Co-catalysis between DABCO and Bronsted acid in the catalytic [4+2] annulation of isatin with but-3-yn-2-one and mechanistic investigation

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Content
1. General Remarks S2
2. General Procedure for the Formation of 3 S2
3. General Procedure for the Screening of Proton Sources S2
4. General Procedure for the Formation of 6a S2
5. General Procedure for the Isotopic Labeling Experiments S3
6. Spectroscopic Data of the Products S5
7. General Procedure and Spectroscopic Data of Compounds 9 and 10 S32
8. References S37
9. X-ray Crystal Data of 5a and 6a S38
General Remarks: 'H NMR spectra were recorded on an Agilent DD2 400-MR spectrometer for solution in CDCl$_3$ with tetramethylsilane (TMS) as the internal standard; $J$-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm$^{-1}$. THF, toluene and Et$_2$O were distilled from sodium (Na) under argon (Ar) atmosphere. CH$_3$CN, 1,2-dichloroethane and dichloromethane were distilled from CaH$_2$ under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General Procedure for the Formation of 3
To a solution of $N$-protected isatin 1 (0.2 mmol), catalyst (0.04 mmol) and 732 cation exchange resin (100 mg) in THF (2.0 mL) were added the but-3-yn-2-one 2a (0.3 mmol). The mixtures were stirred at room temperature for 4.0 h and the reaction was monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EtOAc = 3/1) to give product 3.

General Procedure for the Screening of Proton Sources
To a solution of $N$-protected isatin 1 (0.2 mmol), catalyst (0.04 mmol) and proton source (1.0 eq.) in THF (2.0 mL) were added the but-3-yn-2-one 2a (0.3 mmol). The mixtures were stirred at room temperature for 4.0 h and the reaction was monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EtOAc = 3/1) to give the corresponding products.

General Procedure for the Formation of 6a
To a solution of $N$-protected isatin 1a (0.2 mmol), catalyst (0.04 mmol) and acetic acid (1.0 eq.) in THF (2.0 mL) were added the hex-1-yn-3-one 2b (0.3 mmol). The mixtures were stirred at room temperature for 18 h and the reaction was monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography
General Procedure for the Isotopic Labeling Experiments

The formation of 7a: To a solution of but-3-yn-2-one 2a (5.0 mmol, 340 mg) in THF (20 mL), D$_2$O (5 mmol, 100 mg) and DABCO (0.5 mmol, 55 mg) were added. The reaction mixtures were stirred at room temperature for 15 min. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (PE/EtOAc = 10/1) to give product 7a in 29% yield.

The formation of 8a: To a solution of oct-1-yn-3-one 2c (0.4 mmol, 48 mg) in DCM (2 mL), D$_2$O (0.4 mmol, 8 mg) and DABCO (0.04 mmol, 5 mg) were added. The reaction mixtures were stirred at room temperature for 15 min. Then, the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (PE/EtOAc = 10/1) to give product 8a in 65% yield.

The formation of [D]-3a: To a solution of N-protected isatin 1a (0.2 mmol), D$_2$O (1.0 mmol) and catalyst (0.2 mmol) in THF (2.0 mL) were added but-3-yn-2-one 2a (0.3 mmol). The mixtures were stirred at room temperature for 0.5 h and the reaction was monitored by TLC. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EtOAc = 3/1) to give product [D]-3a in 78% yield.
The formation of [D]-2d: To a solution of 4-phenylbut-3-yn-2-one 2d (0.3 mmol) in THF (3.0 ml), D₂O (0.6 mmol) and DABCO (0.3 mmol) were added. The mixtures were stirred at room temperature for 1.0 h. Then the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (PE/EtOAc = 10/1) to give [D]-2d in 81% yield.
Spectroscopic data of the Products

