Supporting Information
for

The role of the stabilizing/leaving group in palladium catalysed cross-coupling reactions.

Lorenzo Palio[a,b], Francis Bru[a], Tommaso Ruggiero[a], Laurens Bourda[a], Kristof Van Hecke[a], Catherine S. J. Cazin[a], Steven P. Nolan[a]

Department of Chemistry, Ghent University, Ghent, Belgium

[a.] Department of Chemistry, Center for Sustainable Chemistry, Ghent University, Krijgslaan 281 (S-3), 9000, Ghent, Belgium.

[b.] Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS Unit´ e de Catalyse et Chimie Solide, F-59000, Lille, France.

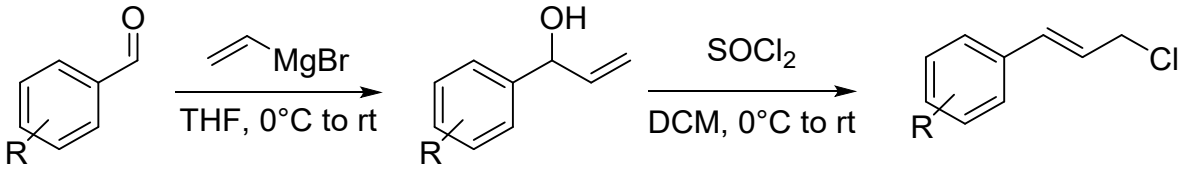
Table of contents

General considerations

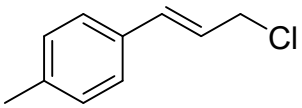
Reagents were used as received. Solvents were dried using activated molecular sieves (3 Å) and bubbled with Ar. ^{1}H and ^{13}C-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker ADVANCE 300 MHz or 400 MHz spectrometer. Spectra were referenced using the residual solvent peak (C_6D_6 : δH = 7.16 ppm; δC = 128.06 ppm and CDCl3: δH = 7.26 ppm; δC = 77.16 ppm) at 298 K.

Synthesis of allyl chlorides

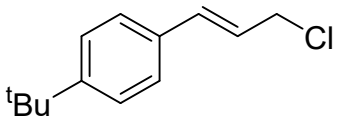
General Procedure



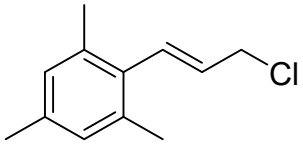
Scheme S1: Synthesis of the allyl chlorides



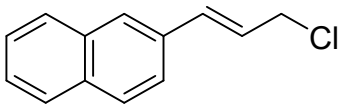
p-tol-allyl chloride (1) was synthesized using the general procedure from tolualdehyde (1 mL, 8.5 mmol), vinylmagnesiumbromide (1.0 M in THF; 10.2 mL, 10.2 mmol) and $SOCl_2$ (2.5 mL, 34 mmol). Purification by vacuum distillation (100°C at 0.7 torr). Isolated as a pale yellow oil; yield: 4.61 mmol (54 %). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ = 2.35 (s, 3H), 4.25 (dd, 2H); 6.27 (dt,1H), 6.63 (d, 1H), 7.14 (d, 2H); 7.29 (d, 2H). The data are in accordance with the literature[1].



p-^{t}Bu-cinnamyl chloride (2) was synthesized using the general procedure from ^{t}butylbenzaldehyde (2 mL, 12 mmol), vinylmagnesiumbromide (1.0 M in THF; 14.4 mL, 14.4 mmol) and $SOCl_2$ (3.5 mL, 48 mmol). Purification by vacuum distillation (120°C at 0.7 torr). Isolated as a pale yellow oil; yield: 7.8 mmol (65 %). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ = 1.33 (s, 9H), 4.25 (dd, 2H); 6.29 (dt,1H), 6.65 (d, 1H), 7.36 (d, 4H). The data are in accordance with the literature[2].



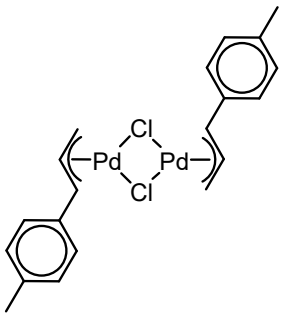
2,4,6-trimethylcinnamyl chloride (3) was synthesized using the general procedure from mesitaldehyde (2 mL, 13.6 mmol), vinylmagnesiumbromide (1.0 M in THF; 16.4 mL, 16.4 mmol) and $SOCl_2$ (4 mL, 54.4 mmol). Purification by vacuum distillation (120°C at 0.7 torr). Isolated as a pale yellow oil; yield: 8.6 mmol (64 %). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ = 2.41 (s, 9H), 4.36 (dd, 2H); 5.96 (dt,1H), 6.76 (d, 1H), 7.00 (s, 2H). The data are in accordance with the literature[3].



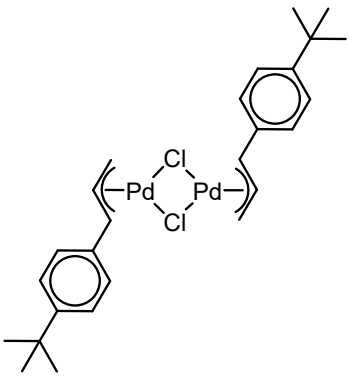
2-(3-chloro-1-propen-1-yl)-naphthalene (4) was synthesized using the general procedure from β-naphtalenaldehyde (0.9934 g, 6.4 mmol), vinylmagnesiumbromide (1.0 M in THF; 7.6 mL, 7.6 mmol) and $SOCl_2$ (0.5 mL, 6.36 mmol). Purification by recrystallization with pentane. Isolated as a off-white powder; yield: 4.1 mmol (64%). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ = 4.31 (dd, 2H), 6.47 (dt, 1H); 6.82 (m, 1H), (m, 7.48, 2H), 7.60 (dd, 1H), 7.76 (m, 1H), 7.81 (m, 3H). The data are in accordance with the literature[4].

Synthesis of [Pd(η^3-R-allyl)(μ-Cl)]$_2$

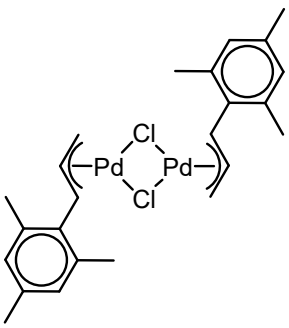
2 $PdCl_2$ + 4 NaCl + 2 R-allylchloride + 2 CO + 2 H_2O → [Pd(η^3-R-allyl)(μ-Cl)]$_2$ + 4 NaCl + 2 CO_2 4 HCl



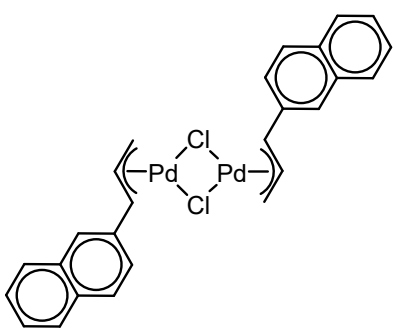
[Pd(η^3-p-tol-allyl)(μ-Cl)]$_2$ (5) was synthesized using the general procedure from p-tol-allyl chloride (500 mg; 3.0 mmol), $PdCl_2$ (532 mg, 3.0 mmol) and NaCl (351 mg, 6 mmol). Isolated as a pale yellow solid; yield: 0.69 mmol (46 %). ^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ = 2.21 (s, 6 H, C*H*$_3$), 3.00 (d, 2H, *J* = 11.9 Hz, C*H* allyl), 3.93 (d, 2H, *J* = 6.7 Hz, C*H* allyl), 4.64 (d, 2H, *J* = 11.9 Hz, C*H* allyl), 5.77 (dt, 2H, *J* = 6.8 Hz, C*H* allyl), 7.07 (d, 4H, *J* = 11.9 Hz, C*H* phenyl), 7.39 (d, 4H, *J* = 11.9 Hz, C*H* phenyl).. ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) δ = 138.6, 134.0, 129.9, 127.9, 105.4, 82.4, 59.1 21.6. Elemental Analysis: calcd for C20H24Cl2Pd2: C, 43.99; H, 4.06; Found: C, 43.88; H: 3.96



Pd(η^3-p-^{t}Bu-cin)(μ-Cl)]$_2$ (6) was synthesized using the general procedure from p-^{t}butylcinnamyl chloride (500 mg; 2.4 mmol), $PdCl_2$ (426 mg, 2.4 mmol) and NaCl (281mg, 4.8 mmol). Isolated as a pale yellow solid; yield: 0.63 mmol (52 %). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ = 1.28 (s, 18 H, C*H*$_3$), 3.01 (d, 2H, *J* = 12.5 Hz, C*H* allyl), 3.94 (d, 2H, *J* = 6.4 Hz, C*H* allyl), 4.66 (d, 2H, *J* = 11.5 Hz, C*H* allyl), 5.76 (dt, 2H, *J* = 6.7 Hz, C*H* allyl), 7.28 (d, 4H, *J* = 8.3 Hz, C*H* phenyl), 7.44 (d, 4H, *J* = 8.3 Hz, C*H* phenyl). ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) δ = 151.6, 134.1, 127.8, 126.1, 105.6, 82.3, 59.1, 31.0. Elemental Analysis: calcd for C26H36Cl2Pd2: C, 49.55; H, 5.44; Found: C, 49.4, H, 5.36.



Pd(η^3-mes-allyl)(μ-Cl)]$_2$ (7) was synthesized using the general procedure from 2,4,6-trimethylcinnamyl chloride (500 mg; 2.57 mmol), $PdCl_2$ (456 mg, 2.57 mmol) and NaCl (300 mg, 5.14 mmol). Isolated as a pale yellow solid; yield: 0.66 mmol (51 %). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ = 2.13 (s, 6 H, p-C*H*$_3$), 2.48 (s, 12 H, o-C*H*$_3$), 2.94 (d, 2H, *J* = 11.6 Hz, C*H* allyl), 3.87 (d, 2H, *J* = 6.5 Hz, C*H* allyl), 4.83 (d, 2H, *J* = 12.1 Hz, C*H* allyl), 5.67 (dt, 2H, *J* = 6.6 Hz, C*H* allyl), 6.78 (s, 4H, C*H* phenyl). ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) δ = 138.0, 137.5, 130.7, 130.2, 107.4, 81.0, 58.2, 22.6, 21.2. Elemental Analysis: calcd for C24H32Cl2Pd2: C, 47.86; H, 5.02; Found: C, 48.10; H, 4.95.



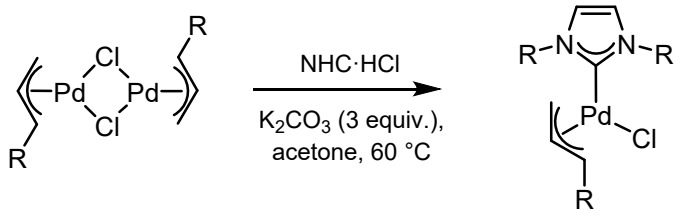
Pd(η^3-2-naph-allyl)(μ-Cl)]$_2$ (8) was synthesized using the general procedure from 2-(3-chloro-1-propen-1-yl)-naphthalene (500 mg; 2.47 mmol), $PdCl_2$ (438 mg, 2.47 mmol) and NaCl (289 mg, 4.94 mmol). Isolated as a pale yellow solid; yield: 0.59 mmol (48 %). ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ = 3.08 (d, 2H, *J* = 11.9 Hz, C*H* allyl), 4.00 (d, 2H, *J* = 6.2 Hz, C*H* allyl), 4.77 (d, 2H, *J* = 11.4 Hz, C*H* allyl),

5.90 (dt, 2H, *J* = 6.7 Hz, C*H* allyl), 7.39-7.57 (m, 6H, C*H* naph), 7.67-7.90 (m, 8H, C*H* naph). ^{13}C-{H}-NMR (400 MHz, DMSO-d_6), 298 K) δ = 135.3, 133.7, 133.1, 128.6, 128.3, 128.2, 127.1, 126.9, 125.8, 113.7, 87.9, 65.0, ,55.1. Elemental Analysis: calcd for C26H24Cl2Pd2: C, 50.52; H, 3.59; Found: C: 50.42; H: 3.47

Synthesis of [(NHC)Pd(η^3-R-allyl)Cl]

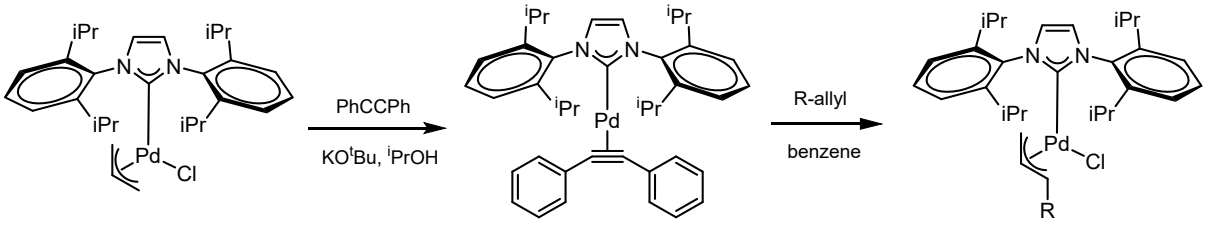
For the synthesis of the Pd-precatalysts, two procedures are possible:

Weak-base route:

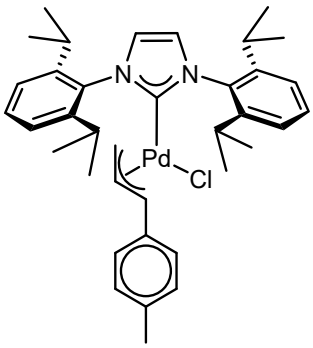


Scheme S2: Synthesis of the [(NHC)Pd(η^3-R-allyl)Cl] via weak base route.

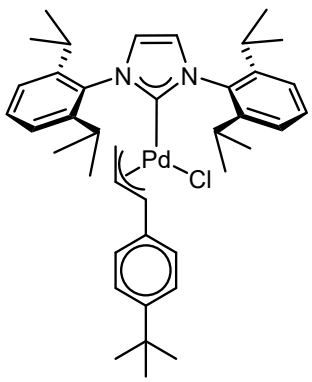
Pd-synthon route:



Scheme S3: Synthesis of the Pd^0-synthon and subsequent oxidative addition of the R-allyl chloride

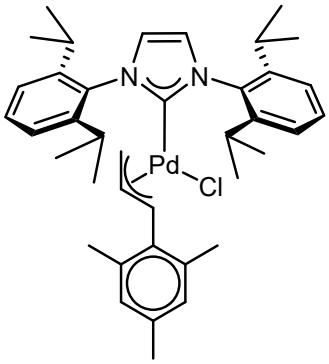


[(IPr)Pd(η^3-p-tol-allyl)Cl] (IPr-1) was synthesized using the weak procedure from [Pd(η^3-p-tol-allyl)(μ-Cl)]$_2$ **(5)** (100 mg; 0.18 mmol), IPr·HCl (184 mg; 0.43 mmol) and K_2CO_3 (75 mg; 0.54 mmol) in mmol 0.45 yield (81 %) or synthesized using the Pd-synthon route using [Pd(IPr)(PhC≡CPh)] (100 mg; 0.15 mmol) and p-tol-allyl chloride **(1)** (25 mg; 0.15 mmol) in 0.13 mmol yield (87 %). Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.37 (t, 2H, *J* = 7.7 Hz), 7.21 (d, 4H, *J* = 7.7 Hz), 7.08 (s, 2H), 6.97 (d, 2H, *J* = 8.1 Hz), 6.87 (d, 2H, *J* = 8.1 Hz), 4.97 (m, 1H), 4.27 (d, 1H, *J* = 12.7 Hz), 2.90 (m, 4H), 2.09 (s, 3H), 1.63 (d, 2H, *J* = 11.7 Hz), 1.30 (m, 12H), 1.07 (s, 6H), 1.05 (s, 6H), 0.99 (d, 1H, *J* = 6.8 Hz). ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) 186.3, 146.1, 136.3, 136.0, 134.9, 129.9, 129.1, 128.8, 127.7, 127.2, 124.2, 123.8, 123.6, 108.2, 90.9, 45.9, 29.3, 28.6, 26.2, 26.0, 23.0, 22.9, 21.3, Elemental Analysis: calcd for C37H48ClN2Pd: C: 67.06, H: 7.30, N:4.23; Found: C: 66.99, H: 7.09, N: 4.19.

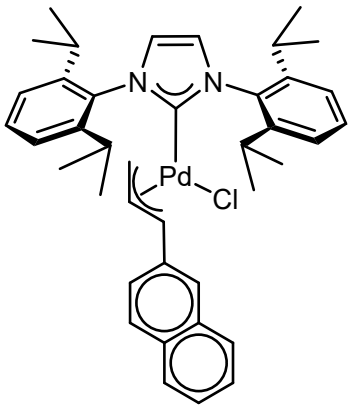


[(IPr)Pd(η^3-p-^{t}Bu-cin)Cl] (IPr-2) was synthesized using the weak procedure from [Pd(η^3-p-^{t}Bu-cin)(μ-Cl)]$_2$ **(6)** (100 mg; 0.16 mmol),

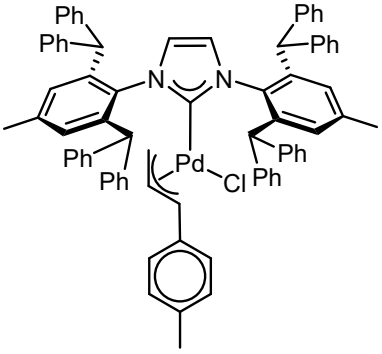
IPr·HCl (119 mg; 0.38 mmol) and K_2CO_3 (48 mg; mmol) in 0.26 mmol yield (81 %) or synthesized using the Pd-synthon route using [Pd(IPr)(PhC≡CPh)] (100 mg; 0.15 mmol) and p-^{t}Bu-cinnamyl chloride **(2)** (31 mg; 0.15 mmol) in 0.14 mmol yield (93 %). Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.38 (t, 2H, *J* = 7.6 Hz), 7.22 (d, 4H, *J* = 7.6 Hz), 7.10 (d, 2H, *J* = 8.4 Hz), 7.09 (s, 2H), 7.03 (d, 2H, *J* = 8.4 Hz), 4.98 (m, 1H), 4.30 (d, 1H, *J* = 12.8 Hz), 3.00 (m, 2H), 2.86 (m, 2H), 2.79 (d, 1H, *J* = 6.7 Hz), 1.60 (d, 2H, *J* = 12.8 Hz), 1.30 (m, 12H), 1.15 (s, 9H), 1.07 (s, 6H), 1.05 (s, 6H). ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) 185.2, 149.3, 146.1, 136.0, 134.9, 129.9, 127.1, 125.3, 124.1, 123.8, 108.5, 91.4, 45.5, 31.2, 31.0, 28.6, 26.2, 25.9, 23.0, 22.9. Elemental Analysis: calcd for C40H54ClN2Pd: C: 68.17, H: 7.72, N:3.97; Found: C: 68.27, H: 7.59, N: 3.98.



[(IPr)Pd(η^3-mes-allyl)Cl] (IPr-3) was synthesized using the weak procedure from [Pd(η^3-mes-allyl)(*μ*-Cl)]$_2$ **(7)** (100 mg; 0.17 mmol), IPr·HCl (123 mg; 0.39 mmol) and K_2CO_3 (0.51 mg; 71 mmol) in 0.29 mmol yield (85 %) or synthesized using the Pd-synthon route using [Pd(IPr)(PhC≡CPh)] (100 mg; 0.15 mmol) and 2,4,6-trimethylcinnamyl chloride **(3)** (30 mg; 0.15 mmol) in 0.14 mmol yield (93 %). Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.38 (t, 2H, *J* = 7.7 Hz), 7.22 (d, 4H, *J* = 7.2 Hz), 7.11 (s, 2H), 6.57 (s, 2H), 4.98 (dt, 1H, J_1 = 13.3 Hz, J_2 = 9.07 Hz), 4.30 (d, 1H, *J* = 13.3 Hz), 3.10 (m, 4H), 2.90 (broad s, 1H), 2.81 (m, 2H), 2.01 (s, 3H), 1.97 (s, 6H), 1.61 (d, 2H, *J* = 9.1 Hz), 1.30 (broad s, 12H), 1.09 (broad s, 6H), 1.03 (broad s, 6H), 1.05 (s, 6H). ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) 186.3, 146.1, 136.3, 136.0, 134.9, 129.9, 129.1, 127.7, 124.1, 123.8, 108.2, 90.9, 45.9, 28.6, 26.2, 26.0, 23.0, 22.9, 21.3, 14.1. Elemental Analysis: calcd for C39H52ClN2Pd: C: 67.82, H: 7.59, N: 4.06; Found: C: 68.18, H: 7.61, N: 3.92.

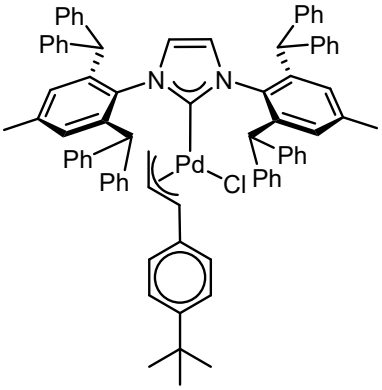


[(IPr)Pd(*η^3*-2-naph-allyl)Cl] (IPr-4) was synthesized using the weak procedure from [Pd(*η^3*-2-naph-allyl)(μ-Cl)]$_2$ **(8)** (100 mg; 0.16 mmol), IPr·HCl (162 mg; 0.38 mmol) and K_2CO_3 (66 mg, 0.48 mmol) in 0.26 mmol yield (79 %) or synthesized using the Pd-synthon route using [Pd(IPr)(PhC≡CPh)] (100 mg; 0.15 mmol) and 2-(3-chloro-1-propen-1-yl)-naphthalene **(4)** (31 mg; 0.15 mmol) in 0.12 mmol yield (80 %). Isolated as yellow solid ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.56 (m, 4H), 7.42 (t, 2H, *J* = 7.7 Hz), 7.27 (m, 6H), 7.16 (dd, 1H, J_1 = 8.5 Hz, J_2 = 1.7 Hz), 7.12 (s, 2H), 5.12 (m, 1H), 4.42 (d, 1H, *J* = 12.6 Hz), 2.95 (m, 5H), 1.79 (d, 1H, *J* = 11.6 Hz), 1.33 (m, 12H), 1.21 (m, 1H), 1.08 (m, 12H). ^{13}C-{H}-NMR (400 MHz, $CDCl_3$, 298 K) 185.0, 146.1, 145.9, 145.7, 145.1, 135.9, 135.7, 133.6, 132.6, 129.9, 127.9, 127.8, 127.6, 126.5, 125.7, 125.3, 125.2, 124.8, 124.2, 123.9, 123.5, 123.4, 108.9, 89.9, 46.7, 28.6, 26.2, 26.1, 23.0, 22.9, 14.1. Elemental Analysis: calcd for C40H48ClN2Pd: C: 68.76, H: 6.92, N: 4.01; Found: C:68.66, H: 7.06, N: 4.00.

