Electronic Supplementary Material (ESI) for Chemical Communications

Single-Step Synthesis of Pyrazoles Using Titanium Catalysis

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Supplementary Information

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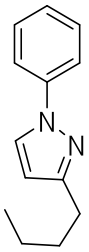
General Considerations: All manipulations of air sensitive compounds were carried out in an MBraun drybox under a purified nitrogen atmosphere. Toluene was purified by sparging with dry N_2 and removing water by running through activated alumina systems purchased from Solv-Tek. ^{1}H and ^{13}C spectra were recorded on Varian VXR-500 spectrometers. Melting points were measured on a Mel-Temp II apparatus with a mercury thermometer and are uncalibrated. 2-(3,5-dimethyl-1H-pyrrol-2-yl)pyridine[1] and cyclohexylisonitrile[2] were made according to the literature procedures. Alkynes were purchased either from Aldrich or from GFS chemicals and were distilled from CaO under dry nitrogen. Phenylhydrazine was purchased from Aldrich, dried over KOH, and distilled under dry nitrogen. (4-bromophenyl)hydrazine, (4-iodophenyl)hydrazine, (4-methoxyphenyl)hydrazine, *p*-tolylhydrazine, and (3,5-dichlorophenyl)hydrazine were made using the typical literature procedure.[3] Neutral alumina was purchased from Sigma-Aldrich Co. and used as received. Hexanes and EtOAc was purchased from Mallinckrodt chemicals and used as received. Anhydrous NH_2NH_2 was prepared using the literature procedure.[4]

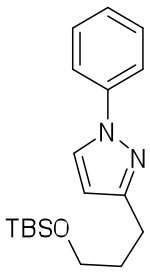
Preparation and Characterization of Compounds

$Ti(NMe_2)_2(pypyr)_2$: A Schlenk flask (250 mL) was loaded with $Ti(NMe_2)_4$ (2.11 g, 9.4 mmol) in toluene (6 mL) and cooled until frozen inside a nitrogen-cooled cold-well. The frozen solution was allowed to warm until stirring, and then a cold toluene (8 mL) solution of 2-(2'-pyridyl)-3,5-dimethylpyrrole (Hpypyr) (3.23 g, 18.8 mmol) was added. The reaction was allowed to warm up to room temperature, was fitted with a septum, removed from the box, and was placed is a 60 °C oil bath to stir for 48 h. The reaction mixture was cooled to room temperature, and volatiles were removed under reduced pressure. The red solid was crystallized from ether/pentane (3.92 g, 7.8 mmol, 84%). M.p.: 199-201 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 2.36 (6 H, s, CH_3), 2.57 (6 H, s, CH_3), 3.19 (12 H, s, $N(CH_3)_2$), 6.0 (2 H, s, 4-CH pyrrole), 6.43-6.46 (2 H, m, Ar-H), 6.99-7.01 (2 H, m, Ar-H), 7.19-7.21 (2 H, m, Ar-H), 7.27-

7.31 (2 H, m, Ar-H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): 14.65, 16.04, 47.66, 113.37, 116.01,116.50, 122.03, 132.53, 136.78, 140.92, 146.79, 154.06.

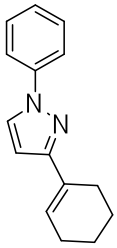


3-butyl-1-phenyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 1-hexyne (82 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (132 mg, 66%) as a yellow oil.[5] ^{1}H NMR ($CDCl_3$, 500 MHz): 0.94 (3 H, t, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.39-1.43 (2 H, m, $CH_2CH_2CH_2CH_3$), 1.64-1.69 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.71 (2 H, t, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 6.23-6.24 (1 H, d, J = 2 Hz, 4-C*H*-pyrazole), 7.18-7.23 (1 H, m, Ar-H), 7.38-7.41 (2 H, m, Ar-H), 7.62-7.64 (2 H, m, Ar-H), 7.79-7.78 (1 H, d, J = 2 Hz, 5-C*H*-pyrazole). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): 13.89, 22.49, 28.10, 31.78, 106.39, 118.86, 125.82, 127.11, 129.29, 140.28, 155.37. MS(EI): m/z 200 (M^+).



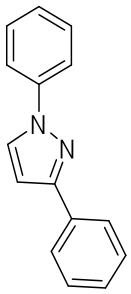
3-(3-(tert-butyldimethylsilyloxy)propyl)-1-phenyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol),

phenylhydrazine (108 mg, 1 mmol), *tert*-butyldimethylsilyloxy-4-pentyne (198 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (224 mg, 71%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.04 (6 H, s, Si-C*H*$_3$), 0.88 (9 H, s, Si-CMe$_2$C*H*$_3$), 1.90-1.93 (2 H, m, CH$_2$C*H*$_2$CH$_2$OTBS), 2.75-2.78 (2 H, t, *J* = 7.5 Hz, C*H*$_2$CH$_2$CH$_2$OTBS), 3.68-3.71 (2 H, t, *J* = 6 Hz, CH$_2$CH$_2$C*H*$_2$OTBS), 6.24-6.25 (1 H, d, *J* = 2 Hz, 4-C*H* pyrazole), 7.22-7.24 (1 H, m, Ar-*H*), 7.38-7.42 (2 H, m, Ar-*H*), 7.62-7.64 (2 H, m, Ar-*H*), 7.79-7.80 (1 H, d, *J* = 2 Hz, 5-C*H* pyrazole). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): 1.01, 18.36, 24.73, 25.27, 25.94, 32.56, 62.64, 106.54, 118.86, 125.88, 127.18, 127.44, 129.32, 154.81.

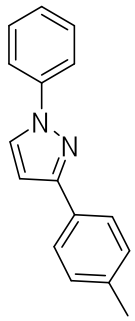


3-cyclohexenyl-1-phenyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 1-ethynylcyclohex-1-ene (106 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (123 mg, 55%) as a yellow oil.[6] ^{1}H NMR ($CDCl_3$, 500 MHz): 1.63-1.67 (2 H, m, C*H*$_2$), 1.72-1.77 (2 H, m, C*H*$_2$), 2.17-2.21 (2 H, m, C*H*$_2$), 2.49-2.53 (2 H, m, C*H*$_2$), 6.35-6.37 (1 H, m, C*H*), 6.46-6.47 (1 H, d, *J* = 2 Hz, 4-C*H*-pyrazole), 7.18-7.36 (1 H, m, Ar-H), 7.37-7.41 (2 H, m, Ar-H), 7.64-7.66 (2 H, m, Ar-H), 7.79-7.80 (1 H, d, *J* = 2 Hz, 5-C*H*-pyrazole).

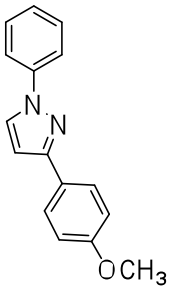
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): 22.32, 22.60, 25.54, 25.85, 103.79, 118.78, 125.33, 125.85, 127.19, 129.29, 130.56, 140.33, 154.97. MS(EI): m/z 224 (M^+).



1,3-diphenyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), phenylacetylene (102 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (105 mg, 48%) as a yellow solid. M.p.: 83-84 °C (Lit M.p.: 84-86).[7] ^{1}H NMR ($CDCl_3$, 500 MHz): 6.76-6.77 (1 H, d, *J* = 2 Hz, 4-C*H*-pyrazole), 7.26-7.29 (2 H, m, Ar-H), 7.31-7.34 (2 H, m, Ar-H), 7.40-7.47 (4 H, m, Ar-H), 7.75-7.77 (2 H, m, Ar-H), 7.90-7.92 (2 H, m, Ar-H), 7.93-7.94 (1 H, d, *J* = 2, Hz, 5-C*H*-pyrazole). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): 104.97, 105.04, 119.03, 125.84, 126.31, 127.92, 128.41, 128.63, 133.13, 140.24, 152.92. MS(EI): m/z 220 (M^+).

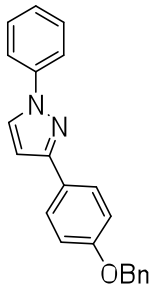


1-phenyl-3-p-tolyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 1-ethynyl-4-methylbenzene (116 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (107 mg, 46%) as a yellow solid. M.p.: 92-94°C (Lit M.p.: 95.5-96).[8] ^{1}H NMR ($CDCl_3$, 500 MHz): 2.43 (3 H, s, CH_3), 6.78-6.79 (1 H, d, J = 4 Hz, 4-C*H* pyrazole), 7.27-7.32 (3 H, m, Ar-*H*), 7.47-7.52 (2 H, m, Ar-*H*), 7.79-7.87 (4 H, m, Ar-*H*), 7.97-7.98 (1 H, d, J = 4 Hz, 5-C*H* pyrazole). ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): 21.29, 104.82, 118.97, 125.51, 125.70, 126.18, 127.85, 129.32, 129.37, 130.30, 137.78, 152.96. MS(EI): m/z 234 (M^+).

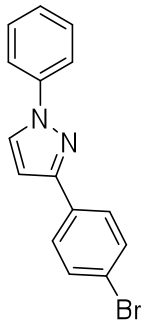


*1-phenyl-4-(4-methoxyphenyl)pyrazole***:** In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 4-methoxyphenylacetylene (132 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was

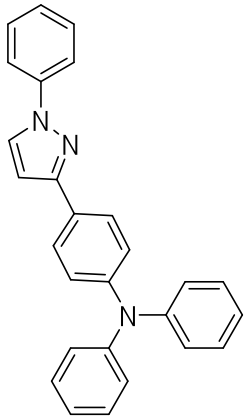
cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (150 mg, 60%) as a yellow solid. M.p.: 100-102 °C (Lit M.p.: 103-104).[9] ^{1}H NMR ($CDCl_3$, 500 MHz): 3.84 (3 H, s, OC*H*$_3$), 6.68-6.69 (1 H, d, J = 2.5 Hz, 4-C*H* pyrazole), 6.94-6.96 (2 H, d, J = 12 Hz, Ar-*H*), 7.24-7.27 (1 H, m, Ar-*H*), 7.42-7.46 (2 H, m, Ar-*H*), 7.74-7.75 (2 H, d, J = 8.5 Hz, Ar-*H*), 7.82-7.85 (2 H, d, *J* = 12 Hz, Ar-*H*), 7.91-7.92 (1 H, d, J = 2.5 Hz, 5-C*H* pyrazole). ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): 55.32, 104.57, 114.03, 118.95, 125.89, 126.16, 127.09, 127.88, 129.38, 140.24, 152.75, 159.59. MS(EI): m/z 250 (M^+).



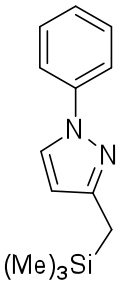
3-(4-(benzyloxy)phenyl)-1-phenyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 1-(benzyloxy)-4-ethynylbenzene (208 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (122 mg, 49%) as a brown solid. M.p.: 116-118 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 5.13 (2 H, s, CH_2), 6.68-6.69 (1 H, d, J = 2.5 Hz, 4-C*H* pyrazole), 7.03-7.04 (2 H, m, Ar-*H*), 7.26-7.28 (1 H, m, Ar-*H*), 7.33-7.37 (1 H, m, Ar-*H*), 7.37-7.43 (2 H, m, Ar-*H*), 7.43-7.46 (4 H, m, Ar-*H*), 7.74-7.76 (2 H, m, Ar-*H*), 7.82-7.85 (2 H, m, Ar-*H*), 7.91-7.92 (1 H, d, J = 2.5 Hz, 5-C*H* pyrazole). ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): 70.02, 104.58, 114.99, 118.92, 126.15, 127.10, 127.49, 127.88, 127.96, 128.57, 129.37, 136.92, 140.20, 152.69, 158.79. MS(EI): m/z 326 (M^+). Elemental Analysis: Found (Expected): %C, (80.96) 80.82; %H, (5.56) 5.72; %N, (8.58) 8.66.



3-(4-bromophenyl)-1-phenyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 1-bromo-4-ethynylbenzene (181 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (179 mg, 60%) as a brown solid. M.p.: 124-126 °C (Lit M.p.: 128).[10] ^{1}H NMR ($CDCl_3$, 500 MHz): 6.73-6.74 (1 H, d, J = 2.5 Hz, 4-C*H* pyrazole), 7.24-7.27 (1 H, m, Ar-*H*), 7.44-7.47 (2 H, m, Ar-*H*), 7.53-7.54 (2 H, m, Ar-*H*), 7.73-7.78 (4 H, m, Ar-*H*), 7.93-7.94 (1 H, d, J = 2.5 Hz, 5-C*H* pyrazole). ^{13}C $\{^1$H$\}$ NMR ($CDCl_3$, 125 MHz): 104.95, 114.06, 119.08, 125.96, 126.52, 127.35, 127.91, 128.18, 129.13, 129.45, 131.75. MS(EI): m/z 299 (M^+). Elemental Analysis: Found (Expected): %C, (60.22) 59.84; %H, (3.71) 3.62; %N, (9.36) 9.51.

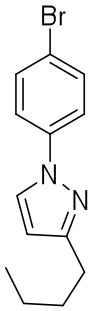


N,N-diphenyl-4-(1-phenyl-pyrazol-3-yl)aniline: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108 mg, 1 mmol), 4-ethynyl-N,N-diphenylaniline (269 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (182 mg, 47%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 6.63-6.64 (1 H, d, J = 2.5 Hz, 4-C*H* pyrazole), 6.94-6.97 (2 H, m, Ar-*H*), 7.05-7.07 (6 H, m, Ar-*H*), 7.17-7.21 (7 H, m, Ar-*H*), 7.37-7.39 (2 H, m, Ar-*H*), 7.67-7.71 (4 H, m, Ar-*H*), 7.86-7.87 (1 H, d, J = 2.5 Hz, 5-C*H* pyrazole). ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): 104.74, 114.07, 118.90, 122.87, 123.88, 124.35, 125.97, 127.38, 127.92, 129.24, 129.39, 139.27, 140.22, 147.64, 152.70. MS(EI): m/z 387 (M^+). Elemental Analysis: Found (Expected): %C, (83.69) 83.74; %H, (5.46) 5.32; %N, (10.84) 10.94.



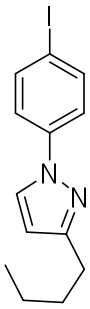
1-phenyl-3-((trimethylsilyl)methyl)-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), phenylhydrazine (108

mg, 1 mmol), trimethyl(prop-2-ynyl)silane (112 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (172 mg, 75%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.07 (9H, s, Si-CH_3), 2.15 (2 H, 2, CH_2), 6.09-6.10 (1 H, d, J = 2 Hz, 4-C*H* pyrazole), 7.18-7.23 (1 H, m, Ar-*H*), 7.37-7.41 (2 H, m, Ar-*H*), 7.61-7.64 (2 H, m, Ar-*H*), 7.75-7.76 (1 H, d, J = 2 Hz, 5-C*H* pyrazole). ^{13}C {^{1}H} NMR ($CDCl_3$, 125 MHz): -1.65, 18.44, 106.84, 118.52, 125.48, 126.92, 129.24, 129.45, 140.29, 152.63. MS(EI): m/z 230 (M^+). Elemental Analysis: Found (Expected): %C, (67.77) 67.54; %H, (7.88) 7.79; %N, (12.16) 12.33.

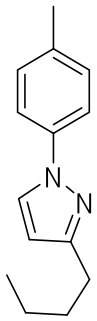


1-(4-bromophenyl)-3-butyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), (4-bromophenyl)hydrazine (187 mg, 1 mmol), hex-1-yne (82 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (145 mg, 52%) as a brown oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.94 (3 H, t, *J* = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.38-1.42 (2 H, m, $CH_2CH_2CH_2CH_3$), 1.64-1.69 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.68 (2 H, t, *J* = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 6.24-6.25 (1 H, d, *J* = 2 Hz, 4-C*H*-pyrazole), 7.51-7.53 (4 H, m, Ar-H), 7.75-7.76 (1 H, d, *J* = 2 Hz, 5-C*H*-pyrazole). ^{13}C{^{1}H} NMR ($CDCl_3$,

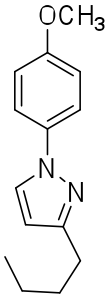
125 MHz):13.90, 22.49, 28.07, 29.69, 31.69, 106.92, 11.87, 120.20, 127.03, 132.32, 139.26, 155.78. MS(EI): m/z 279 (M^+). Elemental Analysis: Found (Expected): %C, (55.93) 56.04; %H, (5.72) 5.63; %N, (10.03) 10.18.



3-butyl-1-(4-iodophenyl)-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), (4-iodophenyl)hydrazine (234 mg, 1 mmol), hex-1-yne (82 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (202 mg, 62%) as a brown oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.93 (3 H, t, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.36-1.43 (2 H, m, $CH_2CH_2CH_2CH_3$), 1.62-1.69 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.68 (2 H, t, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 6.24-6.25 (1 H, d, J = 2.5 Hz, 4-C*H*-pyrazole), 7.39-7.42 (2 H, m, Ar-H), 7.69-7.71 (2 H, m, Ar-H), 7.76-7.77 (1 H, d, J = 2.5 Hz, 5-C*H*-pyrazole). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): 13.90, 22.49, 28.07, 29.69, 89.62, 106.96, 120.45, 126.95, 138.26, 139.92, 155.82. MS(EI): m/z 326 (M^+). Elemental Analysis: Found (Expected): %C, (47.87) 47.58; %H, (4.64) 4.73; %N, (8.59) 8.72.

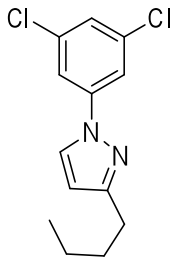


3-butyl-1-p-tolyl-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), *p*-tolylhydrazine (122 mg, 1 mmol), hex-1-yne (82 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (122 mg, 57%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.93 (3 H, t, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.36-1.43 (2 H, m, $CH_2CH_2CH_2CH_3$), 1.62-1.69 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.35 (3 H, s, CH_3), 2.70 (2 H, t, J = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 6.21-6.22 (1 H, d, J = 2.5 Hz, 4-C*H*-pyrazole), 7.18-7.20 (2 H, d, J = 8.5 Hz, Ar-H), 7.50-7.52 (2 H, d, J = 8.5 Hz, Ar-H), 7.74-7.75 (1 H, d, J = 2.5 Hz, 5-C*H*-pyrazole). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): 13.19, 20.86, 22.52, 28.10, 31.85, 106.05, 118.86, 127.08, 129.80, 135.56, 138.05, 155.06. MS(EI): m/z 214 (M^+). Elemental Analysis: Found (Expected): %C, (78.46) 78.23; %H, (8.47) 8.64; %N, (13.07) 13.13.



3-butyl-1-(4-methoxyphenyl)-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), *p*-tolylhydrazine (122 mg, 1

mmol), hex-1-yne (82 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (161 mg, 70%) as a brown oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.93 (3 H, t, *J* = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.39-1.41 (2 H, m, $CH_2CH_2CH_2CH_3$), 1.62-1.69 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.69 (2 H, t, *J* = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 3.81 (3 H, s, OCH_3), 6.20-6.21 (1 H, d, *J* = 2.5 Hz, 4-C*H*-pyrazole), 6.91-6.93 (2 H, d, J = 9 Hz, Ar-H), 7.51-7.53 (2 H, d, J = 9 Hz, Ar-H), 7.74-7.75 (1 H, d, *J* = 2.5 Hz, 5-C*H*-pyrazole). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): 13.93, 22.53, 28.07, 31.89, 55.54, 105.88, 114.41, 120.63, 127.26, 154.92, 157.84. MS(EI): m/z 230 (M^+). Elemental Analysis: Found (Expected): %C, (73.01) 73.19; %H, (7.88) 7.62; %N, (12.16) 12.30.



3-butyl-1-(3,5-dichlorophenyl)-pyrazole: In a N_2 filled glove box, a 40 mL pressure tube, equipped with a magnetic stirbar was loaded with cyclohexylisonitrile (186 µL, 1.5 mmol), (3,5-dichlorophenyl)hydrazine (177 mg, 1 mmol), hex-1-yne (82 mg, 1 mmol), and $Ti(NMe_2)_2(pypyr)_2$ (71.7 mg, 0.15 mmol) in dry toluene (2 mL). The vessel was heated for 36 h at 100 °C in a silicone oil bath. The pressure tube was cooled to room temperature, and volatiles were removed under reduced pressure. Purification was accomplished by column chromatography on neutral alumina. The eluent was hexanes:ethyl acetate 9:1, which afforded the desired compound (121 mg, 45%) as a brown oil. ^{1}H NMR ($CDCl_3$, 500 MHz): 0.93 (3 H, t, *J* = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 1.36-1.41 (2 H, m, $CH_2CH_2CH_2CH_3$), 1.62-1.66 (2 H, m, $CH_2CH_2CH_2CH_3$), 2.69 (2 H, t, *J* = 7.5 Hz, $CH_2CH_2CH_2CH_3$), 6.24-6.25 (1 H, d, *J* = 2Hz, 4-C*H*-pyrazole), 7.15-7.16 (1 H, m, Ar-H), 7.54-7.55 (2 H, m, Ar-H), 7.72-7.73 (1 H, d, *J* = 2 Hz, 5-C*H*-

pyrazole). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): 13.84, 22.41, 27.98, 31.48, 107.56, 116.82, 125.36, 127.06, 135.65, 141.51, 156.29. MS(EI): m/z 269 (M^+). Elemental Analysis: Found (Expected): %C, (58.01) 58.19; %H, (5.24) 5.11; %N, (10.41) 10.69.