**Compound 3a**: A known product.\(^{[1]}\) Yield: 52 mg, 85%. mp. 150-152 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) \(\delta 2.73\) (d, 1H, \(J = 16.8\) Hz), 3.24 (d, 1H, \(J = 16.8\) Hz), 4.87 (d, 1H, \(J = 15.6\) Hz), 4.93 (d, 1H, \(J = 15.6\) Hz), 5.65 (d, 1H, \(J = 6.0\) Hz), 6.76 (d, 1H, \(J = 8.0\) Hz), 7.01-7.05 (m, 1H), 7.26-7.36 (m, 6H), 7.42 (d, 1H, \(J = 6.0\) Hz), 7.49 (d, 1H, \(J = 8.0\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta 41.4, 43.9, 81.4, 107.0, 110.1, 123.6, 124.4, 127.2, 127.4, 128.0, 129.0, 131.2, 134.7, 142.1, 161.3, 172.1, 189.2; IR (CH\(_2\)Cl\(_2\)): \(\nu 2952, 2923, 2851, 1737, 1684, 1602, 1496, 1452, 1398, 1356, 1269, 1222, 1185, 1164, 1126, 1030, 778, 740, 630\) cm\(^{-1}\); MS (% (EI) \(m/z 305\) (M\(^+\), 30.3), 235 (40.0), 91 (100). HRMS (EI) Calcd. for C\(_{19}\)H\(_{15}\)NO\(_3\) requires 305.1052, Found: 305.1053.
Compound 3b: A known product.\textsuperscript{[1]} Yield: 53 mg, 78%. mp. 155-157 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) δ 2.63 (d, 1H, \(J = 17.2 \text{ Hz}\)), 3.78 (d, 1H, \(J = 17.2 \text{ Hz}\)), 4.82 (d, 1H, \(J = 15.6 \text{ Hz}\)), 4.86 (d, 1H, \(J = 15.6 \text{ Hz}\)), 5.62 (d, 1H, \(J = 6.4 \text{ Hz}\)), 6.65 (d, 1H, \(J = 8.0 \text{ Hz}\)), 7.05 (d, 1H, \(J = 8.0 \text{ Hz}\)), 7.20-7.29 (m, 3H), 7.32-7.36 (m, 3H), 7.41 (d, 1H, \(J = 6.4 \text{ Hz}\)); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) δ 38.4, 43.8, 81.2, 106.6, 108.4, 122.8, 124.3, 125.1, 127.2, 128.1, 129.0, 132.2, 134.4, 144.2, 160.6, 172.6, 188.9; IR (CH\textsubscript{2}Cl\textsubscript{2}): ν 2953, 2926, 2853, 1733, 1687, 1608, 1459, 1399, 1344, 1211, 1272, 1222, 1168, 1150, 1033, 990, 893, 873, 779, 736, 700 cm\textsuperscript{-1}; MS (\% (EI) m/z 339 (M\textsuperscript{+}, 0.3), 315 (1.9), 91 (100), 71 (16.2), 57 (35.5), 43 (38.4), 42 (10.5). HRMS (EI) Calcd. for C\textsubscript{19}H\textsubscript{14}NO\textsubscript{3}Cl requires 339.0662, Found: 339.0661.
Compound 3c: A known product.[1] Yield: 52 mg, 68%. mp. 159-163 °C; ¹H NMR (CDCl₃, 400 MHz, TMS) δ 2.55 (d, 1H, J = 17.2 Hz), 3.90 (d, 1H, J = 17.2 Hz), 4.80 (d, 1H, J = 16.0 Hz), 4.86 (d, 1H, J = 16.0 Hz), 5.61 (d, 1H, J = 6.4 Hz), 6.68-6.70 (m, 1H), 7.12-1.16 (m, 1H), 7.21-7.30 (m, 3H), 7.30-7.36 (m, 3H), 7.42 (d, 1H, J = 6.4 Hz); ¹³C NMR (CDCl₃, 100 MHz,
TMS) δ 38.2, 43.7, 81.7, 106.5, 109.0, 120.2, 124.3, 127.2, 127.7, 128.1, 129.0, 132.4, 134.4, 144.4, 160.7, 172.7, 188.9; IR (CH₂Cl₂): ν 2927, 2895, 2853, 1733, 1687, 1608, 1454, 1399, 1344, 1221, 1168, 1150, 1033, 990, 893, 873, 779, 736, 700 cm⁻¹; MS (%) (EI) m/z 383 (M⁺, 7.2), 313 (9.8), 91 (100). HRMS (EI) Calcd. for C₁₉H₁₄NO₃Br requires 383.0157, Found: 383.0161.
Compound 3d: A known product.\textsuperscript{[1]} Yield: 50 mg, 78%. mp. 153-157 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) \(\delta\) 2.72 (d, 1H, \(J = 16.8\) Hz), 3.26 (d, 1H, \(J = 16.8\) Hz), 4.87 (d, 1H, \(J = 15.6\) Hz), 4.92 (d, 1H, \(J = 15.6\) Hz), 5.66 (d, 1H, \(J = 6.4\) Hz), 6.62-6.69 (m, 1H), 6.95-7.01 (m, 1H), 7.23-7.30 (m, 3H), 7.30-7.37 (m, 3H), 7.43 (d, 1H, \(J = 6.4\) Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) \(\delta\) 41.3, 44.1, 81.2, 107.1, 110.8, 110.9 (d, \(J = 7.1\) Hz), 112.7 (d, \(J = 25.3\) Hz), 117.5 (d, \(J\) = 23.1 Hz), 127.1, 128.1, 128.46, 128.54, 129.0, 134.3, 137.9, 159.1 (d, \(J = 242\) Hz), 161.2, 171.9, 188.7; \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz, CFCl\textsubscript{3}) \(\delta\) -118.7; IR (CH\textsubscript{2}Cl\textsubscript{2}): \(\nu\) 2957, 2924, 2853, 1732, 1682, 1600, 1492, 1457, 1400, 1348, 1310, 1271, 1225, 1177, 1033, 876, 816, 757, 738, 701 cm\(^{-1}\); MS (%) (EI) \(m/z\) 323 (M\(^+\), 24.0), 253 (26.8), 91 (100). HRMS (EI) Calcd. for C\textsubscript{19}H\textsubscript{14}NO\textsubscript{3}F requires 323.0958, Found: 323.0960.
**Compound 3e**: A known product.[1] Yield: 48 mg, 75%. mp. 151-155 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) \(\delta\) 2.20 (s, 3H), 2.63 (d, 1H, \(J = 16.4\) Hz), 3.19 (d, 1H, \(J = 16.4\) Hz), 4.78 (d, 1H, \(J = 15.2\) Hz), 4.84 (d, 1H, \(J = 15.2\) Hz), 5.57 (d, 1H, \(J = 6.4\) Hz), 6.56 (d, 1H, \(J = 8.4\) Hz), 6.98-7.00 (m, 1H), 7.19-7.28 (m, 6H), 7.35 (d, 1H, \(J = 6.4\) Hz); \(^1\)C NMR (CDCl\(_3\), 100 MHz,
TMS) δ 21.0, 41.4, 43.9, 81.5, 106.9, 109.8, 125.1, 127.1, 127.4, 127.9, 128.9, 131.4, 133.4, 134.8, 139.6, 161.5, 172.1, 189.4; IR (CH₂Cl₂): ν 2957, 2926, 2856, 1730, 1681, 1600, 1496, 1457, 1376, 1267, 1183, 1097, 1031, 872, 811, 737, 701 cm⁻¹; MS (%) (EI) m/z 319 (M⁺, 28.4), 249 (43.9), 91 (100). HRMS (EI) Calcd. for C₂₀H₁₇NO₃ requires 319.1208, Found: 319.1209.
Compound 3f: A known product.\textsuperscript{[1]} Yield: 48 mg, 68\%. mp. 156-159 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) $\delta$ 2.73 (d, 1H, $J$ = 16.8 Hz), 3.25 (d, 1H, $J$ = 16.8 Hz), 4.86 (d, 1H, $J$ = 15.6 Hz), 4.92 (d, 1H, $J$ = 15.6 Hz), 5.67 (d, 1H, $J$ = 6.4 Hz), 6.67 (d, 1H, $J$ = 7.6 Hz), 7.24-7.27 (m, 3H), 7.30-7.33 (m, 3H), 7.35 (d, 1H, $J$ = 7.6 Hz), 7.48 (s, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) $\delta$ 41.4, 44.0, 81.1, 107.1, 111.2, 124.9, 127.1, 128.1, 128.7, 129.0, 129.1, 131.1, 134.2, 140.5, 161.2, 171.7, 188.6; IR (CH\textsubscript{2}Cl\textsubscript{2}): $\nu$ 2954, 2925, 2854, 1733, 1682, 1602, 1487, 1456, 1399, 1374, 1307, 1269, 1223, 1181, 1035, 817, 741, 702 cm$^{-1}$; MS (EI) m/z 339 (M$^+$, 14.0), 269 (18.6), 91 (100). HRMS (EI) Calcd. for C\textsubscript{19}H\textsubscript{14}NO\textsubscript{3}Cl requires 339.0662, Found: 339.0661.
