Sterically Hindered Mono(phosphines) as Supporting Ligands for the Platinum-Catalyzed Hydroamination of Amino alkenes

Christopher F. Bender, William B. Hudson, and Ross A. Widenhoefer*

Duke University

Department of Chemistry

French Family Science Center

Durham, North Carolina, 27708

Supporting Information

Experimental procedures, spectroscopic data, and scans of NMR spectra (14 pages).

General Methods

Reactions were performed under a nitrogen atmosphere utilizing standard Schlenk and drybox techniques unless specified otherwise. NMR spectra were obtained on Varian spectrometers operating at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR in $CDCl_3$ at 25 °C unless noted otherwise. IR spectra were obtained on a Nicolet Avatar 360-FT IR spectrometer. Gas chromatography was performed on a HP 5890 gas chromatograph equipped with a 15 m or 25 m polydimethylsiloxane capillary column and FID detector. Column chromatography was performed employing 230-400 mesh silica gel (Sorbent Technologies or Silicycle) or 150 mesh activated aluminum oxide, neutral, Brockmann I (Aldrich). Elemental analyses were performed by Complete Analysis Laboratories (Parsippany, NJ). Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} (EMD Chemicals Inc.). All compounds were isolated as colorless oils unless noted otherwise. Room temperature is 22-24 °C.

Tetrahydrofuran (THF) and diethyl ether were distilled from Na^0/benzoquinone, dichloromethane and $CDCl_3$ were distilled from CaH_2 under N_2. All other solvents and reagents were purchased from major chemical suppliers and were used as received. 2-(dicyclohexylphosphino)-2'-isopropylbiphenyl (**5b**)[1] was prepared by a previously described method. All remaining ligands, platinum salts, and reagents were purchased from major suppliers and used as received.

Alkenyl Alkylamines

1-Allylcyclohexylmethylbenzylamine (**1**), benzyl[1-(3-butenyl)cyclohexylmethyl]amine (**8**), benzyl(2,2-diphenyl-4-pentenyl)amine (Table 2, entry 6), benzyl[1-(2-methylallyl)-

cyclohexylmethyl]amine (Table 2, entry 9) were synthesized according to published procedures.[2] (1-Allylcyclohexylmethyl)(4-methoxybenzyl)amine (Table 2, entry 2), (1-allylcyclohexylmethyl)(4-bromobenzyl)amine (Table 2, entry 3), (1-allylcyclohexylmethyl)(4-nitrobenzyl)amine (Table 2, entry 4), (1-allylcyclohexylmethyl)naphthalen-2-ylmethylamine (Table 2, entry 5), (2,2-diphenyl-4-pentenyl)-furan-2-ylmethylamine (Table 2, entry 7), (2,2-diphenyl-4-pentenyl)-thiophen-2-ylmethylamine (Table 2, entry 8), benzyl-4-pentenylamine (Table 2, entry 11), and benzyl-5-hexenylamine (Table 2, entry 12) were synthesized employing a procedure similar to that used to synthesize **1**.

(1-Allylcyclohexylmethyl)(4-methoxybenzyl)amine (Table 2, entry 2). 42%. TLC (EtOAc–hexanes = 1:4): R_f = 0.35. ^{1}H NMR: δ 7.24 (d, *J* = 8.4 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 5.78 (tdd, *J* = 7.5, 9.7, 17.1 Hz, 1 H), 4.98-5.04 (m, 2 H), 3.80 (s, 3 H), 3.70 (s, 2 H), 2.40 (s, 2 H), 2.11 (d, *J* = 7.3 Hz, 2 H), 1.27-1.46 (m, 10 H), 1.07 (br s, 1 H). ^{13}C{^{1}H} NMR: δ 158.6, 135.5, 133.4, 129.2, 116.7, 113.7, 55.9, 55.3, 54.3, 40.8, 36.7, 34.1, 26.5, 21.7. IR (neat, cm^{-1}): 2922, 2851, 1511, 1454, 1244, 1038. Anal. calcd (found) for $C_{18}H_{27}NO$: H, 9.95 (9.87); C, 79.07 (78.75); N, 5.12 (5.00).

(1-Allylcyclohexylmethyl)(4-bromobenzyl)amine (Table 2, entry 3). 58%. TLC (EtOAc-hexanes = 1:6): R_f = 0.39. ^{1}H NMR: δ 7.41-7.45 (m, 2 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 5.77 (tdd, *J* = 7.3, 10.4, 16.6 Hz, 1 H), 4.99-5.03 (m, 2 H), 3.72 (s, 2 H), 2.38 (s, 2 H), 2.11 (d, *J* = 7.5 Hz, 2 H), 1.31-1.42 (m, 11 H). ^{13}C{^{1}H} NMR: δ 140.2, 135.3, 131.3, 129.7, 120.5, 116.7, 55.9, 54.1, 40.7, 36.7, 34.0, 26.5, 21.6. IR (neat, cm-1): 2923, 2852, 1452, 1009, 912, 797. Anal. calcd (found) for $C_{17}H_{24}BrN$: H, 7.51 (7.52); C, 63.35 (63.63); N, 4.35 (4.70).