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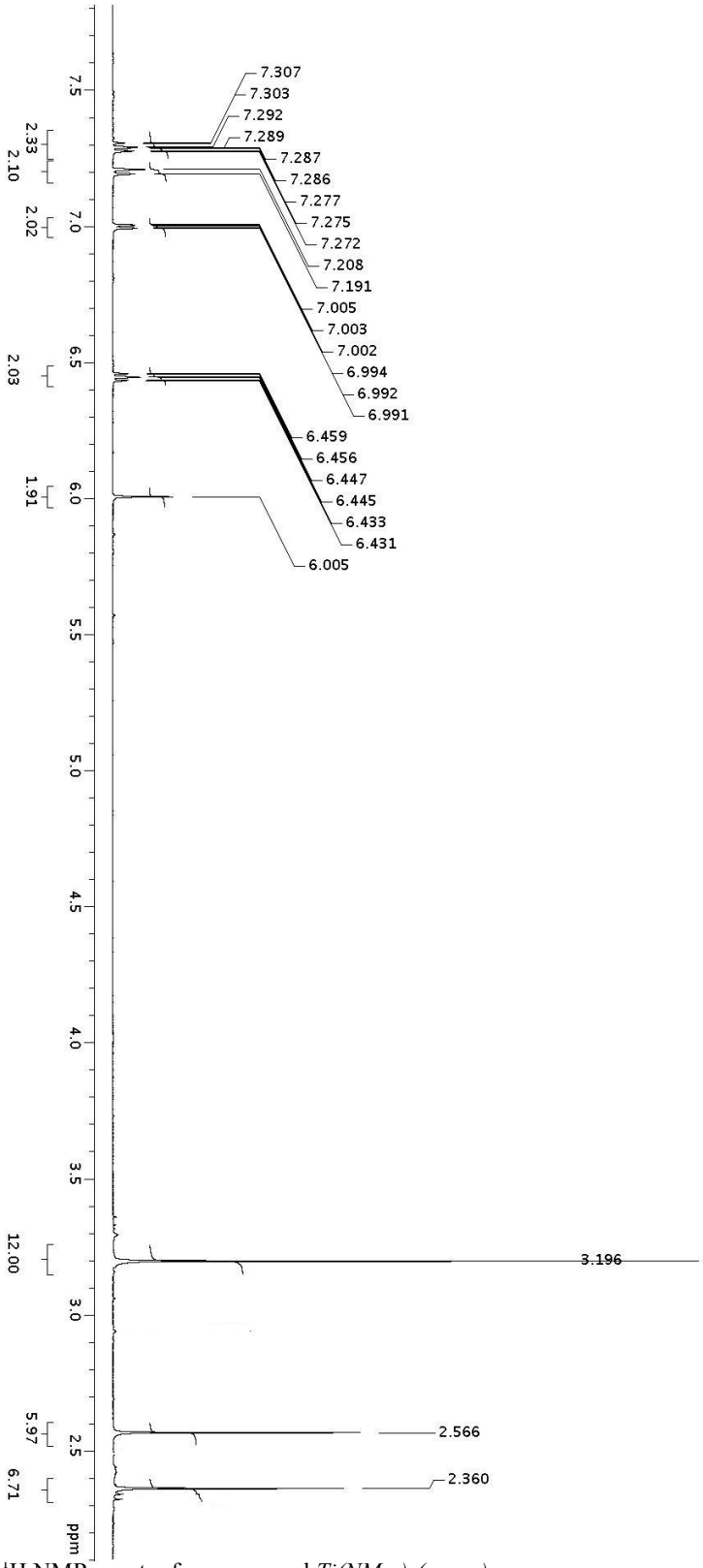

Figure 1. ^{1}H NMR spectra for compound *Ti(NMe$_2$)$_2$(pypyr)$_2$*.

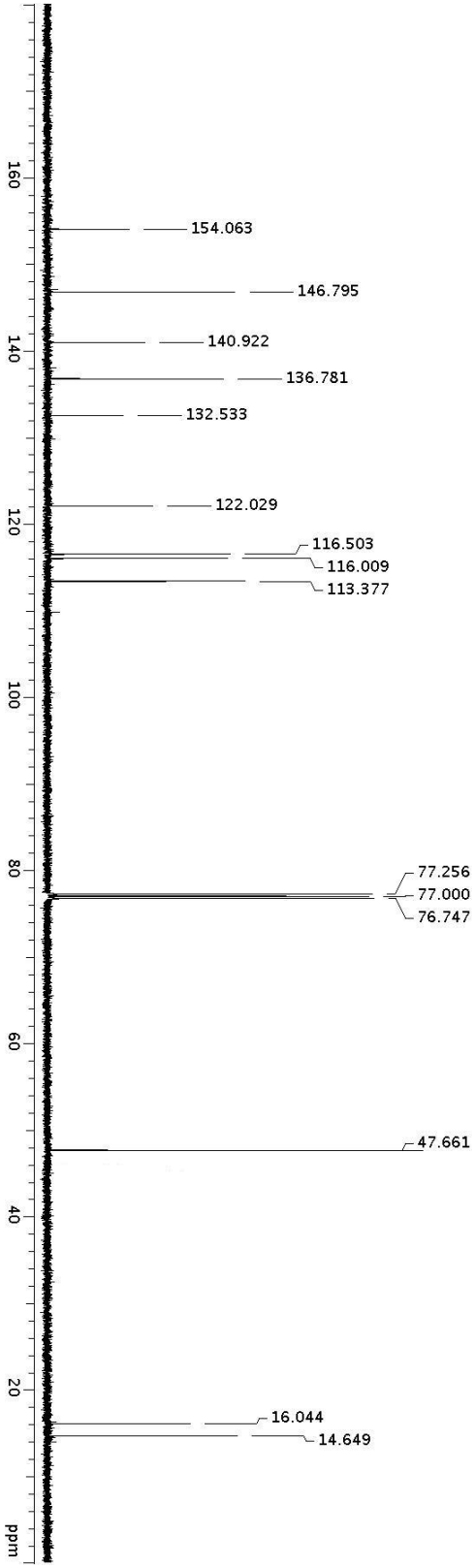

Figure 2. ^{13}C NMR spectra for compound *Ti(NMe$_2$)$_2$(pypyr)$_2$*.

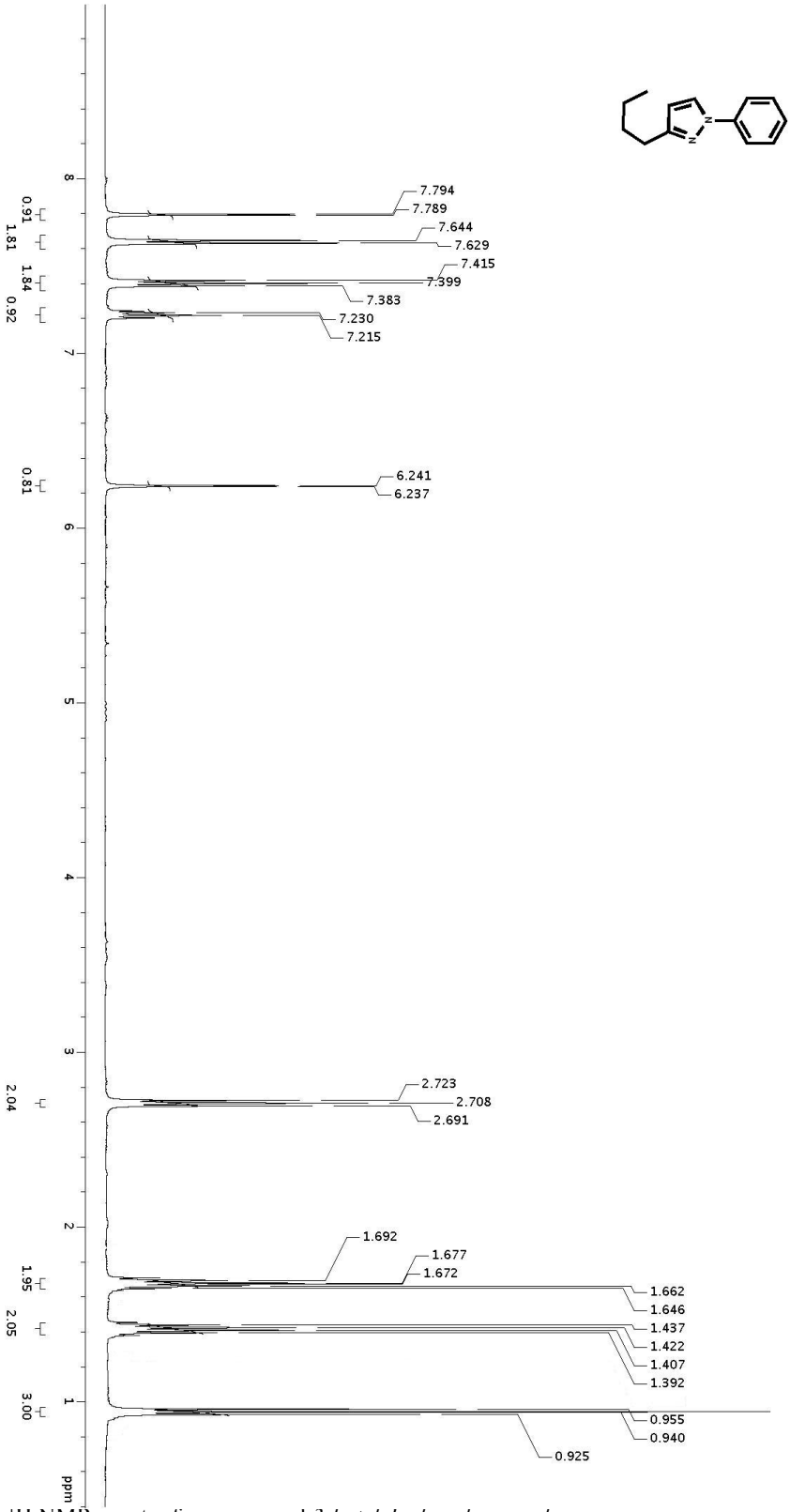

Figure 3. ‘H NMR spectra for compound *3-butyl-1-phenyl-pyrazole.*

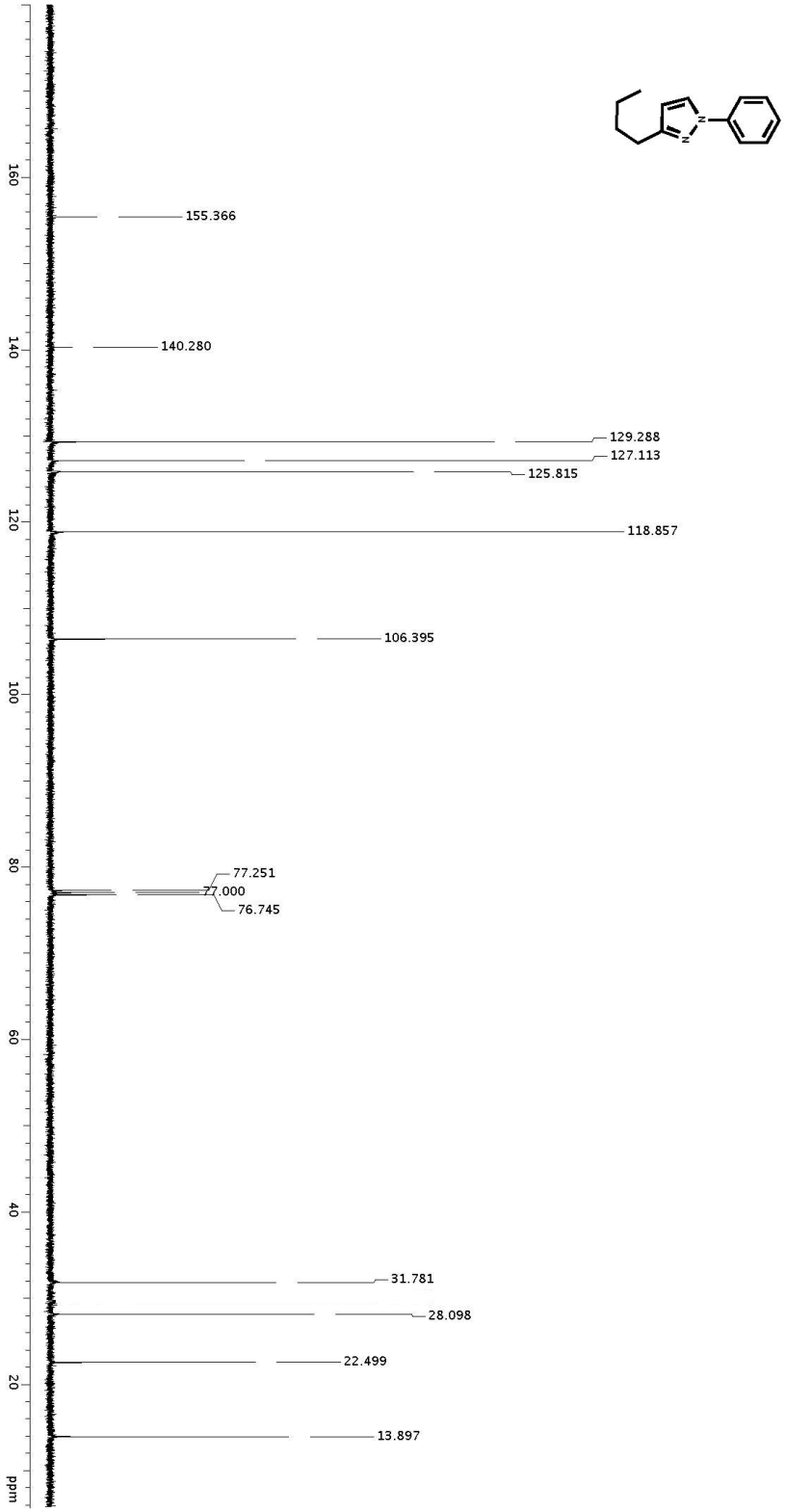

Figure 4. ^{13}C NMR spectra for compound *3-butyl-1-phenyl-pyrazole.*

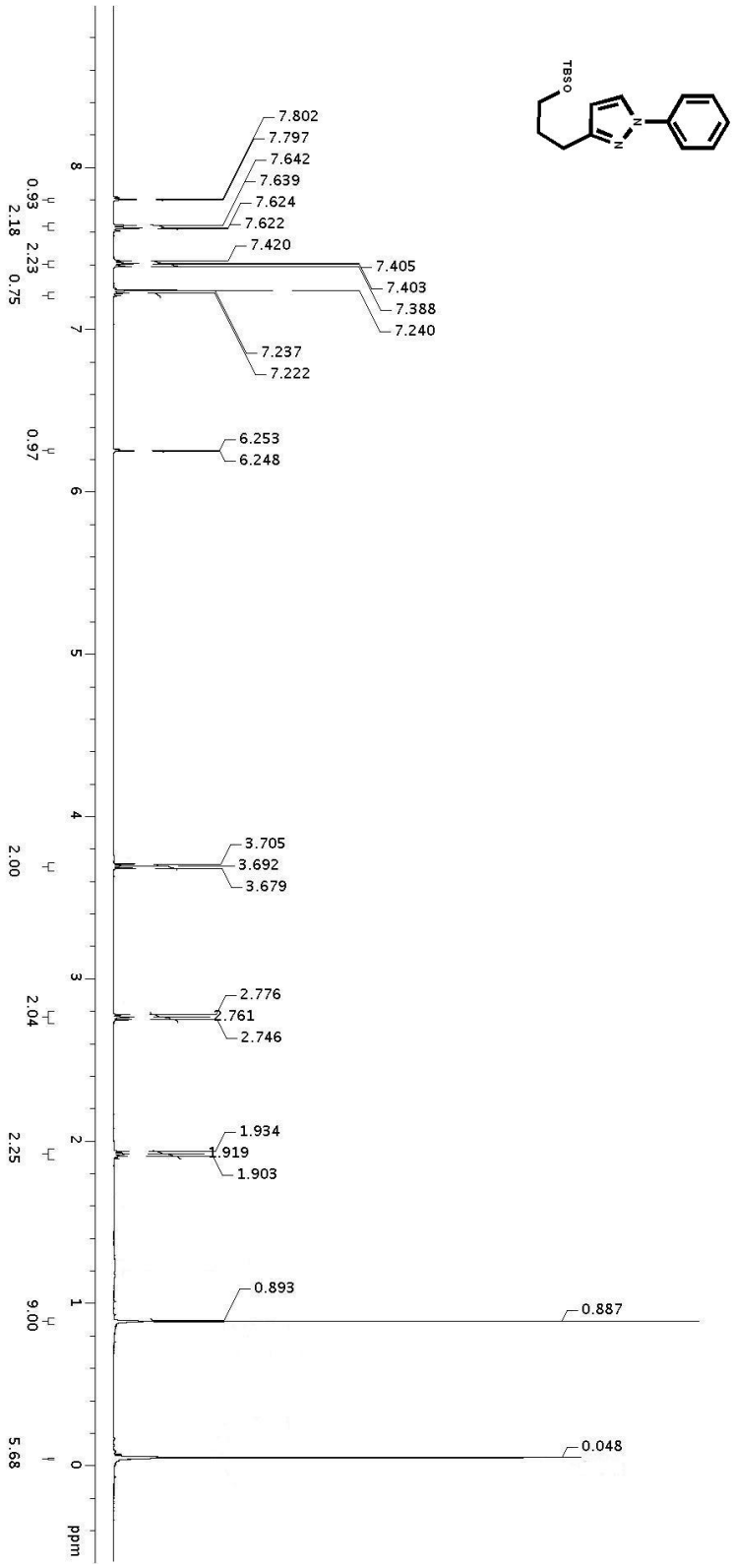

Figure 5. ^{1}H NMR spectra for compound *3-(3-(tert-butyldimethylsilyloxy)propyl)-1-phenyl-pyrazole*.

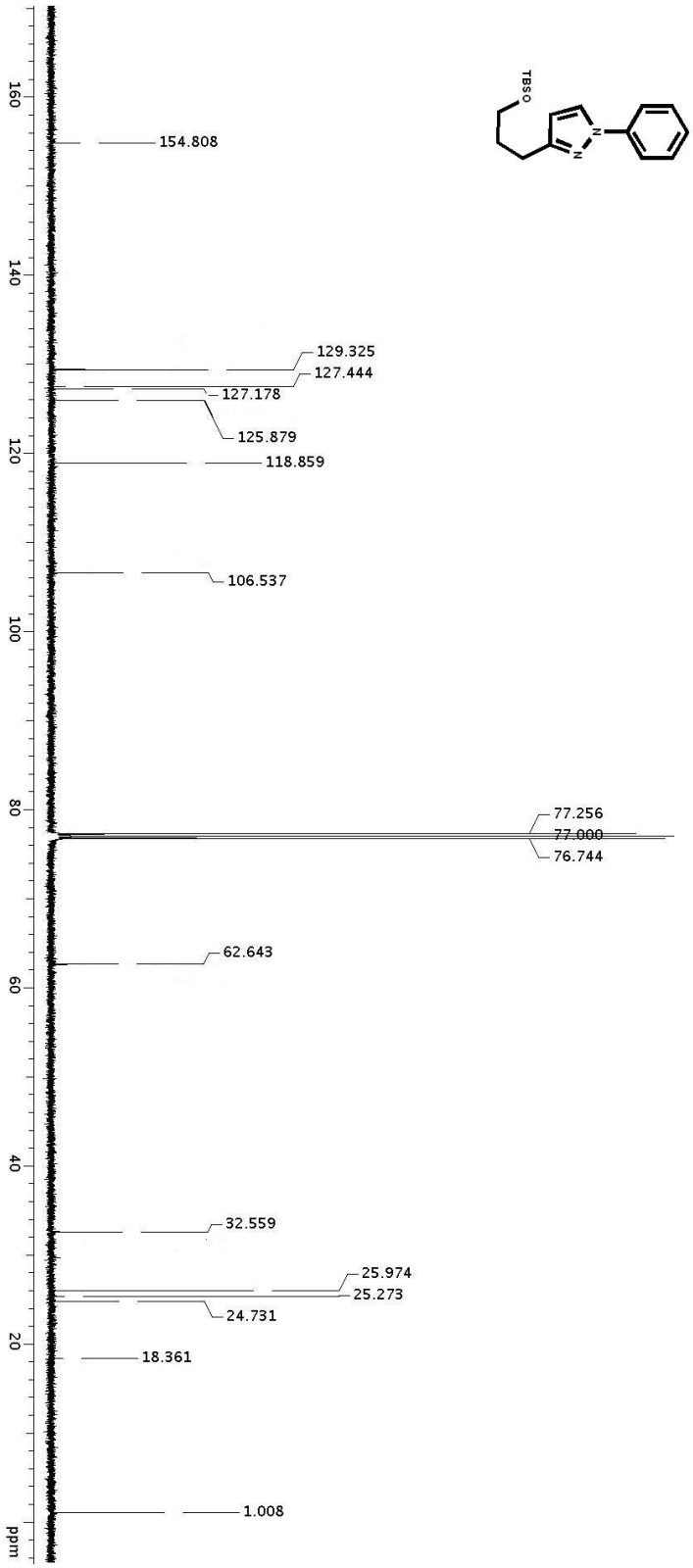

Figure 6. ^{13}C NMR spectra for compound *3-(3-(tert-butyldimethylsilyloxy)propyl)-1-phenyl-pyrazole.*

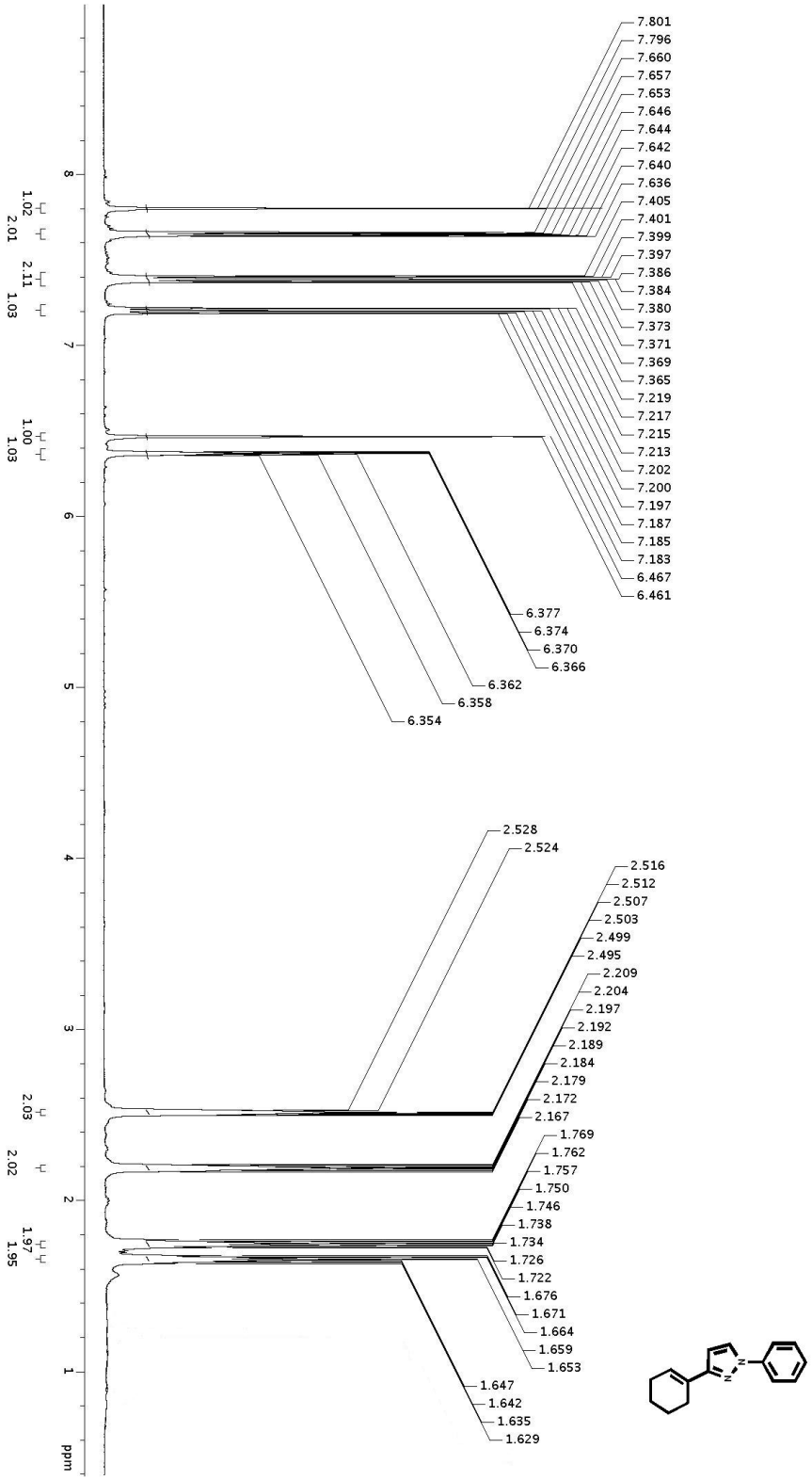

Figure 7. ^{1}H NMR spectra for compound *3-cyclohexenyl-1-phenyl-pyrazole*.

