Supplementary Material (ESI) for Green Chemistry

Towards absolute green protocol: An expeditious, highly efficient, catalyst-free and solvent-free synthesis of nitroamines and nitrosulfides by Michael addition

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Electronic Supplementary Information

Compound 3a. mp 83–85 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.39 (d, 1H, *J* = 4.5 Hz), 4.71 (d, 2H, *J* = 6.5 Hz), 5.17 (q, 1H, *J* = 6.5 Hz), 6.61 (d, 2H, *J* = 8.0 Hz), 6.75 (t, 1H, *J* = 7.0 Hz), 7.14 (t, 2H, *J* = 7.5 Hz), 7.32-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 56.7, 80.0, 113.9, 118.9, 126.5, 128.7, 129.3, 129.4, 137.7, 145.7.

Compound 3b. mp 95–96 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.19 (s, 6H), 4.24 (d, 1H, *J* = 4.5 Hz), 4.69 (s, 1H), 4.70 (d, 1H, *J* = 2.5 Hz), 5.16 (q, 1H, *J* = 6.5 Hz), 6.26 (s, 2H), 6.41 (s, 1H), 7.31-7.35 (m, 1H), 7.37-7.40 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.5, 56.6, 79.9, 111.8, 121.0, 126.5, 128.6, 129.3, 138.0, 139.1, 145.7.

Compound 3c. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.56 (s, 3H), 4.13 (s, 1H), 4.69 (s, 2H), 5.08 (s, 1H), 6.43-6.72 (m, 4H), 7.33-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 55.7, 57.7, 80.1, 114.9, 115.6, 126.5, 128.6, 129.3, 138.0, 139.6, 153.1.

Compound 3d. mp 49–50 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.40 (d, 2H, *J* = 4.0 Hz), 2.55 (d, 2H, *J* = 4.5 Hz), 3.67 (d, 4H, *J* = 3.0 Hz), 4.35-4.38 (m, 1H), 4.60 (dd, 1H, *J* = 5.5, 12.0 Hz), 5.01 (t, 1H, *J* = 10.5 Hz), 7.22 (d, 2H, *J* = 7.0 Hz), 7.38-7.41 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 50.0, 67.0, 67.1, 76.8, 128.7, 129.2, 133.8, 139.1.

Compound 3e. mp 125–126 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.55 (d, 1H, *J* = 5.5 Hz), 4.77 (d, 2H, *J* = 6.0 Hz), 5.27 (q, 1H, *J* = 6.5 Hz), 6.58-6.60 (m, 2H), 6.79 (t, 1H, *J* = 7.5 Hz), 7.14-7.18 (m, 2H), 7.58 (t, 1H *J* = 8.0 Hz), 7.76 (d, 1H *J* = 7.5 Hz), 8.19-8.21 (m, 1H), 8.31 (t, 1H, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 55.9, 79.5,114.0, 119.6, 121.6, 123.8, 129.6, 130.4, 132.8, 140.2, 144.9, 148.9.

Compound 3f. mp 43–44 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.19 (s, 6H), 4.40 (s, 1H), 4.75 (d, 2H, *J* = 5.0 Hz), 5.26 (t, 1H, *J* = 6.0 Hz), 6.23 (s, 2H), 6.45 (s, 1H), 7.58 (t, 1H, *J* = 8.0 Hz), 7.76 (d, 1H, *J* = 7.5 Hz), 8.19-8.21 (m, 1H), 8.30 (t, 1H, *J* = 2.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.4, 55.9, 79.5, 111.9, 121.6, 123.7, 130.4, 132.8, 139.3, 140.4, 145.0, 148.9.

Compound 3g. mp 86–87 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.83-4.88 (m, 2H), 5.02 (dd, 1H, *J* = 4.0, 12.5 Hz), 5.79-5.82 (m, 1H), 6.48-6.49 (m, 2H), 6.73-6.76 (m, 1H), 7.10-7.13 (m, 2H), 7.49-7.53 (m, 1H), 7.60-7.63 (m, 1H), 7.69 (dd, 1H, *J* = 1.0, 7.5 Hz), 8.10 (dd, 1H, *J* = 1.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 52.6, 79.3, 113.6, 119.4, 125.8, 129.0, 129.5, 129.7, 133.4, 134.4, 144.7, 148.6.

Compound 3h. mp 101–102 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.16 (s, 6H), 4.74 (d, 1H, *J* = 7.0 Hz), 4.82 (dd, 1H, *J* = 7.5, 12.5 Hz), 4.98 (dd, 1H, *J* = 3.5, 12.0 Hz), 5.77-5.80 (m, 1H), 6.13 (s, 2H), 6.40 (s, 1H), 7.48-7.52 (m, 1H), 7.60-7.63 (m, 1H), 7.68 (d, 1H, *J* = 7.5 Hz), 8.09 (dd, 1H, *J* = 1.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.4, 52.6, 79.3, 111.6, 121.4, 125.7, 129.0, 129.6, 133.6, 134.4, 139.2, 144.8, 148.6.

