Hypervalent iodine-mediated alkene difunctionalization of vinylphenols: diastereoselective synthesis of substituted indoles and indolizines

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I) General Experimental Methods

All reactions were carried out under a nitrogen or argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF), pentane, diethyl ether (Et₂O), 1,2-dimethoxyethane (DME), 1,4-dioxane, methylene chloride (CH₂Cl₂), chloroform (CHCl₃) obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Ethyl acetate (EtOAc), diethyl ether (Et₂O), N,N-dimethylacetamide (DMA), methylene chloride (CH₂Cl₂), acetone and hexanes were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and an ethanolic solution of ammonium molybdate, anisaldehyde, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on a Bruker AV-400 instrument and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. Melting points (m.p.) are uncorrected, and recorded on a Buchi
B-540 melting point apparatus. High-resolution mass spectra (HRMS) were recorded on an Agilent ESI TOF (time of flight) mass spectrometer at 3500 V emitter voltage.

II) General Experimental Procedures and Characterization data

General procedure for the synthesis of 3-substituted indoles 2a–t through hypervalent iodine-mediated alkene difunctionalization of o-vinylphenols 1:

To a stirred solution of o-vinylphenols 1 (0.2 mmol) and indoles 3 (0.24 mmol) in CH₂Cl₂ (10 mL) at –20 °C was treated with PhI(OAc)₂ (0.24 mmol). The resulting mixture was stirred for 1 h before it was quenched with saturated Na₂S₂O₃ (sat. aq., 10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 20:1) afforded corresponding products 2a–t.

Starting materials: o-Vinylphenols 1a–e, 1s and 1t, indoles 3a and 3f–r were prepared according to the known literature procedures.

5-Butyl-1-methyl-1H-indole (3l): white solid; m.p. 40–42 °C; IR (film) vₘₐₓ 2919, 2594, 1560, 1110, 893, 741 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (s, 1 H), 7.21 (d, J = 8.3 Hz, 1 H), 7.05 (dd, J = 8.3, 1.2 Hz, 1 H), 6.97 (d, J = 3.0 Hz, 1 H), 6.40 (dd, J = 2.9, 0.6 Hz, 1 H), 3.72
(s, 3 H), 2.76–2.61 (m, 2 H), 1.72–1.57 (m, 2 H), 1.37 (dq, \( J = 14.6, 7.3 \) Hz, 2 H), 0.92 ppm (t, \( J = 7.3 \) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 135.3, 133.7, 128.7, 128.6, 122.6, 119.9, 108.8, 100.4, 35.7, 34.5, 32.7, 22.4, 14.0 \) ppm. HRMS (ESI): calcd for C\(_{13}\)H\(_{18}\)N\(^{+}\) [M + H\(^{+}\)] 188.1434, found 188.1435.

5-(2-Methoxyphenyl)-1-methyl-1\(^{1}\)H-indole (3q): white solid; m.p. 117–119 °C; IR (film) \( \nu_{\text{max}} \) 2939, 2907, 1479, 1240, 1026, 886, 802, 748, 721 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.84 \) (s, 1 H), 7.53–7.44 (m, 2 H), 7.44–7.34 (m, 2 H), 7.16–7.09 (m, 2 H), 7.06 (d, \( J = 8.2 \) Hz, 1 H), 6.59 (s, 1 H), 3.87 (s, 3 H), 3.85 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 156.6, 135.9, 132.0, 131.3, 129.7, 129.0, 128.4, 127.9, 123.6, 121.7, 120.7, 111.2, 108.5, 101.2, 55.5, 32.8 ppm. HRMS (ESI): calcd for C\(_{16}\)H\(_{16}\)NO\(^{+}\) [M + H\(^{+}\)] 238.1226, found 238.1228.

5-(Furan-2-yl)-1-methyl-1\(^{1}\)H-indole (3r): white solid; m.p. 70–72 °C; IR (film) \( \nu_{\text{max}} \) 2992, 2907, 1390, 1140, 1022, 986, 876, 738 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.03 \) (s, 1 H), 7.62 (dd, \( J = 8.6, 1.3 \) Hz, 1 H), 7.51 (d, \( J = 0.9 \) Hz, 1 H), 7.35 (d, \( J = 8.6 \) Hz, 1 H), 7.08 (d, \( J = 3.0 \) Hz, 1 H), 6.64 (d, \( J = 3.2 \) Hz, 1 H), 6.56 (d, \( J = 3.0 \) Hz, 1 H), 6.53 (dd, \( J = 3.1, 1.8 \) Hz, 1 H), 3.79 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 155.5, 141.0, 136.2, 129.5, 128.6, 122.8, 118.4, 116.3, 111.5, 109.4, 102.9, 101.4, 32.8 ppm. HRMS (ESI): calcd for C\(_{13}\)H\(_{12}\)NO\(^{+}\) [M + H\(^{+}\)] 198.0913, found 198.0913.

2-((5,5-Dimethyltetrahydrofuran-2-yl)(1-methyl-1\(^{1}\)H-indol-3-yl)methyl)phenol (2a): obtained in 84% yield and >20:1 dr as a white solid; m.p. 112–114 °C; IR (film)
$v_{\text{max}}$ 3232, 3052, 2970, 1612, 1481, 1372, 1232, 1131, 1015, 884, 741 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.84 (s, 1 H), 7.27 (d, $J$ = 8.2 Hz, 1 H), 7.23 (d, $J$ = 7.8 Hz, 1 H), 7.18 (t, $J$ = 7.5 Hz, 1 H), 7.09 (t, $J$ = 7.6 Hz, 1 H), 7.03 (s, 1 H), 6.97 (t, $J$ = 7.5 Hz, 2 H), 6.84 (d, $J$ = 7.6 Hz, 1 H), 6.67 (t, $J$ = 7.4 Hz, 1 H), 4.93 (s, 1 H), 4.82 (td, $J$ = 7.1, 2.3 Hz, 1 H), 3.78 (s, 3 H), 2.16 (dt, $J$ = 13.8, 6.9 Hz, 1 H), 1.96–1.85 (m, 1 H), 1.74–1.63 (m, 1 H), 1.34–1.28 (m, 1 H), 1.27 (s, 3 H), 1.19 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.5, 136.7, 130.9, 127.9(2C), 127.8, 127.0, 121.7, 119.8, 119.6, 118.9, 117.8, 113.2, 108.9, 82.2(2C), 41.4, 38.4, 32.7, 28.2, 27.6, 27.2 ppm; HRMS (ESI): calcd for C$_{22}$H$_{26}$NO$_2$ $^+$ [M + H$^+$] 336.1958, found 336.1963.

2-((5,5-Dimethyltetrahydrofuran-2-yl)(1-methyl-1H-indol-3-yl)methyl)-4-methyl-phenol (2b): obtained in 82% yield and >20:1 dr as a white solid; m.p. 110–112 °C; IR (film) $v_{\text{max}}$ 3235, 2969, 2925, 1614, 1492, 1371, 1229, 1130, 1016, 881, 819, 737 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.69 (s, 1 H), 7.28 (d, $J$ = 8.0 Hz, 1 H), 7.23 (d, $J$ = 10.0 Hz, 1 H), 7.15 (t, $J$ = 7.4 Hz, 1 H), 7.04 (s, 1 H), 6.97 (t, $J$ = 7.4 Hz, 1 H), 6.85 (dt, $J$ = 14.0, 4.9 Hz, 2 H), 6.65 (s, 1 H), 4.82 (d, $J$ = 2.3 Hz, 1 H), 4.74 (td, $J$ = 7.3, 2.6 Hz, 1 H), 3.76 (s, 3 H), 2.11 (dd, $J$ = 13.7, 6.2 Hz, 1 H), 2.05 (s, 3 H), 1.87 (ddd, $J$ = 16.1, 12.5, 7.5 Hz, 1 H), 1.66 (dt, $J$ = 12.2, 7.8 Hz, 1 H), 1.37–1.27 (m, 1 H), 1.23 (s, 3 H), 1.14 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 153.1, 136.7, 131.3, 128.8, 128.5, 128.0, 127.8, 127.2, 121.7, 119.6, 118.9, 117.8, 113.2, 109.0, 82.4, 82.3, 41.8, 38.5, 32.8, 28.5, 27.8, 27.4, 20.6 ppm; HRMS (ESI): calcd for C$_{23}$H$_{28}$NO$_2$ $^+$ [M + H$^+$] 350.2115, found 350.2112.
2-((5,5-Dimethyltetrahydrofuran-2-yl)(1-methyl-1H-indol-3-yl)methyl)-4-fluoro-phenol (2c): obtained in 83% yield and >20:1 dr as a colorless oil; IR (film) \( \nu_{\text{max}} \) 3231, 2969, 2928, 1615, 1373, 1237, 1134, 1017, 879, 821, 741 cm\(^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.60 \) (s, 1 H), 7.33–7.28 (m, 1 H), 7.22 (d, \( J = 7.6 \) Hz, 2 H), 7.04–6.97 (m, 2 H), 6.91 (dd, \( J = 8.8, 5.0 \) Hz, 1 H), 6.78 (td, \( J = 8.3, 3.1 \) Hz, 1 H), 6.53 (dd, \( J = 9.9, 3.1 \) Hz, 1 H), 4.98 (d, \( J = 2.5 \) Hz, 1 H), 4.82 (td, \( J = 7.2, 2.8 \) Hz, 1 H), 3.82 (s, 3 H), 2.20 (dt, \( J = 14.7, 6.9 \) Hz, 1 H), 1.97–1.85 (m, 1 H), 1.80 (s, 1 H), 1.37–1.29 (m, 1 H), 1.27 (s, 3 H), 1.19 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 157.9, 155.6, 151.6 \) (d, \( J_{C-F} = 2.0 \) Hz), 136.8, 129.5 (d, \( J_{C-F} = 6.5 \) Hz), 127.5, 126.8, 122.0, 119.3 (d, \( J_{C-F} = 38.5 \) Hz), 118.7 (d, \( J_{C-F} = 8.0 \) Hz), 116.9 (d, \( J_{C-F} = 23.6 \) Hz), 114.2 (d, \( J_{C-F} = 22.7 \) Hz), 112.6, 109.1, 82.3, 82.1, 40.7, 38.5, 32.8, 27.9, 27.6, 27.1 ppm; HRMS (ESI): calcd for C\(_{22}\)H\(_{25}\)FNO\(_2\)\(^+\) [M + H\(^+\)] 354.1864, found 354.1868.

4-Chloro-2-((5,5-dimethyltetrahydrofuran-2-yl)(1-methyl-1H-indol-3-yl)methyl)-phenol (2d): obtained in 86% yield and >20:1 dr as a white solid; m.p. 107–109 °C; IR (film) \( \nu_{\text{max}} \) 3214, 2970, 2927, 1744, 1613, 1477, 1372, 1264, 1230, 1130, 1017, 881, 822, 740 cm\(^{-1} \); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.89 \) (s, 1 H), 7.30 (d, \( J = 8.2 \) Hz, 1 H), 7.24 (d, \( J = 5.1 \) Hz, 1 H), 7.20 (d, \( J = 7.5 \) Hz, 2 H), 7.04 (dt, \( J = 14.6, 5.6 \) Hz, 2 H), 6.90 (d, \( J = 8.5 \) Hz, 1 H), 6.81 (d, \( J = 2.5 \) Hz, 1 H), 4.92 (d, \( J = 2.4 \) Hz, 1 H), 4.78 (td, \( J = 7.3, 2.6 \) Hz, 1 H), 3.81 (s, 3 H), 2.19 (dd, \( J = 13.1, 6.8 \) Hz, 1 H), 1.96–1.82 (m, 1 H), 1.81–1.67 (m, 1 H), 1.42–1.31 (m, 1 H), 1.27 (s, 3 H), 1.19 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = \)
2-((5,5-Dimethyltetrahydrofuran-2-yl)(1-methyl-1H-indol-3-yl)methyl)-4-Methoxyphenol (2e): obtained in 71% yield and >20:1 dr as a white solid; m.p. 96–98 °C; IR (film) \( \nu_{\text{max}} \) 3229, 3033, 2970, 1612, 1481, 1370, 1132, 1031, 862, 740 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 8.40 (s, 1 H), 7.28–7.25 (m, 2 H), 7.18 (t, \( J = 7.2 \) Hz, 1 H), 7.02 (s, 1 H), 6.99 (dd, \( J = 11.4, 4.4 \) Hz, 1 H), 6.90 (d, \( J = 8.7 \) Hz, 1 H), 6.65 (dd, \( J = 8.7, 3.1 \) Hz, 1 H), 6.43 (d, \( J = 3.1 \) Hz, 1 H), 4.93 (d, \( J = 2.6 \) Hz, 1 H), 4.80 (td, \( J = 7.2, 2.8 \) Hz, 1 H), 3.80 (s, 3 H), 3.58 (s, 3 H), 2.17 (dt, \( J = 14.6, 6.8 \) Hz, 1 H), 1.93 (ddd, \( J = 16.1, 10.6, 7.3 \) Hz, 1 H), 1.75–1.64 (m, 1 H), 1.36–1.28 (m, 1 H), 1.26 (s, 3 H), 1.18 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 153.0, 149.5, 136.8, 129.1, 127.8, 127.0, 121.8, 119.6, 119.0, 118.2, 117.2, 113.0, 112.0, 108.9, 82.4, 82.1, 55.5, 41.1, 38.5, 32.8, 28.2, 27.7, 27.2 ppm; HRMS (ESI): calcd for C\(_{22}\)H\(_{25}\)ClNO\(_2\) \([\text{M + H}^+]\) 370.1568, found 370.1593.

