

Electronic Supplementary Information (ESI) for

CuCl/TMEDA/nor-AZADO-catalyzed aerobic oxidative acylation of amides with alcohols to produce imides

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Yoshiharu Iwabuchi,^c Jun-ya Hasegawa,^d Noritaka Mizuno^a and Kazuya Yamaguchi^{*a}

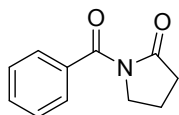
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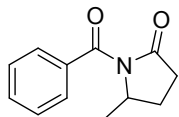
^d Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan.

Spectral Data of Imides



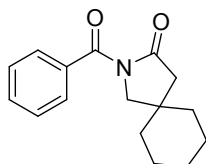
3aa (CAS No. 2399-66-8)

N-Benzoyl-2-pyrrolidone (3aa): ¹H NMR (500 MHz, CDCl₃, TMS): δ 2.09–2.15 (m, 2H), 2.58 (t, *J* = 7.5 Hz, 2H), 3.94 (t, *J* = 7.3 Hz, 2H), 7.39–7.42 (m, 2H), 7.49–7.52 (m, 1H), 7.59–7.61 (m, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃, TMS): δ 17.76, 33.41, 46.65, 127.90, 129.02, 132.03, 134.46, 170.81, 174.70. MS (70 eV, EI): *m/z* (%): 189 (20) [*M*⁺], 106 (10), 105 (100), 77 (56), 51 (19).



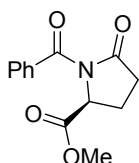
3ab (CAS No. 111607-69-3)

N-Benzoyl-5-methyl-2-pyrrolidone (3ab): ¹H NMR (500 MHz, CDCl₃, TMS): δ 1.42 (d, *J* = 6.0 Hz, 3H), 1.72–1.79 (m, 1H), 2.25–2.32 (m, 1H), 2.45–2.51 (m, 1H), 2.61–2.67 (m, 1H), 4.48–4.55 (m, 1H), 7.38–7.42 (m, 2H), 7.49–7.52 (m, 1H), 7.59–7.61 (m, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃, TMS): δ 20.03, 25.94, 31.89, 54.02, 127.96, 128.95, 132.08, 135.08, 170.98, 175.04. MS (70 eV, EI): *m/z* (%): 203 (22) [*M*⁺], 202 (21), 105 (100), 98 (27), 77 (34).



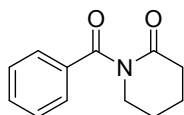
3ac (CAS No. 856069-00-6)

N-Benzoyl-4,4-pentamethylene-2-pyrrolidone (3ac): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.48–1.66 (m, 10H), 2.46 (s, 2H), 3.72 (s, 2H), 7.39–7.42 (m, 2H), 7.49–7.52 (m, 1H), 7.58–7.60 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 22.87, 25.73, 35.52, 36.39, 45.89, 57.06, 127.95, 129.03, 132.07, 134.65, 170.90, 174.10. MS (70 eV, EI): m/z (%): 257 (45) [M^+], 152 (40), 106 (13), 105 (100), 77 (31).



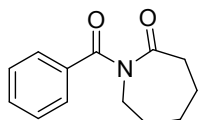
3ad (CAS No. 103322-12-9)

Methyl (S)-1-benzoyl-5-oxopyrrolidine-2-carboxylate (3ad): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.13–2.19 (m, 1H), 2.41–2.49 (m, 1H), 2.55–2.61 (m, 1H), 2.70–2.77 (m, 1H), 3.81 (s, 3H), 4.89–4.91 (dd, J = 9.0 and 3.5 Hz, 1H), 7.40–7.44 (m, 2H), 7.52–7.55 (m, 1H), 7.65–7.67 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 21.98, 31.84, 52.93, 58.81, 128.01, 129.31, 132.48, 133.78, 170.55, 171.71, 173.54. MS (70 eV, EI): m/z (%): 247 (9) [M^+], 188 (23), 105 (100), 77 (39), 51 (11). The enantiomeric excess was >99%*ee*, determined by HPLC analysis (Daicel chiralcel OD-H, *n*-hexane/2-propanol 1:1, 0.5 mL/min). Retention time: 16.6 min.



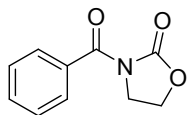
3ae (CAS No. 4252-56-6)

N-Benzoyl-2-piperidone (3ae): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.91–2.00 (m, 4H), 2.56 (t, J = 6.5 Hz, 2H), 3.80 (t, J = 6.0 Hz, 2H), 7.37–7.40 (m, 2H), 7.45–7.49 (m, 1H), 7.54–7.56 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 21.66, 23.01, 34.83, 46.33, 128.05, 128.32, 131.69, 136.29, 173.69, 174.88. MS (70 eV, EI): m/z (%): 203 (18) [M^+], 202 (13), 175 (15), 105 (100), 77 (39).



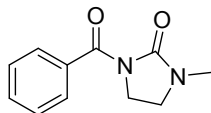
3af (CAS No. 6248-28-8)

N-Benzoylazepan-2-one (3af): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.81–1.89 (m, 6H), 2.68–2.71 (m, 2H), 3.96–3.97 (m, 2H), 7.37–7.40 (m, 2H), 7.45–7.48 (m, 1H), 7.53–7.56 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 23.89, 29.37, 29.77, 38.99, 45.31, 127.84, 128.30, 131.48, 136.75, 174.31, 177.75. MS (70 eV, EI): m/z (%): 217 (18) [M^+], 216 (19), 189 (13), 105 (100), 77 (31).



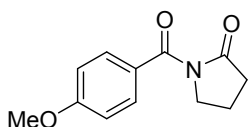
3ag (CAS No. 7007-15-0)

3-Benzoyl-2-oxazolidinone (3ag): MS (70 eV, EI): m/z (%): 191 (17) [M^+], 105 (100), 77 (32).



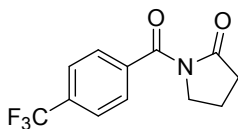
3ah

1-Benzoyl-3-methyl-2-imidazolidinone (3ah): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.86 (s, 3H), 3.49–3.52 (m, 2H), 3.99–4.02 (m, 2H), 7.38–7.42 (m, 2H), 7.46–7.50 (m, 1H), 7.56–7.58 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 30.88, 40.61, 43.30, 127.64, 128.67, 131.28, 134.80, 154.47, 170.52. MS (70 eV, EI): m/z (%): 204 (28) [M^+], 105 (100), 99 (35), 77 (36).



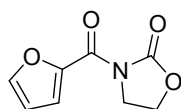
3ba (CAS No. 72432-10-1)

N-(4-Methoxybenzoyl)-2-pyrrolidone (3ba): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.09–2.15 (m, 2H), 2.60 (t, J = 8.0 Hz, 2H), 3.85 (s, 3H), 3.93 (t, J = 7.0 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 17.88, 33.56, 46.97, 55.53, 113.23, 126.31, 131.87, 163.04, 170.20, 174.83. MS (70 eV, EI): m/z (%): 219 (20) [M^+], 135 (100), 92 (12), 77 (15).



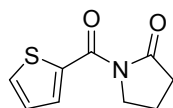
3ca (CAS No. 134407-03-7)

N-[4-(trifluoromethyl)benzoyl]-2-pyrrolidone (3ca): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.14–2.20 (m, 2H), 2.62 (t, J = 8.3 Hz, 2H), 3.98 (t, J = 7.0 Hz, 2H), 7.64–7.71 (m, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 17.75, 33.34, 46.50, 123.87 (q, J = 272.7 Hz), 125.03 (q, J = 3.6 Hz), 129.20, 133.27 (q, J = 32.4 Hz), 138.00, 169.52, 174.80. MS (70 eV, EI): m/z (%): 257 (25) [M^+], 174 (13), 173 (100), 145 (65), 95 (11), 84 (27).



