Air Stable, Sterically Hindered Ferrocenyl Dialkylphosphines for Palladium-Catalyzed C-C, C-N and C-O Bond-Forming Cross-Couplings

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Supporting Information

Triphenylamine (Table 1 entries 1 and 2) Following the reaction procedure of Procedure A, triphenylamine was prepared, and had the following characteristics: ^1H -NMR (400 MHz, CDCl_3): δ 7.26 (t, 6H, $J=7.2$ Hz), 7.11 (d, 6H, $J=7.6$ Hz), 7.02 (app.t, 3H, $J=7.2$ and 7.6 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 147.83, 129.17, 124.14, 122.63. GC/MS (EI): m/z 245 (M^+).

***N*-(4-methoxyphenyl)diphenylamine (Table 1, Entry 3):**¹ According to the general procedure A, 4-chloroanisole (130 mg, 0.92 mmol) reacted with diphenylamine (169 mg, 1.00 mmol) at 80°C for 12 h using 1 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(\text{t-Bu})_2$ catalyst and sodium tert-butoxide to give the title compound (270 mg, 99%) as a solid: ^1H -NMR (300 MHz, CDCl_3): δ 7.30 (app.t, 4H, $J=7.5$ and 8.1 Hz), 7.17 (app.t, 6H, $J=8.4$ and 9.0 Hz), 7.04 (app.t, 2H, $J=7.2$ and 6.9 Hz), 6.94 (d, 2H, $J=9.0$ Hz), 3.88 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 156.11, 148.13, 140.74, 129.04, 127.26, 122.84, 121.78, 114.71, 55.44. GC/MS(EI): m/z 275 (M^+).

***N*-(2-tolyl)diphenylamine (Table 1, Entries 4 and 5):**^{1,2} According to the general procedure A, 2-bromotoluene (188 mg, 1.10 mmol) reacted with diphenylamine (169 mg, 1.00 mmol) to give the title compound (258 mg, 99%) as a white solid at room temperature for 4 h. Reaction of 2-chlorotoluene (70 mg, 0.55 mmol) with diphenylamine (85 mg, 0.50 mmol) proceeded at 80°C for 21 h to give the title compound (134 mg, 99%). ^1H -NMR (400 MHz, CDCl_3): δ 7.14-7.27 (m, 8H), 7.01-6.92 (m, 6H), 2.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 147.46, 145.37,

136.49, 131.67, 129.61, 128.99, 127.33, 125.95, 121.50, 121.33, 18.56. GC/MS(EI): m/z 259 (M^+).

***N*-(4-cyanophenyl)diphenylamine (Table 1, Entry 6):**¹

According to the general procedure A, 4-chlorobenzonitrile (76 mg, 0.55 mmol) reacted with diphenylamine (85 mg, 0.50 mmol) using 1 mol % of catalyst and sodium *tert*-butoxide (72 mg, 0.75 mmol) at 45 °C for 21 h to give the title compound (136 mg, 96%) as a white solid: ¹H-NMR (400 MHz, CDCl₃): δ 7.43 (d, 2H, J =8.8 Hz, Ar-H), 7.35 (m, 4H), 7.17 (m, 6H), 6.97 (d, 2H, J =8.8 Hz). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 151.56, 145.93, 133.16, 129.75, 126.14, 125.11, 119.69, 119.67, 102.46. GC/MS(EI): m/z 270 (M^+).

***N*-(2-methoxyphenyl)diphenylamine (Table 1, Entry 7):**² According to the general procedure A, 2-chloroanisole (143 mg, 1.00 mmol) reacted with diphenylamine (177 mg, 1.05 mmol) using 0.5/1.0 mol % of Pd(dba)₂/Ph₅FcP(*t*-Bu)₂ and sodium *tert*-butoxide (106 mg, 1.10 mmol) in toluene (2 mL) at 100 °C for 5 h to give the title compound (270 mg, 95%): ¹H-NMR (400 MHz, CDCl₃): δ 7.11-7.05 (m, 6H), 6.91-6.89 (m, 4H), 6.85-6.79 (m, 4H), 3.51 (s, 3H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 155.59, 147.62, 135.43, 130.10, 128.75, 126.68, 121.51, 121.49, 121.35, 113.18, 55.76. GC/MS(EI): m/z 244 (M^+ -OMe), 182. Anal. Calcd for C₁₉H₁₇NO. C, 82.88; H, 6.22; N, 5.22. Found C, 83.02; H, 6.21; N, 5.22.

***N*-(4-methoxyphenyl)-*N*-methylaniline (Table 2, Entry 1):**¹ According to the general procedure B, 4-chloroanisole (146 mg, 1.02 mmol) reacted with *N*-methylaniline (130 mg, 1.20 mmol) using 0.5 mol % Pd(OAc)₂, 1 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (115 mg, 1.20 mmol) at 100 °C in toluene to give the title compound (203 mg, 93%) as a colorless oil: ¹H-NMR (400 MHz, CDCl₃): δ 7.24 (t, 2H, J =7.3 Hz), 7.13 (d, 2H, J =8.79 Hz), 6.93 (d, 2H, J =8.79 Hz), 6.82 (app.d, 3H, J =7.4 Hz), 3.85 (s, 3H), 3.29 (s, 3H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 156.23, 149.68, 142.15, 128.88, 126.21, 118.27, 115.62, 114.71, 55.46, 40.44. GC/MS(EI): m/z 213 (M^+). Anal. Calcd for C₁₄H₁₅NO: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.98; H, 7.12; N, 6.63.

***N*-(*o*-tolyl)-*N*-methylaniline (Table 2, Entry 2):**³ According to the general procedure B, 2-chlorotoluene (129 mg, 1.02 mmol) reacted with *N*-methylaniline (133 mg, 1.20 mmol) using 0.5 mol % Pd(OAc)₂, 1 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (120 mg, 1.25 mmol) in toluene at 100 °C to give the title compound (180 mg, 89%) as a colorless oil: ¹H-NMR (400 MHz, CDCl₃): δ 7.37-7.21 (m, 6H), 6.78 (t, 1H, J=7.25 Hz), 6.61 (d, 2H, J=7.86 Hz), 3.30 (s, 3H), 2.22 (s, 3H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 149.08, 146.74, 136.80, 131.32, 128.93, 128.30, 127.46, 126.38, 116.72, 112.76, 39.00, 17.83. GC/MS(EI): m/z 197 (M⁺). Anal. Calcd for C₁₄H₁₅N: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.09; H, 7.71; N, 7.24.

***N*-(4-cyanophenyl)-*N*-methylaniline (Table 2, Entry 3):**⁴ According to the general procedure B, 4-chlorobenzonitrile (74 mg, 0.50 mmol) reacted with *N*-methylaniline (64 mg, 0.60 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 45 °C to give the title compound (102 mg, 91%): ¹H-NMR(400 MHz, CDCl₃): δ 7.47-7.39 (m, 4H), 7.28 (t, 1H), 7.21 (d, 2H), 6.74 (d, 2H, J=9.0 Hz), 3.36 (s, 3H). ¹³C{¹H}-NMR(100 MHz, CDCl₃): δ . GC/MS(EI): m/z 208 (M⁺), 192.

***N*-(4-*tert*-butylphenyl)-*N*-methylaniline (Table 2, Entry 4):**⁵ According to general procedure B, 4-*tert*-butylbromobenzene (117 mg, 0.55 mmol) reacted with *N*-methylaniline (54 mg, 0.50 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 100 °C for 2 h to give the title compound (117 mg, 98%): ¹H-NMR (300 MHz, CDCl₃):δ 7.36 (t, 2H, J=8.1 Hz), 7.29 (t, 2H, J=7.5 and 7.8 Hz), 7.04 (dd, 4H, J=8.1 Hz), 6.94 (t, 1H, J=7.2 Hz and 7.5 Hz), 3.34 (s, 3H), 1.38 (s, 9H). ¹³C{¹H}-NMR (100 MHz, CDCl₃):δ 149.17, 146.36, 144.77, 129.02, 126.05, 121.23, 120.18, 118.94, 40.20, 34.18, 31.45. GC/MS(EI): m/z 239 (M⁺), 224

***N*-(2-methylphenyl)morpholine (Table 3, Entry 1):**¹ According to the general procedure B, 2-bromotoluene (171 mg, 1.00 mmol) reacted with morpholine (104 mg, 1.20 mmol) using 1 mol% Pd(dba)₂ and 2 mol% Ph₅FcP(*t*-Bu)₂ and sodium *tert*-butoxide (134 mg, 1.40 mmol) at room temperature for 43 h to give the title compound (70 mg, 40%) as an oil after purification: ¹H-NMR (300 MHz, CDCl₃): δ 7.22-7.18 (m, 2H), 7.06-7.00 (m, 2H), 3.87 (t, 4H, J=4.5 Hz),

2.93 (t, 4H, $J=4.5$ Hz), 2.34 (s, 3H). GC/MS(EI): m/z 177 (M^+). Alternatively, 2-bromotoluene reacted with *n*-hexylamine in the presence of 5 mol% of $\text{Pd}(\text{OAc})_2$ and $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ in toluene at 100°C for 18 h to give the titled compound in 54% yield.

***N*-(4-methoxyphenyl)morpholine (Table 3, Entry 2):**⁶ According to the general procedure B, 4-chloroanisole (82 mg, 0.55 mmol) reacted with morpholine (46 mg, 0.53 mmol) using 1 mol % $\text{Pd}(\text{dba})_2$ and 2 mol% $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and sodium *tert*-butoxide (63 mg, 0.60 mmol) at 70°C for 27 h to give the title compound (97 mg, 95%) as a solid: ^1H -NMR (400 MHz, CDCl_3): δ 6.92-6.85 (m, 4H), 3.87 (t, 4H, $J=4.8$ Hz), 3.78 (s, 3H), 3.07 (t, 4H, $J=4.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 153.92, 145.60, 117.77, 114.47, 67.00, 55.52, 50.78. GC/MS(EI): m/z 193 (M^+).

***N*-(3-methoxyphenyl)morpholine (Table 3, Entry 3):**⁷ According to the general procedure B, 3-bromoanisole (82 mg, 0.44 mmol) reacted with morpholine (36 mg, 0.41 mmol) using 1 mol % $\text{Pd}(\text{dba})_2$ and 2 mol% $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and sodium *tert*-butoxide (42 mg, 0.44 mmol) at 100°C for 21 h to give the title compound (76 mg, 96%) as an oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.21 (t, 1H, $J=8.1$ and 8.7 Hz), 6.57-6.45 (m, 3H), 3.87 (t, 4H, $J=4.5$ and 5.1 Hz), 3.81 (s, 3H), 3.17 (t, 4H, $J=4.5$ and 5.1 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 160.00, 152.67, 129.83, 108.43, 104.68, 102.18, 66.86, 55.15, 49.25. GC/MS(EI): m/z 193 (M^+).

***N*-(4-*tert*-butylphenyl)morpholine (Table 3, Entry 4):**⁶ According to the general procedure B, 4-*tert*-butylbromobenzene (94 mg, 0.44 mmol) reacted with morpholine (36 mg, 0.41 mmol) using 1 mol % $\text{Pd}(\text{dba})_2$ and 2 mol% $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and sodium *tert*-butoxide (42 mg, 0.44 mmol) at 100°C for 21 h to give the title compound (72 mg, 82%) as a white solid: ^1H -NMR (300 MHz, CDCl_3): δ 7.35 (d, 2H, $J=8.7$ Hz), 6.91 (d, 2H, $J=8.7$ Hz), 3.89 (t, 4H, $J=4.5$ and 4.8 Hz), 3.17 (t, 4H, $J=4.5$ and 4.8 Hz), 1.34 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.89, 142.76, 125.95, 115.38, 66.99, 49.54, 33.94, 31.42. GC/MS(EI): m/z 219 (M^+), 204 ($M^+-\text{CH}_3$), 146 ($M^+-\text{morpholine}$).

***N*-(4-methylphenyl)morpholine (Table 3, Entry 5):**⁶ According to the general procedure B, 4-methylchlorobenzene (71 mg, 0.56 mmol) reacted with morpholine (46 mg, 0.53 mmol) using

1 mol % Pd(dba)₂ and 2 mol% Ph₅FcP(*t*-Bu)₂ and sodium *tert*-butoxide (60 mg, 1.03 mmol) at 70 °C for 27 h to give the title compound (92 mg, 98%) as a solid: ¹H-NMR (300 MHz, CDCl₃): δ 7.12 (d, 2H, J=8.7 Hz), 6.87 (d, 2H, J=8.7 Hz), 3.89 (t, 4H, J=4.8 Hz), 3.14 (t, 4H, J=4.8 Hz), 2.31 (s, 3H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 149.09, 129.64, 129.51, 115.97, 66.90, 49.86, 20.38. GC/MS(EI): m/z 177 (M⁺).

***N*-(4-cyanophenyl)morpholine (Table 3, Entry 6):**⁸ According to the general procedure B, 4-chlorocyanobenzene (71 mg, 0.52 mmol) reacted with morpholine (53 mg, 0.61 mmol) using 1 mol % Pd(dba)₂ and 2 mol% Ph₅FcP(*t*-Bu)₂ and sodium *tert*-butoxide (58 mg, 0.60 mmol) at 45 °C for 27 h to give the title compound (77 mg, 82%) as a solid: ¹H-NMR (400 MHz, CDCl₃): δ 7.49 (d, 2H, J=8.0 Hz), 6.85 (d, 2H, J=8.8 Hz), 3.84 (t, 4H, J=4.8 Hz), 3.27 (t, 4H, J=4.8 Hz). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 153.36, 133.36, 119.76, 113.93, 100.69, 66.31, 47.15. GC/MS(EI): m/z 188 (M⁺).

***N,N*-dibutyl-4-*tert*-butylaniline (Table 4, Entry 1):**⁶ According to the general procedure B, 2-*tert*-butylbromobenzene (213 mg, 1.00 mmol) reacted with *N,N*-di-*n*-butylamine (130 mg, 1.00 mmol) using 1 mol % Pd(dba)₂ and 2 mol% Ph₅FcP(*t*-Bu)₂ and sodium *tert*-butoxide (115 mg, 1.20 mmol) at 60 °C to give the title compound (233 mg, 89%) as an oil: ¹H-NMR (300 MHz, CDCl₃): δ 7.25 (d, 2H, J=8.7 Hz), 6.62 (d, 2H, J=8.7 Hz), 3.25 (t, 4H, J=7.2 and 8.1 Hz), 1.58 (m, 4H), 1.35 (M, 4H), 1.30 (s, 9H), 0.97 (t, 6H, J=7.2 Hz). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 146.01, 137.59, 125.92, 111.29, 50.84, 33.61, 31.56, 29.53, 20.39, 14.02. GC/MS(EI): m/z 261 (M⁺).

***N,N*-dibutyl-(4-phenylcarbonyl)aniline (Table 4, Entry 2):** According to the general procedure B, 2-bromobenzophenone (265 mg, 1.02 mmol) reacted with *N,N*-di-*n*-butylamine (146 mg, 1.13 mmol) using 1 mol % Pd(dba)₂ and 2 mol% Ph₅FcP(*t*-Bu)₂ and sodium *tert*-butoxide (116 mg, 1.20 mmol) at room temperature to give the title compound (310 mg, 99%) as an oil: ¹H-NMR (300 MHz, CDCl₃): δ 7.80 (d, 2H, J=8.7 Hz), 7.74 (d, 2H, J=7.5 Hz), 7.51-7.42 (m, 3H), 6.63 (d, 2H, J=9.0 Hz), 3.35 (t, 4H, J=7.5 and 7.8 Hz), 1.62 (m, 4H), 1.38 (m, 4H), 0.98 (t, 6H, J=7.5 and 7.2 Hz). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 194.67, 151.39, 139.40, 132.91,

130.82, 129.25, 127.87, 123.79, 110.08, 50.67, 29.24, 20.19, 13.88. GC/MS (EI): m/z 309 (M^+), 266, 224, 210, 105, 77. Anal. Calcd for $C_{21}H_{27}NO$: C, 81.51; H, 8.79; N, 4.53. Found: C, 81.26; H, 8.89; N, 4.58.

***N,N*-dibutyl-2-methylaniline (Table 4, Entry 3):**¹ According to the general procedure B, 2-bromotoluene (171 mg, 1.00 mmol) reacted with *N,N*-di-*n*-butylamine (129 mg, 1.00 mmol) using 1 mol % $Pd(dba)_2$ and 2 mol% $Ph_5FcP(t-Bu)_2$ and sodium *tert*-butoxide (115 mg, 1.20 mmol) at 60 °C to give the title compound (79 mg, 37%) as an oil: 1H -NMR (300 MHz, $CDCl_3$): δ 7.20-7.08 (m, 3H), 6.98 (app.t, 1H), 2.94 (t, 4H), 1.41 (m, 4H), 1.27 (m, 4H), 0.88 (t, 6H). GC/MS (EI): m/z 219 (M^+).

***N,N*-dibutyl-4-methoxylaniline (Table 4, Entry 4):**⁹ According to the general procedure B, 4-chloroanisole (150 mg, 1.05 mmol) reacted with *N,N*-di-*n*-butylamine (160 mg, 1.24 mmol) using 1 mol % $Pd(dba)_2$ and 2 mol% $Ph_5FcP(t-Bu)_2$ and sodium *tert*-butoxide (120 mg, 1.25 mmol) at 100 °C for 20 h to give the title compound (230 mg, 93%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 6.74 (d, 2H, $J=9.2$ Hz), 6.58 (d, 2H, $J=9.2$ Hz), 3.68 (s, 3H), 3.11 (t, 4H, $J=8.0$ and 7.2 Hz), 1.45 (m, 4H), 1.26 (m, 4H), 0.86 (t, 6H, $J=7.6$ and 7.2 Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 150.96, 143.33, 114.79, 114.33, 55.82, 51.65, 29.46, 20.40, 14.02. GC/MS (EI): m/z 235 (M^+), 235, 192, 150.

***N,N*-dibutyl-4-methylaniline (Table 4, Entry 5):**¹ According to the general procedure B, 4-bromotoluene (94 mg, 0.55 mmol) reacted with *N,N*-di-*n*-butylamine (65 mg, 0.50 mmol) using 1 mol % $Pd(dba)_2$ and 2 mol% $Ph_5FcP(t-Bu)_2$ and sodium *tert*-butoxide (58 mg, 0.60 mmol) at 40 °C for 24 h to give the title compound (102 mg, 93%) as a colorless oil: 1H -NMR (300 MHz, $CDCl_3$): δ 7.07 (d, 2H, $J=8.4$ Hz), 6.64 (d, 2H, $J=8.4$ Hz), 3.28 (t, 4H, $J=7.2$ and 7.8 Hz), 2.30 (s, 3H), 1.60 (m, 4H), 1.40 (m, 4H), 1.00 (t, 6H, $J=7.5$ and 7.2 Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 146.17, 129.67, 124.34, 112.19, 50.99, 29.41, 20.38, 20.12, 14.01. GC/MS(EI): m/z 219 (M^+), 176, 134.

***N,N*-dibutylaniline (Table 4, Entry 6):**¹⁰ According to the general procedure B, chlorobenzene (117 mg, 1.04 mmol) reacted with *N,N*-di-*n*-butylamine (158 mg, 1.21 mmol)

using 0.5 mol % of $\text{Pd}(\text{OAc})_2$ and 1.0 mol % of ligand and sodium *tert*-butoxide (118 mg, 1.20 mmol) at 100 °C for 20 h to give the title compound (200 mg, 94%) as a colorless oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.29 (m, 2H), 6.69-6.75 (m, 3H), 3.35 (t, 4H, $J=7.5$ and 7.8 Hz), 1.66 (m, 4H), 1.44 (m, 4H), 1.05 (t, 6H, $J=7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.09, 129.12, 114.98, 111.58, 50.71, 29.35, 20.33, 13.99. GC/MS(EI): m/z 205 (M^+), 162, 120, 106, 77.

***N,N*-dibutyl-4-cyanoaniline (Table 4, Entry 7):** According to the general procedure B, 4-chlorobenzonitrile (70 mg, 0.51 mmol) reacted with *N,N*-di-*n*-butylamine (77 mg, 0.60 mmol) using 1 mol % $\text{Pd}(\text{dba})_2$ and 2 mol % $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and K_3PO_4 (254 mg, 1.20 mmol) at 100 °C in DME solvent to give the title compound (110 mg, 94%) as a colorless oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.43 (d, 2H, $J=8.7$ Hz), 6.58 (d, 2H, $J=9.0$ Hz), 3.28 (t, 4H, $J=7.5$ and 8.1 Hz), 1.58 (m, 4H), 1.36 (m, 4H), 0.97 (t, 6H, $J=7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 150.59, 133.52, 120.88, 111.01, 96.20, 50.64, 29.08, 20.20, 13.89. GC/MS(EI): m/z 230 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{N}_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.22; H, 9.75; N, 12.29.

***N,N*-dibutyl-3-methylaniline (Table 4, Entry 8):** According to the general procedure B, 3-chlorotoluene (127 mg, 1.00 mmol) reacted with *N,N*-di-*n*-butylamine (155 mg, 1.20 mmol) using 0.5 mol % $\text{Pd}(\text{OAc})_2$, 1 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (115 mg, 1.20 mmol) at 100 °C for 27 h in toluene to give the title compound (208 mg, 94%) as a colorless oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.15 (t, 1H, $J=$ Hz), 6.53 (app.bd, 3H, $J=3.3$ Hz), 3.31 (t, 4H, $J=7.5$ Hz), 2.37 (s, 3H), 1.63 (m, 4H), 1.42 (m, 4H), 1.02 (t, 6H, $J=7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.27, 138.73, 129.02, 116.05, 112.39, 108.94, 50.74, 29.45, 22.02, 20.36, 14.01. GC/MS (EI): m/z 219 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{N}$: C, 82.13; H, 11.49; N, 6.38. Found: C, 81.85; H, 11.57; N, 6.47.

4-Methoxydiphenylamine (Table 5, Entry 1):¹¹ According to the general procedure B, 4-chloroanisole (72 mg, 0.50 mmol) reacted with aniline (47 mg, 0.50 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (59 mg, 0.60 mmol) in toluene at 70 °C for 15 h to give the title compound (96 mg, 95%): ^1H -NMR (300 MHz, CDCl_3): δ 7.26 (t, 2H, $J=8.4$ and 7.5 Hz), 7.12 (d, 2H, $J=8.7$ Hz), 6.86-6.97 (m, 5H), 5.55 (bs, 1H, -NH-), 3.84 (s,

3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 155.15, 145.07, 135.62, 129.25, 122.11, 119.47, 115.54, 114.58, 55.49. GC/MS(EI): m/z 199 (M^+).

2-Methyldiphenylamine (Table 5, Entry 2):¹² According to the general procedure B, 2-chlorotoluene (65 mg, 0.51 mmol) reacted with aniline (48 mg, 0.52 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (60 mg, 0.60 mmol) in toluene at 70 °C for 15 h to give the title compound (92 mg, 97%) as an oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.19-7.27 (m, 4H, Ar-H), 7.14 (dd, 1H, $J=7.2$ and 7.6 Hz), 6.97-6.88 (m, 4H), 5.36 (bs, 1H, -NH-), 2.25 (s, 3H, Ar- CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 143.86, 141.13, 130.88, 129.25, 128.19, 126.69, 121.89, 120.40, 118.65, 117.37, 17.87. GC/MS(EI): m/z 183 (M^+).

