Supporting information

for

Metal Free One-Pot Synthesis of α-Ketoamides from Terminal Alkenes

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**General considerations**

All reactions were carried out in reaction tubes under aerobic atmosphere unless otherwise mentioned. All the solvents were purchased from commercial sources and used without further purification. Wherever necessary, the solvents were dried by standard literature procedures. Reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and analyzed by UV fluorescence quenching using appropriate mixture of ethyl acetate and hexanes as eluting solvent mixture. Silica gel (particle size 100-200 mesh) purchased from SRL India was used for column chromatography using hexanes and ethyl acetate mixture as eluent. All the chemicals used are purchased from commercially available sources and used without further purification unless otherwise mentioned. IBX was prepared using literature procedure. Reactions were carried out in temperature controlled IKA magnetic stirrers. H and C NMR spectra were recorded on a Bruker 400 or 500 MHz instrument. H NMR spectra were reported relative to Me₄Si (δ 0.0 ppm) or residual CHCl₃ (δ 7.26 ppm). C NMR were reported relative to CDCl₃ (δ 77.16 ppm). FTIR spectra were recorded on a Nicolet 6700 spectrometer and were reported in frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer.

**Typical experimental procedure for α-ketoamides from styrenes**

In a clean reaction tube, I₂ (254 mg, 1.0 mmol) and IBX (280 mg, 1.0 mmol) was taken and dissolved in 2.5 mL of DMSO by stirring for 5 min at rt followed by addition of styrene (1a, 0.05 mL, 0.5 mmol). The mixture was transferred to a 80 °C oil bath and stirred for 3.5 hours. Piperidine (1b, 0.2 mL, 2.0 mmol) was added to the stirring solution slowly and stirred till the reaction was complete. Completion of reaction was monitored using TLC by checking the complete disappearance of the intermediate phenylglyoxal. The reaction was then extracted with ethyl acetate for few times and the combined organic layer was washed with saturated sodium thiosulphate and saturated sodium bicarbonate solutions. It was then dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The crude product was purified using column chromatography (silicagel, petroleum ether:ethyl acetate=85:15) to give the desired tertiary α-ketoamide (2a).
1-Phenyl-2-(piperidin-1-yl)ethane-1,2-dione (2a): yellow solid; mp 94-96 °C, Rf = 0.28 (in 20% ethyl acetate: hexanes); 1H NMR (400 MHz, CDCl3): δ 7.94 (d, J=7.2 Hz, 2H), 7.62 (t, J=7.6 Hz, 1H) 7.50 (t, J=7.6 Hz, 2H), 3.69 (brs, 2H), 3.28 (t, J=5.6 Hz, 2H) 1.68 (t, J=2.8 Hz, 4H), 1.54 (d, J=5.2 Hz, 2H); 13C NMR (100 MHz, CDCl3): δ 192.1, 165.6, 134.8, 133.4, 129.7, 129.1, 47.2, 42.3, 26.3, 25.6, 24.5; FTIR: 3418, 2884, 1733, 1638, 1397, 1264, 1048 cm⁻¹; [M+Na]⁺ calcd. for C13H15NO2Na: 240.0995; found: 240.0998.

1-Morpholino-2-phenylethane-1,2-dione (2b): yellow oil; Rf = 0.35 (in 30% ethyl acetate: hexanes); 1H NMR (400 MHz, CDCl3): δ 7.99-7.93 (m, 2H), 7.69-7.62 (m, 1H), 7.56-7.49 (m, 2H), 3.79 (brs, 4H), 3.68-3.62 (m, 2H), 3.41-3.35 (m, 2H); 13C NMR (100 MHz, CDCl3): δ 191.3, 165.6, 135.1, 133.2, 129.8, 129.2, 66.9, 66.8, 46.4, 41.8; FTIR: 3436, 2862, 1731, 1665, 1636, 1447, 1106 cm⁻¹; [M+H]⁺ calcd. for C12H14NO3: 220.0974; found: 220.0973.

1-Phenyl-2-(pyrrolidin-1-yl)ethane-1,2-dione (2c): Yellow oil; Rf = 0.41 (in 30% ethyl acetate: hexanes); 1H NMR (400 MHz, CDCl3): δ 8.02-7.96 (m, 2H), 7.66-7.59 (m, 1H), 7.54-7.46 (m, 2H), 3.65 (t, J=6.4 Hz, 2H), 3.42 (t, J=6.8 Hz, 2H), 2.02-1.88 (m, 4H); 13C NMR (100 MHz, CDCl3): δ 191.7, 165.1, 134.7, 133.0, 130.1, 129.1, 46.8, 45.4, 26.0, 24.2; FTIR: 2967, 2870, 1672, 1651 cm⁻¹; [M+H]⁺ calcd. for C12H14NO2: 204.1025; found: 204.1021.

