Supporting Information

$Cu(OTf)_2$-Catalyzed Three-Component Annulation Reaction Reaction: One-Pot Synthesis of 4,5-Dihydropyrazole from Aldehydes, Hydrazines and Alkenes

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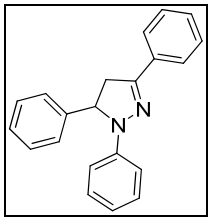
General methods:

Melting points were uncorrected. NMR spectra were in $CDCl_3$ (^1H at 500 MHz and ^{13}C at 125 MHz). Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

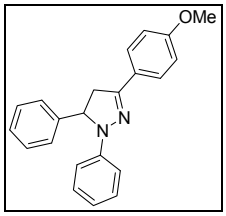
General procedure for $Cu(OTf)_2$-catalyzed synthesis of dihydropyrazole:

A general experimental procedure for the reaction of aldehyde **1**, hydrazine **2** and alkene **3** catalyzed by $Cu(OTf)_2$ is described below: to a 5-mL flask were successively added aldehyde **1** (0.5 mmol), hydrazine **2** (0.5 mmol), alkene **3** (0.6 mmol), dichloromethane (DCM) (2.0 mL) and copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$, 0.1 mmol). The reaction mixture was stirred at room temperature, and monitored periodically by TLC. Upon completion, the dichloromethane was removed under reduced pressure by an aspirator, and then the residue was purified by flash chromatography (hexane/ethyl acetate) on silica gel to afford the substituted 4,5-dihydropyrazole.

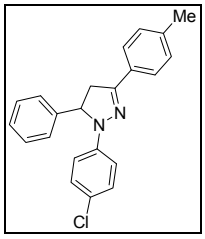


1,3,5-Triphenyl-4,5-dihydro-1*H*-pyrazole (4aa). Following the general procedure for the synthesis of dihydropyrazole, and compound **4aa** was obtained in 89% yield as a yellow solid (134-136 ^oC). **^1H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.83-7.72 (m, 2H), 7.47-7.41 (m, 2H), 7.39 (dd, J = 11.2, 5.4 Hz, 5H), 7.32 (dd, J = 5.7, 2.8 Hz, 1H),

7.27-7.21 (m, 2H), 7.18-7.12 (m, 2H), 6.85-6.83 (m, 1H), 5.29 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.85 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.17 (dd, *J* = 17.0, 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 146.6, 144.8, 142.5, 132.7, 129.1, 128.9, 128.5, 128.4, 127.5, 125.8, 125.7, 119.0, 113.3, 64.4, 43.5; **MS (ESI): [M+H$^+$]** 299.

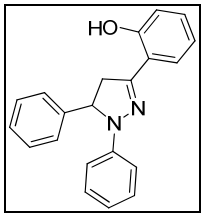


3-(4-Methoxyphenyl)-1,5-diphenyl-4,5-1*H*-dihydropyrazole (4ba). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ba** was obtained in 92% yield as a yellow solid (mp 171-173 °C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.67 (d, *J* = 8.9 Hz, 2H), 7.36-7.32 (m, 5H), 7.22-7.15 (m, 2H), 7.10-7.04 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.78-6.77 (m, 1H), 5.23 (dd, *J* = 12.3, 7.3 Hz, 1H), 3.84 (s, 3H), 3.83 (dd, *J* = 17.0, 12.3 Hz, 1H), 3.12 (dd, *J* = 17.0, 7.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 160.2, 146.8, 145.2, 142.8, 129.1, 128.9, 127.5, 127.2, 125.9, 125.5, 118.9, 114.0, 113.2, 64.4, 55.5, 43.6; **MS (ESI): [M+H$^+$]** 329.

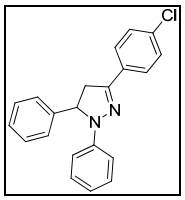


1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-phenyl-4,5-dihydropyrazole (4ca). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ca** was obtained in 83% yield as a pink solid (mp 152-153 °C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.67 (d, *J* = 8.1 Hz, 2H), 7.42-7.33 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 5.19 (dd, *J* = 12.3, 7.2 Hz, 1H),

3.81 (dd, *J* = 17.1, 12.3 Hz, 1H), 3.15 (dd, *J* = 17.1, 7.2 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 147.5, 143.4, 142.1, 138.8, 129.6, 129.2, 129.1, 128.7, 127.6, 125.7, 125.7, 123.5, 114.3, 64.2, 43.7, 21.3; **MS (ESI): [M+H$^+$]** 348; Anal. Calcd for $C_{22}H_{19}ClN_2$: C, 76.18; H, 5.52. Found: C, 76.04; H, 5.78.

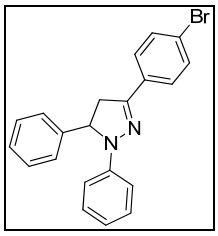


3-(2-Hydroxyphenyl)-1,5-diphenyl-4,5-dihydropyrazole (4da). Following the general procedure for the synthesis of dihydropyrazole, and compound **4da** was obtained in 85% yield as a white solid (mp 178-180 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 10.67 (s, 1H), 7.39-7.35 (m, 2H), 7.32-7.29 (m, 4H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.15-7.10 (m, 3H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.89 (m, 3H), 5.18 (dd, *J* = 12.2, 7.4 Hz, 1H), 3.95 (dd, *J* = 17.3, 12.3 Hz, 1H), 3.26 (dd, *J* = 17.2, 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 157.1, 150.2, 142.5, 141.3, 130.9, 130.7, 129.3, 128.9, 128.5,128.0, 127.2, 125.8, 119.5, 116.6, 114.4, 63.3, 44.0; **MS (ESI)**: [M+H$^+$] 315; Anal. Calcd for $C_{21}H_{18}ON_2$: C, 80.23; H, 5.77. Found: C, 80.40; H, 5.52.

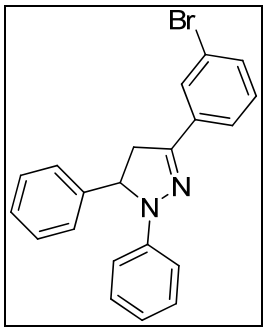


3-(4-Chlorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4ea). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ea** was obtained in 80% yield as a pink solid (mp 143-144 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.64 (d, *J* = 8.7 Hz, 2H), 7.37-7.26 (m, 7H), 7.18 (d, *J* = 8.7 Hz, 2H),

7.07-7.06 (m, 2H), 6.81-6.78 (m, 1H), 5.29 (dd, *J* = 12.4, 7.3 Hz, 1H), 3.81 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.11 (dd, *J* = 17.0, 7.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 147.4, 143.7, 139.8, 136.1, 132.5, 132.4, 130.3, 129.5, 128.8, 127.2, 126.8, 117.5, 113.8, 61.3, 42.4; **MS (ESI): [M+H$^+$]** 334.

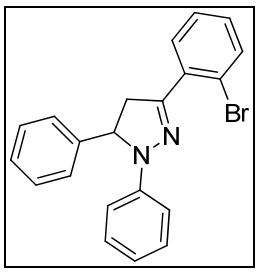


3-(4-Bromophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4fa). Following the general procedure for the synthesis of dihydropyrazole, and compound **4fa** was obtained in 81% yield as a yellow solid (mp 155-156 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.57 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.34-7.25 (m, 5H), 7.19-7.16 (m, 2H), 7.06-7.05 (m, 2H), 6.80-6.79 (m, 1H), 5.28 (dd, *J* = 12.4, 7.3 Hz, 1H), 3.80 (dd, *J* = 17.0, 12.5 Hz, 1H), 3.10 (dd, *J* = 17.0, 7.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 147.4, 143.7, 139.8, 135.1, 132.5, 132.4, 130.5, 129.5, 128.4, 127.2, 123.8, 117.5, 113.8, 61.3, 42.4; **MS (ESI): [M+H$^+$]** 377, 379.

