Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

An Efficient Strategy for the Synthesis of Polysubstituted Chromeno[4,3-*b*]pyrrolidine Derivatives

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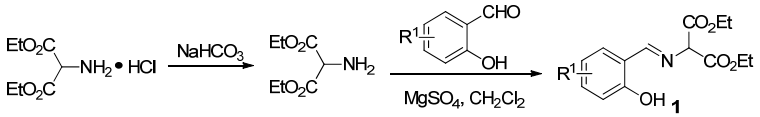
1. General information

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on silicycle silica gel plates with F-254 indicator and the compounds were visualized by irradiation with UV light. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C). The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to either the residual solvent peak (^{13}C) (δ = 77.00 ppm) or TMS (^{1}H) (δ = 0 ppm) as an internal standard. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. IR spectra were recorded using Nicolet NEXUS 670 FT-IR instrument and are reported in wavenumbers (cm^{-1}). HRMS were performed on a Bruker Apex II mass instrument (ESI). Enantiomeric excess values were determined by HPLC employing a Daicel Chirapak AD–H on Agilent 1100 series and eluting with *i*-PrOH and n-hexane solution. Optical rotation was measured on the Perkin Elmer 341 polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is reported in g/100 mL.

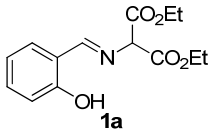
2. General procedure for the synthesis of 1



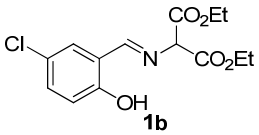
To a stirred solution of diethyl aminomalonate hydrochloride (3 g, 14.2 mmol) and H_2O (30 ml) in a 50ml round-bottomed flask was added $NaHCO_3$ (1.31 g, 15.6mmol), after stirring for 15min, the solution was extracted with AcOEt for 3 times. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum to afford diethyl aminomalonate (2.3 g, 13.1 mmol) which was used without futher purification.

Salicylaldehyde (1.37ml, 13.1mmol) was added to a mixture of diethyl aminomalonate (2.3 g, 13.1 mmol) and $MgSO_4$ (7.86g, 65.5mmol) in CH_2Cl_2 (30 ml). After stirring for 48h, $MgSO_4$ was removed by filtration. The filtrate was concentrated under reduced pressure. The crude product can be purified by flash chromatography on Al_2O_3 or recrystallization (PE/EA) to afford products**1a-e**.

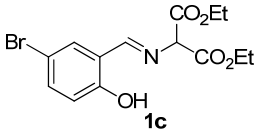
3. Characterization data of 1



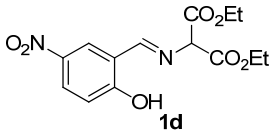
(E)-diethyl 2-((2-hydroxybenzylidene)amino)malonate (1a): yellow solid; Purified by flash chromatography, yield: 56 %; mp 44—46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.70 (s, 1H), 8.47 (s, 1H), 7.37—7.30 (m, 2H), 6.98 (d, *J* = 8.4Hz, 1H), 6.90 (t, *J* = 7.6Hz, 1H), 4.85 (s, 1H), 4.31—4.26 (m, 4H), 1.31 (t, *J* = 7.2Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 166.1, 161.0, 133.3, 132.2, 118.8, 118.5, 117.2, 72.7, 62.3, 13.9; IR (KBr): 3445.3, 2993.4, 1731.5, 1631.9, 1459.4, 1396.9, 1304.2, 1280.4 1174.3, 1085.6, 1024.7, 764.1 cm^{-1}; HRMS (ESI) for $C_{14}H_{17}NO_5$ [M+H] $^+$ calcd 280.1179, found 280.1186.



(E)-diethyl 2-((5-chloro-2-hydroxybenzylidene)amino)malonate (1b): yellow solid; Purified by recrystallization, yield: 63 %; mp 58-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.70 (s, 1H), 8.42 (s, 1H), 7.31–7.29 (m, 2H), 6.95–6.92 (m, 1H), 4.88 (s, 1H), 4.33–4.27 (m, 4H), 1.32 (t, *J* = 7.2Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 165.8, 159.6, 133.2, 131.2, 123.4, 119.2, 118.9, 72.4, 62.4, 13.9; IR (KBr): 3457.9, 2989.9, 1744.8, 1638.4, 1483.1, 1375.9, 1324.9, 1237.4, 1159.9, 1114.3, 1021.1, 829.7 cm^{-1}; HRMS (ESI) for $C_{14}H_{16}ClNO_5$ [M+H] $^+$ calcd 314.0790, found 314.0799.

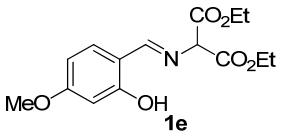


(E)-diethyl 2-((5-bromo-2-hydroxybenzylidene)amino)malonate (1c): yellow solid; Purified by recrystallization, yield: 66 %; mp 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.71 (s, 1H), 8.41 (s, 1H), 7.42–7.41 (m, 2H), 6.89–6.87 (m, 1H), 4.87 (s, 1H), 4.31–4.26 (m, 4H), 1.33–1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 165.8, 160.1, 135.9, 134.2, 119.8, 119.3, 110.2, 72.4, 62.5, 13.9; IR (KBr): 3450.5, 2989.4, 1745.9 1636.6, 1468.6, 1373.9, 1325.6, 1240.7, 1178.7, 1114.7, 1020.7, 820.6 cm^{-1}; HRMS (ESI) for $C_{14}H_{16}BrNO_5$ $[M+H]^+$ calcd 358.0285, found 358.0294.



1d

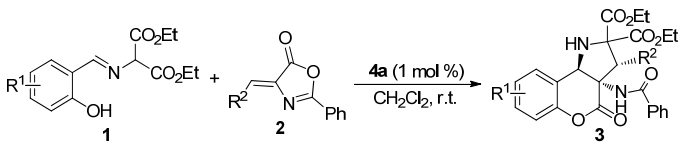
(E)-diethyl 2-((2-hydroxy-5-nitrobenzylidene)amino)malonate (1d): yellow solid; Purified by recrystallization, yield: 59 %; mp 76-78^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.84 (s, 1H), 8.62 (s, 1H), 8.33 (d, *J* = 2.4Hz, 1H), 8.26–8.22 (m, 1H), 7.08–7.05 (m, 1H), 4.99 (s, 1H), 4.36–4.30 (m, 4H), 1.36–1.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.5, 165.4, 139.7, 128.5, 128.4, 118.3, 117.4, 71.7, 62.6, 13.9; IR (KBr): 3445.4, 2994.7, 1733.3, 1639.0, 1482.2, 1335.0, 1300.9, 1243.8, 1100.9, 1029.3, 836.1, 755.5 cm^{-1}; HRMS (ESI) for $C_{14}H_{16}N_2O_7$ $[M+H]^+$ calcd 325.1030, found 325.1032.



1e

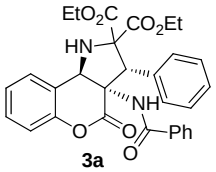
(E)-diethyl 2-((2-hydroxy-4-methoxybenzylidene)amino)malonate (1e): yellow liquid; Purified by flash chromatography, yield: 43 %; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.12 (s, 1H), 8.37 (s, 1H), 7.19 (d, *J* = 8.4Hz, 1H), 6.48–6.45 (m, 2H), 4.80 (s, 1H), 4.31–4.26 (m, 4H), 3.82 (s, 3H), 1.31 (t, *J* = 7.2Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 166.4, 164.0, 163.5, 133.4, 112.4, 106.8, 101.0, 72.5, 62.2, 55.3, 13.9; IR (KBr): 3459.9, 2986.7, 1743.3, 1626.6, 1512.9, 1401.3, 1292.5, 1225.9, 1159.1, 1114.8, 1028.5, 843.1 cm^{-1}; HRMS (ESI) for $C_{15}H_{19}NO_6$ $[M+H]^+$ calcd 310.1285, found 310.1291.

4. General procedure for the synthesis of 3



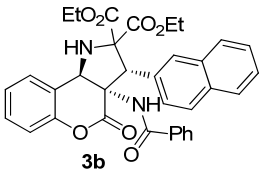
To a solution of catalyst **4a** (1 mol %) and alkylidene azlactone **2** (0.3 mmol) in dry CH_2Cl_2 (1.0 mL) added *o*-hydroxy aromatic aldimine **1** (0.2mmol) with stirring. After **1** disappeared (monitored by TLC), the crude mixture was purified by flash chromatography on silica gel to afford product **3**.

5. Characterization data of 3



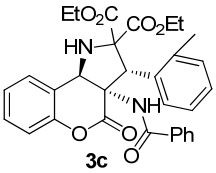
3a

(3R, 3aS, 9bR)-diethyl 3a-benzamido-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-*b*] pyrrole-2,2(*3H*)-dicarboxylate (3a): white solid; $[\alpha]_D^{20}$ = -99.4 (*c* 0.926, $CHCl_3$); mp 70–72 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 14.7 min, $t_{R(major)}$ = 38.2 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6Hz, 2H), 7.48–7.39 (m, 7H), 7.37–7.30 (m, 3H), 7.15–7.09 (m, 2H), 6.77(s, 1H), 5.22 (s, 1H), 4.97 (s, 1H), 4.04–3.93 (m, 3H), 3.91–3.83 (m, 1H), 3.81–3.73 (m, 1H), 1.11 (t, *J* = 7.2Hz, 3H), 0.82 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.2, 167.6, 166.6, 149.4, 132.8, 132.6, 132.1, 130.0, 129.8, 129.2, 129.0, 128.5, 128.3, 126.9, 124.6, 121.8, 116.8, 76.4, 66.1, 63.2, 62.5, 62.4, 57.5, 13.6, 13.2; IR (KBr): 3419.5, 2982.0, 1763.3, 1732.3, 1669.9, 1474.6, 1269.5, 1229.3, 1199.6, 762.2, 710.8 cm^{-1}; HRMS (ESI) for $C_{30}H_{28}N_2O_7$ $[M+H]^+$ calcd 529.1969, found 529.1980.



3b

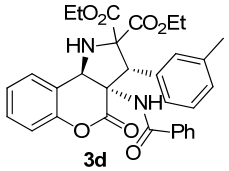
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(naphthalen-2-yl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3b): white solid; $[\alpha]_D^{20}$ = -77.2 (*c* 0.868, $CHCl_3$); mp 78–80 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 254 nm, $t_{R(minor)}$ = 12.5 min, $t_{R(major)}$ = 27.0 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.91 (d, *J* = 8.8Hz, 1H), 7.84 (dd, *J* = 3.2Hz, 6.0Hz, 2H), 7.55–7.51(m, 6H), 7.42 (t, *J* = 7.2Hz, 1H), 7.36–7.28 (m, 3H), 7.17–7.12 (m, 2H), 6.89 (s, 1H), 5.32 (d, *J* = 2.8Hz, 1H), 5.14 (s, 1H), 4.11 (d, *J* = 3.6Hz, 1H), 4.03–3.86 (m, 3H), 3.71–3.63 (m, 1H), 1.13 (t, *J* = 7.2Hz, 3H), 0.68 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.3, 167.8, 166.6, 149.4, 133.3, 133.0, 132.8, 132.1, 130.1, 129.9, 129.7, 128.9, 128.6, 128.4, 127.9, 127.6, 126.94, 126.89, 126.6, 124.6, 121.8, 116.9, 76.5, 66.5, 63.2, 62.6, 62.5, 57.7, 13.7, 13.2; IR (KBr): 3419.7, 2981.2, 1732.0, 1670.3, 1507.5, 1471.4, 1273.7, 1228.6, 1211.3, 760.0, 714.2 cm^{-1}; HRMS (ESI) for $C_{34}H_{30}N_2O_7$ $[M+H]^+$ calcd 579.2126, found 579.2121.



3c

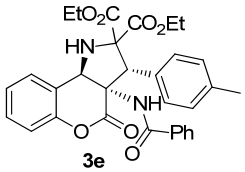
(3R, 3aS, 9bR)-diethyl 3a-benzamido-4-oxo-3-(o-tolyl)-1,3a,4,9b-tetrahydrochromeno[4,3-*b*] pyrrole-2,2(*3H*)-dicarboxylate (3c): white solid; $[\alpha]_D^{20}$ = -140.1 (*c* 0.935, $CHCl_3$); mp 76–78 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 9.5 min, $t_{R(major)}$ = 17.5 min, ee > 99%; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.49–7.43 (m, 5H), 7.35–7.28 (m, 6H), 7.17–7.11 (m, 2H), 6.67 (s, 1H), 5.51 (s, 1H), 5.21 (s, 1H), 3.97–3.88 (m, 3H), 3.83–3.70 (m, 2H), 2.50 (s, 3H), 1.08 (t, *J* = 7.2Hz, 3H), 0.77 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 168.7, 167.7, 167.5, 149.6, 140.0, 132.7, 132.2, 132.1, 131.4, 129.8, 128.9, 128.5, 128.4, 127.6, 126.9, 126.2, 124.6, 121.8, 116.8, 65.2, 63.4, 62.6, 62.2, 51.9, 20.1, 13.6, 13.2; IR (KBr): 3415.2, 2981.2, 1761.8, 1731.9, 1669.1, 1470.6, 1264.6, 1229.2, 1206.9, 760.9, 714.2 cm^{-1}; HRMS (ESI) for $C_{31}H_{30}N_2O_7$ $[M+H]^+$ calcd 543.2126, found 543.2135.



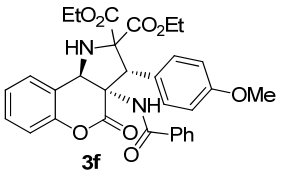
3d

(3R, 3aS, 9bR)-diethyl 3a-benzamido-4-oxo-3-(m-tolyl)-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3d): white solid; $[\alpha]_D^{20}$ = -107.8 (*c* 0.900, $CHCl_3$); mp 70–72 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 9.7 min, $t_{R(major)}$ = 27.1 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.2Hz, 2H), 7.48–7.37 (m, 2H), 7.30–7.22 (m, 4H), 7.15–7.11 (m, 3H), 7.07–7.01 (m, 2H), 6.72 (s, 1H), 5.18 (d, *J* = 2.4Hz, 1H), 4.84 (s, 1H), 3.99–3.84 (m, 3H), 3.83–3.67 (m, 2H), 2.28 (s, 3H), 1.03 (t, *J* = 7.2Hz, 3H), 0.76 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.1, 167.7, 166.7, 149.4, 139.2, 132.9, 132.3, 132.2, 131.1, 129.82, 129.79, 129.1, 128.5, 128.4, 127.0, 126.5, 124.5, 121.7, 116.8, 76.4, 66.2, 63.1, 62.5, 62.4, 57.7, 21.3, 13.6, 13.2; IR (KBr): 3415.4, 2980.7, 1731.7, 1671.3, 1507.2, 1474.1, 1278.1, 1227.4, 1206.4, 761.6, 713.0 cm^{-1}; HRMS (ESI) for $C_{31}H_{30}N_2O_7$ $[M+H]^+$ calcd 543.2126, found 543.2121.



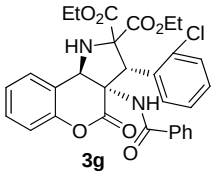
3e

(3R, 3aS, 9bR)-diethyl 3a-benzamido-4-oxo-3-(p-tolyl)-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3e): white solid; $[\alpha]_D^{20}$ = -103.3 (*c* 0.939, $CHCl_3$); mp 70–72 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 12.1 min, $t_{R(major)}$ = 35.4 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2Hz, 2H), 7.39 (t, *J* = 8.0Hz, 2H), 7.28 (t, *J* = 7.6Hz, 2H), 7.23 (d, *J* = 8.0Hz, 3H), 7.14 (d, *J* = 8.0Hz, 2H), 7.06–7.00 (m, 2H), 6.72 (s, 1H), 5.16 (s, 1H), 4.83 (s, 1H), 4.01–3.84 (m, 3H), 3.83–3.72 (m, 1H), 3.72–3.66 (m, 1H), 2.25 (s, 3H), 1.23 (t, *J* = 7.2Hz, 3H), 0.77 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.2, 167.7, 166.5, 149.3, 138.9, 132.9, 132.1, 129.8, 129.75, 129.2, 128.5, 128.3, 126.9, 124.5, 121.8, 116.7, 76.3, 66.3, 63.0, 62.4, 57.2, 20.9, 13.6, 13.2; IR (KBr): 3417.3, 2982.3, 1732.2, 1670.4, 1509.3, 1473.4, 1278.4, 1228.9, 1199.3, 762.3, 713.8 cm^{-1}; HRMS (ESI) for $C_{31}H_{30}N_2O_7$ $[M+H]^+$ calcd 543.2126, found 543.2120.



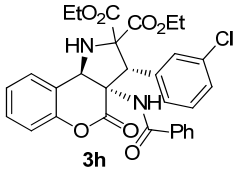
3f

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(4-methoxyphenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3f): white solid; $[\alpha]_D^{20}$ = -81.0 (*c* 0.741, $CHCl_3$); mp 72–74 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 15.3 min, $t_{R(major)}$ = 46.3 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2Hz, 2H), 7.50–7.46 (m, 2H), 7.39–7.30 (m, 5H), 7.15–7.09 (m, 2H), 6.94 (d, *J* = 8.4Hz, 2H), 6.79 (s, 1H), 5.22 (s, 1H), 4.90 (s, 1H), 4.10–3.76 (m, 8H), 1.11 (t, *J* = 7.2Hz, 3H), 0.89 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.3, 167.7, 166.7, 160.0, 149.4, 132.9, 132.2, 131.2, 129.8, 128.6, 128.3, 127.0, 124.6, 124.1, 121.8, 116.8, 114.6, 76.3, 66.2, 63.1, 62.5, 56.9, 55.3, 13.6, 13.4; IR (KBr): 3418.4, 2979.8, 1731.6, 1669.0, 1513.7, 1466.5, 1255.7, 1229.6, 1200.3, 761.9, 713.9 cm^{-1}; HRMS (ESI) for $C_{31}H_{30}N_2O_8$ $[M+H]^+$ calcd 559.2075, found 559.2069.



3g

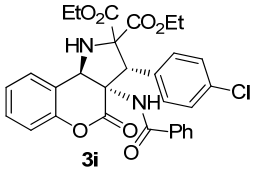
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(2-chlorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3g): white solid; $[\alpha]_D^{20}$ = -162.5 (*c* 0.831, $CHCl_3$); mp 150–152 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 10.9 min, $t_{R(major)}$ = 34.7 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.6Hz, 2H), 7.55–7.48 (m, 4H), 7.40–7.33 (m, 5H), 7.18–7.13 (m, 2H), 6.61 (s, 1H), 5.92 (s, 1H), 5.34, (s, 1H), 4.13–4.04 (m, 2H), 4.01–3.78 (m, 3H), 1.12 (t, *J* = 7.2Hz, 3H), 0.89 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.0, 168.1, 166.3, 149.4, 137.5, 132.9, 132.2, 131.3, 130.4, 130.1, 129.9, 128.9, 128.6, 128.4, 126.9, 126.7, 124.6, 121.5, 116.8, 76.6, 65.9, 62.9, 62.6, 62.5, 51.8, 13.6, 13.3; IR (KBr): 3450.6, 2926.2, 1774.7, 1726.3, 1672.5, 1469.9, 1289.3, 1232.4, 1199.4, 768.2, 715.3 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}ClN_2O_7$ $[M+H]^+$ calcd 563.1580, found 563.1583.



3h

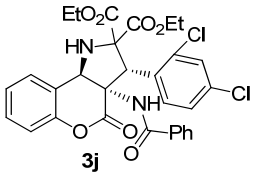
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(3-chlorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3h): white solid; $[\alpha]_D^{20}$ = -78.4 (*c* 0.753, $CHCl_3$); mp 72–74 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 8.1 min, $t_{R(major)}$ = 28.3 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.62 (m, 2H), 7.52–7.48 (m, 3H), 7.42–7.31 (m, 6H), 7.16–7.09

(m, 2H), 6.82 (s, 1H), 5.25 (s, 1H), 4.90 (s, 1H), 4.09–3.81 (m, 5H), 1.14 (t, *J* = 7.2Hz, 3H), 0.90 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.3, 167.7, 166.1, 149.3, 135.0, 134.6, 132.8, 132.3, 130.4, 130.02, 129.96, 129.1, 128.7, 128.3, 128.2, 127.0, 124.7, 121.5, 116.9, 76.3, 66.4, 63.1, 62.8, 62.6, 56.6, 13.7, 13.3; IR (KBr): 3427.5, 2983.4, 1734.1, 1671.4, 1513.2, 1477.4, 1268.8, 1229.8, 1200.4, 762.4, 710.1 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}ClN_2O_7$ $[M+H]^+$ calcd 563.1580, found 563.1574.



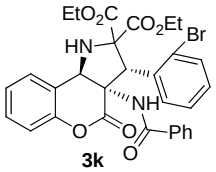
3i

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(4-chlorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3i): white solid; $[\alpha]_D^{20}$ = -61.7 (*c* 0.973, $CHCl_3$); mp 80–82 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 11.1 min, $t_{R(major)}$ = 37.2 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2Hz, 2H), 7.53–7.45 (m, 4H), 7.42–7.39 (m, 4H), 7.33 (t, *J* = 7.6Hz, 1H), 7.17–7.10 (m, 2H), 6.85 (s, 1H), 5.22 (s, 1H), 4.93 (s, 1H), 4.10–3.89 (m, 4H), 3.85–3.77 (m, 1H), 1.14 (t, *J* = 7.2Hz, 3H), 0.91 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.4, 167.6, 166.1, 149.2, 135.0, 132.7, 132.3, 131.3, 131.1, 129.9, 129.2, 128.7, 128.2, 126.9, 124.7, 121.6, 116.9, 76.2, 66.3, 63.2, 62.7, 62.6, 56.2, 13.6, 13.3; IR (KBr): 3427.6, 2926.9, 1734.8, 1670.4, 1490.9, 1464.6, 1266.9, 1229.9, 1144.9, 761.5, 714.6 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}ClN_2O_7$ $[M+H]^+$ calcd 563.1580, found 563.1573.



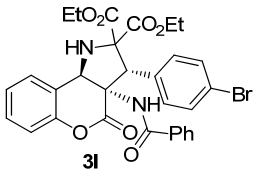
3j

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(2,4-dichlorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3j): white solid; $[\alpha]_D^{20}$ = -130.3 (*c* 0.921, $CHCl_3$); mp 86–88 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 7.9 min, $t_{R(major)}$ = 20.6 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6Hz, 2H), 7.55 (d, *J* = 2.0Hz, 1H), 7.53–7.46 (m, 3H), 7.42–7.38 (m, 2H), 7.36–7.33 (m, 2H), 7.18–7.13 (m, 2H), 6.57 (s, 1H), 5.81 (s, 1H), 5.32 (d, *J* = 3.2Hz, 1H), 4.17–4.09 (m, 2H), 4.01–3.81 (m, 3H), 1.11 (t, *J* = 7.2Hz, 3H), 0.96 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 169.0, 168.1, 166.2, 149.3, 138.2, 135.5, 132.9, 132.3, 130.9, 130.0, 129.8, 129.1, 128.7, 128.4, 126.9, 124.7, 121.4, 116.9, 76.4, 66.0, 62.8, 62.7, 51.3, 13.6, 13.4; IR (KBr): 3432.3, 2982.2, 1737.1, 1671.6, 1471.0, 1265.1, 1229.9, 1141.2, 761.7, 714.5 cm^{-1}; HRMS (ESI) for $C_{30}H_{26}Cl_2N_2O_7$ $[M+H]^+$ calcd 597.1190, found 597.1183.



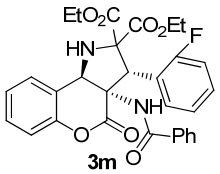
3k

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(2-bromophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3k): white solid; $[\alpha]_D^{20}$ = -163.8 (*c* 0.995, $CHCl_3$); mp 164–166 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 10.1 min, $t_{R(major)}$ = 29.5 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.71 (m, 1H), 7.57–7.46 (m, 5H), 7.42–7.31 (m, 4H), 7.27–7.22 (m, 1H), 7.17–7.12 (m, 2H), 6.59 (s, 1H), 5.89 (s, 1H), 5.32 (d, *J* = 2.8Hz, 1H), 4.10–4.01 (m, 2H), 3.99–3.76 (m, 3H), 1.11 (t, *J* = 7.2Hz, 3H), 0.87 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 168.8, 168.0, 166.4, 149.4, 134.7, 132.9, 132.3, 132.2, 130.3, 129.9, 129.0, 128.6, 128.5, 128.3, 127.3, 126.9, 124.6, 121.5, 116.8, 76.8, 65.8, 62.9, 62.6, 62.5, 54.8, 13.6, 13.3; IR (KBr): 3454.1, 2985.6, 1773.9, 1724.4, 1671.4, 1468.9, 1289.3, 1232.1, 1200.0, 768.4, 717.3 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}BrN_2O_7$ $[M+H]^+$ calcd 607.1074, found 607.1067.



3l

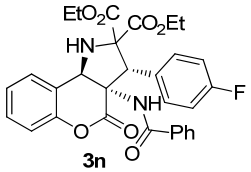
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(4-bromophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3l): white solid; $[\alpha]_D^{20}$ = -51.5 (*c* 0.873, $CHCl_3$); mp 150–152 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 10.5 min, $t_{R(major)}$ = 27.8 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.55–7.45 (m, 4H), 7.42–7.37 (m, 4H), 7.34–7.30 (m, 1H), 7.16–7.09 (m, 2H), 6.83 (s, 1H), 5.20 (s, 1H), 4.89 (s, 1H), 4.10–3.88 (m, 4H), 3.84–3.76 (m, 1H), 1.13 (t, *J* = 7.2Hz, 3H), 0.90 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.4, 167.6, 166.1, 149.2, 132.7, 132.3, 132.2, 131.60, 131.57, 129.9, 128.7, 128.2, 127.0, 124.7, 123.2, 121.6, 116.9, 76.2, 66.3, 63.2, 62.7, 62.6, 56.3, 13.7, 13.4; IR (KBr): 3426.7, 2981.7, 1734.5, 1671.1, 1509.5, 1488.6, 1265.5, 1229.7, 1144.6, 760.1, 712.7 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}BrN_2O_7$ $[M+H]^+$ calcd 607.1074, found 607.1067.



3m

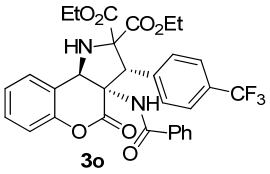
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(2-fluorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3m): white solid; $[\alpha]_D^{20}$ = -118.4 (*c* 1.022, $CHCl_3$); mp 78–80 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 14.1 min, $t_{R(major)}$ = 43.2 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2Hz, 2H), 7.55–7.49 (m, 2H), 7.43–7.27 (m, 6H),

7.20–7.11 (m, 4H), 5.28 (s, 1H), 5.17 (s, 1H), 4.33–4.18 (m, 2H), 4.04–3.89 (m, 3H), 1.13 (t, *J* = 7.2Hz, 3H), 0.96 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.4, 167.8, 165.5, 162.8, 160.4, 149.0, 132.9, 132.5, 132.2, 131.1, 131.0, 129.9, 128.6, 128.4, 127.0, 125.0, 124.97, 124.7, 122.0, 119.1, 118.9, 116.8, 116.4, 116.2, 74.8, 67.5, 62.83, 62.77, 62.5, 13.7, 13.3; IR (KBr): 3427.5, 2982.6, 1770.5, 1732.5, 1671.0, 1490.2, 1274.1, 1231.3, 1209.2, 762.6, 713.9 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}FN_2O_7$ $[M+H]^+$ calcd 547.1875, found 547.1885.



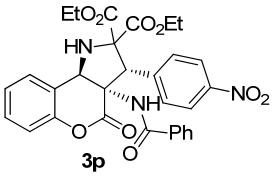
3n

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(4-fluorophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3n): white solid; $[\alpha]_D^{20}$ = -80.0 (*c* 0.912, $CHCl_3$); mp 78–80 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 11.0 min, $t_{R(major)}$ = 54.5 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2Hz, 2H), 7.51–7.45 (m, 4H), 7.40–7.37 (m, 2H), 7.34–7.31 (m, 1H), 7.16–7.09 (m, 4H), 6.80 (s, 1H), 5.20 (s, 1H), 4.94 (s, 1H), 4.07–3.75 (m, 5H), 1.12 (t, *J* = 7.2Hz, 3H), 0.88 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.3, 167.6, 166.4, 164.0, 161.6, 149.3, 132.7, 132.3, 131.9, 131.8, 129.9, 128.6, 128.42, 128.38, 128.2, 126.9, 124.7, 121.7, 116.9, 116.2, 116.0, 76.3, 66.1, 63.2, 62.6, 56.3, 13.6, 13.4; IR (KBr): 3426.2, 2983.0, 1734.3, 1670.2, 1511.5, 1466.5, 1264.6, 1229.6, 1143.8, 761.5, 713.5 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}FN_2O_7$ $[M+H]^+$ calcd 547.1875, found 547.1877.



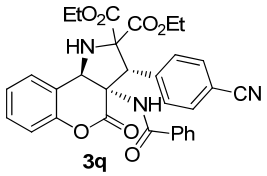
3o

(3R, 3aS, 9bR)-diethyl 3a-benzamido-4-oxo-3-(4-(trifluoromethyl)phenyl)-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3o): white solid; $[\alpha]_D^{20}$ = -55.2 (*c* 1.142, $CHCl_3$); mp 156–158 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 6.5 min, $t_{R(major)}$ = 14.4 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.64 (m, 4H), 7.58 (d, *J* = 7.2Hz, 2H), 7.51–7.45 (m, 2H), 7.39–7.31 (m, 3H), 7.16–7.09 (m, 2H), 6.93 (s, 1H), 5.22 (d, *J* = 2.4Hz, 1H), 5.02 (s, 1H), 4.09–3.92 (m, 4H), 3.81–3.73 (m, 1H), 1.15 (t, *J* = 7.2Hz, 3H), 0.84 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 167.5, 165.8, 149.2, 136.9, 132.7, 132.3, 131.0, 130.7, 130.5, 130.0, 128.6, 128.2, 126.9, 125.74, 125.70, 125.0, 124.7, 122.3, 121.4, 116.9, 76.2, 66.3, 63.3, 62.8, 62.7, 56.0, 13.6, 13.2; IR (KBr): 3434.2, 2988.7, 1739.3, 1641.2, 1465.8, 1328.8, 1298.1, 1213.7, 1169.0, 760.5, 689.1 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}F_3N_2O_7$ $[M+H]^+$ calcd 597.1843, found 597.1838.



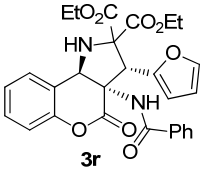
3p

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(4-nitrophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno [4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3p): white solid; $[\alpha]_D^{20}$ = -19.9 (*c* 0.905, $CHCl_3$); mp 96–98 ^oC; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 11.7 min, $t_{R(major)}$ = 36.0 min, ee = 98%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8Hz, 2H), 7.78 (d, *J* = 8.8Hz, 2H), 7.62 (d, *J* = 7.2Hz, 2H), 7.51–7.45 (m, 2H), 7.40–7.32 (m, 3H), 7.16–7.09 (m, 3H), 5.22 (s, 1H), 5.06 (s, 1H), 4.14–3.98 (m, 4H), 3.79–3.71 (m, 1H), 1.19 (t, *J* = 7.2Hz, 3H), 0.90 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.6, 167.4, 165.2, 149.2, 147.6, 140.2, 132.6, 132.4, 131.1, 130.1, 128.7, 128.2, 126.9, 124.8, 123.6, 121.2, 116.9, 76.2, 66.5, 63.4, 63.0, 62.8, 55.2, 13.7, 13.4; IR (KBr): 3432.3, 2982.9, 1736.7, 1668.9, 1523.5, 1463.9, 1349.1, 1266.5, 1230.6, 761.8, 713.1 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}N_3O_9$ $[M+H]^+$ calcd 574.1820, found 574.1815.



3q

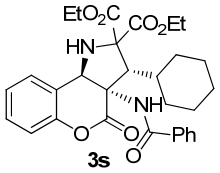
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(4-cyanophenyl)-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3q): white solid; $[\alpha]_D^{20}$ = -24.4 (*c* 0.982, $CHCl_3$); mp 96–98 ^oC; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 12.6 min, $t_{R(major)}$ = 57.8 min, ee > 99%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.4Hz, 17.6Hz, 4H), 7.59 (d, *J* = 7.2Hz, 2H), 7.50 (t, *J* = 7.2Hz, 1H), 7.45 (d, *J* = 7.6Hz, 1H), 7.40–7.32 (m, 3H), 7.14 (t, *J* = 7.2Hz, 1H), 7.09 (d, *J* = 8.0Hz, 1H), 7.03 (s, 1H), 5.19 (s, 1H), 5.01 (s, 1H), 4.11–3.95 (m, 4H), 3.79–3.71 (m, 1H), 1.17 (t, *J* = 7.2Hz, 3H), 0.89 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 167.4, 165.4, 149.2, 138.3, 132.5, 132.4, 132.3, 130.8, 130.1, 128.7, 128.2, 126.9, 124.8, 121.2, 118.0, 116.9, 112.4, 76.2, 66.3, 63.3, 62.9, 62.7, 55.6, 13.7, 13.3; IR (KBr): 3432.0, 2983.2, 1735.9, 1671.9, 1508.9, 1465.5, 1264.1, 1230.2, 1145.9, 761.0, 714.3 cm^{-1}; HRMS (ESI) for $C_{31}H_{27}N_3O_7$ $[M+H]^+$ calcd 554.1922, found 554.1927.



3r

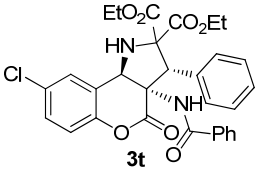
(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-(furan-2-yl)-4-oxo-1,3a,4,9b-tetrahydrochromeno-[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3r): white solid; $[\alpha]_D^{20}$ = -72.9 (*c* 0.796, $CHCl_3$); mp 164–166 ^oC; The enantiomeric excess was determined by HPLC with an AD–H column.

(*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 18.3 min, $t_{R(major)}$ = 64.7 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.85 (d, *J* = 7.6Hz, 2H), 7.55–7.53 (m, 2H), 7.50–7.45 (m, 3H), 7.32 (t, *J* = 7.6Hz, 1H), 7.15–7.08 (m, 2H), 6.43–6.39 (m, 2H), 5.36 (d, *J* = 5.2Hz, 1H), 4.87 (s, 1H), 4.41 (d, *J* = 5.6Hz, 1H), 4.29–4.21 (m, 1H), 4.07 (dd, *J* = 7.2Hz, 14.0Hz, 2H), 3.92–3.84 (m, 1H), 1.18 (t, *J* = 7.2Hz, 3H), 1.04 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 169.2, 167.7, 164.7, 148.8, 146.1, 143.8, 133.4, 132.1, 129.9, 128.7, 128.4, 127.2, 124.7, 122.0, 116.9, 113.3, 111.4, 74.3, 68.3, 63.3, 62.6, 62.4, 49.7, 13.8, 13.5; IR (KBr): 3440.1, 2969.8, 1779.2, 1727.3, 1676.3, 1520.6, 1485.1, 1276.2, 1227.8, 1204.2, 766.6, 708.3 cm^{-1}; HRMS (ESI) for $C_{28}H_{26}N_2O_8$ $[M+H]^+$ calcd 519.1762, found 519.1767.



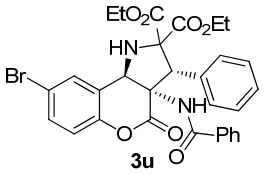
3s

(3R, 3aS, 9bR)-diethyl 3a-benzamido-3-cyclohexyl-4-oxo-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3s): white solid; $[\alpha]_D^{20}$ = -35.4 (*c* 0.905, $CHCl_3$); mp 162–164 ^{o}C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 8.6 min, $t_{R(major)}$ = 29.9 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H), 7.58–7.54 (m, 1H), 7.51–7.47 (m, 2H), 7.42 (m, 1H), 7.29–7.26 (m, 1H), 7.10–7.03 (m, 3H), 5.28 (d, *J* = 4.4Hz, 1H), 4.44–4.40 (m, 1H), 4.31–4.27 (m, 1H), 4.10–4.05 (m, 2H), 3.99 (d, *J* = 5.2Hz, 1H), 3.33 (d, *J* = 6.8Hz, 1H), 2.07 (d, *J* = 12Hz, 1H), 1.80–1.71 (m, 4H), 1.60 (s, 1H), 1.34–1.25 (m, 4H), 1.22–1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 170.3, 166.6, 165.7, 148.7, 133.7, 132.0, 129.6, 128.7, 128.2, 127.0, 124.3, 122.6, 116.3, 75.0, 67.3, 63.4, 63.1, 62.0, 55.2, 37.6, 33.5, 30.0, 26.7, 26.5, 25.6, 13.82, 13.78; IR (KBr): 3449.4, 2925.3, 1773.5, 1718.1, 1672.4, 1504.3, 1478.9, 1278.7, 1235.5, 1205.1, 1144.7, 1100.8, 1025.2, 764.2, 721.3 cm^{-1}; HRMS (ESI) for $C_{30}H_{34}N_2O_7$ $[M+H]^+$ calcd 535.2439, found 535.2426.



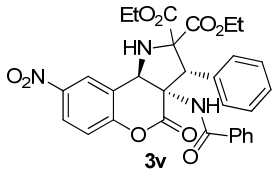
3t

(3R, 3aS, 9bR)-diethyl 3a-benzamido-8-chloro-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3t): white solid; $[\alpha]_D^{20}$ = -76.3 (*c* 1.114, $CHCl_3$); mp 78–80 ^{o}C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 254 nm, $t_{R(minor)}$ = 10.1 min, $t_{R(major)}$ = 29.3 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2H), 7.50–7.47 (m, 2H), 7.42–7.36 (m, 7H), 7.30–7.27 (m, 1H), 7.06 (d, *J* =8.8Hz, 1H), 6.79 (s, 1H), 5.22 (d, *J* = 4.8Hz, 1H), 4.93 (s, 1H), 4.11–3.93 (m, 4H), 3.81–3.73 (m, 1H), 1.18 (t, *J* = 7.2Hz, 3H), 0.83 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.0, 167.9, 166.0, 148.0, 132.6, 132.3, 132.2, 129.9, 129.8, 129.3, 129.2, 128.6, 128.2, 127.0, 123.6, 118.4, 76.5, 66.2, 62.9, 62.8, 62.6, 57.4, 13.7, 13.3; IR (KBr): 3419.0, 2982.3, 1771.5, 1731.5, 1669.7, 1506.1, 1477.5, 1277.7, 1228.4, 1194.6, 711.6 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}ClN_2O_7$ $[M+H]^+$ calcd 563.1580, found 563.1586.



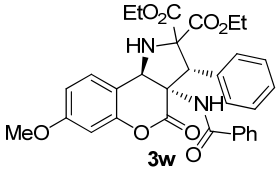
3u

(3R, 3aS, 9bR)-diethyl 3a-benzamido-8-bromo-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3u): white solid; $[\alpha]_D^{20}$ = -63.6 (*c* 1.211, $CHCl_3$); mp 78–80 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 254 nm, $t_{R(minor)}$ = 10.2 min, $t_{R(major)}$ = 27.0 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.6Hz, 1H), 7.58 (d, *J* = 7.2Hz, 2H), 7.50–7.35 (m, 9H), 7.00 (d, *J* =8.8Hz, 1H), 6.79 (s, 1H), 5.22 (d, *J* = 4.4Hz, 1H), 4.93 (s, 1H), 4.11–3.93 (m, 4H), 3.81–3.73 (m, 1H), 1.19 (t, *J* = 7.2Hz, 3H), 0.83 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.0, 167.9, 166.0, 148.5, 132.8, 132.6, 132.3, 132.2, 131.2, 129.9, 129.3, 129.1, 128.6, 127.0, 124.0, 118.7, 117.2, 76.5, 66.2, 62.9, 62.8, 62.6, 57.4, 13.7, 13.3; IR (KBr): 3419.6, 2982.0, 1771.8, 1731.5, 1669.7, 1506.0, 1475.9, 1278.8, 1228.3, 1194.1, 711.5 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}BrN_2O_7$ $[M+H]^+$ calcd 607.1074, found 607.1080.



3v

(3R, 3aS, 9bR)-diethyl 3a-benzamido-8-nitro-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno-[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3v): white solid; $[\alpha]_D^{20}$ = -68.3 (*c* 1.084, $CHCl_3$); mp 84–86 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane: *i*-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 13.3 min, $t_{R(major)}$ = 32.1 min, ee = 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.4Hz, 1H), 8.22 (dd, *J* = 2.4Hz, 8.8Hz, 1H), 7.55–7.35 (m, 10H), 7.25 (d, *J* = 8.8Hz, 1H), 6.82 (s, 1H), 5.25 (d, *J* = 4.8Hz, 1H), 4.95 (s, 1H), 4.17 (d, *J* = 4.8Hz, 1H), 4.17–3.99 (m, 2H), 3.97–3.89 (m, 1H), 3.81–3.73 (m, 1H), 1.14 (t, *J* = 7.2Hz, 3H), 0.84 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 169.0, 167.8, 165.3, 153.9, 144.3, 132.5, 132.2, 131.9, 129.9, 129.4, 129.3, 128.7, 126.9, 125.5, 124.6, 123.7, 118.0, 76.2, 65.9, 63.0, 62.8, 62.7, 57.4, 13.5, 13.2; IR (KBr): 3418.7, 2983.2, 1779.2, 1731.7, 1670.0, 1529.6, 1477.3, 1345.5, 1247.5, 1188.7, 712.3 cm^{-1}; HRMS (ESI) for $C_{30}H_{27}N_3O_9$ $[M+H]^+$ calcd 574.1820, found 574.1826.

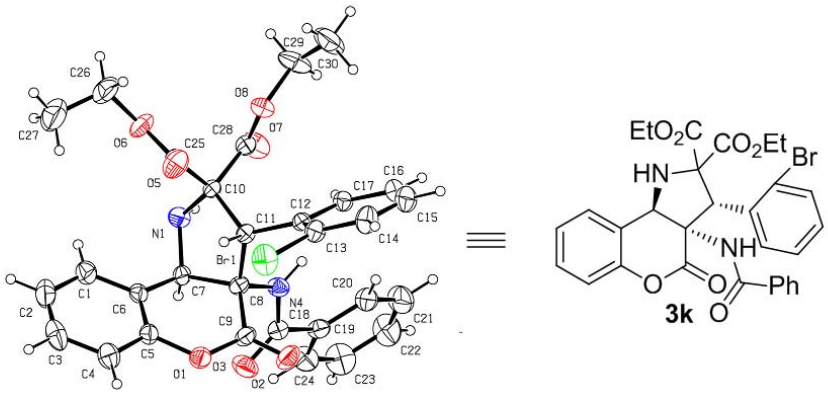


3w

(3R, 3aS, 9bR)-diethyl 3a-benzamido-7-methoxy-4-oxo-3-phenyl-1,3a,4,9b-tetrahydrochromeno[4,3-*b*]pyrrole-2,2(*3H*)-dicarboxylate (3w): white solid; $[\alpha]_D^{20}$ = -83.7 (*c* 1.075, $CHCl_3$); mp 76–78 °C; The enantiomeric excess was determined by HPLC with an AD–H column. (*n*-hexane:

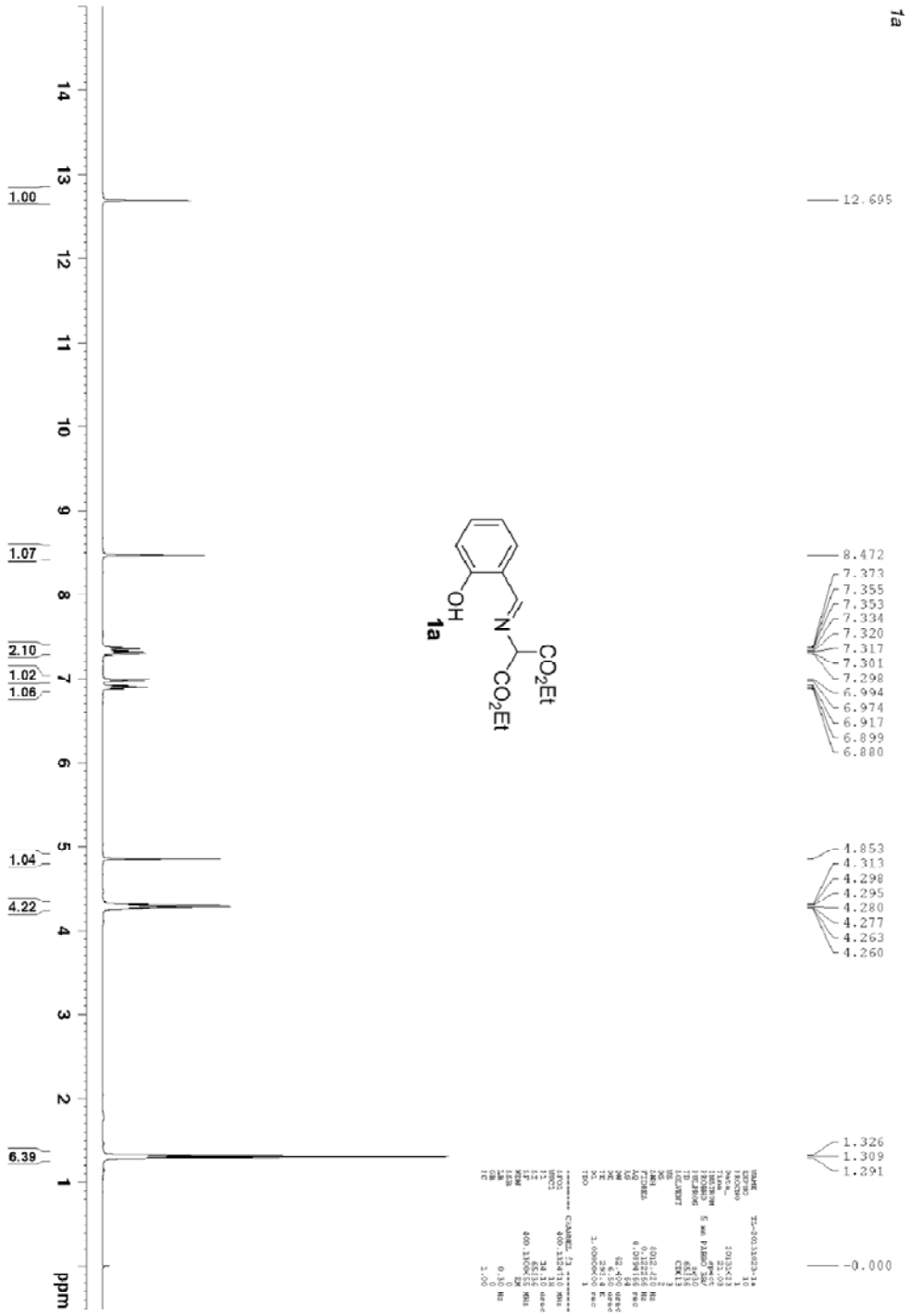
i-PrOH = 70:30), 1.0 mL/min, λ = 230 nm, $t_{R(minor)}$ = 14.2 min, $t_{R(major)}$ = 34.4 min, ee > 99%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6Hz, 2H), 7.48–7.34 (m, 9H), 6.75–6.63 (m, 3H), 5.16 (s, 1H), 4.97 (s, 1H), 4.06–3.87 (m, 4H), 3.80–3.73 (m, 4H), 1.14 (t, *J* = 7.2Hz, 3H), 0.82 (t, *J* = 7.2Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 169.2, 167.6, 166.7, 160.7, 150.2, 132.8, 132.6, 132.1, 130.0, 129.2, 129.1, 129.0, 128.5, 126.9, 113.5, 111.3, 101.6, 76.4, 66.2, 62.9, 62.5, 62.4, 57.5, 55.4, 13.7, 13.2; IR (KBr): 3420.2, 2981.4, 1732.7, 1670.3, 1627.7, 1510.3, 1474.2, 1280.1, 1221.1, 1159.0, 710.9 cm^{-1}; HRMS (ESI) for $C_{31}H_{30}N_2O_8$ $[M+H]^+$ calcd 559.2075, found 559.2083.

