Ruthenium-Catalyzed Direct C3 Alkylation of Indoles with $\alpha,\beta$-Unsaturated Ketones

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Supporting Information

Table of Contents

1. General Methods
2. General procedure for synthesis of 3-alkyl indole and Characterization Data
3. Synthetic Applications, Structure Determination and Characterization Data
4. Mechanism Study
5. NMR Spectra of 3-alkyl indole
1. General Methods

NMR data were obtained for $^1$H at 300 MHz or 400 MHz, and for $^{13}$C at 75 MHz or 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl$_3$ or DMSO-d$_6$ solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with ethyl acetate and petroleum ether. CH$_2$Cl$_2$, CHCl$_3$CHCl$_2$ were distilled over CaH$_2$. All indoles were commercially available and N-methyl indoles were prepared according to the literature procedures.$[^1]$ All $\alpha,\beta$-unsaturated ketones were prepared according to the literature procedures.$[^2]$

2. General Procedure for Synthesis of 3-alkyl indole derivatives and Characterization Data

$N$-CH$_3$ indole 1a (6.6 mg, 0.05 mmol), chalcone 2a (12.1 mg, 0.058 mmol), RuCl$_2$(PPh$_3$)$_3$ (1.4 mg, 3 mol %) and AgSbF$_6$ (3.44 mg, 20 mol %) were stirred in DCM (1.0 mL) at room temperature for 4 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:50) to give the product 3aa as a white solid (16.3 mg, 96%).

$3\text{-}(1\text{-methyl-1}$H-indol-3-yl)-1,3-diphenylpropan-1-one ($3\text{aa}$). 4 h, 96% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 7.6$ Hz, 2H), 7.58-7.54 (m, 1H), 7.49-7.43 (m, 3H), 7.40-7.39 (m, 2H), 7.31-7.27 (m, 3H), 7.23-7.17 (m, 2H), 7.06-7.03 (m, 1H), 6.87 (s, 1H), 5.10 (t, $J = 7.2$ Hz, 1H), 3.81 (ddd, $J = 6.4$, 20.4, 24.4 Hz, 2H), 3.73 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.4, 144.4, 137.3, 137.1, 132.9, 128.5, 128.4, 128.0, 127.8, 126.9, 126.2, 121.6, 119.5, 118.8, 117.7, 109.2, 45.3, 38.0, 32.6 ppm. ESI HRMS: calcd. for C$_{24}$H$_{21}$NO+Na 362.1521, found 362.1515.

3-(2-Chloro-phenyl)-3-(1-methyl-1$^1$H-indol-3-yl)-1-phenyl-propan-1-one ($3\text{ab}$). 8 h, 91% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 7.6$ Hz, 2H), 7.55-7.52 (m, 1H), 7.44-7.41 (m, 3H), 7.39-7.37 (m, 1H), 7.25-7.23 (m, 2H), 7.18-7.15 (m, 1H), 7.11-7.09 (m, 2H), 7.02-6.98 (m, 1H), 6.85 (s, 1H), 5.53 (t, $J = 7.2$ Hz, 1H), 3.73 (ddd, $J = 8.4$, 20.8, 44.4 Hz, 2H), 3.70 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.0, 141.7, 137.2, 136.8, 133.5, 133.0, 129.7, 128.9, 128.6, 128.1, 127.5, 127.0, 126.9, 126.6, 121.7, 119.5, 118.9, 116.1, 109.2, 44.3, 34.7, 32.7 ppm. ESI HRMS: calcd. for C$_{23}$H$_{20}$ClNO+Na 396.1131 found C$_{23}$H$_{20}$ClNNaO 396.1133, C$_{23}$H$_{20}$ClNNaO 398.1105.

3-[1-(3-Chloro-phenyl)-3-phenyl-but-3-enyl]-1-methyl-1$^1$H-indole ($3\text{ac}$). 10 h, 80% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J = 7.6$ Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.44 (m, 3H), 7.36 (s, 1H), 7.29-7.25 (m, 2H), 7.24-7.14 (m, 3H), 7.07-7.04 (m, 1H), 6.87 (s, 1H),
5.07 (t, J = 7.2 Hz, 1H), 3.78 (ddd, J = 6.8, 20, 33.6 Hz, 2H), 3.73 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 197.9, 146.6, 137.3, 136.9, 134.1, 133.1, 129.6, 128.6, 128.0, 127.9, 126.7, 126.4, 126.1, 121.8, 119.3, 118.9, 117.0, 109.2, 44.9, 37.7, 32.7 ppm. ESI HRMS: calcd. for C24H20ClNO+Na 396.1131 found C24H2035ClNNaO 396.1142, C24H2037ClNNaO 398.1096.

3-(4-Chloro-phenyl)-3-(1-methyl-1H-indol-3-yl)-1-phenyl-propan-1-one (3ad). 8 h, 95% yield; 1H NMR (400 MHz, CDCl3): δ 7.92 (d, J = 7.2 Hz, 2H), 7.56-7.52 (m, 1H), 7.45-7.39 (m, 3H), 7.29-7.24 (m, 3H), 7.21-7.17 (m, 3H), 7.04-7.00 (m, 1H), 5.03 (t, J = 7.2 Hz, 1H), 3.74 (ddd, J = 6.4, 20, 29.6 Hz, 2H), 3.73 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 198.2, 142.9, 137.3, 136.9, 133.1, 131.8, 129.1, 128.6, 128.5, 128.0, 126.7, 126.1, 121.8, 119.1, 119.0, 109.3, 45.0, 37.4, 32.7 ppm. ESI HRMS: calcd. for C24H20ClNO+Na 396.1131 found C24H2079BrNNaO 396.1140, C24H2081BrNNaO 398.1090.

3-(4-Methoxy-phenyl)-3-(1-methyl-1H-indol-3-yl)-1-phenyl-propan-1-one (3af). 10 h, 95% yield; 1H NMR (400 MHz, CDCl3): δ 7.92 (d, J = 7.6 Hz, 2H), 7.53-7.50 (m, 1H), 7.44-7.39 (m, 3H), 7.27-7.23 (m, 3H), 7.18-7.15 (m, 1H), 7.02-6.98 (m, 1H), 6.81-6.77 (m, 3H), 5.00 (t, J = 7.2 Hz, 1H), 3.75 (ddd, J = 10.8, 22.2, 31.8 Hz, 2H), 3.73 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 198.6, 157.8, 137.3, 137.0, 136.4, 132.9, 132.9, 131.4, 129.6, 128.6, 128.0, 126.7, 126.1, 121.8, 119.4, 118.9, 117.2, 109.3, 44.9, 37.4, 32.7 ppm. ESI HRMS: calcd. for C25H23NO2+Na 392.1626, found 392.1627.

3-(1-Methyl-1H-indol-3-yl)-1-phenyl-3-(4-trifluoromethyl-phenyl)-propan-1-one (3ag). 12 h, 98% yield; 1H NMR (400 MHz, CDCl3): δ 7.93 (d, J = 7.6 Hz, 2H), 7.56-7.40 (m, 8H), 7.28-7.26 (m, 1H), 7.23-7.18 (m, 1H), 7.05-7.01 (m, 1H), 6.84 (s, 1H), 5.12 (t, J = 7.2 Hz, 1H), 3.79 (ddd, J = 6.4, 20.4, 26 Hz, 2H), 3.72 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3): δ 198.0, 148.5, 137.3, 136.8, 133.2, 128.6, 128.1, 128.0, 126.7, 126.2, 125.4, 125.3, 125.3, 121.2, 119.3,
119.0, 116.9, 109.3, 44.8, 37.8, 32.7 ppm. ESI HRMS: calcd. for C_{23}H_{20}F_{3}NO+Na 430.1395, found 430.1401.

