Supporting Information for

Diastereo- and Enantioselective Construction of Spirooxindole Scaffolds through a Catalytic Asymmetric [3+3] Cycloaddition

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Contents:

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 were $CDCl_3$ and acetone-d_6, using tetramethylsilane as the internal reference. HRMS spectra were recorded on a LTQ-Orbitrap mass spectrometer. Enantiomeric ratios (*er*) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral column used for the determination of Enantiomeric ratioes by chiral HPLC was Chiralpak IC, IA and AD-H columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. Analytical grade solvents for the column chromatography and commercially available reagents were used as received. All starting materials commercially available were used directly. Substrates **1** were synthesized according to the literature methods.[1]

2. General procedure for the catalytic asymmetric synthesis of products 6

After a solution of *N*-methyl-isatins **2** (0.12 mmol), amino ester **3** (0.11 mmol), the catalyst **5** (0.01 mmol), and 3 Å molecular sieves (100 mg) in toluene (4 mL) was stirred at 25 °C for 30 minutes, the solution of 3-substituted-2-indolylmethanols **1** (0.1 mmol) in toluene (4 mL) was added. After being stirred at 50 °C for 12 h, the reaction mixture was filtered to remove molecular sieves and the solid powder was washed with ethyl acetate. The resultant solution was concentrated under the reduced pressure to give the residue, which was purified through flash column chromatography on silica gel to afford pure product **6**.

[1] K. Bera, C. Schneider, *Chem. Eur. J.* **2016**, *22*, 7074.

3. Characterization data of products 6

(1'*S*,4'*S*)-diethyl-1,5'-dimethyl-2-oxo-4'-phenyl-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6aa):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 74% (39.8 mg); yellowish solid, m.p. 118.8-119.5 ^{o}C; $[\alpha]_D^{20}$ = +135.2 (c = 0.59, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.42 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.04 – 6.98 (m, 2H), 6.83 (t, *J* = 7.7 Hz, 1H), 6.20 (d, *J* = 8.3 Hz, 1H), 5.56 (s, 1H), 4.37 – 4.29 (m, 1H), 4.23 – 4.13 (m, 1H), 4.12 – 4.01 (m, 1H), 3.94 – 3.85 (m, 1H), 3.66 (s, 1H), 3.17 (s, 3H), 2.20 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 168.2, 167.7, 144.2, 139.1, 134.9, 132.5, 131.8, 130.7, 128.9, 128.4, 128.1, 127.5, 124.6, 123.8, 121.6, 120.3, 118.7, 110.2, 109.7, 109.2, 72.4, 67.1, 62.5, 62.2, 41.4, 26.1, 13.9, 13.8, 8.1; IR (KBr): 2981, 2935, 1613, 1471, 1493, 1456, 1336, 1367, 1299, 1257, 1242, 1210, 1180, 1095, 1077, 1019, 757 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{31}N_3O_5+H)^+$ requires m/z 538.2342, found m/z 538.2342; Enantiomeric ratio: 82:18, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.10 min (minor), t_R = 5.35 min (major).

(1'*R*,4'*R*)-diethyl-1,5'-dimethyl-2-oxo-4'-(*o*-tolyl)-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (*ent*-6ba):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 56% (30.9 mg); yellowish solid, m.p. 143.7-144.9 ^{o}C; $[\alpha]_D^{20}$ = -103.6 (c = 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.31 – 7.25 (m, 2H), 7.17 – 7.09 (m, 3H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.06 (s, 1H), 5.96 (s, 1H), 4.33 – 4.25 (m, 1H), 4.21 – 4.13 (m, 1H), 3.99 – 3.91 (m, 1H), 3.81 (s, 1H), 3.72 – 3.65 (m, 1H), 3.19 (s, 3H), 2.68 (s, 3H), 2.09 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 168.4, 167.5, 144.1, 137.3, 135.6, 135.1, 134.3, 132.1, 130.5, 129.1, 128.9, 127.4, 127.3, 127.1, 126.4, 124.6, 123.9, 120.9, 119.3, 110.5,

109.7, 109.4, 72.1, 66.7, 62.5, 62.3, 35.6, 26.2, 20.2, 13.9, 13.5, 8.2; IR (KBr): 2920, 1869, 1742, 1614, 1559, 1542, 1508, 1493, 1470, 1368, 1327, 1301, 1252, 1238, 1208, 1173, 1073 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{33}N_3O_5+Na)^+$ requires m/z 574.2318, found m/z 574.2326; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 3.94 min (major), t_R = 9.71 min (minor).

(1'*S*,4'*S*)-diethyl-4'-(2-methoxyphenyl)-1,5'-dimethyl-2-oxo-2'*H*-spiro[indoline-3, 1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ca):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 83% (47.1 mg); yellowish solid, m.p. 118.9-119.6 ^oC; $[\alpha]_D^{20}$ = +132.6 (c = 0.91, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.02 – 6.95 (m, 2H), 6.92 – 6.86 (m, 2H), 6.77 (t, *J* = 7.7 Hz, 1H), 6.27 (s, 1H), 6.14 (d, *J* = 8.3 Hz, 1H), 4.33 – 4.25 (m, 1H), 4.19 – 4.10 (m, 1H), 4.02 – 3.94 (m, 1H), 3.93 (s, 3H), 3.78 – 3.69 (m, 2H), 3.17 (s, 3H), 2.17 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 168.3, 168.0, 156.2, 144.2, 135.0, 133.5, 131.6, 130.7, 130.1, 128.3, 128.2, 127.6, 124.7, 123.6, 121.2, 120.6, 120.1, 118.5, 110.4, 110.1, 109.5, 109.1, 72.4, 66.6, 62.1, 62.0, 55.6, 26.0, 13.9, 13.5, 7.9; IR (KBr): 3565, 3445, 1742, 1614, 1491, 1471, 1456, 1368, 1336, 1301, 1243, 1208, 1094, 1052, 1020, 751, 650 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{33}N_3O_6+Na)^+$ requires m/z 590.2267, found m/z 590.2277; Enantiomeric ratio: 81:19, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.16 min (minor), t_R = 5.58 min (major).

(1'*R*,4'*R*)-diethyl-4'-(2-chlorophenyl)-1,5'-dimethyl-2-oxo-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (*ent*-4da):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 67% (38.3 mg); yellowish oil; $[\alpha]_D^{20}$ = -180.3 (c = 0.24, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.57

(t, *J* = 7.8 Hz, 1H), 7.41 (dd, *J* = 11.3, 7.9 Hz, 2H), 7.26 – 7.10 (m, 3H), 7.04 – 6.97 (m, 2H), 6.80 (t, *J* = 7.7 Hz, 1H), 6.39 (s, 1H), 6.14 (d, *J* = 8.3 Hz, 1H), 4.33 – 4.26 (m, 1H), 4.24 – 4.16 (m, 1H), 4.07 – 3.99 (m, 1H), 3.85 – 3.78 (m, 1H), 3.76 (s, 1H), 3.16 (s, 3H), 2.23 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.0, 167.7, 144.2, 136.9, 135.1, 133.4, 132.5, 131.8, 130.6, 129.5, 128.4, 127.9, 127.1, 124.8, 123.7, 121.6, 120.3, 118.7, 110.6, 110.3, 109.2, 72.3, 66.3, 62.6, 62.2, 36.0, 26.0, 13.9, 13.6, 8.2; IR (KBr): 2979, 2934, 2360, 2340, 1743, 1614, 1494, 1471, 1456, 1368, 1336, 1300, 1259, 1240, 1209, 1182, 1095, 1076, 1038, 1019 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{30}ClN_3O_5+Na)^+$ requires m/z 594.1772, found m/z 594.1766; Enantiomeric ratio: 92:8, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.45 min (major), t_R = 5.32 min (minor).

(1'*R*,4'*R*)-diethyl-4'-(3-fluorophenyl)-1,5'-dimethyl-2-oxo-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (*ent*-6ea):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 53% (29.4 mg); yellowish oil; $[\alpha]_D^{20}$ = -92.0 (c = 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.20 (m, 4H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.97 – 6.91 (m, 1H), 6.82 (t, *J* = 7.7 Hz, 1H), 6.18 (d, *J* = 8.3 Hz, 1H), 5.54 (s, 1H), 4.33 – 4.25 (m, 1H), 4.21 – 4.13 (m, 1H), 4.11 – 4.03 (m, 1H), 3.97 – 3.89 (m, 1H), 3.62 (s, 1H), 3.17 (s, 3H), 2.19 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.0, 167.5, 162.6 (*J* = 246.1 Hz), 144.1, 135.1, 131.8, 130.6, 129.7 (*J* = 8.2 Hz), 127.9, 124.7, 123.8, 121.8, 120.4, 118.8, 116.0 (*J* = 22.1 Hz), 114.4 (*J* = 21.0 Hz), 110.2, 110.0, 109.1, 72.4, 66.8, 62.5, 62.2, 41.0, 26.0, 13.8, 13.7, 8.1; IR (KBr): 2936, 1613, 1588, 1491, 1471, 1456, 1368, 1335, 1300, 1258, 1239, 1208, 1132, 1095, 1077, 1019 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{30}FN_3O_5+Na)^+$ requires m/z 578.2067, found m/z 578.2065; Enantiomeric ratio: 88:12, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.30 min (major), t_R = 4.71 min

(minor).

(1'*S*,4'*S*)-diethyl-4'-(4-fluorophenyl)-1,5'-dimethyl-2-oxo-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6fa):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 53% (29.4 mg); yellowish solid, m.p. 112.3-114.2 ^{o}C; $[\alpha]_D^{20}$ = +156.0 (c = 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.50 – 7.39 (m, 3H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.03 – 6.97 (m, 4H), 6.81 (t, *J* = 7.7 Hz, 1H), 6.17 (d, *J* = 8.3 Hz, 1H), 5.53 (s, 1H), 4.33 – 4.25 (m, 1H), 4.21 – 4.12 (m, 1H), 4.11 – 4.00 (m, 1H), 3.94 – 3.84 (m, 1H), 3.59 (s, 1H), 3.17 (s, 3H), 2.17 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.1, 167.6, 162.0 (*J* = 246.5 Hz), 144.1, 134.9, 134.8, 132.3, 131.8, 130.6, 130.5, 130.4, 127.9, 124.6, 123.7, 121.7, 120.3, 118.7, 115.2 (*J* = 21.4 Hz), 110.2, 109.7, 109.1, 72.4, 66.9, 62.5, 62.2, 40.5, 26.0, 13.9, 13.8, 8.0; IR (KBr): 2980, 2918, 1613, 1506, 1495, 1471, 1456, 1368, 1335, 1300, 1238, 1178, 1159, 1094, 1075, 1018, 739 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{30}FN_3O_5+Na)^+$ requires m/z 578.2067, found m/z 578.2075; Enantiomeric ratio: 85:15, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.07 min (minor), t_R = 5.82 min (major).

(1'*S*,4'*S*)-diethyl-4'-(4-chlorophenyl)-1,5'-dimethyl-2-oxo-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ga):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 45% (25.7 mg); yellowish solid, m.p. 114.8-115.8 ^{o}C; $[\alpha]_D^{20}$ = +103.5 (c = 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 3H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.82 (t, *J* = 7.7 Hz, 1H), 6.18 (d, *J* = 8.3 Hz, 1H), 5.52 (s, 1H), 4.33 – 4.25 (m, 1H), 4.21 – 4.13 (m, 1H), 4.12 – 4.04 (m, 1H), 3.95 – 3.86 (m, 1H), 3.60 (s, 1H), 3.17 (s, 3H), 2.17 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.0, 167.5, 144.1, 137.6,

135.0, 133.3, 132.0, 131.8, 130.5, 130.2, 128.5, 127.9, 124.6, 123.7, 121.8, 120.4, 118.8, 110.2, 109.9, 109.2, 72.4, 66.8, 62.5, 62.2, 40.7, 26.0, 13.8, 13.7, 8.1; IR (KBr): 2979, 2918, 1744, 1614, 1557, 1541, 1521, 1490, 1471, 1456, 1337, 1369, 1300, 1258, 1241, 1210, 1094, 1016 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{30}ClN_3O_5+H)^+$ requires m/z 572.1952, found m/z 572.1944; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.32 min (minor), t_R = 5.94 min (major).

(1'*S*,4'*S*)-diethyl-1,5'-dimethyl-2-oxo-4'-(thiophen-2-yl)-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ha):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 47% (25.5 mg); yellow solid, m.p. 136.5-138.7 ^oC; $[\alpha]_D^{20}$ = +110.9 (c = 0.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.1 Hz, 2H), 7.04 (d, *J* = 3.4 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.94 – 6.89 (m, 1H), 6.81 (t, *J* = 7.7 Hz, 1H), 6.16 (d, *J* = 8.3 Hz, 1H), 5.83 (s, 1H), 4.34 – 4.26 (m, 1H), 4.20 – 4.11 (m, 2H), 4.06 – 3.97 (m, 1H), 3.76 (s, 1H), 3.16 (s, 3H), 2.27 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 167.7, 167.4, 144.0, 141.3, 135.2, 132.3, 131.6, 130.5, 128.1, 126.2, 126.0, 125.4, 125.3, 123.7, 121.8, 120.3, 118.8, 110.3, 109.9, 108.9, 72.5, 66.9, 62.6, 62.2, 37.6, 26.0, 13.9, 13.8, 8.0; IR (KBr): 2921, 1869, 1845, 1793, 1743, 1685, 1559, 1541, 1508, 1473, 1457, 1339, 1259 cm^{-1}; ESI FTMS exact mass calcd for $(C_{30}H_{29}N_3O_5S+H)^+$ requires m/z 544.1906, found m/z 544.1903; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.28 min (minor), t_R = 6.45 min (major).

(1'*S*,4'*S*)-diethyl-5-bromo-1,5'-dimethyl-2-oxo-4'-(o-tolyl)-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ia):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 60% (37.7 mg); yellowish solid, m.p. 76.9-78.1 ^oC; $[\alpha]_D^{20}$ =

+120.5 (c = 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.4 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.10 (m, 3H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 5.98 (d, *J* = 7.9 Hz, 2H), 4.32 – 4.25 (m, 1H), 4.20 – 4.15 (m, 1H), 3.98 – 3.89 (m, 1H), 3.81 (s, 1H), 3.72 – 3.64 (m, 1H), 3.17 (s, 3H), 2.68 (s, 3H), 2.07 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 168.3, 167.4, 144.1, 137.2, 135.6, 135.0, 133.4, 132.3, 132.0, 130.5, 128.8, 127.5, 127.3, 126.4, 124.5, 124.0, 123.9, 121.1, 113.7, 111.6, 109.3, 109.1, 72.0, 66.7, 62.5, 62.3, 26.1, 20.2, 13.9, 13.5, 8.1; IR (KBr): 2979, 2929, 1743, 1613, 1560, 1577, 1492, 1470, 1456, 1368, 1340, 1300, 1254, 1238, 1207, 1095, 1058, 1018 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{32}BrN_3O_5+H)^+$ requires m/z 630.1603, found m/z 630.1601; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 4.19 min (minor), t_R = 6.71 min (major).

(1'*S*,4'*S*)-diethyl-8'-chloro-1,5'-dimethyl-2-oxo-4'-(o-tolyl)-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ja):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 56% (32.8 mg); yellow solid, m.p. 157.7-158.6 ^oC; $[\alpha]_D^{20}$ = +192.2 (c = 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.31 – 7.25 (m, 2H), 7.18 – 7.08 (m, 3H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.07 (s, 1H), 5.96 (s, 1H), 4.34 – 4.25 (m, 1H), 4.22 – 4.14 (m, 1H), 3.98 – 3.89 (m, 1H), 3.81 (s, 1H), 3.73 – 3.64 (m, 1H), 3.19 (s, 3H), 2.68 (s, 3H), 2.09 (s, 3H), 1.26 – 1.22 (t, *J* = 7.0 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 168.3, 167.5, 144.1, 137.3, 135.6, 135.1, 134.3, 132.1, 130.5, 129.1, 128.8, 127.4, 127.3, 127.0, 126.4, 124.5, 123.9, 120.8, 119.2, 110.4, 109.6, 109.4, 72.0, 66.6, 62.5, 62.3, 35.5, 26.1, 20.2, 13.9, 13.5, 8.1; IR (KBr): 3732, 2919, 1742, 1614, 1540, 1557, 1494, 1506, 1520, 1470, 1369, 1327, 1301, 1238, 1260, 1208, 1073 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{32}ClN_3O_5+Na)^+$ requires m/z 608.1928, found m/z 608.1930; Enantiomeric ratio: 80:20, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30

^{o}C, 254 nm): t_R = 3.95 min (minor), t_R = 9.77 min (major).

(1'*S*,4'*S*)-diethyl-4'-(4-methoxyphenyl)-1-methyl-2-oxo-5'-propyl-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ka):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 85% (50.6 mg); yellowish solid, m.p. 102.8-104.3 ^{o}C; $[\alpha]_D^{20}$ = +127.2 (c = 0.81, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.83 – 6.78 (m, 3H), 6.19 (d, *J* = 8.3 Hz, 1H), 5.50 (s, 1H), 4.30 (m, 1H), 4.19 – 4.13 (m, 1H), 4.13 – 4.07 (m, 1H), 3.95 – 3.90 (m, 1H), 3.77 (s, 3H), 3.61 (s, 1H), 3.17 (s, 3H), 2.69 – 2.61 (m, 2H), 1.55 – 1.47 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 168.1, 167.7, 158.8, 144.1, 135.0, 132.8, 131.8, 131.7, 130.2, 129.9, 128.1, 124.5, 123.6, 121.4, 120.1, 119.0, 114.4, 113.6, 110.2, 109.1, 72.4, 67.1, 62.4, 62.1, 55.1, 40.5, 26.1, 26.0, 23.0, 14.3, 13.9, 13.8; IR (KBr): 1743, 1613, 1510, 1494, 1470, 1456, 1368, 1329, 1301, 1244, 1210, 1176, 1092, 1076, 1037, 1022, 740 cm^{-1}; ESI FTMS exact mass calcd for $(C_{35}H_{37}N_3O_6+H)^+$ requires m/z 596.2760, found m/z 596.2765; Enantiomeric ratio: 86:14, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 3.94 min (minor), t_R = 4.62 min (major).

(1'*S*,4'*S*)-diethyl-5'-(4-chlorophenyl)-4'-(4-methoxyphenyl)-1-methyl-2-oxo-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6la):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 74% (49.1 mg); yellowish solid, m.p. 131.5-133.1 ^{o}C; $[\alpha]_D^{20}$ = +72.6 (c = 0.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.44 (m, 1H), 7.40 – 7.32 (m, 4H), 7.23 (t, *J* = 8.6 Hz, 3H), 7.06 – 6.99 (m, 2H), 6.90 – 6.84 (m, 1H), 6.81 – 6.75 (m, 2H), 6.28 (d, *J* = 8.3 Hz, 1H), 5.54 (d, *J* = 21.7 Hz, 1H), 4.34 – 4.26 (m, 1H), 4.17 – 4.05 (m, 2H), 3.96 – 3.88 (m, 1H), 3.76 (s, 3H), 3.64 (s, 1H), 3.20 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* =

7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 168.1, 167.7, 158.8, 144.2, 135.0, 133.8, 132.6, 132.1, 132.0, 131.5, 131.2, 129.9, 129.7, 129.3, 128.5, 128.3, 127.8, 124.6, 123.8, 122.2, 121.2, 119.2, 115.0, 113.7, 110.4, 109.3, 72.9, 67.0, 62.5, 62.1, 55.1, 40.7, 26.1, 13.9; IR (KBr): 3646, 3626, 3564, 3585, 3445, 1732, 1746, 1668, 1682, 1645, 1634, 1398, 669 cm^{-1}; ESI FTMS exact mass calcd for $(C_{38}H_{34}ClN_3O_6+Na)^+$ requires m/z 686.2034, found m/z 686.2017; Enantiomeric ratio: 93:7, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 98/2, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 38.42 min (major), t_R = 46.63 min (minor).

(1'*S*,4'*S*)-diethyl-1,5,5'-trimethyl-2-oxo-4'-phenyl-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ab):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 42% (23.2 mg); yellowish solid, m.p. 133.9-135.1 ^oC; $[\alpha]_D^{20}$ = +154.7 (c = 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.9 Hz, 3H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 7.7 Hz, 1H), 6.21 (d, *J* = 8.3 Hz, 1H), 5.55 (s, 1H), 4.35 – 4.27 (m, 1H), 4.20 – 4.12 (m, 1H), 4.10 – 4.02 (m, 1H), 3.93 – 3.85 (m, 1H), 3.62 (s, 1H), 3.15 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.2, 167.7, 141.7, 139.1, 134.9, 133.3, 132.5, 131.9, 130.6, 128.9, 128.3, 128.0, 127.4, 125.3, 121.5, 120.2, 118.6, 110.2, 109.5, 108.9, 72.5, 67.0, 62.4, 62.1, 41.3, 26.1, 21.2, 13.9, 13.8, 8.0; IR (KBr): 2968, 2920, 1742, 1603, 1501, 1456, 1360, 1327, 1293, 1257, 1242, 1198, 1159, 1103, 1076, 1020, 749, 705 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{33}N_3O_5+H)^+$ requires m/z 552.2498, found m/z 552.2490; Enantiomeric ratio: 96:4, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm): t_R = 3.70 min (minor), t_R = 5.29 min (major).

(1'*S*,4'*S*)-diethyl-5-methoxy-1,5'-dimethyl-2-oxo-4'-phenyl-2'*H*-spiro[indoline-3,1

'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ac):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 64% (36.3 mg); yellowish solid, m.p. 130.3-132.0 ^{o}C; $[\alpha]_D^{20}$ = +185.9 (c = 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.1 Hz, 3H), 7.31 – 7.26 (m, 3H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.06 – 6.98 (m, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.83 (t, *J* = 7.7 Hz, 1H), 6.23 (d, *J* = 8.3 Hz, 1H), 5.53 (s, 1H), 4.35 – 4.27 (m, 1H), 4.19 – 4.11 (m, 1H), 4.09 – 4.01 (m, 1H), 3.93 – 3.87 (m, 1H), 3.82 (s, 3H), 3.60 (s, 1H), 3.15 (s, 3H), 2.18 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 168.1, 167.6, 156.6, 139.0, 137.4, 134.9, 132.4, 130.6, 129.2, 128.9, 128.3, 127.4, 121.6, 120.2, 118.7, 115.8, 111.9, 110.2, 109.6, 109.5, 72.6, 67.0, 62.4, 62.1, 55.8, 41.3, 26.1, 13.8, 13.7, 8.0; IR (KBr): 3735, 2923, 1743, 1604, 1558, 1541, 1498, 1457, 1337, 1363, 1288, 1259, 1240, 1220, 1158, 1076, 1103, 1032 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{33}N_3O_6+H)^+$ requires m/z 568.2447, found m/z 568.2447; Enantiomeric ratio: 90:10, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 4.22 min (minor), t_R = 6.36 min (major).

(1'*S*,4'*S*)-diethyl-1,5',7-trimethyl-2-oxo-4'-phenyl-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ad):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 60% (33.1 mg); yellowish solid, m.p. 122.9-124.0 ^{o}C; $[\alpha]_D^{20}$ = +146.1 (c = 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 6.8 Hz, 3H), 7.30 – 7.19 (m, 4H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.83 (t, *J* = 7.7 Hz, 1H), 6.25 (d, *J* = 8.3 Hz, 1H), 5.55 (s, 1H), 4.34 – 4.26 (m, 1H), 4.18 – 4.11 (m, 1H), 4.07 – 3.98 (m, 1H), 3.90 – 3.81 (m, 1H), 3.58 (s, 1H), 3.42 (s, 3H), 2.67 (s, 3H), 2.16 (s, 3H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 168.1, 167.6, 141.7, 139.0, 135.3, 135.0, 132.5, 130.6, 128.9, 128.8, 128.3, 127.4, 123.7, 122.4, 121.5, 120.9, 120.2, 118.7, 110.3, 109.7, 71.8, 67.1, 62.4, 62.1, 41.3, 29.4, 19.1, 13.8, 13.7, 8.0; IR (KBr): 2978, 2921, 1601, 1522, 1491, 1459, 1357, 1327, 1298, 1244, 1210, 1168, 1104, 1052, 734

cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{33}N_3O_5+H)^+$ requires m/z 552.2498, found m/z 552.2517 Enantiomeric ratio: 86:14, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 3.94 min (minor), t_R = 5.17 min (major).

