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SUPPORTING INFORMATION

Title: Intermolecular $FeCl_3$-Catalyzed Hydroamination of Styrenes
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General Remarks: Reactions were carried out in round bottom flasks equiped with a magnetic stirring bar and capped with a septum. DCE and dioxane was distilled over CaH_2 and Na respectively. TLC analyses were performed on Merck silica gel 60 F_{254} TLC plates. FT-IR spectra were recorded with a Perkin Elmer Spectrum BX spectrometer and 1H and 13C spectra were recorded with Bruker 200, Avance-300 and 500 spectrometers and referenced to $CDCl_3$ unless otherwise noted. Mass spectra were obtained from the mass spectrometry facilities operated by the Institut de Chimie des Substances Naturelles.

General procedure for iron catalyzed hydroamination of vinyl arenes.

To a stirred solution of $TsNH_2$ (5 mmol) and $FeCl_3$ (0.1 mmol) in dioxan (or DCE, 5 mL) was added vinyl arene (1mmol) and the yellow solution was refluxed for 20h (bath temperature: 120°C). After cooling to RT and usual work-up, the residue was purified on silica gel to afford the hydroaminated compound.

N-(1-phenylethyl)-4-methylbenzenesulfonamide (**1**)[1]

(AcOEt/Heptane 3/7)

73% yield, white solid, mp 78-79 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43 (d, J = 6.9 Hz, 3H), 2.39 (s, 3H), 4.47 (quintet, J = 6.8 Hz, 1H), 5.00 (broad d, J = 6.9 Hz, 1H), 7.09-7.14 (m, 2H), 7.16-7.21 (m, 5H), 7.60 (d, J = 8.3 Hz,2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 23.6, 53.7, 126.2, 127.2, 127.5, 128.6, 129.5, 137.8, 142.2, 143.2.

N-(1-phenylethyl)-4-nitroaniline (**2**)

(AcOEt/PE 2/8)

70% yield, yellow solid, mp 81-82 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (d, J = 6.9 Hz, 3H), 4.51 (q, J = 6.8 Hz, 1H), 4.82 (broad s, 1H), 6.38 (d, J = 9.1 Hz, 2H), 7.18-7.27 (m, 5H), 7.92 (d, J = 9.2 Hz, H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 53.3, 111.8, 125.6, 126.2, 127.5, 128.9, 138.1, 143.2, 152.2. MS (CI, NH_3) m/z (%) 502 ($2M+NH_4^+$, 10), 485 ($2M+H^+$, 45), 260 ($M+NH_4^+$, 55), 243 ($M+H^+$, 100), 242 ($M^{\cdot+}$, 45), 227 (10).

N-(1-phenylethyl)-4-methyl-2-nitroaniline (**3**)

(AcOEt/PE 5/95)

41% yield, orange solid, mp 87-88 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (d, *J* = 6.8 Hz, 3H), 2.14 (s, 3H), 4.60 (quintet, *J* = 6.7 Hz, 1H), 6.47 (d, *J* = 8.9 Hz, 1H), 7.01 (dd, *J* = 8.9 and 1.9 Hz, 1H), 7.18-7.20 (m, 2H), 7.25-7-28 (m, 3H), 7.90 (d, *J* = 1.0 Hz, 1H), 8.25 (broad s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.9, 25.1, 53.1, 115.1, 125.1, 125.6, 125.9, 127.3, 128.9, 131.7, 137.5, 142.7, 143.8.

N-[1-(2,4-dimethylphenyl)-ethyl]- 4-methylbenzenesulfonamide (**6**)

(AcOEt/PE 2/8)

59% yield, yellow solid, mp 114-115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (d, *J* = 6.6 Hz, 3H), 2.32 (s, 3H), 2.43 (s, 3H), 4.76 (quintet, *J* = 6.2 Hz, 1H), 5.07 (d, *J* = 5.5 Hz, 1H), 6.42 (d, *J* = 9.2 Hz, 2H), 6.97-7.05 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 9.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 20.9, 22.5, 49.5, 111.5, 124.3, 126.3, 127.4, 131.7, 134.4, 137.0, 137.8, 138.0, 152.2. MS (CI, NH_3) m/z (%) 541 ($2M+NH_4^+$, 100), 420 (10), 403 (25), 288 ($M+NH_4^+$, 10), 271 ($M+H^+$, 30), 270 ($M^{\cdot+}$, 25), 255 (10), 133 (30).