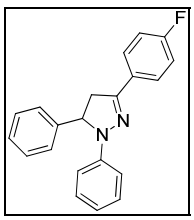


3-(3-Bromophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4ga). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ga** was obtained in 82% yield as a yellow solid (mp 132-134 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$,

δ ppm) 7.90 (t, *J* = 1.7 Hz, 1H), 7.64-7.57 (m, 1H), 7.51-7.43 (m, 1H), 7.35-7.27 (m, 5H), 7.22 (dd, *J* = 17.2, 7.7 Hz, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (dd, *J* = 7.6, 6.9 Hz, 1H), 5.30 (dd, *J* = 12.5, 7.1 Hz, 1H), 3.78 (dd, *J* = 17.0, 12.5 Hz, 1H), 3.10 (dd, *J* = 17.0, 7.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 147.4, 143.7, 139.8, 133.9, 132.8, 132.5, 132.4, 131.5, 129.5, 128.7, 128.1, 127.2, 121.8, 117.5, 113.8, 61.3, 42.4; **MS (ESI): [M+H$^+$]** 377, 379.

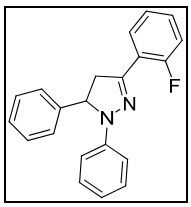


3-(2-Bromophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4ha) Following the general procedure for the synthesis of dihydropyrazole, and compound **4ha** was obtained in 78% yield as a yellow solid (mp 133-135 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.71 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42- 7.27 (m, 6H), 7.21-7.12 (m, 5H), 6.85-6.82 (m, 1H), 5.31 (dd, *J* = 12.2, 7.4 Hz, 1H), 4.06 (dd, *J* = 17.3, 12.2 Hz, 1H), 3.36 (dd, *J* = 17.3, 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 160.6, 157.1, 150.2, 142.5, 131.9, 130.6, 128.9, 128.5, 128.0, 127.2, 125.8, 114.5, 118.2, 116.6, 114.4, 63.3, 44.0; **MS (ESI): [M+H$^+$]** 377, 379.

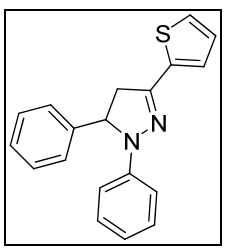


3-(4-Fluorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4ia). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ia** was

obtained in 76% yield as a yellow solid (mp 125-126 ^{o}C)**.** **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.65-7.63 (m, 1H), 7.27-7.23 (m, 4H), 7.22-7.16 (m, 2H), 7.13-7.08 (m, 2H), 7.07-7.03 (m, 4H), 6.71-6.70 (m, 1H), 5.20 (dd, *J* = 12.4, 7.3 Hz, 1H), 3.76 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.05 (dd, *J* = 17.0, 7.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 162.9; 145.7, 144.8, 142.4, 129.1, 129.0, 128.8, 127.6, 127.4, 125.8, 119.1, 115.5, 113.3, 64.5, 43.6; **MS (ESI): [M+H^{+}]** 317.

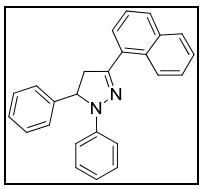


3-(2-Fluorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4ja) Following the general procedure for the synthesis of dihydropyrazole, and compound **4ja** was obtained in 74% yield as a yellow solid (mp 106-107 ^{o}C)**.** **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.98-7.96 (m, 1H). 7.28-7.16 (m, 6H), 7.13-7.08 (m, 3H), 7.00-6.94 (m, 3H), 6.72-6.70 (m, 1H), 5.20 (dd, *J* = 12.5, 7.4 Hz, 1H), 3.88 (dd, *J* = 17.9, 12.5 Hz, 1H), 3.20 (dd, *J* = 17.9, 7.4 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 160.4, 144.6, 143.3, 142.5, 130.0, 129.1, 128.9, 128.3, 127.5, 125.8, 124.2, 120.8, 119.3, 116.3 , 113.4, 64.5, 45.7; **MS (ESI): [M+H^{+}]** 317.

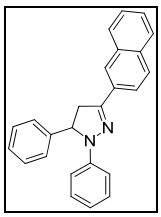


1,5-Diphenyl-3-(2-thiophenyl)-4,5-dihydro-1*H*-pyrazole (4ka). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ka** was obtained in 73% yield as a yellow solid (mp 102-103 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$,

δ ppm) 7.36-7.30 (m, 5H), 7.29-7.27 (m, 1H), 7.19-7.15 (m, 2H), 7.08-6.99 (m, 4H), 6.78 (t, *J* = 7.3 Hz, 1H), 5.26 (dd, *J* = 12.3, 7.3 Hz, 1H), 3.85 (dd, *J* = 16.9, 12.3 Hz, 1H), 3.14 (dd, *J* = 16.9, 7.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 144.7, 142.9, 142.3, 129.2, 128.9, 127.6, 127.3, 126.5, 125.9, 124.9, 124.2, 119.2, 113.9, 64.7, 44.3; **MS (ESI): [M+H$^+$]** 305. Anal. Calcd for $C_{19}H_{16}SN_2$: C, 74.97; H, 5.30. Found: C, 74.75; H, 5.52.

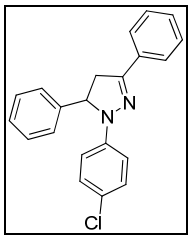


3-(1-Naphthalenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4la) Following the general procedure for the synthesis of dihydropyrazole, and compound **4la** was obtained in 76% yield as a yellow solid (mp 232-233 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.84-7.82 (m, 1H), 7.75-7.72 (m, 2H), 7.65-7.57 (m, 2H), 7.47-7.24 (m, 10H), 7.19-7.18 (m, 2H), 5.28 (dd, *J* = 12.3, 7.1 Hz, 1H), 4.04 (dd, *J* = 16.7, 12.3 Hz, 1H), 3.37 (dd, *J* = 16.7, 7.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 146.8, 144.7, 142.6, 136.8, 133.9, 130.4, 129.2, 128.9, 128.2, 127.8, 127.6, 126.4, 126.9, 125.6, 123.5, 119.2, 113.4, 64.6, 43.5; **MS (ESI): [M+H$^+$]** 349.

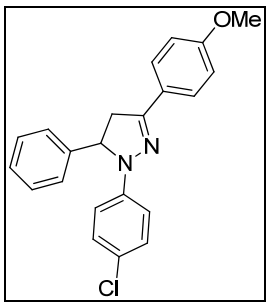


3-(2-Naphthalenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4ma). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ma** was obtained in 78% yield as a yellow solid (mp 256-257 ^{o}C)**. ^{1}H NMR** (500 MHz, $CDCl_3$,

δ ppm) 7.93-7.83 (m, 5H), 7.43-7.27 (m, 8H), 7.23-7.17 (m, 4H), 5.34 (dd, *J* = 12.2, 7.4 Hz, 1H), 3.97 (dd, *J* = 16.9, 12.4 Hz, 1H), 3.28 (dd, *J* = 16.7, 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 146.8, 144.7, 142.6, 133.4, 133.3, 130.4, 129.2, 128.9, 128.1, 127.8, 127.6, 126.4, 126.3, 125.0, 123.5, 119.2, 113.4, 64.6, 43.5; **MS (ESI): [M+H$^+$]** 349.

