Supporting Information
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SUPPORTING INFORMATION

One-Pot Deprotonative Synthesis of Biarylazacyclooctynones

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1 General

Analytical thin layer chromatography (TLC) was performed on Merck 60 F254 aluminum sheets precoated with a 0.25 mm thickness of silica gel. Melting points (m.p.) were measured on a Yanaco MP-J3 and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Alpha with an ATR attachment (Ge) and are reported in wave numbers (cm⁻¹). ¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ¹⁹F NMR (376 MHz) spectra were measured on a JEOL ECZ400 spectrometer. Chemical shifts for ¹H NMR are reported in parts per million (ppm) downfield from tetramethylsilane with the solvent resonance as the internal standard (CHCl₃: δ 7.26 ppm) and coupling constants are in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Chemical shifts for ¹³C NMR are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: δ 77.16 ppm). Chemical shifts for ¹⁹F NMR are reported in ppm from CFCl₃ where C₆F₆ (δ −164.9 ppm) was used as the internal standard. High-resolution mass spectra (HRMS) were performed on a JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment.

2 Materials

Unless otherwise stated, all reactions were conducted in flame-dried glassware under an inert atmosphere of nitrogen. All work-up and purification procedures were carried out with reagent solvents in air. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Flash column chromatography was performed on Wakogel® C-300 (45–75 µm, Wako Pure Chemical Industries, Ltd.). Recycling preparative GPC-HPLC was performed with LC-9201 (Japan Analytical Industry Co., Ltd.) equipped with preparative SEC columns (JAI-GEL-1H and JAI-GEL-2H). Anhydrous THF was purchased from Wako Pure Chemical Industries, Ltd.

3 Synthesis of N-Me BARAC from Enol Triflate (Scheme 2 and Table 1)

Ketolactam 4a was prepared by slightly modifying Bertozzi’s procedure.¹

5,10-Dihydroindeno[1,2-b]indole (2).

A 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a reflux condenser, and an inlet adapter with a three-way stopcock was charged with 1-indanone (3.96 g, 30.0 mmol) in ethanol (21 mL). To the solution was added phenylhydrazine (2.98 mL, 30.3 mmol) followed by acetic acid (10 drops) at room temperature. After stirring at 85 °C (oil bath, reflux) for 15 min, the flask was removed from the oil bath and allowed to cool to room temperature. The precipitated yellow needle crystals were collected by filtration. The crystals were added to a 300-mL round-bottomed flask and dissolved in 2-propanol (102 mL). To the mixture was added conc. sulfuric acid (3.4 mL), and the resulting solution was stirred at 100 °C (oil bath, reflux) for 23 h. Upon cooling to room temperature, the suspension was basified to pH 12 with 1 M aqueous sodium hydroxide to form a brown precipitate. The solid was collected by filtration under reduced pressure and washed

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with ethanol. The title compound was obtained as a grayish brown solid in 87% yield (5.36 g, 26.1 mmol), whose spectroscopic data were consistent with those reported in the literature.\(^1\)

5-Methyl-5,10-dihydropindeno[1,2-b]indole (3a).

A 50-mL one-necked tube equipped with a Teflon-coated magnetic stirring bar was charged with indole 2 (1.00 g, 4.87 mmol) in benzene (6.5 mL). To the solution was added 50 wt% aqueous sodium hydroxide (2.6 mL), tetrabutylammonium iodide (94.2 mg, 0.255 mmol), and iodomethane (2.43 mL, 39.0 mmol). After stirring at 45 °C for 14 h, the mixture was diluted with ethyl acetate and water, and the aqueous layer was extracted twice with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/CH\(_2\)Cl\(_2\) = 1:1) to afford the title compound (0.977 g, 4.46 mmol, 91%) as a pale brown solid, whose spectroscopic data were consistent with those reported in the literature.\(^1\)

5-Methyldibenzo[b,f]azocine-6,12(5H,11H)-dione (4a).

A 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with \(N\)-methylindole 3a (0.999 g, 4.56 mmol), dichloromethane (114 mL), and saturated aqueous sodium bicarbonate (25 mL). After the solution was cooled to 0 °C, \(m\)-CPBA (3.51 g, 13.2 mmol) was added portionwise. The reaction mixture was stirred at 0 °C for 30 min, and the flask was allowed to warm to room temperature for 1 h. The reaction was quenched with 1 M aqueous sodium hydroxide, and the aqueous layer was extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/diethyl ether = 1:1 to 1:3, gradient) to afford the title compound (0.996 g, 3.96 mmol, 87%) as a brown solid, whose spectroscopic data were consistent with those reported in the literature.\(^1\)

5-Methyl-6-oxo-5,6-dihydridibenzo[b,f]azocin-12-yl trifluoromethanesulfonate (5a).

