Supporting Information

Catalytic Asymmetric Interrupted Nazarov-Type Cyclization of 2-Indolylmethanols with Cyclic Enaminones

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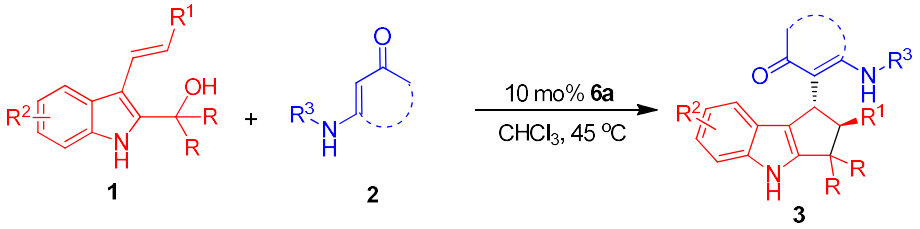
1. General information

^{1}H and ^{13}C NMR spectra were measured respectively at 400 and 100 MHz, respectively. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. HRMS (ESI) was determined by a HRMS/MS instrument. Enantiomeric excesses (*ee*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of enantiomeric excesses by chiral HPLC were Chiralpak columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The X-ray sources used for the single crystal X-ray diffraction analysis of product **3ai** was GaKα (λ = 1.34139), and the thermal ellipsoid was drawn at the 30% probability level. Analytical grade solvents for the column chromatography were distilled before use. All starting materials commercially available were used directly.

2. General procedure for the synthesis of products 3



To the mixture of C3-alkenyl-substituted 2-indolylmethanols **1** (0.11 mmol), cyclic enaminones **2** (0.1 mmol), catalyst **6a** (0.01 mmol) was added chloroform (2 mL). Then, the reaction mixture was stirred at 45 °C for 36 h. After the completion of the reaction indicated by TLC, the reaction mixture was directly purified through preparative thin layer chromatography to afford pure products **3**.

3. Characteristic data of products 3

3-((4-methoxyphenyl)amino)-5,5-dimethyl-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3aa): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 70% yield (44.1 mg); yellow

solid; m.p. 79-80 °C; $[\alpha]_D^{20}$ = +150.0 (c 0.20, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.25 – 7.07 (m, 5H), 7.05 – 6.95 (m, 5H), 6.93 – 6.91 (m, 2H), 6.70 – 6.68 (m, 2H), 6.48 – 6.46 (m, 2H), 6.30 – 6.28 (m, 2H), 5.56 (d, *J* = 9.2 Hz, 1H), 5.37 (d, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 2.28 (d, *J* = 16.8 Hz, 1H), 2.19 – 2.08 (m, 2H), 2.05 (d, *J* = 16.0 Hz, 1H), 1.03 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.4, 157.5, 146.3, 144.8, 141.7, 140.4, 138.0, 131.6, 130.6, 129.6, 128.7, 127.8, 127.3, 127.1, 126.9, 126.7, 126.5, 126.4, 124.3, 122.0, 120.3, 119.0, 118.4, 114.2, 112.2, 107.5, 63.2, 61.8, 55.4, 50.2, 40.8, 36.1, 32.2, 28.1; IR (KBr): 3366, 2923, 1730, 1690, 1595, 1348, 1268, 1032, 989 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{40}N_2O_2\text{-}H)^-$ requires m/z 627.3012, found m/z 627.3029; Enantiomeric excess: 73%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 15.527 min (minor), t_R = 18.253 min (major).

2-((1*R*,2*S*)-3,3-bis(4-fluorophenyl)-2-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ba): thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 57% yield (37.8 mg); yellow solid; m.p. 127-128 °C; $[\alpha]_D^{20}$ = +56.8 (c 0.40, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.57 – 7.48 (m, 3H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.13 (m, 3H), 7.07 – 7.02 (m, 1H), 7.01 – 6.97 (m, 4H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.71 – 6.49 (m, 4H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.22 – 6.18 (m, 2H), 5.53 (d, *J* = 9.6 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 3.74 (s, 3H), 2.28 (d, *J* = 16.8 Hz, 1H), 2.15 – 2.10 (m, 2H), 2.00 (d, *J* = 16.4 Hz, 1H), 1.01 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 161.6 (*J* = 245 Hz), 161.5 (*J* = 245 Hz), 159.6, 157.6, 146.0, 140.5, 140.3, 137.6, 137.1, 131.3 (*J* = 8.0 Hz), 130.4, 129.3 (*J* = 8.9 Hz), 127.1, 127.0, 126.8, 124.1, 122.2, 120.5, 119.0, 118.4, 115.6, 115.4, 114.3, 114.2 (*J* = 21 Hz), 112.3, 107.4, 63.9, 60.8, 55.4, 50.1, 40.7, 35.8, 32.2, 28.1, 28.0; IR (KBr): 3443, 3059, 2928, 1916, 1660, 1395, 1322, 1168, 1032 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{38}F_2N_2O_2\text{-}H)^-$ requires m/z 663.2823, found m/z 663.2849; Enantiomeric excess:

80%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 13.967 min (minor), t_R = 15.637 min (major).

3-((4-methoxyphenyl)amino)-5,5-dimethyl-2-((1*R*,2*S*)-2-phenyl-3,3-di-*p*-tolyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ca): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 69% yield (45.0 mg); yellow solid; m.p. 133-134 °C; $[\alpha]_D^{20}$ = +89.0 (c 0.24, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.53 – 7.47 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.20 – 7.13 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 – 6.91 (m, 5H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.17 (d, *J* = 8.0 Hz, 2H), 5.54 (d, *J* = 9.6 Hz, 1H), 5.32 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 2.31 (s, 3H), 2.29 – 2.25 (d, *J* = 16.4 Hz, 1H), 2.24 (s, 3H), 2.15 (d, *J* = 16.4 Hz, 1H), 2.12 – 2.01 (m, 2H), 1.02 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.4, 157.5, 146.9, 142.0, 140.4, 138.6, 138.1, 136.2, 135.9, 131.6, 130.7, 129.5, 129.3, 127.9, 127.8, 127.1, 126.8, 126.4, 124.3, 121.8, 120.2, 119.0, 118.1, 114.2, 112.2, 107.5, 63.3, 61.1, 55.4, 50.1, 40.8, 36.0, 32.2, 28.2, 28.1, 20.9, 20.8; IR (KBr): 3865, 3389, 1810, 1715, 1690, 1522, 1348, 1261, 1031 cm^{-1}; ESI FTMS exact mass calcd for $(C_{46}H_{44}N_2O_2\text{-}H)^-$ requires m/z 655.3325, found m/z 655.3342; Enantiomeric excess: 52%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.230 min (major), t_R = 15.973 min (minor).

2-((1*R*,2*S*)-3,3-bis(4-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3da): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 62% yield (42.7 mg); yellow solid; m.p. 91-92 °C; $[\alpha]_D^{20}$ = +42.6 (c 0.19, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.55 – 7.46 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.20 – 7.11 (m, 2H), 7.07 – 6.96 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.18 (d, *J* = 8.8 Hz, 2H),

5.53 (d, *J* = 9.6 Hz, 1H), 5.26 (d, *J* = 9.6 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.71 (s, 3H), 2.28 (d, *J* = 16.4 Hz, 1H), 2.17 – 2.07 (m, 2H), 2.03 (d, *J* = 16.4 Hz, 1H), 1.03 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.4, 158.1, 157.4, 147.2, 140.4, 138.1, 136.9, 133.7, 131.6, 130.6, 128.9, 127.0, 126.9, 126.4, 124.3, 121.8, 120.2, 118.9, 117.9, 114.2, 113.9, 112.6, 112.2, 107.5, 63.8, 60.4, 55.4, 55.2, 55.1, 50.1, 40.8, 36.0, 32.2, 28.2, 28.0; IR (KBr): 3633, 3414, 1781, 1719, 1682, 1526, 1348, 1261, 878 cm^{-1}; ESI FTMS exact mass calcd for $(C_{46}H_{44}N_2O_4\text{-}H)^-$ requires m/z 687.3223, found m/z 687.3241; Enantiomeric excess: 70%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 31.233 min (major), t_R = 40.790 min (minor).

2-((1*R*,2*S*)-2-(4-fluorophenyl)-3,3-diphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ea): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 47% yield (30.5 mg); yellow solid; m.p. 112-113 ºC; $[\alpha]_D^{20}$ = +49.1 (c 0.49, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 6.8 Hz, 3H), 7.23 – 7.09 (m, 5H), 7.02 – 6.98 (m, 2H), 6.89 – 6.86 (m, 2H), 6.75 – 6.62 (m, 4H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 7.2 Hz, 2H), 5.50 (d, *J* = 8.8 Hz, 1H), 5.32 (d, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 2.28 (d, *J* = 16.8 Hz, 1H), 2.19 – 2.09 (m, 2H), 2.06 (d, *J* = 16.0 Hz, 1H), 1.03 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 161.8 (*J* = 230 Hz), 159.6, 157.5, 146.2, 144.6, 141.5, 140.4, 132.0 (*J* = 12 Hz), 131.5, 129.6, 128.8, 127.7, 127.4, 127.2, 126.7 (*J* = 16 Hz), 124.2, 122.1, 120.3, 119.0, 118.2, 114.2, 113.6 (*J* = 21 Hz), 112.2, 107.2, 62.3, 61.7, 55.4, 50.1, 40.82, 36.2, 32.2, 28.1, 28.0; IR (KBr): 3638, 3366, 2960, 1744, 1691, 1448, 1268, 1149, 1032 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{39}FN_2O_2\text{-}H)^-$ requires m/z 645.2918, found m/z 645.2909; Enantiomeric excess: 60%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 17.497 min (minor), t_R = 19.450 min (major).

2-((1*R*,2*S*)-2-(4-chlorophenyl)-3,3-diphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3fa): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 46% yield (30.3 mg); yellow solid; m.p. 138-139 ºC; $[\alpha]_D^{20}$= +23.8 (c 0.61, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.09 (m, 3H), 7.04 – 6.98 (m, 2H), 6.96 – 6.93 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.73 – 6.65 (m, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.29 (d, *J* = 7.2 Hz, 2H), 5.51 (d, *J* = 9.6 Hz, 1H), 5.30 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 2.28 (d, *J* = 15.6 Hz, 1H), 2.18 – 2.09 (m, 2H), 2.05 (d, *J* = 15.6 Hz, 1H), 1.03 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.6, 157.6, 146.2, 144.4, 141.4, 140.4, 136.6, 132.3, 131.9, 131.4, 129.5, 128.8, 127.7, 127.5, 127.2, 127.0, 126.8, 126.7, 124.1, 122.1, 120.4, 119.0, 118.2, 114.2, 112.3, 107.1, 62.5, 61.7, 55.4, 50.1, 40.8, 36.2, 32.2, 28.1; IR (KBr): 3306, 2917, 1749, 1611, 1548, 1149, 1032, 987 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{39}ClN_2O_2\text{-}H)^-$ requires m/z 661.2622, found m/z 661.2639; Enantiomeric excess: 60%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 5.780 min (minor), t_R = 6.423 min (major).

2-((1*R*,2*S*)-2-(3-chlorophenyl)-3,3-diphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ga): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 48% yield (31.8 mg); yellow solid; m.p. 122-123 ºC; $[\alpha]_D^{20}$ = -228.3 (c 0.60, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.31 (m, 3H), 7.23 – 7.10 (m, 5H), 7.04 – 7.00 (m, 3H), 6.97 (s, 1H), 6.88 – 6.84 (m, 1H), 6.71 – 6.67 (m, 3H), 6.47 – 6.44 (m, 2H), 6.31 (d, *J* = 7.6 Hz, 2H), 5.51 (d, *J* = 9.6 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 2.29 (d, *J* = 16.8 Hz, 1H), 2.19 – 2.03 (m, 3H), 1.03 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.1, 157.5, 147.0, 145.2, 140.8, 140.5, 137.0, 136.2, 132.2, 131.5, 130.3, 129.1, 128.3, 127.2, 127.1, 126.5, 126.1, 124.6, 124.1, 122.0, 120.2, 118.9, 118.6, 114.3,

112.2, 107.6, 61.9, 55.4, 50.1, 40.7, 38.4, 32.1, 28.1, 27.9, 21.1; ESI FTMS exact mass calcd for $(C_{44}H_{39}ClN_2O_2\text{-}H)^-$ requires m/z 661.2622, found m/z 661.2631; Enantiomeric excess: 63%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 4.290 min (minor), t_R = 5.003 min (major).

2-((1*R*,2*S*)-3,3-diphenyl-2-(m-tolyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ha): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 92% yield (59.2 mg); yellow solid; m.p. 109-110 ºC; $[\alpha]_D^{20}$ = -34.2 (c 0.60, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.54 (d, *J* = 6.0 Hz, 3H), 7.37 (s, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.24 – 7.09 (m, 6H), 7.07 – 7.03 (m, 2H), 6.96 – 6.88 (m, 2H), 6.74 – 6.67 (m, 3H), 6.52 – 6.46 (m, 5H), 5.56 (d, *J* = 9.2 Hz, 1H), 5.50 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 2.27 (d, *J* = 16.8 Hz, 1H), 2.17 (s, 3H), 2.11 (d, *J* = 16.4 Hz, 2H), 1.98 (d, *J* = 16.4 Hz, 1H), 1.01 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.1, 157.5, 147.0, 145.2, 140.8, 140.5, 137.0, 136.2, 132.2, 131.5, 130.3, 129.1, 128.3, 127.2, 127.1, 126.5, 126.1, 124.6, 124.1, 122.0, 120.2, 118.9, 118.6, 114.3, 112.2, 107.6, 61.9, 55.4, 50.1, 40.7, 38.4, 32.1, 28.1, 27.9, 21.1; IR (KBr): 3366, 2923, 1730, 1590, 1495, 1448, 1268, 1032 cm^{-1}; ESI FTMS exact mass calcd for $(C_{45}H_{42}N_2O_2\text{-}H)^-$ requires m/z 641.3168, found m/z 641.3183; Enantiomeric excess: 44%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 5.347 min (minor), t_R = 6.222 min (major).

2-((1*R*,2*R*)-2-(2-fluorophenyl)-3,3-diphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ia): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 62% yield (40.1 mg); yellow solid; m.p. 93-94 ºC; $[\alpha]_D^{20}$ = +26.3 (c 0.4, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.25 – 7.11 (m, 5H), 7.06 – 7.00 (m, 2H), 6.99 – 6.94 (m,

1H), 6.88 – 6.82 (m, 1H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.62 (t, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 7.6 Hz, 2H), 6.39 – 6.35 (m, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 5.47 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 2.27 (d, *J* = 16.0 Hz, 1H), 2.16 – 2.07 (m, 2H), 2.00 (d, *J* = 16.0 Hz, 1H), 1.01 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 158.5 (*J* = 230 Hz), 146.1, 144.8, 142.5, 140.5, 133.5, 131.4, 131.1, 129.7, 128.7, 127.8 (*J* = 9 Hz), 127.6, 127.5, 126.7 (*J* = 8 Hz), 124.1, 122.7, 122.0, 120.3, 119.0, 118.4, 114.2, 113.8 (*J* = 24 Hz), 112.2, 106.6, 61.6, 58.5, 55.4, 53.0, 50.1, 46.1, 40.7, 37.4, 37.3, 35.3, 32.0, 28.4, 27.5; IR (KBr): 3366, 2923, 1730, 1590, 1495, 1448, 1268, 1032 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{39}FN_2O_2\text{-}H)^-$ requires m/z 645.2918, found m/z 645.2926; Enantiomeric excess: 60%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 4.550 min (minor), t_R = 4.987 min (major).

2-((1*R*,2*S*)-3,3-diphenyl-2-(o-tolyl)-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ja): preparative thin layer chromatography (dichloromethane/ethyl acetate = 10/1); 52% yield (33.1 mg); yellow solid; m.p. 119-120 °C; $[\alpha]_D^{20}$ = -20.8 (c 0.66, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.53 (d, *J* = 6.4 Hz, 3H), 7.41 – 7.28 (m, 2H), 7.22 – 7.11 (m, 6H), 7.07 – 7.03 (m, 2H), 6.92 – 6.90 (m, 2H), 6.74 – 6.67 (m, 3H), 6.52 – 6.46 (m, 5H), 5.56 (d, *J* = 9.2 Hz, 1H), 5.49 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 3H), 2.27 (d, *J* = 16.8 Hz, 1H), 2.17 (s, 3H), 2.14 – 2.09 (m, 2H), 1.99 (d, *J* = 16.4 Hz, 1H), 1.01 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 159.1, 157.5, 147.0, 145.2, 140.8, 140.6, 137.0, 136.2, 132.2, 131.5, 130.3, 129.1, 128.3, 127.2, 127.1, 126.5, 126.1, 124.6, 124.1, 122.0, 120.2, 118.9, 118.6, 114.3, 112.2, 107.6, 61.9, 55.4, 50.0, 40.7, 38.4, 32.1, 28.1, 27.9, 21.1; IR (KBr): 3816, 2910, 1765, 1558, 1448, 1268, 1032, 889 cm^{-1}; ESI FTMS exact mass calcd for $(C_{45}H_{42}N_2O_2\text{-}H)^-$ requires m/z 641.3168, found m/z 641.3181; Enantiomeric excess: 52%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.470 min (minor), t_R = 6.360 min (major).

2-((1*R*,2*S*)-7-chloro-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)-3-((4-methoxyphenyl)amino)-5,5-dimethylcyclohex-2-enone (3ka): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 60% yield (40.0 mg); yellow solid; m.p. 78-79 ºC; $[\alpha]_D^{20}$ = -13.1 (c 0.80, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.30 (m, 3H), 7.26 – 7.07 (m, 5H), 7.03 – 7.00 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 7.6 Hz, 2H), 5.51 (d, *J* = 9.6 Hz, 1H), 5.31 (d, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 2.28 (d, *J* = 16.8 Hz, 1H), 2.18 – 2.09 (m, 2H), 2.05 (d, *J* = 16.4 Hz, 1H), 1.03 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 159.8, 157.6, 146.2, 144.5, 141.4, 140.5, 136.6, 132.3, 131.9, 131.4, 129.5, 128.8, 127.7, 127.5, 127.2, 127.0, 126.8, 126.7, 124.1, 122.1, 120.4, 119.0, 118.1, 114.2, 112.3, 107.1, 62.5, 61.7, 55.4, 50.1, 40.8, 36.2, 32.2, 28.1; IR (KBr): 3883, 3419, 2988, 1786, 1521, 1448, 1268, 1032, 917 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{39}ClN_2O_2\text{-}H)^-$ requires m/z 661.2622, found m/z 661.2618; Enantiomeric excess: 65%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 6.823 min (minor), t_R = 7.293 min (major).

3-((4-methoxyphenyl)amino)-5,5-dimethyl-2-((1*R*,2*S*)-7-methyl-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3la): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 78% yield (50.3 mg); yellow solid; m.p. 98-99 ºC; $[\alpha]_D^{20}$ = -375.9 (c 1.0, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.26 – 7.17 (m, 3H), 7.11 – 7.07 (m, 1H), 7.03 – 6.95 (m, 6H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 7.6 Hz, 2H), 5.52 (d, *J* = 9.6 Hz, 1H), 5.36 (d, *J* = 9.6 Hz, 1H), 3.74 (s, 3H), 2.44 (s, 3H), 2.30 (d, *J* = 16.4 Hz, 1H), 2.21 – 2.08 (m, 2H), 2.06 (d, *J* = 16.0 Hz, 1H), 1.04 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.3, 157.4, 146.4, 144.9, 141.8, 138.7, 138.1, 131.7, 130.6,

129.6, 128.7, 127.8, 127.2, 126.9, 126.8, 126.6, 126.4, 126.3, 124.5, 123.5, 118.8, 118.0, 114.2, 111.7, 107.8, 63.1, 61.8, 57.8, 55.4, 54.6, 50.2, 42.1, 40.8, 37.2, 36.0, 32.2, 28.1, 28.0, 21.5; IR (KBr): 3366, 2923, 1730, 1590, 1495, 1448, 1268, 1032 cm^{-1}; ESI FTMS exact mass calcd for $(C_{45}H_{42}N_2O_2\text{-}H)^-$ requires m/z 641.3168, found m/z 641.3182; Enantiomeric excess: 60%, determined by HPLC (Daicel Chiralpak IC, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.337 min (minor), t_R = 19.110 min (major).

3-((4-chlorophenyl)amino)-5,5-dimethyl-2-(2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ab): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 58% yield (36.5 mg); yellow solid; m.p. 90-91 °C; $[\alpha]_D^{20}$ = +38.6 (c 0.2, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 6.8 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.21 – 7.17 (m, 1H), 7.16 – 7.07 (m, 4H), 7.05 – 6.95 (m, 5H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 8.6 Hz, 2H), 6.28 (d, *J* = 7.6 Hz, 2H), 5.56 (d, *J* = 9.6 Hz, 1H), 5.31 (d, *J* = 9.6 Hz, 1H), 2.43 (d, *J* = 16.6 Hz, 1H), 2.18 – 2.05 (m, 3H), 1.06 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 157.7, 146.7, 144.6, 141.6, 140.4, 137.9, 137.6, 130.5, 130.3, 129.5, 129.1, 128.7, 127.8, 12.3, 127.0, 126.7, 126.6, 126.5, 125.4, 124.0, 122.1, 120.4, 118.9, 117.8, 112.3, 109.6, 63.4, 61.9, 50.2, 40.9, 36.1, 32.6, 28.6, 27.6; IR (KBr): 3438, 2918, 1730, 1590, 1418, 1268, 1032, 918 cm^{-1}; ESI FTMS exact mass calcd for $(C_{43}H_{37}ClN_2O\text{-}H)^-$ requires m/z 631.2516, found m/z 631.2528; Enantiomeric excess: 76%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.977 min (minor), t_R = 13.040 min (major).

5,5-dimethyl-3-(*p*-tolylamino)-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ac): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 43% yield (26.2 mg); yellow solid; m.p. 103-104 °C; $[\alpha]_D^{20}$ = +21.2 (c 0.3, acetone); >95:5 dr; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.84 (s, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.21 – 7.13 (m, 2H), 7.12 – 7.07 (m, 1H), 7.05 – 6.89 (m, 9H), 6.39 (d, *J* = 8.41 Hz, 2H), 6.29 (d, *J* = 7.6 Hz, 2H), 5.57 (d, *J* = 9.6 Hz, 1H), 5.37 (d, *J* = 9.6 Hz, 1H), 2.38 (d, *J* = 16.8 Hz, 1H), 2.26 (s, 3H), 2.17 (d, *J* = 16.8 Hz, 2H), 2.06 (d, *J* = 16.4 Hz, 1H), 1.04 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 158.9, 146.4, 144.7, 141.6, 140.4, 138.0, 136.2, 135.0, 130.6, 129.6, 128.7, 127.9, 127.3, 126.9, 126.6, 126.5, 126.4, 125.0, 124.2, 122.0, 120.3, 119.1, 118.3, 112.2, 108.1, 63.2, 61.8, 50.2, 40.9, 36.0, 32.4, 28.3, 27.9, 20.8; IR (KBr): 3441, 3069, 1771, 1640, 1421, 1268, 1032, 887 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{40}N_2O\text{-}H)^-$ requires m/z 611.3063, found m/z 611.3068; Enantiomeric excess: 62%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 11.830 min (minor), t_R = 14.093 min (major).

3-((3-fluorophenyl)amino)-5,5-dimethyl-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ad): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 49% yield (30.3 mg); yellow solid; m.p. 88-89 ºC; $[\alpha]_D^{20}$ = +29.6 (c 0.32, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.43 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.19 – 7.04 (m, 4H), 7.03 – 6.93 (m, 5H), 6.89 (d, *J* = 7.2 Hz, 2H), 6.78 – 6.70 (m, 1H), 6.29 – 6.27 (m, 2H), 6.17 – 6.15 (m, 2H), 5.56 (d, *J* = 9.6 Hz, 1H), 5.32 (d, *J* = 9.6 Hz, 1H), 2.53 (d, *J* = 16.4 Hz, 1H), 2.25 – 2.10 (m, 2H), 2.09 (d, *J* = 16.0 Hz, 1H), 1.08 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 162.8 (*J* = 245 Hz), 146.7, 144.6, 141.5, 140.6 (*J* = 10 Hz), 140.5, 137.9, 130.5, 130.2 (*J* = 10 Hz), 129.6, 128.7, 127.8, 127.3, 127.0, 126.7, 126.6, 126.5, 124.0, 122.2, 120.5, 119.2, 118.9, 117.6, 112.3, 111.3 (*J* = 21 Hz), 110.8 (*J* = 24 Hz), 110.4, 63.5, 61.9, 50.2, 41.0, 36.0, 32.7, 28.8, 27.4; IR (KBr): 3383, 3016, 1809, 1572, 1217, 1032, 917 cm^{-1}; ESI FTMS exact mass calcd for $(C_{43}H_{37}FN_2O\text{-}H)^-$ requires m/z 615.2812, found m/z 615.2823; Enantiomeric excess: 70%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC,

254 nm): t_R = 12.640 min (minor), t_R = 13.900 min (major).

5,5-dimethyl-3-(m-tolylamino)-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ae): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 52% yield (32.9 mg); yellow solid; m.p. 110-111 ºC; $[\alpha]_D^{20}$ = +38.6 (c 0.27, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.25 (m, 2H), 7.23 – 7.15 (m, 2H), 7.14 – 7.06 (m, 2H), 7.05 – 6.94 (m, 6H), 6.92 – 6.86 (m, 3H), 6.37 (d, *J* = 8.0 Hz, 1H), 6.29 (d, *J* = 7.6 Hz, 2H), 6.15 (s, 1H), 5.57 (d, *J* = 9.6 Hz, 1H), 5.36 (d, *J* = 9.6 Hz, 1H), 2.44 (d, *J* = 16.6 Hz, 1H), 2.21 (d, *J* = 9.2 Hz, 1H), 2.17 (s, 3H), 2.15 (s, 1H), 2.07 (d, *J* = 16.4 Hz, 1H), 1.05 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 158.6, 146.5, 144.7, 141.6, 140.4, 139.0, 138.8, 138.0, 130.6, 129.6, 128.7, 128.6, 127.9, 127.3, 126.9, 126.6, 126.5, 126.4, 125.8, 125.3, 124.2, 122.0, 121.7, 120.3, 119.1, 118.2, 112.2, 108.5, 63.3, 61.8, 50.30, 40.9, 36.1, 32.4, 28.4, 27.8, 21.2; IR (KBr): 3617, 3381, 1716, 1622, 1287, 1032, 977 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{40}N_2O\text{-}H)^-$ requires m/z 611.3063, found m/z 611.3081; Enantiomeric excess: 62%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 11.840 min (minor), t_R = 13.767 min (major).

3-((3-methoxyphenyl)amino)-5,5-dimethyl-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3af): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 61% yield (38.3 mg); yellow solid; m.p. 110-111 ºC; $[\alpha]_D^{20}$ = -41.4 (c 0.76, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.38 (s, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.24 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 7.12 – 7.06 (m, 2H), 7.05 – 6.95 (m, 5H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.61 – 6.58 (m, 1H), 6.28 (d, *J* = 7.2 Hz, 2H), 6.21 – 6.13 (m, 1H), 5.81 (s, 1H), 5.56 (d, *J* = 9.6 Hz, 1H), 5.33 (d, *J* = 9.2 Hz, 1H), 3.56 (s, 3H), 2.49 (d, *J* = 16.4 Hz, 1H), 2.25 – 2.12 (m,

2H), 2.08 (d, *J* = 16.4 Hz, 1H), 1.06 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 160.0, 158.3, 146.7, 144.6, 141.6, 140.4, 140.1, 137.9, 130.5, 129.6, 129.5, 128.7, 127.9, 127.3, 126.9, 126.7, 126.5, 126.4, 124.2, 122.0, 120.4, 119.1, 118.0, 116.9, 112.2, 110.8, 109.7, 108.8, 63.4, 61.8, 55.2, 50.3, 40.9, 36.0, 32.5, 28.7, 27.6; IR (KBr): 3854, 3341, 2390, 1717, 1329, 1132, 1012 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{40}N_2O_2\text{-}H)^-$ requires m/z 627.3012, found m/z 627.3024; Enantiomeric excess: 70%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 13.387 min (minor), t_R = 16.577 min (major).

3-((2-chlorophenyl)amino)-5,5-dimethyl-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ag): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 49% yield (30.8 mg); yellow solid; m.p. 87-88 °C; $[\alpha]_D^{20}$ = +29.4 (c 0.39, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.57 – 7.53 (m, 3H), 7.33 – 7.28 (m, 2H), 7.25 – 7.19 (m, 4H), 7.18 – 7.17 (m, 4H), 7.06 – 6.94 (m, 6H), 6.90 – 6.88 (m, 2H), 6.79 (d, *J* = 8.0, 1H), 6.29 (d, *J* = 7.2 Hz, 2H), 5.55 (d, *J* = 9.6 Hz, 1H), 5.48 (d, *J* = 9.6 Hz, 1H), 2.39 (d, *J* = 16.4 Hz, 1H), 2.22 (d, *J* = 16.4 Hz, 1H), 2.13 (d, *J* = 6.8 Hz, 1H), 2.09 (d, *J* = 6.8 Hz, 1H), 1.06 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 157.7, 146.5, 144.5, 141.7, 140.6, 138.0, 136.3, 130.5, 129.9, 129.6, 129.3, 128.5, 127.9, 127.3, 127.2, 127.0, 126.6, 126.5, 126.4, 125.9, 125.7, 124.3, 122.0, 120.2, 119.1, 118.1, 112.0, 110.9, 63.1, 61.8, 50.3, 41.0, 36.0, 32.6, 28.1, 28.0; IR (KBr): 3383, 3016, 1809, 1572, 1217, 1032, 917 cm^{-1}; ESI FTMS exact mass calcd for $(C_{43}H_{37}ClN_2O\text{-}H)^-$ requires m/z 631.2516, found m/z 631.2533; Enantiomeric excess: 50%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 13.853 min (minor), t_R = 16.643 min (major).

5,5-dimethyl-3-(*o*-tolylamino)-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ah): preparative thin layer chromatography (dichloromethane/ethyl acetate = 10/1); 50% yield (30.7 mg); yellow

solid; m.p. 87-88 ºC; $[\alpha]_D^{20}$ = +119.9 (c 0.61, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.61 – 7.51 (m, 3H), 7.30 – 7.28 (m, 1H), 7.26 – 7.16 (m, 4H), 7.15 – 7.05 (m, 5H), 7.04 – 6.95 (m, 6H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.35 – 6.23 (m, 2H), 5.58 (d, *J* = 9.6 Hz, 1H), 5.44 (d, *J* = 9.6 Hz, 1H), 2.29 (d, *J* = 16.4 Hz, 1H), 2.19 (d, *J* = 16.4 Hz, 1H), 2.09 – 2.01 (m, 2H), 1.47 (s, 3H), 1.04 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 159.2, 146.2, 144.7, 141.7, 140.5, 138.1, 137.4, 133.6, 130.7, 130.5, 129.6, 128.6, 127.8, 127.3, 127.0, 126.7, 126.6, 126.5, 126.4, 125.9, 125.8, 124.2, 122.1, 120.3, 119.2, 118.7, 112.1, 108.7, 63.1, 61.8, 50.2, 41.0, 36.1, 32.5, 28.1, 28.0, 17.0; IR (KBr): 3871, 3381, 1716, 1429, 1217, 1031, 981 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{40}N_2O\text{-}H)^-$ requires m/z 611.3063, found m/z 611.3079; Enantiomeric excess: 70%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 11.307 min (minor), t_R = 14.353 min (major).

