Supplementary Information for:

Enantioselective Nazarov cyclization of indole enones cooperatively catalyzed by Lewis acids and chiral Brønsted acids

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1. General Information

Unless otherwise noted, all solvents used in the reactions were distilled from appropriate drying agents prior to use.¹ ZnCl₂ (99.99%) was purchased from Alfa Aesar Chemical Company and sublimated under high vacuum before use. Zn(OTf)₂ (98%) was purchased from Sigma-Aldrich Chemical Company and used without further purification. All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glovebox (MBRAUN LABstar) or using standard Schlenk techniques. ¹H NMR and ¹³C NMR spectra were recorded with a Brucker AV 400 spectrometer at 400 MHz (¹H NMR) and 101 MHz (¹³C NMR) in CDCl₃. Chemical shifts were reported in ppm down field from internal Me₄Si. HRMS were recorded on an Agilent 6520 Q-TOF LC/MS spectrometer with ESI or MALDI-TOF resource. HPLC analysis was performed on an Agilent 1260 Infinity LC chromatography. Melting points were measured on a RY–I or SGW X-4 apparatus and uncorrected. Optical rotations were determined by a Rudolph Autopol VI polarimeter. Infrared spectra were obtained on a Nicolet MAGNA-IR 560 FT-IR spectrometer and peak values are reported in reciprocal centimeters (cm⁻¹).

2. Synthesis and Analytical Data of Substituted Indole Enones

2.1 Synthesis of indole enones

Indole enones were synthesized following the procedures below, while N-substituted indole-2-carbaldehyde, substituted vinyl bromide, α , β -unsaturated aldehyde and Weinreb amide were purchased or synthesized according to literatures. Substrates **2a**–**2i**, **2k**–**2o** were prepared according to route A; substrates **2j** and **2p** were prepared according to route B; substrates **2q**–**2s** were prepared according to route C.



General Method of Route A^{2,3,4}



In an oven dried 100 mL four-necked flask, Mg turnings (1.09 g, 45 mmol) and a small amount of the solution of substituted vinyl bromide (30 mmol) in dry THF (40 mL) was added successively. After initiation automatically, the remaining solution was added alternately to keep the reaction refluxing slightly. After complete addition, the mixture was heated at 45~50 °C for 30 min. The resulting solution was transferred dropwise to a solution of N-substituted indole-2-carbaldehyde (20 mmol) in THF (20 mL). The reaction mixture was stirred for 30 min at room temperature. Saturated aq. NH4Cl (10 mL) was added to quench the reaction. The resulting mixture was then extracted with ethyl acetate and the organic layer was combined and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired indole enol.



To a solution of the Dess-Martin periodinane (DMP, 9.26 g, 21.8 mmol) in DCM (40 mL), pyridine (8.0 mL, 99.3 mmol) was added. The resulting mixture was stirred for 5 min, then a solution of indole enol (19.9 mmol) in DCM (25 mL) was added dropwise. Stirring was continued for another 30 min and the reaction mixture was diluted and washed with the mixture of saturated NaHCO₃ and saturated Na₂S₂O₃ (1:1 v/v) for 3 times, then dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired indole enone.

General Method of Route B^{5,6}



N-substituted indole (15 mmol) was dissolved in dry THF (25 ml) and then "BuLi (7.5 mL, 2.4 M, 18 mmol) was added at 0 °C. The mixture was stirred for 3 h at room temperature. Then the 2-methylene-aldehyde (16.5 mmol) was added slowly, and the resulting mixture was stirred for 12 h at room temperature. The mixture was carefully quenched with saturated aq. NH₄Cl at 0 °C. The organic layer was separated and aqueous layer was extracted with Et₂O twice. The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired indole enol, which subsequently been oxidized to corresponding ketone using the method described in Route A.

General Method of Route C^{7,8}



To a solution of substituted Weinreb amide (15.2 mmol) in dry Et₂O (50 mL) was added ^{*i*}BuLi (38 mL, 1.0 M, 38 mmol) at -78 °C over the course of about 30 min. Upon consumption of the starting material, monitored by TLC, the reaction was allowed to warm to about -50 °C, and saturated aq. NH₄Cl (15 mL) was added slowly to quench the reaction. After the reaction mixture was warmed to room temperature, the organic layer was separated and aqueous layer was extracted with Et₂O twice. The combined organic layer was dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired ketone.



Bis(dimethylamino)methane (17 mL, 125 mmol) and acetic anhydride (12 mL, 125 mmol) was added successively to a solution of ketone (12.5 mmol) dissolved in anhydrous DMF (12 mL). The mixture was stirred at 95 °C until the consumption of starting material, monitored by TLC or ¹H NMR. After cooled to room temperature, the brown mixture was distilled under reduced pressure and the residue was purified by column chromatography on silica gel to afford the desired indole enone.

2.2 Analytical Data of Intermediates

2-methyl-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol

Light yellow solid, mp: 64–65 °C. TLC $R_f = 0.25$ (petroleum ether/ethyl acetate, PE/EA = 10:1, v/v), 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, J = 7.9 Hz, 1H), 7.30 (dd, J =8.2, 0.5 Hz, 1H), 7.21 (ddd, J = 8.2, 5.6, 2.1 Hz, 1H), 7.09 (td, J = 7.5, 1.0 Hz, 1H), 6.42 (s, 1H), 5.30 (s, 1H), 5.22 (d, J = 0.7 Hz, 1H), 5.10 (dd, J = 2.7, 1.4 Hz, 1H), 3.75 (s, 3H), 2.02 (s, 1H), 1.75 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 139.7, 138.2, 127.1, 121.8, 120.7, 119.5, 111.9, 109.1, 100.9, 71.2, 30.1, 19.5. ESI-HRMS calcd for [C₁₃H₁₆NO, M + H]⁺: 202.1226, Found 202.1224.

1-(1-isopropyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol



Colorless solid, mp: 40–42 °C. TLC $R_f = 0.64$ (PE/EA = 4:1, v/v), 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.56–7.48 (m, 2H), 7.16–7.09 (m, 1H), 7.07–7.00 (m, 1H), 6.33 (s, 1H), 5.19

(d, J = 4.5 Hz, 1H), 5.17 (s, 1H), 5.06 (s, 1H), 4.88–4.76 (m, 1H), 2.39–2.24 (m, 1H), 1.69 (s, 3H), 1.58–1.53 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 145.0, 139.1, 135.7, 128.2, 121.1, 121.0, 119.0, 112.1, 111.5, 101.0, 71.2, 47.4, 21.2, 21.1, 19.7. ESI-HRMS calcd for [C₁₅H₂₀NO, M + H]⁺: 230.1539, Found 230.1540.

1-(1-allyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol

Colorless solid, mp: 66–67 °C. TLC $R_f = 0.58$ (PE/EA = 4:1, N/V), 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.8Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 7.20–7.16 (m, 1H), 7.08 (t, J= 7.4 Hz, 1H), 6.42 (s, 1H), 5.97–5.86 (m, 1H), 5.23 (s, 1H), 5.20 (d, J = 4.6 Hz, 1H), 5.09 (d, J = 9.1 Hz, 2H), 4.88–4.71 (m, 3H), 2.22 (d, J = 4.8 Hz, 1H), 1.71 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 139.3, 137.5, 133.8, 127.2, 121.8, 120.8, 119.6, 116.0, 111.7, 109.6, 101.2, 70.7, 45.7, 19.5. ESI-HRMS calcd for [C₁₅H₁₈NO, M + H]⁺: 228.1383, Found 228.1384.

1-(1-benzyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol



6.9 Hz, 2H), 6.52 (s, 1H), 5.45 (dd, J = 39.7, 17.1 Hz, 2H), 5.20 (s, 1H), 5.18 (d, J = 3.7 Hz, 1H), 5.04 (d, J = 1.1 Hz, 1H), 1.96 (s, 1H), 1.68 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 139.7, 138.0, 137.9, 128.7, 127.3, 127.2, 125.8, 122.1, 120.8, 119.8, 111.9, 109.7, 101.4, 70.8, 46.8, 19.4. ESI-HRMS calcd for [C₁₉H₂₀NO, M + H]⁺: 278.1539, Found 278.1542.

2-methyl-1-(1-phenyl-1H-indol-2-yl)prop-2-en-1-ol



Light yellow solid, mp: 111–112 °C. TLC $R_f = 0.47$ (PE/EA = 8:1, v/v), 89% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65–7.63 (m, 1H), 7.54–7.45 (m, 5H), 7.18–7.08 (m, 3H), 6.64 (s, 1H),

5.08 (s, 1H), 5.01 (s, 1H), 4.94 (s, 1H), 1.92–1.73 (m, 1H), 1.69 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 141.1, 138.6, 137.4, 129.3, 128.4, 128.1, 127.3, 122.2, 120.7, 120.2, 111.7, 110.5, 101.2, 70.1, 19.0. ESI-HRMS calcd for [C₁₈H₁₈NO, M + H]⁺: 264.1383, Found 264.1389.

1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-ol

6.96 (d, J = 8.1 Hz, 2H), 6.58 (s, 1H), 5.00 (d, J = 4.5 Hz, 1H), 4.97 (s, 1H), 4.90 (s, 1H), 3.84 (s, 3H), 2.12 (d, J = 5.0 Hz, 1H), 1.65 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 144.9, 141.4, 138.9, 129.9, 129.6, 127.2, 122.0, 120.6, 120.1, 114.4, 111.7, 110.4, 100.7, 70.2, 55.5, 19.0 . ESI-HRMS calcd for [C₁₉H₂₀NO₂, M + H]⁺: 294.1489, Found 294.1492.

2-methyl-1-(1-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)prop-2-en-1-ol



Light yellow solid, mp: 100–101 °C. TLC $R_f = 0.41$ (PE/EA = 8:1, v/v), 93% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.5 Hz, 2H), 7.65–7.61 (m, 1H), 7.57–7.56 (m, 2H), 7.20–7.08 (m, 3H), 6.65 (s, 1H), 5.02 (s, 1H), 5.00 (s, 1H), 4.94 (d, J = 1.0 Hz, 1H), 2.11–2.02 (m, 1H), 1.65 (s, 3H); ¹³C NMR (101

MHz, CDCl₃) δ 144.7, 140.8, 140.6, 138.4, 130.0 (q, J = 33.1 Hz), 128.7, 127.5, 126.5 (q, J = 3.5 Hz), 123.8 (q, J = 273.4 Hz), 122.8, 121.0, 120.8, 111.9, 110.2, 102.5, 70.1, 19.2. ESI-HRMS calcd for [C₁₉H₁₇F₃NO, M + H]⁺: 332.1257, Found 332.1255.

2-methyl-1-(1-(naphthalen-2-yl)-1H-indol-2-yl)prop-2-en-1-ol



Yellow solid, mp: 136–137 °C. TLC $R_f = 0.45$ (PE/EA = 8:1, v/v), 94% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.00–7.88 (m, 4H), 7.69–7.64 (m, 1H), 7.62–7.55 (m, 2H), 7.47 (s, 1H), 7.17–

7.15 (m, 3H), 6.69 (s, 1H), 5.13 (d, J = 5.4 Hz, 1H), 5.02 (s, 1H), 4.94 (s, 1H), 1.91 (d, J = 5.4 Hz, 1H), 1.71 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.0, 141.4, 138.8, 134.8, 133.5, 132.6, 129.3, 128.0, 127.8, 127.5, 126.9, 126.8, 126.7, 126.3, 122.3, 120.8, 120.4, 111.8, 110.5, 101.4, 70.2, 19.1. ESI-HRMS calcd for [C₂₂H₂₀NO, M + H]⁺: 314.1539, Found 314.1538.

1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-ol



1H), 5.35 (d, J = 4.7 Hz, 1H), 5.26 (s, 1H), 5.11 (s, 1H), 3.74 (s, 3H), 2.15–1.96 (m, 3H), 1.05 (t, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 150.7, 139.9, 138.2, 127.1, 121.8, 120.7, 119.5, 109.7, 109.0, 101.0, 70.6, 30.1, 25.6, 12.2. ESI-HRMS calcd for [C₁₄H₁₈NO, M + H]⁺: 216.1383, Found 216.1380.

3-methyl-1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-ol



Yellow solid, mp: 61–62 °C. TLC $R_f = 0.75$ (PE/EA = 10:1, v/v), 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 10.4, 4.6 Hz, 1H),

7.09 (dd, J = 7.7, 7.1 Hz, 1H), 6.39 (s, 1H), 5.37 (d, J = 4.8 Hz, 1H), 5.25 (s, 1H), 5.15 (s, 1H), 3.71 (s, 3H), 2.30–2.19 (m, 1H), 2.08 (d, J = 5.2 Hz, 1H), 1.05 (dd, J = 9.4, 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 155.7, 140.1, 138.2, 127.0, 121.7, 120.7, 119.4, 109.0, 108.5, 101.1, 69.6, 30.6, 30.1, 23.0, 21.9. ESI-HRMS calcd for [C₁₅H₂₀NO, M + H]⁺: 230.1539, Found 230.1545.