Compound 3g: A known product.\textsuperscript{[1]} Yield: 49 mg, 64%. mp. 160-161 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) \(\delta\) 2.73 (d, 1H, \(J = 16.8\) Hz), 3.24 (d, 1H, \(J = 16.8\) Hz), 4.86 (d, 1H, \(J = 16.0\) Hz), 4.91 (d, 1H, \(J = 16.0\) Hz), 5.66 (d, 1H, \(J = 6.0\) Hz), 6.62 (d, 1H, \(J = 7.6\) Hz), 7.24-7.26 (m, 2H), 7.30-7.35 (m, 3H), 7.38-7.41 (m, 2H), 7.43 (d, 1H, \(J = 6.0\) Hz), 7.61 (s, 1H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) \(\delta\) 41.2, 44.0, 81.0, 107.2, 111.6, 116.2, 127.1, 127.5, 128.2, 129.0, 129.1, 134.0, 134.2, 141.0, 161.2, 171.6, 188.6; IR (CH\textsubscript{2}Cl\textsubscript{2}): v 2953, 2924, 2854, 1730, 1605, 1493, 1456, 1375, 1267, 1177, 1029, 742, 701 cm\textsuperscript{-1}; MS (%) (EI) \(m/z\) 383 (M\textsuperscript{+}, 9.1), 315 (11.8), 91 (100). HRMS (EI) Calcd. for C\textsubscript{19}H\textsubscript{14}NO\textsubscript{3}Br requires 383.0157, Found: 383.0154.
Compound 3h: A known product.\textsuperscript{[1]} Yield: 45 mg, 68\%. mp. 160-165 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) δ 2.21 (s, 3H), 2.25 (s, 3H), 2.77 (d, 1H, $J = 16.8$ Hz), 3.22 (d, 1H, $J = 16.8$ Hz), 5.10 (d, 1H, $J = 16.8$ Hz), 5.19 (d, 1H, $J = 15.6$ Hz), 5.63 (d, 1H, $J = 6.4$ Hz), 6.86 (s, 1H), 7.12-7.14 (m, 2H), 7.26-7.28 (m, 1H), 7.30 (s, 1H), 7.32-7.34 (m, 2H), 7.43 (d, 1H, $J = 6.4$ Hz);
$^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 18.6, 20.7, 41.7, 45.1, 80.9, 106.7, 120.6, 122.9, 125.5, 127.5, 128.3, 129.0, 133.5, 135.6, 136.5, 137.6, 161.4, 173.3, 189.4; IR (CH$_2$Cl$_2$): v 2954, 2927, 2853, 1737, 1684, 1602, 1496, 1452, 1398, 1356, 1269, 1222, 1185, 1164, 1126, 1030, 778, 740, 700 cm$^{-1}$; MS (ESI) m/z (%): 356.1 [M + Na]$^+$ (100); MS (ESI) Calcd. for C$_{21}$H$_{19}$NNaO$_3$ [M + Na]$^+$ requires 356.1257, Found: 356.1268.
**Compound 3i**: A known product.\(^2\) Yield: 45 mg, 66%. A light yellow oil. \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) \(\delta\) 2.71 (d, 1H, \(J = 16.8\) Hz), 3.23 (d, 1H, \(J = 16.8\) Hz), 4.85 (d, 1H, \(J = 16.0\) Hz), 4.91 (d, 1H, \(J = 16.0\) Hz), 5.65 (d, 1H, \(J = 6.4\) Hz), 6.75 (d, 1H, \(J = 1.6\) Hz), 7.01 (dd, 1H, \(J = 1.6\) Hz, \(J = 8.0\) Hz), 7.27-7.42 (m, 7H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 41.2, 44.1, 80.8, 107.1, 110.7, 123.5, 125.3, 125.7, 127.1, 128.2, 129.1, 134.2, 137.2, 143.4, 161.2, 172.1, 188.8; IR (CH\(_2\)Cl\(_2\)): \(\nu\) 2954, 2920, 2849, 1734, 1678, 1610, 1490, 1436, 1374, 1274, 1222, 1078, 1035, 763, 748, 703 cm\(^{-1}\); MS (%) (EI) \(m/z\) 339 (M\(^+\), 25.5), 269 (46.1), 91 (100). HRMS (EI) Calcd. for C\(_{19}\)H\(_{14}\)NO\(_3\)Cl requires 339.0662, Found: 339.0660.
Compound 3j: A known product.\textsuperscript{[1]} Yield: 50 mg, 65%. mp. 163-165 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) \(\delta\) 2.70 (d, 1H, \(J = 16.8\) Hz), 3.22 (d, 1H, \(J = 16.8\) Hz), 4.84 (d, 1H, \(J = 15.6\) Hz), 4.90 (d, 1H, \(J = 15.6\) Hz), 5.64 (d, 1H, \(J = 6.4\) Hz), 6.90 (s, 1H), 6.91-7.19 (m, 1H), 7.19-7.28 (m, 2H), 7.31-7.38 (m, 4H), 7.41 (d, 1H, \(J = 6.4\) Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) \(\delta\) 41.2, 44.0, 80.9, 107.1, 113.5, 125.1, 125.6, 126.2, 126.5, 127.1, 128.2, 129.1, 134.2, 143.5, 161.2, 171.9, 188.7; IR (CH\textsubscript{2}Cl\textsubscript{2}): \(\nu\) 2956, 2926, 2853, 1735, 1680, 1604, 1487, 1433, 1398, 1375, 1269, 1223, 1034, 1000, 815, 741, 702 cm\(^{-1}\); MS (\%) (EI) \(m/z\) 383 (M\(^+\), 8.7), 315 (13.7), 91 (100). HRMS (EI) Calcd. for C\textsubscript{19}H\textsubscript{14}NO\textsubscript{3}Br requires 383.0157, Found: 383.0153.
Compound 3k: A known product.\textsuperscript{[2]} Yield: 44 mg, 69%. A light yellow oil. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) δ 2.28 (s, 3H), 2.70 (d, 1H, J = 16.8 Hz), 3.23 (d, 1H, J = 16.8 Hz), 4.85 (d, 1H, J = 15.6 Hz), 4.91 (d, 1H, J = 15.6 Hz), 5.62 (d, 1H, J = 6.4 Hz), 6.57 (s, 1H), 6.83 (d, 1H, J = 7.6 Hz), 7.26-7.37 (m, 6H), 7.41 (d, 1H, J = 6.4 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) δ 21.9, 41.5, 43.8, 81.3, 106.9, 110.7, 124.0, 124.1, 124.5, 127.0, 127.9, 128.9, 134.8, 141.9, 142.2, 161.4, 172.4, 189.4; IR (CH\textsubscript{2}Cl\textsubscript{2}): ν 3062, 3032, 2921, 1724, 1676, 1621, 1596, 1453, 1398, 1381, 1270, 1222, 1155, 1125, 1033, 991, 815, 758, 728, 698 cm\textsuperscript{-1}; MS (ESI) Calcd. for C\textsubscript{20}H\textsubscript{18}NO\textsubscript{3}[M+H]\textsuperscript{+} requires 320.1287, Found: 320.1276.
**Compound 3l**: A known product. Yield: 45 mg, 66%. A light yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz, TMS) $\delta$ 2.77 (d, 1H, $J = 16.8$ Hz), 3.20 (d, 1H, $J = 16.8$ Hz), 5.31 (d, 1H, $J = 16.4$ Hz), 5.37 (d, 1H, $J = 16.4$ Hz), 5.64 (d, 1H, $J = 6.4$ Hz), 7.00 (t, 1H, $J = 7.6$ Hz), 7.20-7.34 (m, 6H), 7.40-7.44 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 41.5, 45.1, 80.5, 106.9, 116.4,
122.9, 124.6, 126.3, 127.5, 128.7, 130.1, 132.6, 136.4, 138.4, 161.1, 172.9, 188.6; IR (CH$_2$Cl$_2$): v 2927, 2853, 2358, 2341, 1738, 1720, 1611, 1454, 1359, 1226, 1137, 1089, 1023, 952, 793, 735 cm$^{-1}$; MS (%) (EI) m/z 339 (M$^+$, 7.3), 242 (79.5), 91 (67.8), 43 (100). HRMS (EI) Calcd. for C$_{19}$H$_{14}$NO$_3$Cl requires 339.0662, Found: 339.0667.