2-((1-Butyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2f): obtained in 80% yield and >20:1 dr as a colorless oil; IR (film) \( \nu_{\text{max}} \) 3256, 3049, 2965, 1738, 1612, 1465, 1369, 1272, 1234, 1134, 1016, 884, 744 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 8.89 (s, 1 H), 7.30 (d, \( J = 8.2 \) Hz, 1 H), 7.24 (d, \( J = 8.8 \) Hz, 1 H), 7.15 (dd, \( J = 11.2, 4.0 \) Hz, 1 H), 7.11–7.08 (m, 2 H), 7.01–6.92 (m, 2 H), 6.83 (dd, \( J = 7.5, 1.3 \) Hz, 1 H), 6.73–6.60 (m, 1 H), 4.92 (d, \( J = 2.0 \) Hz, 1 H), 4.82 (td, \( J = 7.2, 2.5 \) Hz, 1 H), 4.11 (dd, \( J = 7.1, 5.6 \) Hz, 2 H), 2.49 (d, \( J = 6.4 \) Hz, 2 H), 2.17 (dt, \( J = 14.6, 6.8 \) Hz, 1 H), 1.93 (ddd, \( J = 16.1, 10.6, 7.3 \) Hz, 1 H), 1.75–1.64 (m, 1 H), 1.36–1.28 (m, 1 H), 1.26 (s, 3 H), 1.18 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 153.0, 149.5, 136.8, 129.1, 127.8, 127.0, 121.8, 119.6, 119.0, 118.2, 117.2, 113.0, 112.0, 108.9, 82.4, 82.1, 55.5, 41.1, 38.5, 32.8, 28.2, 27.7, 27.2 ppm; HRMS (ESI): calcd for C\(_{23}\)H\(_{28}\)NO\(_3\) \([\text{M + H}^+]\) 366.2064, found 366.2067.
2.17 (dt, $J = 13.3$, 7.3 Hz, 1 H), 1.98–1.88 (m, 1 H), 1.86–1.81 (m, 2 H), 1.74–1.63 (m, 1 H), 1.42–1.31 (m, 3 H), 1.27 (s, 3 H), 1.19 (s, 3 H), 0.96 ppm (t, $J = 7.4$ Hz, 3 H);

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 155.5$, 136.0, 130.9, 128.0(2C), 127.9, 126.0, 121.5, 119.9, 119.7, 118.8, 117.9, 113.0, 109.2, 82.3, 82.2, 46.1, 41.4, 38.5, 32.4, 28.3, 27.7, 27.2, 20.2, 13.7 ppm; HRMS (ESI): calcd for C$_{25}$H$_{32}$NO$_2^+ \ [M + H^+]$ 378.2428, found 378.2428.

2-((1-(Cyclopropylmethyl)-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2g): obtained in 78% yield and >20:1 dr as a white solid; m.p. 121–123 °C; IR (film) $\nu_{\text{max}}$ 3228, 3012, 2969, 1592, 1380, 1372, 1269, 1131, 1015, 854, 741 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.89$ (s, 1 H), 7.32 (d, $J = 8.2$ Hz, 1 H), 7.27–7.22 (m, 1 H), 7.16 (t, $J = 7.6$ Hz, 2 H), 7.13–7.06 (m, 1 H), 6.97 (t, $J = 7.4$ Hz, 2 H), 6.84 (t, $J = 8.3$ Hz, 1 H), 6.68 (t, $J = 7.4$ Hz, 1 H), 4.92 (d, $J = 2.0$ Hz, 1 H), 4.83 (td, $J = 7.2$, 2.5 Hz, 1 H), 3.98 (ddd, $J = 32.0$, 14.3, 6.7 Hz, 2 H), 2.16 (td, $J = 13.7$, 7.1 Hz, 1 H), 1.98–1.85 (m, 1 H), 1.70 (dt, $J = 12.3$, 7.4 Hz, 1 H), 1.38–1.28 (m, 2 H), 1.28 (s, 3 H), 1.19 (s, 3 H), 0.63 (d, $J = 7.8$ Hz, 2 H), 0.38 ppm (d, $J = 4.7$ Hz, 2 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 155.5$, 136.2, 130.9, 128.0, 127.9(2C), 125.8, 121.6, 119.9, 119.6, 118.9, 117.9, 113.1, 109.2, 82.3, 82.2, 50.6, 41.6, 38.5, 28.3, 27.7, 27.3, 11.4, 4.1, 4.0 ppm; HRMS (ESI): calcd for C$_{25}$H$_{30}$NO$_2^+ \ [M + H^+]$ 376.2271, found 376.2272.

2-((1-Benzyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2h): obtained in 75% yield and >20:1 dr as a white solid; m.p. 58–60 °C; IR (film) $\nu_{\text{max}}$ 3201, 2970, 1492, 1431, 1372, 1139, 998, 804, 741 cm$^{-1}$; $^1$H NMR (400 MHz,
CDCl$_3$ $\delta$ = 8.88 (s, 1 H), 7.38–7.26 (m, 3 H), 7.25 (d, $J = 10.1$ Hz, 2 H), 7.18–7.07 (m, 5 H), 6.99 (t, $J = 7.5$ Hz, 2 H), 6.85 (dd, $J = 7.6$, 1.5 Hz, 1 H), 6.69 (td, $J = 7.5$, 1.2 Hz, 1 H), 5.43–5.30 (m, 2 H), 4.95 (d, $J = 2.3$ Hz, 1 H), 4.82 (td, $J = 7.2$, 2.6 Hz, 1 H), 2.13 (dt, $J = 14.6$, 6.8 Hz, 1 H), 1.95–1.80 (m, 1 H), 1.73–1.62 (m, 1 H), 1.29 (dd, $J = 7.3$, 4.9 Hz, 1 H), 1.26 (s, 3 H), 1.15 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.6, 137.7, 136.4, 130.8, 128.8(2C), 128.1, 127.9, 127.8, 127.6, 126.6(2C), 126.4, 122.0, 119.9, 119.8, 119.2, 118.0, 114.0, 109.5, 82.2(2C), 50.0, 41.4, 38.4, 28.2, 27.6, 27.2 ppm; HRMS (ESI): calcd for C$_{28}$H$_{30}$NO$_2$ $^+$ [M + H$^+$] 412.2271, found 412.2276.

2-((1,2-Dimethyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2i): obtained in 72% yield and >20:1 dr as a colorless oil; IR (film) $\nu_{\text{max}}$ 3232, 3052, 2970, 1612, 1481, 1372, 1232, 1131, 1015, 884, 741 cm$^{-1}$; IR (film) $\nu_{\text{max}}$ 3052, 2970, 2886, 1612, 1479, 1352, 1162, 1131, 1015, 894, 745 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.69 (s, 1 H), 7.59 (d, $J = 7.9$ Hz, 1 H), 7.25 (t, $J = 9.0$ Hz, 1 H), 7.15 (dd, $J = 9.0$, 4.4 Hz, 2 H), 7.11–7.00 (m, 2 H), 6.89 (d, $J = 7.5$ Hz, 1 H), 6.70 (t, $J = 7.2$ Hz, 1 H), 4.79 (d, $J = 1.9$ Hz, 1 H), 4.76–4.69 (m, 1 H), 3.64 (s, 3 H), 2.30 (s, 3 H), 2.20 (dt, $J = 12.4$, 6.3 Hz, 1 H), 2.01–1.89 (m, 1 H), 1.71 (dt, $J = 12.2$, 7.8 Hz, 1 H), 1.60–1.46 (m, 1 H), 1.26 (s, 3 H), 1.16 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.0, 136.6, 134.9, 130.9, 127.8, 127.6(2C), 120.4, 119.7, 119.6, 118.9, 117.2, 110.1, 108.7, 82.4, 81.7, 42.1, 38.7, 29.9, 29.6, 27.9, 27.3, 11.1 ppm; HRMS (ESI): calcd for C$_{23}$H$_{28}$NO$_2$ $^+$ [M + H$^+$] 350.2115, found 350.2113.
2-((5,5-Dimethyltetrahydrofuran-2-yl)(1-methyl-2-phenyl-1H-indol-3-yl)methyl)-phenol (2j): obtained in 68% yield and >20:1 dr as a white solid; m.p. 120–122 °C; IR (film) \( \nu_{\text{max}} \) 3206, 3052, 2970, 1607, 1466, 1367, 1240, 1150, 1018, 885, 740 cm\(^{-1}\); \( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.74 \) (s, 1 H), 7.67 (d, \( J = 8.0 \) Hz, 1 H), 7.43 (s, 4 H), 7.35 (d, \( J = 8.2 \) Hz, 1 H), 7.23 (ddd, \( J = 9.6, 9.0, 4.1 \) Hz, 3 H), 7.16–7.01 (m, 2 H), 6.88 (dd, \( J = 8.0, 1.0 \) Hz, 1 H), 6.72–6.64 (m, 1 H), 4.78 (d, \( J = 2.1 \) Hz, 1 H), 4.67–4.46 (m, 1 H), 3.54 (s, 3 H), 1.88 (dt, \( J = 12.3, 5.4 \) Hz, 2 H), 1.68–1.57 (m, 1 H), 1.47 (dd, \( J = 12.2, 8.9, 6.3 \) Hz, 1 H), 1.18 (s, 3 H), 1.15 ppm (s, 3 H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 155.1, 139.2, 137.3, 131.8, 131.0(2C), 130.8, 128.5, 128.4(2C), 127.7, 127.6, 127.2, 121.6, 121.2, 119.6, 119.4, 117.2, 112.4, 109.4, 83.0, 81.4, 42.2, 38.9, 30.9, 29.5, 27.7, 26.9 ppm; HRMS (ESI): calcd for C\(_{28}H_{30}NO_2^+\) [M + H\(^+\)] 412.2271, found 412.2276.

2-((1,4-Dimethyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2k): obtained in 79% yield and >20:1 dr as a white solid; m.p. 120–125 °C; IR (film) \( \nu_{\text{max}} \) 3212, 3022, 2890, 1609, 1521, 1286, 1097, 1015, 885, 738 cm\(^{-1}\); \( ^{1}H \) NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.71 \) (s, 1 H), 7.12 (t, \( J = 6.4 \) Hz, 1 H), 7.07 (dd, \( J = 14.0, 7.7 \) Hz, 2 H), 6.97 (d, \( J = 8.0 \) Hz, 1 H), 6.88 (s, 1 H), 6.71 (d, \( J = 7.0 \) Hz, 1 H), 6.67 (d, \( J = 4.3 \) Hz, 2 H), 5.32 (s, 1 H), 4.89 (td, \( J = 7.0, 2.0 \) Hz, 1 H), 3.79 (s, 3 H), 2.25 (dd, \( J = 13.9, 6.3 \) Hz, 1 H), 2.20 (s, 3 H), 1.94 (ddt, \( J = 12.3, 8.9, 6.1 \) Hz, 1 H), 1.79–1.64 (m, 1 H), 1.29 (d, \( J = 16.7 \) Hz, 1 H), 1.27 (s, 3 H), 1.25 ppm (s, 3 H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)) \( \delta = 155.2, 137.4, 131.8, 131.0, 128.9, 127.7, 126.7, 126.0, 121.9, 121.0, 120.1, 117.7, 114.4, 106.8, 82.7, 81.6,
41.3, 38.5, 32.9, 28.0, 27.4, 26.6, 19.5 ppm; HRMS (ESI): calcd for C$_{23}$H$_{28}$NO$_2^+$ [M + H$^+$] 350.2115, found 350.2120.

2-((5-Butyl-1-methyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)-phenol (2l): obtained in 81% yield and >20:1 dr as a white solid; m.p. 180–182 °C; IR (film) $\nu_{\text{max}}$ 3256, 2964, 2927, 1582, 1487, 1375, 1232, 1148, 1106, 873, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.88 (s, 1 H), 7.20 (d, $J = 8.1$ Hz, 1 H), 7.10 (t, $J = 7.3$ Hz, 1 H), 7.00 (dd, $J = 17.3$, 10.2 Hz, 4 H), 6.87 (d, $J = 7.4$ Hz, 1 H), 6.68 (t, $J = 7.1$ Hz, 1 H), 4.93 (s, 1 H), 4.81 (s, 1 H), 3.77 (s, 3 H), 2.59 (t, $J = 7.4$ Hz, 2 H), 2.17 (dd, $J = 12.4$, 6.6 Hz, 1 H), 2.01–1.82 (m, 1 H), 1.79–1.64 (m, 1 H), 1.54 (dd, $J = 15.6$, 8.2 Hz, 3 H), 1.33 (d, $J = 15.1$ Hz, 1 H), 1.28 (brs, 4 H), 1.20 (s, 3 H), 0.87 ppm (t, $J = 7.2$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 155.5, 135.3, 133.5, 130.9, 127.9(2C), 127.8, 127.1, 122.8, 120.0, 118.8, 117.9, 112.7, 108.6, 82.4, 82.2, 41.2, 38.5, 35.7, 34.5, 32.8, 28.2, 27.7, 27.2, 22.3, 13.9 ppm; HRMS (ESI): calcd for C$_{26}$H$_{34}$NO$_2^+$ [M + H$^+$] 392.2584, found 392.2586.

