Supporting Information

Cooperativity within the catalyst: alkoxyamide as a catalyst for bromocyclization and bromination of (hetero)aromatics

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Experimental Section:

General: All reactions involving air or moisture sensitive reagents were carried out in flame dried glassware under nitrogen atmosphere. Heptane was used as received from the commercial source. All other solvents were obtained from Merck India and were dried according to the standard literature procedure. Reactions were monitored by thin layer chromatography (TLC) using Merck silica gel 60 F254 pre-coated plates (0.25 mm); and visualized under UV light or dipping into KMnO₄ solution. Silica gel (particle size 100-200 mesh) and neutral alumina were purchased from SRL India for performing column chromatography. The ¹H NMR spectroscopic data were recorded with a Bruker 400, 500 or 600 MHz instruments. Proton-decoupled ¹³C NMR spectra (¹³C{¹H}) were similarly recorded with a 101, 126 or 151 MHz instruments by using a broad-band decoupled mode. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton or carbon signals in CDCl₃ (δ = 7.26, 77.16). Coupling constants (J) are reported in Hertz (Hz) and refer to apparent multiplicities. For the description of ¹³C NMR spectra, for two symmetrical carbons ‘2C’ and for four symmetrical carbons ‘4C’ are denoted in the parenthesis next to the respective chemical shift values. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, dd: doublet of doublets dt: doublet of triplets, td: triplet of doublets, ddd: doublet of doublet of doublets, m: multiplet, br: broad. Infrared (IR) spectra were recorded by Perkin Elmer FTIR spectrometer, and reported in terms of wave number (cm⁻¹). High-resolution mass spectra were recorded with the ESI (+ve) method using a time-of-flight (TOF) mass analyzer. Other chemicals were obtained from commercial sources and used without further purification. Starting materials [2a–2d], [2e, 2f], [2g], [2i–2j], [2k, 2l], [2m, 2n, 2o, 2p], [2q] were synthesized according to the standard literature procedure. Compounds [4a and 4b], [4c and 4d], [4e, 4f], [6a-6f] and [8r] were synthesized according to literature reported methods. Starting materials [8a-8q] and [8s-8t] are commercially available.
Synthesis of Alkoxyamide Catalyst (1c): 1-Butanesulfonyl chloride (1.0 mmol, 1.0 equiv.) was dissolved in CH₂Cl₂ (5.0 mL) and N-methoxyamine hydrochloride (1.0 equiv.) was added. Then pyridine (2.0 equiv.) was added and the mixture was stirred at room temperature for 4 h. The mixture was quenched with water, extracted with CH₂Cl₂ (10 mL x 3), dried over anhydrous Na₂SO₄ and solvent was removed under reduced pressure. The crude residue was purified by flash column chromatography and the corresponding alkoxyamide catalyst 1c (151 mg, 90%) was isolated as a light orange oil.

**1H NMR** (600 MHz, CDCl₃): δ (ppm) 7.02 (s, 1H), 3.82 (s, 3H), 3.20 (dd, J = 8.8, 7.2 Hz, 2H), 1.82 – 1.77 (m, 2H), 1.52 – 1.48 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

**13C NMR** (126 MHz, CDCl₃): δ (ppm) 65.3, 48.7, 25.0, 21.7, 13.6. **DEPT 135** (126 MHz, CDCl₃): δ (ppm) 65.3 (CH₃), 48.7 (CH₂), 25.0 (CH₂), 21.7 (CH₂), 13.6 (CH₃). **FTIR**: νmax (neat)/ cm⁻¹ = 3320, 2963, 2877, 1466, 1397, 1328, 1150, 1048. **HRMS (ESI) m/z**: [M + NH₄]⁺ calcd for C₅H₁₇N₂O₃S, 185.0954; found 185.0953. Compounds 1a, 1b and 1d were characterized according to the literature procedure.

**General Procedure for the Alkoxyamide-Catalyzed Bromolactonization (GP I):** To a mixture of alkenoic acid 2 (0.5 mmol, 1.0 equiv) and catalyst 1c (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added N-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na₂SO₃ solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified by flash silica-gel column chromatography to yield the corresponding cyclized products 3.

**General Procedure for Bromo Cycloetherification and Bromo Cycloamination (GP II):** To a mixture of alkenoic acid 4 (0.5 mmol, 1.0 equiv) and catalyst 1c (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added N-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na₂SO₃ solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude residue was purified by flash silica-gel column chromatography to yield the corresponding cyclized products 5.
General Procedure for the Bromocyclization of Tryptophans, Tryptamines and Tryptophols (GP III): To a solution of tryptophan or tryptamine or tryptophol derivative 6 (0.5 mmol, 1.0 equiv) and catalyst 1c (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added N-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na₂SO₃ solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash silica-gel column chromatography to yield the corresponding products 7.

General Procedure for the Bromination of Aromatic and Heteroaromatic Compounds (GP IV): To a mixture of aromatic/ heteroaromatic compound 8 (0.5 mmol, 1.0 equiv) and catalyst 1c (0.025 mmol, 0.05 equiv) in heptane (5 mL) at 25 °C was added N-bromosuccinimide (0.55 mmol, 1.1 equiv). The reaction tube was covered with aluminium foil and the resulting mixture was stirred at 25 °C. After completion of the reaction as monitored by TLC, the reaction was quenched with saturated aqueous Na₂SO₃ solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined extracts were washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash silica-gel column chromatography to yield the corresponding brominated products 9.

5-(Bromomethyl)-5-phenyldihydrofuran-2(3H)-one (3a):³

The titled compound 3a was synthesized according to the GP I and the product was isolated as colourless oil (119.9 mg, 94%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.41 – 7.32 (m, 5H), 3.74 (d, J = 11.6 Hz, 1H), 3.69 (d, J = 11.6 Hz, 1H), 2.86 – 2.75 (m, 2H), 2.60 – 2.48 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 175.6, 140.8, 129.0 (2C), 128.8, 125.0 (2C), 86.5, 41.1, 32.5, 29.2.