(1'*S*,4'*S*)-diethyl-7-methoxy-1,5'-dimethyl-2-oxo-4'-phenyl-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6ae):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 53% (30.1 mg); yellowish solid, m.p. 138.2-139.1 °C; $[\alpha]_D^{20}$ = +94.8 (c = 0.71, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 3H), 7.29 (t, *J* = 6.8 Hz, 3H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 7.7 Hz, 1H), 6.32 (d, *J* = 8.2 Hz, 1H), 5.55 (s, 1H), 4.33 – 4.25 (m, 1H), 4.21 – 4.13 (m, 1H), 4.07 – 4.00 (m, 1H), 3.96 (s, 3H), 3.90 – 3.84 (m, 1H), 3.60 (s, 1H), 3.43 (s, 3H), 2.18 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 168.1, 167.6, 145.9, 139.1, 135.0, 132.5, 131.9, 130.6, 129.5, 128.9, 128.3, 127.4, 124.4, 121.5, 120.2, 118.6, 116.8, 115.4, 110.3, 109.6, 72.2, 67.0, 62.4, 62.1, 56.2, 41.3, 29.4, 13.8, 13.7, 8.1; IR (KBr): 2979, 2934, 1743, 1616, 1603, 1494, 1457, 1362, 1326, 1290, 1259, 1209, 1168, 1128, 1110, 1052, 737 cm^{-1}; ESI FTMS exact mass calcd for $(C_{33}H_{33}N_3O_6+Na)^+$ requires m/z 590.2267, found m/z 590.2256; Enantiomeric ratio: 78:22, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 3.79 min (minor), t_R = 4.70 min (major).

(1'*S*,4'*S*)-diethyl-7-fluoro-1,5'-dimethyl-2-oxo-4'-phenyl-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6af):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 52% (28.9 mg); yellowish solid, m.p. 122.5-123.2 °C; $[\alpha]_D^{20}$ = +112.4 (c = 0.52, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 4H), 7.30 (t, *J* = 7.5 Hz, 3H), 7.25 – 7.13 (m, 2H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.88 (t, *J* = 7.7 Hz,

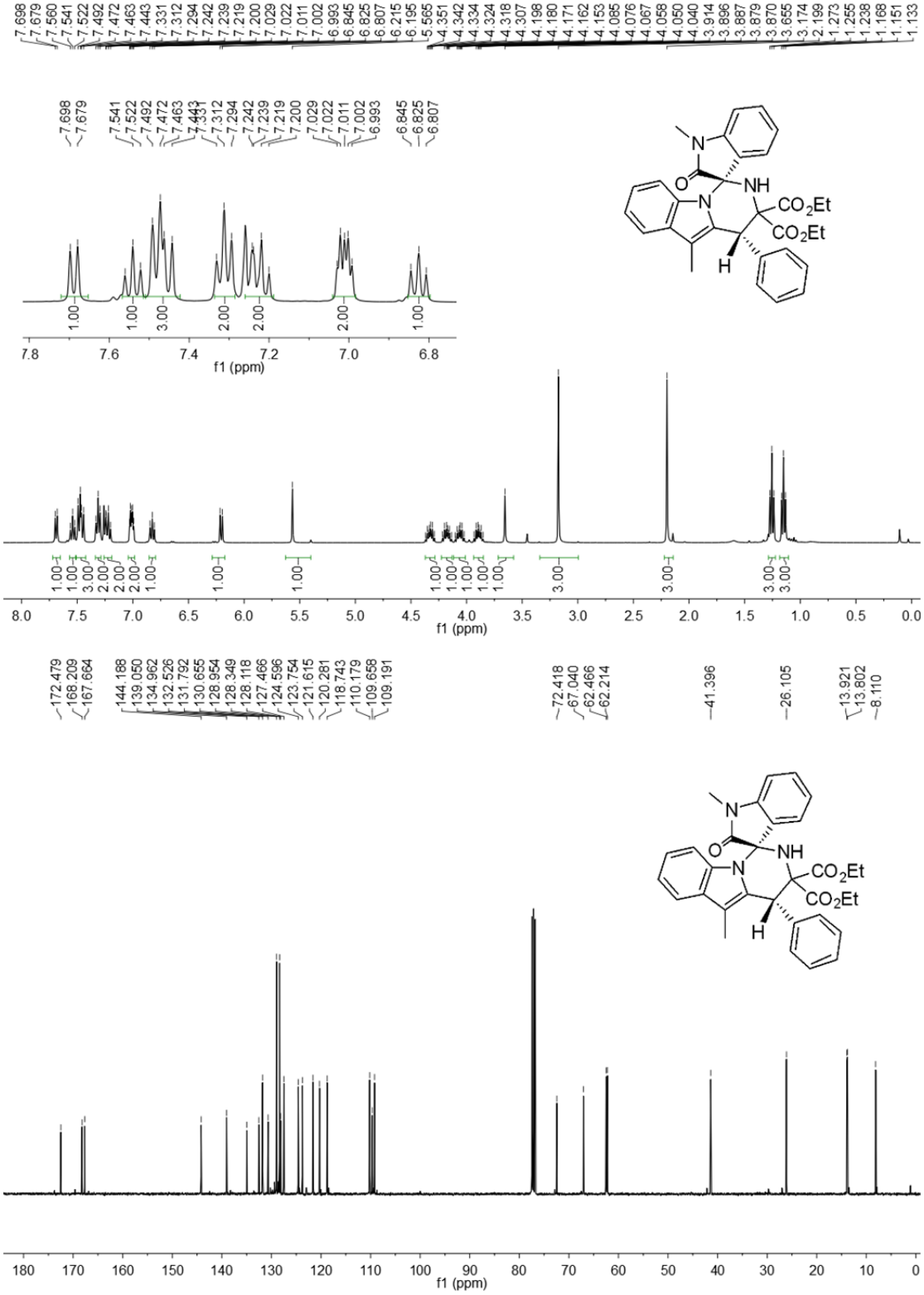
1H), 6.26 (d, *J* = 8.3 Hz, 1H), 5.56 (s, 1H), 4.34 – 4.27 (m, 1H), 4.21 – 4.13 (m, 1H), 4.11 – 4.03 (m, 1H), 3.92 – 3.85 (m, 1H), 3.62 (s, 1H), 3.39 (d, *J* = 1.4 Hz, 3H), 2.19 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 168.0, 167.5, 148.0 (*J* = 245.4 Hz), 138.9, 134.9, 132.3, 131.0, 130.8, 130.6, 128.9, 128.3, 127.5, 124.5 (*J* = 6.3 Hz), 124.4, 121.8, 120.4, 119.8 (*J* = 19.3 Hz), 118.8, 110.1, 110.0, 72.3, 66.9, 62.5, 62.2, 41.3, 13.8, 13.7, 8.0; IR (KBr): 3691, 2979, 1869, 1845, 1793, 1746, 1685, 1559, 1541, 1522, 1508, 1489, 1457, 1364, 1325, 1260, 1242, 1210 cm^{-1}; ESI FTMS exact mass calcd for $(C_{32}H_{30}FN_3O_5+H)^+$ requires m/z 556.2247, found m/z 556.2244; Enantiomeric ratio: 76:24, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 3.79 min (minor), t_R = 5.34 min (major).

(1'*S*,4'*S*)-diethyl-1,5,5'-trimethyl-2-oxo-4'-(*m*-tolyl)-2'*H*-spiro[indoline-3,1'-pyrimido[1,6-a]indole]-3',3'(4'*H*)-dicarboxylate (6mb):

Flash column chromatography eluent, petroleum ether/ethyl acetate = 4/1; Reaction time = 12 h; yield: 59% (33.4 mg); yellowish solid, m.p. 71.9-73.0 ^{o}C; $[\alpha]_D^{20}$ = +88.5 (c = 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 7.24 – 7.16 (m, 2H), 7.06 – 6.98 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 7.7 Hz, 1H), 6.23 (d, *J* = 8.3 Hz, 1H), 5.49 (s, 1H), 4.36 – 4.27 (m, 1H), 4.19 – 4.11 (m, 1H), 4.10 – 4.03 (m, 1H), 3.95 – 3.86 (m, 1H), 3.59 (s, 1H), 3.16 (s, 3H), 2.35 (d, *J* = 8.3 Hz, 6H), 2.18 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.1, 167.7, 141.7, 138.8, 137.6, 134.8, 133.2, 132.5, 131.8, 130.6, 129.6, 128.2, 128.1, 126.0, 125.2, 121.4, 120.1, 118.6, 110.2, 108.9, 72.4, 67.1, 62.3, 62.1, 41.3, 26.1, 21.5, 21.2, 13.9, 13.8, 8.1; IR (KBr): 2920, 1869, 1846, 1793, 1743, 1686, 1604, 1559, 1542, 1522, 1500, 1458, 1363, 1338, 1296, 1259, 1241, 1207 cm^{-1}; ESI FTMS exact mass calcd for $(C_{34}H_{35}N_3O_5+H)^+$ requires m/z 566.2655, found m/z 566.2655; Enantiomeric ratio: 75:25, determined by HPLC (Daicel Chiralpak AD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 3.74 min (minor), t_R = 4.54 min (major).

4. NMR spectra of products 6

6aa



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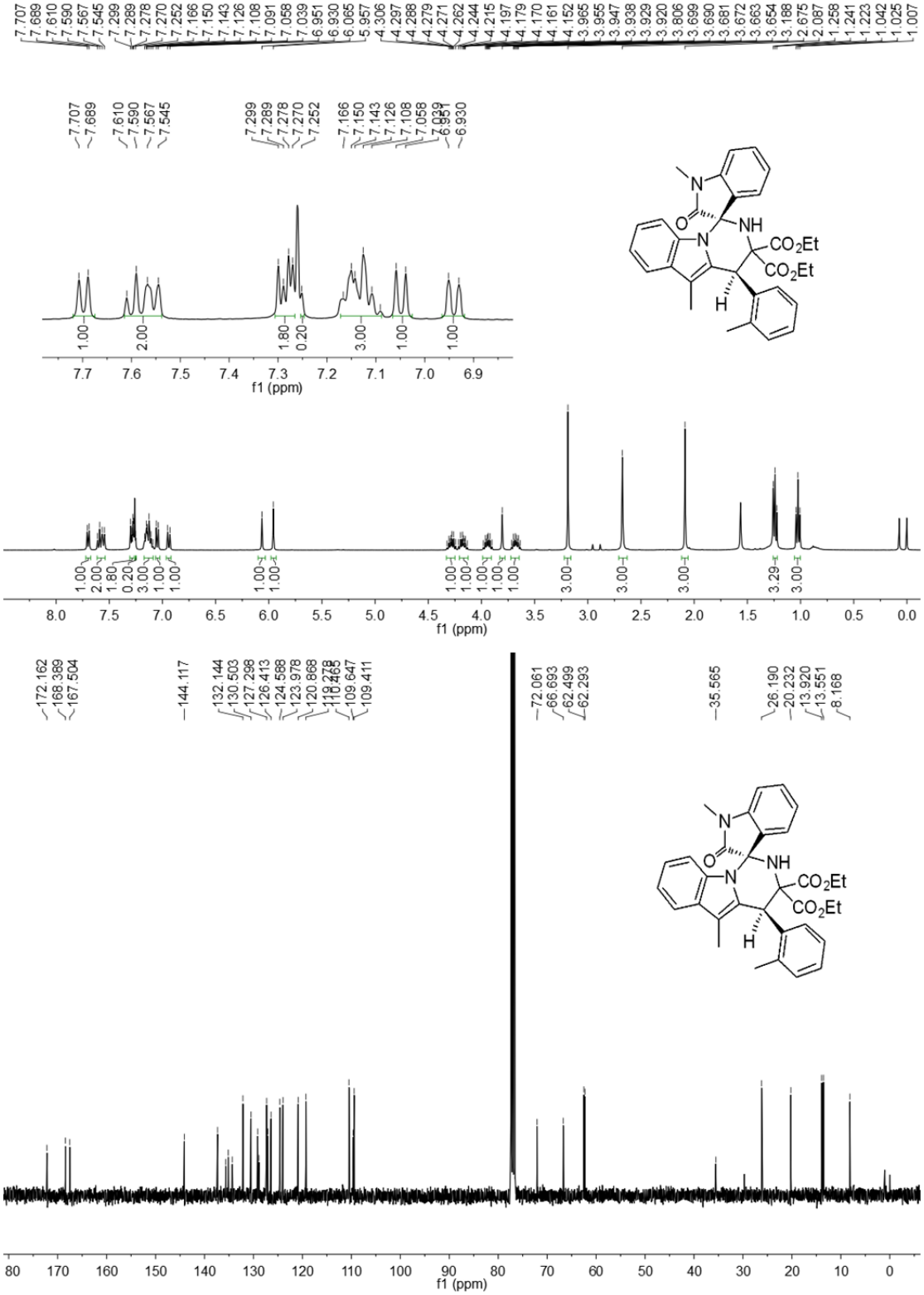
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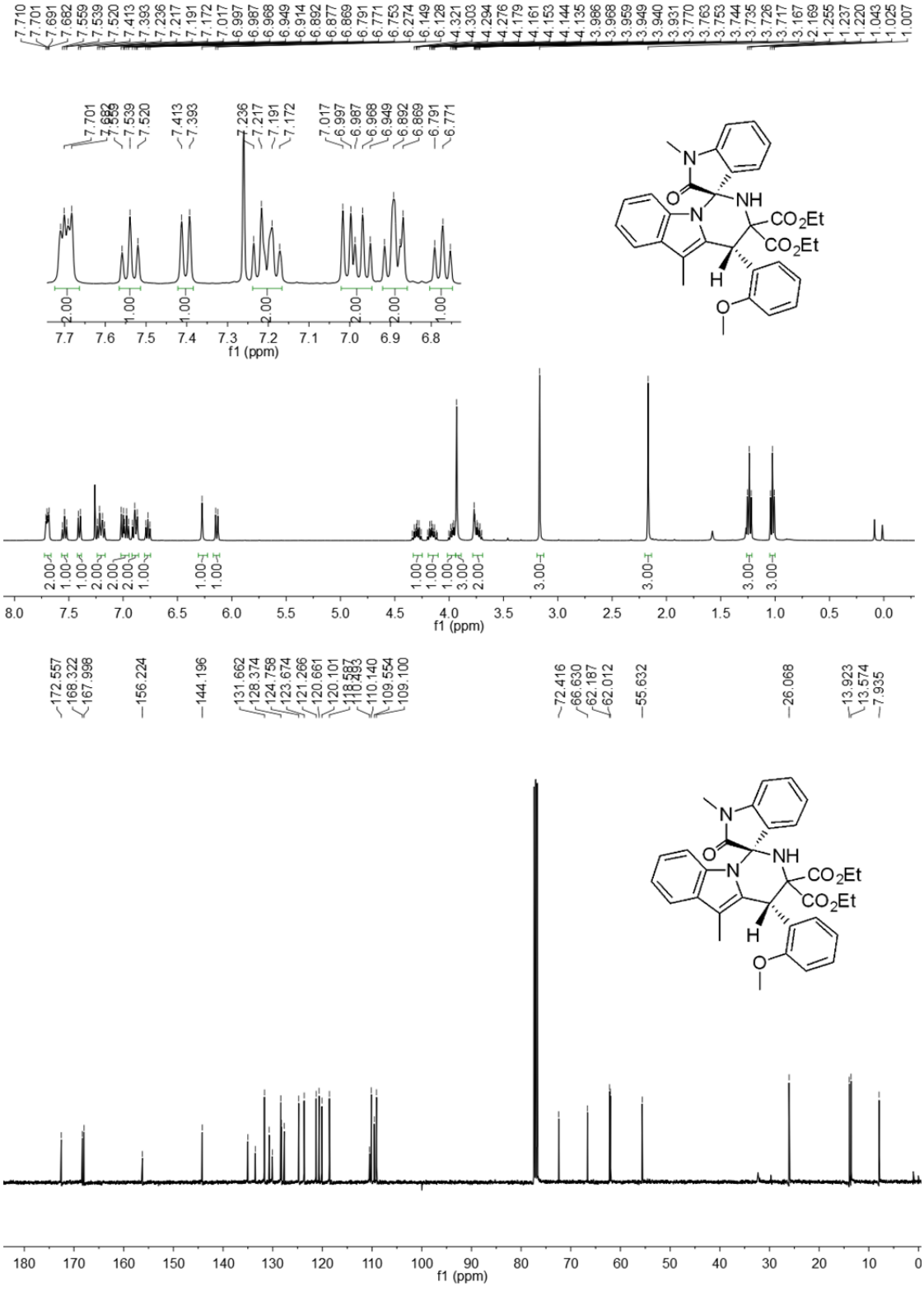
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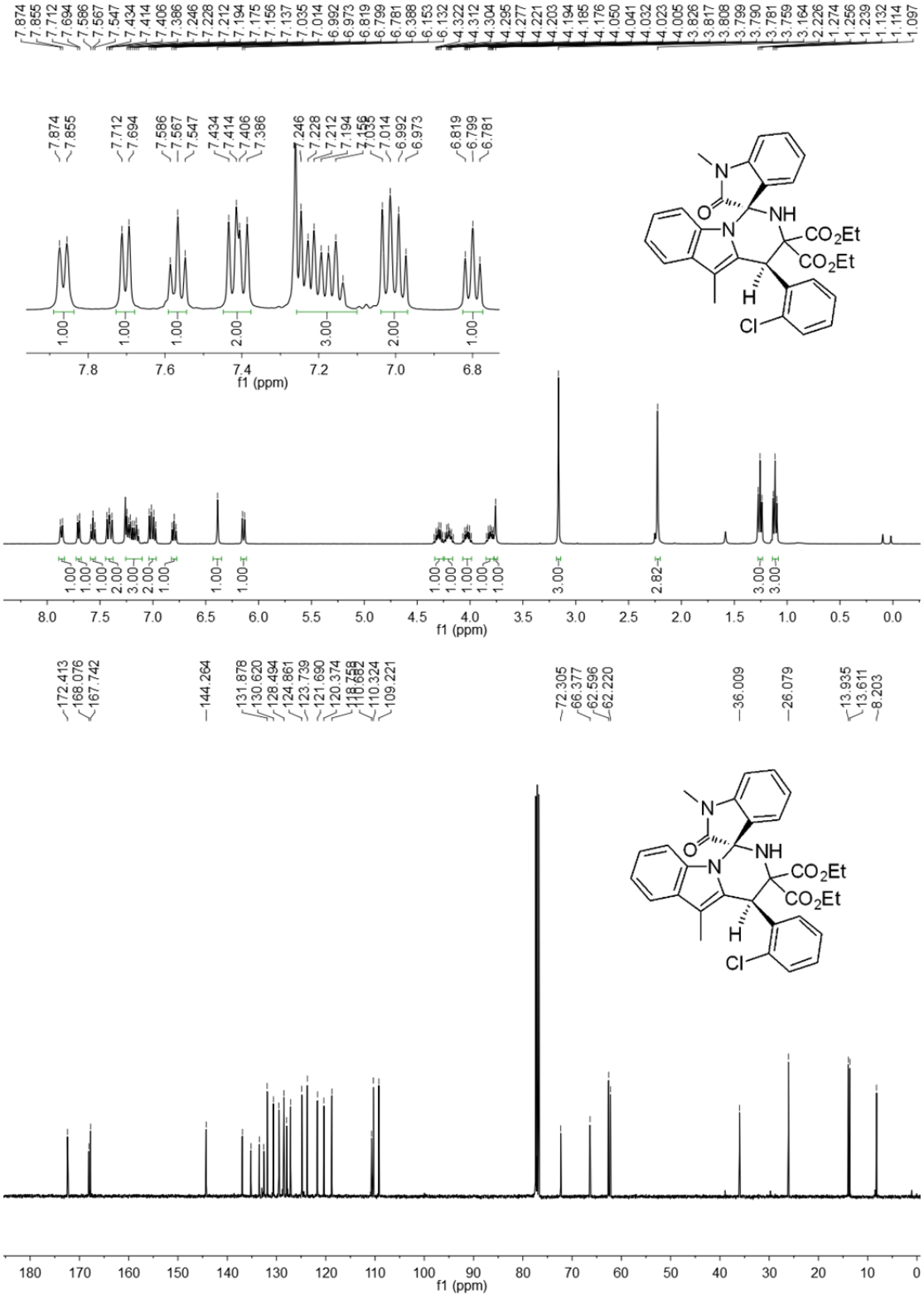
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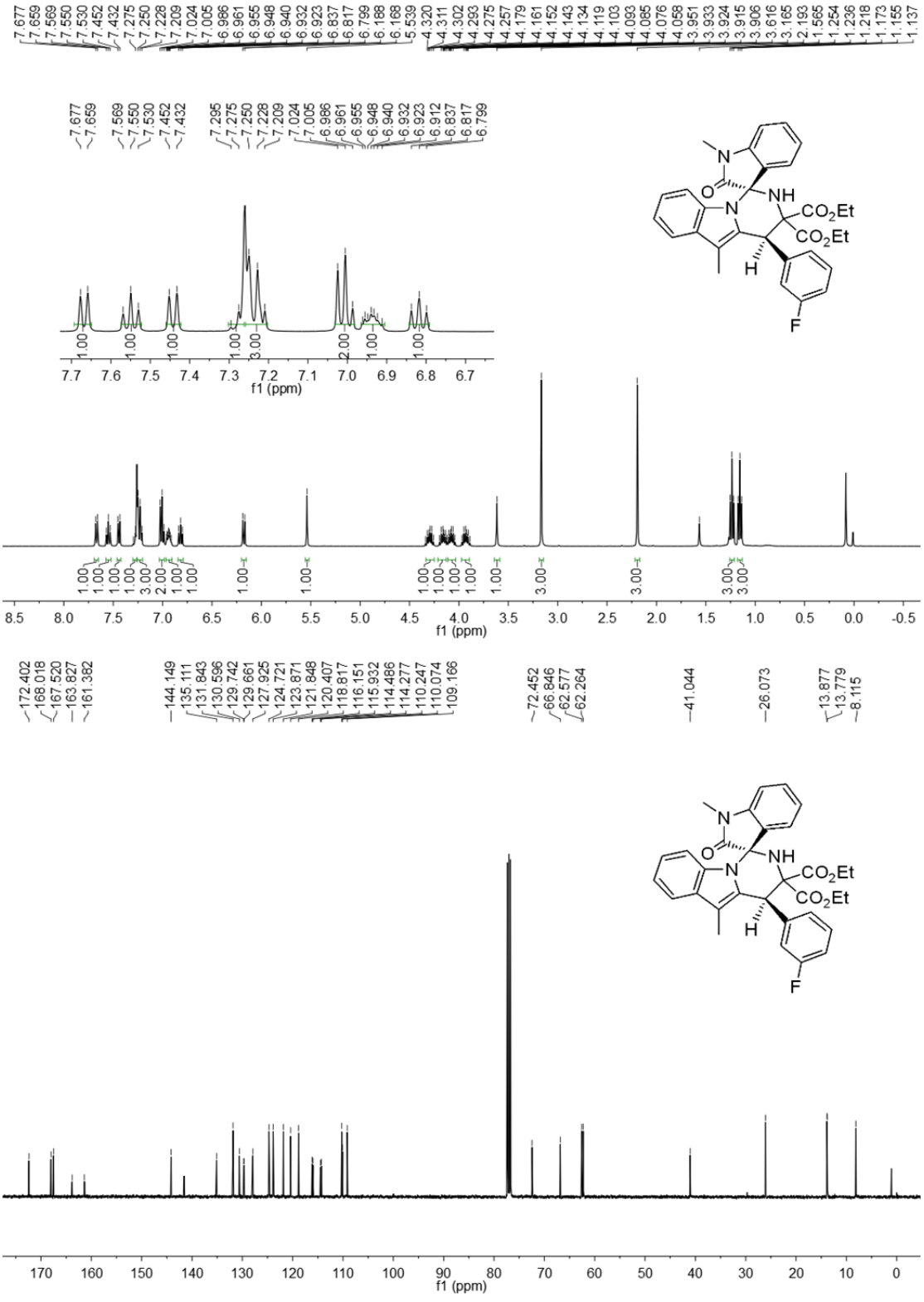
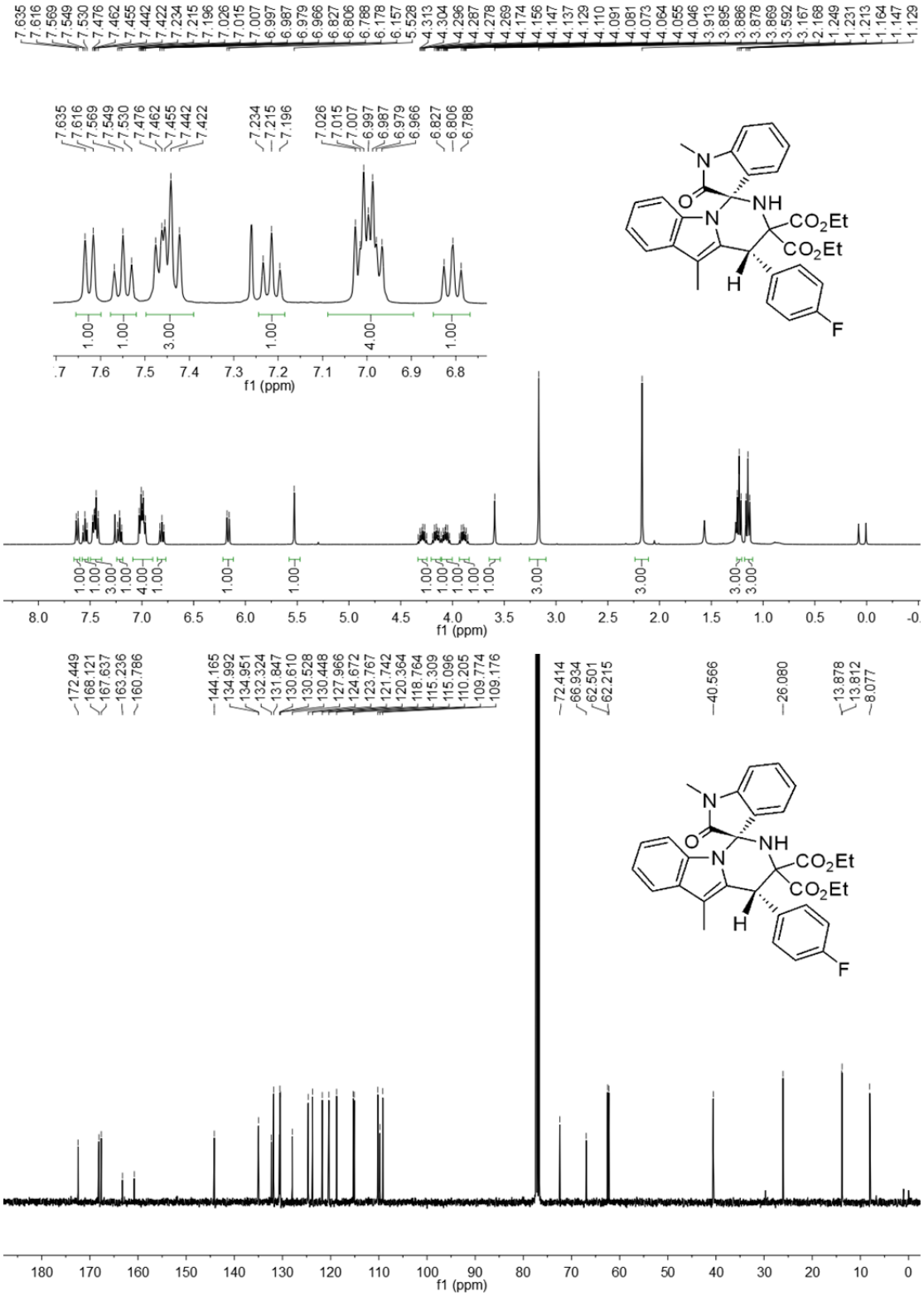