2-((5-Chloro-1-methyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)-phenol (2m): obtained in 76% yield and >20:1 dr as a white solid; m.p. 152–154 °C; IR (film) $\nu_{\text{max}}$ 3262, 2969, 2924, 1583, 1480, 1373, 1267, 1144, 1043, 865, 754 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.84 (s, 1 H), 7.23 (s, 1 H), 7.18 (d, $J = 8.6$ Hz, 1 H), 7.15–7.07 (m, 3 H), 6.97 (d, $J = 8.0$ Hz, 1 H), 6.83 (d, $J = 7.4$ Hz, 1 H), 6.70 (t, $J = 7.4$ Hz, 1 H), 4.80 (s, 1 H), 4.77 (dd, $J = 12.0$, 4.9 Hz, 1 H), 3.78 (s, 3 H), 2.15 (dt, $J = 12.9$, 6.8 Hz, 1 H),
1.87 (dt, $J = 15.8, 7.5$ Hz, 1 H), 1.76–1.66 (m, 1 H), 1.37–1.29 (m, 1 H), 1.27 (s, 3 H), 1.18 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 155.4, 135.1, 130.7, 128.9, 128.4, 128.1, 127.7, 125.0, 122.1, 120.0, 118.9, 118.1, 112.9, 110.1, 82.4, 82.1, 41.6, 38.4, 33.0, 28.4, 27.8, 27.3 ppm; HRMS (ESI): calcd for C$_{22}$H$_{25}$ClNO$_2^{+}$ [M + H$^+$] 370.1568, found 370.1566.

2-((5-Bromo-1-methyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2n): obtained in 73% yield and >20:1 dr as a white solid; m.p. 168–170 °C; IR (film) $\nu_{\text{max}}$ 3220, 2970, 1583, 1373, 1266, 1232, 1145, 1042, 887, 821, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.86$ (s, 1 H), 7.40 (s, 1 H), 7.25 (d, $J = 7.7$ Hz, 1 H), 7.18–7.03 (m, 3 H), 6.97 (d, $J = 7.9$ Hz, 1 H), 6.84 (d, $J = 7.5$ Hz, 1 H), 6.70 (t, $J = 7.4$ Hz, 1 H), 4.80 (s, 1 H), 4.77 (t, $J = 7.3$ Hz, 1 H), 3.77 (s, 3 H), 2.15 (td, $J = 13.4, 6.8$ Hz, 1 H), 1.87 (dt, $J = 15.8, 7.7$ Hz, 1 H), 1.77–1.64 (m, 1 H), 1.40–1.29 (m, 1 H), 1.28 (s, 3 H), 1.19 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 155.4, 135.3, 130.7, 129.6, 128.3, 128.1, 127.7, 124.6, 121.9, 120.0, 118.1, 112.9, 112.5, 110.5, 82.4, 82.1, 41.6, 38.4, 33.0, 28.4, 27.8, 27.3 ppm; HRMS (ESI): calcd for C$_{22}$H$_{25}$BrNO$_2^{+}$ [M + H$^+$] 414.1063, found 414.1068.

2-((5,5-Dimethyltetrahydrofuran-2-yl)(5-methoxy-1-methyl-1H-indol-3-yl)methyl)phenol (2o): obtained in 65% yield and 13:1 dr as a white solid; m.p. 125–127 °C; IR (film) $\nu_{\text{max}}$ 3256, 2968, 2925, 1580, 1489, 1372, 1271, 1224, 1038, 869, 756 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.82$ (s, 1 H), 7.16 (d, $J = 8.8$ Hz, 1 H), 7.09 (t, $J = 7.5$ Hz, 1 H),
7.03–6.94 (m, 2 H), 6.84 (dd, J = 11.5, 4.8 Hz, 2 H), 6.69 (t, J = 7.2 Hz, 1 H), 6.63 (d, J = 1.9 Hz, 1 H), 4.87 (s, 1 H), 4.85–4.75 (m, 1 H), 3.77 (s, 3 H), 3.68 (s, 3 H), 2.16 (dt, J = 19.4, 7.0 Hz, 1 H), 2.00–1.86 (m, 1 H), 1.77–1.64 (m, 1 H), 1.38–1.28 (m, 1 H), 1.27 (s, 3 H), 1.19 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl₃) δ = 155.6, 153.7, 132.2, 130.8, 128.1, 127.9, 127.7, 127.6, 119.90, 117.9, 112.7, 112.1, 109.7, 101.5, 82.3, 82.2, 55.9, 41.3, 38.5, 33.0, 28.2, 27.7, 27.2 ppm; HRMS (ESI): calcd for C₂₃H₂₈NO₃⁺ [M + H⁺] 366.2064, found 366.2060.

2-((5-(Benzyloxy)-1-methyl-1H-indol-3-yl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)phenol (2p): obtained in 63% yield and 15:1 dr as a white solid; m.p. 161–163 °C; IR (film) νmax 3205, 3035, 2970, 1611, 1498, 1372, 1262, 1016, 883, 821, 735, 698 cm⁻¹; ^{1}H NMR (400 MHz, CDCl₃) δ = 9.03 (s, 1 H), 7.27–7.15 (m, 3 H), 7.12 (d, J = 6.5 Hz, 2 H), 7.02–6.90 (m, 3 H), 6.84–6.74 (m, 3 H), 6.60 (dd, J = 10.6, 4.2 Hz, 1 H), 6.34 (d, J = 7.7 Hz, 1 H), 5.37 (d, J = 2.0 Hz, 1 H), 4.99 (q, J = 12.4 Hz, 2 H), 4.62 (td, J = 7.6, 2.2 Hz, 1 H), 3.64 (s, 3 H), 1.97 (dt, J = 12.8, 6.4 Hz, 1 H), 1.90–1.78 (m, 1 H), 1.58 (dt, J = 12.2, 7.6 Hz, 1 H), 1.25 (dd, J = 12.3, 8.9, 6.0 Hz, 1 H), 1.18 (s, 3 H), 1.10 ppm (s, 3 H); ^{13}C NMR (100 MHz, CDCl₃) δ = 155.3, 153.7, 138.2, 137.4, 131.2, 130.0, 128.4(2C), 127.5, 127.4, 127.2(2C), 126.4, 122.2, 119.5, 117.8, 117.7, 113.5, 102.5, 100.8, 82.3, 82.1, 69.7, 42.8, 38.4, 33.0, 28.9, 27.9, 27.4 ppm; HRMS (ESI): calcd for C₂₉H₃₂NO₃⁺ [M + H⁺] 442.2377, found 442.2372.

2-((5,5-Dimethyltetrahydrofuran-2-yl)(5-(2-methoxyphenyl)-1-methyl-1H-indol-3-yl)methyl)phenol (2q): obtained in 75% yield and >20:1 dr as a white solid; m.p.
175–177 °C; IR (film) \( \nu_{\text{max}} \) 3312, 3092, 2988, 1612, 1481, 1472, 1198, 1131, 1015, 834, 728 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 8.89 (s, 1 H), 7.43–7.36 (m, 2 H), 7.30 (d, \( J = 9.0 \) Hz, 1 H), 7.28–7.20 (m, 2 H), 7.13–7.03 (m, 2 H), 7.01–6.84 (m, 4 H), 6.70 (dd, \( J = 10.6, 4.2 \) Hz, 1 H), 4.93 (d, \( J = 1.6 \) Hz, 1 H), 4.81 (td, \( J = 7.3, 2.5 \) Hz, 1 H), 3.80 (s, 3 H), 3.69 (s, 3 H), 2.17 (dq, \( J = 14.2, 6.9 \) Hz, 1 H), 2.03–1.88 (m, 1 H), 1.70 (dt, \( J = 12.3, 7.4 \) Hz, 1 H), 1.39–1.28 (m, 1 H), 1.27 (s, 3 H), 1.20 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 156.5, 155.5, 136.0, 131.8, 131.2, 131.0, 129.3, 128.0, 127.8, 127.8, 127.7, 127.4, 123.9, 120.7, 120.53, 119.9, 117.9, 113.5, 111.1, 108.4, 82.4, 82.2, 55.4, 41.5, 38.5, 32.8, 28.3, 27.7, 27.7 ppm; HRMS (ESI): calcd for C\(_{29}\)H\(_{32}\)NO\(_3^+\) [M + H\(^+\)] 442.2377, found 442.2381.

2-((5,5-Dimethyltetrahydrofuran-2-yl)(5-(furan-2-yl)-1-methyl-1\(H\)-indol-3-yl)methyl)phenol (2r): obtained in 70% yield and >20:1 dr as a white solid; m.p. 134–136 °C; IR (film) \( \nu_{\text{max}} \) 3052, 2970, 2876, 1512, 1381, 1372, 1313, 1015, 984, 785, 741 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 8.99 (s, 1 H), 7.59 (s, 1 H), 7.53 (d, \( J = 8.5 \) Hz, 1 H), 7.40 (s, 1 H), 7.28 (s, 1 H), 7.15–7.07 (m, 2 H), 6.98 (d, \( J = 7.9 \) Hz, 1 H), 6.91 (d, \( J = 7.5 \) Hz, 1 H), 6.69 (t, \( J = 7.3 \) Hz, 1 H), 6.47 (d, \( J = 3.1 \) Hz, 1 H), 6.44–6.39 (m, 1 H), 4.92 (s, 1 H), 4.79 (td, \( J = 7.4, 2.3 \) Hz, 1 H), 3.80 (s, 3 H), 2.17 (td, \( J = 13.0, 6.8 \) Hz, 1 H), 1.99–1.84 (m, 1 H), 1.70 (dt, \( J = 12.2, 7.5 \) Hz, 1 H), 1.39–1.31 (m, 1 H), 1.29 (s, 3 H), 1.20 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 155.5, 155.4, 141.1, 136.2, 130.9, 128.1, 128.0(2C), 127.9, 122.7, 119.9, 118.7, 118.1, 115.0, 113.7, 111.4, 109.3, 103.1,
82.4, 82.3, 41.7, 38.5, 32.9, 28.5, 27.8, 27.3 ppm; HRMS (ESI): calcd for C_{26}H_{28}NO_3^+ [M + H^+] 402.2064, found 402.2070.

2-((1-Methyl-1H-indol-3-yl)(tetrahydrofuran-2-yl)methyl)phenol (2s): obtained in 81% yield and >20:1 dr as a white solid; m.p. 139–141 °C; IR (film) \( \nu_{\text{max}} \) 3205, 3035, 2970, 1611, 1498, 1262, 1016, 883, 735, 698 cm\(^{-1}\);

\( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.77 \) (s, 1 H), 7.26 (dd, \( J = 13.6, 7.8 \) Hz, 2 H), 7.18 (t, \( J = 7.5 \) Hz, 1 H), 7.09 (t, \( J = 7.5 \) Hz, 1 H), 7.03 (s, 1 H), 6.97 (dd, \( J = 17.1, 8.0 \) Hz, 2 H), 6.86 (d, \( J = 7.6 \) Hz, 1 H), 6.68 (t, \( J = 7.4 \) Hz, 1 H), 4.95 (d, \( J = 1.5 \) Hz, 1 H), 4.73 (td, \( J = 7.1, 2.8 \) Hz, 1 H), 3.85 (dd, \( J = 13.6, 7.5 \) Hz, 1 H), 3.78 (s, 3 H), 3.75 (d, \( J = 7.9 \) Hz, 1 H), 2.18–2.03 (m, 1 H), 1.83 (tt, \( J = 14.6, 7.2 \) Hz, 2 H), 1.58–1.46 ppm (m, 1 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 155.4, 136.8, 130.9, 127.9, 127.7, 127.6, 127.0, 121.8, 119.9, 119.6, 119.0, 117.6, 113.1, 109.0, 83.2, 68.4, 41.7, 32.8, 28.0, 26.2 ppm; HRMS (ESI): calcd for C_{20}H_{22}NO_2^+ [M + H^+] 308.1645, found 308.1648.

2-((1-Methyl-1H-indol-3-yl)(tetrahydro-2H-pyran-2-yl)methyl)phenol (2t): obtained in 77% yield and >20:1 dr as a white solid; m.p. 124–126 °C; IR (film) \( \nu_{\text{max}} \) 3232, 3052, 2970, 1612, 1481, 1332, 1231, 1115, 884, 741 cm\(^{-1}\); \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 9.11 \) (s, 1 H), 7.36 (d, \( J = 7.9 \) Hz, 1 H), 7.24 (t, \( J = 10.9 \) Hz, 2 H), 7.16 (t, \( J = 7.5 \) Hz, 1 H), 7.08 (t, \( J = 7.4 \) Hz, 1 H), 7.01 (t, \( J = 7.5 \) Hz, 2 H), 6.89 (d, \( J = 7.8 \) Hz, 1 H), 6.71 (t, \( J = 7.3 \) Hz, 1 H), 4.47 (s, 1 H), 4.14 (dd, \( J = 31.5, 9.8 \) Hz, 2 H), 3.76 (s, 3 H), 3.66–3.54 (m, 1 H), 1.86–1.65 (m, 2 H), 1.54–1.46 ppm (m, 4 H); \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 155.2, 136.5, \ldots \)
131.1, 129.2, 128.3, 128.1, 127.3, 121.5, 119.7, 119.2, 118.8, 117.9, 112.4, 109.0, 82.5, 69.2, 46.1, 32.8, 29.5, 25.4, 23.3 ppm; HRMS (ESI): calcd for C_{21}H_{24}NO_{2}^+ [M + H^+] 322.1802, found 322.1803.

