

Supplementary Information for:

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

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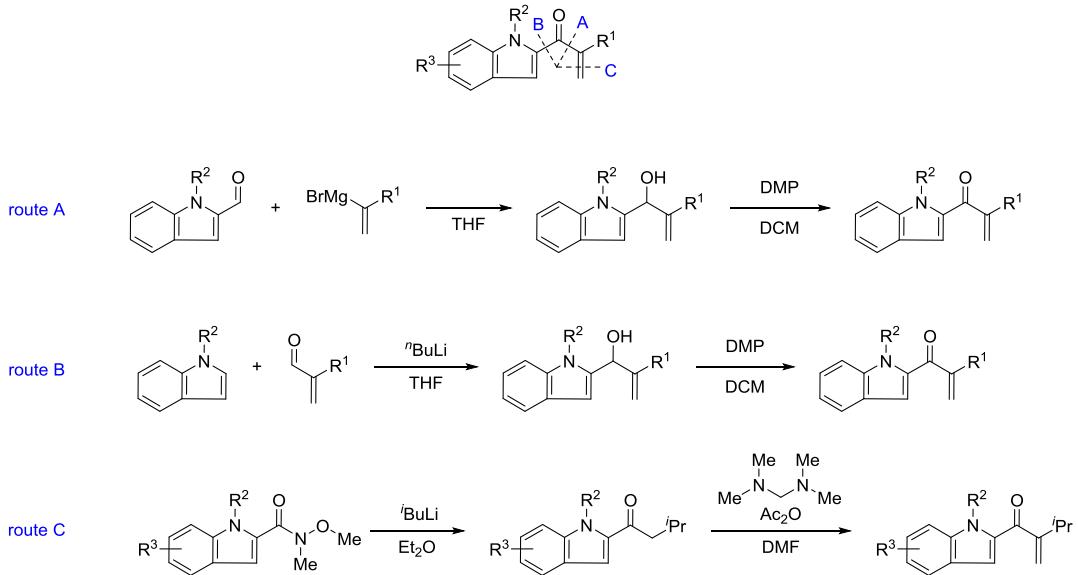
1. General Information

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).

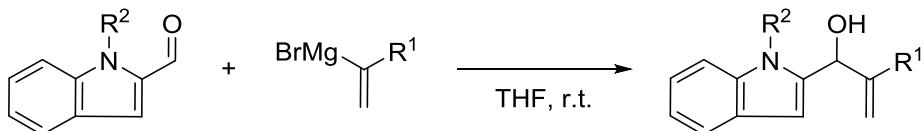
2. Synthesis and Analytical Data of Substituted Indole Enones

2.1 Synthesis of indole enones

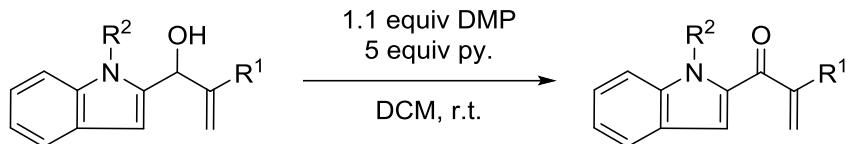
Indole enones were synthesized following the procedures below, while N-substituted indole-2-carbaldehyde, substituted vinyl bromide, α,β -unsaturated aldehyde and Weinreb amide were purchased or synthesized according to literatures. Substrates **2a–2i**, **2k–2o** were prepared according to route A;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

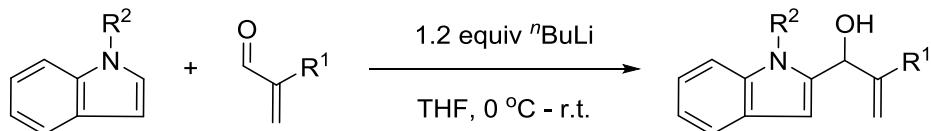


In an oven dried 100 mL four-necked flask, Mg turnings (1.09 g, 45 mmol) and a small amount of the solution of substituted vinyl bromide (30 mmol) in dry THF (40 mL) was added successively. After initiation automatically, the remaining solution was added alternately to keep the reaction refluxing slightly. 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.



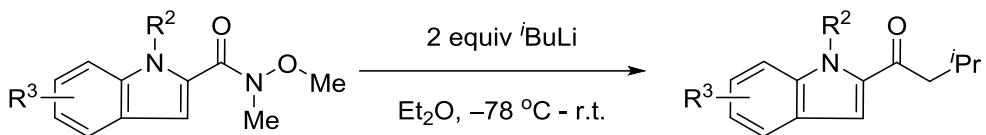
To a solution of the Dess-Martin periodinane (DMP, 9.26 g, 21.8 mmol) in DCM (40 mL), pyridine (8.0 mL, 99.3 mmol) was added. The resulting mixture was stirred for 5 min, then a solution of indole enol (19.9 mmol) in DCM (25 mL) was added dropwise. Stirring was continued for another 30 min and the reaction 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}

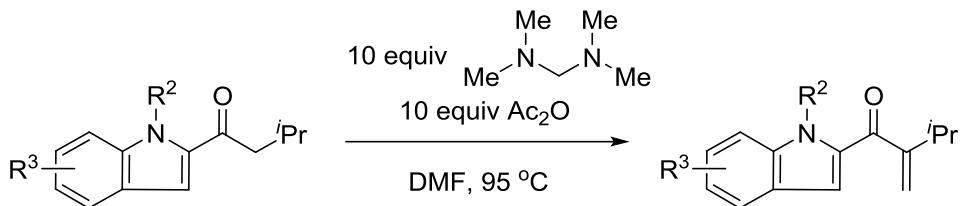


N-substituted indole (15 mmol) was dissolved in dry THF (25 ml) and then ⁿBuLi (7.5 mL, 2.4 M, 18 mmol) was added at 0 °C. The mixture was stirred for 3 h at room temperature. Then the 2-methylene-aldehyde (16.5 mmol) was added slowly, and the resulting mixture was stirred for 12 h at room temperature. 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}



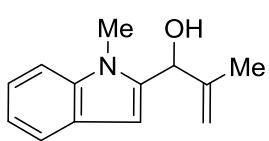
To a solution of substituted Weinreb amide (15.2 mmol) in dry Et₂O (50 mL) was added ⁱBuLi (38 mL, 1.0 M, 38 mmol) at -78 °C over the course of about 30 min. Upon consumption of the starting material, monitored by TLC, the reaction was allowed to warm to about -50 °C, and saturated aq. NH₄Cl (15 mL) 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.

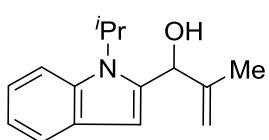
2.2 Analytical Data of Intermediates

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



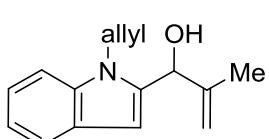
Light yellow solid, mp: 64–65 °C. TLC R_f = 0.25 (petroleum ether/ethyl acetate, PE/EA = 10:1, v/v), 93% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.57 (d, J = 7.9 Hz, 1H), 7.30 (dd, J = 8.2, 0.5 Hz, 1H), 7.21 (ddd, J = 8.2, 5.6, 2.1 Hz, 1H), 7.09 (td, J = 7.5, 1.0 Hz, 1H), 6.42 (s, 1H), 5.30 (s, 1H), 5.22 (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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{13}\text{H}_{16}\text{NO}, \text{M} + \text{H}]^+$: 202.1226, Found 202.1224.

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



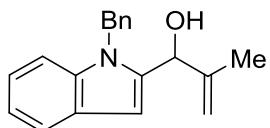
Colorless solid, mp: 40–42 °C. TLC R_f = 0.64 (PE/EA = 4:1, v/v), 95% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.56–7.48 (m, 2H), 7.16–7.09 (m, 1H), 7.07–7.00 (m, 1H), 6.33 (s, 1H), 5.19 (d, J = 4.5 Hz, 1H), 5.17 (s, 1H), 5.06 (s, 1H), 4.88–4.76 (m, 1H), 2.39–2.24 (m, 1H), 1.69 (s, 3H), 1.58–1.53 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{15}\text{H}_{20}\text{NO}, \text{M} + \text{H}]^+$: 230.1539, Found 230.1540.

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



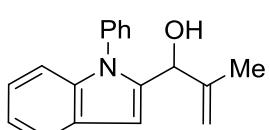
Colorless solid, mp: 66–67 °C. TLC R_f = 0.58 (PE/EA = 4:1, v/v), 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 7.8 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H), 7.20–7.16 (m, 1H), 7.08 (t, J = 7.4 Hz, 1H), 6.42 (s, 1H), 5.97–5.86 (m, 1H), 5.23 (s, 1H), 5.20 (d, J = 4.6 Hz, 1H), 5.09 (d, J = 9.1 Hz, 2H), 4.88–4.71 (m, 3H), 2.22 (d, J = 4.8 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{15}\text{H}_{18}\text{NO}, \text{M} + \text{H}]^+$: 228.1383, Found 228.1384.

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



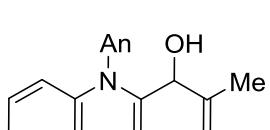
Yellow solid, mp: 79–80 °C. TLC $R_f = 0.30$ (PE/EA = 10:1, v/v), 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.5$ Hz, 1H), 7.27–7.19 (m, 4H), 7.17–7.08 (m, 2H), 6.95 (d, $J = 6.9$ Hz, 2H), 6.52 (s, 1H), 5.45 (dd, $J = 39.7, 17.1$ Hz, 2H), 5.20 (s, 1H), 5.18 (d, $J = 3.7$ Hz, 1H), 5.04 (d, $J = 1.1$ Hz, 1H), 1.96 (s, 1H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{20}\text{NO}, \text{M} + \text{H}]^+$: 278.1539, Found 278.1542.

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



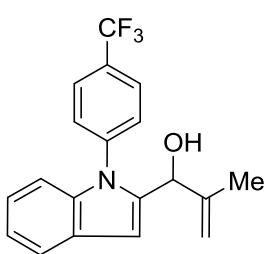
Light yellow solid, mp: 111–112 °C. TLC $R_f = 0.47$ (PE/EA = 8:1, v/v), 89% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.65–7.63 (m, 1H), 7.54–7.45 (m, 5H), 7.18–7.08 (m, 3H), 6.64 (s, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 4.94 (s, 1H), 1.92–1.73 (m, 1H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.9, 141.1, 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 $[\text{C}_{18}\text{H}_{18}\text{NO}, \text{M} + \text{H}]^+$: 264.1383, Found 264.1389.

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



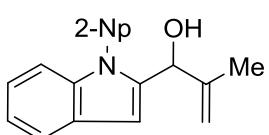
Light yellow solid, mp: 96–97 °C. TLC $R_f = 0.48$ (PE/EA = 4:1, v/v), 91% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.57 (m, 1H), 7.29–7.19 (m, 2H), 7.14–7.09 (m, 2H), 7.07–7.02 (m, 1H), 6.96 (d, $J = 8.1$ Hz, 2H), 6.58 (s, 1H), 5.00 (d, $J = 4.5$ Hz, 1H), 4.97 (s, 1H), 4.90 (s, 1H), 3.84 (s, 3H), 2.12 (d, $J = 5.0$ Hz, 1H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{20}\text{NO}_2, \text{M} + \text{H}]^+$: 294.1489, Found 294.1492.

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



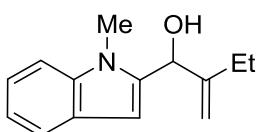
Light yellow solid, mp: 100–101 °C. TLC R_f = 0.41 (PE/EA = 8:1, v/v), 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.5 Hz, 2H), 7.65–7.61 (m, 1H), 7.57–7.56 (m, 2H), 7.20–7.08 (m, 3H), 6.65 (s, 1H), 5.02 (s, 1H), 5.00 (s, 1H), 4.94 (d, J = 1.0 Hz, 1H), 2.11–2.02 (m, 1H), 1.65 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{17}\text{F}_3\text{NO}, \text{M} + \text{H}]^+$: 332.1257, Found 332.1255.

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



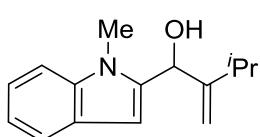
Yellow solid, mp: 136–137 °C. TLC R_f = 0.45 (PE/EA = 8:1, v/v), 94% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.00–7.88 (m, 4H), 7.69–7.64 (m, 1H), 7.62–7.55 (m, 2H), 7.47 (s, 1H), 7.17–7.15 (m, 3H), 6.69 (s, 1H), 5.13 (d, J = 5.4 Hz, 1H), 5.02 (s, 1H), 4.94 (s, 1H), 1.91 (d, J = 5.4 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{22}\text{H}_{20}\text{NO}, \text{M} + \text{H}]^+$: 314.1539, Found 314.1538.

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



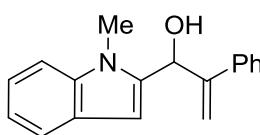
Yellow liquid, TLC R_f = 0.34 (PE/EA = 8:1, v/v), 95% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.24 – 7.07 (m, 1H), 7.10 – 7.07 (m, 1H), 6.41 (s, 1H), 5.35 (d, J = 4.7 Hz, 1H), 5.26 (s, 1H), 5.11 (s, 1H), 3.74 (s, 3H), 2.15–1.96 (m, 3H), 1.05 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{14}\text{H}_{18}\text{NO}, \text{M} + \text{H}]^+$: 216.1383, Found 216.1380.

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



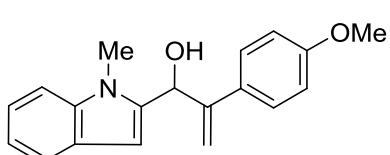
Yellow solid, mp: 61–62 °C. TLC $R_f = 0.75$ (PE/EA = 10:1, v/v), 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.21 (dd, $J = 10.4, 4.6$ Hz, 1H), 7.09 (dd, $J = 7.7, 7.1$ Hz, 1H), 6.39 (s, 1H), 5.37 (d, $J = 4.8$ Hz, 1H), 5.25 (s, 1H), 5.15 (s, 1H), 3.71 (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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{15}\text{H}_{20}\text{NO}, \text{M} + \text{H}]^+$: 230.1539, Found 230.1545.

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



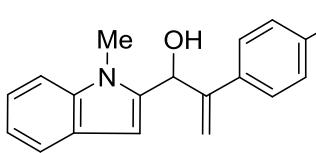
Yellow solid, mp: 96–97 °C. TLC $R_f = 0.53$ (PE/EA = 4:1, v/v), 98% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.9$ Hz, 1H), 7.40 (d, $J = 7.4$ Hz, 2H), 7.32–7.19 (m, 5H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.43 (s, 1H), 5.88 (d, $J = 5.4$ Hz, 1H), 5.66 (s, 1H), 5.51 (s, 1H), 3.80 (s, 3H), 2.14 (d, $J = 5.6$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{18}\text{H}_{18}\text{NO}, \text{M} + \text{H}]^+$: 264.1383, Found 264.1379.

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



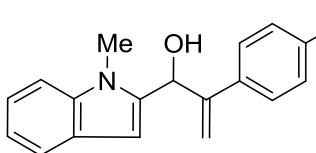
Light green solid, mp: 118–119 °C. TLC $R_f = 0.39$ (PE/EA = 4:1, v/v), 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.8$ Hz, 1H), 7.33–7.28 (m, 3H), 7.21 (dd, $J = 13.2, 5.9$ Hz, 1H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 2H), 6.41 (s, 1H), 5.81 (d, $J = 5.3$ Hz, 1H), 5.57 (s, 1H), 5.40 (s, 1H), 3.76–3.75 (m, 6H), 2.29–2.20 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{20}\text{NO}_2, \text{M} + \text{H}]^+$: 294.1489, Found 294.1497.

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



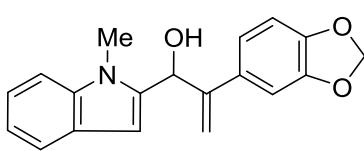
Yellow solid, mp: 109–110 °C. TLC $R_f = 0.41$ (PE/EA = 4:1, v/v), 98% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 7.9$ Hz, 1H), 7.30–7.23 (m, 3H), 7.21–7.16 (m, 1H), 7.08–7.03 (m, 1H), 6.95–6.88 (m, 2H), 6.34 (s, 1H), 5.67 (d, $J = 5.4$ Hz, 1H), 5.55 (s, 1H), 5.44 (s, 1H), 3.66 (s, 3H), 2.55 (d, $J = 5.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{18}\text{H}_{17}\text{FNO}, \text{M} + \text{H}]^+$: 282.1289, Found 282.1284.

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



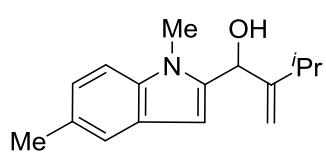
Yellow solid, mp: 130–131 °C. TLC $R_f = 0.43$ (PE/EA = 4:1, v/v), 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.9$ Hz, 1H), 7.32–7.28 (m, 3H), 7.25–7.19 (m, 3H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.38 (s, 1H), 5.80 (d, $J = 5.7$ Hz, 1H), 5.64 (s, 1H), 5.53 (s, 1H), 3.77 (s, 3H), 2.19 (t, $J = 4.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{18}\text{H}_{17}\text{NOCl}, \text{M} + \text{H}]^+$: 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



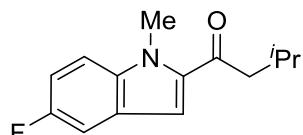
Yellow solid, mp: 116–117 °C. TLC $R_f = 0.59$ (PE/EA = 4:1, v/v), 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 1H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.90 (s, 1H), 6.85 (d, $J = 8.1$ Hz, 1H), 6.70 (d, $J = 8.1$ Hz, 1H), 6.39 (s, 1H), 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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{18}\text{NO}_3, \text{M} + \text{H}]^+$: 308.1281, Found 308.1280.

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



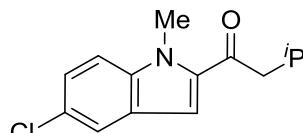
Yellow sticky oil. TLC $R_f = 0.28$ (PE/EA = 10:1, v/v), 92% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 0.6$ Hz, 1H), 7.12 (d, $J = 8.7$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.24 (s, 1H), 5.23 (d, $J = 5.1$ Hz, 1H), 5.17 (s, 1H), 5.09 (s, 1H), 3.57 (s, 3H), 2.41–2.39 (m, 4H), 2.19 (dt, $J = 13.6, 6.8$ Hz, 1H), 1.00 (dd, $J = 8.8, 6.9$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{16}\text{H}_{22}\text{NO}, \text{M} + \text{H}]^+$: 244.1696, Found 244.1698.

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



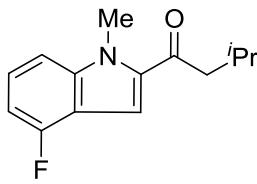
Light green solid, mp: 32–33 °C. TLC $R_f = 0.53$ (PE/EA = 30:1, v/v), 91% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.28 (m, 2H), 7.21 (s, 1H), 7.13 (td, $J = 9.1, 2.4$ Hz, 1H), 4.05 (s, 3H), 2.80 (d, $J = 7.0$ Hz, 2H), 2.31 (dp, $J = 13.5, 6.7$ Hz, 1H), 1.01 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{14}\text{H}_{17}\text{FNO}, \text{M} + \text{H}]^+$: 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, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{14}\text{H}_{17}\text{ClNO}, \text{M} + \text{H}]^+$: 250.0993, Found 250.0997.

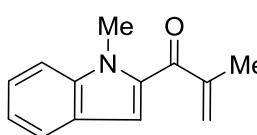
1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



Light yellow solid, mp: 27–28 °C. TLC R_f = 0.41 (PE/EA = 40:1, v/v), 93% yield. ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{14}\text{H}_{17}\text{FNO}, \text{M} + \text{H}]^+$: 234.1289, Found 234.1286.

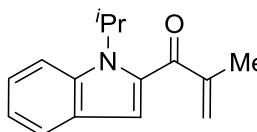
2.3 Analytical Data of Substituted Indole Enones

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



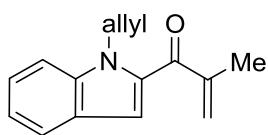
Greenish yellow solid, mp: 77–78 °C. TLC R_f = 0.80 (PE/EA = 10:1, v/v), 82% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 8.0 Hz, 1H), 7.40–7.34 (m, 2H), 7.15 (ddd, J = 8.0, 5.6, 2.3 Hz, 1H), 7.09 (s, 1H), 5.85 (s, 1H), 5.83–5.81 (m, 1H), 4.01 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 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): $\tilde{\nu}$ 3122, 3050, 2962, 2924, 2848, 1629, 800, 753, 743 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{13}\text{H}_{14}\text{NO}, \text{M} + \text{H}]^+$: 200.1070, Found 200.1070.

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



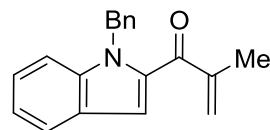
Yellow solid, mp: 31–32 °C. TLC R_f = 0.58 (PE/EA = 20:1, v/v), 84% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.6 Hz, 1H), 7.38–7.32 (m, 1H), 7.17 (t, J = 7.5 Hz, 1H), 7.03 (s, 1H), 5.93–5.92 (m, 2H), 5.38 (hept, J = 7.0 Hz, 1H), 2.14 (s, 3H), 1.70 (d, J = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 3003, 2975, 2934, 2878, 1638, 1623, 789, 757, 747 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{15}\text{H}_{18}\text{NO}, \text{M} + \text{H}]^+$: 228.1383, Found 228.1385.

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



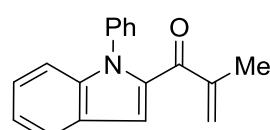
Greenish yellow liquid. TLC $R_f = 0.42$ (PE/EA = 20:1, v/v), 86% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.0$ Hz, 1H), 7.41–7.33 (m, 2H), 7.19–7.14 (m, 1H), 7.12 (s, 1H), 6.02 (ddt, $J = 16.8, 10.2, 5.1$ Hz, 1H), 5.84–5.82 (m, 2H), 5.15–5.08 (m, 3H), 4.93 (dd, $J = 17.2, 1.1$ Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 3083, 3062, 3033, 2983, 2955, 2924, 2852, 1638, 1622, 793, 752, 738 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{15}\text{H}_{16}\text{NO}, \text{M} + \text{H}]^+$: 226.1226, Found 226.1228.

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



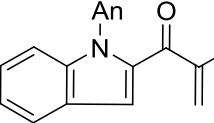
Yellow solid, mp: 62–63 °C. TLC $R_f = 0.74$ (PE/EA = 10:1, v/v), 88% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.0$ Hz, 1H), 7.37–7.29 (m, 2H), 7.26–7.14 (m, 5H), 7.05 (d, $J = 7.3$ Hz, 2H), 5.82 (d, $J = 2.9$ Hz, 2H), 5.76 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 190.3, 145.1, 140.1, 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): $\tilde{\nu}$ 3101, 3084, 3061, 3030, 2952, 2921, 2850, 1635, 1621, 793, 753, 725, 694 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{19}\text{H}_{18}\text{NO}, \text{M} + \text{H}]^+$: 276.1383, Found 276.1385.

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

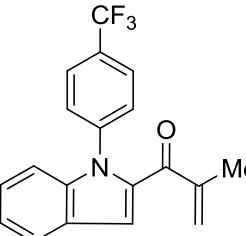


White solid, mp: 59–60 °C. TLC $R_f = 0.59$ (PE/EA = 20:1, v/v), 75% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.41 (t, $J = 7.3$ Hz, 1H), 7.33–7.27 (m, 3H), 7.24–7.17 (m, 3H), 6.01 (s, 1H), 5.88 (s, 1H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 188.9, 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): $\tilde{\nu}$ 3109, 3057, 3029, 2986, 2957, 2918, 1973, 1907, 1873, 1790, 1639, 796, 763, 742, 696 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{18}\text{H}_{16}\text{NO}, \text{M} + \text{H}]^+$: 262.1226, Found 262.1228.

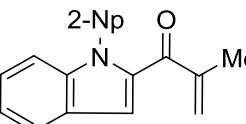
1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-one (2f)

 Light yellow solid, mp: 95–96 °C. TLC R_f = 0.50 (PE/EA = 10:1, v/v), 73% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, J = 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); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 3093, 3064, 2983, 2952, 2936, 2835, 1942, 1902, 1871, 1821, 1643, 1513, 799, 788, 748 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{19}\text{H}_{18}\text{NO}_2, \text{M} + \text{H}]^+$: 292.1332, Found 292.1335.

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

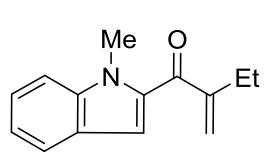
 White solid, mp: 144–145 °C. TLC R_f = 0.58 (PE/EA = 50:1, v/v), 74% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.79 (m, 3H), 7.49 (d, J = 8.2 Hz, 2H), 7.41–7.36 (m, 1H), 7.32–7.26 (m, 3H), 6.11 (s, 1H), 5.99 (s, 1H), 2.07 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 188.6, 144.9, 141.8, 140.3, 135.4, 129.5 (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): $\tilde{\nu}$ 3134, 3094, 3064, 1947, 1930, 1869, 1640, 1122, 1104, 1070, 827, 790, 749, 719 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{19}\text{H}_{15}\text{F}_3\text{NO}, \text{M} + \text{H}]^+$: 330.1100, Found 330.1104.

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

 Light yellow solid, mp: 116–117 °C. TLC R_f = 0.42 (PE/EA = 15:1, v/v), 73% yield. ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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,

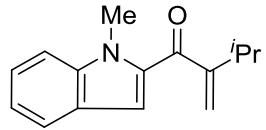
18.3. IR (film): $\tilde{\nu}$ 3106, 3059, 3028, 2961, 2921, 1954, 1910, 1825, 1787, 1638, 817, 756 cm⁻¹. ESI-HRMS calcd for [C₂₂H₁₈NO, M + H]⁺: 312.1383, Found 312.1385.

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



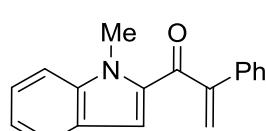
Yellow liquid, TLC R_f = 0.81 (PE/EA = 20:1, v/v), 83% yield.
¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.0 Hz, 1H), 7.41–7.34 (m, 2H), 7.15 (ddd, J = 8.0, 5.4, 2.4 Hz, 1H), 7.09 (s, 1H), 5.78 (s, 1H), 5.73 (d, J = 1.2 Hz, 1H), 4.03 (s, 3H), 2.51 (q, J = 7.4 Hz, 2H), 1.14 (t, J = 7.4 Hz, 3H); ¹³C NMR (101 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): $\tilde{\nu}$ 3058, 2966, 2935, 2874, 1637, 1619, 792, 753, 740 cm⁻¹. ESI-HRMS calcd for [C₁₄H₁₆NO, M + H]⁺: 214.1226, Found 214.1227.

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



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): $\tilde{\nu}$ 3090, 3049, 2969, 2950, 2868, 1632, 1617, 791, 773, 752, 728 cm⁻¹. ESI-HRMS calcd for [C₁₅H₁₈NO, M + H]⁺: 228.1383, Found 228.1388.

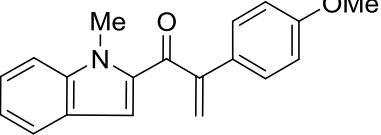
1-(1-methyl-1H-indol-2-yl)-2-phenylprop-2-en-1-one (2k)



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 = 8.1 Hz, 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): $\tilde{\nu}$ 3093, 3040,

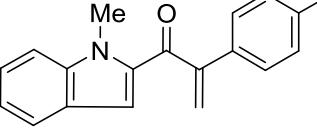
3032, 2949, 1641, 787, 746, 729, 713, 701 cm⁻¹. ESI-HRMS calcd for [C₁₈H₁₆NO, M + H]⁺: 262.1226, Found 262.1228.

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



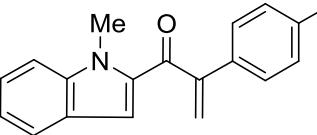
Yellow solid, mp: 74–75 °C. TLC R_f = 0.39 (PE/EA = 20:1, v/v), 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.41–7.39 (m, 4H), 7.18 (s, 1H), 7.14 (t, *J* = 6.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.98 (s, 1H), 5.69 (s, 1H), 4.13 (s, 3H), 3.80 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 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): $\tilde{\nu}$ 3123, 3084, 3009, 2966, 2947, 2836, 1630, 1606, 1509, 846, 805, 788, 742 cm⁻¹. ESI-HRMS calcd for [C₁₉H₁₈NO₂, M + H]⁺: 292.1332, Found 292.1333.

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



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): $\tilde{\nu}$ 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.

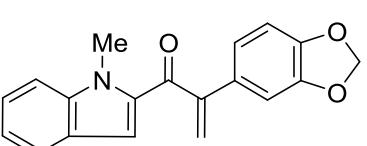
2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2n)



Yellow solid, mp: 101–102 °C. TLC R_f = 0.47 (PE/EA = 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,

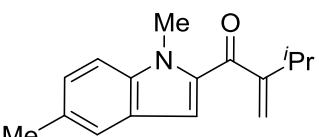
125.7, 123.2, 121.3, 120.9, 115.5, 110.4, 32.1. IR (film): $\tilde{\nu}$ 3065, 2951, 1639, 1614, 987, 915, 843, 748, 729, 647 cm^{-1} . ESI-HRMS calcd for [C₁₈H₁₅ClNO, M + H]⁺: 296.0837, Found 296.0828.

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



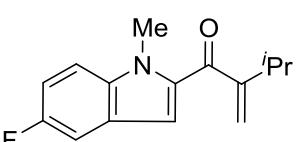
Colorless solid, mp: 117–118 °C. TLC R_f = 0.61 (PE/EA = 10:1, v/v), 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.1 Hz, 1H), 7.42–7.36 (m, 2H), 7.17 (s, 1H), 7.14 (ddd, J = 8.0, 4.9, 3.0 Hz, 1H), 6.97 (d, J = 1.7 Hz, 1H), 6.93 (dd, J = 8.1, 1.8 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 5.95 (s, 2H), 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): $\tilde{\nu}$ 3134, 3087, 2897, 2788, 1622, 1609, 1501, 1486, 894, 870, 743, 691 cm^{-1} . ESI-HRMS calcd for [C₁₉H₁₆NO₃, 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), 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), 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): $\tilde{\nu}$ 3092, 3021, 2962, 2871, 1636, 1621, 793 cm^{-1} . ESI-HRMS calcd for [C₁₆H₂₀NO, M + H]⁺: 242.1539, Found 242.1541.

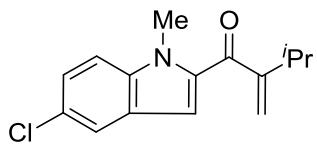
1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2q)



Green liquid. TLC R_f = 0.54 (PE/EA = 20:1, v/v), 68% yield. 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 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): $\tilde{\nu}$ 3092, 3021, 2962, 2871, 1636, 1621, 793 cm^{-1} . ESI-HRMS calcd for [C₁₆H₁₉FNO, M + H]⁺: 259.1459, Found 259.1459.

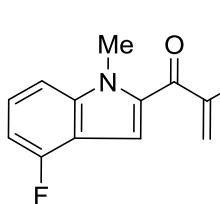
MHz, CDCl₃) δ 191.1, 158.0 (d, *J* = 237.7 Hz), 155.6, 137.0, 136.8, 125.5 (d, *J* = 10.2 Hz), 120.3, 114.7 (d, *J* = 27.1 Hz), 113.3 (d, *J* = 5.5 Hz), 111.2 (d, *J* = 9.5 Hz), 106.8 (d, *J* = 23.1 Hz), 32.0, 29.8, 21.3. IR (film): $\tilde{\nu}$ 3095, 3070, 2963, 2872, 1642, 1516, 1470, 1391, 1193, 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)



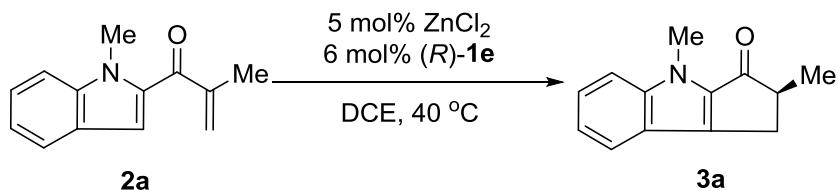
Light green solid, mp: 54–55 °C. TLC *R_f* = 0.47 (PE/EA = 15:1, v/v), 66% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.32 (s, 2H), 6.99 (s, 1H), 5.71 (s, 1H), 5.69 (d, *J* = 0.8 Hz, 1H), 4.03 (s, 3H), 3.04 (hept, *J* = 6.8 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 155.6, 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): $\tilde{\nu}$ 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), 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): $\tilde{\nu}$ 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



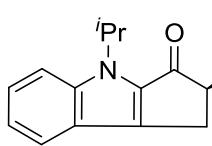
The ZnCl_2 (1.4 mg, 0.01 mmol, 5 mol%) and (R) -**1e** (8.6 mg, 0.012 mmol, 6 mol%) were introduced into an oven-dried Schlenk tube in an argon-filled glovebox. After 2 mL DCE was injected into the Schlenk tube, the mixture was stirred at 40 °C. A solution of **2a** (40 mg, 0.2 mmol) in 1 mL DCE was 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**)

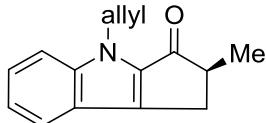
Colorless oil, TLC $R_f = 0.45$ (PE/EA = 10:1, v/v), 98% yield, 91:9 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detector, $t_R = 6.62$ min (major) and $t_R = 7.63$ min (minor). $[\alpha]_D^{27} +3.4$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 3055, 2961, 2928, 2869, 2851, 1678, 1500, 961, 741 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{13}\text{H}_{14}\text{NO}, \text{M} + \text{H}]^+$: 200.1070, Found 200.1071.

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



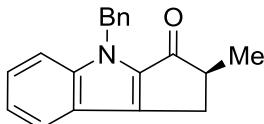
White solid, mp: 77–79 °C. TLC $R_f = 0.62$ (PE/EA = 10:1, v/v), 98% yield, 90:10 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detector, $t_R = 5.16$ min (major) and $t_R = 5.76$ min (minor). $[\alpha]_D^{27} +10.0$ (*c* 1.0, CHCl₃). 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)



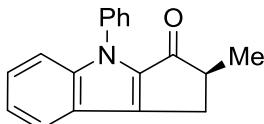
Colorless oil, TLC $R_f = 0.52$ (PE/EA = 10:1, v/v), 93% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detector, $t_R = 5.82$ min (major) and $t_R = 6.95$ min (minor). $[\alpha]_D^{27} +2.6$ (*c* 1.0, CHCl₃). ¹H NMR (400 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): $\tilde{\nu}$ 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)



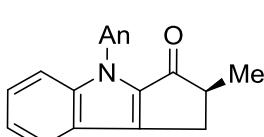
Light yellow solid, mp: 69–72 °C. TLC $R_f = 0.52$ (PE/EA = 10:1, v/v), 87% yield, 88:12 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detector, $t_R = 6.33$ min (minor) and $t_R = 7.35$ min (major). $[\alpha]_D^{27} -1.2$ (*c* 1.0, CHCl₃). 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): $\tilde{\nu}$ 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 detector, $t_R = 5.82$ min (major) and $t_R = 6.90$ min (minor). $[\alpha]_D^{27} +44.7$ (*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): $\tilde{\nu}$ 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.

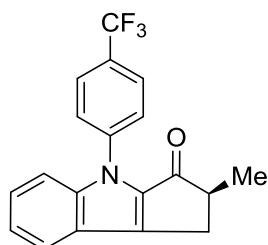
(+)-4-(4-methoxyphenyl)-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3f)



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

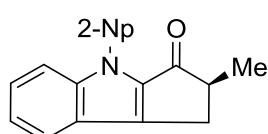
v/v), 95% yield, 92:8 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detecter, t_R = 7.86 min (major) and t_R = 9.24 min (minor). $[\alpha]_D^{27} +35.0$ (c 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 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): $\tilde{\nu}$ 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). $[\alpha]_D^{27} +42.1$ (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): $\tilde{\nu}$ 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_R = 7.53 min (major) and t_R = 8.93 min (minor). $[\alpha]_D^{28} +49.7$ (*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): $\tilde{\nu}$ 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)

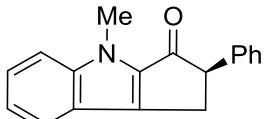
Colorless solid, mp: 83–84 °C. TLC R_f = 0.42 (PE/EA = 10:1, v/v), 93% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 90:10, 1.0 mL/min, 220 nm UV detecter, t_R = 5.95 min (major) and t_R = 6.70 min (minor). $[\alpha]_D^{27} +37.6$ (*c* 1.0, CHCl₃). ¹H 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): $\tilde{\nu}$ 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)

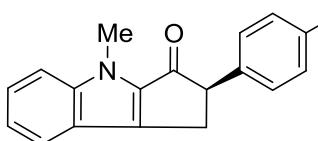
Light yellow oil. TLC R_f = 0.53 (PE/EA = 10:1, v/v), 96% yield, 95:5 er. HPLC condition: Chiralpak AD-3 column (25 cm ×

0.46 cm ID), hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detector, t_R = 6.08 min (minor) and t_R = 6.55 min (major). $[\alpha]_D^{28} +51.1$ (*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): $\tilde{\nu}$ 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)

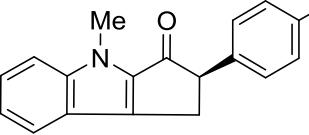
 Light yellow solid, mp: 126–128 °C. TLC R_f = 0.41 (PE/EA = 6:1, v/v), 95% yield, 86:14 er. HPLC condition: Chiraldak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 80:20, 1.0 mL/min, 220 nm UV detector, t_R = 5.88 min (minor) and t_R = 7.93 min (major). $[\alpha]_D^{28} +177.4$ (*c* 1.0, CHCl₃). 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)

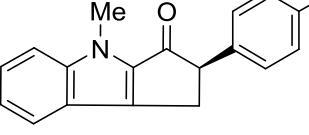
 Light yellow solid, mp: 114–115 °C. TLC R_f = 0.44 (PE/EA = 6:1, v/v), 91% yield, 85:15 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 70:30, 1.0 mL/min, 220 nm UV detector, t_R = 11.05 min (minor) and t_R = 14.68 min (major). $[\alpha]_D^{27} +210.1$ (*c* 1.0, CHCl₃). 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); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 3056, 2954, 2925, 2870, 2852, 1683, 1512, 1248, 891, 837, 746 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{19}\text{H}_{18}\text{NO}_2, \text{M} + \text{H}]^+$: 292.1332, Found 292.1337.

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

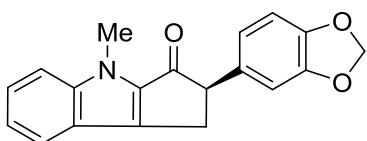
 Light yellow solid, mp: 90–92 °C. TLC R_f = 0.39 (PE/EA = 10:1, v/v), 84% yield, 89:11 er. HPLC condition: Chiralcel OD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 80:20, 1.0 mL/min, 220 nm UV detecter, t_R = 11.09 min (major) and t_R = 12.20 min (minor). $[\alpha]_D^{28} +198.0$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 3066, 3043, 3010, 2949, 2920, 2900, 2858, 1696, 1549, 1511, 1220, 750, 737 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{18}\text{H}_{15}\text{FNO}, \text{M} + \text{H}]^+$: 280.1132, Found 280.1131.

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

 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 × 0.46 cm ID), hexane/2-propanol = 80:20, 1.0 mL/min, 220 nm UV detecter, t_R = 11.11 min (minor) and t_R = 12.35 min (major). $[\alpha]_D^{28} +217.5$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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,

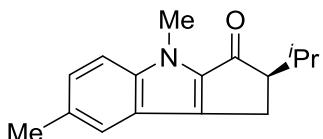
1.6 Hz, 1H), 3.92 (s, 3H), 3.61 (dd, J = 17.1, 6.8 Hz, 1H), 3.10 (dd, J = 17.1 Hz, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 193.6, 145.3, 143.5, 138.6, 137.7, 132.8, 129.1, 128.9, 127.2, 122.8, 121.9, 120.4, 111.1, 57.8, 30.1, 29.7. IR (film): $\tilde{\nu}$ 3051, 3025, 2965, 2923, 2849, 1678, 1615, 1491, 752 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{18}\text{H}_{15}\text{ClNO}, \text{M} + \text{H}]^+$: 296.0837, Found 296.0831.

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



Light yellow solid, mp: 181–182 °C. TLC R_f = 0.39 (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 = 70:30, 1.0 mL/min, 220 nm UV detecter, t_{R} = 14.36 min (minor) and t_{R} = 18.86 min (major). $[\alpha]_D^{27} +241.1$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{16}\text{NO}_3, \text{M} + \text{H}]^+$: 306.1125, Found 306.1132.

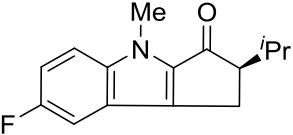
(+)-2-isopropyl-4,7-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3p)



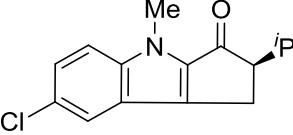
Light yellow liquid. TLC R_f = 0.44 (PE/EA = 15:1, v/v), 83% yield, 92:8 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 95:5, 1.0 mL/min, 220 nm UV detecter, t_{R} = 5.41 min (minor) and t_{R} = 6.85 min (major). $[\alpha]_D^{27} +37.0$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 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)

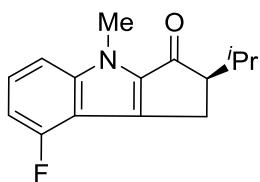
 Colorless solid, mp: 110–112 °C. TLC R_f = 0.44 (PE/EA = 8:1, v/v), 94% yield, 95:5 er. HPLC condition: Chiralpak AD-3 column (25 cm × 0.46 cm ID), hexane/2-propanol = 97:3, 1.0 mL/min, 220 nm UV detector, t_R = 6.83 min (minor) and t_R = 7.29 min (major). $[\alpha]_D^{29} +53.1$ (*c* 1.0, CHCl₃). ¹H 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): $\tilde{\nu}$ 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)

 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 detector, t_R = 7.06 min (minor) and t_R = 7.98 min (major). $[\alpha]_D^{28} +30.8$ (*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): $\tilde{\nu}$ 3059, 2956,

2926, 2870, 1679, 1490, 1467, 1204, 1072, 922, 797, 761, 695, 682 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{15}\text{H}_{17}\text{ClNO}, \text{M} + \text{H}]^+$: 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, $t_{\text{R}} = 5.30$ min (major) and $t_{\text{R}} = 5.84$ min (minor). $[\alpha]_D^{29} +49.3$ (c 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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): $\tilde{\nu}$ 2956, 2926, 2870, 1684, 1631, 1463, 1242, 989, 975, 778, 731 cm^{-1} . ESI-HRMS calcd for $[\text{C}_{15}\text{H}_{17}\text{FNO}, \text{M} + \text{H}]^+$: 246.1289, Found 246.1290.

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

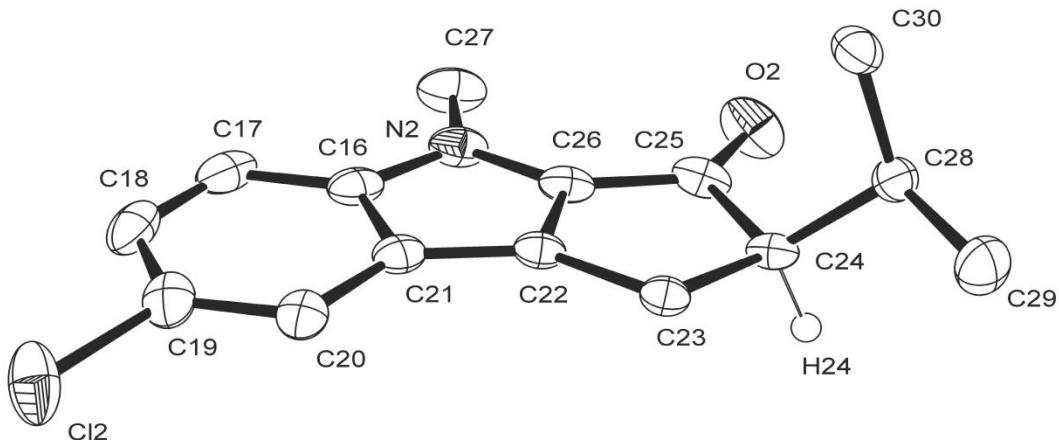


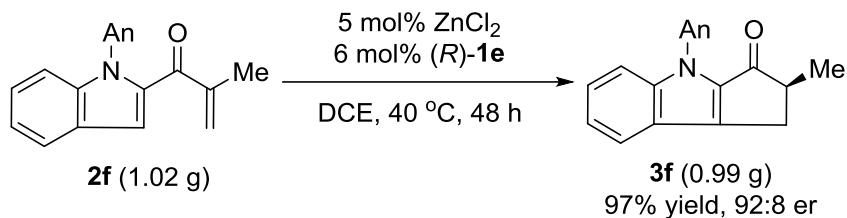
Table S1. Crystal data and structure refinement for (*R*)-3r

Empirical formula	C ₁₅ H ₁₆ ClNO	
Moiety formula	C ₁₅ H ₁₆ ClNO	
Formula weight	261.74	
Temperature	113(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 8.6226(12) Å	alpha = 90 deg.
	b = 13.6329(18) Å	beta = 90 deg.
	c = 22.798(3) Å	gamma = 90 deg.
Volume	2680.0(6) Å ³	
Z	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 [$I > 2\sigma(I)$]	$R_1 = 0.0248, wR_2 = 0.0685$
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. \AA^{-3}

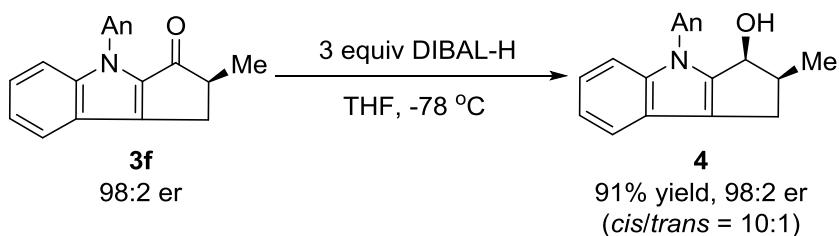
6. Transformations of Cyclization Product

A. Gram-scale experiment



The $ZnCl_2$ (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**)

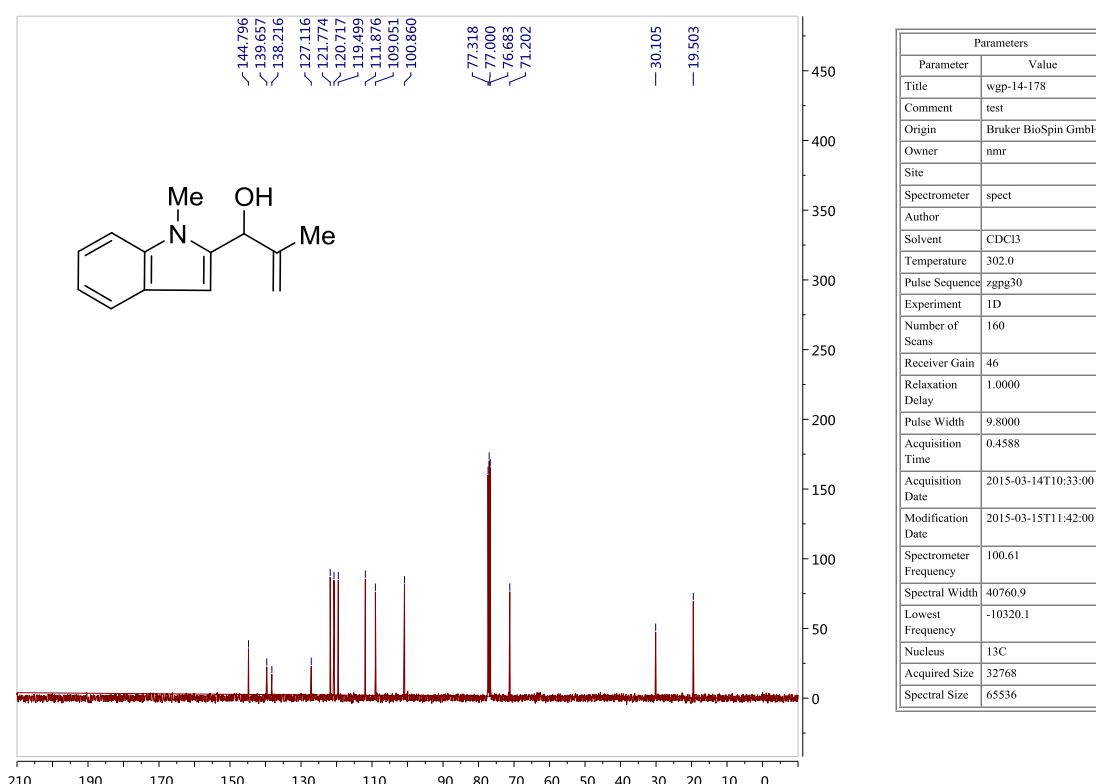
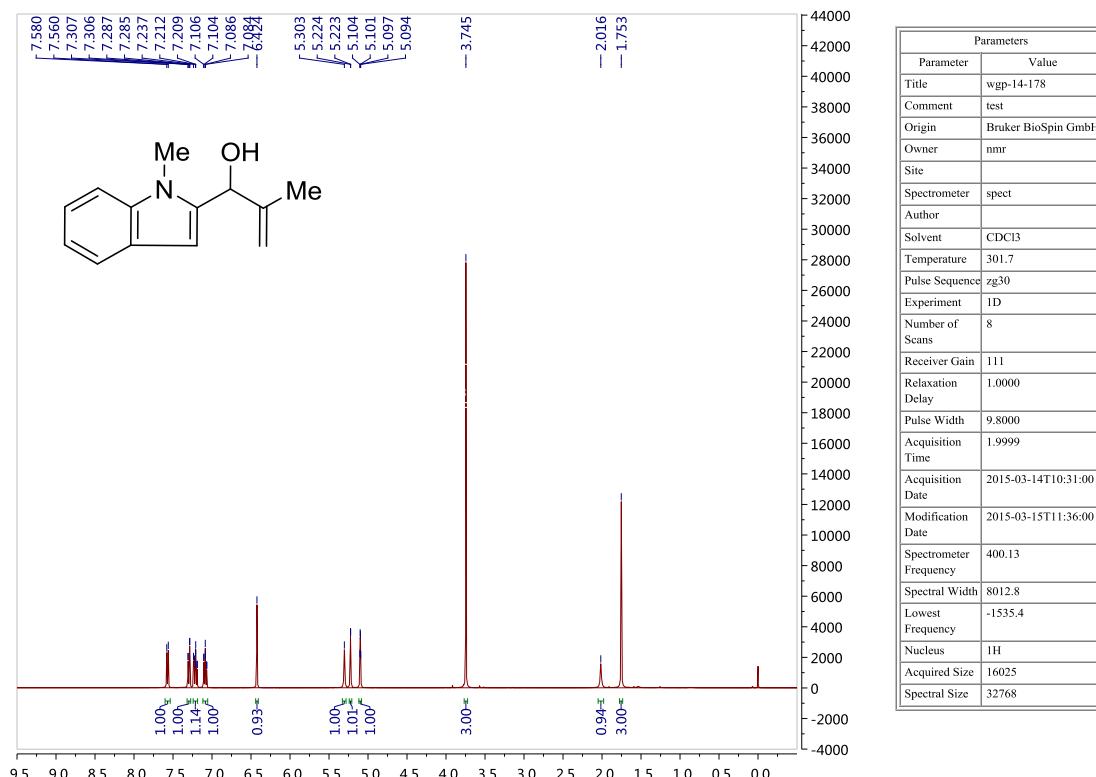


To an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with substrate **3f** (20.4 mg, 0.07 mmol) and dry THF (1.5 mL). After fully cooled to -78 °C, DIBAL-H (0.21 mL, 1.0 M, 0.21 mmol) was dropped into the mixture during 30 min. The solution was stirred at -78 °C until the reaction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

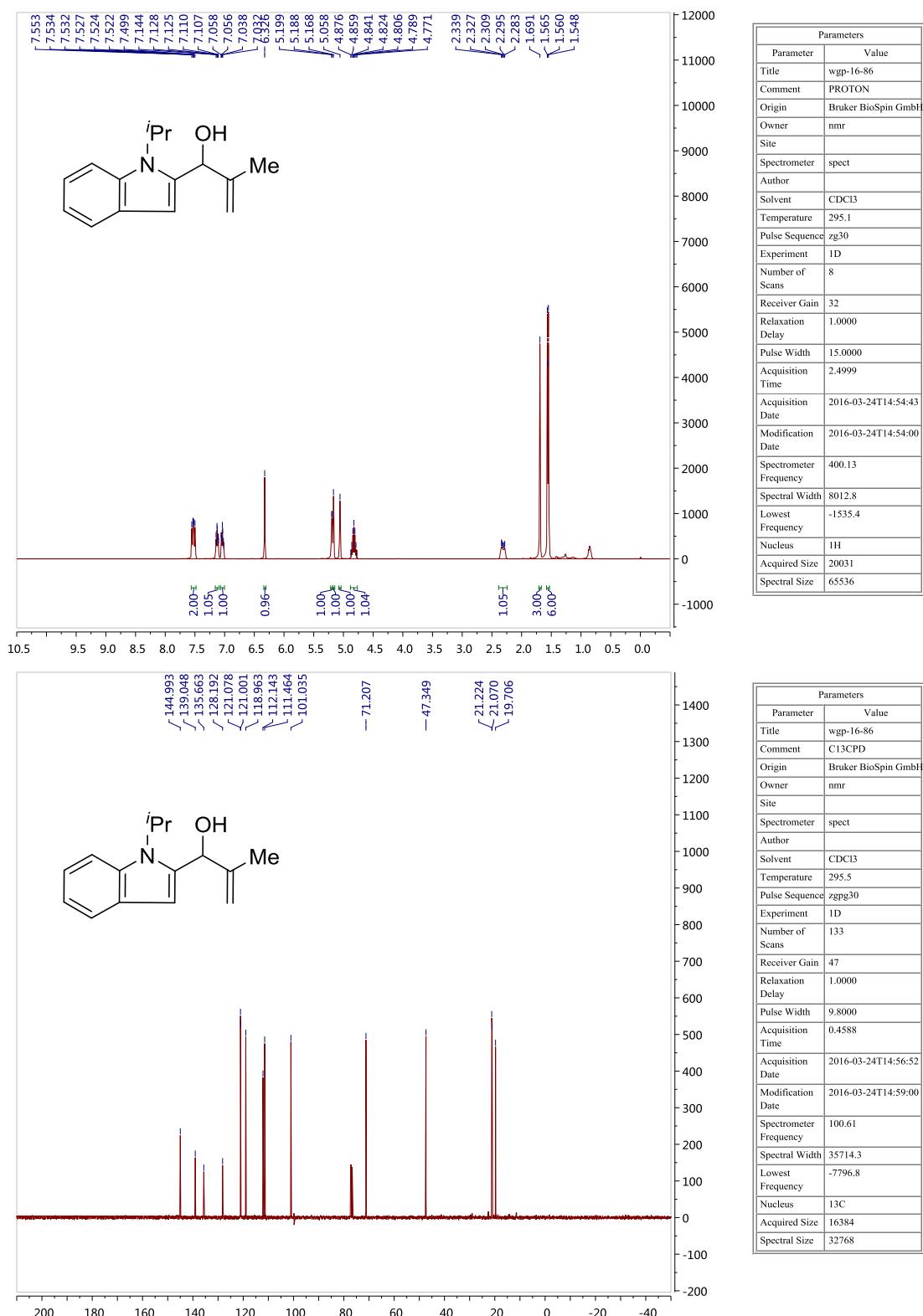
After filtered through a pile of Celite, the solvent was removed by a vacuum pump. ^1H NMR of crude product showed that the value of *cis/trans* was about 10:1. Pure product was obtained by flash chromatography on basic Al_2O_3 (PE/EA = 4:1 to 2:1, v/v). The major product (*cis* isomer) was white solid, 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). $[\alpha]_D^{23} -18.2$ (*c* 1.0, CHCl_3). ^1H NMR (400 MHz, CDCl_3) 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); ^{13}C NMR (101 MHz, CDCl_3) 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 $[\text{C}_{19}\text{H}_{18}\text{NO}, \text{M} - \text{OH}]^+$: 276.1383, Found 276.1385.

