Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Correlation of spectroscopically determined ligand donor strength and nucleophilicity of substituted pyrazoles

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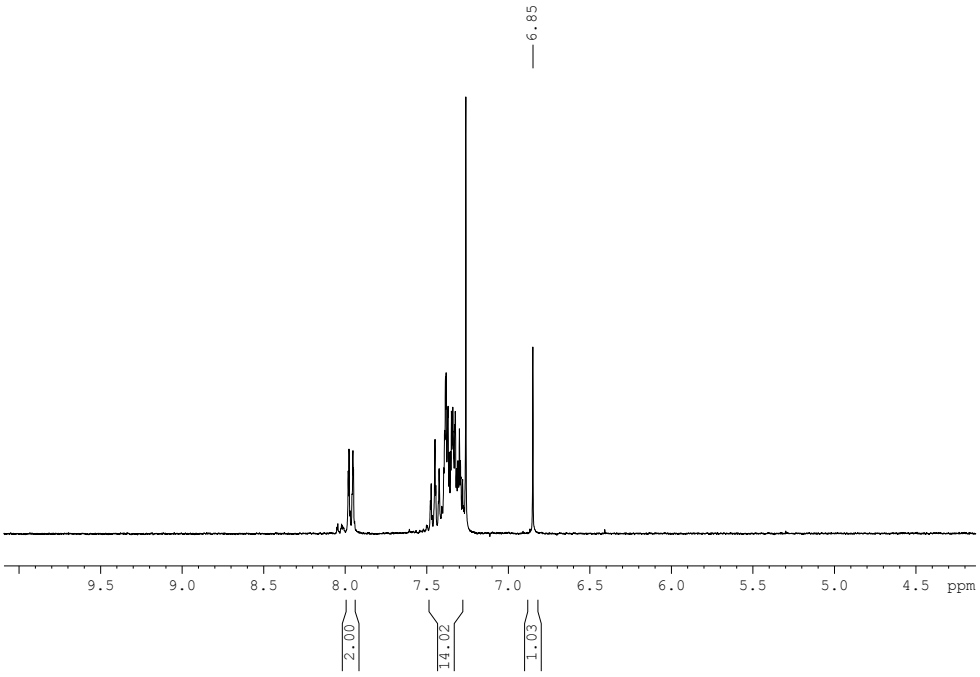
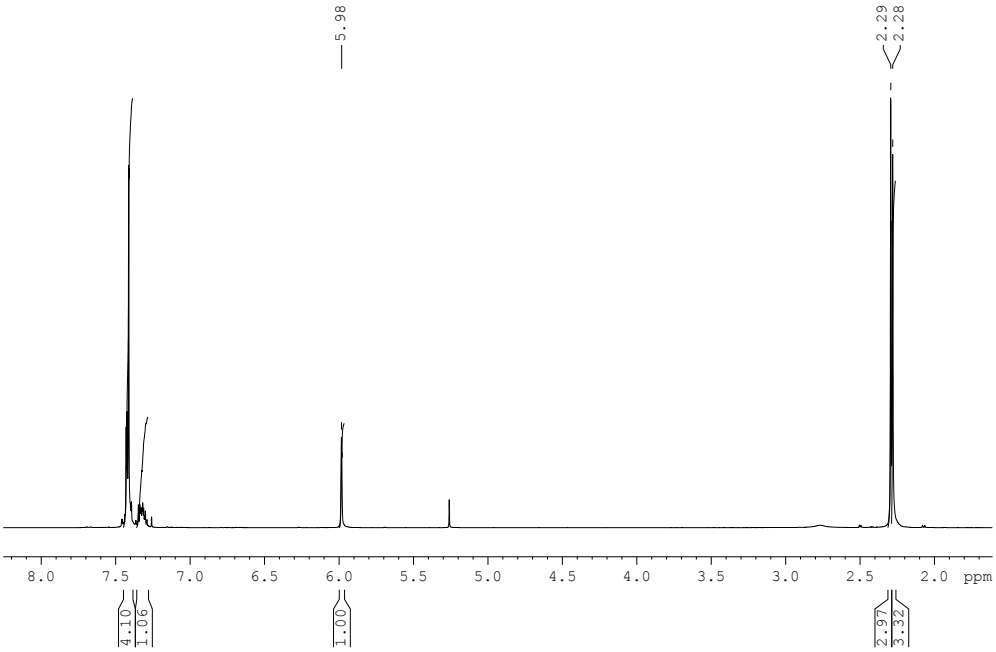
1,3,5-Triphenyl-1*H*-pyrazole (4). Dibenzoylmethane (**1**) (3.00 g, 13.4 mmol, 1.00 eq.) and phenylhydrazine-hydrochloride (2.13 g, 14.7 mmol, 1.10 eq.) were dissolved in 2-propanol (45 mL). The resulting mixture was heated to reflux for 8 h. After that time, it was allowed to cool to ambient temperature, and the solvent was evaporated *in vacuo*. The residue was suspended in dichloromethane (60 mL) and the solution was washed with sodium bicarbonate solution (1 M, 100 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The residue was purified by recrystallization from boiling methanol (100 mL). The product was isolated as pale yellow solid (2.60 g, 65% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (m_C, 2 H, Ar-H), 7.28 – 7.49 (m, 13 H, Ar-H), 6.85 (s, 1 H). The analytical data was in accordance with the reported values.[20]

^{1}H NMR (300 MHz, $CDCl_3$)



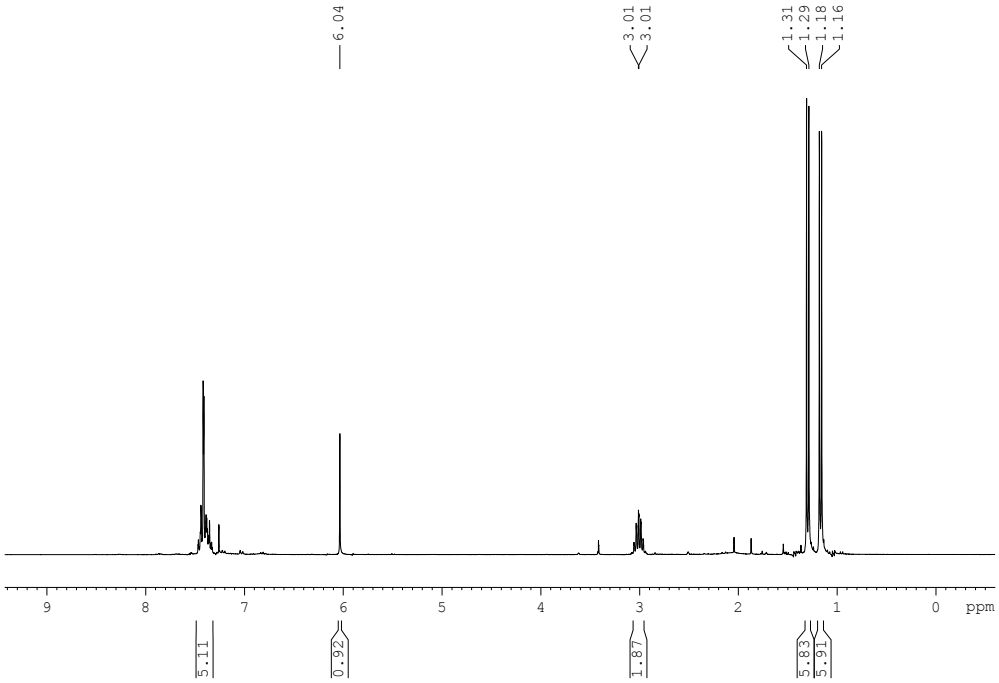
3,5-Dimethyl-1-phenyl-1*H*-pyrazole (5). Acetylacetonate (**2**) (5.00 g, 50.0 mmol, 1.00 eq.) and phenylhydrazine-hydrochloride (7.59 g, 52.5 mmol, 1.05 eq.) were dissolved in absolute ethanol (300 mL). The resulting mixture was heated to reflux for 16 h. After that time, it was allowed to cool to ambient temperature, and the solvent was evaporated *in vacuo*. The residue was suspended in dichloromethane (150 mL) and the solution was washed with sodium bicarbonate solution (1 M, 80 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The residue was purified by Kugelrohr distillation (p = 1 mbar, T = 120 °C). The product was isolated as pale yellow liquid (7.54 g, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.45 (m, 4 H, Ar-H), 7.28 – 7.36 (m, 1 H, Ar-H), 5.98 (s, 1 H), 2.29 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3). The analytical data was in accordance with the reported values.[9]

^{1}H NMR (300 MHz, $CDCl_3$)



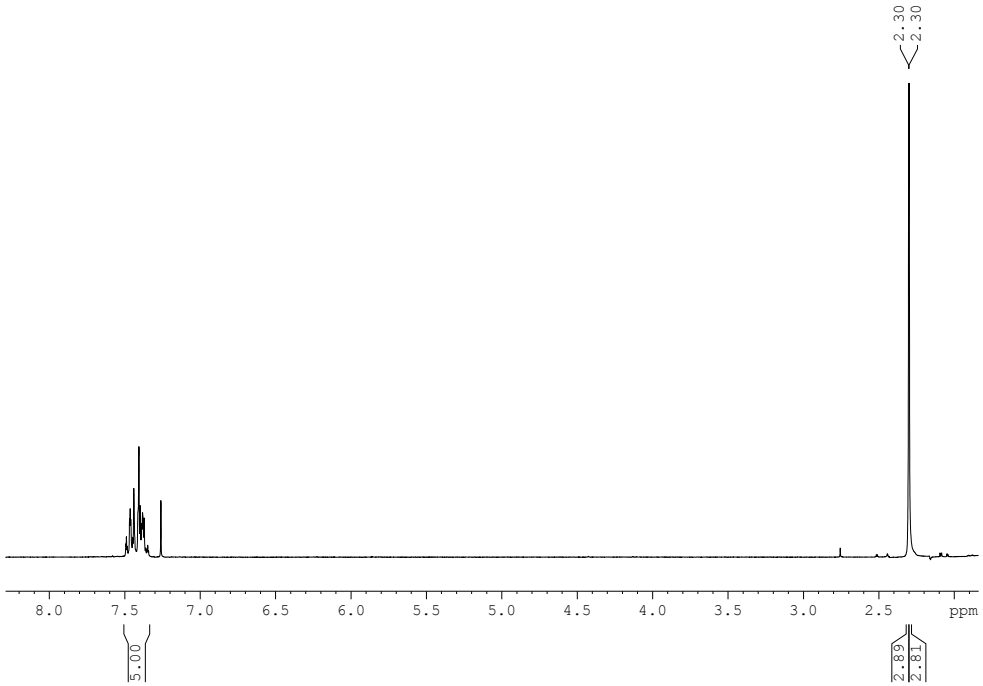
3,5-Diisopropyl-1-phenyl-1*H*-pyrazole (6). 2,6-Dimethyl-3,5-heptandione (**3**) (970 mg, 6.21 mmol, 1.00 eq.) and phenylhydrazine-hydrochloride (988 mg, 6.83 mmol, 1.10 eq.) were dissolved in 2-propanol (14 mL). The resulting mixture was heated to reflux for 14 h. After that time, it was allowed to cool to ambient temperature, and the solvent was evaporated *in vacuo*. The residue was suspended in dichloromethane (30 mL) and the solution was washed with sodium bicarbonate solution (1 M, 30 mL). The organic phase was dried over anhydrous sodium sulfate, filtered, and the solvent was removed *in vacuo*. The product was isolated as an orange liquid (1.32 g, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 – 7.49 (m, 5 H, Ar-H), 6.04 (s, 1 H), 3.00 (sept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1 H, C*H*$(CH_3)_2$, 3.00 (sept, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 1 H, C*H*$(CH_3)_2$), 1.30 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 3 H, CH(C*H*$_3)_2$), 1.17 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 3 H, CH(C*H*$_3)_2$). The analytical data was in accordance with the reported values.[20]

^{1}H NMR (300 MHz, $CDCl_3$)



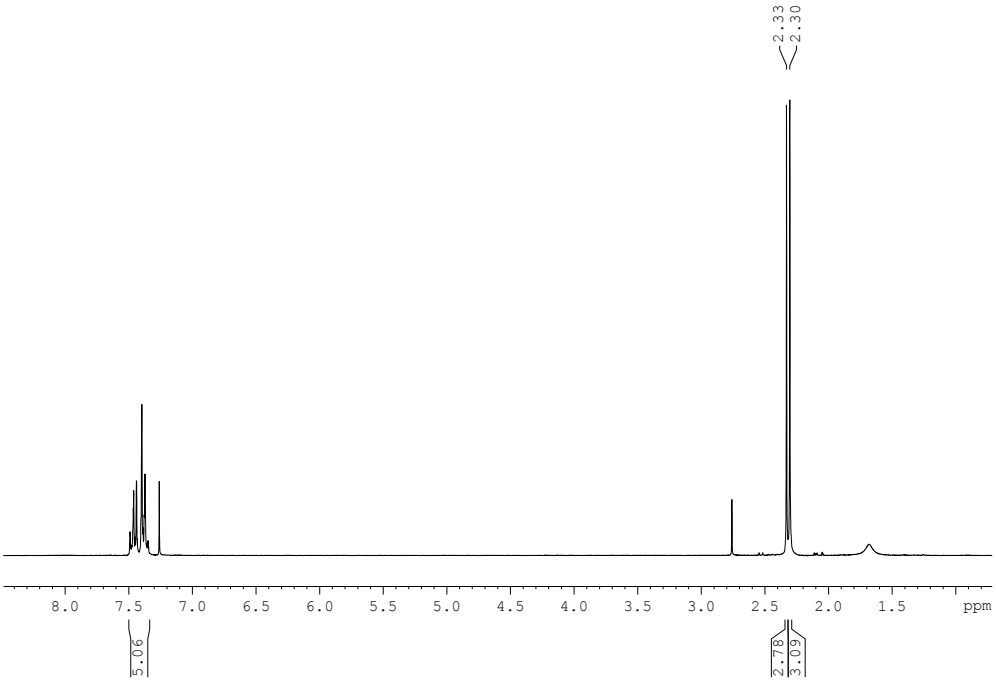
4-Bromo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (8). 3,5-Dimethyl-1-phenyl-1*H*-pyrazole (**5**) (500 mg, 2.90 mmol, 1.00 eq) and N-bromosuccinimide (1.03 g, 5.80 mmol, 2.00 eq) were dissolved in ethyl acetate (13 mL). The solution was sonicated at ambient temperature for 30 min. The reaction mixture was washed with saturated sodium thiosulfate solution (2 × 20 mL) and water (20 mL), dried over sodium sulfate and filtered. The solvent was removed *in vacuo*. The product was obtained as a pale yellow oil (700 mg, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.50 (m, 5 H, Ar-H), 2.30 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3). The analytical data was in accordance with the reported values.[10]