**General procedure for the synthesis of 2-substituted indolizines 5a–e through hypervalent iodine-mediated alkene difunctionalization of o-vinylphenol 1a:**

To a stirred solution of o-vinylphenol 1a (0.2 mmol) and indolizines 4a–e (0.24 mmol) in CH₂Cl₂ (10 mL) at 0 °C was treated with PhI(OAc)₂ (0.24 mmol). The resulting mixture was stirred for 1 h before it was quenched with saturated Na₂S₂O₃ (sat. aq., 10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 20:1) afforded corresponding products 5a–e.

**Starting materials**: Indolizines 4a–e were prepared according to the known literature procedures.³

*Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(2-hydroxyphenyl)methyl) indolizine-1-carboxylate (5a):* obtained in 87% yield and >20:1 dr as a white solid; m.p. 248–250 °C; IR (film) ν_max 3223, 2969, 2868, 1656, 1507, 1456, 1223, 1056, 879, 850, 766, 740 cm⁻¹; ¹H NMR (400
MHz, CDCl₃) δ = 8.42 (s, 1 H), 8.12 (d, J = 8.8 Hz, 1 H), 7.25 (d, J = 6.7 Hz, 1 H), 7.12 (s, 1 H), 7.07 (t, J = 7.2 Hz, 1 H), 7.02–6.89 (m, 2 H), 6.58 (t, J = 7.1 Hz, 1 H), 6.47 (t, J = 6.3 Hz, 1 H), 6.28 (d, J = 7.4 Hz, 1 H), 4.88 (s, 2 H), 3.85 (s, 3 H), 2.39–2.22 (m, 1 H), 1.88 (d, J = 4.9 Hz, 1 H), 1.74–1.62 (m, 1 H), 1.20 (s, 4 H), 1.14 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 165.3, 155.8, 136.0, 129.0, 128.8, 123.6(2C), 123.1, 122.3, 120.8, 119.6, 118.5, 115.3, 112.4, 102.7, 82.2, 81.5, 50.9, 40.6, 38.5, 27.7, 27.4, 26.8 ppm; HRMS (ESI): calcd for C₂₃H₂₆NO₄⁺ [M + H⁺] 380.1856, found 380.1852.

Methyl 7-(tert-butyl)-3-((5,5-dimethyltetrahydrofuran-2-yl)(2-hydroxyphenyl)-methyl)indolizine-1-carboxylate (5b): obtained in 82% yield and >20:1 dr as a white solid; m.p. 270–272 °C; IR (film) νmax 3219, 2969, 2870, 1656, 1507, 1456, 1223, 1135, 860, 766, 740 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 8.50 (s, 1 H), 8.15 (s, 1 H), 7.28 (s, 1 H), 7.18–7.09 (m, 2 H), 7.04 (d, J = 7.9 Hz, 1 H), 6.67 (t, J = 7.1 Hz, 1 H), 6.62 (dd, J = 7.4, 1.8 Hz, 1 H), 6.40 (d, J = 7.6 Hz, 1 H), 4.93 (s, 2 H), 3.92 (s, 3 H), 2.39 (td, J = 14.8, 7.3 Hz, 1 H), 2.03–1.88 (m, 1 H), 1.74 (ddd, J = 13.5, 7.9, 5.9 Hz, 1 H), 1.30 (s, 9 H), 1.27 (s, 4 H), 1.21 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ = 165.5, 155.9, 146.4, 136.6, 129.2, 128.8, 123.9, 123.1, 122.2, 120.8, 118.5, 115.1, 114.0, 111.9, 101.6, 82.2, 81.6, 50.8, 40.6, 38.5, 34.7, 30.5(3C), 27.7, 27.4, 26.8 ppm; HRMS (ESI): calcd for C₂₇H₃₆NO₄⁺ [M + H⁺] 436.2482, found 436.2483.

Methyl 7-benzoyl-3-((S)-((R)-5,5-dimethyltetrahydrofuran-2-yl)(2-hydroxyphenyl)-ethyl)methyl)indolizine-1-carboxylate (5c): obtained in 78% yield and >20:1 dr as a
white solid; m.p. 203–205 °C; IR (film) \( \nu_{\text{max}} \) 3293, 2970, 2865, 1697, 1651, 1449, 1351, 1218, 1111, 1055, 879, 736, 711 cm\(^{-1}\);

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.64 \) (s, 1 H), 8.41 (s, 1 H), 7.81 (d, \( J = 7.1 \) Hz, 2 H), 7.59 (t, \( J = 7.3 \) Hz, 1 H), 7.50 (t, \( J = 7.5 \) Hz, 2 H), 7.43 (d, \( J = 7.3 \) Hz, 1 H), 7.33 (s, 1 H), 7.21–7.09 (m, 2 H), 7.05 (d, \( J = 8.0 \) Hz, 1 H), 6.69 (t, \( J = 7.4 \) Hz, 1 H), 6.35 (d, \( J = 7.6 \) Hz, 1 H), 5.00 (d, \( J = 2.5 \) Hz, 1 H), 4.95 (td, \( J = 6.9, 3.0 \) Hz, 1 H), 3.89 (s, 3 H), 2.38 (td, \( J = 14.5, 7.3 \) Hz, 1 H), 1.96 (ddd, \( J = 15.1, 10.7, 6.6 \) Hz, 1 H), 1.82–1.70 (m, 1 H), 1.38–1.25 (m, 4 H), 1.22 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 194.5, 164.8, 155.7, 137.2, 133.7, 132.5, 130.0(2C), 129.7, 129.1, 128.8, 128.4(2C), 125.8, 124.0, 123.4, 123.2, 121.0, 118.6, 117.1, 111.9, 107.6, 82.4, 81.3, 51.2, 40.7, 38.4, 27.8, 27.5, 26.8 ppm; HRMS (ESI): calcd for C\(_{30}\)H\(_{30}\)NO\(_5\)^{+} [M + H\(^{+}\)] 484.2118, found 484.2123.

**Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(2-hydroxyphenyl)methyl)-6,8-dimethylindolizine-1-carboxylate (5d):** obtained in 80% yield and >20:1 dr as a white solid; m.p. 165–167 °C; IR (film) \( \nu_{\text{max}} \) 2969, 2898, 1556, 1456, 1243, 1056, 880, 871, 740 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.55 \) (s, 1 H), 7.13 (d, \( J = 11.6 \) Hz, 2 H), 7.03 (d, \( J = 7.8 \) Hz, 1 H), 6.97 (s, 1 H), 6.69–6.60 (m, 2 H), 6.37 (d, \( J = 7.3 \) Hz, 1 H), 5.02–4.76 (m, 2 H), 3.87 (s, 3 H), 2.75 (s, 3 H), 2.38 (dt, \( J = 14.8, 7.3 \) Hz, 1 H), 2.04 (s, 3 H), 1.94 (ddd, \( J = 12.8, 8.9, 6.6 \) Hz, 1 H), 1.82–1.63 (m, 1 H), 1.27 (s, 3 H), 1.22 ppm (s, 4 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 165.1, 155.8, 134.1, 129.3, 129.1, 128.7, 126.9, 123.8, 122.1, 121.8, 120.7, 119.3, 118.4, 116.7, 103.7, 82.1, 81.7, 51.0, 40.7, 38.5, 27.8, 27.4,
26.7, 22.0, 18.1 ppm; HRMS (ESI): calcd for C_{25}H_{30}NO_{4}^{+} [M + H^{+}] 408.2169, found 408.2175.

Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(2-hydroxyphenyl)methyl)pyrrolo-[2,1-a]isoquinoline-1-carboxylate (5e): obtained in 72% yield and >20:1 dr as a white solid; m.p. 228–230 °C; IR (film) \( \nu_{\text{max}} \) 3261, 2972, 1699, 1507, 1458, 1203, 1017, 789, 759 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 9.85 \) (d, \( J = 8.3 \) Hz, 1 H), 8.53 (s, 1 H), 7.59 (dd, \( J = 15.6, 7.5 \) Hz, 2 H), 7.52–7.45 (m, 1 H), 7.23–7.12 (m, 3 H), 7.05 (d, \( J = 7.8 \) Hz, 1 H), 6.78 (d, \( J = 7.3 \) Hz, 1 H), 6.66 (t, \( J = 7.3 \) Hz, 1 H), 6.40 (d, \( J = 7.5 \) Hz, 1 H), 5.00 (s, 2 H), 3.97 (s, 3 H), 2.42 (dd, \( J = 12.6, 7.1 \) Hz, 1 H), 2.15–1.90 (m, 1 H), 1.86–1.72 (m, 1 H), 1.30 (s, 4 H), 1.24 ppm (s, 3 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 165.7, 155.7, 132.7, 129.4, 128.9, 128.7, 127.6, 127.5, 127.0, 126.6, 125.6, 124.6, 124.2, 121.5, 120.9, 118.5, 115.5, 113.5, 107.4, 82.2, 81.5, 51.4, 40.7, 38.5, 27.8, 27.4, 26.8 ppm; HRMS (ESI): calcd for C_{27}H_{28}NO_{4}^{+} [M + H^{+}] 430.2013, found 430.2010.

General procedure for the synthesis of 3-substituted indoles 7a–g through hypervalent iodine-mediated alkene difunctionalization of trisubstituted \( \omega \)-vinylphenols 6:
To a stirred solution of trisubstituted o-vinylphenols 6 (0.2 mmol) and indoles 3 (0.24 mmol) in CH₂Cl₂ (10 mL) at –20 °C was treated with PhI(OAc)₂ (0.24 mmol). The resulting mixture was stirred for 1 h before it was quenched with saturated Na₂S₂O₃ (sat. aq., 10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 20:1) afforded corresponding products 7a–g.

Starting materials: Trisubstituted o-vinylphenols 6a–c were prepared according to the known literature procedures.4

(E)-2-(5-Hydroxy-2,5-dimethylhex-1-en-1-yl)phenol (6a): white solid; m.p. 80–82 °C; IR (film) νₘᵡₐₓ 2981, 2886, 1581, 1268, 1150, 945, 816, 740 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.13 (dd, J = 10.9, 4.3 Hz, 1 H), 7.03 (d, J = 7.1 Hz, 1 H), 6.86 (td, J = 8.4, 1.5 Hz, 2 H), 6.20 (s, 1 H), 5.90 (brs, 1 H), 2.44–2.27 (m, 2 H), 1.81–1.72 (m, 2 H), 1.69 (s, 3 H), 1.57 (brs, 1 H), 1.30 ppm (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ = 153.2, 143.9, 129.6, 128.1, 124.7, 119.9, 119.0, 115.0, 71.6, 41.0, 34.7, 29.5(2C), 17.6 ppm; HRMS (ESI): calcd for C₁₄H₂₁O₂⁺ [M + H⁺] 221.1536, found 221.1534.

(E)-2-(5-Hydroxy-2,5-dimethylhex-1-en-1-yl)-4-methylphenol (6b): white solid; m.p. 72–74 °C; IR (film) νₘᵡₐₓ 2998, 2915, 1581, 1310, 1262, 1153, 898, 809, 751 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 6.93 (d, J = 7.5 Hz, 1 H), 6.83 (s, 1 H), 6.77 (d, J = 8.0 Hz, 1 H), 6.17 (s, 1 H), 5.64 (brs, 1 H), 2.40–2.29 (m, 2 H), 2.25 (s, 3 H), 1.78–1.71 (m, 2
H), 1.69 (s, 3 H), 1.29 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 150.9, 143.7, 129.9, 128.9, 128.6, 124.3, 119.1, 114.7, 71.6, 41.1, 34.7, 29.5(2C), 20.5, 17.6 ppm;

HRMS (ESI): calcd for C$_{12}$H$_{22}$O$_2^+$ [M + H$^+$] 235.1693, found 235.1694.

(E)-4-Chloro-2-(5-hydroxy-2,5-dimethylhex-1-en-1-yl)phenol (6c): white solid; m.p. 89–91 °C; IR (film) $\nu_{\text{max}}$ 2971, 2925, 1481, 1411, 1268, 1050, 905, 816, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.09 (dd, $J = 8.6, 2.2$ Hz, 1 H), 7.00 (d, $J = 2.1$ Hz, 1 H), 6.80 (d, $J = 8.6$ Hz, 1 H), 6.11 (s, 1 H), 5.94 (brs, 1 H), 2.35 (t, $J = 7.4$ Hz, 2 H), 1.79–1.71 (m, 2 H), 1.67 (d, $J = 0.9$ Hz, 3 H), 1.30 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 152.1, 145.4, 129.1, 128.0, 126.1, 124.4, 118.0, 116.3, 71.8, 40.6, 34.7, 29.6(2C), 17.6 ppm; HRMS (ESI): calcd for C$_{14}$H$_{20}$ClO$_2^+$ [M + H$^+$] 255.1146, found 255.1143.