7. NMR Spectra of Intermediates and Indole Enones

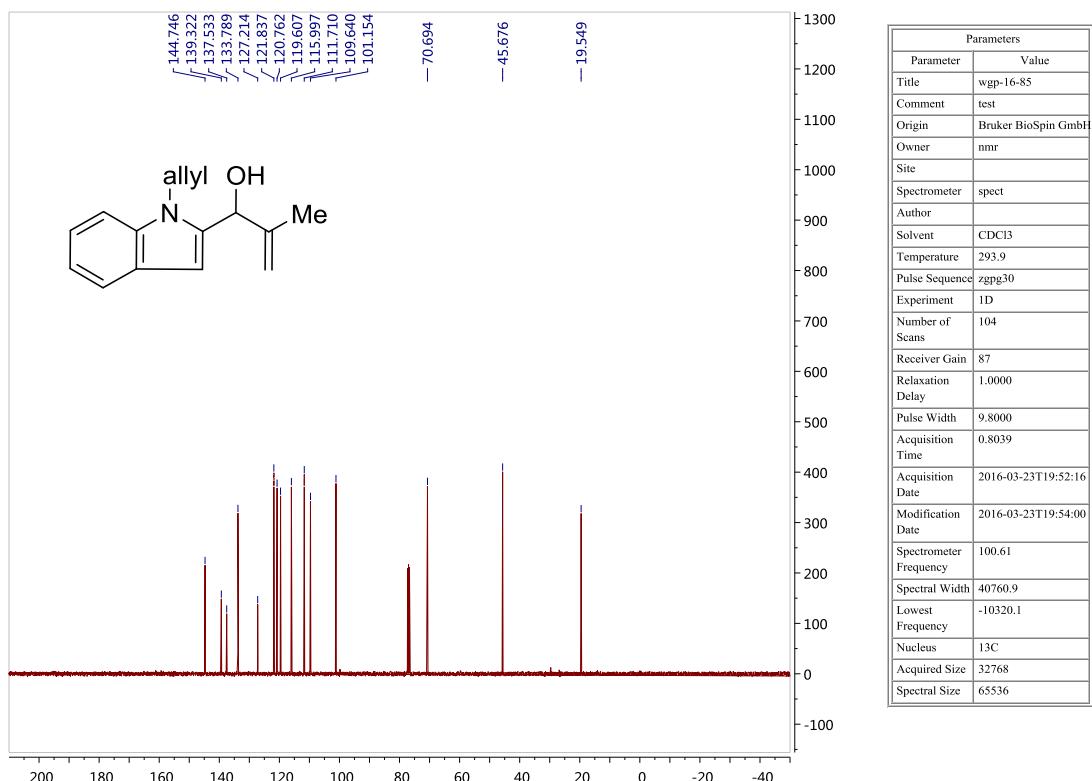
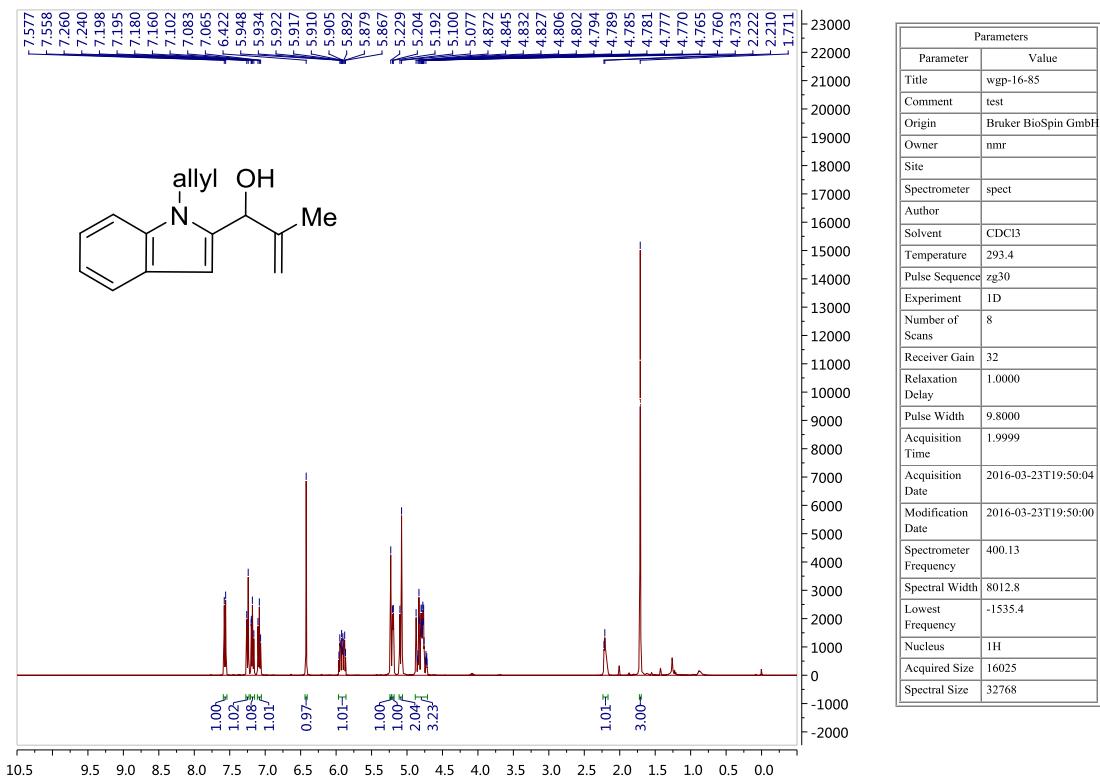
2-methyl-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



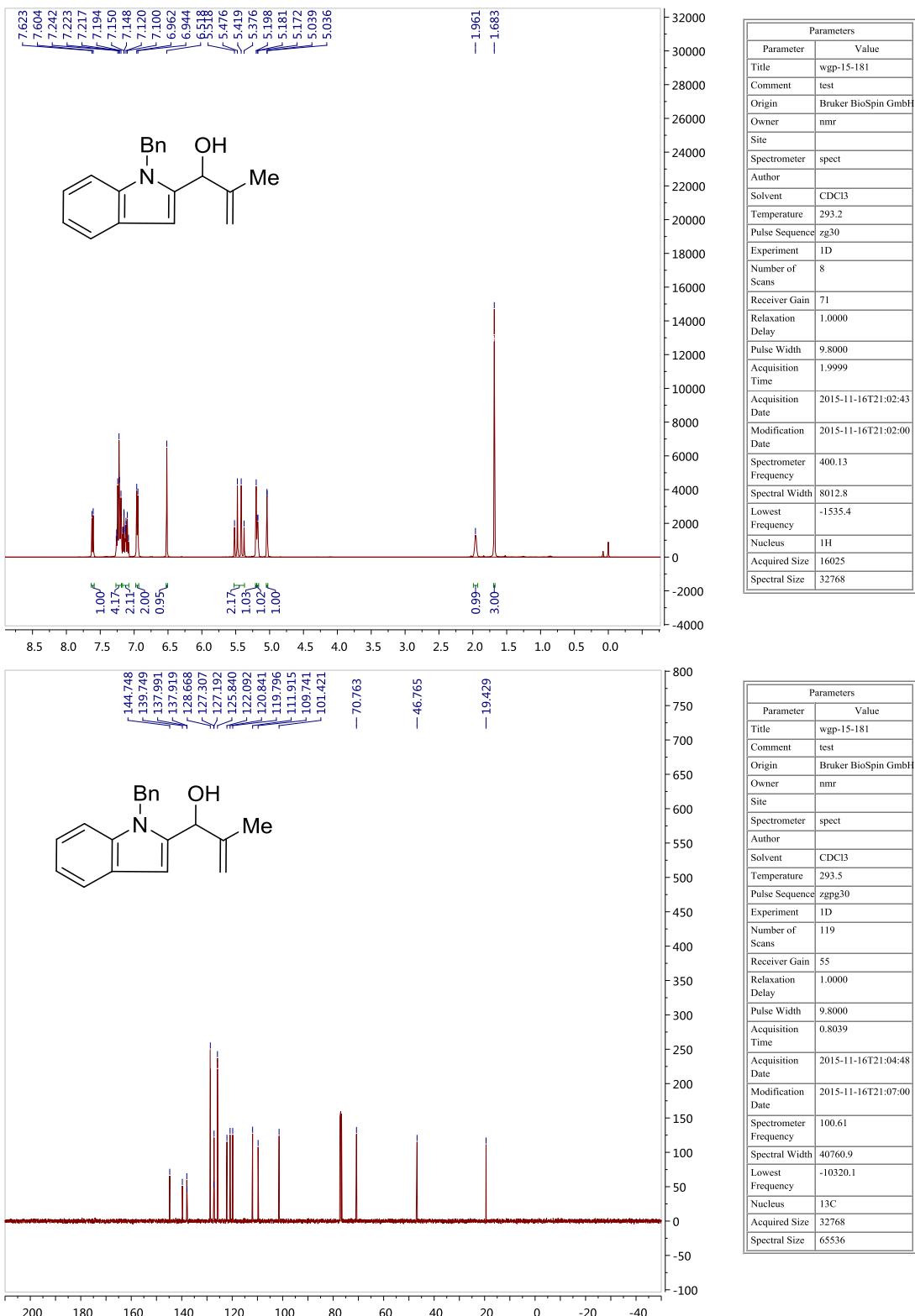
1-(1-isopropyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol



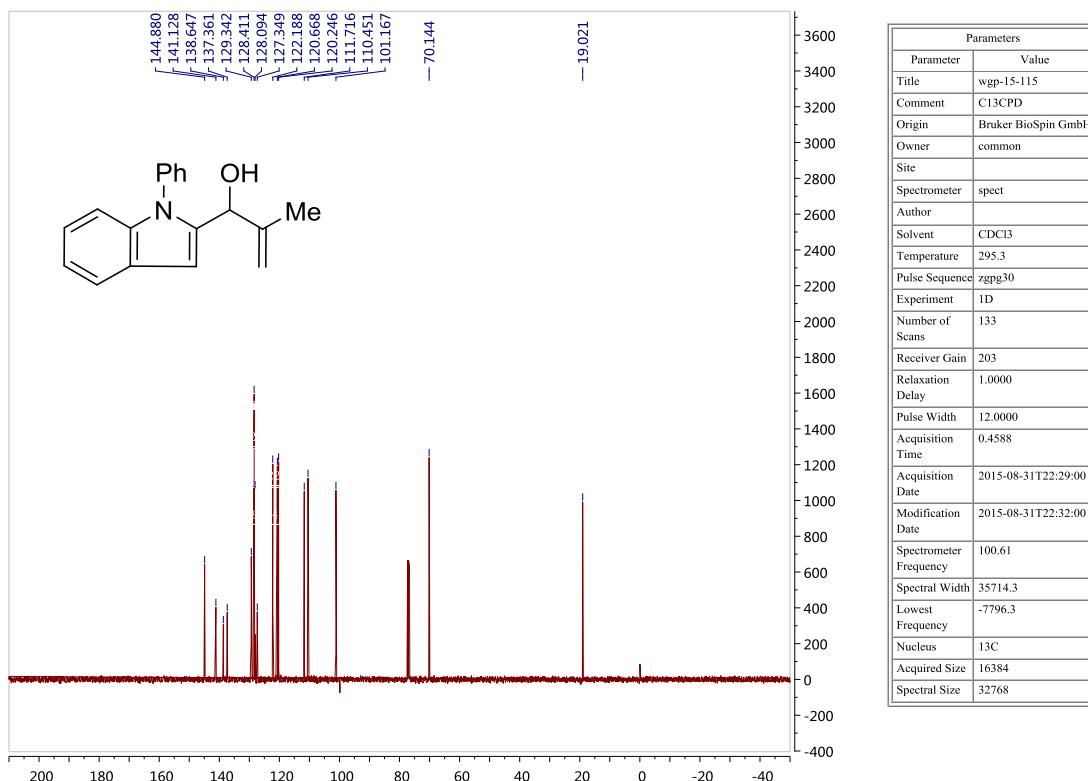
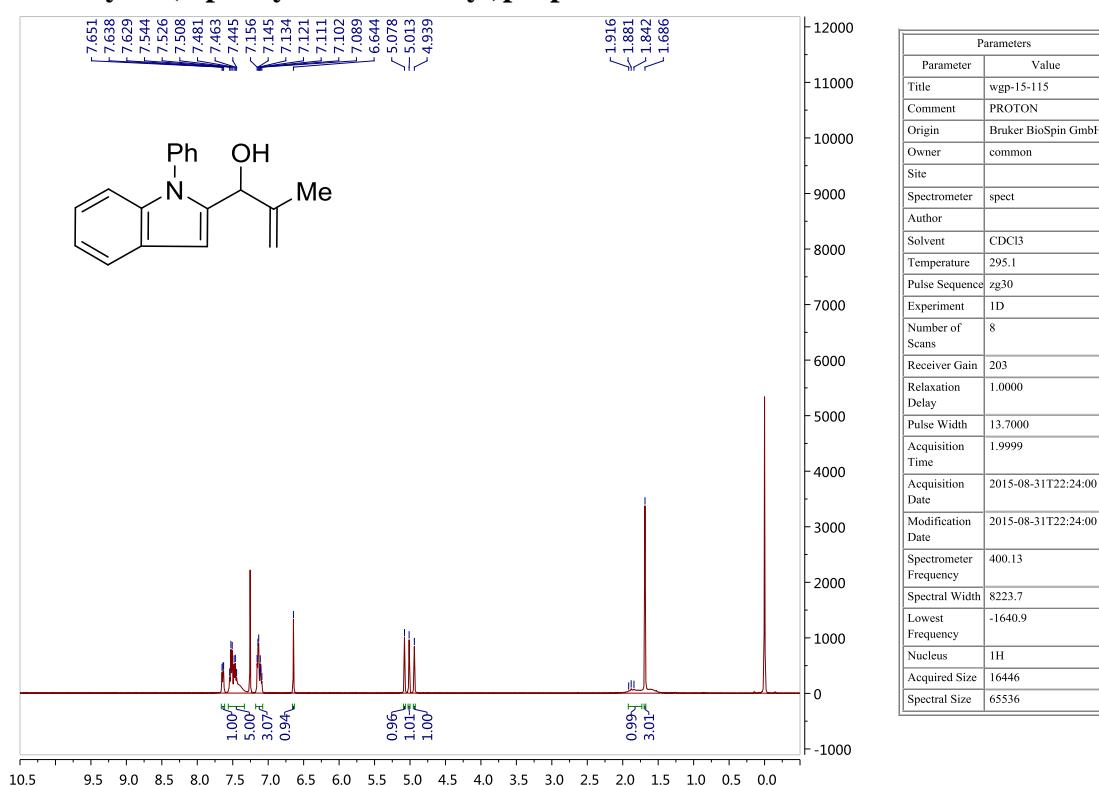
1-(1-allyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol



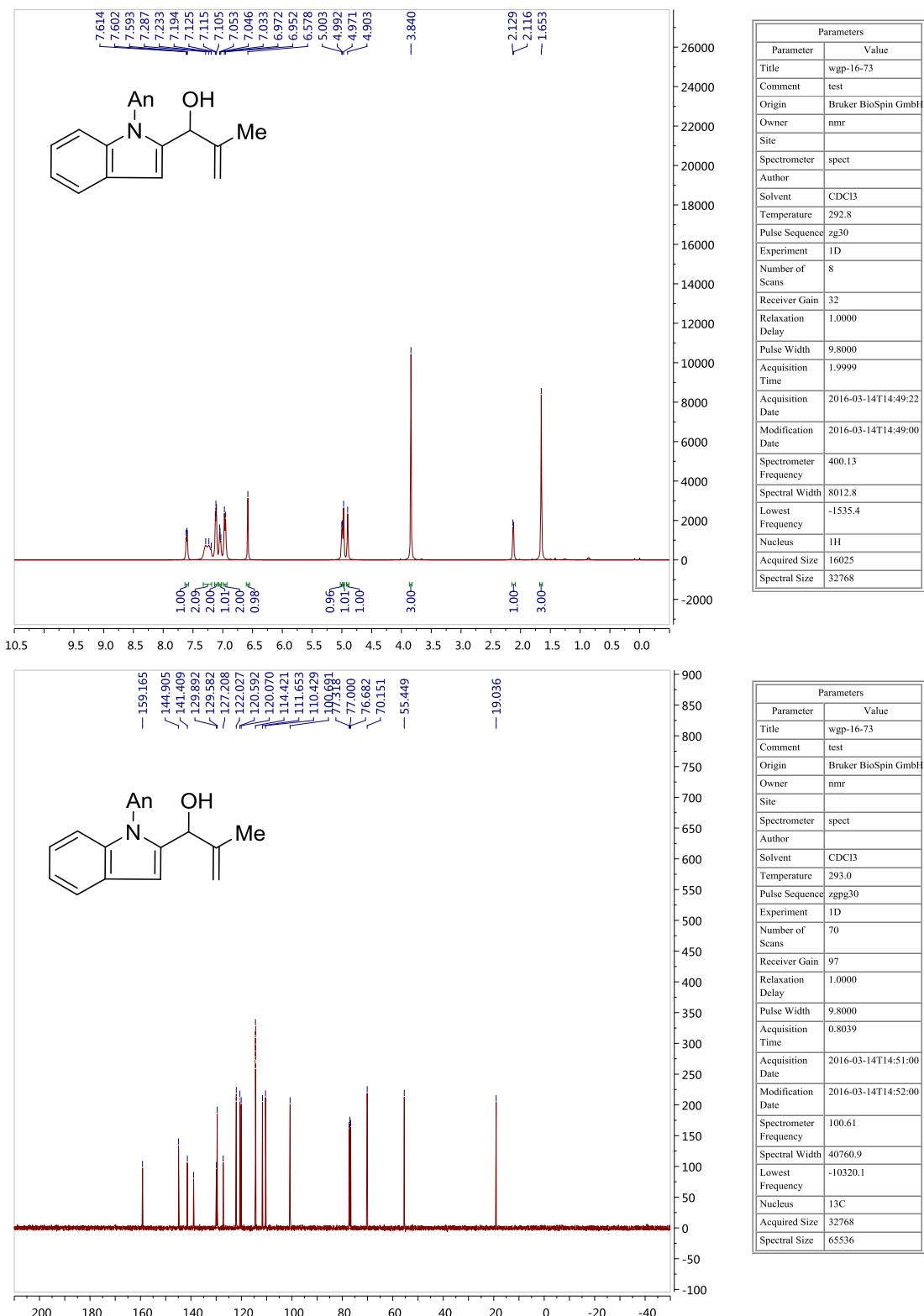
1-(1-benzyl-1H-indol-2-yl)-2-methylprop-2-en-1-ol



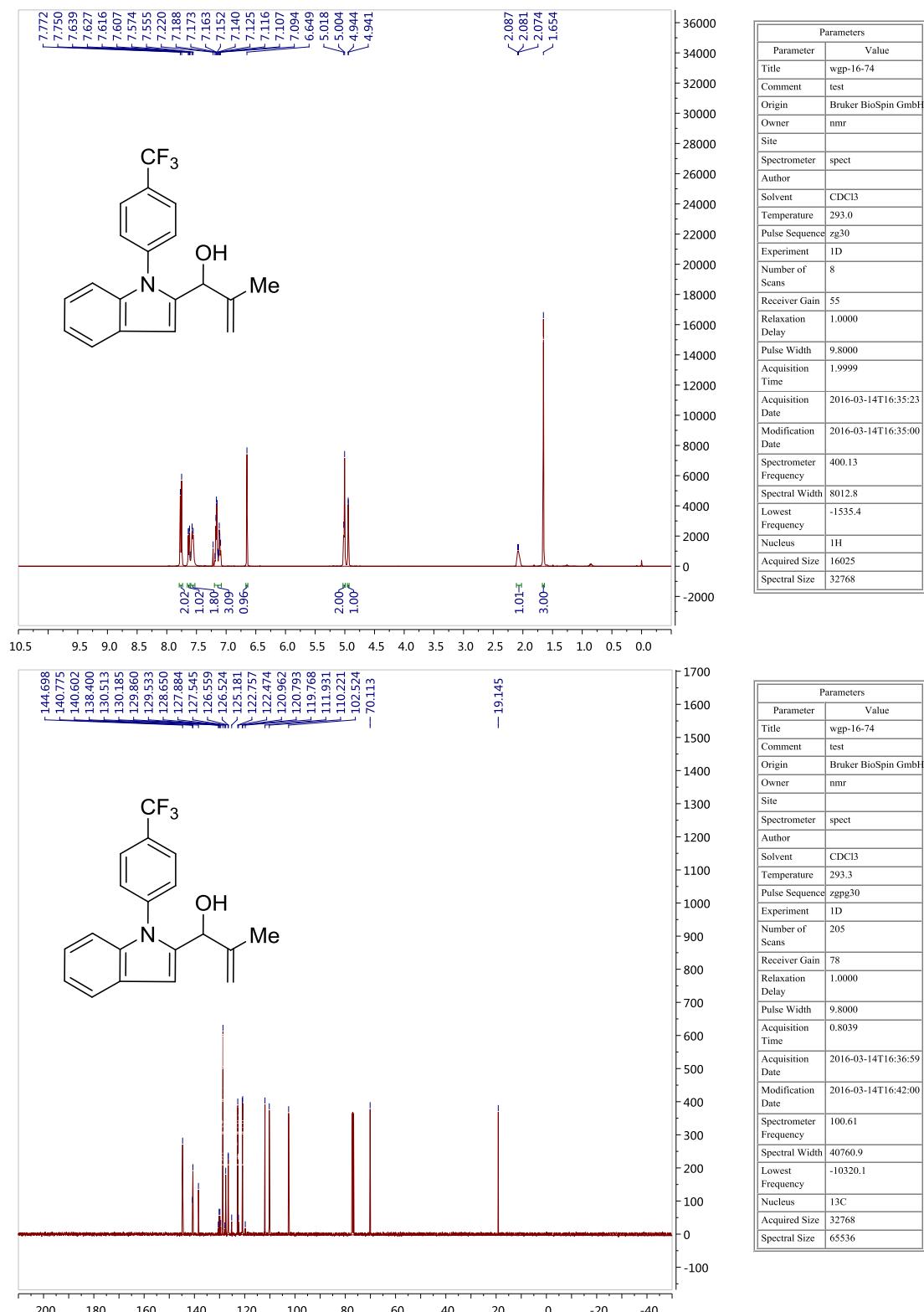
2-methyl-1-(1-phenyl-1H-indol-2-yl)prop-2-en-1-ol



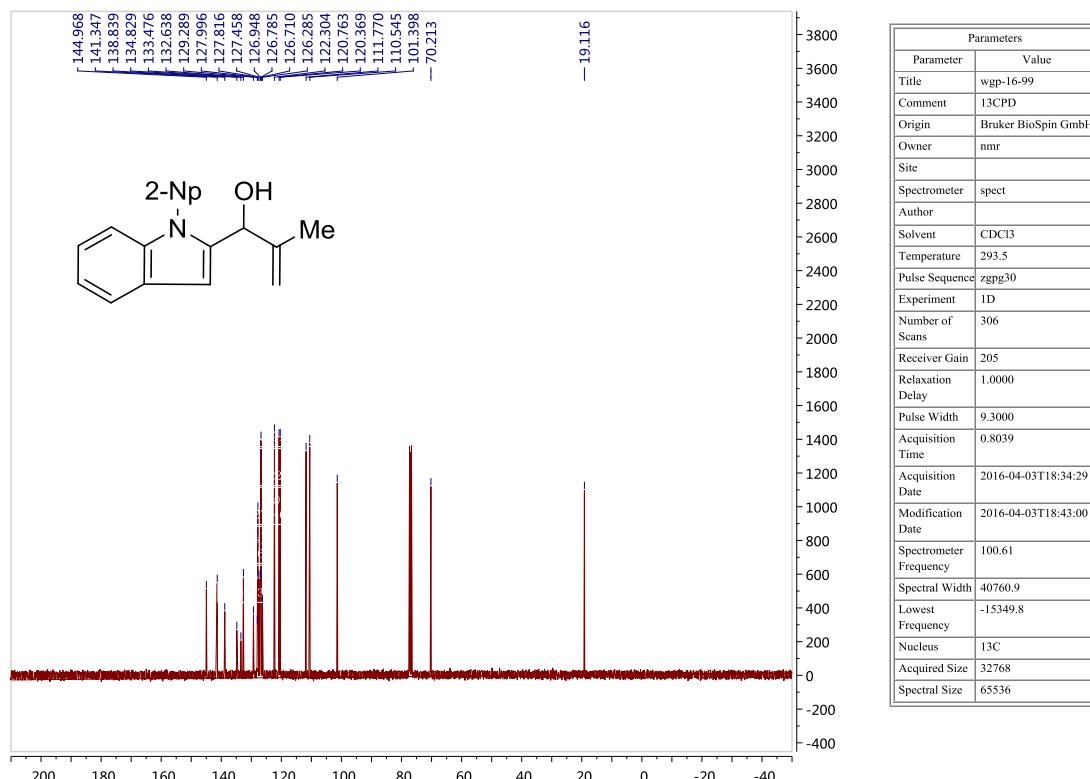
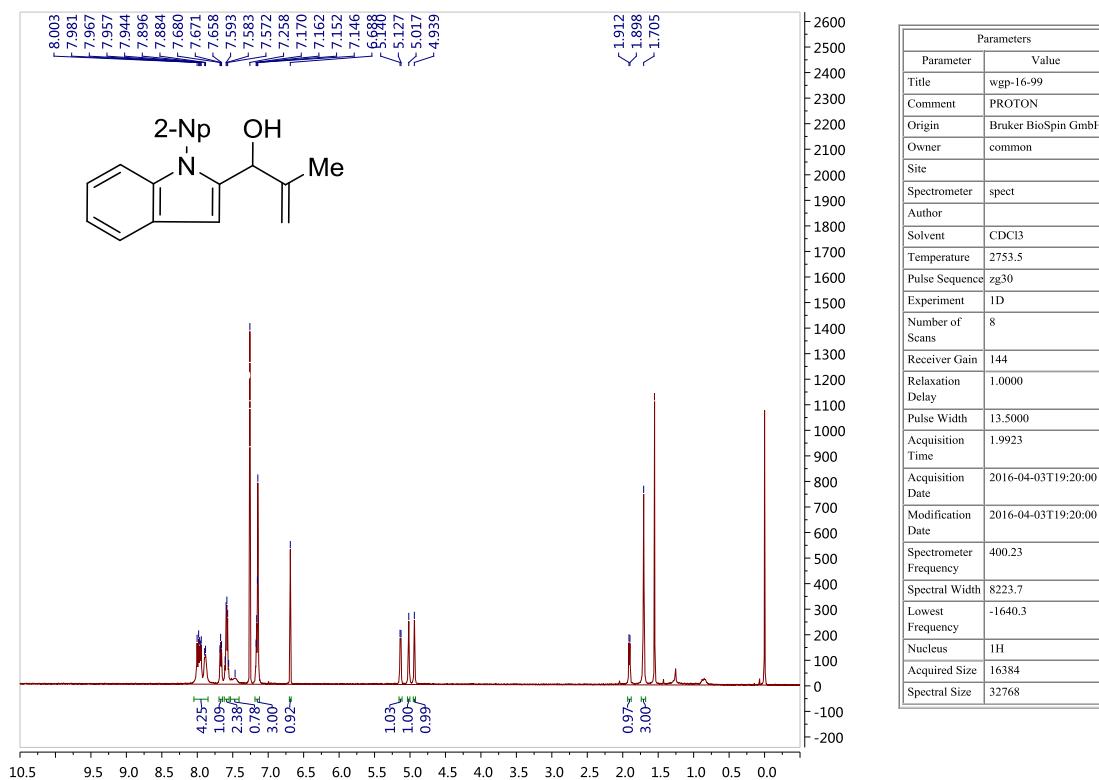
1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-ol



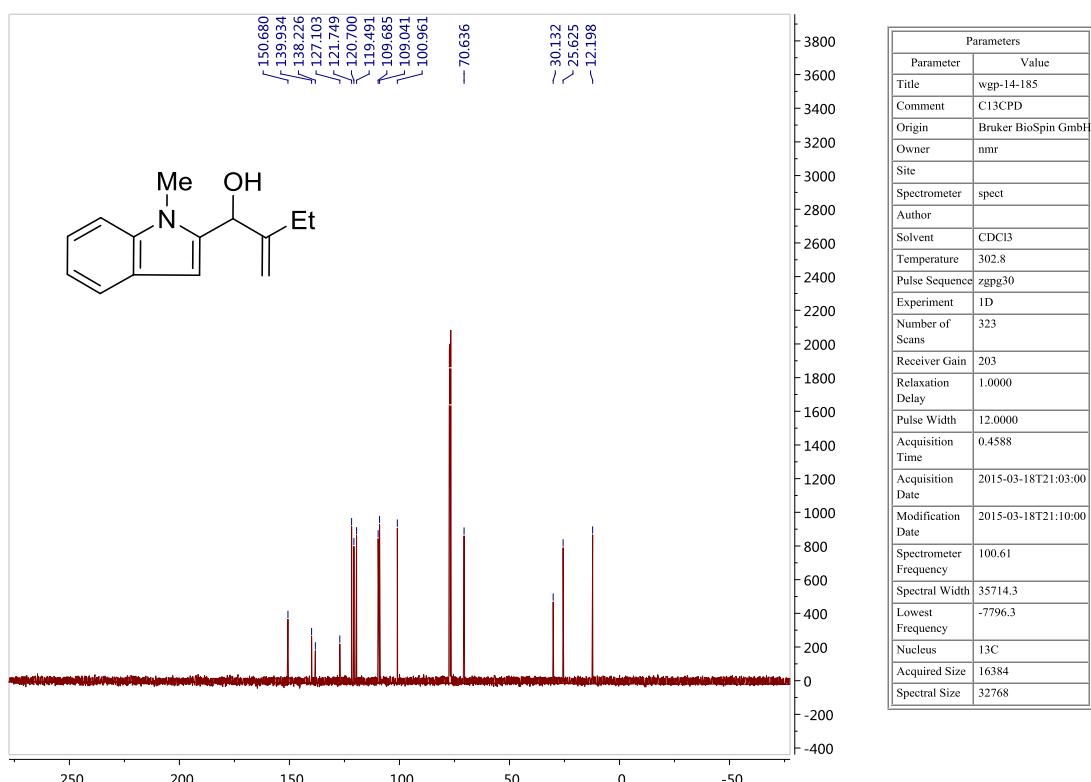
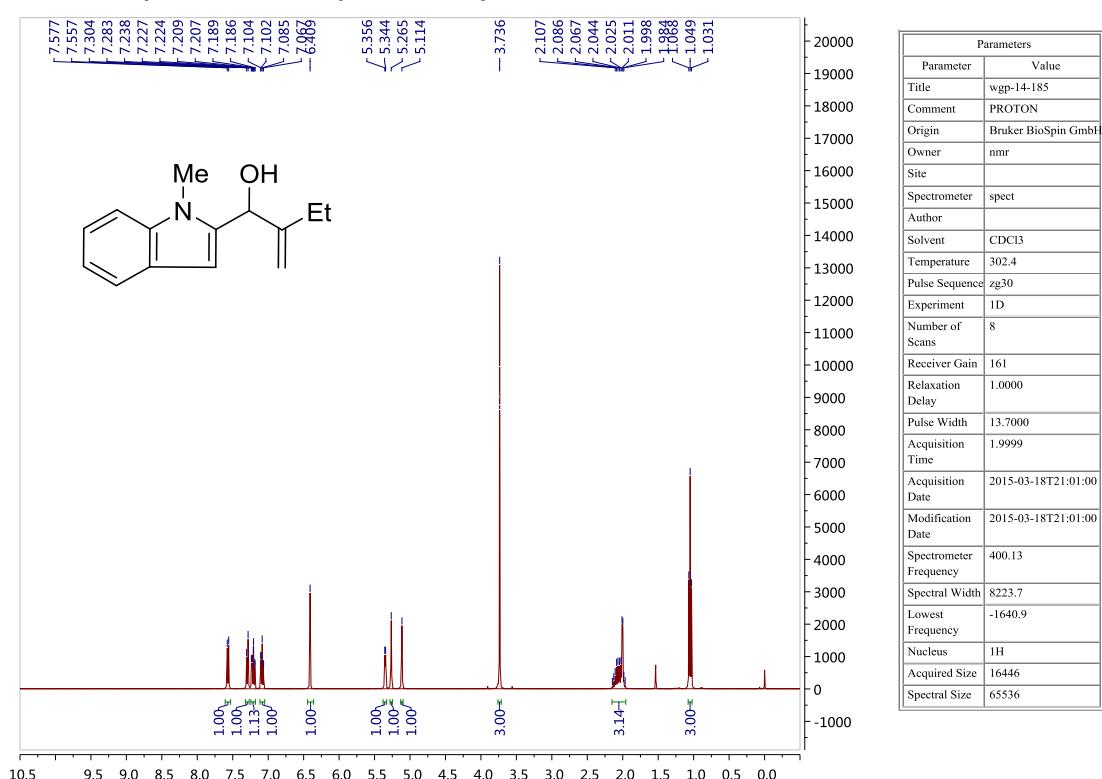
2-methyl-1-(1-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)prop-2-en-1-ol



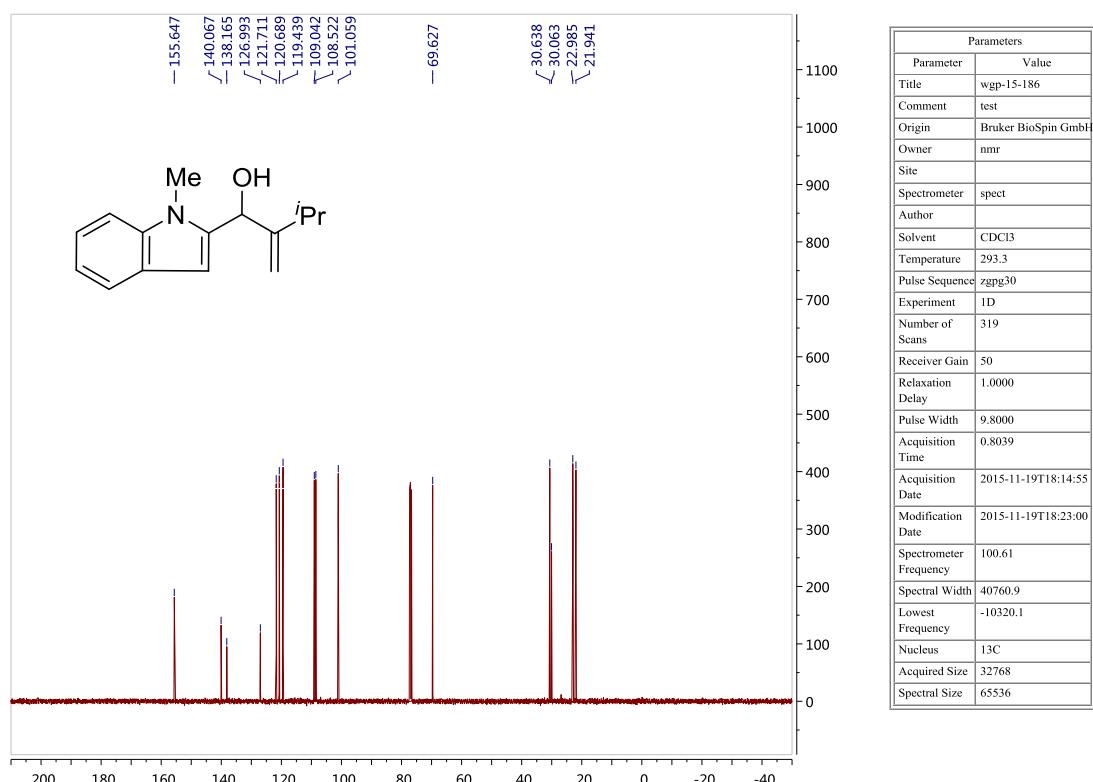
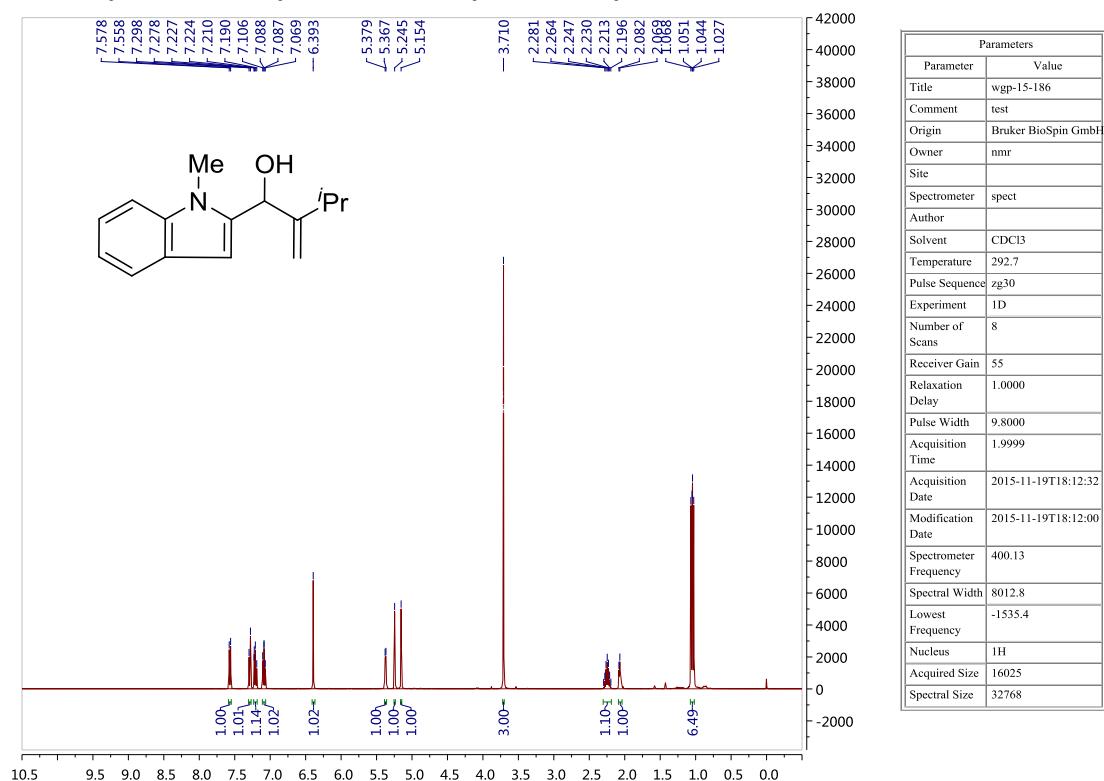
2-methyl-1-(1-(naphthalen-2-yl)-1H-indol-2-yl)prop-2-en-1-ol



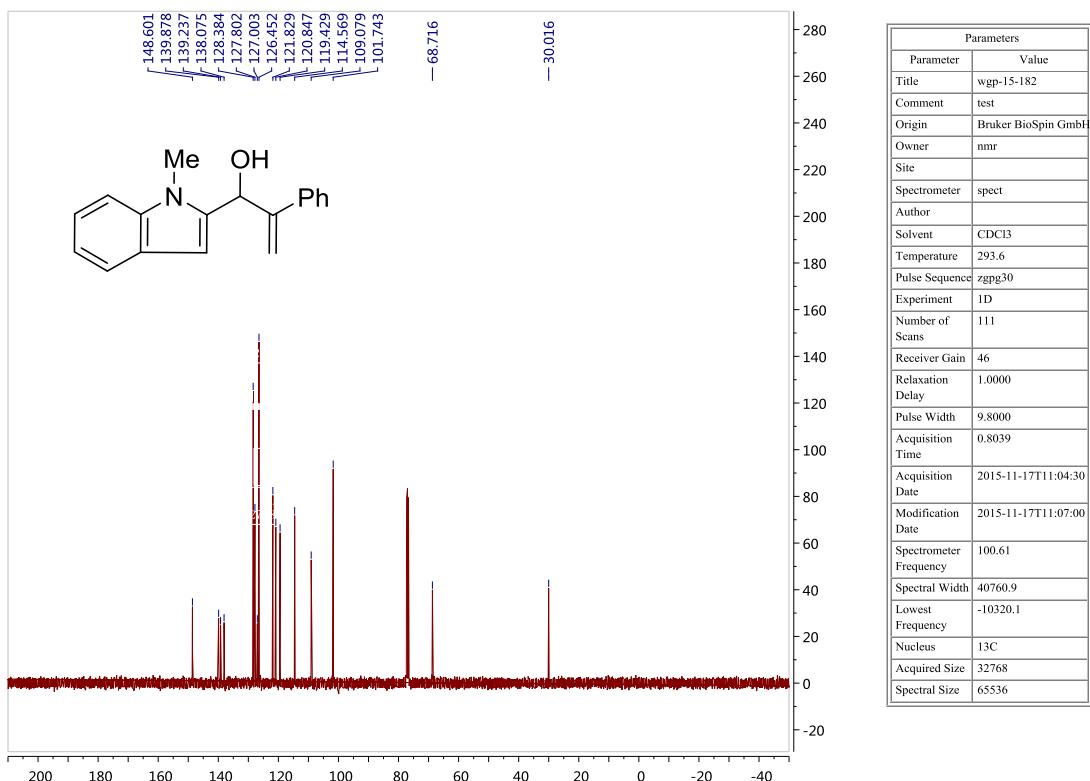
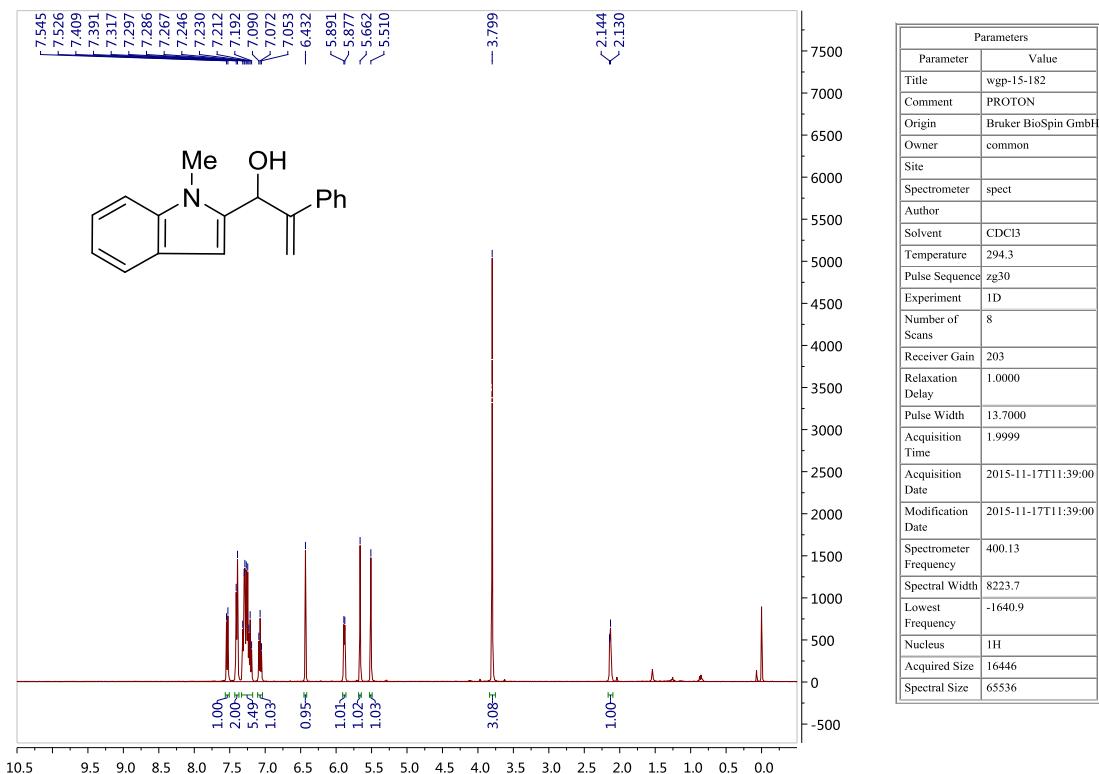
1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-ol



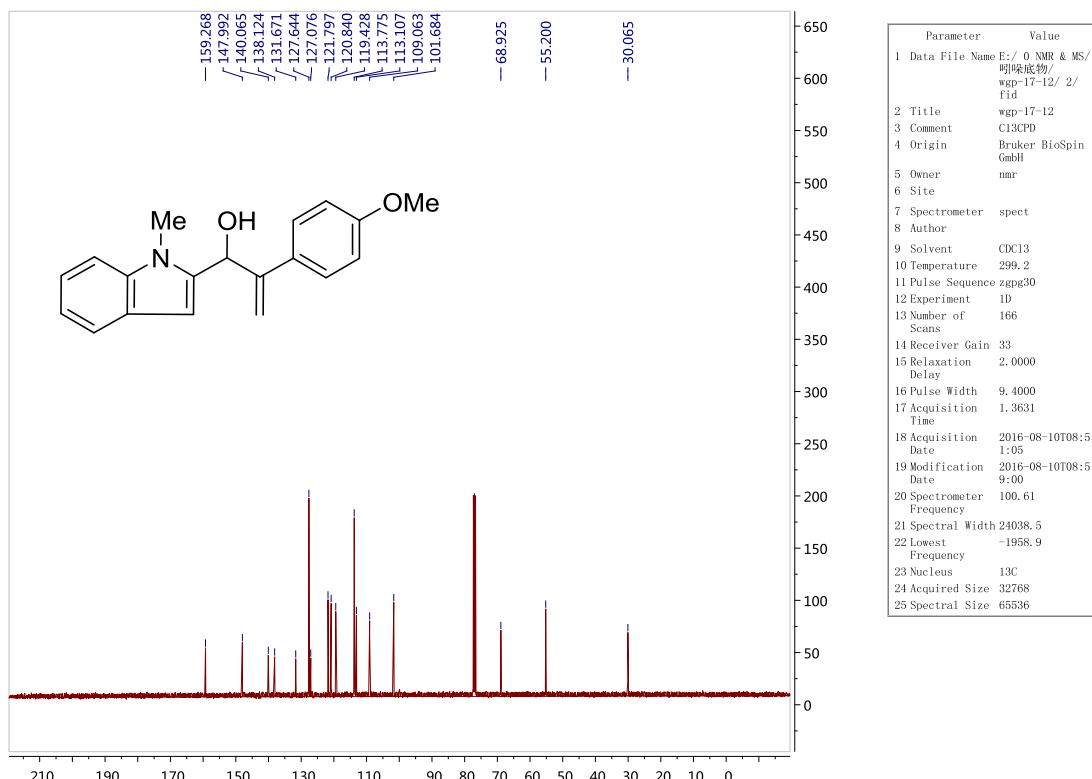
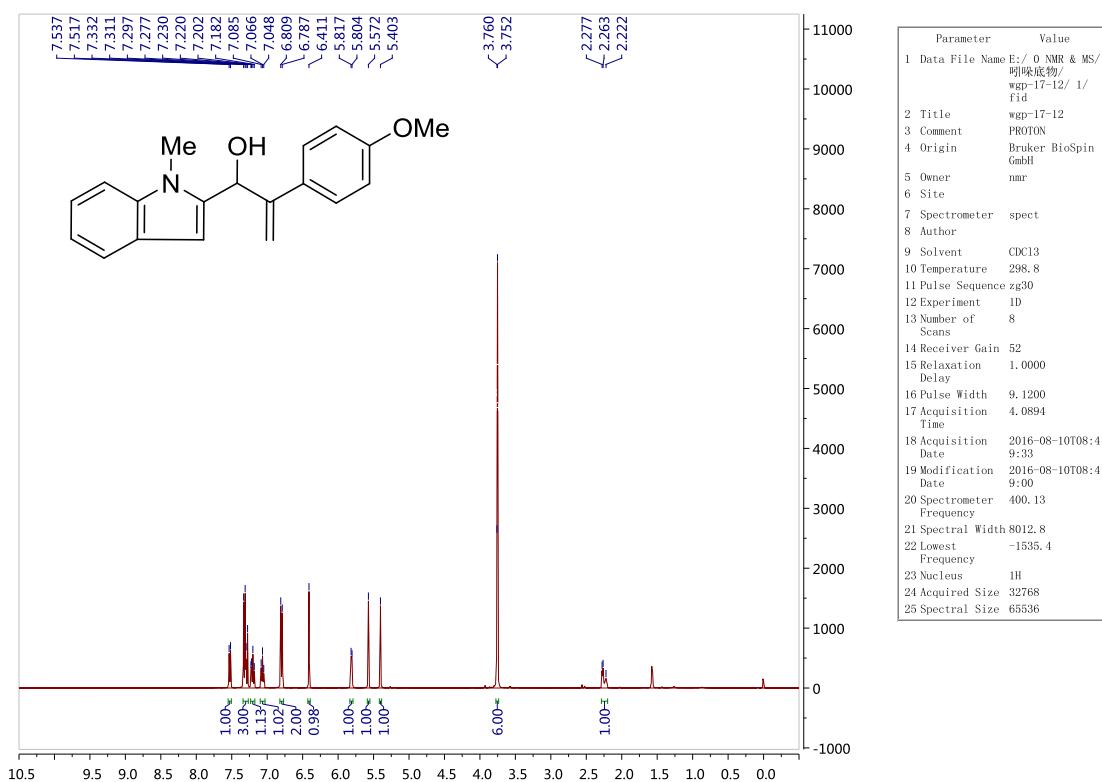
3-methyl-1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-ol