A flame-dried 50-mL two-necked tube equipped with a Teflon-coated magnetic stirring bar, a rubber septum, and a three-way stopcock was charged with KHMDS (1 M in THF, 3.4 mL, 3.4 mmol) and anhydrous THF (4.0 mL). After the resulting solution was cooled to –78 °C, ketolactam 4a (854.7 mg, 3.40 mmol) in THF (13 mL) was added to the solution. After stirring at –78 °C for 1 h, \(N\)-phenyl-bis(trifluoromethanesulfonimide) (1.48 mg, 4.1 mmol) in THF (8.5 mL) was added dropwise to the reaction mixture at –78 °C, and the resulting solution was stirred at room temperature for 1.5 h. The reaction mixture was treated with 1 M aqueous sodium hydroxide (15 mL), and the aqueous layer was extracted twice with diethyl ether (8 mL × 2). The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/diethyl ether = 1:3) to afford the title compound (1.24 g, 3.23 mmol, 95%) as a pale yellow solid. \(R_f = 0.21\) (hexane/diethyl ether = 1:3); M.p. 137–139 °C; IR (ATR, cm\(^{-1}\)) : 2971, 2924, 1738, 1631, 1416, 1216, 1138, 976, 901, 818; \(^1\)H NMR (400 MHz, CDCl\(_3\)) : \(\delta\) 7.46–7.38 (m, 3 H), 7.32–7.25
N-Methyl BARAC 6a.

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with enol triflate 5a (192.1 mg, 0.501 mmol) in THF (1.0 mL). After the resulting solution was cooled to –78 °C, KHMDS (0.50 M in toluene, 1.10 mL, 0.55 mmol) was added dropwise. The reaction mixture was stirred at –78 °C for 40 min, and the reaction was quenched with water (3 mL). The resulting mixture was allowed to warm to room temperature. The mixture was diluted diethyl ether (2 mL), and the aqueous layer was extracted twice with diethyl ether (2 mL × 2). The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/diethyl ether = 1:3) to afford the title compound (97.0 mg, 0.416 mmol, 83%) as a brown solid. Rf = 0.38 (hexane/diethyl ether = 1:3); M.p. decomp. (120 °C); IR (ATR, cm–1): 2924, 1657, 1468, 1447, 1333, 1214, 1180, 1079, 1039, 761, 715, 630; 1H NMR (400 MHz, CDCl3): δ 7.65–7.58 (m, 2H), 7.50–7.35 (m, 6H), 2.73 (s, 3H); 13C{1H} NMR (100 MHz, CDCl3): δ 176.9, 156.6, 149.4, 149.4, 133.3, 121.4, 118.0, 107.9, 103.9, 76.1, 71.5, 63.0; 19F NMR (376 MHz, CDCl3): δ –76.2; HRMS (DART+) m/z: calcd. for C16H12F3NO, 234.0919 [M+H]+; found, 234.0928.

4 One-Pot Synthesis of BARAC Derivatives (Scheme 3 and Table 2)

General Procedure: One-Pot Formation of BARAC from the Corresponding Ketolactam.

A flame-dried 20-mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar and a rubber septum was charged with ketolactam 4 (1.0 equiv) and N-phenyl-bis(trifluoromethanesulfonimide) (1.0 equiv) in THF (0.17 M). After the resulting solution was cooled to –78 °C, KHMDS (0.50 M in toluene, 2.5 equiv) was added dropwise. The reaction mixture was stirred at –78 °C for indicated time, and the reaction mixture was then treated with water. The mixture was allowed to warm to room temperature. The mixture was diluted diethyl ether, and the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography.

Gram-Scale Synthesis of N-Methyl BARAC 6a.

A flame-dried two-necked 500-mL flat-bottomed flask equipped with a Teflon-coated magnetic stirring bar, a rubber septum, and an inlet adapter with a three-way stopcock was charged with ketolactam 4a (1.65 g, 6.56 mmol) and N-phenyl-bis(trifluoromethanesulfonimide) (2.35 g, 6.56 mmol) in THF (39 mL). After the resulting solution was cooled to –78 °C, KHMDS (0.50 M in toluene, 32.8 mL, 16.4 mmol) was added dropwise over 6 min. The reaction mixture was stirred at –78 °C for 1 h, and then the reaction mixture was treated with water (80 mL) and diluted with diethyl ether.
The reaction mixture was allowed to warm to room temperature. The aqueous layer was extracted twice with diethyl ether (15 mL × 2). The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/diethyl ether = 1:3) to afford the N-methyl BARAC 6a (1.45 g, 6.22 mmol, 95%) as a brown solid.

N-Hexyl BARAC 6b.
The title compound was obtained as a brown oil in 64% yield (59.9 mg, 0.197 mmol) from ketolactam 4b (99.5 mg, 0.310 mmol) according to the above procedure (Reaction time: 1 h). R_f = 0.35 (hexane/diethyl ether = 1:1); IR (ATR, cm⁻¹): 2956, 2928, 2858, 1667, 1449, 1354, 1213, 1097, 714; ¹H NMR (400 MHz, CDCl₃): δ 7.62–7.54 (m, 2H), 7.48–7.42 (m, 4H), 7.41–7.34 (m, 2H), 3.05 (dt, 1H, J = 13.2, 7.8 Hz), 2.66 (ddd, 1H, J = 13.2, 8.0, 4.0 Hz), 1.56–1.50 (m, 1H), 1.45–1.17 (m, 7H), 0.85 (t, 3H, J = 6.8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 176.8, 155.1, 149.7, 130.4, 129.4, 129.3, 128.8, 128.1, 127.8, 125.9, 122.7, 122.4, 110.1, 109.3, 51.7, 31.5, 29.1, 26.3, 22.6, 14.1; HRMS (DART⁺) m/z: calcd. for C₂₁H₂₂NO, 304.1701 [M+H]⁺; found, 304.1689.