**Compound 3m:** A known product.$^{[1]}$ Yield: 50 mg, 65%. mp. 163-167 ºC; $^1$H NMR (CDCl$_3$, 400 MHz, TMS) δ 2.77 (d, 1H, J = 17.2 Hz), 3.20 (d, 1H, J = 17.2 Hz), 5.40 (s, 2H), 5.64 (d, 1H, J = 6.8 Hz), 6.92-6.96 (m, 1H), 7.18-7.20 (m, 2H), 7.26-7.34 (m, 2H), 7.41-7.47 (m, 2H), 7.48 (d, 1H, J = 6.8 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 41.5, 44.7, 80.4, 103.4, 107.0, 123.5, 125.0, 126.2, 127.4, 128.8, 130.5, 136.3, 137.2, 139.8, 161.1, 173.1, 188.6; IR (CH$_2$Cl$_2$):
$v$ 2954, 2927, 2853, 1737, 1684, 1602, 1496, 1398, 1356, 1269, 1222, 1185, 1164, 1126, 1030, 778, 740, 700 cm$^{-1}$; MS (ESI) m/z (%) : 406.0 [M + Na]$^+$ (100); MS (ESI) Calcd. for C$_{19}$H$_{14}$BrNNaO$_3$ [M + Na]$^+$ requires 406.0049, Found: 406.0068.