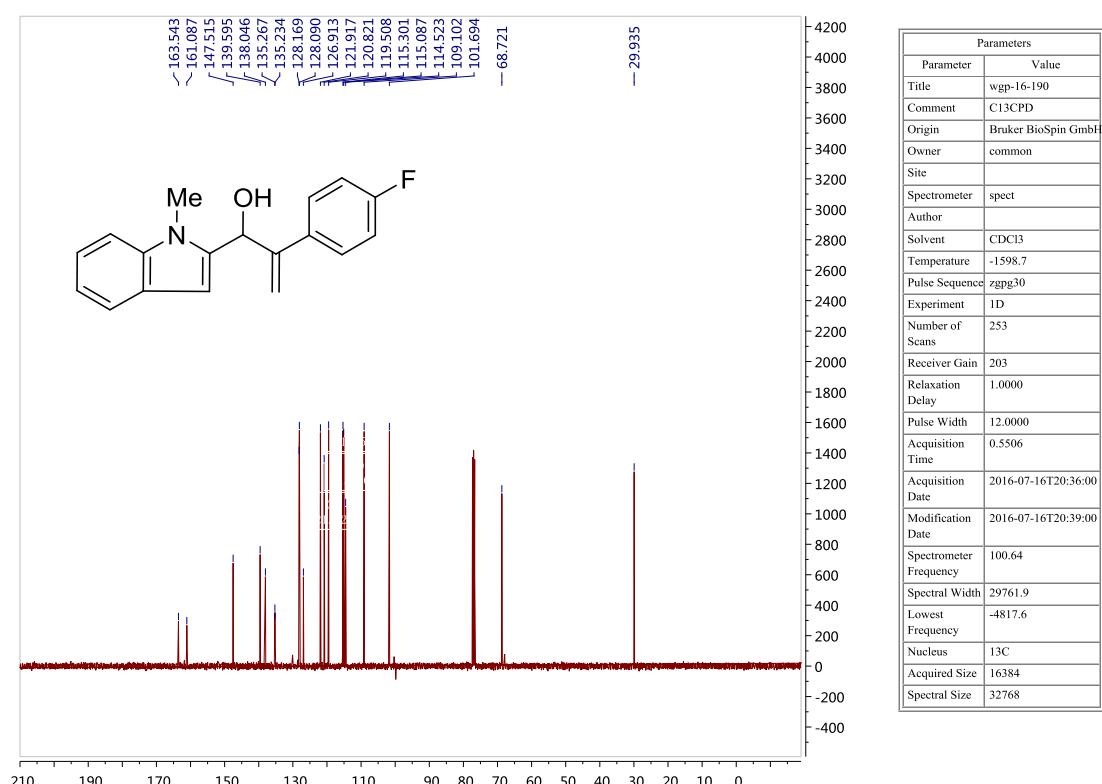
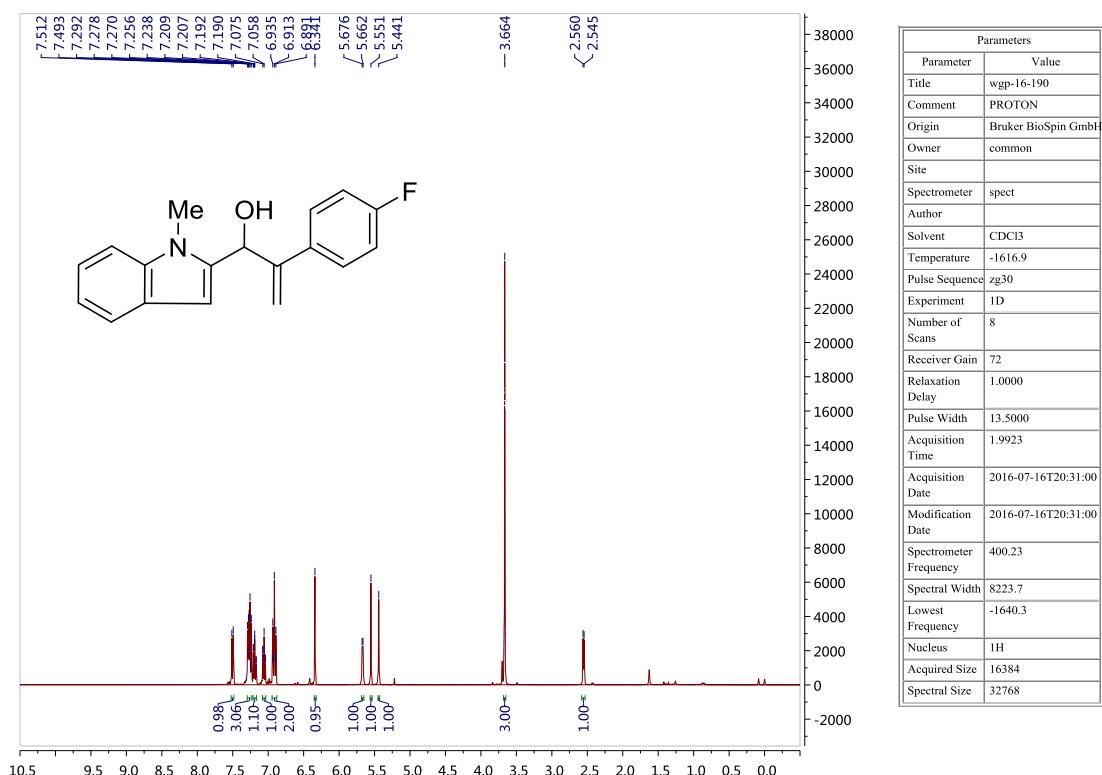
1-(1-methyl-1H-indol-2-yl)-2-phenylprop-2-en-1-ol



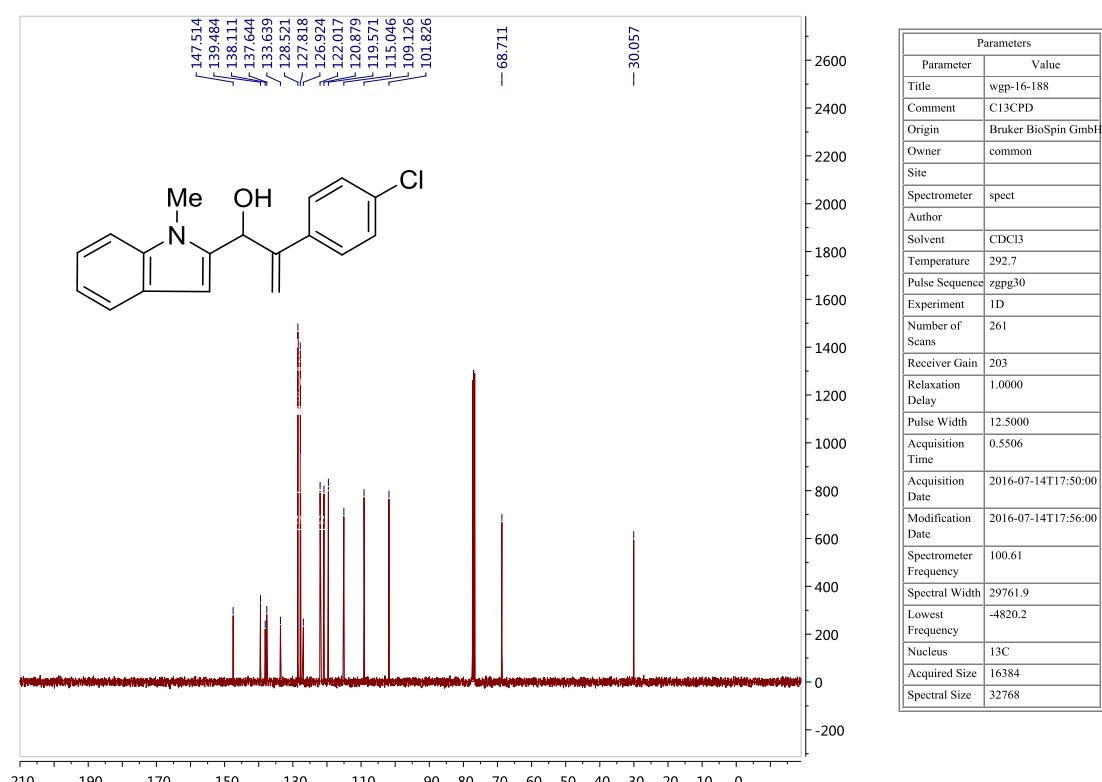
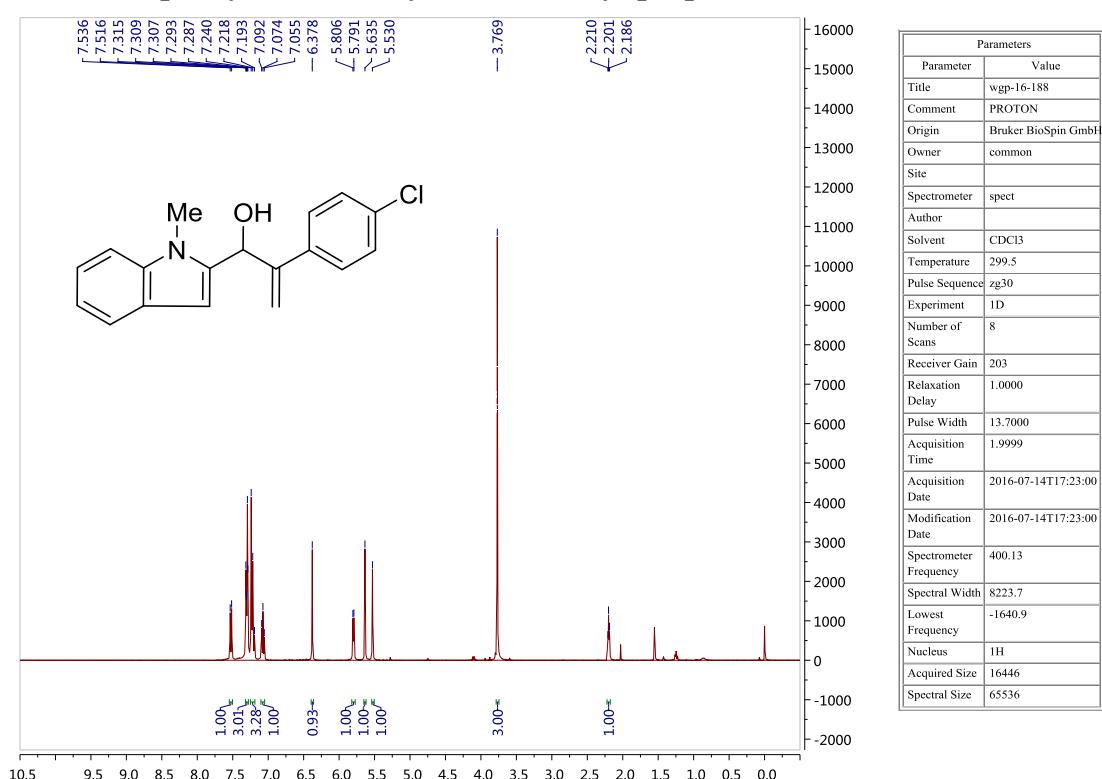
2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



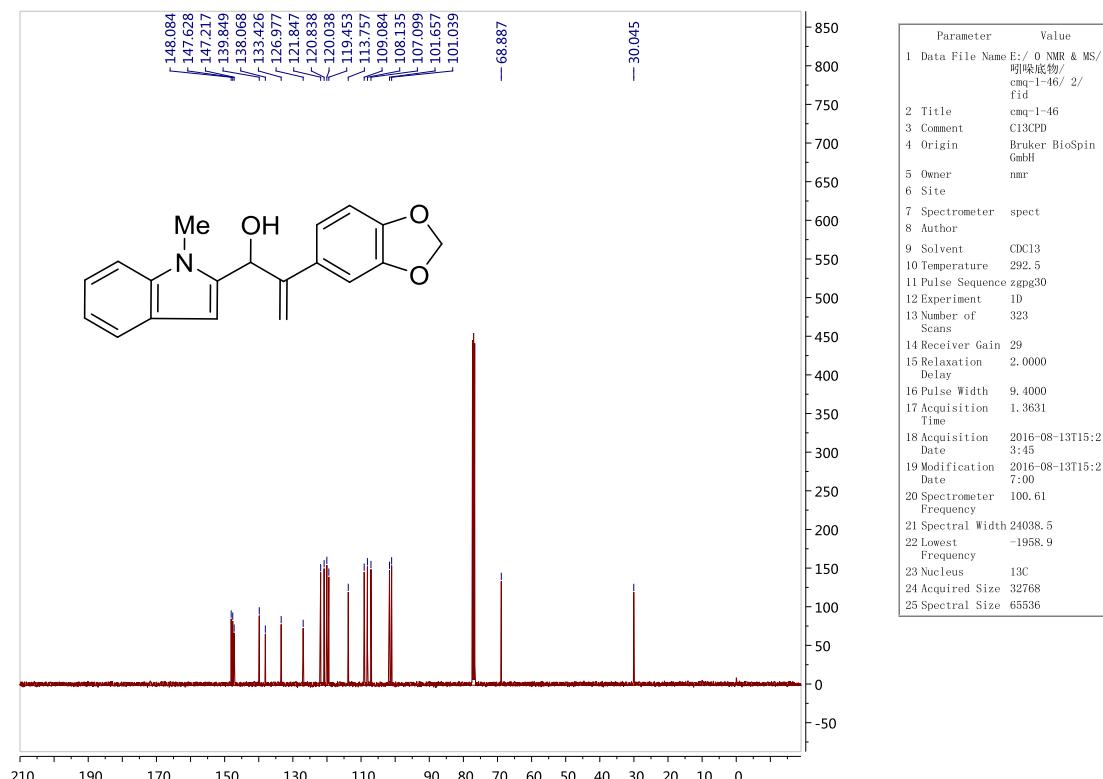
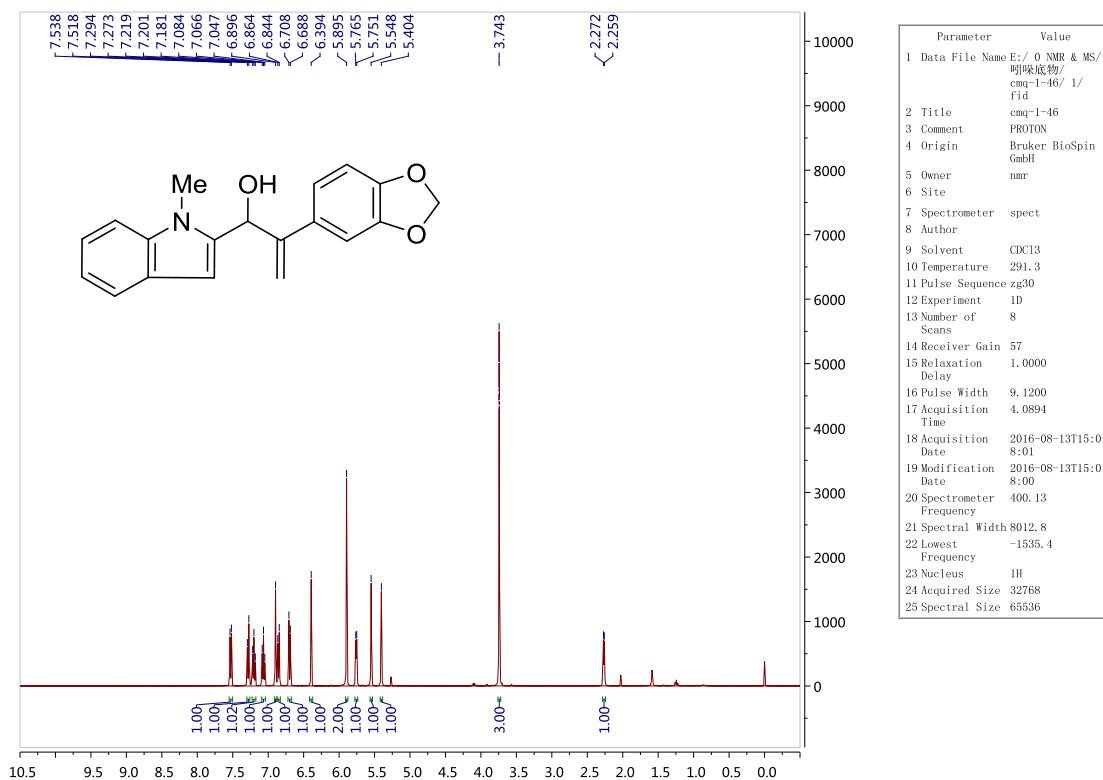
2-(4-fluorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



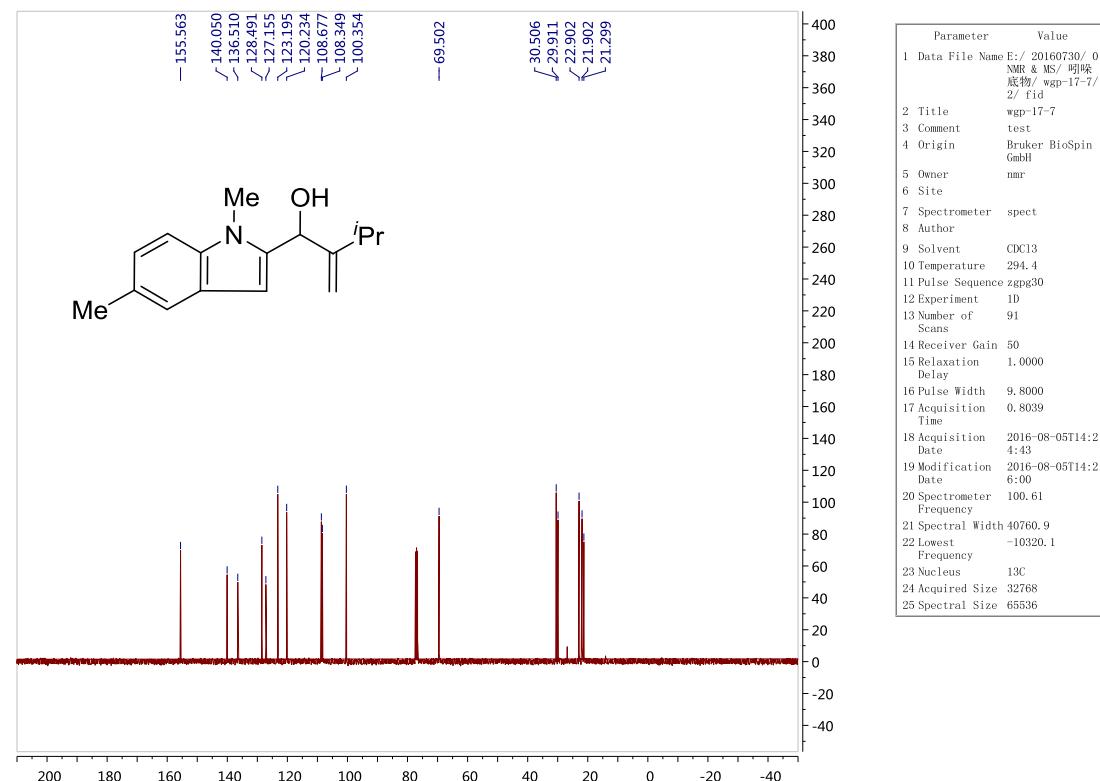
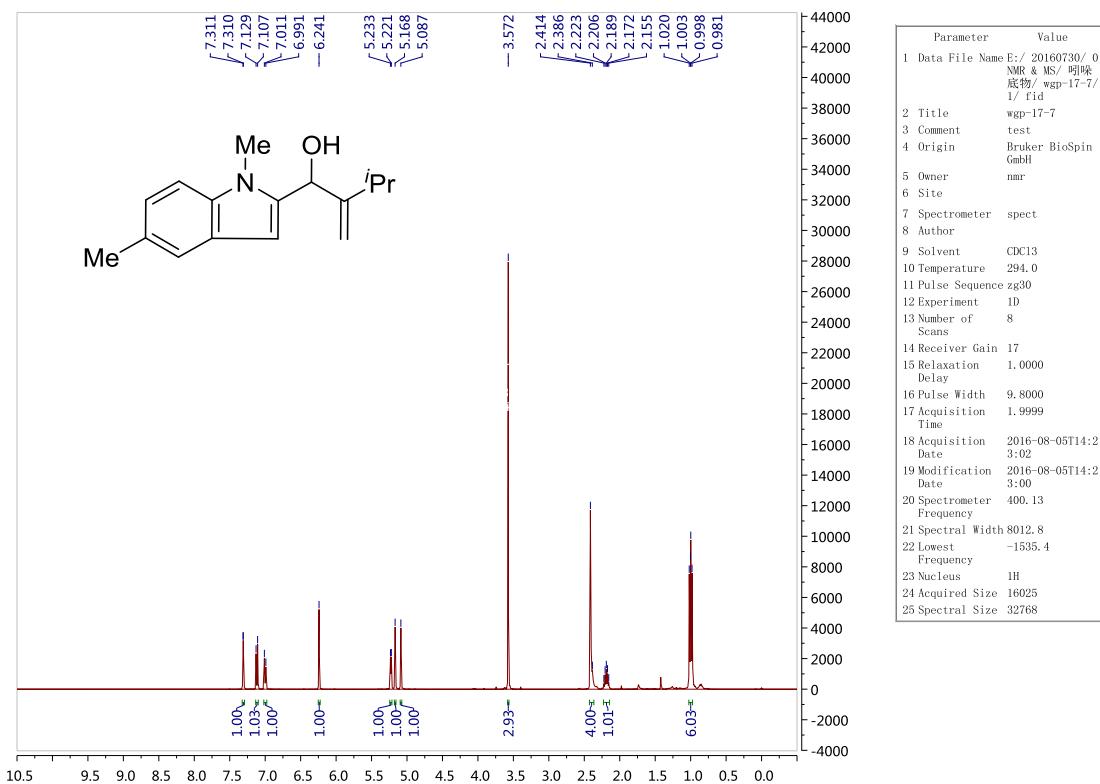
2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



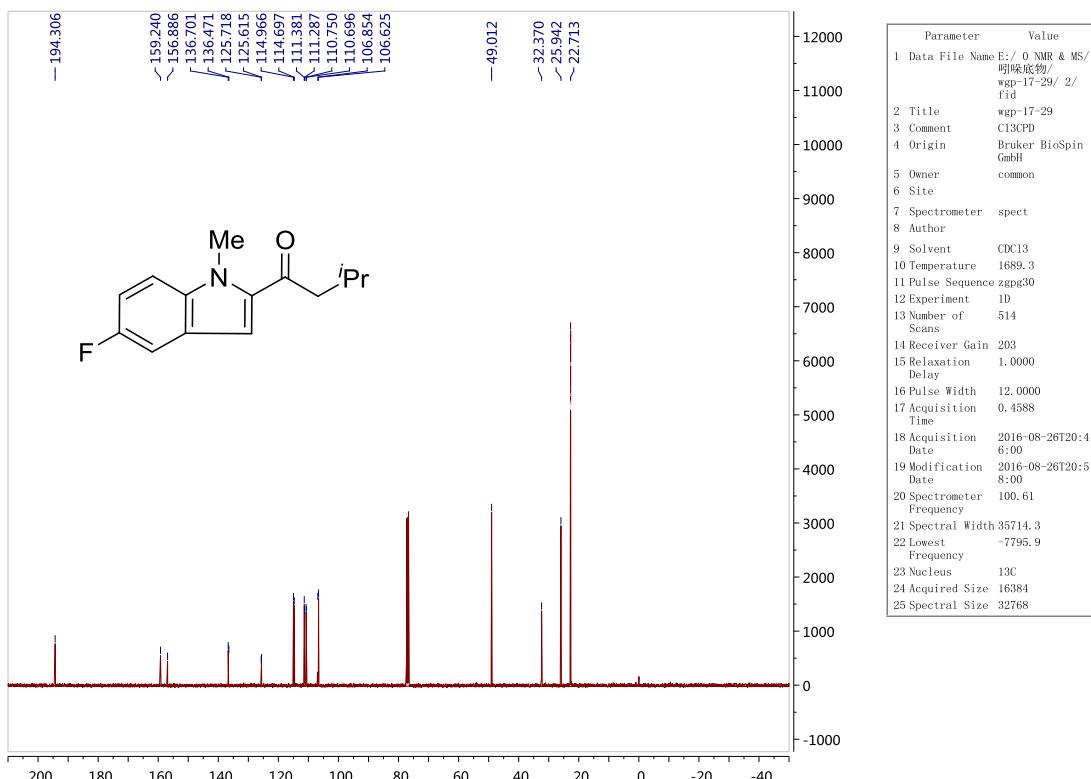
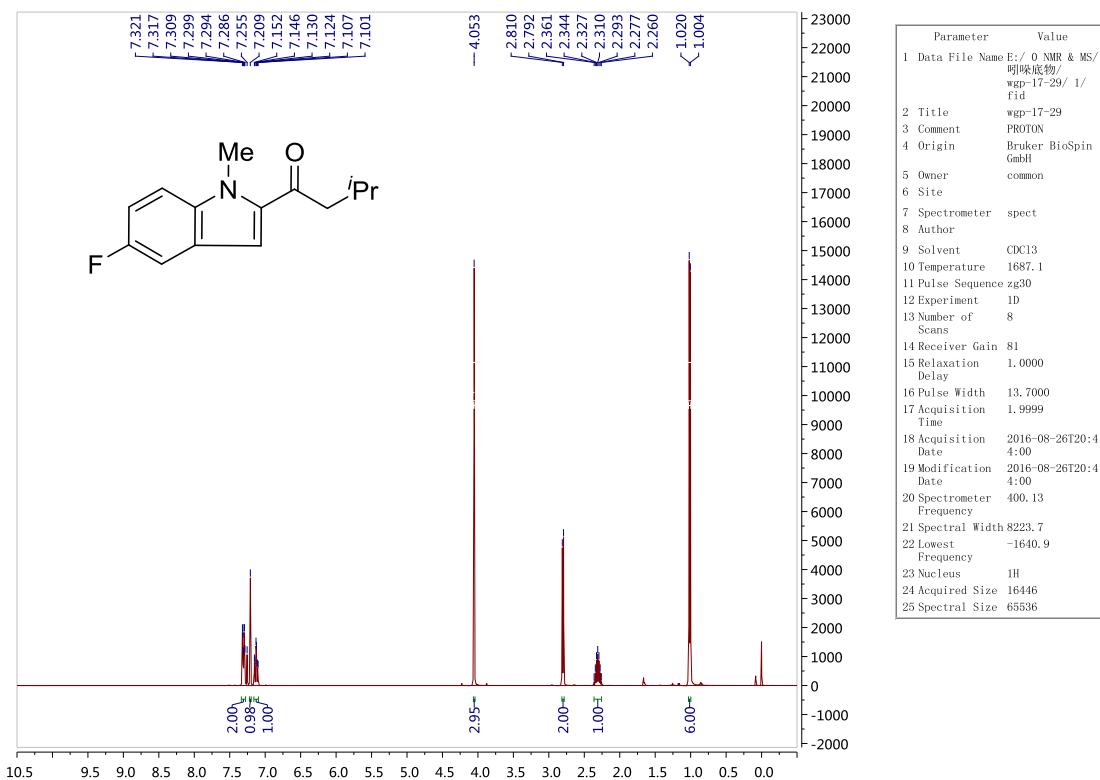
2-(benzo[d][1,3]dioxol-5-yl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-ol



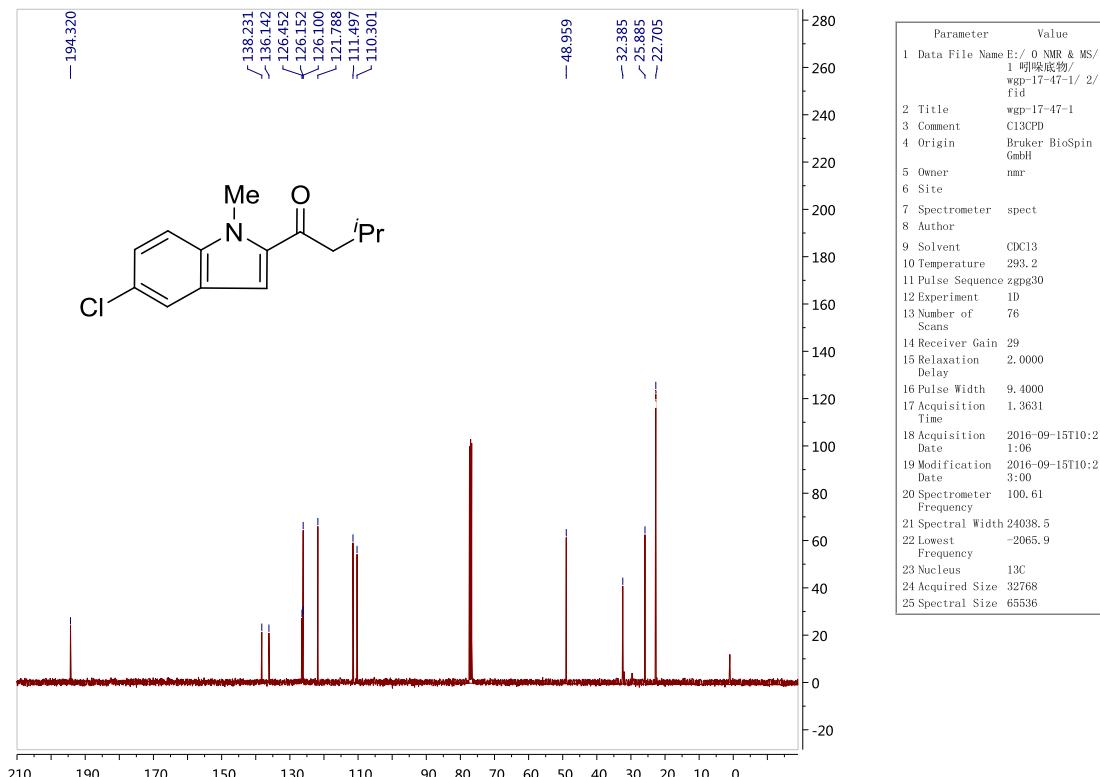
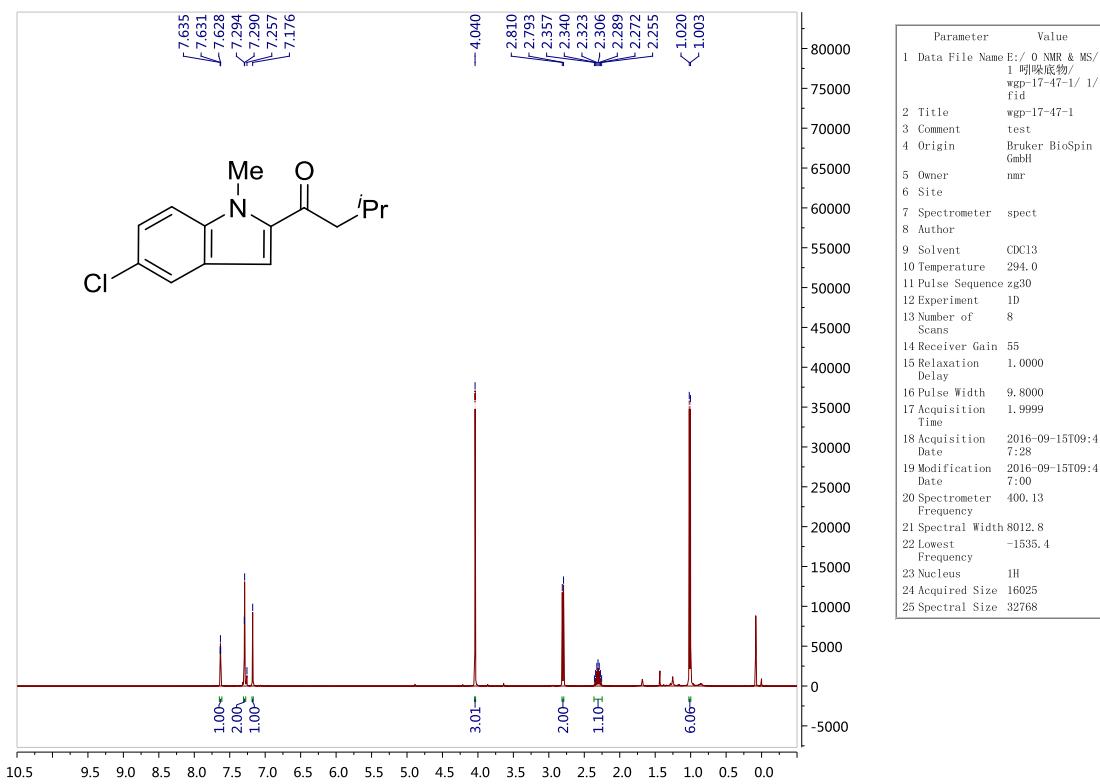
1-(1,5-dimethyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-ol



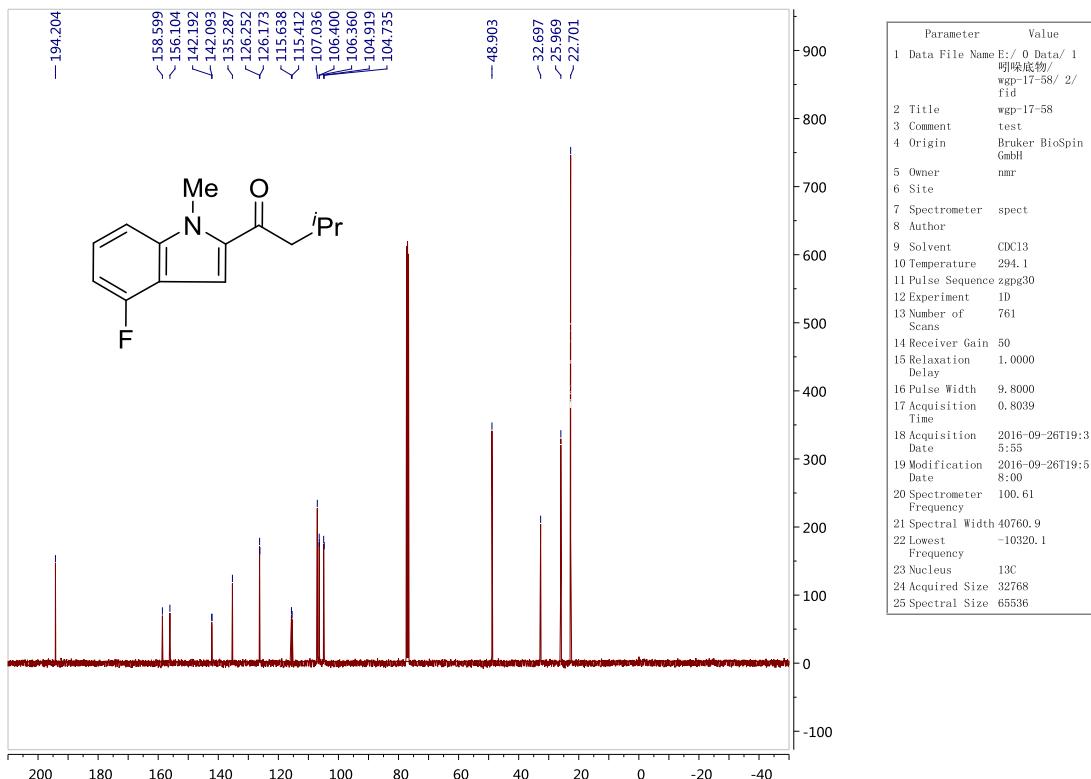
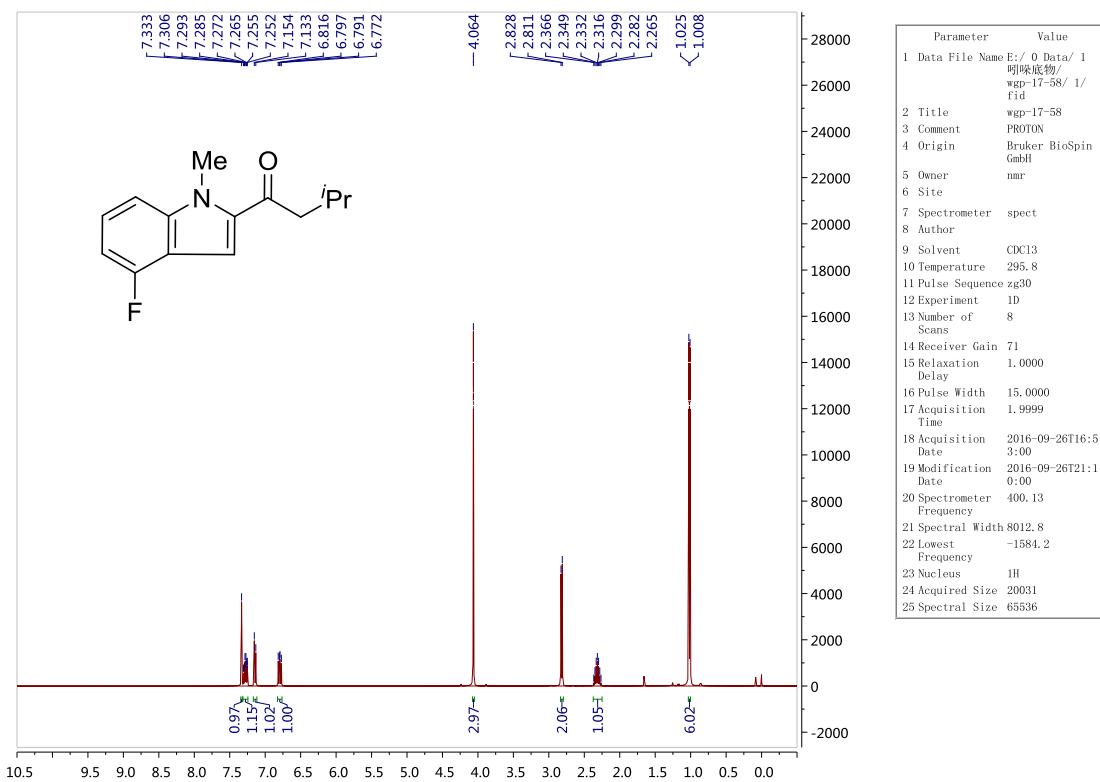
1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



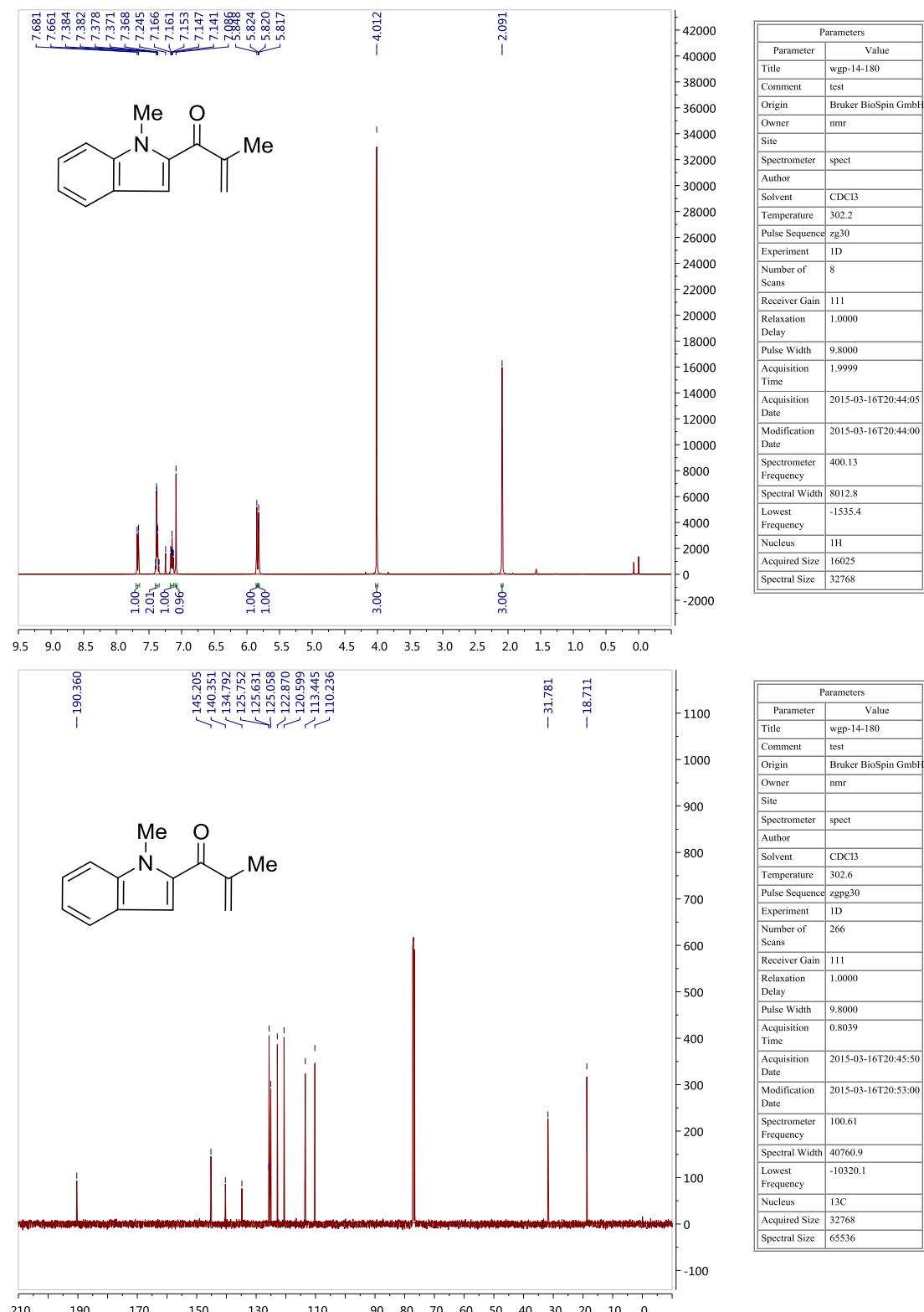
1-(5-chloro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



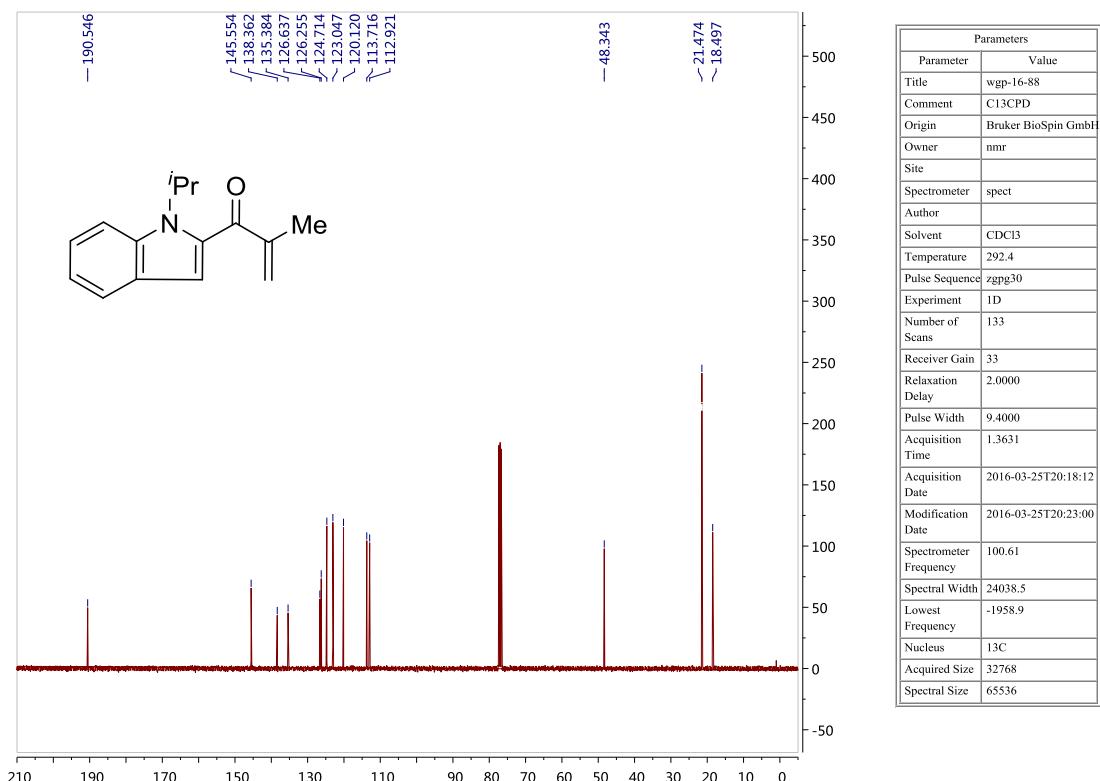
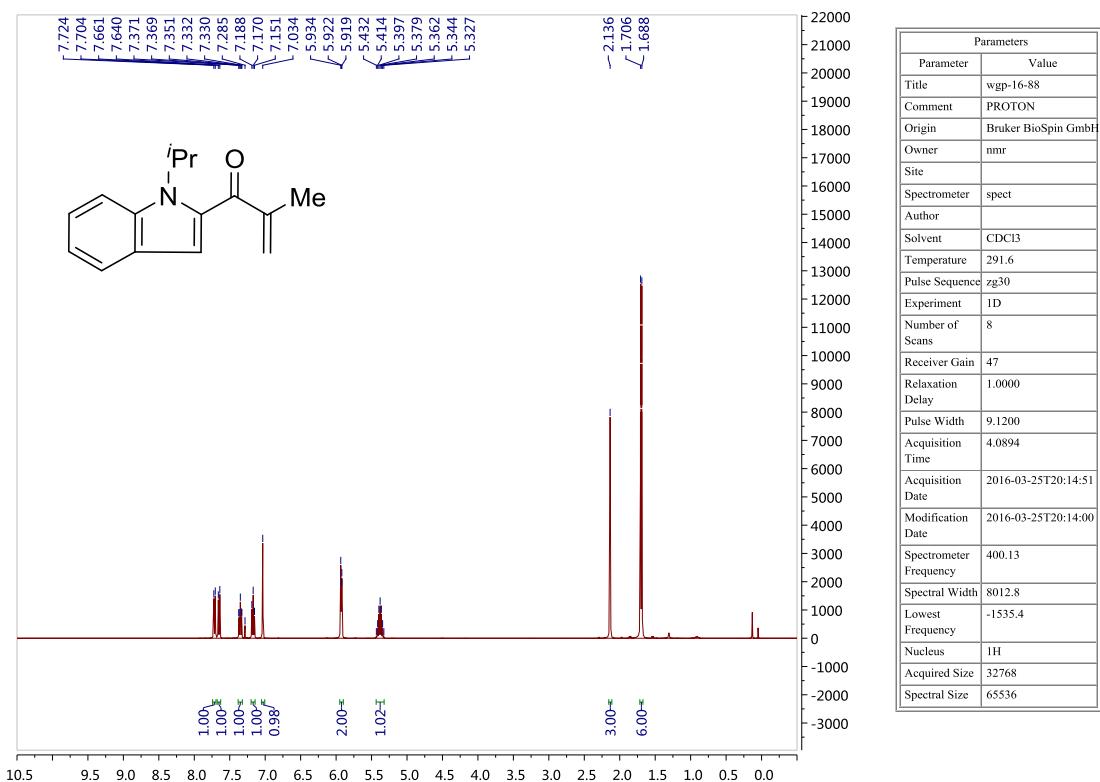
1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methylbutan-1-one



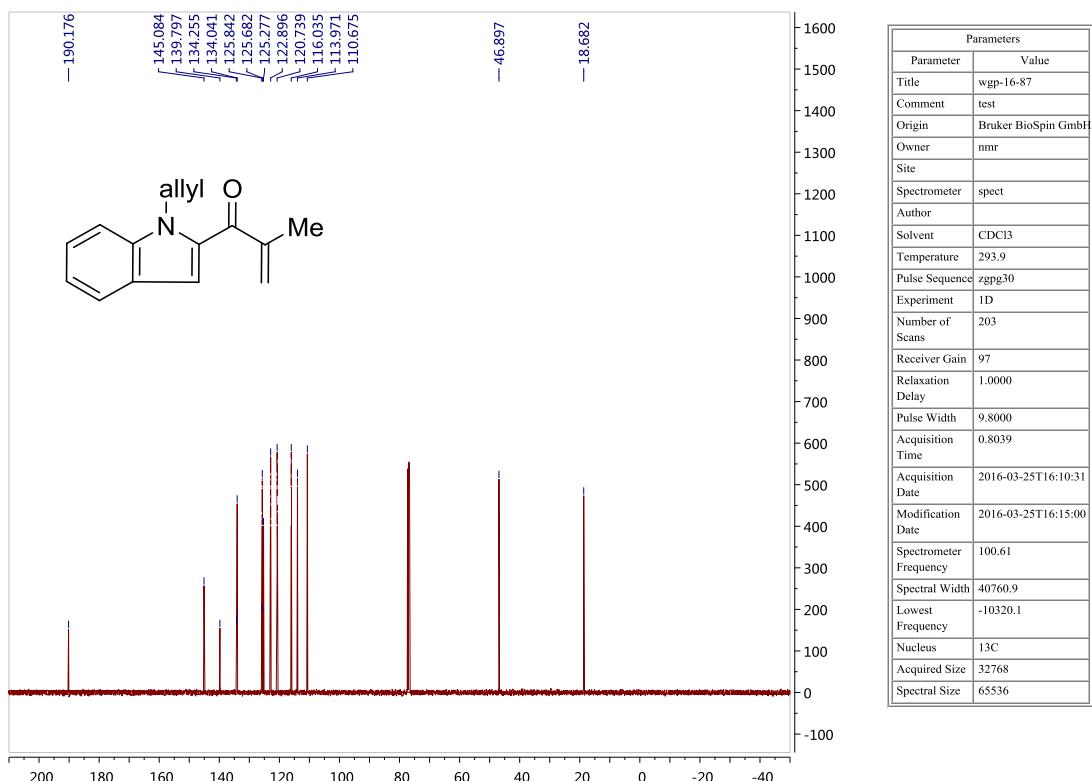
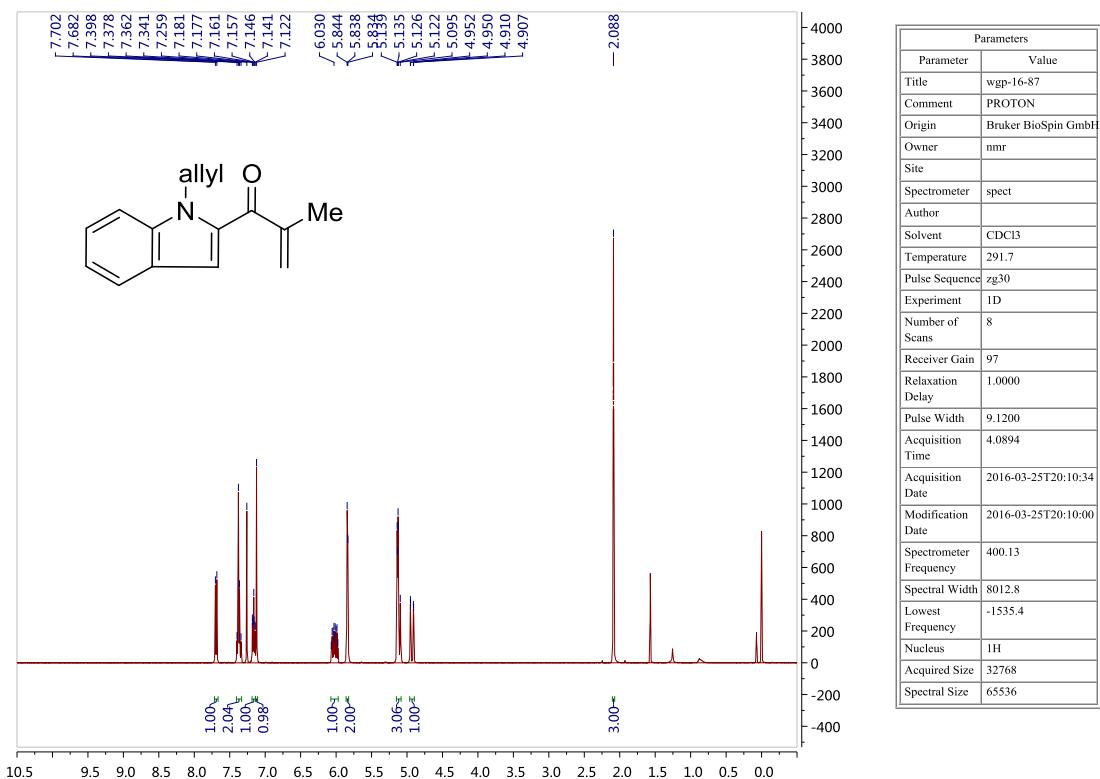
2-methyl-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2a)