5-(Bromomethyl)-5-(p-tolyl)dihydrofuran-2(3H)-one (3b):³

The titled compound 3b was synthesized according to the GP I and the product was isolated as colourless oil (124 mg, 92%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.29 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.37 (d, J = 11.4 Hz, 1H), 3.67 (d, J = 11.4 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.57 – 2.49 (m, 2H), 2.36 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 175.7, 138.8, 137.9, 129.6 (2C), 125.0 (2C), 86.6, 41.2, 32.5, 29.2, 21.2.
5-([1,1'-Biphenyl]-4-yl)-5-(bromomethyl)dihydrofuran-2(3H)-one (3c):¹

The titled compound 3c was synthesized according to the GP I and the product was isolated as white solid (107.6 mg, 65%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.64 – 7.57 (m, 4H), 7.50 – 7.44 (m, 4H), 7.39 – 7.36 (m, 1H), 3.79 (d, J = 11.3 Hz, 1H), 3.73 (d, J = 11.3 Hz, 1H), 2.90 – 2.79 (m, 2H), 2.65 – 2.53 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 175.6, 141.8, 140.2, 139.7, 129.0 (2C), 127.9, 127.7 (2C), 127.3 (2C), 125.6 (2C), 86.5, 41.1, 32.5, 29.2.

5-(Bromomethyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (3d):³

The titled compound 3d was synthesized according to the GP I and the product was isolated as colourless oil (118.3 mg, 83%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.33 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.71 (d, J = 11.3 Hz, 1H), 3.65 (d, J = 11.3 Hz, 1H), 2.82 – 2.75 (m, 2H), 2.57 – 2.50 (m, 2H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 175.7, 159.9, 132.7, 126.4 (2C), 114.3 (2C), 86.5, 55.5, 41.3, 32.3, 29.3.

5-(Bromomethyl)-5-(4-bromophenyl)dihydrofuran-2(3H)-one (3e):²

The titled compound 3e was synthesized according to the GP I and the product was isolated as colourless oil (153.6 mg, 92%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.54 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 3.70 (d, J = 8.7 Hz, 2H), 3.65 (d, J = 8.6 Hz, 1H), 2.85 – 2.75 (m, 2H), 2.57 – 2.48 (m, 2H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 175.2, 140.0, 132.2 (2C), 126.9 (2C), 123.0, 86.1, 40.6, 32.5, 29.1.

5-(Bromomethyl)-5-(4-chlorophenyl)dihydrofuran-2(3H)-one (3f):³

The titled compound 3f was synthesized according to the GP I and the product was isolated as colourless oil (127.4 mg, 88%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.38 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 3.70 (d, J = 11.4 Hz, 1H), 3.65 (d, J = 11.4 Hz, 1H), 2.85 – 2.76 (m, 2H), 2.57 – 2.49 (m, 2H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 175.2, 139.4, 134.9, 129.2 (2C), 126.6 (2C), 86.1, 40.7, 32.5, 29.1.

4-(2-(Bromomethyl)-5-oxotetrahydrofuran-2-yl)benzonitrile (3g):³

The titled compound 3g was synthesized according to the GP I and the product was isolated as white solid (116 mg, 83%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.72 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 3.71 (d, J = 11.4 Hz, 1H), 3.67 (d, J = 11.4 Hz, 1H), 2.89 – 2.79 (m, 2H), 2.60 – 2.52 (m, 2H). ¹³C NMR
(151 MHz, CDCl₃): δ (ppm) 174.8, 146.0, 132.8 (2C), 126.1 (2C), 118.2, 113.0, 85.9, 40.1, 32.6, 28.9.

5-(Bromomethyl)-5-(m-tolyl)dihydrofuran-2(3H)-one (3h):

The titled compound 3h was synthesized according to the GP I and the product was isolated as yellow oil (118.4 mg, 88%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.29 (t, J = 7.8 Hz, 1H), 7.23 (s, 1H), 7.17 (dd, J = 12.9, 7.8 Hz, 2H), 3.73 (d, J = 11.4 Hz, 1H), 3.69 (d, J = 11.4 Hz, 1H), 2.84 – 2.76 (m, 2H), 2.58 – 2.50 (m, 2H), 2.37 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 175.8, 140.8, 138.8, 129.5, 128.9, 125.7, 122.1, 86.6, 41.2, 32.5, 29.2, 21.7. FTIR: νmax (neat)/ cm⁻¹ = 3028, 2924, 1608, 1417, 1242, 1158, 1035. HRMS (ESI) m/z: [M + H]^+ calcd for C₁₂H₁₄BrO₂, 269.0712; found 269.0710.

5-(Bromomethyl)-5-(3-methoxyphenyl)dihydrofuran-2(3H)-one (3i):³

The titled compound 3i was synthesized according to the GP I and the product was isolated as yellow oil (141 mg, 99%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.32 (t, J = 7.8 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.88 (dd, J = 8.1, 2.4 Hz, 1H), 3.82 (s, 3H), 3.74 (d, J = 11.4 Hz, 1H), 3.69 (d, J = 11.4 Hz, 1H), 2.83 – 2.77 (m, 2H), 2.58 – 2.51 (m, 2H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 175.7, 160.1, 142.5, 130.1, 117.2, 114.1, 111.1, 86.5, 55.5, 41.1, 32.6, 29.2.

5-(Bromomethyl)-5-(naphthalen-2-yl)dihydrofuran-2(3H)-one (3j):³

The titled compound 3j was synthesized according to the GP I and the product was isolated as colourless oil (137.3 mg, 90%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.94 (s, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.55 – 7.50 (m, 2H), 7.44 (d, J = 8.6 Hz, 1H), 3.81 (dd, J = 13.8, 11.4 Hz, 2H), 2.93 – 2.81 (m, 2H), 2.70 – 2.65 (m, 1H), 2.60 – 2.54 (m, 1H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 138.0, 133.2, 133.1, 129.1, 128.5, 127.8, 127.0, 124.4, 122.5, 86.7, 40.9, 32.6, 29.2.

