Supporting Information

Palladium Catalyzed Synthesis of a-Iminoamides from Imidoyl Chlorides and a Carbamoylsilane

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General: ^{1}H and ^{13}C NMR spectra were determined in CDCl3 at 4.7 T unless otherwise indicated. IR spectra were determined on neat samples using an FT-IR spectrometer unless otherwise indicated. Boiling points are kugelrohr oven temperatures. Melting points were taken on solidified distillates.

N-Phenylacetimidoyl chloride (1a). Bp 45-50 ^{o}C (0.5 mm Hg). IR: 1692 cm^{-1}. ^{1}H NMR: δ 7.41 (m, 2H), 7.25 (m, 1H), 6.95 (d, J = 9 Hz, 2H), 2.63 (s, 3H). ^{13}C NMR (11.7 T): δ 147.2, 143.1, 128.9, 124.9, 120.3, 30.0.Anal. Calcd for C_8H_8ClN: C, 62.15; H, 5.22; N, 9.06. Found: C, 62.46; H, 4.95; N, 9.19.

N-Phenyl-2-methylpropanimidoyl chloride (1b). Bp 55-60 ^{o}C (0.5 mm Hg). IR: 1704 cm^{-1}. ^{1}H NMR (11.7 T): δ 7.37 (m, 2H), 7.19 (m, 1H), 6.92 (d, J = 7 Hz, 2H), 3.02 (q, J = 7 Hz, 1H), 1.38 (d, J = 7 Hz, 6H). ^{13}C NMR (11.7 T): δ 153.0, 147.0, 128.8, 124.9, 120.4, 41.5, 20.3. Anal. Calcd for $C_{10}H_{12}ClN$: C, 65.75; H, 6.62; N, 7.67. Found: C, 66.08; H, 6.59; N, 7.98.

N-Phenylbutanimidoyl chloride (1c). Bp 50-54 ^{o}C (0.1 mm Hg). IR: 1708, 1693 cm^{-1}. ^{1}H NMR: δ 7.39 (m, 2H), 7.20 (m, 1H), 6.93 (d, J = 8 Hz, 2 H), 2.80 (t, J = 7 Hz, 2H),1.88 (sextet, J = 7 Hz, 2H), 1.09 (t, J = 7 Hz, 3H). ^{13}C NMR: δ 147.4, 147.0, 128.8, 124.9, 120.3, 44.7, 20.0, 13.1. Anal. Calcd for $C_{10}H_{12}ClN$: C, 65.75; H, 6.62; N, 7.67. Found: C, 66.06; H, 6.39; N, 7.32.

N-Phenyl-2,2-dimethylpropanimidoyl chloride (1d). Bp 70-75 ^{o}C (0.1 mm Hg). IR: 1692 cm^{-1}. ^{1}H NMR: δ 7.43 (t, J = 7 Hz, 2H), 7.23 (t, J = 7 Hz, 1H), 6.93 (d, J = 8 Hz, 2H), 1.47 (s, 9H). ^{13}C NMR: δ 154.9, 147.6, 128.8, 124.6, 120.0, 43.9, 28.4. Anal. Calcd for $C_{11}H_{14}ClN$: C, 67.17; H, 7.18; N, 7.12. Found: C, 67.30; H, 7.03; N, 7.87.

N-Phenylbenzimidoyl chloride (1e).[1] Bp 125-130 ºC (0.15 mm Hg); mp 37-38 ºC. IR ($CDCl_3$ solution): 1663 cm^{-1}. ^1H NMR: δ 8.22 (m, 2H), 7.52 (m, 5H), 7.25 (m, 1H), 7.05 (m, 2H). ^{13}C NMR (11.7 T): δ 148.0, 143.3, 135.7, 132.3, 129.8, 129.2, 128.8, 125.4, 120.8.

