# IAN-Amines: Chiral $C_2$-Symmetric Complexes from Readily Modified Axially Chiral $C_1$-Symmetric β-Diketimines

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## General Experimental Details

Flame-dried (under vacuum) glassware was used for all non-aqueous reactions. All reagents and solvents were commercial grade and purified prior to use when necessary. Diethyl ether ($Et_2O$), tetrahydrofuran (THF), dichloromethane ($CH_2Cl_2$), and benzene ($C_6H_6$) were dried by passage through a column of activated alumina as described by Grubbs.[1] Benzene was additionally passed through a column containing activated Q-5 reactant. Solvents other than benzene were degassed using the freeze-pump-thaw method when necessary. All additional solvents were dried by distillation from calcium hydride or Na/benzophenone (hydrocarbon deuterated solvents) when necessary. Magnesium sulfate was used to dry organic solutions unless otherwise noted. Analytical data for **1a** and **12a** has been previously reported.[2] 1-Chloroisoquinoline,[3] 1,5-diphenyl-penta-1,4-dien-3-one (dba),[4] $Pd(dba)_2$ complex,[5] and 2-naphthol triflate[6] were prepared using literature procedures.

Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μ) plates, and flash chromatography utilized 230–400 mesh silica gel from Scientific Adsorbents. Products were visualized by UV light, iodine, and/or the use of ceric ammonium molybdate, potassium permanganate, ninhydrin, *p*-anisaldehyde, and potassium iodoplatinate solutions.

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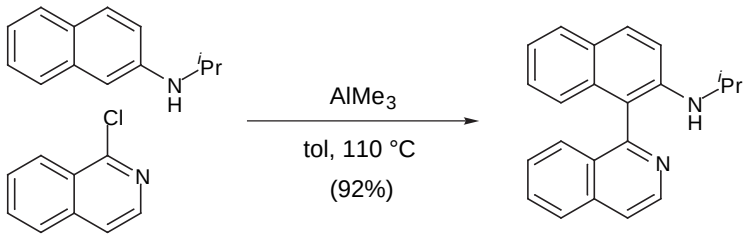
[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. *J. Organometallics* **1996**, *15,* 1518–1520.
[2] Cortright, S. B.; Johnston, J. N. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 345.
[3] a) Alcock, N. W.; Brown, J. M.; Hulmes, D. I. *Tetrahedron: Asymmetry* **1993**, *4*, 743.
[4] C.R. Conard and M.A. Dolliver, in *Organic Syntheses*, A.H. Blatt (ed.), Coll.Vol.2, p.167, Wiley, New York, 1943.
[5] Rettig, M.F.; Maitlis, P.M. *Inorg. Synth*. **1992**, *28*, 110.
[6] Stang, P. J.; Hanack, H.; Subramanian, L. R. *Synthesis* **1982**, 85.

IR spectra were recorded on a Nicolet Avatar 360 spectrophotometer. Liquids and oils were analyzed as neat films on a salt plate (transmission), whereas solids were applied to a diamond plate (ATR). Nuclear magnetic resonance spectra (NMR) were acquired on either a Varian Inova-400 or VXR-400 instrument. Chemical shifts are measured relative to tetramethylsilane, as judged by the residual partially deuterated solvent peak. Mass spectra were obtained using a Kratos MS-80 spectrometer using the ionization technique indicated. Combustion analyses were performed by Atlantic Microlab, Norcross, GA.

**General Procedure for Synthesis of 2-(Alkylamino)-naphthalenes.**[7]

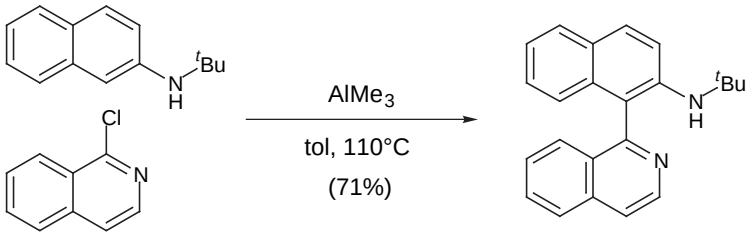
$Pd(dba)_2$ (0.02 equiv), dppf (0.05 equiv), and $NaO^tBu$ (1.5 equiv) were loaded into a round bottom flask in a glove box and then transferred to a hood. Toluene (0.34 equiv) was added to the mixture followed by the primary amine (1.5 equiv) via syringe. 2-Naphthol triflate[6] (1.0 equiv) was dissolved in toluene and added to the solution. The reaction was allowed to stir at 85 °C and monitored by TLC until complete. The reaction was then allowed to cool and was concentrated. The crude mixture was purified by flash chromatography on silica gel.




**$^i$Pr-IAN Amine (1c).** 2-(*N*-Isopropylamino)naphthalene (542.7 mg, 3.317 mmol) and 1-chloroisoquinoline (607.7 mg, 3.280 mmol) were dissolved in toluene (5.0 mL) and treated with $AlMe_3$ (2.3 mL, 2.0 M in toluene) prior to heating at 110 °C for 26 h. The solution was cooled to rt, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, concentrated, and the residue was purified by flash chromatography ($SiO_2$, 20% ethyl acetate in hexanes) to furnish the desired amine as a yellow oil (947.0 mg, 92%). $R_f$ = 0.30 (20% EtOAc/hexanes); IR (film) 3411, 2965, 1620 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 5.6 Hz, 1H), 7.96-7.92 (m, 2H), 7.82-7.78 (m, 2H), 7.69 (ddd, *J* = 8.1, 8.1, 1.2 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.39 (ddd, *J* = 8.1, 8.1, 1.1 Hz, 1H), 7.32 (d, *J* = 9.1 Hz, 1H), 7.21 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.3, 8.3, 1.3 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 3.83 (qq, *J* = 6.3, 6.3 Hz, 1H), 3.51 (br s, 1H), 1.15 (d, *J* = 6.3 Hz, 3H), 1.04 (d, *J* = 6.3 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.1, 143.8, 143.6, 137.0,

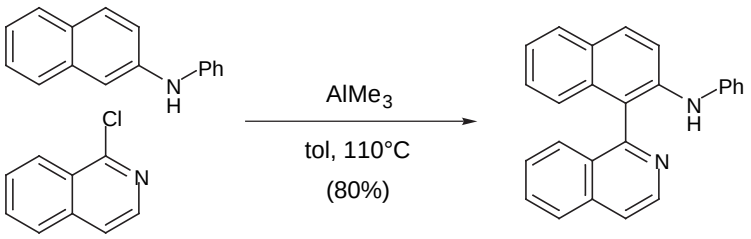
[7] Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1997**, *62*, 1268.