^{1}H NMR (300 MHz, $CDCl_3$)



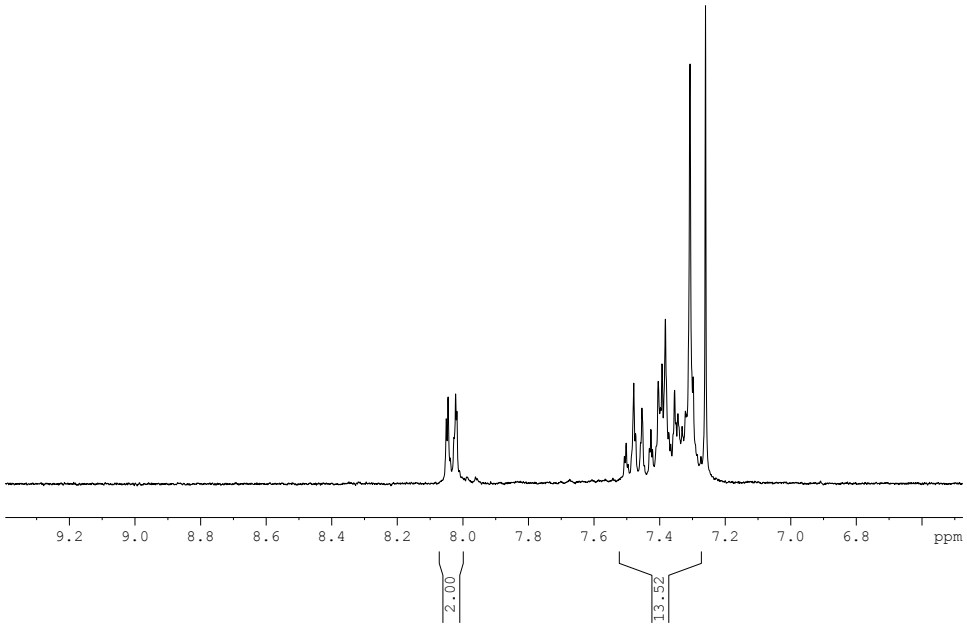
4-Iodo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (9). 3,5-Dimethyl-1-phenyl-1*H*-pyrazole (**5**) (1.50 g, 8.71 mmol, 1.00 eq) and N-iodosuccinimide (2.94 g, 13.1 mmol, 1.50 eq) were dissolved in ethyl acetate (20 mL). The solution was sonicated at ambient temperature for 4 h. The reaction mixture was washed with saturated sodium thiosulfate solution (45 mL). The aqueous phase was extracted with ethyl acetate (50 mL). The combined organic layers were dried over sodium sulfate and filtered. The solvent was removed *in vacuo*. The product was obtained as a light brown oil (2.46 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.50 (m, 5 H, Ar-H), 2.33 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3). The analytical data was in accordance with the reported values.[20]

^{1}H NMR (300 MHz, $CDCl_3$)

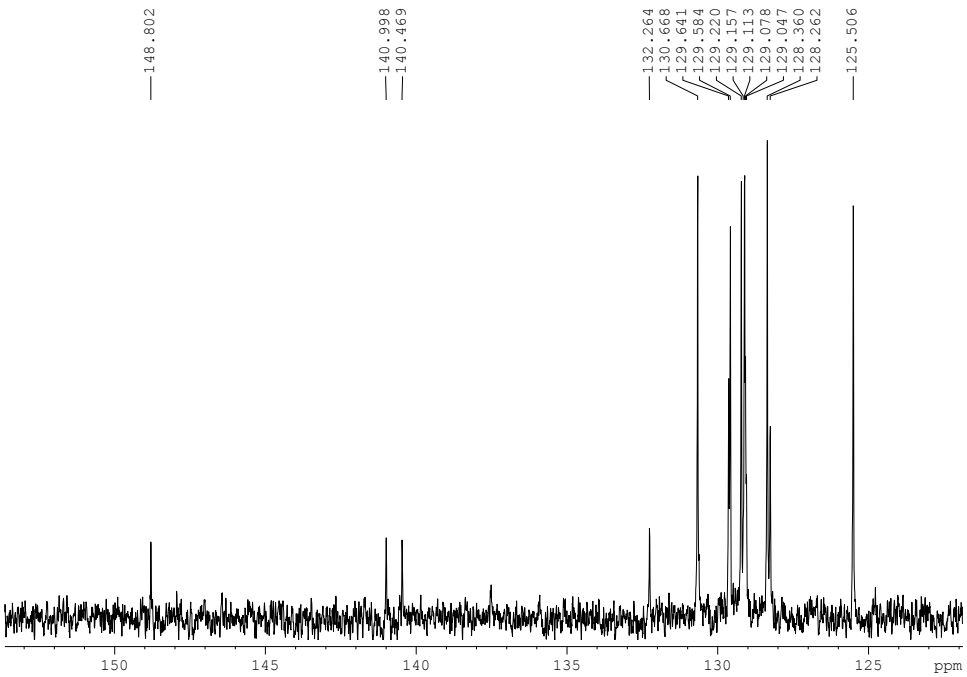


4-Chloro-1,3,5-triphenyl-1*H*-pyrazole (10)

^{1}H NMR (300 MHz, $CDCl_3$)

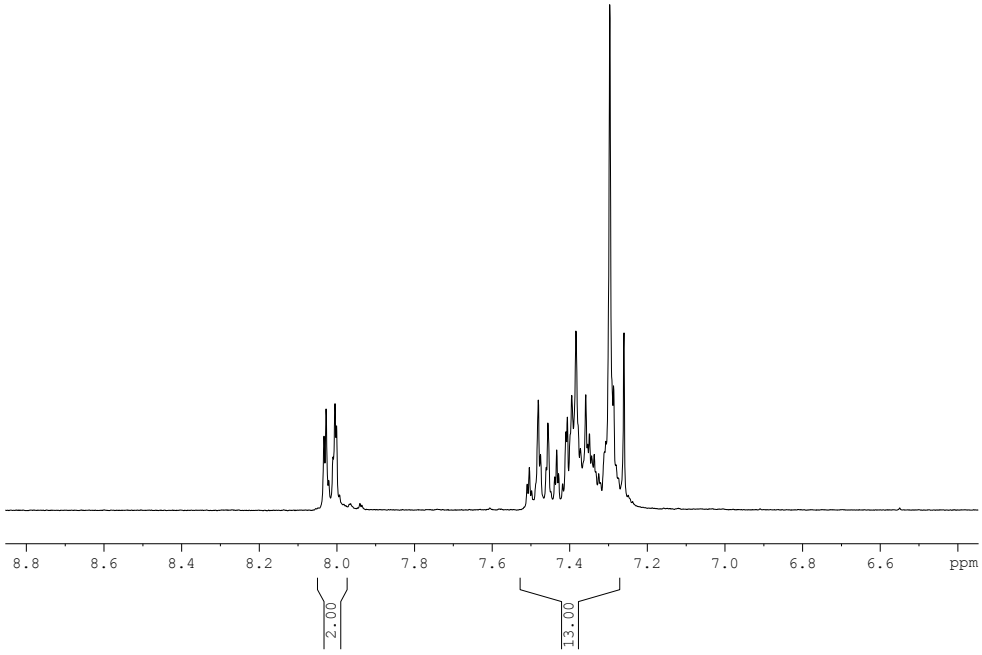


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



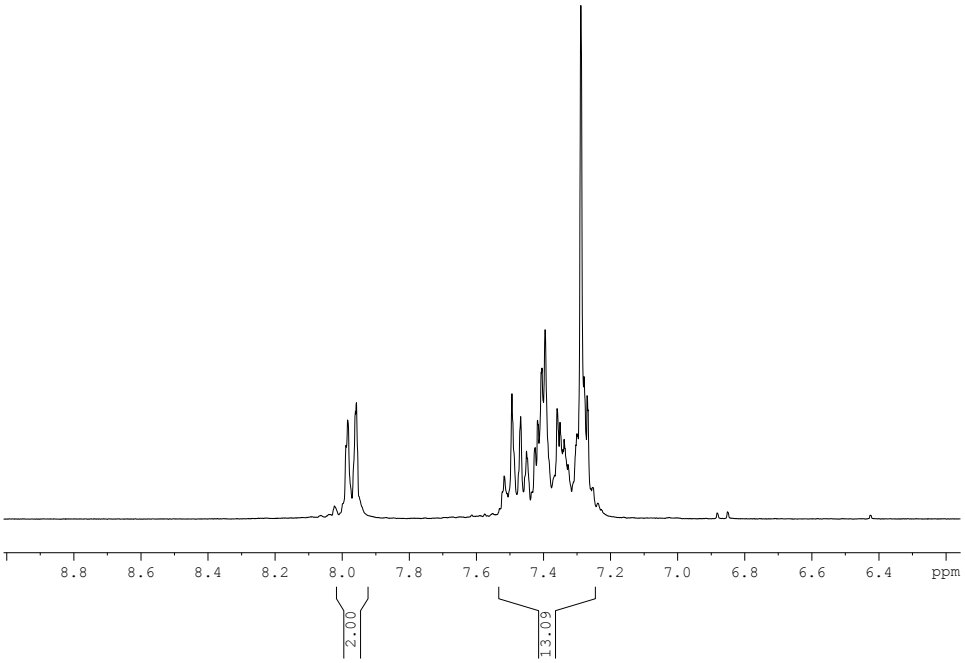
4-Bromo-1,3,5-triphenyl-1*H*-pyrazole (11). 1,3,5-Triphenyl-1*H*-pyrazole (**4**) (500 mg, 1.68 mmol, 1.00 eq) and N-bromosuccinimide (598 mg, 3.36 mmol, 2.00 eq) were dissolved in ethyl acetate (8 mL). The solution was sonicated at ambient temperature for 90 min. The reaction mixture was washed with saturated sodium thiosulfate (2 × 20 mL) and water (20 mL), dried over sodium sulfate and filtered. The solvent was removed *in vacuo*. The product was obtained as an off-white solid (630 mg, > 99% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (m_C, 2 H, Ar-H), 7.27 – 7.53 (m, 13 H, Ar-H). The analytical data was in accordance with the reported values.[12]

^{1}H NMR (300 MHz, $CDCl_3$)



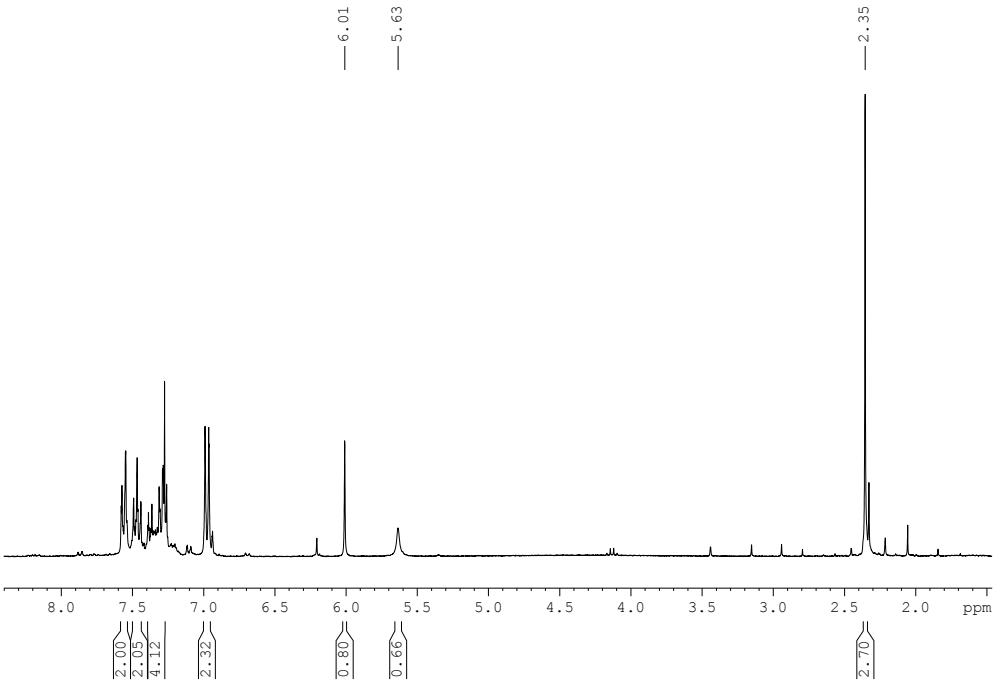
4-Iodo-1,3,5-triphenyl-1*H*-pyrazole (12). 1,3,5-Triphenyl-1*H*-pyrazole (**4**) (2.58 g, 8.71 mmol, 1.00 eq) and N-iodosuccinimide (2.94 g, 13.1 mmol, 1.50 eq) were dissolved in ethyl acetate (20 mL). The solution was sonicated at ambient temperature for 4 h. The reaction mixture was washed with saturated sodium thiosulfate (45 mL). The aqueous phase was extracted with ethyl acetate (50 mL). The combined organic layers were dried over sodium sulfate and filtered. The solvent was removed *in vacuo*. The product was obtained as an off-white solid (3.37 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (m_C, 2 H, Ar-H), 7.27 – 7.52 (m, 13 H, Ar-H). The analytical data was in accordance with the reported values.[20]