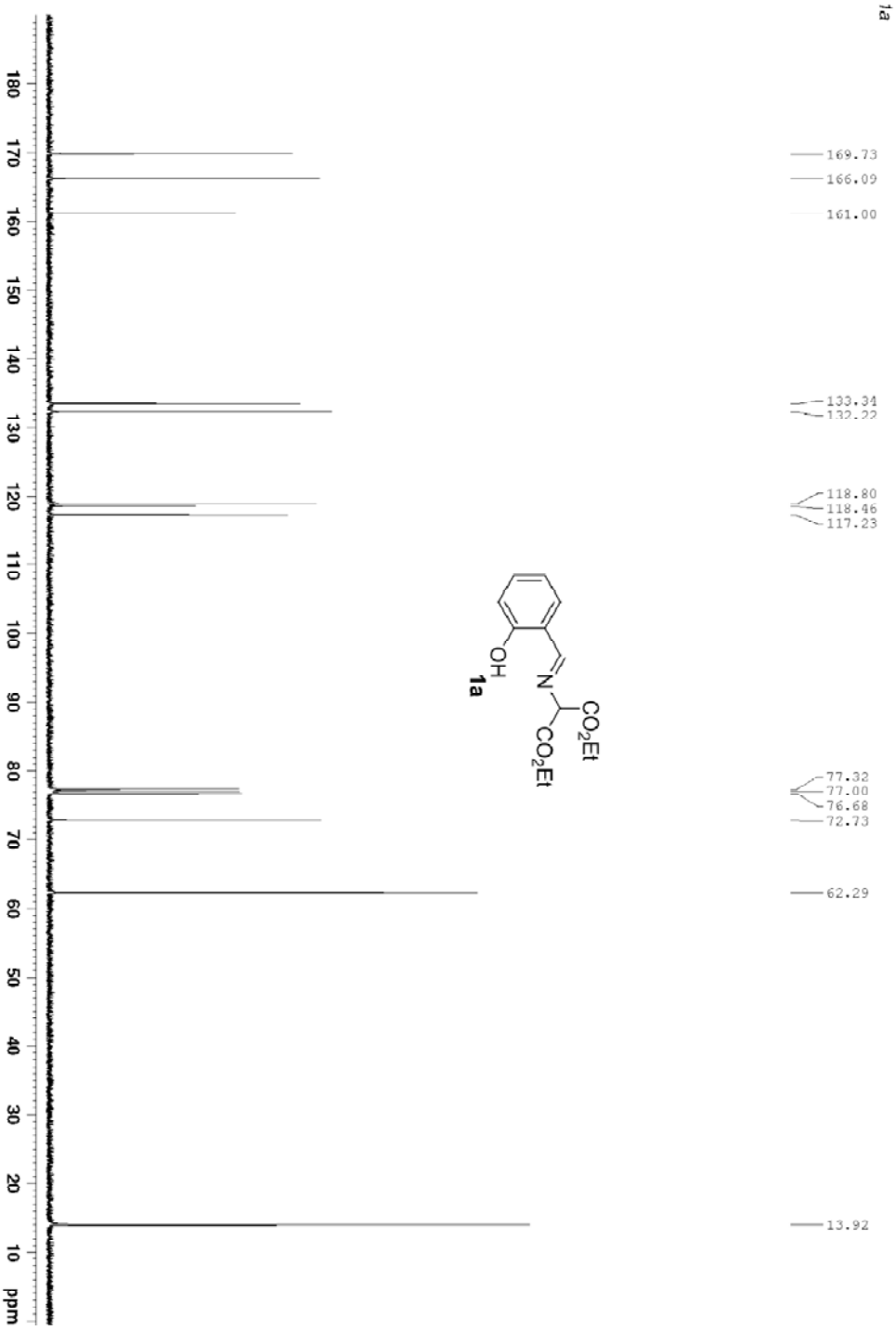
6. X-ray Crystallographic data of 3k



Empirical formula	$C_{30}H_{27}N_2O_7Br$
Formula weight	607.45
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.3949(3)
b/Å	15.4269(5)
c/Å	19.7387(8)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2860.81(17)
Z	4
ρ_{calc}mg/mm^3	1.413
m/mm^{-1}	1.488
F(000)	1248.0
Crystal size/mm^3	0.24 × 0.22 × 0.18
2Θ range for data collection	5.98 to 57.12°
Index ranges	$-11 \le h \le 12$, $-19 \le k \le 18$, $-25 \le l \le 26$
Reflections collected	13749
Independent reflections	6345[R(int) = 0.0599]
Data/restraints/parameters	6345/0/368
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1003
Final R indexes [all data]	R_1 = 0.1185, wR_2 = 0.1274
Largest diff. peak/hole / e Å^{-3}	0.33/-0.52
Flack parameter	-0.007(10)

7. ^{1}H NMR and ^{13}C NMR spectra

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77.00
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72.73
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13.92
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CO2Et
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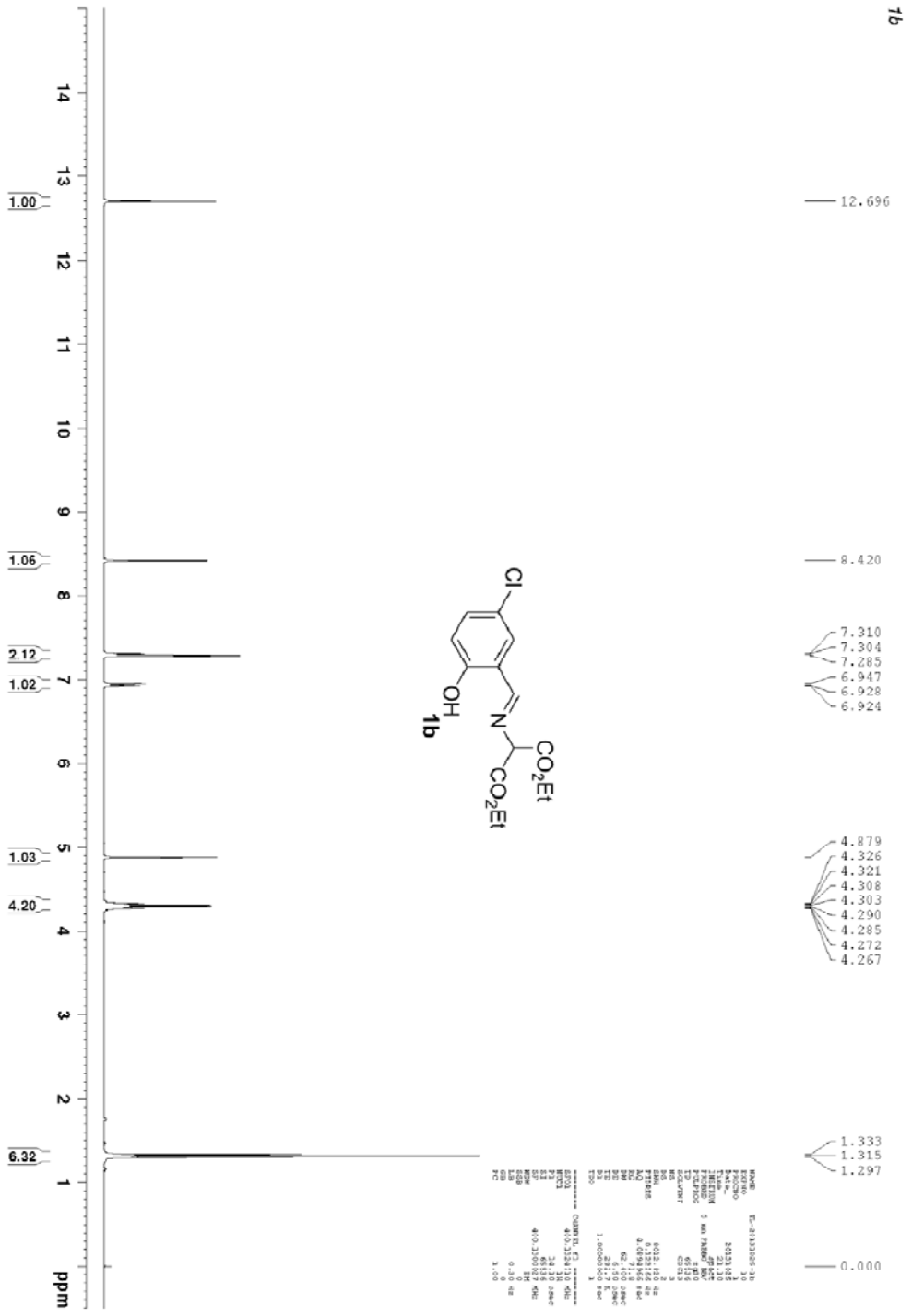
90
80
70
60
50
40
30
20
10
ppm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4.308
4.303
4.290
4.285
4.272
4.267
1.333
1.315
1.297
0.000
1.00
1.06
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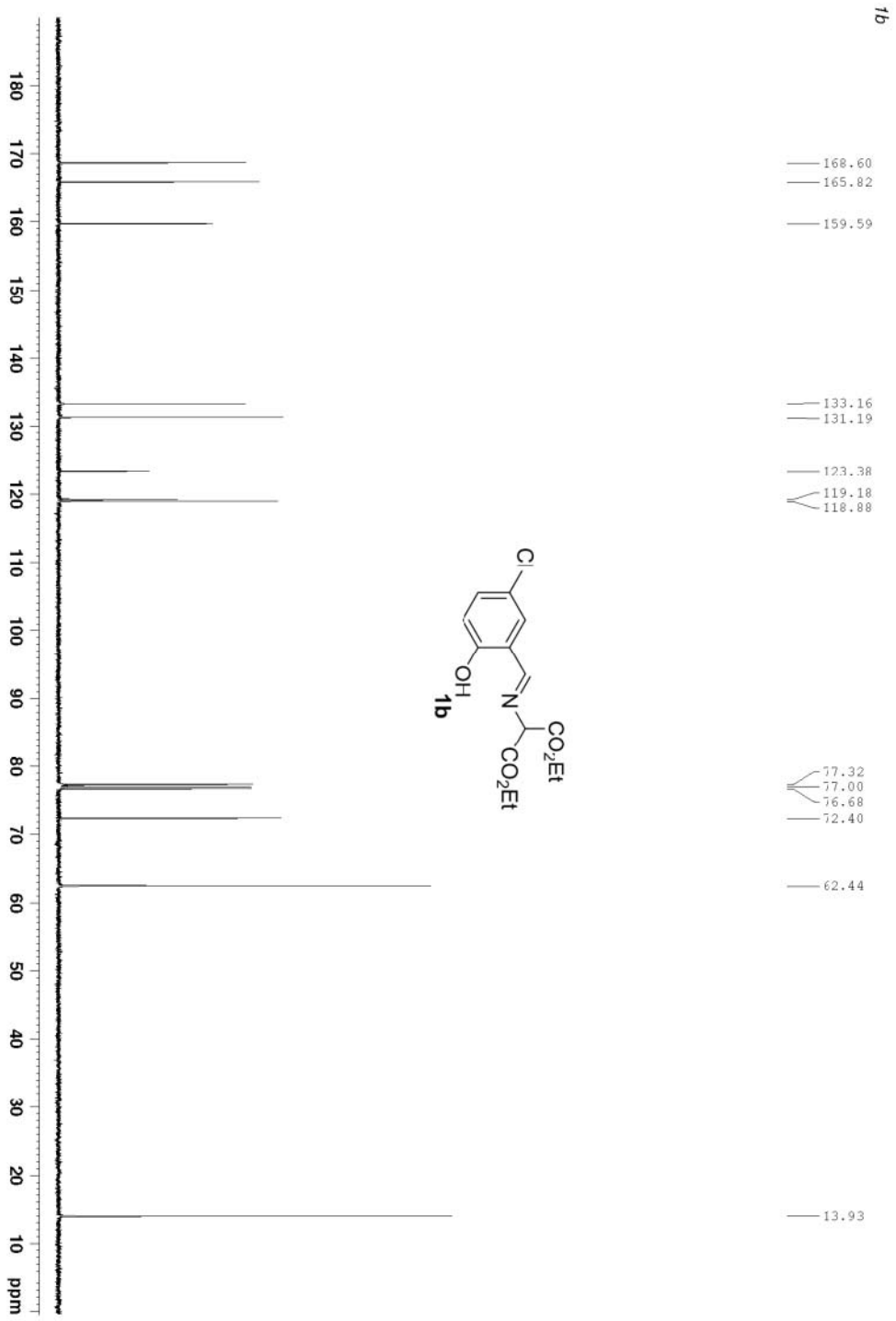
1.02
1.03
4.20
6.32
ppm
Cl
OH
N
CO2Et
CO2Et
1b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62.44
13.93
180
170
160
150
140
130
120
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60
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ppm
Cl
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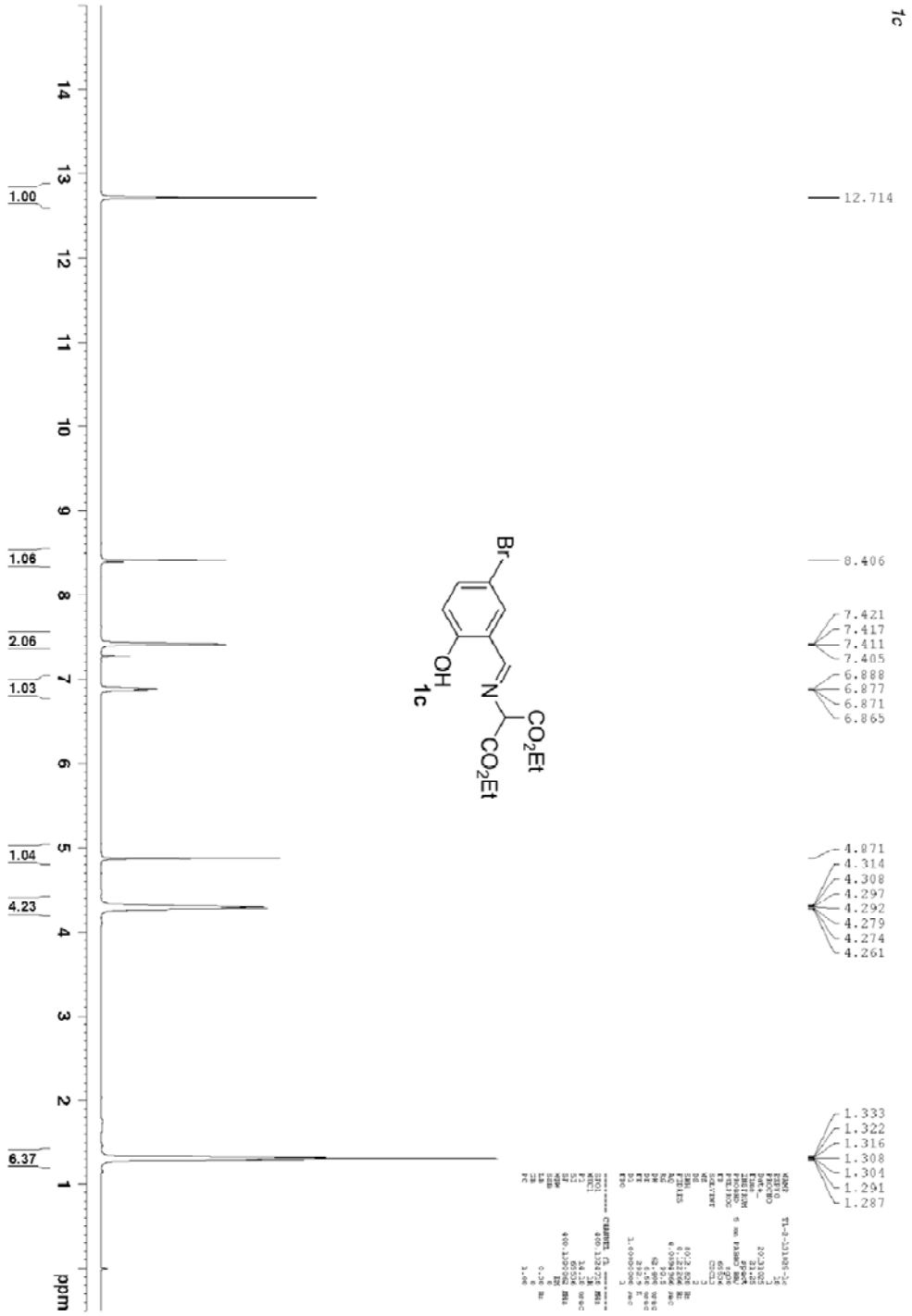
CO2Et
1b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4.308
4.297
4.292
4.279
4.274
4.261
1.333
1.322
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CO2Et
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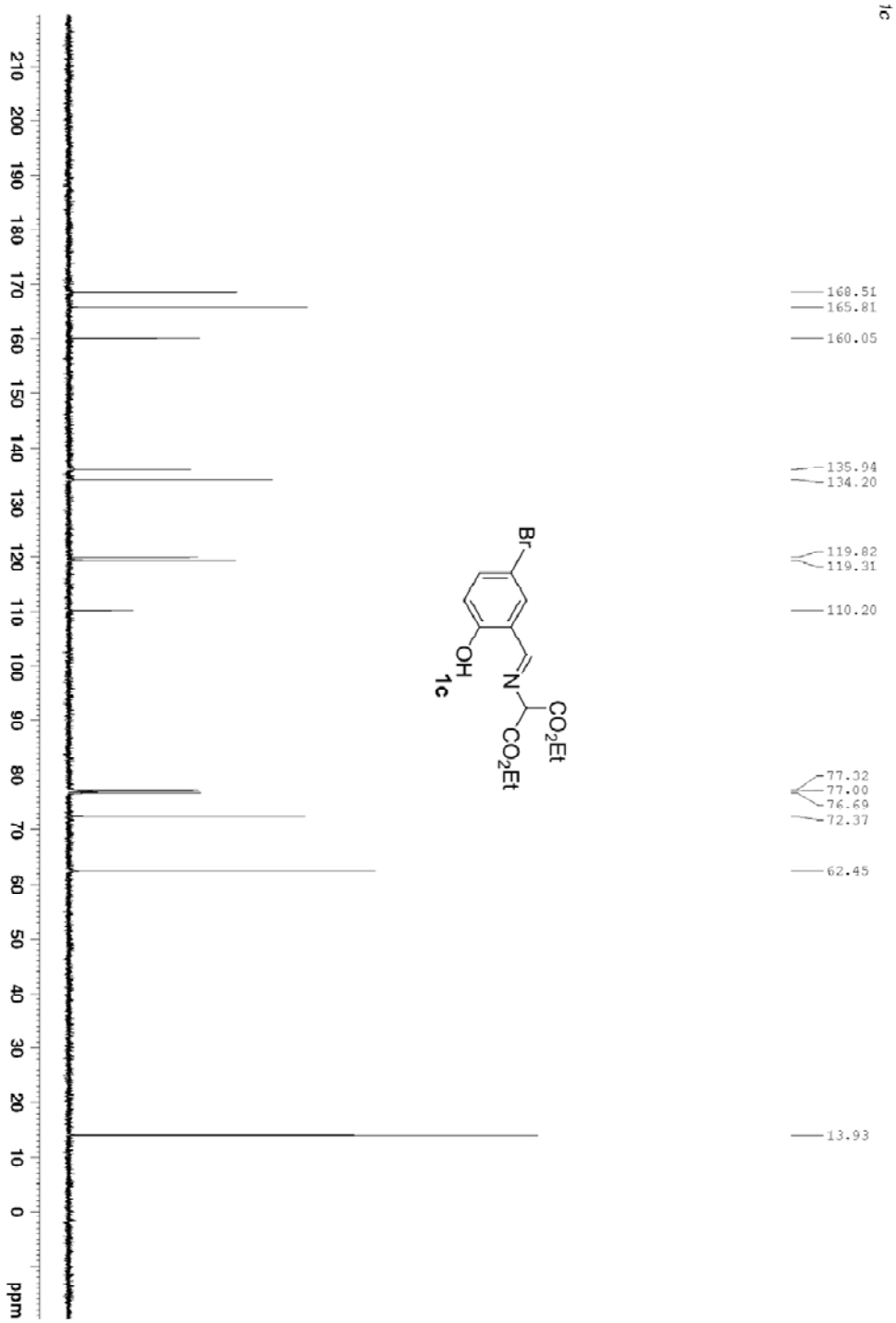
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134.20
119.82
119.31
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77.32
77.00
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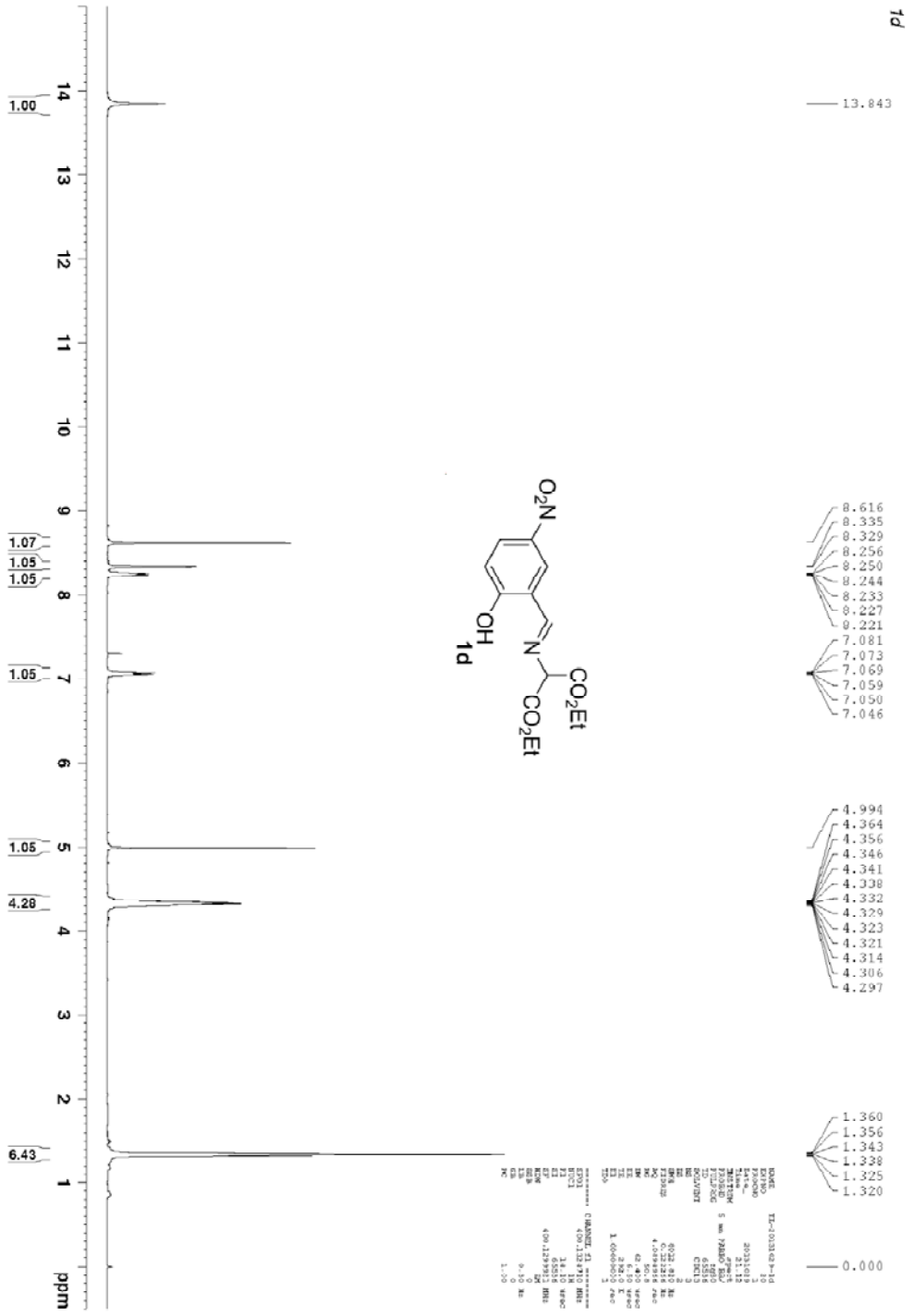
62.45
13.93
Br
OH
N
CO2Et
CO2Et
1c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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4.329
4.323
4.321
4.314
4.306
4.297
1.360
1.356
1.343
1.338
1.325
1.320
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1.00
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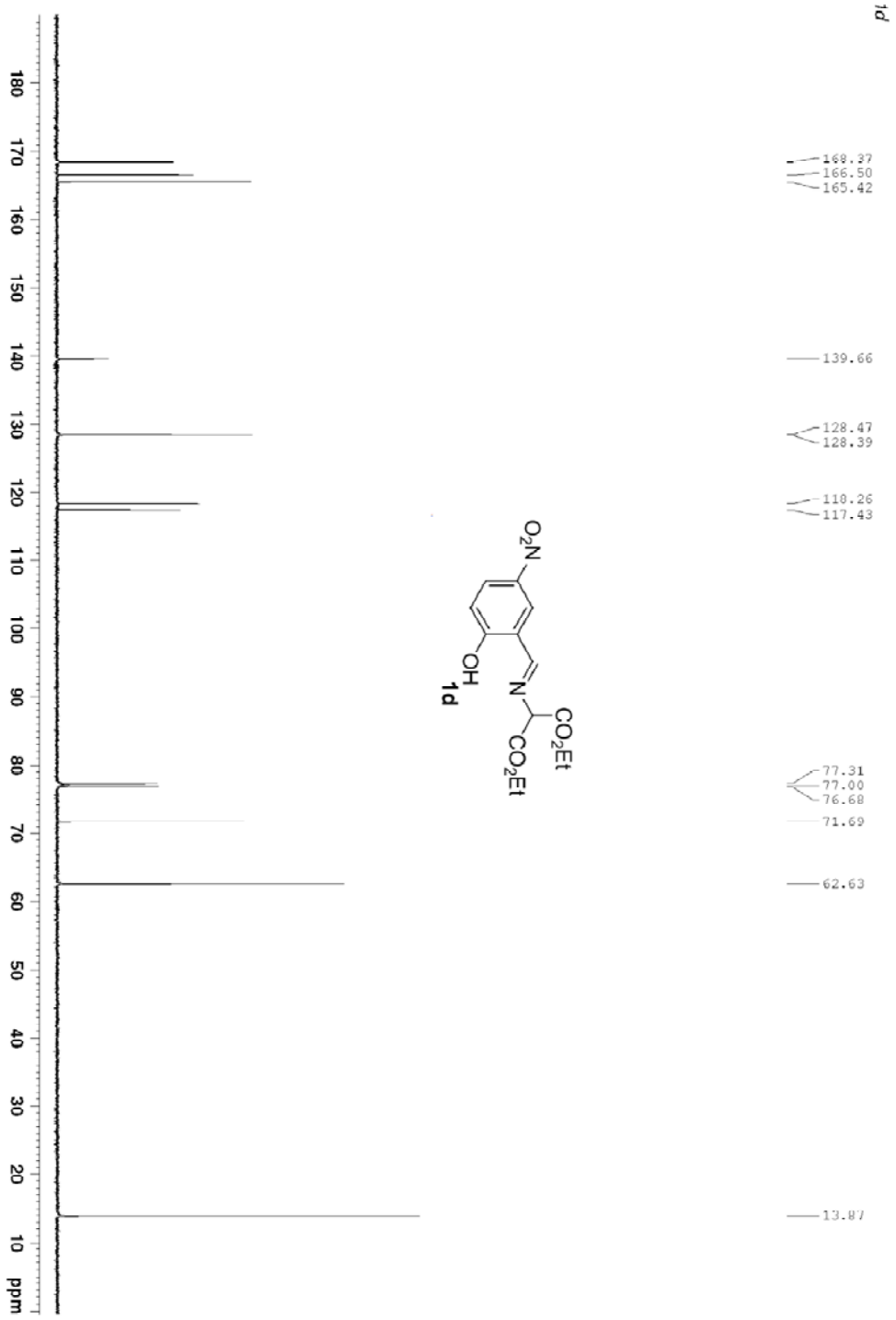
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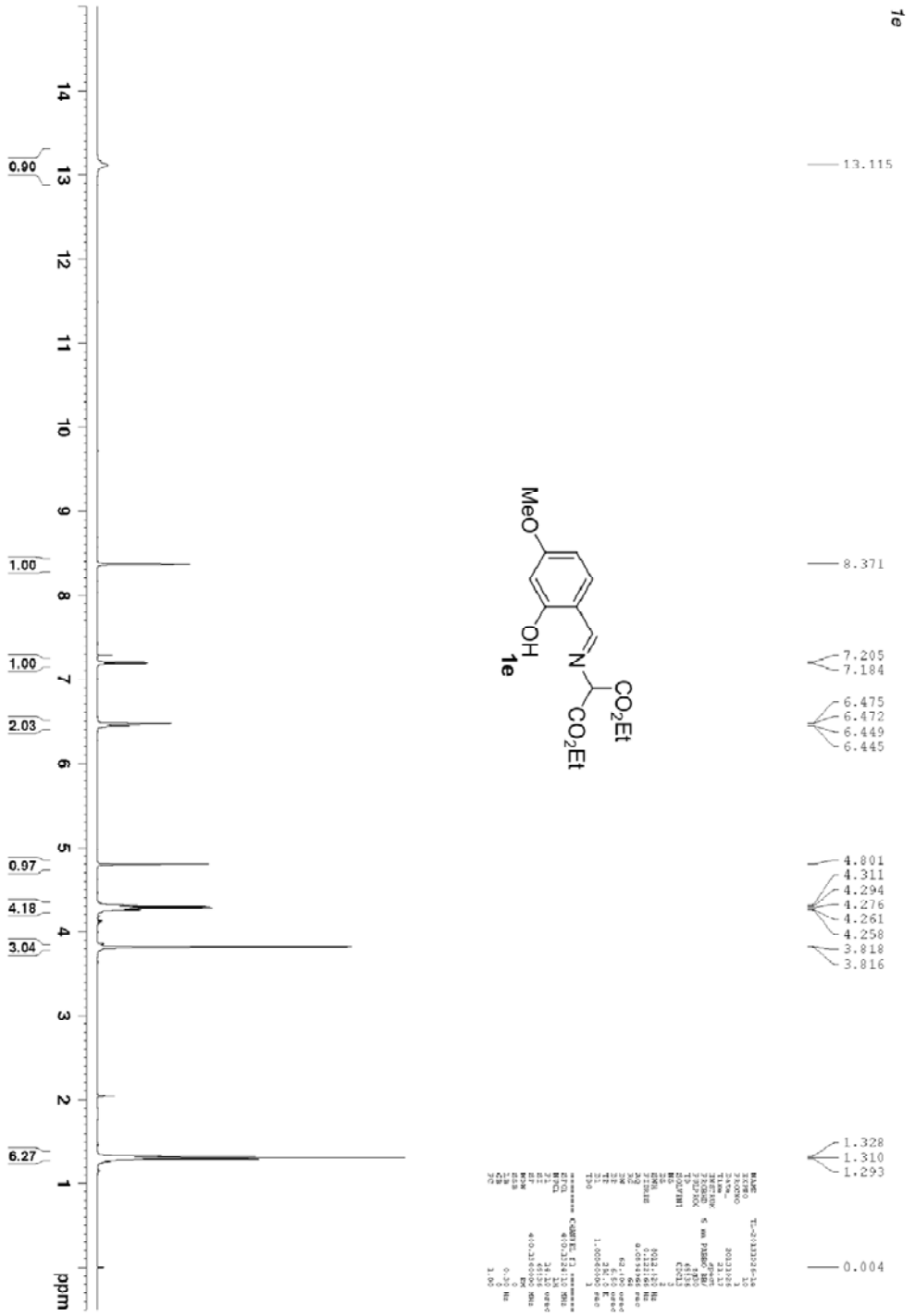
CO2Et
CO2Et
1d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CO2Et
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ppm
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7.205
7.184
6.475
6.472
6.449
6.445
4.801
4.311
4.294
4.276
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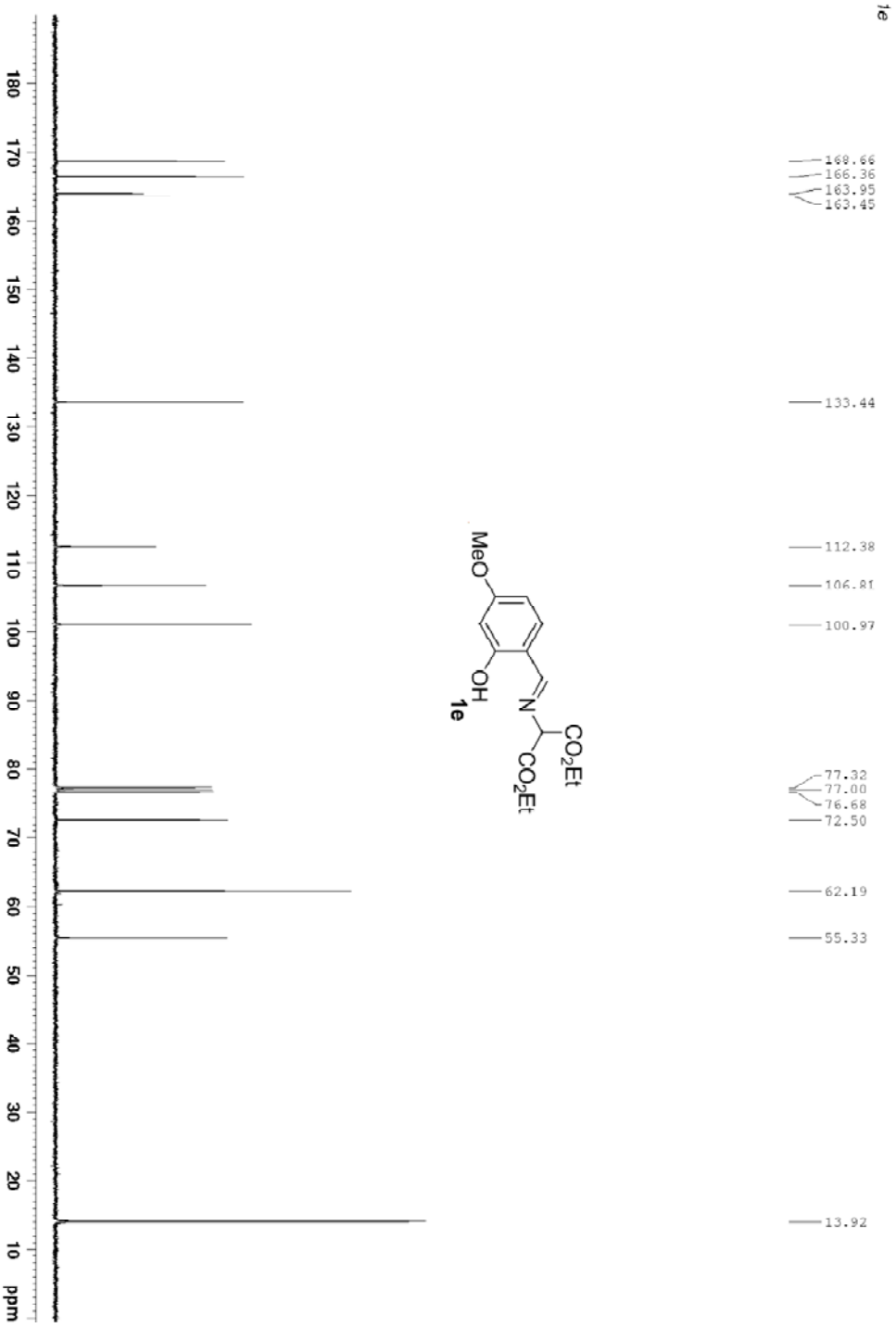
3.818
3.816
1.328
1.310
1.293
0.004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163.95
163.45
133.44
112.38
106.81
100.97
77.32
77.00
76.68
72.50
62.19
55.33
13.92
MeO
OH
N
CO2Et
CO2Et
1e
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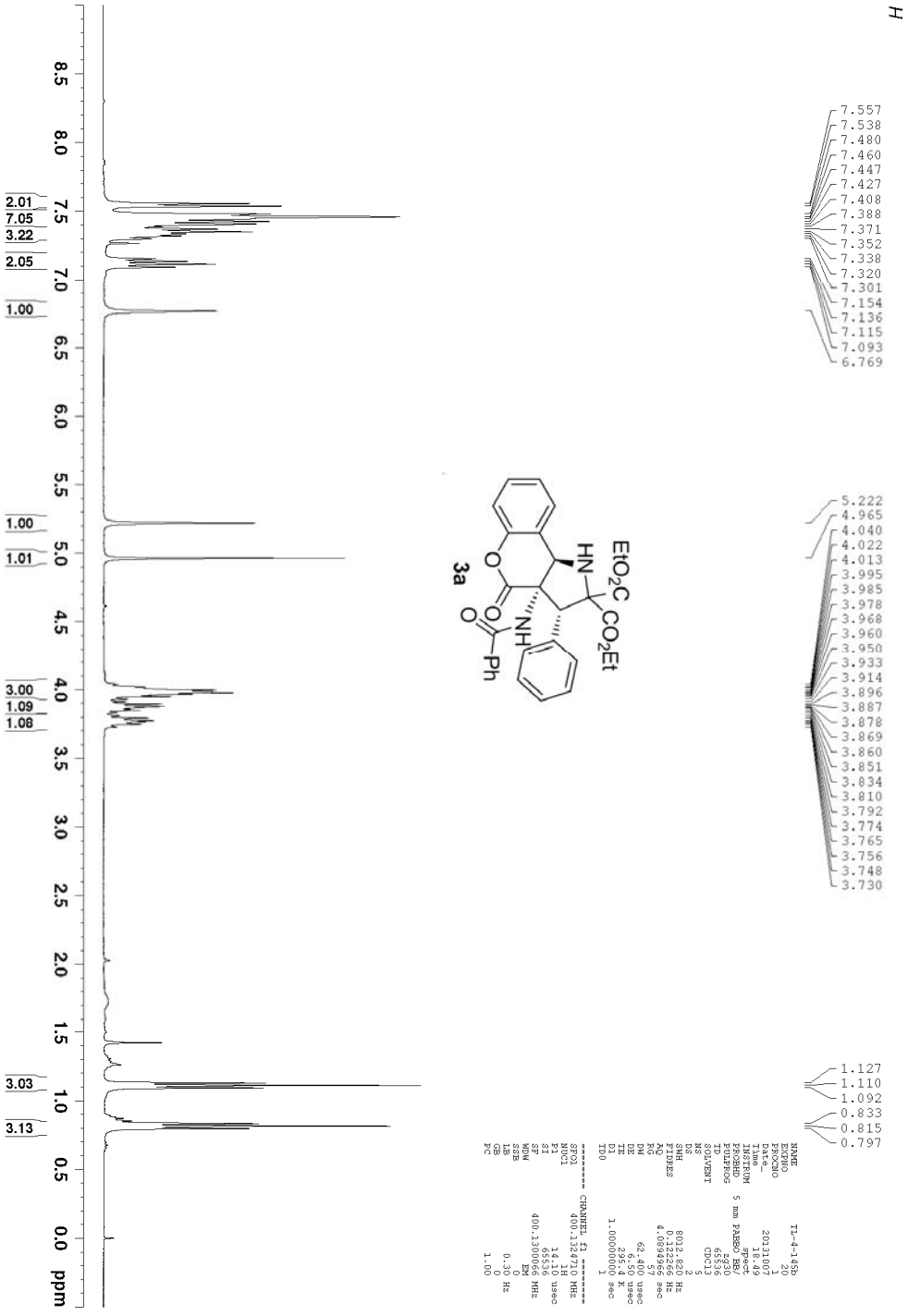
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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EtO2C
CO2Ph
HN
NH
O
O
O
O
Ph
1H
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7.460
7.447
7.427
7.408
7.388
7.371
7.352
7.338
7.320
7.301
7.154
7.136
7.115
7.093
6.769
5.222
4.965
4.040
4.022
4.013
3.995
3.985
3.978
3.968
3.960
3.950
3.933
3.914
3.896
3.887
3.878
3.869
3.860
3.851
3.834
3.810
3.792
3.774
3.765
3.756
3.748
3.730
1.127
1.110
1.092
0.833
0.815
0.797
2.01
7.05
3.22
2.05
1.00
1.00
1.01
3.00
1.09
1.08
3.03
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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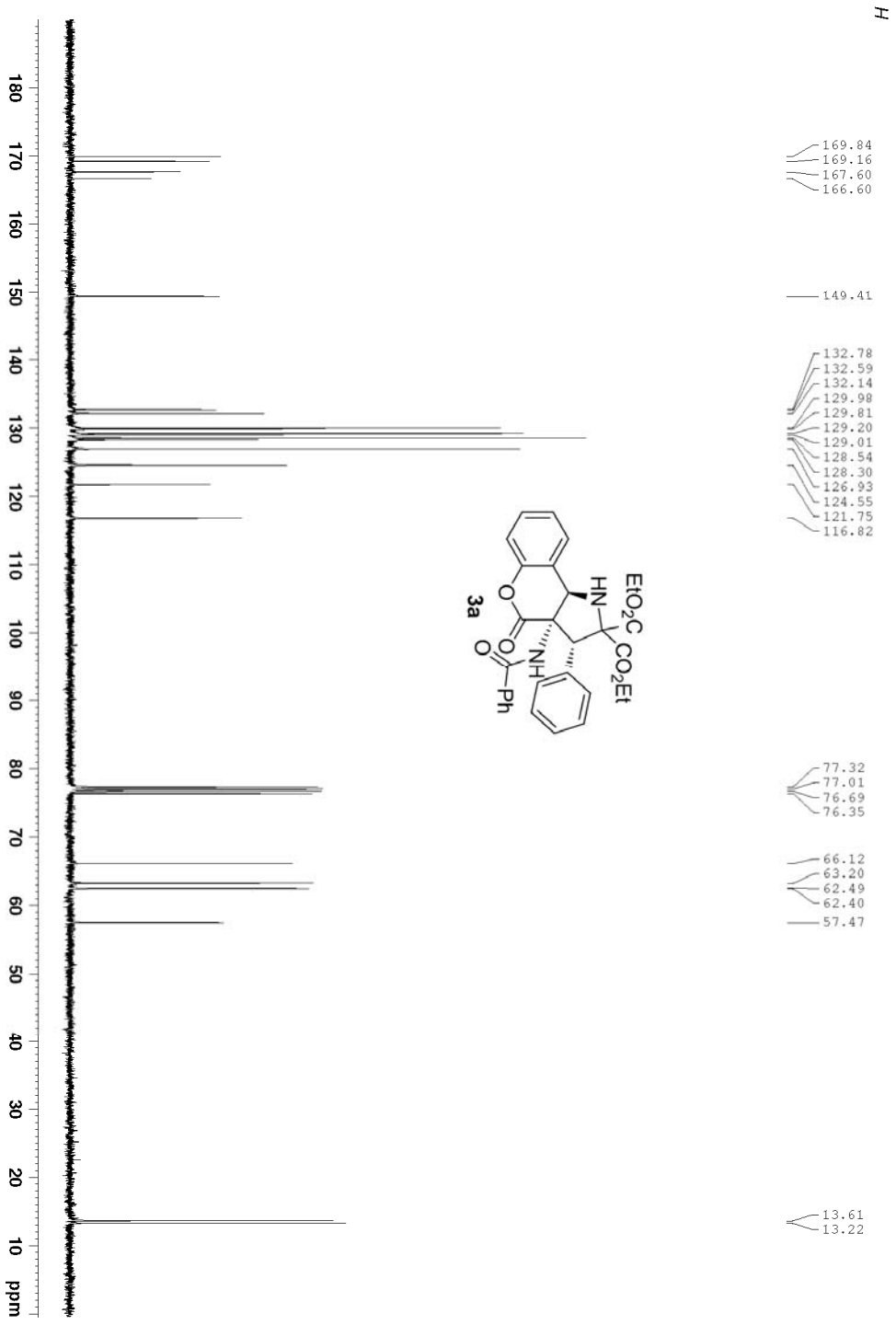
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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167.60
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132.59
132.14
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129.81
129.20
129.01
128.54
128.30
126.93
124.55
121.75
116.82
77.32
77.01
76.69
76.35
66.12
63.20
62.49
62.40
57.47
13.61
13.22
3a
EtO2C
CO2Et
HN
NH
O
O
Ph
H
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170
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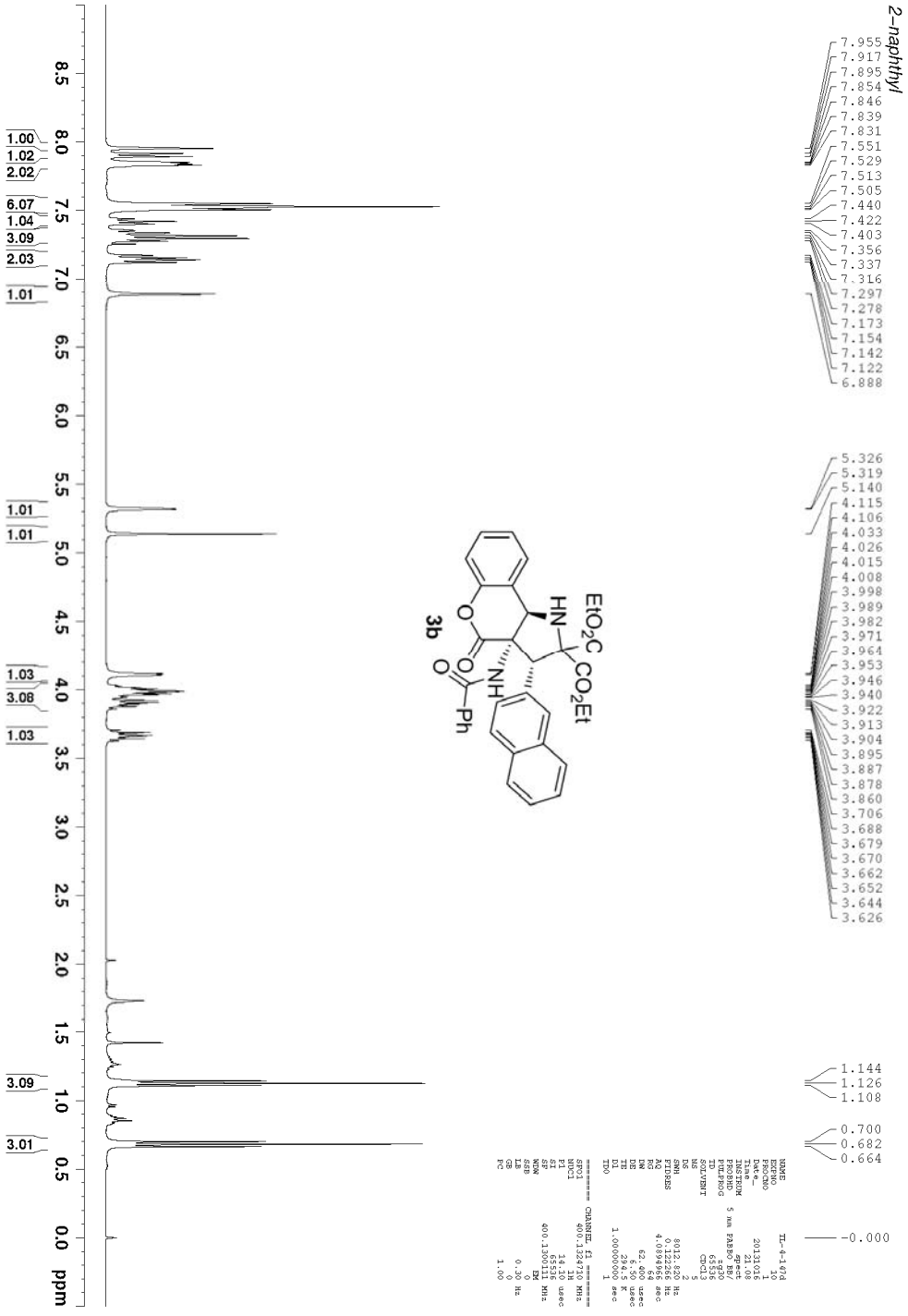
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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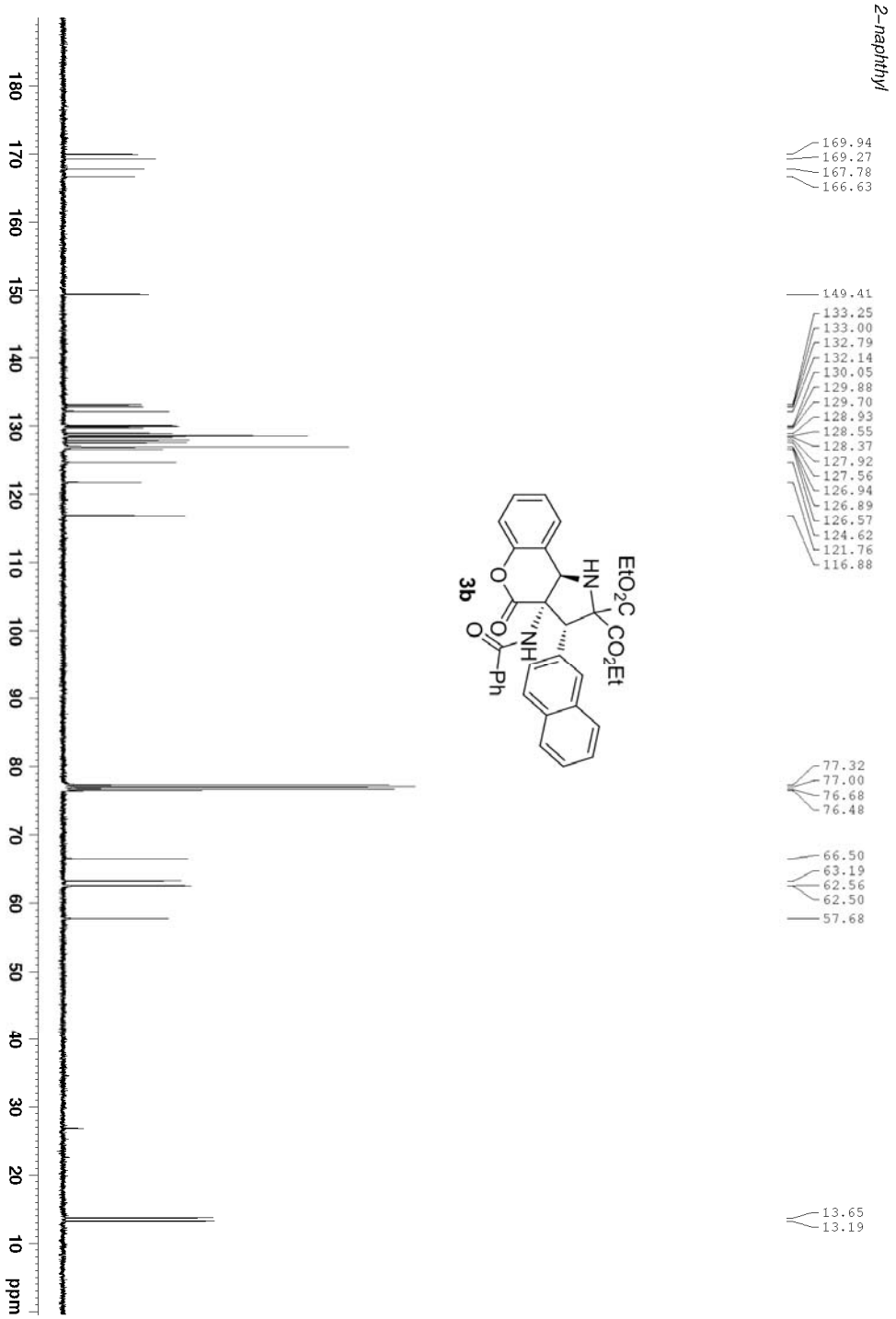
7.917
7.895
7.854
7.846
7.839
7.831
7.551
7.529
7.513
7.505
7.440
7.422
7.403
7.356
7.337
7.316
7.297
7.278
7.173
7.154
7.142
7.122
6.888
5.326
5.319
5.140
4.115
4.106
4.033
4.026
4.015
4.008
3.998
3.989
3.982
3.971
3.964
3.953
3.946
3.940
3.922
3.913
3.904
3.895
3.887
3.878
3.860
3.706
3.688
3.679
3.670
3.662
3.652
3.644
3.626
1.144
1.126
1.108
0.700
0.682
0.664
-0.000
1.00
1.02
2.02
6.07
1.04
3.09
2.03
1.01
1.01
1.01
1.03
3.08
1.03
3.09
3.01
8.5
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
ppm
EtO2C
HN
CO2Et
NH
O
O
O
Ph
3b
NAME
EXPNO
PROCNO
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
D0
======== CHANNEL f1 ========
SFO1
NUC1
P1
PL1
SF
WDW
SSB
LB
GB
PC
TL-4-17d
1
1
20131016
22.10.07
5 mm PABBO BB/
zg30
65536
CDCl3
2
8012.820 Hz
0.122566 Hz
4.089456 sec
64
6.50 usec
298.5 K
1.000000000 sec
1
400.1324710 MHz
1H
14.10 usec
-6.00 dB
400.1300111 MHz
EM
0
0.30 Hz
0
1.00