1-(1-methyl-1H-indol-2-yl)-2-phenylprop-2-en-1-ol



Yellow solid, mp: 96–97 °C. TLC $R_f = 0.53$ (PE/EA = 4:1, v/v), 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 7.9 Hz, 1H), 7.40 (d, J = 7.4 Hz, 2H), 7.32–7.19 (m, 5H), 7.07 (t, J =

7.4 Hz, 1H), 6.43 (s, 1H), 5.88 (d, J = 5.4 Hz, 1H), 5.66 (s, 1H), 5.51 (s, 1H), 3.80 (s, 3H), 2.14 (d, J = 5.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.6, 139.9, 139.2, 138.1, 128.4, 127.8, 127.0, 126.5, 121.8, 120.9, 119.4, 114.6, 109.1, 101.7, 68.7, 30.0. ESI-HRMS calcd for [C₁₈H₁₈NO, M + H]⁺: 264.1383, Found 264.1379.

2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



Light green solid, mp: 118–119 °C. TLC $R_f = 0.39$ (PE/EA = 4:1, v/v), 99% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.8 Hz, 1H), 7.33–7.28 (m, 3H), 7.21 (dd, J = 13.2, 5.9 Hz, 1H), 7.07 (t, J = 7.4 Hz,

1H), 6.80 (d, J = 8.4 Hz, 2H), 6.41 (s, 1H), 5.81 (d, J = 5.3 Hz, 1H), 5.57 (s, 1H), 5.40 (s, 1H), 3.76–3.75 (m, 6H), 2.29–2.20 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 159.3, 148.0, 140.1, 138.1, 131.7, 127.6, 127.1, 121.8, 120.8, 119.4, 113.8, 113.1, 109.1, 101.7, 68.9, 55.2, 30.1. ESI-HRMS calcd for [C₁₉H₂₀NO₂, M + H]⁺: 294.1489, Found 294.1497.

2-(4-fluorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



Yellow solid, mp: 109–110 °C. TLC $R_f = 0.41$ (PE/EA = 4:1, v/v), 98% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.9 Hz, 1H), 7.30–7.23 (m, 3H), 7.21–7.16 (m,

1H), 7.08–7.03 (m, 1H), 6.95–6.88 (m, 2H), 6.34 (s, 1H), 5.67 (d, J = 5.4 Hz, 1H), 5.55 (s, 1H), 5.44 (s, 1H), 3.66 (s, 3H), 2.55 (d, J = 5.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 162.3 (d, J = 248.1 Hz), 147.5, 139.6, 138.1, 135.3 (d, J = 3.3 Hz), 128.1 (d, J = 8.0 Hz), 126.9, 121.9, 120.8, 119.5, 115.2 (d, J = 21.6 Hz), 114.5, 109.1, 101.7, 68.7, 29.9. ESI-HRMS calcd for [C₁₈H₁₇FNO, M + H]⁺: 282.1289, Found 282.1284.

2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol

CI



Yellow solid, mp: 130–131 °C. TLC $R_f = 0.43$ (PE/EA = 4:1, v/v), 99% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.9 Hz, 1H), 7.32–7.28 (m, 3H), 7.25–7.19 (m,

3H), 7.07 (t, J = 7.4 Hz, 1H), 6.38 (s, 1H), 5.80 (d, J = 5.7 Hz, 1H), 5.64 (s, 1H), 5.53 (s, 1H), 3.77 (s, 3H), 2.19 (t, J = 4.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 147.5, 139.5, 138.1, 137.6, 133.6, 128.5, 127.8, 126.9, 122.0, 120.9, 119.6, 115.1, 109.1, 101.8, 68.7, 30.1. ESI-HRMS calcd for [C₁₈H₁₇NOCl, M + H]⁺: 298.0993, Found 298.0997.

2-(benzo[d][1,3]dioxol-5-yl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol

(t, J = 7.6 Hz, 1H), 7.07 (t, J = 7.4 Hz, 1H), 6.90 (s, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.70 (d, J = 8.1 Hz, 1H), 6.39 (s, 1H), 5.90 (s, 2H), 5.76 (d, J = 5.6 Hz, 1H), 5.55 (s, 1H), 5.40 (s, 1H), 3.74 (s, 3H), 2.27 (d, J = 5.1 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 148.1, 147.6, 147.2, 139.9, 138.1, 133.4, 127.0, 121.9, 120.8, 120.0, 119.5, 113.8, 109.1, 108.1, 107.1, 101.7, 101.0, 68.9, 30.1. ESI-HRMS calcd for [C₁₉H₁₈NO₃, M + H]⁺: 308.1281, Found 308.1280.

1-(1,5-dimethyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-ol

MeOH
NYellow sticky oil. TLC $R_f = 0.28$ (PE/EA = 10:1, v/v), 92%
yield. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 0.6 Hz,
1H), 7.12 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H),
6.24 (s, 1H), 5.23 (d, J = 5.1 Hz, 1H), 5.17 (s, 1H), 5.09 (s, 1H), 3.57 (s, 3H), 2.41–
2.39 (m, 4H), 2.19 (dt, J = 13.6, 6.8 Hz, 1H), 1.00 (dd, J = 8.8, 6.9 Hz, 6H); ¹³C NMR
(101 MHz, CDCl₃) δ 155.6, 140.1, 136.5, 128.5, 127.2, 123.2, 120.2, 108.7, 108.4,
100.4, 69.5, 30.5, 29.9, 22.9, 21.9, 21.3. ESI-HRMS calcd for [C₁₆H₂₂NO, M + H]⁺:
244.1696, Found 244.1698.

1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



Light green solid, mp: 32–33 °C. TLC $R_f = 0.53$ (PE/EA = 30:1, v/v), 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.28 (m, 2H), 7.21 (s, 1H), 7.13 (td, J = 9.1, 2.4 Hz, 1H),

4.05 (s, 3H), 2.80 (d, J = 7.0 Hz, 2H), 2.31 (dp, J = 13.5, 6.7 Hz, 1H), 1.01 (d, J = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.3, 158.1(d, J = 237.8 Hz), 136.7, 136.5, 125.7 (d, J = 10.4 Hz), 114.8 (d, J = 27.2 Hz), 111.3 (d, J = 9.5 Hz), 110.7 (d, J = 5.5 Hz), 106.7 (d, J = 23.1 Hz), 49.0, 32.4, 25.9, 22.7. ESI-HRMS calcd for [C₁₄H₁₇FNO, M + H]⁺: 234.1289, Found 234.1291.

1-(5-chloro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



Light yellow solid, mp: 39–40 °C. TLC $R_f = 0.47$ (PE/EA = 15:1, v/v), 94% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (t, J = 1.6 Hz, 1H), 7.29 (d, J = 1.6 Hz, 2H), 7.18 (s, 1H), 4.04

(s, 3H), 2.80 (d, J = 7.0 Hz, 2H), 2.31 (dp, J = 13.5, 6.8 Hz, 1H), 1.01 (d, J = 6.8 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.3, 138.2, 136.1, 126.5, 126.2, 126.1, 121.8, 111.5, 110.3, 49.0, 32.4, 25.9, 22.7. ESI-HRMS calcd for [C₁₄H₁₇ClNO, M + H]⁺: 250.0993, Found 250.0997.

1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



Light yellow solid, mp: 27–28 °C. TLC $R_f = 0.41$ (PE/EA = 40:1, v/v), 93% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.31–7.24 (m, 1H), 7.14 (d, J = 8.4 Hz, 1H), 6.79 (dd, J = 9.9, 7.8 Hz, 1H), 4.06 (s, 3H), 2.82 (d, J = 7.1 Hz, 2H), 2.32 (dp,

J = 13.5, 6.7 Hz, 1H), 1.02 (d, J = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 194.2, 157.4 (d, J = 252.0 Hz), 142.1 (d, J = 10.0 Hz), 135.3, 126.2 (d, J = 7.9 Hz), 115.5 (d, J = 22.8 Hz), 107.0, 106.4 (d, J = 4.0 Hz), 104.8 (d, J = 18.6 Hz), 48.9, 32.7, 26.0, 22.7. ESI-HRMS calcd for [C₁₄H₁₇FNO, M + H]⁺: 234.1289, Found 234.1286.

2.3 Analytical Data of Substituted Indole Enones

2-methyl-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2a)



Greenish yellow solid, mp: 77–78 °C. TLC $R_f = 0.80$ (PE/EA = 10:1, v/v), 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 1H), 7.40–7.34 (m, 2H), 7.15 (ddd, J = 8.0, 5.6, 2.3

Hz, 1H), 7.09 (s, 1H), 5.85 (s, 1H), 5.83–5.81 (m, 1H), 4.01 (s, 3H), 2.09 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.4, 145.2, 140.4, 134.8, 125.8, 125.6, 125.1, 122.9, 120.6, 113.5, 110.2, 31.8, 18.7. IR (film): \tilde{v} 3122, 3050, 2962, 2924, 2848, 1629, 800, 753, 743 cm⁻¹. ESI-HRMS calcd for [C₁₃H₁₄NO, M + H]⁺: 200.1070, Found 200.1070.

1-(1-isopropyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2b)

Yellow solid, mp: 31–32 °C. TLC $R_f = 0.58$ (PE/EA = 20:1, v/v), 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.38–7.32 (m, 1H), 7.17 (t, J

= 7.5 Hz, 1H), 7.03 (s, 1H), 5.93–5.92 (m, 2H), 5.38 (hept, J = 7.0 Hz, 1H), 2.14 (s, 3H), 1.70 (d, J = 7.0 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 190.6, 145.6, 138.4, 135.4, 126.6, 126.3, 124.7, 123.1, 120.1, 113.7, 112.9, 48.3, 21.5, 18.5. IR (film): \tilde{v} 3003, 2975, 2934, 2878, 1638, 1623, 789, 757, 747 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₈NO, M + H]⁺: 228.1383, Found 228.1385.

1-(1-allyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2c)

allyl O N Me

Greenish yellow liquid. TLC $R_f = 0.42$ (PE/EA = 20:1, v/v), 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 1H), 7.41–7.33 (m, 2H), 7.19–7.14 (m, 1H), 7.12 (s, 1H), 6.02 (ddt, J

= 16.8, 10.2, 5.1 Hz, 1H), 5.84–5.82 (m, 2H), 5.15–5.08 (m, 3H), 4.93 (dd, J = 17.2, 1.1 Hz, 1H), 2.09 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.2, 145.1, 139.8, 134.3, 134.0, 125.8, 125.7, 125.3, 122.9, 120.7, 116.0, 114.0, 110.7, 46.9, 18.7. IR (film): \tilde{v} 3083, 3062, 3033, 2983, 2955, 2924, 2852, 1638, 1622, 793, 752, 738 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₆NO, M + H]⁺: 226.1226, Found 226.1228.

1-(1-benzyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2d)



Yellow solid, mp: 62–63 °C. TLC $R_f = 0.74$ (PE/EA = 10:1, v/v), 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.0 Hz, 1H), 7.37–7.29 (m, 2H), 7.26–7.14 (m, 5H), 7.05 (d, J =

7.3 Hz, 2H), 5.82 (d, J = 2.9 Hz, 2H), 5.76 (s, 2H), 2.06 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.3, 145.1, 140.1, 138.3, 134.5, 128.5, 127.1, 126.4, 126.0, 125.9, 125.4, 122.9, 120.9, 114.3, 110.9, 48.0, 18.7. IR (film): \tilde{v} 3101, 3084, 3061, 3030, 2952, 2921, 2850, 1635, 1621, 793, 753, 725, 694 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₈NO, M + H]⁺: 276.1383, Found 276.1385.

2-methyl-1-(1-phenyl-1H-indol-2-yl)prop-2-en-1-one (2e)

White solid, mp: 59–60 °C. TLC $R_f = 0.59$ (PE/EA = 20:1, v/v), 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.33–

7.27 (m, 3H), 7.24–7.17 (m, 3H), 6.01 (s, 1H), 5.88 (s, 1H), 1.99 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.9, 145.2, 140.6, 138.6, 135.7, 129.2, 127.6, 127.2, 126.1, 125.9, 125.9, 122.7, 121.3, 113.9, 111.4, 18.3. IR (film): \tilde{v} 3109, 3057, 3029, 2986, 2957, 2918, 1973, 1907, 1873, 1790, 1639, 796, 763, 742, 696 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₆NO, M + H]⁺: 262.1226, Found 262.1228.

1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-one (2f)

Light yellow solid, mp: 95–96 °C. TLC $R_f = 0.50$ (PE/EA = An 10:1, v/v), 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J Me = 8.3 Hz, 1H), 7.32–7.27 (m, 1H), 7.26–7.16 (m, 5H), 7.02– 6.98 (m, 2H), 5.99 (s, 1H), 5.88 (s, 1H), 3.86 (s, 3H), 2.00 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.9, 158.8, 145.1, 140.9, 135.6, 131.3, 128.3, 125.9, 125.8, 125.7, 122.6, 121.2, 114.3, 113.5, 111.4, 55.4, 18.3. IR (film): v 3093, 3064, 2983, 2952, 2936, 2835, 1942, 1902, 1871, 1821, 1643, 1513, 799, 788, 748 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₈NO₂, M + H]⁺: 292.1332, Found 292.1335.