^{1}H NMR (300 MHz, $CDCl_3$)



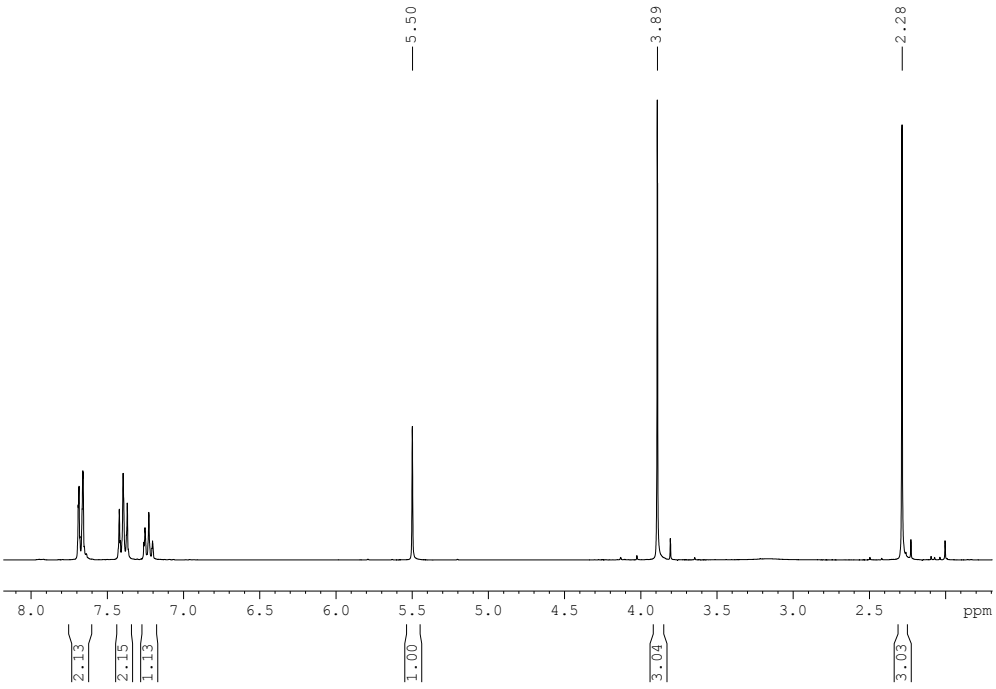
5-Aminophenyl-3-methyl-1-phenyl-1*H*-pyrazole (14)

^{1}H NMR (300 MHz, $CDCl_3$)



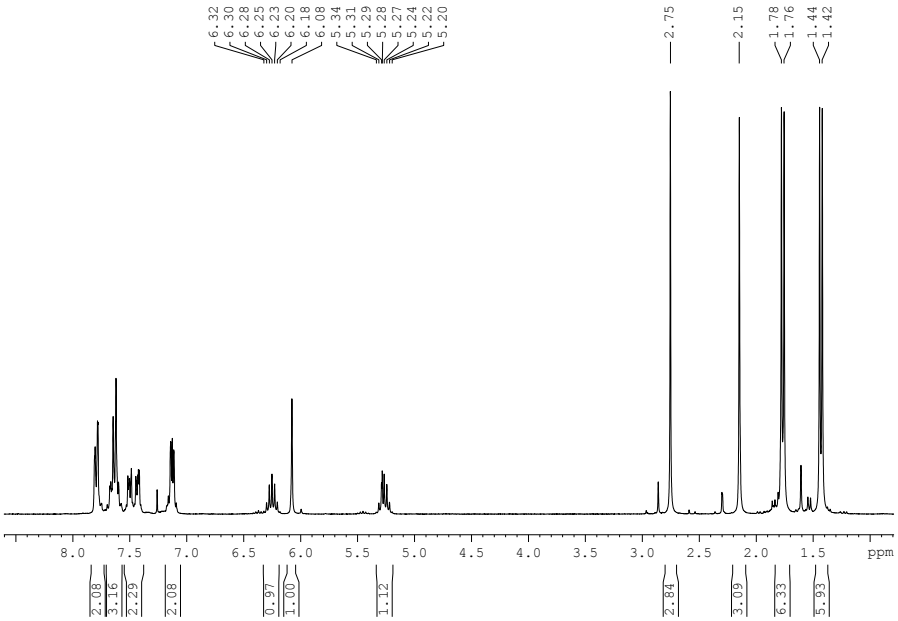
5-Methoxy-3-methyl-1-phenyl-1*H*-pyrazole (15). 3-Methyl-1-phenyl-1*H*-pyrazol-5-one (**13**) (400 mg, 2.30 mmol, 1.00 eq), methanol (91.8 mg, 2.87 mmol, 0.12 mL, 1.25 eq) and triphenylphosphine (902 mg, 3.44 mmol, 1.50 eq) were dissolved in anhydrous toluene under inert atmosphere. Diethyl azodicarboxylate (599 mg, 3.44 mmol, 0.54 mL, 1.50 eq) was added, and the mixture was stirred at ambient temperature for 20 h. After this time, methanol (1 mL) was added, and after 1 min, the solution was poured into water (20 mL). The aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic layers were washed with sodium hydroxide solution (2 M, 20 mL) and water (2 × 20 mL), dried over sodium sulphate, filtered, and the solvent was removed *in vacuo*. The residue was purified by column chromatrography (silica gel, ethyl acetate/hexane 1:3). The product was obtained as pale yellow liquid (202 mg, 47%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 – 7.70 (m, 2 H, Ar-H), 7.39 (m_C, 2 H, Ar-H), 7.23 (m_C, 1 H, Ar-H), 5.50 (s, 1 H), 3.89 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3). The analytical data was in accordance with the reported values.[17]

^{1}H NMR (300 MHz, $CDCl_3$)

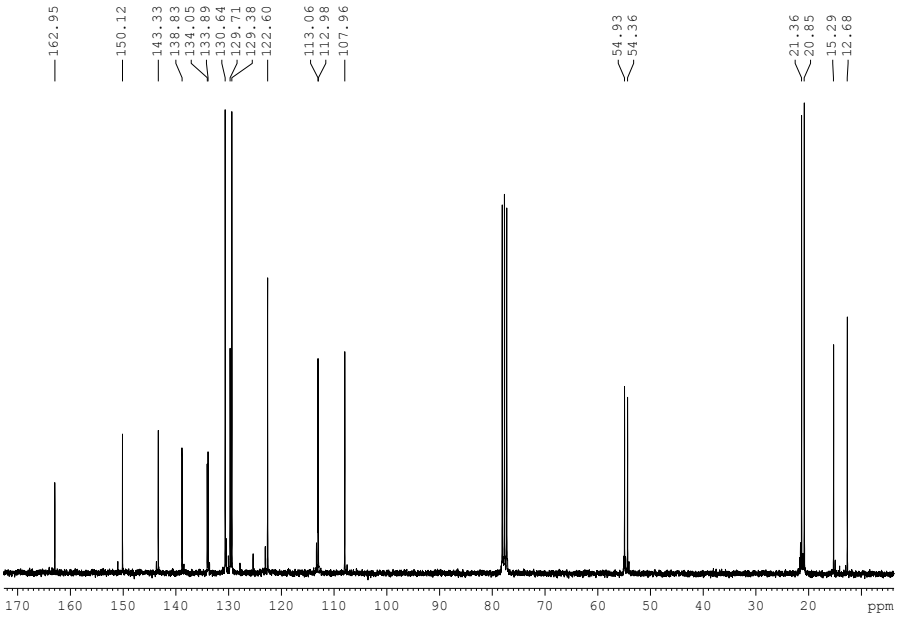


trans-Dibromo(3,5-dimethyl-1-phenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (17)

^{1}H NMR (300 MHz, $CDCl_3$)

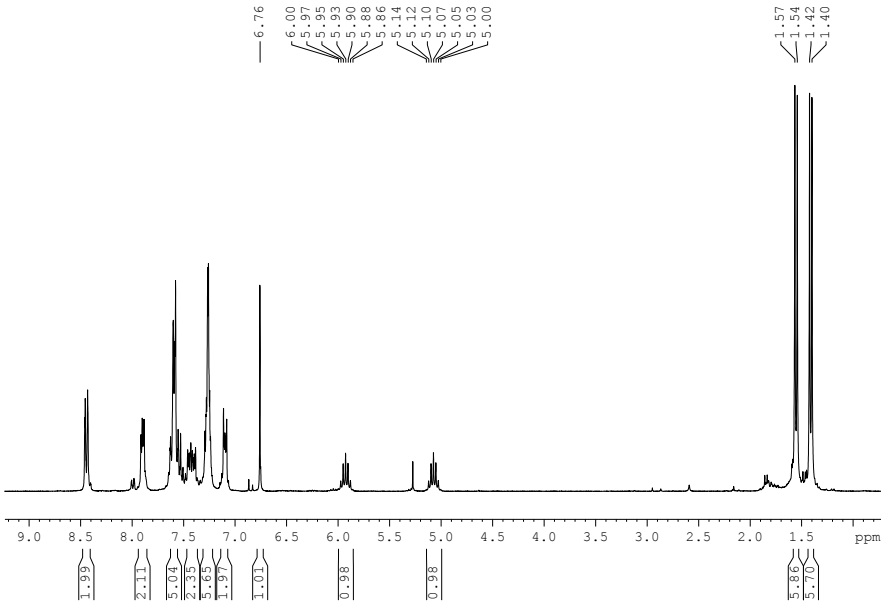


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

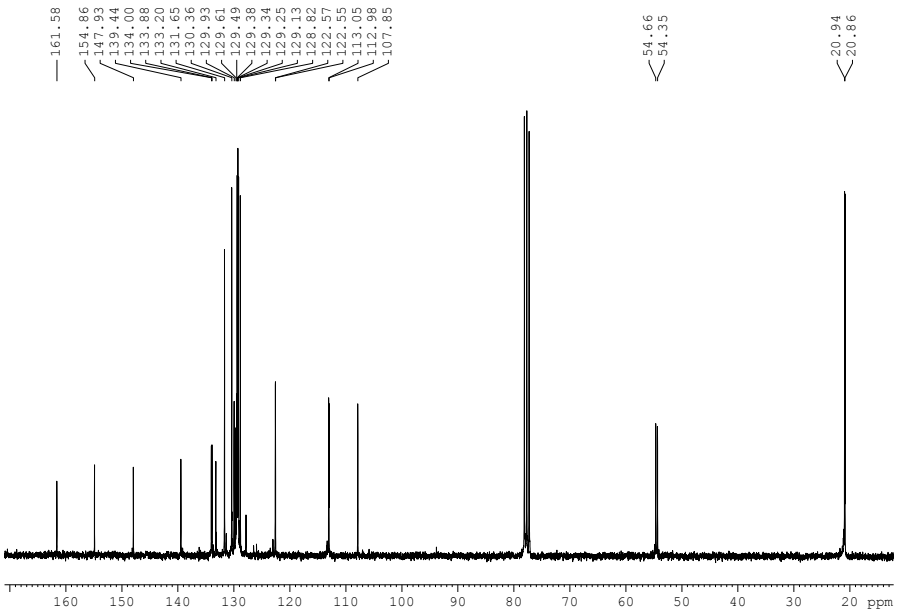


trans-Dibromo(1,3,5-triphenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (18)

^{1}H NMR (300 MHz, $CDCl_3$)

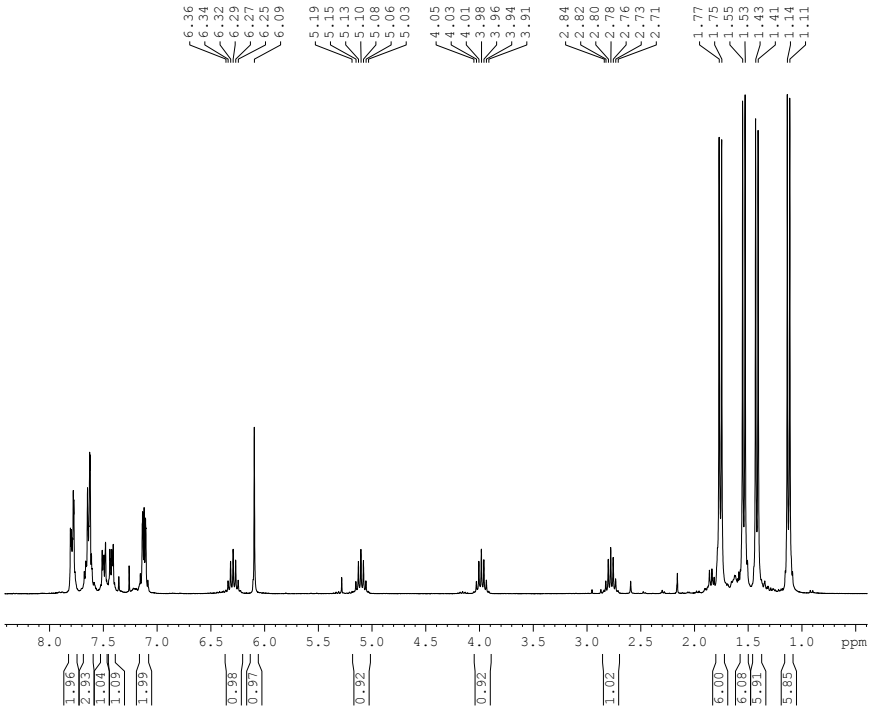


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

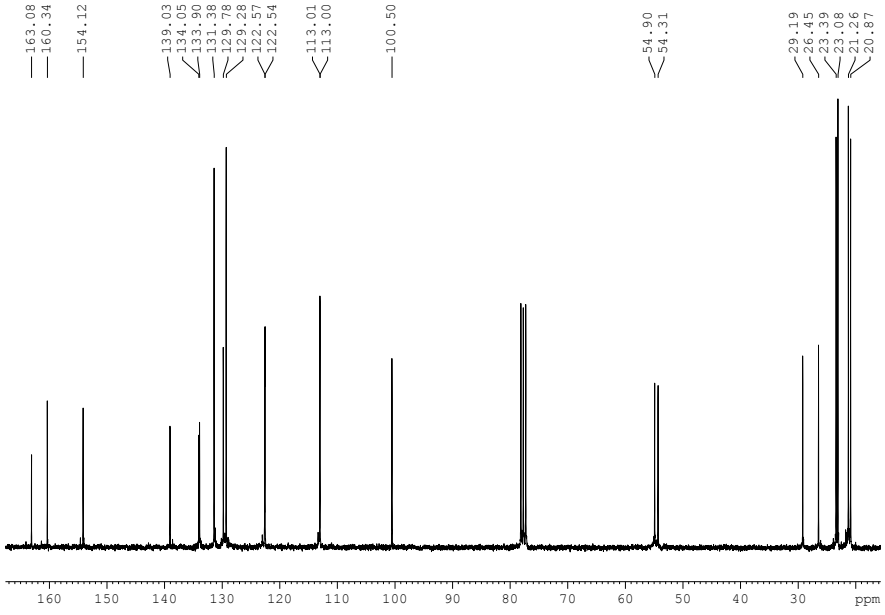


trans-Dibromo(3,5-diisopropyl-1-phenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (19)

