Supporting Information

Metal-free oxidative direct C(sp³)-H bond functionalization of ethers with α,α-diaryl allylic alcohols

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Experimental Section:
General

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in air and using undistilled solvent, without any precautions to exclude air and moisture unless otherwise noted. Melting points were recorded on an Electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. $^1$H, $^{13}$C NMR spectra were recorded in CDCl$_3$ on 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for $^1$H NMR and $^{13}$C NMR. High resolution mass spectra were obtained using a commercial apparatus (ESI or EI Source).

General procedure for alkylation of $\alpha,\alpha$-diaryl allylic alcohols

\[
\begin{array}{c}
\text{H}_2\text{O} \quad \text{Ar}_1^1 \quad \text{Ar}_2^2 \\
\text{O} \quad \text{O} \\
\text{1} \quad \text{2} \quad \text{3} \\
\text{mart-free} \quad \text{Oxidant, 120-150 °C under air} \\
\end{array}
\]

$\alpha,\alpha$-Diaryl allylic alcohol 1 (0.3 mmol), 2 ether (1 mL) and tert-butylperoxybenzoate (0.6 mmol) was stirred at 120°C or 150°C under air for 9-24h. Upon completion of the reaction (indicated by TLC), it was then removal of the organic solvent in vacuum and followed by flash silica gel column chromatographic purification afforded pure product 3 with petroleum/ethyl acetate.

General procedure for the synthesis of serotonin antagonist 5

\[
\begin{array}{c}
\text{O} \quad \text{O} \\
\text{3ae} \\
\text{1. HCIacetone/H}_2\text{O} \\
\text{2. NaBH(OAc)}_3, \text{4} \\
\text{CH}_2\text{CH}_2\text{Cl, rt.} \\
\end{array}
\]

Step 1: ketone 3ae (0.41 mmol) was dissolved in 5 mL acetone and an excess of 2M hydrochloric acid (6 mL) was slowly added to the reaction mixture. The reaction mixture was then stirred at room temperature for 6 hours. Upon completion of the reaction, a sat. aq. NaHCO$_3$ solution (10 mL) was added and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic extracts were dried with sodium sulfate and concentrated to give the crude keto-aldehyde which was used directly without further purification.
**Step 2:** A solution of the crude keto-aldehyde obtained above in dichloroethane (2 mL) was added a solution of 1-(2-methoxyphenyl)piperazine 4 (0.49 mmol) in dichloroethane (2 mL). To this mixture triacetoxy sodium borohydride (0.82 mmol) was added and the mixture was then stirred at room temperature for 6 h. Upon completion of the reaction, a sat. aq. NaHCO₃ solution (5 mL) was added and the mixture was extracted with ethyl acetate (3×5 mL). The combined organic extracts were dried with sodium sulfate and concentrated. The pure product 5 was obtained after purification of the residue by column chromatography (silica gel, ethyl acetate/petroleum ether) as a colourless oil.
Analytical and spectral data for compounds:

3-(1,4-dioxan-2-yl)-1,2-diphenylpropan-1-one (3aa): Yield = 95% (2:3 dr). Colorless oil. IR (KBr) ν = 2953, 2853, 1723, 1677, 940, 869, 760, 742, 696 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.00–7.93 (m, 2H), 7.51–7.43 (m, 1H), 7.41–7.33 (m, 2H), 7.31–7.24 (m, 4H), 7.23–7.16 (m, 1H), 4.94 (dd, J = 11.0, 3.6 Hz, 0.4H), 4.88 (dd, J = 10.2, 4.5 Hz, 0.6H), 3.80–3.71 (m, 1.3H), 3.67–3.53 (m, 4H), 3.35–3.21 (m, 1.7H), 2.45–2.36 (m, 0.4H), 2.12–2.04 (m, 0.6H), 1.97–1.89 (m, 0.6H), 1.71–1.64 (m, 0.4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.8, 199.7, 139.9, 138.8, 137.1, 136.7, 133.1, 133.0, 129.2, 129.0, 128.7, 128.6, 128.2, 127.4, 127.3, 73.6, 72.7, 71.6, 71.5, 66.9, 66.9, 66.7, 49.0, 48.6, 36.3, 35.0 ppm. HRMS m/z: calcd for C₁₉H₂₁O₃ [M+H]+ 297.1491, found: 297.1489.