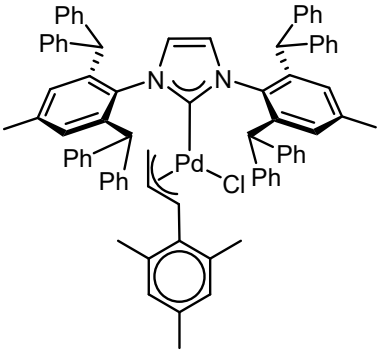


[(IPr*)Pd(η^3-p-tol-allyl)Cl] (IPr*-1) was synthesized using the weak procedure from [Pd(η^3-p-tol-allyl)(*μ*-Cl)]$_2$ **(1)** (100 mg; 0.18 mmol), IPr*·HCl (410 mg; 0.43 mmol) and K_2CO_3 (75 mg; mmol) in 0.32

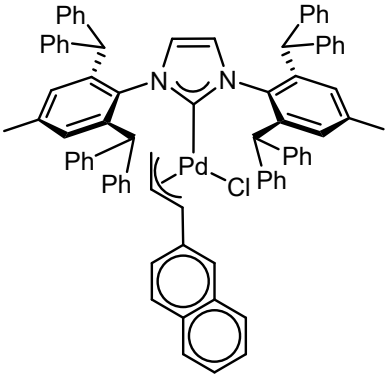
mmol yield (89 %) Isolated as a pale yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.32 (d, 2H, *J* = 7.8 Hz), 7.20 (m, 12H), 7.14 (m, 12H), 7.02 (m, 12H), 6.75 (m, 12H), 5.99 (s, 2H), 5.67 (s, 2H), 4.93 (m, 1H), 4.57 (d, 1H, *J* = 13.1 Hz), 2.48 (d, 1H, *J* = 6.7 Hz), 2.26 (s, 3H), 2.15 (s, 6H), 1.15 (d, 1H, *J* = 11.3 Hz). ^{13}C-{H}-NMR (75 MHz, $CDCl_3$, 298 K) δ 182.9, 144.6, 143.9, 141.4, 140.6, 138.4, 137.0, 135.9, 134.8, 130.6, 130.3, 129.5, 129.3, 129.3, 128.4, 128.3, 127.6, 126.4, 123.5, 108.4, 92.1, 51.5, 47.0, 29.4, 22.0, 21.7. Elemental Analysis: calcd for C37H48ClN2Pd: C: 67.06, H: 7.30, N:4.23; Found: C: 66.99, H: 7.09, N: 4.19.



[(IPr*)Pd(η$_3$-p-^{t}Bu-cin)Cl] (IPr*-2) was synthesized using the weak procedure from [Pd(*η^3*-p-^{t}Bu-cin)(*μ*-Cl)]$_2$ **(2)** (100 mg; 0.16 mmol), IPr*·HCl (mg; 0.38 mmol) and K_2CO_3 (66 mg; 0.48 mmol) in 0.25 mmol yield (79 %) Isolated as a pale yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.38 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.22 (m, 12H), 7.11 (m, 10H), 7.01 (m, 12H), 6.74 (m, 12H), 5.98 (s, 2H), 5.72 (s, 2H), 4.89 (m, 1H), 4.60 (d, 1H, *J* = 13.1 Hz), 2.49 (d, 1H, *J* = 6.4 Hz), 2.15 (s, 6H), 1.29 (s, 9H), 1.14 (d, 1H, *J* = 10.9 Hz). ^{13}C-{H}-NMR (75 MHz, $CDCl_3$, 298 K) δ 182.7, 149.8, 144.5, 143.8, 143.7, 141.2, 140.6, 138.3, 135.9, 134.9, 130.5, 130.3, 129.2, 128.3, 128.1, 127.5, 126.3, 125.6, 123.4, 108.9, 92.1, 51.4, 47.1, 34.7, 31.3, 29.3, 21.9, 21.7. Elemental Analysis: calcd for C37H48ClN2Pd: C: 67.06, H: 7.30, N:4.23; Found: C: 66.99, H: 7.09, N: 4.19.



[(IPr*)Pd(η^3-mes-allyl)Cl] (IPr*-3) was synthesized using the weak procedure from [Pd(*η^3*-p-mes-allyl)(*μ*-Cl)]$_2$ **(3)** (100 mg; 0.17 mmol), IPr*·HCl (378 mg; 0.39 mmol) and K_2CO_3 (71 mg; 0.51 mmol) in 0.28 mmol yield (85 %) Isolated as pale yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K). ^{13}C-{H}-NMR (75 MHz, $CDCl_3$, 298 K) δ 184.4, 144.4, 143.8, 143.5, 138.3, 136.7, 136.0, 135.8, 132.0, 131.9, 129.2, 128.3, 128.1, 127.5, 126.3, 125.6, 123.4, 108.9, 92.1, 51.4, 47.1, 34.7, 31.3, 29.3, 21.9, 21.7. HRMS Analysis: [M+]-Cl for C81H71ClN2Pd: Calcd: [M+]-Cl: 1177.47; Found: 1177.4647.

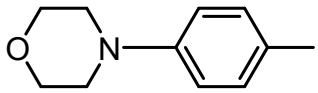


[(IPr*)Pd(*η^3*-2-naph-allyl)Cl] (IPr*-4) was synthesized using the weak procedure from [Pd(*η^3*-2-naph-allyl)(μ-Cl)]$_2$ **(4)** (100 mg; 0.16 mmol), IPr*·HCl (361 mg; 0.38 mmol) and K_2CO_3 (mg; mmol) in mmol yield (%) Isolated as a pale yellow solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.38 (d, 2H, *J* = 8.2 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.22 (m, 12H), 7.11 (m, 10H), 7.01 (m, 12H), 6.74 (m, 12H), 5.98 (s, 2H), 5.72 (s, 2H), 4.89 (m, 1H), 4.60 (d, 1H, *J* = 13.1 Hz), 2.49 (d, 1H, *J* = 6.4 Hz), 2.15 (s, 6H), 1.29 (s, 9H), 1.14 (d, 1H, *J* = 10.9 Hz). ^{13}C-{H}-NMR (75 MHz, $CDCl_3$, 298 K) δ 182.5, 144.5, 143.8, 143.7, 142.9, 142.5, 141.3, 140.6, 138.4, 135.8, 135.5, 133.8, 132.9, 131.9, 130.6, 130.2, 129.8, 129.5, 129.4, 129.2, 128.3, 128.3, 128.2, 128.1, 127.9, 126.3, 126.2, 126.0, 125.8, 125.5,

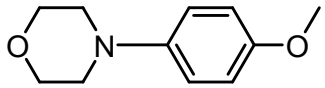
123.4, 108.9, 91.3, 51.5, 47.5, 21.9. Elemental Analysis: calcd for C82H67ClN2Pd: Calcd: [M+]-Cl: 1185.43; Found: 1185.4334.

Buchwald-Hartwig cross-coupling amination

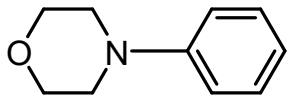
General procedure: In a glovebox, [Pd] (1 mol %), potassium tert-butoxide (0.55 mmol, 62 mg) and anhydrous dimethoxyethane (DME) (0.5 mL) were added in turn to a vial equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. Outside the glovebox, the amine (0.55 mmol) and the aryl halide (0.5 mmol) were injected in turn through the septum. (If one of the two starting materials was a solid, it was added to the vial inside the glovebox and DME and the second starting material were added outside the glovebox under argon). The reaction mixture was then stirred at room temperature. When the reaction reached completion, or no further conversion could be observed by gas chromatography, water was added to the reaction mixture, the organic layer was extracted with diethyl ether, dried over magnesium sulfate and the solvent was evaporated in vacuo. When necessary the product was purified by flash chromatography on silica gel. The reported yields are the average of at least two runs.



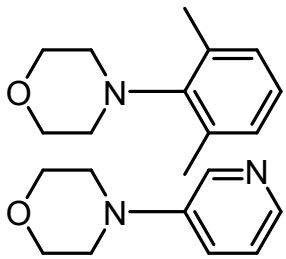
4-(p-tolyl)morpholine (5a) was synthesized using the procedure from 4-methylchlorobenzene and morpholine, in 0.48 mmol yield (96 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.12 (m, 2H), 6.86 (m, 2H), 3.89 (m, 4H), 3.14 (m, 4H), 2.30 (s, 3H). The NMR data are consistent with the reported literature[5].



4-(4-methoxyphenyl)morpholine (5b) was synthesized using the Buchwald-Hartwig procedure from 4-methoxychlorobenzene and morpholine, in 0.49 mmol yield (98 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 6.90 (m, 4H), 3.89 (m, 4H), 3.80 (s, 3H), 3.08 (m, 4H). The NMR data are consistent with the reported literature[6].

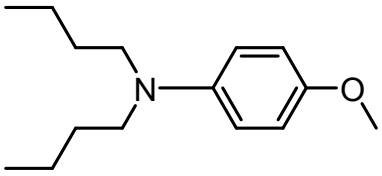


4-phenylmorpholine (5c) was synthesized using the procedure from 4-chlorobenzene and morpholine, in 0.49 mmol yield (98 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.31 (m, 2H), 6.94 (m, 3H), 3.89 (m, 4H), 3.19 (m, 4H). The NMR data are consistent with the reported literature[5].

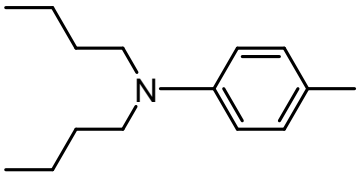


4-(2,6-dimethylphenyl)morpholine (5d) was synthesized using the procedure from 2,6-dichloro-*m*-xylene and morpholine, in 0.5 mmol yield (99 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.02 (m, 3H), 3.83 (m, 4H), 3.13 (m, 4H), 2.37 (s, 6H). The NMR data are consistent with the reported literature[5].

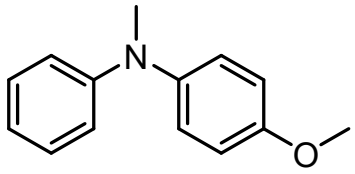
4-(pyridin-3-yl)morpholine (5e) was synthesized using the procedure from 3-chloropyridine and morpholine, in 0.4 mmol yield (80 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 8.24 (S, 1H), 8.06 (s, 1H), 7.11 (m, 2H), 3.81 (m, 4H), 3.12 (m, 4H). The NMR data are consistent with the reported literature[5].



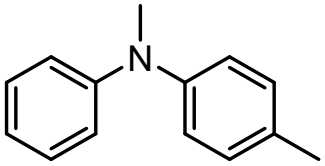
N,N-dibutyl-4-methoxyaniline (5f) was synthesized using the procedure from 4-methoxychlorobenzene and dibutylamine, in 0.46 mmol yield (92 %) Isolated as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 6.82 (m, 2H), 6.65 (d, 2H, *J* = 8.7 Hz), 3.75 (s, 3H), 3.17 (m, 4H), 1.50 (m, 4H), 1.33 (m, 4H), 0.93 (t, 4H, *J* = 7.3 Hz). The NMR data are consistent with the reported literature[7].



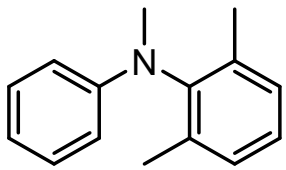
N,N-dibutyl-4-methylaniline (5g) was synthesized using the procedure from 4-methylchlorobenzene and dibutylamine**,** in 0.43 mmol yield (85 %) Isolated as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.01 (m, 2H), 6.58 (d, 2H, *J* = 6.6 Hz), 3.23 (m, 4H), 2.24 (s, 3H), 1.54 (m, 4H), 1.34 (m, 4H), 0.94 (t, 4H, *J* = 7.2 Hz). The NMR data are consistent with the reported literature[7].



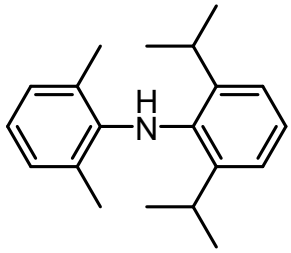
4-methoxy-N-methyl-N-phenylaniline (5h) was synthesized using the procedure from 4-methoxychlorobenzene and N-methylaniline**,** in 0.47 mmol yield (95 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.24 (dd, 2H, J_1 = 8.9 Hz, J_2 = 7.2 Hz), 7.16 (d, 2H, *J* = 8.9 Hz), 6.89 (m, 5H), 3.84 (s, 3H), 3.30 (s, 3H). The NMR data are consistent with the reported literature[5].



4-methoxy-N-methyl-N-phenylaniline (5i) was synthesized using the procedure from 4-methoxychlorobenzene and N-methylaniline**,** in 0.4 mmol yield (80 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.23 (m, 2H), 7.12 (m, 2H), 6.99 (m, 2H), 6.92 (m, 2H), 6.87 (m, 1H), 3.28 (s, 3H), 2.32 (s, 3H). The NMR data are consistent with the reported literature[5].



4-methoxy-N-methyl-N-phenylaniline (5j) was synthesized using the procedure from 4-methoxychlorobenzene and N-methylaniline**,** in 0.48 mmol yield (97 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.28 (m, 4H), 6.82 (m, 2H, J_1 = 7.2 Hz, J_2 = 1.1 Hz), 6.57 (broad s, 1H), 6.92 (m, 2H), 3.34 (s, 3H), 2.25 (s, 6H). The NMR data are consistent with the reported literature[8].

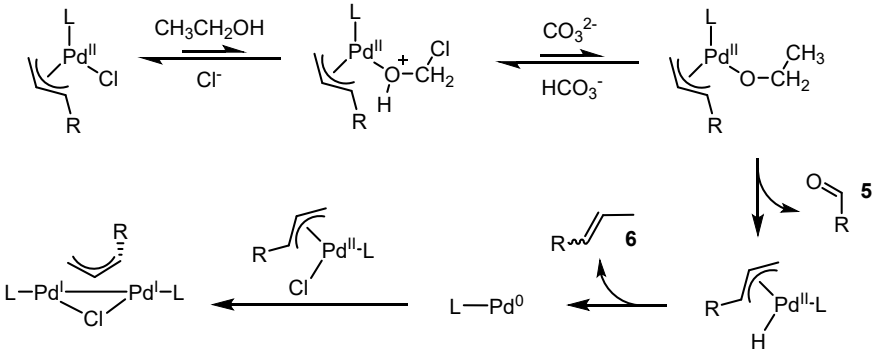


N-(2,6-diisopropylphenyl)-2,6-dimethylaniline (5k) was synthesized using the procedure from 4-methoxychlorobenzene and N-methylaniline**,** in 0.5 mmol yield (99 %) Isolated as an off-white solid. ^{1}H-NMR (300 MHz, $CDCl_3$, 298 K) δ 7.14 (m, 3H), 6.95(m, 2H), 6.74 (m, 1H), 4.81 (broad s, 1H), 3.17

(hept, 2H, *J* = 6.7 Hz), 2.00 (s, 6H), 1.15 (s, 6H), 1.13 (s, 6H). The NMR data are consistent with the reported literature[9].

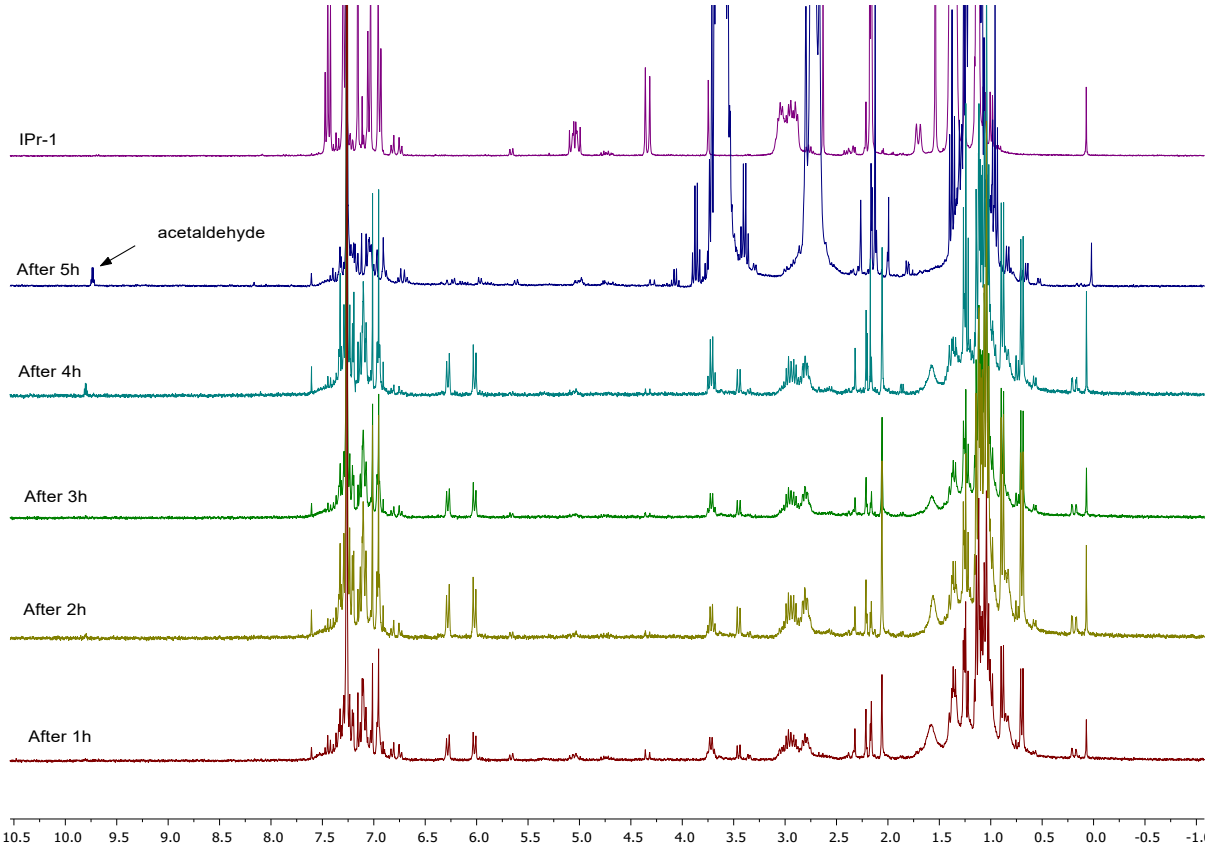
$[Pd^{I}_{2}(NHC)_{2}(\eta^{3}\text{-R-allyl})(\mu\text{-Cl})]$ dimer formation

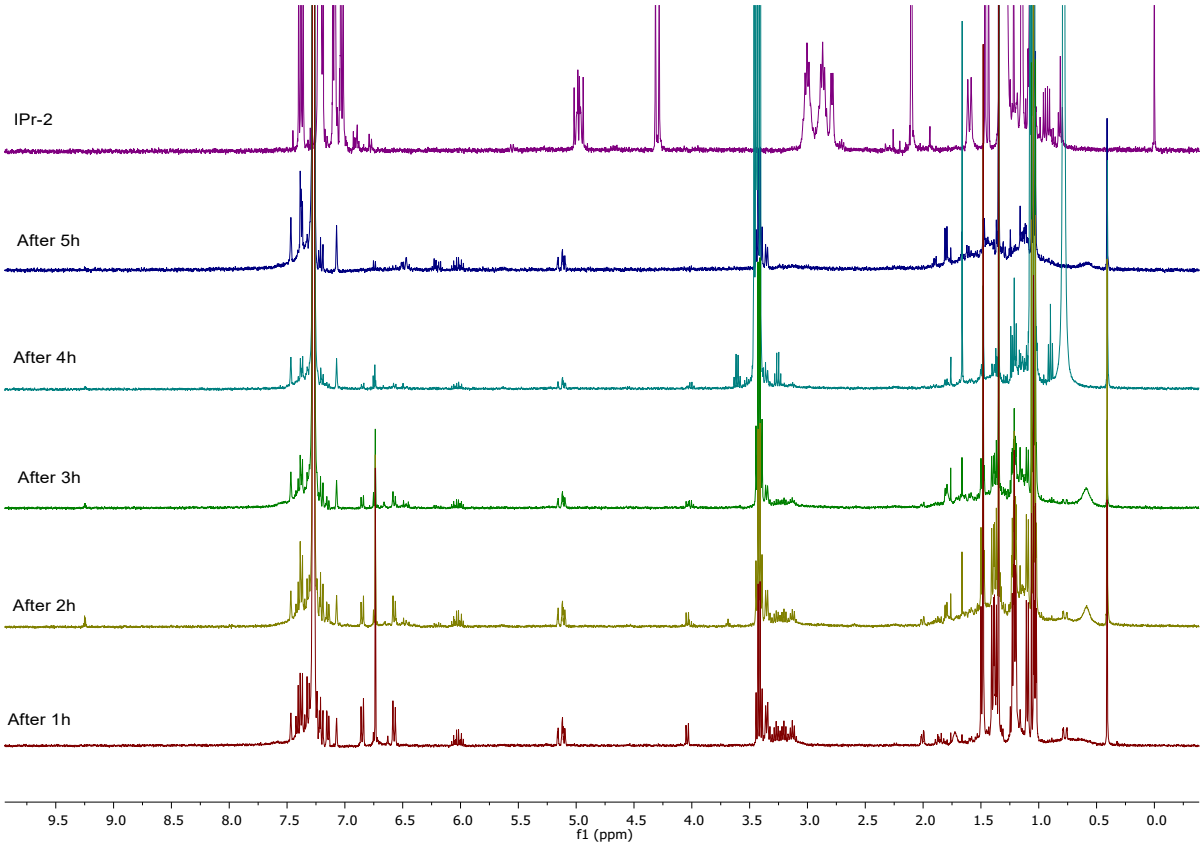
[(NHC)Pd(η^3-R-allyl)Cl] (0.08 mmol, 1 eq), K_2CO_3 (0.24 mmol), and a magnetic stirring bar were charged into a Schlenk flask, followed by 3 vacuum/argon cycles and then the degassed ethanol (3 mL) was transferred into the flask, following the reported procedure. The reaction mixture was stirred at 40 °C for 24 h. A sample of 0.1 mL was taken, the solvent was evaporated in vaccuo, and $CDCl_3$ is added for analysis by ^{1}H NMR. This is done every hour until 5h to check the reaction progress. During the time, the yellow solution turns into brown color[10].