1-Allylcyclohexylmethyl(4-nitrobenzyl)amine (Table 2, entry 4). Pale yellow oil, 59%. TLC (EtOAc–hexanes = 1:4): R_f = 0.33. ^{1}H NMR: δ 8.17 (d, *J* = 8.5 Hz, 2 H), 7.51 (d, *J*

= 8.5 Hz, 2 H), 5.77 (tdd, *J* = 7.5, 10.1, 17.4 Hz, 1 H), 4.99-5.05 (m, 2 H), 3.87 (s, 2 H), 2.39 (s, 2 H), 2.12 (d, *J* = 7.3 Hz, 2 H), 1.31-1.45 (m, 11 H). $^{13}C\{^{1}H\}$ NMR: δ 149.1, 146.9, 135.2, 128.5, 123.5, 116.8, 56.0, 53.9, 40.7, 36.7, 34.0, 26.4, 21.6. IR (neat, cm^{-1}): 2923, 2852, 1518, 1453, 1343, 1108. Anal. calcd (found) for $C_{17}H_{24}N_2O_2$: H, 8.39 (8.41); C, 70.80 (70.98); N, 9.71 (9.86).

(1-Allylcyclohexylmethyl)naphthalen-2-ylmethylamine (Table 2, entry 5). 76%. TLC (EtOAc–hexanes = 1:6): R_f = 0.35. ^{1}H NMR: δ 7.80-7.84 (m, 3 H), 7.76 (s, 1H), 7.43-7.50 (m, 3 H), 5.80 (tdd, *J* = 7.3, 10.1, 17.1 Hz, 1 H), 4.99-5.07 (m, 2 H), 3.95 (s, 2 H), 2.46 (s, 2 H), 2.15 (d, *J* = 7.3 Hz, 2 H), 1.34-1.47 (m, 11 H). $^{13}C\{^{1}H\}$ NMR: δ 138.7, 135.4, 133.5, 132.7, 127.9, 127.7, 127.7, 126.6, 126.3, 125.9, 125.4, 116.7, 56.0, 54.9, 40.7, 36.7, 34.1, 26.5, 21.7. IR (neat, cm^{-1}): 3056, 2922, 2851, 1451, 815, 744. Anal. calcd (found) for $C_{21}H_{27}N$: H, 9.27 (9.31); C, 85.95 (85.67); N, 4.77 (4.99).

(2,2-Diphenyl-4-pentenyl)-furan-2-ylmethylamine (Table 2, entry 7).[3] White solid, 84%. TLC (EtOAc–hexanes = 1:6): R_f = 0.49. ^{1}H NMR: δ 7.14-7.31 (m, 11 H), 6.27 (dd, *J* = 1.7, 3.1 Hz, 1 H), 6.01-6.08 (m, 1 H), 5.33 (tdd, *J* = 7.0, 10.1, 17.3 Hz, 1 H), 4.89-4.99 (m, 2 H), 3.68 (s, 2 H), 3.20 (s, 2 H), 3.00 (d, *J* = 7.2 Hz, 2 H), 0.84 (br s, 1 H). $^{13}C\{^{1}H\}$ NMR: δ 154.4, 146.8, 141.6, 134.9, 128.2, 128.1, 126.1, 117.8, 110.1, 106.8, 55.1, 50.1, 46.7, 41.7. IR (neat, cm^{-1}): 2850, 1440, 1102, 918, 787, 699. HRMS calcd (found) for $C_{22}H_{23}NO^{+}$ (M^{+}): 317.1780 (317.1780).

(2,2-Diphenyl-4-pentenyl)-thiophen-2-ylmethylamine (Table 2, entry 8).[3] White solid, 83%. (EtOAc–hexanes = 1:6): R_f = 0.50. ^{1}H NMR: δ 7.17-7.30 (m, 11 H), 6.92 (dd, *J* = 3.4, 5.1 Hz, 1 H), 6.82-6.83 (m, 1 H), 5.37 (tdd, *J* = 7.2, 10.1, 17.1 Hz, 1 H), 4.91-5.04 (m, 2 H), 3.91 (s, 2 H), 3.27 (s, 2 H), 3.05 (d, *J* = 7.2 Hz, 2 H), 0.90 (br s, 1 H). $^{13}C\{^{1}H\}$ NMR: δ 146.9,

145.1, 135.0, 128.2, 128.1, 126.6, 126.1, 124.5, 124.3, 117.9, 55.3, 50.2, 49.0, 41.7. IR (neat, cm^{-1}): 3338, 2827, 1440, 1096, 920, 697. HRMS calcd (found) for $C_{22}H_{23}NS^+$ (M^+): 333.1551 (333.1553).

Benzyl-4-pentenylamine (Table 2, entry 11).[4] 62%. ^1H NMR: δ 7.23-7.33 (m, 5 H), 5.82 (tdd, *J* = 6.7, 10.3, 16.9 Hz, 1 H), 4.93-5.04 (m, 2 H), 3.80 (s, 2 H), 2.65 (t, *J* = 7.2 Hz, 2 H), 2.08-2.13 (m, 2 H), 1.53-1.66 (m, 3 H). $^{13}C\{^1H\}$ NMR: δ 140.5, 138.6, 128.5, 128.3, 127.1, 114.8, 54.1, 49.0, 31.7, 29.3.