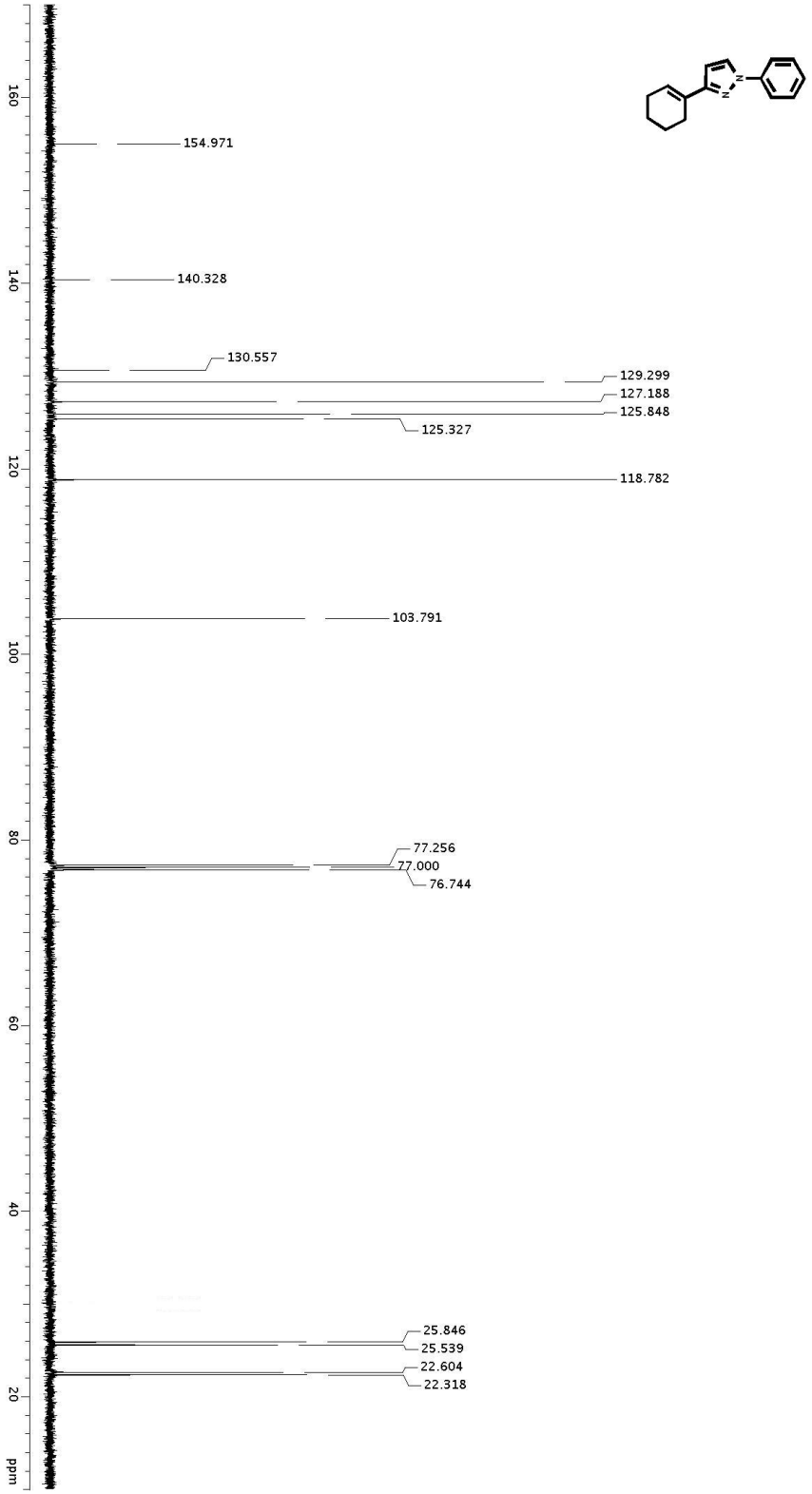

Figure 8. ^{13}C NMR spectra for compound *3-cyclohexenyl-1-phenyl-pyrazole*.

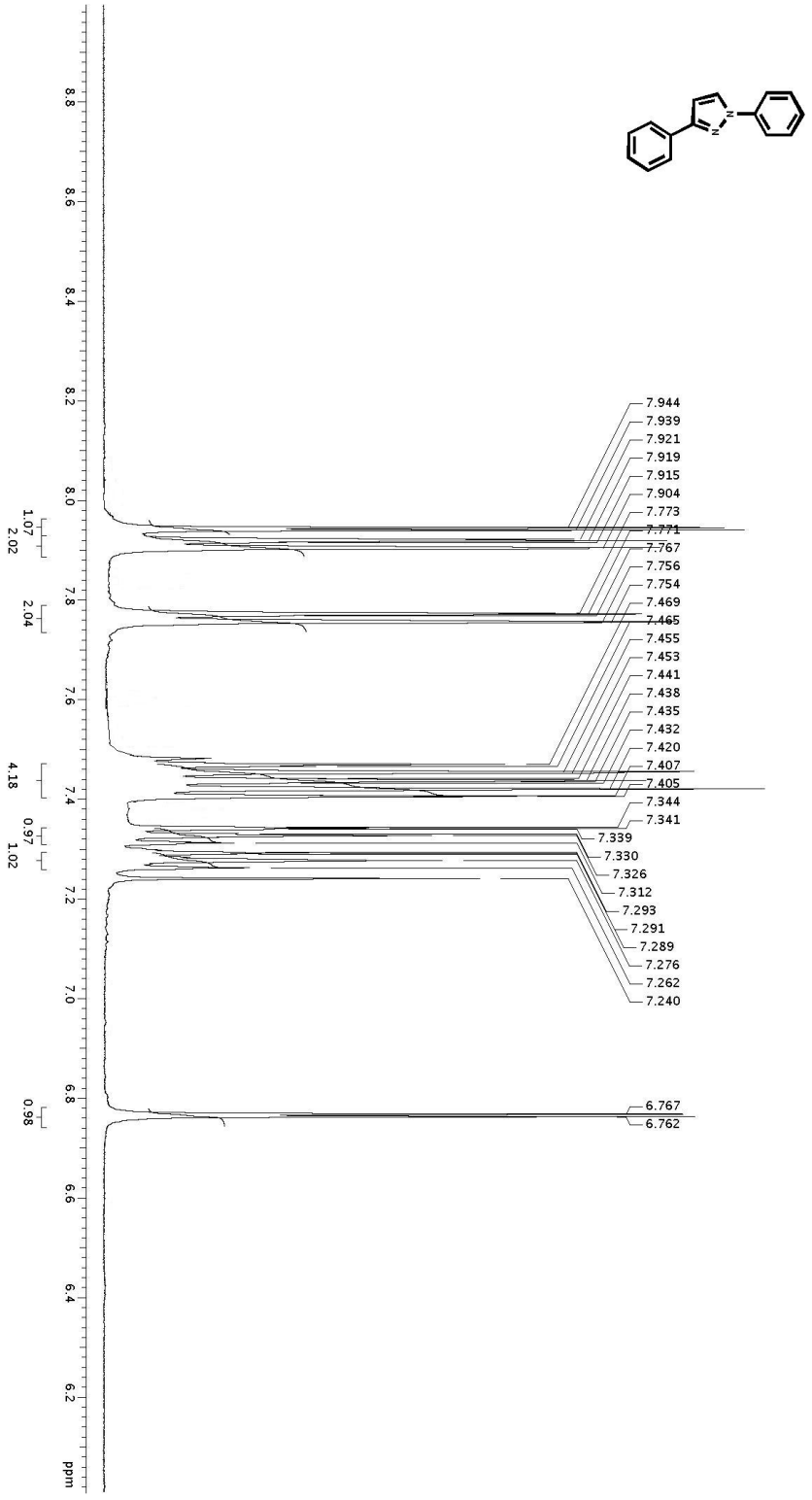

Figure 9. ^{1}H NMR spectra for compound *1,3-diphenyl-pyrazole.*

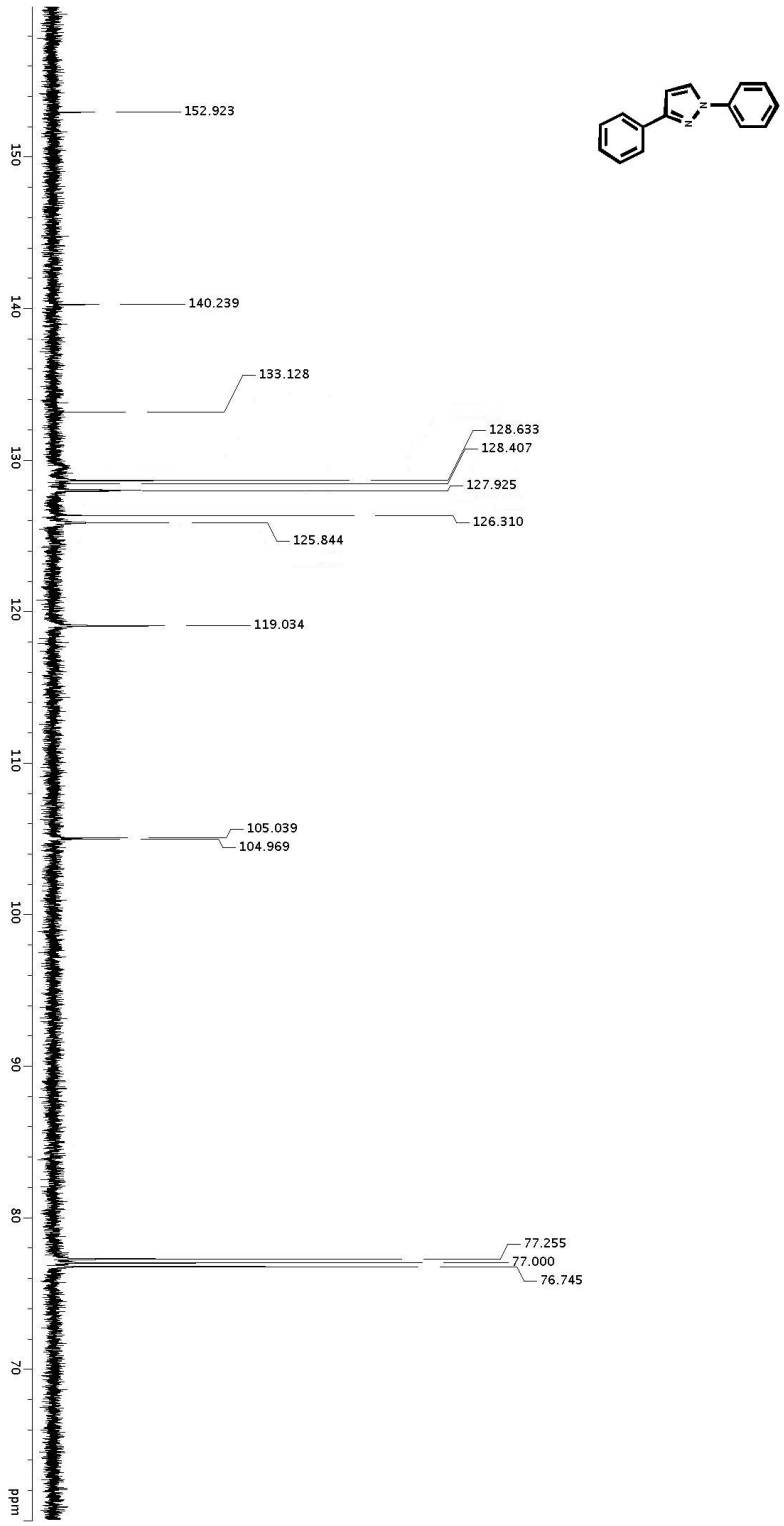

Figure 10. ^{13}C NMR spectra for compound *1,3-diphenyl-pyrazole*.

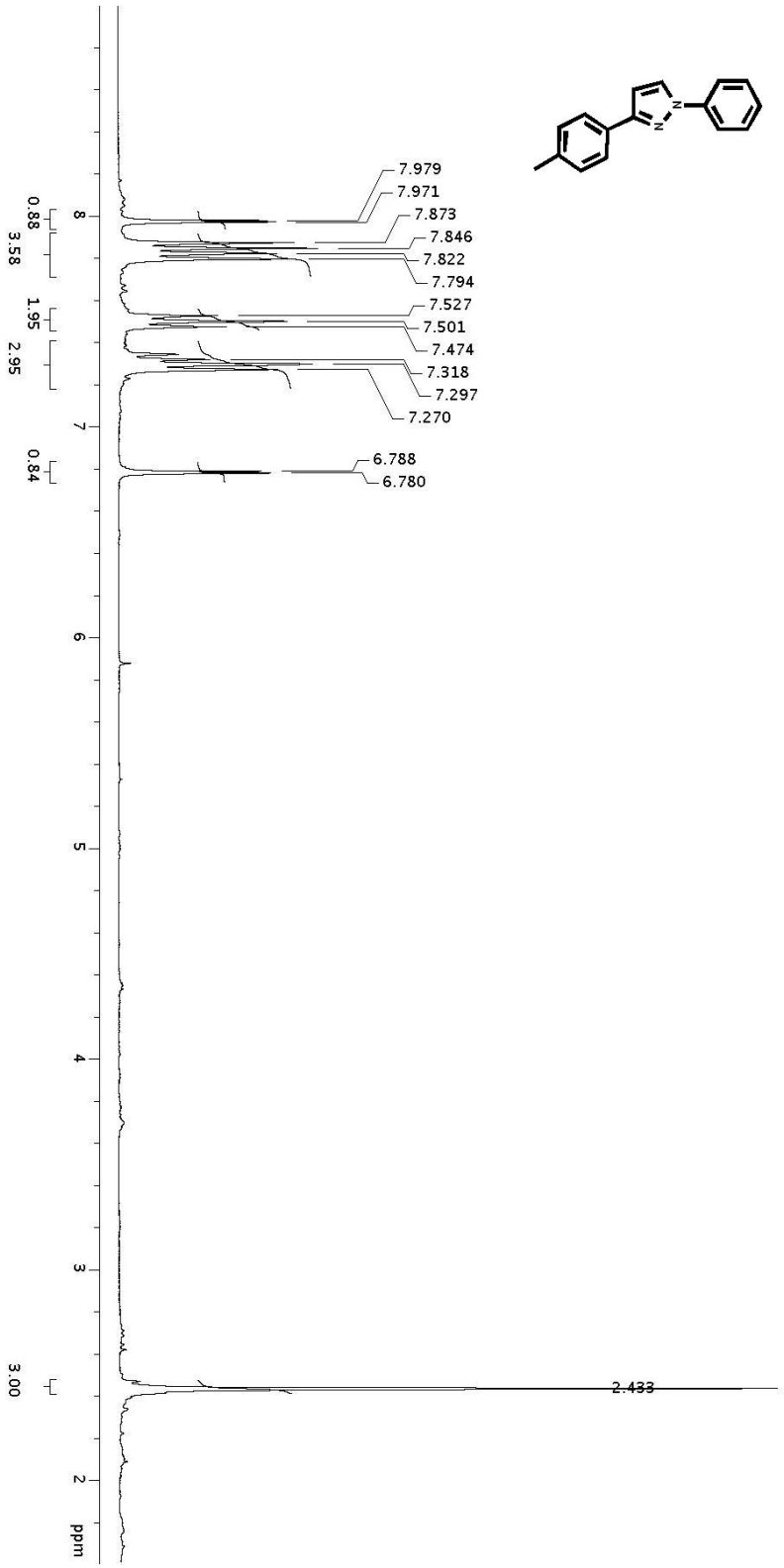

Figure 11. ^{1}H NMR spectra for compound *1-phenyl-3-p-tolyl-pyrazole.*

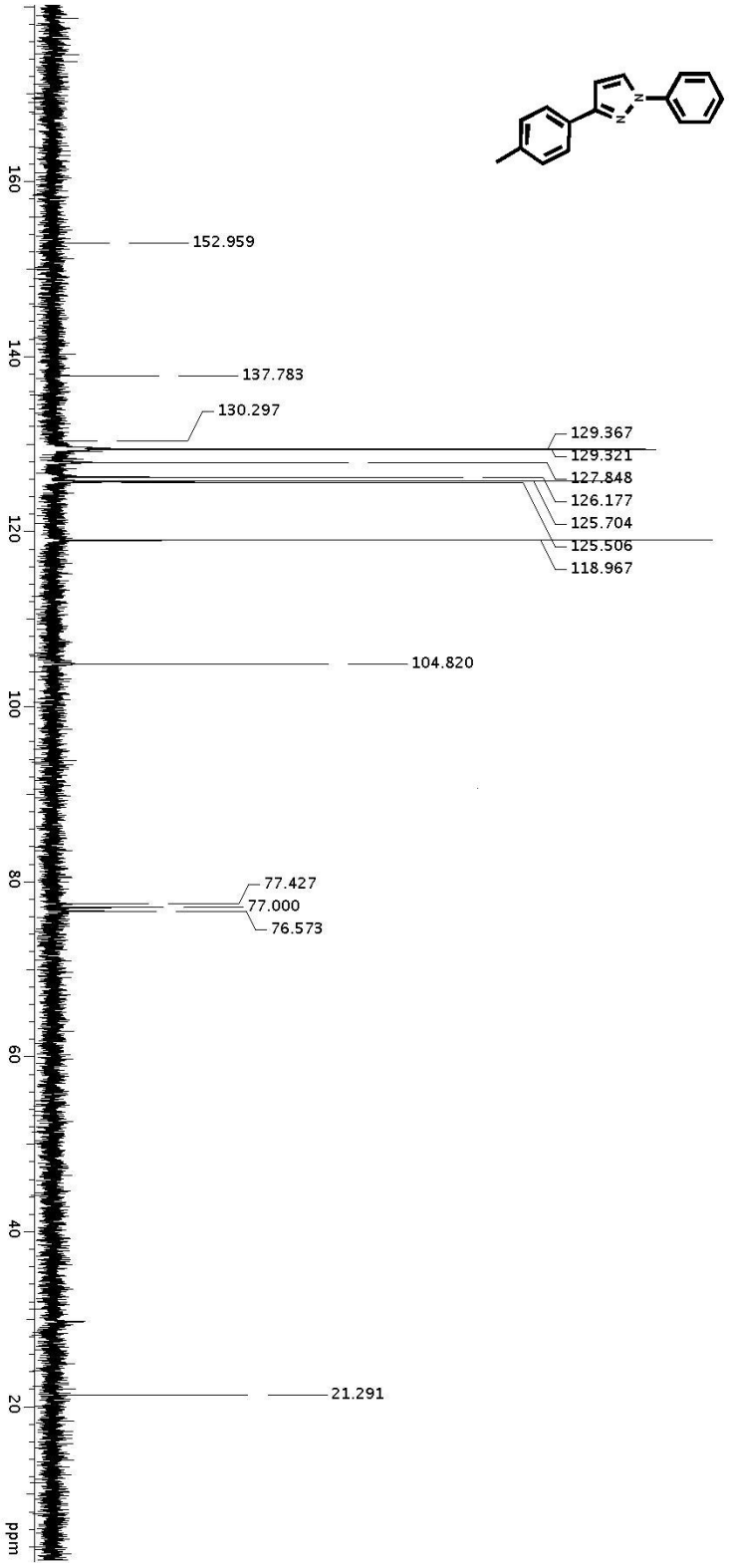

Figure 12. ^{13}C NMR spectra for compound *1-phenyl-3-p-tolyl-pyrazole.*

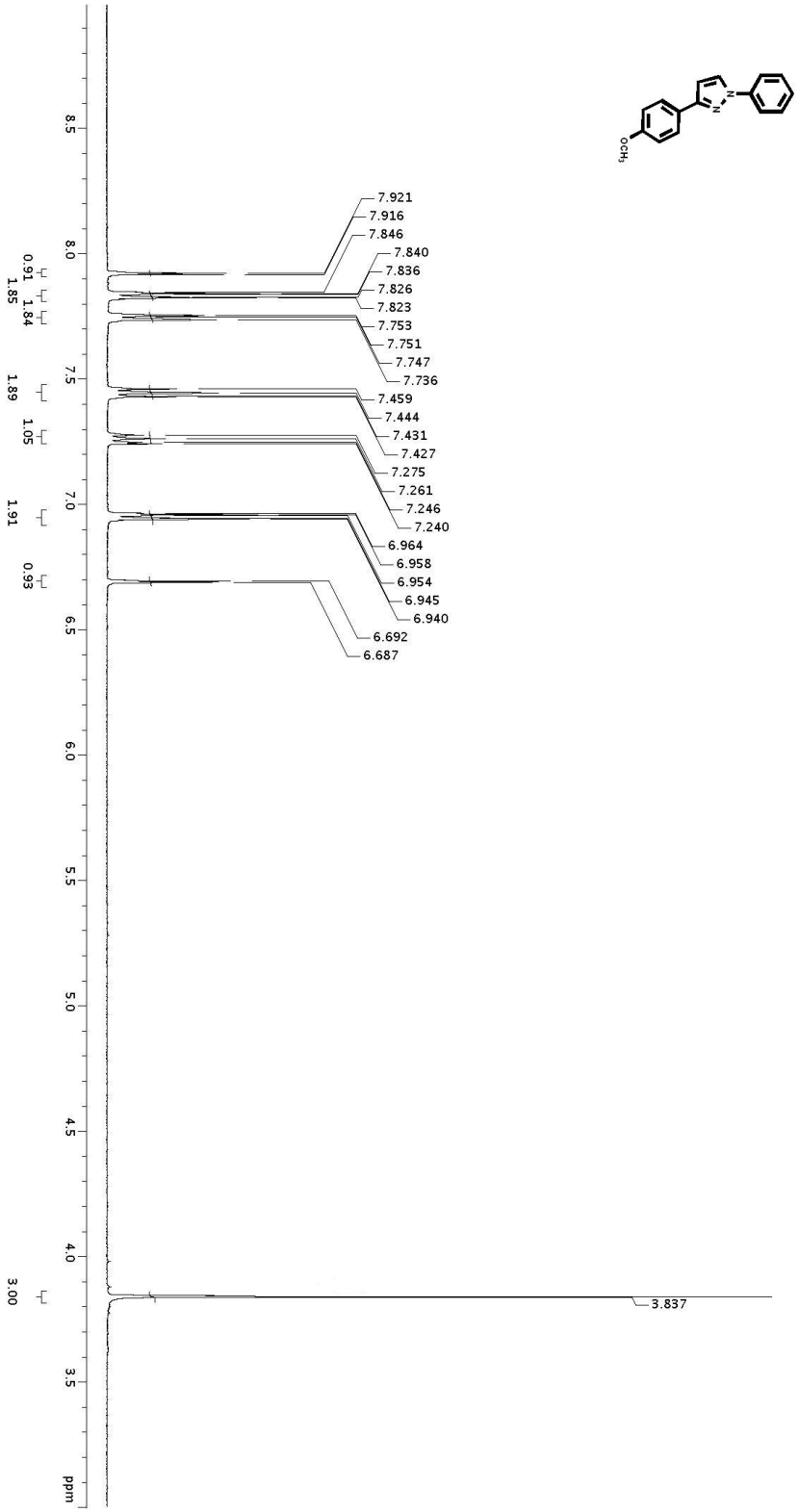

Figure 13. ^{1}H NMR spectra for compound *3-(4-methoxyphenyl)-1-phenyl-pyrazole.*