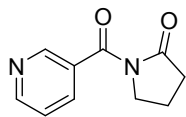
3dg (CAS No. 1394836-09-9)

3-(2-Furoyl)-2-oxazolidinone (3dg): MS (70 eV, EI): m/z (%): 181 (20) [M^+], 95 (100).



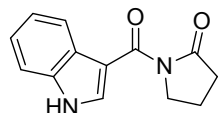
3ea (CAS No. 1394836-00-0)

1-(Thiophene-2-carbonyl)-2-pyrrolidone (3ea): MS (70 eV, EI): m/z (%): 195 (24) [M^+], 111 (100), 84 (11).



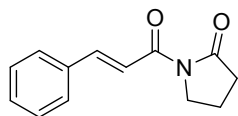
3fa (CAS No. 34236-73-2)

N-(3-Pyridinylcarbonyl)-2-pyrrolidone (3fa): MS (70 eV, EI): m/z (%): 190 (38) [M^+], 162 (20), 107 (16), 106 (100), 84 (14), 79 (24), 78 (75), 51 (36), 50 (11).



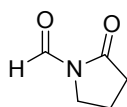
3ga

3-[(2-Pyrrolidonyl)carbonyl]indole (3ga): ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 1.98–2.04 (m, 2H), 2.55 (t, J = 7.8 Hz, 2H), 3.82 (t, J = 7.0 Hz, 2H), 7.16–7.22 (m, 2H), 7.48–7.49 (m, 1H), 8.01–8.02 (m, 1H), 8.11–8.12 (m, 1H), 11.95 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 17.47, 33.20, 46.72, 108.83, 112.21, 120.71, 121.43, 122.38, 126.73, 135.22, 135.80, 164.85, 174.46. MS (70 eV, EI): m/z (%): 228 (32) [M^+], 145 (11), 144 (100), 116 (20), 89 (16).



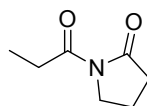
3ha (CAS No. 141236-49-9)

N-Cinnamoyl-2-pyrrolidone (3ha): MS (70 eV, EI): m/z (%): 215 (35) [M^+], 132 (17), 131 (100), 104 (10), 103 (34), 77 (15).



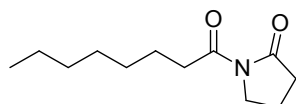
3ia (CAS No. 40321-44-6)

N-Formyl-2-pyrrolidone (3ia): MS (70 eV, EI): m/z (%): 113 (11) [M^+], 85 (100), 84 (18), 57 (27), 56 (22).



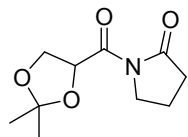
3ja (CAS No. 77015-41-9)

N-Propionyl-2-pyrrolidone (3ja): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.15 (t, J = 7.5 Hz, 3H), 2.01–2.07 (m, 2H), 2.60 (t, J = 8.0 Hz, 2H), 2.91 (q, J = 7.5 Hz, 2H), 3.82 (t, J = 7.3 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 8.48, 17.46, 30.61, 33.92, 45.68, 175.39, 175.61. MS (70 eV, EI): m/z (%): 141 (48) [M^+], 113 (40), 112 (15), 98 (17), 86 (90), 85 (13), 84 (15), 69 (17), 57 (100), 56 (22).

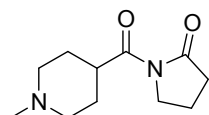


3ka (CAS No. 60437-60-7)

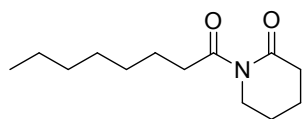
***N*-Octanoyl-2-pyrrolidone (3ka):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.88 (t, J = 6.8 Hz, 3H), 1.28–1.38 (m, 8H), 1.60–1.66 (m, 2H), 2.00–2.06 (m, 2H), 2.60 (t, J = 8.0 Hz, 2H), 2.89 (t, J = 7.5 Hz, 2H), 3.81 (t, J = 7.0 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 14.26, 17.38, 22.79, 24.39, 29.24, 29.34, 31.87, 33.93, 37.00, 45.64, 174.71, 175.50. MS (70 eV, EI): m/z (%): 211 (1) [M^+], 140 (74), 127 (81), 99 (47), 98 (22), 86 (100), 85 (15), 84 (13), 69 (14), 57 (44), 56 (18), 55 (43).

**3la**

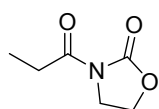
***N*-[(2,2-Dimethyl-1,3-dioxolan-4-yl)carbonyl]-2-pyrrolidone (3la):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.42 (s, 3H), 1.58 (s, 3H), 2.05–2.18 (m, 2H), 2.56–2.67 (m, 2H), 3.80–3.88 (m, 2H), 4.02–4.05 (dd, J = 9.5 and 4.0 Hz, 1H), 4.40–4.43 (dd, J = 9.3 and 7.3 Hz, 1H), 5.38–5.40 (dd, J = 7.3 and 3.8 Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 17.94, 25.63, 26.25, 33.39, 45.51, 68.03, 76.55, 111.68, 172.13, 176.10. MS (70 eV, EI): m/z (%): 198 (40), 155 (33), 138 (64), 101 (100), 100 (10), 86 (57), 85 (19), 83 (11), 73 (30), 69 (11), 56 (18), 55 (14).

**3ma**

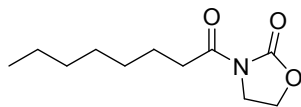
1-Methyl-4-[(2-pyrrolidonyl)carbonyl]piperidine (3ma): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.73–1.85 (m, 4H), 2.01–2.07 (m, 4H), 2.27 (s, 3H), 2.61 (t, J = 8.0 Hz, 2H), 2.87–2.90 (m, 2H), 3.38–3.44 (m, 1H), 3.79–3.82 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 17.31, 28.36, 34.11, 41.28, 45.98, 46.50, 55.24, 175.21, 176.72. MS (70 eV, EI): m/z (%): 210 (33) [M^+], 140 (46), 125 (18), 98 (56), 97 (65), 96 (73), 86 (18), 82 (22), 71 (70), 70 (100), 69 (11), 68 (11), 58 (14), 57 (18), 56 (18), 55 (45).

**3ke (CAS No. 60437-61-8)**

***N*-Octanoyl-2-piperidone (3ke):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.88 (t, J = 6.8 Hz, 3H), 1.24–1.35 (m, 8H), 1.60–1.66 (m, 2H), 1.79–1.87 (m, 4H), 2.54–2.56 (m, 2H), 2.89 (t, J = 7.5 Hz, 2H), 3.72 (t, J = 6.0 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 14.27, 20.47, 22.65, 22.80, 25.13, 29.29, 29.39, 31.90, 35.10, 39.79, 44.05, 173.52, 177.38. MS (70 eV, EI): m/z (%): 225 (2) [M^+], 154 (40), 141 (25), 113 (15), 100 (100), 99 (38), 98 (11), 57 (23), 55 (17).

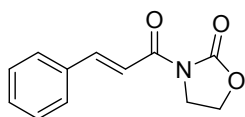
**3jg (CAS No. 60420-27-1)**

3-Propionyl-2-oxazolidinone (3jg): MS (70 eV, EI): m/z (%): 143 (9) [M^+], 115 (24), 88 (51), 57 (100), 56 (15).



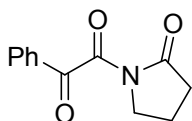
3kg (CAS No. 60420-32-8)

3-Octanoyl-2-oxazolidinone (3kg): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.88 (t, J = 7.0 Hz, 3H), 1.26–1.38 (m, 8H), 1.63–1.69 (m, 2H), 2.91 (t, J = 7.8 Hz, 2H), 4.02 (t, J = 7.8 Hz, 2H), 4.41 (t, J = 7.0 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 14.27, 22.79, 24.43, 29.21, 29.25, 31.85, 35.29, 42.70, 62.18, 153.74, 173.81. MS (70 eV, EI): m/z (%): 213 (0.4) [M^+], 142 (64), 129 (100), 127 (24), 101 (24), 88 (46), 57 (45), 55 (20).



