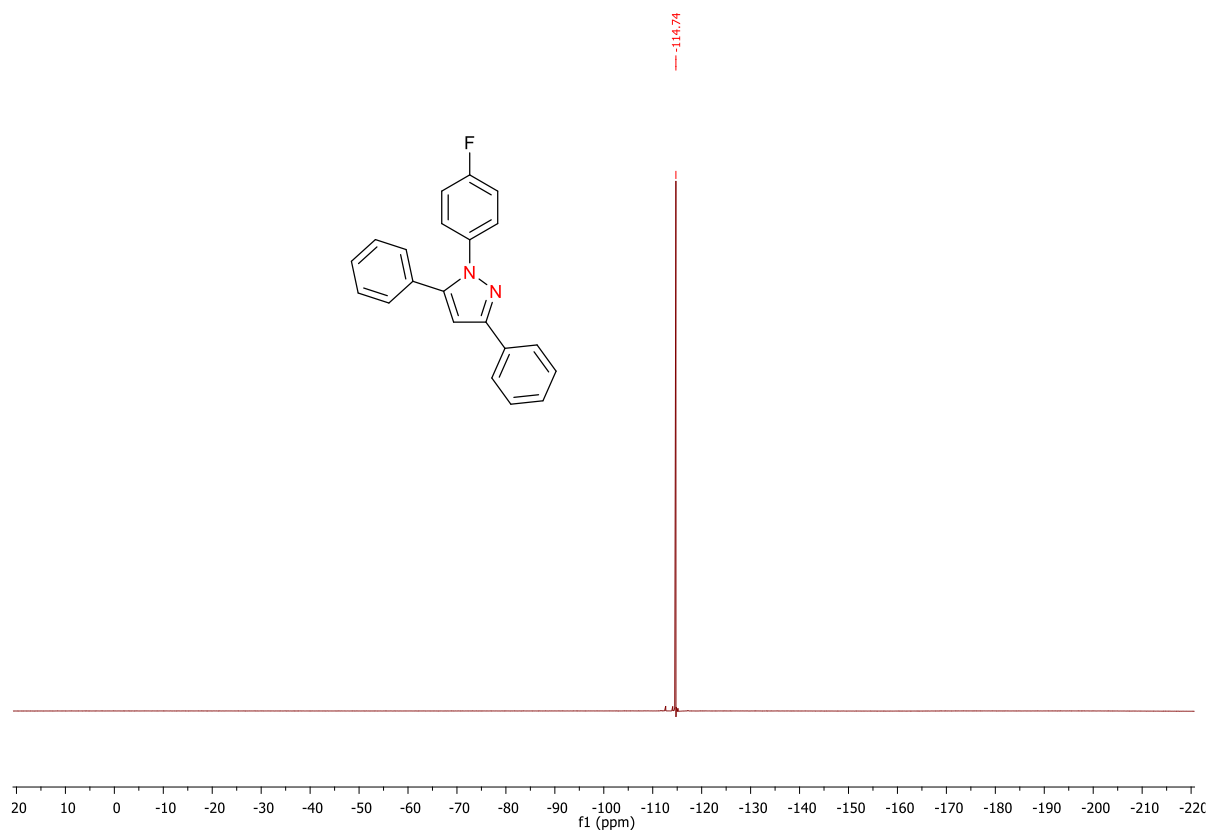


Figure S66. ^{19}F NMR spectrum of **9g** (376 MHz in CDCl_3).



Figure S67. ¹H NMR spectrum of **9h** (400 MHz in CDCl₃).