5-(Bromomethyl)dihydrofuran-2(3H)-one (3k):³

The titled compound 3k was synthesized according to the GP I and the product was isolated as colourless oil (61 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 4.76 – 4.70 (m, 1H), 3.57 – 3.50 (m, 2H), 2.68 – 2.50 (m, 2H), 2.47 – 2.38 (m, 1H), 2.15 – 2.06 (m, 1H). ¹³C NMR (126 MHz, CDCl₃): δ (ppm) 176.2, 78.0, 34.2, 28.4, 26.3.
5-(Bromomethyl)-5-methyldihydrofuran-2(3H)-one (3l): 3

The titled compound 3l was synthesized according to the GP I and the product was isolated as colourless oil (86 mg, 89%). 1H NMR (400 MHz, CDCl3): δ (ppm) 3.53 (d, J = 10.8 Hz, 1H), 3.47 (d, J = 10.8 Hz, 1H), 2.76 – 2.59 (m, 2H), 2.42 – 2.35 (m, 1H), 2.12 – 2.04 (m, 1H), 1.57 (s, 3H). 13C NMR (126 MHz, CDCl3): 175.8, 84.2, 39.5, 31.7, 29.3, 25.6.

(±)-6-Bromohexahydro-2H-3,5-methanocyclopenta[b]furan-2-one (3m): 3

The titled compound 3m was synthesized according to the GP I and the product was isolated as colourless oil (88 mg, 81%). 1H NMR (600 MHz, CDCl3): δ (ppm) 4.93 (d, J = 5.0 Hz, 1H), 3.85 (d, J = 2.2 Hz, 1H), 3.24 (td, J = 4.9, 1.1 Hz, 1H), 2.68 (d, J = 2.9 Hz, 1H), 2.57 (dd, J = 11.2, 4.6 Hz, 1H), 2.34 (dd, J = 11.5, 1.4 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.81 – 1.74 (m, 2H). 13C NMR (126 MHz, CDCl3): δ (ppm) 179.4, 53.6, 46.0, 45.7, 37.7, 35.9, 34.1.

(±)-7-Bromohexahydrobenzofuran-2(3H)-one (3n): 5

The titled compound 3n was synthesized according to the GP I and the product was isolated as colourless oil (101.8 mg, 93%). 1H NMR (600 MHz, CDCl3): δ (ppm) 4.59 (t, J = 4.4 Hz, 1H), 4.45 (dd, J = 8.4, 4.1 Hz, 1H), 2.79 – 2.73 (m, 1H), 2.60 (dd, J = 16.9, 6.9 Hz, 1H), 2.28 (dd, J = 16.9, 3.5 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.96 – 1.92 (m, 1H), 1.80 – 1.75 (m, 2H), 1.56 – 1.51 (m, 1H), 1.34 – 1.28 (m, 1H). 13C NMR (151 MHz, CDCl3): δ (ppm) 176.1, 81.6, 48.5, 36.8, 32.7, 29.5, 26.4, 18.8.

6-(Bromomethyl)-6-phenyltetrahydro-2H-pyran-one (3o): 3

The titled compound 3o was synthesized according to the GP I and the product was isolated as colourless oil (105 mg, 78%). 1H NMR (600 MHz, CDCl3): δ (ppm) 7.42 – 7.34 (m, 5H), 3.68 (d, J = 11.4 Hz, 1H), 3.64 (d, J = 11.4 Hz, 1H), 2.53 – 2.35 (m, 4H), 1.87 – 1.81 (m, 1H), 1.63 – 1.59 (m, 1H). 13C NMR (126 MHz, CDCl3): δ (ppm) 170.6, 140.5, 129.2 (2C), 128.7, 125.6 (2C), 85.3, 41.7, 30.2, 29.2, 16.4.

6-(Bromomethyl)-4-tosylmorpholin-2-one (3p):

The titled compound 3p was synthesized according to the GP I and the product was isolated as gummy liquid (137.5 mg, 79%). 1H NMR (400 MHz, CDCl3): δ (ppm) 7.69 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 4.75 – 4.69 (m, 1H), 4.04 (d, J = 17.6 Hz, 1H), 3.75 – 3.67 (m, 2H), 3.56 – 3.48 (m, 2H), 3.12 (dd, J = 12.9, 7.8 Hz, 3H).
1H), 2.47 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): δ (ppm) 163.5, 145.3, 131.7, 130.5 (2C), 128.0 (2C), 77.1, 47.1, 45.3, 29.5, 21.8. FTIR: $\nu$ max (neat)/ cm$^{-1}$ = 2924, 2854, 1752, 1354, 1255, 1166, 1090, 975. HRMS (ESI) m/z: [M + K]$^+$ calcd for C$_{12}$H$_{14}$BrKNO$_4$S, 385.9458; found 385.9464.

(3S,6S)-6-(Bromomethyl)-3-((S)-sec-butyl)-4-tosylmorpholin-2-one (3q):

The titled compound 3q was synthesized according to the GP I and the product was isolated as gummy liquid (155.6 mg, 77%) with 2:1 diastereomeric ratio. The reported signals are for the major diastereomer and the integration of the total diastereomers are shown because of the overlap of protons of two diastereomers. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.72 (d, $J = 7.9$ Hz, 2H), 7.34 (d, $J = 7.9$ Hz, 2H), 4.34 – 4.33 (m, 1H), 4.19 – 4.12 (m, 1H), 4.10 – 4.02 (m, 1H), 3.39 – 3.34 (m, 3H), 2.44 (s, 3H), 2.07 – 2.01 (m, 1H), 1.67 – 1.59 (m, 2H), 1.04 (d, $J = 6.7$ Hz, 2H), 1.01 – 0.99 (m, 1H), 0.95 – 0.87 (m, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ (ppm) 166.1, 145.0, 136.3, 130.5 (2C), 127.4 (2C), 75.2, 60.2, 42.9, 38.7, 30.8, 26.3, 21.7, 15.9, 11.5. FTIR: $\nu$ max (neat)/ cm$^{-1}$ = 2967, 1746, 1598, 1455, 1349, 1213, 1089, 965. HRMS (ESI) m/z: [M + K]$^+$ calcd for C$_{16}$H$_{22}$BrKNO$_4$S, 442.0084; found 442.0088.