2-methyl-1-(1-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)prop-2-en-1-one (2g)



White solid, mp: 144–145 °C. TLC $R_f = 0.58$ (PE/EA = 50:1, v/v), 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.82–7.79 (m, 3H), 7.49 (d, J = 8.2 Hz, 2H), 7.41–7.36 (m, 1H), 7.32–7.26 (m, 3H), 6.11 (s, 1H), 5.99 (s, 1H), 2.07 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.6, 144.9, 141.8, 140.3, 135.4, 129.5 (q, *J* =

32.9 Hz), 127.5, 126.5, 126.4 (q, J = 4.0 Hz), 126.4, 126.2, 123.9 (q, J = 273.2 Hz), 123.0, 121.8, 115.1, 111.0, 18.3. IR (film): v 3134, 3094, 3064, 1947, 1930, 1869, 1640, 1122, 1104, 1070, 827, 790, 749, 719 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₅F₃NO, M + H]⁺: 330.1100, Found 330.1104.

2-methyl-1-(1-(naphthalen-2-yl)-1H-indol-2-yl)prop-2-en-1-one (2h)

2-Np 0 Me Light yellow solid, mp: 116–117 °C. TLC $R_f = 0.42$ (PE/EA = 15:1, v/v), 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.7 Hz, 1H), 7.91–7.87 (m, 1H), 7.83 (dd, J = 5.7, 3.2 Hz,

1H), 7.80 (s, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.51 (dd, J = 6.1, 3.2 Hz, 2H), 7.38 (dd, J = 8.6, 1.7 Hz, 1H), 7.31–7.17 (m, 4H), 6.05 (s, 1H), 5.88 (s, 1H), 1.97 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 188.8, 145.1, 140.7, 136.1, 135.8, 133.4, 132.5, 129.1, 128.0, 127.8, 126.6, 126.3, 126.2, 126.0, 125.8, 125.2, 122.8, 121.4, 114.1, 111.4,

18.3. IR (film): v 3106, 3059, 3028, 2961, 2921, 1954, 1910, 1825, 1787, 1638, 817, 756 cm⁻¹. ESI-HRMS calcd for $[C_{22}H_{18}NO, M + H]^+$: 312.1383, Found 312.1385.

1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-one (2i)



Yellow liquid, TLC $R_f = 0.81$ (PE/EA = 20:1, v/v), 83% yield. Et ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 1H), 7.41– 7.34 (m, 2H), 7.15 (ddd, J = 8.0, 5.4, 2.4 Hz, 1H), 7.09 (s, 1H), 5.78 (s, 1H), 5.73 (d, J = 1.2 Hz, 1H), 4.03 (s, 3H), 2.51 (q, J = 7.4 Hz, 2H), 1.14 (t, J

= 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.7, 151.2, 140.4, 135.3, 125.7, 125.7, 122.9, 122.3, 120.6, 113.8, 110.3, 31.8, 25.4, 12.5. IR (film): v 3058, 2966, 2935, 2874, 1637, 1619, 792, 753, 740 cm⁻¹. ESI-HRMS calcd for $[C_{14}H_{16}NO, M +$ H]⁺: 214.1226, Found 214.1227.

3-methyl-1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-one (2j)

Me Yellow solid, mp: 50–51 °C. TLC $R_f = 0.59$ (PE/EA = 50:1, v/v), 93% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 1H), 7.40–7.33 (m, 2H), 7.14 (ddd, J = 7.9, 5.0, 2.8 Hz, 1H),

7.08 (s, 1H), 5.69 (s, 1H), 5.64 (s, 1H), 4.05 (s, 3H), 3.05 (hept, J = 6.8 Hz, 1H), 1.15 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.3, 155.8, 140.4, 135.7, 125.8, 125.6, 122.9, 120.6, 119.8, 114.1, 110.2, 31.9, 29.9, 21.4. IR (film): v 3090, 3049, 2969, 2950, 2868, 1632, 1617, 791, 773, 752, 728 cm⁻¹. ESI-HRMS calcd for $[C_{15}H_{18}NO, M + H]^+$: 228.1383, Found 228.1388.

1-(1-methyl-1H-indol-2-yl)-2-phenylprop-2-en-1-one (2k)



Yellow solid, mp: 80–81 °C. TLC $R_f = 0.53$ (PE/EA = 10:1, v/v), 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.1Hz, 1H), 7.47 (dd, J = 8.0, 1.4 Hz, 2H), 7.41–7.31 (m, 5H),

7.18 (s, 1H), 7.15 (ddd, J = 7.9, 5.3, 2.5 Hz, 1H), 6.06 (s, 1H), 5.79 (s, 1H), 4.14 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.1, 149.1, 140.7, 137.4, 135.3, 128.5, 128.3, 127.2, 126.3, 125.7, 123.2, 120.8, 120.7, 115.4, 110.4, 32.1. IR (film): v 3093, 3040, S15

3032, 2949, 1641, 787, 746, 729, 713, 701 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₆NO, M + H]⁺: 262.1226, Found 262.1228.

2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2l)



Yellow solid, mp: 74–75 °C. TLC $R_f = 0.39$ (PE/EA = 20:1, v/v), 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.0 Hz, 1H), 7.41–7.39 (m, 4H), 7.18 (s,

1H), 7.14 (t, J = 6.6 Hz, 1H), 6.89 (d, J = 8.4 Hz, 2H), 5.98 (s, 1H), 5.69 (s, 1H), 4.13 (s, 3H), 3.80 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.4, 159.7, 148.4, 140.6, 135.3, 129.9, 128.4, 126.2, 125.7, 123.2, 120.7, 119.0, 115.3, 113.9, 110.3, 55.3, 32.1. IR (film): v 3123, 3084, 3009, 2966, 2947, 2836, 1630, 1606, 1509, 846, 805, 788, 742 cm^{-1} . ESI-HRMS calcd for $[C_{19}H_{18}NO_2, M + H]^+$: 292.1332, Found 292.1333.

2-(4-fluorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2m)

Me

Bright yellow solid, mp: 65–66 °C. TLC $R_f = 0.44$ (PE/EA = 20:1, v/v), 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd, J = 8.1, 0.7 Hz, 1H), 7.47–7.38 (m,

4H), 7.19–7.11 (m, 2H), 7.05 (t, J = 8.5 Hz, 2H), 6.02 (s, 1H), 5.80 (s, 1H), 4.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 189.7, 162.8 (d, J = 248.9 Hz), 148.0, 140.7, 135.1, 133.5 (d, *J* = 3.2 Hz), 129.0 (d, *J* = 8.2 Hz), 126.4, 125.7, 123.2, 120.9, 120.9, 115.5 (d, J = 21.7 Hz), 115.4, 110.4, 32.1. IR (film): \tilde{v} 3105, 3060, 2951, 1632, 1601, 1505, 1464, 981, 843, 754, 739 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₅FNO, M + H]⁺: 280.1132, Found 280.1135.

2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2n)

Yellow solid, mp: 101–102 °C. TLC $R_f = 0.47$ (PE/EA = CI Me \cap 20:1, v/v), 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.1 Hz, 1H), 7.43–7.39 (m, 4H), 7.33 (d, J =

8.5 Hz, 2H), 7.18–7.12 (m, 2H), 6.05 (s, 1H), 5.82 (s, 1H), 4.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 189.5, 147.9, 140.8, 135.8, 135.1, 134.3, 128.7, 128.6, 126.5,

125.7, 123.2, 121.3, 120.9, 115.5, 110.4, 32.1. IR (film): v 3065, 2951, 1639, 1614, 987, 915, 843, 748, 729, 647 cm⁻¹. ESI-HRMS calcd for $[C_{18}H_{15}CINO, M + H]^+$: 296.0837, Found 296.0828.

2-(benzo[d][1,3]dioxol-5-yl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (20)

Colorless solid, mp: 117–118 °C. TLC $R_f = 0.61$ Me (PE/EA = 10:1, v/v), 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.1 Hz, 1H), 7.42–7.36 (m, 2H),

7.17 (s, 1H), 7.14 (ddd, J = 8.0, 4.9, 3.0 Hz, 1H), 6.97 (d, J = 1.7 Hz, 1H), 6.93 (dd, J= 8.1, 1.8 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.95 (s, 2H), 5.93 (s, 1H), 5.68 (s, 1H), 4.13 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 190.0, 148.7, 147.9, 147.8, 140.7, 135.2, 131.6, 126.3, 125.7, 123.2, 121.3, 120.8, 119.2, 115.4, 110.3, 108.3, 107.5, 101.2, 32.0. IR (film): v 3134, 3087, 2897, 2788, 1622, 1609, 1501, 1486, 894, 870, 743, 691 cm^{-1} . ESI-HRMS calcd for $[C_{19}H_{16}NO_3, M + H]^+$: 306.1125, Found 306.1126.

1-(1,5-dimethyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2p)

Greenish yellow oil. TLC $R_f = 0.66$ (PE/EA = 20:1, v/v), Me 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), Me 7.28 (d, J = 8.6 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.00 (s,

1H), 5.68 (s, 1H), 5.63 (s, 1H), 4.03 (s, 3H), 3.04 (hept, J = 6.8 Hz, 1H), 2.44 (s, 3H), 1.14 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.4, 155.8, 139.1, 135.7, 129.9, 127.8, 125.8, 122.1, 119.6, 113.6, 110.0, 31.9, 29.9, 21.4, 21.3. IR (film): v 3092, 3021, 2962, 2871, 1636, 1621, 793 cm⁻¹. ESI-HRMS calcd for [C₁₆H₂₀NO, M + H]⁺: 242.1539, Found 242.1541.

1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2q)

Green liquid. TLC $R_f = 0.54$ (PE/EA = 20:1, v/v), 68% yield. Me O ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.27 (m, 2H), 7.13 (td, J = 9.1, 2.2 Hz, 1H), 7.01 (s, 1H), 5.71 (s, 1H), 5.67 (s, 1H),

4.03 (s, 3H), 3.04 (hept, J = 6.4 Hz, 1H), 1.14 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 S17

MHz, CDCl₃) δ 191.1, 158.0 (d, J = 237.7 Hz), 155.6, 137.0, 136.8, 125.5 (d, J = 10.2 Hz), 120.3, 114.7 (d, J = 27.1 Hz), 113.3 (d, J = 5.5 Hz), 111.2 (d, J = 9.5 Hz), 106.8 (d, J = 23.1 Hz), 32.0, 29.8, 21.3. IR (film): \tilde{v} 3095, 3070, 2963, 2872, 1642, 1516, 1470, 1391, 1193, 986, 953, 925, 858, 790, 768 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₇FNO, M + H]⁺: 246.1289, Found 246.1294.

1-(5-chloro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2r)

 $\begin{array}{c} \text{Me o} \\ & \text{Ne o} \\ &$

0.8 Hz, 1H), 4.03 (s, 3H), 3.04 (hept, J = 6.8 Hz, 1H), 1.14 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 155.6, 138.6, 136.6, 126.4, 126.2, 126.1, 121.9, 120.5, 112.9, 111.4, 32.1, 29.8, 21.4. IR (film): \tilde{v} 3133, 2961, 2922, 2864, 1638, 1507, 1460, 912, 788, 746, 700 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₇ClNO, M + H]⁺: 262.0993, Found 262.0996.

1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2s)



Colorless solid, mp: 68–69 °C. $R_f = 0.41$ (PE/EA = 40:1, v/v), r 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.25 (m, 1H), 7.17–7.14 (m, 2H), 6.80 (dd, J = 10.0, 7.8 Hz, 1H), 5.73 (s, 1H), 5.69 (d, J = 0.9 Hz, 1H), 4.05 (s, 3H), 3.04 (hept, J = 6.8 Hz,

1H), 1.15 (d, J = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.0, 157.4 (d, J = 252.1 Hz), 155.5, 142.5 (d, J = 10.0 Hz), 135.7, 126.2 (d, J = 8.0 Hz), 120.5, 115.4 (d, J = 22.8 Hz), 109.6, 106.3 (d, J = 4.0 Hz), 104.9 (d, J = 18.6 Hz), 32.4, 29.8, 21.3. IR (film): \tilde{v} 3090, 2957, 2871, 1633, 1622, 1573, 1513, 1468, 1230, 1136, 974, 763, 723, 708 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₇FNO, M + H]⁺: 246.1289, Found 246.1289.

3. Typical Procedure for Nazarov Cyclization of Indole Enones



The ZnCl₂ (1.4 mg, 0.01 mmol, 5 mol%) and (*R*)-1e (8.6 mg, 0.012 mmol, 6 mol%) were introduced into an oven-dried Schlenk tube in an argon-filled glovebox. After 2 mL DCE was injected into the Schlenk tube, the mixture was stirred at 40 °C. A solution of 2a (40 mg, 0.2 mmol) in 1 mL DCE was introduced into the mixture in one portion. The TLC showed that the reaction finished in 48 hours. Then the reaction mixture was concentrated and purified by a flash chromatography on silica gel (PE/EA = 10:1, v/v) to give 3a as a colorless oil.

4. Analytical Data of Cyclization Products

(+)-2,4-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3a)



Colorless oil, TLC $R_f = 0.45$ (PE/EA = 10:1, v/v), 98% yield, 91:9 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm

UV detecter, $t_{\rm R} = 6.62$ min (major) and $t_{\rm R} = 7.63$ min (minor). $[\alpha]_{\rm D}^{27}$ +3.4 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.16 (t, J = 7.3 Hz, 1H), 3.91 (s, 3H), 3.32 (dd, J = 16.7, 6.3 Hz, 1H), 3.06–3.01 (m, 1H), 2.64 (d, J = 16.7 Hz, 1H), 1.37 (d, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.2, 145.5, 143.2, 138.4, 127.1, 123.5, 122.1, 120.5, 111.3, 47.8, 30.4, 29.0, 17.6. IR (film): \tilde{v} 3055, 2961, 2928, 2869, 2851, 1678, 1500, 961, 741 cm⁻¹. ESI-HRMS calcd for [C₁₃H₁₄NO, M + H]⁺: 200.1070, Found 200.1071.