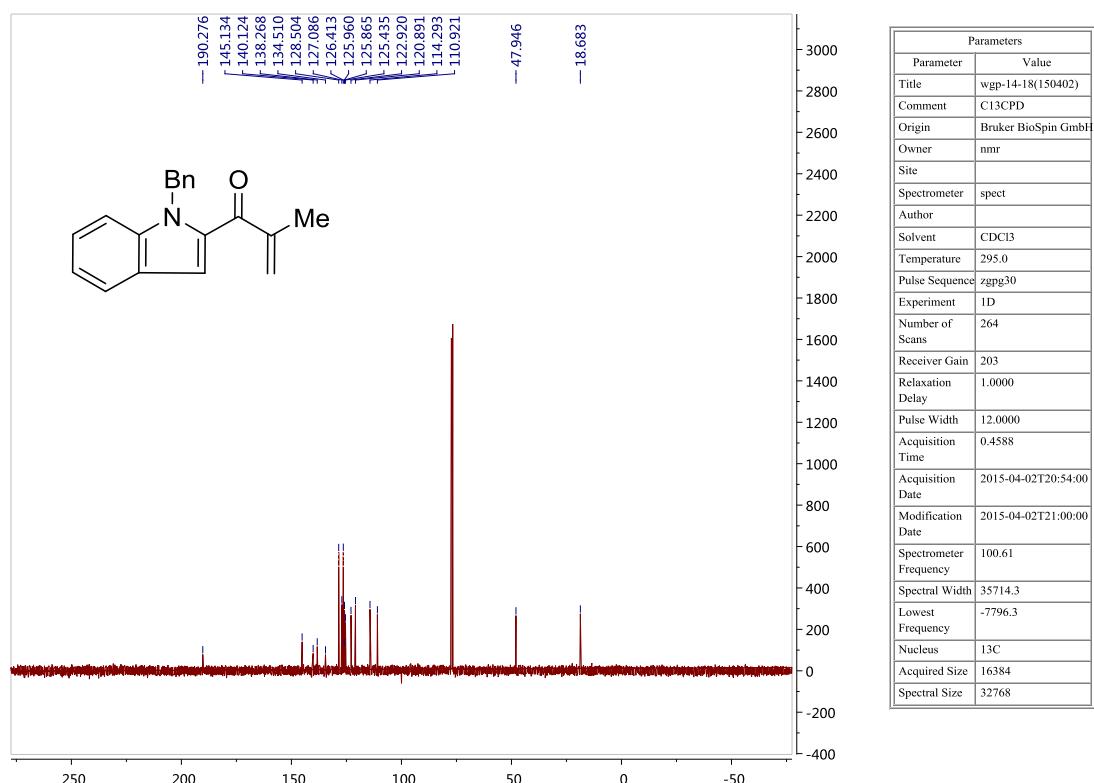
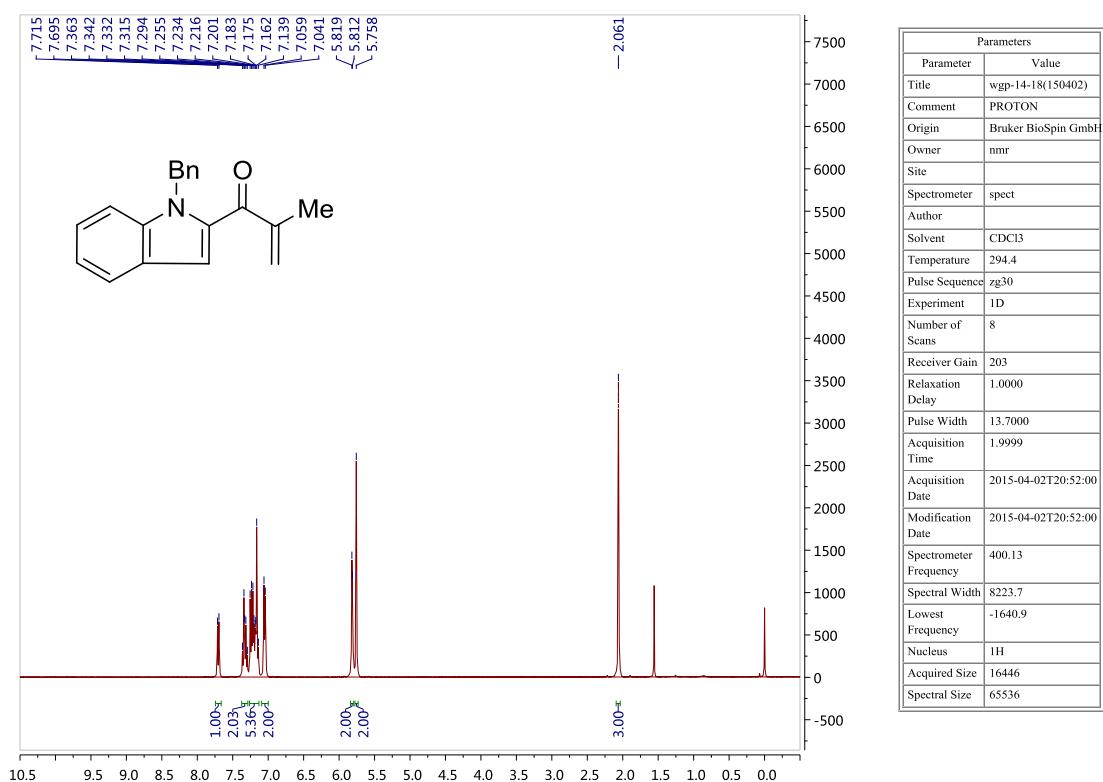
1-(1-isopropyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2b)



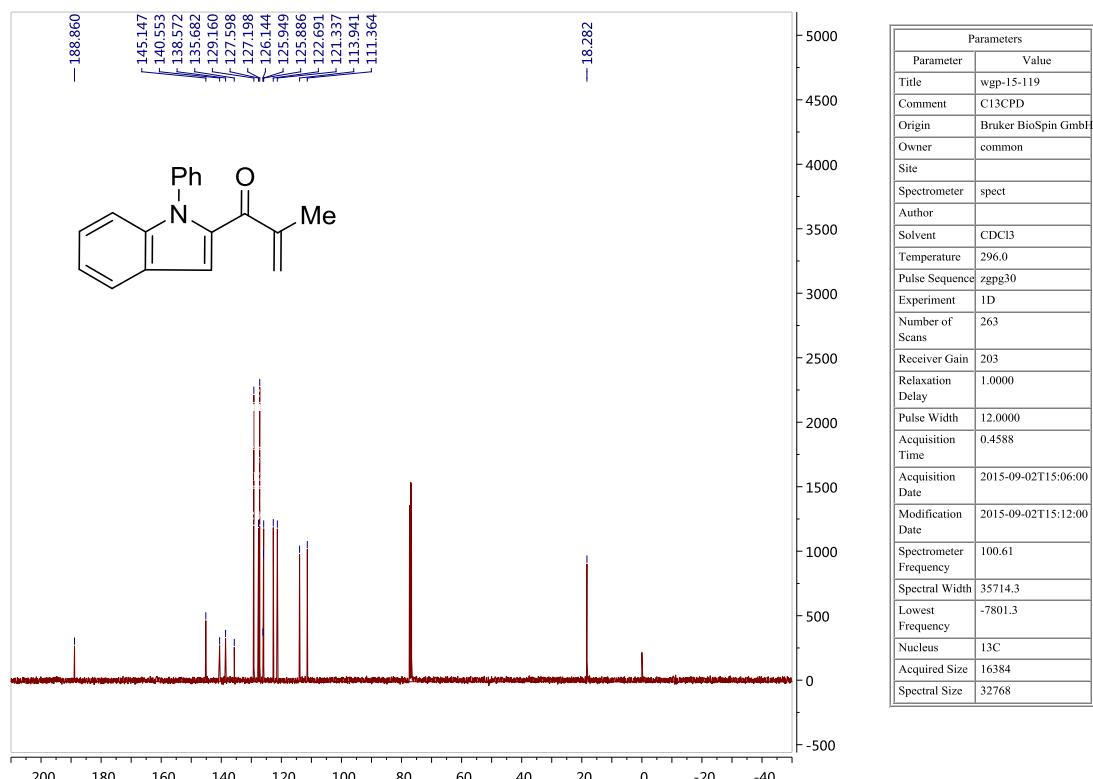
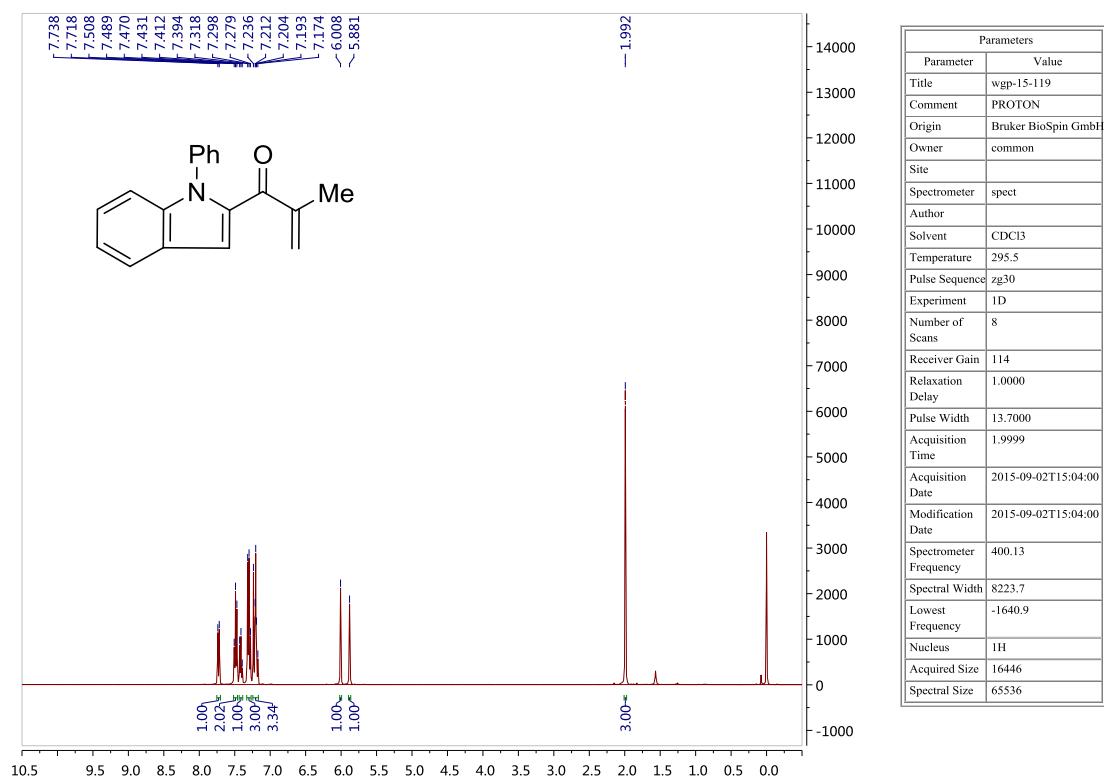
1-(1-allyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2c)



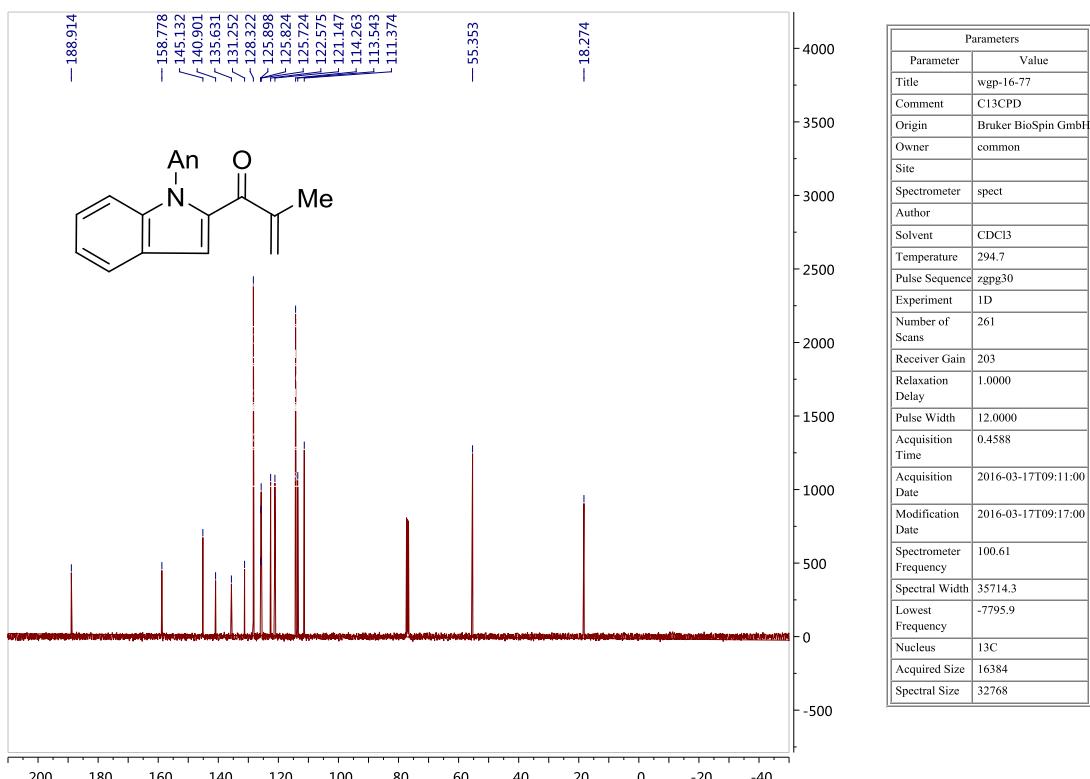
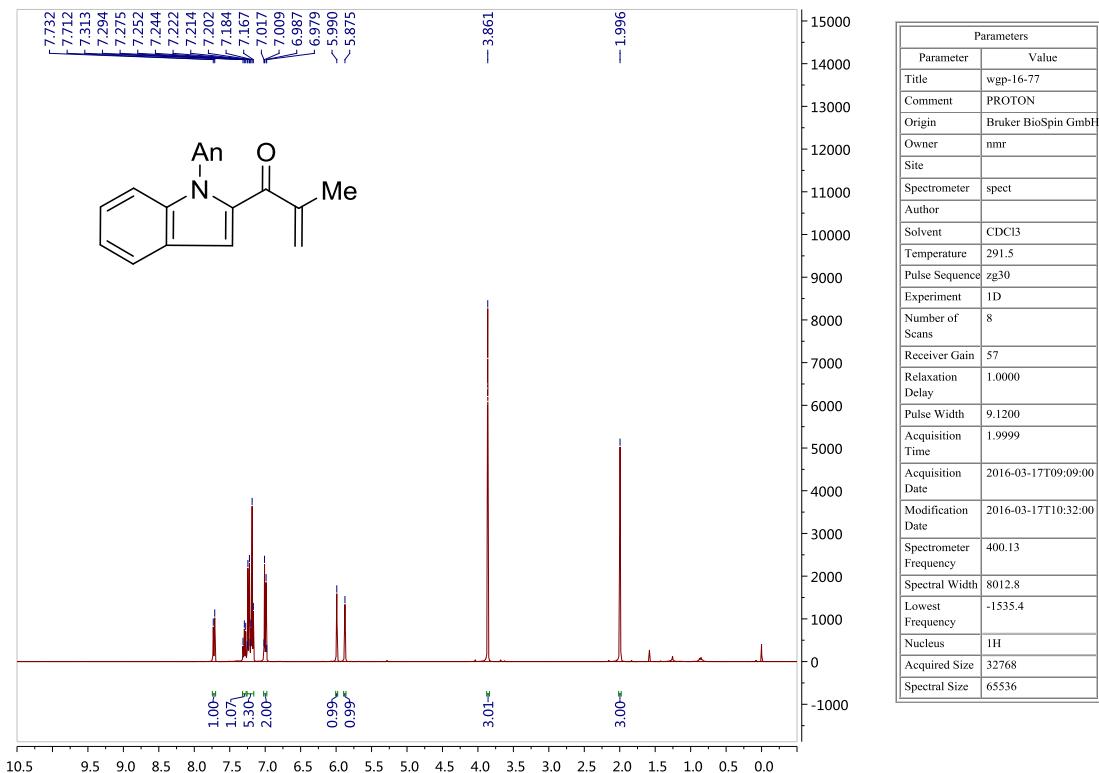
1-(1-benzyl-1H-indol-2-yl)-2-methylprop-2-en-1-one (2d)



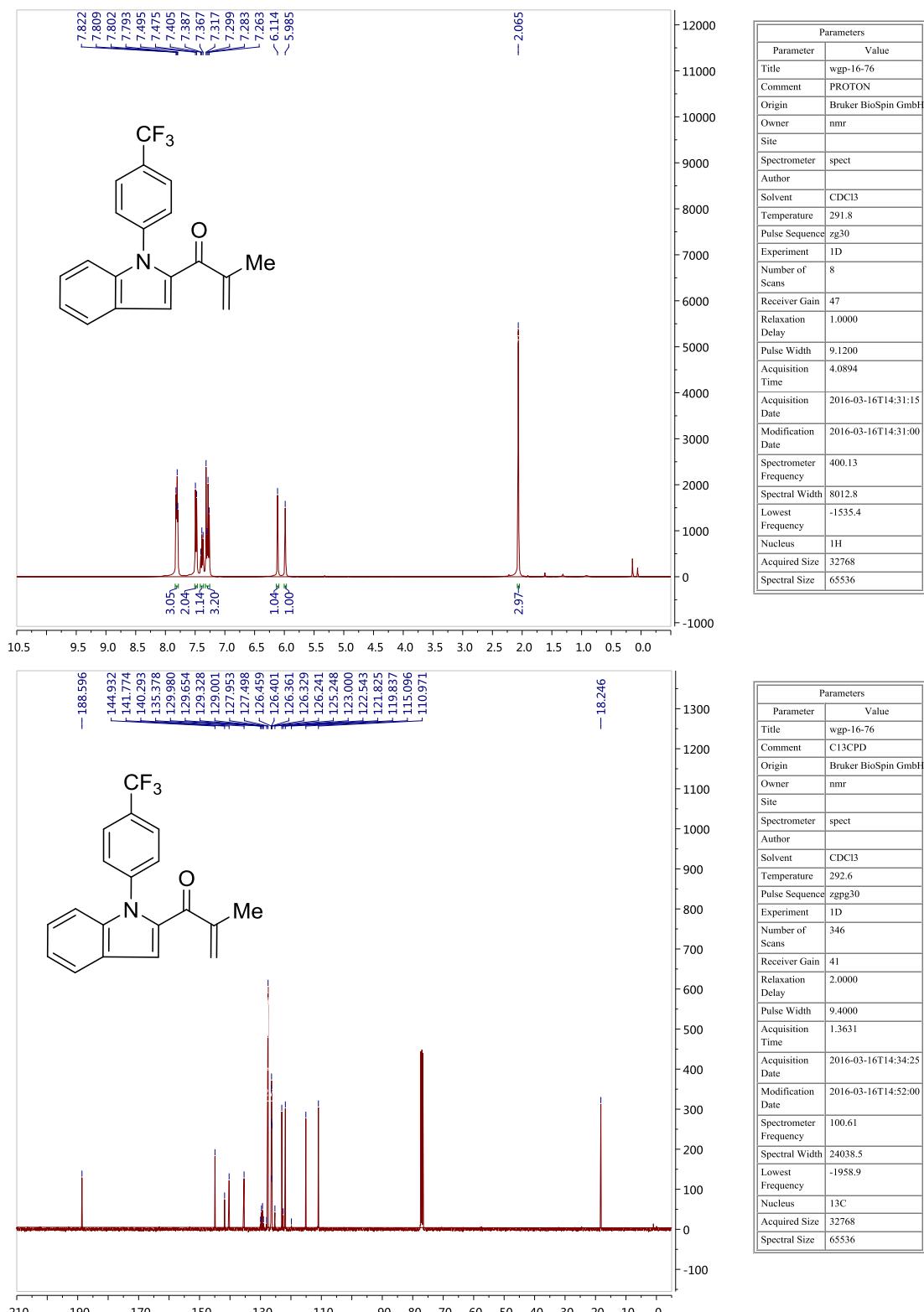
2-methyl-1-(1-phenyl-1H-indol-2-yl)prop-2-en-1-one (2e)



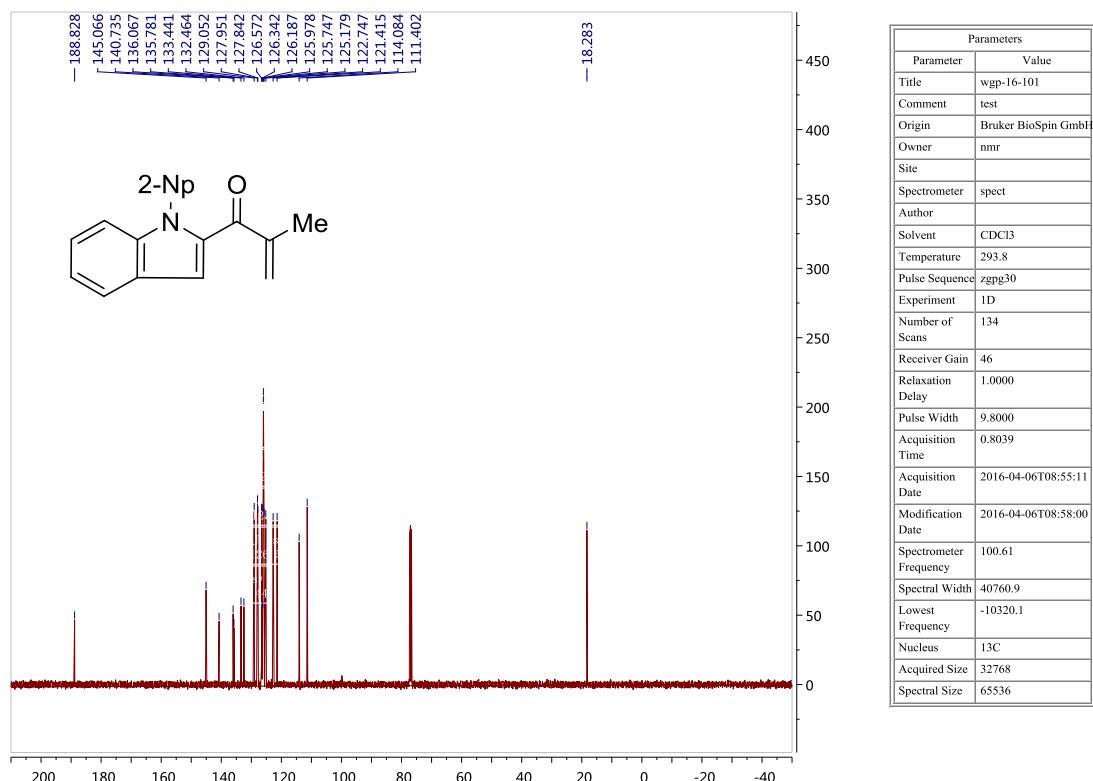
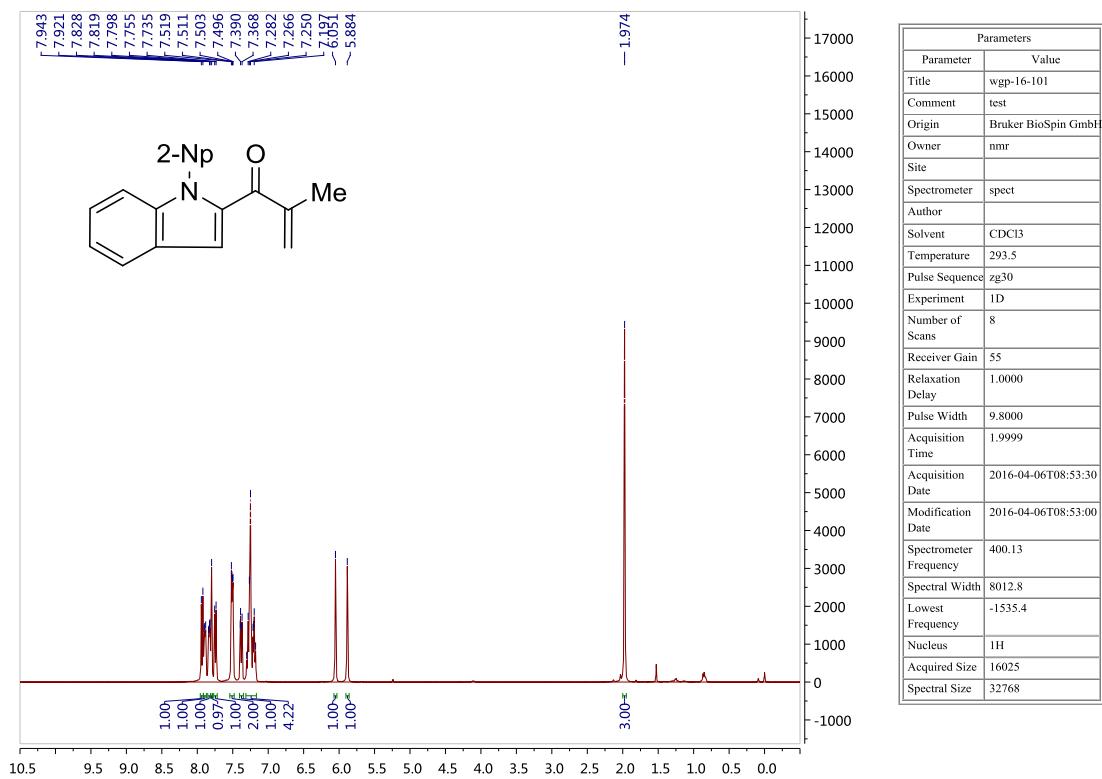
1-(1-(4-methoxyphenyl)-1H-indol-2-yl)-2-methylprop-2-en-1-one (2f)



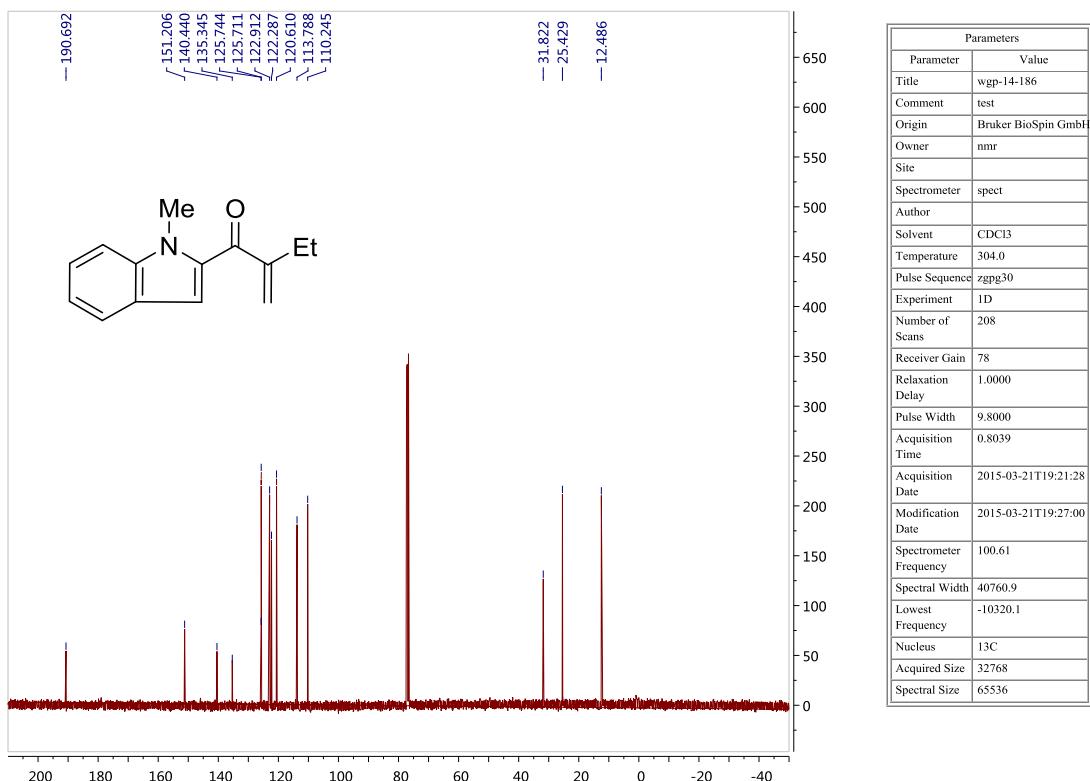
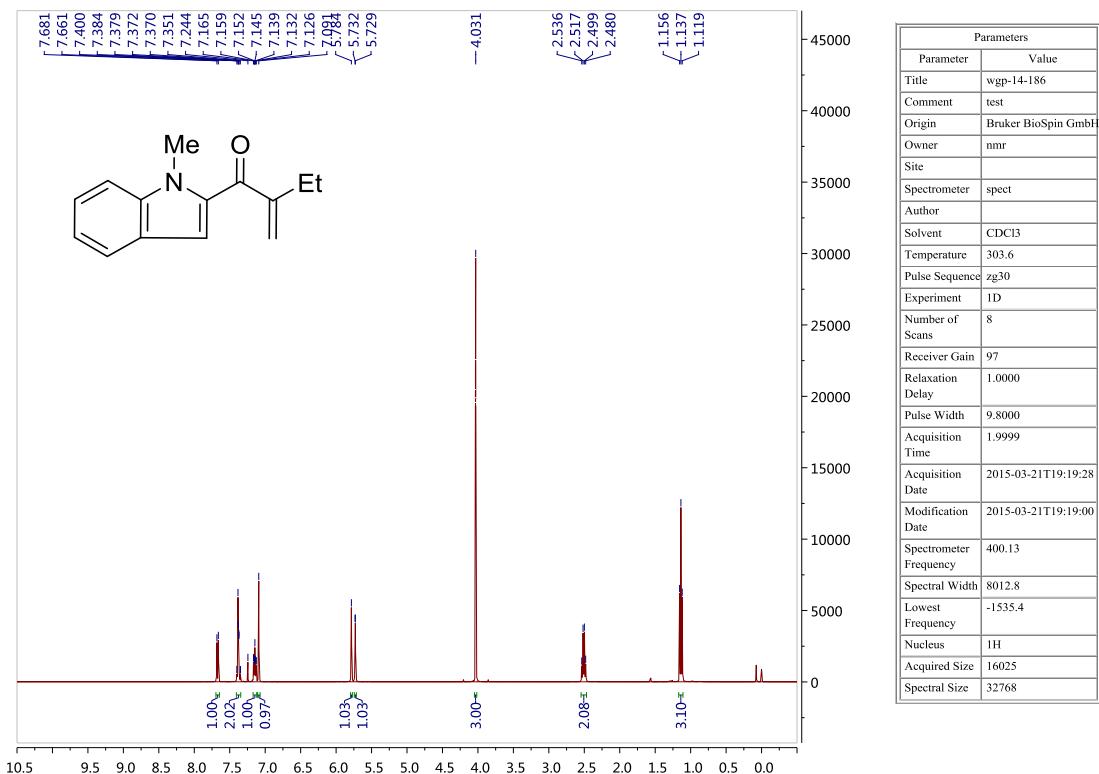
2-methyl-1-(1-(4-(trifluoromethyl)phenyl)-1H-indol-2-yl)prop-2-en-1-one (2g)



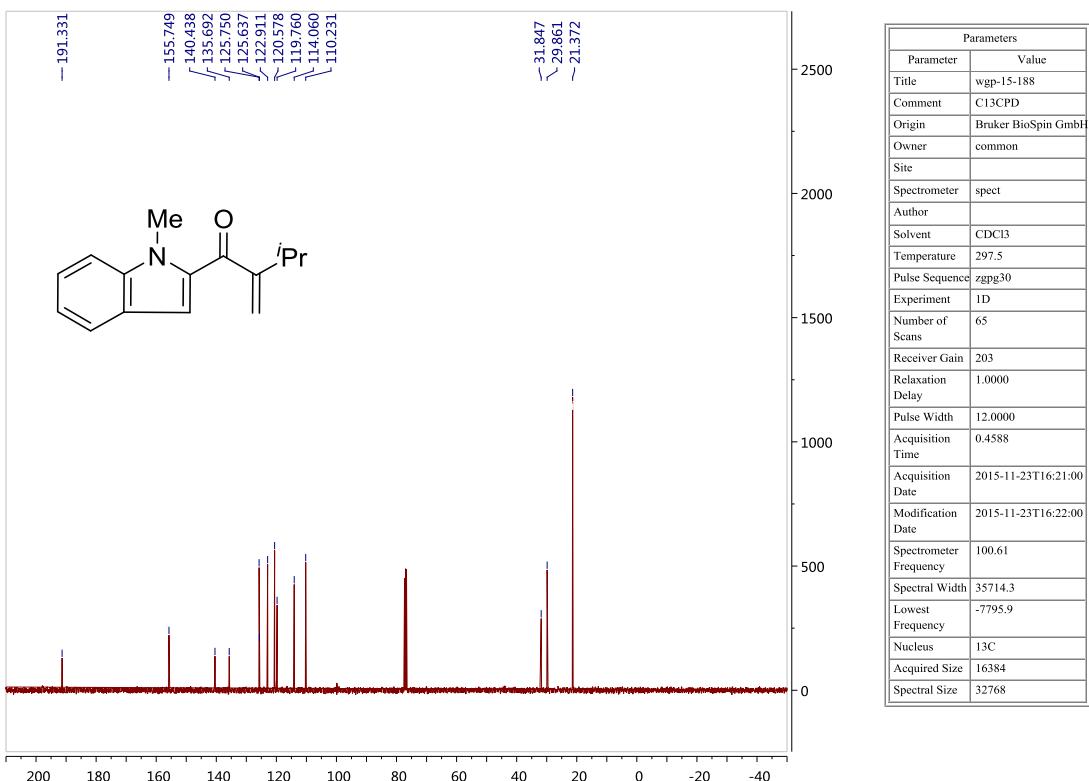
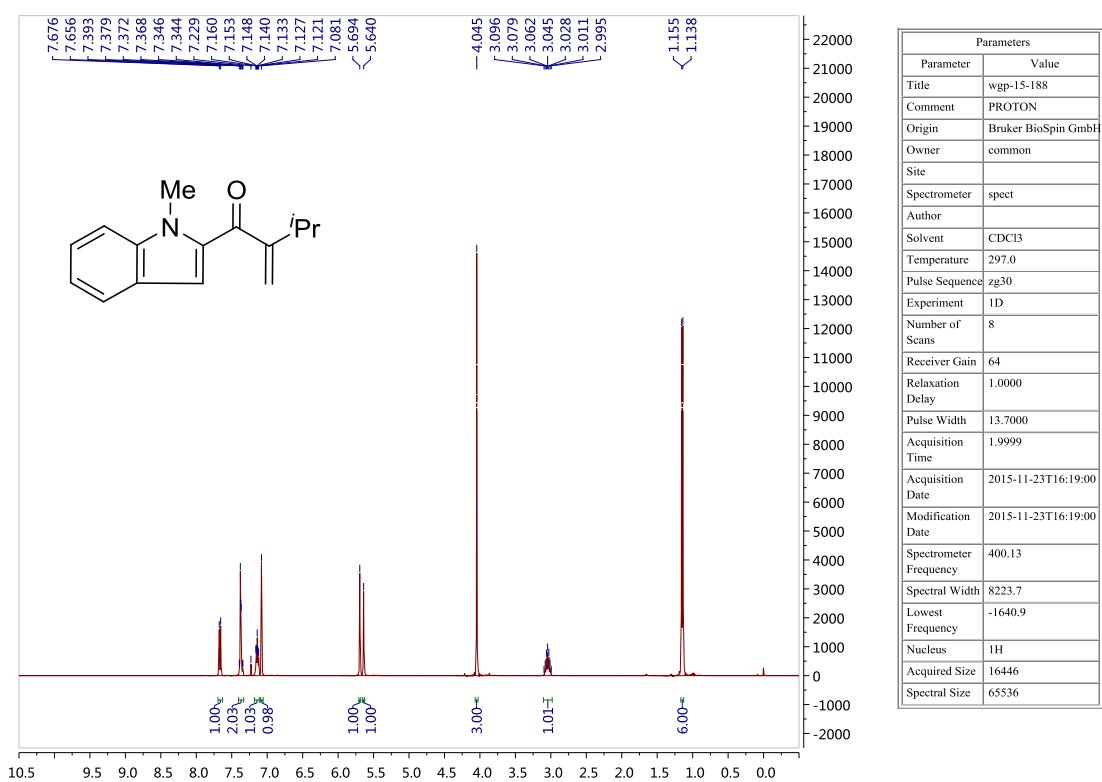
2-methyl-1-(1-(naphthalen-2-yl)-1H-indol-2-yl)prop-2-en-1-one (2h)



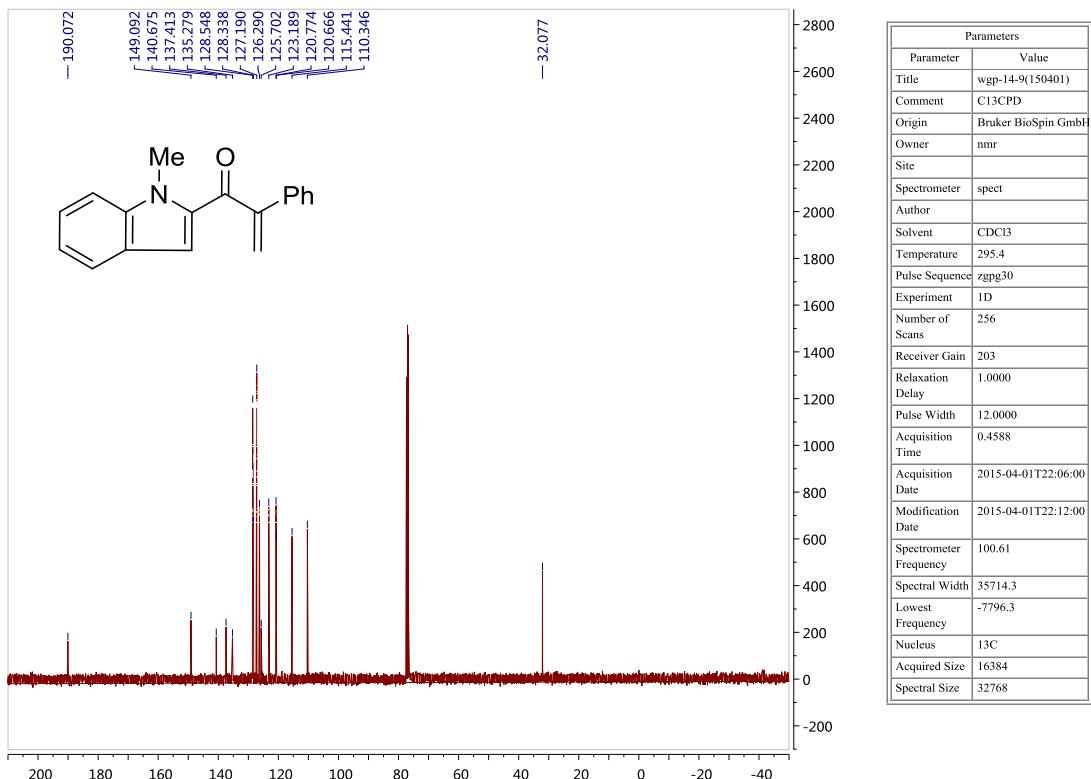
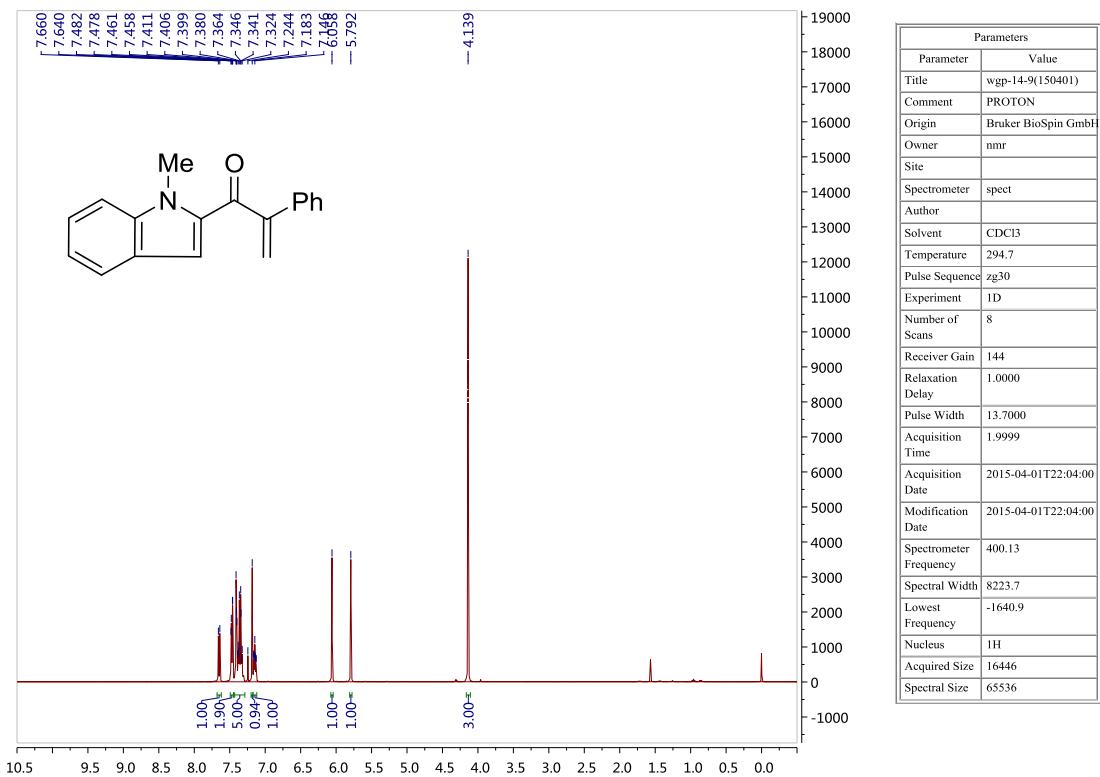
1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-one (2i)



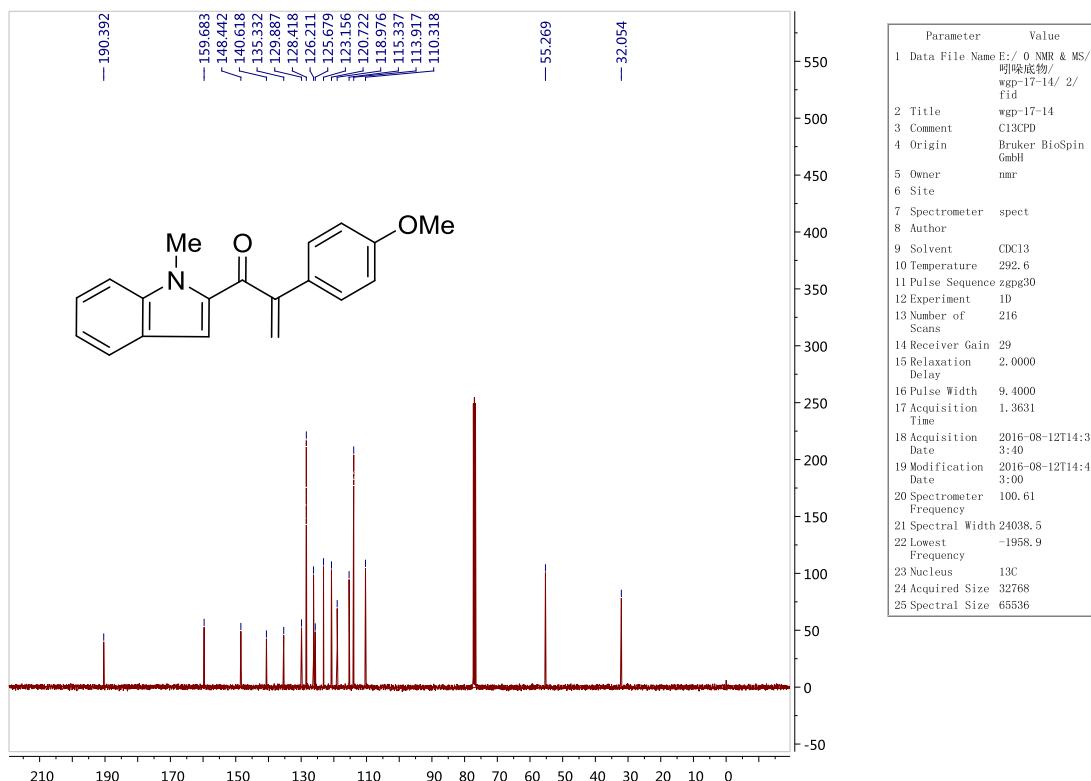
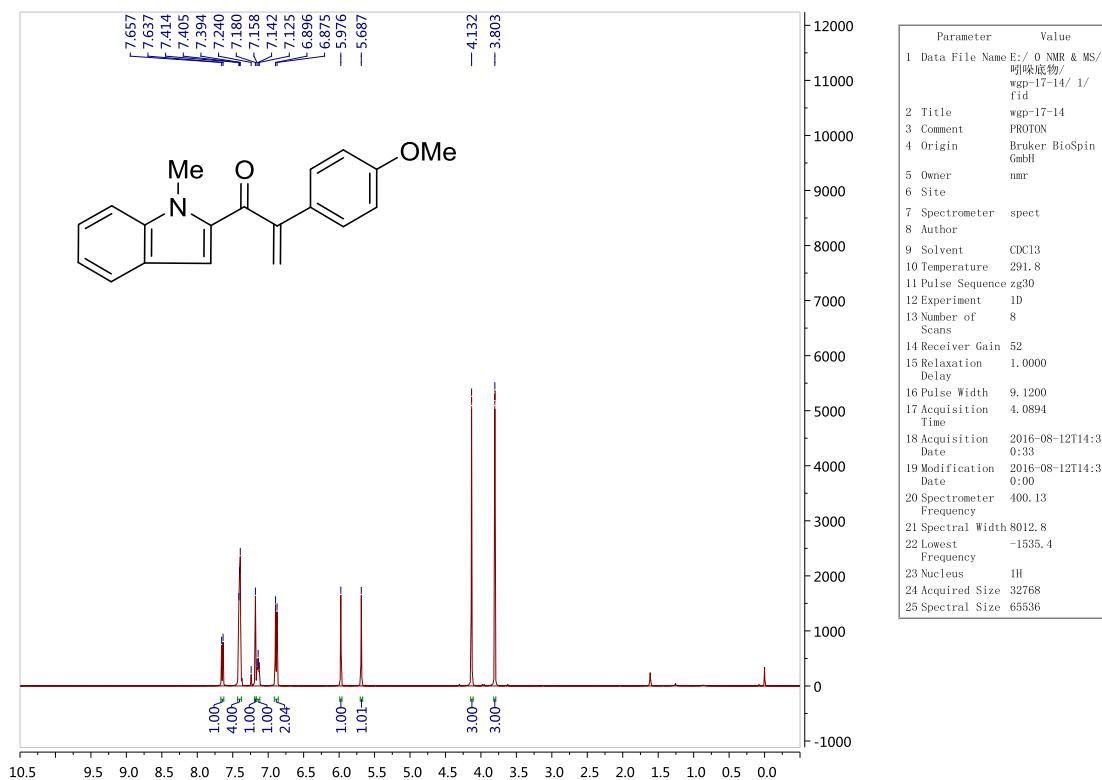
3-methyl-1-(1-methyl-1H-indol-2-yl)-2-methylenebutan-1-one (2j)



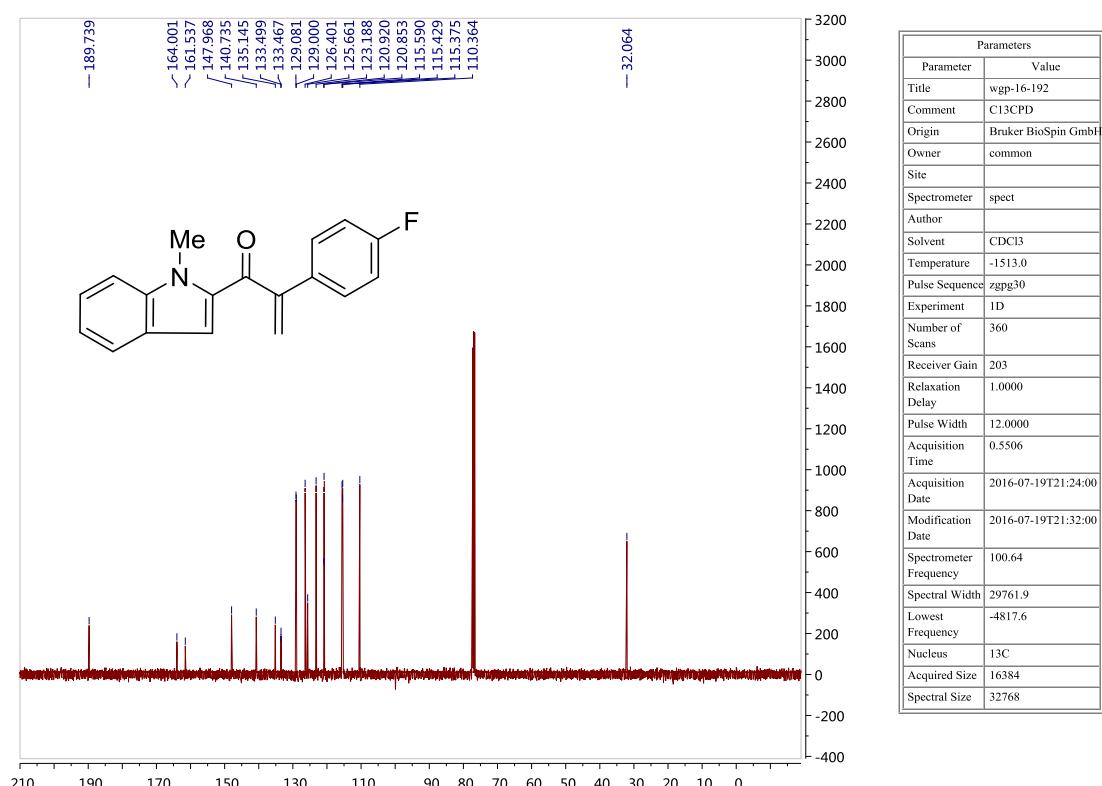
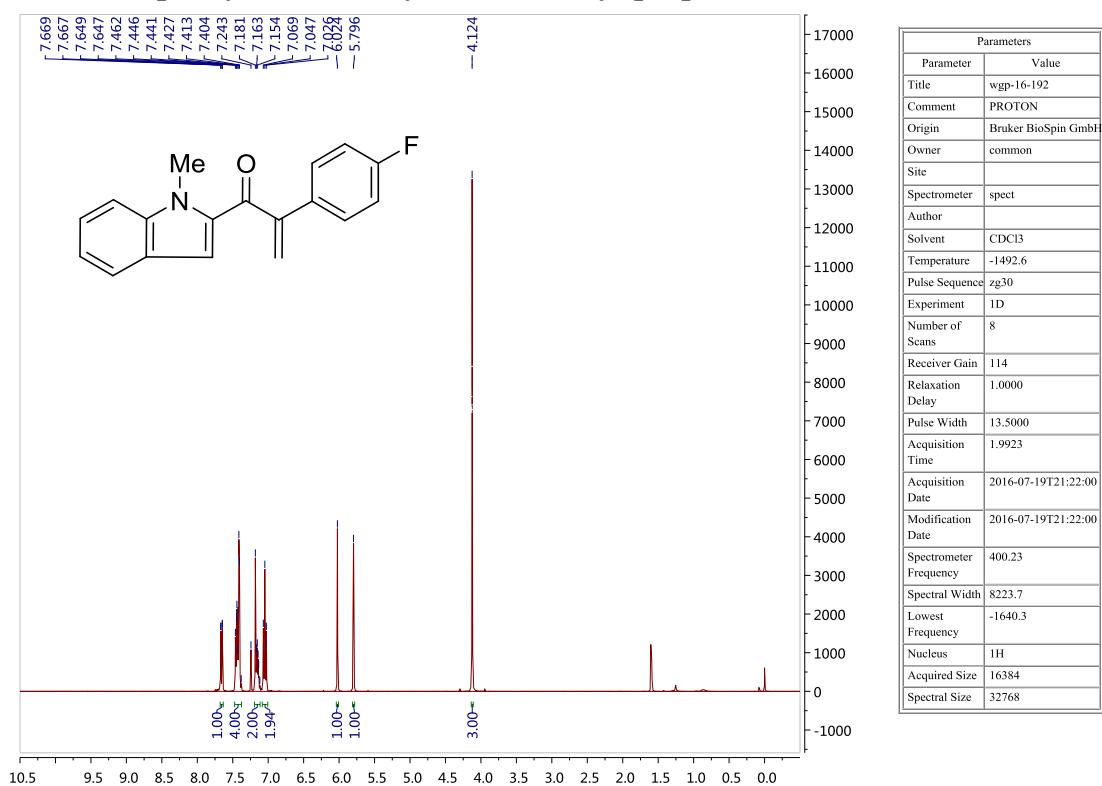
1-(1-methyl-1H-indol-2-yl)-2-phenylprop-2-en-1-one (2k)