(±)-2-(Bromomethyl)-4-phenyltetrahydrofuran (5a):

The titled compound 5a was synthesized according to the GP II and the product was isolated as colourless oil (89.2 mg, 74%). $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 7.34 – 7.31 (m, 2H), 7.26 – 7.23 (m, 3H), 4.37 – 4.32 (m, 1H), 4.24 (t, $J = 8.1$ Hz, 1H), 3.88 (t, $J = 8.8$ Hz, 1H), 3.57 – 3.51 (m, 3H), 2.58 – 2.53 (m, 1H), 1.95 – 1.90 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$): δ (ppm) 140.9, 128.8 (2C), 127.4 (2C), 127.0, 79.1, 75.0, 45.8, 39.6, 36.0.

(±)-(5-(Bromomethyl)tetrahydrofuran-3-yl)methanol (5b):

The titled compound 5b was synthesized according to the GP II and the product was isolated as colourless oil (93 mg, 95%) with 2:1 diastereomeric ratio. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 4.23 (quint, $J = 6.4$ Hz, 1H), 4.13 (q, $J = 6.8$ Hz, 2H), 4.05 (t, $J = 7.8$ Hz, 1H), 3.92 (t, $J = 8.0$ Hz, 2H), 3.78 (t, $J = 7.4$ Hz, 2H), 3.68 – 3.56 (m, 8H), 3.45 (d, $J = 5.4$ Hz, 4H), 3.43 – 3.36 (m, 2H), 2.58 – 2.52 (m, 7.1 Hz, 3H), 2.25 – 2.20 (m, 2H), 1.91 (t, $J = 6.8$ Hz, 2H), 1.81 (s, 4H), 1.47 – 1.41 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ (ppm) 78.7, 78.0, 71.3, 64.7, 64.4, 42.2, 41.8, 35.8, 35.5, 33.8, 33.3.
FTIR: $\nu_{\text{max}}$ (neat)/ cm$^{-1}$ = 3392, 2935, 2870, 1643, 1421, 1361, 1222. HRMS (ESI) m/z: [M + H]$^+$ calcd for C$_6$H$_{12}$BrO$_2$, 195.0015; found 195.0016.

2-(Bromomethyl)-1-tosylpyrrolidine (5c):$^9$

The titled compound 5c was synthesized according to the GP II and the product was isolated as white foam (133.6 mg, 84%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.73 (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 3.85 – 3.81 (m, 1H), 3.77 (dd, $J = 9.8$, 3.2 Hz, 1H), 3.49 – 3.45 (m, 1H), 3.35 (t, $J = 9.7$ Hz, 1H), 3.17 – 3.13 (m, 1H), 2.44 (s, 3H), 1.97 – 1.92 (m, 1H), 1.88 – 1.81 (m, 1H), 1.77 – 1.70 (m, 1H), 1.58 – 1.53 (m, 1H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ (ppm) 143.9, 134.2, 130.0 (2C), 127.7 (2C), 60.5, 49.9, 36.2, 30.4, 23.9, 21.7.

2-(Bromomethyl)-2-methyl-1-tosylpyrrolidine (5d):$^9$

The titled compound 5d was synthesized according to the GP II and the product was isolated as white foam (134.5 mg, 81%). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ (ppm) 7.75 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 3.84 (d, $J = 10.1$ Hz, 1H), 3.75 (d, $J = 10.1$ Hz, 1H), 3.43 – 3.39 (m, 1H), 3.35 – 3.31 (m, 1H), 2.41 (s, 3H), 2.30 – 2.26 (m, 1H), 1.89 – 1.82 (m, 1H), 1.80 – 1.75 (m, 1H), 1.73 – 1.67 (m, 2H), 1.56 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ (ppm) 143.3, 137.9, 129.6 (2C), 127.4 (2C), 67.4, 50.0, 41.1, 39.4, 24.2, 22.6, 21.6.

2-(Bromomethyl)-2-phenyl-1-tosylpyrrolidine (5e):$^{10}$

The titled compound 5e was synthesized according to the GP II and the product was isolated as white solid (118.3 mg, 60%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.33 – 7.32 (m, 2H), 7.26 – 7.24 (m, 5H), 7.09 – 7.07 (m, 2H), 4.47 (d, $J = 10.7$ Hz, 1H), 4.28 (d, $J = 10.7$ Hz, 1H), 4.28 (d, $J = 7.4$ Hz, 1H), 3.69 (q, $J = 7.4$ Hz, 1H), 3.61 (q, $J = 7.3$ Hz, 1H), 2.68 (dt, $J = 14.4$, 7.6 Hz, 1H), 2.36 (s, 3H), 2.24 (dt, $J = 13.3$, 6.8 Hz, 1H), 2.06 – 1.91 (m, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (ppm) 142.7, 141.2, 137.2, 129.0 (2C), 128.1 (2C), 127.4, 127.18 (2C), 127.15 (2C), 71.7, 50.4, 41.9, 39.4, 22.9, 21.4.

5-(Bromomethyl)-3-phenyl-1-tosyl-4,5-dihydro-1H-pyrazole (5f):$^{11}$

The titled compound 5f was synthesized according to the GP II and the product was isolated as white solid (133.7 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.80 (d, $J = 8.3$ Hz, 2H), 7.66 (dd, $J = 7.9$, 1.3 Hz, 2H), 7.44 – 7.36 (m, 3H), 7.30 (d, $J = 8.1$ Hz, 2H), 4.20 – 4.12 (m, 1H), 4.00 (dd, $J = 10.1$, 3.4 Hz, 1H), 3.61 (t, $J = 9.7$ Hz, 1H), 3.28 (dd, $J = 17.5$, 10.9 Hz, 1H), 3.12 (dd, $J = 17.5$, 8.8 Hz, 1H), 2.39 (s, 3H). $^{13}$C
Bromocyclization of Tryptophans, Tryptamines and Tryptophols:

(±)-8-(tert-Butyl) 1-methyl-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (7a): The titled compound 7a was synthesized according to the GP III and the product was isolated as light yellow oil (82.4 mg, 83%).

1H NMR (500 MHz, CDCl3): δ (ppm) 7.64 (d, J = 8.1 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.38 (s, 1H), 3.81 – 3.77 (m, 1H), 3.74 (s, 3H), 2.90 – 2.82 (m, 2H), 2.78 – 2.71 (m, 1H), 1.59 (s, 9H).