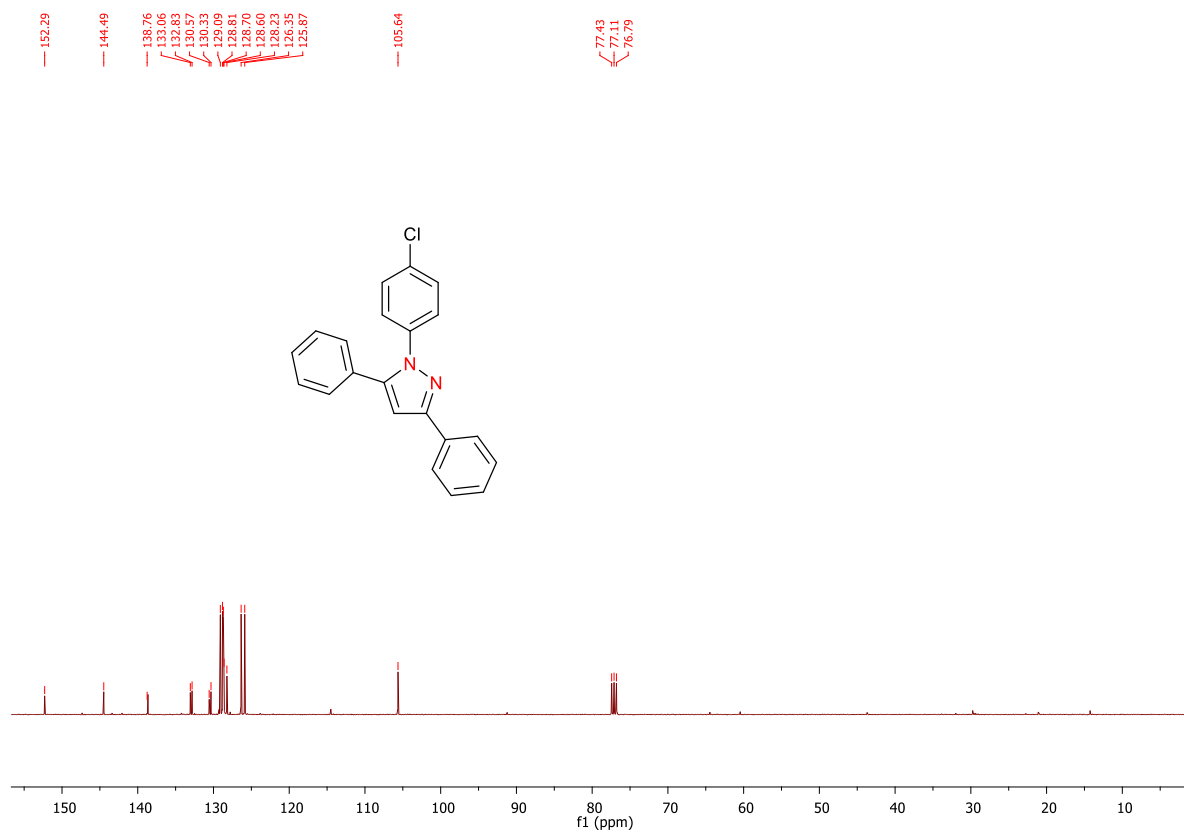


Figure S68. ¹³C NMR spectrum of **9h** (100 MHz in CDCl₃).

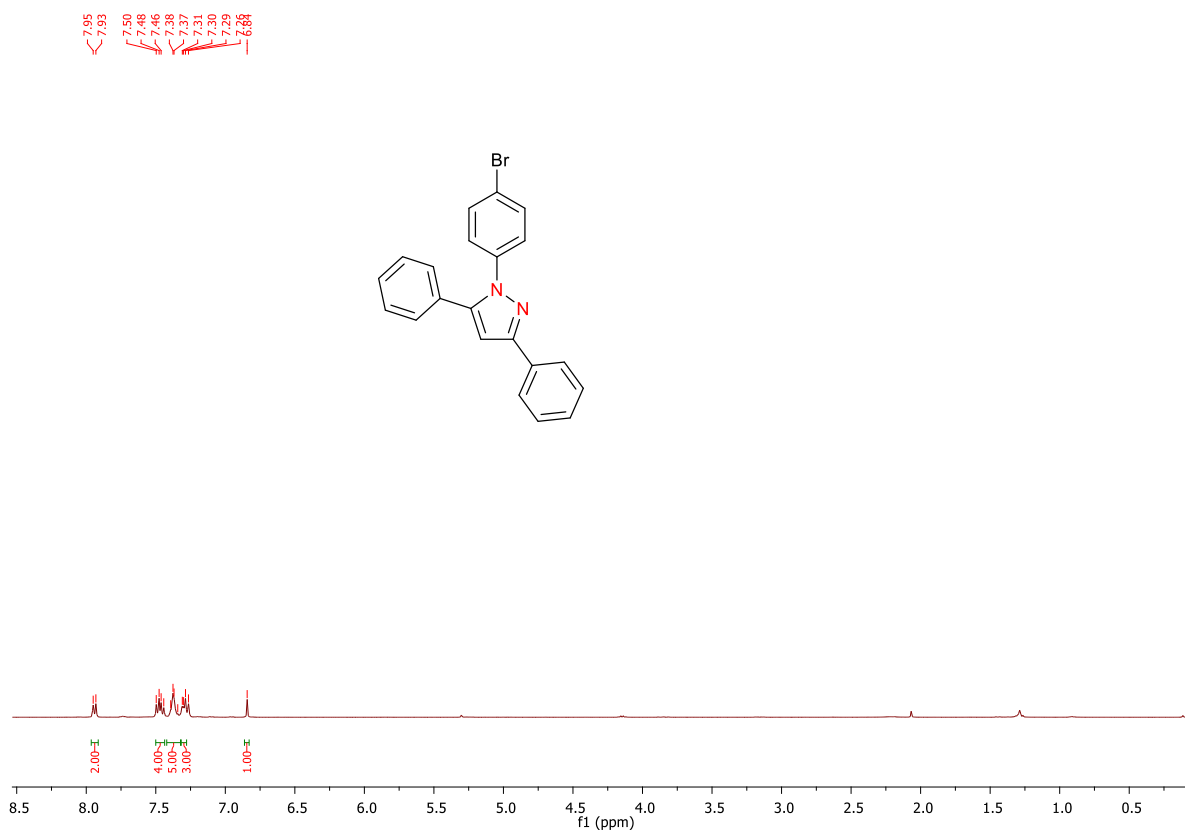


Figure S69. ¹H NMR spectrum of **9i** (400 MHz in CDCl₃).