N-Phenyl-4-methoxybenzimidoyl chloride (1f). Bp 156-159 ºC (0.3 mm Hg; mp 70-72 ºC. IR ($CDCl_3$ solution): 1662 cm^{-1}. ^1H NMR: δ 8.21 (d, J = 9 Hz, 2 H), 7.48 (t, J = 8 Hz, 2 Hz, 2 H), 7.27 (t, J = 8 Hz, 1H), 7.09 (d, J = 8 Hz, 2H), 7.03 (d, J = 8 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR: δ 162.8, 147.8, 142.7, 131.4, 128.9, 127.9, 124.9, 120.7, 113.8, 55.5. Anal. Calcd for $C_{14}H_{12}ClNO$: C, 68.16; H; 4.90, N; 5.68 . Found: C, 68.64; H, 4.85; N, 5.44.

N-Phenyl-4-cyanobenzimidoyl chloride (1g). Mp (sublimed): 93-94 ºC. IR (KBr): 2229, 1656 cm^{-1}. ^1H NMR: δ 8.32 (m, 2 H), 7.82 (m, 2 H), 7.48 (m, 2 H), 7.29 (m, 1 H), 7.08 (m, 2 H). ^{13}C NMR: δ 147.3, 141.7, 139.7, 132.7, 130.3, 129.5, 126.3, 120.9, 118.5, 115.8. Anal. Calcd for $C_{14}H_9ClN_2$: C, 69.86; H, 3.77; N, 11.64. Found: C, 69.48; H, 3.79; N, 11.41.

N-[1-(*S*)-Phenylethyl]butanimidoyl chloride (1h). Bp 75-80 ºC (0.1 mm Hg). IR: 1700 cm^{-1}. ^1H NMR: δ 7.41 (m, 5 H), 5.04 (q, J = 7 Hz, 1 H), 2.69 (t, J = 7 Hz, 2 H), 1.83 (sextet, J = 7 Hz, 2 H), 1.55 (d, J = 7 Hz, 3 H), 1.04 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 144.3, 144.0, 128.9, 127.4, 127.0, 62.9, 45.0, 24.0, 20.4, 13.6. Anal. Calcd for $C_{12}H_{16}ClN$: C, 68.40; H, 7.65; N, 6.65. Found: C, 68.56; H, 7.63; N, 6.90.

N-[1-(*S*)-Phenylethyl]-2,2-dimethylpropanimidoyl chloride (1i). Bp 70-75 ^{o}C (0.5 mm Hg). IR: 1687 cm^{-1}. ^{1}H NMR: δ 7.48 (m, 5 H), 5.08 (q, J = 7 Hz, 1 H), 1.58 (d, J = 7 Hz, 3 H), 1.45 (s, 9 H). ^{13}C NMR: δ 151.0, 144.6, 128.4, 126.9, 126.5, 62.1, 43.8, 28.1, 24.1. Anal. Calcd for $C_{13}H_{18}ClN$: C, 69.47; H, 8.07; N, 6.23. Found: C, 69.77; H, 8.18; N, 6.49.

N-[1-(*S*)-Phenylethyl]benzimidoyl chloride (1j).[2,3] Bp 145-150 ^{o}C (0.5 mm Hg). IR: 1663 cm^{-1}. ^{1}H NMR: δ 7.28-7.70 (m, 10 H), 5.11 (q, J = 7 Hz, 1 H), 1.87 (d, J = 7 Hz, 3 H). ^{13}C NMR: δ 142.9, 132.8, 132.2, 129.2, 128.7, 128.3, 126.5, 118.9, 112.5, 58.8, 26.5. Anal. Calcd for $C_{15}H_{14}ClN$: C, 73.61; H, 5.77; N, 5.72. Found: C, 74.00; H, 6.02; N, 6.04.

N-Phenyl-2-furimidoyl chloride (1k).[4] Bp 157-160 ^{o}C (3 mm Hg). ^{1}H NMR: δ 7.68 (dd, J = 1.8 Hz, J = 0.8 Hz, 1 H), 7.47 (m, 2 H), 7.24 (m, 2 H), 7.10 (m, 2 H), 6.61 (dd, J = 3.4 Hz, J = 1.8 Hz, 1 H).