^{1}H NMR (300 MHz, $CDCl_3$)

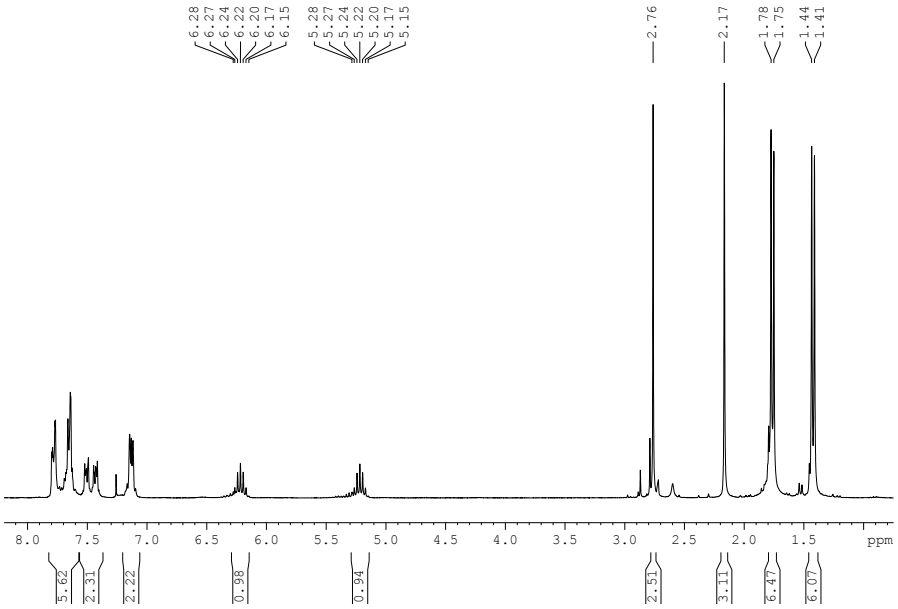


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

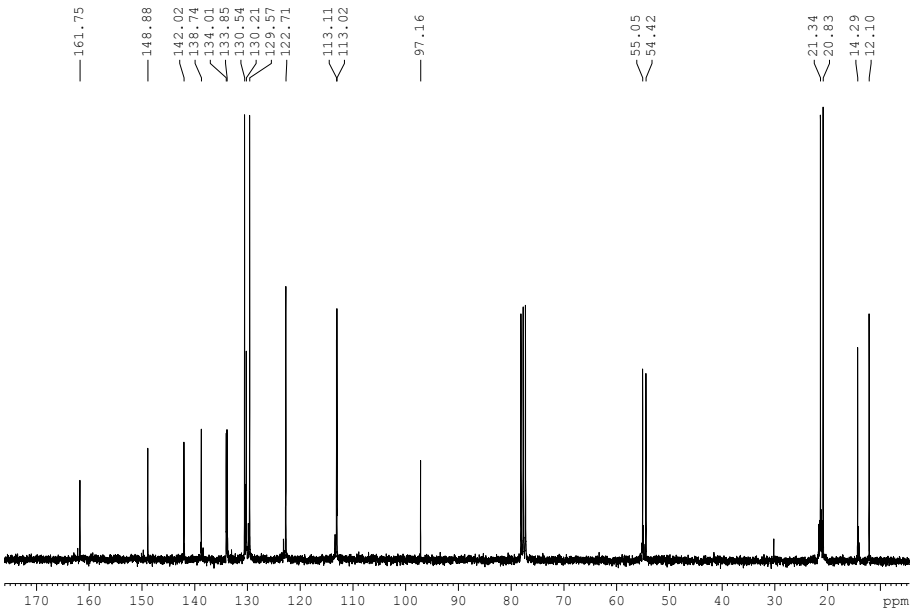


trans-Dibromo(4-bromo-3,5-dimethyl-1-phenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (20)

^{1}H NMR (300 MHz, $CDCl_3$)

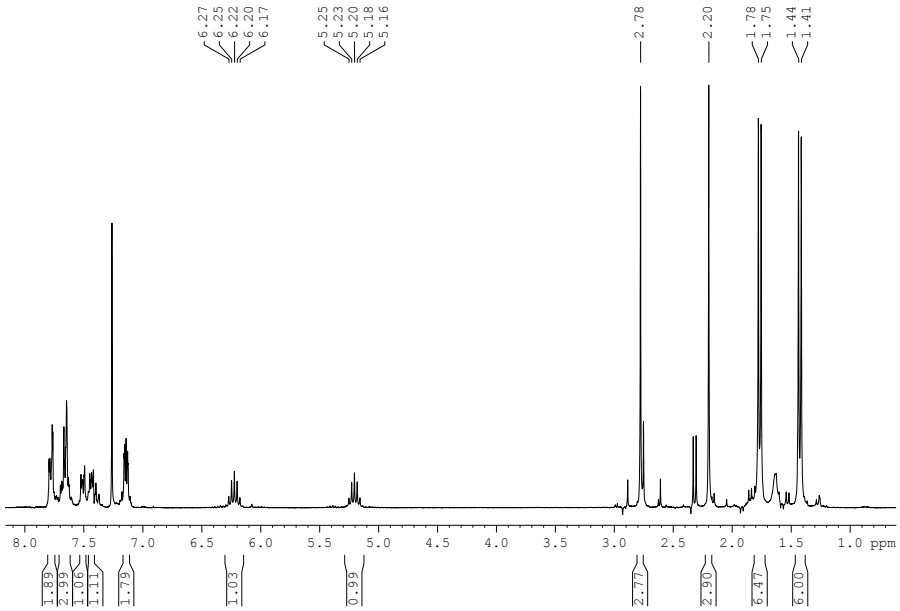


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

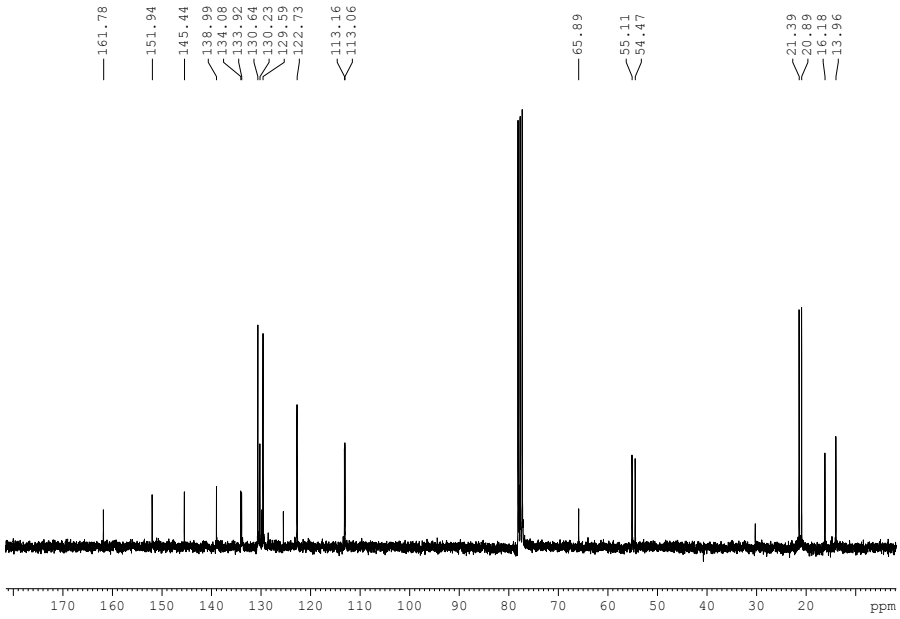


trans-Dibromo(4-iodo-3,5-dimethyl-1-phenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (21)

^{1}H NMR (300 MHz, $CDCl_3$)

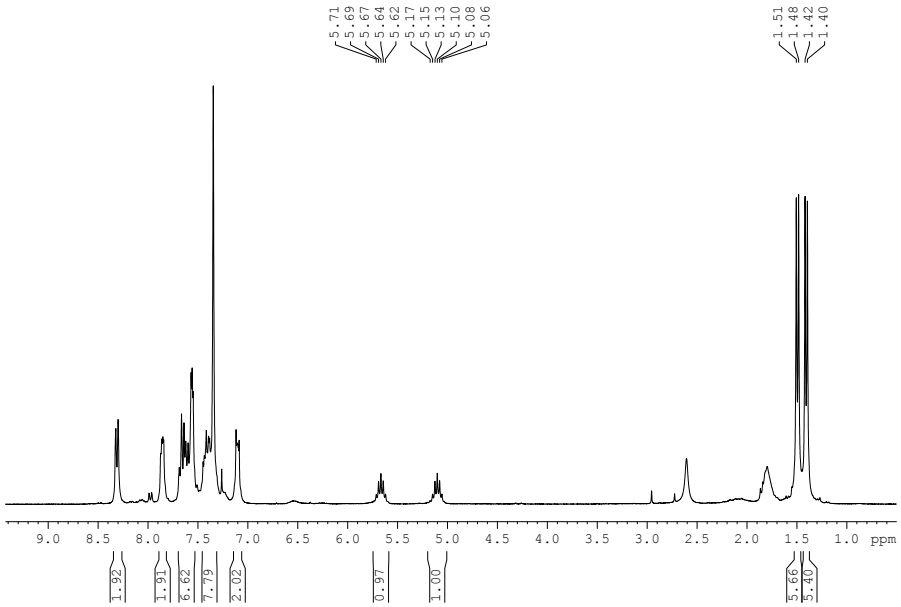


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

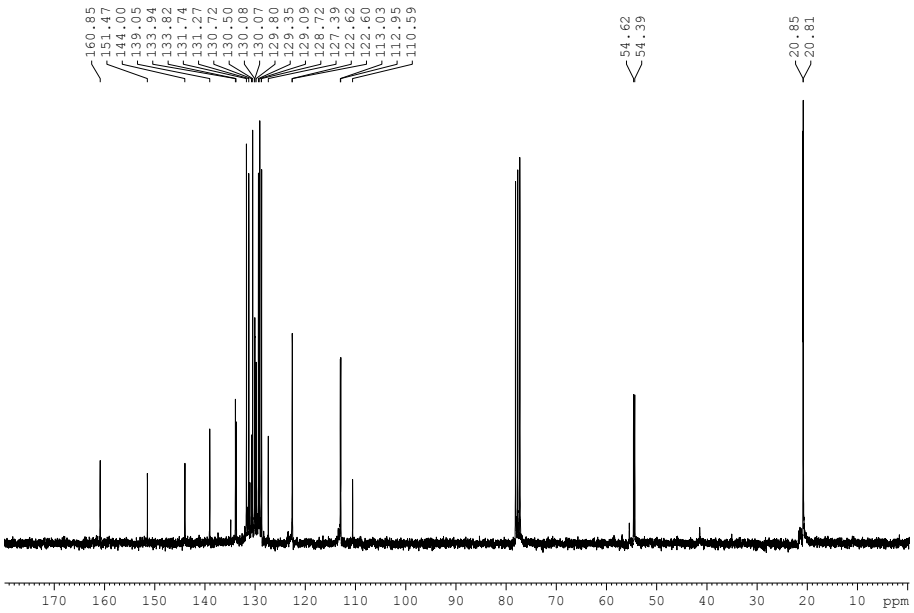


trans-Dibromo(4-chloro-1,3,5-triphenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (22)

^{1}H NMR (300 MHz, $CDCl_3$)