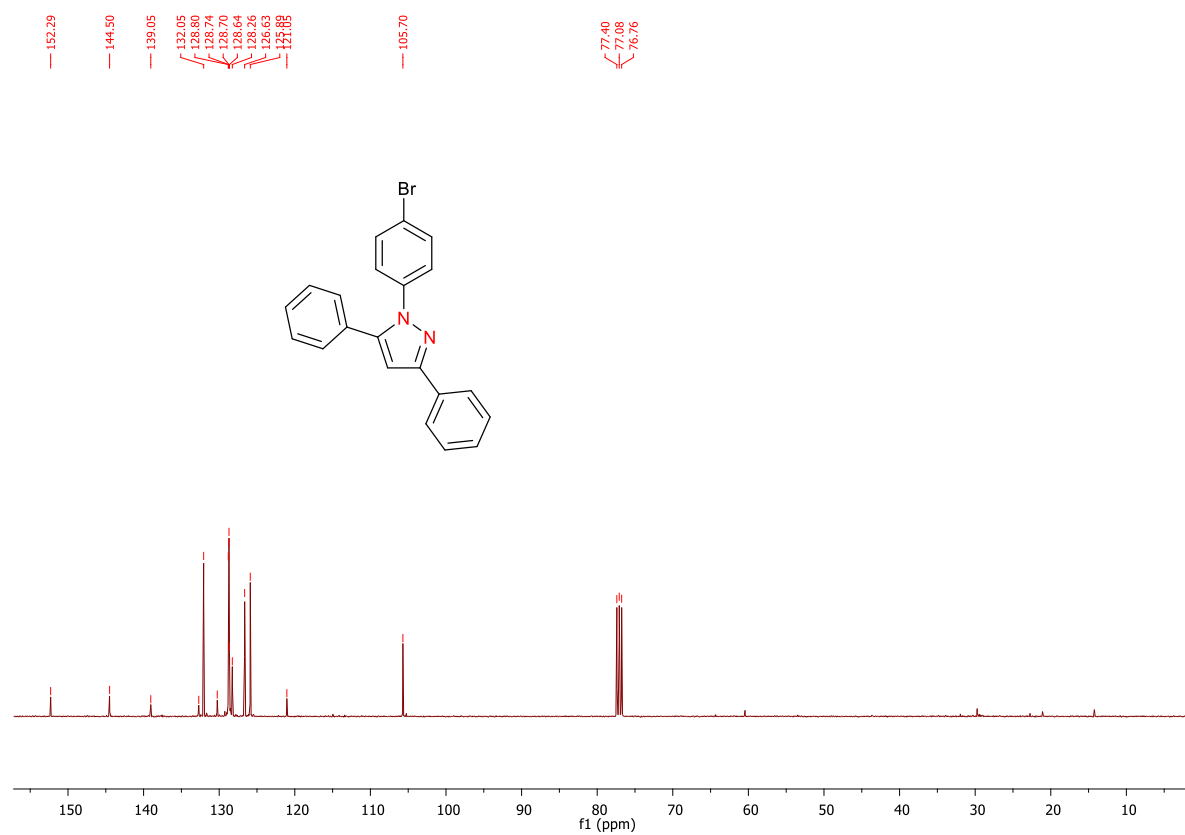


Figure S70. ¹³C NMR spectrum of **9i** (100 MHz in CDCl₃).

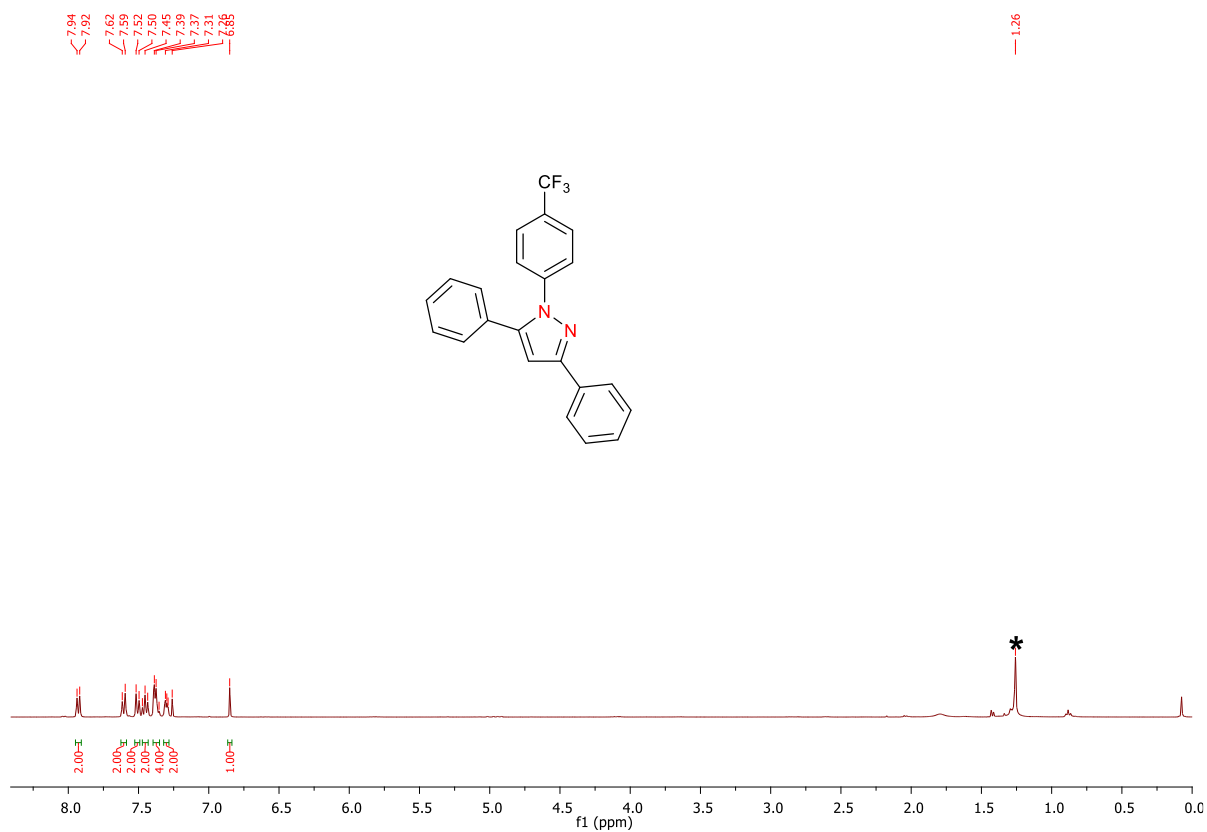


Figure S71. ¹H NMR spectrum of **9j** (400 MHz in CDCl₃). (* hexane)