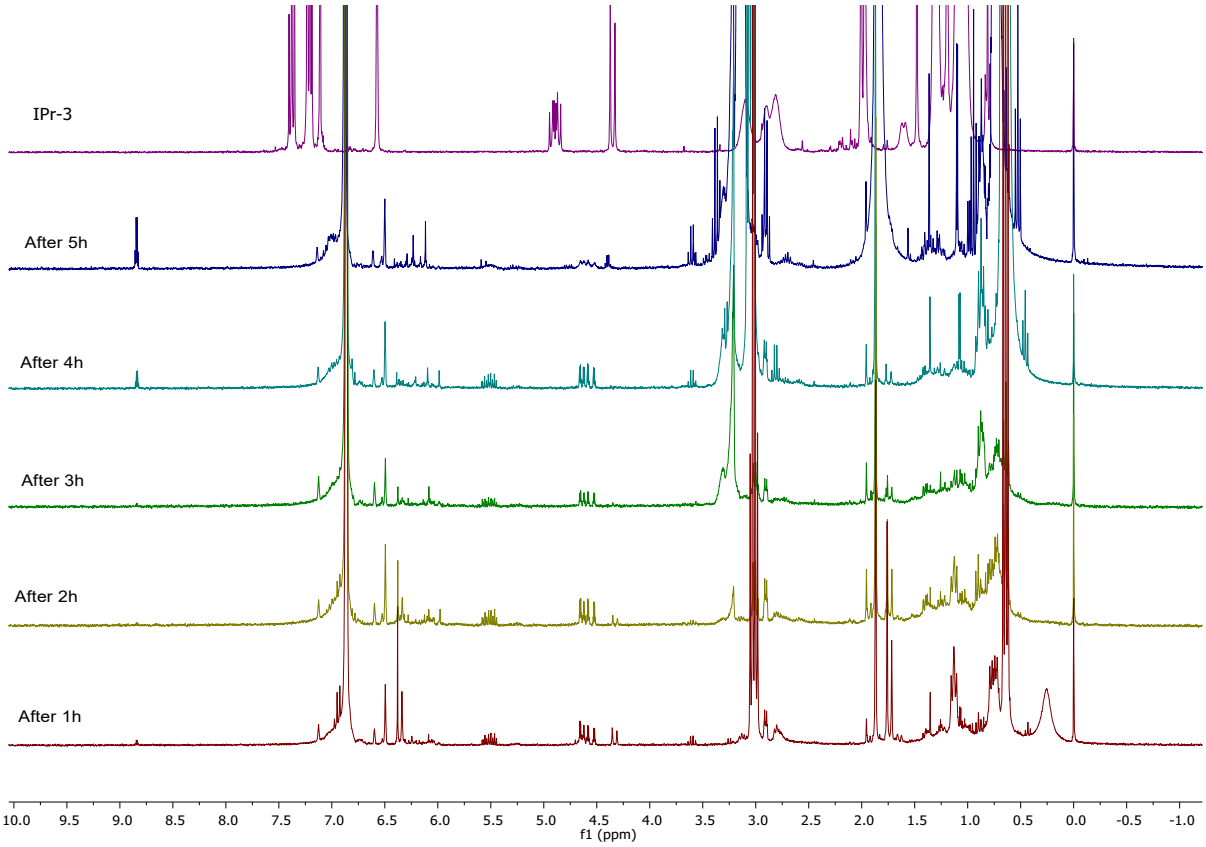


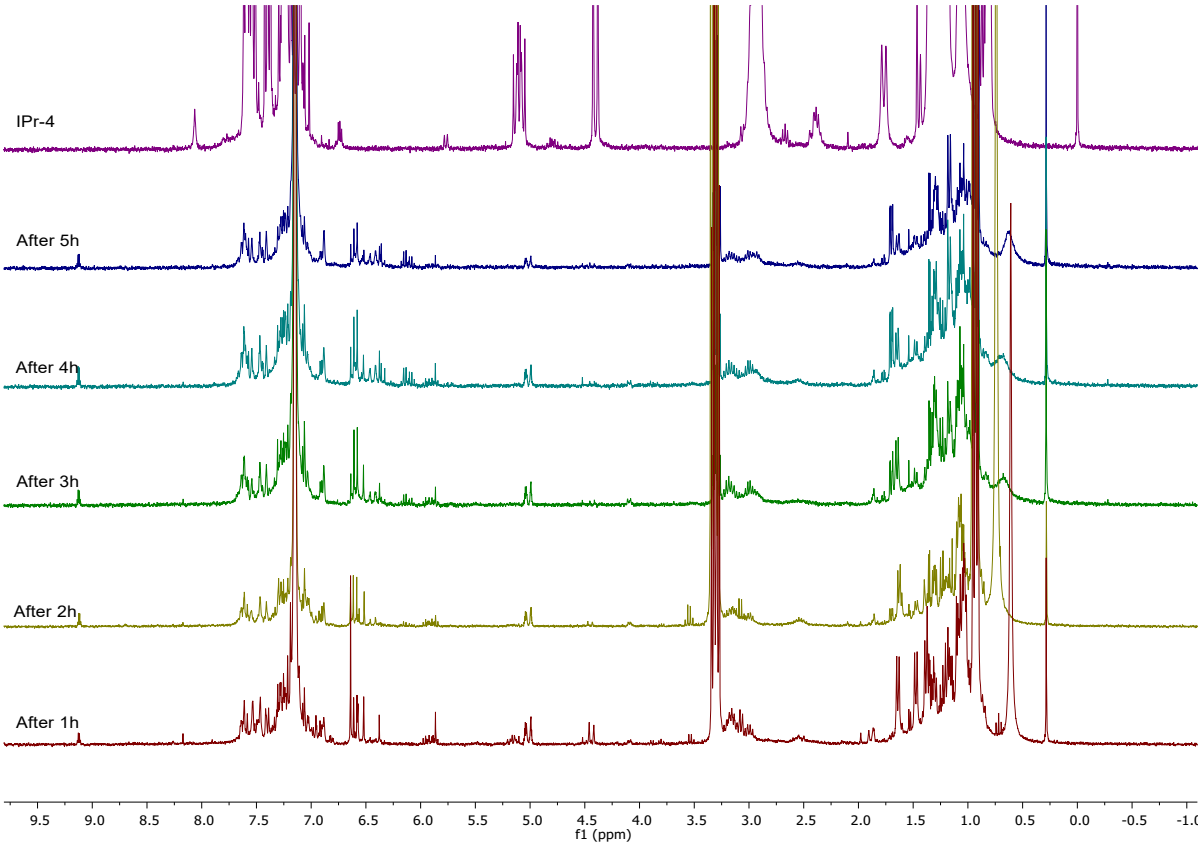
Scheme S4: Proposed mechanism for the formation of the PdI dimers with weak base.

^{1}H NMR spectra of Pd^{I} dimer formation

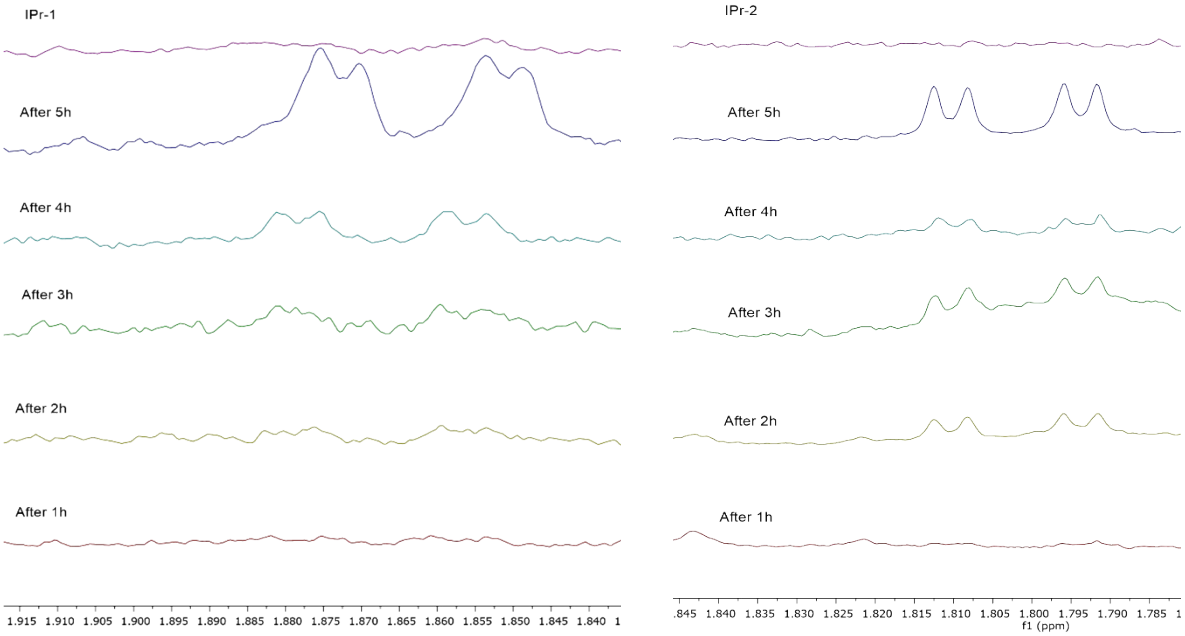

IPr-1
acetaldehyde
After 5h
After 4h
After 3h
After 2h
After 1h
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

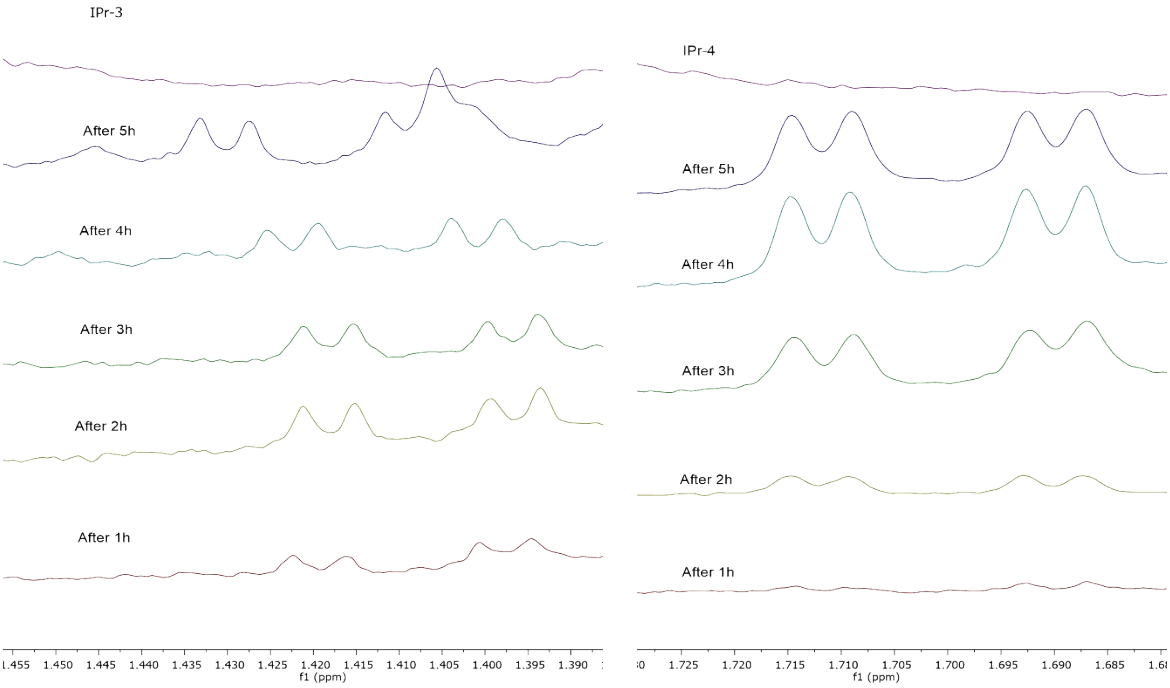

IPr-2
After 5h
After 4h
After 3h
After 2h
After 1h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


IPr-3
After 5h
After 4h
After 3h
After 2h
After 1h
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


IPr-4
After 5h
After 4h
After 3h
After 2h
After 1h
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