1,2-diphenyl-3-(tetrahydro-2H-pyran-2-yl)propan-1-one (3ab): Yield = 63% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2933, 2846, 1719, 1679, 1597, 1580, 1493, 1447, 1272, 1239, 1206, 1175, 1086, 1048, 1032, 757, 742, 696 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.02–7.94 (m, 2H), 7.50–7.43 (m, 1H), 7.43–7.33 (m, 3H), 7.32–7.27 (m, 3H), 7.24–7.14 (m, 1H), 5.01 (dd, J = 11.1, 3.5 Hz, 0.4H), 4.95–4.89 (m, 0.6H), 4.01–3.95 (m, 0.6H), 3.95–3.89 (m, 0.4H), 3.34–3.20 (m, 2H), 3.01–2.93 (m, 0.6H), 2.52–2.44 (m, 0.4H), 2.19–2.10 (m, 0.4H), 2.05–1.97 (m, 0.6H), 1.81–1.62 (m, 2H), 1.57–1.23 (m, 4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 200.7, 200.4, 140.3, 139.4, 137.5, 136.9, 133.0, 132.8, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.3, 127.1, 127.1, 75.9, 74.7, 68.6, 68.5, 49.5, 49.0, 41.7, 40.1, 32.6, 32.4, 26.3, 23.6, 23.6 ppm. HRMS m/z: calcd for C₂₀H₂₂O₂ [M+H]+ 295.1698, found: 295.1703.
1,2-diphenyl-3-(tetrahydrofuran-2-yl)propan-1-one (3ac): Yield = 70\% (1:1.2 dr). Colorless oil. IR (KBr) \(\nu = 2925, 1717, 1678, 1597, 1580, 1493, 1448, 1249, 1174, 1066, 1027, 954, 758, 697\) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 7.99\) (t, \(J = 7.8\) Hz, 2H), 7.50–7.43 (m, 1H), 7.31–7.43 (m, 3H), 7.23–7.75 (m, 1H), 5.91 (dd, \(J = 10.5, 3.9\) Hz, 0.45H), 4.86 (dd, \(J = 9.7, 4.7\) Hz, 0.55H), 3.88–3.60 (m, 3H), 2.63–2.54 (m, 0.55H), 2.24–2.16 (m, 0.55H), 2.13–2.07 (m, 0.55H), 1.93–1.76 (m, 3H), 1.54–1.42 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 200.2, 199.9, 199.7, 199.6, 199.0, 199.0, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 133.1, 129.3, 129.3, 129.2, 129.2, 129.1, 129.1, 129.0, 128.8, 128.7, 128.7, 128.7, 128.4, 128.4, 128.2, 128.2, 127.5, 127.1, 126.2, 111.2, 111.1, 111.1, 110.9, 74.7, 74.1, 73.7, 73.1, 70.1, 70.0, 69.9, 69.7, 50.6, 50.6, 50.6, 50.6, 38.8, 38.6, 37.5, 37.5, 37.1, 33.0, 33.0, 32.2, 32.1, 24.8, 24.8, 24.8, 24.8, 23.9, 23.8, 8.7, 8.6, 8.5, 8.4 ppm. HRMS m/z: calcd for C\(_{19}\)H\(_{21}\)O\(_2\) [M+H]\(^{+}\) 281.1542, found: 281.1538.

3-(2-ethyl-2-methyl-1,3-dioxan-4-yl)-1,2-diphenylpropan-1-one (3ad): Yield = 61\% (3:4:4:4 dr). Colorless oil. IR (KBr) \(\nu = 2976, 2935, 2880, 1724, 1680, 1597, 1492, 1447, 1374, 1249, 1177, 1067, 1030, 1001, 971, 923, 886, 757, 697\) cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.01–7.95\) (m, 2H), 7.49–7.44 (m, 1H), 7.40–7.35 (m, 2H), 7.35–7.32 (m, 2H), 7.30–7.27 (m, 2H), 7.24–7.19 (m, 1H), 4.92–4.81 (m, 1H), 4.12–3.99 (m, 1H), 3.90–3.76 (m, 1H), 3.57–3.40 (m, 1H), 2.64–2.54 (m, 0.5H), 2.27–2.12 (m, 1H), 1.95–1.80 (m, 0.5H), 1.70–1.54 (m, 2H), 1.33 (s, 0.8H), 1.33 (s, 0.8H), 1.25 (s, 0.8H), 1.22 (s, 0.6H), 1.00–0.79 (m, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 199.9, 199.7, 199.6, 199.6, 143.7, 140.0, 139.9, 138.8, 138.8, 137.1, 137.1, 137.0, 136.6, 136.6, 136.6, 133.2, 133.1, 133.1, 133.1, 133.1, 133.1, 129.3, 129.3, 129.2, 129.2, 129.1, 129.1, 129.0, 128.8, 128.7, 128.7, 128.7, 128.4, 128.2, 128.2, 127.5, 127.1, 114.2, 111.2, 111.1, 111.1, 110.9, 74.7, 74.1, 73.7, 73.1, 70.1, 70.0, 69.9, 69.7, 50.6, 50.6, 50.6, 38.8, 38.6, 37.5, 37.5, 37.1, 33.0, 33.0, 32.2, 32.1, 24.8, 24.8, 24.8, 24.8, 23.9, 23.8, 8.7, 8.6, 8.5, 8.4 ppm. HRMS m/z: calcd for C\(_{21}\)H\(_{24}\)O\(_3\) [M]\(^{+}\) 324.1725, found: 324.1718.

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3-(1,3-dioxolan-2-yl)-1,2-diphenylpropan-1-one (3ae): Yield = 43%. White solid. M.p. 36.0–38.0 °C. IR (KBr) ν = 2957, 2929, 1681, 1597, 1447, 1279, 1251, 1175, 1069, 1026, 983, 762, 694 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.01–7.96 (m, 2H), 7.64–7.59 (m, 1H), 7.50–7.49 (m, 2H), 7.39–7.33 (m, 3H), 7.30–7.28 (m, 1H), 7.22–7.16 (m, 1H), 4.90–4.85 (m, 1H), 4.83–4.79 (m, 1H), 3.98–3.91 (m, 1H), 3.89–3.74 (m, 3H), 2.73–2.64 (m, 1H), 2.11–2.12 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 199.4, 139.2, 136.9, 134.0, 133.0, 130.4, 129.2, 129.0, 128.7, 128.5, 127.3, 102.8, 65.1, 65.0, 48.6, 38.0 ppm. HRMS m/z: calcd for C₁₈H₁₉O₃ [M+H]⁺ 283.1334, found: 283.1342.