N-Butenyl BARAC 6c.
The title compound was obtained as a brown oil in 84% yield (66.5 mg, 0.243 mmol) from 4c (84.8 mg, 0.291 mmol) according to the above procedure (Reaction time: 1 h). R_f = 0.28 (hexane/diethyl ether = 1:1); IR (ATR, cm⁻¹): 3069, 2922, 1665, 1449, 1359, 1216, 915, 758, 732; ¹H NMR (400 MHz, CDCl₃): δ 7.63–7.58 (m, 2H), 7.49–7.43 (m, 4H), 7.42–7.34 (m, 2H), 5.71 (ddt, 1H, J = 17.6, 10.8, 6.8 Hz), 5.09–5.01 (m, 2H), 3.15 (dt, 1H, J = 13.2, 8.0 Hz), 2.76 (ddd, 1H, J = 14.0, 8.0, 5.0 Hz), 2.36–2.24 (m, 1H), 2.23–2.12 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 176.7, 154.9, 149.6, 134.9, 130.6, 129.4, 128.9, 128.2, 127.9, 126.5, 126.1, 122.8, 122.3, 117.4, 110.1, 109.2, 51.2, 33.5; HRMS (DART⁺) m/z: calcd. for C₁₉H₁₆NO, 274.1232 [M+H]⁺; found, 274.1232.

N-((3-Triisopropylsiloxy)propyl) BARAC 6d.
The title compound was obtained as a brown oil in 90% yield (83.9 mg, 0.193 mmol) from 4d (97.4 mg, 0.215 mmol) according to the above procedure (Reaction time: 2.5 h). R_f = 0.21 (hexane/diethyl ether = 2:1); IR (ATR, cm⁻¹): 2943, 2866, 1672, 1465, 1377, 1207, 1109, 882, 759, 682; ¹H NMR (400 MHz, CDCl₃): δ 7.62–7.54 (m, 2H), 7.47–7.32 (m, 6H), 3.76 (ddd, 1H, J = 10.8, 6.4, 4.8 Hz), 3.62 (ddd, 1H, J = 10.8, 6.4, 4.4 Hz), 3.37 (dt, 1H, J = 13.2, 7.8 Hz), 2.73 (ddt, 1H, J = 13.2, 8.4, 4.8 Hz), 1.83–1.70 (m, 1H), 1.68–1.56 (m, 1H), 1.10–0.88 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 177.1, 154.9, 149.7, 130.6, 129.4, 129.3, 128.8, 128.2, 127.9, 126.4, 126.0, 122.7, 122.3, 110.2, 109.1, 60.2, 48.4, 32.3, 18.1, 11.9; HRMS (DART⁺) m/z: calcd. for C₁₉H₃₆NO₂Si, 434.2515 [M+H]⁺; found, 434.2517.

N-((11-Triisopropylsiloxy)undecyl) BARAC 6e.
The title compound was obtained as a brown oil in 91% yield (257 mg, 0.471 mmol) from 4e (291 mg, 0.516 mmol) according to the above procedure (Reaction time: 1.5 h, KHMDS 3.0 equiv, PhNTf₂ 1.5 equiv). R_f = 0.26 (hexane/diethyl ether = 2:1); IR (ATR, cm⁻¹): 2923, 2854, 1667, 1465, 1450, 1362,
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1053, 1029; 1H NMR (400 MHz, CDCl3): \(\delta 7.61–7.54 \text{ (m, 2H)}, 7.48–7.41 \text{ (m, 4H)}, 7.41–7.34 \text{ (m, 2H)}, 3.66 \text{ (t, 2H, } J = 6.8 \text{ Hz)}, 3.04 \text{ (dt, 1H, } J = 13.6, 8.0 \text{ Hz)}, 2.70–2.51 \text{ (m, 1H)}, 1.63–1.47 \text{ (m, 4H)}, 1.47–1.14 \text{ (m, 14H)}, 1.14–0.98 \text{ (m, 21H)}; 13C{1H} NMR (100 MHz, CDCl3): \(\delta 176.9, 155.2, 149.8, 130.5, 129.42, 129.39, 128.8, 128.1, 127.9, 126.5, 126.0, 122.7, 122.4, 110.1, 109.3, 63.6, 51.7, 33.2, 29.7, 29.62, 29.59, 29.3, 29.2, 26.7, 25.9, 18.2, 12.1 \text{ (one aliphatic carbon signal is missing due to overlapping)}; HRMS (DART+) \(m/z\): calcd. for C35H52NO2Si, 546.3767 \([M+H]^+\); found, 546.3768.

**N- Allyl BARAC 6f.**

The title compound was obtained as a brown solid in 68% yield as a mixture with tetracyclic compound 7f in 10% yield (44.1 mg, the ratio was determined by 1H NMR.) from ketolactam 4f (60.3 mg, 0.217 mmol) according to the above procedure (Reaction conditions: –60 °C, 10 min). The spectroscopic data were consistent with those reported in the literature.

5 Synthesis of a Coumarin-Tethered BARAC (Scheme 7)

5-(11-Hydroxy)undecyl)dibenzo[b,f]azocine-6,12(5H,11H)-dione (9).