1-(4-Methylpiperidin-1-yl)-2-phenylethane-1,2-dione (2d): yellow oil; Rf = 0.43 (in 20% ethyl acetate: hexane); 1H NMR (400 MHz, CDCl3) δ 7.97-7.91 (m, 2H), 7.66-7.6 (m, 1H), 7.54-7.47 (m, 2H), 4.7-4.55 (m, 1H), 3.6-3.4 (m, 1H), 3.1-2.9 (m, 1H), 2.79 (td, J=12.8 Hz, J2=2.8 Hz, 1H), 2.1-1.5 (m, 3H), 1.40-1.10 (m, 2H), 0.97 (d, J=6.8 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 192.0, 165.6, 134.8, 133.4, 129.7, 129.1, 46.5, 41.7, 34.4, 33.7, 31.2, 21.7; FTIR: 2924, 1741, 1641, 1123 cm⁻¹; [M+Na]⁺ calcd. for C14H17O2 N Na : 254.1152; found: 254.1157.
1-(3-Methylpiperidin-1-yl)-2-phenylethane-1,2-dione (2e): yellow oil; R_f = 0.44 (in 20% ethyl acetate: hexane); mixture of cis and trans isomers. ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.92 (m, 4H), 7.67-7.60 (m, 2H), 7.50 (t, J=7.6Hz, 4H), 4.6-4.40 (m, 2H), 3.55-3.35 (m, 2H), 3.1-2.95 (m, 1H), 2.85-2.75 (m, 1H), 2.75-2.65 (m, 1H), 2.55-2.45 (m, 1H), 1.95-1.70 (m, 5H), 1.6-1.4 (m, 2H), 1.3-1.1 (m, 3H), 0.99 (d, J=6.8Hz, 3H), 0.80 (d, J=6.8Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 192.1, 165.6, 134.8, 133.5, 129.8, 129.1, 53.5, 48.6, 46.7, 41.8, 33.1, 33.0, 31.8, 31.2, 25.8, 24.8, 19.1, 18.8; FTIR: 2923, 1601, 1675, 1176 cm\(^{-1}\); [M+Na]^+ calcd. for C_{14}H_{17}O_2 N Na : 254.1152; found: 254.1156.

1-(3-Nitrophenyl)-2-(piperidin-1-yl)ethane-1,2-dione (2f): yellow oil; R_f = 0.31 (in 30% ethyl acetate: hexanes); ^1H NMR (400 MHz, CDCl_3): δ 8.79-8.67 (m, 1H); 8.51-8.36 (m, 1H); 8.31-8.2 (m, 1H); 7.71 (t, J=8Hz, 1H); 3.78-3.6 (br, 2H), 3.32 (t, J=5.6 Hz, 2H), 1.70 (t, J=1.4Hz, 4H), 1.56 (br, 2H); ^13C NMR (100 MHz, CDCl_3): δ 189.1, 164.1, 148.7, 135.1, 135.0, 130.4, 128.7, 124.3, 47.2, 42.6, 26.5, 25.5, 24.4; FTIR: 3108, 2853, 1681, 1635, 1529, 1445, 1347, 770, 714 cm\(^{-1}\); [M+H]^+ calcd. for C_{13}H_{15}O_4N_2: 263.1032; found: 263.1020.

1-(4-Nitrophenyl)-2-(piperidin-1-yl)ethane-1,2-dione (2g): light yellow solid; mp 94–97 °C; R_f = 0.33 (30% EtOAc in hexanes). ^1H NMR (400 MHz, CDCl_3): δ = 8.38-8.29 (m, 2H), 8.17-8.08 (m, 2H), 7.71 (t, J=8Hz, 1H); 3.78-3.6 (br, 2H), 3.35-3.25 (m, 2H), 1.80–1.65 (m, 4H), 1.60–1.50 (brs, 2H); ^13C NMR (100 MHz, CDCl_3): δ 189.6, 164.2, 151.2, 137.8, 130.8, 124.3, 47.2, 42.6, 26.4, 25.6, 24.4; FTIR: 3102, 2866, 1687, 1638, 1537, 1468, 1346, 12810, 843 cm\(^{-1}\); [M+H]^+ calcd. for C_{13}H_{15}O_4N_2: 263.1032; found: 263.1021.