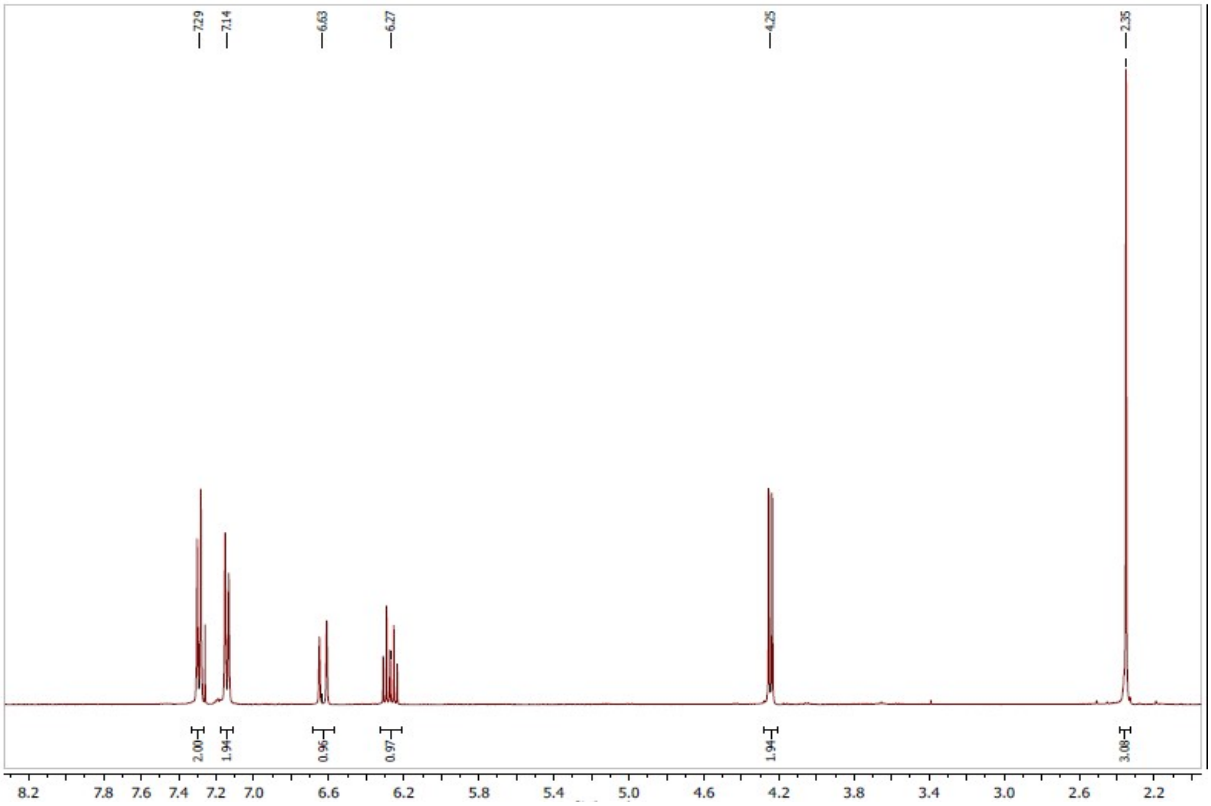
Focus on the central proton peak area



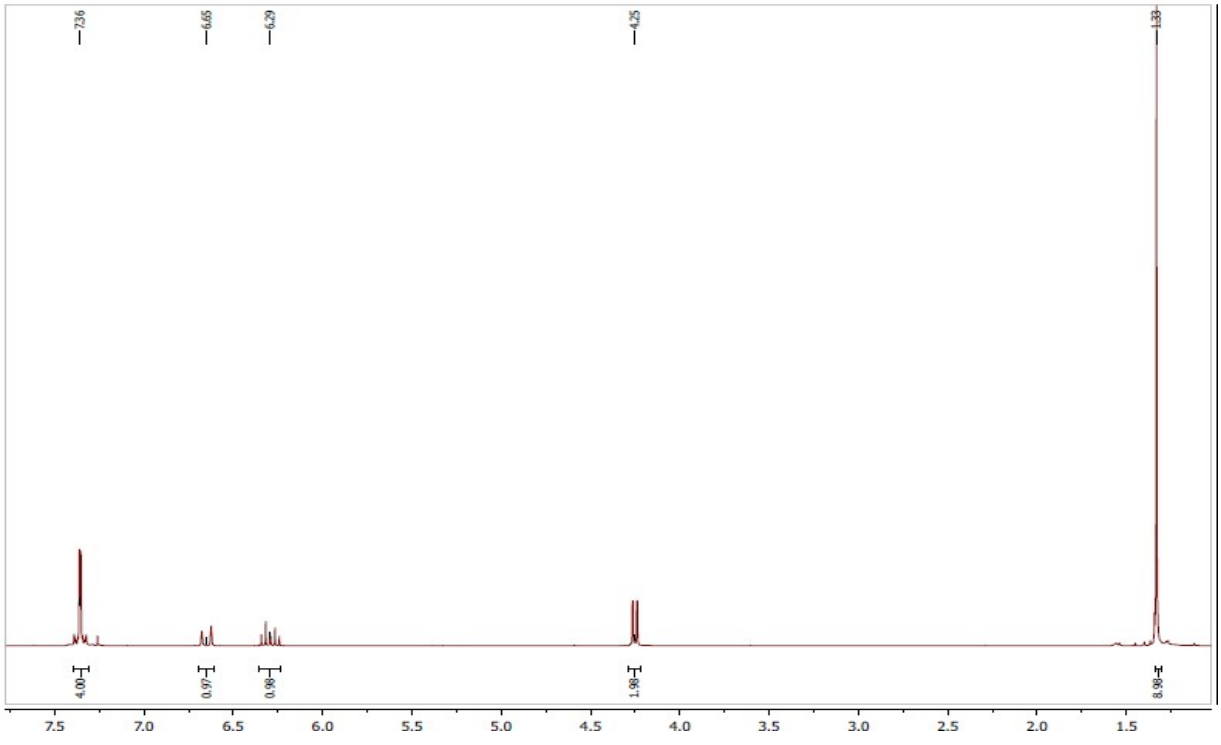


NMR-spectra

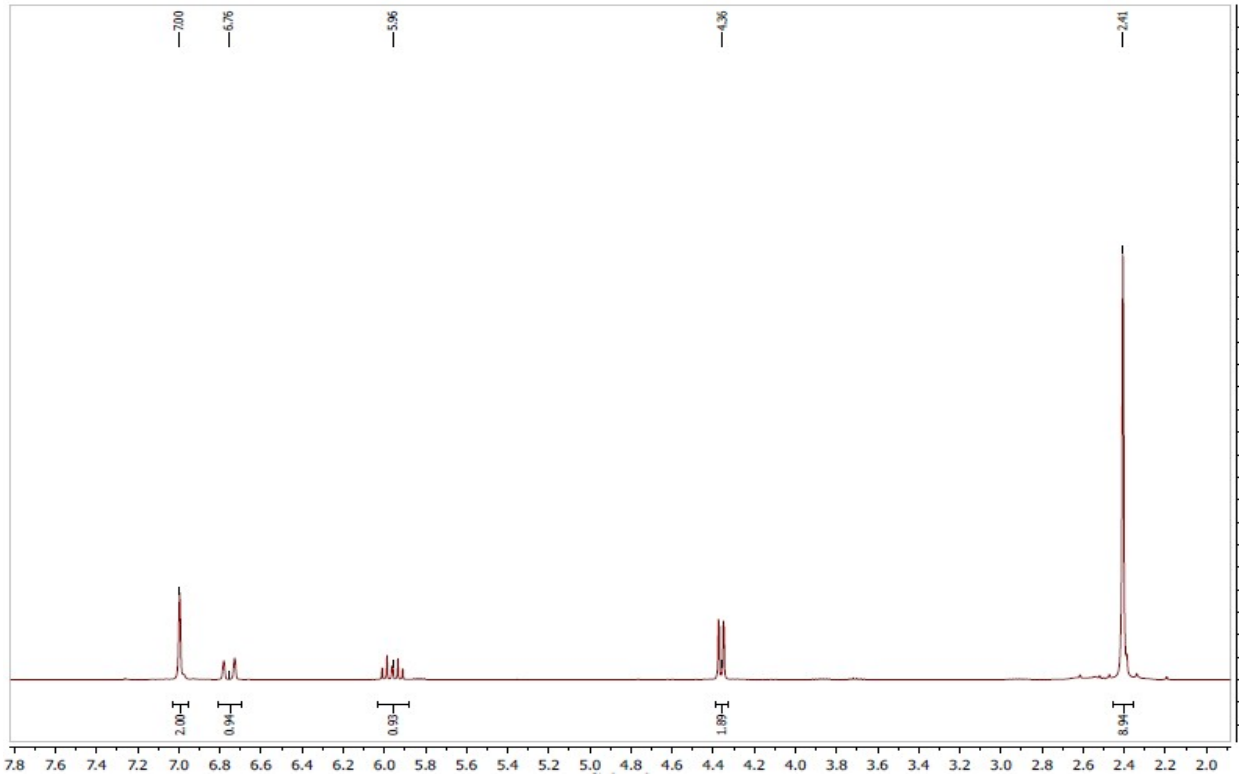
^{1}H NMR (400 MHz, $CDCl_3$) of **1**



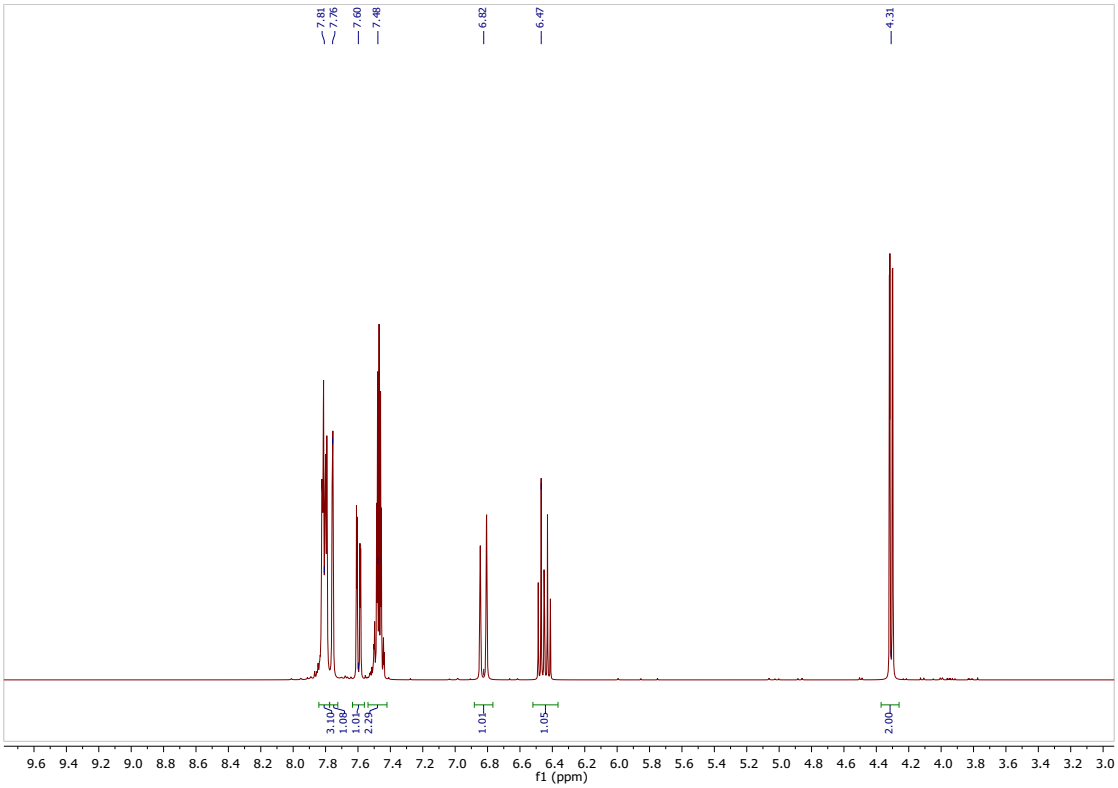
^{1}H NMR (300 MHz, $CDCl_3$) of **2**



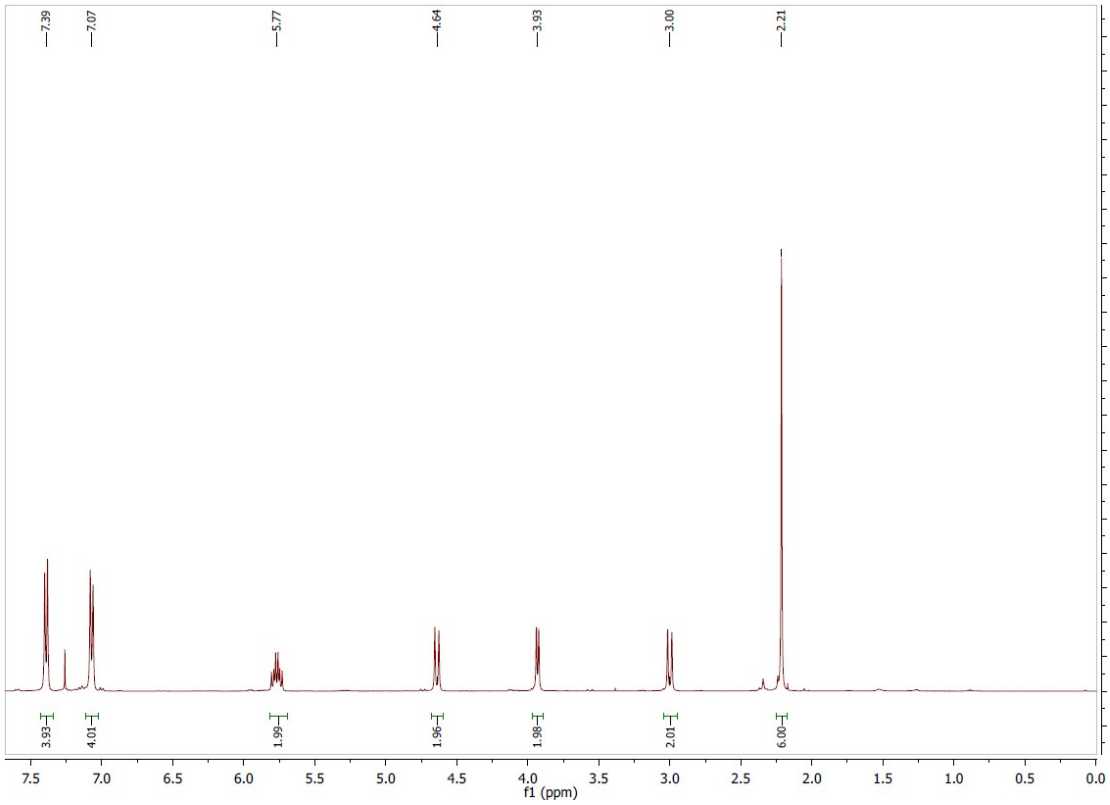
^{1}H NMR (300 MHz, $CDCl_3$) of **3**



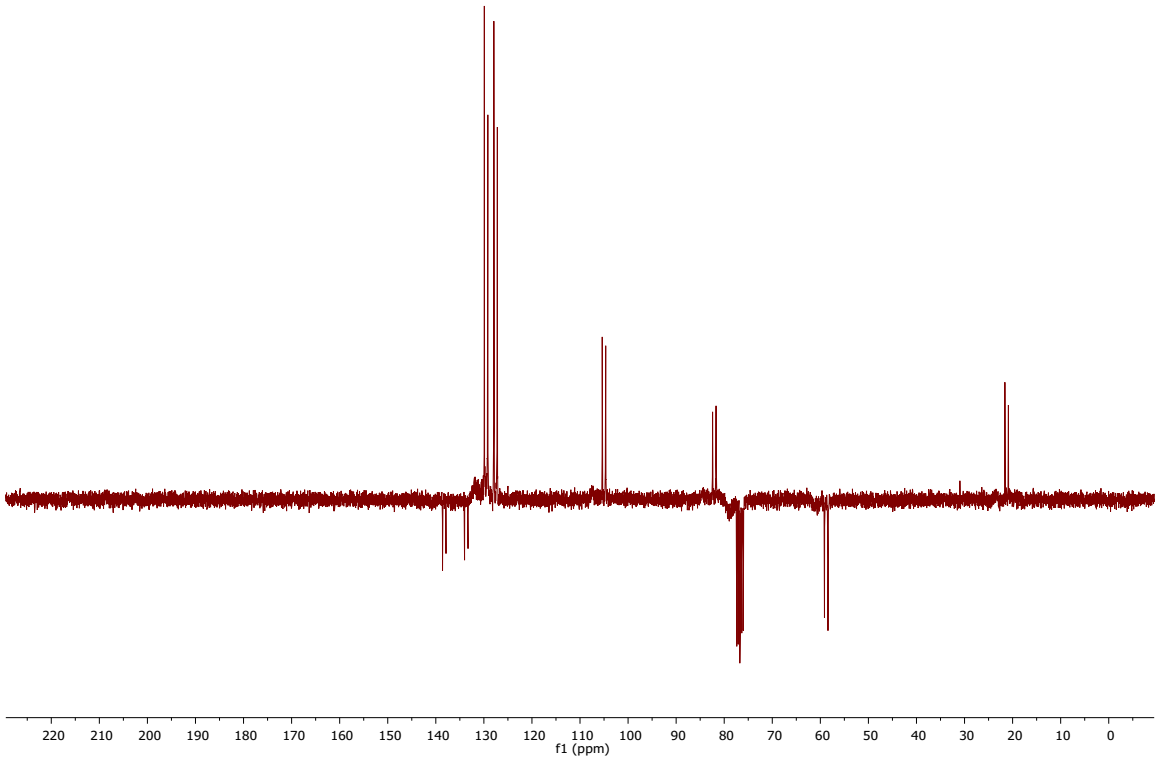
^{1}H NMR (400 MHz, $CDCl_3$) of **4**



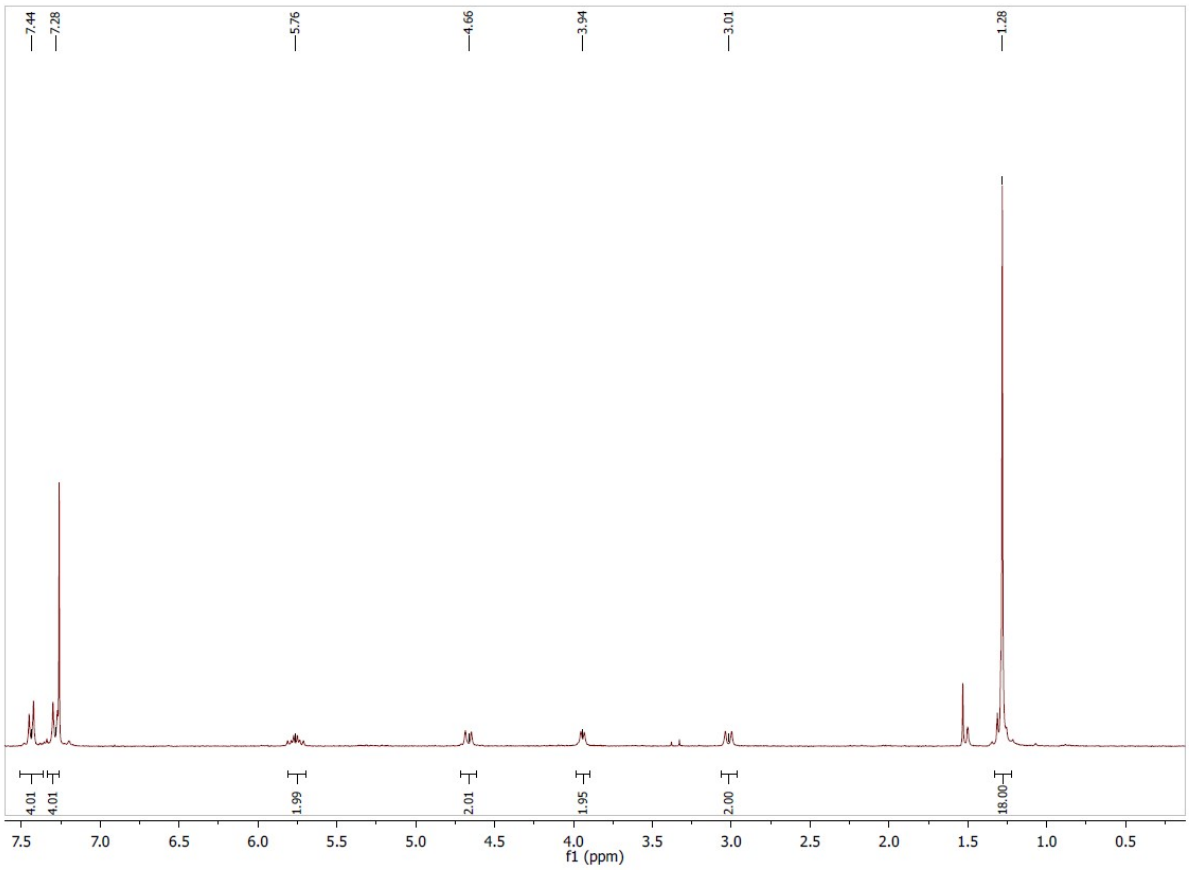
^{1}H NMR (400 MHz, $CDCl_3$) of **5**



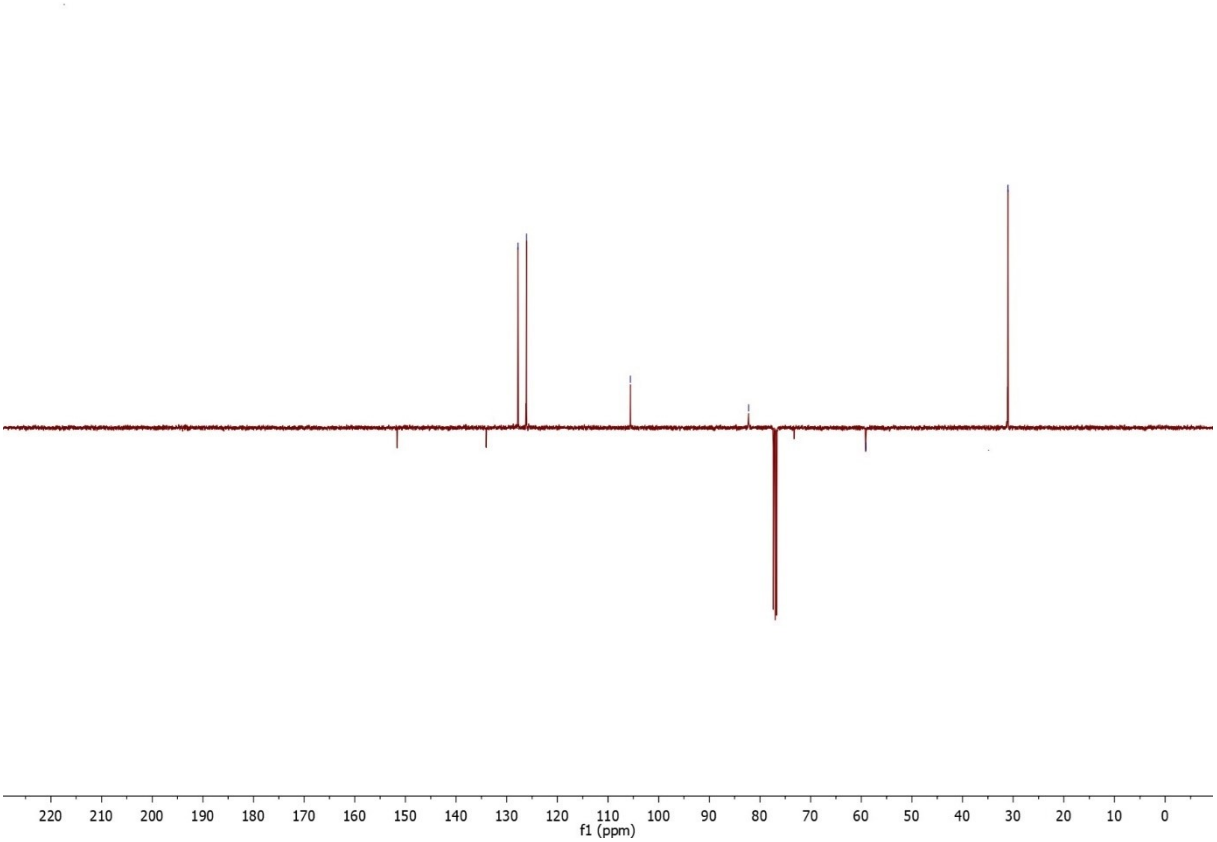
^{13}C NMR (400 MHz, $CDCl_3$) of **5**



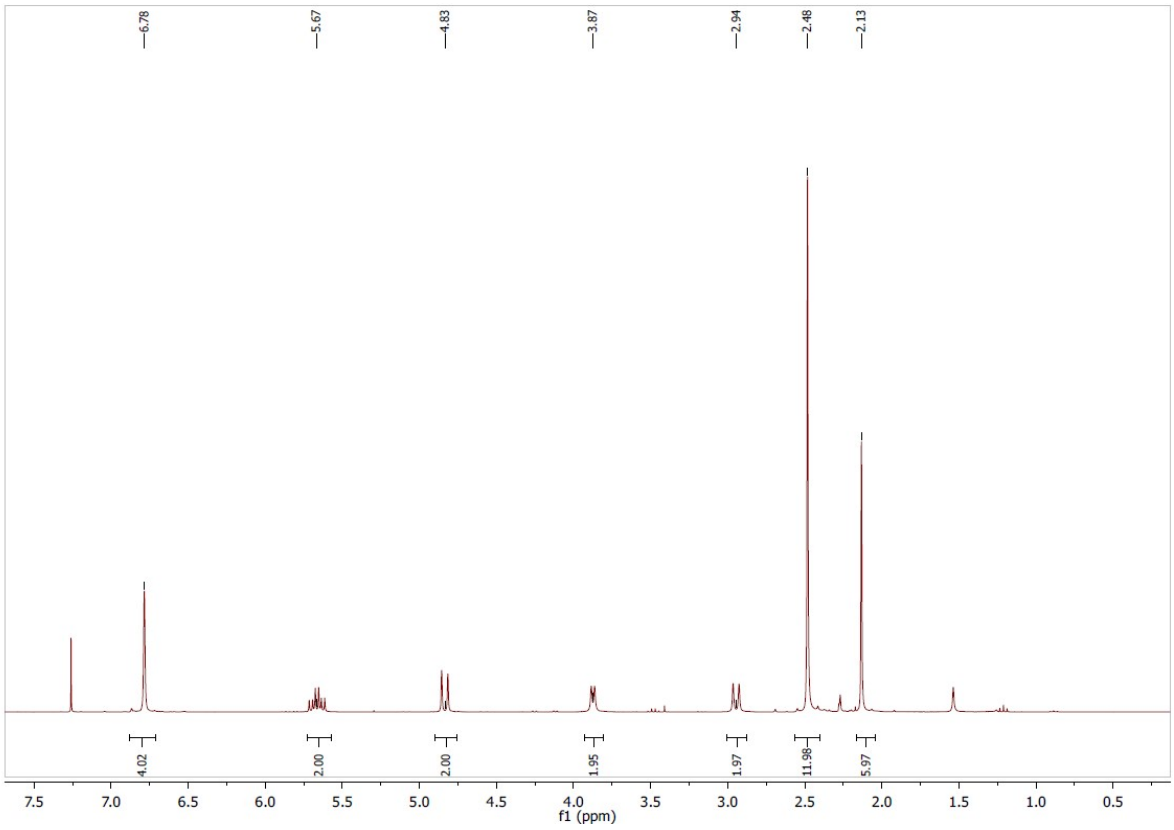
^{1}H NMR (300 MHz, $CDCl_3$) of **6**



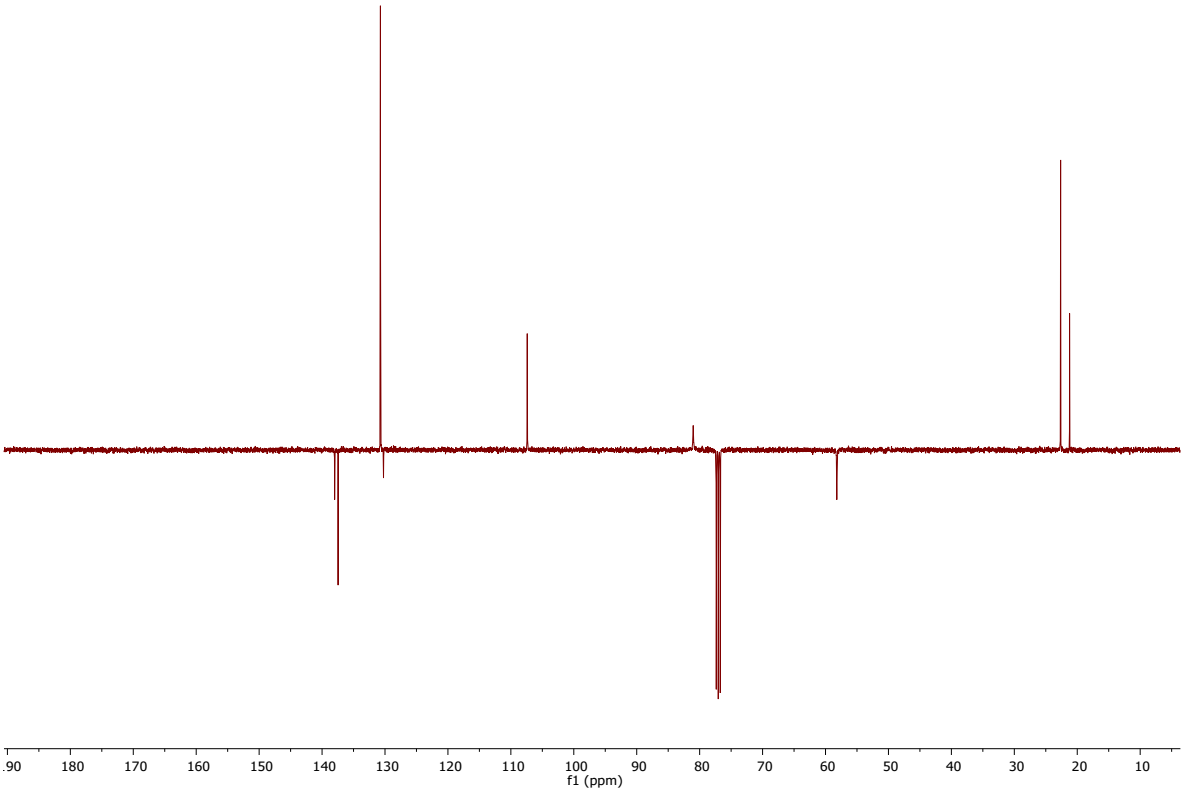
^{13}C NMR (400 MHz, $CDCl_3$) of **6**



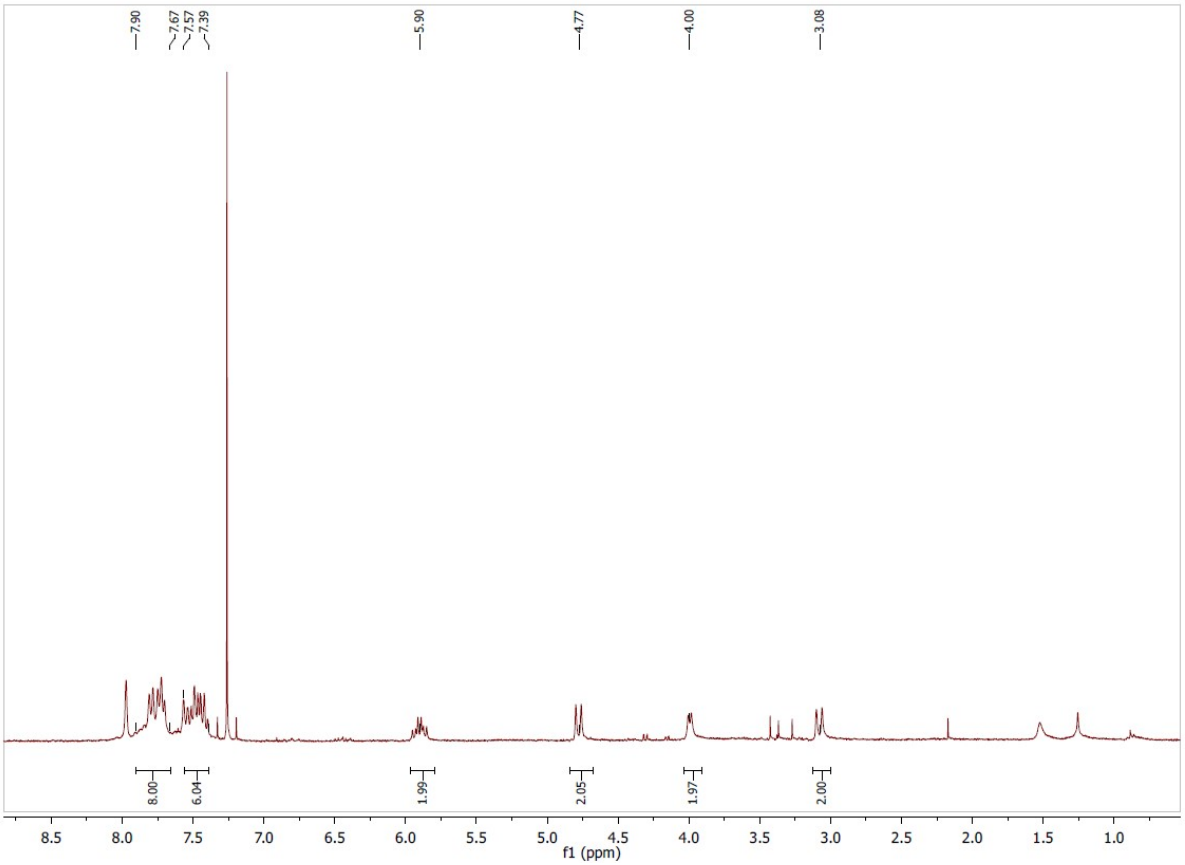