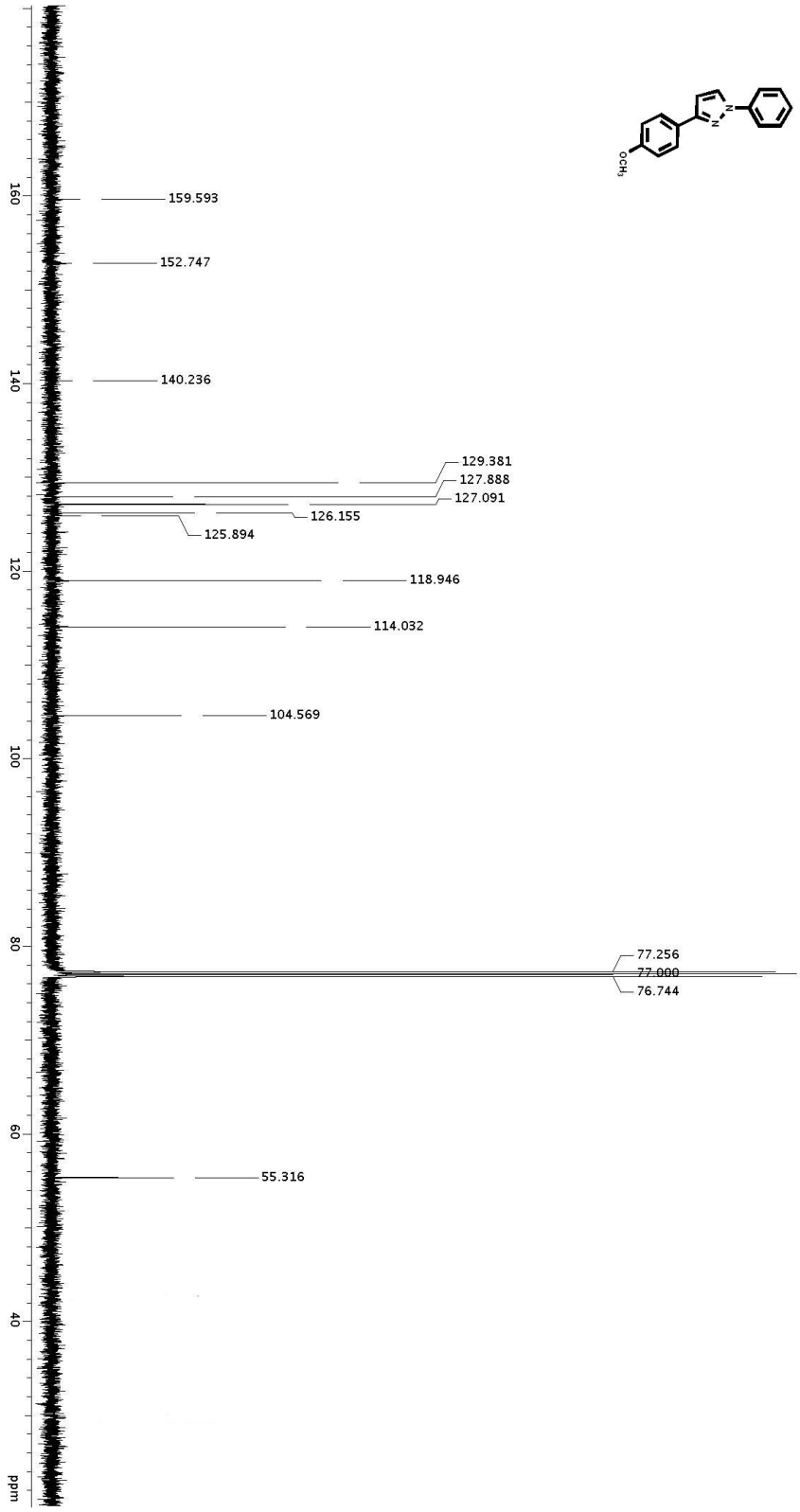

Figure 14. ^{13}C NMR spectra for compound *3-(4-methoxyphenyl)-1-phenyl-pyrazole.*

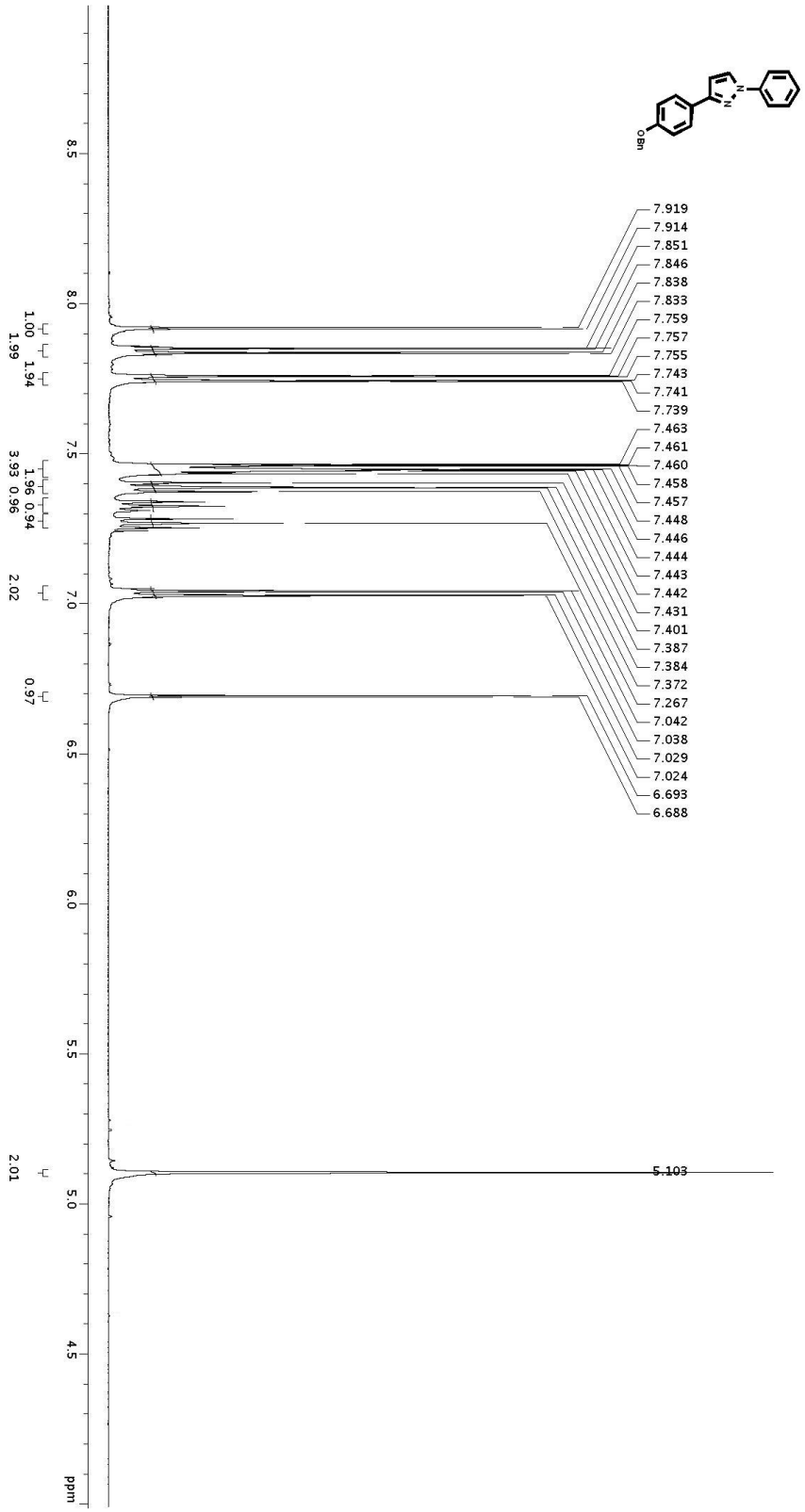

Figure 15. ^{1}H NMR spectra for compound *3-(4-(benzyloxy)phenyl)-1-phenyl-pyrazole.*

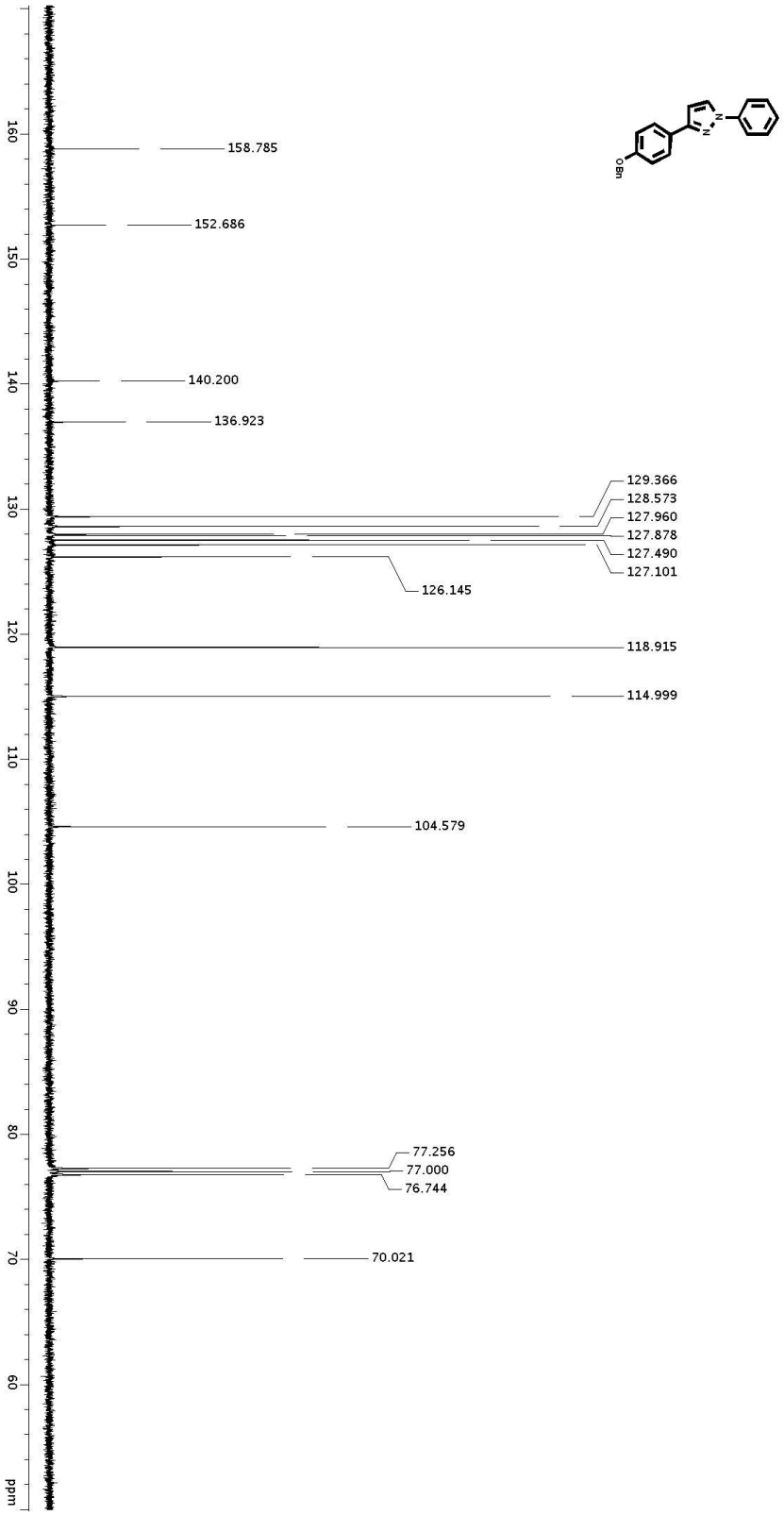

Figure 16. ^{13}C NMR spectra for compound *3-(4-(benzyloxy)phenyl)-1-phenyl-pyrazole.*

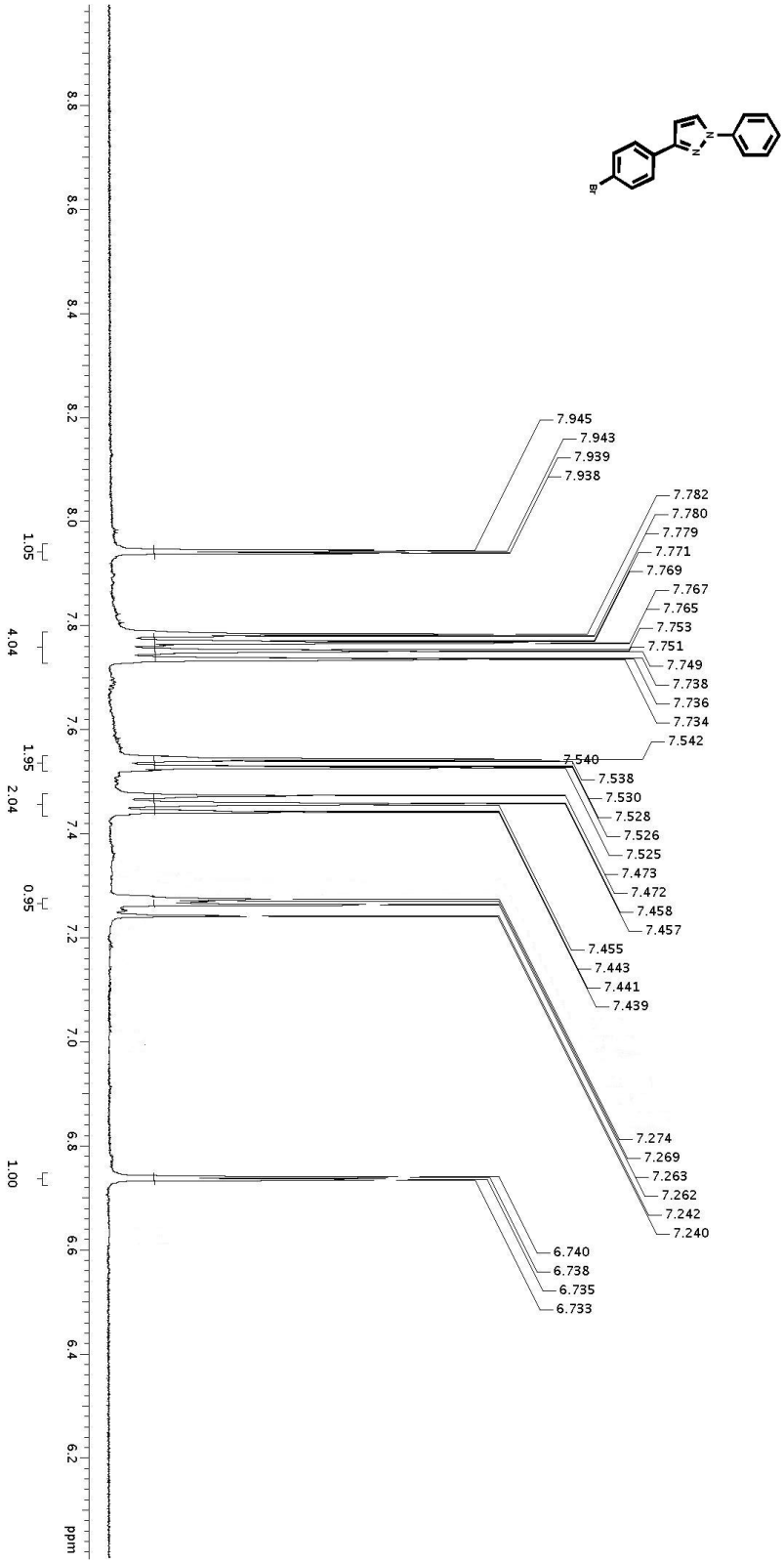

Figure 17. ^{1}H NMR spectra for compound *3-(4-bromophenyl)-1-phenyl-pyrazole.*

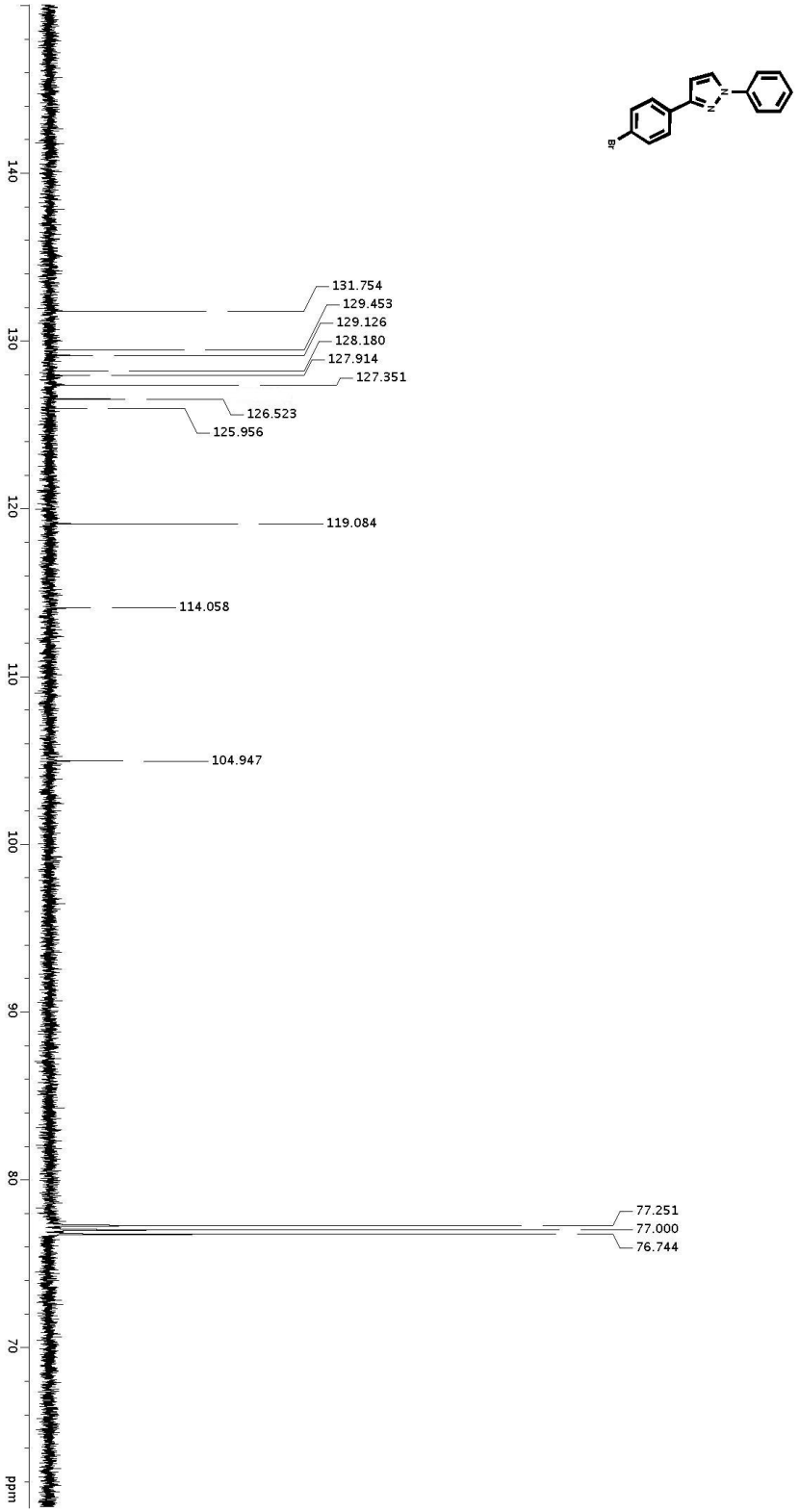

Figure 18. ^{13}C NMR spectra for compound *3-(4-bromophenyl)-1-phenyl-pyrazole*.