2-((1-Methyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methyl)phenol (7a): obtained in 76% yield and >20:1 dr as a white solid; m.p. 186–188 °C; IR (film) $\nu_{\text{max}}$ 2974, 2903, 1583, 1481, 1258, 1066, 880, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 9.40 (s, 1 H), 7.35 (d, $J = 7.9$ Hz, 1 H), 7.28 (s, 1 H), 7.21 (s, 1 H), 7.17 (t, $J = 7.6$ Hz, 1 H), 7.10–7.04 (m, 1 H), 7.00 (t, $J = 7.5$ Hz, 2 H), 6.90 (d, $J = 7.9$ Hz, 1 H), 6.69 (t, $J = 7.4$ Hz, 1 H), 4.64 (s, 1 H), 3.82 (s, 3 H), 2.24–2.08 (m, 1 H), 2.01–1.88 (m, 2 H), 1.83–1.70 (m, 1 H), 1.39 (s, 3 H), 1.38 (s, 3 H), 1.35 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 155.3, 136.3, 131.4, 128.6, 128.4, 127.9, 127.2, 121.6, 119.6, 119.1, 118.9, 118.0, 113.2, 108.9, 89.3, 83.3, 50.4, 38.1, 38.0, 32.9, 30.4, 28.7, 25.1 ppm; HRMS (ESI): calcd for C$_{23}$H$_{28}$NO$_2^+$ [M + H$^+$] 350.2115, found 350.2121.
4-Methyl-2-((1-methyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methy)phenol (7b): obtained in 73% yield and > 20:1 dr as a white solid; m.p. 178–180 °C; IR (film) \( \nu_{\text{max}} \) 2982, 2903, 1483, 1461, 1254, 1126, 786, 739 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 9.16 \) (s, 1 H), 7.39 (d, \( J = 7.9 \) Hz, 1 H), 7.24 (dd, \( J = 7.7, 5.5 \) Hz, 2 H), 7.15 (t, \( J = 7.4 \) Hz, 1 H), 7.00 (t, \( J = 7.3 \) Hz, 1 H), 6.91–6.80 (m, 2 H), 6.76 (d, \( J = 7.9 \) Hz, 1 H), 4.55 (s, 1 H), 3.80 (s, 3 H), 2.24–2.04 (m, 4 H), 1.98–1.81 (m, 2 H), 1.81–1.66 (m, 1 H), 1.36 (s, 3 H), 1.33 ppm (d, \( J = 3.5 \) Hz, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 152.9, 136.2, 131.9, 128.7, 128.4(2C), 128.1, 127.3, 121.5, 119.0, 118.8, 117.8, 113.2, 108.9, 89.3, 83.3, 50.4, 38.0, 37.9, 32.9, 30.5, 28.7, 25.3, 20.7 ppm; HRMS (ESI): calcd for C\(_{24}\)H\(_{30}\)NO\(_2\)^+ [M + H\(^+\)] 364.2271, found 364.2274.

4-Chloro-2-((1-methyl-5-phenyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methyl)phenol (7c): obtained in 80% yield and > 20:1 dr as a white solid; m.p. 208–210 °C; IR (film) \( \nu_{\text{max}} \) 2984, 2873, 1583, 1471, 1258, 1168, 1066, 870, 746, 729 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 9.50 \) (s, 1 H), 7.61–7.52 (m, 3 H), 7.49–7.32 (m, 4 H), 7.30 (d, \( J = 7.2 \) Hz, 1 H), 7.23 (s, 1 H), 7.03 (d, \( J = 5.8 \) Hz, 2 H), 6.85 (d, \( J = 9.2 \) Hz, 1 H), 4.67 (s, 1 H), 3.86 (s, 3 H), 2.21–2.05 (m, 1 H), 2.05–1.86 (m, 2 H), 1.80 (d, \( J = 12.2 \) Hz, 1 H), 1.39 (s, 3 H), 1.38 (s, 3 H), 1.36 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 154.1, 142.4, 135.9, 132.8, 130.7, 130.2, 128.8, 128.6(2C), 127.9, 127.8, 127.4(2C), 126.3, 124.4, 121.8, 119.4, 117.2, 112.9, 109.4, 89.4, 83.7, 50.0, 38.2, 37.9, 33.1, 30.3, 28.7,
25.0 ppm; HRMS (ESI): calcd for C_{29}H_{31}ClNO_2^+ [M + H]^+ 460.2038, found 460.2033.

2-((1-Methyl-2-phenyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methyl)phenol (7d): obtained in 64% yield and >20:1 dr as a white solid; m.p. 163–165 °C; IR (film) ν_{max} 2998, 2883, 1681, 1480, 1260, 1046, 780, 748 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 9.65 (s, 1 H), 7.93 (d, \(J = 8.0\) Hz, 1 H), 7.30–7.26 (m, 3 H), 7.23–7.17 (m, 1 H), 7.11 (dd, \(J = 10.9, 4.3\) Hz, 1 H), 6.98–6.82 (m, 2 H), 6.67 (dd, \(J = 10.8, 4.1\) Hz, 1 H), 4.54 (s, 1 H), 3.60 (s, 3 H), 1.90–1.73 (m, 1 H), 1.66 (ddd, \(J = 15.5, 10.7, 5.9\) Hz, 1 H), 1.53–1.38 (m, 5 H), 1.23 (s, 3 H), 0.85 ppm (s, 3 H); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 155.3, 140.9, 137.7, 131.7, 131.1, 130.4, 128.9, 128.8, 128.4, 127.7, 127.0, 122.3(2C), 121.5, 119.6, 119.2, 117.5, 112.6(2C), 109.7, 89.5, 83.1, 51.4, 37.9, 37.5, 31.1, 30.0, 27.7, 26.8 ppm; HRMS (ESI): calcd for C_{29}H_{32}NO_2^+ [M + H]^+ 426.2428, found 426.2423.

2-((5-(Benzyloxy)-1-methyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methyl)phenol (7e): obtained in 60% yield and 14:1 dr as a white solid; m.p. 134–136 °C; IR (film) ν_{max} 2971, 2925, 1580, 1497, 1377, 1258, 1065, 879, 753, 698 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 9.55 (s, 1 H), 7.40–7.29 (m, 5 H), 7.22 (s, 1 H), 7.02 (dd, \(J = 15.7, 7.7\) Hz, 2 H), 6.93–6.79 (m, 3 H), 6.63 (t, \(J = 7.0\) Hz, 1 H), 6.44 (d, \(J = 7.7\) Hz, 1 H), 5.37 (s, 1 H), 5.12 (q, \(J = 11.9\) Hz, 2 H), 3.76 (s, 3 H), 2.20–2.01 (m, 1 H), 1.95–1.79 (m, 1 H), 1.77–1.62 (m, 2 H), 1.34 (s, 3 H), 1.29 (s, 3 H), 1.20 ppm (s, 3 H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) δ = 155.3, 140.9, 137.7, 131.7, 131.1, 130.4, 128.9, 128.8, 128.4, 127.7, 127.0, 122.3(2C), 121.5, 119.6, 119.2, 117.5, 112.6(2C), 109.7, 89.5, 83.1, 51.4, 37.9, 37.5, 31.1, 30.0, 27.7, 26.8 ppm; HRMS (ESI): calcd for C_{29}H_{32}NO_2^+ [M + H]^+ 426.2428, found 426.2423.
MHz, CDCl$_3$) $\delta = 155.5, 153.9, 137.9, 137.4, 129.4, 128.4(2C), 127.7(3C),
127.5, 126.4, 121.9, 119.2, 117.9, 114.0, 102.5, 100.6, 89.5, 83.3, 69.9, 50.4, 37.9,
37.7, 33.1, 30.5, 29.7, 28.4, 25.7 ppm; HRMS (ESI): calcd for C$_{36}$H$_{34}$NO$_3^+$ [M + H$^+$] 456.2533, found 456.2539.

2-((1-Methyl-5-phenyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methyl)phenol (7f): obtained in 71% yield and >20:1 dr as a white solid; m.p. 70–72 °C; IR (film) $\nu_{\text{max}}$ 2981, 2934, 1569, 1476,
1277, 1253, 1061, 886, 753, 738 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.43$ (s, 1 H), 7.54 (d, $J = 7.2$ Hz, 3 H), 7.41 (dd, $J = 15.4, 8.0$ Hz, 3 H),
7.31 (dd, $J = 17.6, 8.0$ Hz, 2 H), 7.26 (s, 1 H), 7.07 (t, $J = 6.9$ Hz, 2 H), 6.90 (d, $J = 7.5$ Hz, 1 H), 6.72 (t, $J = 7.0$ Hz, 1 H), 4.67 (s, 1 H), 3.85 (s, 3 H), 2.24–2.11 (m, 1 H),
1.96 (ddd, $J = 22.3, 14.7, 7.9$ Hz, 2 H), 1.76 (dd, $J = 15.1, 9.4$ Hz, 1 H), 1.40 (s, 3 H),
1.38 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 155.3, 142.6, 135.9, 132.6, 131.4,
129.6, 129.1, 128.6, 128.3, 128.0(2C), 127.4, 126.2, 121.6, 119.7, 118.1, 117.5, 115.3,
113.6, 109.2, 89.3, 83.4, 50.5, 38.0(2C), 33.0, 30.4, 28.8, 25.3 ppm; HRMS (ESI):
calcd for C$_{29}$H$_{32}$NO$_2$ [M + H$^+$] 426.2428, found 426.2430.

2-((5-(2-Methoxyphenyl)-1-methyl-1H-indol-3-yl)(2,5,5-trimethyltetrahydrofuran-2-yl)methyl)phenol (7g): obtained in 69% yield and >20:1 dr as a white solid; m.p. 154–156 °C; IR (film) $\nu_{\text{max}}$ 2972, 2900,
1582, 1482, 1378, 1252, 1059, 880, 753 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 9.41$ (s, 1 H), 7.50 (s, 1 H), 7.37 (d, $J = 8.4$ Hz, 1 H), 7.30–7.25 (m,
3 H), 7.22 (s, 1 H), 7.06 (t, $J = 7.4$ Hz, 2 H), 7.02–6.92 (m, 2 H), 6.88 (d, $J = 7.9$ Hz, 1
H), 6.71 (t, $J = 7.4$ Hz, 1 H), 4.64 (s, 1 H), 3.83 (s, 3 H), 3.72 (s, 3 H), 2.18 (dd, $J = 20.7$, 12.9 Hz, 1 H), 2.01–1.87 (m, 2 H), 1.82–1.74 (m, 1 H), 1.39 (s, 3 H), 1.36 ppm (s, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta =$ 156.5, 155.3, 135.6, 132.0, 131.5, 131.3, 129.3, 128.6, 128.4, 127.9, 127.7, 127.6, 123.8, 120.7, 120.0, 119.6, 118.0, 113.5, 111.2, 108.4, 89.4, 83.4, 55.5, 50.5, 38.1, 38.0, 32.9, 30.4, 28.7, 25.2 ppm; HRMS (ESI): calcd for C$_{30}$H$_{34}$NO$_3^{+}$ [M + H$^+$] 456.2533, found 456.2528.

Inverse-electron demand Diels–Alder reaction:

To a stirred solution of $o$-vinylphenol 1a (41 mg, 0.20 mmol) and methyl-1-propenyl ether 10 (2.8 mL, 10 mmol, Z/E 2.5:1) in CH$_2$Cl$_2$ (10 mL) at room temperature was added PhI(OAc)$_2$ (77 mg, 0.24 mmol). The resulting mixture was stirred for 4 h before it was quenched with NaHCO$_3$ (sat. aq., 5 mL). The layers were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic layers were dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 80:1) afforded 11 (37.7 mg, 62%, dr = 2.2:1) as a colorless oil.

4-(5,5-Dimethyltetrahydrofuran-2-yl)-2-ethoxy-3-methylchromane (11): IR (film) $\nu_{\text{max}}$ 2970, 2932, 1582, 1486, 1241, 1146, 1110, 1044, 755 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 7.35 (d, $J = 7.5$ Hz, 0.69 H), 7.29 (d, $J =$ 7.6 Hz, 0.31 H), 7.12 (t, $J = 7.0$ Hz, 1 H), 6.85 (dd, $J =$ 13.9, 7.7 Hz, 2
H), 5.14 (d, J = 2.2 Hz, 0.69 H), 5.05 (d, J = 2.1 Hz, 0.31 H), 4.35 (dd, J = 11.5, 6.6 Hz, 0.31 H), 4.17 (dd, J = 11.8, 6.0 Hz, 0.69 H), 4.03–3.88 (m, 1 H), 3.70–3.53 (m, 1 H), 3.09 (t, J = 4.8 Hz, 0.31 H), 2.74 (t, J = 4.6 Hz, 0.69 H), 2.49–2.37 (m, 0.31 H), 2.28–2.18 (m, 0.69 H), 2.16–2.06 (m, 0.31 H), 1.96–1.86 (m, 0.69 H), 1.65 (ddd, J = 15.2, 8.8, 3.1 Hz, 3 H), 1.31 (s, 1 H), 1.28 (s, 2 H), 1.26–1.19 (m, 6 H), 1.07 (d, J = 7.1 Hz, 1 H), 1.01 ppm (d, J = 6.9 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ = 153.0(2C), 130.3, 129.1, 127.6(2C), 123.0, 122.3, 120.3, 120.1, 116.7, 116.4, 101.4, 99.5, 81.20, 80.6, 79.40 77.6, 64.5, 64.4, 45.6, 43.2, 38.9, 38.5, 33.6, 33.0, 30.5, 29.4, 28.9, 28.8, 27.8, 27.1, 15.1(2C), 13.5, 10.3 ppm; HRMS (ESI): calcd for C₁₉H₂₇O₃⁺ [M + H⁺] 291.1955, found 291.1961.