6fa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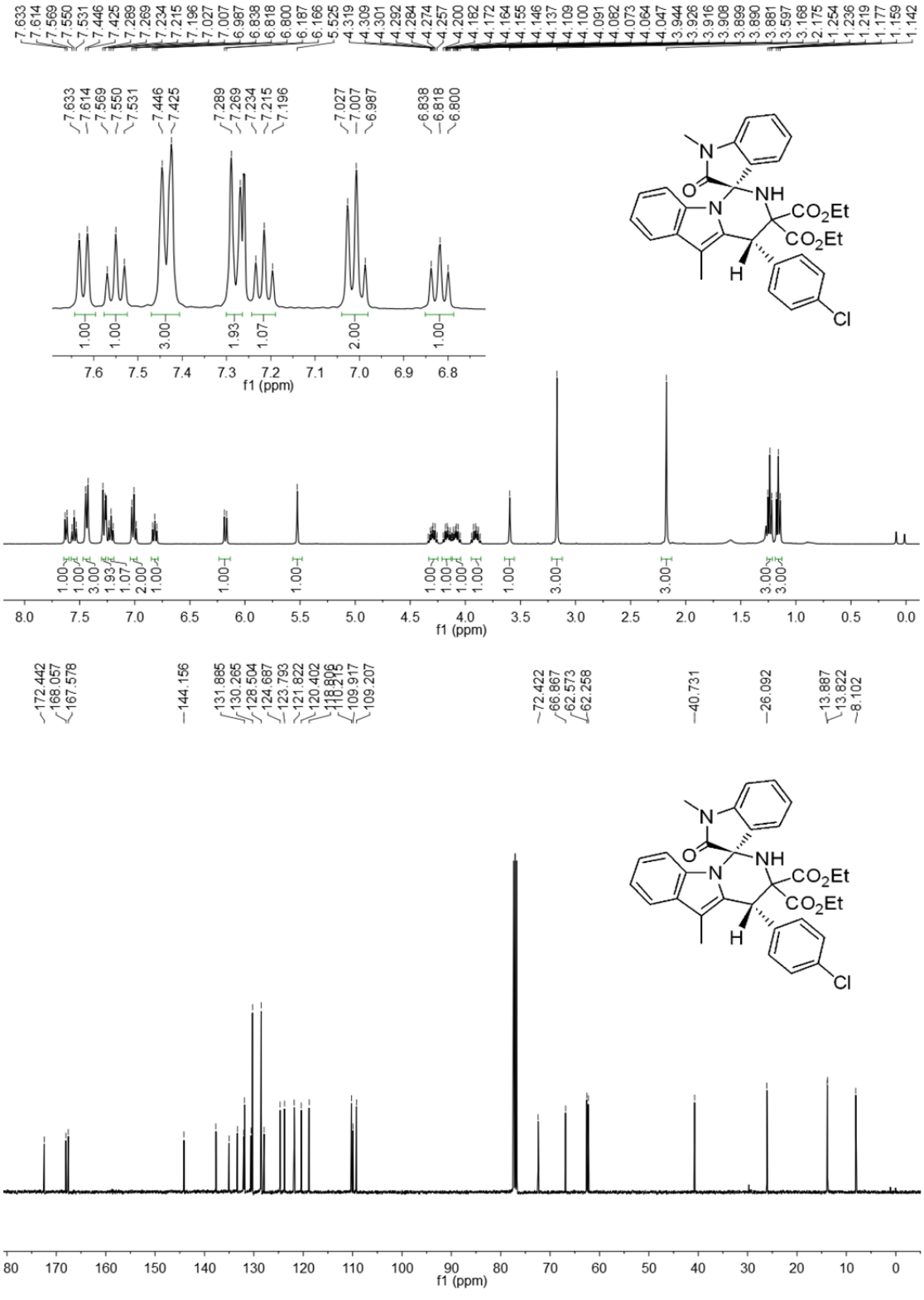
7.455
7.442
7.422
7.234
7.215
7.196
7.026
7.015
7.007
6.997
6.987
6.979
6.966
6.827
6.806
6.788
6.178
6.157
5.528
4.313
4.304
4.296
4.287
4.278
4.269
4.174
4.156
4.147
4.137
4.129
4.110
4.091
4.081
4.073
4.064
4.055
4.046
3.913
3.895
3.886
3.878
3.869
3.592
3.167
2.168
1.249
1.231
1.213
1.164
1.147
1.129
1.00
1.00
3.00
1.00
4.00
1.00
f1 (ppm)
N
O
NH
CO2Et
CO2Et
H
F
172.449
168.121
167.637
163.236
160.786
144.165
134.992
134.951
132.324
131.847
130.610
130.528
130.448
127.966
124.672
123.767
121.742
120.364
118.764
115.309
115.096
110.205
109.774
109.176
72.414
66.934
62.501
62.215
40.566
26.080
13.878
13.812
8.077
f1 (ppm)

6ga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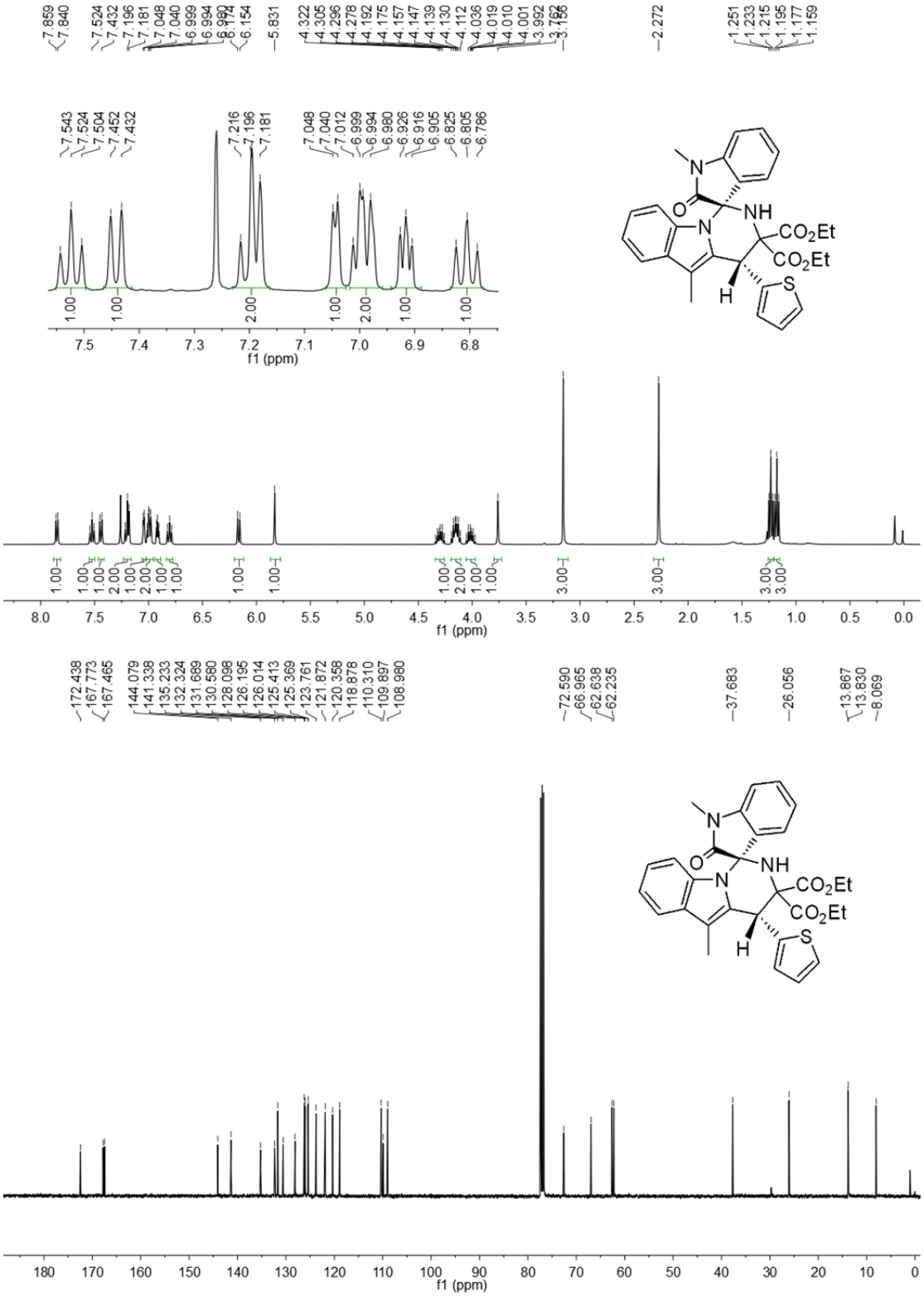
1.00 1.00 3.00 1.93 1.07 2.00 1.00
f1 (ppm)
N
O
NH
N
CO2Et
CO2Et
H
Cl
f1 (ppm)
172.442 168.057 167.578 144.156 131.885 130.265 128.504 124.687 123.793 121.822 120.402 118.806 118.215 109.917 109.207 72.422 66.867 62.573 62.258 40.731 26.092 13.887 13.822 8.102
f1 (ppm)

6ha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7.432
7.196
7.181
7.048
7.040
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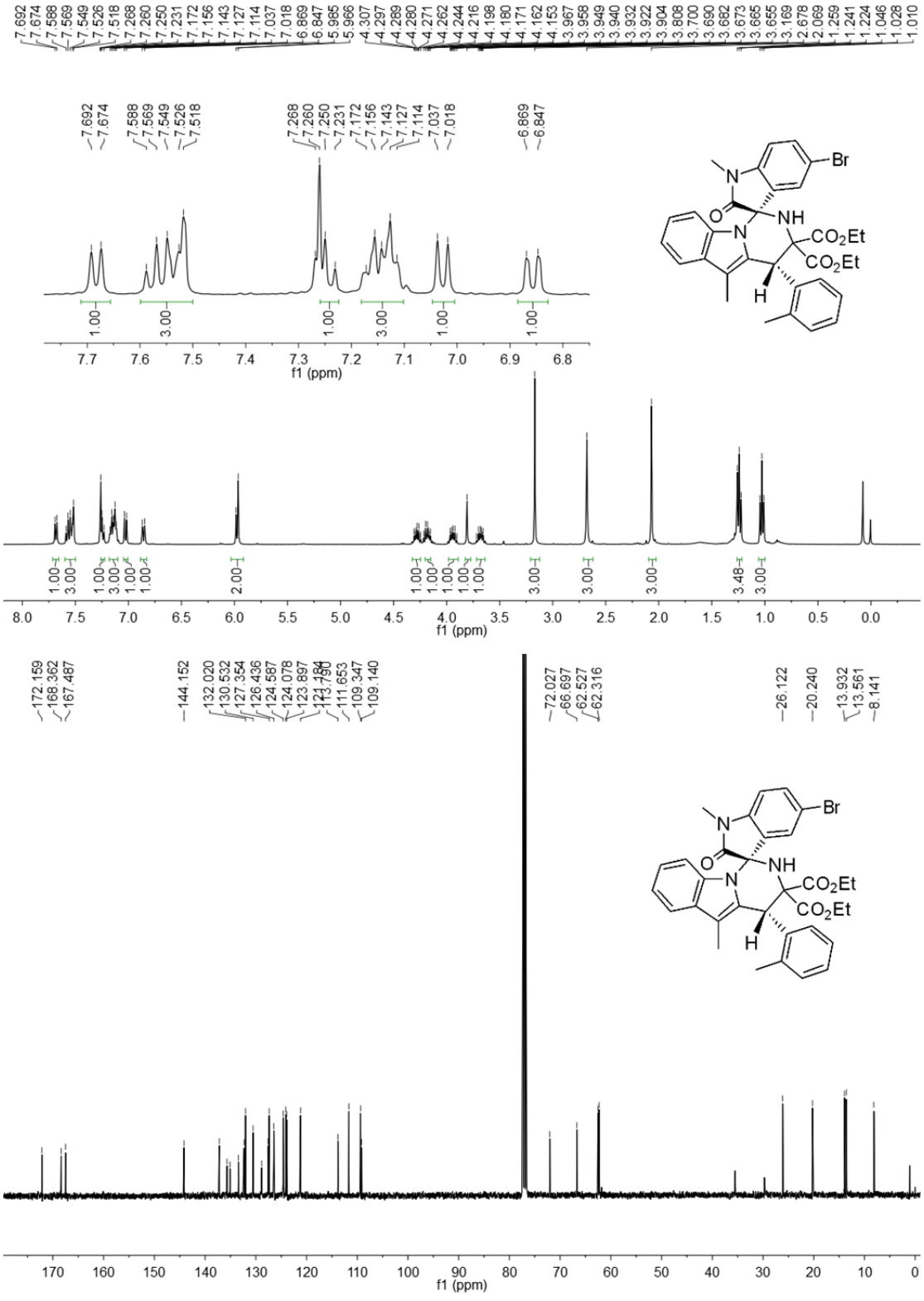
6.994
6.980
6.974
6.154
5.831
4.322
4.305
4.296
4.278
4.192
4.175
4.157
4.147
4.139
4.130
4.112
4.036
4.019
4.010
4.001
3.992
3.762
3.756
2.272
1.251
1.233
1.215
1.195
1.177
1.159
7.543
7.524
7.504
7.452
7.432
7.216
7.196
7.181
7.048
7.040
7.012
6.999
6.994
6.980
6.926
6.916
6.905
6.825
6.805
6.786
1.00
1.00
2.00
1.00
2.00
1.00
1.00
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
N
O
NH
N
CO2Et
CO2Et
H
S
1.00
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
172.438
167.773
167.465
144.079
141.338
135.233
132.324
131.689
130.580
128.098
126.195
126.014
125.413
125.369
123.761
121.872
120.358
118.878
110.310
109.897
108.980
72.590
66.965
62.638
62.235
37.683
26.056
13.867
13.830
8.069
N
O
NH
N
CO2Et
CO2Et
H
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6ia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7.588
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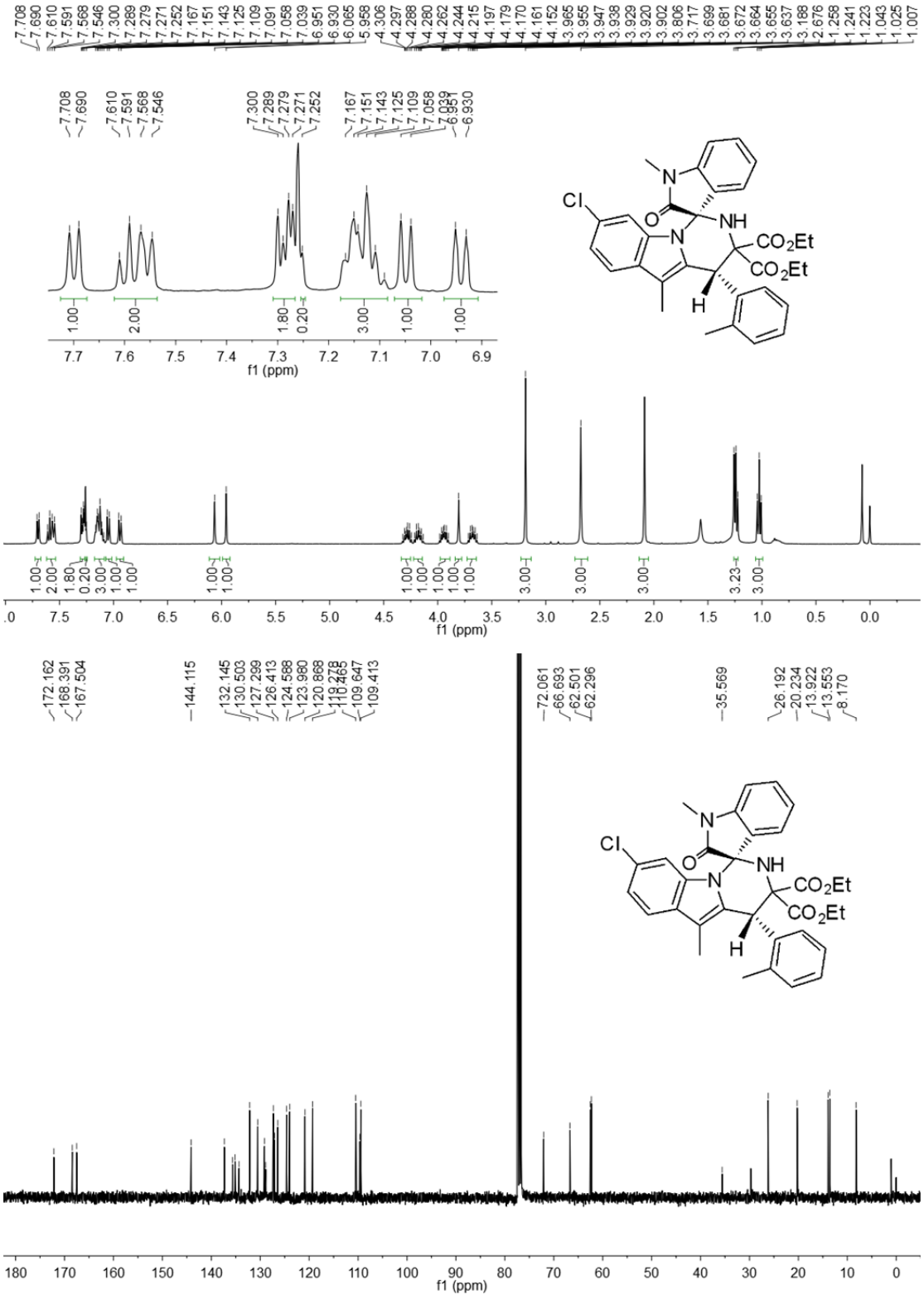
7.549
7.526
7.518
7.268
7.260
7.250
7.231
7.172
7.156
7.143
7.127
7.114
7.037
7.018
6.869
6.847
5.985
5.966
4.307
4.297
4.289
4.280
4.271
4.262
4.244
4.216
4.198
4.180
4.171
4.162
4.153
3.967
3.958
3.949
3.940
3.932
3.922
3.904
3.808
3.700
3.690
3.682
3.673
3.665
3.655
3.169
2.678
2.069
1.259
1.241
1.224
1.046
1.028
1.010
1.00
3.00
1.00
3.00
1.00
1.00
f1 (ppm)
Br
N
O
N
NH
CO2Et
CO2Et
H
1.00
3.00
1.00
3.00
1.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.48
3.00
f1 (ppm)
172.159
168.362
167.487
144.152
132.020
130.532
127.354
126.436
124.567
124.078
123.897
111.653
109.347
109.140
72.027
66.697
62.527
62.316
26.122
20.240
13.932
13.561
8.141
Br
N
O
N
NH
CO2Et
CO2Et
H
f1 (ppm)

6ja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7.568
7.546
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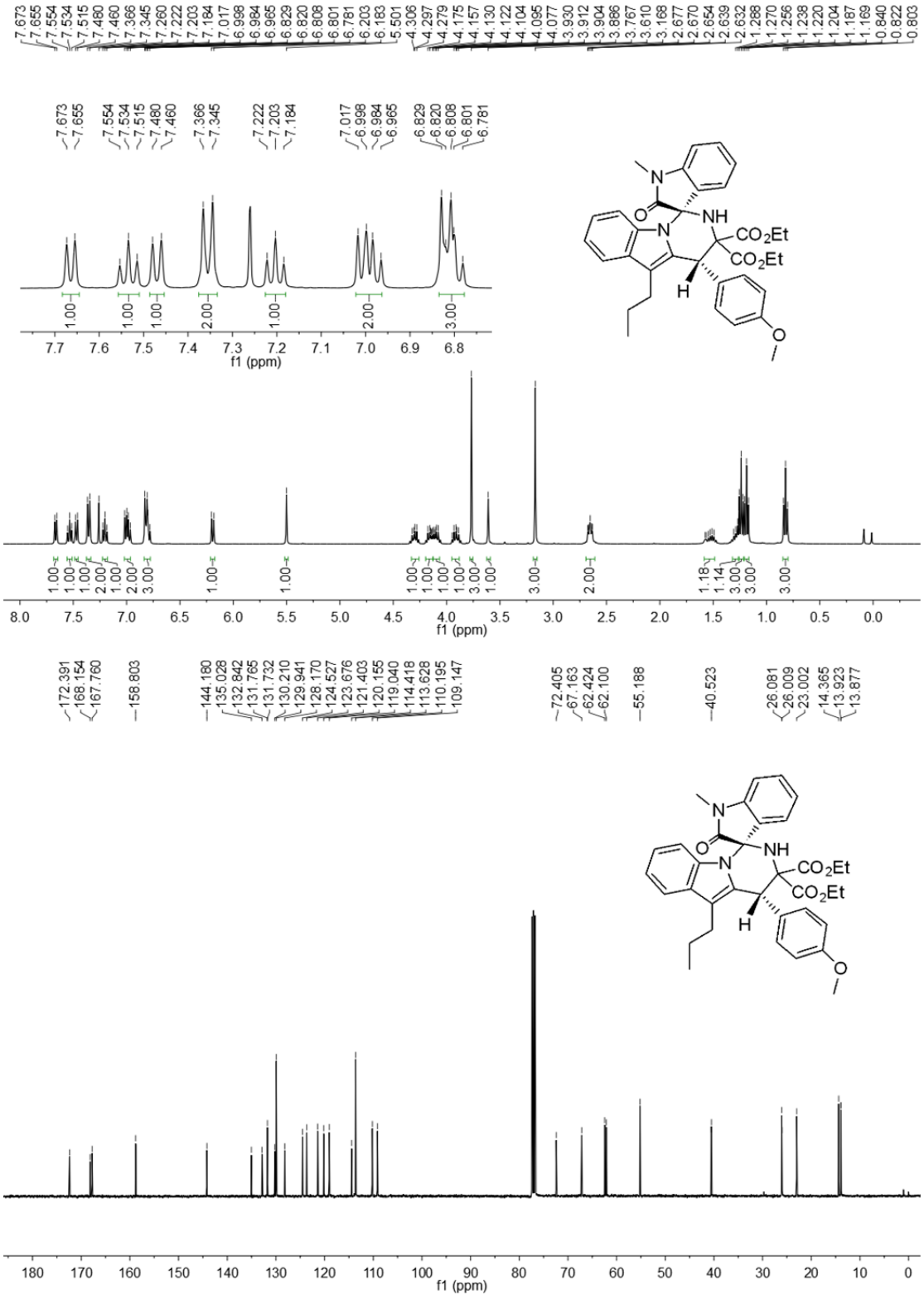
7.289
7.279
7.271
7.252
7.167
7.151
7.143
7.125
7.109
7.091
7.058
7.039
6.951
6.930
6.065
5.958
4.306
4.297
4.288
4.280
4.262
4.244
4.215
4.197
4.179
4.170
4.161
4.152
3.965
3.955
3.947
3.938
3.929
3.920
3.902
3.806
3.717
3.699
3.681
3.672
3.664
3.655
3.637
3.188
2.676
1.258
1.241
1.223
1.043
1.025
1.007
1.00
2.00
1.80
0.20
3.00
1.00
1.00
f1 (ppm)
Cl
N
O
NH
N
CO2Et
CO2Et
H
1.00
2.00
1.80
0.20
3.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.23
3.00
f1 (ppm)
172.162
168.391
167.504
144.115
132.145
130.503
127.299
126.413
124.588
123.980
120.868
110.465
109.647
109.413
72.061
66.693
62.501
62.296
35.569
26.192
20.234
13.922
13.553
8.170
Cl
N
O
NH
N
CO2Et
CO2Et
H
f1 (ppm)

