

## *Supporting Information*

### **Organocatalytic Enantioselective and (Z)-Selective Allylation of 3-Indolylmethanol via Hydrogen-bond Activation**

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#### **List of Contents**

- 1. General method**
- 2. General procedure for the synthesis of products 3 and control experiments**
- 3. Characterization data of products 3**
- 4. Copies of NMR spectra for products 3**
- 5. Chiral HPLC analyses of products 3**
- 6. X-ray single crystal data for product 3qb**

## 1. General method

NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was CDCl<sub>3</sub>, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a micrOTOF-Q II HRMS/MS instrument (Bruker). Enantiomeric excesses (*ee*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak AD-H, IC and IA columns. Optical rotation values were measured with instruments operating at  $\lambda = 589$  nm, corresponding to the sodium D line at the temperatures indicated. Analytic grade solvents for the column chromatography and commercially available reagents were used as received. Substrates **1** and **2** were synthesized according to the literature methods.<sup>1</sup>

## 2. General procedure for the synthesis of products **3** and control experiments

The solution of *o*-hydroxystyrene derivatives **2** (0.1 mmol) in EtOAc (1 mL) was added to the mixture of 3-indolylmethanols **1** (0.15 mmol) and the catalyst **5a** or **6a** (0.01 mmol). After the reaction mixture was stirred at 35 °C for 12 h, the resultant solution was concentrated under the reduced pressure to give the residue, which was purified through preparative thin layer chromatography to afford pure products **3**. In all cases, analytic grade EtOAc was used as received, and the reaction was performed under air.

## 3. Characterization data of products **3**

Note: The proton of the phenol moiety is not observed in <sup>1</sup>H NMR for most compounds.

### (*R*)-1-benzyl-3-(2-(2-hydroxyphenyl)allyl)-3-(1H-indol-3-yl)indolin-2-one (**3aa**):

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 77%; pale yellow solid; m.p. 197.1–198.0; [ $\alpha$ ]<sub>D</sub><sup>20</sup> = +18.0 (c 0.20, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.47 (s, 1H), 7.29–7.27 (m, 3H), 7.25–7.23 (m, 3H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.09–7.00 (m, 3H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 2H), 6.85–6.79 (m, 2H), 6.76–6.70 (m, 2H), 5.90 (s, 1H), 5.22 (s, 1H), 5.02 (s, 1H), 4.87 (d, *J* = 15.5 Hz, 1H), 4.39 (d, *J* = 15.5 Hz, 1H), 4.12 (d, *J* = 13.6 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.9, 152.7, 142.8, 142.0, 136.9, 135.9, 132.1, 128.9, 128.8, 128.7, 128.3, 127.9, 127.8, 127.8, 125.3, 125.1, 123.2, 122.8, 122.1, 120.5, 120.0, 119.8, 119.5, 115.7, 115.3, 111.6, 109.5, 53.0, 44.1, 43.3; IR (KBr):  $\gamma$  3650, 3569, 3399, 2928, 1687, 1611, 1486, 1370, 1234, 1014, 908, 801, 748, 692, 645 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (C<sub>32</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires *m/z* 493.1892, found *m/z* 493.1916; Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*<sub>R</sub> = 14.640 min (minor), *t*<sub>R</sub> = 26.580 min (major).

1. (a) Guo, Q.-X.; Peng, Y.-G.; Zhang, J.-W.; Song, L.; Feng, Z.; Gong, L.-Z. *Org. Lett.* **2009**, *11* (20), 4620–4623; (b) L. Song, Q.-X. Guo, X.-C. Li, J. Tian, Y.-G. Peng, *Angew. Chem. Int. Ed.* **2012**, *51*, 1899.

**(S,Z)-1-benzyl-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3ab):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 71%; >20:1 Z/E; pale yellow sticky oil;  $[\alpha]_D^{20} = +15.6$  (c 0.34, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.12 (s, 1H), 7.32–7.29 (m, 5H), 7.19–7.14 (m, 3H), 7.09–7.00 (m, 2H), 6.97 (d,  $J = 7.5$  Hz, 1H), 6.90–6.81 (m, 5H), 6.71–6.66 (m, 2H), 6.25 (s, 1H), 5.71 (s, 1H), 4.89 (d,  $J = 15.5$  Hz, 1H), 4.66 (d,  $J = 15.4$  Hz, 1H), 4.03 (d,  $J = 13.7$  Hz, 1H), 3.14 (s, 1H), 1.39 (d,  $J = 6.7$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.5, 152.6, 142.1, 136.7, 136.0, 131.9, 130.1, 128.9, 128.8, 128.2, 128.0, 127.7, 127.7, 125.7, 125.3, 124.6, 122.9, 122.7, 121.9, 120.6, 119.6, 119.4, 115.1, 111.3, 109.4, 53.2, 45.4, 44.0, 14.9; IR (KBr):  $\gamma$  3551, 3413, 2924, 1688, 1638, 1614, 1488, 1368, 1263, 1013, 801, 749, 699, 617 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (C<sub>33</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires m/z 507.2048, found m/z 507.2067; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R = 11.130$  min (minor),  $t_R = 12.610$  min (major).

**(S,Z)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)-1-methylindolin-2-one (3bb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 76%; >20:1 Z/E; pale yellow sticky oil;  $[\alpha]_D^{20} = +21.4$  (c 0.14, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.20 (s, 1H), 7.31–7.28 (m, 1H), 7.24–7.19 (m, 2H), 7.10–7.04 (m, 2H), 7.00–6.86 (m, 6H), 6.70–6.64 (m, 2H), 5.68 (s, 1H), 4.03 (d,  $J = 13.8$  Hz, 1H), 3.12 (s, 1H), 3.03 (s, 3H), 1.39 (d,  $J = 6.6$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.3, 152.5, 143.3, 136.8, 132.1, 129.8, 129.1, 128.3, 125.3, 124.6, 122.9, 122.6, 121.9, 120.5, 120.2, 119.6, 119.5, 114.8, 111.4, 108.6, 52.9, 45.4, 26.2, 14.8; IR (KBr):  $\gamma$  3651, 3414, 2972, 1701, 1638, 1618, 1385, 1263, 1133, 749, 619 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (2C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires m/z 839.3573, found m/z 839.3569; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R = 20.473$  min (minor),  $t_R = 31.163$  min (major).

**(S,Z)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)-1-phenylindolin-2-one (3cb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 62%; 5:1 Z/E (inseparable isomers); pale yellow sticky oil;  $[\alpha]_D^{20} = -55.1$  (c 0.12, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.25 (s, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 7.40–7.3 (m, 2H), 7.23–7.21 (m, 2H), 7.15–7.13 (m, 2H), 7.07–7.02 (m, 2H), 7.00–6.88 (m, 6H), 6.71 (t,  $J = 7.4$  Hz, 1H), 6.65–6.62 (m, 1H), 5.84 (s, 1H), 5.75 (s, 1H), 4.11 (d,  $J = 13.8$  Hz, 1H), 3.30 (s, 1H), 1.44 (d,  $J = 6.7$  Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.0, 153.0, 143.2, 136.9, 134.5, 132.2, 130.3, 129.5, 129.4, 129.2, 128.1, 128.0, 126.6, 125.4, 124.8, 123.2, 123.1, 122.0, 120.4, 119.9, 119.6, 115.3, 111.6, 109.9, 53.4, 45.3, 15.0; IR (KBr):

$\gamma$  3550, 3412, 3055, 1702, 1638, 1613, 1499, 1485, 1371, 1292, 1225, 1175, 1013, 742, 698, 614  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{32}\text{H}_{26}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  963.3886, found  $m/z$  963.3905; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm):  $t_R = 10.233\text{ min}$  (major),  $t_R = 20.103\text{ min}$  (minor).

**(*R,Z*)-1-(4-bromobenzyl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3db):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 82%; 8:1 *Z/E* (inseparable isomers); colorless sticky oil;  $[\alpha]_D^{20} = -37.2$  (c 0.42,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.29 (s, 1H), 7.38 (d,  $J = 8.4\text{ Hz}$ , 2H), 7.23–7.19 (m, 2H), 7.15 (d,  $J = 8.4\text{ Hz}$ , 3H), 7.09–7.05 (m, 2H), 7.01–6.99 (m, 2H), 6.88–6.83 (m, 3H), 6.76 (d,  $J = 7.8\text{ Hz}$ , 1H), 6.73–6.66 (m, 2H), 5.70 (s, 1H), 4.83 (d,  $J = 15.7\text{ Hz}$ , 1H), 4.47 (d,  $J = 15.7\text{ Hz}$ , 1H), 4.03 (d,  $J = 13.7\text{ Hz}$ , 1H), 3.18 (s, 1H), 1.39 (d,  $J = 6.8\text{ Hz}$ , 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.6, 178.5, 152.6, 142.0, 136.7, 135.0, 132.0, 131.9, 131.7, 130.0, 129.5, 129.4, 129.1, 128.4, 128.1, 125.2, 124.8, 123.0, 122.9, 122.0, 121.6, 120.4, 119.7, 119.4, 115.0, 111.4, 109.3, 53.1, 45.3, 43.4, 14.9; IR (KBr):  $\gamma$  3527, 3444, 3378, 2978, 1629, 1524, 1388, 1263, 1167, 1012, 803, 749, 692, 556  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{BrN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  585.1154, found  $m/z$  585.1165; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm):  $t_R = 22.923\text{ min}$  (major),  $t_R = 31.977\text{ min}$  (minor).

**(*R,Z*)-1-(4-chlorobenzyl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3eb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 70%; 7:1 *Z/E* (inseparable isomers); colorless sticky oil;  $[\alpha]_D^{20} = -50.1$  (c 0.33,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.23 (s, 1H), 7.23–7.15 (m, 6H), 7.09–6.99 (m, 4H), 6.94–6.83 (m, 4H), 6.77 (d,  $J = 7.8\text{ Hz}$ , 1H), 6.73–6.65 (m, 2H), 5.71 (s, 1H), 4.85 (d,  $J = 15.6\text{ Hz}$ , 1H), 4.50 (d,  $J = 15.6\text{ Hz}$ , 1H), 4.02 (d,  $J = 13.7\text{ Hz}$ , 1H), 3.18 (s, 1H), 1.39 (d,  $J = 6.8\text{ Hz}$ , 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.5, 152.7, 152.6, 142.0, 136.7, 134.5, 133.5, 131.9, 130.1, 129.1, 129.1, 129.0, 128.9, 128.8, 128.4, 128.1, 125.2, 122.9, 122.9, 122.0, 120.4, 119.7, 119.4, 115.0, 111.4, 109.3, 53.1, 45.3, 43.3, 14.9; IR (KBr):  $\gamma$  3526, 3443, 3272, 2925, 1696, 1629, 1576, 1488, 1367, 1263, 1094, 1015, 803, 743, 556  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{ClN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  541.1659, found  $m/z$  541.1639; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm):  $t_R = 22.553\text{ min}$  (major),  $t_R = 30.647\text{ min}$  (minor).

**(*R,Z*)-1-(3-chlorobenzyl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3fb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 64%; 9:1 *Z/E* (inseparable isomers); colorless sticky oil;  $[\alpha]_D^{20} = -101.0$  (c 0.33, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.17 (s, 1H), 7.30 (s, 1H), 7.24–7.19 (m, 4H), 7.17–7.14 (m, 2H), 7.11–6.97 (m, 4H), 6.91–6.87 (m, 3H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.72–6.64 (m, 2H), 5.94 (s, 1H), 5.72 (s, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.55 (d, *J* = 15.7 Hz, 1H), 4.03 (d, *J* = 13.8 Hz, 1H), 3.15 (s, 1H), 1.40 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.5, 152.6, 141.9, 138.0, 136.7, 134.6, 131.9, 130.1, 129.0, 128.3, 128.1, 127.9, 127.7, 125.8, 125.3, 124.7, 124.6, 122.9, 122.0, 120.4, 119.6, 115.2, 115.0, 111.3, 109.3, 53.1, 45.4, 43.4, 14.9; IR (KBr):  $\gamma$  3588, 3440, 3179, 2928, 1700, 1626, 1542, 1508, 1488, 1384, 1169, 749, 680 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (C<sub>33</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires *m/z* 541.1659, found *m/z* 541.1660; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t<sub>R</sub>* = 22.673 min (major), *t<sub>R</sub>* = 31.397 min (minor).

**(*R,Z*)-1-(3,4-dichlorobenzyl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3gb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 68%; 8:1 *Z/E* (inseparable isomers); colorless sticky oil;  $[\alpha]_D^{20} = -22.7$  (c 0.35, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.27 (s, 1H), 7.38 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24–7.19 (m, 2H), 7.09–7.06 (m, 3H), 7.03–6.98 (m, 3H), 6.92–6.85 (m, 3H), 6.76–6.67 (m, 3H), 5.72 (s, 1H), 4.80 (d, *J* = 15.6 Hz, 1H), 4.42 (d, *J* = 15.8 Hz, 1H), 4.04 (d, *J* = 13.7 Hz, 1H), 3.18 (s, 1H), 1.39 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.6, 152.5, 141.9, 136.7, 136.3, 132.8, 131.9, 131.8, 130.7, 130.1, 129.5, 129.4, 129.1, 128.4, 128.2, 127.0, 127.0, 125.2, 124.9, 123.1, 123.0, 122.0, 120.2, 119.7, 119.6, 114.9, 111.4, 109.1, 53.0, 45.4, 42.9, 14.9; IR (KBr):  $\gamma$  3525, 3441, 3276, 2925, 1898, 1697, 1603, 1542, 1487, 1365, 1169, 749, 680 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (C<sub>33</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires *m/z* 575.1269, found *m/z* 575.1241; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC, hexane/isopropanol = 90/ 10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t<sub>R</sub>* = 20.170 min (major), *t<sub>R</sub>* = 31.663 min (minor).

**(*S,Z*)-1-benzyl-5-fluoro-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3hb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 84%; 10:1 *Z/E* (inseparable isomers); pale yellow sticky oil;  $[\alpha]_D^{20} = +166.7$  (c 0.16, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.10 (s, 1H), 7.30–7.28 (m, 5H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.12–7.05 (m, 2H), 7.01–6.94 (m, 2H), 6.89–6.80 (m, 4H), 6.73–6.63 (m, 3H), 6.39 (s, 1H), 5.76 (s, 1H), 4.90 (d, *J* = 15.5 Hz, 1H), 4.69 (d, *J* = 15.5 Hz, 1H), 3.98 (d, *J* = 13.5 Hz, 1H), 3.14 (s, 1H), 1.42 (d, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>,

100 MHz)  $\delta$  (ppm): 178.2, 136.7, 135.7, 131.7, 130.4, 128.8, 128.3, 127.8, 127.8, 125.5, 125.1, 122.9, 122.1, 120.3, 119.7, 119.6, 115.1, 114.4, 114.2, 112.7, 111.4, 109.9, 53.6, 45.3, 44.2, 14.9; IR (KBr):  $\gamma$  3549, 3475, 3008, 1638, 1619, 1489, 1456, 1397, 1264, 749, 616  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{33}\text{H}_{27}\text{FN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1027.4011, found  $m/z$  1027.3988; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30  $^{\circ}\text{C}$ , 254 nm):  $t_R$  = 8.543 min (minor),  $t_R$  = 11.930 min (major).

**(S,Z)-1-benzyl-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)-5-methylindolin-2-one (3ib):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 59%; 15:1 Z/E (inseparable isomers); colorless sticky oil;  $[\alpha]_D^{20}$  = +10.6 (c 0.13,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.18 (s, 1H), 7.36–7.28 (m, 6H), 7.24–7.21 (m, 1H), 7.13–7.05 (m, 2H), 6.99–6.93 (m, 2H), 6.88–6.82 (m, 3H), 6.73–6.62 (m, 3H), 5.72 (s, 1H), 4.88 (d,  $J$  = 15.2 Hz, 1H),  $\delta$  4.77 (d,  $J$  = 15.1 Hz, 1H), 3.95 (d,  $J$  = 13.5 Hz, 1H), 3.10 (s, 1H), 2.12 (s, 3H), 1.39 (d,  $J$  = 6.6 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.6, 152.5, 136.7, 136.1, 132.3, 130.1, 128.8, 128.3, 128.1, 127.9, 127.7, 126.1, 125.4, 123.0, 121.9, 120.6, 119.5, 119.4, 115.1, 111.3, 109.1, 100.0, 53.4, 45.2, 44.1, 21.1, 14.9; IR (KBr):  $\gamma$  3550, 3474, 3416, 2922, 1638, 1619, 1489, 1385, 1261, 749, 615  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1019.4512, found  $m/z$  1019.4486; Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30  $^{\circ}\text{C}$ , 254 nm):  $t_R$  = 10.940 min (minor),  $t_R$  = 18.500 min (major).

**(S,Z)-1-benzyl-6-bromo-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3jb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 45%; 10:1 Z/E (inseparable isomers); pale yellow sticky oil;  $[\alpha]_D^{20}$  = +41.0 (c 0.17,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.08 (s, 1H), 7.30–7.27 (m, 6H), 7.25–7.23 (m, 1H), 7.15–7.07 (m, 2H), 7.01–6.97 (m, 2H), 6.93–6.87 (m, 3H), 6.78 (d,  $J$  = 7.1 Hz, 1H), 6.68–6.63 (m, 2H), 6.12 (s, 1H), 5.74 (s, 1H), 4.87 (d,  $J$  = 15.5 Hz, 1H), 4.63 (d,  $J$  = 15.5 Hz, 1H), 3.96 (d,  $J$  = 13.5 Hz, 1H), 3.13 (s, 1H), 1.41 (d,  $J$  = 6.7 Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.2, 152.4, 136.7, 135.4, 131.7, 128.9, 128.3, 127.9, 127.7, 125.8, 125.5, 125.1, 122.9, 122.2, 121.4, 120.5, 119.7, 115.1, 112.6, 111.3, 52.9, 45.4, 44.1, 14.9; IR (KBr):  $\gamma$  3350, 3475, 3416, 2923, 1638, 1618, 1486, 1385, 1260, 749, 617  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{33}\text{H}_{27}\text{BrN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1147.2410, found  $m/z$  1147.2399; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30  $^{\circ}\text{C}$ , 254 nm):  $t_R$  = 7.967 min (minor),  $t_R$  = 10.853 min (major).

**(S,Z)-1-benzyl-7-fluoro-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3kb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 58%; >20:1 *Z/E*; colorless sticky oil;  $[\alpha]_{\text{D}}^{20} = -105.5$  (c 0.18,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.11 (s, 1H), 7.39 (d,  $J = 5.7$  Hz, 2H), 7.28–7.27 (m, 3H), 7.24–7.15 (m, 2H), 7.11–7.03 (m, 2H), 6.99–6.77 (m, 6H), 6.70–6.65 (m, 2H), 6.30 (s, 1H), 5.69 (s, 1H), 4.98 (d,  $J = 15.0$  Hz, 1H), 4.88 (d,  $J = 15.1$  Hz, 1H), 3.97 (d,  $J = 13.6$  Hz, 1H), 3.09 (s, 1H), 1.37 (d,  $J = 5.2$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.4, 152.8, 149.0, 146.5, 137.2, 136.8, 131.7, 130.5, 128.9, 128.7, 128.4, 128.3, 127.8, 125.6, 125.2, 123.4, 123.1, 122.1, 120.5, 119.7, 119.6, 116.2, 116.0, 115.2, 111.4, 53.5, 45.7, 45.6, 15.0; IR (KBr):  $\gamma$  3549, 3470, 3415, 2930, 1697, 1637, 1487, 1456, 1384, 1243, 1182, 749, 615  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{FN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  525.1954, found  $m/z$  525.1924; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min,  $T = 30$  °C, 254 nm):  $t_{\text{R}} = 7.320$  min (minor),  $t_{\text{R}} = 11.823$  min (major).

**(*S,Z*)-1-benzyl-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(1H-indol-3-yl)-7-methylindolin-2-one (3lb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 71%; >20:1 *Z/E*; colorless sticky oil;  $[\alpha]_{\text{D}}^{20} = +129.3$  (c 0.17,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.25 (s, 1H), 7.24–7.19 (m, 4H), 7.17 (d,  $J = 8.0$  Hz, 1H), 7.13–7.10 (m, 2H), 7.08–6.99 (m, 3H), 6.94–6.86 (m, 5H), 6.73–6.68 (m, 2H), 5.99 (s, 1H), 5.70 (s, 1H), 5.05 (d,  $J = 15.7$  Hz, 1H), 4.86–4.81 (m, 1H), 4.08 (d,  $J = 13.8$  Hz, 1H), 3.15 (s, 1H), 2.33 (s, 3H), 1.42 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 179.8, 152.8, 140.5, 138.0, 136.8, 132.2, 132.1, 130.1, 129.2, 128.8, 128.4, 127.2, 126.1, 125.4, 123.4, 123.3, 122.9, 121.9, 120.8, 120.4, 119.7, 119.4, 115.04, 111.5, 52.5, 46.2, 45.2, 19.2, 15.0; IR (KBr):  $\gamma$  3548, 3476, 3415, 2924, 1688, 1638, 1602, 1486, 1446, 1354, 1262, 1160, 1009, 794, 599, 549  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1019.4512, found  $m/z$  1019.4506; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min,  $T = 30$  °C, 254 nm):  $t_{\text{R}} = 8.240$  min (major),  $t_{\text{R}} = 10.673$  min (minor).

**(*S,Z*)-1-benzyl-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(5-methyl-1H-indol-3-yl)indolin-2-one (3mb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 71%; >20:1 *Z/E*; colorless sticky oil;  $[\alpha]_{\text{D}}^{20} = -45.3$  (c 0.13,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.07 (s, 1H), 7.33–7.28 (m, 4H), 7.25–7.11 (m, 4H), 6.99 (t,  $J = 7.6$  Hz, 1H), 6.91–6.76 (m, 6H), 6.73–6.66 (m, 2H), 5.96 (s, 1H), 5.72 (s, 1H), 4.89 (d,  $J = 15.5$  Hz, 1H), 4.58 (d,  $J = 15.8$  Hz, 1H), 4.02 (d,  $J = 13.6$  Hz, 1H), 3.14 (s, 1H), 2.23 (s, 3H), 1.39 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.6, 152.6, 142.3, 136.0, 135.1, 132.0, 130.0, 128.9, 128.8, 128.5, 128.3, 128.0, 127.7, 127.6, 125.5, 124.6, 123.6, 123.0, 122.7, 120.2, 119.6, 115.0, 110.9, 109.4, 53.1, 45.3, 44.0, 21.7, 14.9; IR

(KBr):  $\gamma$  3548, 3474, 3415, 2928, 1685, 1616, 1487, 1384, 1261, 1169, 1106, 794, 750, 697, 609  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  521.2205, found  $m/z$  521.2199; Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 90/ 10, flow rate 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm):  $t_R = 18.683$  min (major),  $t_R = 22.827$  min (minor).

**(S,Z)-1-benzyl-3-(5-chloro-1H-indol-3-yl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)indolin-2-one (3nb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 54%; 5:1 Z/E (inseparable isomers); colorless sticky oil;  $[\alpha]_D^{20} = +39.4$  (c 0.11,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.38 (s, 1H), 7.32–7.28 (m, 5H), 7.21–7.13 (m, 2H), 7.05–7.02 (m, 2H), 6.97–6.92 (m, 3H), 6.90–6.82 (m, 3H), 6.71–6.61 (m, 2H), 6.21 (s, 1H), 5.70 (s, 1H), 4.90 (d,  $J = 15.6$  Hz, 1H), 4.65 (d,  $J = 15.6$  Hz, 1H), 3.96 (d,  $J = 13.7$  Hz, 1H), 3.06 (s, 1H), 1.39 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.5, 152.5, 135.8, 135.0, 131.6, 128.94, 128.9, 128.3, 127.7, 127.5, 127.4, 126.2, 125.1, 124.5, 123.0, 122.2, 119.8, 119.6, 115.0, 112.3, 109.7, 53.0, 45.5, 44.1, 14.9; IR (KBr):  $\gamma$  3549, 3478, 3416, 2942, 1637, 1618, 1542, 1508, 1385, 1261, 1139, 749, 617  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{ClN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  541.1659, found  $m/z$  541.1659; Enantiomeric excess: 96%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm):  $t_R = 10.160$  min (minor),  $t_R = 15.560$  min (major).

**(S,Z)-1-benzyl-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(6-methyl-1H-indol-3-yl)indolin-2-one (3ob):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 60%; >20:1 Z/E; colorless sticky oil;  $[\alpha]_D^{20} = -146.7$  (c 0.13,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.02 (s, 1H), 7.30–7.27 (m, 5H), 7.23–7.12 (m, 2H), 7.00–6.99 (m, 3H), 6.93–6.79 (m, 4H), 6.74–6.66 (m, 3H), 5.98 (s, 1H), 5.71 (s, 1H), 4.87 (d,  $J = 15.5$  Hz, 1H), 4.62 (d,  $J = 15.2$  Hz, 1H), 3.99 (d,  $J = 13.8$  Hz, 1H), 3.15 (s, 1H), 2.36 (s, 3H), 1.38 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.5, 152.6, 142.2, 137.2, 136.0, 132.0, 131.7, 130.0, 128.9, 128.7, 128.3, 128.0, 127.8, 127.6, 124.6, 123.1, 122.7, 122.3, 121.2, 120.2, 119.6, 115.1, 111.2, 109.4, 53.1, 45.3, 44.0, 21.5, 14.9; IR (KBr):  $\gamma$  3550, 3474, 3416, 2920, 1695, 1616, 1487, 1466, 1384, 1263, 1170, 1106, 799, 749, 698, 609  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  521.2205, found  $m/z$  521.2209; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min,  $T = 30\text{ }^\circ\text{C}$ , 254 nm):  $t_R = 9.497$  min (minor),  $t_R = 13.667$  min (major).

**(S,Z)-1-benzyl-3-(6-fluoro-1H-indol-3-yl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)indolin-2-one (3pb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 87%; >20:1 Z/E; colorless sticky oil;  $[\alpha]_D^{20} = +37.8$  (c 0.14,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm):

8.19 (s, 1H), 7.30–7.27 (m, 6H), 7.18 (t,  $J = 7.2$  Hz, 1H), 7.01–6.93 (m, 3H), 6.85–6.79 (m, 4H), 6.70 (t,  $J = 7.4$  Hz, 1H), 6.65–6.56 (m, 2H), 6.14 (s, 1H), 5.70 (s, 1H), 4.89 (d,  $J = 15.4$  Hz, 1H), 4.63 (d,  $J = 15.3$  Hz, 1H), 3.97 (d,  $J = 13.6$  Hz, 1H), 3.10 (s, 1H), 1.39 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.5, 160.8, 158.4, 152.6, 136.8, 136.7, 135.8, 131.7, 130.2, 128.9, 128.8, 128.3, 128.2, 127.8, 125.5, 124.5, 123.3, 122.8, 121.8, 121.2, 119.7, 115.1, 109.5, 108.2, 108.0, 97.6, 97.3, 53.0, 45.4, 44.0, 14.9; IR (KBr):  $\gamma$  3548, 3472, 3417, 2928, 1638, 1618, 1543, 1509, 1458, 1385, 1262, 749, 613  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{33}\text{H}_{27}\text{FN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1027.4011, found  $m/z$  1027.4017; Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min,  $T = 30$  °C, 254 nm):  $t_R = 13.380$  min (minor),  $t_R = 15.637$  min (major).

**(*S,Z*)-1-benzyl-3-(6-bromo-1H-indol-3-yl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)indolin-2-one (3qb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 64%; >20:1 *Z/E*; pale yellow solid;  $[\alpha]_D^{20} = -85.6$  (c 0.14,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.30 (s, 1H), 7.30–7.28 (m, 7H), 7.20–7.16 (m, 1H), 7.02–6.98 (m, 1H), 6.92–6.84 (m, 6H), 6.74–6.66 (m, 2H), 6.04 (s, 1H), 5.69 (s, 1H), 4.88 (d,  $J = 15.4$  Hz, 1H), 4.62 (d,  $J = 15.3$  Hz, 1H), 3.94 (d,  $J = 13.6$  Hz, 1H), 3.09 (s, 1H), 1.38 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.5, 152.7, 137.6, 135.9, 131.7, 128.9, 128.5, 128.3, 127.9, 127.9, 124.6, 124.3, 123.7, 123.0, 122.8, 121.8, 119.8, 115.7, 115.2, 114.3, 109.7, 53.1, 45.6, 44.2, 15.0; IR (KBr):  $\gamma$  3549, 3478, 3416, 2930, 1684, 1618, 1542, 1508, 1483, 1458, 1364, 1261, 1079, 798, 749, 618  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{BrN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  585.1154, found  $m/z$  585.1141; Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min,  $T = 30$  °C, 254 nm):  $t_R = 17.110$  min (minor),  $t_R = 20.563$  min (major).

**(*S,Z*)-1-benzyl-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)-3-(7-methyl-1H-indol-3-yl)indolin-2-one (3rb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 53%; >20:1 *Z/E*; colorless sticky oil;  $[\alpha]_D^{20} = -76.3$  (c 0.12,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.01 (s, 1H), 7.32–7.28 (m, 5H), 7.25–7.14 (m, 2H), 6.99–6.94 (m, 3H), 6.91–6.76 (m, 5H), 6.69–6.65 (m, 2H), 6.12 (s, 1H), 5.72 (s, 1H), 4.88 (d,  $J = 15.5$  Hz, 1H), 4.64 (d,  $J = 15.5$  Hz, 1H), 4.03 (d,  $J = 13.6$  Hz, 1H), 3.15 (s, 1H), 2.33 (s, 3H), 1.39 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.5, 152.7, 142.2, 136.2, 136.0, 132.0, 130.0, 128.9, 128.7, 128.2, 128.0, 127.8, 127.7, 124.8, 124.6, 122.7, 122.5, 120.3, 119.6, 119.5, 118.3, 115.0, 109.4, 53.2, 45.3, 44.0, 16.5, 14.9; IR (KBr):  $\gamma$  3548, 3475, 4316, 2926, 1638, 1618, 1541, 1507, 1488, 1456, 1397, 1261, 1092, 750, 616  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{34}\text{H}_{30}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1019.4512, found  $m/z$  1019.4502; Enantiomeric excess: 86%,

determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R$  = 10.923 min (minor),  $t_R$  = 12.240 min (major).

**(S,Z)-1-benzyl-3-(7-bromo-1H-indol-3-yl)-3-(2-(2-hydroxyphenyl)but-2-en-1-yl)indolin-2-one (3sb):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 44%; >20:1 Z/E; pale yellow sticky oil;  $[\alpha]_D^{20}$  = -71.4 (c 0.11, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.12 (s, 1H), 7.30–7.28 (m, 6H), 7.23–7.13 (m, 4H), 6.96 (t,  $J$  = 7.6 Hz, 2H), 6.83 (d,  $J$  = 7.7 Hz, 2H), 6.75 (t,  $J$  = 7.9 Hz, 1H), 6.66–6.62 (m, 2H), 6.34 (s, 1H), 5.70 (s, 1H), 4.89 (d,  $J$  = 15.4 Hz, 1H), 4.67 (d,  $J$  = 15.5 Hz, 1H), 3.99 (d,  $J$  = 13.7 Hz, 1H), 3.04 (s, 1H), 1.39 (d,  $J$  = 6.7 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.1, 152.7, 136.0, 135.4, 131.8, 130.5, 128.9, 128.8, 128.4, 128.3, 127.9, 126.7, 124.5, 123.5, 122.9, 120.8, 120.1, 119.7, 115.2, 109.7, 104.9, 53.3, 45.6, 44.1, 15.0; IR (KBr):  $\gamma$  3551, 3492, 3416, 2918, 1637, 1620, 1556, 1539, 1472, 1416, 1258, 1078, 770, 615 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (C<sub>33</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires m/z 585.1154, found m/z 585.1174; Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R$  = 11.860 min (minor),  $t_R$  = 22.987 min (major).

**(R,Z)-1-benzyl-3-(2-(2-hydroxyphenyl)pent-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3ac):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 62%; 6:1 Z/E (inseparable isomers); pale yellow sticky oil;  $[\alpha]_D^{20}$  = -44.2 (c 0.18, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm): 8.16 (s, 1H), 7.30–7.29 (m, 3H), 7.24–7.13 (m, 5H), 7.08–7.03 (m, 2H), 6.97–6.94 (m, 2H), 6.90–6.81 (m, 4H), 6.70–6.64 (m, 2H), 6.20 (s, 1H), 5.55 (s, 1H), 4.90 (d,  $J$  = 15.5 Hz, 1H), 4.59 (d,  $J$  = 15.5 Hz, 1H), 3.98 (d,  $J$  = 13.7 Hz, 1H), 3.05 (s, 1H), 1.72–1.66 (m, 2H), 0.79 (t,  $J$  = 7.4 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm): 178.6, 152.7, 137.8, 136.7, 136.0, 130.1, 129.0, 128.7, 128.6, 128.2, 128.0, 127.8, 127.7, 125.3, 123.1, 122.8, 121.9, 120.5, 119.5, 119.4, 111.3, 109.4, 53.2, 45.3, 44.0, 22.5, 13.7; IR (KBr):  $\gamma$  3651, 3437, 2942, 1700, 1738, 1612, 1543, 1509, 1489, 1458, 1385, 1243, 1098, 748, 698 cm<sup>-1</sup>; ESI FTMS exact mass calcd for (C<sub>34</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>+Na)<sup>+</sup> requires m/z 521.2205, found m/z 521.2192; Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R$  = 25.100 min (minor),  $t_R$  = 29.987 min (major).

**(R,Z)-1-benzyl-3-(2-(2-hydroxyphenyl)-4-phenylbut-2-en-1-yl)-3-(1H-indol-3-yl)indolin-2-one (3ad):**

Preparative thin layer chromatography: dichloromethane/acetic ether = 10/1; Reaction time = 12 h; yield: 75%; 6:1 Z/E (inseparable isomers); colorless oil;  $[\alpha]_D^{20}$  = +48.1 (c 0.16, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (s, 1H), 7.31–7.30 (m, 3H), 7.28–7.24 (m, 7H), 7.22–7.16 (m, 5H), 7.07–7.02 (m, 4H), 6.85 (d,  $J$  = 7.7 Hz, 2H), 6.73 (d,  $J$  = 8.0 Hz, 2H), 5.87 (s, 1H), 5.74 (s, 1H), 4.95 (d,  $J$  = 15.5 Hz, 1H), 4.56 (d,

$J = 12.4$  Hz, 1H), 4.04 (d,  $J = 11.5$  Hz, 1H), 3.16-3.07 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  178.7, 153.1, 140.4, 136.7, 135.9, 134.0, 129.2, 128.7, 128.7, 128.5, 128.4, 128.4, 128.0, 127.7, 127.7, 126.1, 125.9, 125.8, 125.3, 124.6, 123.0, 121.9, 120.5, 119.6, 119.4, 115.5, 111.3, 109.4, 100.0, 53.2, 52.6, 44.0, 35.3; IR (KBr):  $\gamma$  3547, 3474, 3314, 2923, 1686, 1648, 1487, 1451, 1400, 1364, 1168, 1014, 741, 697  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(2\text{C}_{39}\text{H}_{32}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  1143.4825, found  $m/z$  1143.4817; Enantiomeric excess: 90%, determined by HPLC (Daicel Chirapak IA, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min,  $T = 30$  °C, 254 nm):  $t_R = 13.317$  min (minor),  $t_R = 18.390$  min (major).