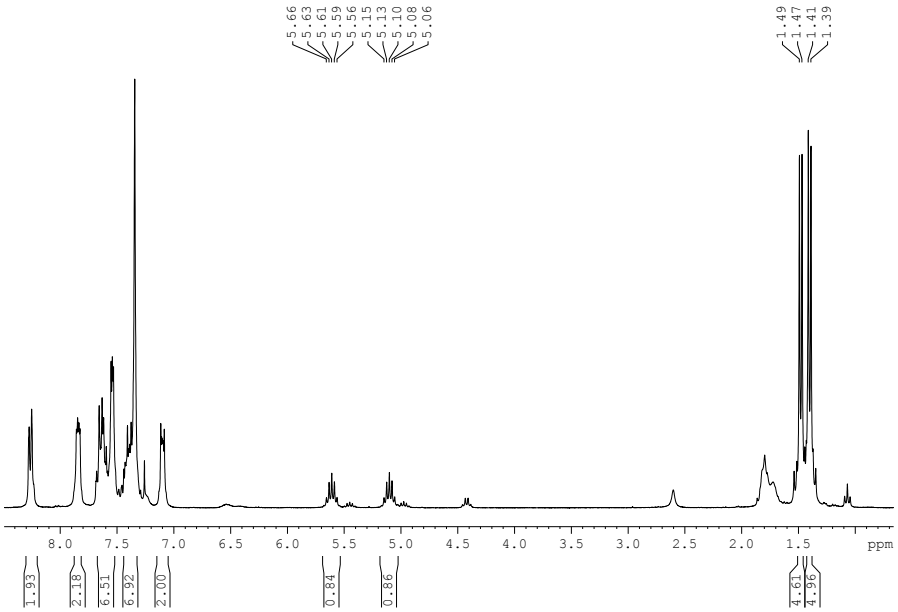


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

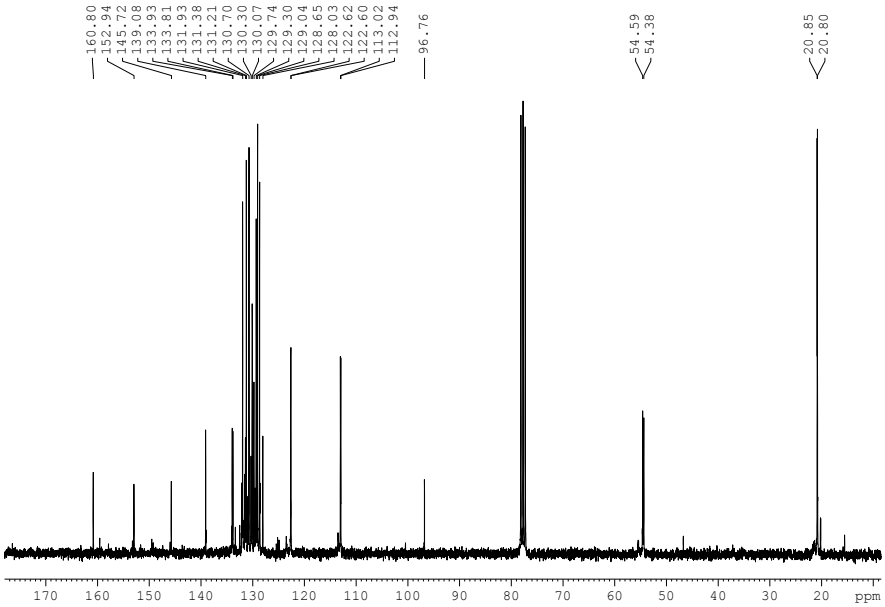


trans-Dibromo(4-bromo-1,3,5-triphenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (23)

^{1}H NMR (300 MHz, $CDCl_3$)

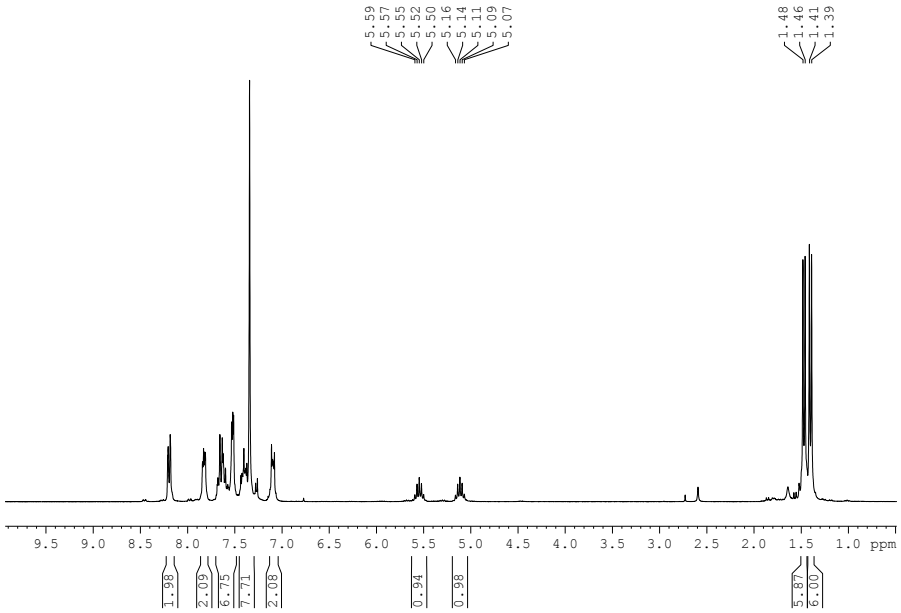


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

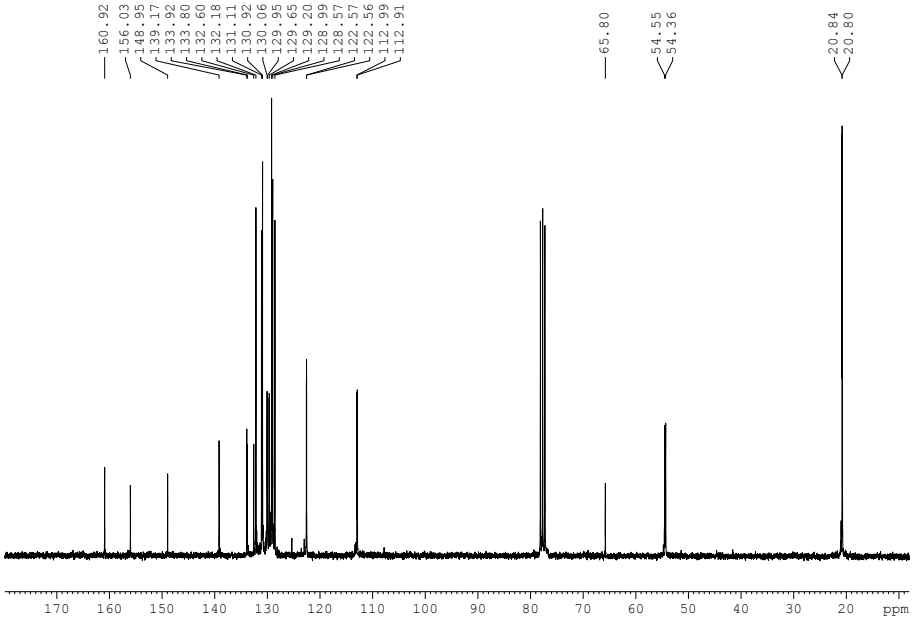


trans-Dibromo(4-iodo-1,3,5-triphenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (24)

^{1}H NMR (300 MHz, $CDCl_3$)

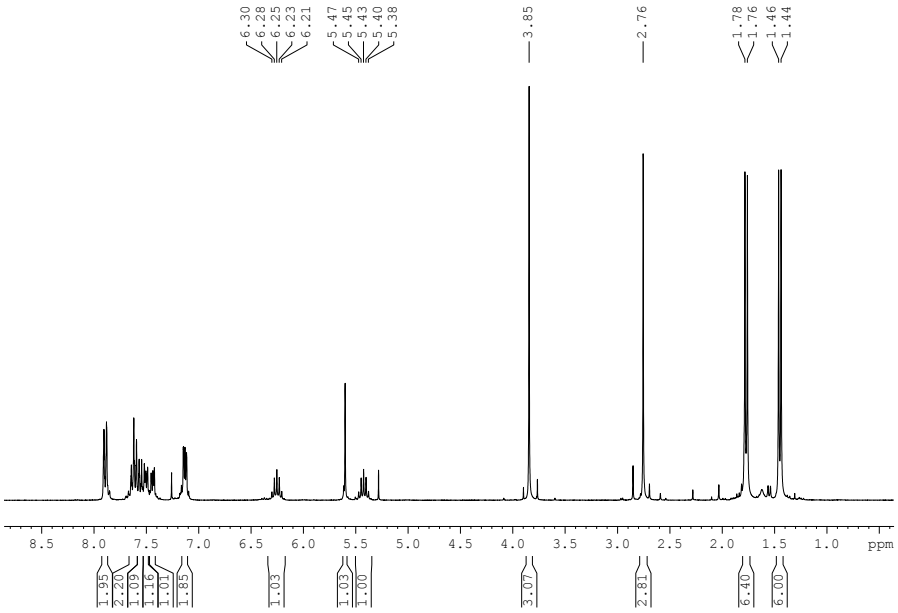


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

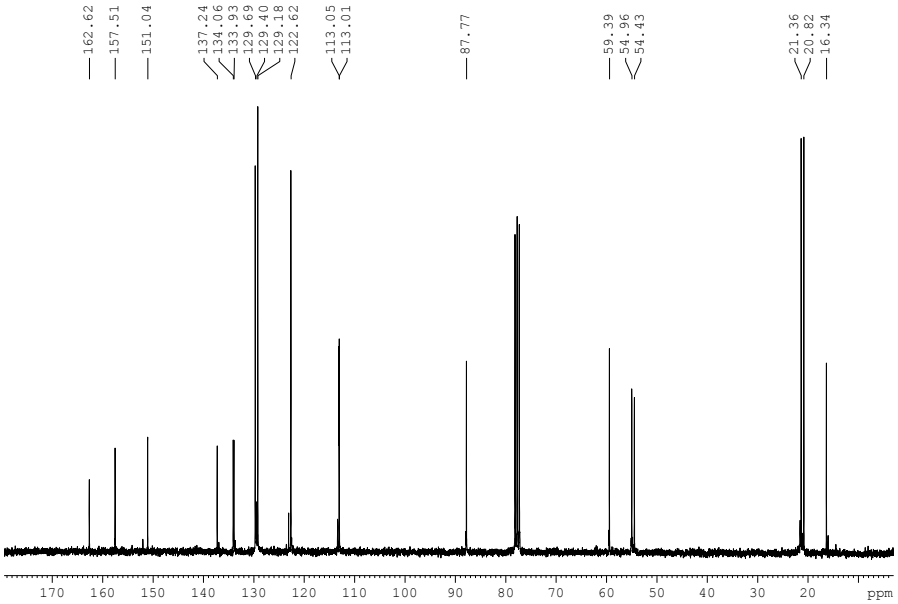


trans-Dibromo(5-methoxy-3-methyl-1-phenyl-1_H_-pyrazole)(1,3-diisopropylbenzimidazolin-2-ylidene)palladium(II) (25)

^{1}H NMR (300 MHz, $CDCl_3$)

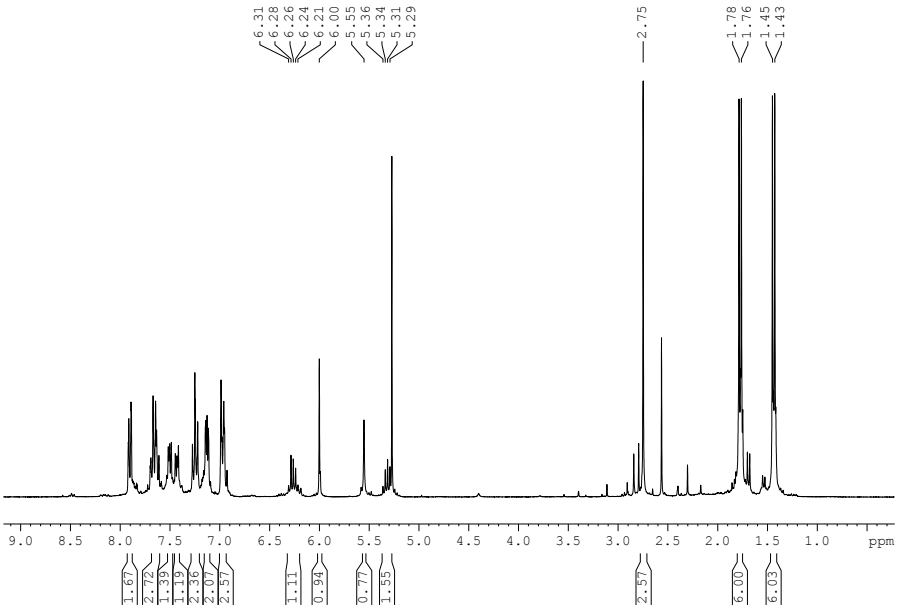


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)

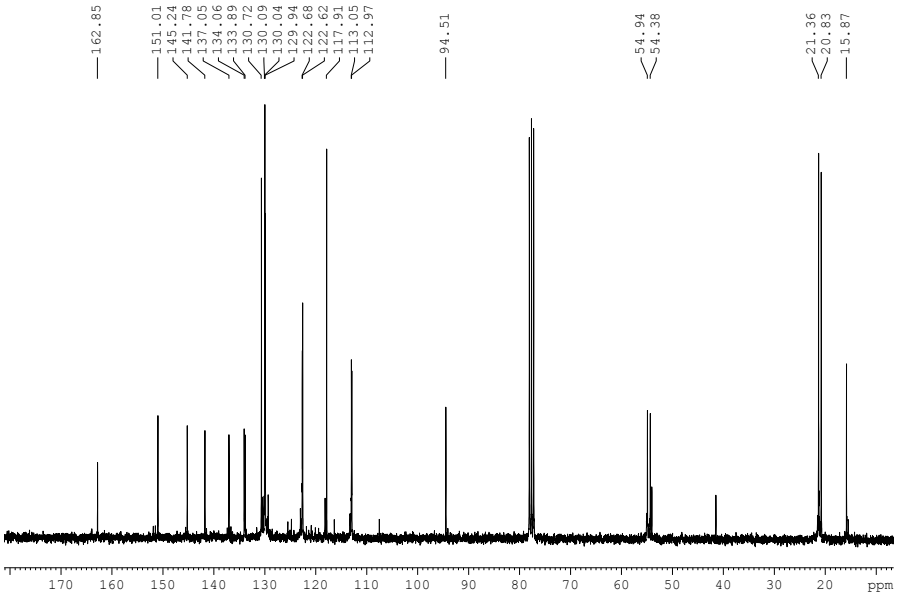


trans-Dibromo(5-aminophenyl-3-methyl-1-phenyl-1_H_-pyrazole)(1,3-diisopropyl-benzimidazolin-2-ylidene)palladium(II) (26)