13C NMR (126 MHz, CDCl3): δ (ppm) 154.9, 152.3, 142.1, 132.5, 130.6, 124.3, 123.8, 117.5, 84.2, 82.3, 62.2, 52.9, 46.4, 41.2, 28.4.

(±)-8-(tert-Butyl) 1-methyl-3a-bromo-8a-methyl-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,8-dicarboxylate (7b): The titled compound 7b was synthesized according to the GP III and the product was isolated as light yellow oil (85.3 mg, 83%).

1H NMR (400 MHz, CDCl3): δ (ppm) 7.72 (s, 1H), 7.34 (d, J = 7.1 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.04 (t, J = 7.1 Hz, 1H), 3.64 (s, 3H), 3.49 – 3.43 (m, 1H), 2.95 – 2.84 (m, 2H), 2.69 – 2.61 (m, 1H), 2.11 (s, 3H), 1.59 (s, 9H).

13C NMR (101 MHz, CDCl3): δ (ppm) 152.1, 142.2, 131.7, 130.4, 123.8, 123.2, 118.3, 88.4, 82.0, 70.4, 52.4, 45.9, 36.1, 28.5, 24.6.

1,8-di-tert-Butyl 2-methyl (2S,3aR,8aR)-3a-bromo-2,3,3a,8a-tetrahydropyrrolo[2,3-b]indole-1,2,8-tricarboxylate (7c): The titled compound 7c was synthesized according to the GP III and the product was isolated as white foam (96.7 mg, 78%).

1H NMR (400 MHz, CDCl3): δ (ppm) 7.56 (s, 1H), 7.37 – 7.30 (m, 2H), 7.12 (td, J = 7.5, 1.0 Hz, 1H), 6.39 (s, 1H), 3.89 (dd, J = 10.3, 6.3 Hz, 1H), 3.74 (s, 3H), 3.21 (dd, J = 12.6, 6.3 Hz, 1H), 2.82 (dd, J = 12.6, 10.3 Hz, 1H), 1.59 (s, 9H), 1.40 (s, 9H).

13C NMR (101 MHz, CDCl3): δ (ppm) 171.5, 152.2, 141.6, 132.9, 130.6, 124.4, 123.2, 118.8, 83.8, 82.3, 81.5, 59.7, 59.5, 52.4, 42.0, 28.3, 28.2.
(3R,5aR,10bR,11aS)-6-Acetyl-10b-bromo-3-isobutyl-2,3,6,10b,11,11a-hexahydro-4H-pyrazino[1',2':1,5]pyrrolo[2,3-b]indole-1,4(5aH)-dione (7d):\(^{12}\)

The titled compound 7d was synthesized according to the GP III followed by treatment with TFA in dichloromethane and the product was isolated after two steps as white solid (37.8 mg, 36%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.01 (d, \(J = 7.9\) Hz, 1H), 7.44 (d, \(J = 7.6\) Hz, 1H), 7.37 (dd, \(J = 11.4, 4.2\) Hz, 1H), 7.21 (t, \(J = 7.5\) Hz, 1H), 6.27 (s, 1H), 6.15 (s, 1H), 3.96 – 3.89 (m, 2H), 3.37 (dd, \(J = 12.9, 5.7\) Hz, 1H), 2.96 (dd, \(J = 12.8, 11.5\) Hz, 1H), 2.70 (s, 3H), 2.04 – 1.97 (m, 1H), 1.76 – 1.69 (m, 1H), 1.57 – 1.50 (m, 1H), 0.99 (d, \(J = 6.5\) Hz, 3H), 0.91 (d, \(J = 6.5\) Hz, 3H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)): \(\delta\) (ppm) 170.7, 167.6, 166.3, 142.1, 131.7, 131.3, 125.8, 123.5, 119.7, 85.2, 59.2, 58.8, 53.3, 43.6, 38.8, 24.6, 23.7, 23.4, 21.2.

(±)-tert-Butyl-3a-bromo-2,3,3a,8a-tetrahydro-8H-furo[2,3-b]indole-8-carboxylate (7e):\(^{12}\)

The titled compound 7e was synthesized according to the GP III and the product was isolated as gummy liquid (84.2 mg, 99%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.77 (s, 1H), 7.36 (d, \(J = 7.5\) Hz, 1H), 7.24 (t, \(J = 7.9\) Hz, 1H), 7.04 (t, \(J = 7.5\) Hz, 1H), 6.16 (s, 1H), 3.96 (t, \(J = 8.1\) Hz, 1H), 3.49 – 3.41 (m, 1H), 2.90 – 2.82 (m, 1H), 2.75 (dd, \(J = 11.7, 4.1\) Hz, 1H), 1.56 (s, 9H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 152.0, 141.8, 131.9, 130.6, 125.0, 123.8, 115.1, 100.9, 82.4, 67.9, 61.8, 45.2, 28.5.

(±)-3a-Bromo-8-tosyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (7f):\(^{12}\)

The titled compound 7f was synthesized according to the GP III and the product was isolated as light yellow foam (77 mg, 78%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.80 (d, \(J = 8.3\) Hz, 2H), 7.46 (d, \(J = 8.2\) Hz, 1H), 7.34 (d, \(J = 7.7\) Hz, 1H), 7.29 – 7.23 (m, 3H), 7.10 (t, \(J = 7.5\) Hz, 1H), 6.24 (s, 1H), 4.03 – 3.98 (m, 1H), 3.43 (dd, \(J = 11.1, 9.2, 4.8\) Hz, 1H), 2.88 – 2.80 (m, 1H), 2.74 – 2.70 (m, 1H), 2.37 (s, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 144.6, 140.7, 135.8, 132.6, 130.8, 129.9 (2C), 127.6 (2C), 125.4, 125.0, 114.4, 103.4, 68.1, 61.5, 44.8, 21.7.

(Hetero)-Aromatic Bromination:

1-Bromo-4-methoxybenzene (9a):\(^{18}\)

The titled compound 9a was synthesized according to the GP IV and the product was isolated as clear liquid (82.2 mg, 88%). \(^{1}H\) NMR (400 MHz,
CDCl₃: δ (ppm) 7.38 (d, J = 8.9 Hz, 2H), 6.78 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 158.9, 132.4 (2C), 115.9 (2C), 113.0, 55.6.