4-Cyanodiphenylamine (Table 5, Entry 3):¹³ According to the general procedure B, 4-chlorobenzonitrile (138 mg, 1.00 mmol) reacted with aniline (112 mg, 1.20 mmol) using 0.5 mol % of $\text{Pd}(\text{dba})_2$, 1 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and K_3PO_4 (640 mg, 3.00 mmol) in DME at 100 °C to give the title compound (190 mg, 97%) as a white solid: ^1H -NMR (400 MHz, CDCl_3): δ 7.47 (d, 2H, $J=8.4$ Hz), 7.37 (t, , $J=7.6$ and 8.4 Hz), 7.18 (d, 2H, $J=8.4$ Hz), 7.13 (t, , $J=7.2$ Hz), 6.99 (d, , $J=8.4$ Hz), 6.28 (bs, 1H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 147.99, 139.92, 133.64, 129.51, 123.77, 121.05, 119.96, 114.77, 101.05. GC/MS(EI): m/z 194 (M^+).

Diphenylamine (Table 5, Entries 4 and 5): According to general procedure B, chlorobenzene (57 mg, 0.50 mmol) reacted with aniline (48 mg, 0.50 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (59 mg, 0.60 mmol) in toluene at 70 °C to give the title compound (73 mg, 86%) as a white solid. The coupling reaction of bromobenzene (158 mg, 1.00 mmol) with aniline (93 mg, 1.00 mmol) occurred at room temperature over 4 h using 1 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ to give the title compound (166 mg, 98%): ^1H -NMR (400 MHz, CDCl_3): δ 7.34 (t, 4H, $J=7.8$ Hz and 7.5 Hz), 7.14 (d, 4H, $J=8.7$ Hz), 7.00 (t, 2H, $J=7.2$ and 7.5 Hz), 5.74 (bs, 1H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 143.09, 129.32, 120.97, 117.78. GC/MS(EI): m/z 169 (M^+).

***N*-(4-methoxyphenyl)benzylamine (Table 6, Entry 1):**¹⁴ According to the general procedure A, 4-chloroanisole (73 mg, 0.51 mmol) reacted with benzylamine (68 mg, 0.63 mmol)

using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (60 mg, 0.63 mmol) in toluene at 100 °C for 4 h to give the title compound (100 mg, 93%) as a solid: ¹H-NMR (500 MHz, CDCl₃): δ 6.63 (d, 2H, J=8.84 Hz), 6.81 (d, 2H, J=8.83 Hz), 7.41-7.35 (m, 4H), 7.30 (t, 1H, J=7.08 and 7.03 Hz), 4.31 (s, 2H), 3.77 (s, 3H). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ 152.18, 142.42, 139.66, 128.56, 127.52, 127.14, 114.89, 114.09, 55.78, 49.23. GC/MS(EI): m/z 213 (M⁺).

***N*-(4-methylphenyl)benzylamine (Table 6, Entry 2):**⁶ According to the general procedure A, 4-chlorotoluene (128 mg, 1.01 mmol) reacted with benzylamine (128 mg, 1.19 mmol) using 1 mol % of Pd(OAc)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (122 mg, 1.27 mmol) in toluene at 100 °C to give the title compound (189 mg, 95%) as a colorless oil: ¹H-NMR (400 MHz, CDCl₃): δ 7.43-7.38 (m, 4H), 7.34-7.30 (m, 1H), 7.04 (d, 2H, J=8.26 Hz), 6.61 (d, 2H, J=8.37 Hz), 4.35 (s, 2H), 3.95 (bs, 1H), 2.29 (s, 3H). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 145.85, 139.59, 129.70, 128.55, 127.45, 127.10, 126.68, 112.93, 48.56, 20.37. GC/MS(EI): m/z 197 (M⁺). Anal. Calcd for C₁₄H₁₅N. C, 85.24; H, 7.66; N, 7.10. Found C, 85.29; H, 7.68; N, 7.14.

***N*-(4-cyanophenyl)benzylamine (Table 6, Entry 3):**⁶ According to the general procedure A, 4-chlorobenzonitrile (69 mg, 0.50 mmol) reacted with benzylamine (54 mg, 0.50 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 50 °C for 24 h to give the title compound (81 mg, 76%) as a solid: ¹H-NMR (300 MHz, CDCl₃): δ 7.41 (d, 2H, J=8.7 Hz), 7.36 (m, 5H), 6.61 (d, 2H, J=8.4 Hz), 4.73 (bs, 1H), 4.39 (d, 2H, J=5.4 Hz). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 151.05, 137.76, 133.67, 128.82, 127.64, 127.26, 120.36, 112.36, 98.99, 47.42. GC/MS(EI): m/z 208 (M⁺), 209.

***N*-phenylbenzylamine (Table 6, Entry 4):**⁶ According to the general procedure A, chlorobenzene (58 mg, 0.51 mmol) reacted with benzylamine (68 mg, 0.64 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and sodium *tert*-butoxide (59 mg, 0.60 mmol) in toluene at 100 °C for 5 h to give the title compound (85 mg, 92%) as an oil. ¹H-NMR (300 MHz, CDCl₃): δ 7.42-7.48 (m, 4H), 7.37 (m, 1H), 7.26-7.29 (m, 2H), 6.82 (t, J=7.5 Hz, 1H), 6.73 (d,

$J=8.5$ Hz, 2H), 4.41 (s, 2H), 4.09 (bs, 1H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 8.06, 139.35, 129.19, 128.55, 127.42, 117.46, 112.74, 48.19. GC/MS (EI): m/z 183 (M^+), 184.

***N*-(*o*-tolyl)benzylamine (Table 6, Entry 5):**¹⁵ According to the general procedure A, 2-chlorotoluene (66 mg, 0.52 mmol) reacted with benzylamine (68 mg, 0.64 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (60 mg, 0.63 mmol) in toluene at 100 °C for 4 h to give the title compound (99 mg, 96%) as a solid after recrystallization from hexane: ^1H -NMR (300 MHz, CDCl_3): δ 7.48-7.35 (m, 5H), 7.14 (m, 2H), 6.75 (t, 1H, $J=7.2$ and 7.5 Hz), 6.68 (d, 1H, $J=7.8$ Hz), 4.44 (s, 2H), 3.93 (bs, 1H), 2.24 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ 146.01, 139.46, 130.02, 128.62, 127.50, 127.20, 127.12, 121.86, 117.13, 109.93, 48.26, 17.52. GC/MS(EI): m/z 197 (M^+), 120, 106. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{N}$: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.98; H, 7.64; N, 7.20.

***N*-*n*-hexyl-4-methoxyaniline (Table 7, Entry 1):**^{16,17} According to the general procedure B, 4-chloroanisole (72 mg, 0.50 mmol) reacted with *n*-hexylamine (80 μl , 0.60 mmol) using 2 mol % of $\text{Pd}(\text{OAc})_2$, 4 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (59 mg, 0.60 mmol) in toluene at 70 °C for 18 h to give the title compound (96 mg, 92% as a colorless oil: ^1H -NMR (400 MHz, CDCl_3): δ 6.79 (d, 2H, $J=8.0$ Hz), 6.60 (d, 2H, $J=8.0$ Hz), 3.76 (s, 3H, ArCH_3), 3.07 (t, 2H, $J=6.8$ Hz), 1.61 (m, 2H), 1.39 (m, 2H), 1.33 (m, 2H), 0.91 (t, 3H, $J=6.4$ and 6.8 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 151.92, 142.77, 114.83, 114.02, 55.80, 45.04, 31.66, 29.61, 26.87, 22.62, 14.05. GC/MS(EI): m/z 207 (M^+), 136. Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.56; H, 10.37; N, 6.78.

***N*-*n*-hexyl-2-methylaniline (Table 7, Entries 2):**¹⁸ According to the general procedure B, 2-chlorotoluene (73 mg, 0.58 mmol) reacted with *n*-hexylamine (80 μl , 0.61 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (59 mg, 0.60 mmol) in toluene at 70 °C for 8 h to give the title compound (102 mg, 92%) as a colorless oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.20 (t, 1H, $J=7.5$ and 7.8 Hz), 7.12 (d, 1H, $J=7.2$ Hz), 6.70 (dd, 2H, $J=7.5$ Hz), 3.51 (bs, 1H), 3.22 (t, 2H, $J=7.2$ Hz), 2.21 (s, 3H), 1.74 (m, 2H), 1.48 (m, 2H), 1.41 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 146.35, 129.94, 127.08, 121.60, 116.53, 109.52, 43.91,

31.64, 29.54, 26.90, 22.62, 17.43, 14.03. GC/MS(EI): m/z 191 (M^+), 121. Anal. Calcd for $C_{13}H_{21}N$: C, 81.62; H, 11.06; N, 7.32. Found: C, 81.52; H, 11.09; N, 7.37.

***N*-*n*-hexyl-4-cyanoaniline (Table 7, Entry 3 and 4):**^{19,20} According to the general procedure B, 4-chlorobenzonitrile (69 mg, 0.50 mmol) reacted with *n*-hexylamine (80 μ l, 0.60 mmol) using 1 mol % of $Pd(dba)_2$, 2 mol % of $Ph_5FcP(t-Bu)_2$, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 70 °C for 8 h or at 100 °C for 13 h to give the title compound as a solid (79 mg, 78%). Alternatively, the reaction of 4-chlorobenzonitrile (69 mg, 0.50 mmol) with *n*-hexylamine (61 mg, 0.60) using K_3PO_4 and DME also occurred in 92% yield to afford the title compound (93 mg) at 100 °C for 13 h. 1H -NMR (300 MHz, $CDCl_3$): δ 7.39 (d, 2H, $J=8.4$ Hz), 6.54 (d, 2H, $J=8.7$ Hz), 4.34 (bs, 1H, -NH-), 3.13 (t, 2H, $J=6.9$ and 7.2 Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 151.43, 133.47, 120.60, 111.56, 97.69, 43.03, 31.37, 28.89, 26.55, 22.43, 13.88. GC/MS(EI): m/z 202 (M^+).

***N*-*n*-hexyl-4-phenylcarbonylaniline (Table 7, Entry 5):**²¹ According to the general procedure B, 4-Bromobenzophenone (131 mg, 0.50 mmol) reacted with *n*-hexylamine (52 mg, 0.52 mmol) using 1 mol % of $Pd(dba)_2$, 2 mol % of $Ph_5FcP(t-Bu)_2$, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 50 °C for 13 h to give the title compound (134 mg, 93%) as a solid: 1H -NMR (300 MHz, $CDCl_3$): δ 7.74, (t, 4H, $J=8.4$ Hz), 7.53-7.43 (m, 3H), 6.58 (d, 2H, $J=8.7$ Hz), 4.46 (bs, 1H), 3.17 (t, 2H, $J=6.6$ Hz), 1.61 (m, 2H), 1.42-1.32 (m, 6H), 0.91 (t, 3H, $J=6.6$ Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 195.00, 152.27, 139.11, 132.93, 131.00, 129.30, 127.89, 125.42, 111.02, 43.17, 31.44, 29.09. GC/MS(EI): m/z 281 (M^+).

***N*-*n*-hexyl-4-*tert*-butylaniline (Table 7, Entry 6):**²² According to the general procedure B, 4-*tert*-butylbromobenzene (108 mg, 0.51 mmol) reacted with *n*-hexylamine (80 μ l, 0.60 mmol) using 1 mol % of $Pd(OAc)_2$, 2 mol % of $Ph_5FcP(t-Bu)_2$, and sodium *tert*-butoxide (59 mg, 0.60 mmol) in THF at 80 °C for 9 h to give the title compound (110 mg, 94%) as a colorless oil: 1H -NMR (300 MHz, $CDCl_3$): δ 7.26 (d, 2H, $J=8.4$ Hz), 6.62 (d, 2H, $J=8.4$ Hz), 3.51 (bs, 1H), 3.14 (t, 2H, $J=7.2$ Hz), 1.66 (m, 2H), 1.34-1.43 (m, 6H), 1.34 (s, 9H, *t*-Bu), 0.96 (t, 3H, $J=6.3$ and 6.9 Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 146.14, 139.75, 125.92, 112.35, 44.11, 33.76, 31.63,

31.53, 29.58, 26.86, 22.62, 14.05. GC/MS(EI): m/z 233 (M^+). Anal. Calcd for $C_{16}H_{27}N$: C, 82.34; H, 11.82; N, 6.00. Found: C, 82.55; H, 11.82; N, 6.06.

***N*-*n*-hexyl-3-methoxyaniline (Table 7, Entries 7 and 8):** 3-Chloroanisole (74 mg, 0.52 mmol) reacted with *n*-hexylamine (65 mg, 0.64 mmol) according to procedure B using 1 mol % of $Pd(dba)_2$, 2 mol % of $Ph_5FcP(t-Bu)_2$, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 100 °C for 24 h to give the title compound (103 mg, 95%) as a colorless oil. Also 3-bromoanisole was converted to the title amine after 10 h at 100 °C in 85% isolated yield by procedure A: 1H -NMR (400 MHz, $CDCl_3$): δ 6.99 (t, 1H, $J=8.0$ Hz), 6.19-6.13 (m, 2H), 6.08 (app.t, 1H, $J=2.4$ Hz), 3.70 (s, 3H), 3.55 (bs, 1H), 3.01 (t, 2H, $J=7.2$ Hz), 1.53 (m, 2H), 1.33 (m, 2H), 1.24 (m, 4H), 0.83 (t, 3H, $J=6.8$ Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 160.81, 149.91, 129.87, 105.86, 102.09, 98.53, 55.01, 43.95, 31.61, 29.47, 26.81, 22.60, 14.01. GC/MS(EI): m/z 207 (M^+), 136. Anal. Calcd for $C_{13}H_{21}NO$: C, 75.23; H, 10.21; N, 6.76. Found: C, 75.25; H, 10.33; N, 6.86.

***N*-*n*-hexyl-2,5-dimethylaniline (Table 7, Entry 9):**⁸ According to the general procedure B, 2-Chloro-*p*-xylene (73 mg, 0.52 mmol) reacted with *n*-hexylamine (62 mg, 0.61 mmol) using 1 mol % of $Pd(dba)_2$, 2 mol % of $Ph_5FcP(t-Bu)_2$, and sodium *tert*-butoxide (60 mg, 0.63 mmol) in toluene at 100 °C for 10 h to give the title compound (90 mg, 87%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 7.00 (d, 1H, $J=7.2$ Hz), 6.54 (d, 1H, $J=7.6$ Hz), 6.51 (s, 1H), 3.45 (bs, 1H), 3.20 (dd, 2H, $J=6.8$ and 7.2 Hz), 2.37 (s, 3H), 2.16 (s, 3H), 1.73 (m, 2H), 1.49 (m, 2H), 1.41 (m, 4H), 0.99 (t, 1H, $J=6.8$ and 7.2 Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 146.23, 136.65, 129.77, 118.61, 117.14, 110.46, 43.92, 31.63, 29.56, 26.90, 22.63, 21.54, 16.98, 14.03. GC/MS(EI): m/z 205 (M^+).

***N*-(2,6-dimethylphenyl)-*n*-hexylamine (Table 7, Entry 10):**⁹ According to the general procedure B, 2-Chloro-*m*-xylene (70 mg, 0.50 mmol) reacted with *n*-hexylamine (80 μ l, 0.60 mmol) using 2 mol % of $Pd(OAc)_2$, 4 mol % of $Ph_5FcP(t-Bu)_2$, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene (1.5 mL) at 100 °C for 10 h to give the title compound (100 mg, 97%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 7.02 (d, 2H, $J=7.2$ Hz), 6.83 (t, 1H, $J=7.2$ Hz), 3.00

(t, 2H, J=7.2 and 7.6 Hz), 3.0 (bs, 1H), 2.32 (s, 6H), 1.61 (m, 2H), 1.45-1.31 (m, 6H), 0.93 (t, 3H, J=5.6 and 7.2 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 146.37, 129.05, 128.75, 121.52, 48.69, 31.73, 31.14, 26.83, 22.62, 18.54, 14.03. GC/MS(EI): m/z 205 (M^+).

***N*-*n*-hexyl-2-methoxyaniline (Table 7, Entry 11):** According to the general procedure B, 2-Chloroanisole (72 mg, 0.51 mmol) reacted with *n*-hexylamine (80 μl , 0.60 mmol) using 1 mol % of $\text{Pd}(\text{OAc})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 100 °C for 16 h to give the title compound (102 mg, 97%) as a colorless oil: ^1H -NMR (400 MHz, CDCl_3): δ 6.93 (t, 1H, J=8.0 Hz, aryl coupling J=0.9 Hz), 6.82 (d, 1H, J=8.0 Hz), 6.66-6.73 (m, 2H), 4.30 (bs, 1H), 3.89 (s, 3H), 3.17 (t, 2H, J=7.2 Hz), 1.71 (m, 2H), 1.51-1.34 (m, 6H), 0.97 (t, 3H, J=6.4 and 6.8 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 146.65, 138.39, 121.23, 116.03, 109.71, 109.24, 55.29, 43.63, 31.63, 29.43, 26.88, 22.58, 14.00. GC/MS(EI): m/z 207 (M^+). Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}$: C, 75.23; H, 10.21; N, 6.76. Found: C, 75.41; H, 10.25; N, 6.69.

2-(3-(*N*-*n*-hexyl)aminophenyl)-1,3-dioxolane (Table 7, Entry 12): According to the general procedure B, 2-(3-bromophenyl)-1,3-dioxolane (115 mg, 0.50 mmol) reacted with *n*-hexylamine (80 μl , 0.60 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (58 mg, 0.60 mmol) in toluene at 100 °C for 16 h to give the title compound (118 mg, 94%) as a colorless oil: ^1H -NMR (300 MHz, CDCl_3): δ 7.19 (t, 1H, J=7.8 Hz), 6.81 (d, 1H, J=6.9 Hz), 6.74 (s, 1H), 6.61 (m, 1H), 5.77 (s, 1H), 4.13 (m, 2H), 4.03 (m, 2H), 3.55 (bs, 1H), 3.13 (t, 2H, J=6.9 and 7.2 Hz), 1.62 (m, 2H), 1.45-1.33 (m, 6H), 0.92 (t, 3H, J=6.0 and 6.9 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.53, 138.85, 129.21, 115.07, 113.48, 110.31, 103.88, 65.15, 43.98, 31.58, 29.43, 26.78, 22.59, 14.01. GC/MS (EI): m/z 249 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.19; H, 9.43; N, 5.70.

***N,N*-di(4-*tert*-butylphenyl)-*n*-hexylamine (Table 7, Entry 13):** According to the general procedure B, 4-*tert*-butylbromobenzene (214 mg, 1.00 mmol) reacted with *n*-hexylamine (66 μl , 0.50 mmol) using 1 mol % of $\text{Pd}(\text{OAc})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and sodium *tert*-butoxide (116 mg, 1.21 mmol) in toluene at 100 °C for 4 h to give the title compound (182 mg, 99%) as

an oil: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.17 (d, 4H, $J=8.4$ Hz), 6.82 (d, 4H, $J=8.8$ Hz), 3.55 (t, 2H, $J=7.2$ and 8.0 Hz), 1.57 (m, 2H), 1.22 (s, 18H), 0.79 (t, 3H, $J=6.4$ and 6.8 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 145.68, 143.41, 125.93, 120.20, 52.38, 34.06, 31.67, 31.49, 27.55, 26.78, 22.70, 14.05. GC/MS(EI): m/z 365 (M^+). Anal. Calcd for $\text{C}_{26}\text{H}_{39}\text{N}$: C, 85.42; H, 10.75; N, 3.83. Found: C, 85.22; H, 10.82; N, 3.86.

***N*-(4-methoxycarbonylphenyl)-*n*-hexylamine (Table 8, Entry 1):** According to the general procedure B, Methyl 4-chlorobenzoate (85 mg, 0.50 mmol) reacted with *n*-hexylamine (80 μL , 0.60 mmol) using 2 mol % of $\text{Pd}(\text{dba})_2$, 4 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, K_3PO_4 (260 mg, 1.23 mmol) in toluene at 100 $^\circ\text{C}$ for 20 h to give the title compound (101 mg, 86%) as a solid: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.90 (d, 2H, $J=8.8$ Hz), 6.54 (d, 2H, $J=8.8$ Hz), 4.17 (bs, 1H), 3.85 (s, 3H, -COOMe), 3.15 (dd, 2H, $J=7.0$ and 12.3 Hz), 1.62 (m, 2H), 1.40 (m, 2H), 1.32 (m, 2H), 0.91 (t, 3H, $J=6.9$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ 167.31, 152.13, 131.47, 117.85, 111.22, 51.38, 43.30, 31.50, 29.21, 26.68, 22.52, 13.94. GC/MS(EI): m/z 235 (M^+), 164. Anal. Calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.54; H, 8.84; N, 5.79.

***N*-(4-methoxycarbonylphenyl)-*N*-methylaniline (Table 8, Entry 2):** According to the general procedure B, methyl 4-chlorobenzoate (172 mg, 1.00 mmol) reacted with *N*-methylaniline (130 mg, 1.20 mmol) using 1 mol % of $\text{Pd}(\text{OAc})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and K_3PO_4 (640 mg, 3.02 mmol) in DME at 100 $^\circ\text{C}$ for 20 h to give the title compound (240 mg, 97%) as a solid: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 7.89 (d, 2H, $J=9.05$ Hz), 7.41 (t, 2H, $J=7.68$ and 8.17 Hz), 7.24-7.21 (m, 3H), 6.79 (d, 2H, $J=9.06$ Hz), 3.88 (s, 3H), 3.37 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ 167.09, 152.44, 147.41, 130.91, 129.70, 125.50, 125.24, 119.08, 113.70, 51.47, 40.09. GC/MS(EI): m/z 241 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.74; H, 6.34; N, 5.80.

4-Methoxycarbonylphenyldiphenylamine (Table 8, Entry 3):²³ According to the general procedure A, methyl 4-chlorobenzoate (88 mg, 0.52 mmol) reacted with aniline (57 mg, 0.61 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2$, 2 mol % of $\text{Ph}_5\text{FcP}(t\text{-Bu})_2$, and K_3PO_4 (260 mg, 1.23 mmol) in DME at 100 $^\circ\text{C}$ for 24 h to give the title compound (111 mg, 96%) as a solid: $^1\text{H-NMR}$ (400

MHz, CDCl₃): δ 7.94 (d, 2H, J=7.6 Hz), 7.35 (t, 2H, J=6.0 and 7.6 Hz), 7.19 (d, 2H, J=7.6 Hz), 7.08 (t, 1H, J=7.6 Hz), 7.01 (d, 2H, J=8.8 Hz), 6.27 (bs, 1H), 3.89 (s, 3H). ¹³C{¹H}-NMR(100 MHz, CDCl₃): δ 166.97, 148.06, 140.75, 131.36, 129.37, 122.91, 120.74, 120.27, 114.41, 51.65. GC/MS(EI): m/z 227 (M⁺).