^{1}H NMR (300 MHz, $CDCl_3$)

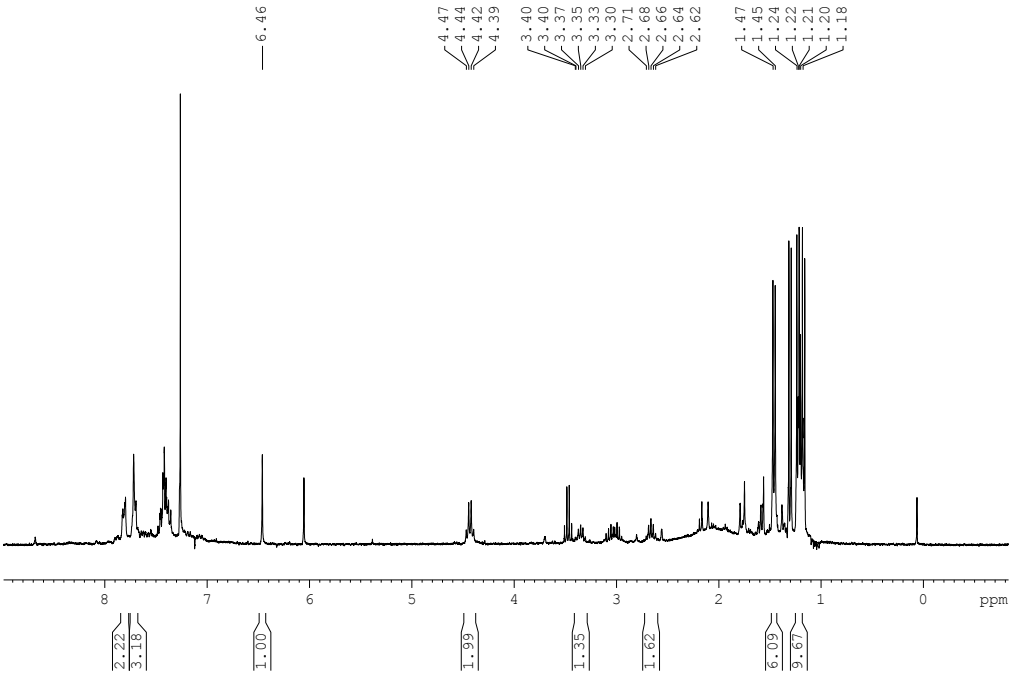


^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$)



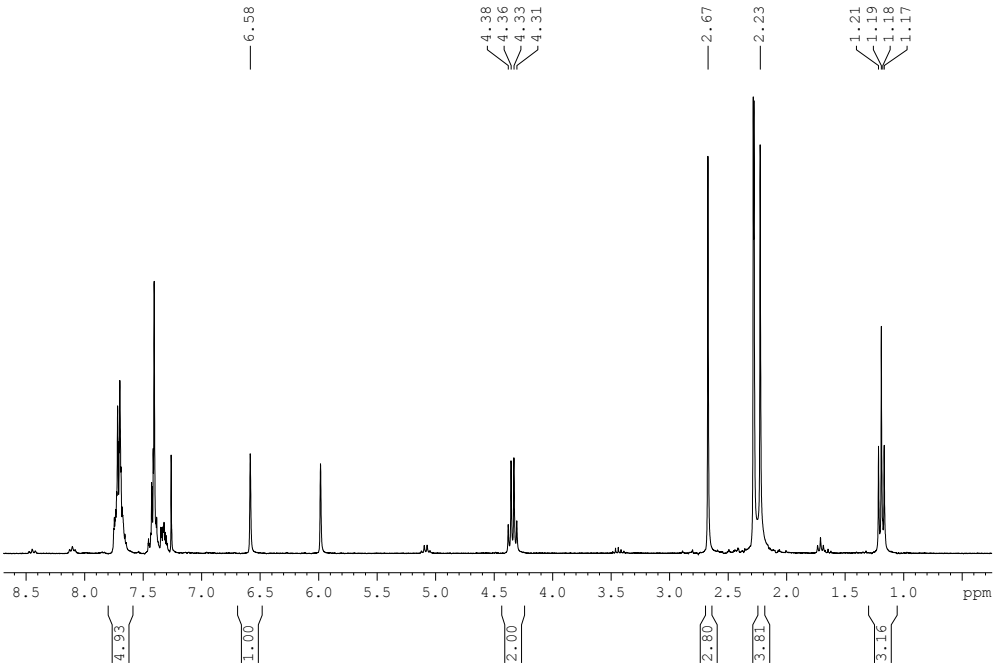
2-Ethyl-3,5-diisopropyl-1-phenyl-1*H*-pyrazolium bromide (27). **27** was prepared using 3,5-diisopropyl-1-phenyl-1*H*-pyrazole (**6**) (342 mg, 1.50 mmol). Trace amounts of a brown solid were obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 – 7.83 (m, 2 H, Ar-H), 7.68 – 7.75 (m, 3 H, Ar-H), 6.46 (s, 1 H), 4.43 (q, *J* = 7.2 Hz, 2 H, C*H*$_2$CH$_3$), 3.35 (sept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.66 (sept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$), 1.44 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.22 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.20 (t, *J* = 7.4 Hz, 3 H, CH$_2$C*H*$_3$).

^{1}H NMR (300 MHz, $CDCl_3$)



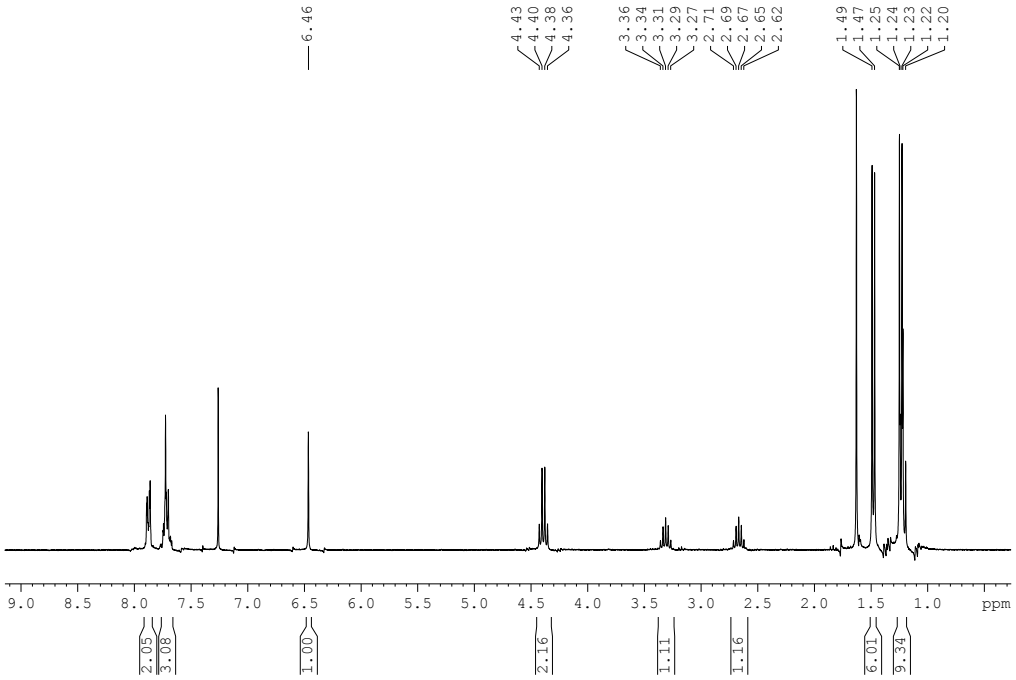
2-Ethyl-3,5-dimethyl-1-phenyl-1*H*-pyrazolium bromide (28). 28 was prepared using 3,5-dimethyl-1-phenyl-1*H*-pyrazole (**5**) (258 mg, 1.50 mmol). 47 mg of an off-white solid were obtained (mixture of starting material and product, 7% yield of product as determined by NMR). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.78 (m, 5 H, Ar-H), 6.59 (s, 1 H), 4.34 (q, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2 H, C*H*$_2$CH$_3$), 2.67 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 1.19 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 3 H, CH_2C*H*$_3$).

^{1}H NMR (300 MHz, $CDCl_3$)



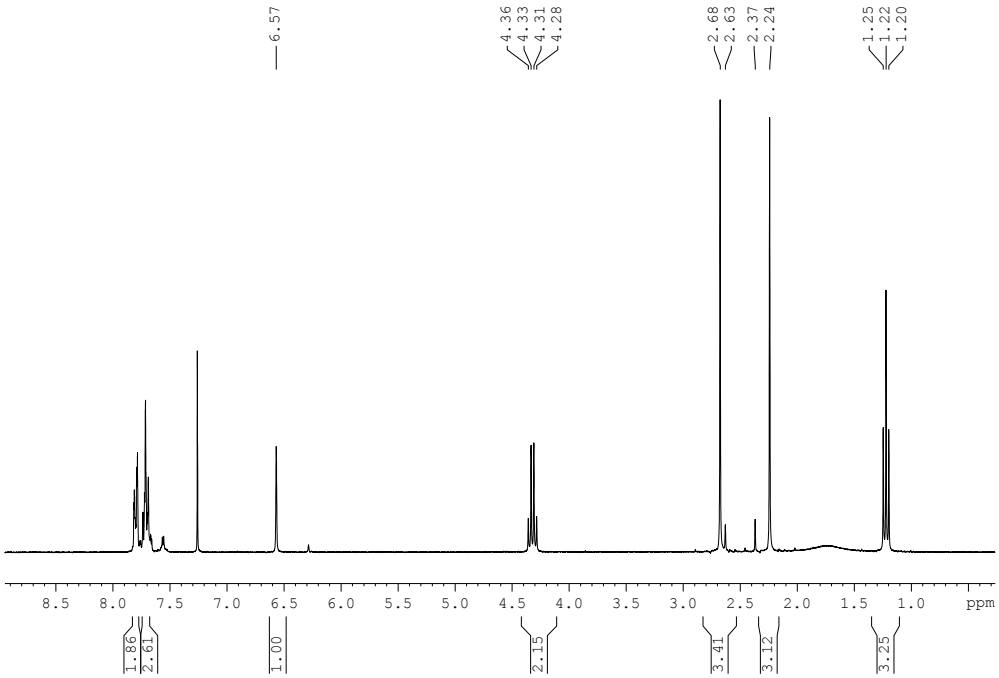
2-Ethyl-3,5-diisopropyl-1-phenyl-1*H*-pyrazolium iodide (29). 29 was prepared using 3,5-diisopropyl-1-phenyl-1*H*-pyrazole (**4**) (228 mg, 1.00 mmol). 433 mg of a light brown solid were obtained (75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.84 – 7.91 (m, 2 H, Ar-H), 7.66 – 7.76 (m, 3 H, Ar-H), 6.46 (s, 1 H), 4.39 (q, J = 7.2 Hz, 2 H, CH_2CH$_3$), 3.31 (sept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1 H, CH(CH$_3$)$_2$), 2.67 (sept, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1 H, CH(CH$_3$)$_2$), 1.48 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6 H, CH(CH_3)$_2$), 1.24 (d, J = 6.9 Hz, 6 H, CH(CH_3)$_2$), 1.22 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 3 H, CH$_2$CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



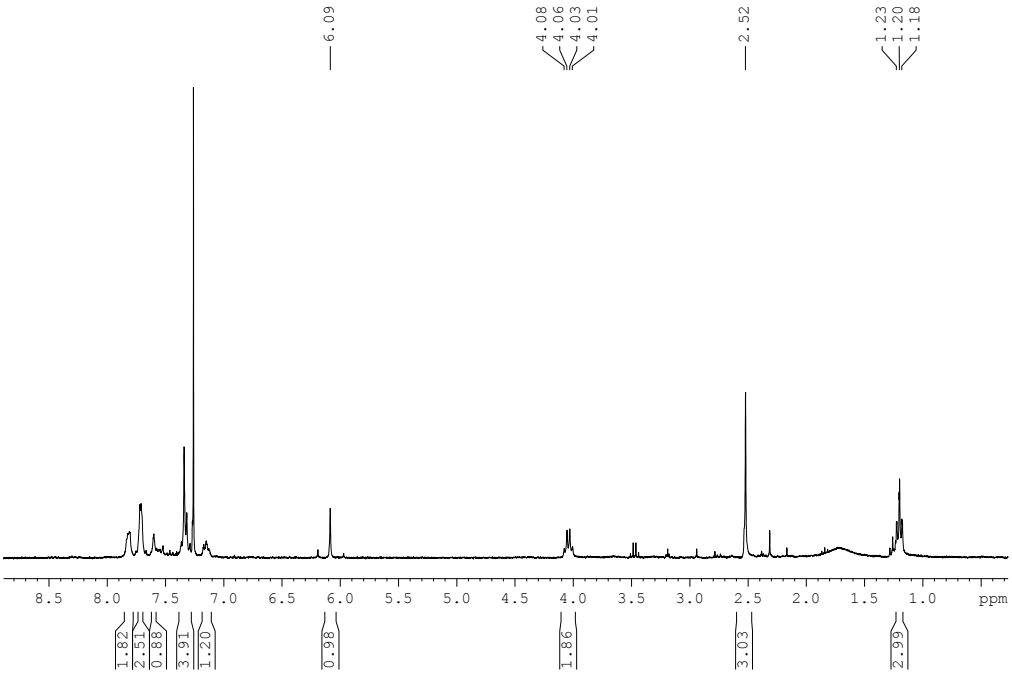
2-Ethyl-3,5-dimethyl-1-phenyl-1*H*-pyrazolium iodide (30). 30 was prepared using 3,5-dimethyl-1-phenyl-1*H*-pyrazole (**5**) (258 mg, 1.50 mmol). 488 mg of a light grey solid were obtainted (99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 – 7.83 (m, 2 H, Ar-H), 7.68 – 7.74 (m, 3 H, Ar-H), 6.57 (s, 1 H), 4.32 (q, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2 H, C*H*$_2$CH$_3$), 2.68 (s, 3 H, CH$_3$), 2.24 (s, 3 H, CH$_3$), 1.22 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 3 H, CH$_2$C*H*$_3$).