1-(Benzyl oxy)-4-bromobenzene (9b):¹⁸

The titled compound 9b was synthesized according to the GP IV and the product was isolated as white solid (114.4 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.43 – 7.32 (m, 7H), 6.86 (d, J = 8.9 Hz, 2H), 5.04 (s, 2H).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 158.0, 136.7, 132.4 (2C), 128.8 (2C), 128.3, 127.6 (2C), 116.8 (2C), 113.3, 70.4.

4-Bromo-1,2-dimethoxybenzene (9c):¹⁸

The titled compound 9c was synthesized according to the GP IV and the product was isolated as colourless oil (95.5 mg, 88%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.02 (dd, J = 8.5, 2.1 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 6.72 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 149.8, 148.4, 123.5, 114.9, 112.8, 112.6, 56.2, 56.1.

4-Bromo-1-methoxy-2-methylbenzene (9d):¹⁸

The titled compound 9d was synthesized according to the GP IV and the product was isolated as colourless oil (75.4 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.25 (d, J = 7.2 Hz, 2H), 6.68 (d, J = 8.9 Hz, 1H), 3.80 (s, 3H), 2.19 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 157.0, 133.3, 129.5, 129.1, 112.5, 111.6, 55.6, 16.2.

5-Bromo-2-methoxybenzaldehyde (9e):¹⁹

The titled compound 9e was synthesized according to the GP IV and the product was isolated as light yellowish solid (80.6 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.37 (s, 1H), 7.90 (d, J = 2.5 Hz, 1H), 7.62 (dd, J = 8.8, 2.5 Hz, 1H), 6.88 (d, J = 8.8 Hz, 1H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ (ppm) 188.5, 160.9, 138.4, 131.1, 126.2, 113.8, 113.6, 56.1.

1-Bromo-2,4-dimethoxybenzene (9f):²⁰

The titled compound 9f was synthesized according to the GP IV and the product was isolated as colourless oil (98.8 mg, 91%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.40 (d, J = 8.6 Hz, 1H), 6.49 (s, 1H), 6.40 (d, J = 8.7 Hz,
1H), 3.87 (s, 3H), 3.79 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ (ppm) 160.5, 156.8, 133.3, 106.3, 102.8, 100.3, 56.4, 55.8.

1-Bromo-2,3,4-trimethoxybenzene (9g):$^{21}$

The titled compound 9g was synthesized according to the GP IV and the product was isolated as light yellow oil (122.3 mg, 99%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.20 (d, $J = 8.9$ Hz, 1H), 6.58 (d, $J = 9.0$ Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): δ (ppm) 160.5, 156.8, 133.3, 106.3, 102.8, 100.3, 56.4, 55.8.

5-Bromo-2-hydroxybenzoic acid (9h):$^{22}$

The titled compound 9h was synthesized according to the GP IV and the product was isolated as white solid (89.6 mg, 85%). The isolated product 9h contained 6% of 8h. $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 10.32 (s, 1H), 8.03 (d, $J = 2.4$ Hz, 1H), 7.60 (dd, $J = 8.9$, 2.4 Hz, 1H), 6.92 (d, $J = 8.9$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ (ppm) 173.6, 161.3, 139.9, 133.2, 120.0, 112.9, 111.4.

6-Bromo-2,3-dihydrobenzo[b][1,4]dioxine (9i):$^{23}$

The titled compound 9i was synthesized according to the GP IV and the product was isolated as colourless oil (100 mg, 93%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.01 (d, $J = 2.3$ Hz, 1H), 6.93 (dd, $J = 8.7$, 2.1 Hz, 1H), 6.73 (d, $J = 8.6$ Hz, 1H), 4.24 (s, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ (ppm) 144.5, 143.0, 124.4, 120.4, 118.7, 112.9, 64.4, 64.3.

tert-Butyl (4-bromophenyl)carbamate (9j):$^{18}$

The titled compound 9j was synthesized according to the GP IV and the product was isolated as white solid (117 mg, 86%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.38 (d, $J = 8.8$ Hz, 2H), 7.25 (d, $J = 7.1$ Hz, 2H), 6.48 (bs, 1H), 1.51 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ (ppm) 152.6, 137.6, 132.0 (2C), 120.2 (2C), 28.4.

$N$-(4-Bromo-2-methylphenyl)pivalamide (9k):$^{24}$

The titled compound 9k was synthesized according to the GP IV and the product was isolated as white solid (124 mg, 92%). $^1$H NMR (600 MHz, CDCl$_3$): δ (ppm) 7.76 (dd, $J = 9.1$, 2.3 Hz, 1H), 7.31 (s, 2H), 7.18 (s, 1H), 2.22 (s, 3H), 1.33 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$): δ (ppm) 176.6, 135.1, 133.1, 130.9, 129.9, 124.4, 117.7, 39.9, 27.8, 17.6.
1-(5-Bromoindolin-1-yl)ethan-1-one (9l): \(^{24}\)

The titled compound 9l was synthesized according to the GP IV and the product was isolated as white solid (102 mg, 85%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ (ppm) 8.06 (d, \(J = 8.4\) Hz, 1H), 7.27 (d, \(J = 9.0\) Hz, 2H), 4.04 (t, \(J = 8.5\) Hz, 2H), 3.16 (t, \(J = 8.5\) Hz, 2H), 2.20 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ (ppm) 168.9, 142.2, 133.5, 130.5, 127.7, 118.4, 116.0, 49.0, 27.8, 24.2.

1-Bromo-4-methoxynaphthalene (9m): \(^{18}\)

The titled compound 9m was synthesized according to the GP IV and the product was isolated as white solid (117 mg, 99%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ (ppm) 8.28 (d, \(J = 8.3\) Hz, 1H), 8.17 (d, \(J = 8.3\) Hz, 1H), 7.67 – 7.59 (m, 2H), 7.54 (d, \(J = 7.5\) Hz, 1H), 6.69 (d, \(J = 7.8\) Hz, 1H), 3.99 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ (ppm) 155.4, 132.6, 129.6, 127.9, 127.0, 126.95, 126.1, 122.6, 113.4, 104.7, 55.8.