3-(1-Methyl-1H-indol-3-yl)-3-naphthalen-1-yl-1-phenyl-propan-1-one (3ah). 10 h, 77% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.30 (d, \(J = 8.8\) Hz, 1H), 7.94 (d, \(J = 7.6\) Hz, 2H), 7.85-7.35 (m, 1H), 7.70 (d, \(J = 8.0\) Hz, 1H), 7.54-7.38 (m, 8H), 7.35-7.31 (m, 1H), 7.24-7.21 (m, 1H), 7.19-7.15 (m, 1H), 6.99 (t, \(J = 7.2\) Hz, 1H), 5.94 (t, \(J = 6.8\) Hz, 1H), 3.88 (ddd, \(J = 7.6, 21.4, 61.8\) Hz, 2H), 3.62 (s, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.3, 140.0, 137.3, 137.0, 134.0, 133.0, 131.4, 128.8, 128.5, 128.0, 127.0, 126.9, 126.1, 125.4, 125.3, 124.2, 123.6, 121.6, 119.5, 118.8, 117.5, 109.2, 44.9, 33.0, 32.6 ppm. ESI HRMS: calcd. for C_{28}H_{23}NO+Na 412.1677, found 412.1675.

3-(1-Methyl-1H-indol-3-yl)-1-phenyl-3-thiophen-2-yl-propan-1-one (3ai). 18 h, 60% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.96 (d, \(J = 7.6\) Hz, 2H), 7.59-7.54 (m, 2H), 7.47-7.43 (m, 2H), 7.31-7.21 (m, 2H), 7.12-7.07 (m, 2H), 6.96-6.95 (m, 2H), 6.91-6.89 (m, 1H), 5.39 (t, \(J = 7.2\) Hz, 1H), 3.86 (ddd, \(J = 7.6, 17.6, 21.2\) Hz, 2H), 3.73 (s, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 197.9, 148.9, 137.2, 136.9, 133.0, 128.5, 128.0, 126.5, 126.3, 124.1, 123.3, 121.7, 119.5, 118.9, 117.4, 109.3, 46.2, 33.3, 32.7 ppm. ESI HRMS: calcd. for C_{22}H_{19}NOS+Na 368.1085, found 368.1093.

3-(1-Methyl-1H-indol-3-yl)-1-phenyl-butan-1-one (3aj). 10 h, 60% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (d, \(J = 7.2\) Hz, 2H), 7.67-7.65 (m, 1H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.29-7.27 (m, 1H), 7.24-7.20 (m, 1H), 7.12-7.08 (m, 1H), 6.88 (s, 1H), 3.81 (m, 1H), 3.73 (s, 3H), 3.34 (ddd, \(J = 5.2, 18.8, 89.4\) Hz, 2H), 1.43 (d, \(J = 6.8\) Hz, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.7, 137.3, 137.2, 132.9, 128.5, 128.1, 126.6, 125.0, 121.5, 120.0, 119.3, 118.6, 109.3, 46.6, 32.6, 29.7, 27.0, 21.1 ppm. ESI HRMS: calcd. for C_{19}H_{19}NO+Na 300.1364, found 300.1366.

3-(1-Methyl-1H-indol-3-yl)-1-naphthalen-2-yl-3-phenyl-propan-1-one (3ak). 12 h, 96% yield; \(^1\)H NMR (400 MHz, DMSO): \(\delta\) 8.79 (s, 1H), 8.13 (d, \(J = 7.6\) Hz, 1H), 7.97-7.95 (m, 3H), 7.68-7.60 (m, 2H), 7.49-7.43 (m, 3H), 7.35-7.33 (m, 2H), 7.25-7.21 (m, 2H), 7.11-7.08 (m, 2H), 6.96-6.92 (m, 1H), 4.94 (t, \(J = 7.2\) Hz, 1H), 4.01 (ddd, \(J = 7.2, 20.8, 32.8\) Hz, 2H), 3.71 (s, 3H) ppm; \(^13\)C NMR (100 MHz, DMSO): \(\delta\) 198.3, 145.4, 136.9, 135.2, 134.3, 132.4, 130.3, 129.8, 128.8, 128.4, 128.3, 128.0, 127.8, 127.1, 126.9, 126.5, 126.1, 123.8, 121.4, 119.2, 118.6, 117.7,
109.8, 44.5, 37.7, 32.5 ppm. ESI HRMS: calcd. for C_{28}H_{23}NO Na 412.1677, found 412.1667.

1-Furan-2-yl-3-(1-methyl-1H-indol-3-yl)-3-phenyl-propan-1-one (3al). 10 h, 96% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.52 (s, 1H), 7.45-7.43 (m, 1H), 7.36-7.34 (m, 2H), 7.26-7.23 (m, 3H), 7.18-7.12 (m, 2H), 7.11-7.10 (m, 1H), 7.02-6.98 (m, 1H), 6.87 (s, 1H), 6.46-6.45 (m, 1H), 5.03 (t, \(J = 7.6\) Hz, 1H), 3.70 (s, 3H), 3.63 (ddd, \(J = 7.6, 19.6, 28.4\) Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 187.6, 152.9, 146.2, 144.1, 137.2, 128.3, 127.8, 126.9, 126.2, 121.6, 119.6, 118.8, 117.4, 117.0, 112.2, 109.1, 45.0, 38.1, 32.6 ppm. ESI HRMS: calcd. for C\(_{22}\)H\(_{19}\)NO\(_2\)Na 352.1313, found 352.1307.

4-(1-Methyl-1H-indol-3-yl)-4-phenyl-butan-2-one (3am). 8 h, 55% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.48-7.46 (m, 1H), 7.36-7.34 (m, 2H), 7.32-7.26 (m, 3H), 7.23-7.18 (m, 2H), 7.07-7.03 (m, 1H), 6.86 (s, 1H), 4.86 (t, \(J = 7.6\) Hz, 1H), 3.74 (s, 3H), 3.23 (ddd, \(J = 7.2, 19.6, 32\) Hz, 2H), 2.10 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 207.6, 144.1, 137.2, 128.4, 127.6, 126.8, 126.3, 126.1, 121.7, 119.4, 118.8, 117.2, 109.2, 50.4, 38.3, 32.6, 30.3 ppm. ESI HRMS: calcd. for C\(_{19}\)H\(_{19}\)NO Na 300.1364, found 300.1360.

5-(1-Methyl-1H-indol-3-yl)-1,5-diphenyl-pent-1-en-3-one (3an). 8 h, 70% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.56 (s, 1H), 7.52-7.48 (m, 3H), 7.42-7.40 (m, 5H), 7.33-7.28 (m, 3H), 7.26-7.19 (m, 2H), 7.09-7.05 (m, 1H), 6.91 (s, 1H), 6.76-6.72 (m, 1H), 5.02 (t, \(J = 7.2\) Hz, 1H), 3.74 (s, 3H), 3.50 (ddd, \(J = 6.8, 19.2, 37.2\) Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.6, 144.2, 142.6, 137.2, 134.4, 130.4, 128.8, 128.4, 128.2, 127.7, 126.9, 126.2, 126.1, 121.6, 119.6, 118.8, 117.5, 109.2, 47.5, 38.4, 32.6 ppm. ESI HRMS: calcd. for C\(_{26}\)H\(_{23}\)NO Na 388.1677, found 388.1676.