5,5-dimethyl-3-(phenylamino)-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)cyclohex-2-enone (3ai): preparative thin layer chromatography (dichloromethane/ethyl acetate = 10/1); 52% yield (30.8 mg); yellow solid; m.p. 109-110 ºC; $[\alpha]_D^{20}$ = -58.4 (c 0.62, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.40 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.11 (m, 7H), 7.10 – 6.93 (m, 7H), 6.91 (d, *J* = 7.2 Hz, 2H), 6.47 (d, *J* = 7.6 Hz, 2H), 6.29 (d, *J* = 7.6 Hz, 2H), 5.57 (d, *J* = 9.6 Hz, 1H), 5.37 (d, *J* = 9.6 Hz, 1H), 2.47 (d, *J* = 16.6 Hz, 1H), 2.27 – 2.16 (m, 2H), 2.08 (d, *J* = 16.4 Hz, 1H), 1.06 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 158.3, 146.5, 144.7, 141.6, 140.4, 138.9, 138.0, 130.5, 129.6, 129.1, 128.7, 127.9, 127.3, 126.9, 126.6, 126.5, 126.4, 124.9, 124.4, 124.2, 122.1, 120.4, 119.0, 118.1, 112.2, 108.9, 63.3, 61.8, 50.3, 41.0, 36.0, 32.5, 28.5, 27.7; IR (KBr): 3391, 3088, 1816, 1489, 1417, 1131, 1028 cm^{-1}; ESI FTMS exact mass calcd for $(C_{43}H_{38}N_2O\text{-}H)^-$ requires m/z 597.2906, found m/z 597.2923; Enantiomeric excess: 70%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 12.623

min (minor), t_R = 14.103 min (major).

5,5-dimethyl-3-(naphthalen-1-ylamino)-2-((1R,2S)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[b]indol-1-yl)cyclohex-2-enone (3aj): preparative thin layer chromatography (dichloromethane/ethyl acetate = 10/1); 48% yield (31.2 mg); yellow solid; m.p. 121-122 ºC; $[\alpha]_D^{20}$ = +53.6 (c 0.48, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.55 (m, 6H), 7.44 – 7.37 (m, 3H), 7.25 – 7.15 (m, 5H), 7.12 – 7.09 (m, 1H), 7.05 – 6.96 (m, 5H), 6.93 (d, *J* = 7.2 Hz, 2H), 6.81 (s, 1H), 6.57 (d, *J* = 8.8, 1H), 6.30 (d, *J* = 7.2 Hz, 2H), 5.61 (d, *J* = 9.6 Hz, 1H), 5.42 (d, *J* = 9.6 Hz, 1H), 2.58 (d, *J* = 16.4 Hz, 1H), 2.29 – 2.18 (m, 2H), 2.12 (d, *J* = 16.4 Hz, 1H), 1.06 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 158.3, 146.7, 144.6, 140.5, 137.9, 136.5, 133.5, 130.7, 130.5, 129.6, 128.9, 128.7, 127.8, 127.6, 127.3, 127.2, 127.0, 126.6, 126.5, 125.4, 124.2, 123.8, 122.2, 121.1, 120.5, 119.2, 118.1, 112.3, 109.3, 63.5, 61.9, 50.3, 41.1, 36.1, 32.6, 28.7, 27.6; IR (KBr): 3188, 2971, 1892, 1549, 1437, 1231, 1058 cm^{-1}; ESI FTMS exact mass calcd for $(C_{47}H_{40}N_2O\text{-}H)^-$ requires m/z 647.3063, found m/z 647.3079; Enantiomeric excess: 62%, determined by HPLC (Daicel Chiralpak IA, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 13.013 min (minor), t_R = 14.823 min (major).

3-((4-methoxyphenyl)amino)-2-((1R,2S)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[b]indol-1-yl)cyclohex-2-enone (3ak): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 60% yield (35.8 mg) as yellow solid; m.p. 112-113 ºC; $[\alpha]_D^{20}$ = +76.2 (c 0.48, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.25 – 7.11 (m, 4H), 7.01 – 6.94 (m, 8H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 8.8 Hz, 2H), 6.30 (d, *J* = 7.8 Hz, 2H), 5.60 (d, *J* = 9.6 Hz, 1H), 5.38 (d, *J* = 9.6 Hz, 1H), 3.74 (d, *J* = 15.2 Hz, 3H), 2.46 – 2.38 (m, 1H), 2.33 – 2.14 (m, 3H), 1.91 – 1.84 (m, 1H), 1.82 – 1.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 161.5, 157.5, 146.2, 144.8, 141.7, 140.5, 138.1, 131.6, 130.5, 129.5, 128.7, 127.9, 127.3, 127.1, 126.9,

126.7, 126.5, 126.4, 124.3, 122.0, 120.3, 119.0, 118.5, 114.1, 112.2, 108.4, 63.1, 62.0, 55.4, 36.8, 36.0, 27.5, 22.0; IR (KBr): 3386, 2963, 1837, 1688, 1591, 1398, 1168, 1032, 879 cm^{-1}; ESI FTMS exact mass calcd for $(C_{44}H_{36}N_2O_2\text{-}H)^-$ requires m/z 599.2699, found m/z 599.2707; Enantiomeric excess: 73%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 15.527 min (minor), t_R = 18.253 min (major).

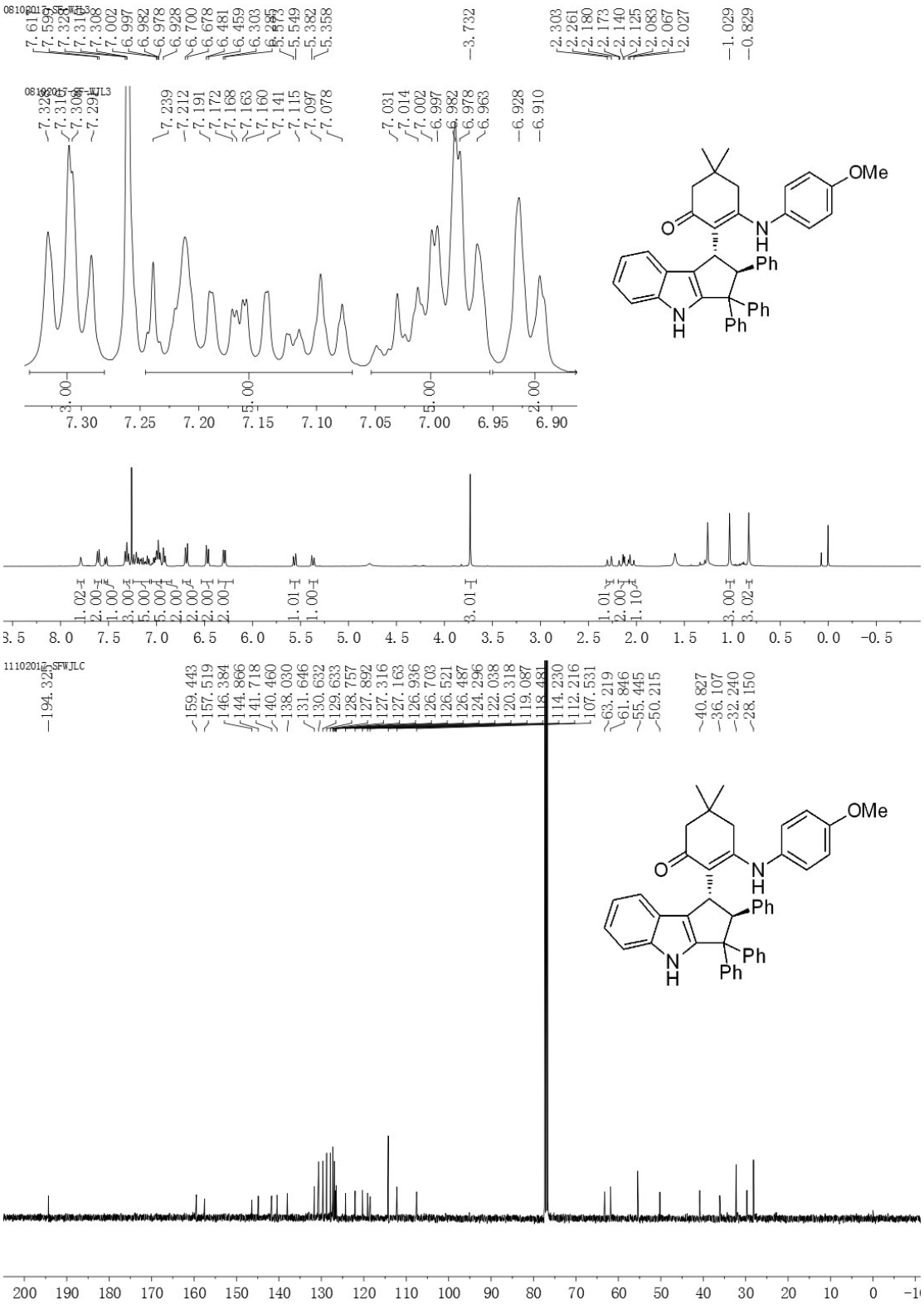
4-((4-methoxyphenyl)amino)-3-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[*b*]indol-1-yl)furan-2(5H)-one (3al): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 55% yield (32.4 mg); yellow solid; m.p. 96-97 °C; $[\alpha]_D^{20}$ = +26.8 (c 0.60, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.32 – 7.28 (m, 1H), 7.25 – 7.16 (m, 2H), 7.14 – 6.91 (m, 8H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 8.8 Hz, 2H), 6.38 – 6.23 (m, 3H), 5.20 (d, *J* = 8.8 Hz, 1H), 4.72 – 4.66 (m, 2H), 4.45 (d, *J* = 15.6 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 162.2, 157.6, 147.2, 144.2, 141.2, 140.2, 137.8, 131.1, 130.1, 129.5, 128.8, 128.0, 127.5, 127.4, 127.0, 126.9, 126.7, 124.5, 124.0, 122.1, 120.6, 118.8, 115.6, 114.6, 114.4, 112.4, 65.5, 61.9, 55.5, 37.4; IR (KBr): 3146, 2923, 1717, 1608, 1533, 1218, 1168, 1032, 981, 879 cm^{-1}; ESI FTMS exact mass calcd for $(C_{40}H_{32}N_2O_3\text{-}H)^-$ requires m/z 587.2335, found m/z 587.2354; Enantiomeric excess: 60%, determined by HPLC (Daicel Chiralpak IA, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.413 min (minor), t_R = 6.383 min (major).

3-((4-methoxyphenyl)amino)-2-((1*R*,2*S*)-2,3,3-triphenyl-1,2,3,4-tetrahydrocyclopenta[b]indol-1-yl)cyclopent-2-enone (3am): preparative thin layer chromatography (dichloromethane / ethyl acetate = 10/1); 55% yield (41.5 mg); yellow solid; m.p. 114-115 °C; $[\alpha]_D^{20}$ = +28.7 (c 0.68, acetone); >95:5 dr; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.11 – 7.05 (m, 2H), 7.04 – 6.96

(m, 6H), 6.84 (s, 1H), 6.72 – 6.69 (m, 2H), 6.51 (d, *J* = 8.4 Hz, 2H), 6.35 – 6.29 (m, 2H), 5.25 (s, 1H), 4.86 (d, *J* = 6.6 Hz, 1H), 3.73 (s, 3H), 2.66 – 2.54 (m, 1H), 2.42 – 2.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 172.4, 157.5, 147.2, 144.5, 141.2, 140.2, 131.6, 130.2, 129.6, 128.7, 128.1, 127.3, 127.2, 126.8, 126.7, 126.5, 125.6, 124.2, 122.0, 120.4, 118.9, 114.2, 112.3, 112.2, 64.7, 62.0, 55.4, 32.6, 25.4; IR (KBr): 3316, 3083, 2961, 1787, 1598, 1521, 1318, 1133, 991, 868 cm^{-1}; ESI FTMS exact mass calcd for $(C_{41}H_{34}N_2O_2\text{-}H)^-$ requires m/z 585.2542, found m/z 585.2559; Enantiomeric excess: 71%, determined by HPLC (Daicel Chiralpak IA, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC, 254 nm): t_R = 4.897 min (minor), t_R = 5.867 min (major).

4. NMR spectra of products 3

3aa



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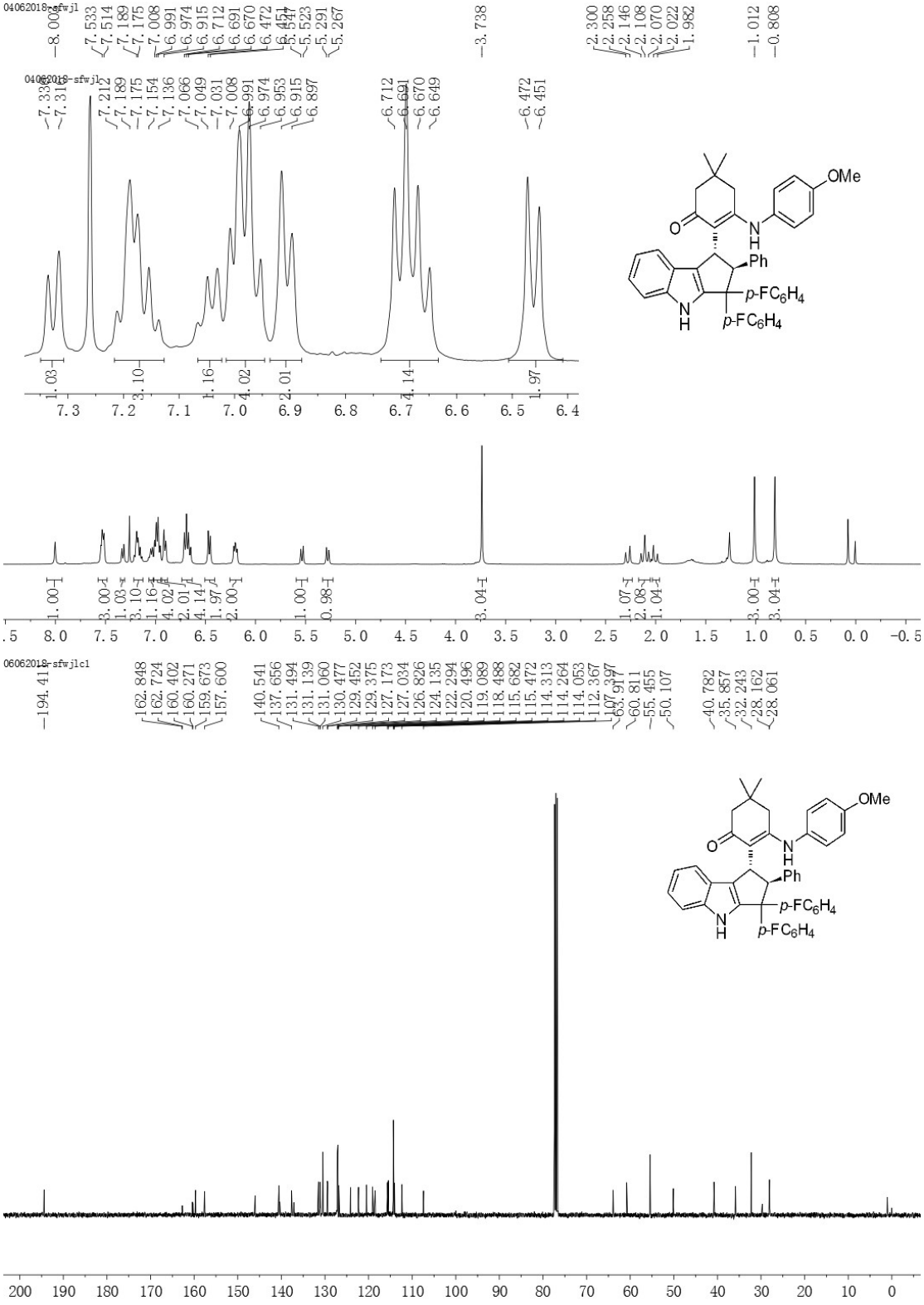
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3.10
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2.01
4.14
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7.1
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6.8
6.7
6.6
6.5
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3.00
3.04
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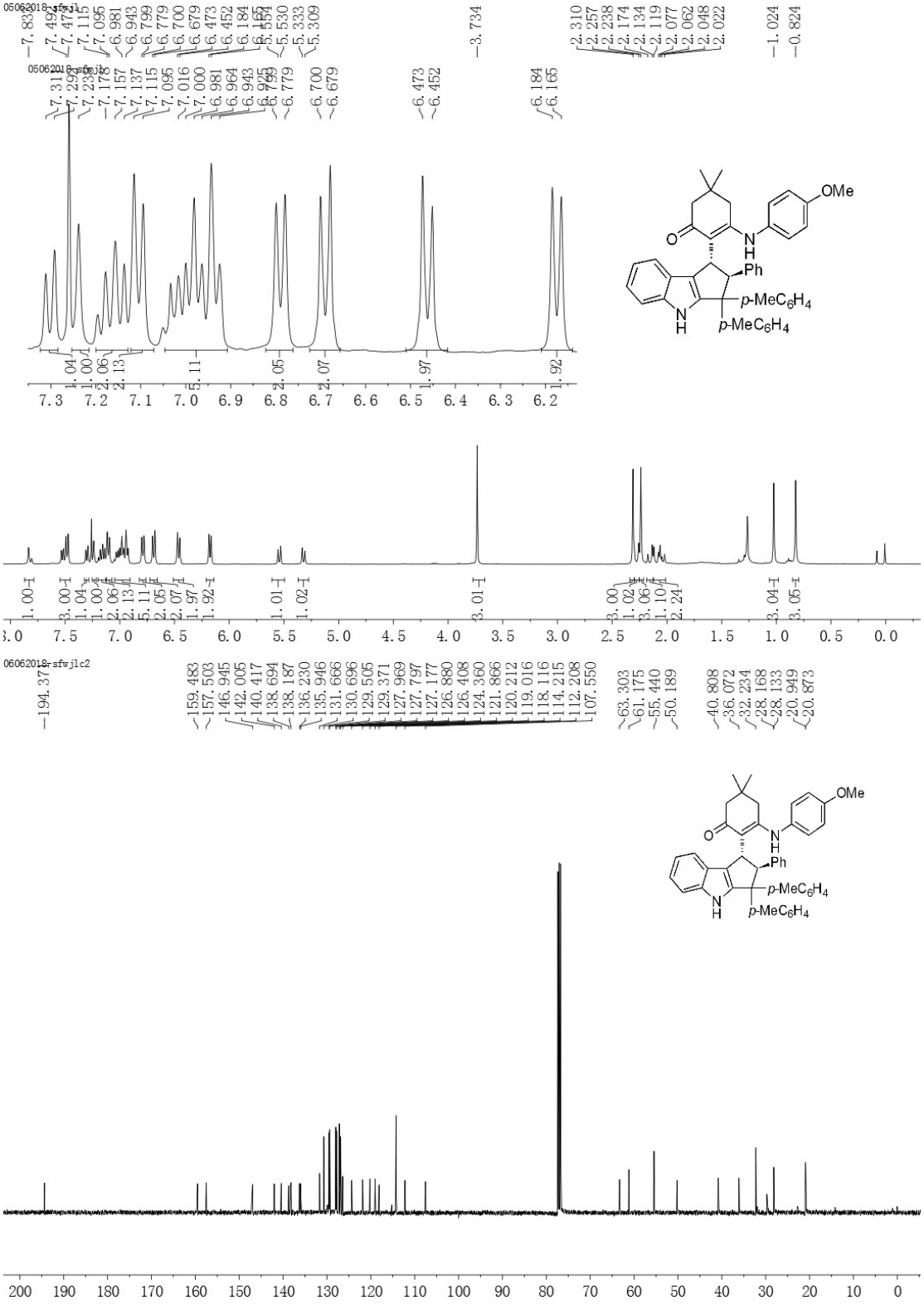

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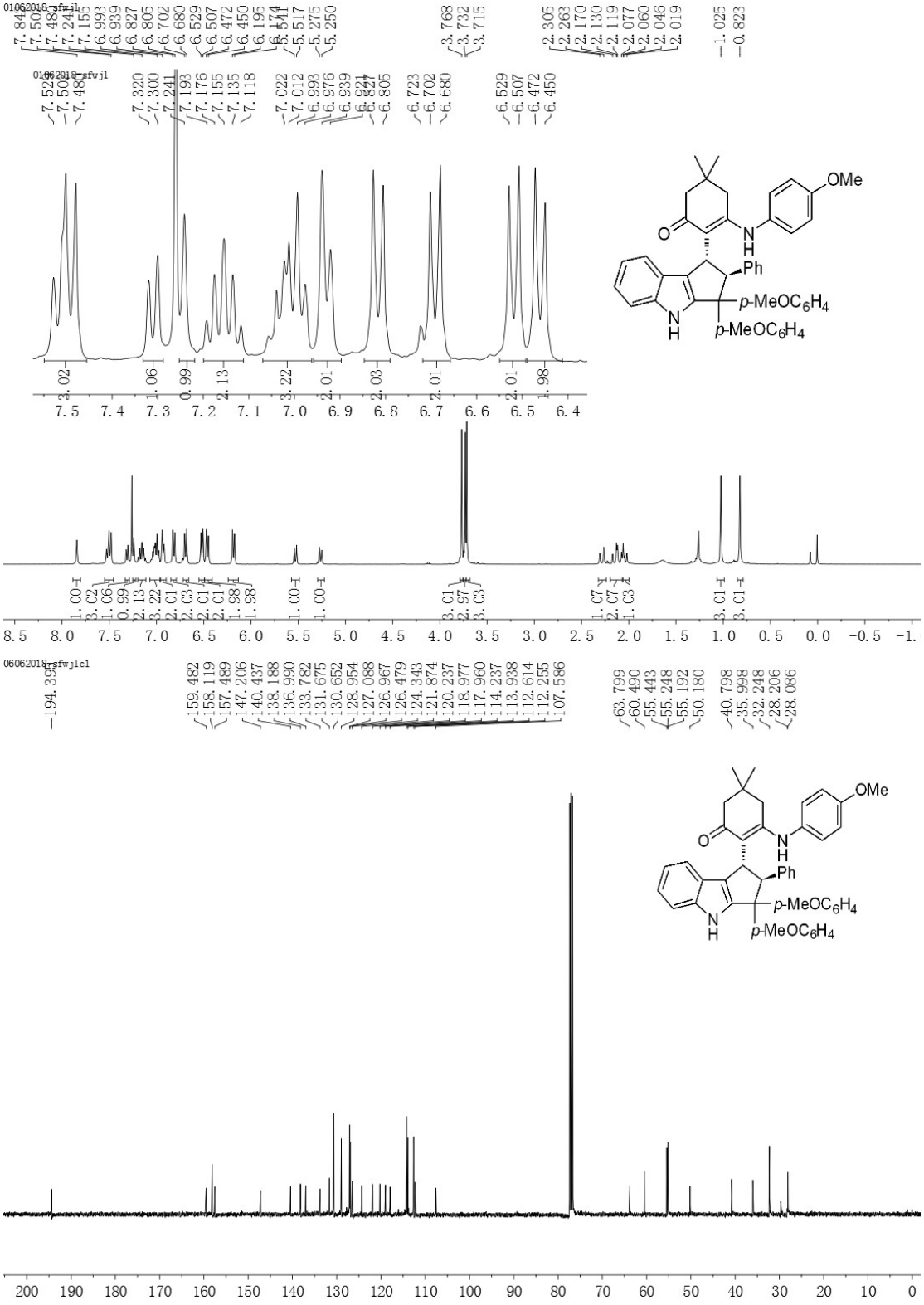

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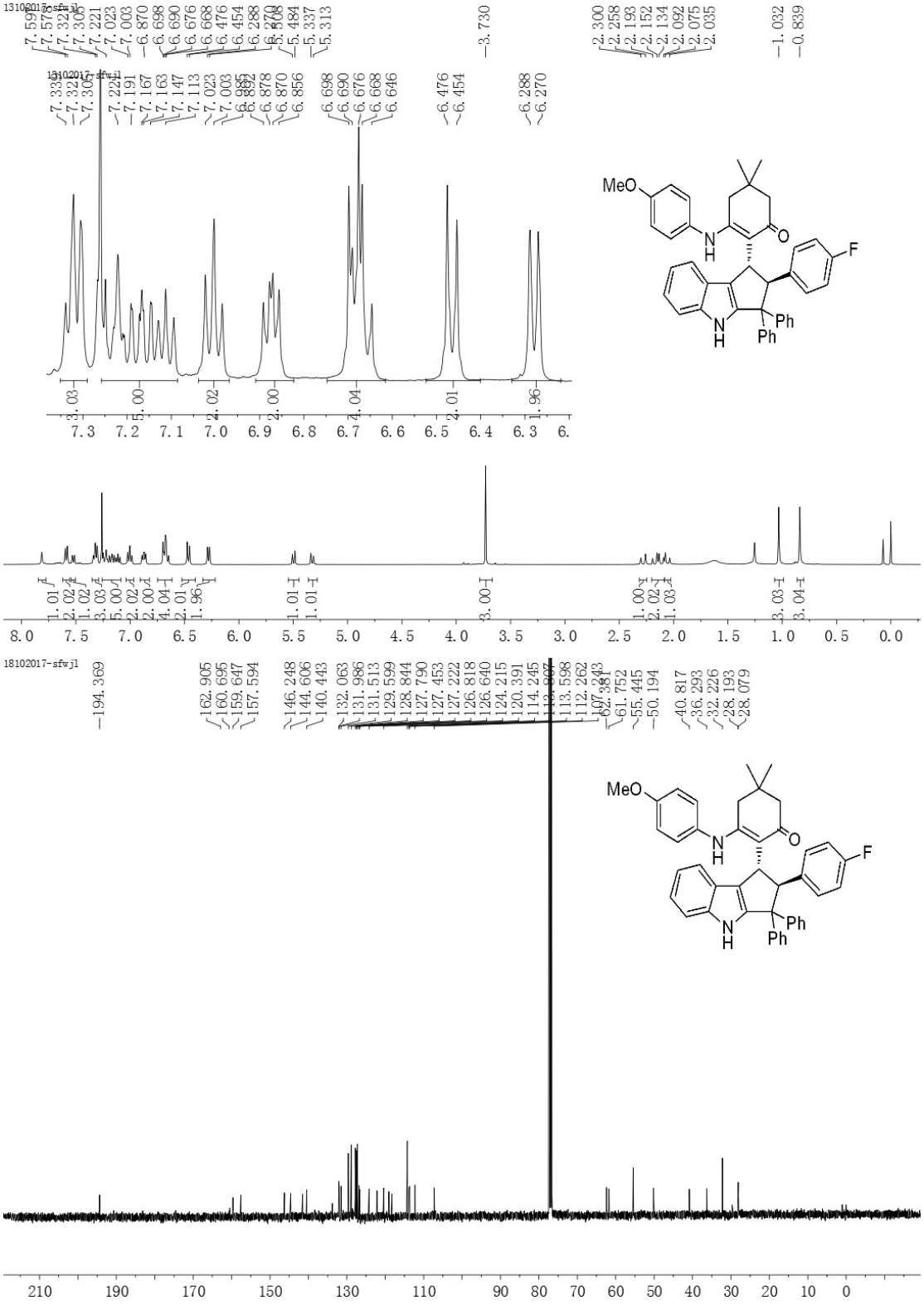