(+)-4-isopropyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3b)



White solid, mp: 77–79 °C. TLC $R_f = 0.62$ (PE/EA = 10:1, v/v), 98% yield, 90:10 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min,

220 nm UV detecter, $t_{\rm R} = 5.16$ min (major) and $t_{\rm R} = 5.76$ min (minor). [α]_D²⁷ +10.0 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.6 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 4.89 (hept, J = 6.8 Hz, 1H), 3.33 (dd, J = 16.7, 6.5 Hz, 1H), 3.08–3.01 (m, 1H), 2.66 (dd, J = 16.7, 2.3 Hz, 1H), 1.61 (dd, J = 6.8, 1.6 Hz, 6H), 1.38 (d, J = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.6, 144.6, 143.5, 137.4, 126.4, 122.8, 121.6, 119.7, 111.8, 47.3, 28.6, 22.1, 22.0, 17.3. IR (film): $\tilde{\nu}$ 2967, 2927, 2870, 1681, 1462, 1343, 968, 741 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₈NO, M + H]⁺: 228.1383, Found 228.1382.

(+)-4-allyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3c)



Colorless oil, TLC $R_f = 0.52$ (PE/EA = 10:1, v/v), 93% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm

UV detecter, $t_{\rm R} = 5.82$ min (major) and $t_{\rm R} = 6.95$ min (minor). $[\alpha]_{\rm D}^{27} + 2.6$ (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 8.0 Hz, 1H), 7.40–7.34 (m, 2H), 7.20–7.14 (m, 1H), 5.97 (ddd, J = 22.3, 10.5, 5.4 Hz, 1H), 5.14 (dd, J = 10.0, 0.8 Hz, 1H), 5.06 (dd, J = 17.1, 0.9 Hz, 1H), 5.01–4.90 (m, 2H), 3.32 (dd, J = 16.7, 6.4 Hz, 1H), 3.08–2.99 (m, 1H), 2.65 (dd, J = 16.8, 2.1 Hz, 1H), 1.37 (d, J = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.4, 144.3, 143.2, 137.5, 133.2, 126.6, 123.2, 121.7, 120.2, 116.9, 111.6, 47.3, 46.0, 28.6, 17.1. IR (film): \tilde{v} 3055, 2962, 2926, 2869, 2852, 1683, 1645, 1614, 1546, 947, 923, 895, 844, 742 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₆NO, M + H]⁺: 226.1226, Found 226.1228.

(-)-4-benzyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3d)



Light yellow solid, mp: 69–72 °C. TLC $R_f = 0.52$ (PE/EA = 10:1, v/v), 87% yield, 88:12 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol =

90:10, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R} = 6.33$ min (minor) and $t_{\rm R} = 7.35$ min (major). [α] $_{\rm D}^{27}$ –1.2 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 1H), 7.35–7.32 (m, 2H), 7.25–7.22 (m, 5H), 7.17–7.14 (m, 1H), 5.56 (d, J = 15.7 Hz, 1H), 5.51 (d, J = 15.7 Hz, 1H), 3.35 (dd, J = 16.8, 6.3 Hz, 1H), 3.12–3.03 (m, 1H), 2.68 (d, J = 16.8 Hz, 1H), 1.39 (d, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.6, 144.4, 143.5, 137.7, 137.4, 128.6, 127.5, 127.3, 126.8, 123.4, 121.8, 120.3, 111.7, 47.5, 47.4, 28.7, 17.1. IR (film): \tilde{v} 3087, 3061, 3031, 2962, 2925, 2869, 2850, 1682, 1614, 1563, 913, 742, 703 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₈NO, M + H]⁺: 276.1383, Found 276.1384.

(+)-2-methyl-4-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3e)



Colorless solid, mp: 94–96 °C. TLC $R_f = 0.48$ (PE/EA = 10:1, v/v), 90% yield, 92:8 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0

mL/min, 220 nm UV detecter, $t_{\rm R} = 5.82$ min (major) and $t_{\rm R} = 6.90$ min (minor). [α]_D²⁷+44.7 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 8.0 Hz, 1H), 7.58– 7.47 (m, 5H), 7.41–7.34 (m, 2H), 7.23 (t, J = 7.4 Hz, 1H), 3.39 (dd, J = 16.9, 6.5 Hz, 1H), 3.13–3.03 (m, 1H), 2.72 (dd, J = 16.9, 2.0 Hz, 1H), 1.38 (d, J = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.0, 145.7, 144.4, 137.3, 136.3, 129.1, 127.3, 127.1, 125.7, 123.6, 121.6, 121.1, 112.3, 47.4, 28.4, 17.3. IR (film): \tilde{v} 3049, 2961, 2924, 2901, 2869, 2839, 1686, 1595, 1542, 1500, 892, 759, 747 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₆NO, M + H]⁺: 226.1226, Found 262.1230.

(+)-4-(4-methoxyphenyl)-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3f)

Colorless solid, mp: 97–99 °C. TLC $R_f = 0.31$ (PE/EA = 10:1,



v/v), 95% yield, 92:8 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R}$ = 7.86 min (major) and $t_{\rm R}$ = 9.24 min (minor). [α]_D²⁷ +35.0 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.47–7.44 (m, 2H), 7.43–7.39 (m, 1H),7.25 (t, *J* = 7.4 Hz, 1H), 7.09–7.04 (m, 2H), 3.90 (s, 3H), 3.42 (dd, *J* = 16.9, 6.5 Hz, 1H), 3.15–3.07 (m, 1H), 2.75 (dd, *J* = 16.9, 2.2 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.1, 158.5, 145.0, 144.7, 137.5, 129.2, 127.2, 127.0, 123.3, 121.5, 120.9, 114.3, 112.2, 55.4, 47.3, 28.3, 17.2. IR (film): \tilde{v} 2958, 2925, 2869, 2852, 1687, 1543, 1514, 1457, 1249, 743 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₈NO₂, M + H]⁺: 292.1332, Found 292.1337.

(+)-2-methyl-4-(4-(trifluoromethyl)phenyl)-1,4-dihydrocyclopenta[b]indol-3(2H)one (3g)



Colorless solid, mp: 136–138 °C. TLC $R_f = 0.36$ (PE/EA = 15:1, v/v), 76% yield, 91:9 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detecter, $t_R = 6.21$ min (major) and $t_R = 6.79$ min (minor). [α]_D²⁷ +42.1 (*c* 1.0, CHCl₃). ¹H NMR (400

MHz, CDCl₃) δ 7.76 (d, *J* = 8.1 Hz, 3H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 3.40 (dd, *J* = 17.0, 6.4 Hz, 1H), 3.13–3.05 (m, 1H), 2.73 (dd, *J* = 17.0, 1.9 Hz, 1H), 1.39 (d, *J* = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.0, 147.0, 144.0, 139.4, 137.0, 128.7 (q, *J* = 32.9 Hz), 127.9, 126.3 (q, *J* = 3.7 Hz), 125.6, 124.0, 123.9 (q, *J* = 273.2 Hz), 121.9, 121.7, 112.0, 47.4, 28.3, 17.2. IR (film): \tilde{v} 3057, 2955, 2923, 2870, 2850, 1684, 1455, 1335, 1114, 849, 762, 747 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₅F₃NO, M + H]⁺: 330.1100, Found 330.1102.

(+)-2-methyl-4-(naphthalen-2-yl)-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3h)



Colorless solid, mp: 119–120 °C. TLC $R_f = 0.36$ (PE/EA = 10:1,

v/v), 92% yield, 92:8 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R}$ = 7.53 min (major) and $t_{\rm R}$ = 8.93 min (minor). [α]_D²⁸ +49.7 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.98–7.92 (m, 2H), 7.86 (dd, *J* = 9.2, 6.6 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64–7.56 (m, 2H), 7.53–7.46 (m, 2H), 7.38 (td, *J* = 7.2, 0.8 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 3.39 (dd, *J* = 16.9, 6.5 Hz, 1H), 3.08 (pd, *J* = 7.4, 2.2 Hz, 1H), 2.72 (dd, *J* = 16.9, 2.2 Hz, 1H), 1.39 (d, *J* = 7.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.0, 145.8, 144.5, 137.5, 133.8, 133.4, 132.1, 129.0, 127.9, 127.7, 127.4, 126.6, 126.1, 124.4, 123.6, 123.5, 121.7, 121.2, 112.3, 47.4, 28.4, 17.2. IR (film): \tilde{v} 3056, 2958, 2925, 2868, 2851, 1684, 1512, 1476, 1451, 969, 743 cm⁻¹. ESI-HRMS calcd for [C₂₂H₁₈NO, M + H]⁺: 312.1383, Found 312.1385.

(+)-2-ethyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3i)



Colorless solid, mp: 83–84 °C. TLC $R_f = 0.42$ (PE/EA = 10:1, v/v), 93% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detecter, $t_R = 5.95$ min (major) and $t_R =$

6.70 min (minor). $[\alpha]_D^{27}$ +37.6 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.17 (t, J = 7.4 Hz, 1H), 3.91 (s, 3H), 3.22 (dd, J = 16.8, 6.3 Hz, 1H), 2.97–2.89 (m, 1H), 2.73 (dd, J = 16.8, 1.5 Hz, 1H), 2.08–1.95 (m, 1H), 1.67–1.55 (m, 1H), 1.03 (t, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.2, 144.9, 143.2, 138.6, 126.7, 123.0, 121.7, 120.1, 110.9, 54.1, 30.0, 25.9, 24.9, 11.4. IR (film): \tilde{v} 3051, 2959, 2932, 2917, 2870, 2847, 1678, 1614, 1560, 1488, 902, 756, 746 cm⁻¹. ESI-HRMS calcd for [C₁₄H₁₆NO, M + H]⁺: 214.1226, Found 214.1227.

(+)-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3j)

0.46 cm ID), hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R}$ = 6.08 min (minor) and $t_{\rm R}$ = 6.55 min (major). [α]_D²⁸ +51.1 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.41 (td, *J* = 8.4, 1.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 3.91 (s, 3H), 3.08–2.97 (m, 2H), 2.83 (d, *J* = 15.3 Hz, 1H), 2.50–2.42 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 144.9, 143.6, 139.3, 126.6, 123.0, 121.7, 120.1, 110.9, 58.4, 30.1, 29.0, 21.5, 20.8, 16.8. IR (film): \tilde{v} 3055, 2955, 2927, 2869, 1672, 1615, 1488, 1202, 1050, 820, 739 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₈NO, M + H]⁺: 228.1383, Found 228.1386.

(+)-4-methyl-2-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3k)



Light yellow solid, mp: 126–128 °C. TLC $R_f = 0.41$ (PE/EA = 6:1, v/v), 95% yield, 86:14 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol =

80:20, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R} = 5.88$ min (minor) and $t_{\rm R} = 7.93$ min (major). [α]_D²⁸ +177.4 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.35–7.28 (m, 2H), 7.26–7.24 (m, 2H), 7.22–7.18 (m, 2H), 4.15 (d, *J* = 4.9 Hz, 1H), 3.91 (s, 3H), 3.59 (dd, *J* = 17.1, 6.8 Hz, 1H), 3.14 (d, *J* = 17.1 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 194.1, 145.2, 143.6, 140.2, 138.0, 128.7, 127.7, 127.0, 127.0, 122.9, 121.9, 120.3, 111.0, 58.5, 30.1, 29.7. IR (film): $\tilde{\nu}$ 3058, 3026, 2954, 2923, 2851, 1682, 1489, 1214, 744, 699 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₆NO, M + H]⁺: 262.1226, Found 262.1228.

(+)-2-(4-methoxyphenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3l)



Light yellow solid, mp: 114–115 °C. TLC $R_f = 0.44$ (PE/EA = 6:1, v/v), 91% yield, 85:15 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm

ID), hexane/2-propanol = 70:30, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R}$ = 11.05 min (minor) and $t_{\rm R}$ = 14.68 min (major). [α]_D²⁷ +210.1 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), S24

7.23–7.12 (m, 3H), 6.86 (d, J = 8.5 Hz, 2H), 4.10 (dd, J = 6.8, 2.0 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 3.57 (dd, J = 17.1, 6.8 Hz, 1H), 3.09 (dd, J = 17.1, 1.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 194.5, 158.5, 145.2, 143.4, 137.9, 132.2, 128.7, 126.9, 122.9, 121.8, 120.3, 114.1, 111.0, 57.8, 55.2, 30.0, 29.8. IR (film): v 3056, 2954, 2925, 2870, 2852, 1683, 1512, 1248, 891, 837, 746 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₈NO₂, M + H]⁺: 292.1332, Found 292.1337.