4-ethoxy-1,2-diphenylpentan-1-one (3af): Yield = 45% (1:1.4 dr). Colorless oil. IR (KBr) ν = 3412, 3027, 2971, 1680, 1597, 1493, 1447, 1372, 1269, 1249, 1140, 1094, 1073, 757, 697 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.99 (t, J = 7.2 Hz, 2H), 7.34–7.30 (m, 2H), 7.30–7.25 (m, 2H), 7.23–7.15 (m, 1H), 4.99 (dd, J = 10.5, 4.1 Hz, 0.4H), 4.88 (dd, J = 9.1, 5.3 Hz, 0.6H), 3.61–3.46 (m, 1H), 3.43–3.37 (m, 0.4H), 3.28–3.09 (m, 1.6H), 2.51–2.42 (m, 0.4H), 2.31–2.22 (m, 0.6H), 2.06–1.97 (m, 0.6H), 1.88–1.79 (m, 0.4H), 1.18 (t, J = 7.0 Hz, 3H), 1.13–1.01 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 200.5, 200.2, 140.1, 139.5, 137.4, 137.0, 133.1, 132.9, 129.1, 129.0, 128.8, 128.8, 128.7, 128.6, 128.4, 127.2, 127.1, 73.2, 72.6, 63.9, 63.8, 50.1, 49.3, 42.2, 41.2, 20.2, 20.0, 15.9, 15.7 ppm. HRMS m/z: calcd for C₁₉H₂₃O₂ [M+H]⁺ 283.1698, found: 283.1699.

4,5-dimethoxy-1,2-diphenylpentan-1-one (3ag): Yield = 42% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2925, 2828, 1723, 1697, 1597, 1448, 1356, 1175, 1124, 1093, 1076, 1058, 925, 759, 697 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.01–7.95 (m, 2H), 7.49–7.43 (m, 1H), 7.42–7.35 (m, 2H), 7.34–7.28 (m, 1H), 7.27–7.21 (m, 2H), 7.18–7.11 (m, 1H), 4.41–4.35 (2H), 3.85–3.77 (2H), 3.83 (s, 3H), 3.77 (s, 3H), 3.63 (2H), 2.04–2.00 (m, 1H), 1.96–1.93 (m, 1H), 1.84–1.81 (m, 1H), 1.77–1.73 (m, 1H), 1.69–1.67 (m, 1H), 1.57–1.53 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 200.5, 199.9, 140.1, 139.5, 137.4, 137.0, 133.1, 132.9, 129.1, 129.0, 128.8, 128.8, 128.7, 128.6, 128.4, 127.2, 127.1, 73.2, 72.6, 63.9, 63.8, 50.1, 49.3, 42.2, 41.2, 20.2, 20.0, 15.9, 15.7 ppm. HRMS m/z: calcd for C₂₀H₂₅O₃ [M+H]⁺ 293.1861, found: 293.1862.
7.34–7.26 (m, 4H), 7.22–7.17 (m, 1H), 4.92 (dd, J = 10.2, 4.4 Hz, 0.45H), 4.87 (dd, J = 8.8, 5.6 Hz, 0.55H), 3.91–3.86 (m, 0.45H), 3.62–3.56 (m, 0.45H), 3.48 (dd, J = 10.1, 3.8 Hz, 0.55H), 3.42 (dd, J = 5.5, 2.3 Hz, 0.55H), 3.38 (s, 1.5H), 3.35 (s, 1.5H), 3.34–3.32 (m, 0.45H), 3.27 (s, 1.5H), 3.27 (s, 1.5H), 3.16–3.09 (m, 0.55H), 2.54–2.44 (m, 0.45H), 2.40–2.31 (m, 0.55H), 2.11–2.02 (m, 0.55H), 2.00–1.91 (m, 0.45H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 200.2, 199.9, 140.0, 139.3, 137.2, 136.9, 133.1, 132.9, 130.1, 129.0, 128.9, 128.8, 128.7, 127.3, 78.0, 77.3, 74.9, 74.5, 59.4, 59.3, 57.8, 57.7, 49.7, 49.3, 36.7, 36.1 ppm. HRMS m/z: calcd for C$_{19}$H$_{23}$O$_3$ [M+H]$^+$ 299.1647, found: 299.1646.

4-(2-methoxyethoxy)-1,2-diphenylbutan-1-one (3ag): Yield = 21%. Colorless oil. IR (KBr) v = 2955, 2850, 1680, 1448, 1352, 1266, 1101, 1081, 964, 756, 741, 697 cm$^{-1}$. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 8.01–7.94 (m, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.33–7.26 (m, 4H), 7.22–7.16 (m, 1H), 4.87 (t, J = 7.3 Hz, 1H), 3.54–3.44 (m, 5H), 3.38 (dd, J = 6.2, 3.5 Hz, 1H), 3.36 (d, J = 4.7 Hz, 3H), 2.48 (dd, J = 13.2, 6.1 Hz, 1H), 2.16–2.02 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 200.1, 139.4, 137.1, 133.0, 129.1, 129.0, 128.7, 127.2, 72.1, 70.2, 68.7, 59.2, 49.9, 33.8 ppm. HRMS m/z: calcd for C$_{19}$H$_{23}$O$_3$ [M+H]$^+$ 299.1647, found: 299.1642.