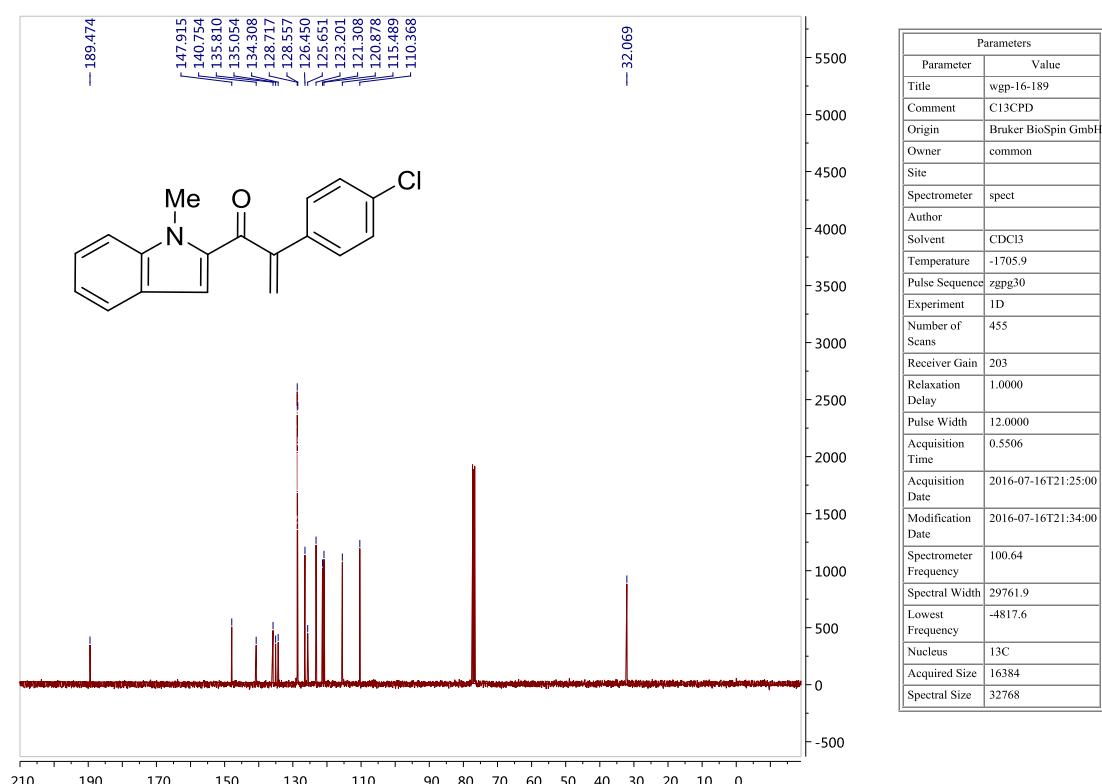
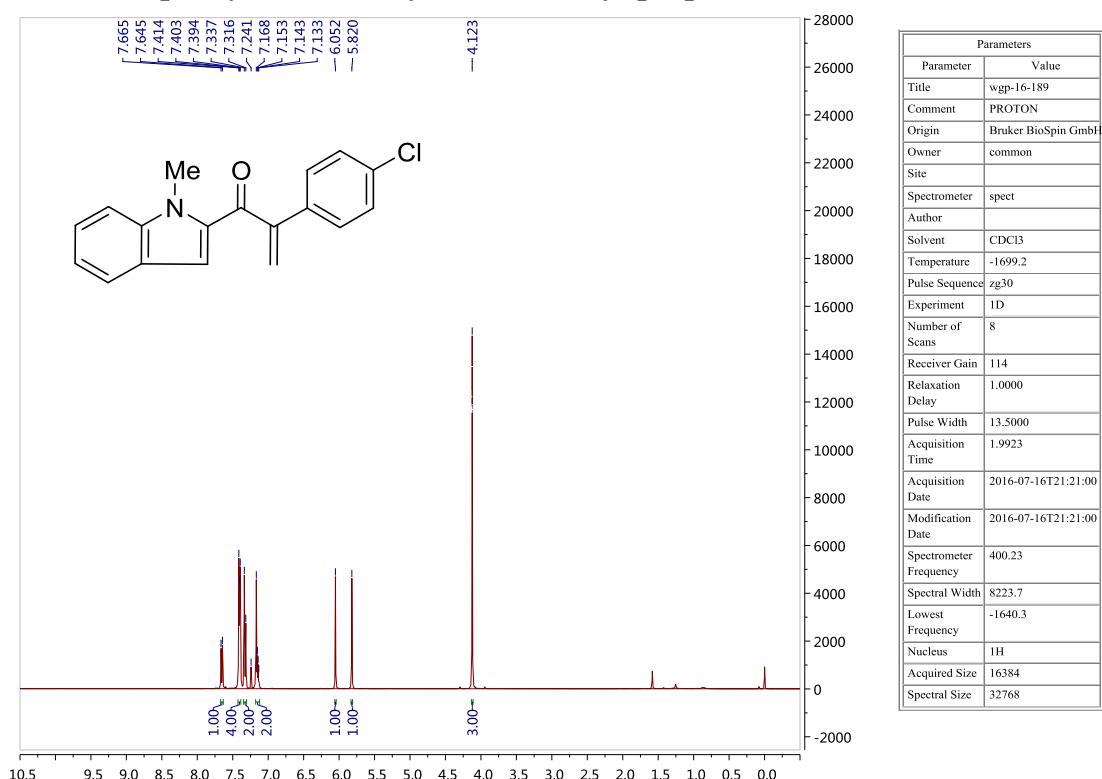
2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2l)



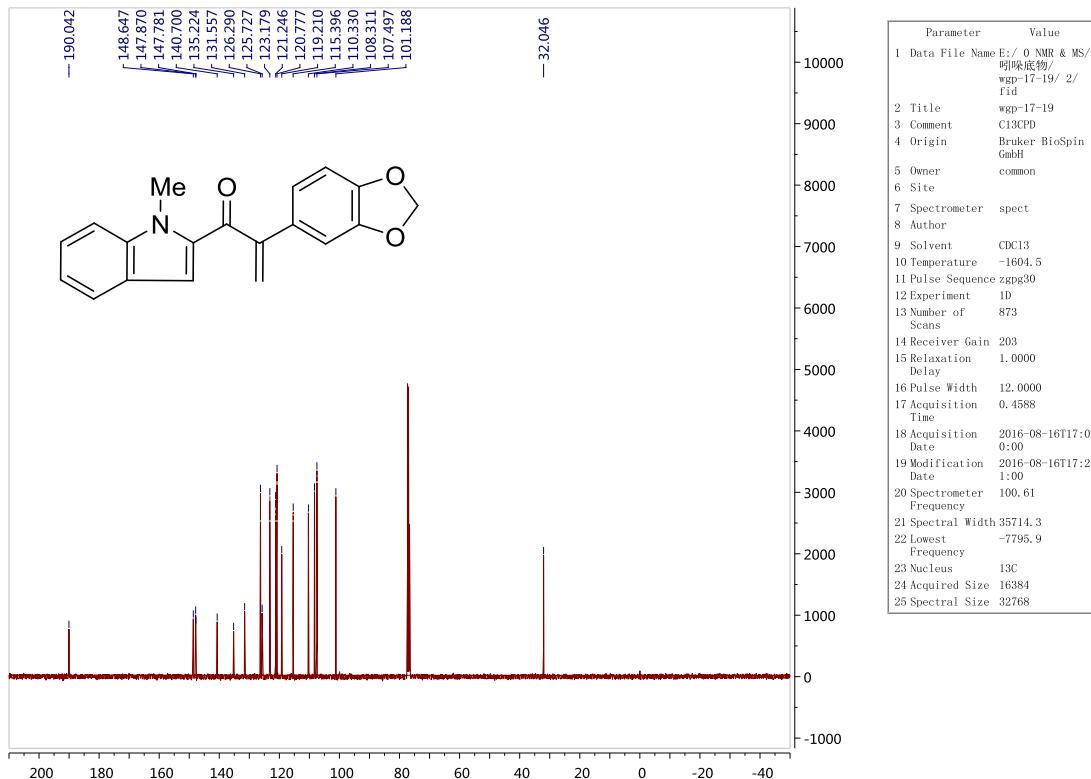
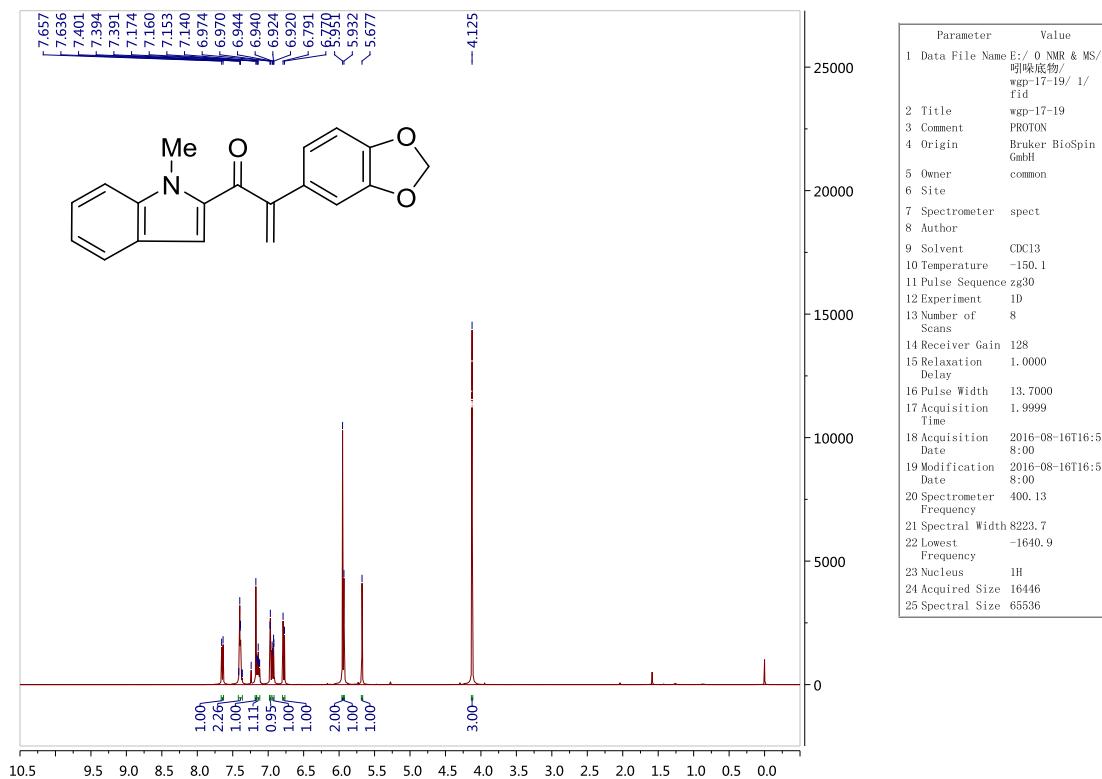
2-(4-fluorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2m)



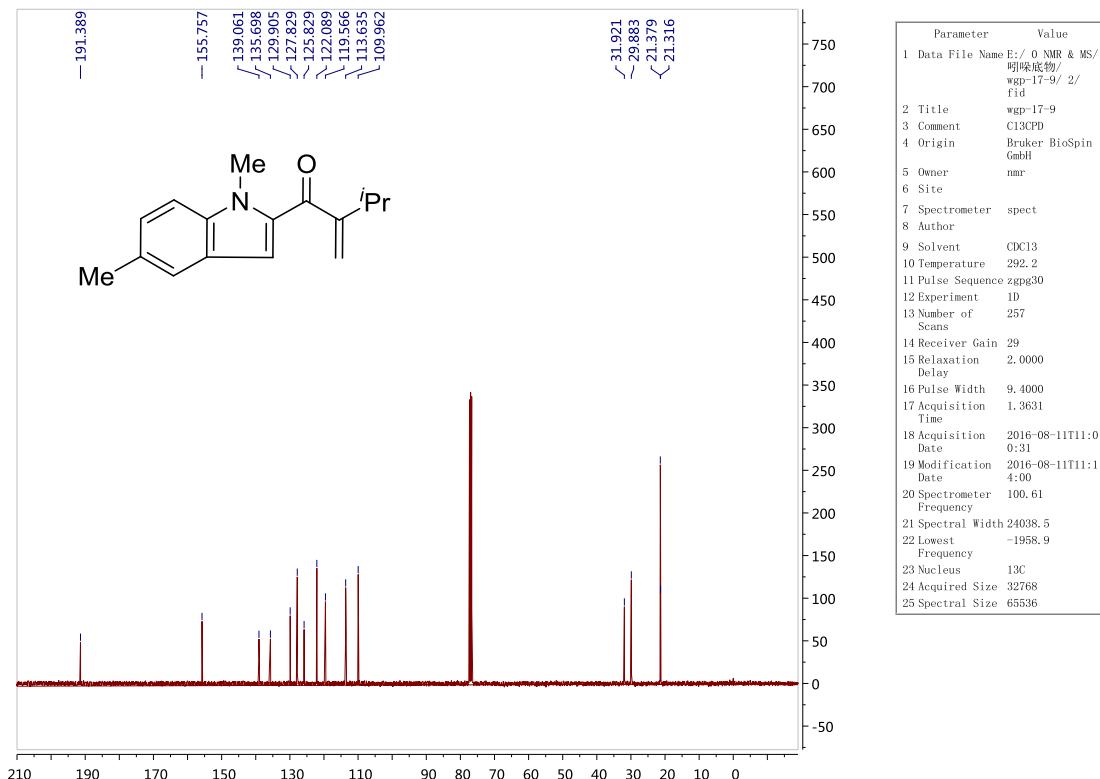
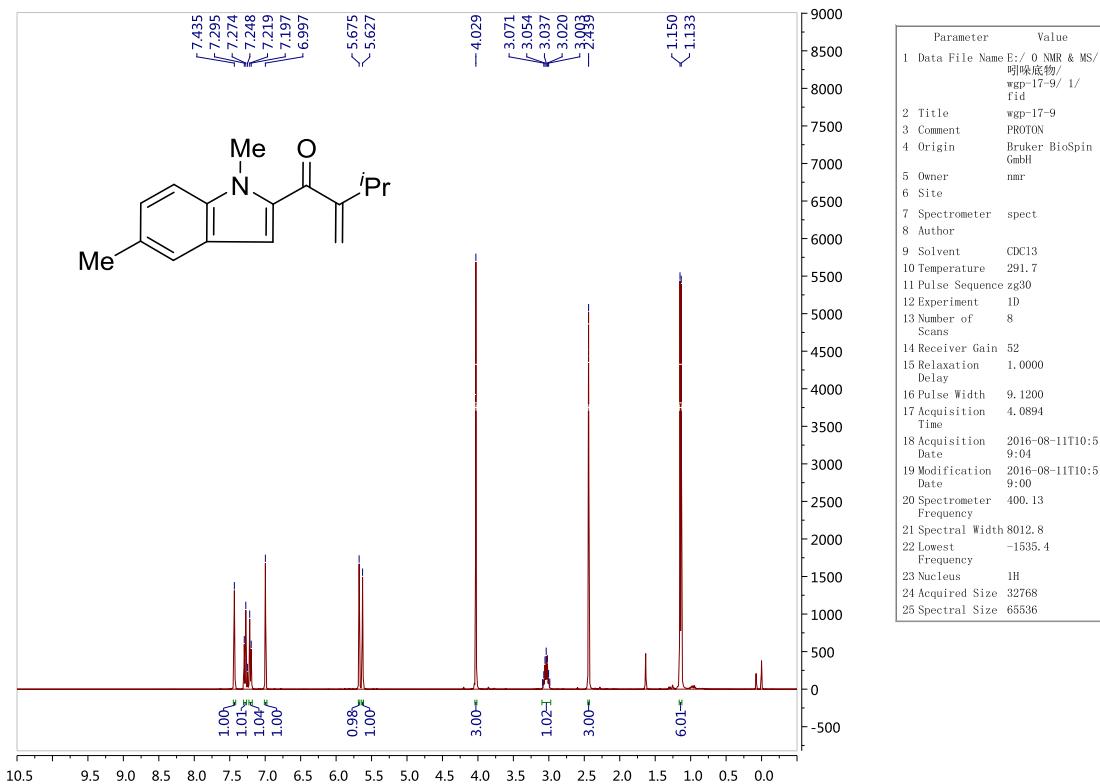
2-(4-chlorophenyl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2n)



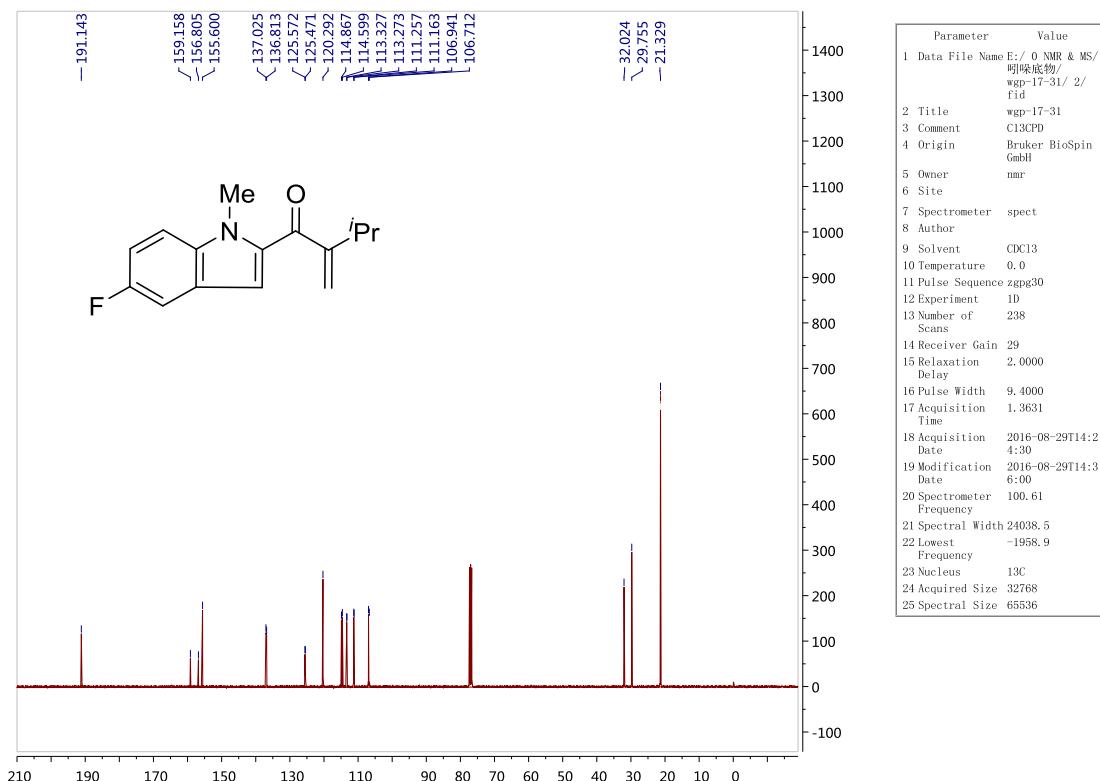
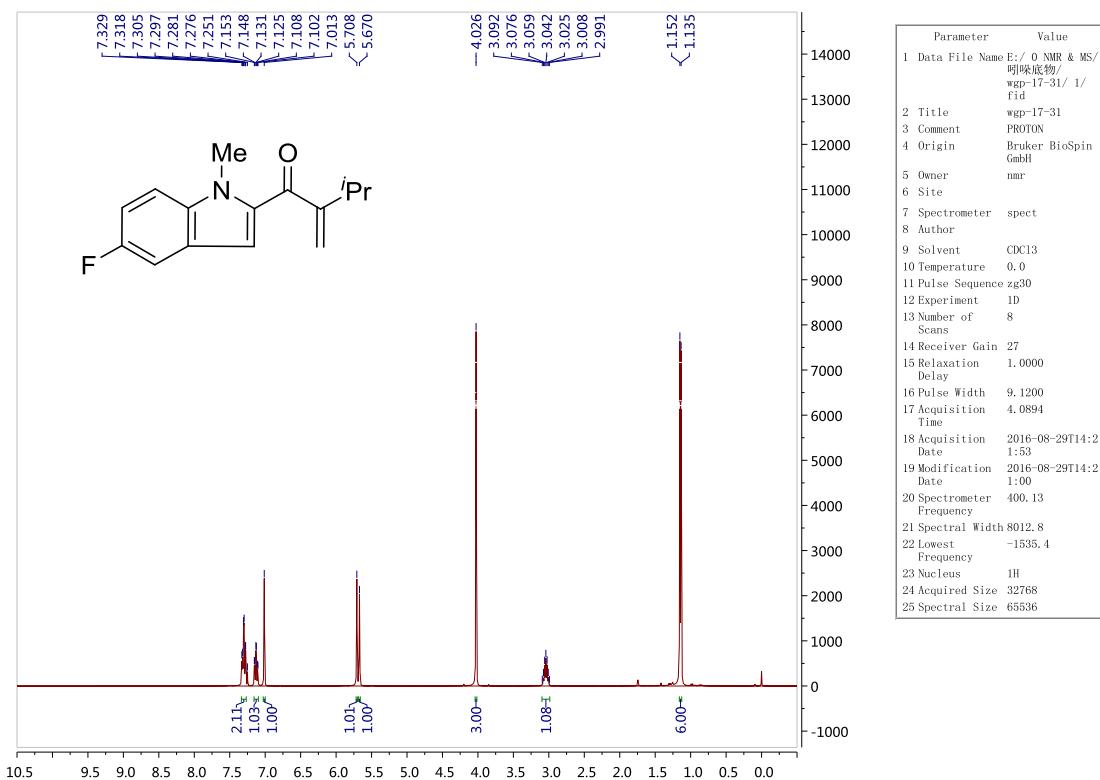
2-(benzo[d][1,3]dioxol-5-yl)-1-(1-methyl-1H-indol-2-yl)prop-2-en-1-one (2o)



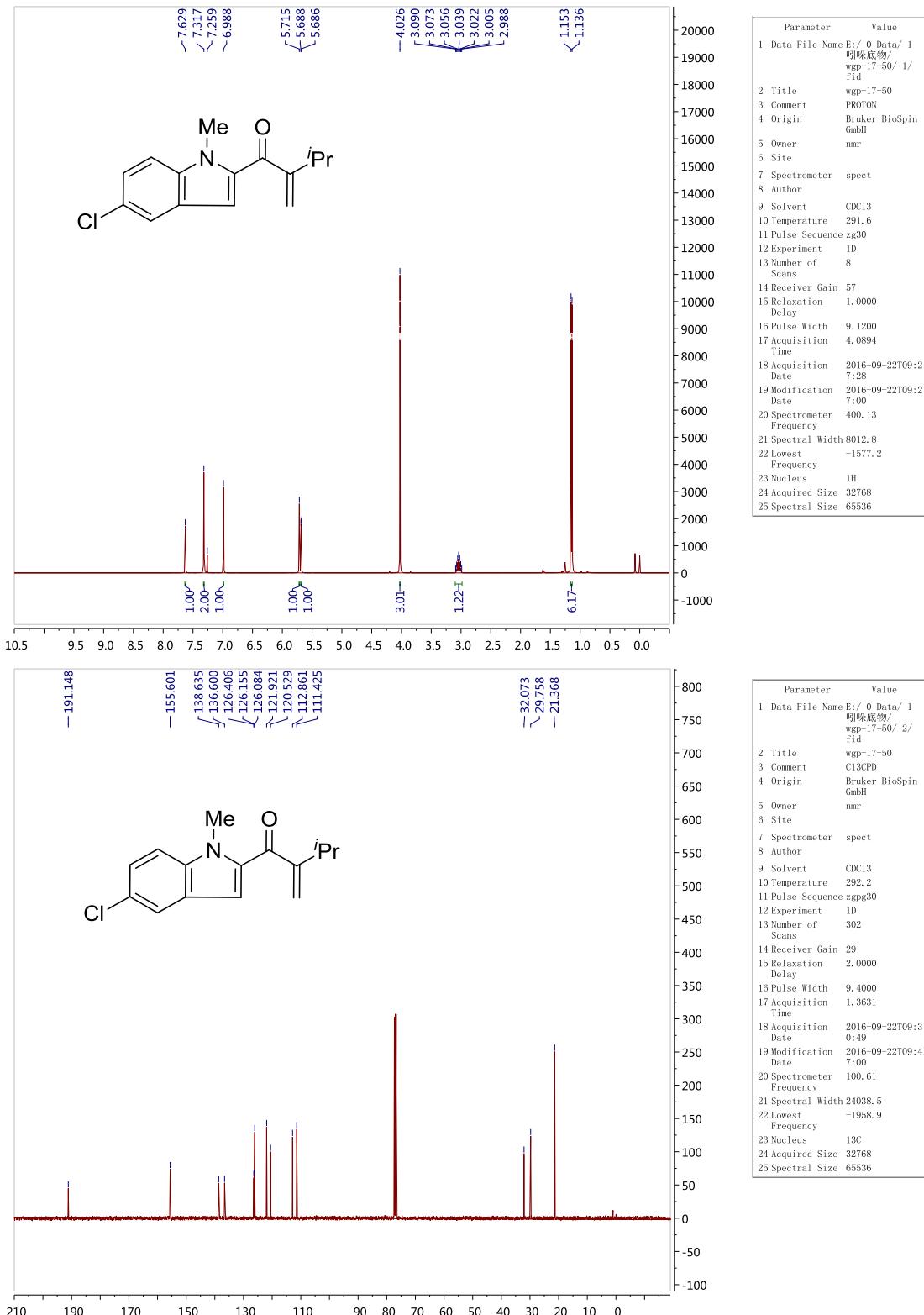
1-(1,5-dimethyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2p)



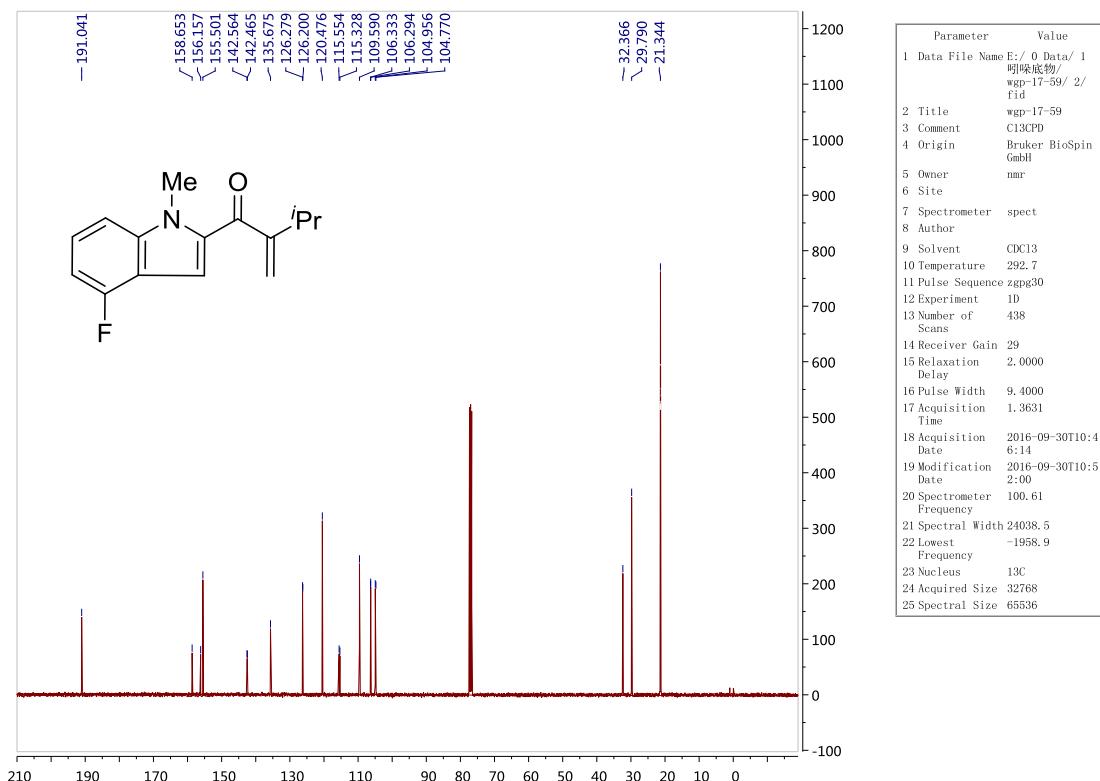
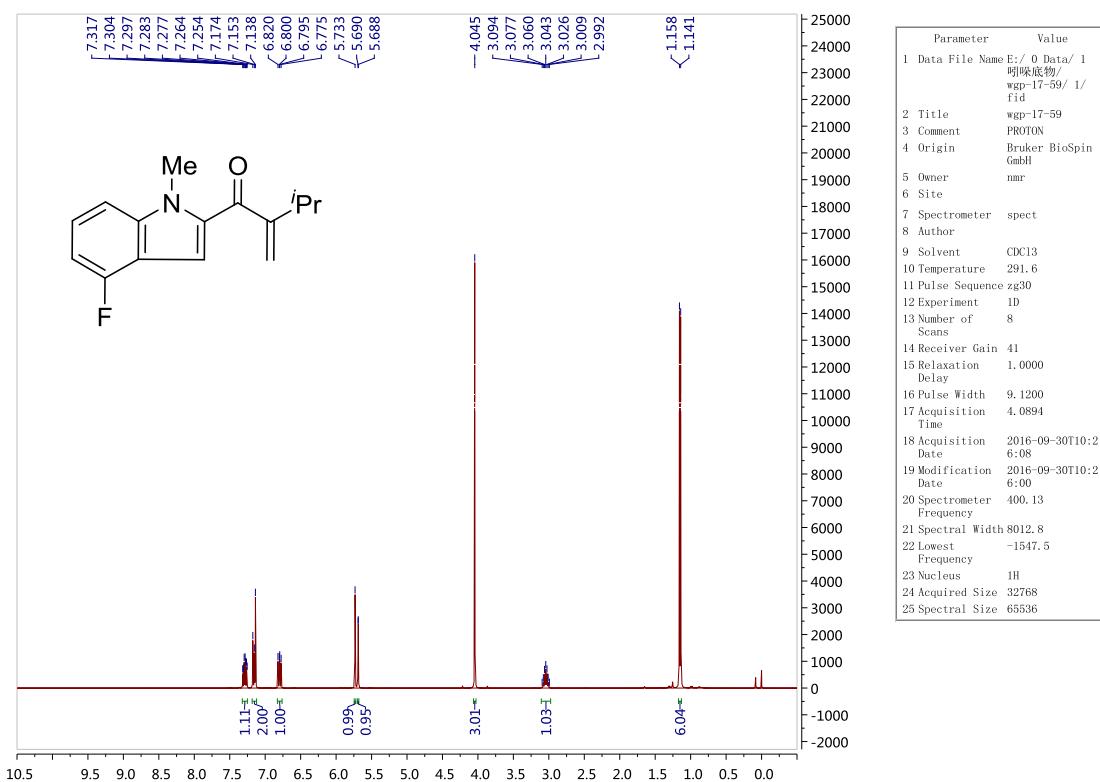
1-(5-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2q)



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



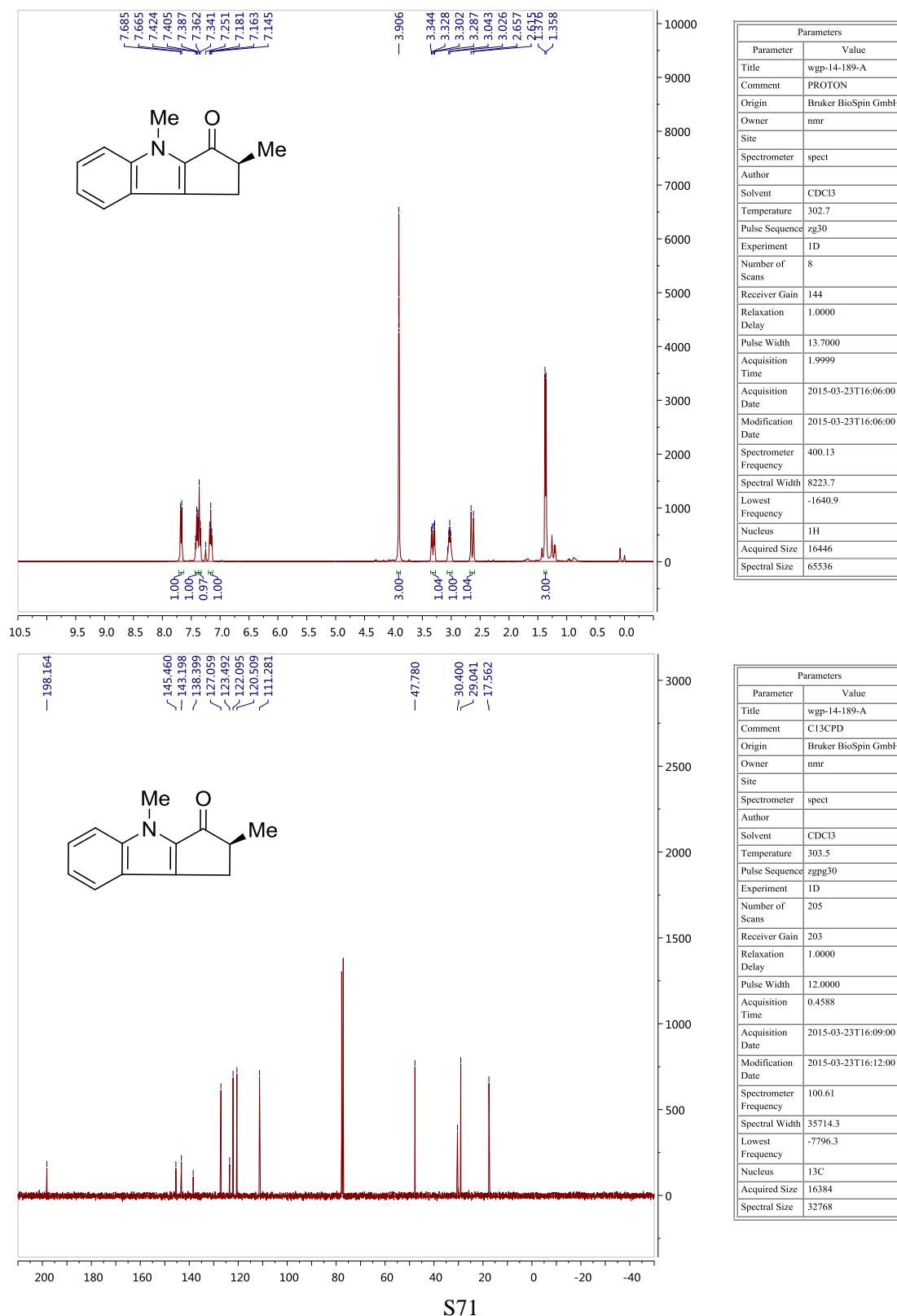
1-(4-fluoro-1-methyl-1H-indol-2-yl)-3-methyl-2-methylenebutan-1-one (2s)



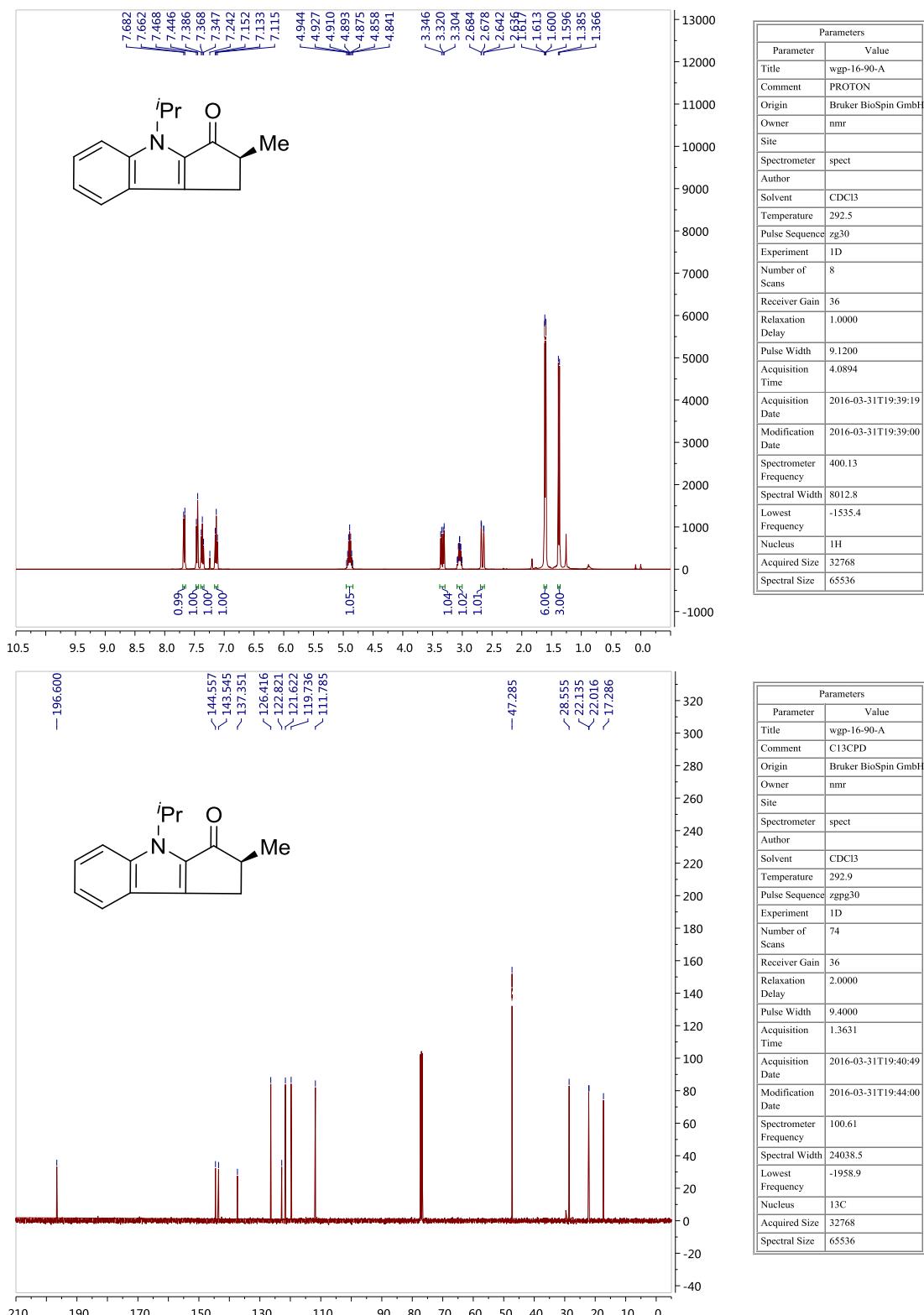
8. NMR Spectra of Cyclization Products and Transformation

Product

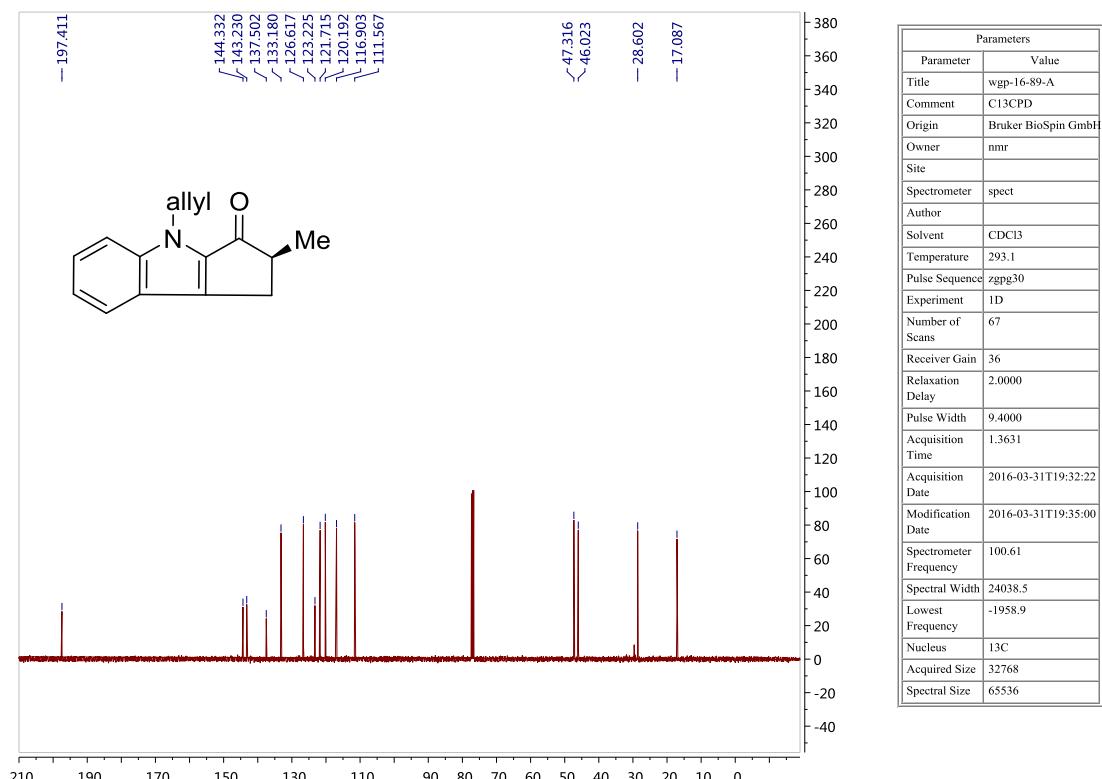
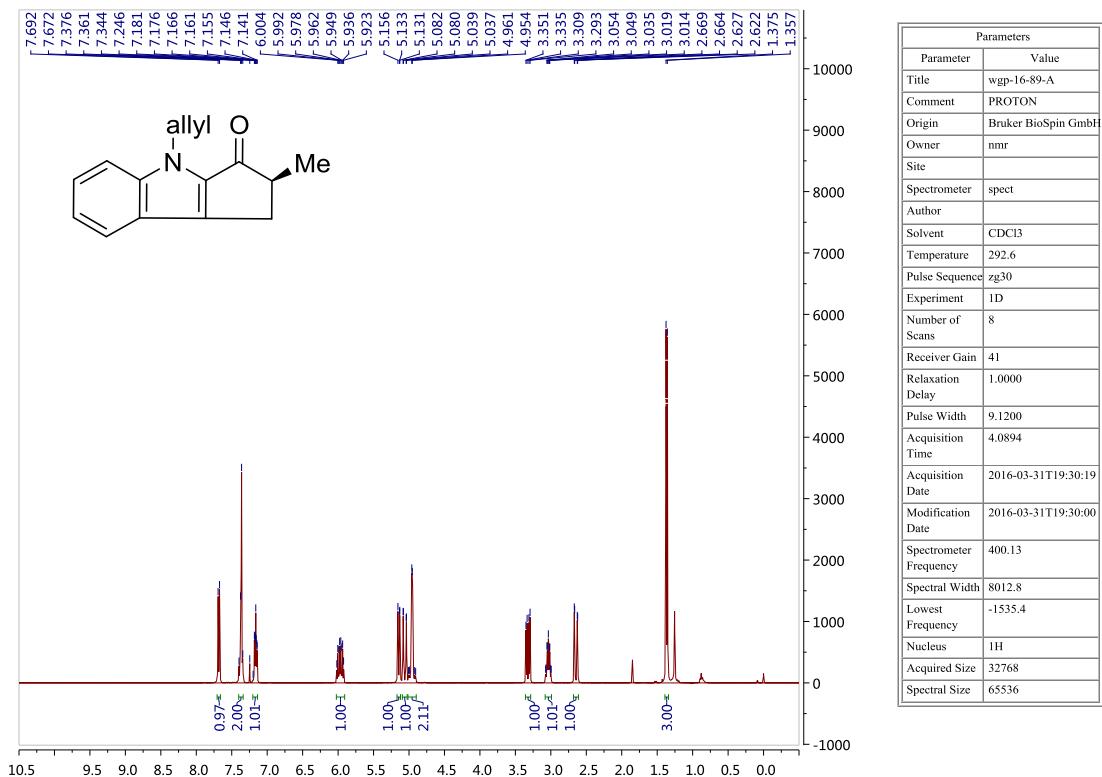
(+)-2,4-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3a)



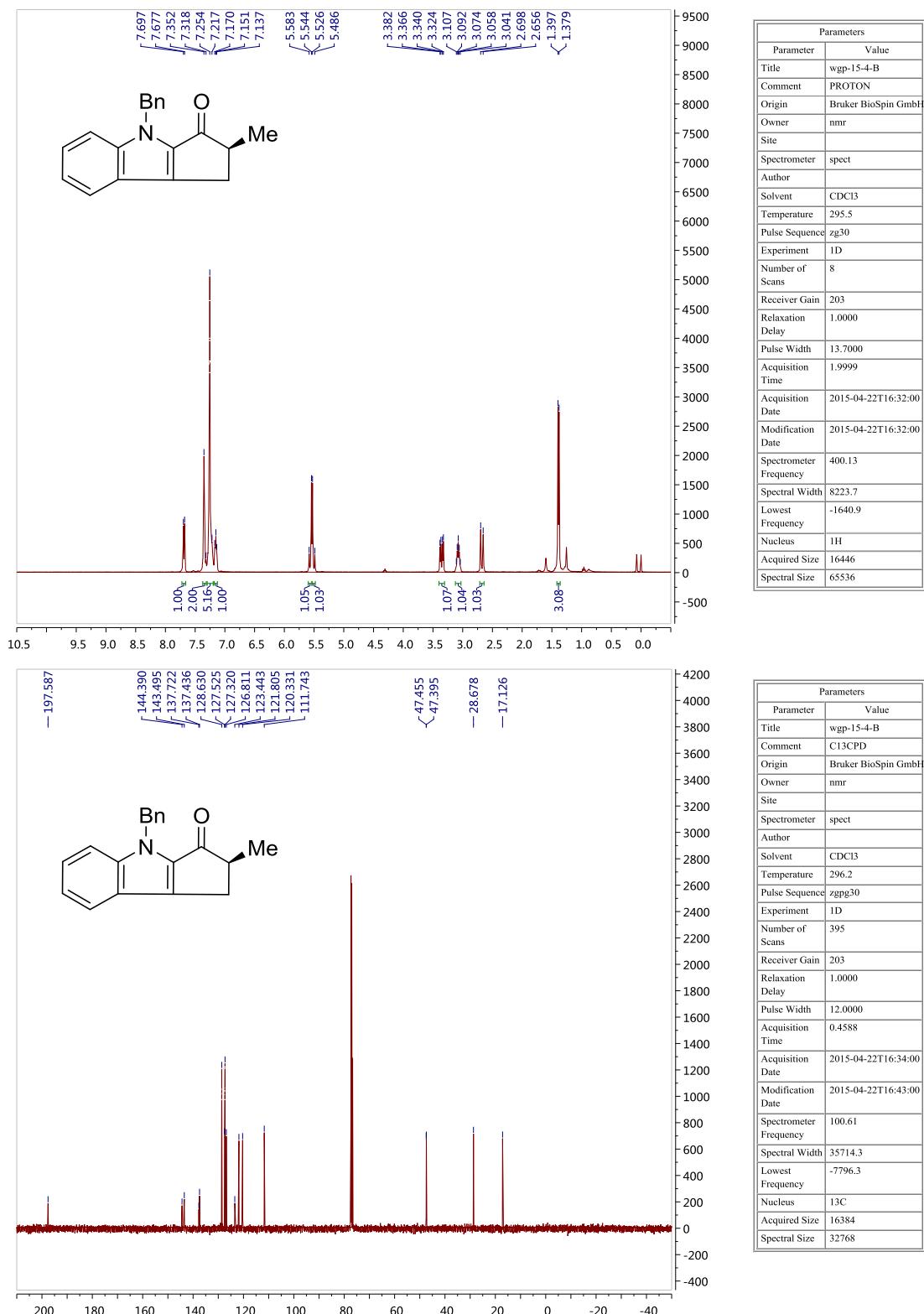
(+)-4-isopropyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3b)



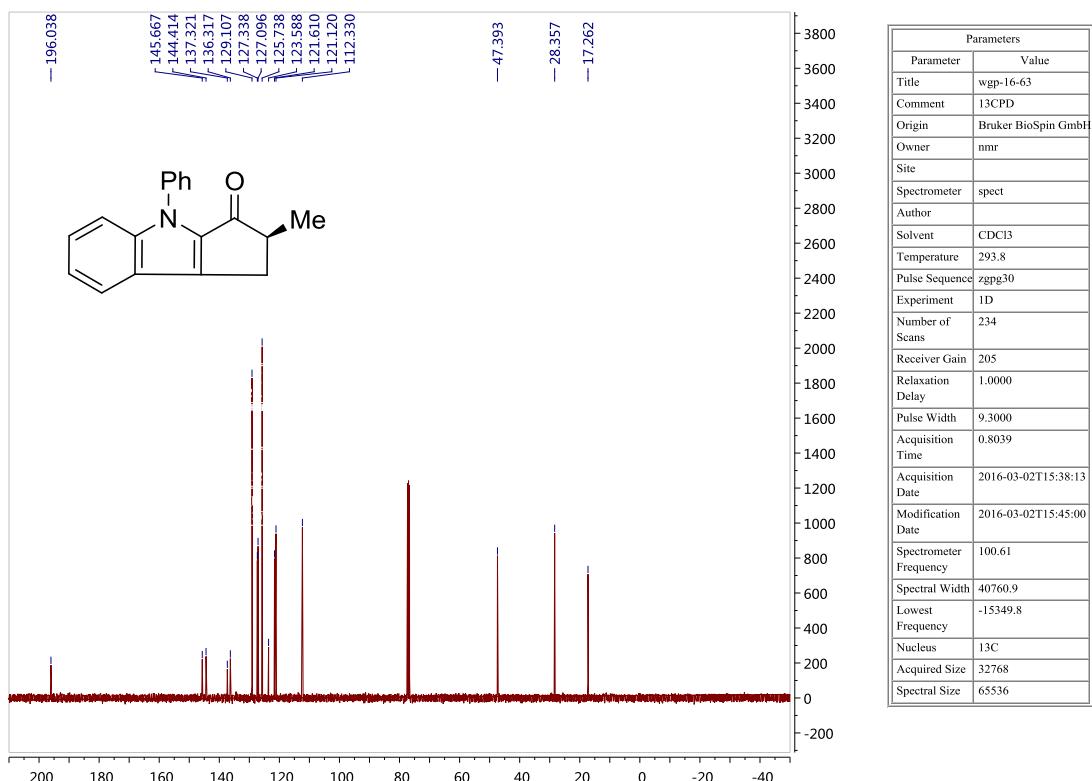
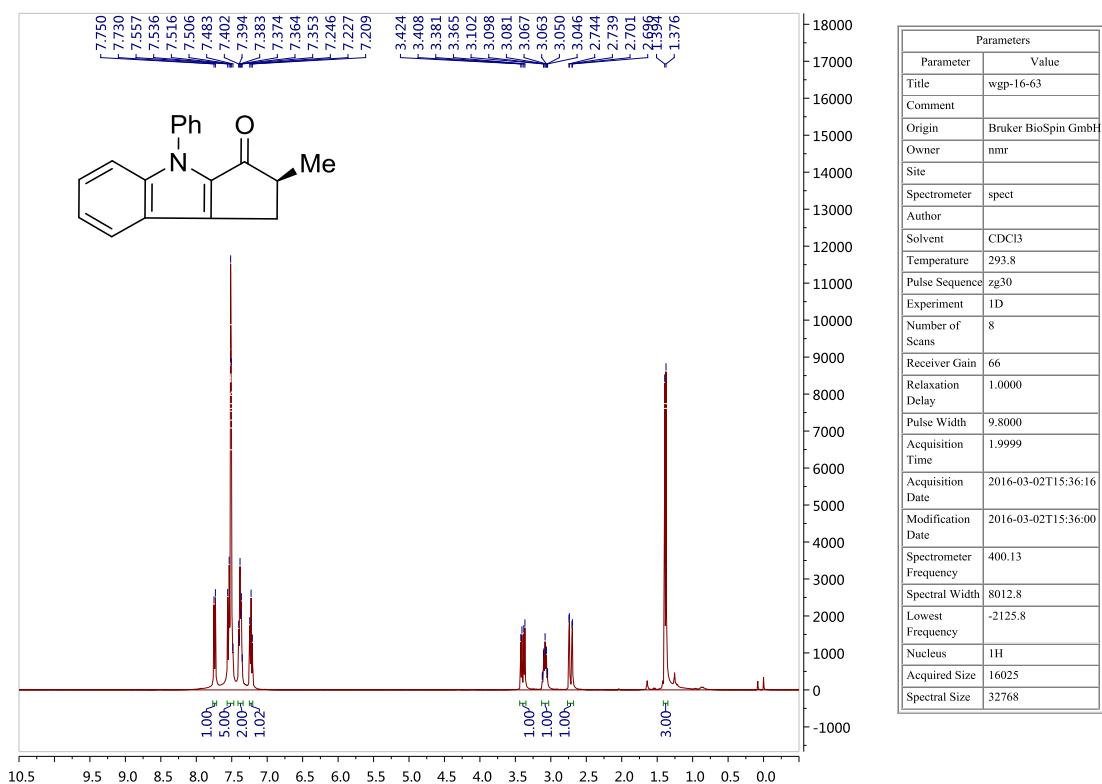
(+)-4-allyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3c)