2-naphthyl
169.94
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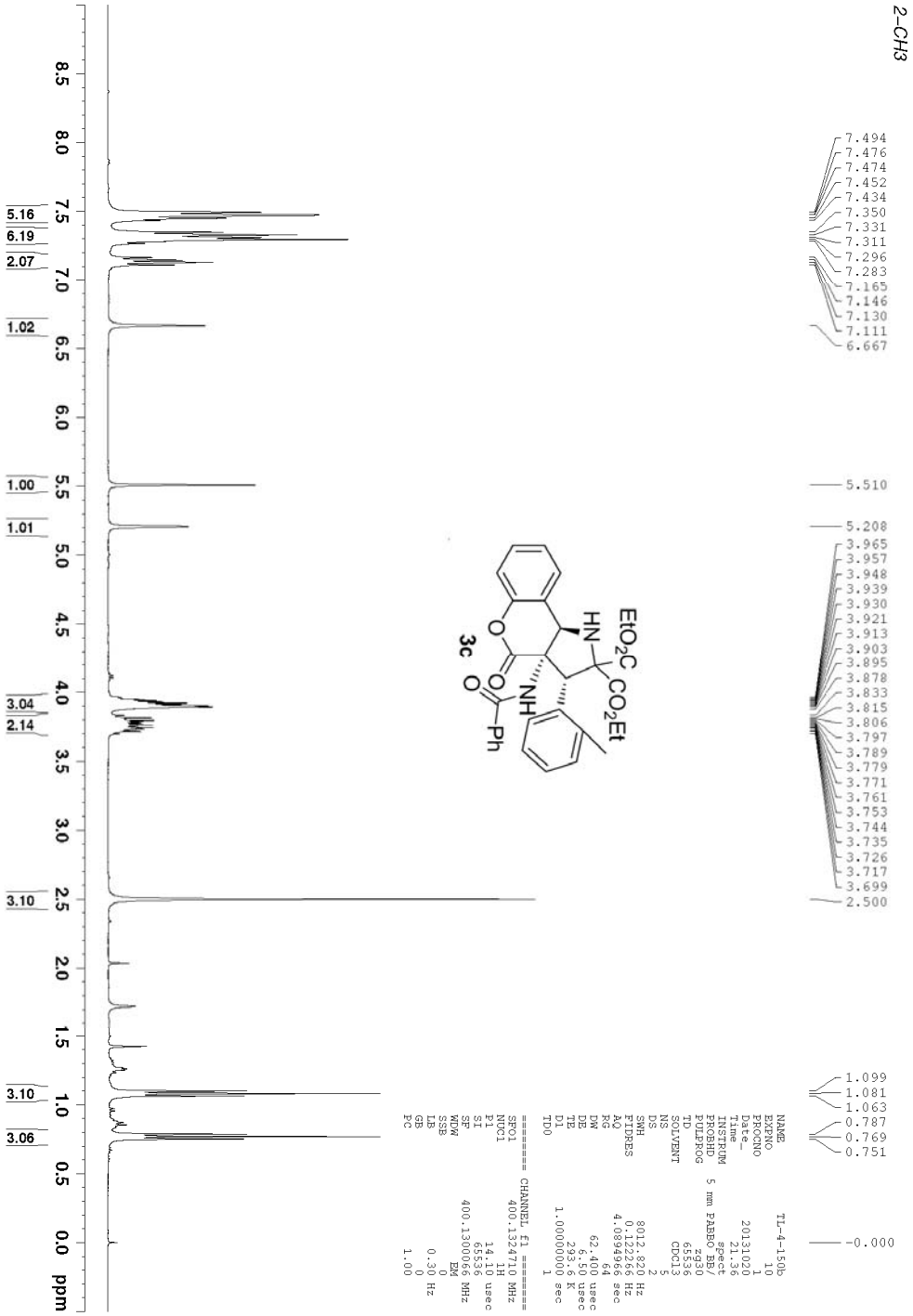
149.41
133.25
133.00
132.79
132.14
130.05
129.88
129.70
128.93
128.55
128.37
127.92
127.56
126.94
126.89
126.57
124.62
121.76
116.88
77.32
77.00
76.68
76.48
66.50
63.19
62.56
62.50
57.68
13.65
13.19
3b
EtO2C
CO2Et
HN
NH
O
O
O
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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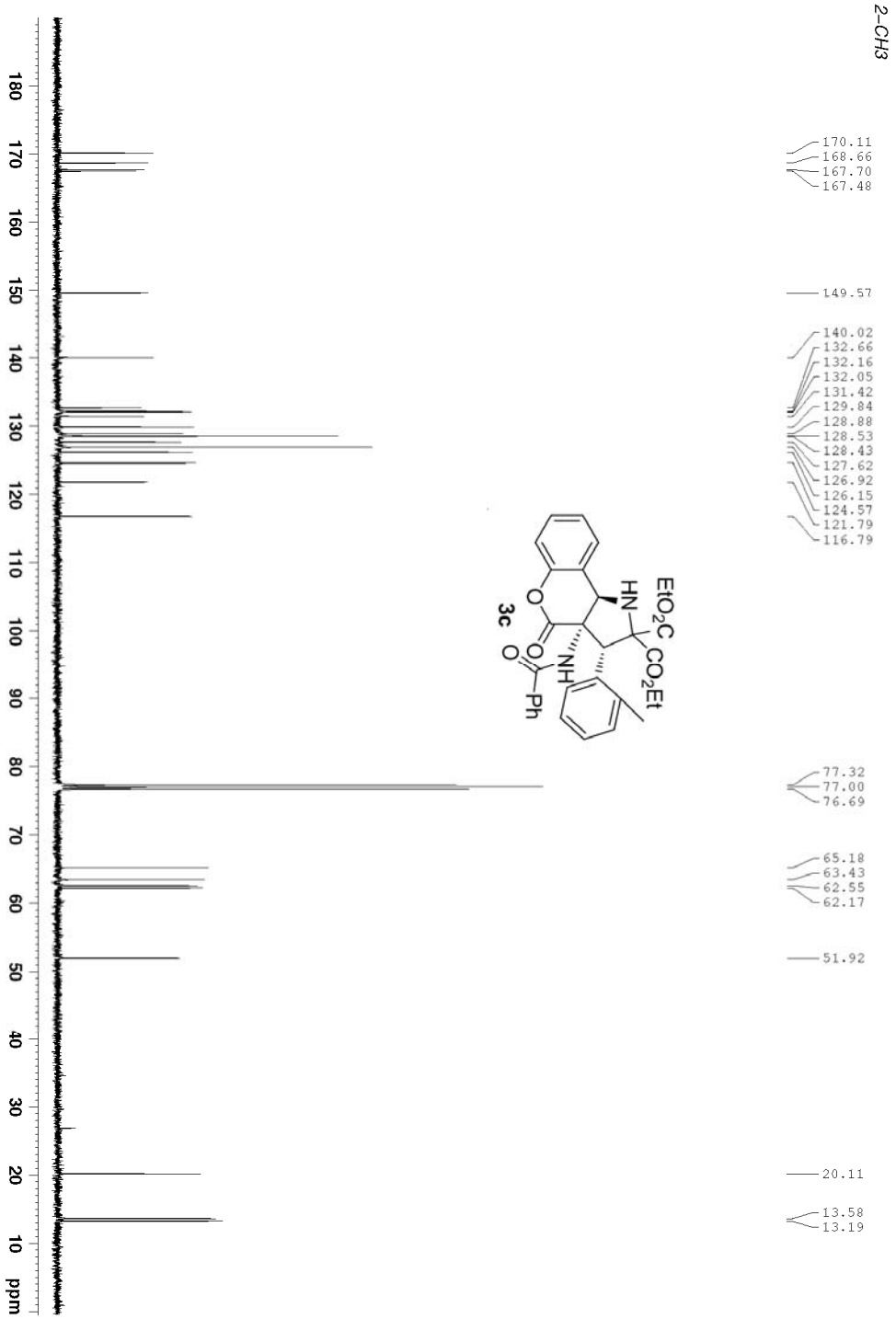
7.476
7.474
7.452
7.434
7.350
7.331
7.311
7.296
7.283
7.165
7.146
7.130
7.111
6.667
5.510
5.208
3.965
3.957
3.948
3.939
3.930
3.921
3.913
3.903
3.895
3.878
3.833
3.815
3.806
3.797
3.789
3.779
3.771
3.761
3.753
3.744
3.735
3.726
3.717
3.699
2.500
1.099
1.081
1.063
0.787
0.769
0.751
-0.000
EtO2C
CO2Et
HN
NH
O
O
O
Ph
3c
5.16
6.19
2.07
1.02
1.00
1.01
3.04
2.14
3.10
3.10
3.06
8.5
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
ppm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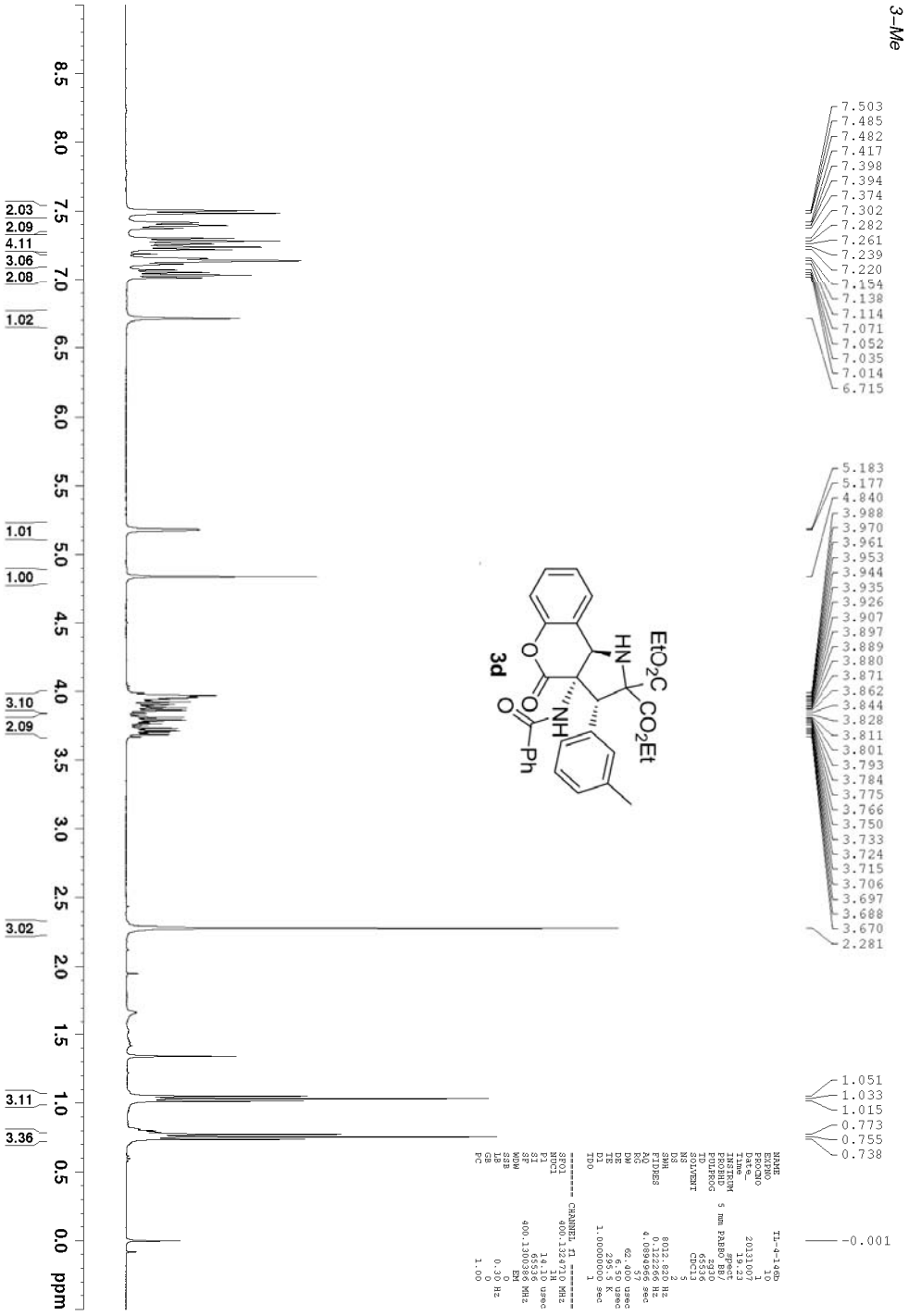
170.11
168.66
167.70
167.48
149.57
140.02
132.66
132.16
132.05
131.42
129.84
128.88
128.53
128.43
127.62
126.92
126.15
124.57
121.79
116.79
77.32
77.00
76.69
65.18
63.43
62.55
62.17
51.92
20.11
13.58
13.19
ppm
3c
EtO2C
CO2Et
HN
NH
O
O
O
Ph


3–Me
3d
EtO2C
CO2Et
HN
NH
O
O
O
Ph
2.03
2.09
4.11
3.06
2.08
1.02
1.01
1.00
3.10
2.09
3.02
3.11
3.36
8.5
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
ppm
7.503
7.485
7.482
7.417
7.398
7.394
7.374
7.302
7.282
7.261
7.239
7.220
7.154
7.138
7.114
7.071
7.052
7.035
7.014
6.715
5.183
5.177
4.840
3.988
3.970
3.961
3.953
3.944
3.935
3.926
3.907
3.897
3.889
3.880
3.871
3.862
3.844
3.828
3.811
3.801
3.793
3.784
3.775
3.766
3.750
3.733
3.724
3.715
3.706
3.697
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3.670
2.281
1.051
1.033
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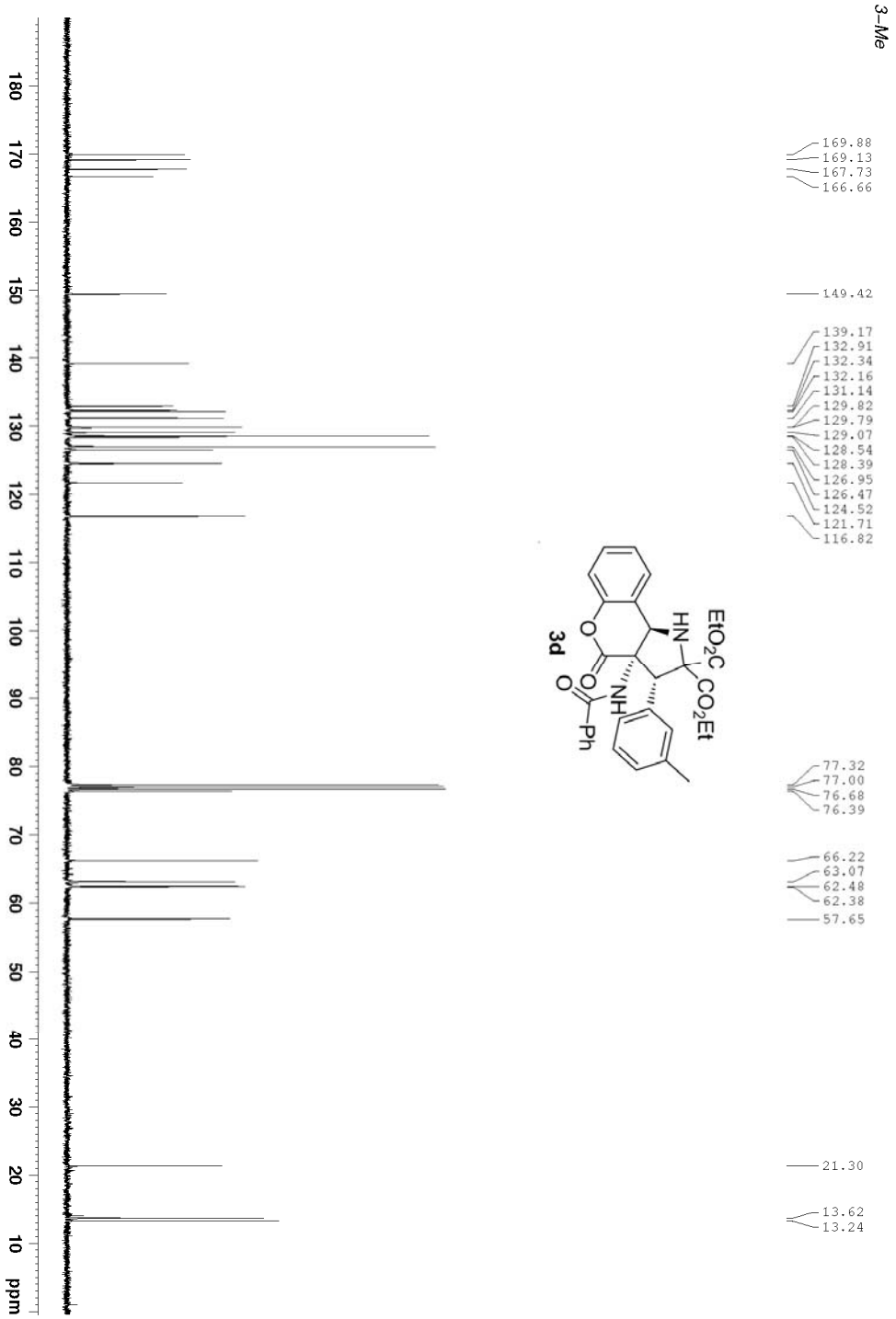
0.738
-0.001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166.66
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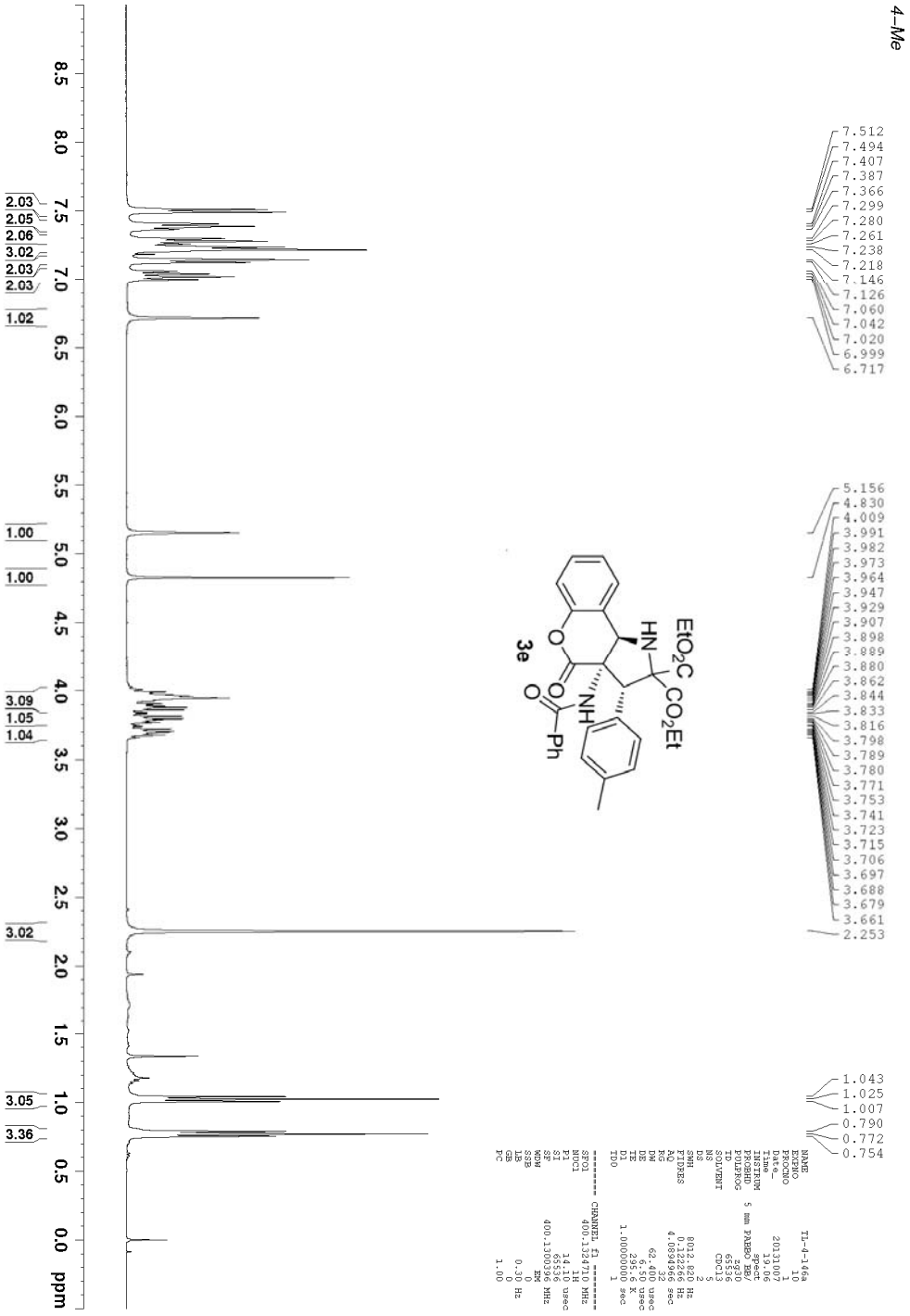
139.17
132.91
132.34
132.16
131.14
129.82
129.79
129.07
128.54
128.39
126.95
126.47
124.52
121.71
116.82
77.32
77.00
76.68
76.39
66.22
63.07
62.48
62.38
57.65
21.30
13.62
13.24
ppm
3d
EtO2C
CO2Et
HN
NH
O
Ph


4_Me
3e
EtO2C
CO2Et
HN
NH
O
Ph
7.512
7.494
7.407
7.387
7.366
7.299
7.280
7.261
7.238
7.218
7.146
7.126
7.060
7.042
7.020
6.999
6.717
5.156
4.830
4.009
3.991
3.982
3.973
3.964
3.947
3.929
3.907
3.898
3.889
3.880
3.862
3.844
3.833
3.816
3.798
3.789
3.780
3.771
3.753
3.741
3.723
3.715
3.706
3.697
3.688
3.679
3.661
2.253
1.043
1.025
1.007
0.790
0.772
0.754
2.03
2.05
2.06
3.02
2.03
2.03
1.02
1.00
1.00
3.09
1.05
1.04
3.02
3.05
3.36
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
0.5
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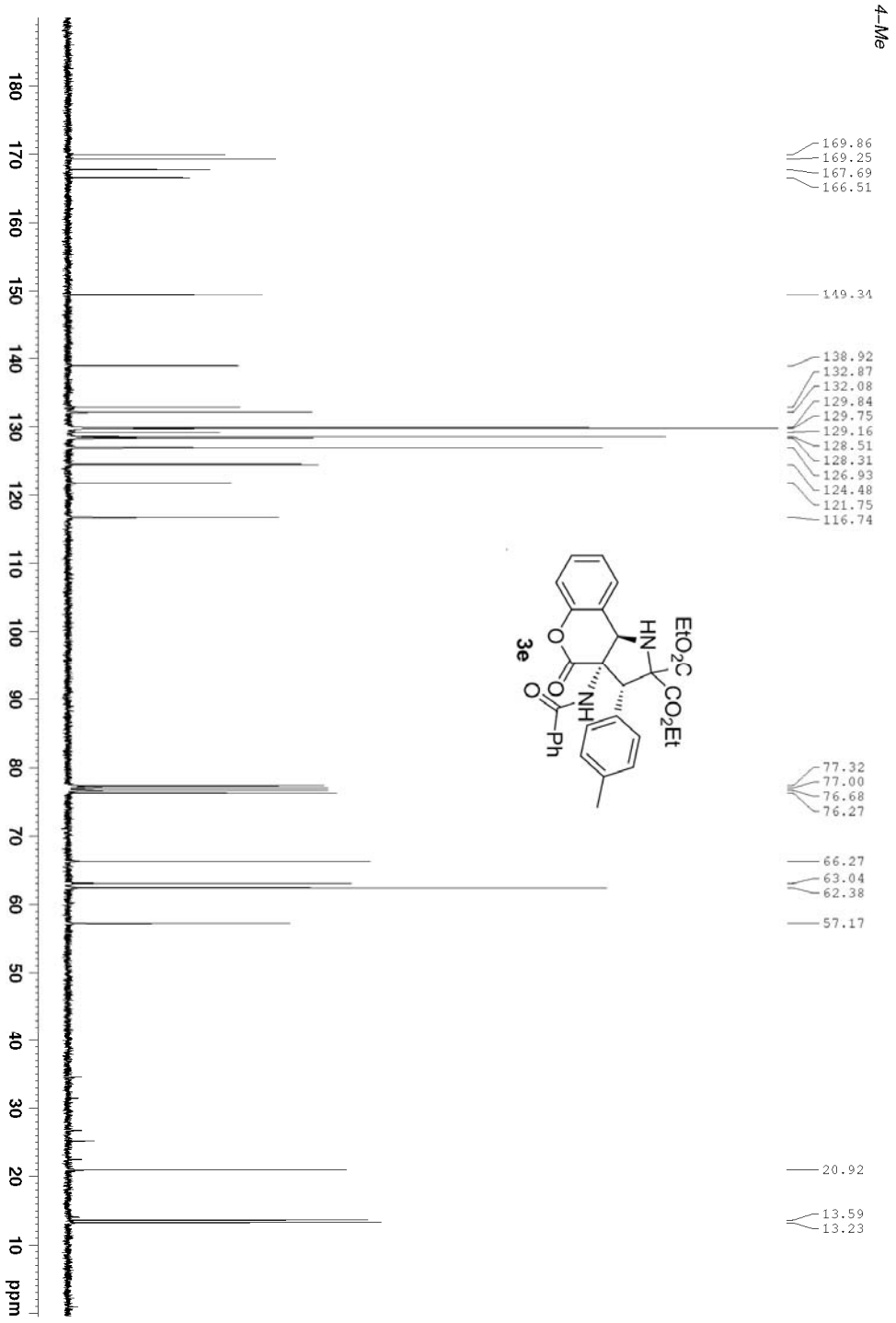
ppm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132.87
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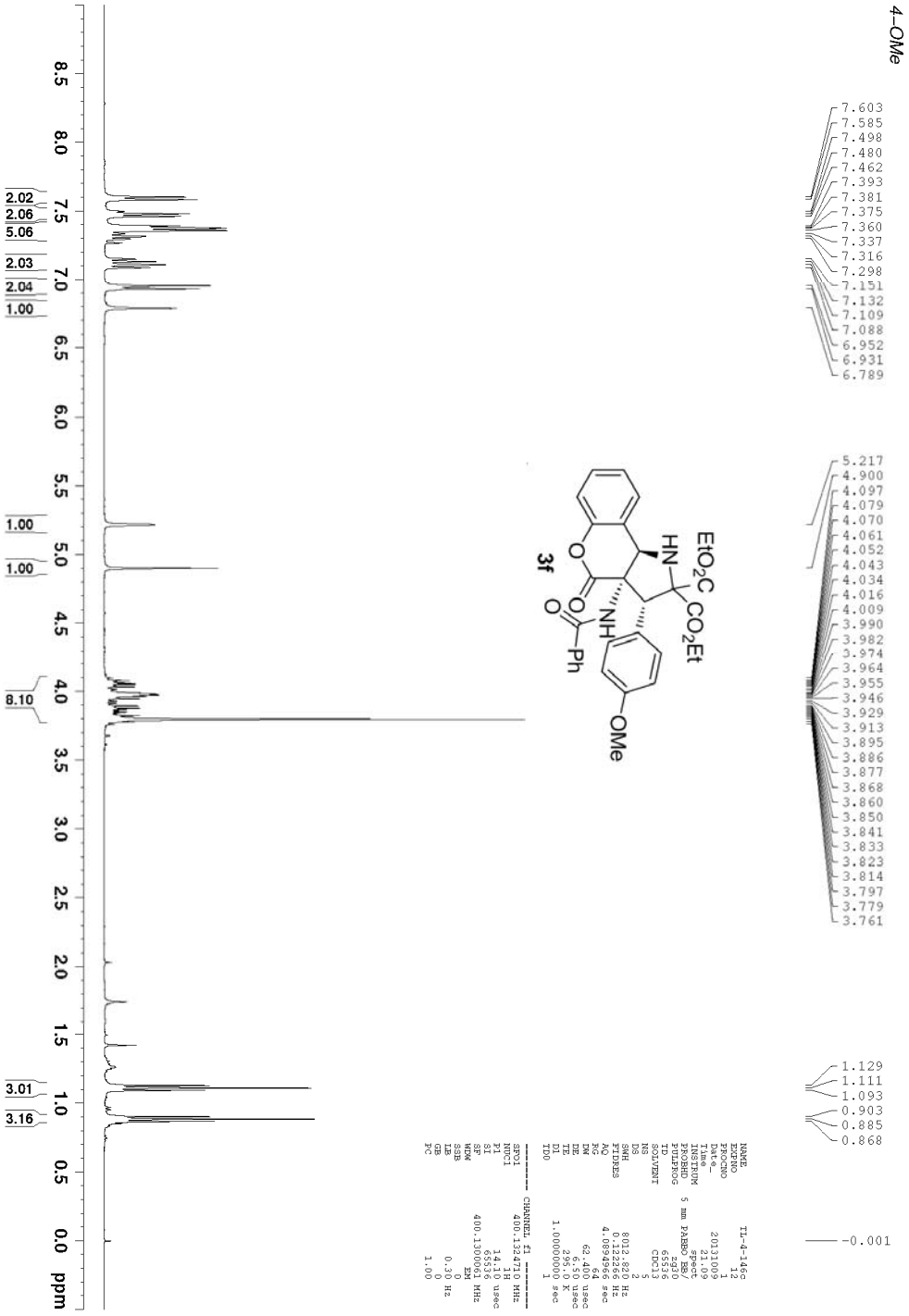
129.84
129.75
129.16
128.51
128.31
126.93
124.48
121.75
116.74
77.32
77.00
76.68
76.27
66.27
63.04
62.38
57.17
20.92
13.59
13.23
ppm
3e
EtO2C
CO2Et
HN
NH
O
Ph


4-OMe
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7.480
7.462
7.393
7.381
7.375
7.360
7.337
7.316
7.298
7.151
7.132
7.109
7.088
6.952
6.931
6.789
5.217
4.900
4.097
4.079
4.070
4.061
4.052
4.043
4.034
4.016
4.009
3.990
3.982
3.974
3.964
3.955
3.946
3.929
3.913
3.895
3.886
3.877
3.868
3.860
3.850
3.841
3.833
3.823
3.814
3.797
3.779
3.761
1.129
1.111
1.093
0.903
0.885
0.868
-0.001
3f
EtO2C
CO2Ph
HN
NH
OMe
O
O
O
O
2.02
2.06
5.06
2.03
2.04
1.00
1.00
1.00
8.10
3.01
3.16
8.5
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
ppm
NAME
EXPNO
PROCNO
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
TD0
CHANNEL f1
SFO1
NUC1
P1
PLW1
SF
WDW
SSB
LB
GB
PC
400.1324710 MHz
1H
14.10 usec
0.53191 W
400.1300061 MHz
EM
0
0.30 Hz
0.00
1.00
TI-4-146c
1
12
20131009
21.09
5 mm PABBO BB/
zg30
65536
CDCl3
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0.122266 Hz
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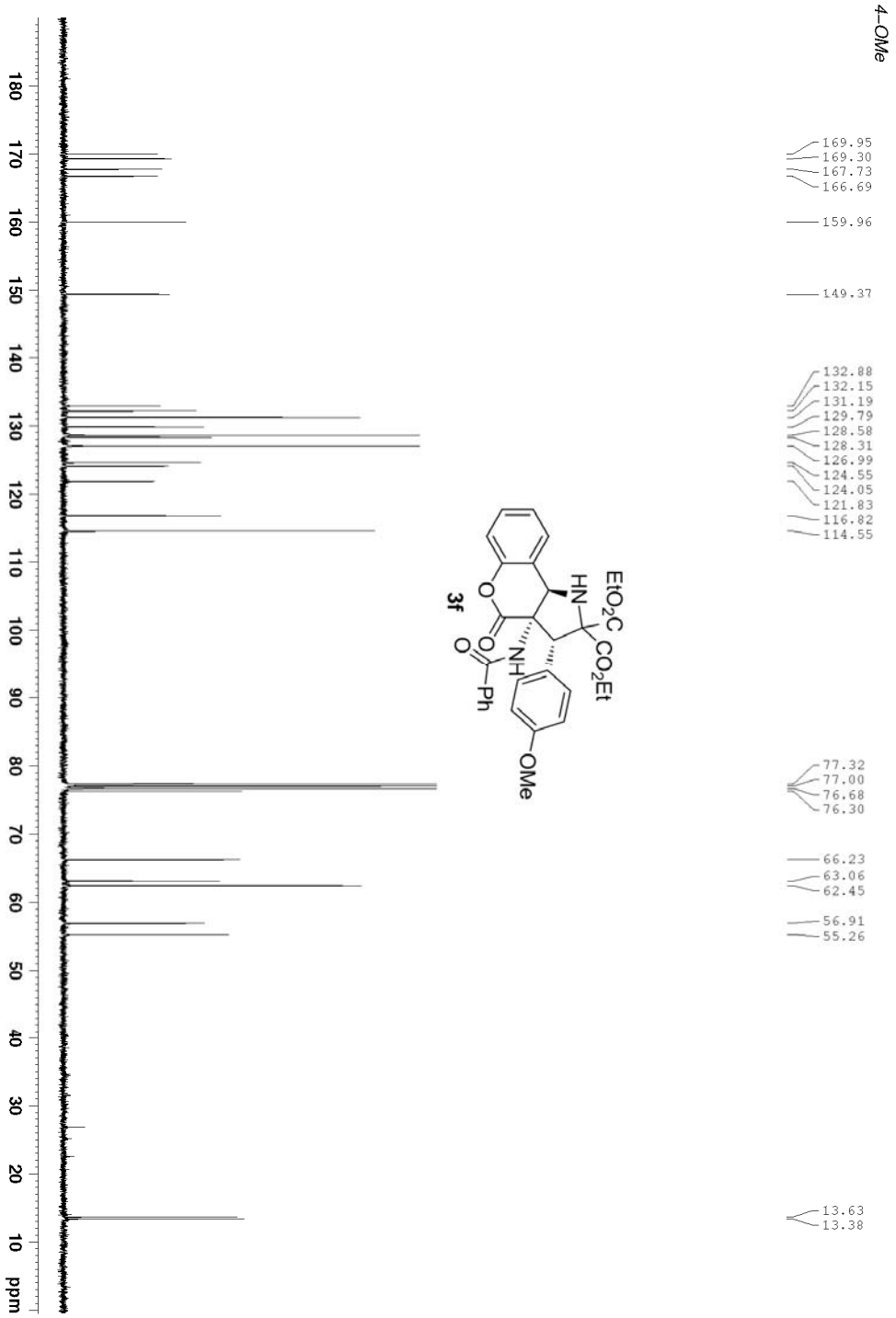
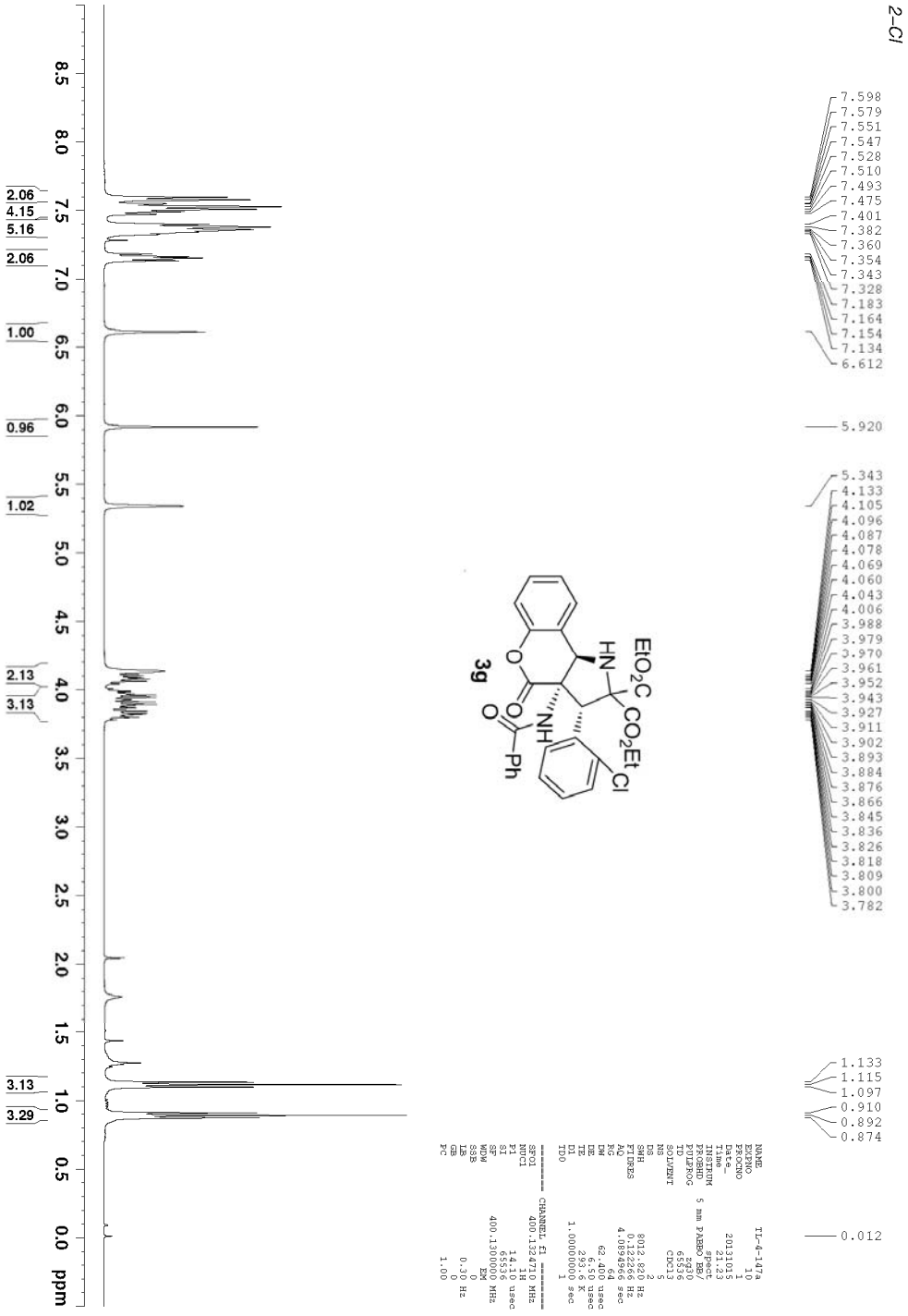
62.400 usec
6.50 usec
2.500 K
1.0000000 sec
1