3-(1,4-dioxan-2-yl)-1,2-bis(4-methoxyphenyl)propan-1-one (3ba): Yield = 80% (1:1.2 dr). Colorless oil. IR (KBr) v = 2956, 2914, 2849, 1720, 1669, 1598, 1574, 1509, 1456, 1420, 1245, 1167, 1119, 1028, 935, 870, 829, 786, 713 cm$^{-1}$. $^1$H NMR (400MHz, CDCl$_3$): $\delta$ = 7.99–7.92 (m, 2H), 7.23–7.18 (m, 2H), 6.89–6.78 (m, 4H), 4.84 (dd, J = 10.9, 3.6 Hz, 0.45H), 4.78 (dd, J = 10.3, 4.4 Hz, 0.55 H), 3.82 (s, 1.3H), 3.81 (s, 1.7H), 3.75 (s, 1.7H), 3.74 (s, 1.3H), 3.72–3.49 (m, 5.5H), 3.35–3.32 (m, 1.5H), 2.40–2.32 (m, 0.45H), 2.06–1.97 (m, 0.55H), 1.93–1.85 (m, 0.55H), 1.68–1.59 (m, 0.45H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 198.4, 198.2, 163.3, 163.2, 158.7, 158.6, 132.2,
131.1, 131.1, 131.0, 129.9, 129.4, 129.0, 114.4, 113.7, 113.6, 73.6, 72.6, 71.4, 71.3, 66.8, 66.7, 66.5, 66.5, 55.4, 55.4, 55.2, 47.5, 47.1, 36.2, 34.8 ppm. HRMS m/z: calcd for C21H25O5 [M+H]+ 357.1702, found: 357.1689.

3-(1,4-dioxan-2-yl)-1,2-dip-tolylpropan-1-one (3ca): Yield = 89% (1:1.5 dr). Colorless oil. IR (KBr) ν = 2955, 2918, 2852, 1724, 1675, 1606, 1510, 1408, 1447, 1242, 1199, 1175, 1121, 1078, 935, 814, 761 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.91–7.84 (m, 2H), 7.20–7.13 (m, 4H), 7.11–7.04 (m, 2H), 4.87 (dd, J = 10.9, 3.6 Hz, 0.4H), 4.80 (dd, J = 10.7, 3.6 Hz, 0.6H), 3.79–3.70 (m, 1H), 2.40 (dd, J = 9.8, 6.6 Hz, 0.4H), 2.35 (s, 1.2H), 2.33 (s, 1.8H), 2.28 (s, 1.8H), 2.26 (s, 1.2H), 2.08–1.99 (m, 0.6H), 1.93–1.85 (m, 0.6H), 1.68–1.60 (m, 0.4H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.6, 199.4, 143.9, 143.7, 137.1, 137.0, 136.9, 136.0, 134.6, 134.1, 129.9, 129.9, 129.4, 129.3, 129.1, 129.1, 128.5, 128.1, 73.7, 72.7, 71.6, 71.5, 67.0, 66.9, 66.7, 66.7, 48.4, 48.1, 36.3, 35.0, 21.8, 21.8, 21.2, 21.2 ppm. HRMS m/z: calcd for C21H25O5 [M+H]+ 325.1804, found: 325.1810.

3-(1,4-dioxan-2-yl)-1,2-bis(4-fluorophenyl)propan-1-one (3da): Yield = 70% (1:1.3 dr). Colorless oil. IR (KBr) ν = 2958, 2917, 2854, 1725, 1680, 1596, 1506, 1409, 1225, 1121, 1078, 993, 912, 833, 799, 773, 685 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 8.02–7.94 (m, 2H), 7.27–7.21 (m, 2H), 7.10–6.94 (m, 4H), 4.89 (dd, J = 11.0, 3.5 Hz, 0.43H), 4.83 (dd, J = 10.2, 4.4 Hz, 0.57H), 3.80–3.49 (m, 5.5H), 3.35–3.20 (m, 1.5H), 2.41–2.32 (m, 0.43H), 2.08–2.00 (m, 0.57H), 1.92–1.84 (m, 0.57H), 1.68–1.60 (m, 0.43H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.2, 198.2, 167.1 (d, J_C,F = 12.9 Hz), 164.6 (d, J_C,F = 12.5 Hz), 163.4 (d, J_C,F = 10.4 Hz), 161.0 (d, J_C,F = 10.2 Hz), 135.5 (d, J_C,F = 3.3 Hz), 134.3 (d, J_C,F = 3.2 Hz), 133.3 (d, J_C,F = 3.0 Hz), 132.8 (d, J_C,F = 3.0 Hz), 131.6 (d, J_C,F = 9.3 Hz), 131.6 (d, J_C,F = 9.3 Hz), 130.2 (d, J_C,F = 8.0 Hz), 129.7 (d, J_C,F = 8.0 Hz), 116.3 (d, J_C,F = 8.0 Hz).
Hz), 116.2 (d, J_{CF} = 21.3 Hz), 116.2 (d, J_{CF} = 21.4 Hz), 115.9 (d, J_{CF} = 21.7 Hz), 73.5, 72.5, 71.5, 71.5, 67.0, 66.9, 66.7, 48.1, 47.7, 36.4, 35.0 ppm. HRMS m/z: calcd for C_{19}H_{19}F_{2}O_{3} [M+H]^+ 333.1302, found: 333.1306.