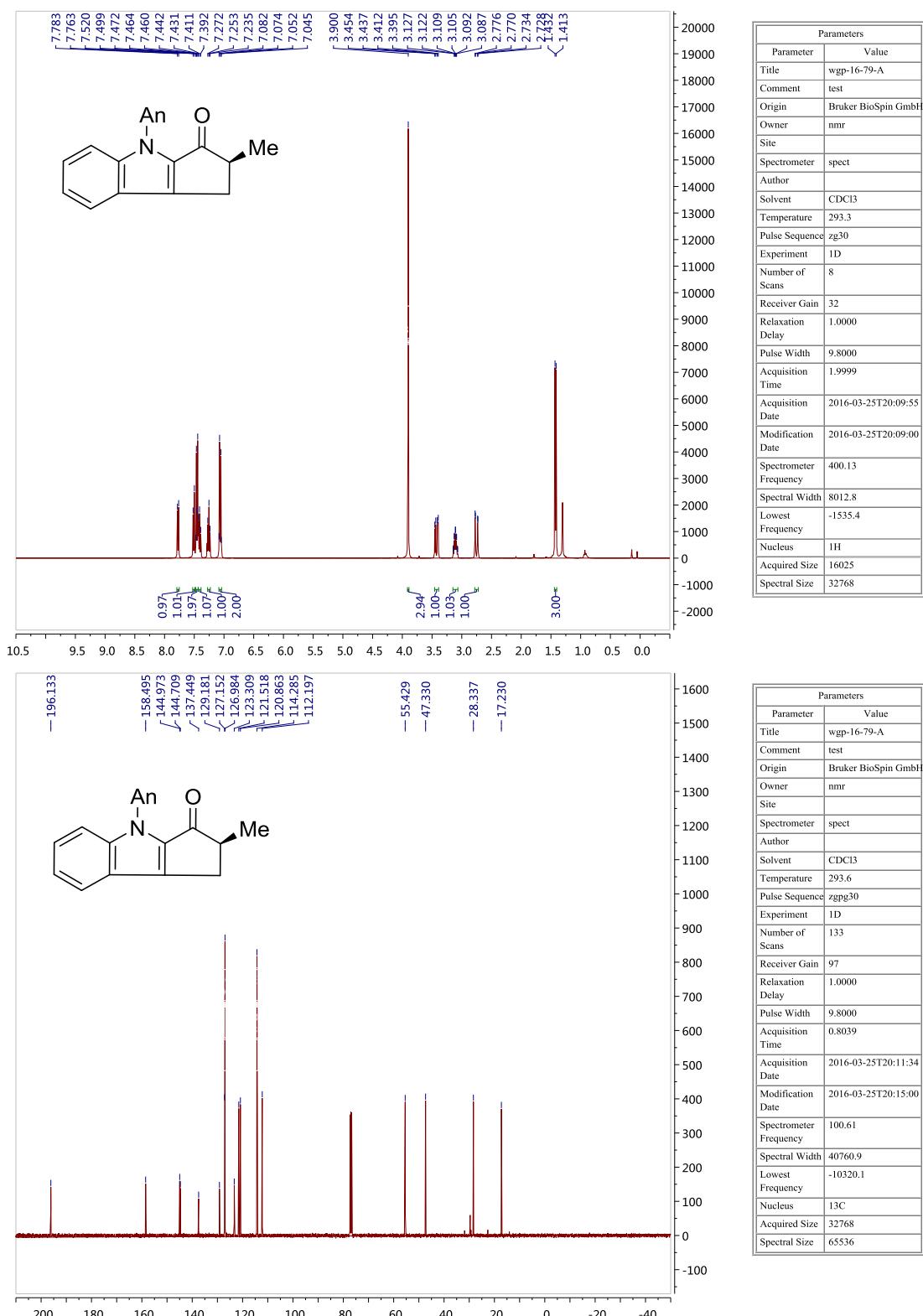
(-)-4-benzyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3d)



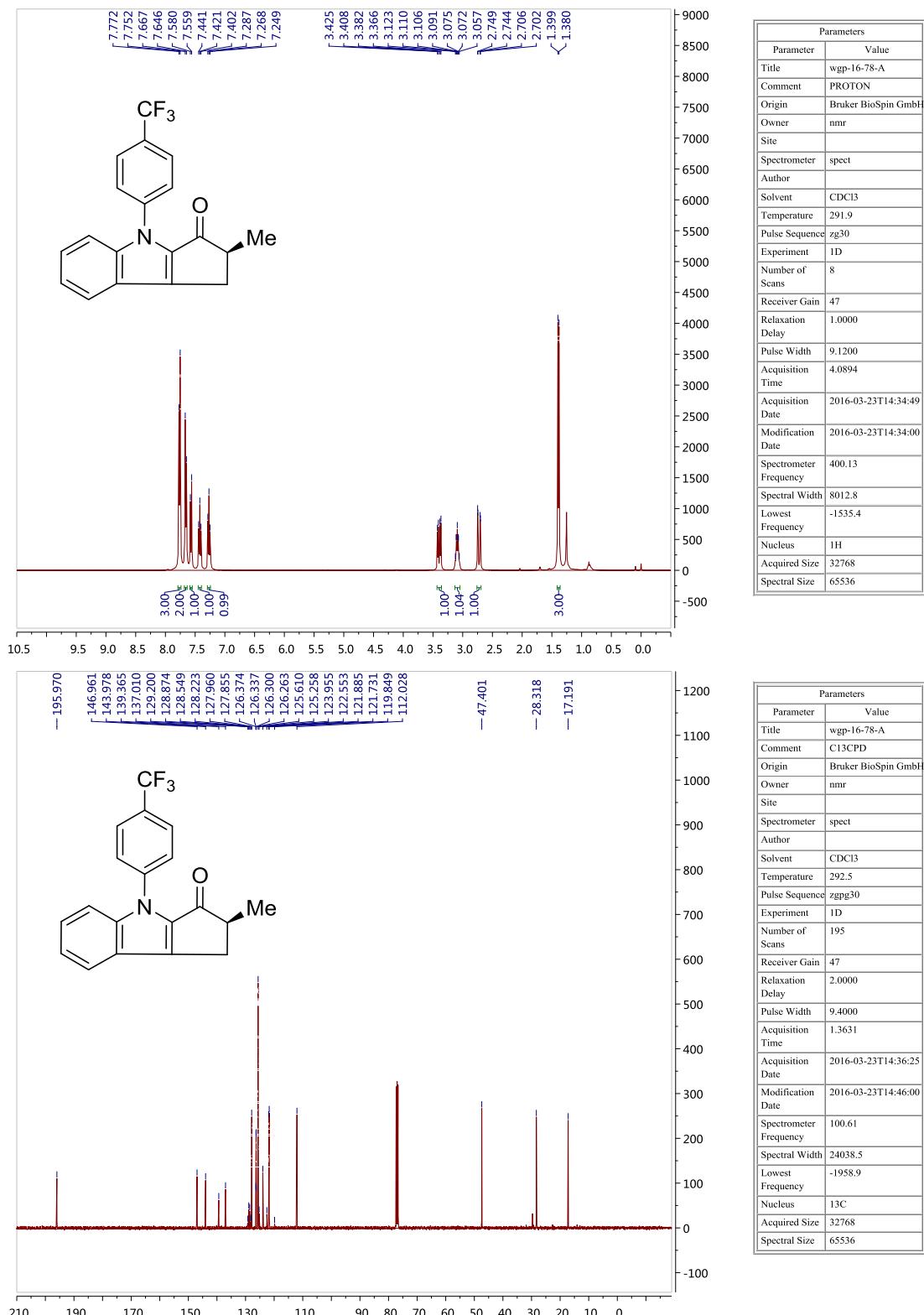
(+)-2-methyl-4-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3e)



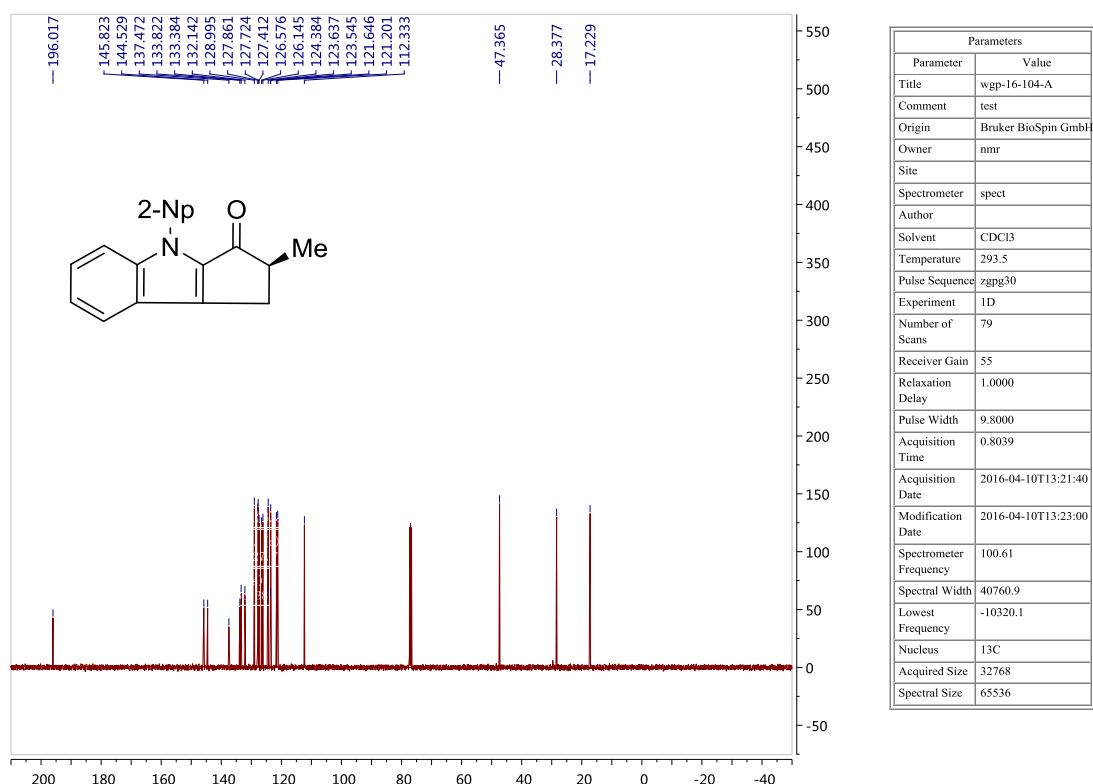
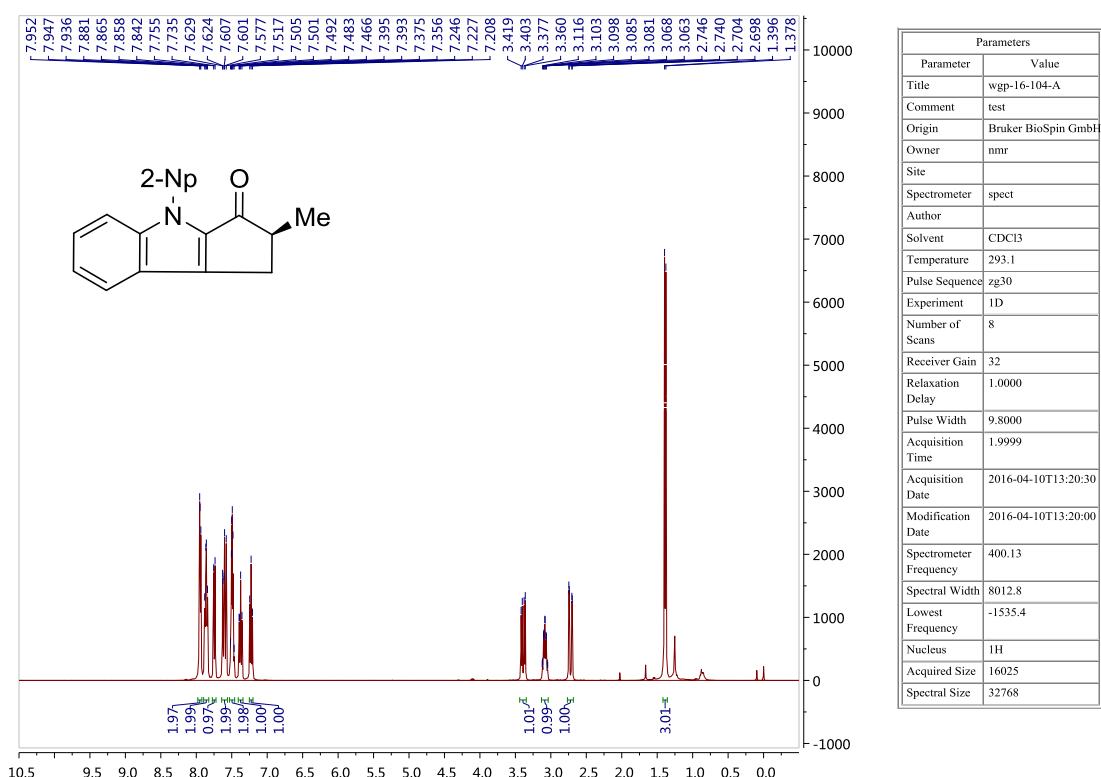
(+)-4-(4-methoxyphenyl)-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3f)



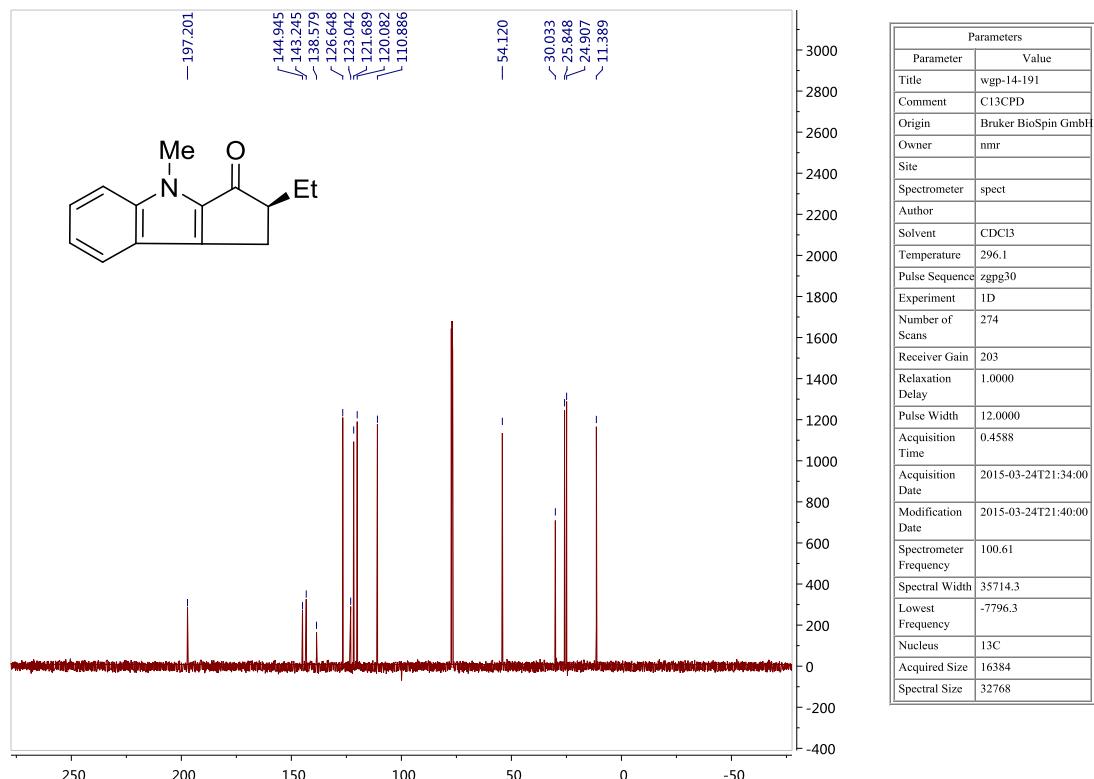
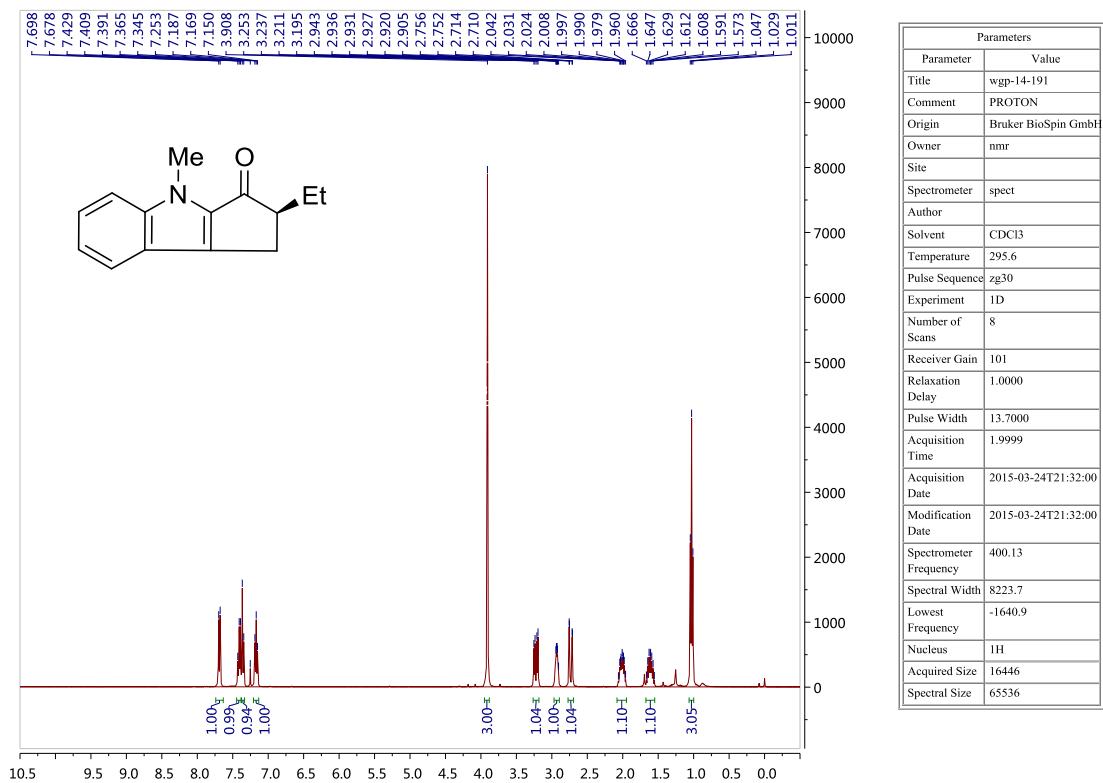
(+)-2-methyl-4-(4-(trifluoromethyl)phenyl)-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3g)



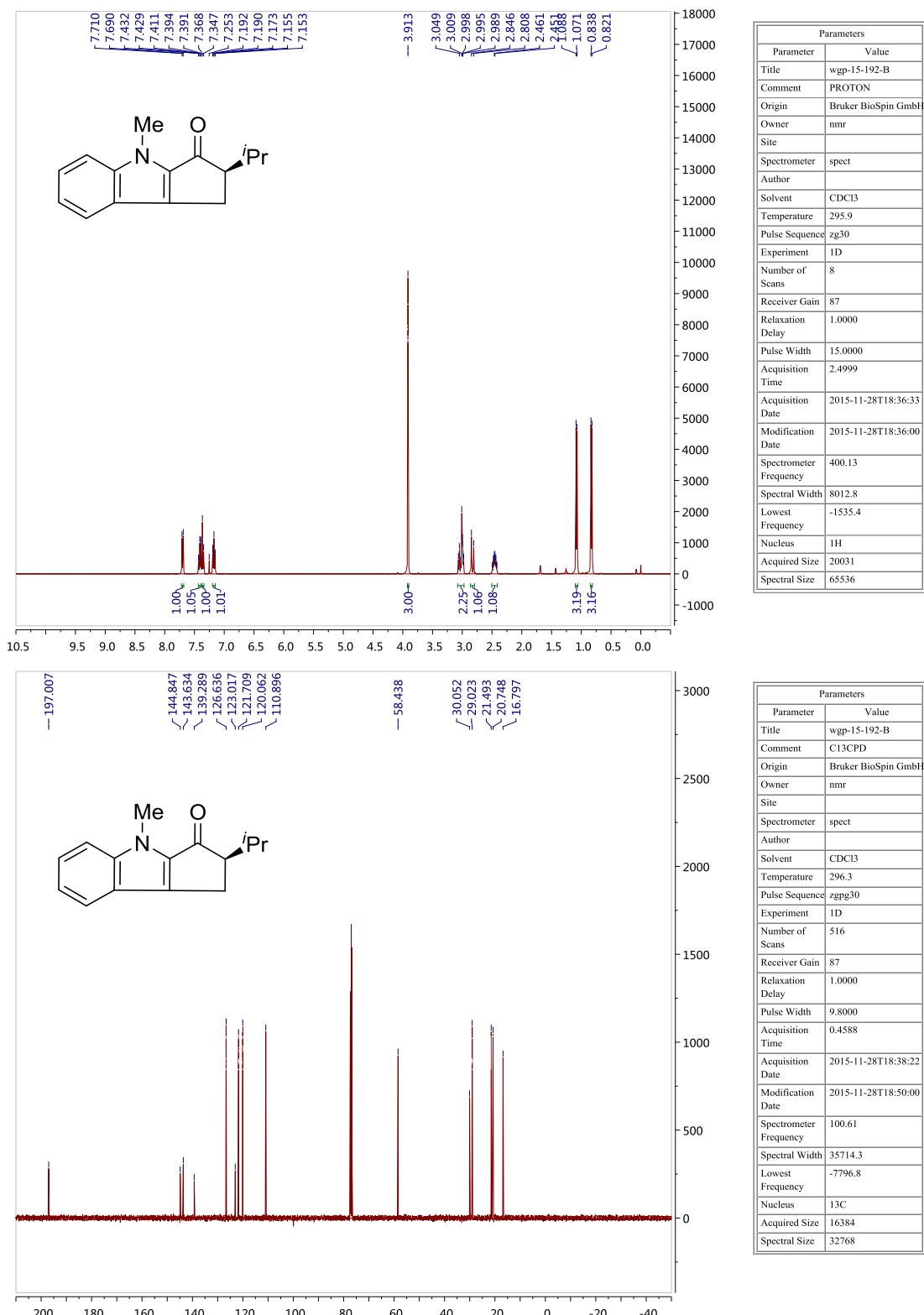
(+)-2-methyl-4-(naphthalen-2-yl)-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3h)



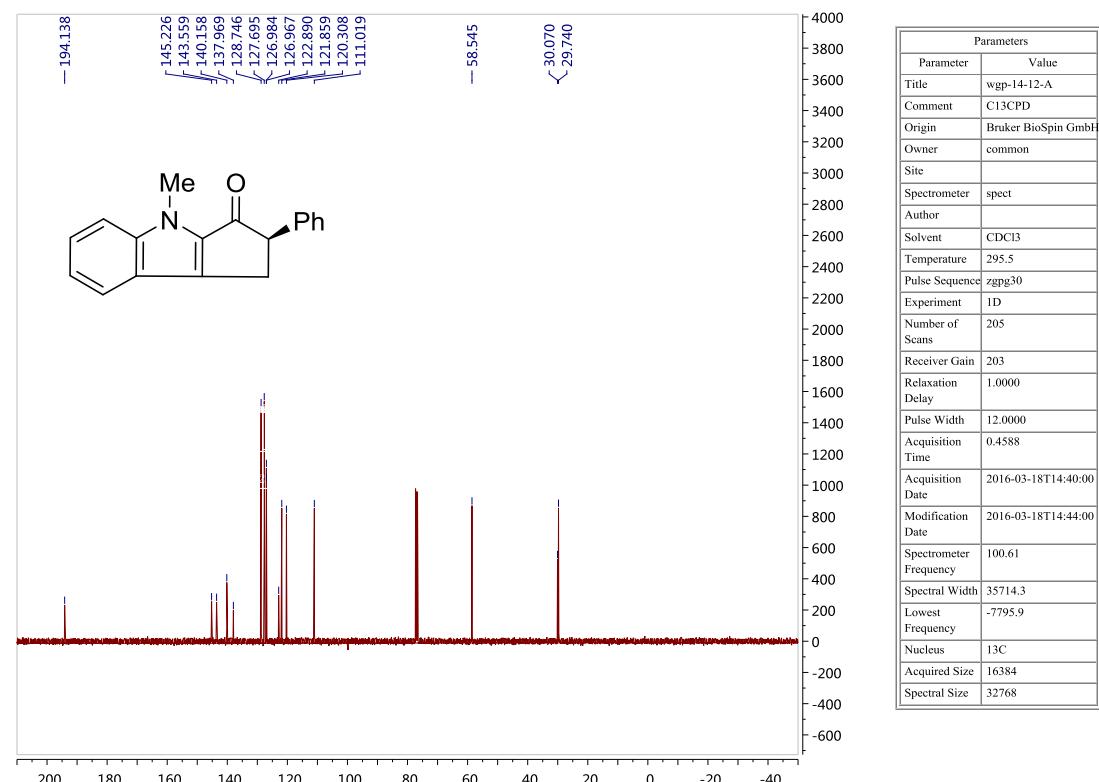
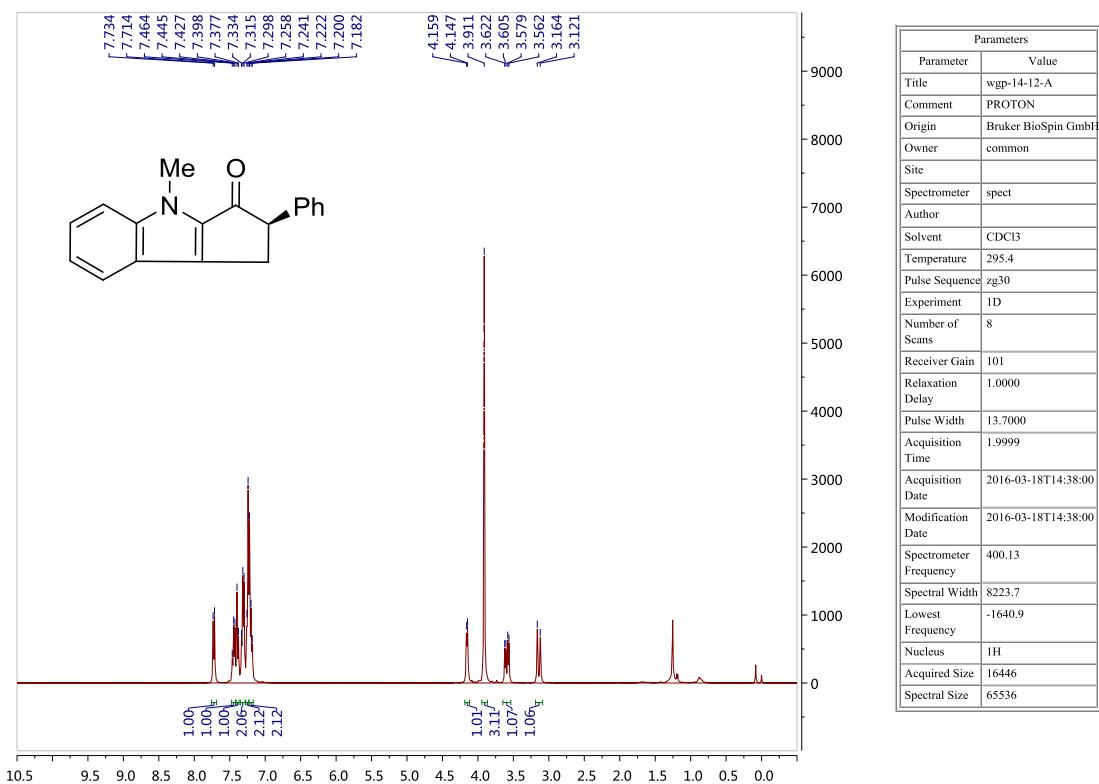
(+)-2-ethyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3i)



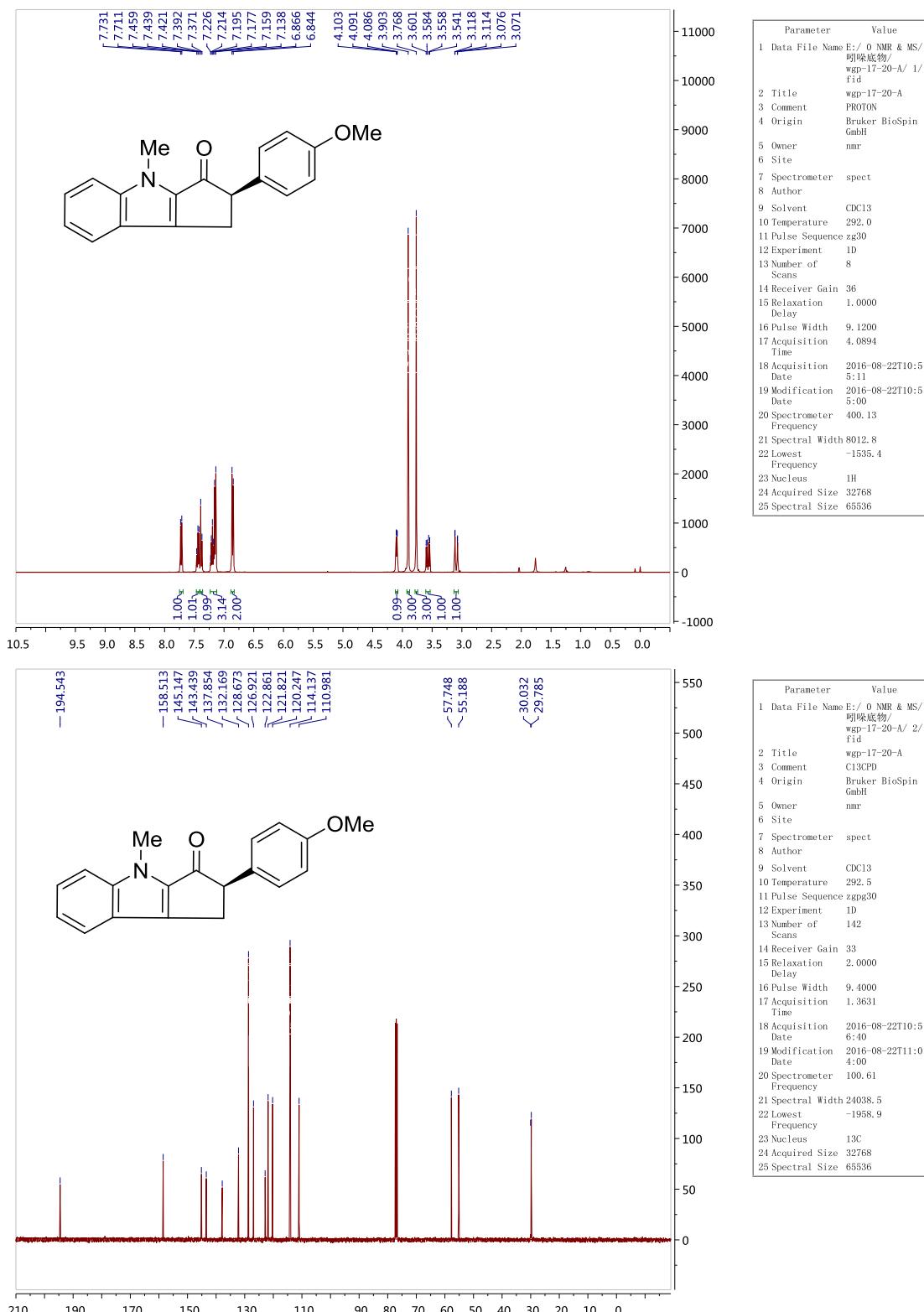
(+)-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3j)



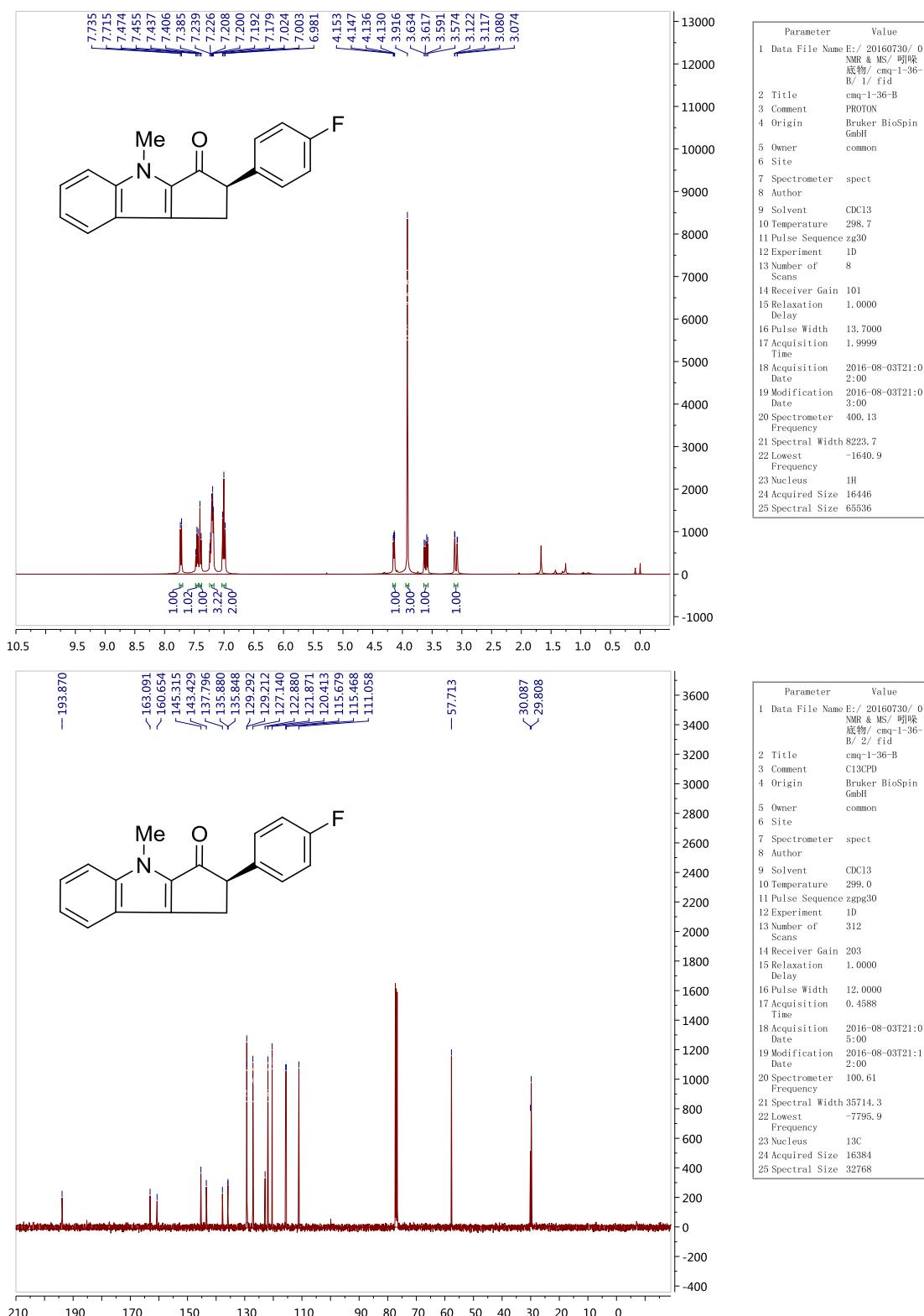
(+)-4-methyl-2-phenyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3k)



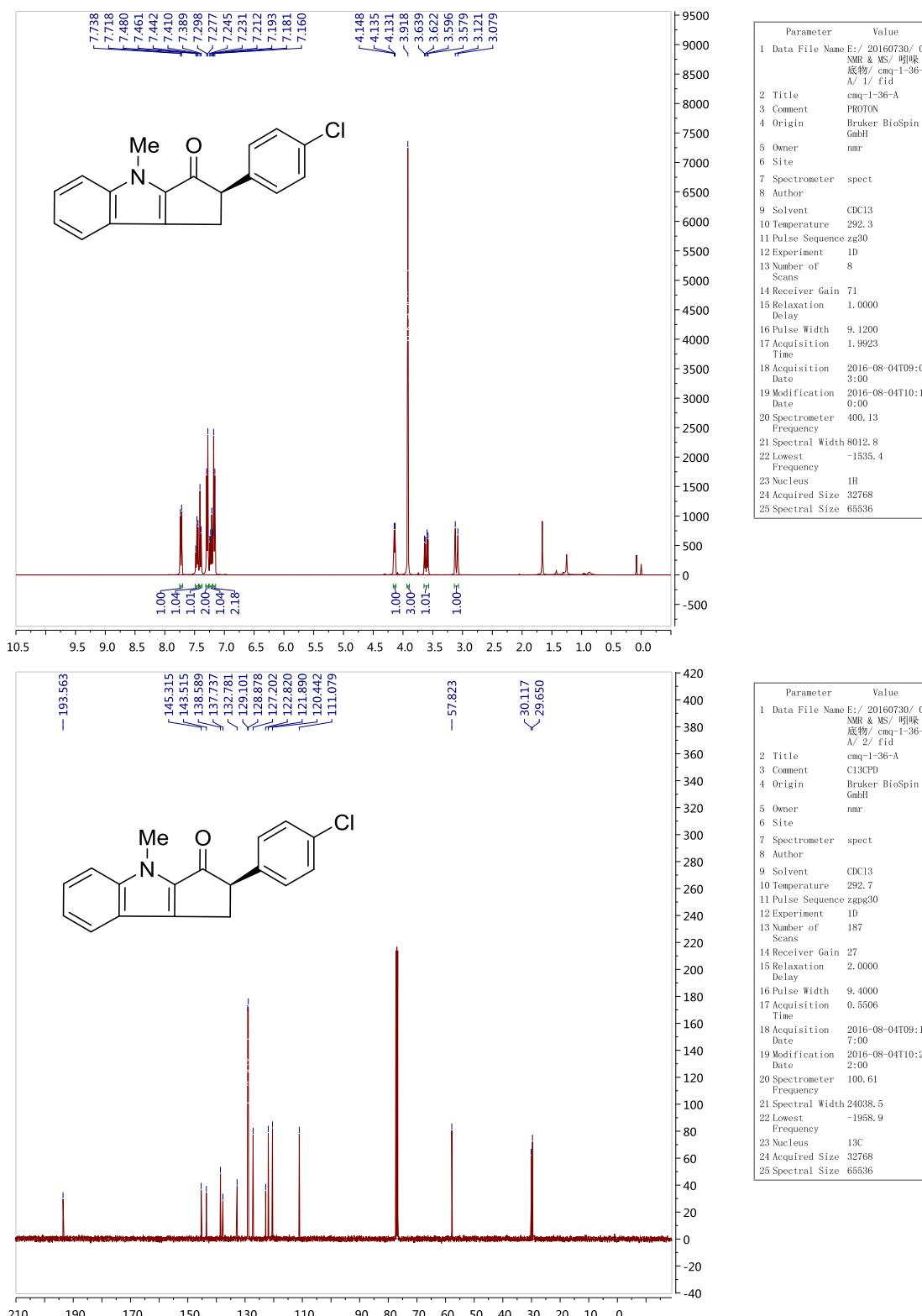
(+)-2-(4-methoxyphenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3l)



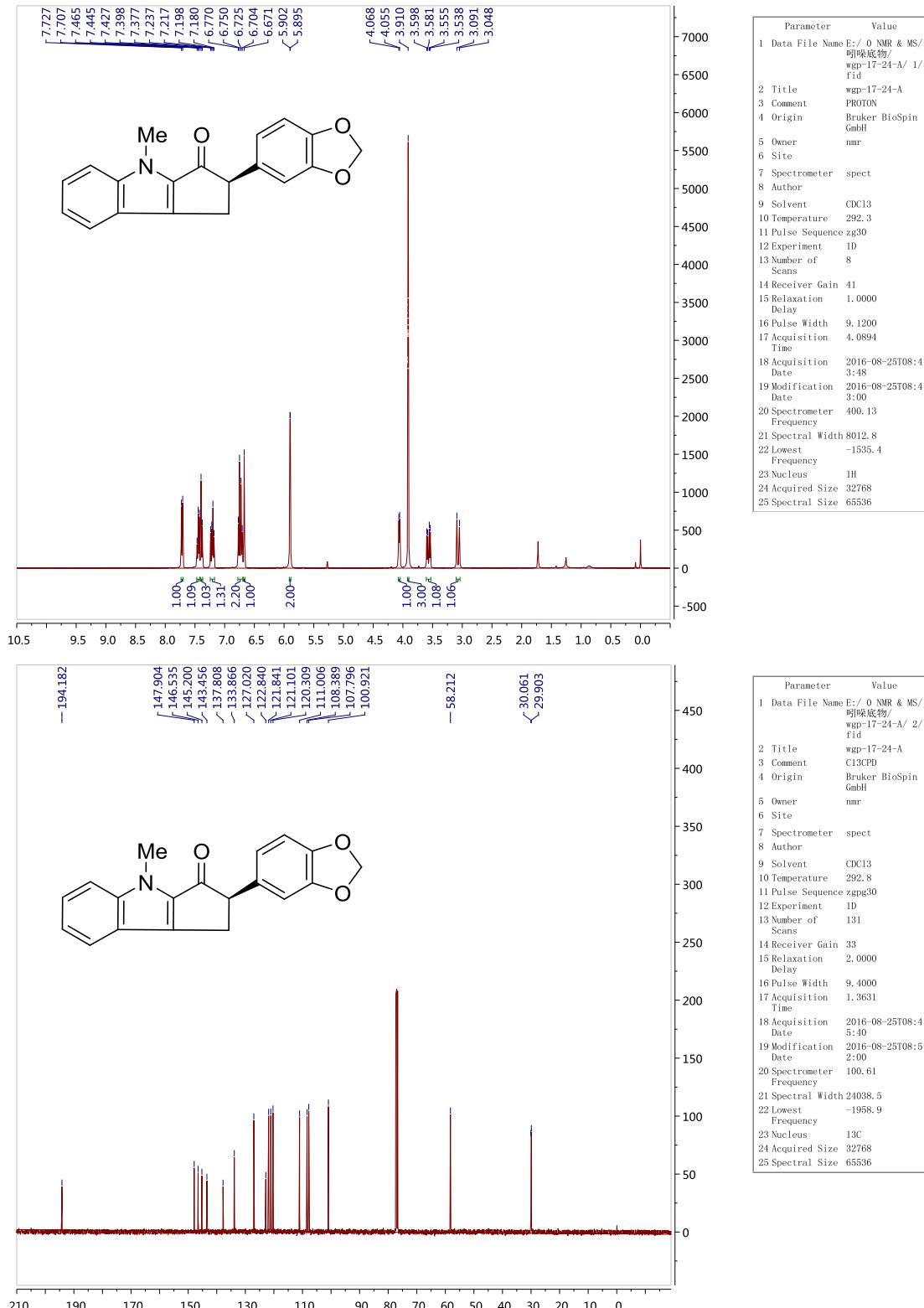
(+)-2-(4-fluorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3m)



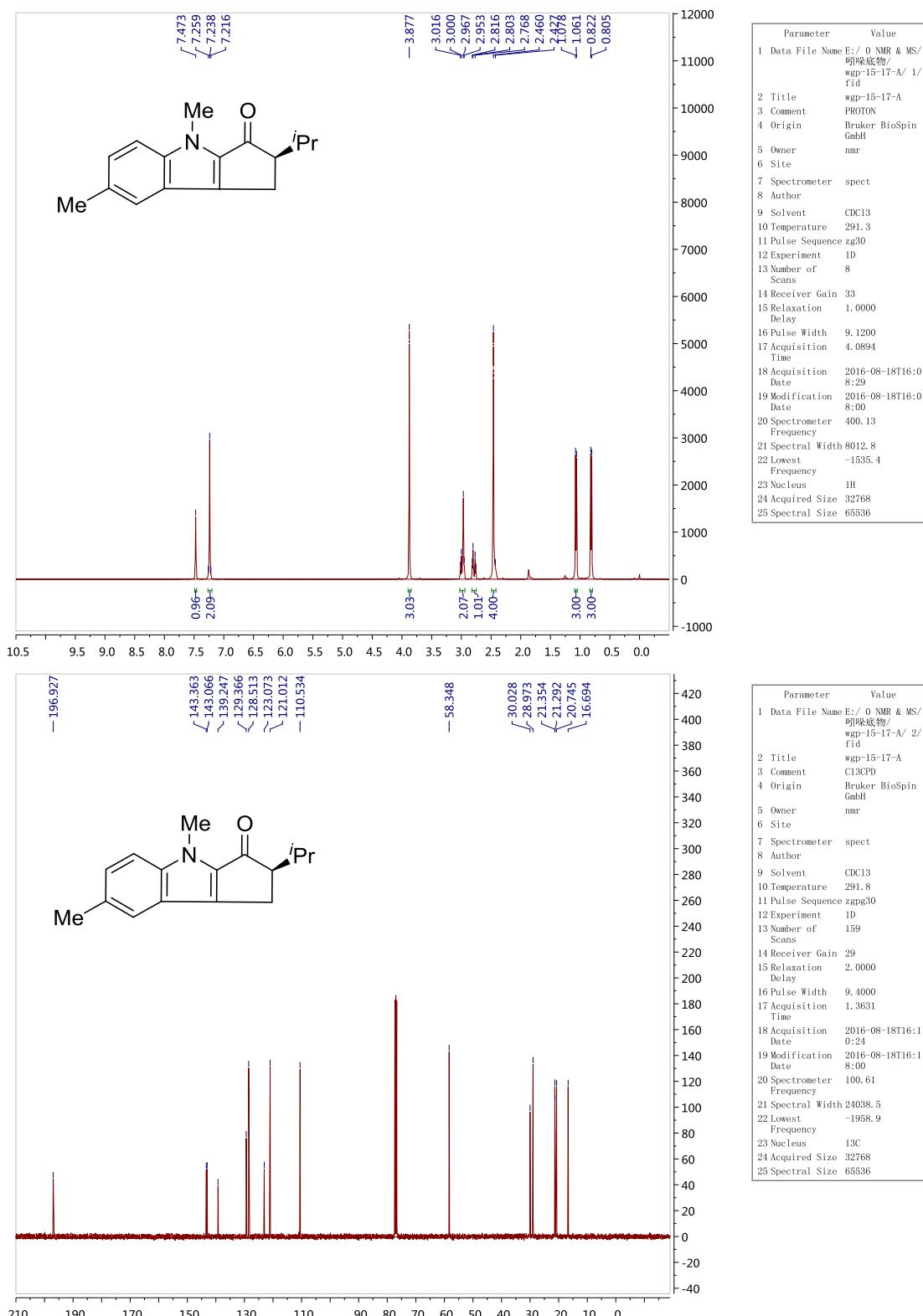
(+)-2-(4-chlorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3n)



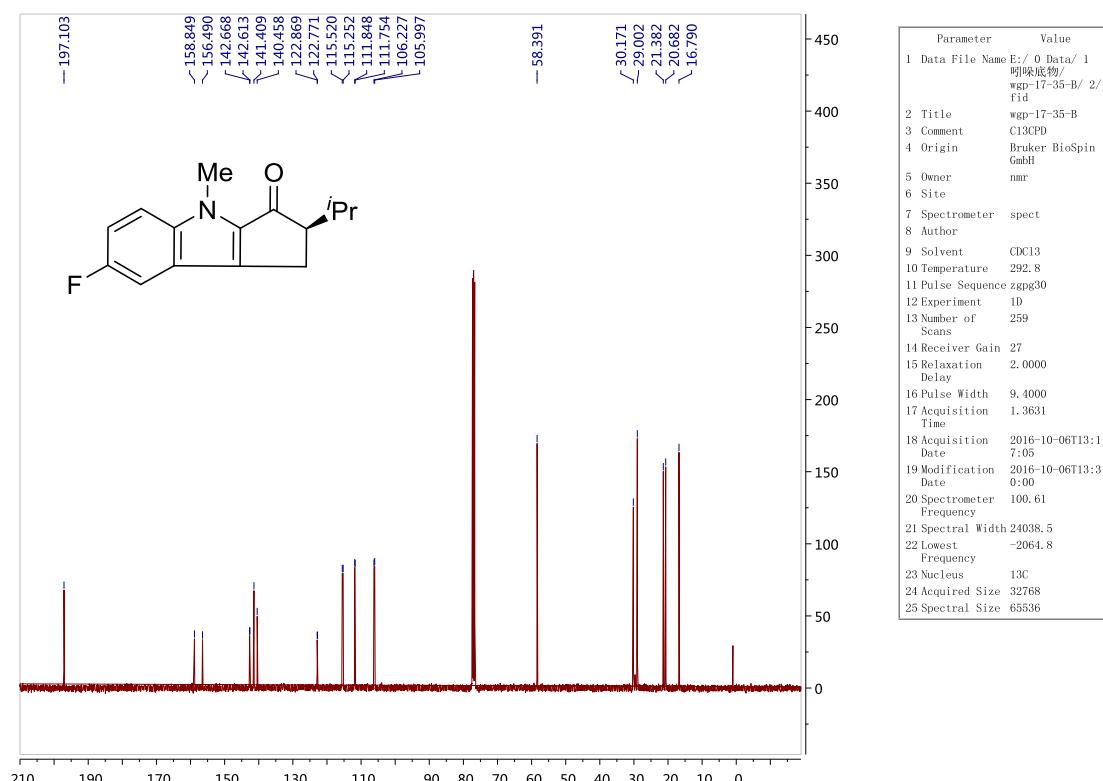
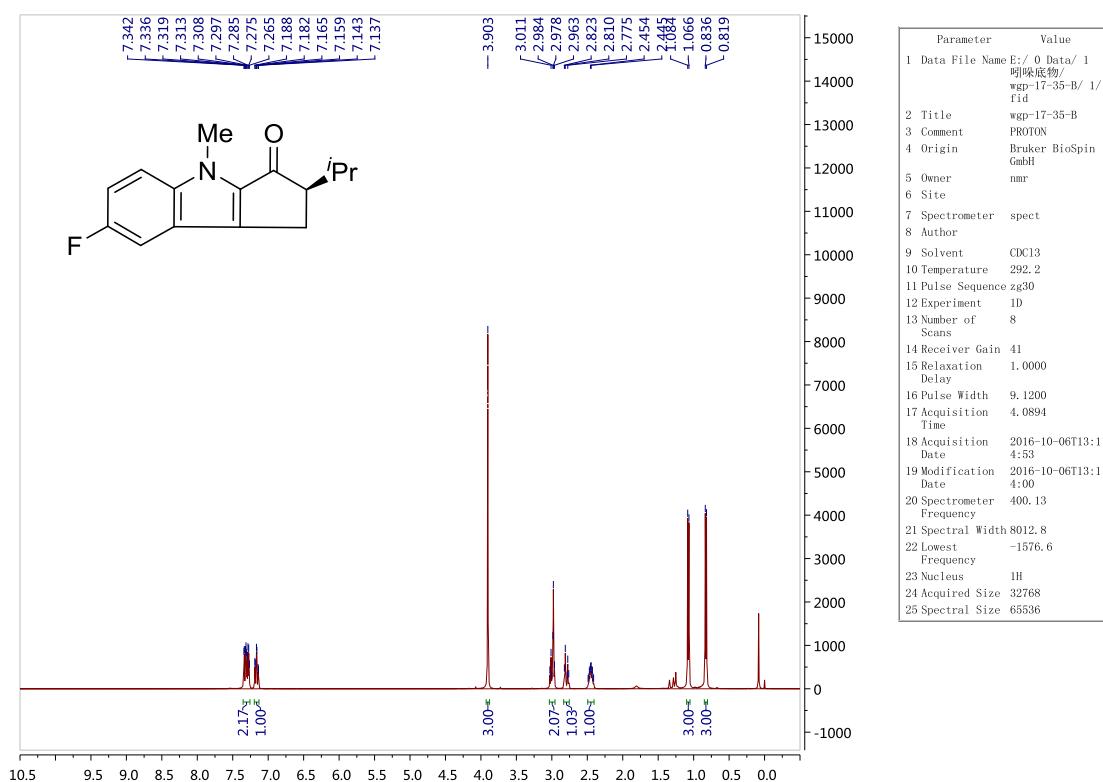
(+)-2-(benzo[d][1,3]dioxol-5-yl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3o)