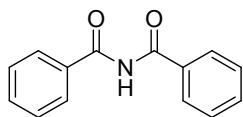
3hg (CAS No. 109299-93-6)

3-Cinnamoyl-2-oxazolidinone (3hg): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 4.13 (t, J = 8.0 Hz, 2H), 4.46 (t, J = 8.0 Hz, 2H), 7.39–7.41 (m, 3H), 7.61–7.64 (m, 2H), 7.85–7.93 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 43.00, 62.27, 116.75, 128.81, 129.07, 130.87, 134.67, 146.47, 153.79, 165.56. MS (70 eV, EI): m/z (%): 217 (25) [M^+], 132 (11), 131 (100), 103 (45), 102 (14), 77 (26), 51 (12).



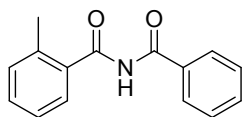
3va (CAS No. 2399-66-8)

1-(2-Oxo-1-pyrrolidinyl)-2-phenyl-1,2-ethanedione (3va): MS (70 eV, EI): m/z (%): 217 (1) [M^+], 189 (15), 105 (100), 77 (44), 51 (16).



3ai (CAS No. 614-28-8)

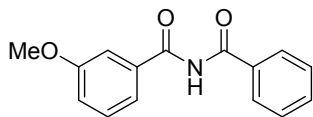
N-Benzoylbenzamide (3ai): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.51 (t, J = 7.5 Hz, 4H), 7.61 (t, J = 7.5 Hz, 2H), 7.86–7.88 (m, 4H), 8.98 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 128.13, 129.10, 133.33, 133.54, 166.55. MS (70 eV, EI): m/z (%): 225 (16) [M^+], 122 (11), 105 (100), 103 (26), 77 (69), 76 (13), 51 (31), 50 (14).



3ni (CAS No. 80791-90-8)

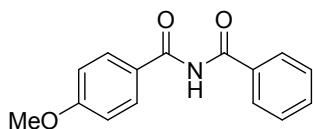
N-Benzoyl-2-methylbenzamide (3ni): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.47 (s, 3H), 7.25–7.27 (m, 2H),

7.37–7.40 (dt, $J = 1.3$ and 7.6 Hz, 1H), 7.44–7.50 (m, 3H), 7.58–7.61 (m, 1H), 7.87–7.89 (m, 2H), 9.11 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 20.02, 125.98, 127.15, 128.13, 129.07, 131.17, 131.41, 132.97, 133.41, 134.90, 136.85, 165.78, 170.10.



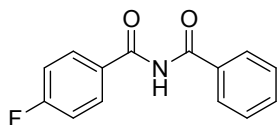
3oi and 3ak (CAS No. 1776069-60-3)

***N*-Benzoyl-3-methoxybenzamide (3oi and 3ak):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.81 (s, 3H), 7.08–7.10 (dd, $J = 8.0$ and 2.0 Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.39–7.40 (m, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H), 7.84 (d, $J = 7.5$ Hz, 2H), 9.30 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 55.56, 113.24, 119.28, 119.80, 128.09, 128.80, 129.86, 133.05, 133.43, 134.77, 159.93, 166.25, 166.74.



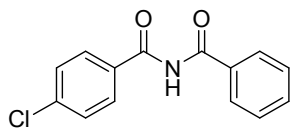
3bi and 3aj (CAS No. 77290-63-2)

***N*-Benzoyl-4-methoxybenzamide (3bi and 3aj):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.84 (s, 3H), 6.93 (d, $J = 8.5$ Hz, 2H), 7.45 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.83–7.85 (m, 4H), 9.20 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 55.55, 114.01, 125.39, 128.06, 128.74, 130.42, 132.89, 133.59, 163.50, 166.02, 166.99.



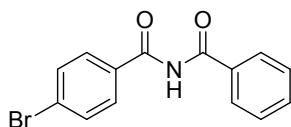
3pi (CAS No. 866353-52-8)

***N*-Benzoyl-4-fluorobenzamide (3pi):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.09–7.12 (m, 2H), 7.42–7.45 (m, 2H), 7.53–7.56 (m, 1H), 7.83–7.90 (m, 4H), 9.47 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 115.71 (d, $J = 21.6$ Hz), 128.07, 128.61, 129.39, 130.87 (d, $J = 8.4$ Hz), 132.96, 133.08, 165.43 (d, $J = 254.3$ Hz), 166.00, 166.86.



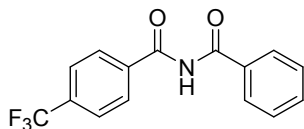
3qi and 3am (CAS No. 58010-69-8)

***N*-Benzoyl-4-chlorobenzamide (3qi and 3am):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.34–7.45 (m, 4H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 2H), 7.83 (d, $J = 8.0$ Hz, 2H), 9.54 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 128.21, 128.79, 128.99, 129.79, 131.77, 133.14, 133.19, 139.40, 166.39, 166.94.



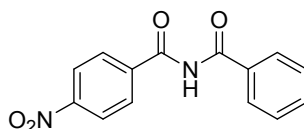
3ri (CAS No. 1590379-99-9)

***N*-Benzoyl-4-bromobenzamide (3ri):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.44 (t, J = 7.5 Hz, 2H), 7.55–7.57 (m, 3H), 7.70 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 9.43 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 128.05, 128.20, 128.85, 129.87, 132.02, 132.25, 133.12, 133.25, 166.55, 166.84.



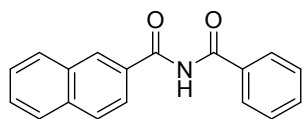
3ci

***N*-Benzoyl-4-(trifluoromethyl)benzamide (3ci):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.48–7.51 (m, 2H), 7.59–7.63 (m, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.86–7.89 (m, 2H), 7.94 (d, J = 8.5 Hz, 2H), 9.32 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 123.58 (q, J = 272.7 Hz), 125.74 (q, J = 3.6 Hz), 128.29, 128.78, 128.93, 132.91, 133.46, 134.31 (q, J = 32.8 Hz), 136.85, 166.78, 166.84.



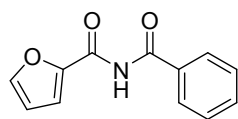
3si (CAS No. 39057-66-4)

***N*-Benzoyl-4-nitrobenzamide (3si):** ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 7.54–7.57 (t, J = 7.3 Hz, 2H), 7.65–7.68 (t, J = 7.3 Hz, 1H), 7.96 (d, J = 7.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H), 8.34 (d, J = 8.0 Hz, 2H), 11.65 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 123.42, 128.45, 128.76, 129.90, 132.94, 133.27, 139.86, 149.42, 167.07, 167.41.



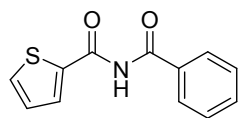
3ti (CAS No. 130956-01-3)

***N*-Benzoyl-2-naphthamide (3ti):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.44 (t, J = 7.5 Hz, 2H), 7.48–7.51 (m, 1H), 7.53–7.57 (m, 2H), 7.81–7.83 (m, 3H), 7.85–7.88 (m, 3H), 8.33 (s, 1H), 9.46 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 124.00, 127.00, 127.79, 128.14, 128.48, 128.65, 128.75, 129.21, 129.24, 130.50, 132.30, 132.99, 133.36, 135.32, 166.78, 166.80.



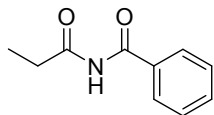
3di (CAS No. 89549-39-3)

***N*-Benzoyl-2-furancarboxamide (3di):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 6.63–6.64 (dd, J = 3.5 and 2.0 Hz, 1H), 7.40–7.41 (dd, J = 3.5 and 1.0 Hz, 1H), 7.57–7.58 (dd, J = 1.5 and 0.5 Hz, 1H), 7.51–7.55 (m, 2H), 7.61–7.64 (tt, J = 7.5 and 1.4 Hz, 1H), 7.89–7.91 (m, 2H), 9.31 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 113.47, 118.22, 127.92, 129.07, 133.29, 133.46, 145.49, 146.70, 155.12, 165.32.