1,2-bis(4-chlorophenyl)-3-(1,4-dioxan-2-yl)propan-1-one (3ea): Yield = 82% (1:1.3 dr).

Colorless oil. IR (KBr) v = 2962, 2922, 2859, 1728, 1688, 1611, 1491, 1449, 1327, 1256, 1163, 1118, 1071, 895, 806, 702, 693 cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 8.28–8.20 (m, 1H), 8.12 (t, J = 8.7 Hz, 1H), 7.81–7.73 (m, 1H), 7.61–7.41 (m, 5H), 5.04 (dd, J = 11.2, 3.3 Hz, 0.4 Hz), 4.95 (dd, J = 9.9, 4.7 Hz, 0.6H), 3.81–3.51 (m, 5.4H), 3.35–3.19 (m, 1.6H), 2.48–2.39 (m, 0.4H), 2.16–2.08 (m, 0.6H), 1.98–1.90 (m, 0.6H), 1.74–1.66 (m, 0.4H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 198.4, 198.4, 138.6, 137.5, 135.5, 135.1, 132.5, 132.2, 132.1, 139.5, 130.4, 139.3, 129.9, 128.7, 128.5, 121.7, 121.6, 73.4, 72.4, 71.5, 71.4, 67.0, 66.9, 66.6, 48.4, 47.9, 36.1, 34.8 ppm. HRMS m/z: calcd for C_{19}H_{19}Cl_{2}O_{3} [M+H]^+ 365.0711, found: 365.0714.

1,2-bis(4-bromophenyl)-3-(1,4-dioxan-2-yl)propan-1-one (3fa): Yield = 78% (1:1.3 dr).

Colorless oil. IR (KBr) v = 2956, 2913, 2851, 1719, 1680, 1584, 1567, 1447, 1396, 1341, 1277, 1121, 1070, 1009, 959, 870, 817, 734, 684 cm\(^{-1}\). \(^1\)H NMR (400MHz, CDCl\(_3\)): \(\delta = 7.92–7.84 (m, 2H), 7.40–7.33 (m, 2H), 7.31–7.25 (m, 2H), 7.23–7.18 (m, 2H), 4.87 (dd, J = 11.0, 3.5 Hz, 0.43H), 4.81 (dd, J = 10.2, 4.4 Hz, 0.57H), 3.79–3.51 (m, 5.4H), 3.34–3.21 (m, 1.6H), 2.41–2.32 (m, 0.43H), 2.09–2.00 (m, 0.57H), 1.91–1.83 (m, 0.57H), 1.67–1.58 (m, 0.43H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 198.3, 198.3, 139.9, 139.7, 138.1, 137.0, 135.2, 134.7, 133.6, 133.5, 130.4, 130.3, 130.0, 129.5, 129.2, 129.1, 73.4, 72.5, 71.5, 71.4, 67.0, 66.9, 66.7, 48.3, 47.9, 36.2, 34.8 ppm. HRMS m/z: calcd for C_{19}H_{19}Br_{2}O_{3} [M+H]^+ 452.9701, found: 452.9721.
3-(1,4-dioxan-2-yl)-1,2-bis(3-(trifluoromethyl)phenyl)propan-1-one (3ga): Yield = 76% (1:1 dr). Colorless oil. IR (KBr) ν = 2957, 2915, 2853, 1724, 1680, 1588, 1488, 1399, 1262, 1121, 1090, 1078, 1013, 960, 870, 745, 713, 690 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.83–7.76 (m, 2H), 7.56–7.50 (m, 2H), 7.46–7.38 (m, 2H), 7.18–7.11 (m, 2H), 4.85 (dd, J = 11.0, 3.5 Hz, 0.43H), 4.79 (dd, J = 10.2, 4.4 Hz, 0.57H), 3.78–3.48 (m, 5.3H), 3.34–3.20 (m, 1.6H), 2.40–2.32 (m, 0.43H), 2.09–2.01 (m, 0.57H), 1.91–1.83 (m, 0.57H), 1.67–1.59 (m, 0.43H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.3, 197.9, 147.7, 144.0, 143.1, 137.3, 135.7, 133.9, 130.4, 130.1, 129.4, 129.1, 128.3, 121.6, 110.2, 108.8, 108.7, 47.7, 38.5, 21.8, 21.2 ppm. HRMS m/z: calcd for C₂₁H₁₉F₆O₃ [M+H]⁺ 433.1238, found: 433.1231.