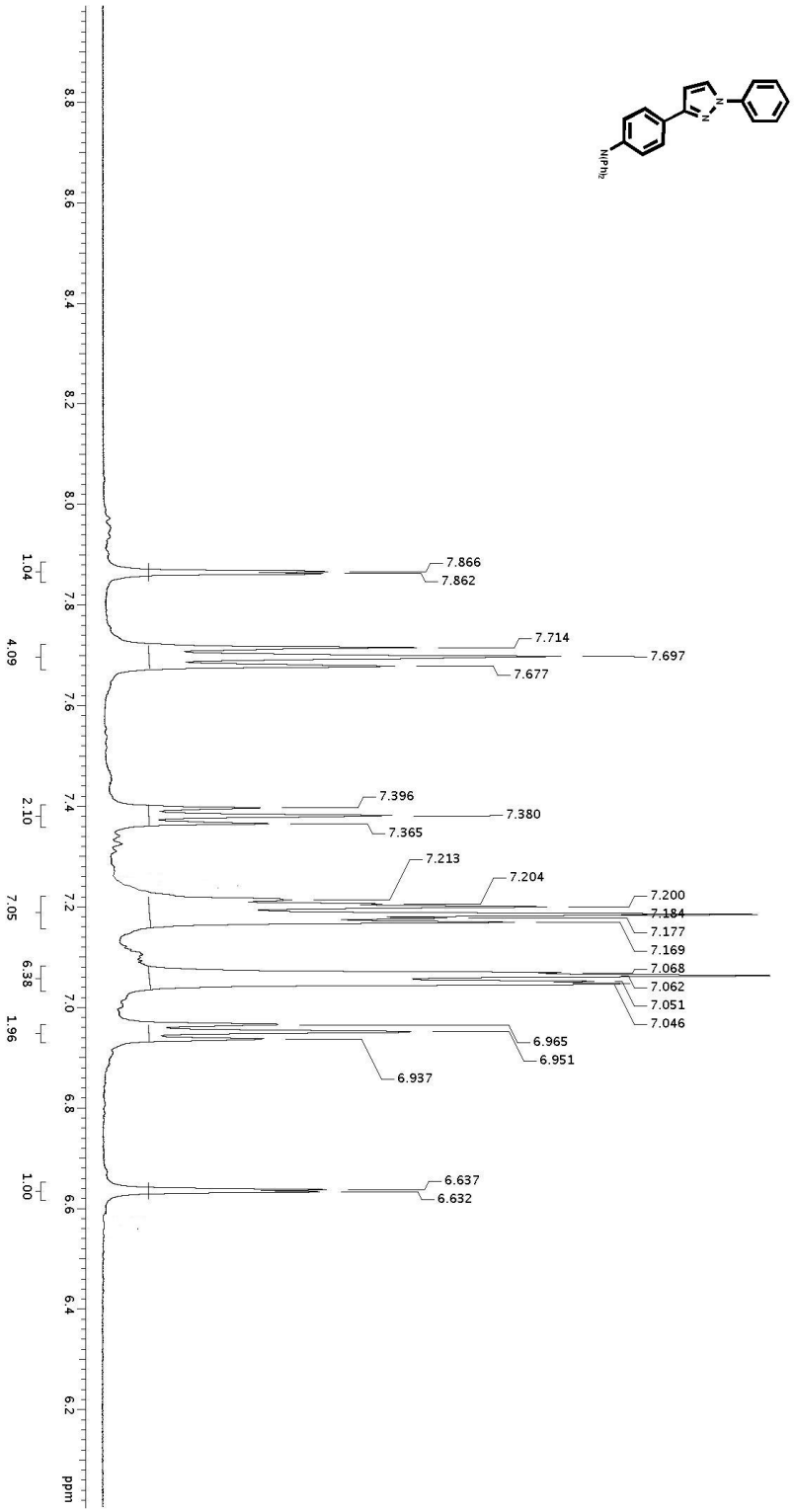

Figure 19. ^{1}H NMR spectra for compound *N,N-diphenyl-4-(1-phenyl-pyrazol-3-yl)aniline.*

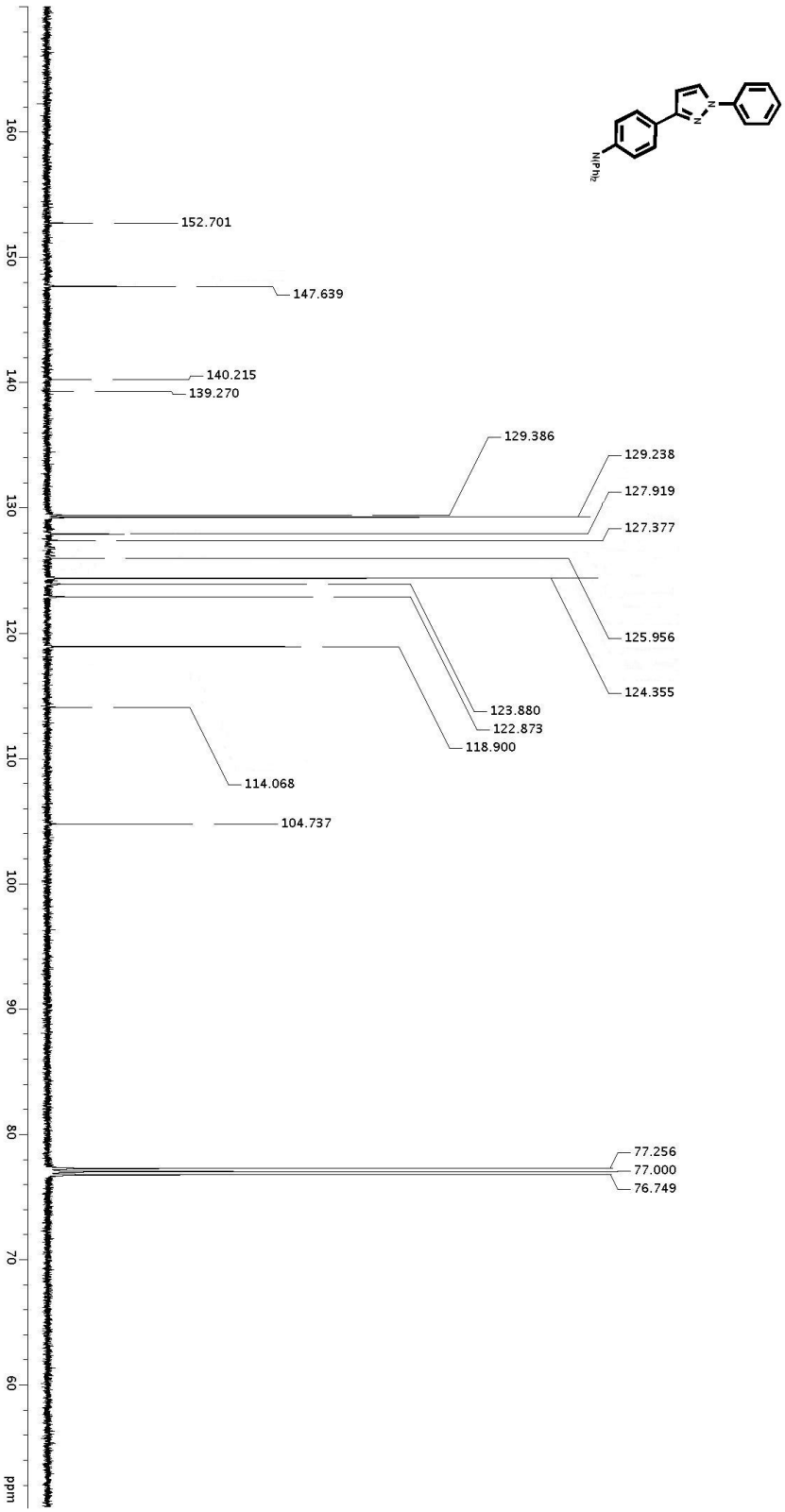

Figure 20. ^{13}C NMR spectra for compound *N,N-diphenyl-4-(1-phenyl-pyrazol-3-yl)aniline.*

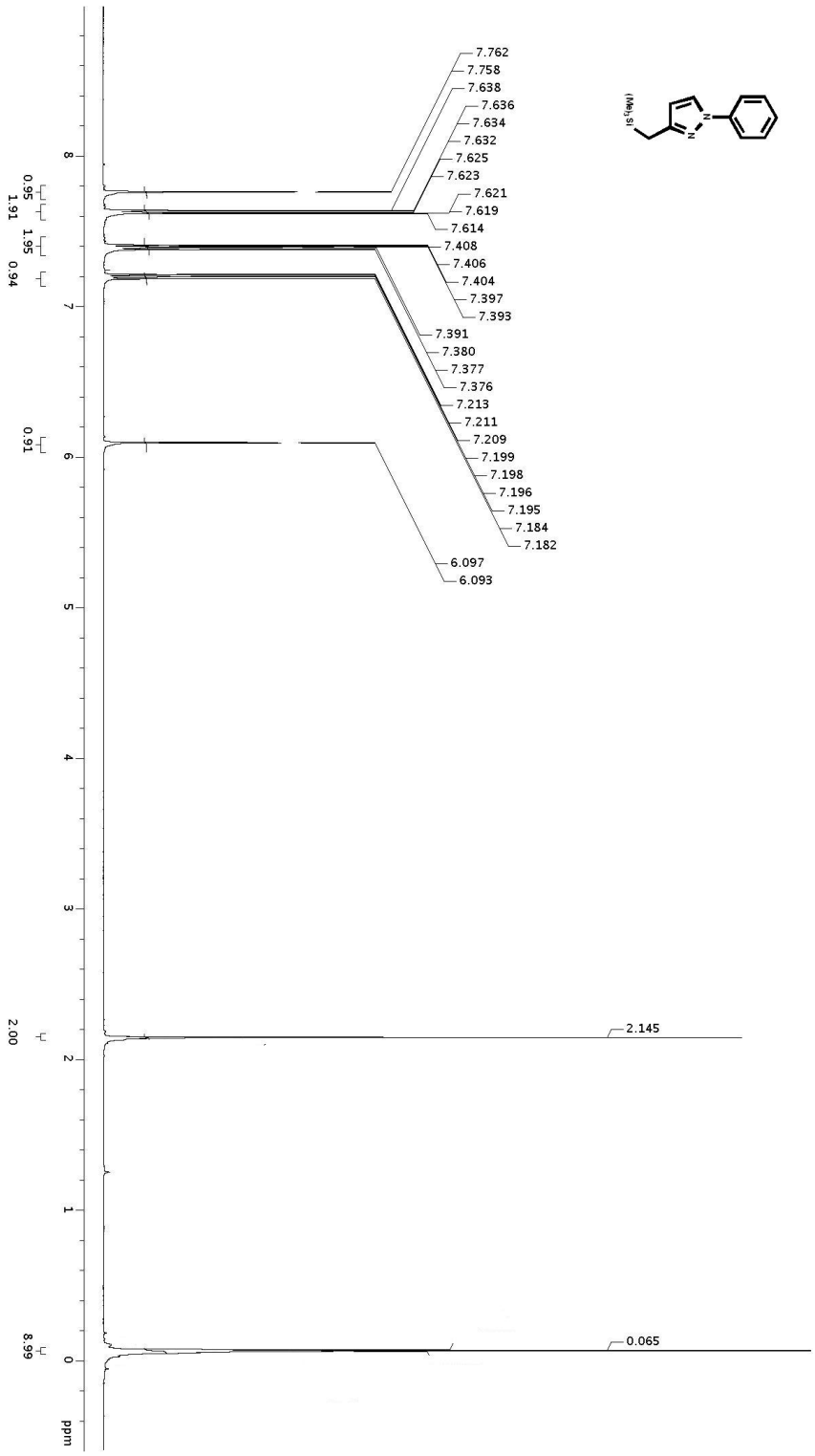

Figure 21. ^{1}H NMR spectra for compound *1-phenyl-3-((trimethylsilyl)methyl)-pyrazole*.

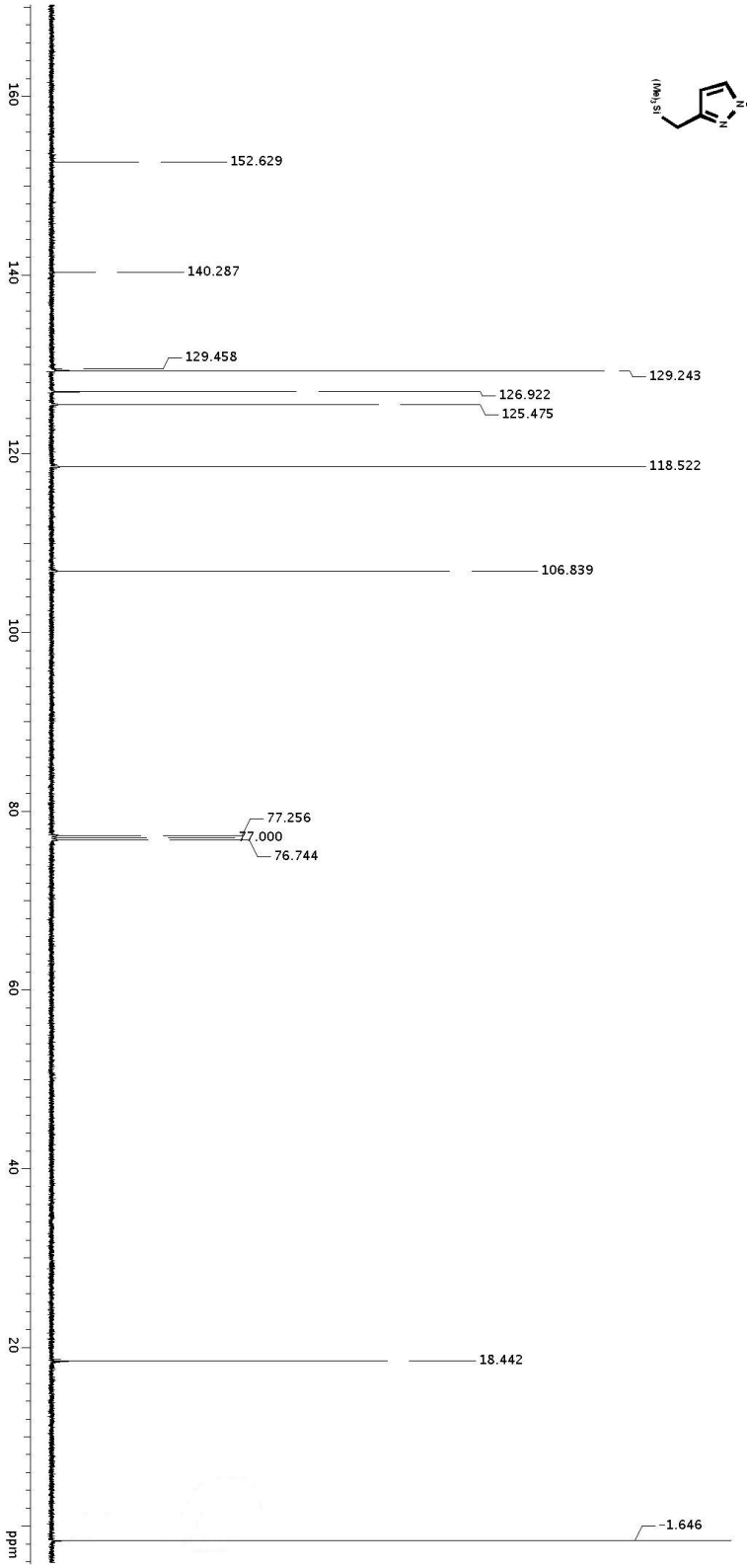

Figure 22. ^{13}C NMR spectra for compound *1-phenyl-3-((trimethylsilyl)methyl)-pyrazole.*