6ka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7.460
7.366
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7.222
7.203
7.184
7.017
6.998
6.984
6.965
6.829
6.820
6.808
6.801
6.781
6.203
6.183
5.501
4.306
4.297
4.279
4.175
4.157
4.130
4.122
4.104
4.095
4.077
3.930
3.912
3.904
3.886
3.767
3.610
3.168
2.677
2.670
2.654
2.639
2.632
1.288
1.270
1.256
1.238
1.220
1.204
1.187
1.169
0.840
0.822
0.803
1.00
1.00
1.00
2.00
1.00
2.00
3.00
f1 (ppm)
NH
CO2Et
CO2Et
H
O
1.00
1.00
1.00
2.00
1.00
1.00
1.00
3.00
1.00
1.00
1.00
1.00
3.00
1.00
3.00
2.00
1.18
1.14
3.00
3.00
3.00
f1 (ppm)
172.391
168.154
167.760
158.803
144.180
135.028
132.842
131.765
131.732
130.210
129.941
128.170
124.527
123.676
121.403
120.155
119.040
114.418
113.628
110.195
109.147
72.405
67.163
62.424
62.100
55.188
40.523
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26.009
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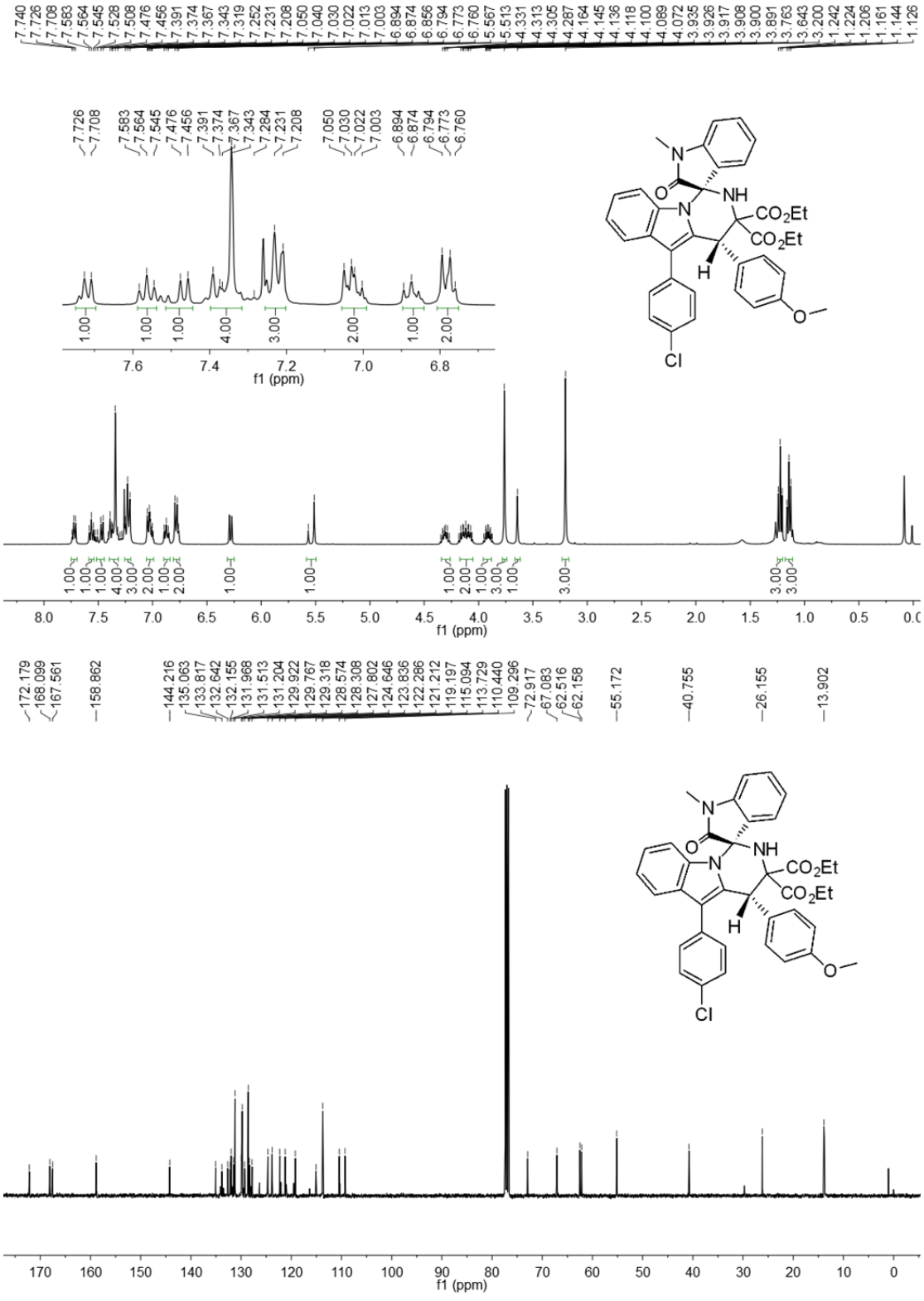
14.365
13.923
13.877
NH
CO2Et
CO2Et
H
O
f1 (ppm)

6la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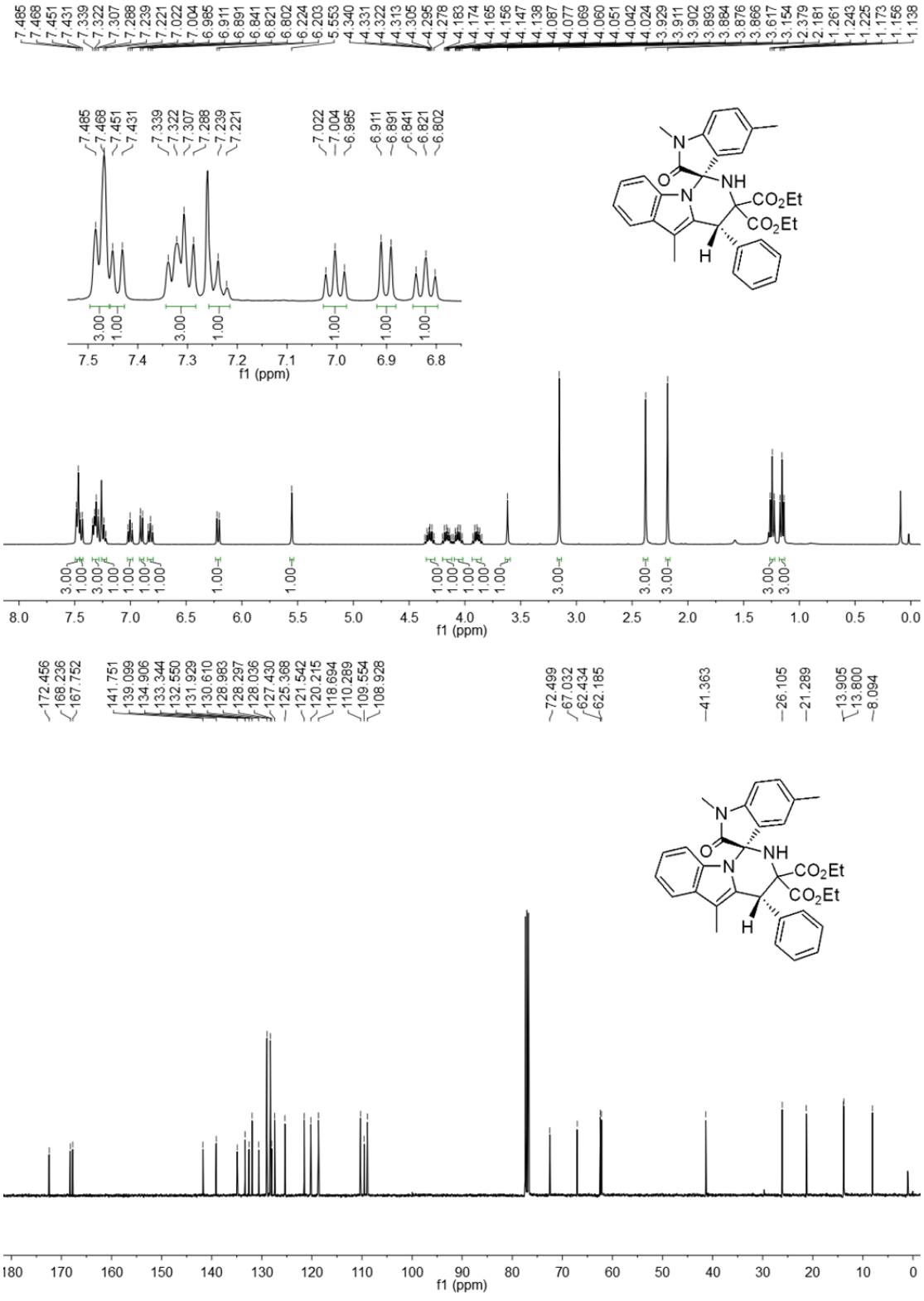
7.726 7.708 7.583 7.564 7.545 7.476 7.456 7.391 7.374 7.367 7.343 7.284 7.231 7.208 7.050 7.030 7.022 7.003 6.894 6.874 6.794 6.773 6.760
1.00 1.00 1.00 4.00 3.00 2.00 1.00 2.00
7.6 7.4 7.2 7.0 6.8
f1 (ppm)
N NH O N CO2Et CO2Et H O Cl
1.00 1.00 1.00 4.00 3.00 2.00 1.00 2.00 1.00 1.00 2.00 1.00 3.00 3.00 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
172.179 168.099 167.561 158.862 144.216 135.063 133.817 132.642 132.155 131.968 131.513 131.204 129.922 129.767 129.318 128.574 128.308 127.802 124.646 123.836 122.286 121.212 119.197 115.094 113.729 110.440 109.296 72.917 67.083 62.516 62.158 55.172 40.755 26.155 13.902
N NH O N CO2Et CO2Et H O Cl
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

6ab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7.431
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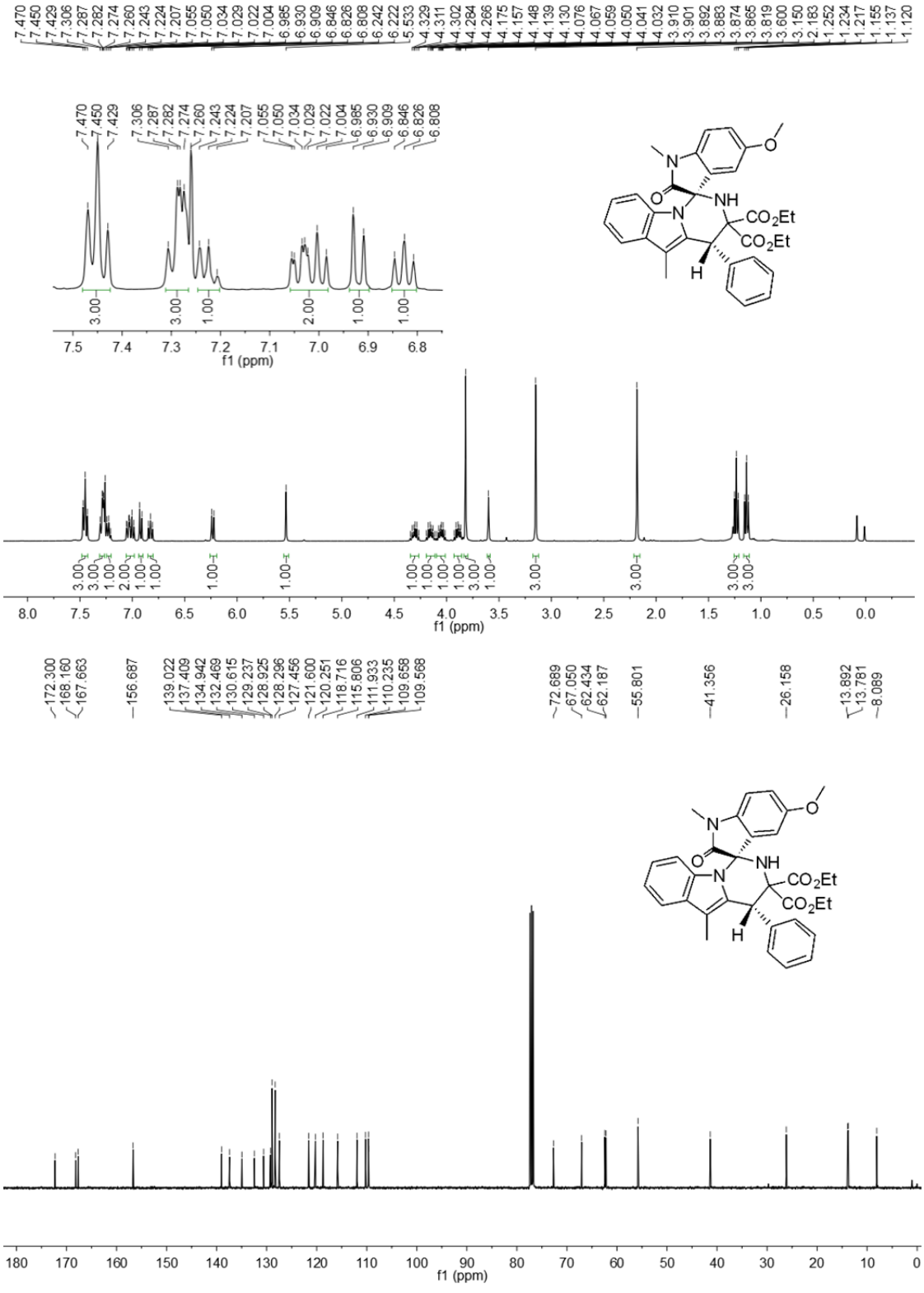
7.322
7.307
7.288
7.239
7.221
7.022
7.004
6.985
6.911
6.891
6.841
6.821
6.802
6.224
6.203
5.553
4.340
4.331
4.322
4.313
4.305
4.295
4.278
4.183
4.174
4.165
4.156
4.147
4.138
4.087
4.077
4.069
4.060
4.051
4.042
4.024
3.929
3.911
3.902
3.893
3.884
3.876
3.866
3.617
3.154
2.379
2.181
1.261
1.243
1.225
1.173
1.156
1.138
3.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
N
O
NH
N
CO2Et
CO2Et
H
3.00
1.00
3.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
172.456
168.236
167.752
141.751
139.099
134.906
133.344
132.550
131.929
130.610
128.983
128.297
128.036
127.430
125.368
121.542
120.215
118.694
110.289
109.554
108.928
72.499
67.032
62.434
62.185
41.363
26.105
21.289
13.905
13.800
8.094
N
O
NH
N
CO2Et
CO2Et
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6ac


7.470 7.450 7.429 7.306 7.287 7.282 7.274 7.260 7.243 7.224 7.207 7.055 7.050 7.034 7.029 7.022 7.004 6.985 6.930 6.909 6.846 6.826 6.808 6.242 6.222 5.533 4.329 4.311 4.302 4.284 4.266 4.175 4.157 4.148 4.139 4.130 4.076 4.067 4.059 4.050 4.041 4.032 3.910 3.901 3.892 3.883 3.874 3.865 3.819 3.600 3.150 2.183 1.252 1.234 1.217 1.155 1.137 1.120
3.00 3.00 1.00 2.00 1.00 1.00
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
O N NH CO2Et CO2Et H
3.00 3.00 1.00 2.00 1.00 1.00 1.00 1.00 1.00 1.00 3.00 1.00 3.00 3.00 3.00 3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
172.300 168.160 167.663 156.687 139.022 137.409 134.942 132.469 130.615 129.237 128.925 128.296 127.456 121.600 120.251 118.716 115.806 111.933 110.235 109.658 109.568 72.689 67.050 62.434 62.187 55.801 41.356 26.158 13.892 13.781 8.089
O N NH CO2Et CO2Et H
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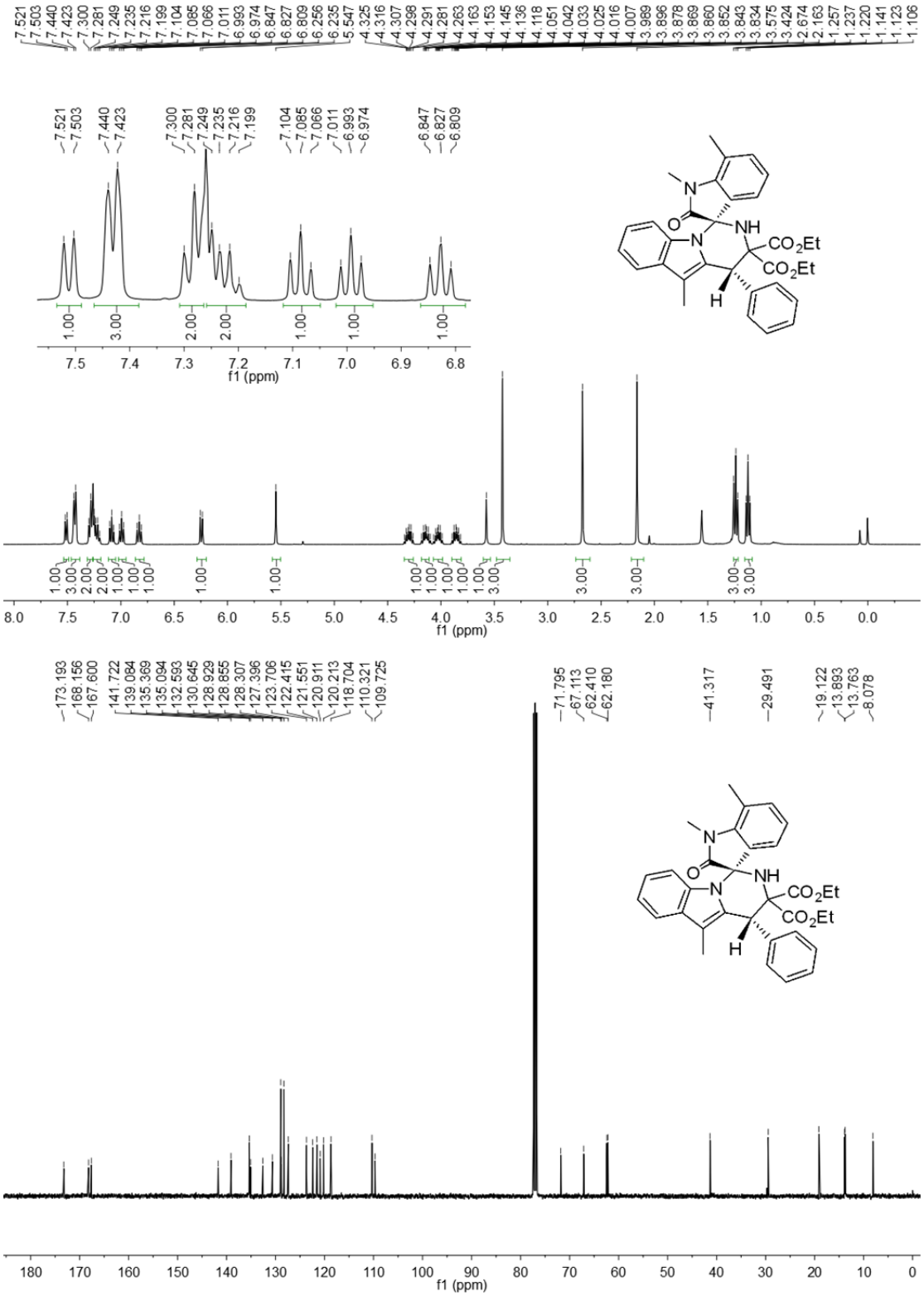
f1 (ppm)

6ad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7.235
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7.199
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7.085
7.066
7.011
6.993
6.974
6.847
6.827
6.809
6.256
6.235
5.547
4.325
4.316
4.307
4.298
4.291
4.281
4.263
4.163
4.153
4.145
4.136
4.118
4.051
4.042
4.033
4.025
4.016
4.007
3.989
3.896
3.878
3.869
3.860
3.852
3.843
3.834
3.575
3.424
2.674
2.163
1.257
1.237
1.220
1.141
1.123
1.106
1.00
3.00
2.00
2.00
1.00
1.00
1.00
f1 (ppm)
N
O
NH
CO2Et
CO2Et
H
1.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)
173.193
168.156
167.600
141.722
139.084
135.369
135.094
132.593
130.645
128.929
128.855
128.307
127.396
123.706
122.415
121.551
120.911
120.213
118.704
110.321
109.725
71.795
67.113
62.410
62.180
41.317
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13.893
13.763
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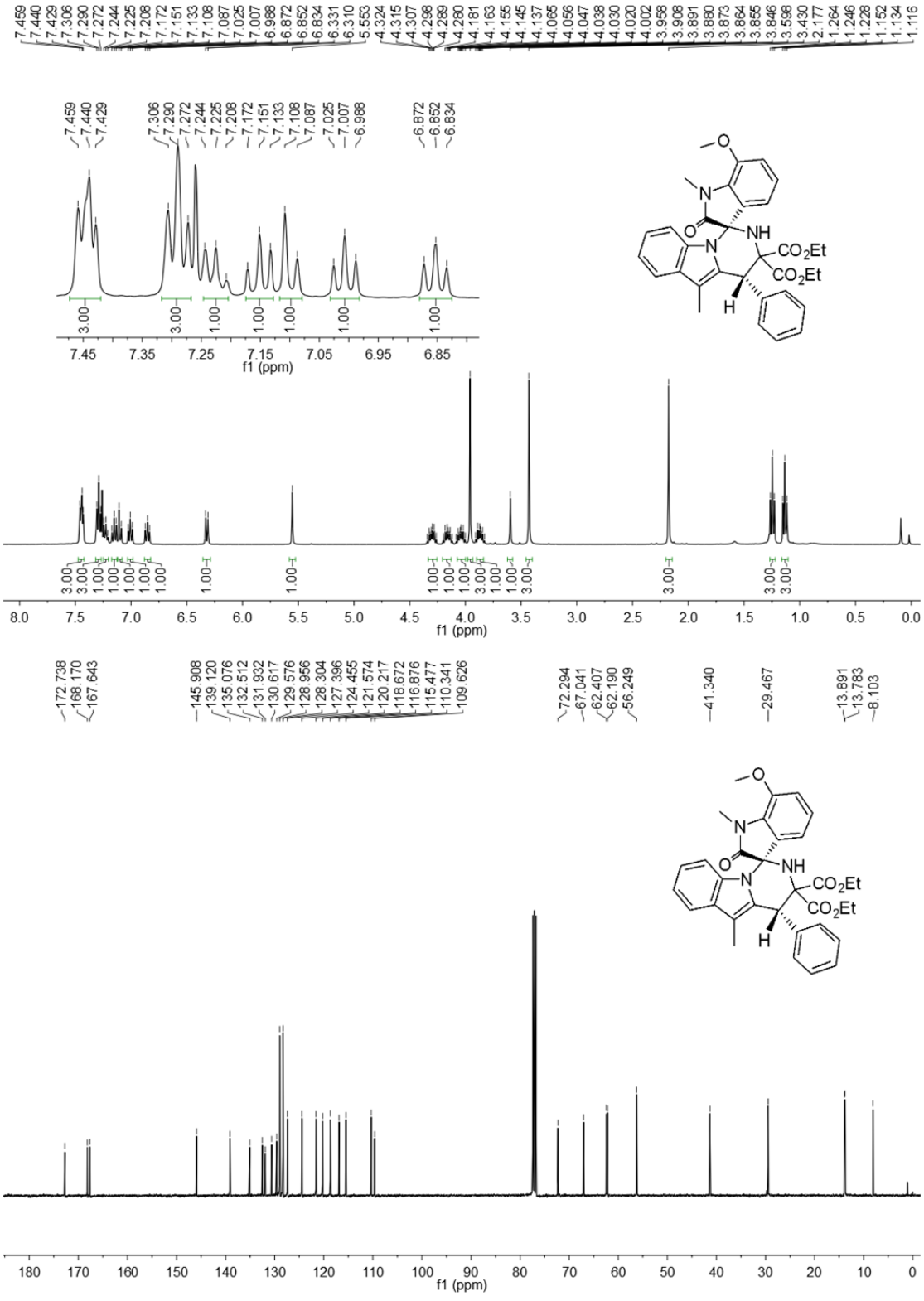
N
O
NH
CO2Et
CO2Et
H
f1 (ppm)