(+)-2-(4-fluorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3m)



Light yellow solid, mp: 90–92 °C. TLC $R_f = 0.39$ (PE/EA = 10:1, v/v), 84% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm \times 0.46 cm ID),

hexane/2-propanol = 80:20, 1.0 mL/min, 220 nm UV detecter, t_R = 11.09 min (major) and $t_{\rm R} = 12.20$ min (minor). $[\alpha]_{\rm D}^{28} + 198.0$ (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.1 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.24– 7.17 (m, 3H), 7.00 (t, J = 8.7 Hz, 2H), 4.14 (dd, J = 6.8, 2.2 Hz, 1H), 3.92 (s, 3H), 3.60 (dd, J = 17.1, 6.9 Hz, 1H), 3.10 (dd, J = 17.1, 2.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 193.9, 161.9 (d, J = 246.1 Hz), 145.3, 143.4, 137.8, 135.9 (d, J = 3.1 Hz), 129.3 (d, J = 8.0 Hz), 127.1, 122.9, 121.9, 120.4, 115.6 (d, J = 21.3 Hz), 111.1, 57.7, 30.1, 29.8. IR (film): v 3066, 3043, 3010, 2949, 2920, 2900, 2858, 1696, 1549, 1511, 1220, 750, 737 cm⁻¹. ESI-HRMS calcd for $[C_{18}H_{15}FNO, M + H]^+$: 280.1132, Found 280.1131.

(+)-2-(4-chlorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3n)

.CI Light yellow solid, mp: 142–143 °C. TLC $R_f = 0.39$ (PE/EA = 10:1, v/v), 78% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm \times 0.46 cm

ID), hexane/2-propanol = 80:20, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R}$ = 11.11 min (minor) and $t_{\rm R} = 12.35$ min (major). $[\alpha]_{\rm D}^{28} + 217.5$ (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.29 (d, J = 8.3 Hz, 2H), 7.25–7.20 (m, 1H), 7.19–7.16 (m, 2H), 4.14 (dd, J = 6.8 Hz, S25

1.6 Hz, 1H), 3.92 (s, 3H), 3.61 (dd, J = 17.1, 6.8 Hz, 1H), 3.10 (dd, J = 17.1 Hz, 1.6 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 193.6, 145.3, 143.5, 138.6, 137.7, 132.8, 129.1, 128.9, 127.2, 122.8, 121.9, 120.4, 111.1, 57.8, 30.1, 29.7. IR (film): \tilde{v} 3051, 3025, 2965, 2923, 2849, 1678, 1615, 1491, 752 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₅ClNO, M + H]⁺: 296.0837, Found 296.0831.

(+)-2-(benzo[d][1,3]dioxol-5-yl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-o ne (30)

ID), hexane/2-propanol = 70:30, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R}$ = 14.36 min (minor) and $t_{\rm R}$ = 18.86 min (major). [α]_D²⁷ +241.1 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.21 (dd, *J* = 15.2, 7.7 Hz, 1H), 6.74 (dd, *J* = 18.2, 8.0 Hz, 2H), 6.67 (s, 1H), 5.90 (d, *J* = 2.6 Hz, 2H), 4.06 (d, *J* = 5.2 Hz, 1H), 3.91 (s, 3H), 3.57 (dd, *J* = 17.1, 6.8 Hz, 1H), 3.07 (d, *J* = 17.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 194.2, 147.9, 146.5, 145.2, 143.5, 137.8, 133.9, 127.0, 122.8, 121.8, 121.1, 120.3, 111.0, 108.4, 107.8, 100.9, 58.2, 30.1, 29.9. IR (film): $\tilde{\nu}$ 2954, 2923, 2851, 1683, 1489, 1243, 1038, 745 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₆NO₃, M + H]⁺: 306.1125, Found 306.1132.

(+)-2-isopropyl-4,7-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3p)

Me O Light yellow liquid. TLC $R_f = 0.44$ (PE/EA = 15:1, v/v), 83% yield, 92:8 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detecter, $t_R = 5.41$ min (minor) and $t_R = 6.85$ min (major). [α] $_D^{27}$ +37.0 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1H), 7.26–7.22 (m, 2H), 3.88 (s, 3H), 3.02–2.95 (m, 2H), 2.79 (dd, J = 19.3, 5.2 Hz, 1H), 2.46–2.43 (m, 4H), 1.07 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.9, 143.4, 143.1, 139.3, 129.4, 128.5, 123.1, 121.0, 110.5, 58.4, 30.0, 29.0, 21.4, 21.3, 20.8, 16.7. IR (film): \tilde{v} 3023, 2956, 2925, 2869, 1678, 1625, 1501, 1218, 794, 761 cm⁻¹. ESI-HRMS calcd for [C₁₆H₂₀NO, M + H]⁺: 242.1539, Found 242.1542.

(+)-7-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3q)



Colorless solid, mp: 110–112 °C. TLC $R_f = 0.44$ (PE/EA = 8:1, v/v), 94% yield, 95:5 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol =

97:3, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R} = 6.83$ min (minor) and $t_{\rm R} = 7.29$ min (major). [α]_D²⁹ +53.1 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.26 (m, 2H), 7.16 (td, J = 9.1, 2.5 Hz, 1H), 3.90 (s, 3H), 3.04–2.96 (m, 2H), 2.83–2.75 (m, 1H), 2.49–2.41 (m, 1H), 1.08 (d, J = 6.9 Hz, 3H), 0.83 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.1, 157.7 (d, J = 238.3 Hz), 142.6 (d, J = 5.5 Hz), 141.4, 140.5, 122.8 (d, J = 9.8 Hz), 115.4 (d, J = 27.1 Hz), 111.8 (d, J = 9.5 Hz), 106.1 (d, J = 23.2 Hz), 58.4, 30.2, 29.0, 21.4, 20.7, 16.8. IR (film): \tilde{v} 2957, 2926, 2871, 1680, 1500, 1161, 943, 798, 763, 752 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₇FNO, M + H]⁺: 246.1289, Found 246.1293.

(*R*)-(+)-7-chloro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3r)

Clock Colorless solid, mp: 110–111 °C. TLC $R_f = 0.44$ (PE/EA = 10:1, v/v), 79% yield, 92:8 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol =

97:3, 1.0 mL/min, 220 nm UV detecter, $t_{\rm R} = 7.06$ min (minor) and $t_{\rm R} = 7.98$ min (major). [α]_D²⁸ +30.8 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 1.7 Hz, 1H), 7.33 (dd, J = 8.9, 1.9 Hz, 1H), 7.27 (d, J = 8.9 Hz, 1H), 3.89 (s, 3H), 3.02–2.95 (m, 2H), 2.82–2.75 (m, 1H), 2.50–2.39 (m, 1H), 1.07 (d, J = 6.9 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 197.0, 143.0, 142.4, 140.2, 126.8, 125.8, 123.7, 120.9, 112.0, 58.4, 30.2, 29.0, 21.4, 20.7, 16.8. IR (film): \tilde{v} 3059, 2956,

2926, 2870, 1679, 1490, 1467, 1204, 1072, 922, 797, 761, 695, 682 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₇ClNO, M + H]⁺: 262.0993, Found 262.0998.

(+)-8-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3s)



Colorless solid, mp: 38–39 °C. TLC $R_f = 0.50$ (PE/EA = 10:1, v/v), 71% yield, 92:8 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detecter, $t_R = 5.30$ min (major) and $t_R =$

5.84 min (minor). $[\alpha]_D^{29}$ +49.3 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.34– 7.26 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 10.0, 7.9 Hz, 1H), 3.91 (s, 3H), 3.14 (dd, *J* = 17.0, 6.2 Hz, 1H), 3.01–2.97 (m, 1H), 2.94 (dd, *J* = 17.1, 2.2 Hz, 1H), 2.51–2.39 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 196.9, 157.8 (d, *J* = 252.4 Hz), 146.7 (d, *J* = 10.5 Hz), 140.9, 139.2, 127.3 (d, *J* = 8.1 Hz), 112.9 (d, *J* = 23.0 Hz), 106.8 (d, *J* = 4.0 Hz), 104.9 (d, *J* = 18.5 Hz), 58.6, 30.4, 29.0, 22.3, 20.7, 16.8. IR (film): \tilde{v} 2956, 2926, 2870, 1684, 1631, 1463, 1242, 989, 975, 778, 731 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₇FNO, M + H]⁺: 246.1289, Found 246.1290.

5. X-Ray Diffraction Analysis of (R)-3r



Empirical formula	C15 H16 Cl N O
Moiety formula	C ₁₅ H ₁₆ ClNO
Formula weight	261.74
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = $8.6226(12)$ A alpha = 90 deg. b = $13.6329(18)$ A beta = 90 deg. c = $22.798(3)$ A gamma = 90 deg. 2680 0(6) A^3
7.	8
Calculated density	1.297 Mg/m ³
Absorption coefficient	0.272 mm ⁻¹
F(000)	1104
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	3.07 to 27.51°
Limiting indices	-11<=h<=10, -17<=k<=17, -29<=l<=29
Reflections collected / unique	29367 / 6127 [R(int) = 0.0274]

Completeness to theta $= 25.242$	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9680 and 0.9475
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6127 / 0 / 331
Goodness-of-fit on F ²	1.058
Final R indices [I>2sigma(I)]	$R_1 = 0.0248, wR_2 = 0.0685$
R indices (all data)	$R_1 = 0.0272, wR_2 = 0.0696$
Absolute structure parameter	0.01(3)
Largest diff. peak and hole	0.211 and -0.219 e.Å ⁻³

6. Transformations of Cyclization Product

A. Gram-scale experiment



The ZnCl₂ (23.9 mg, 0.175 mmol, 5 mol%) and (*R*)-**1e** (151.0 mg, 0.21 mmol, 6 mol%) were introduced into an oven-dried Schlenk flask in an argon-filled glovebox. After 35 mL DCE was injected into the Schlenk tube, the mixture was stirred at 40 °C. A solution of **2f** (1.020 g, 3.5 mmol) in 17.5 mL DCE was introduced into the mixture. After 48 hours, the reaction mixture was concentrated and purified by a flash chromatography on silica gel (PE/EA = 8:1, v/v) to give **3f** as a colorless solid, 0.989 g, 97% yield, 92:8 er. After recrystallization from a mixed solution (PE/EA = 25:1, v/v) twice, crystal blocks were obtained with 60% yield, 98:2 er.

B. Synthesis of (-)-4-(4-methoxyphenyl)-2-methyl-1,2,3,4-tetrahydrocyclopenta[b] indol-3-ol (4)



To an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with substrate **3f** (20.4 mg, 0.07 mmol) and dry THF (1.5 mL). After fully cooled to -78 °C, DIBAL-H (0.21 mL, 1.0 M, 0.21 mmol) was dropped into the mixture during 30 min. The solution was stirred at -78 °C until the reaction finished (monitored by TLC, about 30 min). 50 µL water was dropped into the Schlenk tube to quench the reaction.

After filtered through a pile of Celite, the solvent was removed by a vacuum pump. ¹H NMR of crude product showed that the value of *cis/trans* was about 10:1. Pure product was obtained by flash chromatography on basic Al₂O₃ (PE/EA = 4:1 to 2:1, v/v). The major product (*cis* isomer) was white solid, mp: 97–98 °C. TLC R_f = 0.57 (PE/EA = 4:1, v/v), 18.6 mg, 91% yield, 98:2 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detecter, t_R = 14.64 min (major) and t_R = 16.07 min (minor). [α]_D²³ –18.2 (*c* 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.55–7.48 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.19–7.11 (m, 2H), 7.03–6.98 (m, 2H), 4.90 (t, *J* = 5.8 Hz, 1H), 3.86 (s, 3H), 3.03–2.93 (m, 2H), 2.64–2.55 (m, 1H), 1.43–1.39 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 146.1, 141.3, 131.4, 126.5, 124.0, 122.3, 122.0, 120.0, 119.7, 114.6, 111.3, 71.1, 55.5, 43.9, 30.9, 14.6. ESI-HRMS calcd for [C₁₉H₁₈NO, M – OH]⁺: 276.1383, Found 276.1385.