Compound 3n: A known product.$^{[2]}$ Yield: 42 mg, 65%. A light yellow oil. $^1$H NMR (CDCl$_3$,
400 MHz, TMS) δ 2.72 (d, 1H, J = 16.8 Hz), 3.21 (d, 1H, J = 16.8 Hz), 5.01 (d, 1H, J = 16.4 Hz), 5.07 (d, 1H, J = 16.4 Hz), 5.64 (d, 1H, J = 6.4 Hz), 6.97-7.09 (m, 2H), 7.26-7.33 (m, 6H), 7.40 (d, 1H, J = 6.4 Hz); ¹³C NMR (CDCl₃, 100 MHz, TMS) δ 41.4, 45.6 (d, J = 4.8 Hz), 81.1 (d, J = 2.3 Hz), 107.0, 119.4 (d, J = 19.3 Hz), 120.3 (d, J = 3.3 Hz), 124.6 (d, J = 6.7 Hz), 127.4, 127.9, 128.8, 128.9, 130.1 (d, J = 2.2 Hz), 136.0, 147.5 (d, J = 244.7 Hz), 161.1, 171.9, 188.7; ¹⁹F NMR (CDCl₃, 376 MHz, CFCl₃) δ -131.78—-131.74 (m); IR (CH₂Cl₂): ν 3063, 3033, 2929, 1676, 1630, 1596, 1487, 1398, 1471, 1347, 1264, 1219, 1179, 1028, 925, 880, 774, 727, 697 cm⁻¹; MS (ESI) Calcd. for C₁₀H₁₈FN₂O₃ [M+NH₄]⁺ requires 341.1296, Found: 341.1297.
**Compound 3o:** A known product.\(^1\) Yield: 40 mg, 87%. mp. 147-152 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) \(\delta\) 2.66 (d, 1H, \(J = 16.8\) Hz), 3.20 (d, 1H, \(J = 16.8\) Hz), 3.23 (s, 3H), 5.62 (d, 1H, \(J = 6.0\) Hz), 6.88 (d, 1H, \(J = 8.0\) Hz), 7.05-7.27 (m, 1H), 7.43-7.48 (m, 2H), 7.49 (d, 1H, \(J = 6.0\) Hz); \(^13\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 26.5, 41.3, 81.3, 106.9, 109.0, 123.6, 124.3, 127.4, 131.3, 143.0, 161.4, 171.9, 189.3; IR (CH\(_2\)Cl\(_2\)): \(\nu\) 2957, 2924, 2854, 1732, 1683, 1615, 1494, 1471, 1376, 1275, 1183, 1094, 1037, 872, 811, 737, 701 \(\text{cm}^{-1}\); MS (%) (EI) \(m/\text{z}\) 229 (M\(^+\), 61.5), 200 (17.5), 159 (100), 130 (56.7), 91 (13.9), 71 (33.6). HRMS (EI) Calcd. for C\(_{13}\)H\(_{11}\)NO\(_3\) requires 229.0739, Found: 229.0740.
**Compound 3p**: A known product.\(^1\) Yield: 48 mg, 94%. mp. 141-145 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) δ 2.69 (d, 1H, \(J = 16.8\) Hz), 3.21 (d, 1H, \(J = 16.8\) Hz), 4.33-4.35 (m, 2H), 5.22-5.30 (m, 2H), 5.63 (d, 1H, \(J = 6.4\) Hz), 5.79-5.89 (m, 1H), 6.87 (d, 1H, \(J = 8.0\) Hz), 7.04-
7.08 (m, 1H), 7.27-7.48 (m, 2H), 7.50 (d, 1H, J = 6.4 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 41.3, 42.5, 81.3, 106.9, 109.9, 118.2, 123.6, 124.4, 127.4, 130.4, 131.2, 142.2, 161.4, 171.7, 189.2; IR (CH$_2$Cl$_2$): $\nu$ 2959, 2915, 2855, 1731, 1682, 1613, 1489, 1468, 1400, 1369, 1274, 1224, 1201, 1104, 1034, 993, 929, 894, 784, 757, 731, 618 cm$^{-1}$; MS (%) (EI) m/z 255 (M$^+$, 78.2), 185 (100), 156 (34.3), 130 (26.2), 41 (24.7). HRMS (EI) Calcd. for C$_{15}$H$_{13}$NO$_3$ requires 255.0895, Found: 255.0893.
**Compound 3q**: A known product.\textsuperscript{[2]} Yield: 41 mg, 71%. A light yellow oil. \( ^1\)H NMR (CDCl\textsubscript{3}, 400 MHz, TMS) \( \delta \) 2.82 (d, 1H, \( J = 16.8 \) Hz), 3.29 (d, 1H, \( J = 16.8 \) Hz), 5.65 (d, 1H, \( J = 6.4 \) Hz), 6.85 (d, 1H, \( J = 8.0 \) Hz), 7.10 (t, 1H, \( J = 7.6 \) Hz), 7.33 (t, 1H, \( J = 7.6 \) Hz), 7.41-7.46 (m, 4H), 7.52-7.57 (m, 3H); \( ^{13}\)C NMR (CDCl\textsubscript{3}, 100 MHz, TMS) \( \delta \) 41.4, 81.4, 106.9, 110.3, 124.0, 124.6, 126.3, 127.1, 128.6, 129.7, 131.2, 133.2, 143.0, 161.3, 171.2, 189.1; IR (CH\textsubscript{2}Cl\textsubscript{2}): \( \nu \) 3058, 2955, 2922, 1735, 1676, 1596, 1498, 1371, 1262, 1224, 1027, 801, 754, 699 cm\textsuperscript{-1}; MS (%) (EI) \( m/z \) 291 (M\textsuperscript{+}, 51.1), 221 (100), 193 (73). HRMS (EI) Calcd. for C\textsubscript{18}H\textsubscript{13}NO\textsubscript{3} requires 291.0895, Found: 291.0897.
Compound 4b: A known product. Yield 21 mg, 55%. $^1$H NMR (CDCl$_3$, 400 MHz, TMS) $\delta$ 2.35 (s, 3H), 6.18 (d, 1H, $J = 13.2$ Hz), 7.50 (t, 2H, $J = 8.0$ Hz), 7.53 (t, 1H, $J = 8.0$ Hz), 8.09 (d, 2H, $J = 8.0$ Hz), 8.50 (d, 1H, $J = 13.2$ Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 27.5, 115.7, 127.5, 128.8, 130.3, 134.5, 149.7, 162.7, 197.4.
Compound 4c: A known product.[3] Yield 15 mg, 47%. $^1$H NMR (CDCl$_3$, 400 MHz, TMS) δ 2.23 (s, 3H), 5.91 (d, 1H, $J = 12.4$ Hz), 7.08 (t, 2H, $J = 8.0$ Hz), 7.21 (d, 2H, $J = 8.0$ Hz), 7.40 (d, 1H, $J = 8.0$ Hz), 7.75 (d, 1H, $J = 12.4$ Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 28.2, 111.6, 118.0, 125.1, 129.9, 155.6, 159.0, 197.2.
Compound 4d: A known product. Yield 18 mg, 52%. $\textsuperscript{1}H$ NMR (CDCl$_3$, 400 MHz, TMS) $\delta$ 2.18 (s, 3H), 4.91 (s, 2H), 5.70 (d, 1H, $J = 12.8$ Hz), 7.26-7.41 (m, 5H), 7.62 (d, 1H, $J = 12.8$ Hz); $\textsuperscript{13}C$ NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 27.8, 72.8, 107.9, 134.9, 162.0, 197.2.
Compound 5a: A known product.\[^{[4]}\] \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) \(\delta\) 2.25 (s, 3H), 6.01 (d, 1H, \(J = 12.0\) Hz), 7.57 (d, 1H, \(J = 12.0\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 28.7, 113.0, 156.9, 196.5.