4-OMe
169.95
169.30
167.73
166.69
159.96
149.37
132.88
132.15
131.19
129.79
128.58
128.31
126.99
124.55
124.05
121.83
116.82
114.55
77.32
77.00
76.68
76.30
66.23
63.06
62.45
56.91
55.26
13.63
13.38
3f
EtO2C
CO2Et
HN
NH
OMe
Ph
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.401
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7.360
7.354
7.343
7.328
7.183
7.164
7.154
7.134
6.612
5.920
5.343
4.133
4.105
4.096
4.087
4.078
4.069
4.060
4.043
4.006
3.988
3.979
3.970
3.961
3.952
3.943
3.927
3.911
3.902
3.893
3.884
3.876
3.866
3.845
3.836
3.826
3.818
3.809
3.800
3.782
1.133
1.115
1.097
0.910
0.892
0.874
0.012
3g
EtO2C
CO2Et
HN
NH
Ph
Cl
O
2.06
4.15
5.16
2.06
1.00
0.96
1.02
2.13
3.13
3.13
3.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
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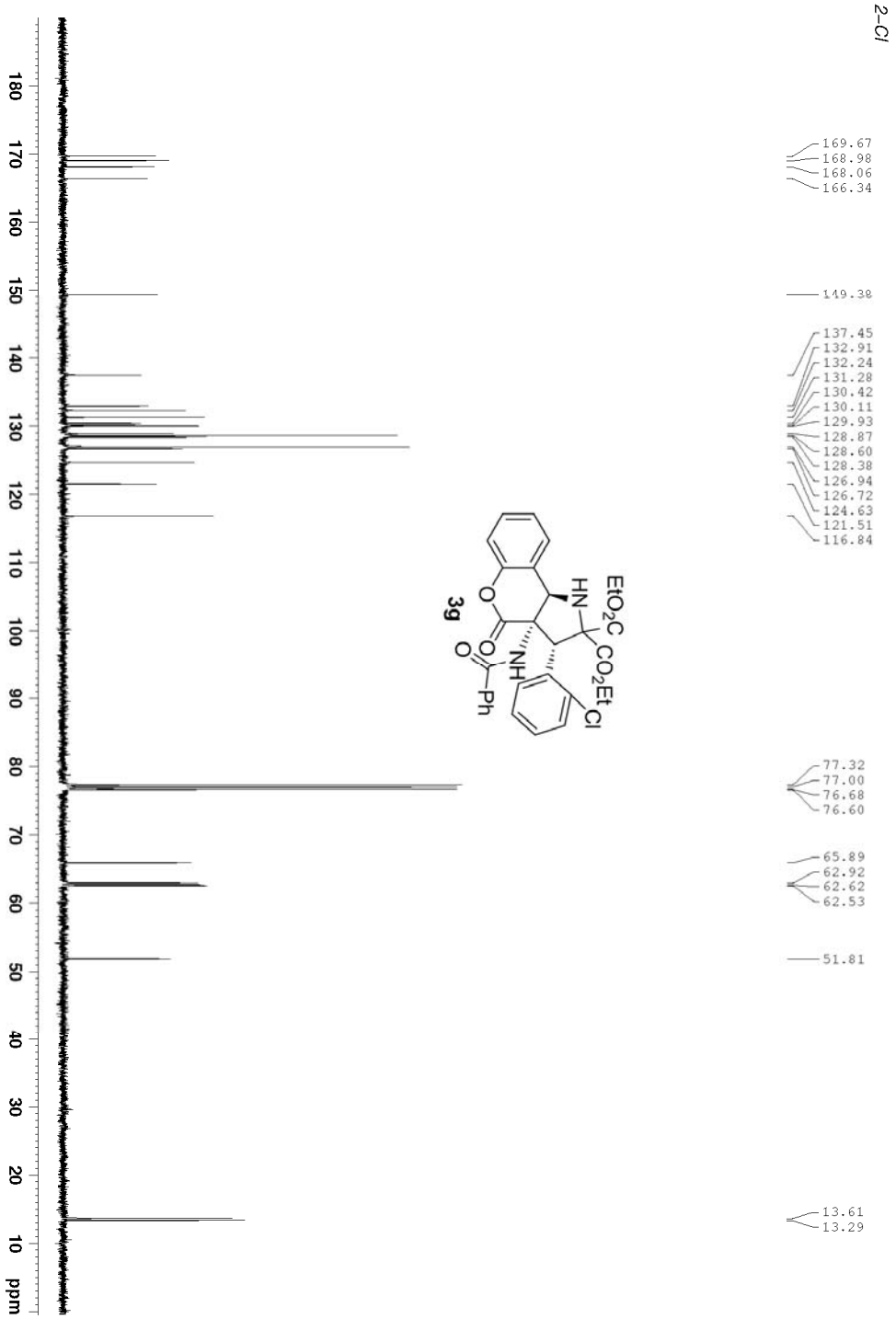
1.5
1.0
0.5
0.0
ppm


2-Cl
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132.91
132.24
131.28
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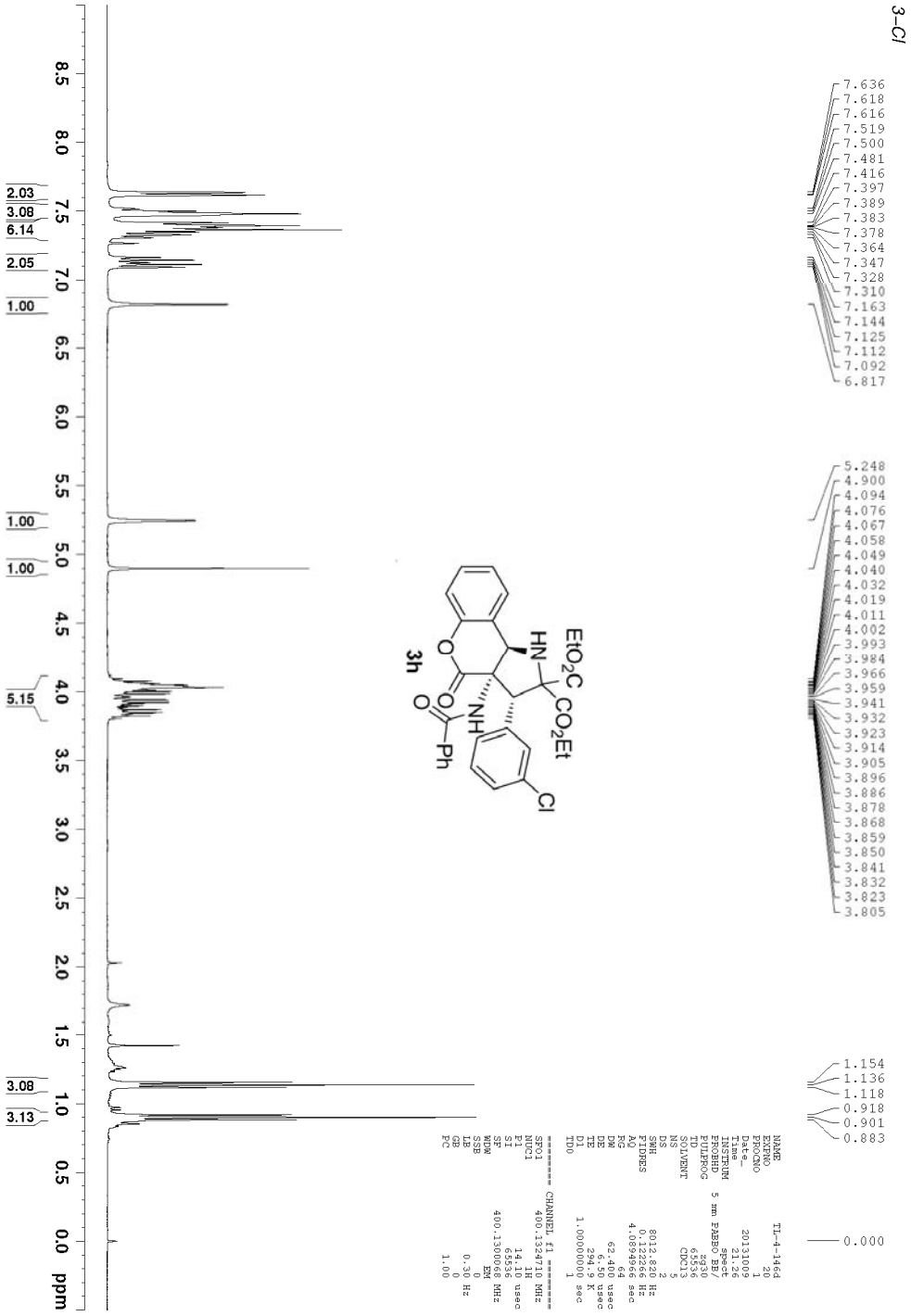
130.11
129.93
128.87
128.60
128.38
126.94
126.72
124.63
121.51
116.84
77.32
77.00
76.68
76.60
65.89
62.92
62.62
62.53
51.81
13.61
13.29
3g
EtO2C
HN
CO2Et
Cl
NH
Ph
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


3–Cl
3h
EtO2C
CO2Ph
HN
NH
CO2Et
Cl
O
O
O
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7.618
7.616
7.519
7.500
7.481
7.416
7.397
7.389
7.383
7.378
7.364
7.347
7.328
7.310
7.163
7.144
7.125
7.112
7.092
6.817
5.248
4.900
4.094
4.076
4.067
4.058
4.049
4.040
4.032
4.019
4.011
4.002
3.993
3.984
3.966
3.959
3.941
3.932
3.923
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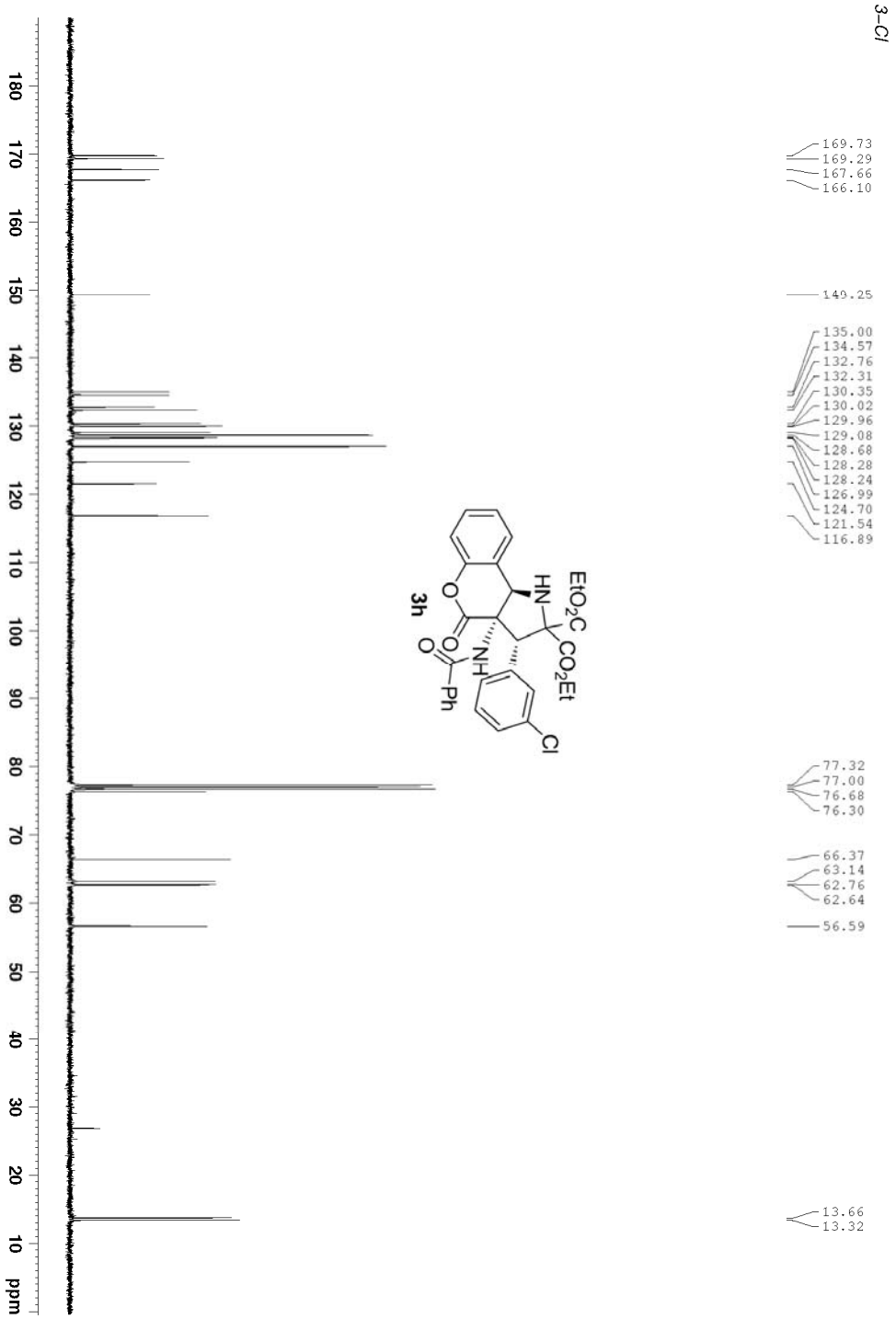
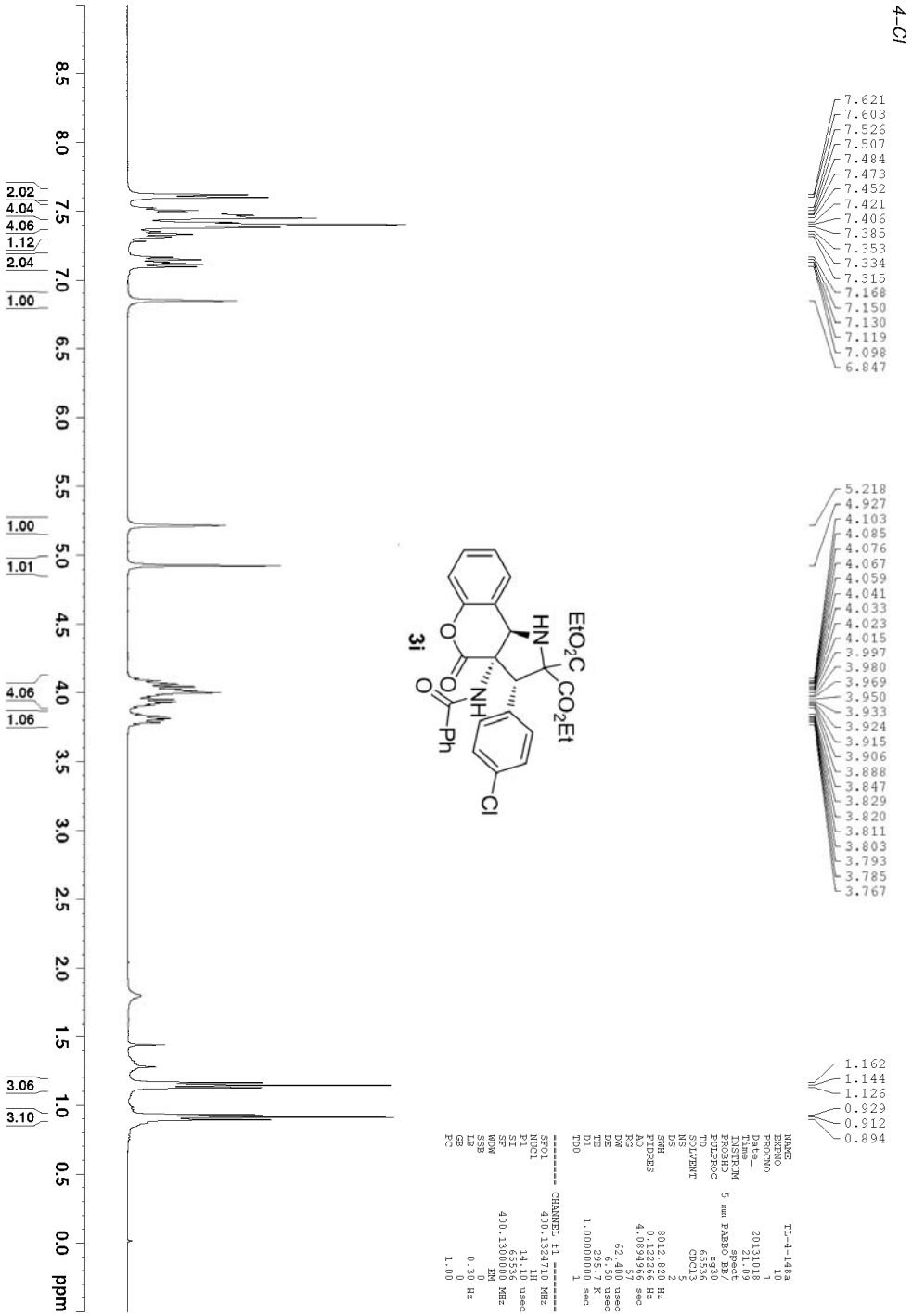
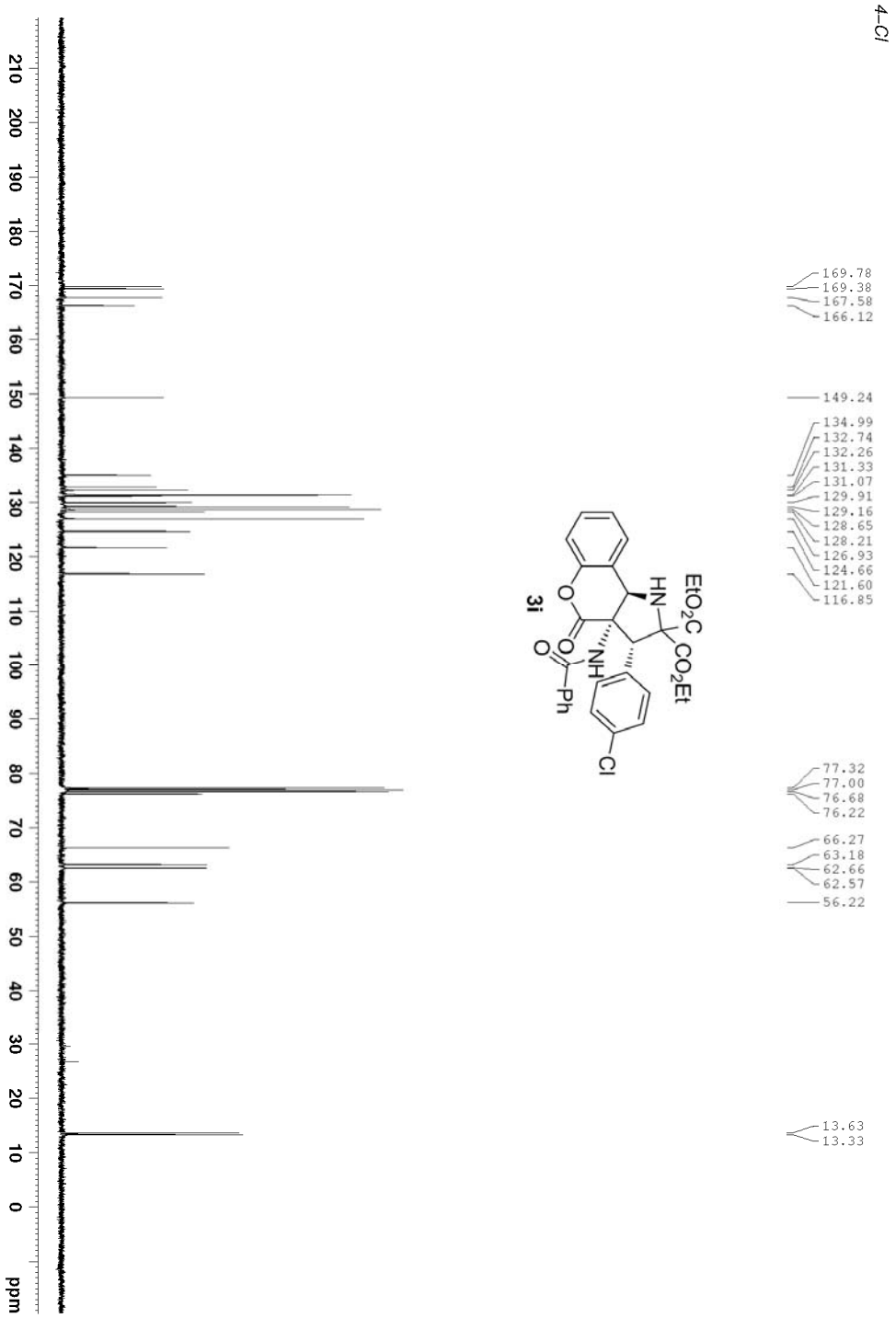
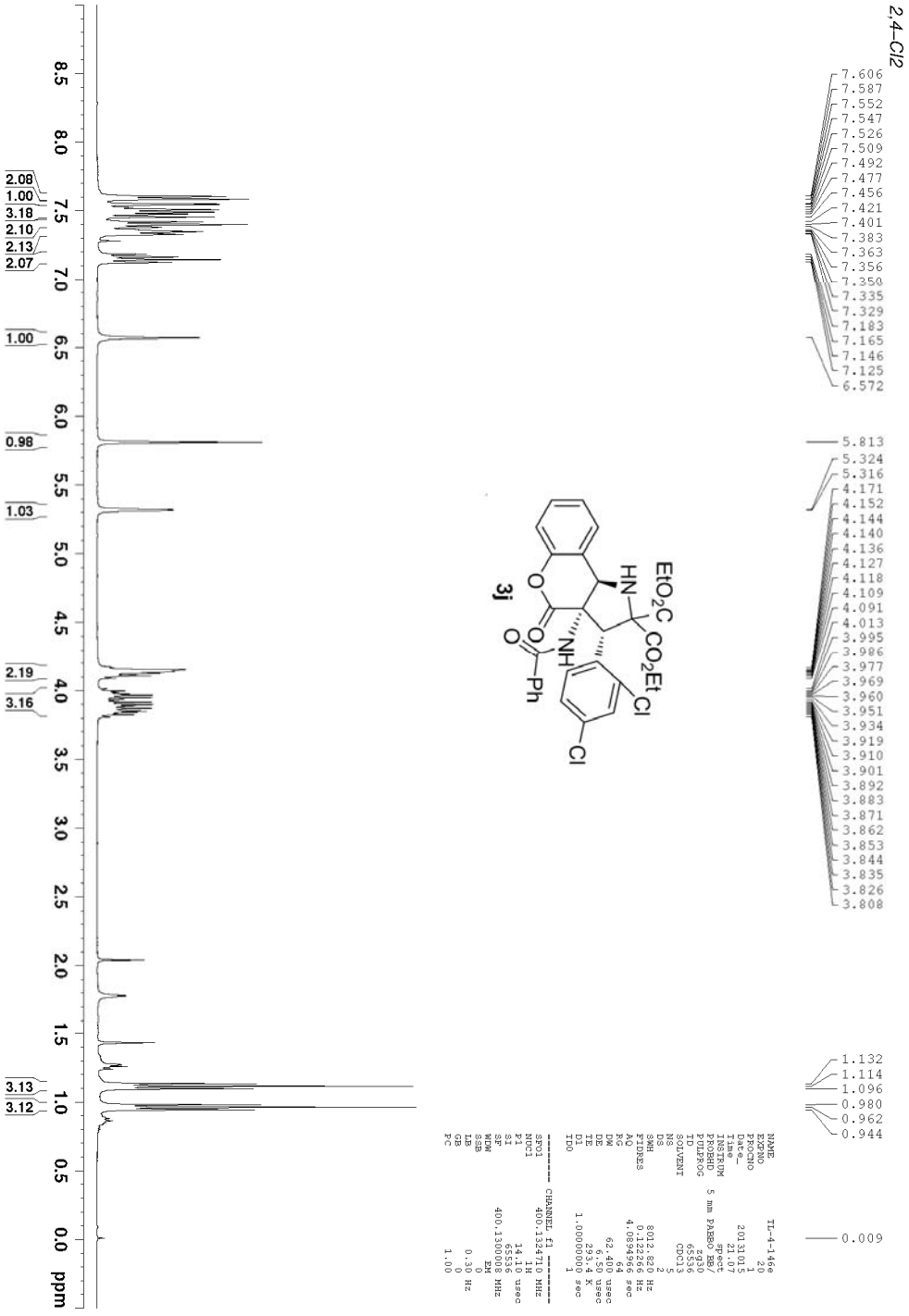
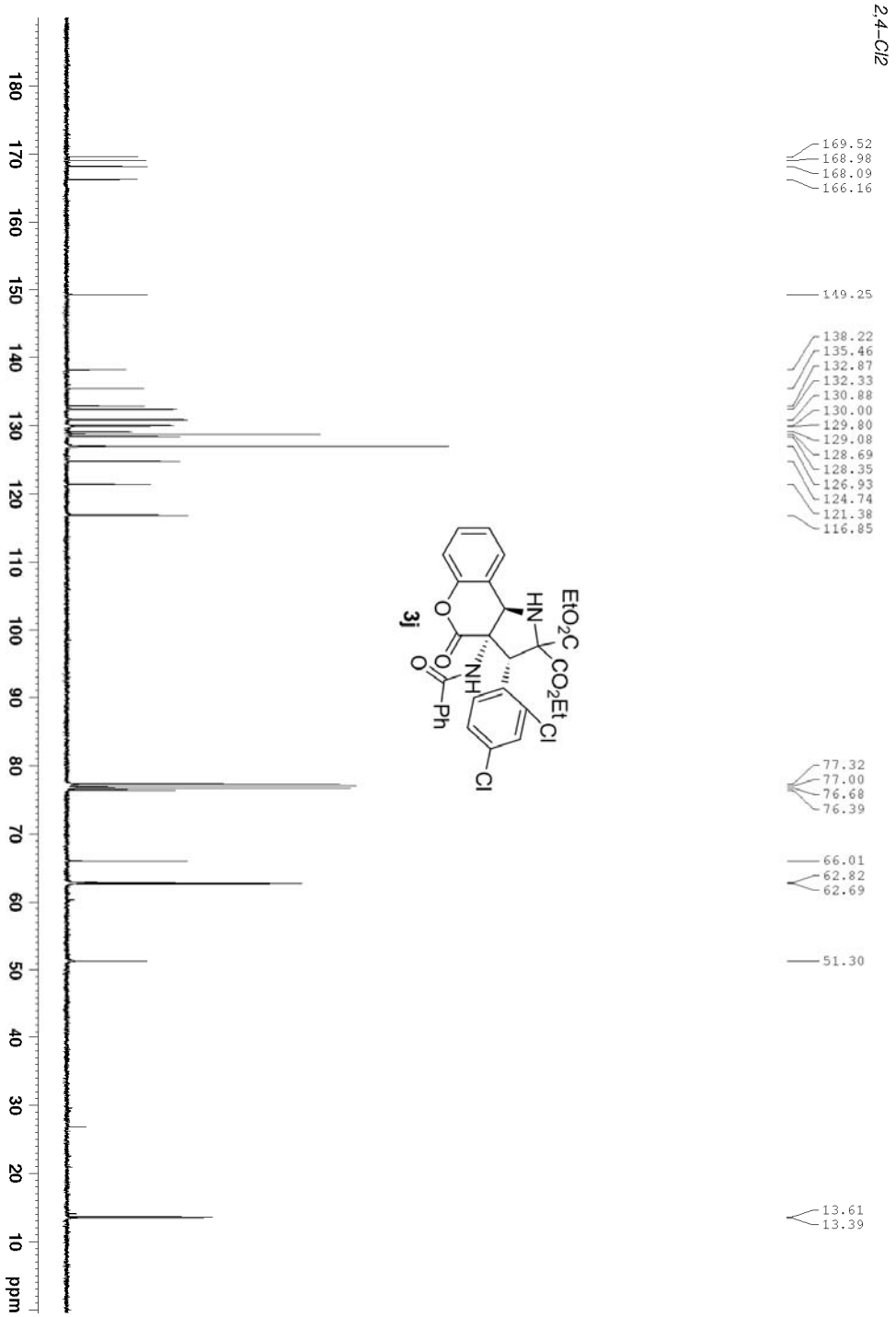
3.905
3.896
3.886
3.878
3.868
3.859
3.850
3.841
3.832
3.823
3.805
1.154
1.136
1.118
0.918
0.901
0.883
0.000
2.03
3.08
6.14
2.05
1.00
1.00
1.00
5.15
3.08
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
NAME TL-4-146d
EXPNO 20
PROCNO 1
Date_ 20131009
Time 21.25
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894964 sec
RG 62.400
DW 62.400 usec
DE 6.50 usec
TE 294.9 K
D1 1.00000001 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

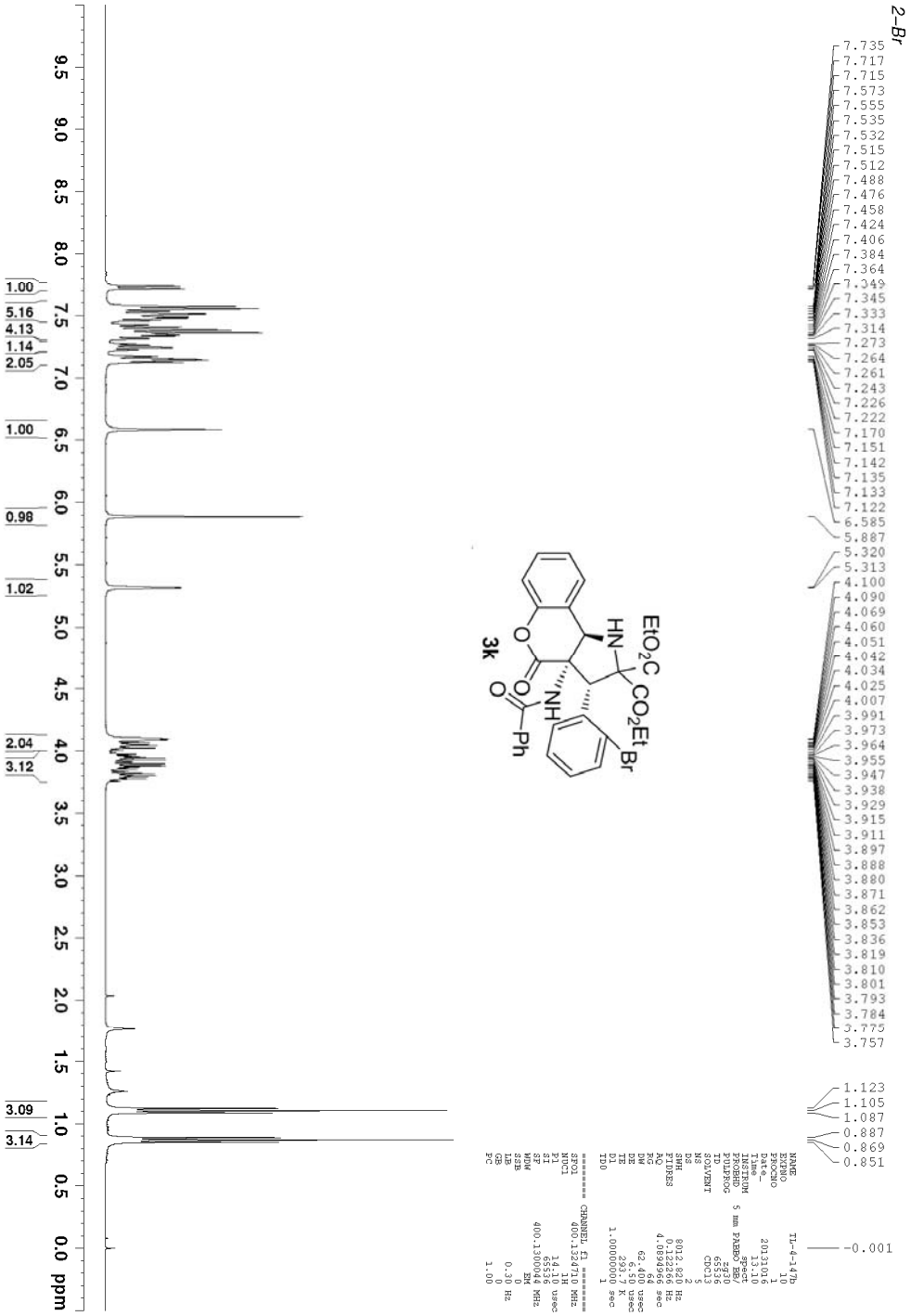

3-Cl
169.73
169.29
167.66
166.10
149.25
135.00
134.57
132.76
132.31
130.35
130.02
129.96
129.08
128.68
128.28
128.24
126.99
124.70
121.54
116.89
77.32
77.00
76.68
76.30
66.37
63.14
62.76
62.64
56.59
13.66
13.32
3h
EtO2C
CO2Et
HN
NH
O
O
O
Ph
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

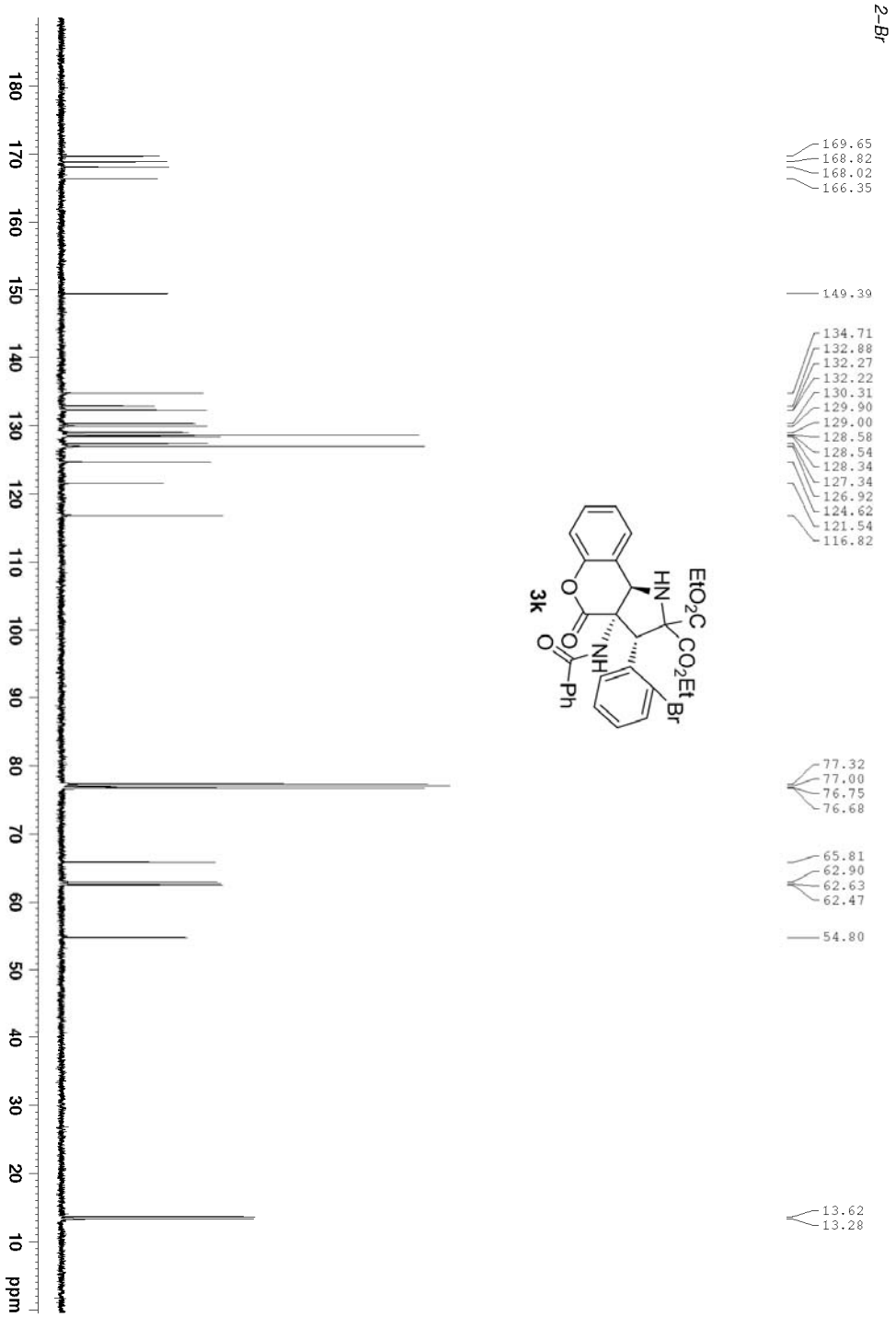

4-Cl
7.621
7.603
7.526
7.507
7.484
7.473
7.452
7.421
7.406
7.385
7.353
7.334
7.315
7.168
7.150
7.130
7.119
7.098
6.847
5.218
4.927
4.103
4.085
4.076
4.067
4.059
4.041
4.033
4.023
4.015
3.997
3.980
3.969
3.950
3.933
3.924
3.915
3.906
3.888
3.847
3.829
3.820
3.811
3.803
3.793
3.785
3.767
1.162
1.144
1.126
0.929
0.912
0.894
3i
EtO2C
CO2Et
HN
NH
Ph
Cl
2.02
4.04
4.06
1.12
2.04
1.00
1.00
1.01
4.06
1.06
3.06
3.10
8.5
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
ppm

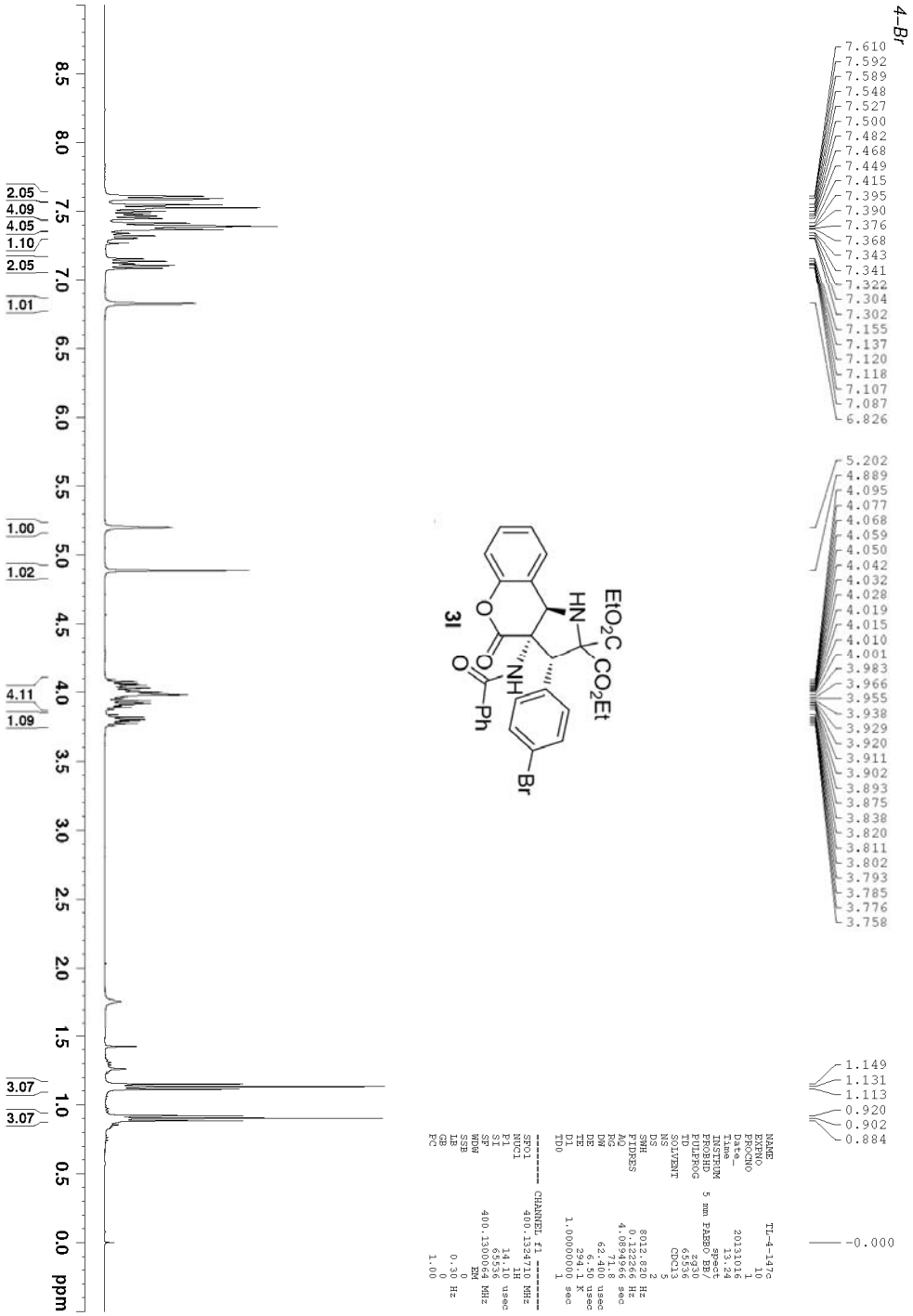

4-Cl
169.78
169.38
167.58
166.12
149.24
134.99
132.74
132.26
131.33
131.07
129.91
129.16
128.65
128.21
126.93
124.66
121.60
116.85
77.32
77.00
76.68
76.22
66.27
63.18
62.66
62.57
56.22
13.63
13.33
3i
EtO2C
CO2Et
HN
NH
O
O
O
Ph
Cl
ppm

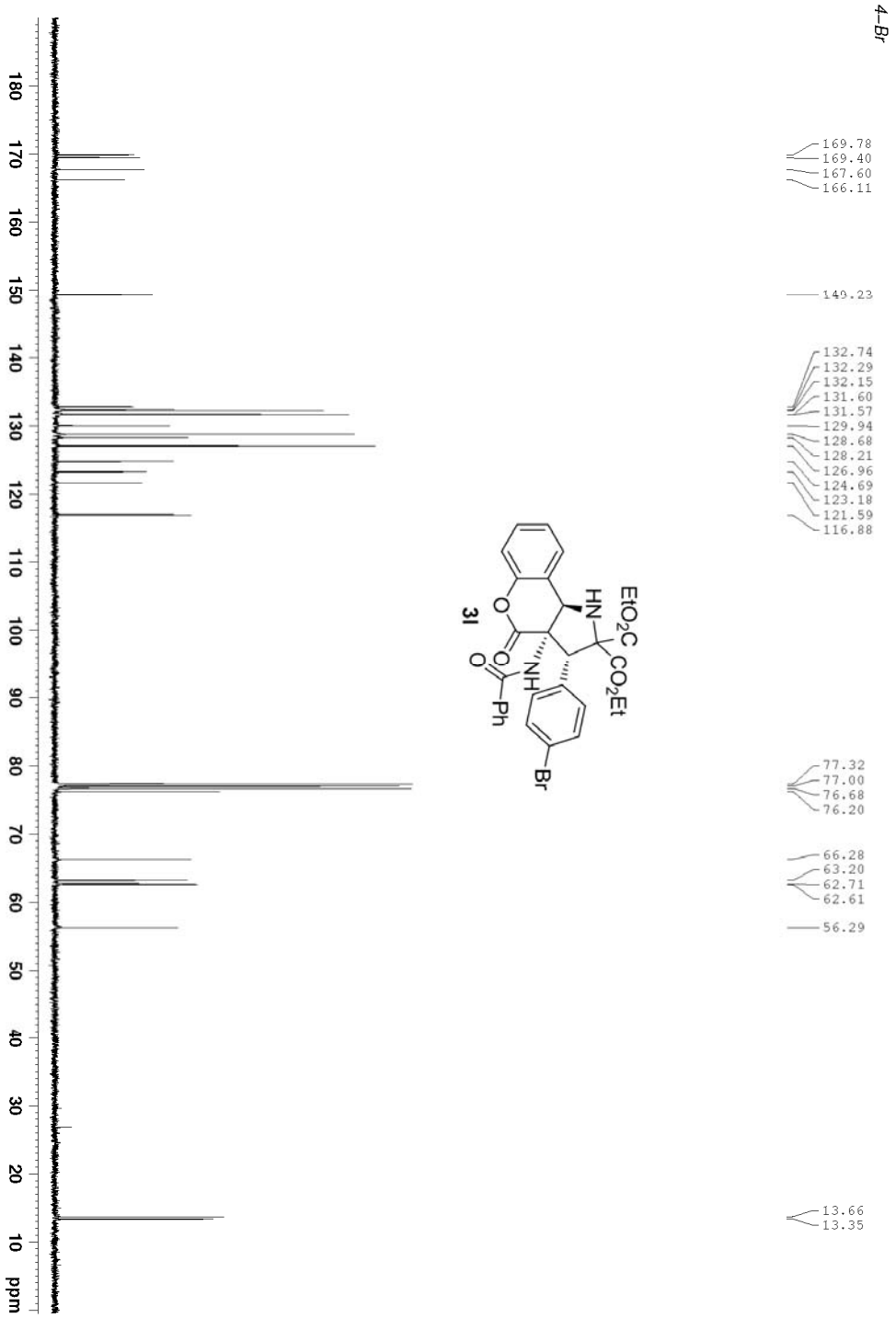

2,4-Cl2
3j
EtO2C
HN
CO2Et
Cl
NH
O
O
O
Ph
Cl
7.606
7.587
7.552
7.547
7.526
7.509
7.492
7.477
7.456
7.421
7.401
7.383
7.363
7.356
7.350
7.335
7.329
7.183
7.165
7.146
7.125
6.572
5.813
5.324
5.316
4.171
4.152
4.144
4.140
4.136
4.127
4.118
4.109
4.091
4.013
3.995
3.986
3.977
3.969
3.960
3.951
3.934
3.919
3.910
3.901
3.892
3.883
3.871
3.862
3.853
3.844
3.835
3.826
3.808
1.132
1.114
1.096
0.980
0.962
0.944
0.009
2.08
1.00
3.18
2.10
2.13
2.07
1.00
0.98
1.03
2.19
3.16
3.13
3.12
8.5
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
ppm