1-morpholino-2-(4-nitrophenyl) ethane-1,2-dione (2h): light yellow solid; mp 137-139 °C; R_f = 0.33 (30% Ethyl acetate : hexanes). ^1H NMR (400 MHz, CDCl_3): δ = 8.78 (s, 1H), 8.54-8.45 (m, 1H), 8.30 (d, J=8Hz, 1H), 7.74 (t, J=8Hz, 1H), 3.82 (brs, 4H), 3.69 (t, J=4.8Hz, n2H), 3.47-3.40(m, 2H), ^13C NMR (100 MHz, CDCl_3): δ 188.3,
164.0, 148.8, 139.4, 135.2, 130.5, 129.0, 124.7, 66.9, 66.8, 46.5, 42.1, 24.6; FTIR : 3075, 2864, 1682, 1527, 1455, 1345, 1115, 836 cm⁻¹;

1-(4-Bromophenyl)-2-(piperidin-1-yl)ethane-1,2-dione  (2i):³ white solid; m.p. 88-90, Rф = 0.33 (in 30% ethyl acetate: hexane); ¹H NMR (400 MHz, CDCl3): δ= 7.81 (d, J= 8.4 Hz, 2H), 7.65 (d, J=8.4 Hz, 2H), 3.70-3.69 (t, J=4.8 Hz, 2H), 1.69 (br, 4H), 1.55 (br, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 190.9, 165.0, 132.5, 132.3, 131.1, 130.2, 47.2, 42.4, 26.4, 25.6, 24.5; FTIR : 3445, 3072, 2947, 2840, 1668, 1631, 1109, 842, 753 cm⁻¹; [M+Na]⁺ calcd. for C₁₃H₁₄O₂NBr : 318.0100; found: 318.0107.

1-(3-Bromophenyl)-2-(piperidin-1-yl)ethane-1,2-dione  (2j):⁴ yellow liquid; Rф = 0.56 (in 30% Ethyl acetate : hexane); ¹H NMR (400 MHz, CDCl₃): δ 8.12-8.03 (m, 1 H), 7.84 (d, J = 7.6 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H), 7.39 (t, J=7.6 Hz, 1H), 3.67 (brs, 2H), 3.32-3.2 (m, 2H), 1.75–1.62 (m, 4H), 1.6–1.5 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 190.4, 164.8, 137.5, 135.2, 132.3, 128.3, 123.4, 47.2, 42.4, 26.3, 25.5, 24.4; FTIR : 3069, 2943, 1684, 1634, 1281, 746 cm⁻¹; [M+Na]⁺ calcd. for C₁₃H₁₄O₂NBr Na:318.0100; found:318.0104.

1-(4-Methoxyphenyl)-2-(piperidin-1-yl)ethane-1,2-dione  (2k):⁵ yellow liquid, Rф = 0.30 (in 30% ethyl acetate: hexanes); ¹H NMR (400 MHz, CDCl₃): δ 7.89 (d, J=7.2Hz, 2H); 6.95 (d, J=7.2, 2H); 3.14 (s, 3H); 3.68-3.67 (t, J=4Hz, 2H); 3.26 (t, J=4.8Hz, 2H); 1.67-1.66 (m, 4H); 1.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 190.8, 165.9, 164.9, 132.1, 126.5, 114.4, 55.7, 42.1, 26.3, 25.6, 24.5; FTIR: 3071, 2863, 1682, 1641, 1526, 1453, 1346, 1115, 836 cm⁻¹ (m/z): [M+H]⁺ calcd. for C₁₄H₁₈NO₃:248.1287, found: 248.1283.
1-(Piperidin-1-yl)-2-(p-tolyl)ethane-1,2-dione (2l): 5 yellow oil; \( R_f = 0.38 \) (in 30% ethyl acetate: hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.82 \) (d, \( J=8\) Hz, 2H), 7.29 (d, \( J=8\) Hz, 2H), 3.68 (brs, 2H); 3.26 (t, \( J=5.6 \) Hz, 2H); 2.24 (s, 3H), 1.68-1.67 (m, 4H), 1.53-1.51(m, 2H), \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 191.9, 165.8, 146, 131, 129.8, 129.8, 47.1, 42.2, 26.3, 25.6, 24.49, 21.98; FTIR : 3038, 2861, 1668, 1641, 1454, 851 cm\(^{-1}\); [M+Na\(^+\)] calcd. for C\(_{14}\)H\(_{17}\)O\(_2\)N Na: 254.1152; found: 254.1156.

1-Morpholino-2-(p-tolyl)ethane-1,2-dione (2m): 5 yellow oil; \( R_f = 0.18 \) (in 30% ethyl acetate: hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.84 \) (d, \( J=8\) Hz, 2H), 7.3 (d, \( J=7.6\) Hz, 2H), 3.77 (br, 2H), 3.64 (t, \( J=5.6 \) Hz, 2H), 3.39-3.33 (m, 2H), \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 191.0, 165.8, 146.4, 130.1, 130, 129.78, 66.9, 66.8. 46.4, 41.7, 22.0; FTIR : 3103, 2867, 1686, 1637, 1536, 1468, 1346, 1281, 844 cm\(^{-1}\);