Benzyl 5-hexenylamine (Table 2, entry 12).[4] 62%. TLC (MeOH–CH_2Cl_2 = 1:19): R_f = 0.29. ^1H NMR: δ 7.23-7.33 (m, 5 H), 5.82 (tdd, *J* = 6.7, 10.3, 17.1 Hz, 1 H), 4.94-5.04 (m, 2 H), 3.80 (s, 2 H), 2.63 (t, *J* = 7.2 Hz, 2 H), 2.05-2.11 (m, 2 H), 1.40-1.58 (m, 4 H), 1.26 (br s, 1 H). $^{13}C\{^1H\}$ NMR: δ 140.7, 138.9, 128.4, 128.2, 126.9, 114.6, 54.2, 49.4, 33.7, 29.7, 26.7.

Nitrogen heterocycles

2-Benzyl-3-methyl-2-aza-spiro[4.5]decane (2).[2] A suspension of **1** (184 mg, 0.76 mmol), $PtCl_2$ (10.0 mg, 0.038 mmol), and **6c** (12.6 mg, 0.037 mmol) in diglyme (0.75 mL) was stirred at 60 °C for 10 h. The resulting mixture was concentrated and the resulting oily residue was purified by bulb to bulb distillation (90 °C, 75 mtorr) to give **2** (158 mg, 86%) as a colorless oil. TLC (EtOAc–hexanes = 1:6): R_f = 0.45. ^1H NMR: δ 7.21-7.34 (m, 5 H), 4.01 (d, *J* = 13.3 Hz, 1 H), 3.09 (d, *J* = 13.3 Hz, 1 H), 2.77 (d, *J* = 9.2 Hz, 1 H), 2.44-2.52 (m, 1 H), 1.86 (d, *J* = 9.2 Hz, 1 H), 1 H (dd, *J* = 7.0, 12.5 Hz, 1 H), 1.25-1.45 (m, 11 H), 1.14 (d, *J* = 6.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR: δ 140.1, 128.8, 128.2, 126.7, 66.8, 59.1, 58.1, 47.1, 39.4, 38.6, 26.2, 23.8, 23.6, 19.4.

3-Methyl-2-(4-methoxybenzyl)-2-aza-spiro[4.5]decane (Table 2, entry 2), 3-methyl-2-(2-naphthyl)-2-aza-spiro[4.5]decane (Table 2, entry 5), and **9** were synthesized employing a procedure analogous to that used to synthesize **2**. 3-Methyl-2-(4-bromobenzyl)-2-aza-spiro[4.5]decane (Table 2, entry 3), benzyl-4,4-diphenyl-2-methylpyrrolidine (Table 2, entry 6), 1-furan-2-ylmethyl-2-methyl-4,4-diphenylpyrrolidine (Table 2, entry 7),[3] 2-methyl-4,4-diphenyl-1-thiophen-2-ylmethylpyrrolidine (Table 2, entry 8),[3] 2-benzyl-3,3-dimethyl-2-aza-spiro[4.5]decane (Table 2, entry 9),[2] 1-benzyl-2-methylpyrrolidine (Table 2, entry 11),[5] and 1-benzyl-2-methyl-piperidine (Table 2, entry 12)[6] were prepared by a manner analogous to that used to synthesize 3-methyl-2-(4-nitrobenzyl)-2-aza-spiro[4.5]decane (Table 2, entry 4; see below).

2-(4-Methoxybenzyl)-3-methyl-2-aza-spiro[4.5]decane (Table 2, entry 2). TLC (EtOAc–hexanes = 1:1): R_f = 0.39. ^{1}H NMR: δ 7.24 (d, *J* = 8.5 Hz, 2 H), 6.85 (d, *J* = 8.5 Hz, 2 H), 3.95 (d, *J* = 13.0 Hz, 1 H), 3.81 (s, 3 H), 3.05 (d, *J* = 13.0 Hz, 1 H), 2.76 (d, *J* = 9.4 Hz, 1 H), 2.40-2.51 (m, 1 H), 1.87 (d, *J* = 9.4 Hz, 1 H), 1.75 (dd, *J* = 7.0, 12.5 Hz, 1 H), 1.25-1.46 (m, 11 H), 1.14 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 158.5, 132.1, 129.9, 113.6, 66.7, 58.9, 57.3, 55.3, 47.1, 39.4, 39.3, 38.7, 26.2, 23.8, 23.7, 19.4. IR (neat, cm^{-1}): 2922, 2849, 1511, 1244, 1038, 825. Anal. calcd (found) for $C_{18}H_{27}NO^+$ (M^+): H, 9.95 (10.00); C, 79.07 (78.95).

2-(4-Bromobenzyl)-3-methyl-2-aza-spiro[4.5]decane (Table 2, entry 3). Yellow oil. TLC (Et_3N–EtOAc–hexanes = 1:3:90): R_f = 0.11. ^{1}H NMR (Figure S1): δ 7.41-7.43 (m, 2 H), 7.22 (d, *J* = 8.2 Hz, 2 H), 3.94 (d, *J* = 13.3 Hz, 1 H), 3.04 (d, *J* = 13.5 Hz, 1 H), 2.74 (d, *J* = 9.2 Hz, 1 H), 2.45-2.55 (m, 1 H),1.84 (d, *J* = 9.4 Hz, 1 H), 1.75 (dd, *J* = 7.0 Hz, 12.5 Hz, 1 H), 1.26-1.46 (m, 11 H), 1.13 (d, *J* = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S2): δ 139.2, 131.3, 130.4, 120.4, 66.7, 59.2, 57.4, 47.0, 39.5,39.3, 38.6, 31.0, 26.1, 23.7, 19.4. IR (neat, cm^{-1}): 2922,

2850, 2787, 1485, 1448, 798. HRMS calcd (found) for $C_{17}H_{24}N^{81}Br$ (M^+): 323.1072, (323.1068).