Compound 3i. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.69 (s, 3H), 4.59 (d, 1H, *J* = 5.5 Hz), 4.82 (dd, 1H, *J* = 7.5, 12.5 Hz), 4.99 (dd, 1H, *J* = 3.5, 12.5 Hz), 5.71 (d, 1H, *J* = 3.0 Hz), 6.45-6.47 (m, 2H), 6.68-6.71 (m, 2H), 7.48-7.51 (m, 1H), 7.61 (t, 1H, *J* = 7.5 Hz), 7.69 (d, 1H, *J* = 8.0 Hz), 8.07 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 53.5, 55.6, 79.3, 115.0, 115.3, 125.7, 129.0, 129.6, 133.5, 134.3, 138.7, 148.7, 153.3.

Compound 3j. mp 78–79 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.85 (dd, 1H, *J* = 7.5, 12.5 Hz), 4.90 (d, 1H, *J* = 7.0 Hz), 5.01 (dd, 1H, *J* = 3.5, 12.5 Hz), 5.74-5.77 (m, 1H), 6.40-6.43 (m, 2H), 7.04-7.08 (m, 2H), 7.52-7.54 (m, 1H), 7.61-7.65 (m, 2H), 8.09-8.11 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 52.8, 79.1, 114.8, 124.2, 125.9, 128.9, 129.4, 129.9, 132.8, 134.4, 143.4, 148.6.

Compound 3k. mp 118–120 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.44-2.50 (m, 4H), 3.61-3.63 (m, 4H), 4.78-4.83 (m, 1H), 4.92-4.96 (m, 2H), 7.48-7.55 (m, 2H), 7.58-7.62 (m, 1H), 7.80 (dd, 1H, *J* = 1.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 50.2, 61.5, 66.7, 75.3, 125.0, 128.7, 129.4, 131.1, 132.5, 150.4.

Compound 3l. mp 86–87 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.36-2.39 (m, 2H), 2.47-2.51 (m, 2H), 3.64-3.68 (m, 4H), 4.27-4.30 (m, 1H), 4.54 (dd, 1H, *J* = 6.0, 12.0 Hz), 4.91-4.95 (m, 1H),

7.10 (d, 2H, *J* = 8.5 Hz), 7.52 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 50.1, 66.5, 66.9, 76.6, 122.8, 129.9, 132.0, 133.2.

Compound 3m. mp 119–121 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.22 (s, 6H), 4.27 (s, 1H), 4.67 (s, 1H), 4.69 (d, 1H, *J* = 2.0 Hz), 5.13 (s, 1H), 6.22 (s, 2H), 6.43 (s, 1H), 7.33-7.37 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.5, 56.0, 79.8, 111.8, 121.2, 127.9, 129.5, 134.4, 136.5, 139.2, 145.4.

Compound 3n. mp 91–92 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.36-2.38 (m, 2H), 2.48-2.51 (m, 2H), 3.64-3.68 (m, 4H), 4.30 (dd, 1H, *J* = 6.0, 8.5 Hz), 4.54 (dd, 1H, *J* = 6.5, 12.5 Hz), 4.94 (dd, 1H, *J* = 9.0, 12.5 Hz), 7.16 (d, 2H, *J* = 8.5 Hz), 7.36 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 50.1, 66.5, 66.9, 76.7, 129.0, 129.6, 132.6, 134.7.

Compound 3o. mp 112–113 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.15 (s, 6H), 4.35 (d, 1H, *J* = 3.5 Hz), 4.68 (dd, 1H, *J* = 8.5, 12.5 Hz), 4.94 (dd, 1H, *J* = 4.5, 12.5 Hz), 5.98-6.00 (m, 1H), 6.24 (s, 2H), 6.40 (s, 1H), 7.44 (t, 1H, *J* = 7.5 Hz), 7.56-7.59 (m, 1H), 7.64-7.67 (m, 2H), 7.83 (d, 1H, *J* = 8.0 Hz), 7.94 (d, 1H, *J* = 8.0 Hz), 8.19 (d, 1H, *J* = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.4, 53.1, 79.0, 111.6, 121.0, 121.7, 123.8, 125.7, 126.1, 127.3, 129.3, 129.5, 130.4, 132.7, 134.2, 139.2, 145.7

Compound 5a. mp 72 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.75 (dd, 1H, *J* = 6, 12.5 Hz), 4.85-4.93 (m, 2H), 7.29-7.30 (m, 2H), 7.33-7.38 (m, 6H), 7.42-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.9, 78.5, 127.7, 128.7, 128.8, 129.0, 129.4, 131.9, 133.8, 136.3.