^{1}H NMR (300 MHz, $CDCl_3$) of **7**



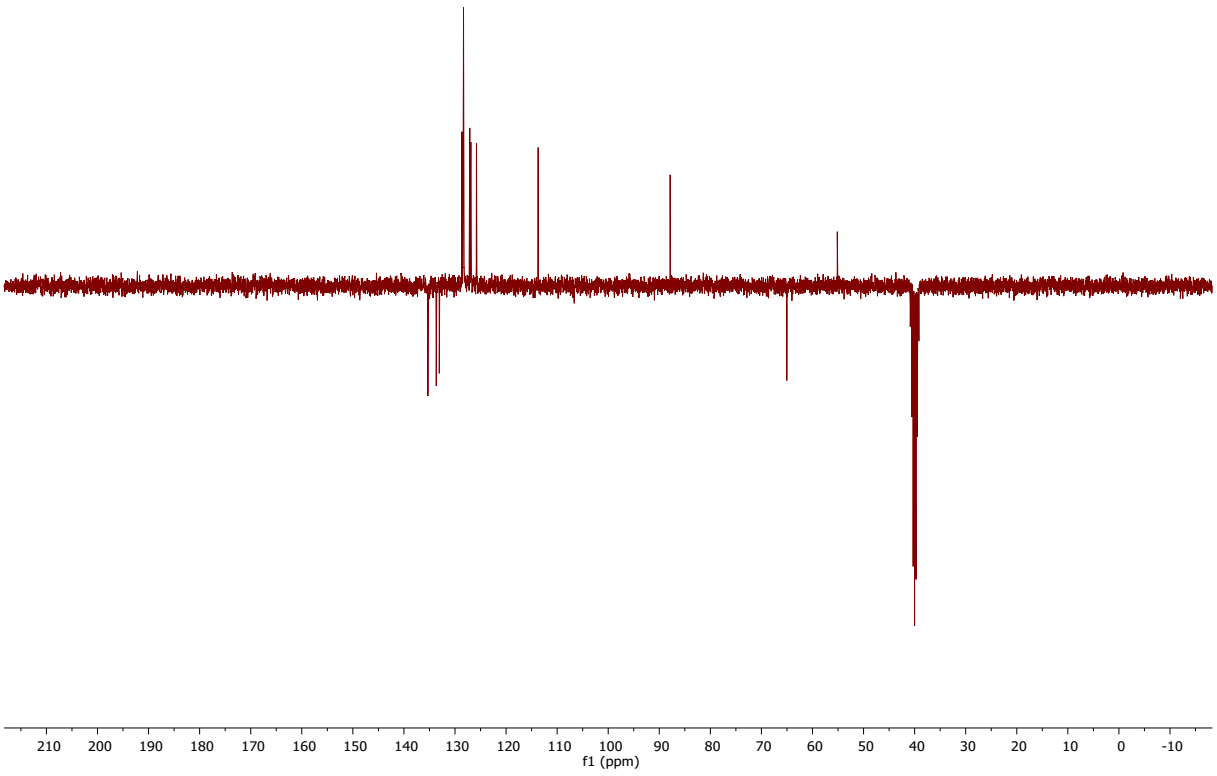
^{13}C NMR (400 MHz, $CDCl_3$) of **7**



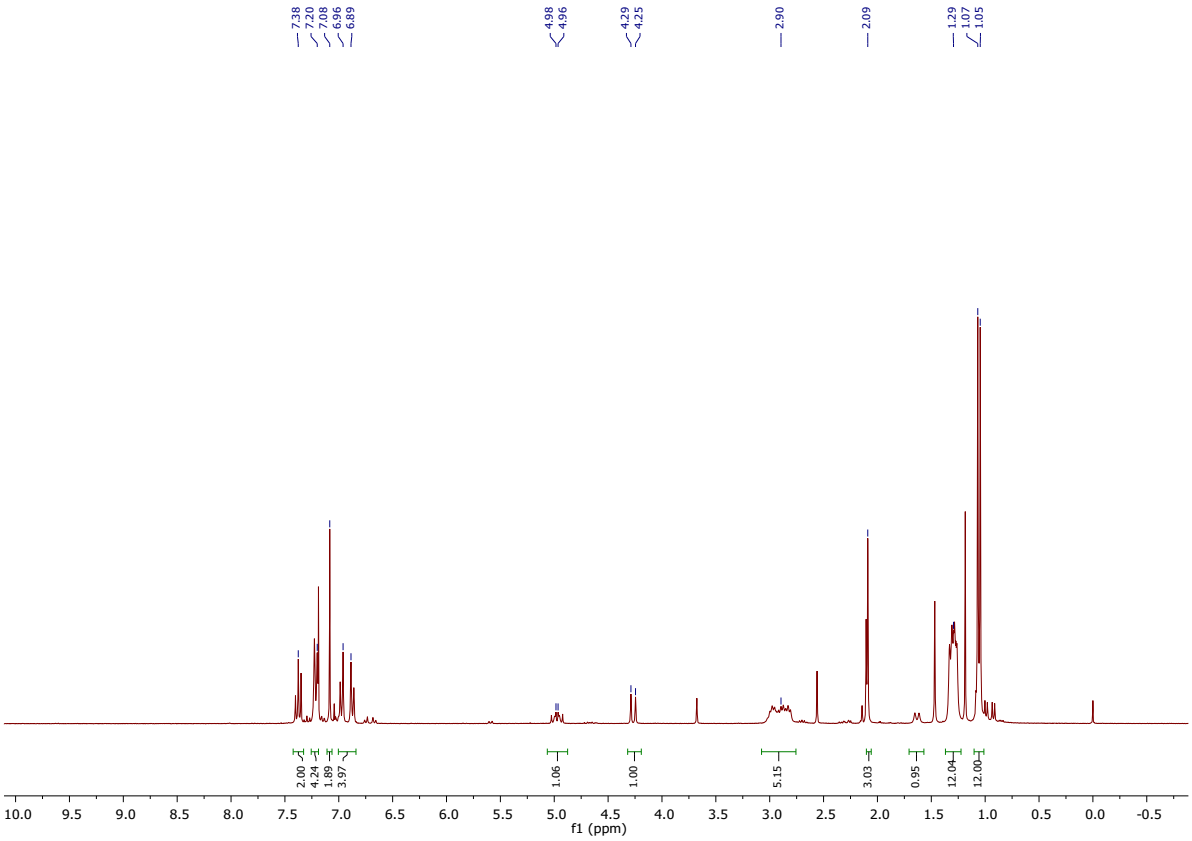
^{1}H NMR (300 MHz, $CDCl_3$) of **8**



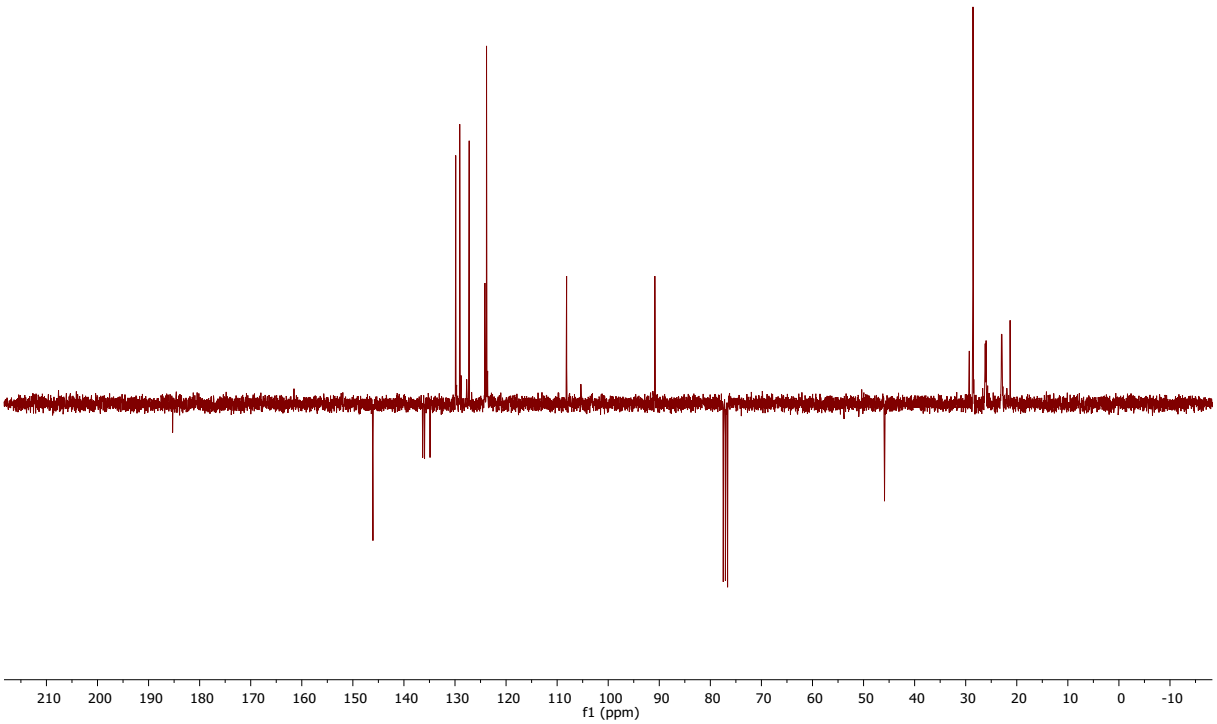
^{13}C NMR (400 MHz, DMSO-d_6) of **8**



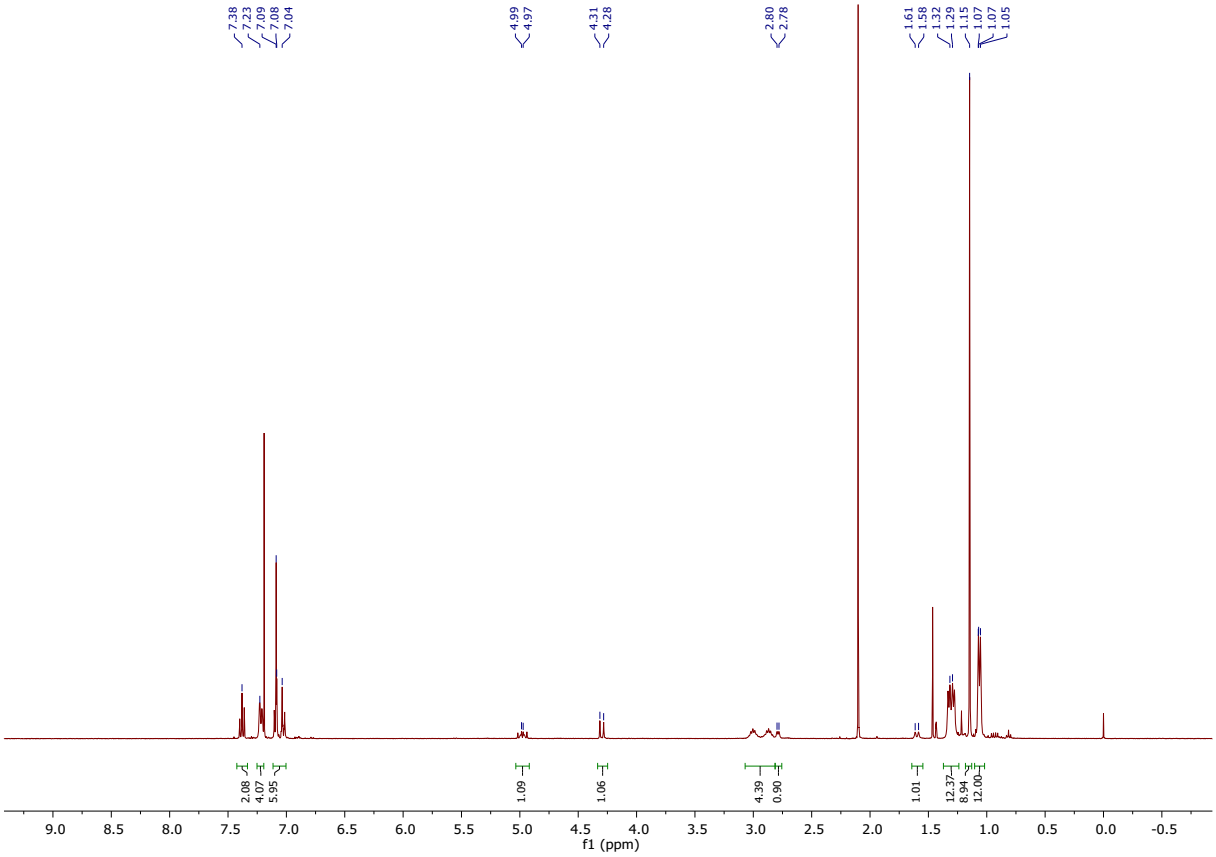
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-1**



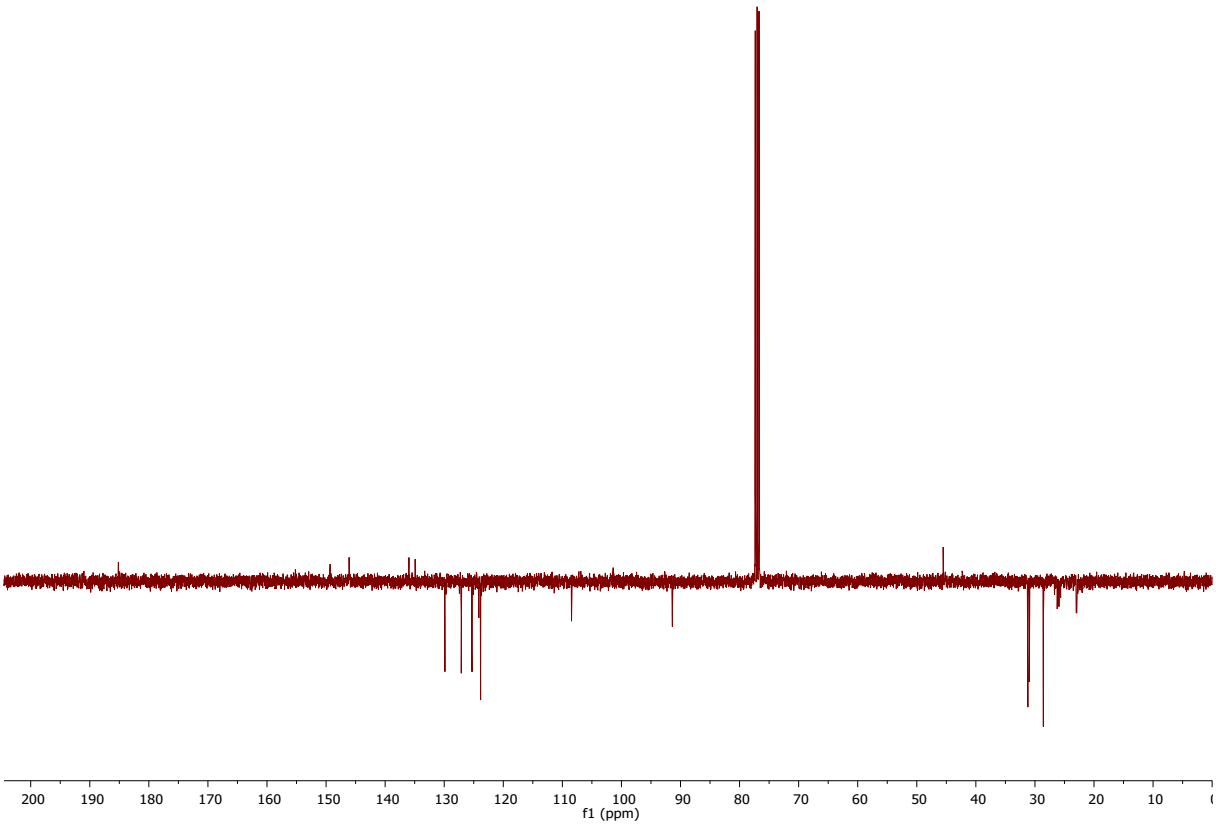
^{13}C NMR (300 MHz, $CDCl_3$) of **IPr-1**



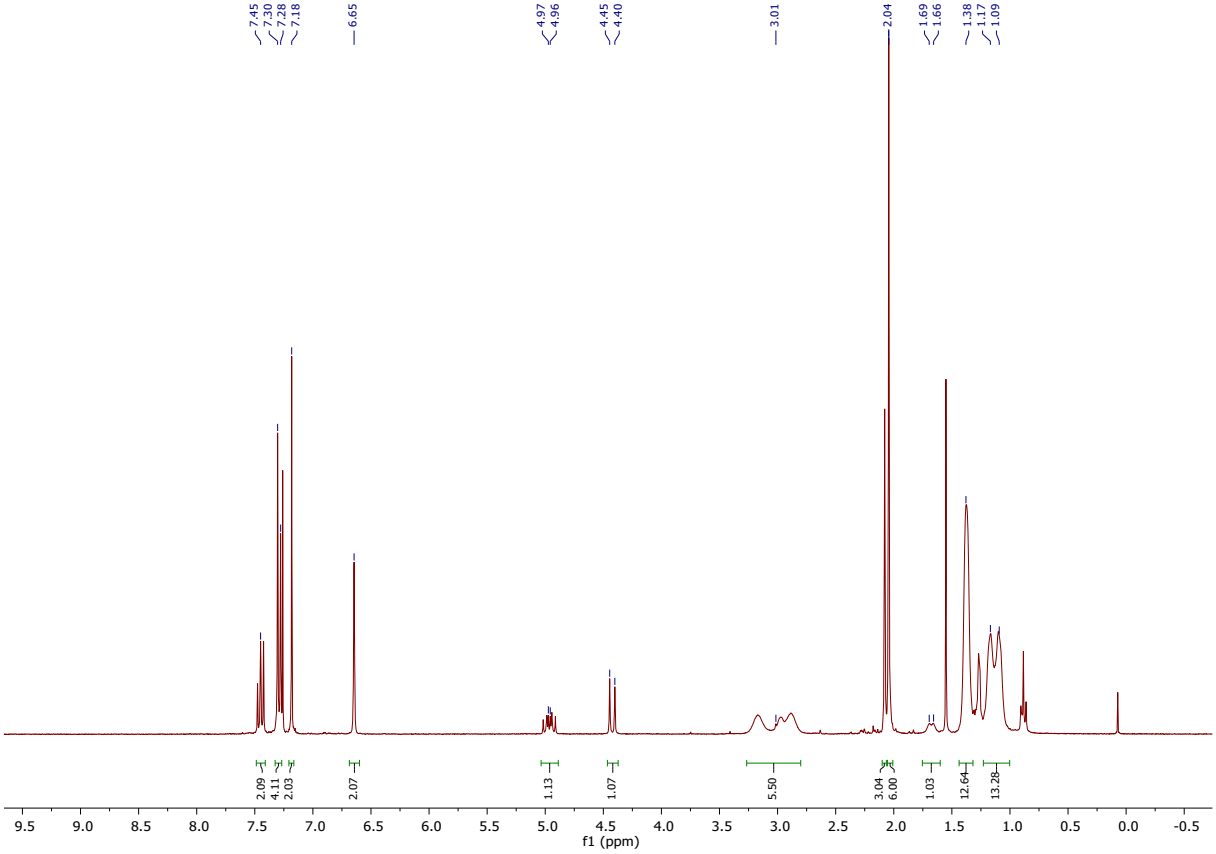
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-2**



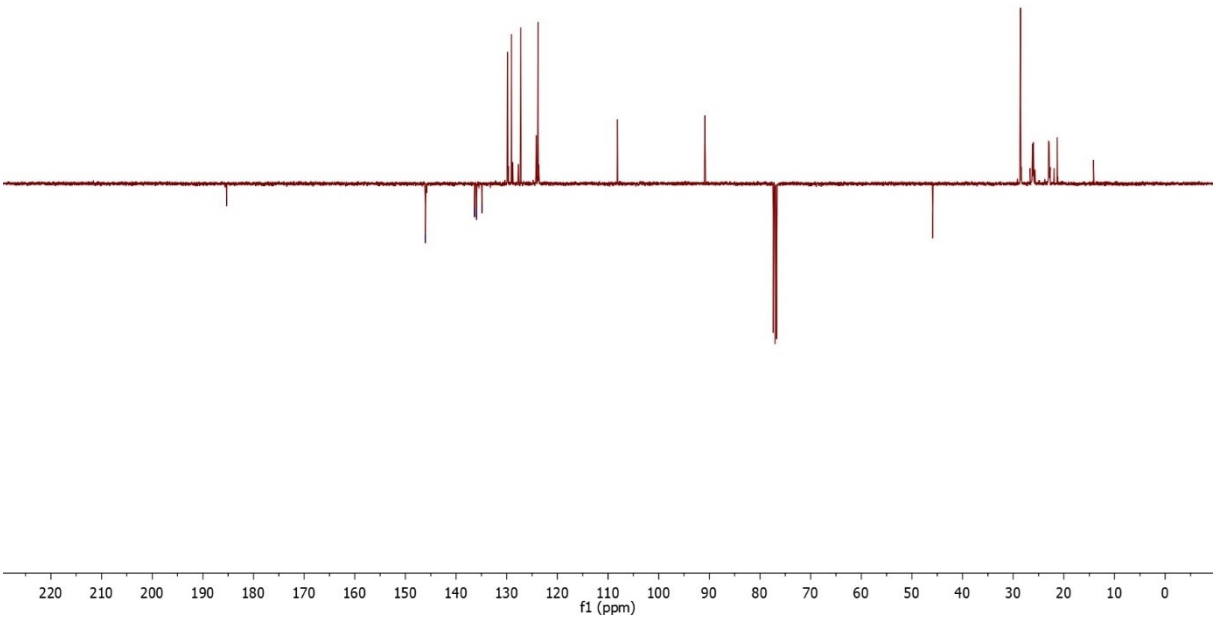
^{13}C NMR (400 MHz, $CDCl_3$) of **IPr-2**



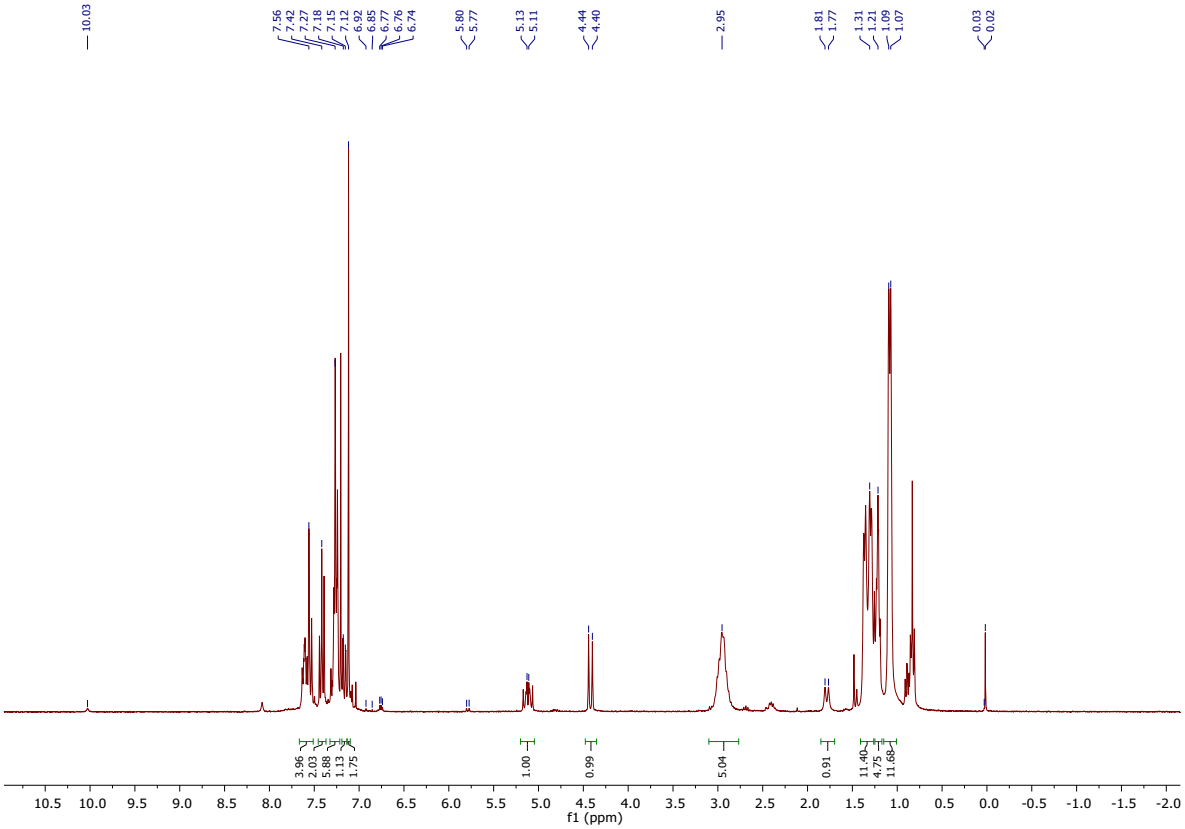
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-3**



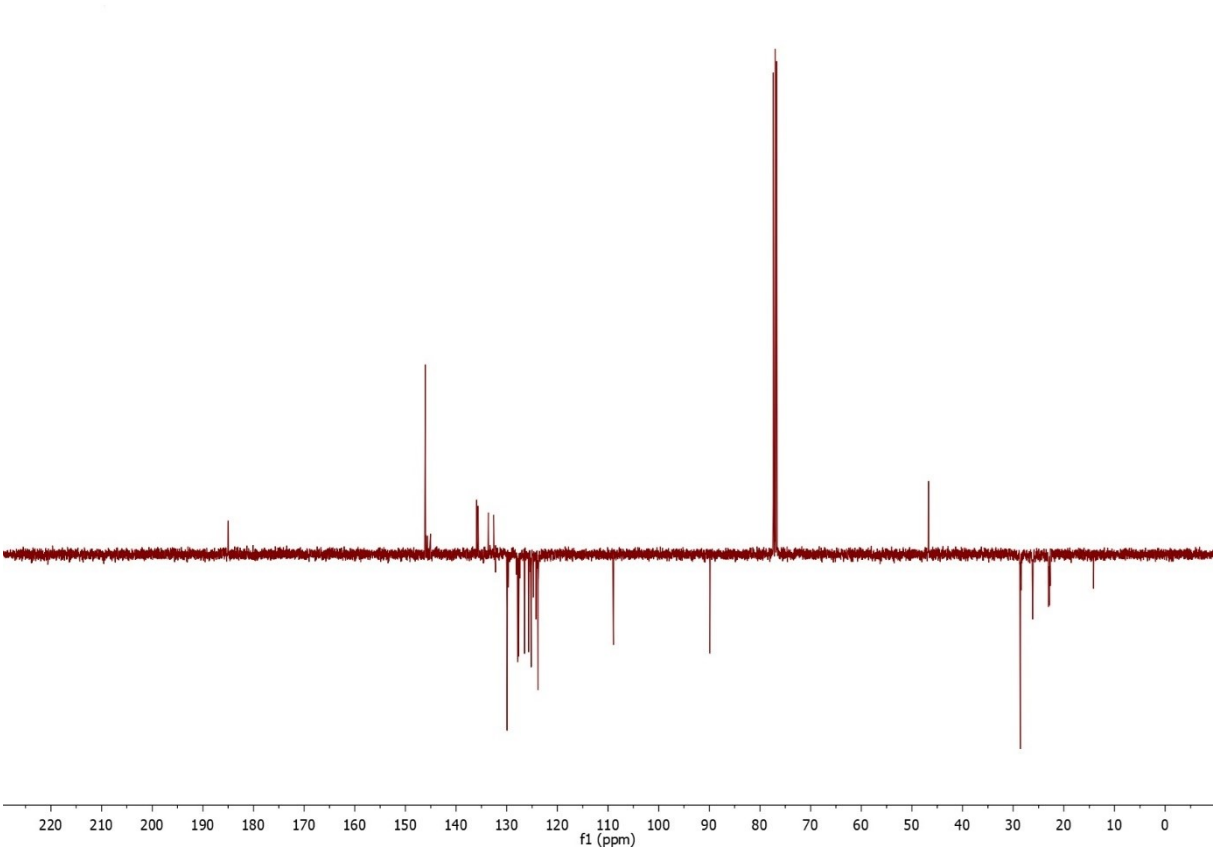
^{13}C NMR (300 MHz, $CDCl_3$) of **IPr-3**