2-(1-Methyl-1H-indol-3-yl)-1,4-diphenyl-butane-1,4-dione (3ao). 6 h, 98% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.07-8.05 (m, 2H), 7.98-7.96 (m, 2H), 7.78-7.76 (m, 1H), 7.54-7.50 (m, 1H), 7.46-7.39 (m, 3H), 7.37-7.33 (m, 2H), 7.28-7.22 (m, 2H), 7.18-7.15 (m, 1H), 6.88 (s, 1H), 5.59 (dd, \(J = 3.6, 10.4\) Hz, 1H), 4.24 (dd, \(J = 10.4, 18.4\) Hz, 1H), 3.42 (dd, \(J = 3.2, 18\) Hz, 1H), 3.66 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.1, 198.6, 137.1, 136.5, 136.4, 133.1, 132.6, 128.7, 128.5, 128.4, 128.1, 127.4, 126.4, 122.0, 119.5, 118.7, 111.4, 109.5, 43.1, 39.4, 32.7 ppm. ESI HRMS: calcd. for C\(_{25}\)H\(_{21}\)NO\(_2\) Na 390.1470, found 390.1465.
1-(1-Methyl-1H-indol-3-yl)-pentan-3-one (3ap). 8 h, 75% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (d, $J = 8.0$ Hz, 1H), 7.28-7.19 (m, 2H), 7.12-7.08 (m, 1H), 6.82 (s, 1H), 3.70 (s, 3H), 3.03 (t, $J = 7.6$ Hz, 2H), 2.79 (t, $J = 7.6$ Hz, 2H), 2.39 (q, $J = 7.2$ Hz, 2H), 1.03 (t, $J = 7.2$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 211.3, 136.9, 127.5, 126.3, 121.5, 118.7, 118.6, 113.7, 109.1, 42.9, 35.9, 32.5, 19.2, 7.7 ppm. ESI HRMS: calcd. for C$_{14}$H$_{17}$NO+Na 238.1208, found 238.1210.

4-(1-Methyl-1H-indol-3-yl)-pentan-2-one (3aq). 8 h, 71% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.64-7.62 (m, 1H), 7.29-7.27 (m, 1H), 7.24-7.20 (m, 1H), 7.12-7.09 (m, 1H), 6.82 (s, 1H), 3.72 (s, 3H), 3.65-3.60 (m, 1H), 2.81 (ddd, $J = 6.0, 19, 86.6$ Hz, 2H), 2.09 (s, 3H), 1.37 (d, $J = 6.8$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 208.6, 137.1, 126.5, 124.9, 121.5, 119.4, 119.1, 118.6, 109.3, 51.6, 32.5, 30.3, 26.9, 21.4 ppm. ESI HRMS: calcd. for C$_{14}$H$_{17}$NO+Na 238.1208, found 238.1205.

4-Methyl-3-(1-methyl-1H-indol-3-yl)-phenol (3ar). 12 h, 42% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.69 (d, $J = 8.0$ Hz, 1H), 7.52-7.50 (m, 1H), 7.43-7.38 (m, 1H), 7.32-7.26 (m, 2H), 7.16 (s, 1H), 7.05-7.04 (m, 1H), 6.89-6.86 (m, 1H), 5.23 (s, 1H), 3.93 (s, 3H), 2.20 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.3, 136.6, 135.6, 131.3, 128.6, 127.6, 127.3, 121.7, 120.2, 119.4, 117.4, 115.6, 113.4, 109.3, 32.8, 19.8 ppm. ESI HRMS: calcd. for C$_{16}$H$_{15}$NO+Na 260.1051, found 260.1048.

3-(1H-Indol-3-yl)-cyclohexanone (3as). 4 h, 33% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63 (d, $J = 7.6$ Hz, 1H), 7.32-7.30 (m, 1H), 7.27-7.23 (m, 1H), 7.14-7.11 (m, 1H), 6.84 (s, 1H), 3.76 (s, 3H), 3.49-3.44 (m, 1H), 2.82-2.81 (m, 1H), 2.66-2.60 (m, 1H), 2.50-2.37 (m, 2H), 2.27-2.24 (m, 1H), 2.09-2.02 (m, 1H), 1.99-1.93 (m, 1H), 1.88-1.82 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 211.8, 170.6, 137.0, 126.4, 125.2, 121.7, 119.0, 118.0, 118.1, 109.3, 48.1, 41.5, 35.8, 32.6, 31.8, 24.8 ppm. ESI HRMS: calcd. for C$_{15}$H$_{17}$NO+Na 250.1208, found 250.1196.

3-(1-methyl-1H-indol-3-yl)cyclopentanone (3at). 4 h, 66% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.57 (d, $J = 8.0$ Hz, 1H), 7.28-7.26 (m, 1H), 7.22-7.19 (m, 1H), 7.10-7.06 (m, 1H), 6.78 (s, 1H), 3.70 (s, 3H), 3.66-3.64 (m, 1H), 2.73-2.66 (m, 1H), 2.49-2.44 (m, 1H), 2.43-2.34 (m, 2H), 2.31-2.22 (m, 1H), 2.12-2.04 (m, 1H) ppm; $^{13}$C NMR (75 MHz, DMSO): $\delta$ 218.3, 136.9, 126.8, 125.6, 121.2, 118.9, 118.4, 116.5, 109.7, 44.9, 37.9, 33.1, 32.3, 29.7 ppm. ESI HRMS: calcd. For C$_{14}$H$_{15}$NO+Na 236.1051, found 236.1042.
3-(4-Bromo-1-methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3ba). 10 h, 70% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.96 (d, $J$ = 7.6 Hz, 2H), 7.56-7.53 (m, 1H), 7.46-7.42 (m, 2H), 7.39-7.37 (m, 2H), 7.32-7.25 (m, 3H), 7.22-7.20 (m, 2H), 7.05-7.00 (m, 1H), 6.74 (s, 1H), 5.82 (t, $J$ = 7.2 Hz, 1H), 3.82 (ddd, $J$ = 5.6, 20.4, 27.2 Hz, 2H), 3.67 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.9, 144.3, 138.5, 137.0, 132.9, 128.5, 128.3, 128.1, 128.0, 126.1, 124.8, 123.8, 122.4, 118.8, 114.3, 108.5, 46.7, 36.9, 32.9 ppm. ESI HRMS: calcd. for C$_{24}$H$_{20}$BrNO+Na 440.0626, found C$_{24}$H$_{20}$BrNO 440.0620, C$_{24}$H$_{20}$BrNO 442.0612.

3-(1,4-Dimethyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3ca). 8 h, 79% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J$ = 8.0 Hz, 2H), 7.59-7.55 (m, 1H), 7.48-7.45 (m, 2H), 7.31-7.25 (m, 4H), 7.19-7.14 (m, 1H), 7.12-7.08 (m, 2H), 6.86 (s, 1H), 6.79 (d, $J$ = 6.4 Hz, 1H), 5.45 (t, $J$ = 7.2 Hz, 1H), 3.74 (ddd, $J$ = 6.8, 24.6, 33 Hz, 2H), 3.72 (s, 3H), 2.57 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.2, 145.4, 137.6, 137.1, 133.0, 131.2, 128.6, 128.4, 128.0, 127.9, 126.5, 126.1, 125.8, 121.7, 120.8, 118.1, 107.0, 47.1, 38.6, 32.8, 20.7 ppm. ESI HRMS: calcd. for C$_{25}$H$_{23}$NO+Na 376.1677, found 376.1680.