6ae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7.208
7.172
7.151
7.133
7.108
7.087
7.025
7.007
6.988
6.872
6.852
6.834
6.331
6.310
5.553
4.324
4.315
4.307
4.298
4.289
4.280
4.181
4.163
4.155
4.145
4.137
4.065
4.056
4.047
4.038
4.030
4.020
4.002
3.958
3.908
3.891
3.880
3.873
3.864
3.855
3.846
3.598
3.430
2.177
1.264
1.246
1.228
1.152
1.134
1.116
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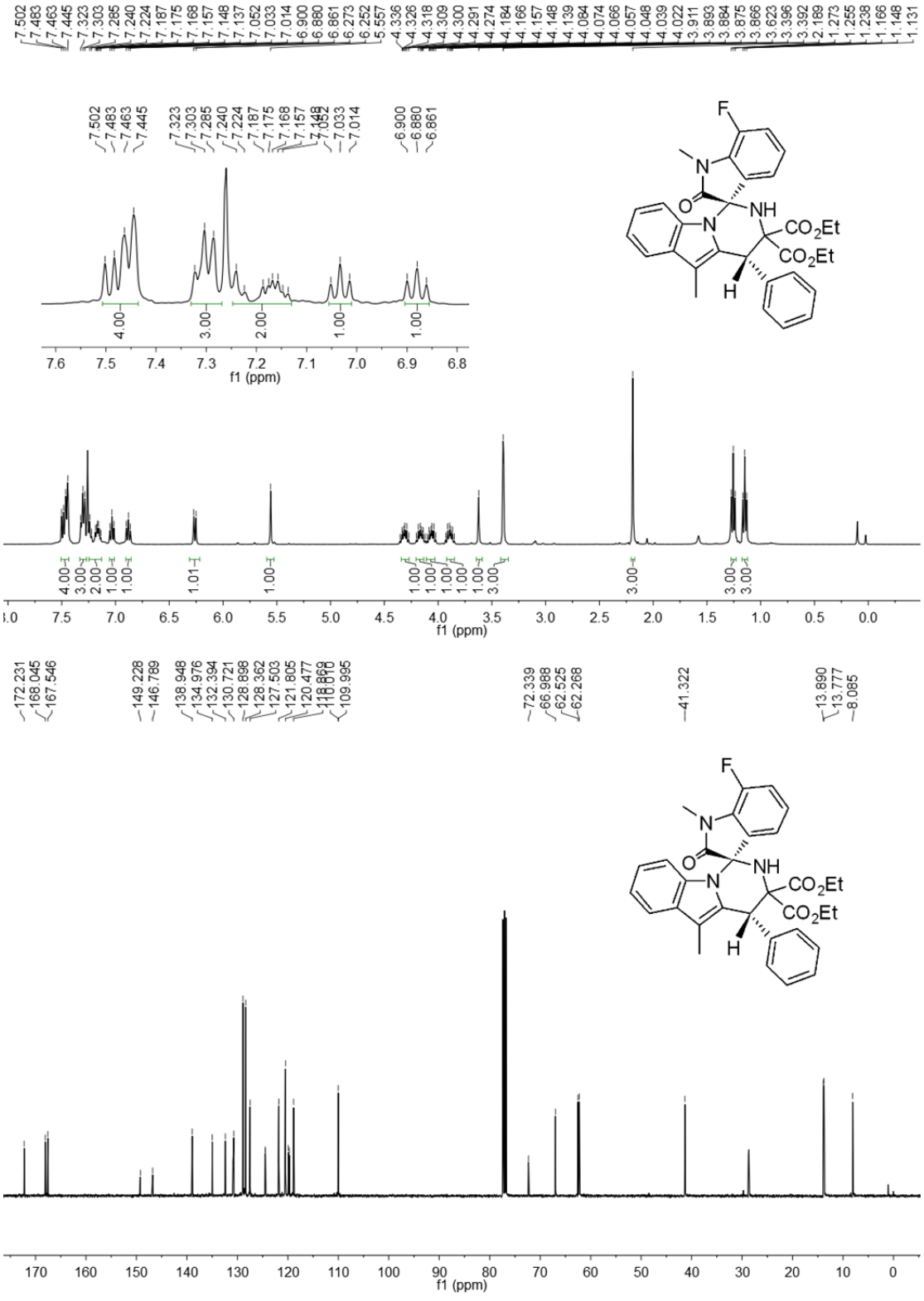
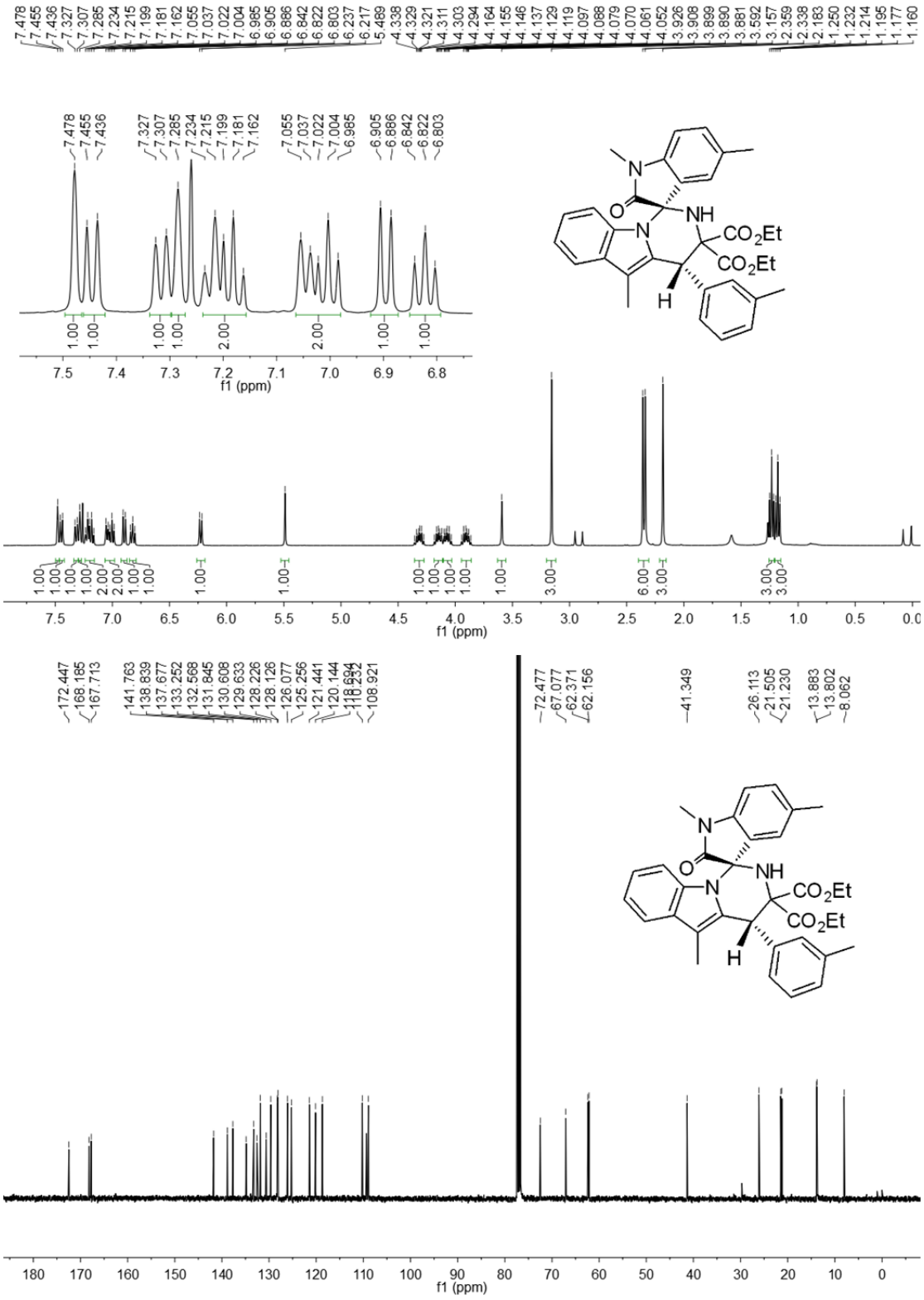
3.00
1.00
1.00
1.00
1.00
1.00
7.45
7.35
7.25
7.15
7.05
6.95
6.85
f1 (ppm)
O
N
O
NH
N
CO2Et
CO2Et
H
3.00
3.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
172.738
168.170
167.643
145.908
139.120
135.076
132.512
131.932
130.617
129.576
128.956
128.304
127.396
124.455
121.574
120.217
118.672
116.876
115.477
110.341
109.626
72.294
67.041
62.407
62.190
56.249
41.340
29.467
13.891
13.783
8.103
O
N
O
NH
N
CO2Et
CO2Et
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

6af

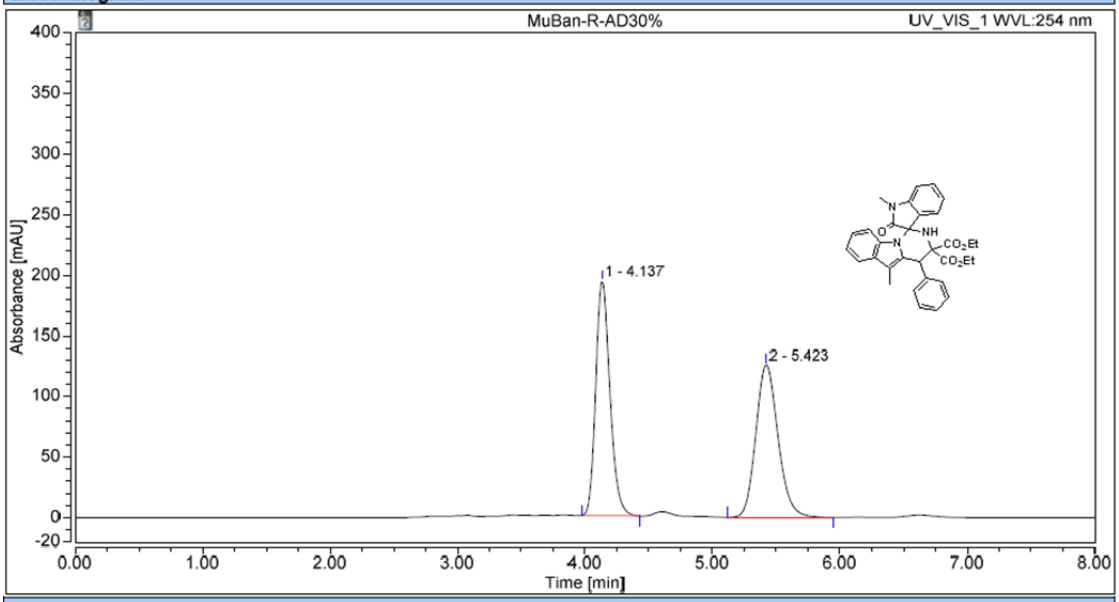


6mb


7.478 7.455 7.436 7.327 7.307 7.285 7.234 7.215 7.199 7.181 7.162 7.055 7.037 7.022 7.004 6.985 6.905 6.886 6.842 6.822 6.803 6.237 5.489 4.338 4.329 4.321 4.311 4.303 4.294 4.164 4.155 4.146 4.137 4.129 4.119 4.097 4.088 4.079 4.070 4.061 4.052 3.926 3.908 3.899 3.890 3.881 3.592 3.157 2.359 2.338 2.183 1.250 1.232 1.214 1.195 1.177 1.160
1.00 1.00 1.00 1.00 2.00 2.00 1.00 1.00
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
N
O
NH
N
CO2Et
CO2Et
H
1.00 1.00 1.00 1.00 2.00 2.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 3.00 6.00 3.00 3.00 3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
172.447 168.185 167.713 141.763 138.839 137.677 133.252 132.568 131.845 130.608 129.633 128.226 128.126 126.077 125.256 121.441 120.144 118.694 118.232 108.921 72.477 67.077 62.371 62.156 41.349 26.113 21.505 21.230 13.883 13.802 8.062
N
O
NH
N
CO2Et
CO2Et
H
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

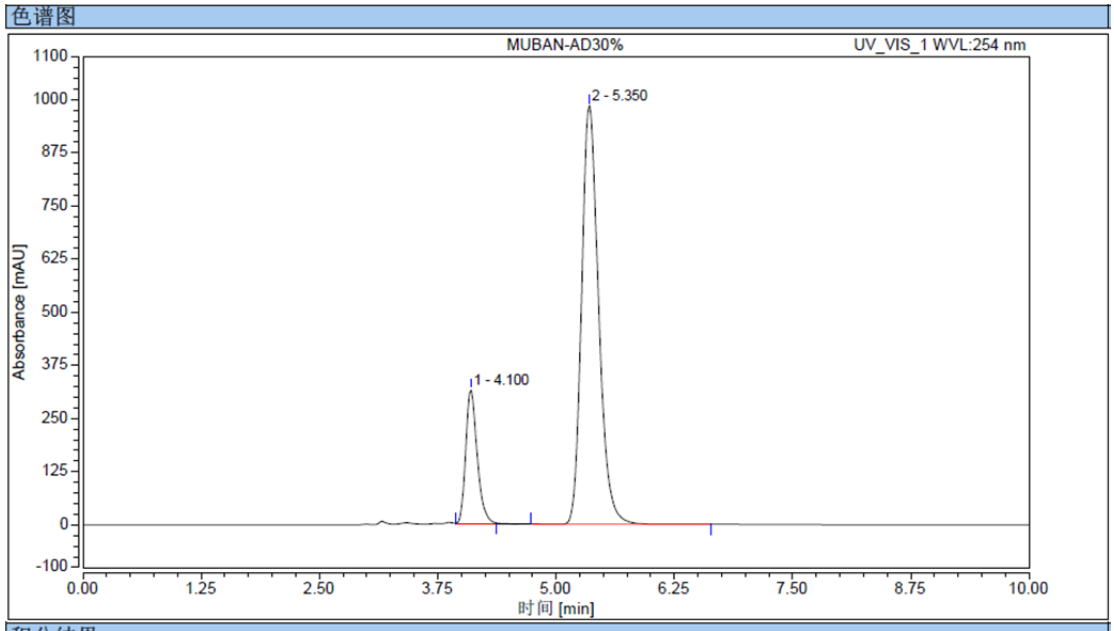
5. HPLC spectra of products 6

6aa



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.137	25.062	193.620	49.67	60.62	n.a.
2		5.423	25.399	125.760	50.33	39.38	n.a.
Total:			**50.461**	**319.379**	**100.00**	**100.00**	

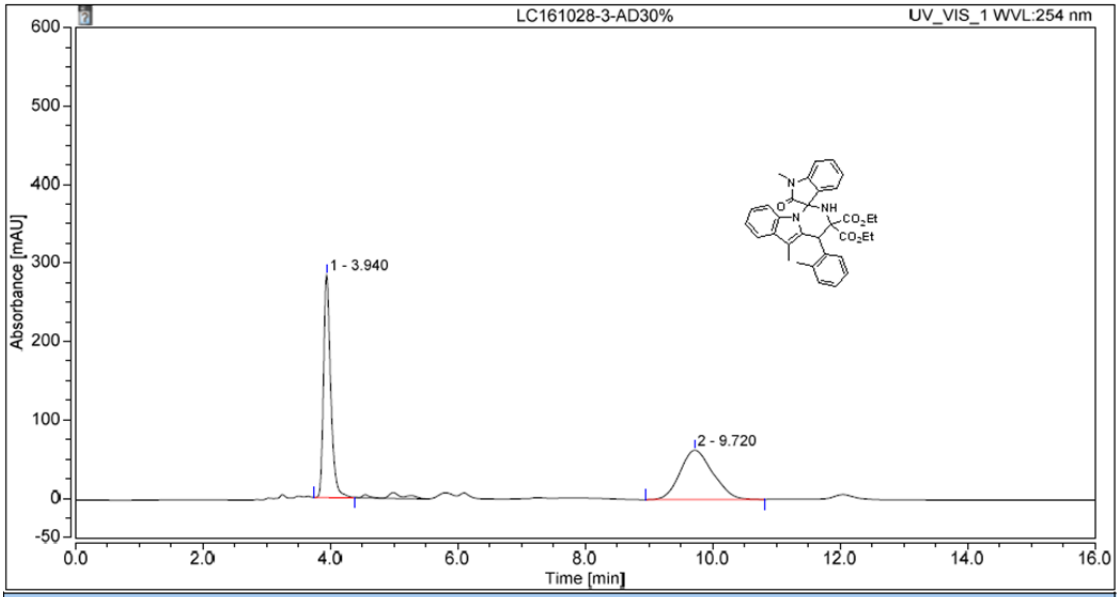


积分结果

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		4.100	44.503	316.299	17.82	24.32	n.a.
2		5.350	205.292	984.392	82.18	75.68	n.a.
总和:			**249.795**	**1300.691**	**100.00**	**100.00**	

ent-6ba

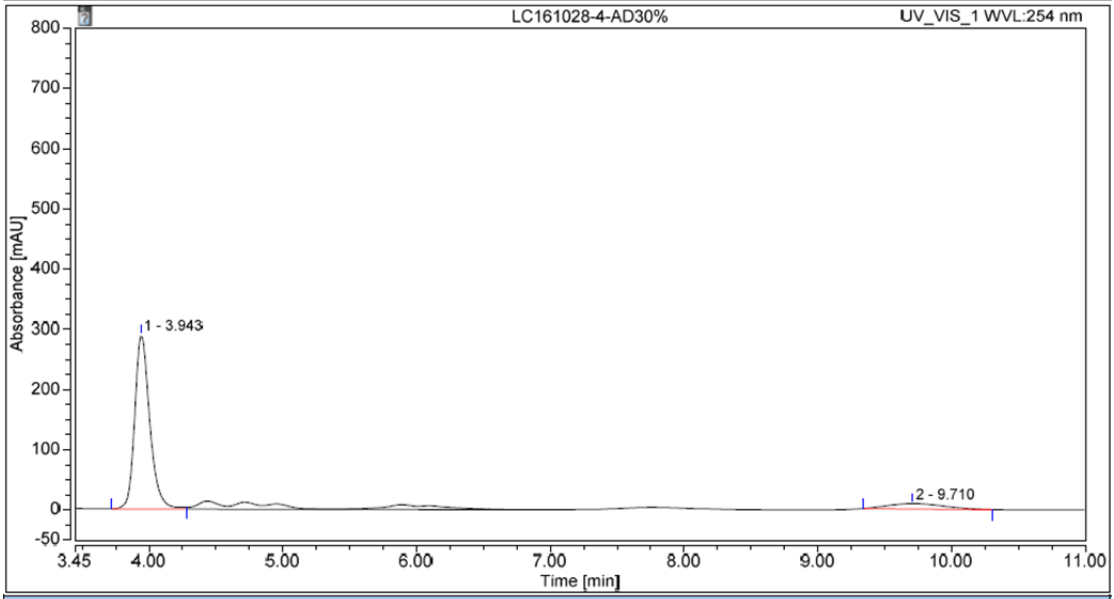
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.940	37.224	283.807	50.01	81.89	n.a.
2		9.720	37.204	62.761	49.99	18.11	n.a.
Total:			**74.429**	**346.568**	**100.00**	**100.00**	

Chromatogram

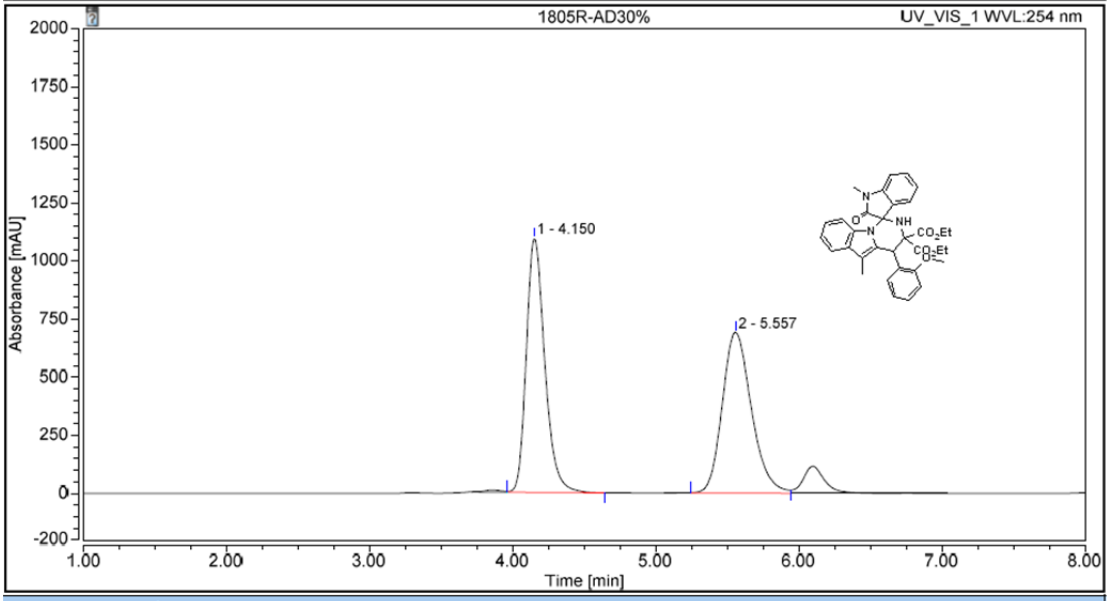


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.943	37.679	288.723	89.98	97.08	n.a.
2		9.710	4.194	8.682	10.02	2.92	n.a.
Total:			**41.873**	**297.405**	**100.00**	**100.00**	

6ca

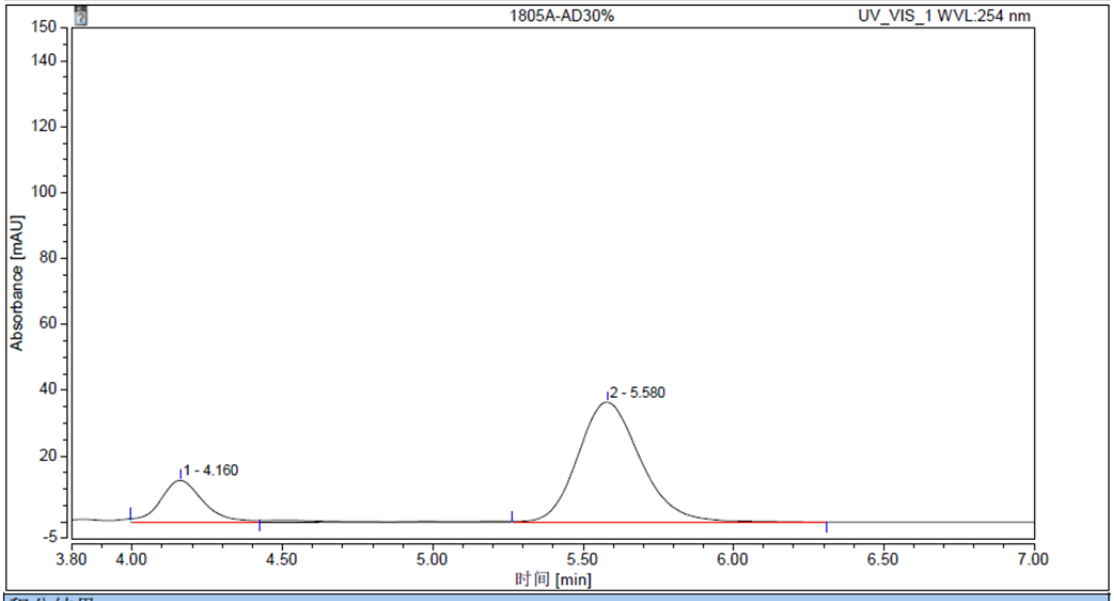
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.150	163.616	1092.764	50.06	61.22	n.a.
2		5.557	163.203	692.311	49.94	38.78	n.a.
Total:			**326.819**	**1785.076**	**100.00**	**100.00**	