**(R)-1-(4-chlorobenzyl)-3-(2-(2-hydroxy-5-methylphenyl)allyl)-3-(1H-indol-3-yl)indolin-2-one (3ed):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 47%; colorless sticky oil;  $[\alpha]_{\text{D}}^{20} = -70.4$  (c 0.25,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.49 (s, 1H), 7.25–7.16 (m, 6H), 7.10–7.05 (m, 2H), 6.98 (d,  $J = 2.6$  Hz, 1H), 6.91–6.78 (m, 2H), 6.85–6.79 (m, 2H), 6.73 (d,  $J = 7.8$  Hz, 1H), 6.61 (d,  $J = 8.2$  Hz, 1H), 6.54 (d,  $J = 1.8$  Hz, 1H), 5.74 (s, 1H), 5.20 (s, 1H), 5.00 (d,  $J = 1.6$  Hz, 1H), 4.84 (d,  $J = 15.6$  Hz, 1H), 4.32 (d,  $J = 15.6$  Hz, 1H), 4.10 (d,  $J = 13.5$  Hz, 1H), 3.40 (d,  $J = 13.6$  Hz, 1H), 2.15 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.8, 150.3, 142.4, 142.2, 136.8, 134.4, 133.5, 132.1, 129.4, 129.2, 129.1, 128.8, 128.7, 128.2, 127.4, 125.1, 125.1, 123.1, 122.9, 122.0, 120.2, 119.7, 119.4, 115.3, 115.1, 111.5, 109.1, 52.8, 43.3, 43.1, 20.4; IR (KBr):  $\gamma$  3527, 3442, 3275, 2925, 1701, 1629, 1598, 1542, 1265, 1200, 1015, 814, 744, 556  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{ClN}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  541.1659, found  $m/z$  541.1641; Enantiomeric excess: 89%, determined by HPLC (Daicel Chirapak AD-H, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min,  $T = 30$  °C, 254 nm):  $t_R = 15.590$  min (minor),  $t_R = 36.027$  min (major).

**(R)-1-(4-bromobenzyl)-3-(2-(2-hydroxy-5-methoxyphenyl)allyl)-3-(1H-indol-3-yl)indolin-2-one (3de):**

Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 47%; colorless sticky oil;  $[\alpha]_{\text{D}}^{20} = -111.7$  (c 0.20,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.48 (s, 1H), 7.39 (d,  $J = 8.3$  Hz, 2H), 7.31–7.26 (m, 2H), 7.21 (d,  $J = 8.3$  Hz, 2H), 7.09–7.00 (m, 2H), 6.90 (d,  $J = 7.3$  Hz, 1H), 6.76–6.69 (m, 4H), 6.54–6.47 (m, 2H), 5.70 (d,  $J = 2.9$  Hz, 1H), 5.18 (s, 1H), 4.93 (d,  $J = 1.8$  Hz, 1H), 4.74 (d,  $J = 15.6$  Hz, 1H), 4.56 (d,  $J = 15.7$  Hz, 1H), 4.00 (d,  $J = 13.1$  Hz, 1H), 3.76 (d,  $J = 13.0$  Hz, 1H), 3.45 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 179.2, 151.9, 147.0, 144.1, 142.1, 136.8, 134.9, 132.0, 131.4, 129.6, 129.4, 127.5, 124.9, 124.8, 122.9, 122.5, 121.2, 119.6, 119.0, 118.5, 115.4, 114.7, 113.9, 113.7, 111.2, 108.4, 55.0, 53.1, 43.1, 41.3; IR (KBr):  $\gamma$  3527, 3444, 3269, 2962, 1698, 1541, 1487, 1260, 1092, 1017, 869, 799, 744, 556  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{27}\text{BrN}_2\text{O}_3+\text{Na})^+$  requires  $m/z$  601.1103, found  $m/z$  601.1102; Enantiomeric excess: 89%, determined by HPLC (Daicel

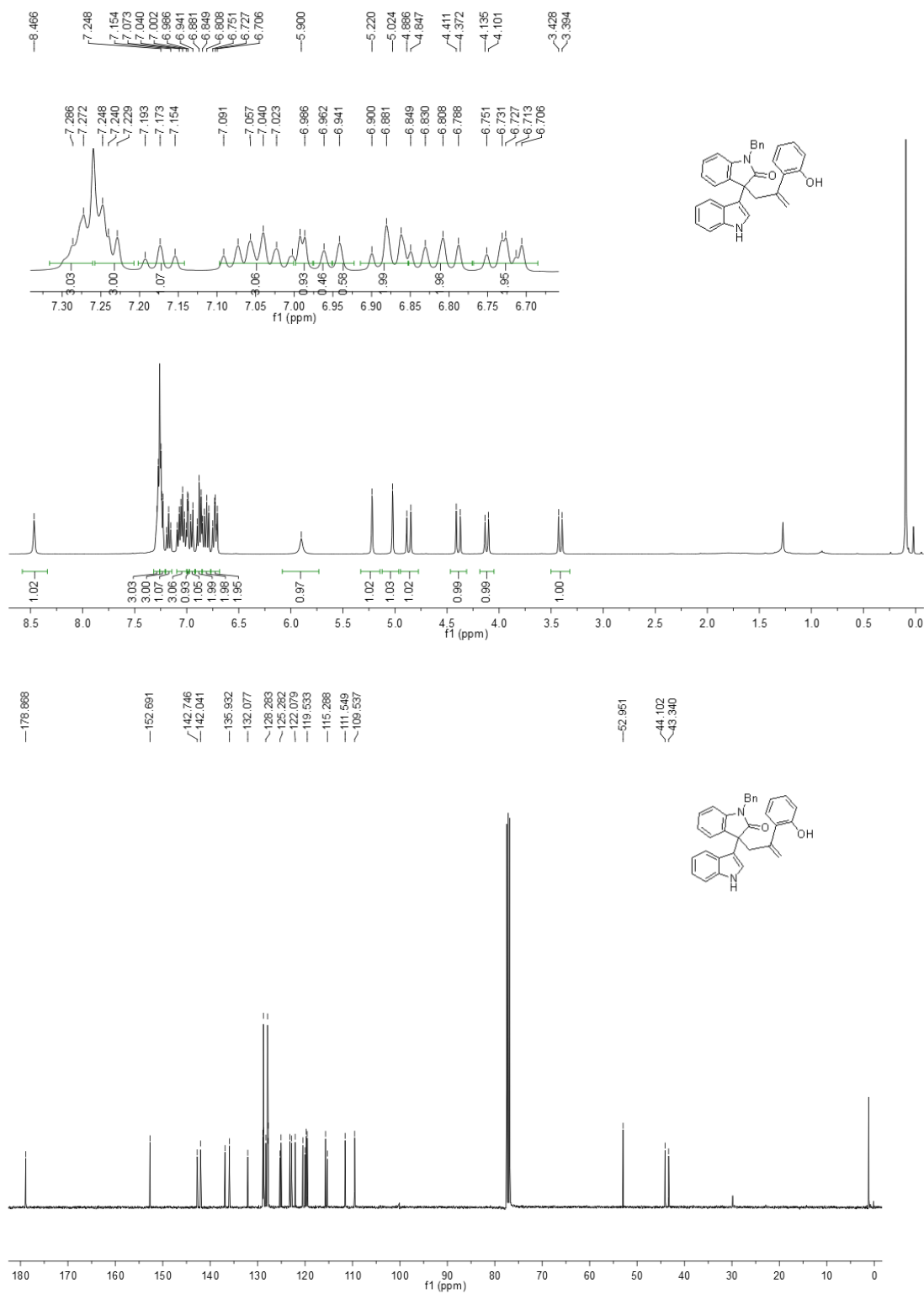
Chirapak IC, hexane/ isopropanol = 70/ 30, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R$  = 6.737 min (major),  $t_R$  = 7.470 min (minor).

**1-benzyl-3-(1H-indol-3-yl)-3-(2-(2-methoxyphenyl)allyl)indolin-2-one (3af):**

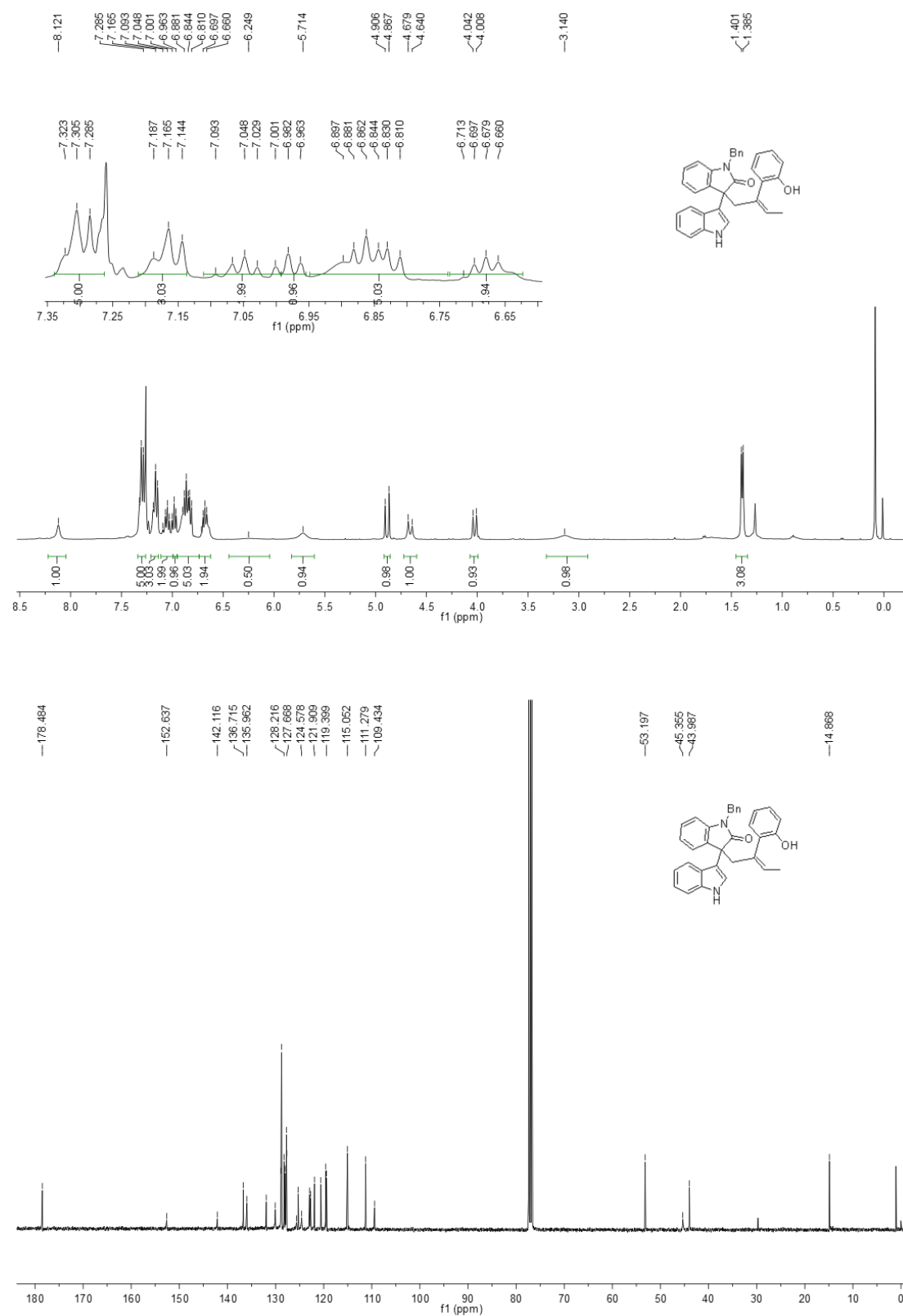
Preparative thin layer chromatography: toluene/acetic ether = 5/1; Reaction time = 12 h; yield: 29%; colorless sticky oil;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 8.21 (s, 1H), 7.29–7.27 (m, 3H), 7.25–7.21 (m, 3H), 7.10–7.03 (m, 5H), 6.91 (d,  $J$  = 7.3 Hz, 1H), 6.83 (t,  $J$  = 7.6 Hz, 1H), 6.72 (t,  $J$  = 7.5 Hz, 1H), 6.66 (t,  $J$  = 8.6 Hz, 2H), 6.56 (t,  $J$  = 7.4 Hz, 1H), 6.22 (d,  $J$  = 7.4 Hz, 1H), 5.22 (s, 1H), 4.93 (s, 1H), 4.82 (d,  $J$  = 15.5 Hz, 1H), 4.38 (d,  $J$  = 15.6 Hz, 1H), 4.10 (d,  $J$  = 13.2 Hz, 1H), 3.79 (s, 3H), 3.62 (d,  $J$  = 13.2 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 178.3, 156.2, 144.4, 143.1, 136.8, 136.2, 131.7, 131.1, 129.7, 128.5, 128.2, 127.8, 127.7, 127.5, 125.4, 125.1, 122.6, 122.0, 120.9, 119.9, 119.6, 119.4, 116.5, 111.2, 109.9, 108.6, 55.2, 53.0, 43.9, 41.9; IR (KBr):  $\gamma$  3677, 3630, 3414, 1700, 1638, 1612, 1543, 1489, 1458, 1385, 1243, 1098, 748, 698  $\text{cm}^{-1}$ ; ESI FTMS exact mass calcd for  $(\text{C}_{33}\text{H}_{28}\text{N}_2\text{O}_2+\text{Na})^+$  requires  $m/z$  507.2048, found  $m/z$  507.2046; Enantiomeric excess: 4%, determined by HPLC (Daicel Chirapak IC, hexane/ isopropanol = 80/ 20, flow rate 1.0 mL/min, T = 30 °C, 254 nm):  $t_R$  = 8.973 min (minor),  $t_R$  = 16.283 min (major).

## Copies of NMR spectra for products 3

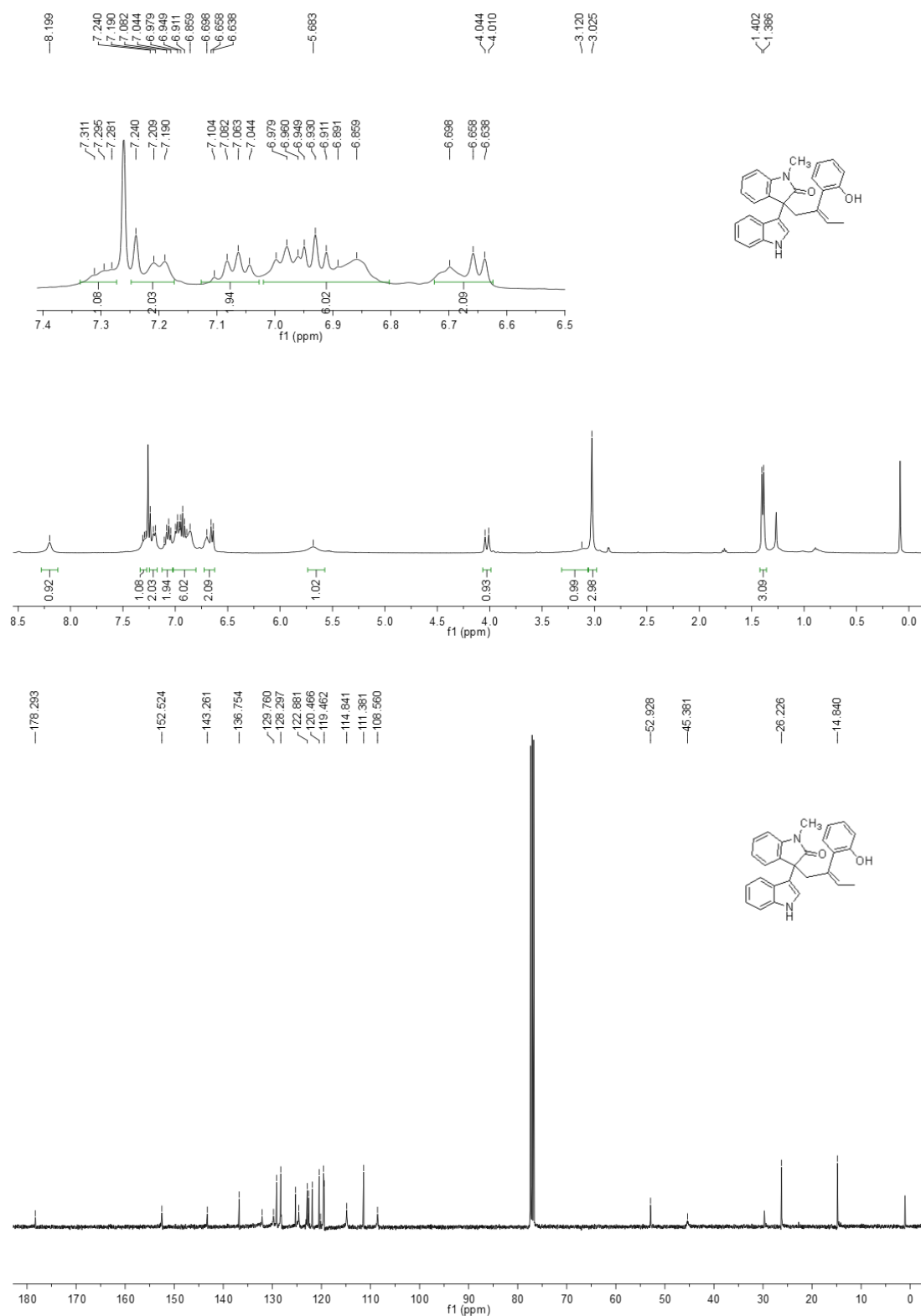
**3aa :**



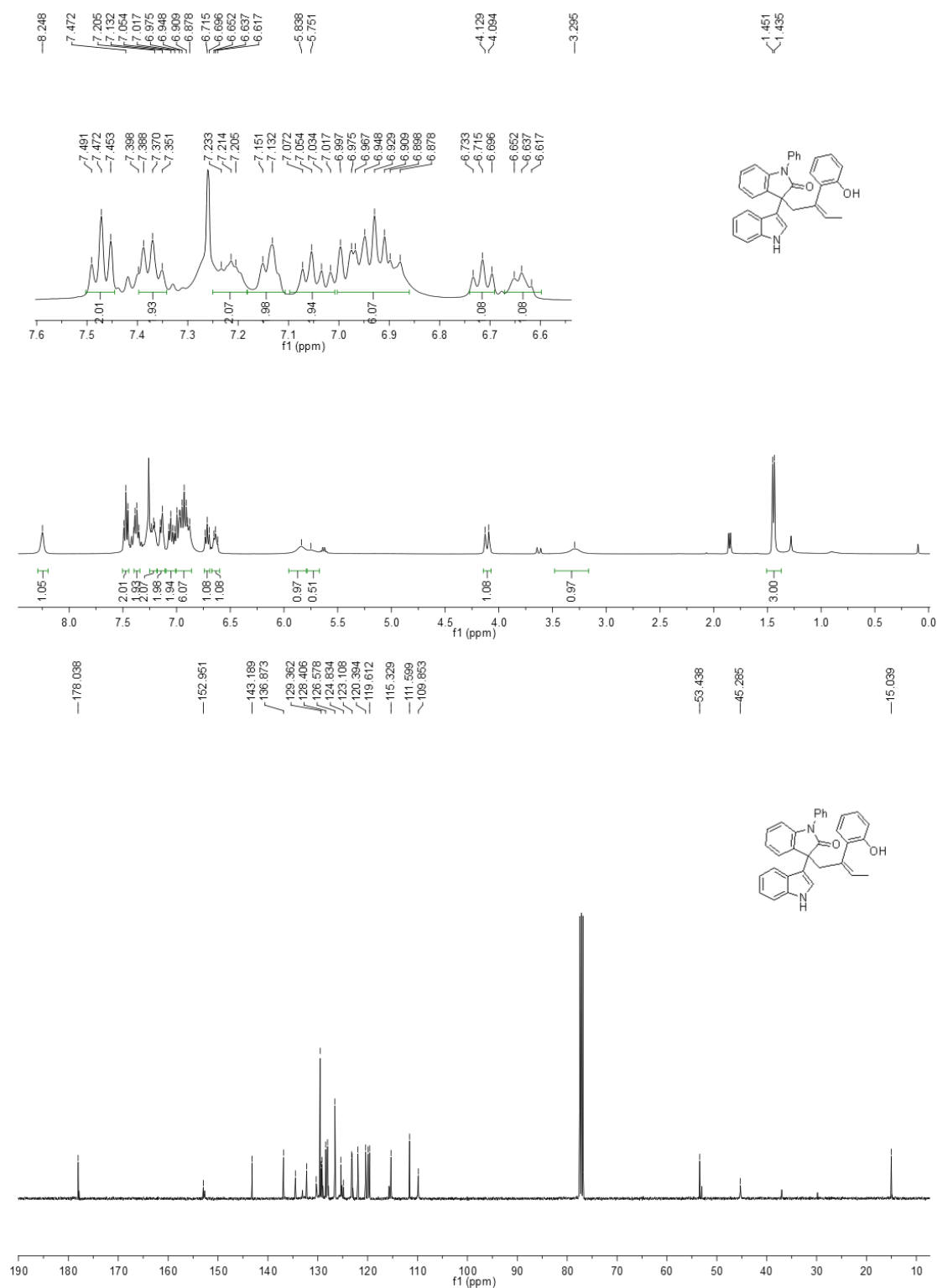
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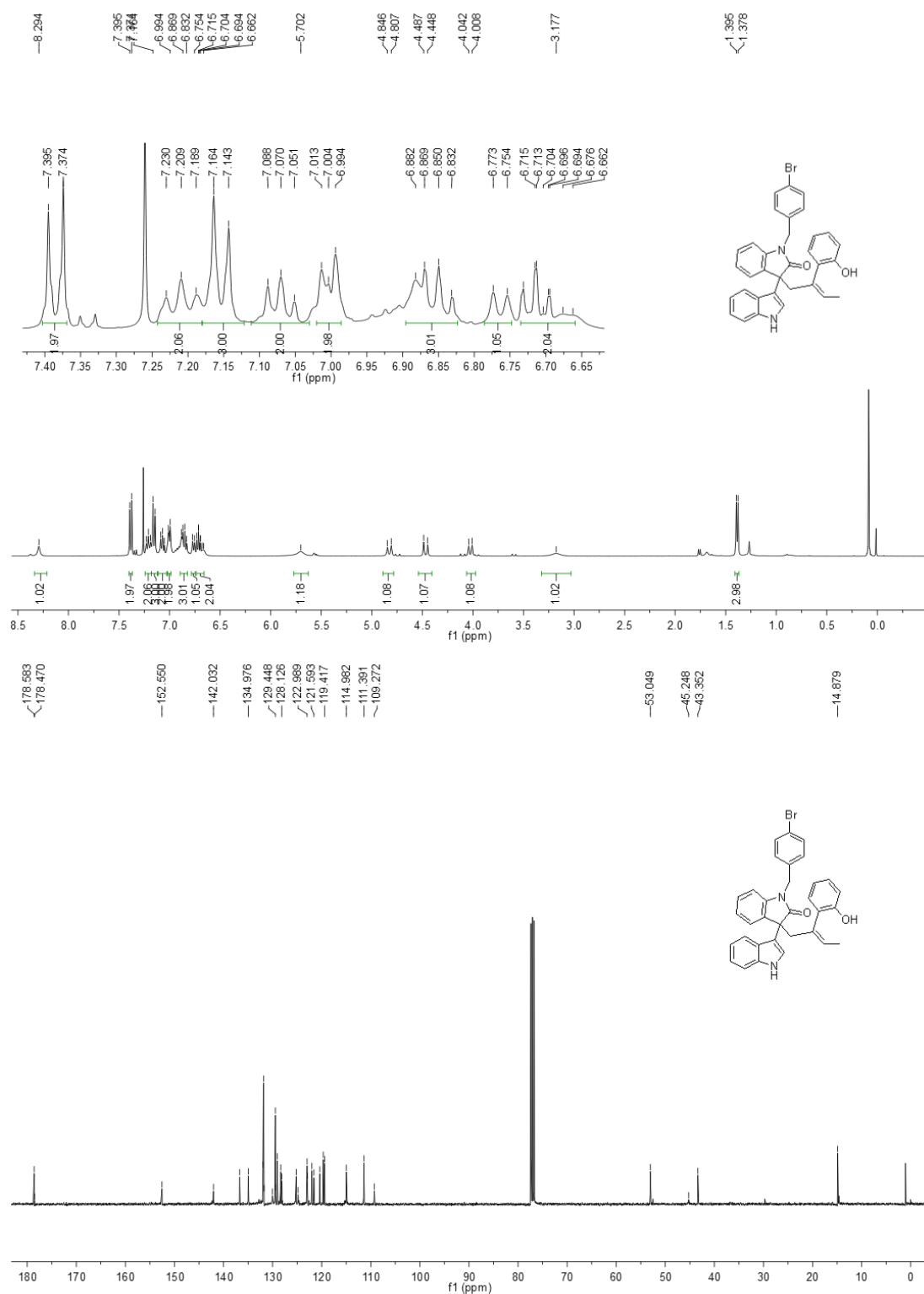
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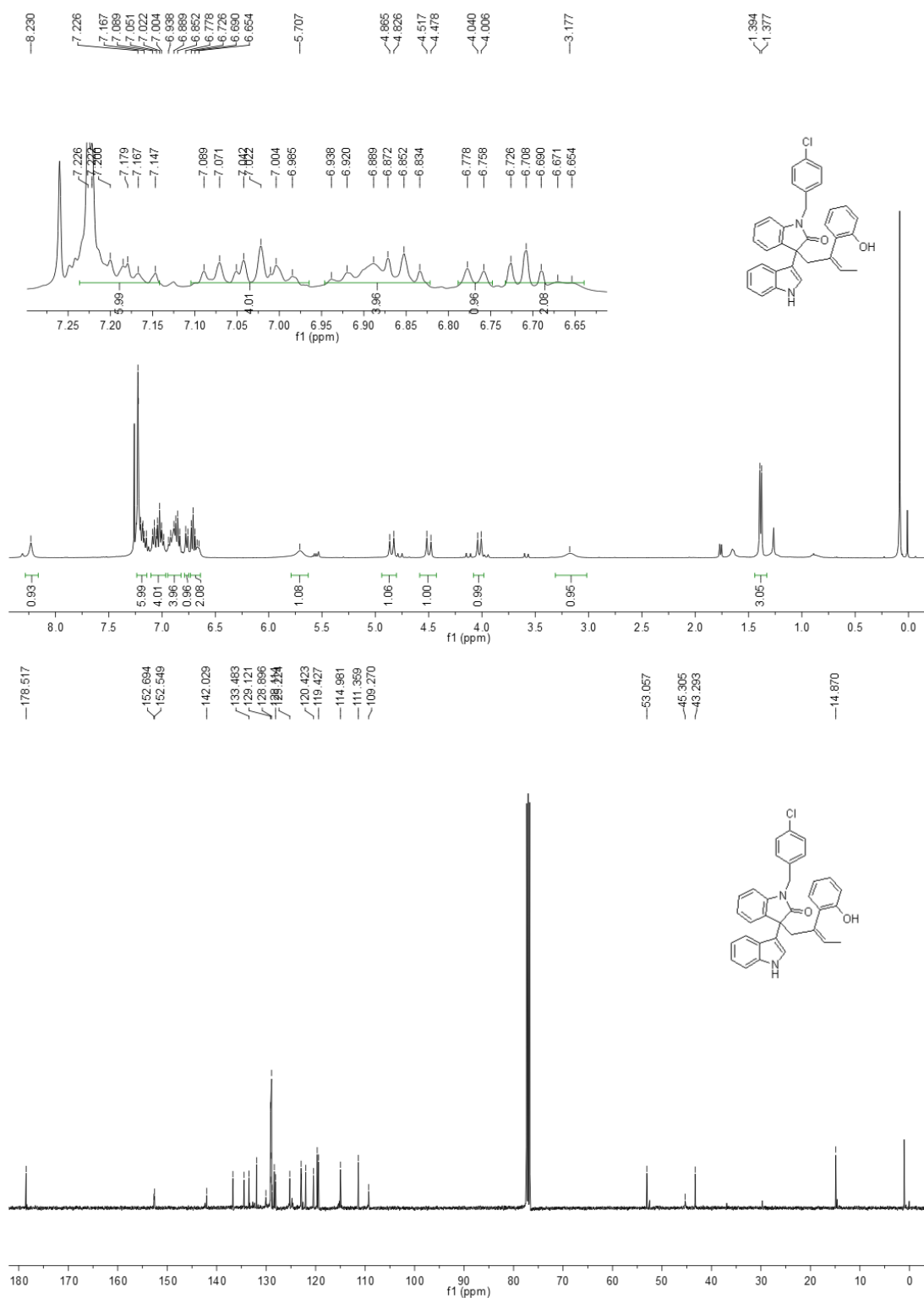
**3cb:** (inseparable 5:1 *Z/E* isomers)



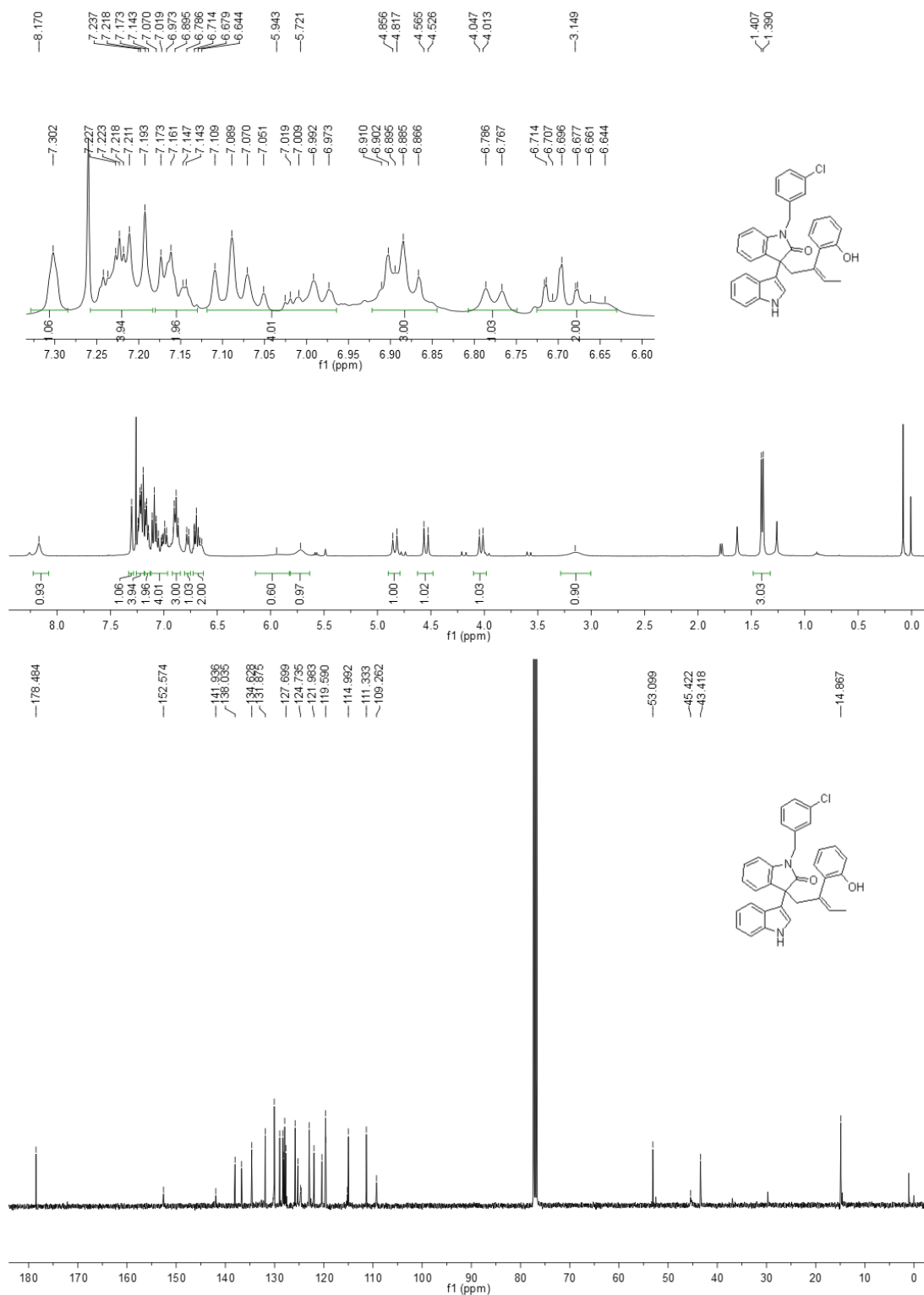
**3db:** (inseparable 8:1 *Z/E* isomers)