3-(5-Methoxy-1-methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3da). 8 h, 96% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J$ = 7.6 Hz, 2H), 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 7.41-7.39 (m, 2H), 7.31-7.26 (m, 2H), 7.21-7.15 (m, 2H), 6.89-6.83 (m, 3H), 5.05 (t, $J$ = 7.2 Hz, 1H), 3.81 (ddd, $J$ = 6.8, 20.2, 29.2 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.5, 153.5, 144.3, 137.0, 132.9, 132.6, 128.5, 128.4, 128.0, 127.7, 127.2, 126.7, 126.2, 117.2, 111.7, 109.9, 101.4, 55.8, 45.2, 37.9, 32.8 ppm. ESI HRMS: calcd. for C$_{25}$H$_{23}$NO$_2$+Na 392.1626, found 392.1632.

3-(5-Bromo-1-methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3ea). 8 h, 80% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.91 (d, $J$ = 7.6 Hz, 2H), 7.54-7.50 (m, 2H), 7.43-7.39 (m, 2H), 7.33-7.31 (m, 2H), 7.27-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.08-7.05 (m, 1H), 6.83 (s, 1H), 4.98 (t, $J$ = 7.6 Hz, 1H), 3.72 (ddd, $J$ = 7.2, 20.4, 27.6 Hz, 2H), 3.63 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.1, 143.9, 136.9, 135.9, 133.0, 128.5, 128.4, 128.0, 127.6, 127.3, 126.4, 124.4, 121.9, 117.3, 112.2, 110.7, 45.2, 37.8, 32.8 ppm. ESI HRMS: calcd. for C$_{24}$H$_{20}$BrNO+Na 440.0626 found C$_{24}$H$_{20}$BrNO 440.0626, C$_{24}$H$_{20}$BrNO 442.0608.
3-(6-Methoxy-1-methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3fa). 8 h, 86% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 (d, $J = 7.2$ Hz, 2H), 7.53-7.49 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.33 (m, 2H), 7.28-7.22 (m, 3H), 7.16-7.12 (m, 1H), 6.71-6.65 (m, 3H), 5.00 (t, $J = 7.2$ Hz, 1H), 3.82 (s, 3H), 3.74 (ddd, $J = 6.8$, 20.2, 27.4 Hz, 2H), 3.62 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.5, 156.3, 144.4, 138.0, 137.0, 132.9, 128.5, 128.4, 128.0, 127.7, 126.2, 125.0, 121.4, 120.2, 117.7, 108.6, 92.73, 55.60, 45.3, 38.1, 32.6 ppm. ESI HRMS: calcd. for C$_{25}$H$_{23}$NO$_2$+Na 392.1626 found 392.1621.

3-(7-Methoxy-1-methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3ga). 8 h, 91% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 7.2$ Hz, 2H), 7.49-7.45 (m, 2H), 7.37-7.34 (m, 4H), 7.24-7.19 (m, 3H), 7.14-7.07 (m, 2H), 7.00-6.96 (m, 1H), 5.12 (t, $J = 7.2$ Hz, 1H), 3.93 (ddd, $J = 7.6$, 17.2, 20 Hz, 2H), 3.58 (s, 3H), 2.41 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 199.0, 144.4, 137.1, 136.8, 133.6, 132.8, 128.4, 128.2, 128.0, 127.5, 126.4, 125.8, 120.2, 119.1, 118.7, 112.9, 108.7, 43.7, 37.0, 29.4, 10.5 ppm. ESI HRMS: calcd. for C$_{25}$H$_{23}$NO$_2$+Na 392.1626 found 392.1619.

1,3-diphenyl-3-(1-phenyl-1H-indol-3-yl)propan-1-one (3ha). 20 h, 60% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (d, $J = 7.6$ Hz, 2H), 7.58-7.48 (m, 4H), 7.53-7.44 (m, 8H), 7.37-7.30 (m, 3H), 7.26-7.20 (m, 3H), 7.13-7.09 (m, 1H), 5.18 (t, $J = 7.2$ Hz, 1H), 3.86 (ddd, $J = 6.4$, 20.4, 22.8 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.3, 143.9, 139.7, 137.0, 136.3, 132.9, 129.5, 128.5, 128.4, 128.0, 127.8, 126.4, 126.2, 125.2, 124.1, 122.6, 120.3, 120.0, 119.8, 110.5, 45.1, 38.0 ppm. ESI HRMS: calcd. for C$_{29}$H$_{23}$NO+Na 424.1677, found 424.1674.

3-(1-Methyl-2-phenyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (3ia). 14 h, 73% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.86 (d, $J = 7.6$ Hz, 2H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.54-7.48 (m, 4H), 7.41-7.36 (m, 7H), 7.30-7.25 (m, 3H), 7.20-7.14 (m, 2H), 5.07 (t, $J = 7.2$ Hz, 1H), 3.92 (ddd, $J = 7.2$, 15.6, 20.4 Hz, 2H), 3.56 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.4, 144.6, 138.3, 137.3, 136.8, 132.7, 131.8, 130.8, 128.3, 128.2, 128.0, 127.5, 126.4, 125.7, 121.4, 120.1, 119.2, 114.6, 109.5, 44.2, 37.5, 30.6 ppm. ESI HRMS: calcd. for C$_{30}$H$_{25}$NO+Na 438.1834 found 438.1833.

3-(1H-Indol-3-yl)-1,3-diphenyl-propan-1-one (5aa). 12 h, 90% yield; $^1$H NMR (400 MHz, DMSO): $\delta$ 10.9 (s, 1H), 8.03 (d, $J = 7.2$ Hz, 2H), 7.63-7.61 (m, 1H), 7.54-7.50 (m, 2H), 7.46-7.42 (m, 3H), 7.38-7.33 (m, 2H), 7.26-7.22 (m, 2H), 7.13-7.12 (m, 1H), 7.06-7.03 (m,
1H), 6.93-6.90 (m, 1H), 4.90 (t, \( J = 6.4 \) Hz, 1H), 3.90 (ddd, \( J = 6.8, 20, 40.8 \) Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, DMSO): \( \delta \) 214.7, 198.6, 145.5, 137.1, 136.6, 133.3, 128.9, 128.3, 128.0, 126.6, 126.0, 122.1, 121.2, 118.9, 118.5, 118.2, 111.6, 44.5, 37.9 ppm. ESI HRMS: calcd. for C\(_{23}\)H\(_{19}\)NO+Na 348.1364, found 348.1365.

3-(2-Chloro-phenyl)-3-(1H-indol-3-yl)-1-phenyl-propan-1-one (5ab). 12 h, 93% yield; \(^{1}\)H NMR (400 MHz, DMSO): \( \delta \) 10.93 (s, 1H), 8.03 (d, \( J = 7.2 \) Hz, 2H), 7.65-7.62 (m, 1H), 7.54-7.50 (m, 2H), 7.46-7.42 (m, 3H), 7.34-7.30 (m, 2H), 7.23-7.15 (m, 2H), 7.07-7.03 (m, 1H), 6.94-6.91 (m, 1H), 5.38 (t, \( J = 7.2 \) Hz, 1H), 4.02 (dd, \( J = 7.2, 16.8 \) Hz, 1H), 3.72 (dd, \( J = 6.4, 17.6 \) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, DMSO): \( \delta \) 203.1, 147.4, 141.8, 141.4, 138.3, 137.7, 134.5, 134.4, 133.8, 133.2, 132.7, 132.3, 131.5, 127.8, 127.7, 126.3, 123.6, 121.8, 116.6, 48.8, 39.9 ppm. ESI HRMS: calcd. for C\(_{23}\)H\(_{18}\)ClNO+Na 382.0975, found C\(_{23}\)H\(_{18}\)\(_{35}\)ClNNaO 382.0967, C\(_{23}\)H\(_{18}\)\(_{37}\)ClNNaO 384.0947.