A 30-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with TIPS ether 4e (1.07 g, 1.90 mmol) and THF (4.7 mL). To the resulting solution was added 1.0 M THF solution of TBAF (5.7 mL, 5.7 mmol), and the mixture was stirred at room temperature for 30 min. The reaction mixture was treated with water, and the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (diethyl ether) to afford the title compound (0.682 g, 1.67 mmol, 88%) as a yellow oil, which solidified on standing in a refrigerator. \(R_f = 0.32 \text{ (diethyl ether)}\); IR (ATR, cm\(^{-1}\)): 3438, 2927, 2854, 1688, 1650, 1595, 1482, 1454, 1392, 771, 747, 720; 1H NMR (400 MHz, CDCl3): \(\delta 7.47–7.36 \text{ (m, 3H)}, 7.29–7.24 \text{ (m, 1H)}, 7.23–7.16 \text{ (m, 2H)}, 7.12 \text{ (d, 1H, } J = 8.0 \text{ Hz)}), 7.07–7.01 \text{ (m, 1H)}, 4.57 \text{ (ddd, 1H, } J = 13.2, 9.6, 6.4 \text{ Hz)}, 4.32 \text{ (d, 1H, } J = 17.0 \text{ Hz)}, 3.83 \text{ (d, 1H, } J = 17.0 \text{ Hz)}, 3.63 \text{ (t, 2H, } J = 6.6 \text{ Hz)}, 3.23 \text{ (ddd, 1H, } J = 13.2, 9.6, 4.8 \text{ Hz)}, 1.58–1.16 \text{ (m, 19H)}; 13C{1H} NMR (100 MHz, CDCl3): \(\delta 200.8, 169.8, 140.6, 137.0, 136.0, 133.2, 132.4, 130.2, 129.4, 129.2, 128.8, 128.2, 127.9, 127.4, 63.2, 50.2, 49.8, 32.9, 29.6, 29.49, 29.46, 29.3, 27.9, 27.2, 25.8 \text{ (one aliphatic carbon signal is missing due to overlapping)}; HRMS (DART+) \(m/z\): calcd. for C26H34NO3, 408.2539 \([M+H]^+\); found, 408.2558.

5-(11-Azido)undecyl)dibenzo[b,f]azocine-6,12(5H,11H)-dione (10).

A 10-mL screw-capped test tube equipped with a Teflon-coated magnetic stirring bar was charged with alcohol 9 (300.2 mg, 0.737 mmol) and dichloromethane (1.8 mL). The resulting solution was cooled to 0 °C, methanesulfonyl chloride (63 µL, 0.81 mmol) and triethylamine (154 µL, 1.11 mmol) were added successively. After the resulting mixture was stirred at 0 °C for 20 min, the mixture was treated with water, and the aqueous layer was extracted twice with dichloromethane. The combined

organic extracts were washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude mesylate, which was used directly in the next step without further purification.

A 10-mL screw-capped test tube equipped with a Teflon-coated magnetic stirring bar was charged with the crude mesylate (368 mg) and DMF (2.8 mL). To the resulting solution was added sodium azide (96.9 mg, 1.48 mmol), and the reaction mixture was stirred at 80 °C for 1 h, at which time the reaction mixture was treated with water and diluted with diethyl ether. The aqueous layer was extracted with diethyl ether three times. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/diethyl ether = 2:1) to afford the title compound (0.268 g, 0.620 mmol, 84%) as a yellow oil, which solidified on standing in a refrigerator. $R_f = 0.20$ (hexane/diethyl ether = 2:1); IR (ATR, cm$^{-1}$): 2927, 2855, 2095, 1689, 1653, 1595, 1453, 1279, 770, 746, 719; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46–7.36 (m, 3H), 7.30–7.24 (m, 1H), 7.23–7.16 (m, 2H), 7.12 (d, 1H, $J = 8.0$ Hz), 7.07–7.01 (m, 1H), 4.57 (ddd, 1H, $J = 16.0, 10.0, 6.0$ Hz), 4.32 (d, 1H, $J = 16.8$ Hz), 3.83 (d, 1H, $J = 16.8$ Hz), 3.29–3.19 (m, 3H), 1.64–1.16 (m, 18H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 200.7, 169.8, 140.7, 137.0, 136.1, 133.2, 132.4, 130.2, 129.4, 129.2, 128.8, 128.2, 127.9, 127.4, 51.6, 50.2, 49.9, 29.5, 29.3, 29.2, 28.9, 27.9, 27.2, 26.8 (two aliphatic carbon signals are missing due to overlapping); HRMS (DART$^+$) $m/z$: calcd. for C$_{26}$H$_{33}$N$_4$O$_2$, 433.2604 [M+H]$^+$; found, 433.2599.

5-(11-(4-(2-Oxo-2H-chromen-7-yl)-1H-1,2,3-triazol-1-yl)undecyl)dibenzo[b,f]azocine-6,12(5H,11H)-dione (12).