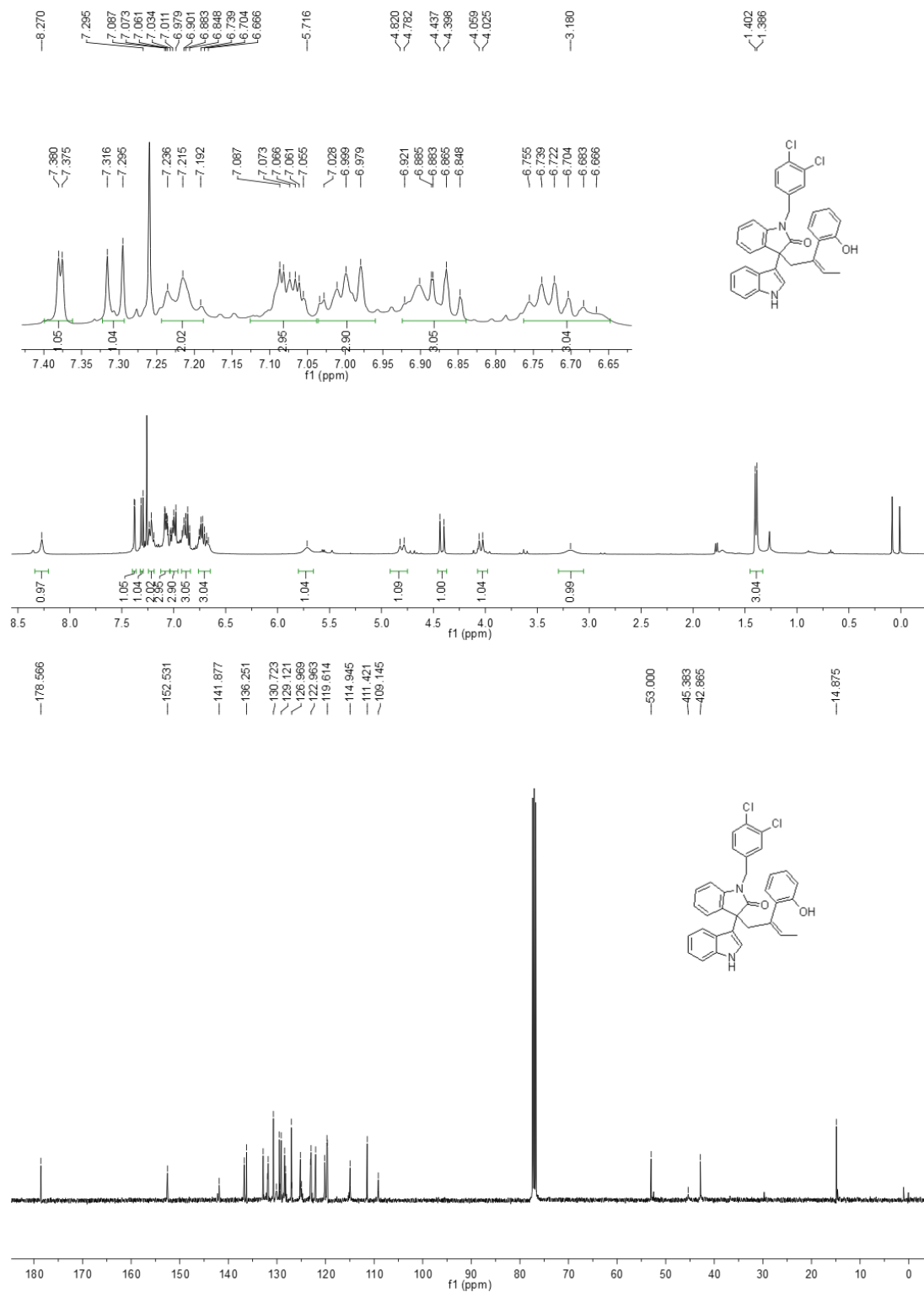
**3eb:** (inseparable 7:1 *Z/E* isomers)



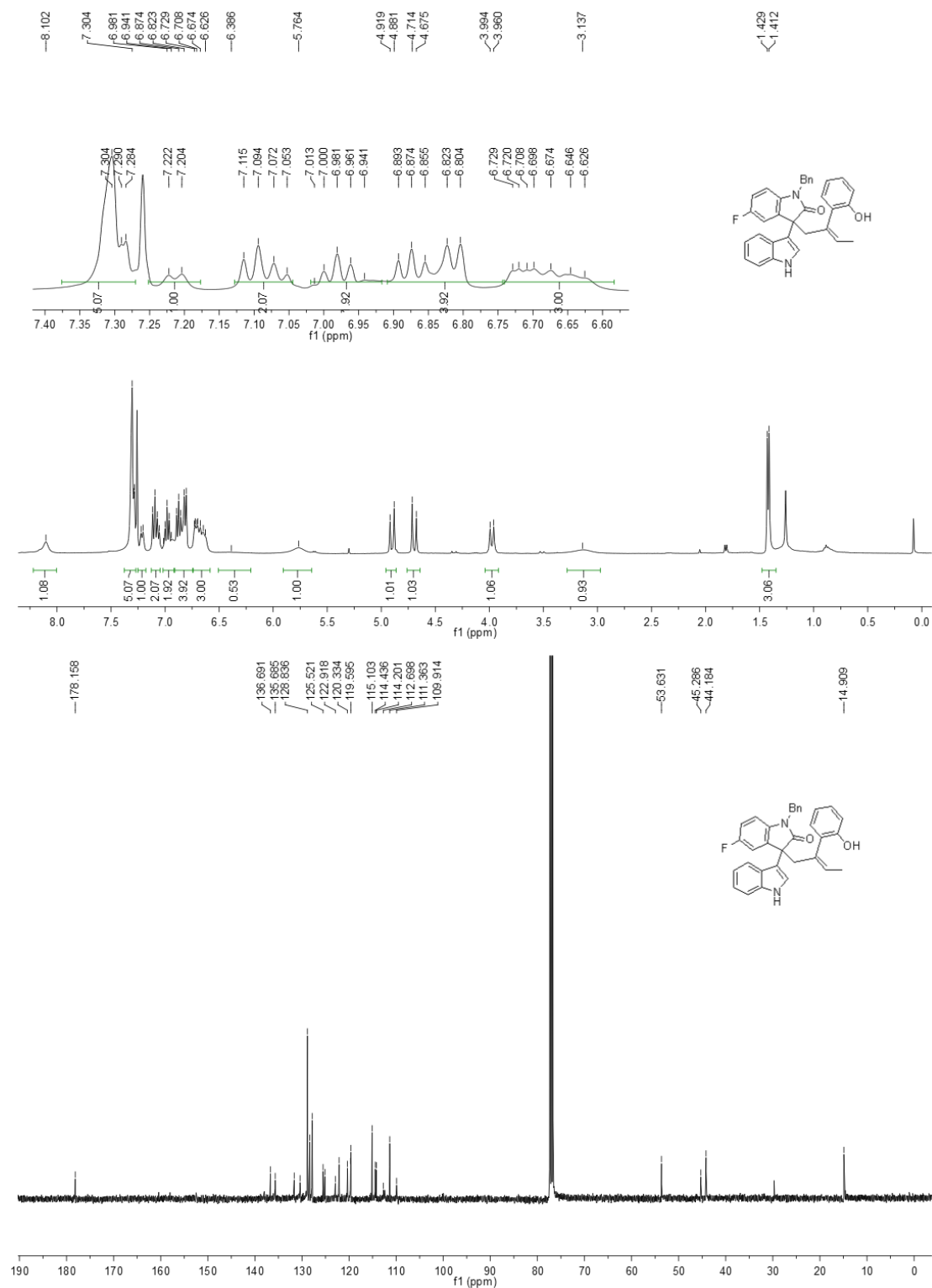
**3fb:** (inseparable 9:1 *Z/E* isomers)



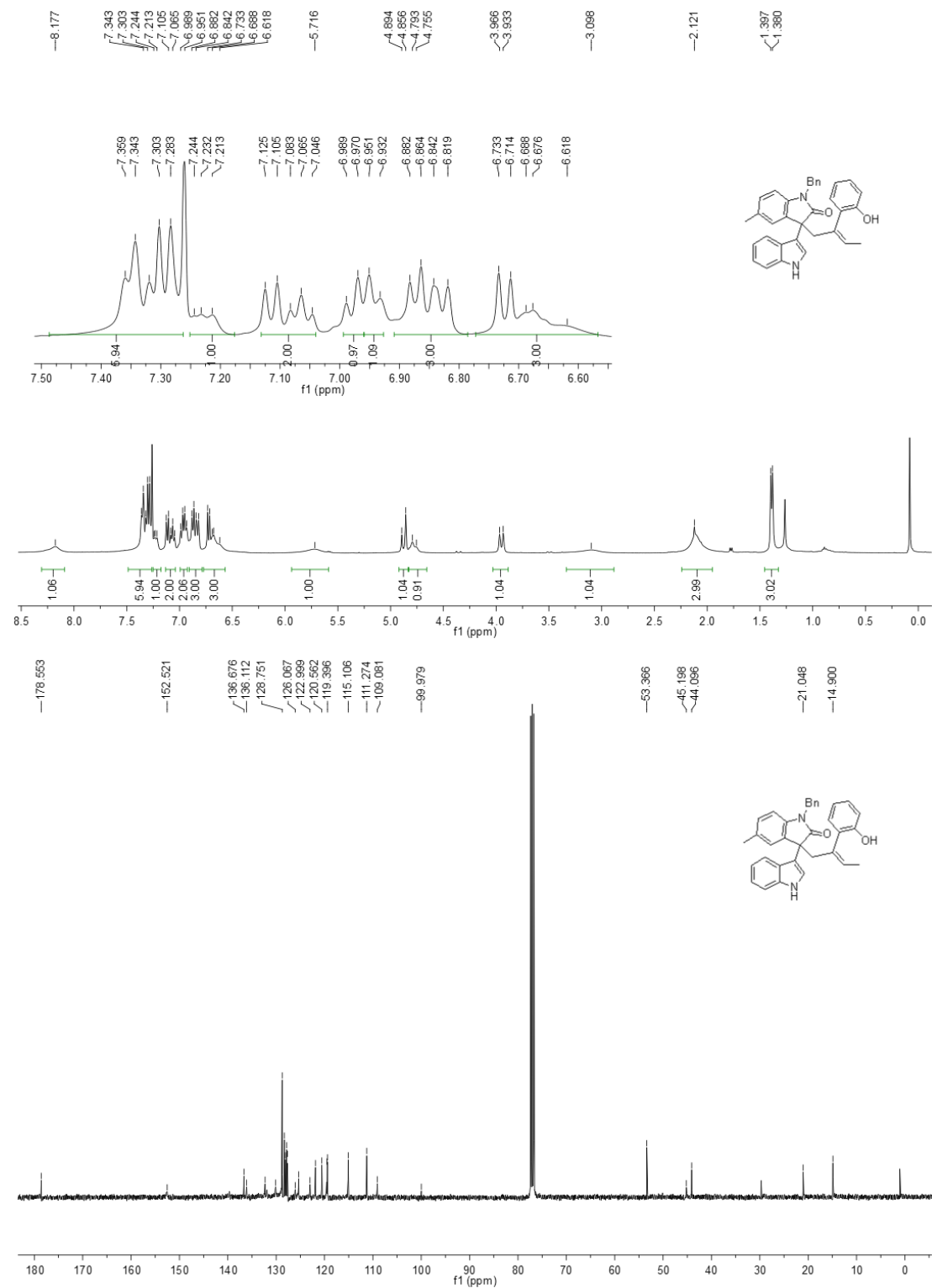
**3gb:** (inseparable 8:1 Z/E isomers)



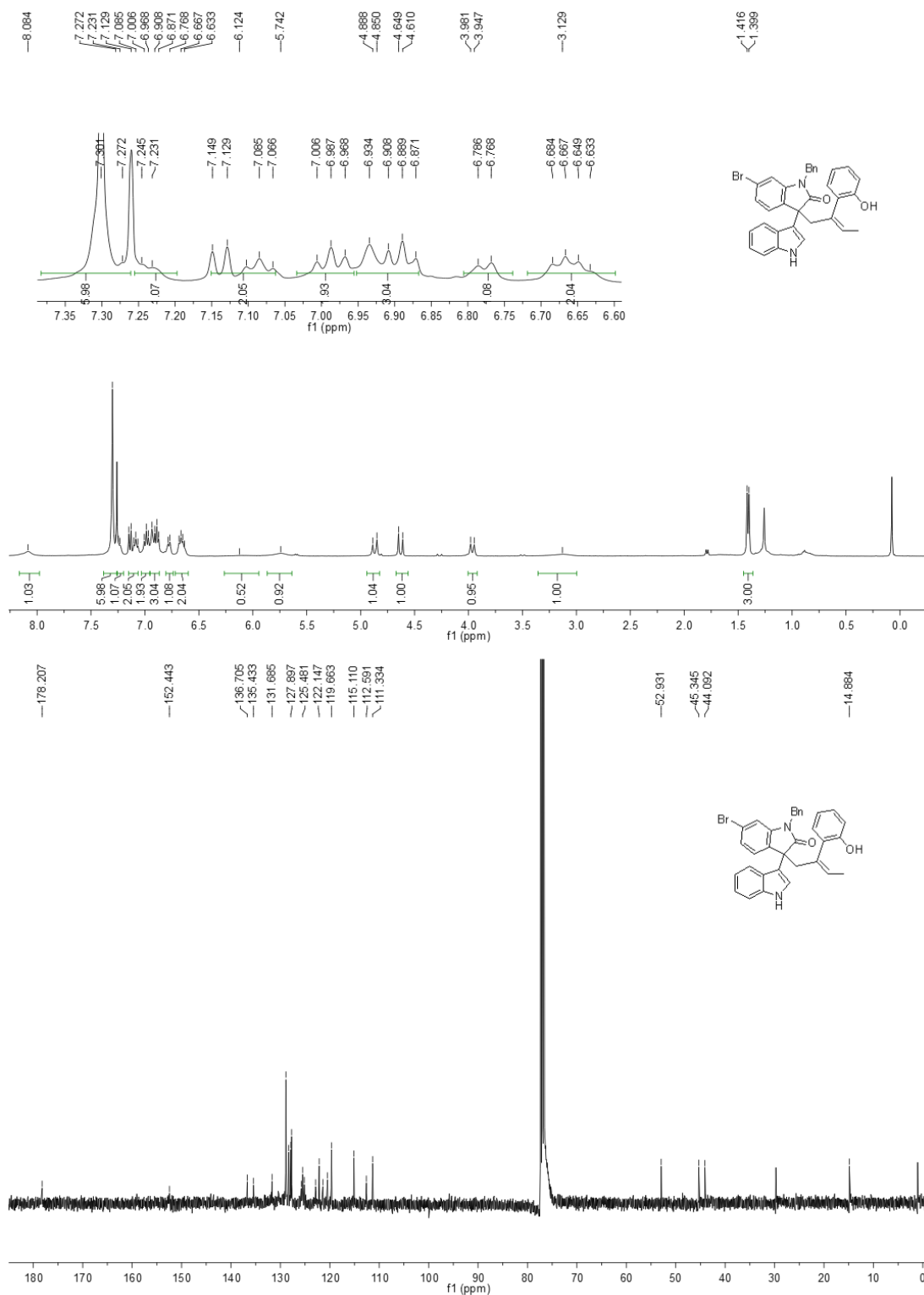
**3hb:** (inseparable 10:1 Z/E isomers)



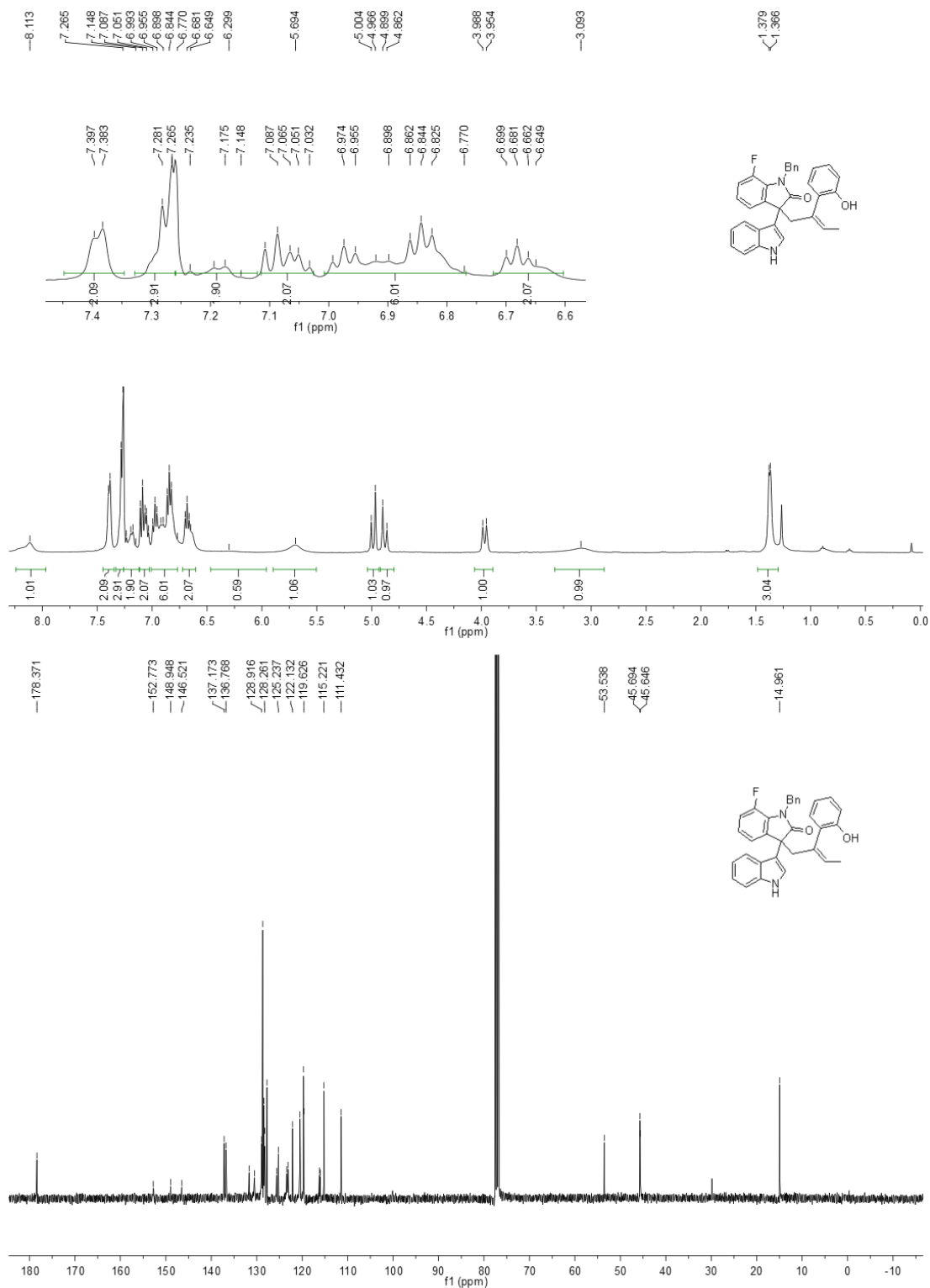
**3ib:** (inseparable 15:1 *Z/E* isomers)



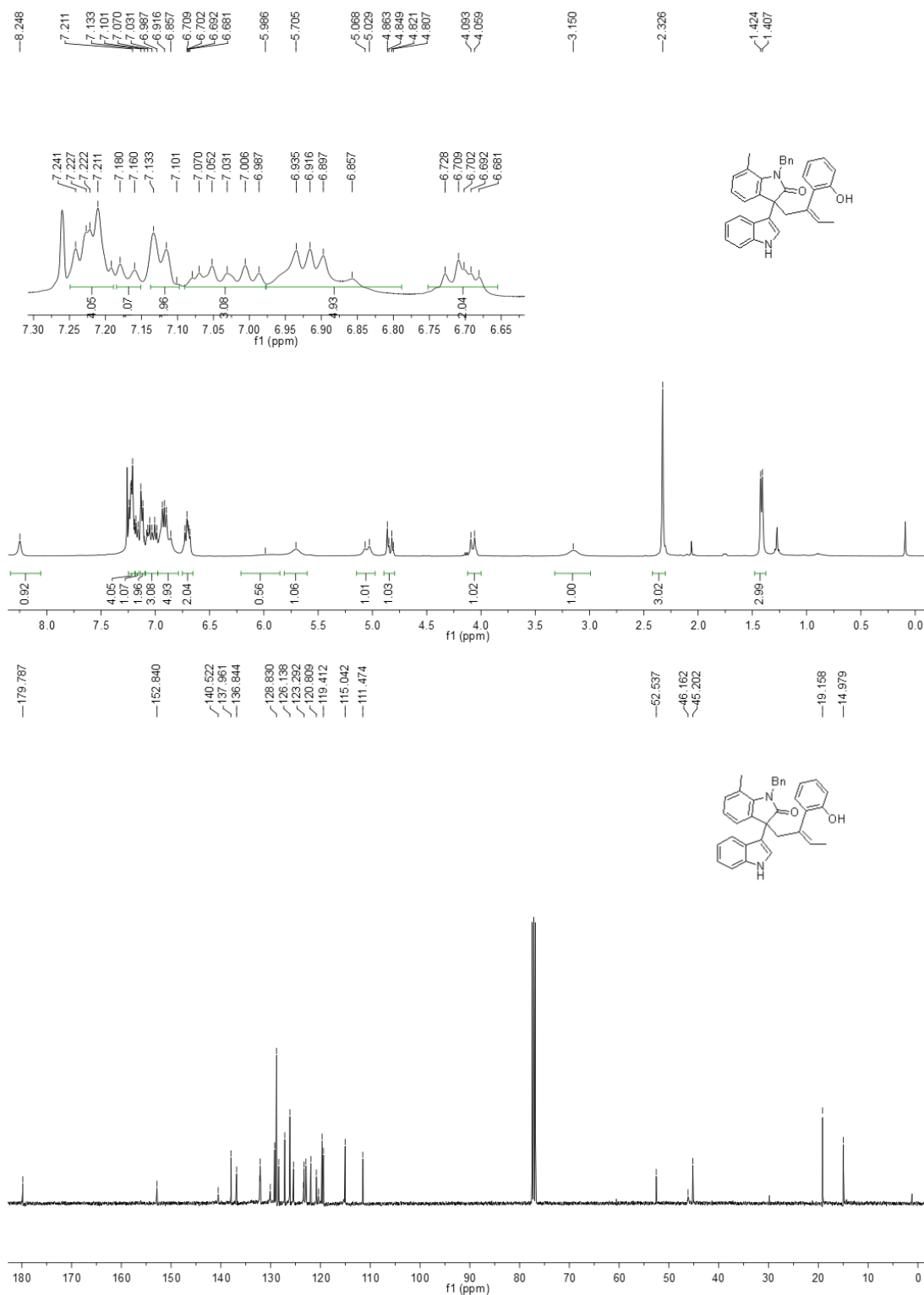
**3jb:** (inseparable 10:1 *Z/E* isomers)



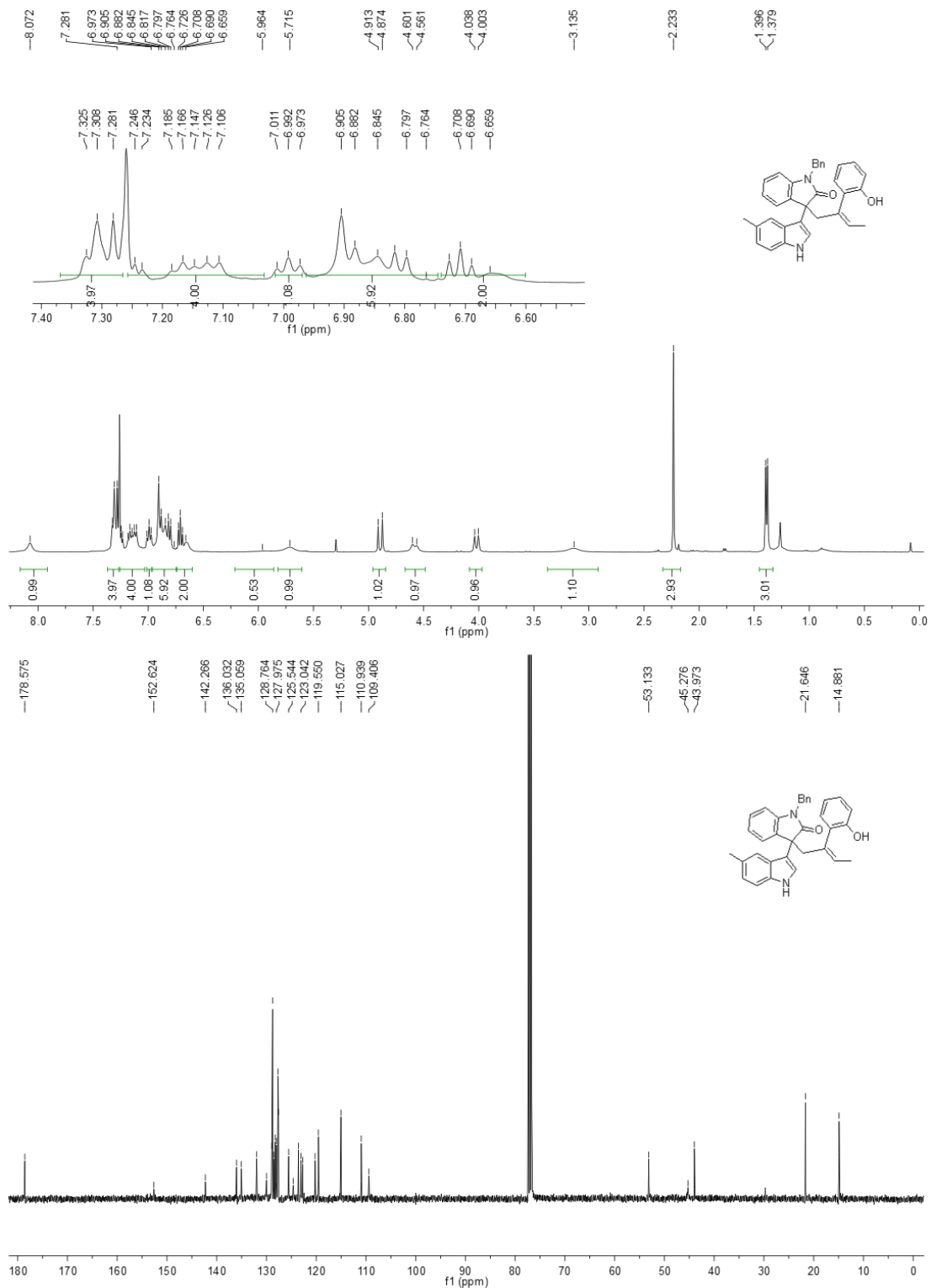
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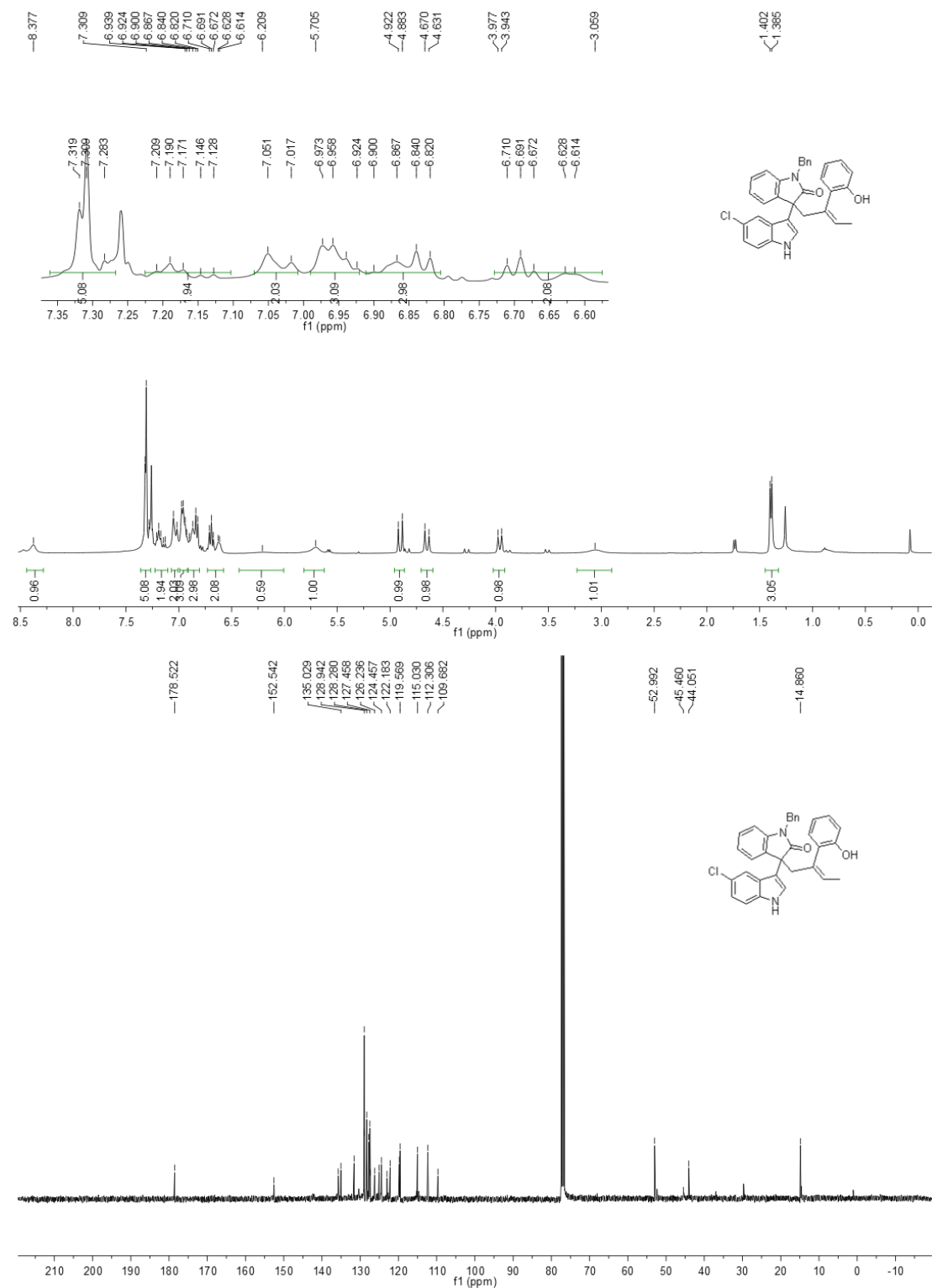
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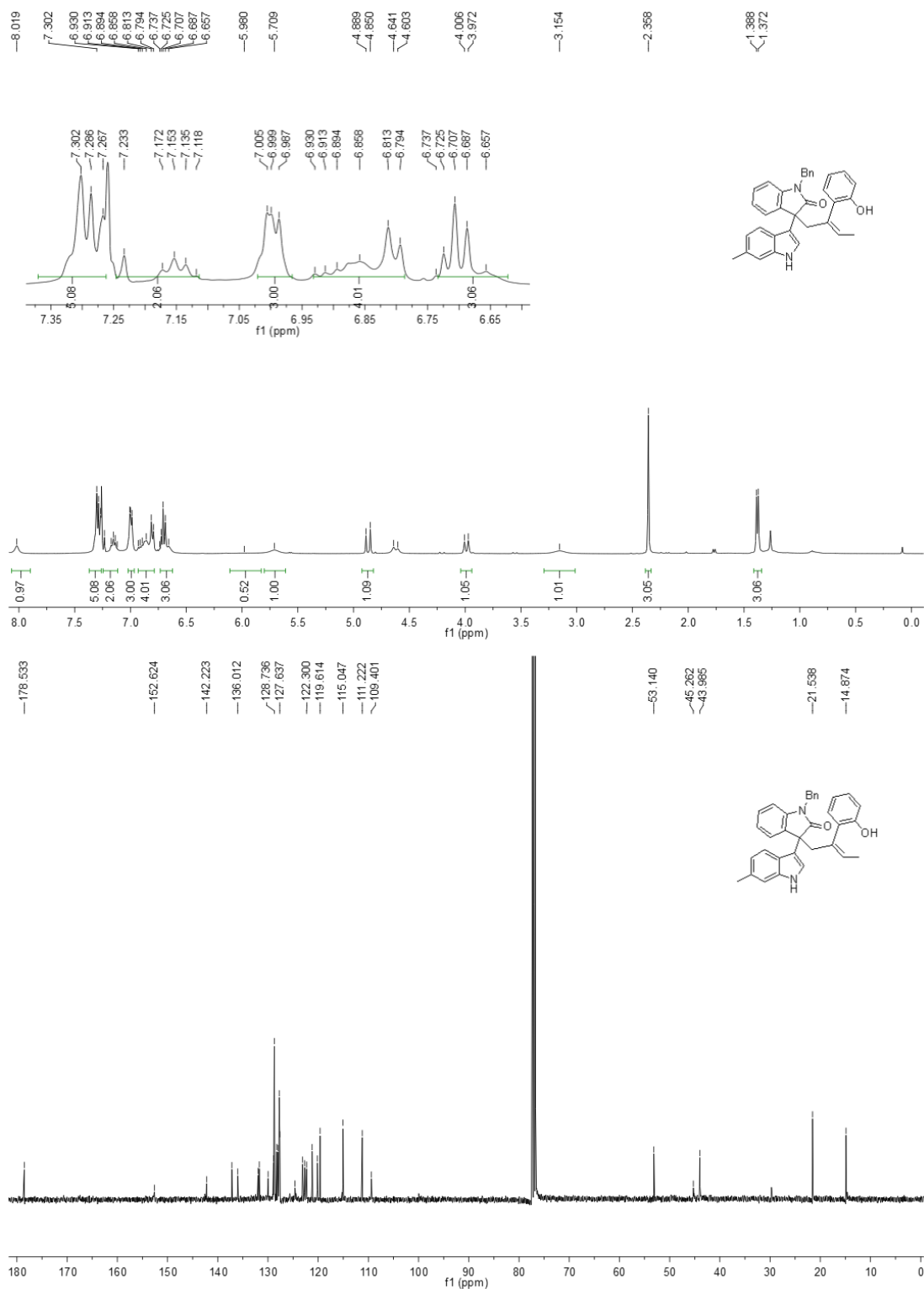
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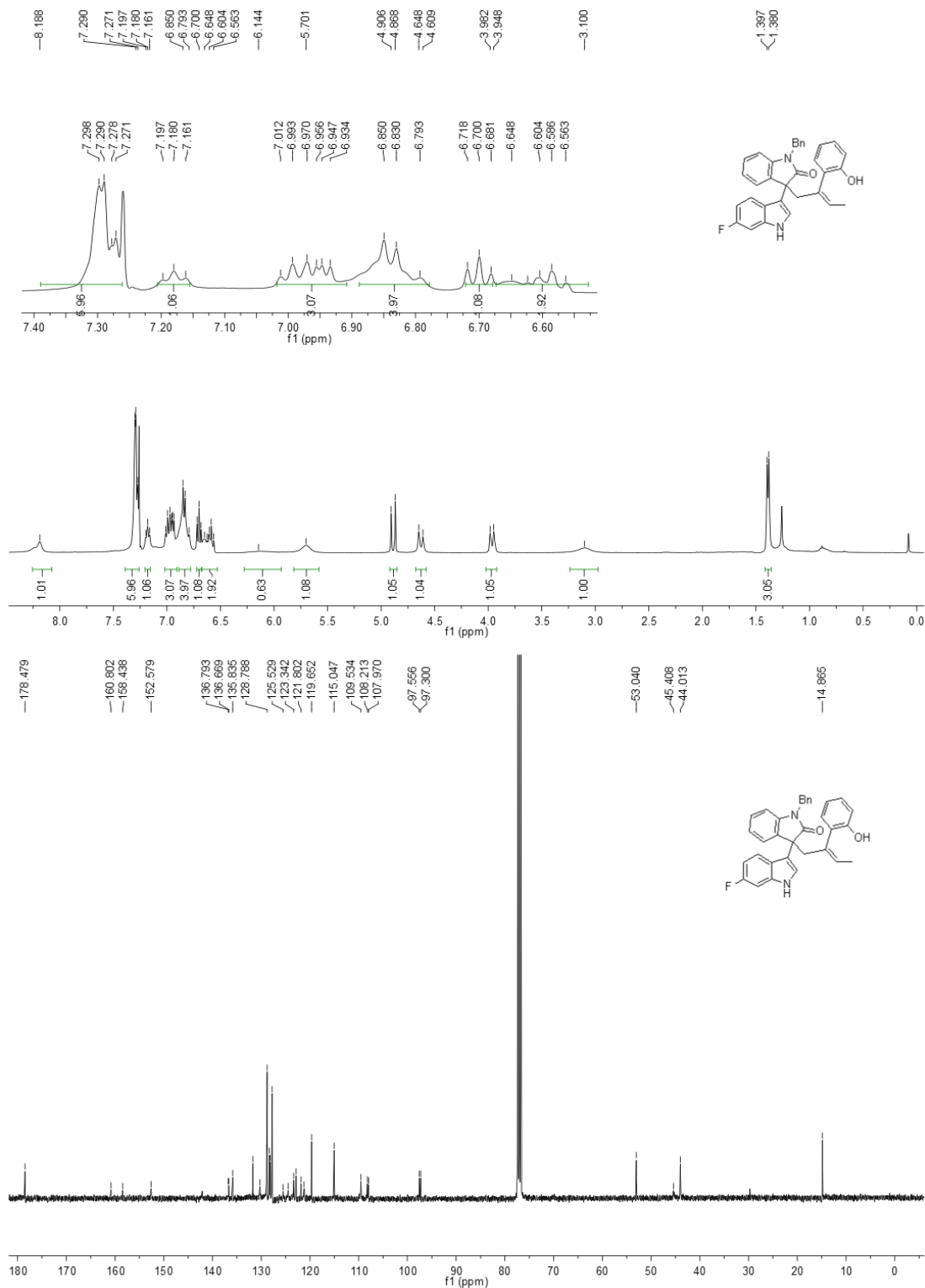
**3nb:** (inseparable 5:1 *Z/E* isomers)