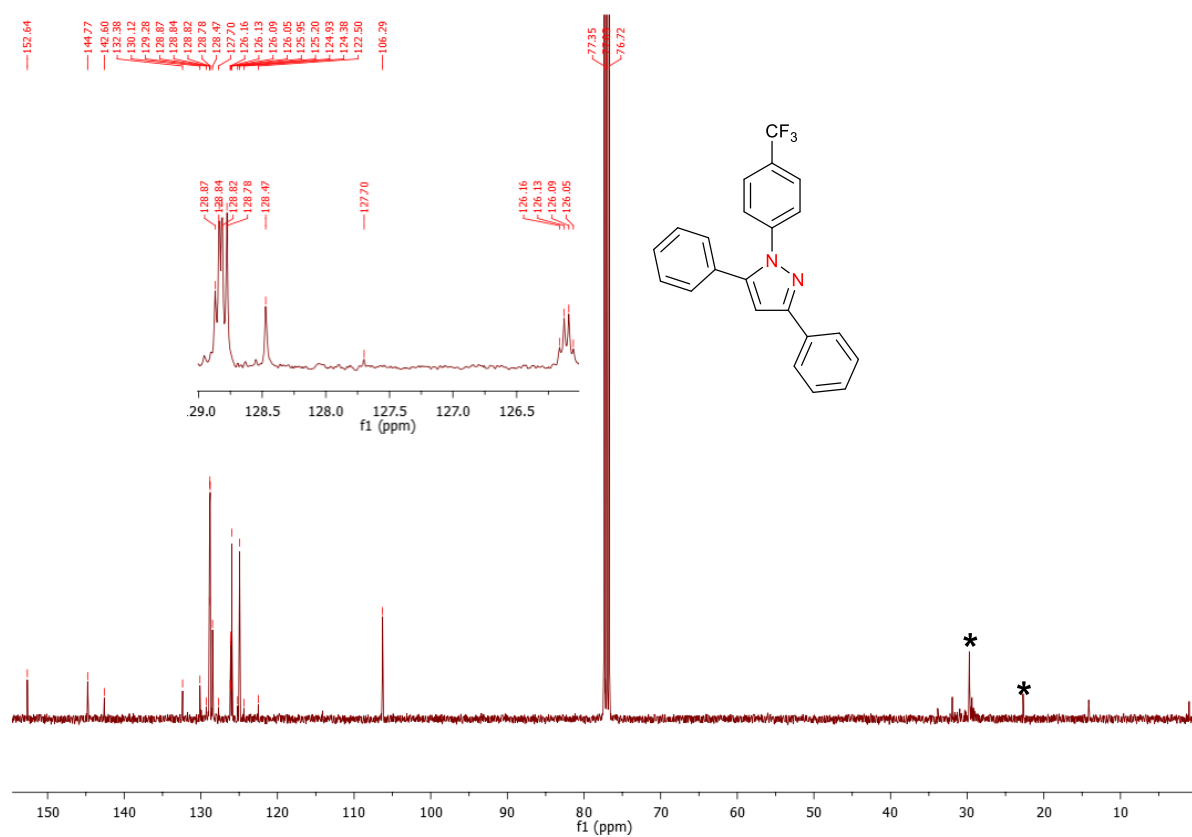


Figure S72. ¹³C NMR spectrum of **9j** (100 MHz in CDCl₃) (* hexane).

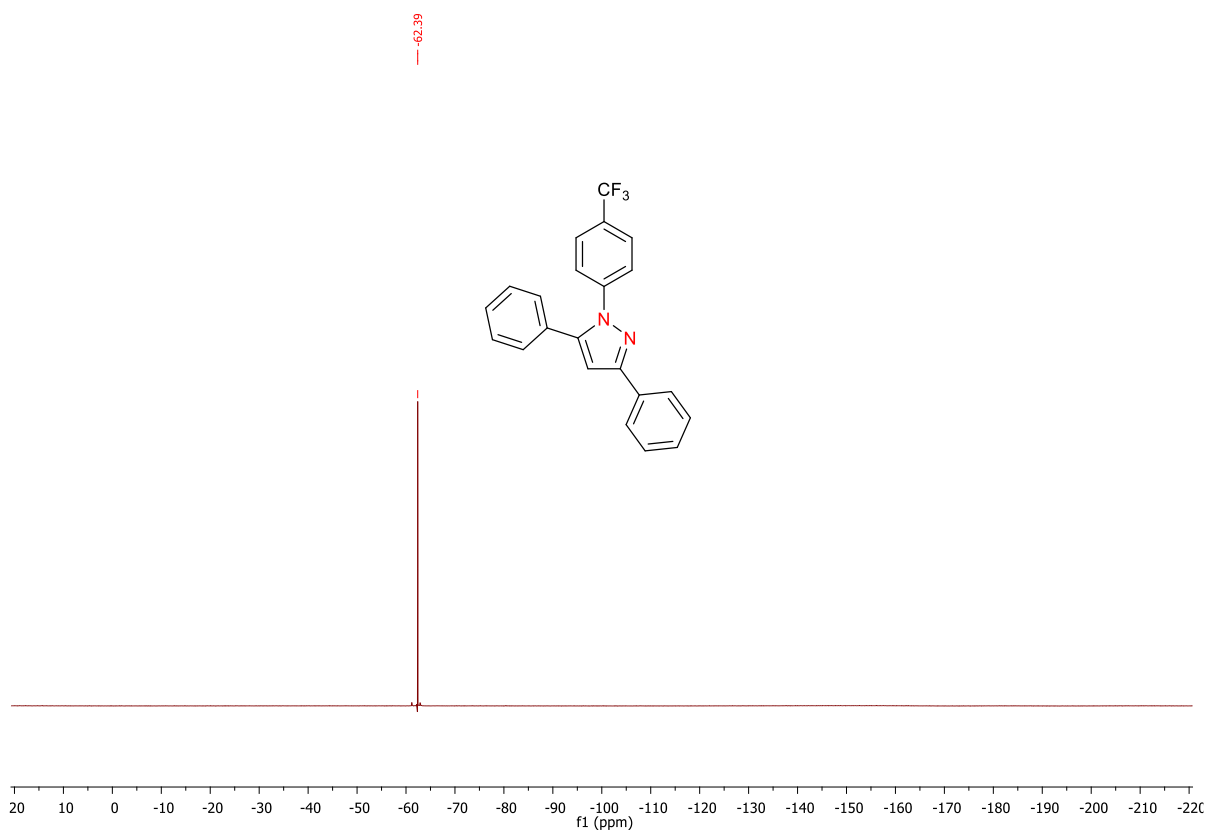


Figure S73. ^{19}F NMR spectrum of **9j** (376 MHz in CDCl_3).