General procedure for the synthesis of 2-substituted indolizines 13a–j through hypervalent iodine-mediated alkene difunctionalization of p-vinylphenols 12:

To a stirred solution of p-vinylphenol 12 (0.2 mmol) and indolizines 4 (0.24 mmol) in CH₂Cl₂ (10 mL) at 10 °C was treated with PhI(OAc)₂ (0.24 mmol). The resulting mixture was stirred for 1 h before it was quenched with saturated Na₂S₂O₃ (sat. aq., 10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated in
vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 20:1) afforded corresponding products 13a–j.

Starting materials: p-Vinylphenols 12a–d were synthesized according to the known literature procedures.1

4-(5-Hydroxy-5-methylhex-1-en-1-yl)phenol (12a): ca. 6.7:1 inseparable mixture of Z/E isomers; white solid; m.p. 110–112 °C; IR (film) υ \text{max} 2992, 2899, 1594, 1312, 1263, 1235, 1124, 1022, 882, 741 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), Z isomer) δ = 7.16 (d, J = 8.5 Hz, 2 H), 6.79 (d, J = 8.6 Hz, 2 H), 6.34 (d, J = 11.7 Hz, 1 H), 6.00 (s, 1 H), 5.55 (dt, J = 11.6, 7.2 Hz, 1 H), 2.42 (td, J = 8.7, 1.6 Hz, 2 H), 1.68–1.62 (m, 2 H), 1.60 (s, 1 H), 1.24 ppm (s, 6 H); \(^13\)C NMR (100 MHz, CDCl\(_3\), Z isomer) δ = 154.6, 130.9, 130.1(2C), 128.6, 115.2(2C), 71.6, 43.7, 43.1, 29.2(2C), 23.6 ppm; HRMS (ESI): calcd for C\(_{13}\)H\(_{19}\)O\(_2\) [M + H\(^+\)] 207.1380, found 207.1381.

(Z)-4-(5-Hydroxy-5-methylhex-1-en-1-yl)-2,6-dimethylphenol (12b): white solid; m.p. 84–85 °C; IR (film) υ \text{max} 3322, 2942, 2889, 1564, 1502, 1363, 1135, 1101, 896, 759 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ = 6.93 (s, 2 H), 6.30 (d, J = 11.6 Hz, 1 H), 5.54 (dt, J = 11.6, 7.3 Hz, 1 H), 4.95 (s, 1 H), 2.42 (ddd, J = 8.7, 8.1, 1.5 Hz, 2 H), 2.24 (s, 6 H), 1.70–1.61 (m, 2 H), 1.24 ppm (s, 6 H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) δ = 151.0, 130.6(2C), 129.6, 129.0(2C), 128.7, 122.8, 71.2, 43.7, 29.1(2C), 23.7, 16.0(2C) ppm; HRMS (ESI): calcd for C\(_{15}\)H\(_{23}\)O\(_2\) [M + H\(^+\)] 235.1693, found 235.1695.
2-Bromo-4-(5-hydroxy-5-methylhex-1-en-1-yl)phenol (12c): ca. 4:1 mixture of Z/E isomers; white solid; m.p. 147–149 °C; IR (film) \( \nu_{\text{max}} \) 3372, 2983, 2882, 1578, 1498, 1231, 1082, 1042, 856, 818, 738 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 7.43 \) (d, \( J = 1.9 \) Hz, 0.2 H), 7.39 (d, \( J = 1.8 \) Hz, 0.8 H), 7.17 (dd, \( J = 8.6, 2.0 \) Hz, 0.2 H), 7.13 (dd, \( J = 8.4, 1.8 \) Hz, 0.8 H), 6.96 (d, \( J = 8.4 \) Hz, 0.8 H), 6.92 (d, \( J = 8.4 \) Hz, 0.2 H), 6.28 (d, \( J = 11.5 \) Hz, 1 H), 6.08 (dt, \( J = 15.7, 6.8 \) Hz, 0.2 H), 5.83 (s, 0.8 H), 5.76 (s, 0.2 H), 5.61 (dt, \( J = 11.5, 7.3 \) Hz, 0.8 H), 2.44–2.33 (m, 1.6 H), 2.33–2.23 (m, 0.4 H), 1.63 (dd, \( J = 9.7, 6.9 \) Hz, 2 H), 1.43 (s, 1 H), 1.26 (s, 1.2 H), 1.23 (s, 4.8 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 151.3, 151.0, 132.4, 132.1, 131.6(2C), 130.1, 129.5, 129.3, 128.0, 127.2, 126.7, 116.1, 115.8, 110.4, 110.0, 71.2(2C), 43.6, 43.2, 29.3(2C), 29.2(2C), 27.9, 23.6 ppm; HRMS (ESI): calcd for C\(_{13}\)H\(_{18}\)BrO\(_2\)\(^+\) [M + H\(^+\)] 285.0485, found 285.0489.

2-Ethoxy-4-(5-hydroxy-5-methylhex-1-en-1-yl)phenol (12d): ca. 7.7:1 mixture of Z/E isomers; colorless oil; IR (film) \( \nu_{\text{max}} \) 3392, 2972, 2929, 1594, 1512, 1263, 1235, 1122, 1042, 826, 749 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), Z isomer) \( \delta = 6.88 \) (d, \( J = 8.0 \) Hz, 1 H), 6.82 (dd, \( J = 15.9, 8.1 \) Hz, 2 H), 6.32 (d, \( J = 11.5 \) Hz, 1 H), 5.54 (dt, \( J = 11.6, 7.2 \) Hz, 1 H), 4.08 (q, \( J = 6.9 \) Hz, 2 H), 2.41 (dd, \( J = 15.3, 7.2 \) Hz, 2 H), 1.63 (dd, \( J = 9.6, 6.8 \) Hz, 2 H), 1.42 (t, \( J = 7.0 \) Hz, 3 H), 1.21 ppm (s, 6 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), Z isomer) \( \delta = 145.4, 144.5, 130.9, 129.8, 128.7, 121.8, 114.4, 112.3, 70.8, 64.3, 43.6, 29.1(2C), 23.6, 14.8 ppm; HRMS (ESI): calcd for C\(_{15}\)H\(_{23}\)O\(_3\)\(^+\) [M + H\(^+\)] 251.1642, found 251.1643.
Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(4-hydroxyphenyl)methyl)indolizine-1-carboxylate (13a): obtained in 83% yield and >20:1 dr as a white solid; m.p. 216–218 °C; IR (film) $\nu_{\text{max}}$ 2971, 2925, 1692, 1663, 1510, 1259, 1227, 1058, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.16 (d, $J$ = 9.0 Hz, 1 H), 7.62 (d, $J$ = 7.1 Hz, 1 H), 7.30 (s, 1 H), 6.98 (t, $J$ = 10.9 Hz, 3 H), 6.71 (d, $J$ = 8.5 Hz, 2 H), 6.54 (t, $J$ = 6.8 Hz, 1 H), 5.11 (brs, 1 H), 4.66 (dd, $J$ = 13.7, 6.5 Hz, 1 H), 4.20 (d, $J$ = 6.1 Hz, 1 H), 3.91 (s, 3 H), 1.94 (dt, $J$ = 12.3, 6.9 Hz, 1 H), 1.80 (dt, $J$ = 16.0, 7.7 Hz, 1 H), 1.65 (dd, $J$ = 12.0, 7.7 Hz, 1 H), 1.44–1.31 (m, 1 H), 1.26 (s, 3 H), 1.15 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 165.7, 154.8, 136.1, 130.1, 129.9(2C), 125.7, 123.7, 121.8, 119.6, 115.3(2C), 115.0, 112.0, 102.6, 81.2, 80.0, 50.9, 47.7, 38.2, 30.0, 28.6, 27.8 ppm; HRMS (ESI): calecd for C$_{23}$H$_{26}$NO$_4$ $^+$ [M + H$^+$] 380.1856, found 380.1860.

Methyl 7-(tert-butyl)-3-((5,5-dimethyltetrahydrofuran-2-yl)(4-hydroxyphenyl)methyl)indolizine-1-carboxylate (13b): obtained in 80% yield and >20:1 dr as a white solid; m.p. 221–223 °C; IR (film) $\nu_{\text{max}}$ 2981, 2919, 1691, 1563, 1510, 1351, 1219, 1158, 751 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.09 (s, 1 H), 7.53 (d, $J$ = 7.3 Hz, 1 H), 7.22 (s, 1 H), 6.97 (d, $J$ = 8.1 Hz, 2 H), 6.71 (d, $J$ = 8.1 Hz, 2 H), 6.60 (d, $J$ = 6.1 Hz, 1 H), 5.74 (brs, 1 H), 4.64 (d, $J$ = 6.4 Hz, 1 H), 4.18 (d, $J$ = 5.7 Hz, 1 H), 3.91 (s, 3 H), 1.94 (dd, $J$ = 12.4, 6.4 Hz, 1 H), 1.77 (dd, $J$ = 19.9, 7.7 Hz, 1 H), 1.68–1.55 (m, 1 H), 1.42–1.25 (m, 13 H), 1.13 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 166.1, 155.0, 145.9, 136.7, 130.1, 129.7(2C), 124.9, 123.3, 115.3(2C), 114.7, 114.0, 111.4,
101.4, 81.1, 79.9, 50.8, 47.5, 38.2, 34.6, 30.4(3C), 29.7, 28.5, 27.8 ppm; HRMS (ESI): calcd for C_{27}H_{34}NO_{4}^{+} [M + H^{+}] 436.2482, found 436.2487.

Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(4-hydroxyphenyl)methyl)-6,8-dimethylindolizine-1-carboxylate (13c): obtained in 77% yield and >20:1 dr as a white solid; m.p. 164–166 °C; IR (film) \( \nu_{\text{max}} \) 2981, 2885, 1611, 1413, 1262, 1058, 789, 741 cm\(^{-1}\); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 7.28 (s, 1 H), 7.25 (s, 1 H), 7.01 (d, \( J = 8.5 \) Hz, 2 H), 6.70 (d, \( J = 8.5 \) Hz, 2 H), 6.59 (s, 1 H), 4.94 (brs, 1 H), 4.65 (dd, \( J = 13.3, 6.7 \) Hz, 1 H), 4.16 (d, \( J = 6.1 \) Hz, 1 H), 3.85 (s, 3 H), 2.72 (s, 3 H), 2.08 (s, 3 H), 1.96 (td, \( J = 12.6, 6.5 \) Hz, 1 H), 1.86–1.74 (m, 1 H), 1.64 (dd, \( J = 12.1, 7.6 \) Hz, 1 H), 1.37–1.28 (m, 1 H), 1.25 (s, 3 H), 1.16 ppm (s, 3 H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 165.5, 154.7, 134.1, 130.2(2C), 129.4, 126.3, 124.7, 121.2, 119.4, 116.3, 115.2(2C), 103.8, 81.0, 80.1, 51.0, 47.7, 38.2, 29.9(2C), 28.6, 27.8, 22.0, 18.2 ppm; HRMS (ESI): calcd for C_{25}H_{30}NO_{4}^{+} [M + H^{+}] 408.2169, found 408.2173.

Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(4-hydroxyphenyl)methyl)pyrrolo[2,1-a]isoquinoline-1-carboxylate (13d): obtained in 70% yield and >20:1 dr as a white solid; m.p. 151–153 °C; IR (film) \( \nu_{\text{max}} \) 3272, 2903, 1509, 1258, 1207, 1051, 887, 760 cm\(^{-1}\); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 9.82 (d, \( J = 8.3 \) Hz, 1 H), 7.54 (dd, \( J = 17.6, 9.7 \) Hz, 3 H), 7.48–7.40 (m, 1 H), 7.25 (d, \( J = 10.9 \) Hz, 1 H), 7.01 (d, \( J = 7.8 \) Hz, 2 H), 6.77 (d, \( J = 7.4 \) Hz, 1 H), 6.70 (d, \( J = 7.7 \) Hz, 2 H), 5.22 (brs, 1 H), 4.70 (dd, \( J = 12.7, 6.3 \) Hz, 1 H), 4.26 (d, \( J = 5.7 \) Hz, 1 H), 3.95 (s, 3 H), 2.06–1.93 (m, 1 H),
1.82 (dd, $J = 19.9, 7.5$ Hz, 1 H), 1.65 (s, 1 H), 1.35 (dd, $J = 12.3, 7.0$ Hz, 1 H), 1.28 (s, 3 H), 1.18 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 166.1, 154.9, 132.6, 130.1(2C), 128.6, 127.3(2C), 127.0(3C), 126.5, 125.8, 121.8, 115.3, 115.2, 113.0(2C), 107.4, 81.2, 79.9, 51.4, 47.6, 38.2, 29.9, 28.6, 27.8 ppm; HRMS (ESI): calcd for C$_{27}$H$_{28}$NO$_4$$^+$ [M + H$^+$] 430.2013, found 430.2017.