3-(benzo[d][1,3]dioxol-2-yl)-1,2-dip-tolylpropan-1-one (3ci): Yield = 71%. Colorless oil. IR (KBr) ν = 2922, 2855, 1676, 1606, 1482, 1460, 1231, 1176, 1096, 1018, 964, 813, 737, 681 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.85 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.11–7.08 (m, 1H), 6.80–6.72 (m, 3H), 6.72–6.68 (m, 1H), 6.02–5.98 (m, 1H), 4.88 (t, J = 7.3 Hz, 1H), 2.84 (dd, J = 13.9, 7.6 Hz, 1H), 2.43–2.38 (m, 1H), 2.33 (s, 3H), 2.27 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.3, 147.7, 144.0, 143.1, 137.3, 135.7, 133.9, 130.4, 130.1, 129.4, 129.1, 128.3, 121.6, 110.2, 108.8, 108.7, 47.7, 38.5, 21.8, 21.2 ppm. HRMS m/z: calcd for C₂₄H₂₁O₃ [M+H]⁺ 359.1647, found: 359.1655.
3-(benzo[d][1,3]dioxol-2-yl)-1-(4-(benzylxyloxy)phenyl)-2-phenylpropan-1-one (3hi) and 3-(benzo[d][1,3]dioxol-2-yl)-2-(4-(benzylxyloxy)phenyl)-1-phenylpropan-1-one (3hi'): Yield = 49% (3hi:3hi'=4:1). Colorless oil. IR (KBr) ν = 3062, 3031, 2927, 1673, 1597, 1508, 1482, 1453, 1351, 1230, 1167, 1096, 1005, 965, 831, 803, 735, 696 cm⁻¹. The ¹H NMR spectrum of the isolated product showed a 4:1 mixture of 3hi and its isomer 3hi'. ¹H NMR (400MHz, CDCl₃) 3hi: δ = 7.95–7.92 (m, 2H), 7.48–7.42 (m, 1H), 7.39–7.37 (m, 4H), 7.36–7.34 (m, 2H), 7.34–7.32 (m, 2H), 7.31–7.28 (m, 2H), 7.23–7.18 (m, 1H), 6.78–6.75 (m, 3H), 6.70–6.67 (m, 1H), 6.02 (t, J = 2.2 Hz, 1H), 5.07 (s, 2H), 4.89 (t, J = 4.9 Hz, 1H), 2.91–2.85 (m, 1H), 2.47–2.42 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.8, 197.1, 162.8, 158.4, 147.7, 147.7, 147.6, 138.9, 136.4, 136.3, 131.4, 129.6, 129.5, 129.4, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.7, 127.7, 127.6, 121.6, 115.7, 114.8, 114.6, 110.1, 108.8, 108.7, 70.3, 70.2, 47.9, 47.3, 38.7, 38.6 ppm. HRMS m/z: calcd for C₂₉H₂₉O₄ [M+H]^+ 437.1753, found: 437.1742.

3-(benzo[d][1,3]dioxol-2-yl)-1-(3,4-dimethylphenyl)-2-phenylpropan-1-one (3ii) and 3-(benzo[d][1,3]dioxol-2-yl)-2-(3,4-dimethylphenyl)-1-phenylpropan-1-one (3ii'): Yield = 53% (3ii:3ii'=1.6:1). Colorless oil. IR (KBr) ν = 2921, 1676, 1727, 1482, 1448, 1351, 1231, 1117, 1096, 1021, 970, 862, 809, 735, 699 cm⁻¹. The ¹H NMR spectrum of the isolated product showed a 1.6:1 mixture of 3ii and its isomer 3ii'. ¹H NMR (400MHz, CDCl₃) 3ii and 3ii': δ = 7.95 (dd, J = 5.2, 3.3 Hz, 0.7H), 7.80–7.76 (m, 0.3H), 7.74–7.71 (m, 0.5H), 7.68 (m, 0.5H), 7.63–7.44 (m, 1H), 7.39–7.32 (m, 2H), 7.31–7.27(m, 1H), 7.23–7.17 (m, 0.7H), 7.13–7.05 (m, 1.3H), 6.79–6.72 (m, 3H), 6.71–6.66 (m, 1H), 6.03–6.00 (m, 0.6H), 6.01–5.99 (m, 0.4H), 4.93 (t, J = 7.3 Hz, 0.6H), 4.88 (t, J = 7.3 Hz, 0.4H),
2.92–2.86 (m, 0.6H), 2.87–2.82 (m, 0.4H), 2.48–2.42 (m, 0.6H), 2.44–2.39 (m, 0.4H), 2.25 (s, 2H), 2.24 (s, 2H), 2.20 (s, 1H), 2.18 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) 3ii and 3ii': $\delta$ = 198.8, 198.5, 147.7, 147.7, 142.9, 138.8, 137.7, 137.1, 136.5, 136.0, 135.8, 134.2, 133.1, 130.6, 130.2, 129.9, 129.4, 129.3, 129.0, 128.7, 128.4, 127.5, 126.8, 125.9, 121.6, 110.2, 110.1, 108.8, 108.8, 108.7, 48.0, 47.8, 38.6, 38.6, 20.2, 20.2, 20.0, 20.0 ppm. HRMS m/z: calcd for C$_{24}$H$_{23}$O$_3$ [M+H]$^+$ 359.1647, found: 359.1633.