3-Methyl-2-(4-nitrobenzyl)-2-aza-spiro[4.5]decane (Table 2, entry 4). A suspension of (1-allylcyclohexylmethyl)(4-nitrobenzyl)amine (144 mg, 0.50 mmol), $PtCl_2$ (6.9 mg, 0.26 mmol), **6a** (11.0 mg, 0.26 mmol), and diglyme (1.0 mL) was heated at 60 °C for 13 h. The reaction mixture was concentrated and the resultant residue was chromatographed (Et_3N–EtOAc–hexanes = 1:3:96) to yield 3-methyl-2-(4-nitrobenzyl)-2-aza-spiro[4.5]decane (121 mg, 84 %) as a pale yellow oil. TLC (Et_3N–EtOAc–hexanes = 1:3:96): R_f = 0.15. ^{1}H NMR (Figure S3): δ 8.11 (d, *J* = 8.7 Hz, 2 H), 7.47 (d, *J* = 8.5 Hz, 2 H), 4.01 (d, *J* = 14.4 Hz, 1 H), 3.16 (d, *J* = 14.2 Hz, 1 H,), 2.50-2.52 (m, 1 H), 1.81 (d, *J* = 9.2 Hz, 1 H), 1.73 (dd, *J* = 7.0, 12.5 Hz, 1 H), 1.22-1.42 (m, 11 H), 1.09 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR (Figure S4): δ 148.5, 147.0, 129.1, 123.5, 66.9, 59.4, 57.5, 46.9, 39.6, 39.3, 38.5, 26.1, 23.7, 23.6, 19.4. IR (neat, cm^{-1}): 2923, 2851, 2790, 1518, 1343, 851. HRMS calcd (found) for $C_{17}H_{24}N_2O_2^+$ (M^+): 288.1838 (288.1834).

3-Methyl-2-(2-naphthyl)-2-aza-spiro[4.5]decane (Table 2, entry 5). TLC (EtOAc–hexanes = 1:1): R_f = 0.77. ^{1}H NMR: δ 7.75-7.84 (m, 4 H), 7.42-7.53 (m, 3 H), 4.18 (d, *J* = 13.2 Hz, 1 H), 3.25 (d, *J* = 13.3 Hz, 1 H), 2.79 (d, *J* = 9.1 Hz, 1 H), 2.51-2.60 (m, 1 H), 1.93 (d, *J* = 9.2 Hz, 1 H), 1.78 (dd, *J* = 6.8, 12.3 Hz, 1 H), 1.26-1.50 (m, 11 H), 1.20 (d, *J* = 6.0 Hz, 3 H). ^{13}C{^{1}H} NMR: δ 137.8, 133.5, 132.8, 127.8, 127.8, 127.8, 127.5, 127.0, 125.9, 125.5, 66.9, 59.4, 58.4, 47.1, 39.5, 39.4, 38.6, 26.2, 23.8, 23.6, 19.4. IR (neat, cm^{-1}): 2922, 2851, 2785, 1447, 1148, 745. Anal. calcd (found) for $C_{21}H_{27}N$: H, 9.27 (9.22); C, 85.95 (85.80).

1-Benzyl-2-methyl-4,4-diphenyl-pyrrolidine (Table 2, entry 6).[2] White solid. TLC (Et_3N-EtOAc-hexanes = 1:3:90): R_f = 0.09. ^{1}H NMR: δ 7.13-7.43 (m, 15 H), 4.14 (d, *J* = 13.2,

1 H), 3.69 (d, *J* = 9.7, 1 H), 3.30 (d, *J* = 13.2, 1 H), 2.94-2.99 (m, 1 H), 2.82-2.91 (m, 2 H), 2.26 (dd, *J* = 7.7,12.6, 1 H), 1.21 (d, *J* = 6.0, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 150.9, 148.9, 140.3, 128.8, 128.4, 128.3, 128.0, 127.6, 127.4, 127.0, 126.0, 125.6, 66.6, 59.9, 58.2, 52.7, 48.2, 19.7.

1-Furan-2-ylmethyl-2-methyl-4,4-diphenylpyrrolidine (Table 2, entry 7).[3] Waxy yellow solid. TLC (Et_3N–EtOAc–hexanes = 1:9:90): R_f = 0.29. ^{1}H NMR: δ 7.35-7.36 (m, 1 H), 7.08-7.59 (m, 10 H), 6.30 (dd, *J* = 1.5, 3.1 Hz, 1 H), 6.17 (d, *J* = 2.9 Hz, 1 H), 3.93 (d, *J* = 14.4 Hz, 1 H), 3.73 (d, *J* = 10.1 Hz, 1 H), 3.48 (d, *J* = 14.4 Hz, 1 H), 2.97 (d, *J* = 10.0 Hz, 1 H), 2.76-2.86 (m, 2 H), 2.15-2.20 (dd, *J* = 7.5, 12.1 Hz, 1 H), 1.13 (d, *J* = 5.8 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 153.2, 150.5, 148.9, 142.0, 128.4, 128.2, 127.6, 127.4, 126.0, 125.7, 110.3, 108.0, 66.3, 59.0, 52.6, 49.5, 48.1, 19.4.