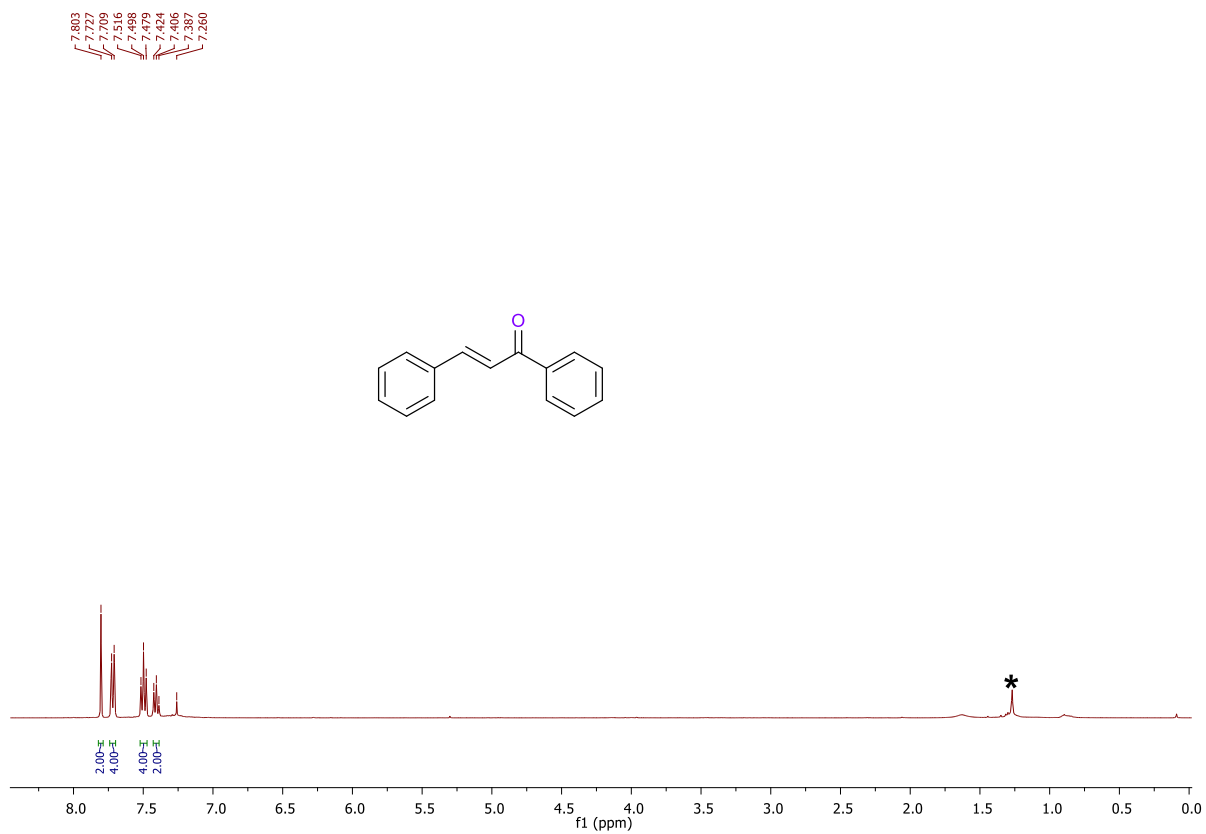


Figure S74. ¹H NMR spectrum of **10** (400 MHz in CDCl₃). (*hexane)