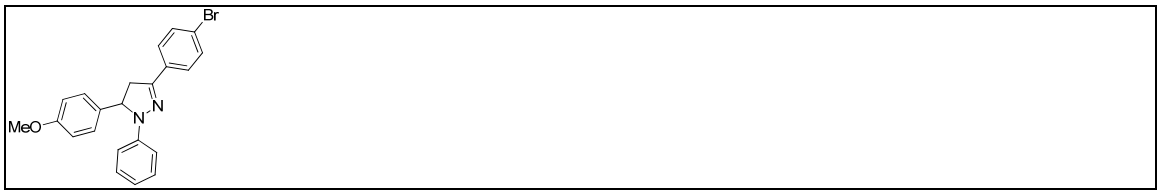


1-(4-Chlorophenyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (4aba). Following the general procedure for the synthesis of dihydropyrazole, and compound **4aba** was obtained in 86% yield as a yellow solid (mp 162-163 ^{o}C)**. ^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.71 (m, 2H), 7.47-7.26 (m, 8H), 7.11 (d, *J* = 9.1 Hz, 2H), 6.98 (d, *J* = 9.1 Hz, 2H), 5.25 (dd, *J* = 12.3, 7.1 Hz, 1H), 3.86 (dd, *J* = 17.1, 12.3 Hz, 1H), 3.16 (dd, *J* = 17.1, 7.1 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 148.5, 142.6, 141.8, 131.5, 129.6, 128.9, 128.6, 127.5, 125.6, 122.3, 114.2, 63.2, 43.3; **MS (ESI): [M+H$^+$]** 345.



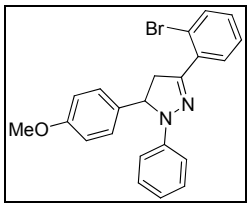
1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-5-phenyl-4,5-dihydropyrazole (4bba). Following the general procedure for the synthesis of dihydropyrazole, and compound **4bba** was obtained in 90% yield as a yellow solid (mp 168-170 ^{o}C). **^{1}H NMR** (500 MHz,

$CDCl_3$, δ ppm) 7.66 (d, *J* = 8.9 Hz, 2H), 7.35-7.27 (m, 5H), 7.10 (d, *J* = 9.1 Hz, 2H), 6.96 (d, *J* = 9.1 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 5.19 (dd, *J* = 12.2, 7.2 Hz, 1H), 3.84 (s, 3H), 3.81 (dd, *J* = 10.4, 1.8 Hz, 1H), 3.13 (dd, *J* = 17.0, 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 160.3, 147.4, 143.7, 142.2, 129.2, 128.7, 127.7, 127.3, 125.8, 125.2, 123.5, 114.3, 114.0, 64.4, 55.3, 43.9; **MS (ESI): [M+H$^+$]** 364. Anal. Calcd for $C_{22}H_{19}ClON_2$: C, 72.82; H, 5.28. Found: C, 72.65; H, 5.45.



3-(4-bromophenyl)-5-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole (4fb).

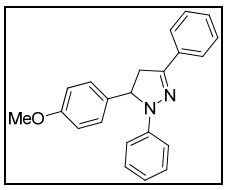
Following the general procedure for the synthesis of dihydropyrazole, and compound **4fb** was obtained in 85% yield as a yellow solid (mp 176-178 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.57 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.19 (m, 5H), 7.07 (d, *J* = 7.7 Hz, 2H), 6.86 (d, *J* = 7.7 Hz, 2H), 5.25 (dd, *J* = 12.4, 7.3 Hz, 1H), 3.80 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.78 (s, 3H), 3.08 (dd, *J* = 17.0, 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 147.6, 143.5, 139.9, 135.1, 132.5, 132.4, 130.2, 129.8, 128.4, 127.2, 123.8, 117.5, 113.8, 61.3, 55.5, 42.4; **MS (ESI): [M+H$^+$]** 407, 409.



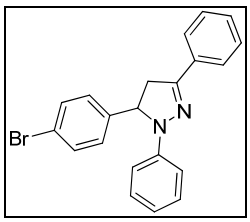
3-(2-bromophenyl)-5-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole (4hb).

Following the general procedure for the synthesis of dihydropyrazole, and compound **4hb** was obtained in 82 % yield as a yellow solid (mp 154-156 ^{o}C). **^{1}H NMR** (500

MHz, $CDCl_3$, δ ppm) 7.67 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.19-7.15 (m, 3H), 7.08-7.06 (m, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.24 (dd, *J* = 12.1, 7.3 Hz, 1H), 4.00 (dd, *J* = 17.3, 12.1 Hz, 1H), 3.77 (s, 3H), 3.31 (dd, *J* = 17.3, 7.3 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 158.9, 146.7, 144.7, 134.2, 134.1, 133.6, 130.4, 129.5, 128.9, 127.3, 127.1, 121.1, 119.4, 114.4, 113.6, 64.4, 55.2, 46.1; **MS (ESI): [M+H$^+$]** 407, 409; Anal. Calcd for $C_{22}H_{19}BrON_2$: C, 64.87; H, 4.70. Found: C, 65.05; H, 4.55.

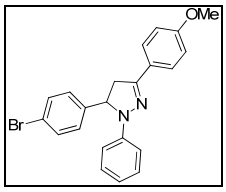


5-(4-methoxyphenyl)-1,3-diphenyl-4,5-dihydropyrazole (4ab). Following the general procedure for the synthesis of dihydropyrazole, and compound **4ab** was obtained in 87% yield as a yellow solid (mp 142-143 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.76 (d, *J* = 7.1 Hz, 2H), 7.45-7.35 (m, 5H), 7.25-7.13 (m, 5H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.24 (dd, *J* = 12.4, 7.0 Hz, 1H), 3.84 (dd, *J* = 17.0, 12.4 Hz, 1H), 3.79 (s, 3H), 3.13 (dd, *J* = 17.0, 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 159.4, 146.7, 145.5, 134.9, 133.5, 129.2, 128.7, 128.6, 127.2, 126.1, 119.5, 114.7, 114.0, 64.1, 54.6, 43.4; **MS (ESI): [M+H$^+$]** 329.



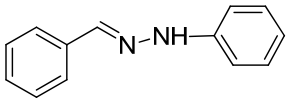
5-(4-bromophenyl)-1,3-diphenyl-4,5-dihydropyrazole (4ac). Following the general

procedure for the synthesis of dihydropyrazole, and compound **4aaa** was obtained in 81% yield as a yellow solid (mp 142-143 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.74 (d, *J* = 8.1 Hz, 2H), 7.48-7.34 (m, 6H), 7.24-7.19 (m, 4H), 7.07 (d, *J* = 8.7 Hz, 2H), 5.23 (dd, *J* = 12.4, 7.1 Hz, 1H), 3.83 (dd, 17.0, 12.4 Hz, 1H), 3.10 (dd, *J* = 17.0, 7.2 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 146.6, 144.5, 141.5, 132.4, 132.2, 128.9, 128.6, 128.5, 127.6, 125.6, 121.3, 119.3, 113.3 63.8, 43.3; **MS (ESI): [M+H^{+}]** 377, 379.



5-(4-bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole(4bc).