134.3, 130.8, 130.2, 128.8, 128.2, 127.8 (2C), 127.3, 127.2, 126.7, 124.1, 122.0, 120.6, 116.6, 115.4, 45.0, 23.6, 23.5; HRMS (CI, $CH_4$): Exact mass calcd for $C_{22}H_{20}N_2$ $[M]^+$ 312.1626. Found 312.1619. *Anal*. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found C, 84.47, H, 6.72, N, 8.70.

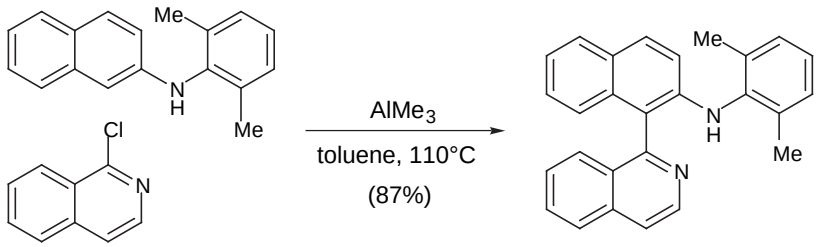



**$^t$Bu-IAN Amine (1d).**[8] 2-(*N*-*tert*-Butylamino)naphthalene (27.0 mg, 135 μmol) and 1-chloroisoquinoline (22.2 mg, 136 μmol) were dissolved in toluene (2.0 mL) and treated with $AlMe_3$ (0.20 mL, 2.0 M in toluene) prior to heating at 100 °C for 12 h. The solution was cooled to rt, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, concentrated, and the residue was purified by flash chromatography ($SiO_2$, 5% ethyl acetate in hexanes) to give the desired amine as a yellow oil (31.5 mg, 71%). $R_f$ = 0.30 (20% EtOAc/hexanes); IR (film) 3404, 2963, 1619 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.8 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.69 (ddd, *J* = 8.2, 8.2, 1.2 Hz, 1H), 7.53-7.50 (m, 2H); 7.40 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.20 (ddd, *J* = 8.1, 8.1, 1.2 Hz, 1H), 7.12 (ddd, *J* = 8.2, 8.2, 1.3 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 3.62 (br s, 1H), 1.16 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.8, 143.5, 136.9, 134.2, 130.8, 129.3, 128.9, 128.04, 127.95, 127.81, 127.77, 127.3, 126.5, 124.6, 122.5, 120.5, 120.3, 119.6, 52.2, 31.0; HRMS (CI, $CH_4$): Exact mass calcd for $C_{23}H_{22}N_2$ $[M]^+$ 326.1783. Found 326.1784. *Anal*. Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found C, 84.65, H, 6.84, N, 8.52.

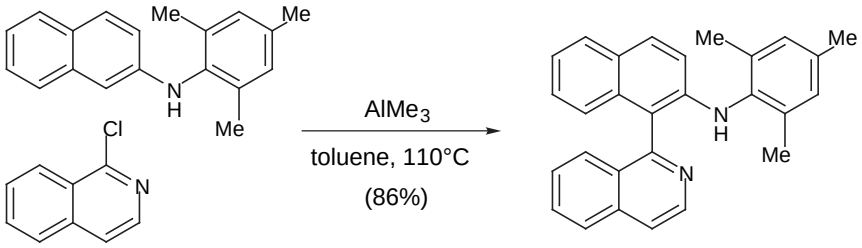
[8] Adapted from Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1144.




**Ph-IAN Amine (1e)**. *N*-2-Naphthylaniline (10.40 g, 47.4 mmol) and 1-chloroisoquinoline (7.77 g, 47.5 mmol) were dissolved in toluene (75 mL) and treated with $AlMe_3$ (38.0 mL, 2.0 M in toluene) prior to heating at 110 °C for 24 h. The solution was cooled to rt, added to 6 M aq NaOH and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and concentrated, and the residue was purified by flash chromatography ($SiO_2$, 20% ethyl acetate in hexanes) to furnish the desired amine (13.09 g, 80%). Alternately, the crude product may be purified by crystallization, from a hot toluene solution with an equivalent volume of hexanes added, to give a tan powder. Mp 163-164 °C; $R_f$ = 0.30 (20% EtOAc/hexanes); IR (film) 3405, 3051, 1595 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 5.6 Hz, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 5.8 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.68 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.39 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.30 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.21-7.17 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.88 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.07 (br s, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.7, 143.2, 143.0, 139.5, 137.0, 134.1, 130.9, 129.8 (2C), 129.5, 128.7, 128.3, 127.9, 127.6, 127.3, 126.9, 125.1, 123.7, 122.0, 121.5, 120.8, 119.2, 118.9; HRMS (CI, $CH_4$): Exact mass calcd for $C_{25}H_{18}N_2$ $[M]^+$ 346.1470. Found 346.1577. *Anal*. Calcd for $C_{25}H_{18}N_2$: C, 86.68; H, 5.24; N, 8.09. Found C, 86.68; H, 5.37; N, 7.96.