***N,N*-Di-*n*-butyl(4-methoxycarbonyl)aniline (Table 8, Entry 4):** According to the general procedure A, methyl 4-chlorobenzoate (86 mg, 0.50 mmol) reacted with di-*n*-butylamine (77 mg, 0.60 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and K₃PO₄ (255 mg, 1.20 mmol) in DME at 100 °C to give the title compound (128 mg, 96%) as an oil: ¹H-NMR (400 MHz, CDCl₃): δ 7.87 (d, 2H, J=8.8 Hz), 6.58 (d, 2H, J=8.8 Hz), 3.85 (s, 3H), 3.32 (t, 4H, J=7.6 and 8.0 Hz), 1.60 (m, 4H), 1.37 (m, 4H), 0.97 (t, 6H, J=7.2 and 7.6 Hz). ¹³C{¹H}-NMR (100 MHz, CDCl₃): δ 167.40, 151.26, 131.36, 115.78, 110.13, 51.33, 50.63, 29.20, 20.20, 13.91. GC/MS(EI): m/z 232 (M⁺-OMe), 220 (M⁺-propyl), 178. Anal. Calcd for C₁₆H₂₅NO₂: C, 72.96; H, 9.57; N, 5.32. Found: C, 73.06; H, 9.44; N, 5.35.

4-Nitrophenylmorpholine (Table 8, Entry 5):²⁴ According to the general procedure B, 4-chloronitrobenzene (80 mg, 0.51 mmol) reacted with morpholine (53 mg, 0.60 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and K₃PO₄ (256 mg, 1.21 mmol) in DME at 100 °C to give the title compound (58 mg, 56%) as a yellow solid: ¹H-NMR (400 MHz, CDCl₃): δ 8.11 (d, 2H, J=9.6 Hz), 6.82 (d, 2H, J=9.6 Hz), 3.85 (t, 4H, J=5.2 Hz), 3.37 (t, 4H, J=5.2 Hz). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ 154.91, 138.80, 125.76, 112.50, 66.26, 47.00. GC/MS(EI): m/z 208 (M⁺).

4-Nitrodiphenylamine (Table 8, Entry 6): According to the general procedure B, 4-chloronitrobenzene (80 mg, 0.51 mmol) reacted with aniline (57 mg, 0.60 mmol) using 1 mol % of Pd(dba)₂, 2 mol % of Ph₅FcP(*t*-Bu)₂, and K₃PO₄ (254 mg, 1.21 mmol) in DME at 100 °C to give the title compound (102 mg, 95%) as a yellow solid: ¹H-NMR (400 MHz, CDCl₃): δ 8.12 (d, 2H, J=7.2 Hz), 7.40 (t, 2H, J=7.2 and 8.8 Hz), 6.96 (d, 2H, J=7.2 Hz), 7.24-7.18 (m, 3H), 6.48 (bs, 1H). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ 150.26, 139.51, 139.44, 129.64, 126.18, 124.54,

121.83, 113.59. GC/MS(EI): m/z 214 (M^+). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.45; H, 4.75; N, 13.02.

Reactions of Aryl Halides with Boronic Acids:

4-(2-Methylphenyl)benzophenone (Table 10, Entry 1): Prepared as described in the general procedure A. 1H -NMR (300 MHz, $CDCl_3$): δ 7.91 (m, 4H), 7.60-7.50 (m, 5H), 7.33 (m, 4H), 2.35 (s, 3H, Ar- CH_3). GC/MS(EI): m/z 272 (M^+). Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.47; H, 6.09.

4-Phenylbenzophenone (Table 10, Entry 2):²⁵ According to the general procedure, 4-Bromobenzophenone (131 mg, 0.50 mmol) reacted with phenylboronic acid (92 mg, 0.75 mmol) using 0.0005 mol % of $Pd(dba)_2$, 0.002 mol % of $Ph_5FcP(t-Bu)_2$, and K_3PO_4 (318 mg, 1.50 mmol) in toluene solvent at 100°C for 1 h to give the title compound (121 mg, 94%) as a solid: 1H -NMR (400 MHz, $CDCl_3$): δ 7.92 (d, 2H, $J=8.4$ Hz), 7.87 (d, 2H, $J=7.2$ Hz), 7.73 (d, 2H, $J=8.4$ Hz), 7.18 (d, 2H, $J=6.8$ Hz), 7.63 (m, 1H), 7.51 (m, 3H), 7.43 (m, 2H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 196.30, 145.16, 139.89, 137.68, 136.15, 132.34, 130.69, 129.96, 128.92, 128.26, 128.14, 127.25, 126.91. GC/MS(EI): m/z 181 ($M-77^+$). Anal. Calcd for $C_{19}H_{14}O$: C, 88.34; H, 5.46. Found: C, 88.26; H, 5.62.

4-(4-Trifluoromethylphenyl)benzonitrile (Table 10, Entry 3):²⁶ 4-Chlorobenzonitrile (141 mg, 1.02 mmol) reacted with *p*-trifluoromethylphenylboronic acid using by 1/2 mol % of $Pd(OAc)_2/Ph_5FcP(t-Bu)_2$ and KF (182 mg, 3.00 mmol) in THF solvent to give the title compound (236 mg, 96%) as a white solid after recrystallization from hexane: 1H -NMR (500 MHz, $CDCl_3$): δ 7.78 (d, 2H, $J=8.23$ Hz), 7.76 (d, 2H, $J=8.48$ Hz), 7.71 (app.d, 4H, $J=8.18$ Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 111.92, 118.57, 142.61, 144.09, 123.95 (q, $J=270.2$ Hz), 126.04 (q, $J=3.6$ Hz), 127.60, 127.93, 130.63 (q, $J=32.5$ Hz), 132.76. $^{19}F\{^1H\}$ -NMR ($CDCl_3$): δ -63.0. GC/MS(EI): m/z 247 (M^+).

4-(4-Methoxyphenyl)benzonitrile (Table 10, Entry 4):²⁷ 4-Chlorobenzonitrile (140 mg, 1.02 mmol) reacted with *p*-methoxyphenylboronic acid (200 mg, 1.32 mmol) using 1/2 mol % of $Pd(OAc)_2/Ph_5FcP(t-Bu)_2$ and KF (182 mg, 3.00 mmol) in THF solvent to give the title compound

(197 mg, 94%) as white solid after recrystallization from hexane: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.70 (d, 2H, $J=8.41$ Hz), 7.65 (d, 2H, $J=8.40$ Hz), 7.55 (d, 2H, $J=8.80$ Hz), 7.02 (d, 2H, $J=8.79$ Hz), 3.88 (s, 3H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, CDCl_3): δ 160.18, 145.17, 132.52, 131.45, 128.31, 127.06, 119.04, 114.52, 110.07, 55.35. GC/MS(EI): m/z (M^+).

4-(4-Cyanophenyl)benzaldehyde (Table 10, Entry 5):²⁶ 4-Bromobenzonitrile (73 mg, 0.40 mmol) reacted with 4-formylphenylboronic acid (90 mg, 0.60 mmol) using 0.5/1.0 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (70 mg, 1.21 mmol) in THF solvent at 40°C to give the title compound (83 mg, 97%) as a white solid: $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 10.10 (s, 1H), 8.01 (d, 2H, $J=8.25$ Hz), 7.80-7.74 (m, 6H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, CDCl_3): δ 191.57, 144.90, 144.14, 136.14, 132.78, 130.41, 128.03, 127.91, 118.52, 112.17. GC/MS(EI): m/z 207 (M^+), 206.

4-(4-Methoxyphenyl)nitrobenzene (Table 10, Entry 6):^{28,29} 4-Chloronitrobenzene (164 mg, 1.04 mmol) reacted with *p*-methoxyphenylboronic acid (200 mg, 1.32 mmol) using 1/2 mol % of $\text{Pd}(\text{OAc})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (182 mg, 3.00 mmol) in THF solvent at 50°C for 17 h to give the title compound (234 mg, 98%) as a solid: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.27 (d, 2H, $J=8.76$ Hz), 7.69 (d, 2H, $J=8.76$ Hz), 7.59 (d, 2H, $J=8.70$ Hz), 7.03 (d, 2H, $J=8.71$ Hz), 3.88 (s, 3H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3): δ 160.40, 147.15, 146.47, 130.99, 128.52, 127.01, 124.10, 114.56, 55.39. GC/MS(EI): m/z 139, 229 (M^+).

4-(2-Methylphenyl)nitrobenzene (Table 10, Entry 7):³⁰ 4-Chloronitrobenzene (80 mg, 0.51 mmol) reacted with *o*-methylphenylboronic acid (85 mg, 0.63 mmol) using 0.5/1.0 mol % of $\text{Pd}(\text{OAc})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (87 mg, 1.55 mmol) in THF solvent at 50°C for 22 h to give the title compound (107 mg, 98%): $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ 8.30 (d, 2H, $J=6.90$ Hz, aryl coupling 1.8 Hz), 7.51 (d, 2H, $J=6.92$ Hz, aryl coupling 1.8 Hz), 7.35-7.23 (m, 4H), 2.29 (s, 3H, Ar- CH_3). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, CDCl_3): δ 148.80, 146.86, 139.60, 135.04, 130.70, 130.09, 129.39, 128.45, 126.11, 123.40, 20.31. GC/MS(EI): m/z 213 (M^+), 165, 152.

4-(4-Chlorophenyl)benzaldehyde (Table 10, Entry 8):³¹ 4-Bromobenzaldehyde (95 mg, 0.51 mmol) reacted with 4-chlorophenylboronic acid (101 mg, 0.65 mmol) using 0.5/1.0 mol %

of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (87 mg, 1.55 mmol) in THF solvent at room temperature to give the title compound (110 mg, 99%) as a white solid: ^1H -NMR (400 MHz, CDCl_3): δ 10.07 (s, 1H, -CHO), 7.96 (d, 2H, $J=7.04$ Hz), 7.73 (d, 2H, $J=7.04$ Hz), 7.58 (d, 2H, $J=7.16$ Hz), 7.46 (d, 2H, $J=7.27$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 191.80, 145.84, 138.10, 135.35, 134.70, 130.34, 129.20, 128.58, 127.51. GC/MS(EI): m/z 216 (M^+), 218, 152.

2-Methylbiphenyl (Table 10, Entry 9):³² 2-Bromobenzene (80 mg, 0.51 mmol) reacted with 2-methylphenylboronic acid (90 mg, 0.66 mmol) using 1.0 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (87 mg, 1.55 mmol) in THF solvent at room temperature to give the title compound (80 mg, 95%) as a colorless oil: ^1H -NMR (400 MHz, CDCl_3): δ 7.51-7.47 (m, 2H), 7.44-7.40 (m, 3H), 7.36-7.32 (m, 4H), 2.36 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 141.91, 141.89, 135.30, 130.27, 129.76, 129.16, 128.03, 127.22, 126.72, 125.73, 20.46. GC/MS(EI): m/z 168 (M^+), 153.

4-Methoxybiphenyl (Table 10, Entry 10):³³ Bromobenzene (79 mg, 0.50 mmol) reacted with 4-methoxyphenylboronic acid (99 mg, 0.65 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (87 mg, 1.50 mmol) in THF solvent at room temperature to give the title compound (87 mg, 95%) as a white solid. The reaction of 4-chloroanisole (71 mg, 0.50 mmol) with phenylboronic acid (92 mg, 0.75 mmol) gave the title compound (74 mg, 80%) using 1/2 mol% of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF in THF solvent at 40°C. ^1H -NMR (400 MHz, CDCl_3): δ 7.61 (m, 4H), 7.48 (t, 2H, $J=7.6$ Hz), 7.37 (app.t, 1H, $J=7.2$ Hz), 7.04 (d, 2H, $J=8.8$ Hz), 3.90 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 159.09, 140.76, 133.69, 128.66, 128.08, 126.67, 126.60, 114.14, 55.26. GC/MS(EI): m/z 184 (M^+). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.75; H, 6.56. Found: C, 84.86; H, 6.76.

1-Phenylnaphthalene (Table 10, Entry 11):^{34,35} Bromobenzene (82 mg, 0.52 mmol) reacted with 1-naphthylboronic acid (110 mg, 0.64 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (90 mg, 1.55 mmol) in THF (2 mL) at room temperature to give the title compound (106 mg, 99%) as a colorless oil: ^1H -NMR (400 MHz, CDCl_3): δ 7.99-7.91 (m, 3H), 7.60-7.47 (m, 9H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 140.71, 140.21, 133.75, 131.57, 130.05, 128.23, 127.60,

127.21, 126.90, 125.99, 125.74, 125.36. GC/MS(EI): m/z 204 (M^+). Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 93.96; H, 6.11.

1,1'-Bisnaphthalene (Table 10, Entry 12):³⁶ 1-Bromonaphthalene (108 mg, 0.52 mmol) reacted with 1-naphthylboronic acid (112 mg, 0.65 mmol) using 1 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (87 mg, 1.50 mmol) in THF (2 mL) at room temperature to give the title compound (128 mg, 97%) as a solid: 1H -NMR (400 MHz, $CDCl_3$): δ 7.98 (d, 1H, $J=3.45$ Hz), 7.96 (d, 1H, $J=3.39$ Hz), 7.61 (t, 1H, $J=7.30$ and 7.83 Hz), 7.52-7.47 (m, 2H), 7.41 (d, 1H, $J=8.36$ Hz), 7.31 (t, 1H, $J=7.39$ and 7.62 Hz). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 138.43, 133.49, 132.82, 128.12, 127.87, 127.81, 126.54, 125.95, 125.78, 125.36. GC/MS(EI): m/z (M^+).

4-Chloro-1,1'-biphenyl (Table 10, Entry 13):^{37,38} Bromobenzene (80 mg, 0.51 mmol) reacted with 4-chlorophenylboronic acid (103 mg, 0.66 mmol) using 0.5/1.0 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and K_3PO_4 (318 mg, 1.50 mmol) in toluene at 100 °C for 17 h to give the title compound (75 mg, 78%) as a white solid: 1H -NMR (400 MHz, $CDCl_3$): δ 7.41-7.62 (m, 9H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 139.95, 139.62, 133.33, 128.88, 128.86, 128.36, 127.56, 126.96. GC/MS(EI): m/z 188 (M^+), 152

2, 2'-Dimethyl-1,1'-biphenyl (Table 10, Entry 14):^{39,40} 2-Bromotoluene (87 mg, 0.51 mmol) reacted with 2-methylphenylboronic acid (88 mg, 0.65 mmol) using 1 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (87 mg, 1.50 mmol) in THF solvent at room temperature for 14 h to give the title compound (91 mg, 98%) as a colorless oil: 1H -NMR (300 MHz, $CDCl_3$): δ 7.29-7.35 (m, 6H), 7.20 (d, 2H, $J=6.3$ Hz), 2.15 (s, 6H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 141.56, 135.76, 129.77, 129.25, 127.12, 125.51, 19.81. GC/MS(EI): m/z 182 (M^+).

2-Methoxy-2'-methyl-1,1'-biphenyl (Table 11, Entry 1): 2-Bromoanisole (187 mg, 1.00 mmol) reacted with 2-methylphenylboronic acid (150 mg, 1.10 mmol) using 1 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (116 mg, 2.0 mmol) in toluene at 100°C to give the title compound (193 mg, 98%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 7.43 (t, 1H, $J=8.2$ Hz, aryl coupling $J=1.75$ Hz), 7.36-7.24 (m 5H), 7.10 (t, 1H, $J=7.4$ Hz, aryl coupling 0.91 Hz), 7.05 (d, 1H, $J=8.2$ Hz), 3.84 (s, 3H), 2.24 (s, 3H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 156.53,

138.58, 136.77, 130.95, 130.77, 129.95, 129.52, 128.51, 127.25, 125.40, 120.38, 110.56, 55.31, 19.89. GC/MS(EI): m/z 198 (M^+). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.97; H, 7.11.

2-Methoxy-4'-chloro-1,1'-biphenyl (Table 11, Entry 2): 2-Bromoanisole (97 mg, 0.52 mmol) reacted with 4-chlorophenylboronic acid (102 mg, 0.65 mmol) using 0.5/1.0 mol % of $Pd(dba)_2/Ph_3FcP(t-Bu)_2$ and KF (88 mg, 1.57 mmol) in THF (2 mL) at room temperature to give the title compound (108 mg, 95%): 1H -NMR (400 MHz, $CDCl_3$): δ 7.51 (d, 2H, $J=8.4$ Hz), 7.42 (d, 2H, $J=8.0$ Hz), 7.46-7.32 (m, 2H), 7.08 (t, 1H, $J=7.6$ Hz, aryl coupling $J=1.2$ Hz), 7.03 (d, 1H, $J=8.0$ Hz), 3.85 (s, 3H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 156.27, 136.86, 132.79, 130.81, 130.60, 129.33, 128.94, 128.10, 120.85, 111.16, 55.47. GC/MS(EI): m/z 218 (M^+), 220 (M^++2 , Cl isotope peak), 168, 139. Anal. Calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.07. Found: C, 71.47; H, 5.21.

1-(3-Methoxyphenyl)naphthalene (Table 11, Entry 3):⁴¹ 3-Bromoanisole (75 mg, 0.40 mmol) reacted with 1-naphthylboronic acid (103 mg, 0.60 mmol) using 0.5/1.0 mol % of $Pd(dba)_2/Ph_3FcP(t-Bu)_2$ and KF (70 mg, 1.20 mmol) in 1,2-dioxane at 100°C to give the title compound (108 mg, 99%) as a colorless oil: 1H -NMR (500 MHz, $CDCl_3$): δ 7.96 (d, 2H, $J=8.49$ Hz), 7.93 (d, 2H, $J=7.96$ Hz), 7.89 (d, 2H, $J=8.20$ Hz), 7.56-7.50 (m, 2H), 7.48-7.41 (m, 3H), 7.13-7.11 (m, 1H), 7.08 (m, 1H), 7.03-7.00 (m, 1H), 3.88 (s, 3H). $^{13}C\{^1H\}$ -NMR (125 MHz, $CDCl_3$): δ 159.45, 142.15, 140.09, 133.75, 131.57, 129.20, 128.22, 127.67, 126.74, 126.04, 126.01, 125.75, 125.31, 122.57, 115.61, 112.86, 55.28. GC/MS(EI): m/z 234 (M^+), 203, 189.

2-Methyl-3',4'-methylenedioxy-1,1'-biphenyl (Table 11, Entry 4): 4-Bromo-1,2-(methylenedioxy)benzene (201 mg, 1.02 mmol) reacted with 2-methylphenylboronic acid (150 mg, 1.10 mmol) using 1 mol % of $Pd(dba)_2/Ph_3FcP(t-Bu)_2$ and KF (116 mg, 2.00 mmol) in toluene at room temperature for 3 h to give the title compound (218 mg, 99%) : 1H -NMR (300 MHz, $CDCl_3$): δ 7.31-7.27 (m, 4H), 6.94-6.82 (m, 3H), 6.04 (s, 2H), 2.35 (s, 3H). $^{13}C\{^1H\}$ -NMR (125 MHz, $CDCl_3$): δ 147.24, 146.39, 141.52, 135.84, 135.42, 130.26, 129.79, 127.10, 125.69,

122.44, 109.76, 107.98, 100.95, 20.45. GC/MS(EI): m/z 212 (M^+), 181, 153. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.23; H, 5.70. Found: C, 79.36; H, 5.73.

4-Formyl-3',4'-methylenedioxybiphenyl (Table 11, Entry 5): 4-Bromo-1,2-(methylenedioxy)benzene (80 mg, 0.40 mmol) reacted with 4-chlorophenylboronic acid (90 mg, 0.60 mmol) using 1/2 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (70 mg, 1.20 mmol) in 1,2-dioxane at 100 °C to give the title compound (77 mg, 85%) as a solid: 1H -NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1H), 7.93 (d, 2H, $J=8.0$ Hz), 7.68 (d, 2H, $J=7.6$ Hz), 7.14 (d, 2H), 7.13 (bs, 1H), 6.04 (s, 2H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 191.84, 148.38, 148.08, 146.81, 134.83, 133.88, 130.28, 127.26, 121.25, 108.78, 107.63, 101.41. GC/MS(EI): m/z 226 (M^+), 139. Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.19; H, 4.67.

2-Methyl-4'-tert-butylbiphenyl (Table 11, Entry 6): 4-*tert*-butylbromobenzene (220 mg, 1.03 mmol) reacted with 2-methylphenylboronic acid (178 mg, 1.31 mmol) using 1 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and K_3PO_4 (424 mg, mmol) in toluene at 80 °C to give the title compound (223 mg, 97%) as a colorless oil: 1H -NMR (300 MHz, $CDCl_3$): δ 7.49 (d, 2H, $J=8.4$ Hz), 7.34-7.30 (m, 6H), 2.36 (s, 3H), 1.44 (s, 9H). $^{13}C\{^1H\}$ -NMR (125 MHz, $CDCl_3$): δ 149.50, 141.79, 138.88, 135.42, 130.26, 129.88, 128.81, 127.00, 125.69, 124.92, 34.51, 31.42, 20.58. GC/MS(EI): m/z (M^+). Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.72; H, 8.88.

2, 5-Dimethyl-4'-chlorobiphenyl (Table 11, Entry 7):⁴² 2-Bromo-*p*-xylene (77 mg, 0.42 mmol) reacted with 4-chlorophenylboronic acid (94 mg, 0.60 mmol) using 1/2 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and K_3PO_4 (254 mg, 1.20 mmol) in toluene at 100 °C to give the title compound (85 mg, 95%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 7.27 (d, 2H, $J=8.0$ Hz), 7.14 (d, 2H, $J=8.0$ Hz), 7.06 (d, 1H, $J=7.6$ Hz), 6.98 (bs, 1H), 6.92 (s, 1H), 2.25 (s, 3H), 2.11 (s, 3H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 140.44, 135.30, 132.66, 132.04, 130.46, 130.33, 128.23, 128.18, 20.88, 19.88. GC/MS(EI): m/z 216 (M^+), 181, 166, 89.

2, 6-Dimethyl-2'-methyl-1,1'-biphenyl (Table 11, Entry 8):⁴⁰ 2-Bromo-*m*-xylene (186 mg, 1.01 mmol) reacted with 2-methylphenylboronic acid (164 mg, 1.21 mmol) using 2/4 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and K_3PO_4 (640 mg, 3.00 mmol) in toluene at 100 °C for 48 h to give

the title compound (170 mg, 87%) as a colorless oil: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.31-7.25 (m, 3H), 7.20-7.11 (m, 3H), 7.03 (m, 1H), 1.98 (s, 3H), 1.96 (s, 6H).

2-Chloro-1,1'-biphenyl (Table 11, Entry 9):⁴³ 2-Bromochlorobenzene (96 mg, 0.50 mmol) reacted with phenylboronic acid (79 mg, 0.65 mmol) using 1/2 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (87 mg, 1.50 mmol) in THF at room temperature to give the title compound (88 mg, 93%) as a white solid: $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.40-7.19 (m, 9H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3): δ 140.45, 139.33, 132.43, 131.32, 129.88, 129.39, 128.47, 127.99, 127.55, 126.77. GC/MS(EI): 188 (M^+), 190, 152, 76.

2,6-Dichloro-2'-methyl-1,1'-biphenyl (Table 11, Entry 10): 1-Bromo-2,6-dichlorobenzene (90 mg, 0.40 mmol) reacted with 2-methylphenylboronic acid (82 mg, 0.60 mmol) using 2/4 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and K_3PO_4 (254 mg, 1.20 mmol) in toluene at 100 °C to give the title compound (88 mg, 76%): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.07 (d, 2H, $J=8.07$ Hz), 7.28-7.18 (m, 3H), 7.15 (t, 1H, $J=8.13$ Hz), 7.00 (d, 1H, $J=7.25$ Hz), 1.99 (s, 3H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, CDCl_3): δ 139.23, 136.91, 136.16, 135.09, 129.90, 129.04, 129.01, 128.39, 127.88, 125.81, 19.30. GC/MS(EI): 236 (M^+), 238 (M^++2), 240, 165, 166. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{Cl}_2$: C, 65.85; H, 4.25. Found: C, 65.72; H, 4.46.