1-Bromo-2-methoxynaphthalene (9n): \(^{18}\)

The titled compound 9n was synthesized according to the GP IV and the product was isolated as white solid (109 mg, 92%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ (ppm) 8.23 (d, \(J = 8.6\) Hz, 1H), 7.83 – 7.78 (m, 2H), 7.57 (t, \(J = 7.7\) Hz, 1H), 7.40 (t, \(J = 7.4\) Hz, 1H), 7.28 (d, \(J = 9.3\) Hz, 1H), 4.03 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ (ppm) 153.9, 133.3, 130.0, 129.1, 128.2, 127.9, 126.3, 124.4, 113.8, 108.8, 57.2.

9-Bromoanthracene (9o): \(^{20}\)

The titled compound 9o was synthesized according to the GP IV and the product was isolated as yellow solid (104 mg, 81%). In a second fraction, dibrominated product 9p was also isolated (10.5 mg, 8% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ (ppm) 8.52 (d, \(J = 8.9\) Hz, 2H), 8.45 (s, 1H), 8.00 (d, \(J = 8.4\) Hz, 2H), 7.62 – 7.59 (m, 2H), 7.53 – 7.49 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): δ (ppm) 132.3, 130.7, 128.8 (2C), 127.8 (2C), 127.4 (2C), 127.3, 125.8 (2C), 122.5.
9,10-Dibromoanthracene (9p):\(^{20}\)

The titled compound 9p was synthesized according to the GP IV and the product was isolated as yellow solid (143 mg, 85%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.61 – 8.57 (m, 4H), 7.65 – 7.61 (m, 4H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 131.2 (4C), 128.4 (4C), 127.6 (4C), 123.7 (2C).

3-Bromo-2-methyl-4H-chromen-4-one (9q):\(^{25}\)

The titled compound 9q was synthesized according to the GP IV and the product was isolated as white solid (59.7 mg, 50%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.23 (dd, \(J = 7.9, 1.2\) Hz, 1H), 7.68 (ddd, \(J = 8.5, 7.4, 1.5\) Hz, 1H), 7.45 – 7.40 (m, 2H), 2.66 (s, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 172.4, 164.1, 155.5, 134.0, 126.6, 125.7, 122.0, 117.7, 109.9, 21.8.

Ethyl 3-Bromo-1H-indole-2-carboxylate (9r):\(^{26}\)

The titled compound 9r was synthesized according to the GP IV and the product was isolated as white solid (110 mg, 82%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.07 (bs, 1H), 7.68 (d, \(J = 8.1\) Hz, 1H), 7.41 – 7.36 (m, 2H), 7.23 – 7.21 (m, 1H), 4.46 (q, \(J = 7.1\) Hz, 2H), 1.46 (t, \(J = 7.1\) Hz, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 161.1, 135.4, 128.2, 126.7, 124.3, 121.6, 121.5, 112.1, 98.5, 61.6, 14.5.

3-Bromo-1-tosyl-1H-indole (9s):\(^{27}\)

The titled compound 9s was synthesized according to the GP IV and the product was isolated as white solid (89 mg, 51%). \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.00 (d, \(J = 8.3\) Hz, 1H), 7.77 (d, \(J = 8.2\) Hz, 2H), 7.63 (s, 1H), 7.49 (d, \(J = 7.7\) Hz, 1H), 7.38 (t, \(J = 7.7\) Hz, 1H), 7.31 (t, \(J = 7.5\) Hz, 1H), 7.23 (d, \(J = 8.2\) Hz, 2H), 2.34 (s, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta\) (ppm) 145.5, 134.9, 134.4, 130.2 (2C), 129.9, 127.0 (2C), 125.9, 124.9, 124.0, 120.2, 113.7, 99.7, 21.7.
Control Experiments:
Bromocyclization Using Stoichiometric Amount of 10:

In a reaction tube, 1.1 equiv. of NBS was added to a solution of 1c (83.6 mg, 0.5 mmol) in heptane. The reaction tube was covered with aluminium foil and the reaction was stirred for 5 min at room temperature. After completion, the insoluble succinimide was filtered and the filtrate was collected. Then 0.5 mmol of the alkenoic acid 8l was added to the solution and the mixture was stirred for 15 minutes at room temperature. The reaction was quenched with saturated solution of Na2S2O3. The reaction mixture was concentrated and purified by column chromatography to isolate 88% of 9l and catalyst 1c was recovered (79.4 mg, 95%) almost in quantitative yield.

Figure S1. 1H NMR study of crude 10.

Alternatively, we also attempted to isolate the intermediate 10 by following the same procedure as discussed above to obtain 10 as a solution in heptane. The solvent was then evaporated and the crude residue containing 10 was quickly re-dissolved in CDCl3 and NMR was recorded immediately. The 1H NMR analysis of crude 10 revealed that N-H peak of 1c at 7.05 ppm disappeared (Figure S1). It was found that although the intermediate 10 is stable in heptane...
solution for some time, it undergoes rapid decomposition in the absence of any solvent. The stability of 10 also varies from solvent to solvent.

**Chromatography-Free Gram-Scale Synthesis:**

To a solution of N-Boc tryptophol 6e (1.3 g, 5 mmol) in 25 mL hexane, 1 mol % of 1c (8.4 mg) and NBS (1.1 equiv., 0.98 g) were added. After stirring the resulting mixture at room temperature for 1 h, the insoluble succinimide was separated by filtration. The filtrate was then concentrated to obtain tetrahydrofuroindoline 7e (1.6 g, 95%) in analytically pure form as indicated by $^1$H NMR analysis (Figure S2). Pure succinimide (confirmed by $^1$H NMR analysis) was recovered in 97% yield. No column chromatography was performed in this entire isolation process.
**Figure S2:** Chromatography-free gram-scale synthesis.

**Kinetic Studies:**

**Effect of Catalyst on the Reaction Profile: Catalyzed vs Uncatalyzed Reaction of Anisole Bromination:**

**Anisole Bromination in the Presence of Catalyst:** Anisole (1 mmol) was dissolved in 10 ml of heptane and 5 mol % of 1c and 1.05 mmol of NBS were added successively. The reaction mixture was stirred in the absence of light. Periodically, aliquots of the reaction mixture were taken and quenched with Na₂S₂O₃ solution. The conversion from 8a to 9a was followed up by ¹H NMR analysis of aliquots. Product conversion was plotted as a function of time.