N-Phenyl-2-thienimidoyl chloride (1l). Bp 150-155 ^{o}C (0.5 mm Hg). ^{1}H NMR: δ 7.88 (dd, J = 3.8 Hz, J = 1.2 Hz, 1 H), 7.61 (dd, J = 5.1 Hz, J = 1.2 Hz, 1 H), 7.47 (m, 2 H), 7.28 (m, 1 H), 7.14 (m, 3H). ^{13}C NMR: δ 147.2, 140.8, 136.6, 133.4, 132.6, 129.3, 128.0,
125.8, 121.5. Anal. Calcd for $C_{11}H_{8}ClNS$: C,59.59; H, 3.64; N, 6.32. Found: C, 59.43; H, 3.66; N, 6.49.

N-Phenyl-4-pyridimidoyl chloride (1m). Mp 57-58 ^{o}C. IR ($CDCl_3$): 1664 cm^{-1}. ^{1}H NMR: δ 8.86 (m, 2 H), 8.21 (m, 2 H), 7.50 (m, 2 H), 7.35 (m, 1 H), 7.13 (m, 2H). ^{13}C NMR: δ 150.3, 146.7, 142.7, 141.1, 129.0, 125.9, 122.7, 120.4.

N,N-Dimethyl 2-(N'-phenylimino)-3,3-dimethylbutanamide (3d). IR: 1635(s) cm^{-1}. ^{1}H NMR: δ 7.29 (t, J = 9 Hz, 2H), 7.10 (t, J = 7 Hz, 1H), 6.94 (d, J = 7.5 Hz, 2H), 2.67 (s, 3H), 2.57 (s, 3H), 1.35 (s, 9H). ^{13}C NMR: δ 175.3, 167.2, 149.7, 128.9, 124.9, 120.4, 39.2, 37.3, 33.3, 28.6. Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.51; H, 8.70; N, 11.93.

N, N-Dimethyl 2-phenyl-2-(N'-phenylimino)ethanamide (3e). Mp 88-89 ^{o}C. IR: 1701(m), 1682(m), 1655(s) cm^{-1}. ^{1}H NMR: δ 7.96 (d, J = 6 Hz, 2H), 7.11-7.55 (m, 8H), 2.88 (s, 3H), 2.71 (s, 3H). ^{13}C NMR: δ 166.5, 162.7, 149.3, 134.6, 131.6, 128.8, 128.1, 127.5, 125.1, 120.3, 36.9, 33.5. Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.23; H, 6.41; N, 11.15.

N,N-Dimethyl 2-[N'-(4-cyanophenyl)imino]-2-phenylethanamide (3g). Mp 96-98 ^{o}C. IR: 1726(m), 1672(m), 1642(s) cm^{-1}. ^{1}H NMR: δ 8.09 (d, J = 9 Hz, 2H), 7.79 (d, J = 9 Hz), 2H), 7.12-7.41 (m, 5 H), 2.90 (s, 3H), 2.65 (s, 3H). ^{13}C NMR: δ 166.1, 161.0, 148.9, 139.0, 132.9, 129.4, 129.0, 126.4, 120.8, 118.8, 115.2, 37.2, 34.1. Anal. Calcd for $C_{17}H_{15}N_3O$: C, 73.63; H, 5.45; N, 15.15. Found: C, 73.27; H, 5.70; N, 15.40

N,N-Dimethyl 2-{N'-[1-(*S*)-phenylethyl]imino}-3,3-dimethylbutanamide (3i). IR: 1656(s) cm^{-1}. ^{1}H NMR: δ 7.28-7.40 (m, 5H), 4.30 (q, J = 6 Hz, 1H), 3.00 (s, 3H), 2.50 (s,
3H), 1.43 (d, J = 6 Hz, 3H), 1.27 (s, 9H). ^{13}C NMR: δ 172.0, 167.9, 145.7, 128.2, 126.6, 126.2, 62.7, 61.8, 37.4, 32.9, 28.4, 26.0. Anal. Calcd for $C_{16}H_{24}N_2O$: C, 73.81; H, 9.29; N, 10.76. Found: C, 74.03; H, 9.07; 10.71.