7. NMR Spectra of Intermediates and Indole Enones



2-methyl-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol

Р	arameters
Parameter	Value
Title	wgp-14-178
Comment	test
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	302.0
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	160
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	9.8000
Acquisition Time	0.4588
Acquisition Date	2015-03-14T10:33:00
Modification Date	2015-03-15T11:42:00
Spectrometer Frequency	100.61
Spectral Width	40760.9
Lowest Frequency	-10320.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameters

nmr

spect

CDCl3

301.7 Pulse Sequence zg30

1D

8

1.0000

9.8000

1.9999

400.13

8012.8

1H

-1535.4

2015-03-14T10:31:00

2015-03-15T11:36:00

wgp-14-178

Value

Bruker BioSpin GmbH

Parameter

Title

Comment Origin

Owner

Author

Solvent

Spectrometer

Temperature

Experiment

Number of Scans

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Spectral Width

Acquired Size 16025

Spectral Size 32768

Lowest Frequency

Nucleus

Receiver Gain 111 Relaxation Delay

Site



200

180

160

140

120

100

60

80

40

20

0

-20

-40

1-(1-isopropyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol

P	arameters
Parameter	Value
Title	wgp-16-86
Comment	PROTON
Origin	Bruker BioSpin Gmbl
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zg30
Experiment	1D
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	15.0000
Acquisition Time	2.4999
Acquisition Date	2016-03-24T14:54:43
Modification Date	2016-03-24T14:54:00
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1535.4
Nucleus	1H
Acquired Size	20031
Spectral Size	65536
Р	arameters
Parameter	Value
Title	wgp-16-86
Comment	C13CPD
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDC13
Temperature	295.5
Dulas Camanas	zene30

1D

133

1.0000

9.8000

0.4588

100.61

-7796.8

13C

2016-03-24T14:56:52

2016-03-24T14:59:00

Experiment

Number of Scans

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Nucleus

Spectral Width 35714.3 Lowest Frequency

Acquired Size 16384 Spectral Size 32768

Receiver Gain 47 Relaxation Delay

Parameters



1-(1-allyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol

Comment	test
Origin	Bruker BioSpin GmbI
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Number of Scans	8
Receiver Gain	32
Relaxation Delay	1.0000
Pulse Width	9.8000
Acquisition Time	1.9999
Acquisition Date	2016-03-23T19:50:04
Modification Date	2016-03-23T19:50:00
Spectrometer Frequency	400.13
Spectral Width	8012.8
-	
Lowest	-1535.4
Lowest Frequency	-1535.4
Lowest Frequency Nucleus	-1535.4 1H
Lowest Frequency Nucleus Acquired Size	-1535.4 1H 16025
Lowest Frequency Nucleus Acquired Size Spectral Size	-1535.4 1H 16025 32768
Lowest Frequency Nucleus Acquired Size Spectral Size	-1535.4 1H 16025 32768
Lowest Frequency Nucleus Acquired Size Spectral Size	-1535.4 1H 16025 32768
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter	-1535.4 1H 16025 32768 arameters Value
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title	-1:3:3:4 1H 16025 32768 arameters Value wgp-16-85
Lowest Frequency Nucleus Acquired Size Spectral Size Parameter Title Comment	-1535.4 1H 16025 32768 arameters Value wgp-16-85 test
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title Comment Origin	arameters Value wgp-16-85 test Bruker BioSpin Gmbl
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title Comment Origin Owner	-1535.4 1H 16025 32768 arameters Value wgp-16-85 test Bruker BioSpin Gmbl nmr
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title Comment Origin Owner Site	+1535,4 1H 16025 32768 32768 value wgp-16-85 test Bruker BioSpin Gmbl mmr
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title Comment Origin Owner Site	-1535.4 1H 16025 32768 arameters Value wgp-16-85 test Bruker BioSpin GmbI nmr spect
Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title Comment Origin Owner Site Spectrometer Author	III 16025 32768 arameters Value wgp-16-85 test Bruker BioSpin Gmbl nmr
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size P Parameter Title Origin Owner Origin Owner Site Spectrometer Author	-1535,4 IH 16025 32768 arameters Value wgp-16-85 Bruker BioSpin Gmbb mur spect CDCI3
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size P Parameter Title Comment Comment Comment Ovner Site Spectrometer Author Solvent Temperature	-1535,4 1H 16025 32768 32768 value wgp-16-85 test Bruker BioSpin Gmbbl nmr spect CDCI3 293,9
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Site Site Site Solvent Temperature Pulse Sequence	III 353,4 IH 16025 32768 32768 32768 value wgp-16-85 test Bruker BioSpin Gmbl mm spect CDCI3 293,9 zgpg30
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Origin Owner Origin Owner Site Spectrometer Author Solvent Temperature Paules Sequence Paules Sequence	III -1535,4 III 16025 32768 32768 32768 spect 420 5990 CDCI3 293.9 293.9 1D
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Comment Over Site Over Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans	-1535,4 1H 16025 32768 32768 32768 value wgp-16-85 test Braker BioSpin Gmb nmr spect CDCI3 203,9 229290 1D 104
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Site Solvent Salvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain	1-153,4 1H 16025 32768 32768 32768 value wgp-16-85 test Bruker BioSpin Gmbl mm Spect CDCI3 203,9 20,
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size P Parameter Title Origin Owner Comment Origin Owner Comment Origin Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay	-1535,4 1H 16025 32768 32768 42708 427
Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Ovner Ovner Site Ovner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay	-153,4 1H 16025 32768 32768 32768 4200 42

Acquisition Date

Modification Date

Spectrometer Frequency

Lowest Frequency

Nucleus

Spectral Width

2016-03-23T19:52:16

2016-03-23T19:54:00

100.61

40760.9

-10320.1

13C Acquired Size 32768 Spectral Size 65536

Parameters

wgp-16-85

Value

Parameter

Title

S35



1-(1-benzyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol




Р	arameters
Parameter	Value
Title	wgp-15-115
Comment	C13CPD
Origin	Bruker BioSpin Gn
Owner	common
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	295.3
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	133
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	12.0000
Acquisition Time	0.4588
Acquisition Date	2015-08-31T22:29
Modification Date	2015-08-31T22:32:
Spectrometer Frequency	100.61
Spectral Width	35714.3
Lowest Frequency	-7796.3
Nucleus	13C
Acquired Size	16384
Spectral Size	32768

Parameters Value

wgp-15-115

Bruker BioSpin GmbH

PROTON

common

spect

CDCI3

295.1

1D

8

1.0000

13.7000

1.9999

400.13

-1640.9

 $1 \mathrm{H}$

2015-08-31T22:24:00

2015-08-31T22:24:00



1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-ol

Value

-1535.4

Value

100.61

-10320.1



2-methyl-1-(1-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)prop-2-en-1-ol



2-methyl-1-(1-(naphthalen-2-yl)-1H-indol-2-yl)prop-2-en-1-ol

Date	
Spectrometer Frequency	400.23
Spectral Width	8223.7
Lowest Frequency	-1640.3
Nucleus	1H
Acquired Size	16384
Spectral Size	32768
Р	arameters
Parameter	Value
Title	wgp-16-99
Comment	13CPD
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDC13
Temperature	293.5
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	306
Receiver Gain	205
Relaxation Delay	1.0000
Pulse Width	9.3000
Acquisition Time	0.8039
Acquisition Date	2016-04-03T18:34:2
Modification Date	2016-04-03T18:43:0
Spectrometer Frequency	100.61
Spectral Width	40760.9
Lowest Frequency	-15349.8
Nucleus	13C
	32768
Acquired Size	

Parameters

wgp-16-99

PROTON

common

CDCl3

2753.5

1D

8

1.0000

1.9923

Modification 2016-04-03T19:20:00

2016-04-03T19:20:00

Parameter

Spectrometer spect

Pulse Sequence zg30 Experiment

Receiver Gain 144

Pulse Width 13.5000

Title

Comment

Origin Owner

Site

Author

Solvent

Temperature

Number of Scans

Relaxation Delay

Acquisition Time

Acquisition Date

Value

Bruker BioSpin GmbH



1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-ol

Duite	
Modification Date	2015-03-18T21:01:00
Spectrometer Frequency	400.13
Spectral Width	8223.7
Lowest	-1640.9
Frequency	
Nucleus	1H
Acquired Size	16446
Spectral Size	65536
Р	arameters
Parameter	Value
Title	wgp-14-185
Comment	C13CPD
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	302.8
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	323
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	12.0000
Acquisition Time	0.4588
Acquisition Date	2015-03-18T21:03:0
Modification	2015-03-18T21:10:00
Date	
Date Spectrometer Frequency	100.61
Date Spectrometer Frequency Spectral Width	100.61 35714.3
Date Spectrometer Frequency Spectral Width Lowest Frequency	100.61 35714.3 -7796.3
Date Spectrometer Frequency Spectral Width Lowest Frequency Nucleus	100.61 35714.3 -7796.3 13C
Date Spectrometer Frequency Spectral Width Lowest Frequency Nucleus Acquired Size	100.61 35714.3 -7796.3 13C 16384

Parameters

wgp-14-185

PROTON Bruker BioSpin GmbH

nmr

CDC13

302.4

zg30

1.0000

1.9999

2015-03-18T21:01:00

1D

Value

Parameter

Title

Comment

Origin

Owner

Author

Solvent

Temperature

Pulse Sequence

Experiment

Relaxation Delay

Acquisition Time

Acquisition Date

Number of Scans 8 Receiver Gain 161

Pulse Width 13.7000

Site Spectrometer spect



3-methyl-1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-ol



Parameters

test Bruker BioSpin GmbH

nmr

CDC13

292.7

zg30

1D

8

1.0000

9.8000

1.9999

400.13

8012.8

 $1\mathrm{H}$

-1535.4

2015-11-19T18:12:32

2015-11-19T18:12:00

wgp-15-186

Value

Parameter

Site





Value
wgp-15-182
PROTON
Bruker BioSpin Gmb
common
spect
CDCl3
294.3
zg30
1D
8
203
1.0000
13.7000
1.9999
2015-11-17T11:39:00
2015-11-17T11:39:00
400.13
8223.7
-1640.9
1H
16446

Р	arameters
Parameter	Value
Title	wgp-15-182
Comment	test
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	111
Receiver Gain	46
Relaxation Delay	1.0000
Pulse Width	9.8000
Acquisition Time	0.8039
Acquisition Date	2015-11-17T11:04:3
Modification Date	2015-11-17T11:07:0
Spectrometer Frequency	100.61
Spectral Width	40760.9
Lowest Frequency	-10320.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



2-(4-fluorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol

Value

Bruker BioSpin GmbH

wgp-16-190

PROTON

common

CDC13

-1616.9

zg30

1D

8

1.0000

1.9923

400.23

8223.7

 $1\mathrm{H}$

-1640.3

2016-07-16T20:31:00

2016-07-16T20:31:00

Value

Bruker BioSpin GmbH

wgp-16-190

C13CPD

common

spect

CDCl3

-1598.7

1.0000

12.0000

0.5506

100.64

-4817.6

13C

2016-07-16T20:36:00

2016-07-16T20:39:00

1D



2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol

Modification Date	2016-07-14T17:23:0
Spectrometer Frequency	400.13
Spectral Width	8223.7
Lowest	-1640.9
Frequency	
Nucleus	1H
Acquired Size	16446
Spectral Size	65536
p	
P	Value
Title	wen-16-188
Comment	C13CPD
Origin	Bruker BioSpin Gmb
Owner	common
Site	
Spectrometer	spect
Author	1.1
Solvent	CDCl3
Temperature	292.7
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	261
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	12.5000
Acquisition Time	0.5506
Acquisition Date	2016-07-14T17:50:0
Modification Date	2016-07-14T17:56:0
Spectrometer Frequency	100.61
Spectral Width	29761.9
Lowest	-4820.2
Frequency	
Frequency Nucleus	13C
Frequency Nucleus Acquired Size	13C 16384

Parameters

wgp-16-188

PROTON Bruker BioSpin GmbH

common

CDC13

299.5

1D

1.0000 Pulse Width 13.7000

1.9999

2016-07-14T17:23:00

Value

Parameter

Spectrometer spect

Pulse Sequence zg30 Experiment

 Number of Scans
 8

 Receiver Gain
 203

Relaxation Delay

Acquisition Time

Acquisition Date

Title

Comment

Origin

Owner

Author

Solvent

Temperature

Site



2-(benzo[d][1,3]dioxol-5-yl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



1-(1,5-dimethyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-ol

Value

. Bruker BioSpin GmbH

Value

wgp-17-7 test Bruker BioSpin GmbH

nmr

test

nmr

spect

CDC13

1D

8



1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one

Value

Value



1-(5-chloro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



2-methyl-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2a)

Value

wgp-14-180

-1535.4

Value

100.61

-10320.1



1-(1-isopropyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2b)