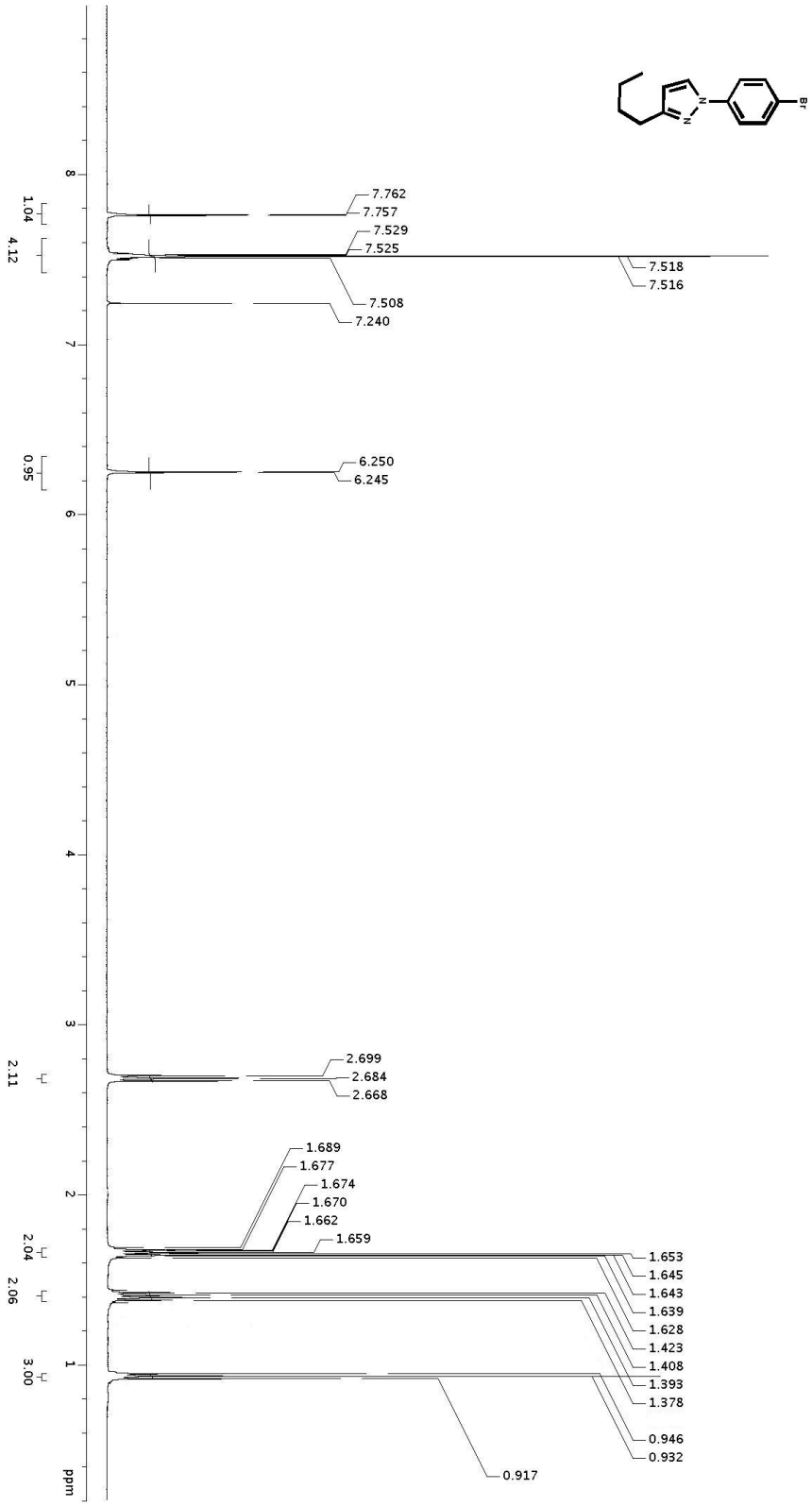

Figure 23. ^{1}H NMR spectra for compound *1-(4-bromophenyl)-3-butyl-pyrazole.*

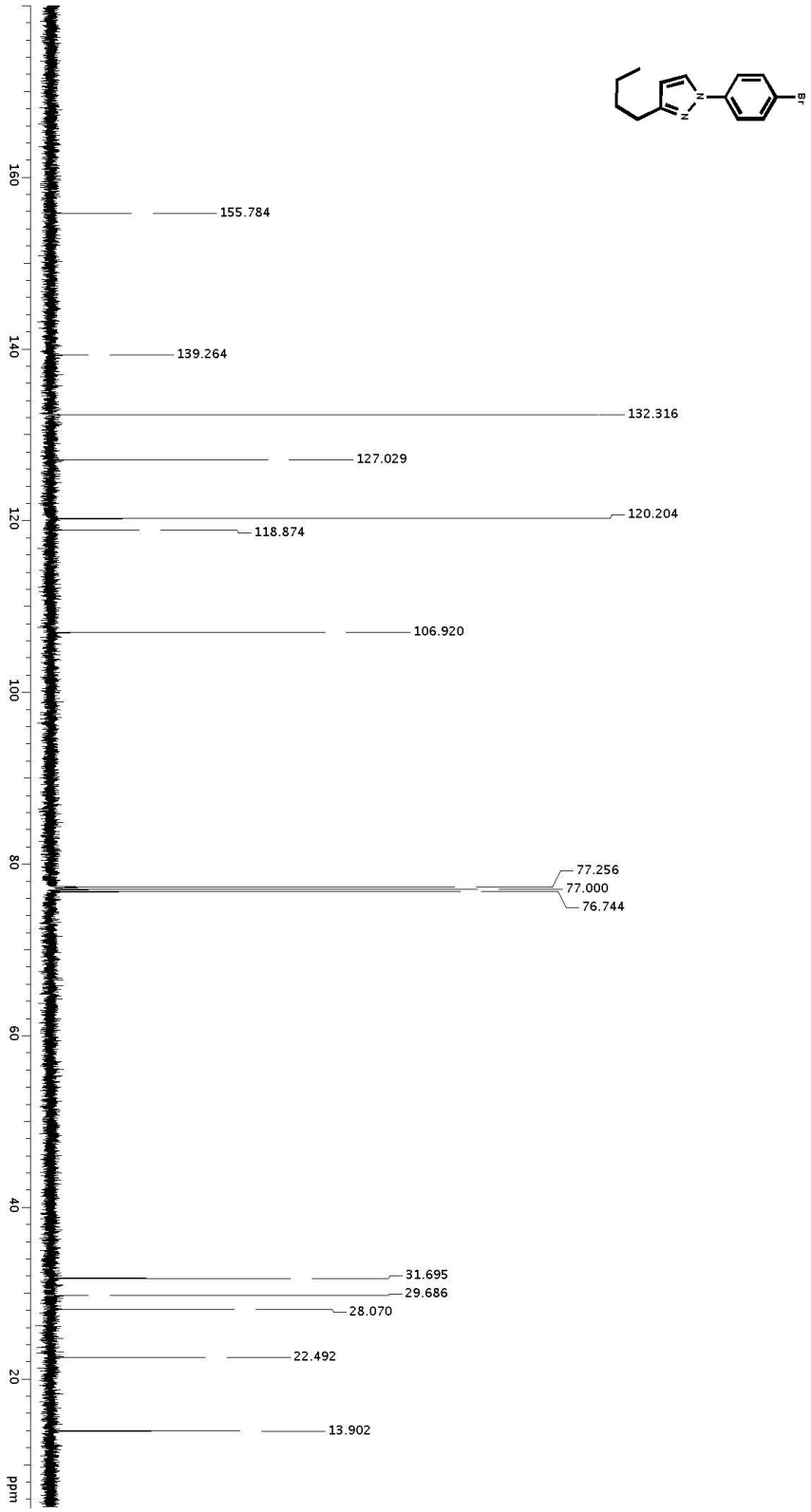

Figure 24. ^{13}C NMR spectra for compound *1-(4-bromophenyl)-3-butyl-pyrazole.*

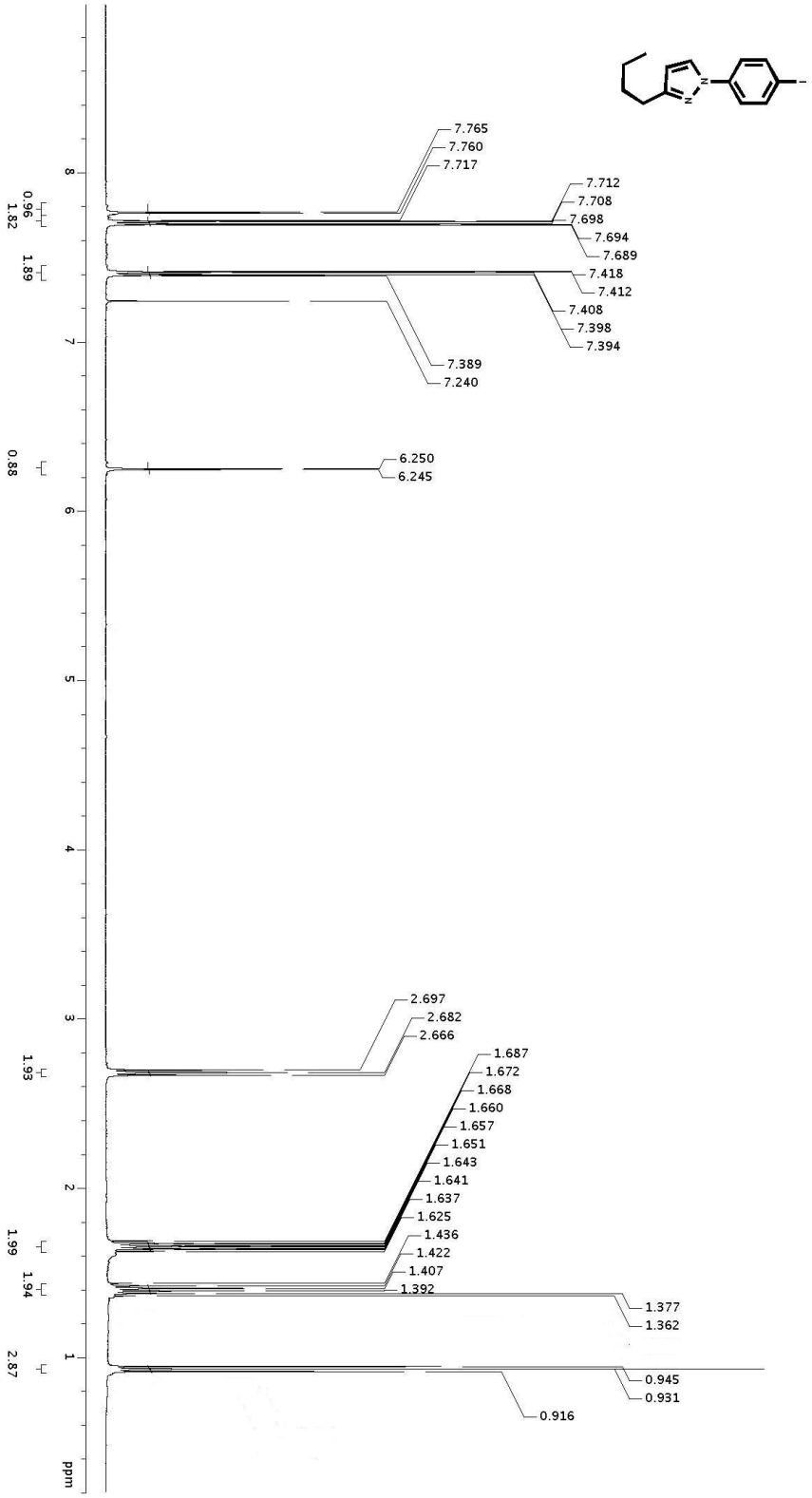

Figure 25. ^{1}H NMR spectra for compound *3-butyl-1-(4-iodophenyl)-pyrazole.*

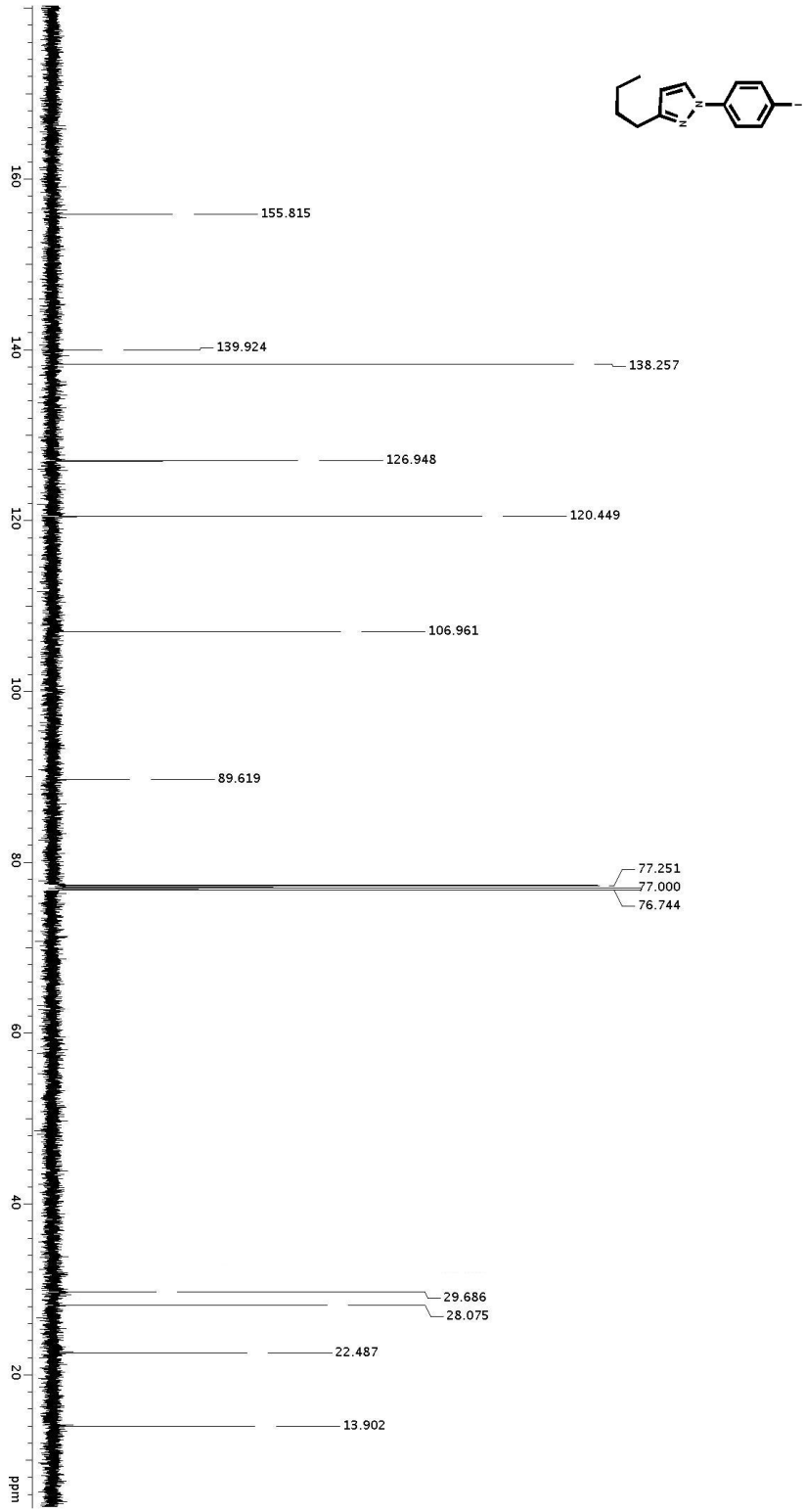

Figure 26. ^{13}C NMR spectra for compound *3-butyl-1-(4-iodophenyl)-pyrazole.*

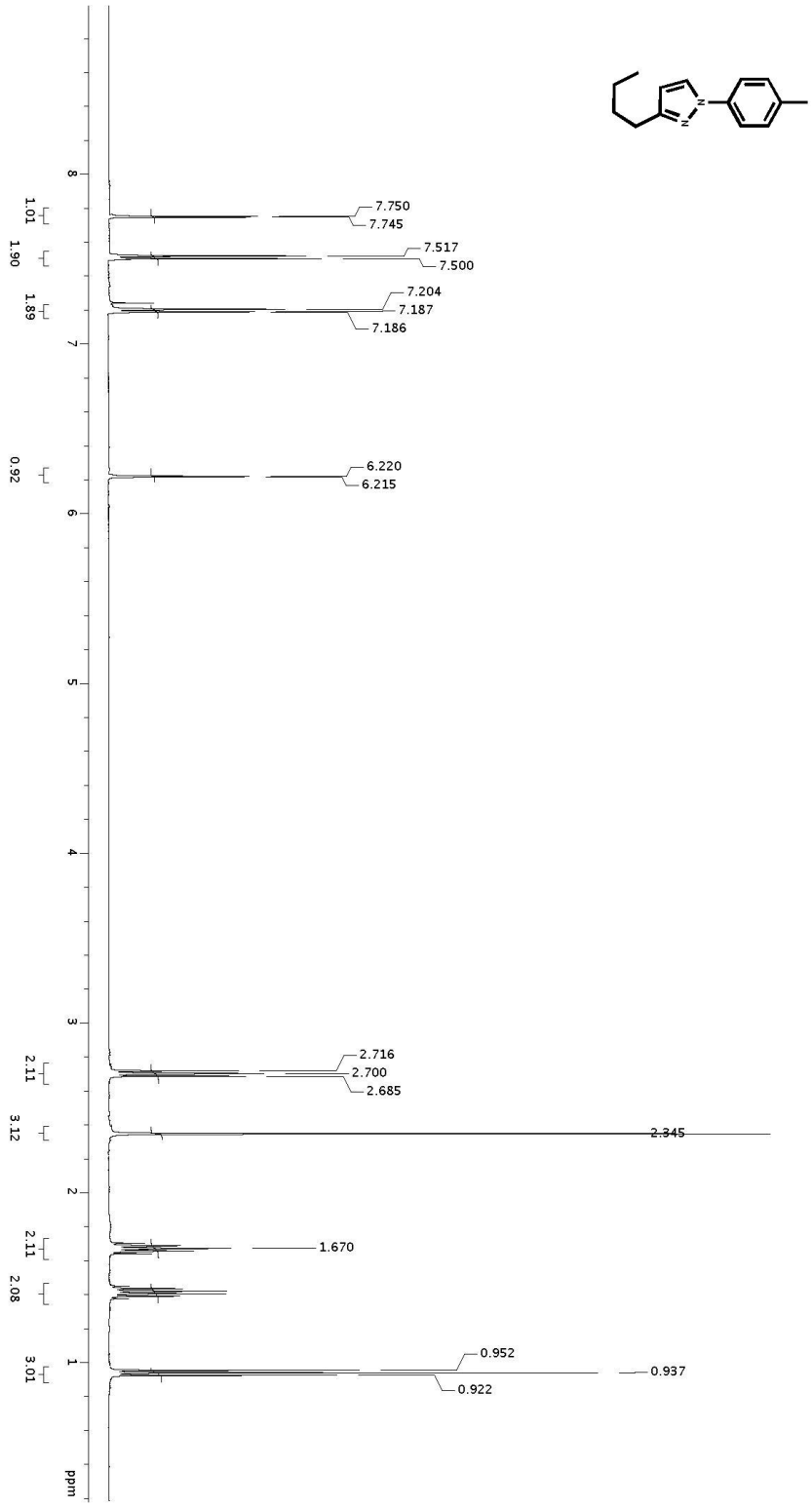

Figure 27. ^{1}H NMR spectra for compound *3-butyl-1-p-tolyl-pyrazole.*

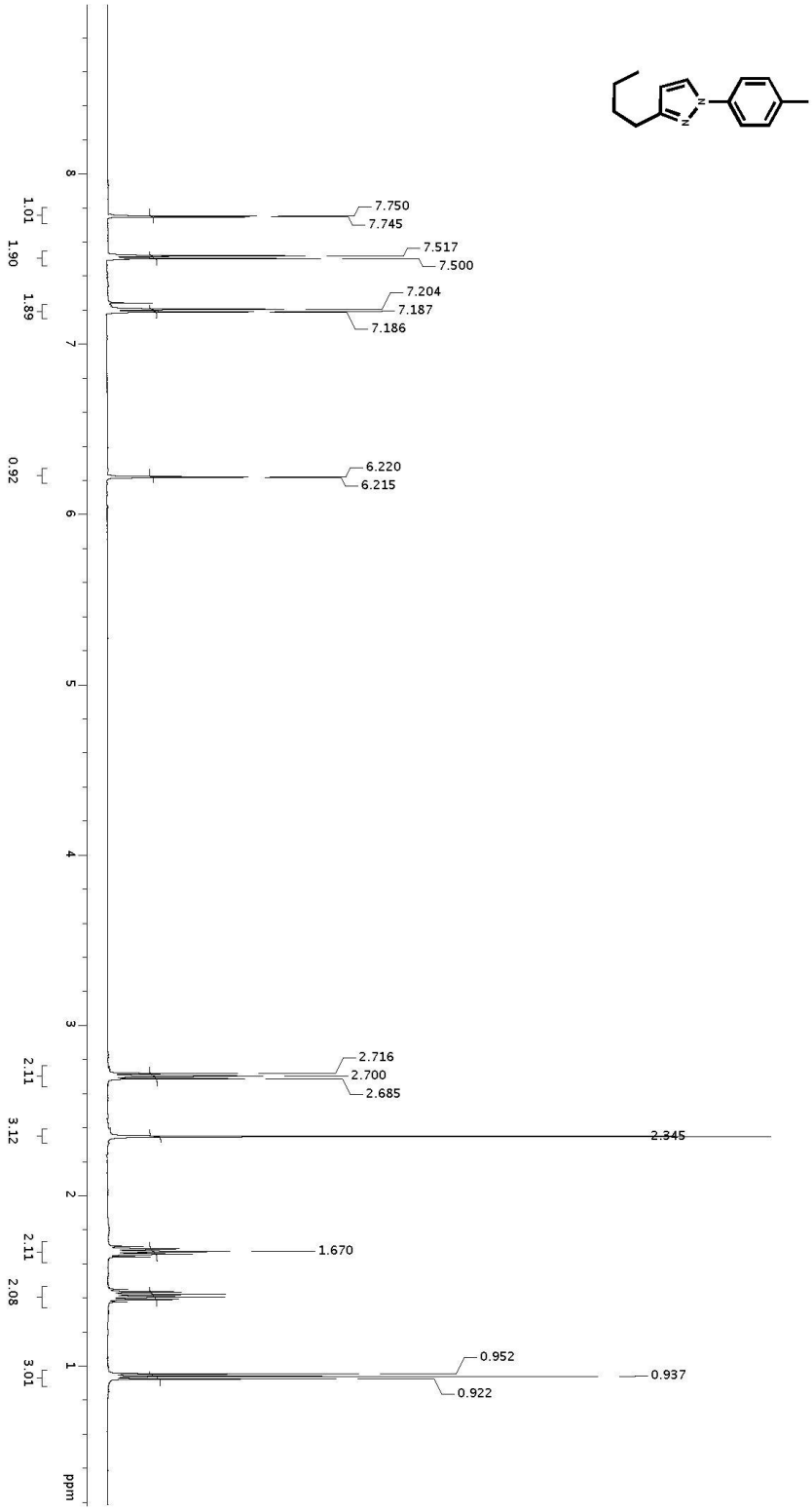

Figure 28. ^{13}C NMR spectra for compound *3-butyl-1-p-tolyl-pyrazole.*

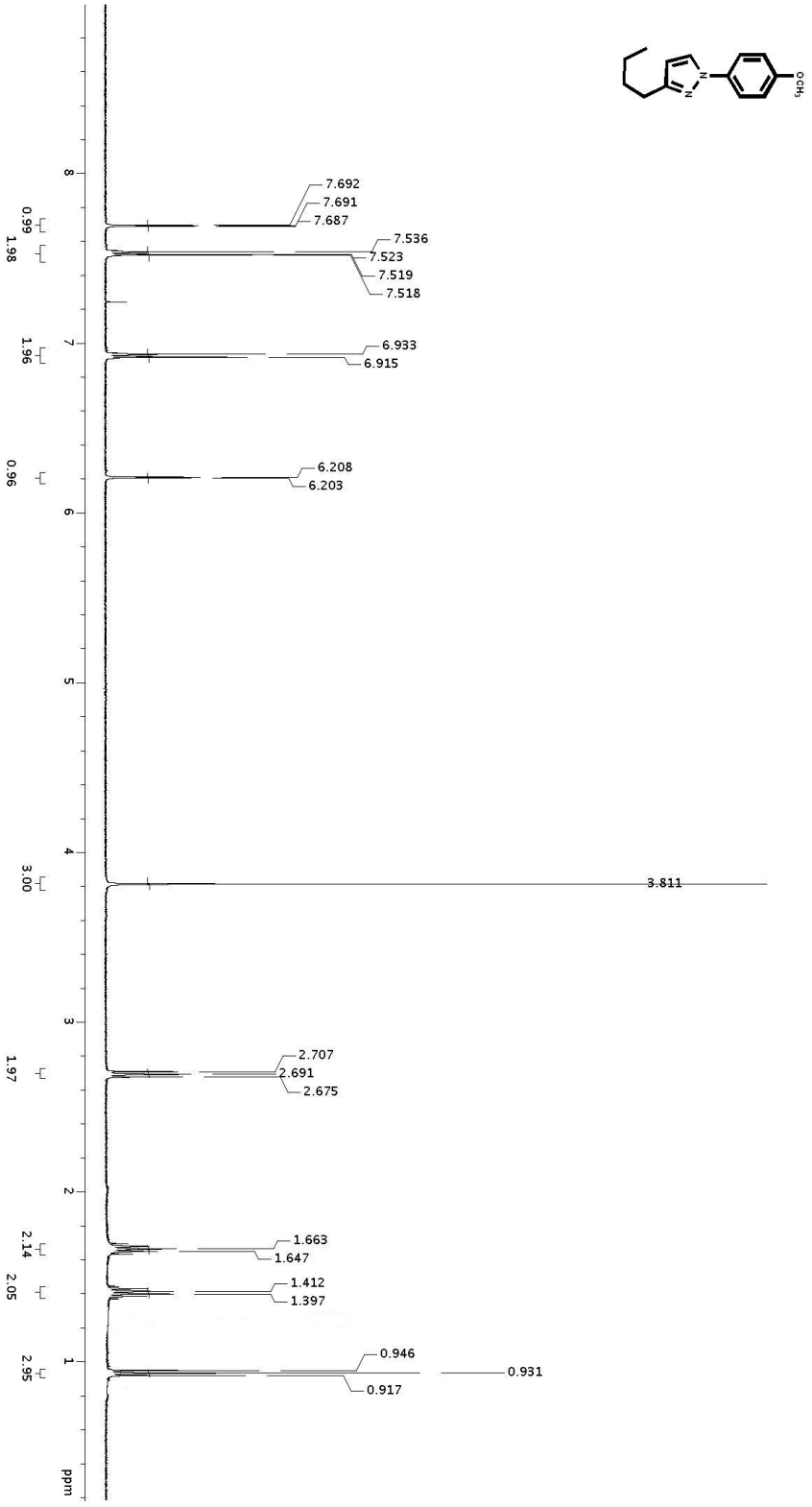

Figure 29. ^{1}H NMR spectra for compound *3-butyl-1-(4-methoxyphenyl)-pyrazole.*

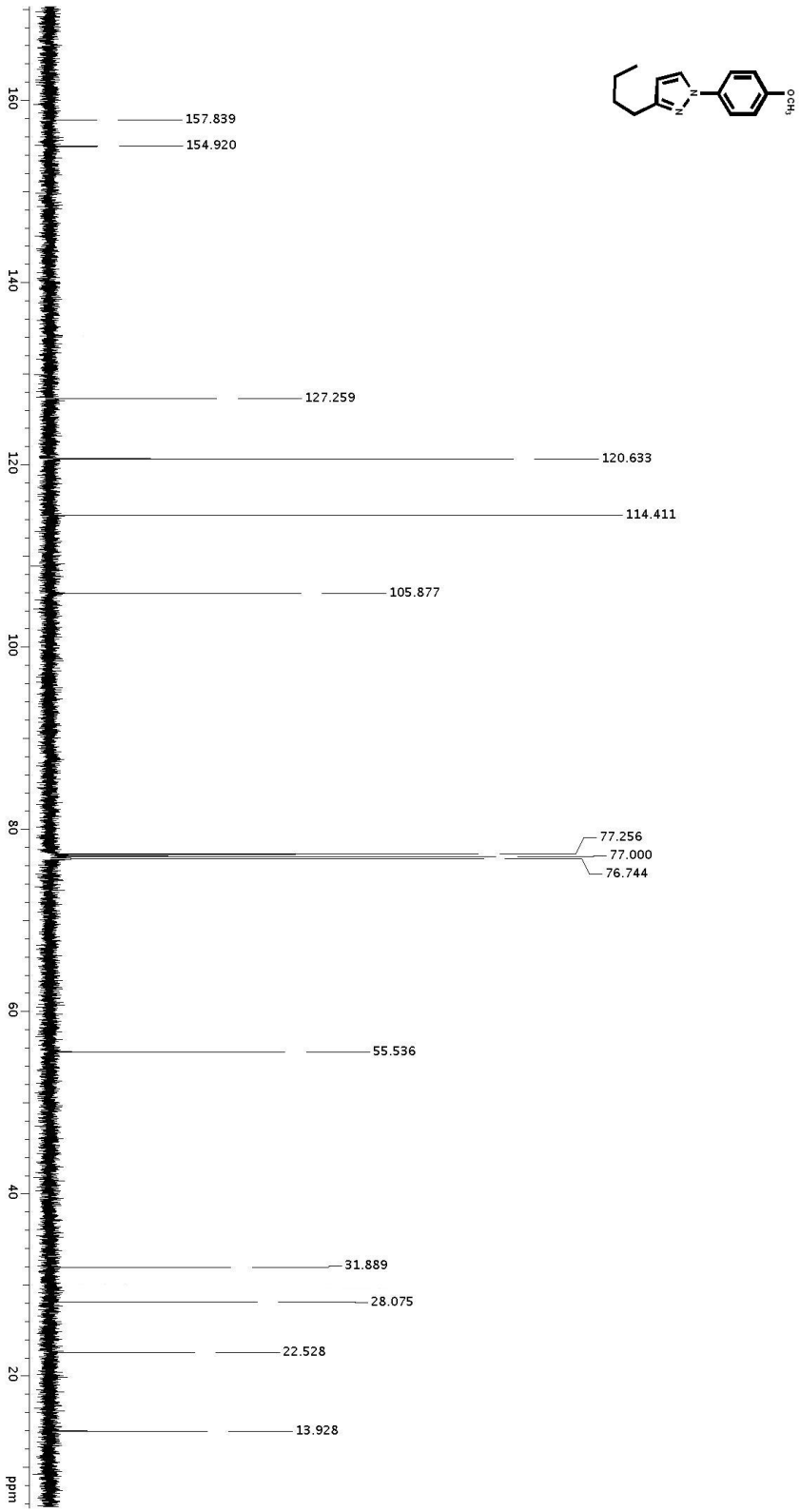

Figure 30. ^{13}C NMR spectra for compound *3-butyl-1-(4-methoxyphenyl)-pyrazole.*