N,N-Dimethyl 2-(2-furanyl)-2-(N'-phenylimino)ethanamide (3k). IR: 1646(s) cm^{-1}. ^{1}H NMR: δ 7.67 (d, J = 1.8 Hz, 1H), 7.15-7.67 (m, 5H), 7.00 (d, J = 3.4 Hz, 1H), 6.60 (dd, J = 1.8 Hz, 3.4 Hz, 1H), 2.87 (s, 3H), 2.69 (s, 3H). ^{13}C NMR: δ 165.3, 153.2, 150.5, 149.0, 146.5, 129.2, 125.8, 121.2, 116.8, 112.7, 37.3, 34.2. Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.57; H, 6.08; N, 11.19.

N,N-Dimethyl 2-(N'-phenylimino)-2-(2-thienyl)ethanamide (3l). Mp 77-78 ^{o}C. IR: 1643(s) cm^{-1}. ^{1}H NMR: δ 7.50 (d, J = 5.0 Hz, 1 H), 7.39 (d, J = 3.7 Hz, 1H), 7.06-7.30 (m, 7 H), 2.81 (s, 3H), 2.64 (s, 3H). ^{13}C NMR: δ 166.0, 157.7, 149.0, 141.9, 131.8, 131.7, 129.2, 128.4, 125.8, 121.2, 37.4, 34.1. Anal. Calcd for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.84. Found: C, 64.62; H, 5.84; N, 11.07.

N,N-Dimethyl 2-(N'-phenylimino)-2-(4-pyridyl)ethanamide (3m). Mp 112-113 ^{o}C. IR: 1642(s) cm^{-1}. ^{1}H NMR: δ 8.77 (d, J = 4.6 Hz, 2H), 7.79 (d, J = 4.6 Hz, 2H), 7.10-7.42 (m, 5H), 2.88 (s, 3H), 2.62 (s, 3H). ^{13}C NMR: δ 165.9, 161.0, 151.0, 148.8, 142.1, 129.4, 126.5, 122.0, 120.7, 37.2, 34.0. Anal. Calcd for $C_{15}H_{15}N_3O$: C, 71.13; H, 5.97; N, 16.59. Found: C, 71.02; H, 6.02; N, 16.57.

N,N-Dimethyl 2-(4-methoxyphenyl)-2-oxoethanamide (4). Mp 75-76 ^{o}C. Yield: 30%. IR ($DCCl_3$): 1668, 1644, 1599 cm^{-1}. ^{1}H NMR: δ 7.93 (dd J = 5 Hz, J = 2 Hz, 2H), 6.99 (dd, J = 5 Hz, J = 2 Hz, 2H), 3.91 (s, 3H), 3.13 (s, 3H), 2.98 (s, 3H). ^{13}C NMR: δ 191.5, 165.0, 165.5, 132,5, 127.0, 114.7, 56.1, 37.5, 34.4. Anal. Calcd for $C_{11}H_{13}NO_3$: C,
63.76:, H, 6.32; N, 6.76. Found: C, 63.45; H, 6.27; N, 6.62.

Reduction of 3e to 2-(*R,S)*-N, N-Dimethyl-2-phenyl-2-(N'-phenylamino)acetamide (8).[5]

A solution of 252 mg (1.0 mmol) of **3e** in 10 mL of dry methanol was treated with 114 mg (4.0 mmol) of $NaBH_4$ at 0 ^oC over 5 min. The reaction was stirred 1 h at 0 ^oC, an additional 1 h at 25 ^oC (reaction progress was monitored by TLC), and water was then added. The ethyl acetate extract (3 x 20 ml) was dried (Na_2SO_4), evaporated and chromatographed (silica gel, EtOAc:hexane, 1:4) to give 244 mg (96%) of **8**, mp 155-156 ^oC.

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