Methyl-4,4-diphenyl-1-thiophen-2-ylmethyl-pyrrolidine (Table 2, entry 8).[3] White solid. TLC (Et_3N–EtOAc–hexanes = 1:9:90): R_f = 0.37. ^{1}H NMR: δ 7.07-7.28 (m, 11 H), 6.89-6.93 (m, 2 H), 4.15 (d, *J* = 14.0 Hz), 3.75 (d, *J* = 9.7 Hz, 1 H), 3.58 (d, *J* = 13.8 Hz, 1 H), 2.79-2.92 (m, 3 H), 2.17 (dd, *J* = 7.5, 12.5 Hz, 1 H), 1.14 (d, *J* = 6.0 Hz, 3 H). $^{13}C\{^{1}H\}$ NMR: δ 150.8, 148.8, 143.8, 128.4, 128.1, 127.6, 127.5, 126.5, 126.0, 125.7, 125.1, 124.9, 66.6, 59.5, 52.6, 52.4, 48.2, 19.6.

2-Benzyl-3,3-dimethyl-2-aza-spiro[4.5]decane (Table 2, entry 9).[2] TLC (Et_3N–EtOAc–hexanes = 1:3:90): R_f = 0.44. ^{1}H NMR: δ 7.18-7.36 (m, 5 H), 3.50 (s, 2 H), 2.41 (s, 2 H), 1.55 (s, 2H), 1.26-1.42 (m, 10 H), 1.08 (s, 6 H). $^{13}C\{^{1}H\}$ NMR: δ 141.8, 128.2, 128.1, 126.4, 62.8, 60.1, 53.9, 52.2, 39.3, 39.1, 26.2, 24.8, 23.9.

2-Benzyl-3-methyl-2-aza-spiro[5.5]undecane (9). TLC (EtOAc–hexanes = 1:5): R_f = 0.73. ^{1}H NMR: δ 7.20-7.35 (m, 5 H), 4.00 (d, *J* = 13.8 Hz, 1 H), 3.05 (d, *J* = 13.8 Hz, 1 H), 2.52 (d, *J* = 11.4 Hz, 1 H), 2.21-2.27 (m, 1 H), 1.62 (d, *J* = 11.6 Hz, 1 H), 1.04-1.57 (m, 17 H).

$^{13}C\{^1H\}$ NMR: δ 140.8, 128.7, 128.1, 126.5, 61.8, 58.4, 57.4, 38.1, 34.9, 33.3, 31.0, 27.1, 21.8, 19.3.

Benzyl 2-methylpyrrolidine (Table 2, entry 11).[5] Pale yellow oil. TLC (Et_3N–EtOAc–hexanes = 1:3:96): R_f = 0.13. ^1H NMR: δ 7.20-7.30 (m, 5 H), 3.99 (d, *J* = 12.8 Hz, 1 H), 3.11 (d, *J* = 9.8 Hz, 1 H), 2.85-2.90 (m, 1 H), 2.31-2.40 (m, 1 H), 2.07 (q, *J* = 8.9 Hz, 1 H), 1.86-1.95 (m, 1 H), 1.51-1.74 (m, 2 H), 1.38-1.47 (m, 1 H), 1.15 (d, *J* = 6.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR: δ 139.8, 129.3, 128.3, 126.9, 59.8, 58.6, 54.2, 32.9, 21.7, 19.4.

Benzyl 2-methylpiperidine (Table 2, entry 12).[6] Pale yellow oil. TLC (Et_3N–EtOAc–hexanes = 1:3:96): R_f = 0.14. ^1H NMR: δ 7.25-7.31 (m, 4 H), 7.20-7.22 (m, 1 H), 3.97 (d, *J* = 13.3 Hz), 3.17 (d, *J* = 13.5 Hz, 1 H), 2.70 (td, *J* = 3.8, 11.4 Hz, 1 H), 2.23-2.32 (m, 1 H), 1.91 (dt, *J* = 3.4, 11.4 Hz, 1 H), 1.59-1.64 (m, 2 H), 1.20-1.50 (m, 4 H), 1.13-1.15 (m, 15 H). $^{13}C\{^1H\}$ NMR: δ 129.3, 128.4, 126.8, 58.7, 56.6, 52.4, 34.9, 26.3, 24.2, 19.8.

Optimization Reactions Employing $PtCl_2$ and Mono(phosphines).

n-Hexadecane (60 μL, 0.20 mmol) and **1** (181 mg, 0.74 mmol) were added to a suspension of $PtCl_2$ (10.1 mg, 0.038 mmol) and **6c** (13.0 mg, 0.038 mmol) in diglyme (1.5 mL) in a 3 mL scintillation vial fitted with a septum and the reaction mixture was heated at 80 °C. Aliquots (50 μL) were taken after 6 h and analyzed by GC.

Figure S1. ^{1}H NMR spectrum of 2-(4-bromobenzyl)-3-methyl-2-aza-spiro[4.5]decane.