3-(3-Chloro-phenyl)-3-(1H-indol-3-yl)-1-phenyl-propan-1-one (5ac). 12 h, 90% yield; \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.08 (s, 1H), 7.95 (d, \( J = 7.6 \) Hz, 2H), 7.58-7.55 (m, 1H), 7.47-7.43 (m, 3H), 7.35-7.30 (m, 2H), 7.28-7.26 (m, 1H), 7.21-7.14 (m, 3H), 7.08-7.04 (m, 1H), 6.95-6.94 (m, 1H), 5.07 (t, \( J = 7.2 \) Hz, 1H), 3.77 (ddd, \( J = 6.4, 20.4, 44.4 \) Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 198.2, 146.4, 136.8, 136.5, 134.1, 133.2, 129.6, 128.6, 128.0, 127.9, 126.5, 126.1, 122.2, 121.4, 119.5, 119.2, 118.4, 111.2, 44.8, 37.8 ppm. ESI HRMS: calcd. for C\(_{23}\)H\(_{18}\)ClNO+Na 382.0975, found C\(_{23}\)H\(_{18}\)\(_{35}\)ClNNaO 382.0967, C\(_{23}\)H\(_{18}\)\(_{37}\)ClNNaO 384.0947.

3-(4-chlorophenyl)-3-(1H-indol-3-yl)-1-phenylpropan-1-one (5ad). 12 h, 87% yield; \(^{1}\)H NMR (400 MHz, DMSO): \( \delta \) 10.91 (s, 1H), 8.02 (d, \( J = 7.6 \) Hz, 2H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 2H), 7.44-7.42 (m, 3H), 7.38 (s, 1H), 7.33-7.31 (m, 1H), 7.28-7.26 (m, 2H), 7.04 (t, \( J = 7.2 \) Hz, 1H), 6.90 (t, \( J = 7.6 \) Hz, 1H), 4.89 (t, \( J = 7.2 \) Hz, 1H), 3.89 (ddd, \( J = 6.8, 20.8, 35.2 \) Hz, 2H) ppm; \(^{13}\)C NMR (100 MHz, DMSO): \( \delta \) 198.4, 144.5, 137.0, 136.6, 133.4, 130.5, 129.9, 128.9, 128.3, 128.2, 126.4, 122.2, 121.3, 118.8, 118.6, 117.8, 111.6, 44.2, 37.2 ppm. ESI HRMS: calcd. for C\(_{23}\)H\(_{18}\)ClNO+Na 382.0975, found C\(_{23}\)H\(_{18}\)\(_{35}\)ClNNaO 382.0967, C\(_{23}\)H\(_{18}\)\(_{37}\)ClNNaO 384.0940.

3-(4-Bromo-phenyl)-3-(1H-indol-3-yl)-1-phenyl-propan-1-one (5ae). 14 h, 90% yield; \(^{1}\)H NMR (400 MHz, DMSO): \( \delta \) 10.91 (s, 1H), 8.02-8.00 (m , 2H), 7.63-7.60 (m, 1H), 7.52-7.48 (m, 2H), 7.44-7.42 (m, 3H), 7.38 (s, 1H), 7.33-7.31 (m, 1H), 7.28-7.26 (m, 2H), 7.03 (t, \( J = 7.2 \) Hz, 1H), 6.90 (t, \( J = 7.2\)Hz, 1H), 4.87 ppm; \(^{13}\)C NMR (100 MHz, DMSO): \( \delta \) 214.7, 198.6, 145.5, 137.1, 136.6, 133.3, 128.9, 128.3, 128.0, 126.6, 126.0, 122.1, 121.2, 118.9, 118.5, 118.2, 111.6, 44.5, 37.9 ppm. ESI HRMS: calcd. for C\(_{23}\)H\(_{19}\)NO+Na 348.1364, found 348.1365.
(t, J = 5.6 Hz, 1H), 3.88 (ddd, J = 6.4, 20.4, 33.6 Hz, 2H) ppm; \(^{13}C\) NMR (100 MHz, DMSO): \(\delta\) 198.4, 145.0, 137.0, 136.6, 133.4, 131.1, 130.3, 128.9, 128.3, 126.4, 122.2, 121.3, 119.0, 118.8, 118.6, 117.8, 111.6, 44.2, 37.2 ppm. ESI HRMS: calcd. for C\(_{23}\)H\(_{18}\)BrNO+Na 426.0469, found C\(_{23}\)H\(_{18}\)BrNNaO 426.0483, C\(_{23}\)H\(_{18}\)BrNNaO 428.3361.

3-(1H-indol-3-yl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (5af). 26 h, 63% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.00 (s, 1H), 7.91 (d, J = 7.6 Hz, 2H), 7.51-7.49 (m, 1H), 7.42-7.48 (m, 3H), 7.27-7.22 (m, 3H), 7.13-7.09 (m, 1H), 7.01-6.98 (m, 1H), 6.90 (s, 1H), 6.77 (d, J = 8.4 Hz, 2H), 5.00 (t, J = 7.2 Hz, 1H), 3.71 (ddd, J = 6.4, 20, 30 Hz, 2H), 3.70 (s, 3H) ppm; \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.8, 157.8, 137.0, 136.6, 133.0, 128.7, 128.5, 128.0, 126.5, 122.0, 121.3, 119.5, 119.4, 119.2, 113.7, 111.1, 55.1, 45.3, 37.4 ppm. ESI HRMS: calcd. for C\(_{24}\)H\(_{21}\)NO\(_2\)+Na 378.1470, found 378.1466.

3-(1H-indol-3-yl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (5ag). 26 h, 70% yield; \(^1\)H NMR (400 MHz, DMSO): \(\delta\) 10.96 (s, 1H), 8.04 (d, J = 7.6 Hz, 2H), 7.67-7.65 (m, 3H), 7.62-7.58 (m, 2H), 7.54-7.50 (m, 2H), 7.54-7.50 (m, 2H), 7.48-7.43 (m, 2H), 7.34-7.32 (m, 1H), 7.06-7.03 (m, 1H), 6.94-6.90 (m, 1H), 4.99 (s, 1H), 3.97 (ddd, J = 6.8, 21.2, 24.4 Hz, 2H) ppm; \(^{13}C\) NMR (100 MHz, DMSO): \(\delta\) 198.3, 150.4, 136.9, 136.5, 133.4, 128.9, 128.8, 128.3, 126.4, 125.2, 125.2, 122.4, 121.3, 118.7, 118.7, 117.4, 111.6, 44.0, 37.6 ppm. ESI HRMS: calcd. for C\(_{24}\)H\(_{18}\)F\(_3\)NO+Na 416.1238, found 416.1240.

3-(1H-indol-3-yl)-3-naphthalen-1-yl-1-phenyl-propan-1-one (5ah). 12 h, 87% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.35-8.33 (m, 1H), 7.97-7.95 (m, 2H), 7.90-7.87 (m, 2H), 7.75-7.73 (m, 1H), 7.58-7.54 (m, 1H), 7.50-7.44 (m, 5H), 7.42-7.33 (m, 2H), 7.29-7.26 (m, 1H), 7.17-7.14 (m, 1H), 7.04-7.00 (m, 1H), 6.77-6.76 (m, 1H), 5.97 (t, J = 6.8 Hz, 1H), 3.89 (ddd, J = 8.0, 21.2, 77.2 Hz, 2H) ppm; \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 198.5, 139.9, 137.0, 136.6, 134.0, 133.1, 131.4, 128.8, 128.6, 128.0, 127.0, 126.6, 126.1, 125.5, 125.3, 124.3, 123.6, 122.2, 122.0, 119.4, 119.3, 118.9, 111.1, 44.6, 33.2 ppm. ESI HRMS: calcd. for C\(_{27}\)H\(_{21}\)NO+Na 398.1521, found 398.1530.