^{1}H NMR (300 MHz, $CDCl_3$)



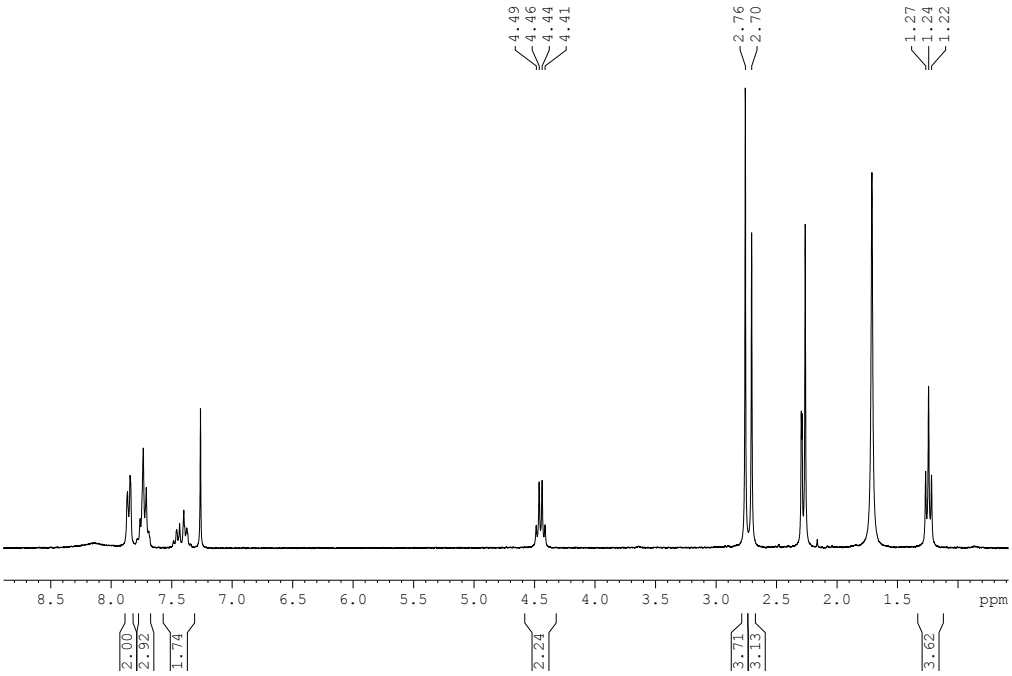
5-Aminophenyl-2-ethyl-3-methyl-1-phenyl-1*H*-pyrazolium iodide (31). 31 was prepared using 5-aminophenyl-3-methyl-1-phenyl-1*H*-pyrazole (**14**)(150 mg, 0.60 mmol). 142 mg of a light brown solid were obtainted (58%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 – 7.85 (m, 2 H, Ar-H), 7.69 – 7.73 (m, 2 H, Ar-H), 7.58 – 7.62 (m, 1 H, Ar-H), 7.28 – 7.38 (m, 4 H, Ar-H), 7.11 – 7.19 (m, 1 H, Ar-H), 6.09 (s, 1 H), 4.04 (q, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 2 H, CH_2CH$_3$), 2.52 (s, 3 H, CH_3), 1.20 (t, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 3 H, CH$_2$CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



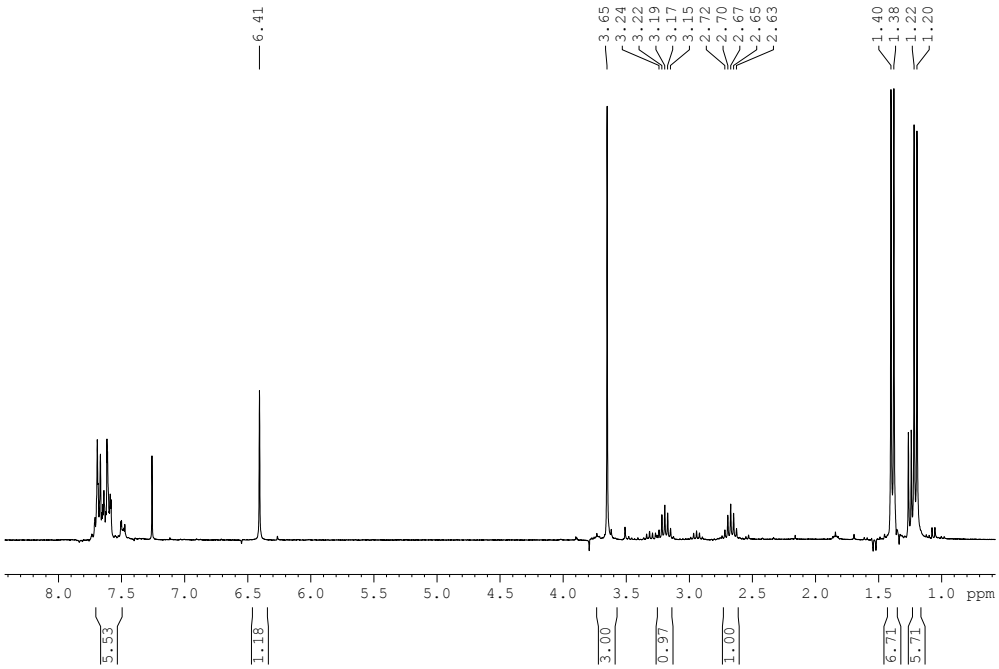
4-Bromo-2-ethyl-3,5-dimethyl-1-phenyl-1*H*-pyrazolium iodide (32). 32 was prepared using 4-bromo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (**8**) (126 mg, 0.50 mmol). 60 mg of a light brown solid were obtainted (mixture of starting material and product, 24% yield of product as determined by NMR). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 – 7.89 (m, 2 H, Ar-H), 7.67 – 7.77 (m, 3 H, Ar-H), 4.45 (q, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 2 H, C*H*$_2$CH$_3$), 2.76 (s, 3 H, CH$_3$), 2.70 (s, 3 H, CH$_3$), 1.24 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 3 H, CH$_2$C*H*$_3$).

^{1}H NMR (300 MHz, $CDCl_3$)



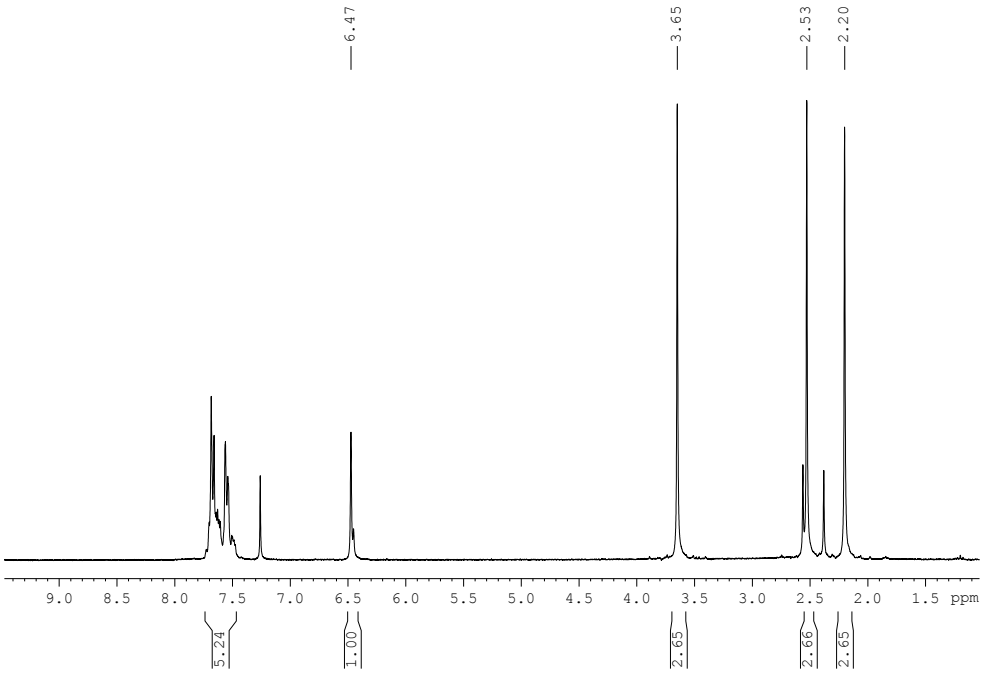
3,5-Diisopropyl-2-methyl-1-phenyl-1*H*-pyrazolium tetrafluoroborate (33). 33 was prepared using 3,5-dipropyl-1-phenyl-1*H*-pyrazole (**6**) (342 mg, 1.50 mmol). 234 mg of a brown solid were obtained (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 – 7.73 (m, 5 H, Ar-H), 6.41 (s, 1 H), 3.65 (s, 3 H, CH_3), 3.20 (sept, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 1 H, C*H*(CH_3)$_2$), 2.68 (sept, *J* = 7.0 Hz, 1 H, C*H*(CH_3)$_2$), 1.39 (d, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.21 (d, *J* = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$).

^{1}H NMR (300 MHz, $CDCl_3$)



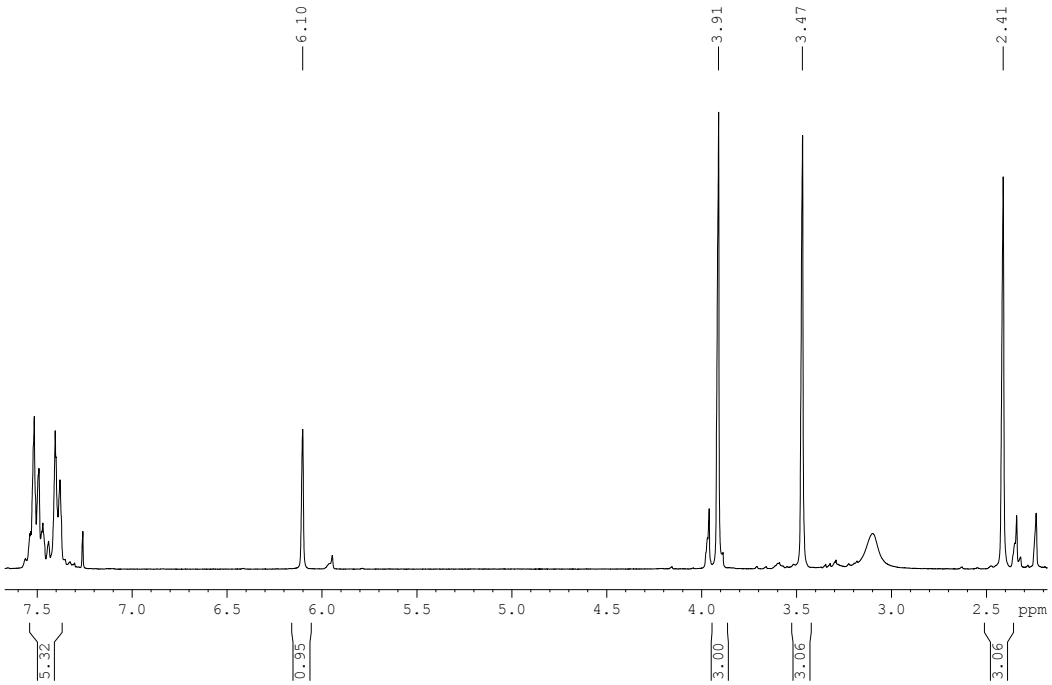
2,3,5-Trimethyl-1-phenyl-1*H*-pyrazolium tetrafluoroborate (34). 34 was prepared using 3,5-dimethyl-1-phenyl-1*H*-pyrazole (**5**) (172 mg, 1.50 mmol). 210 mg of a white solid were obtained (77% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 – 7.74 (m, 5 H, Ar-H), 6.48 (s, 1 H), 3.65 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