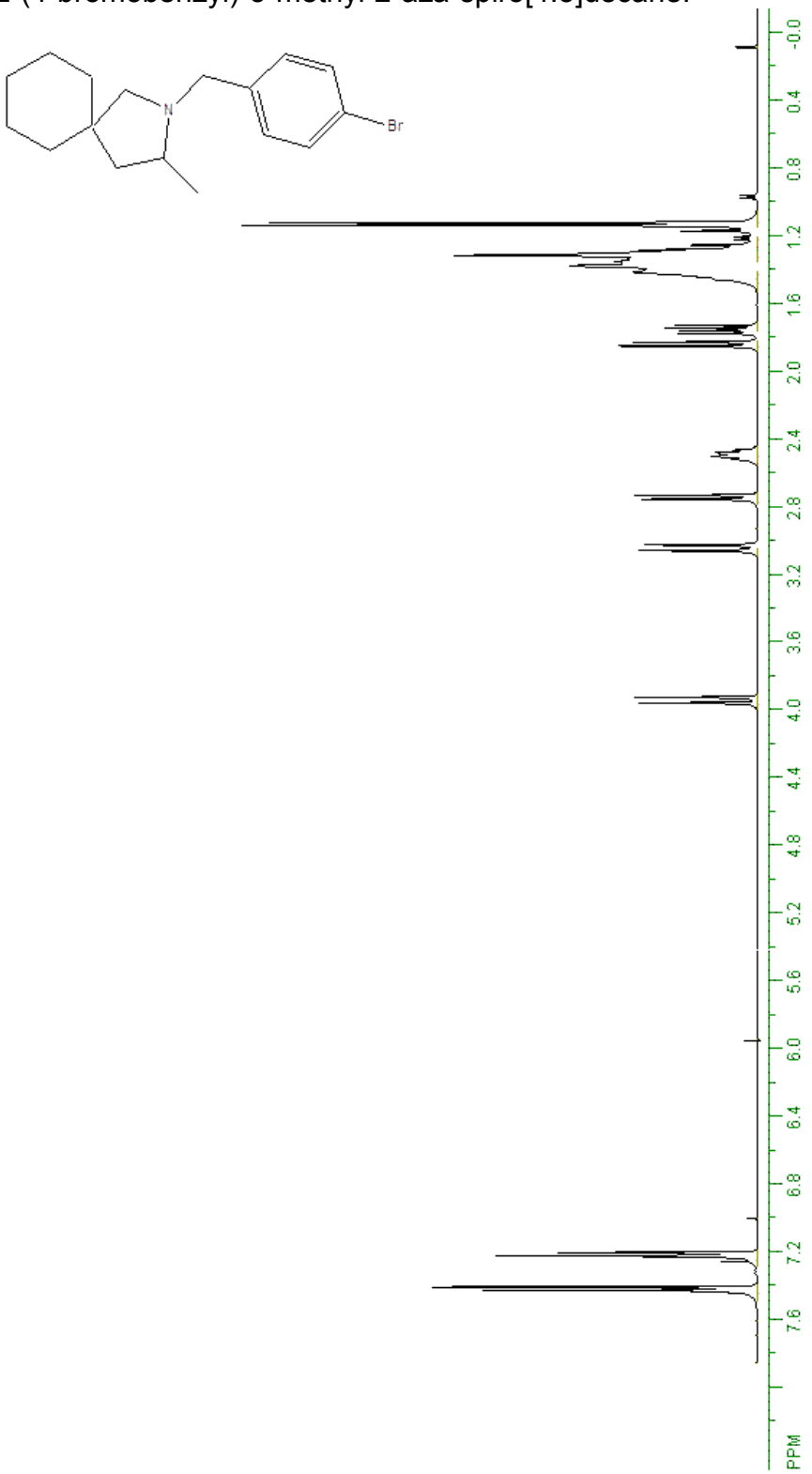


Figure S2. ^{13}C NMR spectrum of 2-(4-bromobenzyl)-3-methyl-2-aza-spiro[4.5]decane.