**Methyl 7-(tert-butyl)-3-((5,5-dimethyltetrahydrofuran-2-yl) (4-hydroxy-3,5-dimethylphenyl)methyl)indolizine-1-carboxylate (13e):**

![Methyl 7-(tert-butyl)-3-((5,5-dimethyltetrahydrofuran-2-yl) (4-hydroxy-3,5-dimethylphenyl)methyl)indolizine-1-carboxylate (13e)](image)

obtained in 76% yield and >20:1 dr as a white solid; m.p. 98–100 °C; IR (film) $\nu_{\text{max}}$ 2971, 2845, 1510, 1459, 1227, 1168, 887, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.12$ (s, 1 H), 7.60 (d, $J = 7.3$ Hz, 1 H), 7.23 (s, 1 H), 6.74 (s, 2 H), 6.62 (d, $J = 6.9$ Hz, 1 H), 4.73–4.55 (m, 2 H), 4.08 (d, $J = 6.2$ Hz, 1 H), 3.91 (s, 3 H), 2.16 (s, 6 H), 1.91 (dt, $J = 12.6, 6.3$ Hz, 1 H), 1.80 (dt, $J = 14.8, 7.6$ Hz, 1 H), 1.63 (dt, $J = 15.0, 7.6$ Hz, 1 H), 1.42–1.21 (m, 13 H), 1.14 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 165.9, 151.2, 145.7, 136.6, 129.5, 129.0(2C), 125.1, 123.3, 122.8(2C), 114.5, 114.0, 111.3, 101.5, 81.0, 80.1, 50.7, 47.8, 38.2, 34.6, 30.5(3C), 30.0, 28.6, 27.9, 15.9(2C) ppm; HRMS (ESI): calcd for C$_{29}$H$_{38}$NO$_4$$^+$ [M + H$^+$] 464.2795, found 464.2789.

**Methyl 3-((3-bromo-4-hydroxyphenyl)(5,5-dimethyltetrahydrofuran-2-yl) methyl)indolizine-1-carboxylate (13f):**

![Methyl 3-((3-bromo-4-hydroxyphenyl)(5,5-dimethyltetrahydrofuran-2-yl) methyl)indolizine-1-carboxylate (13f)](image)

obtained in 78% yield and >20:1 dr as a white solid; m.p. 155–157 °C; IR (film) $\nu_{\text{max}}$ 2988, 2875, 1563, 1310, 1126, 1058, 738 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.18$ (d, $J = 9.0$ Hz, 1 H), 7.60 (d, $J = 7.0$ Hz, 1 H), 7.29 (d, $J = 3.5$ Hz, 2 H), 7.05–
6.98 (m, 1 H), 6.94 (d, \( J = 8.3 \) Hz, 1 H), 6.88 (d, \( J = 8.3 \) Hz, 1 H), 6.58 (t, \( J = 6.7 \) Hz, 1 H), 5.67 (s, 1 H), 4.66 (dd, \( J = 13.0 \), 6.6 Hz, 1 H), 4.22 (d, \( J = 5.7 \) Hz, 1 H), 3.92 (s, 3 H), 2.02 (td, \( J = 13.0 \), 6.7 Hz, 1 H), 1.78 (td, \( J = 15.7 \), 7.7 Hz, 1 H), 1.66 (dd, \( J = 10.0 \), 5.3 Hz, 1 H), 1.36–1.28 (m, 1 H), 1.26 (s, 3 H), 1.15 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 165.6, 151.5, 136.2, 132.3, 131.4, 129.5, 124.7, 123.5, 122.0, 119.7, 115.9, 115.2, 112.2, 110.2, 102.8, 81.2, 79.7, 50.9, 47.1, 38.2, 29.7, 28.5, 27.7 ppm; HRMS (ESI): calcd for \( \text{C}_{23}\text{H}_{25}\text{BrNO}_{4}^+ \) [M + H\(^+\)] 458.0961, found 458.0964.

**Methyl 3-((3-bromo-4-hydroxyphenyl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)-7-(tert-butyl)indolizine-1-carboxylate (13g):** obtained in 75% yield and >20:1 dr as a white solid; m.p. 210–212 °C; IR (film) \( \nu_{\text{max}} \) 3321, 2987, 2922, 1655, 1540, 1259, 1231, 1059, 866, 748 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.14 \) (s, 1 H), 7.52 (d, \( J = 7.4 \) Hz, 1 H), 7.31 (d, \( J = 1.5 \) Hz, 1 H), 7.21 (s, 1 H), 6.94 (dd, \( J = 8.2 \), 1.7 Hz, 1 H), 6.88 (d, \( J = 8.3 \) Hz, 1 H), 6.65 (dd, \( J = 7.3 \), 1.7 Hz, 1 H), 5.70 (s, 1 H), 4.66 (dd, \( J = 12.6 \), 6.7 Hz, 1 H), 4.21 (d, \( J = 5.4 \) Hz, 1 H), 3.91 (s, 3 H), 2.04 (td, \( J = 13.2 \), 7.0 Hz, 1 H), 1.84–1.70 (m, 1 H), 1.70–1.58 (m, 1 H), 1.35–1.25 (m, 13 H), 1.14 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 165.7, 151.5, 146.1, 136.7, 132.4, 131.6, 129.6, 123.8, 123.0, 115.8, 114.9, 114.1, 111.7, 110.2, 101.7, 81.1, 79.6, 50.8, 46.9, 38.2, 34.6, 30.5(3C), 29.5, 28.4, 27.7 ppm; HRMS (ESI): calcd for \( \text{C}_{27}\text{H}_{33}\text{BrNO}_{4}^+ \) [M + H\(^+\)] 514.1587, found 514.1592.

**Methyl 3-((3-bromo-4-hydroxyphenyl)(5,5-dimethyltetrahydrofuran-2-yl)methyl)pyrrolo[2,1-a]isoquinoline-1-carboxylate (13h):** obtained in 67% yield and >20:1 dr
as a white solid; m.p. 144–146 °C; IR (film) \( \nu_{\text{max}} \) 2988, 2925, 1695, 1633, 1410, 1259, 1227, 1058, 744 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 10.27 (d, \( J = 8.3 \) Hz, 1 H), 8.05–7.98 (m, 2 H), 7.91 (t, \( J = 7.7 \) Hz, 2 H), 7.75 (d, \( J = 1.6 \) Hz, 1 H), 7.71 (s, 1 H), 7.44–7.38 (m, 1 H), 7.32 (d, \( J = 8.4 \) Hz, 1 H), 7.26 (d, \( J = 7.4 \) Hz, 1 H), 5.88 (s, 1 H), 5.14 (dd, \( J = 12.6, 6.7 \) Hz, 1 H), 4.73 (d, \( J = 5.3 \) Hz, 1 H), 4.39 (s, 3 H), 2.50 (td, \( J = 13.1, 6.7 \) Hz, 1 H), 2.24 (dt, \( J = 15.5, 7.4 \) Hz, 1 H), 2.17–2.05 (m, 1 H), 1.74 (d, \( J = 8.8 \) Hz, 1 H), 1.71 (s, 3 H), 1.61 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 165.9, 151.4, 132.7, 132.3, 131.8, 129.7, 128.6, 127.5, 127.4, 127.0, 126.6, 125.9, 125.8, 121.6, 115.9, 115.5, 113.3, 110.3, 107.6, 81.2, 79.6, 51.4, 47.0, 38.2, 29.6, 28.4, 27.7 ppm; HRMS (ESI): calcd for C\(_{27}\)H\(_{27}\)BrNO\(_4\)\(^+\) [M + H\(^+\)] 508.1118, found 508.1125.

**Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(3-ethoxy-4-hydroxyphenyl)methyl)indolizine-1-carboxylate (13i):** obtained in 63% yield and >20:1 dr as a white solid; m.p. 176–178 °C; IR (film) \( \nu_{\text{max}} \) 2971, 2925, 1692, 1663, 1510, 1259, 1227, 1128, 890, 740 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) = 8.17 (d, \( J = 9.0 \) Hz, 1 H), 7.63 (d, \( J = 7.0 \) Hz, 1 H), 7.31 (s, 1 H), 7.03–6.93 (m, 1 H), 6.80 (d, \( J = 8.1 \) Hz, 1 H), 6.65 (d, \( J = 8.1 \) Hz, 1 H), 6.58 (s, 1 H), 6.54 (t, \( J = 6.8 \) Hz, 1 H), 5.61 (s, 1 H), 4.66 (dd, \( J = 13.4, 6.7 \) Hz, 1 H), 4.17 (d, \( J = 6.2 \) Hz, 1 H), 4.00 (dd, \( J = 16.0, 7.0 \) Hz, 2 H), 3.91 (s, 3 H), 1.95 (dt, \( J = 12.6, 6.6 \) Hz, 1 H), 1.88–1.75 (m, 1 H), 1.66 (dt, \( J = 12.3, 7.7 \) Hz, 1 H), 1.43–1.32 (m, 4 H), 1.27 (s, 3 H), 1.16 ppm (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) = 165.6, 145.8, 144.9, 136.1, 129.6, 125.6, 123.8, 121.7(2C), 119.6, 114.9, 114.1, 111.9(2C), 102.6, 81.1,
Methyl 3-((5,5-dimethyltetrahydrofuran-2-yl)(3-ethoxy-4-hydroxyphenyl)methyl)pyrrolo[2,1-a]isoquinoline-1-carboxylate (13j): obtained in 55% yield and >20:1 dr as a white solid; m.p. 220–222 °C; IR (film) $\nu_{\text{max}}$ 2991, 2875, 1676, 1310, 1254, 1217, 1058, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.84 (d, $J$ = 8.3 Hz, 1 H), 7.55 (dd, $J$ = 15.0, 8.5 Hz, 3 H), 7.45 (t, $J$ = 7.4 Hz, 1 H), 7.29 (s, 1 H), 6.79 (t, $J$ = 8.3 Hz, 2 H), 6.72–6.58 (m, 2 H), 5.58 (s, 1 H), 4.70 (dd, $J$ = 13.1, 6.5 Hz, 1 H), 4.25 (d, $J$ = 5.8 Hz, 1 H), 4.09–3.82 (m, 5 H), 2.00 (td, $J$ = 12.9, 6.5 Hz, 1 H), 1.85 (td, $J$ = 15.7, 7.9 Hz, 1 H), 1.74–1.61 (m, 1 H), 1.36 (t, $J$ = 6.9 Hz, 4 H), 1.29 (s, 3 H), 1.18 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 166.0, 145.7, 144.9, 132.5, 130.0, 128.6, 127.3(2C), 126.9(2C), 126.5, 125.8, 121.9, 121.8, 115.2, 114.1, 113.0, 112.1, 107.4, 81.0, 79.9, 64.4, 51.3, 48.1, 38.2, 30.0, 28.7, 27.8, 14.8 ppm; HRMS (ESI): calcd for C$_{29}$H$_{32}$NO$_5^+$ [M + H$^+$] 474.2275, found 474.2278.
Synthetic application of indole derivative 2a

Preparation of triflate 14: To a stirred solution of indole 2a (335 mg, 1.0 mmol) in CH₂Cl₂ (5 mL) at 0°C were added pyridine (0.19 mL, 2.4 mmol) and Tf₂O (0.20 mL, 1.2 mmol). The resulting mixture was warmed to room temperature and stirred for further 1 h before it was quenched with NH₄Cl (sat. aq., 10 mL). The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 5 mL). The combined organic layers were dried (Na₂SO₄) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 10:1) afforded triflate 14 (430 mg, 92%) as a colorless oil.

2-((5,5-Dimethyltetrahydrofuran-2-yl)(1-methyl-1H-indol-3-yl)methyl)phenyl trifluoromethanesulfonate (14): IR (film) νmax 2970, 2875, 1481, 1416, 1211, 1141, 1070, 891, 766, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ = 7.56 (dd, J = 6.4, 2.8 Hz, 1 H), 7.44 (d, J = 8.0 Hz, 1 H), 7.25–7.18 (m, 5 H), 7.15 (t, J = 7.5 Hz, 1 H), 7.00 (t, J = 7.5 Hz, 1 H), 4.70 (d, J = 6.3 Hz, 1 H), 4.61 (dd, J = 14.2, 6.4 Hz, 1 H), 3.76 (s, 3 H), 1.93–1.84 (m, 1 H), 1.84–
1.73 (m, 1 H), 1.72–1.56 (m, 2 H), 1.25 (s, 3 H), 1.20 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 147.4, 136.7, 136.5, 131.2, 128.2, 128.0, 127.9, 127.8, 121.4, 120.9, 119.5, 118.8, 118.6 ($J_{C-F} = 318$ Hz), 113.6, 108.9, 81.5, 81.2, 40.9, 38.2, 32.8, 30.6, 28.9, 28.3 ppm; HRMS (ESI): calcd for C$_{23}$H$_{25}$F$_3$NO$_4$S$^+$ [M + H$^+$] 468.1451, found 468.1453.