3-(1H-indol-3-yl)-1-phenyl-3-(thiophen-2-yl)propan-1-one (5ai). 48 h, 40% yield; \(^1\)H NMR (400 MHz, DMSO): \(\delta\) 10.92 (s, 1H), 8.02 (d, J = 7.2Hz, 2H), 7.64-7.60 (m, 1H), 7.51 (t, J = 7.2 Hz, 3H), 7.35-7.33 (m, 2H), 7.23-7.22 (m, 1H), 7.08-7.04 (m, 1H), 7.00-6.99 (m, 1H), 6.95 (t, J = 7.2 Hz, 1H), 6.88-6.86 (m, 1H), 5.20 (t, J = 7.2 Hz, 1H), 3.92 (d, J = 7.2 Hz, 2H) ppm; \(^{13}C\) NMR
(100 MHz, DMSO): $\delta$ 198.2, 149.9, 136.9, 136.6, 133.4, 128.9, 128.3, 126.7, 126.3, 124.1, 123.8, 122.4, 121.3, 118.9, 118.7, 117.9, 111.7, 45.4, 32.9 ppm. ESI HRMS: calcd. for C$_{21}$H$_{17}$NOS+Na 354.0929, found 354.0930.

$\text{3-(1H-Indol-3-yl)-1-naphthalen-2-yl-3-phenyl-propan-1-one (5ak).}$ 11 h, 80% yield; $^1$H NMR (400 MHz, DMSO): $\delta$ 10.89 (s, 1H), 8.81 (s, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 7.98-7.07 (m, 3H), 7.68-7.60 (m, 2H), 7.47-7.45 (m, 3H), 7.39 (m, 1H), 7.34-7.32 (m, 1H), 7.24 (t, $J = 7.2$ Hz, 2H), 7.11 (t, $J = 7.2$Hz, 1H), 7.06-7.02 (m, 1H), 6.93-6.89 (m, 1H), 4.97 (t, $J = 7.2$Hz, 1H), 4.02 (ddd, $J = 7.2$, 20.8, 66.8 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO): $\delta$ 198.5, 145.5, 136.6, 135.2, 134.4, 132.4, 130.3, 129.8, 128.8, 128.4, 128.3, 128.0, 127.8, 127.1, 126.6, 126.0, 123.8, 122.1, 121.2, 118.9, 118.5, 118.2, 111.6, 44.4, 38.0 ppm. ESI HRMS: calcd. for C$_{27}$H$_{21}$NO+Na 398.1521, found 398.1511.

$\text{3-(1H-Indol-3-yl)-1-naphthalen-2-yl-3-phenyl-propan-1-one (5ak).}$ 11 h, 80% yield; $^1$H NMR (400 MHz, DMSO): $\delta$ 10.89 (s, 1H), 8.81 (s, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 7.98-7.07 (m, 3H), 7.68-7.60 (m, 2H), 7.47-7.45 (m, 3H), 7.39 (m, 1H), 7.34-7.32 (m, 1H), 7.24 (t, $J = 7.2$ Hz, 2H), 7.11 (t, $J = 7.2$Hz, 1H), 7.06-7.02 (m, 1H), 6.93-6.89 (m, 1H), 4.97 (t, $J = 7.2$Hz, 1H), 4.02 (ddd, $J = 7.2$, 20.8, 66.8 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO): $\delta$ 198.5, 145.5, 136.6, 135.2, 134.4, 132.4, 130.3, 129.8, 128.8, 128.4, 128.3, 128.0, 127.8, 127.1, 126.6, 126.0, 123.8, 122.1, 121.2, 118.9, 118.5, 118.2, 111.6, 44.4, 38.0 ppm. ESI HRMS: calcd. for C$_{27}$H$_{21}$NO+Na 398.1521, found 398.1511.

$\text{1-Furan-2-yl-3-(1H-indol-3-yl)-3-phenyl-propan-1-one (5al).}$ 16 h, 73% yield; $^1$H NMR (400 MHz, DMSO): $\delta$ 10.88 (s, 1H), 7.95 (s, 1H), 7.60-7.59 (m, 1H), 7.43-7.38 (m, 3H), 7.33-7.30 (m, 2H), 7.24-7.20 (m, 2H), 7.12-7.08 (m, 1H), 7.04-7.00 (m, 1H), 6.91-6.88 (m, 1H), 6.69-6.68 (m, 1H), 4.85 (s, 1H), 3.64 (ddd, $J = 6.4$, 19.6, 60 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO): $\delta$ 186.9, 152.4, 148.1, 148.0, 145.1, 136.5, 128.4, 127.9, 126.5, 126.1, 122.1, 121.3, 119.3, 118.9, 118.6, 117.8, 112.7, 112.7, 111.6, 44.2, 38.0 ppm. ESI HRMS: calcd. for C$_{21}$H$_{17}$NO$_2$+Na 338.1157, found 338.1157.

$\text{5-(1H-Indol-3-yl)-1,5-diphenyl-pent-1-en-3-one (5an).}$ 12 h, 62% yield; $^1$H NMR (400 MHz, DMSO): $\delta$ 10.88 (s, 1H), 7.69-7.67 (m ,2H), 7.63 (s , 1H), 7.43-7.38 (m, 6H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 2H), 7.13-7.09 (m, 1H), 7.05-7.01 (m, 1H), 6.96 (s, 1H), 6.92-6.88 (m, 1H), 4.84 (t, $J = 7.6$ Hz, 1H), 3.52 (ddd, $J = 7.6$, 20, 66.4 Hz, 2H) ppm; $^{13}$C NMR (100 MHz, DMSO): $\delta$ 198.7, 145.4, 142.4, 136.6, 134.7, 130.6, 129.1, 128.6, 128.3, 127.9, 126.9, 126.6, 126.0, 122.1, 121.2, 118.9, 118.4, 118.0, 111.6, 46.5, 38.0 ppm. ESI HRMS: calcd. for C$_{25}$H$_{21}$NO+Na 374.1521, found 374.1514.

$\text{2-(1H-Indol-3-yl)-1,4-diphenyl-butane-1,4-dione (5ao).}$ 12 h, 99% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.27 (s, 1H), 8.04-8.02 (m, 2H), 7.95-7.93 (m, 2H), 7.77-7.75 (m, 1H), 7.53-7.49 (m, 1H), 7.43-7.37 (m, 3H), 7.32-7.27 (m, 2H), 7.22-7.14 (m, 2H), 6.92 (s, 1H), 5.58 (dd, $J = 3.2$, 10.4 Hz, 1H), 4.24 (dd, $J = 10.4$, 18.4 Hz, 1H) 3.40 (dd, $J = 3.6$, 18.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 199.2, 198.8, 136.4, 136.4, 133.2, 132.7, 128.7, 128.5, 128.4, 128.1, 125.9, 122.8, 122.4, 119.9, 118.6, 112.9, 111.5, 42.8, 39.6 ppm. ESI HRMS: calcd. for C$_{24}$H$_{19}$NO$_2$+Na 376.1313,
1-(1H-Indol-3-yl)-pentan-3-one (5ap). 12 h, 91% yield; \(^1\)H NMR (400 MHz, DMSO): \(\delta\) 10.77 (s, 1H), 7.53-7.51 (m, 1H), 7.35-7.33 (m, 1H), 7.09-7.05 (m, 2H), 6.99-6.96 (m, 1H), 2.90 (t, \(J = 7.2\) Hz, 2H), 2.80 (t, \(J = 7.2\) Hz, 2H), 2.45 (q, \(J = 7.2\) Hz, 2H), 0.93 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, DMSO): \(\delta\) 210.9, 136.5, 127.2, 122.4, 121.2, 118.5, 118.4, 113.8, 111.5, 42.4, 35.2, 19.3, 7.8 ppm. ESI HRMS: calcd. for C\(_{13}\)H\(_{15}\)NO+Na 224.1051, found 224.1044.