4-Cyano-2'-methyl-1,1'-biphenyl (Table 12, Entry 1): 4-Chlorobenzonitrile (55 mg, 0.40 mmol) reacted with 2-methylphenylboronic acid (82 mg, 0.60 mmol) using 1 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (70 mg, 1.21 mmol) in THF at 45 °C to give the title compound (72 mg, 94%) as a white solid: $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ 7.73 (d, 2H, $J=8.1$ Hz), 7.46 (d, 2H, $J=8.4$ Hz), 7.27-7.34 (m, 3H), 7.21 (d, 1H, $J=6.9$ Hz), 2.80 (s, 3H). $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (100 MHz, CDCl_3): δ 146.76, 139.97, 135.00, 131.94, 130.64, 129.97, 129.39, 128.26, 126.07, 118.93, 110.70, 20.28. GC/MS (EI): m/z 193 (M^+), 165. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}$: C, 87.01; H, 5.74; N, 7.25. Found: C, 86.85; H, 5.99; N, 7.24.

4-Formyl-2'-methyl-1,1'-biphenyl (Table 12, Entry 2): 4-Chlorobenzaldehyde (144 mg, 1.02 mmol) reacted with 2-methylphenylboronic acid (204 mg, 1.50 mmol) using 1/2 mol % of $\text{Pd}(\text{OAc})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (180 mg, 3.10 mmol) in THF at 50 °C to give the title

compound (189 mg, 96%) as a white solid: ^1H -NMR (400 MHz, CDCl_3): δ 9.98 (s, 1H), 7.85 (d, 2H, $J=8.2$ Hz), 7.41 (d, 2H, $J=8.1$ Hz), 7.22-7.13 (m, 4H), 2.19 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 191.98, 148.36, 140.51, 135.06, 134.87, 130.54, 129.88, 129.55, 129.42, 128.03, 125.94, 20.34. GC/MS(EI): m/z 196 (M^+), 165, 167, 152. Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{O}$: C, 85.68; H, 6.16. Found: C, 85.64; H, 6.39.

4-Formyl-1,1'-biphenyl (Table 12, Entry 3): 4-Chlorobenzaldehyde (144 mg, 1.02 mmol) reacted with phenylboronic acid (185 mg, 1.36 mmol) using 1/2 mol % of $\text{Pd}(\text{OAc})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (178 mg, 3.18 mmol) in THF at 50 °C to give the title compound (180 mg, 96%) as a colorless oil: ^1H -NMR (400 MHz, CDCl_3): δ 8.05 (s, 1H), 7.96 (d, 2H, $J=8.32$ Hz), 7.76 (d, 2H, $J=8.22$ Hz), 7.65 (d, 2H, $J=7.08$ Hz), 7.52-7.41 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 191.88, 147.10, 139.62, 135.11, 130.21, 128.96, 128.42, 127.61, 127.30. GC/MS(EI): m/z 182 (M^+), 152. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{O}$: C, 85.69; H, 5.53. Found: C, 85.69; H, 5.77.

4-Methyloxycarbonyl-4'-methoxy-1,1'-biphenyl (Table 12, Entry 4):⁴¹ Methyl 4-chlorobenzoate (171 mg, 1.00 mmol) reacted with 4-methoxyphenylboronic acid (200 mg, 1.31 mmol) using 1/2 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (180 mg, 3.10 mmol) in THF at 100 °C for 4 h to give the title compound (210 mg, 89%) as a white solid: ^1H -NMR (500 MHz, CDCl_3): δ 8.09 (d, 2H, $J=8.35$ Hz), 7.63 (d, 2H, $J=8.30$ Hz), 7.59 (d, 2H, $J=8.71$ Hz), 7.01 (d, 2H, $J=8.73$ Hz), 3.95 (s, 3H), 3.88 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 167.02, 159.77, 145.14, 132.32, 130.05, 128.31, 128.16, 126.40, 114.31, 55.32, 52.03. GC/MS (EI): m/z 242 (M^+), 211, 139.

4-Methyloxycarbonyl-2'-methyl-1,1'-biphenyl (Table 12, Entry 5): Methyl 4-chlorobenzoate (172 mg, 1.01 mmol) reacted with 2-methylphenylboronic acid (210 mg, 1.54 mmol) using 1/2 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_5\text{FcP}(t\text{-Bu})_2$ and KF (190 mg, 3.39 mmol) in THF at 100 °C to give the title compound (209 mg, 92%) as a colorless oil: ^1H -NMR (400 MHz, CDCl_3): δ 8.13 (d, 2H, $J=8.24$ Hz), 7.44 (d, 2H, $J=8.20$ Hz), 7.33-7.25 (m, 4H), 3.98 (s, 3H), 2.30 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 166.98, 146.69, 140.79, 135.10, 130.44, 129.47, 129.36,

129.21, 128.53, 127.78, 125.85, 52.06, 20.33. GC/MS(EI): m/z 226 (M^+), 195, 165, 152. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found C, 79.33; H, 6.26.

1,1'-Biphenyl (Table 12, Entry 6):⁴³ Chlorobenzene (56 mg, 0.50 mmol) reacted with phenylboronic acid (92 mg, 0.75 mmol) using 0.5/1.0 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (87 mg, 1.50 mmol) in THF solvent at 45 °C for 20 h to give the title compound (74 mg, 96%) as a white solid.

2-Methyl-4'-methoxybiphenyl (Table 12, Entry 7):³⁰ 4-Chloroanisole (74 mg, 0.52 mmol) reacted with 2-methylphenylboronic acid (102 mg, 0.75 mmol) using 1 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (87 mg, 1.50 mmol) in toluene at 80 °C to give the title compound (104 mg, 99%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 7.35-7.31 (m, 6H), 7.04 (d, 2H, $J=8.8$ Hz), 3.92 (s, 3H), 2.37 (s, 3H). $^{13}C\{^1H\}$ -NMR (125 MHz, $CDCl_3$): δ 158.43, 141.47, 135.40, 134.28, 130.25, 130.19, 129.85, 126.91, 125.71, 113.41, 55.19, 20.52. GC/MS(EI): m/z 198 (M^+).

3-Methoxy-2'-methyl-1,1'-biphenyl (Table 12, Entry 8): 3-Chloroanisole (71 mg, 0.50 mmol) reacted with 2-methylphenylboronic acid (82 mg, 0.60 mmol) using 3 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and K_3PO_4 (318 mg, 1.50 mmol) in toluene at 80 °C to give the title compound (86 mg, 87%) as a colorless oil: 1H -NMR (400 MHz, $CDCl_3$): δ 7.39 (t, 1H, $J=7.6$ and 8.0 Hz), 7.33-7.30 (m, 4H), 6.99-6.94 (m, 3H), 3.89 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ -NMR (100 MHz, $CDCl_3$): δ 159.23, 143.32, 141.75, 135.27, 130.25, 129.60, 129.00, 127.26, 125.67, 121.63, 114.78, 112.23, 55.16, 20.42. GC/MS (EI): m/z 198 (M^+), 167 (M^+-OMe). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found C, 84.72; H, 7.09.

3-Methoxy-4'-methoxy-1,1'-biphenyl (Table 12, Entry 9): 3-Chloroanisole (76 mg, 0.54 mmol) reacted with 4-methoxyphenylboronic acid (117 mg, 0.77 mmol) using 1 mol % of $Pd(dba)_2/Ph_5FcP(t-Bu)_2$ and KF (87 mg, 1.50 mmol) in toluene at 80 °C to give the title compound (112 mg, 97%) as a colorless oil: 1H -NMR (300 MHz $CDCl_3$): δ 7.57 (d, 2H, $J=8.7$ Hz), 7.37 (t, 1H, $J=7.8$ and 8.1 Hz), 7.17 (m, 2H), 7.01 (d, 2H, $J=8.7$ Hz), 6.88-6.97 (m, 1H),

3.89 (s, 3H), 3.88 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 159.86, 159.17, 142.28, 135.51, 129.66, 128.13, 119.21, 114.09, 112.44, 111.93. GC/MS (EI): m/z 214 (M^+), 199, 171, 128. Anal. Calcd for $\text{C}_{14}\text{H}_4\text{O}_2$: C, 78.48; H, 6.59. Found C, 78.46; H, 6.62.

2,5-dimethyl-2'-methylbiphenyl (Table 12, Entry 10):⁴⁴ 2-Chloro-p-xylene (56 mg, 0.40 mmol) reacted with 2-methylphenylboronic acid (82 mg, 0.60 mmol) using 2.5/5.0 mol % of $\text{Pd}(\text{dba})_2/\text{Ph}_3\text{FcP}(t\text{-Bu})_2$ and Cs_2CO_3 (391 mg, 1.20 mmol) in 1,2-dioxane at 100 °C to give the title compound (63 mg, 80%): ^1H -NMR (300 MHz, CDCl_3): δ 7.12-7.18 (m, 6H), 6.97 (s, 1H), 2.37 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ 141.74, 141.45, 135.77, 134.86, 132.60, 129.94, 129.72, 129.65, 129.26, 127.81, 127.02, 125.47, 20.92, 19.81, 19.28. GC/MS(EI): m/z 196 (M^+).

4-tert-butyl-1-n-butylbenzene (Table 13, Entry 1):⁴⁵ Synthesis of this compound followed procedure B at 100 °C for 2.5 h. ^1H -NMR(400 MHz, CDCl_3): δ 7.39 (d, 2H, $J=8.2$ Hz), 7.21 (d, 2H, $J=8.2$ Hz), 2.67 (t, 2H, $J=7.6$ and 8.0 Hz), 1.69 (m, 2H), 1.45 (m, 2H), 1.40 (s, 9H), 1.02 (t, 3H, $J=7.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.23, 139.80, 128.01, 125.07, 35.12, 34.29, 33.67, 31.42, 22.48, 14.00. GC/MS (EI): m/z 190 (M^+), 175 (M^+-CH_3). Anal. Calcd. for $\text{C}_{14}\text{H}_{22}$: C, 88.35; H, 11.65. Found: C, 88.05; H, 11.56.

4-n-butylnisole (Table 13, Entry 2):⁴⁶ According to the procedure B at 100 °C for 30 h, 4-bromoanisole was converted to the title compound as a colorless oil (132 mg, 83%): ^1H -NMR (500 MHz, CDCl_3): δ 7.13 (d, 2H, $J=8.48$ Hz), 6.86 (d, 2H, $J=8.55$ Hz), 3.82 (s, 3H), 2.59 (t, 2H, $J=7.65$ and 7.79 Hz), 1.60 (m, 2H), 1.40 (m, 2H), 0.96 (t, 3H, $J=7.34$ Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ 157.59, 134.99, 129.22, 113.62, 55.20, 34.70, 33.89, 22.29, 13.63. GC/MS (EI): m/z 164 (M^+), 121 (M^+-propyl), 91. Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: C, 80.18; H, 9.87.

2-n-butylnisole (Table 13, Entry 3):⁴⁶ According to the procedure B at 100 °C for 18 h, 2-chloroanisole was converted to the title compound as a colorless oil (80 mg, 94%): ^1H -NMR (400 MHz, CDCl_3): δ 7.22-7.15 (m, 2H), 6.91 (t, 1H, $J=7.2$ Hz, aryl coupling 0.8 Hz), 6.87 (d, 2H, $J=8.0$ Hz), 3.85 (s, 3H), 2.64 (t, 2H, $J=7.2$ and 8.0 Hz), 1.58 (m, 2H), 1.40 (m, 2H), 0.96 (t,

3H, J=7.2 and 7.6 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 157.39, 131.27, 129.70, 126.71, 120.24, 110.14, 55.22, 32.05, 29.84, 22.66, 14.03. GC/MS (EI): m/z 164 (M^+), 121 (M^+ -propyl). Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.82. Found: C, 80.64; H, 9.96.

4-*n*-butylcyanobenzene (Table 13, Entry 4):⁴⁷ According to the procedure B above at 100 °C for 12 h, 4-chlorobenzonitrile was converted to the title compound as a colorless oil (80 mg, 97%): ^1H -NMR (400 MHz, CDCl_3): δ 7.55 (d, 2H, J=7.6 Hz), 7.27 (d, 2H, J=7.6 Hz), 2.66 (t, 2H, J=7.6 Hz), 1.60 (m, 2H), 1.35 (m, 2H), 0.93 (t, 3H, J=7.2 and 7.6 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.48, 131.96, 129.10, 119.10, 109.31, 35.70, 32.99, 22.15, 13.77. GC/MS (EI): m/z 159 (M^+), 117. Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{N}$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.19; H, 8.25; N, 8.83.

3-*n*-butylanisole (Table 13, Entry 5):⁴⁸ According to the procedure B above at 100 °C for 48 h, 3-chloroanisole was converted to the title compound as a colorless oil (161 mg, 94%): ^1H -NMR (400 MHz, CDCl_3): δ 7.55 (d, 2H, J=7.6 Hz), 7.27 (d, 2H, J=7.6 Hz), 2.66 (t, 2H, J=7.6 Hz), 1.60 (m, 2H), 1.35 (m, 2H), 0.93 (t, 3H, J=7.2 and 7.6 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 159.52, 144.56, 129.12, 120.84, 114.16, 110.75, 55.07, 35.70, 33.53, 22.36, 13.94. GC/MS (EI): m/z 164 (M^+), 122.

2-*n*-butyltoluene (Table 13, Entry 6):⁴⁹ According to the procedure B, 2-chlorotoluene was converted to the title compound as a colorless oil (65 mg, 88 %): ^1H -NMR (400 MHz, CDCl_3): δ 7.14 (m, 4H), 2.63 (t, 2H, J=7.6 and 8.0 Hz), 2.34 (s, 3H), 1.61 (m, 2H), 1.45 (m, 2H), 0.99 (t, 3H, J=6.8 and 7.2 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 141.06, 135.80, 130.04, 128.77, 125.79, 125.67, 33.02, 32.46, 22.75, 19.26, 14.02.

4-*tert*-butyl-1-*iso*-butylbenzene (Table 13, Entry 7):⁴⁶ According to the procedure B above using isobutyl boronic acid as reagent at 100 °C for 22 h, 4-*tert*-butylbromobenzene was converted to the title compound as a colorless oil (105 mg, 55%): ^1H -NMR (400 MHz, CDCl_3): δ 7.35 (d, 2H, J=7.24 Hz), 7.16 (d, 2H, J=7.61 Hz), 2.62 (m, 1H), 1.62 (m, 2H), 1.36 (s, 9H), 1.27 (d, 3H, J=6.28 Hz), 0.88 (t, 3H, J=6.90 and 7.08 Hz). $^{13}\text{C}\{^1\text{H}\}$ -NMR (100 MHz, CDCl_3): δ 148.35, 144.56, 126.59, 125.02, 41.03, 34.29, 31.42, 31.21, 21.66, 12.31. GC/MS (EI): m/z 190 (M^+), 175 (M^+ - CH_3), 161. Anal. Calcd. for $\text{C}_{14}\text{H}_{22}$: C, 88.35; H, 11.65. Found: C, 88.09; H, 11.68.

Etherification of Aryl Halides:⁵⁰

***tert*-Butoxybenzene (Table 14, Entry 1):** 96 % yield. ^1H NMR (300 MHz, CDCl_3): δ 7.28 (t, 2H, $J = 7.5$ Hz), 7.90 (t, 1H, $J = 7.5$ Hz), 7.11 (d, 2H, $J = 7.5$ Hz), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.33, 128.79, 124.21, 123.29, 78.33, 28.86.

2-*tert*-Butoxytoluene (Table 14, Entry 2): 79% yield, eluted from silica gel using ethyl acetate/hexane (0 to 10% gradient). ^1H NMR (300 MHz, CDCl_3): δ 7.20-6.95 (m, 4H), 2.28 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 154.35, 132.03, 130.84, 126.02, 122.54, 122.18, 78.87, 29.18, 17.21. GC/MS: m/z 149 (M^+)

2-(*tert*-Butyl-dimethylsilyloxy)toluene (Table 14, Entry 3): 99% yield. ^1H NMR (300 MHz, CDCl_3): δ 7.17-6.80 (m, 4H), 2.24 (s, 3H), 1.05 (s, 9H), 0.25 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.85, 130.92, 128.91, 126.55, 120.93, 118.47, 25.78, 18.25, 16.80, -3.46. GC/MS: m/z 222 (M^+).

4-Methoxyphenoxy-2-methylbenzene (Table 14, entry 4): Reaction of 2-bromotoluene (86 mg, 0.5 mmol) with sodium *p*-methoxyphenoxide (88 mg, 0.60 mmol) by the general procedure gave 106 mg (99%) of diarylether after chromatography with ethyl acetate/hexanes (0 to 10% gradient). ^1H NMR (CDCl_3) δ 2.33 (s, 3H), 3.83 (s, 3H), 6.83-6.96 (m, 5H), 7.05 (t, 7.4 Hz, 1H), 7.16 (t, 7.7 Hz, 1H), 7.27 (d, 7.3 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 16.19, 55.59, 114.71, 117.93, 119.27, 123.01, 126.91, 128.99, 131.23, 151.00, 155.21, 155.74.

3-*tert*-Butoxyanisole (Table 14, Entries 5 and 7): 77% yield from 3-Bromoanisole and 92% yield from 3-Chloroanisole, eluted from silica gel using ethyl acetate/hexane (0 to 10% gradient). ^1H NMR (300 MHz, CDCl_3): δ 7.17 (t, 1H, $J = 8.1$ Hz), 6.64 (t, 2H, $J = 8.4$ and 2.1 Hz), 6.58 (d, 1H, $J = 2.1$ Hz), 3.79 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.10, 156.58, 129.04, 116.31, 110.03, 108.71, 78.48, 55.15, 28.86. GC/MS: m/z 180 (M^+)

3-(*tert*-Butyl-dimethylsilyloxy)anisole (Table 14, Entries 6 and 8): 79% yield from 3-bromoanisole and 78% yield from 3-chloroanisole, eluted from silica gel using ethyl acetate/hexanes (0 to 10% gradient). ^1H NMR (300 MHz, CDCl_3): δ 7.15 (m, 1H), 6.57-6.43 (m, 3H), 3.80 (s, 3H), 1.02 (s, 9H), 0.24 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 160.59, 156.74, 129.61, 112.50, 106.73, 106.23, 55.13, 25.62, 18.14, -3.58. GC/MS: m/z 238 (M^+).

4-*tert*-Butoxyanisole (Table 14, Entry 9): 81% yield, eluted from silica gel using ethyl acetate/hexane (0 to 10% gradient). ¹H NMR (300 MHz, CDCl₃): δ 6.94 (d, 2H, *J* = 9.0 Hz), 6.81 (d, 2H, *J* = 9.0 Hz), 3.79 (s, 3H), 1.32 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 155.72, 148.55, 125.30, 113.75, 77.98, 55.42, 28.67. GC/MS: *m/z* 180 (M⁺).

4-*tert*-Butoxybenzophenone (Table 14, Entries 10 and 12): 98% yield from 4-Bromobenzophenone and 98% yield from 4-Chlorobenzophenone, eluted from silica gel using ethyl acetate/hexane (0 to 10% gradient). ¹H NMR (300 MHz, CDCl₃): δ 7.78 (app. d, 4H, *J* = 8.4 Hz), 7.57-7.45 (m, 3H), 7.06 (app. d, 2H, *J* = 6.9, 1.8 Hz), 1.44 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 195.70, 159.96, 138.03, 131.92, 131.68, 131.64, 129.72, 128.12, 122.11, 79.54, 28.87. GC/MS: *m/z* 254 (M⁺).

4-(*tert*-Butyl-dimethylsilyloxy)benzophenone (Table 14, Entry 11): 94% yield, eluted from silica gel using ethyl acetate/hexanes (0 to 10% gradient). ¹H NMR (300 MHz, CDCl₃): δ 7.82-7.77 (m, 4H), 7.61-7.56 (m, 1H), 7.51-7.47 (m, 2H), 6.94-6.92 (m, 2H), 1.02 (s, 9H), 0.27 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 195.65, 159.91, 138.16, 132.43, 131.78, 130.63, 129.72, 128.14, 119.67, 25.57, 18.22, -3.45. GC/MS: *m/z* 312 (M⁺).

4-*tert*-Butoxy-1-nitrobenzene (Table 14, Entries 13, 14): 98% yield from 4-Bromo-1-nitrobenzene and 93% yield from 4-Chloro-1-nitrobenzene, eluted from silica gel using ethyl acetate/hexane (0 to 10% gradient). ¹H NMR (300 MHz, CDCl₃): δ 8.16 (d, 2H, *J* = 9.0 Hz), 7.05 (d, 2H, *J* = 9.0 Hz), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 161.87, 142.35, 125.16, 121.62, 80.56, 28.78.

2,3-Dihydrobenzo[b]furan (Table 14, entry 15): 58% yield, eluted from silica gel using 5% ethyl acetate in hexanes. ¹H NMR (300 MHz, CDCl₃): δ 7.22 (d, 1H, *J* = 7.2 Hz), 7.14 (app.t, 1H, *J* = 7.5 Hz), 6.85 (app.q, 2H, *J* = 7.5 Hz), 4.58 (app.t, 2H, *J* = 8.7 Hz), 3.24 (app.t, 2H, *J* = 8.7 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 159.96, 127.87, 127.27, 124.85, 120.29, 109.30, 70.96, 29.70. GC/MS: *m/z* 120 (M⁺).

2-Methyl-2,3-dihydrobenzo[b]furan (Table 14, entry 16): 59% yield, eluted from silica gel using 5% ethyl acetate in hexanes. ¹H NMR (300 MHz, CDCl₃): δ 7.19-7.11 (m, 2H), 6.78-

6.88 (m, 2H), 4.94 (m, 1H), 3.34 (dd, 1H, $J = 8.7, 15.3$ Hz), 2.84 (dd, 1H, $J = 7.5, 15.6$ Hz), 1.50 (d, 3H, $J = 6.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 159.46, 127.91, 126.99, 124.92, 120.11, 109.27, 79.43, 37.09, 20.71. GC/MS: m/z 134 (M^+).

2-Methylchroman (Table 14, entry 17): 64% yield, eluted from silica gel using 5% ethyl acetate in hexanes. ^1H NMR (300 MHz, CDCl_3): δ 7.14-7.07 (m, 2H), 6.88-6.82 (m, 2H), 4.18 (m, 1H), 2.86 (m, 2H), 2.04 (m, 1H), 1.80 (m, 1H), 1.43 (d, 3H, $J = 6.3$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 154.97, 129.50, 127.20, 121.78, 119.92, 116.62, 72.11, 29.16, 24.85, 21.37. GC/MS: m/z 148 (M^+).

2,2-Dimethyl-2,3-dihydrobenzo[b]furan (Table 14, entry 18): 77% yield, eluted from silica gel using 5% ethyl acetate in hexanes. ^1H NMR (300 MHz, CDCl_3): δ 7.15 (m, 2H), 6.85 (t, 1H, $J = 7.2$ Hz), 6.77 (d, 1H, $J = 8.1$ Hz), 3.04 (s, 2H), 1.51 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.79, 127.91, 127.03, 125.10, 119.87, 109.46, 86.42, 42.82, 28.17. GC/MS: m/z 148 (M^+).