N-[1-(2,4-dimethylphenyl)-ethyl]- 4-nitroaniline (**9**)

(AcOEt/PE 2/8)

43% yield, white solid, mp 85-86 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (d, *J* = 6.8 Hz, 3H), 2.15 (s, 3H), 2.25 (s, 3H), 2.39 (s, 3H), 4.68 (quintet, *J* = 6.8 Hz, 1H), 4.82 (broad d, *J* = 6.4 Hz, 1H), 6.86 (d, *J* = 6.4 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 20.8, 21.4, 23.1, 49.5, 125.2, 126.9, 127.0, 129.3, 131.1, 134.4, 136.9, 137.2, 137.6, 143.0.

N-[1-(2,4-dimethylphenyl)-ethyl]-4-methyl-2-nitroaniline (**10**)

(AcOEt/PE 5/95)

57% yield, orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.50 (d, J = 6.6 Hz, 3H), 2.13 (s, 3H), 2.21 (s, 3H), 2.34 (s, 3H), 4.73 (quintet, J = 6.6 Hz, 1H), 6.31 (d, J = 8.7 Hz, 1H), 6.86-6.93 (m, 2H), 7.00 (dd, J = 8.9 and 2.1 Hz, 1H), 7.10 (d, J = 7.9 Hz, 1H), 7.89 (s, 1H), 8.24 (broad s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.8, 19.9, 20.9, 23.1, 49.5, 114.8, 124.5, 124.9, 125.9, 127.5, 127.6, 131.6, 134.0, 136.7, 137.6, 138.5, 142.7.

N-(1-(4-fluorophenyl)ethyl)-4-methylbenzenesulfonamide (**12**) [1]

63% yield, white solid, mp 115-116 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (d, J = 6.9 Hz, 3H), 2.38 (s, 3H), 4.45 (quintet, J = 7.0 Hz, 1H), 5.76 (d, J = 7.3 Hz, 1H), 6.83 (t, J = 8.7 Hz, 2H), 7.08 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 23.6, 53.0, 115.2 (d, $J_{F\text{-}C}$ = 21.6 Hz), 127.1, 127.9 (d, $J_{F\text{-}C}$ = 8.4 Hz), 129.4, 137.6, 138.1, 143.2, 161.9 (d, $J_{F\text{-}C}$ = 245.0 Hz)

N-(1-methyl-1-phenylethyl)-4-nitroaniline (**14**)

(AcOEt/PE 2/8)

12% yield, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 6H), 4.90 (broad s, 1H), 6.19 (d, J = 9.2 Hz, 2H), 7.18-7.36 (m, 5H), 7.82 (d, J = 9.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.4, 56.5, 113.4, 125.2, 125.7, 127.0, 128.9, 137.8, 145.3, 151.5. MS (CI, NH_3) m/z (%) 513 ($2M+NH_4^+$, 85), 392 (10), 274 ($M+NH_4^+$, 30), 257 ($M+H^+$, 100), 256 ($M^{\cdot+}$, 40), 119 (10).

N-(3-vinylbenzyl)-4-nitroaniline (**18**)

(AcOEt/PE 2/8)

15% yield, yellow solid, mp 58-59 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.35 (d, J = 5.2 Hz, 2H), 4.80 (broad s, 1H), 5.21 (d, J = 10.8 Hz, 1H), 5.69 (d, J = 17.7 Hz, 1H), 6.51 (d, J = 9.2 Hz, 2H), 6.64 (dd, J = 10.8 and 17.7 Hz, 1H), 7.16 (m, 1H), 7.19-7.31 (m, 3H), 8.01 (d, J = 9.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 47.6, 111.3, 114.6, 125.2, 125.7, 126.4, 126.7, 129.2, 136.3, 137.6, 138.3, 138.4, 153.0. MS (CI, NH_3, neg) m/z (%) 253 ($M-H^-$, 100), 137 (10).

N,N'-di-4-nitrophenyl-1-(aminomethylphenyl)-ethylamine (mixture *m/p*) (**19**)

(AcOEt/PE 1/1)

43% yield, yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (m, 3H), 4.34 (s, 2H), 4.52 (m, 1H), 4.73 (broad s, 1H), 6.37 (m, 2H), 6.48 (m, 2H), 7.16-7.32 (m, 4H), 7.92 (m, 2H), 8.00 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.6, 47.2, 47.5, 52.9, 53.1, 111.3, 111.8, 124.4, 125.2, 126.1, 126.2, 126.3, 126.4, 126.5, 128.0, 129.6, 136.7, 138.1, 138.2, 138.3, 143.1, 144.2, 152.1, 153.0.

[1] Nishimura, T.; Yasuhara, Y.; Hayashi, T. *Org. Lett.* **2006**, *8*, 979.