Compound 6a: Yield: 15 mg, 23%. A yellow solid. mp. 107-109 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz, TMS) \(\delta\) 1.02 (t, 3H, \(J = 7.6\) Hz), 1.74-1.83 (m, 2H), 2.72 (t, 2H, \(J = 7.6\) Hz), 4.90 (s, 2H), 6.72 (d, 1H, \(J = 7.6\) Hz), 6.95 (t, 1H, \(J = 7.6\) Hz), 7.19 (d, 1H, \(J = 7.6\) Hz), 7.27-7.37 (m, 5H), 11.2 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz, TMS) \(\delta\) 13.5, 16.3, 43.7, 45.8, 110.0, 119.0, 123.1, 125.5, 127.9, 128.9, 133.4, 134.8, 143.1, 145.0, 166.7, 191.2, 204.2; IR (CH\(_2\)Cl\(_2\)) 2961, 2930,
2873, 1699, 1659, 1605, 1351, 1177, 1107, 1027, 928, 731, 747, 696 cm$^{-1}$; HRMS (ESI) Calcd. for C$_{21}$H$_{20}$NO$_{3}$ [M + H]$^+$ requires 334.1438, Found: 334.1439.

Compound [D]-3a: Yield: 48 mg, 26%.
General procedure and spectroscopic data of compounds 9 and 10