Compound 5b. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.63 (AB quartet, 2H, *J* = 13.5, 43.5 Hz), 4.41 (dd, 1H, *J* = 7.0, 9.0 Hz), 4.62-4.71 (m, 2H), 7.23-7.28 (m, 5H), 7.30-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.1, 46.0, 79.1, 127.5, 127.8, 128.5, 128.7, 128.9, 129.1, 136.9, 137.1.

Compound 5c. mp 109–110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.73-4.77 (m, 1H), 4.86-4.90 (m, 1H), 4.98-5.01 (m, 1H), 7.30-7.34 (m, 5H), 7.44 (d, 1H, *J* = 8.5 Hz), 7.51-7.53 (m, 2H),

7.73-7.84 (m, 3H), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.9, 78.6, 126.9, 127.1, 127.7, 127.8, 128.7, 129.0, 129.1, 129.2, 130.2, 133.0, 133.2, 133.6, 136.3.

Compound 5d. mp 81–82 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.39 (s, 3H), 4.66-4.72 (m, 1H), 4.79-4.85 (m, 2H), 7.12 (d, 2H, *J* = 7.5 Hz), 7.24-7.33 (m, 7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.2, 50.2, 78.6, 127.7, 128.2, 128.5, 128.9, 130.1, 134.3, 136.5, 139.2.

Compound 5e. mp 49–51 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.78-4.82 (m, 1H), 4.85-4.89 (m, 1H), 4.95 (dd, 1H, *J* = 6.0, 9.5 Hz), 7.32-7.39 (m, 5H), 7.52 (t, 1H, *J* = 8.0 Hz), 7.58 (dd, 1H, *J* = 1.5, 6.5 Hz), 8.10 (t, 1H, *J* = 2.0 Hz), 8.16-8.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.2, 77.8, 122.7, 123.6, 129.5, 129.6, 130.0, 130.5, 133.8, 134.4, 138.8, 148.4.

Compound 5f. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.70 (AB quartet, 2H, *J* = 14.0, 56.0 Hz), 4.46-4.49 (m, 1H), 4.69 (s, 1H), 4.71 (d, 1H, *J* = 1.5 Hz), 7.22-7.24 (m, 2H), 7.28-7.34 (m, 3H), 7.51 (t, 1H, *J* = 8.0 Hz), 7.56 (td, 1H, *J* = 1.5, 3.0, 8.0 Hz), 8.12 (t, 1H, *J* = 1.5 Hz), 8.14-8.16 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.4, 45.2, 78.4, 122.9, 123.4, 127.8, 128.9, 130.1, 133.9, 136.3, 139.7, 148.5.

Compound 5g. mp 125–126 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.81-4.93 (m, 2H), 5.06 (dd, 1H, *J* = 6.0, 8.5 Hz), 7.42 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.49-7.60 (m, 4H), 7.76-7.90 (m, 4H), 8.17-8.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.2, 77.9, 122.8, 123.6, 127.1, 127.4, 127.7, 127.8, 129.5, 130.0, 130.3, 133.2, 133.5, 133.8, 134.2, 138.7.

Compound 5h. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.80 (s, 3H), 4.78-4.86 (m, 3H), 6.82-6.85 (m, 2H), 7.26-7.29 (m, 2H), 7.50-7.53 (m, 2H), 8.03-8.04 (m, 1H), 8.15-8.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.7, 55.4, 77.7, 115.1, 120.4, 122.7, 123.4, 129.9, 133.8, 137.2, 138.9, 148.4, 161.1.

Compound 5i. mp 62–63 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.76-4.80 (m, 1H), 4.83-4.87 (m, 1H), 4.93 (dd, 1H, *J* = 6.0, 9.0 Hz), 7.22-7.24 (m, 2H), 7.45-7.47 (m, 2H), 7.53-7.55 (m, 2H), 8.14 (t, 1H, *J* = 1.5 Hz), 8.19 (td, 1H, *J* = 2.0, 4.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.3, 77.7, 122.7, 123.7, 124.2, 129.6, 130.1, 132.8, 133.7, 135.7, 138.5, 148.5.

Compound 5j. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.81 (dd, 1H, *J* = 6.5, 14.0 Hz), 4.97 (dd, 1H, *J* = 9.5, 14.0 Hz), 5.69 (dd, 1H, *J* = 6.0, 9.0 Hz), 7.31-7.36 (m, 3H), 7.40-7.43 (m, 3H), 7.46-7.49 (m, 1H), 7.57-7.58 (m, 1H), 7.96 (dd, 1H, *J* = 1.5, 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 44.5, 77.6, 125.6, 128.7, 129.3, 129.4, 129.6, 131.0, 131.6, 133.4, 134.3, 148.9.

