

Convenient and Clean Synthesis of Imines from Primary Benzylamines

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General experimental information

All of the chemicals were obtained from commercial sources or prepared according to standard methods. The ¹H-NMR (400 MHz) and ¹³C-NMR (100 MHz) were recorded on a Bruker AM-400 spectrometer. Chemical shifts (δ) are reported relative to TMS (¹H) or CDCl₃ (¹³C). Mass spectra (ESI) were obtained on a Finnigan LCQ Advantage MAX spectrometer. Elemental analyses for C, H and N were performed on a Yanaco CHNCORNER MF-3 elemental analyzer, and the analytical results were within ±0.4% of the theoretical values.

General procedure for the preparation of imines in water

In a round bottom flask, benzylamine (200 mg, 1 equiv.), V₂O₅ (0.08 equiv) was suspended in water (5 ml) with vigorous stirring. H₂O₂ (30% solution in water) (3 equiv.) was added to the reaction mixture. The solid imine was filtered to afford pure product when the reaction completed (monitored by TLC). The oily product was extracted with EtOAc (2 × 5 mL). The extract was washed with water (2 × 3 mL), dried over anhydrous Na₂SO₄. The solvent was concentrated in vacuum to give pure product without further purification.

N-(4-Chlorobenzyl) 4-chlorobenzaldimine (2a): ^1H NMR (d_6 -DMSO, 400 MHz) δ 8.52 (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.55-7.35 (m, 6H), 4.77 (s, 2H).

N-Benzylbenzaldimine (2b): ^1H NMR (CDCl_3 , 400 MHz) δ 8.41 (s, 1H), 7.80-7.78 (m, 2H), 7.44-7.35 (m, 8H), 4.84 (s, 2H).

N-(3-Fluorobenzyl) 3-fluorobenzaldimine (2c): ^1H NMR (CDCl_3 , 400 MHz) δ 8.39 (s, 1H), 7.58-7.28 (m, 4H), 7.18-6.95 (m, 4H), 4.84 (s, 2H).

N-(2-Chlorobenzyl) 2-chlorobenzaldimine (2d): ^1H NMR (CDCl_3 , 400 MHz) δ 8.89 (s, 1H), 8.14 (d, J = 9.2 Hz, 1H), 7.46-7.23 (m, 7H), 4.97 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.8, 136.8, 135.3, 133.4, 133.1, 131.7, 129.8, 129.7, 129.4, 128.5, 128.3, 127.0, 126.9, 62.2; MS (ESI): m/z (%) $[\text{M} + \text{H}]^+$ =264 (100), 265 (18), 266 (60); Anal. Calcd. For $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N}$: C, 63.66; H, 4.20; N, 5.30 Found: C, 63.74; H, 4.10; N, 5.22.

N-(3-Chlorobenzyl) 3-chlorobenzaldimine (2e): ^1H NMR (CDCl_3 , 400 MHz) δ 8.36 (s, 1H), 7.84 (s, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.45-7.23 (m, 6H), 4.81 (s, 2H).

N-(3-Bromobenzyl) 3-bromobenzaldimine (2f): ^1H NMR (CDCl_3 , 400 MHz) δ 8.34 (s, 1H), 7.99 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.34-7.22 (m, 3H), 4.80 (s, 2H).

N-(2,3-Dichlorobenzyl) 2,3-dichlorobenzaldimine (2g): ^1H NMR (CDCl_3 , 400 MHz) δ 8.91 (s, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.30-7.21 (m, 2H), 4.99 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.9, 139.0, 135.1, 133.5, 133.4, 133.1, 132.4, 131.6, 129.1, 127.6, 127.4, 127.3, 126.7, 62.7; MS (ESI): m/z (%) $[\text{M} + \text{H}]^+$ = 332 (78), 334 (100), 336 (47); Anal. Calcd. For $\text{C}_{14}\text{H}_9\text{Cl}_4\text{N}$: C, 50.49; H, 2.72; N, 4.21 Found: C, 50.61; H, 2.67; N, 4.30.

N-(2,4-Dichlorobenzyl) 2,4-dichlorobenzaldimine (2h): ^1H NMR (CDCl_3 , 400 MHz) δ 8.82 (s, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.45-7.26 (m, 5H), 4.90 (s, 2H).

N-(4-Ethoxycarbonylbenzyl) 4-ethoxycarbonylbenzaldimine (2i): ^1H NMR (CDCl_3 , 400 MHz) δ 8.48 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 8.05 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 4.92 (s, 2H), 4.42 (m, 4H), 1.42 (m, 6H).

N-(3-Nitrobenzyl) 3-nitrobenzaldimine (2j): ^1H NMR (CDCl_3 , 400 MHz) δ 8.65 (s, 1H), 8.56 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 8.25 (s, 1H), 8.18 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 4.98 (s, 2H).

General procedure for the preparation of aromatic aldehydes in water

In a round bottom flask, benzylamine (200 mg, 1 equiv.), V₂O₅ (0.08 equiv) was suspended in water (5 ml) with vigorous stirring. H₂O₂ (30% solution in water) (3 equiv.) was added to the reaction mixture. The system was heated to 50°C and monitored by TLC to completion. The mixture was extracted with EtOAc (2 × 5 mL). The extract was washed with water (2 × 3 mL), dried over anhydrous Na₂SO₄. The solvent was concentrated in vacuum to give crude product, which was then filtered through a silica gel pad with petroleum ether to afford aromatic aldehydes.

4-Methylbenzaldehyde (3k): ¹H NMR (CDCl₃, 400 MHz) δ 9.98 (s, 1H), 7.79 (d, J= 7.6 Hz, 2H), 7.35 (d, J= 7.6 Hz, 2H), 2.46 (s, 3H).

4-Methoxybenzaldehyde (3l): ¹H NMR (CDCl₃, 400 MHz) δ 9.65 (s, 1H), 7.61 (d, J= 7.2 Hz, 2H), 6.79 (d, J= 7.2 Hz, 2H), 3.67(s, 3H).

5-Formyl-2-methoxyphenyl acetate (3m): ¹H NMR (CDCl₃, 400 MHz) δ 9.88 (s, 1H), 7.78 (dd, J= 2.0 Hz, J= 8.4 Hz, 1H), 7.60 (d, J= 2.0 Hz, 1H), 7.09 (d, J= 8.4 Hz, 1H), 3.93 (s, 3H), 2.35 (s, 3H).

1-Naphthaldehyde (3n): ¹H NMR (CDCl₃, 400 MHz) δ 9.88 (s, 1H), 9.28 (d, J= 8.8 Hz, 1H), 8.11(d, J= 8.0 Hz, 1H), 8.00 (d, J= 7.2 Hz, 1H), 7.94 (d, J= 8.0 Hz, 1H), 7.74-7.60 (m, 3H).





