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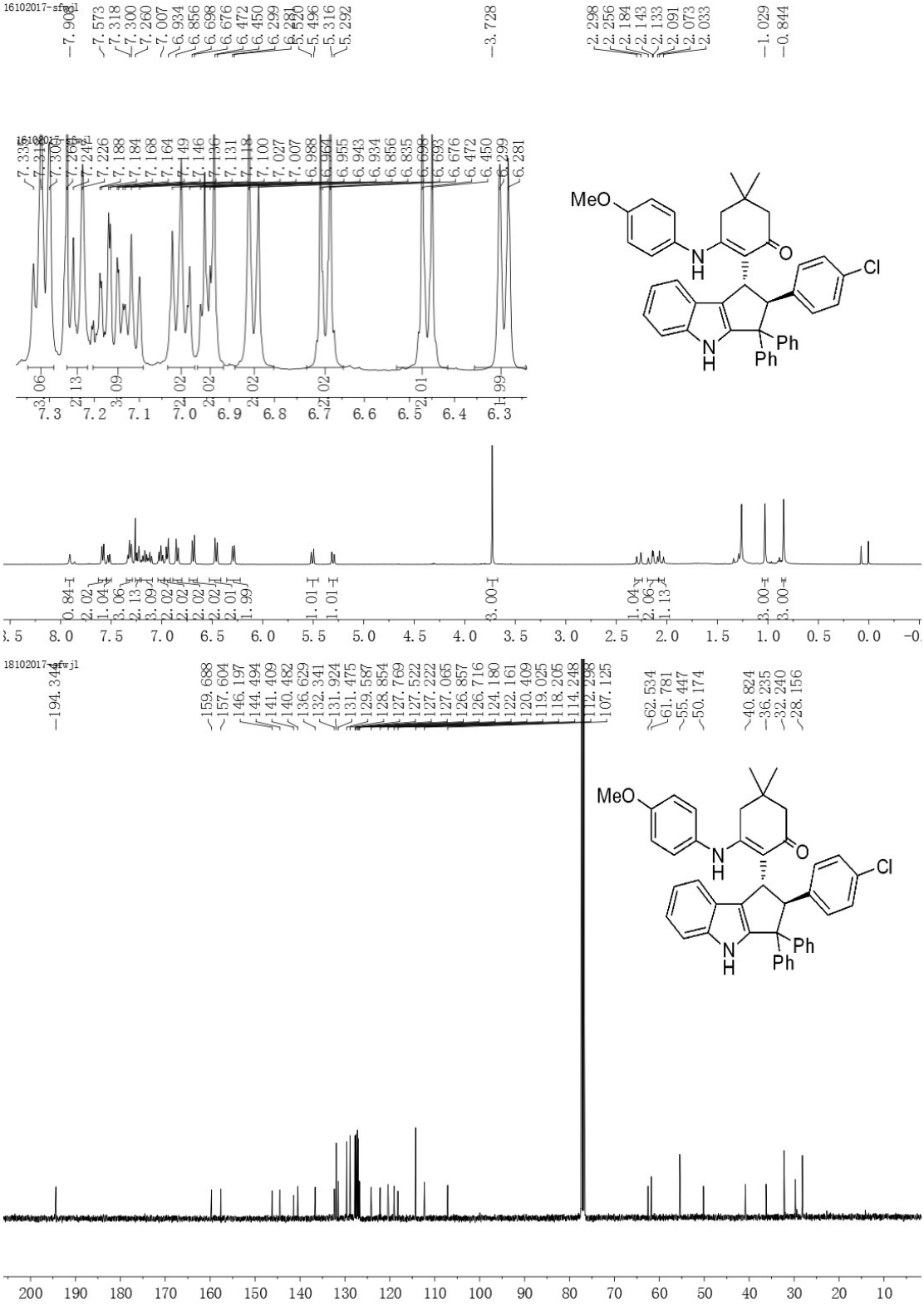
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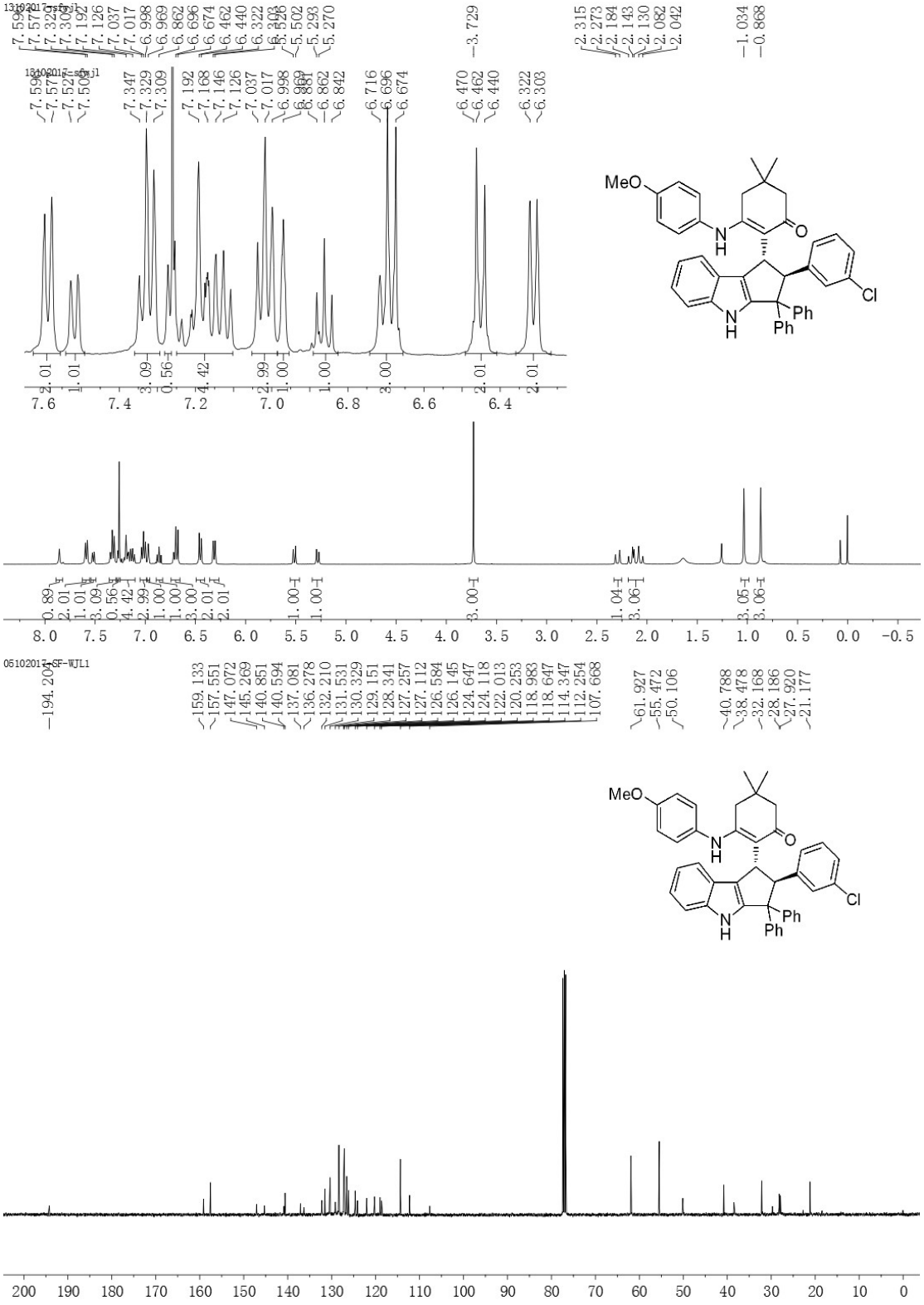

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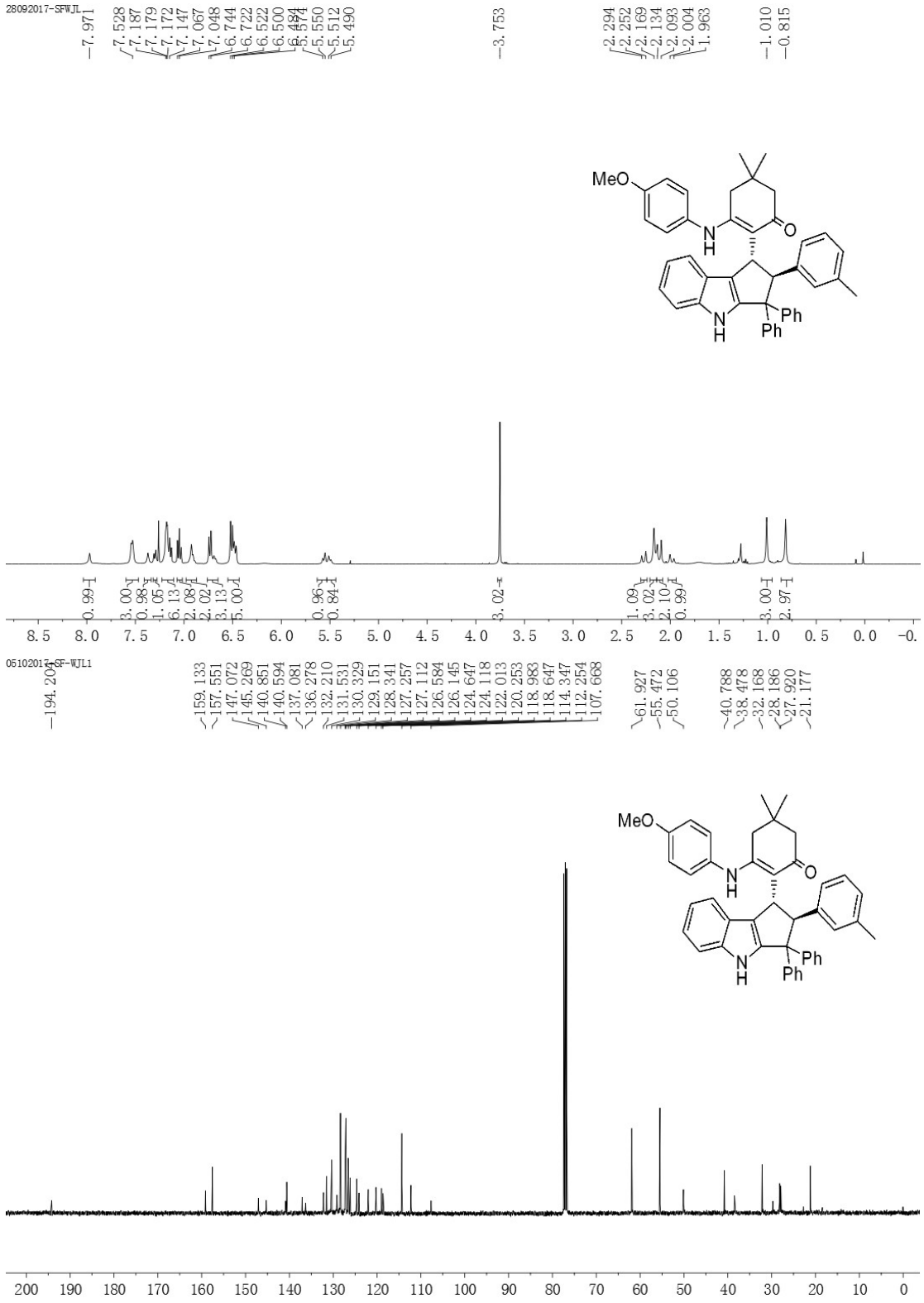
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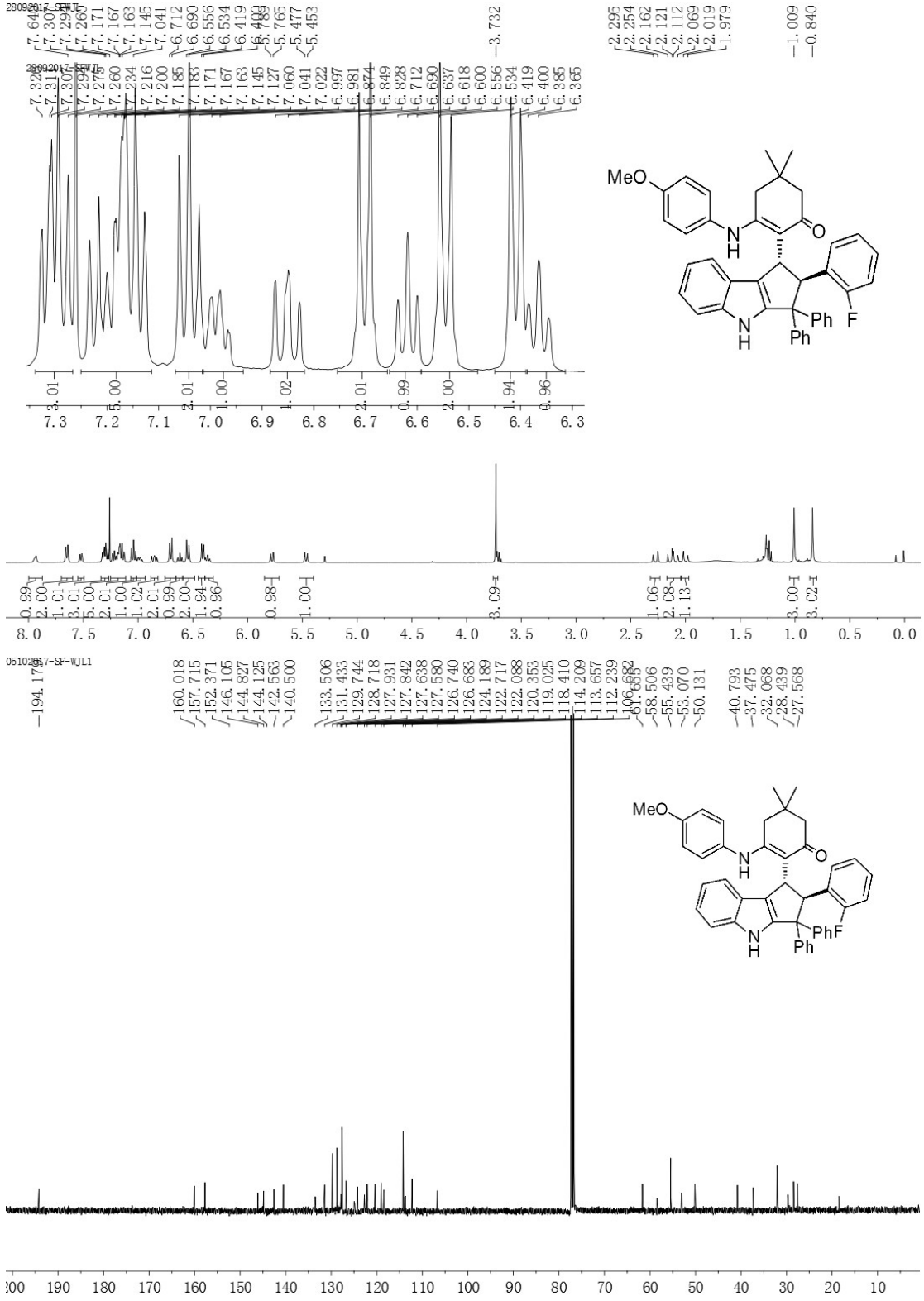

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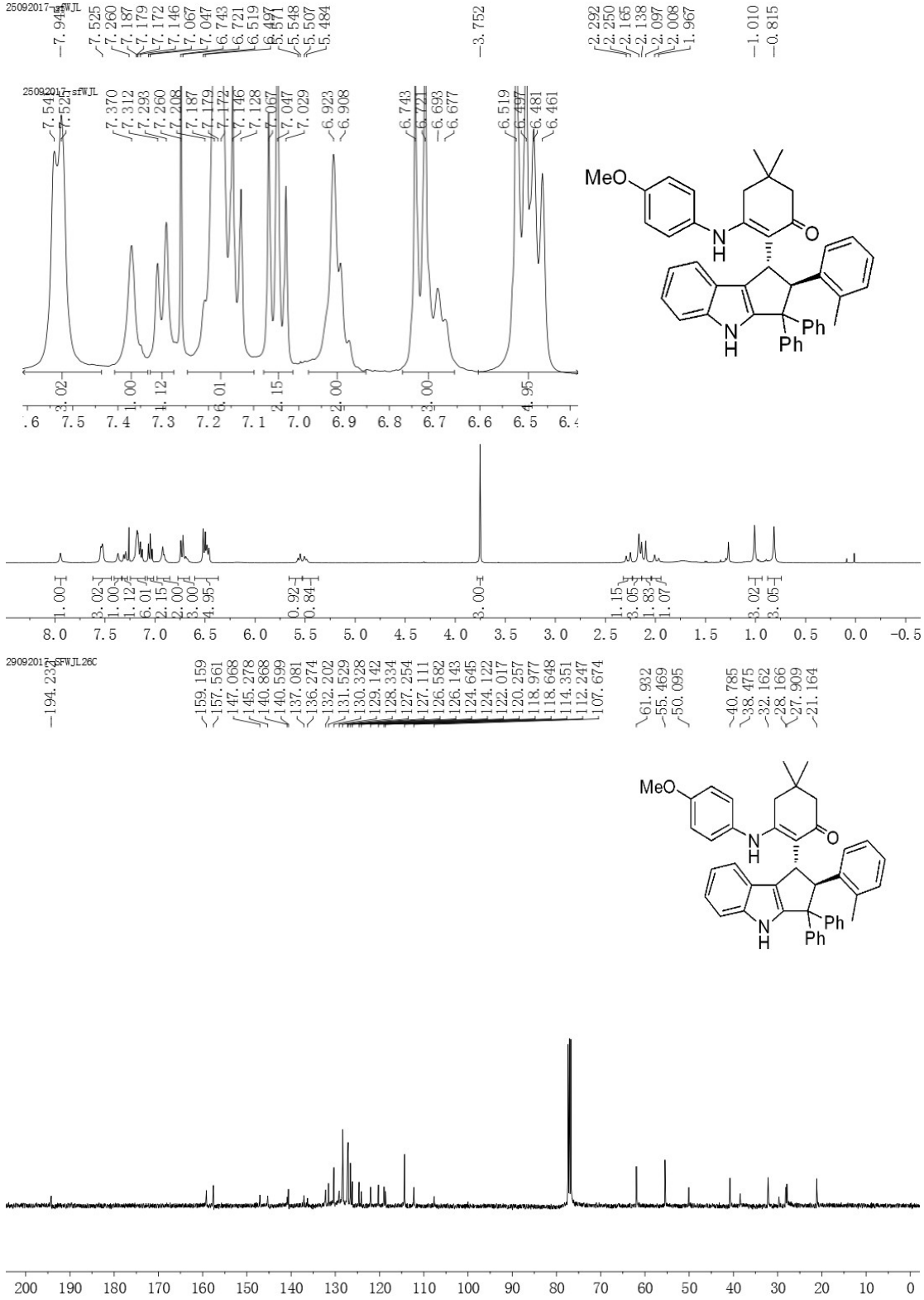

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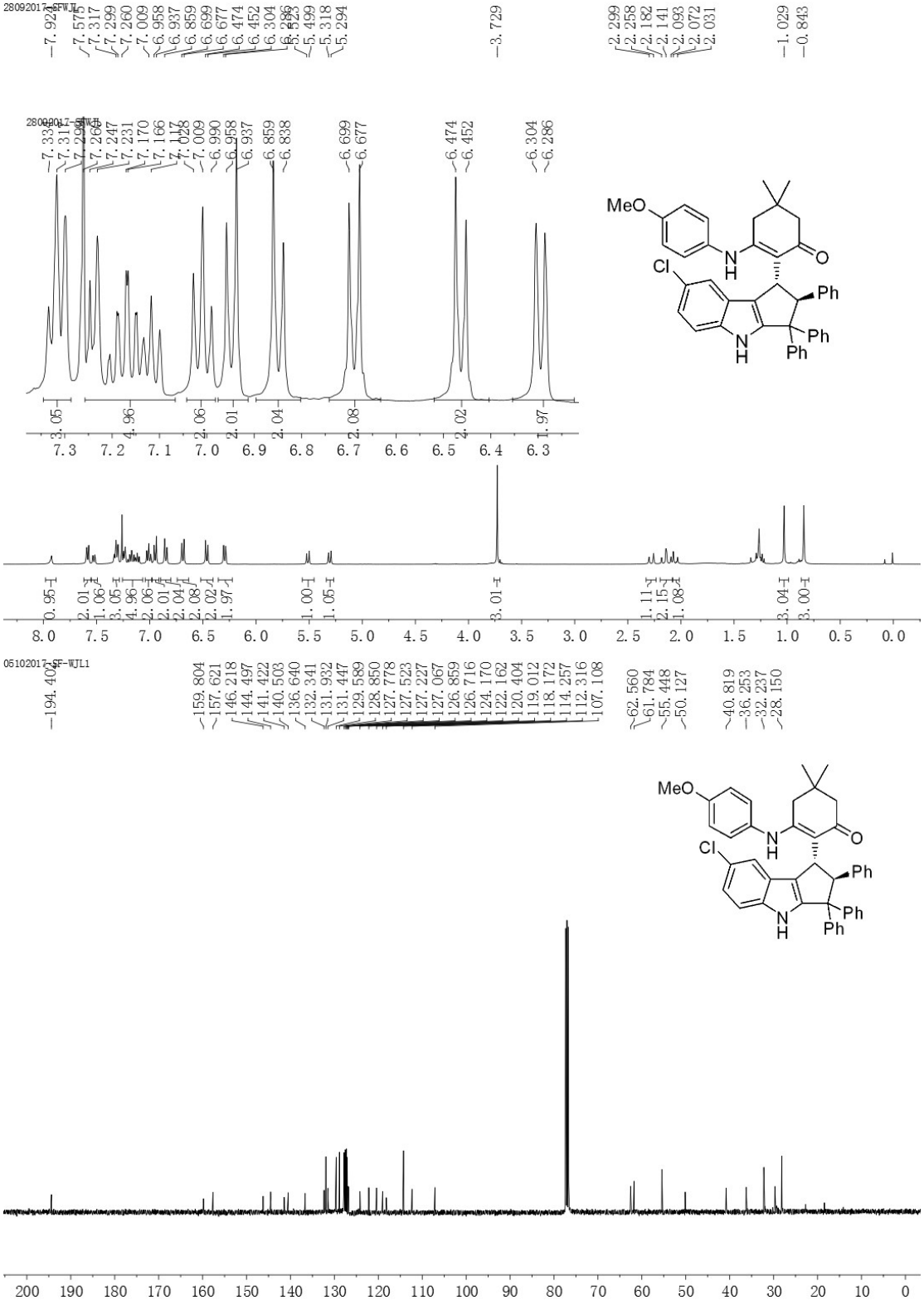

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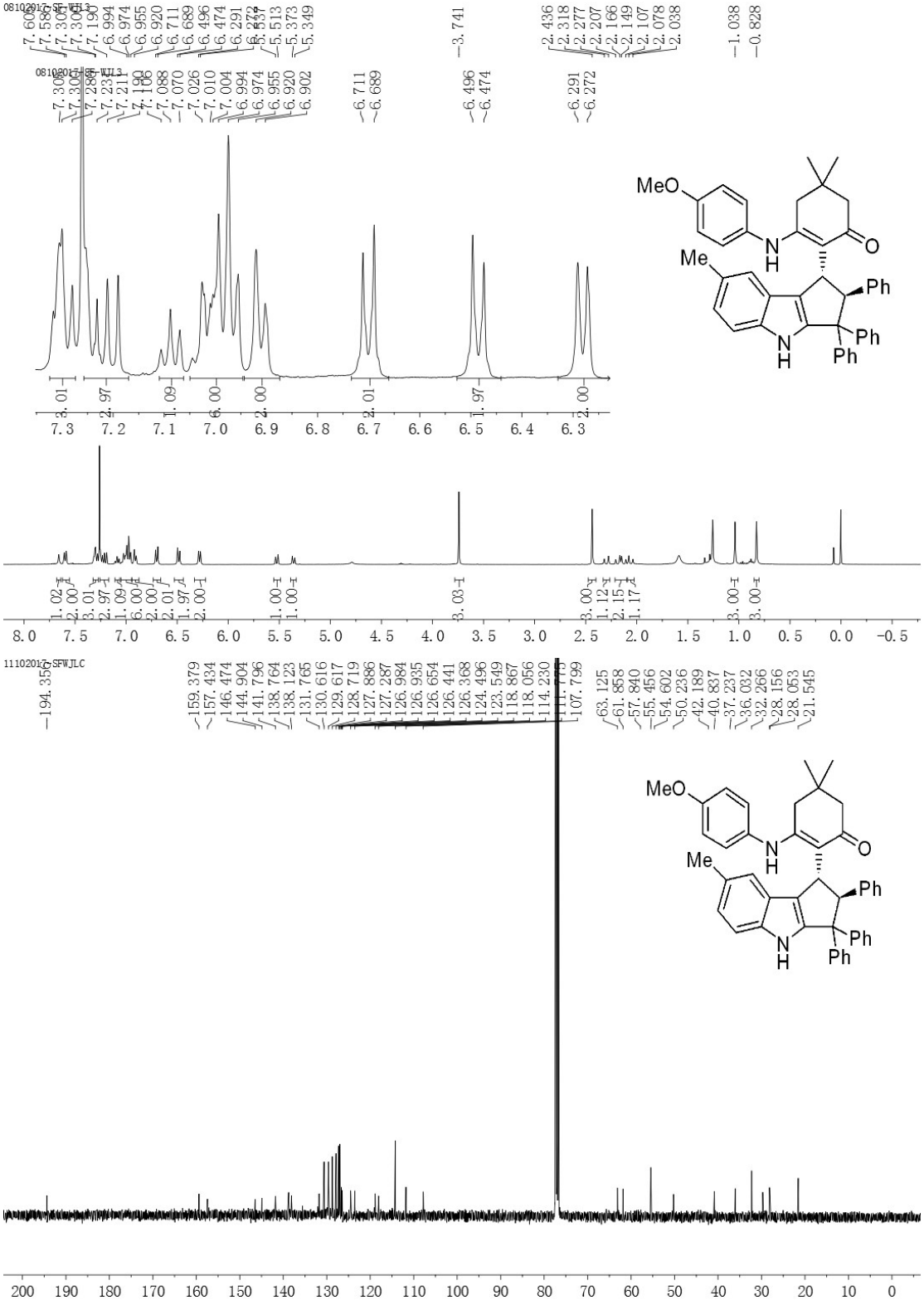

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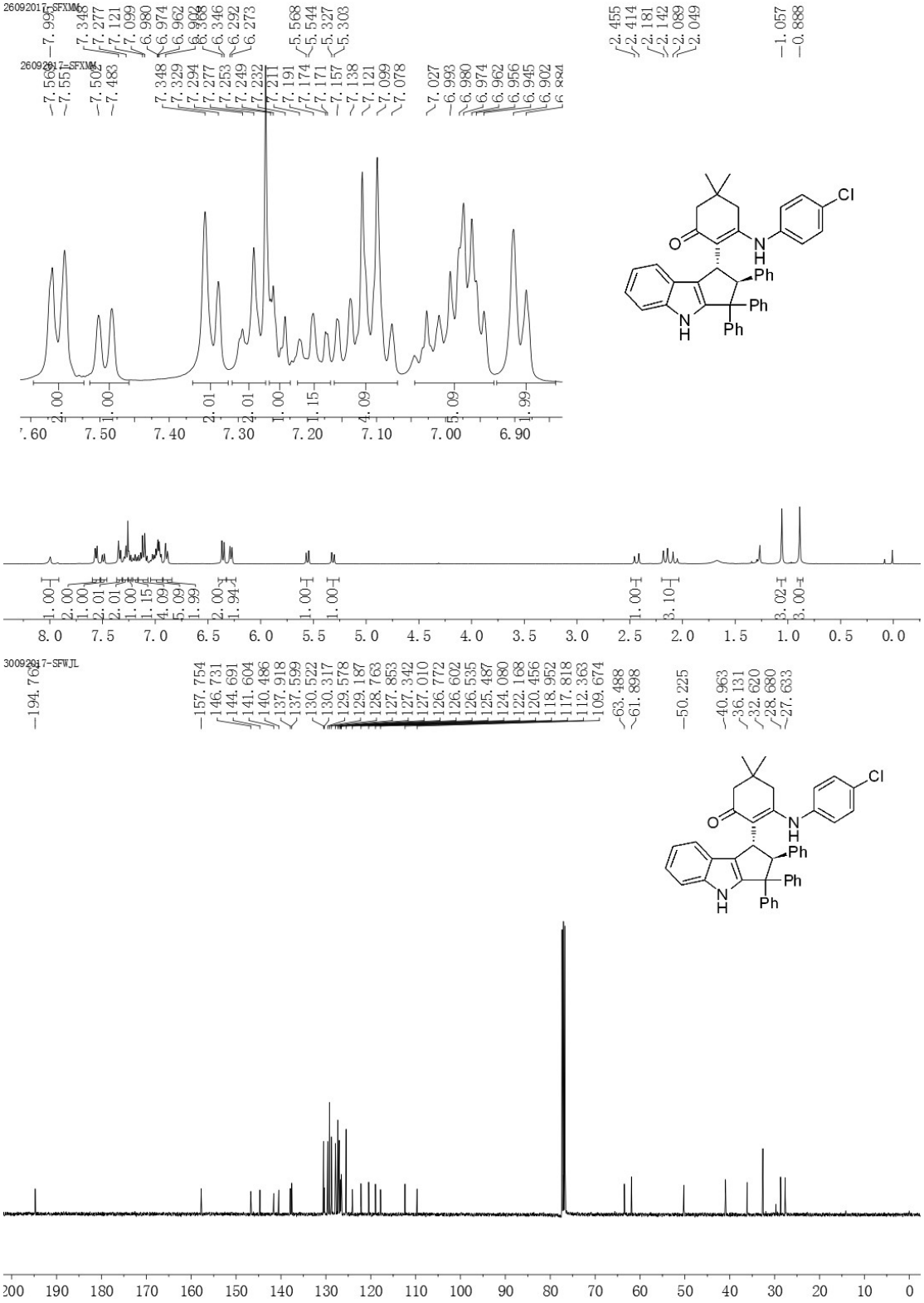

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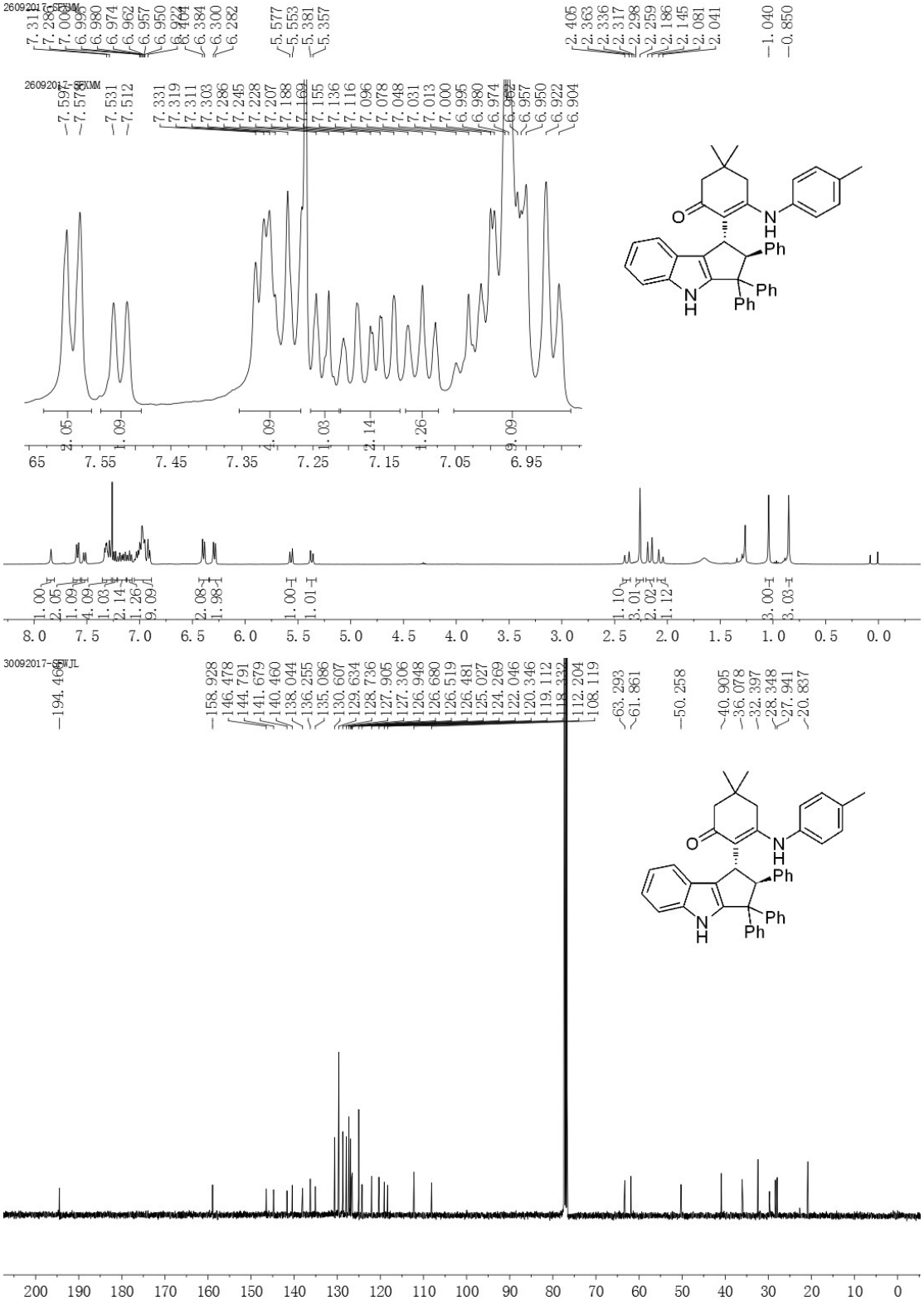