Following the general procedure for the synthesis of dihydropyrazole, and compound **4bc** was obtained in 83% yield as a yellow solid (mp 155-157 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 7.62 (d, *J* = 9.0 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 7.21-7.10 (m, 5H), 6.82 (d, *J* = 10.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 4.58 (dd, *J* = 12.5, 7.5 Hz, 1H), 3.29 (s, 3H), 3.03 (dd, *J* = 16.5, 12.5 Hz, 1H), 2.50 (dd, *J* = 17.0, 7.5 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 160.8, 146.7, 145.6, 142.1, 132.4, 129.3, 127.7, 125.9, 121.4, 119.6, 114.4, 113.8, 64.0, 54.8, 43.5; **MS (ESI): [M+H^{+}]** 407,409.



N-Benzylidene-N'-phenylhydrazine (6a). A yellow solid (mp 155-157 ^{o}C). **^{1}H NMR** (500 MHz, $CDCl_3$, δ ppm) 10.34 (s, 1H), 7.86 (s, 1H), 7.64 (m, 2H), 7.38 (m, 2H), 7.29-7.06 (m, 5H), 6.74 (m, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$, δ ppm) 145.6,

136.5, 135.7, 129.8, 128.6, 128.1, 125.7, 118.9, 112.3; **MS (ESI): [M+H$^+$]** 197.

References available for known products

No.	Products	Reference
1	1,3,5-Triphenyl-4,5-dihydro-1*H*-pyrazole **(4aa)**	[S1]
2	3-(4-Methoxyphenyl)-1,5-diphenyl-4,5-dihydropyrazole **(4ba)**	[S2]
3	1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-phenyl-4,5-dihydropyrazole **(4ca)**	NO
4	3-(2-Hydroxyphenyl)-1,5-diphenyl-4,5-dihydropyrazole **(4da)**	NA
5	3-(4-Chlorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4ea)**	[S3]
6	3-(4-Bromophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4fa)**	[S3]
7	3-(3-Bromophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4ga)**	[S4]
8	3-(2-Bromophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4ha)**	[S5]
9	3-(4-Fluorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4ia)**	[S6]
10	3-(2-Fluorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (**4ja**)	[S6]
11	1,5-Diphenyl-3-(2-thiophenyl)-4,5-dihydro-1*H*-pyrazole **(4ka)**	NA
12	3-(1-Naphthalenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4la)**	[S7]
13	3-(2-Naphthalenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4ma)**	[S8]
14	1-(4-Chlorophenyl)-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole **(4aba)**	[S9]
15	1-(4-Chlorophenyl)-3-(4-methoxyphenyl)-5-phenyl-4,5-dihydropyrazole **(4bba).**	NO
16	3-(4-Bromophenyl)-5-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole **(4fb)**	[S10]
17	3-(2-Bromophenyl)-5-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole **(4hb)**	NO
18	5-(4-Methoxyphenyl)-1,3-diphenyl-4,5-dihydropyrazole **(4ab)**	[S2]
19	5-(4-Bromophenyl)-1,3-diphenyl-4,5-dihydropyrazole **(4ac)**	[S11]
20	5-(4-Bromophenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole **(4bc)**.	[S12]
21	N-Benzylidene-N'-phenylhydrazine **(6a)**	[S13]

NA: Not available;
NO: No reference was found *via* SciFinder.

References:

[S1] M. Kidwai, S. Kukreja, R. Thakur, *Lett. Org. Chem.,* 2006, **3**, 135.

[S2] Y. -R. Huang and J. A. Katzenellenbogen, *Org. Lett.,* 2010, **18**, 2833.

[S3] R. Fazaeli, H. Aliyan, M. Bordbar, and E. Mohammadi, *Open Catalysis Journal*,

2010, **3**, 79.

[S4] R. Fazaeli, H.Aliyan, S. Mallakpour, Z. Rafiee, M. Bordbar, *Cuihua Xuebao*,

2011, **32**, 582.

[S5] X.-J. Liu, X.-L. Huang, W.-H. Lin, D.-Y. Wang, Y.-Y.Diao, H.-L.Li, X.-Y. Hui, Y. Wang, A.-M. Xu, D.-H. Wu, D. Ke, *Bioorg. Med. Chem Lett.,* 2011, **21**, 2949.

[S6] M. Verma, A. F. Chaudhry, C. J. Fahrni, *Org.Biomol. Chem.,* 2009, **7**, 1536.

[S7] L.-T. Kang, Y. Chen, D.-B. Xiao, A.-D. Peng, F.-G. Shen,; X. Kuang, H.-B. Fu, J.-N. Yao, *Chem. Commun.* 2007, 2695.

[S8] A. Levai, J. J. Jeko, *Heterocycl. Chem.,* 2006, **43**, 111.

[S9] X.-Y. Zhu, Z.-H. Li, C. Jin, L. Xu, Q.-Q. Wu and W.-K.Su, *Green Chem.,* 2009, **11**, 163.

[S10] V. D. Orlov, A. P. Shkumat, V. N. Kotlyar, *Visnik Kharkivs'kogo Universitetu*, 1999, **437**, 99.

[S11] Y. Chen, Y.-L. Lam, and Y.-H. Lai, *Org. Lett.,* 2003, **2**, 2833.

[S12] Y.-Z. Wang, C. I. Rivera Vera,. Q. Lin, *Org. Lett.,* 2007, **9**, 4155.

[S13]R. J. Lundgren and M.Stradiotto, *Angew. Chem. Int. Ed.* 2010, **49**, 8686.

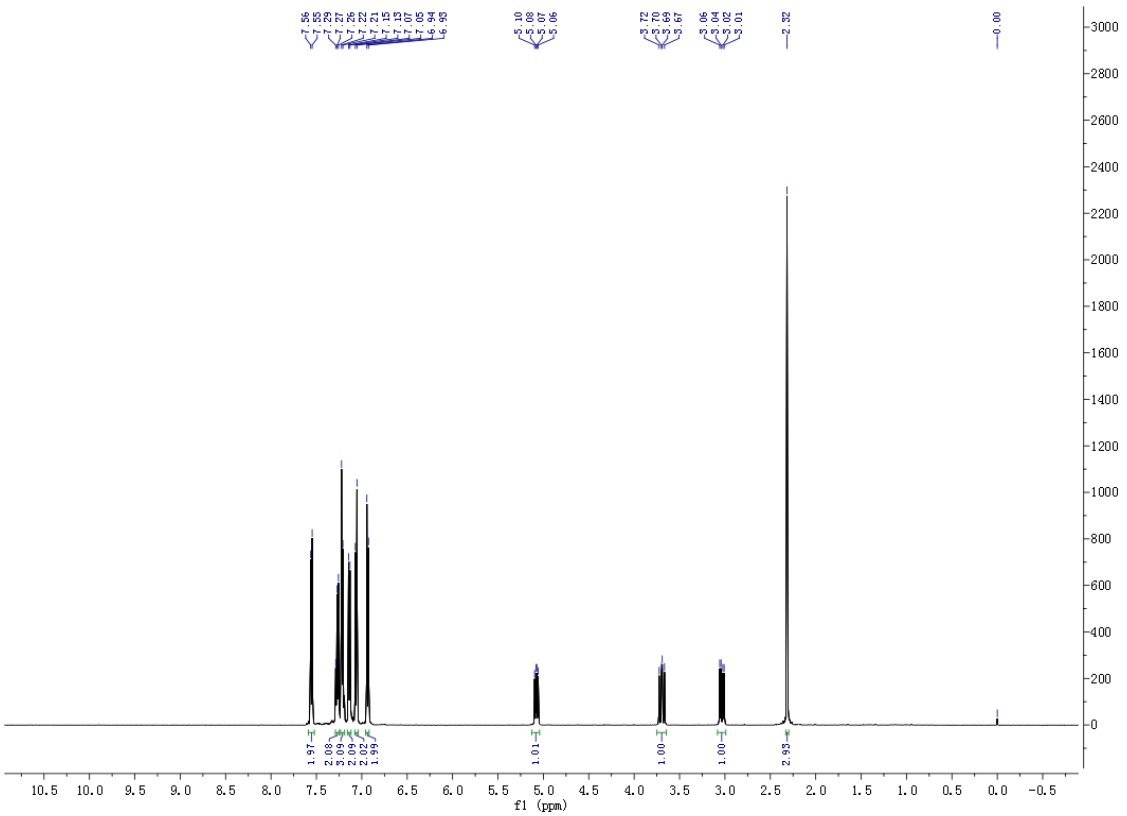


Figure 1. [1]H NMR of 1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-phenyl-4,5-dihydropyrazole (**4ca**).