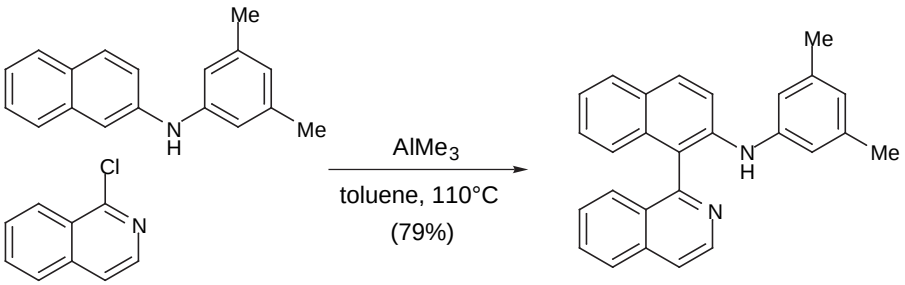



**2,6-Me$_2$Ph-IAN Amine (1f).** 2-(*N*-(2,6-Dimethylphenyl)amino)naphthalene (129.8 mg, 525 μmol) and 1-chloroisoquinoline (85.9 mg, 525 μmol) were dissolved in toluene (5.0 mL) and treated with $AlMe_3$ (0.40 mL, 2.0 M in toluene) via syringe prior to heating at 110 °C for 24 h. The solution was cooled to rt, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and concentrated and the residue was purified by flash chromatography ($SiO_2$, 10% ethyl acetate in hexanes) to give the desired amine as a yellow powder (170.1 mg, 87%). Mp 186.5-187.5 °C; $R_f$ = 0.08 (20% EtOAc/hexanes); IR (film) 3398, 3050, 1620 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.83 (d, *J* = 5.6 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.81-7.69 (m, 5H), 7.45 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.22-7.18 (m, 2H), 7.05 (d, *J* = 5.2 Hz, 2H), 7.05-7.03 (m, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.75 (d, *J* = 8.9 Hz, 1H), 5.39 (s, 1H), 2.17-2.14 (br s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.2, 143.5, 142.3, 138.1, 137.1, 135.9, 134.1, 130.8, 130.0, 128.7 (2C), 128.2, 128.0, 127.8 (2C), 127.3, 126.8, 125.8, 124.2, 122.4, 120.7, 117.1, 115.4, 18.7; HRMS (CI, $CH_4$): Exact mass calcd for $C_{27}H_{22}N_2$ $[M]^+$ 374.1783. Found 374.1778. *Anal.* Calcd for $C_{27}H_{22}N_2$: C, 86.60; H, 5.92; N, 7.48. Found C, 86.36; H, 5.99; N, 7.46.



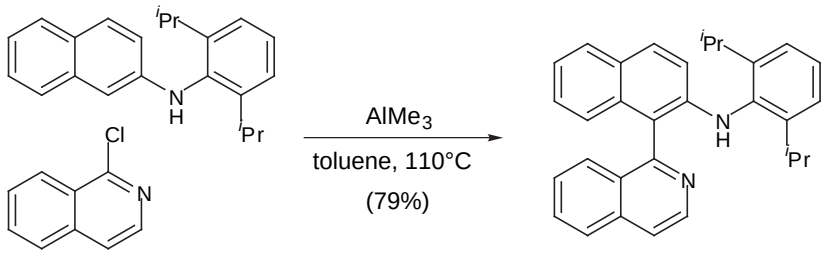

**2,4,6-Me$_3$Ph-IAN Amine (1g).** 2-(*N*-(2,4,6-Trimethylphenyl)amino)naphthalene (181.0 mg, 693 μmol) and 1-chloroisoquinoline (112.7 mg, 689 μmol) were dissolved in toluene (4.0 mL)

and treated with $AlMe_3$ (0.53 mL, 2.0 M in toluene) via syringe prior to heating at 110 °C for 24 h. The solution was cooled to rt, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and concentrated and the residue was purified by flash chromatography ($SiO_2$, 10% ethyl acetate in hexanes) to give the amine as a yellow foam (229.5 mg, 86%). A small amount of the crude product was purified by crystallization, from a hot toluene solution with an equivalent volume of hexanes added, to give a yellow powder. Mp 157-158 °C; $R_f$ = 0.08 (20% EtOAc/hexanes); IR (film) 3402, 3052, 1620 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 5.8 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.83-7.72 (m, 5H), 7.47 (dd, *J* = 8.1, 8.1 Hz, 1H), 7.26-7.20 (m, 2H), 6.97 (d, *J* = 7.5 Hz, 1H), 6.92 (s, 2H), 6.79 (d, *J* = 9.0 Hz, 1H), 5.30 (s, 1H), 2.31 (s, 3H), 2.26-2.10 (br s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 159.3, 143.6, 142.8, 137.2, 136.1, 135.6, 135.5, 134.3, 130.9, 130.1, 129.4, 128.9, 128.2, 128.0, 127.9, 127.8, 127.4, 126.8, 124.2, 122.3, 120.7, 116.8, 115.3, 21.2, 18.6; HRMS (EI): Exact mass calcd for $C_{28}H_{24}N_2$ $[M]^+$ 388.1939. Found 388.1925. *Anal.* Calcd for $C_{28}H_{24}N_2$: C, 86.56; H, 6.23; N, 7.21. Found C, 86.28; H, 6.20; N, 7.17.



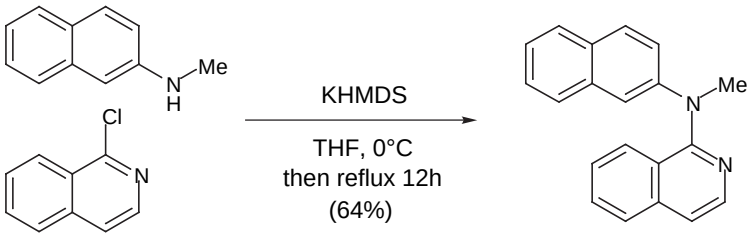

**3,5-$Me_2$Ph-IAN Amine (1h).** 2-(*N*-(3,5-Dimethylphenyl)amino)naphthalene (301.9 mg, 1.22 mmol) and 1-chloroisoquinoline (201.0 mg, 1.23 mmol) were dissolved in toluene (6.0 mL) and treated with $AlMe_3$ (1.85 mL, 2.0 M in toluene) prior to heating at 110 °C for 24 h. The solution was cooled to rt, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and

concentrated. Purification by flash chromatography ($SiO_2$, 10% ethyl acetate in hexanes) gave the desired amine as a yellow powder (359.6 mg, 79%). Mp 174.5-175.5 °C, $R_f$ = 0.34 (20% EtOAc/hexanes); IR (film) 3408, 3052, 1594 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 5.8 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 5.6 Hz, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.68 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.39 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.28 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 7.19 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.64 (s, 2H), 6.54 (s, 1H), 5.97 (br s, 1H), 2.21 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 158.7, 143.2, 142.8, 139.7, 139.1, 137.0, 134.1, 130.8, 129.7, 129.3, 128.7, 128.2, 127.8, 127.6, 127.2, 126.7, 125.0, 123.5, 123.4, 121.7, 120.7, 119.3, 116.6, 21.5; HRMS (CI, $CH_4$): Exact mass calcd for $C_{27}H_{22}N_2$ $[M]^+$ 374.1783. Found 374.1808.