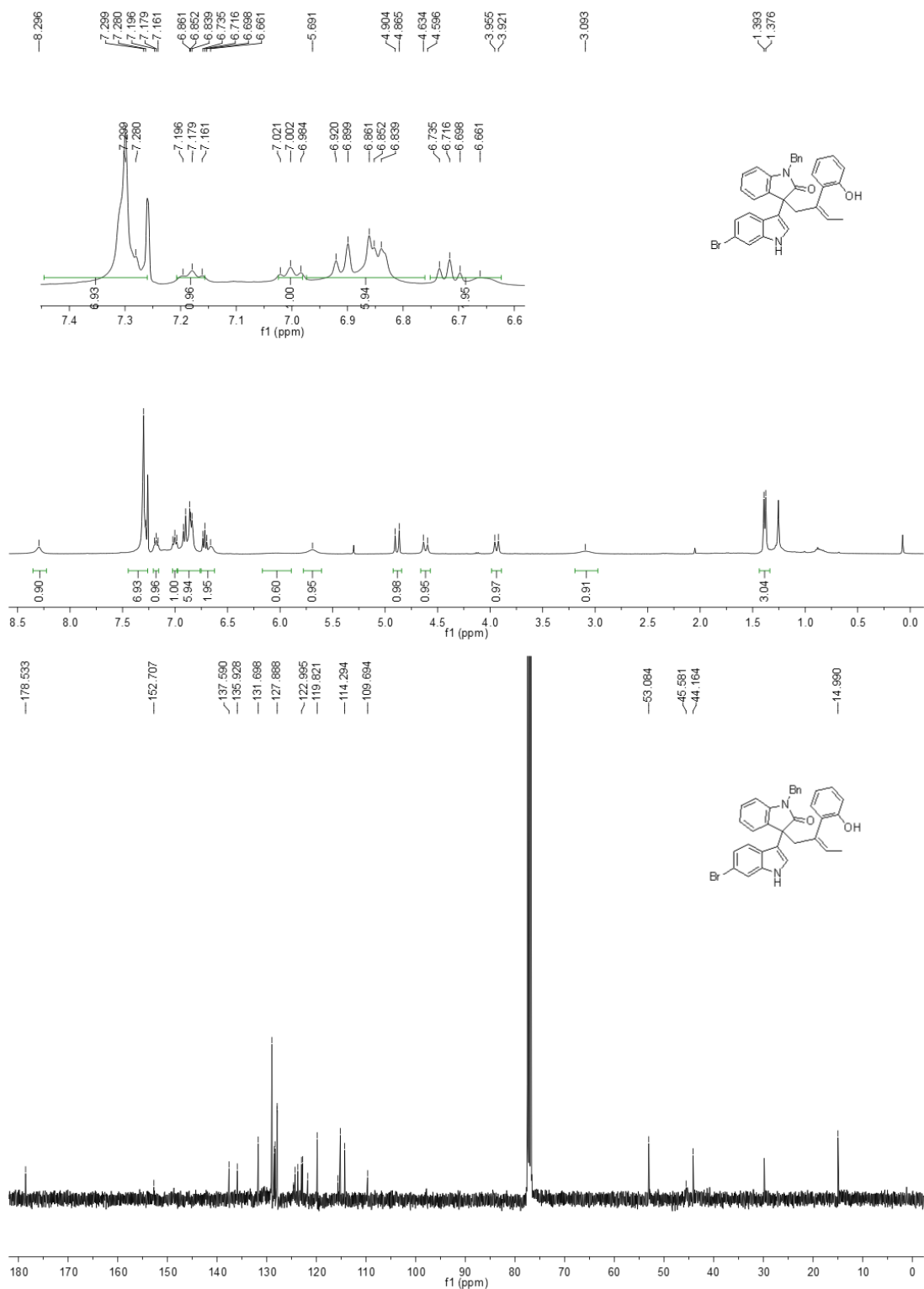
### 3ob:



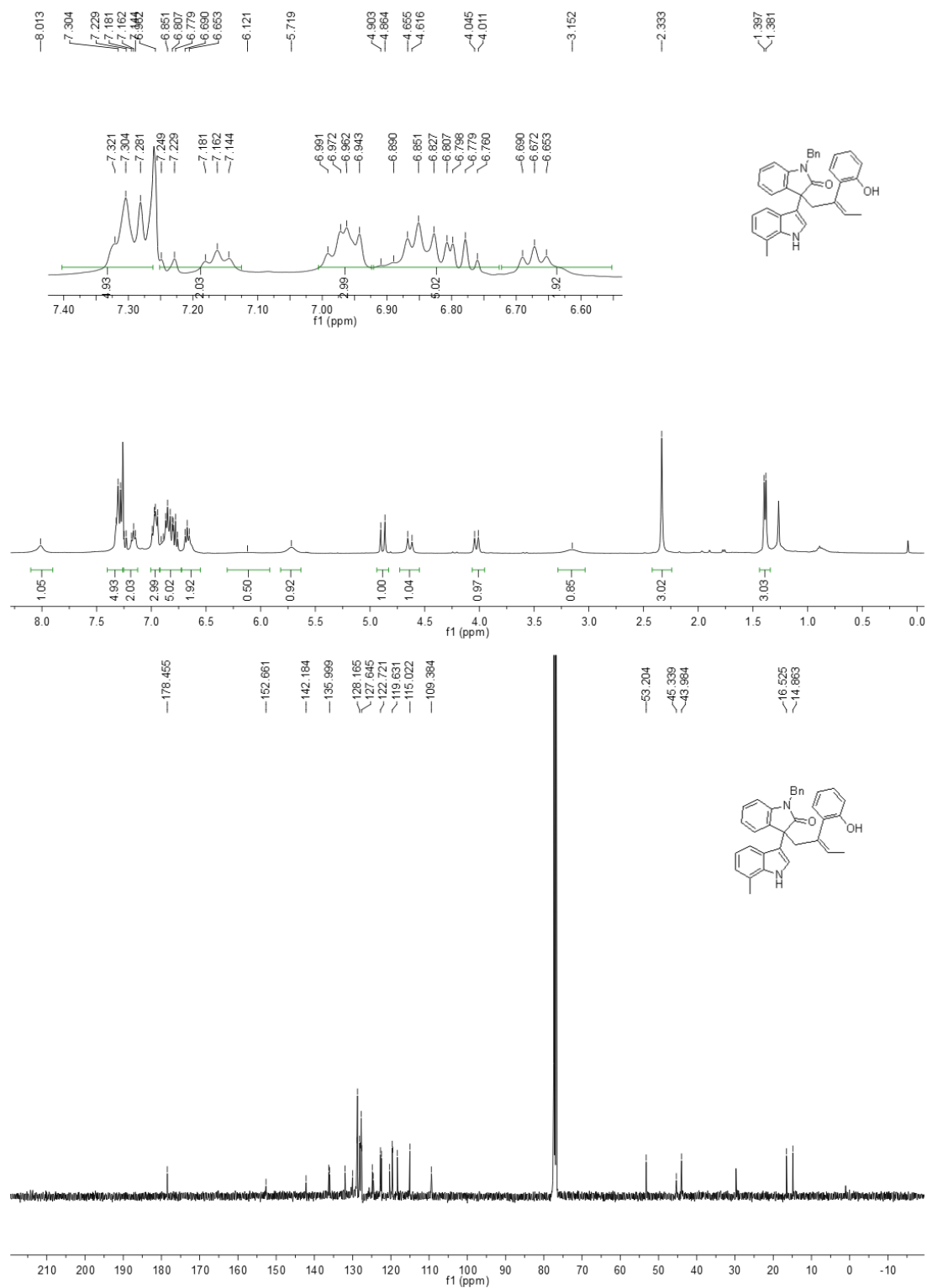
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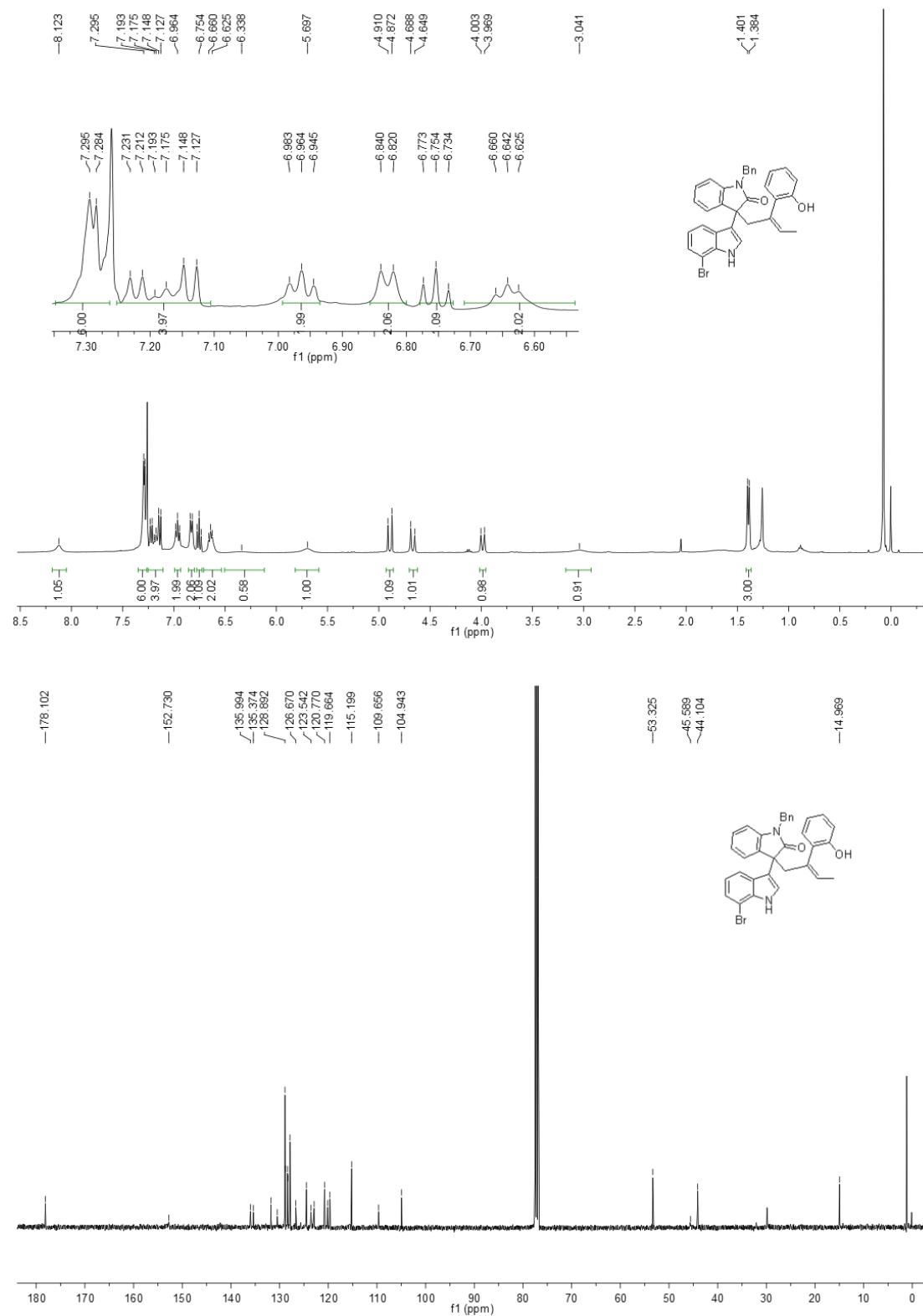
3qb:



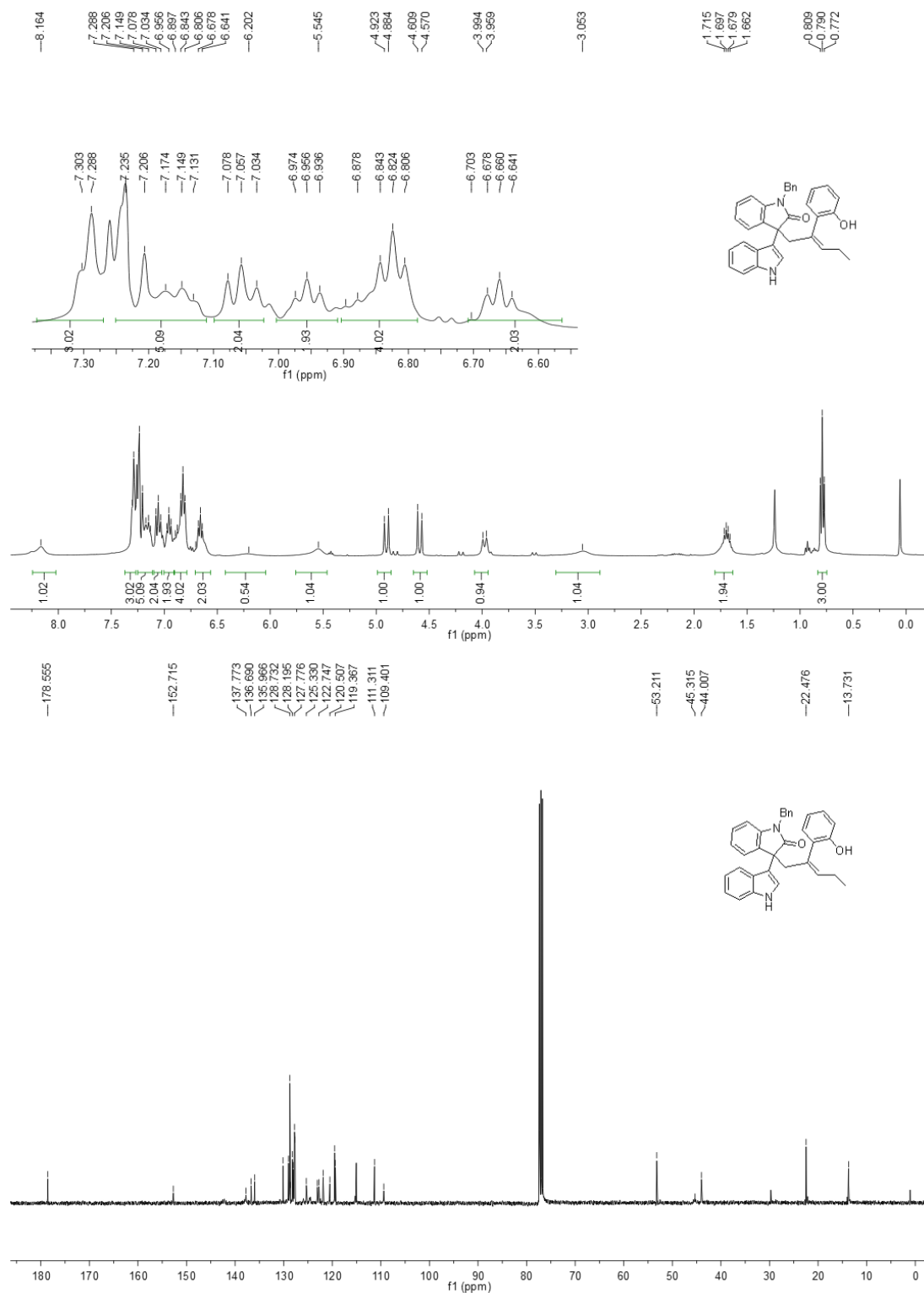
**3rb :**



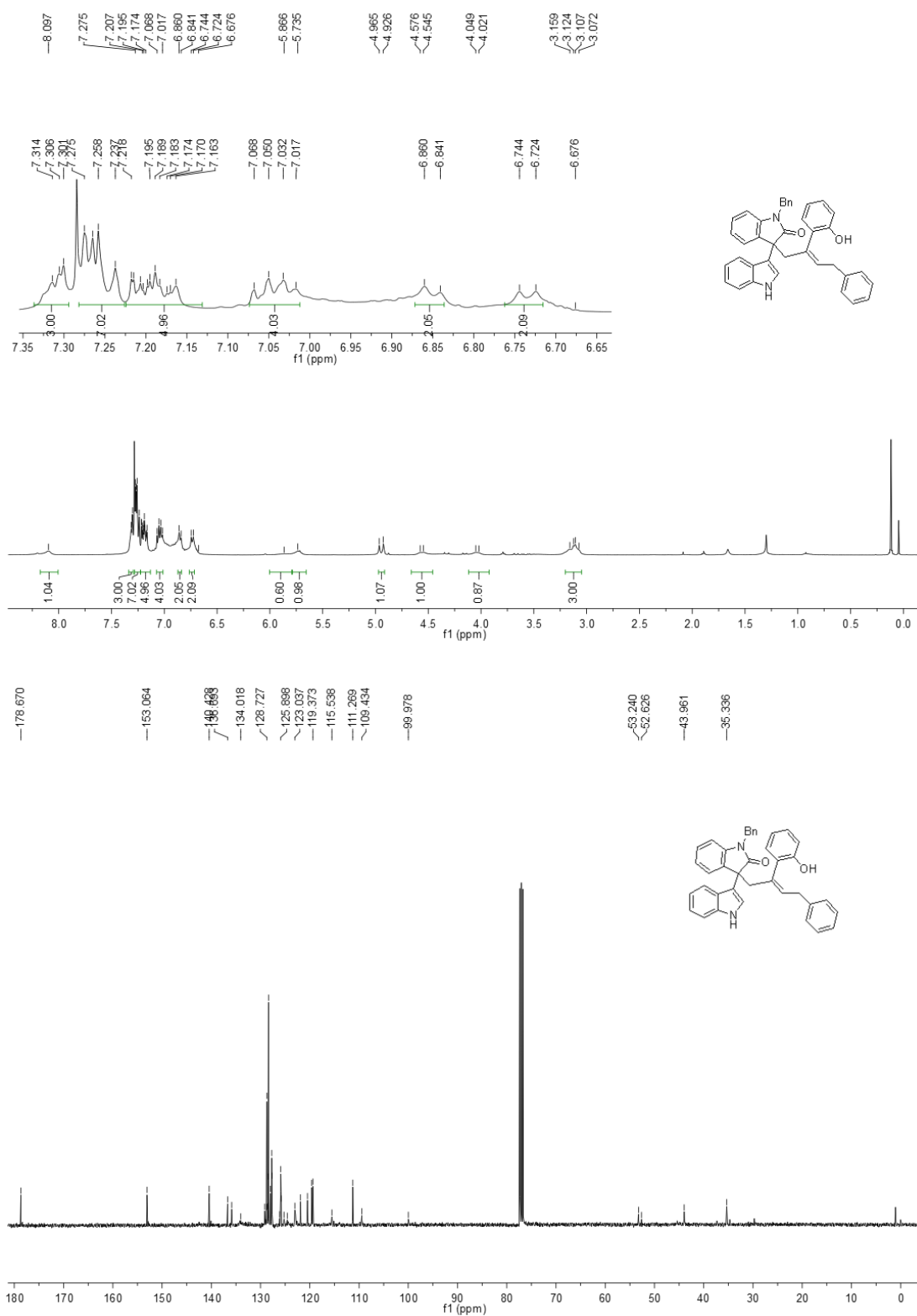
**3sb:**



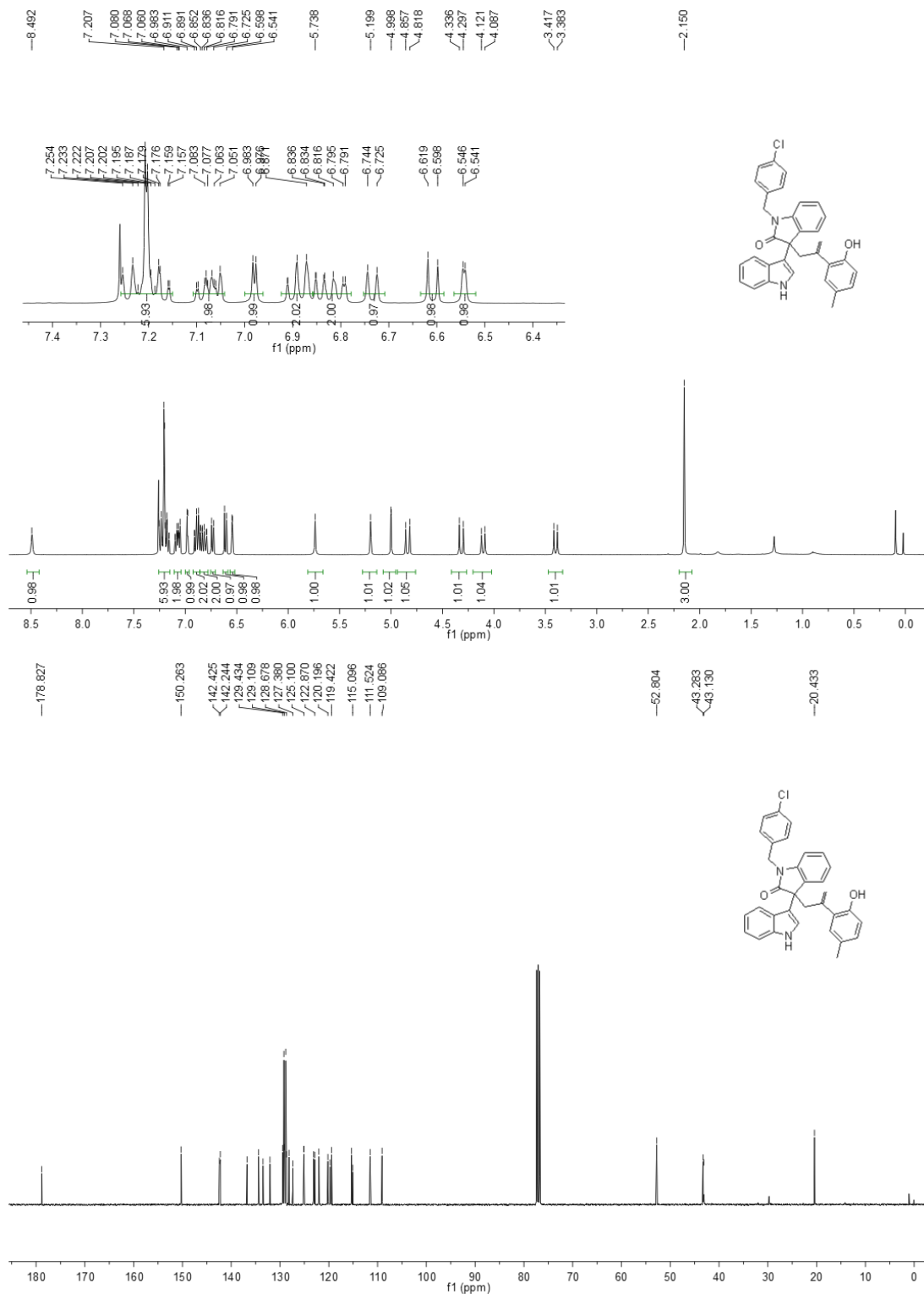
**3ac:** (inseparable 6:1 *Z/E* isomers)

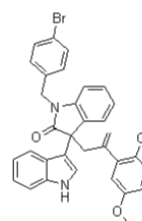
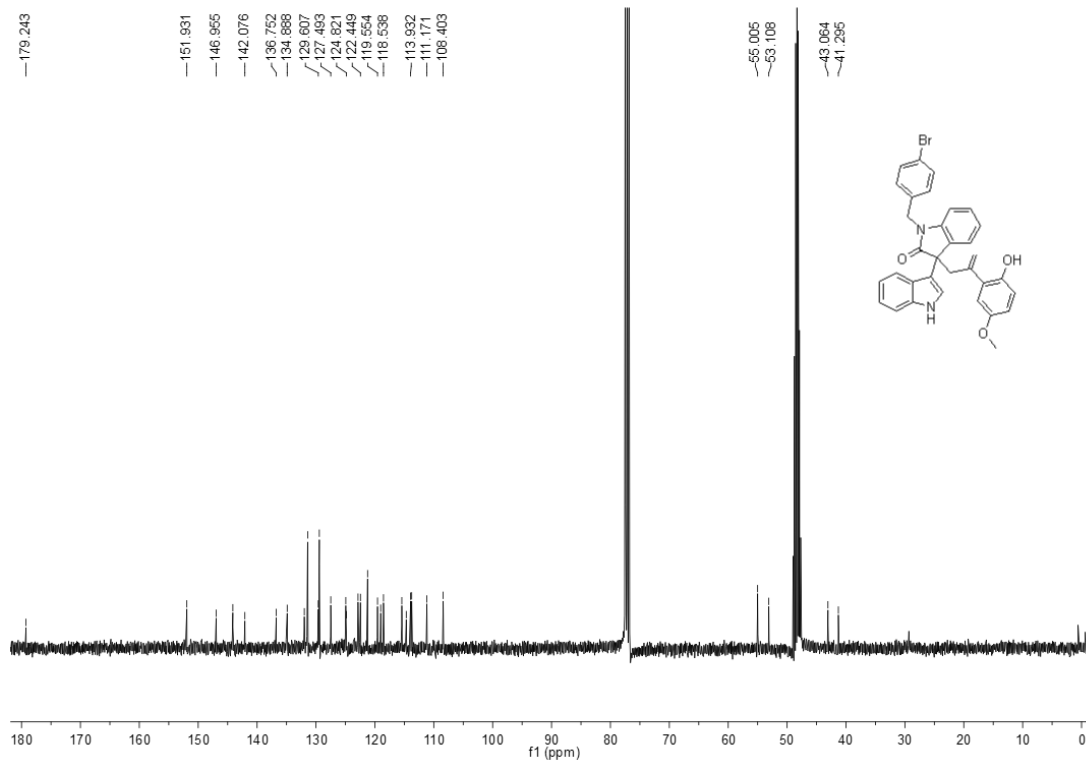
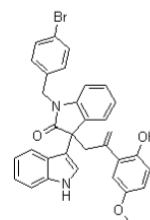


**3ad:** (ins separable 6:1 *Z/E* isomers)

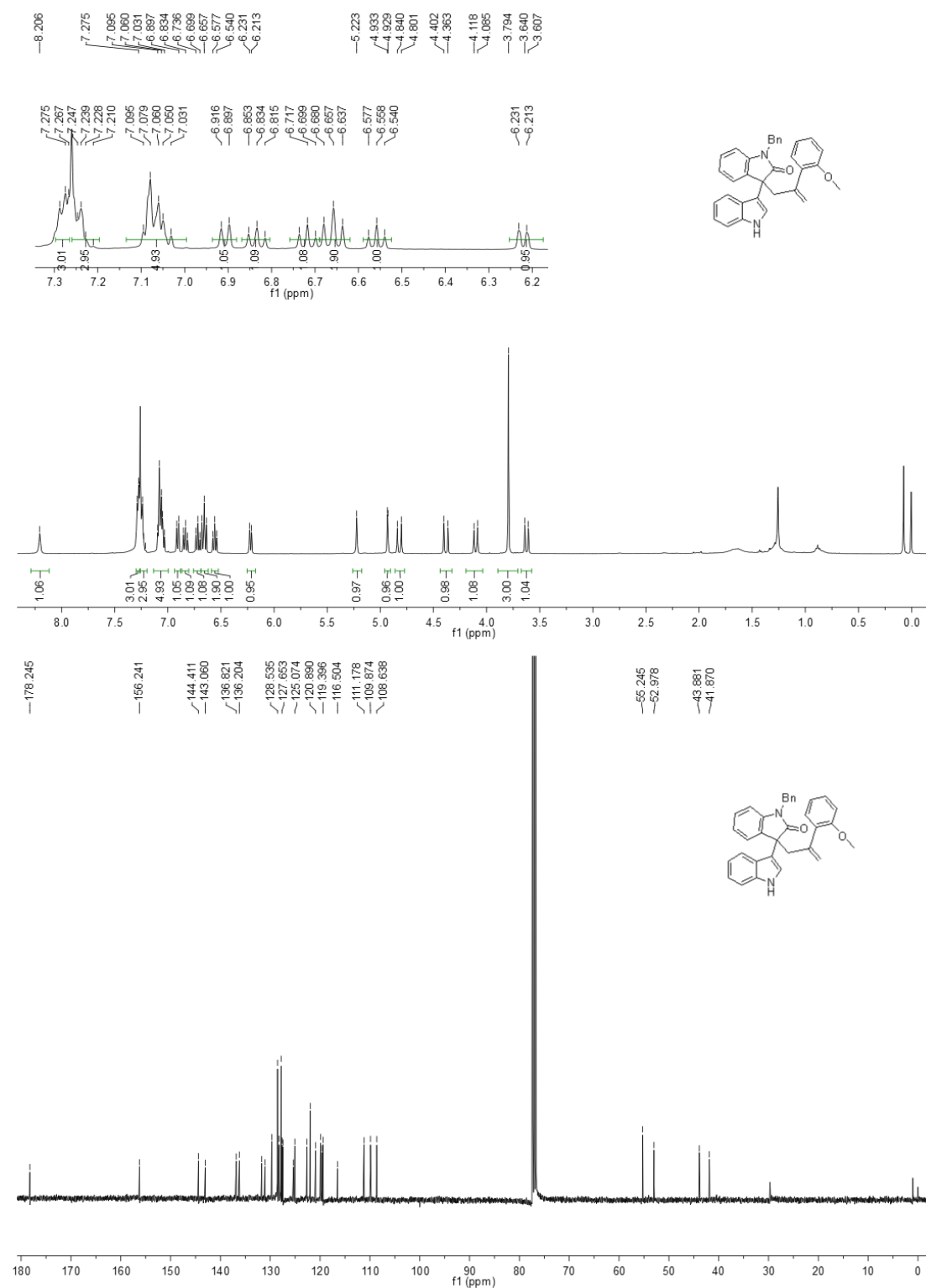


3ed:



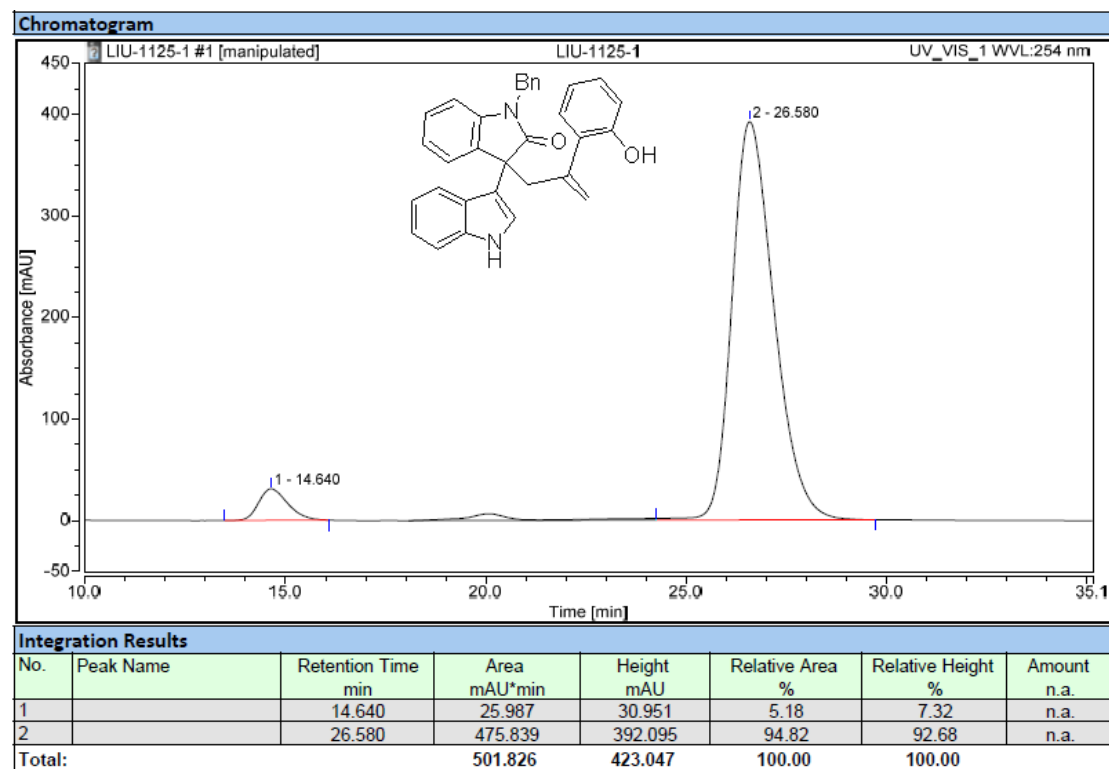
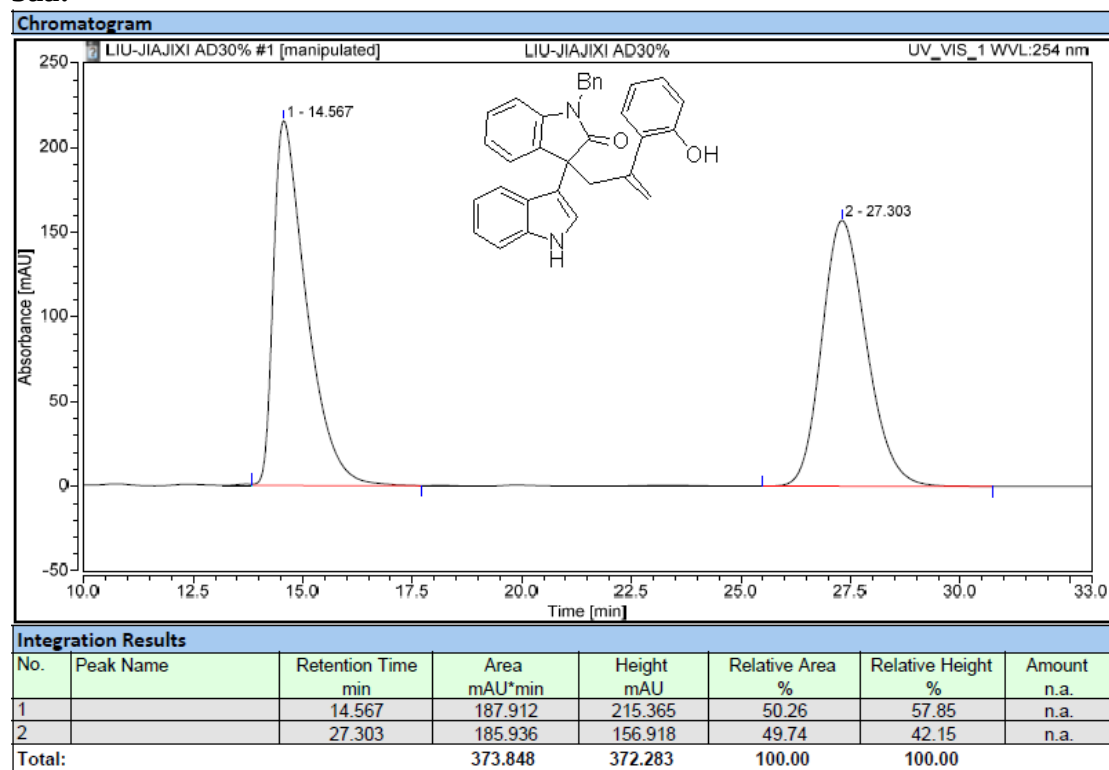
$$\begin{array}{r} \int_1^1 1 \, dx \\ \int_1^2 2x \, dx \\ \int_1^3 3x^2 \, dx \\ \int_1^4 4x^3 \, dx \\ \int_1^5 5x^4 \, dx \end{array} \quad \begin{array}{r} \sim 7.036 \\ -6.886 \\ -6.887 \\ -6.520 \\ -6.488 \\ -6.474 \\ -6.466 \end{array} \quad \begin{array}{r} \int_1^5 5x^4 \, dx \\ \int_1^6 6x^5 \, dx \\ \int_1^7 7x^6 \, dx \\ \int_1^8 8x^7 \, dx \\ \int_1^9 9x^8 \, dx \end{array} \quad \begin{array}{r} \sim 5.707 \\ -5.700 \\ -5.184 \\ -4.932 \\ -4.927 \\ -4.720 \\ -4.579 \\ -4.540 \end{array} \quad \begin{array}{r} \int_1^{10} 10x^9 \, dx \\ \int_1^{11} 11x^{10} \, dx \\ \int_1^{12} 12x^{11} \, dx \\ \int_1^{13} 13x^{12} \, dx \\ \int_1^{14} 14x^{13} \, dx \end{array} \quad \begin{array}{r} \sim 4.015 \\ -3.963 \\ -3.780 \\ -3.747 \\ -3.452 \end{array}$$


**3af:**

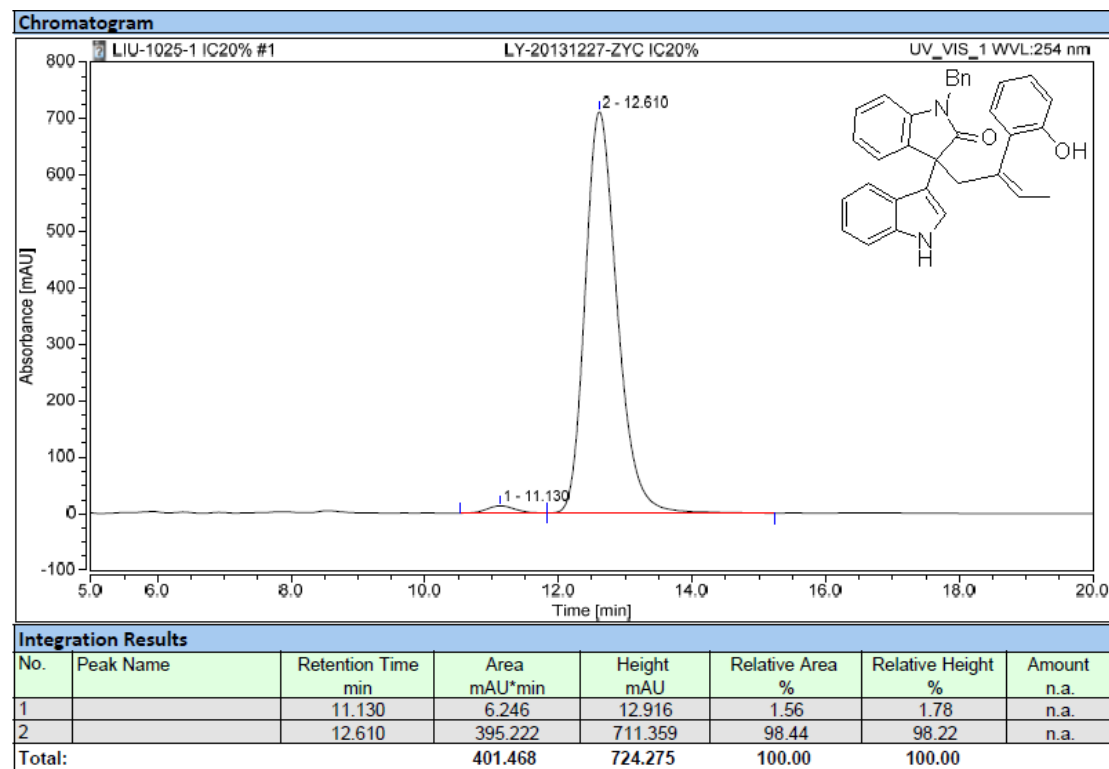
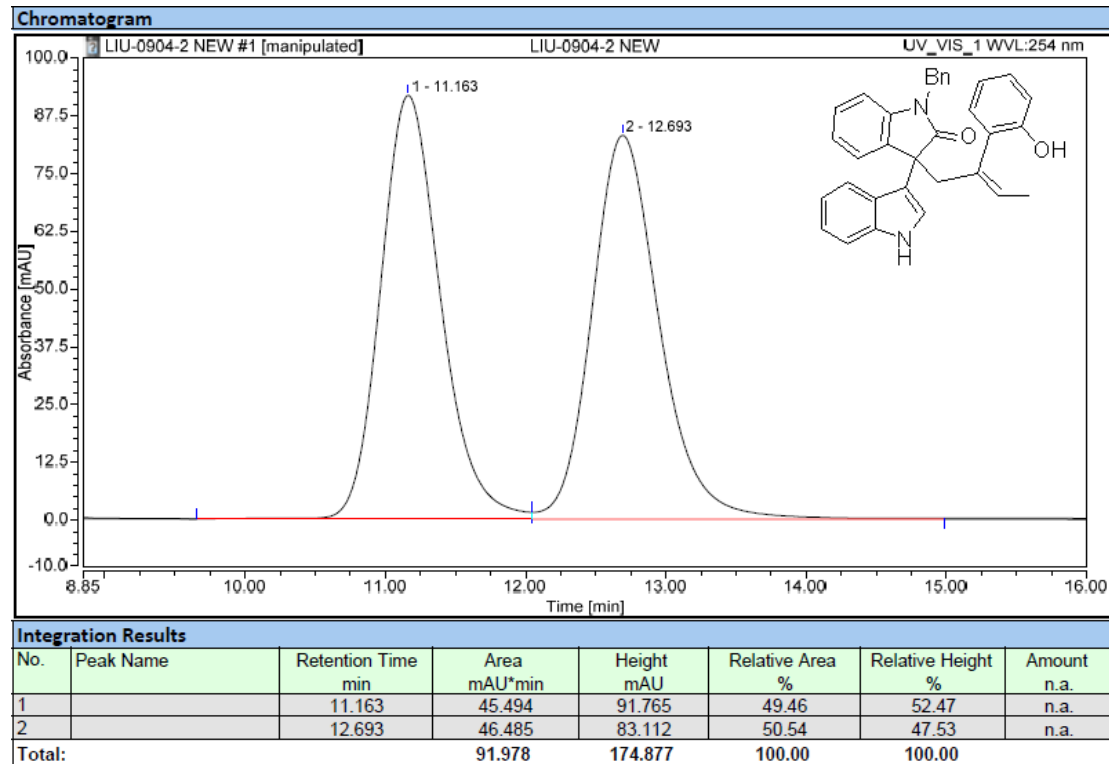


### Chiral HPLC analyses of products 3

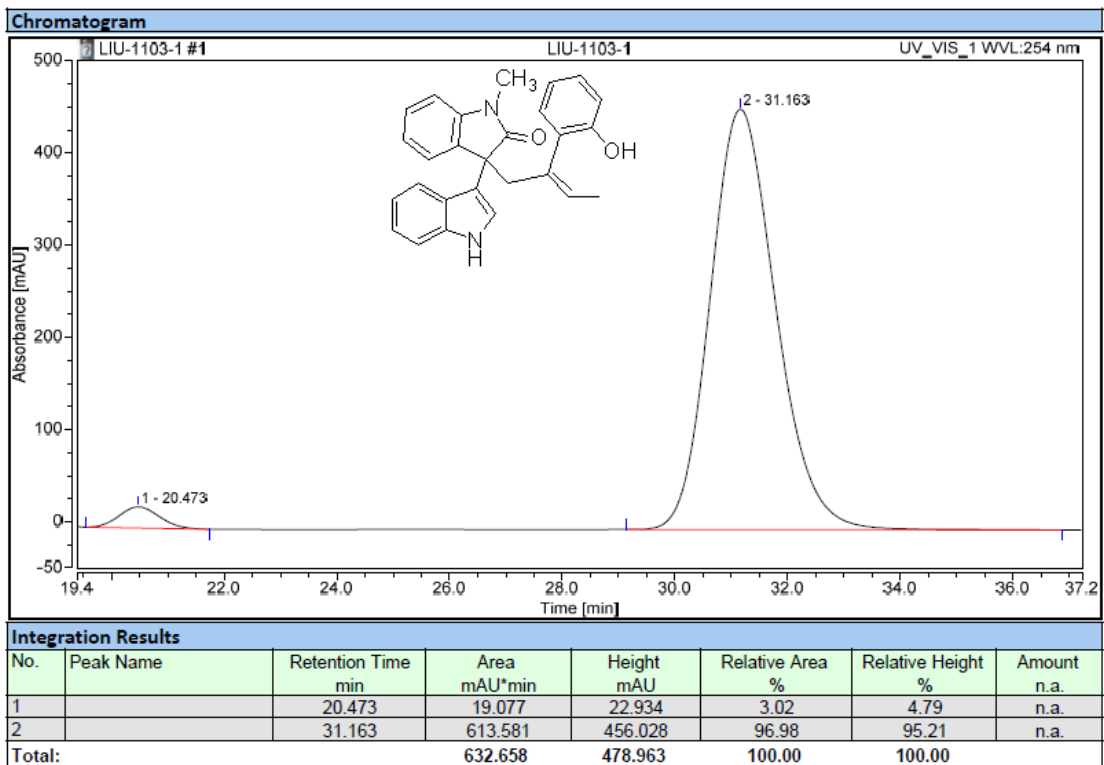
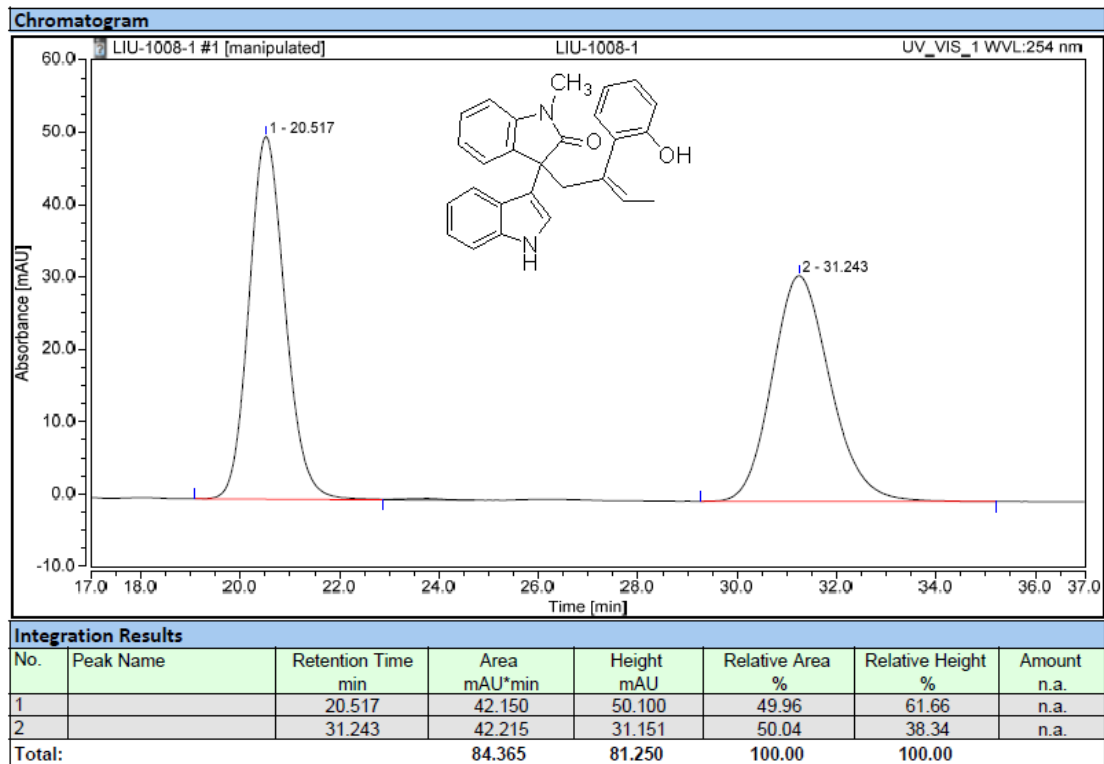
**3aa:**



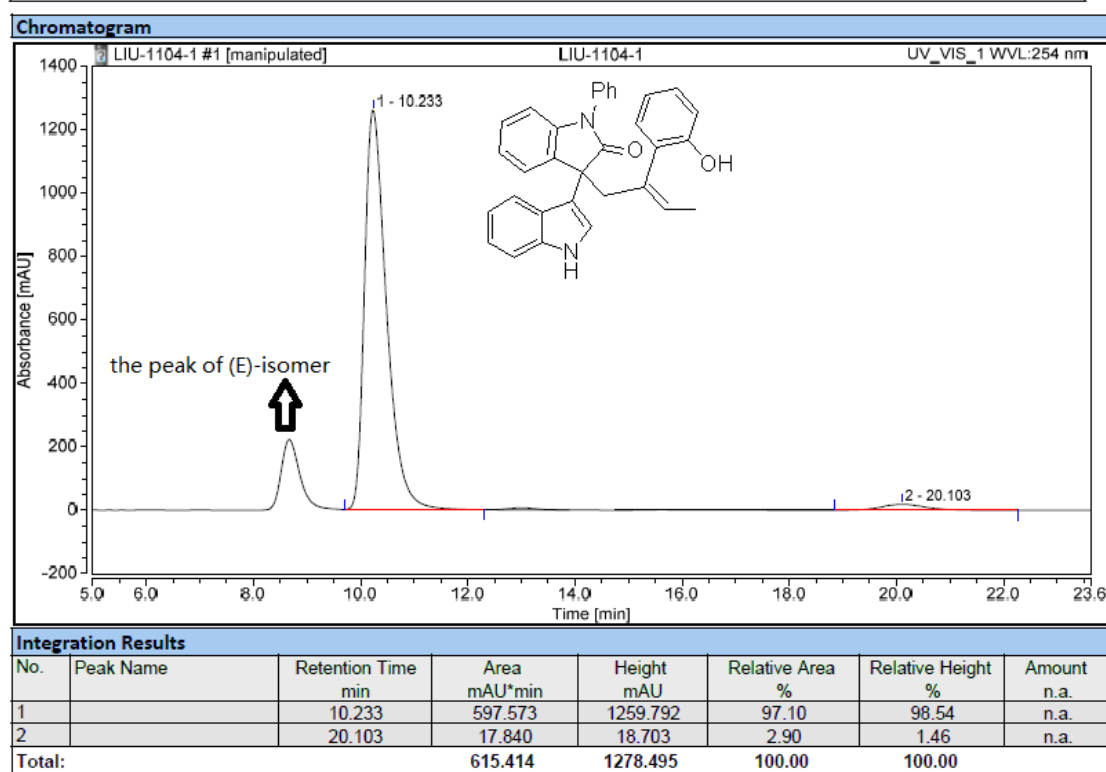
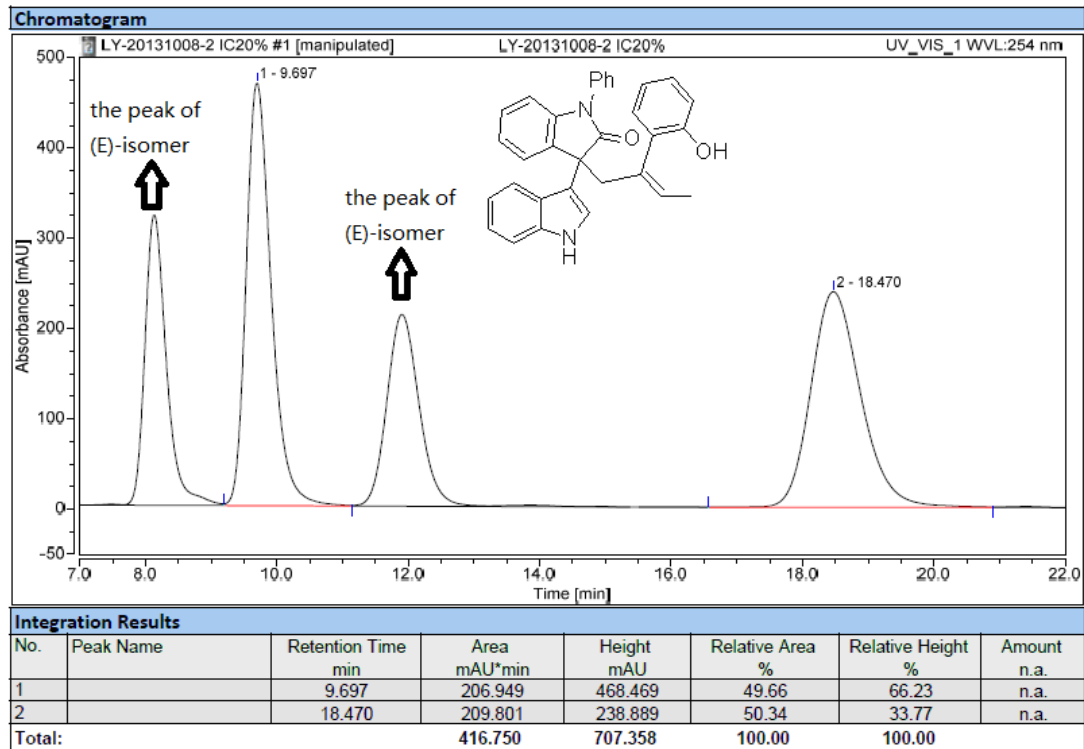
3ab:



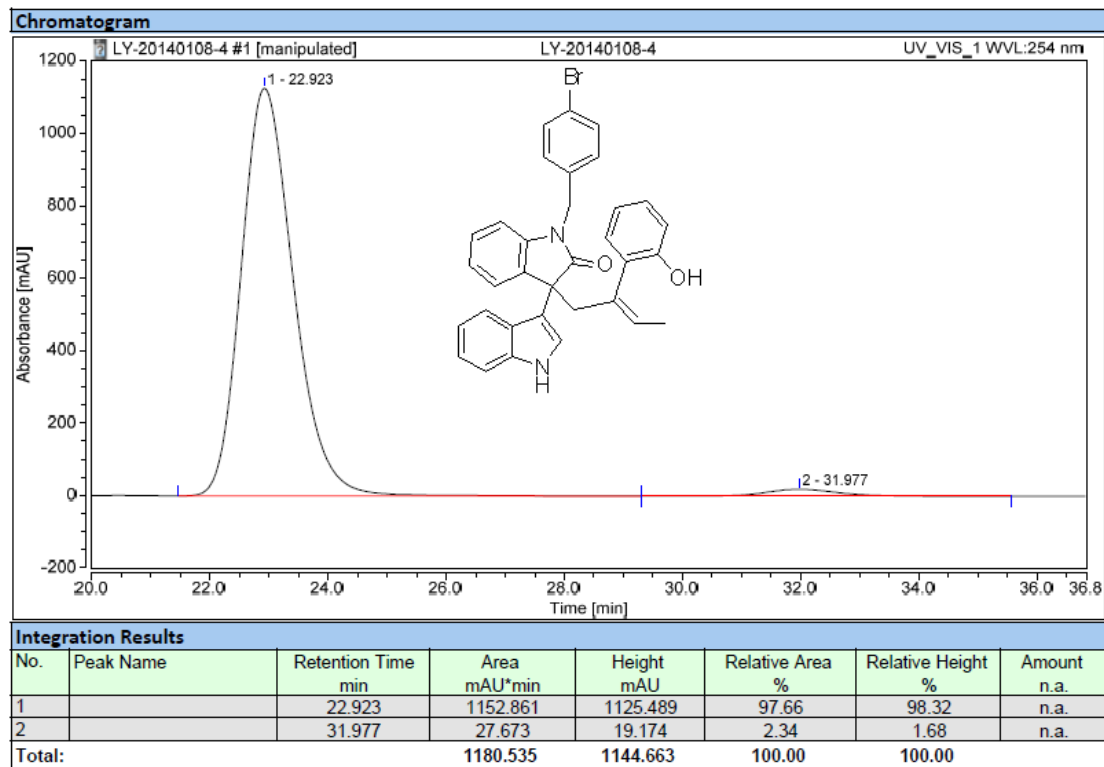
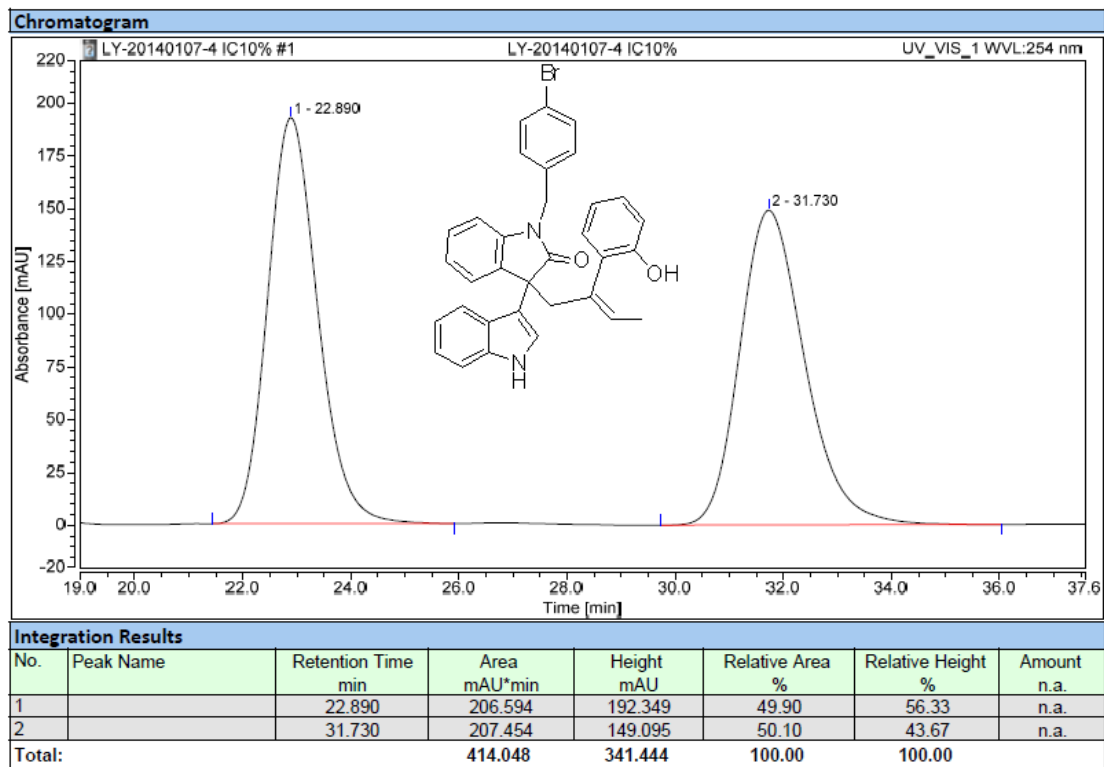
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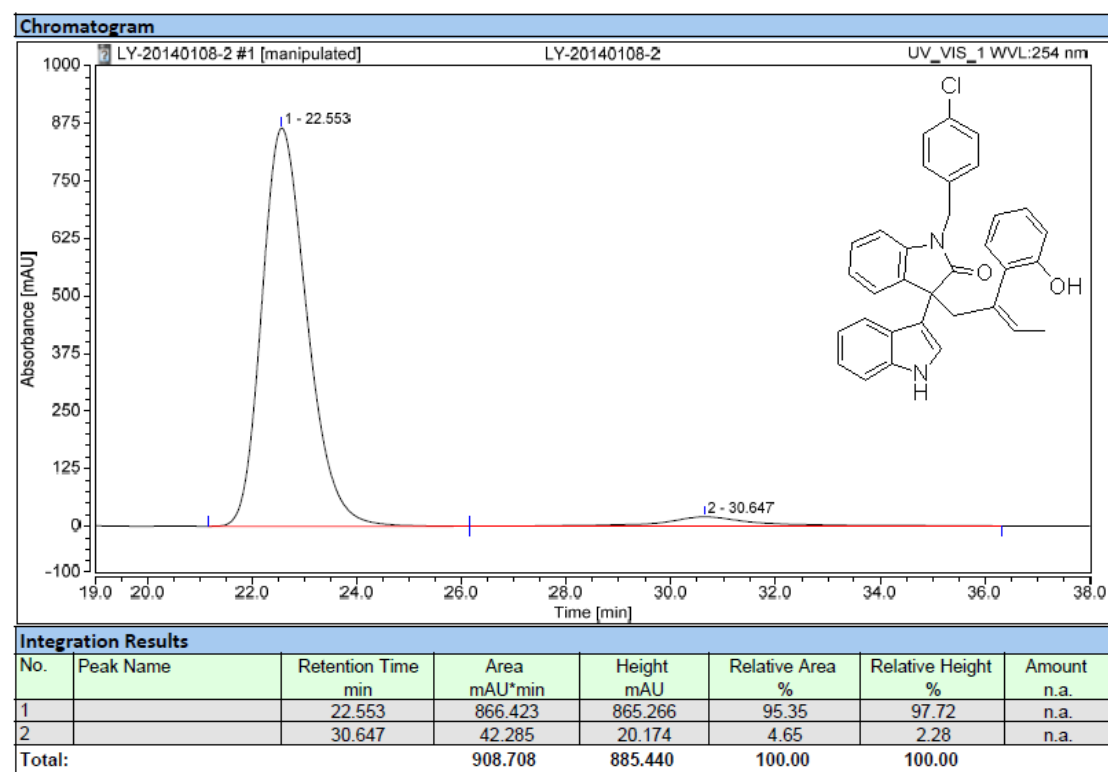
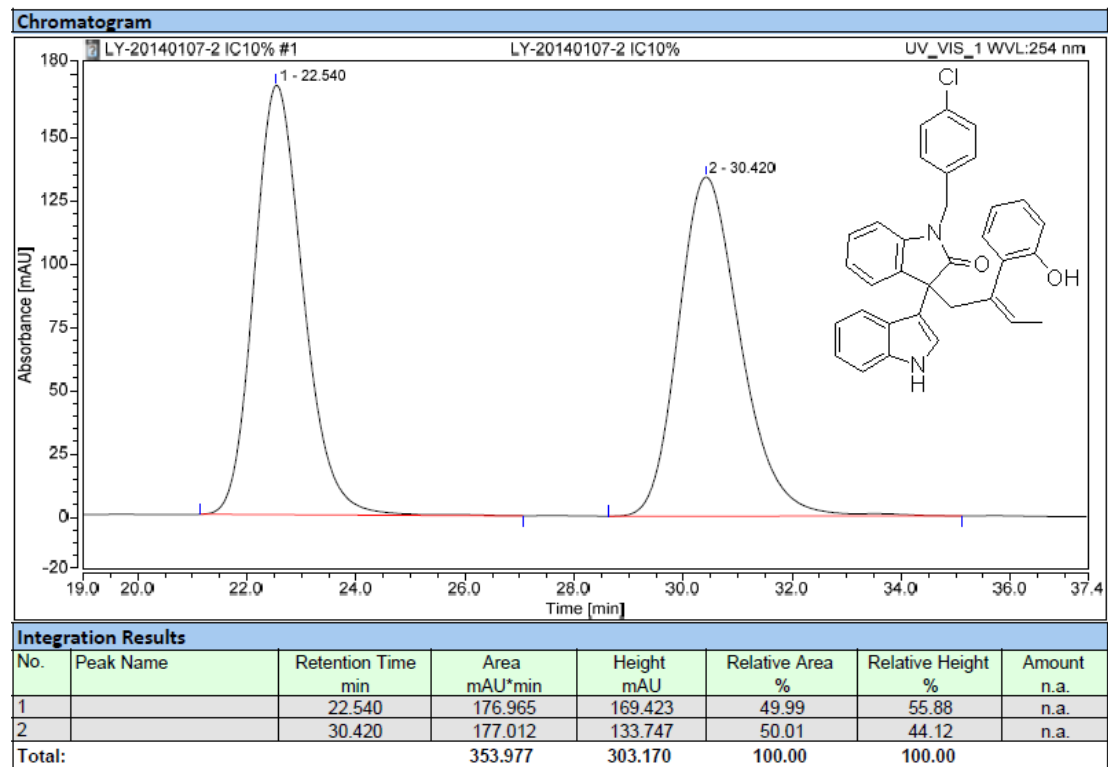
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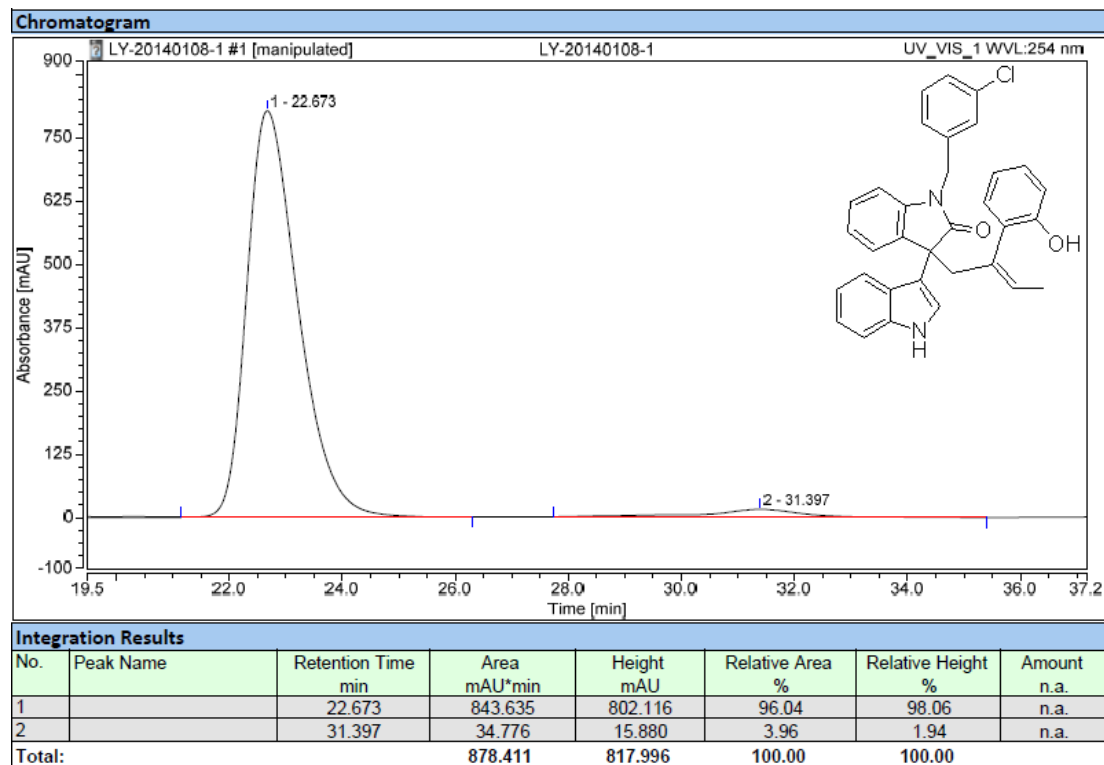
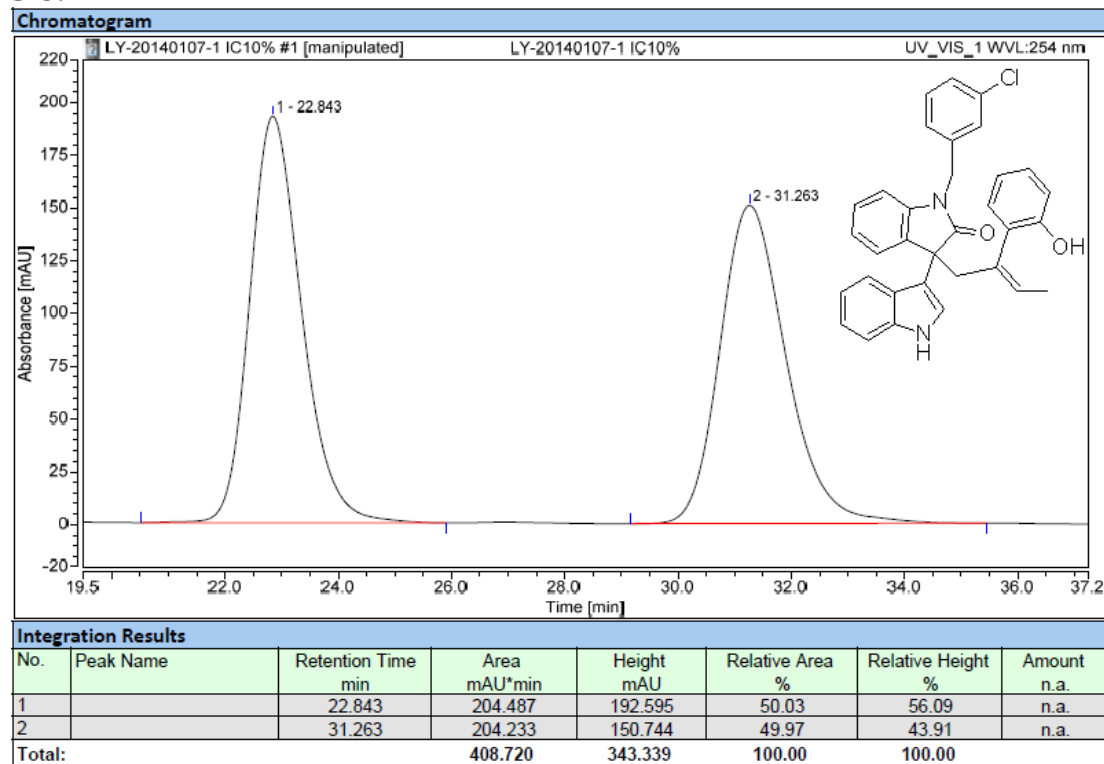
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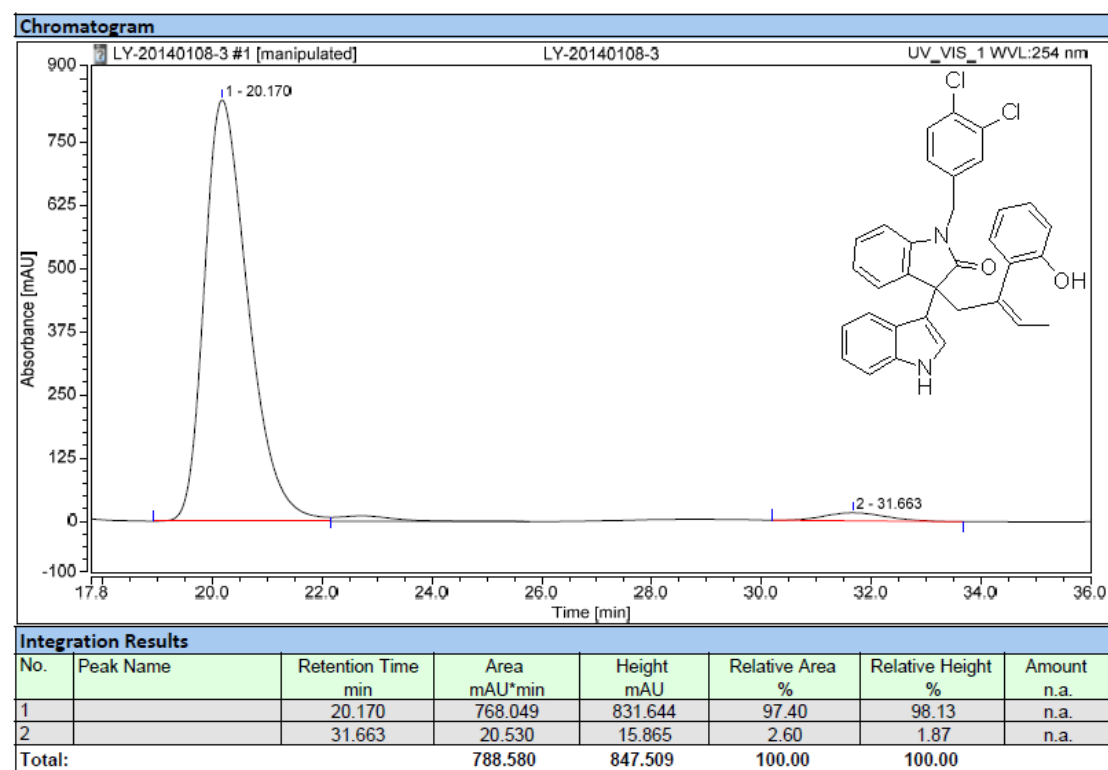
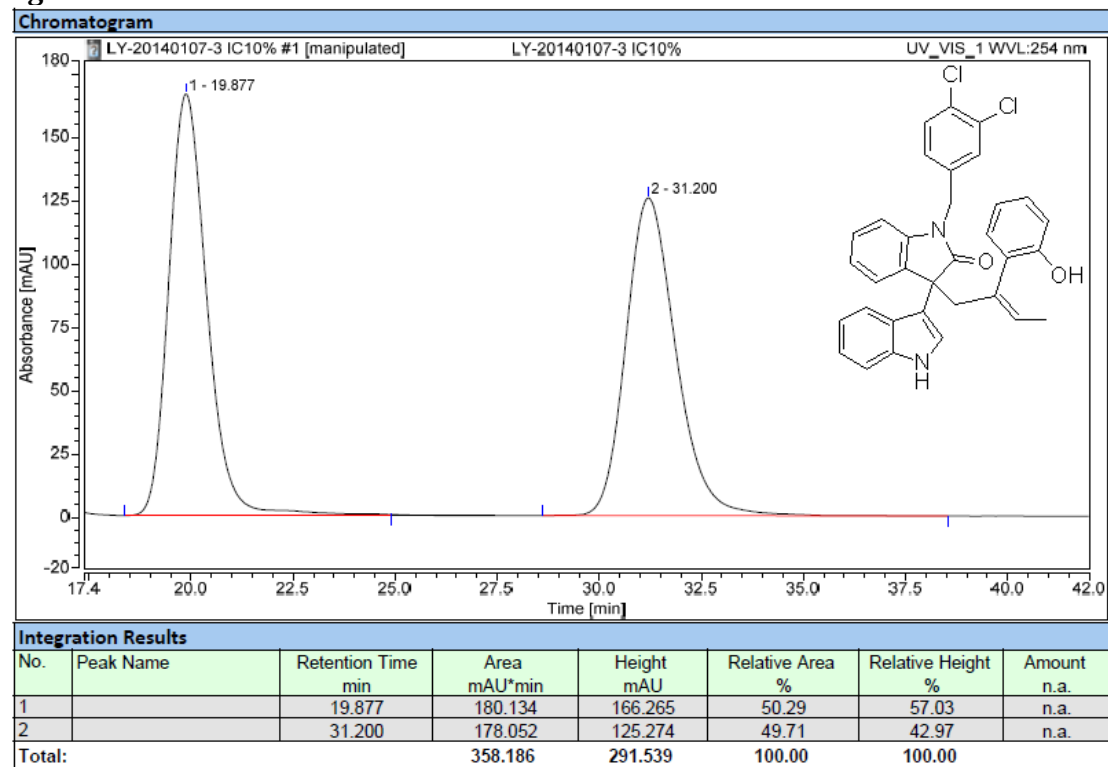
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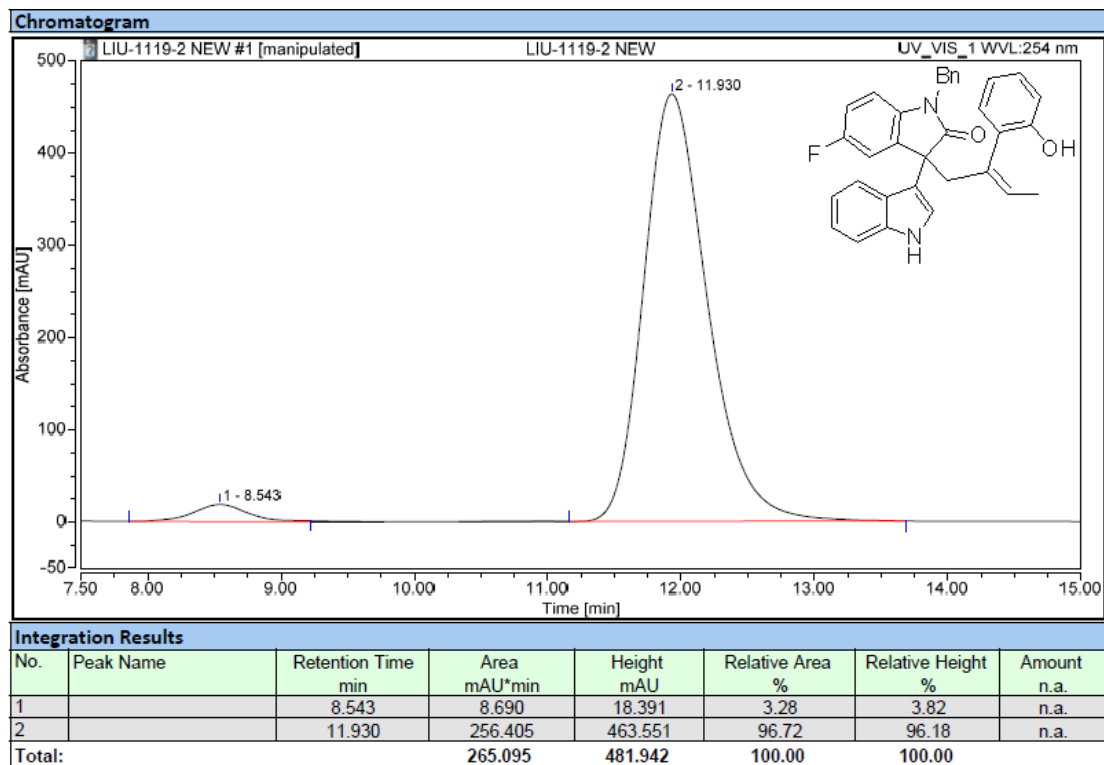
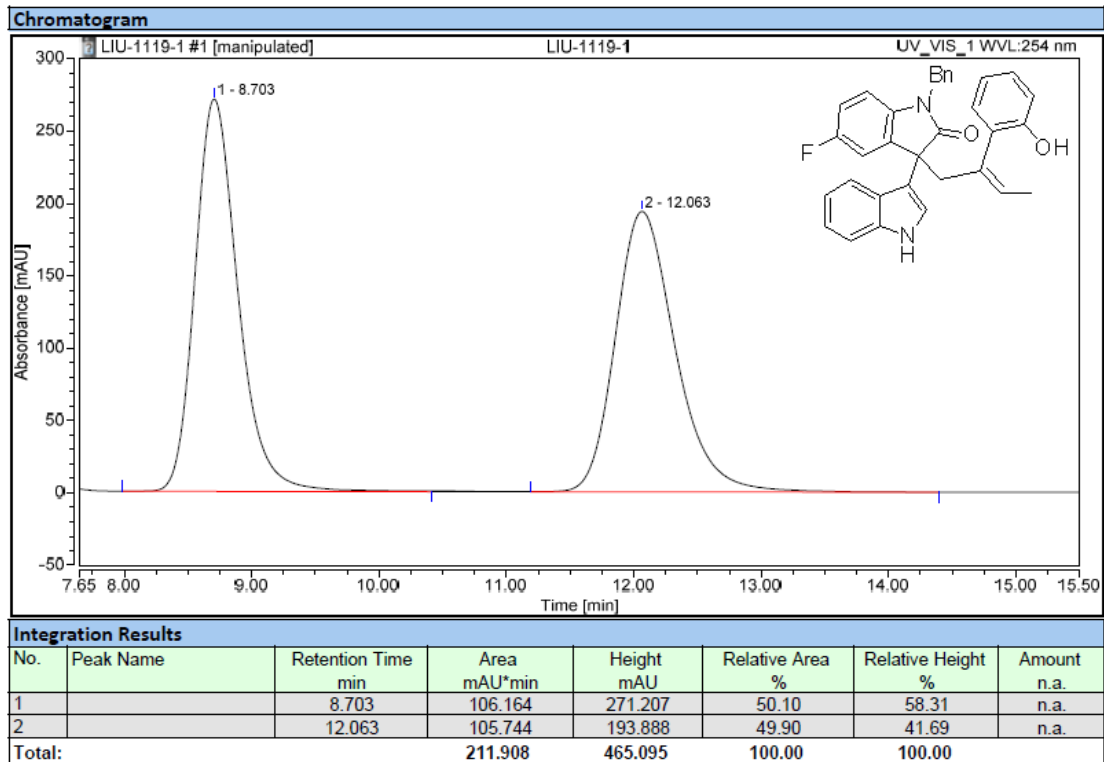
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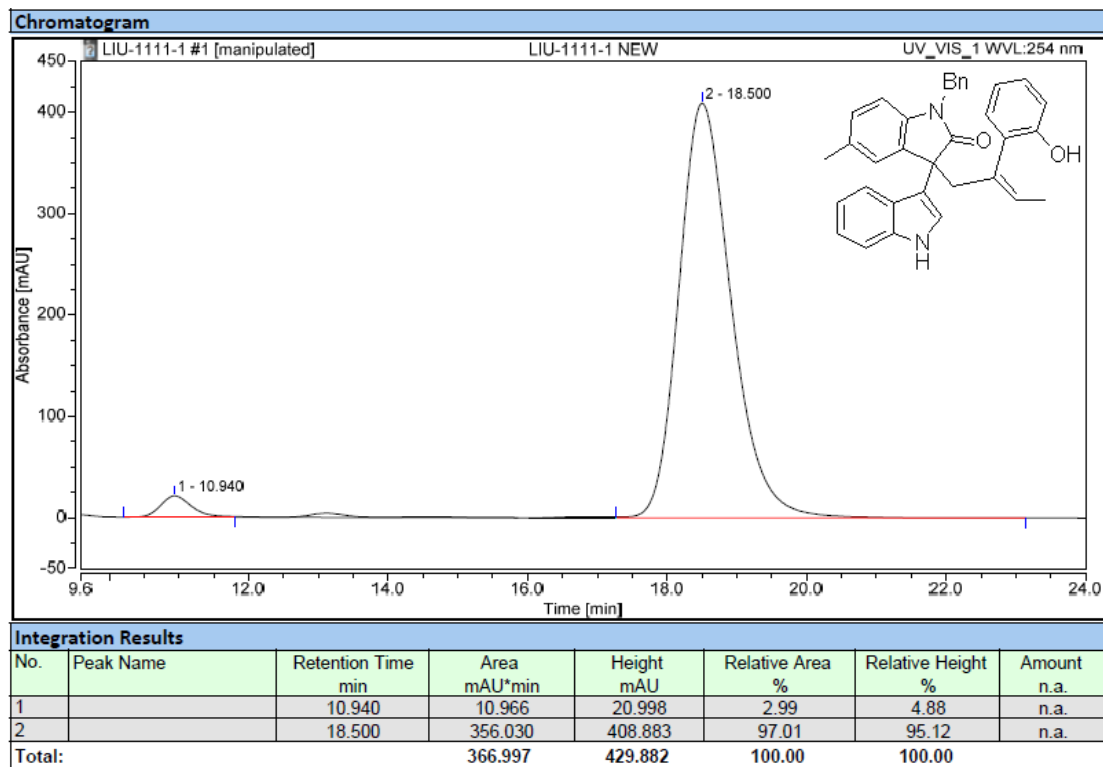
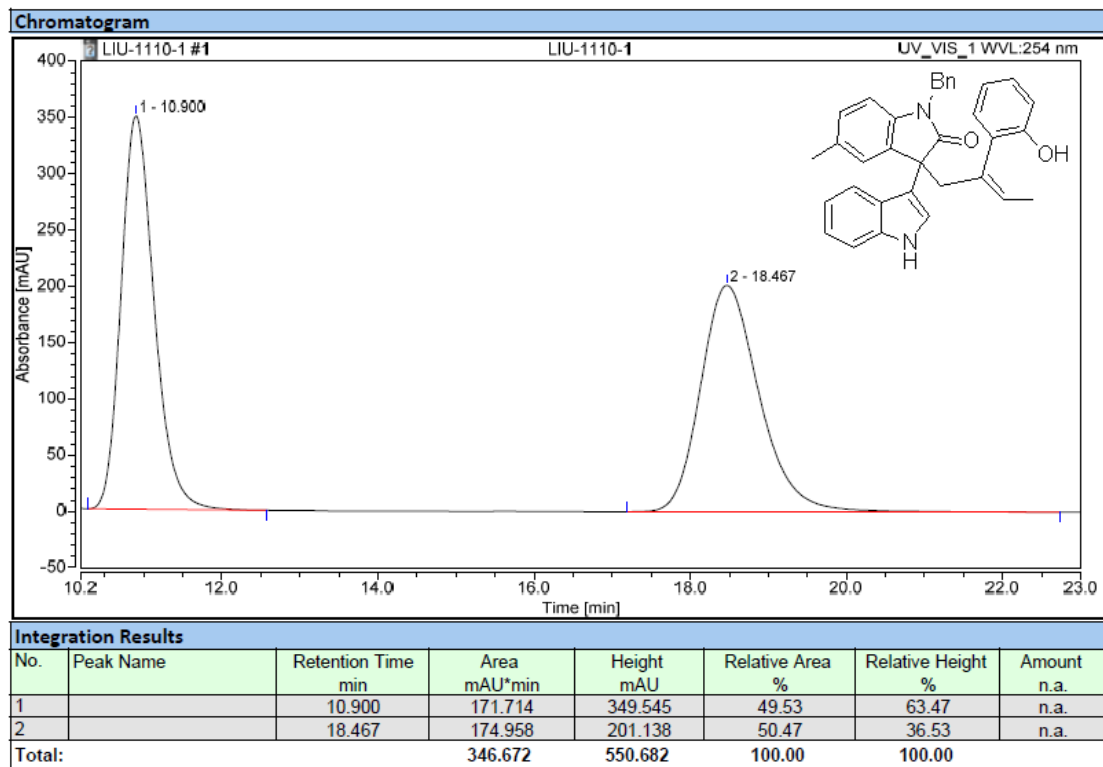
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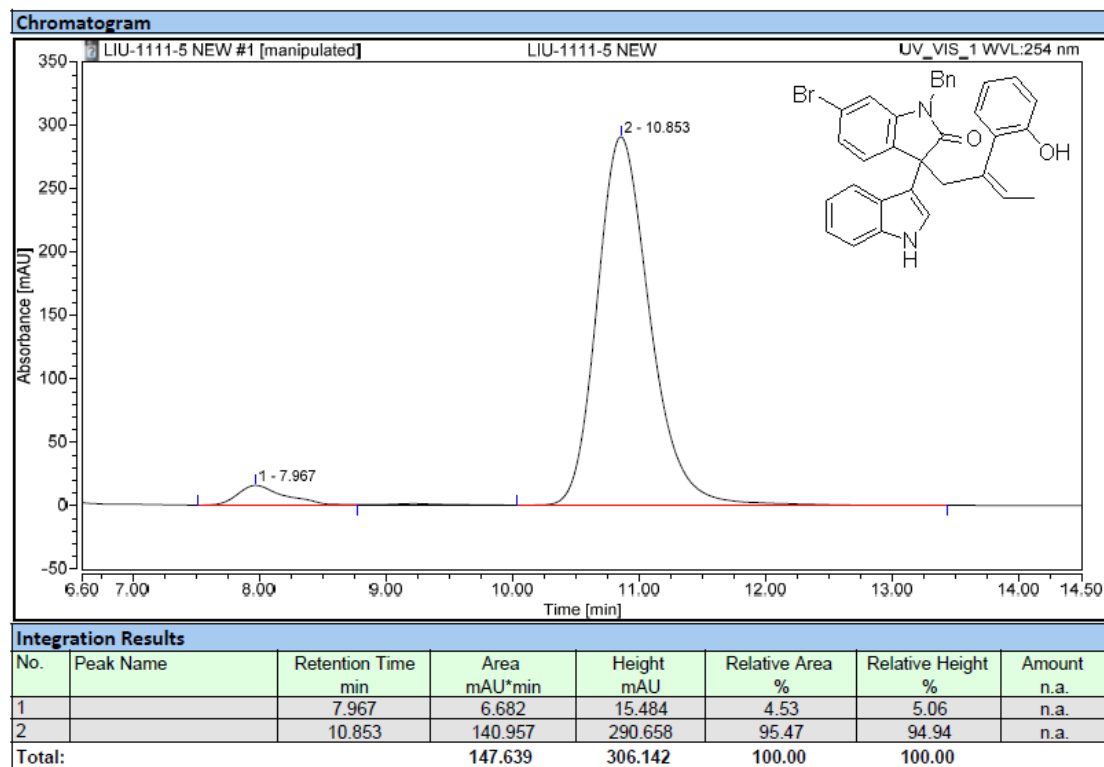
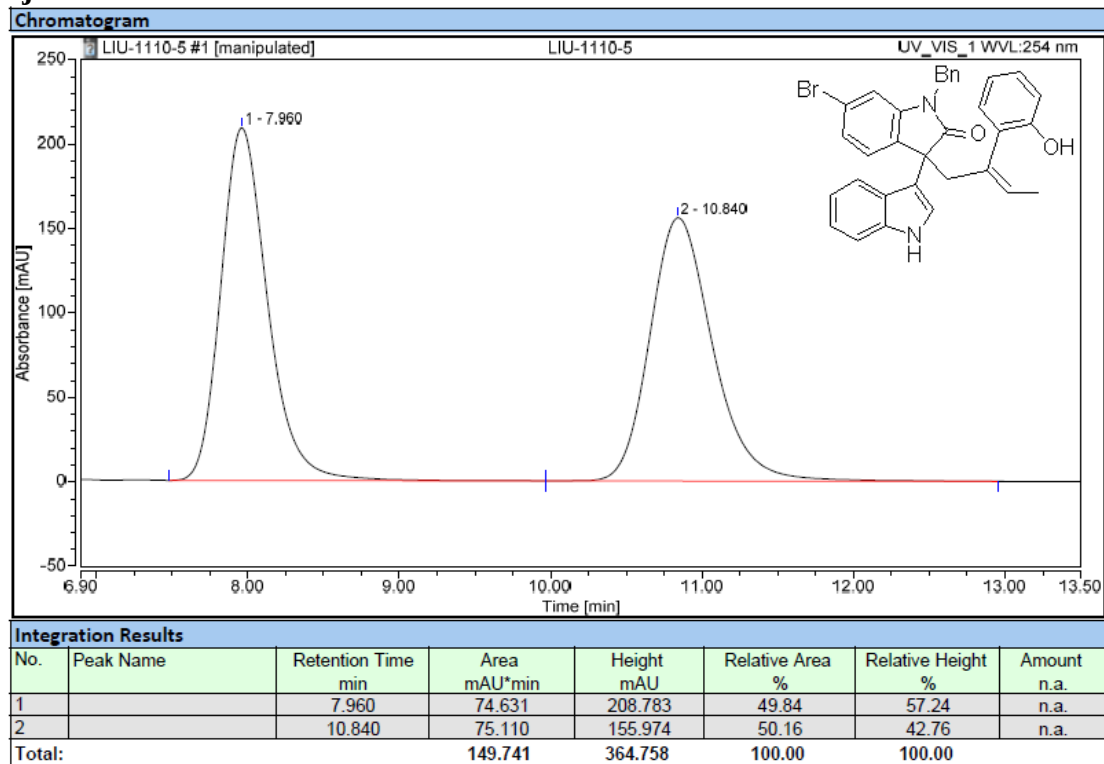
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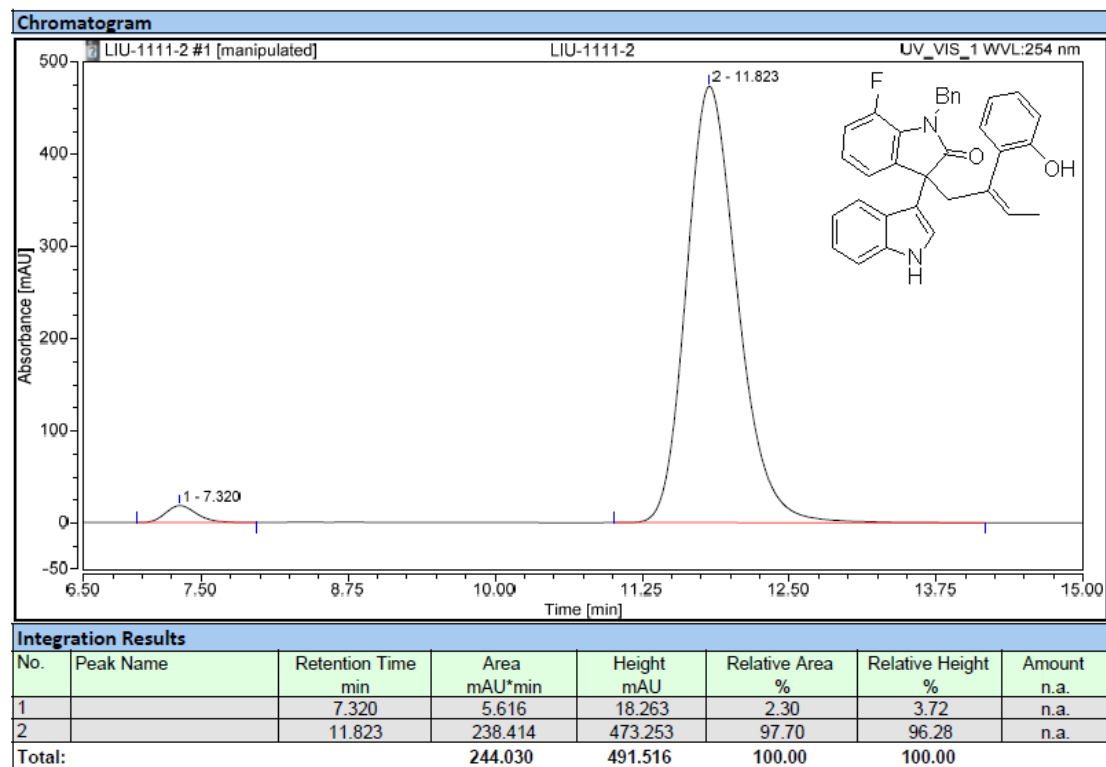
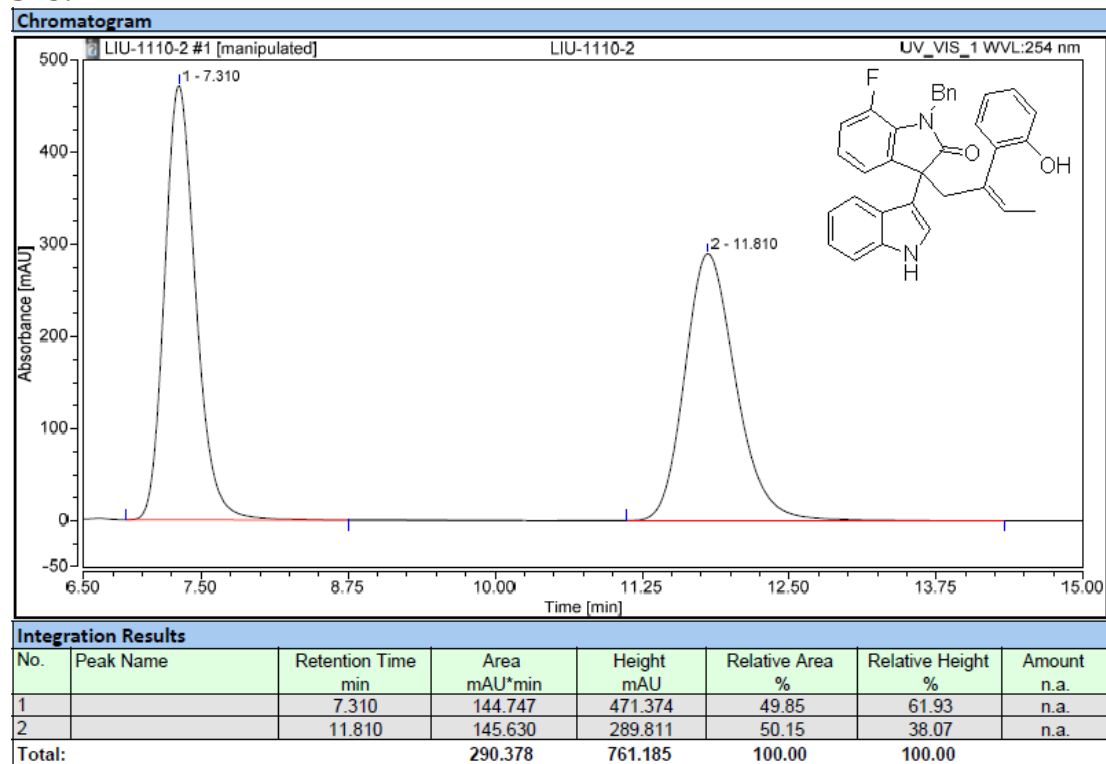
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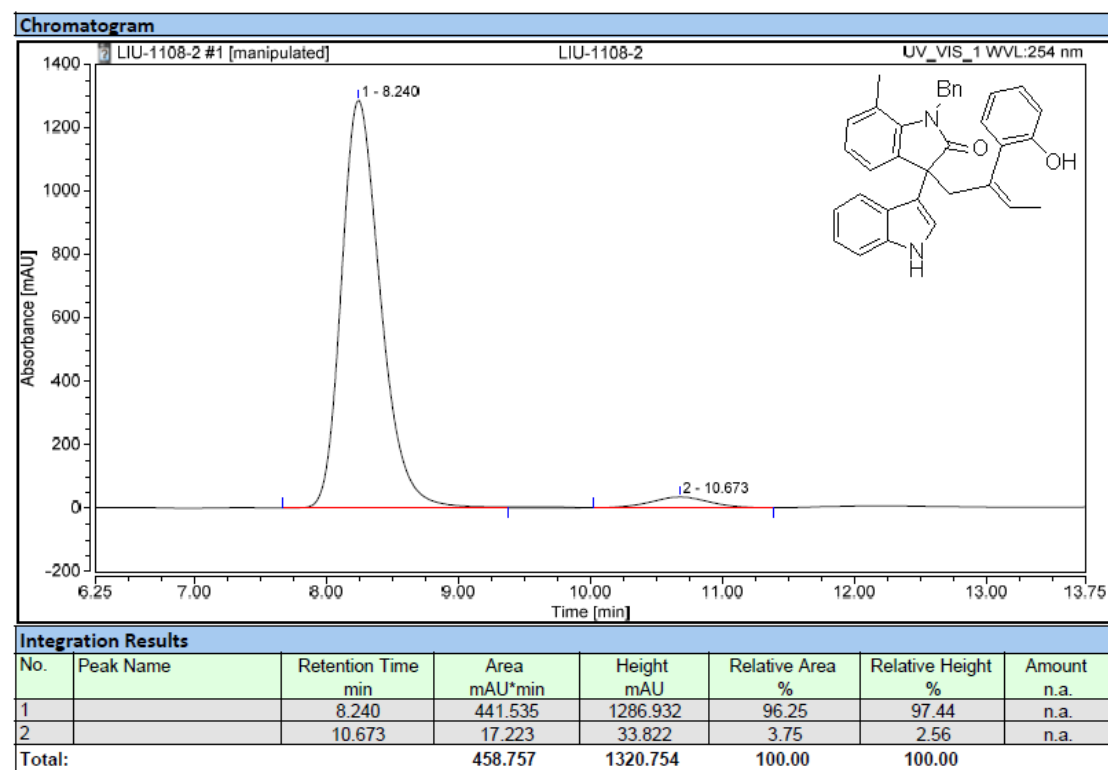
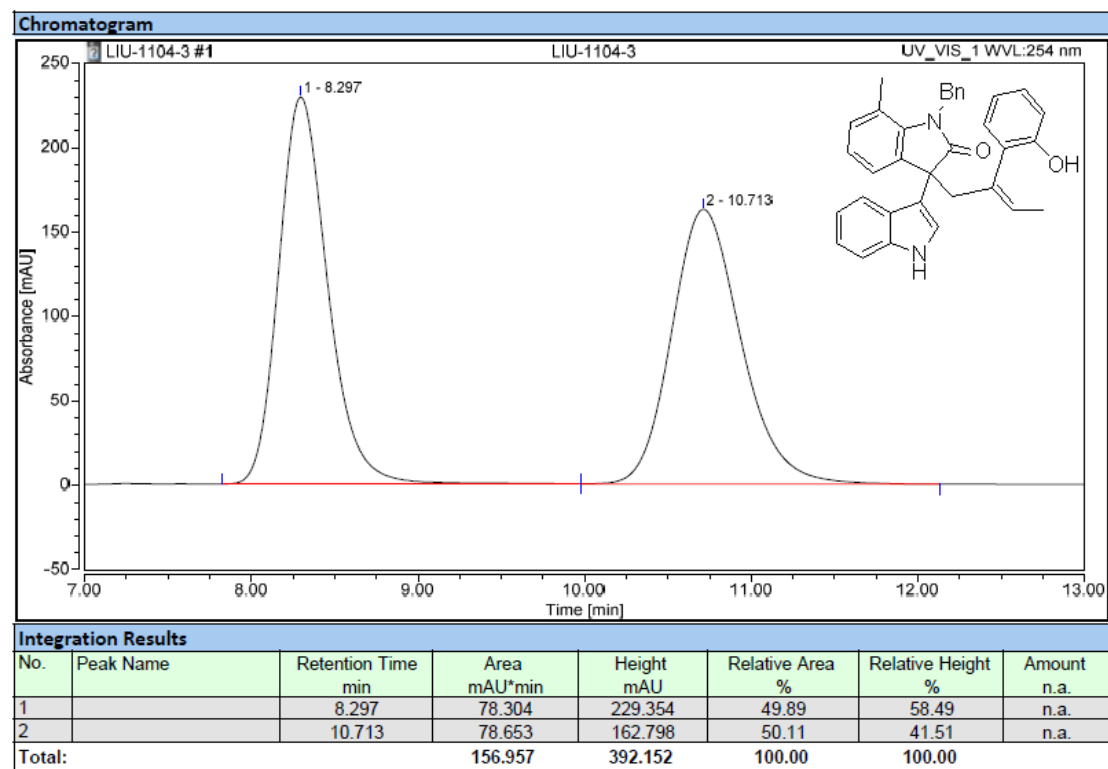
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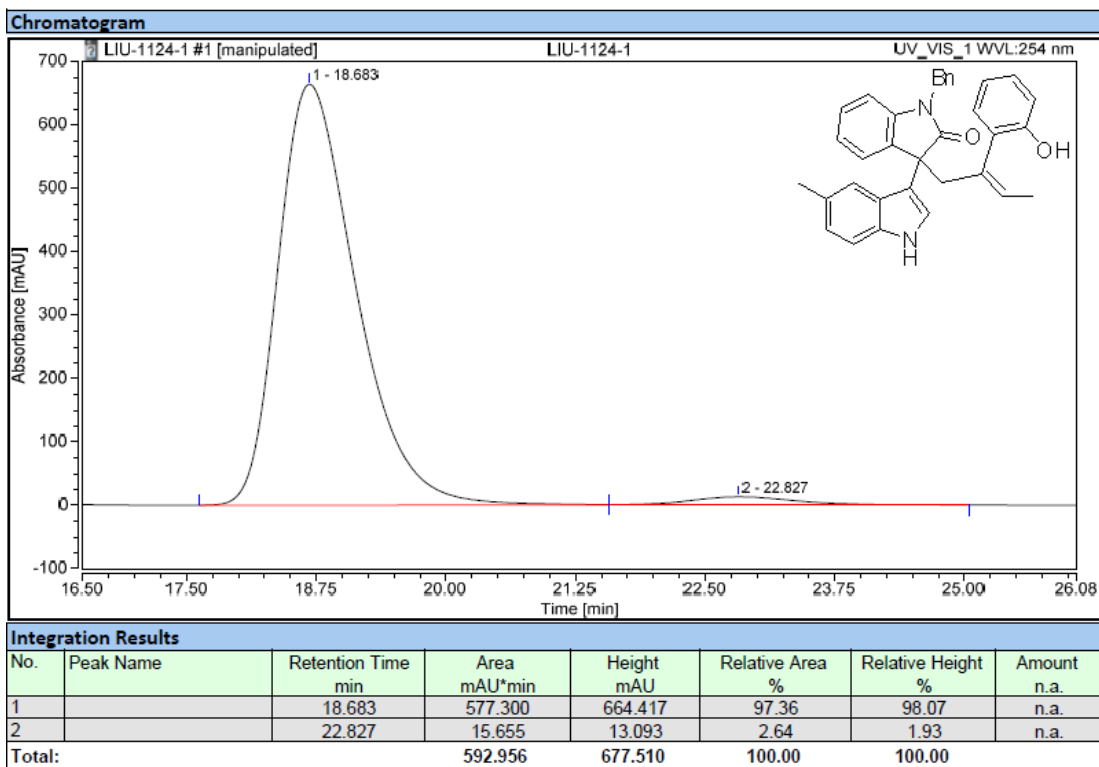
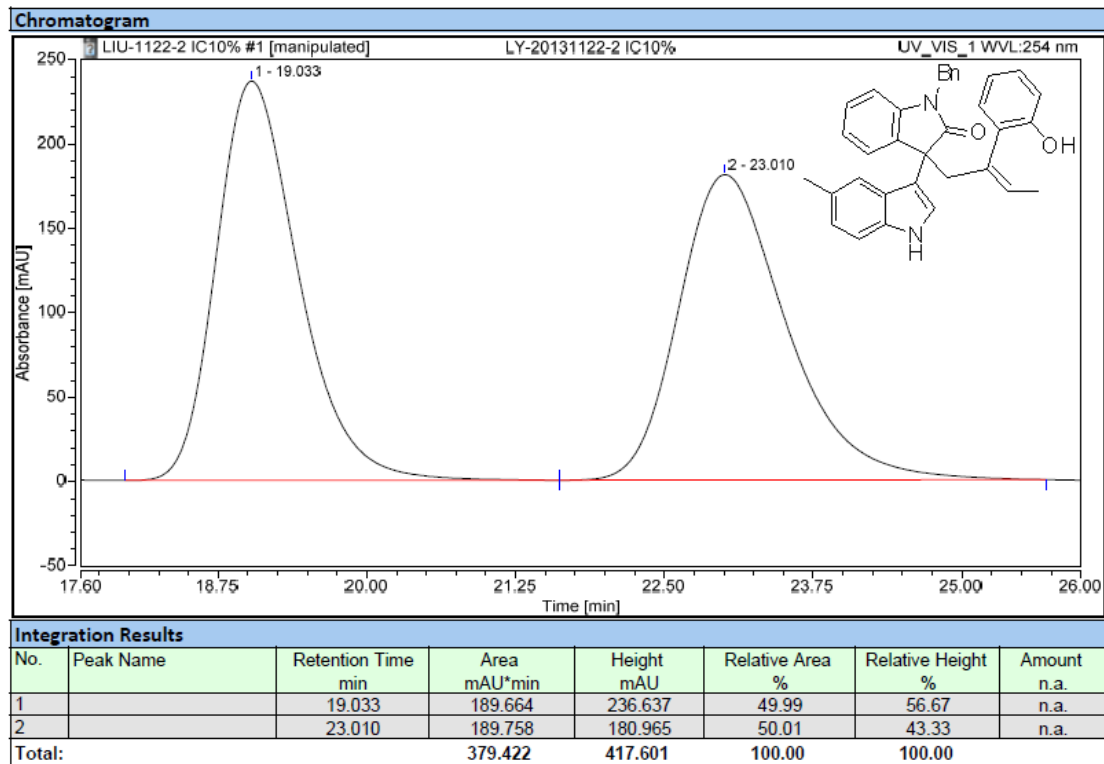
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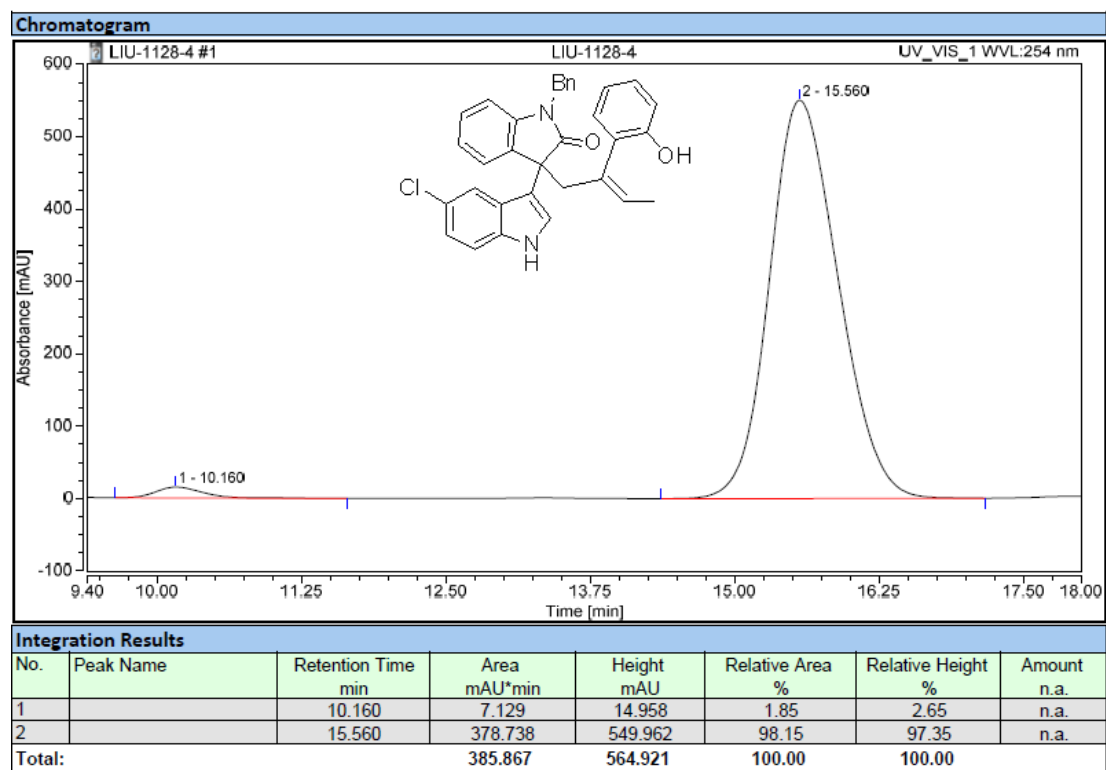