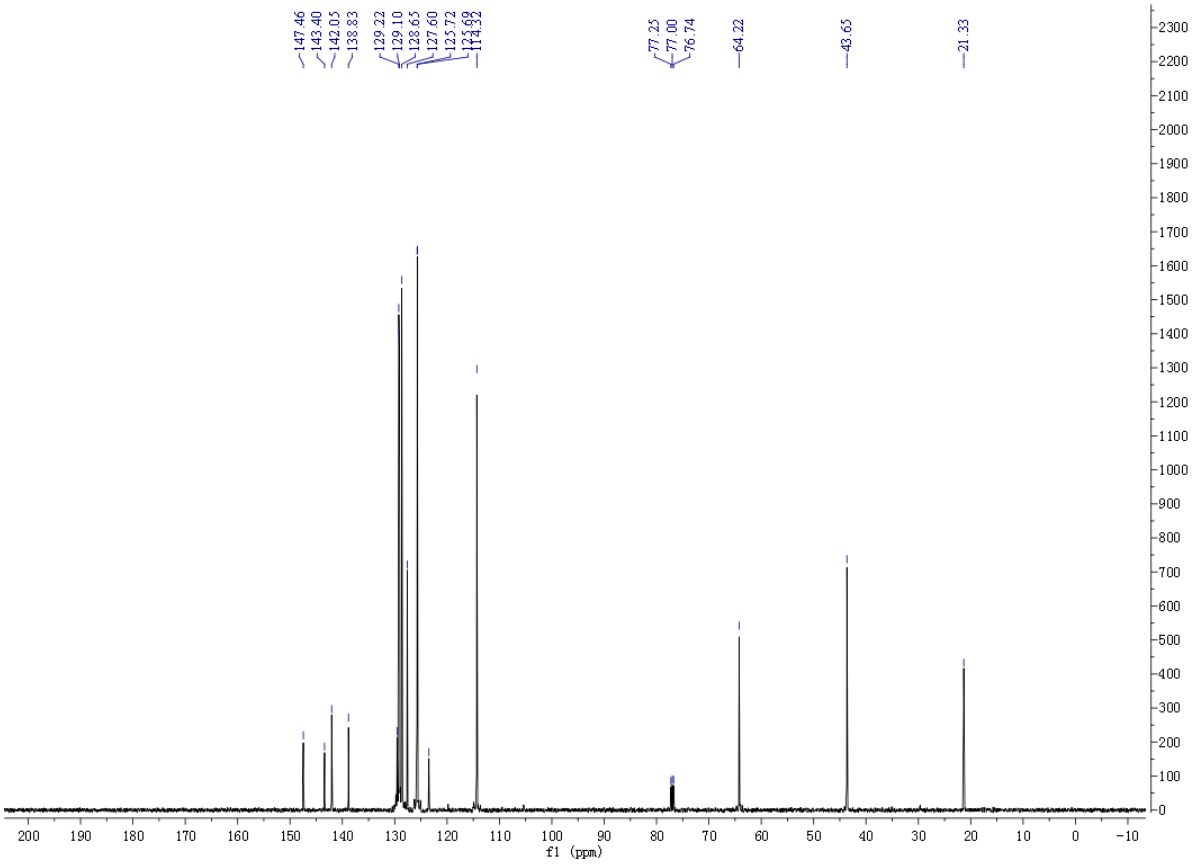


Figure 2. [13]C NMR of 1-(4-Chlorophenyl)-3-(4-methylphenyl)-5-phenyl-4,5-dihydropyrazole (**4ca**).

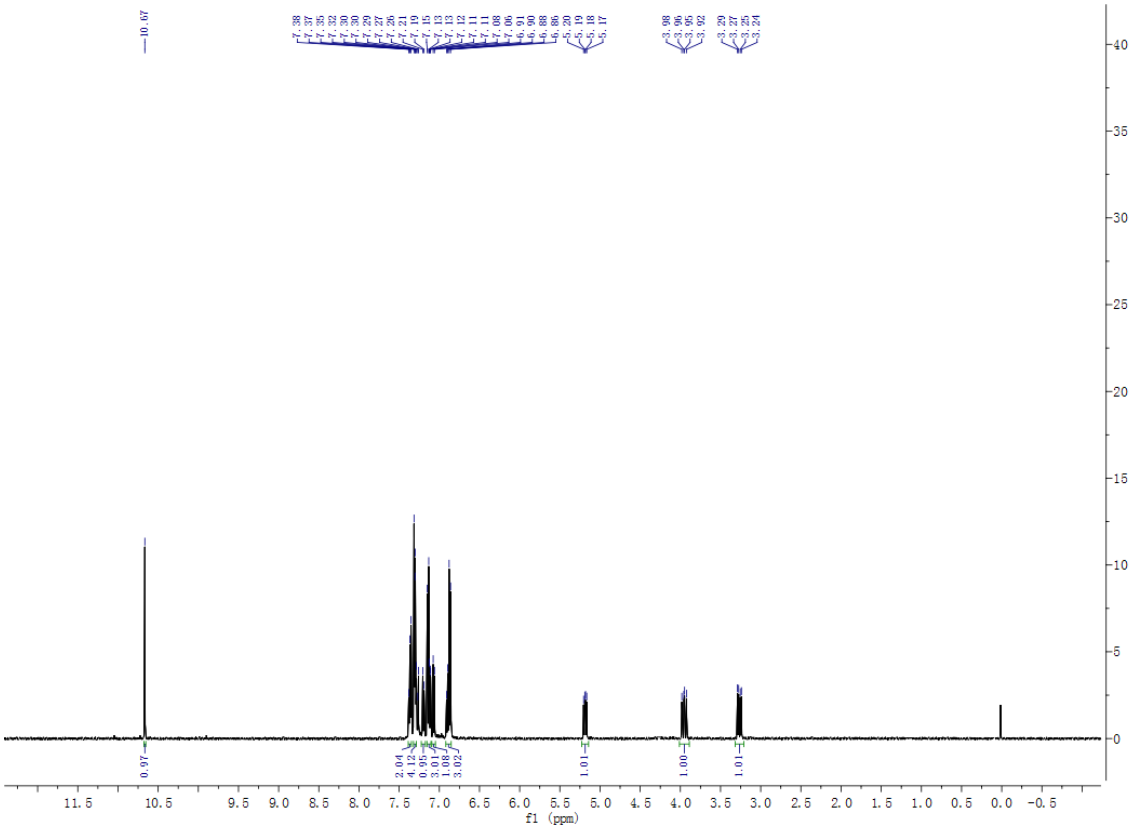


Figure 3. [1]H NMR of 3-(2-Hydroxyphenyl)-1,5-diphenyl-4,5-dihydropyrazole **(4da).**