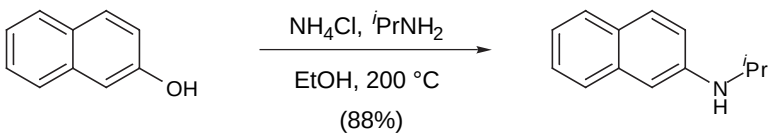



**2,6-$^i$Pr$_2$Ph-IAN Amine (1i).** 2-(*N*-(2,6-Diisopropylphenyl)amino)naphthalene (158.7 mg, 523 μmol) and 1-chloroisoquinoline (87.5 mg, 535 μmol) were dissolved in toluene (6.0 mL) and treated with $AlMe_3$ (0.79 mL, 2.0 M in toluene) via syringe prior to heating at 110 °C for 26 h. The solution was cooled to rt, added to 6 M aq NaOH, and diluted with EtOAc and Rochelle's salt solution. The mixture was stirred for 30 min, the phases were separated, and the aqueous layer was further extracted with EtOAc. The combined organic layers were dried, filtered, and concentrated and the residue was purified by flash chromatography ($SiO_2$, 2% ethyl acetate in hexanes) to give the amine as a yellow powder (176.8 mg, 79%). Mp 171.5-172.5 °C; $R_f$ = 0.18 (20% EtOAc/hexanes); IR (film) 3412, 2962, 1620 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 5.6 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 5.8 Hz, 1H), 7.77-7.71 (m, 4H), 7.46 (ddd, *J* = 8.1, 8.1, 1.1 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.21-7.15 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H),

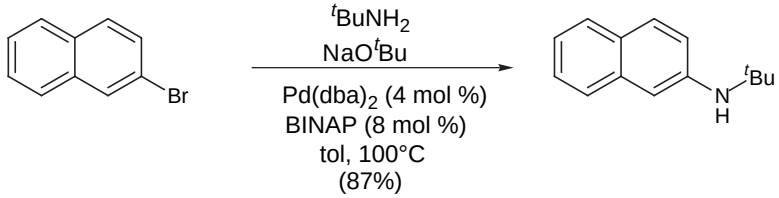
6.95-6.92 (m, 1H), 6.71 (d, *J* = 9.0 Hz, 1H), 5.14 (s, 1H), 3.29 (qq, *J* = 6.8, 6.8 Hz, 1H), 3.00 (qq, *J* = 6.8, 6.8 Hz, 1H), 1.15 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.67 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.9, 147.6, 143.9, 143.6, 137.2, 135.4, 134.1, 130.9, 130.0, 128.9, 128.2 (2C), 127.8, 127.7 (2C), 127.4, 127.3, 126.9, 124.2, 124.1, 123.9, 122.2, 120.7, 115.2, 28.5, 28.4, 24.5, 24.3, 23.4, 23.0; HRMS (CI, $CH_4$): Exact mass calcd for $C_{31}H_{30}N_2$ $[M]^+$ 430.2409. Found 430.2404. *Anal.* Calcd for $C_{31}H_{30}N_2$: C, 86.47; H, 7.02; N, 6.51. Found C, 86.18; H, 7.03; N, 6.40.




**Isoquinolin-1-yl-methyl-naphthalen-2-yl-amine (10).** 2-(*N*-Methylamino)naphthalene (68.4 mg, 435 μmol) was dissolved in THF (1.5 mL) and stirred at 0 °C. KHMDS (1.00 mL, 0.5 M in toluene) was added and the solution became dark red. 1-Chloroisoquinoline (72.4 mg, 443 μmol) was added and the solution was heated at reflux for 12 h. After cooling to rt, $H_2O$ and EtOAc were added. The organic layer was collected, dried, filtered, and concentrated. Purification by flash chromatography ($SiO_2$, 10% ethyl acetate in hexanes) gave the amine as a yellow oil (79.5 mg, 64%). $R_f$ = 0.36 (20% EtOAc/hexanes); IR (film) 3050, 1623 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 5.8 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.55 (ddd, *J* = 7.1, 7.1, 1.1 Hz, 1H), 7.40 (d, *J* = 5.8 Hz, 1H), 7.41-7.39 (m, 1H), 7.34 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.24 (ddd, J = 7.1, 7.1, 1.2 Hz, 1H), 7.06 (dd, *J* = 8.9 Hz, 2.3 Hz, 1H), 3.69 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.8, 148.4, 141.6, 138.6, 134.7, 129.9, 129.8, 129.1, 127.8, 127.2 (2C), 126.9, 126.6, 126.5, 124.4, 123.4, 122.2, 117.4, 116.3, 76.9; HRMS (CI, $CH_4$): Exact mass calcd for $C_{20}H_{16}N_2$ $[M]^+$ 284.1313. Found 284.1307.