A 10-mL screw-capped test tube equipped with a Teflon-coated magnetic stirring bar was charged with azide 10 (232 mg, 0.536 mmol), 7-ethynylcoumarin (11) (93.2 mg, 0.55 mmol), and THF (4.1 mL). To the resulting solution was added the aqueous solution of CuSO$_4$·5H$_2$O (67.2 mg, 0.27 mmol in 0.55 mL distilled H$_2$O) and the aqueous of sodium ascorbate (106 mg, 0.54 mmol in 0.55 mL distilled H$_2$O). The reaction mixture was stirred at 65 °C for 19.5 h, at which time the reaction mixture was treated with saturated aqueous ammonium chloride and diluted with diethyl ether. The aqueous layer was extracted twice with diethyl ether/THF = 1:1 and once with dichloromethane. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/methyl acetate = 1:1) to afford the title compound (287 mg, 0.476 mmol, 89%) as a pale green solid. $R_f = 0.18$ (diethyl ether); M.p. 117–120 °C; IR (ATR, cm$^{-1}$): 2927, 2855, 1733, 1688, 1649, 1621, 1453, 1103, 938, 845, 771; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88–7.84 (m, 2H), 7.74–7.69 (m, 2H), 7.54 (d, 1H, $J = 8.4$ Hz), 7.45–7.37 (m, 3H), 7.32–7.24 (m, 1H), 7.23–7.17 (m, 2H), 7.12 (d, 1H, $J = 7.6$ Hz), 7.07–7.02 (m, 1H), 6.42 (d, 1H, $J = 9.6$ Hz), 4.57 (ddd, 1H, $J = 13.6, 10.0, 6.8$ Hz), 4.43 (t, 2H, $J = 7.6$ Hz), 4.32 (d, 1H, $J = 16.8$ Hz), 3.83 (d, 1H, $J = 16.8$ Hz), 3.28–3.18 (m, 1H), 2.02–1.92 (m, 2H), 1.40–1.15 (m, 16H); $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$): $\delta$ 200.8, 169.8, 160.9, 154.6, 146.2, 143.2, 140.6, 137.0, 136.0, 134.6, 133.2, 132.3, 130.2, 129.3, 129.2, 128.8, 128.5, 128.2, 127.9, 127.4, 121.9, 120.7, 118.5, 116.5, 113.5, 50.8, 50.1, 49.8, 30.4, 29.41,
29.38, 29.32, 29.0, 27.9, 27.1, 26.6; HRMS (DART+) m/z: calcd. for C_{37}H_{39}N_{4}O_{4}, 603.2971 [M+H]^+; found, 603.2975.

5-(11-(4-(2-Oxo-2H-chromen-7-yl)-1H-1,2,3-triazol-1-yl)undecyl) BARAC 13.

The title compound was obtained as a pale yellow solid in 51% yield (26.0 mg, 44.5 µmol) from 12 (52.5 mg, 87.1 µmol) according to the above procedure (Reaction time: 4 h, KHMS 4.0 equiv, PhNTf₂ 2.0 equiv). R_f = 0.21 (diethyl ether); M.p. decom. (155 °C); IR (ATR, cm⁻¹): 2925, 2854, 1733, 1661, 1621, 1465, 1449, 1225, 1101, 938, 846, 758, 626; ¹H NMR (400 MHz, CDCl₃): δ 7.87–7.83 (m, 2H), 7.74–7.69 (m, 2H), 7.61–7.51 (m, 3H), 7.48–7.33 (m, 6H), 6.43 (d, 1H, J = 10.0 Hz), 4.42 (t, 2H, J = 7.2 Hz), 3.08–2.99 (m, 1H), 2.70–2.61 (m, 1H), 2.01–1.91 (m, 2H), 1.41–1.13 (m, 16H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 176.9, 160.9, 155.1, 154.6, 149.7, 146.2, 143.2, 134.5, 130.4, 129.42, 129.36, 128.8, 128.5, 128.1, 127.9, 126.5, 125.9, 122.7, 122.4, 121.9, 120.7, 118.5, 116.5, 113.5, 110.1, 109.3, 51.6, 50.7, 30.4, 29.52, 29.48, 29.41, 29.2, 29.10, 29.07, 26.62, 26.57; HRMS (DART+) m/z: calcd. for C_{37}H_{37}N_{4}O_{3}, 585.2866 [M+H]^+; found, 585.2864.

6 Preparation of Ketolactams

5-Hexyl-5,10-dihydroindeno[1,2-b]indole (3b).

A flame-dried 50-mL two-necked tube equipped with a Teflon-coated magnetic stirring bar, a rubber septum, and a three-way stopcock was charged with indole 2 (604 mg, 2.94 mmol) and THF (9 mL). To the resulting suspension was added potassium tert-butoxide (366 mg, 3.23 mmol), and the reaction was stirred at room temperature for 1 h, at which time 1-bromohexane (0.50 mL, 3.5 mmol) was added to the mixture. After stirring at reflux for 14 h, the reaction mixture was treated with water. The aqueous layer was extracted with diethyl ether three times. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/dichloromethane = 5:1) to afford the title compound (421.3 mg, 1.46 mmol, 50%) as a brown solid, whose spectroscopic data were corresponding with those reported in the literature.³

5-Butenyl-5,10-dihydroindeno[1,2-b]indole (3c).

A flame-dried 20-mL two-necked tube equipped with a Teflon-coated magnetic stirring bar, a rubber septum, and a three-way stopcock was charged with sodium hydride (93.9 mg, 2.35 mmol) and DMF (9 mL). To the resulting solution was added a solution of indole 2 (439 mg, 2.14 mmol) in DMF (5.0 mL), and the resulting mixture was stirred at room temperature for 30 min, at which time 4-bromo-1-butene (216 µL, 2.14 mmol) was added to the suspension. After stirring at room temperature for 49 h, the reaction mixture was treated with water, and the aqueous layer was extracted with diethyl ether three times. The combined organic extracts were washed with brine three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/dichloromethane = 5:1) to afford the title compound (421.3 mg, 1.46 mmol, 50%) as a brown solid, whose spectroscopic data were corresponding with those reported in the literature.³