1-(4-Bromophenyl)-2-morpholinoethane-1,2-dione (2n): 3 white solid; mp 122-124 °C; \( R_f = 0.34 \) (in 30% ethyl acetate: hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.84-7.79 (m, 2H), 7.69-7.64 (m, 2H), 3.82-3.74 (m, 4H), 3.67-3.62 (m, 2H), 3.69 (t, \( J=5.2 \) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 190.0, 165, 132.6, 131.2, 130.6, 66.9, 66.8, 46.4, 41.9; FTIR : 3448, 3073, 2947, 2838, 1671, 1629, 1569, 1109, 842, 756 cm\(^{-1}\); [M+H\(^+\)] calcd. for C\(_{12}\)H\(_{13}\)NO\(_3\)Br: 298.0079; found: 298.0067.

2-Iodo-1-phenylethanol (1d): Colourless liquid; \( R_f \) 0.32 (in 10% Ethyl acetate: hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz, ppm): \( \delta \) 7.25-7.37 (m, 5H), 4.81-4.84 (m, 1H), 3.51-3.38 (m, 2H), 2.518 (br, s, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 141.1, 128.7, 128.3, 125.7, 74.06, 15.32. FTIR: 3430, 2867, 1731, 1447, 1102 cm\(^{-1}\); MS(EI) 247.9636 (M\(^+\)).

2-Iodo-1-phenylethanone (1e): 6 yellow solid; m.p. 36-38 °C; \( R_f \) 0.66 (in 10% Ethyl acetate: hexanes); \(^1\)H NMR (CDCl\(_3\), 400 MHz,
ppm): \( \delta 7.86-7.84 \) (d, \( J=7.2 \) Hz, 2H), 7.58-7.54 (t, \( J=7.4 \), 1H), 7.45-7.42 (m, 2H), 4.81 (s, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 198.3, 134.2, 133.41, 128.9, 127.6, 30.1; FTIR: 2865, 1716, 1665, 1447, 1112 cm\(^{-1}\); MS(EI) 245.9540(M\(^+\)).

References

**Figure 1:** 400 MHz $^1$H NMR spectrum of 2a in CDCl$_3$

**Figure 2:** 100 MHz $^{13}$C NMR spectrum of 2a in CDCl$_3$
Figure 3: 400 MHz $^1$H NMR spectrum of 2b in CDCl$_3$

Figure 4: 100 MHz $^{13}$C NMR spectrum of 2b in CDCl$_3$
Figure 5: 400 MHz $^1$H NMR spectrum of 2c in CDCl$_3$

Figure 6: 100 MHz $^{13}$C NMR spectrum of 2c in CDCl$_3$
Figure 7: 400 MHz $^1$H NMR spectrum of 2d in CDCl$_3$

Figure 8: 100 MHz $^{13}$C NMR spectrum of 2d in CDCl$_3$
Figure 9: 400 MHz $^1$H NMR spectrum of 2e in CDCl$_3$

Figure 10: 100 MHz $^{13}$C NMR spectrum of 2e in CDCl$_3$
Figure 11: 400 MHz $^1$H NMR spectrum of 2f in CDCl$_3$
Figure 12: 400 MHz $^{13}$C NMR spectrum of 2f in CDCl$_3$

Figure 13: 400 MHz $^1$H NMR spectrum of 2g in CDCl$_3$

Figure 14: 100 MHz $^{13}$C NMR spectrum of 2g in CDCl$_3$
**Figure 15:** 400 MHz $^1$H NMR spectrum of 2i in CDCl$_3$

**Figure 16:** 100 MHz $^1$H NMR spectrum of 2i in CDCl$_3$
Figure 17: 400 MHz $^1$H NMR spectrum of 2j in CDCl$_3$
Figure 18: 100 MHz $^1$H NMR spectrum of 2j in CDCl$_3$

Figure 19: 400 MHz $^1$H NMR spectrum of 2h in CDCl$_3$
Figure 20: 100 MHz $^1$H NMR spectrum of 2h in CDCl$_3$

Figure 21: 400 MHz $^1$H NMR spectrum of 2k in CDCl$_3$

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Figure 26: 100 MHz $^1$H NMR spectrum of 2l in CDCl$_3$.
Figure 27: 400 MHz $^1$H NMR spectrum of 2n in CDCl$_3$

Figure 28: 100 MHz $^{13}$C NMR spectrum of 2n in CDCl$_3$
Figure 29: 100 MHz $^{13}$C NMR spectrum of 1d in CDCl$_3$

Figure 30: 400 MHz $^1$H NMR spectrum of 1d in CDCl$_3$
Figure 31: 400 MHz $^1$H NMR spectrum of 1e in CDCl$_3$

Figure 32: 100 MHz $^{13}$C NMR spectrum of 1e in CDCl$_3$