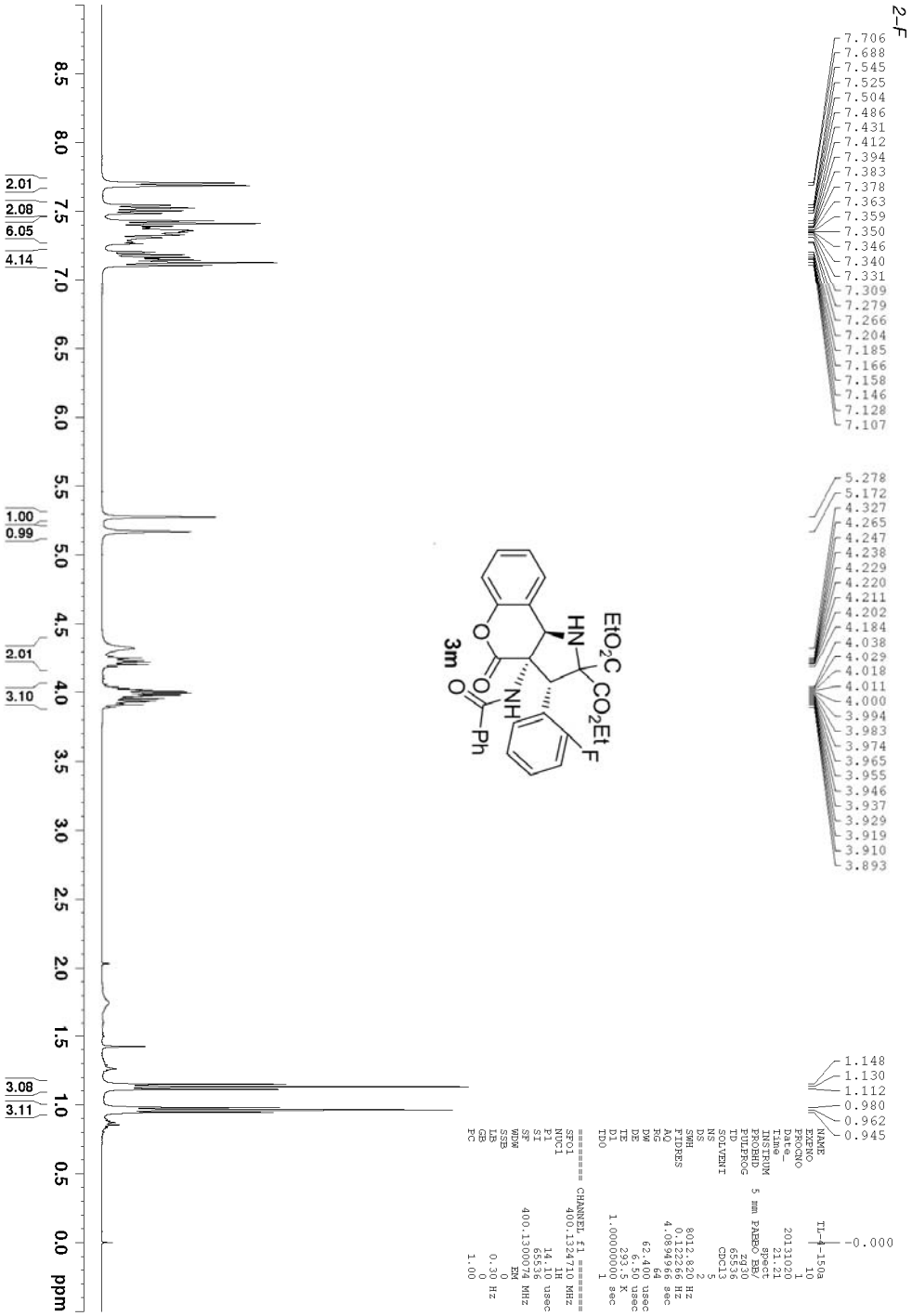

2,4-Cl2
169.52
168.98
168.09
166.16
149.25
138.22
135.46
132.87
132.33
130.88
130.00
129.80
129.08
128.69
128.35
126.93
124.74
121.38
116.85
77.32
77.00
76.68
76.39
66.01
62.82
62.69
51.30
13.61
13.39
3j
EtO2C
CO2Et
HN
NH
O
O
O
Ph
Cl
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

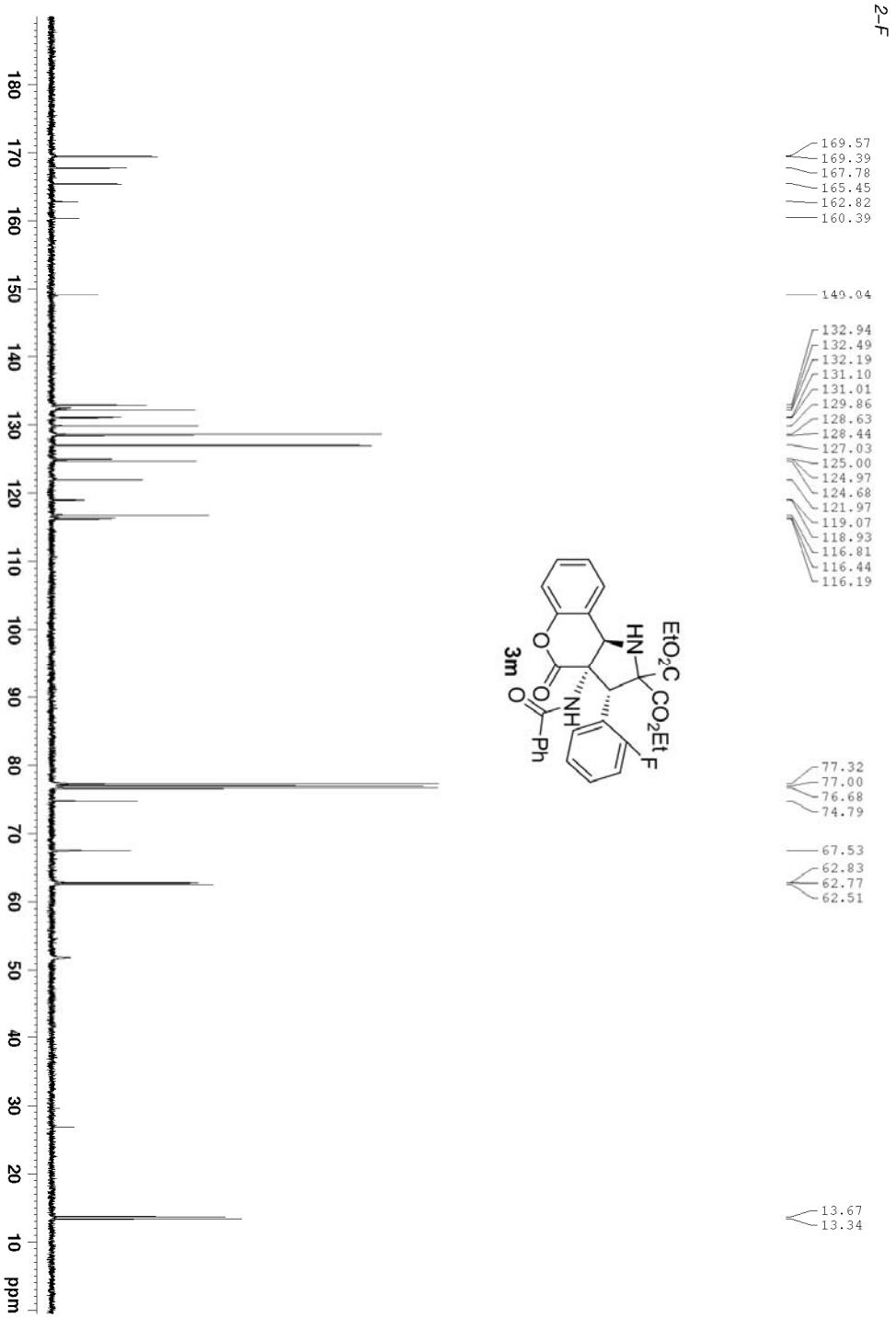

2-Br
3k
EtO2C
CO2Et
HN
NH
Br
Ph
O
7.735
7.717
7.715
7.573
7.555
7.535
7.532
7.515
7.512
7.488
7.476
7.458
7.424
7.406
7.384
7.364
7.349
7.345
7.333
7.314
7.273
7.264
7.261
7.243
7.226
7.222
7.170
7.151
7.142
7.135
7.133
7.122
6.585
5.887
5.320
5.313
4.100
4.090
4.069
4.060
4.051
4.042
4.034
4.025
4.007
3.991
3.973
3.964
3.955
3.947
3.938
3.929
3.915
3.911
3.897
3.888
3.880
3.871
3.862
3.853
3.836
3.819
3.810
3.801
3.793
3.784
3.775
3.757
1.123
1.105
1.087
0.887
0.869
0.851
-0.001
1.00
5.16
4.13
1.14
2.05
1.00
0.98
1.02
2.04
3.12
3.09
3.14
9.5
9.0
8.5
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
ppm

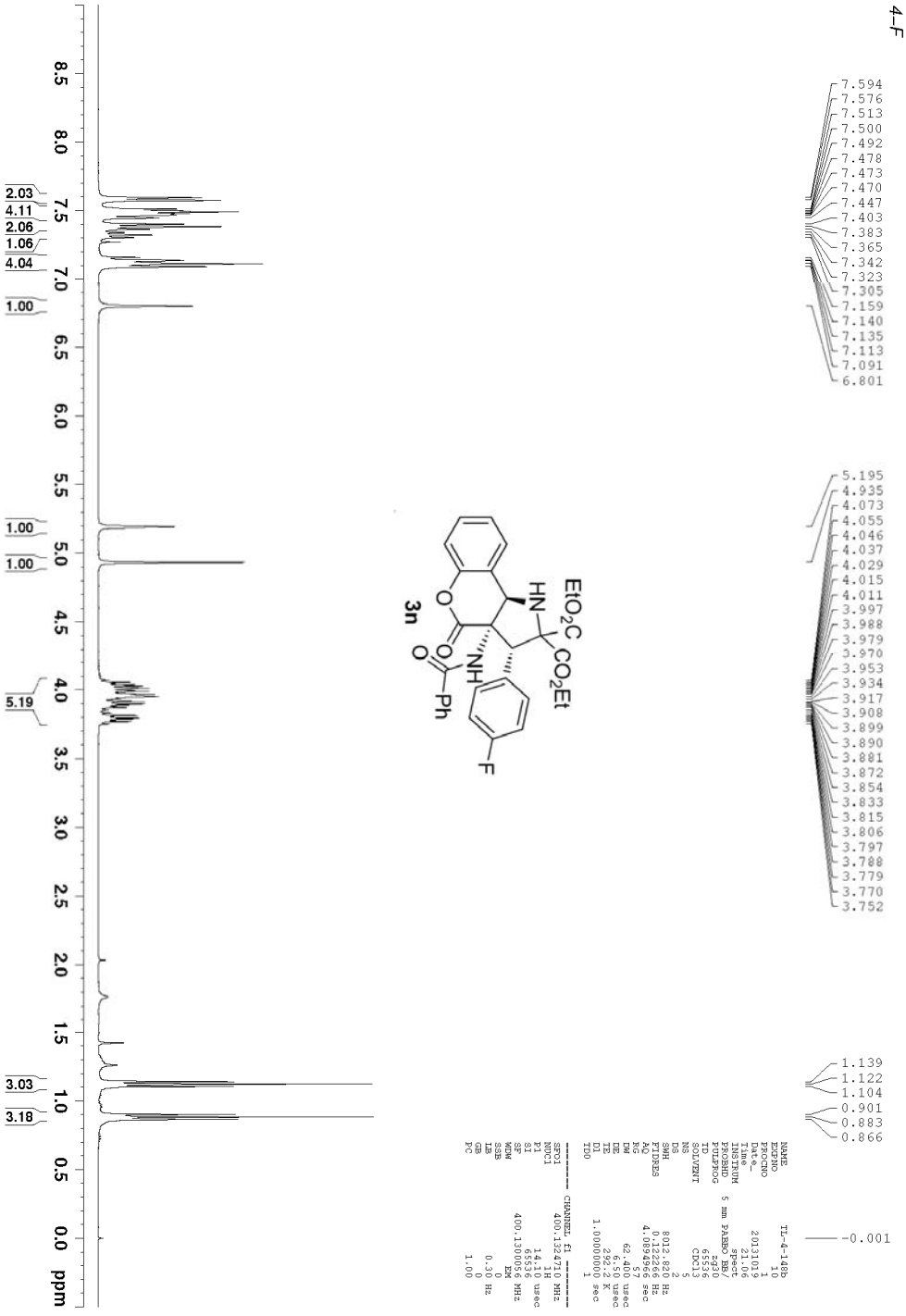

2-Br
169.65
168.82
168.02
166.35
149.39
134.71
132.88
132.27
132.22
130.31
129.90
129.00
128.58
128.54
128.34
127.34
126.92
124.62
121.54
116.82
77.32
77.00
76.75
76.68
65.81
62.90
62.63
62.47
54.80
13.62
13.28
3k
EtO2C
CO2Et
HN
NH
Ph
Br
O
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

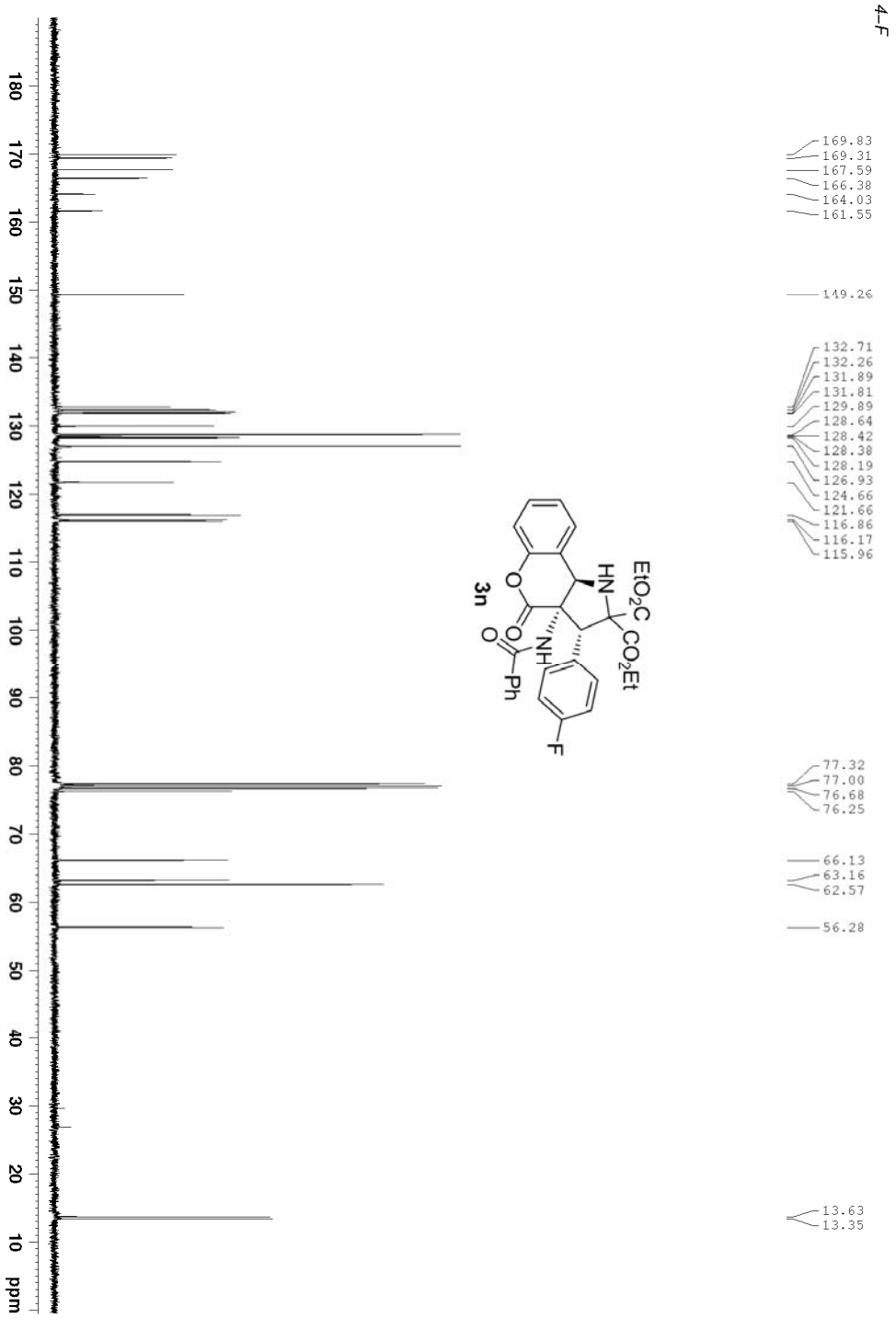

4_Br
7.610
7.592
7.589
7.548
7.527
7.500
7.482
7.468
7.449
7.415
7.395
7.390
7.376
7.368
7.343
7.341
7.322
7.304
7.302
7.155
7.137
7.120
7.118
7.107
7.087
6.826
5.202
4.889
4.095
4.077
4.068
4.059
4.050
4.042
4.032
4.028
4.019
4.015
4.010
4.001
3.983
3.966
3.955
3.938
3.929
3.920
3.911
3.902
3.893
3.875
3.838
3.820
3.811
3.802
3.793
3.785
3.776
3.758
1.149
1.131
1.113
0.920
0.902
0.884
-0.000
3I
EtO2C
CO2Et
HN
NH
O
O
O
Ph
Br
2.05
4.09
4.05
1.10
2.05
1.01
1.00
1.02
4.11
1.09
3.07
3.07
8.5
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
ppm
NAME TL-4-147c
EXPNO 10
PROCNO 1
Date_ 20131016
Time 13.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894266 sec
RG 71.8
DW 62.400 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000001 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300064 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

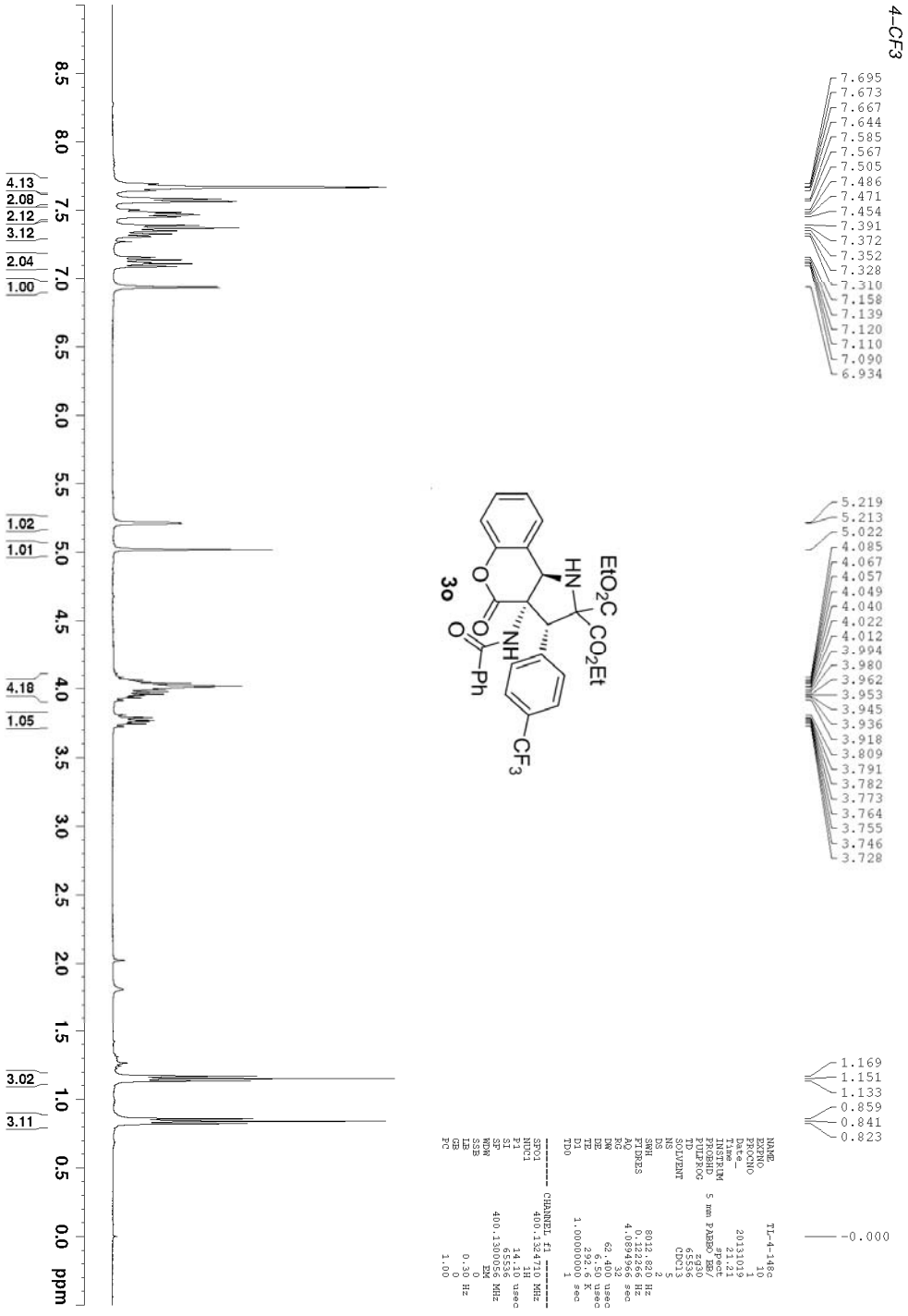

4-Br
169.78
169.40
167.60
166.11
149.23
132.74
132.29
132.15
131.60
131.57
129.94
128.68
128.21
126.96
124.69
123.18
121.59
116.88
77.32
77.00
76.68
76.20
66.28
63.20
62.71
62.61
56.29
13.66
13.35
ppm
3l
EtO2C
CO2Et
HN
NH
O
O
O
Ph
Br

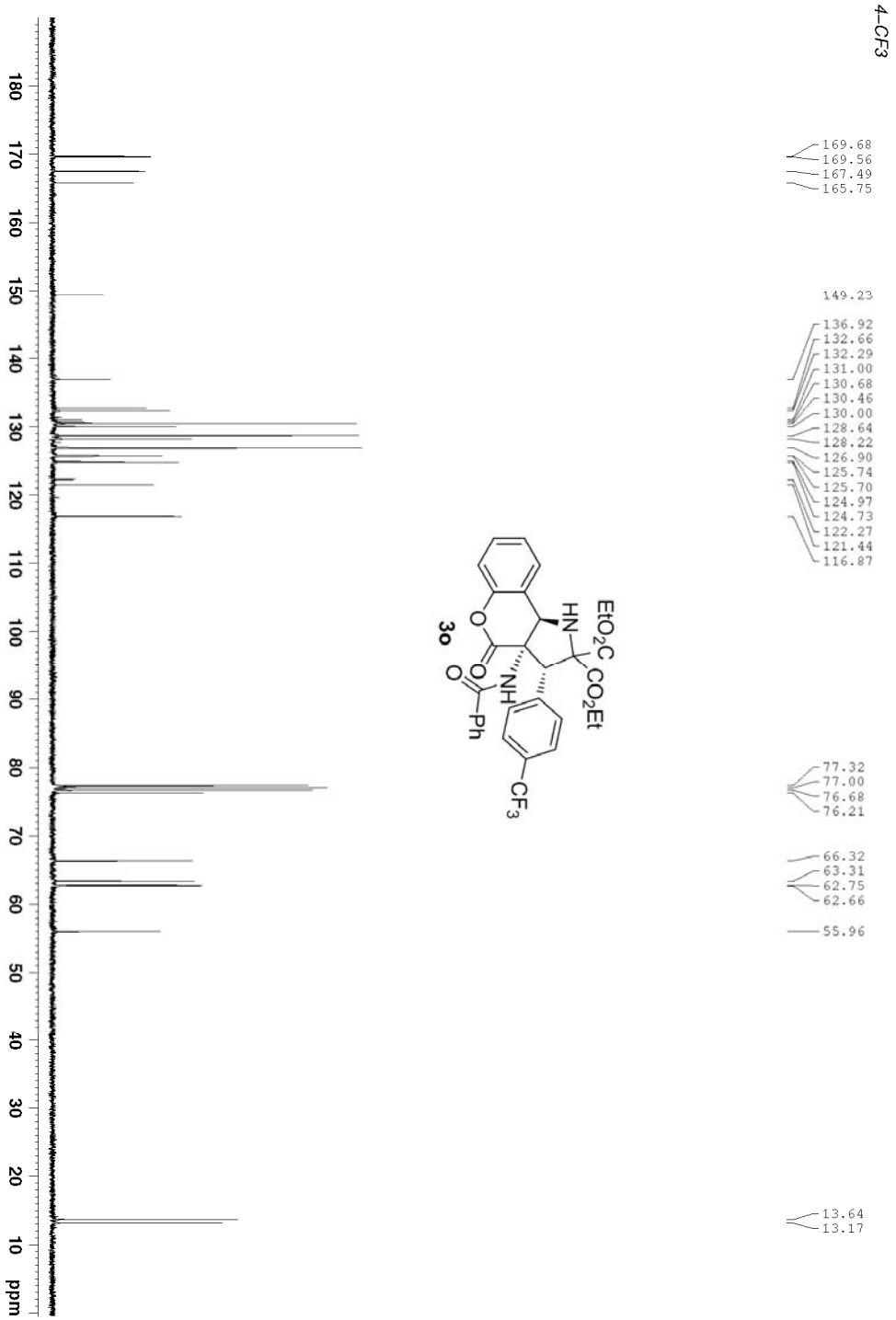

2-F
3m
EtO2C
CO2Et
HN
NH
O
Ph
F
2.01
2.08
6.05
4.14
1.00
0.99
2.01
3.10
3.08
3.11
ppm

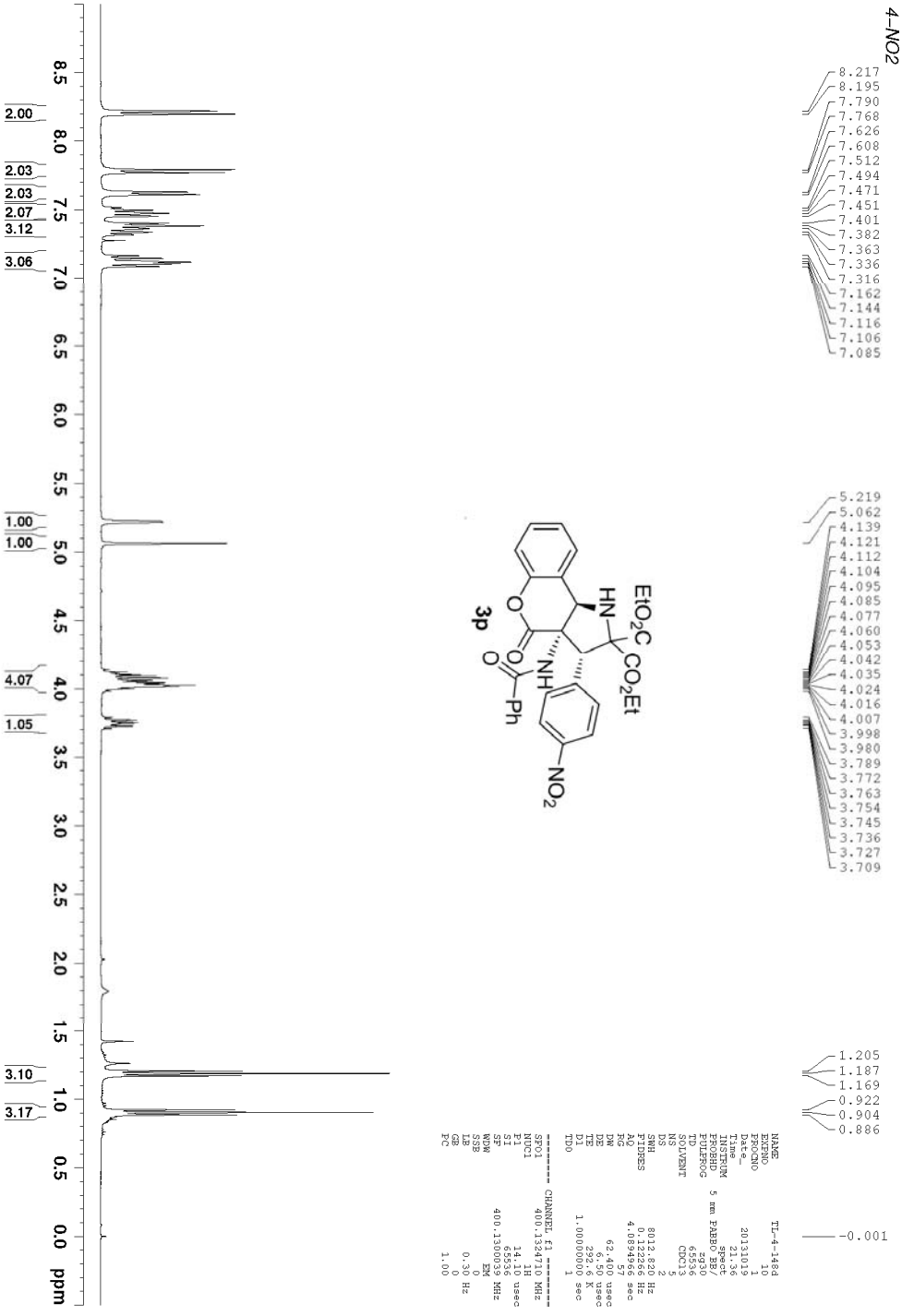

2-F
169.57
169.39
167.78
165.45
162.82
160.39
149.04
132.94
132.49
132.19
131.10
131.01
129.86
128.63
128.44
127.03
125.00
124.97
124.68
121.97
119.07
118.93
116.81
116.44
116.19
77.32
77.00
76.68
74.79
67.53
62.83
62.77
62.51
13.67
13.34
3m
EtO2C
CO2Et
HN
NH
O
Ph
F
ppm


4-F
3n
Ph
NH
HN
O
EtO_2C
CO_2Et
F
7.594
7.576
7.513
7.500
7.492
7.478
7.473
7.470
7.447
7.403
7.383
7.365
7.342
7.323
7.305
7.159
7.140
7.135
7.113
7.091
6.801
5.195
4.935
4.073
4.055
4.046
4.037
4.029
4.015
4.011
3.997
3.988
3.979
3.970
3.953
3.934
3.917
3.908
3.899
3.890
3.881
3.872
3.854
3.833
3.815
3.806
3.797
3.788
3.779
3.770
3.752
1.139
1.122
1.104
0.901
0.883
0.866
-0.001
2.03
4.11
2.06
1.06
4.04
1.00
1.00
1.00
5.19
3.03
3.18
8.5
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
ppm


4-F
169.83
169.31
167.59
166.38
164.03
161.55
149.26
132.71
132.26
131.89
131.81
129.89
128.64
128.42
128.38
128.19
126.93
124.66
121.66
116.86
116.17
115.96
77.32
77.00
76.68
76.25
66.13
63.16
62.57
56.28
13.63
13.35
3n
EtO2C
CO2Et
HN
NH
O
O
O
Ph
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


4_CF3
7.695
7.673
7.667
7.644
7.585
7.567
7.505
7.486
7.471
7.454
7.391
7.372
7.352
7.328
7.310
7.158
7.139
7.120
7.110
7.090
6.934
5.219
5.213
5.022
4.085
4.067
4.057
4.049
4.040
4.022
4.012
3.994
3.980
3.962
3.953
3.945
3.936
3.918
3.809
3.791
3.782
3.773
3.764
3.755
3.746
3.728
1.169
1.151
1.133
0.859
0.841
0.823
-0.000
4.13
2.08
2.12
3.12
2.04
1.00
1.02
1.01
4.18
1.05
3.02
3.11
8.5
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
ppm
3o
EtO2C
CO2Et
HN
NH
Ph
CF3
NAME TL-4-148c
EXPNO 10
PROCNO 1
Date_ 20131019
Time 21.21
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 62.400
DW 62.400 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300056 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


4-CF3
169.68
169.56
167.49
165.75
149.23
136.92
132.66
132.29
131.00
130.68
130.46
130.00
128.64
128.22
126.90
125.74
125.70
124.97
124.73
122.27
121.44
116.87
77.32
77.00
76.68
76.21
66.32
63.31
62.75
62.66
55.96
13.64
13.17
3o
EtO2C
CO2Et
HN
NH
O
O
Ph
CF3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


4-NO2
8.217
8.195
7.790
7.768
7.626
7.608
7.512
7.494
7.471
7.451
7.401
7.382
7.363
7.336
7.316
7.162
7.144
7.116
7.106
7.085
5.219
5.062
4.139
4.121
4.112
4.104
4.095
4.085
4.077
4.060
4.053
4.042
4.035
4.024
4.016
4.007
3.998
3.980
3.789
3.772
3.763
3.754
3.745
3.736
3.727
3.709
1.205
1.187
1.169
0.922
0.904
0.886
-0.001
3p
EtO2C
CO2Ph
HN
NH
NO2
2.00
2.03
2.03
2.07
3.12
3.06
1.00
1.00
4.07
1.05
3.10
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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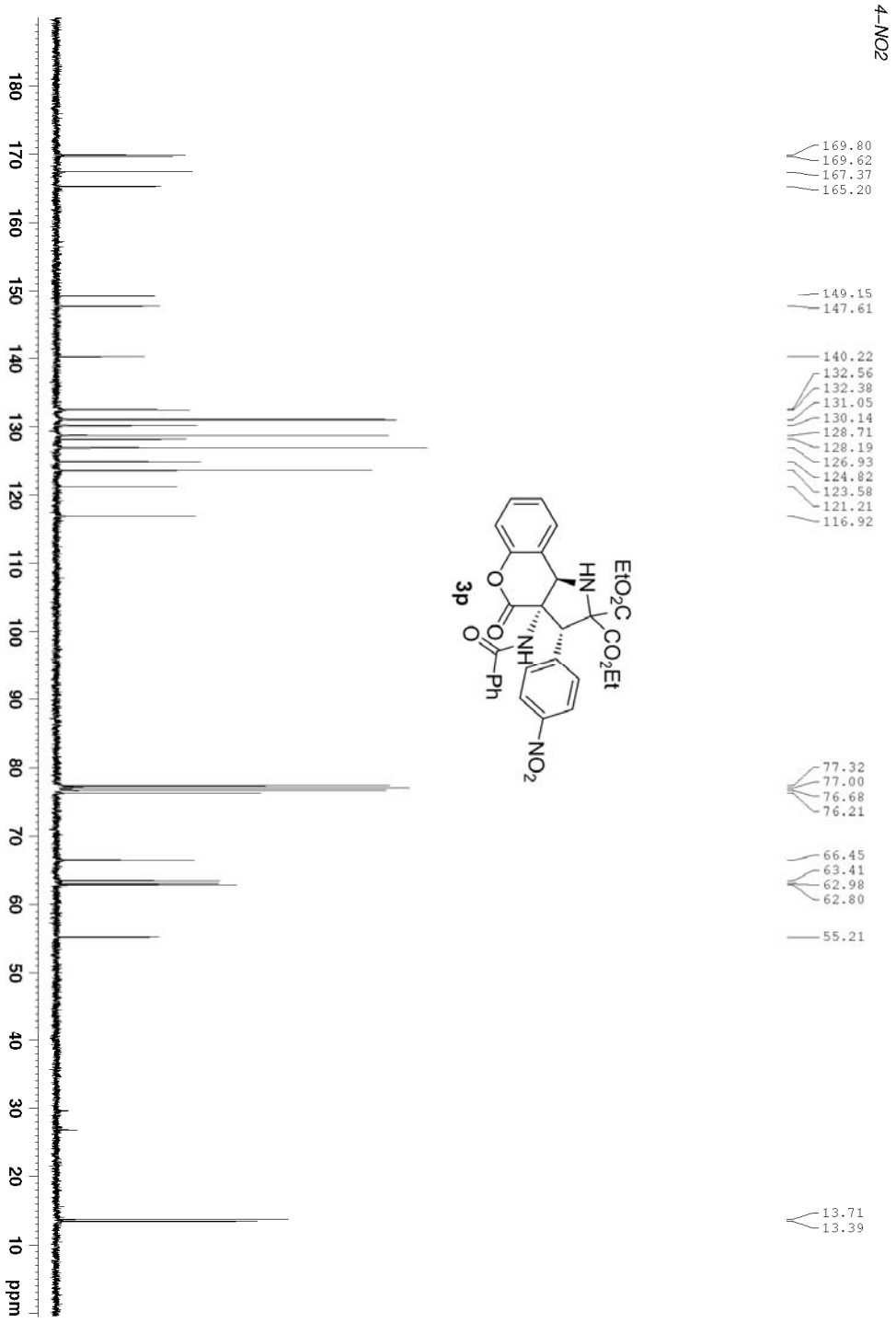
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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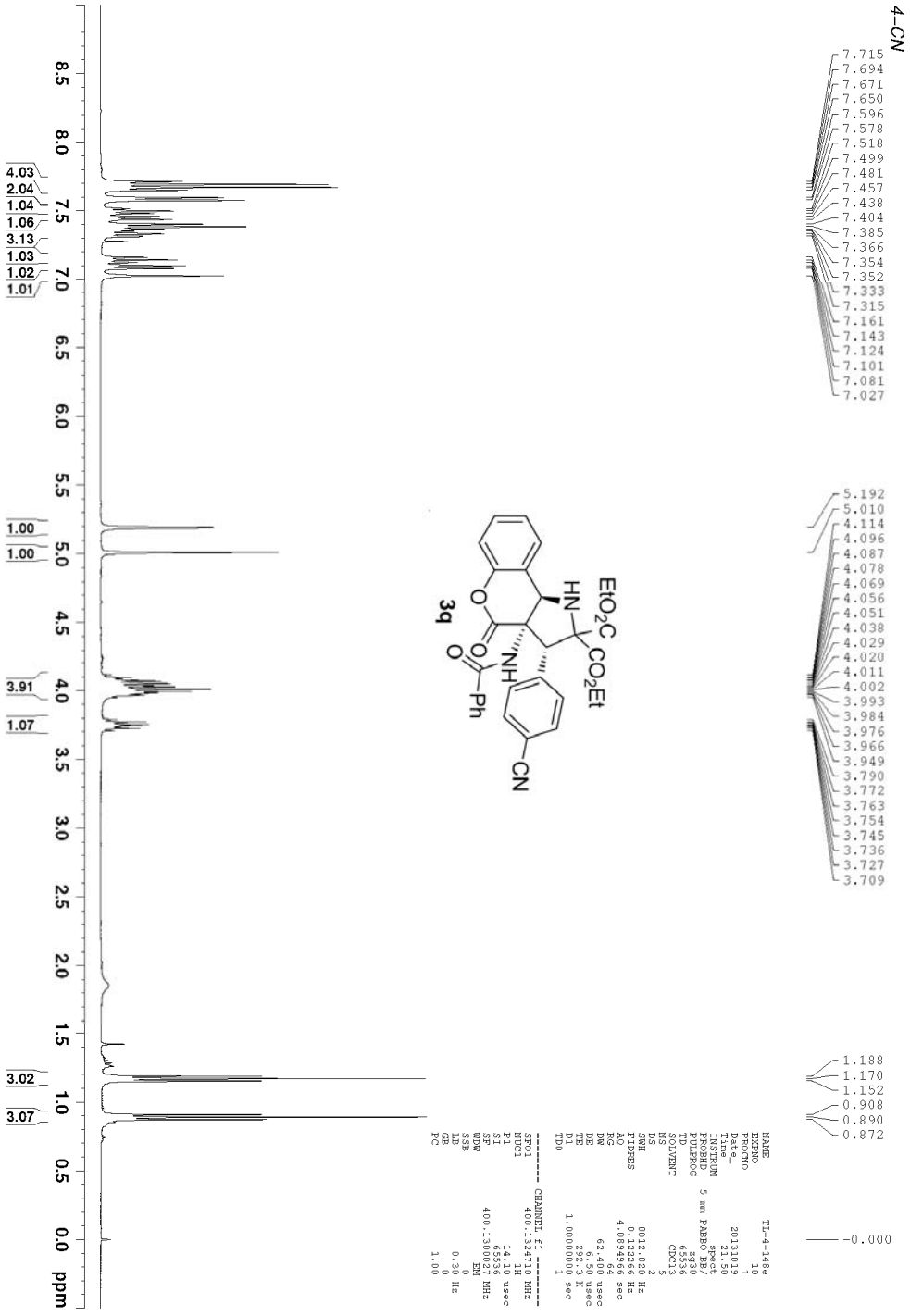
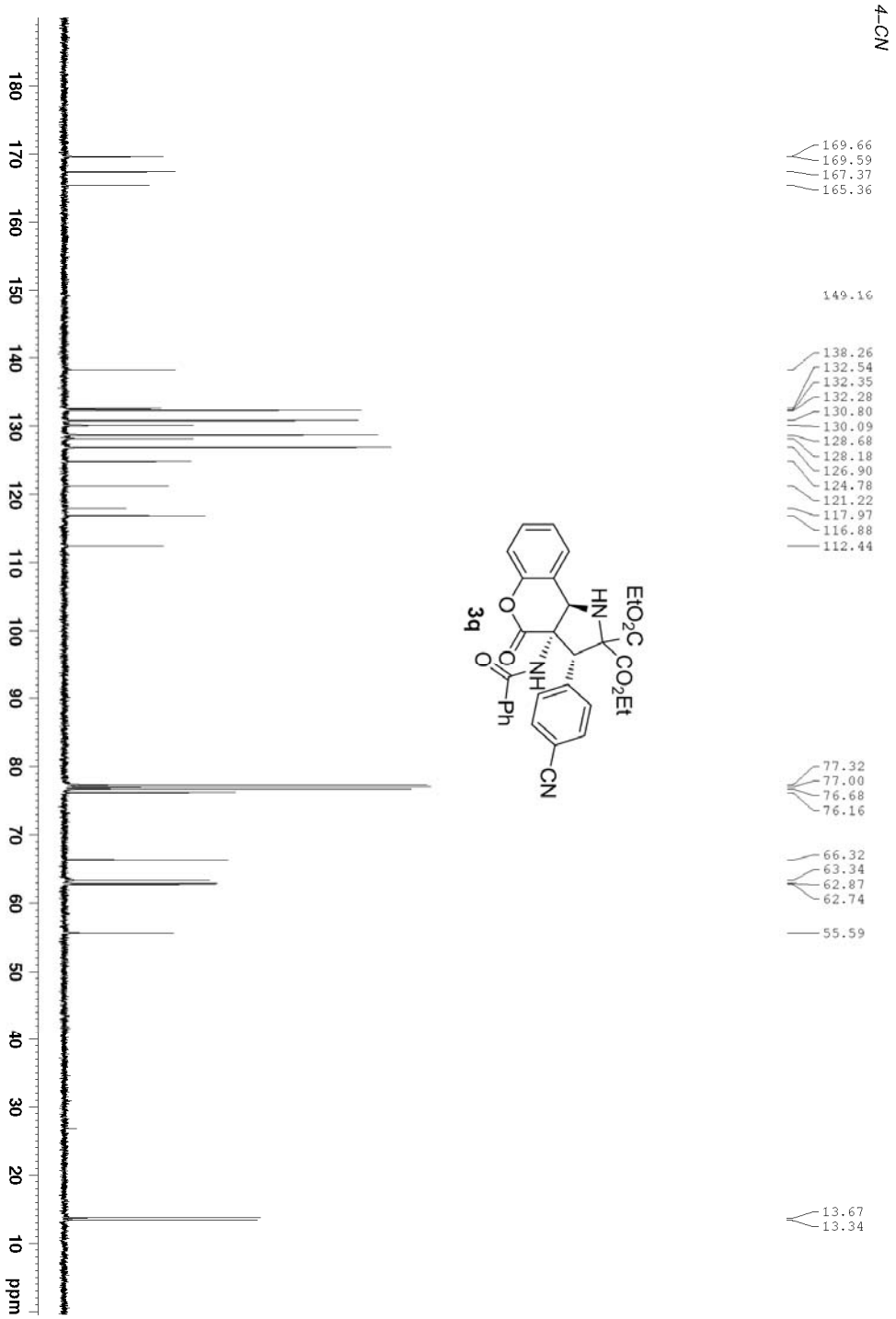
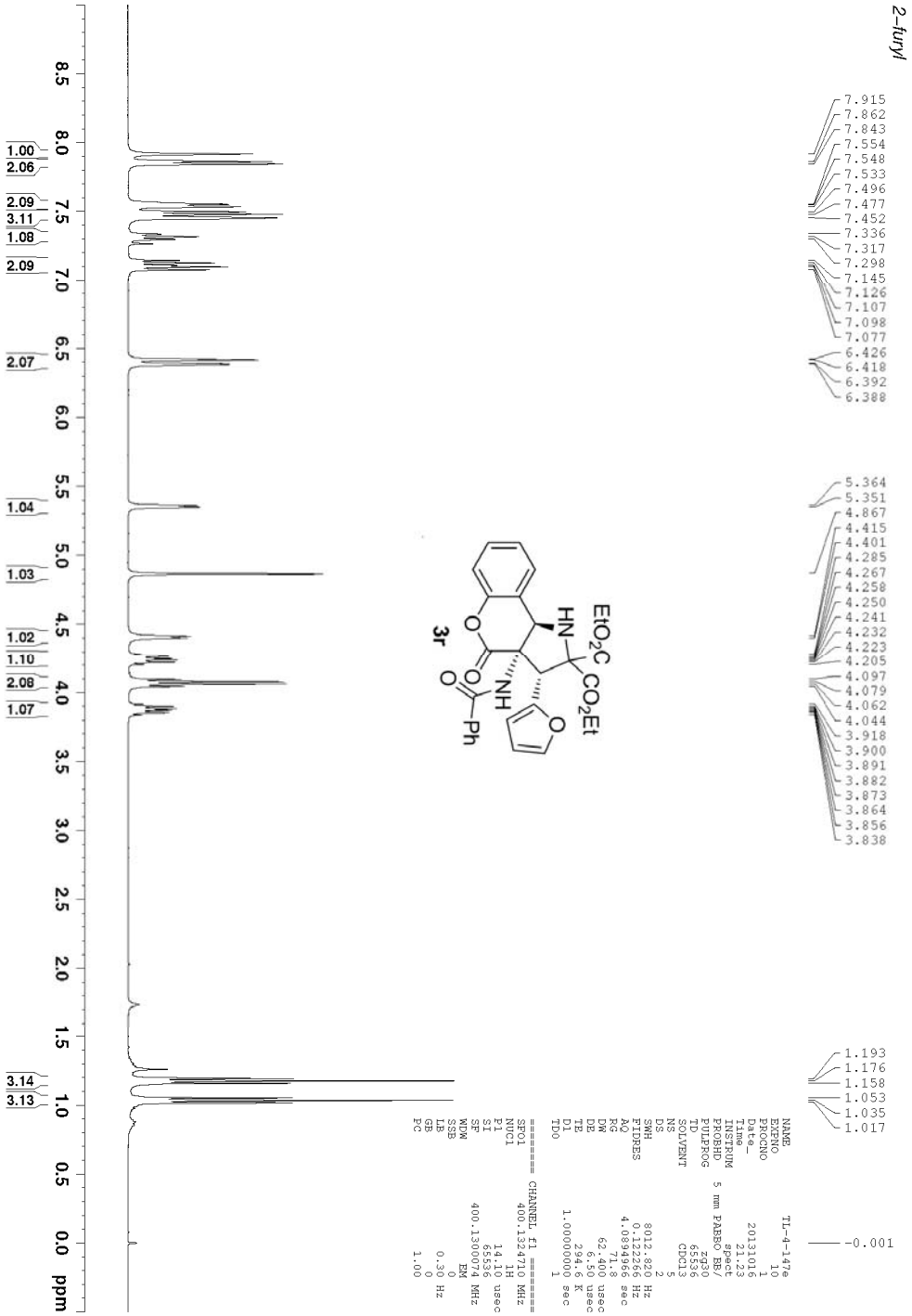
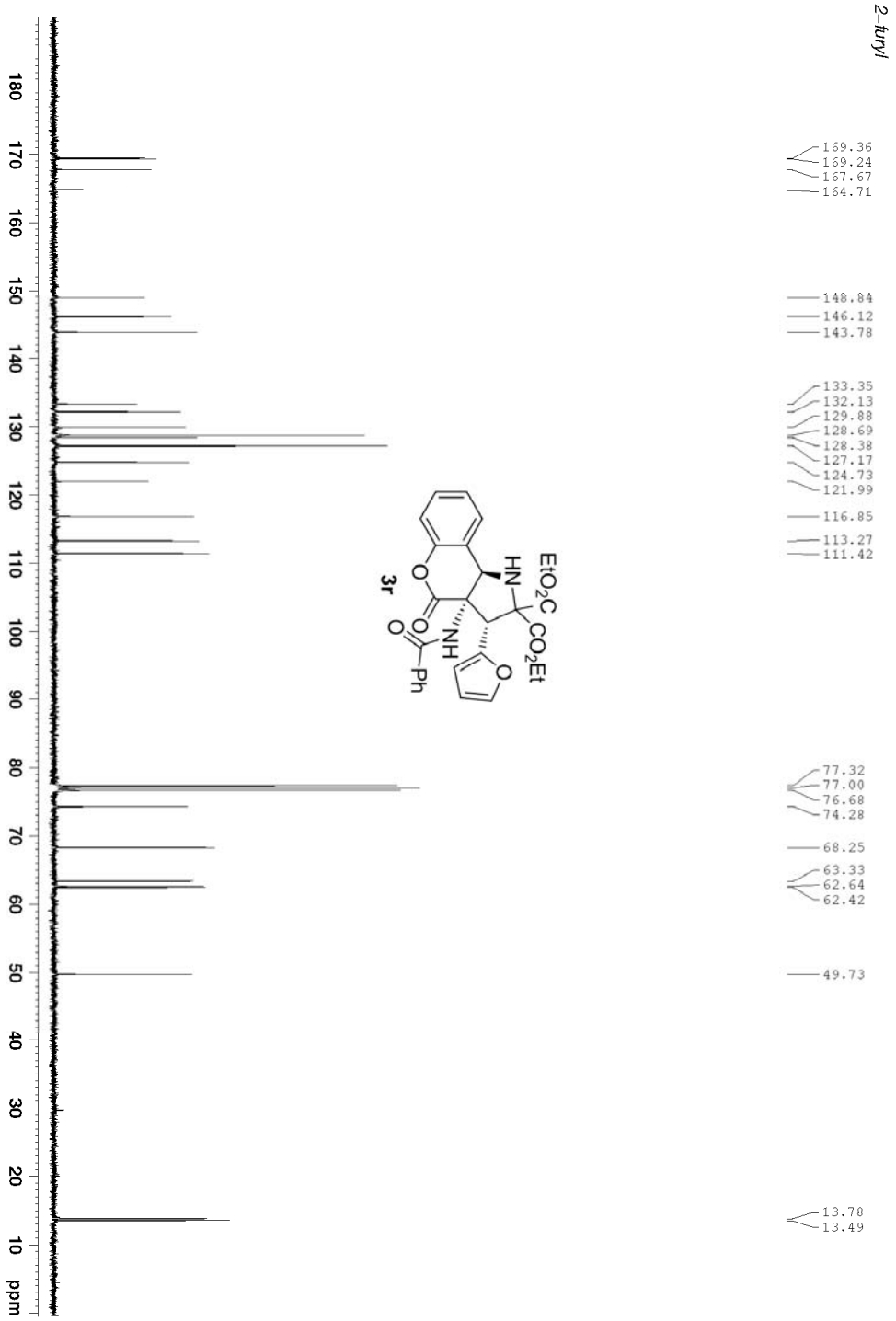
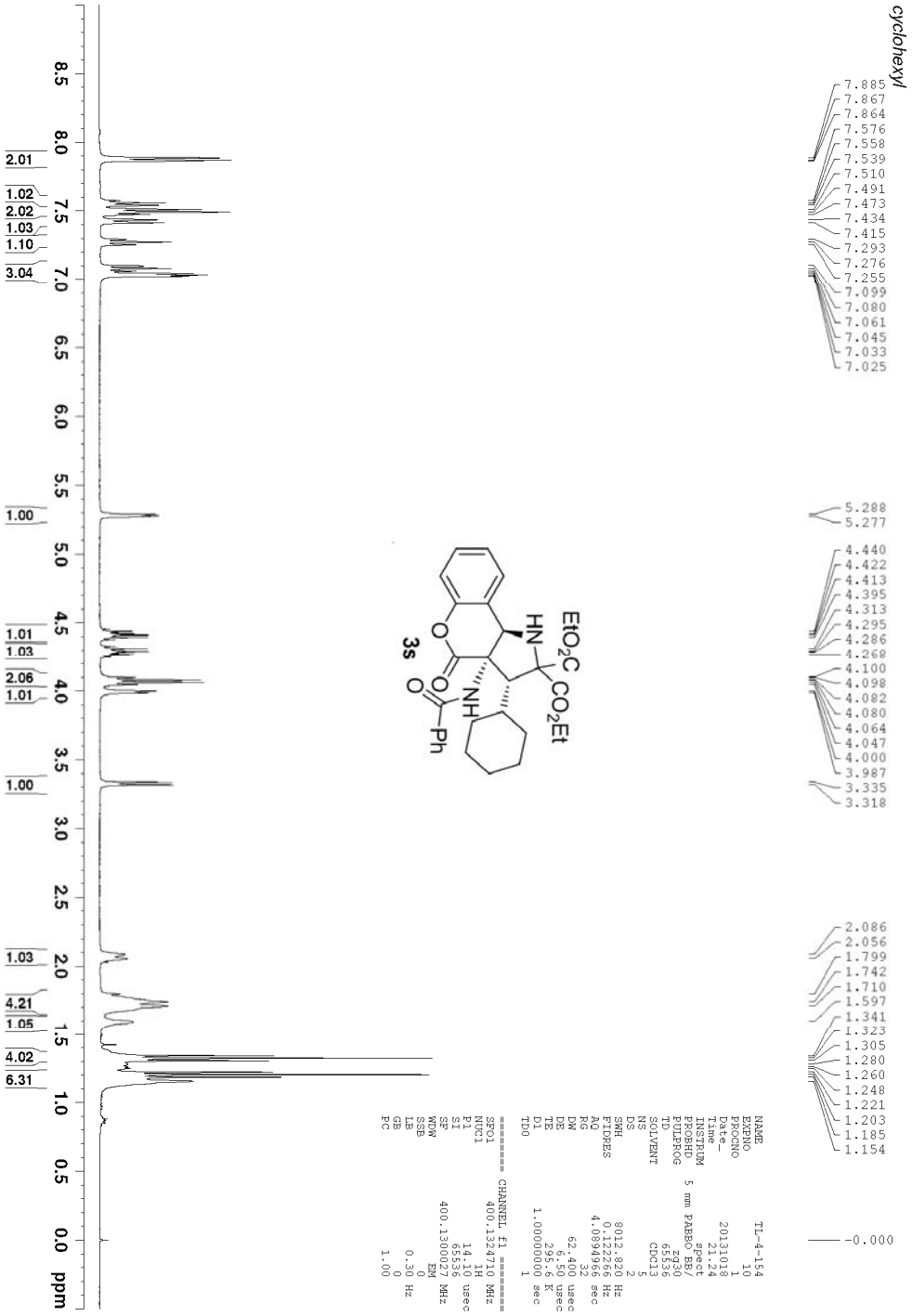
169.80
169.62
167.37
165.20
149.15
147.61
140.22
132.56
132.38
131.05
130.14
128.71
128.19
126.93
124.82
123.58
121.21
116.92
77.32
77.00
76.68
76.21
66.45
63.41
62.98
62.80
55.21
13.71
13.39
3p
EtO2C
CO2Et
HN
NH
NO2
Ph
O
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