4-(1H-Indol-3-yl)-pentan-2-one (5aq). 12 h, 76% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.05 (s, 1H), 7.64 (d, \(J = 8.0\) Hz, 1H), 7.33-7.32 (m, 1H), 7.20-7.16 (m, 1H), 7.13-7.09 (m, 1H), 6.93 (s, 1H), 3.66-3.60 (m, 1H), 2.81 (ddd, \(J = 6.0, 18.8, 86.4\) Hz, 2H), 2.08 (s, 3H), 1.37 (d, \(J = 6.8\) Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 208.8, 136.4, 126.2, 121.9, 120.8, 120.1, 119.1, 119.0, 111.3, 51.4, 30.4, 26.9, 21.2 ppm. ESI HRMS: calcd. for C\(_{13}\)H\(_{15}\)NO+Na 224.1051, found 224.1042.

3-(1H-Indol-3-yl)-cyclohexanone (5as). 16 h, 41% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.18 (s, 1H), 7.66 (d, \(J = 8.0\) Hz, 1H), 7.39 (d, \(J = 8.0\) Hz, 1H), 7.27-7.22 (m, 1H), 7.18-7.14 (m, 1H), 6.98 (s, 1H), 3.51-3.44 (m, 1H), 2.86-2.81 (m, 1H), 2.69-2.63 (m, 1H), 2.53-2.39 (m, 2H), 2.31-2.27 (m, 1H), 2.11-1.95 (m, 2H), 1.91-1.81 (m, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 212.0, 136.4, 126.0, 122.1, 120.3, 119.5, 119.3, 118.9, 111.3, 48.0, 41.5, 35.9, 31.6, 24.8 ppm. ESI HRMS: calcd. for C\(_{14}\)H\(_{15}\)NO+Na 236.1051, found 236.1043.

3-(1H-Indol-3-yl)-cyclopentanone (5at). 16 h, 51% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.15 (s, 1H), 7.64-7.62 (m, 1H), 7.38-7.36 (m, 1H), 7.24-7.20 (m, 1H), 7.16-7.20 (m, 1H), 6.96-6.95 (m, 1H), 3.75-3.67 (m, 1H), 2.79-2.72 (m, 1H), 2.56-2.50 (m, 1H), 2.50-2.41 (m, 2H), 2.40-2.27 (m, 1H), 2.17-2.08 (m, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 219.6, 136.6, 126.5, 122.2, 119.9, 119.4, 119.0, 118.4, 111.3, 45.2, 38.1, 33.6, 29.8 ppm. ESI HRMS: calcd. for C\(_{13}\)H\(_{13}\)NO+Na 222.0895, found 222.0892.

3-(2-Methyl-1H-indol-3-yl)-1,3-diphenyl-propan-1-one (5ba). 16 h, 76% yield; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.86 (d, \(J = 7.2\) Hz, 2H), 7.75 (s, 1H), 7.50-7.46 (m, 2H), 7.38-7.34 (m, 4H), 7.25-7.18 (m, 3H), 7.15-7.11 (m, 1H), 7.06-7.03 (m, 1H), 7.00-6.96 (m, 1H), 5.08 (t, \(J = 6.8\) Hz, 1H), 3.92 (ddd, \(J = 7.6, 24.8, 26\) Hz, 2H), 2.36 (s, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 199.1, 144.2, 137.1, 135.4, 132.9, 131.7, 128.4, 128.2, 128.0, 127.5, 127.4, 125.8, 120.6, 119.1, 119.1, 113.5, 110.4,
1,3-Diphenyl-3-(1H-pyrazol-4-yl)-propan-1-one (5ca). 10 h, 30% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 7.6$ Hz, 2H), 7.57-7.49 (m, 3H), 7.45-7.42 (m, 2H), 7.33-7.32 (m, 4H), 7.30-7.25 (m, 1H), 6.23 (s, 1H), 5.2 (dd, $J = 5.2$, 8.4 Hz, 1H), 4.49 (q, $J = 8.8$ Hz, 1H) 3.64 (dd, $J = 4.8$, 17.6 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 196.6, 140.7, 139.2, 136.4, 133.3, 129.7, 128.8, 128.6, 128.2, 127.9, 126.6, 105.5, 60.7, 44.1 ppm. ESI HRMS: calcd. for C$_{24}$H$_{21}$NO$^+$$\text{Na}$ 362.1521, found 362.1508.

1,3-Diphenyl-3-(1H-pyrrol-2-yl)-1,3-diphenylpropan-1-one (7a). 8 h, 33% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J = 7.2$ Hz, 2H), 7.57-7.55 (m, 1H), 7.46-7.42 (m, 2H), 7.32-7.17 (m, 5H), 6.54 (s, 1H), 6.08 (s, 2H), 4.81 (t, $J = 7.2$ Hz, 1H), 3.80 (dd, $J = 7.2$, 17.2 Hz, 1H), 3.50 (dd, $J = 7.2$, 17.2 Hz, 1H), 3.38 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.8, 143.2, 137.0, 134.3, 133.0, 128.6, 128.5, 128.0, 127.9, 126.4, 121.9, 106.3, 105.6, 45.5, 38.2, 33.9 ppm. ESI HRMS: calcd. for C$_{20}$H$_{19}$NO$^+$$\text{Na}$ 312.1364, found 312.1365.

1,3-Diphenyl-3-(1H-pyrrol-3-yl)-1,3-diphenylpropan-1-one (7b). 8 h, 6% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.93 (d, $J = 7.6$ Hz, 2H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.32-7.30 (m, 3H), 7.28-7.26 (m, 1H), 7.18-7.14 (m, 1H), 6.48 (s, 1H), 6.32 (s, 1H), 5.97 (s, 1H), 4.69 (t, $J = 7.2$ Hz, 1H), 3.62 (ddd, $J = 6.4$, 20.4, 91.6 Hz, 4H), 3.05 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.9, 143.3, 137.1, 134.4, 132.9, 128.5, 128.4, 127.9, 127.8, 126.4, 104.2, 45.4, 38.6, 30.6 ppm. ESI HRMS: calcd. for C$_{20}$H$_{19}$NO$^+$$\text{Na}$ 312.1364, found 312.1364.

(3R,3'S)-3,3'-(1-methyl-1H-pyrrole-2,5-diyl)bis(1,3-diphenylpropan-1-one) (7c). 8 h, 16% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.90 (d, $J = 7.2$ Hz, 4H), 7.55-7.52 (m, 2H), 7.44-7.41 (m, 4H), 7.27-7.23 (m, 4H), 7.18-7.14 (m, 6H), 6.04 (s, 2H), 4.71 (t, $J = 7.2$ Hz, 2H), 3.61 (ddd, $J = 6.4$, 20.4, 91.6 Hz, 4H), 3.05 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.9, 143.3, 137.1, 134.4, 132.9, 128.5, 128.4, 127.9, 127.8, 126.4, 104.2, 45.4, 38.6, 30.6 ppm. ESI HRMS: calcd. for C$_{35}$H$_{31}$NO$_2$$^+$$\text{Na}$ 520.2252, found 520.2250.