Spectrometer	speer
Author	
Solvent	CDCl3
Temperature	291.6
Pulse Sequence	zg30
Experiment	1D
Number of Scans	8
Bossivos Gein	47
Receiver Galli Relevation	47
Delay	1.0000
Pulse Width	9.1200
Acquisition Time	4.0894
Acquisition Date	2016-03-25T20:14:51
Modification Date	2016-03-25T20:14:00
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest	-1535.4
Frequency	
Maria	1H
Nucleus	32768
Acquired Size	
Acquired Size Spectral Size	65536
Acquired Size Spectral Size	arameters
Acquired Size Spectral Size P Parameter	arameters Value
Acquired Size Spectral Size P Parameter Title	arameters Value wgp-16-88
Acquired Size Spectral Size P Parameter Title Comment	arameters Value wgp-16-88 C13CPD
Acquired Size Spectral Size P Parameter Title Comment Origin	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl
Acquired Size Spectral Size Parameter Title Comment Origin Owner	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl nmr
Acquired Size Acquired Size Spectral Size P Parameter Title Corrigin Owner Site	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl nmr
Acquired Size Spectral Size P Parameter Title Comment Origin Owner Site Spectrometer	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl nmr spect
Acquired Size Spectral Size Spectral Size Parameter Title Comment Origin Owner Site Site Spectrometer Author	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl nmr spect
Acquired Size Spectral Size P Parameter Title Origin Owner Site Spectrometer Author Solvent	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbbl nmr spect CDC13
Acquired Size Spectral Size Pertan Size Parameter Title Comment Comment Origin Owner Site Spectrometer Author Solvent Temperature	arameters Value wgp-16-88 Cl3CPD Bruker BioSpin Gmbl nmr spect CDCl3 292.4
Acquired Size Spectral Size P Parameter Title Comment Origin Owner Site Spectrometer Author Temperature Pulse Sequence	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl nmr spect CDC13 292.4 zgpg30
Acquired Size Spectral Size P P Parameter Title Comment Origin Owner Site Spectrometer Author Solvent Temperature P Pulse Sequence Experiment	arameters Value wgp-16-88 CI3CPD Bruker BioSpin Gmbl nmr spect CDCI3 292.4 292.4 292.4 1D
Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Comment Site Spectrometer Author Site Spectrometer Author Pulse Sequence Experiment Number of Scans	arameters Value wgp-16-88 Cl3CPD Bruker BioSpin Gmbl nmr CDCl3 292.4 292930 1D 133
Acquired Size Spectral Size Spectral Size Parameter Title Comment Origin Owner Site Solvent Salvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain	65536 arameters Value wgp-16-88 Cl3CPD Bruker BioSpin Gmbl nmr spect CDCl3 292.4 292.4 292.4 292.4 292.4 10 133 33
Aucteus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Owner Ovner Origin Owner Ovner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxion Delay	65536 Value Value wgp-16-88 C13CPD Bruker BioSpin Gmb mmr Spect CDC13 292.4 zgpg30 1D 133 33 2.0000
Acquired Size Spectral Size Spectral Size Parameter Title Commert Commert Owner Site Owner Site Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay	65536 arameters Value wgp-16-88 Cl3CPD Bruker BioSpin Gmbl nmr spect CDCl3 202.4 zgpg30 1D 133 3.3 2.0000 9.4000
Aucheus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Origin Owner Comment Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmb mm cpc1/3 20224 zgpg30 1D 133 33 2.0000 9.4000 1.3631
Aucheus Acquired Size Spectral Size Spectral Size Parameter Title Origin Owner Origin Owner Site Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Receiver Gain Delay Palse Width Acquisition Time Acquisition Date	arameters Value wgp-16-88 C13CPD Bruker BioSpin Gmbl nmr speci CDC13 292.4 292.4 10 133 2.0000 9.4000 1.3631 201-03-25T20: 18:12
Acquired Size Spectral Size Spectral Size Parameter Title Comment Comm	65536 4720000 4720000 4720000 472000 472000 47200000 472000000 472000000000000000000000000000000000000

Spectral Width 24038.5

-1958.9 13C

Lowest Frequency

Nucleus13CAcquired Size32768Spectral Size65536

Parameters

wgp-16-88

PROTON Bruker BioSpin GmbH

nmr

Value

Parameter

Title

Origin Owner

Site

Comment



1-(1-allyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2c)

Spectral Width	8012.8
Lowest Frequency	-1535.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536
Р	arameters
Parameter	Value
Title	wgp-16-87
Comment	test
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDC13
Temperature	293.9
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	203
Receiver Gain	97
Relaxation Delay	1.0000
Pulse Width	9.8000
Acquisition Time	0.8039
Acquisition Date	2016-03-25T16:10:3
Modification Date	2016-03-25T16:15:00
Spectrometer Frequency	100.61
Spectral Width	40760.9
Lowest Frequency	-10320.1
Nucleus	13C
Acquired Size	32768
	(***)(

Parameters

wgp-16-87

PROTON

nmr

spect

CDCI3

Experiment 1D

1.0000

9.1200

4.0894

400.13

2016-03-25T20:10:34

2016-03-25T20:10:00

Value

Bruker BioSpin GmbH

Parameter

Title

Origin

Owner

Author

Solvent

Number of Scans

Relaxation Delay

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Receiver Gain 97

Spectrometer

Temperature 291.7 Pulse Sequence 2g30

Site

Comment



1-(1-benzyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2d)

Parameters

PROTON

nmr

spect

CDCI3

294.4

1D

1.0000

13.7000

1.9999

400.13 8223.7

-1640.9

1H

Parameters

C13CPD Bruker BioSpin GmbH

nmr

CDCI3

295.0

zgpg30

1D

264

1.0000

12.0000

0.4588

100.61

-7796.3

13C

2015-04-02T20:54:00

2015-04-02T21:00:00

Value

wgp-14-18(150402)

2015-04-02T20:52:00

2015-04-02T20:52:00

Value

wgp-14-18(150402)

Bruker BioSpin GmbH



2-methyl-1-(1-phenyl-1H-indol-2-yl)prop-2-en-1-one (2e)

Value

wgp-15-119

PROTON Bruker BioSpin GmbH

common

spect

CDCI3

1.0000

13.7000

1.9999

400.13

-1640.9

1H

2015-09-02T15:04:00

2015-09-02T15:04:00

Value

wgp-15-119

C13CPD Bruker BioSpin GmbI

common

CDCI3

1D 263

1.0000

12.0000

0.4588

100.61

-7801.3

13C

2015-09-02T15:06:00

2015-09-02T15:12:00



1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-one (2f)



2-methyl-1-(1-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)prop-2-en-1-one (2g)



2-methyl-1-(1-(naphthalen-2-yl)-1H-indol-2-yl)prop-2-en-1-one (2h)



1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-one (2i)



3-methyl-1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-one (2j)



1-(1-methyl-1H-indol-2-yl)-2-phenylprop-2-en-1-one (2k)



2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2l)



2-(4-fluorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2m)



2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2n)



2-(benzo[d][1,3]dioxol-5-yl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (20)



1-(1,5-dimethyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2p)



1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2q)



1-(5-chloro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2r)

Value



1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2s)

8. NMR Spectra of Cyclization Products and Transformation Product



(+)-2,4-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3a)



(+)-4-isopropyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3b)

Title	wgp-16-90-A
Comment	PROTON
Origin	Bruker BioSpin Gmb
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDC13
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Number of Scans	8
Receiver Gain	36
Relaxation Delay	1.0000
Pulse Width	9.1200
Acquisition Time	4.0894
Acquisition Date	2016-03-31T19:39:19
Modification Date	2016-03-31T19:39:00
Spectrometer	400.13
. reducine à	
Spectral Width	8012.8
Spectral Width Lowest Frequency	8012.8 -1535.4
Spectral Width Lowest Frequency Nucleus	8012.8 -1535.4 1H
Spectral Width Lowest Frequency Nucleus Acquired Size	8012.8 -1535.4 1H 32768
Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	8012.8 -1535.4 11H 32768 65536
Spectral Width Lowest Nucleus Acquired Size Spectral Size	8012.8 -1535.4 1H 32768 65536 arameters
Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter	8012.8 -1535.4 1H 32768 65536 arameters Value
Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size P Parameter Title	8012.8 -1535.4 IH 32768 65536 arameters Value wgp-16-90-A
Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Parameter Title Comment	8012.8 -1535.4 1H 32768 65536 arameters Value wgp-16-90-A C13CPD
Request Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Perameter Title Comment Origin	8012.8 -1535.4 1H 32768 65536 45536 45536 400 400 400 400 400 400 400 40
Peperameter Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Perameter Title Comment Origin Owner	8012.8 -1535.4 1H 32768 65536 arameters Value wgp-16-90-A C13CPD Bruker BioSpin Gmb nmr
Prepetral Width Lowest Frequency Nucleus Acquired Size Spectral Size Parameter Title Comment Origin Owner Site	8012.8 -1535.4 1H 32768 65536 65536 arameters Value wgp-16-90-A C13CPD Bruker BioSpin Gmb nmr
Pectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Parameter Title Comment Comment Origin Size	8012.8 -1535.4 1H 32768 65536 4 4 4 4 4 5 5 5 4 5 5 5 5 5 5 5 5 5 5 5 5 5
Perspectral Width Lowest Frequency Nucleus Acquired Size Spectral Size P P Parameter Title Comment Origin Owner Site Spectranderet Author	8012.8 -1535.4 1H 32768 65536 65536 value wgp-16-90-A C13CPD Bruker BioSpin Gmb nm spect
Perspectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size P Parameter Title Comment Origin Owner Site Spectrometer Author Solvent	8012.8 -1535.4 1H 32768 65536 45566 455666 455666 455666 455666 455666 455666 455666 455666 4
Pequency Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Origin Owner Origin Owner Site Spectrometer Author Solvent Temperature	8012.8 -1535.4 1H 32768 65536 arameters Value wgp-16-90-A C13CPD Bruker BioSpin Gmb nmr
Prepetral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Gower Site Solvent Temperature Pulse Sequence	8012.8 8012.8 -1535.4 1H 32768 65536 45566 455666 455666 455666 455666 455666 455666 455666 455666
Perspectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Parameter Title Comment Origin Ovane Site Spectraneter Author Solvent Temperature Pushs Sequence Experiment	8012.8 -1535.4 1H 32768 65536 65536 45566 455666 455666 455666 455666 455666 455666 455666 455666 4
Pectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Owner Comment Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans	8012.8 8012.8 -1535.4 1H 32768 65536
Prepeteral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Parameter Title Comment Comment Comment Site Solvent Salvent Temperature Palse Sequence Experiment Number of Scans Receiver Gain	8012.8 111 12768 65536 45566 455666 455666 455666 455666 455666 455666 455666 455666 455666 4
Person Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Spectral Size Spectral Size Comment Origin Owner Origin Owner Comment Origin Owner Solvent Solvent Temperature Pulse Sequence Experiment Number of Scans	8012.8 -1535.4 1H 32768 65536

1.3631

100.61

-1958.9

13C

2016-03-31T19:40:49

2016-03-31T19:44:00

Parameters

Parameter


(+)-4-allyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3c)

Parameters			
Parameter	Value		
Title	wgp-16-89-A		
Comment	C13CPD		
Origin	Bruker BioSpin Gm		
Owner	nmr		
Site			
Spectrometer	spect		
Author			
Solvent	CDC13		
Temperature	293.1		
Pulse Sequence	zgpg30		
Experiment	1D		
Number of Scans	67		
Receiver Gain	36		
Relaxation Delay	2.0000		
Pulse Width	9.4000		
Acquisition Time	1.3631		
Acquisition Date	2016-03-31T19:32:		
Modification Date	2016-03-31T19:35:		
Spectrometer Frequency	100.61		
Spectral Width	24038.5		
Lowest Frequency	-1958.9		
Nucleus	13C		
Acquired Size	32768		
Spectral Size	65536		

Parameters

Value

Bruker BioSpin GmbH

wgp-16-89-A

PROTON

nmr

spect

CDCI3

1D

1.0000

9.1200

4.0894

400.13

8012.8

1HAcquired Size 32768

-1535.4

2016-03-31T19:30:19

2016-03-31T19:30:00

Parameter

Title

Origin

Owner

Author

Solvent

Number of Scans Receiver Gain 41 Relaxation Delay

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Nucleus

Spectral Width Lowest Frequency

Spectral Size 65536

Site

Comment

Spectrometer

Temperature 292.6 Pulse Sequence zg30 Experiment



(-)-4-benzyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3d)