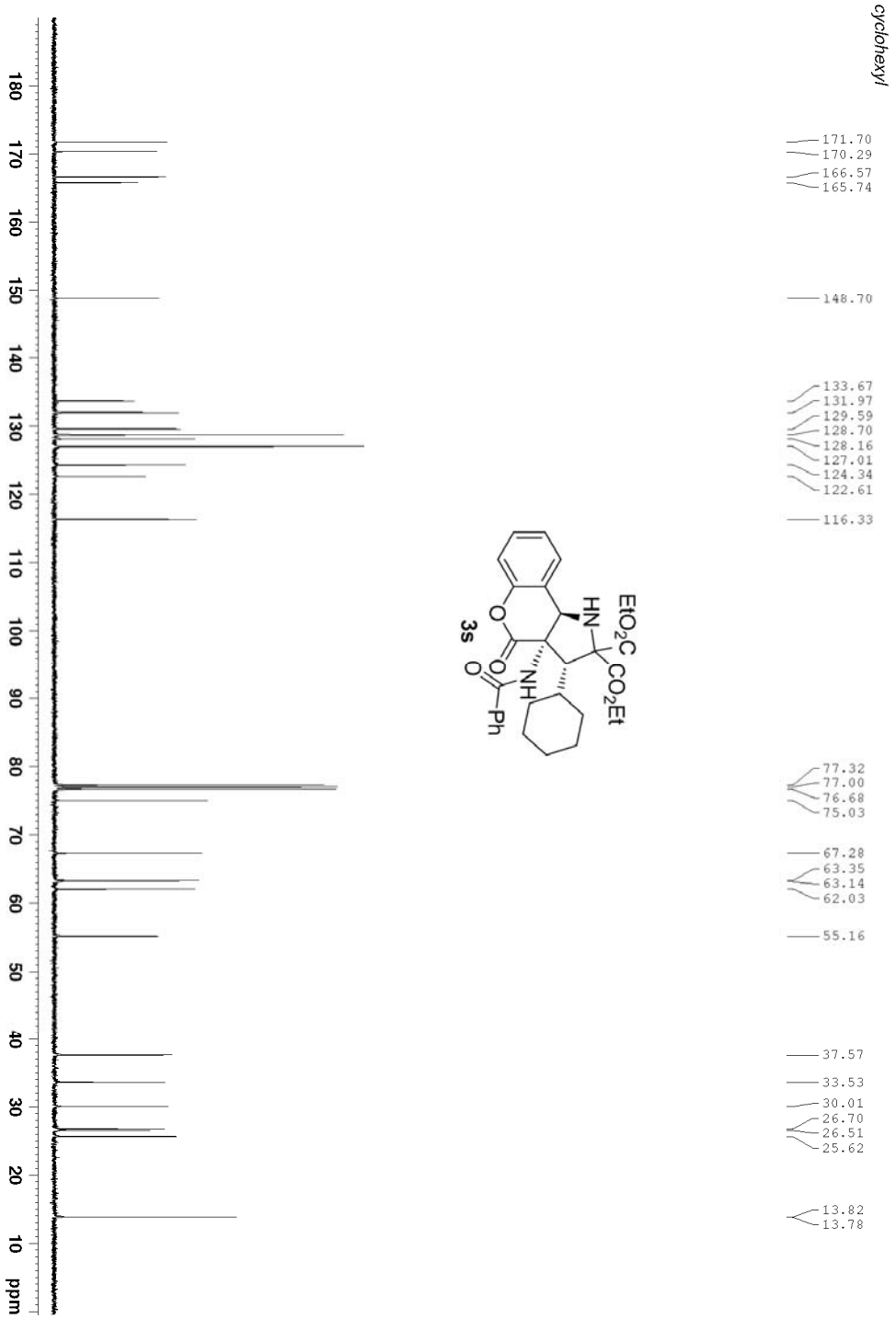

4-CN
3q
EtO2C
CO2Ph
CN
NH
HN
4.03
2.04
1.04
1.06
3.13
1.03
1.02
1.01
1.00
1.00
3.91
1.07
3.02
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
7.715
7.694
7.671
7.650
7.596
7.578
7.518
7.499
7.481
7.457
7.438
7.404
7.385
7.366
7.354
7.352
7.333
7.315
7.161
7.143
7.124
7.101
7.081
7.027
5.192
5.010
4.114
4.096
4.087
4.078
4.069
4.056
4.051
4.038
4.029
4.020
4.011
4.002
3.993
3.984
3.976
3.966
3.949
3.790
3.772
3.763
3.754
3.745
3.736
3.727
3.709
1.188
1.170
1.152
0.908
0.890
0.872
-0.000
NAME TI-4-148e
EXPNO 10
PROCNO 1
Date_ 20131019
Time 21.50
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.089856 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 292.5 K
D1 1.00000010 sec
TD0 1
SF01 CHANNEL f1
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300027 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

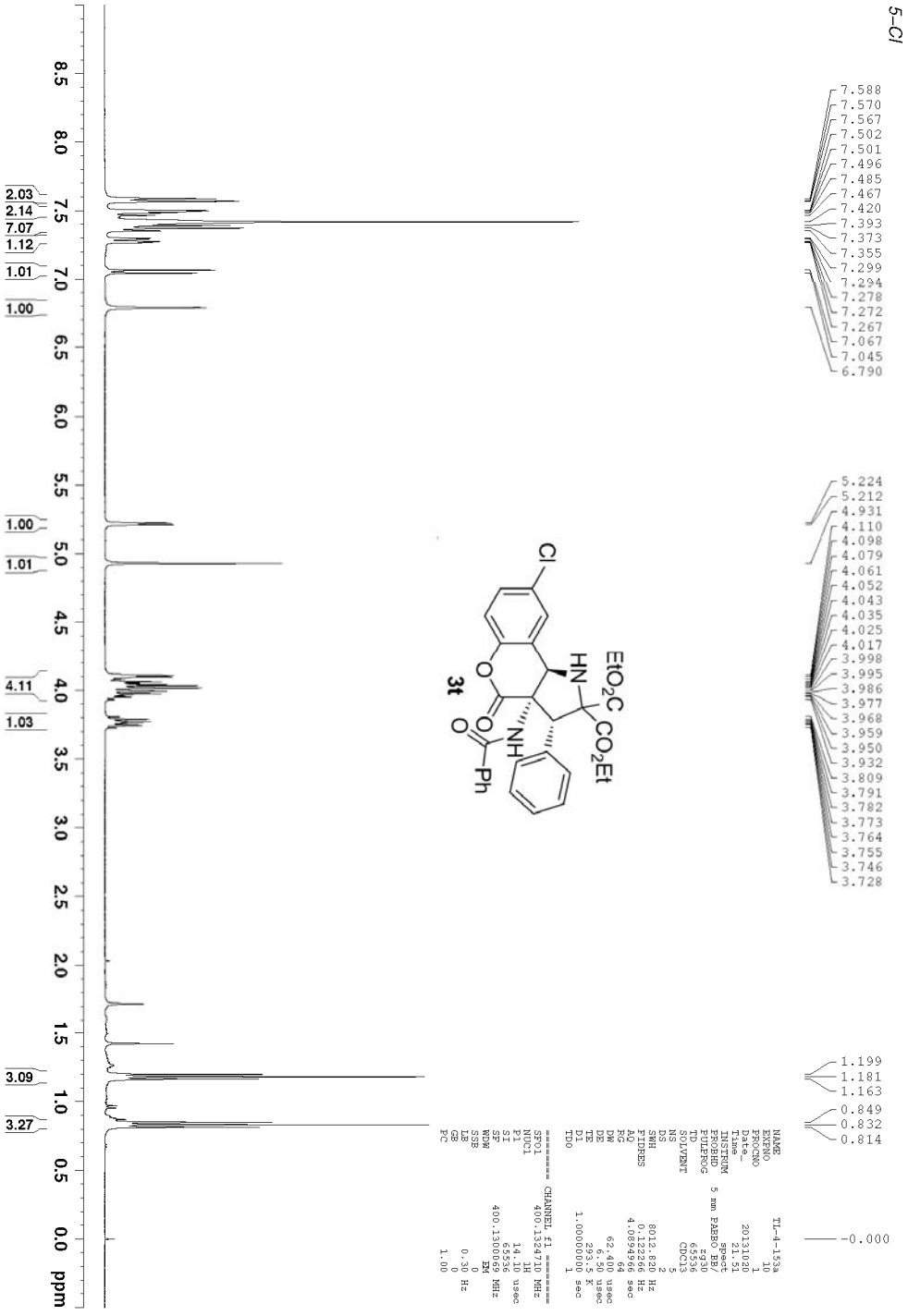

4-CN
169.66
169.59
167.37
165.36
149.16
138.26
132.54
132.35
132.28
130.80
130.09
128.68
128.18
126.90
124.78
121.22
117.97
116.88
112.44
77.32
77.00
76.68
76.16
66.32
63.34
62.87
62.74
55.59
13.67
13.34
3q
EtO2C
CO2Et
HN
NH
O
O
Ph
CN
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

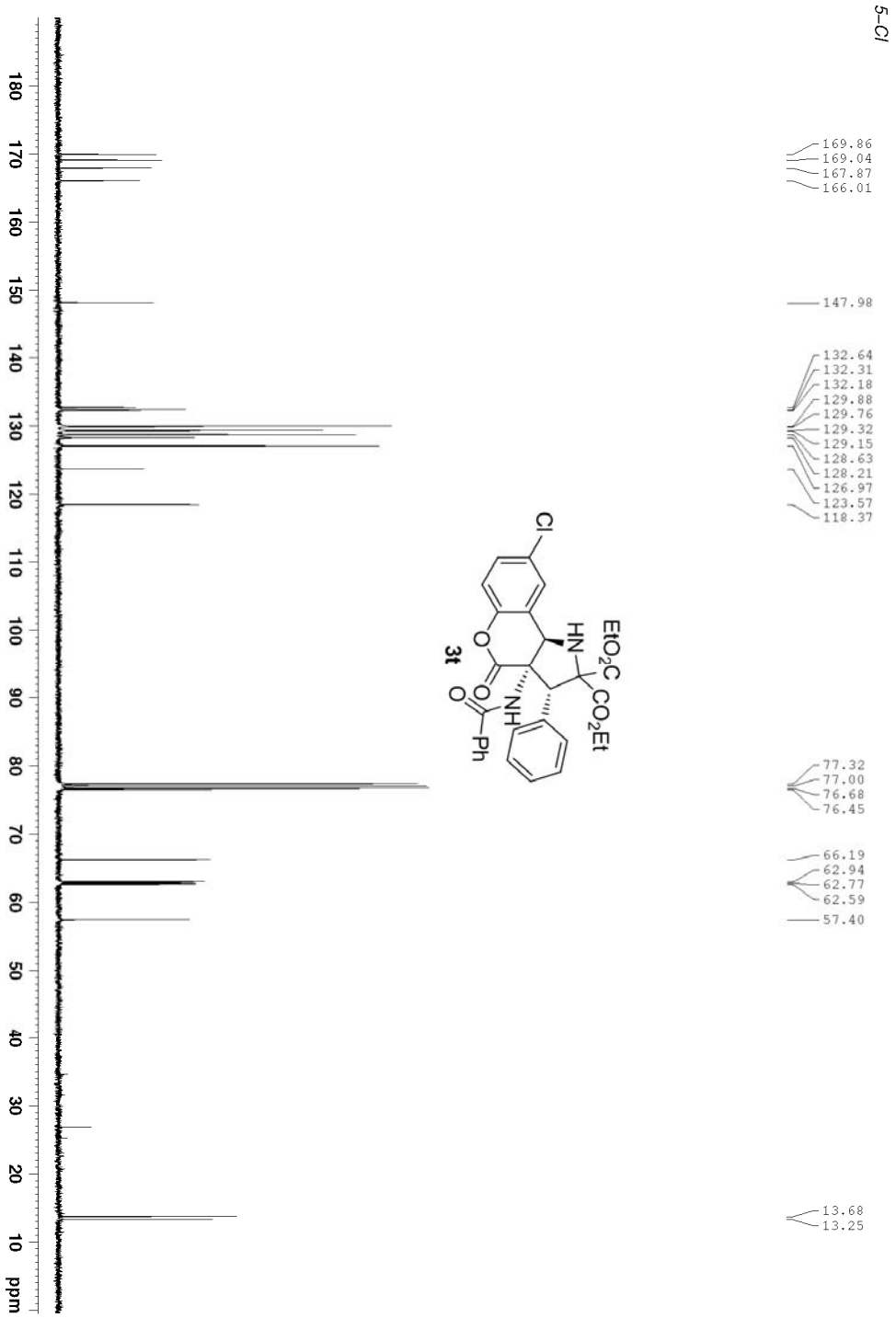

2-furyl
7.915
7.862
7.843
7.554
7.548
7.533
7.496
7.477
7.452
7.336
7.317
7.298
7.145
7.126
7.107
7.098
7.077
6.426
6.418
6.392
6.388
5.364
5.351
4.867
4.415
4.401
4.285
4.267
4.258
4.250
4.241
4.232
4.223
4.205
4.097
4.079
4.062
4.044
3.918
3.900
3.891
3.882
3.873
3.864
3.856
3.838
1.193
1.176
1.158
1.053
1.035
1.017
-0.001
3r
EtO2C
CO2Et
HN
NH
O
Ph
1.00
2.06
2.09
3.11
1.08
2.09
2.07
1.04
1.03
1.02
1.10
2.08
1.07
3.14
3.13
8.5
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
ppm
NAME TL-4-147e
EXPNO 10
PROCNO 1
Date_ 20131016
Time 21.23
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 71.8
DW 62.400 usec
DE 6.50 usec
TE 294.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300074 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

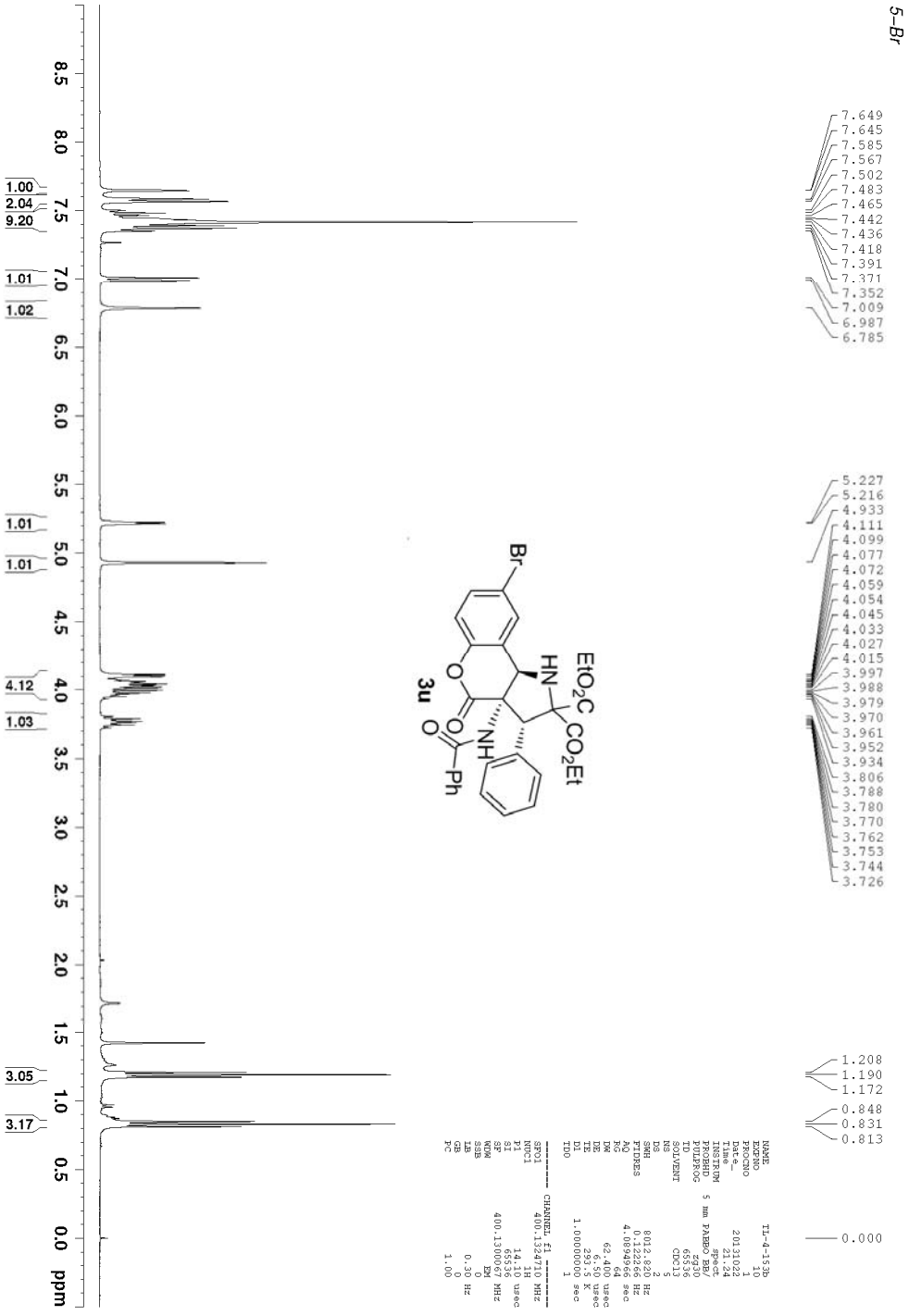

2-furyl
169.36
169.24
167.67
164.71
148.84
146.12
143.78
133.35
132.13
129.88
128.69
128.38
127.17
124.73
121.99
116.85
113.27
111.42
77.32
77.00
76.68
74.28
68.25
63.33
62.64
62.42
49.73
13.78
13.49
ppm
3r
EtO2C
CO2Et
HN
NH
O
Ph

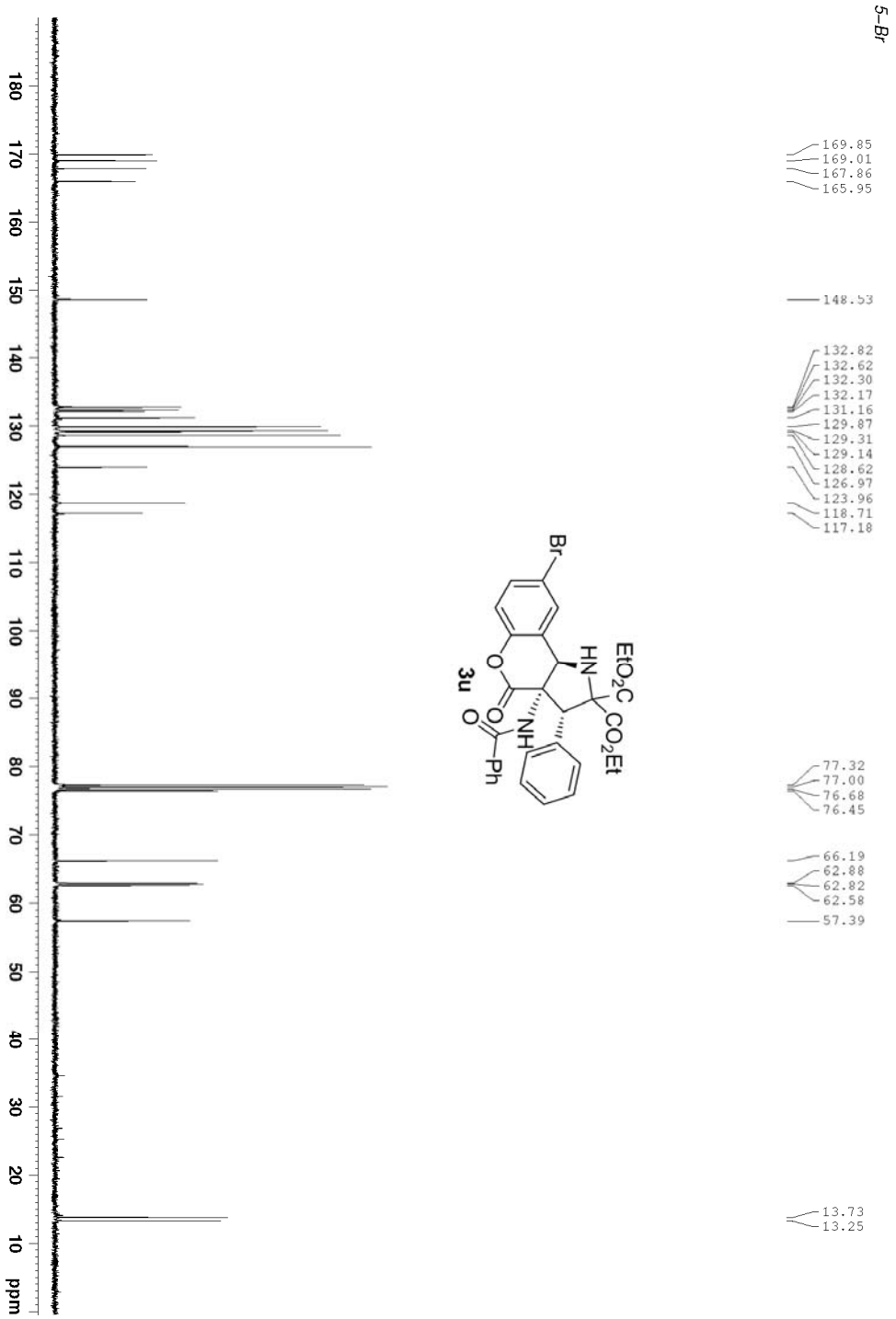

cyclohexyl
7.885
7.867
7.864
7.576
7.558
7.539
7.510
7.491
7.473
7.434
7.415
7.293
7.276
7.255
7.099
7.080
7.061
7.045
7.033
7.025
5.288
5.277
4.440
4.422
4.413
4.395
4.313
4.295
4.286
4.268
4.100
4.098
4.082
4.080
4.064
4.047
4.000
3.987
3.335
3.318
2.086
2.056
1.799
1.742
1.710
1.597
1.341
1.323
1.305
1.280
1.260
1.248
1.221
1.203
1.185
1.154
-0.000
EtO2C
CO2Et
HN
NH
O
O
O
Ph
3s
2.01
1.02
2.02
1.03
1.10
3.04
1.00
1.01
1.03
2.06
1.01
1.00
1.03
4.21
1.05
4.02
6.31
8.5
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
ppm
NAME TL-4-154
EXPNO 10
PROCNO 1
Date_ 20131018
Time 21.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122766 Hz
AQ 4.083496 sec
RG 32
DW 62.400 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300027 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

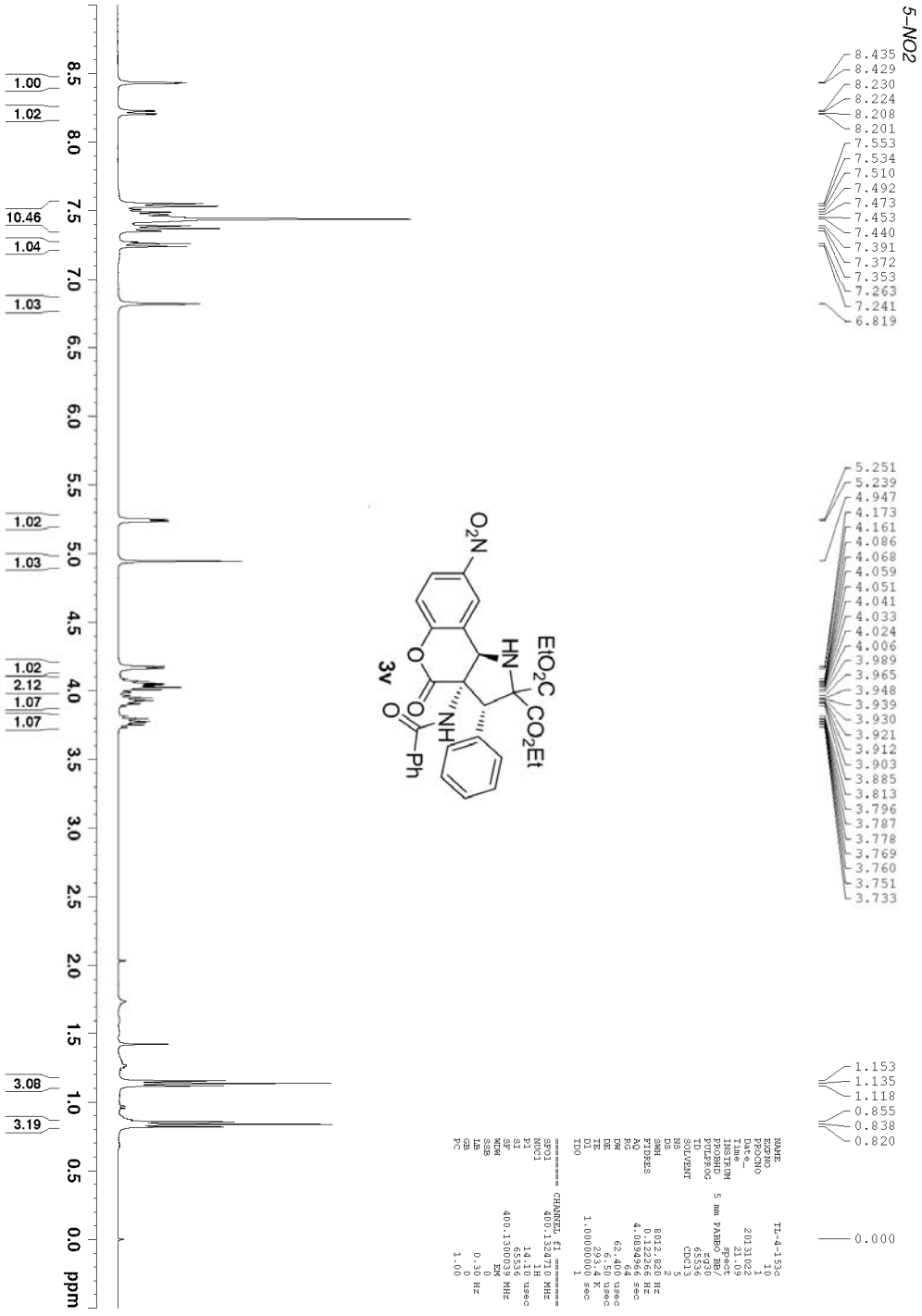

cyclohexyl
171.70
170.29
166.57
165.74
148.70
133.67
131.97
129.59
128.70
128.16
127.01
124.34
122.61
116.33
77.32
77.00
76.68
75.03
67.28
63.35
63.14
62.03
55.16
37.57
33.53
30.01
26.70
26.51
25.62
13.82
13.78
3s
EtO2C
CO2Et
HN
NH
O
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

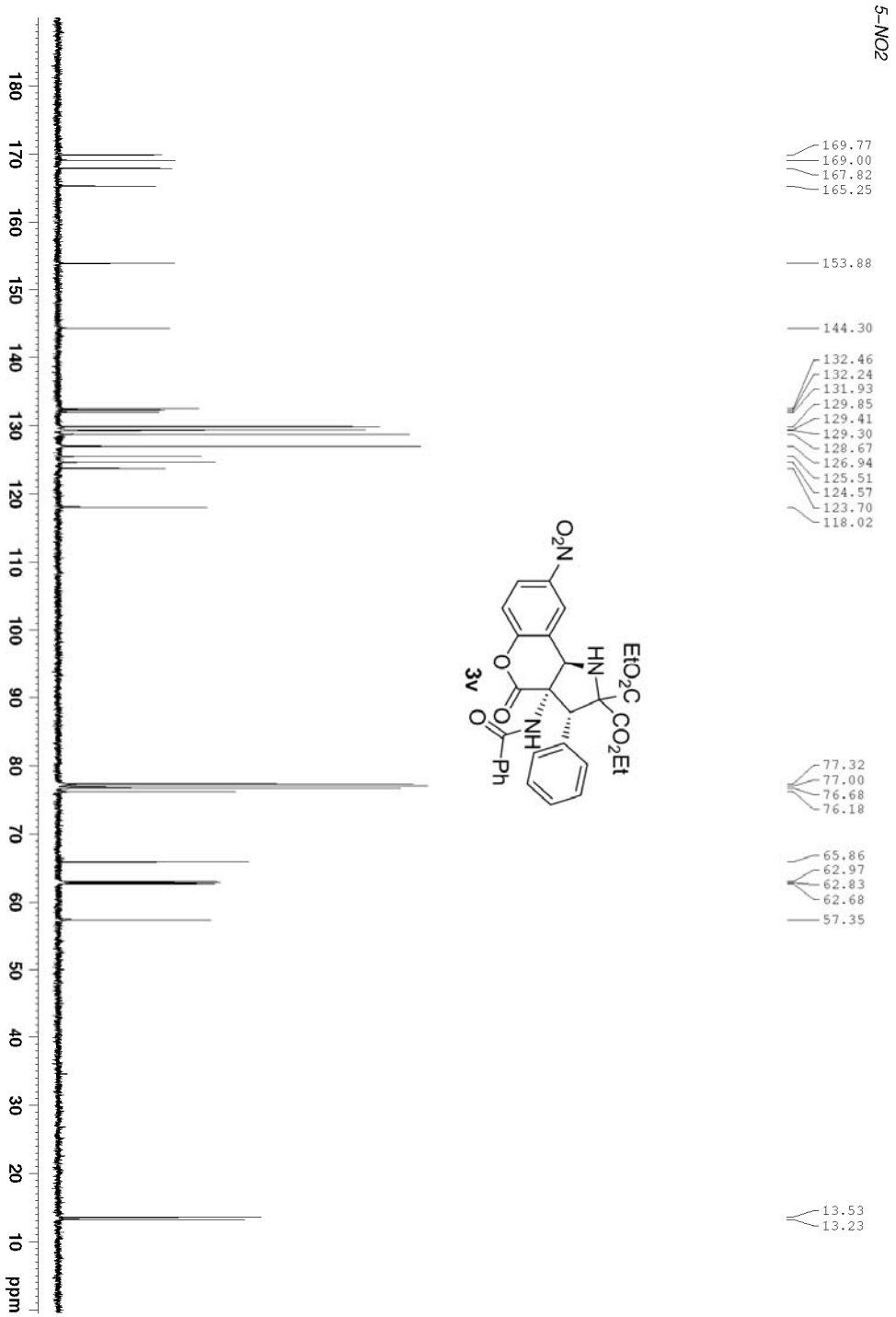

5–Cl
7.588
7.570
7.567
7.502
7.501
7.496
7.485
7.467
7.420
7.393
7.373
7.355
7.299
7.294
7.278
7.272
7.267
7.067
7.045
6.790
5.224
5.212
4.931
4.110
4.098
4.079
4.061
4.052
4.043
4.035
4.025
4.017
3.998
3.995
3.986
3.977
3.968
3.959
3.950
3.932
3.809
3.791
3.782
3.773
3.764
3.755
3.746
3.728
1.199
1.181
1.163
0.849
0.832
0.814
-0.000
2.03
2.14
7.07
1.12
1.01
1.00
1.00
1.01
4.11
1.03
3.09
3.27
8.5
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
ppm
Cl
HN
EtO2C
CO2Et
O
3t
O
NH
O
Ph
NAME TL-4-153a
EXPNO 10
PROCNO 1
Date_ 20131010
Time 21.51
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894976 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300069 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

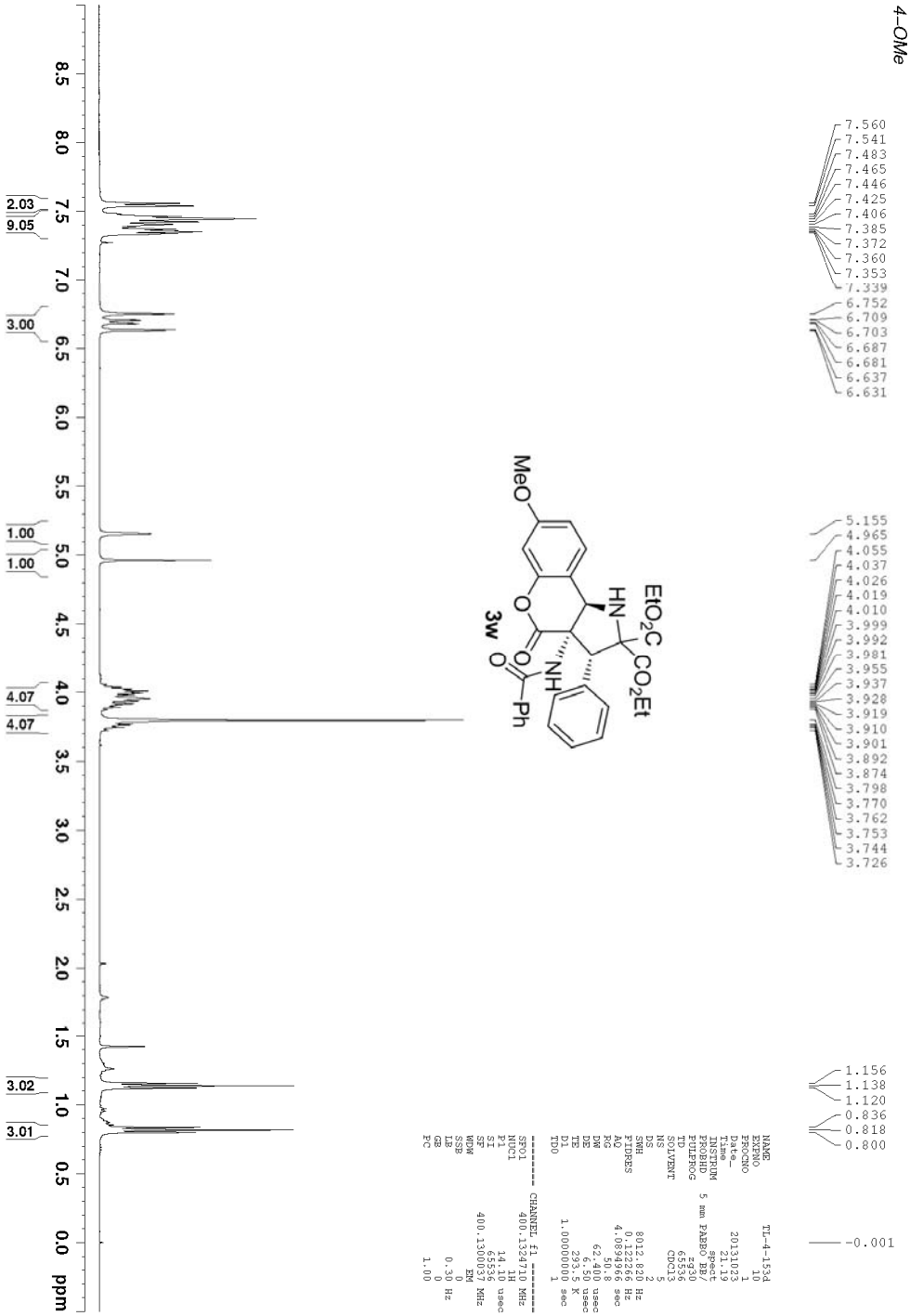

5-Cl
169.86
169.04
167.87
166.01
147.98
132.64
132.31
132.18
129.88
129.76
129.32
129.15
128.63
128.21
126.97
123.57
118.37
77.32
77.00
76.68
76.45
66.19
62.94
62.77
62.59
57.40
13.68
13.25
Cl
EtO2C
CO2Et
HN
NH
O
O
O
Ph
3t
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


5–Br
7.649
7.645
7.585
7.567
7.502
7.483
7.465
7.442
7.436
7.418
7.391
7.371
7.352
7.009
6.987
6.785
5.227
5.216
4.933
4.111
4.099
4.077
4.072
4.059
4.054
4.045
4.033
4.027
4.015
3.997
3.988
3.979
3.970
3.961
3.952
3.934
3.806
3.788
3.780
3.770
3.762
3.753
3.744
3.726
1.208
1.190
1.172
0.848
0.831
0.813
0.000
1.00
2.04
9.20
1.01
1.02
1.01
1.01
4.12
1.03
3.05
3.17
8.5
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
ppm
Br
EtO2C
HN
CO2Et
O
3u
O
NH
O
Ph
NAME TI-4-153b
EXPNO 10
PROCNO 1
Date_ 20131021
Time_ 21.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 2
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 62.400
DW 62.400 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SI 65536
SF 400.1300067 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


5-Br
169.85
169.01
167.86
165.95
148.53
132.82
132.62
132.30
132.17
131.16
129.87
129.31
129.14
128.62
126.97
123.96
118.71
117.18
77.32
77.00
76.68
76.45
66.19
62.88
62.82
62.58
57.39
13.73
13.25
Br
HN
EtO2C
CO2Et
O
3u
O
NH
O
Ph
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


5–NO2
8.435
8.429
8.230
8.224
8.208
8.201
7.553
7.534
7.510
7.492
7.473
7.453
7.440
7.391
7.372
7.353
7.263
7.241
6.819
5.251
5.239
4.947
4.173
4.161
4.086
4.068
4.059
4.051
4.041
4.033
4.024
4.006
3.989
3.965
3.948
3.939
3.930
3.921
3.912
3.903
3.885
3.813
3.796
3.787
3.778
3.769
3.760
3.751
3.733
1.153
1.135
1.118
0.855
0.838
0.820
0.000
1.00
1.02
10.46
1.04
1.03
1.02
1.03
1.02
2.12
1.07
1.07
3.08
3.19
8.5
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
ppm
O2N
EtO2C
CO2Et
HN
NH
O
O
O
Ph
3v
NAME TI-4-153c
EXPNO 10
PROCNO 1
Date_ 20130221
Time 21.09
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 5
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 64
DW 62.400 usec
DE 6.50 usec
TE 293.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 14.10 usec
SF 400.1300039 MHz
SFB 0
WDW EM
SSB 0.30 Hz
LB 0
GB 1.00
PC