(3R,3'R)-3,3'-(1-methyl-1H-pyrrole-2,5-diyl)bis(1,3-diphenylpropan-1-one) (7d). 8 h, 17% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92-7.90 (m, 4H), 7.55-7.52 (m, 2H), 7.44-7.41 (m, 4H), 7.26-7.15 (m, 4H), 7.11-7.09 (m, 6H), 6.00 (s, 2H), 4.75 (t, $J = 7.2$ Hz, 2H), 3.75 (dd, $J = 7.2$, 17.2 Hz, 2H), 3.43 (dd, $J = 7.2$, 17.2 Hz, 2H), 2.99 (s, 3H) ppm; $^{13}$C NMR
[75 MHz, DMSO]: \( \delta \) 197.8, 143.7, 136.7, 134.2, 133.2, 128.7, 128.2, 128.0, 127.7, 126.1, 104.2, 44.6, 37.9, 30.2 ppm. ESI HRMS: calcd. for C_{35}H_{31}NO_{2}^{+}Na 520.2252, found 520.2258.

### 3. Synthetic Applications and Characterization Data

**General Procedure for Synthesis of Compound 8a:**

1. **1b** (20.9 mg, 0.1 mmol) and **2p** (9.2 mg, 0.11 mmol) worked under standard conditions to produce **3bp** (60% yield). To the MeOH (1.5 mL) solution of **3bp** (17.6 mg, 0.06 mmol) at r.t. was added NaBH\(_4\) (2.3 mg, 0.06 mmol). The resulting mixture was further stirred at room temperature for 2 h, then quenched with water. The aqueous layer was extracted further with ethyl acetate three times; then the combined organic layer was washed with brine and dried over Na\(_2\)SO\(_4\). Then the organic layer was concentration in vacuo. In this step, **3bp** would convert to **3bp-a** completely.

2. To a mixture of **3bp-a** (17.7 mg, 0.06 mmol), K\(_2\)CO\(_3\) (16.6 mg, 0.12 mmol), KI (19.8 mg, 0.12 mmol) and CuI (2.9 mg, 0.015 mmol) in anhydrous dioxane (0.8 mL), in a dry flask under nitrogen atmosphere, was added TMEDA (3.5 mg, 0.03 mmol), and the reaction mixture was stirred at 140 °C for 48 h. Then the mixture quenched with water. The aqueous layer was extracted further with ethyl acetate three times; then the combined organic layer was washed with brine and dried over Na\(_2\)SO\(_4\), and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate: petroleum ether = 1: 200) to give compound **8a** (80% conversion) as white solid.\(^3\)

The general procedure for synthesis of compound **8b** was same as compound **8a**.
General Procedure for Synthesis of Compound 8c and 8d:

1b (20.9 mg, 0.1 mmol) and 2n (25.7 mg, 0.11 mmol) worked under standard conditions to produce 3bn (58% yield). To the DMF (1.0 mL) solution of 3bn (27 mg, 0.058 mmol) was added Pd(OAc)$_2$ (1.9 mg, 0.0087 mmol), PPh$_3$ (7.6 mg, 0.029 mmol), DIEA (15 mg, 0.116 mmol). The mixture was stirred at 100 °C under Ar atmosphere for 18 h. Then the mixture quenched with water. The aqueous layer was extracted further with ethyl acetate three times; then the combined organic layer was washed with brine and dried over Na$_2$SO$_4$, and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate: petroleum ether = 1: 50) to give compound 8c (57.3% yield) and 8d (28.7% yield) as yellow solid.[4]

2-ethyl-6-methyl-2,3,4,6-tetrahydrooxepino[4,3,2-cd]indole (8a). 48 h, 80% conversion; $^1$H NMR (300 MHz, DMSO): δ 7.00 (s, 1H), 6.99-6.89 (m, 2H), 6.45-6.42 (m, 1H), 3.96-3.92 (m, 1H), 3.68 (s, 3H), 3.03-2.98 (m, 1H), 2.75-2.74 (m, 1H), 2.15-2.10 (m, 1H), 1.86-1.69 (m, 3H), 1.05-0.99 (m, 3H) ppm; $^{13}$C NMR (75 MHz, DMSO): δ 152.0, 138.8, 124.6, 121.6, 117.4, 112.0, 105.0, 101.9, 83.7, 34.9, 32.4, 29.4, 24.6, 10.0 ppm. ESI HRMS: calcd. for C$_{14}$H$_{18}$NO+H 216.1388, found 216.1386.

6-methyl-2,4-diphenyl-2,3,4,6-tetrahydrooxepino[4,3,2-cd]indole (8b). 48 h, 72% conversion; $^1$H NMR (400 MHz, CDCl$_3$): δ 7.30-7.24 (m, 4H), 7.23-7.17 (m, 4H), 7.15-7.13 (m, 1H), 7.11-7.09 (m, 2H), 6.96-6.94 (m, 1H), 6.72-6.70 (m, 2H), 5.44 (d, $J = 7.2$ Hz, 1H), 4.72 (t, $J = 4.0$ Hz, 1H), 3.74 (s, 3H), 3.01 (ddd, $J = 4.4$, 9.8, 13 Hz, 1H), 2.60 (dd, $J = 4.0$, 14.8 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ 152.5, 146.7, 143.6, 139.2, 128.3, 126.9, 126.1, 125.4, 122.6, 118.2, 115.1, 106.3, 102.0, 78.8, 46.6, 40.6, 33.0 ppm. ESI HRMS: calcd. for C$_{24}$H$_{22}$NO+H 340.1701, found 340.1700.
(Z)-1-methyl-3,7-diphenyl-3,4-dihydrocycloocta[cd]indol-5(1H)-one (8c) & (E)-1-methyl-3,7-diphenyl-3,4-dihydrocycloocta[cd]indol-5(1H)-one (8d), (8c : 8d = 2 : 1). 18 h, 86% yield; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38-7.29 (m, 8H, 8c and 3H, 8d), 7.28-7.24 (m, 2H, 8c and 1H, 8d), 7.18-7.15 (m, 3H, 8c and 2H, 8d), 7.06-7.02 (m, 1H, 8c), 6.95-6.92 (m, 1H, 8d), 6.43 (s, 1H, 8c), 6.35 (s, 1H, 8d), 4.74-4.71 (m, 1H, 8d), 4.66 (d, J = 10.4 Hz, 1H, 8c), 3.74 (s, 3H, 8c), 3.69 (s, 2H, 8d), 3.56-3.48 (m, 2H, 8c), 3.26-3.20 (m, 1H, 8d) ppm. ESI HRMS (8c): calcd. for C$_{26}$H$_{21}$NO$^+$Na 386.1521, found 386.1521.

**Structure Determination**

The structure of compound 8c and compound 8d were determined by NOE.
irradiation of $\text{H}_a$ at 6.44 ppm
noe of $\text{H}_c$ at 7.34 ppm
noe of $\text{H}_d$ at 4.68 ppm

irradiation of $\text{H}_b$ at 6.35 ppm
noe of $\text{H}_e$ at 7.36 ppm
Reference


4. Mechanism Study

Deuterium-labeling experiments were carried out to study the mechanism of this alkylation reaction. 1a was stirred in the absence of alkynes for 2.5 h, then D$_2$O was added and stirred for 0.5 h. $^1$H NMR indicated the possibility of the reaction pathway via C-H activation.
5. NMR Spectra of 3-alkyl indole
noe of H_b at 6.55 ppm
noe of H_a at 4.82 ppm
noe of H_c at 6.55 ppm

irradiation of H_a at 3.38 ppm
Irradiation of H\textsubscript{a} at 3.04 ppm
defines the area

Noe of H\textsubscript{b} at 4.70 ppm

Noc of H\textsubscript{c} at 7.16 ppm