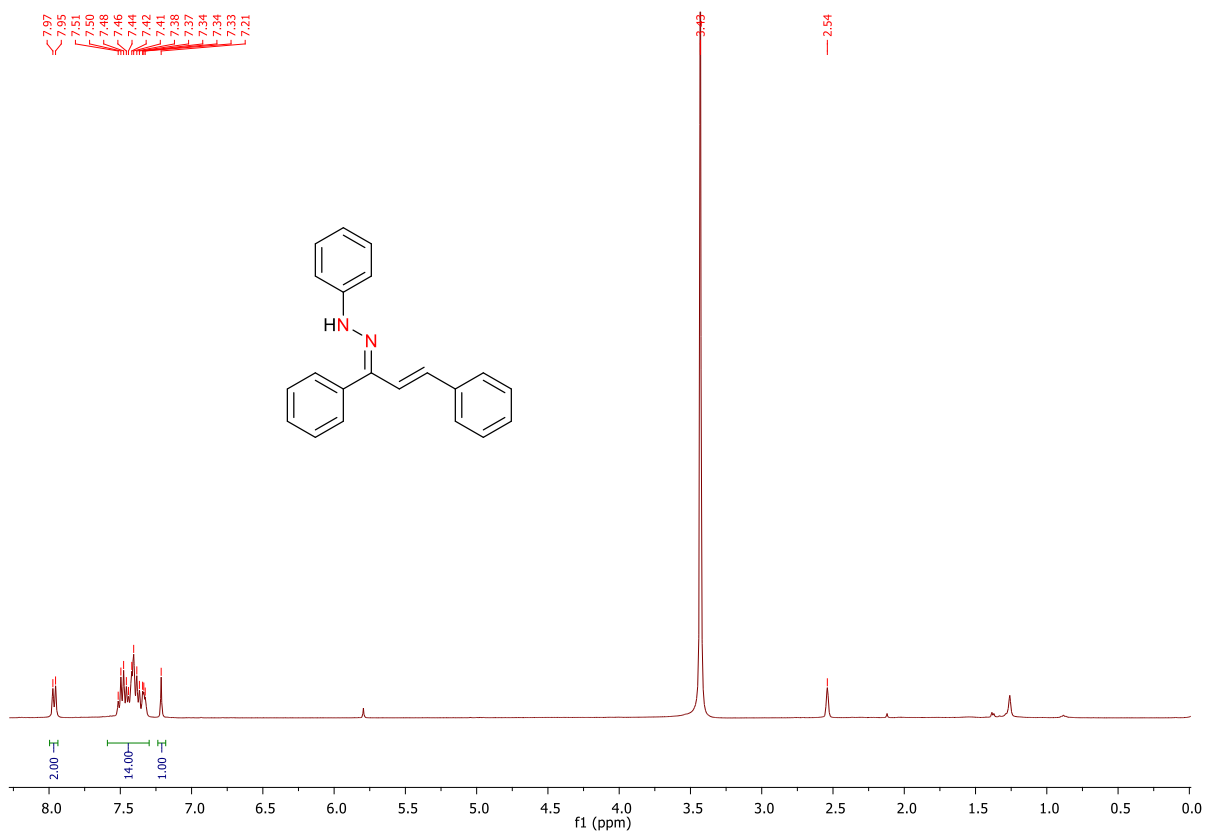


Figure S75. ¹H NMR spectrum of **11** (400 MHz in DMSO-d⁶).

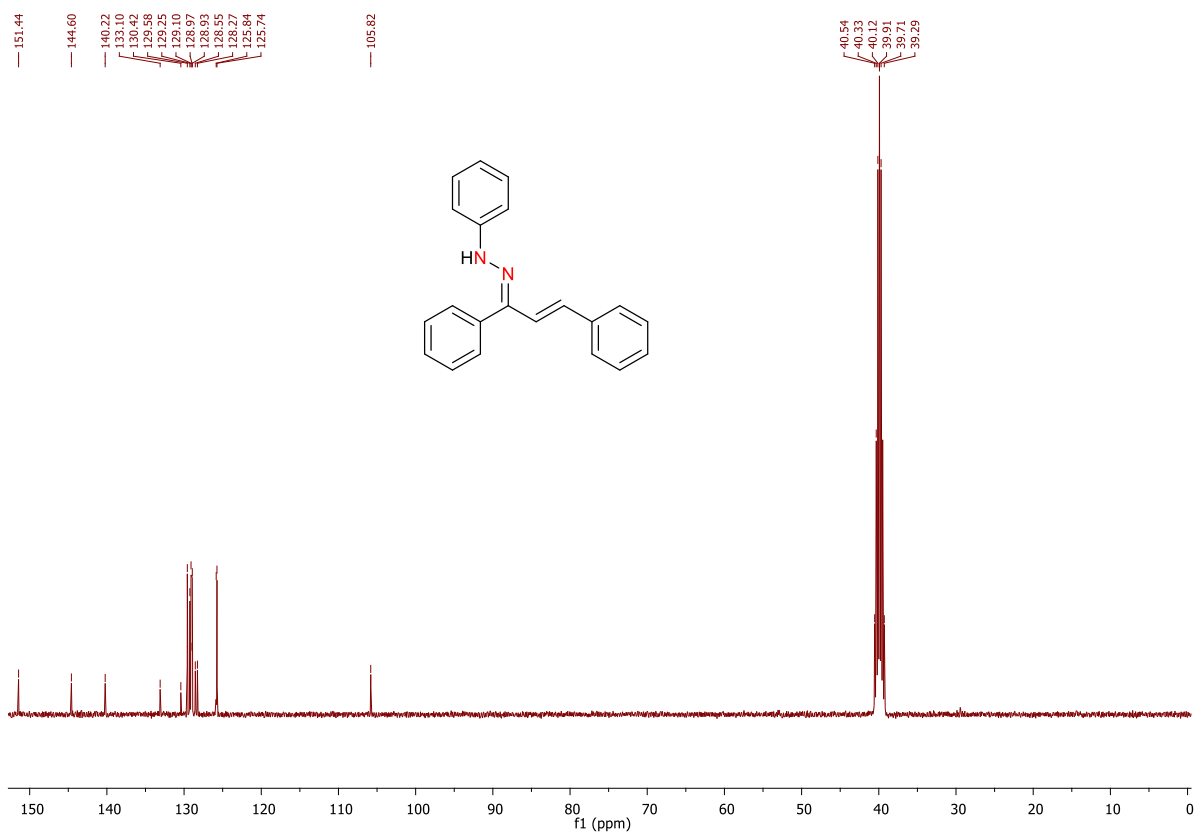


Figure S76. ¹³C NMR spectrum of **11** (100 MHz in DMSO-d⁶).