Preparation of Substrates for Intramolecular Etherification.

2-Bromophenethyl alcohol (Table 14, Entry 15): To a solution of 2-bromophenylacetic acid (3.96 g, 18.42 mmol) in 60 mL of anhydrous THF was added slowly at room temperature 24.0 mL (23.95 mmol) of a 1 M solution BH_3/THF . After finishing the addition of BH_3/THF , the solution was stirred at room temperature for 1 h and then heated at 100 °C for 2 h. After this time, the solution was cooled to room temperature, and a mixture of THF and water (20 mL) was added. Potassium carbonate was then added, along with 60 mL of ether. The organic layer was separated from the mixture, and this layer was washed with water (60 mL), aqueous NaHCO_3 (60 mL), and brine (60 mL) before it was dried over magnesium sulfate, filtered, and concentrated to give the crude product. This crude product was purified by silica gel flash chromatography eluting with hexanes and a 5 to 10% gradient of ethyl acetate to give 3.47 g (94%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.57 (d, 1H, $J = 7.8$ Hz), 7.31-7.21 (m, 2H), 7.14-7.08 (m, 1H), 3.90 (app. t, 2H, $J = 6.6, 6.9$ Hz), 3.05 (app. t, 2H, $J = 6.6$ Hz), 1.51 (bs, 1H). ^{13}C NMR

(100 MHz, CDCl_3): δ 137.76, 132.95, 131.25, 128.19, 127.44, 124.67, 62.04, 39.30. Anal. Calc'd. for $\text{C}_8\text{H}_9\text{BrO}$: C, 47.79; H, 4.51. Found: C, 47.75; H, 4.50.

1-(2-Bromophenyl)-2-propanol (Table 14, Entry 16): To a solution of 2-(2-bromophenyl)methyl acetate (4.4 g, 19.21 mmol) in 50 mL of anhydrous toluene was added slowly at -78°C under a nitrogen atmosphere 13.6 mL (20.1 mmol) of a 1 M solution of DIBAL in Toluene. After 2 h, anhydrous methanol (7.8 mL) was added slowly to avoid increasing the temperature and to avoid rapid evolution of gas. The solution was allowed to stand at -78°C for 1 hr. The mixture was then warmed to room temperature and stirred for an additional 30 min. The solution was diluted with ether (200 mL), washed with brine, and dried with MgSO_4 . After evaporating the solvent, 2-(2-bromophenyl)methylaldehyde was obtained (3.42 g, 89% yield) as a colorless oil. This aldehyde was used without further purification. ^1H NMR (300 MHz, CDCl_3): δ 9.78 (s, 1H), 7.64 (d, 1H, $J = 8.1$ Hz), 7.34-7.18 (m, 3H), 3.89 (s, 2H). To a solution of methyl magnesium chloride (8.8 mL, 25.65 mmol) in anhydrous THF was added at -20°C a solution of 2-(2-bromophenyl)methylaldehyde in anhydrous ether (50 mL). The mixture was stirred at -20°C for 0.5 h and at room temperature for 1 h. The resulting solution was carefully poured into a mixture of ether (100 mL) and water (100 mL). The organic layer was separated, washed with brine, and dried with anhydrous magnesium sulfate. After evaporation of the solvent, 1-(2-bromophenyl)-2-propanol was purified by flash chromatography on silica gel using ethyl acetate/hexanes (5 to 10%) as eluent to afford 2.67 g (73% yield) of colorless oil. ^1H NMR (300 MHz, CDCl_3): δ 7.57 (d, 1H, $J = 7.8$ Hz), 7.27 (d, 2H, $J = 4.2$ Hz), 7.12 (m, 1H), 4.12 (m, 1H), 2.98 (dd, 1H, $J = 13.5, 4.8$ Hz), 2.85 (dd, 1H, $J = 13.5, 8.1$ Hz), 1.59 (bs, 1H), 1.29 (d, 3H, $J = 6.3$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 138.11, 132.99, 131.68, 128.16, 127.38, 124.87, 67.47, 45.62, 22.97. Anal. Calc'd. for $\text{C}_9\text{H}_9\text{BrO}$: C, 50.26; H, 5.15. Found: C, 50.06; H, 5.06.

4-(2-Bromophenyl)-2-butanol (Table 14, Entry 17): This material was prepared by literature procedures.⁵¹ ^1H NMR (400 MHz, CDCl_3): δ 7.55 (d, 1H, $J = 7.6$ Hz), 7.28-7.23 (m, 2H), 7.11-7.05 (m, 1H), 3.92-3.86 (m, 1H), 2.95-2.77 (m, 2H), 1.83-1.75 (m, 2H), 1.55 (bs, 1H),

1.28 (d, 3H, $J = 6.0$ Hz). ^{13}C -NMR (100 MHz, CDCl_3): δ 141.31, 132.78, 130.35, 127.57, 127.47, 124.36, 67.48, 39.23, 32.42, 23.57.

2-Methyl-1-(2-bromophenyl)-2-propanol (Table 14, Entry 18): This material was prepared by literature procedures (Bacon, R. G. R.; Rennison, S. C. *J. Chem. Soc. (C)* **1969**, 312-315). ^1H NMR (300 MHz, CDCl_3): δ 7.59 (d, 1H, $J = 7.8$ Hz), 7.37 (dd, 1H, $J = 7.6, 1.8$ Hz), 7.27 (m, 1H), 7.11 (t, 1H, $J = 7.8, 1.8$ Hz), 3.03 (s, 2H), 1.53 (bs, 1H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.66, 133.02, 132.38, 128.10, 127.10, 125.95, 69.83, 47.93, 29.50, 29.43. Anal. Calc'd. for $\text{C}_{10}\text{H}_{13}\text{BrO}$: C, 52.42; H, 5.72. Found: C, 52.20; H, 5.63.

4-(2-Bromophenyl)-2-methyl-2-butanol (Table 14, Entry 19): This material was prepared by literature procedures.⁵¹ ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, 1H, $J = 7.2$ Hz), 7.31-7.24 (m, 2H), 7.09-7.06 (m, 1H), 2.87-2.82 (m, 2H), 1.80-1.75 (m, 2H), 1.43 (bs, 1H), 1.34 (s, 6H). ^{13}C -NMR (100 MHz, CDCl_3): δ 141.71, 132.78, 130.24, 127.54, 127.52, 124.34, 70.91, 44.00, 31.30, 29.19. Calcd for $\text{C}_{11}\text{H}_{15}\text{BrO}$: C, 54.34; H, 6.22. Found: C, 54.52; H, 6.30.

X-ray Structure of $(\text{Ph}_5\text{Fc})\text{P}(t\text{-Bu})_2$

Data Collection: A red prism crystal of $\text{C}_{96}\text{H}_{94}\text{P}_2\text{Fe}_2$ having approximate dimensions of 0.20 x 0.21 x 0.24 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo- $\text{K}\alpha$ radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in ω , 10 s exposure, de-zingered) data frames, corresponded to a primitive monoclinic cell with dimensions: $a = 19.4129(3)$ Å, $b = 18.0760(4)$ Å, $\beta = 104.744(1)^\circ$, $c = 22.333(1)$ Å, and $V = 7578.6(3)$ Å³. For $Z = 4$ and F.W. = 1421.44, the calculated density is 1.25 g/cm³. The systematic absences of: $h0l$: $h+l = 2n+1$, $0k0$: $k = 2n+1$; uniquely determine the space group to be: $\text{P}2_1/n$ (#14). There are two independent, but essentially identical, molecules per asymmetric unit.

The data were collected at a temperature of -90 ± 1 °C to a maximum 2θ value of 54.9° . Two omega scans consisting of 75 and 69 data frames, respectively, were collected with a scan width of 1.6° and a detector-to-crystal distance, D_x , of 40 mm. Each frame was exposed twice

(for the purpose of de-zingering) for 96 s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction: A total of 17663 reflections were collected. No decay correction was applied. The linear absorption coefficient, μ , for Mo-K α radiation is 4.7 cm⁻¹ and no absorption correction was applied. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement: The structure was solved by heavy-atom Patterson methods⁵² and expanded using Fourier techniques.⁵³ The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement⁵⁴ was based on 9620 observed reflections ($I > 5.00\sigma(I)$) and 901 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.037$$

$$R_w = [(\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2} = 0.041$$

The standard deviation of an observation of unit weight⁵⁵ was 2.21. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and -0.31 e⁻/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.⁵⁶ Anomalous dispersion effects were included in Fcalc⁵⁷ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁵⁸ The values for the mass attenuation coefficients are those of Creagh and Hubbel.⁵⁹ All calculations were performed using the teXsan⁶⁰ crystallographic software package of Molecular Structure Corporation.

Experimental Details for the Structure Solution of (Ph₅Fc)P(t-Bu)₂

A. Crystal Data

Empirical Formula	C ₉₆ H ₉₄ P ₂ Fe ₂
Formula Weight	1421.44
Crystal Color, Habit	red, prism
Crystal Dimensions	0.20 X 0.21 X 0.24 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 19.4129(3) Å b = 18.0760(4) Å c = 22.333(1) Å β = 104.744(1)° V = 7578.6(3) Å ³
Space Group	P2 ₁ /n (#14)
Z value	4
D _{calc}	1.246 g/cm ³
F ₀₀₀	3008.00
μ(MoK _α)	4.73 cm ⁻¹

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoK _α (λ = 0.71069 Å) graphite monochromated
Take-off Angle	2.8°
Crystal to Detector Distance	40 mm
Temperature	-90.0 °C
Scan Rate	96 s/frame
Scan Width	1.6°/frame
2θ _{max}	54.9°
No. of Reflections Measured	Total: 17663
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF92 PATTY)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (F _o - F _c) ²
Least Squares Weights	1/σ ² (F _o)

p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 5.00 \sigma(I)$)	9620
No. Variables	901
Reflection/Parameter Ratio	10.68
Residuals: R; R_w	0.037 ; 0.041
Goodness of Fit Indicator	2.21
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.35 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.31 e ⁻ /Å ³

Table S1. Atomic coordinates and Biso/Beq of (Ph₃Fc)P(*t*-Bu)₂.

atom	x	y	z	Beq
Fe(1)	0.26232(2)	0.25837(2)	0.95196(2)	1.954(8)
Fe(2)	0.23714(2)	0.18521(2)	0.35051(2)	2.033(8)
P(1)	0.08241(3)	0.16814(4)	0.93159(3)	2.42(2)
P(2)	0.04398(3)	0.24458(4)	0.30066(3)	2.74(2)
C(1)	0.2761(1)	0.3186(1)	0.8776(1)	1.91(5)
C(2)	0.2709(1)	0.2409(1)	0.8627(1)	1.90(5)
C(3)	0.3281(1)	0.2037(1)	0.9062(1)	1.87(5)
C(4)	0.3672(1)	0.2580(1)	0.9478(1)	1.88(5)
C(5)	0.3359(1)	0.3290(1)	0.9304(1)	1.93(6)
C(6)	0.2335(1)	0.3798(1)	0.8419(1)	2.07(6)
C(7)	0.2062(1)	0.4373(1)	0.8706(1)	2.48(6)
C(8)	0.1707(1)	0.4961(1)	0.8360(1)	3.18(7)
C(9)	0.1615(1)	0.4979(2)	0.7730(2)	3.76(8)
C(10)	0.1879(1)	0.4414(2)	0.7438(1)	3.65(7)
C(11)	0.2238(1)	0.3827(1)	0.7780(1)	2.78(6)
C(12)	0.2169(1)	0.2081(1)	0.8103(1)	1.93(5)
C(13)	0.1465(1)	0.2332(1)	0.7949(1)	2.47(6)
C(14)	0.0963(1)	0.2041(2)	0.7453(1)	3.09(7)
C(15)	0.1146(1)	0.1479(2)	0.7102(1)	3.39(7)
C(16)	0.1838(1)	0.1211(1)	0.7252(1)	3.12(7)
C(17)	0.2343(1)	0.1516(1)	0.7742(1)	2.47(6)
C(18)	0.3548(1)	0.1265(1)	0.9065(1)	1.98(6)
C(19)	0.3243(2)	0.0668(2)	0.9275(1)	3.87(8)
C(20)	0.3535(2)	-0.0033(2)	0.9296(1)	5.31(10)
C(21)	0.4160(2)	-0.0136(2)	0.9125(2)	5.11(9)
C(22)	0.4469(1)	0.0449(2)	0.8910(2)	5.14(9)
C(23)	0.4168(1)	0.1145(1)	0.8881(1)	3.46(7)
C(24)	0.4349(1)	0.2441(1)	0.9959(1)	2.01(6)
C(25)	0.4980(1)	0.2690(1)	0.9851(1)	3.20(7)
C(26)	0.5628(1)	0.2580(2)	1.0279(1)	3.89(8)
C(27)	0.5645(1)	0.2223(2)	1.0826(1)	3.64(7)
C(28)	0.5026(1)	0.1961(2)	1.0939(1)	3.68(7)
C(29)	0.4381(1)	0.2063(2)	1.0501(1)	3.03(7)
C(30)	0.3647(1)	0.4005(1)	0.9590(1)	2.00(6)

C(31)	0.3744(1)	0.4595(1)	0.9218(1)	2.39(6)
C(32)	0.4022(1)	0.5260(1)	0.9480(1)	2.88(7)
C(33)	0.4211(1)	0.5347(1)	1.0113(1)	2.93(7)
C(34)	0.4127(1)	0.4765(2)	1.0487(1)	2.97(7)
C(35)	0.3850(1)	0.4099(1)	1.0227(1)	2.50(6)
C(36)	0.1674(1)	0.2139(1)	0.9689(1)	1.97(6)
C(37)	0.2289(1)	0.1945(1)	1.0172(1)	2.48(6)
C(38)	0.2630(1)	0.2603(2)	1.0442(1)	2.82(6)
C(39)	0.2247(1)	0.3212(1)	1.0125(1)	2.82(6)
C(40)	0.1676(1)	0.2928(1)	0.9659(1)	2.32(6)
C(41)	0.0397(1)	0.1756(1)	0.9996(1)	2.94(7)
C(42)	0.0767(2)	0.1374(2)	1.0586(1)	4.69(8)
C(43)	0.0359(2)	0.2572(2)	1.0146(2)	6.8(1)
C(44)	-0.0370(2)	0.1483(3)	0.9782(2)	8.9(1)
C(45)	0.0990(1)	0.0675(1)	0.9188(1)	2.93(7)
C(46)	0.1451(2)	0.0225(2)	0.9717(2)	5.31(9)
C(47)	0.1333(2)	0.0657(2)	0.8650(1)	5.05(9)
C(48)	0.0269(2)	0.0287(2)	0.8974(2)	7.8(1)
C(49)	0.2806(1)	0.2842(1)	0.3888(1)	1.93(5)
C(50)	0.2948(1)	0.2259(1)	0.4344(1)	1.93(5)
C(51)	0.3345(1)	0.1689(1)	0.4125(1)	1.82(5)
C(52)	0.3442(1)	0.1920(1)	0.3536(1)	1.88(5)
C(53)	0.3115(1)	0.2632(1)	0.3392(1)	1.90(5)
C(54)	0.2430(1)	0.3541(1)	0.3954(1)	2.24(6)
C(55)	0.2675(1)	0.4219(1)	0.3796(1)	2.94(6)
C(56)	0.2321(2)	0.4870(2)	0.3879(1)	4.18(8)
C(57)	0.1741(2)	0.4848(2)	0.4131(1)	4.45(8)
C(58)	0.1500(1)	0.4178(2)	0.4286(1)	3.89(8)
C(59)	0.1832(1)	0.3530(1)	0.4195(1)	2.83(6)
C(60)	0.2798(1)	0.2273(1)	0.4963(1)	2.05(6)
C(61)	0.2510(1)	0.1667(1)	0.5204(1)	2.45(6)
C(62)	0.2422(1)	0.1680(2)	0.5798(1)	2.91(7)
C(63)	0.2606(1)	0.2298(2)	0.6167(1)	3.28(7)
C(64)	0.2884(1)	0.2909(2)	0.5934(1)	3.22(7)
C(65)	0.2979(1)	0.2894(1)	0.5342(1)	2.59(6)
C(66)	0.3635(1)	0.1002(1)	0.4462(1)	2.06(6)
C(67)	0.3592(1)	0.0318(1)	0.4164(1)	2.56(6)

C(68)	0.3868(1)	-0.0315(1)	0.4484(1)	2.96(7)
C(69)	0.4200(1)	-0.0278(2)	0.5106(1)	3.12(7)
C(70)	0.4262(1)	0.0392(2)	0.5408(1)	2.85(7)
C(71)	0.3986(1)	0.1031(1)	0.5093(1)	2.33(6)
C(72)	0.3873(1)	0.1547(1)	0.3165(1)	2.12(6)
C(73)	0.4576(1)	0.1350(1)	0.3444(1)	2.92(6)
C(74)	0.5005(1)	0.1039(2)	0.3107(1)	3.79(8)
C(75)	0.4748(2)	0.0926(2)	0.2484(2)	4.09(8)
C(76)	0.4057(2)	0.1126(2)	0.2198(1)	4.31(8)
C(77)	0.3622(1)	0.1434(2)	0.2534(1)	3.16(7)
C(78)	0.3202(1)	0.3089(1)	0.2863(1)	2.06(6)
C(79)	0.3880(1)	0.3303(2)	0.2839(1)	3.56(7)
C(80)	0.3980(2)	0.3728(2)	0.2352(2)	4.51(9)
C(81)	0.3413(2)	0.3936(2)	0.1884(1)	4.49(9)
C(82)	0.2742(2)	0.3729(2)	0.1900(1)	4.88(9)
C(83)	0.2643(1)	0.3307(2)	0.2388(1)	3.90(8)
C(84)	0.1244(1)	0.1876(1)	0.3099(1)	2.20(6)
C(85)	0.1623(1)	0.1554(1)	0.2689(1)	2.60(6)
C(86)	0.2011(1)	0.0934(1)	0.2980(1)	2.90(7)
C(87)	0.1900(1)	0.0867(1)	0.3578(1)	2.87(6)
C(88)	0.1449(1)	0.1454(1)	0.3658(1)	2.47(6)
C(89)	-0.0259(1)	0.1705(2)	0.2682(1)	3.29(7)
C(90)	-0.0092(1)	0.1011(2)	0.3089(2)	5.18(9)
C(91)	-0.0982(1)	0.1986(2)	0.2740(2)	5.79(10)
C(92)	-0.0316(1)	0.1451(2)	0.2023(1)	4.79(8)
C(93)	0.0409(1)	0.3159(2)	0.2379(1)	3.00(6)
C(94)	-0.0347(2)	0.3478(2)	0.2174(2)	5.89(10)
C(95)	0.0628(1)	0.2930(2)	0.1797(1)	4.04(7)
C(96)	0.0898(2)	0.3781(2)	0.2693(1)	4.65(8)
H(1)	0.2119	0.4362	0.9141	2.9755
H(2)	0.1528	0.5353	0.8560	3.8119
H(3)	0.1370	0.5381	0.7496	4.5125
H(4)	0.1815	0.4427	0.7002	4.3766
H(5)	0.2420	0.3440	0.7576	3.3311
H(6)	0.1329	0.2711	0.8192	2.9591
H(7)	0.0490	0.2227	0.7351	3.7085
H(8)	0.0801	0.1278	0.6761	4.0730

H(9)	0.1965	0.0817	0.7019	3.7436
H(10)	0.2818	0.1337	0.7834	2.9671
H(11)	0.2820	0.0737	0.9409	4.6412
H(12)	0.3304	-0.0442	0.9429	6.3733
H(13)	0.4375	-0.0611	0.9157	6.1333
H(14)	0.4893	0.0378	0.8778	6.1734
H(15)	0.4391	0.1549	0.8732	4.1462
H(16)	0.4970	0.2942	0.9475	3.8359
H(17)	0.6057	0.2750	1.0195	4.6645
H(18)	0.6085	0.2158	1.1126	4.3723
H(19)	0.5039	0.1710	1.1315	4.4178
H(20)	0.3956	0.1870	1.0577	3.6366
H(21)	0.3617	0.4541	0.8781	2.8680
H(22)	0.4082	0.5658	0.9220	3.4513
H(23)	0.4398	0.5806	1.0291	3.5207
H(24)	0.4260	0.4821	1.0924	3.5644
H(25)	0.3797	0.3701	1.0489	2.9986
H(26)	0.2443	0.1456	1.0291	2.9794
H(27)	0.3043	0.2629	1.0778	3.3794
H(28)	0.2355	0.3720	1.0211	3.3871
H(29)	0.1343	0.3219	0.9367	2.7874
H(30)	0.0502	0.1443	1.0886	5.6332
H(31)	0.0803	0.0860	1.0510	5.6332
H(32)	0.1231	0.1576	1.0737	5.6332
H(33)	0.0827	0.2764	1.0290	8.1163
H(34)	0.0115	0.2831	0.9784	8.1163
H(35)	0.0110	0.2630	1.0458	8.1163
H(36)	-0.0605	0.1562	1.0101	10.7066
H(37)	-0.0611	0.1748	0.9422	10.7066
H(38)	-0.0372	0.0970	0.9689	10.7066
H(39)	0.1235	0.0215	1.0053	6.3768
H(40)	0.1497	-0.0265	0.9580	6.3768
H(41)	0.1909	0.0446	0.9847	6.3768
H(42)	0.1374	0.0159	0.8528	6.0599
H(43)	0.1047	0.0927	0.8312	6.0599
H(44)	0.1793	0.0875	0.8773	6.0599
H(45)	0.0049	0.0266	0.9308	9.3970

H(46)	-0.0027	0.0555	0.8641	9.3970
H(47)	0.0337	-0.0201	0.8841	9.3970
H(48)	0.3081	0.4239	0.3633	3.5269
H(49)	0.2482	0.5331	0.3762	5.0146
H(50)	0.1510	0.5292	0.4196	5.3449
H(51)	0.1100	0.4162	0.4457	4.6672
H(52)	0.1653	0.3071	0.4298	3.3972
H(53)	0.2373	0.1239	0.4955	2.9417
H(54)	0.2233	0.1258	0.5954	3.4914
H(55)	0.2543	0.2305	0.6575	3.9388
H(56)	0.3008	0.3339	0.6182	3.8603
H(57)	0.3173	0.3315	0.5189	3.1062
H(58)	0.3369	0.0287	0.3734	3.0779
H(59)	0.3829	-0.0776	0.4274	3.5533
H(60)	0.4385	-0.0714	0.5327	3.7478
H(61)	0.4496	0.0417	0.5836	3.4166
H(62)	0.4035	0.1490	0.5306	2.7923
H(63)	0.4763	0.1432	0.3876	3.5092
H(64)	0.5481	0.0902	0.3307	4.5454
H(65)	0.5043	0.0712	0.2251	4.9122
H(66)	0.3878	0.1051	0.1765	5.1709
H(67)	0.3147	0.1569	0.2330	3.7938
H(68)	0.4280	0.3157	0.3159	4.2775
H(69)	0.4447	0.3876	0.2344	5.4104
H(70)	0.3485	0.4223	0.1549	5.3856
H(71)	0.2344	0.3873	0.1576	5.8526
H(72)	0.2173	0.3165	0.2394	4.6798
H(73)	0.1614	0.1729	0.2286	3.1151
H(74)	0.2298	0.0618	0.2804	3.4796
H(75)	0.2092	0.0494	0.3873	3.4428
H(76)	0.1305	0.1552	0.4026	2.9647
H(77)	-0.0468	0.0663	0.2962	6.2200
H(78)	0.0341	0.0798	0.3049	6.2200
H(79)	-0.0047	0.1143	0.3510	6.2200
H(80)	-0.0951	0.2111	0.3159	6.9472
H(81)	-0.1114	0.2412	0.2487	6.9472
H(82)	-0.1330	0.1611	0.2609	6.9472