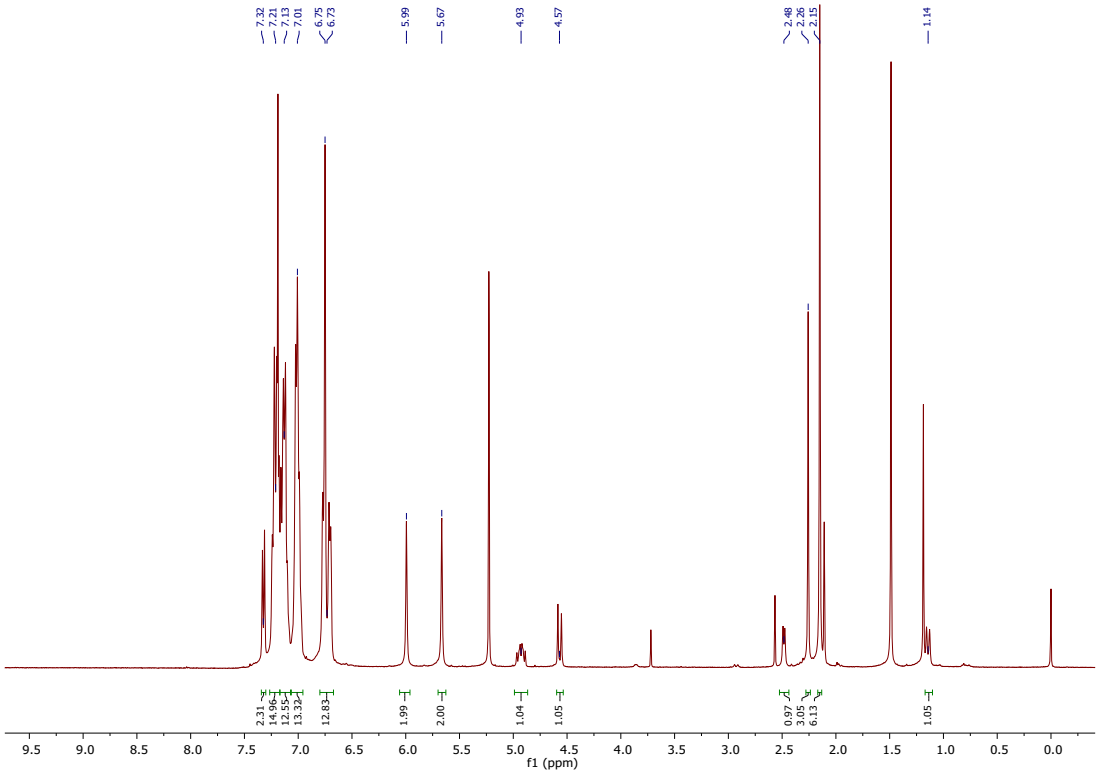
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-4**



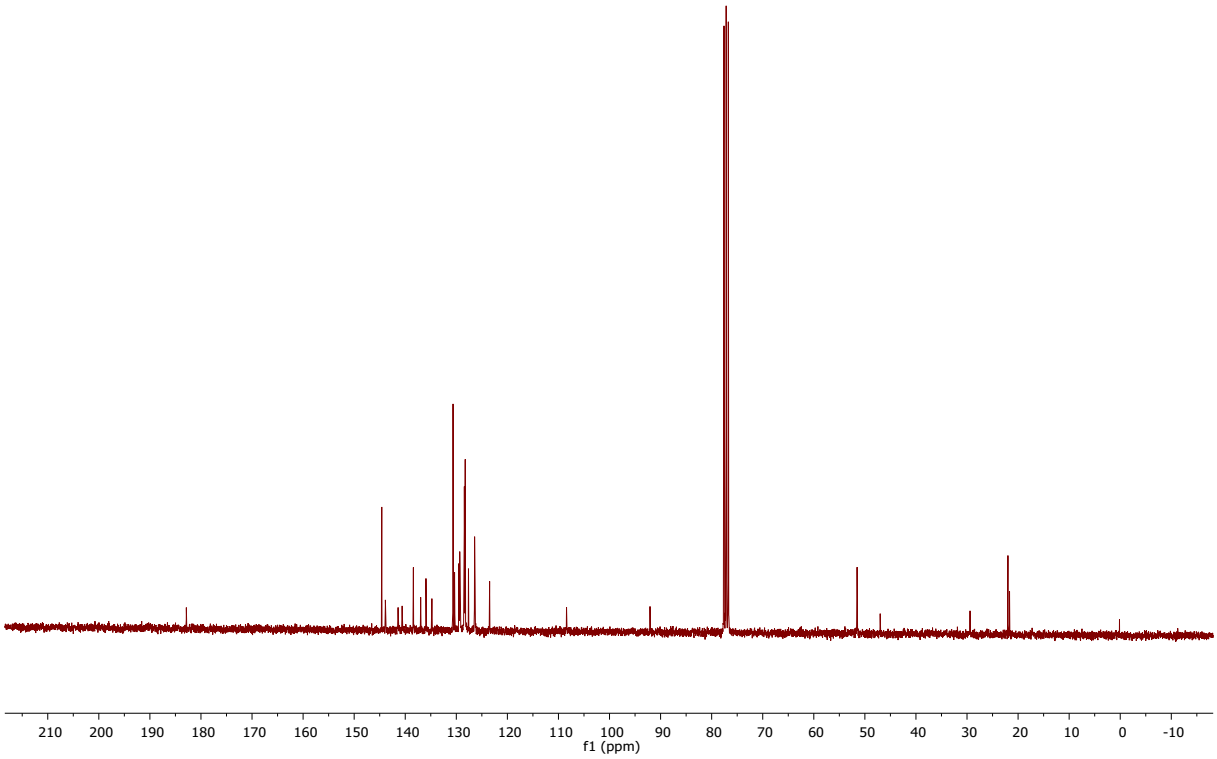
^{13}C NMR 4300 MHz, $CDCl_3$) of **IPr-4**



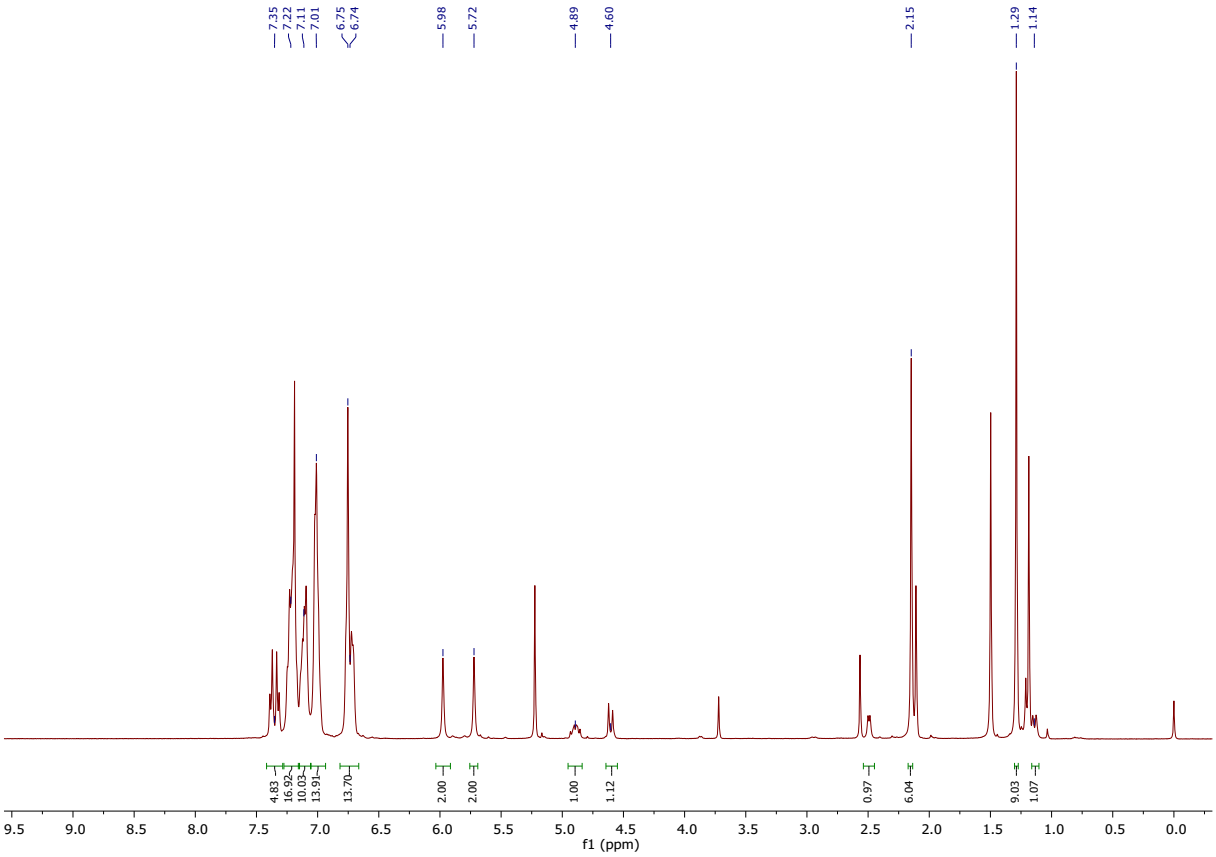
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr*-1**



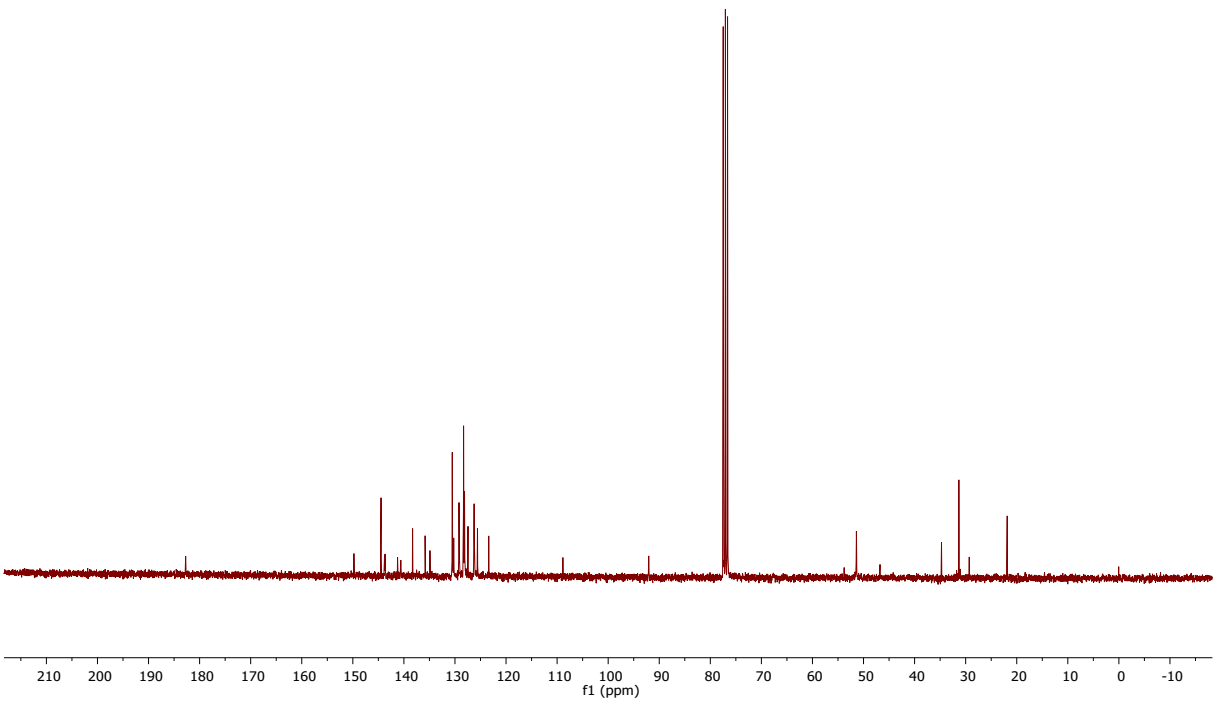
^{13}C NMR (300 MHz, $CDCl_3$) of **IPr*-1**



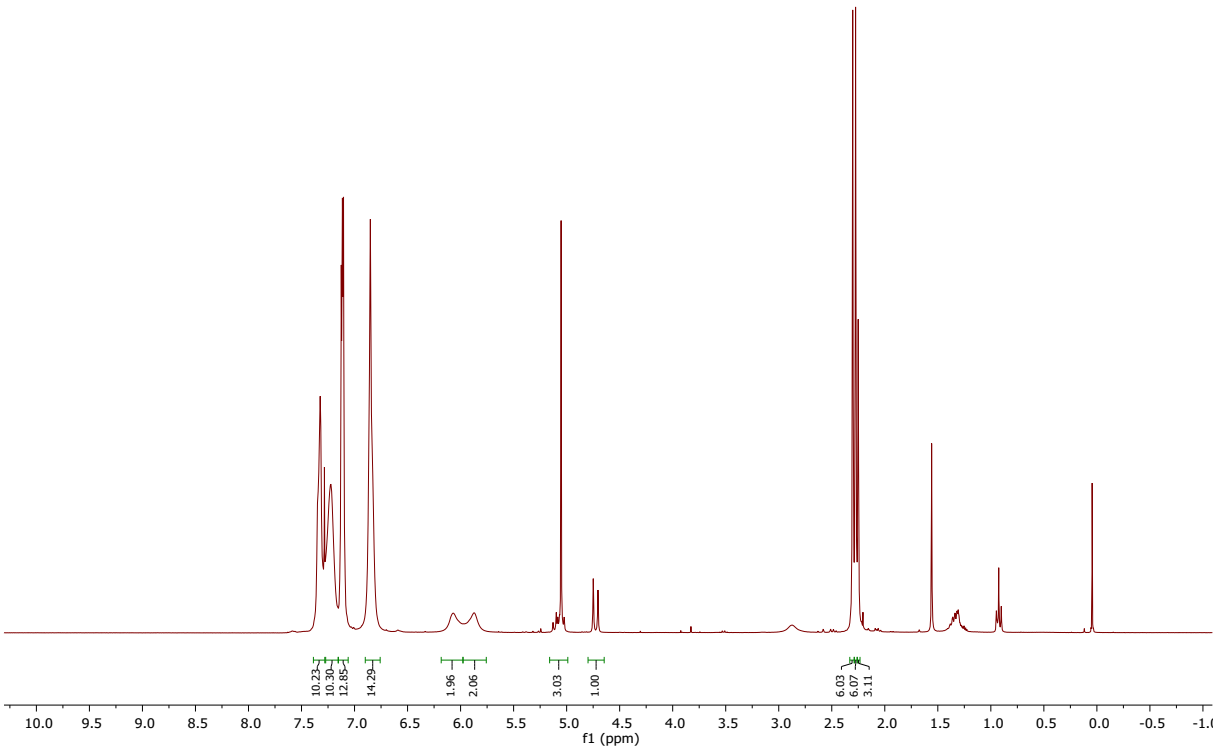
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr*-2**



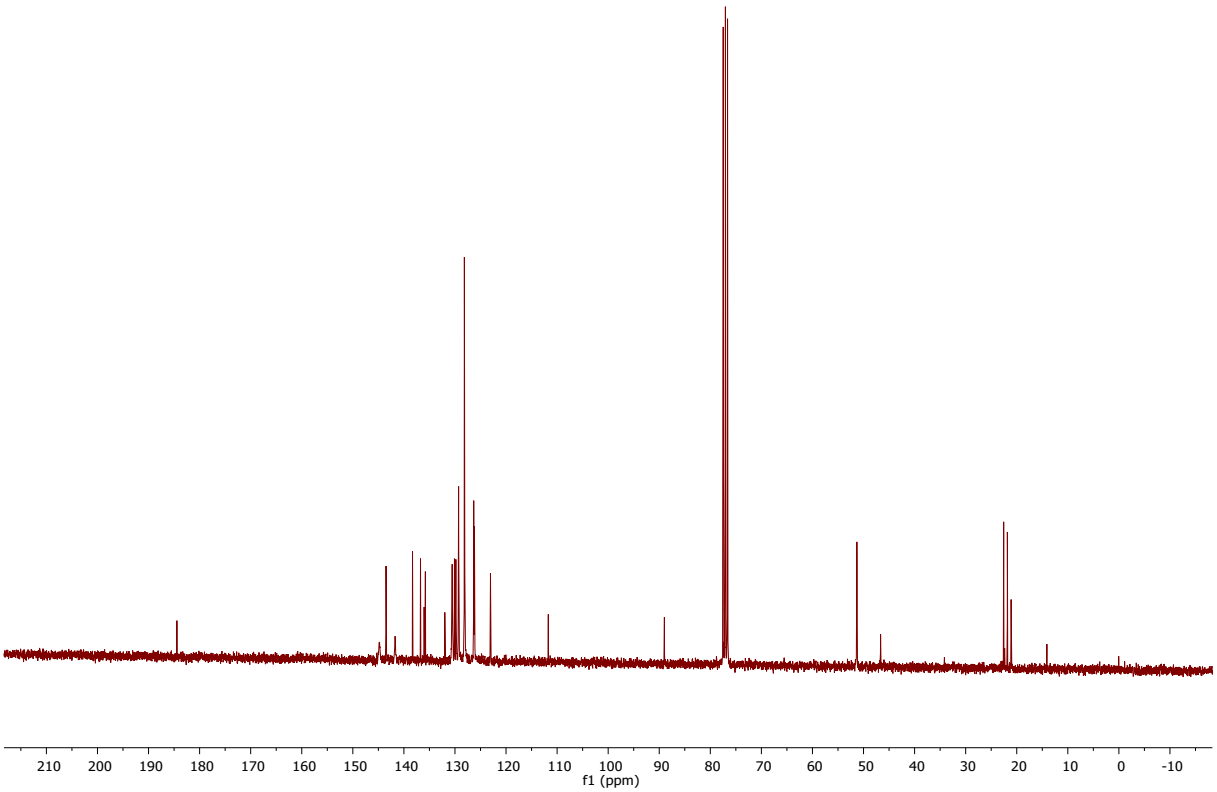
^{13}C NMR (300 MHz, $CDCl_3$) of **IPr*-2**



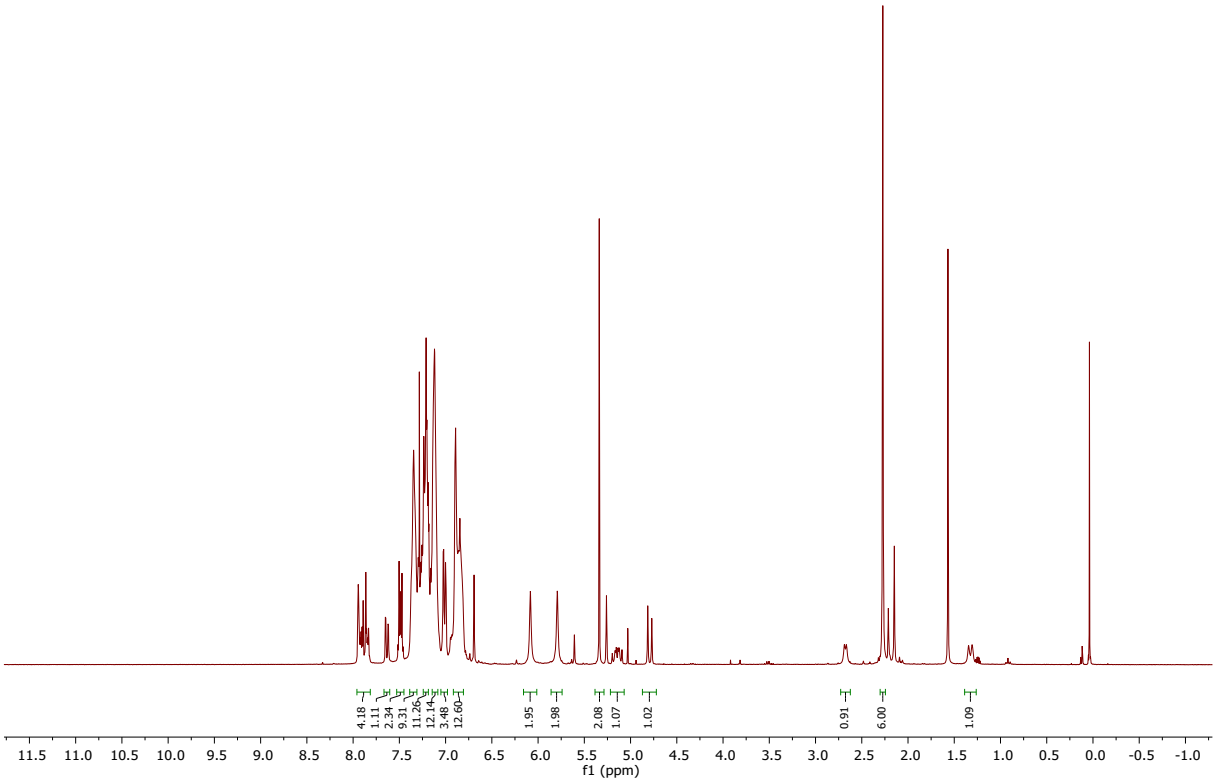
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr*-3**



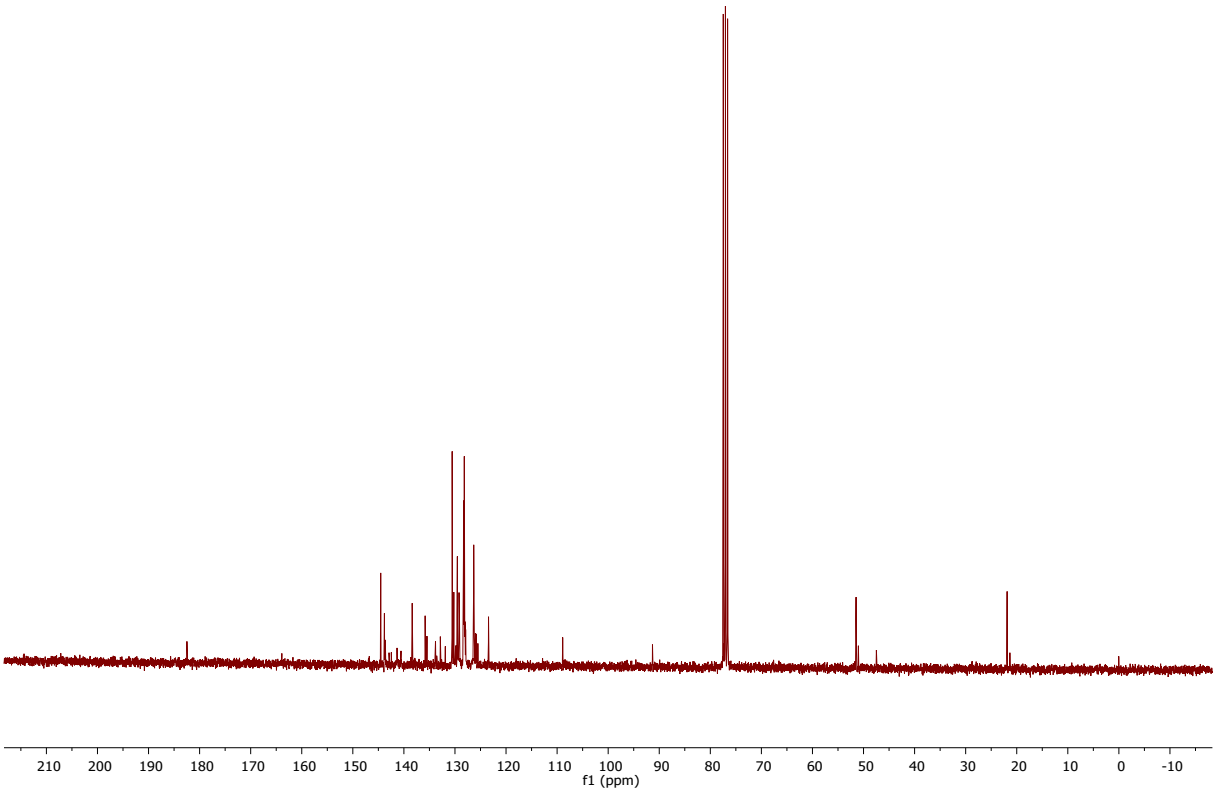
^{13}C NMR (300 MHz, $CDCl_3$) of **IPr*-3**