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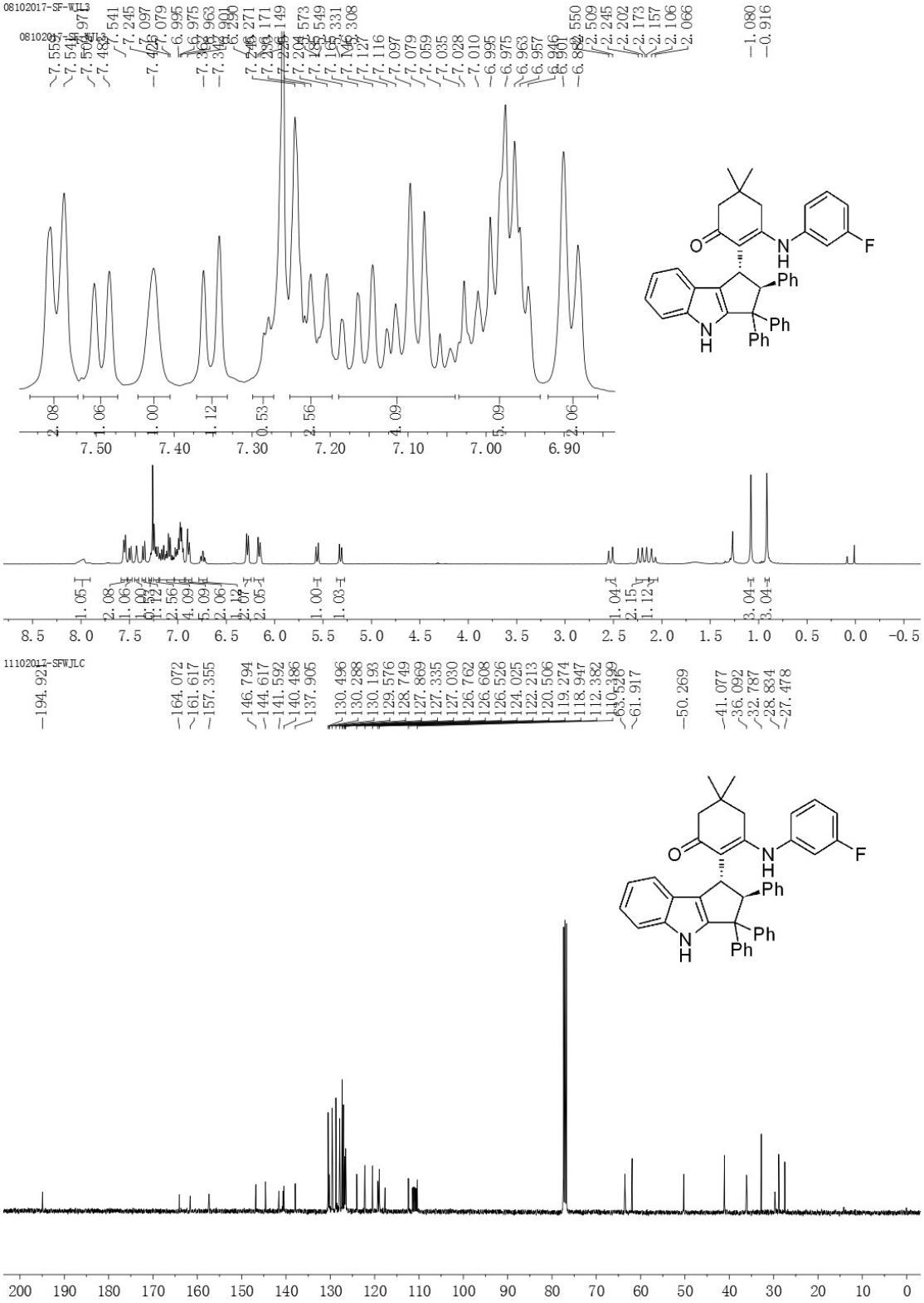

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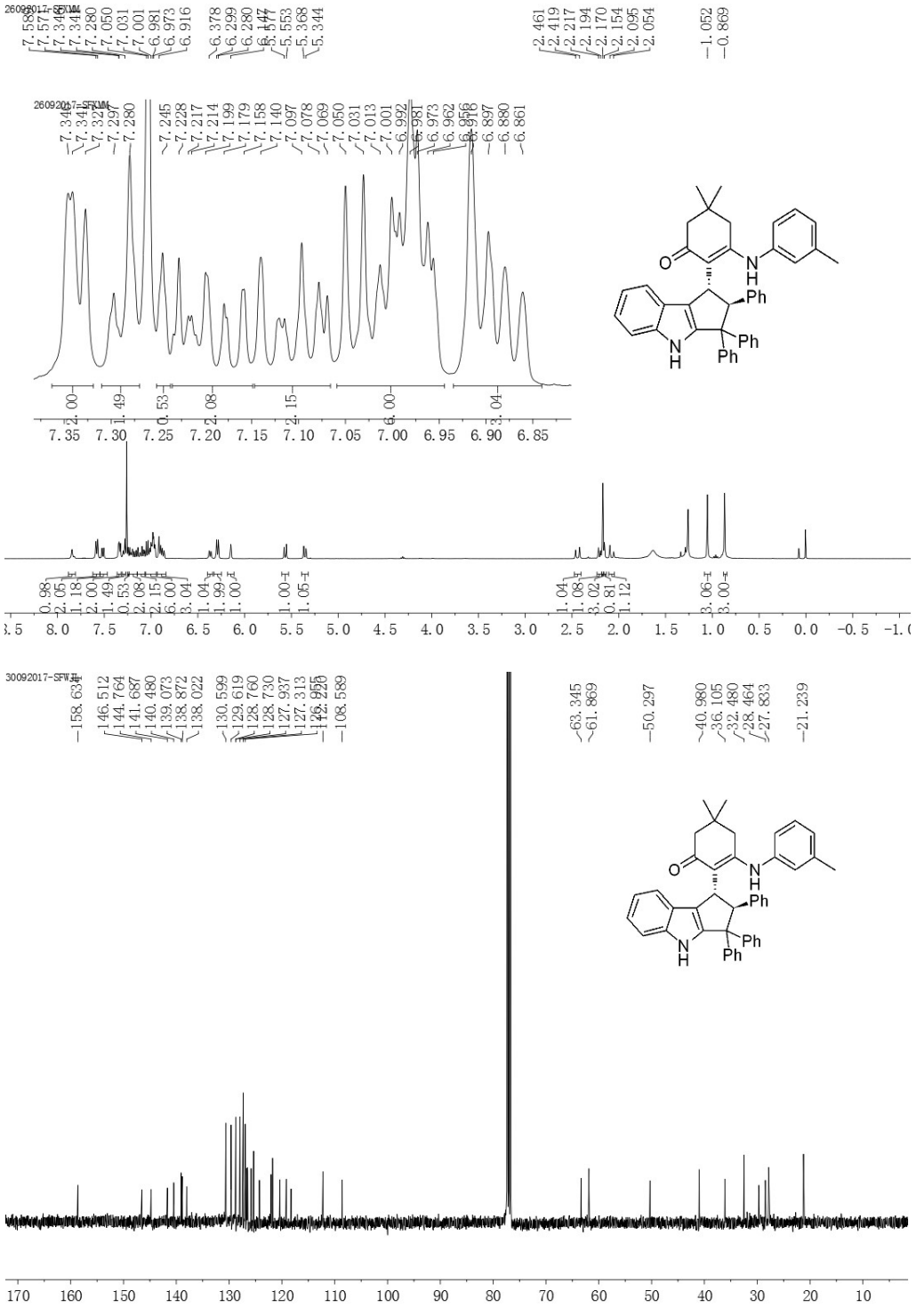
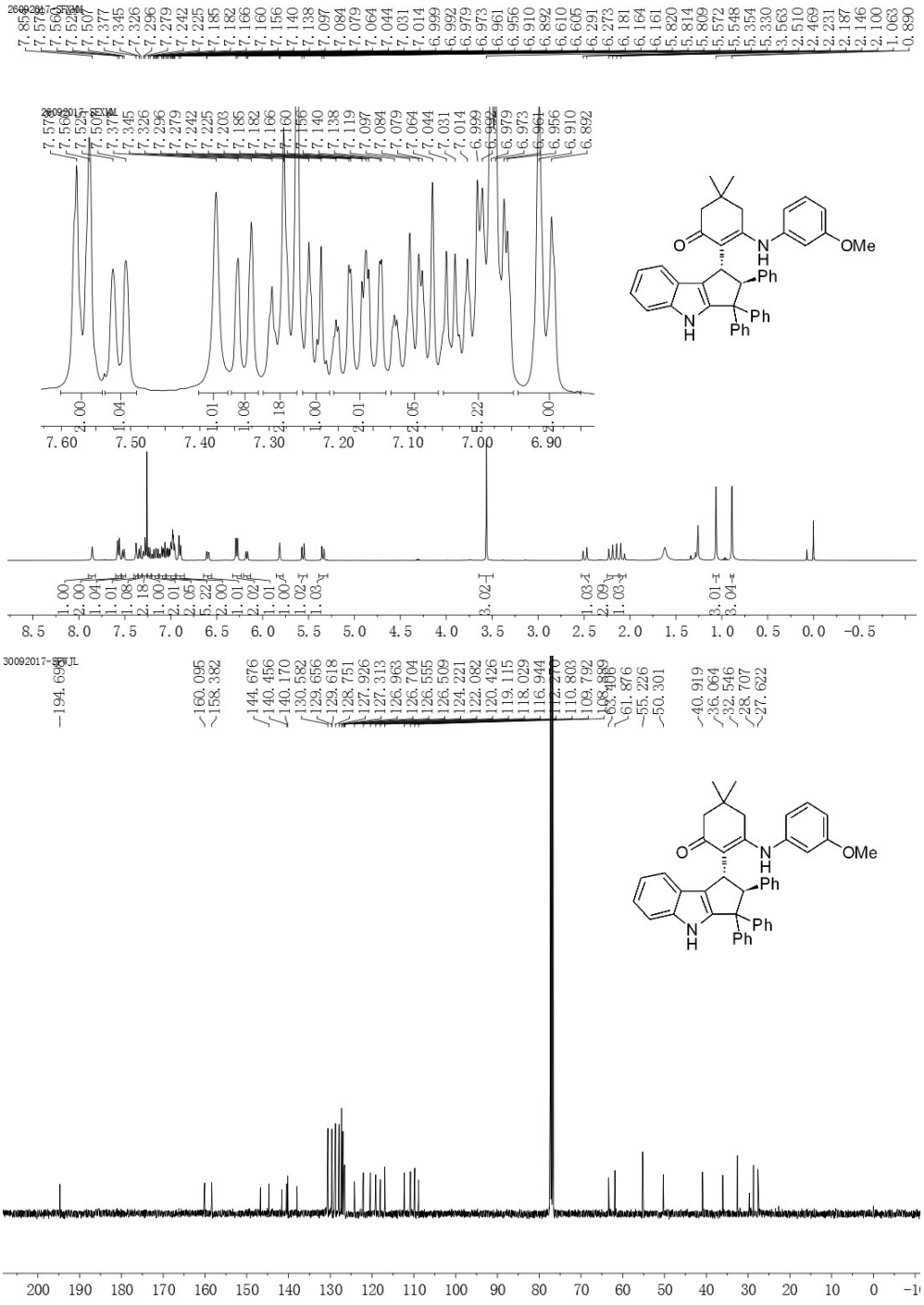
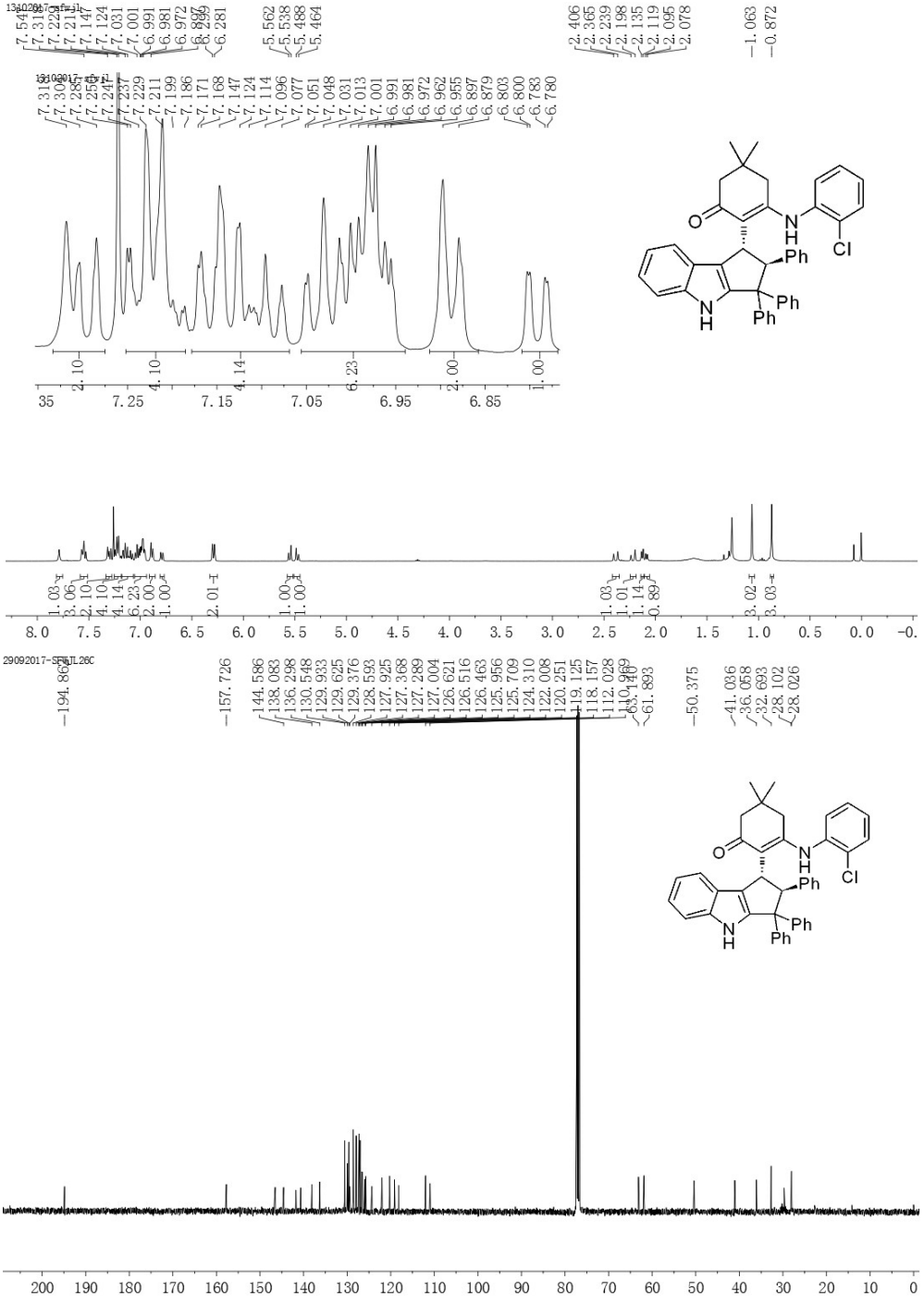