3-(benzo[d][1,3]dioxol-2-yl)-2-(4-bromophenyl)-1-phenylpropan-1-one (3ji) and 3-(benzo[d][1,3]dioxol-2-yl)-1-(4-bromophenyl)-2-phenylpropan-1-one (3ji'): Yield = 60% (3ji:3ji'=1:1). Colorless oil. IR (KBr) $\nu$ = 2926, 1718, 1584, 1482, 1447, 1396, 1265, 1231, 1174, 1096, 1070, 1010, 989, 964, 805, 737, 700, 669 cm$^{-1}$. The $^1$H NMR spectrum of the isolated product showed a 1.1:1 mixture of 3ji and its isomer 3ji'. $^1$H NMR (400MHz, CDCl$_3$) 3ji and 3ji': $\delta$ = 7.93–7.88 (m, 1H), 7.80–7.76 (m, 0.6H), 7.70–7.58 (m, 0.6H), 7.53–7.46 (m, 1.4H), 7.45–7.36 (m, 2.6H), 7.31–7.29 (m, 1H), 7.24–7.19 (m, 1.4H), 7.16–7.11 (m, 0.4H), 6.88–6.72 (m, 3H), 6.69–6.66 (m, 1H), 6.04–6.02 (m, 0.5H), 6.02–5.98 (m, 0.5H), 4.93 (t, $J$ = 7.2 Hz, 0.5H), 4.89–4.85 (m, 0.5H). 2.94–2.85 (m, 1H), 2.48–2.39 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) 3ji and 3ji': $\delta$ = 198.3, 197.6, 147.6, 147.5, 138.2, 137.5, 136.1, 135.1, 135.1, 133.5, 132.9, 132.5, 132.1, 131.8, 131.6, 131.6, 130.5, 130.2, 129.9, 129.5, 129.0, 128.8, 128.6, 128.5, 128.4, 127.9, 127.8, 121.8, 121.7, 109.9, 109.8, 108.8, 108.7, 48.2, 47.4, 38.5, 38.4 ppm. HRMS m/z: calcd for C$_{22}$H$_{18}$BrO$_3$ [M+H]$^+$ 409.0439, found: 409.0454/411.0439.

3-(benzo[d][1,3]dioxol-2-yl)-1-phenyl-2-(3-(trifluoromethyl)phenyl)propan-1-one (3ki): Yield = 43%. Colorless oil. IR (KBr) $\nu$ = 3065, 2933, 1682, 1596, 1483, 1448, 1351, 1327, 1164, 1121, 1102, 1088, 1066, 1015, 990, 974, 949, 914, 805 cm$^{-1}$. $^1$H NMR (400MHz, CDCl$_3$) 3ki: $\delta$ = 7.89–7.86 (m, 1H), 7.77–7.72 (m, 0.4H), 7.71–7.49 (m, 1.4H), 7.47–7.37 (m, 2.6H), 7.30–7.28 (m, 1H), 7.25–7.19 (m, 1.4H), 7.16–7.11 (m, 0.4H), 6.88–6.72 (m, 3H), 6.69–6.66 (m, 1H), 6.04–6.02 (m, 0.5H), 6.02–5.98 (m, 0.5H), 4.93 (t, $J$ = 7.2 Hz, 0.5H), 4.89–4.85 (m, 0.5H). 2.94–2.85 (m, 1H), 2.48–2.39 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) 3ki: $\delta$ = 198.8, 198.5, 147.7, 147.7, 142.9, 138.8, 137.7, 137.1, 136.6, 136.0, 135.8, 134.2, 133.1, 130.6, 130.2, 129.9, 129.4, 129.3, 129.0, 128.7, 128.5, 128.4, 127.9, 127.8, 121.8, 121.7, 109.9, 109.8, 108.8, 108.7, 48.2, 47.4, 38.5, 38.4 ppm. HRMS m/z: calcd for C$_{22}$H$_{18}$BrO$_3$ [M+H]$^+$ 409.0439, found: 409.0454/411.0439.
The $^1$H NMR spectrum of the crude product showed a 2.2:1 mixture of 3ki and its isomer 3ki'. Flash chromatography on silica gel afforded ketone 3ki. $^1$H NMR (400MHz, CDCl$_3$): $\delta = 7.95–7.91$ (m, 2H), 7.62–7.60 (m, 1H), 7.56–7.47 (m, 3H), 7.45–7.37 (m, 3H), 6.80–6.72 (m, 3H), 6.68–6.64 (m, 1H), 6.05 (dd, $J = 8.8$, 4.2 Hz, 1H), 5.05 (dd, $J = 7.7$, 6.7 Hz, 1H), 3.02–2.93 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 198.2$, 147.5, 147.5, 139.6, 136.0, 133.6, 131.8, 129.8, 128.9, 128.9, 125.3 (dd, $J_{C,F} = 7.6$, 3.7 Hz), 124.6 (dd, $J_{C,F} = 7.3$, 3.8 Hz), 121.8, 121.8, 109.6, 108.8, 47.4, 38.7 ppm. HRMS m/z: calcd for C$_{23}$H$_{18}$F$_3$O$_3$ [M+H]$^+$ 399.1208, found: 399.1216.