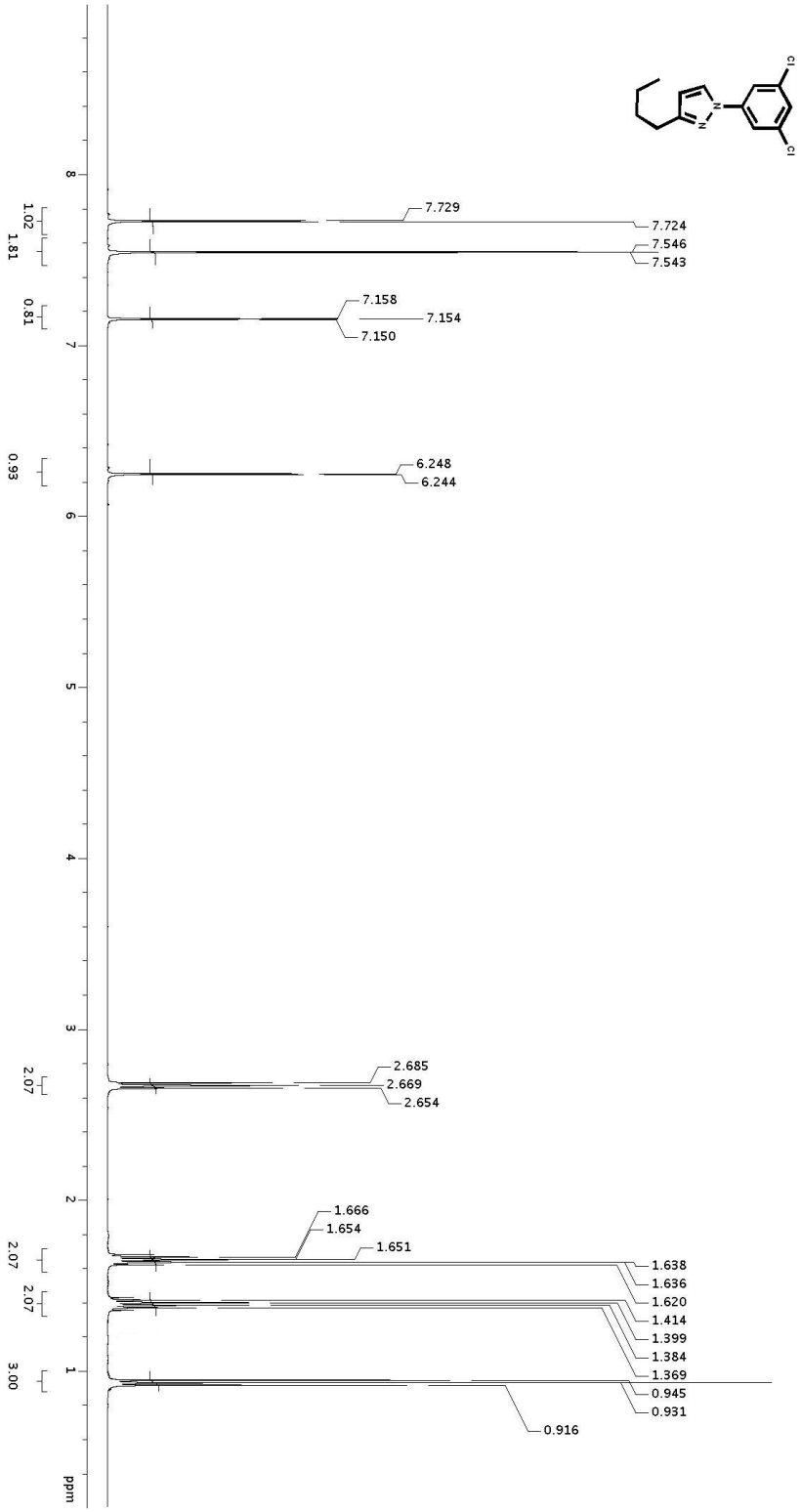

Figure 31. ^{1}H NMR spectra for compound *3-butyl-1-(3,5-dichlorophenyl)-pyrazole.*

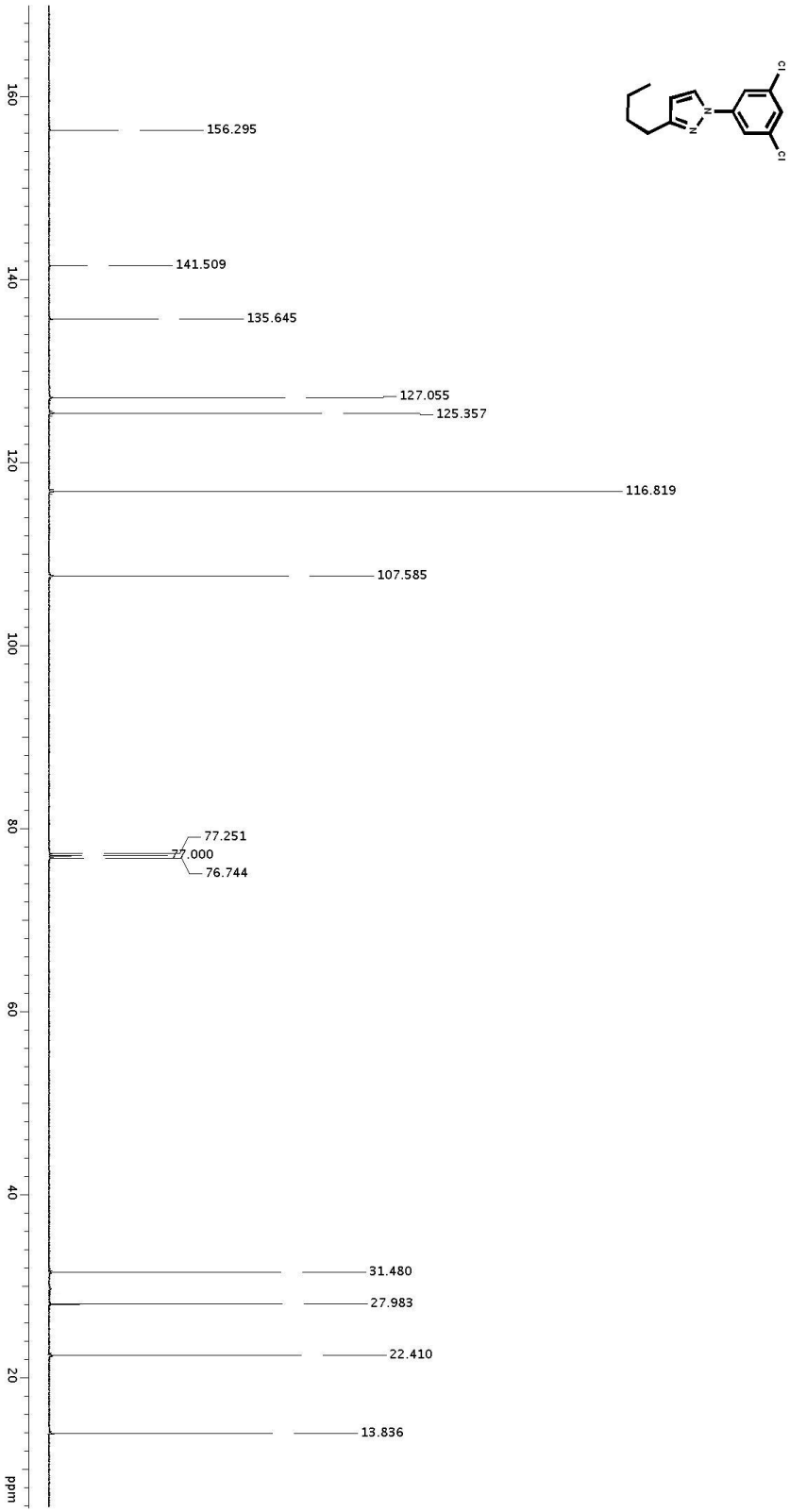

Figure 32. ^{13}C NMR spectra for compound *3-butyl-1-(3,5-dichlorophenyl)-pyrazole.*

Structural Data

Date: September 13, 2011

Submitter: Amila Dissanayake

Sample Reference Number: AD_VII_154

X-ray Number: ADD9sept11

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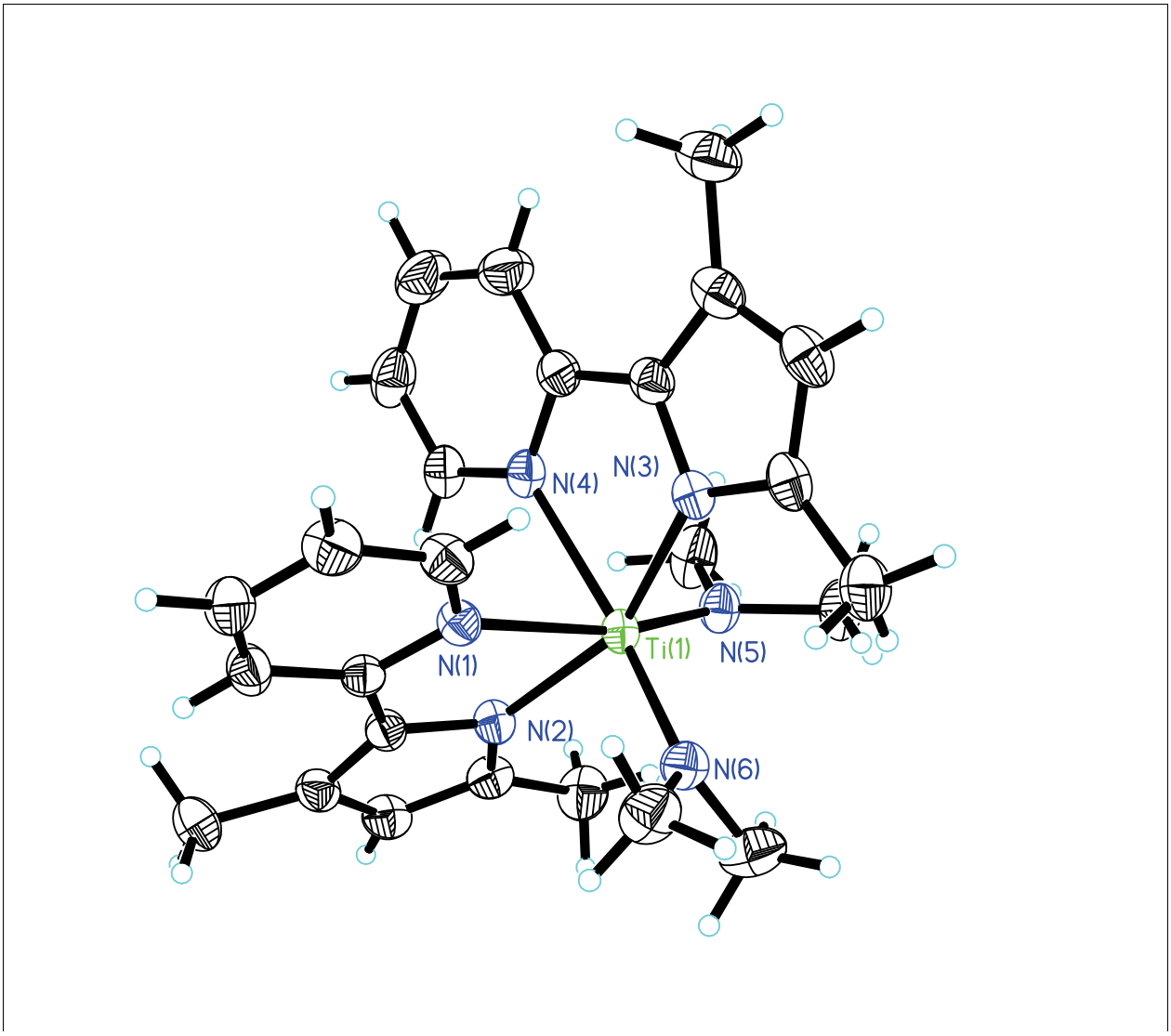


Introduction:

Single crystal study to confirm the identity of the sample submitted.

Experimental Section:

A red block crystal with dimensions 0.48 x 0.28 x 0.23 mm was mounted on a glass fiber using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 10 s. The total number of images was based on results from the program COSMO[1] where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software[2] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[3] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[4] multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL- 97, which are incorporated in SHELXTL-PC V 6.10.[5]

The structure was solved in the space group $P2_1/c$ (# 14). All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids.

Acknowledgement. The CCD based x-ray diffractometer at Michigan State University were upgraded and/or replaced by departmental funds.

References

1. COSMO V1.61, *Software for the CCD Detector Systems for Determining Data Collection Parameters.* Bruker Analytical X-ray Systems, Madison, WI (2009).

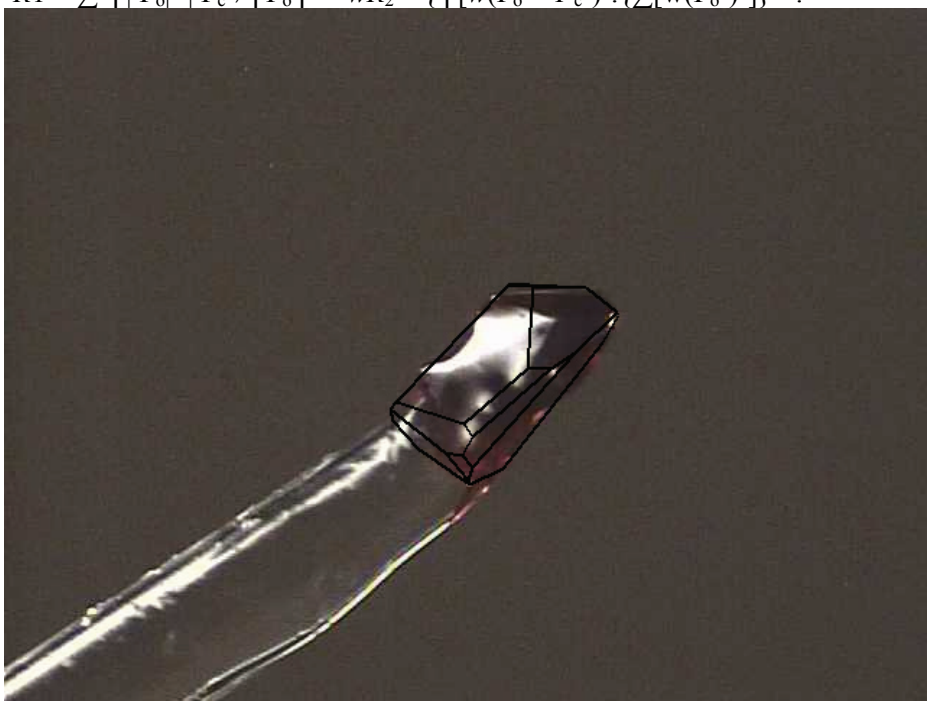
2. APEX2 V2010.11-3. Software *for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (2010).

3. SAINT V 7.68A Software *for the Integration of CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2010).

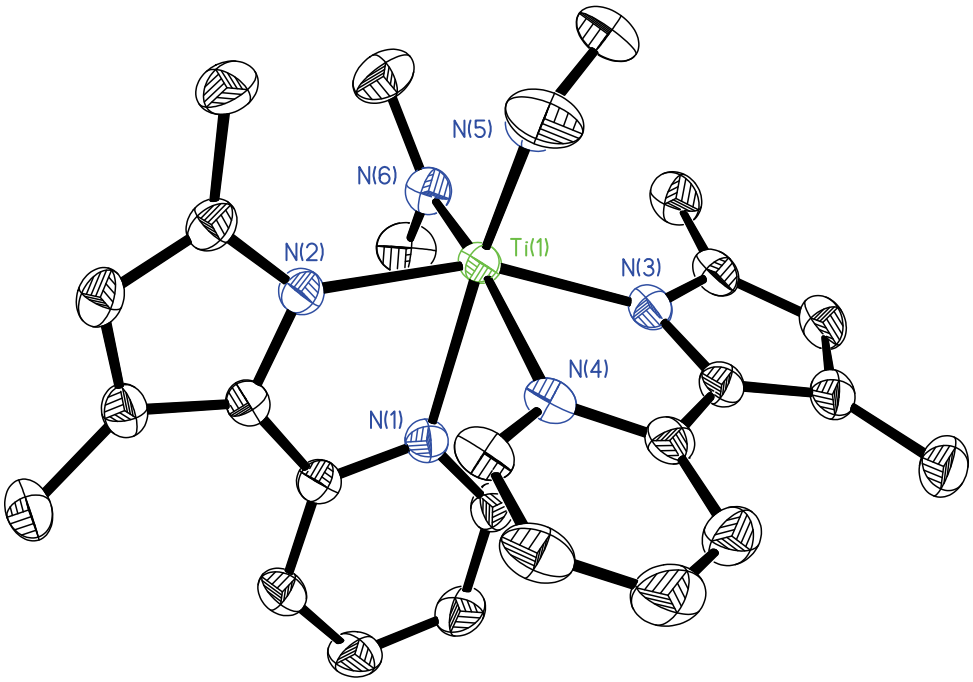
4. SADABS V2.008/2 Program for absorption corrections using Bruker-AXS CCD based on the method of Robert Blessing; Blessing, R.H. Acta Cryst. A51, 1995, 33-38.

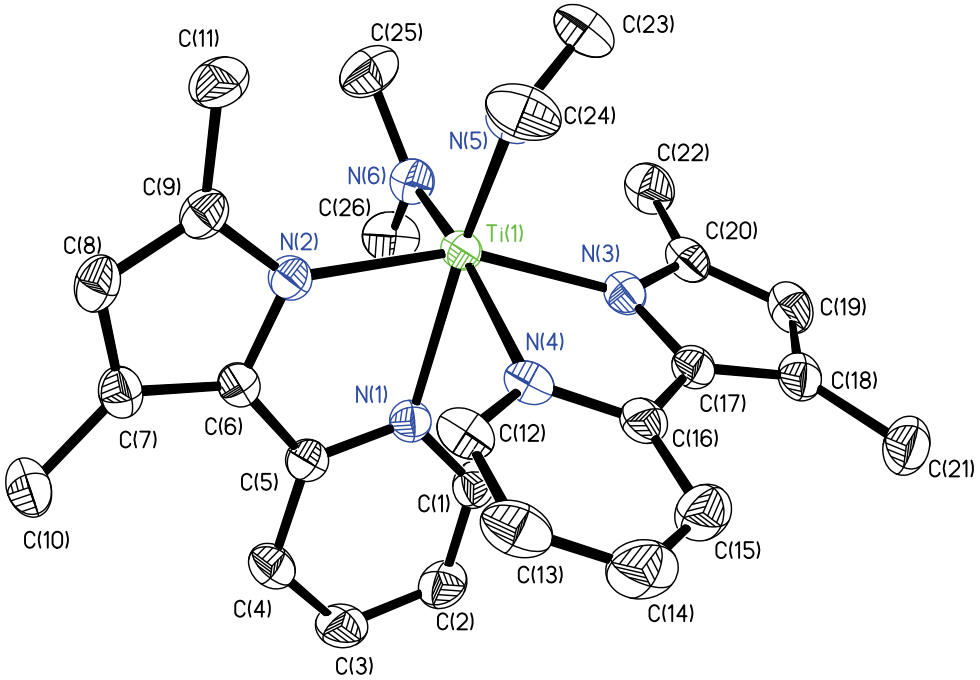
5. Sheldrick, G.M. "A short history of SHELX". *Acta Cryst*. **A64**, 2008, 112-122.

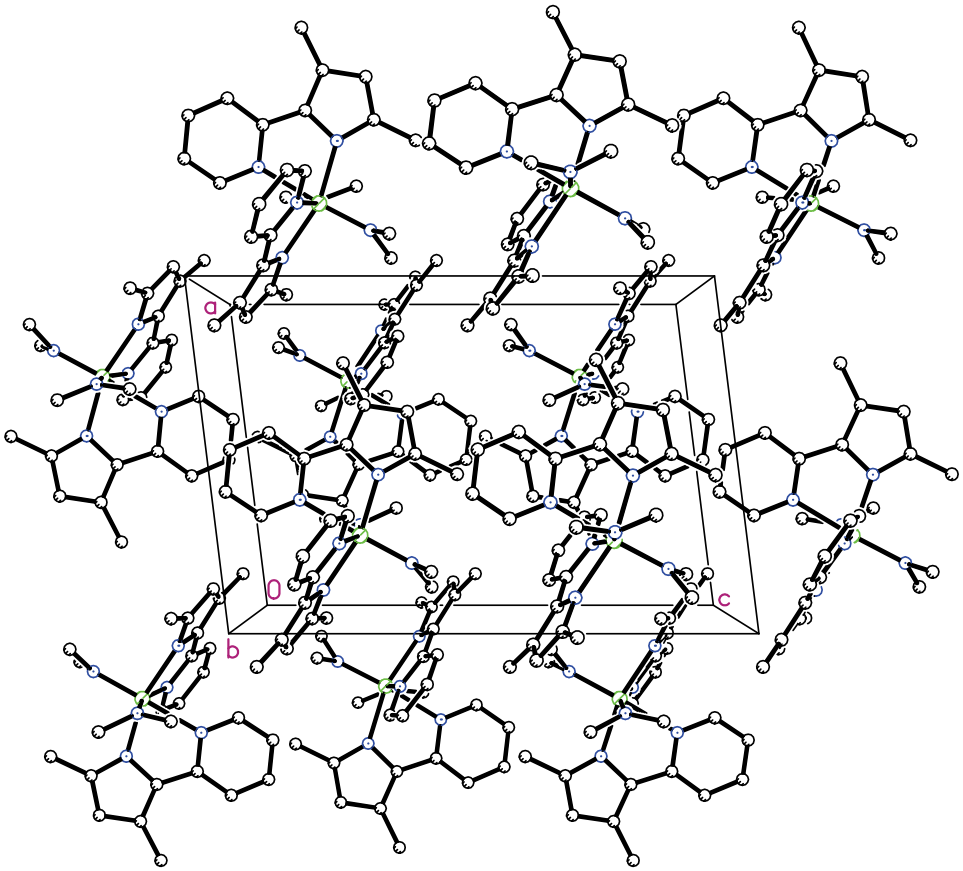
[a] Obtained with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation.
[b] $R1 = \sum \big| |F_o| - |F_c| / |F_o| \big|$ [c] $wR_2 = \{ \big| [w(F_o^2 - F_c^2)^2 . \{\sum [w(F_o^2)^2]\}^{1/2}$.