H(83)	-0.0685	0.1094	0.1907	5.7505
H(84)	-0.0422	0.1863	0.1751	5.7505
H(85)	0.0123	0.1238	0.1998	5.7505
H(86)	-0.0489	0.3649	0.2527	7.0697
H(87)	-0.0354	0.3878	0.1897	7.0697
H(88)	-0.0667	0.3104	0.1972	7.0697
H(89)	0.0334	0.2533	0.1601	4.8430
H(90)	0.0575	0.3338	0.1521	4.8430
H(91)	0.1111	0.2774	0.1906	4.8430
H(92)	0.1373	0.3603	0.2821	5.5810
H(93)	0.0875	0.4178	0.2410	5.5810
H(94)	0.0751	0.3949	0.3044	5.5810

$$\text{Beq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S2. Anisotropic Displacement Parameters for (Ph₃Fc)P(*t*-Bu)₃.

atom	U11	U22	U33	U12	U13	U23
Fe(1)	0.0252(2)	0.0231(2)	0.0284(2)	0.0007(2)	0.0112(2)	-0.0007(2)
Fe(2)	0.0221(2)	0.0256(2)	0.0289(2)	0.0000(2)	0.0053(2)	0.0008(2)
P(1)	0.0301(3)	0.0297(4)	0.0346(4)	-0.0028(3)	0.0128(3)	0.0035(3)
P(2)	0.0263(3)	0.0484(5)	0.0285(4)	0.0072(3)	0.0051(3)	-0.0015(4)
C(1)	0.022(1)	0.023(1)	0.029(1)	0.003(1)	0.010(1)	0.004(1)
C(2)	0.023(1)	0.025(1)	0.026(1)	0.002(1)	0.011(1)	0.002(1)
C(3)	0.025(1)	0.022(1)	0.027(1)	0.001(1)	0.012(1)	0.002(1)
C(4)	0.024(1)	0.022(1)	0.028(1)	-0.001(1)	0.011(1)	0.000(1)
C(5)	0.025(1)	0.022(1)	0.028(1)	0.000(1)	0.011(1)	0.001(1)
C(6)	0.020(1)	0.022(1)	0.036(2)	0.000(1)	0.006(1)	0.006(1)
C(7)	0.025(1)	0.027(2)	0.043(2)	-0.001(1)	0.011(1)	0.002(1)
C(8)	0.025(1)	0.027(2)	0.070(2)	0.004(1)	0.015(2)	0.007(2)
C(9)	0.031(1)	0.040(2)	0.071(2)	0.006(1)	0.013(2)	0.026(2)
C(10)	0.039(2)	0.053(2)	0.047(2)	0.007(2)	0.010(1)	0.023(2)
C(11)	0.032(1)	0.034(2)	0.040(2)	0.005(1)	0.012(1)	0.011(1)
C(12)	0.028(1)	0.023(1)	0.025(1)	0.001(1)	0.011(1)	0.005(1)
C(13)	0.034(1)	0.029(2)	0.031(2)	-0.001(1)	0.008(1)	0.000(1)
C(14)	0.035(1)	0.043(2)	0.038(2)	-0.001(1)	0.005(1)	0.006(2)
C(15)	0.043(2)	0.053(2)	0.029(2)	-0.011(2)	0.001(1)	-0.004(2)
C(16)	0.050(2)	0.043(2)	0.028(2)	-0.003(1)	0.015(1)	-0.007(1)
C(17)	0.033(1)	0.035(2)	0.028(2)	0.002(1)	0.012(1)	0.001(1)
C(18)	0.027(1)	0.026(2)	0.021(1)	0.002(1)	0.004(1)	-0.002(1)
C(19)	0.072(2)	0.032(2)	0.055(2)	-0.001(2)	0.040(2)	0.001(2)
C(20)	0.133(3)	0.026(2)	0.051(2)	0.001(2)	0.038(2)	0.007(2)
C(21)	0.089(3)	0.035(2)	0.055(2)	0.029(2)	-0.010(2)	-0.007(2)
C(22)	0.040(2)	0.048(2)	0.104(3)	0.011(2)	0.012(2)	-0.031(2)
C(23)	0.038(2)	0.030(2)	0.067(2)	0.000(1)	0.022(2)	-0.009(2)
C(24)	0.028(1)	0.020(1)	0.029(1)	0.003(1)	0.006(1)	-0.002(1)
C(25)	0.032(1)	0.041(2)	0.045(2)	-0.007(1)	0.003(1)	0.009(2)
C(26)	0.033(2)	0.046(2)	0.063(2)	-0.005(1)	0.001(2)	0.011(2)
C(27)	0.037(2)	0.041(2)	0.049(2)	0.006(1)	-0.009(2)	-0.006(2)
C(28)	0.054(2)	0.051(2)	0.034(2)	0.020(2)	0.010(2)	0.011(2)
C(29)	0.035(1)	0.044(2)	0.038(2)	0.009(1)	0.013(1)	0.009(2)
C(30)	0.019(1)	0.022(1)	0.034(2)	0.001(1)	0.007(1)	-0.001(1)
C(31)	0.023(1)	0.030(2)	0.038(2)	0.000(1)	0.007(1)	0.002(1)

C(32)	0.032(1)	0.025(2)	0.054(2)	0.001(1)	0.013(1)	0.009(2)
C(33)	0.033(1)	0.025(2)	0.056(2)	-0.004(1)	0.016(1)	-0.008(2)
C(34)	0.037(1)	0.038(2)	0.041(2)	-0.007(1)	0.014(1)	-0.007(1)
C(35)	0.032(1)	0.027(2)	0.037(2)	-0.004(1)	0.011(1)	0.001(1)
C(36)	0.027(1)	0.025(1)	0.027(1)	0.001(1)	0.015(1)	0.001(1)
C(37)	0.033(1)	0.034(2)	0.033(2)	0.004(1)	0.017(1)	0.007(1)
C(38)	0.033(1)	0.050(2)	0.025(2)	0.000(1)	0.011(1)	-0.005(1)
C(39)	0.037(1)	0.034(2)	0.043(2)	-0.003(1)	0.021(1)	-0.015(1)
C(40)	0.027(1)	0.025(2)	0.039(2)	0.004(1)	0.014(1)	0.000(1)
C(41)	0.034(1)	0.039(2)	0.045(2)	0.002(1)	0.022(1)	0.006(1)
C(42)	0.080(2)	0.063(2)	0.048(2)	0.017(2)	0.039(2)	0.012(2)
C(43)	0.138(3)	0.058(2)	0.093(3)	0.038(2)	0.089(3)	0.023(2)
C(44)	0.046(2)	0.225(5)	0.079(3)	-0.036(3)	0.036(2)	-0.021(3)
C(45)	0.045(2)	0.029(2)	0.042(2)	-0.006(1)	0.019(1)	0.002(1)
C(46)	0.111(3)	0.035(2)	0.066(2)	0.021(2)	0.041(2)	0.008(2)
C(47)	0.115(3)	0.033(2)	0.058(2)	-0.008(2)	0.048(2)	-0.005(2)
C(48)	0.069(2)	0.041(2)	0.186(5)	-0.026(2)	0.029(3)	-0.025(3)
C(49)	0.021(1)	0.025(1)	0.026(1)	0.000(1)	0.004(1)	0.000(1)
C(50)	0.019(1)	0.026(1)	0.028(1)	-0.003(1)	0.005(1)	0.003(1)
C(51)	0.020(1)	0.024(1)	0.024(1)	-0.002(1)	0.003(1)	0.003(1)
C(52)	0.021(1)	0.025(2)	0.023(1)	0.000(1)	0.002(1)	0.000(1)
C(53)	0.020(1)	0.025(1)	0.024(1)	-0.002(1)	0.002(1)	0.004(1)
C(54)	0.030(1)	0.029(2)	0.023(1)	0.005(1)	-0.001(1)	-0.001(1)
C(55)	0.046(2)	0.029(2)	0.033(2)	0.003(1)	0.004(1)	-0.001(1)
C(56)	0.079(2)	0.030(2)	0.042(2)	0.008(2)	0.000(2)	-0.001(2)
C(57)	0.070(2)	0.052(2)	0.041(2)	0.033(2)	0.003(2)	-0.008(2)
C(58)	0.045(2)	0.061(2)	0.039(2)	0.023(2)	0.005(1)	-0.006(2)
C(59)	0.034(1)	0.043(2)	0.029(2)	0.009(1)	0.004(1)	-0.001(1)
C(60)	0.017(1)	0.035(2)	0.025(1)	0.003(1)	0.003(1)	0.004(1)
C(61)	0.021(1)	0.037(2)	0.035(2)	0.000(1)	0.007(1)	0.004(1)
C(62)	0.026(1)	0.050(2)	0.035(2)	-0.001(1)	0.009(1)	0.016(2)
C(63)	0.030(1)	0.068(2)	0.028(2)	0.000(1)	0.009(1)	0.004(2)
C(64)	0.034(1)	0.055(2)	0.032(2)	-0.003(1)	0.006(1)	-0.010(2)
C(65)	0.028(1)	0.037(2)	0.032(2)	-0.003(1)	0.005(1)	0.002(1)
C(66)	0.020(1)	0.027(2)	0.032(2)	0.001(1)	0.008(1)	0.006(1)
C(67)	0.027(1)	0.032(2)	0.038(2)	0.002(1)	0.007(1)	0.005(1)
C(68)	0.030(1)	0.025(2)	0.058(2)	0.002(1)	0.013(1)	0.004(2)

C(69)	0.029(1)	0.037(2)	0.053(2)	0.004(1)	0.012(1)	0.019(2)
C(70)	0.024(1)	0.049(2)	0.035(2)	0.002(1)	0.006(1)	0.015(2)
C(71)	0.022(1)	0.035(2)	0.032(2)	0.002(1)	0.008(1)	0.006(1)
C(72)	0.028(1)	0.022(1)	0.033(2)	-0.001(1)	0.010(1)	0.003(1)
C(73)	0.031(1)	0.043(2)	0.037(2)	0.009(1)	0.008(1)	0.005(1)
C(74)	0.036(2)	0.055(2)	0.057(2)	0.016(1)	0.019(2)	0.003(2)
C(75)	0.055(2)	0.048(2)	0.063(2)	0.009(2)	0.036(2)	-0.009(2)
C(76)	0.059(2)	0.065(2)	0.042(2)	-0.001(2)	0.018(2)	-0.017(2)
C(77)	0.037(1)	0.051(2)	0.033(2)	0.002(1)	0.009(1)	-0.008(2)
C(78)	0.030(1)	0.024(1)	0.025(1)	0.002(1)	0.007(1)	0.001(1)
C(79)	0.042(2)	0.047(2)	0.047(2)	-0.002(1)	0.014(1)	0.016(2)
C(80)	0.058(2)	0.057(2)	0.067(2)	-0.002(2)	0.036(2)	0.021(2)
C(81)	0.091(2)	0.042(2)	0.047(2)	0.013(2)	0.037(2)	0.018(2)
C(82)	0.071(2)	0.066(2)	0.043(2)	0.012(2)	0.003(2)	0.025(2)
C(83)	0.042(2)	0.059(2)	0.045(2)	0.002(2)	0.007(2)	0.018(2)
C(84)	0.023(1)	0.030(2)	0.029(1)	-0.002(1)	0.004(1)	-0.003(1)
C(85)	0.027(1)	0.038(2)	0.031(2)	-0.002(1)	0.002(1)	-0.004(1)
C(86)	0.030(1)	0.032(2)	0.047(2)	-0.001(1)	0.007(1)	-0.010(1)
C(87)	0.025(1)	0.027(2)	0.052(2)	-0.006(1)	0.001(1)	0.005(1)
C(88)	0.023(1)	0.038(2)	0.032(2)	-0.005(1)	0.006(1)	0.002(1)
C(89)	0.023(1)	0.063(2)	0.037(2)	-0.004(1)	0.006(1)	0.000(2)
C(90)	0.043(2)	0.079(3)	0.069(2)	-0.029(2)	0.003(2)	0.006(2)
C(91)	0.030(2)	0.106(3)	0.085(3)	-0.001(2)	0.015(2)	-0.019(2)
C(92)	0.048(2)	0.077(3)	0.059(2)	-0.026(2)	0.017(2)	-0.023(2)
C(93)	0.034(1)	0.046(2)	0.031(2)	0.012(1)	0.003(1)	0.000(1)
C(94)	0.057(2)	0.101(3)	0.066(2)	0.038(2)	0.014(2)	0.029(2)
C(95)	0.056(2)	0.058(2)	0.036(2)	0.001(2)	0.005(1)	0.004(2)
C(96)	0.080(2)	0.045(2)	0.043(2)	0.004(2)	0.000(2)	0.004(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table S3. Bond Lengths(Å) for (Ph₅Fc)P(*t*-Bu)₂.

atom	atom	distance		atom	atom	distance
Fe(1)	C(1)	2.059(2)		Fe(1)	C(2)	2.066(2)
Fe(1)	C(3)	2.077(2)		Fe(1)	C(4)	2.061(2)
Fe(1)	C(5)	2.063(2)		Fe(1)	C(36)	2.131(2)
Fe(1)	C(37)	2.087(2)		Fe(1)	C(38)	2.057(3)
Fe(1)	C(39)	2.038(2)		Fe(1)	C(40)	2.038(2)
Fe(2)	C(49)	2.069(2)		Fe(2)	C(50)	2.059(2)
Fe(2)	C(51)	2.061(2)		Fe(2)	C(52)	2.065(2)
Fe(2)	C(53)	2.079(2)		Fe(2)	C(84)	2.145(2)
Fe(2)	C(85)	2.092(2)		Fe(2)	C(86)	2.049(3)
Fe(2)	C(87)	2.028(2)		Fe(2)	C(88)	2.037(2)
P(1)	C(36)	1.844(2)		P(1)	C(41)	1.911(3)
P(1)	C(45)	1.883(3)		P(2)	C(84)	1.838(2)
P(2)	C(89)	1.912(3)		P(2)	C(93)	1.894(3)
C(1)	C(2)	1.441(3)		C(1)	C(5)	1.441(3)
C(1)	C(6)	1.485(3)		C(2)	C(3)	1.443(3)
C(2)	C(12)	1.483(3)		C(3)	C(4)	1.429(3)
C(3)	C(18)	1.489(3)		C(4)	C(5)	1.431(3)
C(4)	C(24)	1.492(3)		C(5)	C(30)	1.486(3)
C(6)	C(7)	1.395(3)		C(6)	C(11)	1.391(3)
C(7)	C(8)	1.389(3)		C(8)	C(9)	1.372(4)
C(9)	C(10)	1.379(4)		C(10)	C(11)	1.388(3)
C(12)	C(13)	1.397(3)		C(12)	C(17)	1.394(3)
C(13)	C(14)	1.380(3)		C(14)	C(15)	1.383(4)
C(15)	C(16)	1.386(3)		C(16)	C(17)	1.383(3)
C(18)	C(19)	1.370(3)		C(18)	C(23)	1.385(3)
C(19)	C(20)	1.384(4)		C(20)	C(21)	1.374(4)
C(21)	C(22)	1.363(4)		C(22)	C(23)	1.381(4)
C(24)	C(25)	1.383(3)		C(24)	C(29)	1.377(3)
C(25)	C(26)	1.386(3)		C(26)	C(27)	1.375(4)
C(27)	C(28)	1.372(4)		C(28)	C(29)	1.392(3)
C(30)	C(31)	1.393(3)		C(30)	C(35)	1.388(3)
C(31)	C(32)	1.383(3)		C(32)	C(33)	1.377(4)
C(33)	C(34)	1.379(4)		C(34)	C(35)	1.384(3)
C(36)	C(37)	1.434(3)		C(36)	C(40)	1.428(3)
C(37)	C(38)	1.418(3)		C(38)	C(39)	1.413(3)

C(39)	C(40)	1.411(3)		C(41)	C(42)	1.499(4)
C(41)	C(43)	1.519(4)		C(41)	C(44)	1.525(4)
C(45)	C(46)	1.522(4)		C(45)	C(47)	1.513(4)
C(45)	C(48)	1.529(4)		C(49)	C(50)	1.443(3)
C(49)	C(53)	1.439(3)		C(49)	C(54)	1.485(3)
C(50)	C(51)	1.445(3)		C(50)	C(60)	1.484(3)
C(51)	C(52)	1.438(3)		C(51)	C(66)	1.486(3)
C(52)	C(53)	1.435(3)		C(52)	C(72)	1.481(3)
C(53)	C(78)	1.487(3)		C(54)	C(55)	1.391(3)
C(54)	C(59)	1.399(3)		C(55)	C(56)	1.398(4)
C(56)	C(57)	1.382(4)		C(57)	C(58)	1.373(4)
C(58)	C(59)	1.375(4)		C(60)	C(61)	1.397(3)
C(60)	C(65)	1.396(3)		C(61)	C(62)	1.379(3)
C(62)	C(63)	1.381(4)		C(63)	C(64)	1.386(4)
C(64)	C(65)	1.382(3)		C(66)	C(67)	1.397(3)
C(66)	C(71)	1.401(3)		C(67)	C(68)	1.382(3)
C(68)	C(69)	1.376(4)		C(69)	C(70)	1.376(4)
C(70)	C(71)	1.387(3)		C(72)	C(73)	1.396(3)
C(72)	C(77)	1.385(3)		C(73)	C(74)	1.378(3)
C(74)	C(75)	1.367(4)		C(75)	C(76)	1.380(4)
C(76)	C(77)	1.380(4)		C(78)	C(79)	1.387(3)
C(78)	C(83)	1.368(3)		C(79)	C(80)	1.384(4)
C(80)	C(81)	1.363(4)		C(81)	C(82)	1.365(4)
C(82)	C(83)	1.384(4)		C(84)	C(85)	1.435(3)
C(84)	C(88)	1.432(3)		C(85)	C(86)	1.413(3)
C(86)	C(87)	1.411(4)		C(87)	C(88)	1.415(3)
C(89)	C(90)	1.536(4)		C(89)	C(91)	1.529(4)
C(89)	C(92)	1.518(4)		C(93)	C(94)	1.535(4)
C(93)	C(95)	1.524(4)		C(93)	C(96)	1.522(4)

Table S4. Bond Angles($^{\circ}$) for $(\text{Ph}_5\text{Fc})\text{P}(t\text{-Bu})_2$.

atom	atom	atom	angle		atom	atom	atom	angle
C(1)	Fe(1)	C(2)	40.88(8)		C(1)	Fe(1)	C(3)	68.45(9)
C(1)	Fe(1)	C(4)	68.48(9)		C(1)	Fe(1)	C(5)	40.93(8)
C(1)	Fe(1)	C(36)	129.65(9)		C(1)	Fe(1)	C(37)	169.24(9)
C(1)	Fe(1)	C(38)	146.1(1)		C(1)	Fe(1)	C(39)	112.5(1)
C(1)	Fe(1)	C(40)	105.57(9)		C(2)	Fe(1)	C(3)	40.77(8)
C(2)	Fe(1)	C(4)	68.50(9)		C(2)	Fe(1)	C(5)	68.82(9)
C(2)	Fe(1)	C(36)	113.54(9)		C(2)	Fe(1)	C(37)	134.78(10)
C(2)	Fe(1)	C(38)	170.80(10)		C(2)	Fe(1)	C(39)	148.8(1)
C(2)	Fe(1)	C(40)	119.38(9)		C(3)	Fe(1)	C(4)	40.39(8)
C(3)	Fe(1)	C(5)	68.31(9)		C(3)	Fe(1)	C(36)	125.19(9)
C(3)	Fe(1)	C(37)	114.80(9)		C(3)	Fe(1)	C(38)	130.72(10)
C(3)	Fe(1)	C(39)	163.77(9)		C(3)	Fe(1)	C(40)	155.73(10)
C(4)	Fe(1)	C(5)	40.61(8)		C(4)	Fe(1)	C(36)	156.29(9)
C(4)	Fe(1)	C(37)	121.03(9)		C(4)	Fe(1)	C(38)	106.89(9)
C(4)	Fe(1)	C(39)	123.80(9)		C(4)	Fe(1)	C(40)	161.30(10)
C(5)	Fe(1)	C(36)	163.07(9)		C(5)	Fe(1)	C(37)	149.57(10)
C(5)	Fe(1)	C(38)	113.30(10)		C(5)	Fe(1)	C(39)	101.33(9)
C(5)	Fe(1)	C(40)	123.48(10)		C(36)	Fe(1)	C(37)	39.73(8)
C(36)	Fe(1)	C(38)	67.26(9)		C(36)	Fe(1)	C(39)	67.66(9)
C(36)	Fe(1)	C(40)	39.97(9)		C(37)	Fe(1)	C(38)	40.01(9)
C(37)	Fe(1)	C(39)	67.5(1)		C(37)	Fe(1)	C(40)	67.05(9)
C(38)	Fe(1)	C(39)	40.37(10)		C(38)	Fe(1)	C(40)	67.57(10)
C(39)	Fe(1)	C(40)	40.49(9)		C(49)	Fe(2)	C(50)	40.93(9)
C(49)	Fe(2)	C(51)	68.79(9)		C(49)	Fe(2)	C(52)	68.54(9)
C(49)	Fe(2)	C(53)	40.60(9)		C(49)	Fe(2)	C(84)	114.95(9)
C(49)	Fe(2)	C(85)	134.65(10)		C(49)	Fe(2)	C(86)	168.8(1)
C(49)	Fe(2)	C(87)	150.6(1)		C(49)	Fe(2)	C(88)	121.29(10)
C(50)	Fe(2)	C(51)	41.06(8)		C(50)	Fe(2)	C(52)	68.85(9)
C(50)	Fe(2)	C(53)	68.57(9)		C(50)	Fe(2)	C(84)	129.59(9)
C(50)	Fe(2)	C(85)	168.92(9)		C(50)	Fe(2)	C(86)	146.9(1)
C(50)	Fe(2)	C(87)	113.1(1)		C(50)	Fe(2)	C(88)	105.70(9)
C(51)	Fe(2)	C(52)	40.79(8)		C(51)	Fe(2)	C(53)	68.40(9)
C(51)	Fe(2)	C(84)	161.74(9)		C(51)	Fe(2)	C(85)	149.75(10)
C(51)	Fe(2)	C(86)	112.95(10)		C(51)	Fe(2)	C(87)	100.14(9)
C(51)	Fe(2)	C(88)	122.10(10)		C(52)	Fe(2)	C(53)	40.52(9)