3-(benzo[d][1,3]dioxol-2-yl)-1-(2-fluorophenyl)-2-phenylpropan-1-one (3li) and 3-(benzo[d][1,3]dioxol-2-yl)-2-(2-fluorophenyl)-1-phenylpropan-1-one (3li'): Yield = 48% (3li:3li' = 2.7:1). Colorless oil. IR (KBr) $\nu = 2930$, 1682, 1608, 1481, 1449, 1351, 1273, 1230, 1096, 1033, 966, 736, 698 cm$^{-1}$. The $^1$H NMR spectrum of the isolated product showed a 1.1:1 mixture of 3li and its isomer 3li'. $^1$H NMR (400MHz, CDCl$_3$) 3li and 3li': $\delta = 7.98–7.93$ (m, 0.5H), 7.77–7.71 (m, 0.5H), 7.50–7.35 (m, 2H), 7.28 (m, 3H), 7.23–6.98 (m, 3H), 6.87–6.72 (m, 3H), 6.72–6.66 (m, 1H), 6.09 (t, $J = 4.9$ Hz, 0.3H), 6.05–6.00 (m, 0.7H), 5.34–5.29 (m, 0.3H), 4.88 (t, $J = 7.3$ Hz, 0.7H), 2.98–2.88 (m, 1H), 2.46–2.37 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) 3li and 3li': $\delta = 197.6$, 197.6, 147.7, 147.6, 147.6, 137.6, 134.6, 134.5, 133.5, 131.4, 131.3, 129.5, 129.4, 129.1, 128.8, 127.7, 125.1, 125.1, 121.7, 121.6, 121.6, 121.6, 117.0, 116.7, 116.2, 116.0, 110.0, 109.8, 108.7, 52.1, 52.1, 38.4 ppm. HRMS m/z: calcd for C$_{22}$H$_{18}$F$_3$O [M+H]$^+$ 349.1240, found: 349.1241.

3-(benzo[d][1,3]dioxol-2-yl)-1-phenyl-2-(3-(trifluoromethyl)phenyl)propan-1-one (3mi): Yield
= 60%. White solid. M.p. = 148.8-149.9 °C. IR (KBr) v = 2961, 2911, 1680, 1485, 1338, 1261, 1231, 1175, 1123, 1075, 873, 799, 759, 718, 669 cm⁻¹. The ¹H NMR spectrum of the crude product showed a 2:3:1 mixture of 3mi and its isomer 3mi¹, flash chromatography on silica gel afforded ketone 3mi. ¹H NMR (400MHz, CDCl₃): δ = 8.64 (d, J = 1.9 Hz, 1H), 8.48 (dd, J = 4.7, 1.4 Hz, 1H), 7.95–7.90 (m, 2H), 7.70–7.64 (m, 1H), 7.54–7.48 (m, 1H), 7.39 (dd, J = 10.6, 4.8 Hz, 2H), 7.23 (dd, J = 7.9, 4.9 Hz, 1H), 6.82–6.72 (m, 3H), 6.69–6.65 (m, 1H), 6.07 (t, J = 4.7 Hz, 1H), 5.02 (dd, J = 7.6, 6.7 Hz, 1H), 3.02–2.93 (m, 1H), 2.50–2.42 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.1, 150.2, 149.1, 147.5, 147.4, 135.9, 135.6, 134.4, 133.7, 129.0, 128.9, 124.2, 121.8, 121.8, 109.5, 108.9, 108.8, 45.0, 38.4 ppm. HRMS m/z: calcd for C₂₁H₁₈NO₃ [M+H]⁺ 332.1287, found: 332.1279.

4-(4-(2-methoxyphenyl)piperazin-1-yl)-1,2-diphenylbutan-1-one (5): Yield = 54%. Colorless oil. IR (KBr) v = 2935, 2813, 1678, 1595, 1499, 1447, 1238, 1138, 1024, 746, 696 cm⁻¹. ¹H NMR (400MHz, CDCl₃): δ = 7.99 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.00–6.95 (m, 1H), 6.93–6.88 (m, 2H), 6.84 (d, J = 8.0 Hz, 1H), 4.74 (t, J = 7.0 Hz, 1H), 3.83 (s, 3H), 3.08–2.89 (m, 4H), 2.68–2.47 (m, 5H), 2.44–2.36 (m, 2H), 2.02–1.94 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 199.7, 152.4, 141.6, 139.8, 137.3, 132.9, 129.0, 128.9, 128.6, 128.5, 127.2, 123.0, 121.1, 118.3, 111.4, 56.4, 55.5, 53.4, 51.5, 50.7, 31.5 ppm. HRMS m/z: calcd for C₂₇H₃₁N₂O₂ [M+H]⁺ 415.2386, found: 415.2387.
The $^1$H, $^{13}$C spectra of compounds:
Figure 1. X-ray structure of 3mi

Crystal Number: CCDC 1006442
Empirical formula: C21H17NO3
Formula weight: 357.4019
Unit cell parameters: a = 10.2758 (3) Å, b = 8.6059 (15) Å,
c = 10.5383 (3) Å, α = 90.00, β = 118.016(4), γ = 90.00,
space group P 1 2 1 1.
Temperature: 223(2) K
Wavelength: 1.54184 Å
Crystal system: Monoclinic
Volume: 822.72(4) Å³
Z: 2

Calculated density: 1.338 Mg/m³
Absorption coefficient: 0.725 mm⁻¹
F (000): 348
Crystal size: 0.80×0.60×0.50 mm³
Correction-type: multi-scan
h, k, l max: 11, 7, 12
Tmin, Tmax: 0.73309/1.00000
R₁ = 0.0456, wR₂ = 0.1061.