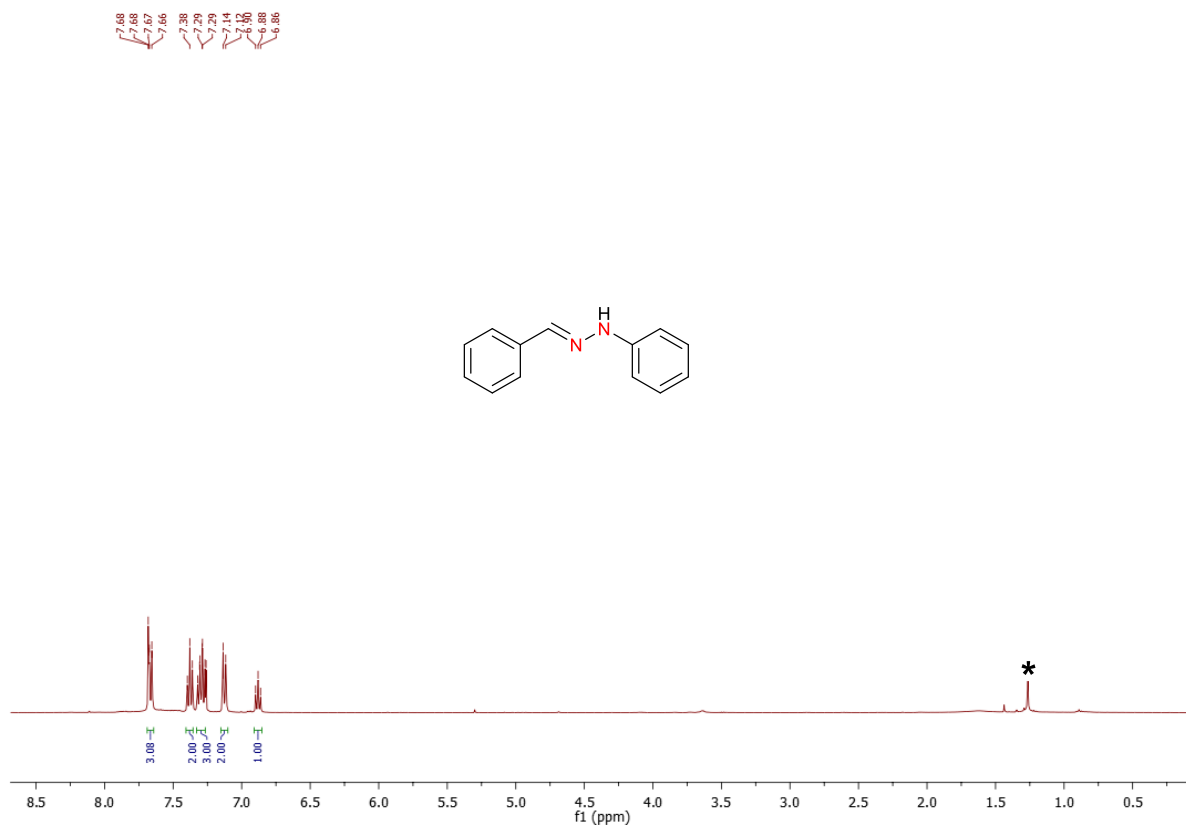


Figure S77. ¹H NMR spectrum of **12** (400 MHz in CDCl₃). (* hexane)

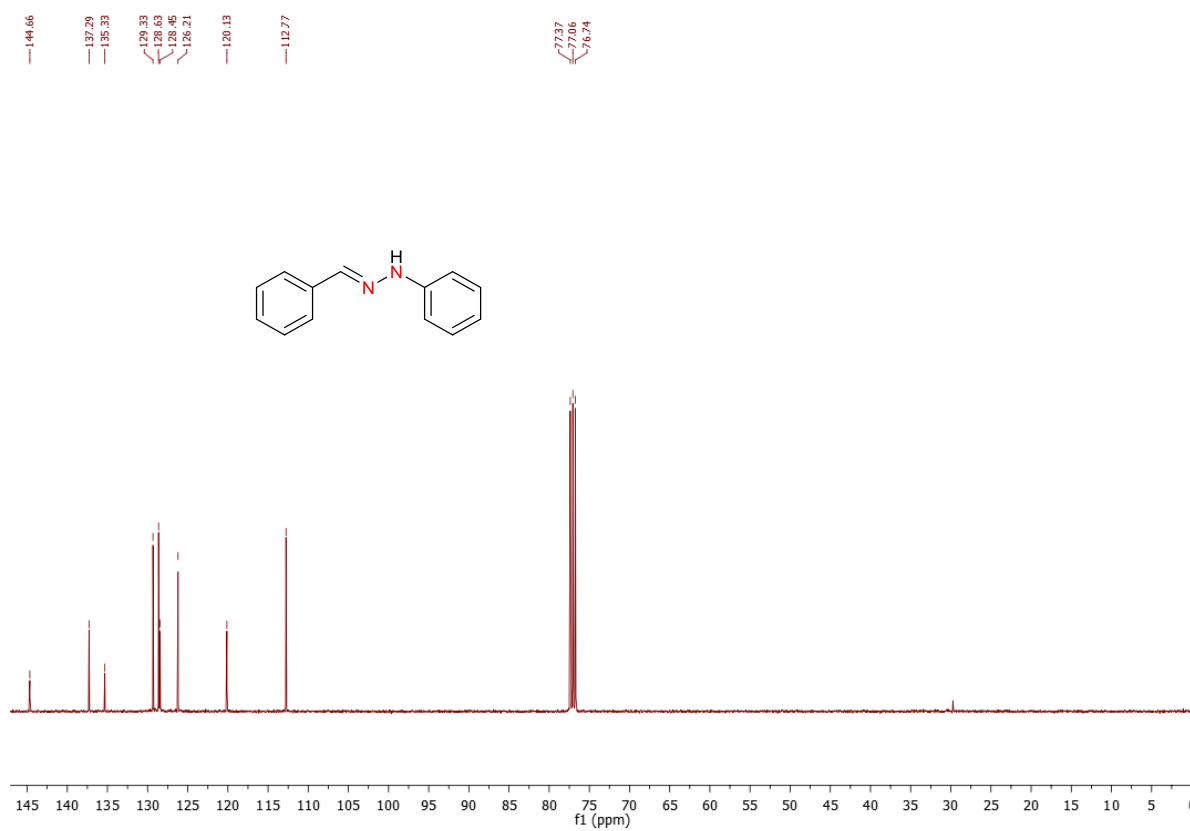


Figure S78. ¹³C NMR spectrum of **12** (100 MHz in CDCl₃).