5-NO2
169.77
169.00
167.82
165.25
153.88
144.30
132.46
132.24
131.93
129.85
129.41
129.30
128.67
126.94
125.51
124.57
123.70
118.02
77.32
77.00
76.68
76.18
65.86
62.97
62.83
62.68
57.35
13.53
13.23
ppm
3v


4-OMe
7.560
7.541
7.483
7.465
7.446
7.425
7.406
7.385
7.372
7.360
7.353
7.339
6.752
6.709
6.703
6.687
6.681
6.637
6.631
5.155
4.965
4.055
4.037
4.026
4.019
4.010
3.999
3.992
3.981
3.955
3.937
3.928
3.919
3.910
3.901
3.892
3.874
3.798
3.770
3.762
3.753
3.744
3.726
1.156
1.138
1.120
0.836
0.818
0.800
-0.001
MeO
EtO2C
HN
CO2Et
NH
O
O
O
Ph
3w
2.03
9.05
3.00
1.00
1.00
4.07
4.07
3.02
3.01
8.5
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
ppm
NAME TL-4-153d
EXPNO 10
PROCNO 1
Date_ 20131023
Time 21.59
INSTRUM spect
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PULPROG zg30
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SOLVENT CDCl3
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DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 203.8
DW 62.400 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
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PL1 -6.55 dB
SF 400.1300037 MHz
WDW EM
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LB 0.30 Hz
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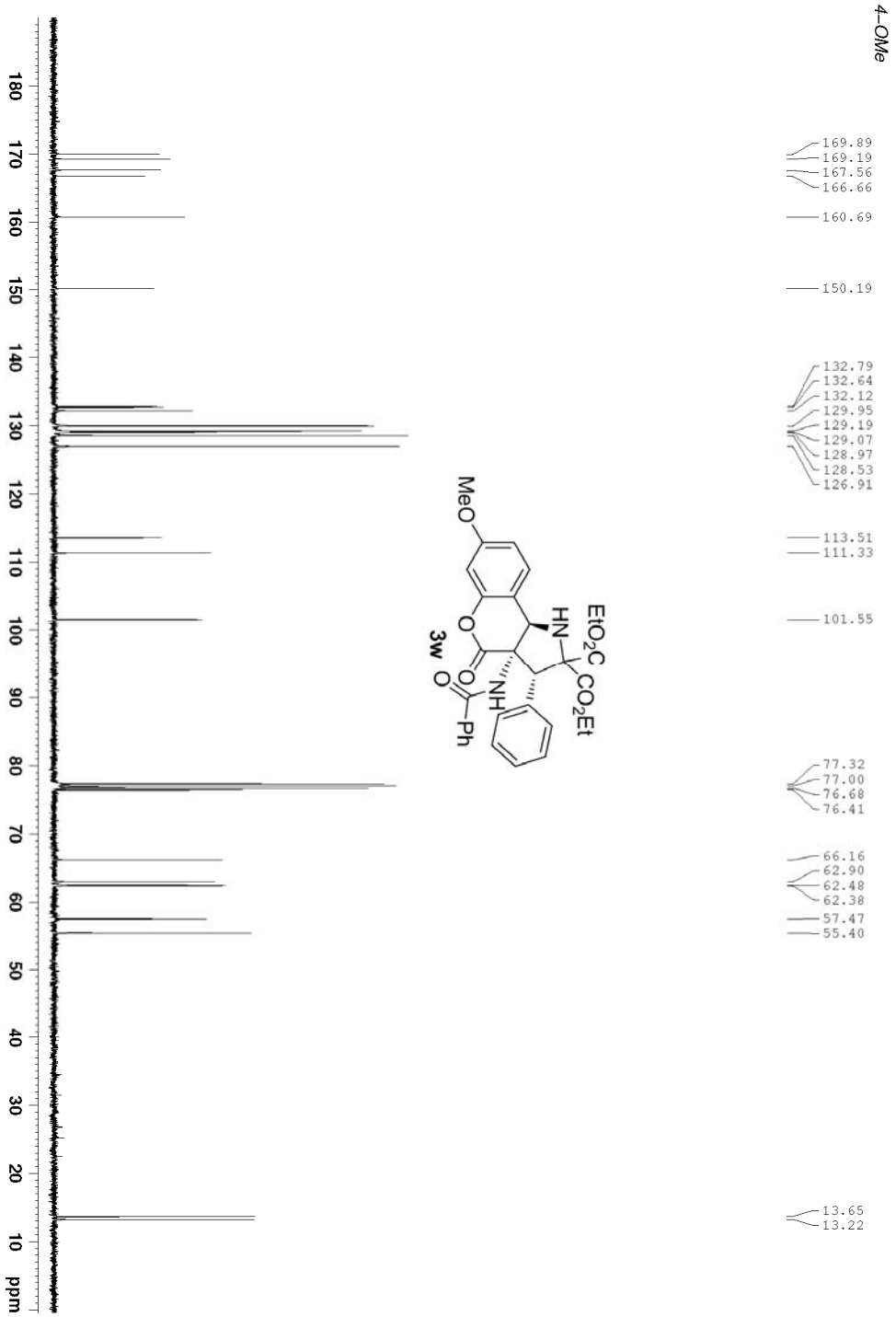
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HN
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CO2Et
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180
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120
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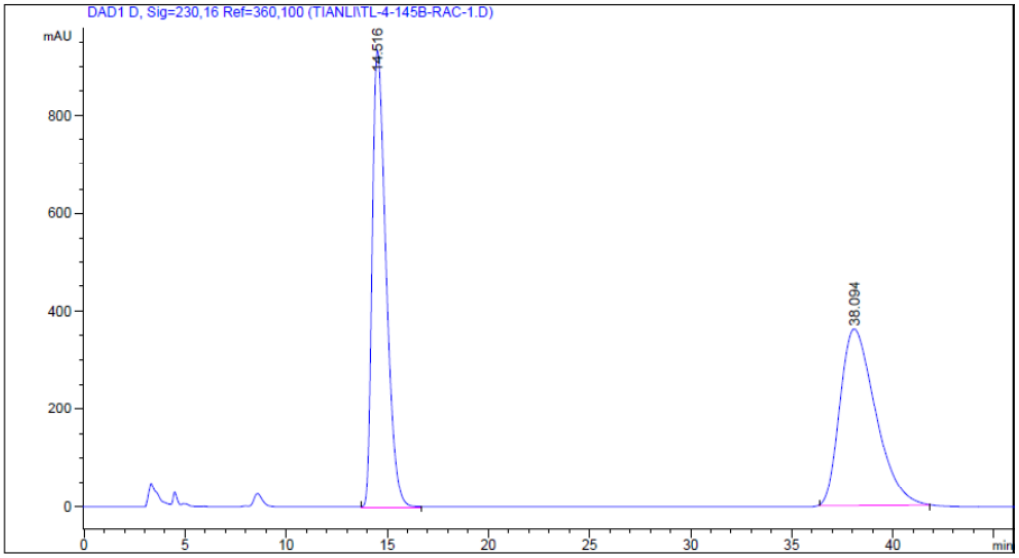
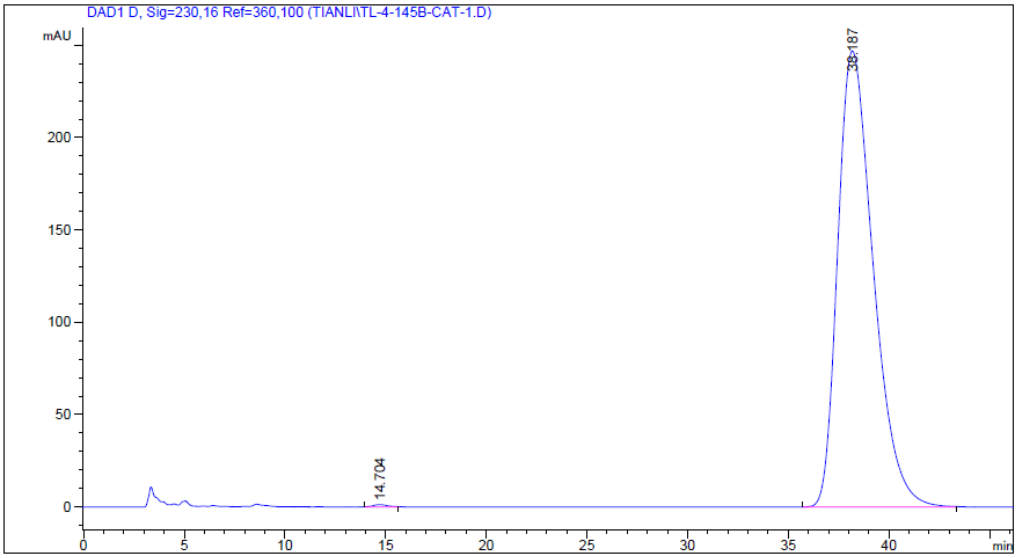
10
ppm

8. HPLC spectra

3a: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

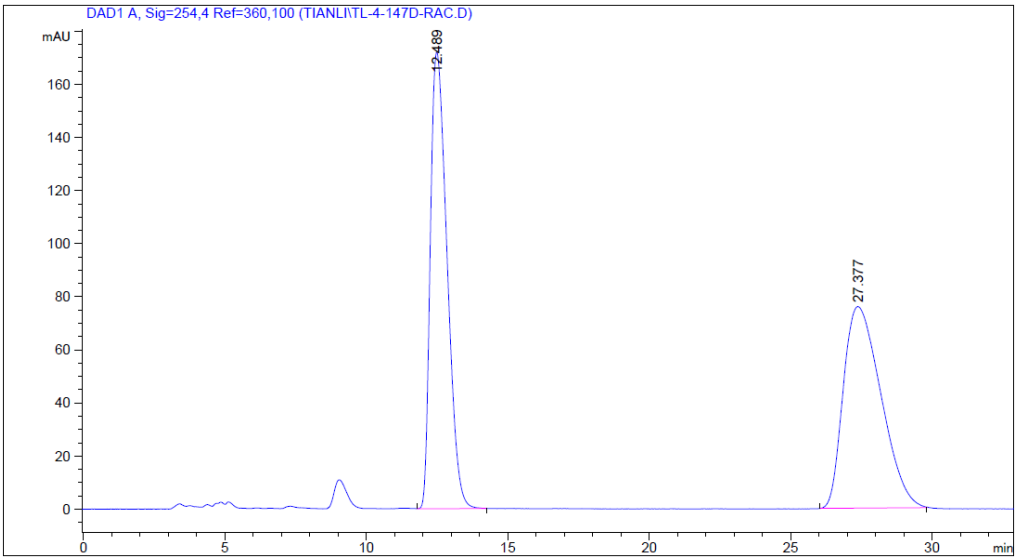


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	14.516	4.42561e4	931.22510	50.0543
2	DAD 230.16 nm	38.094	4.41601e4	360.54883	49.9457

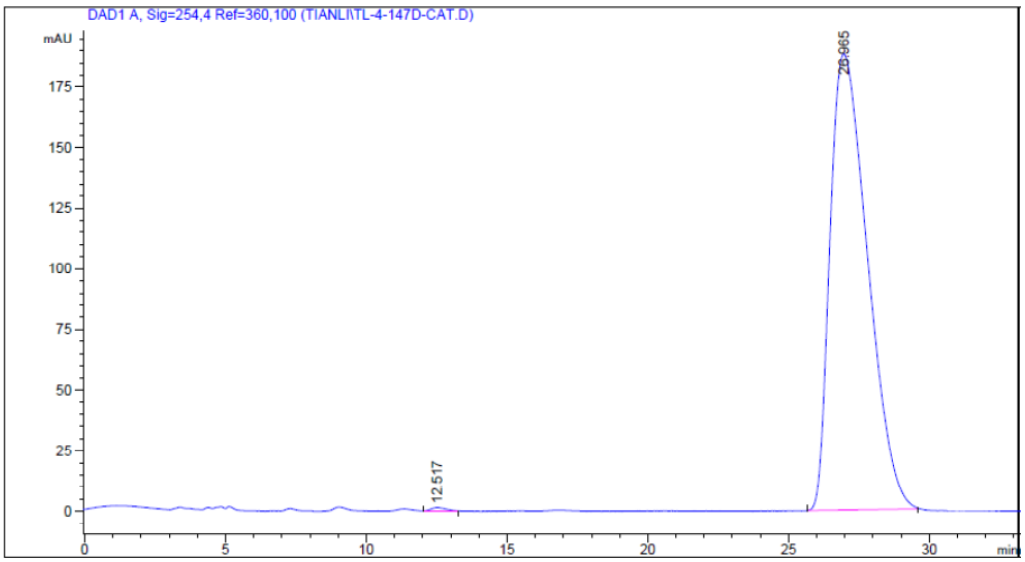


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	14.704	65.72226	1.32549	0.2164
2	DAD 230.16 nm	38.187	3.03025e4	246.92838	99.7836

3b: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

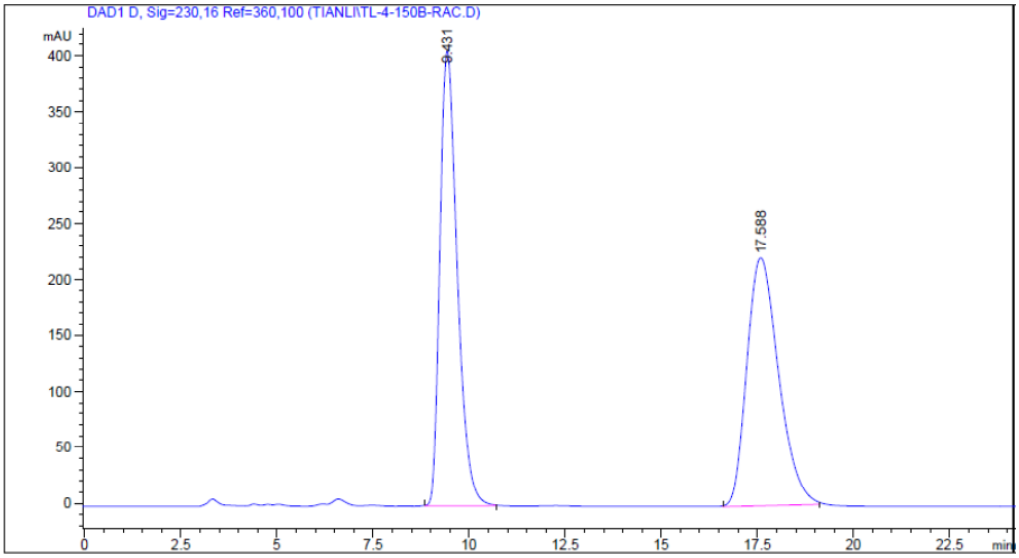


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.489	7043.68359	172.06007	50.0770
2	DAD 254.4 nm	27.377	7022.02246	75.90296	49.9230

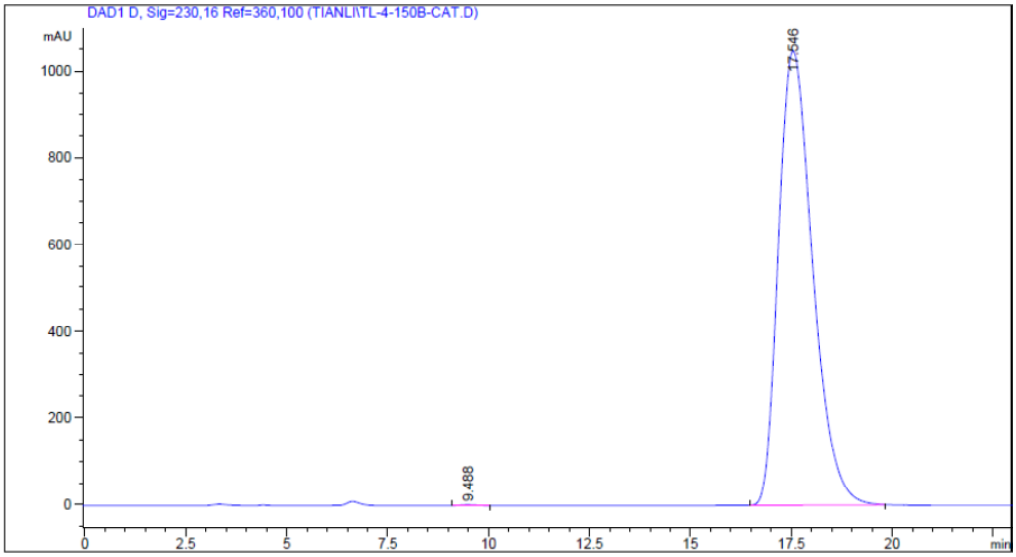


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	12.517	58.06630	1.44128	0.3331
2	DAD 254.4 nm	26.965	1.73717e4	188.06601	99.6669

3c: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

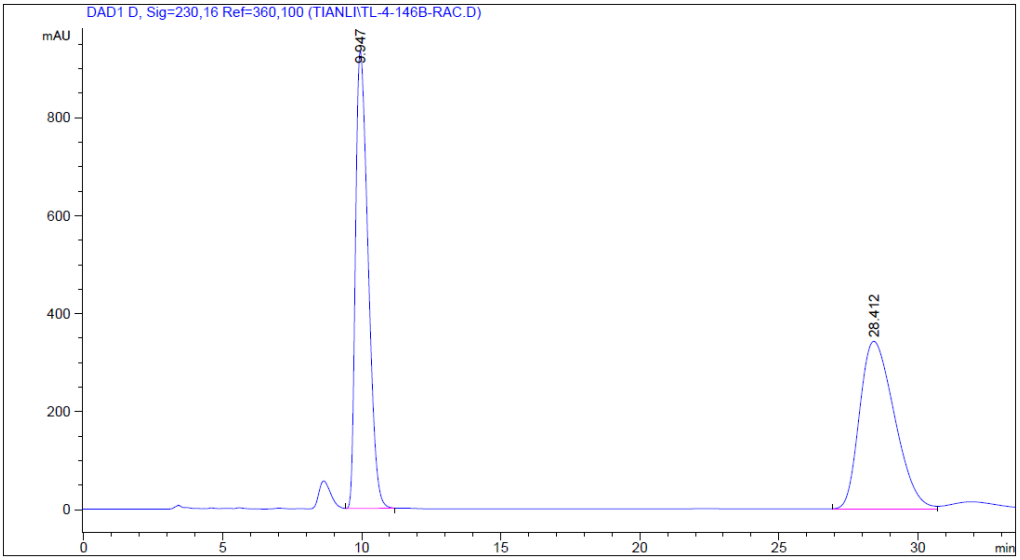


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	9.431	1.27384e4	406.55832	50.0512
2	DAD 230.16 nm	17.588	1.27123e4	221.79678	49.9488

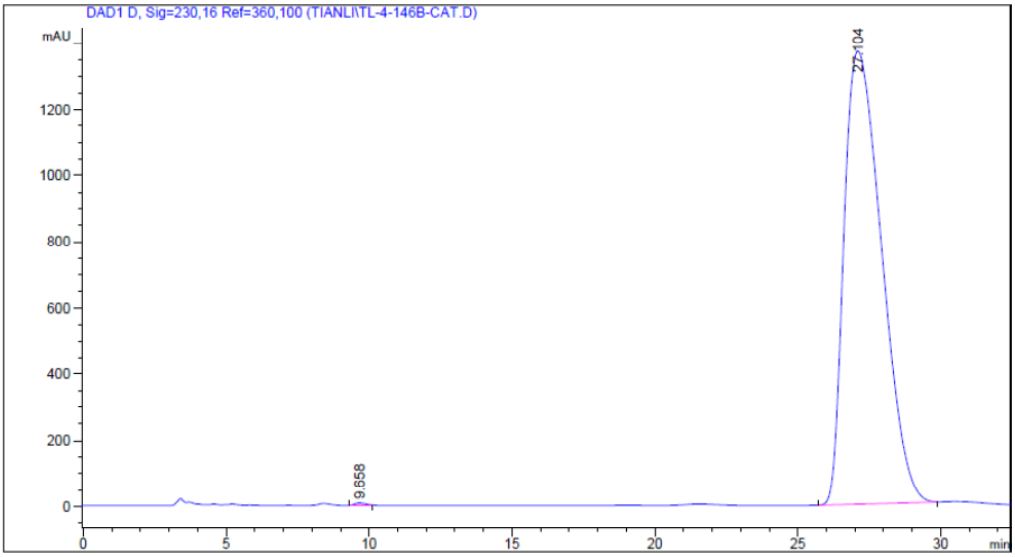


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	9.488	47.91438	1.70864	0.0776
2	DAD 230.16 nm	17.546	6.17004e4	1046.78967	99.9224

3d: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

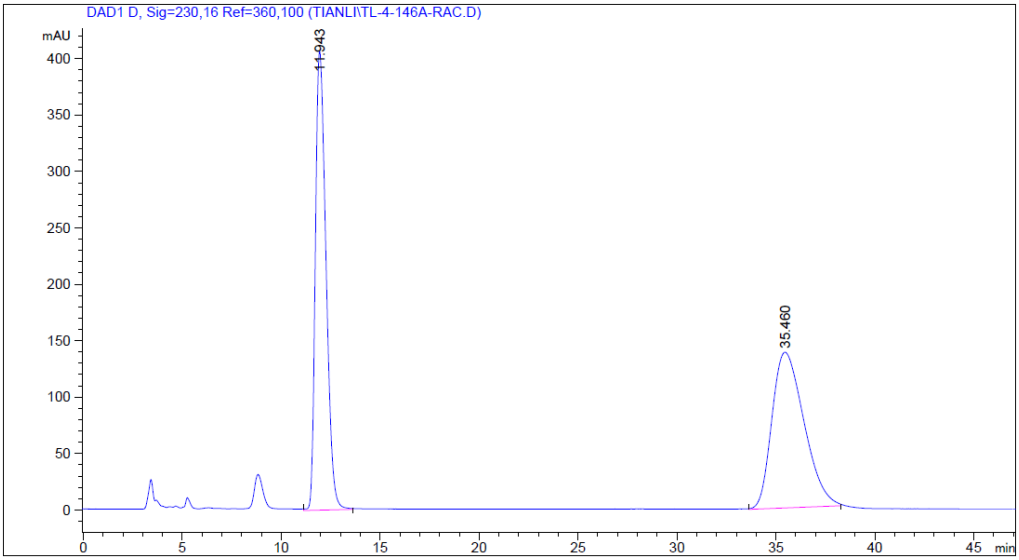


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	9.947	2.93854e4	933.64313	49.6160
2	DAD 230.16 nm	28.412	2.98403e4	342.00146	50.3840

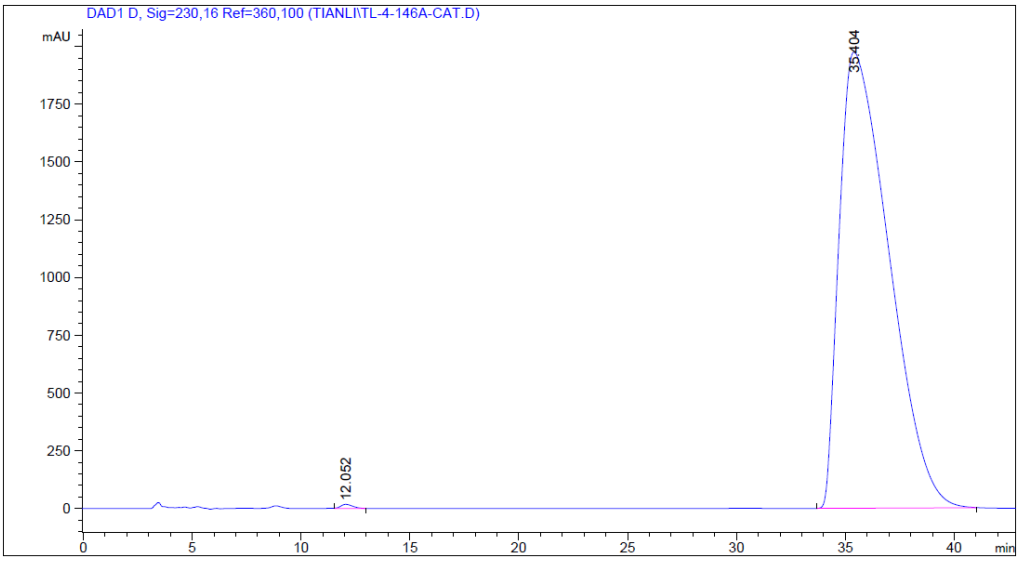


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	9.658	229.77553	7.98003	0.1836
2	DAD 230.16 nm	27.104	1.24909e5	1368.79395	99.8164

3e: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

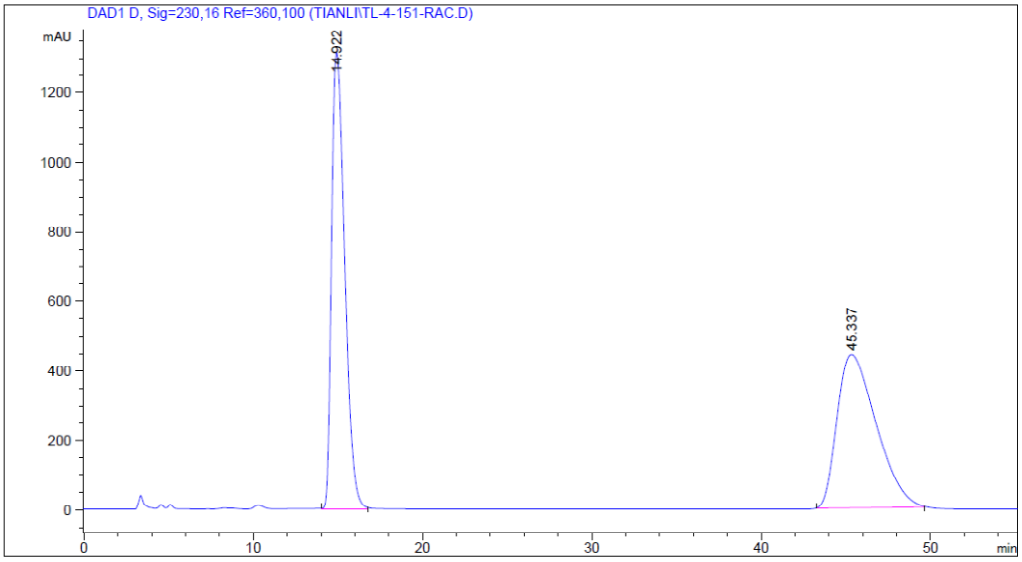


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	11.943	1.51561e4	406.85596	49.3734
2	DAD 230.16 nm	35.460	1.55408e4	138.02827	50.6266

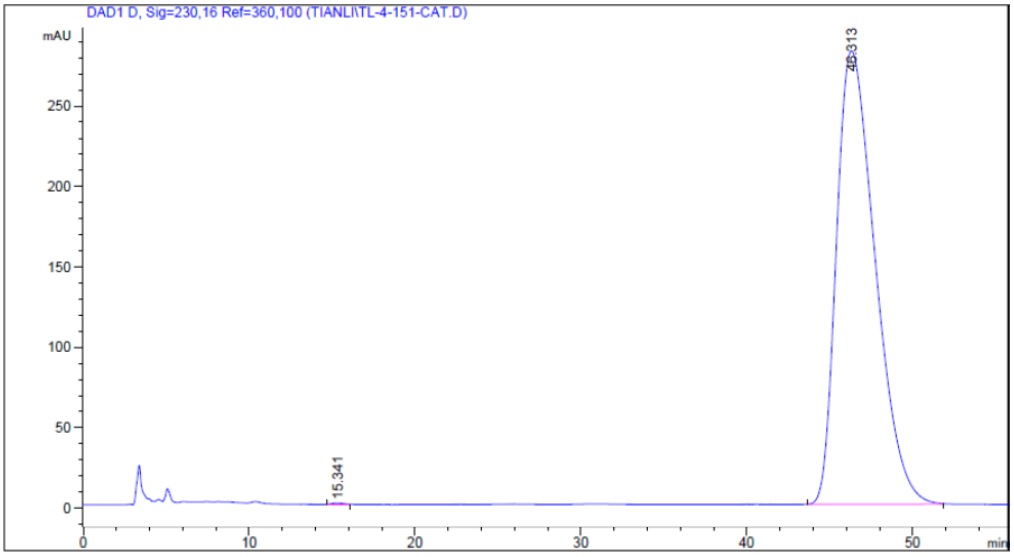


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	12.052	699.63135	17.98186	0.2232
2	DAD 230.16 nm	35.404	3.12771e5	1974.31396	99.7768

3f: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

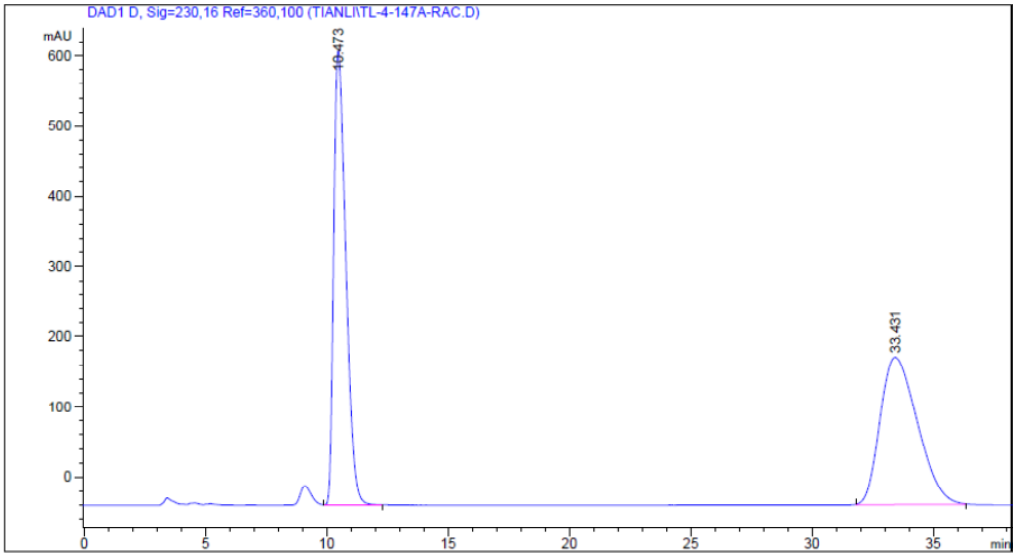


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	14.922	7.09226e4	1316.09509	50.0516
2	DAD 230.16 nm	45.337	7.07763e4	441.24490	49.9484

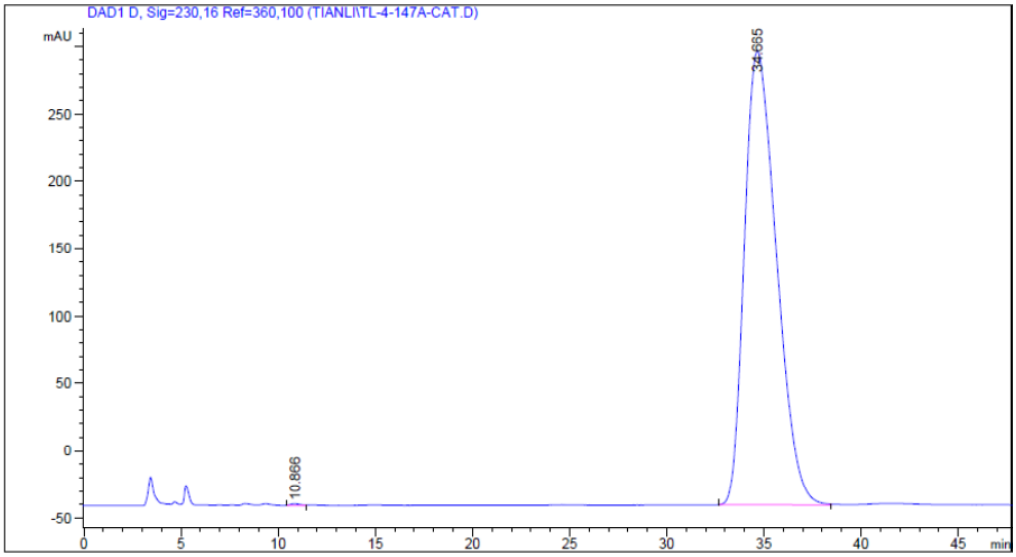


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	15.341	53.95940	1.05002	0.1183
2	DAD 230.16 nm	46.313	4.55607e4	281.78635	99.8817

3g: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

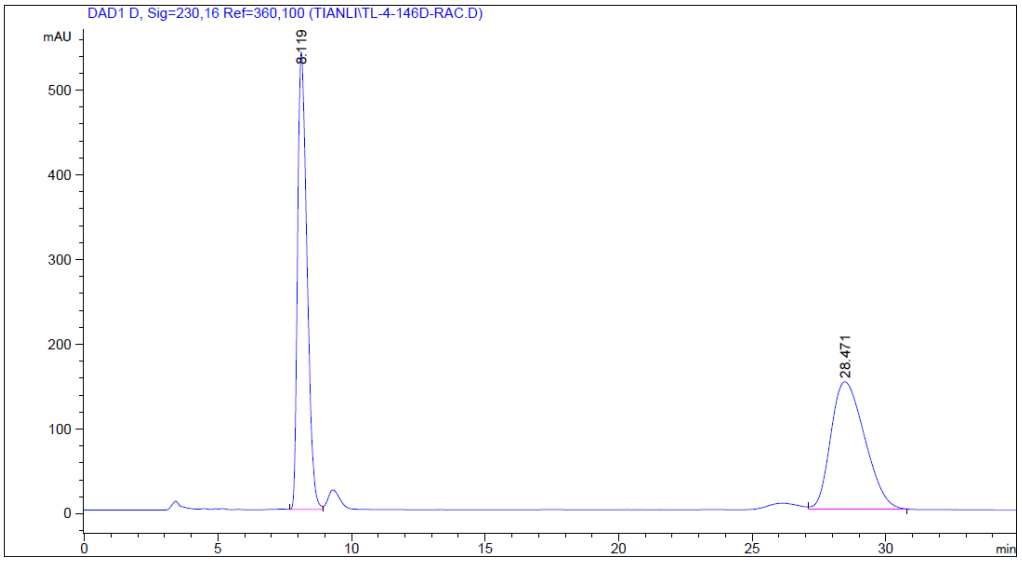


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	10.473	2.24628e4	646.72772	50.0281
2	DAD 230.16 nm	33.431	2.24376e4	209.84456	49.9719

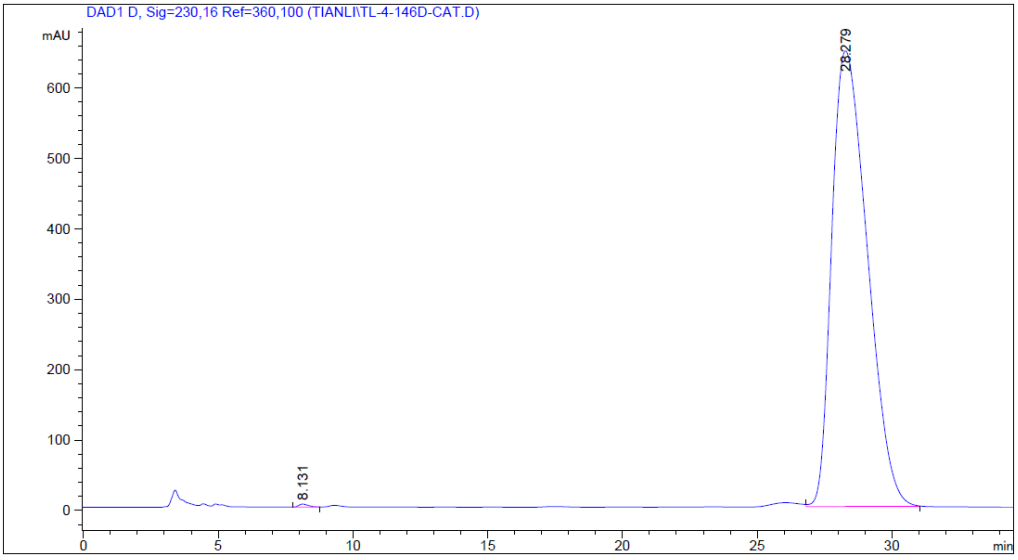


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	10.866	48.91969	1.32402	0.1267
2	DAD 230.16 nm	34.665	3.85705e4	336.63397	99.8733

3h: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

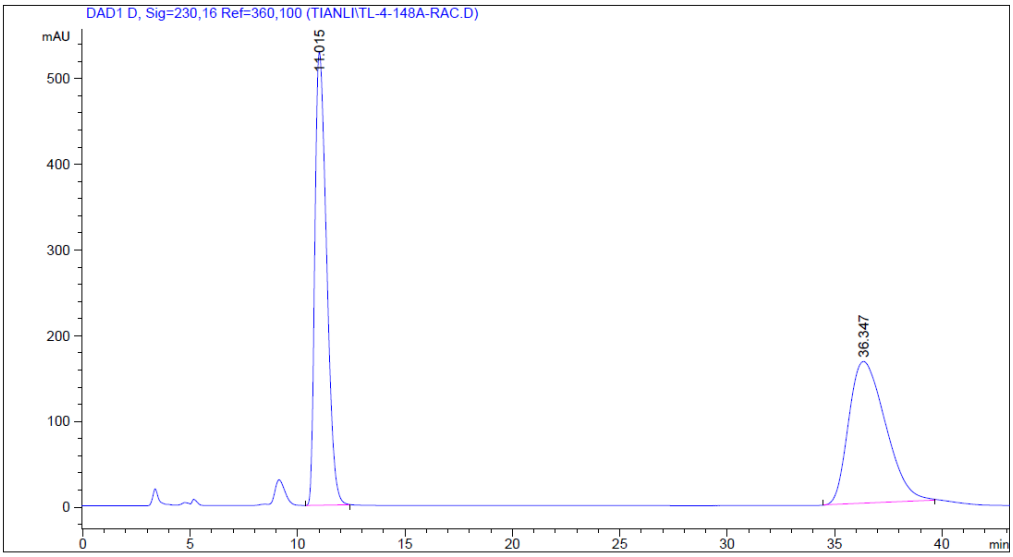


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	8.119	1.32298e4	540.00916	49.9065
2	DAD 230.16 nm	28.471	1.32793e4	150.43208	50.0935

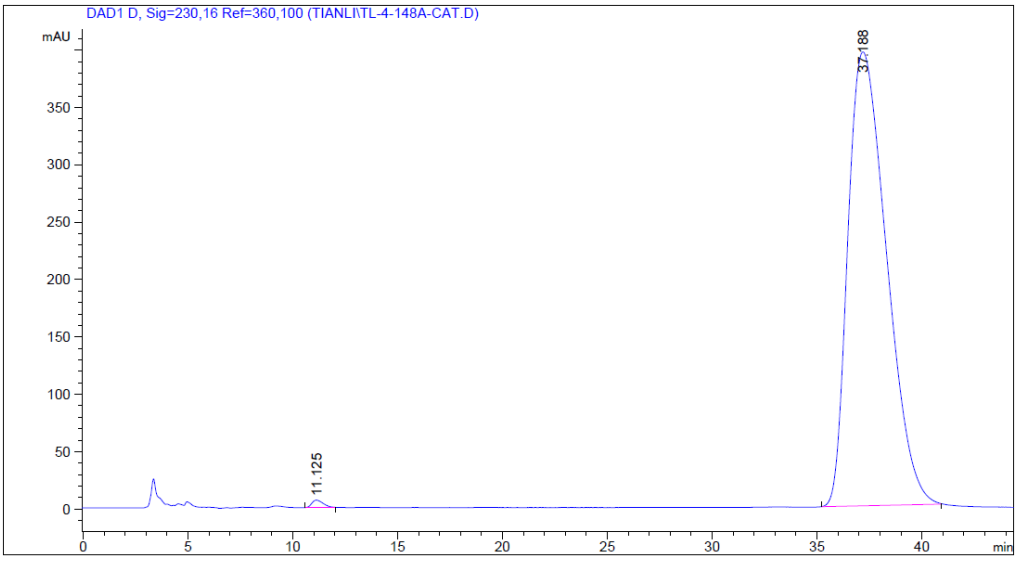


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	8.131	100.70414	4.14770	0.1697
2	DAD 230.16 nm	28.279	5.92512e4	647.06018	99.8303

3i: HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

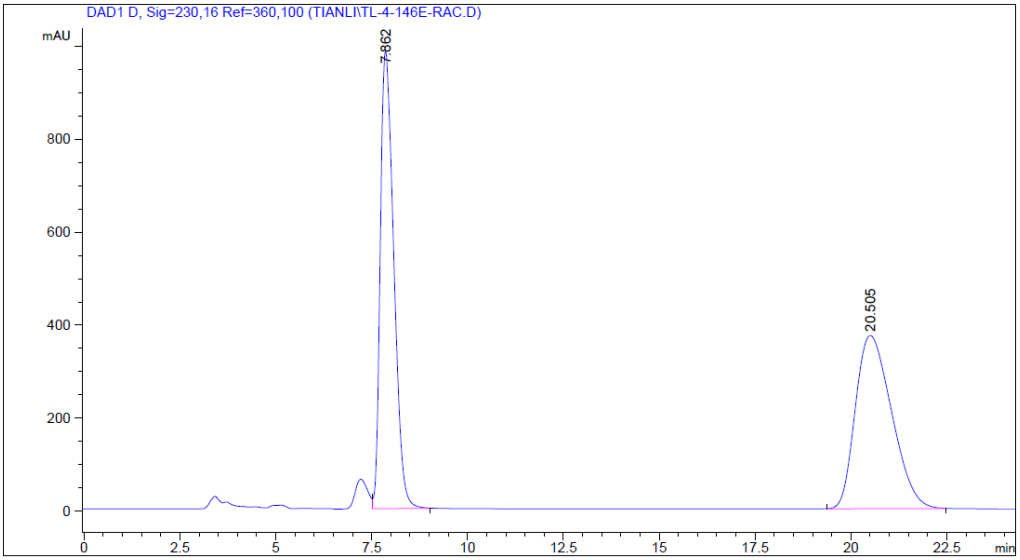


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	11.015	2.00165e4	529.26758	50.4564
2	DAD 230.16 nm	36.347	1.96543e4	165.33336	49.5436

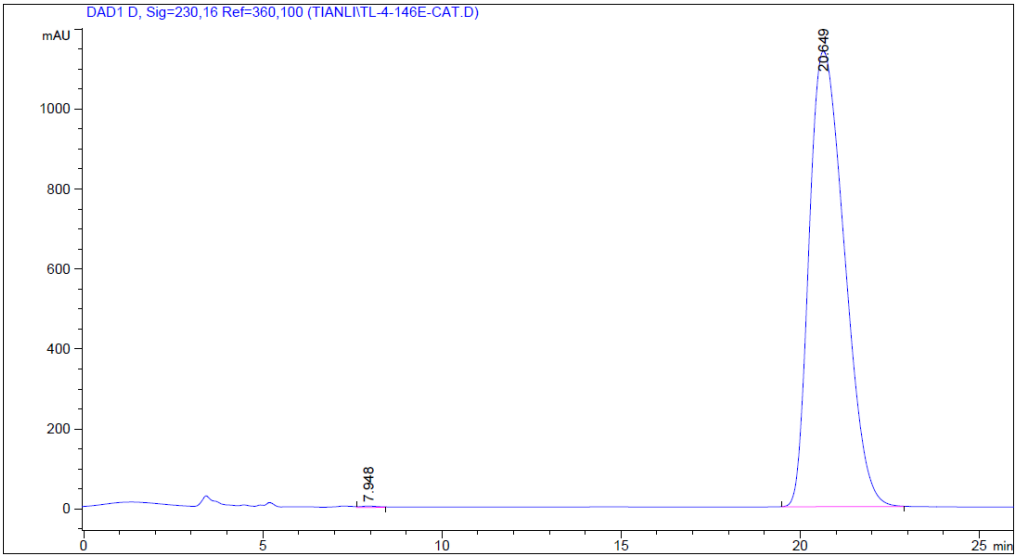


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	11.125	239.04121	6.43722	0.4699
2	DAD 230.16 nm	37.188	5.06324e4	395.58185	99.5301

3j:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

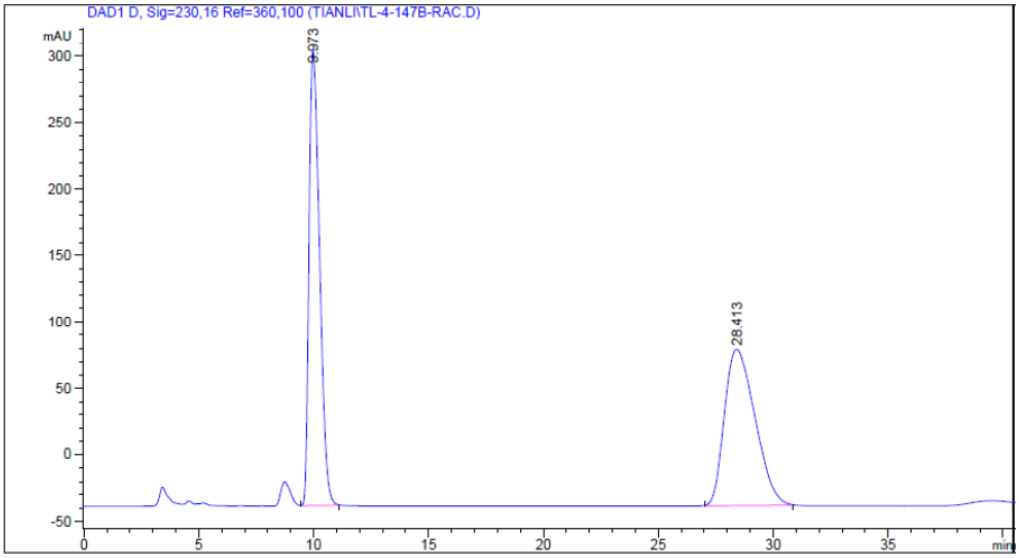


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	7.862	2.40812e4	984.50940	49.5573
2	DAD 230.16 nm	20.505	2.45115e4	372.62677	50.4427