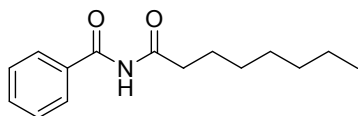


3ei (CAS No. 1590380-00-9)

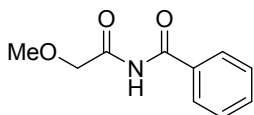
N-Benzoyl-2-thiophenecarboxamide (3ei): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.12–7.14 (m, 1H), 7.43–7.47 (m, 2H), 7.54–7.57 (m, 1H), 7.63–7.65 (m, 1H), 7.81–7.86 (m, 3H), 9.24 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 128.18, 128.32, 128.87, 131.47, 133.13, 133.54, 133.65, 137.78, 160.24, 166.79.

**3ji (CAS No. 28358-79-4)**

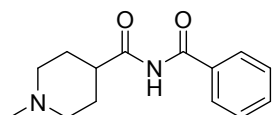
N-Propionylbenzamide (3ji): MS (70 eV, EI): m/z (%): 177 (29) [M^+], 149 (15), 122 (27), 105 (100), 77 (33), 57 (12).

**3ki and 3as (CAS No. 695203-41-9)**

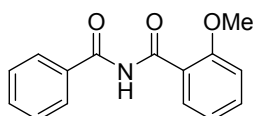
N-Octanoylbenzamide (3ki and 3as): MS (70 eV, EI): m/z (%): 247 (3) [M^+], 176 (27), 163 (32), 162 (14), 122 (36), 105 (100), 77 (44), 57 (14), 55 (12), 51 (10).

**3ui (CAS No. 959095-81-9)**

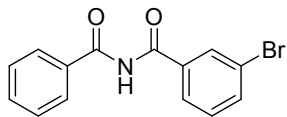
N-(2-Methoxyacetyl)-benzamide (3ui): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.53 (s, 3H), 4.40 (s, 2H), 7.49–7.53 (m, 2H), 7.60–7.63 (m, 1H), 7.87–7.89 (m, 2H), 9.42 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 59.58, 73.13, 127.94, 129.16, 132.57, 133.52, 165.29, 171.14. MS (70 eV, EI): m/z (%): 193 (5) [M^+], 178 (11), 163 (16), 105 (100), 77 (54), 51 (19).

**3mi**

N-Benzoyl-1-methyl-4-piperidinecarboxamide (3mi): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.79–1.87 (m, 2H), 1.96–1.99 (m, 2H), 2.04–2.10 (m, 2H), 2.29 (s, 3H), 2.90–2.93 (m, 2H), 3.37–3.43 (tt, J = 11.3 and 3.7 Hz, 1H), 7.48–7.51 (m, 2H), 7.58–7.62 (m, 1H), 7.91–7.93 (m, 2H), 9.32 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 28.36, 42.41, 46.55, 55.26, 128.00, 129.02, 132.95, 133.32, 165.83, 178.92. MS (70 eV, EI): m/z (%): 246 (18) [M^+], 176 (19), 105 (43), 98 (20), 97 (55), 96 (100), 82 (13), 77 (31), 71 (27), 70 (60), 57 (10), 55 (25), 51 (11).

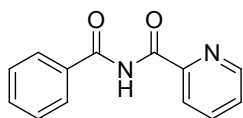
**3al (CAS No. 92552-95-9)**

***N*-Benzoyl-2-methoxybenzamide (3al):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 4.09 (s, 3H), 7.06 (d, J = 8.0 Hz, 1H), 7.10–7.13 (m, 1H), 7.50–7.56 (m, 3H), 7.58–7.61 (m, 1H), 7.89–7.90 (m, 2H), 8.25–8.27 (dd, J = 8.0 and 1.5 Hz, 1H), 11.23 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 56.66, 111.80, 120.72, 122.03, 127.49, 128.97, 132.88, 133.24, 134.17, 134.69, 157.37, 162.93, 165.19.



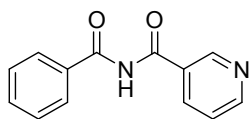
3an (CAS No. 109312-13-2)

***N*-Benzoyl-3-bromobenzamide (3an):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.32 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.65–7.67 (m, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.84–7.86 (m, 2H), 7.96–7.97 (m, 1H), 9.40 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 122.96, 126.81, 128.28, 128.95, 130.38, 131.36, 133.14, 133.37, 135.47, 135.99, 165.92, 166.79.



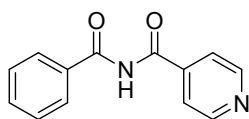
3ao (CAS No. 956028-68-5)

***N*-Benzoyl-2-pyridinecarboxamide (3ao):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.53–7.65 (m, 4H), 7.94–8.02 (m, 3H), 8.33–8.35 (m, 1H), 8.66–8.67 (m, 1H), 11.55 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 123.44, 127.91, 127.96, 129.10, 133.25, 133.57, 138.22, 148.46, 148.69, 162.13, 164.96.



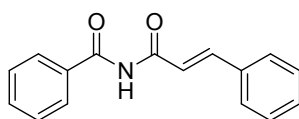
3ap (CAS No. 756488-91-2)

***N*-Benzoyl-3-pyridinecarboxamide (3ap):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.35–7.38 (m, 1H), 7.42–7.46 (m, 2H), 7.54–7.57 (m, 1H), 7.86–7.88 (m, 2H), 8.12–8.14 (m, 1H), 8.65–8.67 (m, 1H), 8.99 (m, 1H), 10.04 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 123.58, 128.37, 128.90, 129.81, 132.97, 133.44, 136.50, 149.20, 153.08, 166.80, 167.10.



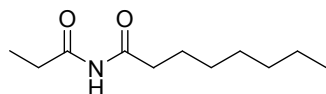
3aq

***N*-Benzoyl-4-pyridinecarboxamide (3aq):** ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 7.53–7.56 (m, 2H), 7.65–7.68 (m, 1H), 7.78–7.79 (m, 2H), 7.95–7.97 (m, 2H), 8.78–8.79 (m, 2H), 11.61 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, $(\text{CD}_3)_2\text{SO}$, TMS): δ 121.97, 128.46, 128.78, 132.96, 133.27, 141.34, 150.16, 167.12, 167.36.



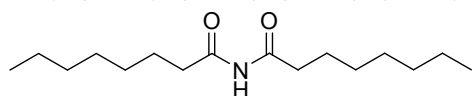
3ar (CAS No. 173909-83-6)

***N*-Cinnamoylbenzamide (3ar):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 7.40–7.42 (m, 3H), 7.52 (t, J = 7.8 Hz, 2H), 7.56–7.65 (m, 3H), 7.84–7.97 (m, 4H), 9.28 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 119.65, 128.11, 128.82, 129.07, 129.09, 130.87, 133.14, 133.40, 134.76, 146.82, 166.31, 168.23.



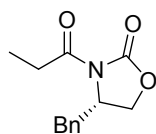
3js (CAS No. 109777-03-9)

***N*-Propionyloctaneamide (3js):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.88 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H), 1.28–1.36 (m, 8H), 1.62–1.68 (m, 2H), 2.58–2.68 (m, 4H), 9.13 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 8.53, 14.23, 22.77, 24.62, 29.17, 29.25, 30.90, 31.84, 37.58, 174.94, 175.83. MS (70 eV, EI): m/z (%): 199 (3) [M^+], 156 (11), 144 (15), 142 (11), 128 (61), 127 (22), 126 (11), 115 (100), 98 (10), 87 (24), 86 (10), 74 (62), 73 (95), 72 (47), 60 (12), 59 (64), 57 (100), 55 (21).