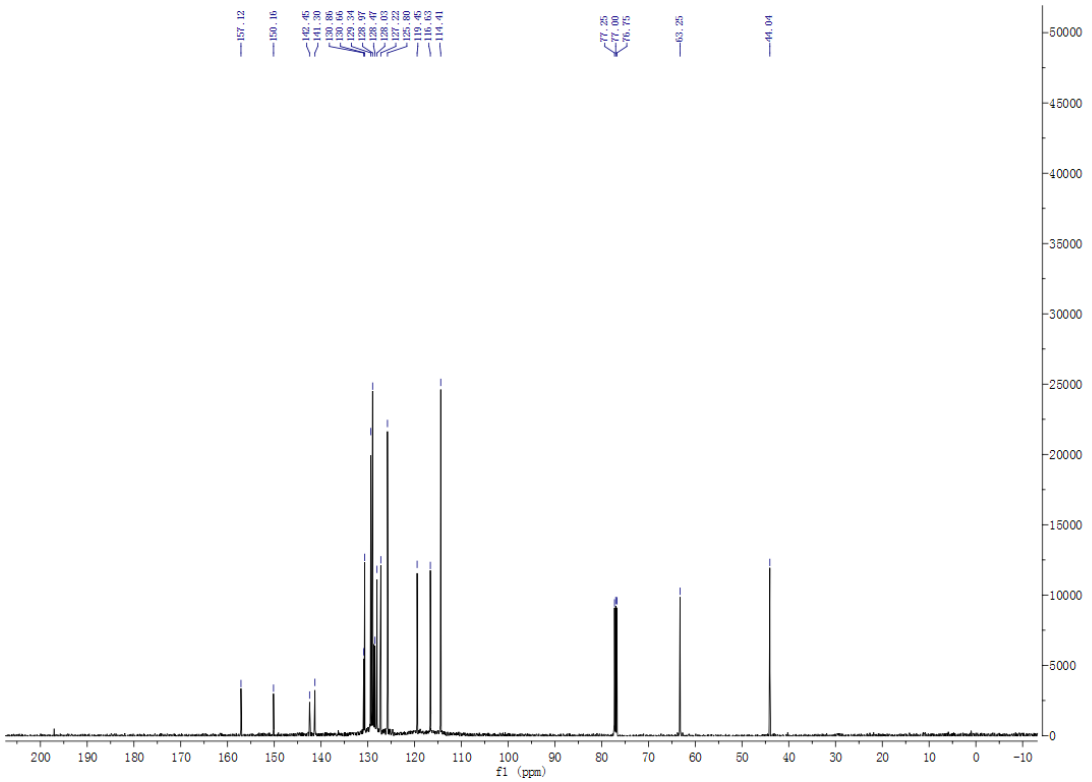


Figure 4. [13]C NMR of 3-(2-Hydroxyphenyl)-1,5-diphenyl-4,5-dihydropyrazole **(4da).**

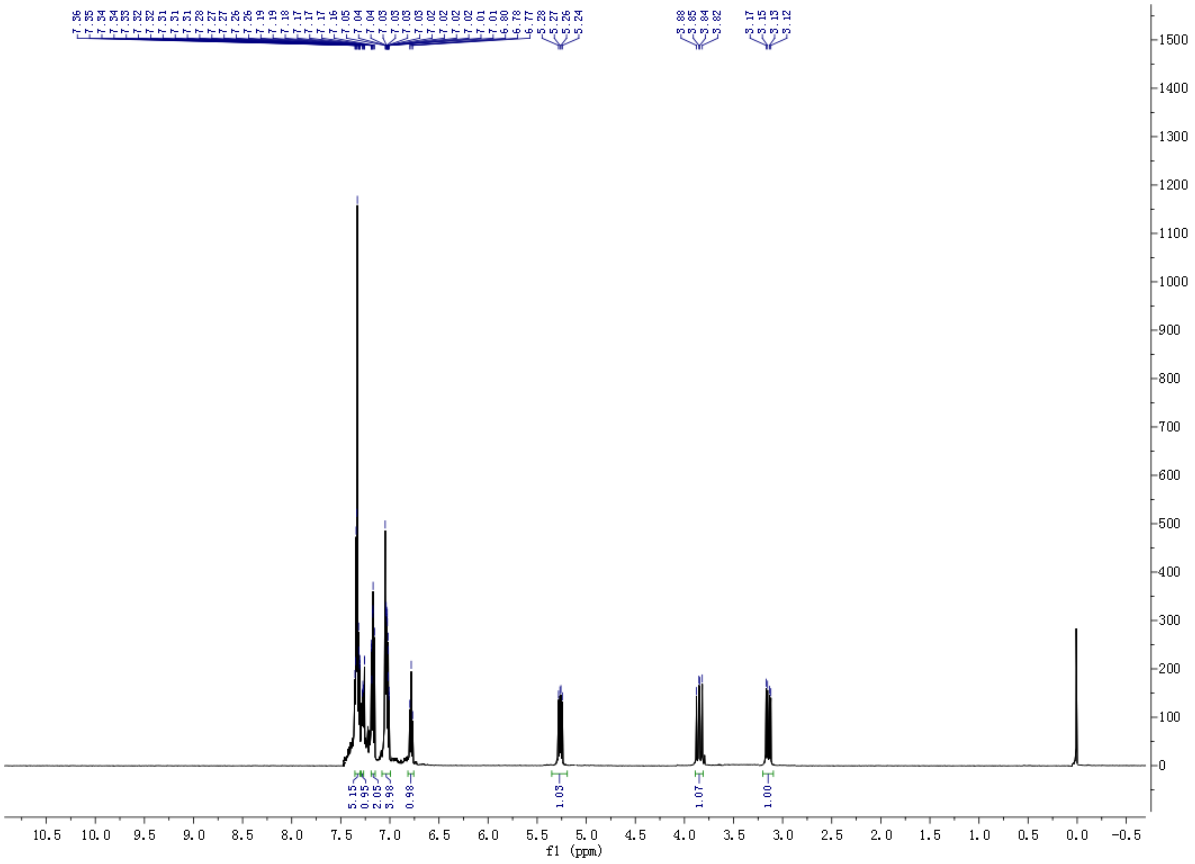


Figure 5. ^{1}H NMR of 1,5-Diphenyl-3-(2-thiophenyl)-4,5-dihydro-1*H*-pyrazole **(4ka).**