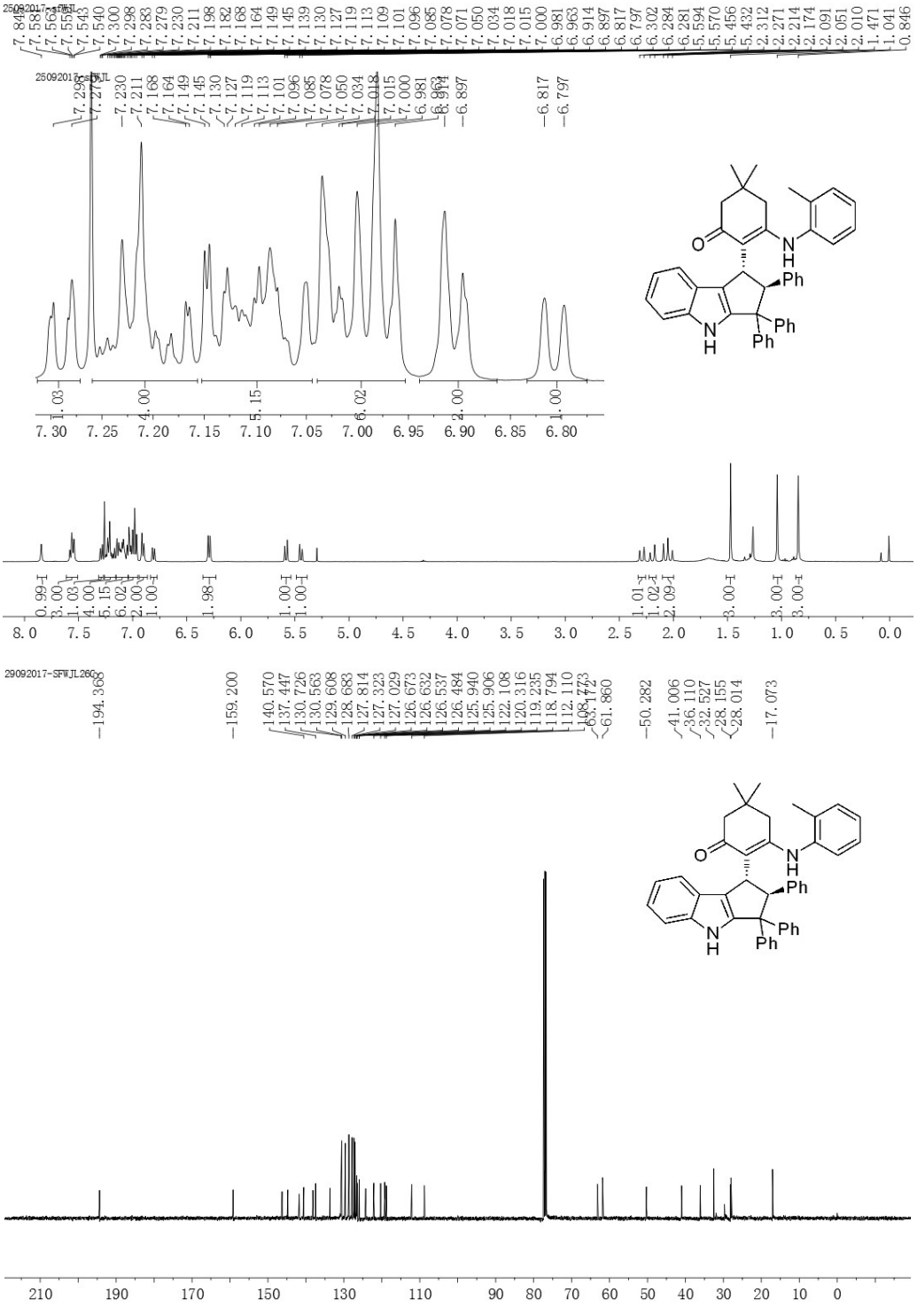
3af



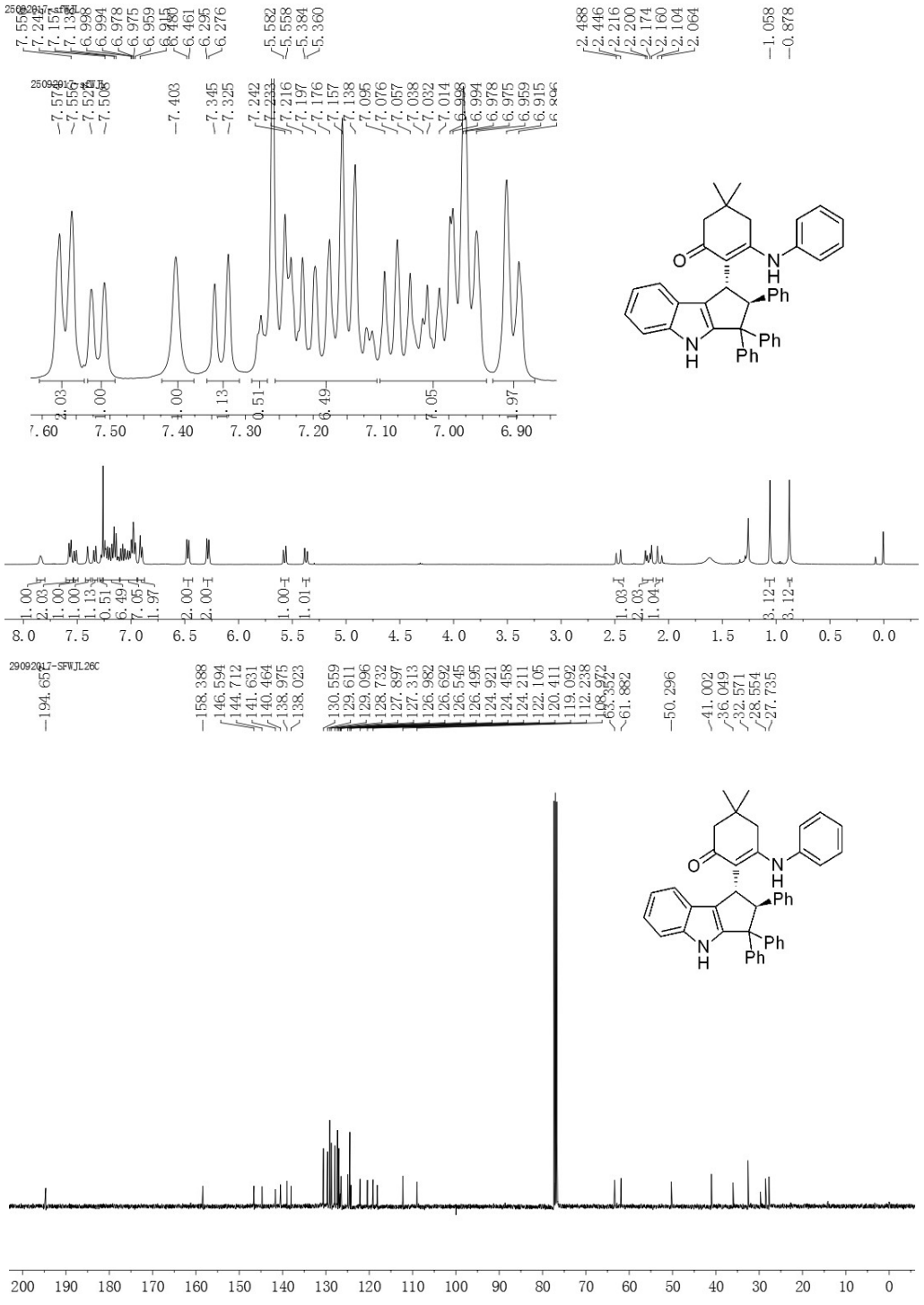
3ag



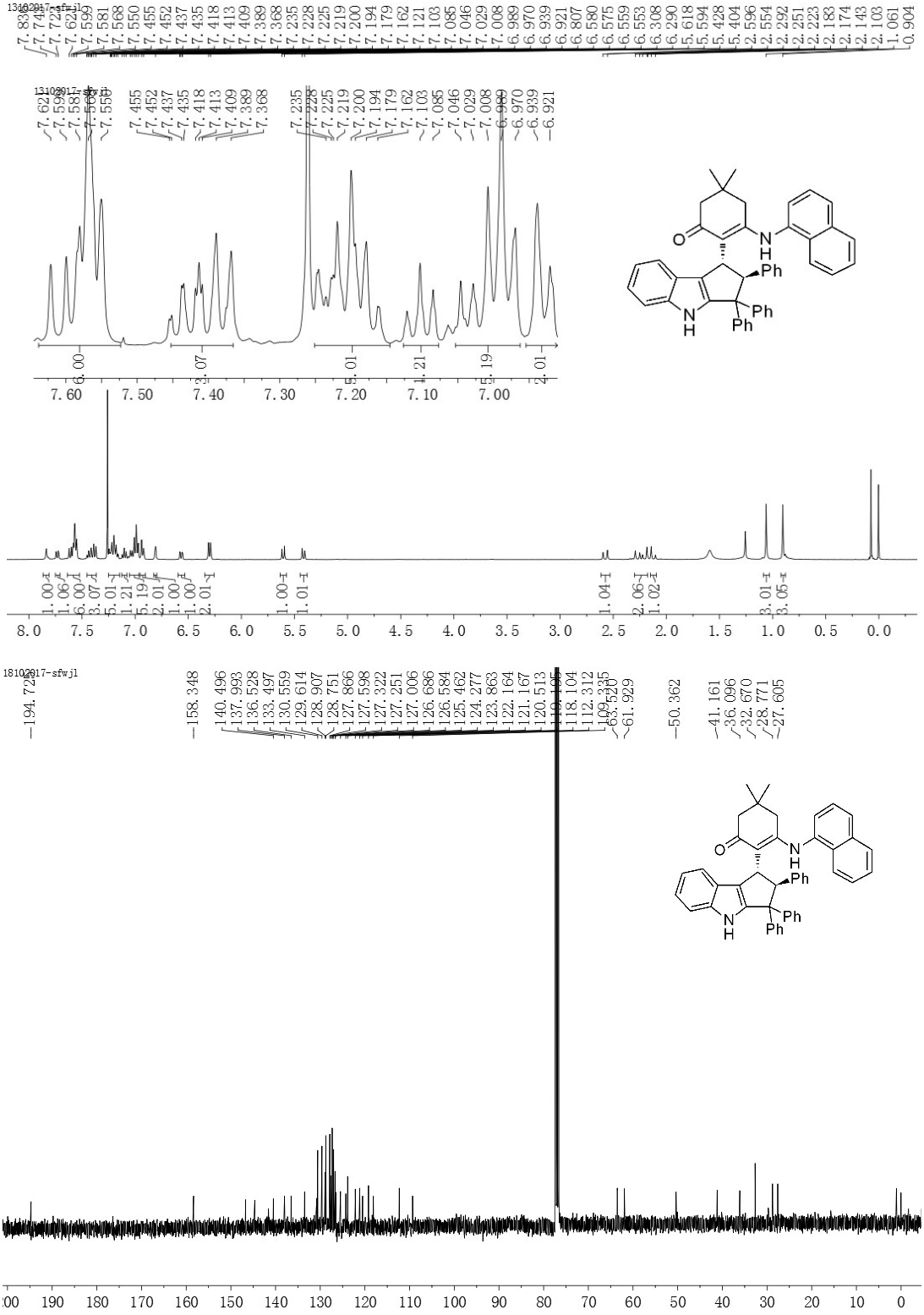
3ah



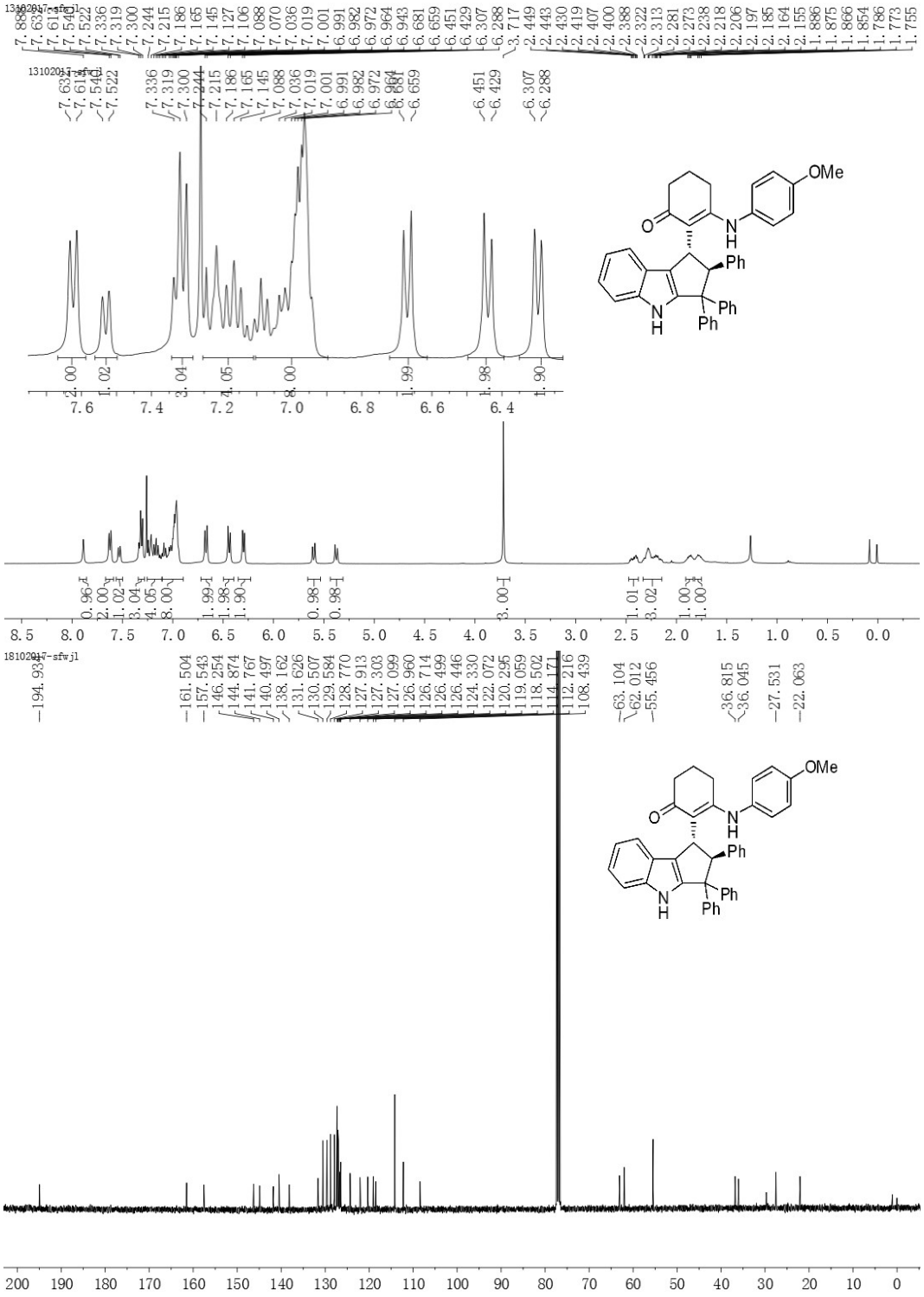
3ai



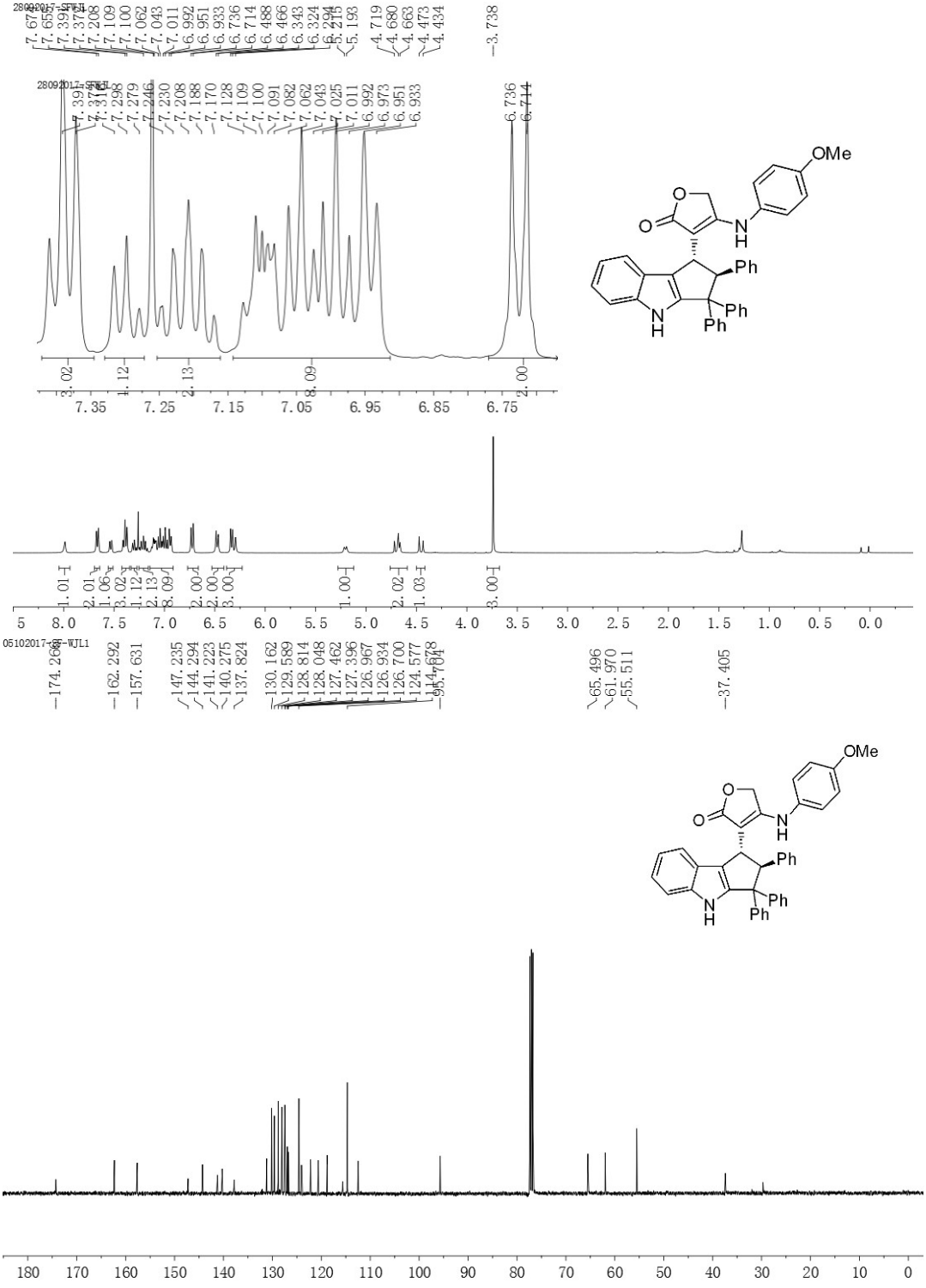
3aj



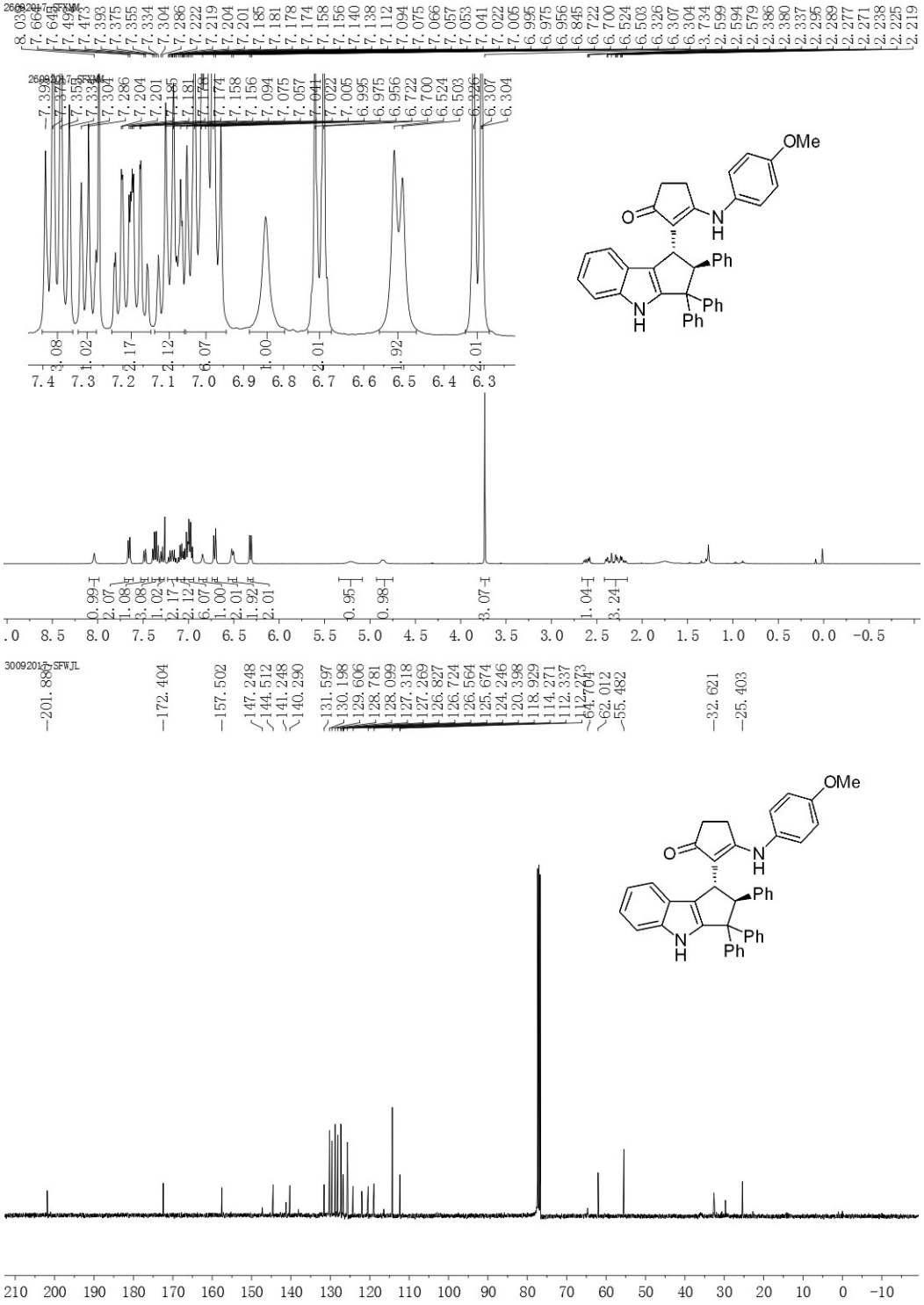
3ak



3al



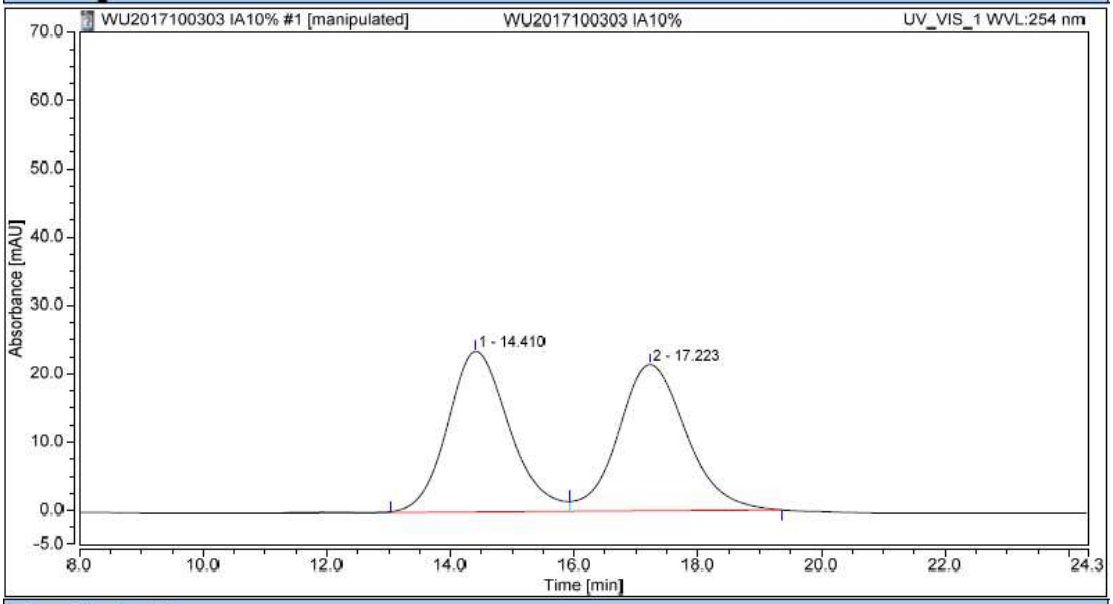
3am



5. HPLC spectra of products 3

3aa

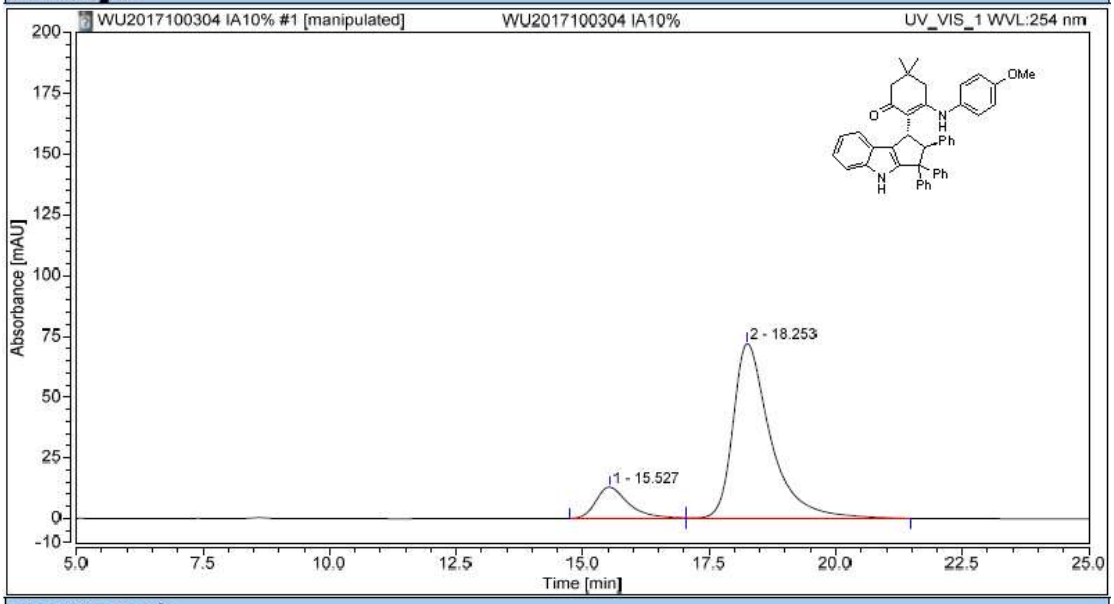
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.410	27.178	23.505	49.91	52.33	n.a.
2		17.223	27.275	21.408	50.09	47.67	n.a.
Total:			54.453	44.913	100.00	100.00	

Chromatogram

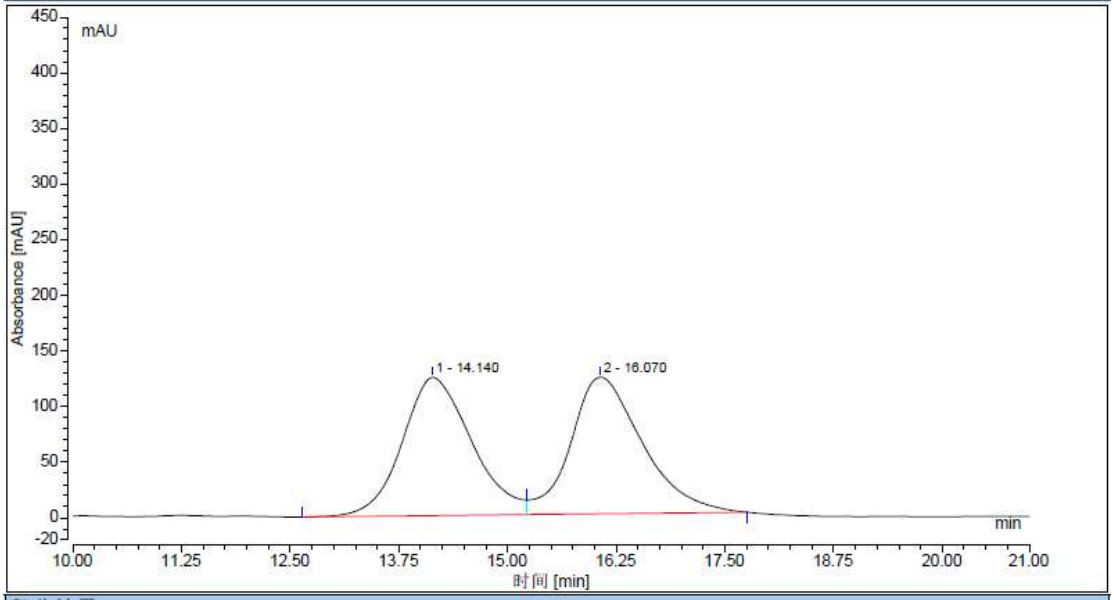


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.527	9.700	12.888	13.50	15.18	n.a.
2		18.253	62.129	72.019	86.50	84.82	n.a.
Total:			71.828	84.907	100.00	100.00	

3ba

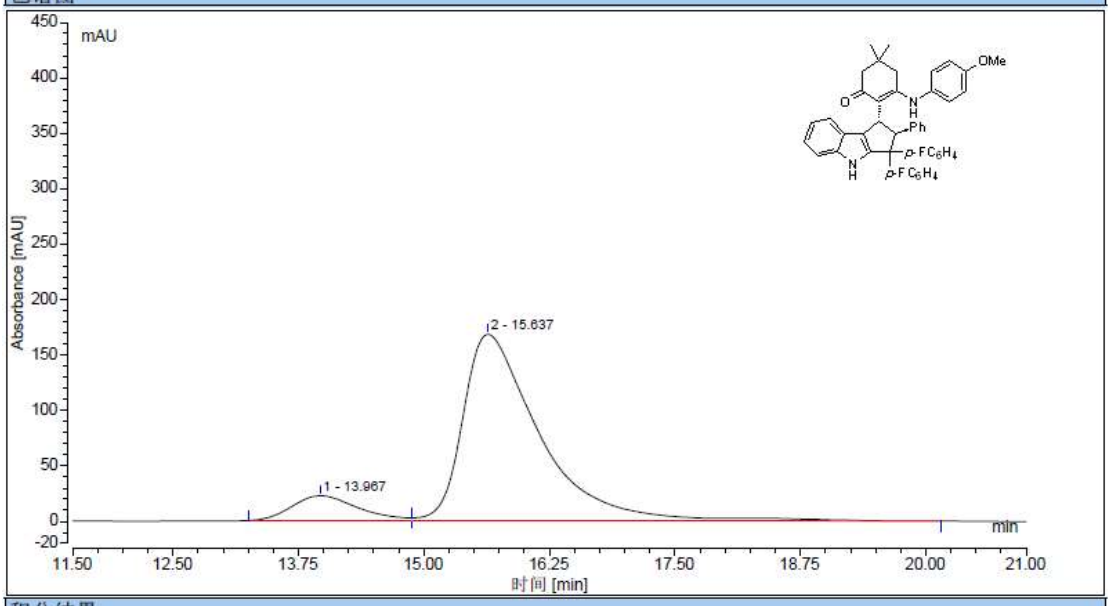
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.140	114.849	124.182	49.45	50.29	n.a.
2		16.070	117.397	122.744	50.55	49.71	n.a.
总和:			232.246	246.926	100.00	100.00	

色谱图

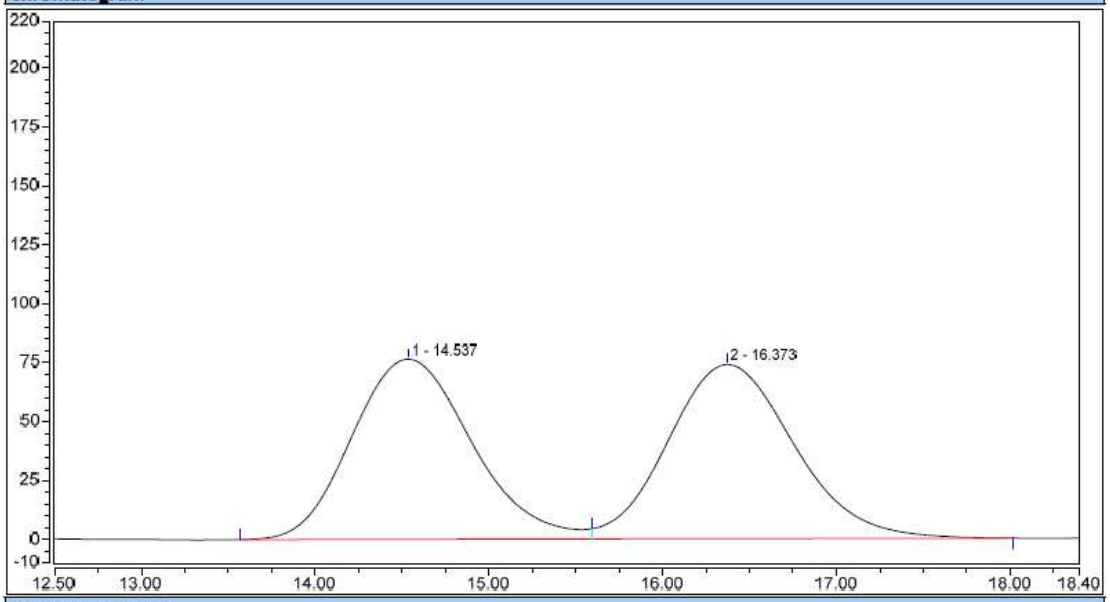


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.967	16.942	22.370	10.25	11.75	n.a.
2		15.637	148.356	168.021	89.75	88.25	n.a.
总和:			165.298	190.391	100.00	100.00	

3ca

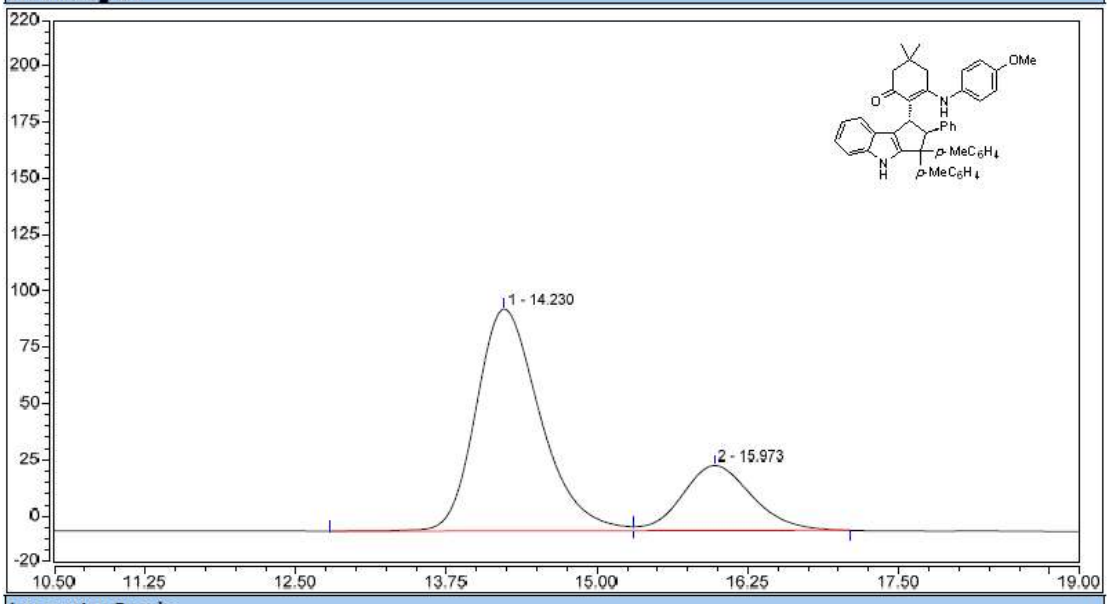
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.537	61.082	76.400	49.60	50.83	n.a.
2		16.373	62.066	73.911	50.40	49.17	n.a.
Total:			123.148	150.312	100.00	100.00	

Chromatogram

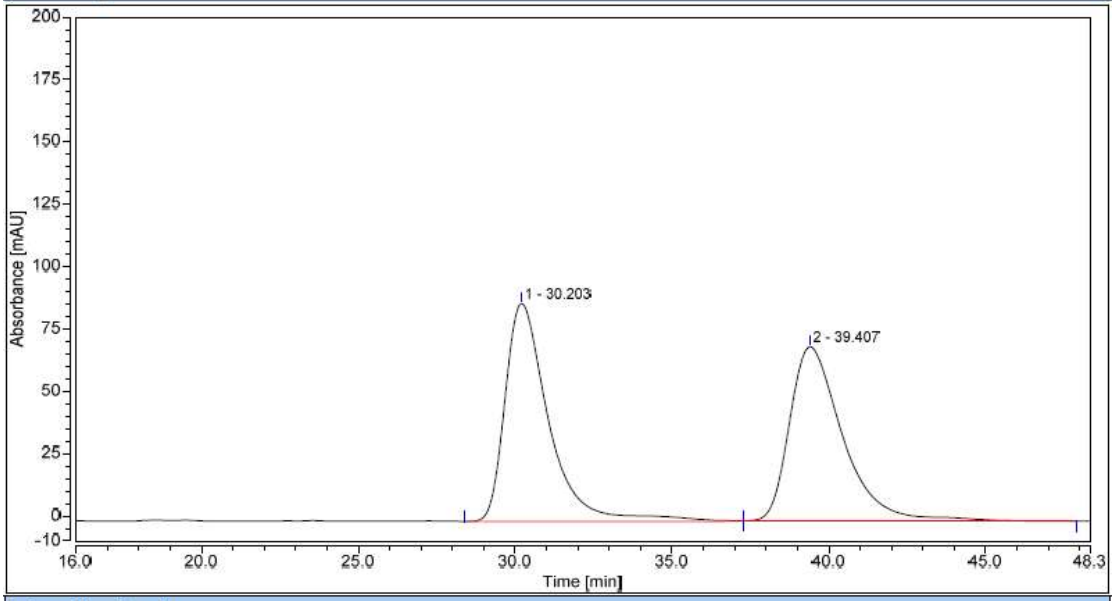


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.230	60.718	98.409	75.86	77.34	n.a.
2		15.973	19.326	28.836	24.14	22.66	n.a.
Total:			80.044	127.245	100.00	100.00	

3da

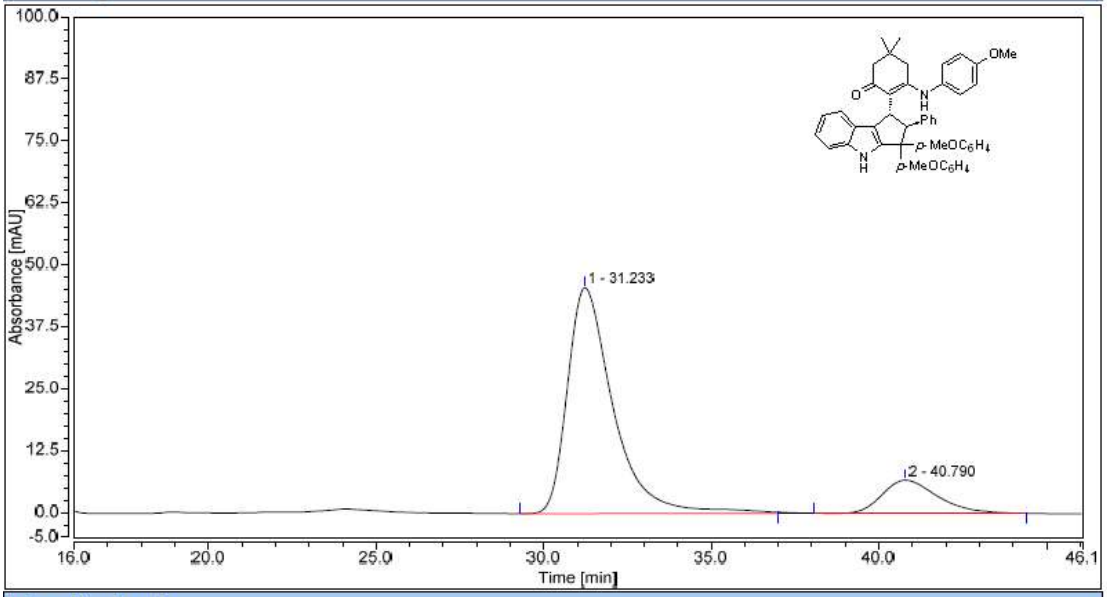
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.203	141.395	87.367	50.56	55.53	n.a.
2		39.407	138.244	69.961	49.44	44.47	n.a.
Total:			**279.638**	**157.329**	**100.00**	**100.00**	

Chromatogram

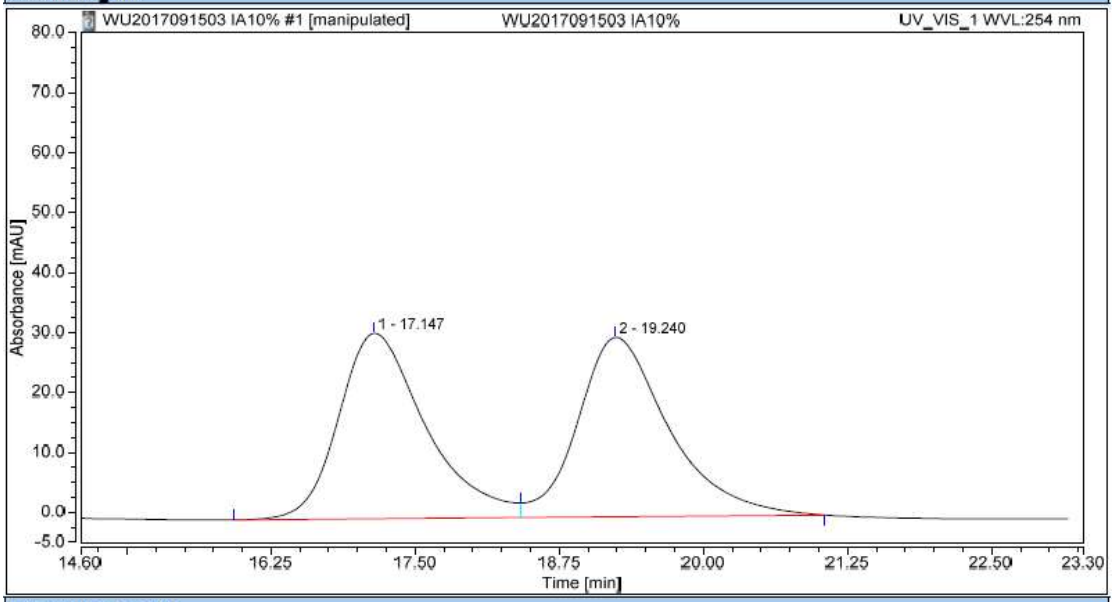


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		31.233	72.247	45.557	84.96	87.17	n.a.
2		40.790	12.788	6.704	15.04	12.83	n.a.
Total:			**85.035**	**52.260**	**100.00**	**100.00**	

3ea

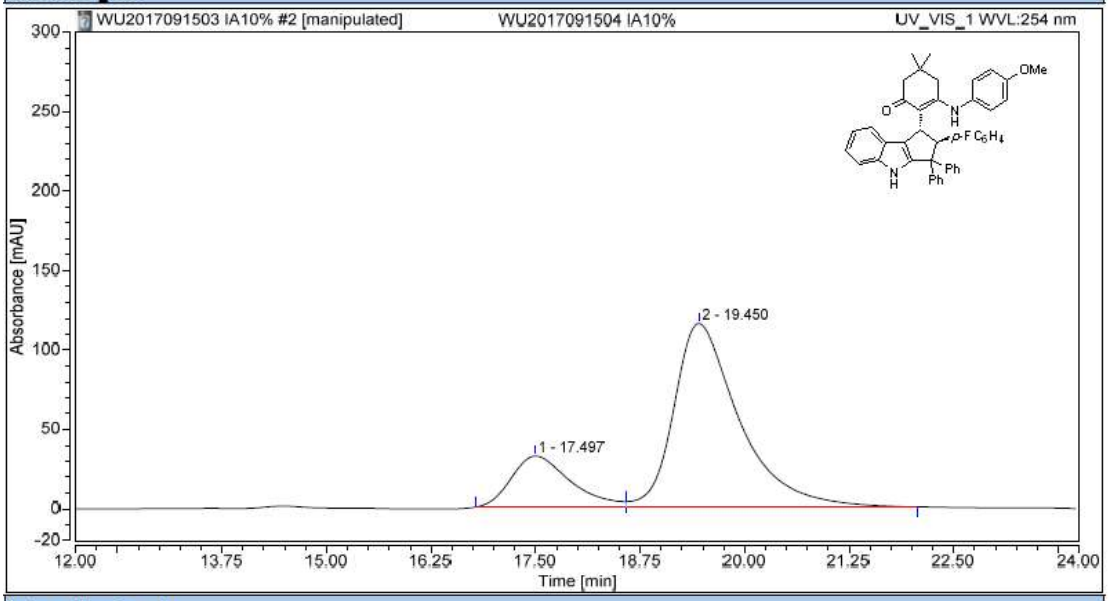
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.147	27.113	30.921	49.74	50.82	n.a.
2		19.240	27.402	29.923	50.26	49.18	n.a.
Total:			**54.514**	**60.844**	**100.00**	**100.00**	

Chromatogram

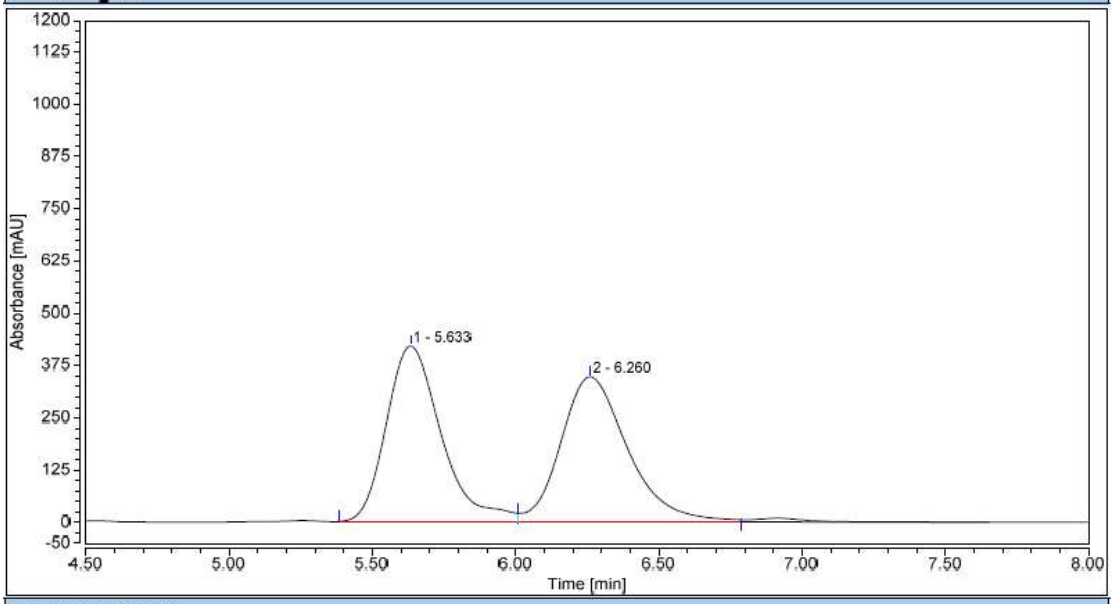


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.497	26.258	32.089	20.05	21.74	n.a.
2		19.450	104.696	115.489	79.95	78.26	n.a.
Total:			**130.953**	**147.578**	**100.00**	**100.00**	

3fa

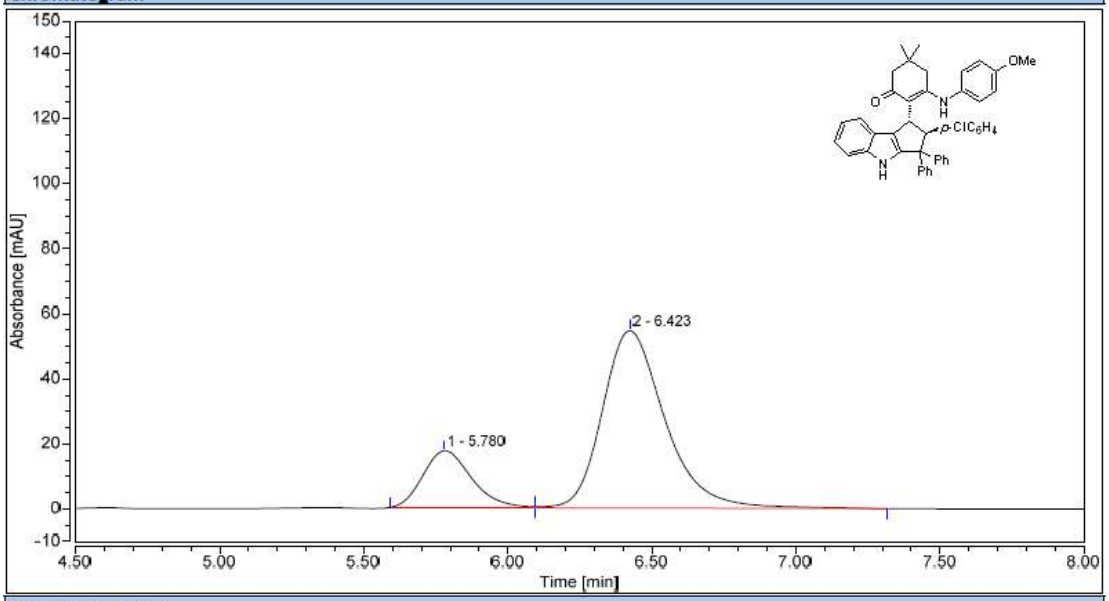
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.633	93.190	420.255	49.88	54.79	n.a.
2		6.260	93.620	346.724	50.12	45.21	n.a.
Total:			**186.809**	**766.979**	**100.00**	**100.00**	

Chromatogram

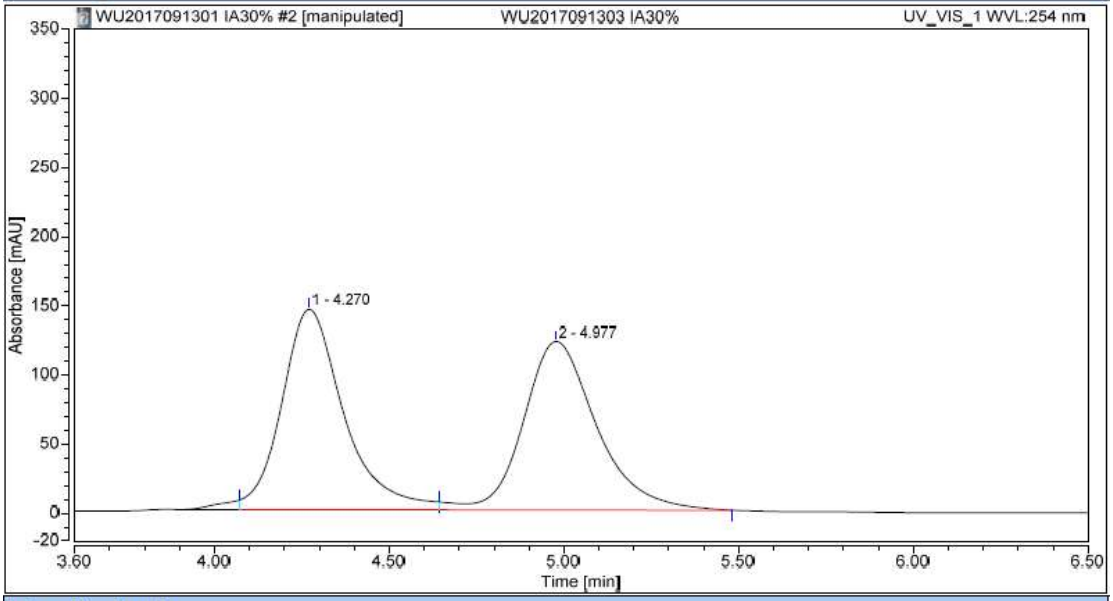


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.780	3.415	17.485	19.90	24.29	n.a.
2		6.423	13.748	54.502	80.10	75.71	n.a.
Total:			**17.163**	**71.987**	**100.00**	**100.00**	

3ga

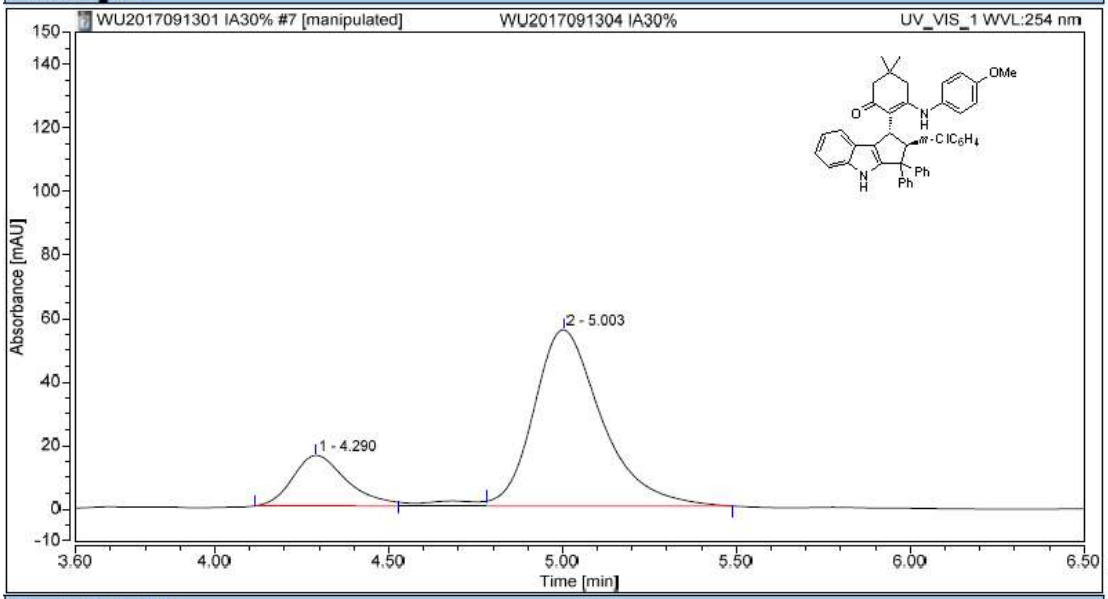
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.270	29.850	144.933	50.16	54.32	n.a.
2		4.977	29.664	121.859	49.84	45.68	n.a.
Total:			**59.515**	**266.792**	**100.00**	**100.00**	

Chromatogram

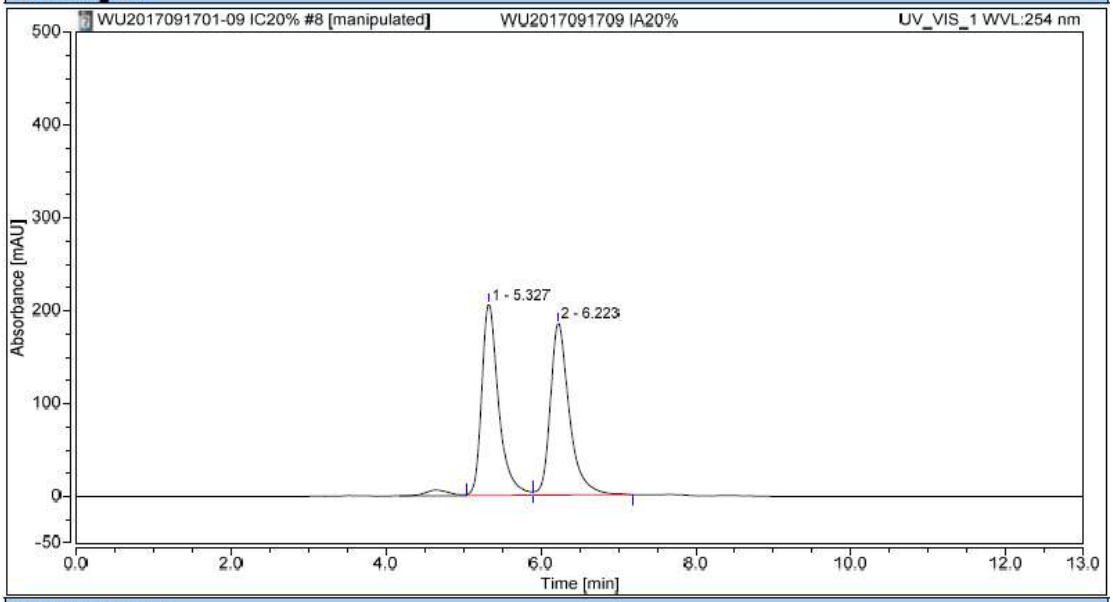


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.290	2.854	15.879	18.53	22.26	n.a.
2		5.003	12.550	55.471	81.47	77.74	n.a.
Total:			**15.404**	**71.350**	**100.00**	**100.00**	

3ha

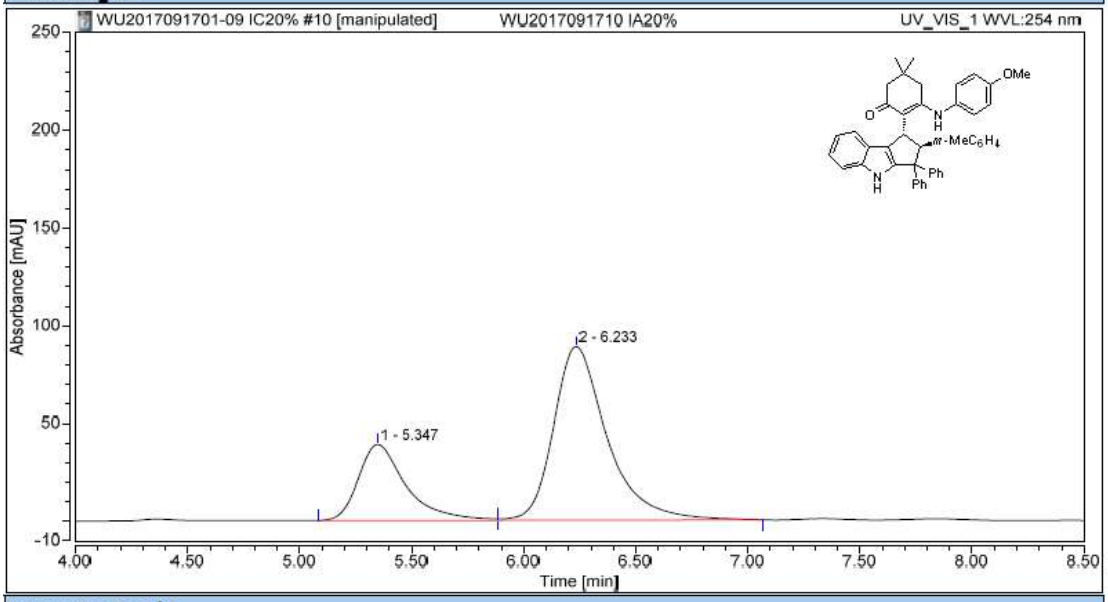
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.327	52.146	206.173	49.72	52.66	n.a.
2		6.223	52.731	185.364	50.28	47.34	n.a.
Total:			104.877	391.538	100.00	100.00	

Chromatogram

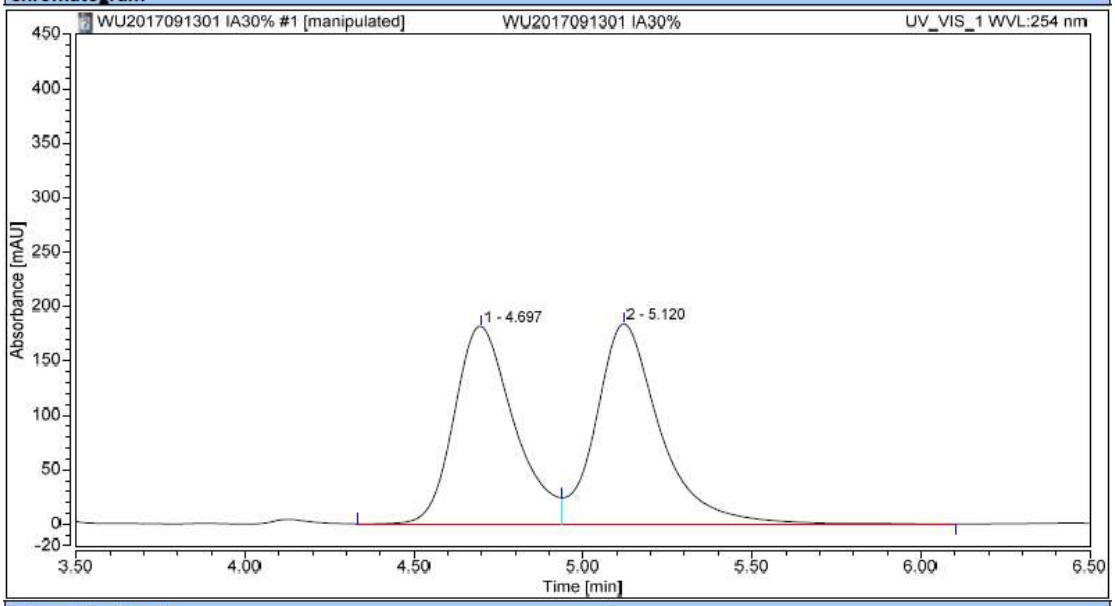


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.347	9.523	38.809	27.91	30.43	n.a.
2		6.233	24.593	88.720	72.09	69.57	n.a.
Total:			34.115	127.529	100.00	100.00	

3ia

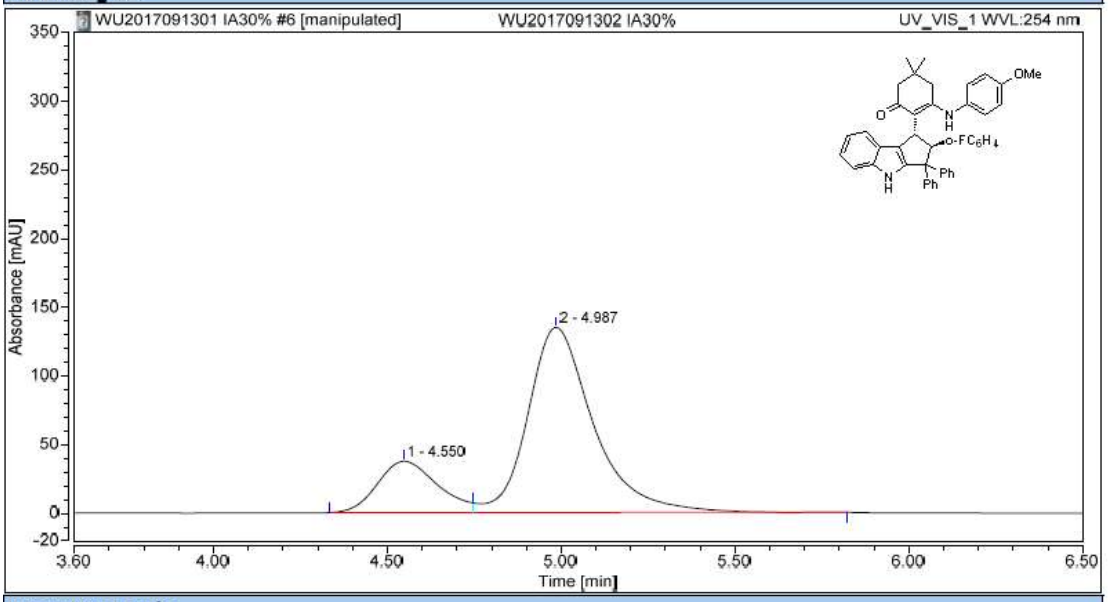
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.697	37.101	181.619	47.93	49.70	n.a.
2		5.120	40.301	183.801	52.07	50.30	n.a.
Total:			**77.402**	**365.420**	**100.00**	**100.00**	

Chromatogram

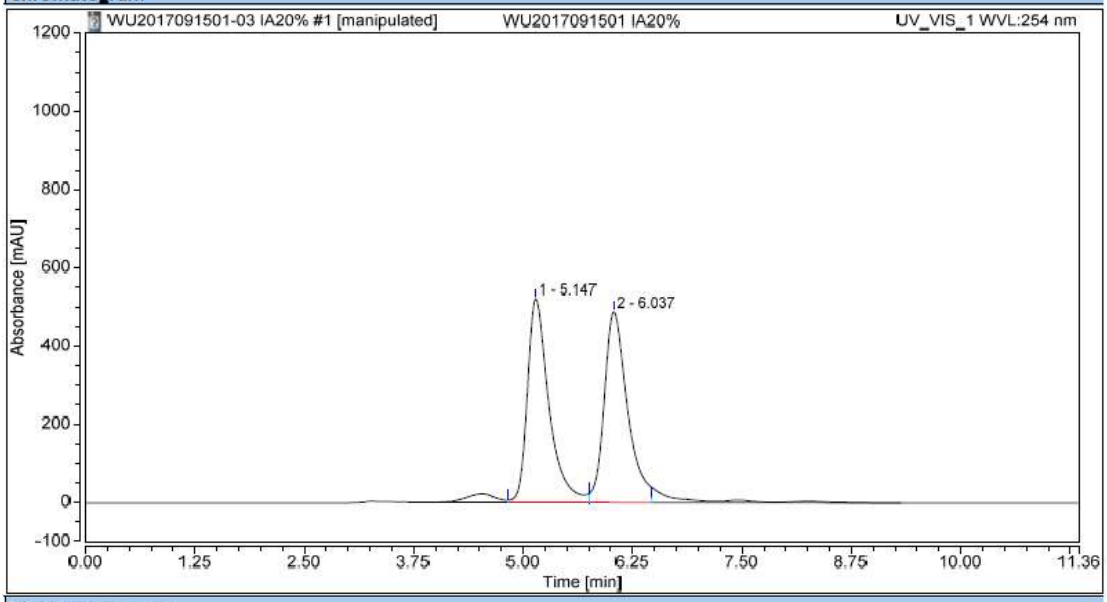


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.550	7.423	37.339	20.12	21.70	n.a.
2		4.987	29.477	134.714	79.88	78.30	n.a.
Total:			**36.900**	**172.054**	**100.00**	**100.00**	

3ja

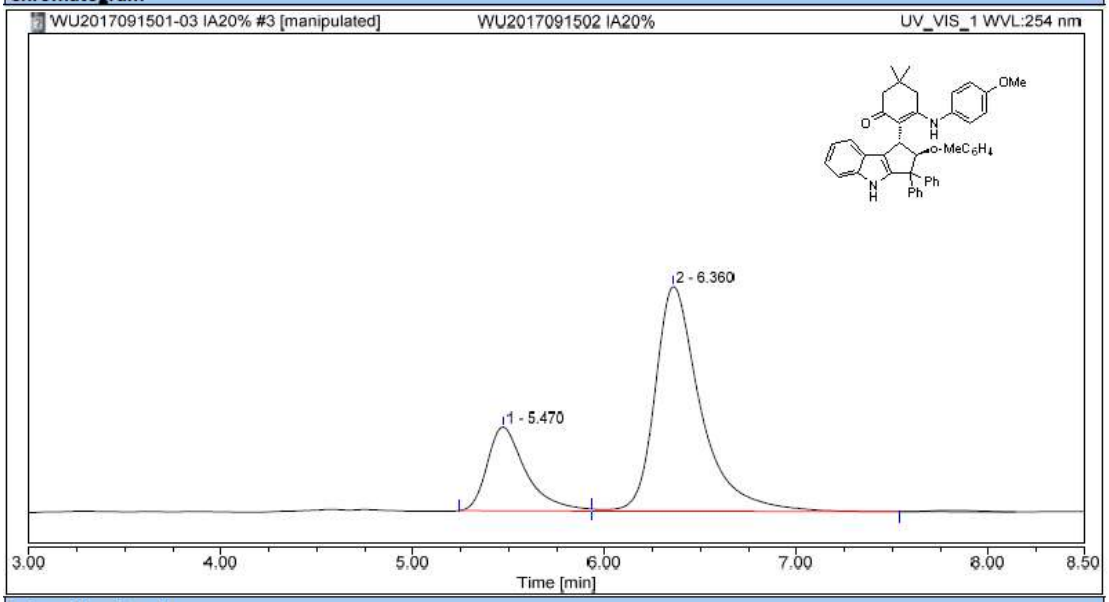
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.147	149.032	519.585	50.00	51.59	n.a.
2		6.037	149.021	487.594	50.00	48.41	n.a.
Total:			**298.053**	**1007.179**	**100.00**	**100.00**	

Chromatogram

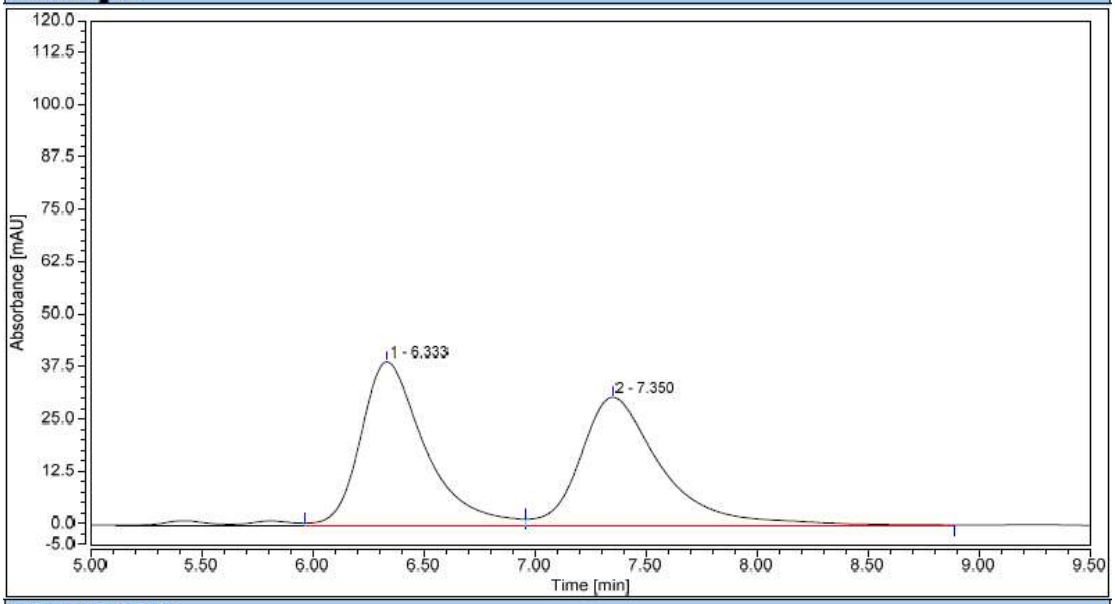


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.470	32.704	140.037	24.02	27.15	n.a.
2		6.360	103.465	375.714	75.98	72.85	n.a.
Total:			**136.169**	**515.751**	**100.00**	**100.00**	

3ka

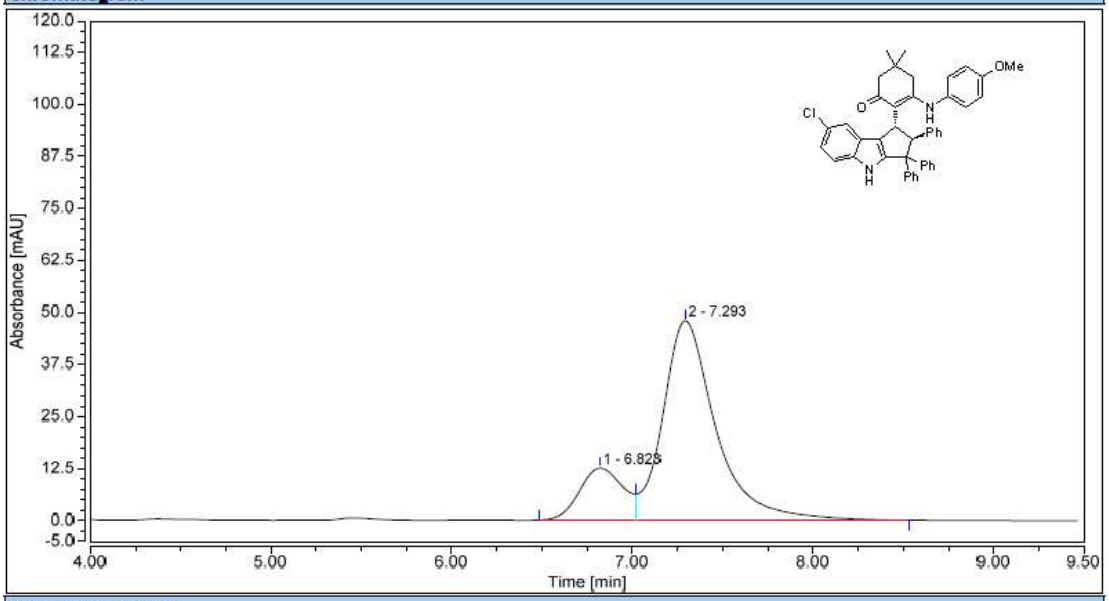
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.333	13.018	38.980	50.46	56.09	n.a.
2		7.350	12.783	30.519	49.54	43.91	n.a.
Total:			**25.801**	**69.499**	**100.00**	**100.00**	

Chromatogram

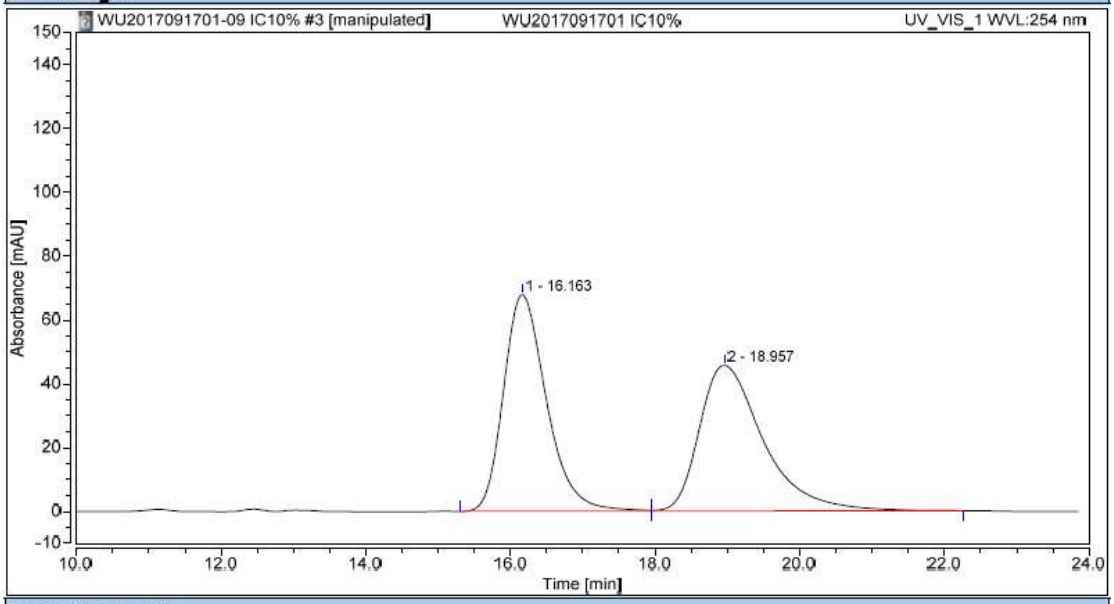


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.823	3.461	12.506	17.52	20.70	n.a.
2		7.293	16.291	47.909	82.48	79.30	n.a.
Total:			**19.752**	**60.415**	**100.00**	**100.00**	

3la

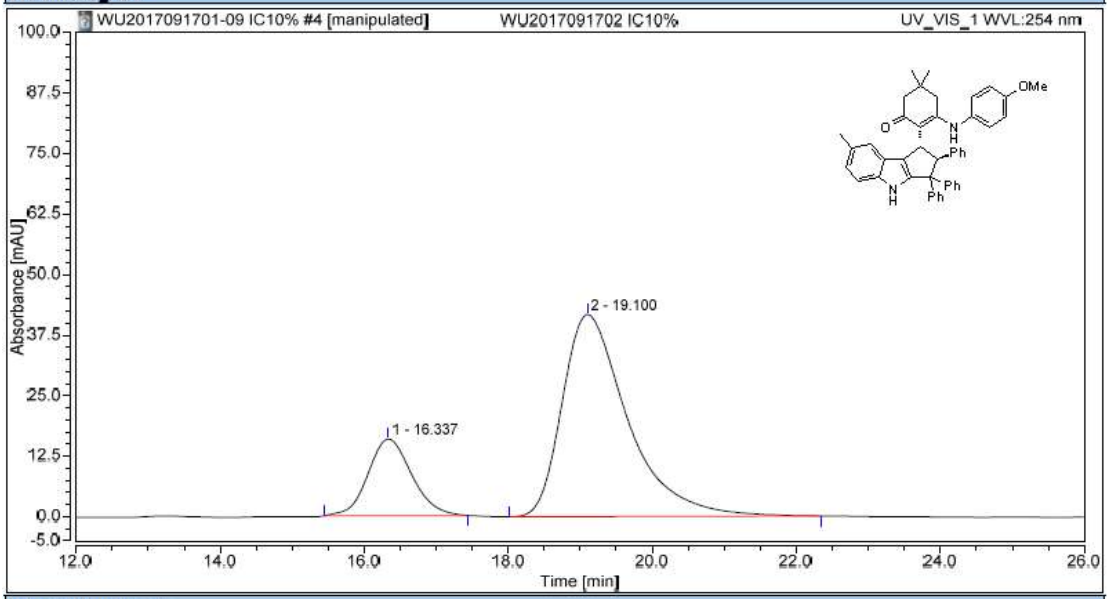
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.163	46.646	67.887	50.01	59.79	n.a.
2		18.957	46.633	45.647	49.99	40.21	n.a.
Total:			93.278	113.534	100.00	100.00	