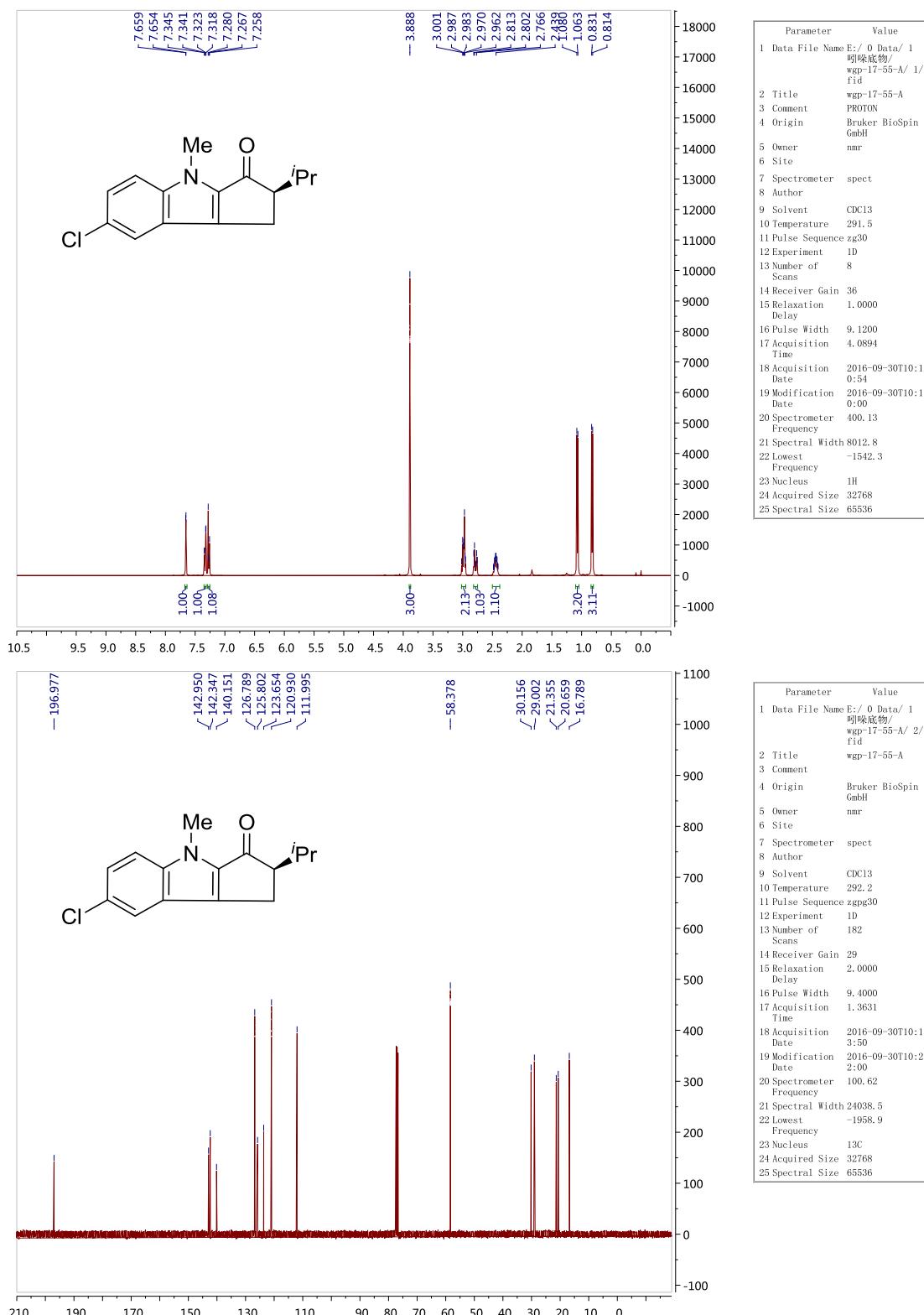
(+)-2-isopropyl-4,7-dimethyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3p)



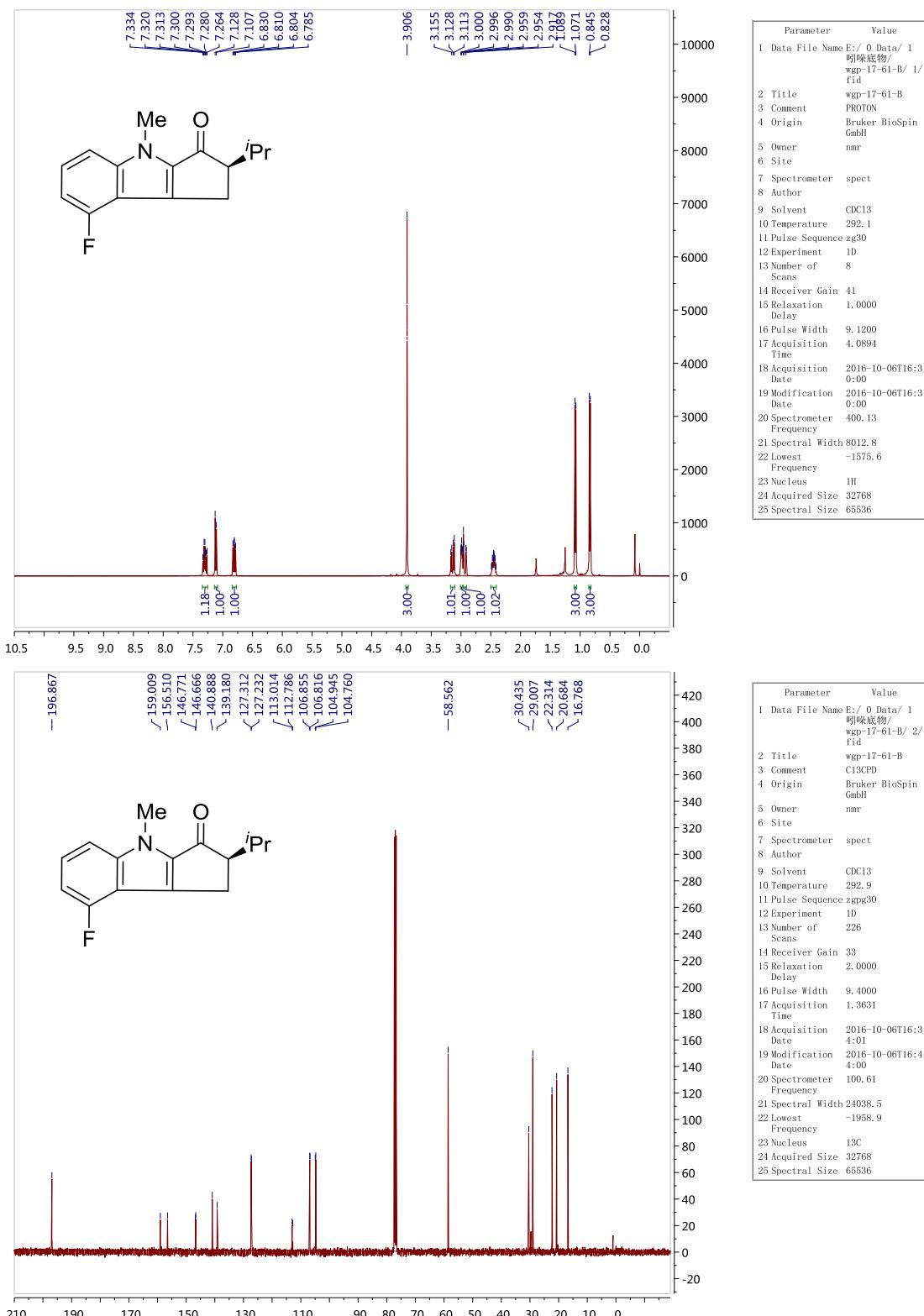
(+)-7-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3q)



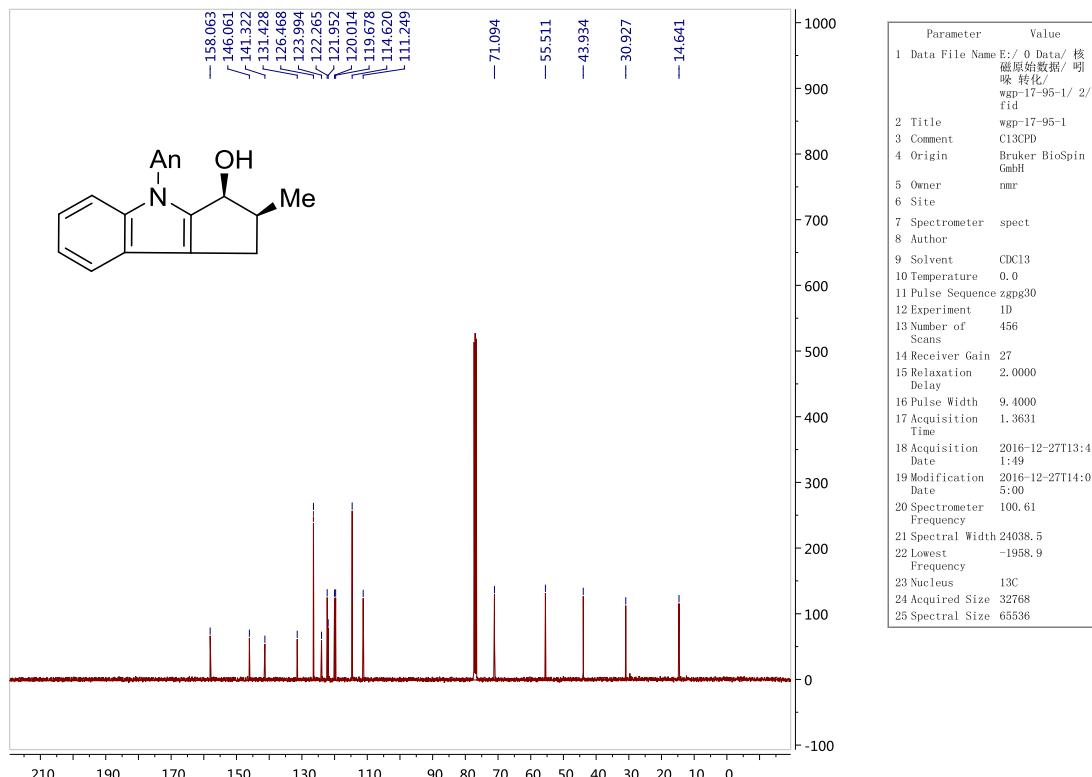
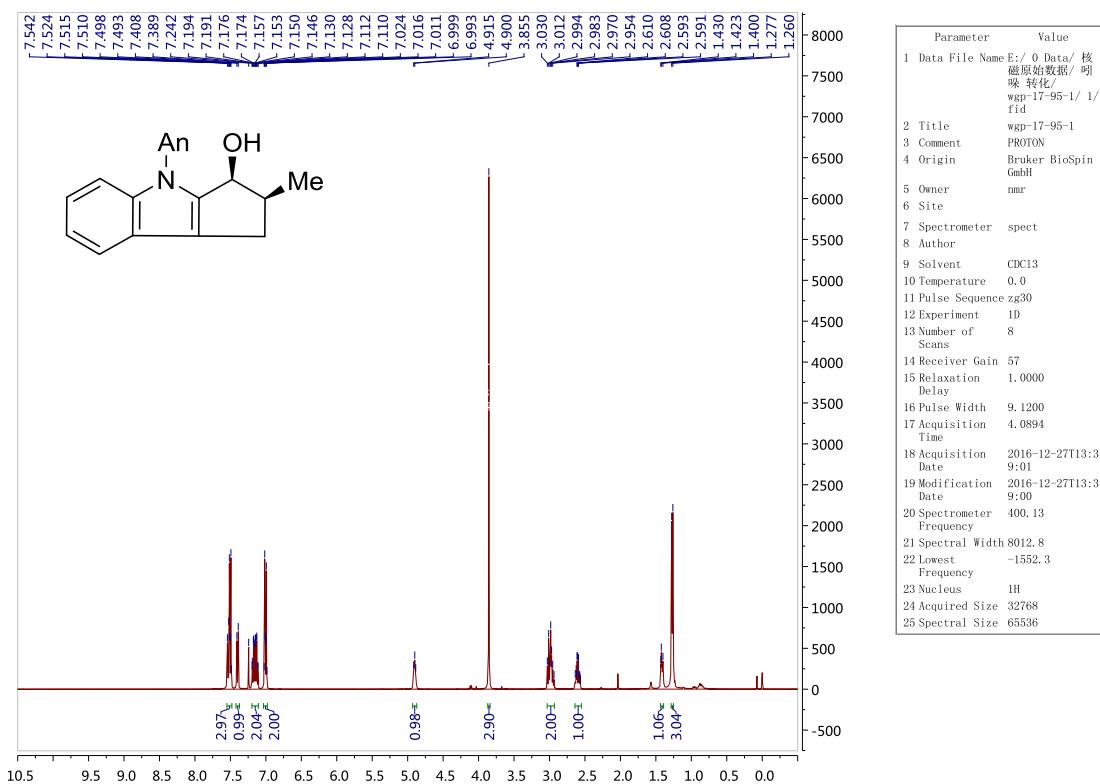
**(R)-(+)-7-chloro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one
(3r)**

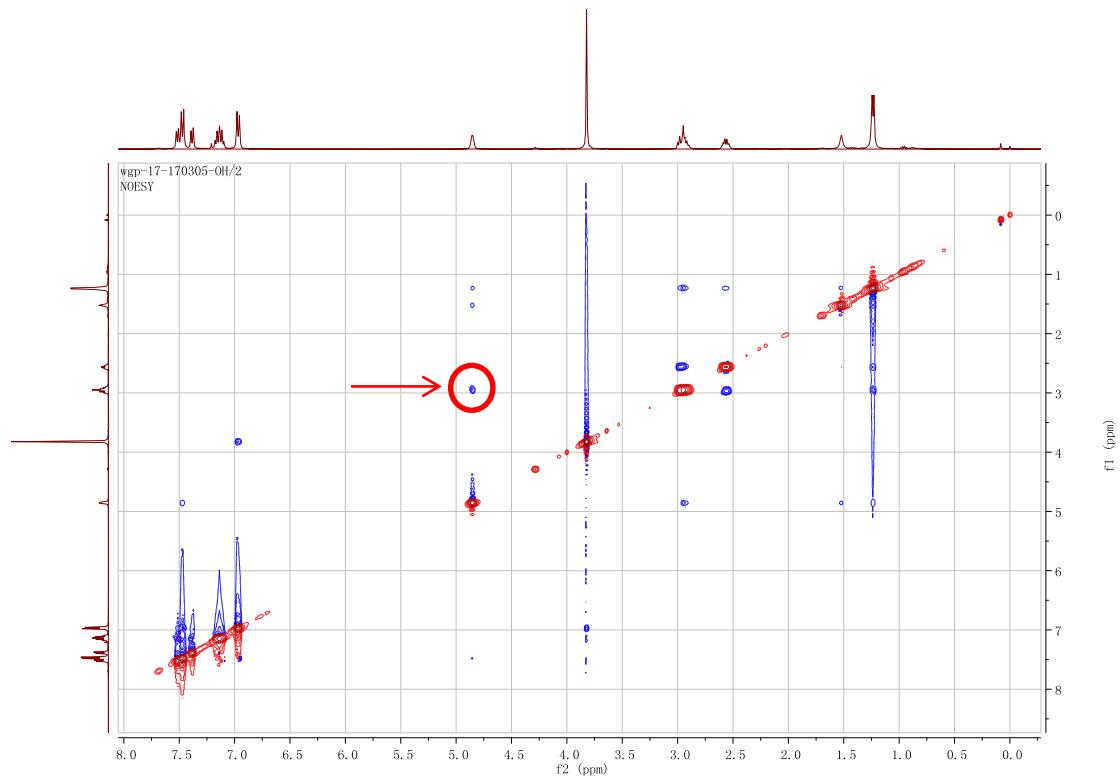


(+)-8-fluoro-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3s)



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

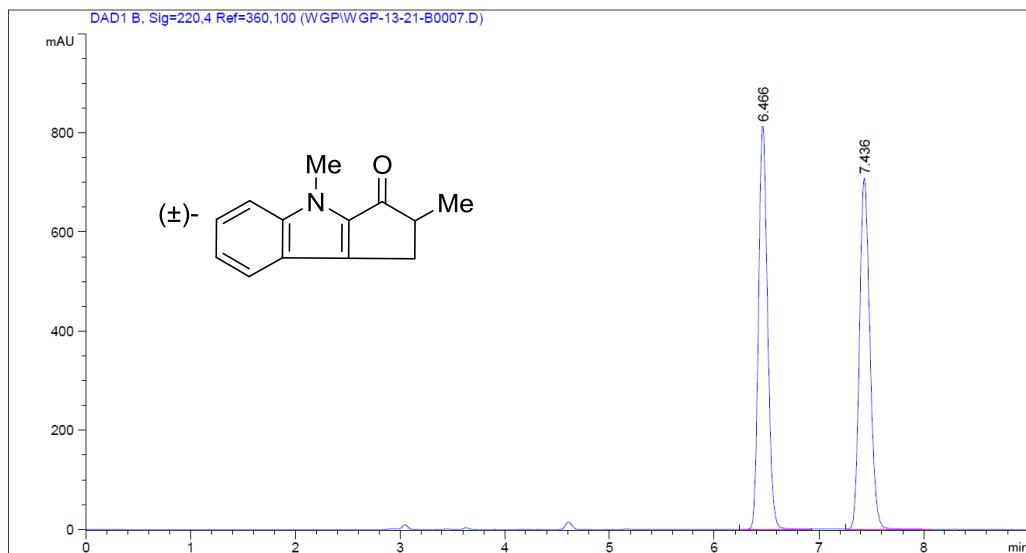




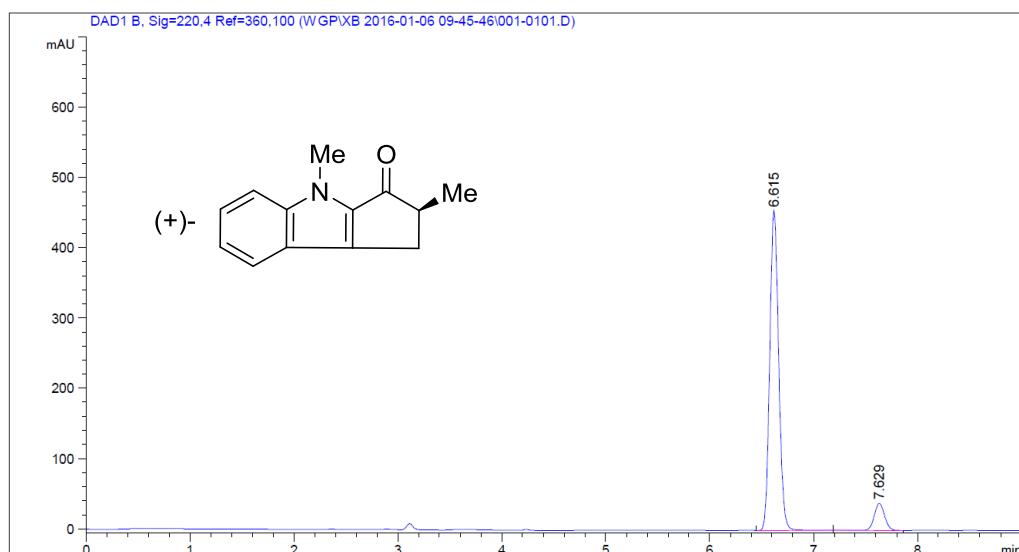
9. HPLC Charts of Cyclization Products and Transformation

Product

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

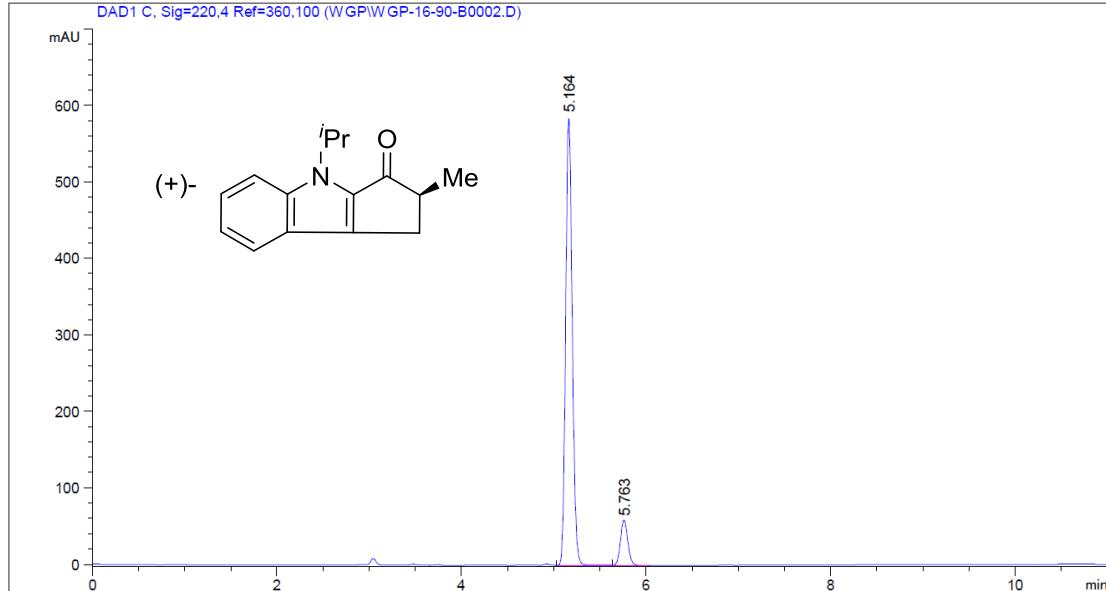
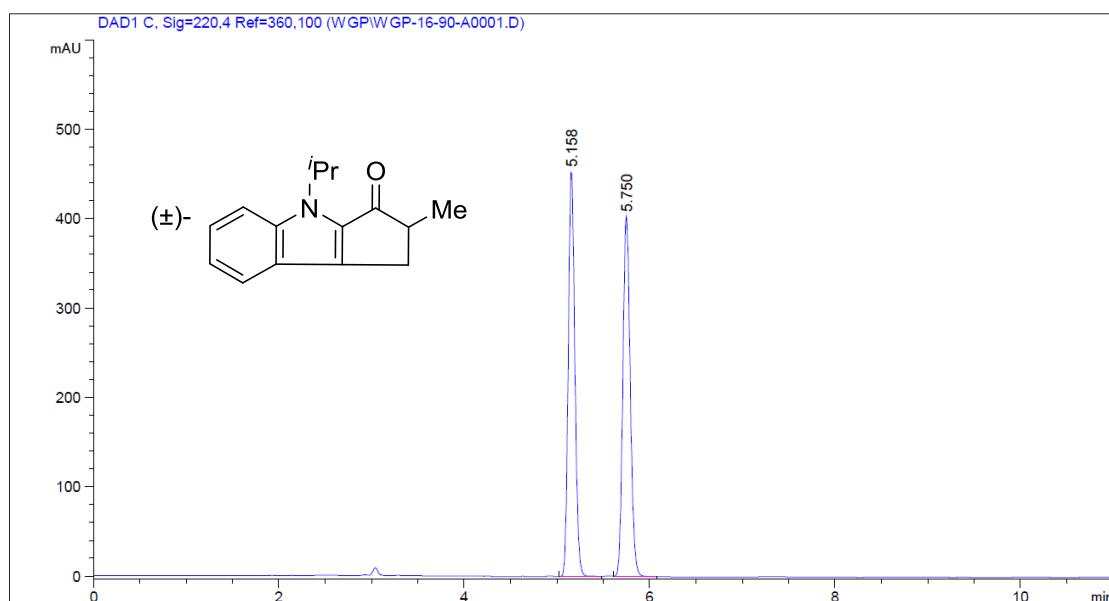


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.466	BB	0.0936	4867.17529	815.72778	49.8979
2	7.436	BB	0.1065	4887.09375	708.57227	50.1021

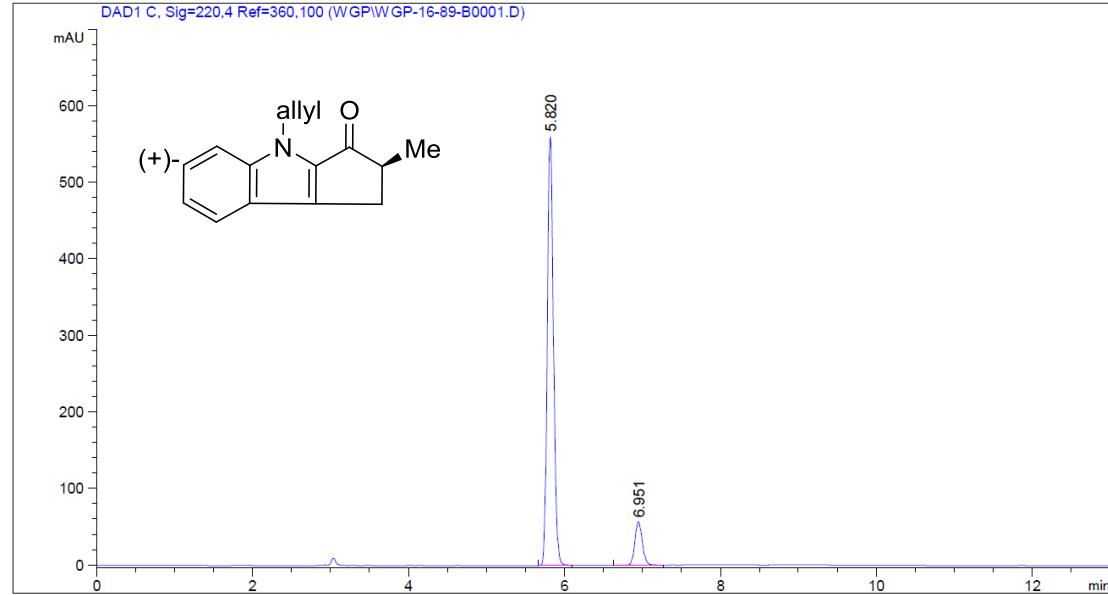
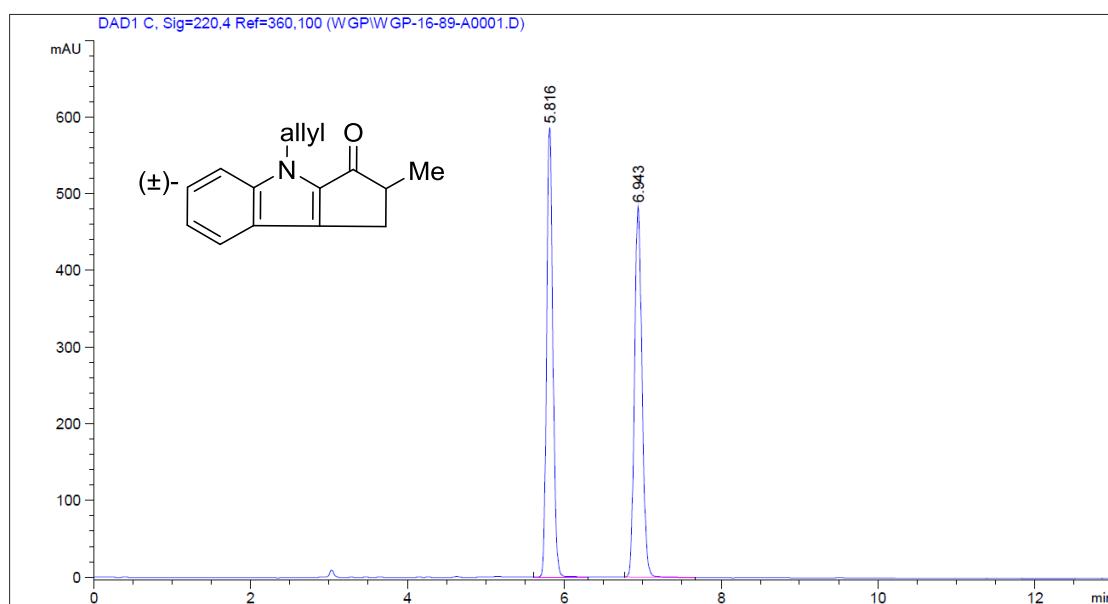


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.615	BB	0.0915	2709.63696	455.02417	90.9136
2	7.629	BB	0.1077	270.81601	38.67042	9.0864

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

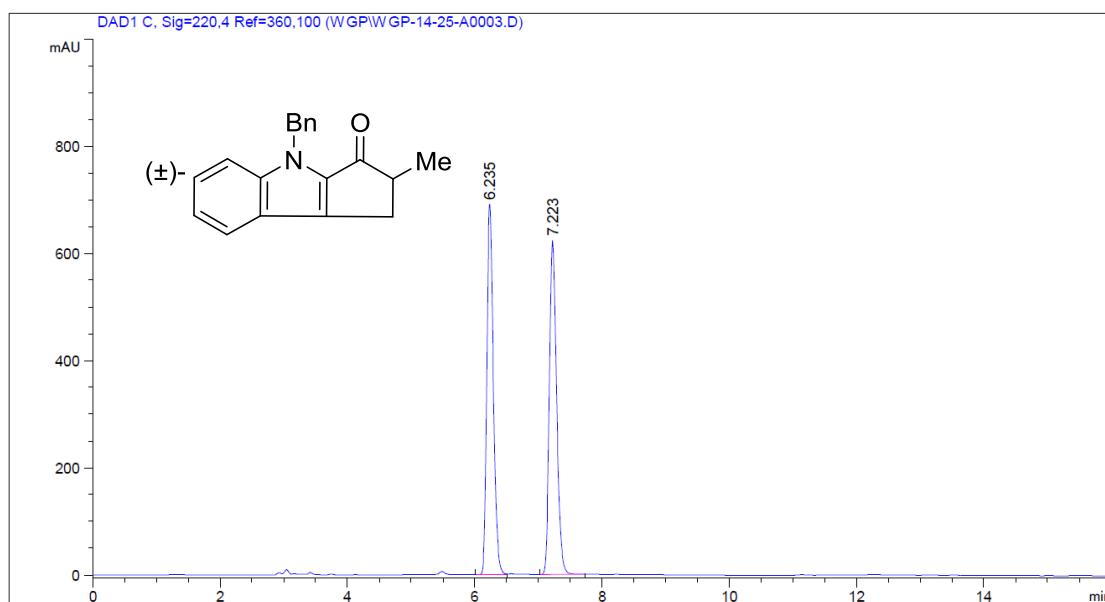


(+)-4-allyl-2-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3c)

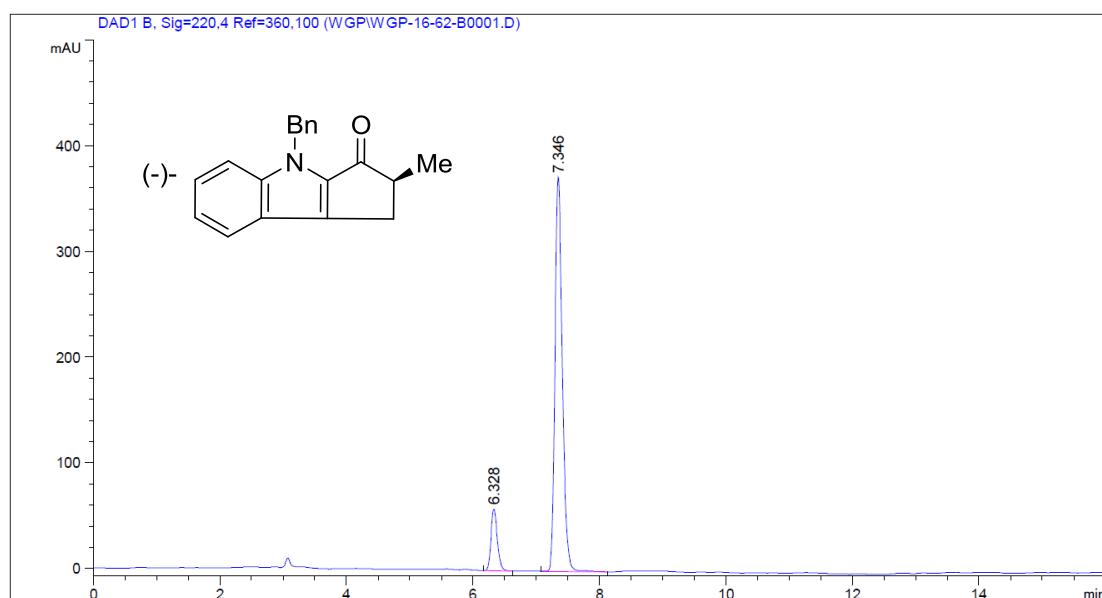


Peak	RetTime	Type	Width	Area	Height	Area %
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.820	BB	0.0857	3063.91016	560.94293	89.0622
2	6.951	BB	0.1035	376.28085	56.63813	10.9378

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

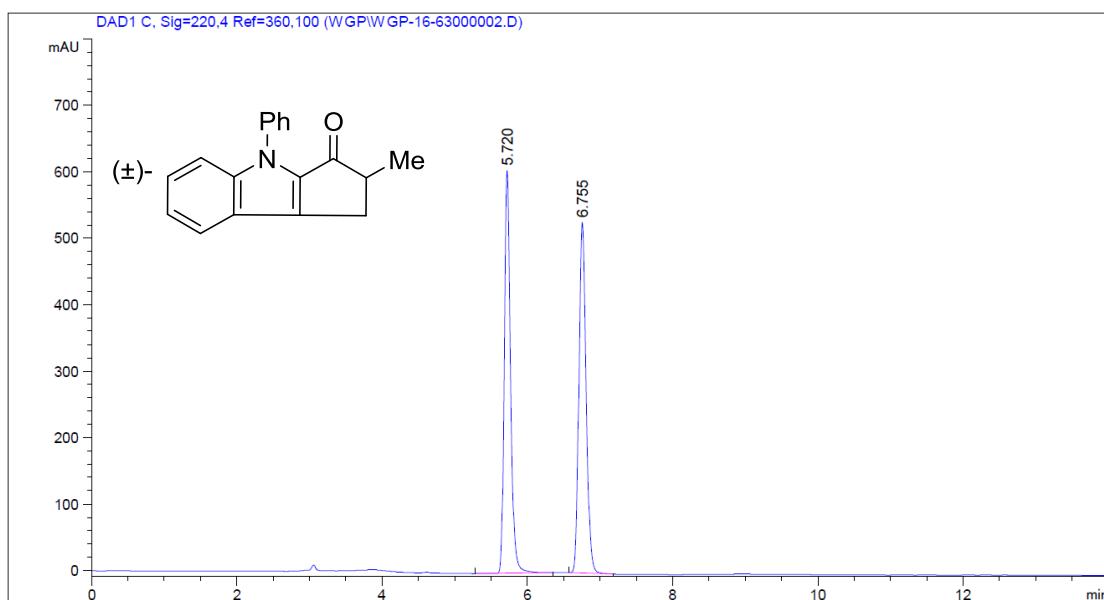


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.235	BV	0.1111	4934.35742	692.75580	49.9591
2	7.223	BB	0.1203	4942.43164	624.85785	50.0409

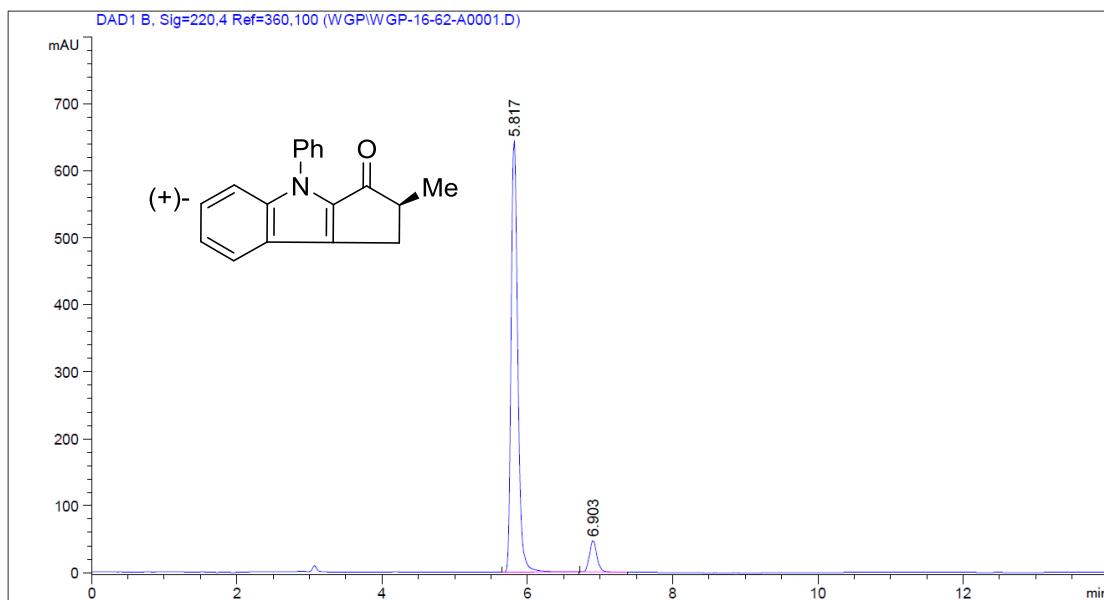


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.328	BB	0.1041	401.74609	58.48005	11.7360
2	7.346	BB	0.1245	3021.44604	373.21472	88.2640

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

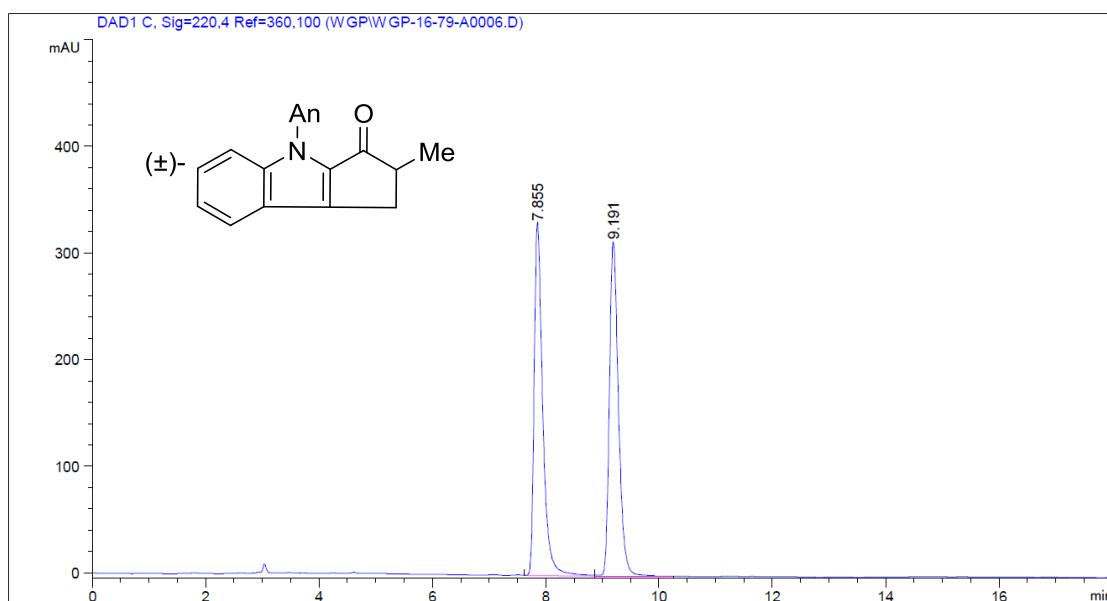


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.720	BB	0.0925	3667.38599	606.57990	50.0780
2	6.755	BB	0.1088	3655.96875	528.13989	49.9220

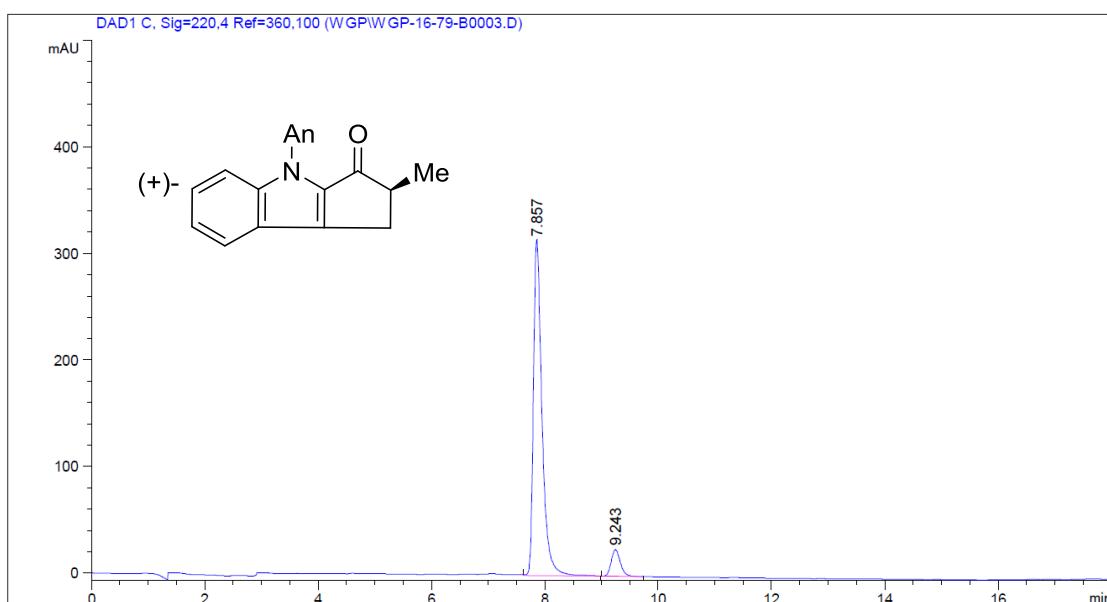


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.817	BB	0.0973	4046.63794	644.17590	92.2467
2	6.903	BB	0.1123	340.11893	47.06593	7.7533

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

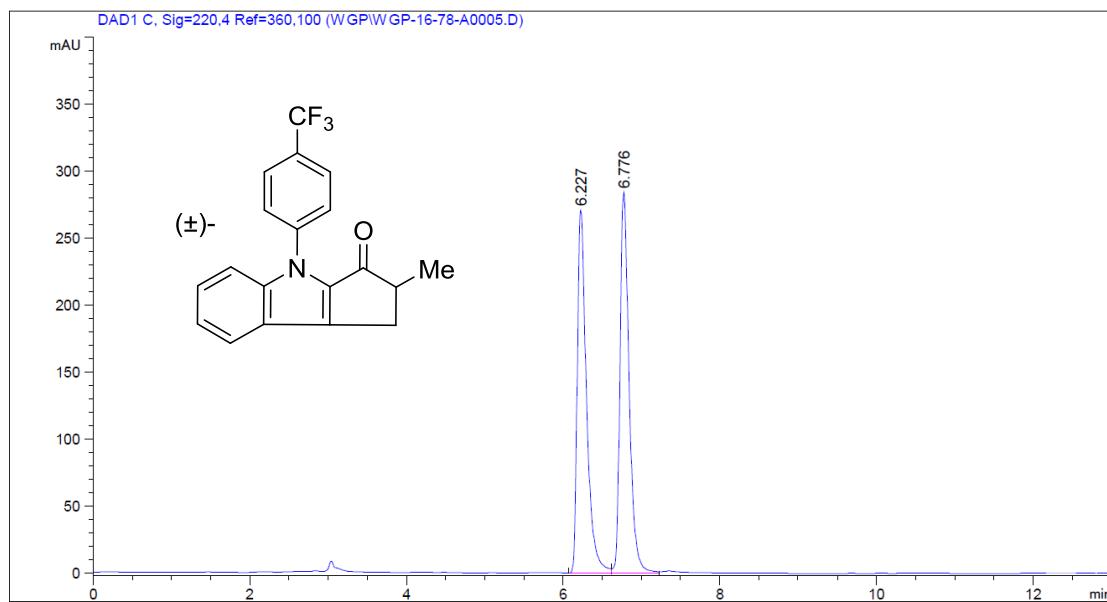


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.855	VV	0.1634	3478.91333	328.91351	49.9364
2	9.191	VB	0.1744	3487.77856	312.07806	50.0636

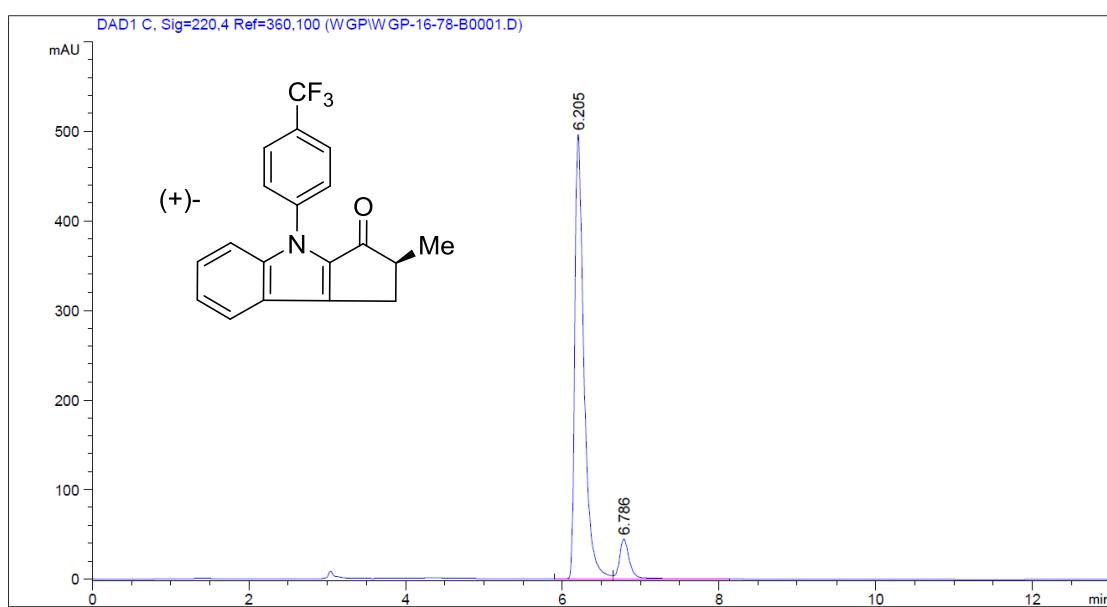


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.857	VB	0.1590	3310.79541	314.10974	92.1710
2	9.243	BB	0.1752	281.21967	25.01088	7.8290

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

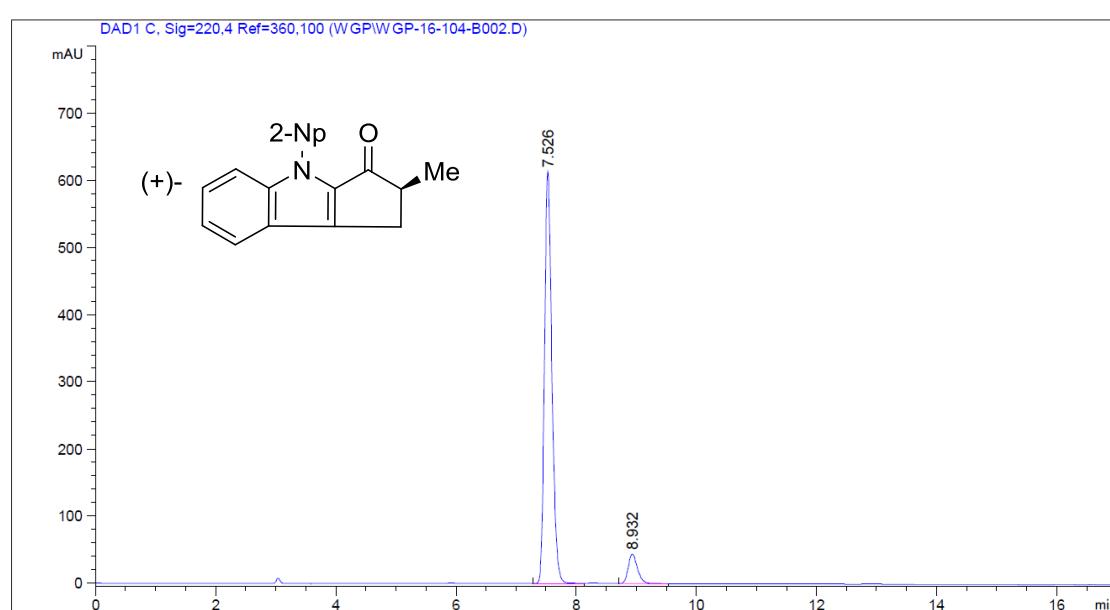
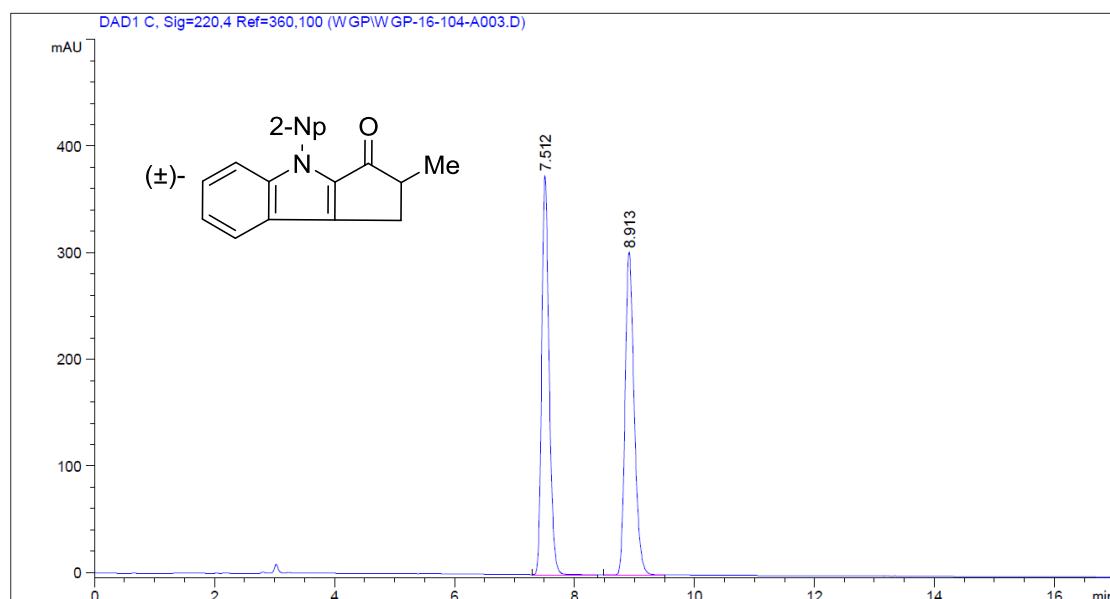


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.227	BV	0.1238	2222.37671	270.74310	49.1373
2	6.776	VV	0.1244	2300.40942	284.19302	50.8627