**Synthesis of indole 9**: To a stirred solution of triflate 14 (46.7 mg, 0.1 mmol) in MeOH (1 mL) at room temperature were added Pd/C (5 mg, 10% wt/wt), magnesium metal (3 mg, 0.12 mmol) and ammonium acetate (7.8 mg, 0.1 mmol). The resulting mixture was stirred for 5 h before it was filtered through a short pad of celite. The filtrate was concentrated *in vacuo*. Flash column chromatography (silica gel, hexanes:EtOAc 1:1) afforded 9 (27 mg, 85%) as a white solid.

**3-((5,5-Dimethyltetrahydrofuran-2-yl)(phenyl)methyl)-1-methyl-1H-indole** (9):

m.p. 108–110 °C; IR (film) $\nu_{\text{max}}$ 2967, 2929, 2863, 1467, 1366, 1143, 1052, 906, 739, 703 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.28 (t, $J$ = 6.3 Hz, 2 H), 7.26–7.18 (m, 4 H), 7.18–7.07 (m, 3 H), 6.92 (t, $J$ = 7.4 Hz, 1 H), 4.61 (q, $J$ = 7.1 Hz, 1 H), 4.28 (d, $J$ = 7.1 Hz, 1 H), 3.77 (s, 3 H), 1.76 (dq, $J$ = 12.4, 7.5 Hz, 2 H), 1.64 (dt, $J$ = 12.0, 7.9 Hz, 1 H), 1.54–1.45 (m, 1 H), 1.27 (s, 3 H), 1.20 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 142.9, 136.9, 129.0(2C), 128.1, 128.0(2C), 126.9, 126.1, 121.2, 119.8, 118.4, 115.9, 108.8, 81.4, 81.0, 48.6, 38.3, 32.7, 30.7, 29.0, 28.2 ppm; HRMS (ESI): calcd for C$_{22}$H$_{26}$NO$^+$ [M + H$^+$] 320.2009, found 320.2012.
Synthesis of tetracycle 15. To a stirred solution of triflate 14 (46.7 mg, 0.1 mmol) in N,N-dimethylacetamide (1 mL) were added Pd(OAc)$_2$ (2.0 mg, 0.01 mmol), Cy$_3$P (5.6 mg, 0.02 mmol) and Et$_2$NH (20.6 μL, 0.2 mmol). The resulting mixture was stirred at 100 °C for 5 h before it was cooled to room temperature and concentrated in in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 10:1) afforded tetracycle 15 (28 mg, 75%) as a white solid.

10-(5,5-Dimethyltetrahydrofuran-2-yl)-5-methyl-5,10-dihydroindeno[1,2-b]-indole (15): m.p. 120–122 °C; IR (film) $\nu_{\text{max}}$ 2961, 2926, 2856, 1462, 1261, 1134, 1049, 802, 745 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.79 (d, $J$ = 7.5 Hz, 1 H), 7.71 (d, $J$ = 7.8 Hz, 1 H), 7.63 (d, $J$ = 7.5 Hz, 1 H), 7.36 (t, $J$ = 8.2 Hz, 2 H), 7.25–7.12 (m, 3 H), 4.76 (dt, $J$ = 11.9, 6.0 Hz, 1 H), 4.21 (d, $J$ = 5.3 Hz, 1 H), 4.06 (s, 3 H), 1.64–1.55 (m, 2 H), 1.51–1.42 (m, 1 H), 1.40 (s, 3 H), 1.30 (s, 3 H), 1.16–1.05 ppm (m, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 148.9, 144.1, 142.0, 136.1, 127.1(2C), 124.5, 124.1, 122.04, 121.2, 119.6(2C), 117.5, 109.7, 81.1, 79.8, 46.9, 38.5, 31.1, 28.7, 27.6, 27.5 ppm; HRMS (ESI): calcd for C$_{22}$H$_{24}$NO$^+ [M + H^+]$ 318.1852, found 318.1853.

Synthesis of ester 16. To a stirred solution of triflate 14 (46.7 mg, 0.1 mmol) in MeOH/DMSO (1.5 mL, 1:2) were added Pd(OAc)$_2$ (2.0 mg, 0.01 mmol), dpdp (4.1 mg, 0.01 mmol) and Et$_3$N (27.7μL, 0.2 mmol). The resulting mixture was stirred under CO atmosphere at 70 °C for 12 h before it was cooled to room temperature and concentrated in in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 10:1) afforded ester 16 (31 mg, 81%) as a while solid.
Methyl 2-((5,5-dimethyltetrahydrofuran-2-yl)(1-methyl-1H-indol-3-yl)methyl)-benzoate (16): m.p. 93–95 °C; IR (film) $\nu_{\text{max}}$ 2929, 2868, 1750, 1373, 1237, 1134, 879, 741 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.74 (d, $J$ = 7.6 Hz, 1 H), 7.36 (dd, $J$ = 15.0, 7.8 Hz, 2 H), 7.22 (dq, $J$ = 14.5, 7.5 Hz, 4 H), 7.12 (t, $J$ = 7.5 Hz, 1 H), 6.93 (t, $J$ = 7.4 Hz, 1 H), 5.48 (d, $J$ = 6.7 Hz, 1 H), 4.59 (q, $J$ = 6.9 Hz, 1 H), 3.92 (s, 3 H), 3.77 (s, 3 H), 1.85–1.70 (m, 2 H), 1.69–1.55 (m, 1 H), 1.55–1.45 (m, 1 H), 1.25 (s, 3 H), 1.17 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 169.3, 143.6, 136.8, 131.2(2C), 129.9, 129.5, 128.2, 127.3, 125.7, 121.2, 119.9, 118.5, 115.9, 108.7, 81.7, 81.1, 52.1, 42.4, 38.3, 32.8, 30.0, 28.8, 28.2 ppm; HRMS (ESI): calcd for C$_{24}$H$_{28}$NO$_3$ $^{+}$ [M + H$^+$] 378.2064, found 378.2060.

**Synthesis of tetracycles 17a and 17b:** To a stirred solution of indole 2a (33.5 mg, 0.1 mmol) in CH$_2$Cl$_2$ (2 mL) at –78 °C was added a solution of DMDO in acetone (0.06 M, 3.3 mL, 0.2 mmol). The resulting mixture was stirred for 1 h before it was diluted with CH$_2$Cl$_2$ (5 mL) and quenched with H$_2$O (5 mL). The layers were separated, and the organic layer was washed with brine (10 mL). The organic layer was dried (Na$_2$SO$_4$) and concentrated in vacuo. Flash column chromatography (silica gel, hexanes:EtOAc 80:1) afforded tetracycles 17a and 17b (78%, dr = 1:1) as colorless oils.

(5a,10b)-11-(5,5-Dimethyltetrahydrofuran-2-yl)-6-methyl-5a,6,10b,11-tetrahydrochromeno[2,3-b]indol-10b-ol (17a): IR (film) $\nu_{\text{max}}$ 2971, 2885, 1657, 1510, 1359, 1246, 1055, 890, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 7.45 (d, $J$ = 7.3 Hz, 1 H), 7.10 (t, $J$ = 7.4 Hz, 1 H), 6.98...
(dd, J = 13.1, 7.7 Hz, 2 H), 6.86 (t, J = 7.5 Hz, 1 H), 6.78 (d, J = 7.5 Hz, 1 H), 6.57 (t, J = 7.4 Hz, 1 H), 6.15 (d, J = 7.8 Hz, 1 H), 5.88 (s, 1 H), 5.47 (s, 1 H), 4.99–4.82 (m, 1 H), 3.20 (d, J = 10.5 Hz, 1 H), 2.86 (s, 3 H), 2.61 (td, J = 11.5, 4.8 Hz, 1 H), 1.93 (s, 3 H), 1.48 (s, 3 H), 1.45 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 154.5, 151.3, 129.3, 128.8, 127.4, 127.2, 125.3, 125.1, 122.8, 118.7, 116.9, 104.7, 103.8, 85.8, 82.6, 77.3, 48.5, 38.0, 33.0, 30.3, 28.8, 27.3 ppm; HRMS (ESI): calcd for C$_{22}$H$_{26}$NO$_3$ $^+$ [M + H$^+$] 352.1907, found 352.1912.

(5a,10b)-11-(5,5-Dimethyltetrahydrofuran-2-yl)-6-methyl-5a,6,10b,11-tetrahydrochloromeno[2,3-b]indol-10b-ol (17b): IR (film) $\nu_{\text{max}}$ 2979, 2897, 1657, 1599, 1501, 1344, 1242, 1151, 883, 741 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.10 (d, J = 7.2 Hz, 1 H), 6.98 (dt, J = 12.6, 7.5 Hz, 2 H), 6.87 (d, J = 6.7 Hz, 1 H), 6.81 (d, J = 7.9 Hz, 1 H), 6.75 (t, J = 7.3 Hz, 1 H), 6.56 (t, J = 7.3 Hz, 1 H), 6.50 (s, 1 H), 6.23 (d, J = 7.8 Hz, 1 H), 5.57 (s, 1 H), 4.59 (dd, J = 14.3, 8.5 Hz, 1 H), 3.27 (d, J = 9.8 Hz, 1 H), 2.97 (s, 3 H), 1.89–1.61 (m, 4 H), 1.42 (s, 3 H), 1.33 ppm (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 153.9, 150.9, 131.3, 129.4, 129.2, 128.2, 126.7, 122.6, 122.3, 117.9, 117.6, 105.2, 101.2, 83.5, 83.2, 80.1, 51.2, 37.2, 32.6, 30.0, 29.3, 28.5 ppm; HRMS (ESI): calcd for C$_{22}$H$_{26}$NO$_3$ $^+$ [M + H$^+$] 352.1907, found 352.1910.
III) References


IV) $^1$H and $^{13}$C NMR Spectra of Compounds

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

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

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

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

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
\[ \text{\textsuperscript{1}H NMR spectrum (400 MHz, CDCl}_3] \]

\[ \text{\textsuperscript{13}C NMR spectrum (100 MHz, CDCl}_3] \]
\( ^1H \) NMR spectrum (400 MHz, CDCl\(_3\))

\( ^{13}C \) NMR spectrum (100 MHz, CDCl\(_3\))
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

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

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

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

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

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

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

13C NMR spectrum (100 MHz, CDCl₃)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$\text{H NMR spectrum (400 MHz, CDCl}_3$)

$\text{C NMR spectrum (100 MHz, CDCl}_3$)
\[ ^1\text{H NMR spectrum (400 MHz, CDCl}_3) \]

\[ ^{13}\text{C NMR spectrum (100 MHz, CDCl}_3) \]
$^1$H NMR spectrum (400 MHz, CDCl₃)

$^{13}$C NMR spectrum (100 MHz, CDCl₃)
$^{1}\text{H NMR spectrum (400 MHz, CDCl}_3\text{)}$

$^{13}\text{C NMR spectrum (100 MHz, CDCl}_3\text{)}$
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

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

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

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

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

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

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

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

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

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
\textbf{\textsuperscript{1}H NMR spectrum (400 MHz, CDCl$_3$)}

\textbf{\textsuperscript{13}C NMR spectrum (100 MHz, CDCl$_3$)}
$^{1}$H NMR spectrum (400 MHz, CDCl$_3$)

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

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

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
\(^1\)H NMR spectrum (400 MHz, CDCl\(_3\))

\(^{13}\)C NMR spectrum (100 MHz, CDCl\(_3\))
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

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

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

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

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

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

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)
(ca. 2.2:1 mixture of diastereomers)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
(ca. 2.2:1 mixture of diastereomers)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)
(ca. 6.7:1 mixture of Z/E isomers)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
(ca. 6.7:1 mixture of Z/E isomers)
$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$^1$H NMR spectrum (400 MHz, CDCl$_3$)
(ca. 4:1 mixture of $Z$/$E$ isomers)

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
(ca. 4:1 mixture of $Z$/$E$ isomers)
$\text{EtO} \quad \text{OH}$

12d

$^1$H NMR spectrum (400 MHz, CDCl$_3$)
(ca. 7.7:1 mixture of Z/E isomers)

13C NMR spectrum (100 MHz, CDCl$_3$)
(ca. 7.7:1 mixture of Z/E isomers)
$^{1}H$ NMR spectrum (400 MHz, CDCl$_3$)

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

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

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
$\text{1H NMR spectrum (400 MHz, CDCl}_3\text{)}$

$\text{13C NMR spectrum (100 MHz, CDCl}_3\text{)}$
$^{1}$H NMR spectrum (400 MHz, CDCl$_3$)

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

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

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

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

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

$^{13}$C NMR spectrum (100 MHz, CDCl$_3$)
\[ ^{1}H \text{ NMR spectrum (400 MHz, CDCl}_3] \]

\[ ^{13}C \text{ NMR spectrum (100 MHz, CDCl}_3] \]
$^1$H NMR spectrum (400 MHz, CDCl$_3$)

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

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