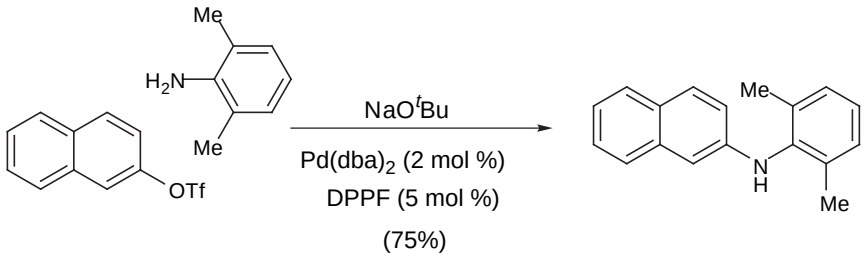



**2-(*N*-isopropylamino)naphthalene (12c).** 2-Naphthol (314.5 mg, 2.181 mmol), ammonium chloride (168.6 mg, 3.152 mmol), isopropylamine (5.8 mL, 68.6 mmol), and ethanol (1.0 mL) were combined. The solution was heated at 200 °C by a Wood's metal bath (in a sealed tube for 40 h). After cooling to room temperature, the mixture was concentrated, removing the excess isopropylamine. The residue was diluted with EtOAc, washed with 6 M aq NaOH, dried ($Na_2SO_4$), filtered, and concentrated. The brown liquid was purified by flash chromatography ($SiO_2$, 5% ethyl acetate in hexanes) to furnish the product as a brown liquid (354.9 mg, 88%). $R_f$ = 0.49 (20% EtOAc/hexanes); IR (film) 3402, 2965, 1627 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.73-7.71 (m, 2H), 7.47 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.30 (dd, *J* = 7.9, 7.9 Hz, 1H), 6.93-6.90 (m, 2H), 3.85 (sept, *J* = 6.3 Hz, 1H), 3.70 (br s, 1H), 1.36 (d, *J* = 6.2 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 145.5, 135.7, 129.3, 128.0, 127.6, 126.6, 126.2, 122.1, 118.7, 105.2, 44.5, 23.2; HRMS (CI, $CH_4$): Exact mass calcd for $C_{13}H_{15}N$ $[M]^+$ 185.1204. Found 185.1209.

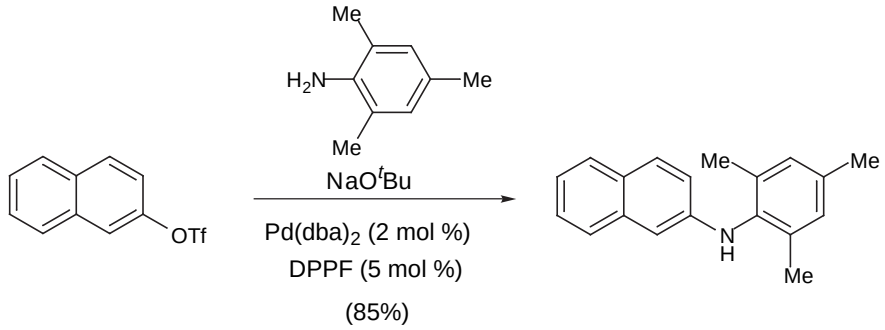



**2-(*N*-*tert*-butylamino)naphthalene (12d).**[8] BINAP (23.5 mg, 37.8 μmol) and sodium *tert*-butoxide (53.2 mg, 554 μmol) were weighed into a flame-dried flask in an inert atmosphere. $Pd(dba)_2$ (11.3 mg, 19.7 μmol) and 2-bromonaphthalene (96.7 mg, 467 μmol) were dissolved in toluene and cannulated into the reaction flask. Then, *tert*-butylamine (5.90 μL, 561 μmol) was added. The solution was heated at 100 °C for 24 h. The reaction was cooled to rt, concentrated, filtered through Celite with EtOAc, then concentrated a final time. Purification by flash

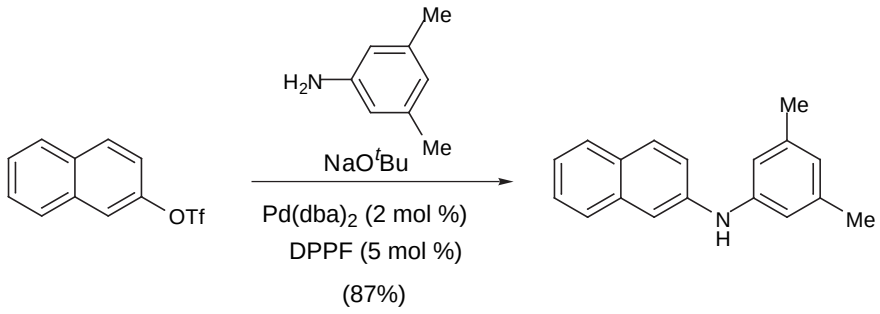
chromatography ($SiO_2$, 5% diethyl ether in hexanes) gave the naphthylamine as a brown oil (80.7 mg, 87%). $R_f$ = 0.41 (20% EtOAc/hexanes); IR (film) 3407, 2971, 1628 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 1H), 7.63-7.60 (m, 2H), 7.36 (ddd, *J* = 8.1, 8.1, 1.1 Hz, 1H), 7.21 (ddd, *J* = 8.1, 8.1, 1.1 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 6.91 (dd, *J* = 8.9, 2.1 Hz, 1H), 1.43 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 135.1, 128.8 (2C), 127.8, 126.4 (2C), 122.5, 121.2, 109.7, 107.1, 51.9, 30.1; HRMS (CI, $CH_4$): Exact mass calcd for $C_{14}H_{17}N$ $[M]^+$ 199.1361. Found 199.1354.




**(2,6-Dimethyl-phenyl)-naphthalen-2-yl-amine** (**12f**)**.** According to the general procedure, triflate (305 mg, 1.11 mmol) and aniline (204.2 μL, 1.658 mmol) combined to give **12f** as a light yellow solid (205 mg, 75%) after chromatography ($SiO_2$, 5% ether in hexanes). Mp 118-120 ˚C; $R_f$ = 0.53 (20% EtOAc/hexanes); IR (film) 3392, 3055, 1632 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.33 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.19 (m, 4H), 6.97 (m, 1H), 6.58 (d, *J* = 1.8 Hz, 1H), 5.28 (s, 1H), 2.26 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 144.1, 138.2, 136.3, 135.2, 129.4, 128.9, 128.2, 127.9, 126.5, 126.2 (2C), 122.5, 117.8, 106.5, 18.6; HRMS (CI, $CH_4$): Exact mass calcd for $C_{18}H_{17}N$ $[M]^+$ 247.1361. Found 247.1370.