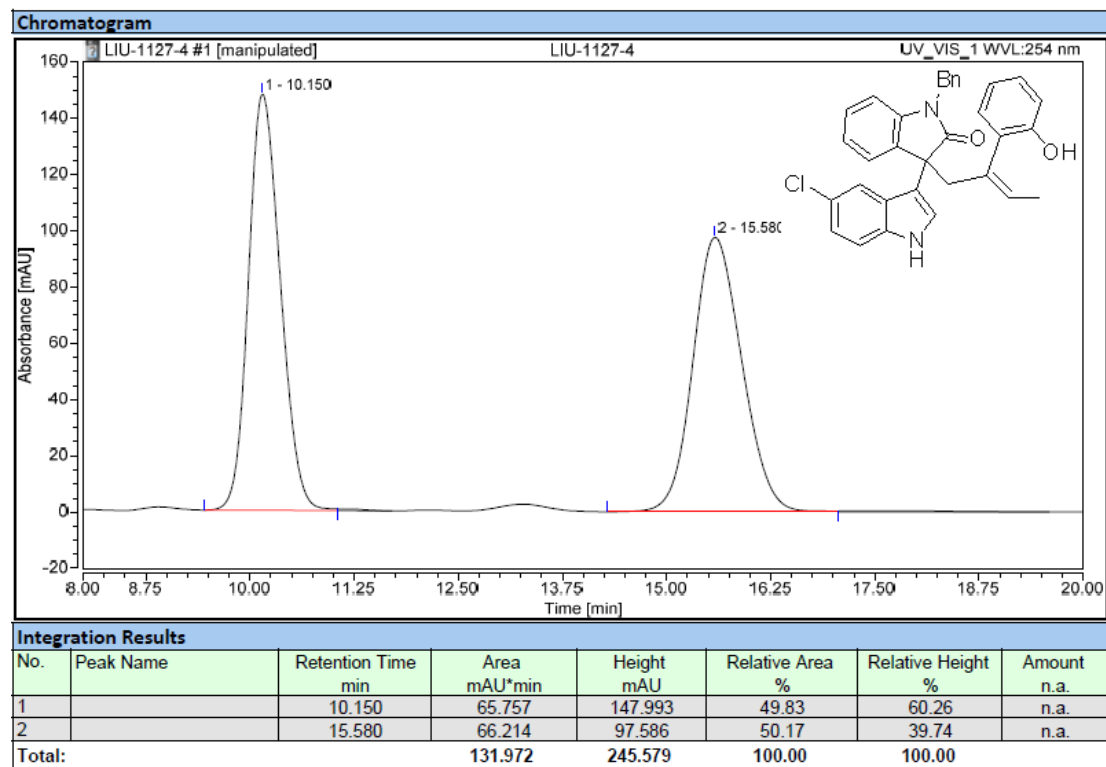
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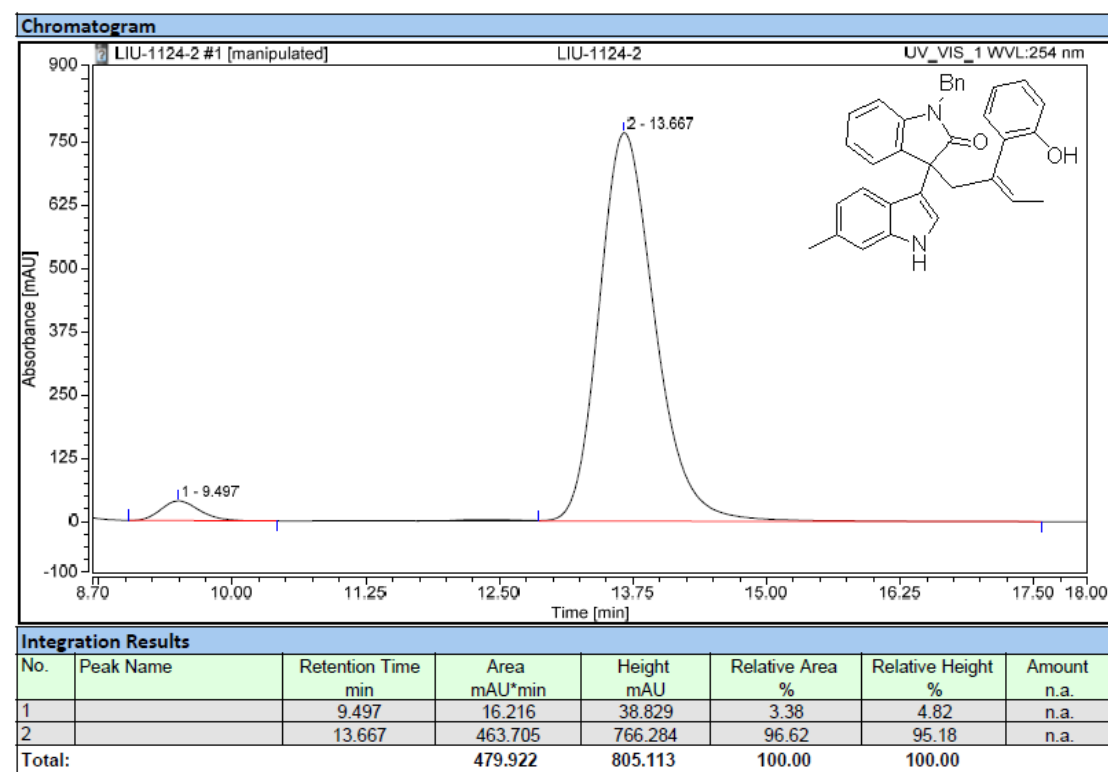
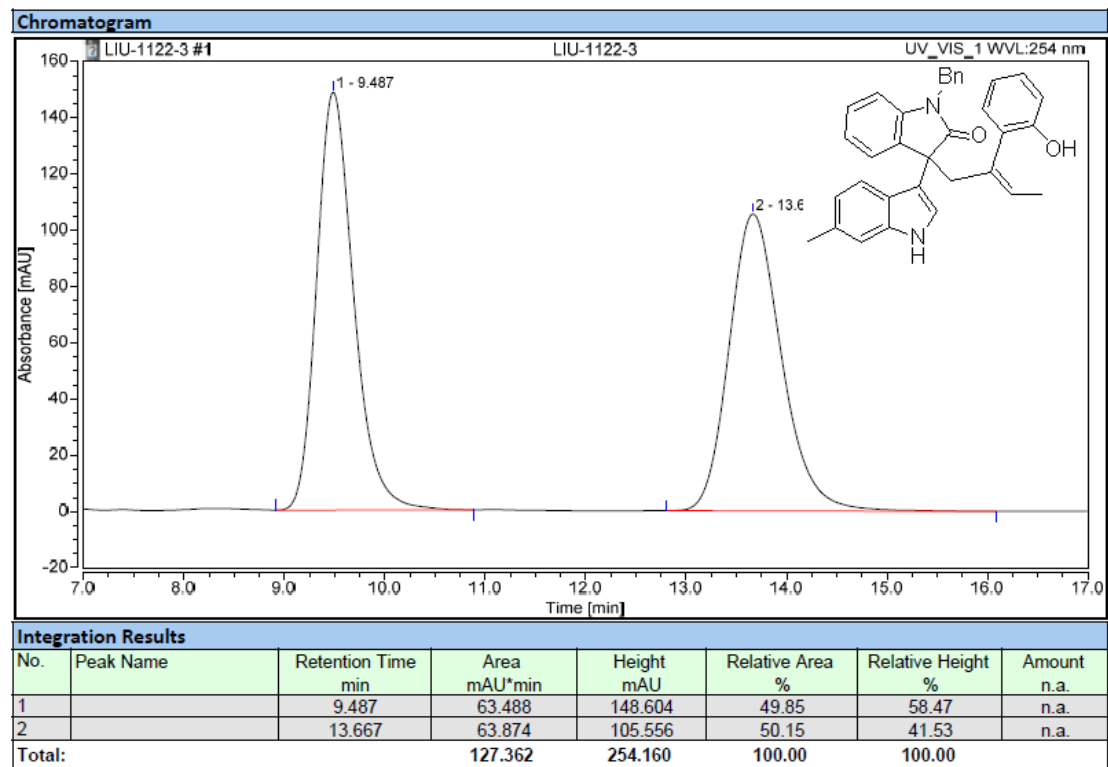
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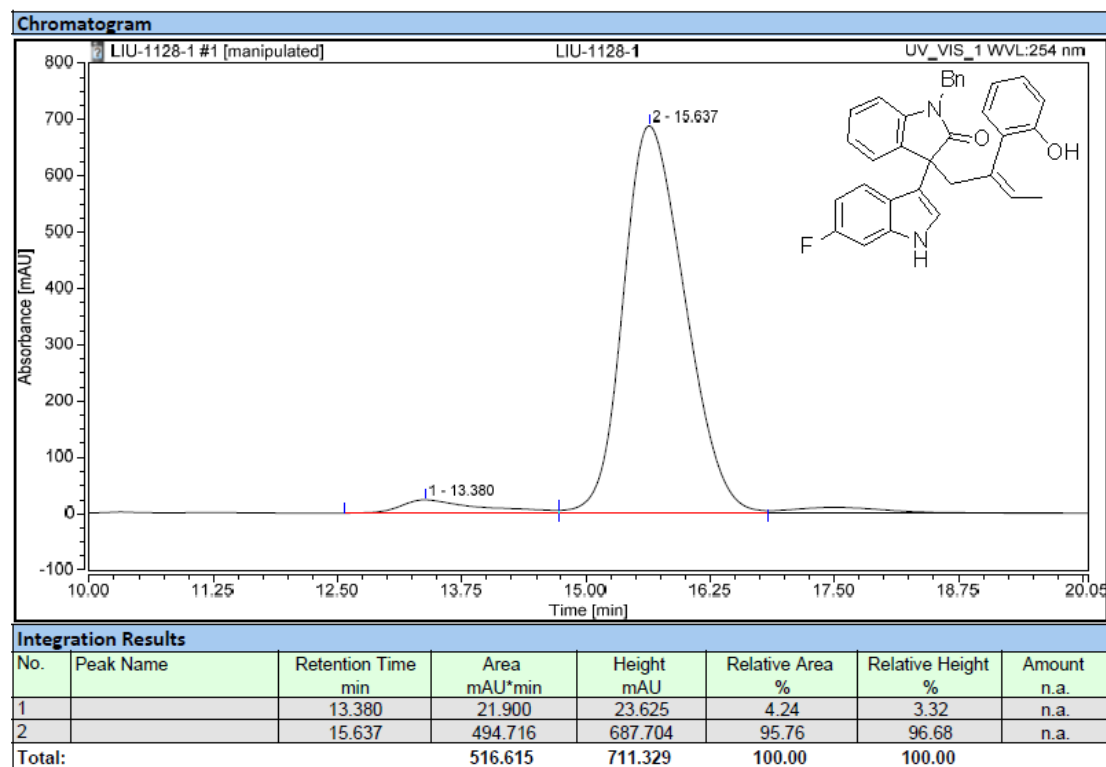
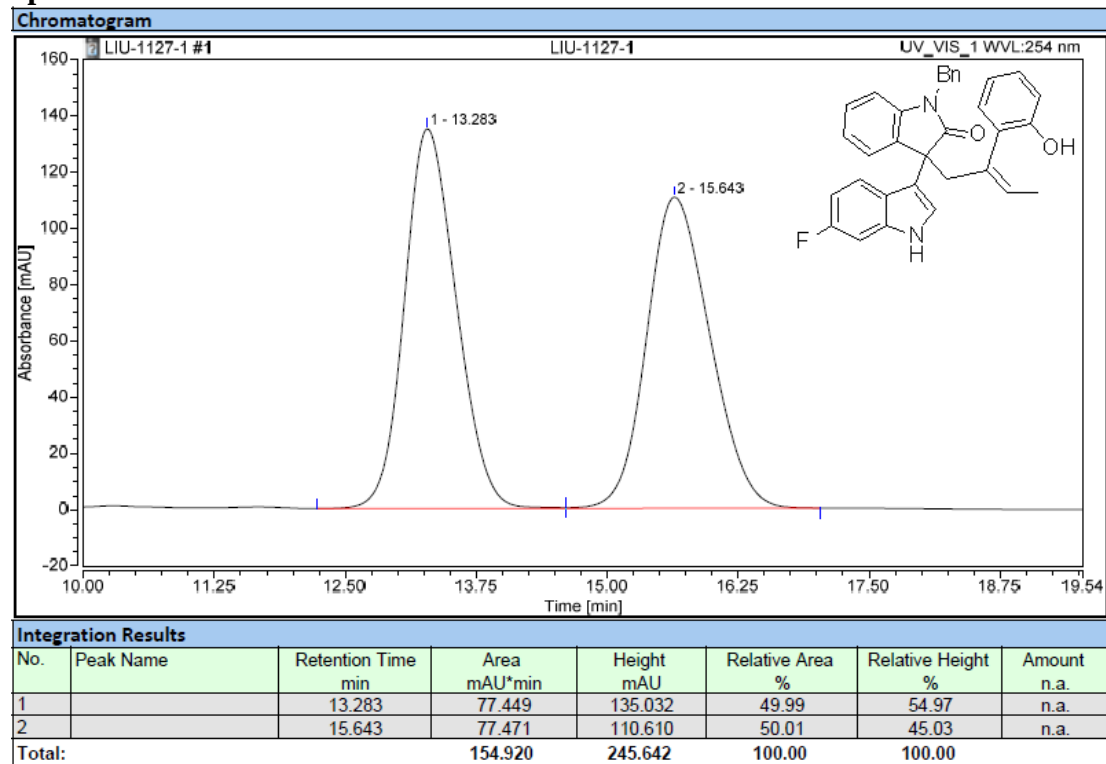
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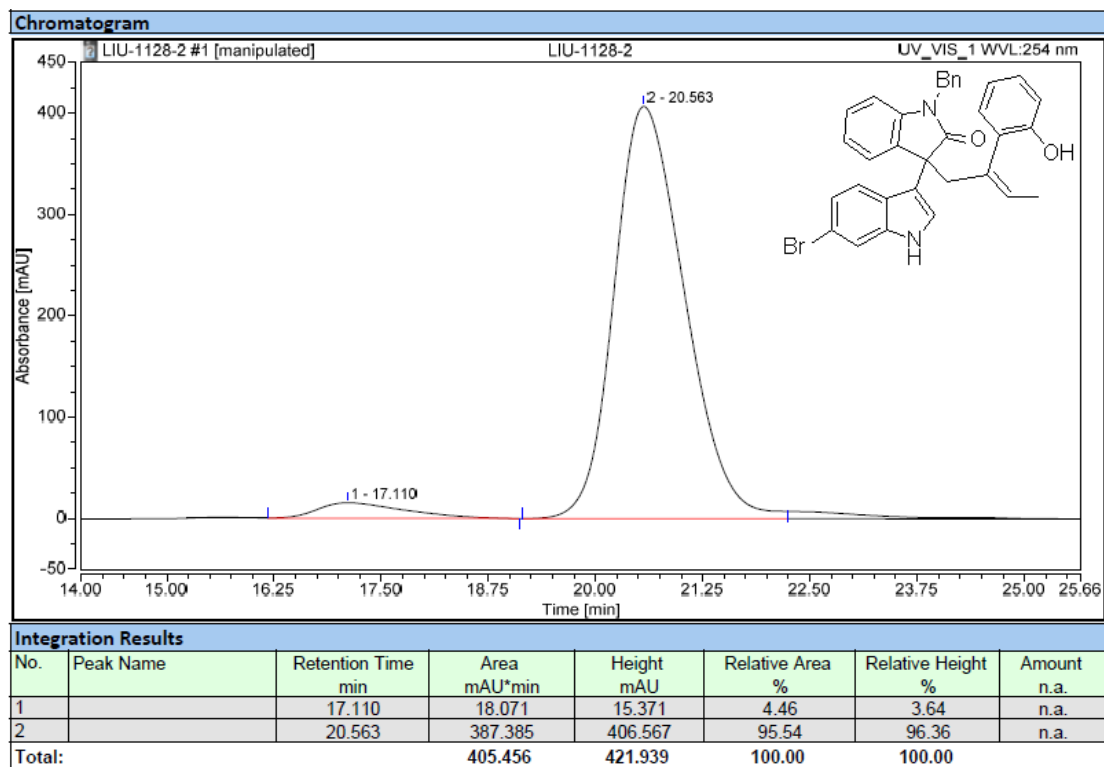
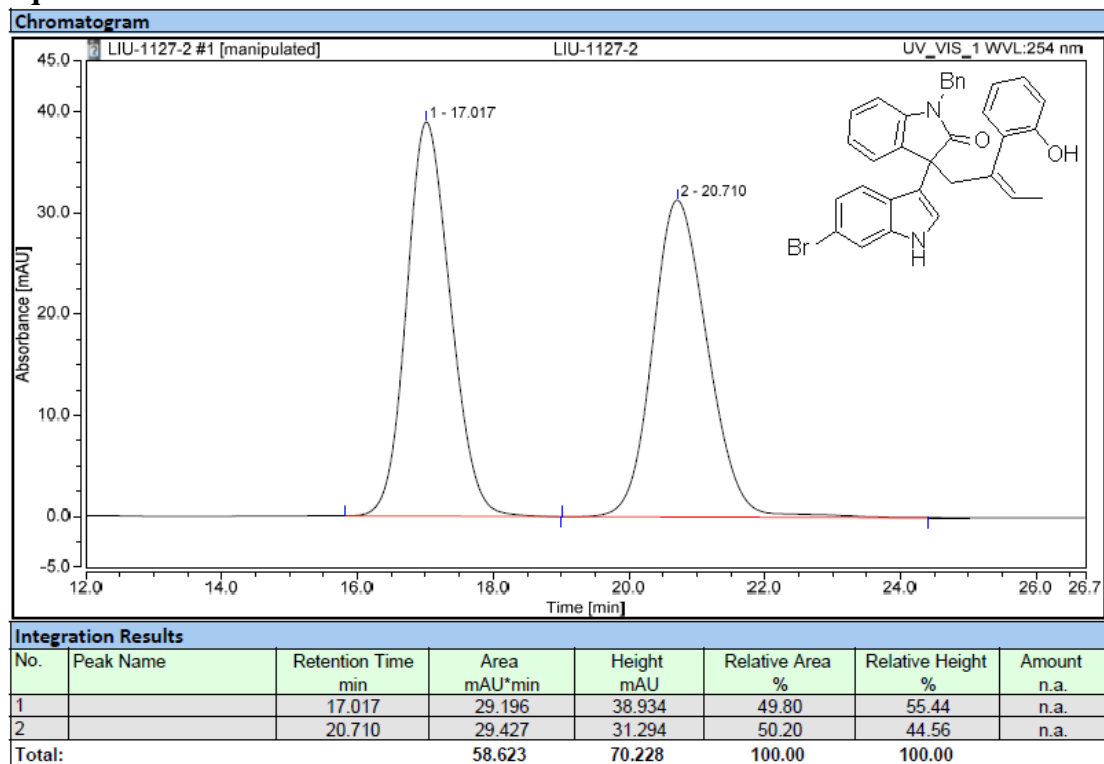
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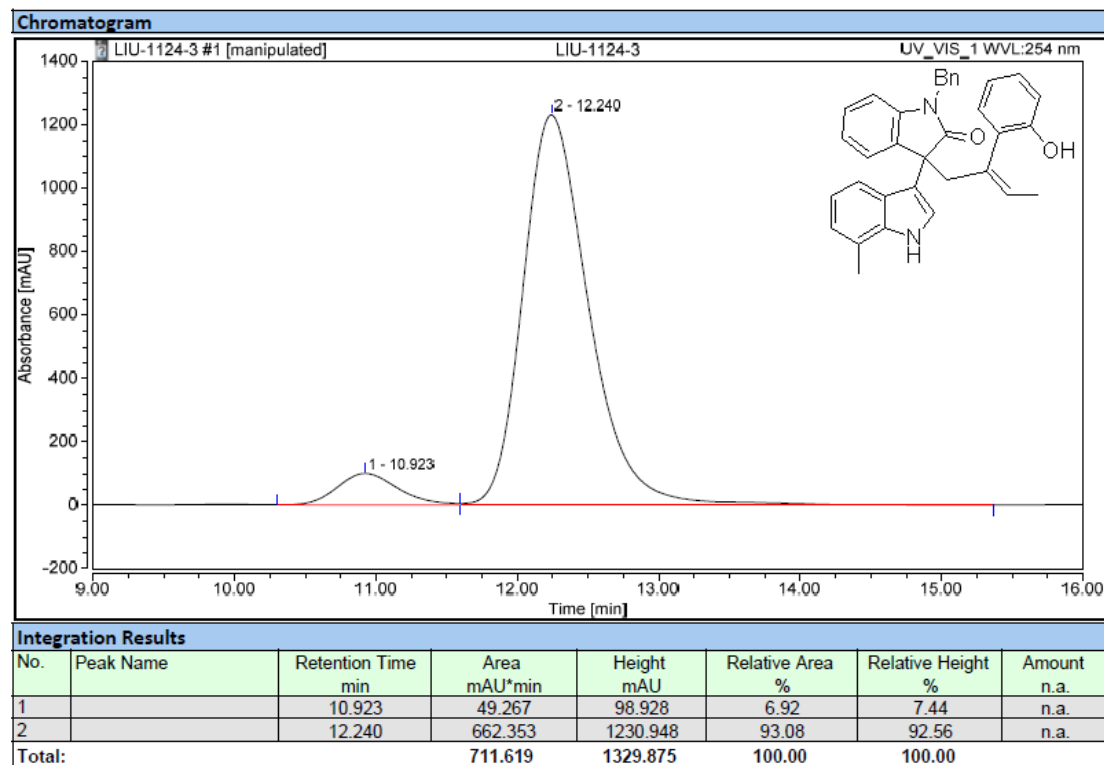
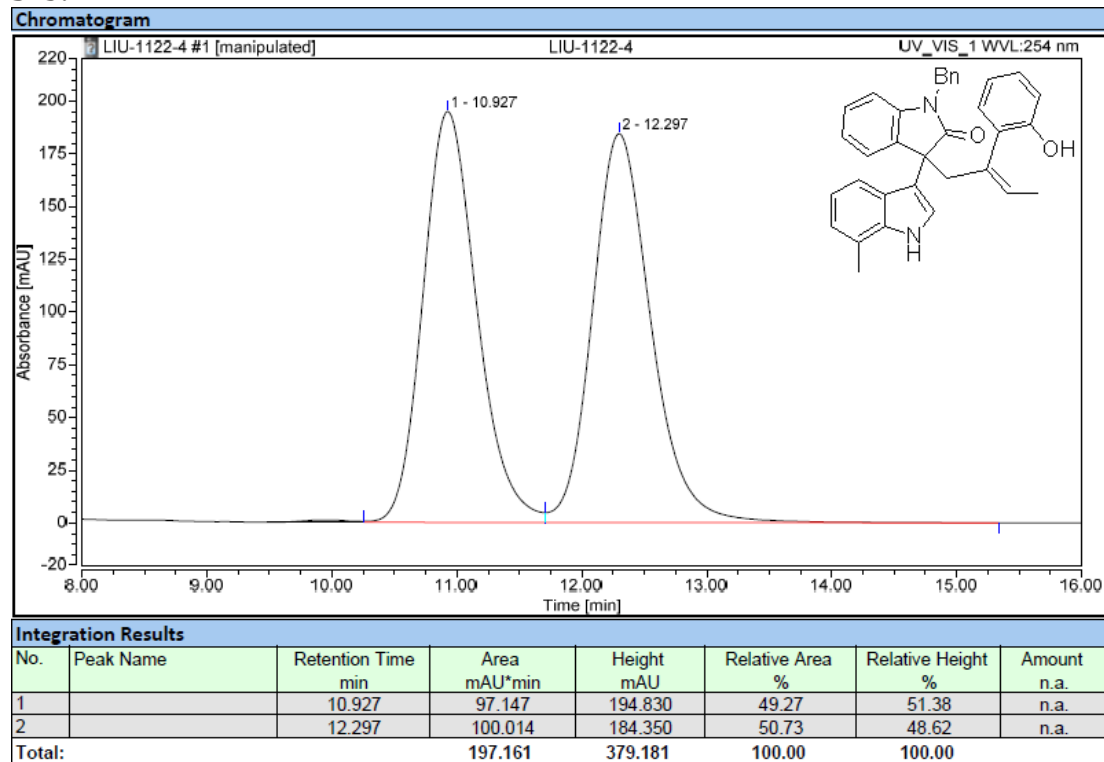
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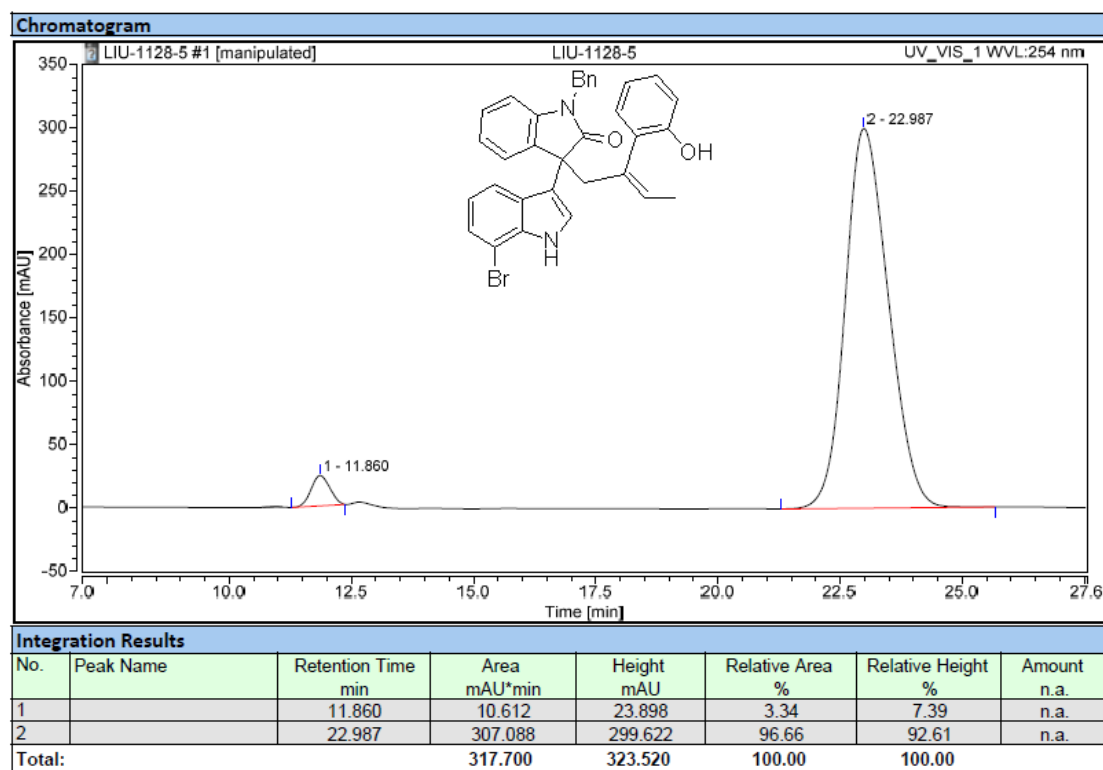
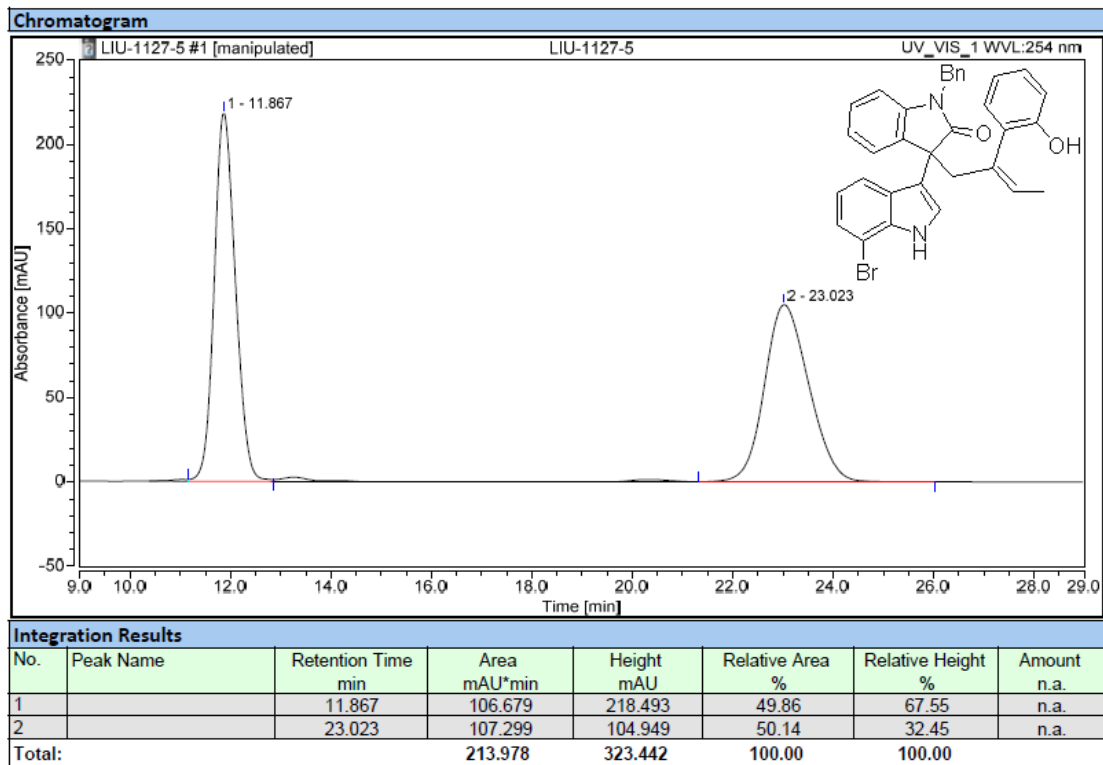
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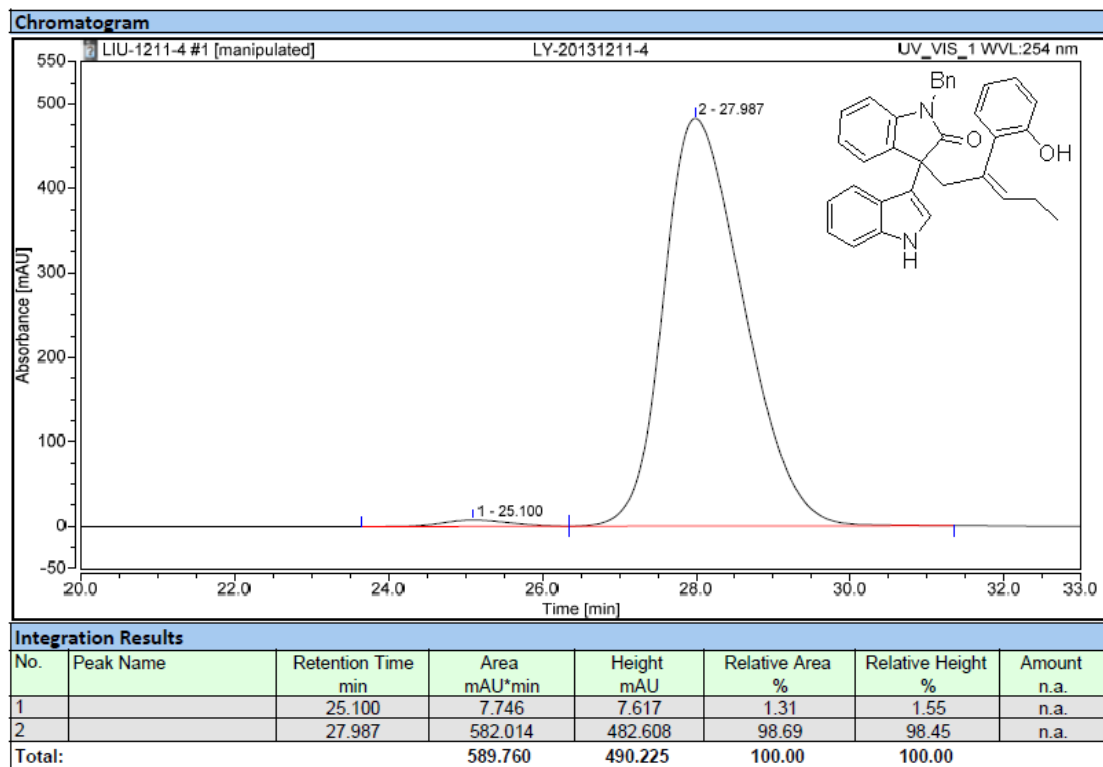
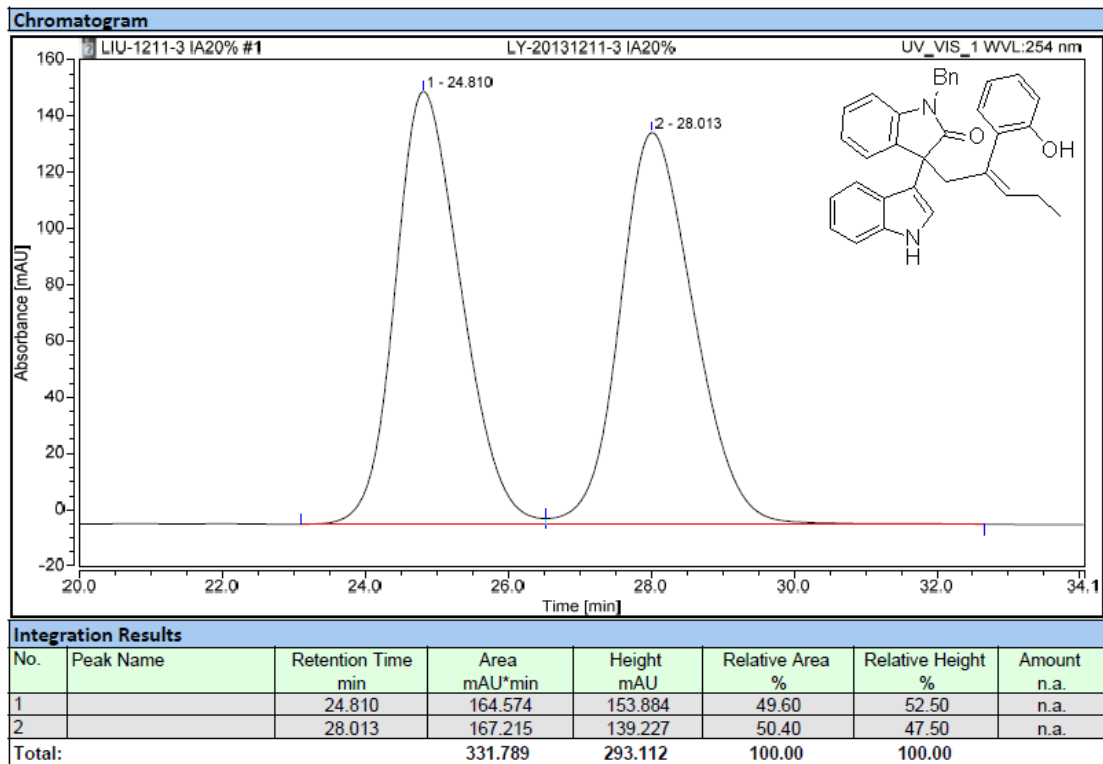
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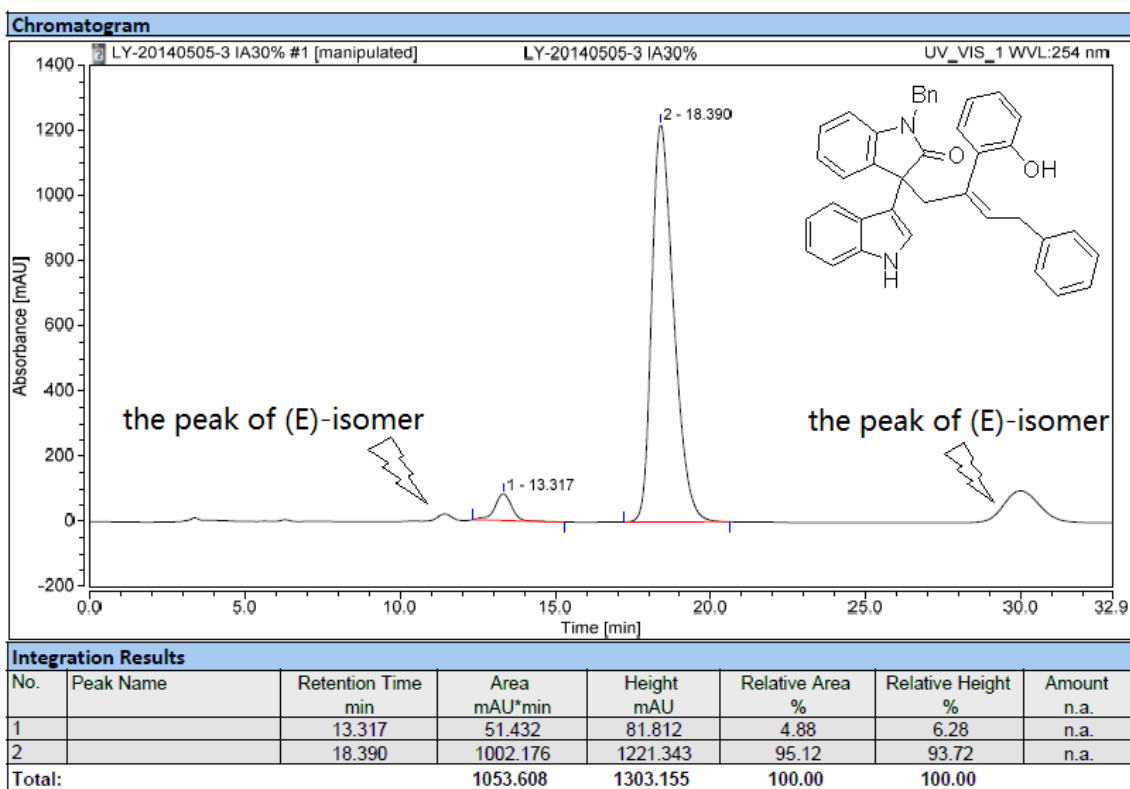
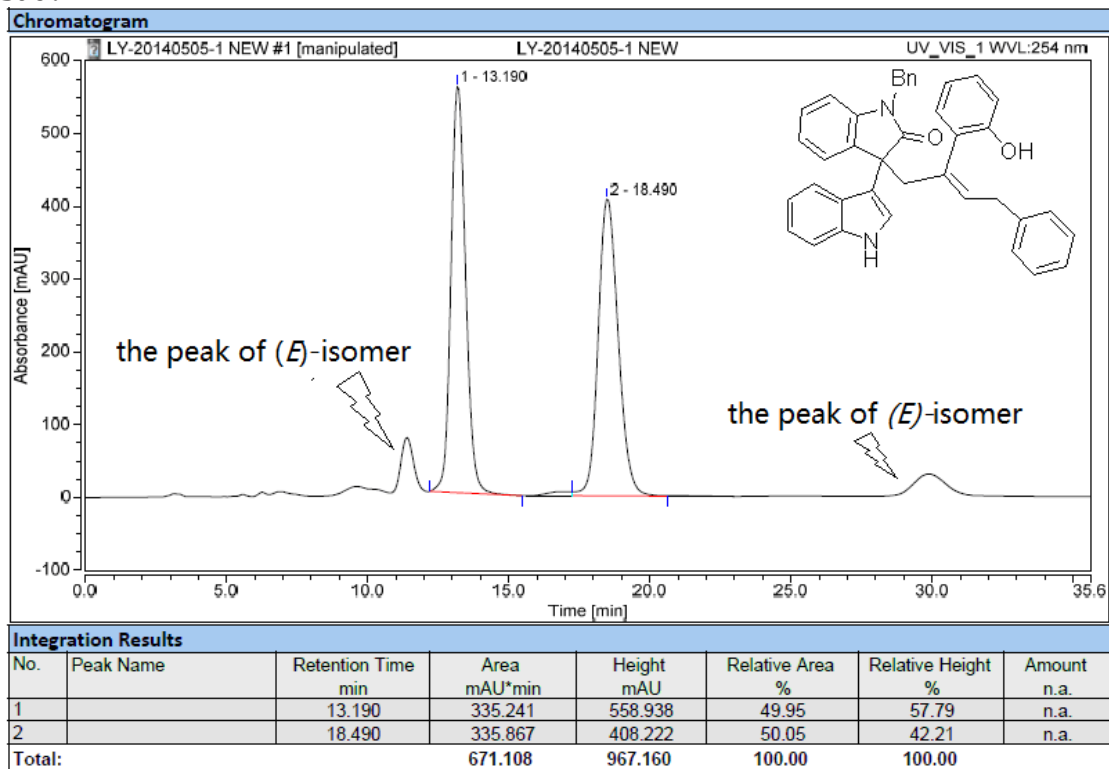
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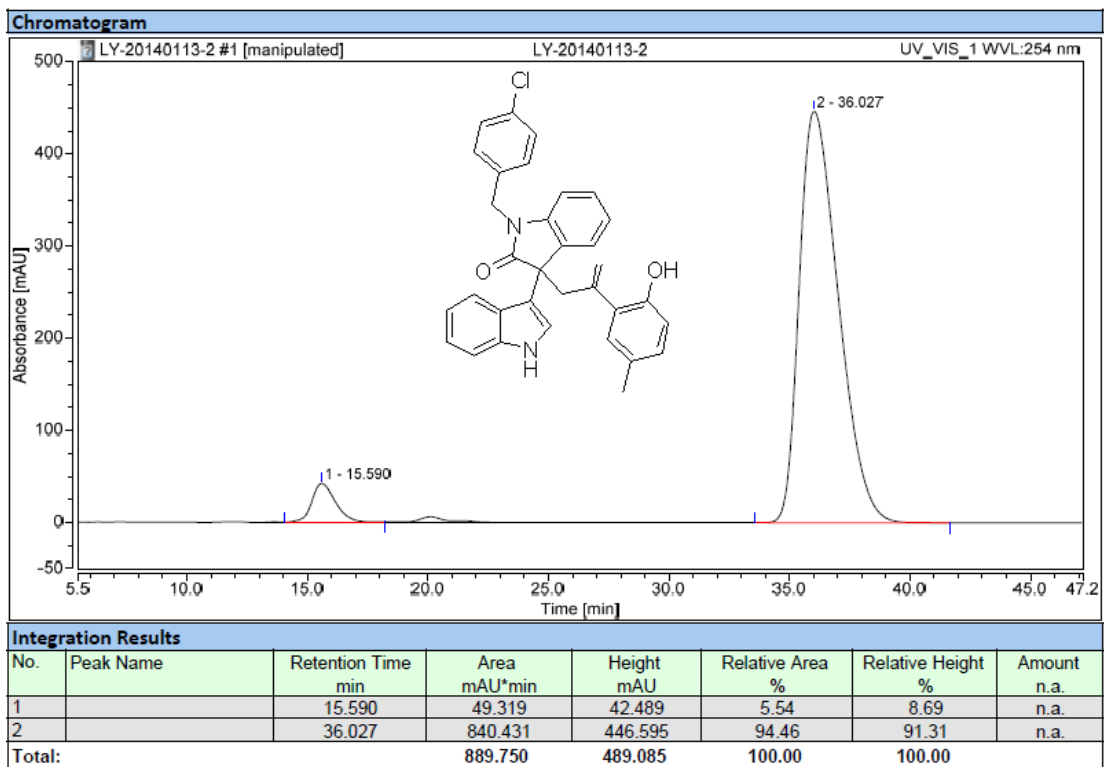
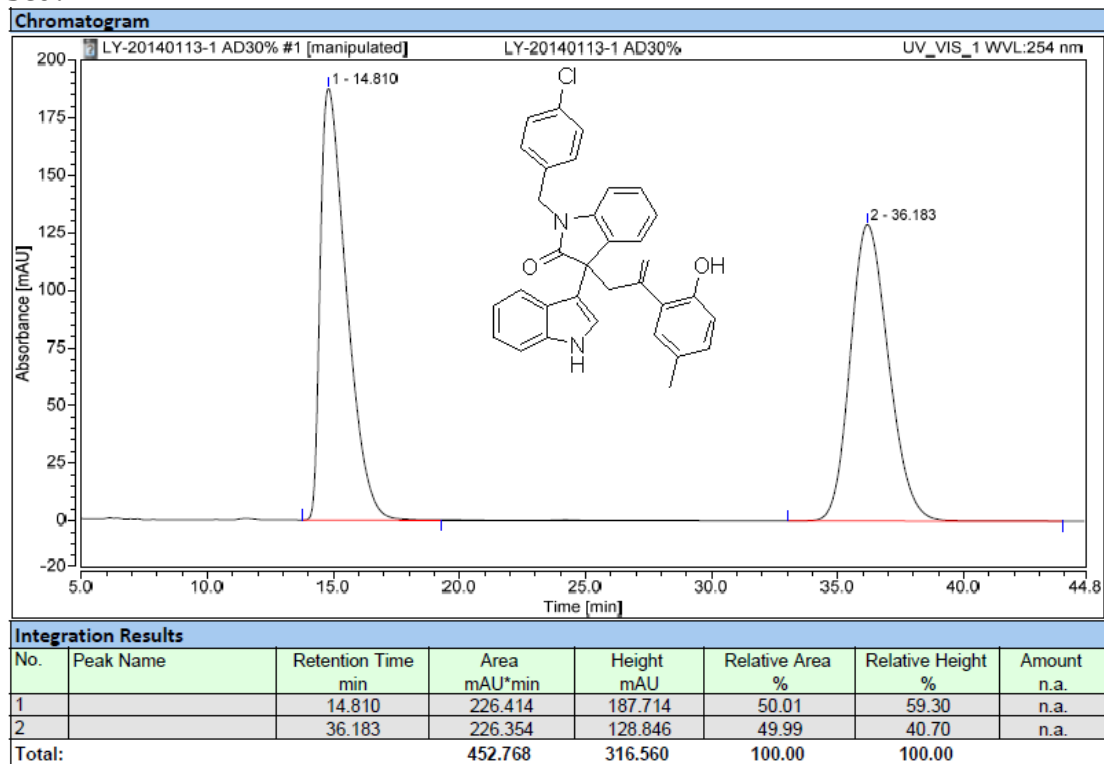
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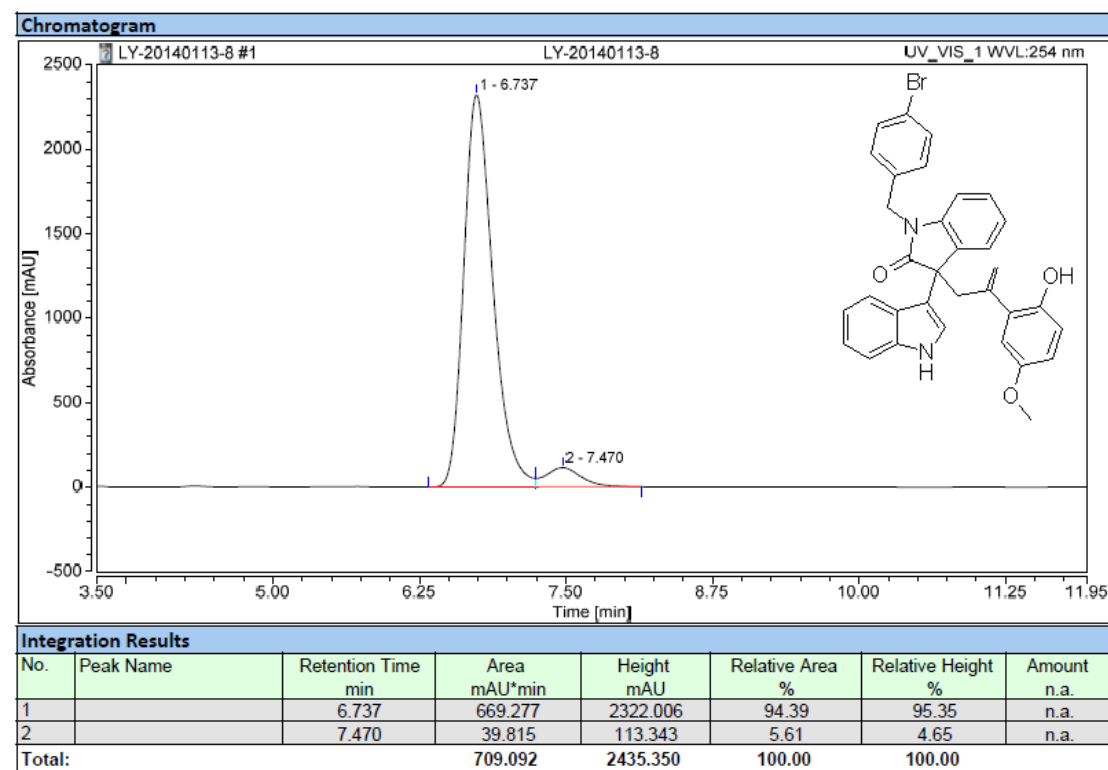
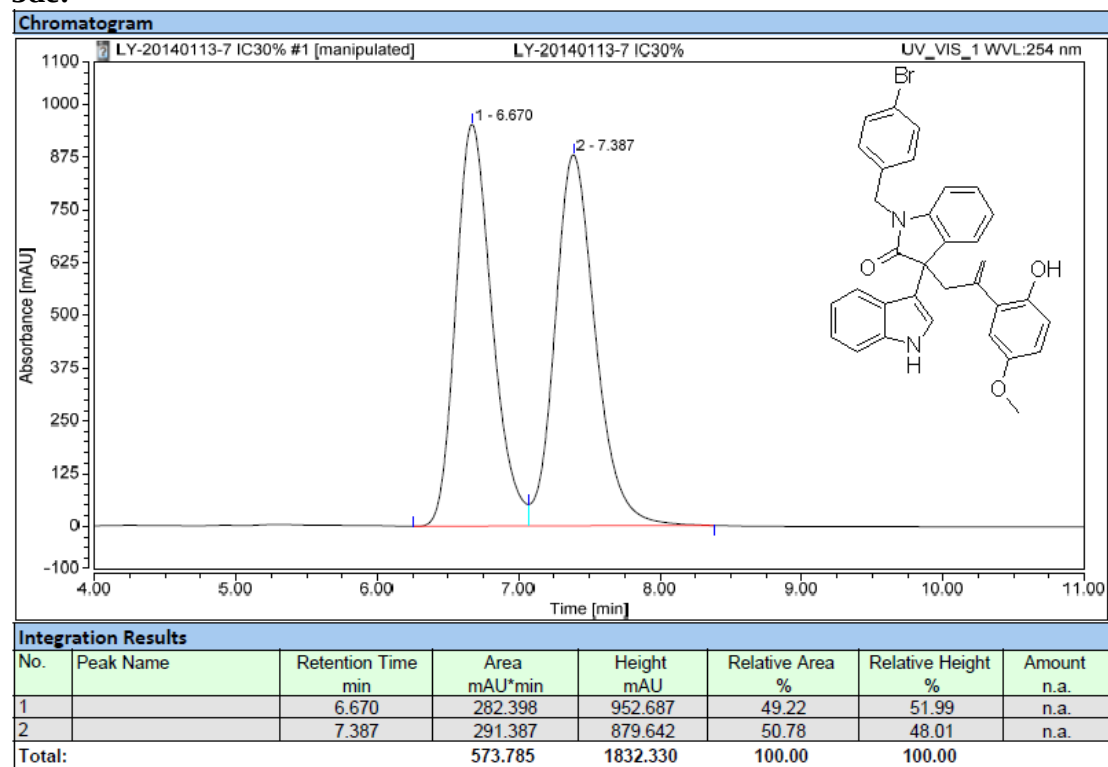
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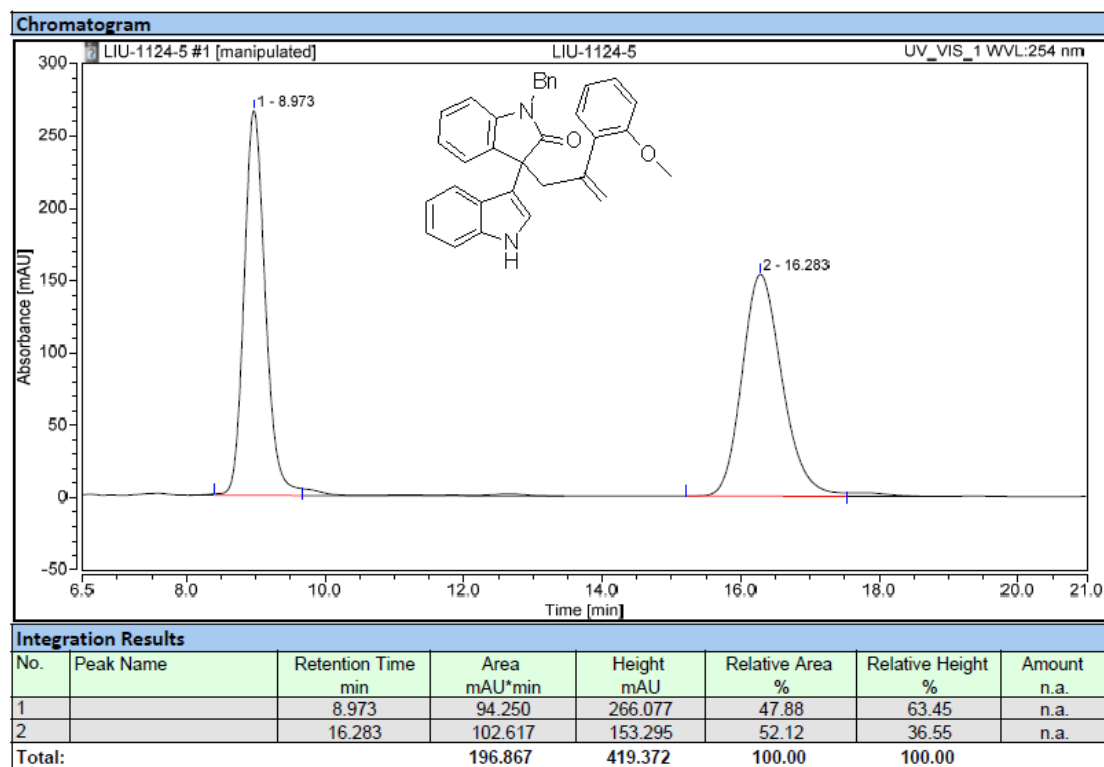
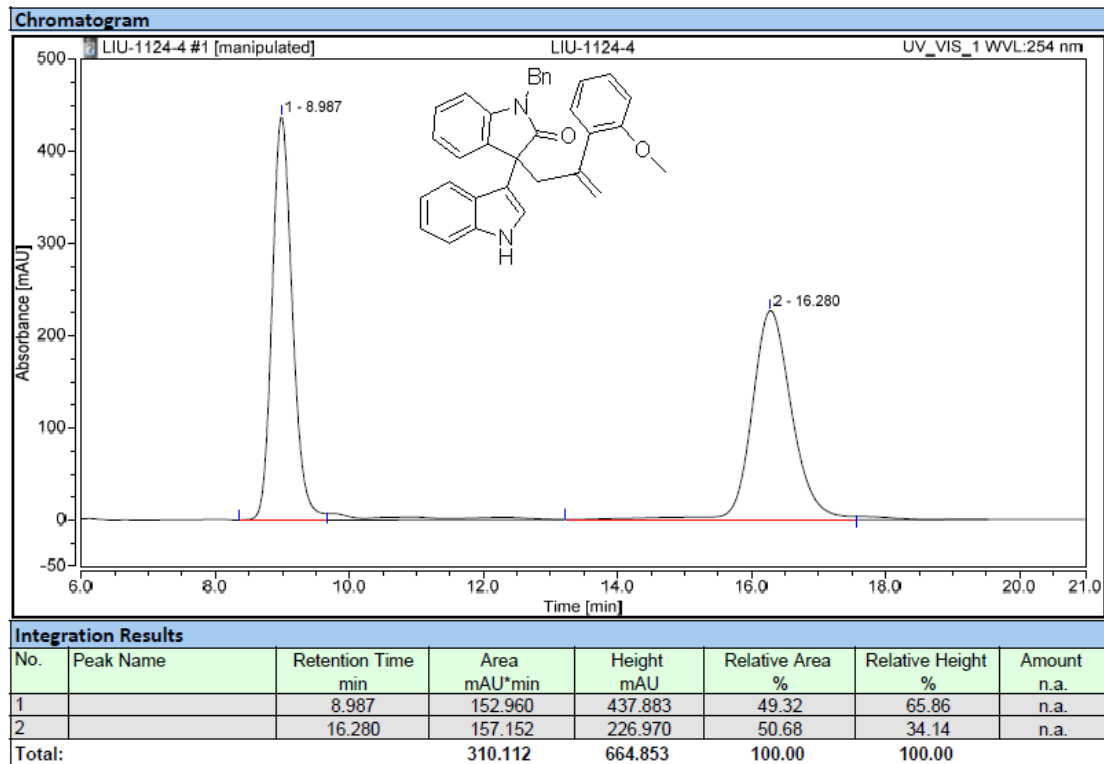
3ed:



3de:

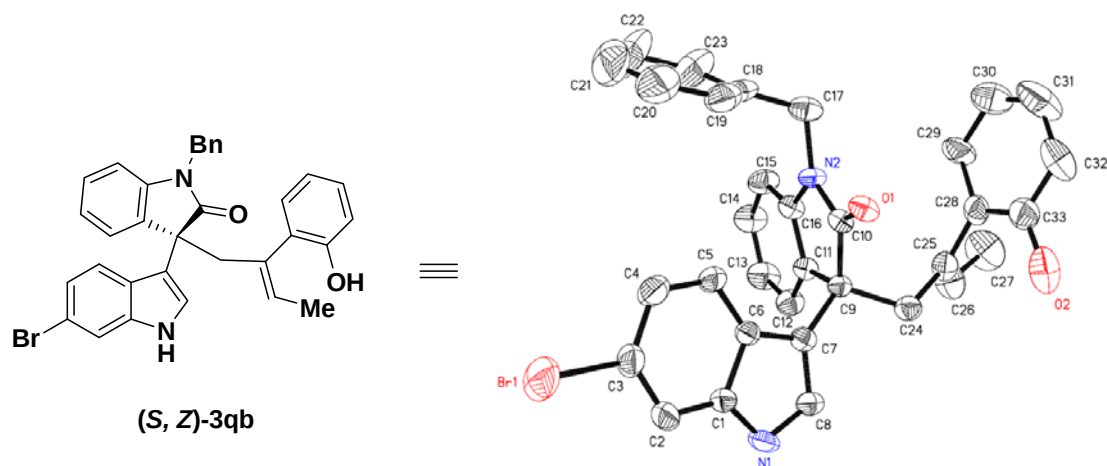


3af:



## X-ray single crystal data for 3qb:

### Absolute configuration and olefin geometry of 3qb:



|                               |                                                                                                 |
|-------------------------------|-------------------------------------------------------------------------------------------------|
| Crystal system                | orthorhombic                                                                                    |
| Space group                   | P 21 21 21                                                                                      |
| Hall group                    | P 2ac 2ab                                                                                       |
| Unit cell dimensions          | $a = 8.9032(6)$ $\alpha = 90$<br>$b = 11.1649(7)$ $\beta = 90$<br>$c = 27.772(2)$ $\gamma = 90$ |
| Volume                        | 2760.6(3)                                                                                       |
| Z                             | 4                                                                                               |
| Density (calculated)          | 1.356                                                                                           |
| Mu (mm <sup>-1</sup> )        | 1.521                                                                                           |
| $F(000)$                      | 1160.0                                                                                          |
| h,k,lmax                      | 11,14,35                                                                                        |
| Nref                          | 6298                                                                                            |
| Tmin,Tmax                     | 0.603,0.741                                                                                     |
| Data completeness             | 1.76/0.99                                                                                       |
| Theta(max)                    | 27.474                                                                                          |
| R(reflections)                | 0.0580( 2682)                                                                                   |
| wR2(reflections)              | 0.1508( 6298)                                                                                   |
| refine ls abs structure Flack | 0.025(9)                                                                                        |