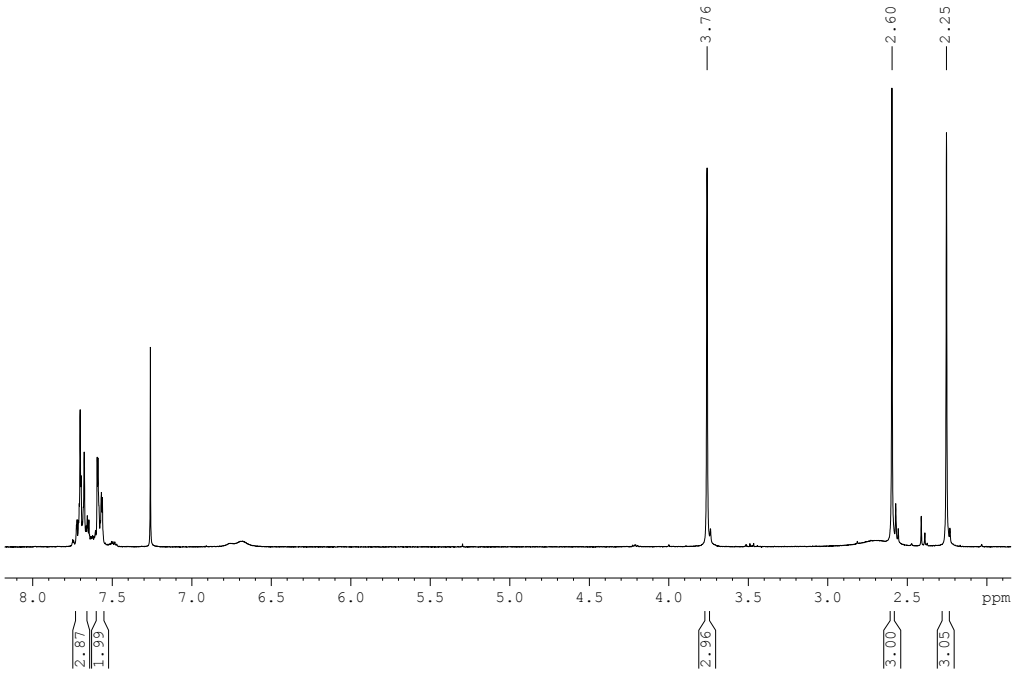
2,3-Dimethyl-5-methoxy-1-phenyl-1*H*-pyrazolium tetrafluoroborate (35). 35 was prepared using 3-methyl-5-methoxy-1-phenyl-1*H*-pyrazole (**15**) (49 mg, 0.26 mmol). 47 mg of a white solid were obtained (62% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.55 (m, 5 H, Ar-H), 6.10 (s, 1 H), 3.91 (s, 3 H, CH_3), 3.47 (s, 3 H, CH_3), 2.41 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



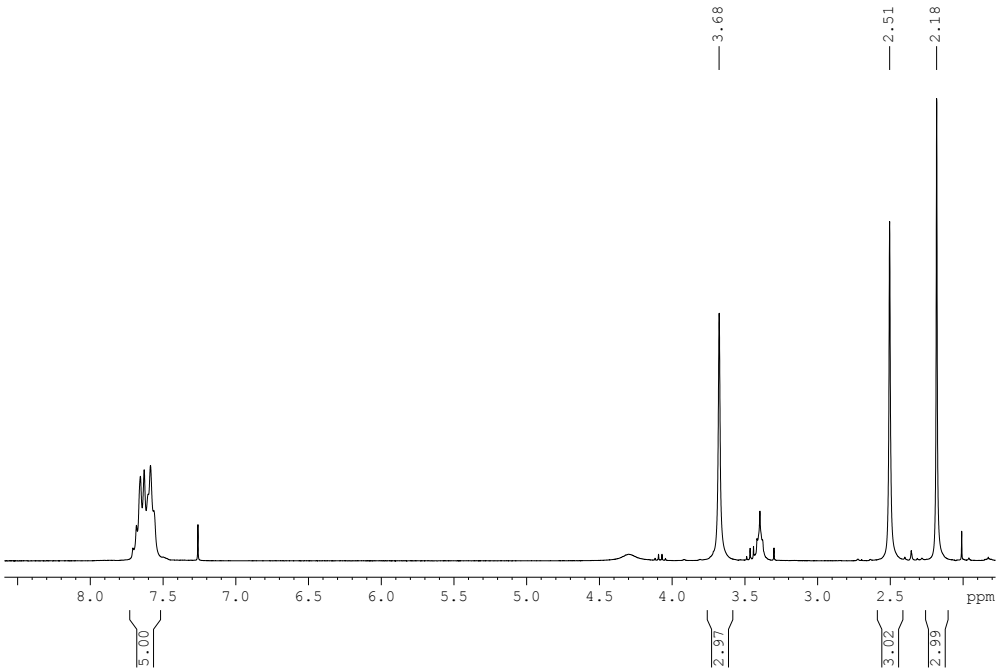
4-Iodo-2,3,5-trimethyl-1-phenyl-1*H*-pyrazolium tetrafluoroborate (36). 36 was prepared using 4-iodo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (**9**) (700 mg, 2.35 mmol). 760 mg of an off-white solid were obtained (80% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 – 7.73 (m, 3 H, Ar-H), 7.55 – 7.60 (m, 2 H, Ar-H), 3.76 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



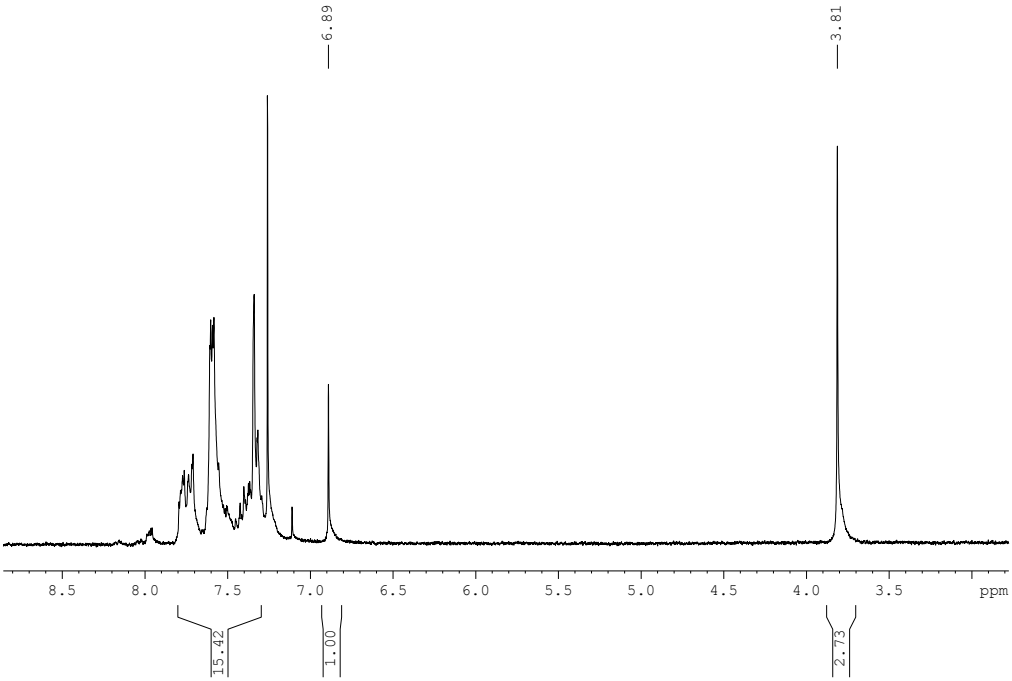
4-Bromo-2,3,5-trimethyl-1-phenyl-1*H*-pyrazolium tetrafluoroborate (37). 37 was prepared using 4-bromo-3,5-dimethyl-1-phenyl-1*H*-pyrazole (**8**) (700 mg, 2.79 mmol). 501 mg of a white solid were obtained (51% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 – 7.73 (m, 5 H, Ar-H), 3.68 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



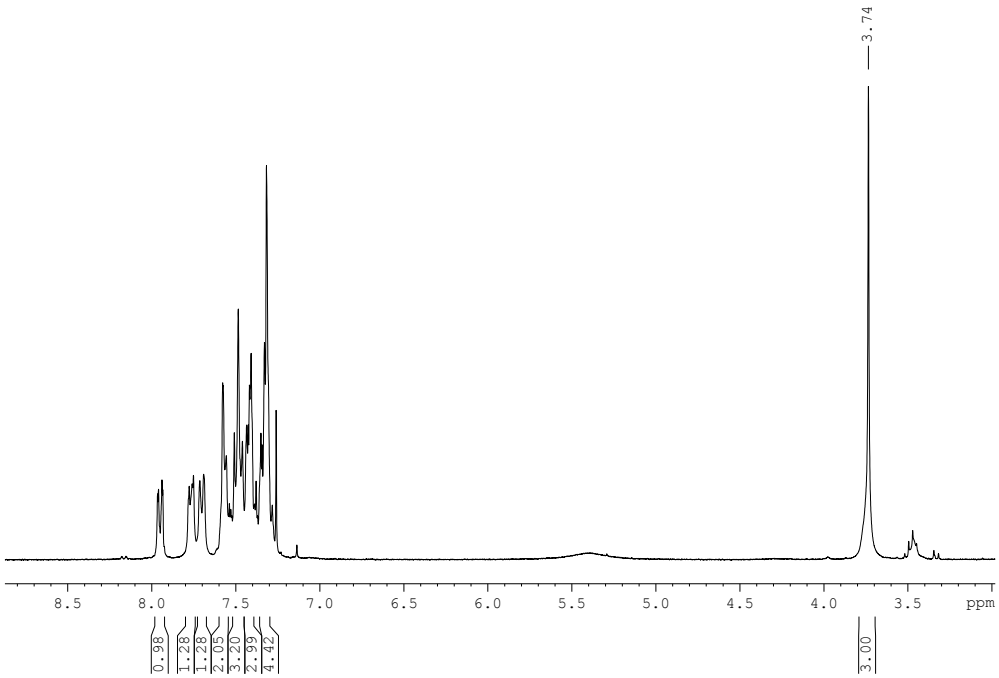
2-Methyl-1,3,5-triphenyl-1*H*-pyrazolium tetrafluoroborate (38). 38 was prepared using 1,3,5-triphenyl-1*H*-pyrazole (**4**) (296 mg, 1.00 mmol). 221 mg of an off-white solid were obtained (55% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ =7.31 – 7.80 (m, 15 H, Ar-H) 6.89 (s, 1 H), 3.81 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



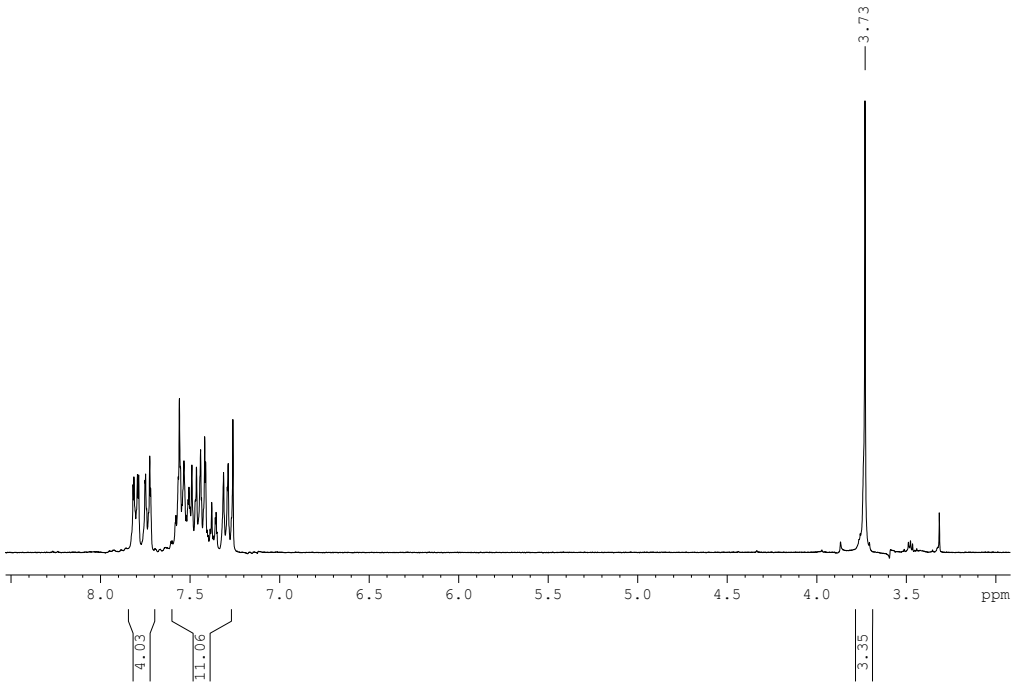
4-Iodo-2-Methyl-1,3,5-triphenyl-1*H*-pyrazolium tetrafluoroborate (39). 39 was prepared using 4-iodo-1,3,5-triphenyl-1*H*-pyrazole (**12**) (641 mg, 1.52 mmol). 530 mg of a white solid were obtained (67% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 – 7.98 (m, 1 H, Ar-H), 7.74 – 7.79 (m, 1 H, Ar-H), 7.68 – 7.73 (m, 1 H, Ar-H), 7.54 – 7.60 (m, 2 H, Ar-H), 7.45 – 7.52 (m, 3 H, Ar-H), 7.39 – 7.45 (m, 3 H, Ar-H), 7.29 – 7.37 (m, 4 H, Ar-H), 3.74 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



4-Chloro-2-methyl-1,3,5-triphenyl-1*H*-pyrazolium tetrafluoroborate (40). 40 was prepared using 4-chloro-1,3,5-triphenyl-1*H*-pyrazole (**10**) (165 mg, 0.50 mmol). 79 mg of a white solid were obtained (37% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 – 7.84 (m, 4 H, Ar-H), 7.27 – 7.61 (m, 11 H, Ar-H), 3.73 (s, 3 H, CH_3).

^{1}H NMR (300 MHz, $CDCl_3$)



4-Bromo-2-Methyl-1,3,5-triphenyl-1*H*-pyrazolium tetrafluoroborate (41). 41 was prepared using 4-bromo-1,3,5-triphenyl-1*H*-pyrazole (**11**) (555 mg, 1.55 mmol). 521 mg of a white solid were obtained (70% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 – 7.87 (m, 4 H, Ar-H), 7.40 – 7.59 (m, 8 H, Ar-H), 7.34 – 7.39 (m, 1 H, Ar-H), 7.24 – 7.31 (m, 2 H, Ar-H), 3.73 (s, 3 H, CH_3).

^{1}H-NMR (300 MHz, $CDCl_3$)