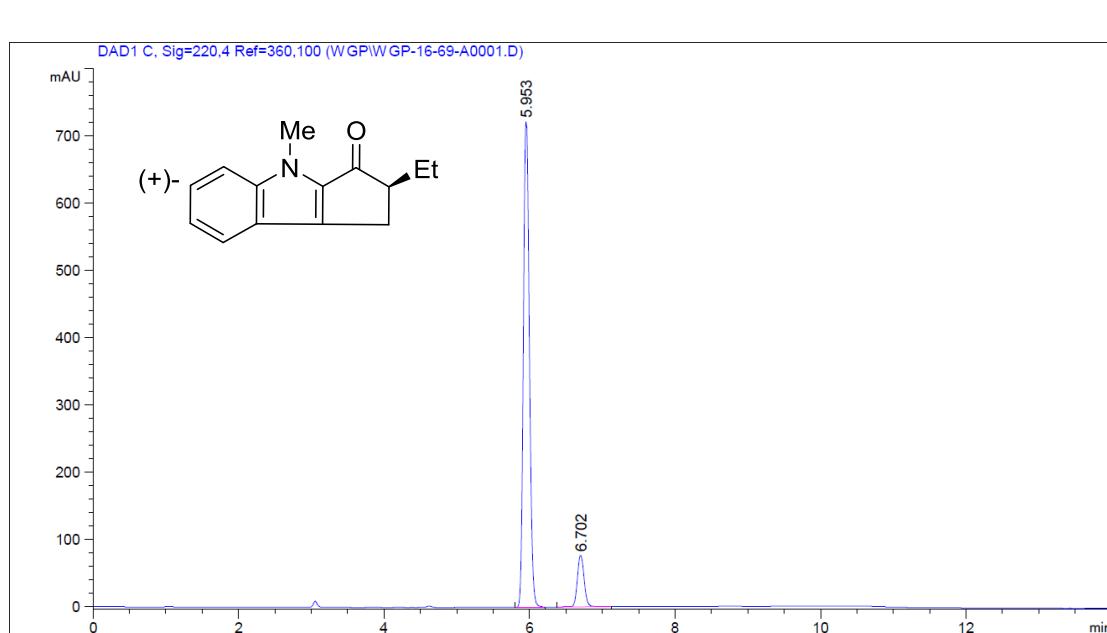
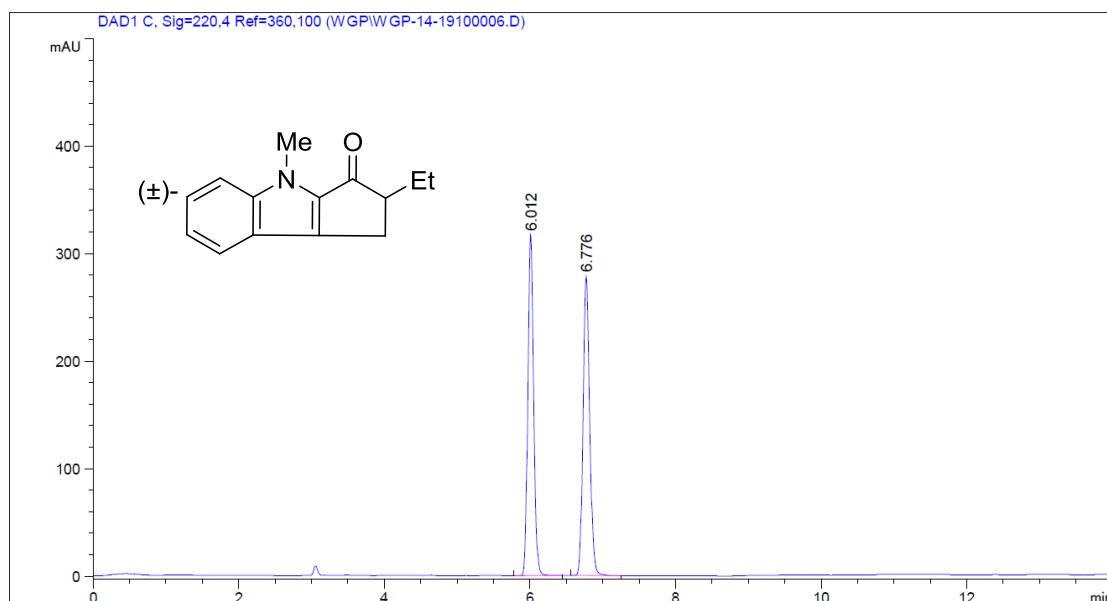


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.205	BV	0.1227	4026.77759	496.19296	90.9884
2	6.786	VB	0.1345	398.81454	44.53178	9.0116

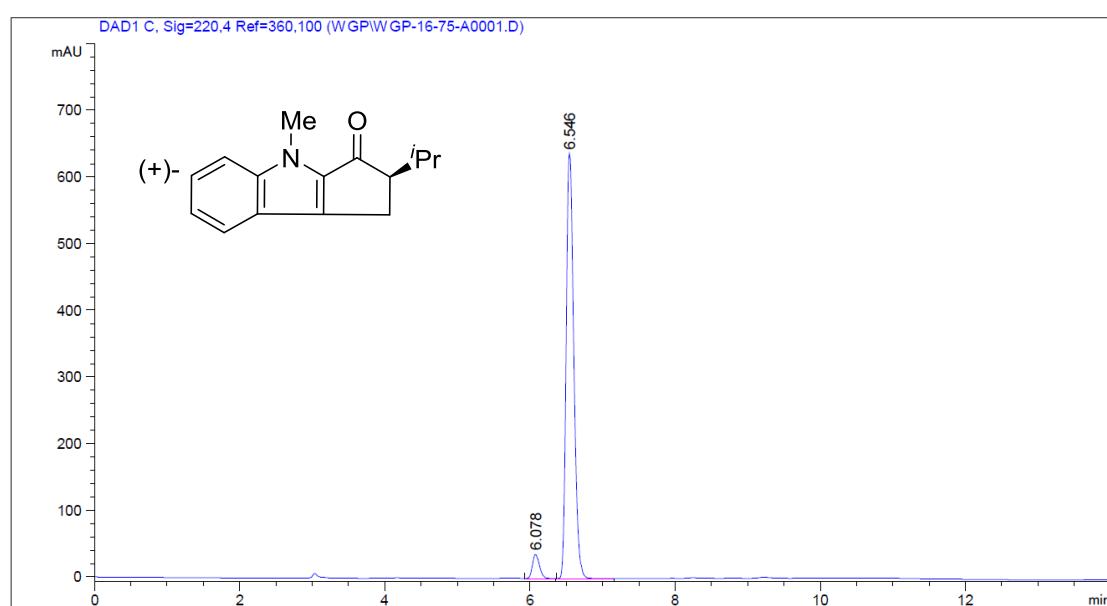
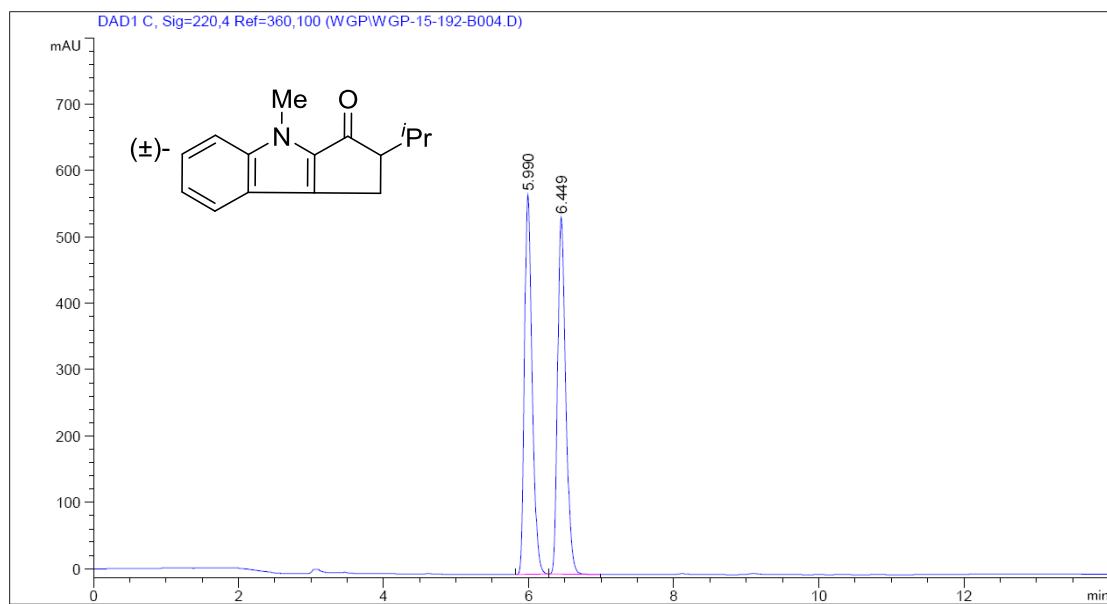
(+)-2-methyl-4-(naphthalen-2-yl)-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3h)



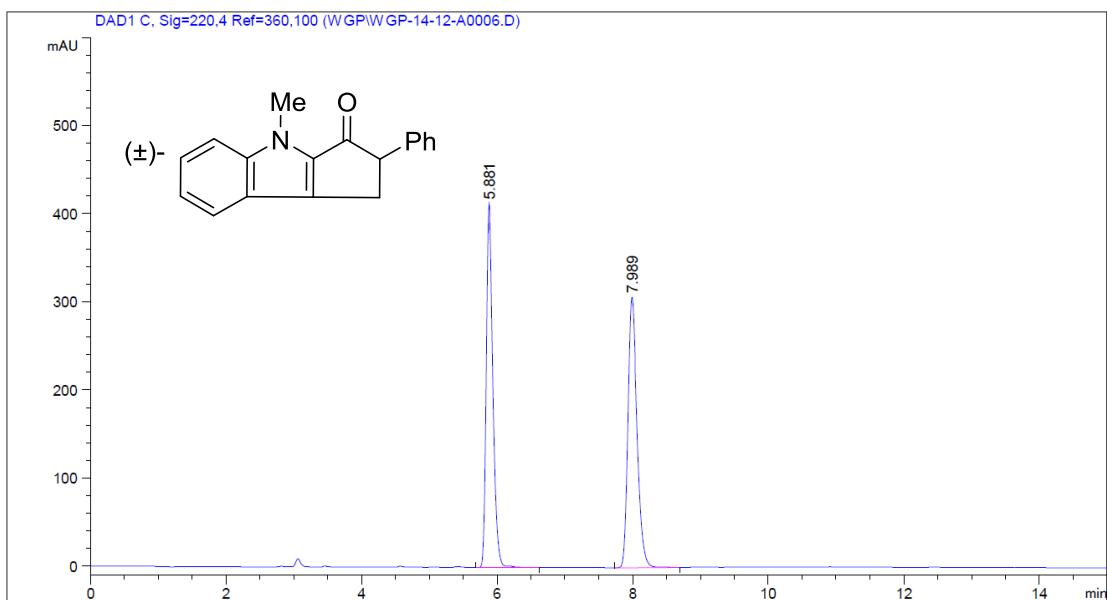
(+)-2-ethyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3i)



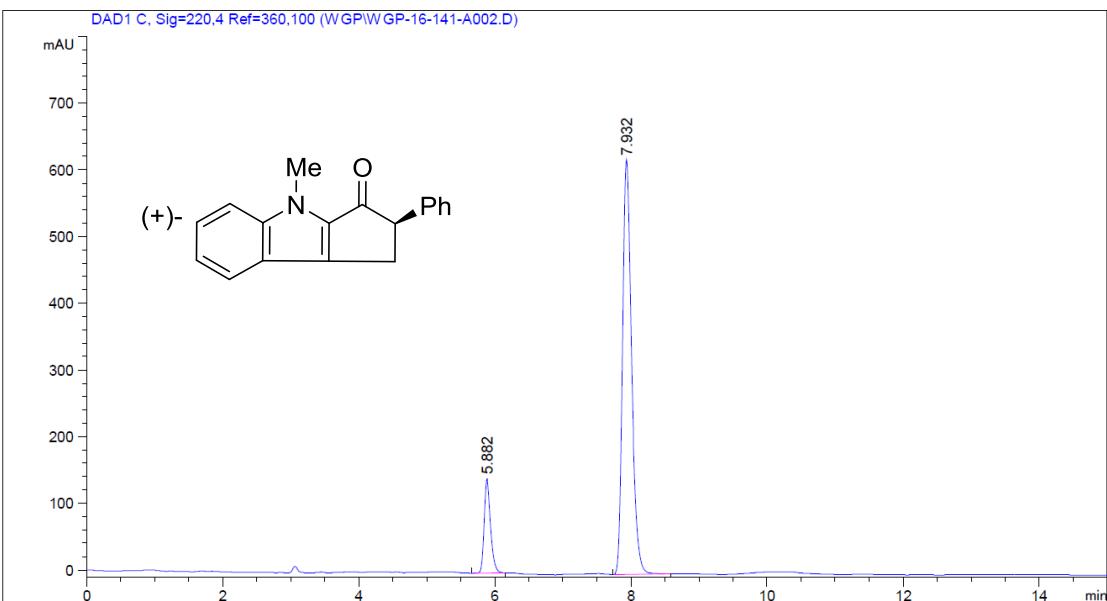
(+)-2-isopropyl-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3j)



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

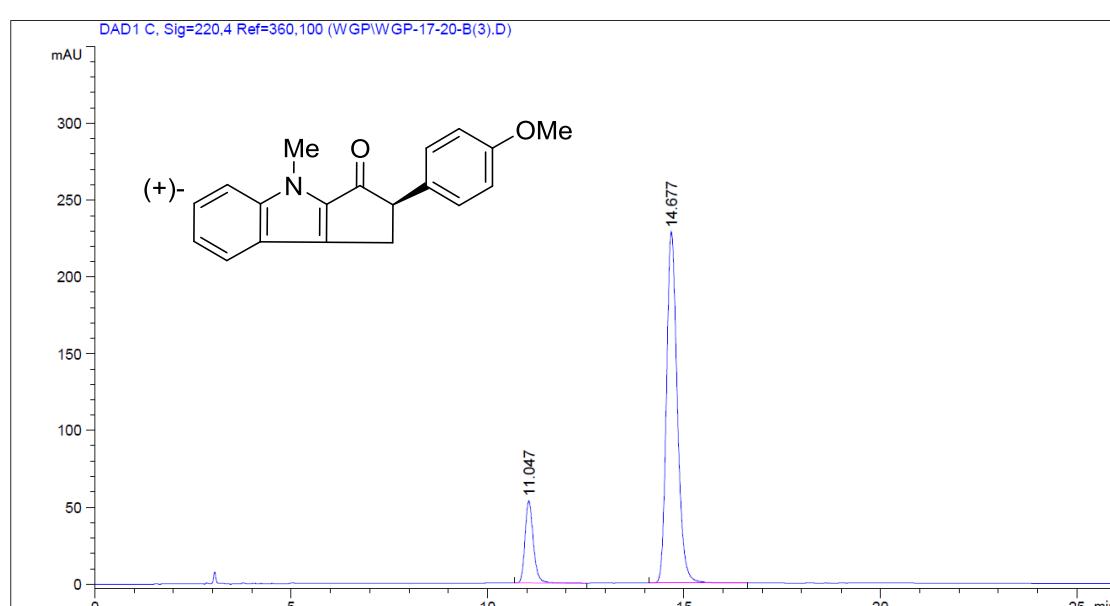
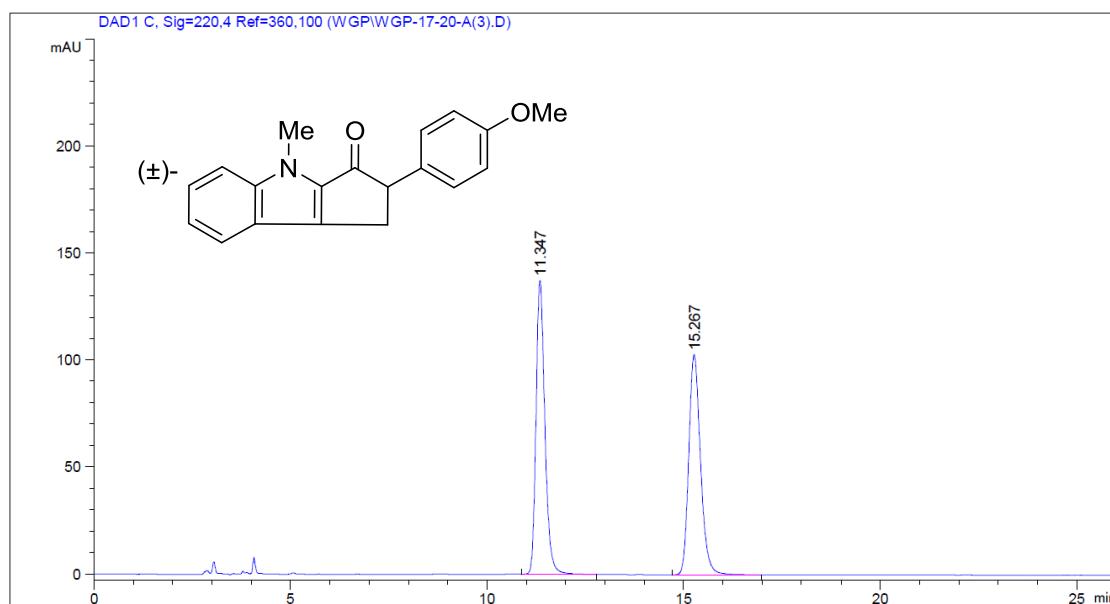


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.881	BB	0.1069	2860.16919	412.65671	49.9539
2	7.989	BB	0.1428	2865.44922	307.12250	50.0461

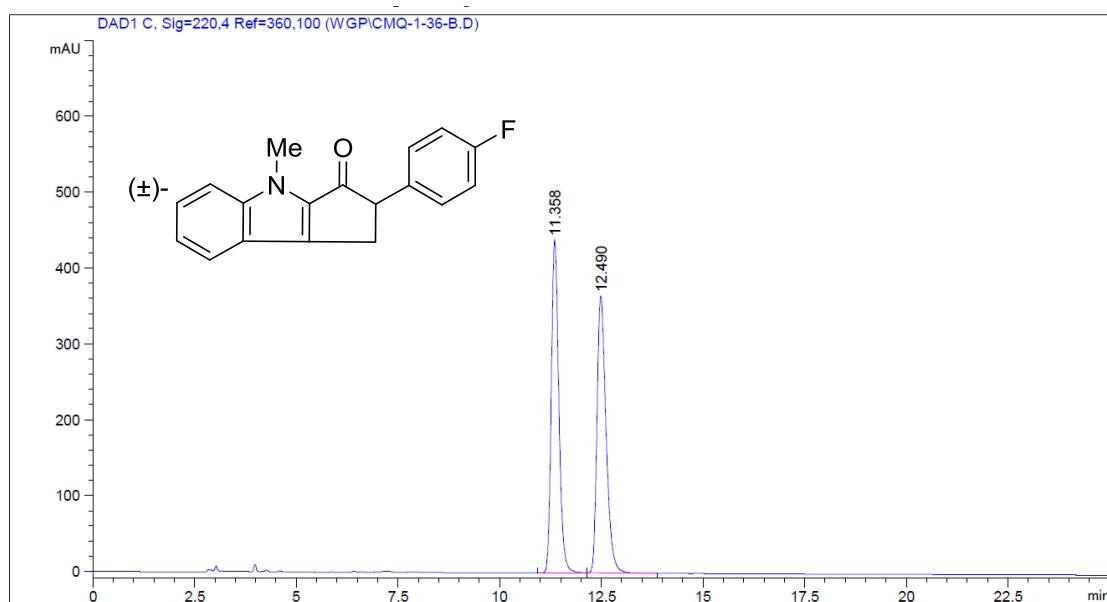


Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.882	BB	0.1012	938.11768	141.71437	14.1556
2	7.932	BB	0.1407	5689.06592	621.92834	85.8444

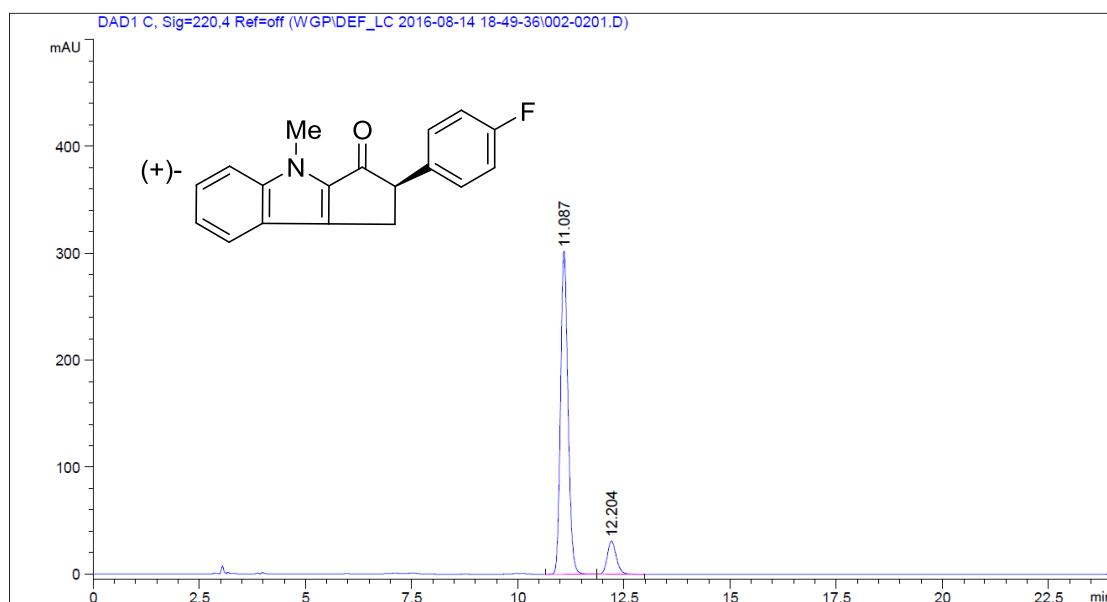
(+)-2-(3-methoxyphenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one(3l)



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

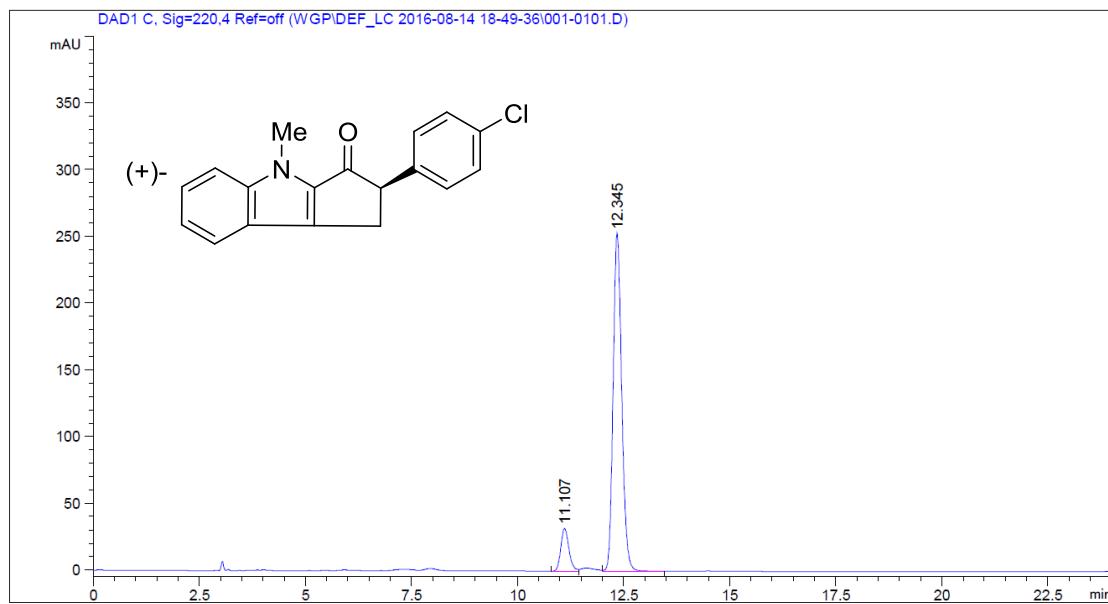
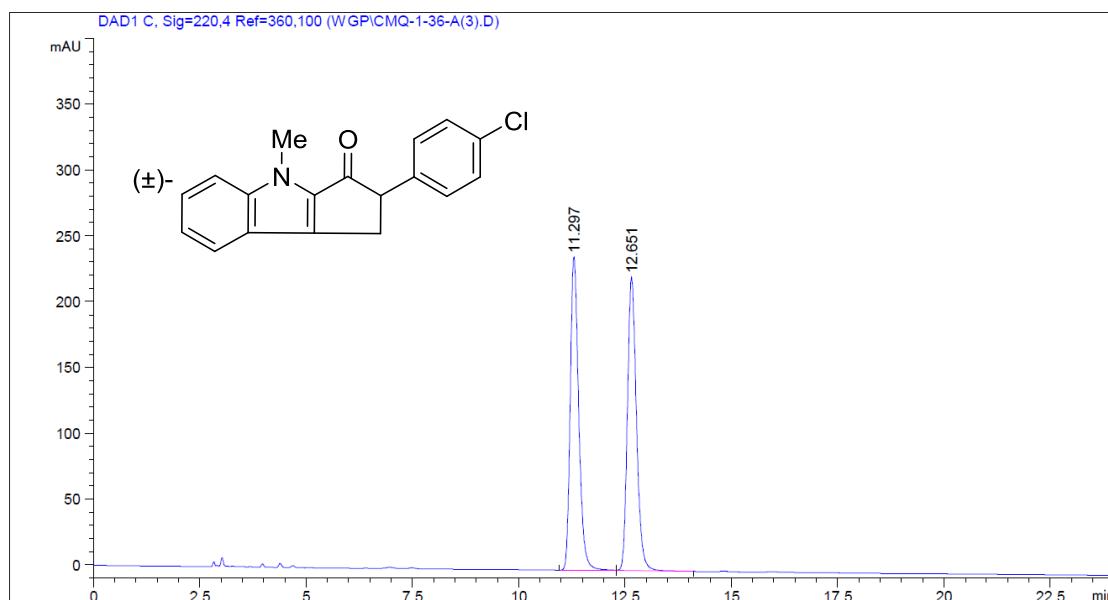


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.358	BB	0.1983	5653.51416	438.91394	50.0182
2	12.490	BB	0.2365	5649.40723	365.24557	49.9818

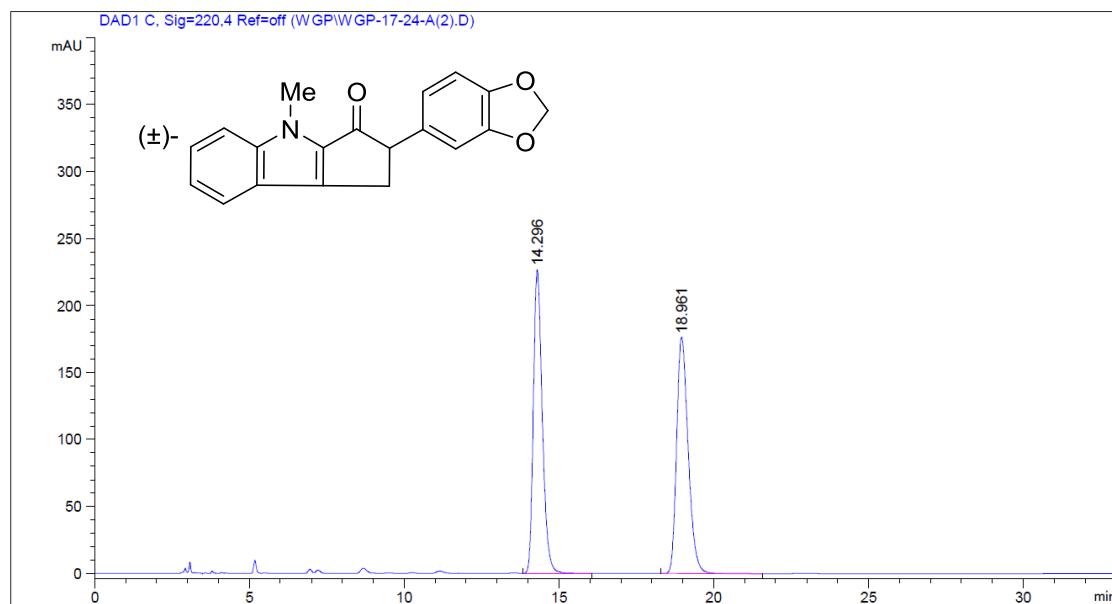


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.087	BB	0.1890	3699.49390	301.81158	88.9780
2	12.204	BB	0.2261	458.26645	31.07299	11.0220

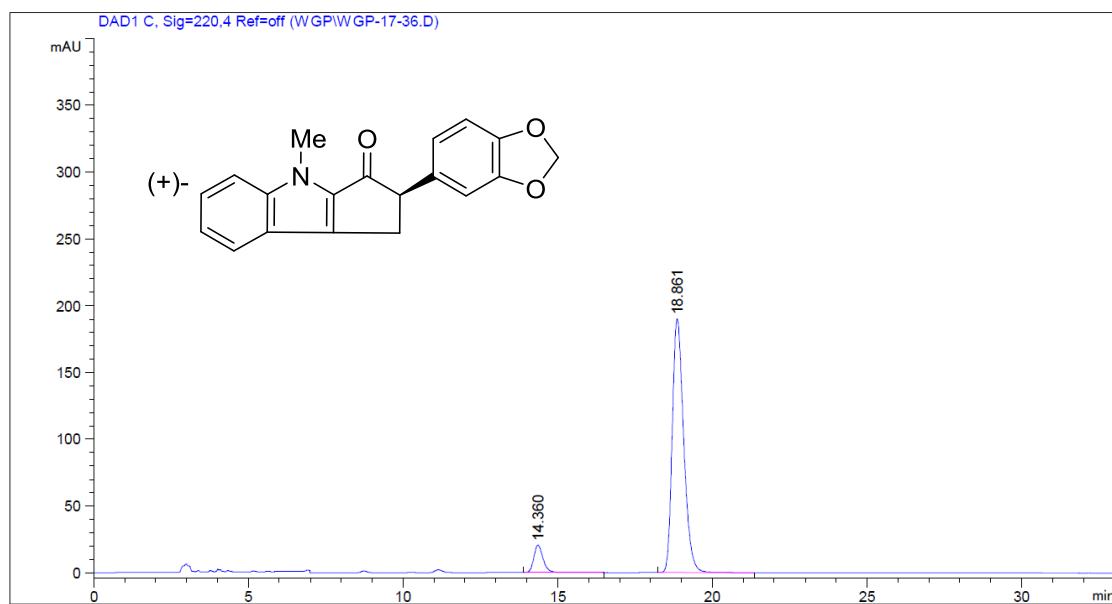
(+)-2-(3-chlorophenyl)-4-methyl-1,4-dihydrocyclopenta[b]indol-3(2H)-one (3n)



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

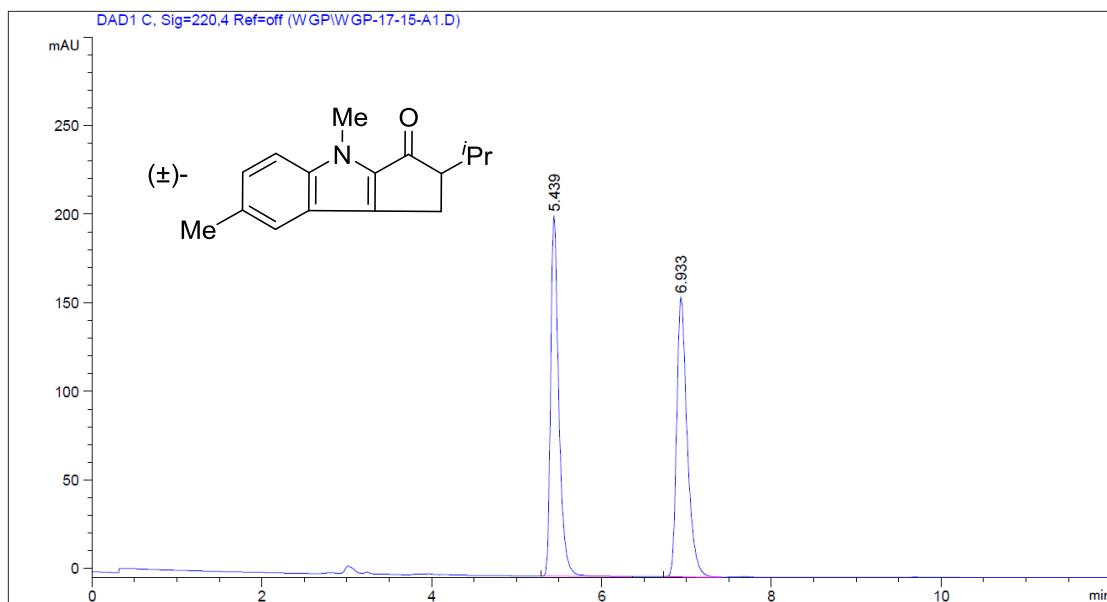


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.296	BB	0.3086	4557.24170	226.62152	49.8959
2	18.961	BB	0.3983	4576.25244	176.58572	50.1041

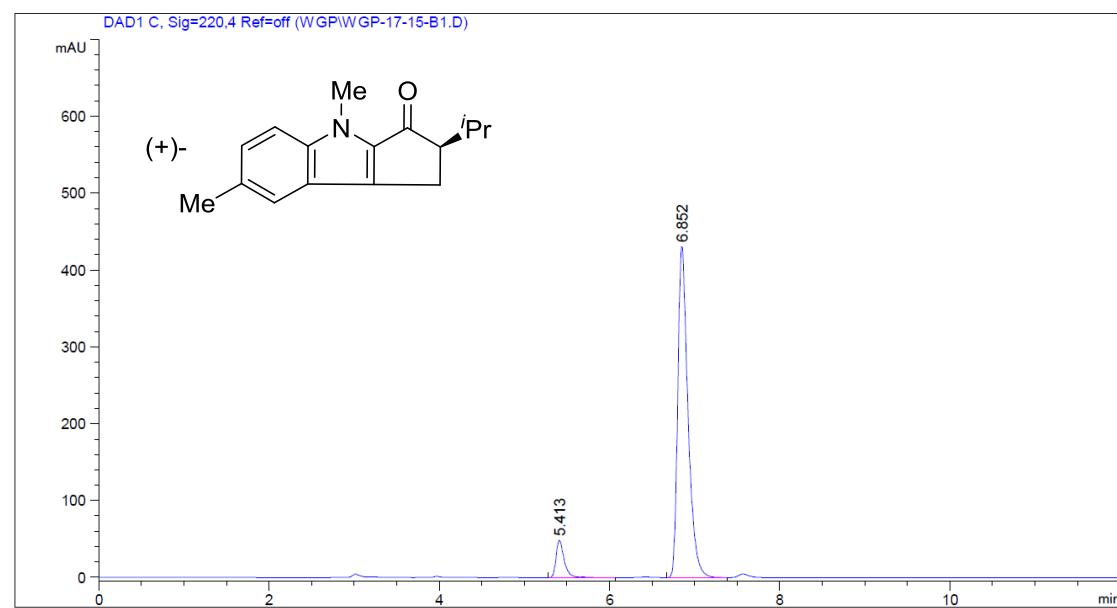


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.360	BB	0.3181	430.48038	20.57157	8.1107
2	18.861	BB	0.3953	4877.05273	190.11383	91.8893

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

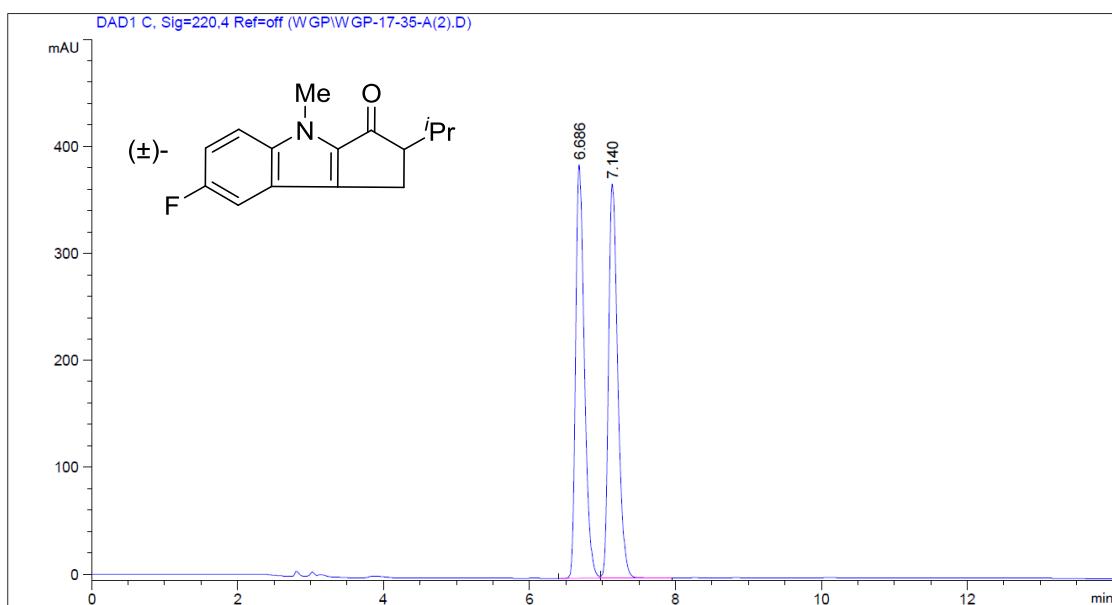


Peak	RetTime	Type	Width	Area	Height	Area %
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.439	BB	0.0998	1358.27197	203.56589	50.0870
2	6.933	BB	0.1301	1353.55603	157.78421	49.9130

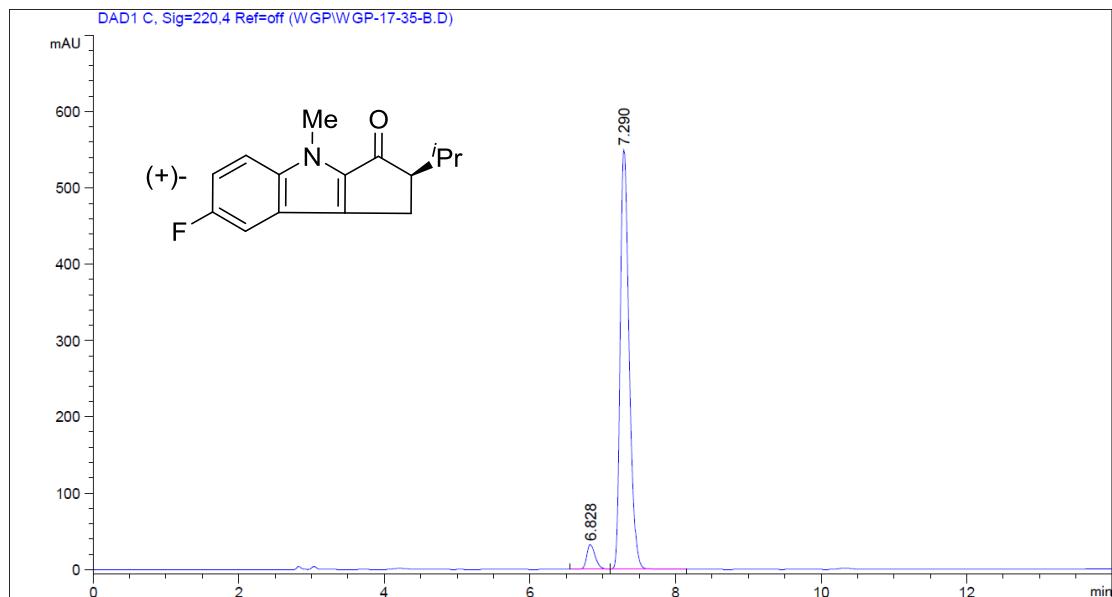


Peak	RetTime	Type	Width	Area	Height	Area %
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.413	BB	0.0989	321.01346	48.69363	8.2061
2	6.852	BB	0.1251	3590.88110	431.42349	91.7939

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

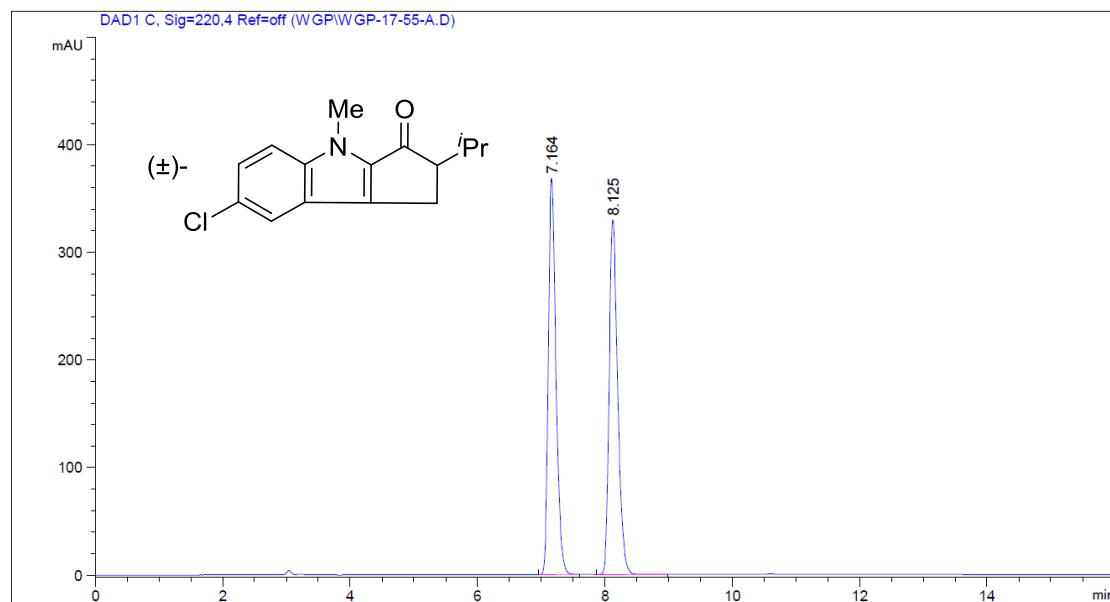


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.686	BV	0.1246	3208.80200	387.34805	49.8647
2	7.140	VB	0.1339	3226.21753	369.28119	50.1353

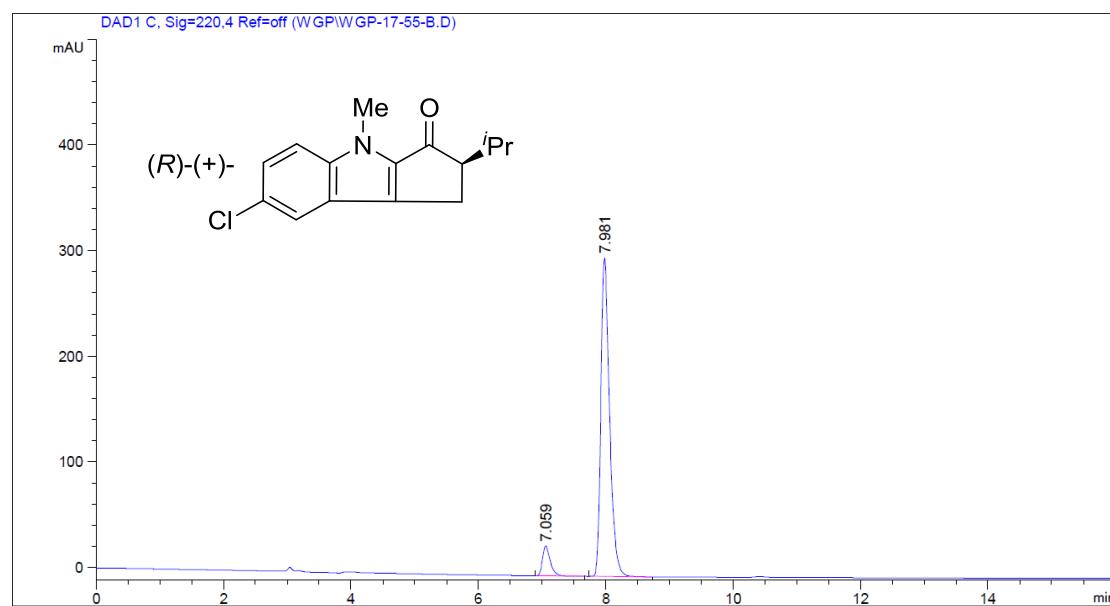


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.828	BV	0.1224	264.10773	32.64989	5.3645
2	7.290	VB	0.1289	4659.09668	549.42303	94.6355

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

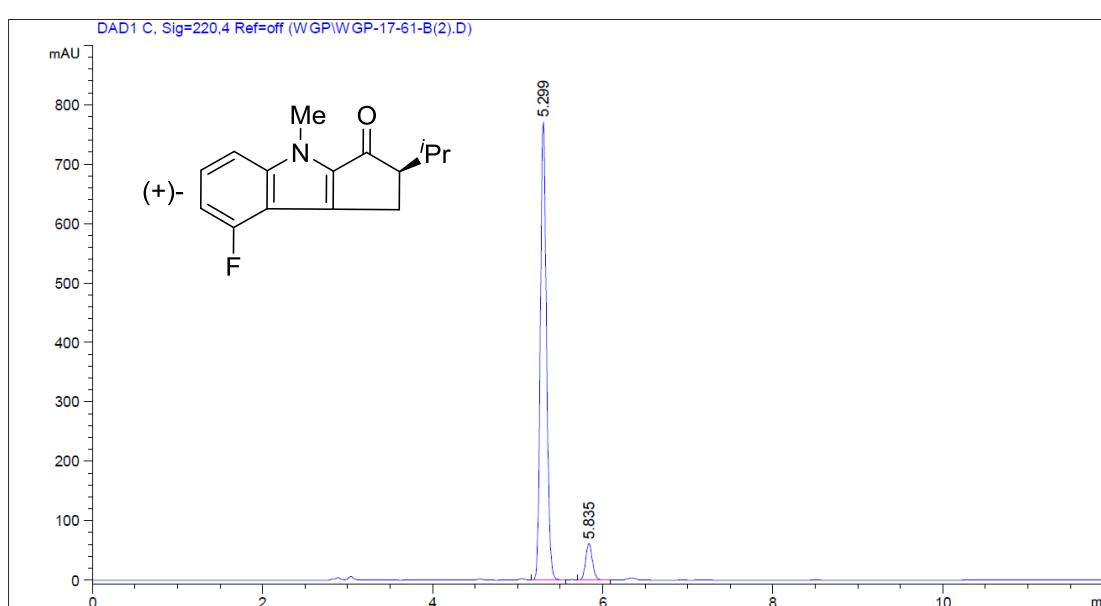
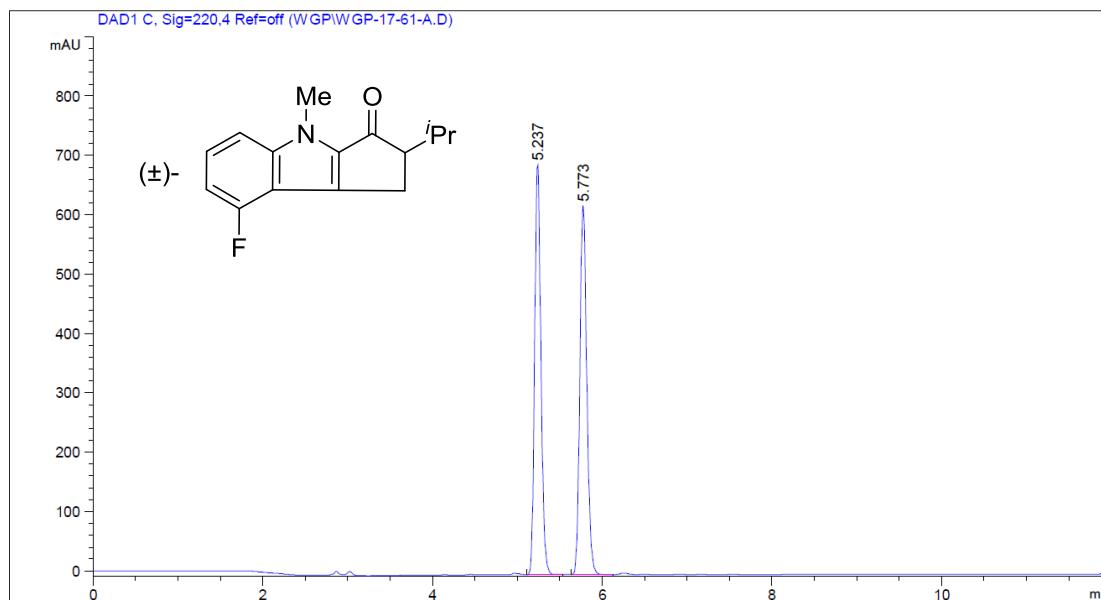


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.164	BB	0.1246	3054.42822	368.89114	49.8458
2	8.125	BB	0.1407	3073.32520	329.81360	50.1542



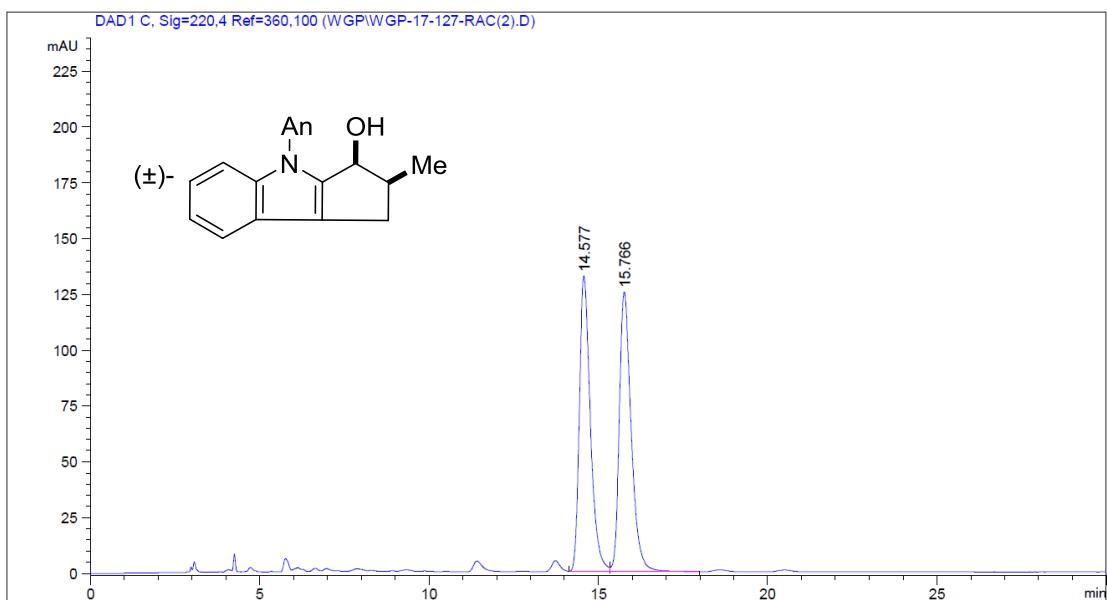
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.059	BB	0.1267	239.48936	28.29431	7.7251
2	7.981	BB	0.1447	2860.64624	301.52655	92.2749

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

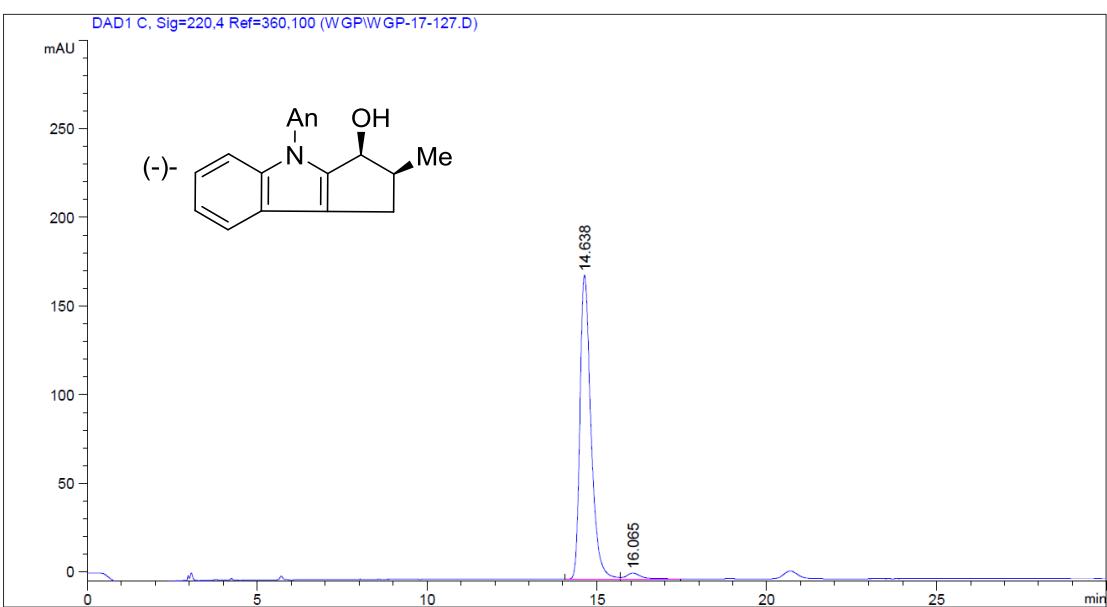


Peak	RetTime	Type	Width	Area	Height	Area %
#	[min]		[min]	[mAU*s]	[mAU]	%
1	5.299	BV	0.0760	3831.00122	771.13232	91.8609
2	5.835	VB	0.0842	339.43655	61.64135	8.1391

(-)4-(4-methoxyphenyl)-2-methyl-1,2,3,4-tetrahydropyran-3-ol (4)



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.577	VV	0.3438	2995.34644	132.46559	49.4498
2	15.766	VB	0.3709	3062.00269	125.37962	50.5502



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	14.638	BV	0.3421	3851.26782	171.45178	97.5308
2	16.065	VB	0.4261	97.50146	3.32474	2.4692

10. References

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