**Anisole Bromination in the Absence of Catalyst:** Anisole (1 mmol) was dissolved in 10 ml of heptane and 1.05 mmol of NBS was added. The reaction mixture was stirred in the absence of light. Periodically, aliquots of the reaction mixture were taken and quenched with Na₂S₂O₃ solution. The conversion from 8a to 9a was followed up by NMR analysis of aliquots.
### Figure S3. Effect of catalyst on the reaction profile: catalyzed vs uncatalyzed reaction of anisole bromination.

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<th>Time (h)</th>
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Stacked NMR spectra of anisole bromination in presence of catalyst
Stacked NMR spectra of anisole bromination without catalyst
References

$^1$H, $^{13}$C and DEPT 135 NMR Spectra of Compound 1c
$^1$H and $^{13}$C NMR Spectra of Compound 3a
$^1$H and $^{13}$C NMR Spectra of Compound 3b
$^1$H and $^{13}$C NMR Spectra of Compound 3c

[Graph showing NMR spectra with peaks and chemical shifts]
$^1$H and $^{13}$C NMR Spectra of Compound 3d
H and $^{13}$C NMR Spectra of Compound 3e
$^1$H and $^{13}$C NMR Spectra of Compound 3f

![NMR Spectra](image)
$^1$H and $^{13}$C NMR Spectra of Compound 3g
$^1$H and $^{13}$C NMR Spectra of Compound 3h
$^1$H and $^{13}$C NMR Spectra of Compound 3i

**$^1$H NMR Spectra**

- 5.15 (s, 1H)
- 7.51 (d, 1H, J = 8.0 Hz)
- 7.53 (d, 1H, J = 8.0 Hz)
- 7.59 (s, 1H)
- 7.72 (d, 1H, J = 8.0 Hz)
- 7.73 (d, 1H, J = 8.0 Hz)
- 7.83 (s, 1H)
- 8.19 (d, 1H, J = 8.0 Hz)

**$^{13}$C NMR Spectra**

- 56.0 (CH)
- 120.1 (CH)
- 120.4 (CH)
- 130.3 (CH)
- 141.1 (CH)
- 155.1 (CO)
- 155.4 (CO)
- 166.4 (CO)
- 171.4 (CO)
- 174.1 (CO)
- 224.2 (CO)

**Chemical Shifts**

- 3.15 (s, 3H)
- 3.42 (s, 3H)
- 7.72 (d, 1H, J = 8.0 Hz)
- 7.83 (s, 1H)
- 8.19 (d, 1H, J = 8.0 Hz)
$^1$H and $^{13}$C NMR Spectra of Compound 3j
$^1$H and $^{13}$C NMR Spectra of Compound 3k
$^1$H and $^{13}$C NMR Spectra of Compound 3i
H and $^{13}$C NMR Spectra of Compound 3m

M S Haji

$^1$H NMR (300 MHz, CDCl$_3$)  $^13$C NMR (75 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR Spectra of Compound 3n
$^1$H and $^{13}$C NMR Spectra of Compound 3o

**M S Magh**

$^1$H NMR (500 MHz) / $^{13}$C NMR (126 MHz) 293

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$^1$H and $^{13}$C NMR Spectra of Compound 3p

![NMR Spectra Image]
$^1$H and $^{13}$C NMR Spectra of Compound 3q
$^1$H and $^{13}$C NMR Spectra of Compound 5a

Chemistry M S Mphi

S41
$^1$H and $^{13}$C NMR Spectra of Compound 5b
$^1$H and $^{13}$C NMR Spectra of Compound 5c
$^1$H and $^{13}$C NMR Spectra of Compound 5d
$^1$H and $^{13}$C NMR Spectra of Compound 5e
$^1$H and $^{13}$C NMR Spectra of Compound 5f
$^1$H and $^{13}$C NMR Spectra of Compound 7a
$^1$H and $^{13}$C NMR Spectra of Compound 7b

[Chemical structures and spectra images are shown here, but not transcribed due to the nature of the content.]
$^1$H and $^{13}$C NMR Spectra of Compound 7c

![NMR Spectra](image_url)
$^1$H and $^{13}$C NMR Spectra of Compound 7d
$^1$H and $^{13}$C NMR Spectra of Compound 7f
$^1$H and $^{13}$C NMR Spectra of Compound 9a

MeO-Br

9a

1.48, 2.89, 3.14

1.06, 1.18, 2.17, 7.57, 7.75

MeO-Br

9a

126.27, 128.28, 146.49, 77.56, 55.16
$^1$H and $^{13}$C NMR Spectra of Compound 9b

[Image of NMR spectra]

S54
H and $^{13}$C NMR Spectra of Compound 9c
$^1$H and $^{13}$C NMR Spectra of Compound 9d

S56
$^1$H and $^{13}$C NMR Spectra of Compound 9f
$^1$H and $^{13}$C NMR Spectra of Compound 9g
$^1$H and $^{13}$C NMR Spectra of Compound 9h

[Diagram showing NMR spectra with peak assignments]
$^1$H and $^{13}$C NMR Spectra of Compound 9i
$^1$H and $^{13}$C NMR Spectra of Compound 9j
$^1$H and $^{13}$C NMR Spectra of Compound 9k

Chemistry M S Majhi

1H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 7.18 (s, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.92 (s, 1H), 6.85 (t, J = 7.2 Hz, 1H), 2.45 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.9, 134.2, 133.2, 130.1, 128.8, 128.5, 125.2, 124.4, 124.0, 117.7, 117.5, 21.9.
$^1$H and $^{13}$C NMR Spectra of Compound 91
$^1$H and $^{13}$C NMR Spectra of Compound 9m
§H and ¹³C NMR Spectra of Compound 9n

![NMR Spectra Diagram]
$^1$H and $^{13}$C NMR Spectra of Compound 9o
$^1$H and $^{13}$C NMR Spectra of Compound 9p
$^1$H and $^{13}$C NMR Spectra of Compound 9q
$^1$H and $^{13}$C NMR Spectra of Compound 9r

![NMR Spectra](image_url)
$^1$H and $^{13}$C NMR Spectra of Compound 9s

[Image of NMR spectra]

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