色谱图

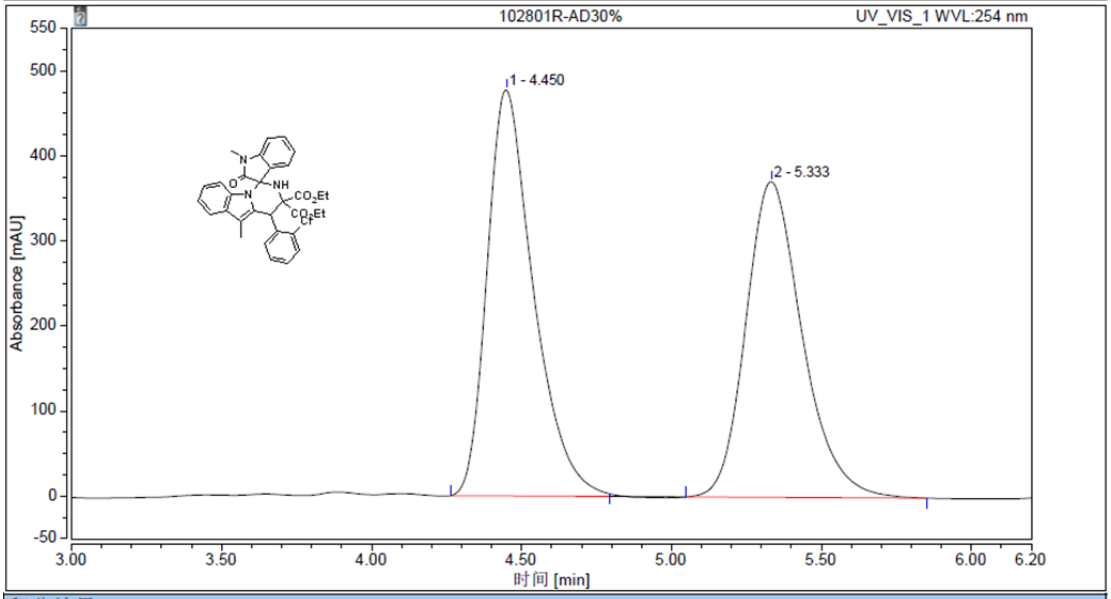


积分结果

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		4.160	2.083	12.725	19.16	25.89	n.a.
2		5.580	8.788	36.430	80.84	74.11	n.a.
总和:			**10.871**	**49.154**	**100.00**	**100.00**	

***ent*-6da**

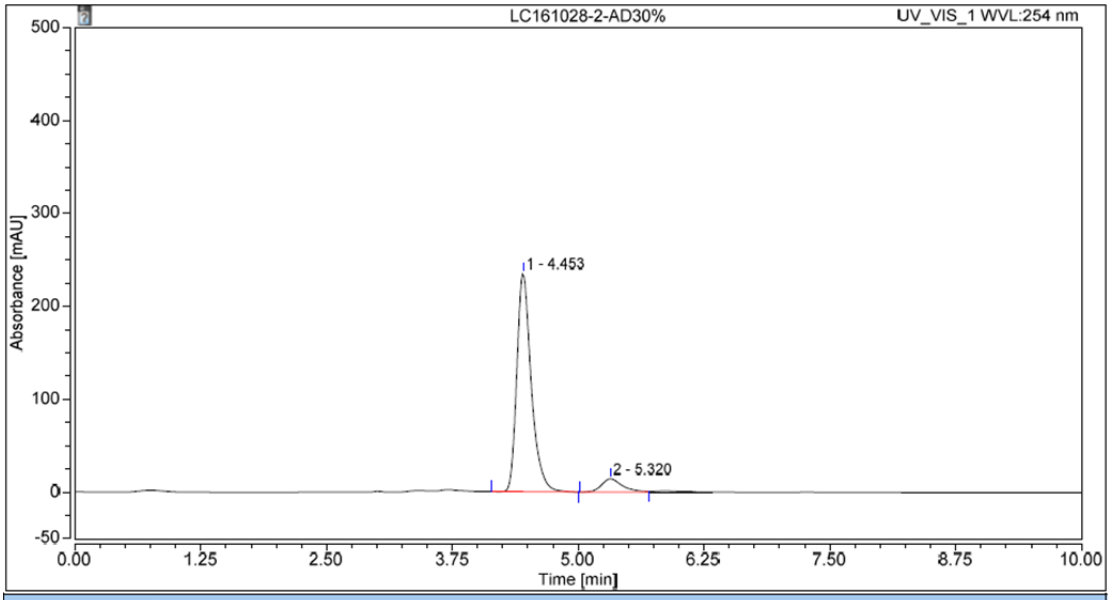
色谱图



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		4.450	85.581	477.576	51.39	56.27	n.a.
2		5.333	80.953	371.123	48.61	43.73	n.a.
总和:			**166.535**	**848.699**	**100.00**	**100.00**	

Chromatogram

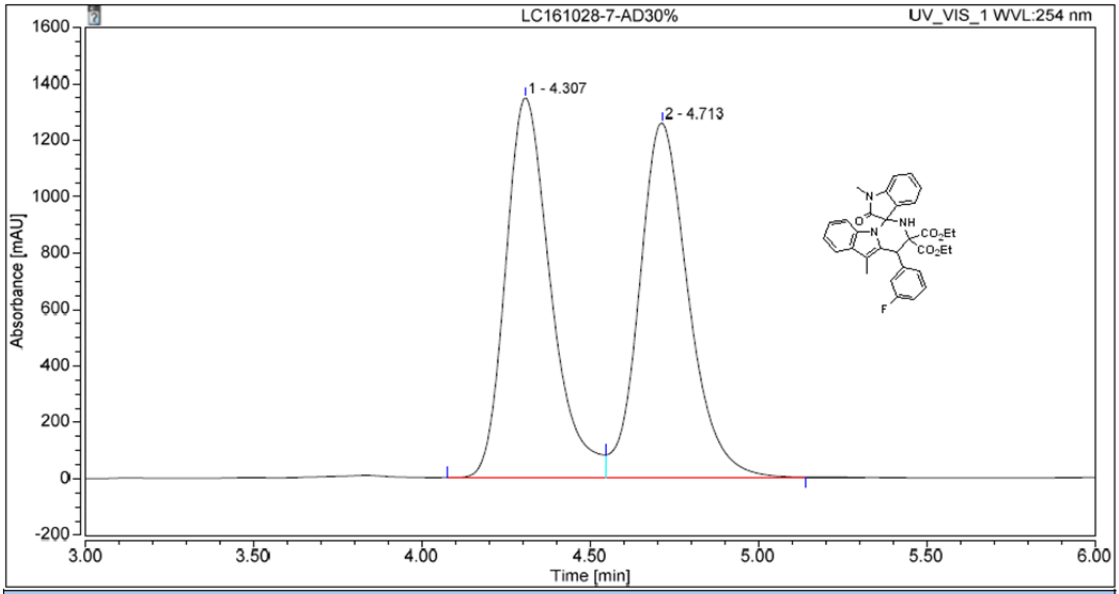


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.453	38.963	235.020	91.94	94.28	n.a.
2		5.320	3.414	14.250	8.06	5.72	n.a.
Total:			**42.377**	**249.270**	**100.00**	**100.00**	

ent-6ea

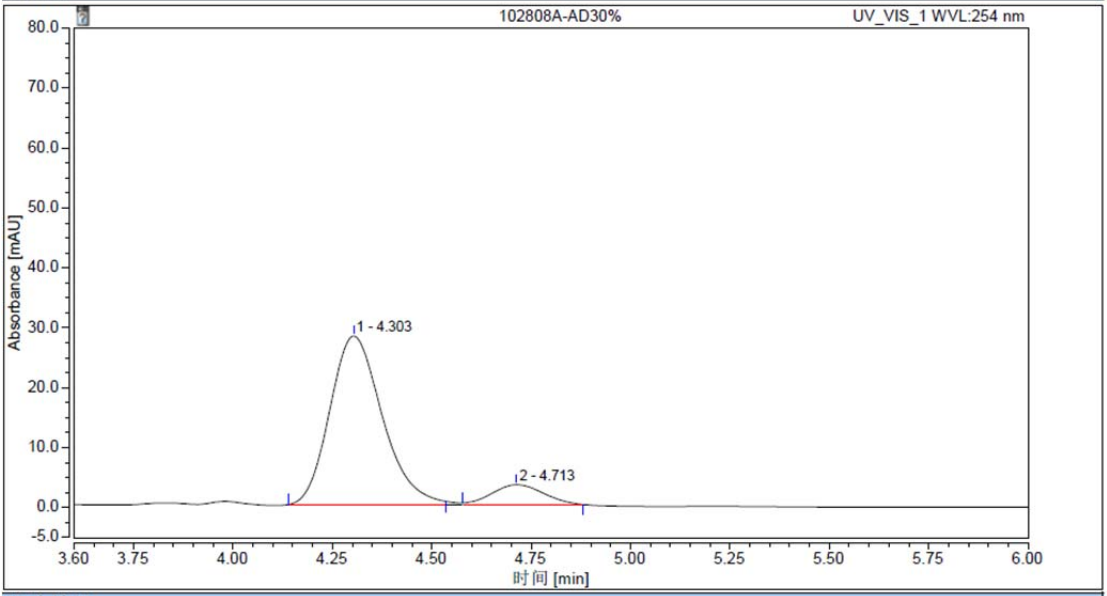
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.307	208.578	1346.872	49.64	51.72	n.a.
2		4.713	211.610	1257.443	50.36	48.28	n.a.
Total:			**420.188**	**2604.315**	**100.00**	**100.00**	

色谱图

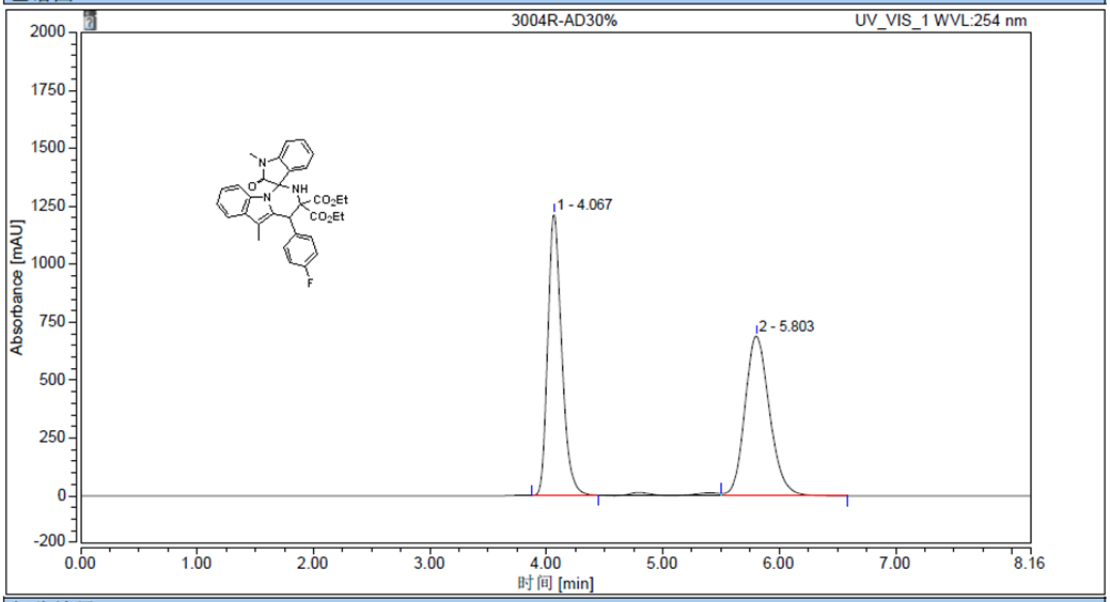


积分结果

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		4.303	4.300	28.169	89.64	89.46	n.a.
2		4.713	0.497	3.317	10.36	10.54	n.a.
总和:			**4.797**	**31.487**	**100.00**	**100.00**	

6fa

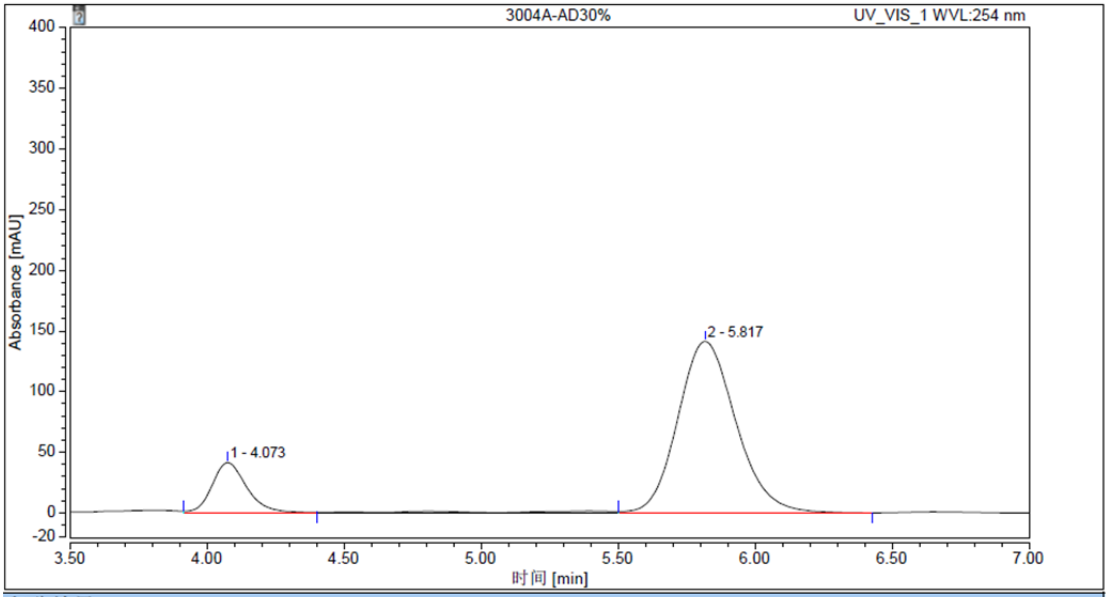
色谱图



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		4.067	168.736	1215.983	49.94	63.78	n.a.
2		5.803	169.160	690.452	50.06	36.22	n.a.
总和:			**337.895**	**1906.435**	**100.00**	**100.00**	

色谱图

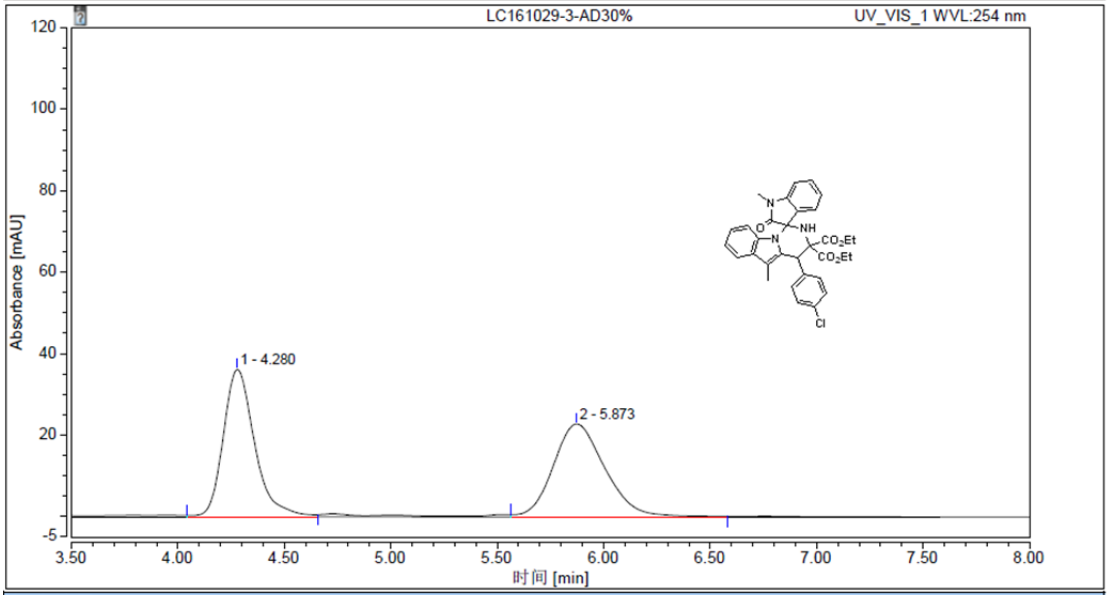


积分结果

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		4.073	6.197	41.555	15.10	22.72	n.a.
2		5.817	34.855	141.369	84.90	77.28	n.a.
总和:			**41.053**	**182.924**	**100.00**	**100.00**	

6ga

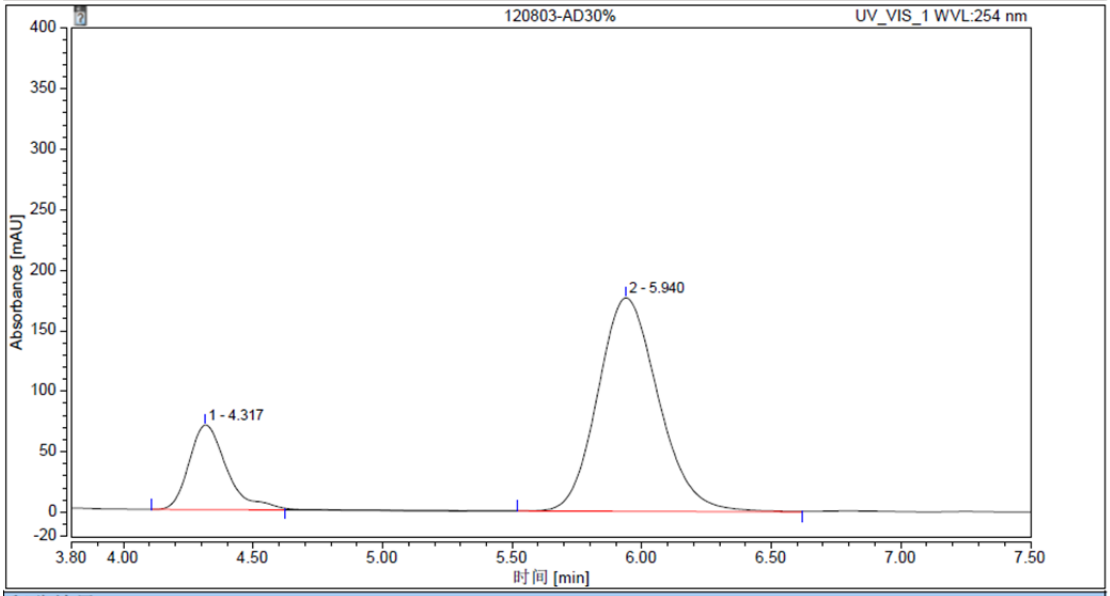
色谱图



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		4.280	6.185	36.203	49.08	61.33	n.a.
2		5.873	6.416	22.828	50.92	38.67	n.a.
总和:			**12.600**	**59.031**	**100.00**	**100.00**	

色谱图

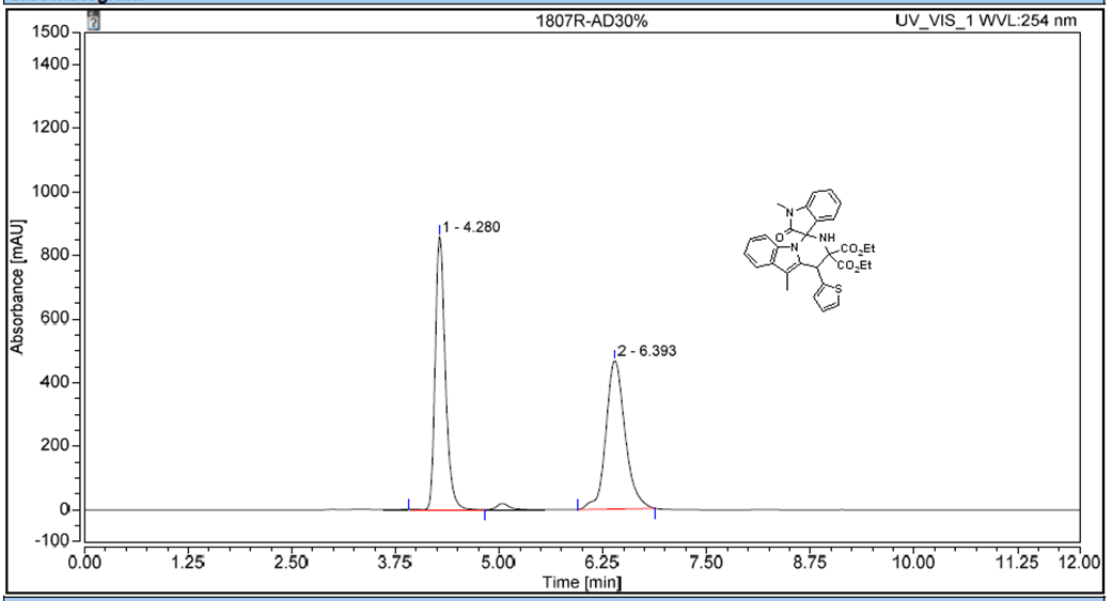


积分结果

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		4.317	11.809	69.978	19.81	28.42	n.a.
2		5.940	47.801	176.230	80.19	71.58	n.a.
总和:			**59.610**	**246.208**	**100.00**	**100.00**	

6ha

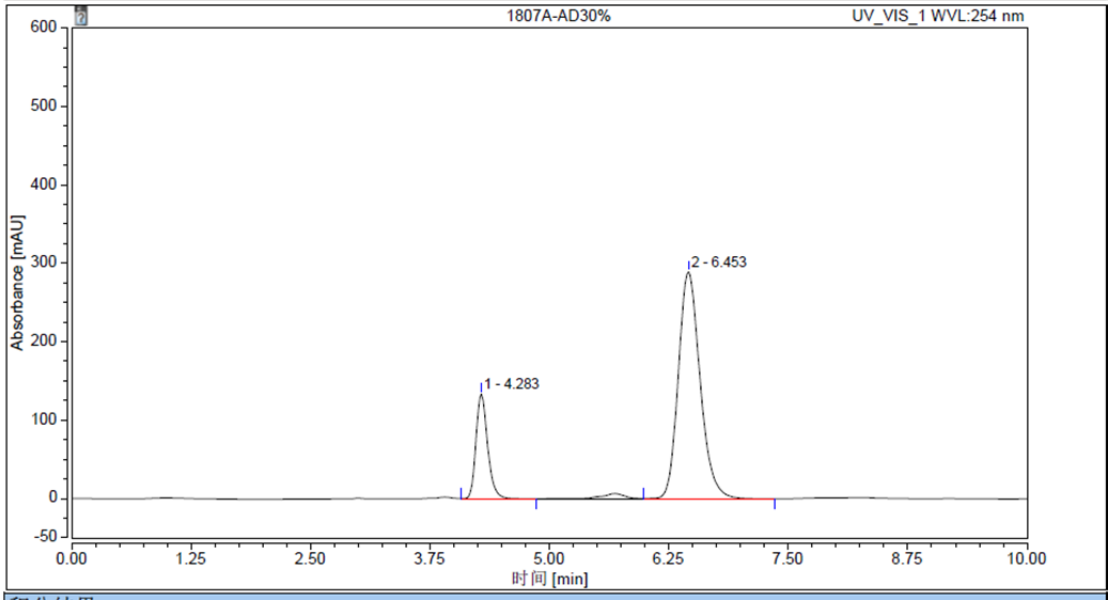
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.280	121.643	860.191	49.24	64.82	n.a.
2		6.393	125.377	466.870	50.76	35.18	n.a.
Total:			**247.020**	**1327.061**	**100.00**	**100.00**	