The following are 50% thermal ellipsoidal drawings of the molecule in the asymmetric cell with various amount of labeling.







This is a drawing of the packing along the b-axis.

Table 1. Crystal data and structure refinement for AAD9sept11_0m.

Identification code	aad9sept11_0m	
Empirical formula	C26 H34 N6 Ti	
Formula weight	478.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.7933(11) Å	α= 90°.
	b = 14.4889(14) Å	β= 97.0720(10)°.
	c = 15.8761(16) Å	γ = 90°.
Volume	2463.9(4) $Å^3$	
Z	4	
Density (calculated)	1.290 Mg/m^3	
Absorption coefficient	0.373 mm^{-1}	
F(000)	1016	
Crystal size	0.42 x 0.28 x 0.23 mm^3	
Theta range for data collection	1.90 to 25.36°.	
Index ranges	-12<=h<=12, -17<=k<=17, -19<=l<=19	
Reflections collected	22406	
Independent reflections	4497 [R(int) = 0.0333]	
Completeness to theta = 25.36°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9184 and 0.8594	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4497 / 0 / 306	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0330, wR2 = 0.0875	
R indices (all data)	R1 = 0.0403, wR2 = 0.0928	
Largest diff. peak and hole	0.255 and -0.327 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for AAD9sept11_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	7425(1)	882(1)	2468(1)	24(1)
N(1)	7597(1)	2384(1)	2836(1)	26(1)
N(2)	9065(1)	957(1)	3349(1)	27(1)
N(3)	5592(1)	1198(1)	1939(1)	27(1)
N(4)	6349(1)	1037(1)	3597(1)	28(1)
N(5)	7149(1)	-418(1)	2495(1)	30(1)
N(6)	8250(1)	1071(1)	1484(1)	31(1)
C(1)	6774(2)	3057(1)	2572(1)	32(1)
C(2)	6876(2)	3948(1)	2870(1)	37(1)
C(3)	7876(2)	4161(1)	3474(1)	37(1)
C(4)	8726(2)	3490(1)	3750(1)	32(1)
C(5)	8576(2)	2588(1)	3429(1)	26(1)
C(6)	9380(2)	1825(1)	3696(1)	26(1)
C(7)	10483(2)	1762(1)	4258(1)	30(1)
C(8)	10840(2)	836(1)	4244(1)	33(1)
C(9)	9976(2)	361(1)	3686(1)	30(1)
C(10)	11207(2)	2500(1)	4763(1)	41(1)
C(11)	10046(2)	-635(1)	3452(1)	42(1)
C(12)	6820(2)	989(1)	4422(1)	33(1)
C(13)	6106(2)	1112(1)	5074(1)	42(1)
C(14)	4847(2)	1298(2)	4868(1)	49(1)
C(15)	4342(2)	1354(1)	4032(1)	41(1)
C(16)	5112(2)	1223(1)	3391(1)	30(1)
C(17)	4694(2)	1284(1)	2496(1)	28(1)
C(18)	3513(2)	1410(1)	2040(1)	33(1)
C(19)	3707(2)	1393(1)	1187(1)	36(1)
C(20)	4969(2)	1266(1)	1136(1)	31(1)
C(21)	2266(2)	1510(2)	2356(2)	45(1)
C(22)	5578(2)	1217(2)	341(1)	41(1)
C(23)	6651(2)	-892(1)	1718(1)	42(1)
C(24)	6982(2)	-985(1)	3227(1)	45(1)

C(25)	9013(2)	367(2)	1152(1)	48(1)
C(26)	8457(2)	1958(1)	1094(1)	44(1)

Table 3. Bond lengths [Å] and angles [°] for AAD9sept11_0m.

Ti(1)-N(5)	1.9081(15)
Ti(1)-N(6)	1.9111(15)
Ti(1)-N(3)	2.1025(14)
Ti(1)-N(2)	2.1195(14)
Ti(1)-N(1)	2.2559(14)
Ti(1)-N(4)	2.2634(15)
N(1)-C(1)	1.350(2)
N(1)-C(5)	1.358(2)
N(2)-C(9)	1.367(2)
N(2)-C(6)	1.398(2)
N(3)-C(20)	1.369(2)
N(3)-C(17)	1.397(2)
N(4)-C(12)	1.347(2)
N(4)-C(16)	1.362(2)
N(5)-C(24)	1.452(2)
N(5)-C(23)	1.456(2)
N(6)-C(25)	1.450(2)
N(6)-C(26)	1.457(2)
C(1)-C(2)	1.375(3)
C(1)-H(1)	0.9500
C(2)-C(3)	1.389(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.371(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.405(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.437(2)
C(6)-C(7)	1.400(2)
C(7)-C(8)	1.396(3)
C(7)-C(10)	1.498(2)
C(8)-C(9)	1.388(3)
C(8)-H(8)	0.9500
C(9)-C(11)	1.495(3)
C(10)-H(10A)	0.9800

C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.376(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.384(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.373(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.403(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.440(2)
C(17)-C(18)	1.398(2)
C(18)-C(19)	1.396(3)
C(18)-C(21)	1.500(3)
C(19)-C(20)	1.386(3)
C(19)-H(19)	0.9500
C(20)-C(22)	1.494(3)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800

C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800

N(5)-Ti(1)-N(6)	104.45(6)
N(5)-Ti(1)-N(3)	94.75(6)
N(6)-Ti(1)-N(3)	98.76(6)
N(5)-Ti(1)-N(2)	98.96(6)
N(6)-Ti(1)-N(2)	95.51(6)
N(3)-Ti(1)-N(2)	157.07(6)
N(5)-Ti(1)-N(1)	162.73(6)
N(6)-Ti(1)-N(1)	92.37(6)
N(3)-Ti(1)-N(1)	86.35(5)
N(2)-Ti(1)-N(1)	75.18(5)
N(5)-Ti(1)-N(4)	89.07(6)
N(6)-Ti(1)-N(4)	165.75(6)
N(3)-Ti(1)-N(4)	75.27(5)
N(2)-Ti(1)-N(4)	86.62(5)
N(1)-Ti(1)-N(4)	74.51(5)
C(1)-N(1)-C(5)	119.00(15)
C(1)-N(1)-Ti(1)	125.89(11)
C(5)-N(1)-Ti(1)	114.89(11)
C(9)-N(2)-C(6)	106.59(14)
C(9)-N(2)-Ti(1)	136.73(12)
C(6)-N(2)-Ti(1)	116.67(10)
C(20)-N(3)-C(17)	106.50(14)
C(20)-N(3)-Ti(1)	135.86(12)
C(17)-N(3)-Ti(1)	117.28(11)
C(12)-N(4)-C(16)	119.00(16)
C(12)-N(4)-Ti(1)	126.55(13)
C(16)-N(4)-Ti(1)	114.42(11)
C(24)-N(5)-C(23)	110.06(15)
C(24)-N(5)-Ti(1)	127.67(12)
C(23)-N(5)-Ti(1)	119.22(12)
C(25)-N(6)-C(26)	110.05(16)
C(25)-N(6)-Ti(1)	122.63(13)
C(26)-N(6)-Ti(1)	125.81(12)

N(1)-C(1)-C(2)	123.30(17)
N(1)-C(1)-H(1)	118.3
C(2)-C(1)-H(1)	118.3
C(1)-C(2)-C(3)	118.03(17)
C(1)-C(2)-H(2)	121.0
C(3)-C(2)-H(2)	121.0
C(4)-C(3)-C(2)	119.66(17)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	120.11(17)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
N(1)-C(5)-C(4)	119.90(15)
N(1)-C(5)-C(6)	115.35(14)
C(4)-C(5)-C(6)	124.74(15)
N(2)-C(6)-C(7)	109.79(15)
N(2)-C(6)-C(5)	117.83(14)
C(7)-C(6)-C(5)	132.37(16)
C(8)-C(7)-C(6)	105.54(15)
C(8)-C(7)-C(10)	124.55(16)
C(6)-C(7)-C(10)	129.88(17)
C(9)-C(8)-C(7)	108.73(15)
C(9)-C(8)-H(8)	125.6
C(7)-C(8)-H(8)	125.6
N(2)-C(9)-C(8)	109.34(16)
N(2)-C(9)-C(11)	124.63(16)
C(8)-C(9)-C(11)	125.97(16)
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5

C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(4)-C(12)-C(13)	123.04(18)
N(4)-C(12)-H(12)	118.5
C(13)-C(12)-H(12)	118.5
C(12)-C(13)-C(14)	118.12(19)
C(12)-C(13)-H(13)	120.9
C(14)-C(13)-H(13)	120.9
C(15)-C(14)-C(13)	120.09(19)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	119.52(19)
C(14)-C(15)-H(15)	120.2
C(16)-C(15)-H(15)	120.2
N(4)-C(16)-C(15)	120.21(17)
N(4)-C(16)-C(17)	115.31(16)
C(15)-C(16)-C(17)	124.47(17)
N(3)-C(17)-C(18)	110.07(16)
N(3)-C(17)-C(16)	117.55(15)
C(18)-C(17)-C(16)	132.37(17)
C(19)-C(18)-C(17)	105.29(17)
C(19)-C(18)-C(21)	125.05(18)
C(17)-C(18)-C(21)	129.63(18)
C(20)-C(19)-C(18)	109.00(16)
C(20)-C(19)-H(19)	125.5
C(18)-C(19)-H(19)	125.5
N(3)-C(20)-C(19)	109.14(16)
N(3)-C(20)-C(22)	124.47(16)
C(19)-C(20)-C(22)	126.38(16)
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
N(5)-C(23)-H(23A)	109.5
N(5)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
N(5)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
N(5)-C(24)-H(24A)	109.5
N(5)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
N(5)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
N(6)-C(25)-H(25A)	109.5
N(6)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
N(6)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
N(6)-C(26)-H(26A)	109.5
N(6)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
N(6)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for AAD9sept11_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	26(1)	21(1)	23(1)	-1(1)	0(1)	0(1)
N(1)	26(1)	24(1)	28(1)	1(1)	2(1)	0(1)
N(2)	27(1)	25(1)	28(1)	0(1)	0(1)	1(1)
N(3)	28(1)	26(1)	27(1)	-1(1)	0(1)	-2(1)
N(4)	34(1)	23(1)	25(1)	-2(1)	2(1)	-3(1)
N(5)	37(1)	24(1)	28(1)	-1(1)	2(1)	-2(1)
N(6)	31(1)	32(1)	28(1)	2(1)	3(1)	0(1)
C(1)	28(1)	28(1)	39(1)	3(1)	0(1)	2(1)
C(2)	36(1)	26(1)	50(1)	5(1)	5(1)	6(1)
C(3)	43(1)	22(1)	48(1)	-4(1)	9(1)	-2(1)
C(4)	35(1)	28(1)	33(1)	-3(1)	3(1)	-6(1)
C(5)	26(1)	27(1)	25(1)	0(1)	6(1)	-2(1)
C(6)	26(1)	27(1)	24(1)	0(1)	3(1)	-2(1)
C(7)	27(1)	37(1)	26(1)	1(1)	2(1)	-3(1)
C(8)	28(1)	40(1)	30(1)	6(1)	0(1)	5(1)
C(9)	29(1)	32(1)	28(1)	5(1)	3(1)	6(1)
C(10)	34(1)	46(1)	40(1)	-3(1)	-6(1)	-5(1)
C(11)	44(1)	33(1)	46(1)	0(1)	0(1)	13(1)
C(12)	42(1)	28(1)	28(1)	-1(1)	2(1)	-5(1)
C(13)	61(1)	38(1)	27(1)	-2(1)	8(1)	-7(1)
C(14)	58(1)	53(1)	41(1)	-5(1)	24(1)	-6(1)
C(15)	38(1)	43(1)	45(1)	-2(1)	14(1)	-1(1)
C(16)	32(1)	22(1)	35(1)	-2(1)	7(1)	-6(1)
C(17)	27(1)	21(1)	35(1)	-1(1)	3(1)	-3(1)
C(18)	29(1)	21(1)	49(1)	2(1)	0(1)	-1(1)
C(19)	34(1)	29(1)	42(1)	5(1)	-10(1)	-1(1)
C(20)	35(1)	24(1)	31(1)	2(1)	-6(1)	-3(1)
C(21)	30(1)	41(1)	65(1)	2(1)	5(1)	2(1)
C(22)	45(1)	46(1)	29(1)	0(1)	-6(1)	0(1)
C(23)	56(1)	36(1)	33(1)	-6(1)	1(1)	-11(1)
C(24)	71(2)	29(1)	35(1)	2(1)	7(1)	-6(1)

C(25)	46(1)	46(1)	56(1)	4(1)	21(1)	9(1)
C(26)	55(1)	38(1)	40(1)	5(1)	15(1)	-4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for AAD9sept11_0m.

	x	y	z	U(eq)
H(1)	6090	2907	2159	38
H(2)	6280	4404	2668	45
H(3)	7972	4770	3696	45
H(4)	9417	3634	4159	39
H(8)	11556	575	4565	40
H(10A)	11464	2972	4378	61
H(10B)	11949	2228	5087	61
H(10C)	10683	2782	5154	61
H(11A)	9838	-1018	3923	63
H(11B)	10894	-780	3332	63
H(11C)	9453	-759	2946	63
H(12)	7685	864	4560	40
H(13)	6466	1070	5650	50
H(14)	4332	1388	5305	59
H(15)	3478	1479	3889	49
H(19)	3077	1458	718	43
H(21A)	2093	960	2681	68
H(21B)	1616	1582	1873	68
H(21C)	2275	2056	2723	68
H(22A)	6063	1780	285	61
H(22B)	4936	1159	-149	61
H(22C)	6133	680	367	61
H(23A)	7128	-1458	1658	63
H(23B)	6716	-488	1230	63
H(23C)	5772	-1048	1742	63
H(24A)	6088	-1063	3264	68
H(24B)	7378	-683	3744	68
H(24C)	7366	-1590	3168	68
H(25A)	8737	276	547	72
H(25B)	8931	-213	1457	72

H(25C)	9889	564	1229	72
H(26A)	9300	2179	1297	65
H(26B)	7841	2405	1248	65
H(26C)	8370	1888	476	65

Table 6. Torsion angles [°] for AAD9sept11_0m.

N(5)-Ti(1)-N(1)-C(1)	-104.8(2)
N(6)-Ti(1)-N(1)-C(1)	88.13(15)
N(3)-Ti(1)-N(1)-C(1)	-10.51(14)
N(2)-Ti(1)-N(1)-C(1)	-176.80(15)
N(4)-Ti(1)-N(1)-C(1)	-86.22(14)
N(5)-Ti(1)-N(1)-C(5)	69.7(2)
N(6)-Ti(1)-N(1)-C(5)	-97.41(12)
N(3)-Ti(1)-N(1)-C(5)	163.96(12)
N(2)-Ti(1)-N(1)-C(5)	-2.33(11)
N(4)-Ti(1)-N(1)-C(5)	88.24(12)
N(5)-Ti(1)-N(2)-C(9)	19.29(18)
N(6)-Ti(1)-N(2)-C(9)	-86.31(18)
N(3)-Ti(1)-N(2)-C(9)	145.30(17)
N(1)-Ti(1)-N(2)-C(9)	-177.32(18)
N(4)-Ti(1)-N(2)-C(9)	107.82(17)
N(5)-Ti(1)-N(2)-C(6)	-162.12(12)
N(6)-Ti(1)-N(2)-C(6)	92.27(12)
N(3)-Ti(1)-N(2)-C(6)	-36.1(2)
N(1)-Ti(1)-N(2)-C(6)	1.27(11)
N(4)-Ti(1)-N(2)-C(6)	-73.60(12)
N(5)-Ti(1)-N(3)-C(20)	-87.73(17)
N(6)-Ti(1)-N(3)-C(20)	17.71(17)
N(2)-Ti(1)-N(3)-C(20)	145.58(16)
N(1)-Ti(1)-N(3)-C(20)	109.55(17)
N(4)-Ti(1)-N(3)-C(20)	-175.51(17)
N(5)-Ti(1)-N(3)-C(17)	84.36(12)
N(6)-Ti(1)-N(3)-C(17)	-170.20(12)
N(2)-Ti(1)-N(3)-C(17)	-42.3(2)
N(1)-Ti(1)-N(3)-C(17)	-78.36(12)
N(4)-Ti(1)-N(3)-C(17)	-3.43(11)
N(5)-Ti(1)-N(4)-C(12)	88.39(14)
N(6)-Ti(1)-N(4)-C(12)	-109.8(2)
N(3)-Ti(1)-N(4)-C(12)	-176.45(15)
N(2)-Ti(1)-N(4)-C(12)	-10.64(14)

N(1)-Ti(1)-N(4)-C(12)	-86.19(14)
N(5)-Ti(1)-N(4)-C(16)	-93.55(12)
N(6)-Ti(1)-N(4)-C(16)	68.3(3)
N(3)-Ti(1)-N(4)-C(16)	1.60(11)
N(2)-Ti(1)-N(4)-C(16)	167.42(12)
N(1)-Ti(1)-N(4)-C(16)	91.86(12)
N(6)-Ti(1)-N(5)-C(24)	155.79(17)
N(3)-Ti(1)-N(5)-C(24)	-103.89(17)
N(2)-Ti(1)-N(5)-C(24)	57.68(17)
N(1)-Ti(1)-N(5)-C(24)	-10.9(3)
N(4)-Ti(1)-N(5)-C(24)	-28.75(17)
N(6)-Ti(1)-N(5)-C(23)	-46.05(15)
N(3)-Ti(1)-N(5)-C(23)	54.28(15)
N(2)-Ti(1)-N(5)-C(23)	-144.16(14)
N(1)-Ti(1)-N(5)-C(23)	147.25(18)
N(4)-Ti(1)-N(5)-C(23)	129.41(15)
N(5)-Ti(1)-N(6)-C(25)	-27.53(16)
N(3)-Ti(1)-N(6)-C(25)	-124.78(15)
N(2)-Ti(1)-N(6)-C(25)	73.21(15)
N(1)-Ti(1)-N(6)-C(25)	148.55(15)
N(4)-Ti(1)-N(6)-C(25)	171.2(2)
N(5)-Ti(1)-N(6)-C(26)	167.90(15)
N(3)-Ti(1)-N(6)-C(26)	70.65(15)
N(2)-Ti(1)-N(6)-C(26)	-91.35(15)
N(1)-Ti(1)-N(6)-C(26)	-16.02(15)
N(4)-Ti(1)-N(6)-C(26)	6.7(3)
C(5)-N(1)-C(1)-C(2)	0.4(3)
Ti(1)-N(1)-C(1)-C(2)	174.61(14)
N(1)-C(1)-C(2)-C(3)	-0.2(3)
C(1)-C(2)-C(3)-C(4)	0.3(3)
C(2)-C(3)-C(4)-C(5)	-0.7(3)
C(1)-N(1)-C(5)-C(4)	-0.7(2)
Ti(1)-N(1)-C(5)-C(4)	-175.57(12)
C(1)-N(1)-C(5)-C(6)	177.85(15)
Ti(1)-N(1)-C(5)-C(6)	2.98(18)
C(3)-C(4)-C(5)-N(1)	0.9(3)

C(3)-C(4)-C(5)-C(6)	-177.52(17)
C(9)-N(2)-C(6)-C(7)	-0.63(19)
Ti(1)-N(2)-C(6)-C(7)	-179.62(11)
C(9)-N(2)-C(6)-C(5)	178.83(15)
Ti(1)-N(2)-C(6)-C(5)	-0.15(19)
N(1)-C(5)-C(6)-N(2)	-2.0(2)
C(4)-C(5)-C(6)-N(2)	176.51(16)
N(1)-C(5)-C(6)-C(7)	177.36(17)
C(4)-C(5)-C(6)-C(7)	-4.2(3)
N(2)-C(6)-C(7)-C(8)	0.2(2)
C(5)-C(6)-C(7)-C(8)	-179.17(18)
N(2)-C(6)-C(7)-C(10)	178.18(18)
C(5)-C(6)-C(7)-C(10)	-1.2(3)
C(6)-C(7)-C(8)-C(9)	0.3(2)
C(10)-C(7)-C(8)-C(9)	-177.80(17)
C(6)-N(2)-C(9)-C(8)	0.8(2)
Ti(1)-N(2)-C(9)-C(8)	179.51(13)
C(6)-N(2)-C(9)-C(11)	-176.52(17)
Ti(1)-N(2)-C(9)-C(11)	2.2(3)
C(7)-C(8)-C(9)-N(2)	-0.7(2)
C(7)-C(8)-C(9)-C(11)	176.57(18)
C(16)-N(4)-C(12)-C(13)	0.5(3)
Ti(1)-N(4)-C(12)-C(13)	178.48(13)
N(4)-C(12)-C(13)-C(14)	-0.3(3)
C(12)-C(13)-C(14)-C(15)	0.2(3)
C(13)-C(14)-C(15)-C(16)	-0.2(3)
C(12)-N(4)-C(16)-C(15)	-0.6(2)
Ti(1)-N(4)-C(16)-C(15)	-178.77(13)
C(12)-N(4)-C(16)-C(17)	178.60(15)
Ti(1)-N(4)-C(16)-C(17)	0.39(18)
C(14)-C(15)-C(16)-N(4)	0.4(3)
C(14)-C(15)-C(16)-C(17)	-178.65(18)
C(20)-N(3)-C(17)-C(18)	-0.33(19)
Ti(1)-N(3)-C(17)-C(18)	-174.59(11)
C(20)-N(3)-C(17)-C(16)	179.20(15)
Ti(1)-N(3)-C(17)-C(16)	4.94(19)

N(4)-C(16)-C(17)-N(3)	-3.4(2)
C(15)-C(16)-C(17)-N(3)	175.73(16)
N(4)-C(16)-C(17)-C(18)	176.01(17)
C(15)-C(16)-C(17)-C(18)	-4.9(3)
N(3)-C(17)-C(18)-C(19)	0.41(19)
C(16)-C(17)-C(18)-C(19)	-179.02(18)
N(3)-C(17)-C(18)-C(21)	178.36(17)
C(16)-C(17)-C(18)-C(21)	-1.1(3)
C(17)-C(18)-C(19)-C(20)	-0.3(2)
C(21)-C(18)-C(19)-C(20)	-178.41(17)
C(17)-N(3)-C(20)-C(19)	0.11(19)
Ti(1)-N(3)-C(20)-C(19)	172.77(12)
C(17)-N(3)-C(20)-C(22)	179.60(17)
Ti(1)-N(3)-C(20)-C(22)	-7.7(3)
C(18)-C(19)-C(20)-N(3)	0.1(2)
C(18)-C(19)-C(20)-C(22)	-179.33(17)

Symmetry transformations used to generate equivalent atoms: