Supporting Information

Organocatalytic asymmetric synthesis of arylindolyl indolin-3-ones with both axial and central chirality

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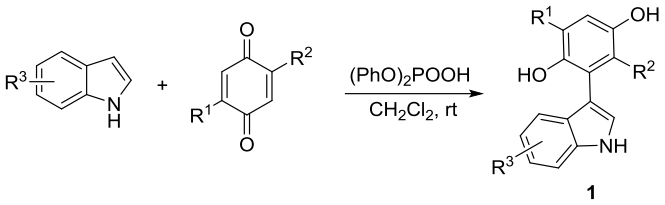
1. General procedures

All reactions were carried out in dry solvents under an argon atmosphere. The reagents were purchased and used without further purification. The reactions were monitored by thin layer chromatography (TLC), and the products were isolated by silica gel column chromatography or preparative silica gel thin layer chromatography (*p*-TLC). Melting points were recorded on a Beijing Tech X-4 melting point apparatus. High-resolution mass spectra (HRMS) were recorded on LCMS-IT/TOF (SHIMADZU, Japan) with an electrospray ionization source. ^{1}H NMR, ^{13}C NMR spectra were recorded on JNM-ECS 400 using tetramethylsilane (TMS) as the internal standard. Chiral HPLC analysis was achieved using an Agilent 1100 Infinity series normal phase HPLC unit and Agilent Chemstation software. Daicel Chiralpak columns (250 × 4.6 mm) were used as specified in the text. Solvents were used of HPLC grade (Sigma Aldrich); all eluent systems were isocratic. Single crystal X-ray data were collected on a Bruker APEXII X-ray diffractometer equipped with a CMOS PHOTON 100 detector with a Cu K_α X-ray source (K_α = 1.54178 Å). Data were indexed, integrated and scaled using DENZO and SCALEPACK from the HKL program suite (Otwinowski & Minor, 1997). Structure of (S_a,*R*)-**3a** was solved through direct method (SHELXS-97) and refined by full-matrix least-squares (SHELXL-2014) on F^2. Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. The data obtained were deposited at the Cambridge Crystallographic Data Centre.

2. General procedure for the synthesis of compounds 1a-1t, 2, and 5

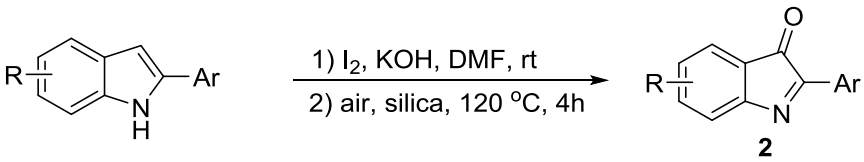


1

To solution of indole or indole derivative (1.5 mmol) and $(PhO)_2POOH$ (10 mmol%, 0.1 mmol) in CH_2Cl_2 (10 mL) was added quinone derivative (1 mmol) at 0 °C, then the solution was stirred at room temperature for 12-36 h, and the reaction was monitored by TLC until completion. The resulting solution was concentrated, and the residue was purified by flash chromatography on silica gel eluted with petroleum ether (PE)/ethyl acetate (EA) to afford pure product (**1a-1t** and **5**).[1,2]

Substrates **2** were synthesized according to the previous method.[3]

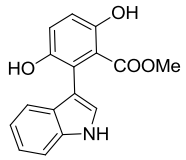
General procedure:



2

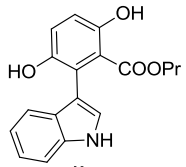
A solution of I_2 (4.38 g, 17.2 mmol) in DMF (30 mL) was dropped into 2-aryl indoles(17.1 mmol) and KOH (2.39 g, 42.7 mmol) in DMF (30 mL) at room temperature (rt), and the resulting solution was stirred for 2 h. The mixture was then purged with air, silica (7.1 g) was added, and the mixture heated to 120 ℃ for 4 h. After cooling, water (200 mL) was added, and the mixture extracted with ethyl acetate (3 × 100 mL). The organic extracts were combined, dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by flash chromatography on silica with petroleum ether/ethyl acetate the eluent gave **2** as the red solids.

3. Characterization data of compounds 1a-1t and 5



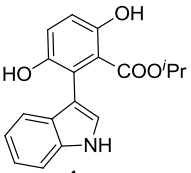
1a

Methyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1a): pale yellow solid, mp = 149-150 ºC. 220.8 mg, 78% yield. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.34 (s, 1H), 8.40 (s, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.22 – 7.15 (m, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.18 (s, 1H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.2, 155.6, 147.4, 136.3, 127.5, 123.2, 123.0, 122.2, 120.7, 119.5, 119.3, 118.3, 113.4, 111.4, 110.6, 51.9. HRMS (ESI): calcd for $[C_{16}H_{12}NO_4]^-$ [M-H]$^-$ *m/z* 282.0772; found: 282.0771.



1b

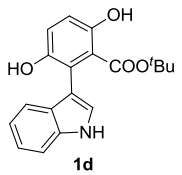
Propyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1b): pale yellow solid, mp = 152-153 ºC. 227.1 mg, 73% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.64 (s, 1H), 8.42 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 9.3 Hz, 1H), 7.21 – 7.14 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.18 (s, 1H), 3.69 (ddt, *J* = 47.9, 10.8, 6.6 Hz, 2H), 0.72 (dtt, *J* = 21.0, 13.9, 6.8 Hz, 2H), 0.32 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.1, 155.9, 147.4, 136.4, 127.8, 123.1, 122.9, 122.1, 120.7, 119.5, 119.4, 118.4, 113.4, 111.3, 111.0, 67.0, 20.8, 9.9. HRMS (ESI): calcd for $[C_{18}H_{16}NO_4]^-$ [M-H]$^-$ *m/z* 310.1085; found: 310.1081.



1c

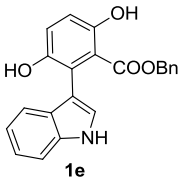
Isopropyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1c): pale yellow solid, mp = 188-189 ºC. 199.1 mg, 64% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.71 (s, 1H), 8.43 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.19 – 7.14 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.20 (s, 1H),

4.77 (p, *J* = 6.2 Hz, 1H), 0.66 (d, *J* = 6.2 Hz, 3H), 0.33 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 170.3, 155.9, 147.5, 136.4, 128.3, 123.1, 122.8, 121.9, 120.6, 119.7, 119.4, 118.4, 113.8, 111.2, 111.0, 68.7, 21.1, 20.2. HRMS (ESI): calcd for $[C_{18}H_{16}NO_4]^-$ $[M-H]^-$ *m/z* 310.1085; found: 310.1078.



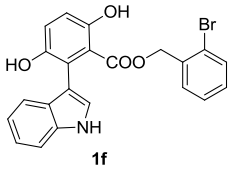
1d

***tert*-Butyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1d):** white solid, mp = 175-176 °C. 247.1 mg, 76% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.71 (s, 1H), 8.44 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.20 – 7.04 (m, 3H), 7.02 – 6.91 (m, 1H), 5.19 (s, 1H), 0.85 (s, 9H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 170.2, 155.7, 147.2, 136.5, 128.2, 123.2, 122.4, 121.5, 120.6, 119.7, 119.3, 118.3, 114.7, 111.5, 111.3, 82.4, 27.2. HRMS (ESI): calcd for $[C_{19}H_{18}NO_4]^-$ $[M-H]^-$ *m/z* 324.1241; found: 324.1241.



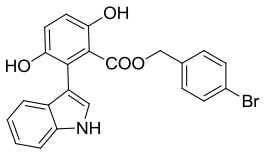
1e

Benzyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1e): brown solid, mp = 99-100 °C. 247.8 mg 69% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.51 (s, 1H), 8.12 (s, 1H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.21-7.15 (m, 2H), 7.10 (dt, *J* = 22.6, 7.5 Hz, 3H), 7.03 – 6.99 (m, 2H), 6.50 (d, *J* = 7.5 Hz, 2H), 5.14 (s, 1H), 4.90 (d, *J* = 12.1 Hz, 1H), 4.62 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 170.8, 155.9, 147.5, 136.3, 134.3, 128.2, 128.2, 128.0, 127.5, 123.2, 123.0, 122.3, 120.7, 119.5, 119.3, 118.4, 113.3, 111.6, 110.4, 67.3. HRMS (ESI): calcd for $[C_{22}H_{16}NO_4]^-$ $[M-H]^-$ *m/z* 358.1085; found: 358.1075.



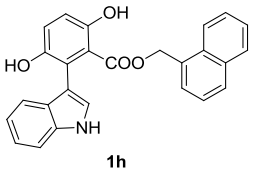
1f

2-Bromobenzyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1f): brown solid, mp = 82-83 ºC. 222.9 mg 51% yield, 1H NMR (400 MHz, chloroform-*d*) δ 10.49 (s, 1H), 8.11 (s, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.22 – 7.14 (m, 3H), 7.10 – 7.00 (m, 4H), 6.89 (t, J = 7.5 Hz, 1H), 6.27 (d, J = 7.6 Hz, 1H), 5.11 (s, 1H), 5.06 (d, J = 12.8 Hz, 1H), 4.74 (d, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 170.6, 156.1, 147.6, 136.2, 133.9, 132.4, 131.1, 129.8, 129.5, 128.9, 127.3, 127.2, 123.4, 122.9, 122.5, 120.7, 119.5, 119.3, 118.5, 113.0, 111.5, 110.3, 66.6. HRMS (ESI): calcd for $[C_{22}H_{15}BrNO_4]^-$ $[M-H]^-$ *m/z* 436.0190, 438.0172; found: 436.0170, 438.0179.



1g

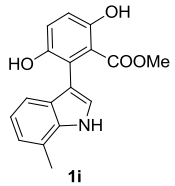
4-Bromobenzyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1g): brown solid, mp = 191-192 ºC. 249.1 mg 57% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.45 (s, 1H), 8.11 (s, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.21 – 7.13 (m, 3H), 7.12 – 7.07 (m, 1H), 7.06 – 6.96 (m, 2H), 6.32 (d, *J* = 8.3 Hz, 2H), 5.08 (s, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.1, 148.5, 147.1, 136.4, 135.8, 131.4, 129.8, 127.6, 124.7, 124.2, 121.5, 121.2, 121.0, 120.7, 119.0, 117.6, 115.3, 111.8, 111.0, 65.2. HRMS (ESI): calcd for $[C_{22}H_{15}BrNO_4]^-$ $[M-H]^-$ *m/z* 436.0190, 438.0172; found: 436.0177, 438.0179.



1h

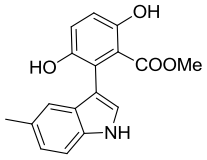
Naphthalene-1-ylmethyl-3,6-dihydroxy-2-(1*H*-indol-3-yl)benzoate (1h): white solid, mp = 190-191ºC. 331.4 mg, 81% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.60 (s, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.39 – 7.29 (m, 2H), 7.21 – 7.12 (m, 3H), 7.09 – 6.90 (m, 4H), 6.72 (d, *J* = 6.9 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 5.50 (d, *J* = 12.2 Hz, 1H), 5.01 (s, 1H), 4.95 (d, *J* = 12.2 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 170.8, 156.1, 147.5, 135.9, 133.4,

131.5, 130.0, 129.1, 128.4, 127.8, 127.0, 126.3, 125.8, 125.4, 123.6, 123.3, 122.7, 122.3, 120.4, 119.6, 118.9, 118.4, 113.1, 111.2, 110.0, 65.1. HRMS (ESI): calcd for $[C_{26}H_{18}NO_4]^-$ [M-H]$^-$ *m/z* 408.1241; found: 408.1242.



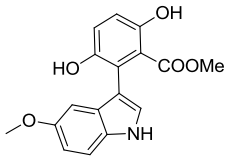
1i

Methyl-3,6-dihydroxy-2-(7-methyl-1*H*-indol-3-yl)benzoate (1i): white solid, mp = 165-166 ºC. 202.0 mg, 68% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.31 (s, 1H), 8.41 (s, 1H), 7.21 – 7.12 (m, 3H), 7.05 (q, *J* = 7.7, 7.1 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.23 (s, 1H), 3.27 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.3, 155.5, 147.4, 136.0, 127.0, 123.5, 122.9, 122.2, 120.9, 120.6, 119.8, 118.2, 117.0, 113.4, 111.0, 52.0, 16.7. HRMS (ESI): calcd for $[C_{17}H_{14}NO_4]^-$ [M-H]$^-$ *m/z* 296.0928; found: 296.0927.



1j

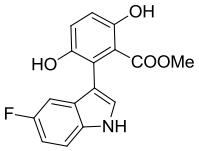
Methyl-3,6-dihydroxy-2-(5-methyl-1*H*-indol-3-yl)benzoate (1j): light brown solid, mp = 172-173 ºC. 213.9 mg, 72% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.30 (s, 1H), 8.28 (s, 1H), 7.33 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 2H), 7.02 – 6.97 (m, 1H), 5.16 (s, 1H), 3.28 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.3, 155.6, 147.4, 134.6, 130.1, 127.6, 124.7, 123.2, 122.1, 119.6, 118.8, 118.3, 113.4, 111.0, 110.1, 51.9, 21.5. HRMS (ESI): calcd for $[C_{17}H_{14}NO_4]^-$ [M-H]$^-$ *m/z* 296.0928; found: 296.0927.



1k

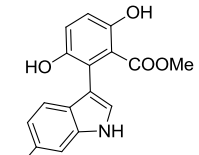
Methyl-3,6-dihydroxy-2-(5-methoxy-1*H*-indol-3-yl)benzoate (1k): white solid, mp = 169-170 ºC. 234.8 mg, 75% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.28 (s, 1H), 8.38 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.21 – 7.10 (m, 2H), 7.00 (d, *J* = 8.9 Hz,

1H), 6.90 (d, *J* = 8.8 Hz, 1H), 6.70 (s, 1H), 5.23 (s, 1H), 3.75 (s, 3H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.3, 155.5, 155.0, 147.4, 131.3, 127.9, 123.8, 122.2, 119.6, 118.3, 113.7, 113.4, 112.3, 110.3, 100.3, 55.9, 52.0. HRMS (ESI): calcd for $[C_{17}H_{14}NO_5]^-$ [M-H]$^-$ *m/z* 312.0877; found: 312.0878.



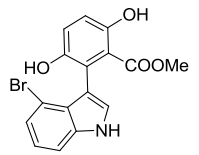
1l

Methyl-2-(5-fluoro-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (1l): white solid, mp = 160-161 °C. 195.7 mg, 65% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.38 (s, 1H), 8.44 (s, 1H), 7.36 (dd, *J* = 8.8, 4.2 Hz, 1H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.17 (d, *J* = 9.0 Hz, 1H), 7.05 – 6.89 (m, 3H), 5.08 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.0, 158.5 (d, $^1J_{C\text{-}F}$ = 236.4 Hz), 155.8, 147.4, 132.7, 128.1 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 124.9, 122.4, 118.8, 118.7, 113.1, 112.2 (d, $^3J_{C\text{-}F}$ = 9.5 Hz), 111.6 (d, $^2J_{C\text{-}F}$ = 26.4 Hz), 110.8, 104.3 (d, $^2J_{C\text{-}F}$ = 23.8 Hz), 52.0. ^{19}F NMR (376 MHz, chloroform-*d*) δ –122.9. HRMS (ESI): calcd for $[C_{16}H_{11}FNO_4]^-$ [M-H]$^-$ *m/z* 300.0678; found: 300.0678.



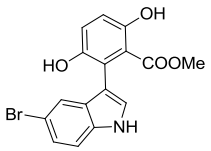
1m

Methyl-2-(6-chloro-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (1m): pale yellow solid, mp = 215-216 °C. 164.9 mg, 52% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.36 (s, 1H), 8.37 (s, 1H), 7.45 (s, 1H), 7.23 – 7.14 (m, 3H), 7.12 – 7.05 (m, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.04 (s, 1H), 3.27 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.0, 155.8, 147.4, 136.6, 129.1, 126.2, 123.7, 122.4, 121.6, 120.4, 118.7, 113.1, 111.4, 111.0, 52.0. HRMS (ESI): calcd for $[C_{16}H_{11}ClNO_4]^-$ [M-H]$^-$ *m/z* 316.0382; found: 316.0379.



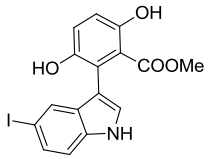
1n

Methyl-2-(4-bromo-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (1n): brown solid, mp = 198-199 °C. 231.0 mg, 64% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.75 (s, 1H), 8.52 (s, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.18 – 7.12 (m, 2H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 1H), 4.91 (s, 1H), 3.28 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.3, 156.0, 148.1, 137.2, 125.9, 124.7, 123.8, 122.0, 119.8, 118.9, 114.5, 114.1, 111.0, 110.8, 51.9. HRMS (ESI): calcd for $[C_{16}H_{11}BrNO_4]^-$ $[M-H]^-$ *m/z* 359.9877, 361.9858; found: 359.9879, 361.9853.



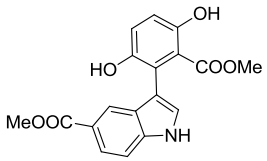
1o

Methyl-2-(5-bromo-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (1o): white solid, mp = 194-195 °C. 249.1 mg, 69% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.42 (s, 1H), 8.51 (s, 1H), 7.42 (s, 1H), 7.35 – 7.28 (m, 2H), 7.17 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 1H), 5.02 (s, 1H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.0, 155.8, 147.5, 134.9, 129.2, 126.0, 124.5, 122.5, 121.9, 118.8, 118.6, 114.0, 113.1, 112.9, 110.3, 52.0. HRMS (ESI): calcd for $[C_{16}H_{11}BrNO_4]^-$ $[M-H]^-$ *m/z* 359.9877, 361.9858; found: 359.9880, 361.9840.



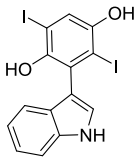
1p

Methyl-3,6-dihydroxy-2-(5-iodo-1*H*-indol-3-yl)benzoate (1p): yellow solid, mp = 217-218 °C. 290.4 mg, 71% yield, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.33 – 11.14 (m, 1H), 9.27 (s, 1H), 8.85 (s, 1H), 7.54 (d, *J* = 1.2 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 6.67 (d, *J* = 8.7 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 148.2, 146.9, 135.4, 130.0, 129.4, 129.3, 125.6, 124.4, 119.7, 117.5, 115.5, 114.5, 110.3, 82.8, 52.0. HRMS (ESI): calcd for $[C_{16}H_{11}INO_4]^-$ $[M-H]^-$ *m/z* 407.9738; found: 407.9738.



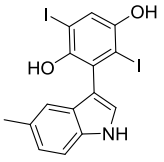
1q

Methyl-3,6-dihydroxy-2-(5-methoxy-1*H*-indol-3-yl)benzoate (1q): white solid, mp = 219-220 °C. 194.4 mg, 57% yield, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.45 (s, 1H), 9.30 (s, 1H), 8.87 (s, 1H), 7.97 (s, 1H), 7.68 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.19 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 6.70 (d, *J* = 8.7 Hz, 1H), 3.76 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 168.0, 148.3, 146.9, 139.0, 127.0, 126.2, 124.5, 123.7, 122.5, 120.5, 119.5, 117.5, 115.7, 112.4, 112.0, 52.2, 52.0. HRMS (ESI): calcd for $[C_{18}H_{14}NO_6]^-$ [M-H]$^-$ *m/z* 340.0827; found: 340.0827.



1r

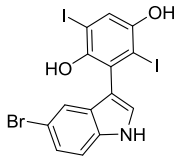
3-(1*H*-Indol-3-yl)-2,5-Diiodobenzene-1,4-diol (1r): White solid, mp = 209-210 °C. 381.4 mg, 80% yield, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 – 10.99 (m, 1H), 9.70 (s, 1H), 7.69 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.95 – 6.86 (m, 2H), 6.82 – 6.75 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.4, 148.0, 136.4, 128.7, 126.8, 125.8, 122.9, 121.4, 119.7, 119.1, 114.5, 112.0, 95.1, 86.4. HRMS (ESI): calcd for $[C_{14}H_8I_2NO_2]^-$ [M-H]$^-$ *m/z* 475.8650; found: 475.8649.



1s

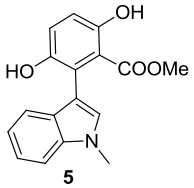
2,5-Diiodo-3-(5-methyl-1*H*-indol-3-yl)benzene-1,4-diol (1s): White solid, mp = 190-191 °C. 407.4 mg, 83% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.39 (s, 1H), 7.48 (s, 1H), 7.36 (d, *J* = 9.0 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 5.34 (s, 1H), 5.08 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 149.6, 147.9, 134.5, 130.5, 125.8, 125.2, 125.0, 124.6, 124.0, 119.3, 113.4, 111.4,

95.0, 82.8, 21.6. HRMS (ESI): calcd for $[C_{15}H_{10}I_2NO_2]^-$ [M-H]$^-$ *m/z* 489.8806; found: 489.8806.



1t

3-(5-Bromo-1*H*-indol-3-yl)-2,5-diiodobenzene-1,4-diol (1t): White solid, mp = 216-217 ^{o}C. 338.4 mg, 61% yield, ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (s, 1H), 9.76 (s, 1H), 7.84 (s, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 7.11 (s, 1H), 7.04 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.98 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.5, 148.0, 135.2, 128.7, 128.1, 127.6, 123.8, 123.2, 121.7, 114.5, 114.0, 111.8, 95.0, 87.0. HRMS (ESI): calcd for $[C_{14}H_7BrI_2NO_2]^-$ [M-H]$^-$ *m/z* 553.7755, 555.7735; found: 553.7755, 555.7734.

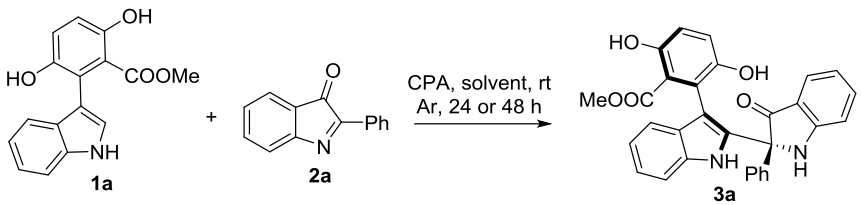


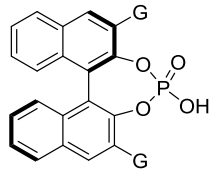
5

Methyl-3,6-dihydroxy-2-(1-methyl-1*H*-indol-3-yl)benzoate (5): light yellow oil, 124.8 mg, 42% yield, ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.24 (s, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.05 (s, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 5.23 (s, 1H), 3.87 (s, 3H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 171.2, 155.5, 147.4, 137.3, 128.0, 127.7, 122.5, 122.1, 120.3, 119.6, 119.5, 118.1, 113.4, 109.5, 108.9, 51.8, 33.1. HRMS (ESI): calcd for $[C_{17}H_{14}NO_4]^-$ [M-H]$^-$ *m/z* 296.0928; found: 296.0926.

4. Optimization of reaction conditions

Table S1. Optimization of reaction conditions for synthesis of arylindolyl indolin-3-ones with both axial and central chirality **3a-3z** and **3aa-3af**.





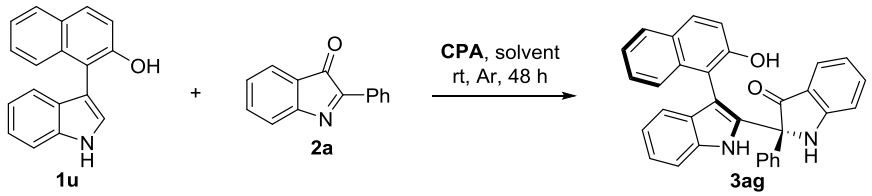
(*R*)-**CPA**

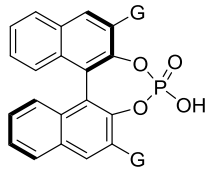
4a, G = 9-Phenanthrenyl
4b, G = 9-Anthracenyl
4c, G = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$
4d, G = SiPh$_3$
4e, G = 2,4,6-(Cy)$_3$C$_6$H$_2$
4f, G = 2,3,4,5,6-F$_5$C$_6$
4g, G = 3,5-(CF$_3$)$_2$C$_6$H$_3$
4h, G = 1-Napthyl
4i, G = 2-Napthyl
4j, G = 4-ClC$_6$H$_4$
4k, G = 2,4,6-(Me)$_3$C$_6$H$_2$
4l, G = 3,5-(Me)$_2$C$_6$H$_3$

Entry	CPA	Solvent	Time (h)	Yield of **3a** (%)[b]	ee of **3a** (%)[c]
1	**4a**	toluene	24	86	90
2	**4b**	toluene	48	80	90
3	**4c**	toluene	48	93	60
4	**4d**	toluene	48	11	75
5	**4e**	toluene	48	81	44
6	**4f**	toluene	48	91	38
7	**4g**	toluene	48	5	58
8	**4h**	toluene	48	4	89
9	**4i**	toluene	48	11	59
10	**4k**	toluene	48	39	88
11	**4l**	toluene	48	39	88
12	**4m**	toluene	48	87	75
13	**4a**	CH_2Cl_2	48	86	87
14	**4a**	$CHCl_3$	24	90	91
15	**4a**	DCE	24	89	89
16[d]	**4a**	$CHCl_3$	24	92	92
17[d,e]	**4a**	$CHCl_3$	24	85	92
18[d,f]	**4a**	$CHCl_3$	24	90	92
19[d,g]	**4a**	$CHCl_3$	24	98 (95[h])	94
20[d,g,i]	**4a**	$CHCl_3$	24	94	93

[a]Reaction conditions: under argon atmosphere, **1a** (0.1 mmol, 1.0 equiv), **2a** (0.12 mmol, 1.2 equiv), catalyst (**4a-4l**) (0.01 mmol, 10 mol%), solvent (1.0 mL), temperature (rt, ~25 ^oC), time (24 or 48 h) in a sealed Schlenk tube. [b]Conversion yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as the internal standard. [c]The ee values were determined by HPLC analysis on a chiral stationary phase using a Daicel Chiralpak ID column. [d]Solvent (2.0 mL). [e]Temperature (0 ^oC). [f]Temperature (35 ^oC). [g] (**1a**) (0.12 mmol, 1.2 equiv), **2a** (0.1 mmol, 1.0 equiv). [h]Isolated yield. [i]**4a** (5 μmol, 5 mol%). The dr values were determined by ^1H NMR analysis of the crude reaction mixture after removal of solvent, and the results showed dr > 20:1. DCE = 1,2-dichloroethane.

Table S2. Optimization of reaction conditions for synthesis of arylindolyl indolin-3-ones with both axial and central chirality **3ag-3ak**.





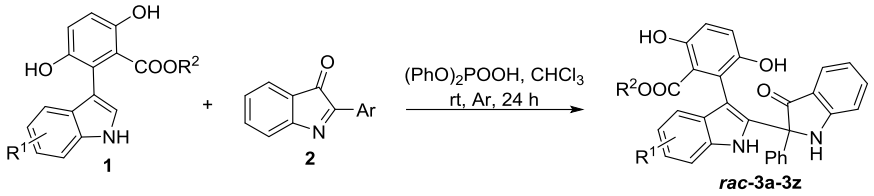
(*R*)-**CPA**

4a, G = 9-Phenanthrenyl
4b, G = 9-Anthracenyl
4c, G = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$
4d, G = SiPh$_3$
4e, G = 2,4,6-(Cy)$_3$C$_6$H$_2$
4f, G = 2,3,4,5,6-F$_5$C$_6$
4g, G = 3,5-(CF$_3$)$_2$C$_6$H$_3$
4h, G = 1-Napthyl
4i, G = 2-Napthyl
4j, G = 4-ClC$_6$H$_4$
4k, G = 2,4,6-(Me)$_3$C$_6$H$_2$
4l, G = 3,5-(Me)$_2$C$_6$H$_3$

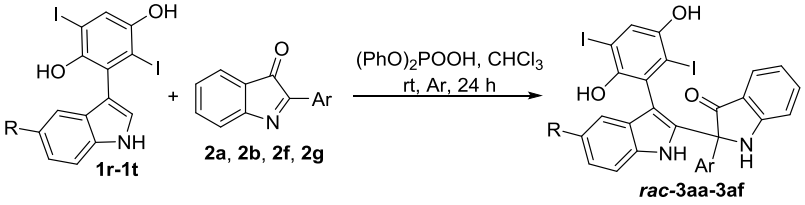
Entry	CPA	Solvent	Yield of **3a** (%)[b]	ee of **3ag** (%)[c]	dr of **3a** (%)[d]
1	**4a**	toluene	71	84	>20:1
2	**4b**	toluene	58	76	>20:1
3	**4c**	toluene	70	26	>20:1
4	**4d**	toluene	29	43	10:1
5	**4e**	toluene	69	15	>20:1
6	**4f**	toluene	54	16	3:1
7	**4g**	toluene	24	50	7:1
8	**4h**	toluene	trace	-	-
9	**4i**	toluene	42	62	7:1
10	**4j**	toluene	trace	-	-
11	**4k**	toluene	83	90	>20:1
12	**4l**	toluene	59	83	>20:1
13	**4k**	DCM	74	86	>20:1
14	**4k**	$CHCl_3$	78	76	>20:1
15	**4k**	DCE	76	88	>20:1
16	**4k**	THF	trace	-	-
17[f]	**4k**	toluene	91(88)[e]	90	>20:1
18[g]	**4k**	toluene	68	89	>20:1
19[f,h]	**4k**	toluene	90	89	>20:1
20[f,i]	**4k**	toluene	86	90	>20:1

[a]Reaction conditions: under argon atmosphere, **1a** (0.1 mmol, 1.0 equiv), **2a** (0.1 mmol, 1 equiv), catalyst (**4a-4l**) (0.01 mmol, 10 mol%), solvent (1.0 mL), temperature (rt, ~25 ^oC), time (24 or 48 h) in a sealed Schlenk tube. [b]Yields were determined from the ^1H NMR spectra using 1,3,5-trimethoxybenzene as the internal standard. [c]Determined by HPLC analysis on a chiral stationary phase using Daicel Chiralpak AY column. [d]The dr. value was determined by ^1H NMR [e]Isolated yield. [f]Sovent: 0.5 mL toluene. [g]Sovent: 2 mL toluene. [h]**1a** (0.12 mmol, 1.2 equiv), **2a** (0.1 mmol, 1.0 equiv). [i]**1a** (0.1 mmol, 1 equiv), **2a** (0.12 mmol, 1.2 equiv).

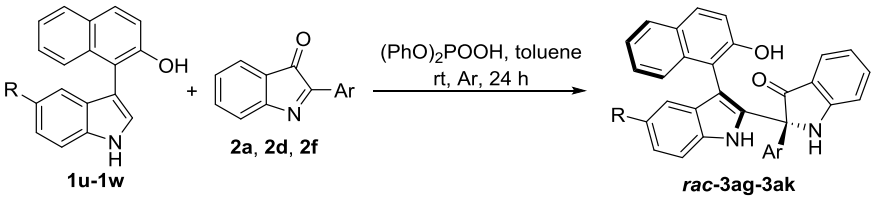
5. General procedures for preparation of racemic products



In an oven dried Schlenk tube, diphenyl phosphate (10 mol%), **1** (0.1 mmol) and **2** (0.1mmol) were dissolved in anhydrous $CHCl_3$ (2 mL). After stirred under argon atmosphere at room temperature for 24 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford pure product (***rac*-3a-3z**).

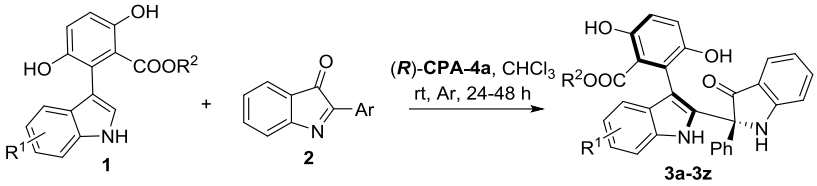


In an oven dried Schlenk tube, diphenyl phosphate (10 mol%), **1** (0.1 mmol) and **2** (0.1mmol) were dissolved in anhydrous $CHCl_3$ (2 mL). After stirred under argon atmosphere at room temperature for 24 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford pure product (***rac*-3aa-3af**).

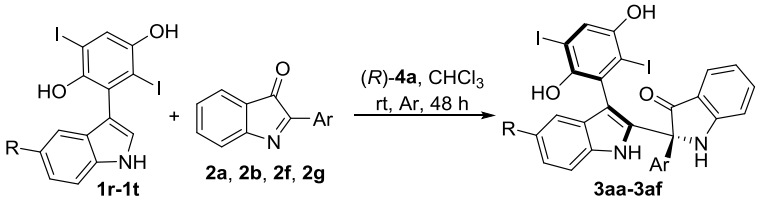


In an oven dried Schlenk tube, chiral phophoric acid **4k** (10 mol%), **1** (0.1 mmol) and **2** (0.1 mmol) were dissolved in anhydrous toluene (0.5 mL). After stirred under argon atmosphere at room temperature for 24 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford pure product (***rac*-3ag-3ak**).

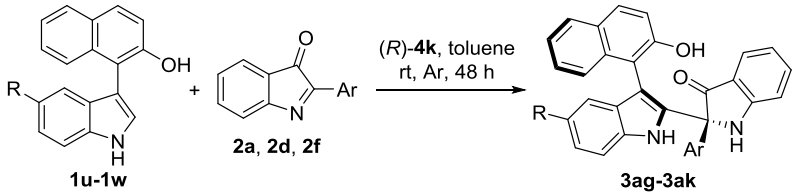
6. General procedures for the synthesis of products 3a-3z, 3aa-3ak



In an oven dried Schlenk tube, chiral phophoric acid (*R*)-**4a** (10 mol%), **1** (0.12 mmol) and **2** (0.1mmol) were dissolved in anhydrous $CHCl_3$ (2 mL). After stirred under argon atmosphere at room temperature for 24-48 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford pure product (**3a**-**3z**).

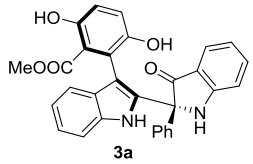


In an oven dried Schlenk tube, chiral phophoric acid (*R*)-**4a** (10 mol%), **1** (0.1 mmol) and **2** (0.1mmol) were dissolved in anhydrous $CHCl_3$ (2 mL). After stirred under argon atmosphere at room temperature for 48 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford pure product (**3aa**-**3af**).



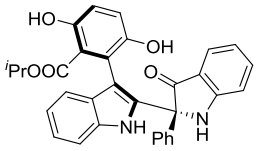
In an oven dried Schlenk tube, chiral phophoric acid **4k** (10 mol%), **1** (0.1 mmol) and **2** (0.1 mmol) were dissolved in anhydrous toluene (0.5 mL). After stirred under argon atmosphere at room temperature for 48 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford pure product(**3ag**-**3ak**).

7. Characterization data of products 3a-3z, 3aa-3ak



3a

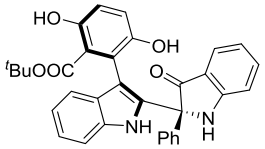
(S_a,*R*)-Methyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3a): Reaction time 24 h, yellow solid, mp = 184-185 ºC. 46.6 mg, 95% yield, 94% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 214 nm, t (minor) = 14.608 min, t (major) = 25.193 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.82 (s, 1H), 8.93 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.40 (ddd, J = 8.3, 7.0, 1.3 Hz, 1H), 7.30 (s, 6H), 7.20 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H), 7.15 (d, J = 9.0 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.97 (d, J = 9.0 Hz, 1H), 6.86 – 6.76 (m, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.10 (s, 1H), 4.98 (s, 1H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.8, 170.6, 160.4, 156.7, 146.9, 139.4, 138.5, 136.0, 132.1, 129.3, 128.9, 128.0, 126.8, 124.9, 123.3, 122.7, 120.6, 119.8, 119.0, 118.8, 112.6, 112.3, 111.3, 107.9, 71.8, 51.9. HRMS (ESI): calcd for $[C_{30}H_{22}N_2O_5+H]^+$ $[M+H]^+$ *m/z* 491.1601, found 491.1605.



3b

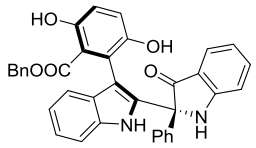
(S_a,*R*)-Isopropyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3b): Reaction time 24 h, yellow solid, mp = 200-201 ºC. 50.1 mg, 96% yield, 90% ee [Daicel Chiralpak IF, hexane/2-propanol = 95/5, ν = 1.0 mL/min, λ = 254 nm, t (minor = 18.569 min, t (major) = 20.533 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.93 (s, 1H), 9.23 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.22 (t, J = 7.6 Hz, 1H), 7.11 (dd, J = 15.3, 8.5 Hz, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 9.0 Hz, 1H), 6.81 (t, J = 7.4 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 5.16 (s, 1H), 4.88 (s, 1H), 4.42 (hept, J = 6.2 Hz, 1H), 0.26 (d, J = 6.2 Hz, 3H), 0.15 (d, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.8, 169.7, 160.8, 156.6, 147.0, 139.2, 138.6, 135.7, 131.6, 129.3, 129.1, 128.8, 126.3, 125.4, 123.4, 122.5, 120.6, 119.9, 119.4, 119.4, 119.1, 118.3,

113.4, 112.3, 111.2, 108.4, 71.5, 68.9, 20.4, 20.2. HRMS (ESI): calcd for $[C_{32}H_{26}N_2O_5+H]^+$ $[M+H]^+$ *m/z* 519.1914, found 519.1908.



3c

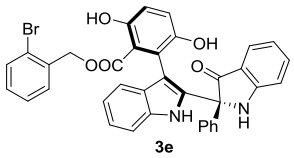
(*S*$_a$,*R*)-*tert*-Butyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3c): Reaction time 24 h, yellow solid, mp = 116-117 ºC. 41.5 mg, 78% yield, 94% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 8.334 min, t (major) = 10.364 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 11.09 (s, 1H), 9.32 (s, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.36 – 7.26 (m, 5H), 7.23 (t, J = 7.6 Hz, 1H), 7.15 (d, J = 7.9 Hz, 1H), 7.10 – 7.03 (m, 2H), 6.99 (d, J = 9.0 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.57 (d, J = 8.3 Hz, 1H), 5.21(s, 1H), 4.74 (s, 1H), 0.54 (s, 9H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.9, 169.8, 161.0, 156.7, 146.9, 139.2, 138.6, 135.8, 131.4, 129.2, 128.9, 128.8, 126.2, 125.5, 123.5, 122.2, 120.7, 119.8, 119.3, 119.2, 119.2, 118.2, 114.2, 112.3, 111.3, 108.7, 82.6, 71.4, 26.8. HRMS (ESI): calcd for $[C_{33}H_{27}N_2O_5]^-$ $[M-H]^-$ *m/z* 531.1925; found: 531.1923.



3d

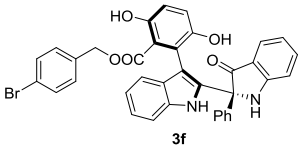
(*S*$_a$,*R*)-Benzyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3d): Reaction time 48 h, yellow solid, mp = 115-116 ºC. 55.5 mg, 98% yield, 91% ee [Daicel Chiralpak ID, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 254 nm, t (major) = 17.777 min, t (minor) = 23.450 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.94 (s, 1H), 8.82 (s, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.27 – 7.19 (m, 7H), 7.14 – 7.06 (m, 3H), 7.03 (m, 1H), 7.00 – 6.93 (m, 3H), 6.88 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 8.3 Hz, 1H), 6.21 (d, J = 7.5 Hz, 2H), 5.07 (s, 1H), 4.91 (s, 1H), 4.62 (d, J = 11.9 Hz, 1H), 4.15 (d, J = 12.0 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.6, 170.3, 160.5, 156.9, 147.2, 139.1, 138.5, 135.7, 133.7, 132.0,

129.1, 128.8, 128.2, 128.1, 128.1, 127.9, 126.4, 125.3, 123.2, 122.9, 120.6, 119.9, 119.5, 119.2, 119.1, 118.6, 112.7, 112.4, 111.6, 108.0, 71.4, 67.2. HRMS (ESI): calcd for $[C_{36}H_{25}N_2O_5]^-$ [M-H]$^-$ *m/z* 565.1769; found: 565.1764.



3e

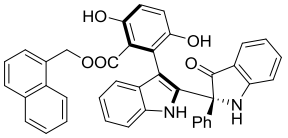
(*S*$_a$,*R*)-2-Bromobenzyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3e): Reaction time 48 h, yellow solid, mp = 145-146 ºC. 53.5 mg, 83% yield, 90% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (major) = 13.352 min, t (minor) = 16.166 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.91 (s, 1H), 8.90 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.28-7.22 (m, 5H), 7.20 – 7.09 (m, 5H), 7.05 – 6.99 (m, 2H), 6.95 (td, J = 7.7, 1.2 Hz, 1H), 6.89 (t, J = 7.4 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 6.02 (d, J = 7.6 Hz, 1H), 5.05 (s, 1H), 4.89 (s, 1H), 4.85 (d, J = 12.9 Hz, 1H), 4.17 (d, J = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.9, 170.1, 160.5, 157.0, 147.2, 139.2, 138.6, 135.5, 133.4, 132.3, 131.9, 129.5, 129.4, 129.2, 128.8, 128.0, 127.1, 126.4, 125.2, 123.4, 123.1, 122.9, 120.8, 120.1, 119.4, 119.3, 119.2, 118.6, 112.7, 112.5, 111.3, 108.1, 71.5, 66.5. HRMS (ESI): calcd for $[C_{36}H_{24}BrN_2O_5]^-$ [M-H]$^-$ *m/z* 643.0874, 645.0861; found: 643.0878, 645.0866.



3f

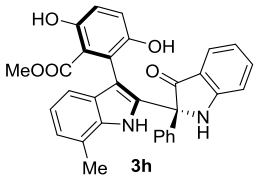
(*S*$_a$,*R*)-4-Bromobenzyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3f): Reaction time 48 h, yellow solid, mp = 185-186 ºC. 55.4 mg, 86% yield, 92% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 9.755 min, t (minor) = 15.167 min]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.83 (s, 1H), 8.76 (s, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 7.31 – 7.25 (m, 3H), 7.24 – 7.16 (m, 4H), 7.11 (d, J = 9.1 Hz, 1H), 7.08 – 6.94 (m, 5H), 6.87 (t, J = 7.4 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 6.11 (d, J = 8.3 Hz, 2H), 5.03 (s, 1H), 4.87 (s, 1H), 4.59 (d, J = 11.9 Hz, 1H), 4.01 (d, J = 11.9 Hz, 1H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.5, 170.0, 160.4, 156.9, 147.1, 139.1, 138.6, 135.6, 132.6, 131.8, 131.2, 129.8, 129.2, 128.9, 128.1, 126.5, 125.1, 123.3, 123.0, 122.2, 120.7, 119.9, 119.5, 119.2, 119.0, 118.6, 112.5, 112.4, 111.6, 107.9, 71.4, 66.4. HRMS (ESI): calcd for $[C_{36}H_{24}BrN_2O_5]^-$ *m/z* $[M-H]^-$ 643.0874, 645.0861; found: 643.0876, 645.0865.



3g

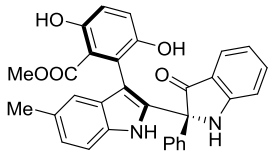
(*S*$_a$,*R*)-Naphthalen-1-ylmethyl-3,6-dihydroxy-2-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3g): Reaction time 24 h, yellow solid, mp = 105-106 ^{o}C. 46.6 mg, 76% yield, 91% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 17.235 min, t (major) = 19.534 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.88 (s, 1H), 8.56 (s, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.24-7.08 (m, 8H), 7.05 (d, J = 9.0 Hz, 1H), 6.99 – 6.83 (m, 5H), 6.82-6.72 (m, 1H), 6.62 (dd, J = 11.4, 7.6 Hz, 2H), 5.14 – 5.03 (m, 2H), 4.79 (s, 1H), 4.71 (d, J = 12.1 Hz, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.8, 170.5, 160.4, 156.7, 147.3, 138.6, 138.5, 135.2, 133.3, 131.7, 131.2, 129.6, 129.2, 128.9, 128.7, 128.5, 128.1, 128.1, 126.4, 126.4, 125.7, 125.3, 125.0, 123.1, 123.0, 123.0, 120.5, 120.0, 119.5, 119.0, 118.7, 118.6, 112.9, 112.5, 110.9, 108.4, 71.5, 64.8. HRMS (ESI): calcd for $[C_{40}H_{28}N_2O_5+H]^+$ $[M+H]^+$ *m/z* 617.2071, found 617.2079.



3h

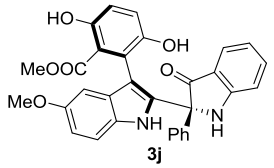
(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(7-methyl-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)benzoate (3h): Reaction time 24 h, yellow solid, mp = 104-105 ^{o}C. 56.1 mg, 96% yield, 95% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (major) = 7.340 min, t (minor) = 8.889 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.82 (s, 1H), 8.94 (s, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.36-7.27 (m, 5H), 7.14 (d, J = 9.0 Hz, 1H), 7.07 – 7.01 (m, 1H), 7.01 – 6.94

(m, 3H), 6.83 (t, J = 7.4 Hz, 1H), 6.49 (d, J = 8.3 Hz, 1H), 5.09 (s, 1H), 4.95 (s, 1H), 2.88 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 200.2, 170.7, 160.5, 156.7, 146.9, 139.6, 138.6, 135.6, 131.6, 129.3, 128.9, 127.5, 126.7, 125.0, 124.0, 122.7, 120.9, 120.6, 120.0, 119.8, 119.0, 118.8, 116.7, 112.7, 112.4, 108.6, 71.9, 51.9, 16.8. HRMS (ESI): calcd for $[C_{31}H_{24}N_2O_5+Na]^+$ $[M+Na]^+$ *m/z* 527.1577, found 527.1555.



3i

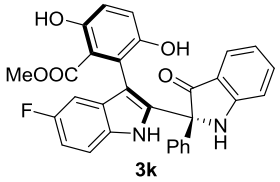
(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(5-methyl-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)benzoate (3i): Reaction time 24 h, yellow solid, mp = 122-123 ^{o}C. 46.7 mg, 93% yield, 94% ee [Daicel Chiralpak IB, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 8.212 min, t (major) = 9.580 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.85 (s, 1H), 8.88 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.29 (s, 5H), 7.21 (d, J = 8.3 Hz, 1H), 7.14 (d, J = 9.0 Hz, 1H), 7.03 (dd, J = 8.3, 1.2 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 6.87 (s, 1H), 6.81 (t, J = 7.4 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.11 (s, 1H), 5.00 (s, 1H), 2.89 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.9, 170.7, 160.4, 156.7, 146.9, 139.5, 138.5, 134.3, 132.0, 130.0, 129.2, 128.9, 128.1, 126.7, 125.0, 124.9, 122.6, 120.1, 119.8, 119.0, 118.8, 118.5, 112.6, 112.3, 111.0, 107.4, 71.8, 51.9, 21.5. HRMS (ESI): calcd for $[C_{31}H_{24}N_2O_5+Na]^+$ $[M+Na]^+$ *m/z* 527.1577, found 527.1581.



3j

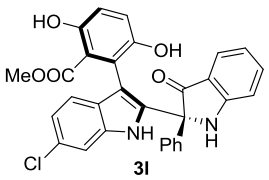
(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(5-methoxy-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)benzoate (3j): Reaction time 24 h, yellow solid, mp = 169-170 ^{o}C. 51.0 mg, 98% yield, 94% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 19.476 min, t (major) = 36.388 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.82 (s, 1H), 8.83 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.7

Hz, 1H), 7.30 (s, 5H), 7.20 (d, J = 8.9 Hz, 1H), 7.15 (d, J = 9.0 Hz, 1H), 6.97 (d, J = 9.0 Hz, 1H), 6.86 (dd, J = 8.9, 2.4 Hz, 1H), 6.81 (t, J = 7.4 Hz, 1H), 6.48 (d, J = 2.3 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.09 (s, 1H), 5.04 (s, 1H), 3.69 (s, 3H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.8, 170.7, 160.4, 156.7, 154.9, 146.9, 139.4, 138.5, 132.6, 131.0, 129.2, 128.9, 128.5, 126.7, 124.9, 122.6, 119.9, 119.8, 119.0, 118.8, 113.8, 112.7, 112.3, 112.2, 107.6, 100.1, 71.8, 55.8, 51.9. HRMS (ESI): calcd for $[C_{31}H_{24}N_2O_6+Na]^+$ $[M+Na]^+$ *m/z* 543.1527, found 543.1525.



3k

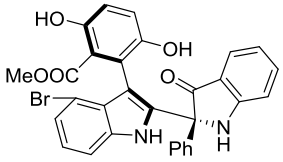
(*S*$_a$,*R*)-Methyl-2-(5-fluoro-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3k): Reaction time 24 h, yellow solid, mp = 187-188 ºC. 50.3 mg, 99% yield, 94% ee [Daicel Chiralpak IB, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 9.604 min, t (major) = 12.406 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.79 (s, 1H), 8.93 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.43-7.37 (m, 1H), 7.29 (s, 5H), 7.24 – 7.19 (m, 1H), 7.13 (d, J = 9.1 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.81 (t, J = 7.3 Hz, 1H), 6.73 (dd, J = 9.1, 2.4 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.12 (s, 1H), 5.01 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.6, 170.5, 160.4, 158.3 (d, $^1J_{C\text{-}F}$ = 236.7 Hz), 156.8, 146.8, 139.1, 138.6, 134.0, 132.4, 129.3, 129.0, 128.6 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 126.7, 124.9, 122.8, 120.0, 119.4, 119.3, 118.7, 112.5, 112.3, 112.1 (d, $^3J_{C\text{-}F}$ = 9.4 Hz), 111.8 (d, $^2J_{C\text{-}F}$ = 26.4 Hz), 108.2 (d, $^4J_{C\text{-}F}$ = 4.7 Hz), 103.9 (d, $^2J_{C\text{-}F}$ = 23.9 Hz), 71.7, 51.9. ^{19}F NMR (376 MHz, chloroform-*d*) δ –122.7. HRMS (ESI): calcd for $[C_{30}H_{20}FN_2O_5]^-$ *m/z* $[M-H]^-$ 507.1362; found: 507.1350.



3l

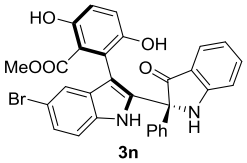
(*S*$_a$,*R*)-Methyl-2-(6-chloro-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3l): Reaction time 24 h, yellow solid, mp = 150-151 ºC. 41.0 mg, 78% yield, 90% ee [Daicel Chiralpak IB, hexane/2-propanol = 90/10, ν = 1.0 mL/min,

λ = 254 nm, t (minor) = 10.516 min, t (major) = 11.741 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.79 (s, 1H), 8.92 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.44-7.38 (m, 1H), 7.34-7.26 (m, 6H), 7.13 (d, J = 9.1 Hz, 1H), 7.03 – 6.93 (m, 3H), 6.82 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.07 (s, 1H), 4.99 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.6, 170.5, 160.4, 156.8, 146.8, 139.1, 138.7, 136.2, 132.9, 129.3, 129.2, 129.0, 126.7, 126.6, 124.9, 122.8, 121.4, 120.0, 120.0, 119.3, 119.2, 118.7, 112.5, 112.4, 111.3, 108.3, 71.7, 52.0. HRMS (ESI): calcd for $[C_{30}H_{21}ClN_2O_5+H]^+$ $[M+H]^+$ *m/z* 525.1212, found 525.1211.



3m

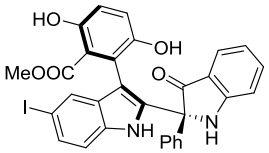
(*S*$_a$,*R*)-Methyl-2-(4-bromo-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3m): Reaction time 48 h, yellow solid, mp = 108-109 ^{o}C. 53.0 mg, 93% yield, 90% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 10.976 min, t (major) = 18.611 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.85 (s, 1H), 9.02 (s, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.32 (s, 5H), 7.29 (d, J = 8.2 Hz, 1H), 7.20 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 9.0 Hz, 1H), 7.02 (t, J = 7.9 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 6.81 (t, J = 7.5 Hz, 1H), 6.43 (d, J = 8.3 Hz, 1H), 5.07 (s, 1H), 4.82 (s, 1H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.5, 170.7, 160.3, 156.8, 147.6, 139.0, 138.6, 136.8, 133.3, 129.3, 129.0, 126.8, 125.7, 124.9, 123.9, 122.4, 120.4, 119.9, 119.3, 118.5, 113.9, 113.3, 112.3, 110.7, 108.2, 71.6, 51.9. HRMS (ESI): calcd for $[C_{30}H_{21}BrN_2O_5+H]^+$ $[M+H]^+$ *m/z* 569.0707, 571.0691, found 569.0699, 571.0696.



3n

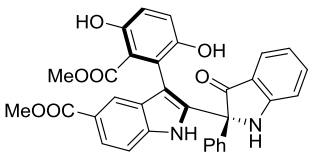
(*S*$_a$,*R*)-Methyl-2-(5-bromo-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3n): Reaction time 24 h, yellow solid, mp = 143-144 ^{o}C. 47.3 mg, 83% yield, 96% ee [Daicel Chiralpak IB, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 10.486 min, t (major) = 12.949 min]. ^{1}H NMR (400 MHz,

chloroform-*d*) δ 10.83 (s, 1H), 8.99 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.33 – 7.26 (m, 6H), 7.23 – 7.16 (m, 2H), 7.13 (d, J = 9.1 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.10 (s, 1H), 4.96 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.6, 170.5, 160.4, 156.9, 146.8, 139.1, 138.7, 134.5, 133.5, 129.7, 129.4, 129.0, 126.7, 126.2, 124.9, 122.9, 121.5, 120.0, 119.4, 119.1, 118.7, 113.9, 112.9, 112.4, 112.4, 107.7, 71.7, 52.0. HRMS (ESI): calcd for $[C_{30}H_{21}BrN_2O_5+H]^+$ $[M+H]^+$ *m/z m/z* 569.0707, 571.0691, found *m/z* 569.0672, 571.0691.



3o

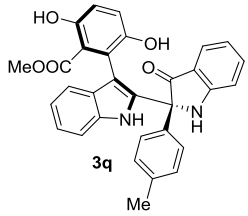
(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(5-iodo-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)benzoate (3o): Reaction time 24 h, yellow solid, mp = 127-128 ºC. 60.0 mg, 97% yield, 94% ee [Daicel Chiralpak IB, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 10.616 min, t (major) = 12.412 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.83 (s, 1H), 9.00 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.47 – 7.37 (m, 3H), 7.33-7.26 (m, 5H), 7.11 (dd, J = 12.2, 8.8 Hz, 2H), 6.95 (d, J = 9.0 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.45 (d, J = 8.3 Hz, 1H), 5.10 (s, 1H), 4.97 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.6, 170.5, 160.4, 156.9, 146.8, 139.1, 138.7, 135.0, 133.1, 131.7, 130.5, 129.3, 129.0, 127.7, 126.7, 124.9, 122.9, 120.0, 119.4, 119.1, 118.7, 113.4, 112.5, 112.4, 107.4, 84.1, 71.6, 52.0. HRMS (ESI): calcd for $[C_{30}H_{21}IN_2O_5+H]^+$ $[M+H]^+$ *m/z* 617.0568, found 617.0567.



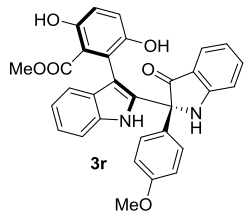
3p

(*S*$_a$,*R*)-Methyl-3-(3,6-dihydroxy-2-(methoxycarbonyl)phenyl)-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indole-5-carboxylate (3p): Reaction time 48 h, yellow solid, mp = 217-218 ºC. 44.8 mg, 82% yield, 98% ee [Daicel Chiralpak AD, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 254 nm, t (major) = 22.867 min, t (minor) = 27.862 min].

^{1}H NMR (400 MHz, chloroform-*d*) δ 10.84 (s, 1H), 9.10 (s, 1H), 7.87 – 7.78 (m, 2H), 7.54 (d, J = 7.8 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.35 – 7.26 (m, 6H), 7.10 (d, J = 9.0 Hz, 1H), 6.96 (d, J = 9.0 Hz, 1H), 6.81 (t, J = 7.4 Hz, 1H), 6.43 (d, J = 8.3 Hz, 1H), 5.29 (s, 1H), 5.17 (s, 1H), 3.77 (s, 3H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.7, 170.4, 167.9, 160.4, 156.9, 147.0, 139.0, 138.7, 138.5, 133.5, 129.3, 129.0, 127.9, 126.9, 124.9, 124.6, 123.2, 122.5, 122.0, 119.9, 119.3, 119.2, 118.7, 112.4, 110.9, 109.9, 71.8, 52.0, 51.9. HRMS (ESI): calcd for $[C_{32}H_{24}N_2O_7+H]^+$ $[M+H]^+$ *m/z* 549.1656, found 549.1653.

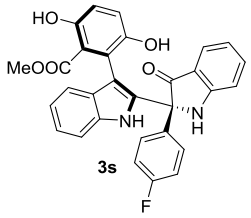


(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(2-(3-oxo-2-(p-tolyl)indolin-2-yl)-1*H*-indol-3-yl)benzoate (3q): Reaction time 24 h, yellow solid, mp = 133-134 ºC. 50.0 mg, 99% yield, 92% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (major) = 14.835 min, t (minor) = 22.364 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.82 (s, 1H), 8.92 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.39 (td, J = 7.7, 7.2, 1.2 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.22 – 7.01 (m, 8H), 6.96 (d, J = 9.0 Hz, 1H), 6.80 (t, J = 7.3 Hz, 1H), 6.43 (d, J = 8.3 Hz, 1H), 5.08 (s, 1H), 5.01 (s, 1H), 2.87 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.9, 170.7, 160.4, 156.7, 146.9, 138.9, 138.5, 136.4, 136.0, 132.3, 129.9, 128.0, 126.7, 124.9, 123.5, 122.6, 120.6, 120.0, 119.7, 119.0, 118.9, 118.8, 112.6, 112.3, 111.3, 107.8, 71.7, 51.9, 21.2. HRMS (ESI): calcd for $[C_{31}H_{24}N_2O_5+H]^+$ $[M+H]^+$ *m/z* 505.1758, found 505.1761.



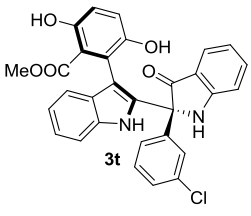
(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(2-(2-(4-methoxyphenyl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)benzoate (3r): Reaction time 24 h, yellow solid, mp = 135-136 ºC. 50.8 mg, 98% yield, 91% ee [Daicel Chiralpak IF, hexane/2-propanol = 85/15, ν = 1.0 mL/min,

λ = 254 nm, t (major) = 14.572 min, t (minor) = 23.695 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.80 (s, 1H), 8.90 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.15 (d, J = 9.0 Hz, 1H), 7.05 (dt, J = 14.6, 7.4 Hz, 2H), 6.96 (d, J = 9.0 Hz, 1H), 6.84 – 6.76 (m, 3H), 6.43 (d, J = 8.3 Hz, 1H), 5.05 (s, 1H), 4.99 (s, 1H), 3.75 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 200.0, 170.6, 160.3, 159.9, 156.7, 146.9, 138.5, 135.9, 132.4, 131.4, 128.1, 128.0, 124.9, 123.3, 122.6, 120.6, 120.0, 119.7, 119.0, 119.0, 118.8, 114.6, 112.6, 112.3, 111.3, 107.8, 71.5, 55.4, 51.9. HRMS (ESI): calcd for $[C_{31}H_{24}N_2O_6+Na]^+$ $[M+Na]^+$ *m/z* 543.1527, found 543.1524.



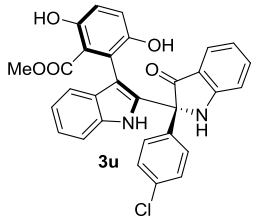
3s

(*S*$_a$,*R*)-Methyl-2-(2-(2-(4-fluorophenyl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3s): Reaction time 24 h, yellow solid, mp = 169-170 ºC. 44.5 mg, 88% yield, 90% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 10.382 min, t (major) = 13.018 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.78 (s, 1H), 8.93 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.36 – 7.28 (m, 3H), 7.21 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.15 (d, J = 9.0 Hz, 1H), 7.11 – 6.96 (m, 5H), 6.82 (t, J = 7.4 Hz, 1H), 6.46 (d, J = 8.3 Hz, 1H), 5.10 (s, 1H), 4.89 (s, 1H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.7, 170.5, 162.8 (d, $^{1}J_{C\text{-}F}$ = 248.6 Hz), 160.4, 156.8, 146.84, 138.7, 135.9, 135.2, 131.8, 128.7 (d, $^{3}J_{C\text{-}F}$ = 8.4 Hz), 128.0, 125.0, 123.5, 122.7, 120.8, 120.0, 119.6, 119.1 (d, $^{2}J_{C\text{-}F}$ = 18.0 Hz), 118.6, 116.2 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 112.6, 112.3, 111.3, 108.0, 71.2, 51.9. ^{19}F NMR (376 MHz, chloroform-*d*) δ –112.3. HRMS (ESI): calcd for $[C_{30}H_{20}FN_2O_5]^-$ $[M-H]^-$ *m/z* 507.1362; found: 507.1360.



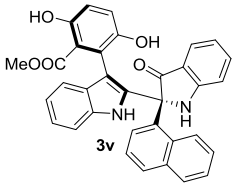
3t

(*S*$_a$,*R*)-Methyl-2-(2-(2-(3-chlorophenyl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3t): Reaction time 24 h, yellow solid, mp = 142-143 ºC. 46.2 mg, 88% yield, 87% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 11.154 min, t (major) = 12.607 min]. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 10.65 (s, 1H), 9.29 (s, 1H), 8.33 (s, 1H), 7.48 (s, 1H), 7.41 – 7.21 (m, 7H), 7.00 (t, J = 7.3 Hz, 1H), 6.90 – 6.79 (m, 2H), 6.74 – 6.59 (m, 4H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 199.3, 169.1, 161.5, 149.0, 148.3, 141.8, 138.3, 136.4, 133.3, 132.4, 130.2, 128.9, 128.2, 128.1, 126.2, 124.9, 121.9, 121.3, 120.8, 119.5, 119.0, 118.8, 118.8, 118.4, 116.4, 113.0, 111.8, 109.6, 71.6, 51.6. HRMS (ESI): calcd for [$C_{30}H_{21}ClN_2O_5$+H]$^+$ [M+H]$^+$ *m/z* 525.1212; found: 525.1029.



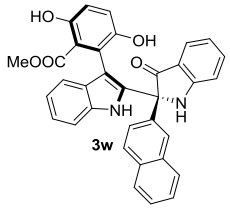
3u

(*S*$_a$,*R*)-Methyl-2-(2-(2-(4-chlorophenyl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3u): Reaction time 24 h, yellow solid, mp = 130-131 ºC. 52.0 mg, 99% yield, 90% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (major) = 11.312 min, t (minor) = 16.036 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.78 (s, 1H), 8.93 (s, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.27 (s, 4H), 7.21 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 9.1 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.98 (d, J = 8.9 Hz, 1H), 6.82 (t, J = 7.4 Hz, 1H), 6.47 (d, J = 8.3 Hz, 1H), 5.12 (s, 1H), 4.88 (s, 1H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.4, 170.5, 160.4, 156.8, 146.9, 138.7, 137.8, 135.9, 134.9, 131.5, 129.4, 128.2, 128.0, 125.0, 123.5, 122.8, 120.8, 120.1, 119.5, 119.3, 119.0, 118.5, 112.6, 112.3, 111.4, 108.1, 71.2, 51.9. HRMS (ESI): calcd for [$C_{30}H_{21}ClN_2O_5$+H]$^+$ [M+H]$^+$ *m/z* 525.1212, found 525.1208.



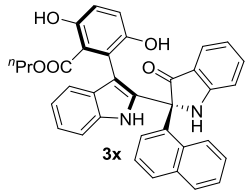
3v

(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(2-(2-(naphthalen-1-yl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)benzoate (3v): Reaction time 48 h, yellow solid, mp = 204-205 ^{o}C. 52.3 mg, 92% yield, 95% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (major) = 11.796 min, t (minor) = 18.540 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.78 (s, 1H), 8.48 (s, 1H), 7.90 – 7.78 (m, 3H), 7.62 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.46 – 7.32 (m, 4H), 7.23 (s, 1H), 7.19 – 7.10 (m, 3H), 7.06 – 6.99 (m, 1H), 6.86 (dd, J = 8.3, 5.1 Hz, 2H), 6.42 (d, J = 8.3 Hz, 1H), 5.60-5.35 (m, 2H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.1, 170.5, 160.2, 156.8, 146.9, 138.4, 136.0, 134.9, 133.2, 132.4, 131.7, 130.3, 129.8, 128.6, 127.1, 126.8, 126.1, 125.2, 125.0, 124.0, 123.1, 123.0, 120.5, 120.4, 120.3, 119.2, 119.1, 118.7, 112.9, 112.3, 111.2, 108.3, 73.0, 51.8. HRMS (ESI): calcd for $[C_{34}H_{24}N_2O_5+Na]^+$ $[M+Na]^+$ *m/z* 563.1577, found 563.1567.

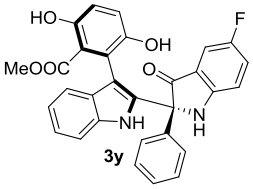


3w

(*S*$_a$,*R*)-Methyl-3,6-dihydroxy-2-(2-(2-(naphthalen-2-yl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)-benzoate (3w): Reaction time 24 h, yellow solid, mp = 117-118 ^{o}C. 50.0 mg, 93% yield, 90% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 13.420 min, t (minor) = 21.308 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.81 (s, 1H), 8.93 (s, 1H), 7.86 (d, J = 1.5 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.60 (d, J = 7.7 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.41 (ddd, J = 8.4, 7.3, 1.2 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.21 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.13 (t, J = 9.1 Hz, 2H), 7.08 – 7.01 (m, 1H), 6.95 (d, J = 9.0 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 6.46 (d, J = 8.3 Hz, 1H), 5.21 (s, 1H), 5.07 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.6, 170.6, 160.4, 156.8, 146.9, 138.6, 136.3, 136.1, 133.2, 132.1, 129.4, 128.4, 128.1, 127.7, 127.0, 126.8, 125.9, 124.9, 124.3, 123.4, 122.6, 120.7, 119.9, 119.0, 118.9, 112.6, 112.4, 111.4, 108.0, 71.9, 51.9. HRMS (ESI): calcd for $[C_{34}H_{24}N_2O_5+H]^+$ $[M+H]^+$ *m/z* 541.1758, found 541.1764.

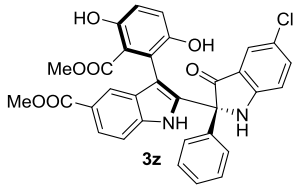


(*S*$_a$,*R*)-Propyl-3,6-dihydroxy-2-(2-(2-(naphthalen-1-yl)-3-oxoindolin-2-yl)-1*H*-indol-3-yl)benzoate (3x): Reaction time 48 h, yellow solid, mp = 150-151 ºC, 52.2 mg, 92% yield, 93% ee [Daicel Chiralpak IB, hexane/2-propanol = 93/7, ν = 1.0 mL/min, λ = 254 nm, t (minor) = 9.900 min, t (major) = 33.868 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.99 (s, 1H), 8.55 (s, 1H), 7.85 (dd, *J* = 16.6, 8.0 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.39 (m, 3H), 7.38 – 7.31 (m, 2H), 7.24 (d, *J* = 4.2 Hz, 1H), 7.19 – 7.11 (m, 3H), 7.07 – 6.99 (m, 1H), 6.93 – 6.82 (m, 2H), 6.43 (d, *J* = 8.3 Hz, 1H), 5.44 (d, *J* = 33.6 Hz, 2H), 3.58 (dt, *J* = 10.6, 7.2 Hz, 1H), 3.13 (ddd, *J* = 10.6, 7.0, 5.8 Hz, 1H), 0.67 (tq, *J* = 14.1, 7.3 Hz, 1H), 0.40 (dh, *J* = 14.5, 7.3 Hz, 1H), 0.13 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.1, 170.3, 160.1, 157.0, 146.9, 138.5, 136.1, 134.8, 133.3, 131.9, 131.6, 130.3, 129.7, 128.9, 127.1, 127.0, 126.1, 125.2, 125.1, 124.0, 123.3, 122.9, 120.6, 120.3, 120.2, 119.4, 119.2, 118.8, 112.9, 112.4, 111.2, 108.7, 73.1, 67.1, 20.4, 9.7. HRMS (ESI): calcd for $[C_{36}H_{28}N_2O_5+Na]^+$ $[M+Na]^+$ *m/z* 591.1890, found 591.1887.



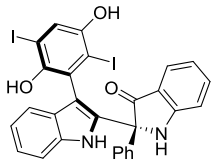
(*S*$_a$,*R*)-Methyl-2-(5-fluoro-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)-3,6-dihydroxybenzoate (3y): Reaction time 24 h, yellow solid, mp = 125-126 ºC, 50.4 mg, 99% yield, 90% ee [Daicel Chiralpak AD, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 10.936 min, t (minor) = 14.554 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.73 (s, 1H), 8.80 (s, 1H), 7.34-7.28 (m, 6H), 7.23 – 7.12 (m, 4H), 7.10 – 7.02 (m, 2H), 6.96 (d, J = 9.1 Hz, 1H), 6.42 (dd, J = 8.7, 3.6 Hz, 1H), 5.02 (s, 1H), 4.94 (s, 1H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.4, 170.6, 157.0, 156.9 (d, $^1J_{C\text{-}F}$ = 241.4 Hz) 156.6, 146.9, 139.0, 136.0, 131.8, 129.3, 129.0, 128.0, 126.7, 126.5, 123.5, 122.6, 120.7, 119.8, 119.2 (d, $^3J_{C\text{-}F}$ = 7.4 Hz), 119.1, 113.6

(d, $^{3}J_{C\text{-}F}$ = 7.4 Hz), 112.7, 111.3, 109.4 (d, $^{2}J_{C\text{-}F}$ = 22.7 Hz), 108.0, 72.9, 51.9. ^{19}F NMR (376 MHz, chloroform-*d*) δ –123.2. HRMS (ESI): calcd for $[C_{30}H_{20}FN_2O_5]^-$ $[M\text{-}H]^-$ *m/z* 507.1362; found: 507.1356.



3z

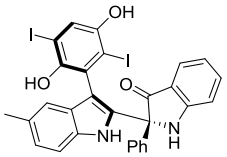
(*S*$_a$,*R*)-Methyl-2-(5-chloro-3-oxo-2-phenylindolin-2-yl)-3-(3,6-dihydroxy-2-(methoxycarbonyl)phenyl)-1*H*-indole-5-carboxylate (3z): Reaction time 48 h, yellow solid, mp = 162-163 ºC solid, mp = 162-163 ºC, 50.6 mg, 87% yield, 99% ee [Daicel Chiralpak AD, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 9.783 min, t (minor) = 14.098 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 10.78 (s, 1H), 8.99 (s, 1H), 7.89 – 7.76 (m, 2H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.27 (m, 7H), 7.10 (d, *J* = 9.0 Hz, 1H), 6.97 (d, *J* = 9.0 Hz, 1H), 6.40 (d, *J* = 8.7 Hz, 1H), 5.21 (s, 2H), 3.78 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 198.4, 170.4, 167.9, 158.6, 156.8, 146.9, 138.5, 133.0, 129.4, 129.2, 127.8, 126.8, 125.2, 124.8, 124.0, 123.1, 122.6, 122.0, 119.7, 119.4, 119.0, 113.5, 112.4, 111.0, 110.0, 72.6, 52.0, 52.0. HRMS (ESI): calcd for $[C_{32}H_{23}ClN_2O_7+H]^+$ $[M+H]^+$ *m/z* 583.1267, found 583.1267.



3aa

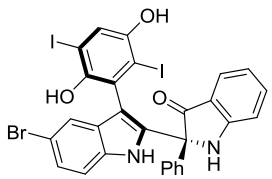
(*S*$_a$,R)-2-(3-(2,5-Dihydroxy-3,6-diiodophenyl)-1*H*-indol-2-yl)-2-phenylindolin-3-one. Reaction time 48 h, yellow solid, mp = 190-191 ºC. 63.6 mg, 93% yield, 93% ee [Daicel Chiralpak AD, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 13.388 min, t (minor) = 24.929 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.96 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.27 (m, 3H), 7.24 – 7.19 (m, 1H), 7.12 – 7.03 (m, 2H), 6.83 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.24 (m, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.5, 160.9, 149.6, 147.7, 138.6, 138.2, 135.7, 132.6, 129.1, 129.0, 127.3, 126.8, 125.7, 125.4, 123.7, 123.6, 120.8,

120.2, 119.5, 119.1, 113.0, 112.6, 111.6, 96.0, 84.0, 71.7. HRMS (ESI): calcd for $[C_{28}H_{18}I_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 684.9480, found 684.9478.



3ab

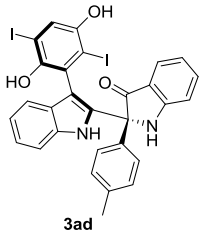
(*S*$_a$,*R*)-2-(3-(2,5-Dihydroxy-3,6-diiodophenyl)-5-methyl-1*H*-indol-2-yl)-2-phenylindolin-3-one. Reaction time 48 h, yellow solid, mp = 252-253 ^oC. 66.3 mg, 95% yield, 96% ee [Daicel Chiralpak ID, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 254 nm, t (major) = 13.811 min, t (minor) = 18.805 min]. ^1H NMR (400 MHz, chloroform-*d*) δ 8.89 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.34 (m, 4H), 7.31 – 7.24 (m, 4H), 7.09 – 6.99 (m, 1H), 6.84 (dd, *J* = 14.0, 6.5 Hz, 2H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.22 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.5, 160.9, 149.6, 147.7, 138.6, 138.4, 134.0, 132.6, 130.3, 129.1, 128.9, 127.5, 126.8, 125.7, 125.6, 125.3, 123.7, 120.2, 119.1, 118.9, 112.6, 112.4, 111.2, 96.1, 83.8, 71.7, 21.6. HRMS (ESI): calcd for $[C_{29}H_{20}I_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 698.9636, found 698.9634.



3ac

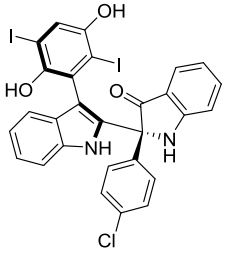
(*S*$_a$,*R*)-2-(5-Bromo-3-(2,5-dihydroxy-3,6-diiodophenyl)-1*H*-indol-2-yl)-2-phenylindolin-3-one. Reaction time 48 h, yellow solid, mp = 207-208 ^oC. 66.3 mg, 87% yield, 93% ee [Daicel Chiralpak AD, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 10.437 min, t (minor) = 16.190 min]. ^1H NMR (400 MHz, chloroform-*d*) δ 9.01 (s, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.37 – 7.33 (m, 3H), 7.28 (m, 4H), 7.24 – 7.19 (m, 2H), 6.85 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.20 (m, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.4, 160.9, 149.7, 147.6, 138.7, 138.0, 134.2, 133.9, 129.2, 129.1, 126.8, 126.5, 125.7, 124.8, 123.9, 121.9, 120.4, 119.1, 114.1, 113.1, 113.0, 112.7, 96.0, 84.6, 71.7. HRMS (ESI): calcd

for $[C_{28}H_{17}BrI_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 762.8585, 764.8564, found 762.8581, 764.8561.



3ad

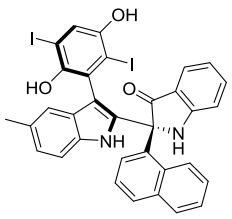
(S_a,*R*)-2-(3-(2,5-Dihydroxy-3,6-diiodophenyl)-1*H*-indol-2-yl)-2-(*p*-tolyl)indolin-3-one. Reaction time 48 h, yellow solid, mp = 182-183 ºC. 60.7 mg, 87% yield, 91% ee [Daicel Chiralpak AD, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 14.370 min, t (minor) = 30.594 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.93 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.34 (m, 2H), 7.26 (m, 2H), 7.23 – 7.17 (m, 1H), 7.07 (m, 4H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 5.24 (m, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.7, 160.9, 149.6, 147.7, 138.9, 138.6, 135.7, 135.1, 132.9, 129.7, 127.3, 126.8, 125.7, 125.5, 123.6, 123.5, 120.8, 120.2, 119.5, 119.2, 113.0, 112.6, 111.6, 96.1, 84.0, 71.6, 21.2. HRMS (ESI): calcd for $[C_{29}H_{20}I_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 698.9636, found 698.9634.



3ae

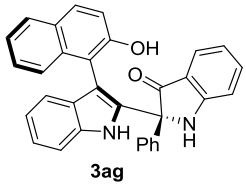
(S_a,*R*)-2-(4-Chlorophenyl)-2-(3-(2,5-dihydroxy-3,6-diiodophenyl)-1*H*-indol-2-yl)indolin-3-one. Reaction time 48 h, yellow solid, mp = 185-186 ºC. 64.6 mg, 90% yield, 92% ee [Daicel Chiralpak AD, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 10.678 min, t (minor) = 33.291 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.93 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.39 – 7.32 (m, 4H), 7.23 (m, 3H), 7.11 – 7.05 (m, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 5.57 (s, 1H), 5.23 (s, 1H), 5.10 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 199.1, 160.8, 149.7, 147.6, 138.8, 136.7, 135.6, 135.0, 132.1, 129.1, 128.3, 127.2, 125.7, 125.1, 123.8, 121.0, 120.4, 119.5, 118.9, 113.2, 112.7, 111.6,

95.9, 84.3, 71.0. HRMS (ESI): calcd for $[C_{28}H_{17}ClI_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 718.9090, found 718.9088.



3af

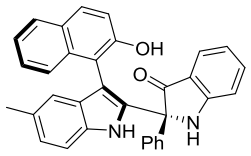
(*S*$_a$,*R*)-2-(3-(2,5-Dihydroxy-3,6-diiodophenyl)-5-methyl-1*H*-indol-2-yl)-2-(naphthalen-1-yl)indolin-3-one. Reaction time 48 h, yellow solid, mp = 234-235 ^oC. 51.6 mg, 69% yield, 90% ee [Daicel Chiralpak ID, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 254 nm, t (major) = 6.349 min, t (minor) = 15.267 min]. ^1H NMR (400 MHz, chloroform-*d*) δ 8.51 (s, 1H), 7.88 (dd, *J* = 19.9, 8.2 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 25.9, 7.3 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.40 – 7.32 (m, 3H), 7.21 (s, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 7.05 – 6.96 (m, 1H), 6.87 (m, 2H), 6.49 (m, 2H), 5.67 (s, 1H), 4.96 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 198.9, 160.5, 149.4, 147.5, 138.5, 134.8, 134.1, 132.5, 132.4, 131.6, 130.3, 130.0, 129.7, 128.0, 127.7, 127.1, 126.0, 125.9, 125.8, 125.1, 125.1, 124.7, 123.0, 120.5, 119.6, 119.4, 112.9, 112.5, 111.2, 95.9, 84.5, 73.1, 21.6. HRMS (ESI): calcd for $[C_{33}H_{22}I_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 748.9793, found 748.9789.



3ag

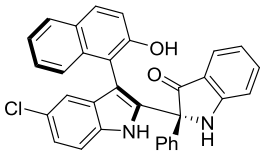
(*S*$_a$,*R*)-2-(3-(2-Hydroxynaphthalen-1-yl)-1*H*-indol-2-yl)-2-phenylindolin-3-one. Reaction time 48 h, yellow solid, mp = 236-237 ^oC. 41.0 mg, 88% yield, 90% ee [Daicel Chiralpak AY, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 7.284 min, t (minor) = 14.354 min]. ^1H NMR (400 MHz, Chloroform-d) δ 9.60 (s, 1H), 7.86 – 7.77 (m, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 7.28 (m, 4H), 7.24 – 7.16 (m, 5H), 7.08 – 6.99 (m, 4H), 6.72 (t, J = 7.5 Hz, 1H), 5.98 (d, J = 8.3 Hz, 1H), 5.10 (s, 2H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 200.3, 161.1, 152.5, 139.4, 138.2, 135.6, 134.7, 134.4, 130.3, 129.0, 128.6, 128.0, 126.7, 126.0,

125.4, 125.1, 123.5, 120.8, 119.7, 119.6, 118.1, 117.5, 112.2, 112.0, 111.6, 105.6, 71.3. HRMS (ESI): calcd for $[C_{32}H_{22}N_2O_2+H]^+$ $[M+H]^+$ *m/z* 467.1754, found 467.1756.



3ah

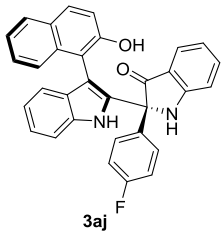
(*S*$_a$,*R*)-2-(3-(2-Hydroxynaphthalen-1-yl)-5-methyl-1*H*-indol-2-yl)-2-phenylindolin-3-one. Reaction time 48 h, yellow solid, mp = 154-155 ºC. 43.7 mg, 91% yield, 85% ee [Daicel Chiralpak IF, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 254 nm, t (major) = 9.351 min, t (minor) = 23.563 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 9.53 (s, 1H), 7.82 (m, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.27 (m, 3H), 7.24 – 7.15 (m, 5H), 7.12 – 7.02 (m, 3H), 6.85 – 6.78 (m, 1H), 6.72 (t, *J* = 7.6 Hz, 1H), 5.97 (d, *J* = 8.3 Hz, 1H), 5.17 (s, 1H), 5.08 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 200.3, 161.1, 152.5, 139.5, 138.2, 134.7, 134.4, 133.9, 130.3, 129.3, 129.0, 128.5, 128.1, 126.7, 125.9, 125.4, 125.2, 125.1, 123.5, 119.5, 119.1, 118.1, 117.5, 112.2, 111.2, 104.9, 71.3, 21.4. HRMS (ESI): calcd for $[C_{33}H_{24}N_2O_2+H]^+$ $[M+H]^+$ *m/z* 481.1911, found 481.1912.



3ai

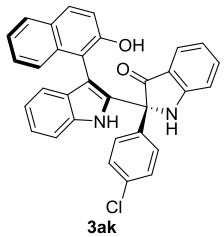
(*S*$_a$,*R*)-2-(5-Chloro-3-(2-hydroxynaphthalen-1-yl)-1*H*-indol-2-yl)-2-phenylindolin-3-one. Reaction time 48 h, yellow solid, mp = 160-161 ºC. 38.0 mg, 76% yield, 90% ee [Daicel Chiralpak ID, hexane/2-propanol = 70/30, ν = 1.0 mL/min, λ = 254 nm, t (major) = 6.640 min, t (minor) = 15.896 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 9.64 (s, 1H), 7.81 (m, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.27 (m, 3H), 7.24 – 7.13 (m, 6H), 7.09 (td, *J* = 7.5, 6.8, 1.1 Hz, 1H), 7.03 – 6.93 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.01 (d, *J* = 8.3 Hz, 1H), 5.19 (s, 1H), 5.08 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 200.1, 161.1, 152.5, 139.7, 139.0, 138.4, 136.2, 134.2, 133.9, 130.6, 130.2, 129.1, 129.0, 128.7, 128.1, 126.9, 126.7, 125.9, 125.4, 124.8, 123.9,

123.6, 119.8, 119.0, 118.0, 117.6, 112.7, 112.2, 111.4, 105.5, 71.2. HRMS (ESI): calcd for $[C_{32}H_{21}ClN_2O_2+H]^+$ $[M+H]^+$ *m/z* 501.1364, found 501.1366.



3aj

(*S*$_a$,*R*)-2-(4-Fluorophenyl)-2-(3-(2-hydroxynaphthalen-1-yl)-1*H*-indol-2-yl)indolin-3-one. Reaction time 48 h, yellow solid, mp = 151-152 ºC. 40.2 mg, 83% yield, 85% ee [Daicel Chiralpak ID, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 254 nm, t (major) = 7.760 min, t (minor) = 35.935 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 9.56 (s, 1H), 7.83 (m, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.24 – 7.16 (m, 2H), 7.11 – 7.01 (m, 4H), 6.91 – 6.84 (m, 2H), 6.78 – 6.71 (m, 1H), 6.01 (d, *J* = 8.3 Hz, 1H), 5.21 (s, 1H), 5.12 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ 200.2, 162.6 (d, $^1J_{C\text{-}F}$ = 248.1 Hz), 161.1, 152.5, 138.4, 135.6, 135.1, 135.1, 134.4, 134.3, 130.4, 129.0 (d, $^3J_{C\text{-}F}$ = 6.5 Hz), 128.1, 127.9 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 126.8, 125.4, 124.9, 123.7, 123.6, 120.9, 119.8, 119.7, 118.0, 117.5, 115.8 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 112.3, 111.9, 111.6, 105.8, 77.5, 70.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.2. HRMS (ESI): calcd for $[C_{32}H_{21}FN_2O_2+H]^+$ $[M+H]^+$ *m/z* 485.1660, found 485.1662.

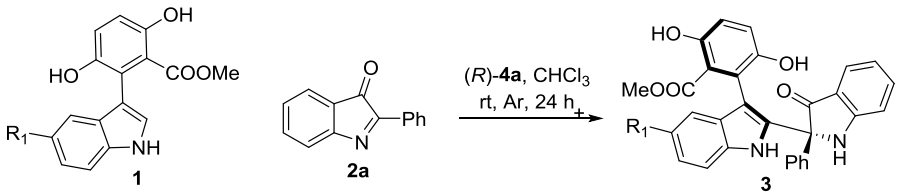


3ak

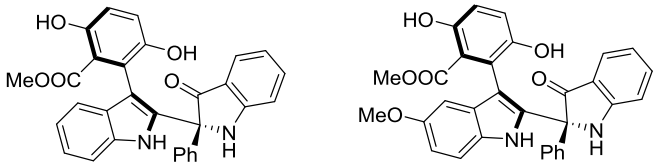
(*S*$_a$,*R*)-2-(4-Chlorophenyl)-2-(3-(2-hydroxynaphthalen-1-yl)-1*H*-indol-2-yl)indolin-3-one. Reaction time 48 h, yellow solid, mp = 164-165 ºC. 44.5 mg, 89% yield, 86% ee [Daicel Chiralpak ID, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 6.479 min, t (minor) = 12.058 min]. ^{1}H NMR (400 MHz, chloroform-*d*) δ 9.57 (s, 1H), 7.83 (m, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 7.11 – 7.01 (m, 4H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 1H), 5.13 (s, 1H). ^{13}C NMR (100 MHz,

chloroform-*d*) δ 199.9, 161.1, 152.5, 138.4, 137.8, 135.6, 134.5, 134.3, 134.2, 130.5, 129.1, 128.2, 127.5, 126.8, 125.5, 124.9, 123.7, 123.6, 120.9, 119.9, 119.7, 117.9, 117.6, 112.3, 111.8, 111.6, 105.8, 70.8. HRMS (ESI): calcd for $[C_{32}H_{21}ClN_2O_2+H]^+$ $[M+H]^+$ *m/z* 501.1364, found 501.1366.

8. Scale up synthesis of 3a, 3j and 3ag



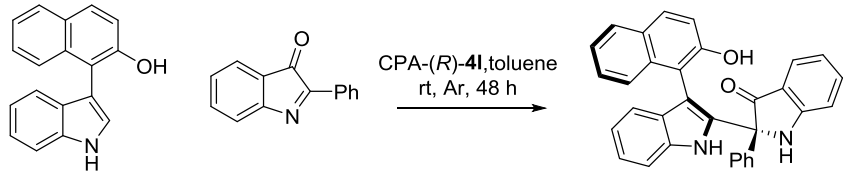
In an oven dried round-bottom flask, chiral phophoric acid (*R*)-**4a** (10 mol%), **1a** or **1j** (1.2 mmol) and **2a** (1 mmol) were dissolved in anhydrous $CHCl_3$ (20 mL). After stirred under argon atmosphere at room temperature for 24 h (monitored by TLC), the solution was concentrated and purified by silica gel column chromatography to afford pure product **3a** or **3j**.



3a, 456 mg (93% yield)
93% ee, dr > 20:1

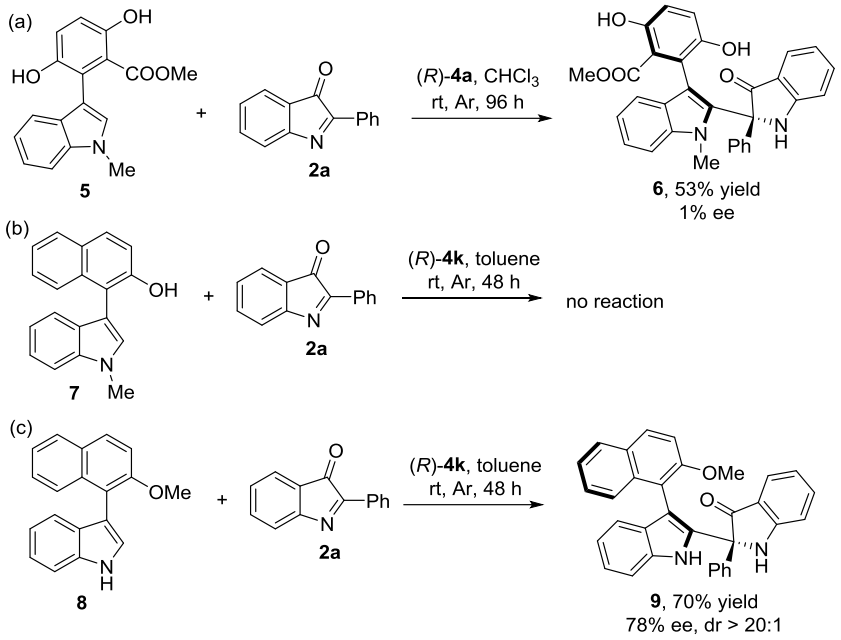
3j, 499 mg (96% yield)
94% ee, dr > 20:1

In an oven dried round-bottom flask, chiral phophoric acid (*R*)-**4a** (10 mol%), **1u** (1 mmol) and **2a** (1 mmol) were dissolved in anhydrous toluene (5 mL). After stirred under argon atmosphere at room temperature for 48 h (monitored by TLC), the solution was concentrated and purified by silica gel column chromatography to afford pure product **3ag.**



3ag,424.2mg, 91% yield
90% ee, dr > 20:1

9. Control experiments



To gain some insights into the activation mode of catalyst **CPA** on the substrates, we performed the control experiments. We attempted treatment of methyl 3,6-dihydroxy-2-(1-methyl-1*H*-indol-3-yl)benzoate (**5**) with 2-phenyl-3*H*-indol-3-ones (**2a**) under the standard conditions, the reaction afforded product **6** in 53% yield almost without enantioselectivity, and a long time (96 h) was needed. Further, reaction of **7** with **2a** did not work under the standard conditions Finally, we attempted reaction of **8** with **2a** under the standard conditions, and product **9** was obtained in 70% yield with 78% ee. These result indicated that the N-H group of indole ring was necessary for the reactivity and enantioselectivity, which showed that a hydrogen-bond between NH in the indole (**1**) and (*R*)-CPA was important.

In an oven dried Schlenk tube, chiral phophoric acid (*R*)-**4a** (10 mol%), **5** (0.12 mmol) and **2a** (0.1 mmol) were dissolved in anhydrous $CHCl_3$ (2 mL). After stirred under argon atmosphere at room temperature for 96 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford **6**.

Methyl-3,6-dihydroxy-2-(1-methyl-2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl) benzoate (6): Yellow solid, mp = 137-138 ^{o}C, 26.7 mg, 53% yield, 1% ee [Daicel Chiralpak IF, hexane/2-propanol = 90/10, ν = 1.0 mL/min, λ = 254 nm, t (major) =

8.481 min, t (minor) = 11.906 min]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.73 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.25 (m, 8H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.09 – 7.01 (m, 2H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.14 (d, *J* = 8.2 Hz, 1H), 5.05 (s, 1H), 4.77 (s, 1H), 3.56 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.2, 170.5, 158.6, 156.8, 146.0, 140.3, 138.9, 138.2, 133.7, 129.6, 128.7, 126.6, 124.3, 123.0, 122.5, 122.0, 120.4, 119.6, 119.0, 118.0, 112.3, 112.0, 109.5, 108.7, 72.8, 51.8, 33.5. HRMS (ESI): calcd for $[C_{31}H_{24}N_2O_5+Na]^+$ $[M+Na]^+$ *m/z* 527.1577, found 527.1577.

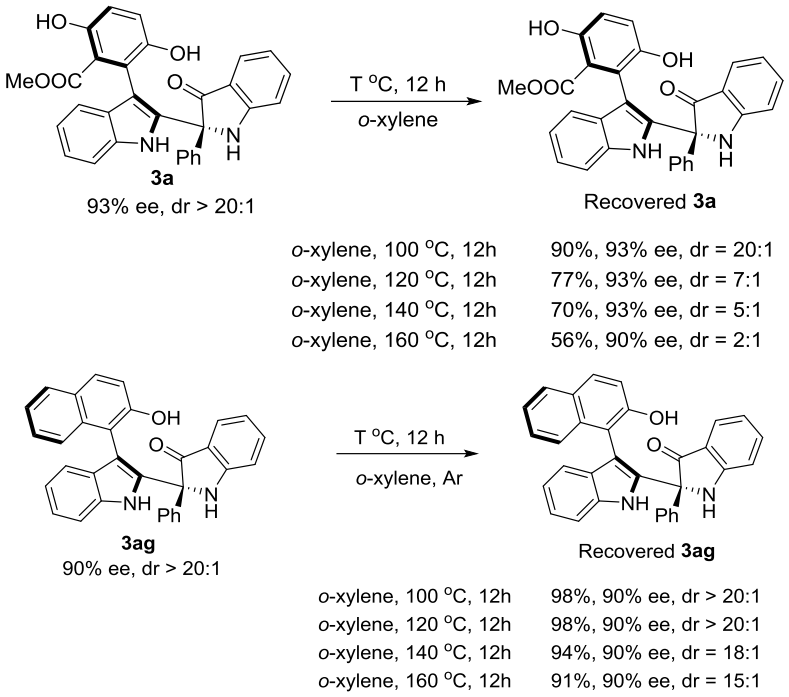
In an oven dried Schlenk tube, chiral phophoric acid (*R*)-**4k** (10 mol%), **7** or **8** (0.1mmol) and **2a** (0.1mmol) were dissolved in anhydrous toluene (0.5 mL). After stirred under argon atmosphere at room temperature for 48 h (monitored by TLC), the solution was concentrated and purified by preparative silica gel thin layer chromatography (*p*-TLC) to afford **9**.

(*S*$_a$,*R*)-2-(3-(2-Methoxynaphthalen-1-yl)-1*H*-indol-2-yl)-2-phenylindolin-3-one (9): Yellow solid, mp = 146-147 ºC. 33.6 mg, 70% yield, 78% ee [Daicel Chiralpak AY, hexane/2-propanol = 75/25, ν = 1.0 mL/min, λ = 254 nm, t (major) = 8.034 min, t (minor) = 16.140 min]. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.44 – 7.25 (m, 6H), 7.24 – 7.11 (m, 3H), 7.06 (m, 3H), 6.97 (d, *J* = 4.0 Hz, 2H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.42 (d, *J* = 8.3 Hz, 1H), 5.48 (s, 1H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.8, 165.6, 161.1, 155.5, 139.7, 137.9, 135.6, 134.2, 132.7, 129.6, 129.4, 129.0, 128.4, 127.9, 127.8, 126.6, 126.4, 125.8, 125.5, 123.7, 122.7, 120.0, 119.7, 119.1, 117.2, 113.4, 112.1, 111.4, 109.5, 71.6, 56.3. HRMS (ESI): calcd for $[C_{33}H_{24}N_2O_2+H]^+$ $[M+H]^+$ *m/z* 481.1911, found 481.1912.

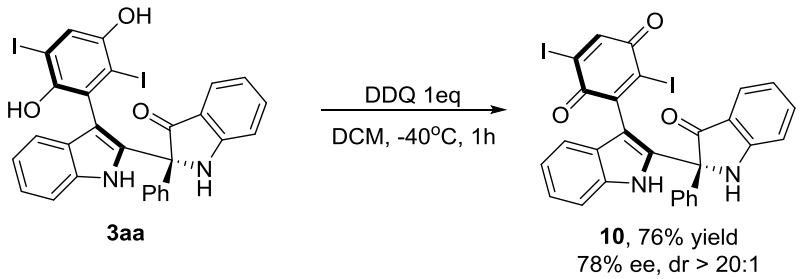
10. Investigation on conformational stability of product 3a and 3ag

We investigated the stability for products **3a** and **3ag** (0.1 mmol scale)**,** and the treatment was carried out in *o*-xylene (2 mL) at various temperatures under Ar

atmosphere for 12 h. The experiment results showed that the axially chiral products were of good conformational stability, especially, compound **3ag**.



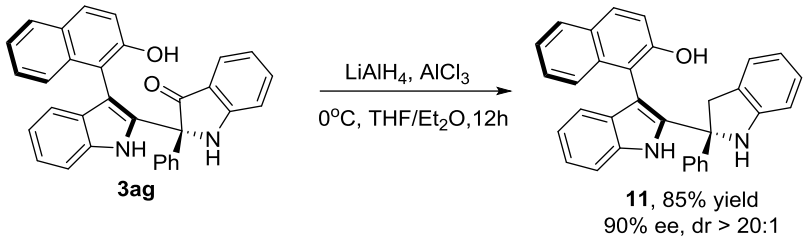
11. Derivatization of chiral products



In an oven dried Schlenk tube containing **3aa** (0.1mmol) in anhydrous CH_2Cl_2 (DCM) (3 mL), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (22.7 mg, 0.1 mmol) was added in one portion at -40 °C. After the reaction completed (about 1 hour), the solvent was removed and the residue was purified by preparative silica gel thin layer chromatography (*p*-TLC) (EA/DCM = 1/30) to afford **10.**[4]

(*S*$_a$,*R*)-2,5-Diiodo-3-(2-(3-oxo-2-phenylindolin-2-yl)-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (10): Brown solid, mp = 262-263 °C. 51.8 mg, 76% yield, 91% ee [Daicel Chiralpak IF, hexane/2-propanol = 80/20, ν = 1.0 mL/min, λ = 254 nm, t (major) = 18.189 min, t (minor) = 23.887 min]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.05 (s, 1H), 8.00 (s, 1H), 7.85 (s, 1H), 7.40 – 7.31 (m, 7H), 7.15 (d, *J* = 7.9 Hz, 1H),

7.05 (t, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 1H), 5.71 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 199.2, 179.4, 177.6, 161.3, 149.5, 144.2, 139.3, 138.3, 137.5, 137.3, 133.7, 133.5, 129.3, 129.0, 128.4, 125.3, 122.3, 121.0, 120.6, 120.3, 119.9, 119.7, 119.5, 113.6, 112.9, 112.5, 72.4, 55.5. HRMS (ESI): calcd for $[C_{28}H_{16}I_2N_2O_3+H]^+$ $[M+H]^+$ *m/z* 682.9323, found 682.9322.



3ag (46.6 mg, 0.1 mmol) was dissolved to THF/Et_2O (1/1, 1.5 mL) and $LiAlH_4$ (19.0 mg, 0.5 mmol) was added to the solution at 0 °C. After being stirred for 1 h, $AlCl_3$ (80.0 mg, 0.6 mmol) was added at 0 °C under Ar atmosphere. After being stirred for 12 h, the reaction was quenched by adding H_2O. The mixture was extracted with CH_2Cl_2 three times, then combined organic phase was dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by preparative silica gel thin layer chromatography (*p*-TLC) (PE/EA = 2/1) to afford the product **11**.[5]

(*S*$_a$,*R*)-1-(2-(2-Phenylindolin-2-yl)-1*H*-indol-3-yl)naphthalen-2-ol (11): White solid, mp = 264-265 °C. 38.4 mg, 85% yield, 90% ee [Daicel Chiralpak ID, hexane/2-propanol = 85/15, ν = 1.0 mL/min, λ = 254 nm, t (major) = 15.190 min, t (minor) = 22.073 min]. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (s, 1H), 8.96 (s, 1H), 7.77 (m, 2H), 7.42 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.10 – 7.05 (m, 3H), 7.01 – 6.93 (m, 3H), 6.75 – 6.65 (m, 3H), 6.50 – 6.39 (m, 2H), 5.94 (d, *J* = 7.8 Hz, 1H), 5.80 (s, 1H), 5.58 (d, *J* = 6.4 Hz, 1H), 4.73 (d, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.7, 150.0, 141.5, 140.6, 135.9, 135.3, 131.3, 129.8, 129.2, 128.9, 128.7, 128.5, 128.1, 127.3, 126.6, 125.8, 125.7, 125.3, 122.7, 121.6, 119.2, 119.1, 118.7, 118.2, 114.9, 111.5, 109.7, 107.2, 77.1, 74.8. HRMS (ESI): calcd for $[C_{32}H_{24}N_2O+H]^+$ $[M+H]^+$ *m/z* 453.1961, found 453.1960.

12. X-Ray crystallographic data for 3a with 50% probability displacement ellipsoids (CCDC 1955097).

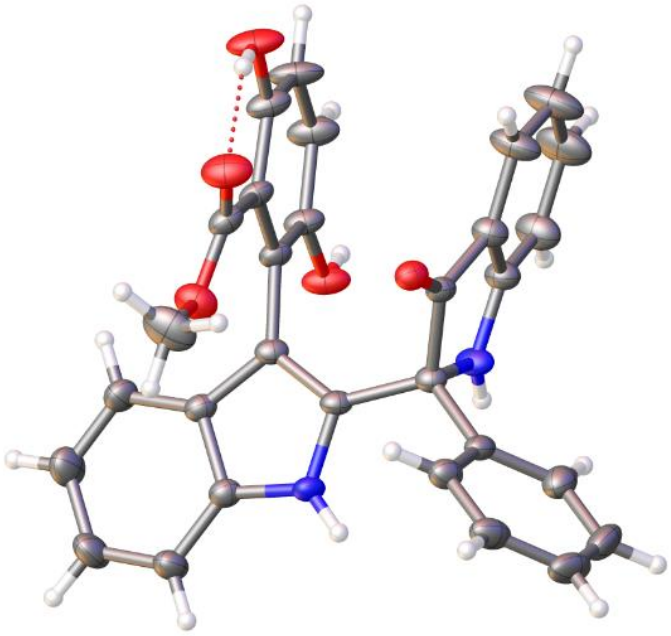


Table S3 Crystal data and structure refinement for 3a (CCDC 1955097).

Identification code	CCDC 1955097
Empirical formula	$C_{30}H_{22}N_2O_5$
Formula weight	490.49
Temperature/K	173.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.8477(2)
b/Å	14.2309(2)
c/Å	9.63710(10)
α/°	90
β/°	95.549(2)
γ/°	90
Volume/Å^3	1207.73(3)
Z	2
ρ_{calc}g/cm^3	1.349
μ/mm^{-1}	0.758
F(000)	512.0
Crystal size/mm^3	0.35 × 0.3 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.22 to 142.818
Index ranges	$-10 \le h \le 10$, $-17 \le k \le 10$, $-11 \le l \le 11$

Reflections collected	7961
Independent reflections	3401 [R_{int} = 0.0298, R_{sigma} = 0.0346]
Data/restraints/parameters	3401/1/337
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1= 0.0350, wR_2 = 0.0922
Final R indexes [all data]	R_1= 0.0360, wR_2 = 0.0937
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.31
Flack parameter	0.02(16)

Table S4 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$ ×10^3) for 3a (CCDC 1955097) U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O001	4283.5(18)	3595.7(12)	4131.9(16)	24.5(4)
O002	727(2)	4391.0(14)	3844.5(19)	34.8(4)
O003	4287(2)	7229.5(13)	4179.0(17)	32.9(4)
O004	1283(2)	3691.8(15)	5888.6(19)	41.2(5)
O005	2487(3)	4642.5(14)	7938.7(17)	43.0(5)
N006	2700(2)	5348.5(15)	830.7(18)	23.6(4)
N007	6050(2)	5593.0(16)	2774.4(19)	28.0(5)
C008	5061(3)	4282.8(17)	3908(2)	21.3(5)
C009	3361(2)	5275.1(17)	2186(2)	21.1(4)
C00A	2545(3)	5782.3(16)	3050(2)	22.0(5)
C00B	1336(3)	6225.9(18)	2197(2)	23.7(5)
C00C	1435(3)	4359.1(19)	5117(2)	26.8(5)
C00D	1448(3)	5917.9(17)	821(2)	24.4(5)
C00E	2384(3)	5188.6(17)	5538(2)	24.3(5)
C00F	2873(3)	5863.4(17)	4589(2)	22.9(5)
C00G	5337(3)	4160.4(19)	1372(2)	25.4(5)
C00H	4914(3)	4839.3(17)	2504(2)	22.2(5)
C00I	6716(3)	5527(2)	4132(2)	28.3(5)
C00J	6259(3)	4727.9(19)	4809(2)	28.0(5)
C00K	4353(3)	3423.9(19)	952(3)	29.4(6)
C00L	3773(3)	6609.3(18)	5112(2)	27.6(5)
C00M	6705(3)	4241(2)	784(3)	35.2(6)
C00N	2852(3)	5273.5(19)	6966(2)	31.9(6)
C00O	230(3)	6891(2)	2451(3)	31.2(6)
C00P	4732(3)	2776(2)	-35(3)	38.1(7)
C00Q	433(3)	6214(2)	-289(3)	33.0(6)
C00R	-759(3)	7196(2)	1351(3)	41.8(7)

C00S	6826(4)	4522(2)	6180(3)	42.5(7)
C00T	-670(3)	6852(2)	-2(3)	40.8(7)
C00U	3730(4)	6040(2)	7452(3)	41.5(7)
C00V	7070(4)	3579(3)	-208(3)	46.0(8)
C00W	6094(4)	2857(2)	-622(3)	44.1(8)
C00X	7721(3)	6166(2)	4828(3)	39.6(7)
C00Y	4180(4)	6695(2)	6542(3)	38.7(7)
C00Z	-154(4)	3566(2)	3410(4)	51.8(8)
C010	8279(4)	5941(3)	6167(3)	52.6(9)
C011	7860(4)	5127(3)	6844(3)	55.8(9)

Table S5 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3a (CCDC 1955097). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	30.7(8)	20.3(8)	22.7(8)	1.1(6)	4.0(6)	1.3(7)
O002	41.9(10)	27.3(10)	33.6(9)	0.0(8)	-4.2(7)	-7.5(8)
O003	56.6(11)	22.9(9)	19.2(8)	0.7(7)	3.7(7)	-12.9(8)
O004	61.6(12)	32.2(11)	30.4(9)	4.0(8)	7.1(8)	-16.3(10)
O005	81.3(15)	30.3(11)	18.6(8)	2.2(7)	11.1(9)	-15.5(11)
N006	29.5(9)	26.0(10)	15.5(8)	-1.9(8)	2.4(7)	3.6(9)
N007	32.8(10)	30.6(12)	20.4(9)	4.9(8)	2.1(8)	-9.5(9)
C008	26.7(11)	20.4(12)	16.9(9)	0.8(9)	3.2(8)	4.1(9)
C009	28.3(11)	19.3(11)	15.6(9)	1.9(9)	2.1(8)	0.4(9)
C00A	29.9(11)	18.7(11)	17.5(10)	2.2(9)	2.9(8)	-0.3(9)
C00B	28.4(11)	23.6(12)	19.5(10)	-1.2(9)	4.1(9)	1.0(10)
C00C	33.8(12)	24.8(13)	23.1(10)	-1.4(10)	9.9(9)	-0.3(10)
C00D	28.9(11)	23.3(12)	21.1(10)	-1.7(9)	3.3(9)	1.3(10)
C00E	33.3(12)	21.3(12)	19.4(10)	-2.0(9)	8.7(8)	0.2(10)
C00F	30.7(11)	21.3(12)	17.2(10)	-1.8(9)	4.9(8)	3.0(10)
C00G	29.3(11)	30.4(13)	16.3(9)	1.3(9)	1.6(8)	7.5(11)
C00H	26.3(11)	21.9(12)	18.5(10)	2.0(9)	2.4(8)	-0.6(9)
C00I	31.0(12)	31.3(14)	22.1(11)	2.3(10)	1.1(9)	-3.1(11)
C00J	33.1(12)	26.5(13)	23.8(11)	1.6(10)	-0.8(9)	-1.9(10)
C00K	34.7(13)	29.6(14)	23.6(11)	-2.5(10)	0.4(9)	8.3(11)
C00L	43.0(14)	22.1(12)	18.6(11)	0.6(10)	7.0(10)	-3.7(11)
C00M	35.5(13)	42.8(16)	28.0(12)	5.9(12)	7.3(10)	8.2(13)
C00N	53.3(15)	23.2(13)	20.6(11)	0.5(10)	11.0(10)	-3.0(12)

C00O	34.2(13)	33.0(14)	26.7(12)	-6.2(11)	5.1(10)	6.1(11)
C00P	51.3(17)	36.1(15)	25.5(12)	-5.2(11)	-3.7(11)	15.5(13)
C00Q	35.2(13)	39.5(15)	23.2(11)	-3.9(11)	-2.7(9)	8.6(12)
C00R	40.9(15)	42.7(17)	41.0(15)	-7.8(13)	-0.4(12)	16.8(13)
C00S	56.1(17)	40.3(17)	27.4(13)	8.5(12)	-13.8(12)	-12.9(14)
C00T	39.3(14)	48.0(18)	32.7(13)	-2.5(13)	-8.9(11)	16.2(14)
C00U	77(2)	32.0(15)	15.2(10)	-2.2(11)	4.8(12)	-11.6(15)
C00V	47.8(16)	60(2)	33.1(14)	7.8(14)	19.7(12)	23.4(17)
C00W	61.5(19)	46.8(19)	24.2(12)	-4.7(12)	5.9(12)	26.1(16)
C00X	42.5(15)	39.6(16)	35.2(14)	4.4(13)	-4.3(11)	-14.6(13)
C00Y	65.4(19)	28.2(14)	22.7(12)	-2.9(11)	5.0(12)	-15.3(14)
C00Z	59.9(19)	38.8(18)	52.6(18)	-1.6(15)	-16.0(15)	-16.9(16)
C010	61(2)	52(2)	40.0(15)	1.8(14)	-16.9(14)	-24.9(17)
C011	72(2)	57(2)	32.8(14)	9.7(14)	-22.0(14)	-21.5(19)

Table S6 Bond Lengths for 3a (CCDC 1955097).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C008	1.227(3)	C00E	C00N	1.403(3)
O002	C00C	1.322(3)	C00F	C00L	1.392(3)
O002	C00Z	1.448(4)	C00G	C00H	1.531(3)
O003	C00L	1.369(3)	C00G	C00K	1.397(4)
O004	C00C	1.222(3)	C00G	C00M	1.390(3)
O005	C00N	1.359(3)	C00I	C00J	1.391(4)
N006	C009	1.383(3)	C00I	C00X	1.397(4)
N006	C00D	1.371(3)	C00J	C00S	1.398(3)
N007	C00H	1.476(3)	C00K	C00P	1.388(4)
N007	C00I	1.385(3)	C00L	C00Y	1.396(3)
C008	C00H	1.562(3)	C00M	C00V	1.402(4)
C008	C00J	1.449(3)	C00N	C00U	1.394(4)
C009	C00A	1.360(3)	C00O	C00R	1.378(4)
C009	C00H	1.511(3)	C00P	C00W	1.385(4)
C00A	C00B	1.432(3)	C00Q	C00T	1.380(4)
C00A	C00F	1.488(3)	C00R	C00T	1.402(4)
C00B	C00D	1.409(3)	C00S	C011	1.369(4)
C00B	C00O	1.400(4)	C00U	C00Y	1.366(4)
C00C	C00E	1.483(3)	C00V	C00W	1.376(5)
C00D	C00Q	1.394(3)	C00X	C010	1.375(4)
C00E	C00F	1.422(3)	C010	C011	1.397(5)

Table S7 Bond Angles for 3a (CCDC 1955097).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00C	O002	C00Z	115.7(2)	N007	C00H	C00G	112.02(18)
C00D	N006	C009	108.58(18)	C009	C00H	C008	112.45(18)
C00I	N007	C00H	109.76(19)	C009	C00H	C00G	113.22(18)
O001	C008	C00H	123.7(2)	C00G	C00H	C008	106.97(18)
O001	C008	C00J	129.3(2)	N007	C00I	C00J	112.4(2)
C00J	C008	C00H	107.0(2)	N007	C00I	C00X	127.1(2)
N006	C009	C00H	121.05(18)	C00J	C00I	C00X	120.5(2)
C00A	C009	N006	109.71(19)	C00I	C00J	C008	107.8(2)
C00A	C009	C00H	128.2(2)	C00I	C00J	C00S	121.4(2)
C009	C00A	C00B	107.07(19)	C00S	C00J	C008	130.5(2)
C009	C00A	C00F	126.0(2)	C00P	C00K	C00G	120.7(2)
C00B	C00A	C00F	127.0(2)	O003	C00L	C00F	117.9(2)
C00D	C00B	C00A	106.7(2)	O003	C00L	C00Y	121.4(2)
C00O	C00B	C00A	133.9(2)	C00F	C00L	C00Y	120.6(2)
C00O	C00B	C00D	119.3(2)	C00G	C00M	C00V	119.3(3)
O002	C00C	C00E	115.6(2)	O005	C00N	C00E	123.5(2)
O004	C00C	O002	121.4(2)	O005	C00N	C00U	116.6(2)
O004	C00C	C00E	123.0(2)	C00U	C00N	C00E	119.9(2)
N006	C00D	C00B	107.92(19)	C00R	C00O	C00B	118.8(2)
N006	C00D	C00Q	130.1(2)	C00W	C00P	C00K	120.1(3)
C00Q	C00D	C00B	121.9(2)	C00T	C00Q	C00D	117.4(2)
C00F	C00E	C00C	124.1(2)	C00O	C00R	C00T	121.1(3)
C00N	C00E	C00C	116.3(2)	C011	C00S	C00J	118.1(3)
C00N	C00E	C00F	119.6(2)	C00Q	C00T	C00R	121.4(2)
C00E	C00F	C00A	123.1(2)	C00Y	C00U	C00N	120.4(2)
C00L	C00F	C00A	118.0(2)	C00W	C00V	C00M	121.3(3)
C00L	C00F	C00E	118.8(2)	C00V	C00W	C00P	119.4(3)
C00K	C00G	C00H	119.4(2)	C010	C00X	C00I	117.0(3)
C00M	C00G	C00H	121.4(2)	C00U	C00Y	C00L	120.7(3)
C00M	C00G	C00K	119.1(2)	C00X	C010	C011	123.0(3)
N007	C00H	C008	102.55(17)	C00S	C011	C010	120.0(3)
N007	C00H	C009	109.1(2)				

Table S8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3a (CCDC 1955097).

Atom	*x*	*y*	*z*	U(eq)
H003	4782	7644	4602	49
H005	2030	4199	7551	64
H006	3020	5082	114	28
H007	6266	6010	2179	34
H00K	3434	3367	1338	35
H00M	7372	4728	1047	42
H00O	165	7123	3345	37
H00P	4070	2287	-302	46
H00Q	496	5990	-1188	40
H00R	-1497	7638	1508	50
H00S	6509	3989	6629	51
H00T	-1369	7057	-720	49
H00U	4011	6106	8402	50
H00V	7990	3629	-595	55
H00W	6347	2428	-1289	53
H00X	8000	6718	4404	48
H00Y	4765	7204	6879	46
H00A	-598	3649	2469	78
H00B	-943	3478	4014	78
H00C	496	3025	3459	78
H010	8967	6349	6644	63
H011	8282	4997	7744	67

13. References

1 Y.-H. Chen, D.-J. Cheng, J. Zhang, Y. Wang, X.-Y. Liu and B. Tan, *J. Am. Chem. Soc.*, 2015, **137**, 15062.

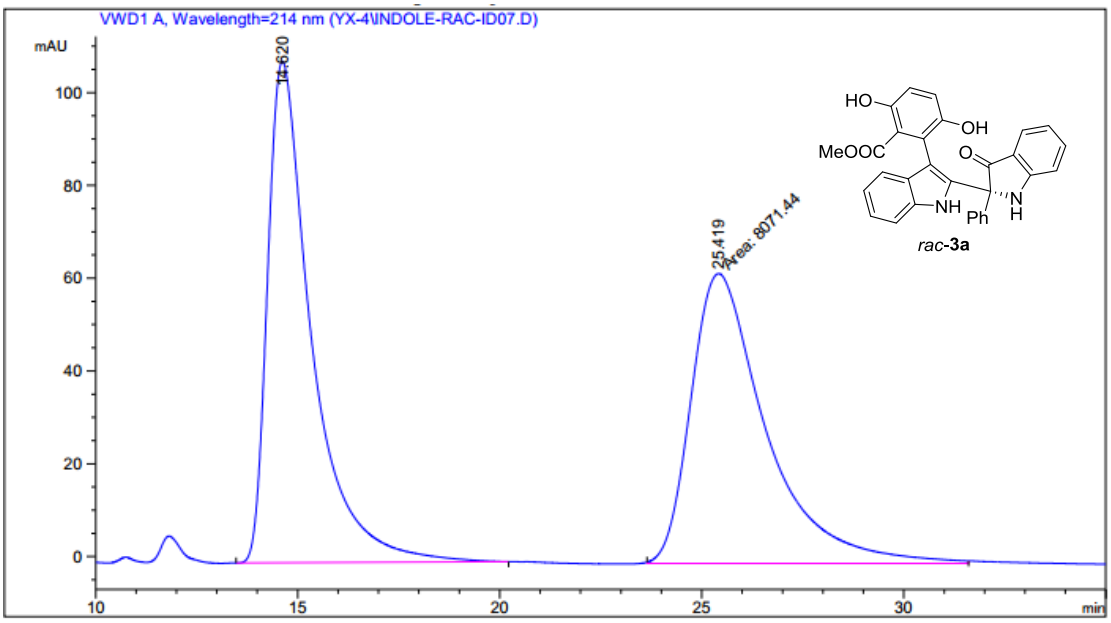
2 D.-L. Lu, Y.-H. Chen, S.-H. Xiang, P.-Y. Yu, B. Tan and S.-Y. Li, *Org. Lett.*, 2019, **21**, 6000.

3 J.-S. Li, Y.-J. Liu, G.-W. Zhang and J.-A. Ma, *Org. Lett.*, 2017, **19**, 6364.

4 Y.-H. Chen, H.-H. Li, X. Zhang, S.-H. Xiang, S.-Y. Li and B. Tan, *Angew. Chem., Int. Ed.*, 2020, **59**, 11347.

5 Li, Y.-J. Liu, S. Li and J.-A. Ma, *Chem. Commun.*, 2018, **54**, 9151.

14. HPLC analysis of products 3a-3z, 3aa-3ak, 6, 9, 10, 11



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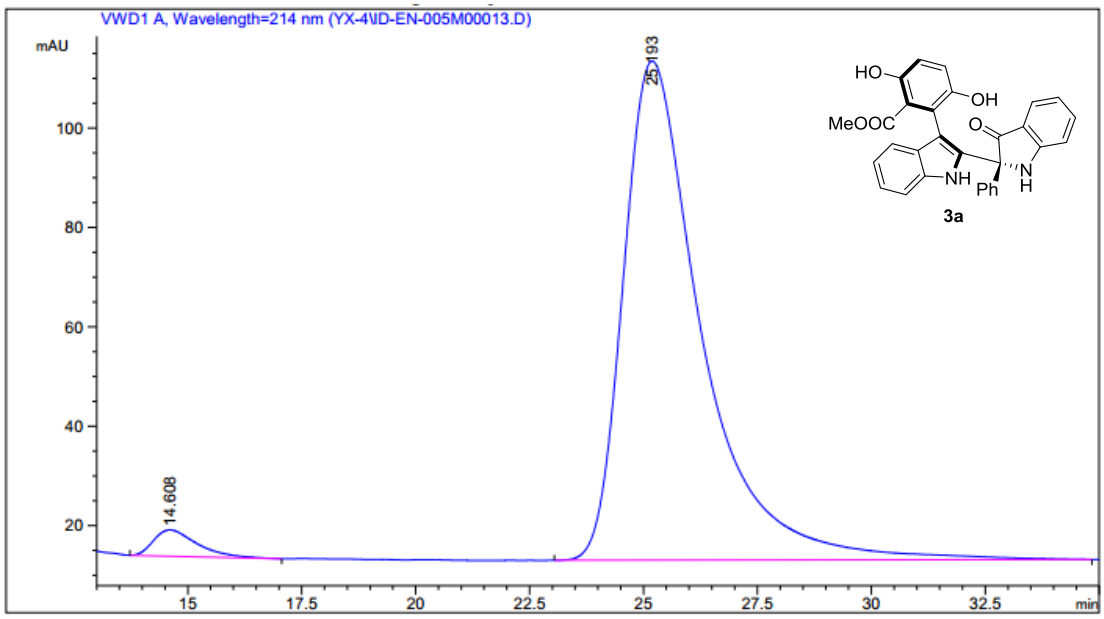

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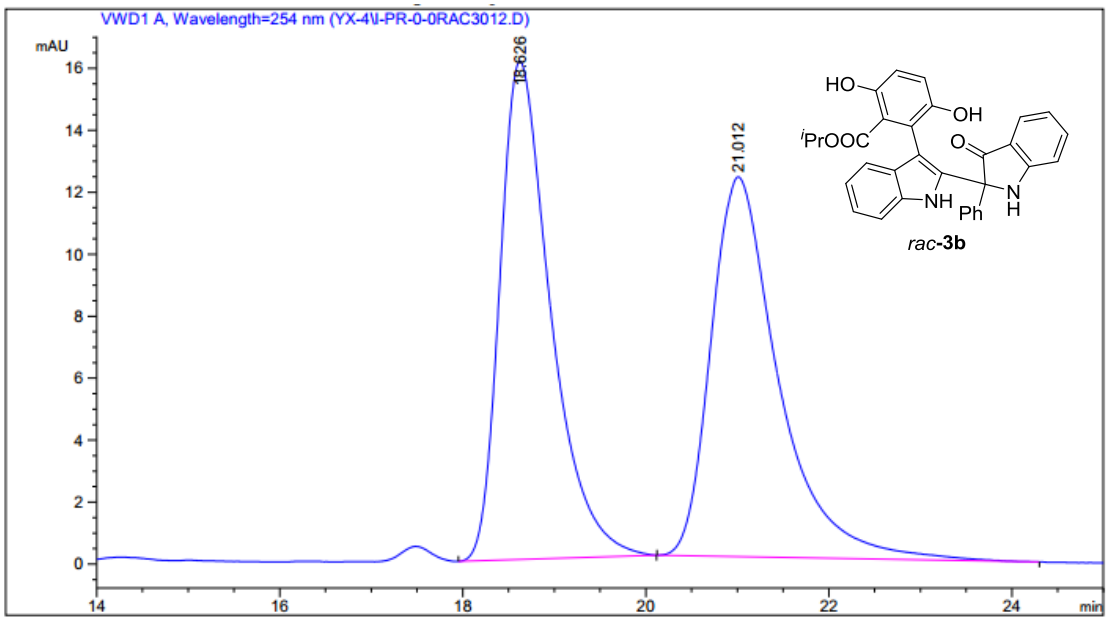
2	25.193	BB	1.7713	1.20502e4	100.41355	97.1766



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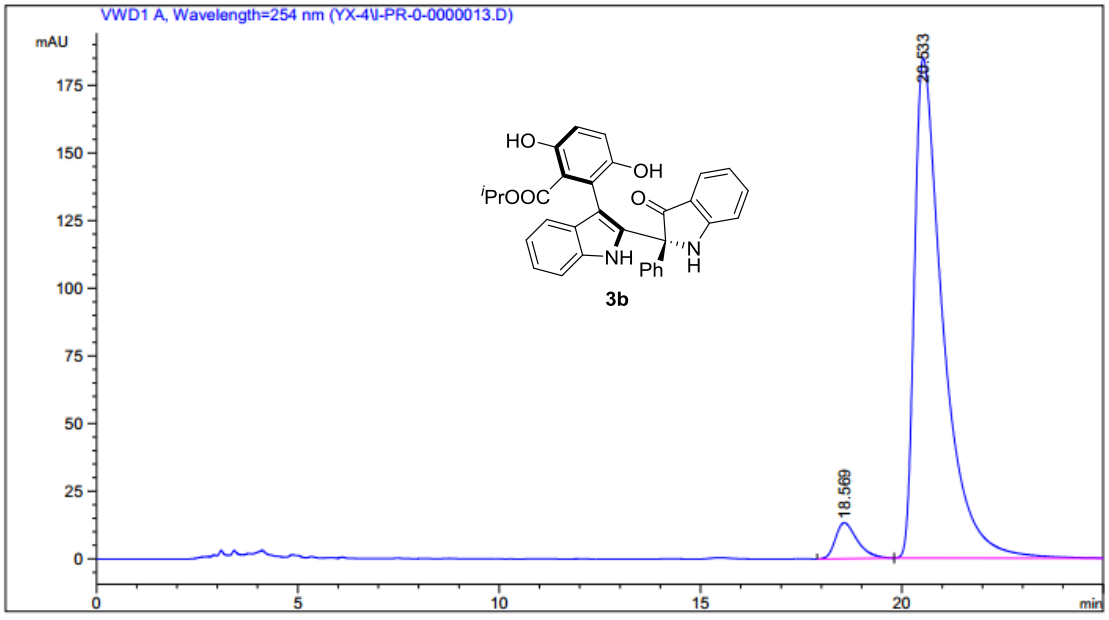
1	18.626	BB	0.5783	618.25549	16.07358	49.5148
2	21.012	BB	0.7646	630.37262	12.25510	50.4852



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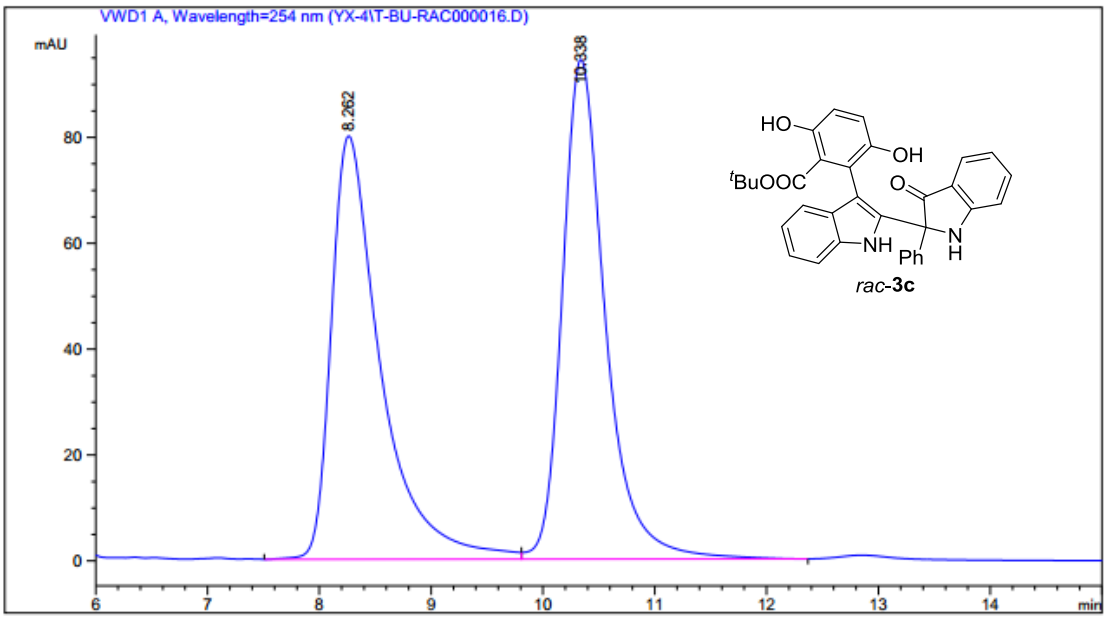
1	18.569	BB	0.5619	498.02985	13.26279	5.1792
2	20.533	BB	0.7211	9117.87695	184.84509	94.8208



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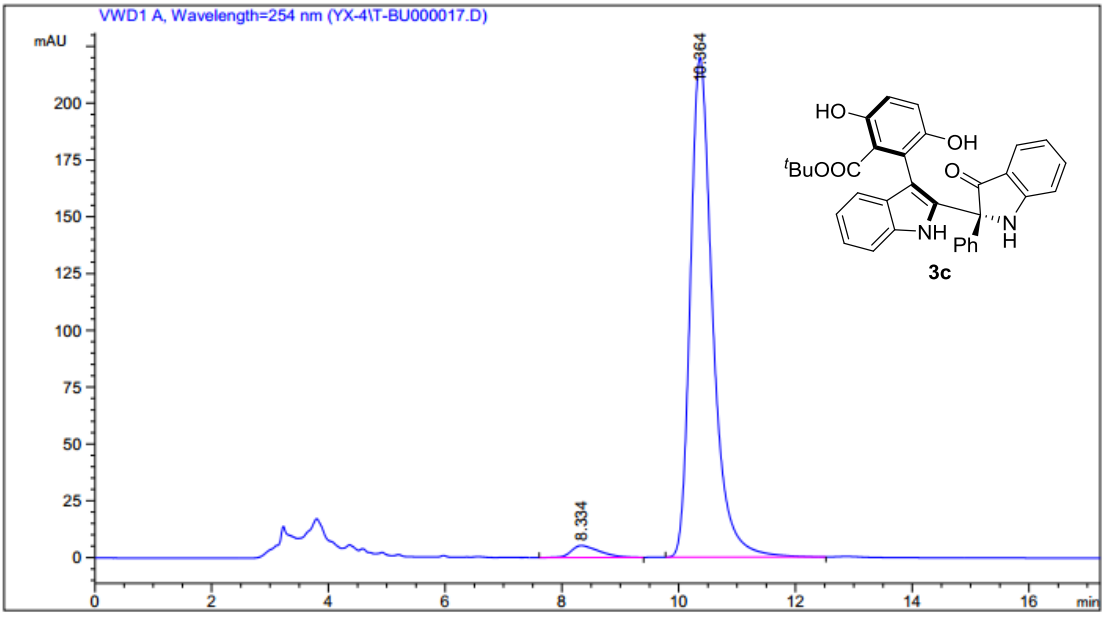
1	8.262	BV	0.4484	2453.38403	79.93375	49.2724
2	10.338	VB	0.4041	2525.84619	94.32701	50.7276



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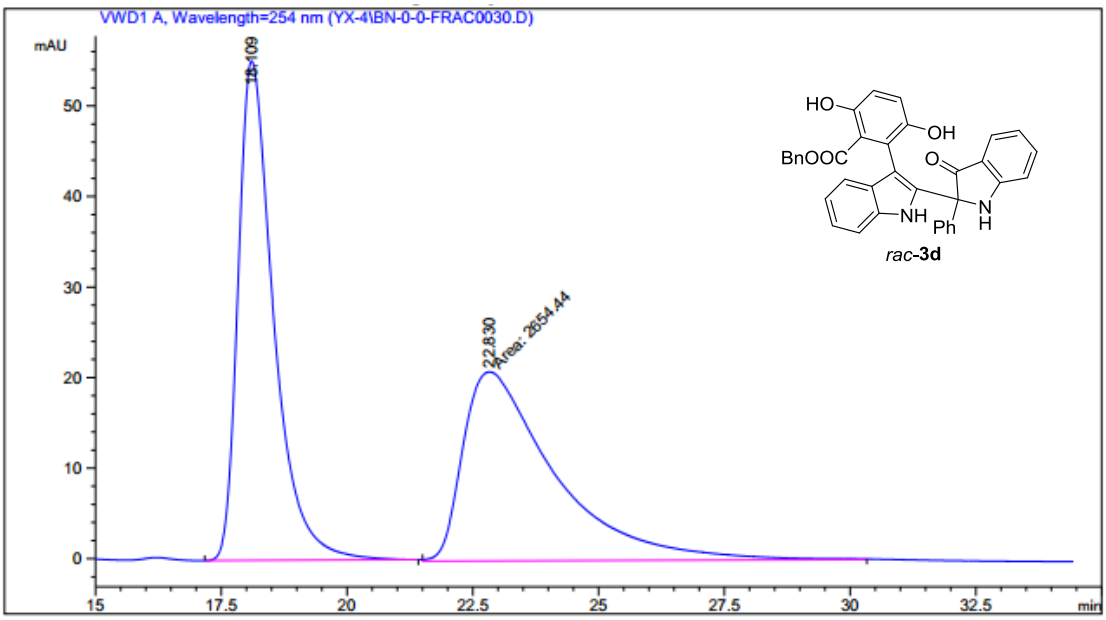
1	8.334	BB	0.4711	175.85371	5.28680	2.9228
2	10.364	BB	0.4031	5840.85254	219.86156	97.0772



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1	18.109	BB	0.7396	2711.58276	55.15127	50.5325
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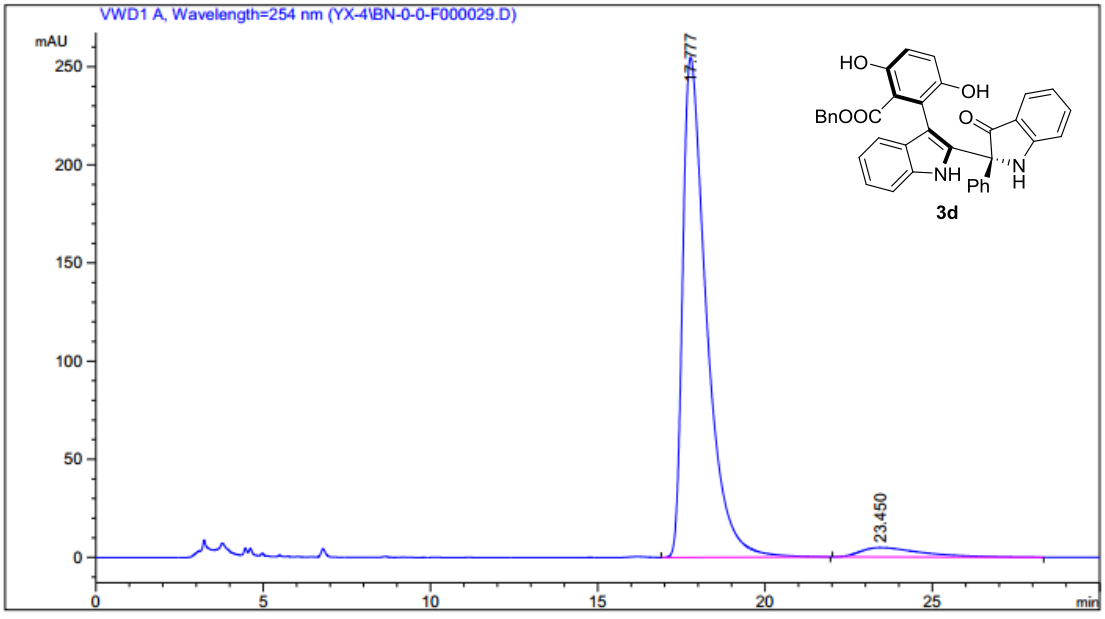

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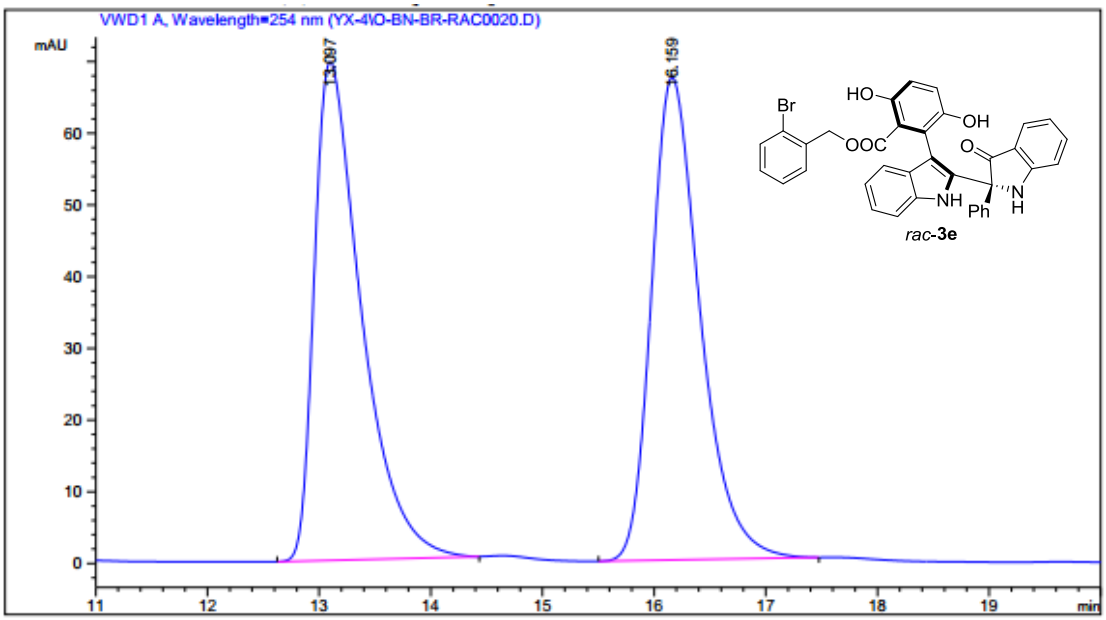

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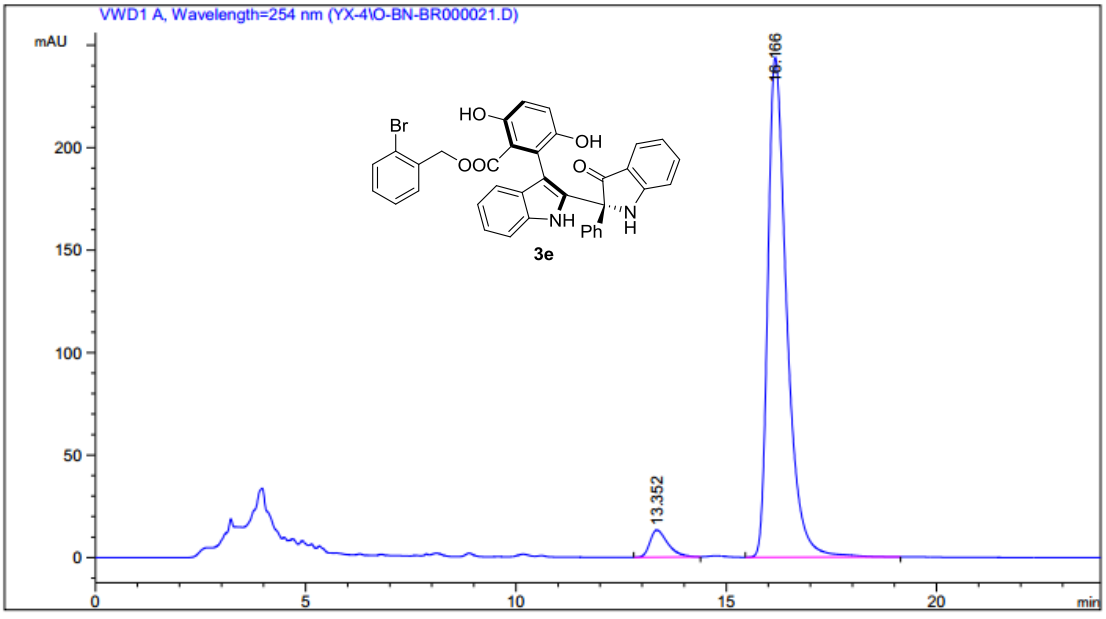
2	16.159	BB	0.4614	2040.88928	67.33466	50.0696



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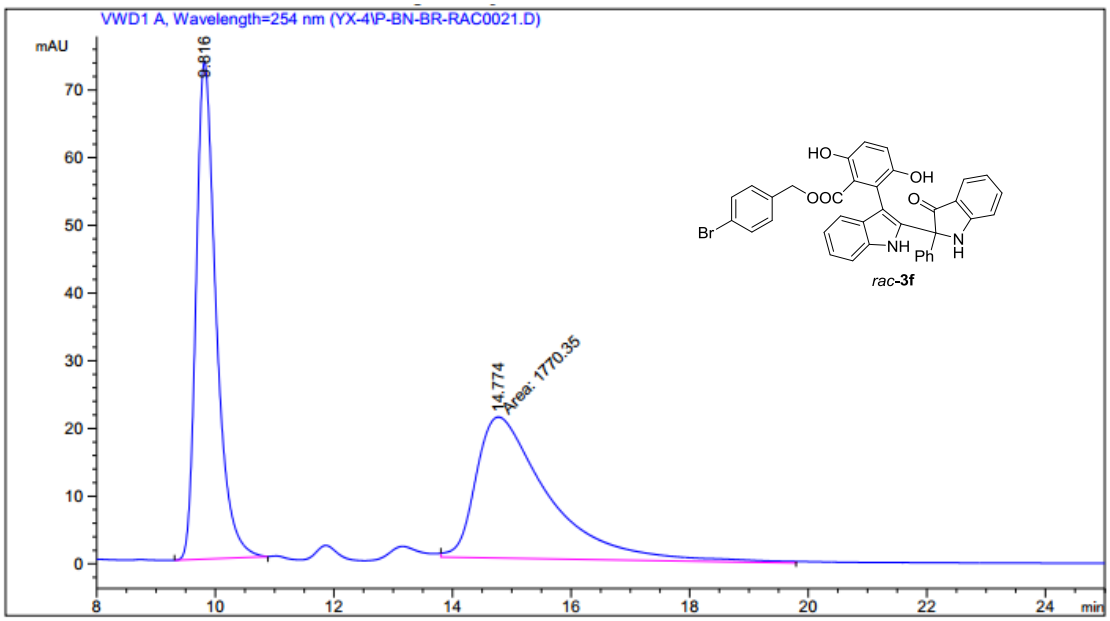
2	16.166	BB	0.4706	7584.63574	243.84946	95.1321



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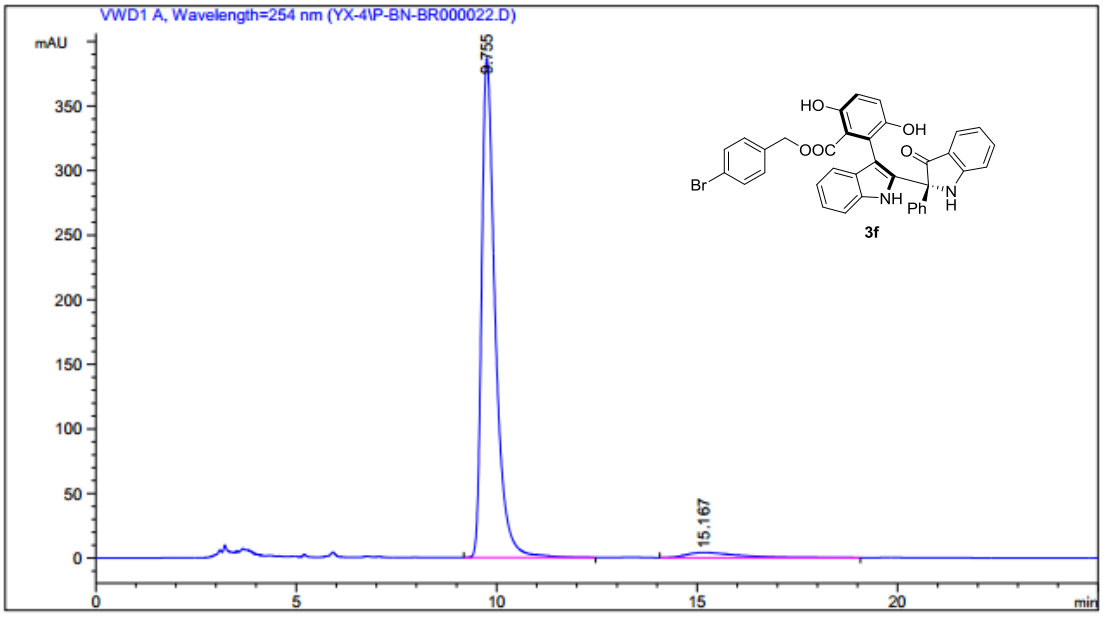
1	9.816	BB	0.3546	1720.40723	73.51584	49.2847
2	14.774	MM	1.4158	1770.34668	20.83963	50.7153



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1	9.755	BB	0.3528	9083.71094	386.54514	96.1341
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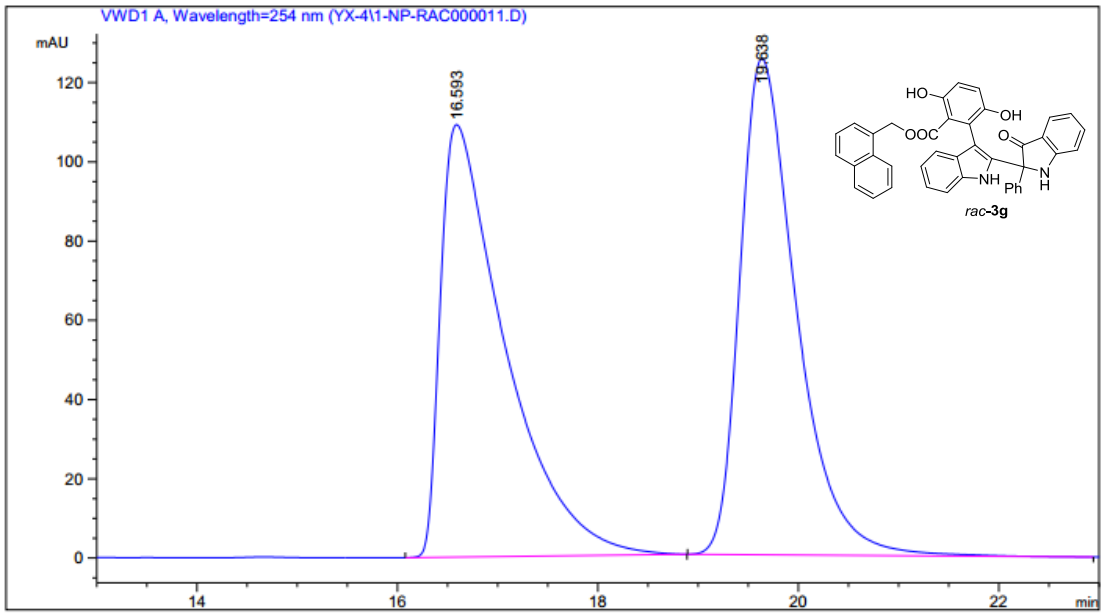

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1	16.593	BB	0.6411	4880.74268	109.13976	49.8278
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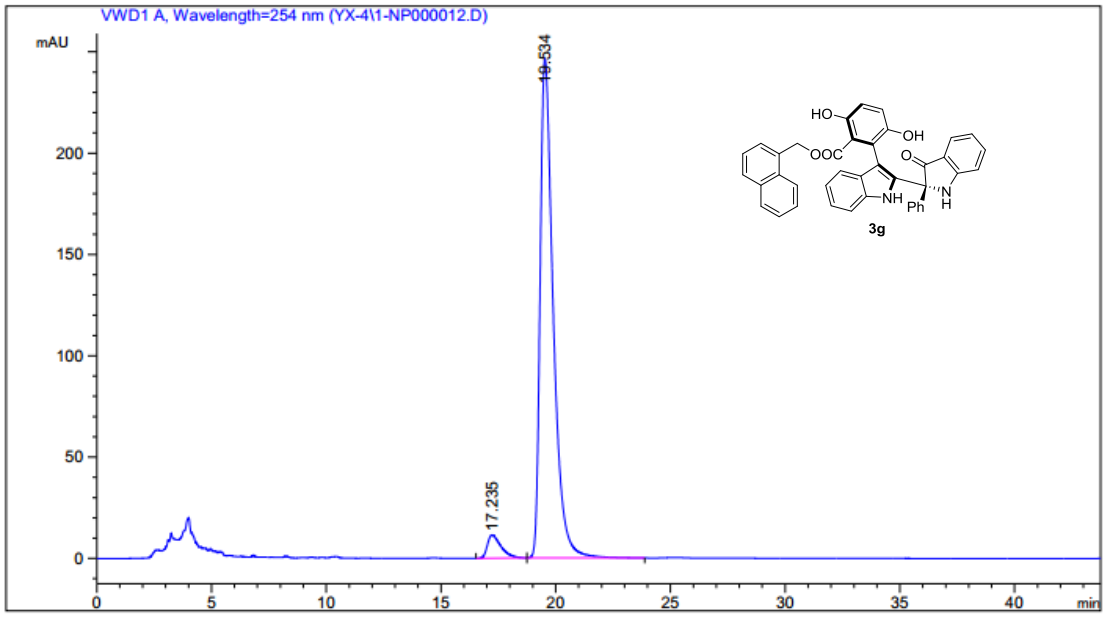

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1	17.235	BB	0.6081	472.34323	11.51522	4.6166
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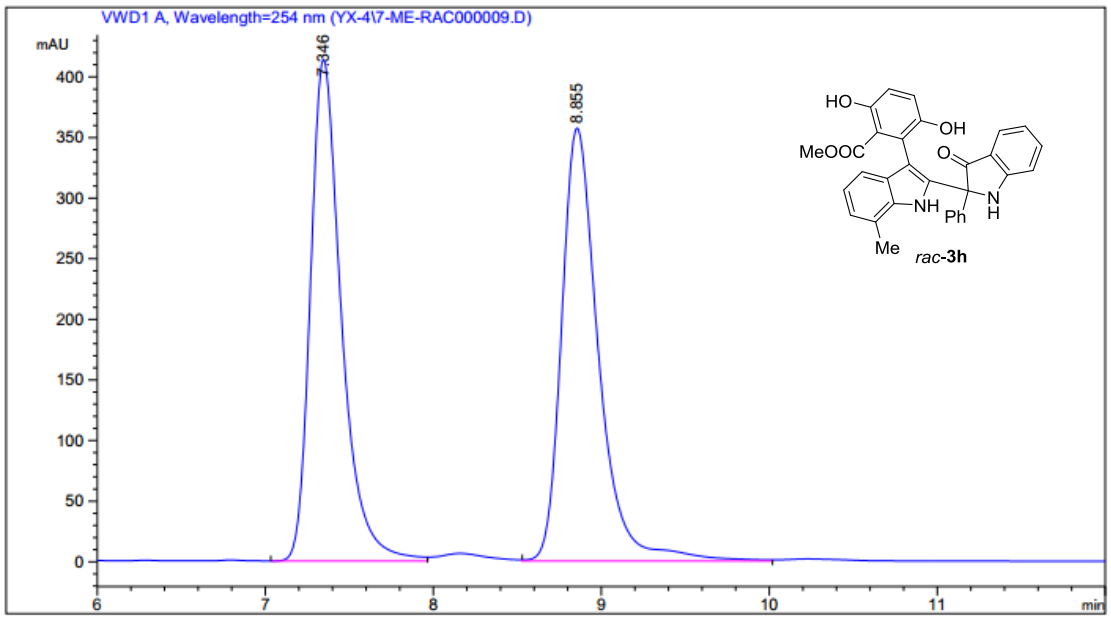

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1	7.346	BV	0.1935	5314.51416	413.74097	49.2268
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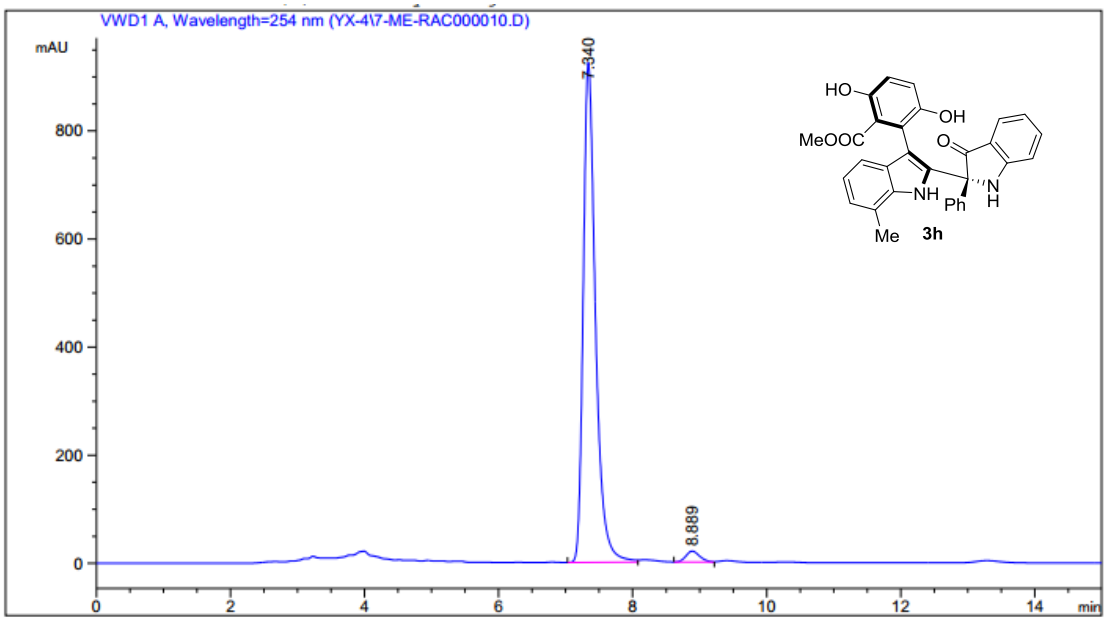

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1	7.340	BV	0.1918	1.17408e4	924.57397	97.5974
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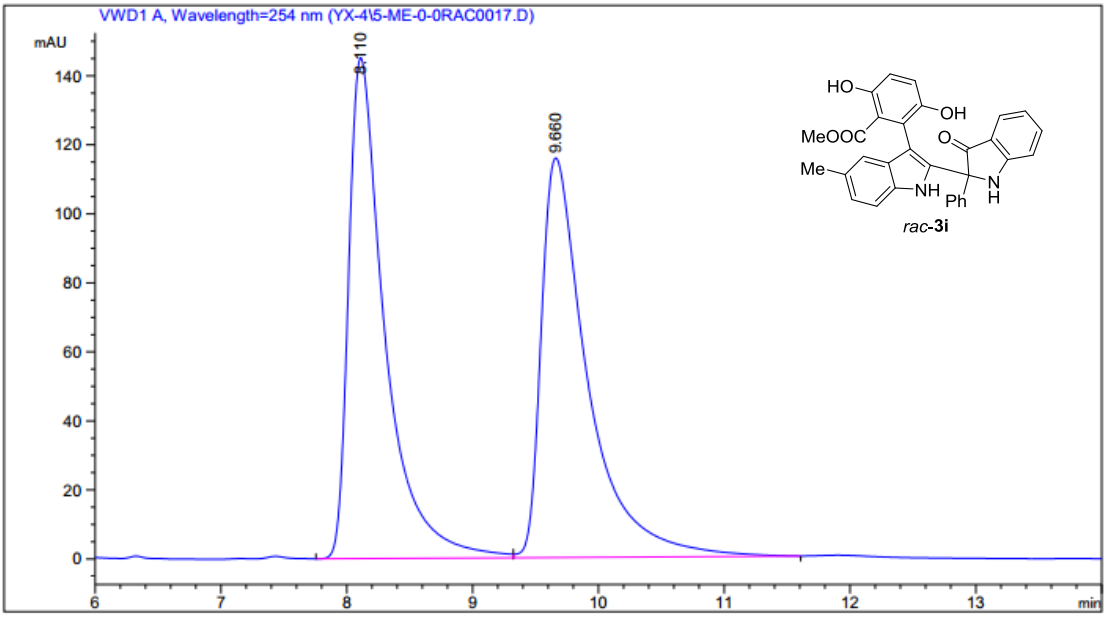

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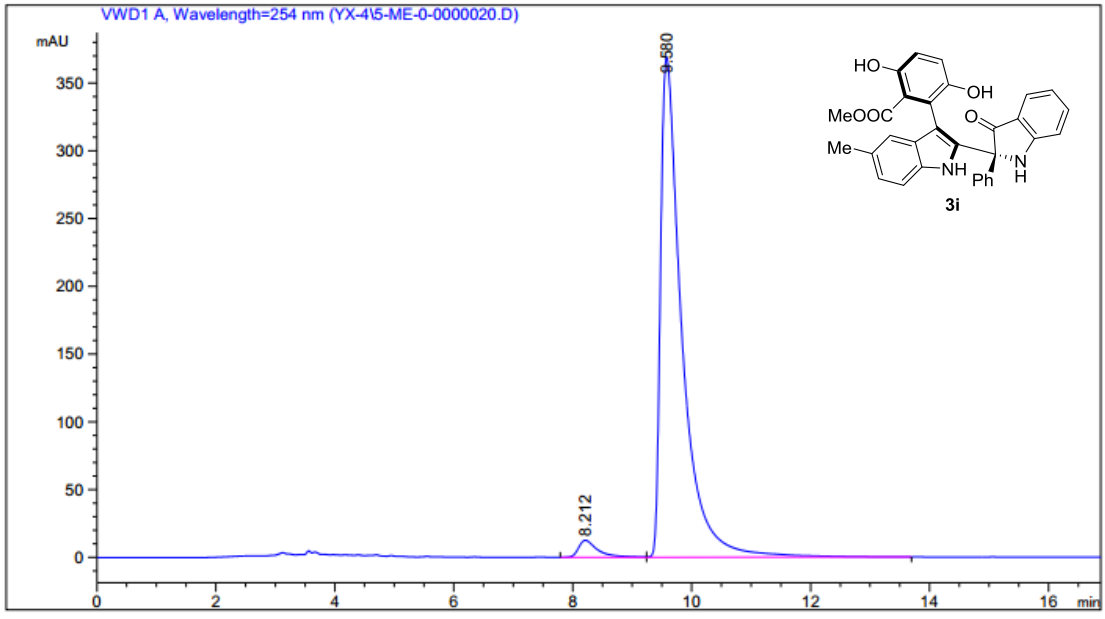
1	8.110	BV	0.2942	2917.03638	145.12740	49.5773
2	9.660	VB	0.3748	2966.78101	115.74433	50.4227



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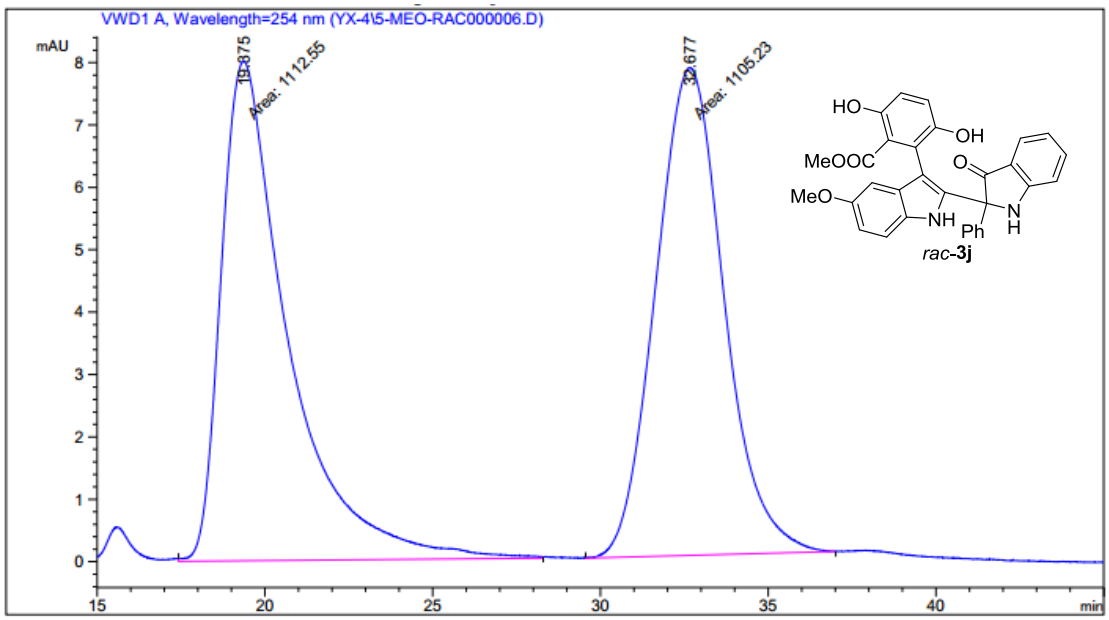
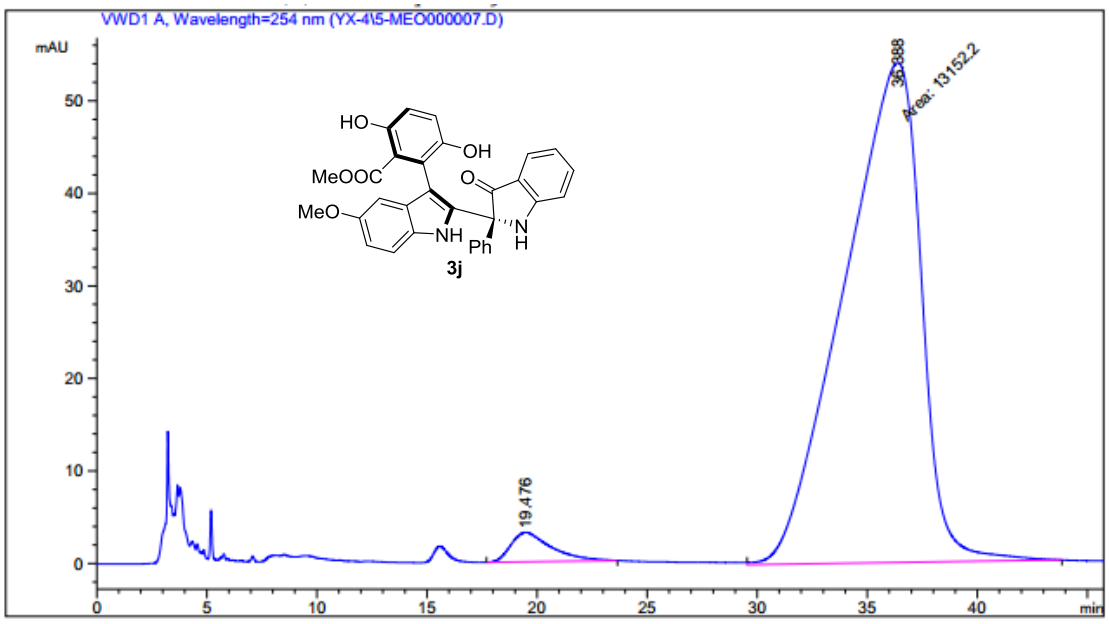
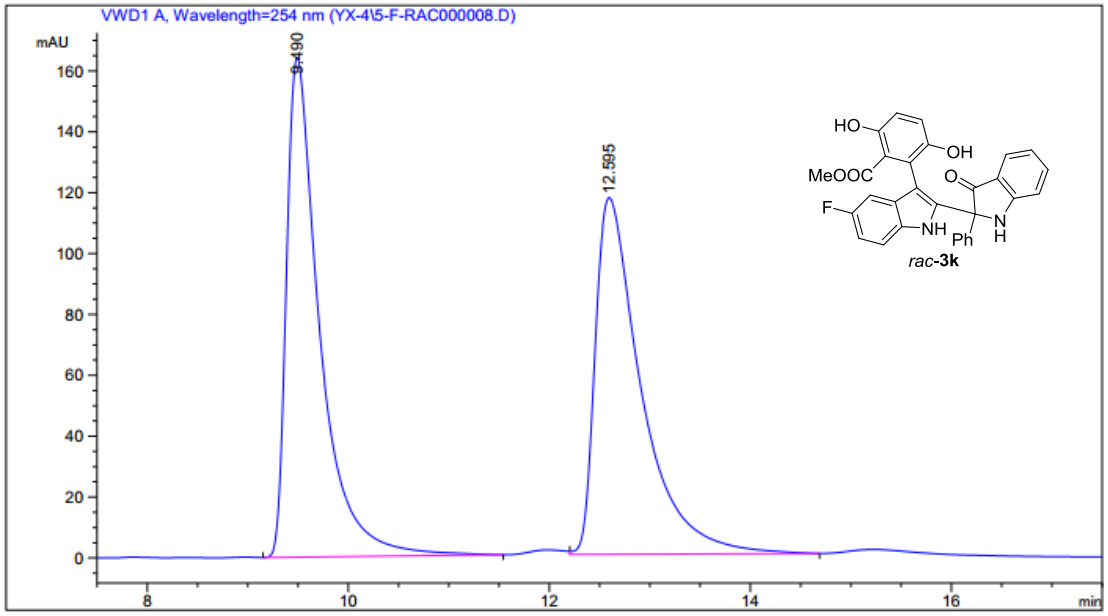
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.212	BV	0.3295	282.14917	12.53846	2.9630
2	9.580	VB	0.3650	9240.33496	368.91638	97.0370



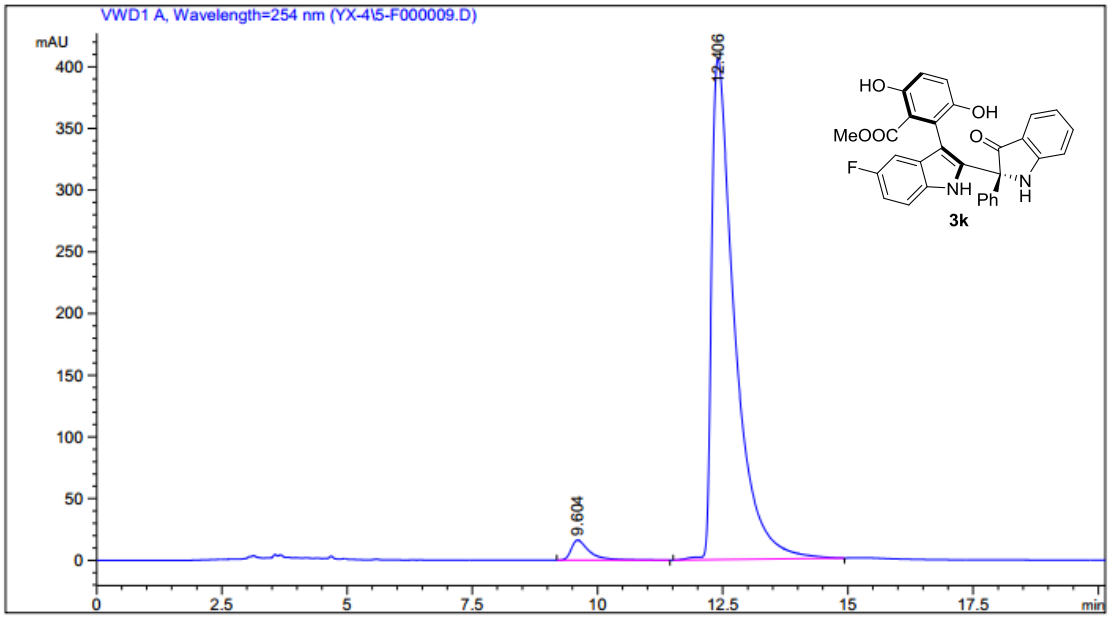
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.375	MM	2.3161	1112.55383	8.00603	50.1651
2	32.677	MM	2.3569	1105.22900	7.81568	49.8349



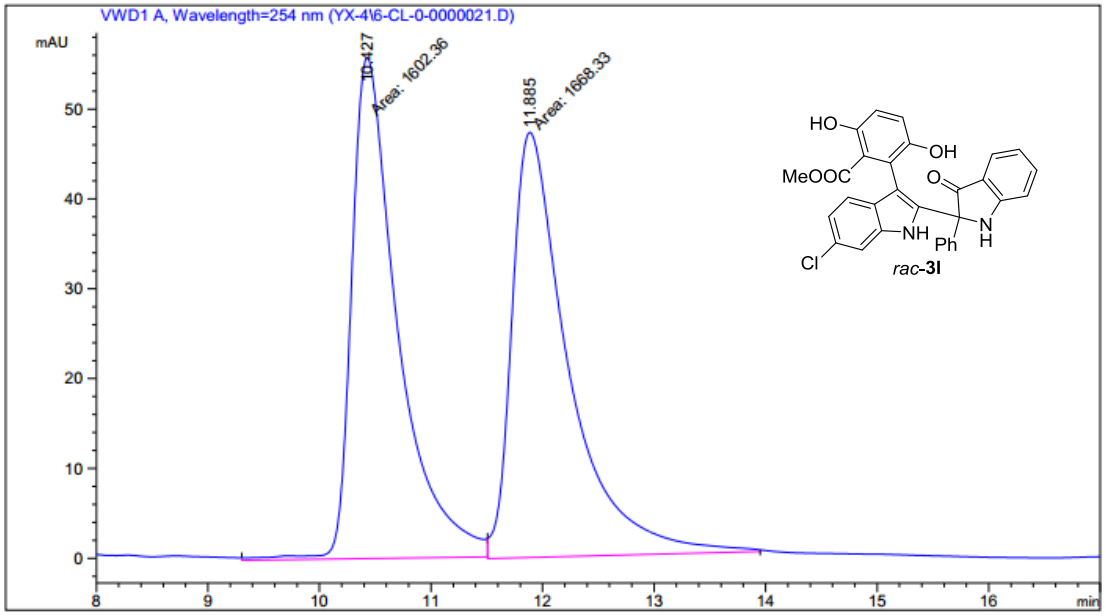
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.476	BB	1.5186	404.68591	3.17596	2.9920
2	36.388	MM	4.0531	1.31211e4	53.95518	97.0080



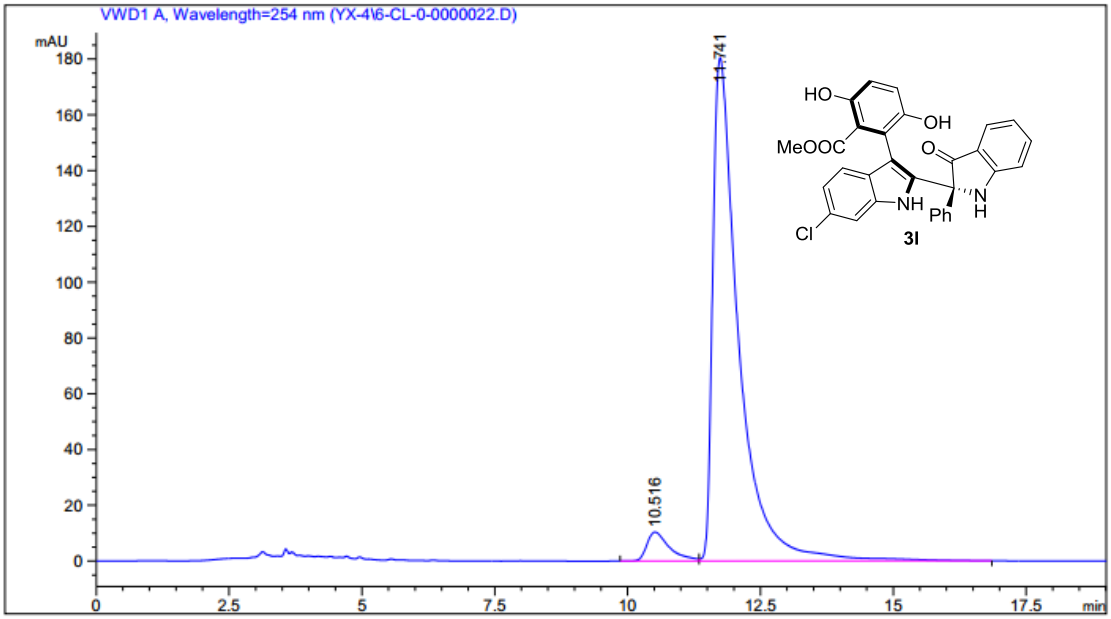
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.490	BB	0.3377	3767.04199	164.10654	50.3075
2	12.595	VB	0.4667	3720.99438	117.14586	49.6925



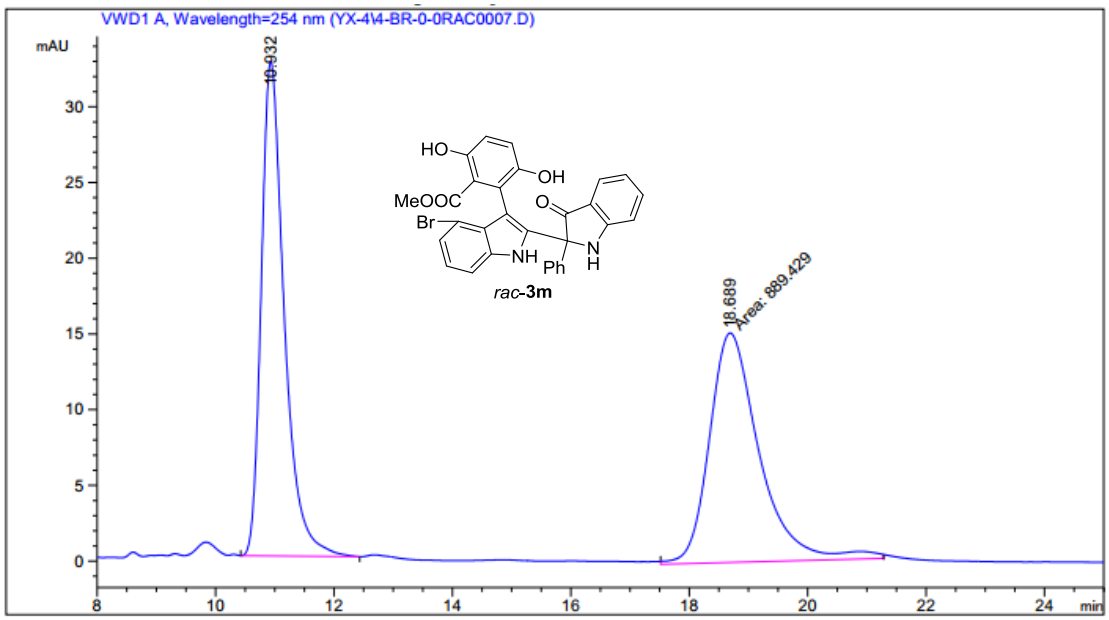
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.604	BB	0.3712	409.11880	16.23581	3.0554
2	12.406	BB	0.4688	1.29807e4	406.33759	96.9446



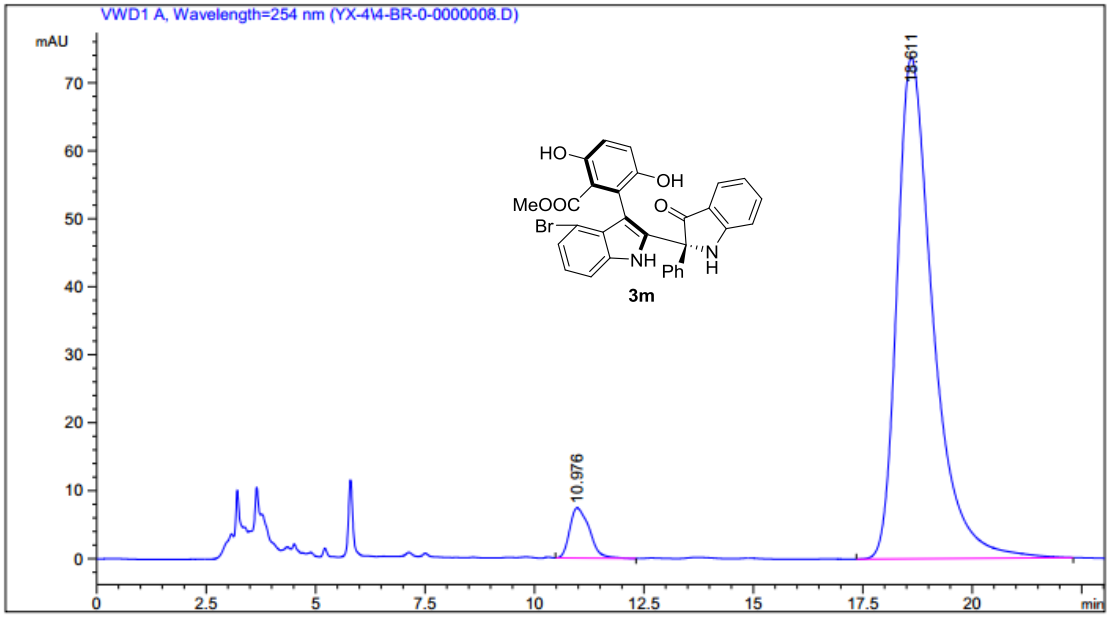
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.427	MM	0.4790	1602.35999	55.75388	48.9915
2	11.885	MM	0.5876	1668.33179	47.32104	51.0085



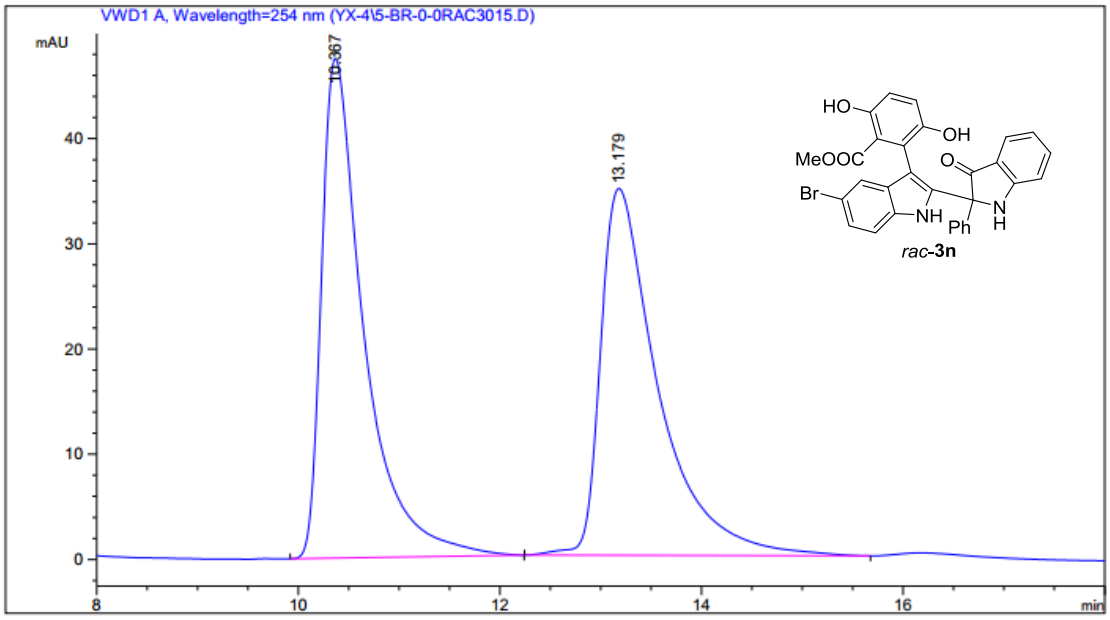
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.516	BV	0.4385	306.84308	10.36574	4.7630
2	11.741	VB	0.4942	6135.34326	180.45930	95.2370



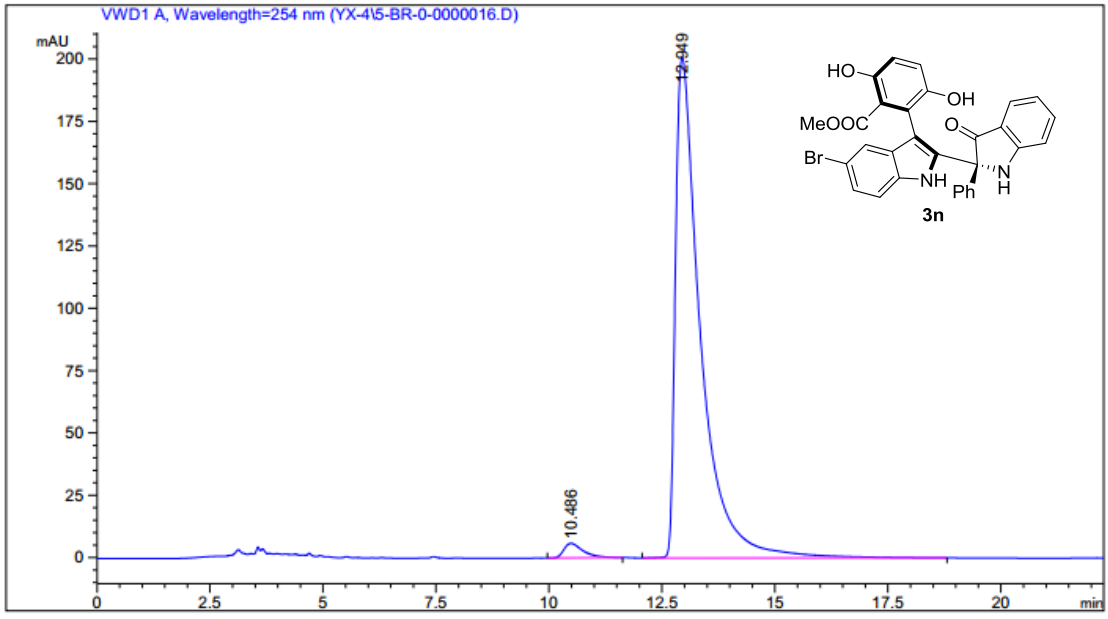
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.932	BB	0.4058	879.24554	32.66433	49.7121
2	18.689	MM	0.9782	889.42932	15.15395	50.2879



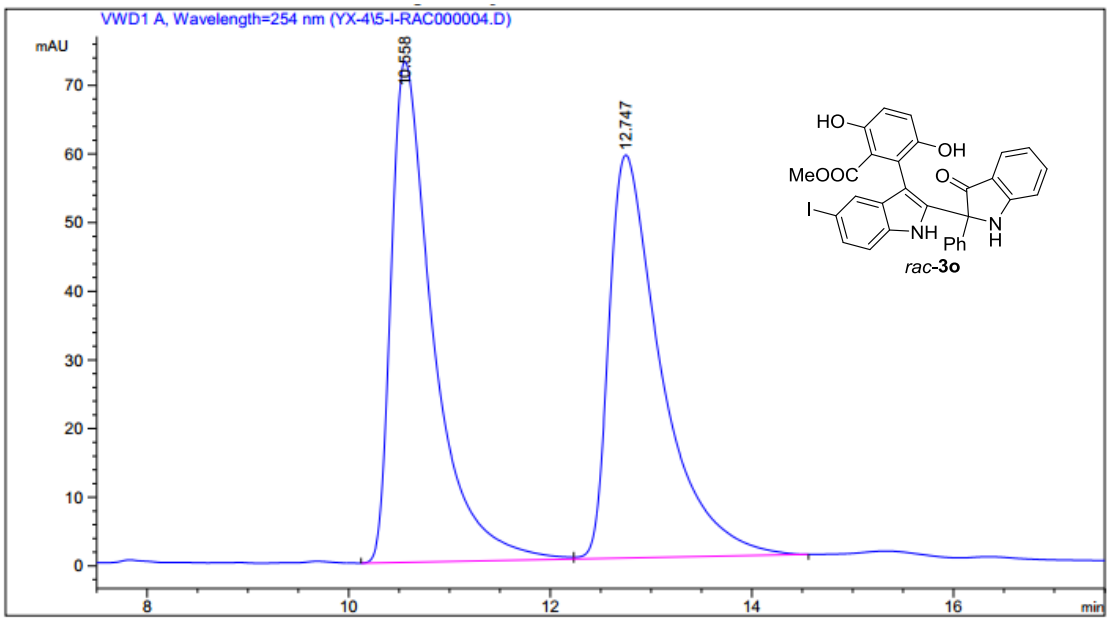
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.976	BB	0.4492	230.39452	7.39839	5.1928
2	18.611	BB	0.8596	4206.39307	73.68790	94.8072



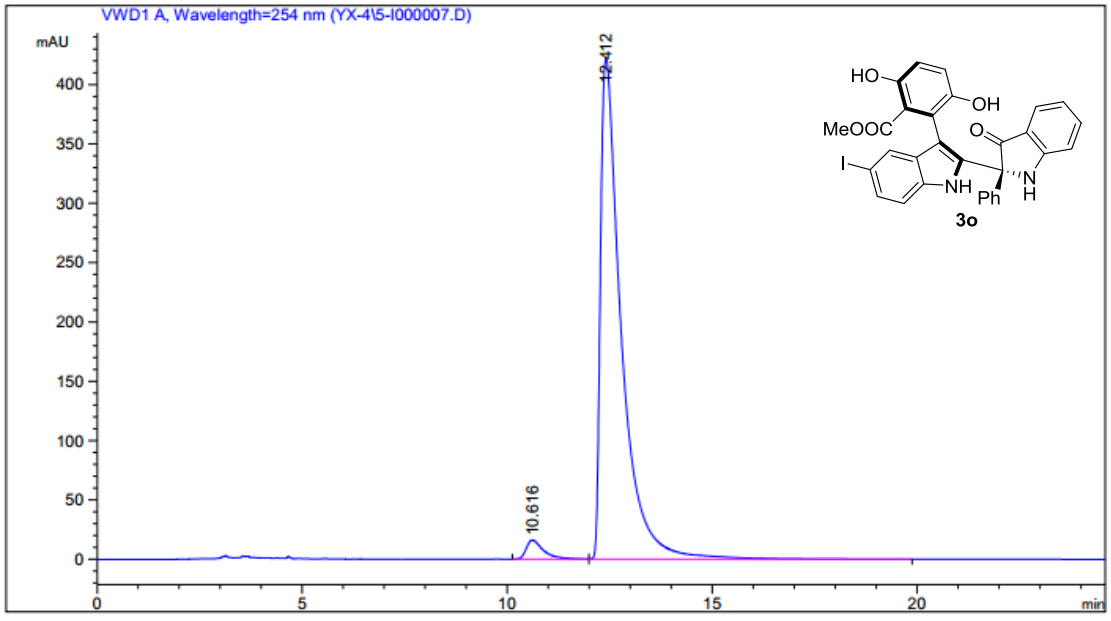
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.367	BB	0.4279	1385.60608	47.46967	50.0044
2	13.179	BB	0.5817	1385.36426	34.85355	49.9956



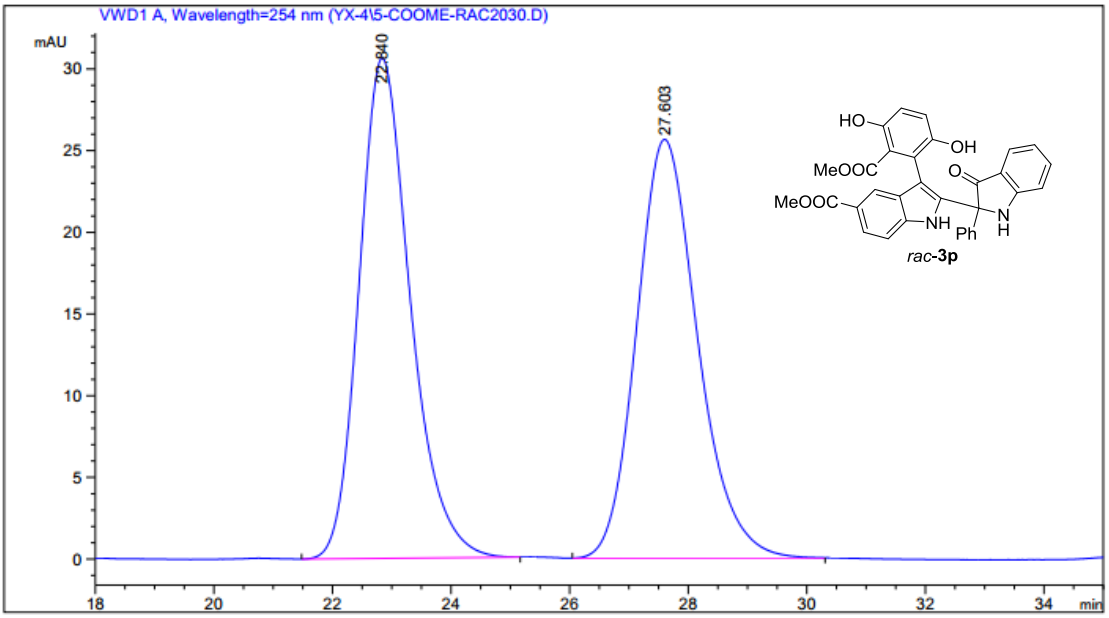
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.486	BB	0.4396	172.86182	5.87121	2.1796
2	12.949	BB	0.5600	7758.08789	200.77359	97.8204



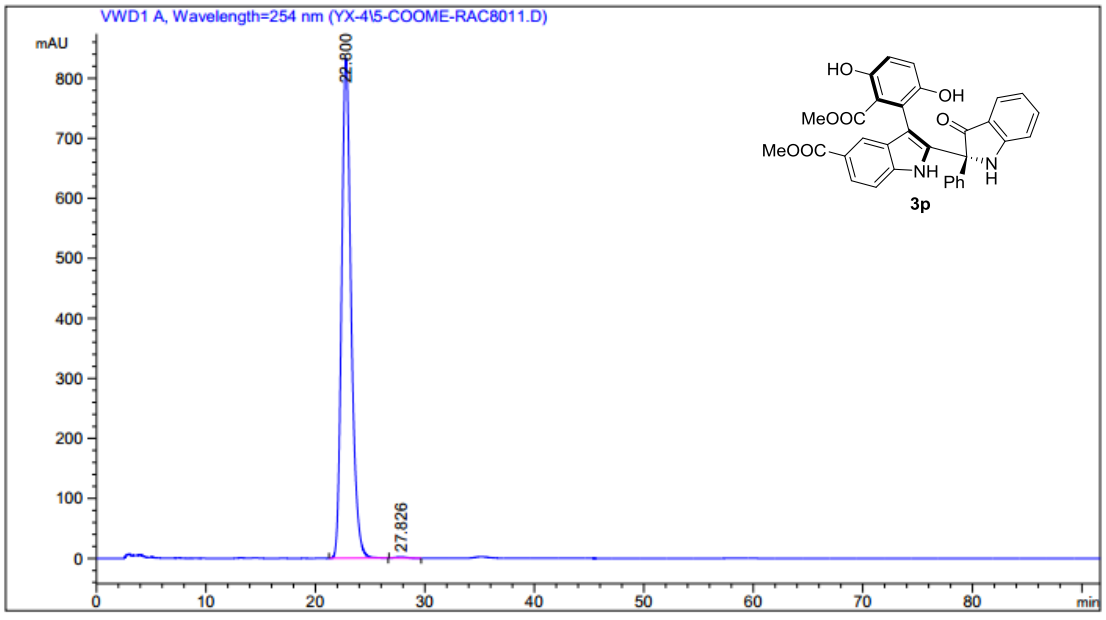
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.558	BV	0.4256	2105.87866	72.95094	50.0765
2	12.747	VB	0.5266	2099.44189	58.67856	49.9235



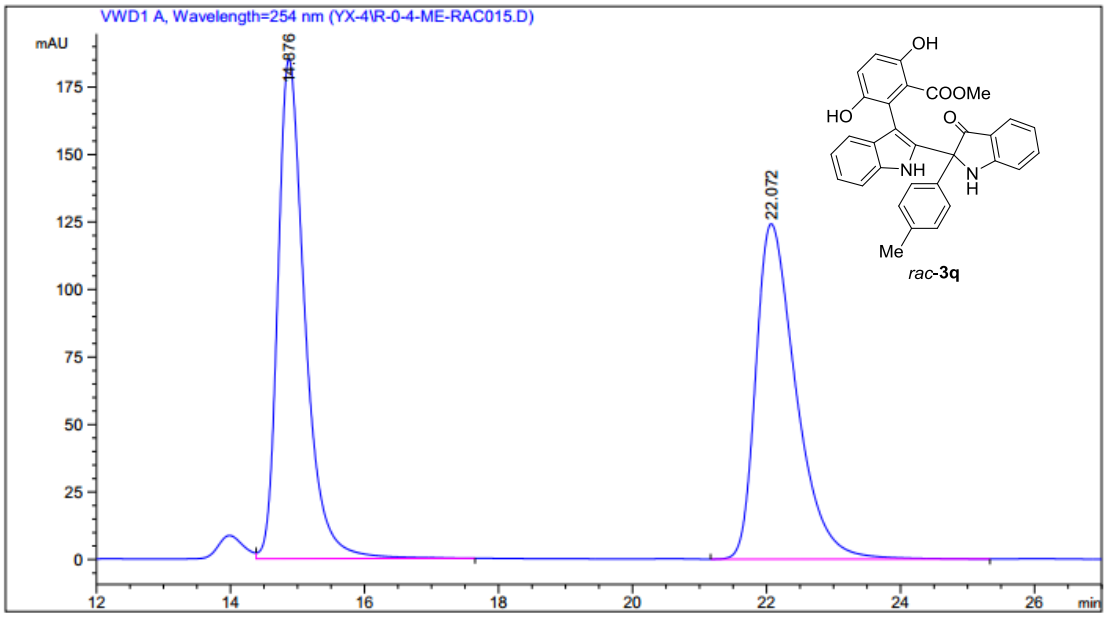
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.616	BV	0.4362	473.45621	16.03344	3.0730
2	12.412	VB	0.5144	1.49334e4	422.34329	96.9270



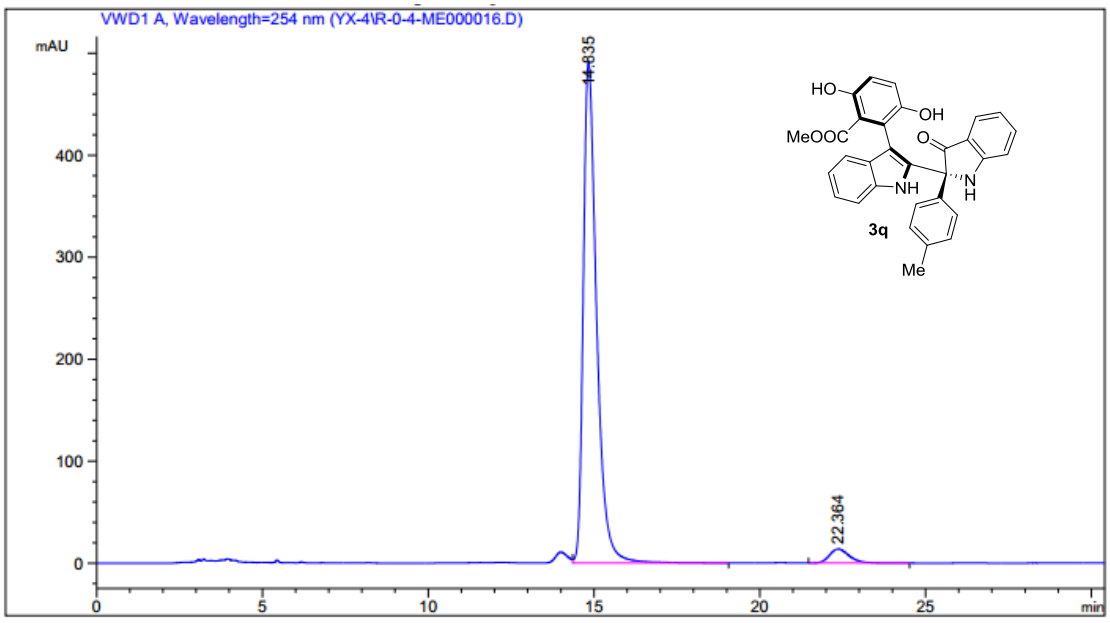
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.840	BB	0.9072	1837.71582	30.61035	50.0948
2	27.603	BB	1.0594	1830.75916	25.61953	49.9052



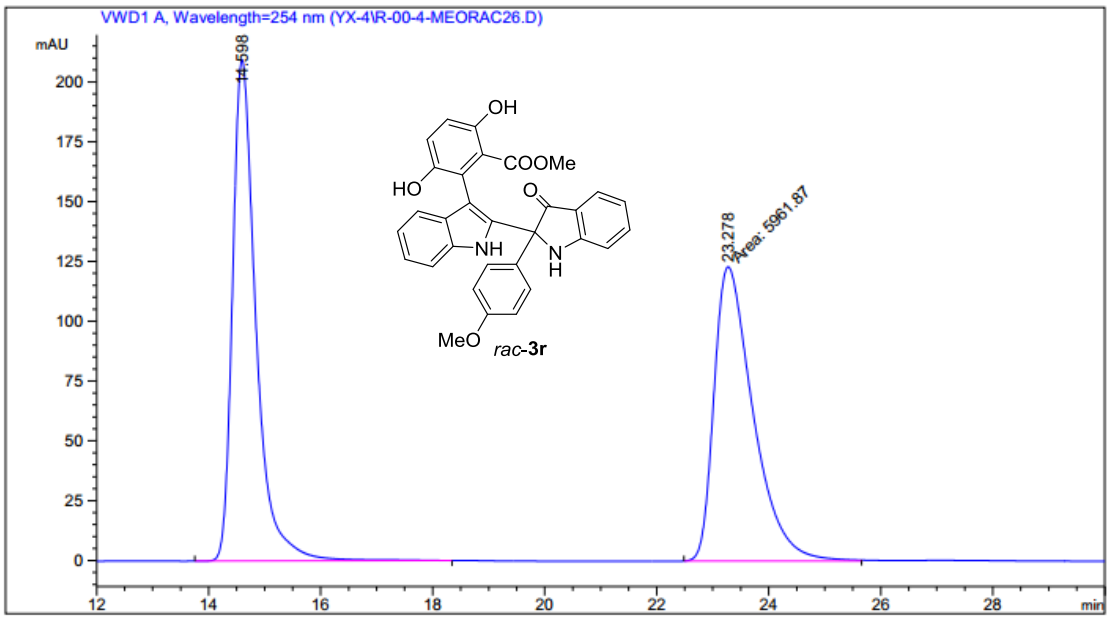
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.800	BB	0.9189	5.02914e4	832.37427	99.7376
2	27.826	BB	0.8130	132.33586	1.95135	0.2624



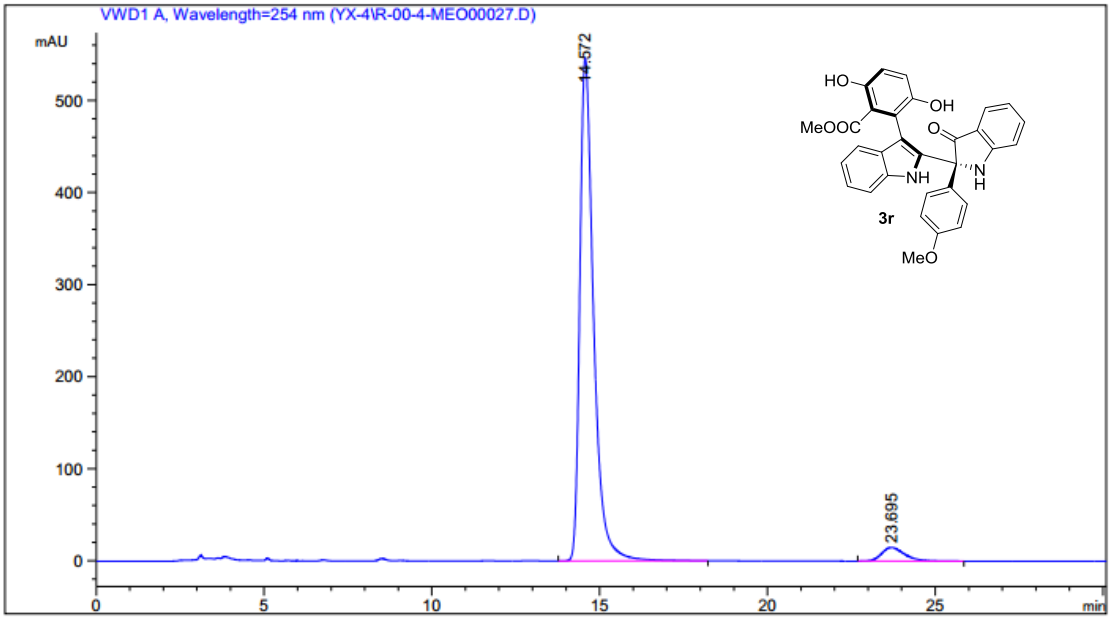
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.876	VB	0.4229	5186.77832	185.19170	50.0833
2	22.072	BB	0.6327	5169.51465	124.18867	49.9167



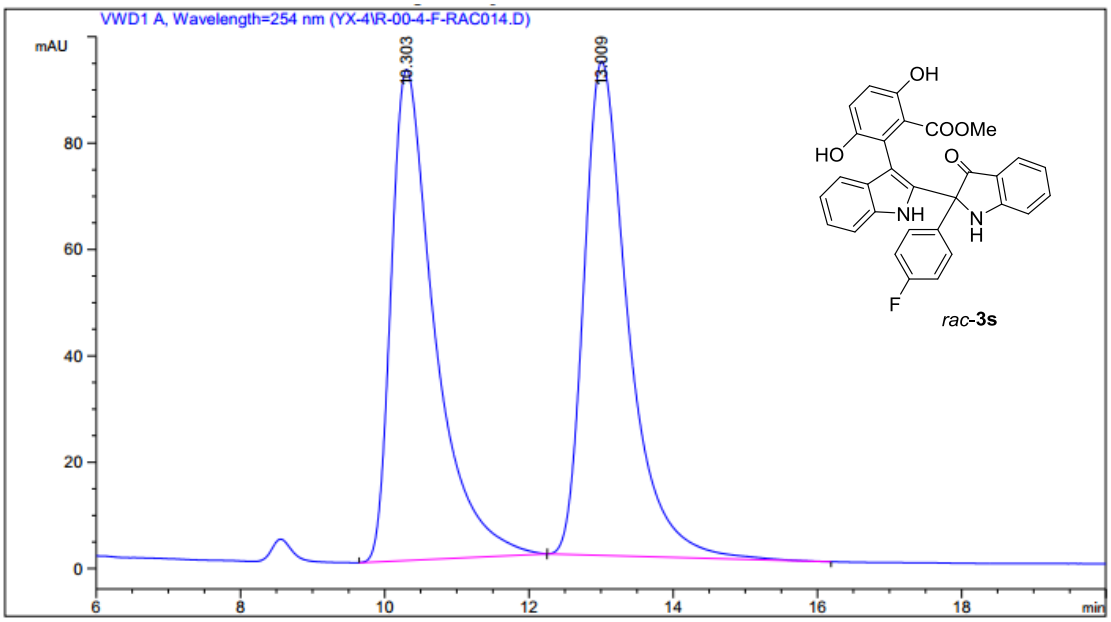
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.835	VB	0.4213	1.37121e4	491.97015	95.9766
2	22.364	BB	0.6400	574.81677	13.80967	4.0234



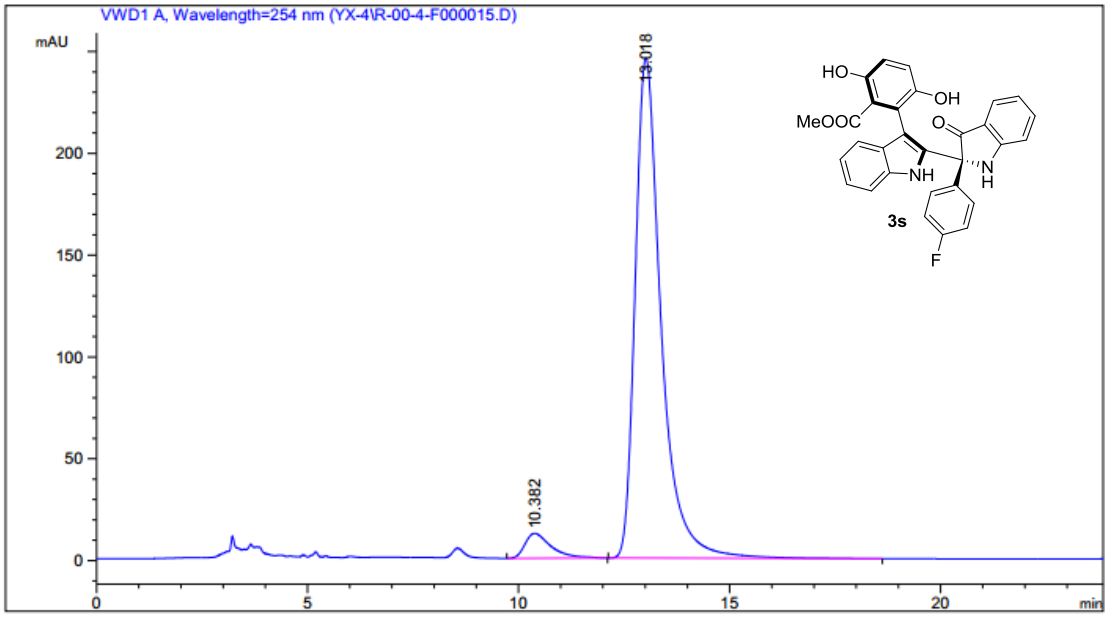
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.598	BB	0.4384	6092.76514	209.46140	50.5429
2	23.278	MM	0.8083	5961.86865	122.93170	49.4571



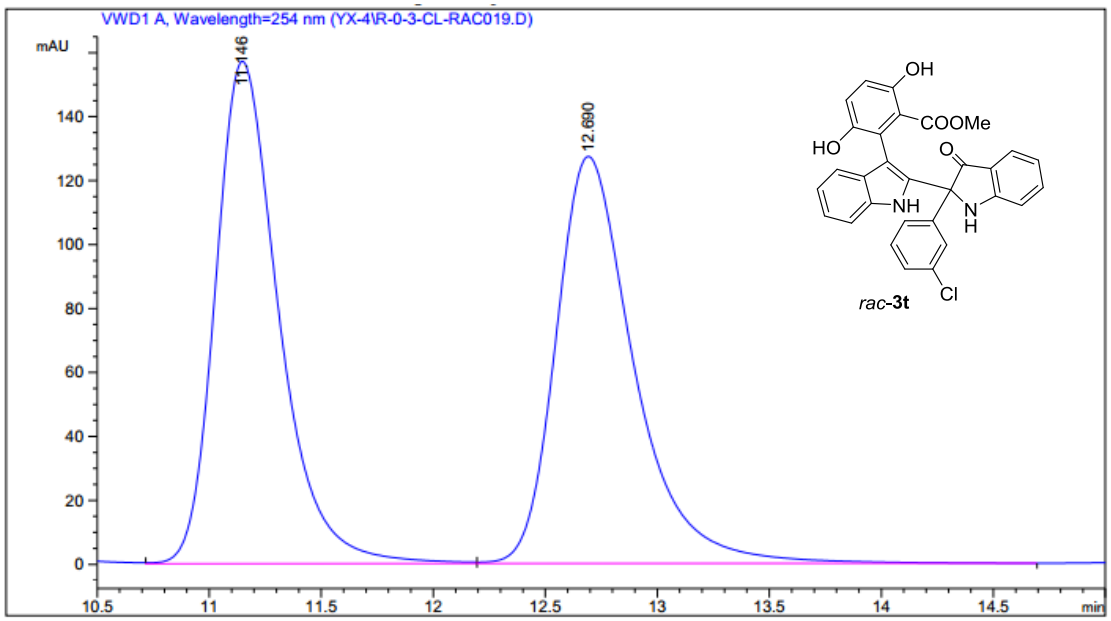
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.572	BB	0.4293	1.55437e4	546.55426	95.6667
2	23.695	BB	0.7257	704.07422	14.79140	4.3333



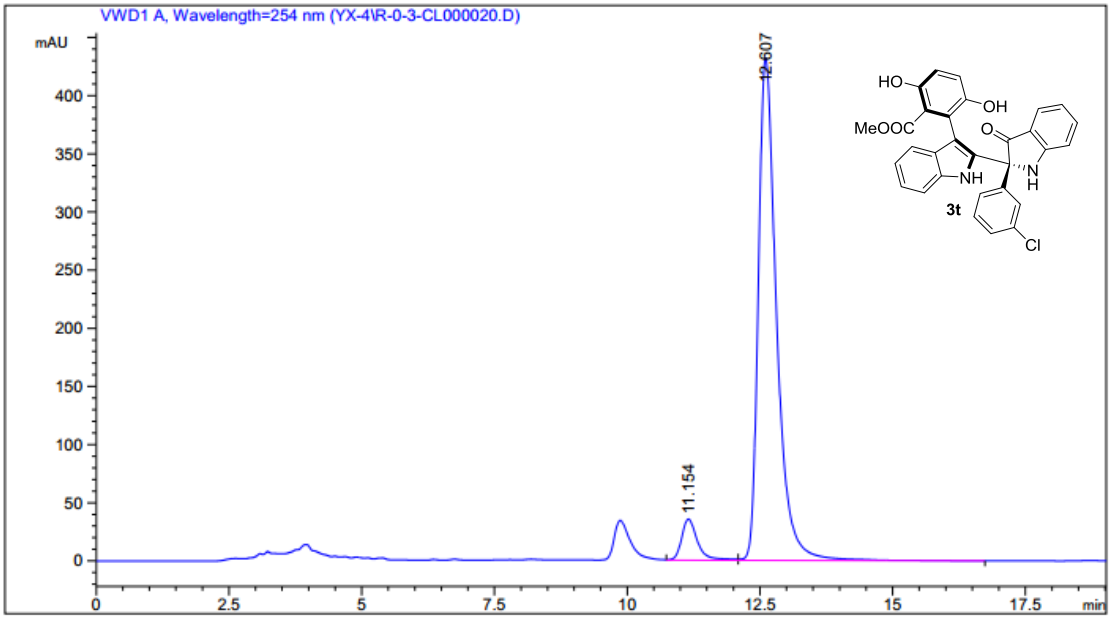
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.303	BB	0.6205	3848.68457	92.28810	49.3409
2	13.009	BB	0.6405	3951.50293	92.87514	50.6591



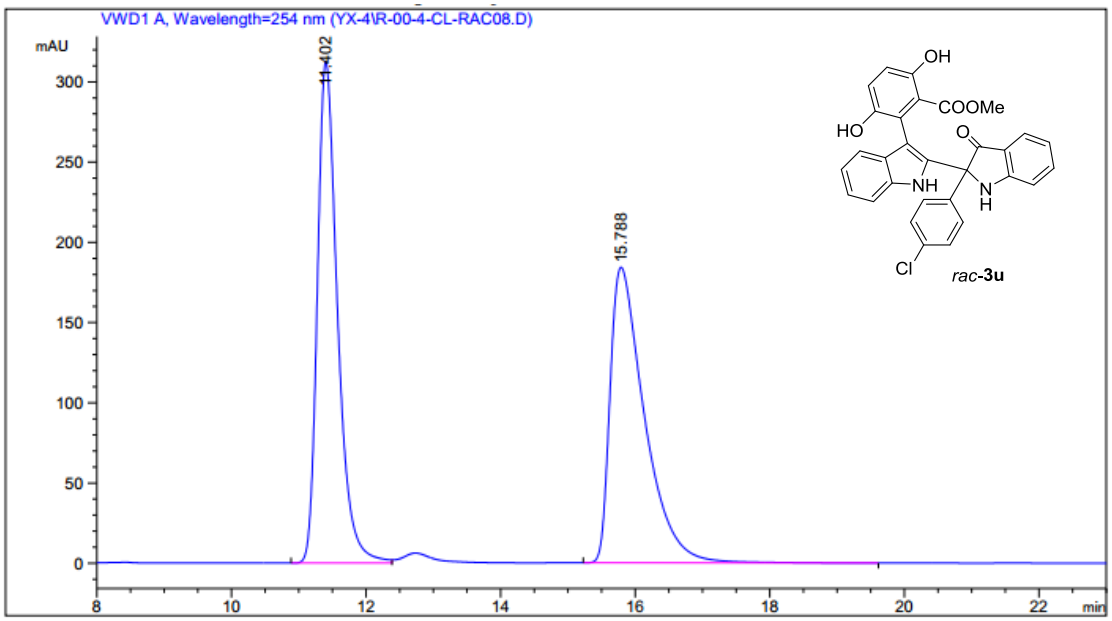
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.382	BB	0.6340	528.49762	12.22451	4.7893
2	13.018	BB	0.6431	1.05064e4	245.66069	95.2107



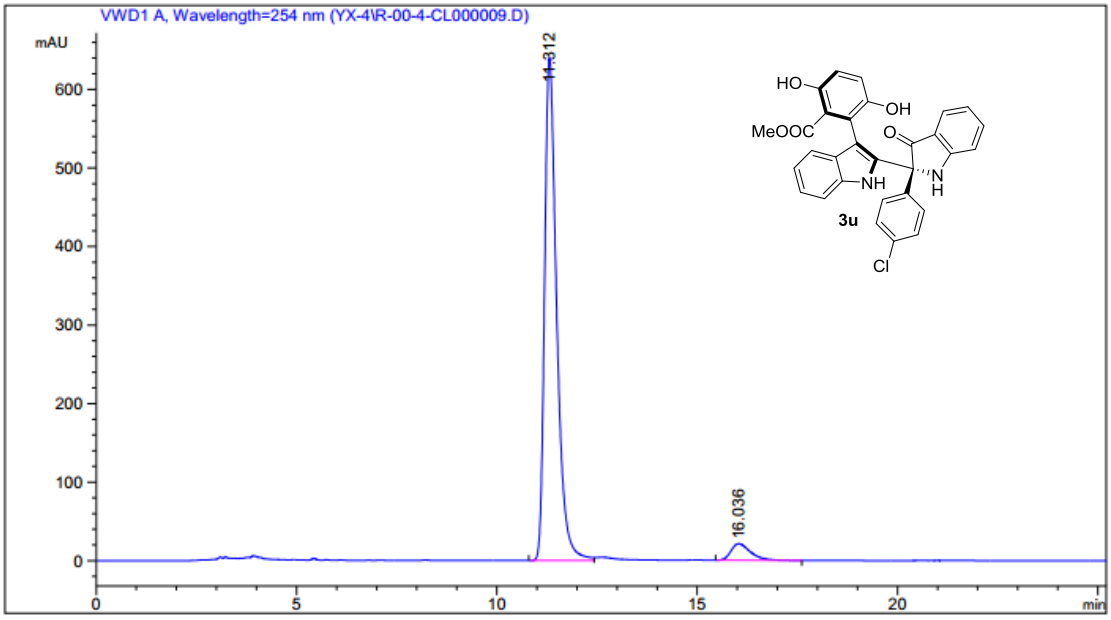
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.146	VV	0.2993	3087.91528	157.06271	49.9560
2	12.690	VB	0.3679	3093.35620	127.29810	50.0440



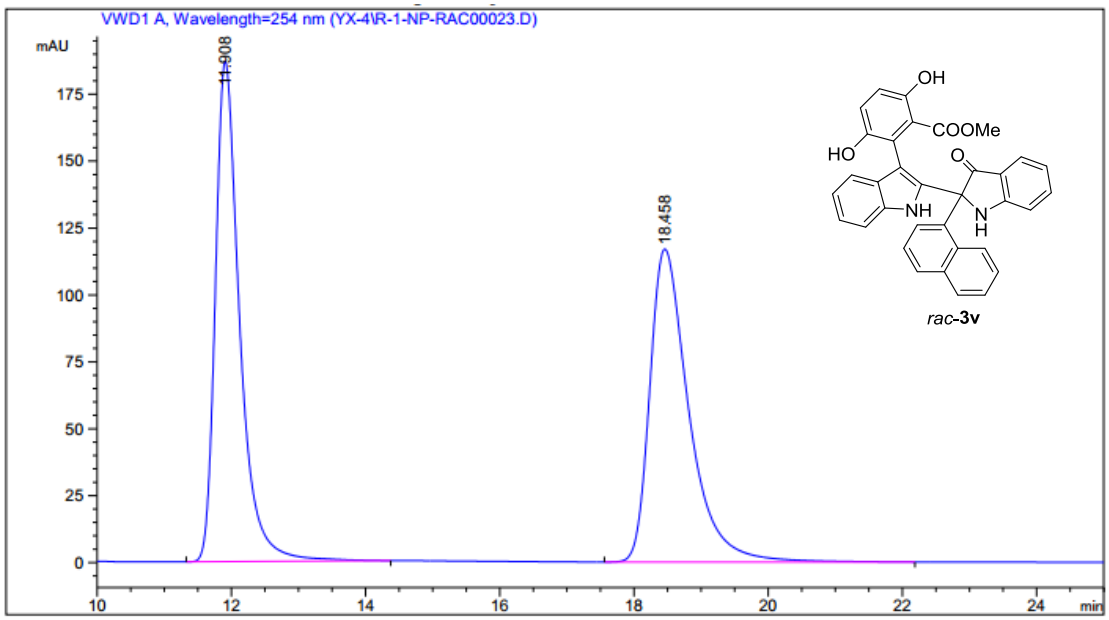
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.154	VV	0.3142	735.82166	35.35518	6.6495
2	12.607	VB	0.3591	1.03299e4	431.89703	93.3505



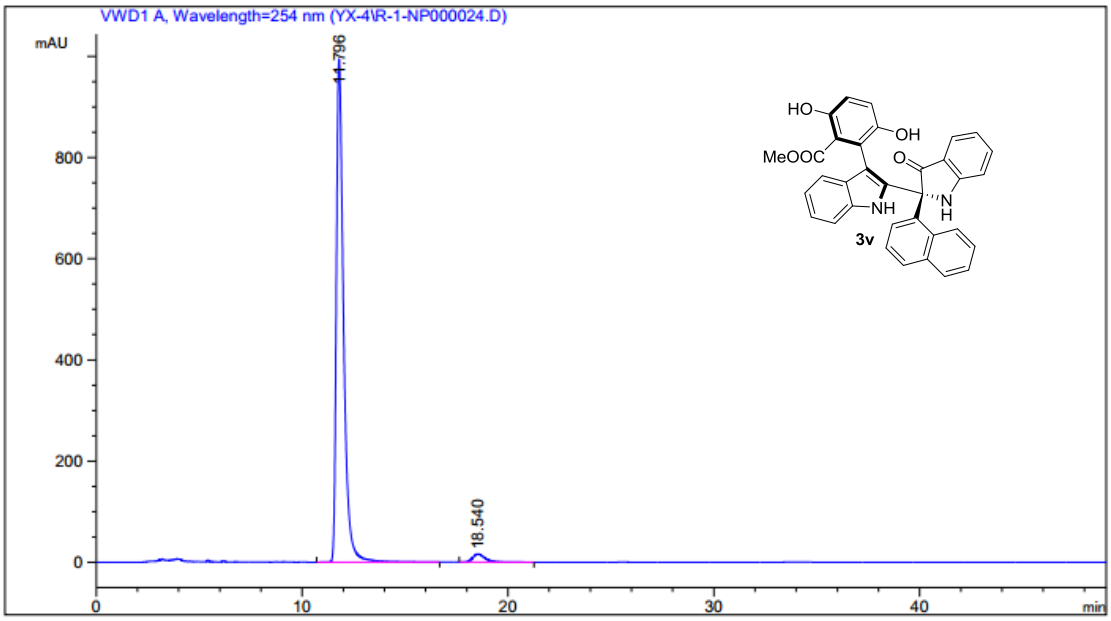
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.402	BV	0.3151	6492.41846	312.61066	49.7993
2	15.788	BB	0.5295	6544.74365	184.21657	50.2007



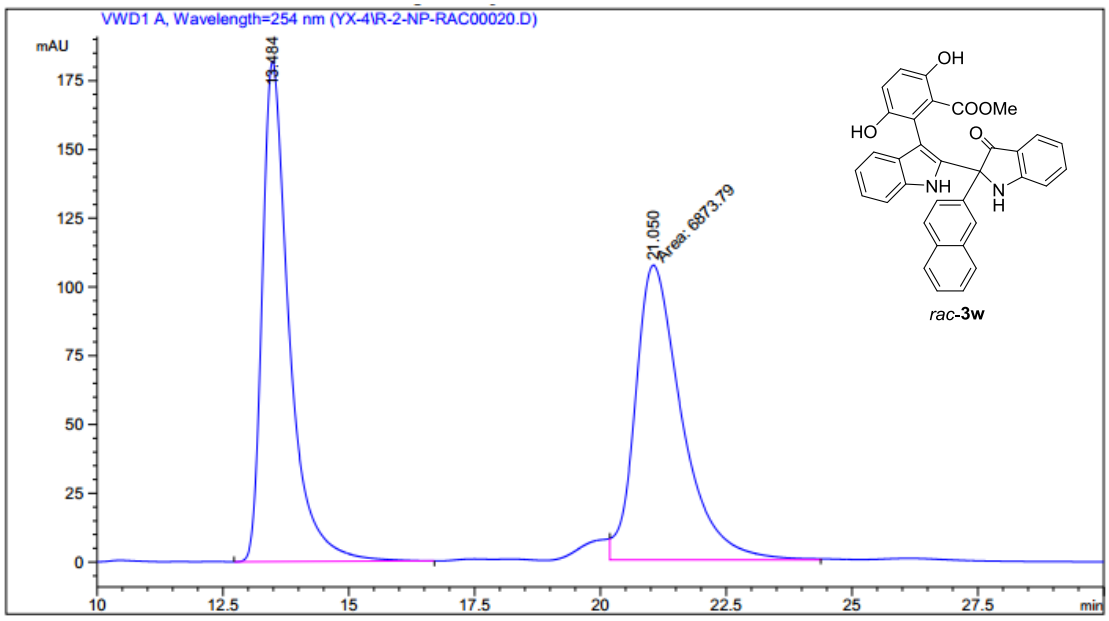
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.312	BV	0.3186	1.34010e4	639.91412	94.9601
2	16.036	BB	0.5140	711.24072	21.10635	5.0399



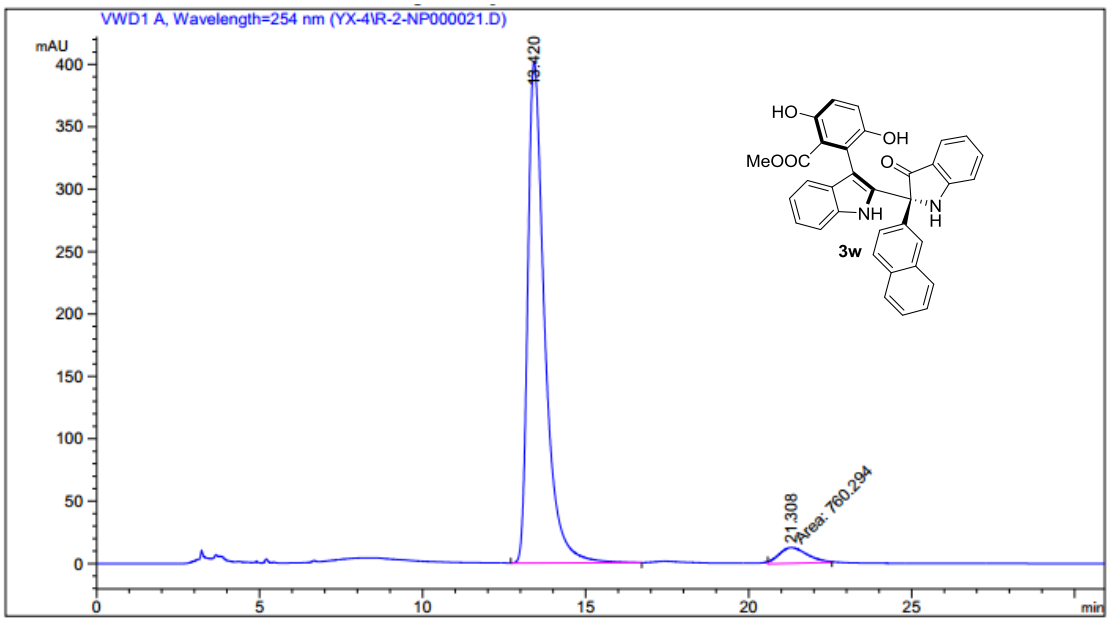
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.908	BB	0.3777	4700.03271	186.97446	49.8099
2	18.458	BB	0.6079	4735.90918	116.93082	50.1901



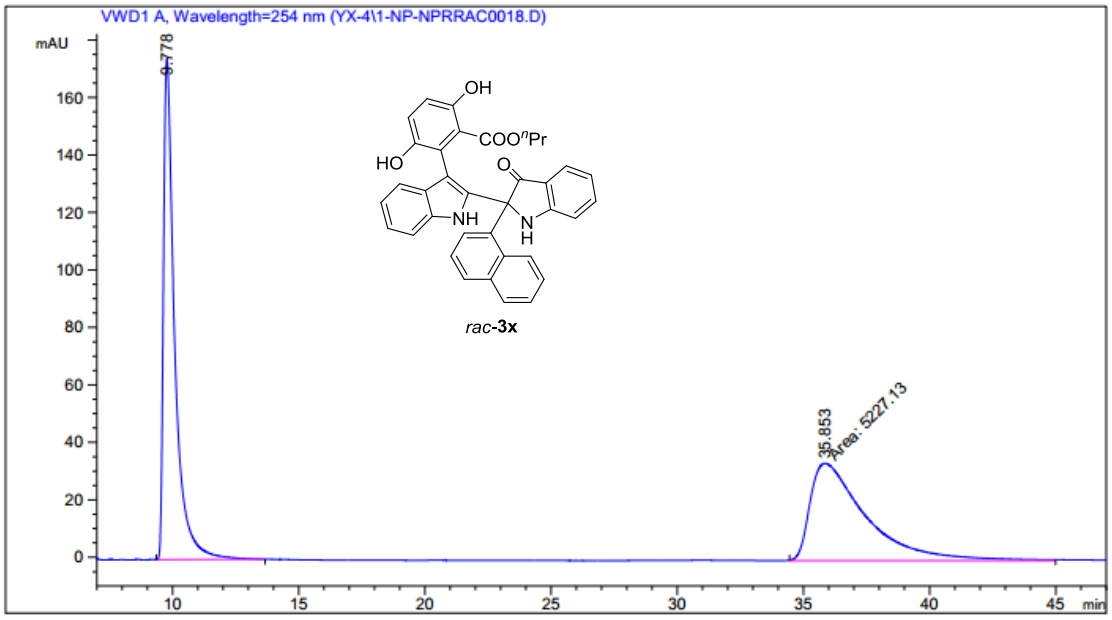
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.796	BB	0.3656	2.42169e4	994.64929	97.3129
2	18.540	BB	0.6312	668.70453	15.97061	2.6871



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.484	BB	0.5543	6758.97803	181.90408	49.5789
2	21.050	MM	1.0693	6873.78613	107.13533	50.4211



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.420	BB	0.5386	1.44434e4	401.92358	94.9993
2	21.308	MM	1.0036	760.29376	12.62575	5.0007



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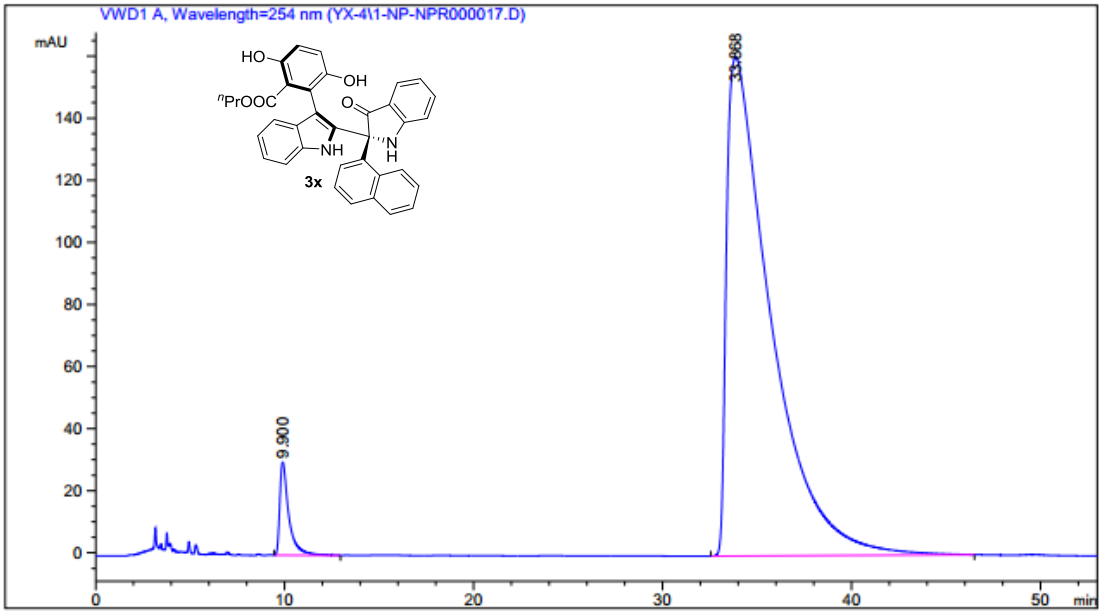
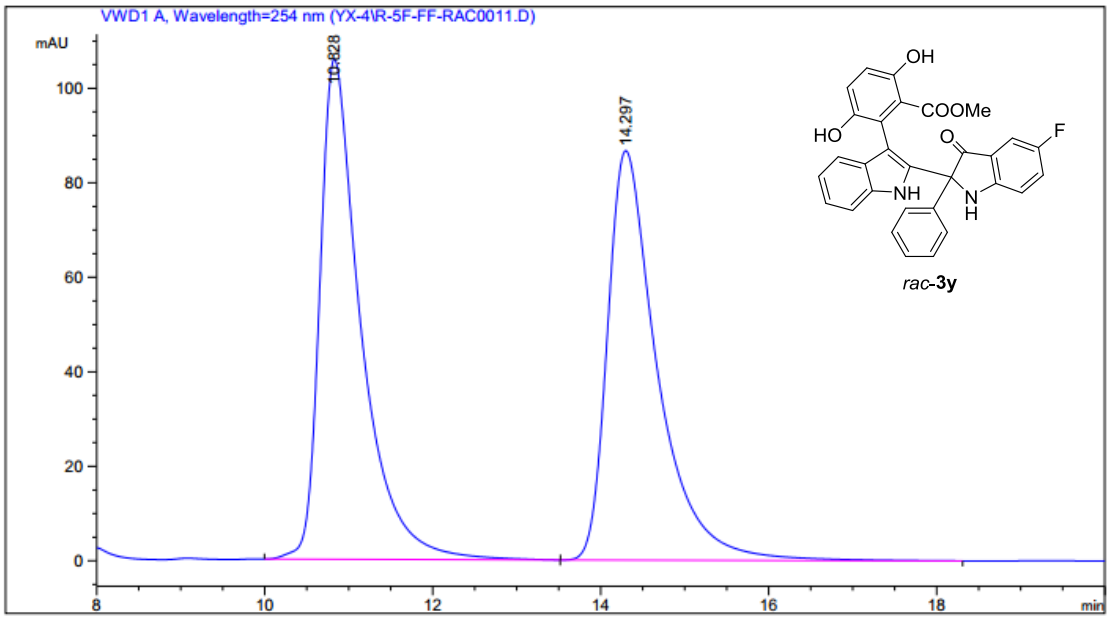
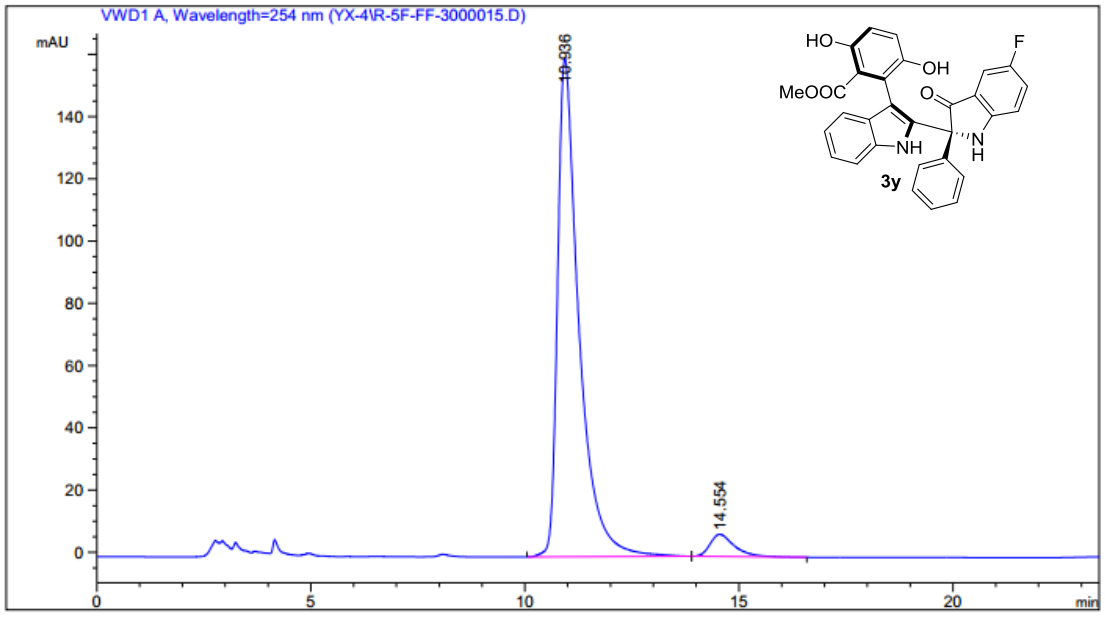
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.778	BB	0.4496	5366.45410	174.23270	50.6576
2	35.853	MM	2.5732	5227.13135	33.85683	49.3424



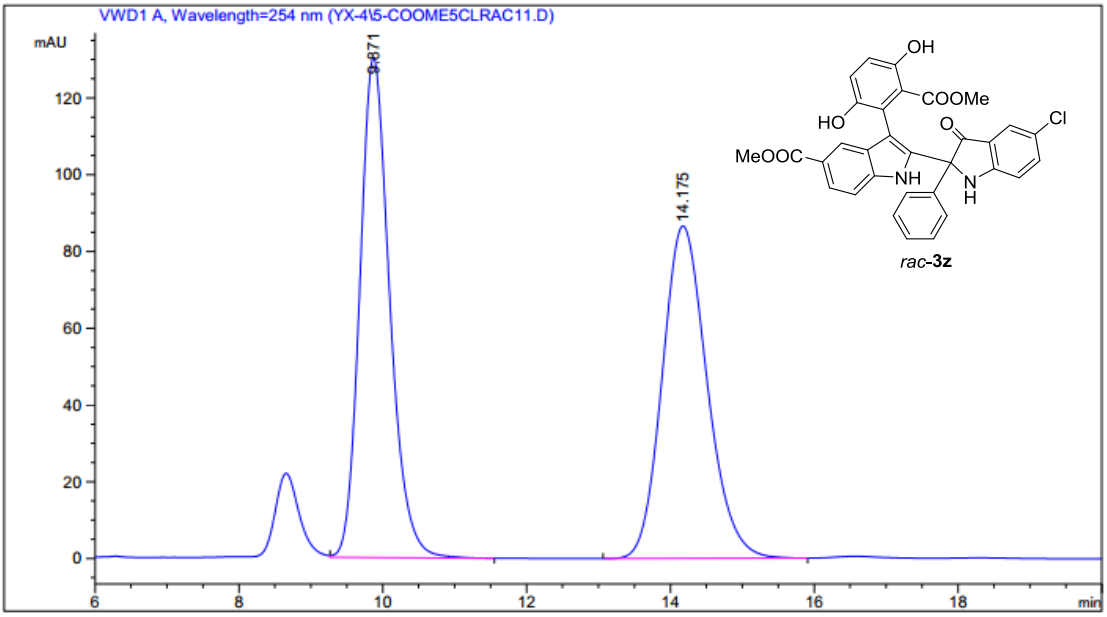
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.900	BB	0.4877	998.32208	29.96308	3.6807
2	33.868	BB	2.1655	2.61248e4	160.61575	96.3193



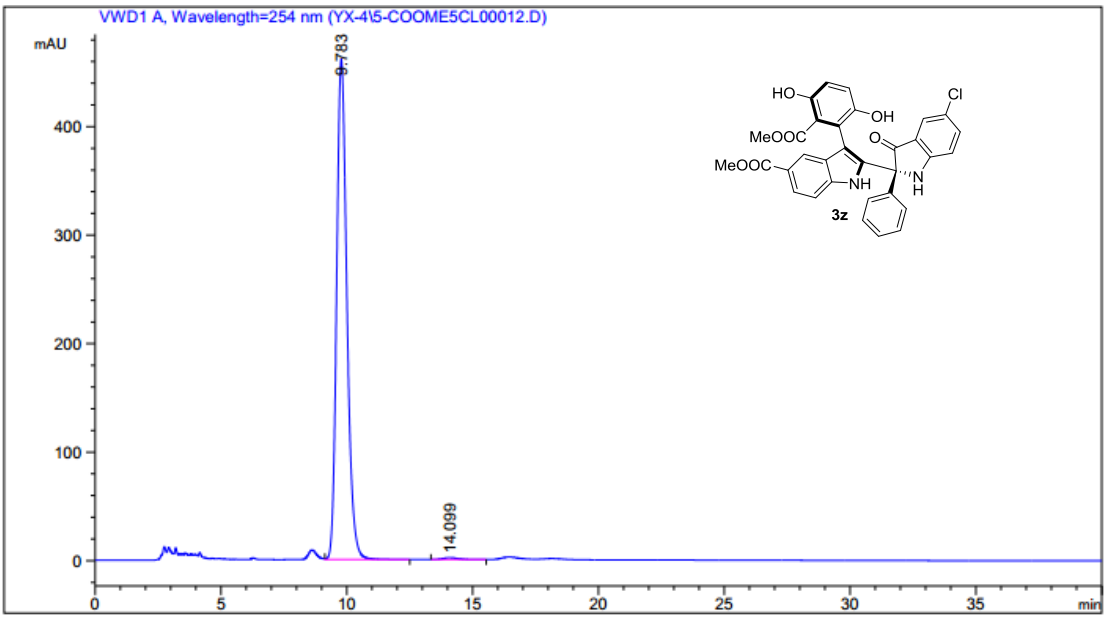
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.828	BB	0.4974	3601.04614	105.84821	50.1449
2	14.297	BB	0.6102	3580.23657	86.64684	49.8551



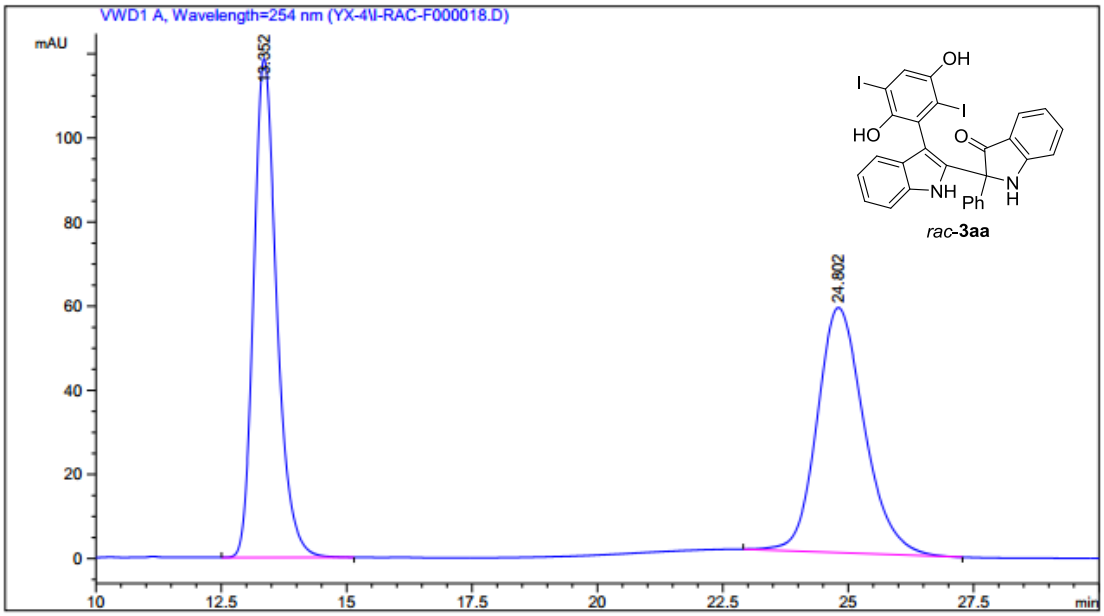
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.936	BB	0.5052	5555.90771	160.13596	95.1359
2	14.554	BB	0.5883	284.05966	7.13443	4.8641



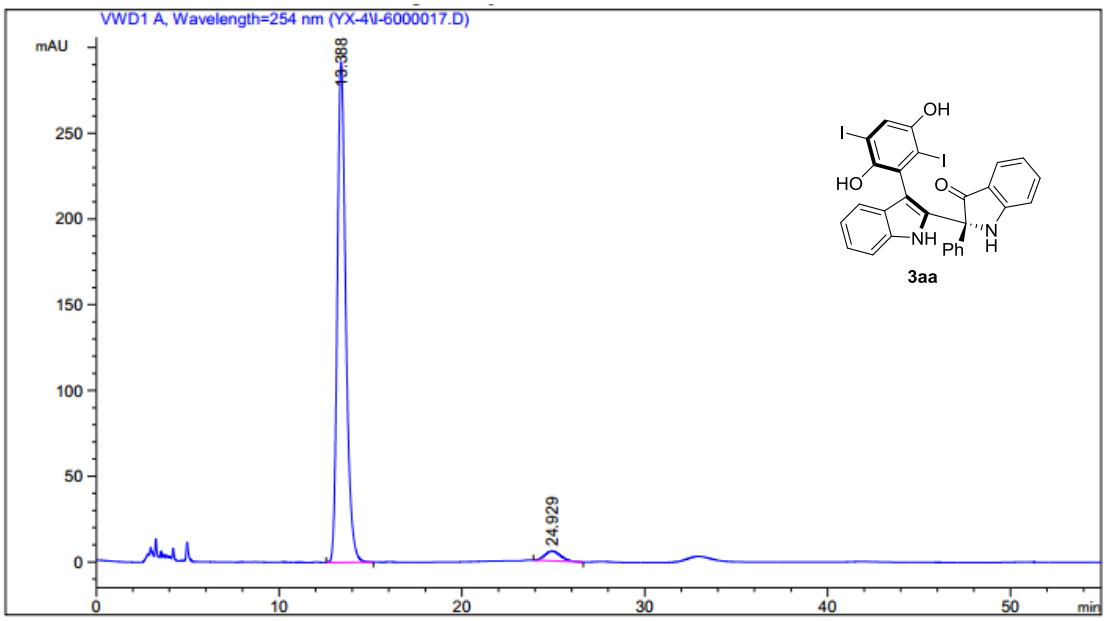
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.871	VB	0.4424	3753.00562	130.25272	49.9948
2	14.175	BB	0.6686	3753.78906	86.63263	50.0052



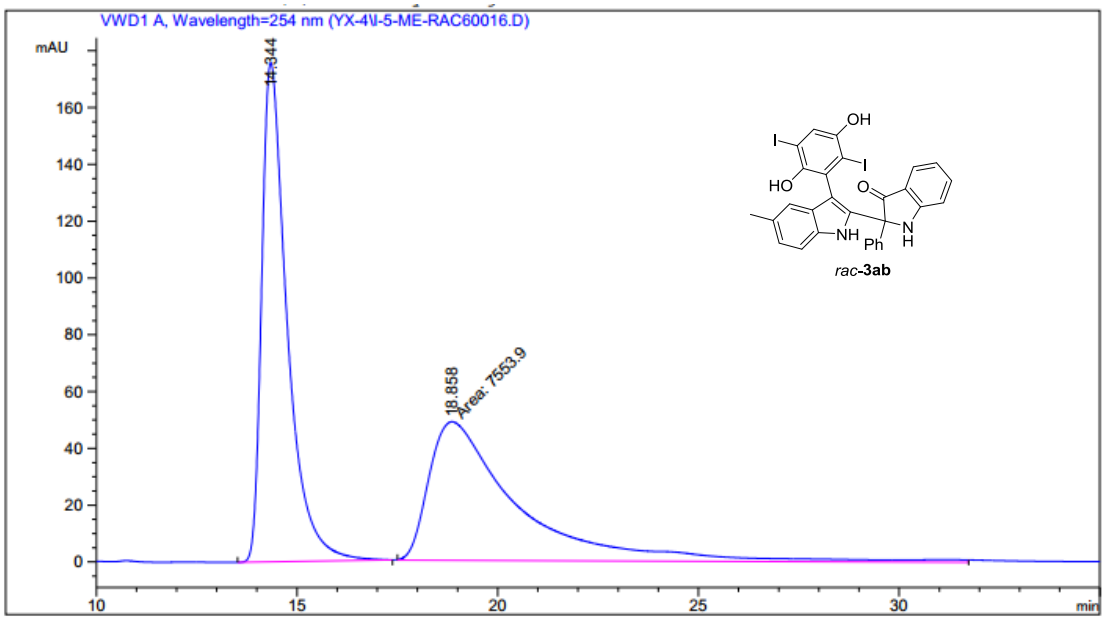
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.783	VB	0.4336	1.29943e4	461.10974	99.4644
2	14.099	BB	0.6282	69.97574	1.66166	0.5356



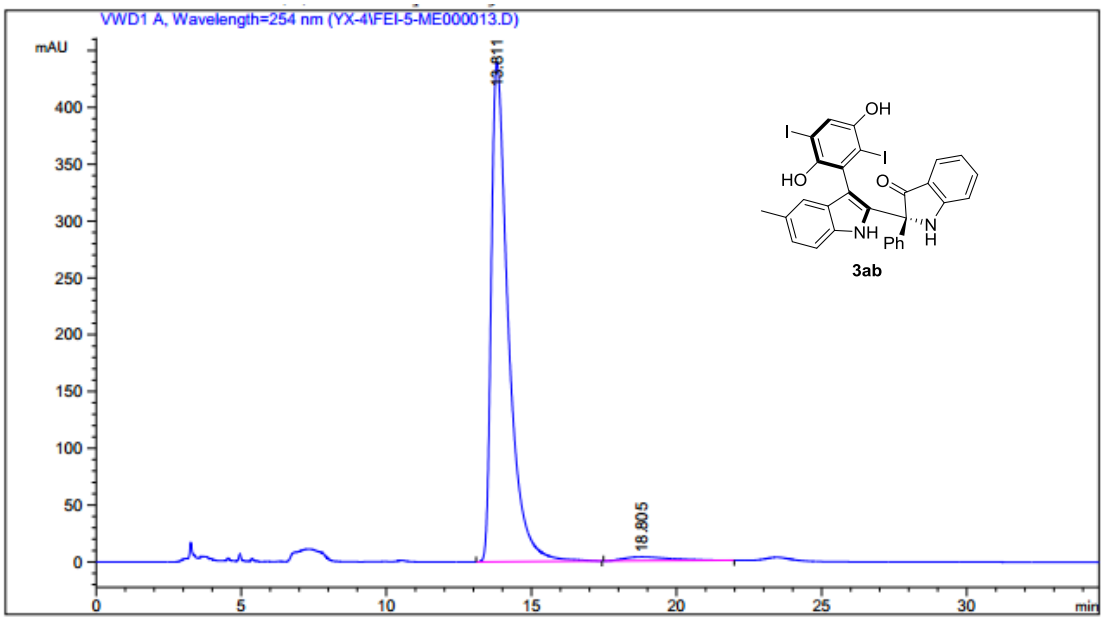
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.352	BB	0.4857	3783.59717	118.62504	49.8211
2	24.802	BB	0.9976	3810.76294	58.25714	50.1789



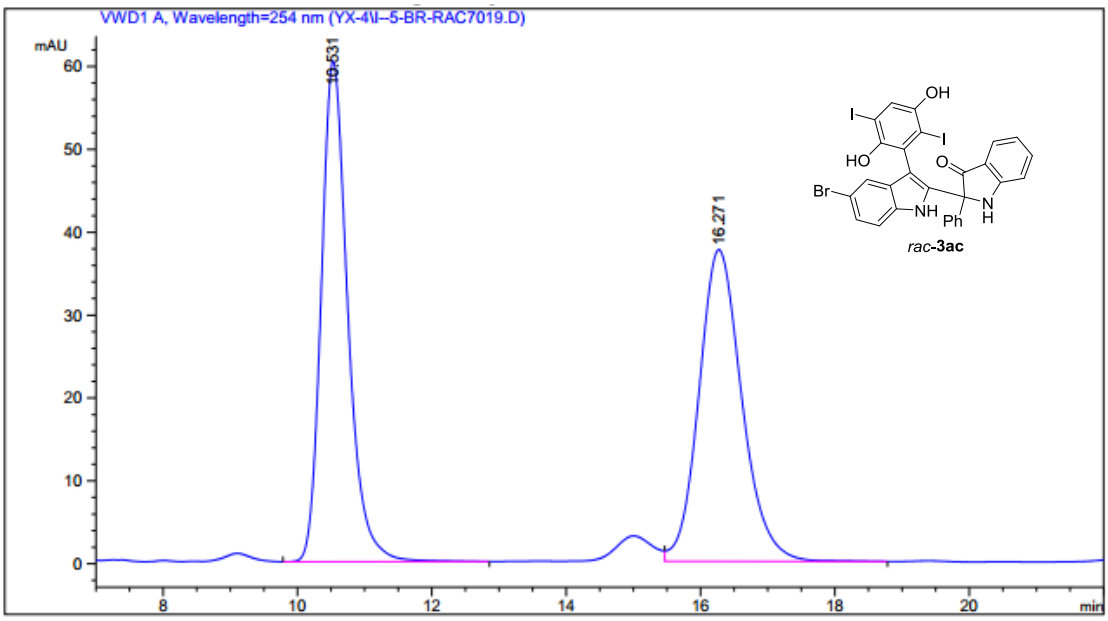
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.388	BB	0.4936	9395.99414	291.81784	96.4652
2	24.929	BB	0.8791	344.29498	5.72617	3.5348



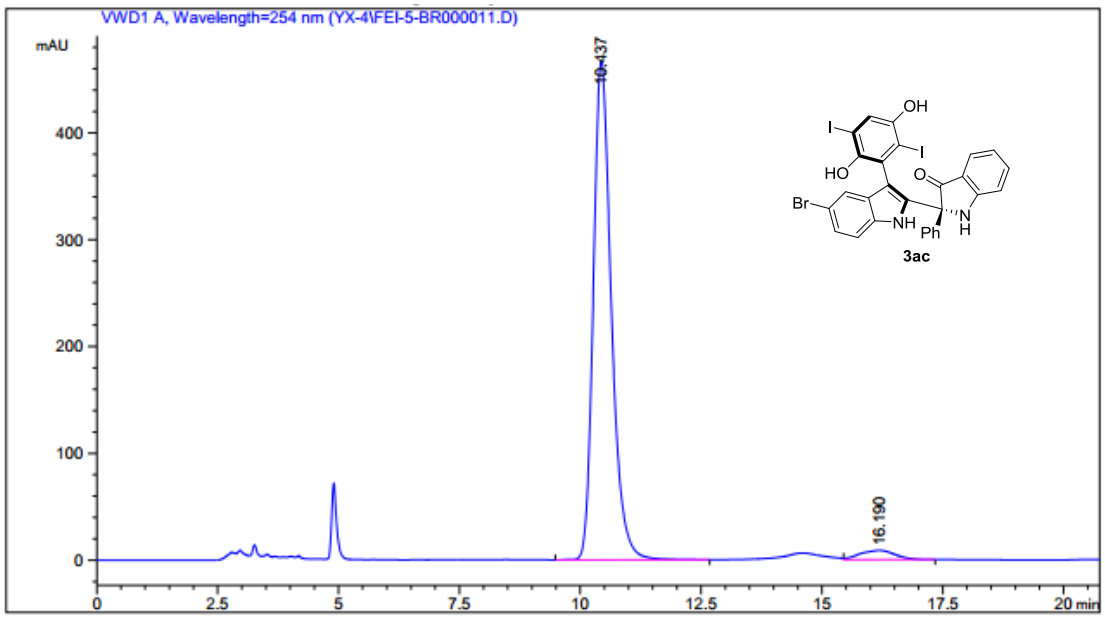
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.344	BB	0.6556	7748.81104	175.74043	50.6369
2	18.858	MM	2.5780	7553.89893	48.83524	49.3631



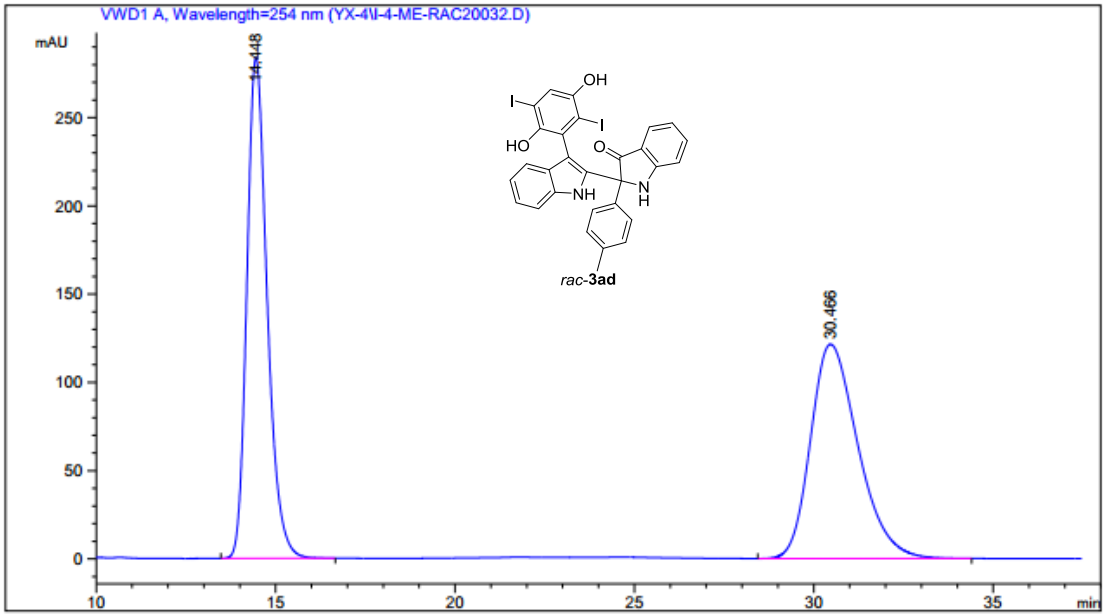
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.811	BB	0.6067	1.79664e4	439.34872	97.9063
2	18.805	BB	1.3499	384.20679	3.38257	2.0937



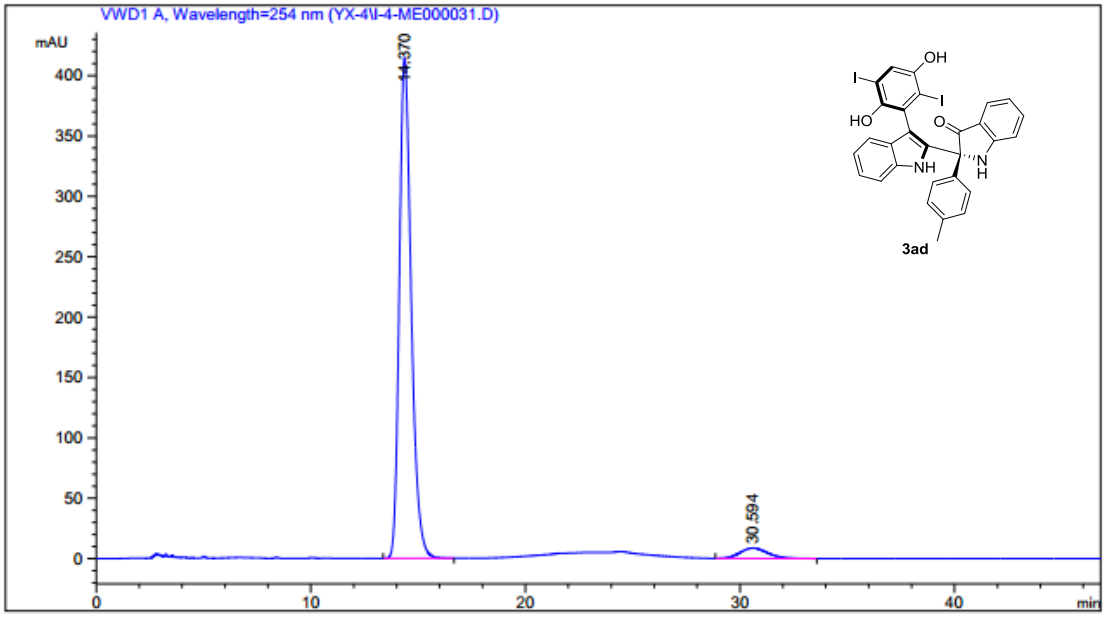
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.531	BB	0.4190	1657.20435	60.41360	49.8024
2	16.271	VB	0.6769	1670.35620	37.60455	50.1976



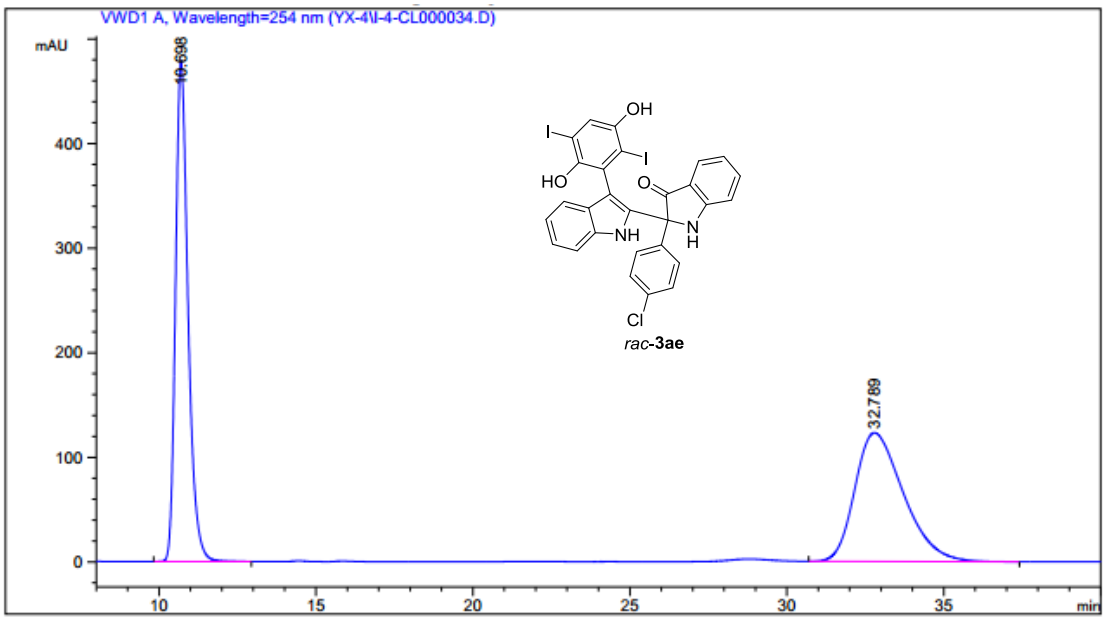
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.437	BB	0.3940	1.20461e4	467.12329	96.5272
2	16.190	VB	0.7176	433.38727	8.59881	3.4728



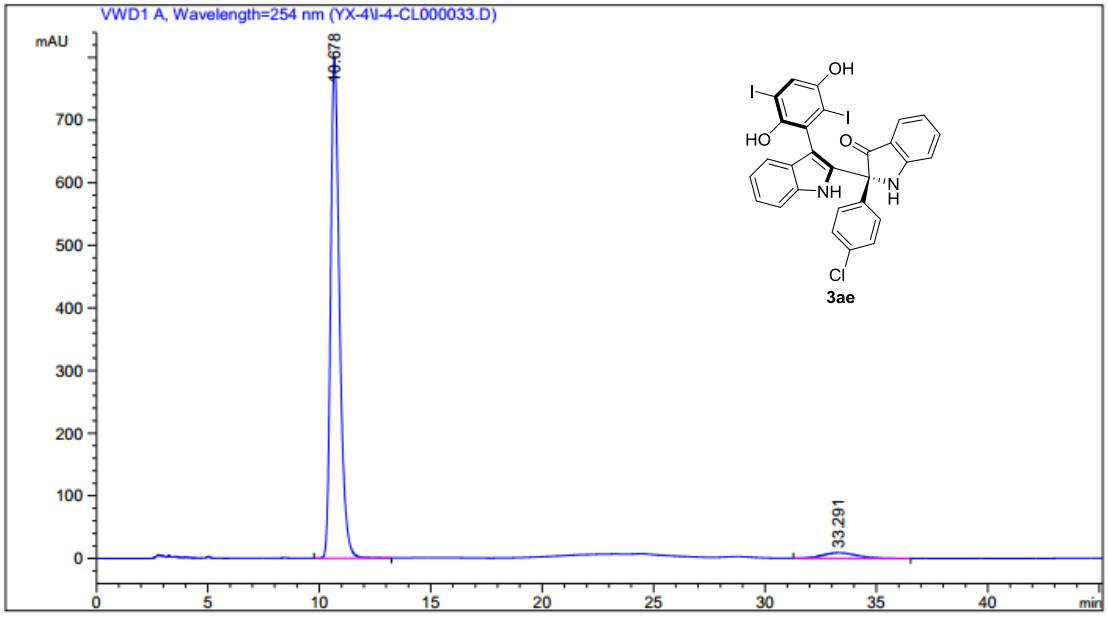
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.448	BB	0.6004	1.11282e4	283.66238	49.9497
2	30.466	BB	1.4007	1.11506e4	121.38960	50.0503



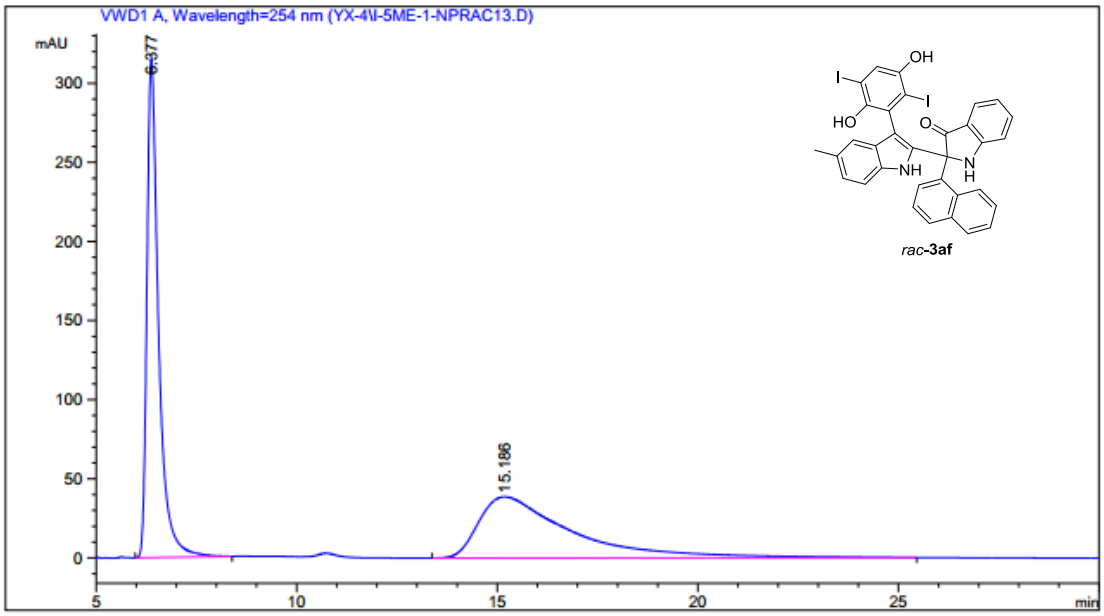
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.370	BB	0.5887	1.59540e4	414.64532	95.4298
2	30.594	BB	1.1677	764.04633	8.57429	4.5702



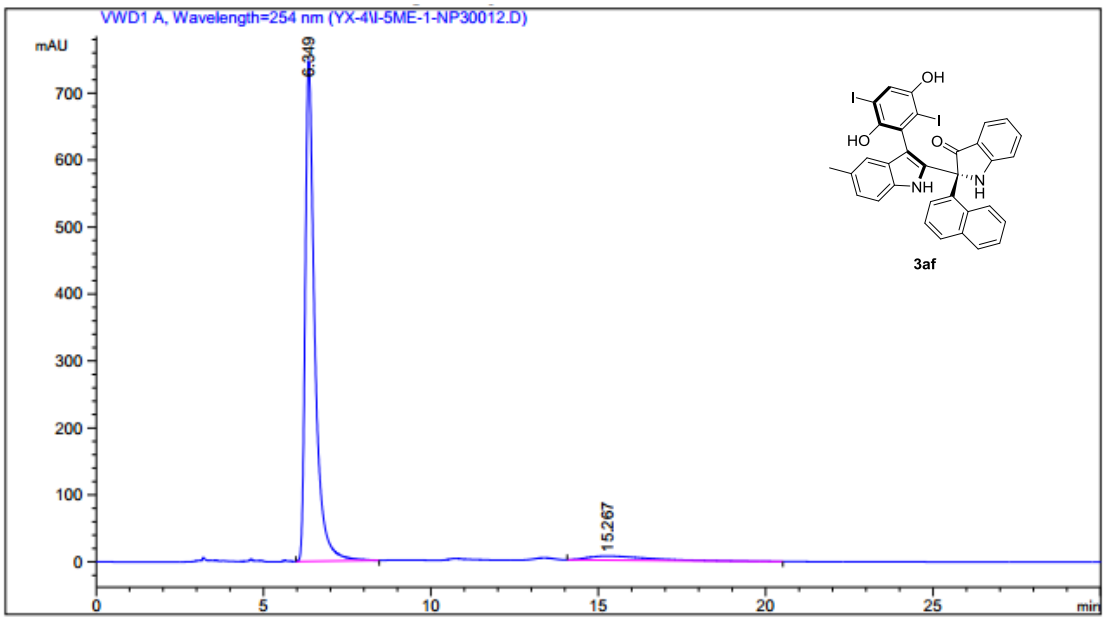
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.698	BB	0.4225	1.32695e4	478.52667	50.0534
2	32.789	BB	1.6063	1.32412e4	123.04992	49.9466



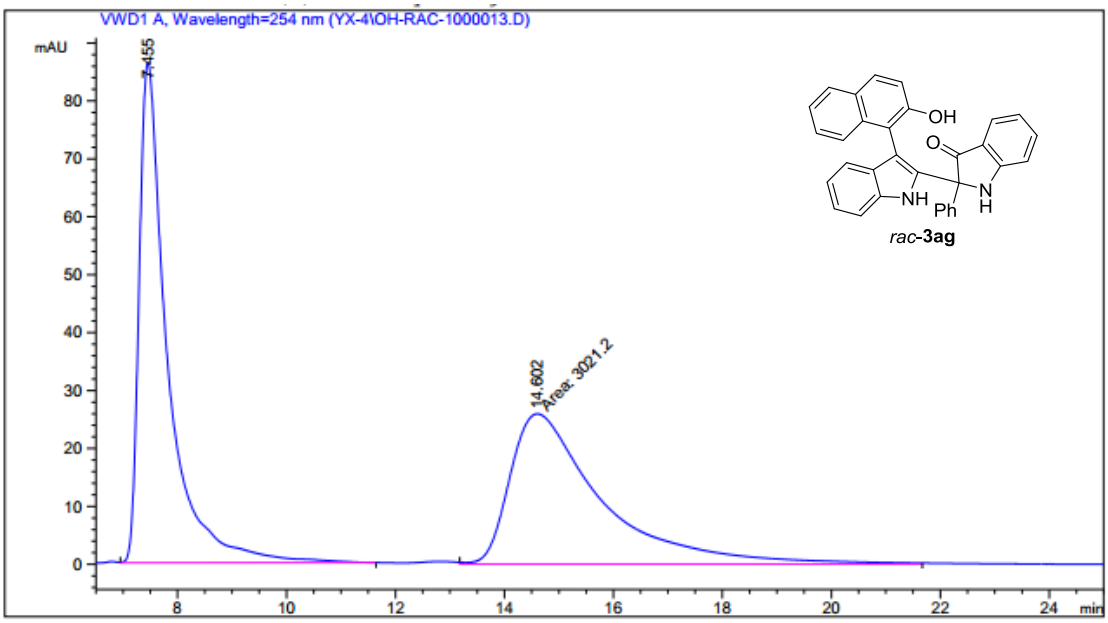
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.678	BB	0.4196	2.20666e4	799.48462	95.9866
2	33.291	BB	1.3306	922.64624	8.79223	4.0134



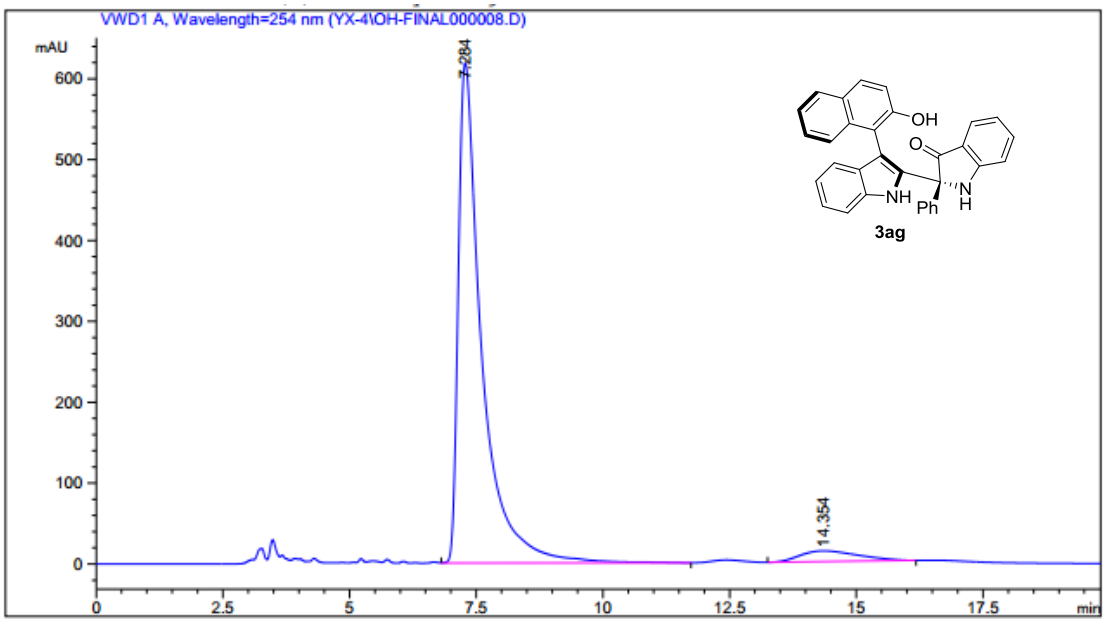
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.377	BB	0.2998	6372.34180	315.31796	50.9824
2	15.186	BB	2.1961	6126.75293	38.58557	49.0176



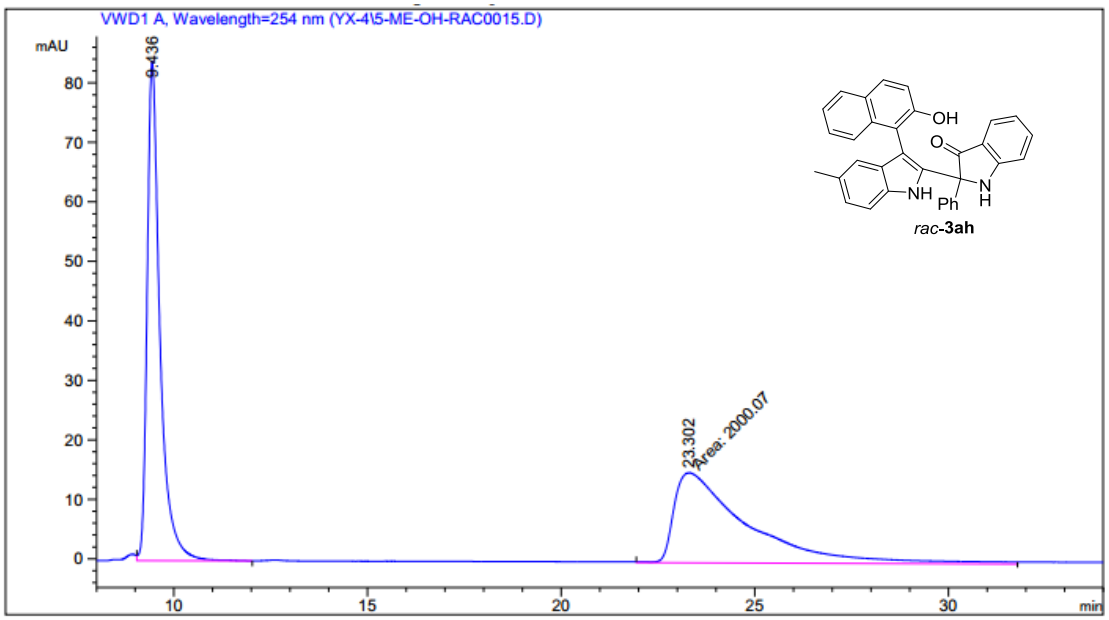
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.349	BB	0.2930	1.48516e4	747.27643	94.8094
2	15.267	BB	1.5508	813.09393	6.22206	5.1906



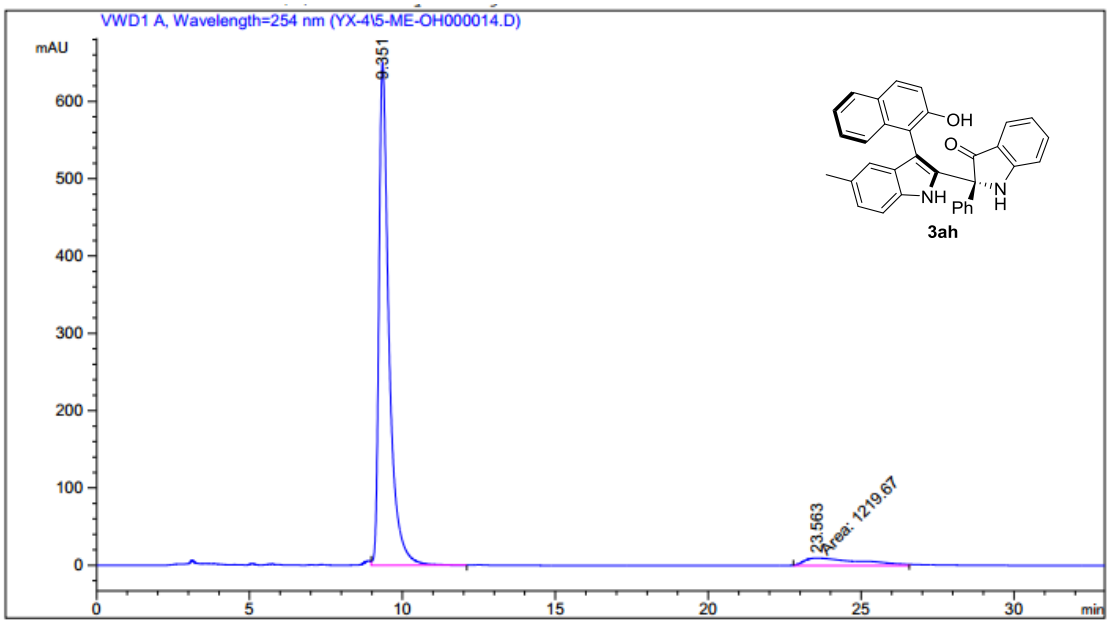
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.403	MM	0.5713	2419.58374	70.59116	50.9773
2	14.345	MM	1.7192	2326.81128	22.55686	49.0227



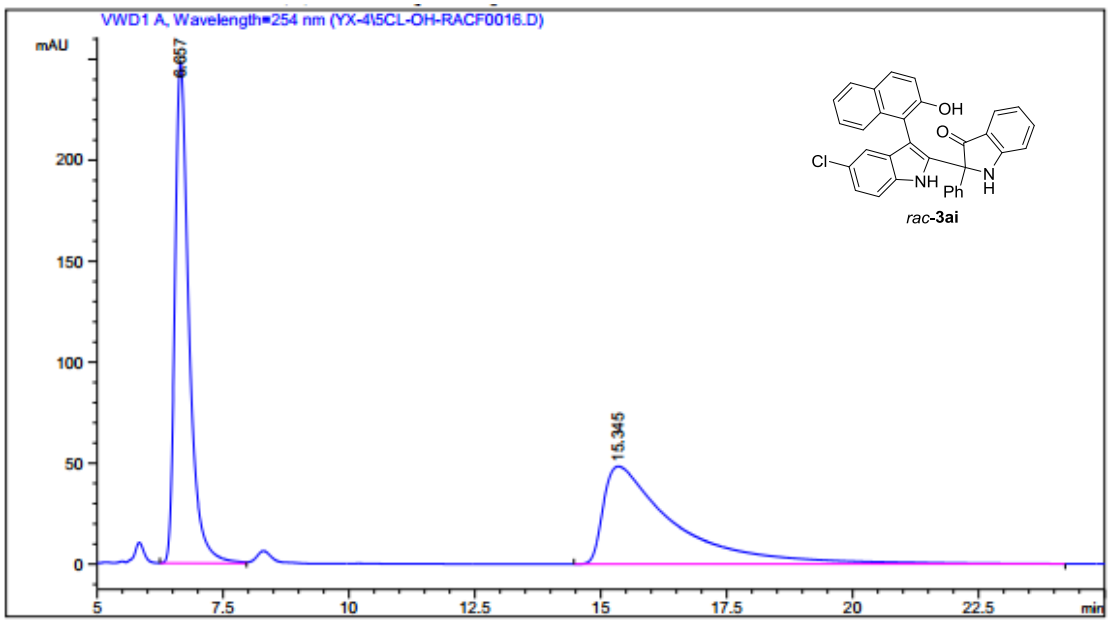
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.284	VB	0.4625	1.98917e4	618.60876	94.9439
2	14.354	BB	1.1557	1059.30579	13.28806	5.0561



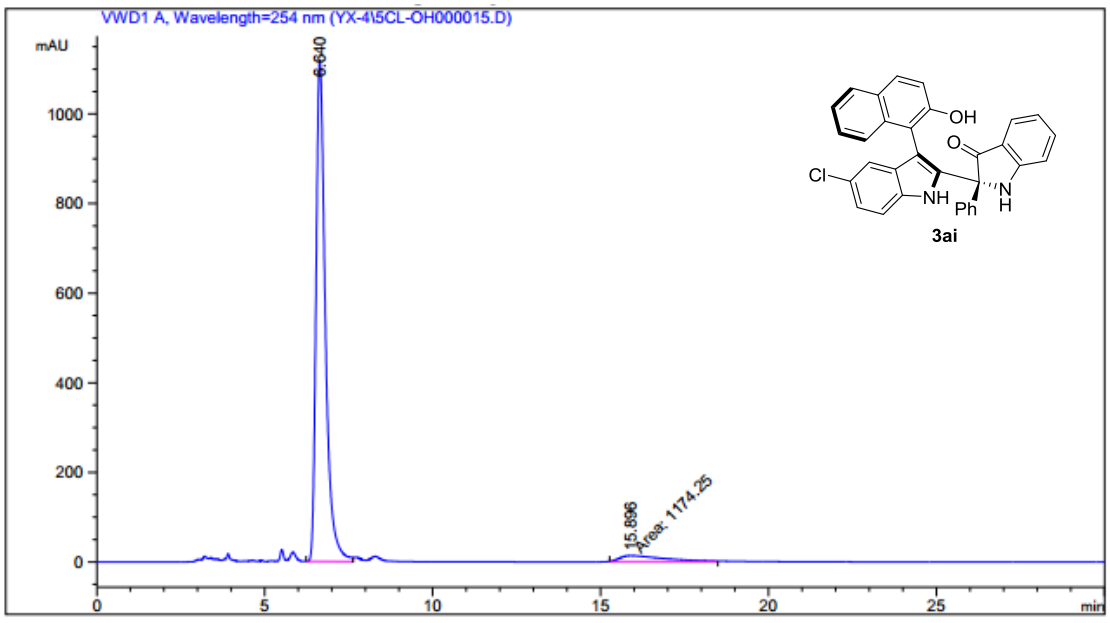
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.436	VB	0.3410	1929.37561	83.93239	49.1004
2	23.302	MM	2.2023	2000.07251	15.13643	50.8996



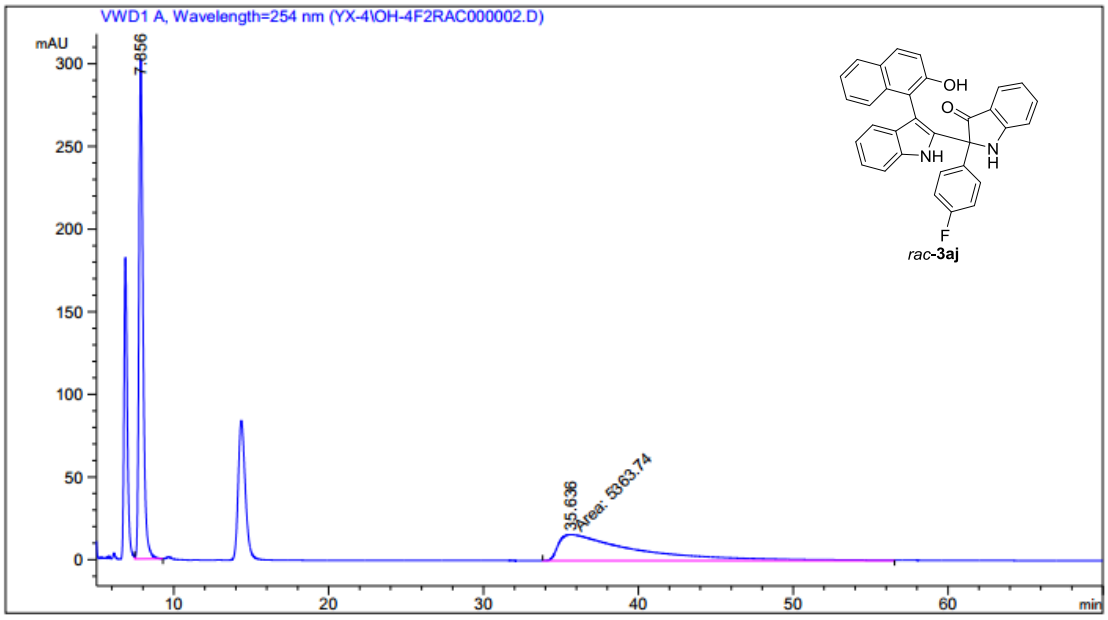
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.351	VB	0.3376	1.48256e4	649.52539	92.3986
2	23.563	MM	2.1136	1219.67407	9.61753	7.6014



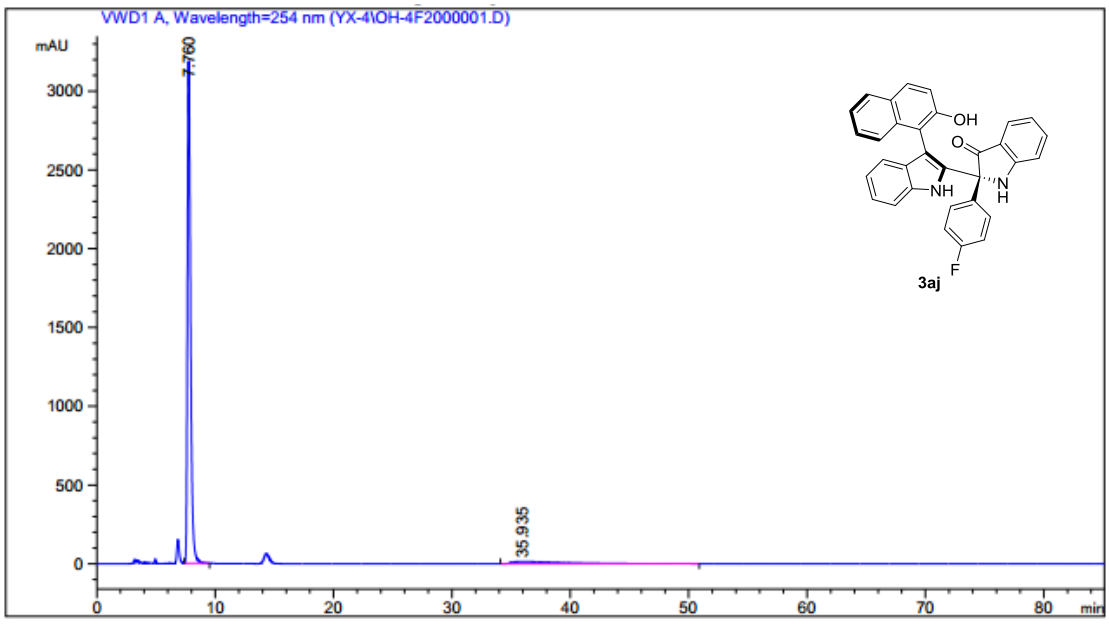
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.657	BV	0.2903	4809.94043	248.02786	50.4965
2	15.345	BB	1.3410	4715.35791	48.37654	49.5035



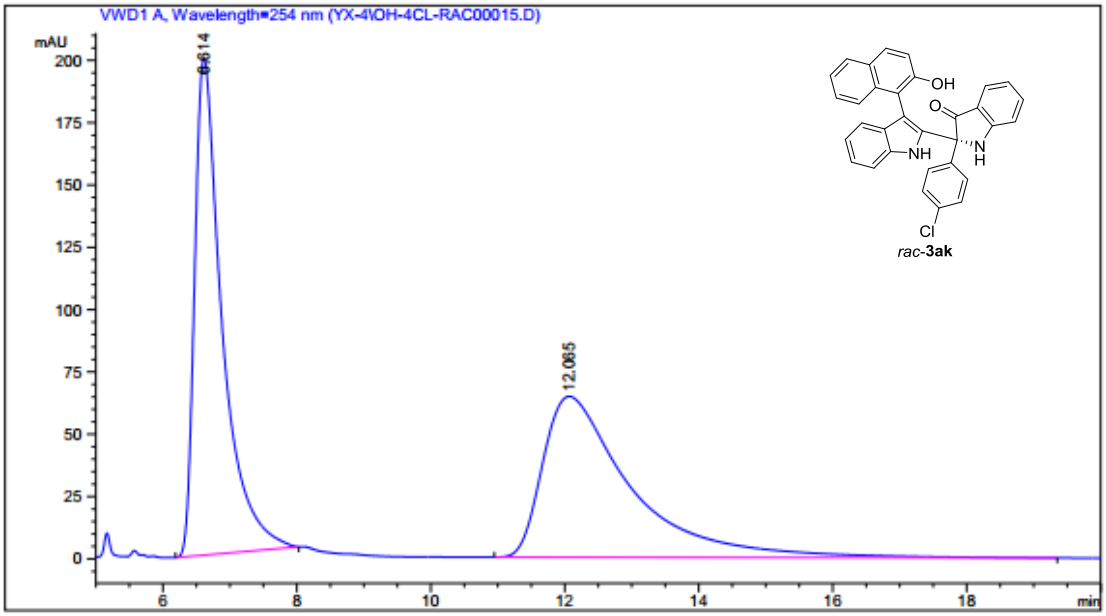
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.640	BV	0.2924	2.15851e4	1116.97229	94.8406
2	15.896	MM	1.5201	1174.24780	12.87435	5.1594



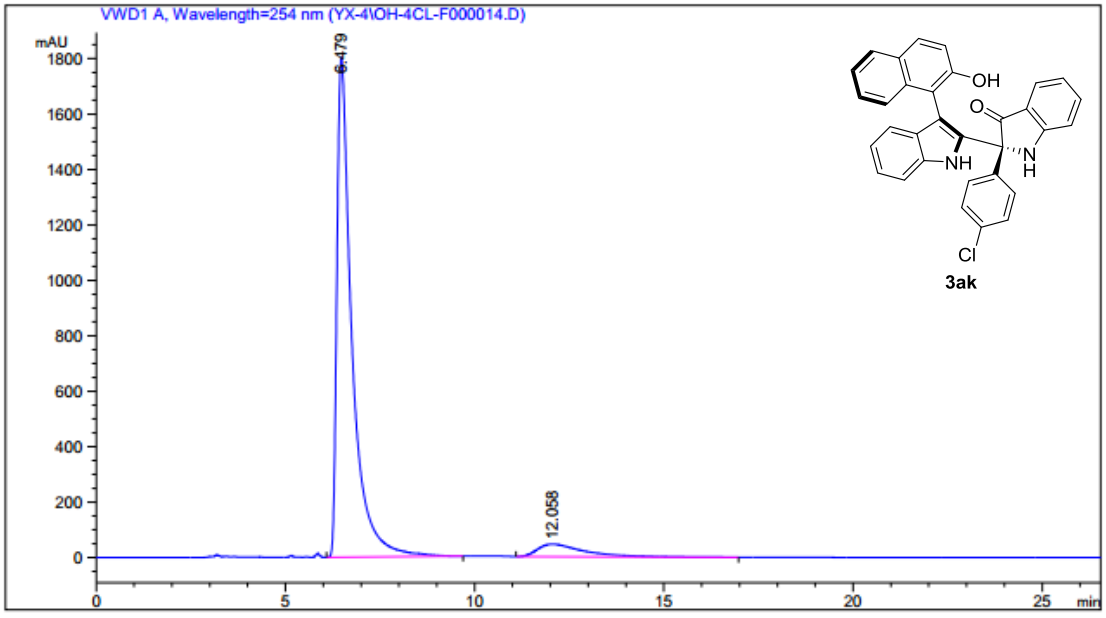
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.856	VB	0.2777	5541.70996	302.61761	50.8160
2	35.636	MM	5.6920	5363.74268	15.70540	49.1840



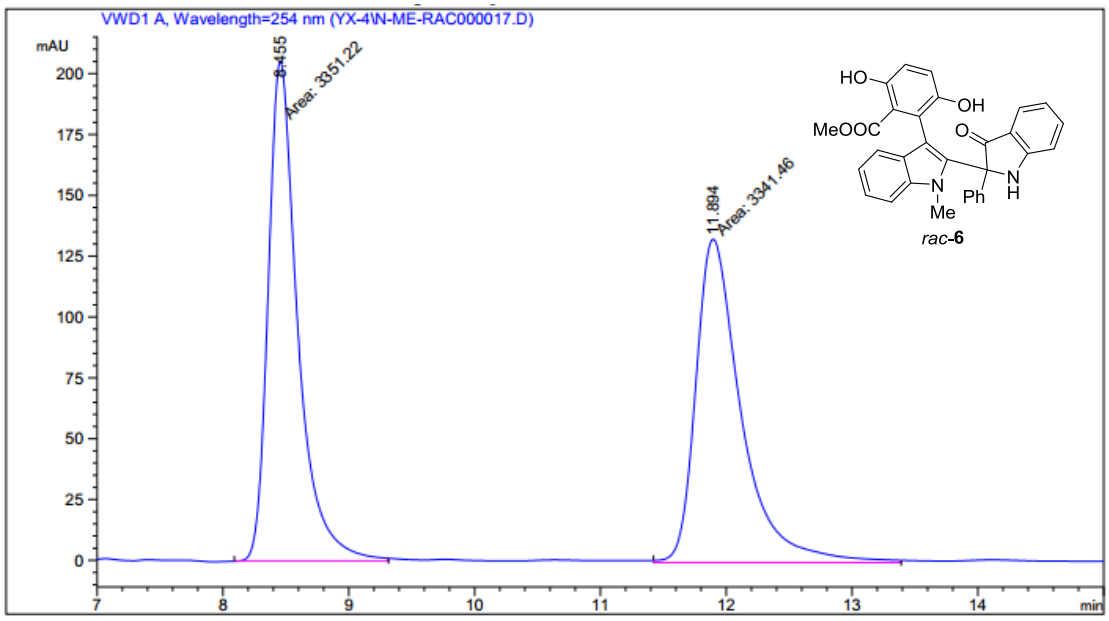
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.760	VB	0.2839	5.92673e4	3187.87012	92.5693
2	35.935	BB	3.8264	4757.49756	14.54434	7.4307



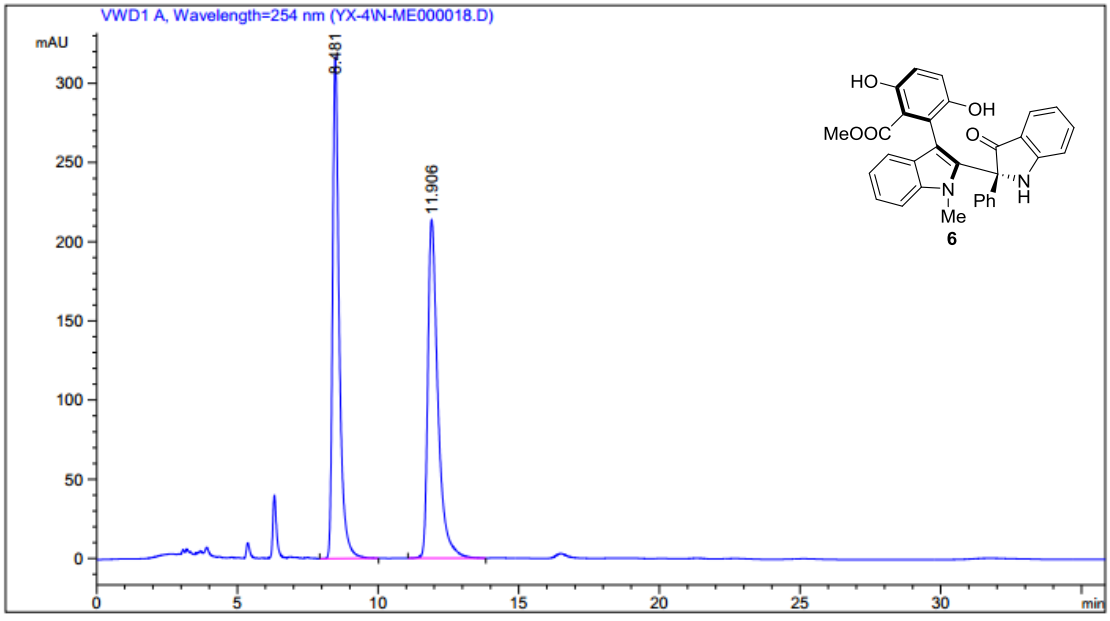
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.614	BB	0.4187	5690.28027	199.47795	49.1344
2	12.065	BB	1.3341	5890.76367	64.54748	50.8656



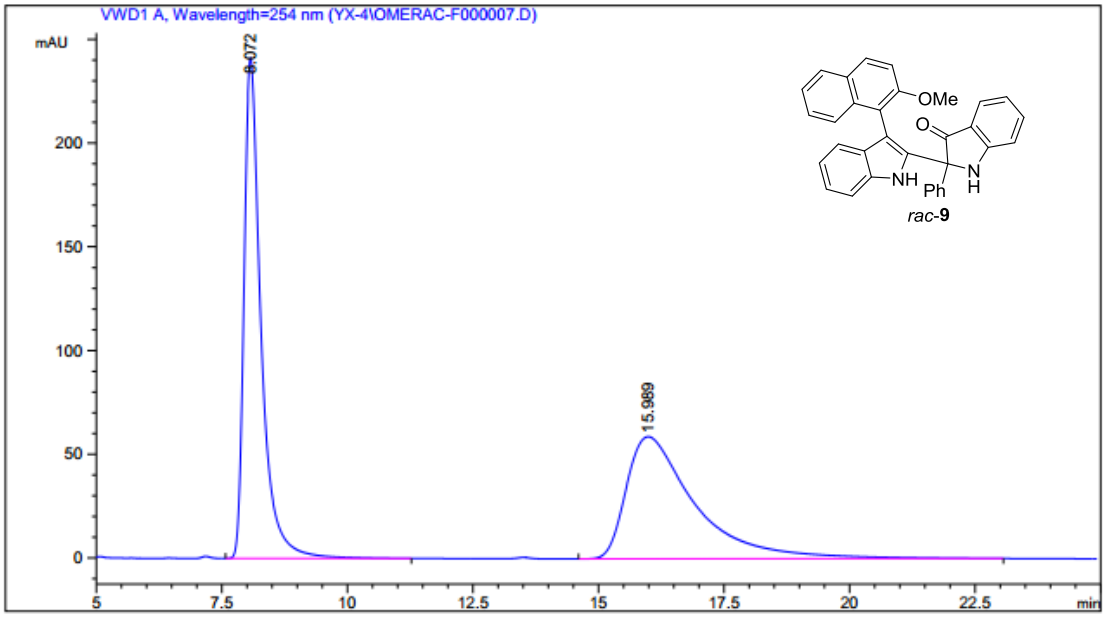
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.479	BB	0.3989	4.97197e4	1802.66101	92.8168
2	12.058	BB	1.2355	3847.86255	45.17378	7.1832



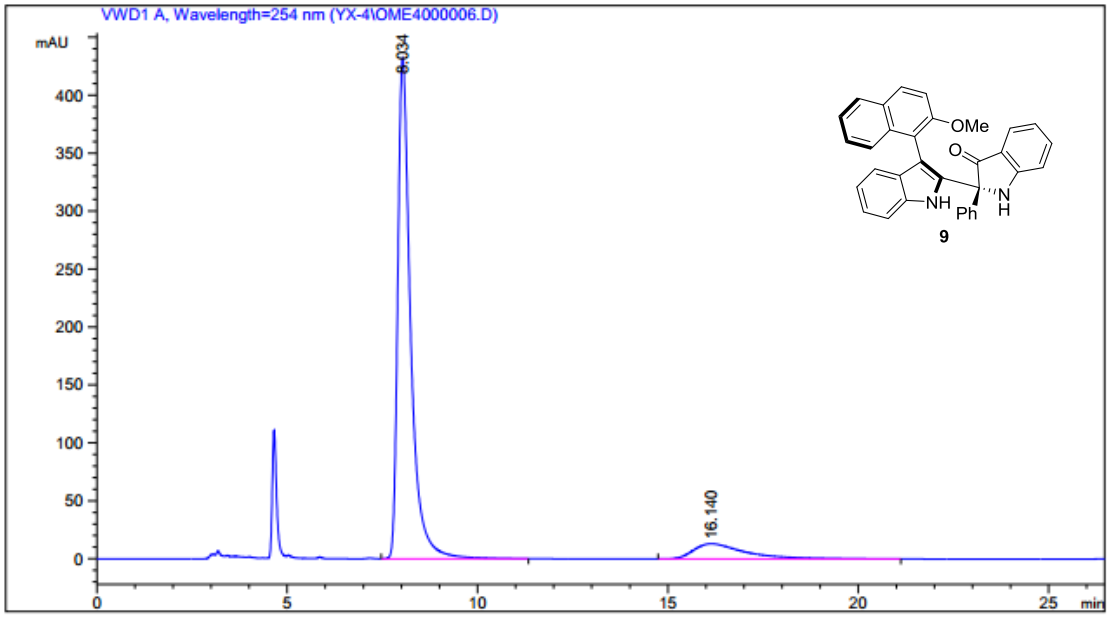
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.455	MM	0.2721	3351.22046	205.29593	50.0729
2	11.894	MM	0.4192	3341.46021	132.85701	49.9271



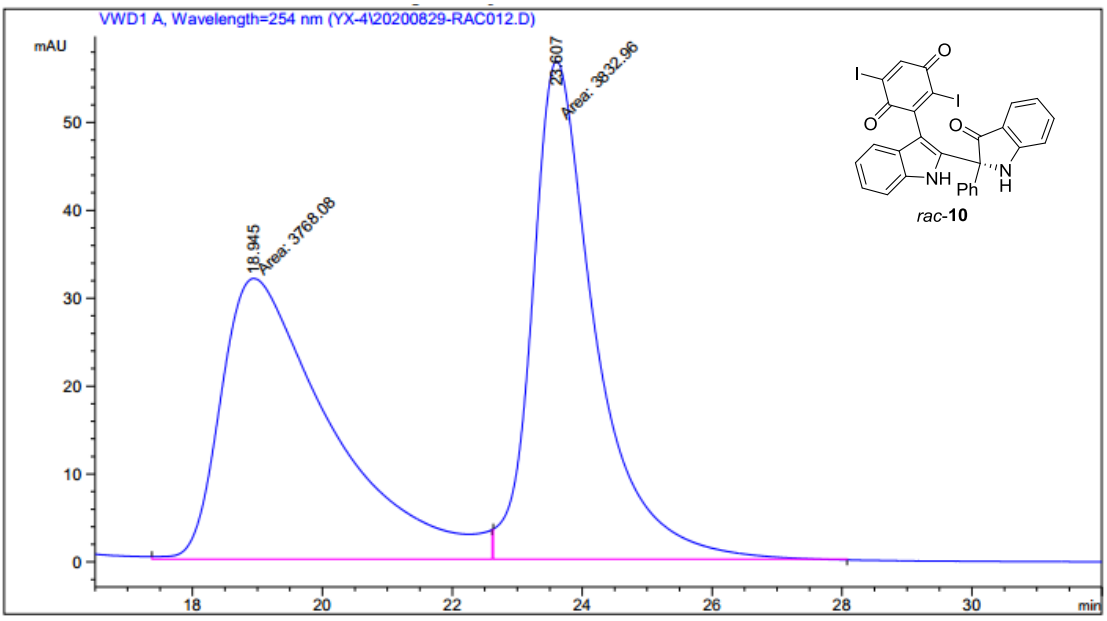
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.481	BB	0.2449	5177.96680	316.28656	49.4175
2	11.906	BB	0.3706	5300.04199	213.91086	50.5825



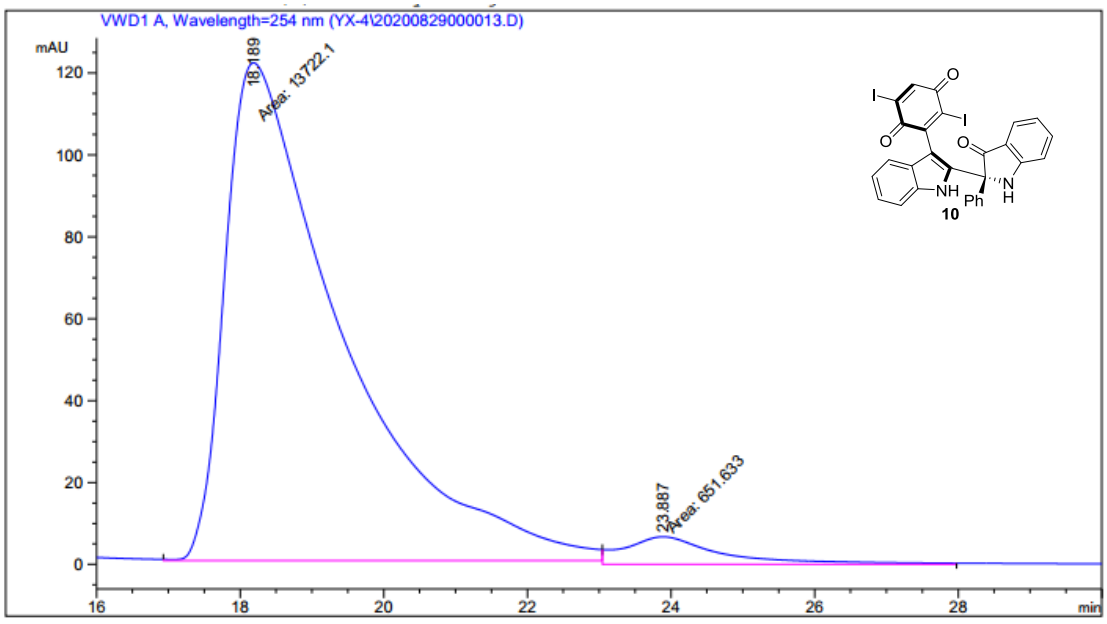
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.072	BB	0.3511	5695.37256	241.29538	50.4257
2	15.989	BB	1.3718	5599.20313	58.86565	49.5743



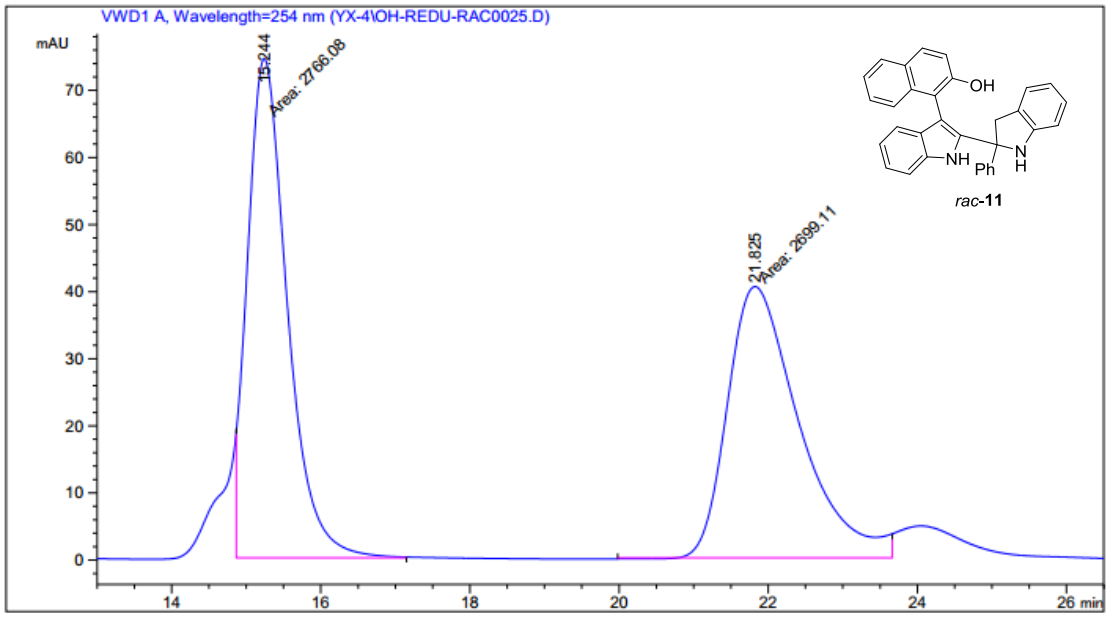
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.034	BB	0.3475	1.01216e4	432.20853	89.0331
2	16.140	BB	1.3230	1246.75842	13.09854	10.9669



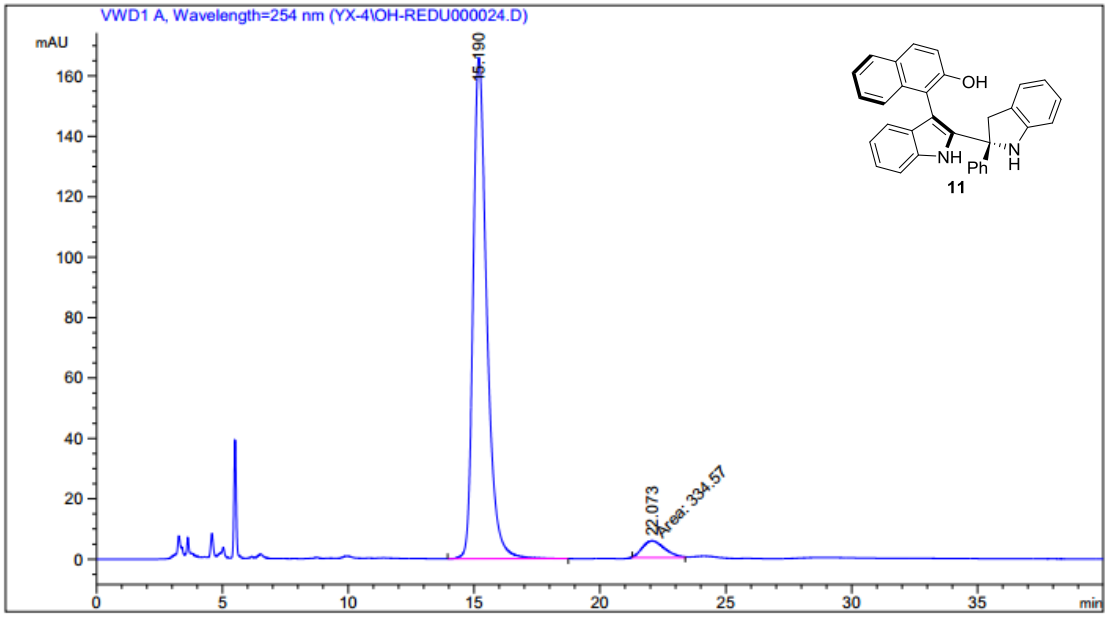
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.945	MM	1.9660	3768.07593	31.94295	49.5732
2	23.607	MM	1.1276	3832.95581	56.65447	50.4268



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.189	MM	1.8819	1.37221e4	121.52431	95.4665
2	23.887	MM	1.6105	651.63257	6.74360	4.5335

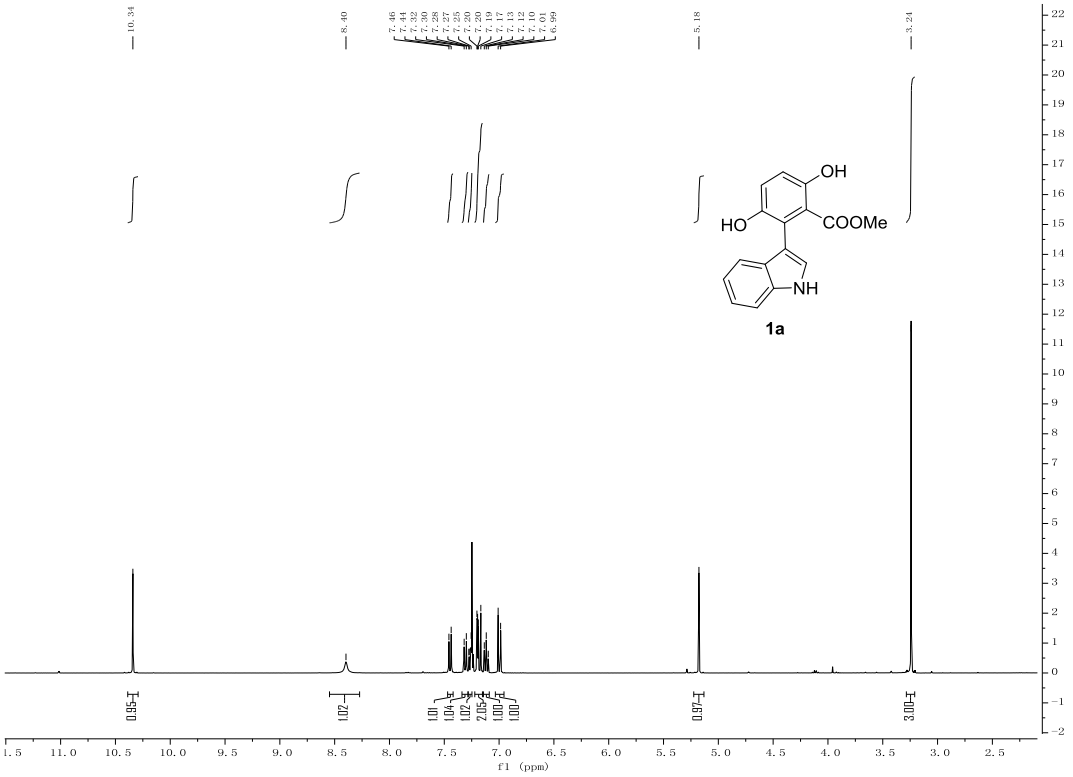


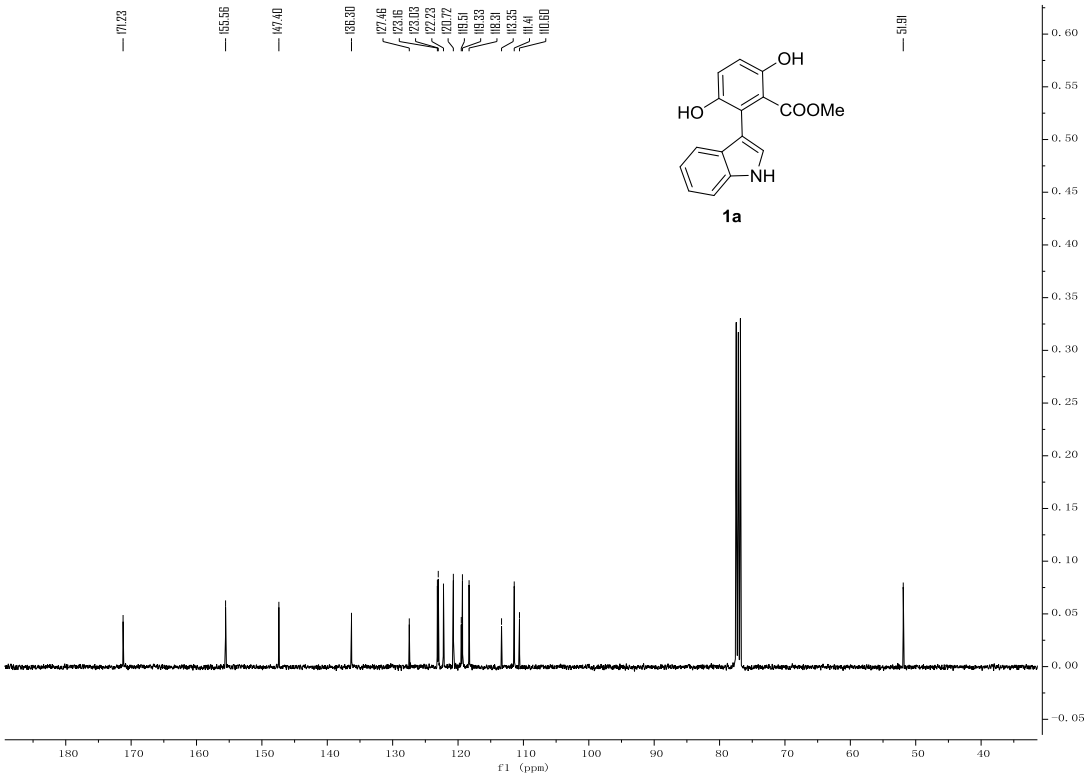
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.244	MM	0.6197	2766.08374	74.39885	50.6127
2	21.825	MM	1.1128	2699.11157	40.42588	49.3873

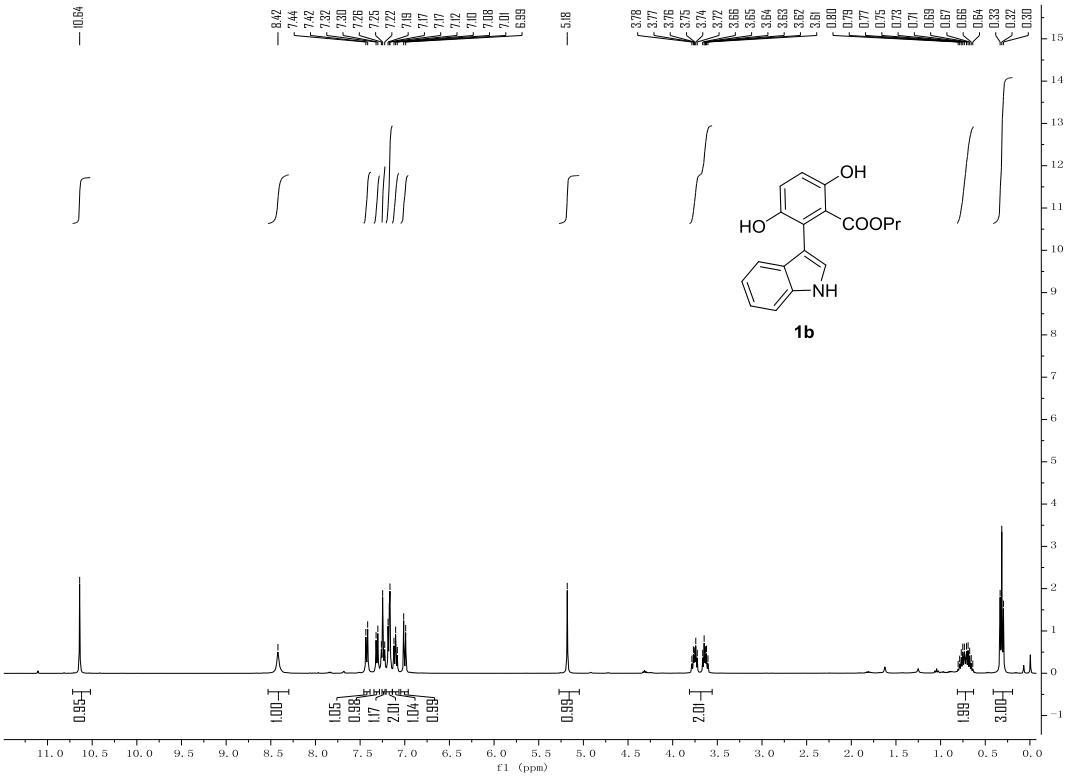


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.190	BB	0.5713	6238.75098	165.86638	94.9102
2	22.073	MM	1.0147	334.57040	5.49550	5.0898

15. NMR Spectra of 1a-1t, 5, 3a-3z, 3aa-3ak, 6, 9, 10, 11



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7.17
7.17
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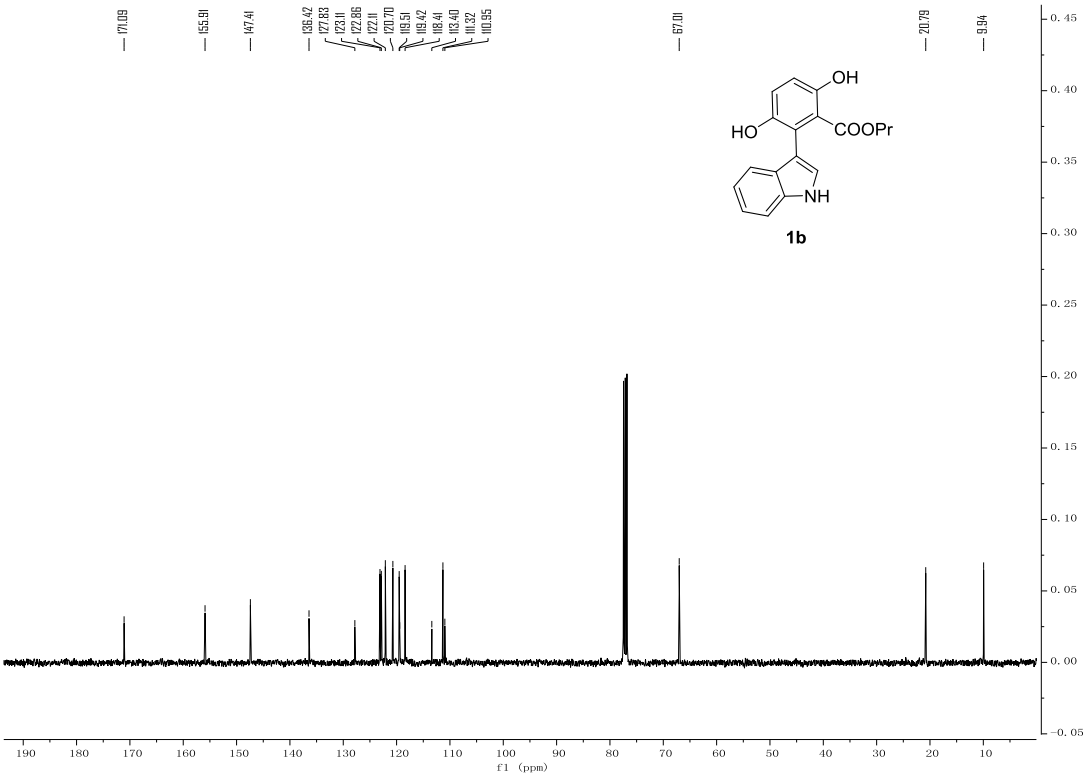
7.10
7.08
7.01
6.99
5.18
3.78
3.77
3.76
3.75
3.74
3.72
3.66
3.65
3.64
3.63
3.62
3.61
0.80
0.79
0.77
0.75
0.73
0.71
0.69
0.67
0.66
0.64
0.33
0.32
0.30
OH
HO
COOPr
NH
1b
0.95
1.00
1.05
0.98
1.17
2.01
1.04
0.99
0.99
2.01
1.99
3.00
f1 (ppm)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119.42
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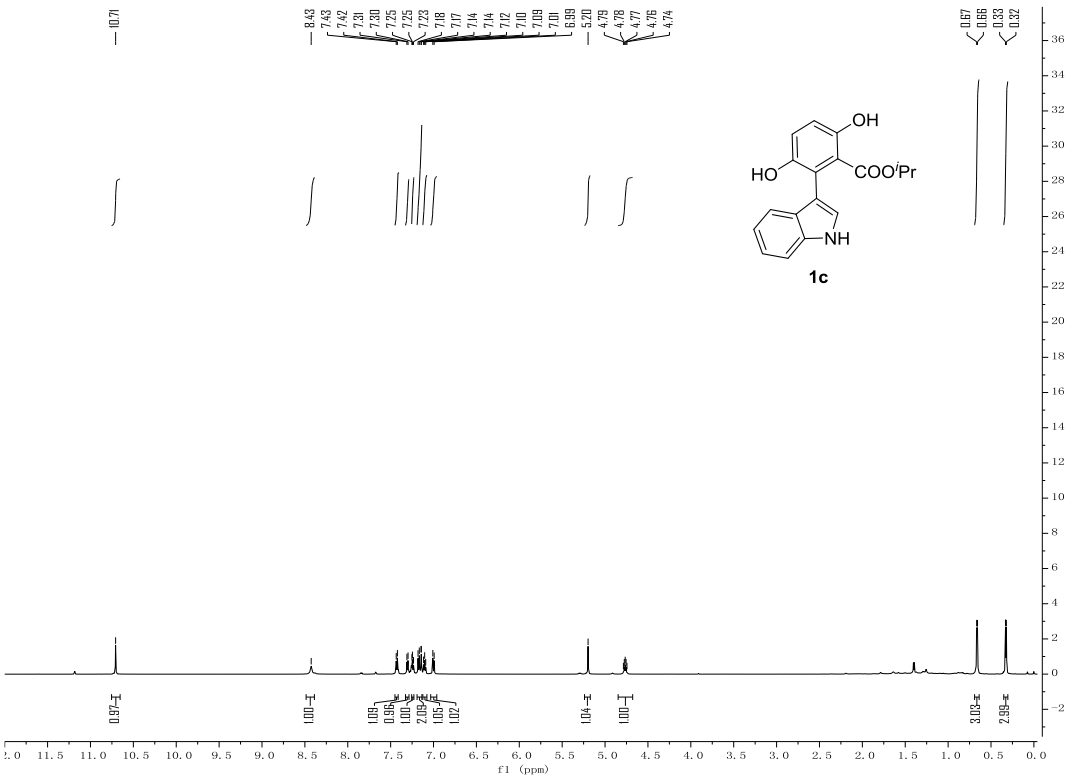
9.94
OH
HO
COOPr
NH
1b
f1 (ppm)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7.18
7.17
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7.12
7.10
7.09
7.01
6.99
5.20
4.79
4.78
4.77
4.76
4.74
0.87
0.66
0.33
0.32
OH
HO
COO^{i}Pr
NH
1c
0.97
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0.96
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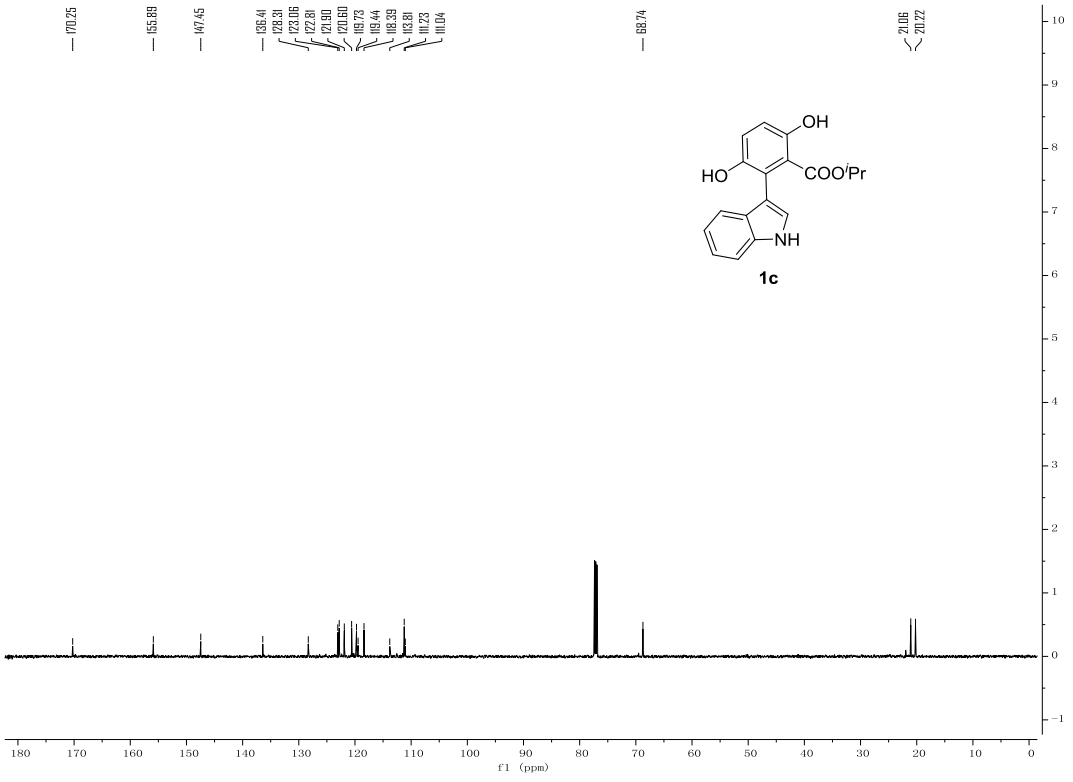
2.09
1.05
1.02
1.04
1.00
3.03
2.89
f1 (ppm)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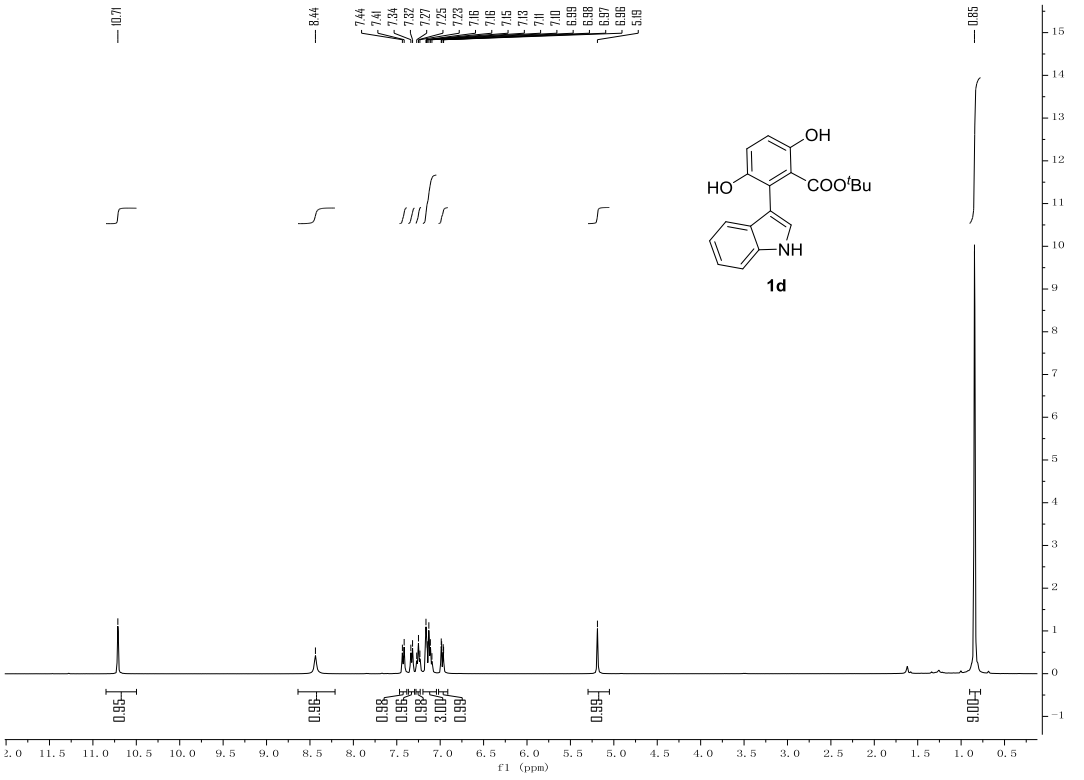
111.04
68.74
21.06
20.72
OH
HO
COO^{i}Pr
NH
1c
f1 (ppm)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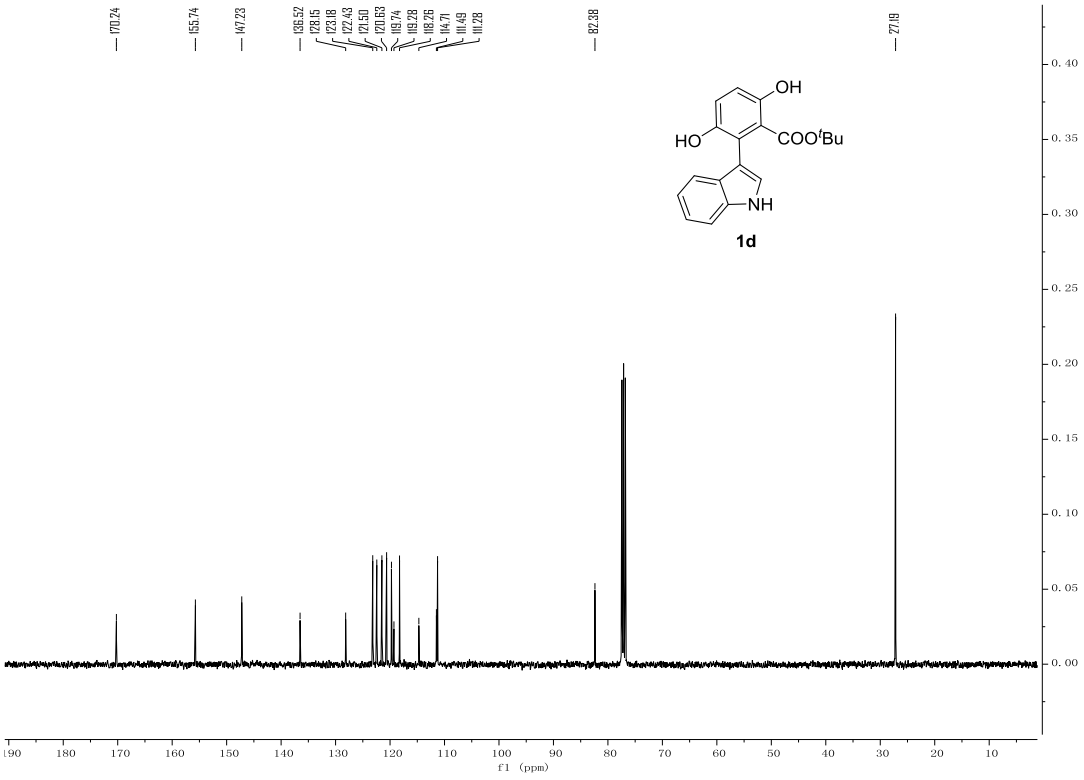
7.44
7.41
7.34
7.32
7.27
7.25
7.23
7.16
7.16
7.15
7.13
7.11
7.10
6.99
6.98
6.97
6.96
5.19
0.85
OH
HO
COO^{t}Bu
NH
1d
0.95
0.96
0.98
0.96
0.98
3.00
0.99
0.99
9.00
f1 (ppm)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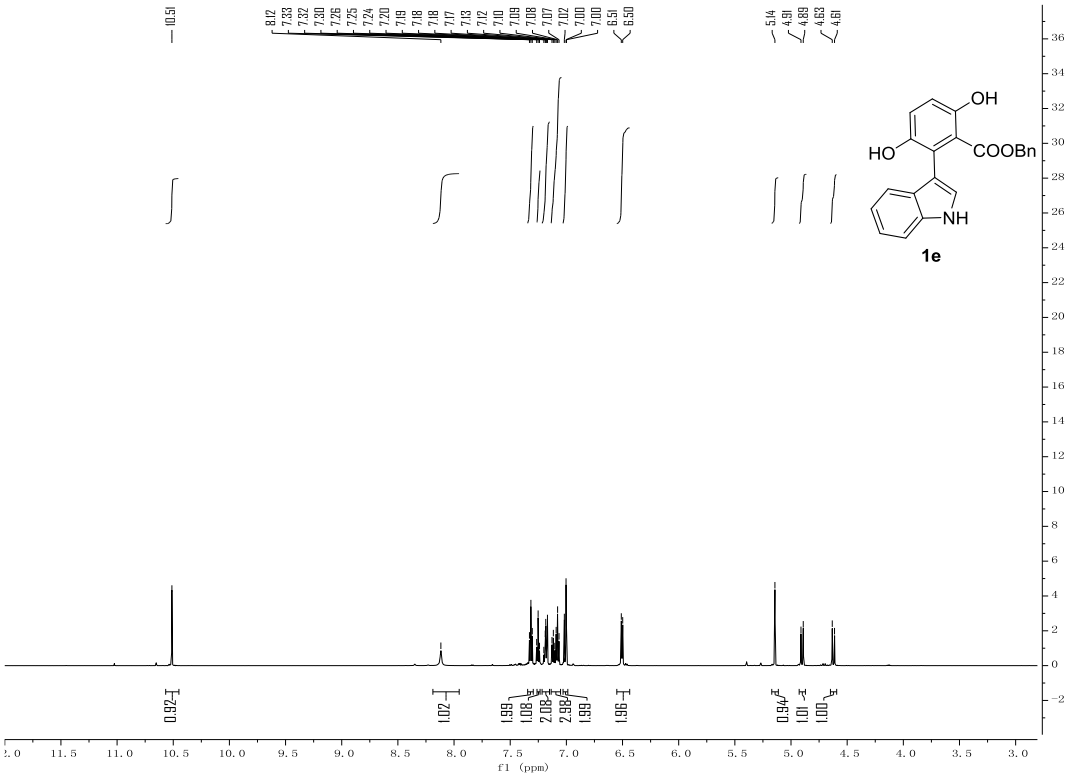
155.74
147.23
135.52
128.15
123.18
122.43
121.50
120.63
119.74
119.28
118.26
114.71
111.49
111.28
82.38
27.19
OH
HO
COO^{t}Bu
NH
1d
f1 (ppm)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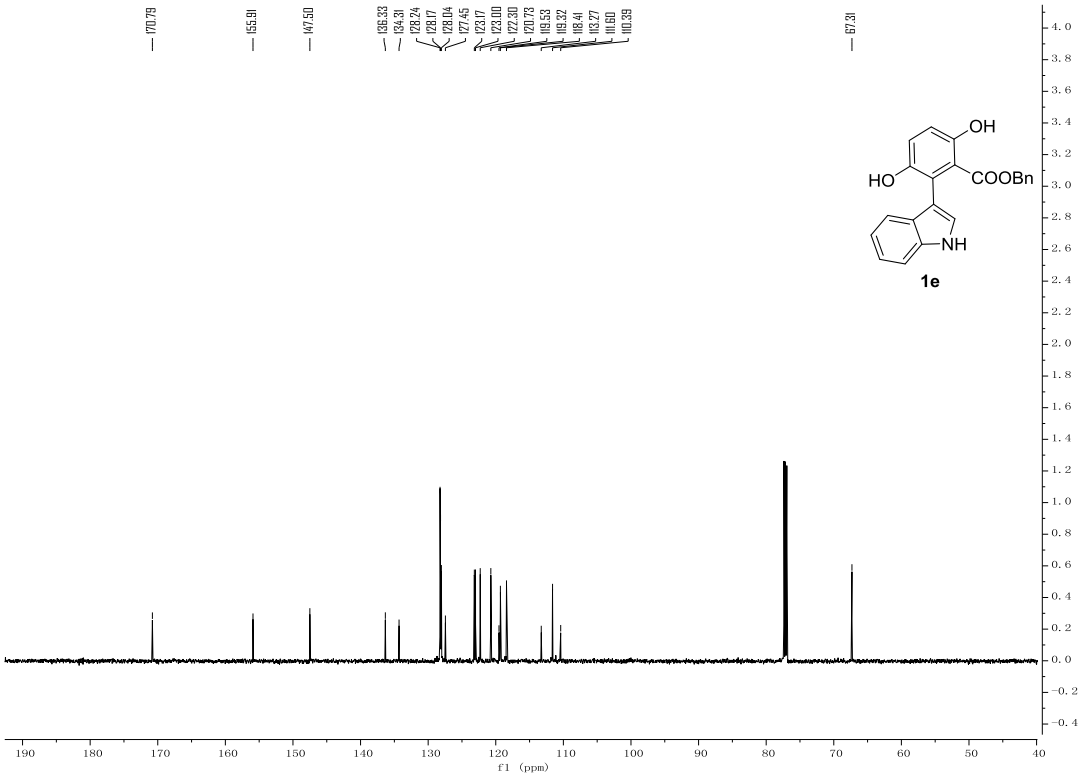
7.24
7.20
7.19
7.18
7.18
7.17
7.13
7.12
7.10
7.09
7.08
7.07
7.02
7.00
7.00
6.51
6.50
5.14
4.91
4.89
4.63
4.61
OH
HO
COOBn
NH
1e
0.32
1.07
1.99
1.08
2.08
2.98
1.99
1.96
0.94
1.01
1.00
f1 (ppm)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128.04
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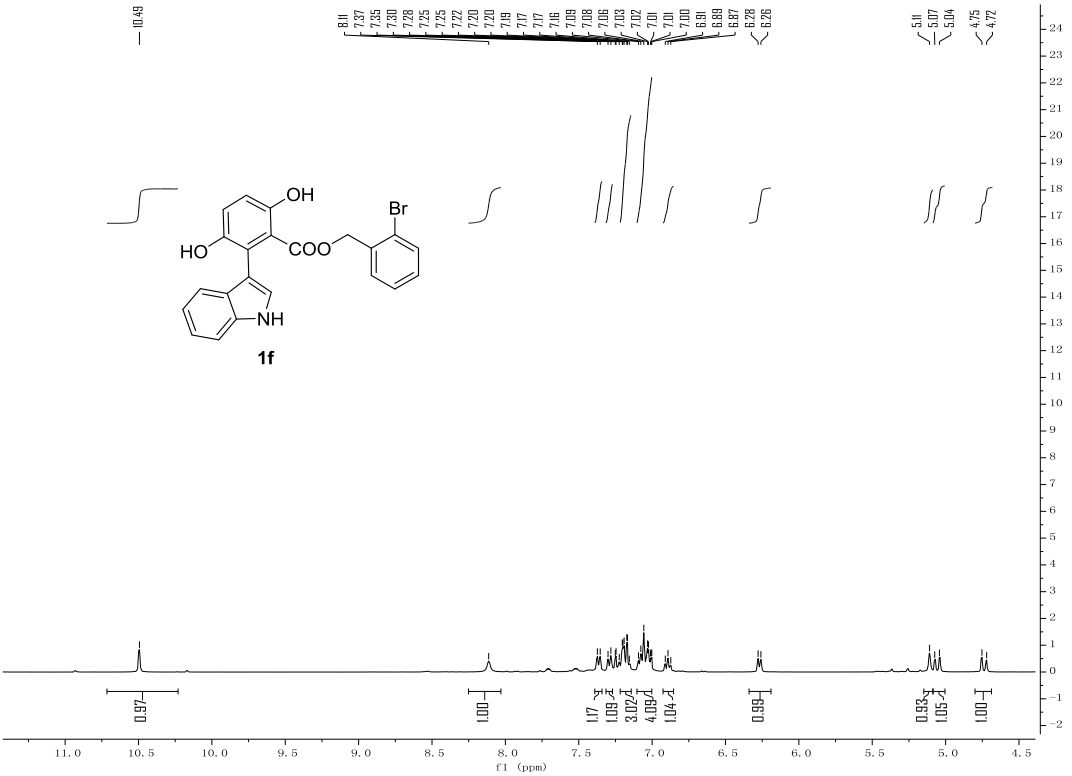
123.17
123.00
122.30
120.73
119.53
119.32
118.41
113.27
111.60
110.39
67.31
OH
HO
COOBn
NH
1e
f1 (ppm)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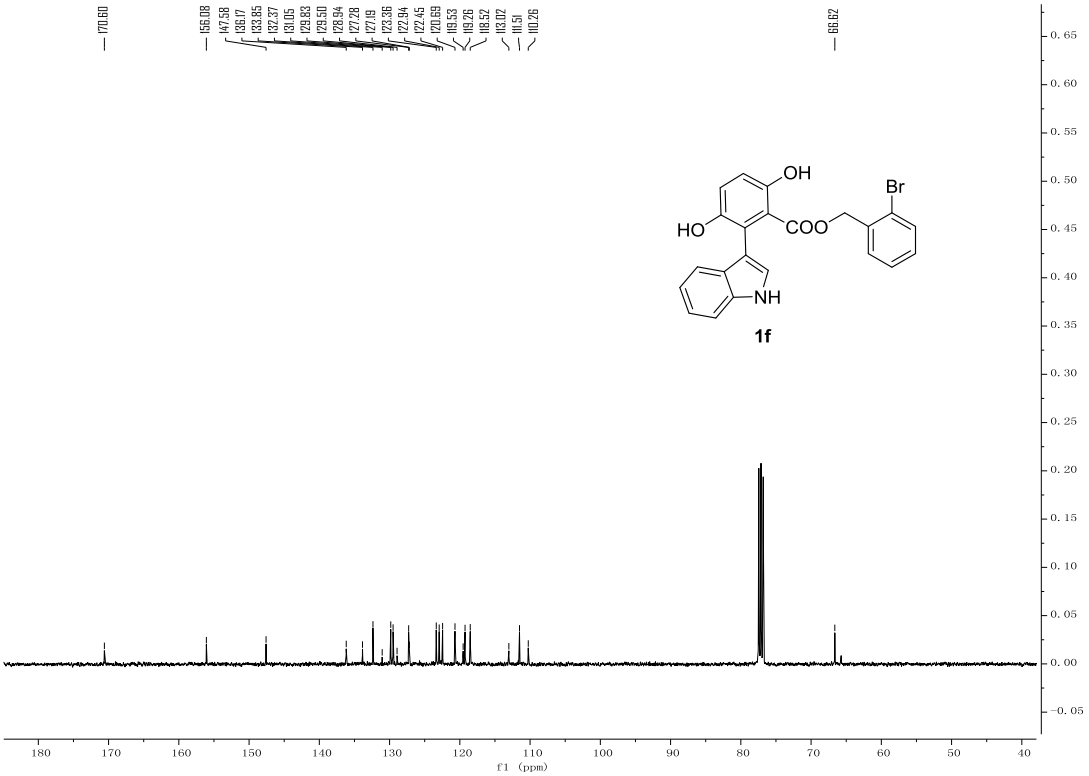
7.28
7.25
7.25
7.22
7.20
7.20
7.19
7.17
7.17
7.16
7.09
7.08
7.06
7.03
7.02
7.01
7.01
7.00
6.91
6.89
6.87
6.78
6.76
5.11
5.07
5.04
4.75
4.72
OH
HO
COO
Br
NH
1f
0.97
1.00
1.17
1.09
3.02
4.09
1.04
0.99
0.93
1.05
1.00
f1 (ppm)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129.83
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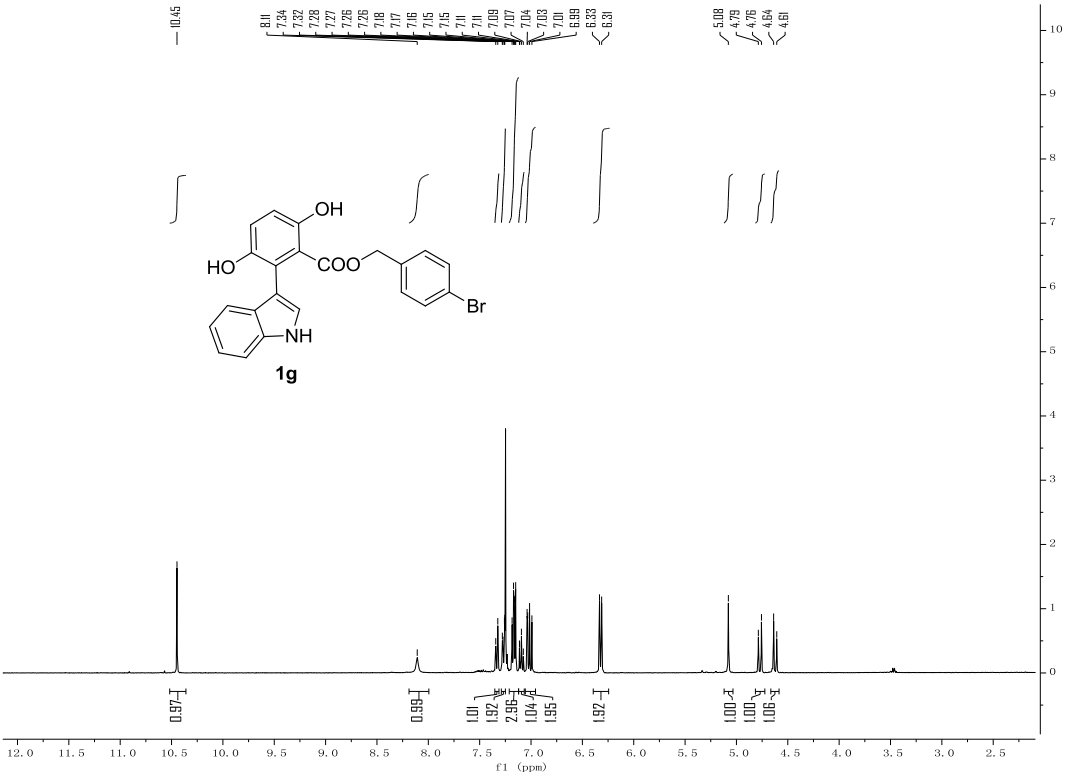
128.94
127.28
127.19
123.38
122.94
122.45
120.69
119.53
119.26
118.52
113.02
111.51
110.26
66.62
OH
HO
COO
Br
NH
1f
f1 (ppm)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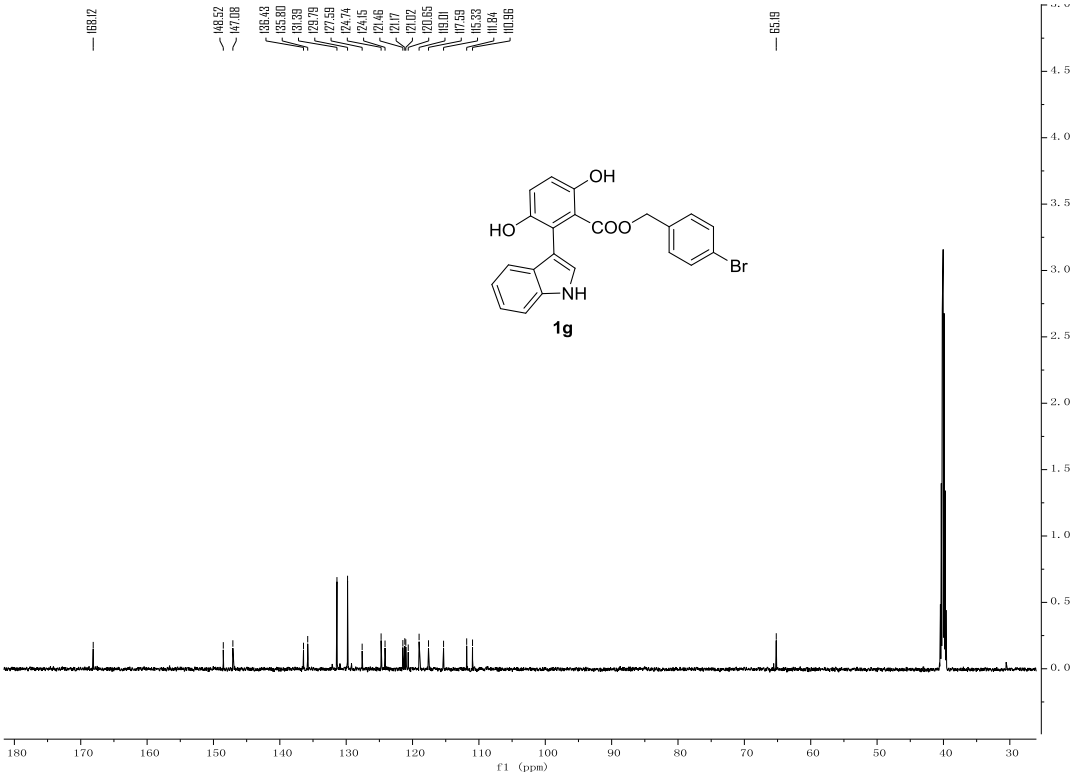
7.27
7.26
7.25
7.18
7.17
7.16
7.15
7.15
7.11
7.11
7.09
7.07
7.04
7.03
7.01
6.99
6.33
6.31
5.08
4.79
4.76
4.64
4.61
OH
HO
COO
Br
NH
1g
0.97
0.99
1.01
1.92
2.96
1.04
1.95
1.92
1.00
1.00
1.06
f1 (ppm)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148.52
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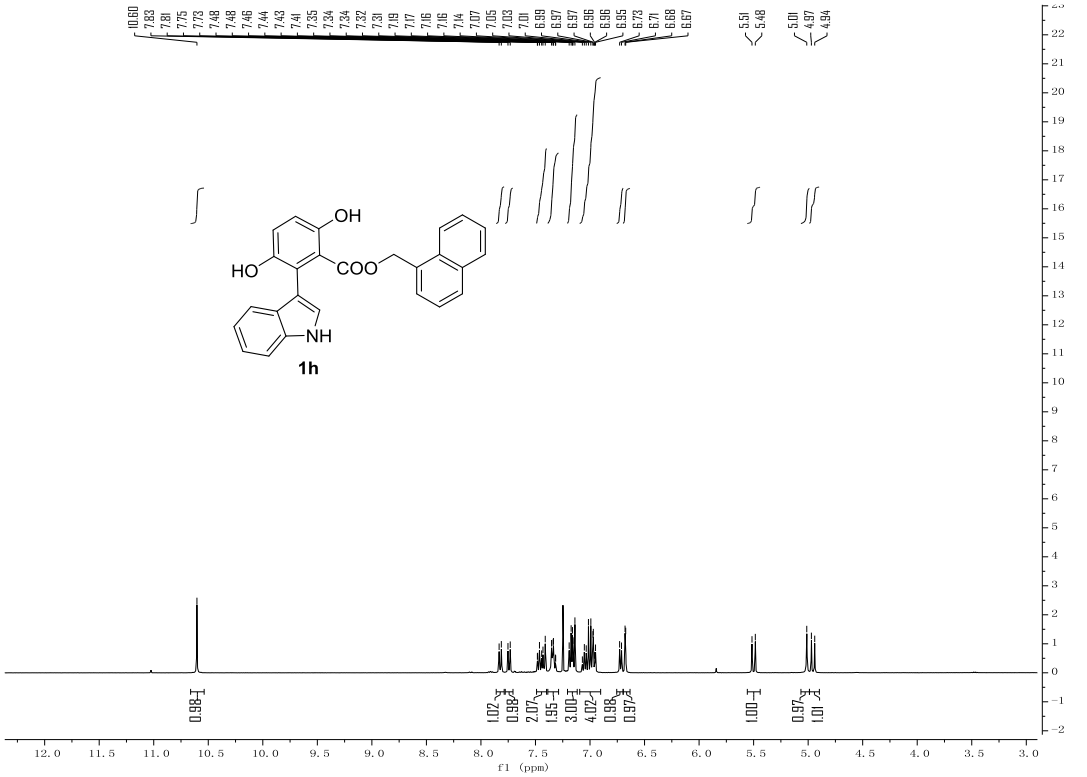
131.39
129.79
127.59
124.74
124.15
121.46
121.17
121.02
120.65
119.01
117.59
115.33
111.84
110.96
65.19
OH
HO
COO
Br
NH
1g
f1 (ppm)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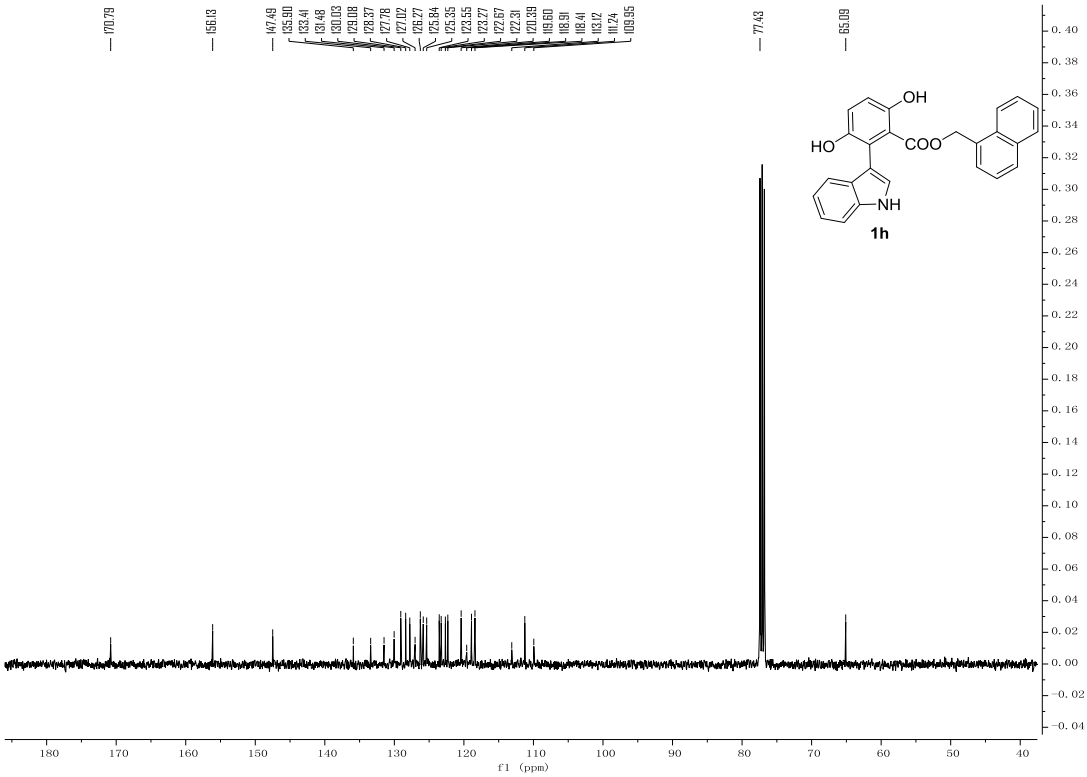
7.73
7.48
7.48
7.46
7.44
7.43
7.41
7.35
7.34
7.34
7.32
7.31
7.19
7.17
7.16
7.16
7.14
7.07
7.05
7.03
7.01
6.99
6.97
6.97
6.96
6.96
6.95
6.73
6.71
6.68
6.67
5.51
5.48
5.01
4.97
4.94
OH
HO
COO
NH
1h
0.98
1.02
0.99
2.07
1.95
3.00
4.02
0.98
0.97
1.00
0.97
1.01
f1 (ppm)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156.13
147.49
135.90
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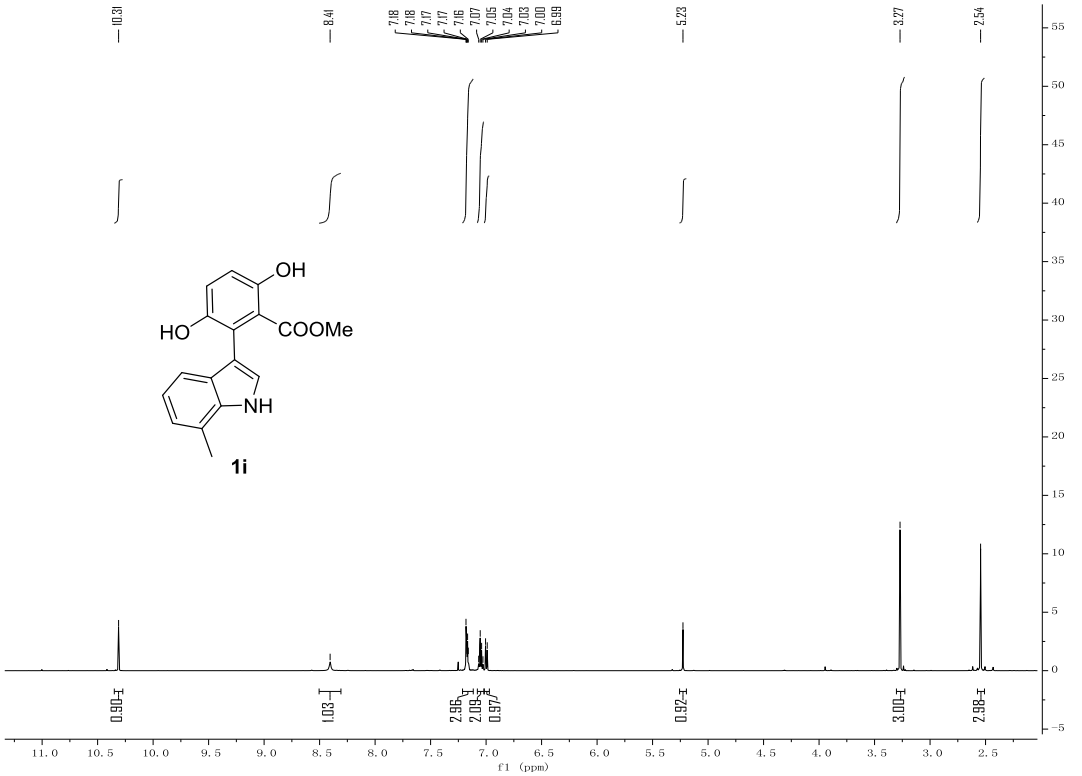
131.48
130.03
129.08
128.37
127.78
127.02
126.27
125.84
125.35
123.55
123.27
122.67
122.31
120.93
119.60
118.91
118.41
113.12
111.24
109.95
77.43
65.09
OH
HO
COO
NH
1h
f1 (ppm)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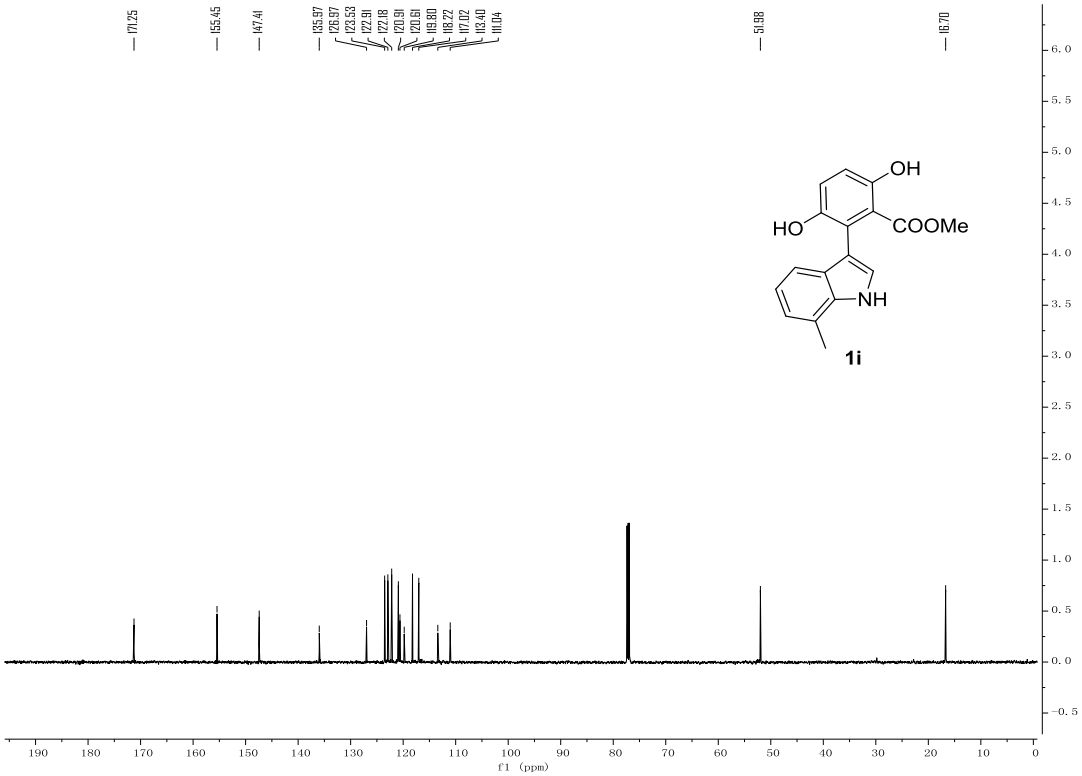
8.41
7.18
7.18
7.17
7.17
7.16
7.07
7.05
7.04
7.03
7.00
6.99
5.23
3.27
2.54
OH
HO
COOMe
NH
1i
0.90
1.03
2.95
2.09
0.97
0.92
3.00
2.98
f1 (ppm)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155.45
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135.97
126.97
123.53
122.91
122.18
120.91
120.61
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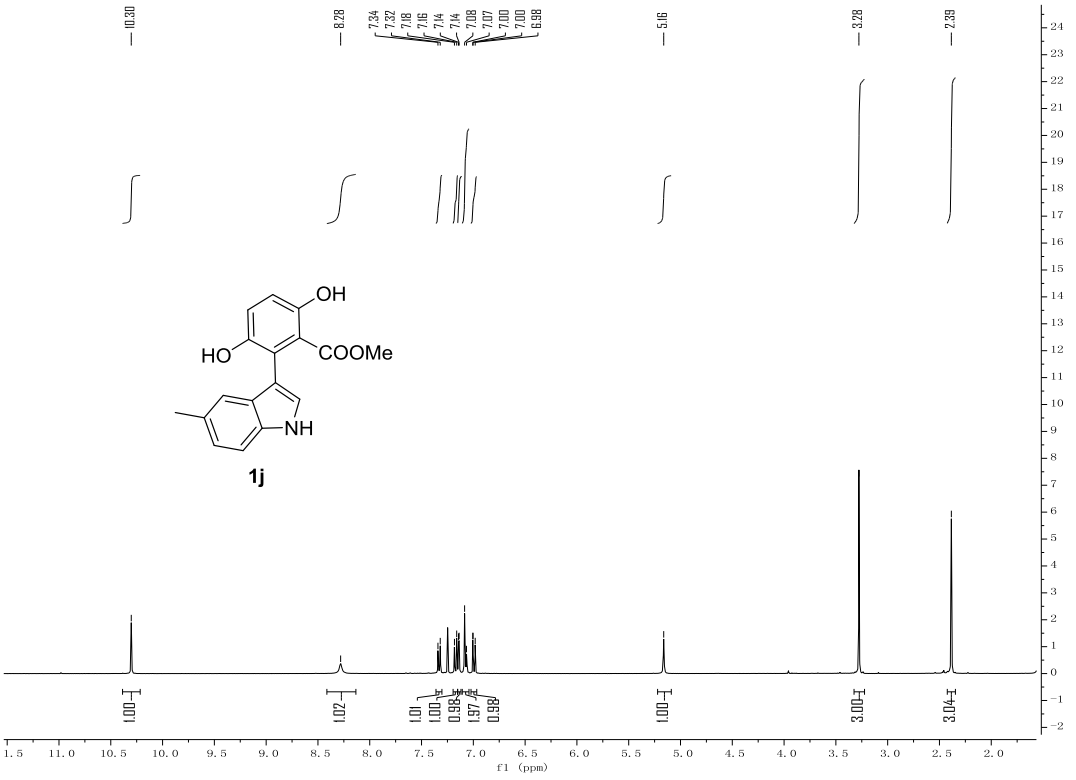
118.22
117.02
113.40
111.04
51.98
16.70
OH
HO
COOMe
NH
1i
f1 (ppm)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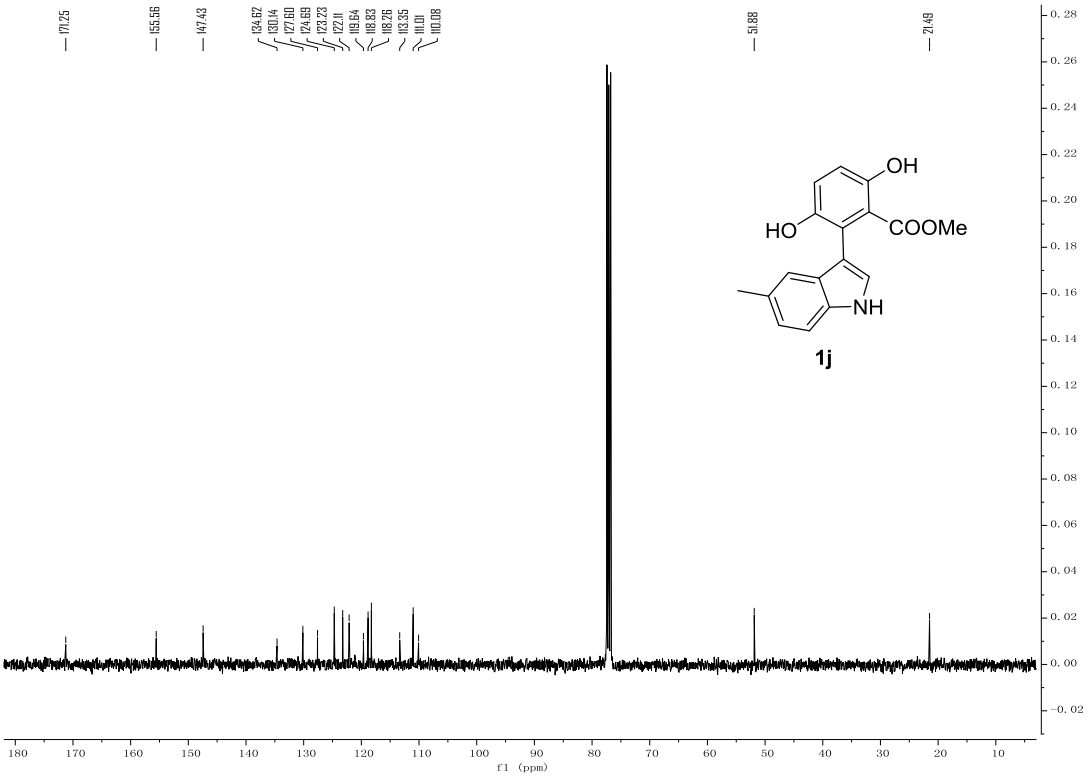
8.228
7.34
7.32
7.18
7.16
7.14
7.14
7.08
7.07
7.00
7.00
6.98
5.161
3.228
2.389
OH
HO
COOMe
NH
1j
1.00
1.02
1.01
1.00
0.98
1.97
0.98
1.00
3.00
3.04
f1 (ppm)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147.43
134.62
130.14
127.60
124.69
123.23
122.11
119.64
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111.01
110.08
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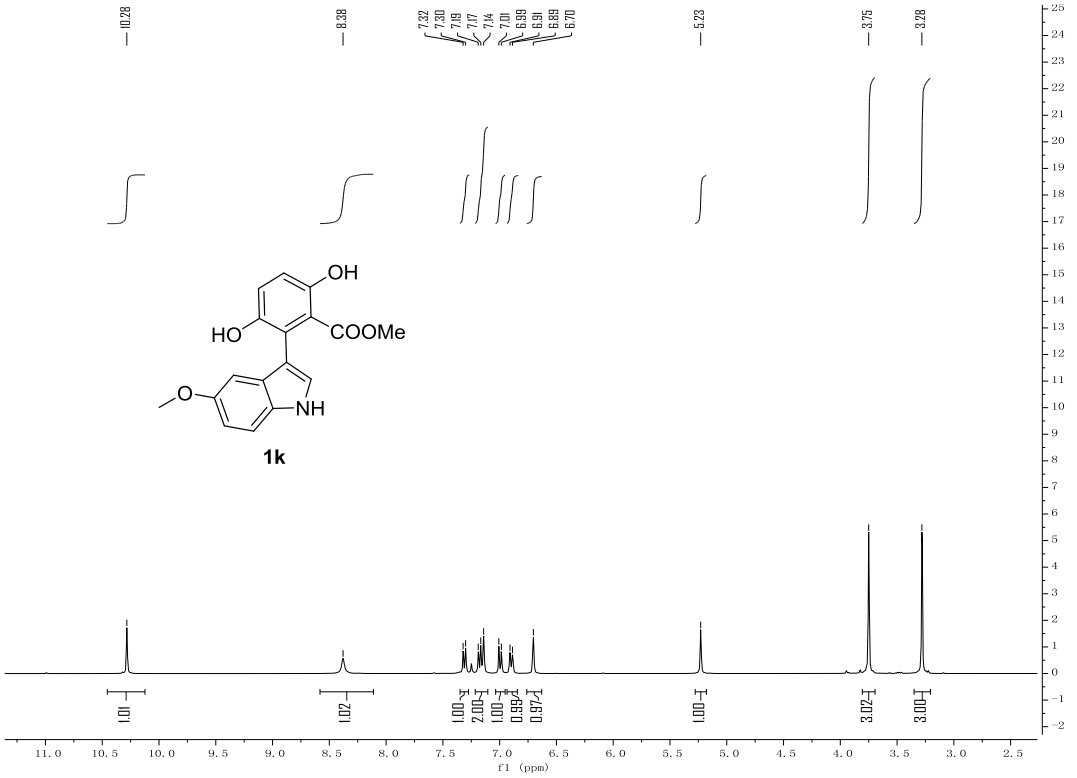
21.449
OH
HO
COOMe
NH
1j
f1 (ppm)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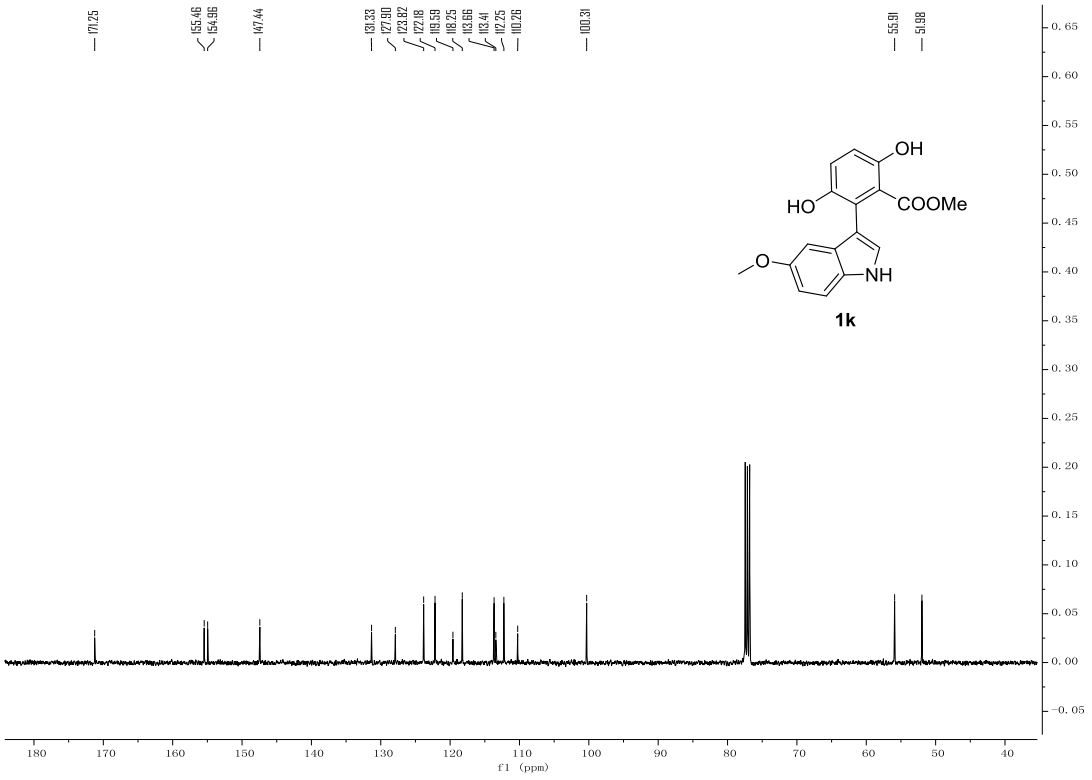
8.38
7.32
7.30
7.19
7.17
7.14
7.01
6.93
6.91
6.89
6.70
5.23
3.75
3.28
OH
HO
COOMe
O
NH
1k
1.01
1.02
1.00
2.05
1.00
0.99
0.97
1.00
3.02
3.00
f1 (ppm)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154.95
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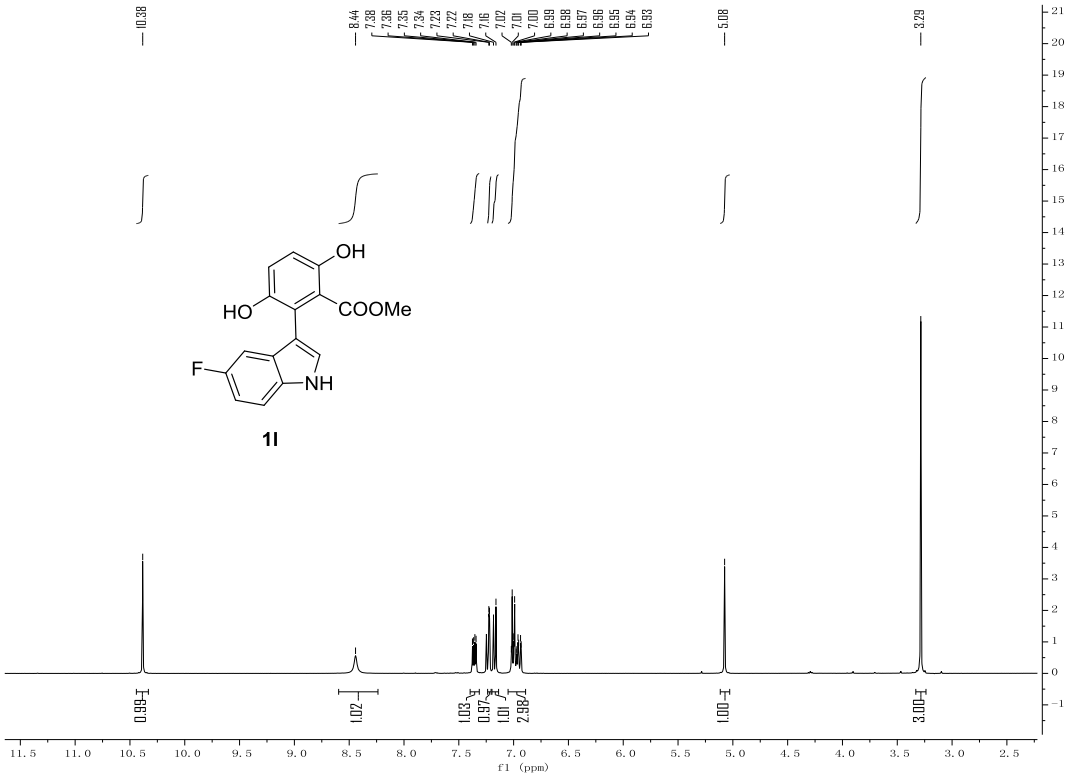
127.90
123.82
122.18
119.59
118.25
113.66
113.41
112.25
110.26
100.31
55.91
51.98
OH
HO
COOMe
O
NH
1k
f1 (ppm)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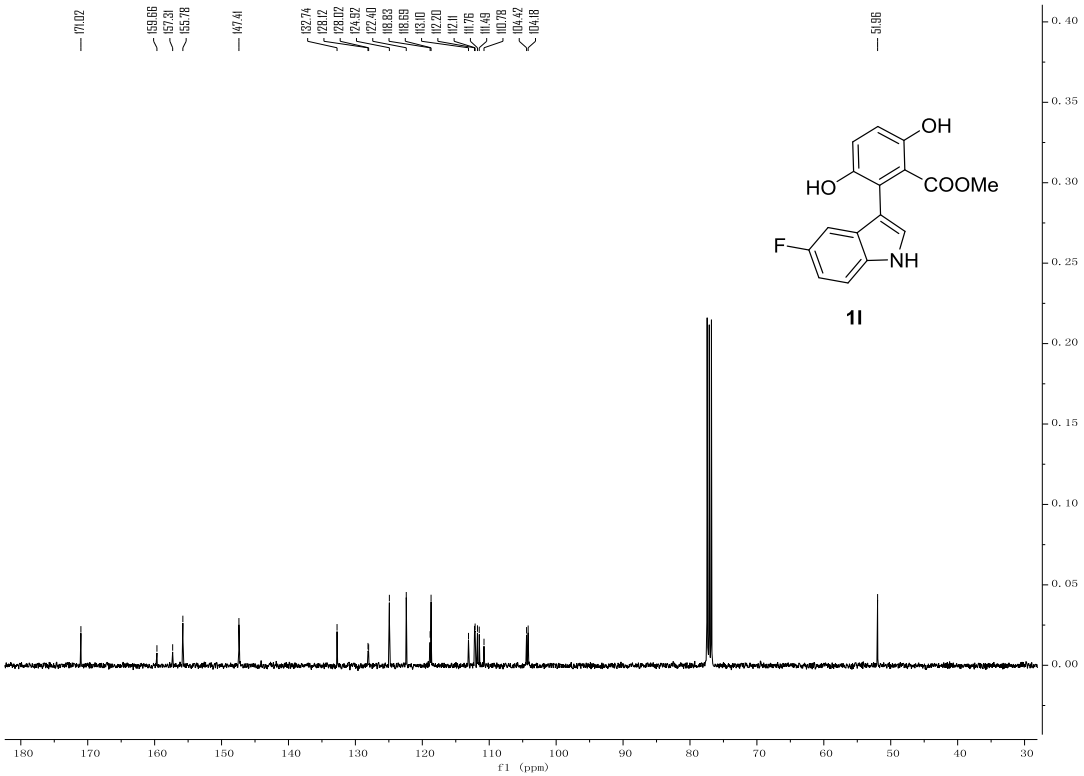
8.44
7.38
7.36
7.35
7.34
7.23
7.22
7.18
7.16
7.02
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.93
5.08
3.29
OH
HO
COOMe
F
NH
1I
0.99
1.02
1.03
0.97
1.01
2.98
1.00
3.00
f1 (ppm)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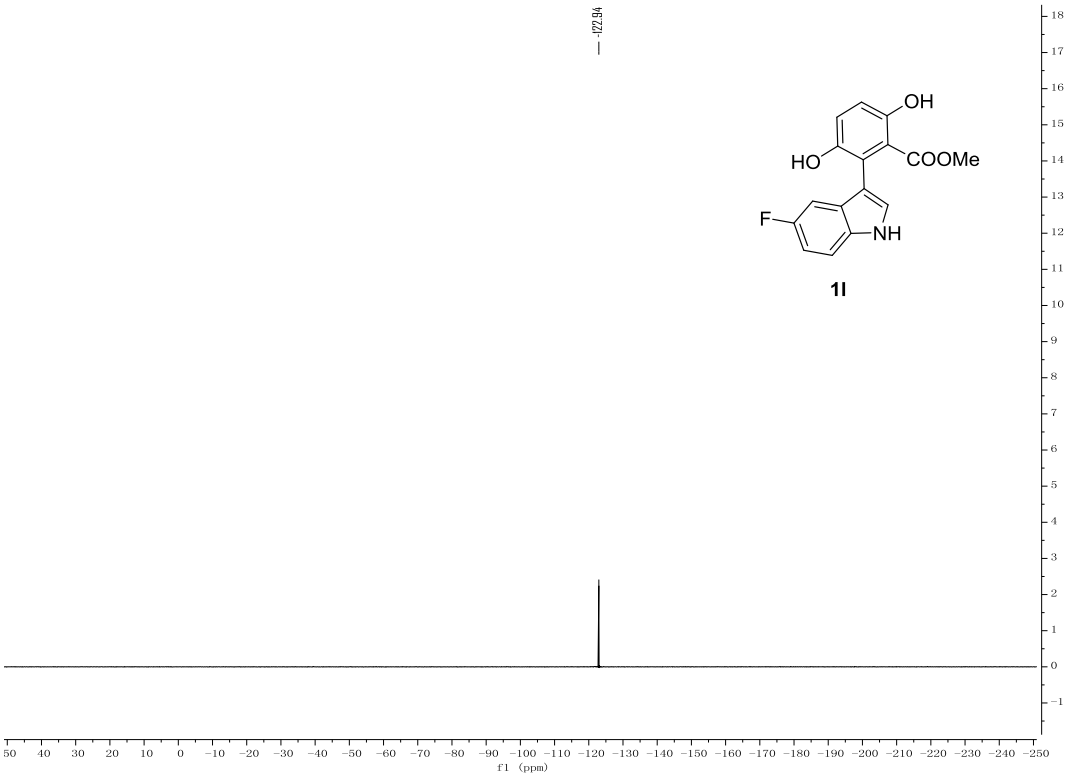
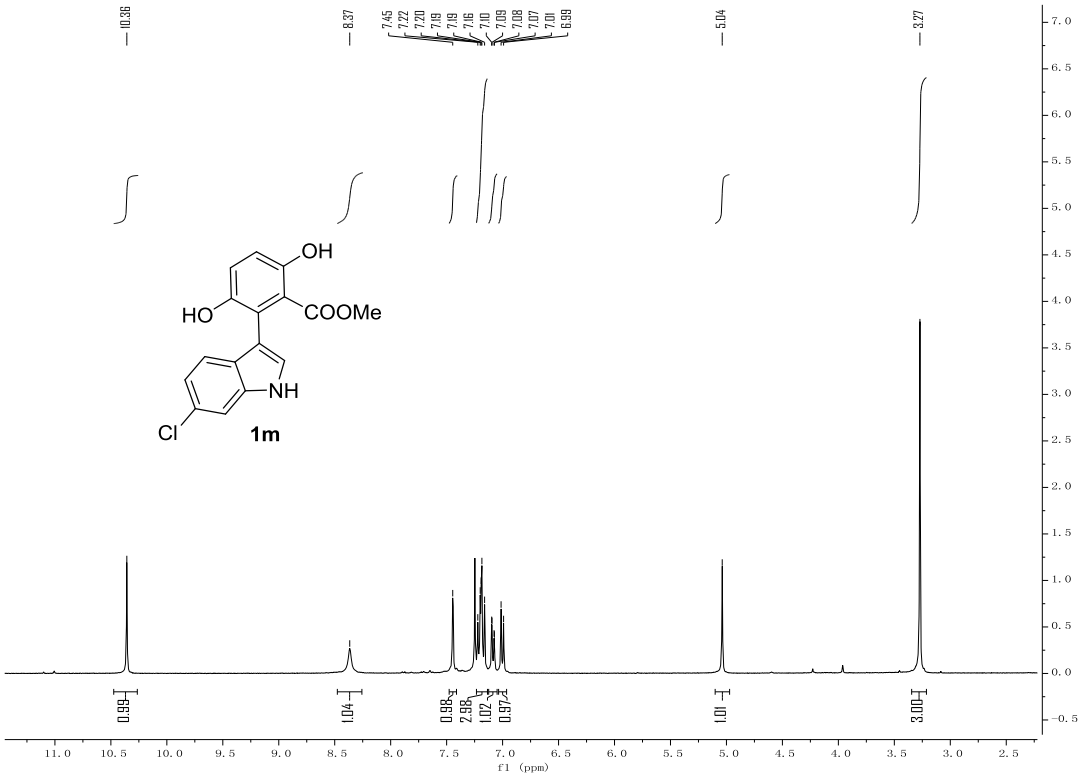
159.66
157.31
155.78
147.41
132.74
128.12
124.02
124.92
122.40
118.83
118.69
113.10
112.20
112.11
111.76
111.49
110.78
104.42
104.18
51.96
OH
HO
COOMe
F
NH
1I
f1 (ppm)


-122.94
OH
HO
COOMe
F
NH
1l
18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250
f1 (ppm)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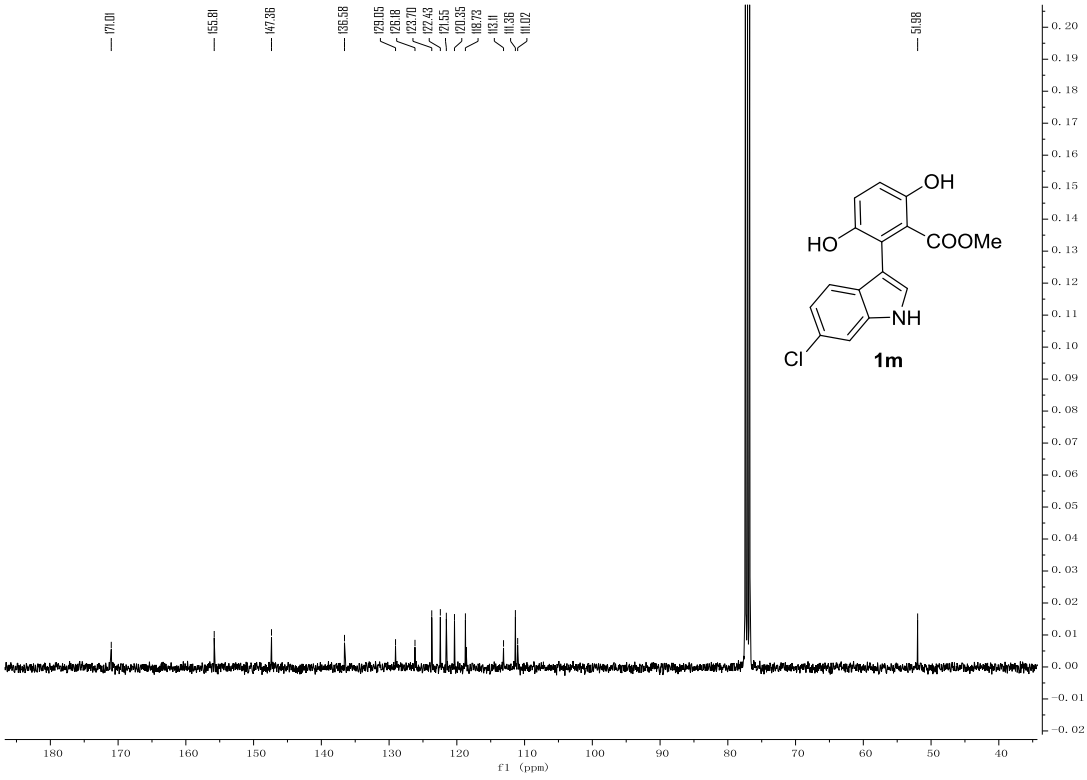
7.45
7.22
7.20
7.18
7.19
7.16
7.10
7.09
7.08
7.07
7.01
6.99
5.04
3.27
OH
HO
COOMe
NH
Cl
1m
0.99
1.04
0.98
2.98
1.02
0.97
1.01
3.00
f1 (ppm)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136.58
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126.18
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122.43
121.55
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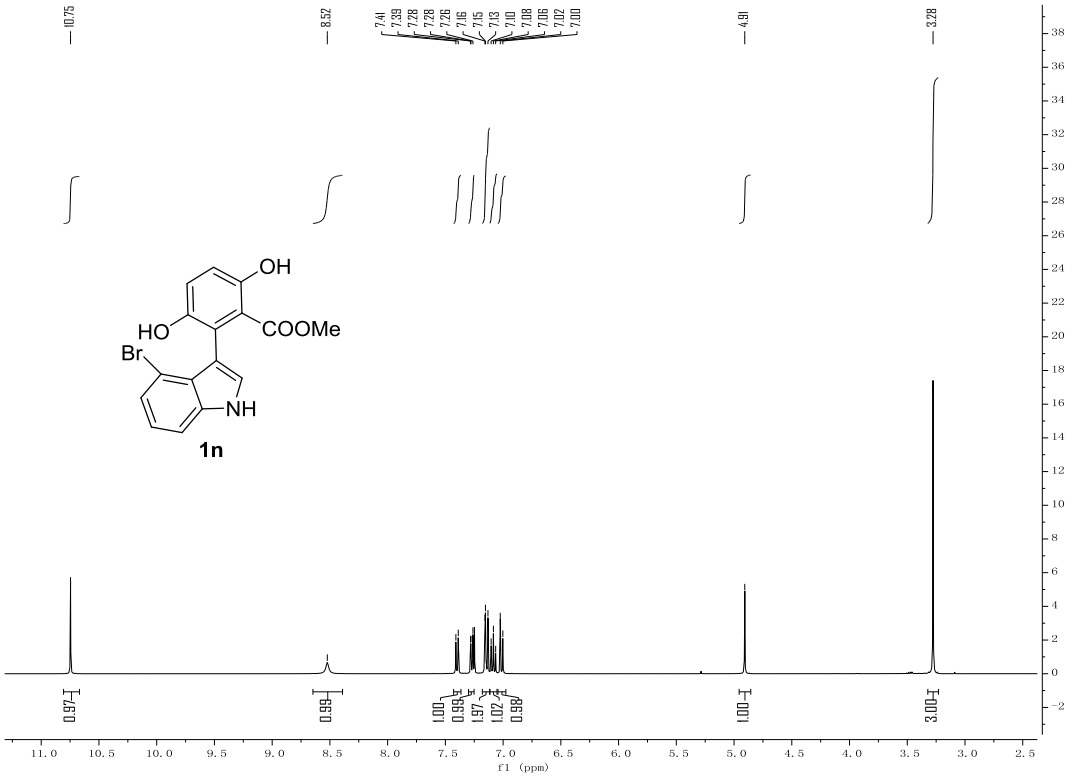
113.11
111.36
111.02
51.98
OH
HO
COOMe
NH
Cl
1m
f1 (ppm)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7.28
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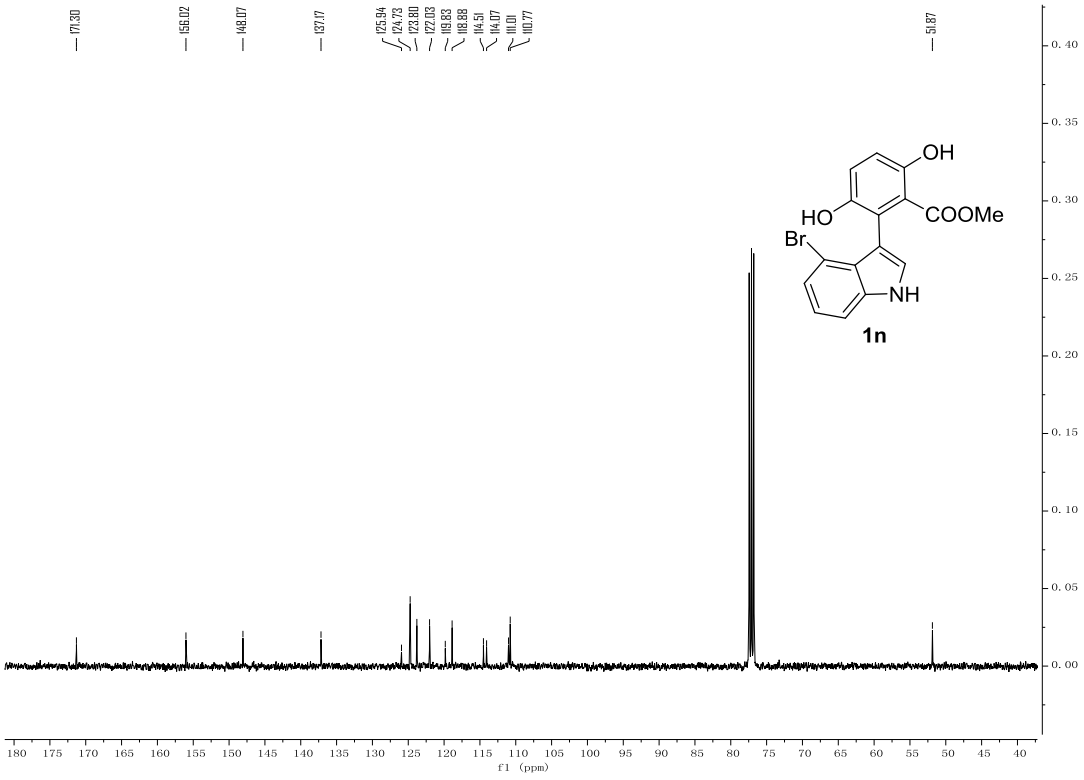
7.26
7.16
7.15
7.13
7.10
7.08
7.06
7.02
7.00
4.91
3.28
OH
HO
COOMe
Br
NH
1n
0.97
0.99
1.00
0.99
1.97
1.02
0.98
1.00
3.00
f1 (ppm)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156.02
148.07
137.17
125.94
124.73
123.80
122.03
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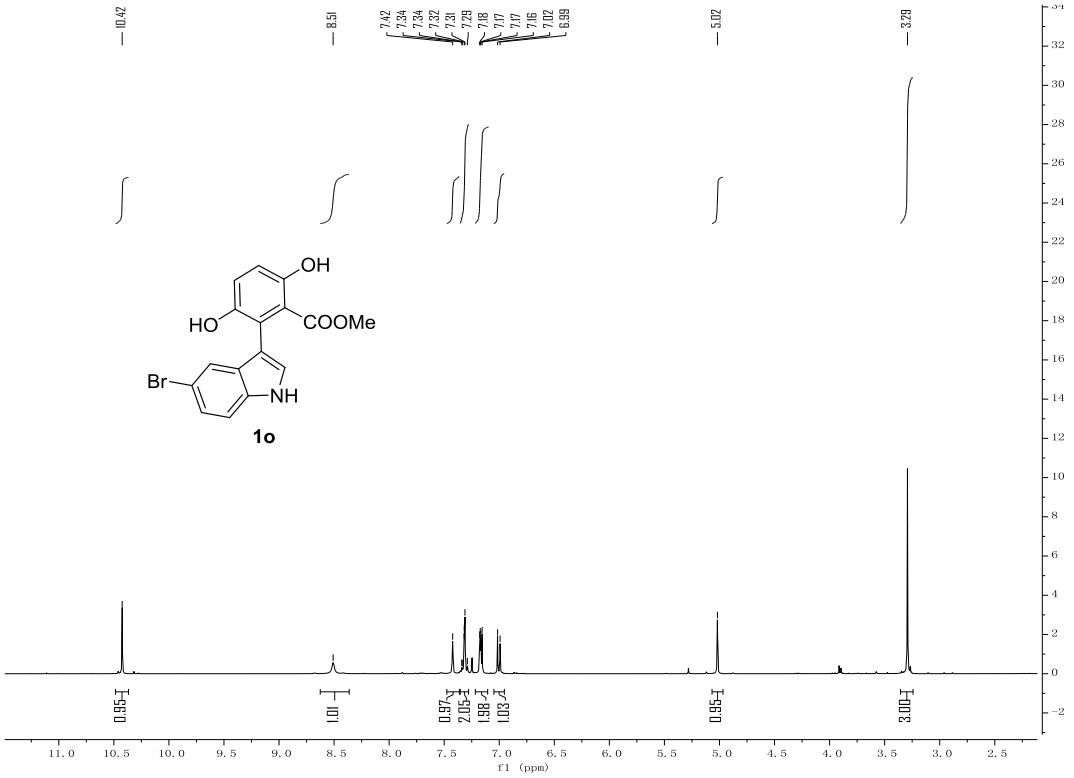
114.07
111.01
110.77
51.87
OH
HO
COOMe
Br
NH
1n
f1 (ppm)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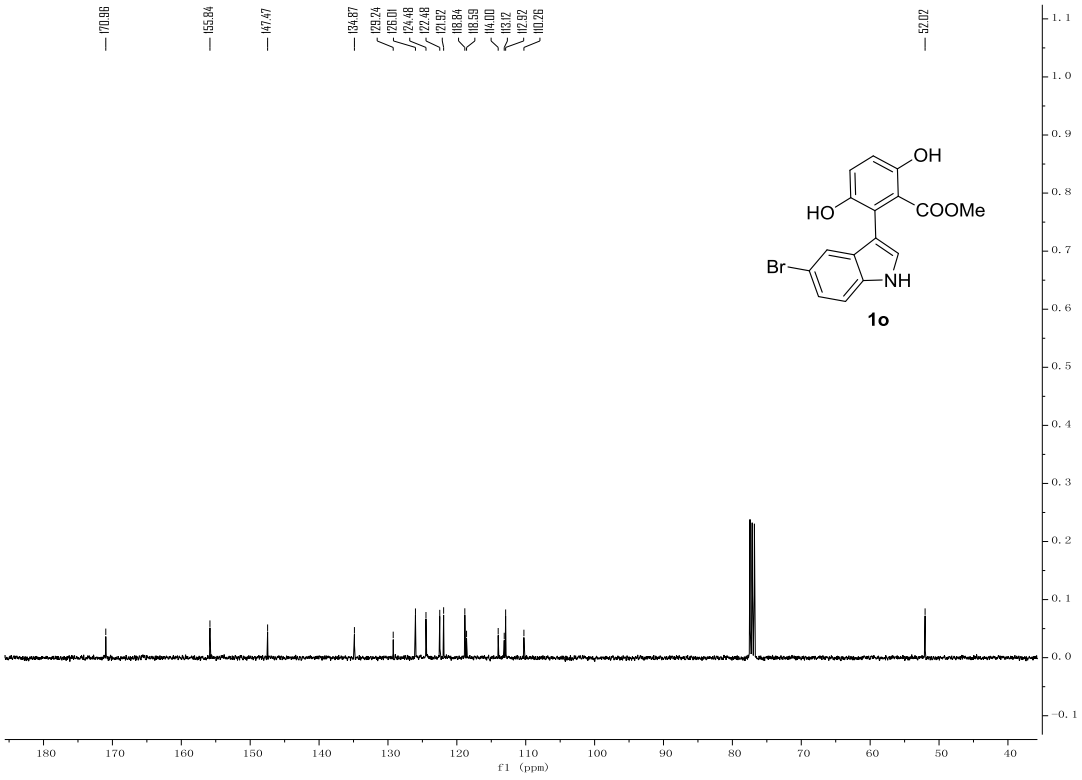
7.34
7.32
7.31
7.29
7.18
7.17
7.17
7.16
7.02
6.99
5.02
3.28
OH
HO
COOMe
Br
NH
1o
0.95
1.01
0.97
2.05
1.98
1.03
0.95
3.00
f1 (ppm)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134.87
129.24
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124.48
122.48
121.92
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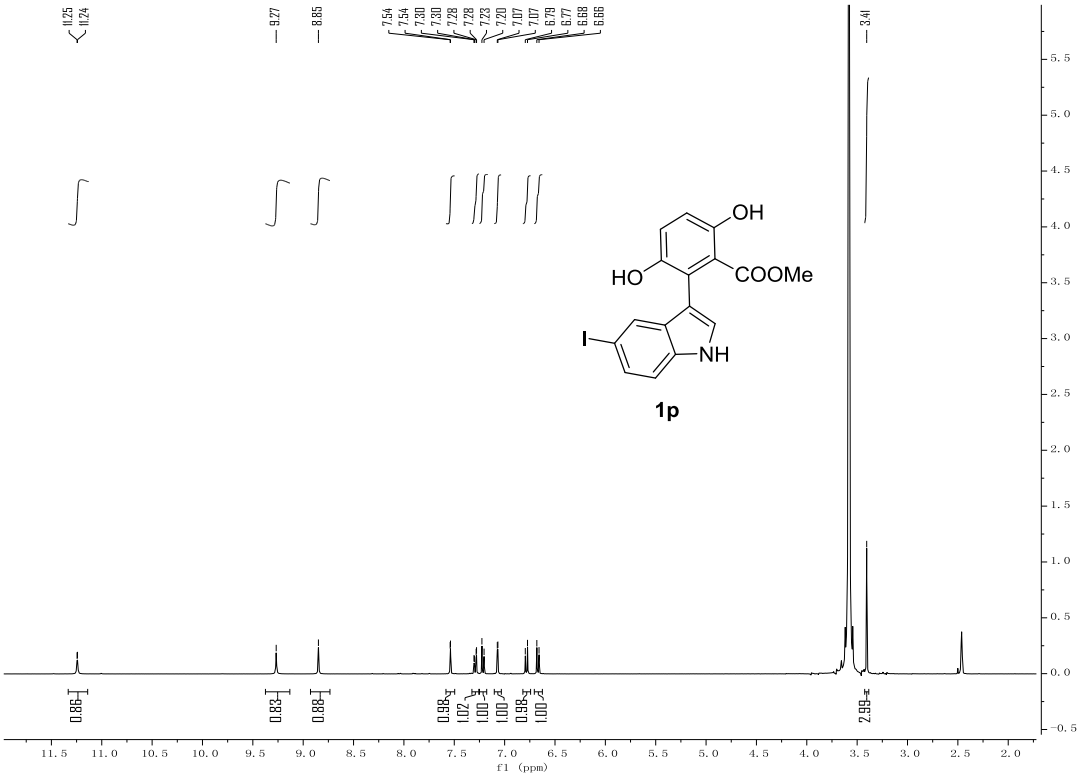
114.00
113.12
112.92
110.26
52.02
OH
HO
COOMe
Br
NH
1o
f1 (ppm)


11.25
11.24
9.27
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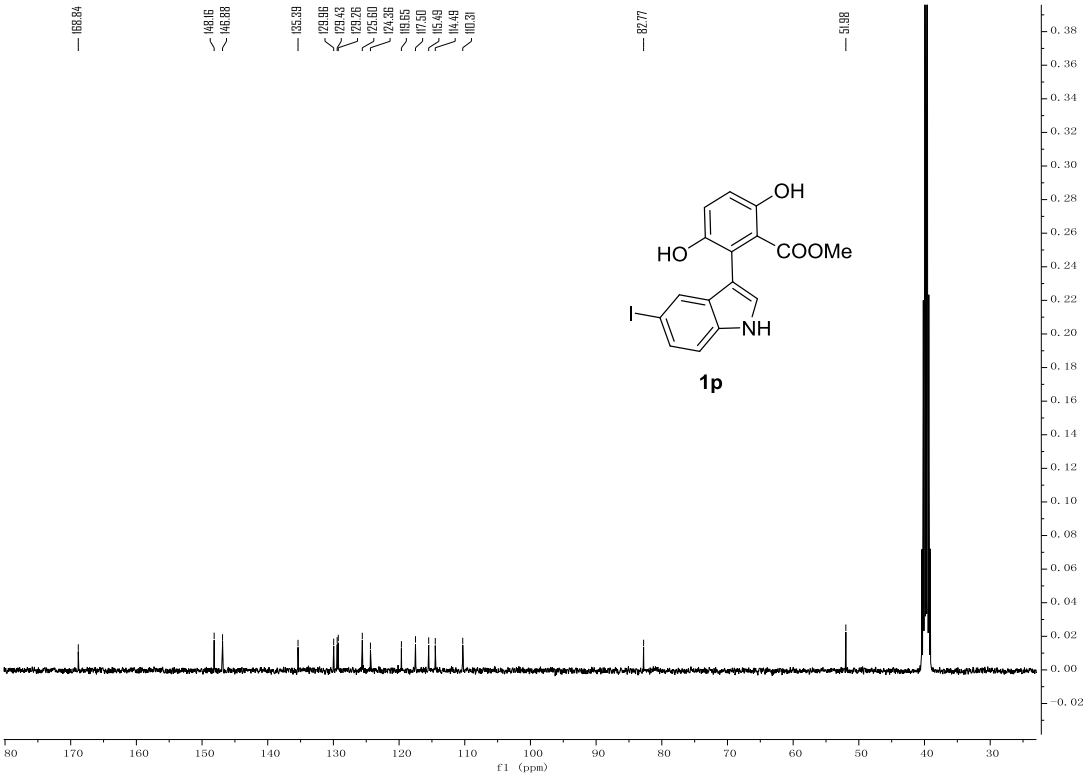
7.54
7.54
7.30
7.30
7.28
7.28
7.23
7.20
7.07
7.07
6.78
6.77
6.68
6.66
3.41
OH
HO
COOMe
I
NH
1p
0.86
0.83
0.88
0.98
1.02
1.00
1.00
0.98
1.00
2.99
f1 (ppm)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135.39
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129.43
129.26
125.60
124.38
119.65
117.50
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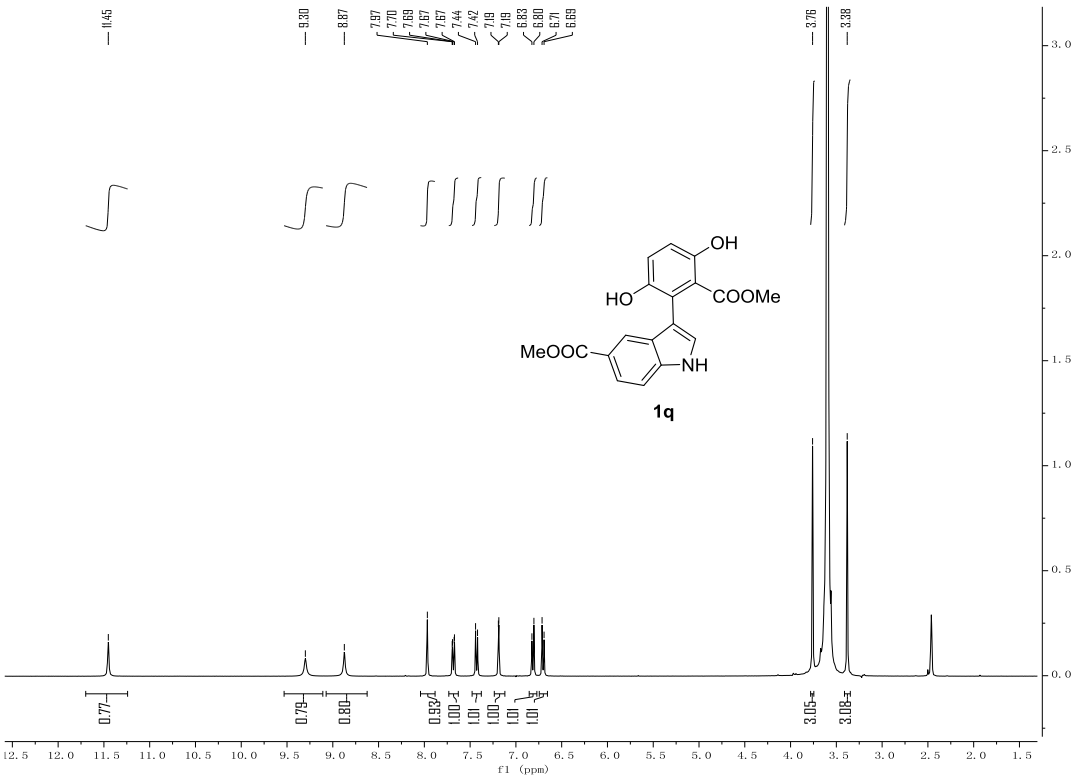
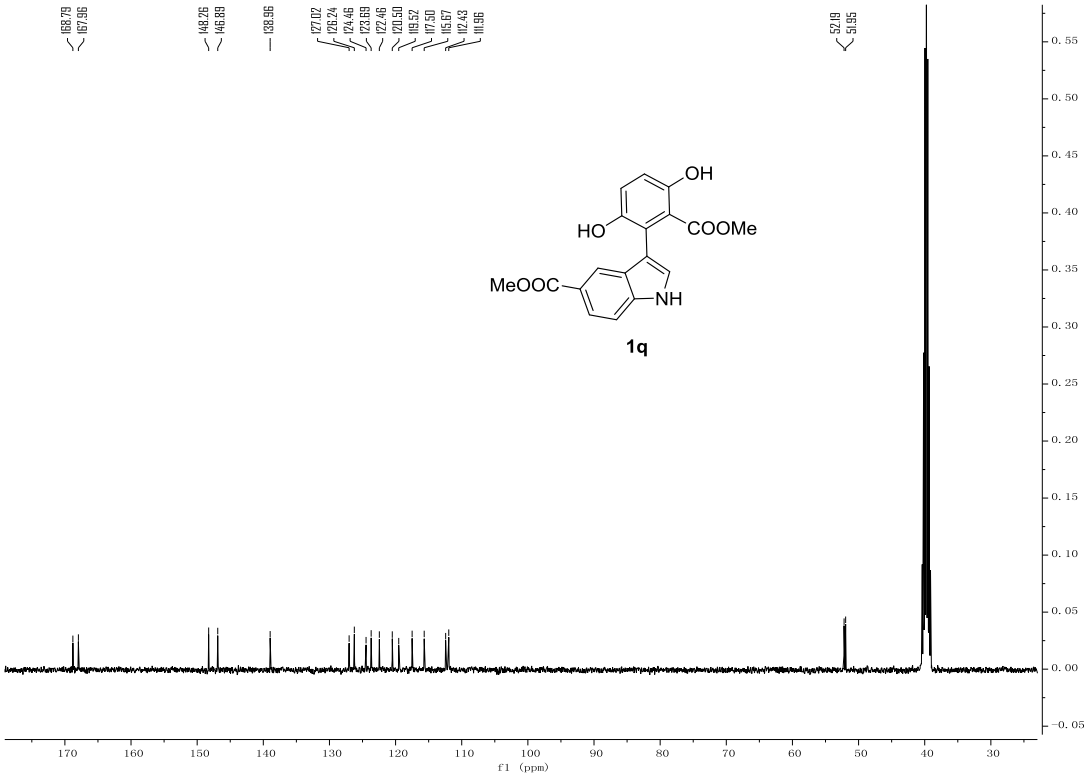
114.49
110.31
82.77
51.98
OH
HO
COOMe
I
NH
1p
f1 (ppm)


11.45
9.30
8.87
7.97
7.70
7.69
7.67
7.67
7.67
7.44
7.42
7.19
7.19
6.83
6.80
6.71
6.69
3.76
3.38
OH
HO
COOMe
MeOOC
NH
1q
0.77
0.79
0.80
0.93
1.00
1.01
1.00
1.01
1.01
3.05
3.08
f1 (ppm)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167.96
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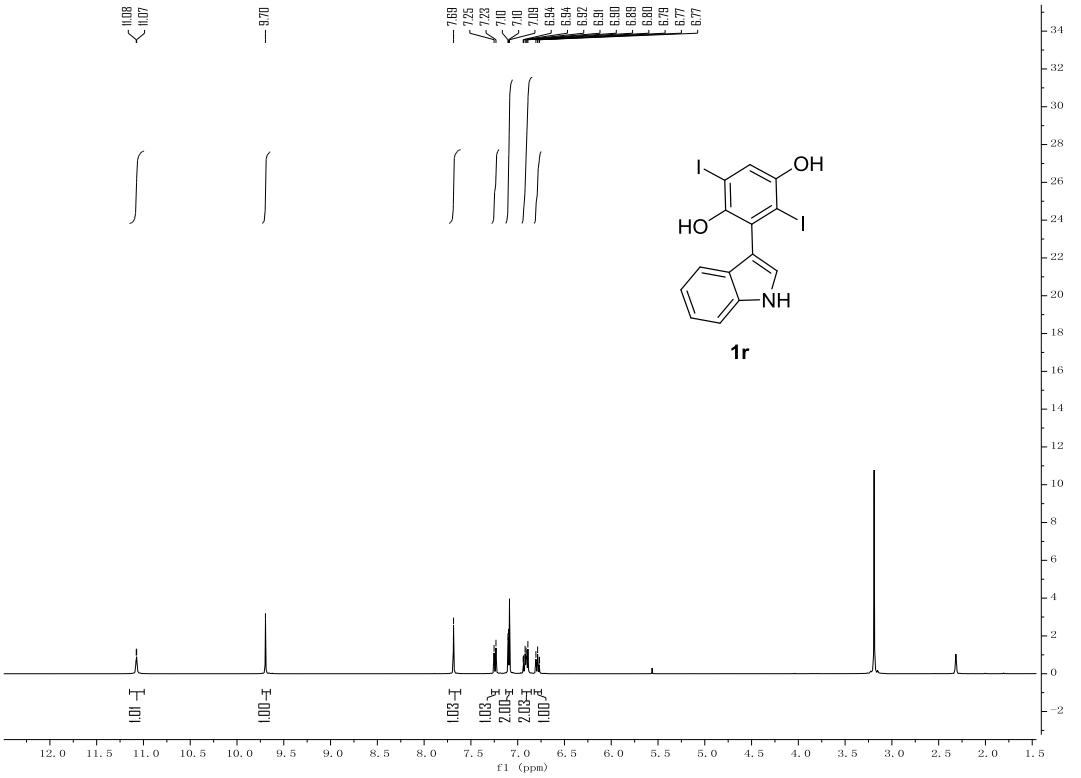
126.24
124.45
123.83
122.46
120.50
119.52
117.50
115.67
112.43
111.96
52.19
51.95
OH
HO
COOMe
MeOOC
NH
1q
f1 (ppm)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9.700
7.683
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7.323
7.110
7.101
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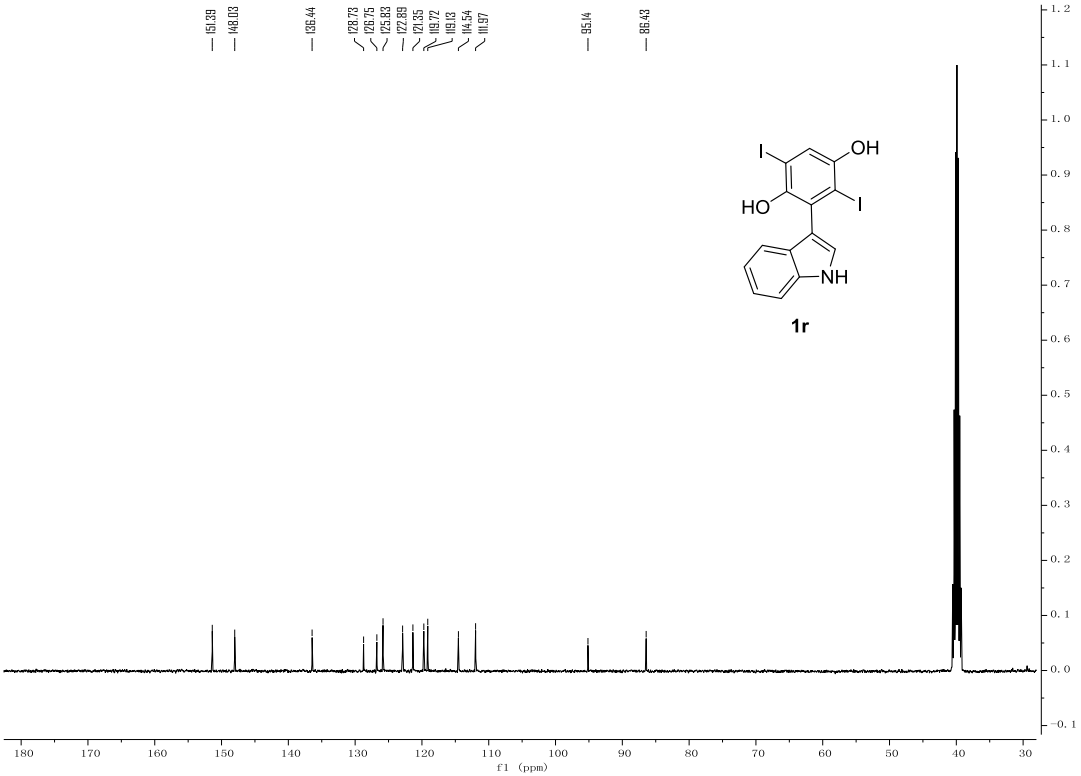
6.934
6.934
6.912
6.910
6.909
6.909
6.680
6.679
6.677
6.677
I
OH
HO
I
NH
1r
1.01
1.00
1.03
1.03
2.004
2.03
1.00
f1 (ppm)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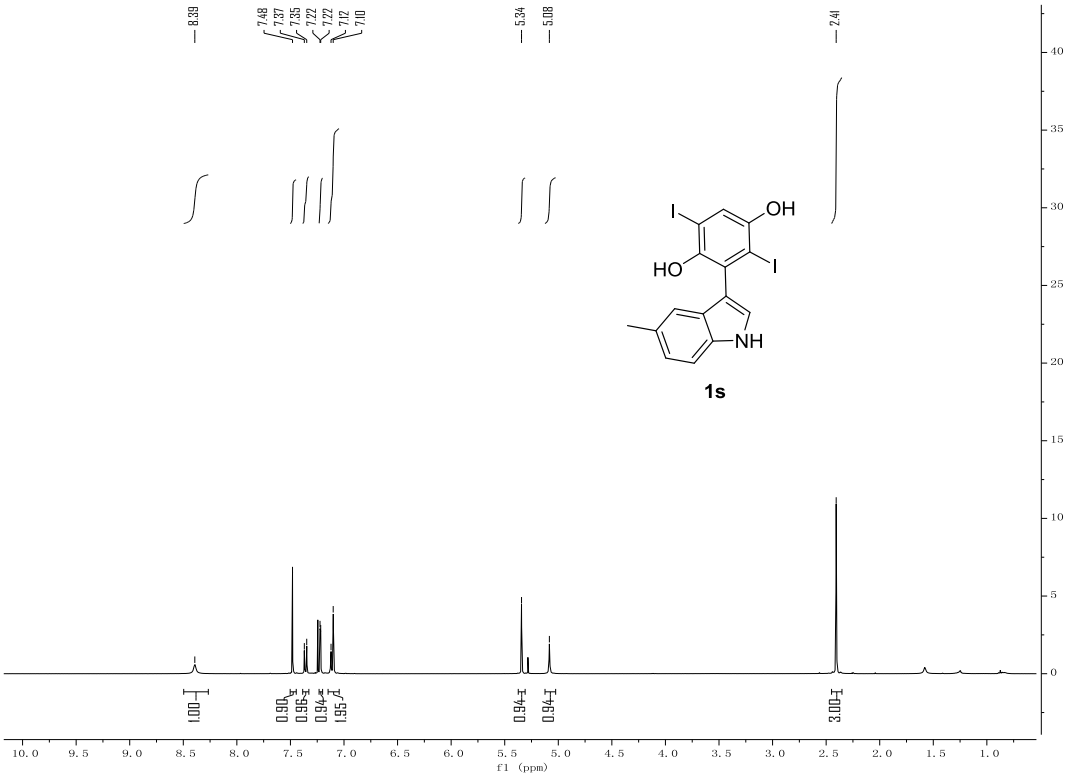
114.544
111.977
95.140
86.432
I
OH
HO
I
NH
1r
f1 (ppm)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7.22
7.22
7.12
7.10
5.34
5.08
2.41
1.00
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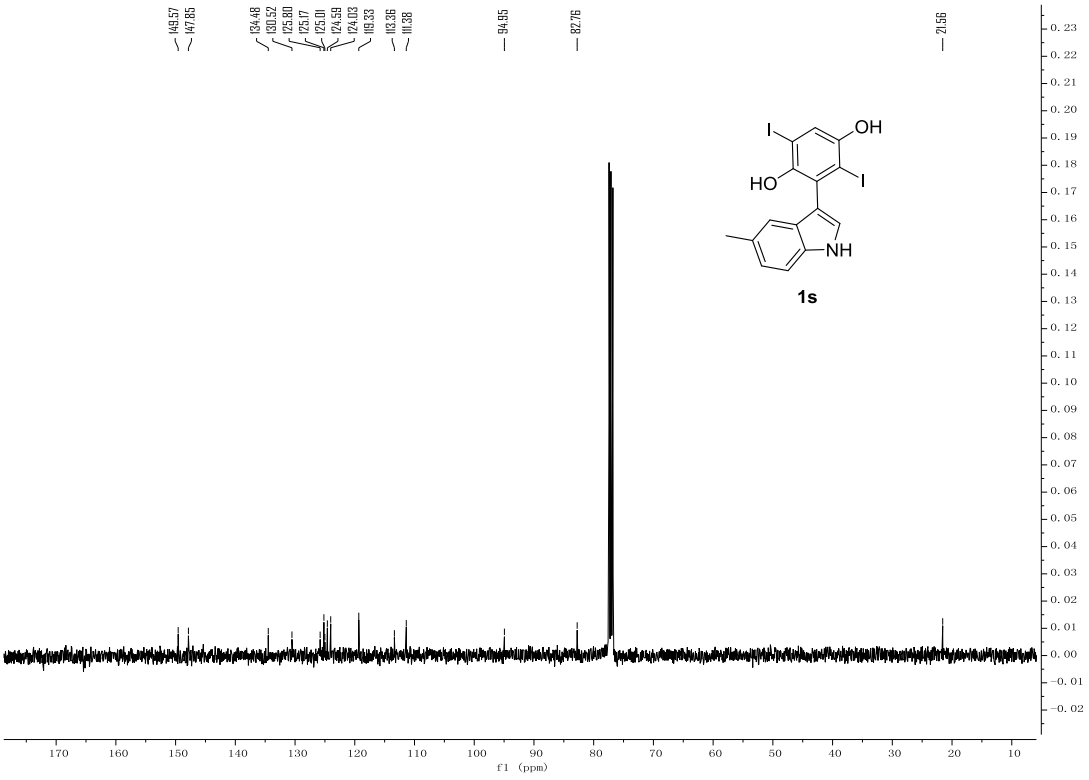
0.96
0.94
1.95
0.94
0.94
3.00
I
OH
HO
I
NH
1s
f1 (ppm)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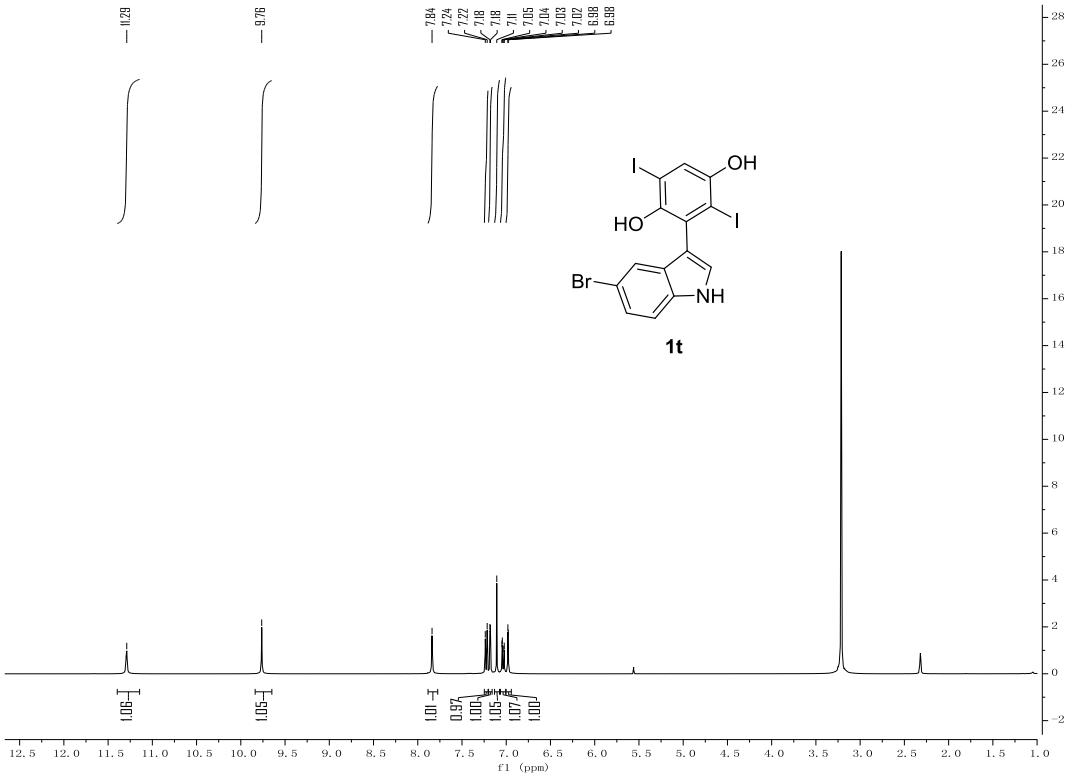
125.17
125.01
124.58
124.03
119.33
113.36
111.38
94.95
82.76
21.56
I
OH
HO
I
NH
1s
f1 (ppm)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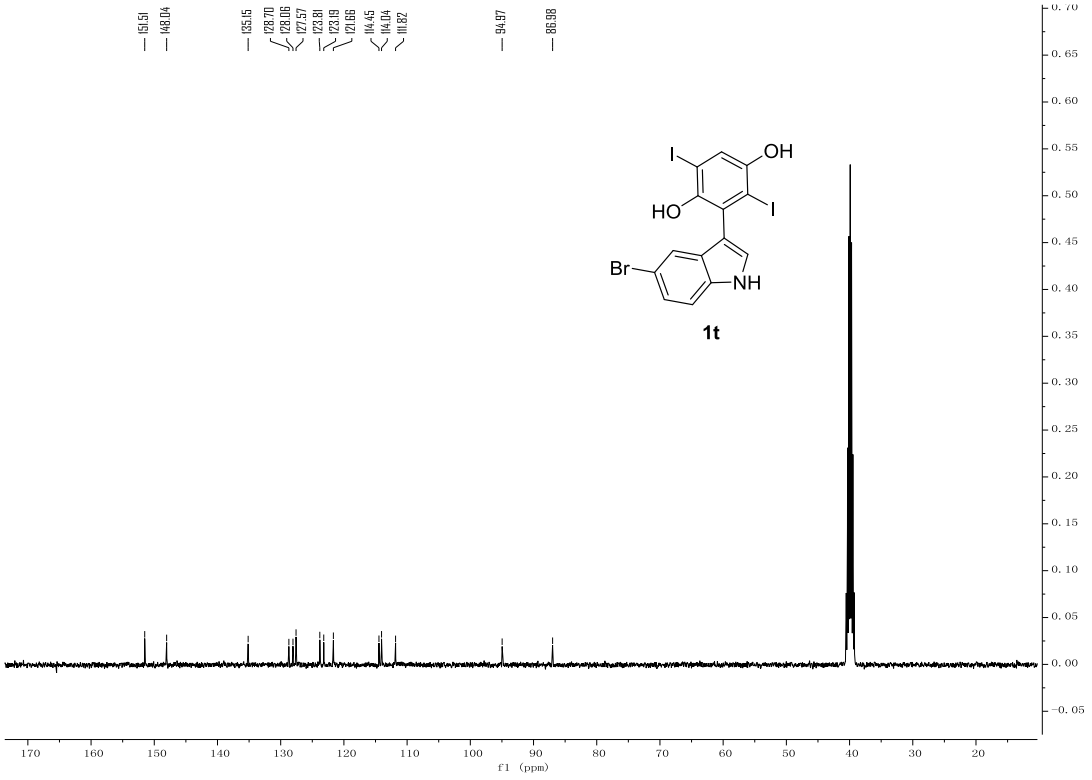
7.18
7.18
7.11
7.05
7.04
7.03
7.02
6.98
6.98
OH
I
HO
I
Br
NH
1t
1.06
1.05
1.01
0.97
1.00
1.05
1.07
1.00
f1 (ppm)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128.70
128.06
127.57
123.81
123.19
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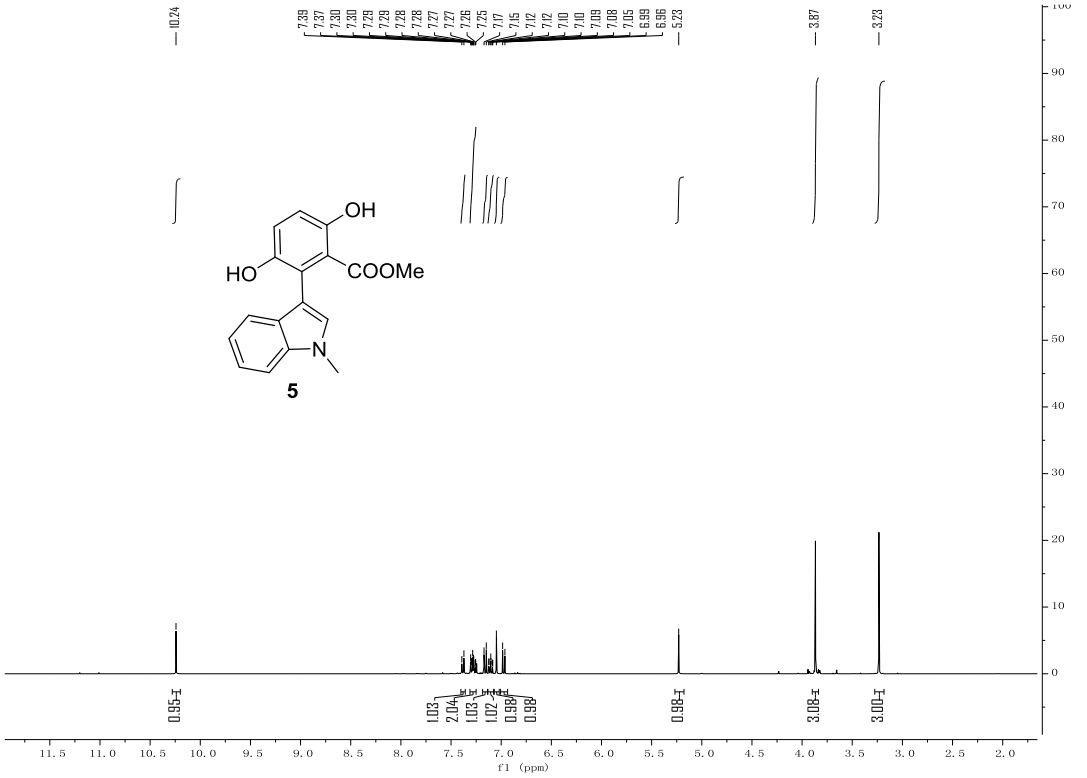
114.04
111.82
94.57
86.98
OH
I
HO
I
Br
NH
1t
f1 (ppm)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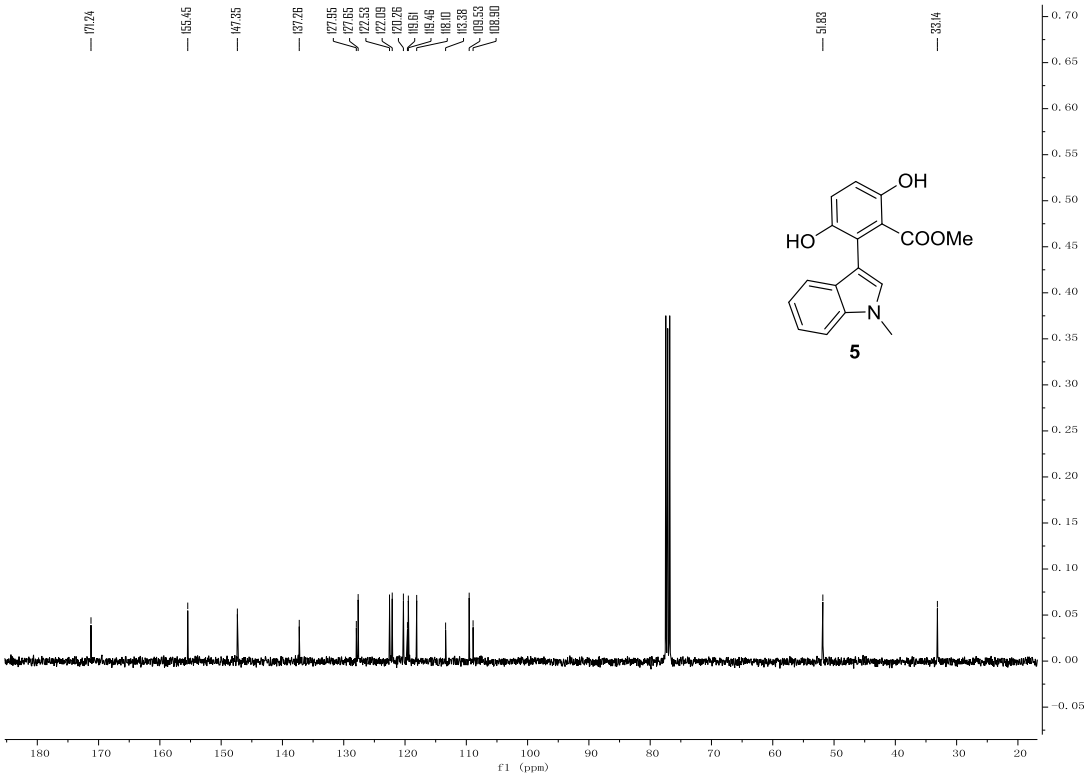
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.17
7.15
7.12
7.12
7.10
7.10
7.09
7.08
7.05
6.99
6.96
5.23
3.87
3.23
OH
HO
COOMe
N
5
0.95
1.03
2.04
1.03
1.02
0.98
0.98
0.98
3.08
3.00
f1 (ppm)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155.45
147.35
137.26
127.55
127.55
122.53
122.09
120.26
119.61
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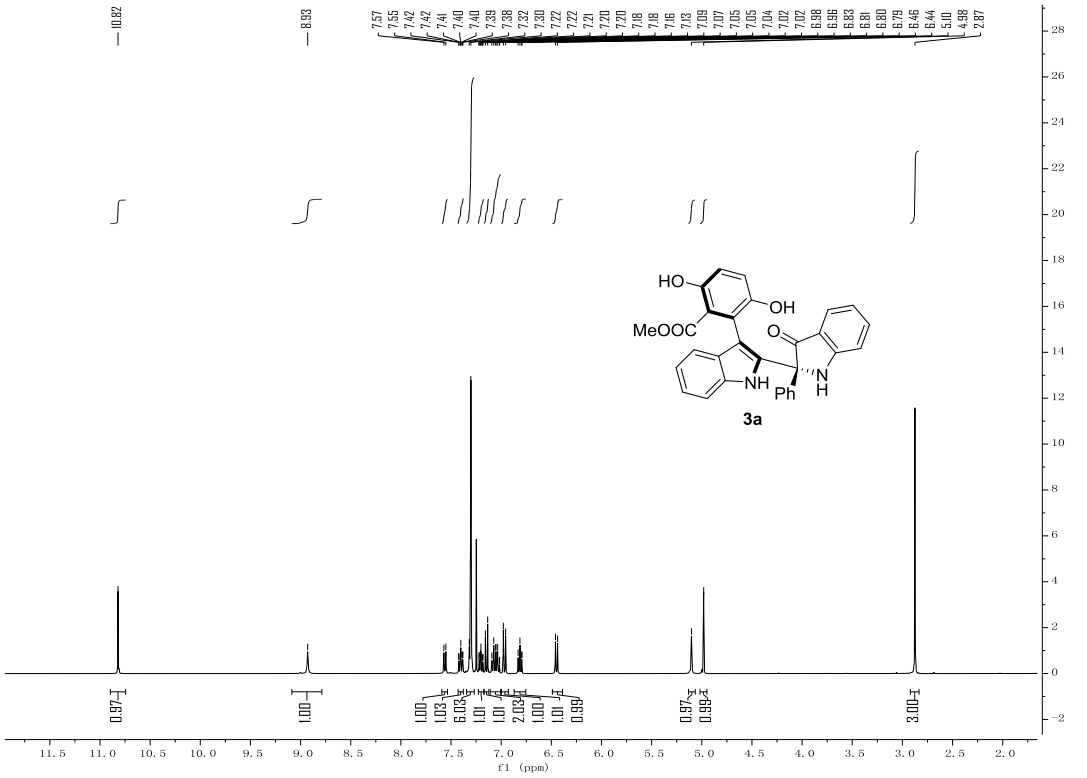
113.38
109.53
109.50
51.83
33.14
OH
HO
COOMe
N
5
f1 (ppm)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7.41
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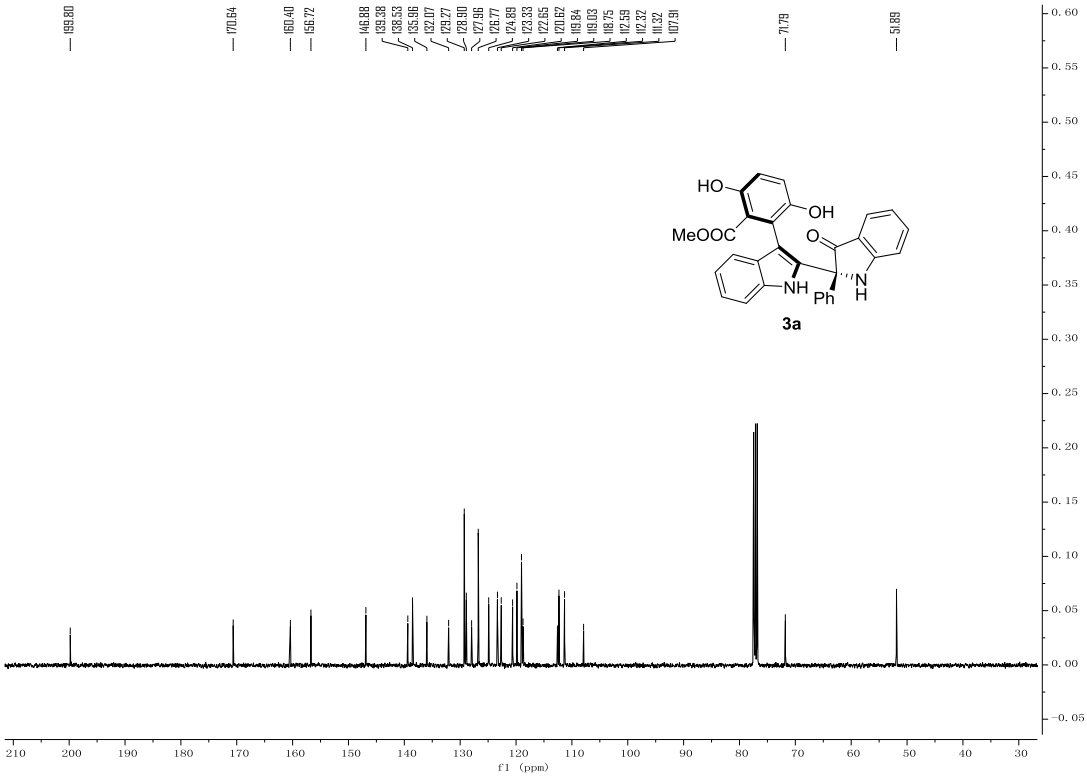
7.39
7.38
7.32
7.30
7.22
7.21
7.20
7.18
7.16
7.13
7.09
7.07
7.05
7.04
7.02
6.98
6.96
6.83
6.81
6.80
6.79
6.46
6.44
5.10
4.98
2.87
HO
OH
MeOOC
O
NH
Ph
N
H
3a
0.97
1.00
1.00
1.03
6.03
1.01
1.01
2.03
1.00
1.01
0.99
0.97
0.99
3.00
f1 (ppm)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133.38
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135.96
132.07
129.27
128.90
127.96
126.77
124.83
123.33
122.65
120.62
119.84
119.03
118.75
117.58
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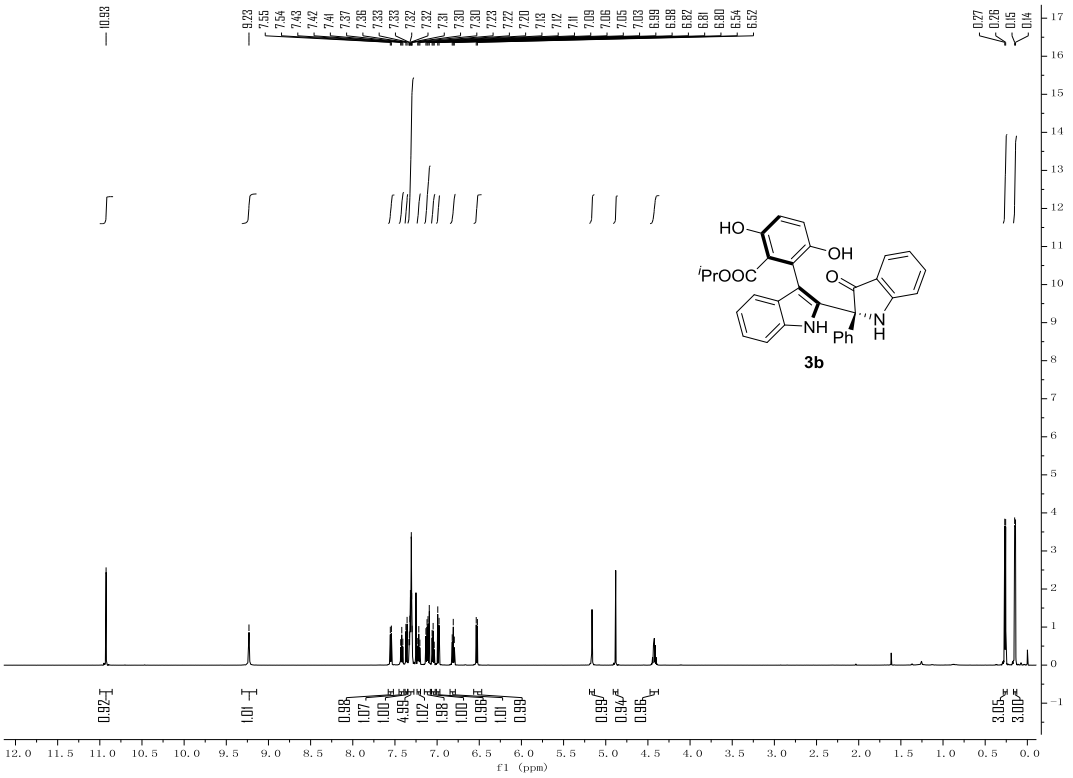
71.79
51.88
HO
OH
MeOOC
O
NH
Ph
N
H
3a
f1 (ppm)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7.37
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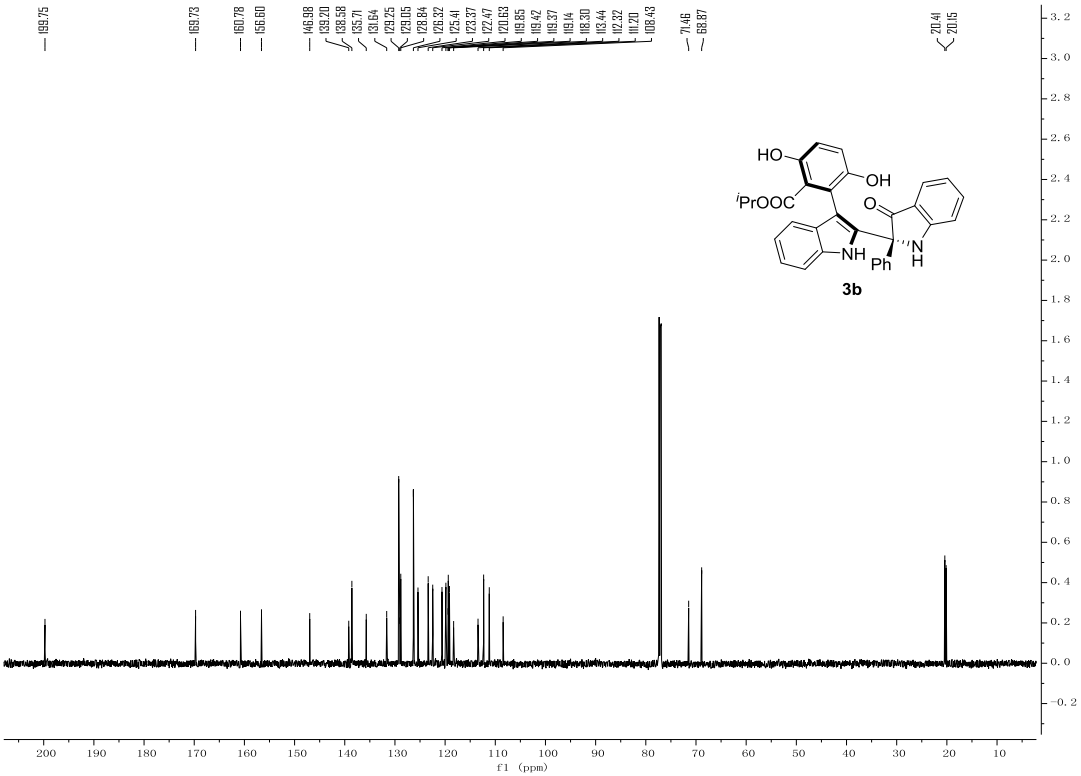
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.23
7.22
7.20
7.13
7.12
7.11
7.09
7.06
7.05
7.03
6.99
6.98
6.82
6.81
6.80
6.54
6.52
0.27
0.26
0.15
0.14
HO
OH
iPrOOC
O
NH
Ph
N
H
3b
0.92
1.01
0.98
1.07
1.00
4.95
1.02
1.98
1.00
0.96
1.01
0.99
0.99
0.94
0.95
3.05
3.00
f1 (ppm)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129.25
129.05
128.84
126.32
125.41
123.37
122.47
120.83
119.85
119.42
119.37
119.14
118.30
113.44
112.32
111.20
108.43
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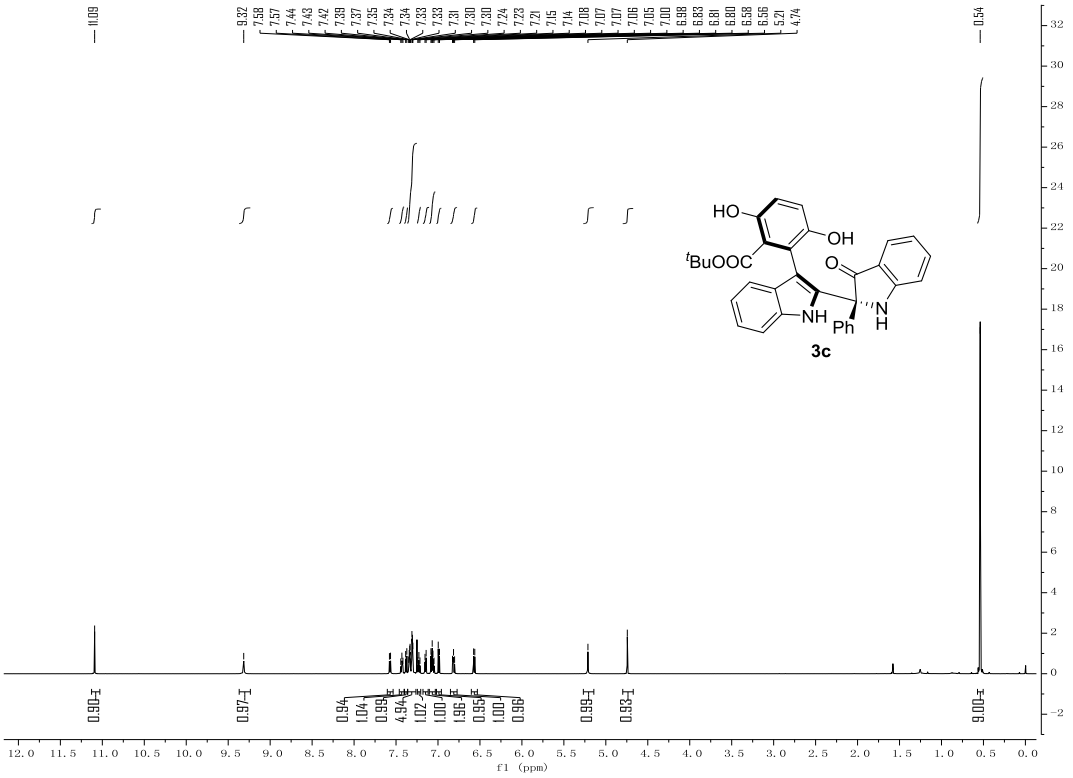
68.87
20.41
20.15
HO
OH
iPrOOC
O
NH
Ph
N
H
3b
f1 (ppm)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9.32
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7.39
7.37
7.35
7.34
7.34
7.33
7.33
7.31
7.30
7.30
7.24
7.23
7.21
7.15
7.14
7.08
7.07
7.07
7.06
7.05
7.00
6.98
6.83
6.81
6.80
6.58
6.56
5.21
4.74
0.54
HO
OH
tBuOOC
O
NH
Ph
N
H
3c
0.90
0.97
0.94
1.04
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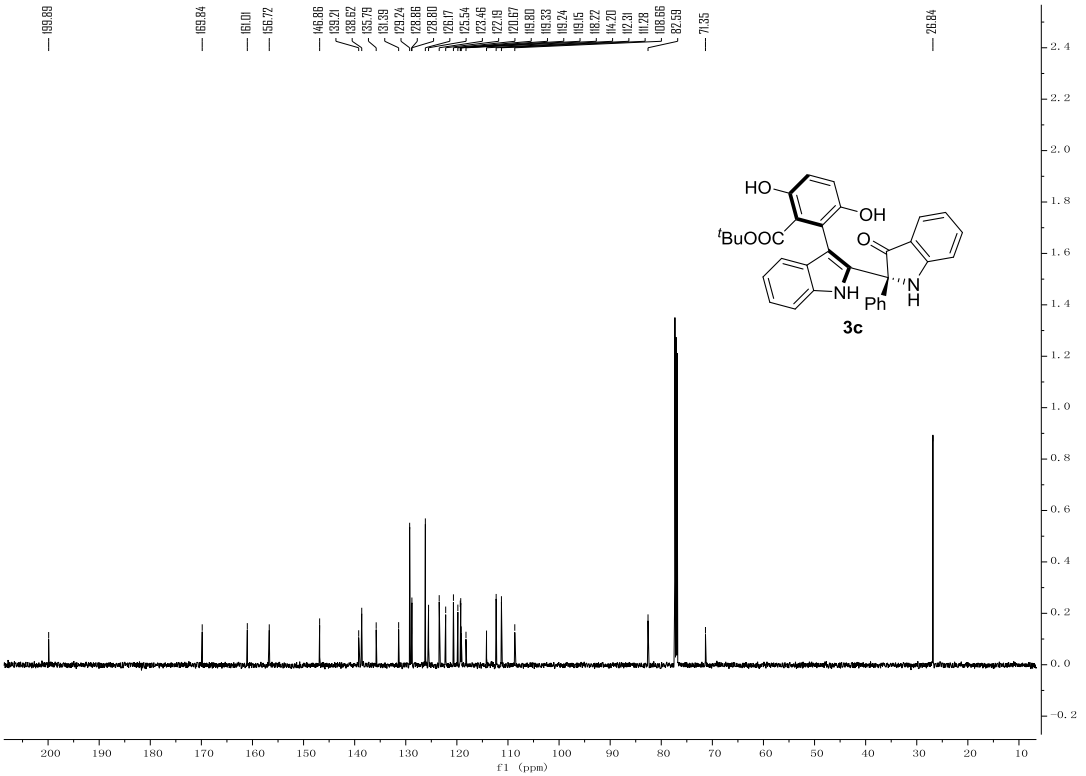
1.02
1.00
1.96
0.95
1.00
0.98
0.99
0.93
9.00
f1 (ppm)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135.79
131.39
129.24
128.86
128.80
126.17
125.54
123.46
122.19
120.67
119.80
119.33
119.24
119.15
118.22
114.20
112.31
111.28
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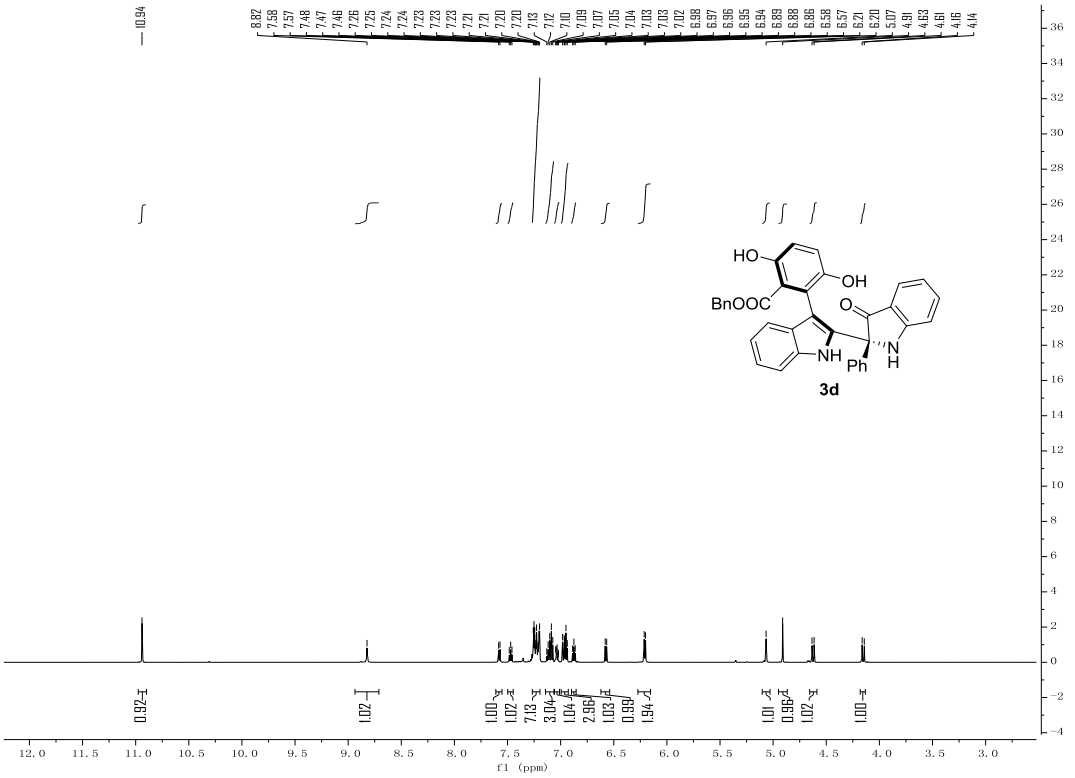
77.35
26.84
HO
OH
tBuOOC
O
NH
Ph
N
H
3c
f1 (ppm)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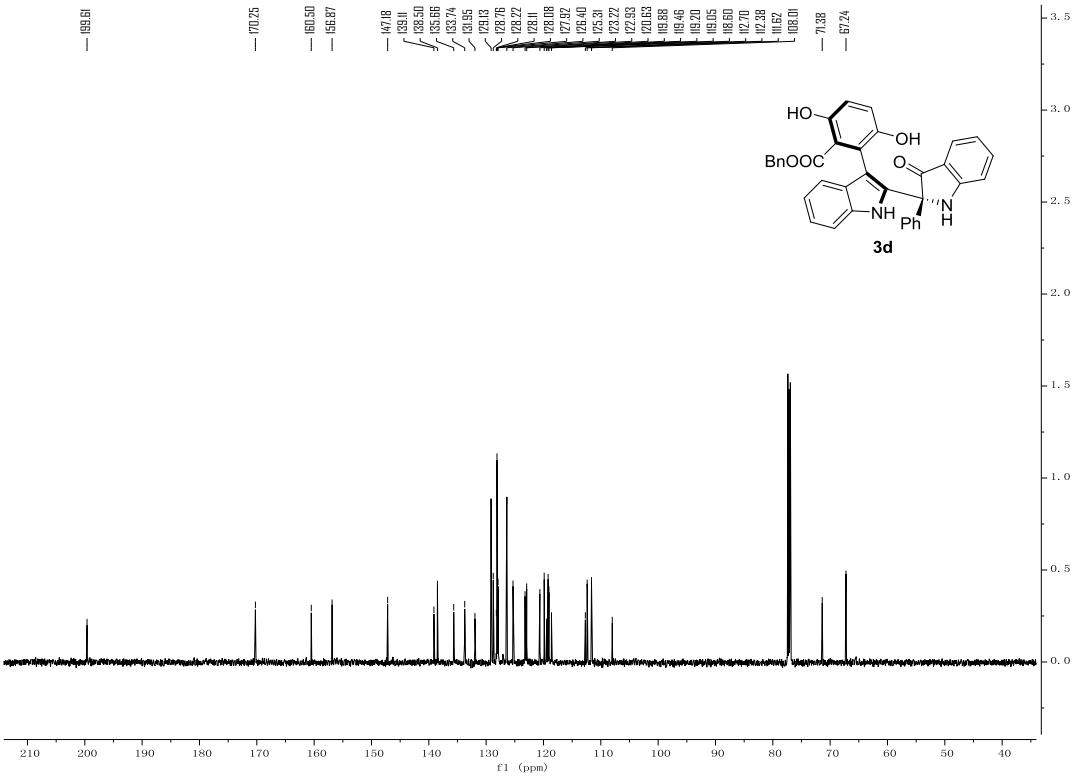
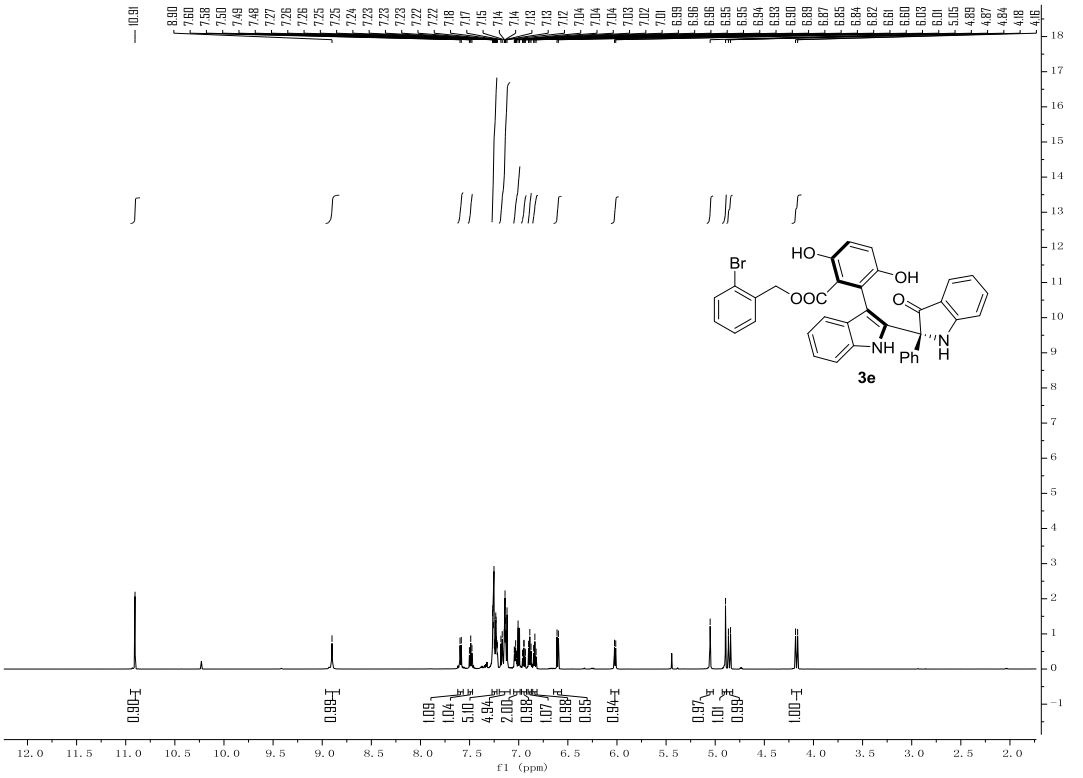
O
NH
Ph
N
H
3d


HO
OH
BnOOC
O
NH
Ph
N
H
3d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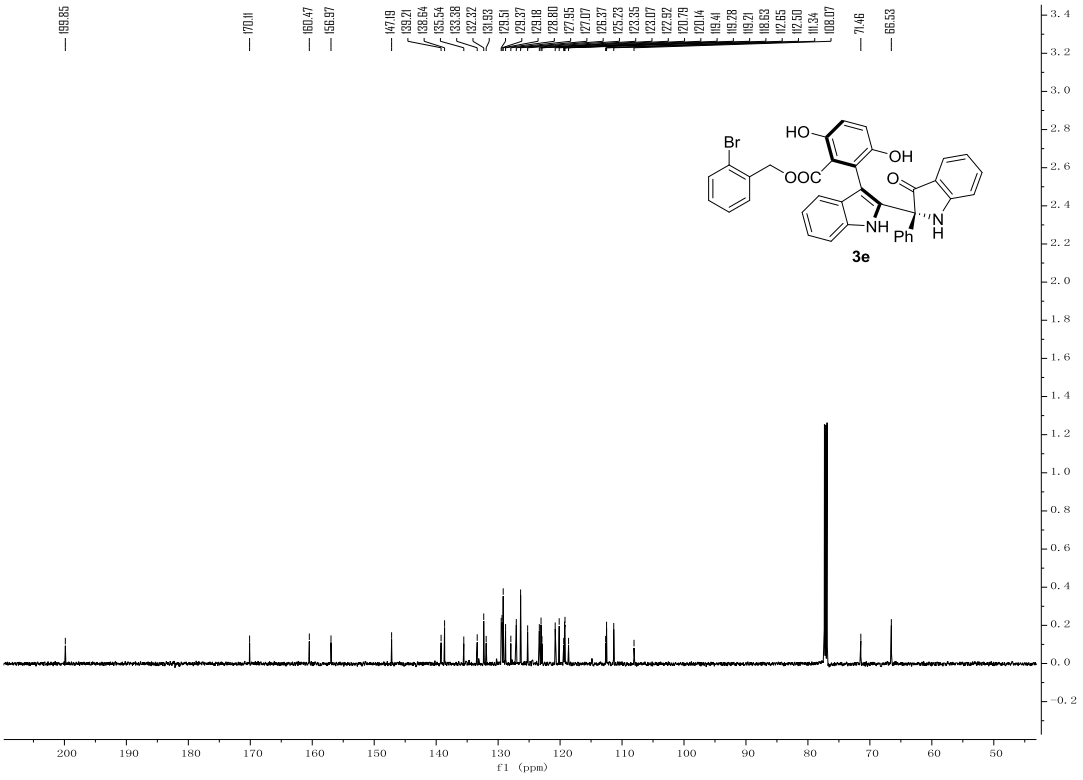
7.24
7.23
7.23
7.23
7.22
7.22
7.18
7.17
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.04
7.04
7.04
7.03
7.02
7.01
6.99
6.96
6.96
6.95
6.95
6.94
6.93
6.90
6.89
6.87
6.85
6.84
6.82
6.81
6.80
6.03
6.01
5.05
4.89
4.87
4.84
4.18
4.16
0.90
0.89
1.09
1.04
5.10
4.94
2.00
0.98
1.07
0.99
0.95
0.94
0.97
1.01
0.99
1.00
f1 (ppm)
Br
HO
OH
OOC
O
NH
Ph
N
H
3e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135.54
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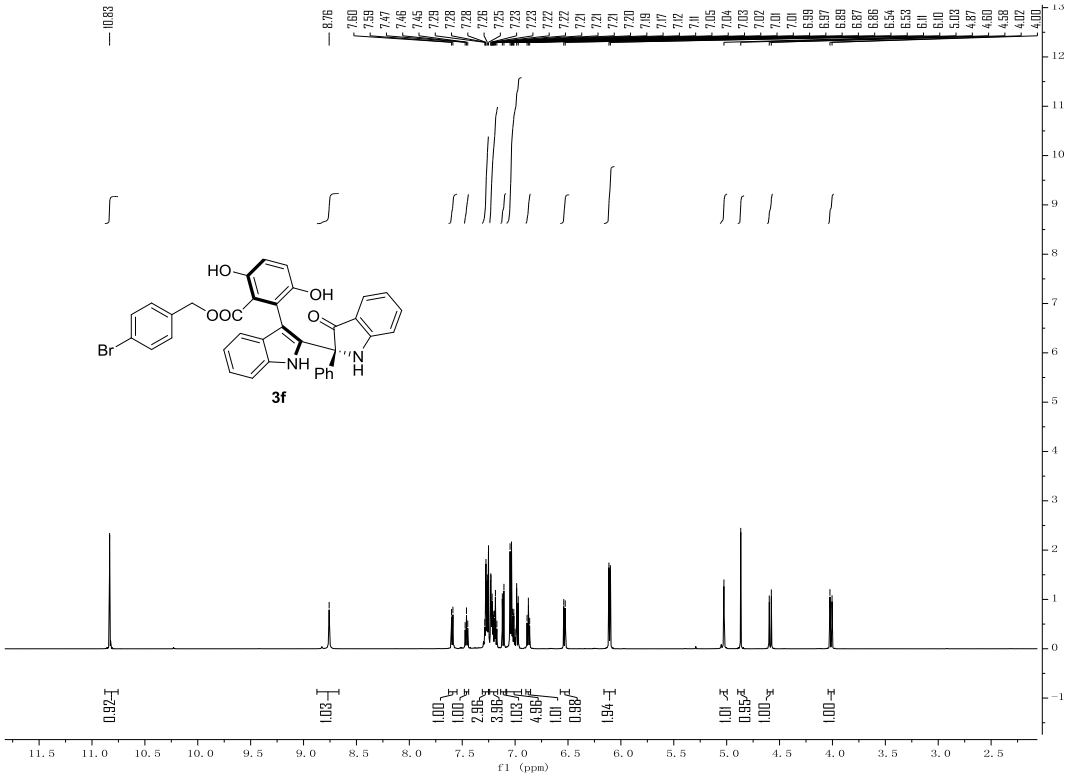
132.32
131.93
129.51
129.37
129.18
128.80
127.95
127.07
125.37
125.23
123.35
123.07
122.92
120.79
120.14
119.41
119.28
119.21
118.63
112.85
112.50
111.34
108.07
71.46
66.53
f1 (ppm)
Br
HO
OH
OOC
O
NH
Ph
N
H
3e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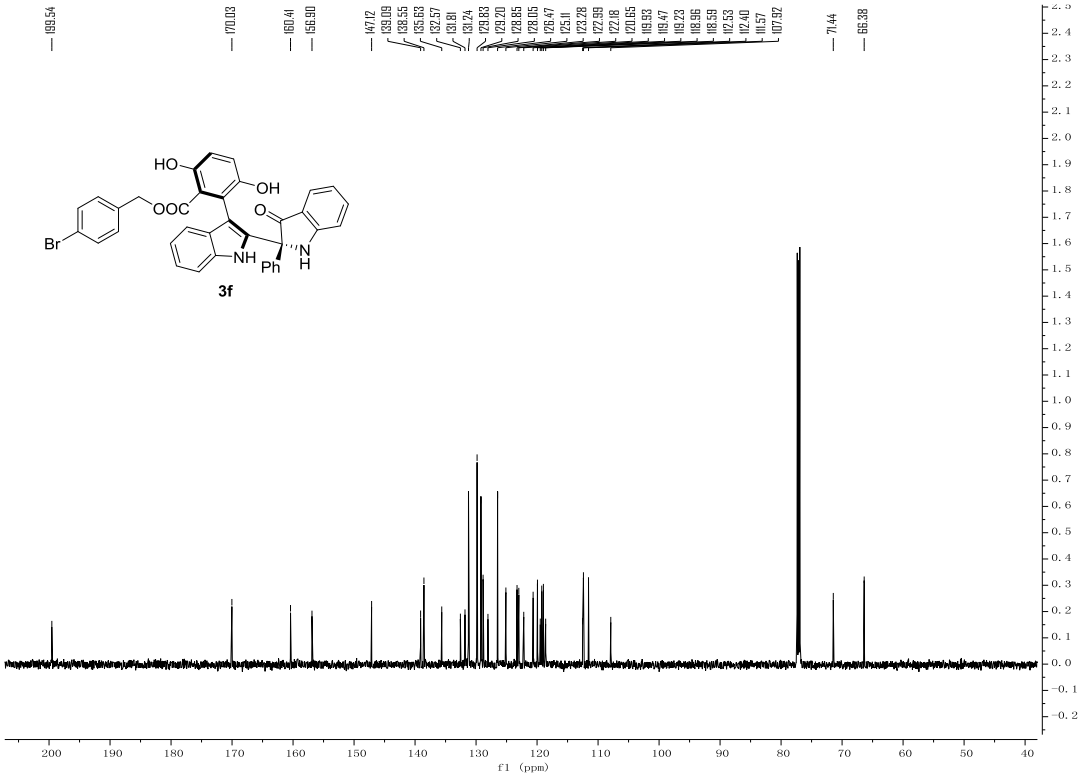
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.19
7.17
7.12
7.11
7.05
7.04
7.03
7.02
7.01
7.01
6.99
6.97
6.89
6.87
6.86
6.54
6.53
6.11
6.10
5.03
4.87
4.60
4.58
4.02
4.00
HO
OH
OOC
O
Br
NH
Ph
N
H
3f
0.92
1.03
1.00
1.00
2.95
3.96
1.03
4.95
1.01
0.98
1.94
1.01
0.95
1.00
1.00
f1 (ppm)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128.85
128.05
126.47
125.11
123.28
122.59
122.18
120.65
119.53
119.47
119.23
118.96
118.58
112.53
112.40
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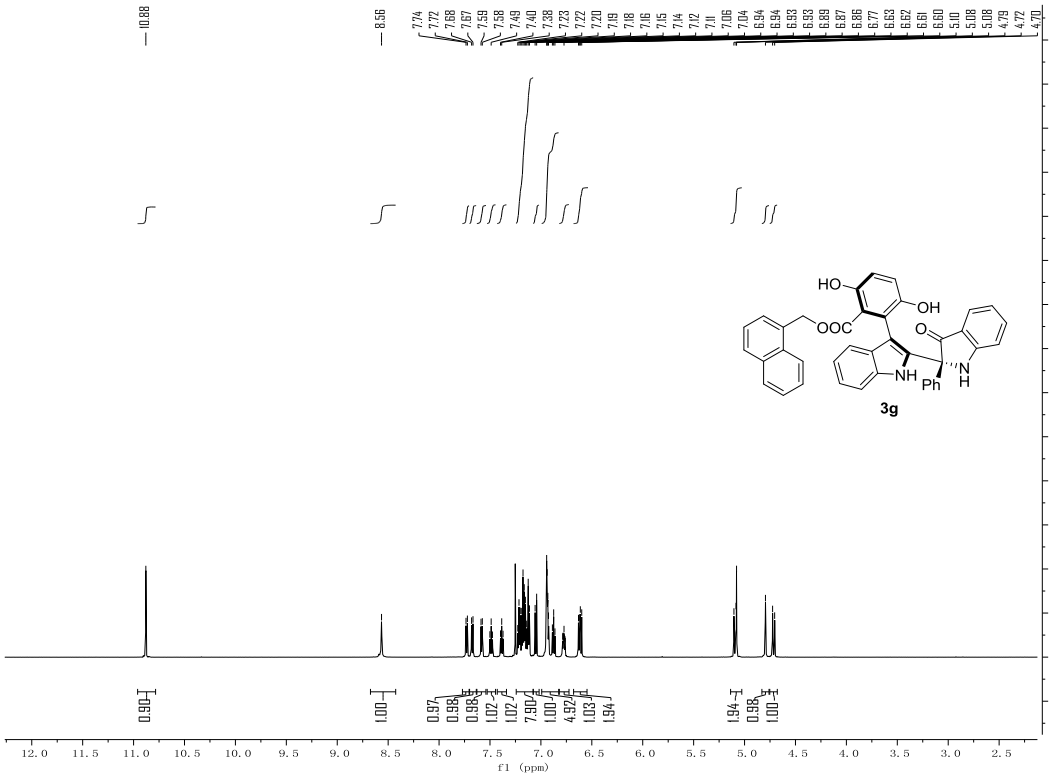
66.38
HO
OH
OOC
O
Br
NH
Ph
N
H
3f
f1 (ppm)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7.20
7.19
7.18
7.16
7.15
7.14
7.12
7.11
7.06
7.04
6.94
6.94
6.93
6.93
6.89
6.87
6.86
6.77
6.63
6.62
6.61
6.60
5.41
5.08
5.08
4.79
4.72
4.70
0.90
1.00
0.97
0.98
0.98
1.02
1.02
7.90
1.00
4.57
1.03
1.94
1.94
0.98
1.00
f1 (ppm)
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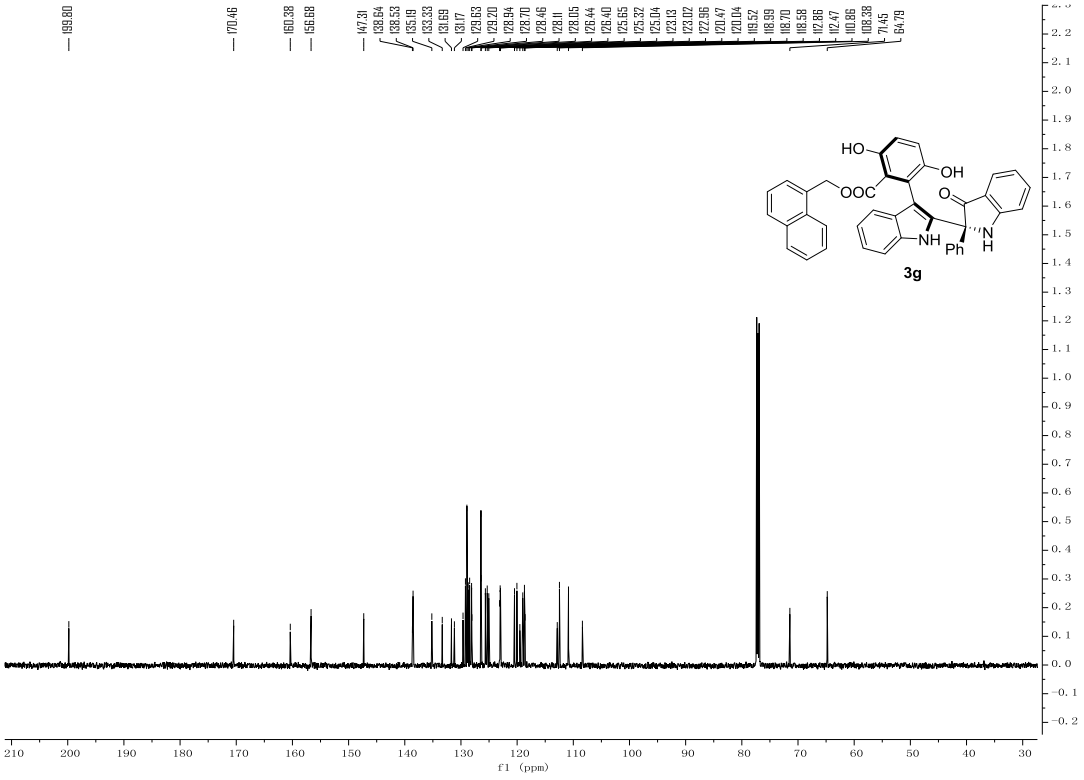
OH
OOC
O
NH
Ph
N
H
3g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131.17
129.83
129.20
128.94
128.70
128.46
128.11
128.05
126.44
126.40
125.65
125.32
125.04
123.13
123.02
122.96
121.47
121.04
119.52
118.99
118.70
118.58
112.86
112.47
110.96
108.38
71.45
64.79
f1 (ppm)
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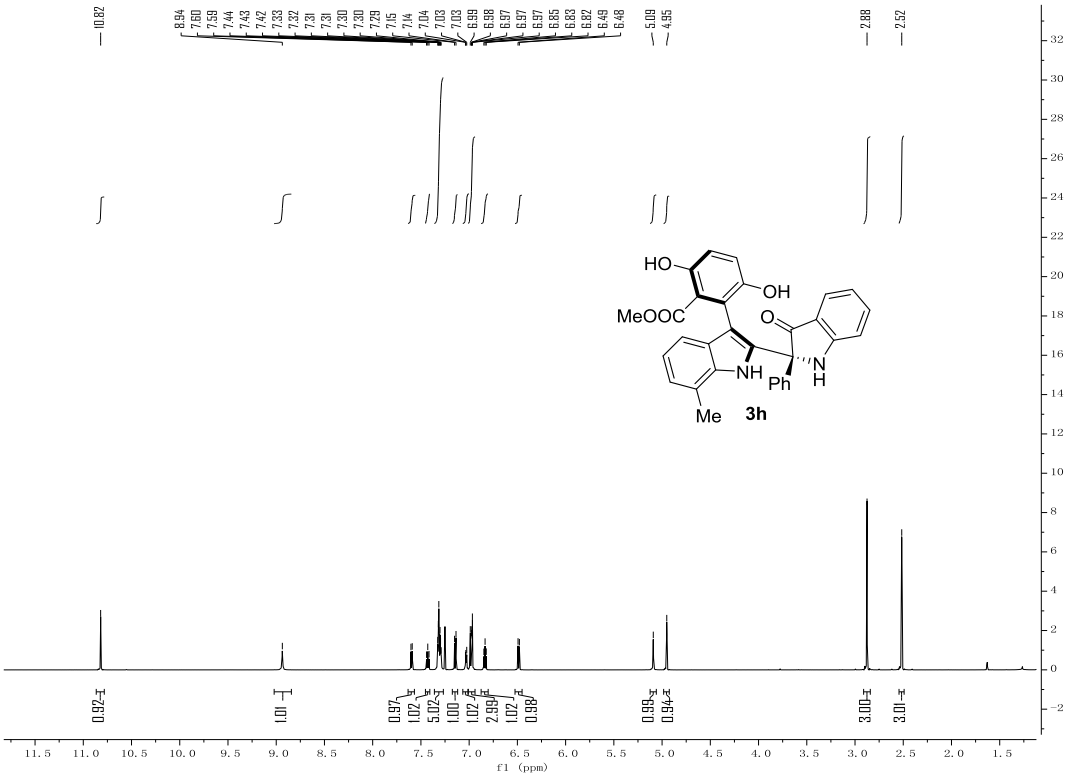
OH
OOC
O
NH
Ph
N
H
3g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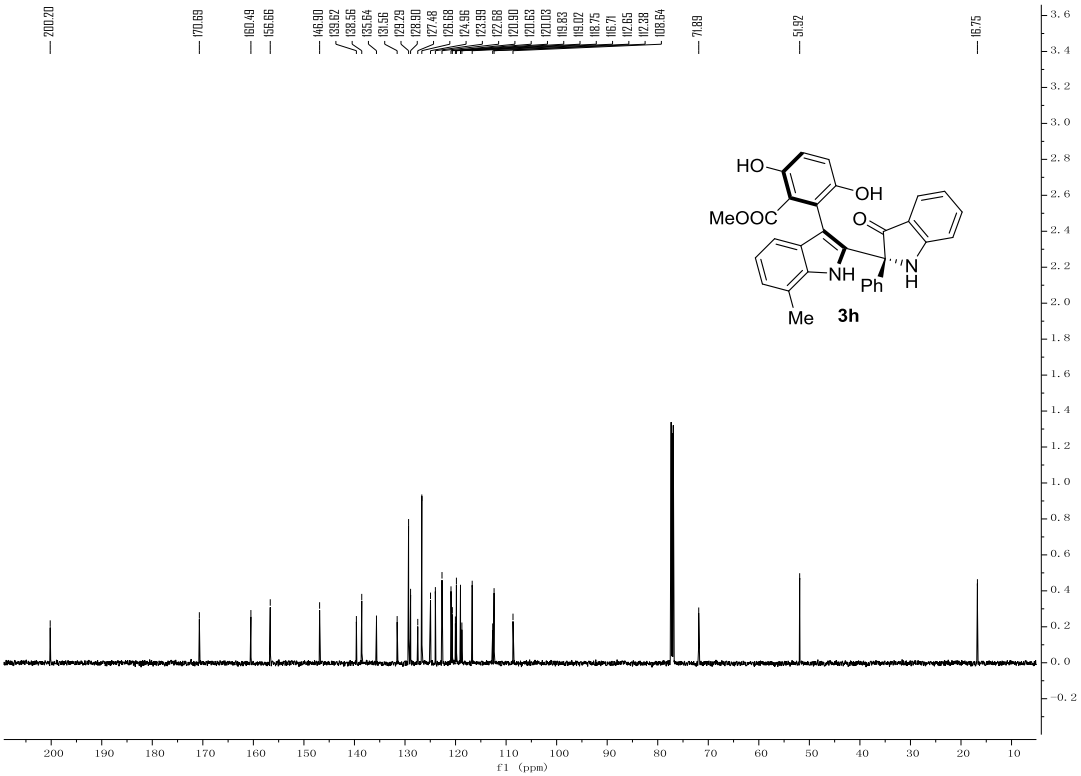
7.29
7.15
7.14
7.04
7.03
7.03
6.99
6.98
6.97
6.97
6.97
6.85
6.83
6.82
6.48
6.48
5.08
4.95
2.88
2.52
HO
OH
MeOOC
O
NH
Ph
N
H
Me
3h
0.92
1.01
0.97
1.02
5.02
1.00
1.02
2.99
1.02
0.98
0.99
0.94
3.00
3.01
f1 (ppm)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131.56
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124.95
123.99
122.68
121.90
121.63
121.03
119.83
119.02
118.75
116.71
112.65
112.38
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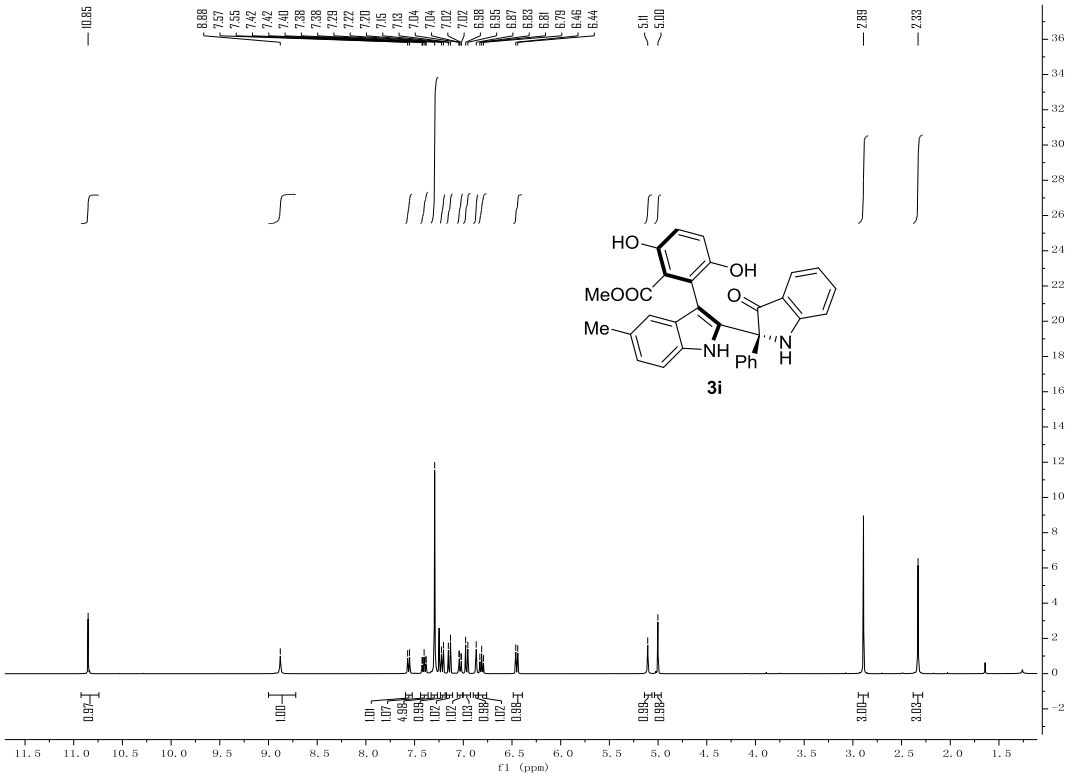
71.89
51.92
16.75
HO
OH
MeOOC
O
NH
Ph
N
H
Me
3h
f1 (ppm)


10.85
8.88
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7.42
7.42
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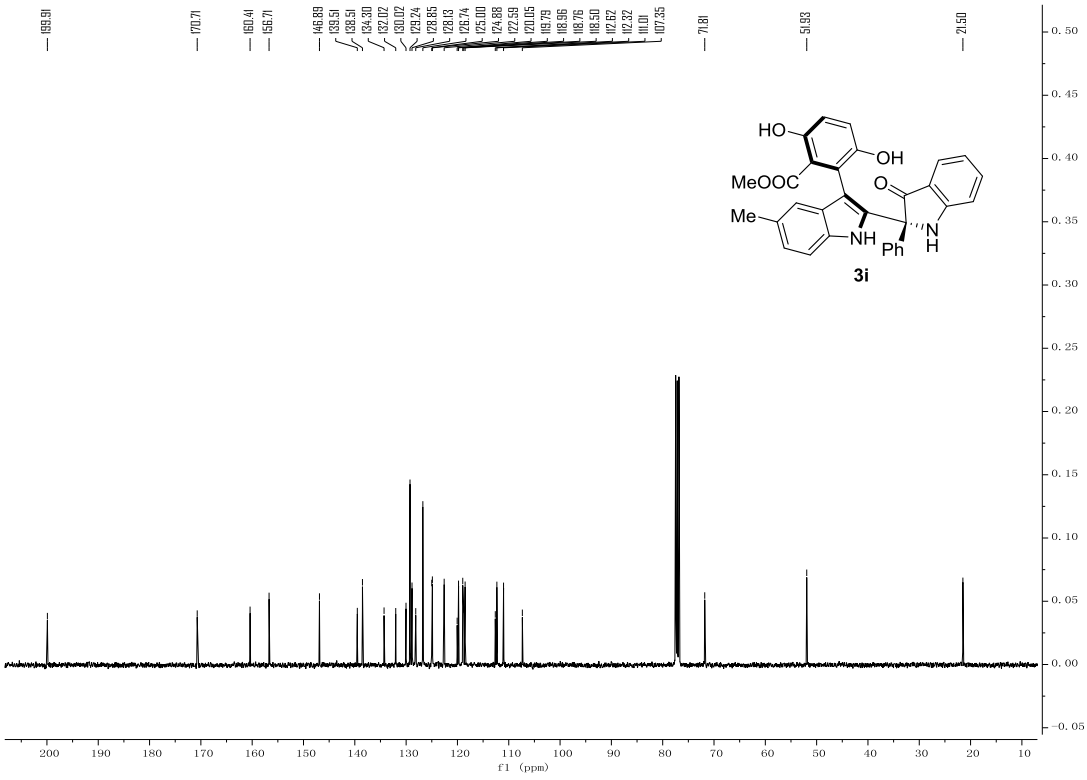
7.29
7.22
7.20
7.15
7.13
7.04
7.04
7.02
7.02
6.98
6.95
6.87
6.83
6.81
6.79
6.46
6.44
5.11
5.00
2.89
2.33
HO
OH
MeOOC
O
Me
NH
Ph
N
H
3i
0.97
1.00
1.01
1.07
4.98
0.95
1.02
1.02
1.03
0.98
1.02
0.99
0.89
0.89
3.00
3.03
f1 (ppm)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128.13
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125.00
124.88
122.59
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118.96
118.76
118.50
117.67
112.32
111.01
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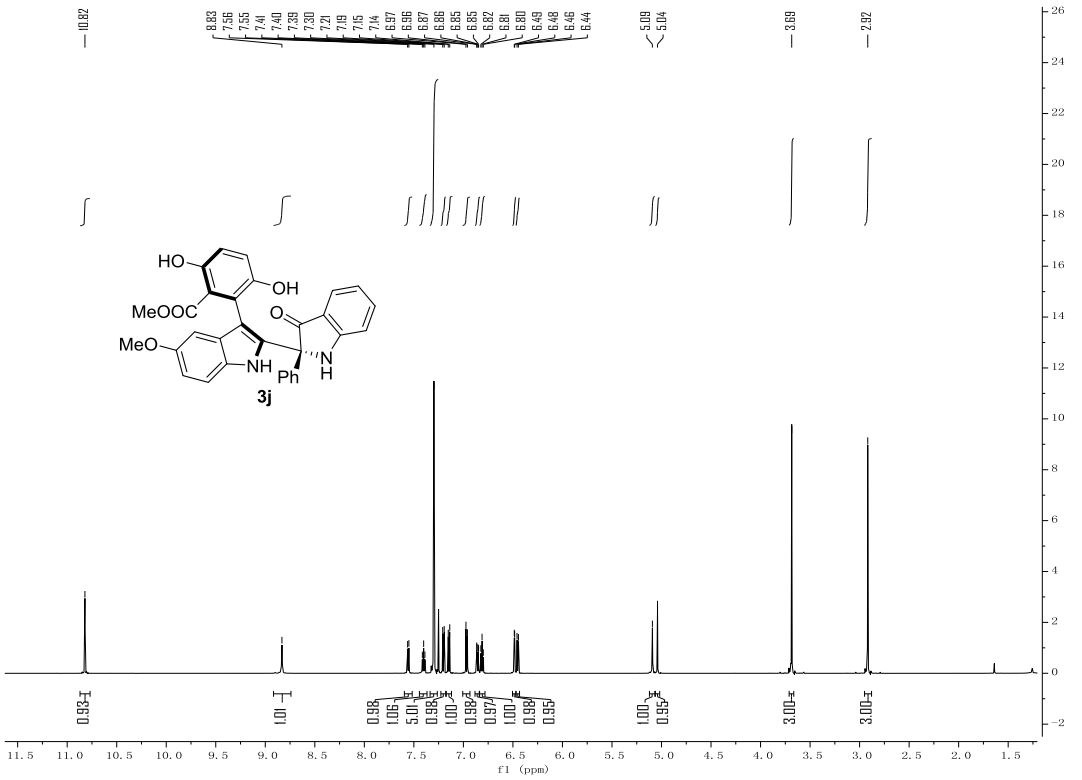
OH
MeOOC
O
Me
NH
Ph
N
H
3i
f1 (ppm)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6.82
6.81
6.80
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6.48
6.46
6.44
5.09
5.04
3.68
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OH
MeOOC
O
MeO
NH
Ph
N
H
3j
0.93
1.01
0.98
1.06
5.01
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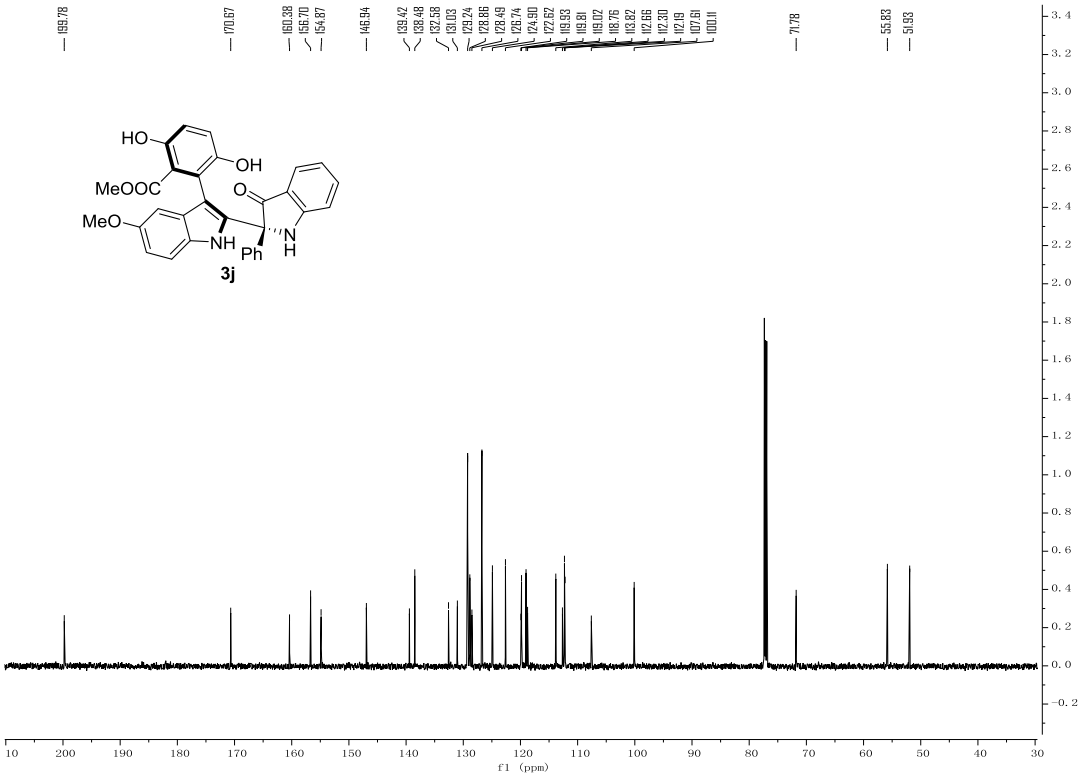
3.00
f1 (ppm)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119.02
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112.30
112.19
107.61
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51.93
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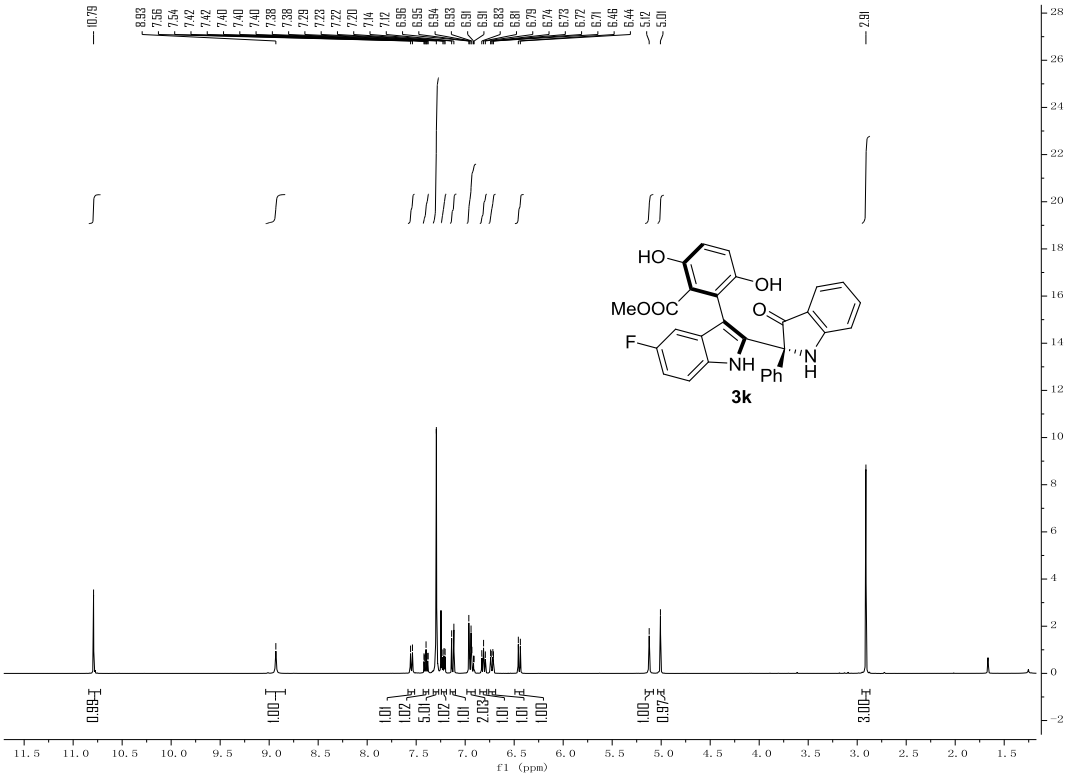
OH
MeOOC
O
MeO
NH
Ph
N
H
3j
f1 (ppm)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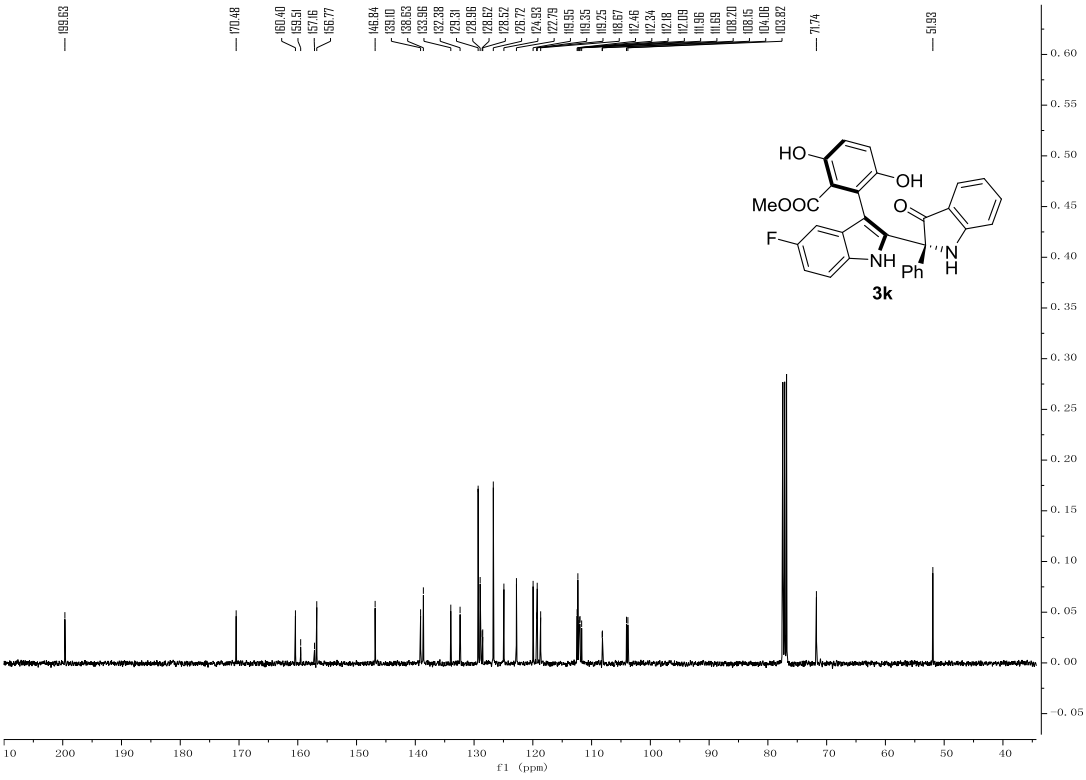
O
F
NH
Ph
N
H
3k
f1 (ppm)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F
NH
Ph
N
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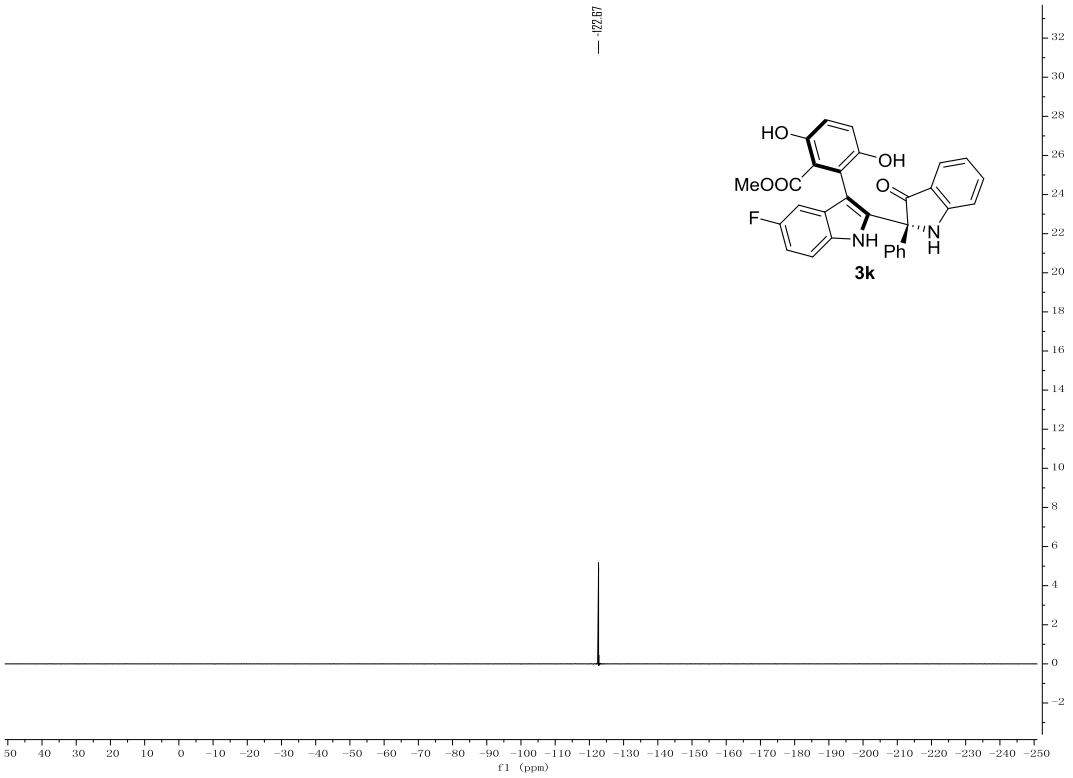
3k
f1 (ppm)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OH
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NH
Ph
N
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3k
32
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28
26
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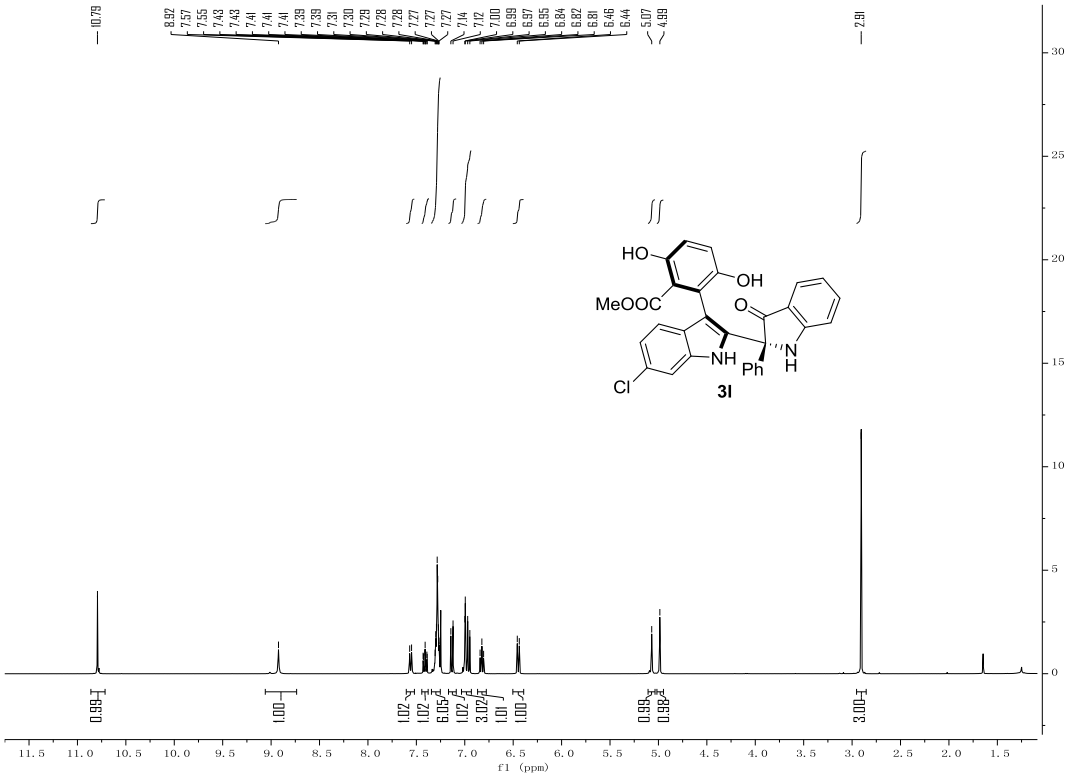
22
20
18
16
14
12
10
8
6
4
2
0
-2
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)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7.27
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7.27
7.27
7.14
7.12
7.00
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6.97
6.95
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6.82
6.81
6.46
6.44
5.07
4.99
2.91
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O
NH
Ph
N
H
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3l
0.99
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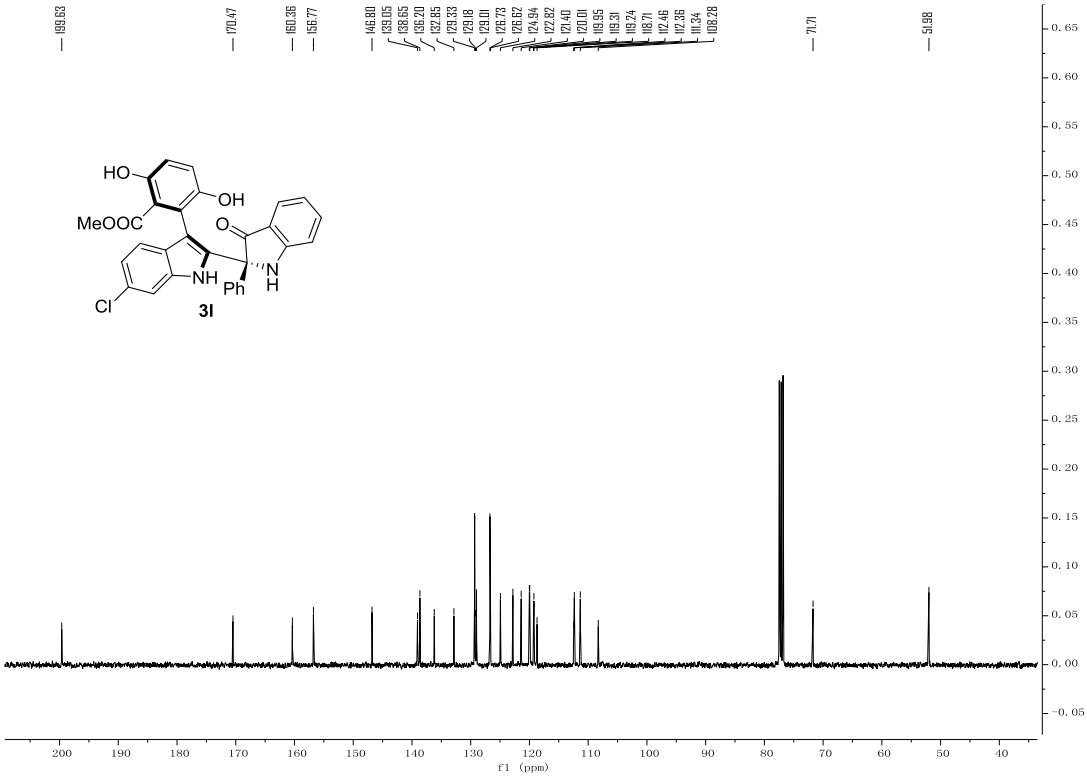
3.00
f1 (ppm)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122.82
121.40
120.01
119.95
119.31
119.24
118.71
112.46
112.36
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51.98
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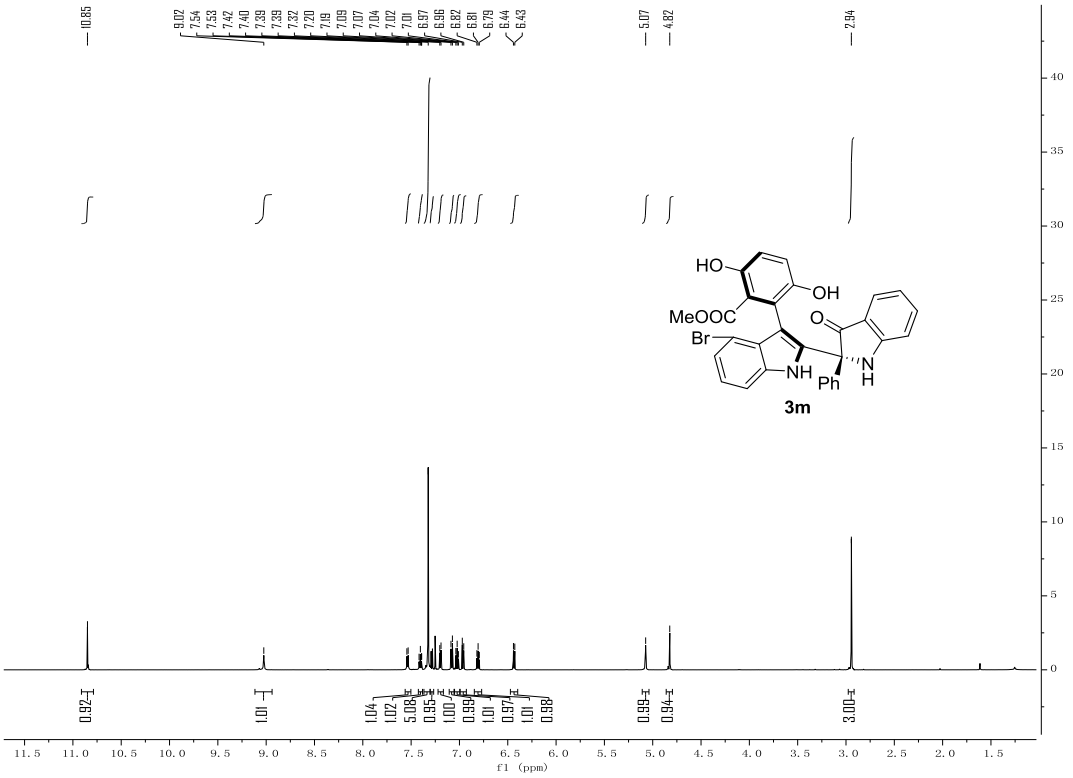
OH
MeOOC
O
NH
Ph
N
H
Cl
3l
f1 (ppm)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7.20
7.19
7.09
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7.02
7.01
6.97
6.96
6.82
6.81
6.79
6.44
6.43
5.07
4.82
2.94
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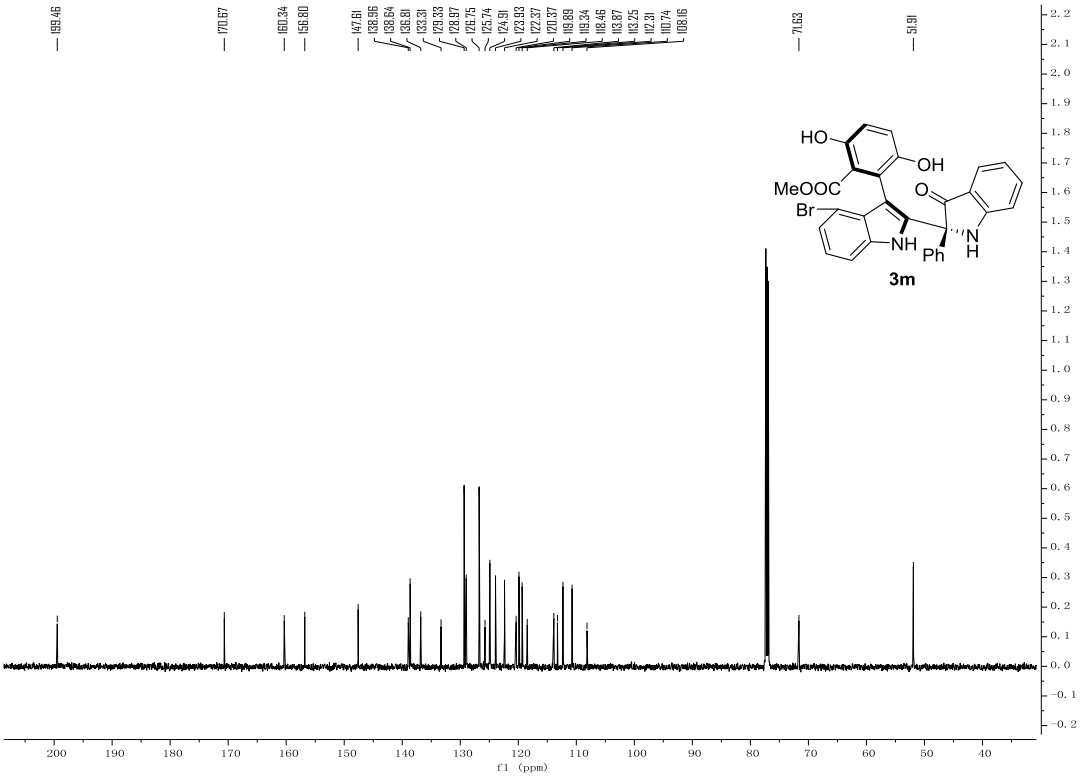
OH
MeOOC
O
Br
NH
Ph
N
H
3m
f1 (ppm)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120.37
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119.34
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112.31
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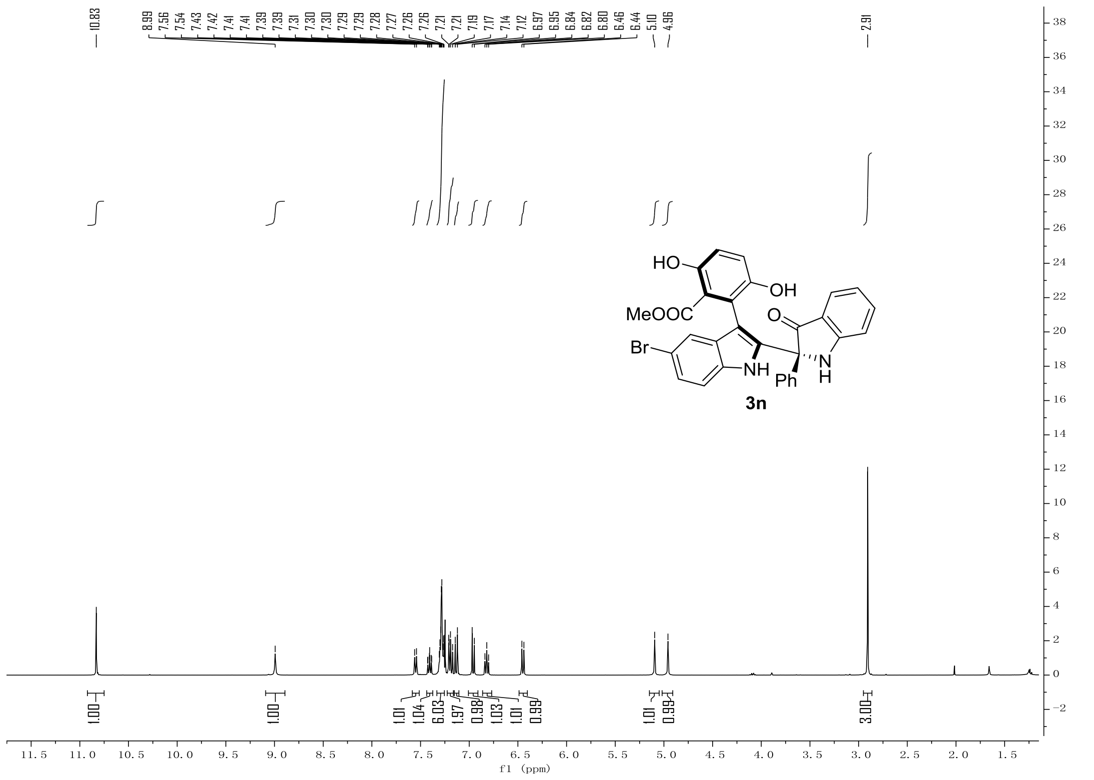
Br
NH
Ph
N
H
3m
f1 (ppm)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5.10
4.96
2.91
HO
OH
MeOOC
O
Br
NH
Ph
N
H
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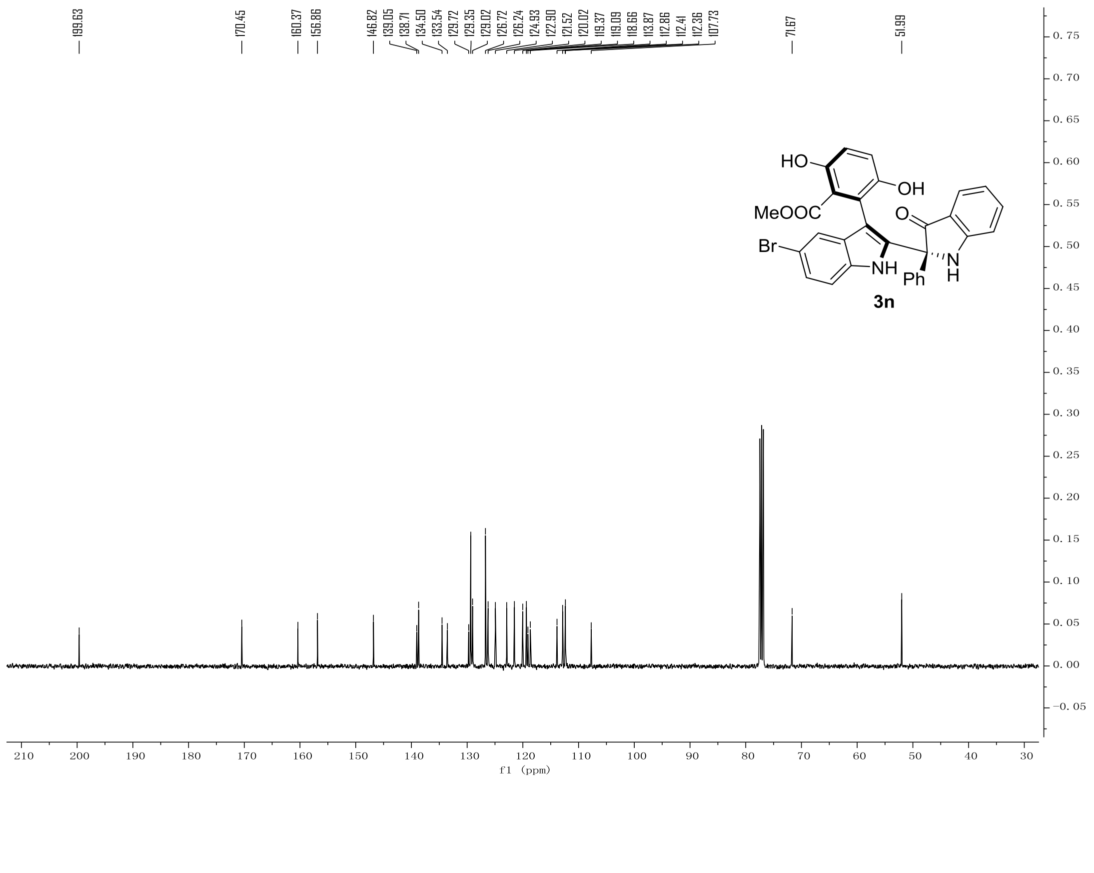
1.00
1.01 1.04 6.03 1.97 0.98 1.03 1.01 0.99
1.01 0.99
3.00
f1 (ppm)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156.86
146.82 139.05 138.71 134.50 133.54 129.72 129.35 129.02 126.72 126.24 124.93 122.90 121.52 120.02 119.37 119.09 118.66 113.87 112.86 112.41 112.36 107.73
71.67
51.99
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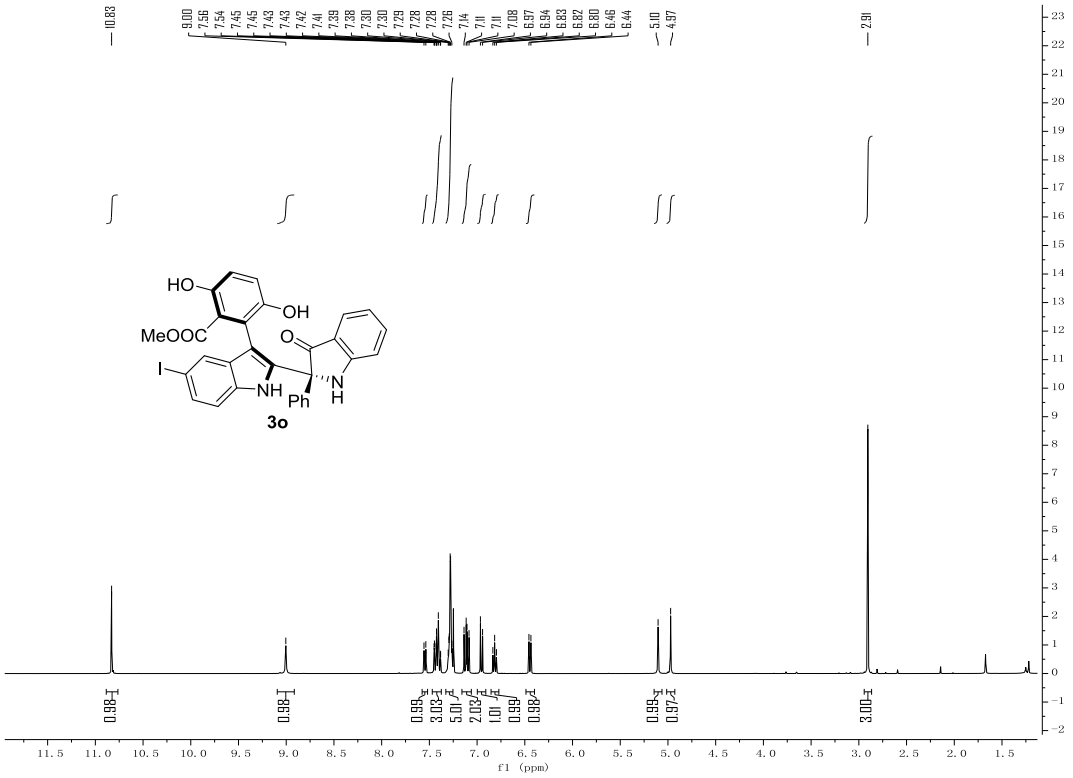
OH
MeOOC
O
Br
NH
Ph
N
H
3n
f1 (ppm)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7.26
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7.08
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6.94
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OH
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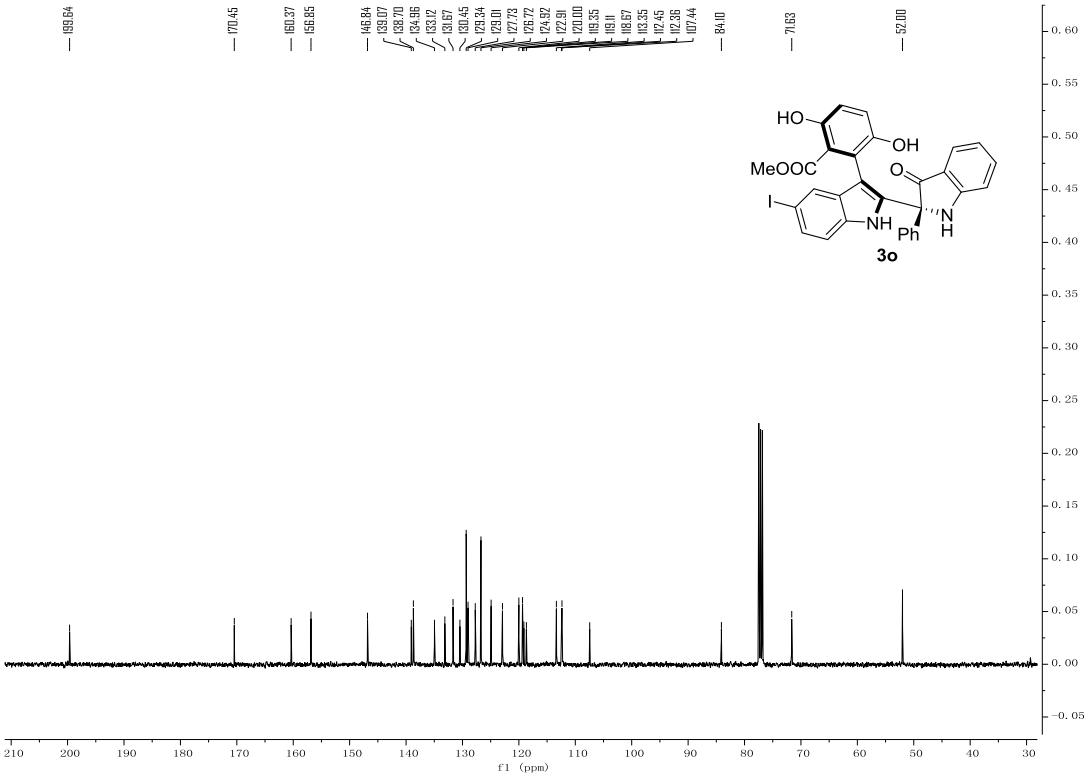
f1 (ppm)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121.00
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119.11
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113.35
112.45
112.36
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52.00
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OH
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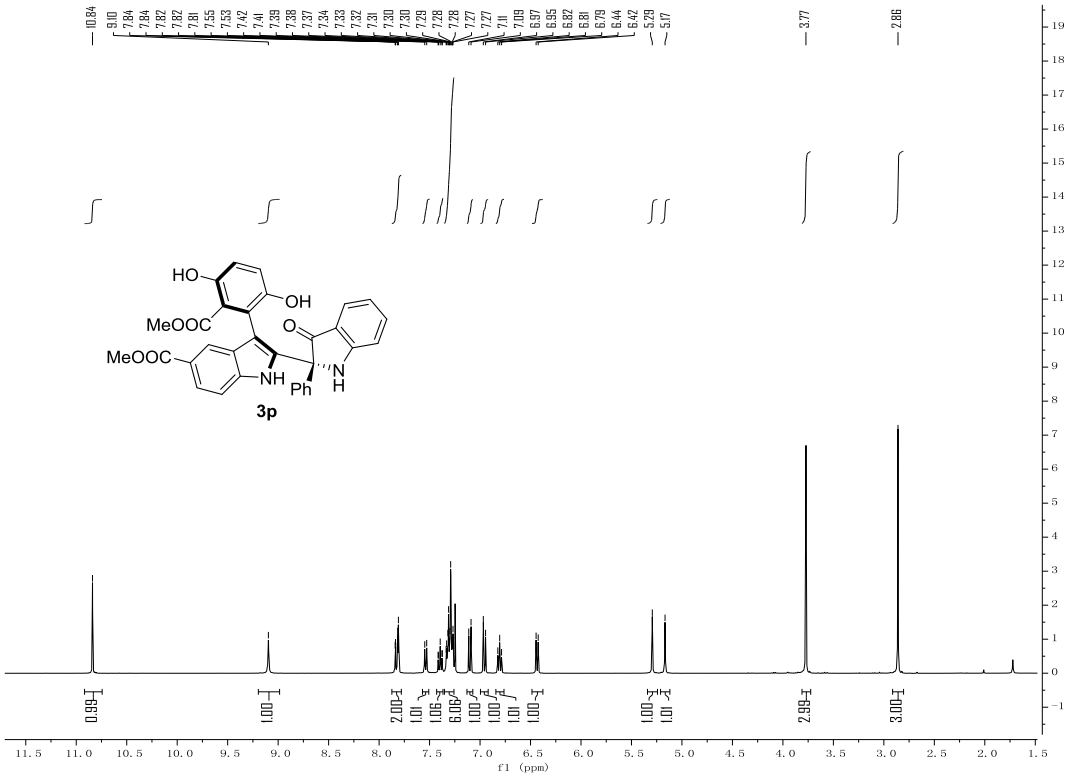
NH
Ph
N
H
3o
f1 (ppm)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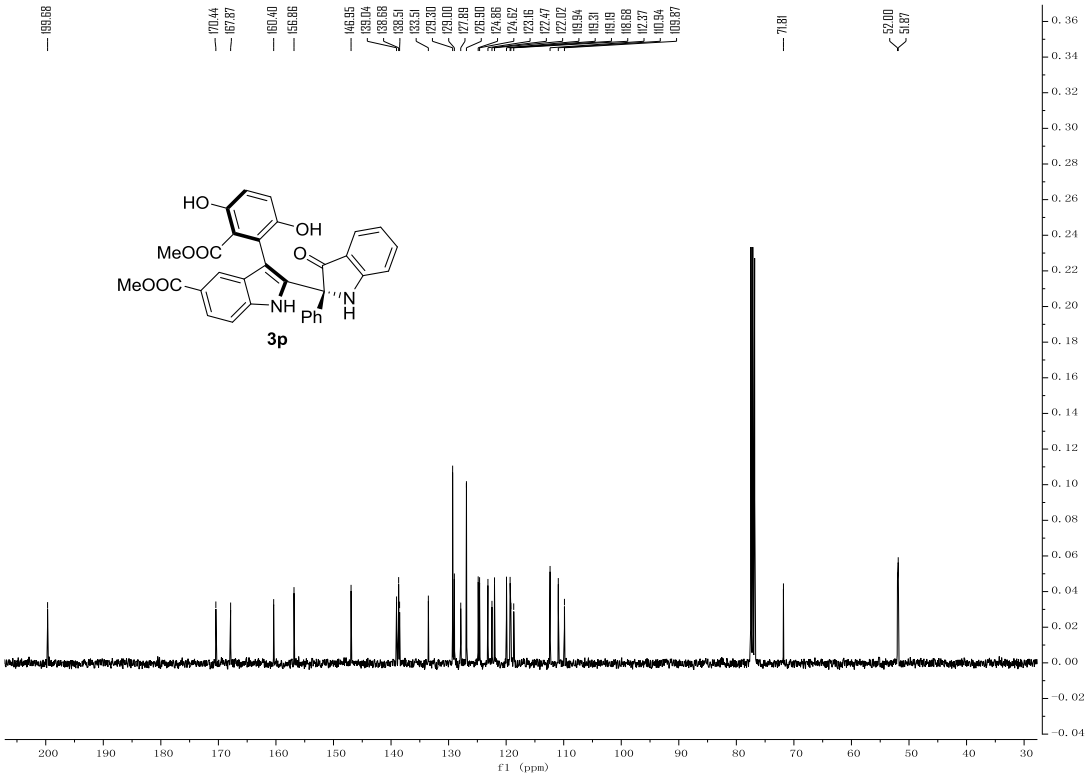
f1 (ppm)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Ph
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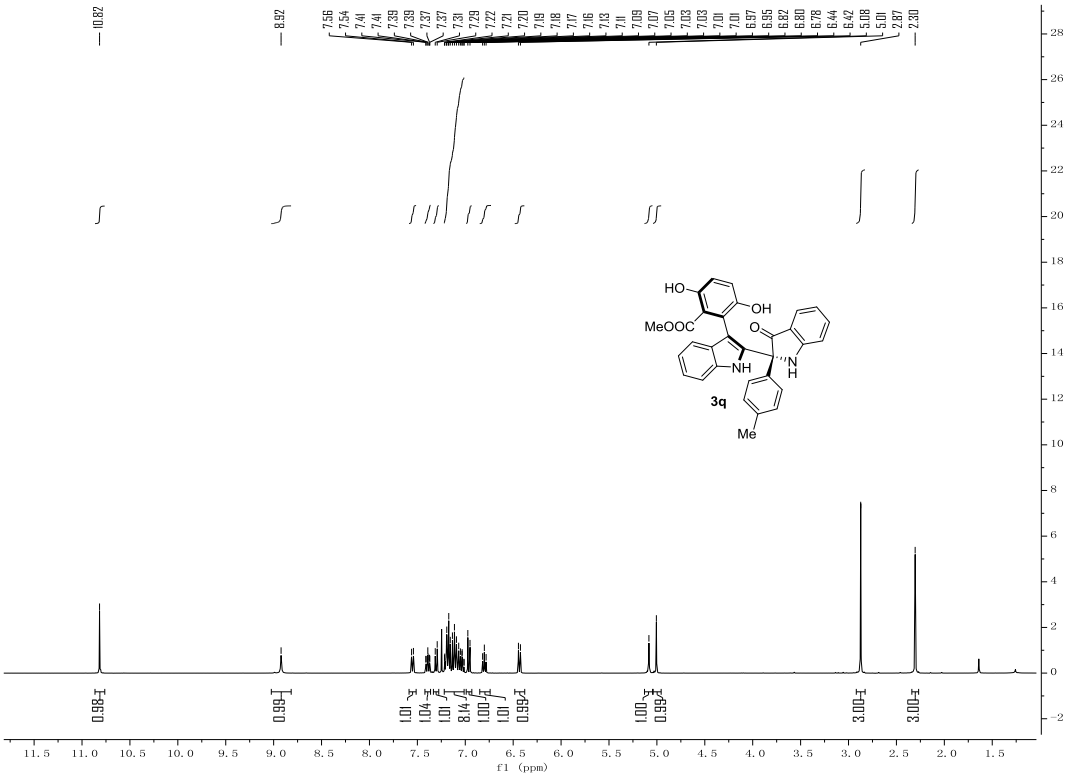
f1 (ppm)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7.11
7.09
7.07
7.05
7.03
7.03
7.01
7.01
6.97
6.95
6.82
6.80
6.78
6.44
6.42
5.08
5.01
2.87
2.30
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OH
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O
NH
N
H
3q
Me
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3.00
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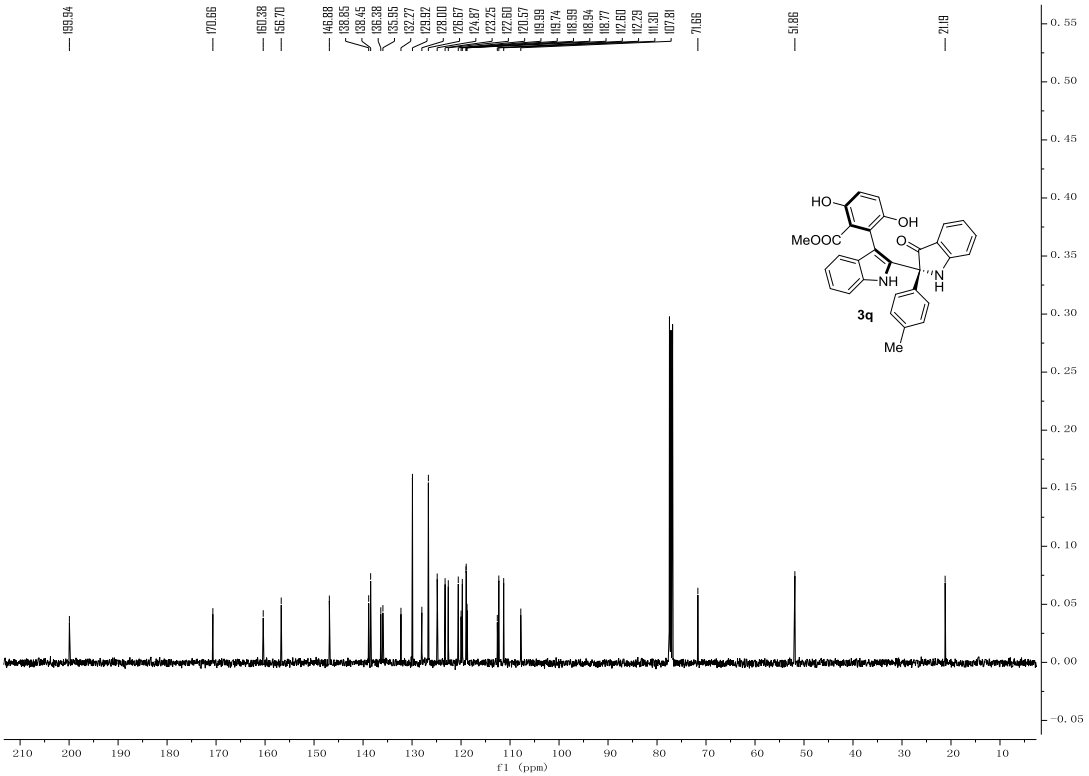
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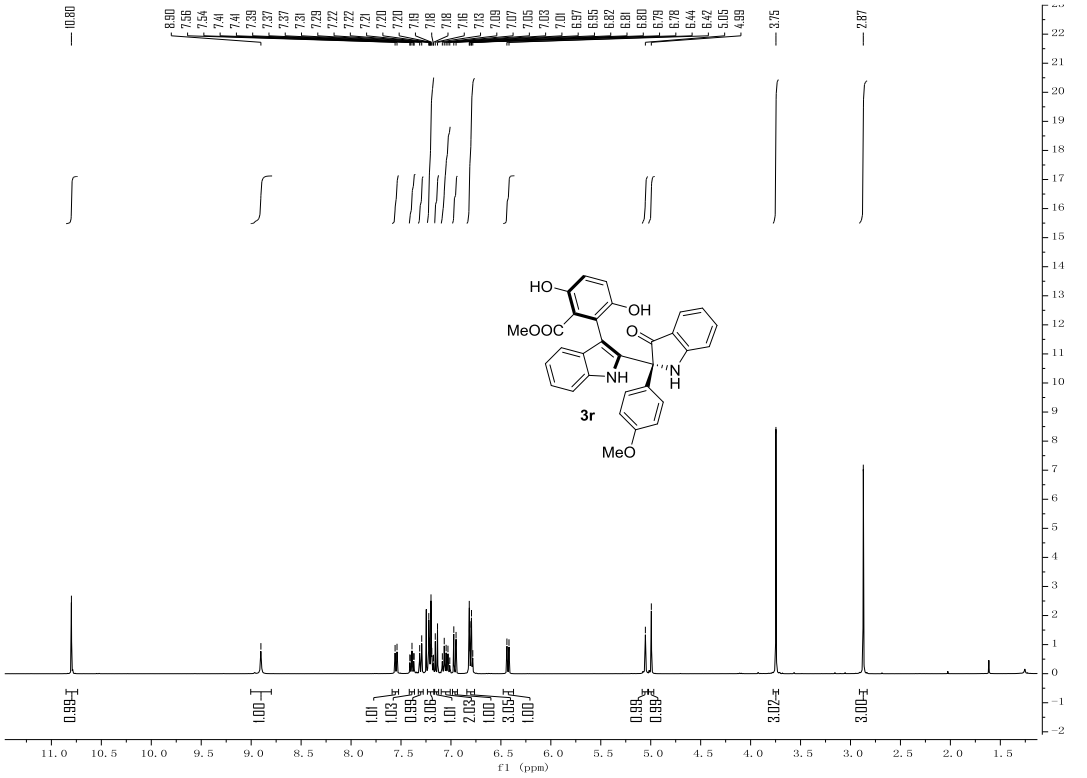
Me
f1 (ppm)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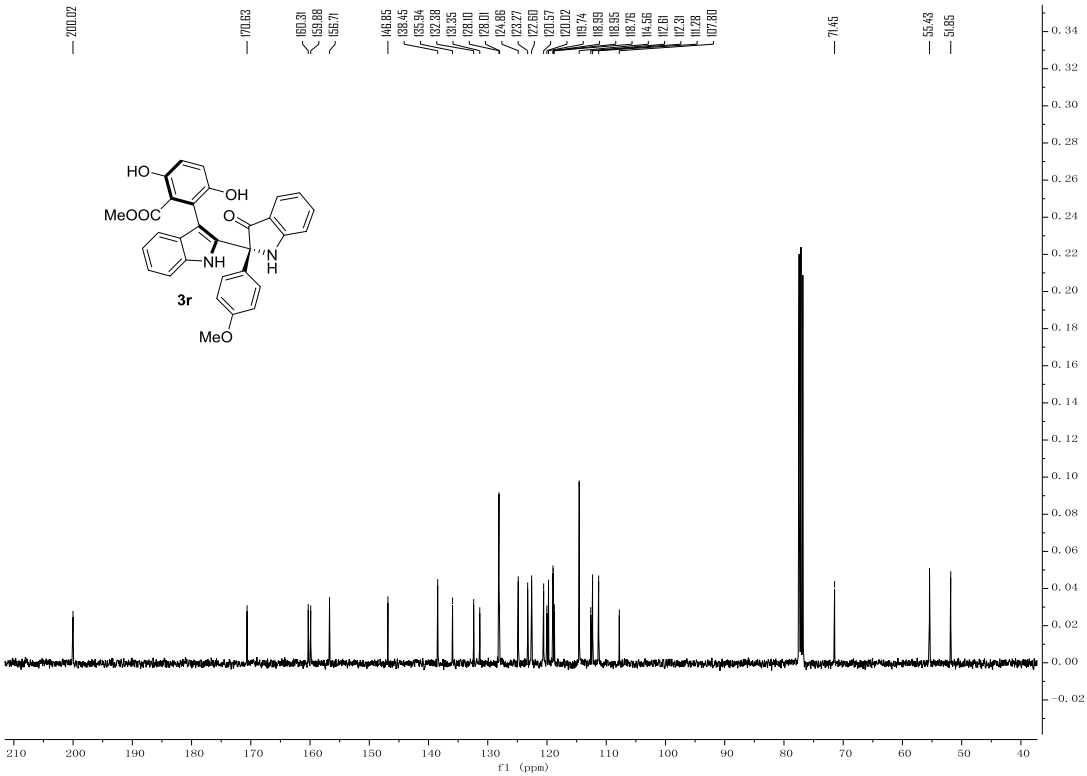
f1 (ppm)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123.27
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118.95
118.76
114.56
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112.31
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55.43
51.85
HO
OH
MeOOC
O
NH
N
H
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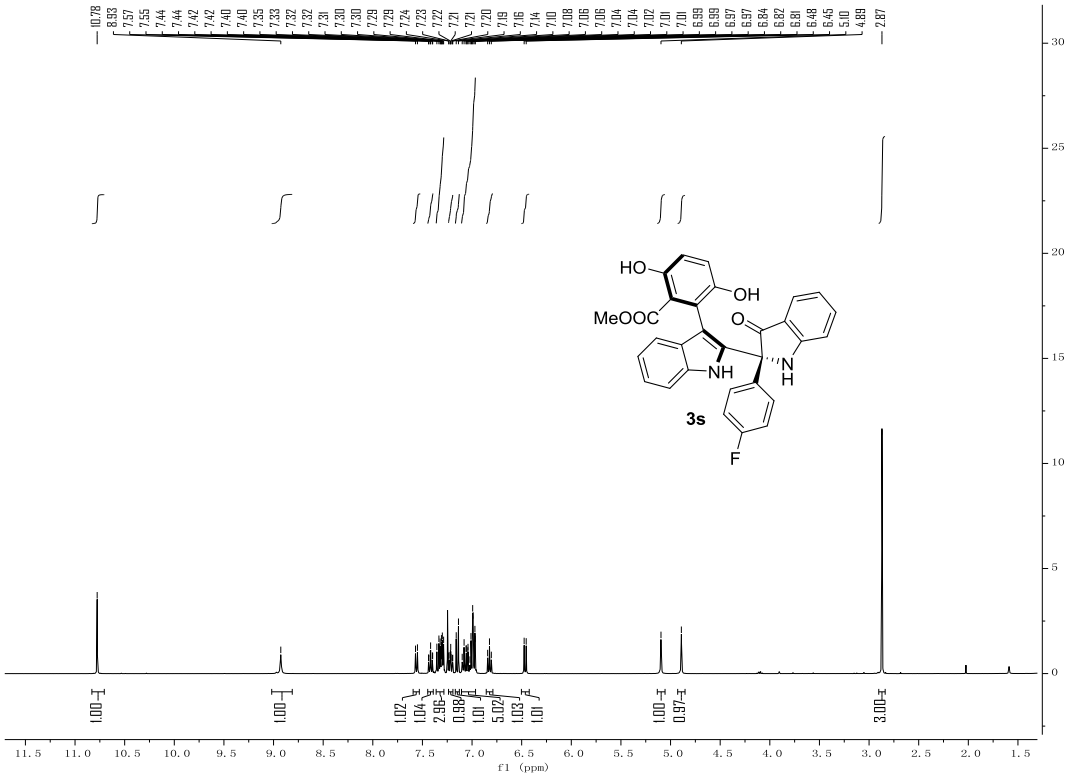
MeO
f1 (ppm)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2.87
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OH
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NH
N
H
3s
F
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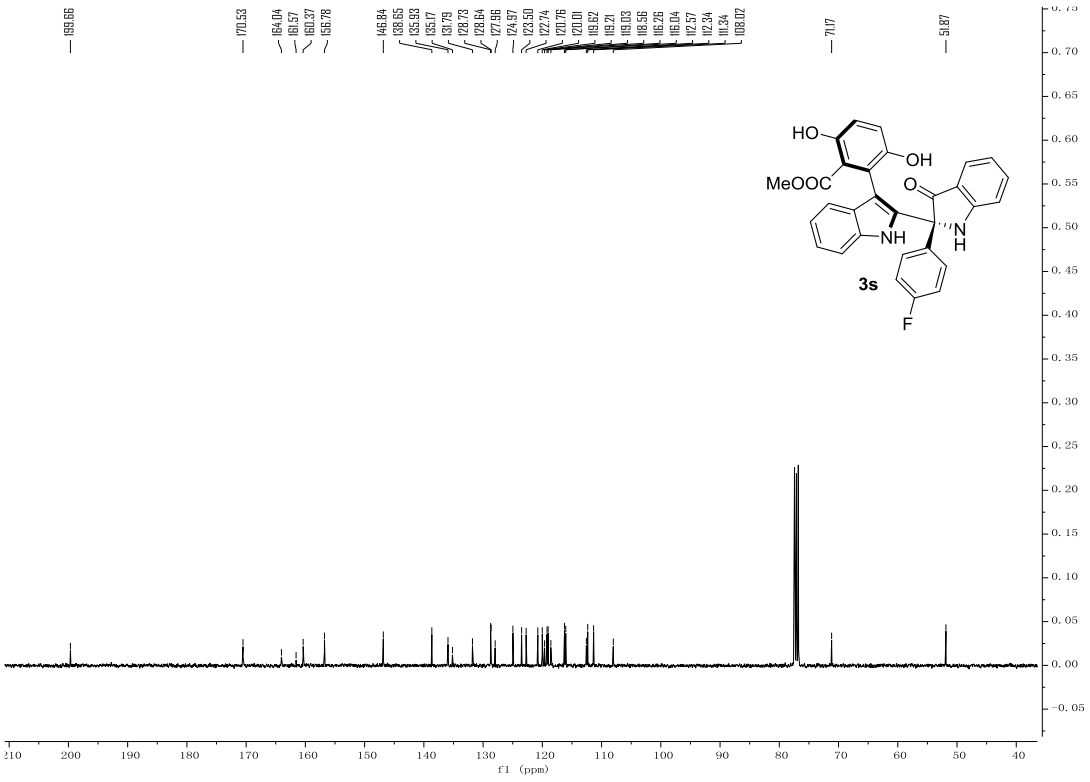
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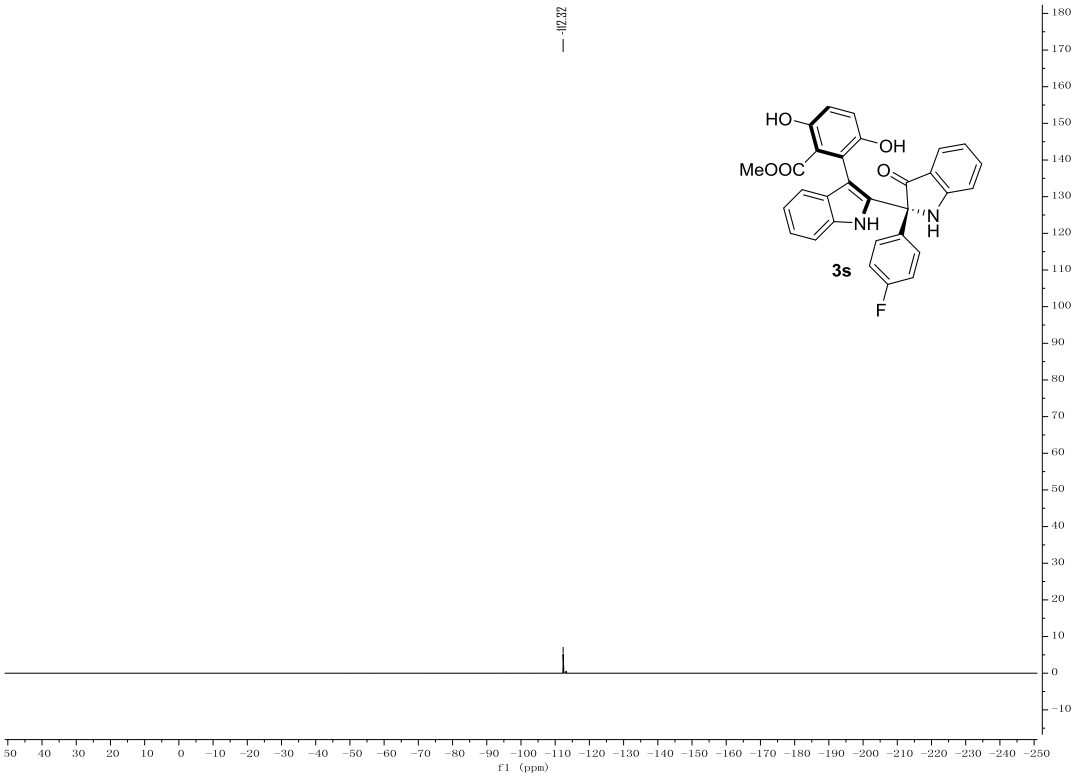
3s
F
f1 (ppm)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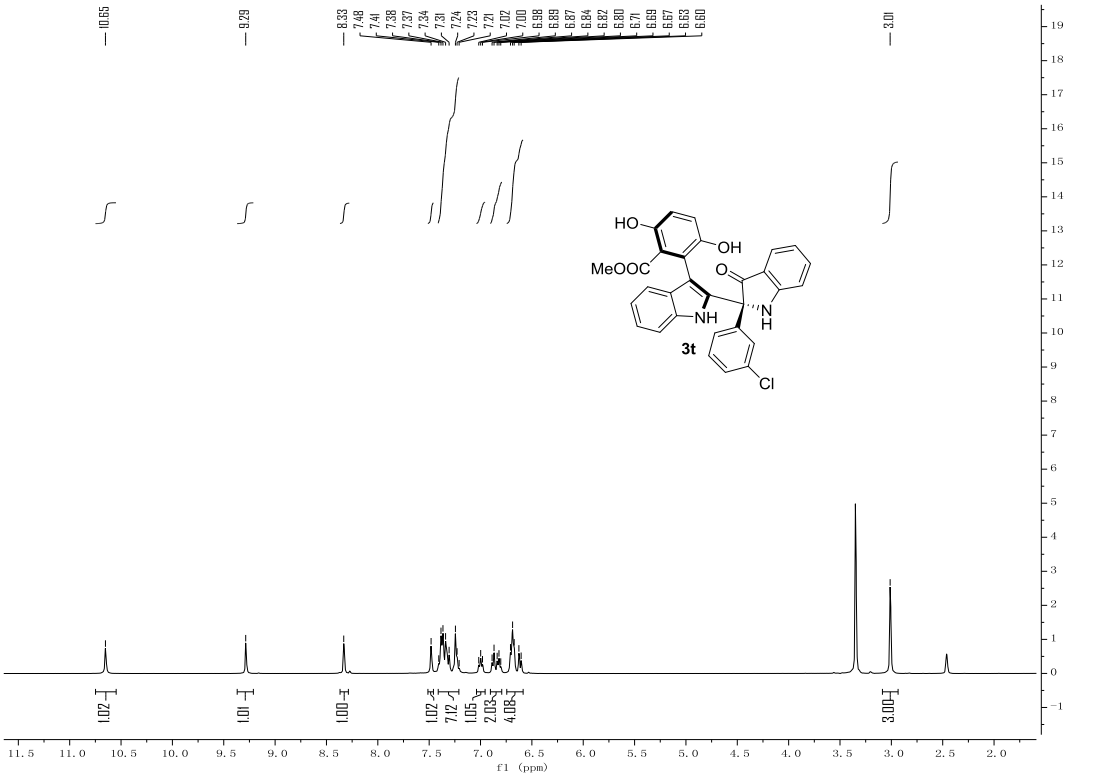
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6.69
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O
NH
N
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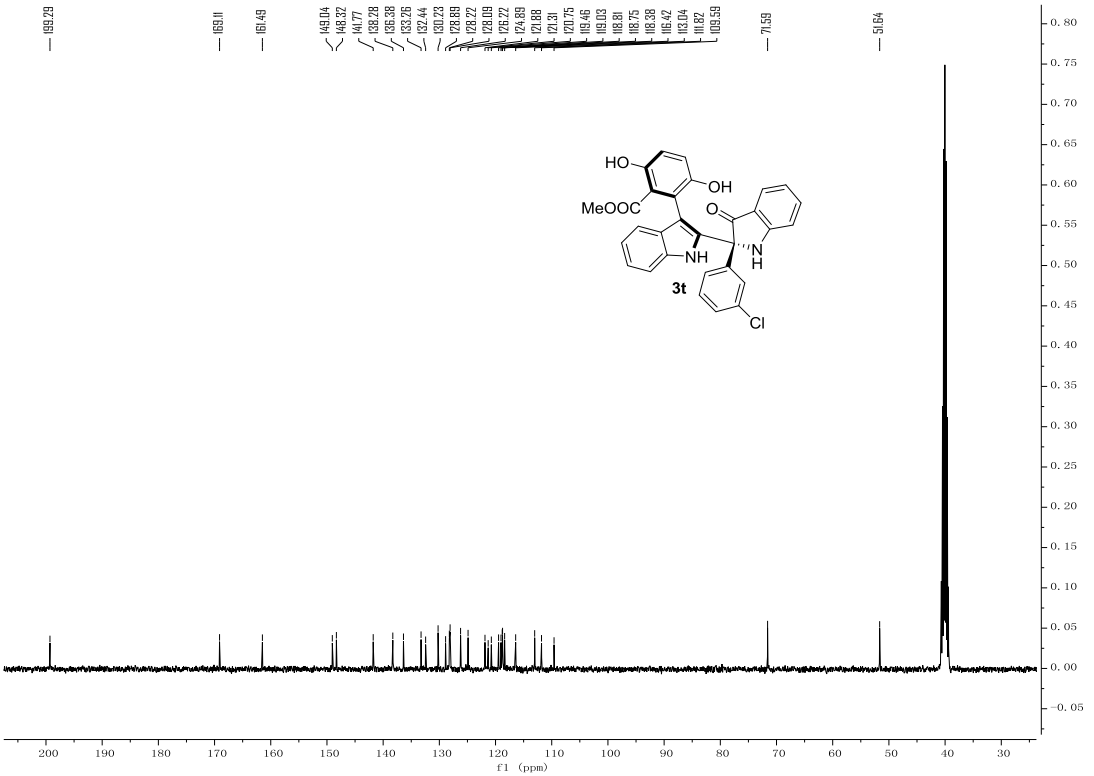
3.00
f1 (ppm)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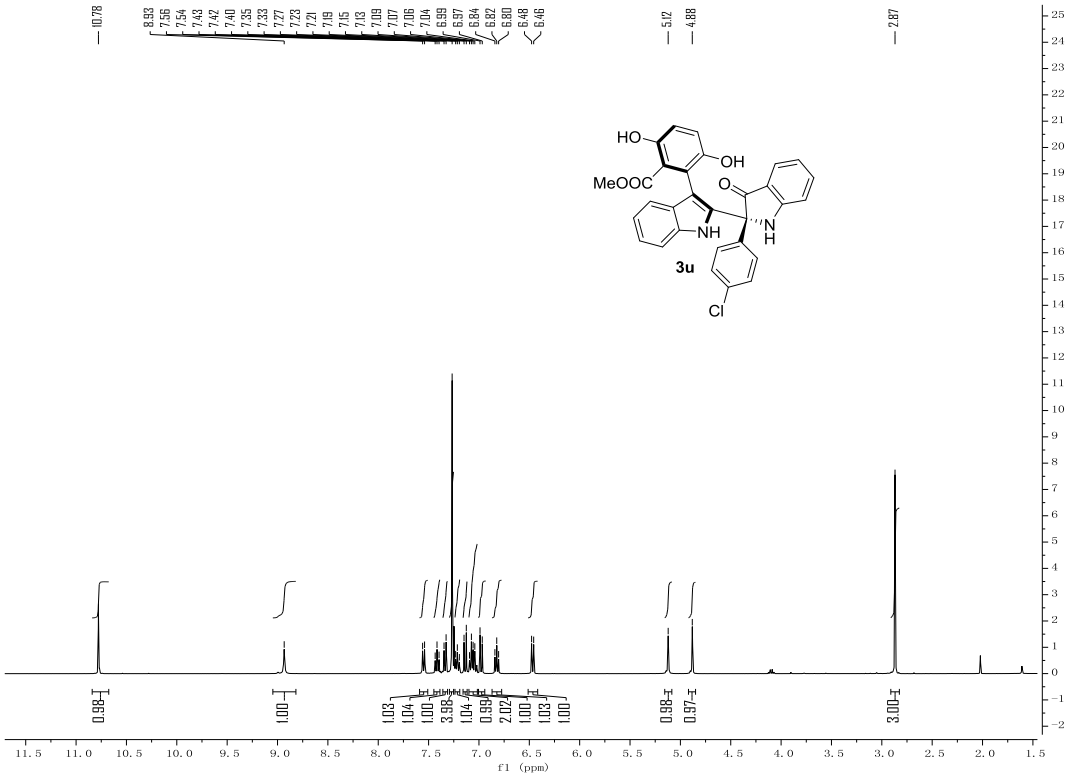
Cl
f1 (ppm)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HO
OH
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NH
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Cl
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1.03
1.04
1.00
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1.04
0.99
2.02
1.00
1.03
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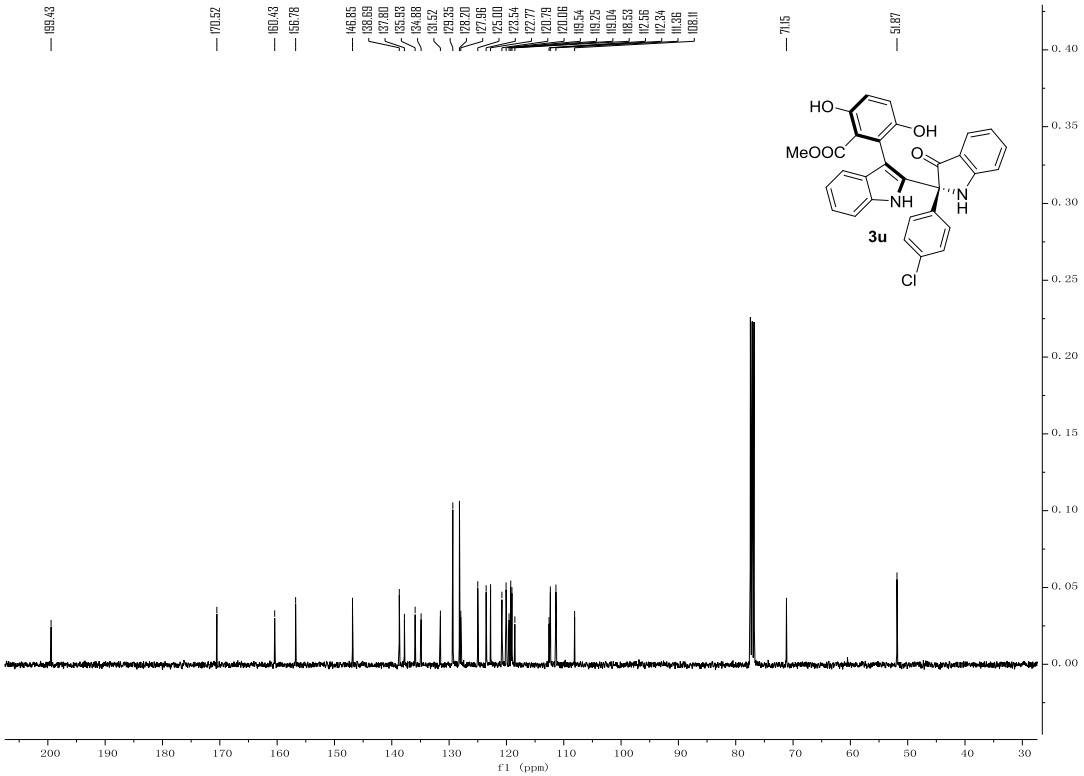
0.97
3.00
f1 (ppm)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122.77
120.79
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119.25
119.04
118.53
112.56
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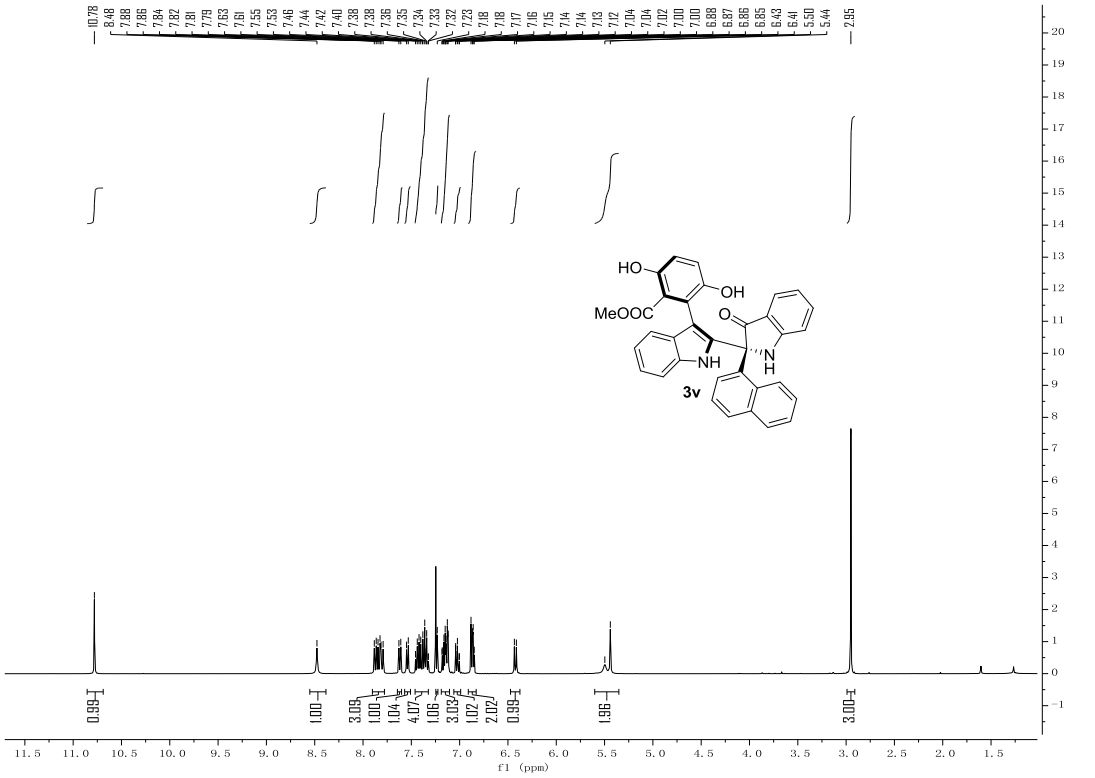
O
NH
N
H
Cl
3u
f1 (ppm)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7.38
7.36
7.35
7.34
7.33
7.32
7.23
7.18
7.18
7.17
7.16
7.15
7.14
7.14
7.13
7.12
7.04
7.04
7.02
7.00
7.00
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6.87
6.86
6.85
6.43
6.41
5.50
5.44
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OH
MeOOC
O
NH
N
H
3v
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1.02
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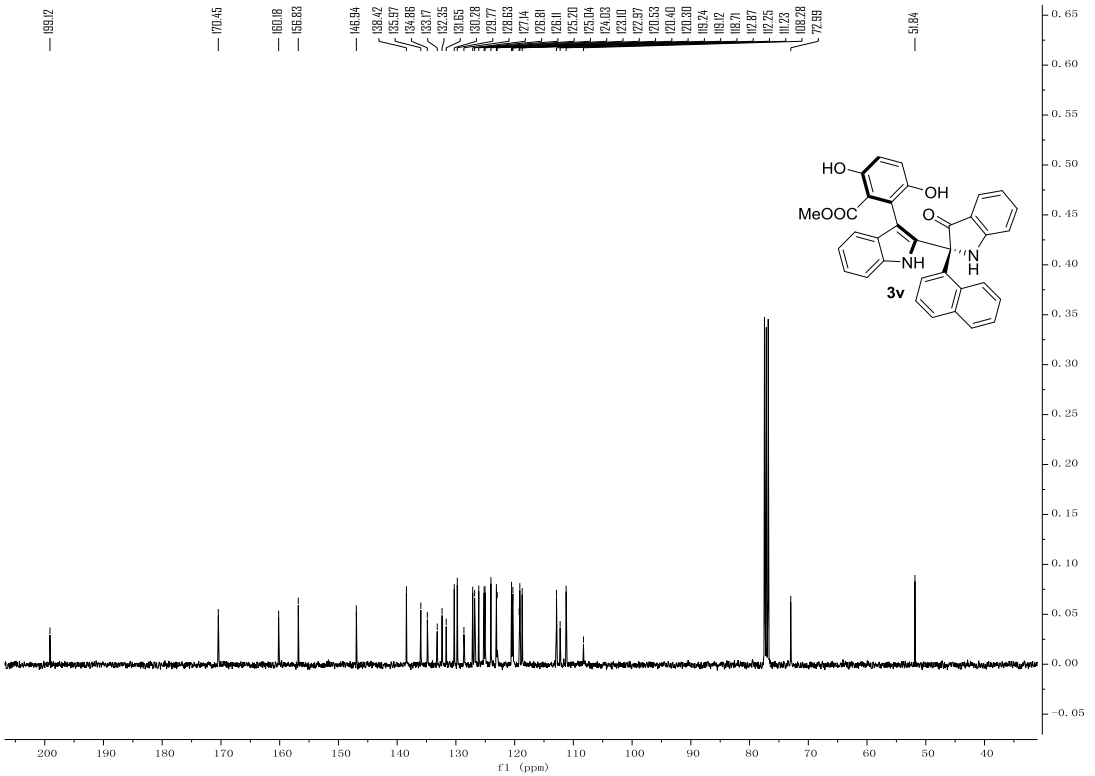
3.00
f1 (ppm)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119.12
118.71
112.87
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OH
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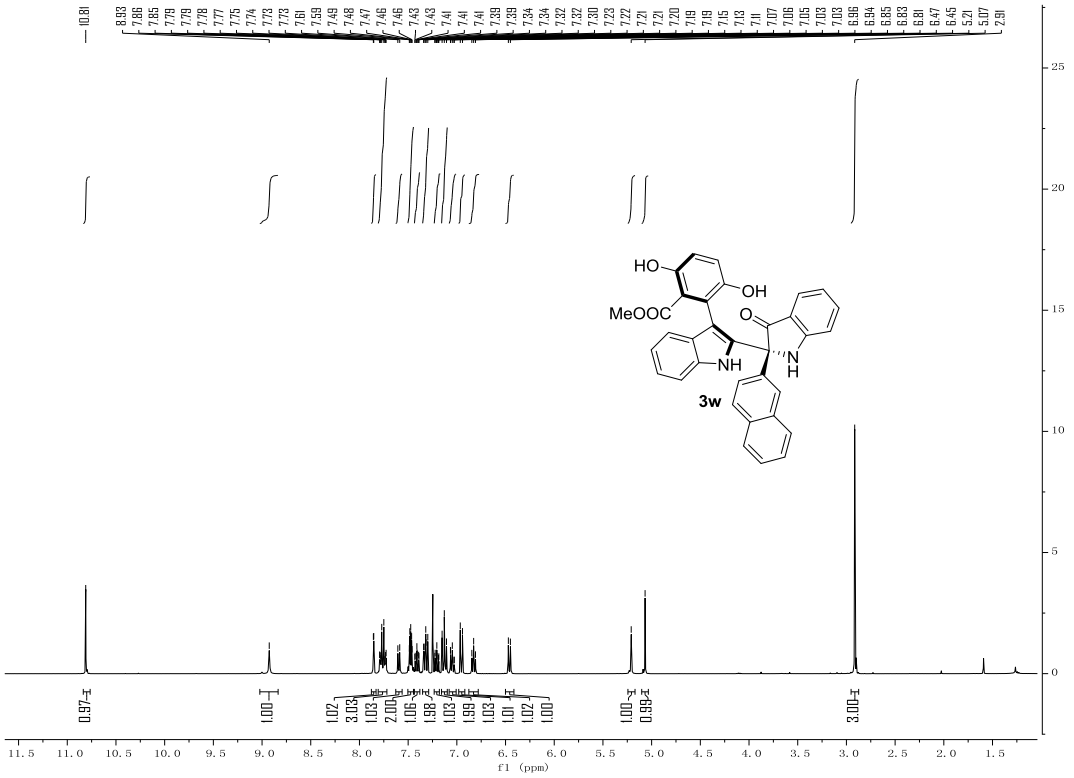
O
NH
N
H
3v
f1 (ppm)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7.41
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7.03
7.03
6.96
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H
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1.03
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1.02
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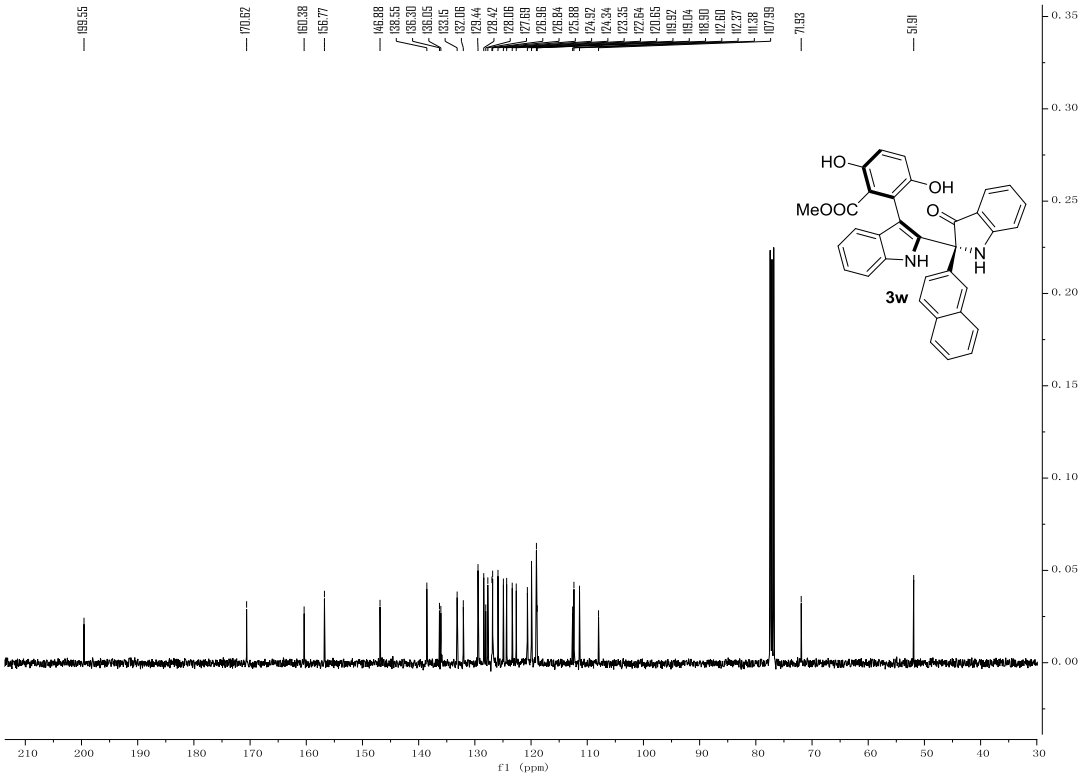
f1 (ppm)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OH
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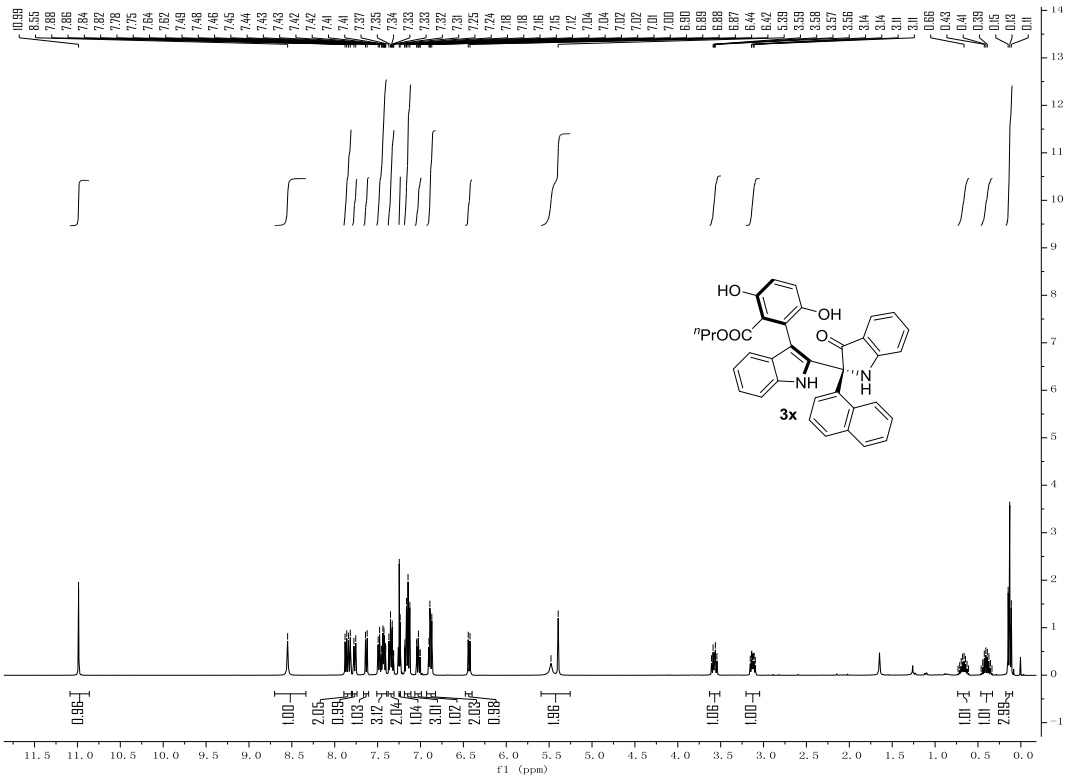
O
NH
N
H
3w
f1 (ppm)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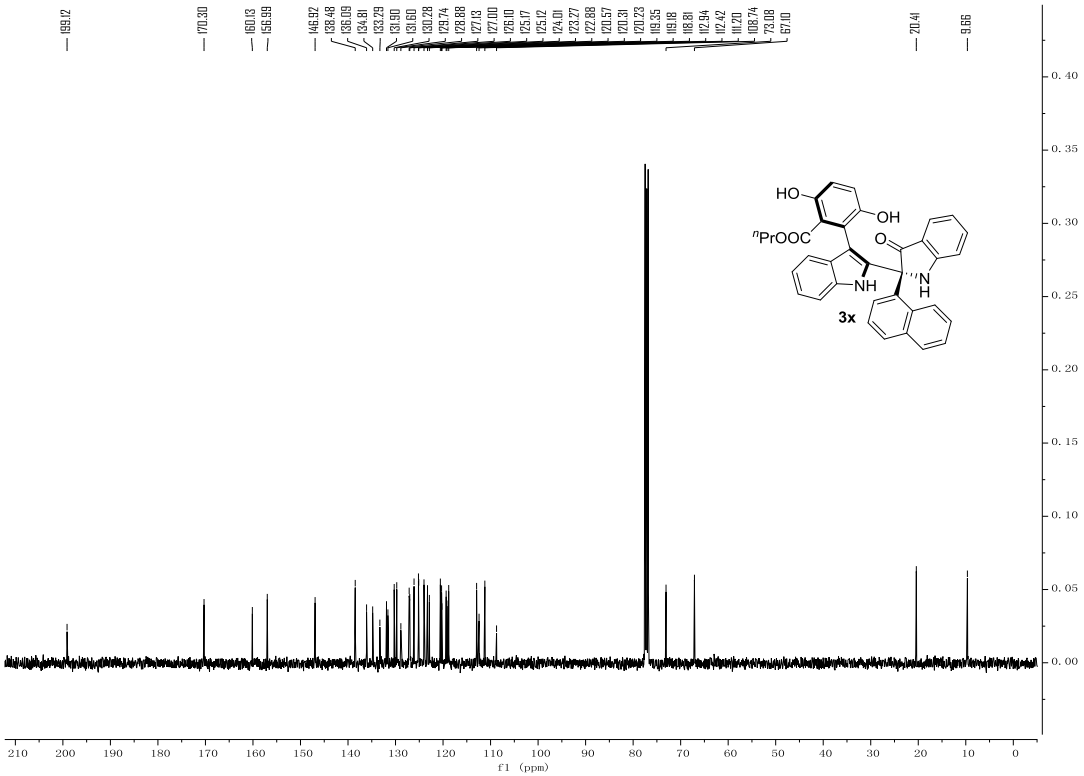
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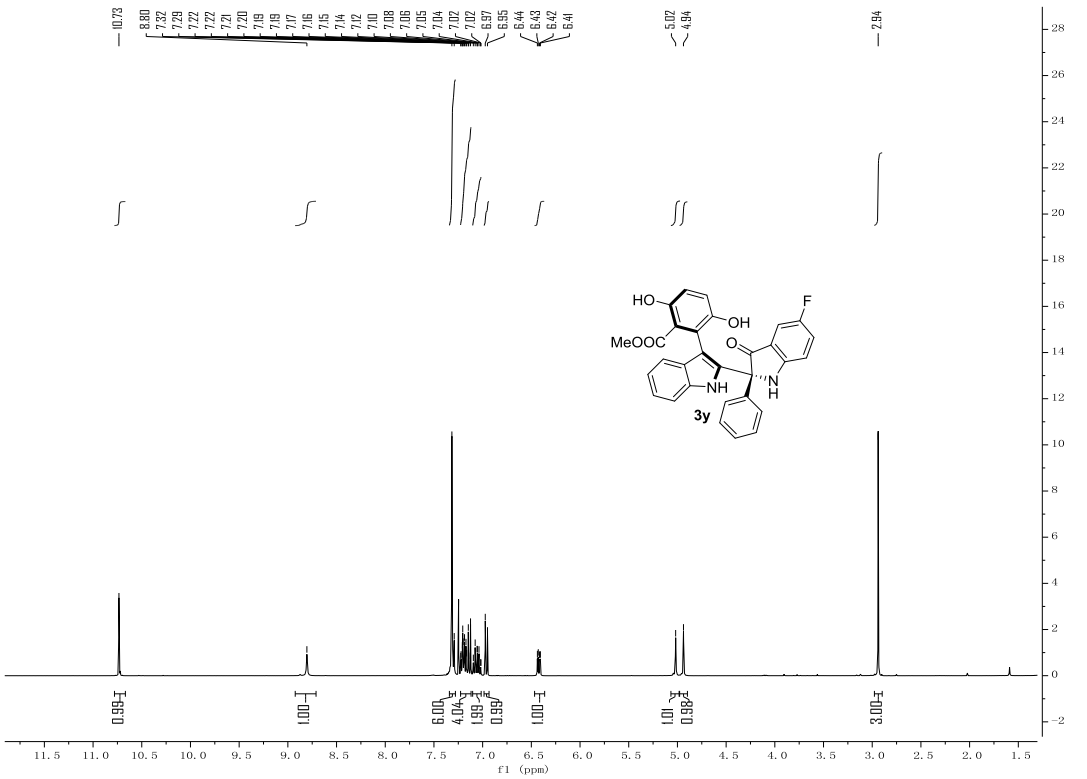
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7.14
7.12
7.10
7.08
7.06
7.05
7.04
7.02
7.02
6.97
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6.43
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4.94
2.94
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MeOOC
O
NH
N
H
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6.00
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1.00
1.01
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3.00
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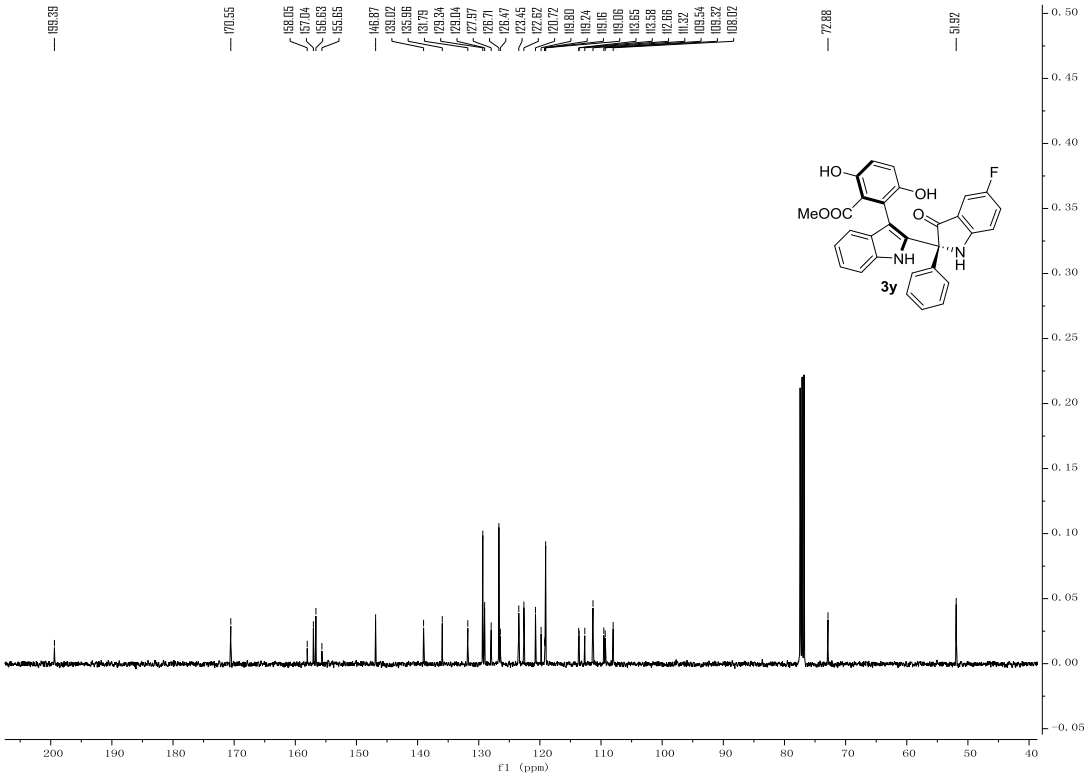
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OH
F
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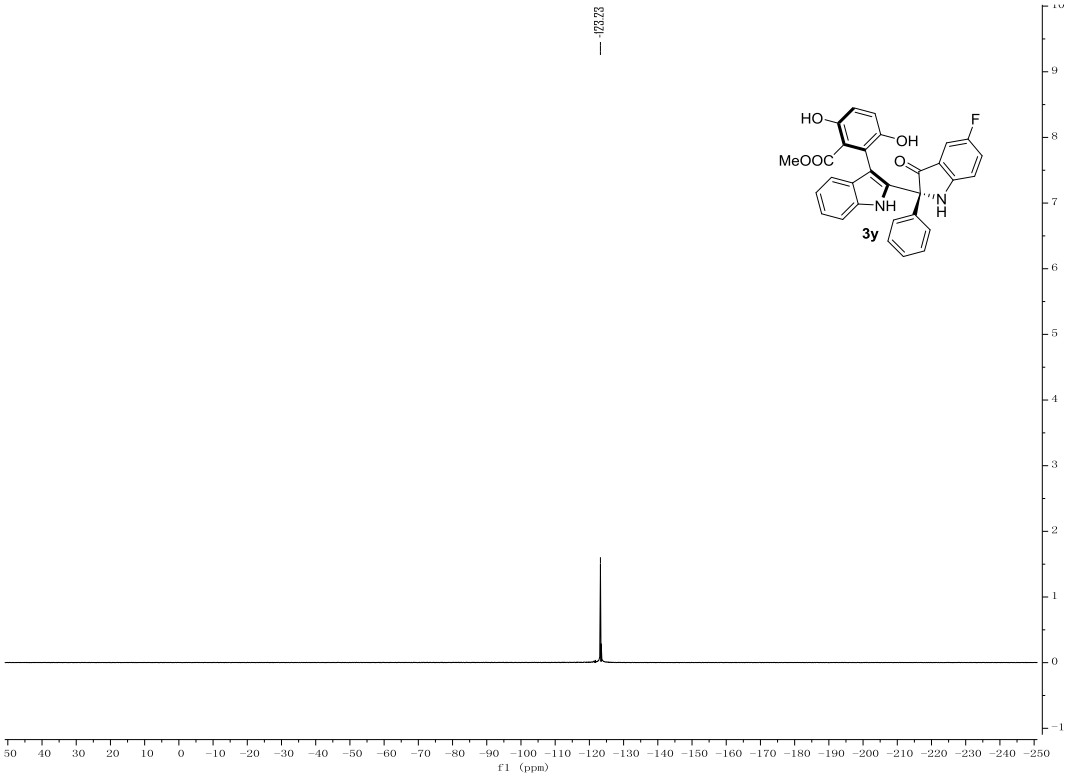
O
NH
N
H
3y
f1 (ppm)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F
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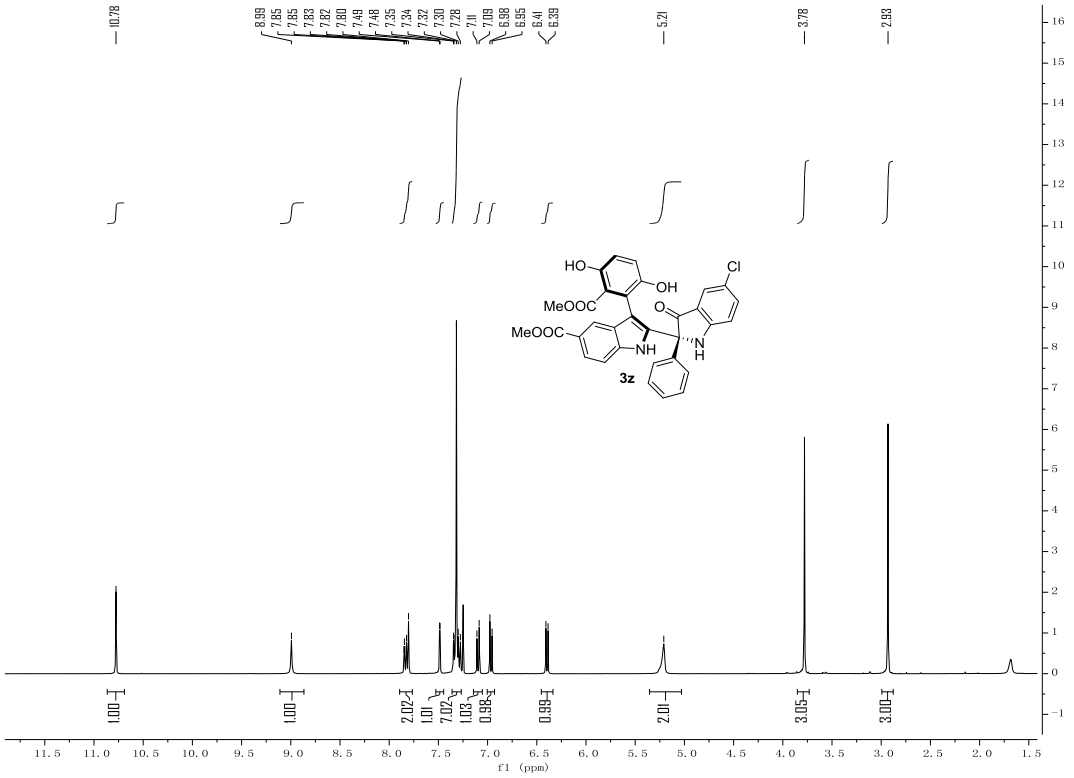
O
NH
N
H
3y
10
9
8
7
6
5
4
3
2
1
0
-1
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)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7.34
7.32
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7.28
7.11
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OH
Cl
MeOOC
O
MeOOC
NH
N
H
3z
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1.01
7.02
1.03
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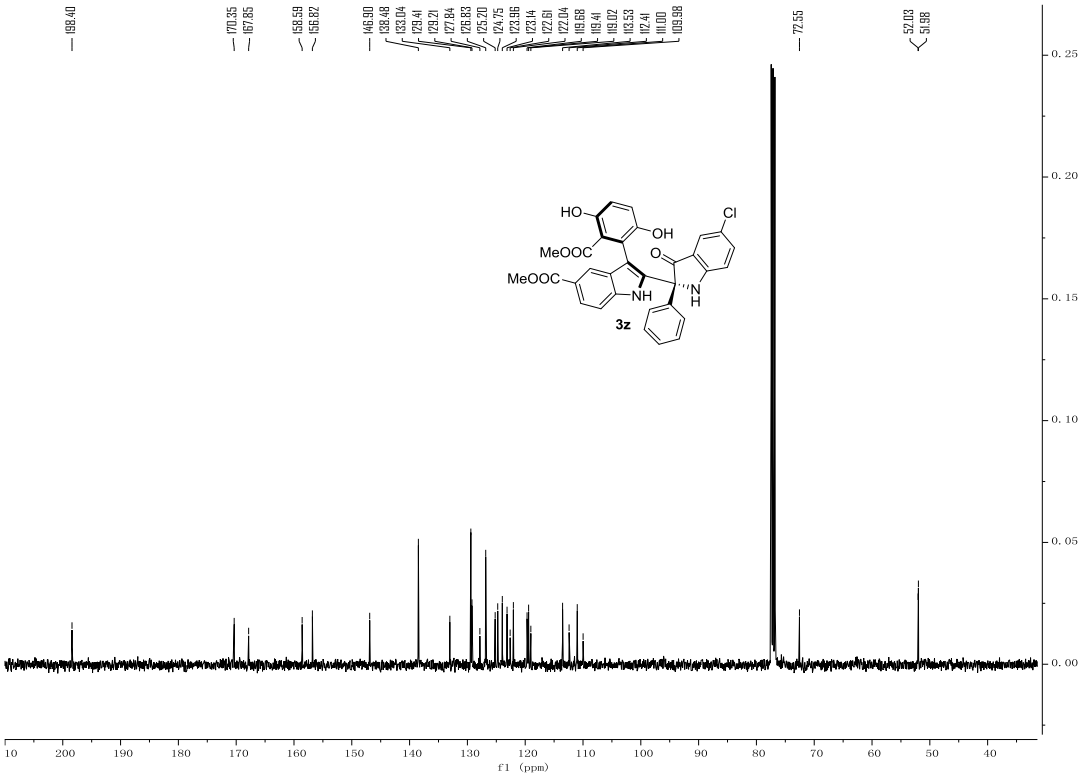
0.99
2.01
3.05
3.00
f1 (ppm)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123.14
122.61
122.04
119.68
119.41
119.02
113.53
112.41
111.00
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51.88
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OH
Cl
MeOOC
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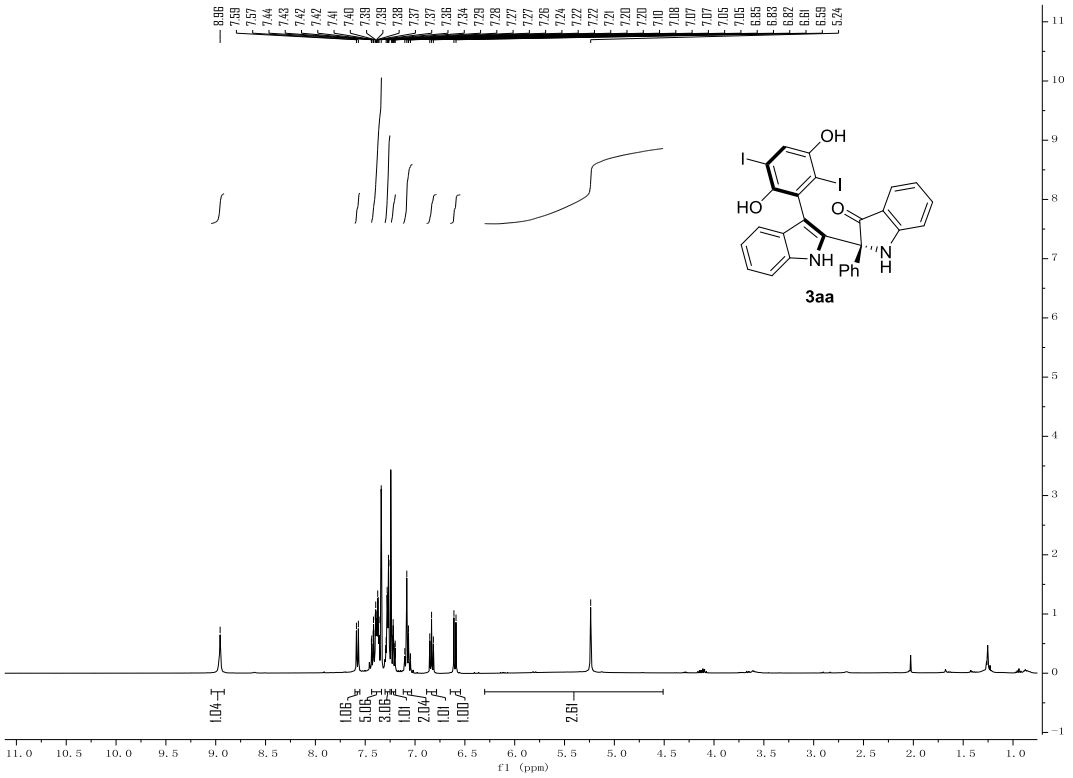
MeOOC
NH
N
H
3z
f1 (ppm)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7.337
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7.097
7.097
7.095
7.095
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6.882
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I
HO
O
NH
Ph
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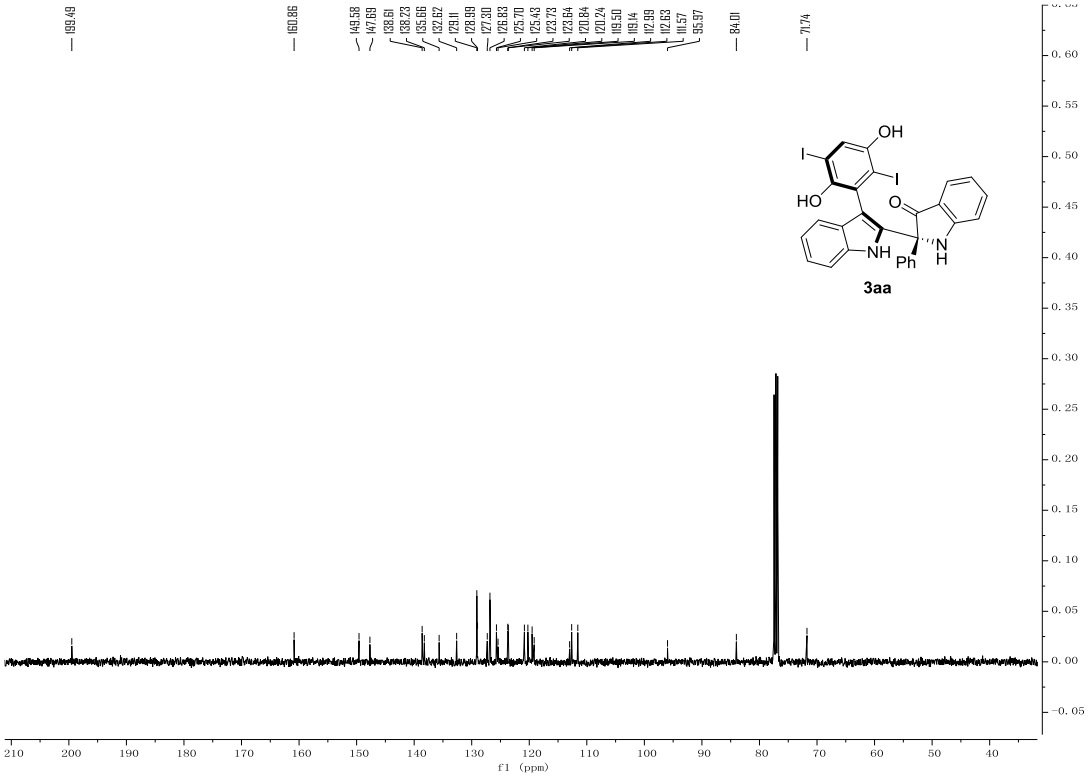
2.61
f1 (ppm)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126.83
125.70
125.43
123.73
123.64
120.84
120.24
119.50
118.14
112.99
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84.01
71.74
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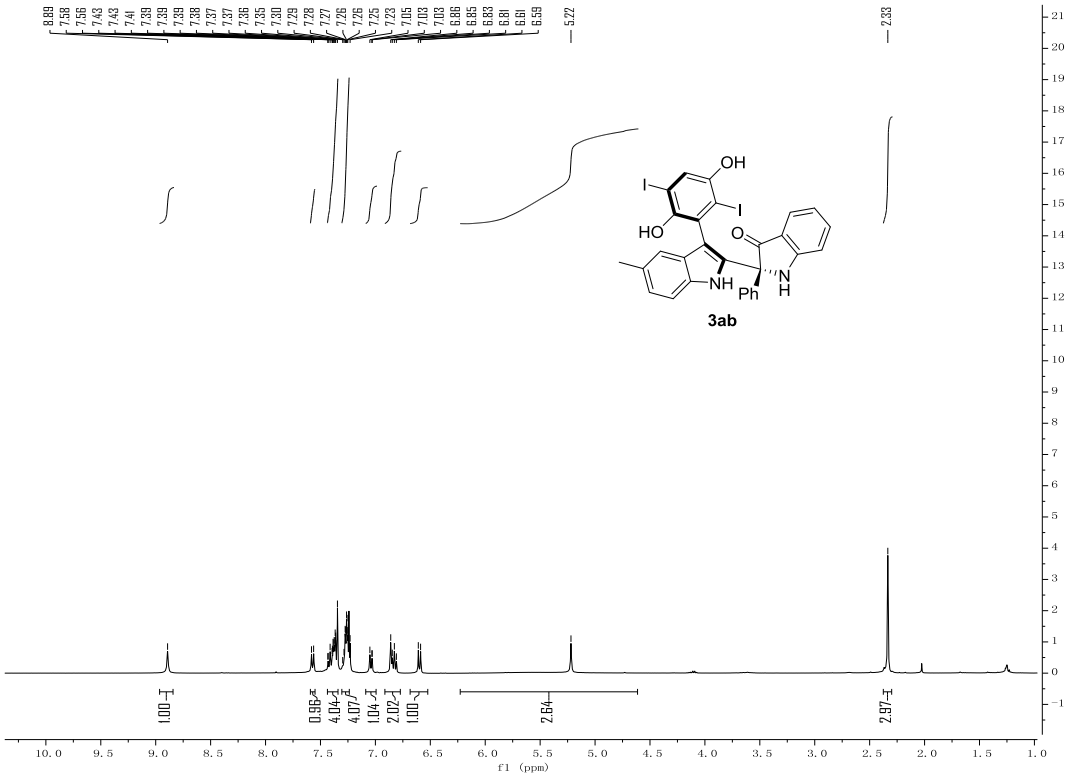
I
HO
O
NH
Ph
N
H
3aa
f1 (ppm)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7.327
7.326
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7.325
7.323
7.015
7.013
7.013
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6.885
6.883
6.881
6.861
6.559
5.722
2.333
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I
HO
O
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Ph
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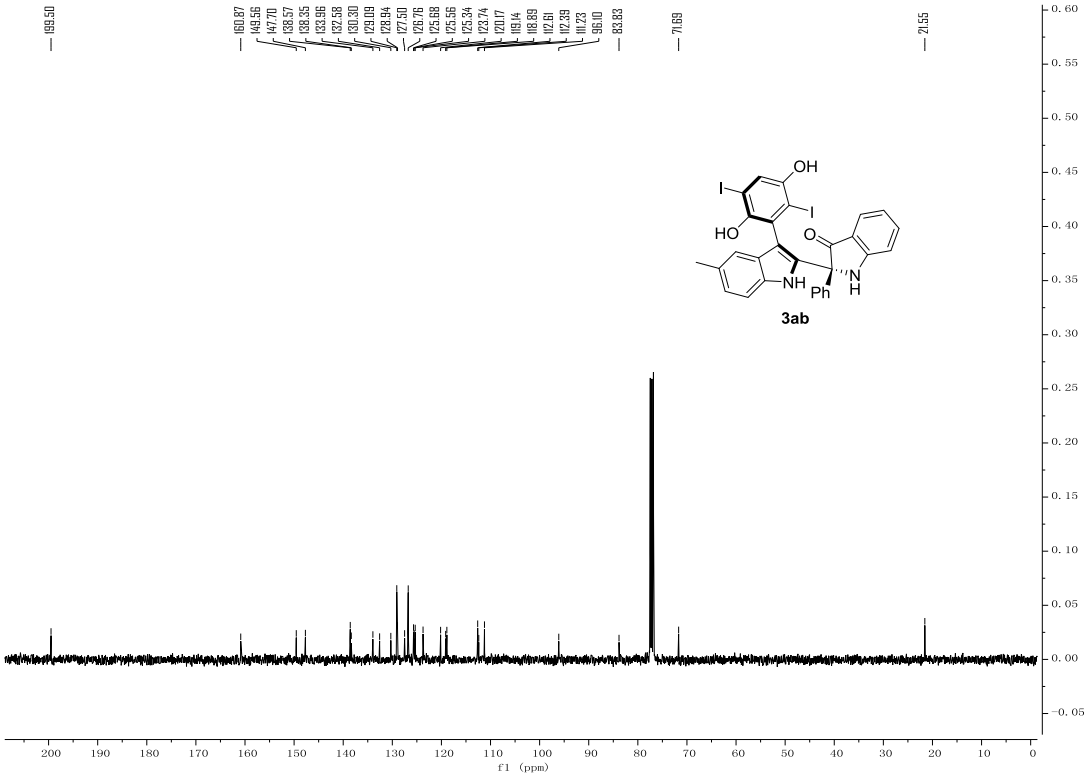
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125.56
125.34
123.74
120.17
119.14
118.89
112.61
112.39
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71.69
21.55
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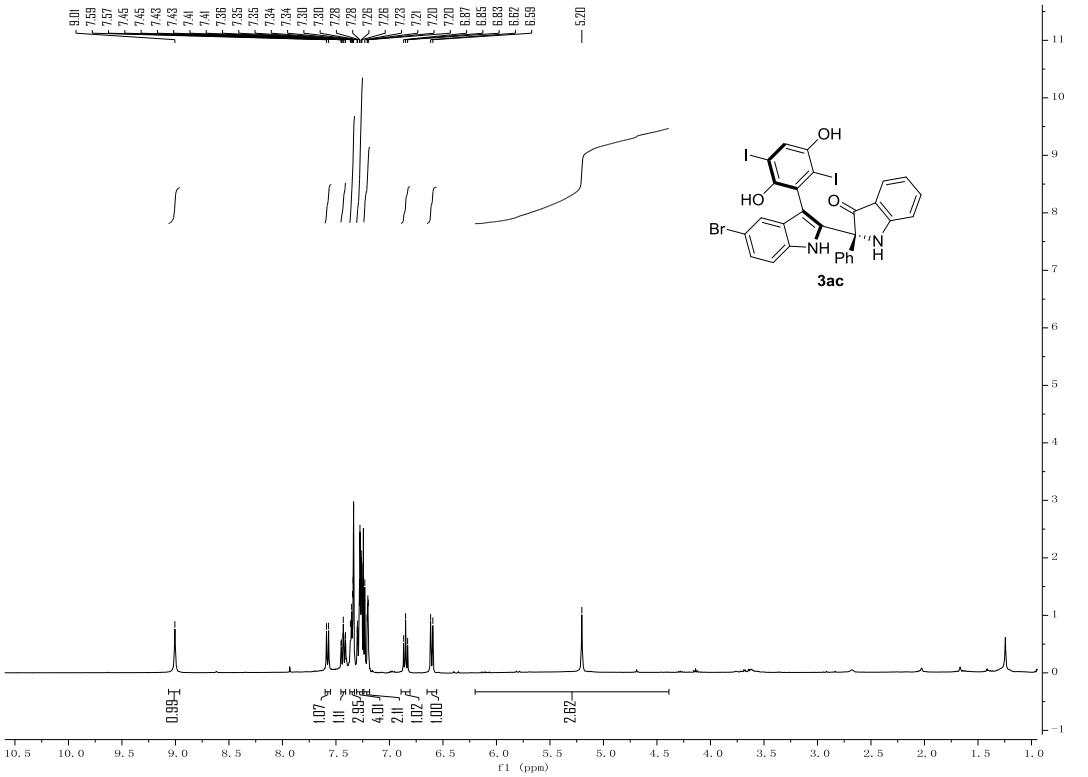
I
HO
O
NH
Ph
N
H
3ab
f1 (ppm)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7.35
7.34
7.34
7.30
7.30
7.28
7.28
7.26
7.26
7.23
7.21
7.20
7.20
6.87
6.85
6.83
6.82
6.59
5.20
OH
I
I
HO
O
Br
NH
Ph
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1.02
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2.67
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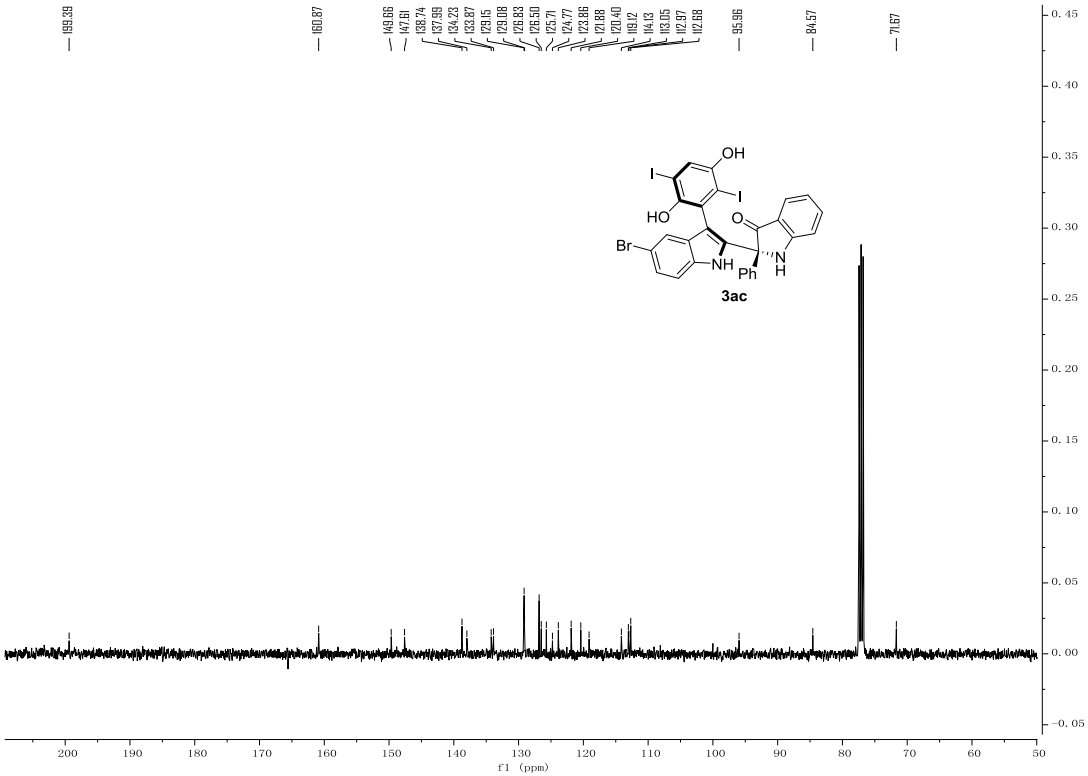
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124.77
123.88
121.88
120.40
119.12
114.13
113.05
112.97
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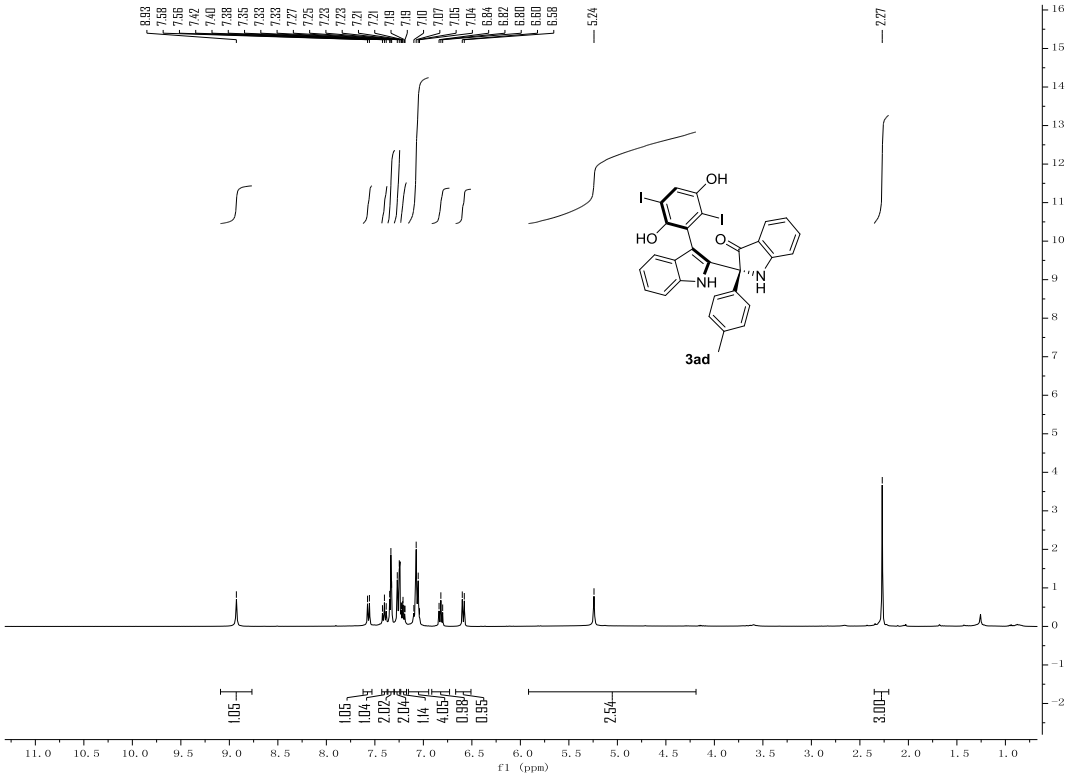
71.67
OH
I
I
HO
O
Br
NH
Ph
N
H
3ac
f1 (ppm)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7.23
7.23
7.21
7.21
7.19
7.19
7.10
7.07
7.05
7.04
6.84
6.82
6.80
6.60
6.58
5.24
2.27
OH
I
I
HO
O
NH
N
H
3ad
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1.05
1.04
2.02
2.04
1.14
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0.95
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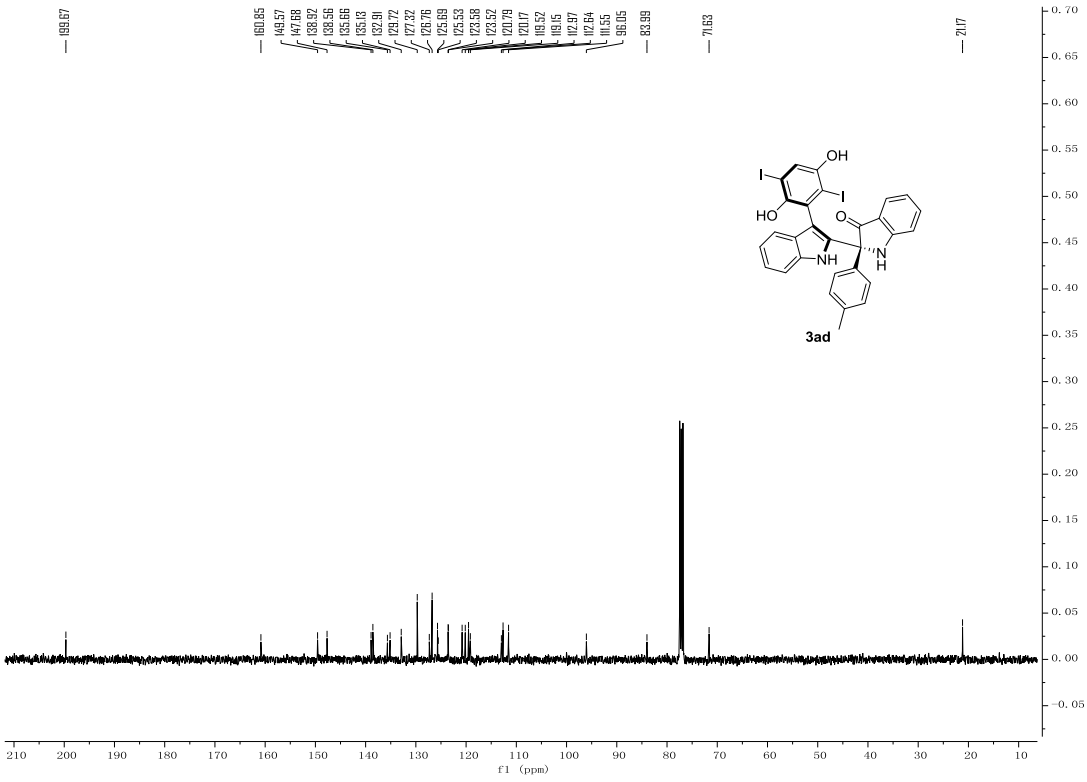
3.00
f1 (ppm)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119.52
119.15
112.97
112.64
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HO
O
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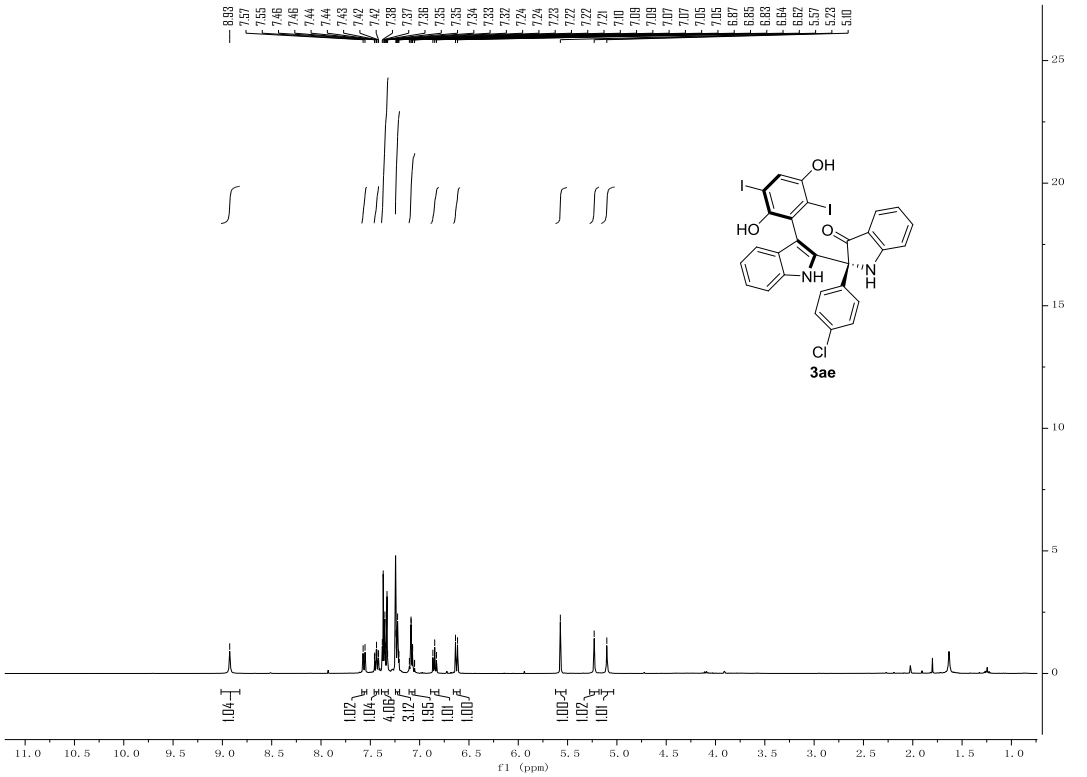
N
H
3ad
f1 (ppm)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7.34
7.33
7.32
7.24
7.24
7.23
7.22
7.22
7.21
7.10
7.08
7.08
7.07
7.07
7.05
7.05
6.87
6.85
6.83
6.64
6.62
5.57
5.23
5.10
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I
I
HO
O
NH
N
H
Cl
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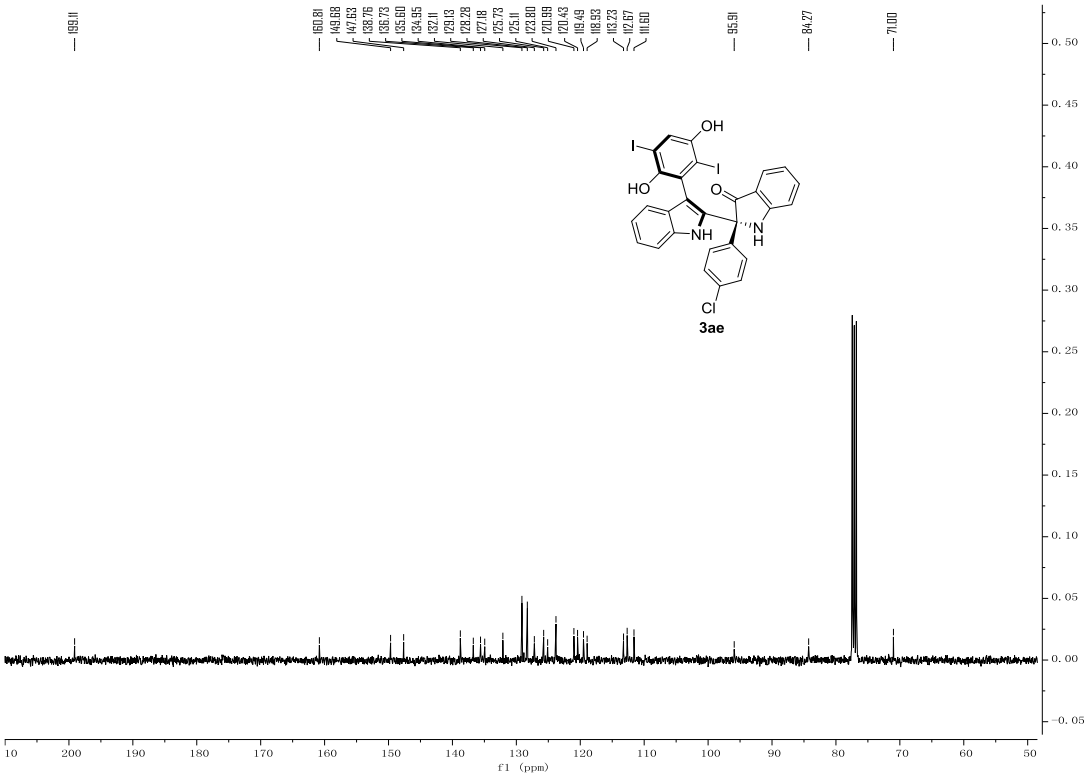
1.00
1.02
1.01
f1 (ppm)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125.73
125.11
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120.43
119.49
118.53
113.23
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71.00
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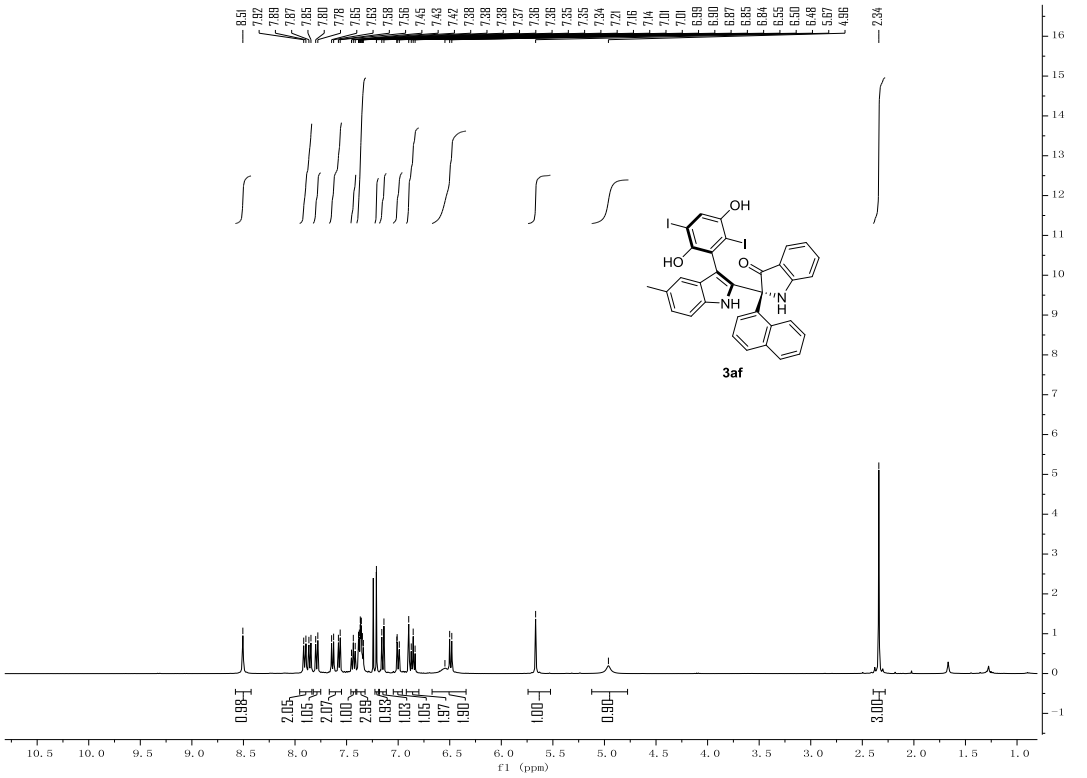
HO
O
NH
N
H
Cl
3ae
f1 (ppm)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7.38
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7.36
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7.16
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I
HO
O
NH
N
H
3af
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1.00
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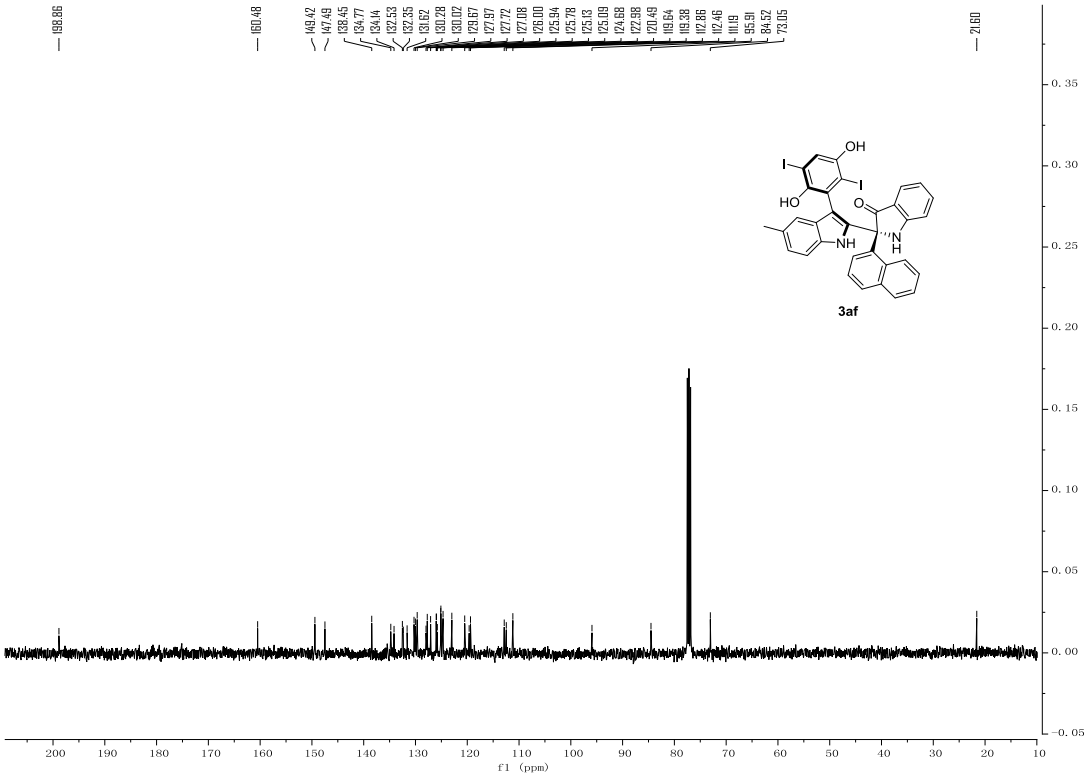
3.00
f1 (ppm)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130.02
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127.72
127.08
126.00
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125.13
125.09
124.68
122.98
120.43
119.64
119.38
112.86
112.46
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73.05
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OH
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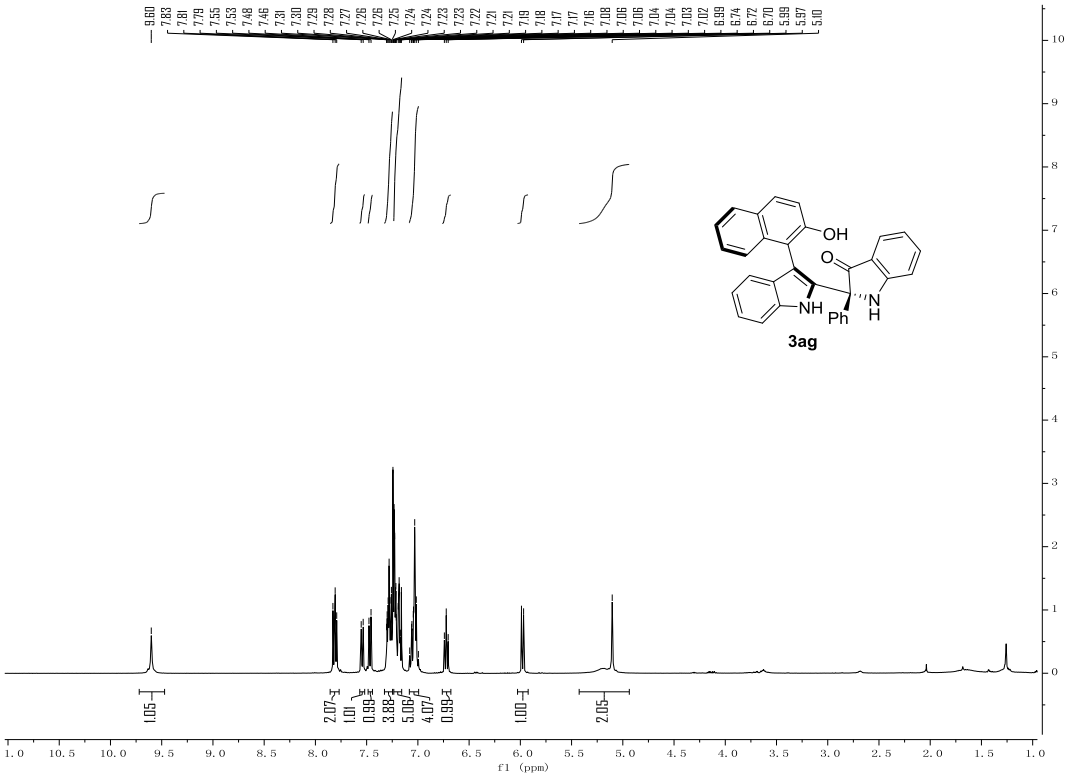
I
HO
O
NH
N
H
3af
f1 (ppm)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7.81
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7.27
7.26
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7.25
7.24
7.24
7.24
7.23
7.23
7.22
7.21
7.21
7.19
7.18
7.17
7.17
7.16
7.08
7.06
7.06
7.04
7.04
7.03
7.02
6.89
6.74
6.72
6.70
5.99
5.57
5.10
OH
O
NH
Ph
N
H
3ag
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1.01
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5.06
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0.99
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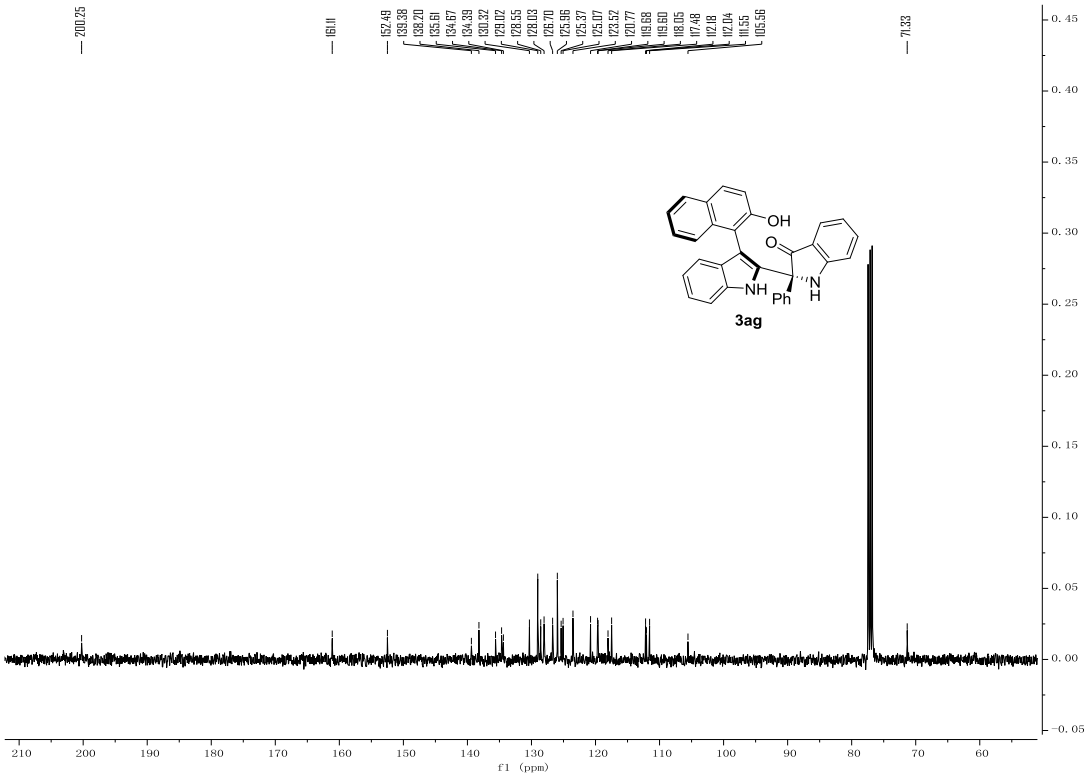
2.05
f1 (ppm)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134.39
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128.03
126.70
125.96
125.37
125.07
123.52
120.77
119.68
119.60
118.05
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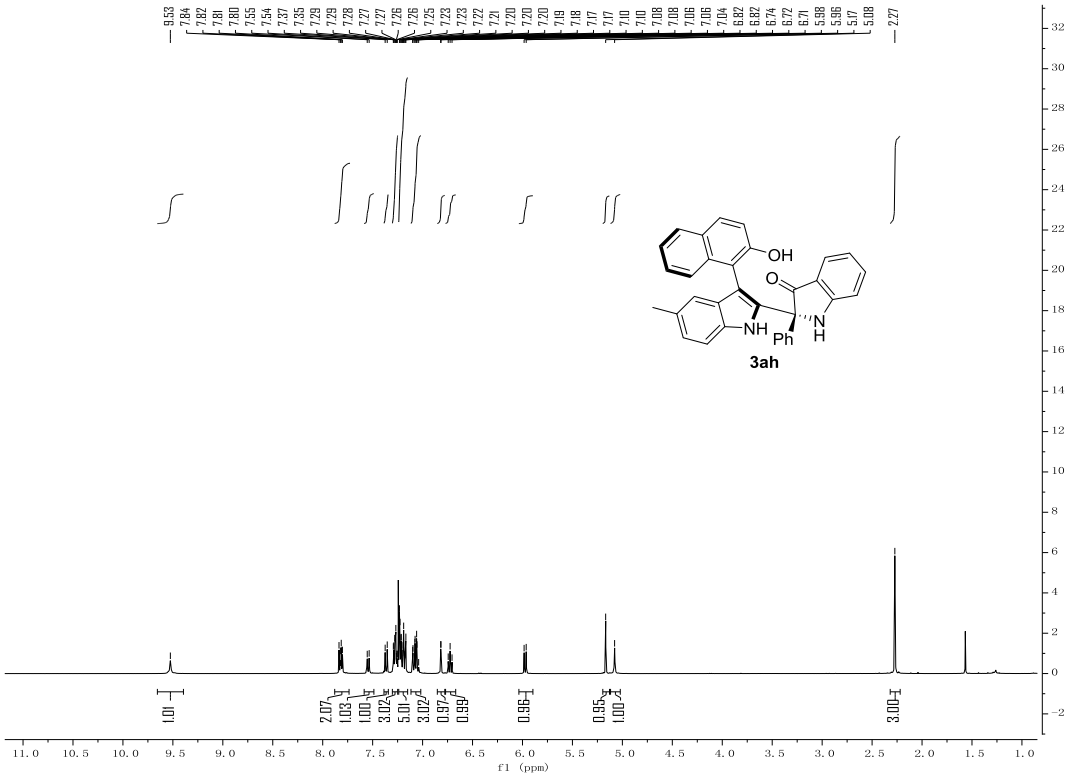
112.04
111.55
105.56
71.33
OH
O
NH
Ph
N
H
3ag
f1 (ppm)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7.26
7.25
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.10
7.08
7.06
7.04
6.82
6.74
6.72
6.71
5.96
5.17
5.08
2.27
OH
O
NH
Ph
N
H
3ah
1.01
2.07
1.03
1.00
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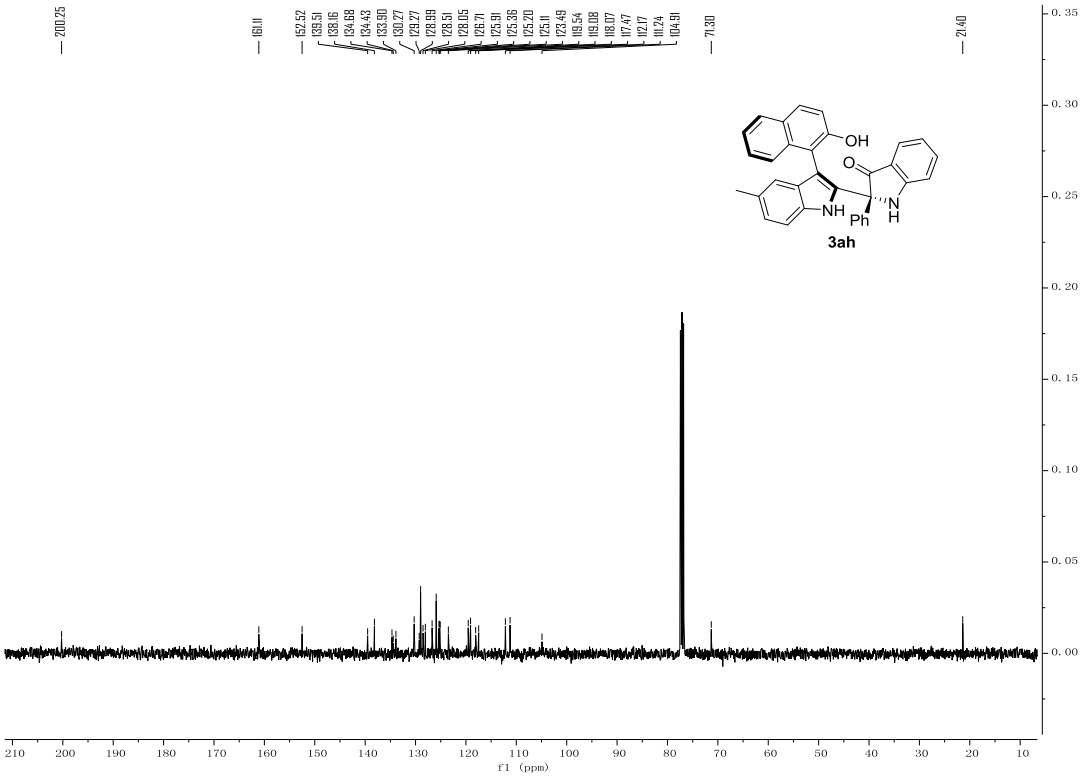
3.02
0.97
0.99
0.96
0.95
1.00
3.00
f1 (ppm)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126.71
125.91
125.38
125.20
125.11
123.49
119.54
119.08
118.07
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104.91
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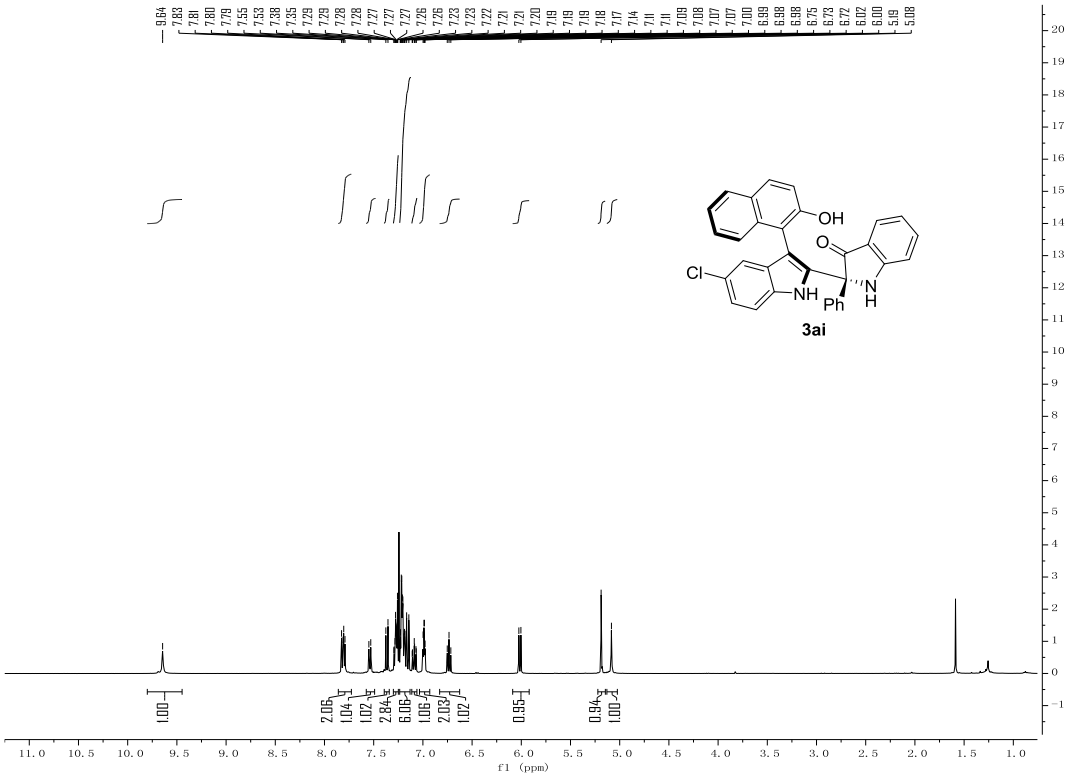
21.40
OH
O
NH
Ph
N
H
3ah
f1 (ppm)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7.21
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7.19
7.19
7.19
7.18
7.17
7.14
7.11
7.11
7.08
7.08
7.07
7.07
7.00
6.99
6.98
6.98
6.75
6.73
6.72
6.02
6.00
5.49
5.08
OH
O
Cl
NH
Ph
N
H
3ai
1.00
2.05
1.04
1.02
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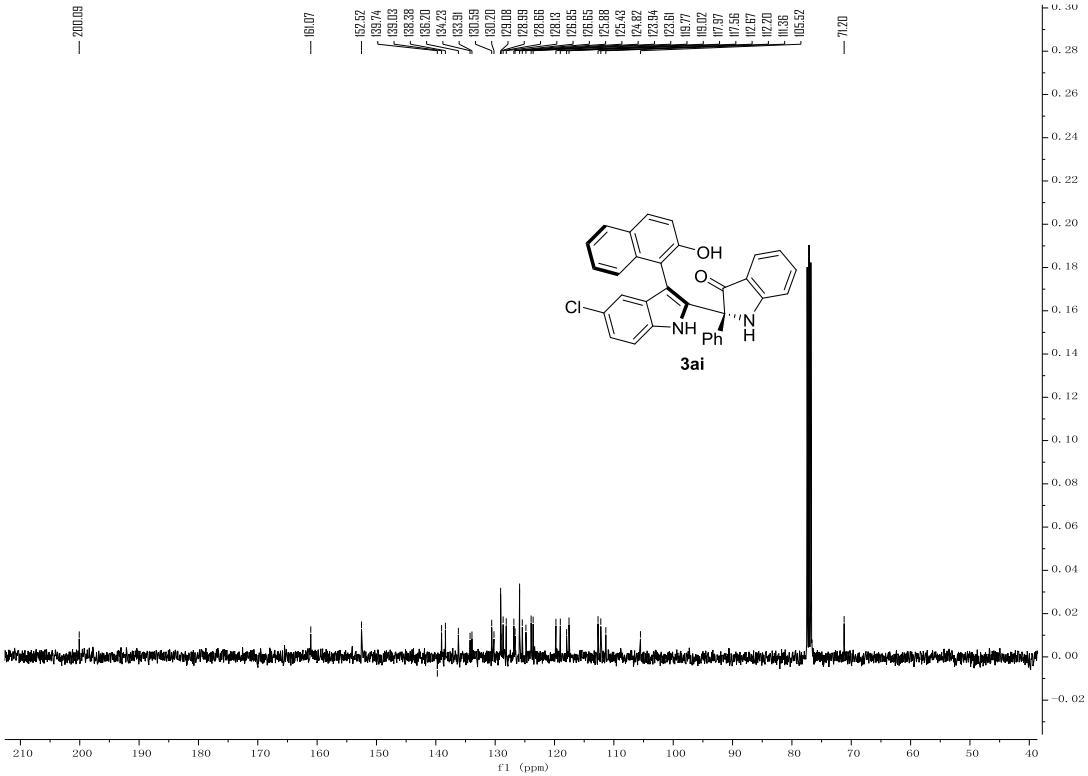
6.06
1.06
2.03
1.02
0.95
0.94
1.00
f1 (ppm)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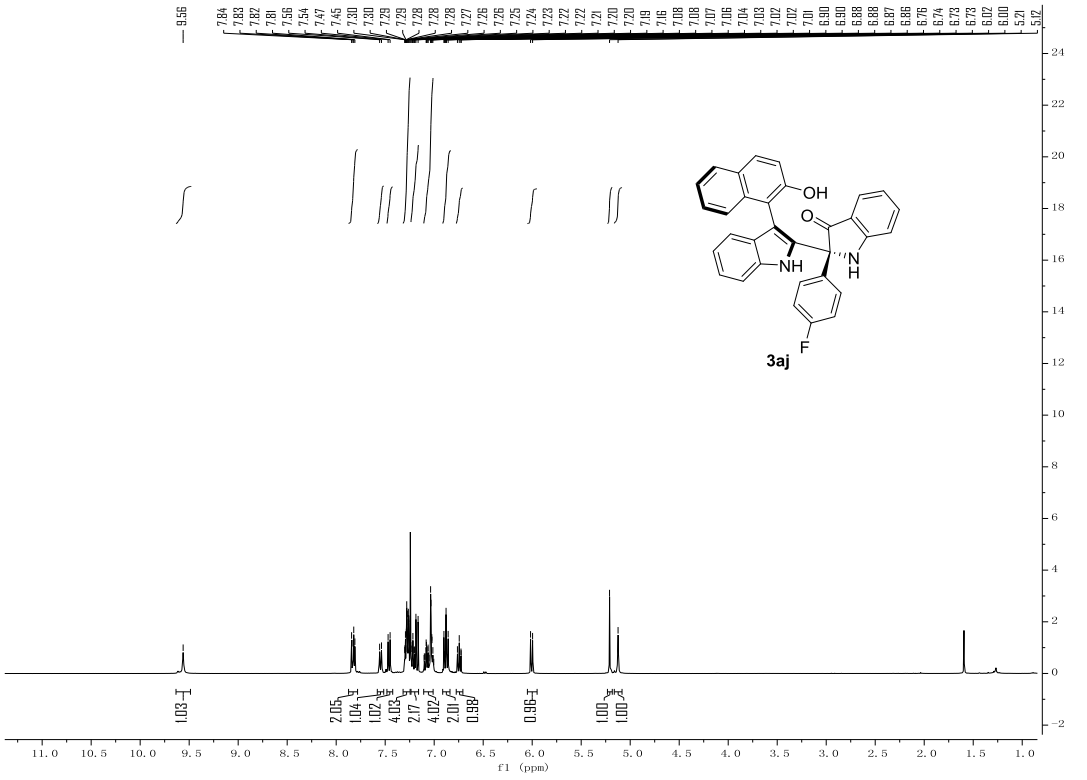
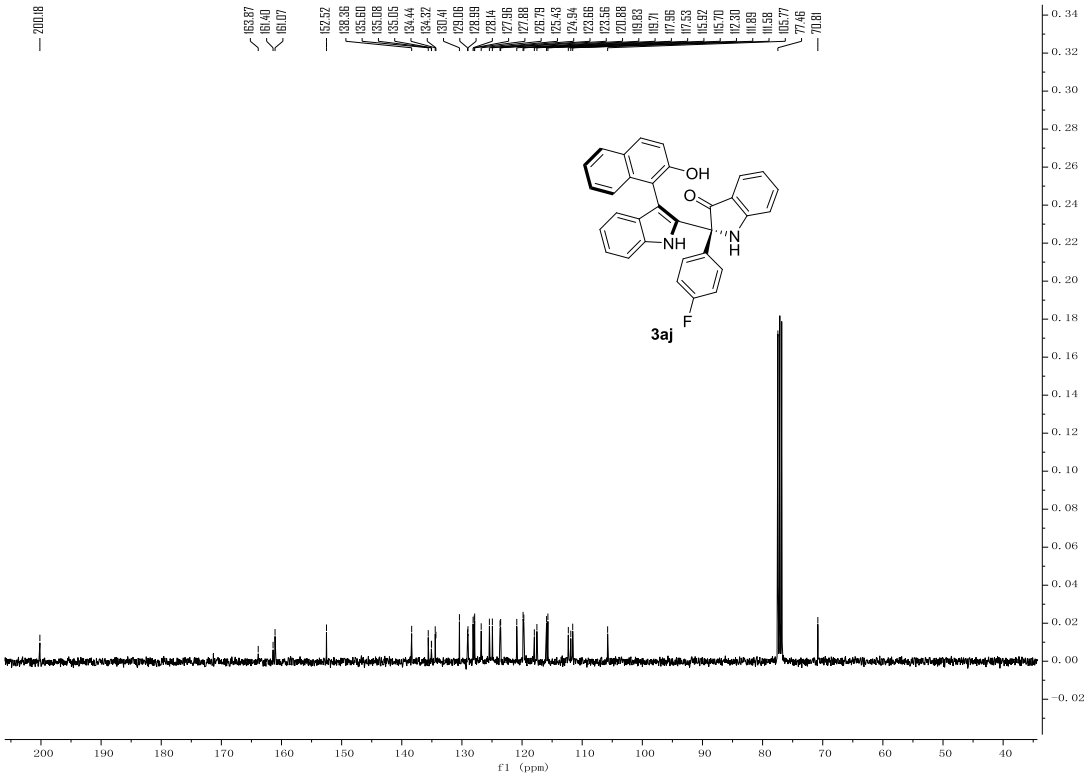
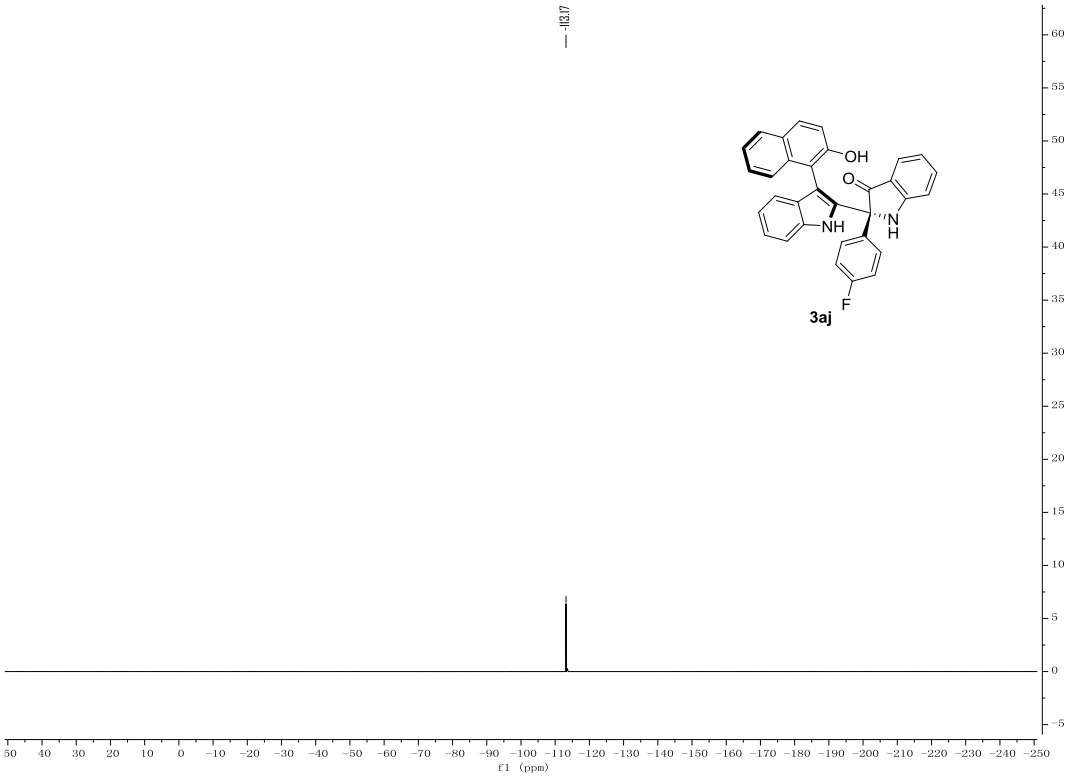
129.08
128.59
128.56
128.13
126.85
126.65
125.88
125.43
124.82
123.94
123.61
119.77
119.02
117.97
117.56
112.67
112.20
111.36
105.52
71.20
OH
O
Cl
NH
Ph
N
H
3ai
f1 (ppm)


OH
O
NH
N
H
F
3aj
f1 (ppm)


OH
O
NH
N
H
F
3aj
f1 (ppm)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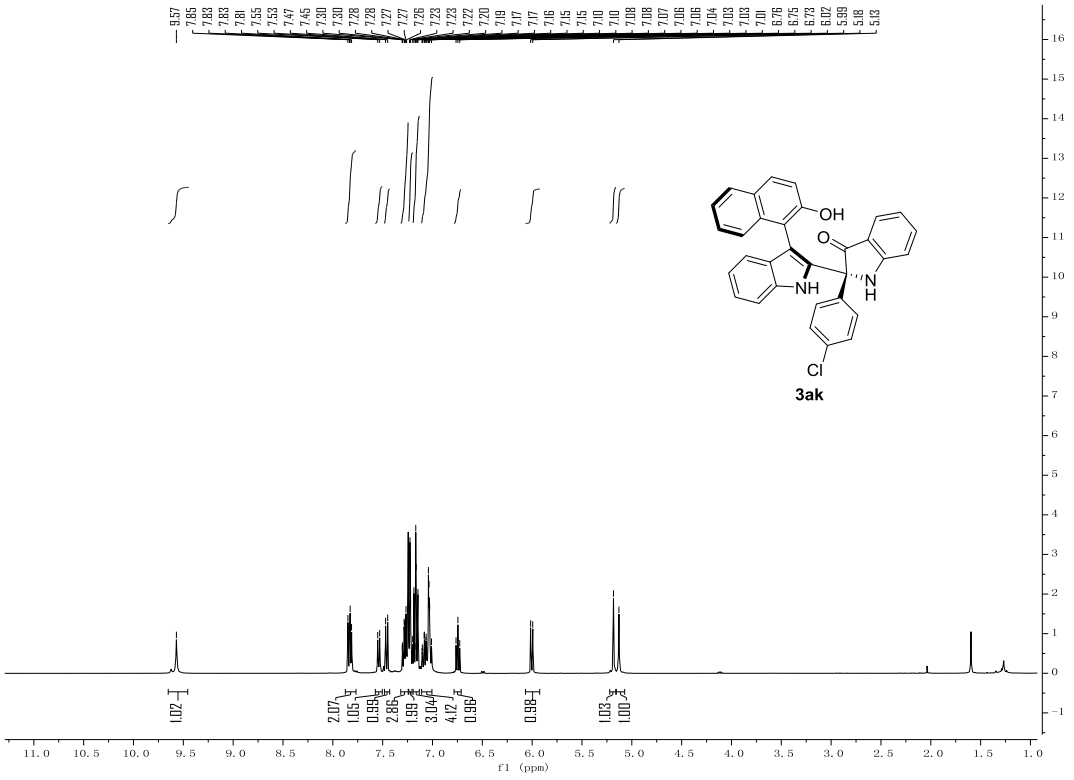
NH
N
H
F
3aj
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250
f1 (ppm)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7.17
7.16
7.15
7.15
7.10
7.10
7.08
7.08
7.07
7.06
7.06
7.04
7.03
7.03
7.01
6.76
6.75
6.73
6.02
5.89
5.18
5.13
OH
O
NH
N
H
Cl
3ak
1.02
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2.86
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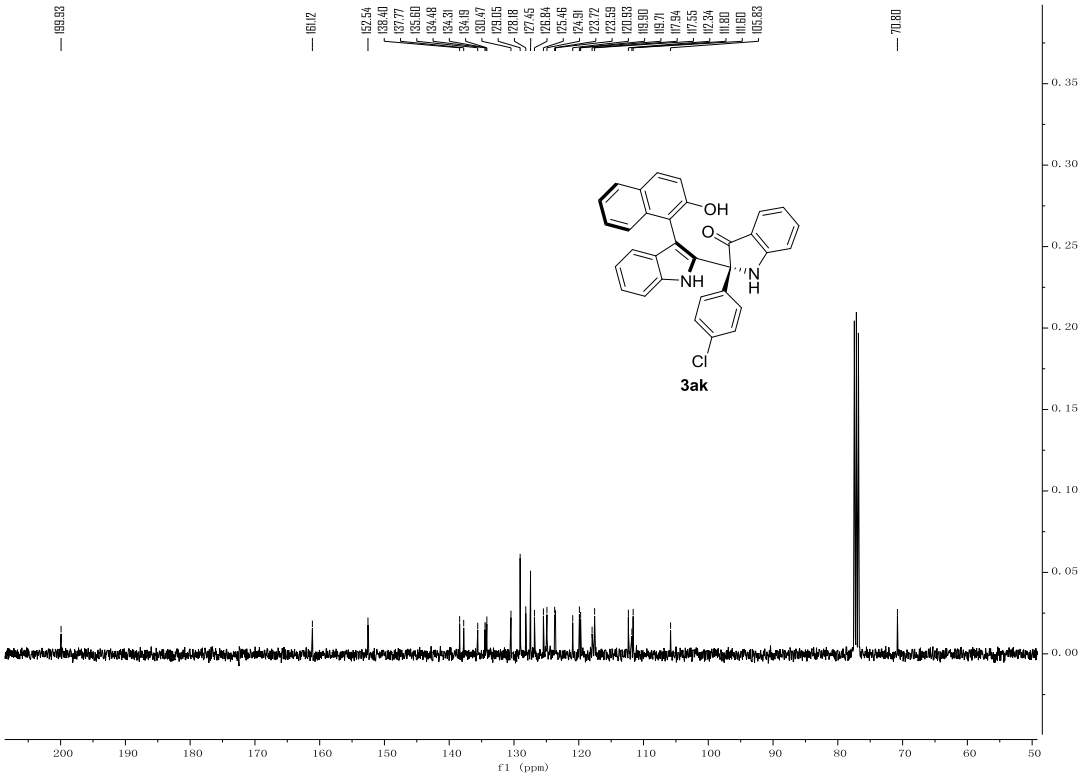
3.04
4.12
0.96
0.98
1.03
1.00
f1 (ppm)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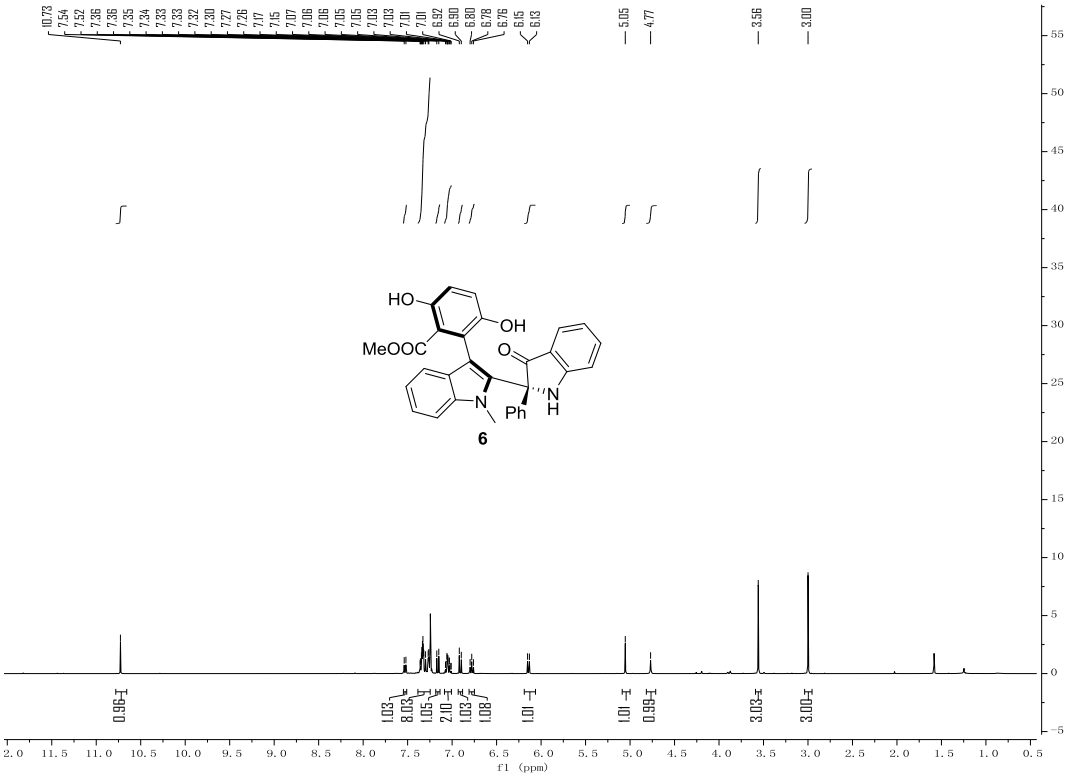
134.19
130.47
129.05
128.18
127.45
126.84
125.46
124.91
123.72
123.59
120.53
119.90
119.71
117.94
117.55
112.34
111.80
111.60
105.83
70.80
OH
O
NH
N
H
Cl
3ak
f1 (ppm)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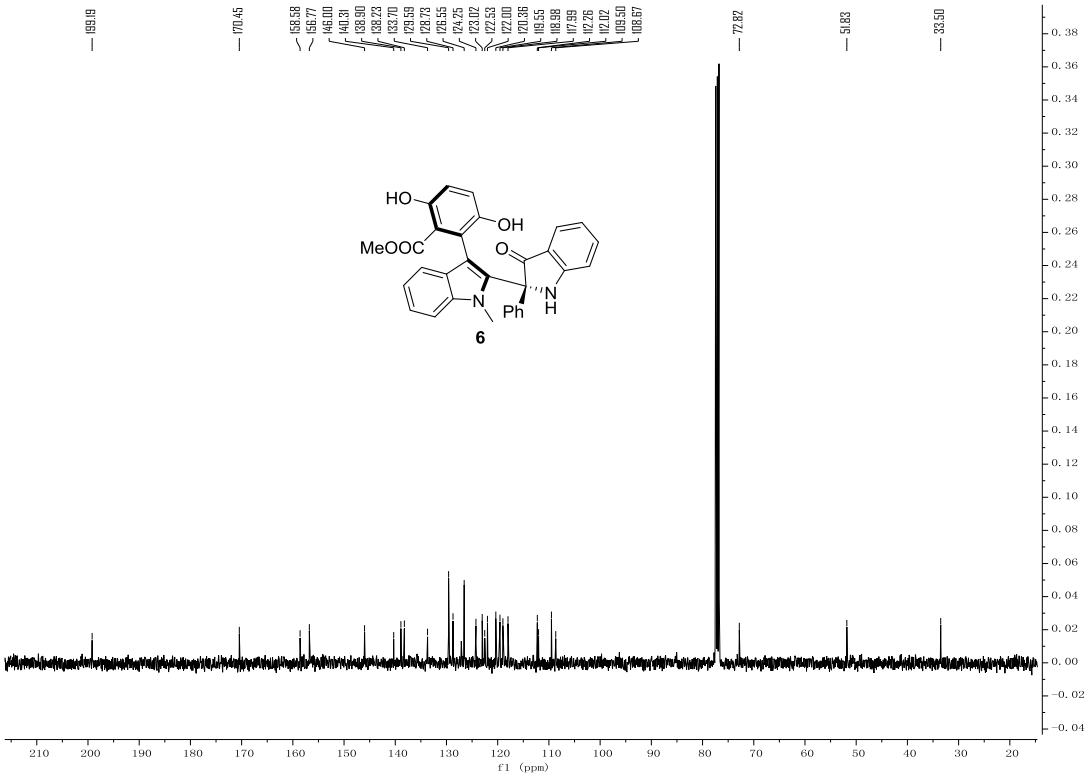
7.33
7.33
7.32
7.30
7.27
7.26
7.17
7.15
7.07
7.06
7.05
7.05
7.03
7.03
7.01
7.01
6.92
6.90
6.80
6.78
6.76
6.15
6.13
5.05
4.77
3.56
3.00
HO
OH
MeOOC
O
N
Ph
N
H
6
0.96
1.03
8.03
1.05
2.10
1.03
1.08
1.01
1.01
0.99
3.03
3.00
f1 (ppm)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138.23
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128.73
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124.25
123.02
122.53
122.00
120.36
119.55
118.98
117.99
112.26
112.02
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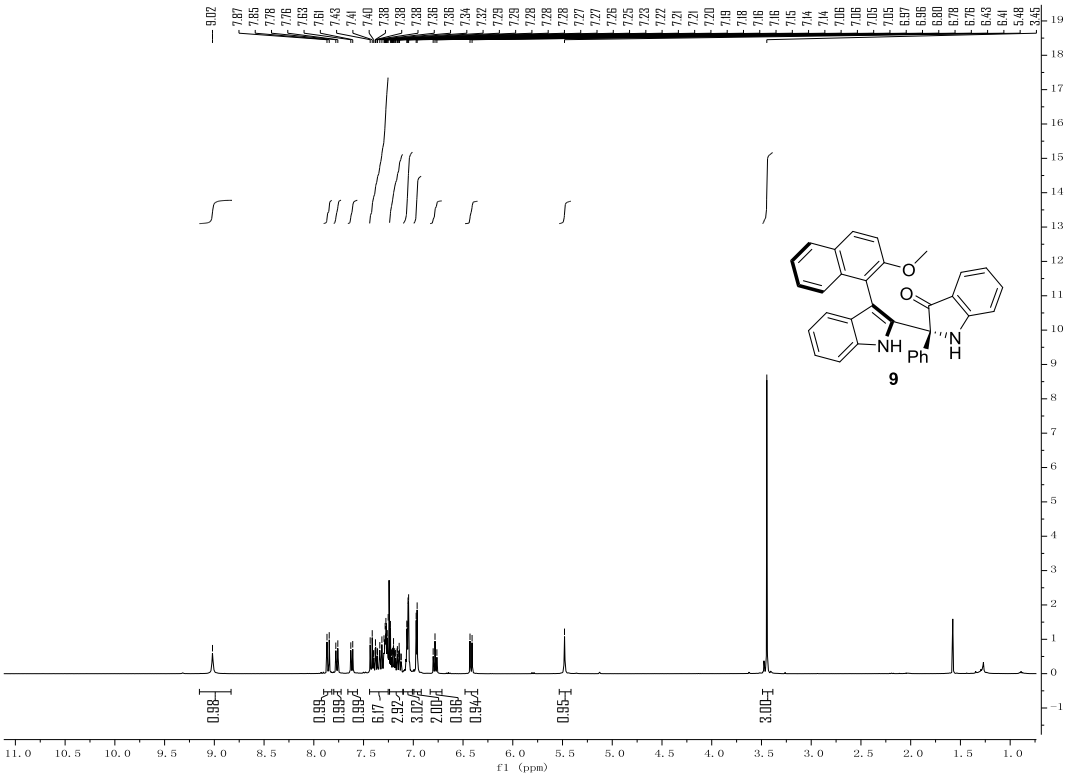
108.67
77.82
51.83
33.50
HO
OH
MeOOC
O
N
Ph
N
H
6
f1 (ppm)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7.28
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7.27
7.27
7.26
7.25
7.23
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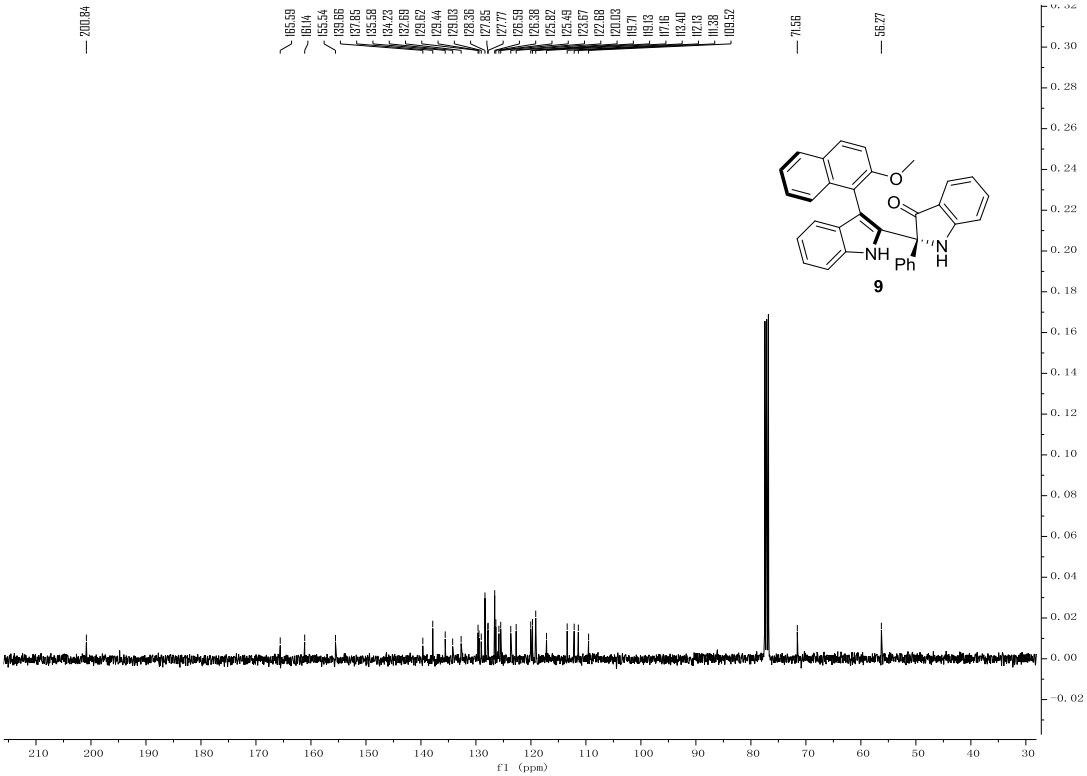
7.21
7.21
7.20
7.19
7.18
7.16
7.16
7.15
7.14
7.14
7.06
7.06
7.05
7.05
6.97
6.96
6.80
6.78
6.76
6.63
6.41
5.48
3.45
0.98
0.99
0.99
0.99
6.17
2.92
3.02
2.00
0.96
0.94
0.95
3.00
O
O
NH
Ph
N
H
9
f1 (ppm)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132.69
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128.36
127.85
127.77
126.59
126.38
125.82
125.43
123.67
122.68
121.03
119.71
119.13
117.16
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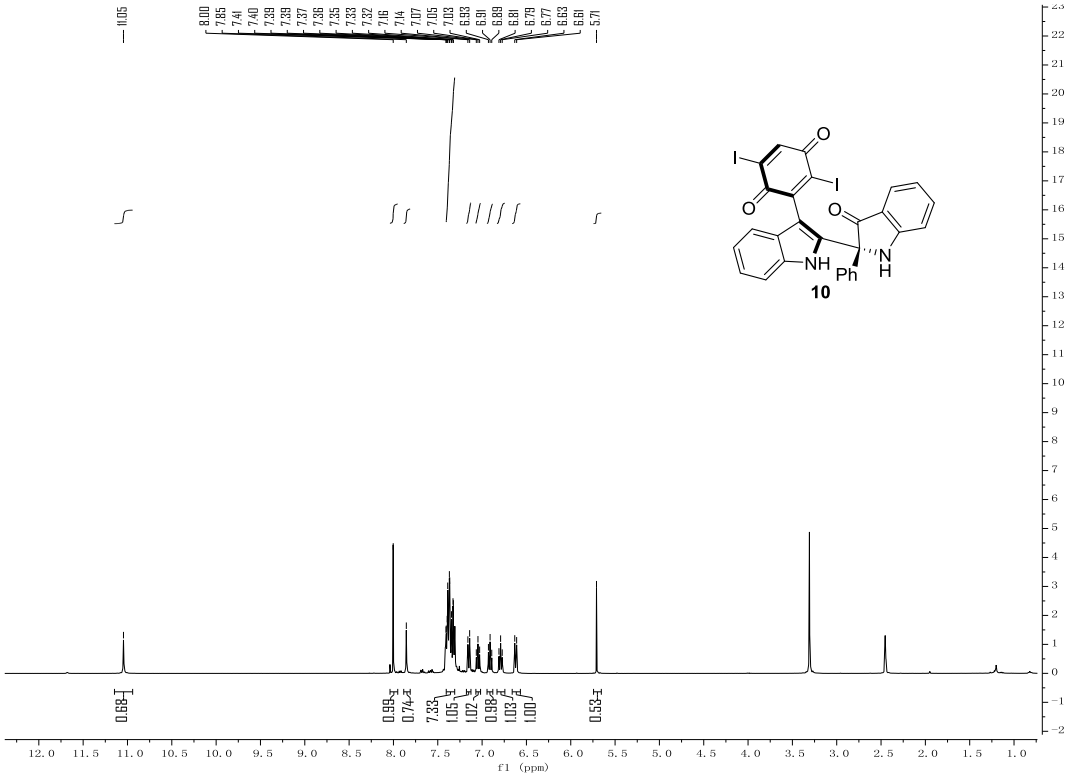
111.38
109.52
71.56
58.27
O
O
NH
Ph
N
H
9
f1 (ppm)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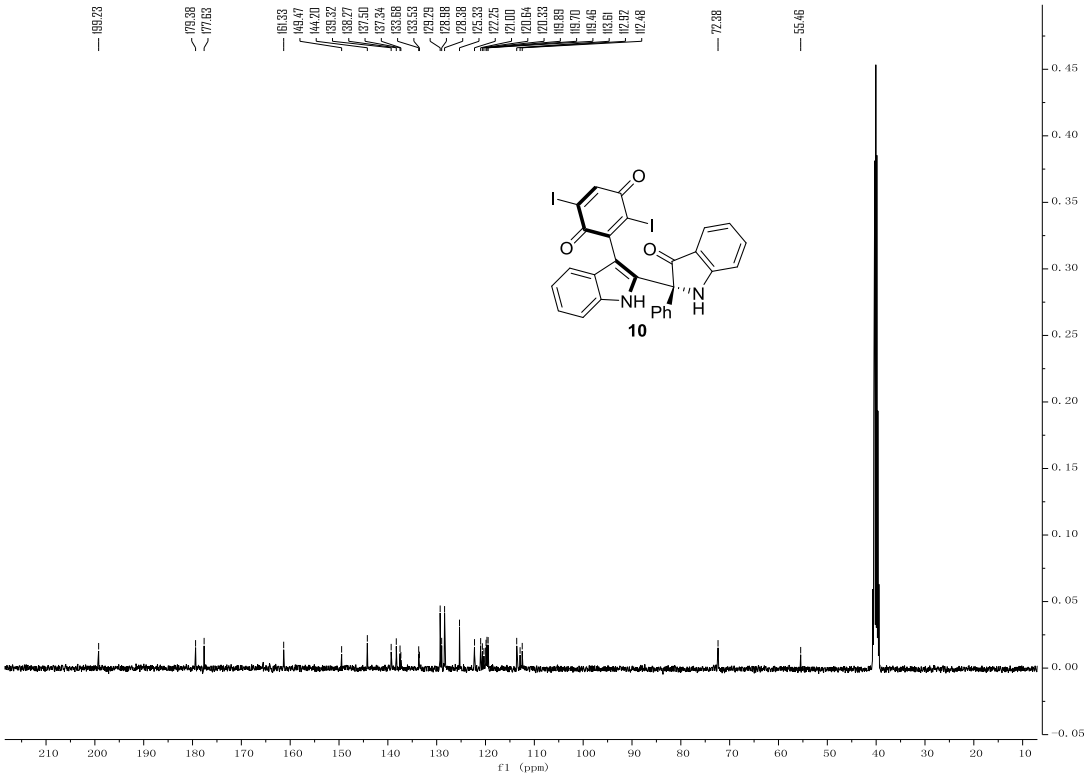
7.36
7.35
7.33
7.32
7.16
7.14
7.07
7.05
7.03
6.93
6.91
6.89
6.81
6.79
6.77
6.63
6.61
5.71
0.68
0.99
0.74
7.33
1.05
1.02
0.98
1.03
1.00
0.53
f1 (ppm)
10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177.63
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144.20
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138.27
137.50
137.34
133.68
133.53
129.29
129.88
128.38
125.33
122.25
121.00
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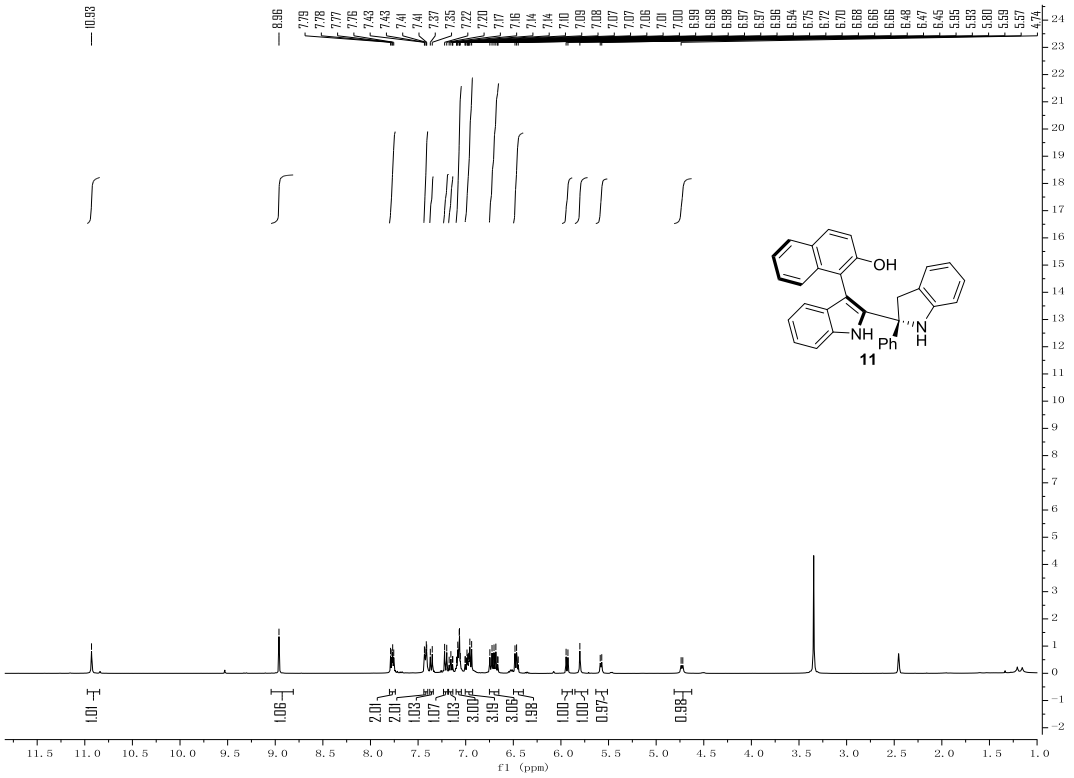
119.70
119.46
113.61
112.82
112.48
72.38
55.46
f1 (ppm)
10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7.375
7.222
7.220
7.197
7.196
7.174
7.174
7.010
7.009
7.008
7.007
7.007
7.006
7.001
7.000
6.999
6.998
6.997
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6.668
6.666
6.666
6.648
6.647
6.645
5.915
5.913
5.810
5.559
5.557
4.474
OH
NH
Ph
N
H
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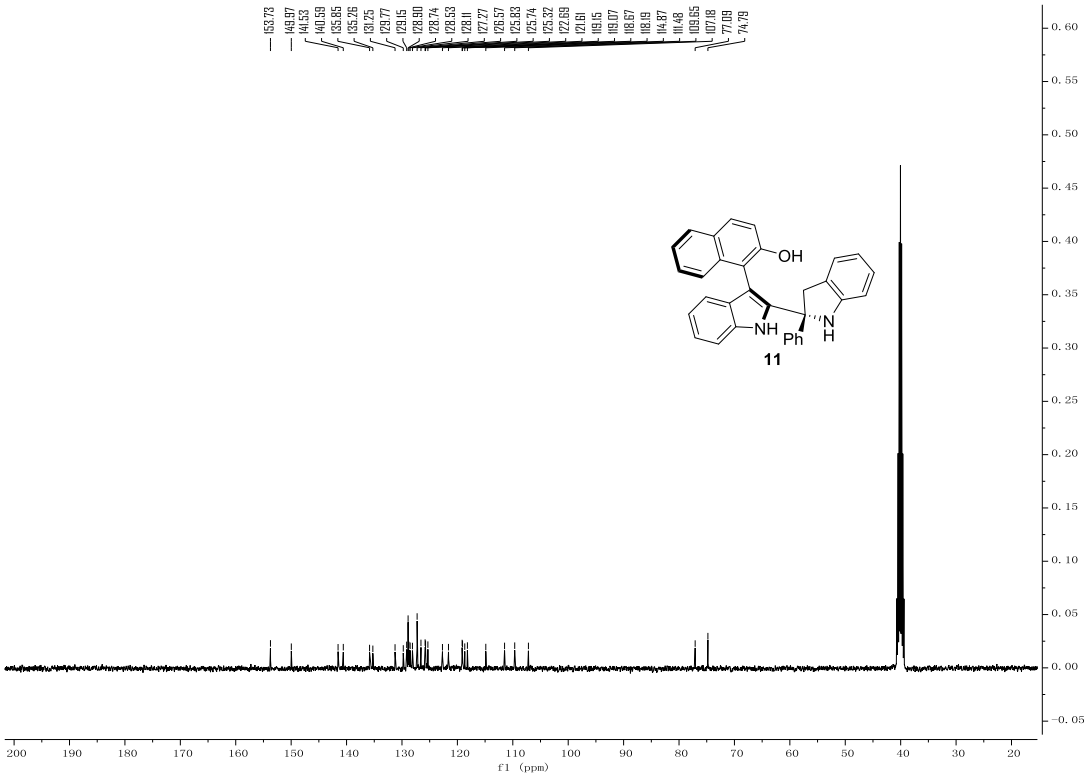
1.06
2.01
2.01
1.03
1.07
1.03
3.00
3.19
3.09
1.98
1.00
1.00
0.97
0.98
f1 (ppm)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128.53
128.11
127.27
126.57
125.83
125.74
125.32
122.69
121.61
119.15
119.07
118.67
118.19
114.87
111.48
109.65
107.18
77.09
74.79
OH
NH
Ph
N
H
11
f1 (ppm)