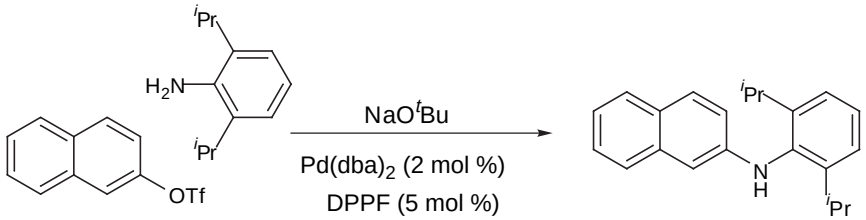



**Naphthalen-2-yl-(2,4,6-trimethyl-phenyl)-amine** (**12g**)**.** According to the general procedure, triflate (305 mg, 1.11 mmol) and aniline (232.7 μL, 1.658 mmol) combined to give **12g** as a dark red oil (245 mg, 85%). $R_f$ = 0.67 (20% EtOAc/hexanes); IR (film) 3392, 2915, 1632 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.31 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.19 (m, 1H), 6.98 (s, 2H), 6.94 (m, 1H), 6.54 (m, 1H), 5.26 (s, 1H), 2.34 (s, 3H), 2.20 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 144.6, 136.3, 135.9, 135.6, 135.3, 129.6, 129.4, 128.1, 128.0, 126.5, 126.2, 122.4, 117.7, 106.0, 21.2, 18.5; HRMS (CI, $CH_4$): Exact mass calcd for $C_{19}H_{19}N$ $[M]^+$ 261.1517. Found 261.1523.

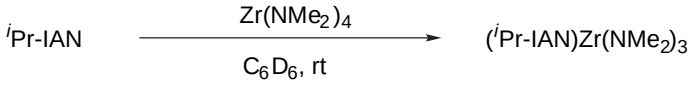



**(3,5-Dimethyl-phenyl)-naphthalen-2-yl-amine (12h).** According to the general procedure, dppf (39.3 mg, 70.9 μmol), sodium *tert*-butoxide (201.2 mg, 2.094 mmol), $Pd(dba)_2$ (16.3 mg, 28.4 μmol), 2-naphthyl triflate (401.5 mg, 1.455 mmol), and 3,5-dimethylaniline (260.0 μL, 2.085 mmol) were combined to give, after purification by flash chromatography ($SiO_2$, 5% ethyl acetate in hexanes), the desired naphthylamine as a brown oil (313.5 mg, 87%). $R_f$ = 0.59 (20% EtOAc/hexanes); IR (film) 3395, 2917, 1597 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 5.6

Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.52-7.49 (m, 2H), 7.39 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.87 (s, 2H), 6.74 (s, 1H), 5.83 (br s, 1H), 2.40 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 143.2, 141.5, 139.4, 135.0, 129.4 (2C), 128.0, 126.8, 126.7, 123.7, 123.6, 120.5, 116.5, 112.0, 21.8; HRMS (CI, $CH_4$): Exact mass calcd for $C_{18}H_{17}N$ $[M]^+$ 247.1361. Found 247.1367.

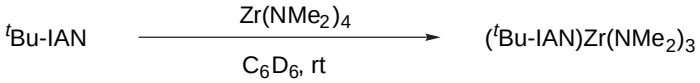



**(2,6-Diisopropyl-phenyl)-naphthalen-2-yl-amine** (**12i**)**.** According to the general procedure, triflate (305 mg, 1.11 mmol) and aniline (312.9 µL, 1.658 mmol) combined to give **12i** as a yellowish solid (250 mg, 75%). Mp 110-112 ˚C; $R_f$ = 0.67 (20% EtOAc/hexanes); IR (film) 3399, 3051, 1631 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.35 (m, 4H), 7.24 (m, 1H), 6.99 (m, 1H), 6.60 (s, 1H), 5.33 (s, 1H), 3.28 (m, 2H), 1.20 (d, *J* = 6.8 Hz, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.0, 135.3, 135.2, 129.4, 128.0, 127.9, 127.7, 126.6, 126.2, 124.3, 122.4, 117.4, 106.1, 28.6, 24.2; HRMS (CI, $CH_4$): Exact mass calcd for $C_{22}H_{25}N$ $[M]^+$ 303.1987. Found 303.1973.

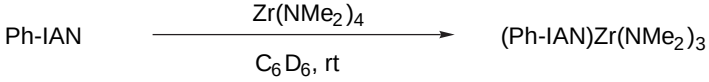



**(*i*Pr-IAN)Zr(NMe$_2$)$_3$ (15c).** *i*Pr-IAN Amine (15.6 mg, 49.9 µmol) and Zr(NMe$_2$)$_4$ (13.4 mg, 50.0 µmol) were weighed into a flame-dried vial in a glovebox. $d_6$-Benzene was then added and the clear orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.33 (d, *J* = 6.2 Hz, 1H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.56-7.50 (m, 3H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.09 (d, *J* = 5.9 Hz, 1H),

7.03-6.97 (m, 2H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.82 (dd, *J* = 8.3, 8.3 Hz, 1H), 6.68 (dd, *J* = 8.6, 8.6 Hz, 1H), 4.22 (qq, *J* = 6.0, 6.0 Hz, 1H), 3.00 (s, 18H), 1.40 (d, *J* = 6.0 Hz, 3H), 0.71 (d, *J* = 6.0 Hz, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 158.5, 148.1, 140.3, 136.8, 135.4, 131.4, 130.8, 129.9, 128.3 (2C), 127.4 (2C), 126.7, 126.5, 126.0, 122.5 (2C), 120.1, 119.3, 50.3, 43.6, 24.5, 24.2.