**Compound 9:** Yield: 229 mg, 51%. A white solid. mp. 103-105 °C. $^1$H NMR (CDCl$_3$, 400 MHz, TMS) $\delta$ 1.03-1.12 (m, 21H), 3.28 (d, 1H, $J = 16.8$ Hz), 3.50 (d, 1H, $J = 16.8$ Hz), 3.94 (brs, 1H), 4.84 (d, 1H, $J = 16.0$ Hz), 4.97 (d, 1H, $J = 16.0$ Hz), 6.96 (d, 1H, $J = 8.0$ Hz), 7.03 (t, 1H, $J = 8.0$ Hz), 7.20 (t, 1H, $J = 8.0$ Hz), 7.25-7.34 (m, 5H), 7.40 (d, 1H, $J = 8.0$ Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 10.9, 18.4, 43.9, 51.6, 73.9, 98.2, 103.9, 109.8, 123.2, 124.1, 127.6, 128.8, 129.0, 130.0, 135.2, 142.8, 176.1, 183.4; IR (neat): ν 3356, 2940, 2863, 2148, 1698, 1683, 1619, 1469, 1390, 1333, 1177, 1060, 997, 882, 737 cm$^{-1}$; HRMS (ESI) Calcd. for C$_{28}$H$_{36}$NO$_3$Si [M + H]$^+$ requires 462.2459, Found: 462.2457.
1-benzyl-3-hydroxy-3-(2-oxobut-3-yn-1-yl)indolin-2-one: A light yellow solid. mp. 113-116 °C. $^1$H NMR (CDCl$_3$, 400 MHz, TMS) δ 3.26 (s, 1H), 3.34 (d, 1H, $J = 16.8$ Hz), 3.51 (d, 1H, $J = 16.8$ Hz), 4.83 (d, 1H, $J = 16.0$ Hz), 4.97 (d, 1H, $J = 16.0$ Hz), 6.71 (d, 1H, $J = 7.6$ Hz), 7.04 (t, 1H, $J = 7.6$ Hz), 7.18-7.04 (m, 7H); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) δ 44.0, 51.6, 73.7, 80.2, 81.1, 109.9, 123.3, 124.0, 127.3, 127.7, 128.7, 128.8, 130.2, 135.2, 142.9, 176.2, 183.1; IR (neat): ν 3296, 2895, 2097, 1697, 1686, 1614, 1467, 1337, 1177, 1065, 1004, 861, 695, 641 cm$^{-1}$; HRMS (ESI) Calcd. for C$_{19}$H$_{16}$NO$_3$ [M + H]$^+$ requires 306.1125, Found: 306.112.
**Compound 10**: Yield: 30 mg, 98%. HRMS (ESI) Calcd. for C$_{19}$H$_{14}$D$_1$N$_1$Na$_1$O$_3$ [M + Na]$^+$ requires 329.1107, Found: 329.1017.