Chromatogram

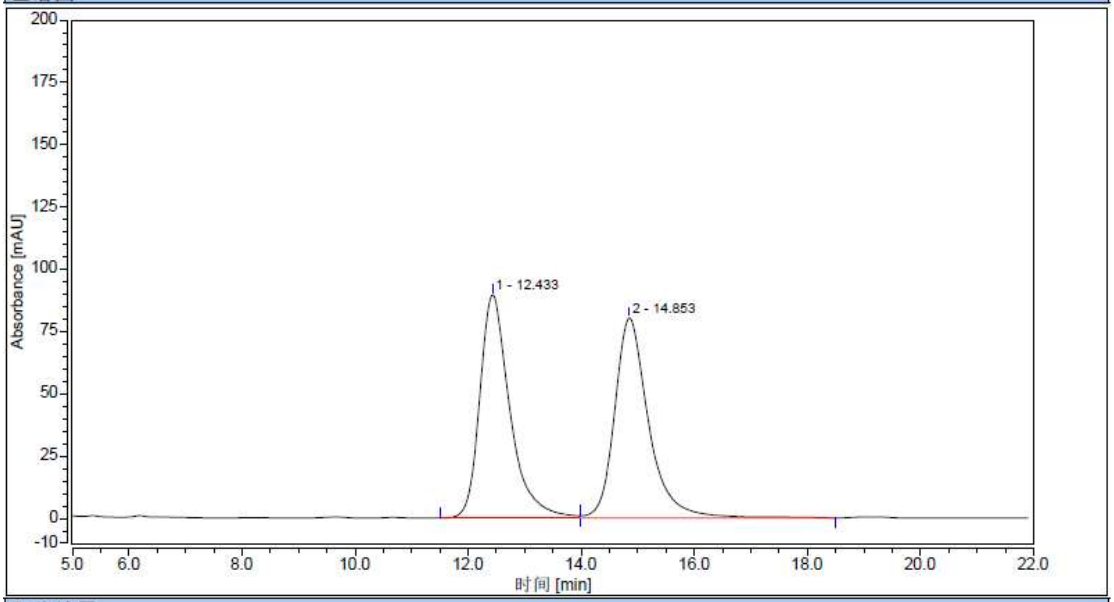


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.337	11.098	15.822	20.18	27.50	n.a.
2		19.100	43.893	41.710	79.82	72.50	n.a.
Total:			54.992	57.533	100.00	100.00	

3ab

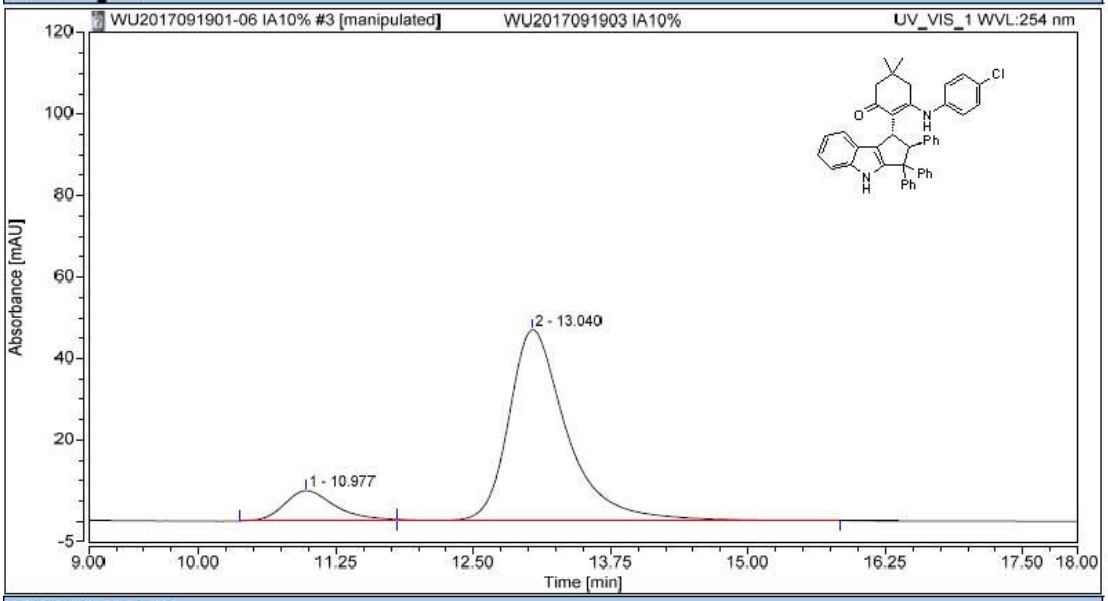
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.433	55.376	89.629	49.68	52.73	n.a.
2		14.853	56.085	80.345	50.32	47.27	n.a.
总和:			**111.461**	**169.974**	**100.00**	**100.00**	

Chromatogram

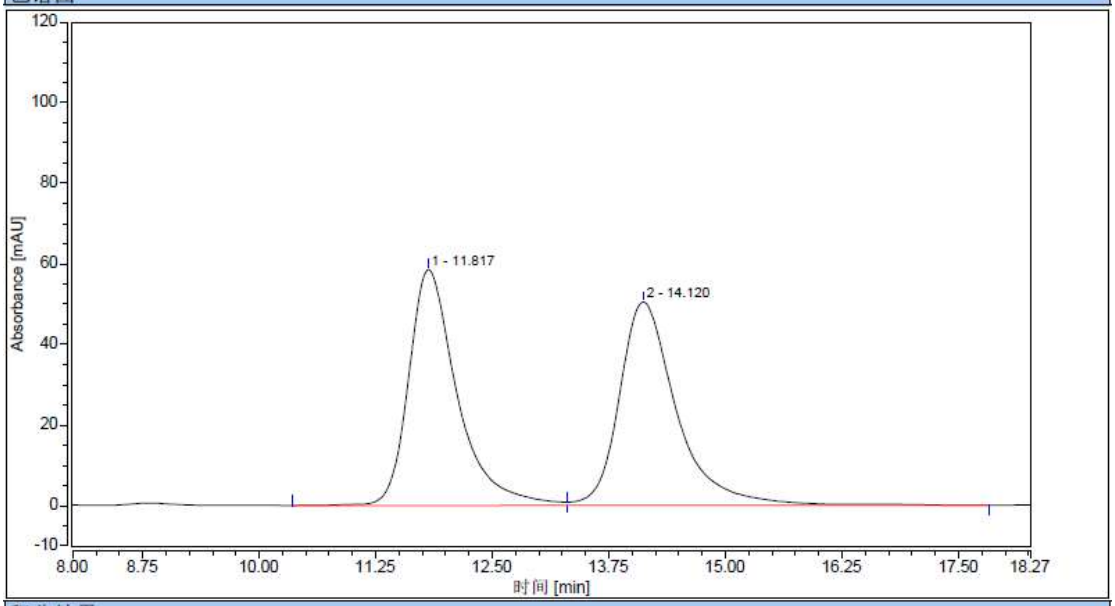


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.977	4.031	7.429	12.16	13.67	n.a.
2		13.040	29.115	46.923	87.84	86.33	n.a.
Total:			**33.146**	**54.352**	**100.00**	**100.00**	

3ac

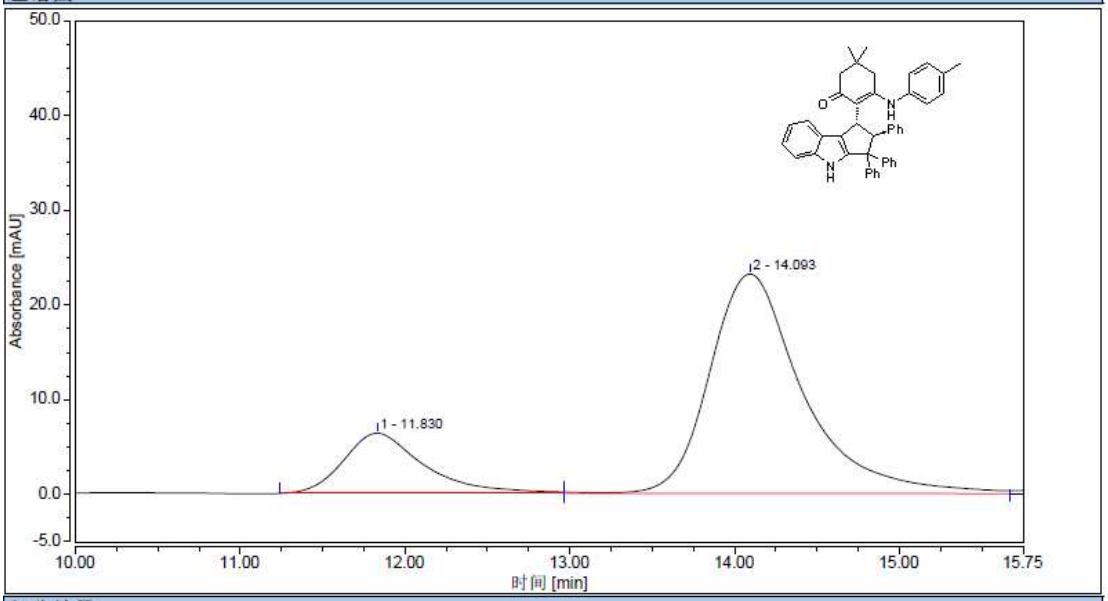
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.817	35.352	58.510	49.61	53.70	n.a.
2		14.120	35.901	50.452	50.39	46.30	n.a.
总和:			**71.253**	**108.962**	**100.00**	**100.00**	

色谱图

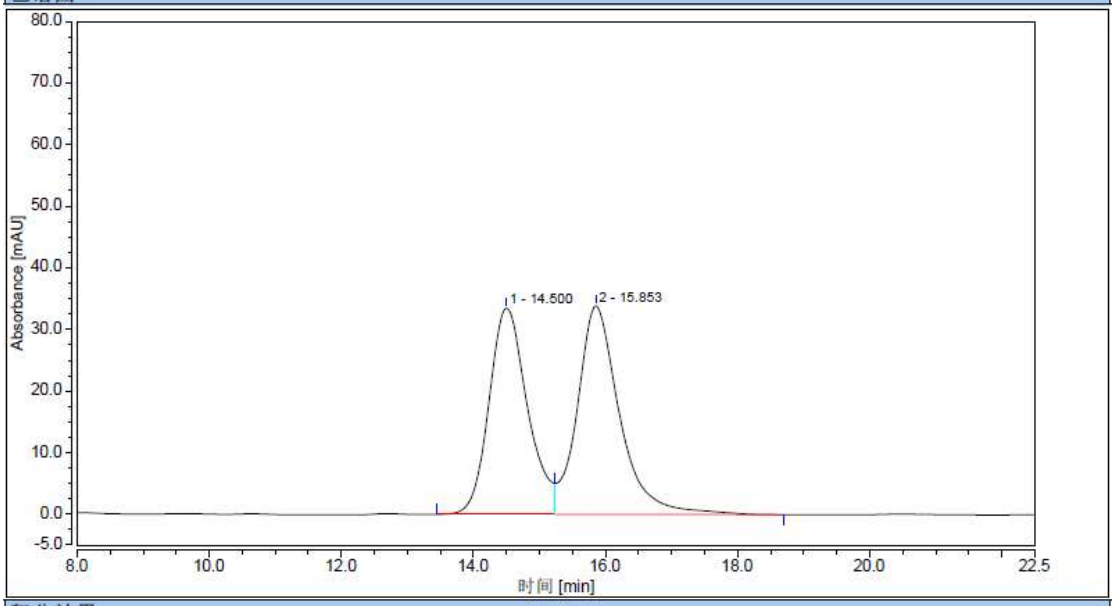


积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		11.830	3.595	6.353	19.13	21.54	n.a.
2		14.093	15.201	23.146	80.87	78.46	n.a.
总和:			**18.795**	**29.500**	**100.00**	**100.00**	

3ad

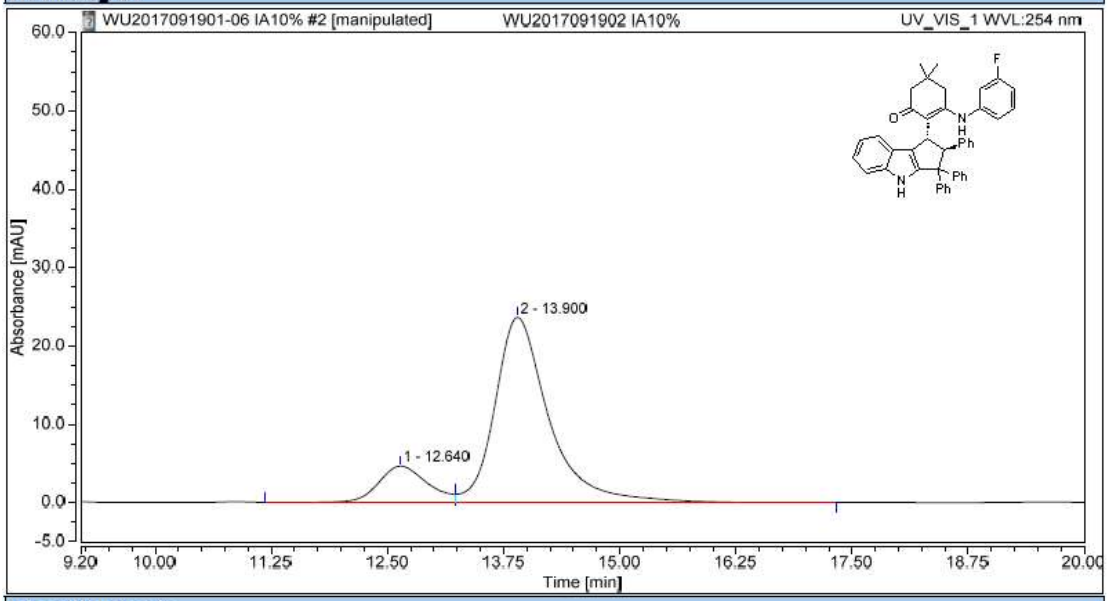
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.500	22.558	33.471	47.28	49.72	n.a.
2		15.853	25.157	33.852	52.72	50.28	n.a.
总和:			**47.715**	**67.323**	**100.00**	**100.00**	

Chromatogram

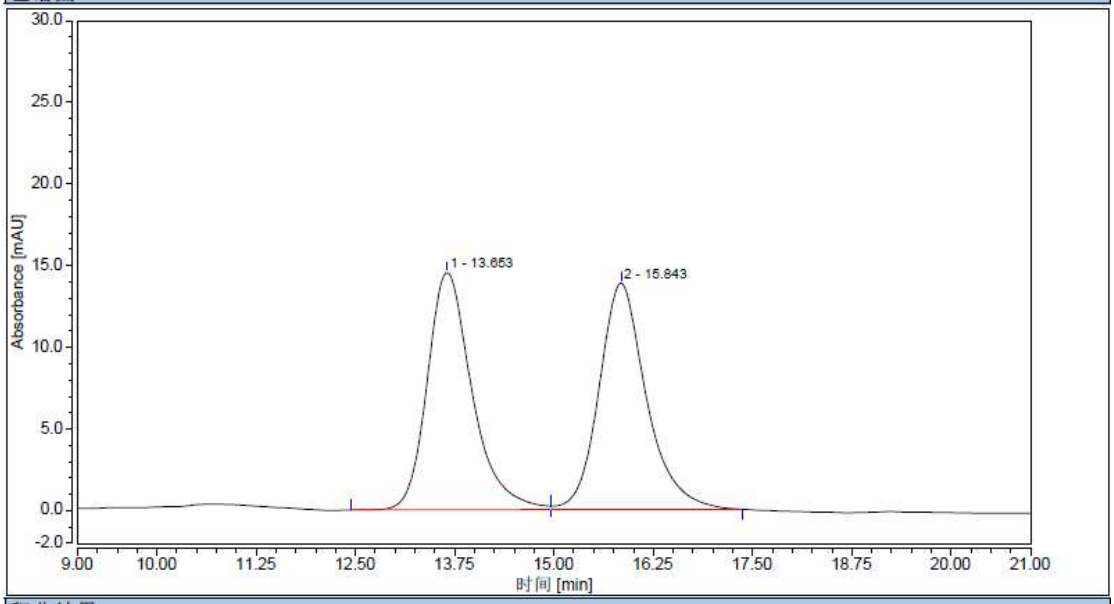


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.640	2.775	4.603	14.90	16.32	n.a.
2		13.900	15.852	23.604	85.10	83.68	n.a.
Total:			**18.627**	**28.207**	**100.00**	**100.00**	

3ae

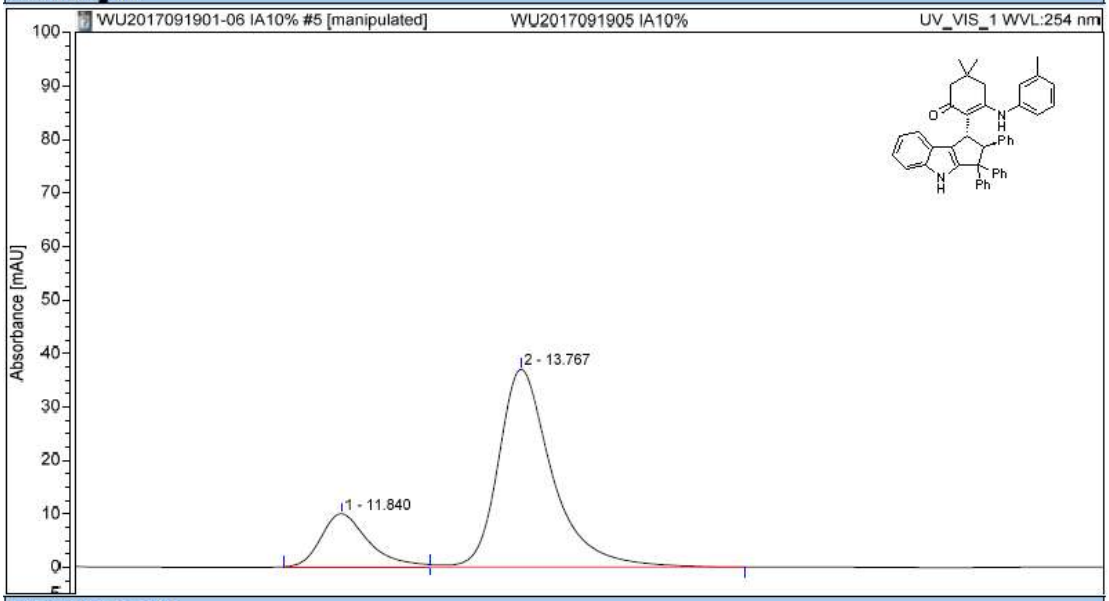
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.653	9.515	14.511	49.84	51.15	n.a.
2		15.843	9.575	13.859	50.16	48.85	n.a.
总和:			**19.090**	**28.370**	**100.00**	**100.00**	

Chromatogram

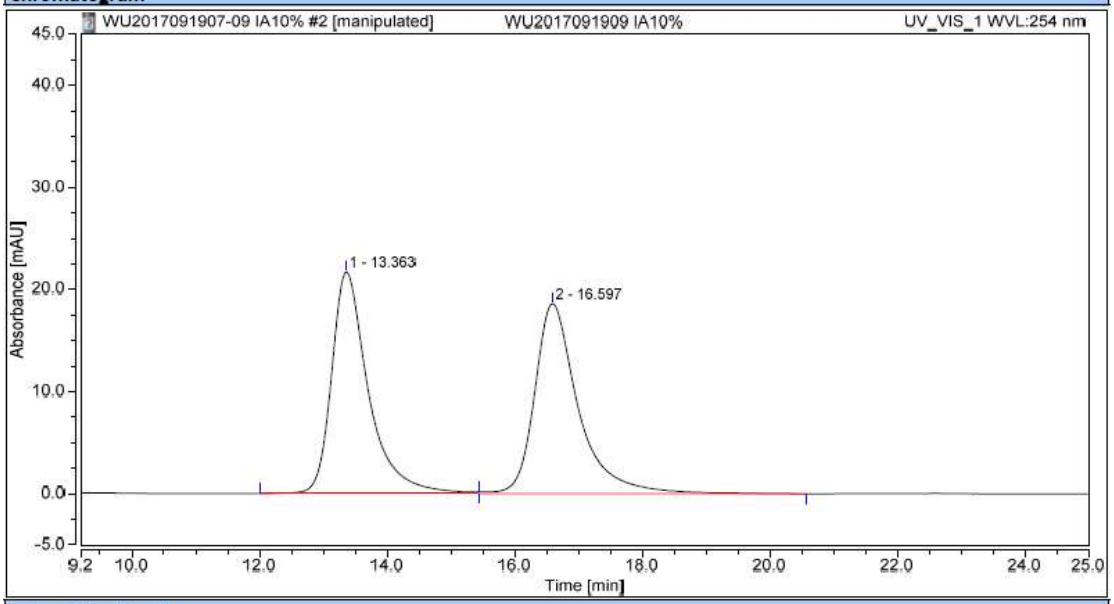


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.840	5.829	9.932	19.09	21.18	n.a.
2		13.767	24.700	36.971	80.91	78.82	n.a.
Total:			**30.529**	**46.903**	**100.00**	**100.00**	

3af

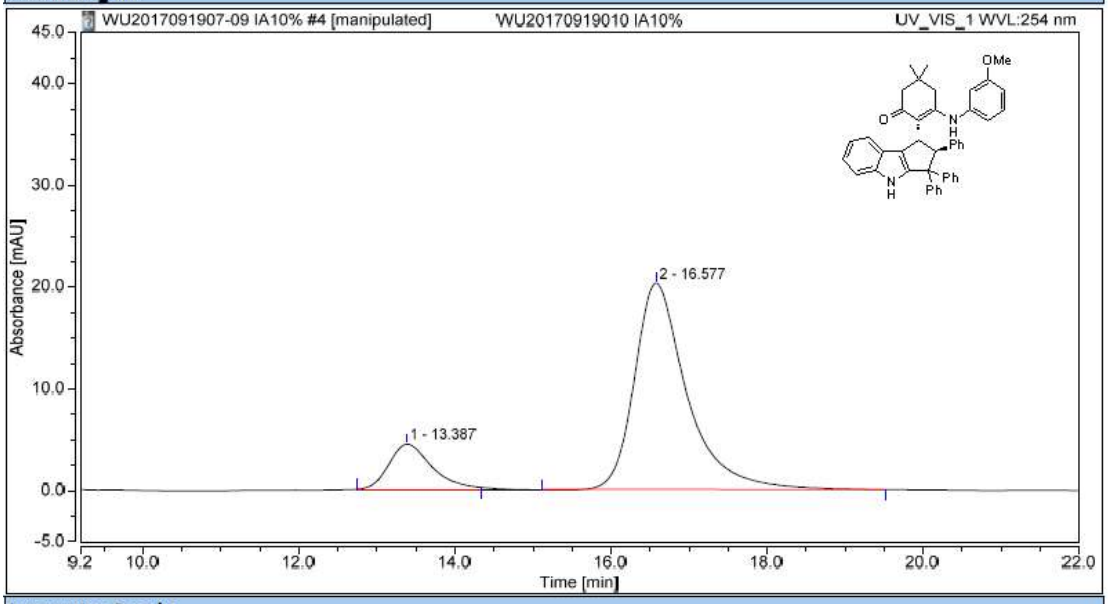
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.363	14.525	21.695	49.62	53.85	n.a.
2		16.597	14.747	18.594	50.38	46.15	n.a.
Total:			**29.272**	**40.288**	**100.00**	**100.00**	

Chromatogram

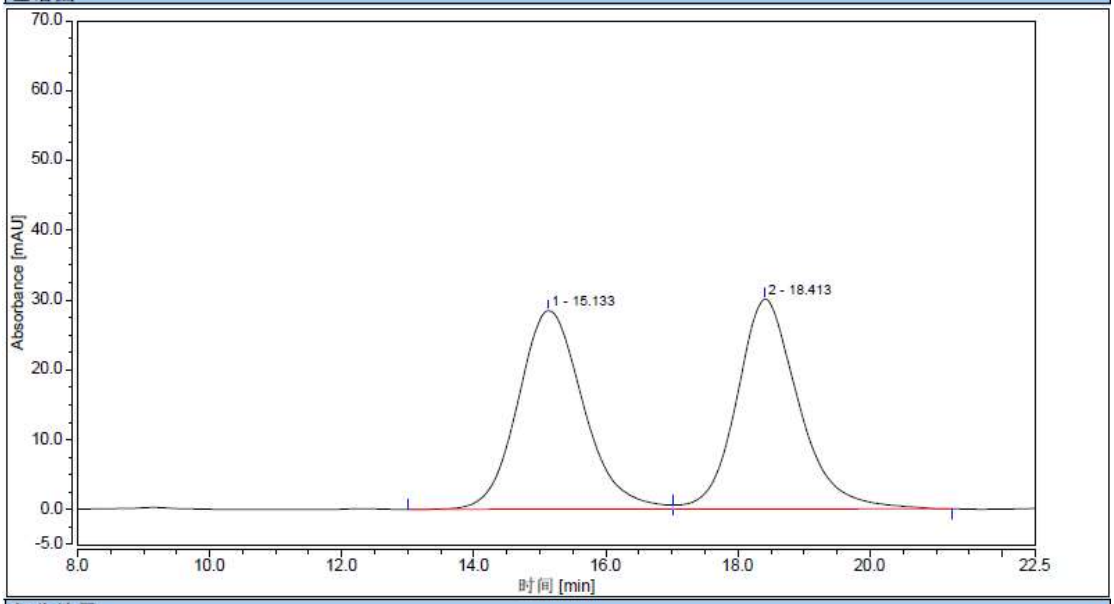


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.387	2.811	4.423	15.15	17.93	n.a.
2		16.577	15.739	20.247	84.85	82.07	n.a.
Total:			**18.550**	**24.669**	**100.00**	**100.00**	

3ag

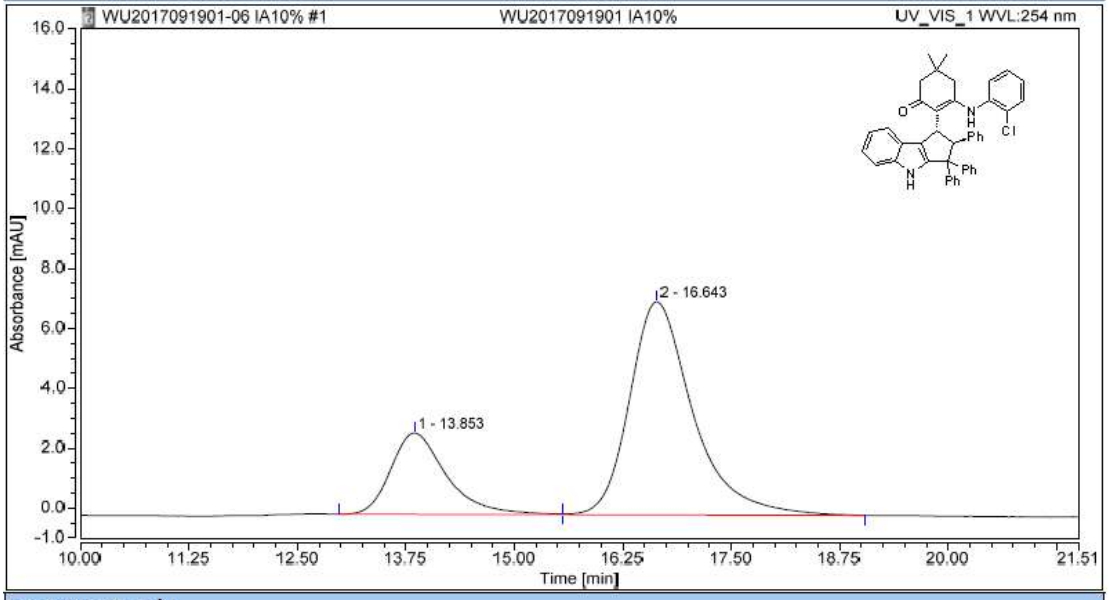
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		15.133	32.614	28.415	49.94	48.58	n.a.
2		18.413	32.687	30.079	50.06	51.42	n.a.
总和:			65.301	58.494	100.00	100.00	

Chromatogram

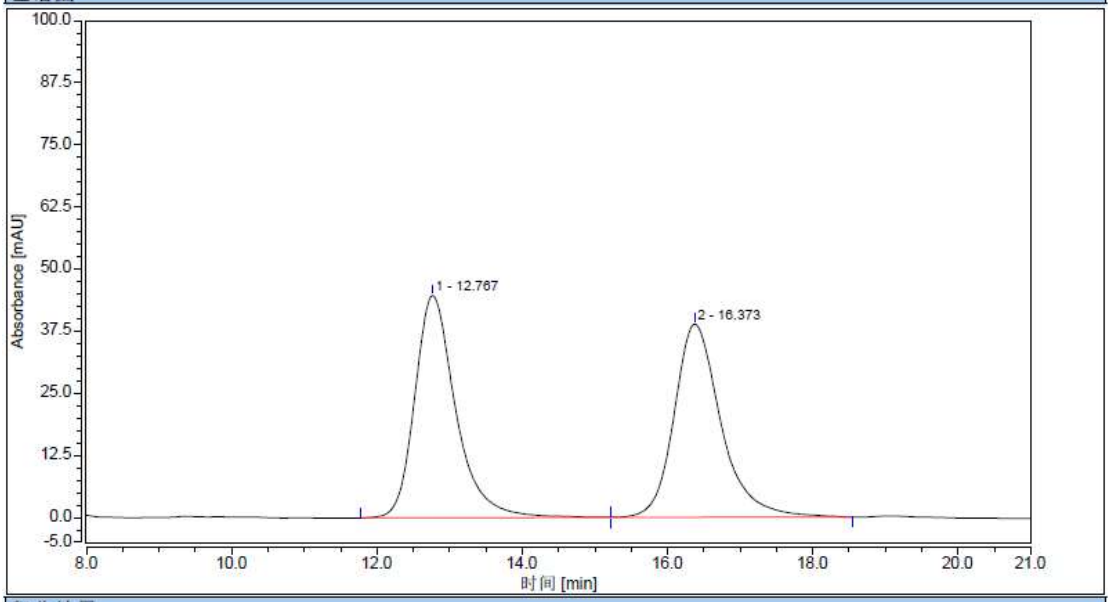


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.853	2.021	2.719	25.08	27.65	n.a.
2		16.643	6.037	7.115	74.92	72.35	n.a.
Total:			8.059	9.834	100.00	100.00	