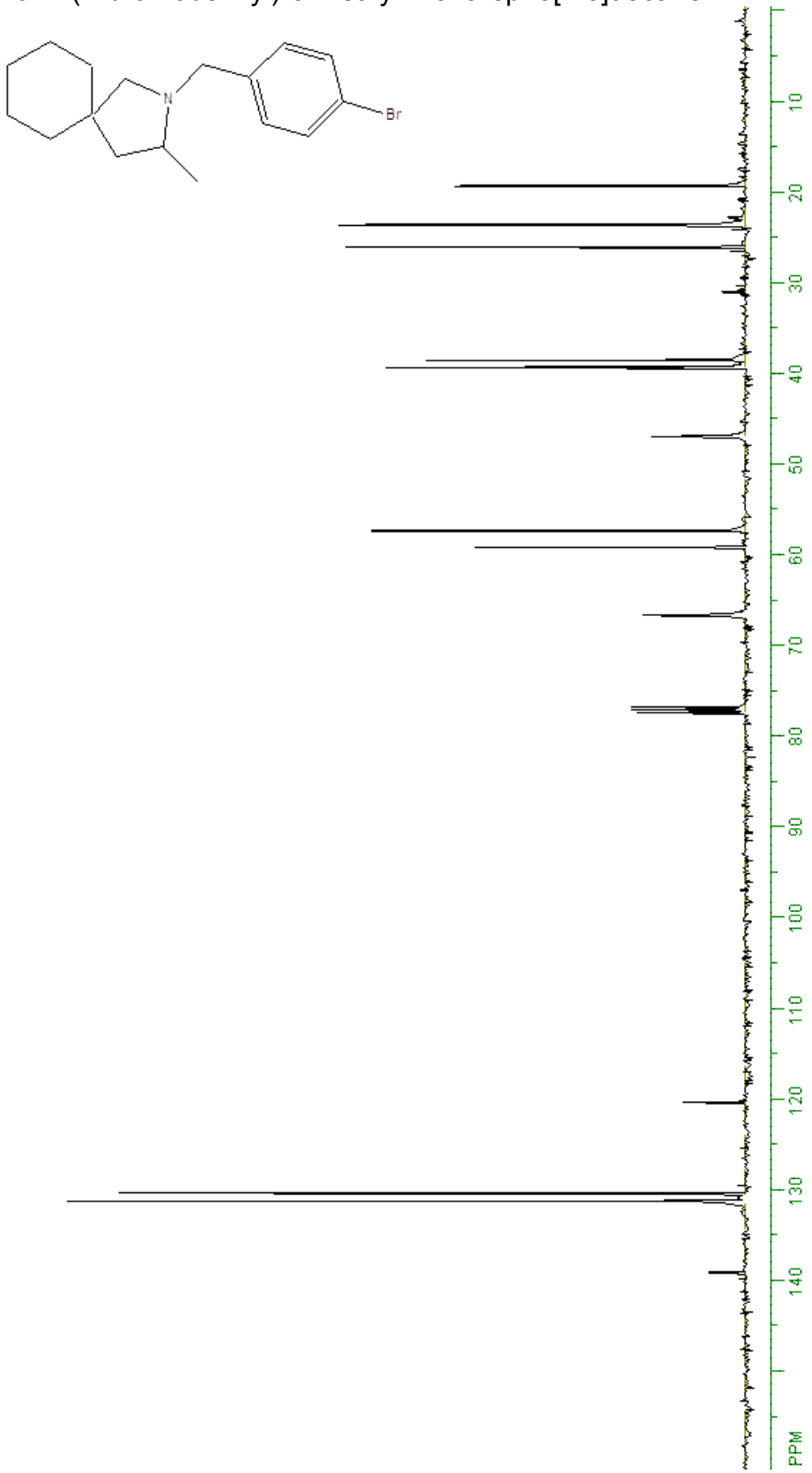


Figure S3. ^{1}H NMR spectrum of (1-allylcyclohexylmethyl)(4-nitrobenzyl)amine.