5:1) to afford the title compound (65.2 mg, 0.251 mmol, 12%) as a pale yellow solid. R_f = 0.40 (hexane/dichloromethane = 5:1); M.p. 41–42 °C; IR (ATR, cm–1): 3056, 1609, 1526, 1497, 1461, 1439, 1347, 1017, 735; ¹H NMR (400 MHz, CDCl₃): δ 7.77–7.62 (m, 1H), 7.60–7.54 (m, 2H), 7.40 (d, 1H, J = 8.0 Hz), 7.35 (dd, 1H, J = 7.2, 7.2 Hz), 7.25–7.18 (m, 2H), 7.18–7.12 (m, 1H), 5.88 (ddt, 1H, J = 17.2, 10.0, 6.8 Hz), 5.19–5.11 (m, 1H), 5.09–5.04 (m, 1H), 4.50 (t, 2H, J = 7.6 Hz), 3.73 (s, 2H), 2.67 (dt, 2H, J = 7.2, 6.8 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.4, 144.2, 141.5, 135.5, 134.7, 126.7, 125.7, 124.7, 124.5, 121.4, 120.8, 119.8, 119.3, 117.8, 117.4, 110.1, 44.4, 35.1, 30.2; HRMS (DART+) m/z: calcd. for C₁₉H₁₈N, 260.1439 [M+H]^+; found, 260.1444.

5-((3-Triisopropylsiloxy)propyl)-5,10-dihydroindeno[1,2-b]indole (3d).
A flame-dried 20-mL two-necked tube equipped with a Teflon-coated magnetic stirring bar, a rubber septum, and a three-way stopcock was charged with sodium hydride (91.8 mg, 2.30 mmol) and DMF (2.0 mL). To the resulting solution was added a solution of indole (430 mg, 2.10 mmol) in DMF (5.0 mL), and the resulting mixture was stirred at room temperature for 30 min, at which time 1-bromo-3-(triisopropylsiloxy)propane (629 mg, 2.1 mmol) was added to the suspension. After stirring at room temperature for 1 h, the reaction mixture was treated with water, and the aqueous layer was extracted with diethyl ether three times. The combined organic extracts were washed with brine three times, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/dichloromethane = 5:1) to afford the title compound (471 mg, 1.12 mmol, 53%) as a pale yellow solid. R_f = 0.39 (hexane/dichloromethane = 5:1); M.p. 46–47 °C; IR (ATR, cm–1): 2942, 2891, 2865, 1610, 1462, 1384, 1347, 1099, 1069, 882; ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, 1H, J = 7.6 Hz), 7.62 (d, 1H, J = 7.2 Hz), 7.54 (d, 1H, J = 8.0 Hz), 7.47 (d, 1H, J = 8.0 Hz), 7.32 (dd, 1H, J = 7.6, 7.6 Hz), 7.24–7.18 (m, 2H), 7.13 (dd, 1H, J = 7.2, 7.2 Hz), 4.60 (t, 2H, J = 7.2 Hz), 3.82 (t, 2H, J = 5.6 Hz), 3.73 (s, 2H), 2.17–2.08 (m, 2H), 1.21–1.03 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.3, 144.4, 141.5, 135.5, 126.7, 125.6, 124.7, 124.2, 121.2, 120.5, 119.6, 119.1, 118.1, 110.2, 60.5, 41.7, 34.2, 30.3, 18.2, 12.1; HRMS (DART+) m/z: calcd. for C₂₇H₃₈NOSi, 420.2723 [M+H]^+; found, 420.2706.

11-((Triisopropylsiloxy)undecyl) bromide.
A 300-mL round-bottomed flask equipped with a Teflon-coated magnetic stirring bar was charged with 11-bromo-1-undecanol (2.06 g, 8.22 mmol), imidazole (1.40 g, 20.6 mmol), and dichloromethane (42 mL). To the solution was added triisopropylsilyl chloride (1.92 mL, 9.0 mmol) dropwise. After stirring at room temperature for 3 h, the reaction mixture was treated with water, and the aqueous layer was extracted twice with dichloromethane. The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/diethyl ether = 9:1) to afford the title compound (3.27 g, 8.02 mmol, 98%) as a colorless oil. R_f = 0.29 (hexane); IR (ATR, cm–1): 2927, 2864, 1462 1346, 1103, 882; ¹H NMR (400 MHz, CDCl₃): δ 3.66 (t, 2H, J = 6.8 Hz), 3.41 (t, 2H, J = 6.8 Hz), 3.18 (t, 2H, J = 6.8 Hz), 1.85 (tt, 2H, J = 6.8, 6.8 Hz), 1.58–1.49 (m, 2H), 1.46–1.38 (m, 2H), 1.37–1.24 (m, 12H), 1.14–0.99 (m, 21H); ¹³C{¹H} NMR (100 MHz,
A flame-dried 50-mL two-necked tube equipped with a Teflon-coated magnetic stirring bar, a rubber septum, and a three-way stopcock was charged with sodium hydride (72.0 mg, 1.8 mmol) and DMF (1.8 mL). To the resulting solution was added the solution of indole 2 (326 mg, 1.59 mmol) in DMF (4.5 mL), and the resulting mixture was stirred at room temperature for 30 min, at which time 11-(triisopropylsiloxy)undecyl bromide (0.70 g, 1.72 mmol) was added to the suspension. After stirring at room temperature for 1 h, the reaction mixture was treated with water, and the aqueous layer was extracted twice with diethyl ether. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a crude material, which was purified by silica gel column chromatography (hexane/dichloromethane = 5:1) to afford the title compound (611 mg, 1.15 mmol, 72%) as a yellow oil. R_f = 0.33 (hexane/dichloromethane = 5:1); IR (ATR, cm⁻¹): 2927, 2864, 1462, 1103, 882, 735, 681; ¹H NMR (400 MHz, CDCl₃): δ 7.63 (d, 1H, J = 8.0 Hz), 7.56 (dd, 2H, J = 8.6, 8.6 Hz), 7.39 (d, 1H, J = 8.0 Hz), 7.35 (dd, 1H, J = 7.6, 7.6 Hz), 7.24–7.17 (m, 2H), 7.16–7.10 (m, 1H), 4.42 (t, 2H, J = 7.2 Hz), 3.73 (s, 2H), 3.65 (t, 2H, J = 6.8 Hz), 1.91 (tt, 2H, J = 7.2, 7.2 Hz), 1.59–1.47 (m, 2H), 1.47–1.37 (m, 2H), 1.36–1.19 (m, 12H), 1.13–1.00 (m, 21H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 148.4, 144.3, 141.4, 135.6, 126.7, 125.8, 124.7, 124.2, 121.2, 120.5, 119.6, 119.2, 117.9, 110.1, 110.0, 63.6, 45.0, 33.2, 31.0, 30.3, 29.73, 29.67, 29.61, 29.58, 29.56, 27.2, 25.9, 18.2, 12.2; HRMS (DART⁺) m/z: calcd. for C₃₅H₅₄NOSi, 532.3975 [M+H]⁺; found, 532.3975.