**Compound 6a**: Yield: 100 mg, 23%.
Compound [D]-2d: Yield: 35 mg, 81%.

(1E)-1-(oct-3-en-1-yn-3-yloxy)hept-1-en-3-one:

The isomeric ratio of this isolated product is 3:1, but we can not confirm the corresponding Z or E isomer on the basis of $^1$H NMR spectroscopic data.

A light yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz, TMS) $\delta$ 0.88-0.94 (m, 6H), 1.26-1.45 (m, 8H), 1.59-1.66 (m, 2H), 2.15-2.27 (m, 2H), 2.43-2.48 (m, 2H), 3.18 (s, 0.63H), 3.42 (s, 0.19H), 5.52 (t, 0.68H, $J$ = 8.0 Hz), 5.75 (t, 0.21H, $J$ = 8.0 Hz), 5.82-5.89 (m, 0.91H), 7.74 (d, 0.19H, $J$ = 12.0 Hz), 7.83 (d, 0.71H, $J$ = 12.0 Hz); $^{13}$C NMR (CDCl$_3$, 100 MHz, TMS) $\delta$ 13.76, 13.80, 13.9, 22.1, 22.2, 22.5, 24.2, 25.0, 27.3, 30.7, 31.1, 31.4, 41.56, 41.63, 74.5, 76.3, 80.6, 85.2,
109.47, 109.58, 125.4, 125.9, 133.2, 134.6, 156.9, 157.3, 200.06, 200.11; IR (neat): ν 3267, 2956, 2931, 2872, 2094, 1719, 1615, 1466, 1378, 1120, 1052, 728 cm⁻¹; HRMS (ESI) Calcd. for C₁₆H₂₅O₂ [M + H]⁺ requires 249.1849, Found: 249.1849.

Compound 8a: Yield: 32 mg, 65%.
References:


X-ray Crystal Data of 5a and 6a

The crystal data of compound 5a have been deposited in CCDC with number 914026. Empirical Formula: C_{8}H_{10}O_{3}; Formula Weight: 154.16; Crystal Color, Habit: colorless; Crystal Dimensions: 0.15 x 0.10 x 0.02 mm; Crystal System: Triclinic; Lattice Parameters: a = 3.90450(10)Å, b = 9.1939(3)Å, c = 22.5383(7)Å, α = 88.422(2)°, β = 88.1310(10)°, γ = 78.1610(10)°, V = 791.26(4)Å³; Space group: P-1; Z = 4; D_{calc}= 1.294 g/cm³; F_{000} = 328; Final R indices [I>2σ(I)]: R1 = 0.0481; wR2 = 0.1457.

The crystal data of compound 6a have been deposited in CCDC with number 936172. Empirical Formula: C_{21}H_{19}NO_{3}; Formula Weight: 333.37; Crystal Color, Habit: colorless; Crystal Dimensions: 0.217 x 0.158 x 0.123 mm; Crystal System: Triclinic; Lattice Parameters: a = 8.1086(14)Å, b = 8.8324(16)Å, c = 13.260(2)Å, α = 108.838(3)°, β = 97.636(4)°, γ = 94.663(4)°, V = 883.0(3)Å³; Space group: P-1; Z = 2; D_{calc}= 1.254 g/cm³; F_{000} = 352; Final R indices [I>2σ(I)]: R1 = 0.0682; wR2 = 0.1926.