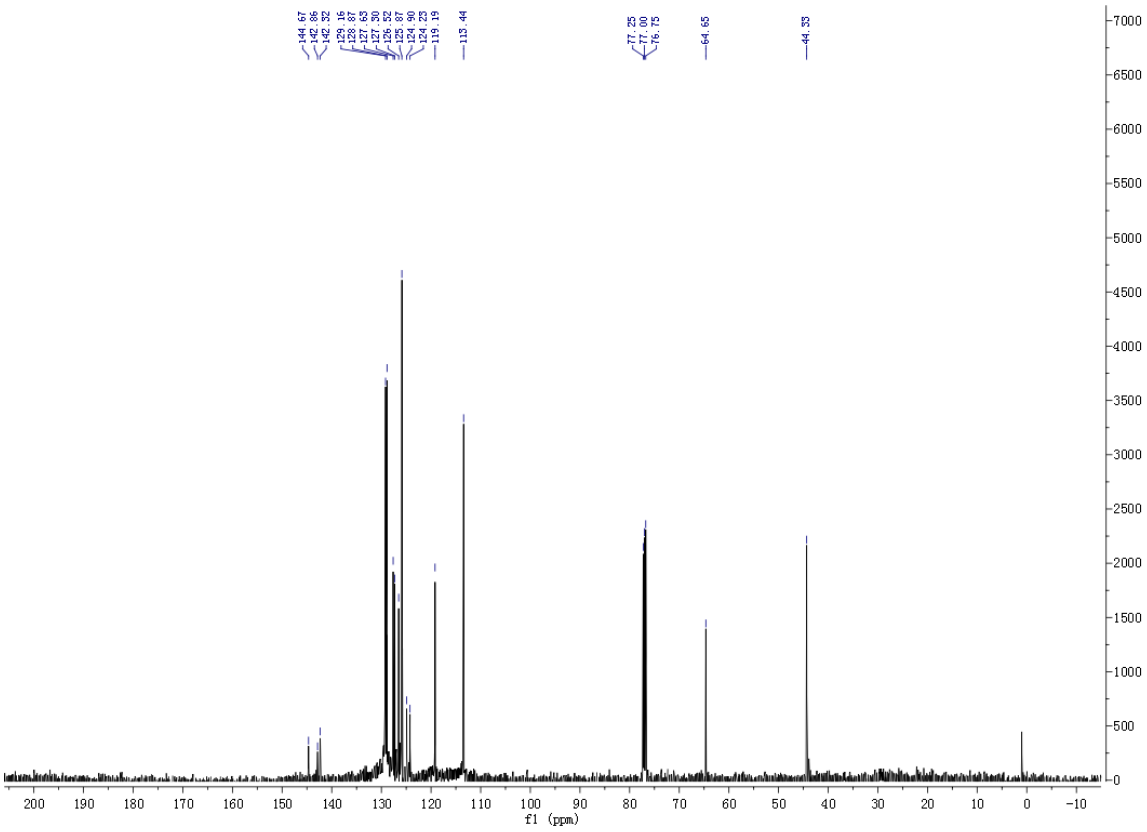


Figure 6. ^{13}C NMR of 1,5-Diphenyl-3-(2-thiophenyl)-4,5-dihydro-1*H*-pyrazole **(4ka).**

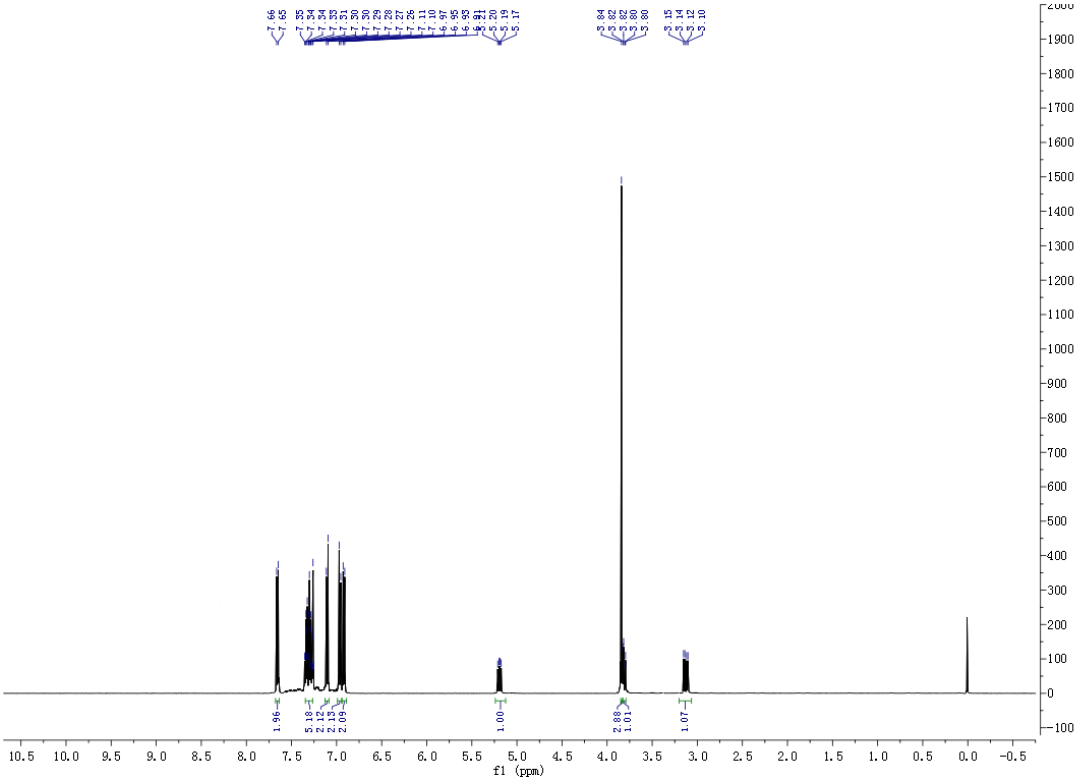


Figure 7. ^{1}H NMR of 1-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-phenyl-4,5-dihydropyrazole **(4bba).**

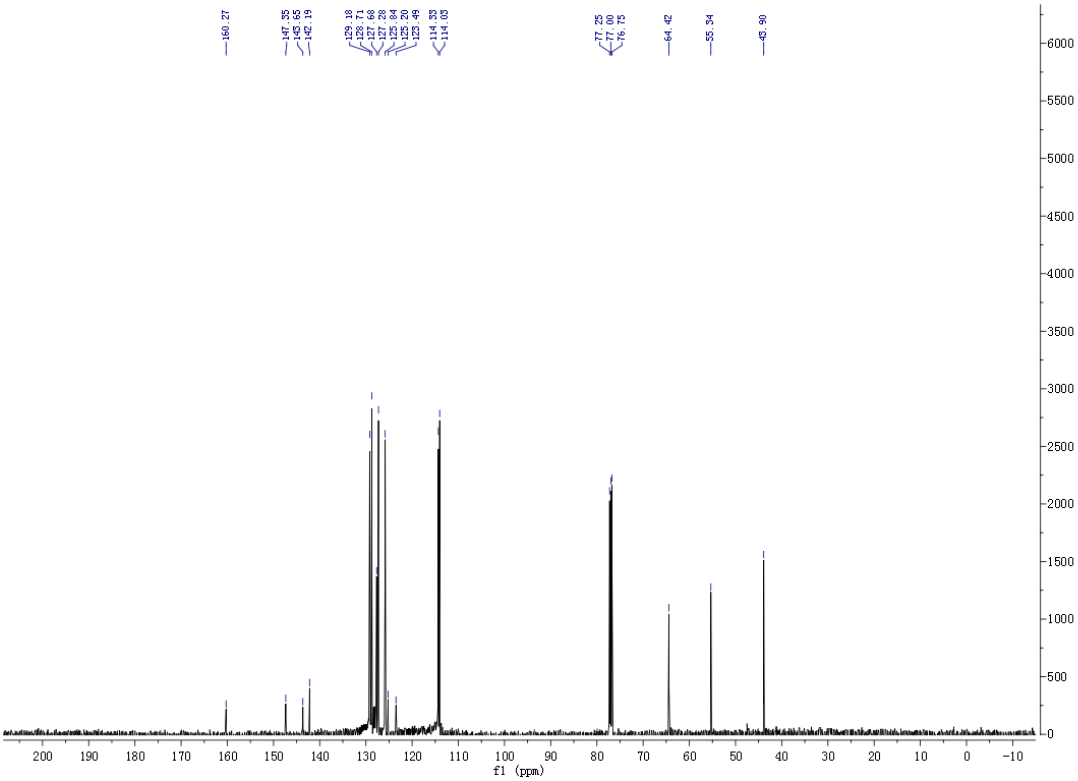


Figure 8. ^{13}C NMR of 1-(4-chlorophenyl)-3-(4-methoxyphenyl)-5-phenyl-4,5-dihydropyrazole **(4bba).**