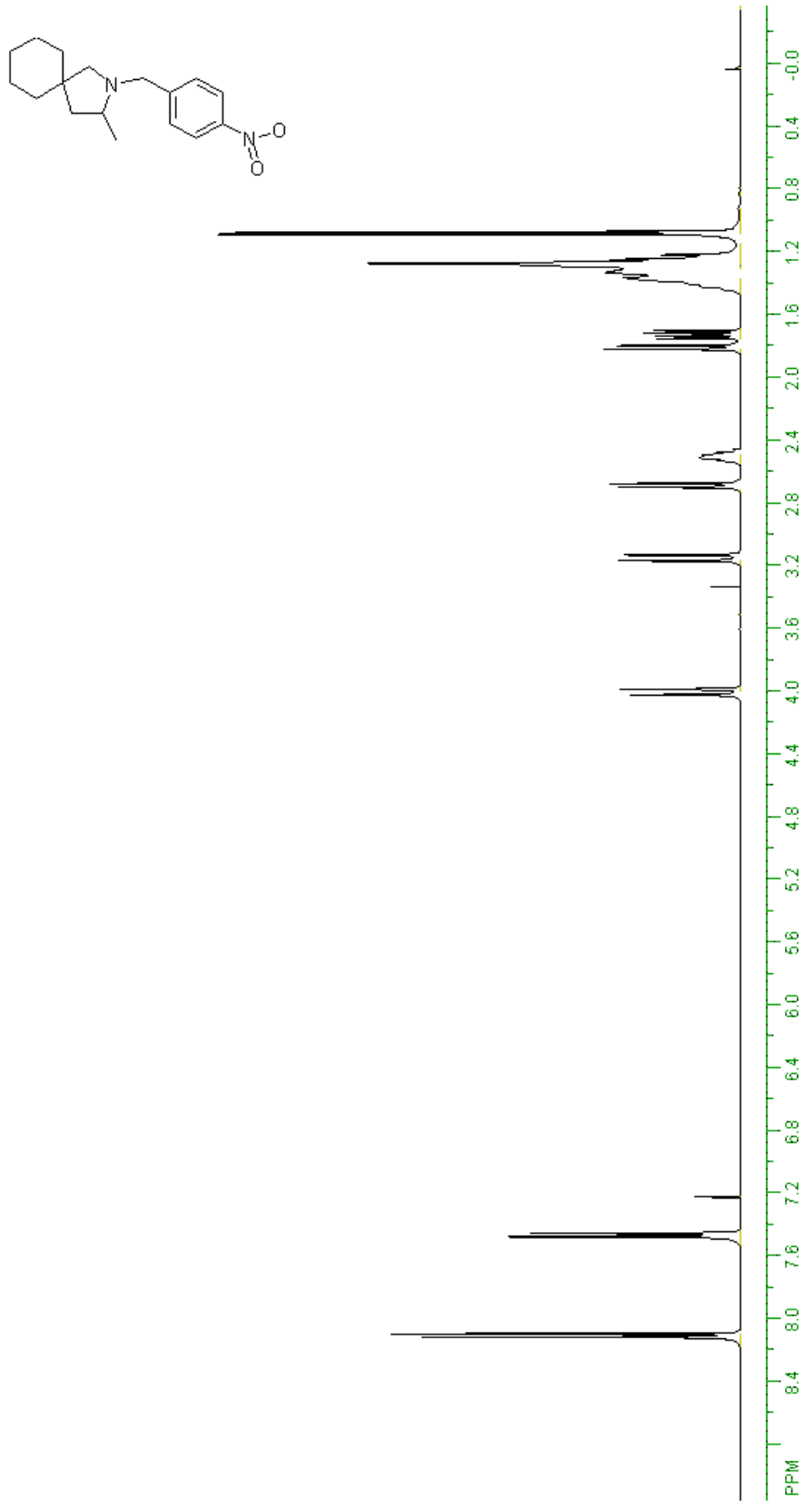
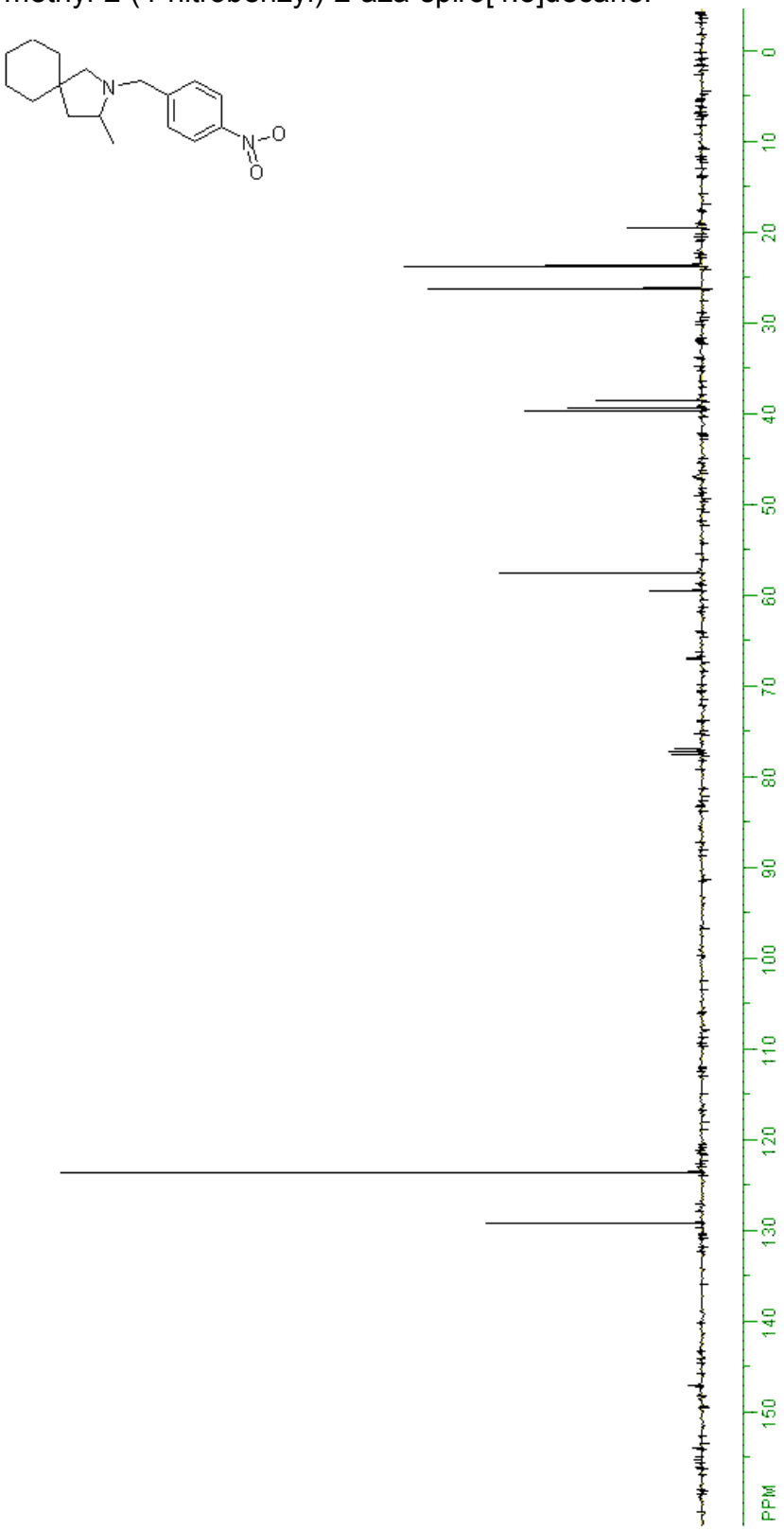


Figure S4. ^{13}C NMR spectrum of 3-methyl-2-(4-nitrobenzyl)-2-aza-spiro[4.5]decane.



References

1) Tomori, H.; Fox, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334.

2) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc*. **2005**, *127*, 1070.

3) Dochnahl, M.; Pissarek, J-W.; Blechert, S.; Loehnwitz, K.; Roesky, P. W. *Chem. Commun*. **2006**, 3405.

4) Lorthiois, E., Marek, I., Normant, J. F. *J. Org. Chem.* **1998**, *63*, 566.

5) Gribkov, D. V., Hultzsch, K. C. *Angew. Chem. Int. Ed.* **2004**, *43*, 5542.

6) Pearson, W. H., Fang, W.-k. *J. Org. Chem.* **1995**, *60*, 4960.