3ah

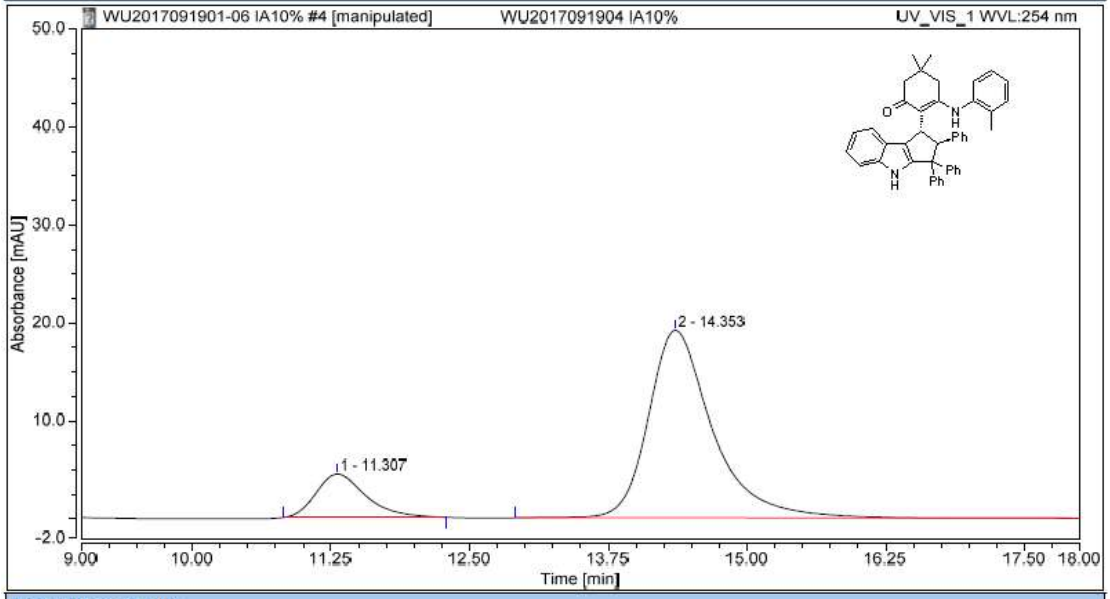
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		12.767	29.313	44.694	50.19	53.48	n.a.
2		16.373	29.090	38.882	49.81	46.52	n.a.
总和:			**58.403**	**83.576**	**100.00**	**100.00**	

Chromatogram

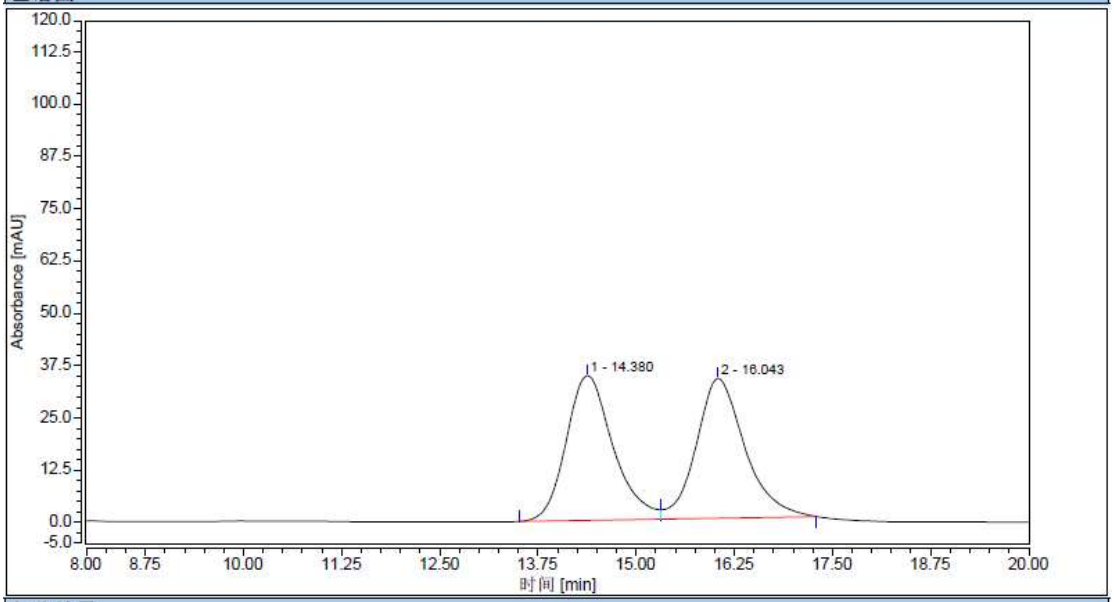


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.307	2.295	4.430	15.06	18.79	n.a.
2		14.353	12.939	19.151	84.94	81.21	n.a.
Total:			**15.234**	**23.581**	**100.00**	**100.00**	

3ai

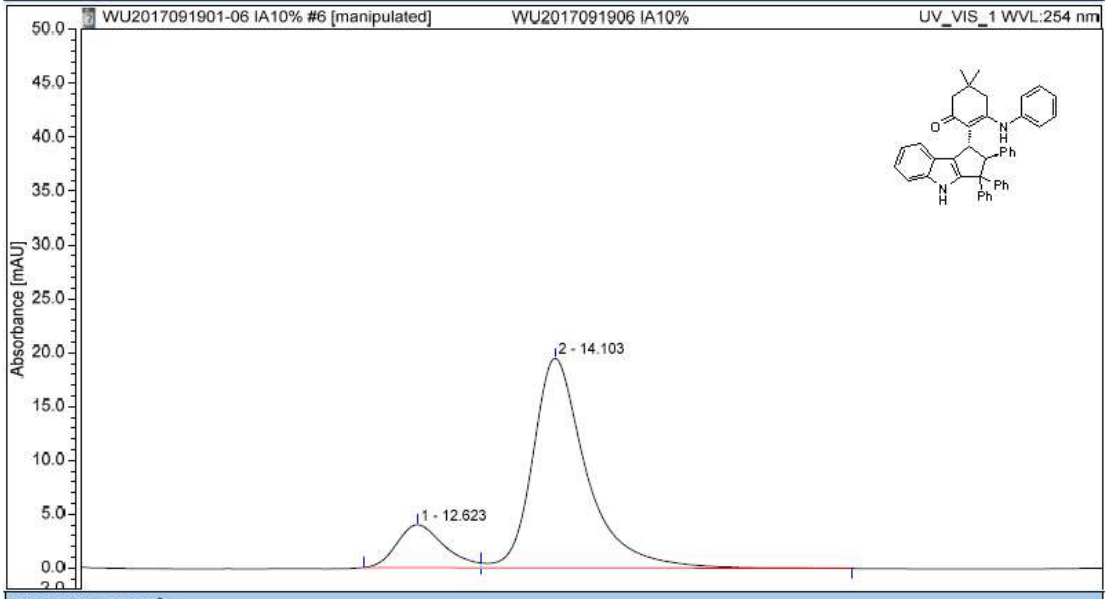
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		14.380	23.901	34.566	49.94	50.86	n.a.
2		16.043	23.962	33.394	50.06	49.14	n.a.
总和:			**47.863**	**67.960**	**100.00**	**100.00**	

Chromatogram

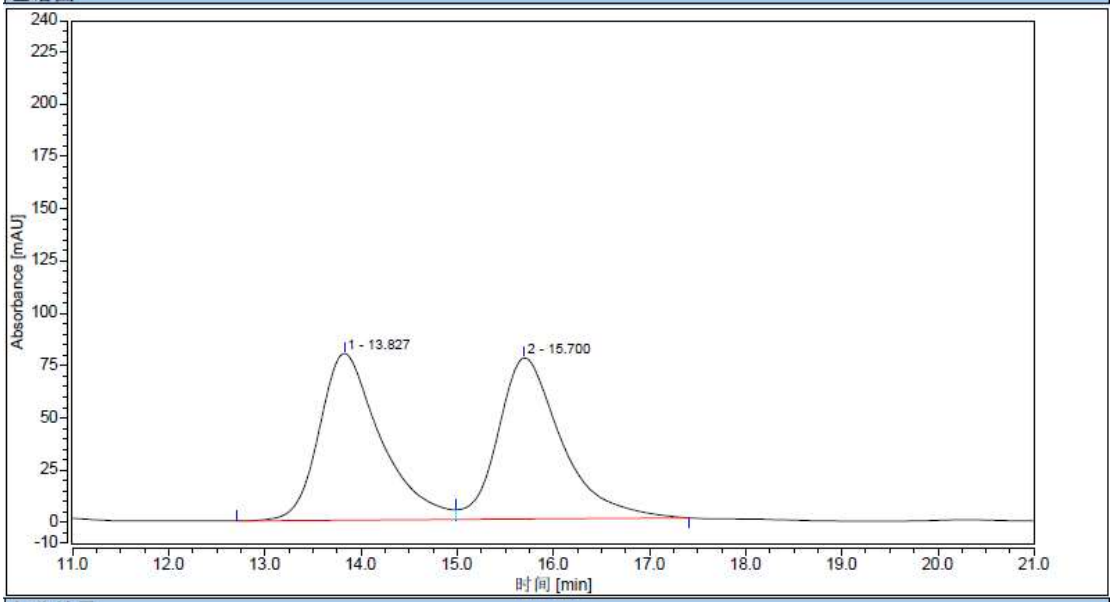


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.623	2.320	3.970	15.12	16.95	n.a.
2		14.103	13.018	19.450	84.88	83.05	n.a.
Total:			**15.338**	**23.420**	**100.00**	**100.00**	

3aj

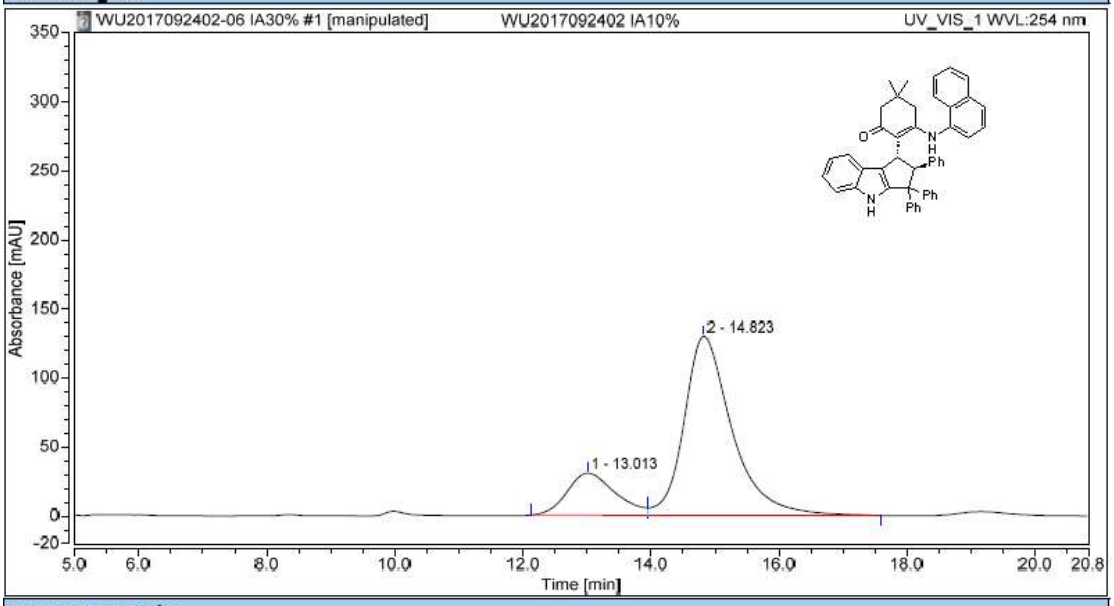
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		13.827	59.082	79.764	50.05	50.89	n.a.
2		15.700	58.956	76.972	49.95	49.11	n.a.
总和:			**118.038**	**156.736**	**100.00**	**100.00**	

Chromatogram

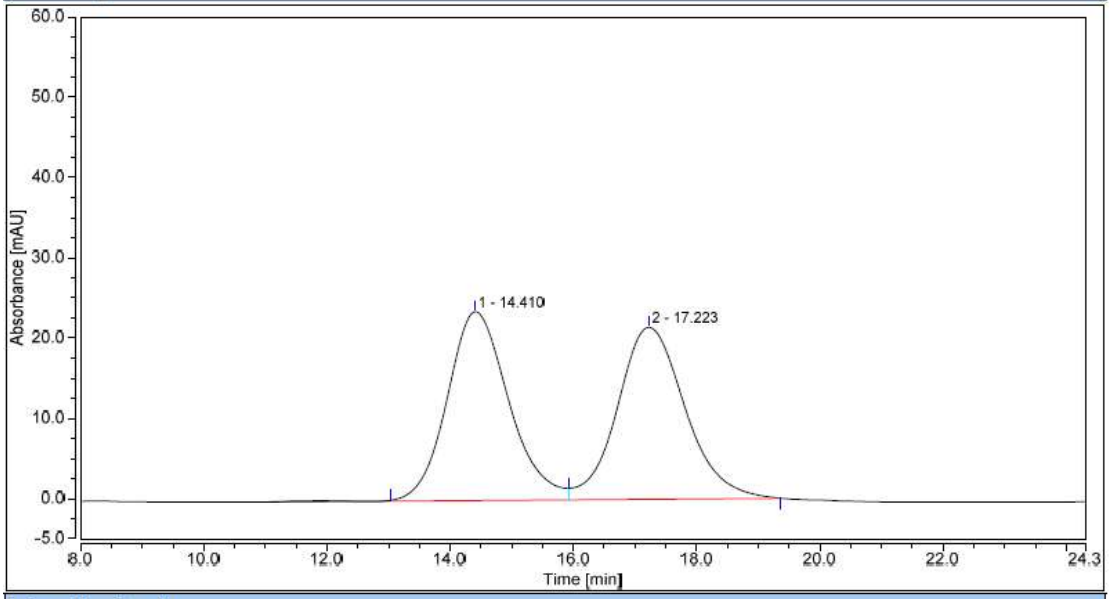


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.013	26.546	30.432	19.11	19.03	n.a.
2		14.823	112.388	129.487	80.89	80.97	n.a.
Total:			**138.934**	**159.920**	**100.00**	**100.00**	

3ak

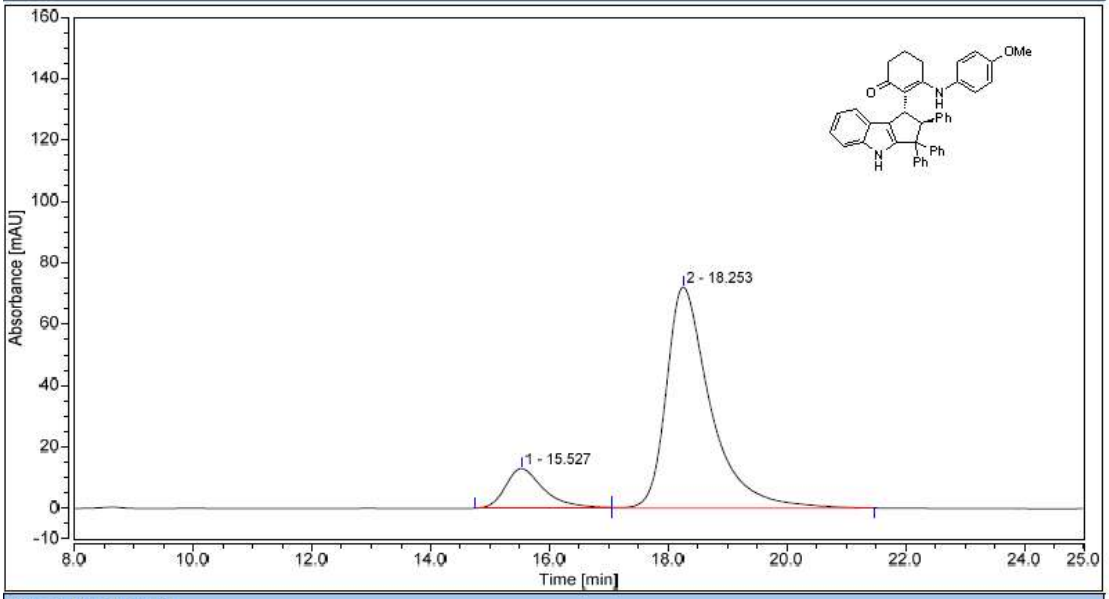
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.410	27.178	23.505	49.91	52.33	n.a.
2		17.223	27.275	21.408	50.09	47.67	n.a.
Total:			**54.453**	**44.913**	**100.00**	**100.00**	

Chromatogram

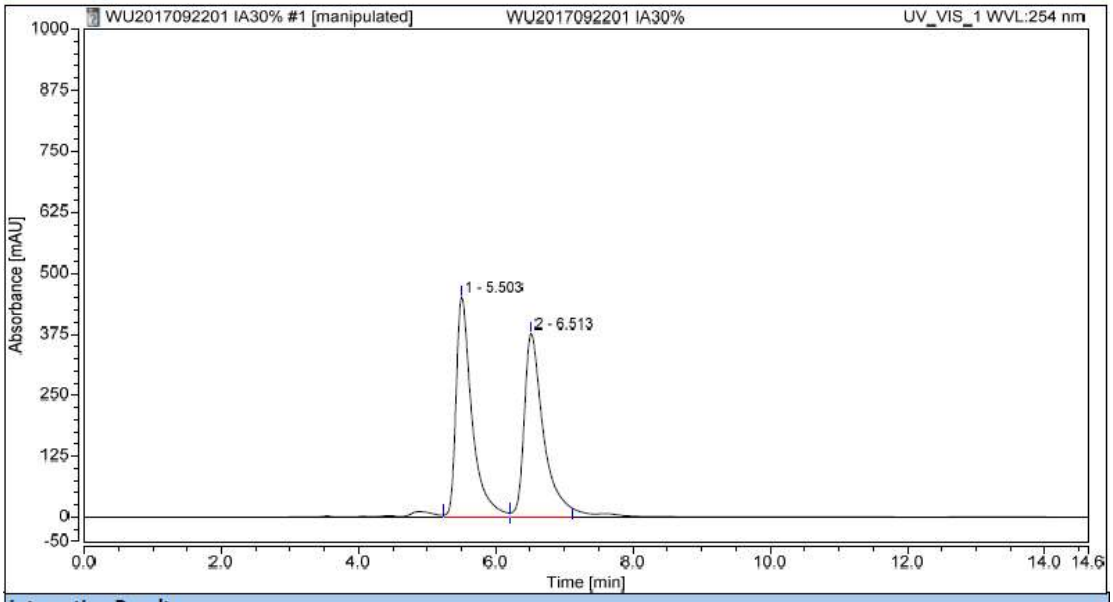


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.527	9.700	12.888	13.50	15.18	n.a.
2		18.253	62.129	72.019	86.50	84.82	n.a.
Total:			**71.828**	**84.907**	**100.00**	**100.00**	

3al

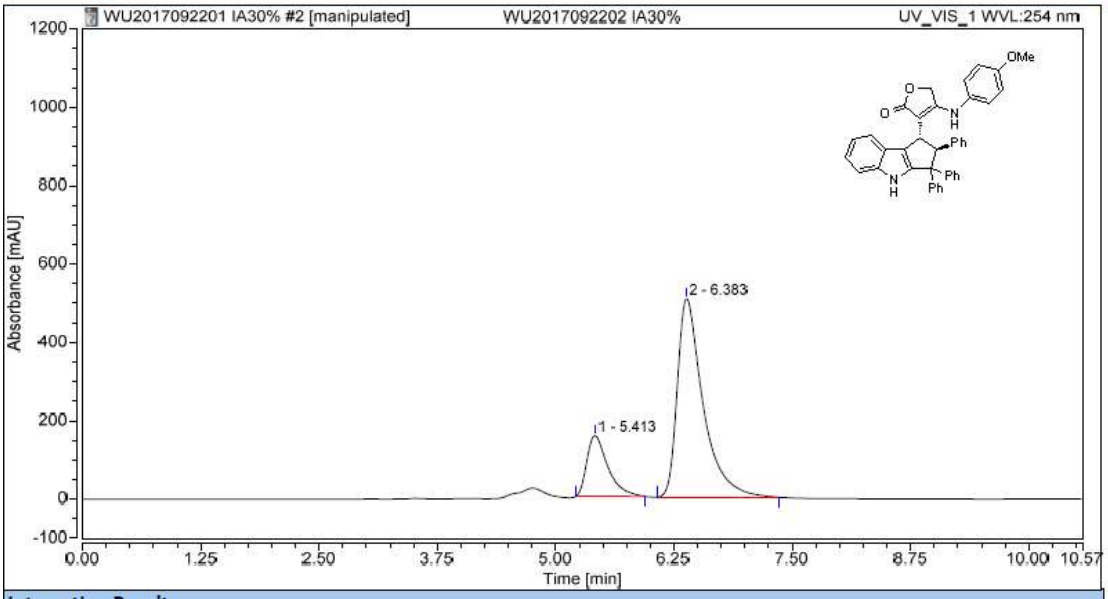
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.503	121.442	451.847	49.92	54.53	n.a.
2		6.513	121.818	376.749	50.08	45.47	n.a.
Total:			243.260	828.597	100.00	100.00	

Chromatogram

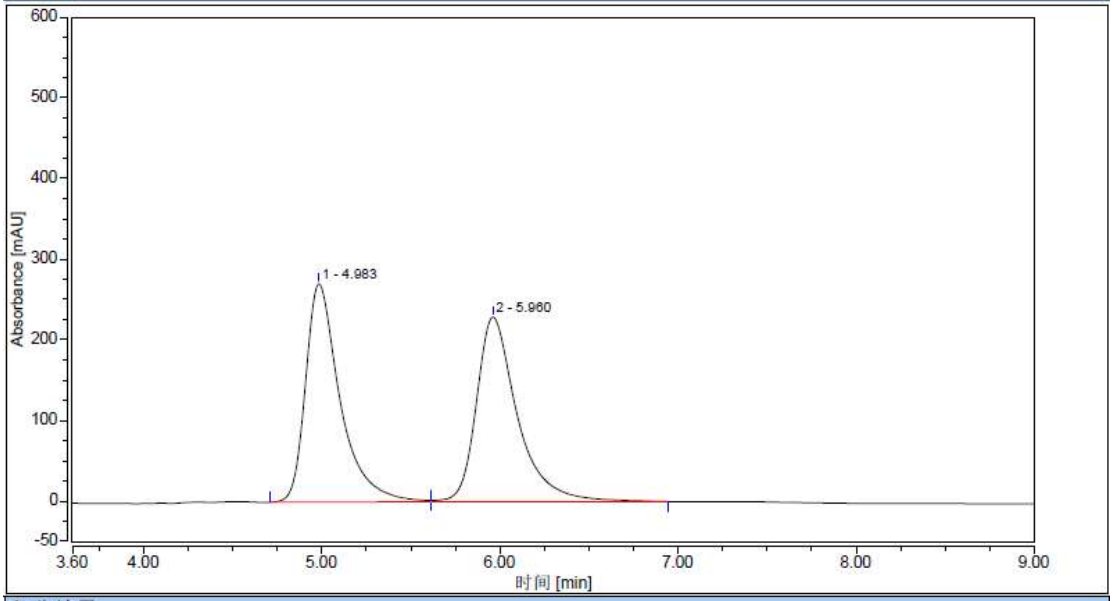


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.413	39.529	154.806	19.82	23.40	n.a.
2		6.383	159.884	506.859	80.18	76.60	n.a.
Total:			199.413	661.665	100.00	100.00	

3am

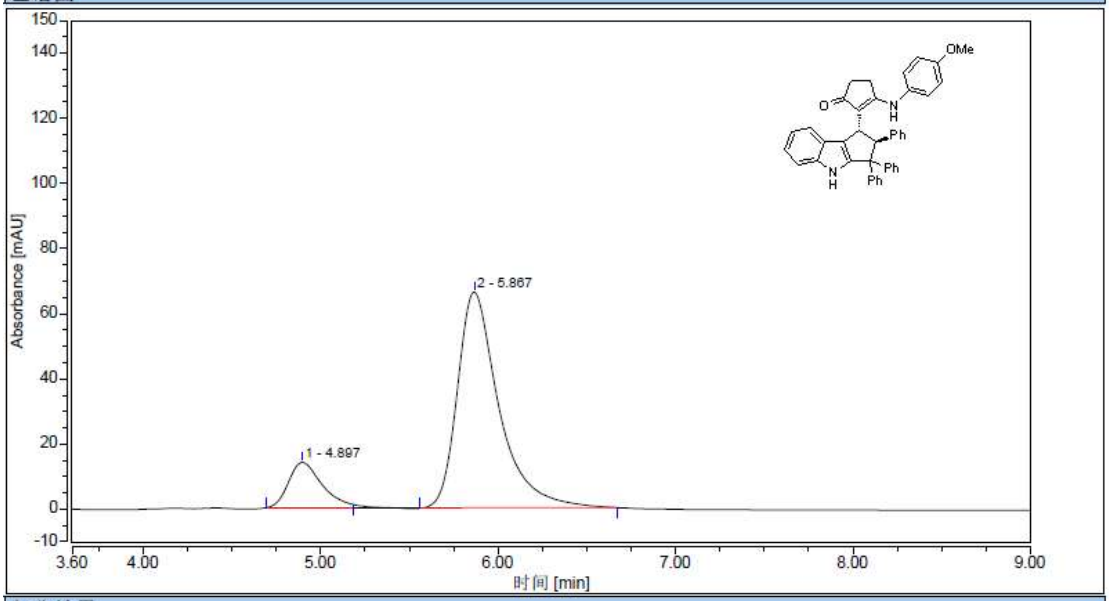
色谱图



积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.983	60.795	270.681	49.92	54.17	n.a.
2		5.960	60.988	228.999	50.08	45.83	n.a.
总和:			**121.783**	**499.680**	**100.00**	**100.00**	

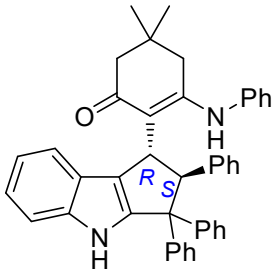
色谱图



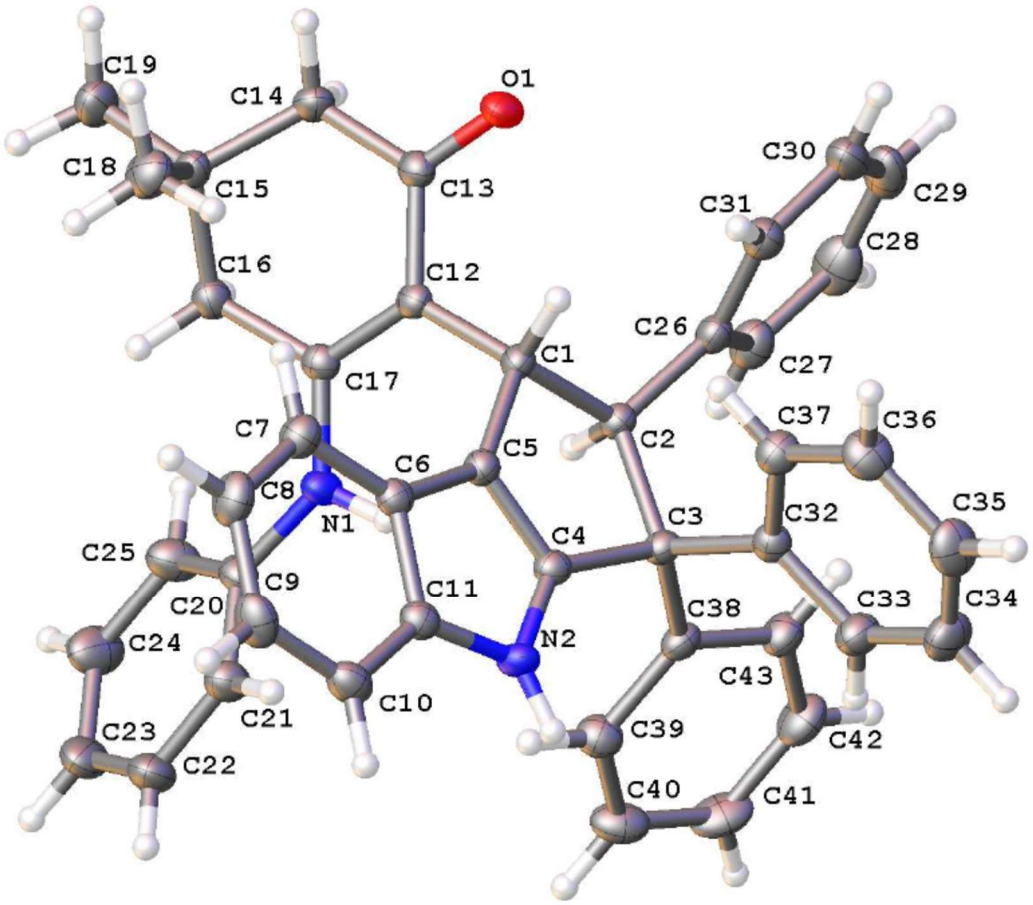
积分结果

序号	峰名称	保留时间 min	峰面积 mAU*min	峰高 mAU	相对峰面积 %	相对峰高 %	样品量 n.a.
1		4.897	3.038	13.943	14.51	17.41	n.a.
2		5.867	17.907	66.153	85.49	82.59	n.a.
总和:			**20.945**	**80.096**	**100.00**	**100.00**	

6. X-ray single crystal data for product 3ai



(1*R*,2*S*)-3ai



The thermal ellipsoid was drawn at the 30% probability level.

Empirical formula	C43 H38 N2 O	
Formula weight	598.75	
Temperature	173 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.7773(4) Å	α= 90°.
	b = 16.6542(8) Å	β= 90°.

	c = 21.9525(10) Å γ = 90°.
Volume	3209.0(3) $Å^3$
Z	4
Density (calculated)	1.239 Mg/m^3
Absorption coefficient	0.364 mm^{-1}
F(000)	1272
Crystal size	0.15 x 0.1 x 0.08 mm^3
Theta range for data collection	2.898 to 60.734°.
Index ranges	-11<=h<=11, -21<=k<=21, -26<=l<=28
Reflections collected	35258
Independent reflections	7382 [R(int) = 0.0450]
Completeness to theta = 53.594°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7519 and 0.6558
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7382 / 0 / 417
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0814
R indices (all data)	R1 = 0.0421, wR2 = 0.0850
Absolute structure parameter	-0.10(14)
Extinction coefficient	n/a
Largest diff. peak and hole	0.185 and -0.164 $e.Å^{-3}$