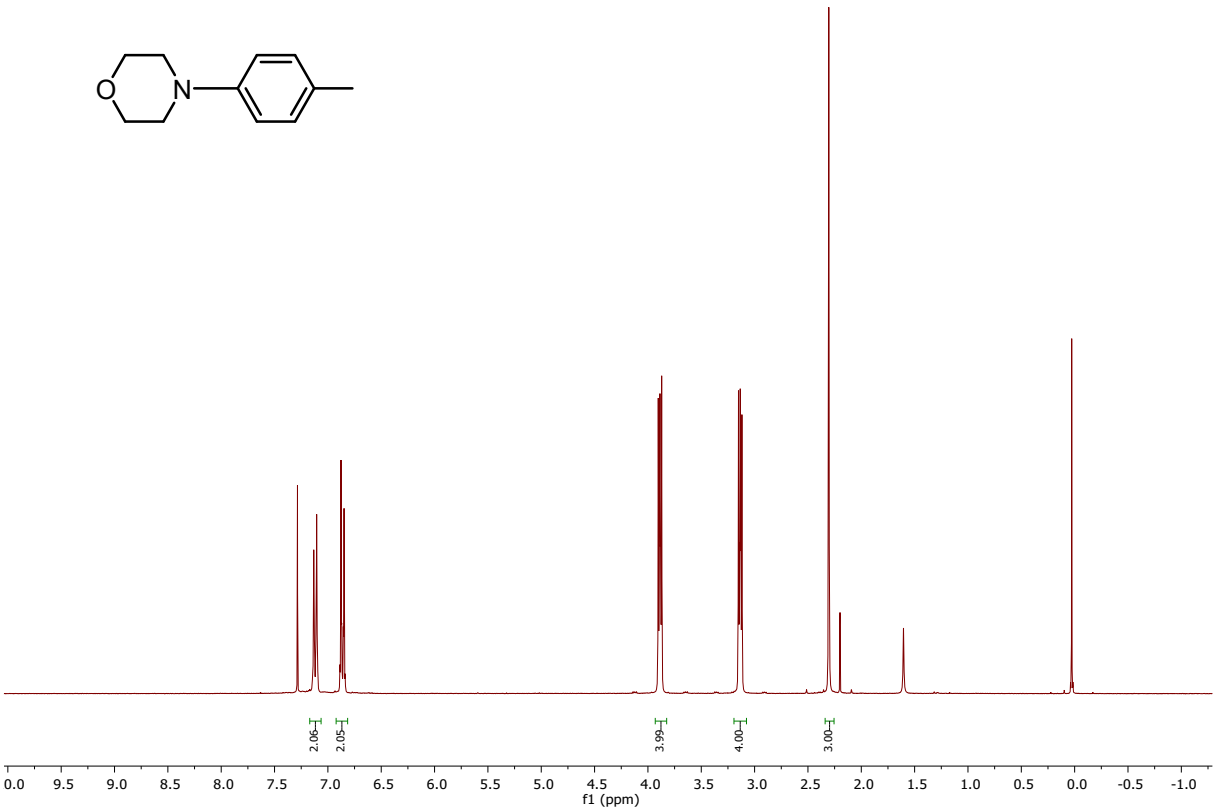
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr*-4**



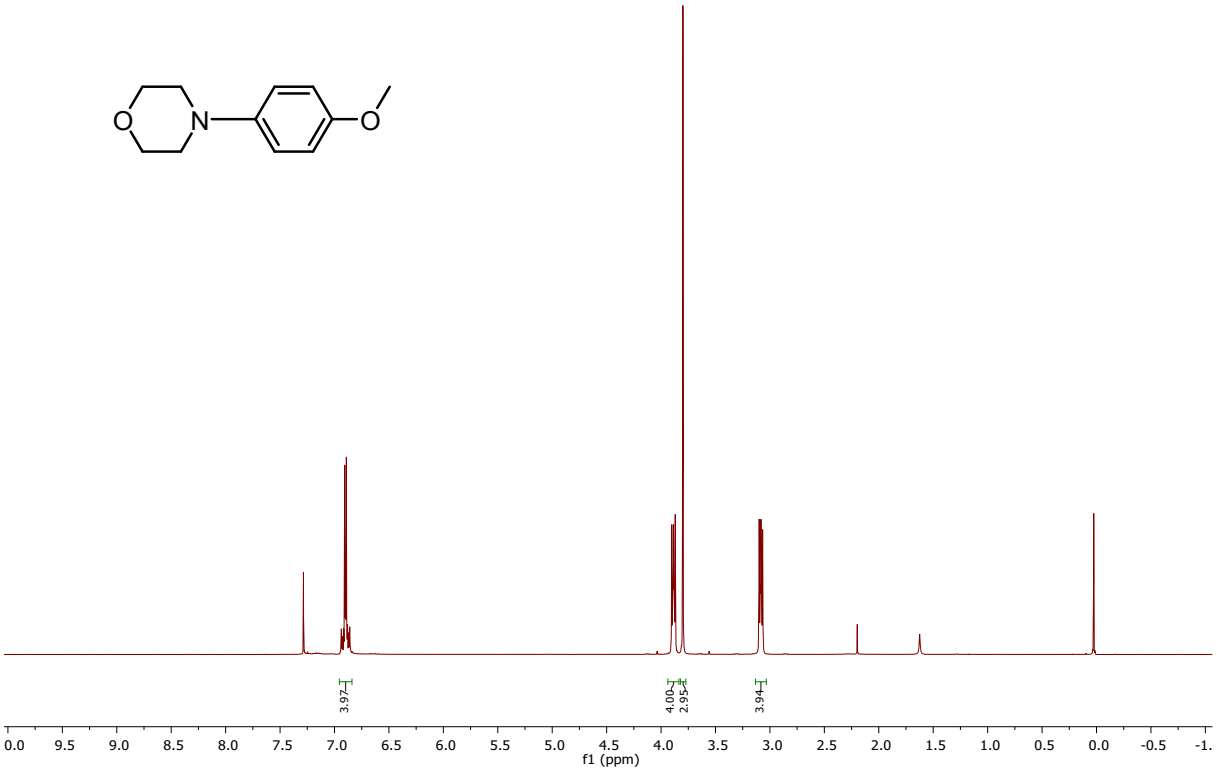
^{13}C NMR (300 MHz, $CDCl_3$) of **IPr*-4**