色谱图

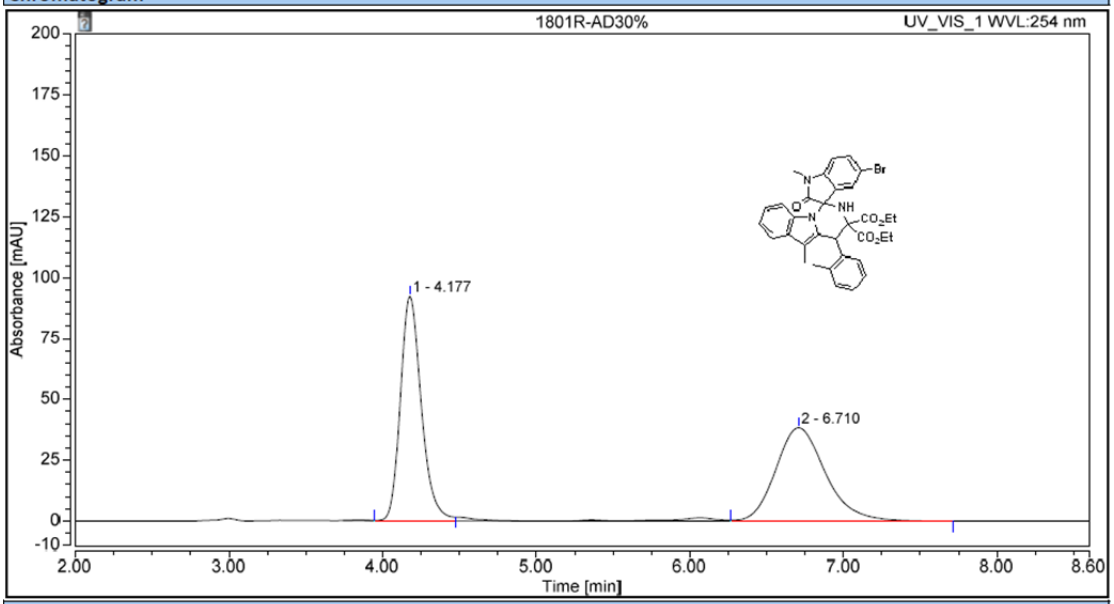


积分结果

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		4.283	19.006	133.845	19.89	31.61	n.a.
2		6.453	76.562	289.581	80.11	68.39	n.a.
总和:			**95.568**	**423.426**	**100.00**	**100.00**	

6ia

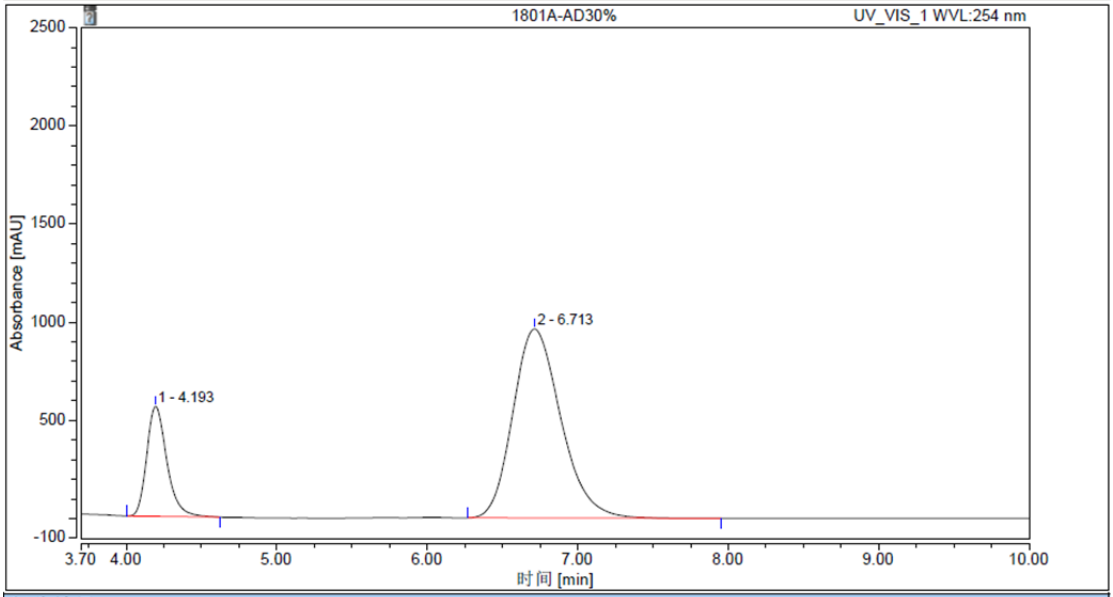
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.177	14.541	92.074	50.30	70.61	n.a.
2		6.710	14.366	38.327	49.70	29.39	n.a.
Total:			**28.907**	**130.401**	**100.00**	**100.00**	

色谱图

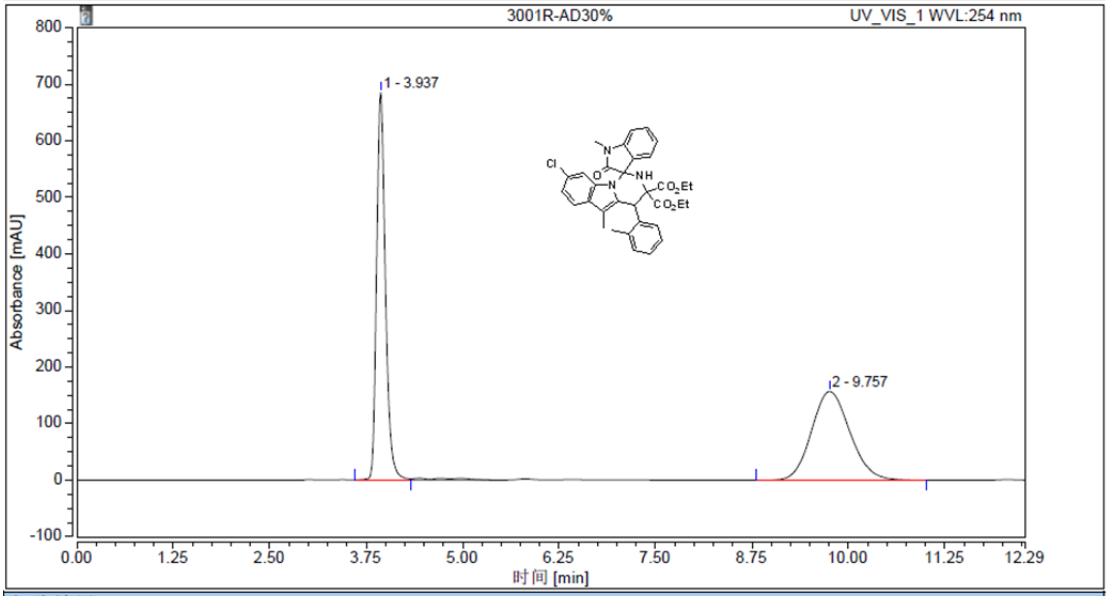


积分结果

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		4.193	86.994	560.208	19.67	36.79	n.a.
2		6.713	355.271	962.574	80.33	63.21	n.a.
总和:			**442.264**	**1522.782**	**100.00**	**100.00**	

6ja

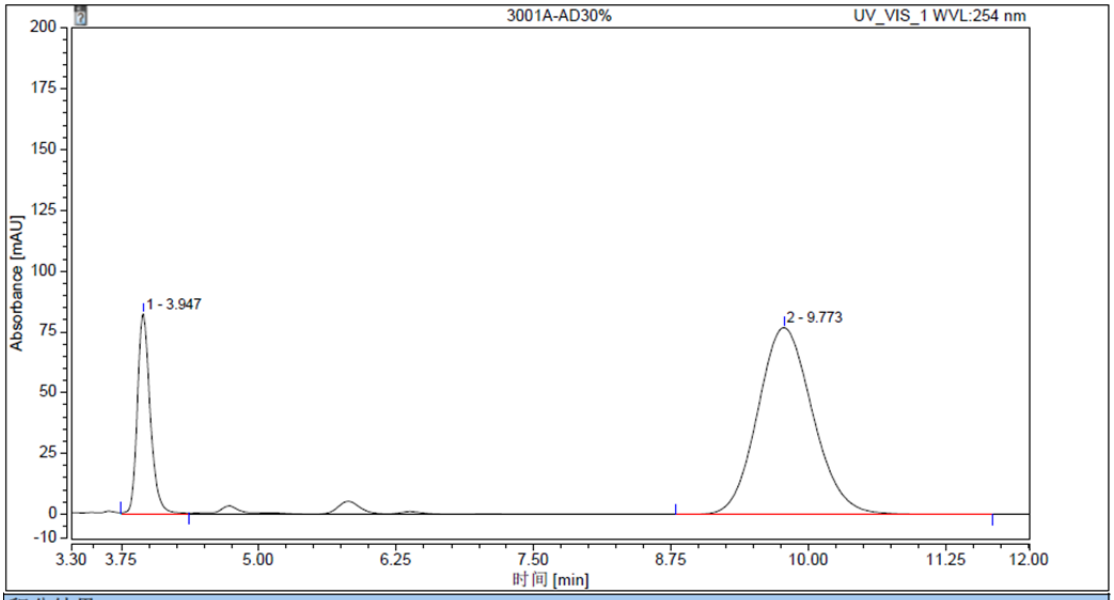
色谱图



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		3.937	90.089	684.800	49.89	81.37	n.a.
2		9.757	90.494	156.826	50.11	18.63	n.a.
总和:			**180.583**	**841.626**	**100.00**	**100.00**	

色谱图

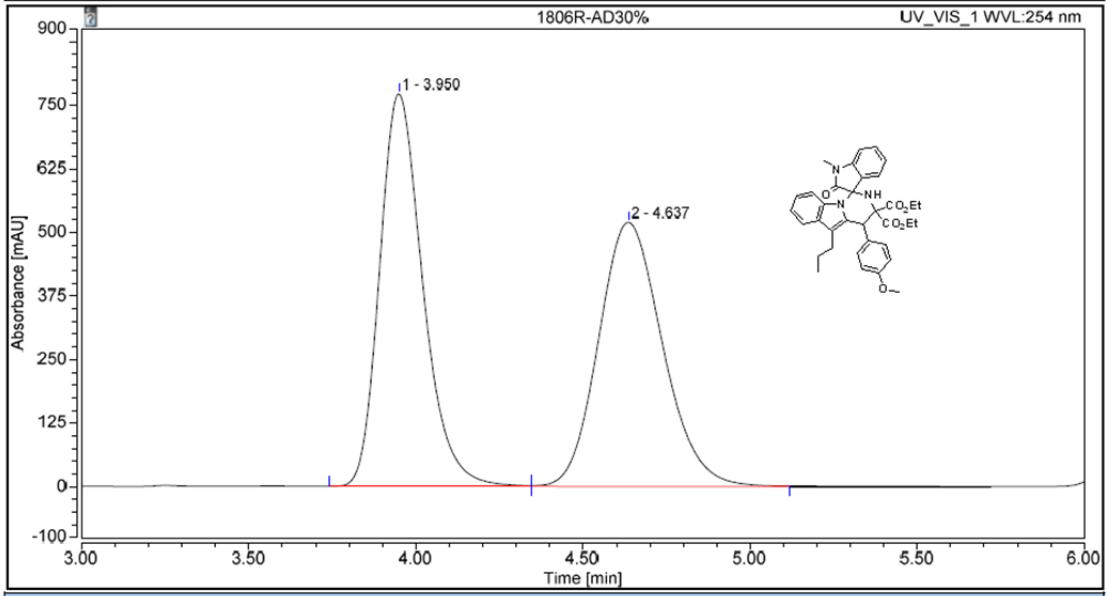


积分结果

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		3.947	11.318	82.531	20.32	51.80	n.a.
2		9.773	44.384	76.784	79.68	48.20	n.a.
总和:			**55.703**	**159.315**	**100.00**	**100.00**	

6ka

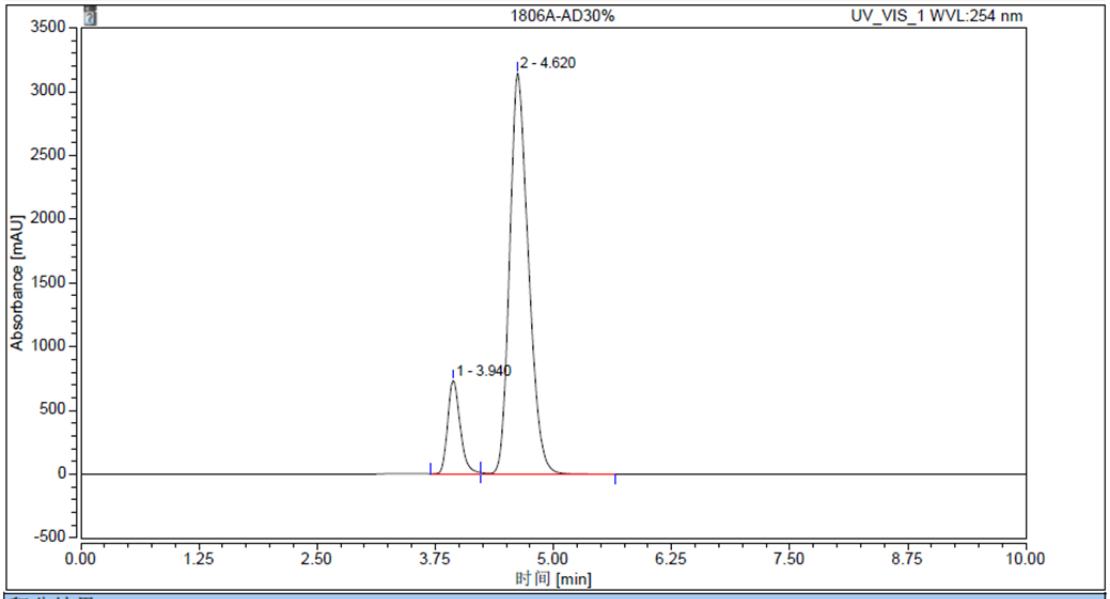
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.950	115.460	771.975	50.03	59.78	n.a.
2		4.637	115.309	519.339	49.97	40.22	n.a.
Total:			**230.769**	**1291.315**	**100.00**	**100.00**	

色谱图

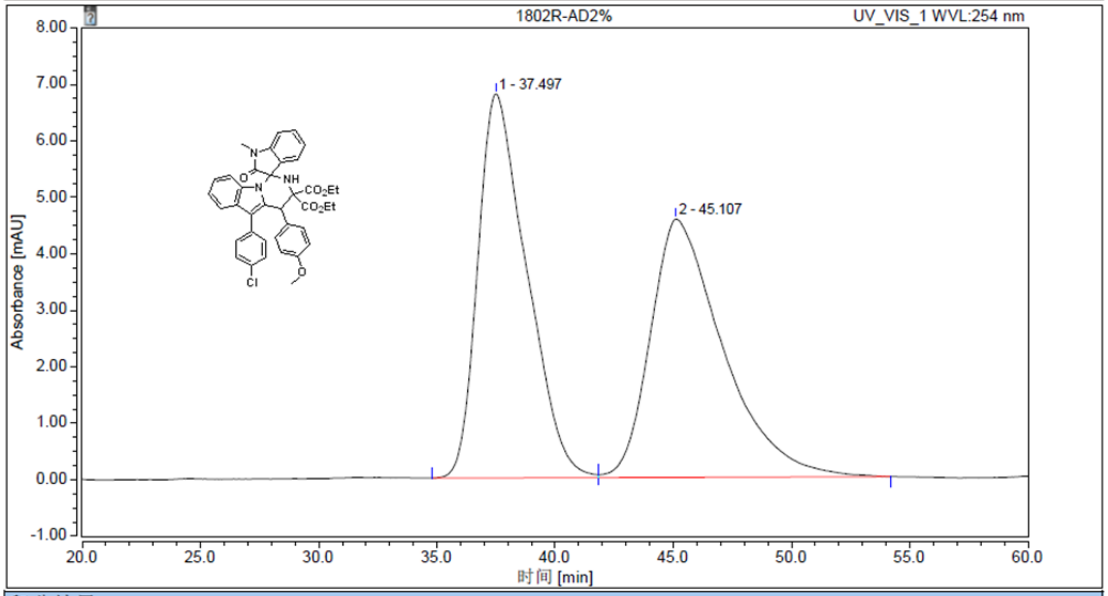


积分结果

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		3.940	113.715	736.765	13.54	18.98	n.a.
2		4.620	726.021	3145.452	86.46	81.02	n.a.
总和:			**839.736**	**3882.217**	**100.00**	**100.00**	

6la

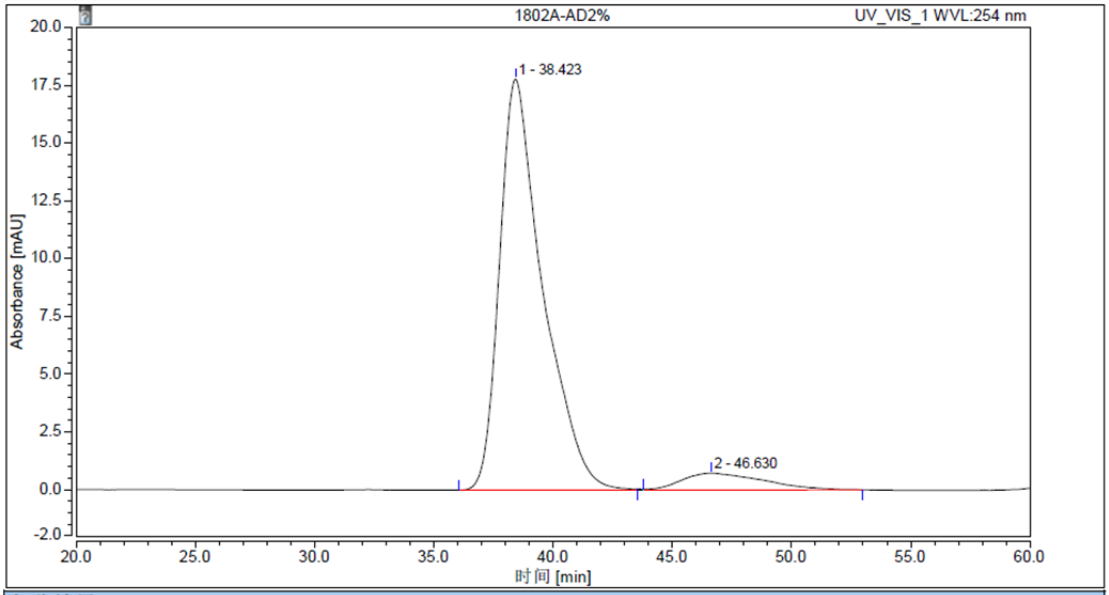
色谱图



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		37.497	16.273	6.805	50.00	59.78	n.a.
2		45.107	16.274	4.578	50.00	40.22	n.a.
总和:			**32.546**	**11.382**	**100.00**	**100.00**	

色谱图

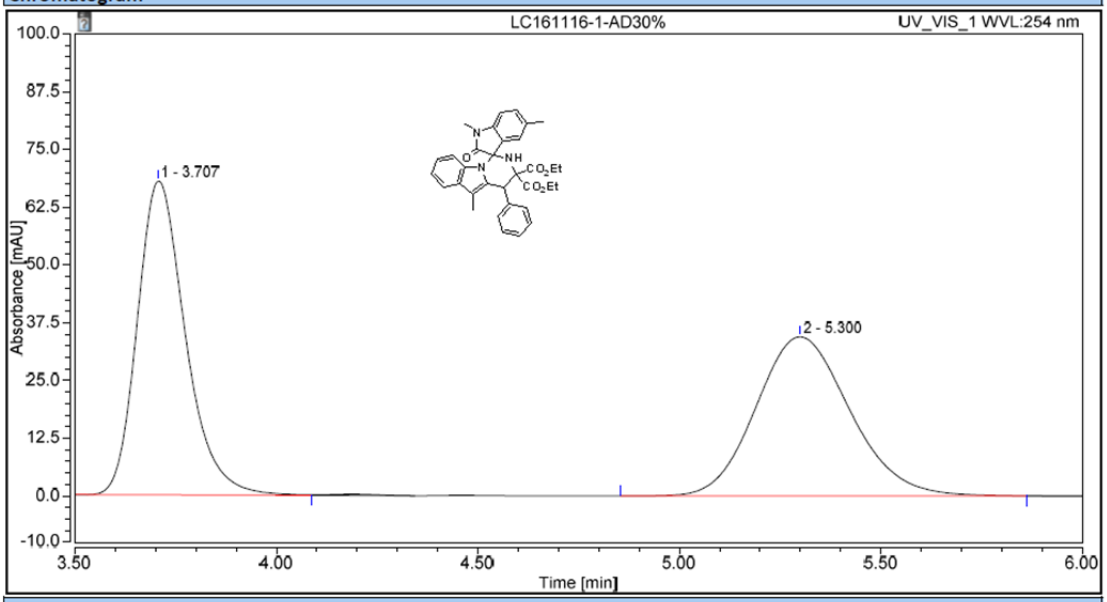


积分结果

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		38.423	37.359	17.793	92.77	96.05	n.a.
2		46.630	2.910	0.731	7.23	3.95	n.a.
总和:			**40.269**	**18.524**	**100.00**	**100.00**	

6ab

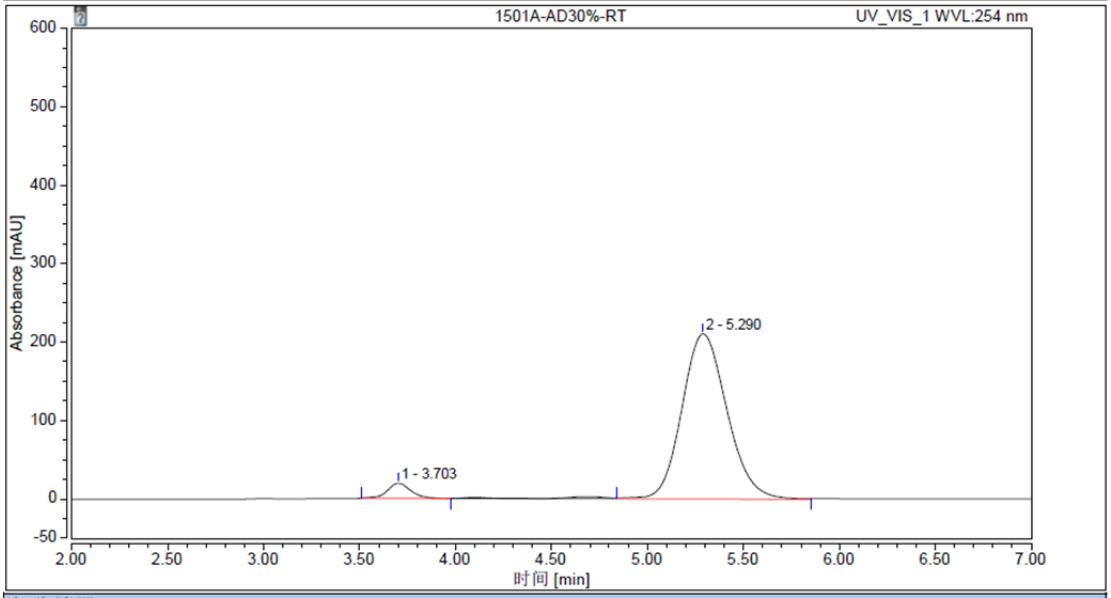
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.707	9.379	67.966	50.14	66.36	n.a.
2		5.300	9.326	34.459	49.86	33.64	n.a.
Total:			**18.705**	**102.425**	**100.00**	**100.00**	

色谱图

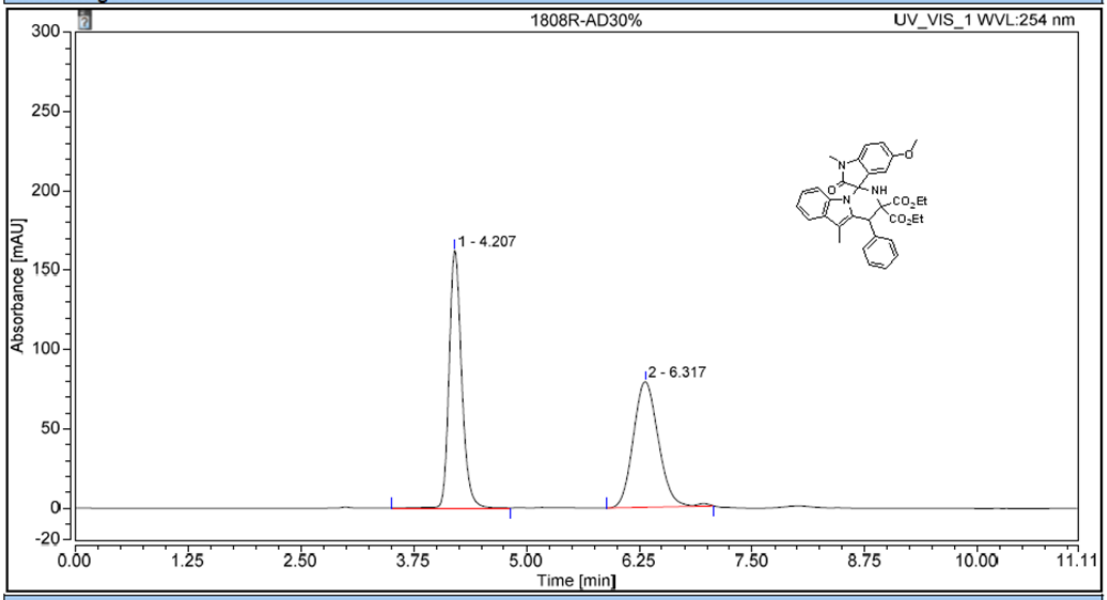


积分结果

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		3.703	2.629	19.020	4.39	8.29	n.a.
2		5.290	57.245	210.519	95.61	91.71	n.a.
总和:			**59.874**	**229.539**	**100.00**	**100.00**	