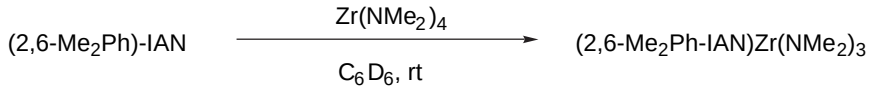



**($^t$Bu-IAN)Zr(NMe$_2$)$_3$ (15d).** $^t$Bu-IAN Amine (9.4 mg, 28.8 µmol) and Zr(NMe$_2$)$_4$ (7.9 mg, 29.5 µmol) were weighed into a flame-dried vial in a glovebox. $d_6$-Benzene was then added and the clear orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.43 (d, *J* = 6.2 Hz, 1H), 7.80 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.16-7.14 (m, 1H), 7.10-7.03 (m, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.85-6.83 (m, 1H), 6.73-6.71 (m, 1H), 3.02 (s, 18H), 1.13 (s, 9H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 159.6, 147.7, 146.5, 141.4, 136.6, 134.6, 130.8, 130.1, 129.6, 129.5, 129.3, 128.2, 127.5, 127.1, 126.7, 126.5, 126.4, 123.6, 120.0, 58.1, 44.2, 32.3.

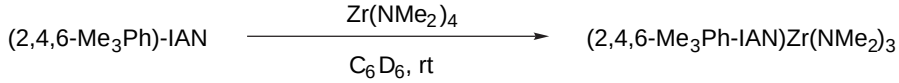



**(Ph-IAN)Zr(NMe$_2$)$_3$ (15e).** Ph-IAN Amine (16.3 mg, 47.1 µmol) and Zr(NMe$_2$)$_4$ (12.6 mg, 47.1 µmol) were weighed into a flame-dried vial in a glovebox. $d_6$-Benzene was then added and the clear orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.17 (d, *J* = 6.2 Hz, 1H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.16-7.11 (m, 4H), 7.09-6.95 (m, 4H), 6.82 (dd, *J* = 8.1, 8.1 Hz, 1H), 6.72 (dd, *J* = 8.1, 8.1 Hz, 1H), 6.68-6.65 (m, 1H), 2.98 (s, 18H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 157.6,

154.2 (2C), 145.6, 140.5, 136.8, 134.7, 131.8, 131.1, 129.6, 129.5 (2C), 128.4, 127.9, 127.7, 126.8, 126.5, 126.1, 124.1, 123.9, 120.8, 119.7, 118.3, 42.8.

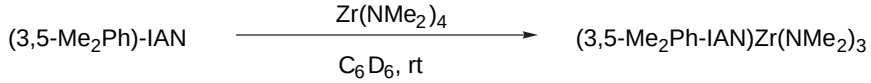



**(2,6-Me$_2$Ph-IAN)Zr(NMe$_2$)$_3$ (15f).** 2,6-Me$_2$Ph-IAN Amine (9.5 mg, 25.4 μmol) and Zr(NMe$_2$)$_4$ (6.8 mg, 25.4 μmol) were weighed into a flame-dried vial in the glovebox. $d_6$-Benzene was then added and the clear red-orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.37 (d, *J* = 6.3 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 9.3 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.09-7.05 (m, 3H), 6.99-6.94 (m, 3H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.82-6.78 (m, 1H), 6.70 (ddd, *J* = 7.8, 7.8, 1.3 Hz, 1H), 2.79 (s, 18H), 2.42 (s, 3H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 169.8, 167.0, 148.2, 139.7, 136.5, 131.2, 131.1, 130.9, 129.3 (2C), 128.9, 128.5, 128.0, 127.2, 126.4, 126.1 (2C), 126.0 (2C), 124.4, 121.8 (2C), 119.3, 118.0, 112.5, 43.1, 19.1, 18.7.

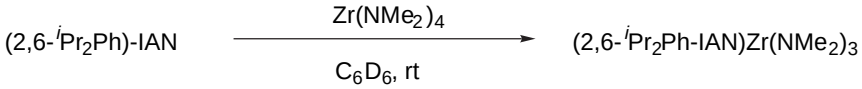



**(2,4,6-Me$_3$Ph-IAN)Zr(NMe$_2$)$_3$ (15g).** 2,4,6-Me$_3$Ph-IAN Amine (12.7 mg, 32.7 μmol) and Zr(NMe$_2$)$_4$ (8.8 mg, 32.9 μmol) were weighed into a flame-dried vial in the glovebox. $d_6$-Benzene was then added and the clear red-orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.39 (d, *J* = 6.2 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.52-7.48 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.11-7.01 (m, 4H), 6.97 (ddd, *J* = 6.8, 6.8, 1.3 Hz, 1H), 6.90-6.87 (m, 2H), 6.81 (ddd, *J* = 7.7, 7.7, 1.3 Hz, 1H), 6.71 (ddd, *J* = 7.0, 7.0, 1.3 Hz, 1H), 2.82 (s, 18H), 2.42 (s, 3H), 2.22 (s, 3H), 1.91 (s, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 161.1, 151.1, 145.2, 139.7, 137.3, 136.8, 136.5, 134.5, 133.1, 131.2, 131.0, 130.9, 129.6, 129.3, 128.0, 127.3 (2C), 127.1, 126.4, 126.04, 125.97,

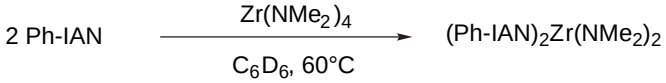
121.8, 119.4, 117.9, 112.6, 43.1, 20.8, 19.0, 18.6.



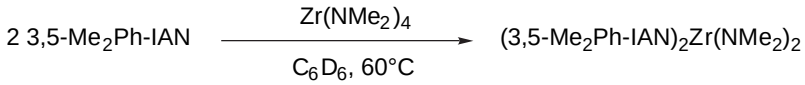

**(3,5-Me$_2$Ph-IAN)Zr(NMe$_2$)$_3$ (15h).** 3,5-Me$_2$Ph-IAN Amine (12.0 mg, 32.0 μmol) and Zr(NMe$_2$)$_4$ (9.1 mg, 34.0 μmol) were weighed into a flame-dried vial in a glovebox. $d_6$-Benzene was then added and the clear orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.23 (d, *J* = 6.0 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.58 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.06-6.99 (m, 4H), 6.87 (s, 2H), 6.85-6.82 (m, 1H), 6.72 (ddd, *J* = 7.3, 7.3, 1.0 Hz, 1H), 6.40 (s, 1H), 3.04 (s, 18H), 2.16 (s, 6H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 157.6, 154.1, 145.8, 140.5, 138.3, 136.8, 134.8, 131.6, 131.0, 129.6, 129.5, 128.4, 128.0, 127.7, 126.8, 126.4, 126.1 (2C), 123.8, 123.5, 120.7, 120.4, 117.9, 42.9, 21.7.