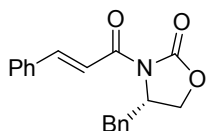
3ks (CAS No. 13916-42-2)

***N*-Octanoyloctaneamide (3ks):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.88 (t, J = 7.0 Hz, 6H), 1.28–1.36 (m, 16H), 1.61–1.67 (m, 4H), 2.60 (t, J = 2.3 Hz, 4H), 8.89 (brs, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 14.26, 22.80, 24.59, 29.21, 29.26, 31.87, 37.63, 174.90. MS (70 eV, EI): m/z (%): 269 (10) [M^+], 226 (22), 212 (12), 198 (60), 185 (25), 144 (100), 143 (17), 142 (19), 128 (17), 127 (63), 126 (61), 114 (49), 101 (20), 100 (21), 98 (21), 86 (26), 84 (14), 73 (11), 72 (99), 60 (31), 59 (53), 57 (78), 55 (28).



3jt (CAS No. 101711-78-8)

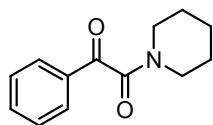
(*S*)-4-Benzyl-3-propionyl-2-oxazolidinone (3jt): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.21 (t, J = 7.3 Hz, 3H), 2.75–2.80 (dd, J = 13.3 and 9.8 Hz, 1H), 2.89–3.03 (m, 2H), 3.29–3.32 (dd, J = 13.5 and 3.5 Hz, 1H), 4.16–4.22 (m, 2H), 4.65–4.70 (m, 1H), 7.21–7.22 (m, 2H), 7.26–7.29 (m, 1H), 7.32–7.35 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 8.48, 29.40, 38.10, 55.36, 66.40, 127.53, 129.15, 129.61, 135.52, 153.71, 174.27. MS (70 eV, EI): m/z (%): 233 (14) [M^+], 142 (24), 91 (19), 57 (100). The enantiomeric excess was >99%*ee*, determined by HPLC analysis (Daicel chiralcel OD-H, *n*-hexane/2-propanol 1:1, 0.5 mL/min). Retention time: 12.6 min.



3ht (CAS No. 128891-66-7)

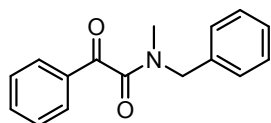
(*S*)-4-Benzyl-3-cinnamoyl-2-oxazolidinone (3ht): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 2.83–2.88 (dd, J = 13.3 and 9.3 Hz, 1H), 3.36–3.39 (dd, J = 13.3 and 3.3 Hz, 1H), 4.20–4.27 (m, 2H), 4.78–4.83 (m, 1H), 7.24–7.42 (m, 8H), 7.62–7.66 (m, 2H), 7.89–7.96 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , TMS): δ 38.11, 55.62, 66.37, 117.16, 127.54, 128.88, 129.10, 129.17, 129.67, 130.94, 134.72, 135.53, 146.68, 153.74, 165.40.

MS (70 eV, EI): m/z (%): 307 (17) [M^+], 132 (10), 131 (100), 103 (31), 77 (18). The enantiomeric excess was >99%*ee*, determined by HPLC analysis (Daicel chiralcel OD-H, *n*-hexane/2-propanol 1:1, 0.5 mL/min). Retention time: 18.9 min.



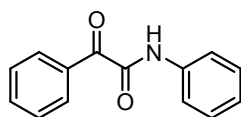
8va (CAS No. 14377-63-0)

1-(Phenylglyoxylyl)piperidine (8va): MS (70 eV, EI): m/z (%): 217 (6) [M^+], 112 (100), 105 (54), 84 (18), 77 (38), 69 (57), 51 (14).



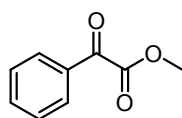
8vb (CAS No. 95725-09-0)

N-Benzyl-N-methyl-2-oxo-2-phenylacetamide (8vb): MS (70 eV, EI): m/z (%): 253 (3) [M^+], 148 (10), 120 (54), 105 (89), 91 (100), 77 (45), 65 (12), 51 (14).



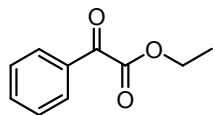
8vc (CAS No. 4732-66-5)

2-Oxo-N,2-diphenylacetamide (8vc): MS (70 eV, EI): m/z (%): 225 (22) [M^+], 119 (10), 105 (100), 77 (52), 51 (15).



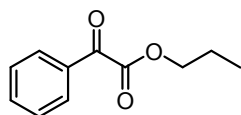
9vi (CAS No. 15206-55-0)

Methyl phenylglyoxylate (9vi): ^1H NMR (500 MHz, CDCl_3 , TMS): δ 3.99 (s, 3H), 7.51–7.54 (m, 2H), 7.66–7.69 (m, 1H), 8.02–8.03 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 52.81, 128.92, 130.10, 132.41, 135.02, 164.04, 186.06. MS (70 eV, EI): m/z (%): 164 (1) [M^+], 105 (100), 77 (62), 51 (25).



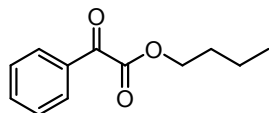
9vy (CAS No. 1603-79-8)

Ethyl phenylglyoxylate (9vy): ^1H NMR (500MHz, CDCl_3 , TMS): δ 1.43 (t, J = 7.3 Hz, 3H), 4.46 (q, J = 7.2 Hz, 2H), 7.51–7.54 (m, 2H), 7.65–7.68 (m, 1H), 8.01–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 14.14, 62.37, 128.90, 130.56, 132.47, 134.92, 163.84, 186.44. MS (70 eV, EI): m/z (%): 178 (0.5) [M^+], 105 (100), 77 (49), 51 (20).



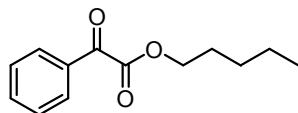
9vj (CAS No. 31197-63-4)

***n*-Propyl phenylglyoxylate (9vj):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 1.02 (t, $J = 7.3$ Hz, 3H), 1.82 (sext, $J = 7.1$ Hz, 2H), 4.36 (t, $J = 6.8$ Hz, 2H), 7.51–7.54 (m, 2H), 7.65–7.68 (m, 1H), 8.00–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 10.32, 21.89, 67.79, 128.91, 130.02, 132.49, 134.91, 164.02, 186.51. MS (70 eV, EI): m/z (%): 192 (0.4) [M^+], 105 (100), 77 (42), 51 (13).



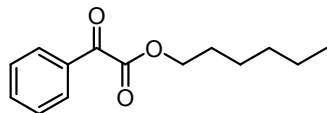
9vz (CAS No. 5524-55-0)

***n*-Butyl phenylglyoxylate (9vz):** ^1H NMR (500 MHz, CDCl_3 , TMS): δ 0.97 (t, $J = 7.3$, 3H), 1.46 (sext, $J = 7.5$, 2H), 1.77 (quin, $J = 7.1$, 2H), 4.40 (t, $J = 6.8$, 2H), 7.51–7.54 (m, 2H), 7.67–7.68 (m, 1H), 8.00–8.02 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3 , TMS): δ 13.65, 19.04, 30.47, 66.12, 128.90, 130.02, 132.49, 134.90, 164.02, 186.51. MS (70 eV, EI): m/z (%): 206 (0.4) [M^+], 105 (100), 77 (35), 51 (12).



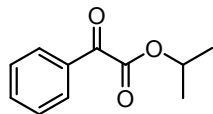
9va (CAS No. 31197-64-5)

Pentyl phenylglyoxylate (9va): MS (70 eV, EI): m/z (%): 220 (0.3) [M^+], 105 (100), 77 (33), 51 (10).



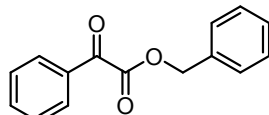
9vβ (CAS No. 31197-65-6)

Hexyl phenylglyoxylate (9vβ): MS (70 eV, EI): m/z (%): 234 (0.3) [M^+], 105 (100), 77 (27).