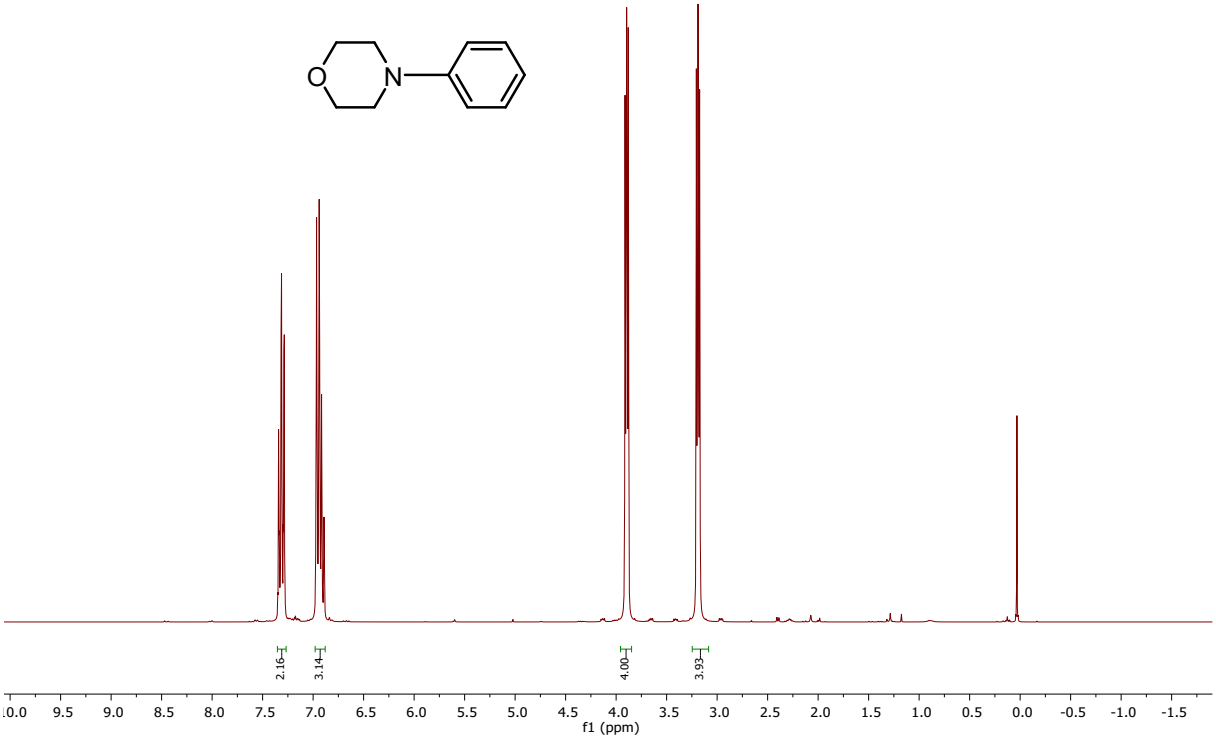
^{1}H NMR (300 MHz, $CDCl_3$) of **1a**



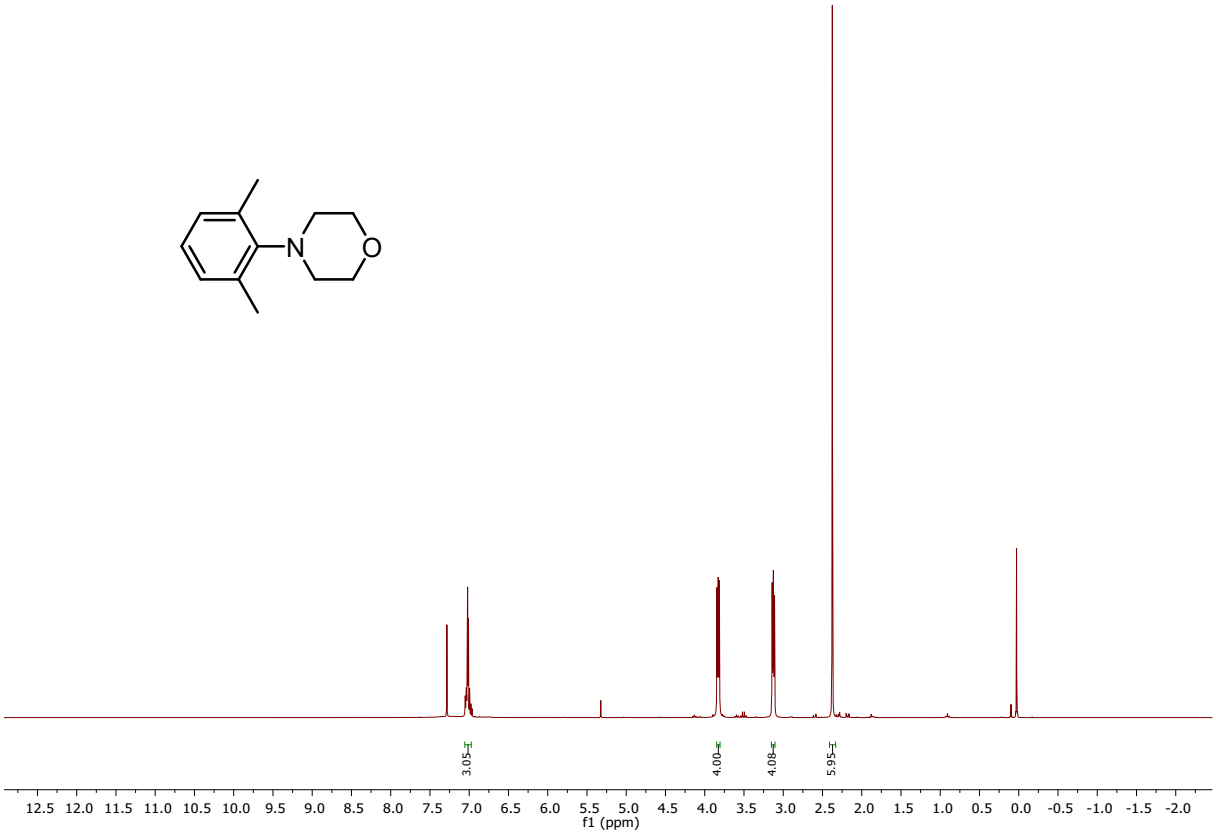
^{1}H NMR (300 MHz, $CDCl_3$) of **1b**



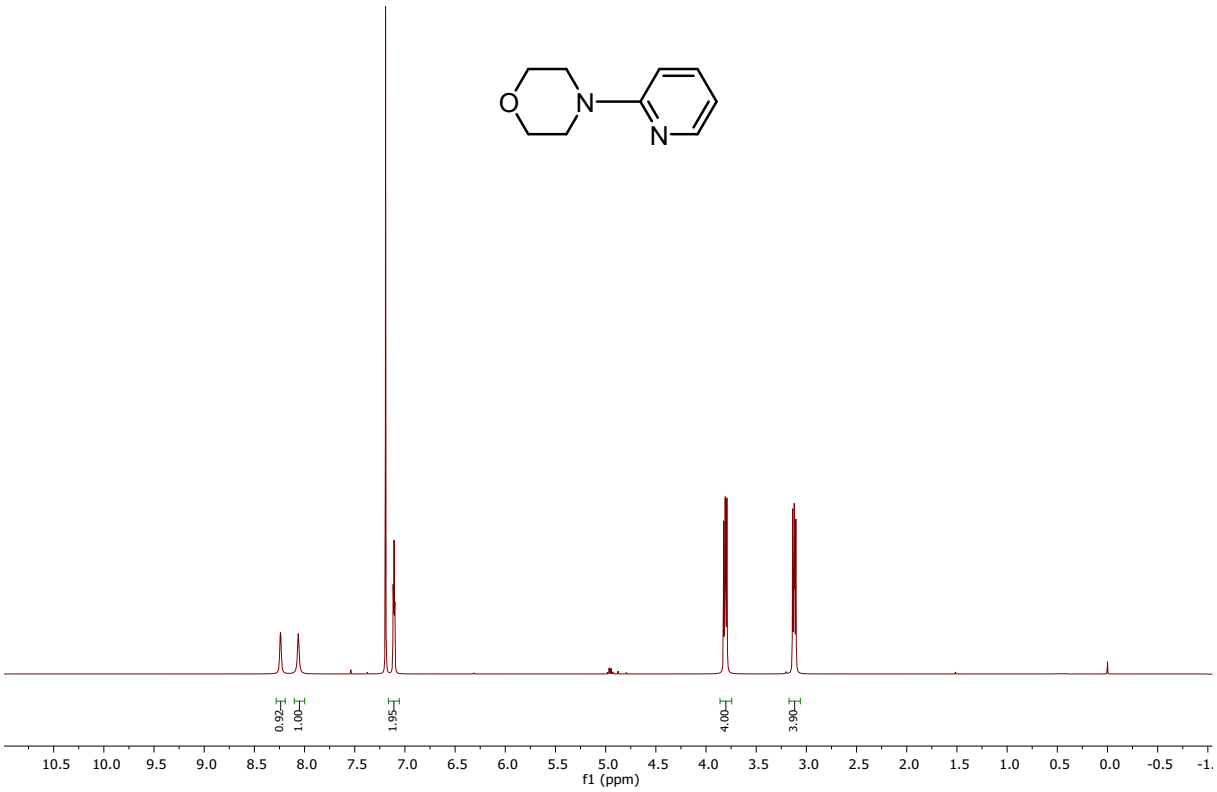
^{1}H NMR (300 MHz, $CDCl_3$) of **1c**



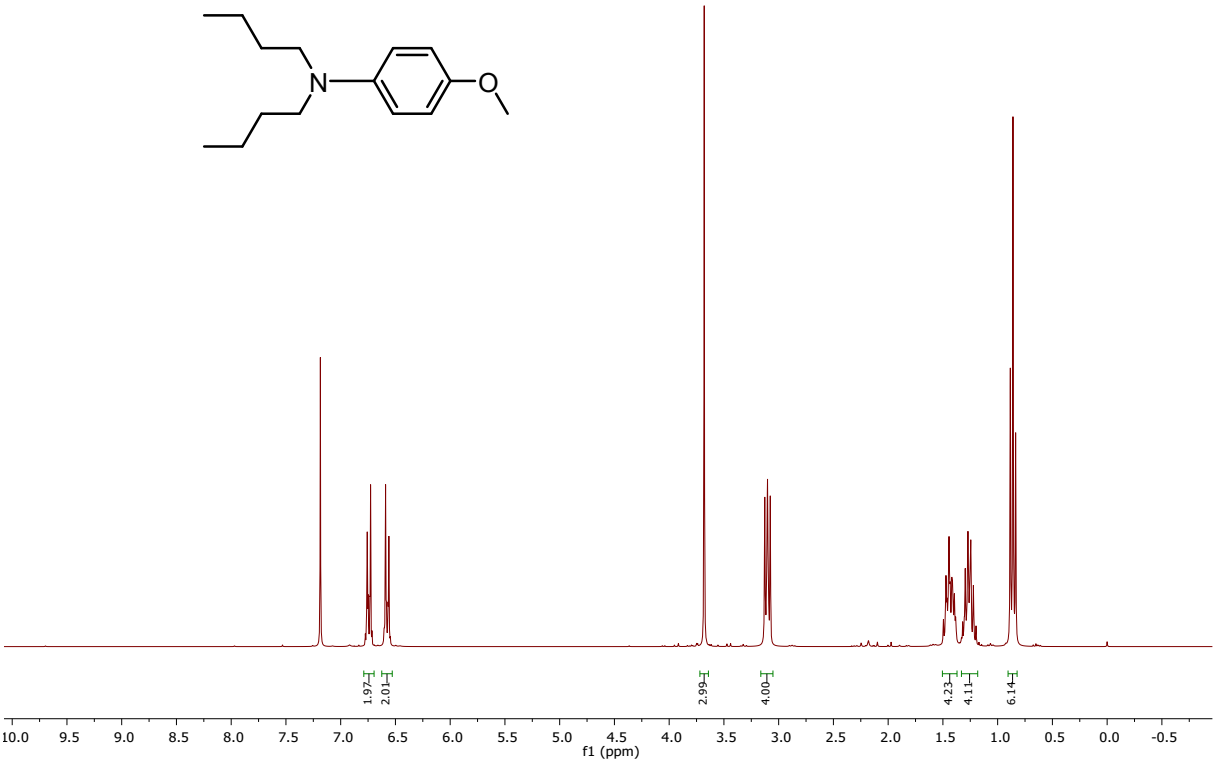
^{1}H NMR (300 MHz, $CDCl_3$) of **1d**



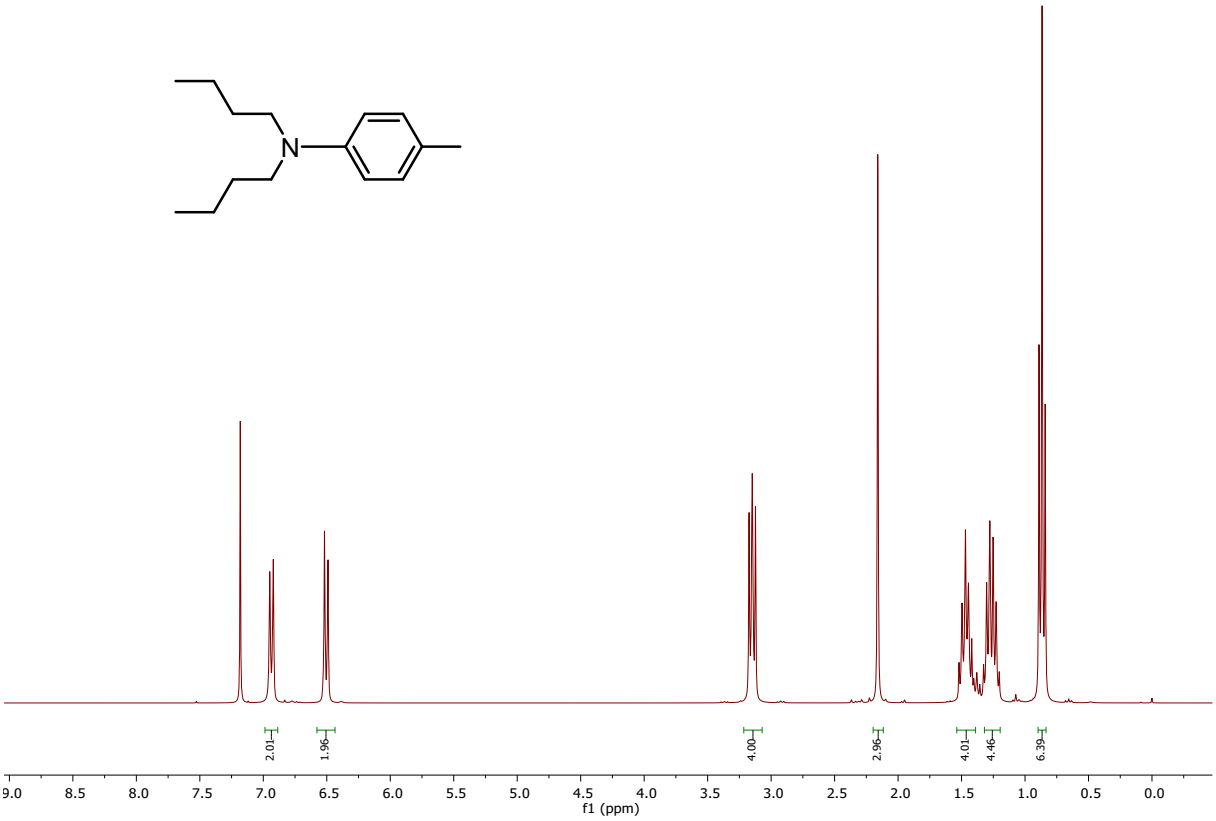
^{1}H NMR (300 MHz, $CDCl_3$) of **1e**



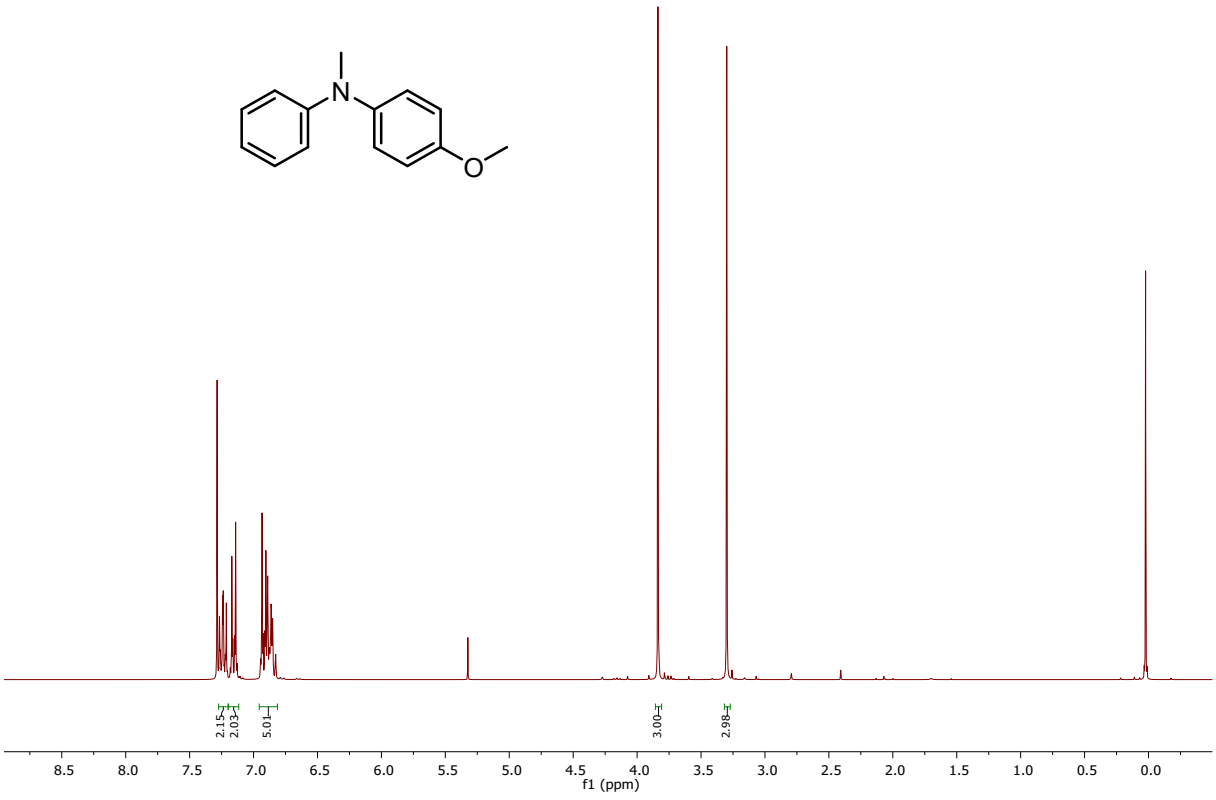
^{1}H NMR (300 MHz, $CDCl_3$) of **1f**



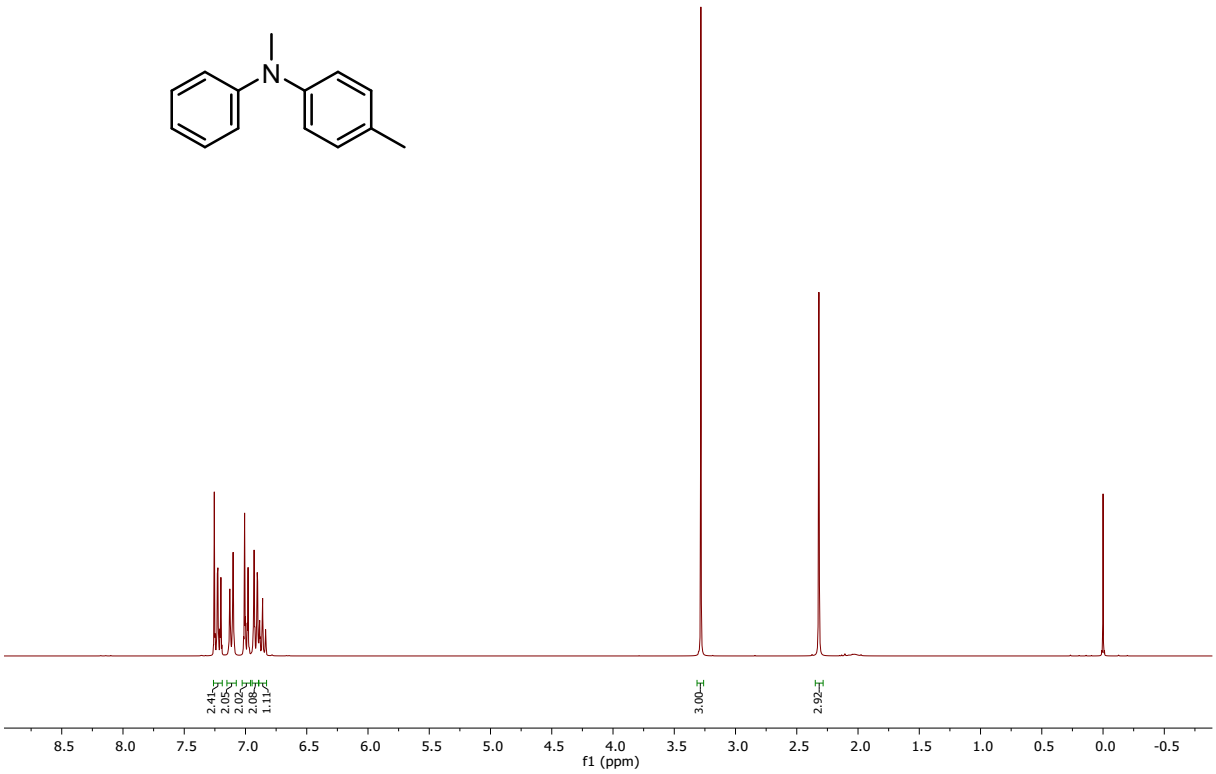
^{1}H NMR (300 MHz, $CDCl_3$) of **1g**



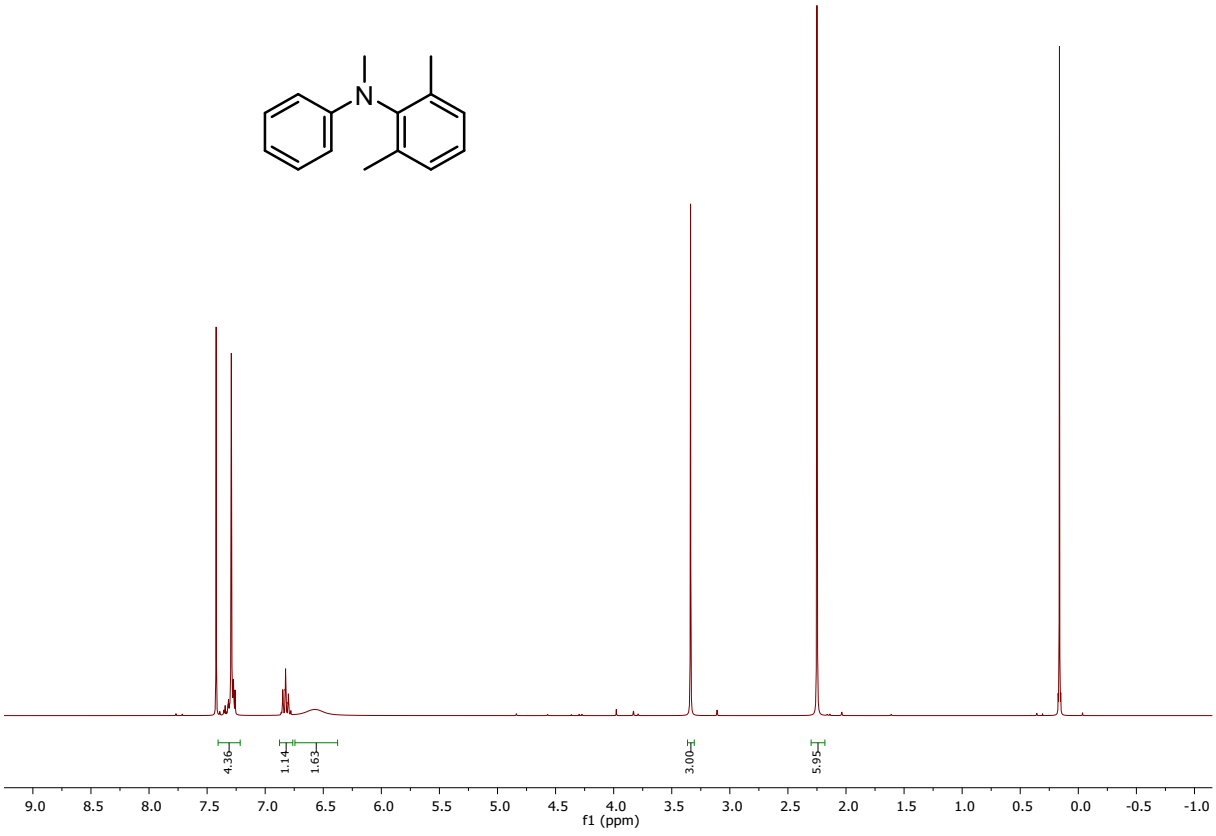
^{1}H NMR (300 MHz, $CDCl_3$) of **1h**



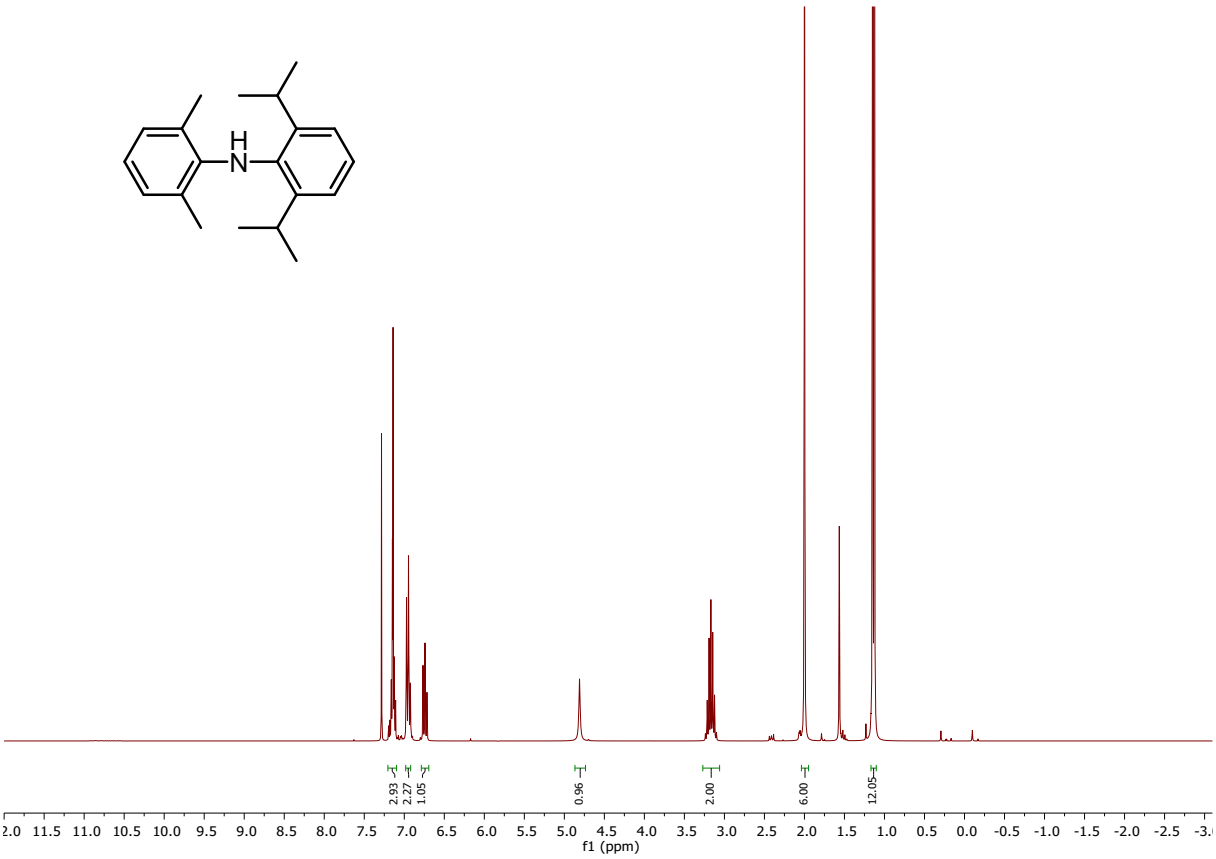
^{1}H NMR (300 MHz, $CDCl_3$) of **1i**



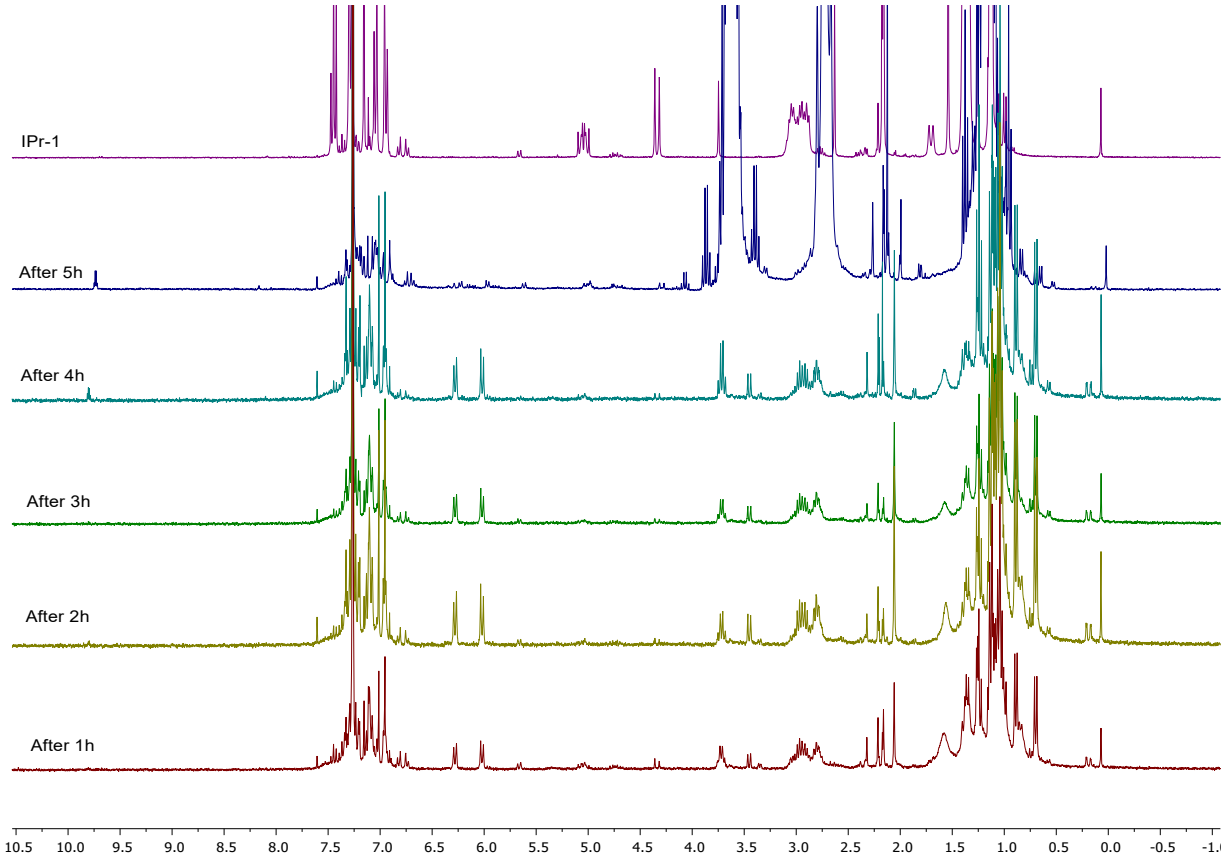
^{1}H NMR (300 MHz, $CDCl_3$) of **1j**



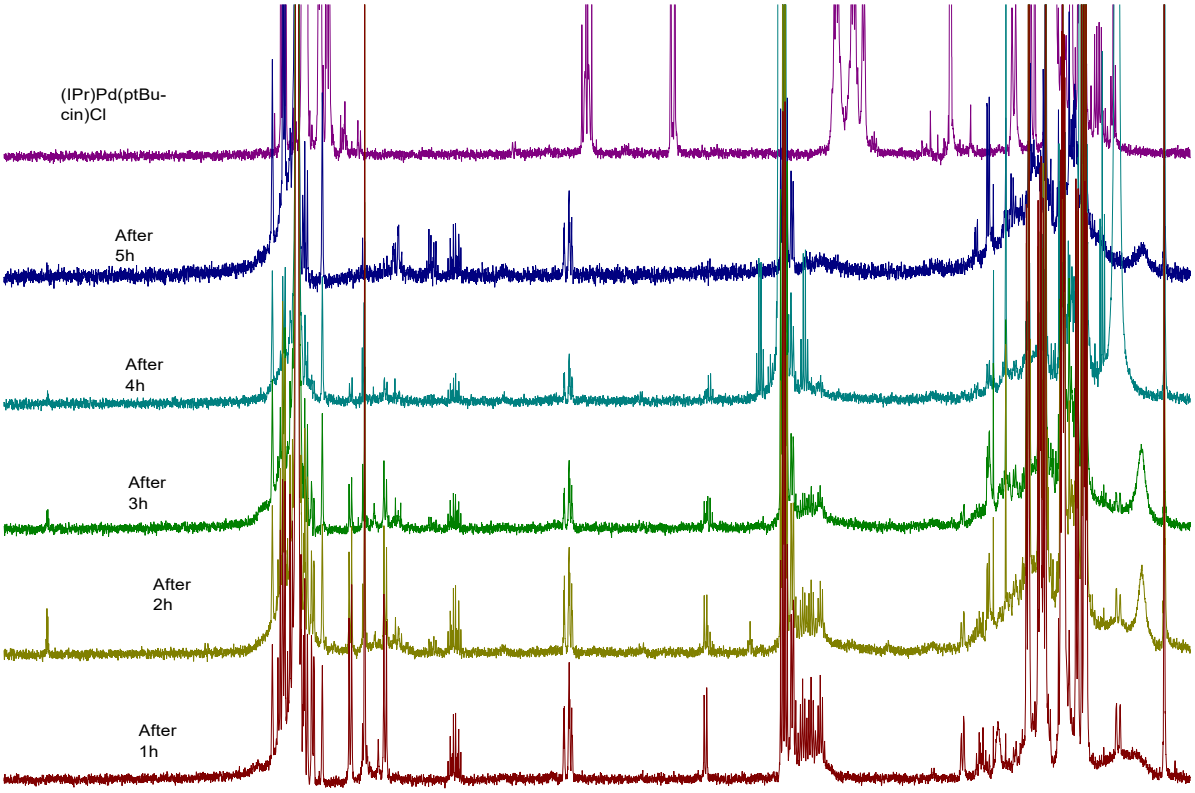
^{1}H NMR (300 MHz, $CDCl_3$) of **1k**



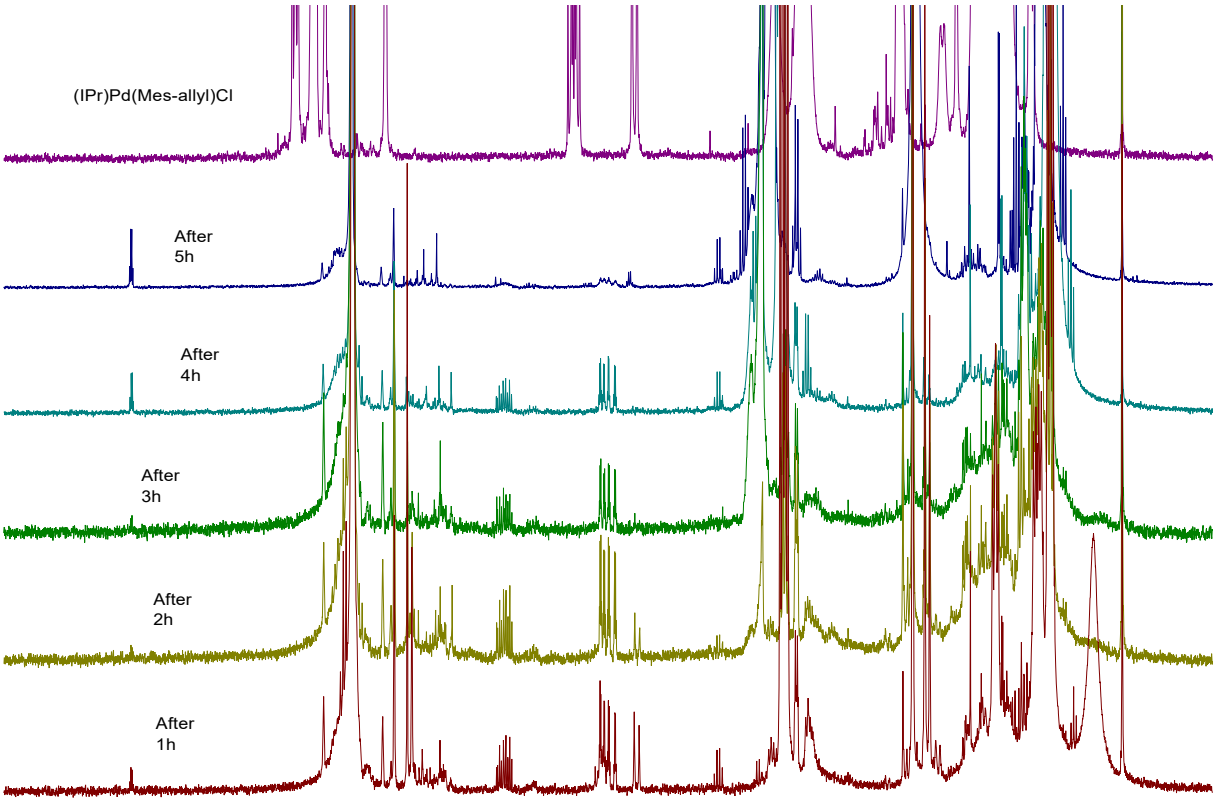
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-1** Pd(I) dimer formation



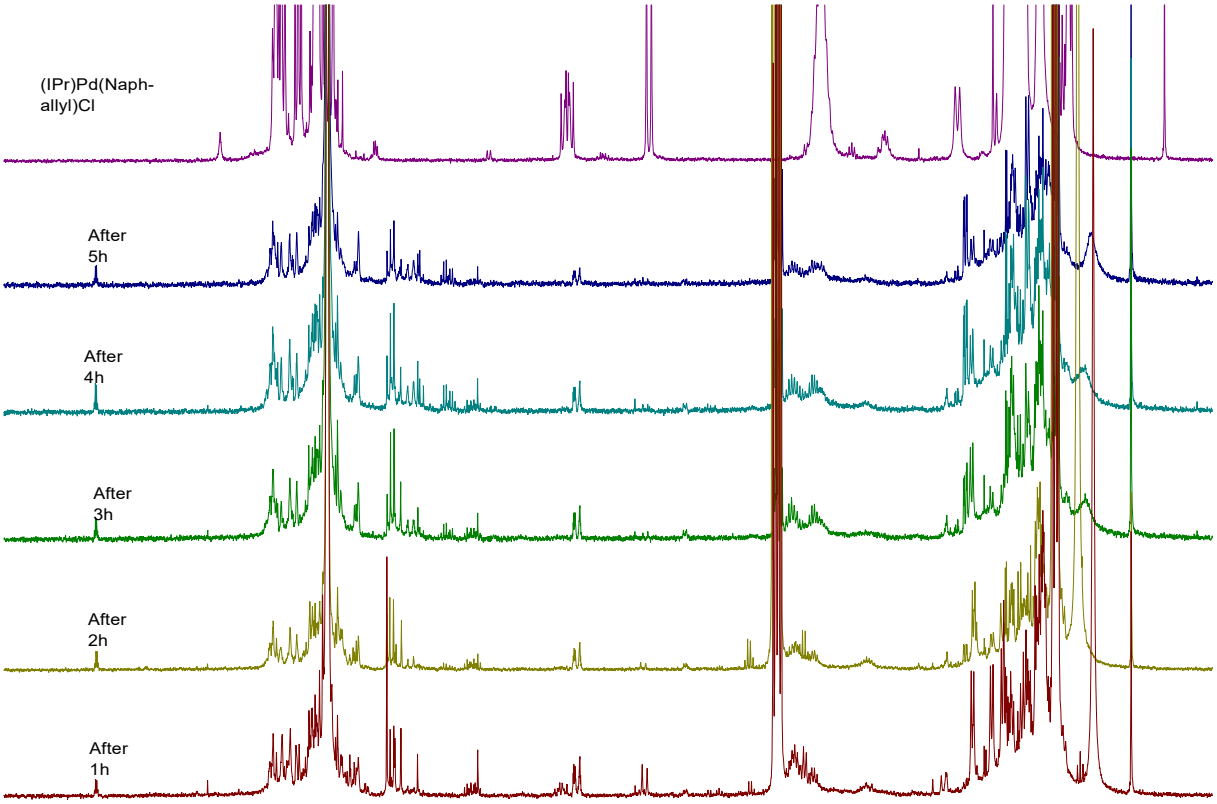
^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-2** Pd(I) dimer formation



^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-3** Pd(I) dimer formation



^{1}H NMR (300 MHz, $CDCl_3$) of **IPr-4** Pd(I) dimer formation



References

1 W. Lölsberg, S. Ye and H.-G. Schmalz, *Advanced Synthesis & Catalysis*, 2010, **352**, 2023–2031.
2 N. W. J. Ang, J. C. A. Oliveira and L. Ackermann, *Angewandte Chemie International Edition*, 2020, **59**, 12842–12847.
3 W.-F. Wang, J.-B. Peng, X. Qi, J. Ying and X.-F. Wu, *Chemistry – A European Journal*, 2019, **25**, 3521–3524.
4 C. I. Jette, Z. J. Tong, R. G. Hadt and B. M. Stoltz, *Angewandte Chemie International Edition*, 2020, **59**, 2033–2038.
5 M. Kim, T. Shin, A. Lee and H. Kim, *Organometallics*, 2018, **37**, 3253–3258.
6 N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott and S. P. Nolan, *J. Am. Chem. Soc.*, 2006, **128**, 4101–4111.
7 W.-J. Xiong, L. Li, J.-T. Li, S.-Q. Zhang, J.-L. Tang and T. Zhou, *Tetrahedron Letters*, 2023, **127**, 154684.
8 S. Meiries, A. Chartoire, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2012, **31**, 3402–3409.
9 S. Meiries, K. Speck, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2013, **32**, 330–339.
10 Y. Liu, V. A. Voloshkin, T. Scattolin, L. Cavallo, B. Dereli, C. S. J. Cazin and S. P. Nolan, *Dalton Trans.*, 2021, **50**, 5420–5427.