6ac

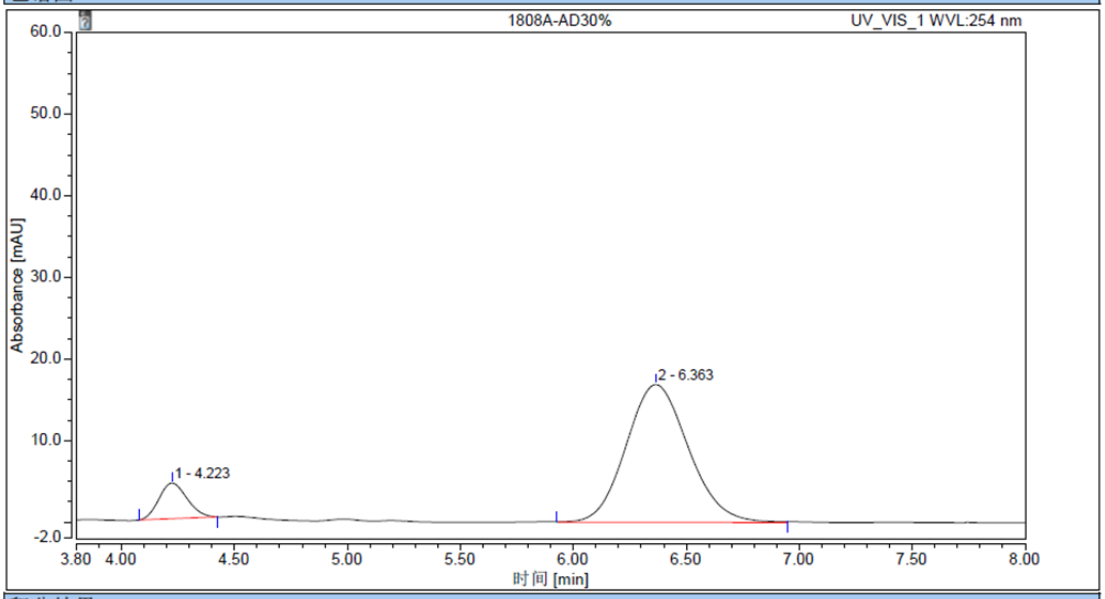
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.207	26.078	162.147	50.45	67.19	n.a.
2		6.317	25.617	79.180	49.55	32.81	n.a.
Total:			**51.695**	**241.326**	**100.00**	**100.00**	

色谱图

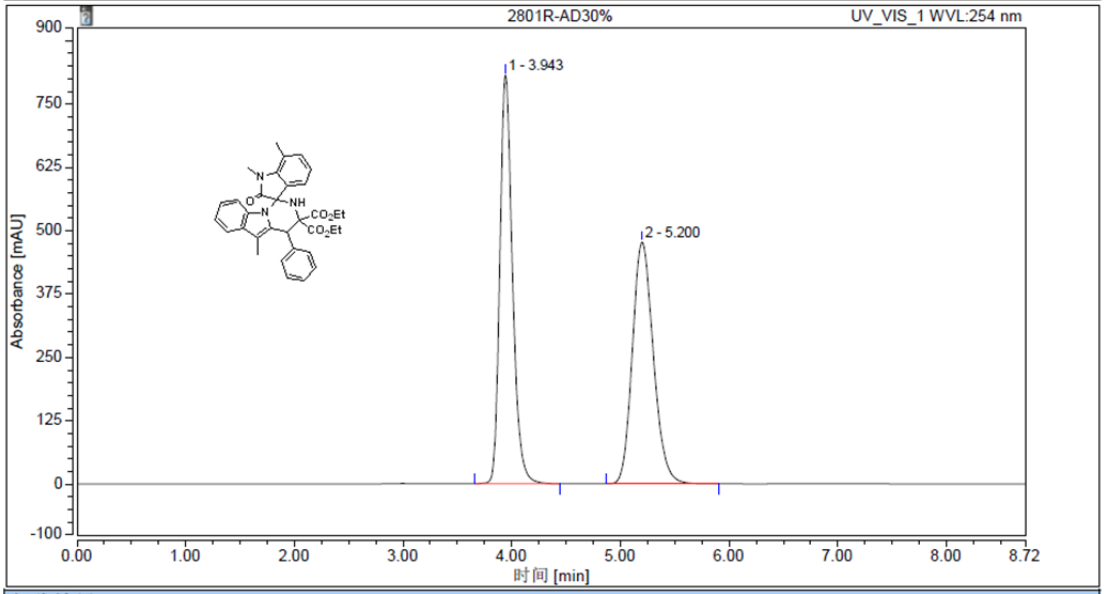


积分结果

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		4.223	0.627	4.344	10.40	20.47	n.a.
2		6.363	5.403	16.873	89.60	79.53	n.a.
总和:			**6.030**	**21.217**	**100.00**	**100.00**	

6ad

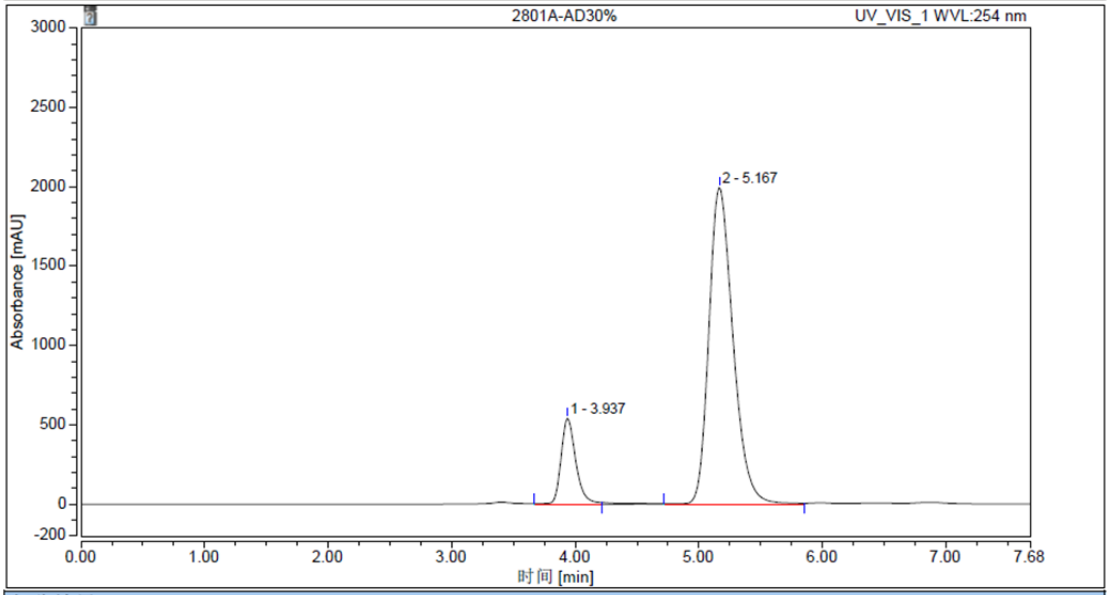
色谱图



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		3.943	108.079	806.207	50.28	62.79	n.a.
2		5.200	106.874	477.733	49.72	37.21	n.a.
总和:			**214.952**	**1283.940**	**100.00**	**100.00**	

色谱图

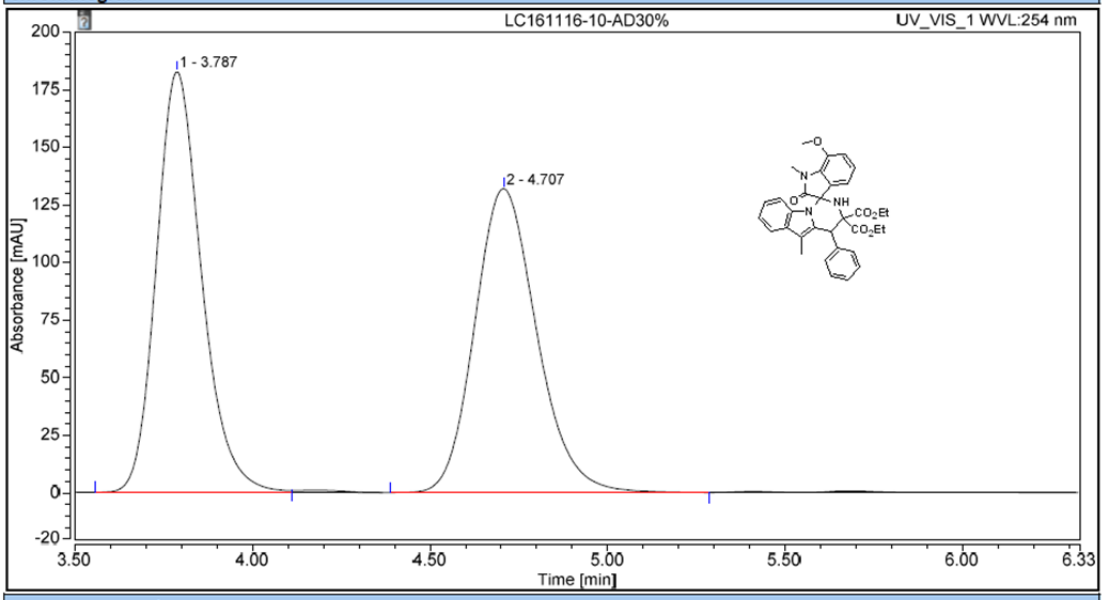


积分结果

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		3.937	74.383	541.012	14.14	21.34	n.a.
2		5.167	451.580	1994.720	85.86	78.66	n.a.
总和:			**525.963**	**2535.732**	**100.00**	**100.00**	

6ae

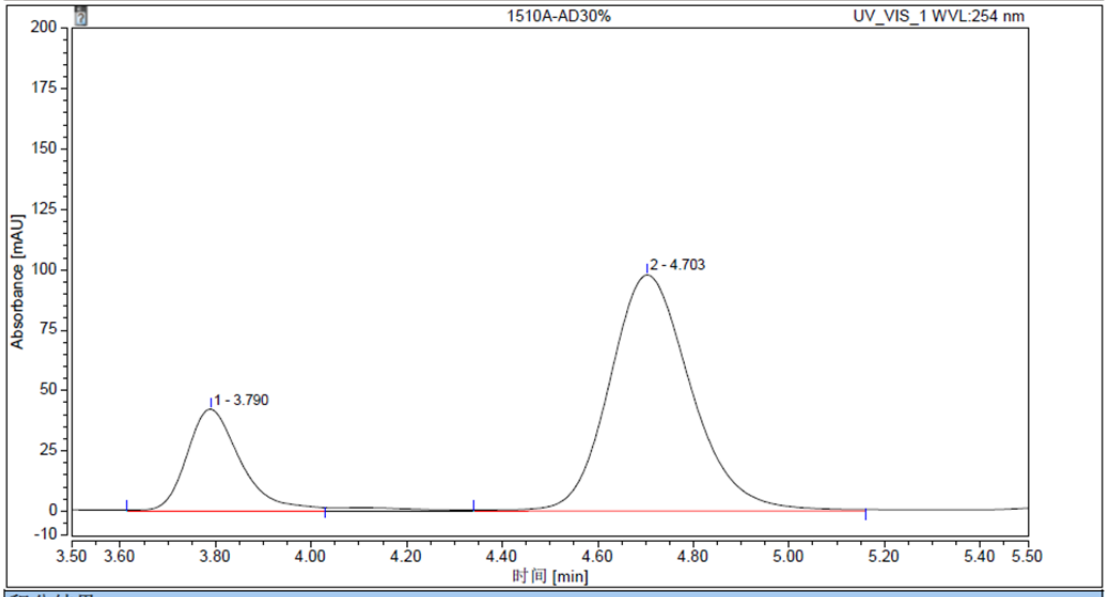
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		3.787	26.953	182.642	50.21	58.06	n.a.
2		4.707	26.724	131.924	49.79	41.94	n.a.
Total:			**53.676**	**314.566**	**100.00**	**100.00**	

色谱图

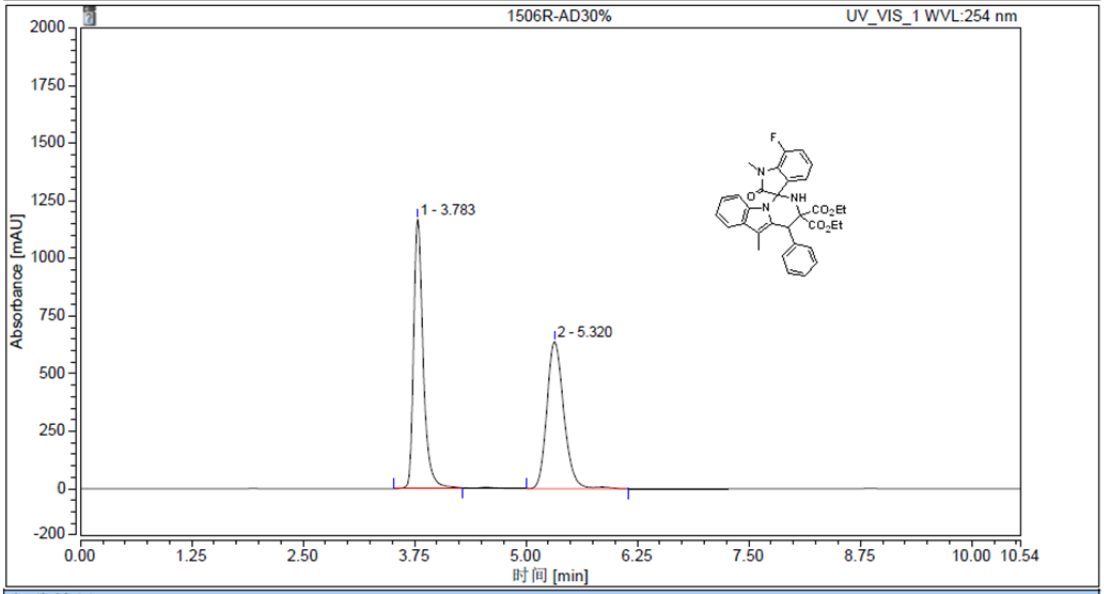


积分结果

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		3.790	5.516	42.196	22.21	30.17	n.a.
2		4.703	19.315	97.677	77.79	69.83	n.a.
总和:			**24.830**	**139.874**	**100.00**	**100.00**	

6af

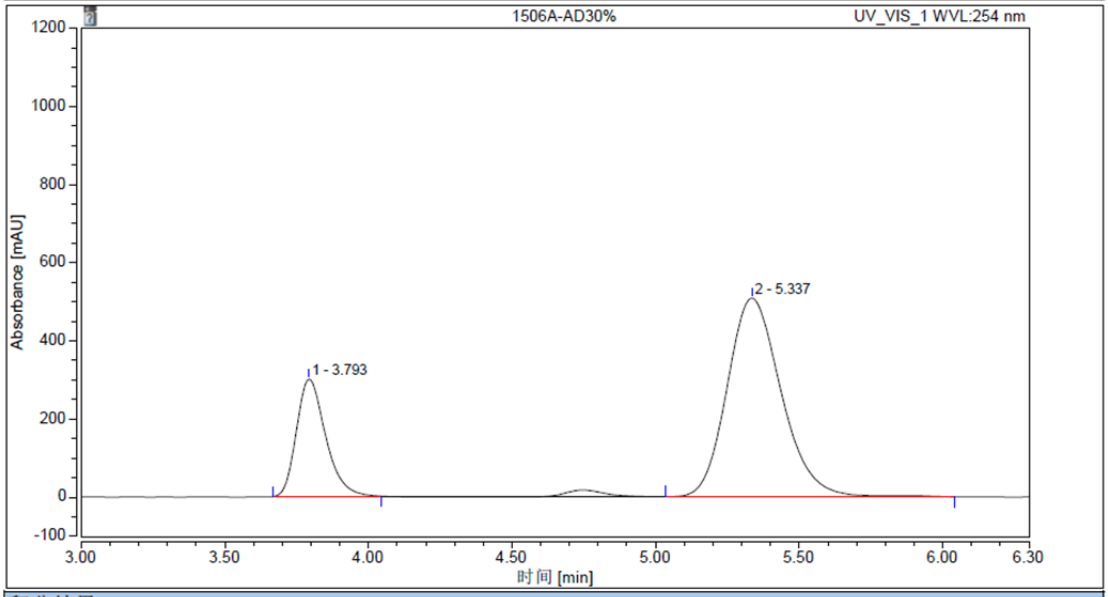
色谱图



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		3.783	145.971	1169.629	50.72	64.67	n.a.
2		5.320	141.802	639.078	49.28	35.33	n.a.
总和:			**287.772**	**1808.707**	**100.00**	**100.00**	

色谱图

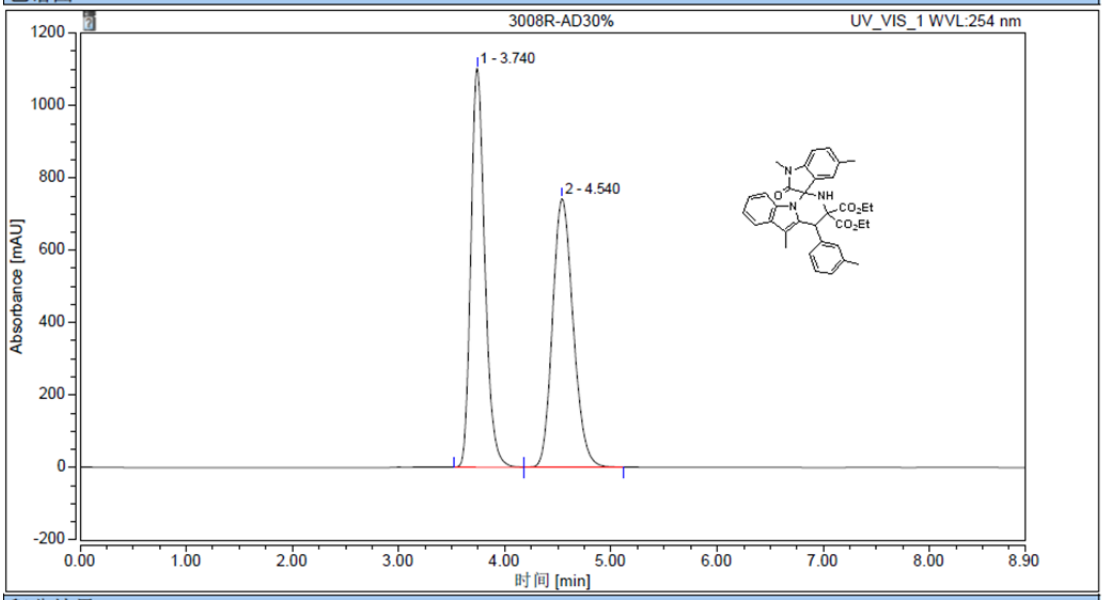


积分结果

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		3.793	35.555	301.033	24.28	37.21	n.a.
2		5.337	110.858	507.889	75.72	62.79	n.a.
总和:			**146.413**	**808.922**	**100.00**	**100.00**	

6mb

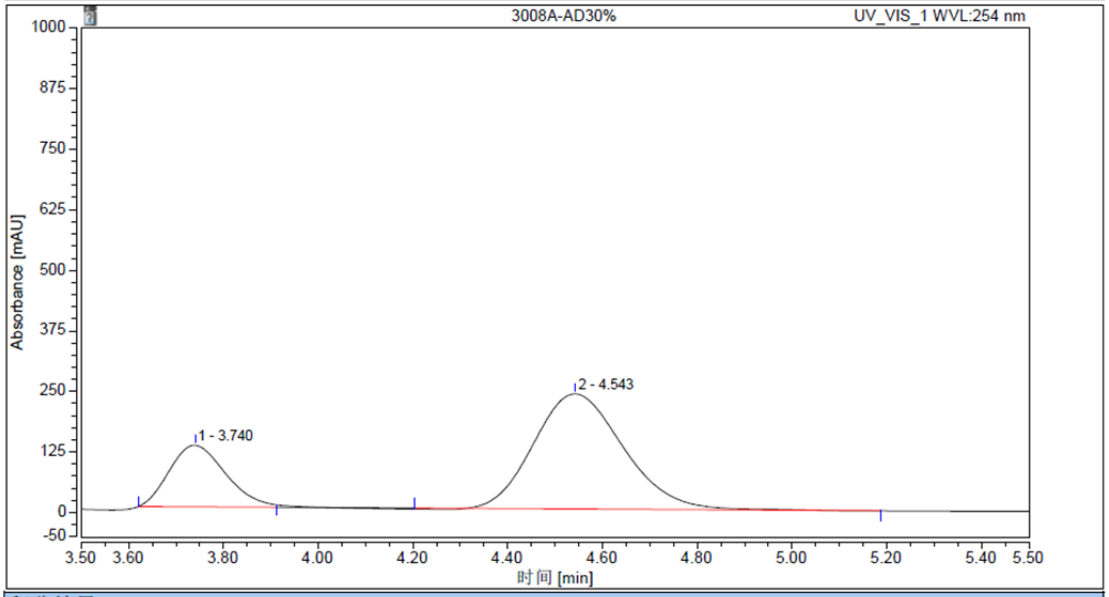
色谱图



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		3.740	167.464	1102.331	50.05	59.74	n.a.
2		4.540	167.109	742.852	49.95	40.26	n.a.
总和:			**334.573**	**1845.183**	**100.00**	**100.00**	

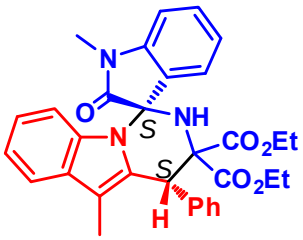
色谱图



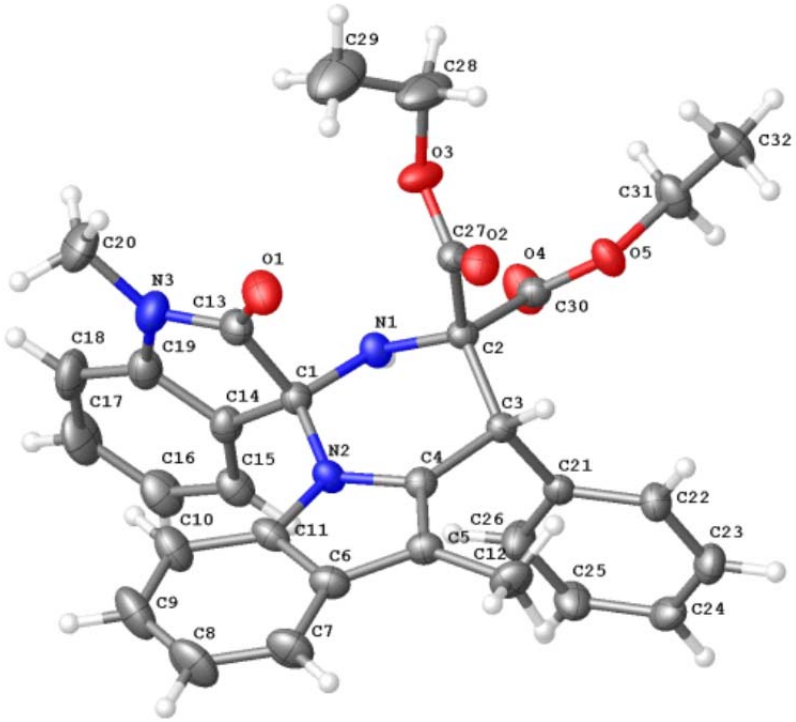
积分结果

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		3.740	17.489	127.091	25.16	34.86	n.a.
2		4.543	52.030	237.463	74.84	65.14	n.a.
总和:			**69.519**	**364.554**	**100.00**	**100.00**	

6. X-ray single crystal data for product 6aa



(*S*,*S*)-6aa



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

Empirical formula	C32 H31 N3 O5	
Formula weight	537.60	
Temperature	130 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 31.9591(4) Å	α= 90°.
	b = 33.2764(4) Å	β= 90°.
	c = 10.32080(10) Å	γ = 90°.
Volume	10976.0(2) $Å^3$	
Z	16	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	0.720 mm^{-1}	
F(000)	4544	
Crystal size	0.2 x 0.18 x 0.15 mm^3	

Theta range for data collection	3.835 to 69.544°.
Index ranges	-38<=h<=37, -39<=k<=39, -12<=l<=12
Reflections collected	20326
Independent reflections	4942 [R(int) = 0.0460]
Completeness to theta = 67.679°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.5856
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4942 / 1 / 369
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1130
R indices (all data)	R1 = 0.0436, wR2 = 0.1149
Absolute structure parameter	-0.02(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.581 and -0.257 e.$Å^{-3}$