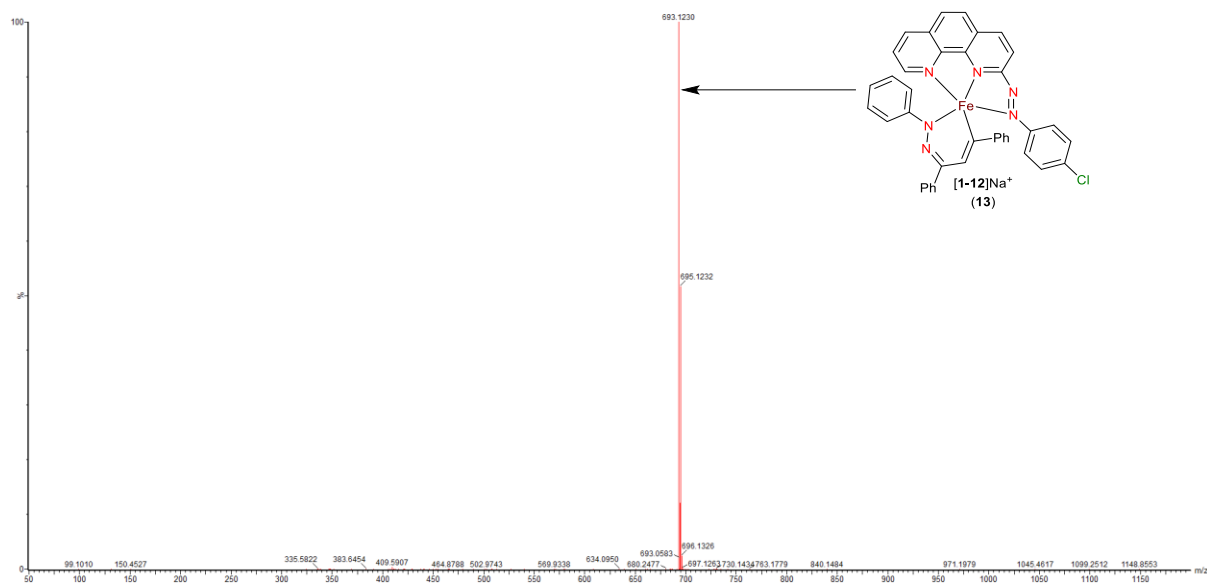
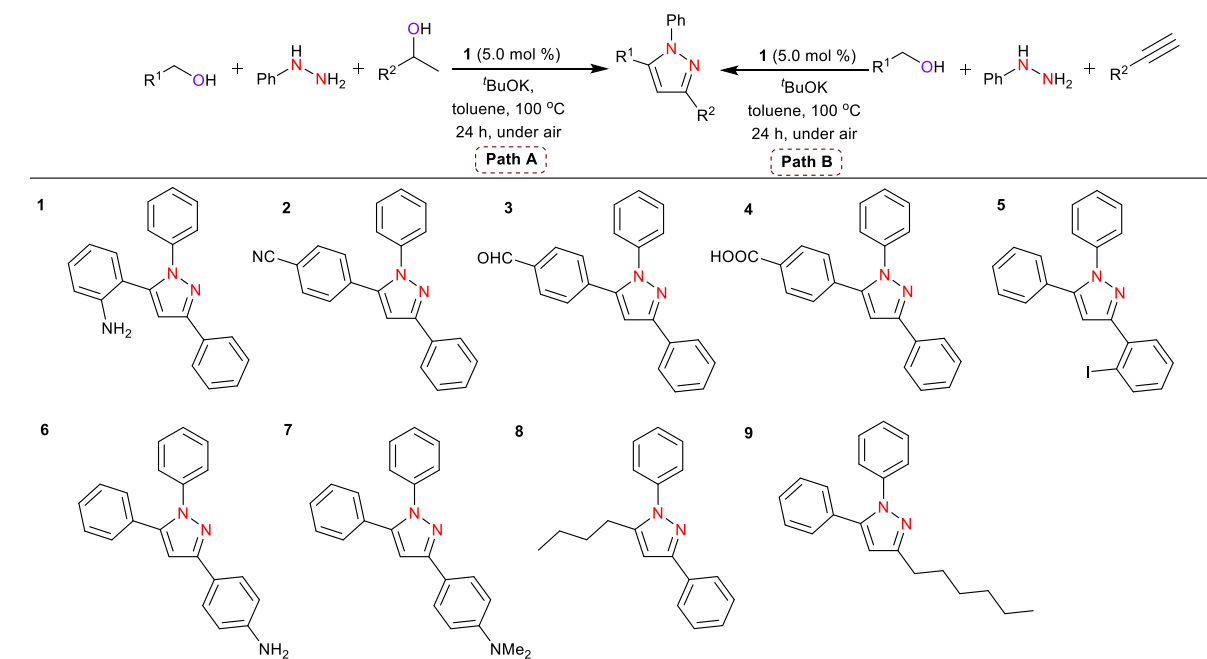


Figure S79. HRMS analysis of the reaction mixture for the detection of adducts **13**.

Table S1. Unsuccessful substrates scope.



References

1. S. Sinha, S. Das, R. Sikari, S. Parua, P. Brandaõ, S. Demeshko, F. Meyer, and N. D. Paul, Redox noninnocent azo-aromatic pincers and their iron complexes. Isolation, characterization, and catalytic alcohol oxidation, *Inorg. Chem.*, 2017, **56**, 14084–14100.
2. Y. Ding, H. Li, Y. Meng, T. Zhang, J. Li, Q-Y. Chen, and C. Zhu, Direct synthesis of hydrazones by visible light mediated aerobic oxidative cleavage of the C=C bond, *Org. Chem. Front.*, 2017, **4**, 1611–1614.