5-Allyl-5,10-dihydroindeno[1,2-b]indole (3f).
The title compound was obtained as a white solid in 51% yield (628 mg, 2.56 mmol) from indole 2 (1.03 g, 5.0 mmol) according to the reported in the literature.⁴

The title compound was obtained as a pale yellow solid in 62% yield (301 mg, 0.937 mmol) from indole 3b (421 mg, 1.50 mmol) according to the synthesis of 4a. R_f = 0.29 (hexane/diethyl ether = 1:1); M.p. 107–108 °C; IR (ATR, cm⁻¹): 2957, 2926, 2859, 1682, 1652, 1594, 1370, 1309, 1106, 771, 748, 725; ¹H NMR (400 MHz, CDCl₃): δ 7.46–7.37 (m, 3H), 7.31–7.24 (m, 1H), 7.23–7.17 (m, 2H), 7.15–7.11 (m, 1H), 7.07–7.02 (m, 1H), 4.57 (ddd, 1H, J = 13.2, 10.0, 6.4 Hz), 4.33 (d, 1H, J = 17.0 Hz), 3.83 (d, 1H, J = 17.0 Hz), 3.24 (ddd, 1H, J = 13.2, 9.6, 5.0 Hz), 1.60–1.37 (m, 2H), 1.35–1.17 (m, 6H), 0.85 (t, 3H, J = 7.6 Hz); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 200.7, 169.8, 140.6, 137.0, 136.0, 133.2, 132.4, 130.2, 129.4, 129.2, 128.8, 128.2, 127.9, 127.4, 50.2, 49.8, 31.5, 27.9, 26.9, 22.6, 14.1; HRMS (DART⁺) m/z: calcd. for C₂₁H₂₅NO₂, 322.1807 [M+H]⁺; found, 322.1812.

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5-Butenylidenobenzof[bf]azocine-6,12(5H,11H)-dione (4c).
The title compound was obtained as a pale yellow solid in 90% yield (194 mg, 0.666 mmol) from indole 3c (194 mg, 0.736 mmol) according to the synthesis of 4a. R_f = 0.22 (hexane/diethyl ether = 1:1); M.p. 99–101 °C; IR (ATR, cm⁻¹): 2923, 2853, 1683, 1646 1453, 1366, 1274, 775, 745; ¹H NMR (400 MHz, CDCl₃): δ 7.45 (dd, 1H, J = 8.0, 8.0, 1.6 Hz), 7.43–7.38 (m, 2H), 7.28 (dd, 1H, J = 8.0, 7.2, 0.8 Hz), 7.23–7.16 (m, 2H), 7.14 (d, 1H, J = 7.2 Hz), 7.07–7.01 (m, 1H), 5.73 (ddt, 1H, J = 17.0, 10.0, 6.8 Hz), 5.10–5.05 (m, 1H), 5.05–5.01 (m, 1H), 4.79 (dt, 1H, J = 13.6, 7.6 Hz), 4.38 (d, 1H, J = 16.6 Hz), 3.80 (d, 1H, J = 16.6 Hz), 3.35 (ddd, 1H, J = 13.6, 7.6, 5.4 Hz), 2.36–2.15 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 200.5, 170.1, 140.5, 136.8, 136.0, 134.9, 133.3, 132.5, 130.3, 129.6, 129.2, 128.8, 128.2, 127.8, 127.5, 117.8, 50.2, 49.4; HRMS (DART⁺) m/z: calcd. for C₁₀H₁₈NO₂Si, 292.1338 [M+H]⁺; found, 292.1332.