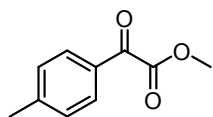
9vγ (CAS No. 31197-66-7)

Isopropyl phenylglyoxylate (9vγ): MS (70 eV, EI): m/z (%): 192 (0.4) [M^+], 105 (100), 77 (40), 51 (16).



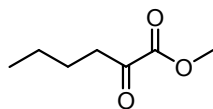
9va (CAS No. 62977-82-6)

Benzyl phenylglyoxylate (9va): MS (70 eV, EI): m/z (%): 105 (100), 91 (88), 77 (53), 65 (12), 51 (20).



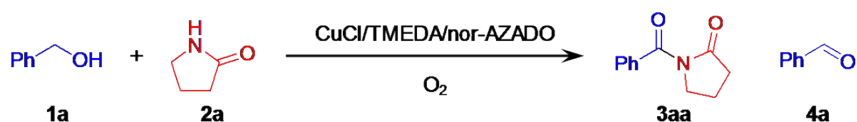
9wi (CAS No. 34966-53-5)

Methyl (4-methylphenyl)glyoxylate (9wi): MS (70 eV, EI): m/z (%): 178 (2) [M^+], 119 (100), 91 (53), 65 (21).



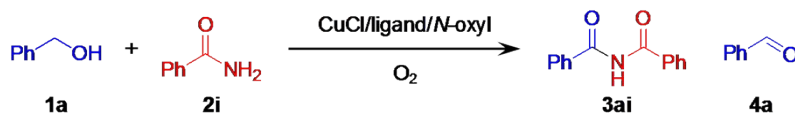
9xi (CAS No. 6395-83-1)

Methyl 2-oxohexanoate (9xi): MS (70 eV, EI): m/z (%): 144 (8) [M^+], 85 (84), 57 (100), 55 (10).

Table S1 Solvent effect^a

Entry	Solvent	Conv. of 1a (%)	Yield (%)	
			3aa	4a
1	THF	>99	>99	<1
2	DCM	>99	13	78
3	MeCN	84	1	72

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), CuCl (5 mol%), TMEDA (5 mol%), nor-AZADO (3 mol%), MS 3A (200 mg), solvent (2.5 mL), O₂ (balloon), room temp. (ca. 23°C), 5 min. Conversions and yields were determined by GC analysis.

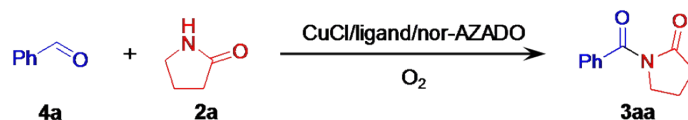
Table S2 Optimization of the reaction conditions for the reaction of benzyl alcohol (**1a**) and benzamide (**2i**)^a

Entry	Ligand	<i>N</i> -Oxyl	Base	Conv. of 1a (%)	Yield (%)	
					3ai	4a
1 ^b	TMEDA	nor-AZADO	none	>99	12	74
2 ^c	TMEDA	nor-AZADO	none	>99	24	73
3 ^d	TMEDA	nor-AZADO	none	>99	84	12
4 ^{c,e}	TMEDA	nor-AZADO	none	83	<1	70
5^c	TMEDA	nor-AZADO	^tBuOK	>99	>99	<1
6	bpy	nor-AZADO	^t BuOK	>99	13	81
7	⁴ Me ₆ bpy	nor-AZADO	^t BuOK	82	1	63
8	⁶ Me ₆ bpy	nor-AZADO	^t BuOK	85	1	77
9	⁴ MeO ₆ bpy	nor-AZADO	^t BuOK	>99	51	42
10	phen	nor-AZADO	^t BuOK	>99	44	47
11	^{MeO} phen	nor-AZADO	^t BuOK	46	<1	33
12	TMEDA	nor-AZADO	^tBuOK	>99	72	25
13^f	TMEDA	nor-AZADO	^tBuOK	>99	>99	<1
14	TEEDA	nor-AZADO	^t BuOK	>99	60	35
15	TMEDA	TEMPO	^t BuOK	43	<1	30
16	TMEDA	ABNO	^t BuOK	>99	26	61
17	TMEDA	keto-ABNO	^t BuOK	34	<1	24
18	TMEDA	AZADO	^t BuOK	>99	69	24

19	TMEDA	1-Me-AZADO	^t BuOK	>99	29	46
20	TMEDA	5-F-AZADO	^t BuOK	>99	67	26
21	TMEDA	4-Cl-AZADO	^t BuOK	>99	16	64
22	TMEDA	nor-AZADO	DBU	>99	10	77
23	TMEDA	nor-AZADO	DMAP	>99	5	80
24	TMEDA	nor-AZADO	K ₂ CO ₃	>99	13	74

^aReaction conditions for entries 1–5: **1a** (0.5 mmol), **2i** (0.55 mmol), CuCl, TMEDA (1 eq.), nor-AZADO (5 mol%), MS 3A (200 mg), THF (2.5 mL), O₂ (balloon), room temp. (ca. 23°C), 1 h; for 6–24: **1a** (0.5 mmol), **2i** (0.55 mmol), CuCl (5 mol%), ligand (5 mol%), *N*-oxyl (3 mol%), base (1 eq.), MS 3A (200 mg), THF (2.5 mL), O₂ (balloon), room temp. (ca. 23°C), 1 h. Conversions and yields were determined by GC and HPLC analysis. ^bCuCl (10 mol%). ^cCuCl (20 mol%). ^dCuCl (100 mol%). ^e**3ai** (20 mol%), half scale. ^f4 h.

Table S3 Control experiments for the reaction of benzaldehyde (**4a**) and 2-pyrrolidone (**2a**)^a



Entry	Cu source	Ligand	<i>N</i> -Oxyl	Time (min)	Conv. of 4a (%)	Yield of 3aa (%)
1	CuCl	TMEDA	nor-AZADO	2.5	98	98
2	CuCl	bpy	nor-AZADO	2.5	25	17
3	CuCl	TMEDA	nor-AZADO	5	>99	>99
4	–	TMEDA	nor-AZADO	5	21	<1
5	CuCl	–	nor-AZADO	5	19	<1
6	CuCl	TMEDA	–	5	24	<1
7 ^b	CuCl	TMEDA	nor-AZADO	5	24	6
8 ^c	CuCl	TMEDA	nor-AZADO	5	7	1

^aReaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), CuCl (5 mol%), ligand (5 mol%), nor-AZADO (3 mol%), MS 3A (200 mg), THF (2.5 mL), O₂ (balloon), room temp. (ca. 23°C). Conversion and yields were determined by GC analysis. ^bWithout MS 3A. ^cAr (1 atm).

Table S4 Effect of copper sources for the reaction of benzaldehyde (**4a**) and benzamide (**2i**) in the presence of ^tBuOK^a

$\text{Ph-CH}_2\text{OH} + \text{Ph-CO-NH}_2 \xrightarrow[\text{O}_2]{\text{Cu/TMEDA/nor-AZADO}/^t\text{BuOK}} \text{Ph-CO-NH-CH}_2\text{Ph} + \text{Ph-CHO}$

1a **2i** **3ai** **4a**

Entry	Cu source	Time (h)	Conv. of 1a (%)	Yield (%)	
				3ai	4a
1	CuCl	1	>99	72	25
2	CuCl	4	>99	>99	<1
3	CuBr	1	>99	75	23
4	CuBr	4	>99	>99	<1
5	CuI	1	>99	66	27
6	CuI	4	>99	>99	<1
7	CuOAc	1	>99	69	28
8	CuOAc	4	>99	>99	<1
9	CuCl ₂	1	>99	74	22
10	CuCl ₂	4	>99	>99	<1

^aReaction conditions: **1a** (0.5 mmol), **2i** (0.55 mmol), Cu source (5 mol%), TMEDA (5 mol%), nor-AZADO (3 mol%), ^tBuOK (1 eq.), MS 3A (200 mg), THF (2.5 mL), O₂ (balloon), room temp. (ca. 23°C). Conversion and yields were determined by GC and HPLC analysis.