Compound 5k. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.77 (d, 2H, *J* = 2.5 Hz), 4.58 (dd, 1H, *J* = 7.0, 13.5 Hz), 4.81 (dd, 1H, *J* = 7.5, 13.5 Hz), 5.11 (t, 1H, *J* = 7.5 Hz), 7.18-7.19 (m, 2H), 7.23-7.28 (m, 3H), 7.42-7.45 (m, 1H), 7.57-7.61 (m, 2H), 7.88 (dd, 1H, *J* = 0.5, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 37.4, 41.4, 78.6, 125.1, 127.7, 128.5, 128.8, 129.1, 129.4, 129.9, 132.8, 133.5, 136.3, 148.9.

Compound 5l. mp 105–106 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.84 (dd, 1H, *J* = 6.5, 14.0 Hz), 5.00 (dd, 1H, *J* = 9.0, 14.0 Hz), 5.80 (dd, 1H, *J* = 6.0, 9.0 Hz), 7.43-7.50 (m, 3H), 7.52-7.58 (m, 3H), 7.76-7.84 (m, 3H), 7.90 (s, 1H), 7.98 (dd, 1H, *J* = 1.0, 9.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 44.5, 77.6, 125.6, 127.0, 127.3, 127.8, 128.2, 128.7, 129.4, 129.4, 130.3, 131.6, 133.2, 133.4, 133.5, 134.0, 149.0.

Compound 5m. mp 51–52 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.80 (dd, 1H, *J* = 6.5, 13.5 Hz), 4.96 (dd, 1H, *J* = 9.0, 14.0 Hz), 5.64-5.67 (m, 1H), 7.25-7.27 (m, 2H), 7.42-7.45 (m, 3H), 7.48-7.51 (m, 1H), 7.58-7.62 (m, 1H), 7.97 (dd, 1H, *J* = 1.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 44.8, 77.6, 124.0, 125.6, 128.7, 129.5, 130.2, 131.4, 132.7, 133.5, 135.6, 148.9.

Compound 5n. mp 68–69 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.69-4.72 (m, 1H), 4.76-4.84 (m, 2H), 7.12-7.14 (m, 2H), 7.32-7.39 (m, 5H), 7.45-7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.3, 78.2, 122.7, 129.1, 129.3, 129.5, 131.3, 132.2, 134.0, 135.5.

Compound 5o. mp 122–123 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.72-4.76 (m, 1H), 4.80-4.84 (m, 1H), 4.94 (dd, 1H, *J* = 6.5, 9.5 Hz), 7.15-7.18 (m, 2H), 7.42 (dd, 1H, *J* = 1.5, 8.5 Hz), 7.45-7.47 (m, 2H), 7.52-7.55 (m, 2H), 7.77-7.85 (m, 3H), 7.89 (d, 1H, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.3, 78.3, 122.7, 127.0, 127.2, 127.7, 127.8, 128.6, 129.2, 129.3, 130.2, 132.2, 133.1, 133.5, 135.5.

Compound 5p. mp 60–61 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.69-4.73 (m, 1H), 4.77-4.86 (m, 2H), 7.18 (d, 2H, J = 8.5 Hz), 7.30-7.39 (m, 7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.3, 78.3, 129.0, 129.1, 129.2, 129.5, 131.4, 134.0, 134.5, 134.9.

Compound 5q. oily liquid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.63 (AB quartet, 2H, J = 13.5, 53.0 Hz), 4.35-4.38 (m, 1H), 4.62 (s, 1H), 4.64 (d, 1H, J = 2.0 Hz), 7.19-7.24 (m, 4H), 7.28-7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.1, 45.3, 78.9, 127.7, 128.8, 128.9, 129.2, 129.2, 134.4, 135.7, 136.7.

Compound 5r. mp 123–124 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 4.72-4.76 (m, 1H), 4.80-4.85 (m, 1H), 4.95 (dd, 1H, J = 6.0, 9.5 Hz), 7.22-7.23 (m, 2H), 7.29-7.31 (m, 2H), 7.42 (dd, 1H, J = 2.0, 8.5 Hz), 7.52-7.54 (m, 2H), 7.77-7.84 (m, 3H), 7.89 (d, 1H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 49.3, 78.4, 127.0, 127.2, 127.7, 127.8, 128.6, 129.0, 129.2, 129.2, 130.2, 133.1, 133.5, 133.6, 134.6, 134.9.