C(52)	Fe(2)	C(84)	157.26(9)		C(52)	Fe(2)	C(85)	120.95(9)
C(52)	Fe(2)	C(86)	105.15(9)		C(52)	Fe(2)	C(87)	121.37(10)
C(52)	Fe(2)	C(88)	159.20(10)		C(53)	Fe(2)	C(84)	126.87(9)
C(53)	Fe(2)	C(85)	114.76(9)		C(53)	Fe(2)	C(86)	128.8(1)
C(53)	Fe(2)	C(87)	161.29(10)		C(53)	Fe(2)	C(88)	157.98(10)
C(84)	Fe(2)	C(85)	39.57(9)		C(84)	Fe(2)	C(86)	67.14(9)
C(84)	Fe(2)	C(87)	67.61(9)		C(84)	Fe(2)	C(88)	39.93(9)
C(85)	Fe(2)	C(86)	39.89(9)		C(85)	Fe(2)	C(87)	67.4(1)
C(85)	Fe(2)	C(88)	67.06(10)		C(86)	Fe(2)	C(87)	40.49(10)
C(86)	Fe(2)	C(88)	67.86(10)		C(87)	Fe(2)	C(88)	40.72(9)
C(36)	P(1)	C(41)	97.4(1)		C(36)	P(1)	C(45)	109.6(1)
C(41)	P(1)	C(45)	108.3(1)		C(84)	P(2)	C(89)	98.7(1)
C(84)	P(2)	C(93)	109.3(1)		C(89)	P(2)	C(93)	108.1(1)
Fe(1)	C(1)	C(2)	69.8(1)		Fe(1)	C(1)	C(5)	69.7(1)
Fe(1)	C(1)	C(6)	131.2(2)		C(2)	C(1)	C(5)	108.1(2)
C(2)	C(1)	C(6)	127.2(2)		C(5)	C(1)	C(6)	124.4(2)
Fe(1)	C(2)	C(1)	69.3(1)		Fe(1)	C(2)	C(3)	70.0(1)
Fe(1)	C(2)	C(12)	127.5(2)		C(1)	C(2)	C(3)	107.5(2)
C(1)	C(2)	C(12)	124.6(2)		C(3)	C(2)	C(12)	127.9(2)
Fe(1)	C(3)	C(2)	69.2(1)		Fe(1)	C(3)	C(4)	69.2(1)
Fe(1)	C(3)	C(18)	134.5(2)		C(2)	C(3)	C(4)	108.0(2)
C(2)	C(3)	C(18)	130.4(2)		C(4)	C(3)	C(18)	121.0(2)
Fe(1)	C(4)	C(3)	70.4(1)		Fe(1)	C(4)	C(5)	69.8(1)
Fe(1)	C(4)	C(24)	131.9(2)		C(3)	C(4)	C(5)	108.7(2)
C(3)	C(4)	C(24)	125.2(2)		C(5)	C(4)	C(24)	125.6(2)
Fe(1)	C(5)	C(1)	69.4(1)		Fe(1)	C(5)	C(4)	69.6(1)
Fe(1)	C(5)	C(30)	130.2(2)		C(1)	C(5)	C(4)	107.6(2)
C(1)	C(5)	C(30)	127.0(2)		C(4)	C(5)	C(30)	125.2(2)
C(1)	C(6)	C(7)	122.2(2)		C(1)	C(6)	C(11)	119.4(2)
C(7)	C(6)	C(11)	118.3(2)		C(6)	C(7)	C(8)	120.5(2)
C(7)	C(8)	C(9)	120.3(3)		C(8)	C(9)	C(10)	120.1(3)
C(9)	C(10)	C(11)	120.0(3)		C(6)	C(11)	C(10)	120.8(3)
C(2)	C(12)	C(13)	120.9(2)		C(2)	C(12)	C(17)	121.5(2)
C(13)	C(12)	C(17)	117.6(2)		C(12)	C(13)	C(14)	121.2(2)
C(13)	C(14)	C(15)	120.3(2)		C(14)	C(15)	C(16)	119.5(2)
C(15)	C(16)	C(17)	120.0(2)		C(12)	C(17)	C(16)	121.4(2)
C(3)	C(18)	C(19)	124.1(2)		C(3)	C(18)	C(23)	118.2(2)

C(19)	C(18)	C(23)	117.6(2)		C(18)	C(19)	C(20)	121.6(3)
C(19)	C(20)	C(21)	119.8(3)		C(20)	C(21)	C(22)	119.6(3)
C(21)	C(22)	C(23)	120.3(3)		C(18)	C(23)	C(22)	121.2(3)
C(4)	C(24)	C(25)	118.5(2)		C(4)	C(24)	C(29)	123.4(2)
C(25)	C(24)	C(29)	118.1(2)		C(24)	C(25)	C(26)	121.4(2)
C(25)	C(26)	C(27)	119.5(2)		C(26)	C(27)	C(28)	120.1(2)
C(27)	C(28)	C(29)	119.9(3)		C(24)	C(29)	C(28)	120.9(2)
C(5)	C(30)	C(31)	120.2(2)		C(5)	C(30)	C(35)	121.7(2)
C(31)	C(30)	C(35)	118.1(2)		C(30)	C(31)	C(32)	120.7(2)
C(31)	C(32)	C(33)	120.5(2)		C(32)	C(33)	C(34)	119.5(2)
C(33)	C(34)	C(35)	120.2(2)		C(30)	C(35)	C(34)	121.0(2)
Fe(1)	C(36)	P(1)	143.5(1)		Fe(1)	C(36)	C(37)	68.5(1)
Fe(1)	C(36)	C(40)	66.5(1)		P(1)	C(36)	C(37)	135.1(2)
P(1)	C(36)	C(40)	116.1(2)		C(37)	C(36)	C(40)	105.5(2)
Fe(1)	C(37)	C(36)	71.8(1)		Fe(1)	C(37)	C(38)	68.9(1)
C(36)	C(37)	C(38)	108.9(2)		Fe(1)	C(38)	C(37)	71.1(1)
Fe(1)	C(38)	C(39)	69.1(1)		C(37)	C(38)	C(39)	108.1(2)
Fe(1)	C(39)	C(38)	70.5(1)		Fe(1)	C(39)	C(40)	69.7(1)
C(38)	C(39)	C(40)	107.5(2)		Fe(1)	C(40)	C(36)	73.5(1)
Fe(1)	C(40)	C(39)	69.8(1)		C(36)	C(40)	C(39)	109.8(2)
P(1)	C(41)	C(42)	117.3(2)		P(1)	C(41)	C(43)	107.4(2)
P(1)	C(41)	C(44)	108.3(2)		C(42)	C(41)	C(43)	107.0(3)
C(42)	C(41)	C(44)	109.8(3)		C(43)	C(41)	C(44)	106.5(3)
P(1)	C(45)	C(46)	119.1(2)		P(1)	C(45)	C(47)	105.5(2)
P(1)	C(45)	C(48)	108.2(2)		C(46)	C(45)	C(47)	108.3(2)
C(46)	C(45)	C(48)	108.0(3)		C(47)	C(45)	C(48)	107.2(3)
Fe(2)	C(49)	C(50)	69.2(1)		Fe(2)	C(49)	C(53)	70.1(1)
Fe(2)	C(49)	C(54)	128.2(1)		C(50)	C(49)	C(53)	107.9(2)
C(50)	C(49)	C(54)	124.2(2)		C(53)	C(49)	C(54)	127.8(2)
Fe(2)	C(50)	C(49)	69.9(1)		Fe(2)	C(50)	C(51)	69.5(1)
Fe(2)	C(50)	C(60)	131.6(2)		C(49)	C(50)	C(51)	107.7(2)
C(49)	C(50)	C(60)	126.7(2)		C(51)	C(50)	C(60)	125.1(2)
Fe(2)	C(51)	C(50)	69.4(1)		Fe(2)	C(51)	C(52)	69.8(1)
Fe(2)	C(51)	C(66)	128.6(2)		C(50)	C(51)	C(52)	107.9(2)
C(50)	C(51)	C(66)	126.2(2)		C(52)	C(51)	C(66)	125.8(2)
Fe(2)	C(52)	C(51)	69.5(1)		Fe(2)	C(52)	C(53)	70.3(1)
Fe(2)	C(52)	C(72)	131.4(2)		C(51)	C(52)	C(53)	108.2(2)

C(51)	C(52)	C(72)	127.2(2)		C(53)	C(52)	C(72)	124.3(2)
Fe(2)	C(53)	C(49)	69.3(1)		Fe(2)	C(53)	C(52)	69.2(1)
Fe(2)	C(53)	C(78)	134.1(2)		C(49)	C(53)	C(52)	108.2(2)
C(49)	C(53)	C(78)	128.3(2)		C(52)	C(53)	C(78)	122.9(2)
C(49)	C(54)	C(55)	121.1(2)		C(49)	C(54)	C(59)	120.2(2)
C(55)	C(54)	C(59)	118.7(2)		C(54)	C(55)	C(56)	119.8(2)
C(55)	C(56)	C(57)	120.5(3)		C(56)	C(57)	C(58)	119.5(3)
C(57)	C(58)	C(59)	120.7(3)		C(54)	C(59)	C(58)	120.7(3)
C(50)	C(60)	C(61)	122.5(2)		C(50)	C(60)	C(65)	119.9(2)
C(61)	C(60)	C(65)	117.5(2)		C(60)	C(61)	C(62)	121.1(2)
C(61)	C(62)	C(63)	120.7(2)		C(62)	C(63)	C(64)	119.2(2)
C(63)	C(64)	C(65)	120.2(3)		C(60)	C(65)	C(64)	121.4(2)
C(51)	C(66)	C(67)	122.0(2)		C(51)	C(66)	C(71)	120.1(2)
C(67)	C(66)	C(71)	117.8(2)		C(66)	C(67)	C(68)	121.2(2)
C(67)	C(68)	C(69)	120.1(3)		C(68)	C(69)	C(70)	119.8(2)
C(69)	C(70)	C(71)	120.7(2)		C(66)	C(71)	C(70)	120.3(2)
C(52)	C(72)	C(73)	119.6(2)		C(52)	C(72)	C(77)	122.3(2)
C(73)	C(72)	C(77)	117.9(2)		C(72)	C(73)	C(74)	121.2(2)
C(73)	C(74)	C(75)	120.1(2)		C(74)	C(75)	C(76)	119.5(3)
C(75)	C(76)	C(77)	120.7(3)		C(72)	C(77)	C(76)	120.5(2)
C(53)	C(78)	C(79)	119.1(2)		C(53)	C(78)	C(83)	123.3(2)
C(79)	C(78)	C(83)	117.6(2)		C(78)	C(79)	C(80)	120.6(2)
C(79)	C(80)	C(81)	120.5(3)		C(80)	C(81)	C(82)	119.7(3)
C(81)	C(82)	C(83)	119.7(3)		C(78)	C(83)	C(82)	121.8(3)
Fe(2)	C(84)	P(2)	143.6(1)		Fe(2)	C(84)	C(85)	68.2(1)
Fe(2)	C(84)	C(88)	66.0(1)		P(2)	C(84)	C(85)	135.6(2)
P(2)	C(84)	C(88)	115.8(2)		C(85)	C(84)	C(88)	105.5(2)
Fe(2)	C(85)	C(84)	72.2(1)		Fe(2)	C(85)	C(86)	68.4(1)
C(84)	C(85)	C(86)	109.1(2)		Fe(2)	C(86)	C(85)	71.7(1)
Fe(2)	C(86)	C(87)	69.0(1)		C(85)	C(86)	C(87)	108.2(2)
Fe(2)	C(87)	C(86)	70.5(1)		Fe(2)	C(87)	C(88)	70.0(1)
C(86)	C(87)	C(88)	107.7(2)		Fe(2)	C(88)	C(84)	74.1(1)
Fe(2)	C(88)	C(87)	69.3(1)		C(84)	C(88)	C(87)	109.5(2)
P(2)	C(89)	C(90)	109.0(2)		P(2)	C(89)	C(91)	108.2(2)
P(2)	C(89)	C(92)	116.7(2)		C(90)	C(89)	C(91)	106.3(2)
C(90)	C(89)	C(92)	106.3(3)		C(91)	C(89)	C(92)	109.9(2)
P(2)	C(93)	C(94)	108.9(2)		P(2)	C(93)	C(95)	118.9(2)

P(2)	C(93)	C(96)	105.3(2)		C(94)	C(93)	C(95)	107.5(2)
C(94)	C(93)	C(96)	107.3(2)		C(95)	C(93)	C(96)	108.5(2)

Experimental Details for the Structure Solution of $(\text{Ph}_5\text{Fc})\text{P}(\text{t-Bu})_2$

Data Collection: An orange plate crystal of $\text{C}_{42}\text{H}_{43}\text{PFe}$ having approximate dimensions of 0.08 x 0.20 x 0.23 mm was mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo-K α radiation.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using ten (1° in ω , 10 s exposure, de-zingered) data frames, corresponded to a primitive triclinic cell with dimensions:

$$a = 10.3484(3) \text{ \AA} \quad \alpha = 88.715(2)^\circ$$

$$b = 12.5331(3) \text{ \AA} \quad \beta = 78.692(2)^\circ$$

$$c = 13.3058(4) \text{ \AA} \quad \gamma = 79.560(2)^\circ$$

$$V = 1664.06(8) \text{ \AA}^3$$

For $Z = 2$ and F.W. = 634.62, the calculated density is 1.27 g/cm³. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: P_{-1} (#2).

The data were collected at a temperature of $-90 \pm 1^\circ\text{C}$ to a maximum 2θ value of 55.1° . Five omega scans consisting of 55, 51, 33, 40 and 20 data frames, respectively, were collected with a scan width of 2.0° and a detector-to-crystal distance, D_x , of 33 mm. Each frame was exposed twice (for the purpose of de-zingered) for 120 s. The data frames were processed and scaled using the DENZO software package. (Z. Otwinowski and W. Minor, "Processing of X-Ray Diffraction Data Collected in Oscillation Mode," Methods in Enzymology, vol. 276: Macromolecular Crystallography, part A, 307-326, 1997, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press).

Data Reduction: A total of 7626 reflections was collected. No decay correction was applied. The linear absorption coefficient, μ , for Mo-K α radiation is 5.3 cm⁻¹. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement: The structure was solved by direct methods and expanded using Fourier techniques.⁵³ The non-hydrogen atoms were refined anisotropically.

Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement⁵⁴ was based on 5135 observed reflections ($I > 3.00\sigma(I)$) and 569 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.041$$

$$R_w = [(\Sigma w (|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2} = 0.040$$

The standard deviation of an observation of unit weight⁵⁵ was 1.69. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. Plots of $\Sigma w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.30 and -0.45 $e^-/\text{\AA}^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.⁵⁶ Anomalous dispersion effects were included in F_{calc} ;⁵⁷ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.⁵⁸ The values for the mass attenuation coefficients are those of Creagh and Hubbel.⁵⁹ All calculations were performed using the teXsan⁶⁰ crystallographic software package of Molecular Structure Corporation.

Experimental details for $\text{Ph}_4\text{FcP}(t\text{-Bu})_2$

A. Crystal Data

Empirical Formula	$\text{C}_{42}\text{H}_{43}\text{PFe}$
Formula Weight	634.62
Crystal Color, Habit	orange, plate
Crystal Dimensions	0.08 X 0.20 X 0.23 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	$a = 10.3484(3) \text{ \AA}$ $b = 12.5331(3) \text{ \AA}$ $c = 13.3058(4) \text{ \AA}$ $\alpha = 88.715(2)^\circ$ $\beta = 78.692(2)^\circ$ $\gamma = 79.560(2)^\circ$ $V = 1664.06(8) \text{ \AA}^3$
Space Group	P_{-1} (#2)
Z value	2
D _{calc}	1.266 g/cm ³
F ₀₀₀	672.00
$\mu(\text{MoK}\alpha)$	5.30 cm ⁻¹

B. Intensity Measurements

Diffractometer	Nonius KappaCCD
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Take-off Angle	2.8 $^\circ$
Crystal to Detector Distance	33 mm
Temperature	-90.0 $^\circ\text{C}$
Scan Rate	120 s/frame
Scan Width	2.0 $^\circ$ /frame
$2\theta_{\text{max}}$	55.1 $^\circ$
No. of Reflections Measured	Total: 7626
Corrections	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w (F_o - F_c)^2$

Least Squares Weights	$1/\sigma^2(F_o)$
p-factor	0.0100
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00_\sigma(I)$)	5135
No. Variables	569
Reflection/Parameter Ratio	9.02
Residuals: R; R_w	0.041 ; 0.040
Goodness of Fit Indicator	1.69
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	$0.30 \text{ e}^-/\text{\AA}^3$
Minimum peak in Final Diff. Map	$-0.45 \text{ e}^-/\text{\AA}^3$

Table S5. Atomic coordinates and Biso/Beq of Ph₄FcP(*t*-Bu)₂.

atom	x	y	z	Beq
Fe(1)	0.52098(3)	0.29811(2)	0.73249(2)	1.890(7)
P(1)	0.22348(6)	0.22914(4)	0.89799(4)	2.08(1)
C(1)	0.4035(2)	0.4121(2)	0.6602(2)	2.00(5)
C(2)	0.4919(2)	0.3391(2)	0.5861(2)	2.00(5)
C(3)	0.6263(2)	0.3448(2)	0.5955(2)	2.06(5)
C(4)	0.6204(2)	0.4218(2)	0.6764(2)	1.99(5)
C(5)	0.4795(2)	0.4638(2)	0.7162(2)	2.01(5)
C(6)	0.4483(2)	0.2724(2)	0.5128(2)	2.08(5)
C(7)	0.3348(3)	0.3130(2)	0.4734(2)	2.62(6)
C(8)	0.2876(3)	0.2519(2)	0.4085(2)	3.27(7)
C(9)	0.3554(3)	0.1495(2)	0.3795(2)	3.68(7)
C(10)	0.4688(3)	0.1077(2)	0.4170(2)	3.51(7)
C(11)	0.5151(3)	0.1683(2)	0.4838(2)	2.77(6)
C(12)	0.7477(2)	0.2881(2)	0.5238(2)	2.40(5)
C(13)	0.8552(3)	0.2222(2)	0.5566(2)	2.93(6)
C(14)	0.9625(3)	0.1681(2)	0.4853(2)	3.82(7)
C(15)	0.9637(3)	0.1799(3)	0.3817(2)	4.16(7)
C(16)	0.8610(3)	0.2461(2)	0.3487(2)	3.74(7)
C(17)	0.7538(3)	0.3001(2)	0.4186(2)	2.90(6)
C(18)	0.7352(2)	0.4560(2)	0.7104(2)	2.18(5)
C(19)	0.8491(2)	0.4701(2)	0.6394(2)	2.65(6)
C(20)	0.9539(3)	0.5074(2)	0.6694(2)	3.52(7)
C(21)	0.9470(3)	0.5313(2)	0.7709(2)	3.81(8)
C(22)	0.8362(3)	0.5174(2)	0.8423(2)	3.24(7)
C(23)	0.7313(3)	0.4792(2)	0.8132(2)	2.70(6)
C(24)	0.4161(2)	0.5535(2)	0.7911(2)	2.02(5)
C(25)	0.4629(3)	0.6508(2)	0.7842(2)	2.52(6)
C(26)	0.3947(3)	0.7387(2)	0.8464(2)	2.82(6)
C(27)	0.2796(3)	0.7307(2)	0.9144(2)	2.83(6)
C(28)	0.2315(3)	0.6344(2)	0.9226(2)	2.96(6)
C(29)	0.2999(3)	0.5461(2)	0.8610(2)	2.63(6)
C(30)	0.4025(2)	0.2141(2)	0.8414(2)	1.90(5)
C(31)	0.4891(2)	0.1424(2)	0.7646(2)	2.31(5)
C(32)	0.6229(3)	0.1497(2)	0.7644(2)	2.81(6)
C(33)	0.6235(3)	0.2268(2)	0.8392(2)	2.65(6)

C(34)	0.4895(2)	0.2677(2)	0.8855(2)	2.28(5)
C(35)	0.1436(2)	0.1677(2)	0.8018(2)	2.53(5)
C(36)	0.1772(3)	0.2283(3)	0.7019(2)	3.73(8)
C(37)	-0.0088(3)	0.1974(3)	0.8387(2)	3.85(8)
C(38)	0.1801(4)	0.0459(2)	0.7801(3)	3.82(8)
C(39)	0.2349(2)	0.1315(2)	1.0094(2)	2.61(5)
C(40)	0.2928(5)	0.1865(3)	1.0871(2)	4.86(9)
C(41)	0.0946(3)	0.1158(3)	1.0608(3)	4.47(8)
C(42)	0.3235(4)	0.0212(3)	0.9820(3)	4.92(9)
H(1)	0.308(2)	0.424(1)	0.671(1)	1.0(4)
H(2)	0.293(2)	0.380(2)	0.492(2)	2.9(5)
H(3)	0.211(2)	0.283(2)	0.383(2)	3.1(5)
H(4)	0.332(2)	0.106(2)	0.333(2)	3.9(6)
H(5)	0.519(2)	0.039(2)	0.400(2)	2.8(5)
H(6)	0.596(2)	0.138(2)	0.510(2)	2.7(5)
H(7)	0.852(2)	0.215(2)	0.631(2)	3.0(5)
H(8)	1.032(3)	0.122(2)	0.509(2)	3.9(6)
H(9)	1.036(3)	0.139(2)	0.339(2)	3.6(6)
H(10)	0.864(2)	0.253(2)	0.275(2)	4.2(6)
H(11)	0.682(2)	0.346(2)	0.396(2)	3.4(6)
H(12)	0.859(2)	0.455(2)	0.570(2)	2.7(5)
H(13)	1.028(2)	0.523(2)	0.622(2)	3.2(6)
H(14)	1.016(2)	0.553(2)	0.790(2)	2.7(5)
H(15)	0.824(2)	0.534(2)	0.911(2)	3.0(5)
H(16)	0.654(2)	0.470(2)	0.864(2)	2.5(5)
H(17)	0.532(2)	0.656(2)	0.740(2)	2.1(5)
H(18)	0.429(2)	0.803(2)	0.841(2)	2.7(5)
H(19)	0.235(2)	0.791(2)	0.959(2)	3.8(6)
H(20)	0.155(2)	0.630(2)	0.965(2)	2.4(5)
H(21)	0.265(2)	0.482(2)	0.867(2)	2.5(5)
H(22)	0.460(2)	0.100(2)	0.721(2)	2.0(5)
H(23)	0.696(2)	0.115(2)	0.721(2)	2.4(5)
H(24)	0.691(2)	0.249(2)	0.853(2)	2.2(5)
H(25)	0.462(2)	0.320(2)	0.931(2)	1.6(5)
H(26)	0.147(2)	0.310(2)	0.717(2)	3.8(6)
H(27)	0.271(3)	0.211(2)	0.672(2)	3.1(5)
H(28)	0.123(3)	0.208(2)	0.653(2)	4.5(6)

H(29)	-0.036(3)	0.279(3)	0.845(2)	8.0(9)
H(30)	-0.052(3)	0.173(2)	0.787(2)	4.3(6)
H(31)	-0.042(3)	0.159(2)	0.896(2)	4.2(6)
H(32)	0.149(2)	0.006(2)	0.837(2)	3.0(6)
H(33)	0.132(3)	0.035(2)	0.722(2)	5.6(7)
H(34)	0.278(3)	0.019(2)	0.761(2)	5.3(7)
H(35)	0.231(3)	0.254(2)	1.104(2)	3.9(7)
H(36)	0.293(3)	0.140(2)	1.144(2)	7.0(8)
H(37)	0.393(4)	0.192(3)	1.054(3)	7.4(9)
H(38)	0.056(3)	0.076(2)	1.017(2)	6.2(8)
H(39)	0.034(3)	0.190(2)	1.075(2)	6.3(8)
H(40)	0.099(3)	0.076(2)	1.125(2)	4.6(6)
H(41)	0.297(4)	-0.019(3)	0.937(3)	10(1)
H(42)	0.410(4)	0.025(3)	0.946(3)	7.3(10)
H(43)	0.325(3)	-0.017(2)	1.046(2)	5.5(7)