5-(3-Triisopropylsiloxy)propylidenobenzof[bf]azocine-6,12(5H,11H)-dione (4d).
The title compound was obtained as a pale yellow solid in 80% yield (323 mg, 0.716 mmol) from indole 3d (375 mg, 0.894 mmol) according to the synthesis of 4a. R_f = 0.35 (hexane/diethyl ether = 1:1); M.p. 85–86 °C; IR (ATR, cm⁻¹): 2943, 2867, 1681 1645, 1453, 1391, 1106, 883, 678; ¹H NMR (400 MHz, CDCl₃): δ 7.47–7.37 (m, 3H), 7.31–7.23 (m, 1H), 7.22–7.13 (m, 3H), 7.07–7.02 (m, 1H), 4.75–4.66 (m, 1H), 4.32 (d, 1H, J = 16.8 Hz), 3.83 (d, 1H, J = 16.8 Hz), 3.74–3.63 (m, 2H), 3.49–3.40 (m, 1H), 1.85–1.63 (m, 2H), 1.11–0.93 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 200.4, 169.8, 140.7, 136.9, 135.8, 133.2, 132.3, 130.2, 129.4, 129.1, 128.7, 128.1, 127.8, 127.4, 60.8, 49.8, 47.4, 31.2, 18.0, 11.9; HRMS (DART⁺) m/z: calcd. for C₂₇H₃₈NO₃Si, 452.2621 [M+H]⁺; found, 452.2605.

The title compound was obtained as a pale brown solid in 62% yield (383 mg, 0.679 mmol) from indole 3e (584 mg, 1.10 mmol) according to the synthesis of 4a. R_f = 0.29 (hexane/diethyl ether = 2:1); M.p. 67–68 °C; IR (ATR, cm⁻¹): 2928, 2863, 1690, 1656, 1596, 1455, 1387, 1103, 882, 680; ¹H NMR (400 MHz, CDCl₃): δ 7.47–7.36 (m, 3H), 7.30–7.24 (m, 1H), 7.22–7.16 (m, 2H), 7.12 (d, 1H, J = 7.6 Hz), 7.07–7.00 (m, 1H), 4.56 (dd, 1H, J = 13.2, 10.4, 6.4 Hz), 4.32 (d, 1H, J = 17.0 Hz), 3.83 (d, 1H, J = 17.0 Hz), 3.65 (t, 2H, J = 6.8 Hz), 3.23 (ddd, 1H, J = 13.2, 10.0, 4.8 Hz), 1.57–1.36 (m, 4H), 1.35–1.17 (m, 14H), 1.14–0.97 (m, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 200.7, 169.8, 140.7, 137.0, 136.0, 133.2, 132.4, 130.2, 129.4, 129.2, 128.8, 128.2, 127.9, 127.4, 63.7, 50.2, 49.9, 33.2, 29.7, 29.6, 29.4, 28.0, 27.2, 26.0, 18.2, 12.2 (two aliphatic carbon signals are missing due to overlapping); HRMS (DART⁺) m/z: calcd. for C₁₃H₃₆NO₃Si, 564.3873 [M+H]⁺; found, 564.3886.

The title compound was obtained as a pale yellow solid in 99% yield (137 mg, 0.494 mmol) from indole 3f (122 mg, 0.497 mmol) according to the synthesis of 4a. R_f = 0.23 (hexane/diethyl ether = 1:1); M.p. 89–91 °C; IR (ATR, cm⁻¹): 2910, 1687, 1649, 1453, 1384, 1280, 1025, 778, 746, 668; ¹H NMR (400 MHz, CDCl₃): δ 7.47–7.36 (m, 3H), 7.30–7.24 (m, 1H), 7.24–7.18 (m, 2H), 7.14 (dd, 1H, J = 7.8, 1.0 Hz), 7.07–7.02 (m, 1H), 5.85 (ddt, 1H, J = 17.6, 10.0, 6.8 Hz), 5.17–5.08 (m, 2H), 4.98 (dd, 1H, J = 14.4, 6.8 Hz), 4.32 (d, 1H, J = 16.8 Hz), 4.00 (dd, 1H, J = 14.4, 6.8 Hz), 3.82 (d, 1H, J = 16.8
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Hz; \(^{13}\)C\(^{1}H\) NMR (100 MHz, CDCl\(_3\)): \(\delta\) 200.3, 169.6, 140.2, 136.6, 135.9, 133.1, 132.5, 131.9, 130.4, 129.5, 129.3, 128.9, 128.2, 128.1, 127.4, 120.4, 52.8, 49.7; HRMS (DART\(^{+}\)) \(m/z\): calcd. for C\(_{18}\)H\(_{15}\)NO\(_2\), 278.1181 [M+H]\(^{+}\); found, 278.1183.
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{5a}$
$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^6c$
$^1$H NMR (400 MHz, CDCl$_3$)

![NMR Spectrum](image)

X : parts per Million : Proton

1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6

Abundance

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X : parts per Million : Proton
$^{13}$C NMR (100 MHz, CDCl$_3$)

X: parts per Million: Carbon13
$^1$H NMR (400 MHz, CDCl$_3$)

S25
$^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$

![Chemical Structure](image)

X : parts per Million : Carbon13

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S27
$^1$H NMR (400 MHz, CDCl$_3$)

![Chemical Structure](image)

**X : parts per Million : Proton**

**Abundance**

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**S28**
$^1\text{H NMR (400 MHz, CDCl}_3\text{)}$

3c
$^{13}$C NMR (100 MHz, CDCl$_3$)

3c
$^1$H NMR (400 MHz, CDCl$_3$)

X : parts per Million : Proton
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

4c
\[ ^{13}\text{C NMR (100 MHz, CDCl}_3) \]

![Chemical Structure](image)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$C NMR (100 MHz, CDCl$_3$)
$^1H$ NMR (400 MHz, CDCl$_3$)

![NMR spectrum of compound 4f](image)