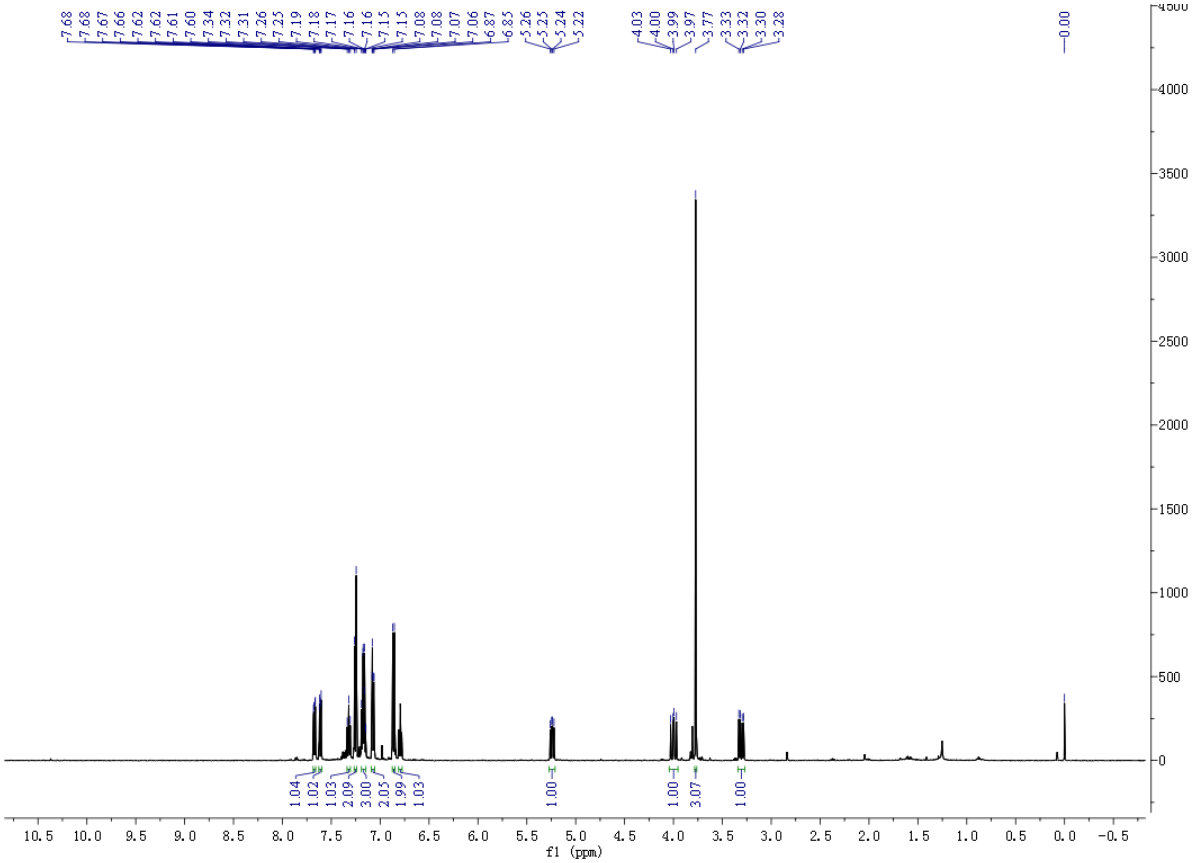


Figure 9. [1]H NMR of 3-(2-bromophenyl)-5-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole **(4hb).**

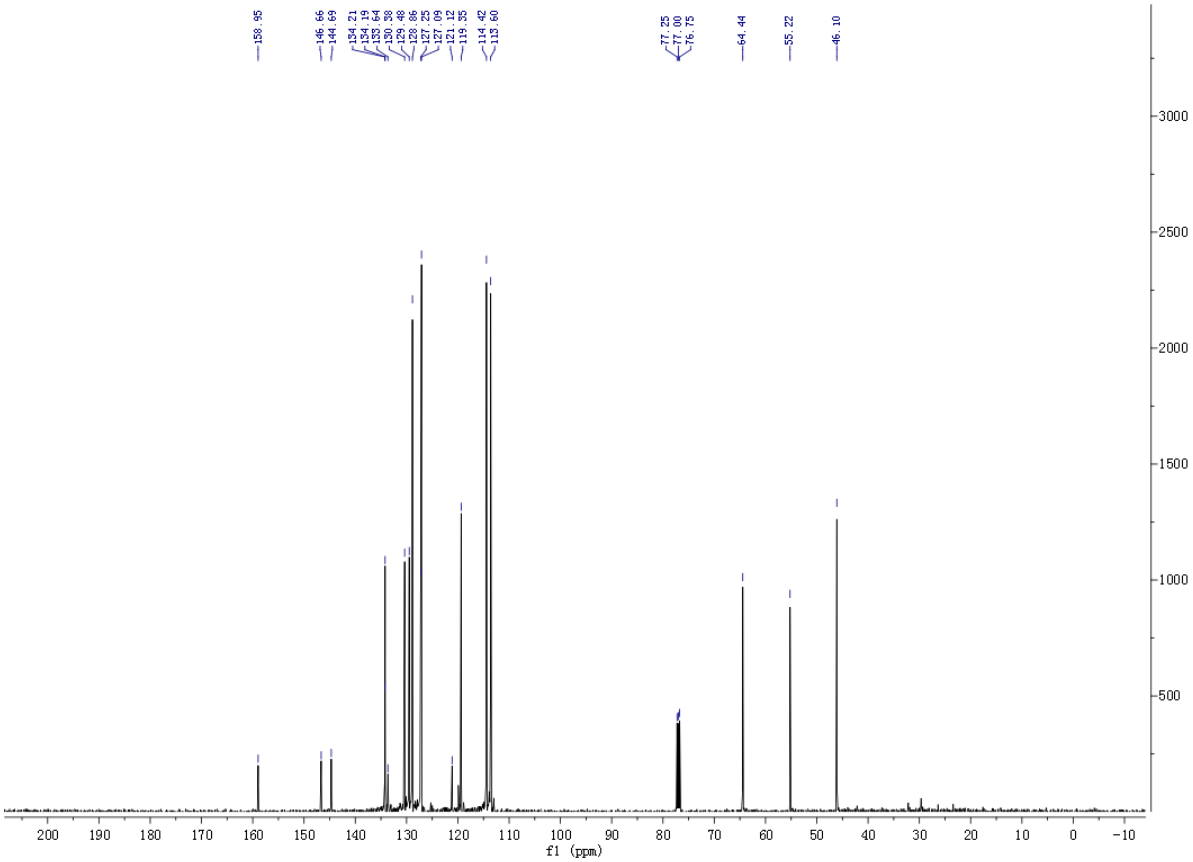


Figure 10. [13]C NMR of 3-(2-bromophenyl)-5-(4-methoxyphenyl)-1-phenyl-4,5-dihydropyrazole **(4hb).**