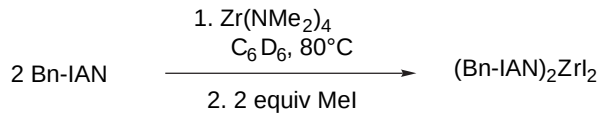

**(2,6-$^i$Pr$_2$Ph-IAN)Zr(NMe$_2$)$_3$ (15i).** 2,6-$^i$Pr$_2$Ph-IAN Amine (18.9 mg, 43.9 μmol) and Zr(NMe$_2$)$_4$ (11.9 mg, 44.5 μmol) were weighed into a flame-dried vial in the glovebox. $d_6$-Benzene was then added and the clear red-orange solution was transferred to a J-Young tube. $^1$H NMR, analyzed 5 min after mixing, revealed complete complexation. $^1$H NMR (400 MHz, $C_6D_6$) δ 8.31 (d, *J* = 6.2 Hz, 1H), 7.52-7.48 (m, 2H), 7.43 (d, *J* = 9.3 Hz, 1H), 7.32 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.18-7.11 (m, 3H), 7.10-6.95 (m, 4H), 6.90 (ddd, *J* = 8.3, 8.3, 1.2 Hz, 1H), 6.65 (ddd, *J* = 7.0, 7.0, 1.2 Hz, 1H), 3.63 (qq, *J* = 6.8, 6.8 Hz, 1H), 2.85 (s, 18 H), 2.27 (qq, *J* = 6.8, 6.8 Hz, 1H), 1.45 (d, *J* = 6.8 Hz, 3H), 1.44 (d, *J* = 6.8 Hz, 3H), 0.65 (d, *J* = 6.8 Hz, 3H), 0.51 (d, *J* = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 158.2, 152.3, 146.8, 146.7, 145.0, 138.3, 137.1, 136.6, 131.3, 130.9, 130.5, 128.6, 127.3, 126.8, 126.7 (3C), 126.2, 125.2, 124.2, 123.8, 122.6, 122.1, 119.4, 109.7, 43.1, 28.6, 28.0, 26.5, 25.0, 24.6, 22.8.




**(Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (16e).** Ph-IAN amine (20.2 mg, 58.3 μmol) and Zr(NMe$_2$)$_4$ (7.8 mg, 29.2 μmol) were combined in a flame dried vial in the glovebox. Benzene was added and the clear red solution was transferred to a J-Young tube and heated in an oil bath at 60°C for 12 h. The solvent was removed, leaving the desired product as a red powder. (A minor product also formed in ~15%). $^1$H NMR (400 MHz, $C_6D_6$) δ 8.77 (d, *J* = 6.2 Hz, 2H), 7.45-7.35 (m, 4H), 7.30-7.19 (m, 6H), 7.10-7.02 (m, 4H), 6.96 (d, *J* = 6.2 Hz, 2H), 6.91-6.80 (m, 6H), 6.71-6.63 (m, 4H), 6.52 (dd, *J* = 8.1, 8.1 Hz, 2H), 6.16 (dd, *J* = 8.1 Hz, 2H), 5.51 (d, *J* = 8.6 Hz, 2H), 2.74 (s, 12H). $^{13}$C NMR (100 MHz, $C_6D_6$) δ 159.2, 155.9, 153.0, 140.4, 136.1, 134.3, 130.7, 130.0, 128.9 (2C), 128.2, 127.9, 127.5, 127.1, 127.0, 126.5, 126.0, 125.7, 124.1 (2C), 122.7, 120.1, 119.1, 46.5.




**(3,5-Me$_2$Ph-IAN)$_2$Zr(NMe$_2$)$_2$ (16h).** 3,5-Me$_2$Ph-IAN Amine (16.3 mg, 42.7 μmol) and Zr(NMe$_2$)$_4$ (6.0 mg, 22.4 μmol) were combined in a flame-dried vial in the glovebox. Benzene was added and the clear red solution was transferred to a J-Young tube and heated in an oil bath at 60°C for 15 h. The solvent was removed, leaving the desired product as a red powder. (A minor product also formed in ~10%). $^1$H NMR (400 MHz, $C_6D_6$) δ 8.86 (d, *J* = 6.4 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.20-7.10 (m, 4H), 7.10 (d, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 6.4 Hz, 2H), 6.84 (dd, *J* = 7.3, 7.3 Hz, 2H), 6.65 (ddd, *J* = 7.3, 7.3, 0.8 Hz, 2H), 6.58 (s, 2H), 6.53 (dd, *J* = 7.3, 7.3, Hz, 2H), 6.17 (dd, *J* = 7.3, 7.3 Hz, 2H), 5.56 (d, *J* = 8.3 Hz, 2H), 2.85 (s, 12H), 2.22 (s, 12H); $^{13}$C NMR (100 MHz, $C_6D_6$) δ 159.3, 155.7, 153.3, 140.5, 137.9, 136.2, 134.3, 130.6, 130.2, 129.8, 129.1, 128.2, 127.4 (2C), 127.2, 126.9, 126.5, 125.9, 123.9, 122.6, 122.5, 122.4, 119.0, 47.0, 21.7.




**(Bn-IAN)$_2$ZrI$_2$ (18b).** Bn-IAN amine (26.5 mg, 73.5 μmol) and Zr(NMe $_2$)$_4$ (10.4 mg, 38.9 μmol) were dissolved in d$_6$-benzene and transferred to a J-Young tube. The clear, red solution was heated at 80 °C for 12 h. Then, MeI (4.6 μL, 73.9 μmol) was added and the solution stirred for 30 min. The solution lightened from a clear deep red to an opaque orange-red, with a large amount of an orange powder present. An X-ray quality crystal was obtained from this d$_6$-benzene solution.