Table S5 Control experiments for the reaction of benzaldehyde (**4a**) and benzamide (**2i**)^a

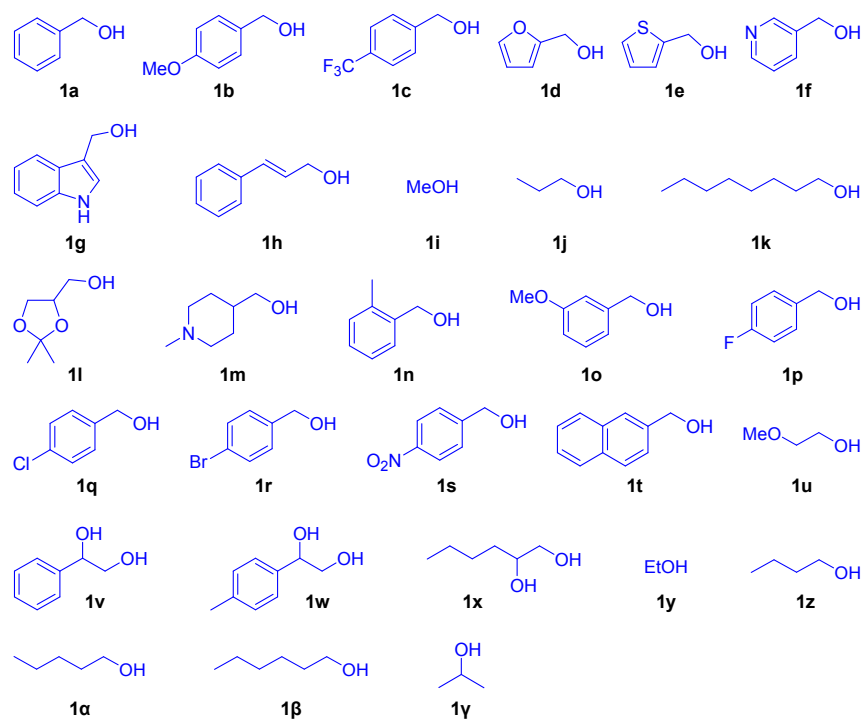
$\text{Ph-CHO} + \text{Ph-CO-NH}_2 \xrightarrow[\text{O}_2]{\text{CuCl/TMEDA/nor-AZADO}} \text{Ph-CO-NH-CH}_2\text{Ph} + \text{Ph-COOH} + \text{Ph-CH=N-CO-Ph}$

4a **2i** **3ai** **5a** **6ai**

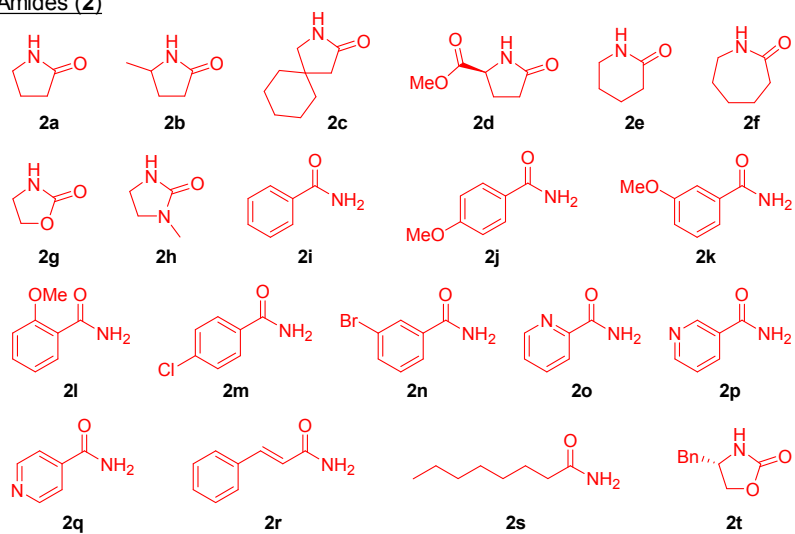
Entry	Cu source	Ligand	N-Oxyl	Conv. of 4a (%)	Yield (%)		
					3ai	5a	6ai
1	CuCl	TMEDA	nor-AZADO	69	54	<1	14
2	—	TMEDA	nor-AZADO	10	<1	<1	<1
3	CuCl	—	nor-AZADO	42	28	<1	7
4	CuCl	TMEDA	—	34	<1	<1	24
5 ^b	CuCl	TMEDA	nor-AZADO	34	14	7	<1
6 ^c	CuCl	TMEDA	nor-AZADO	13	2	<1	<1

^aReaction conditions: **4a** (0.5 mmol), **2i** (0.55 mmol), CuCl (5 mol%), TMEDA (5 mol%), nor-AZADO (3 mol%), ^tBuOK (1 eq.), MS 3A (200 mg), THF (2.5 mL), O₂ (balloon), room temp. (ca. 23°C), 1 h. Conversion and yields were determined by GC and HPLC analysis. ^bWithout MS 3A. ^cAr (1 atm).

Alcohols (1)



Amides (2)



Amines (7)

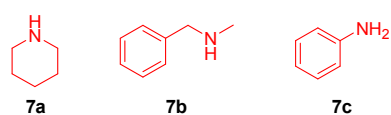


Fig. S1 Substrates used in this study.