Temperature	295.5		
Pulse Sequence	zg30		
Experiment	1D		
Number of Scans	8		
Receiver Gain	203		
Relaxation Delay	1.0000		
Pulse Width	13,7000		
Acquisition Time	1.9999		
Acquisition Date	2015-04-22T16:32:0		
Modification Date	2015-04-22T16:32:00		
Spectrometer Frequency	400.13		
Spectral Width	8223.7		
Lowest Frequency	-1640.9		
Nucleus	1H		
Acquired Size	16446		
Spectral Size	65536		
	Parameters		
Paramatar	arameters Value		
P Parameter Title	arameters Value		
P Parameter Title Comment	arameters Value wgp-15-4-B		
P Parameter Title Comment Origin	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb		
Parameter Title Comment Origin Owner	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr		
P Parameter Title Comment Origin Owner Site	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr		
Parameter Title Comment Origin Owner Site Spectrometer	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr spect		
Parameter Title Comment Origin Owner Site Spectrometer Author	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr spect		
Parameter Title Comment Origin Owner Site Spectrometer Author Solvent	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr spect CDCl3		
P Parameter Title Comment Origin Owner Site Site Site Site Site Site Site Site	arameters Value wgp-15-4-B Cl3CPD Bruker BioSpin Gmb nmr spect CDCl3 296.2		
P Parameter Title Comment Origin Owner Site Site Spectrometer Author Solvent Temperature Pulse Sequence	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr spect CDC13 206.2 zgpg30		
P Parameter Title Comment Origin Owner Site Site Solvent Author Solvent Temperature Pulse Sequence Experiment	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nm spect CDC13 296.2 2gpg30 D		
P Parameter Title Comment Origin Owner Site Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr Bruker BioSpin Gmb nmr Spect CDC13 296.2 296.2 zgpg30 1D 1D		
P Parameter Title Comment Origin Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr spect DCC13 296.2 296.2 2gg30 1D 395 203		
P Parameter Title Comment Origin Owner Site Site Solectometer Author Solvent Temperature Palse Sequence Experiment Number of Gas Seas Seas ReceiverGain Reclaxation Delay	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr Bruker BioSpin Gmb nmr CDC13 296.2 296.2 296.2 296.2 299.3 1D 203 1.0000		
P Parameter Title Comment Origin Owner Site Site Sapeetrometer Author Solvent Temperature Pulse Sequence Experiment Russer Scans Receiver Gain Relaxation Relaxation Delay	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr Spect CDC13 206.2 205.2 20		
P Parameter Title Comment Origin Owner Site Site Spectrometer Author Solvent Temperature Palse Sequence Experiment Receiver Gain Receiver Gain Receiver Gain Receiver Gain Calas Hole Delay Palse Width Acquisition	arameters Value Wgp-15-4-B C13CPD Bruker BioSpin Gmb mm spect CDC13 206.2 226.2 228p230 10 205.2 205.		
P Parameter Title Comment Origin Owner Site Spectrometer Author Solvent Author Solvent Temperature Pulse Sequence Experiment Number of Seans Receiver Gain Relaxation Delay Pulse Width Acquisition Time	arameters Value wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr spect 200C13 2050-2 2030 1D 2030 1.0000 2030 1.0000 0.4588 2015-04-22T16:34:00		
P Parameter Title Origin Owner Site Site Soletometer Author Solvent Temperature Pulse Sequence Experiment Number of Experiment Number of Seans Receiver Gall Receiver Gall	arameters Value Value Value C13CPD Bruker BioSpin Gmb nmr Bruker BioSpin Gmb nmr CDC13 296.2 296.2 205.2 205.2 205.2 203 10 203 1.0000 0.4588 2015-04-22T16:34:00 2015-04-2015-04-2015-04-2015-04-2015-04-2015-04-2015-04-2015-04-2015-04-2015-0		
P Parameter Title Comment Origin Owner Site Sopectometer Author Laberer Relaxation Receiver Gain Rec	arameters Value Wgp-15-4-B C13CPD Bruker BioSpin Gmb nmr Spect CDC13 206.2 2289240 2015 203 1.0000 12.0000 0.4588 2015-04-22T16-34-00 2015-04-22T16-34-00 100.61		
P Parameter Title Comment Origin Owner Site Sopectrometer Factor Solvent Temperature Pulse Sequence Experiment Experiment Receiver Gain Receiver Gain Receiver Gain Acquisition Delay Pulse Width Acquisition Time Sopectrometer Faceucere Spectrameter Faceucere Spectrameter Faceucere Spectrameter Faceucere Fa	arameters Value Wgp-15-4-B C13CPD C13CPD Bruker BioSpin Gmb nmr Spect 2005 2015 2026 203 203 203 203 203 203 203 203 203 203		
P Parameter Tide Comment Origin Owner Site Owner Solvent Solvent Author Palse Sequence Experiment Number of Palse Sequence Experiment Receiver Gain Receiver Gain Receiver Gain Calastion Delay Palse Width Acquisition Time Secton ter Secton ter	arameters Value Value C13CPD Bruker BioSpin Gmb mmr Bruker BioSpin Gmb nmr CDC13 296.2 296.2 296.2 296.2 296.2 296.2 203 1D 203 1D 203 1.0000 203 1.0000 203 203 203 203 203 203 203 203 203		
P Parameter Title Comment Origin Owner Site Owner Author Solvent Solvent Temperature Pulse Sequence Experiment Pulse Sequence Experiment Receiver Gain Receiver Gain Receiver Gain Receiver Gain Acquisition Delay Pulse Width Acquisition Delay Mudification Date Spectrometer Frequency Spectral Width Lowest Spectral Width	arameters Value Wgp-15-4-B C13CPD C13CPD Bruker BioSpin Gmb nmr Spect 2005 2015 2026 203 203 203 203 203 203 203 203 203 203		
P Parameter Title Comment Comment Site Site Spectrometer Factories Author Author Solvent Palse Solvent Palse Solvent Palse Solvent Seare S	arameters Value Wgp-15.4-B C13CPD Bruker BioSpin Gmb nmr Bruker BioSpin Gmb nmr CDC13 CDC13 206.2 CDC13 2096.2 CDC13 2096.2 CDC13 2095 CD1 2000 C05588 2015-04-22T16-34:00 2015-04-22T16-34:00 2015-04-22T16-34:00 2015-04-22T16-34:00 10.0.61 35714.3 CD1 10.0 CD1 10		

Parameters

PROTON

nmr

spect

CDC13

Value wgp-15-4-B

Bruker BioSpin GmbH

Parameter

Title

Comment

Origin

Owner

Solvent

Site Spectrometer Author



(+)-2-methyl-4-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3e)

Parameters			
Parameter	Value		
Title	wgp-16-63		
Comment	13CPD		
Origin	Bruker BioSpin Gml		
Owner	nmr		
Site			
Spectrometer	spect		
Author			
Solvent	CDC13		
Temperature	293.8		
Pulse Sequence	zgpg30		
Experiment	1D		
Number of Scans	234		
Receiver Gain	205		
Relaxation Delay	1.0000		
Pulse Width	9.3000		
Acquisition Time	0.8039		
Acquisition Date	2016-03-02T15:38:1		
Modification Date	2016-03-02T15:45:0		
Spectrometer Frequency	100.61		
Spectral Width	40760.9		
Lowest Frequency	-15349.8		
Nucleus	13C		
Acquired Size	32768		
Spectral Size	65536		

Parameters

nmr

spect

CDCI3

293.8

1.0000

9.8000

1.9999

400.13

-2125.8

1H Acquired Size 16025

2016-03-02T15:36:16

2016-03-02T15:36:00

wgp-16-63

Value

Bruker BioSpin GmbH

Parameter

Title

Comment

Origin

Owner

Author Solvent

Temperature

Number of Scans

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Lowest Frequency

Nucleus

Spectral Width 8012.8

Spectral Size 32768

Pulse Sequence zg30 Experiment 1D

Receiver Gain 66 Relaxation Delay

Site Spectrometer



(+)-4-(4-methoxyphenyl)-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3f)



Parameters

test Bruker BioSpin GmbH

nmr

spect

CDCl3

293.3 Pulse Sequence zg30

1D

1.0000

Value

wgp-16-79-A

Parameter

Title

Comment

Origin

Owner

Author

Solvent

Spectrometer

Temperature

Experiment

Receiver Gain 32

Number of Scans

Site



(+)-2-methyl-4-(4-(trifluoromethyl)phenyl)-1,4-dihydrocyclopenta[b]indol-3(2H)-

Parameters

PROTON

nmr

spect

CDC13

291.9

zg30

1D

47

1.0000

9.1200 4.0894

400.13

-1535.4

 $1 \mathrm{H}$

Parameters

Value

vgp-16-78-A

C13CPD Bruker BioSpin GmbH

nmr

spect

CDCl3

292.5

1D

195

47

2.0000

9.4000

1.3631

100.61

-1958.9

13C

2016-03-23T14:36:25

2016-03-23T14:46:00

2016-03-23T14:34:49

2016-03-23T14:34:00

Value wgp-16-78-A

Bruker BioSpin GmbH

one (3g)



(+)-2-methyl-4-(naphthalen-2-yl)-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3h)

Title	wgp-16-104-A
Comment	test
Origin	Bruker BioSpin Gmbl
Owner	nmr
Site	
Spectrometer	spect
Author	
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgpg30
Experiment	1D
Number of Scans	79
Receiver Gain	55
Relaxation Delay	1.0000
Pulse Width	9.8000
Acquisition Time	0.8039
Acquisition Date	2016-04-10T13:21:40
Modification Date	2016-04-10T13:23:00
Spectrometer Frequency	100.61
Spectral Width	40760.9
Lowest Frequency	-10320.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Parameters

test

nmr

CDC13

293.1

zg30

1.0000

9.8000

1.9999

400.13

8012.8

 $1\mathrm{H}$

Parameters Value

1535.4

2016-04-10T13:20:30

2016-04-10T13:20:00

1D

Value

Bruker BioSpin GmbH

wgp-16-104-A



(+)-2-ethyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3i)

Parameter	Value		
Title	wgp-14-191		
Comment	C13CPD		
Origin	Bruker BioSpin Gmb		
Owner	nmr		
Site			
Spectrometer	spect		
Author			
Solvent	CDC13		
Temperature	296.1		
Pulse Sequence	zgpg30		
Experiment	1D		
Number of Scans	274		
Receiver Gain	203		
Relaxation Delay	1.0000		
Pulse Width	12.0000		
Acquisition Time	0.4588		
Acquisition Date	2015-03-24T21:34:00		
Modification Date	2015-03-24T21:40:00		
Spectrometer Frequency	100.61		
Spectral Width	35714.3		
Lowest Frequency	-7796.3		
Nucleus	13C		
Acquired Size	16384		
Spectral Size	32768		

Parameters

wgp-14-191

PROTON Bruker BioSpin GmbH

nmr

spect

CDCl3

295.6 Pulse Sequence zg30

1D

1.0000

13.7000

1.9999

400.13

8223.7

-1640.9

1H Acquired Size 16446

Parameters

2015-03-24T21:32:00

2015-03-24T21:32:00

Value

Parameter

Title

Comment

Spectrometer

Temperature

Experiment Number of Scans Receiver Gain 101

Relaxation Delay

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Spectral Width

Spectral Size 65536

Lowest Frequency

Nucleus

Origin Owner

Site

Author

Solvent



(+)-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3j)

Parameters

Parameter

Title

Origin

Owner

Author

Solvent Temperature

Number of Scans

Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Spectral Width Lowest Frequency

Spectral Size 65536

Parameter

Spectrometer spect Author Solvent

Temperature

Pulse Sequenc

Experiment

Number of

Receiver Gain 87 Relaxation

Scans

Delay Pulse Width

Acquisition Time

Acquisition Date

Modification Date

Spectrometer Frequency

Nucleus

Spectral Width 35714.3 Lowest Frequency

Acquired Size 16384 Spectral Size 32768

Title

Comment

Origin

Owner

Site

Nucleus Acquired Size 20031

Site

Comment

Spectrometer

Pulse Sequence zg30 Experiment 1D

Receiver Gain 87 Relaxation Delay

Value

Bruker BioSpin GmbH

wgp-15-192-B

PROTON

nmr

spect

CDCI3

295.9

1.0000

15.0000

2015-11-28T18:36:33

2015-11-28T18:36:00

2.4999

400.13

8012.8

-1535.4

1H

Parameters

C13CPD

nmr

CDCI3

296.3

zgpg30

1D

516

1.0000

9.8000

0.4588

100.61

-7796.8

13C

2015-11-28T18:38:22

2015-11-28T18:50:00

Value wgp-15-192-B

Bruker BioSpin GmbI



(+)-4-methyl-2-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3k)



(+)-2-(4-methoxyphenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3l)



(+)-2-(4-fluorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3m)



(+)-2-(4-chlorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3n)

	Parameter	Value
1	Data File Name	E:/ 20160730/ NMR & MS/ 吲哚 底物/ cmq-1-36 A/ 2/ fid
2	Title	cmq-1-36-A
3	Comment	C13CPD
4	Origin	Bruker BioSpin GmbH
5	Owner	nmr
6	Site	
7	Spectrometer	spect
8	Author	
9	Solvent	CDC13
10	Temperature	292.7
11	Pulse Sequence	zgpg30
12	Experiment	1D
13	Number of Scans	187
14	Receiver Gain	27
15	Relaxation Delay	2.0000
16	Pulse Width	9.4000
17	Acquisition Time	0.5506
18	Acquisition Date	2016-08-04T09: 7:00
19	Modification Date	2016-08-04T10: 2:00
20	Spectrometer Frequency	100.61
21	Spectral Width	24038.5
22	Lowest Frequency	-1958. 9
23	Nucleus	130
24	Acquired Size	32768
25	Spectral Size	65536

Value

Bruker BioSpin GmbH

nmr

-1535.4

Parameter



(+) - 2 - (benzo[d][1,3] dioxol - 5 - yl) - 4 - methyl - 1, 4 - dihydrocyclopenta[b] indol - 3(2H) - o a constraint of the second sec

ne (30)



(+)-2-isopropyl-4,7-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3p)



(+)-7-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3q)



(*R*)-(+)-7-chloro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3r)



(+)-8-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3s)



(-)-4-(4-methoxyphenyl)-2-methyl-1,2,3,4-tetrahydrocyclopenta[b] indol-3-ol (4)



9. HPLC Charts of Cyclization Products and Transformation Product



(+)-2,4-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3a)

0.1077 270.81601

0.0915 2709.63696 455.02417

90.9136

9.0864

38.67042

1

2

6.615 BB

7.629 BB



(+)-4-isopropyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3b)



(+)-4-allyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3c)



(-)-4-benzyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3d)





Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	olo
1	5.817	BB	0.0973	4046.63794	644.17590	92.2467
2	6.903	BB	0.1123	340.11893	47.06593	7.7533



(+)-4-(3-methoxyphenyl)-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3f)

(+) - 2 - methyl - 4 - (3 - (trifluoromethyl)phenyl) - 1, 4 - dihydrocyclopenta[b]indol - 3(2H) - 1, 4 - dihy







(+)-2-methyl-4-(naphthalen-2-yl)-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3h)



(+)-2-ethyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3i)



(+)-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3j)



(+)-4-methyl-2-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3k)



(+)-2-(3-methoxyphenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one(3l)



(+)-2-(3-fluorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3m)



(+)-2-(3-chlorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3n)









(+)-2-isopropyl-4,7-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3p)



(+)-7-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3q)


(*R*)-(+)-7-chloro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3r)

0.1447 2860.64624 301.52655

92.2749

7.981 BB

2



(+)-8-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3s)



(-)4-(4-methoxyphenyl)-2-methyl-1,2,3,4-tetrahydrocyclopenta[b] indol-3-ol (4)

10. References

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