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S6. Anisotropic Displacement Parameters of Ph₄FcP(*t*-Bu)₂.

atom	U11	U22	U33	U12	U13	U23
Fe(1)	0.0239(2)	0.0242(2)	0.0242(2)	-0.0055(1)	-0.0051(1)	0.0021(1)
P(1)	0.0253(3)	0.0267(3)	0.0256(3)	-0.0045(3)	-0.0018(3)	-0.0005(2)
C(1)	0.024(1)	0.025(1)	0.028(1)	-0.005(1)	-0.008(1)	0.0046(10)
C(2)	0.028(1)	0.024(1)	0.024(1)	-0.004(1)	-0.007(1)	0.0028(9)
C(3)	0.029(1)	0.026(1)	0.024(1)	-0.005(1)	-0.006(1)	0.0036(9)
C(4)	0.025(1)	0.028(1)	0.025(1)	-0.008(1)	-0.0058(10)	0.0051(9)
C(5)	0.030(1)	0.025(1)	0.023(1)	-0.007(1)	-0.006(1)	0.0032(9)
C(6)	0.029(1)	0.031(1)	0.021(1)	-0.011(1)	-0.004(1)	0.0055(10)
C(7)	0.037(2)	0.035(1)	0.029(1)	-0.009(1)	-0.009(1)	0.005(1)
C(8)	0.046(2)	0.049(2)	0.039(2)	-0.021(1)	-0.020(1)	0.010(1)
C(9)	0.070(2)	0.053(2)	0.030(1)	-0.033(2)	-0.021(1)	0.003(1)
C(10)	0.064(2)	0.035(2)	0.035(2)	-0.012(1)	-0.008(1)	-0.008(1)
C(11)	0.041(2)	0.035(1)	0.030(1)	-0.007(1)	-0.009(1)	-0.003(1)
C(12)	0.031(1)	0.033(1)	0.028(1)	-0.011(1)	-0.003(1)	0.001(1)
C(13)	0.033(2)	0.046(2)	0.033(1)	-0.010(1)	-0.005(1)	0.001(1)
C(14)	0.033(2)	0.055(2)	0.053(2)	-0.001(1)	-0.005(1)	-0.006(1)
C(15)	0.035(2)	0.074(2)	0.044(2)	-0.008(2)	0.007(1)	-0.023(2)
C(16)	0.046(2)	0.071(2)	0.027(1)	-0.022(2)	-0.002(1)	-0.006(1)
C(17)	0.036(2)	0.046(2)	0.030(1)	-0.014(1)	-0.006(1)	0.003(1)
C(18)	0.031(1)	0.023(1)	0.031(1)	-0.006(1)	-0.008(1)	0.0041(10)
C(19)	0.035(2)	0.035(1)	0.032(1)	-0.012(1)	-0.005(1)	0.002(1)
C(20)	0.035(2)	0.046(2)	0.053(2)	-0.017(1)	-0.004(1)	0.006(1)
C(21)	0.043(2)	0.047(2)	0.067(2)	-0.020(1)	-0.027(2)	0.006(1)
C(22)	0.052(2)	0.040(1)	0.040(2)	-0.016(1)	-0.021(1)	0.004(1)
C(23)	0.039(2)	0.034(1)	0.032(1)	-0.014(1)	-0.008(1)	0.005(1)
C(24)	0.027(1)	0.027(1)	0.023(1)	-0.005(1)	-0.006(1)	0.0019(9)
C(25)	0.030(1)	0.034(1)	0.031(1)	-0.009(1)	0.000(1)	-0.001(1)
C(26)	0.040(2)	0.027(1)	0.042(2)	-0.011(1)	-0.010(1)	-0.005(1)
C(27)	0.042(2)	0.033(1)	0.031(1)	-0.002(1)	-0.007(1)	-0.007(1)
C(28)	0.034(2)	0.043(2)	0.029(1)	-0.004(1)	0.006(1)	0.001(1)
C(29)	0.036(2)	0.027(1)	0.036(1)	-0.008(1)	-0.002(1)	0.002(1)
C(30)	0.025(1)	0.023(1)	0.025(1)	-0.0057(10)	-0.0050(10)	0.0040(9)
C(31)	0.033(2)	0.023(1)	0.032(1)	-0.008(1)	-0.006(1)	0.002(1)
C(32)	0.027(2)	0.033(1)	0.041(2)	0.001(1)	0.000(1)	0.011(1)
C(33)	0.030(2)	0.041(1)	0.037(2)	-0.014(1)	-0.017(1)	0.014(1)

C(34)	0.035(2)	0.030(1)	0.023(1)	-0.009(1)	-0.008(1)	0.005(1)
C(35)	0.024(1)	0.044(1)	0.030(1)	-0.012(1)	-0.003(1)	-0.002(1)
C(36)	0.038(2)	0.075(2)	0.036(2)	-0.021(2)	-0.014(1)	0.010(1)
C(37)	0.031(2)	0.074(2)	0.044(2)	-0.016(2)	-0.008(1)	0.005(2)
C(38)	0.049(2)	0.054(2)	0.046(2)	-0.026(2)	-0.003(2)	-0.009(2)
C(39)	0.032(1)	0.040(1)	0.029(1)	-0.014(1)	-0.005(1)	0.007(1)
C(40)	0.089(3)	0.075(2)	0.034(2)	-0.037(2)	-0.025(2)	0.017(2)
C(41)	0.052(2)	0.083(2)	0.038(2)	-0.029(2)	-0.005(2)	0.024(2)
C(42)	0.076(3)	0.047(2)	0.056(2)	0.004(2)	-0.012(2)	0.026(2)

The general temperature factor expression:

$$\exp(-2\pi^2(a^2U_{11}h^2 + b^2U_{22}k^2 + c^2U_{33}l^2 + 2a*b*U_{12}hk + 2a*c*U_{13}hl + 2b*c*U_{23}kl))$$

Table S7. Bond Lengths(Å) of Ph₄FcP(*t*-Bu)₂.

atom	atom	distance		atom	atom	distance
Fe(1)	C(1)	2.052(2)		Fe(1)	C(2)	2.068(2)
Fe(1)	C(3)	2.063(2)		Fe(1)	C(4)	2.059(2)
Fe(1)	C(5)	2.058(2)		Fe(1)	C(30)	2.101(2)
Fe(1)	C(31)	2.059(2)		Fe(1)	C(32)	2.045(2)
Fe(1)	C(33)	2.032(2)		Fe(1)	C(34)	2.036(2)
P(1)	C(30)	1.835(2)		P(1)	C(35)	1.899(2)
P(1)	C(39)	1.909(2)		C(1)	C(2)	1.425(3)
C(1)	C(5)	1.424(3)		C(2)	C(3)	1.435(3)
C(2)	C(6)	1.483(3)		C(3)	C(4)	1.446(3)
C(3)	C(12)	1.493(3)		C(4)	C(5)	1.455(3)
C(4)	C(18)	1.485(3)		C(5)	C(24)	1.488(3)
C(6)	C(7)	1.388(3)		C(6)	C(11)	1.386(3)
C(7)	C(8)	1.378(3)		C(8)	C(9)	1.371(4)
C(9)	C(10)	1.376(4)		C(10)	C(11)	1.388(3)
C(12)	C(13)	1.396(3)		C(12)	C(17)	1.395(3)
C(13)	C(14)	1.391(4)		C(14)	C(15)	1.381(4)
C(15)	C(16)	1.363(4)		C(16)	C(17)	1.380(4)
C(18)	C(19)	1.393(3)		C(18)	C(23)	1.397(3)
C(19)	C(20)	1.385(4)		C(20)	C(21)	1.375(4)
C(21)	C(22)	1.374(4)		C(22)	C(23)	1.384(4)
C(24)	C(25)	1.385(3)		C(24)	C(29)	1.385(3)
C(25)	C(26)	1.388(3)		C(26)	C(27)	1.365(4)
C(27)	C(28)	1.381(4)		C(28)	C(29)	1.388(3)
C(30)	C(31)	1.430(3)		C(30)	C(34)	1.432(3)
C(31)	C(32)	1.403(3)		C(32)	C(33)	1.403(4)
C(33)	C(34)	1.410(3)		C(35)	C(36)	1.529(4)
C(35)	C(37)	1.535(4)		C(35)	C(38)	1.525(4)
C(39)	C(40)	1.525(4)		C(39)	C(41)	1.524(4)
C(39)	C(42)	1.523(4)				

Table S8. Bond Lengths(Å) for the Hydrogen Atoms of Ph₄FcP(*t*-Bu)₂.

atom	atom	distance		atom	atom	distance
C(1)	H(1)	0.96(2)		C(7)	H(2)	0.89(2)
C(8)	H(3)	0.94(2)		C(9)	H(4)	0.92(2)
C(10)	H(5)	0.93(2)		C(11)	H(6)	0.98(2)
C(13)	H(7)	0.99(2)		C(14)	H(8)	0.94(2)
C(15)	H(9)	0.93(2)		C(16)	H(10)	0.97(3)
C(17)	H(11)	0.95(2)		C(19)	H(12)	0.93(2)
C(20)	H(13)	0.94(2)		C(21)	H(14)	0.89(2)
C(22)	H(15)	0.93(2)		C(23)	H(16)	0.97(2)
C(25)	H(17)	0.84(2)		C(26)	H(18)	0.94(2)
C(27)	H(19)	0.96(2)		C(28)	H(20)	0.88(2)
C(29)	H(21)	0.93(2)		C(31)	H(22)	0.92(2)
C(32)	H(23)	0.90(2)		C(33)	H(24)	0.85(2)
C(34)	H(25)	0.88(2)		C(36)	H(26)	1.02(2)
C(36)	H(27)	0.96(3)		C(36)	H(28)	0.99(3)
C(37)	H(29)	1.01(3)		C(37)	H(30)	0.98(3)
C(37)	H(31)	0.93(3)		C(38)	H(32)	0.93(2)
C(38)	H(33)	1.03(3)		C(38)	H(34)	0.99(3)
C(40)	H(35)	0.96(2)		C(40)	H(36)	0.95(3)
C(40)	H(37)	1.05(4)		C(41)	H(38)	0.96(3)
C(41)	H(39)	1.02(3)		C(41)	H(40)	0.98(3)
C(42)	H(41)	0.90(4)		C(42)	H(42)	0.94(4)
C(42)	H(43)	0.97(3)				

Table S9. Bond Angles($^{\circ}$) of $\text{Ph}_4\text{FcP}(t\text{-Bu})_2$.

atom	atom	atom	angle		atom	atom	atom	angle
C(1)	Fe(1)	C(2)	40.47(8)		C(1)	Fe(1)	C(3)	68.17(9)
C(1)	Fe(1)	C(4)	68.74(9)		C(1)	Fe(1)	C(5)	40.54(8)
C(1)	Fe(1)	C(30)	110.88(9)		C(1)	Fe(1)	C(31)	125.24(9)
C(1)	Fe(1)	C(32)	158.78(10)		C(1)	Fe(1)	C(33)	160.63(9)
C(1)	Fe(1)	C(34)	126.01(9)		C(2)	Fe(1)	C(3)	40.66(8)
C(2)	Fe(1)	C(4)	69.00(8)		C(2)	Fe(1)	C(5)	68.66(8)
C(2)	Fe(1)	C(30)	126.85(9)		C(2)	Fe(1)	C(31)	110.19(9)
C(2)	Fe(1)	C(32)	122.02(9)		C(2)	Fe(1)	C(33)	155.65(10)
C(2)	Fe(1)	C(34)	163.06(9)		C(3)	Fe(1)	C(4)	41.06(8)
C(3)	Fe(1)	C(5)	68.93(8)		C(3)	Fe(1)	C(30)	161.98(8)
C(3)	Fe(1)	C(31)	124.51(9)		C(3)	Fe(1)	C(32)	106.15(9)
C(3)	Fe(1)	C(33)	119.07(10)		C(3)	Fe(1)	C(34)	154.89(9)
C(4)	Fe(1)	C(5)	41.37(8)		C(4)	Fe(1)	C(30)	156.73(8)
C(4)	Fe(1)	C(31)	158.91(9)		C(4)	Fe(1)	C(32)	121.30(9)
C(4)	Fe(1)	C(33)	104.20(10)		C(4)	Fe(1)	C(34)	119.61(9)
C(5)	Fe(1)	C(30)	122.91(8)		C(5)	Fe(1)	C(31)	159.43(9)
C(5)	Fe(1)	C(32)	158.56(10)		C(5)	Fe(1)	C(33)	122.47(10)
C(5)	Fe(1)	C(34)	107.31(9)		C(30)	Fe(1)	C(31)	40.20(8)
C(30)	Fe(1)	C(32)	67.86(9)		C(30)	Fe(1)	C(33)	68.13(10)
C(30)	Fe(1)	C(34)	40.46(8)		C(31)	Fe(1)	C(32)	39.98(9)
C(31)	Fe(1)	C(33)	67.4(1)		C(31)	Fe(1)	C(34)	67.45(9)
C(32)	Fe(1)	C(33)	40.26(10)		C(32)	Fe(1)	C(34)	67.81(10)
C(33)	Fe(1)	C(34)	40.55(9)		C(30)	P(1)	C(35)	106.31(10)
C(30)	P(1)	C(39)	98.99(10)		C(35)	P(1)	C(39)	108.4(1)
Fe(1)	C(1)	C(2)	70.4(1)		Fe(1)	C(1)	C(5)	70.0(1)
C(2)	C(1)	C(5)	109.5(2)		Fe(1)	C(2)	C(1)	69.2(1)
Fe(1)	C(2)	C(3)	69.5(1)		Fe(1)	C(2)	C(6)	127.5(1)
C(1)	C(2)	C(3)	107.5(2)		C(1)	C(2)	C(6)	124.6(2)
C(3)	C(2)	C(6)	127.9(2)		Fe(1)	C(3)	C(2)	69.8(1)
Fe(1)	C(3)	C(4)	69.3(1)		Fe(1)	C(3)	C(12)	131.7(1)
C(2)	C(3)	C(4)	108.5(2)		C(2)	C(3)	C(12)	123.4(2)
C(4)	C(3)	C(12)	127.8(2)		Fe(1)	C(4)	C(3)	69.6(1)
Fe(1)	C(4)	C(5)	69.3(1)		Fe(1)	C(4)	C(18)	128.2(1)
C(3)	C(4)	C(5)	107.1(2)		C(3)	C(4)	C(18)	127.1(2)
C(5)	C(4)	C(18)	125.8(2)		Fe(1)	C(5)	C(1)	69.5(1)

Fe(1)	C(5)	C(4)	69.4(1)		Fe(1)	C(5)	C(24)	132.0(1)
C(1)	C(5)	C(4)	107.5(2)		C(1)	C(5)	C(24)	122.2(2)
C(4)	C(5)	C(24)	129.9(2)		C(2)	C(6)	C(7)	119.8(2)
C(2)	C(6)	C(11)	122.1(2)		C(7)	C(6)	C(11)	118.0(2)
C(6)	C(7)	C(8)	121.6(2)		C(7)	C(8)	C(9)	119.8(3)
C(8)	C(9)	C(10)	119.7(3)		C(9)	C(10)	C(11)	120.6(3)
C(6)	C(11)	C(10)	120.2(2)		C(3)	C(12)	C(13)	123.4(2)
C(3)	C(12)	C(17)	118.6(2)		C(13)	C(12)	C(17)	118.0(2)
C(12)	C(13)	C(14)	120.3(2)		C(13)	C(14)	C(15)	120.1(3)
C(14)	C(15)	C(16)	120.2(3)		C(15)	C(16)	C(17)	120.3(3)
C(12)	C(17)	C(16)	121.1(2)		C(4)	C(18)	C(19)	120.7(2)
C(4)	C(18)	C(23)	121.6(2)		C(19)	C(18)	C(23)	117.7(2)
C(18)	C(19)	C(20)	121.3(2)		C(19)	C(20)	C(21)	120.0(3)
C(20)	C(21)	C(22)	119.8(3)		C(21)	C(22)	C(23)	120.6(3)
C(18)	C(23)	C(22)	120.6(3)		C(5)	C(24)	C(25)	120.5(2)
C(5)	C(24)	C(29)	120.4(2)		C(25)	C(24)	C(29)	118.6(2)
C(24)	C(25)	C(26)	120.6(2)		C(25)	C(26)	C(27)	120.2(2)
C(26)	C(27)	C(28)	120.0(2)		C(27)	C(28)	C(29)	119.9(3)
C(24)	C(29)	C(28)	120.6(2)		Fe(1)	C(30)	P(1)	135.7(1)
Fe(1)	C(30)	C(31)	68.3(1)		Fe(1)	C(30)	C(34)	67.3(1)
P(1)	C(30)	C(31)	132.8(2)		P(1)	C(30)	C(34)	121.2(2)
C(31)	C(30)	C(34)	105.2(2)		Fe(1)	C(31)	C(30)	71.5(1)
Fe(1)	C(31)	C(32)	69.5(1)		C(30)	C(31)	C(32)	109.5(2)
Fe(1)	C(32)	C(31)	70.6(1)		Fe(1)	C(32)	C(33)	69.4(1)
C(31)	C(32)	C(33)	108.0(2)		Fe(1)	C(33)	C(32)	70.3(1)
Fe(1)	C(33)	C(34)	69.9(1)		C(32)	C(33)	C(34)	108.0(2)
Fe(1)	C(34)	C(30)	72.2(1)		Fe(1)	C(34)	C(33)	69.6(1)
C(30)	C(34)	C(33)	109.2(2)		P(1)	C(35)	C(36)	105.9(2)
P(1)	C(35)	C(37)	107.0(2)		P(1)	C(35)	C(38)	119.2(2)
C(36)	C(35)	C(37)	106.6(2)		C(36)	C(35)	C(38)	109.2(2)
C(37)	C(35)	C(38)	108.4(2)		P(1)	C(39)	C(40)	106.7(2)
P(1)	C(39)	C(41)	109.5(2)		P(1)	C(39)	C(42)	115.4(2)
C(40)	C(39)	C(41)	107.8(3)		C(40)	C(39)	C(42)	107.8(3)
C(41)	C(39)	C(42)	109.4(3)					

Table S10. Bond Angles(^o) for the Hydrogen Atoms of Ph₄FcP(*t*-Bu)₂.

atom	atom	atom	angle		atom	atom	atom	angle
Fe(1)	C(1)	H(1)	125(1)		C(2)	C(1)	H(1)	125(1)
C(5)	C(1)	H(1)	124(1)		C(6)	C(7)	H(2)	117(1)
C(8)	C(7)	H(2)	120(1)		C(7)	C(8)	H(3)	118(1)
C(9)	C(8)	H(3)	121(1)		C(8)	C(9)	H(4)	124(1)
C(10)	C(9)	H(4)	116(1)		C(9)	C(10)	H(5)	123(1)
C(11)	C(10)	H(5)	115(1)		C(6)	C(11)	H(6)	119(1)
C(10)	C(11)	H(6)	120(1)		C(12)	C(13)	H(7)	117(1)
C(14)	C(13)	H(7)	121(1)		C(13)	C(14)	H(8)	118(1)
C(15)	C(14)	H(8)	121(1)		C(14)	C(15)	H(9)	115(1)
C(16)	C(15)	H(9)	124(1)		C(15)	C(16)	H(10)	118(1)
C(17)	C(16)	H(10)	121(1)		C(12)	C(17)	H(11)	118(1)
C(16)	C(17)	H(11)	120(1)		C(18)	C(19)	H(12)	122(1)
C(20)	C(19)	H(12)	116(1)		C(19)	C(20)	H(13)	122(1)
C(21)	C(20)	H(13)	117(1)		C(20)	C(21)	H(14)	119(1)
C(22)	C(21)	H(14)	120(1)		C(21)	C(22)	H(15)	124(1)
C(23)	C(22)	H(15)	115(1)		C(18)	C(23)	H(16)	119(1)
C(22)	C(23)	H(16)	120(1)		C(24)	C(25)	H(17)	118(1)
C(26)	C(25)	H(17)	120(1)		C(25)	C(26)	H(18)	119(1)
C(27)	C(26)	H(18)	120(1)		C(26)	C(27)	H(19)	120(1)
C(28)	C(27)	H(19)	119(1)		C(27)	C(28)	H(20)	119(1)
C(29)	C(28)	H(20)	120(1)		C(24)	C(29)	H(21)	120(1)
C(28)	C(29)	H(21)	118(1)		Fe(1)	C(31)	H(22)	124(1)
C(30)	C(31)	H(22)	124(1)		C(32)	C(31)	H(22)	126(1)
Fe(1)	C(32)	H(23)	122(1)		C(31)	C(32)	H(23)	126(1)
C(33)	C(32)	H(23)	125(1)		Fe(1)	C(33)	H(24)	123(1)
C(32)	C(33)	H(24)	127(1)		C(34)	C(33)	H(24)	124(1)
Fe(1)	C(34)	H(25)	121(1)		C(30)	C(34)	H(25)	124(1)
C(33)	C(34)	H(25)	126(1)		C(35)	C(36)	H(26)	107(1)
C(35)	C(36)	H(27)	111(1)		C(35)	C(36)	H(28)	108(1)
H(26)	C(36)	H(27)	111(2)		H(26)	C(36)	H(28)	107(1)
H(27)	C(36)	H(28)	109(2)		C(35)	C(37)	H(29)	109(1)
C(35)	C(37)	H(30)	108(1)		C(35)	C(37)	H(31)	114(1)
H(29)	C(37)	H(30)	107(2)		H(29)	C(37)	H(31)	115(2)
H(30)	C(37)	H(31)	101(2)		C(35)	C(38)	H(32)	111(1)
C(35)	C(38)	H(33)	103(1)		C(35)	C(38)	H(34)	113(1)

H(32)	C(38)	H(33)	109(2)		H(32)	C(38)	H(34)	106(2)
H(33)	C(38)	H(34)	112(2)		C(39)	C(40)	H(35)	104(1)
C(39)	C(40)	H(36)	106(1)		C(39)	C(40)	H(37)	108(1)
H(35)	C(40)	H(36)	111(2)		H(35)	C(40)	H(37)	116(2)
H(36)	C(40)	H(37)	108(2)		C(39)	C(41)	H(38)	111(1)
C(39)	C(41)	H(39)	109(1)		C(39)	C(41)	H(40)	109(1)
H(38)	C(41)	H(39)	107(2)		H(38)	C(41)	H(40)	109(2)
H(39)	C(41)	H(40)	110(2)		C(39)	C(42)	H(41)	115(2)
C(39)	C(42)	H(42)	113(2)		C(39)	C(42)	H(43)	106(1)
H(41)	C(42)	H(42)	99(3)		H(41)	C(42)	H(43)	110(3)
H(42)	C(42)	H(43)	112(2)					

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 and $s^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L_p^2$
 S = Scan rate
 C = Total integrated peak count
 R = Ratio of scan time to background counting time
 B = Total background count
 L_p = Lorentz-polarization factor
 p = p-factor leastsquares.
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