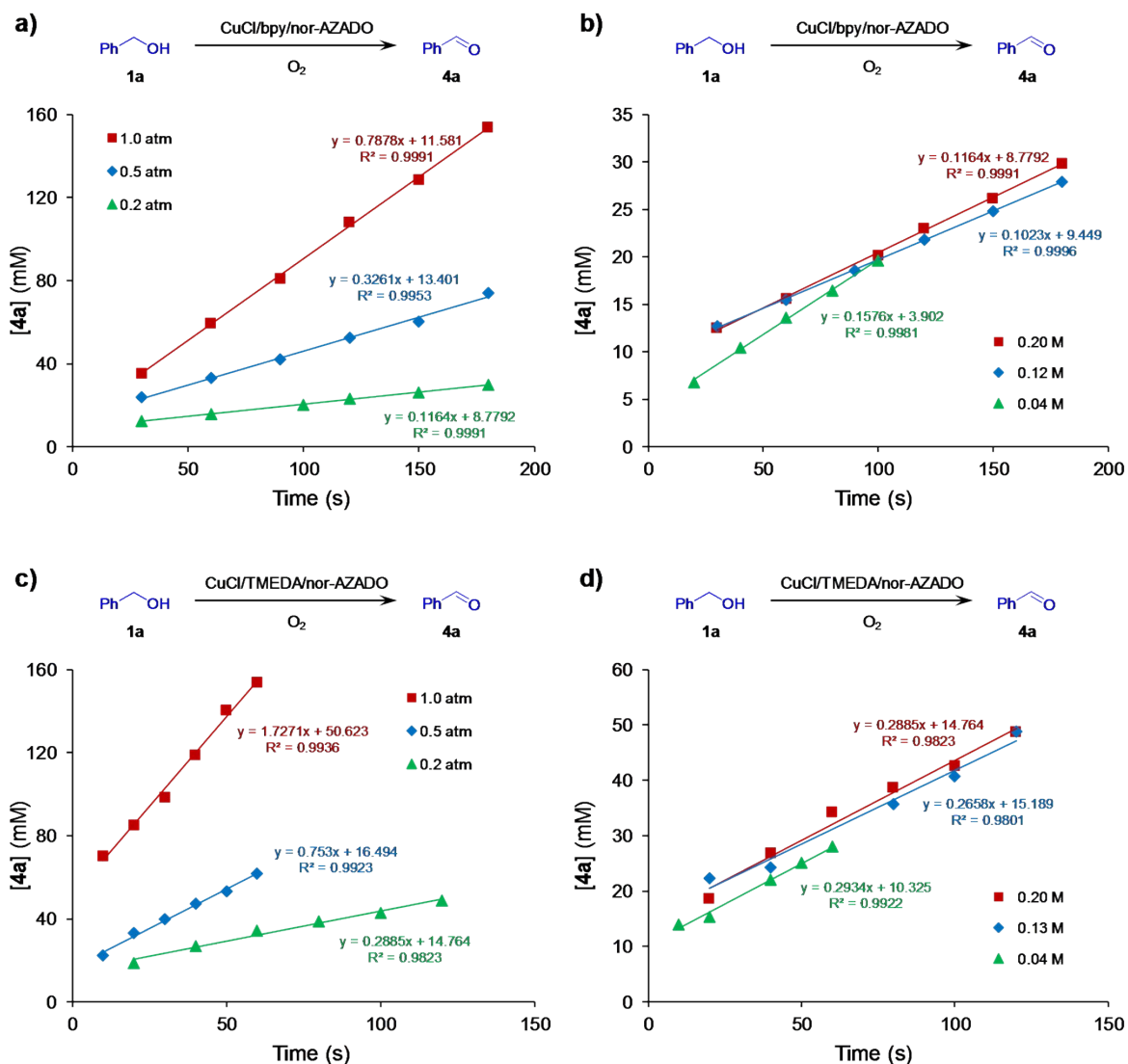


Fig. S2 Reaction profiles for a) the yield of **4a** with different partial pressure of O₂ in the presence of CuCl/bpy/nor-AZADO catalyst, b) the yield of **4a** with different initial concentrations of **1a** in the presence of CuCl/bpy/nor-AZADO catalyst, c) the yield of **4a** with different partial pressure of O₂ in the presence of CuCl/TMEDA/nor-AZADO catalyst, and d) the yield of **4a** with different initial concentrations of **1a** in the presence of CuCl/TMEDA/nor-AZADO catalyst. Reaction conditions for a): **1a** (0.2 M), CuCl (10 mM), bpy (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.2–1.0 atm), room temp. (ca. 23°C); for b): **1a** (0.04–0.20 M), CuCl (10 mM), bpy (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.2 atm), room temp. (ca. 23°C); for c): **1a** (0.2 M), CuCl (10 mM), TMEDA (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.2–1.0 atm), room temp. (ca. 23°C); for d): **1a** (0.04–0.20 M), CuCl (10 mM), TMEDA (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.2 atm), room temp. (ca. 23°C). Yields were determined by GC analysis.

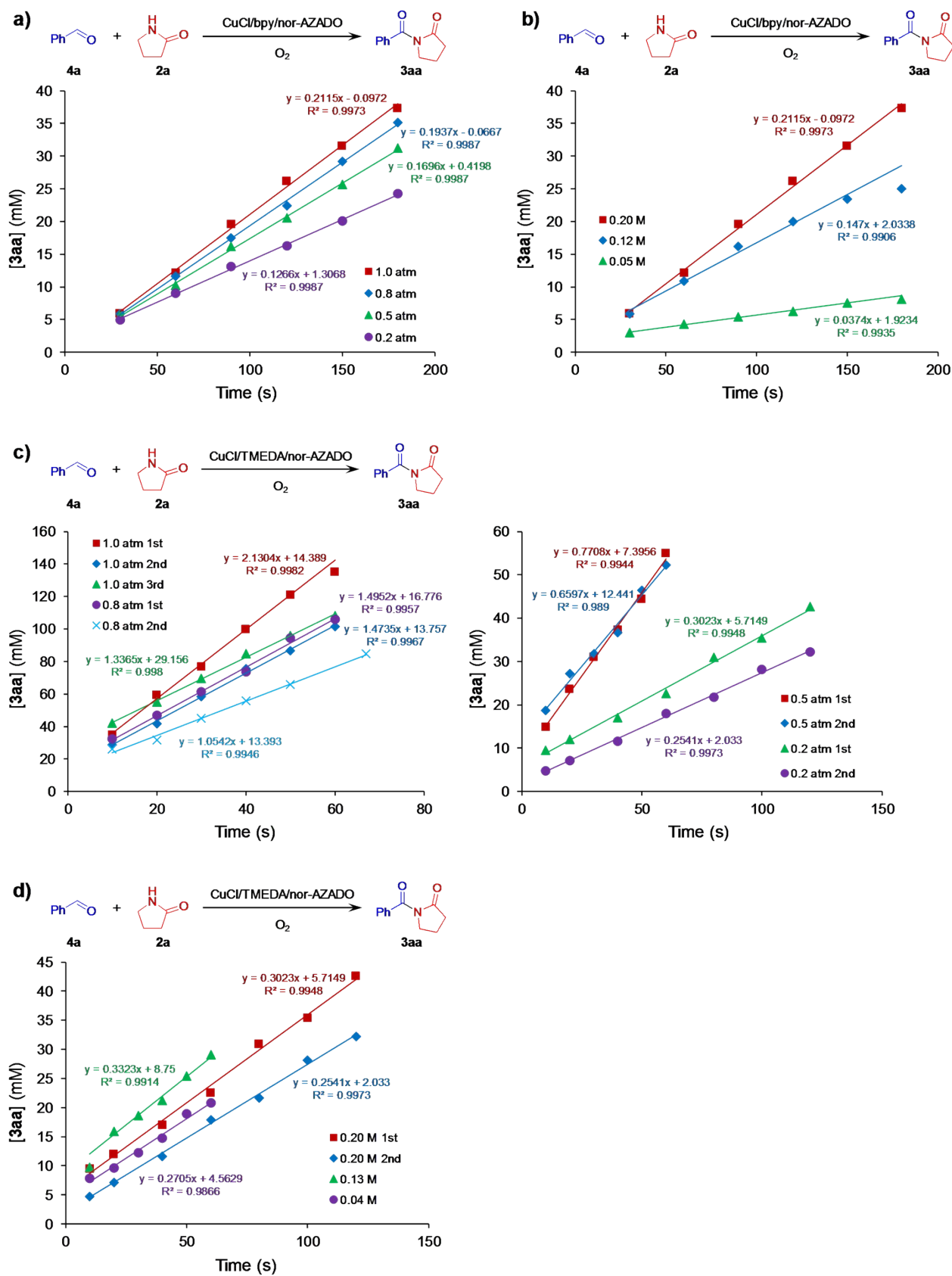


Fig. S3 Reaction profiles for a) the yield of **3aa** with different partial pressure of O_2 in the presence of $\text{CuCl/bpy/nor-AZADO}$ catalyst, b) the yield of **3aa** with different initial concentrations of **4a** in the presence

of CuCl/bpy/nor-AZADO catalyst, c) the yield of **3aa** with different partial pressure of O₂ in the presence of CuCl/TMEDA/nor-AZADO catalyst, and d) the yield of **3aa** with different initial concentrations of **4a** in the presence of CuCl/TMEDA/nor-AZADO catalyst. Reaction conditions for a): **4a** (0.20 M), **2a** (0.22 M), CuCl (10 mM), bpy (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.1–1.0 atm), room temp. (ca. 23°C); for b): **4a** (0.05–0.20 M), **2a** (0.22 M), CuCl (10 mM), bpy (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (1.0 atm), room temp. (ca. 23°C); for c): **4a** (0.20 M), **2a** (0.22 M), CuCl (10 mM), bpy (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.1–1.0 atm), room temp. (ca. 23°C); for d): **4a** (0.04–0.20 M), **2a** (0.22 M), CuCl (10 mM), bpy (10 mM), nor-AZADO (6 mM), MS 3A (200 mg), THF (2.5 mL), O₂ (0.2 atm), room temp. (ca. 23°C). Yields were determined by GC analysis.