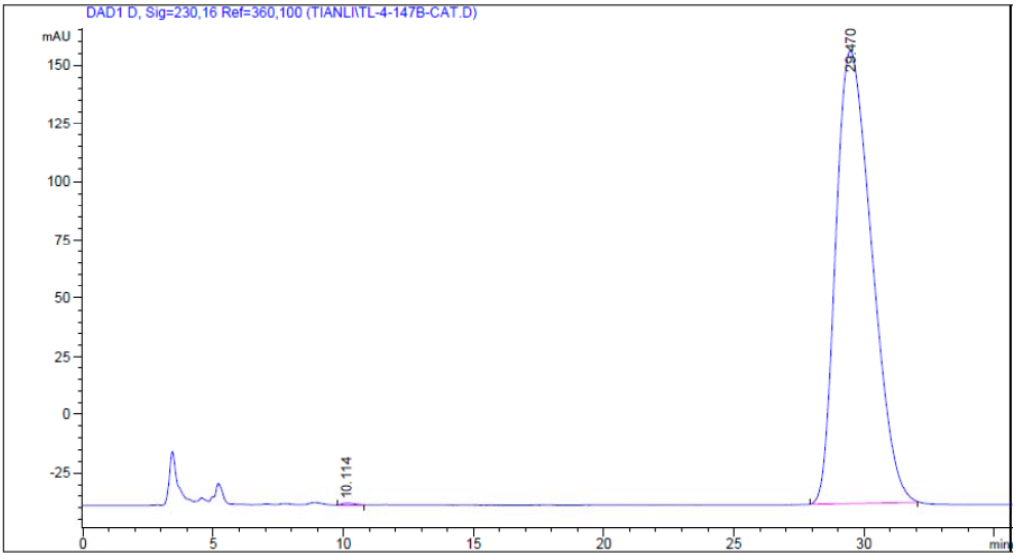


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	7.948	118.13894	3.60138	0.1517
2	DAD 230.16 nm	20.649	7.77663e4	1140.08362	99.8483

3k:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

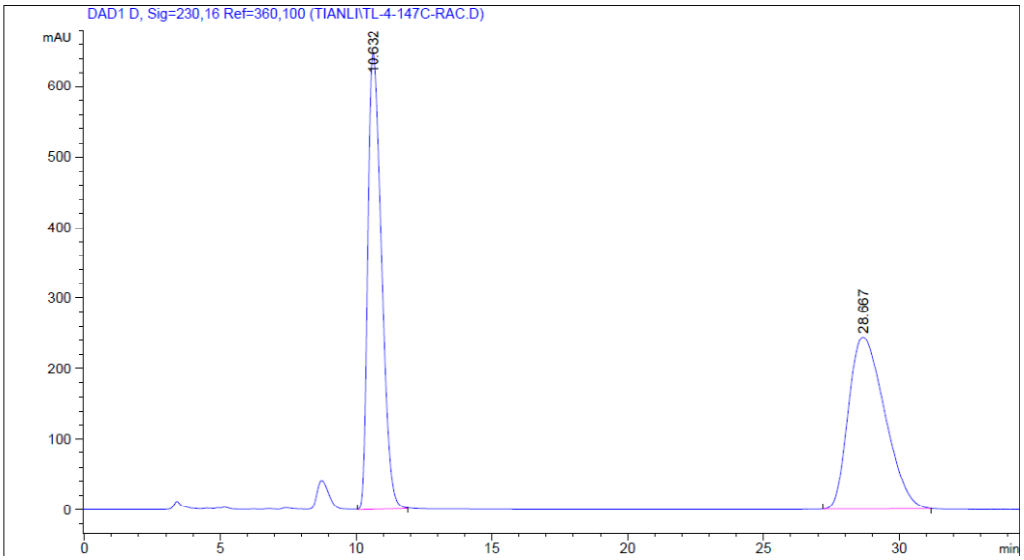


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	9.973	1.08838e4	341.89804	50.0379
2	DAD 230.16 nm	28.413	1.08673e4	117.58463	49.9621

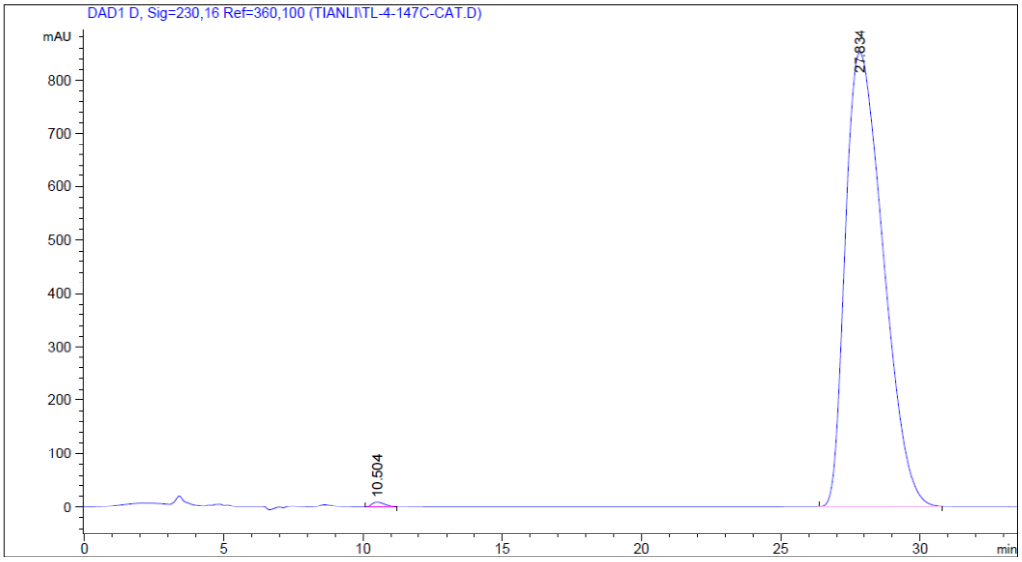


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	10.114	42.15909	1.07290	0.2252
2	DAD 230.16 nm	29.470	1.86825e4	194.16730	99.7748

3l:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

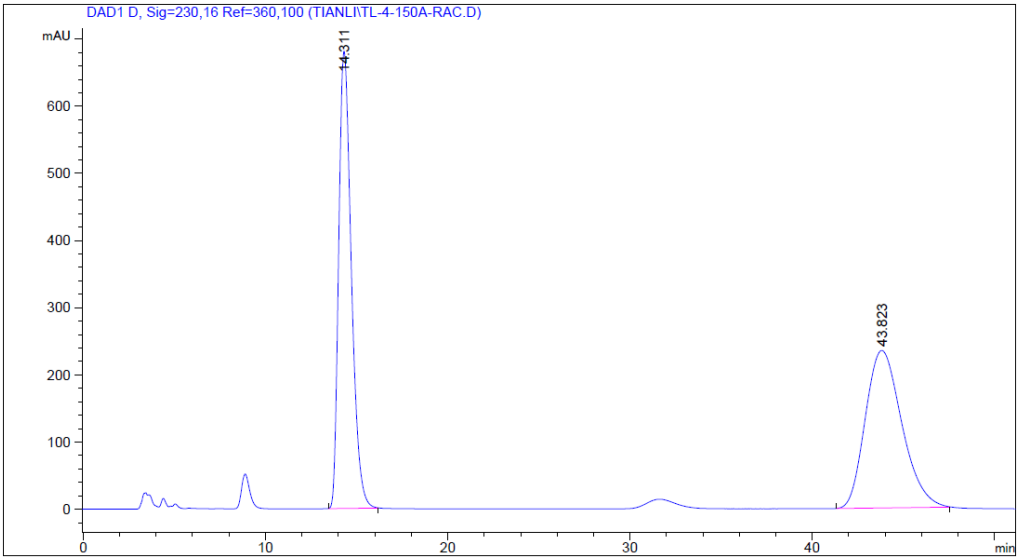


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	10.632	2.26649e4	648.13892	50.0079
2	DAD 230.16 nm	28.667	2.26577e4	244.10370	49.9921

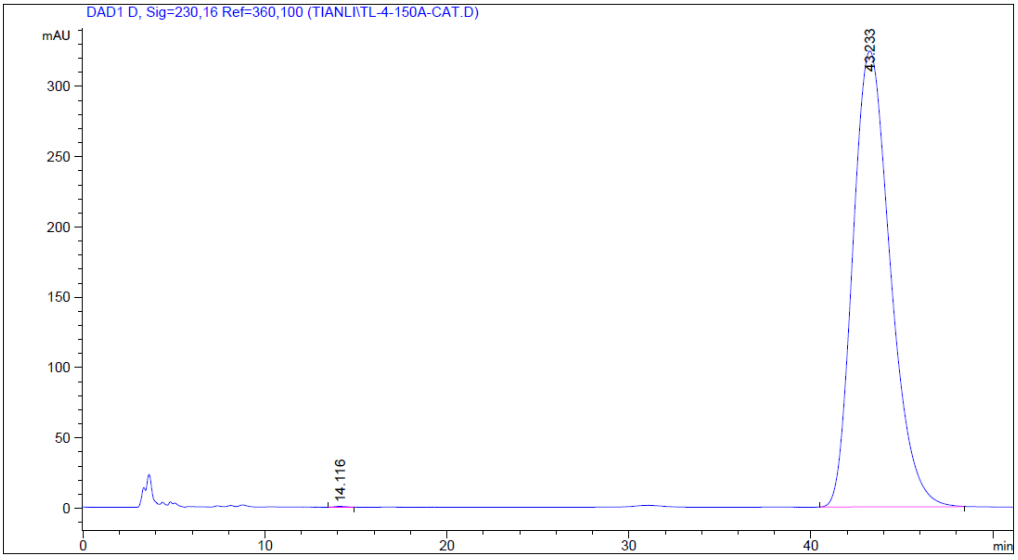


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	10.504	319.44400	9.45661	0.3971
2	DAD 230.16 nm	27.834	8.01273e4	850.75189	99.6029

3m:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

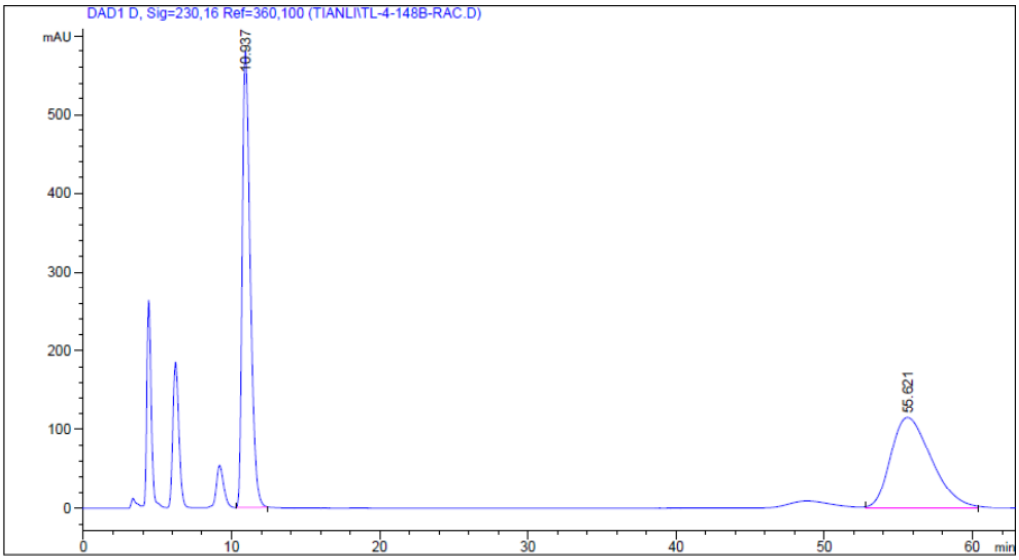


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	14.311	3.26665e4	680.86188	50.0742
2	DAD 230.16 nm	43.823	3.25697e4	234.41856	49.9258

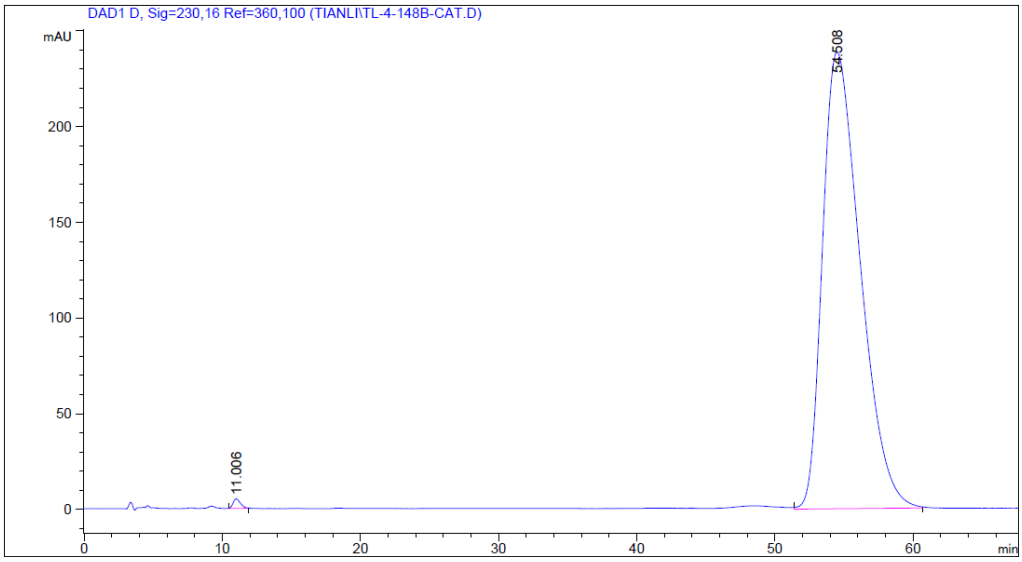


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	14.116	28.79625	6.40862e-1	0.0622
2	DAD 230.16 nm	43.233	4.62597e4	324.35739	99.9378

3n:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

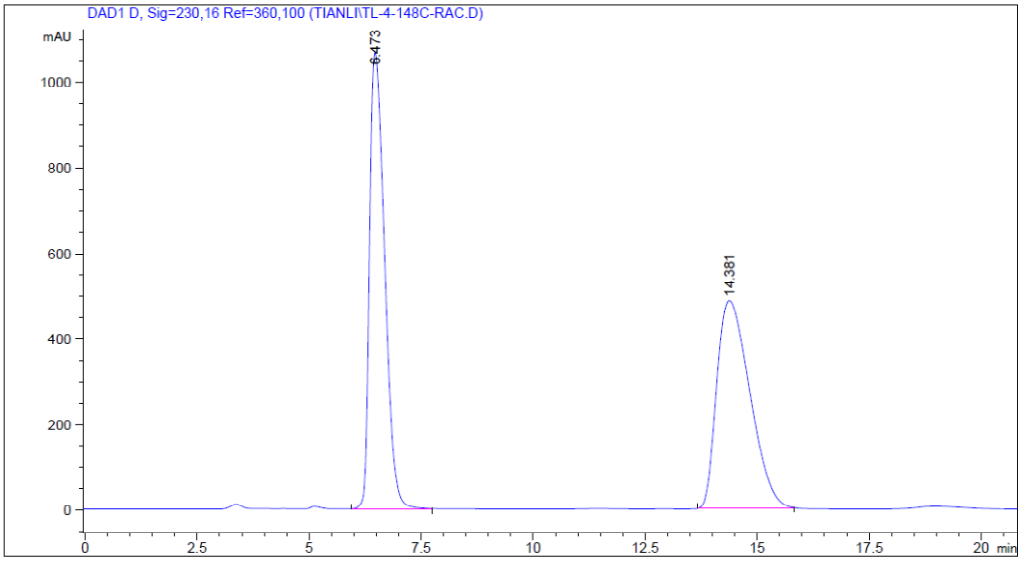


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	10.937	2.17395e4	578.34674	50.2087
2	DAD 230.16 nm	55.621	2.15588e4	113.59769	49.7913

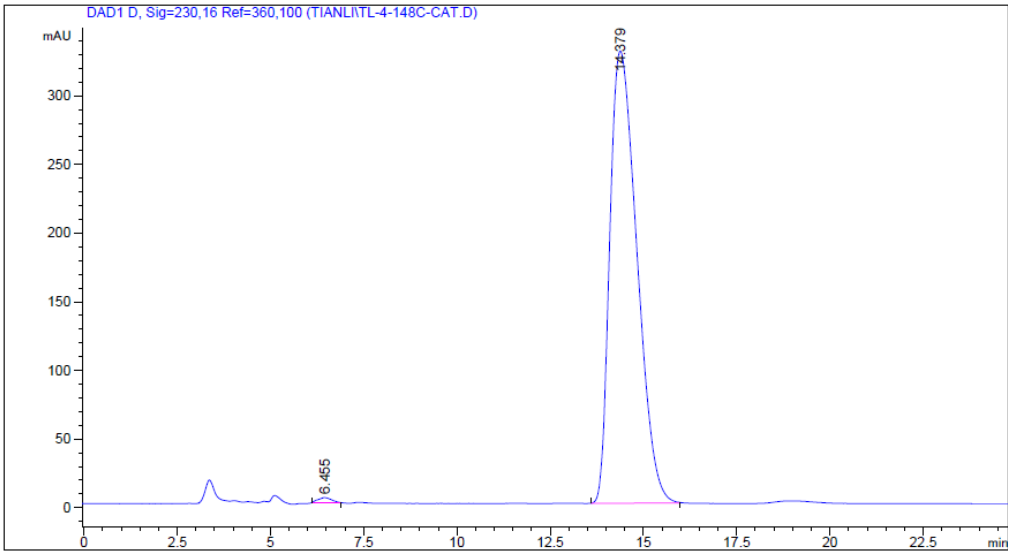


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	11.006	181.87411	4.94089	0.4010
2	DAD 230.16 nm	54.508	4.51783e4	238.48979	99.5990

3o:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

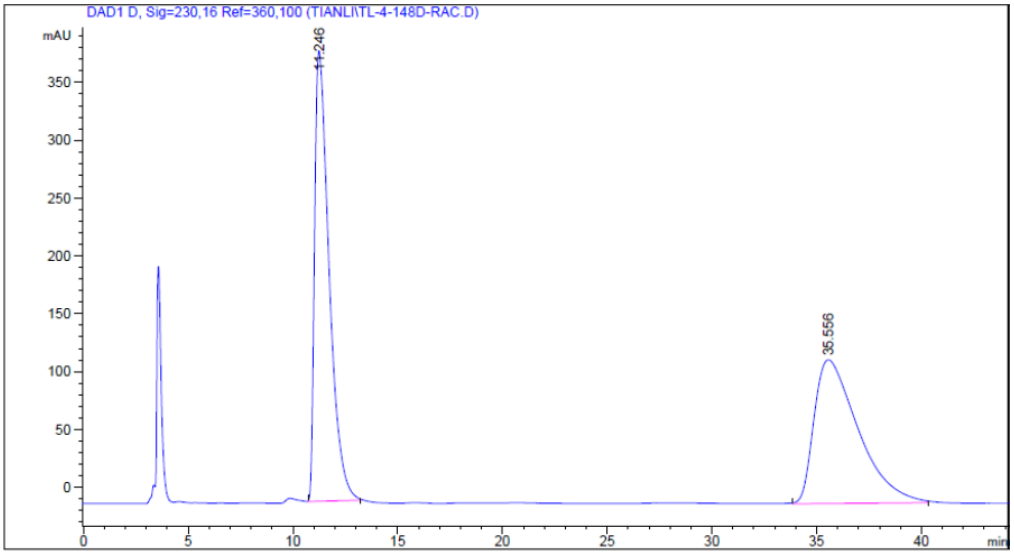


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	6.473	2.49199e4	1067.90808	50.0339
2	DAD 230.16 nm	14.381	2.48860e4	484.83890	49.9661

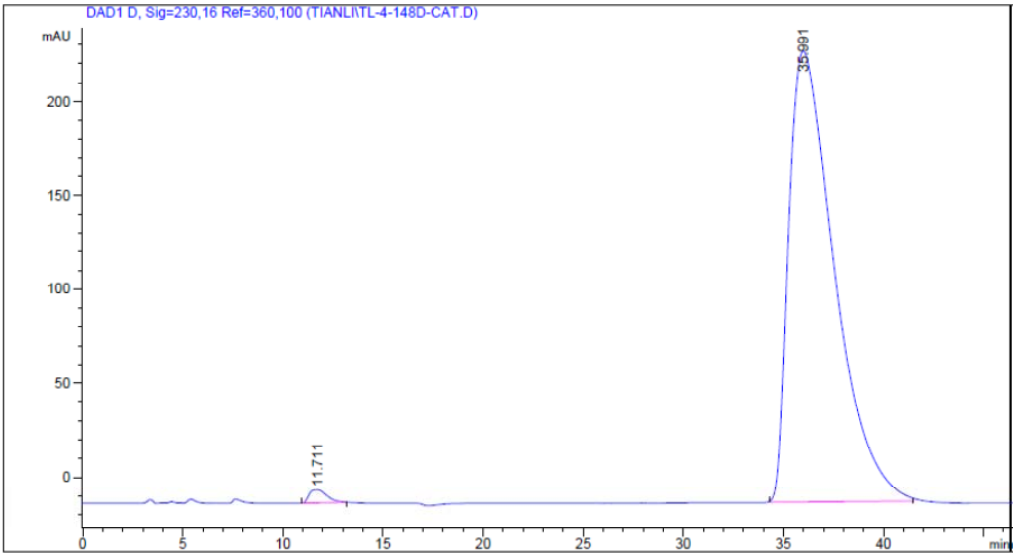


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	6.455	110.25813	4.12542	0.6595
2	DAD 230.16 nm	14.379	1.66078e4	329.38794	99.3405

3p:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

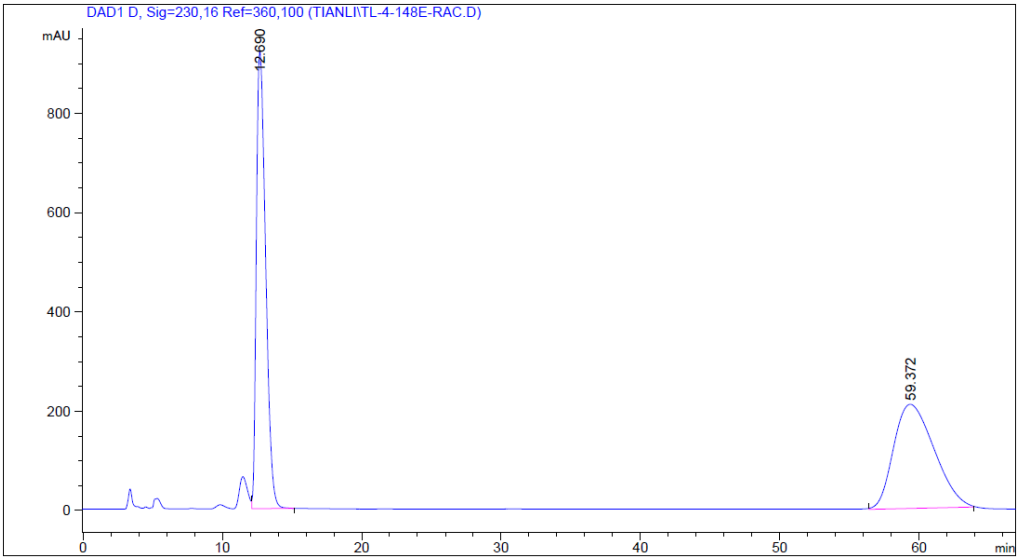


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	11.246	1.87441e4	389.62531	50.7824
2	DAD 230.16 nm	35.556	1.81665e4	124.27949	49.2176

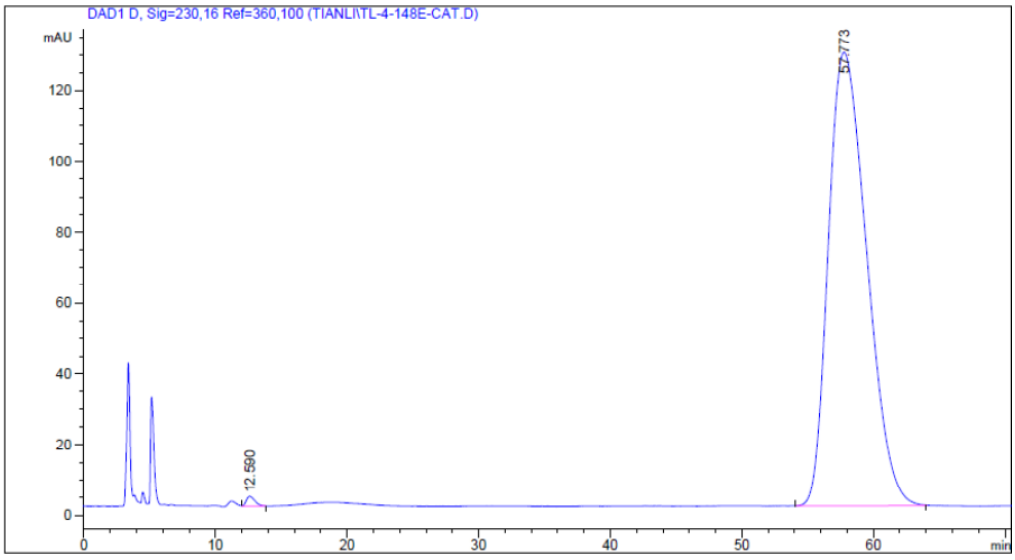


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	11.711	429.86615	6.96837	1.1178
2	DAD 230.16 nm	35.991	3.80263e4	239.78430	98.8822

3q:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

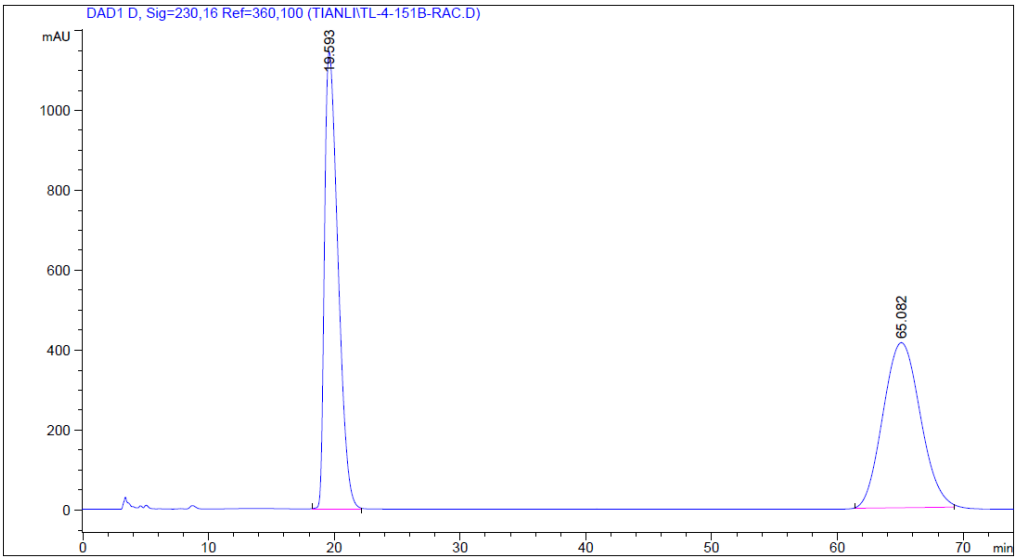


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	12.690	4.25759e4	922.08051	50.1293
2	DAD 230.16 nm	59.372	4.23563e4	209.81834	49.8707

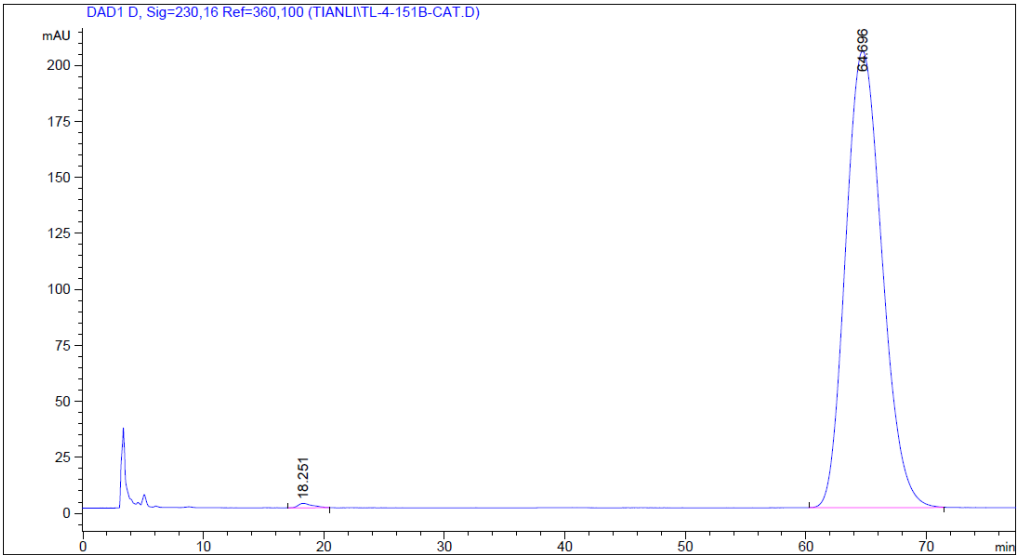


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	12.590	121.49043	2.71774	0.4664
2	DAD 230.16 nm	57.773	2.59255e4	128.00862	99.5336

3r:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

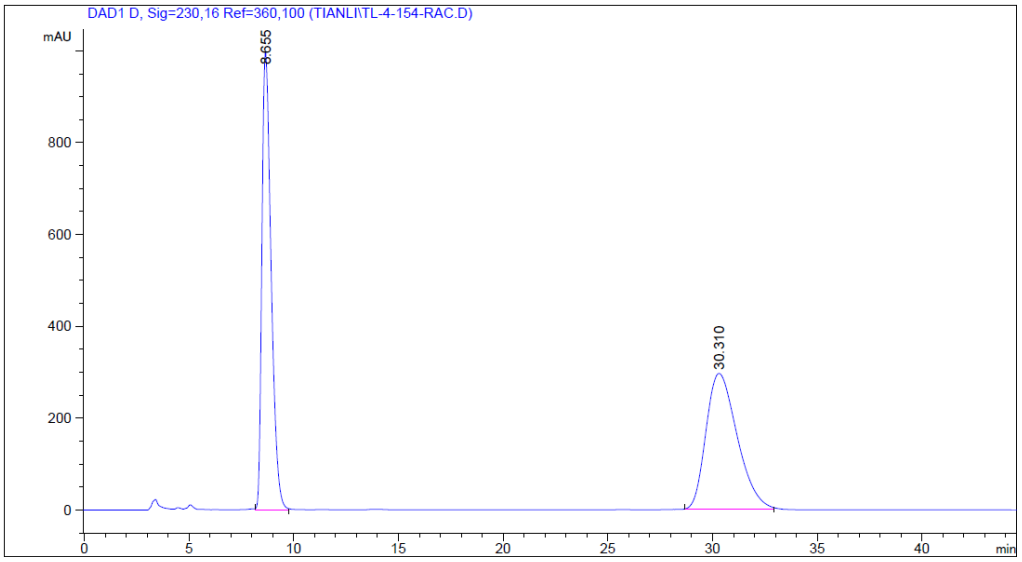


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	19.593	8.54262e4	1144.53760	50.1086
2	DAD 230.16 nm	65.082	8.50560e4	412.88434	49.8914

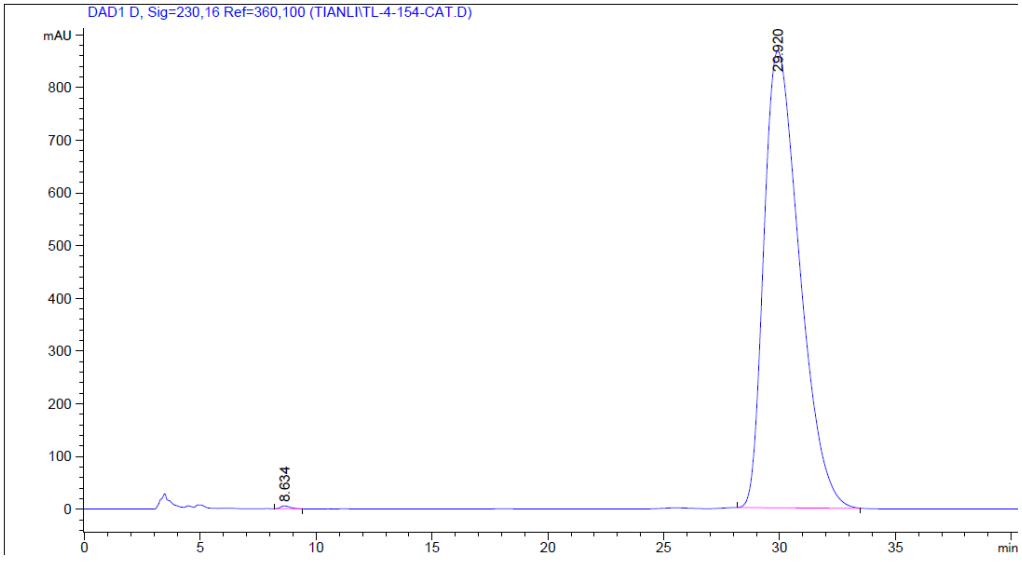


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	18.251	166.70596	2.00678	0.3872
2	DAD 230.16 nm	64.696	4.28897e4	203.96678	99.6128

3s:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

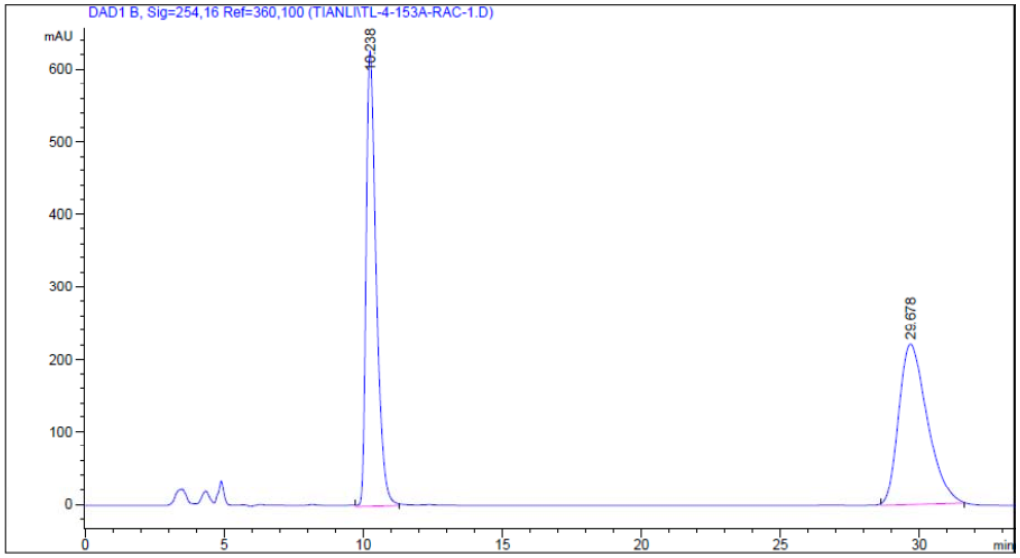


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	8.655	3.06431e4	998.09821	50.0975
2	DAD 230.16 nm	30.310	3.05239e4	295.44714	49.9025

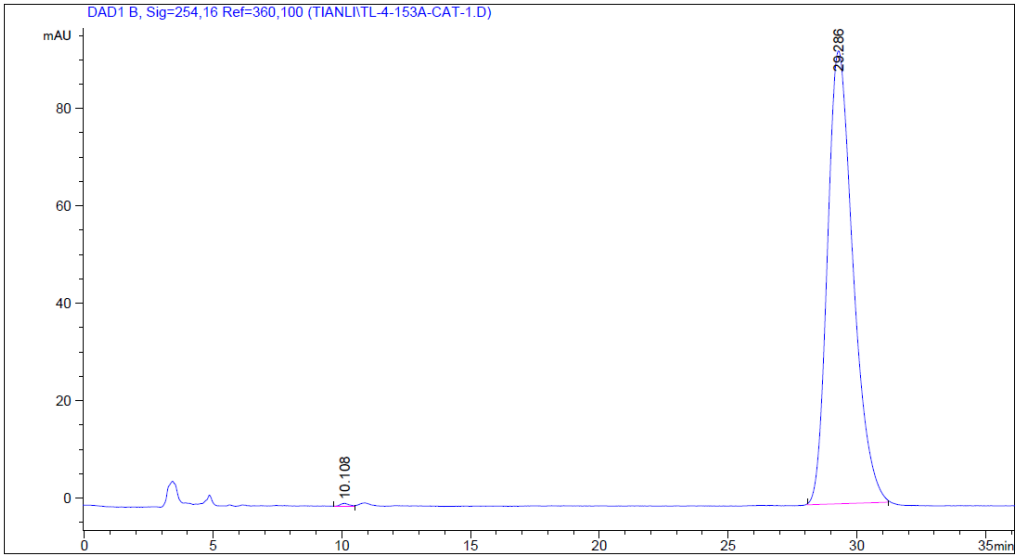


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	8.634	158.97664	5.39230	0.1715
2	DAD 230.16 nm	29.920	9.25320e4	866.61578	99.8285

3t:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

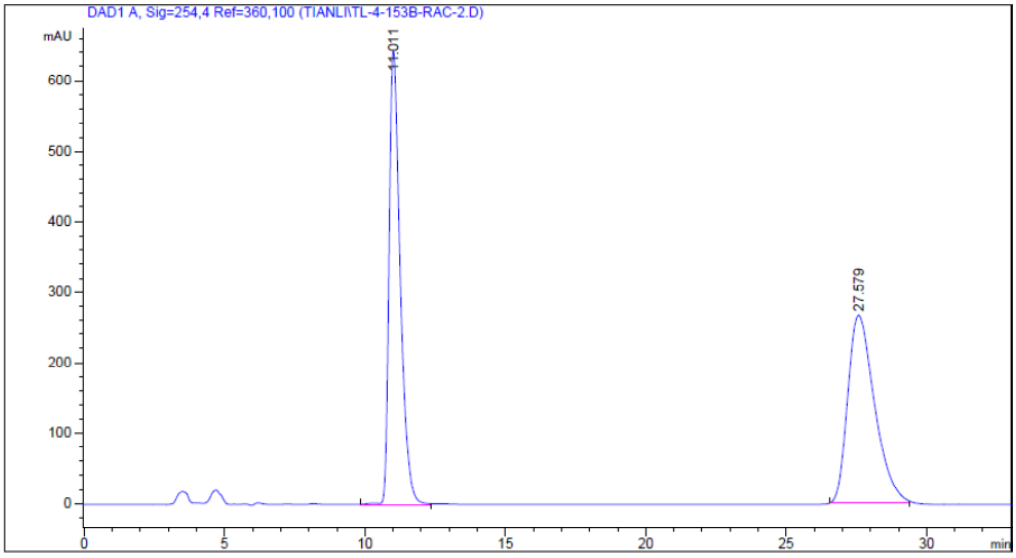


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.16 nm	10.238	1.58218e4	627.70129	50.0031
2	DAD 254.16 nm	29.678	1.58198e4	221.13376	49.9969

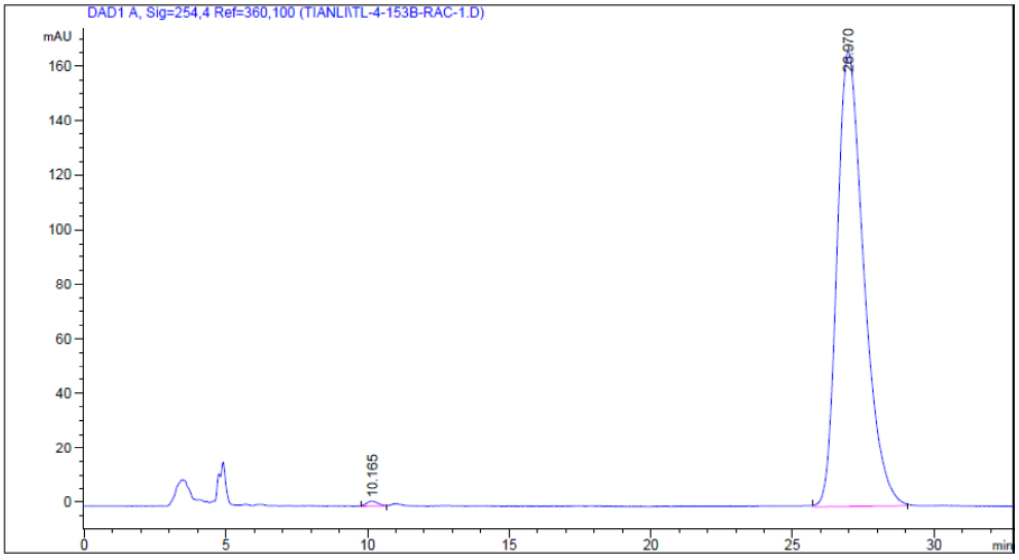


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.16 nm	10.108	15.22353	6.26461e-1	0.2360
2	DAD 254.16 nm	29.286	6435.04883	93.01656	99.7640

3u:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

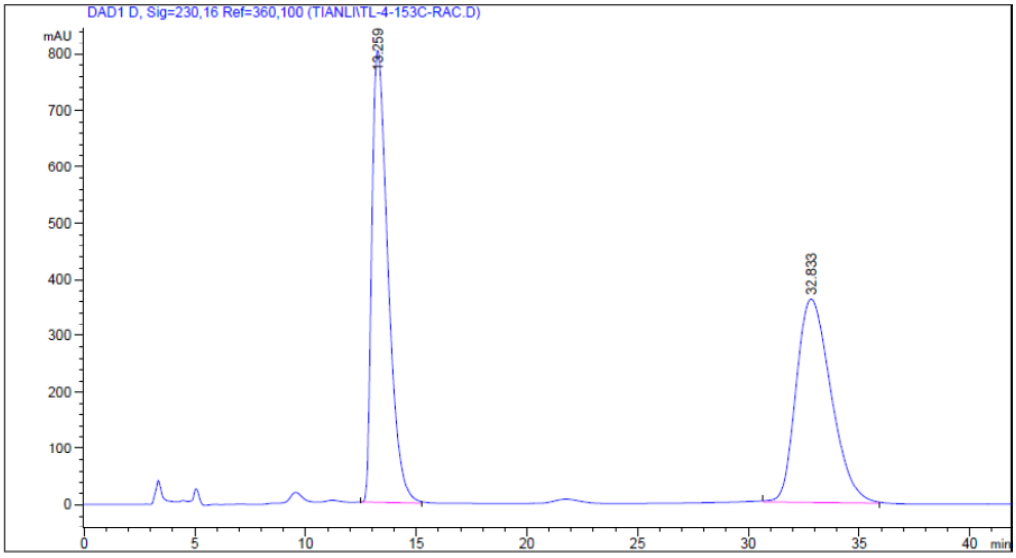


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	11.011	1.77310e4	643.92480	50.0365
2	DAD 254.4 nm	27.579	1.77051e4	266.57214	49.9635

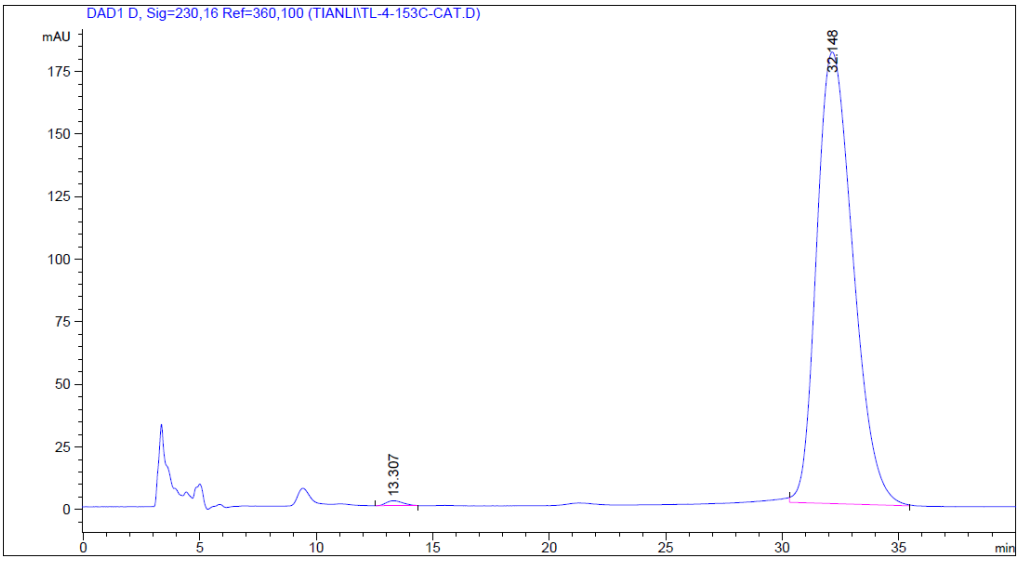


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 254.4 nm	10.165	48.94022	1.76480	0.4435
2	DAD 254.4 nm	26.970	1.09855e4	166.81984	99.5565

3v:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)

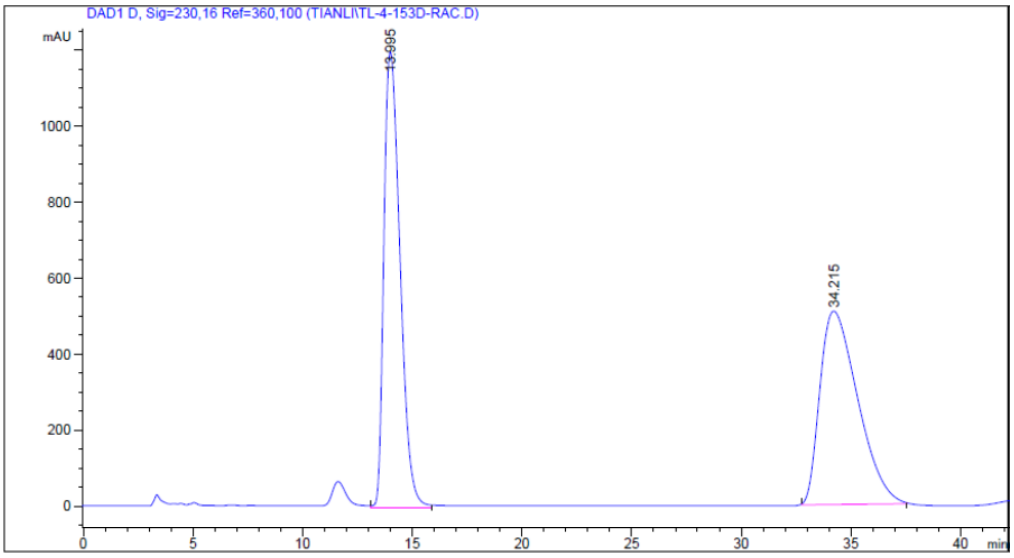


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	13.259	4.06633e4	801.24097	50.7586
2	DAD 230.16 nm	32.833	3.94478e4	360.46756	49.2414

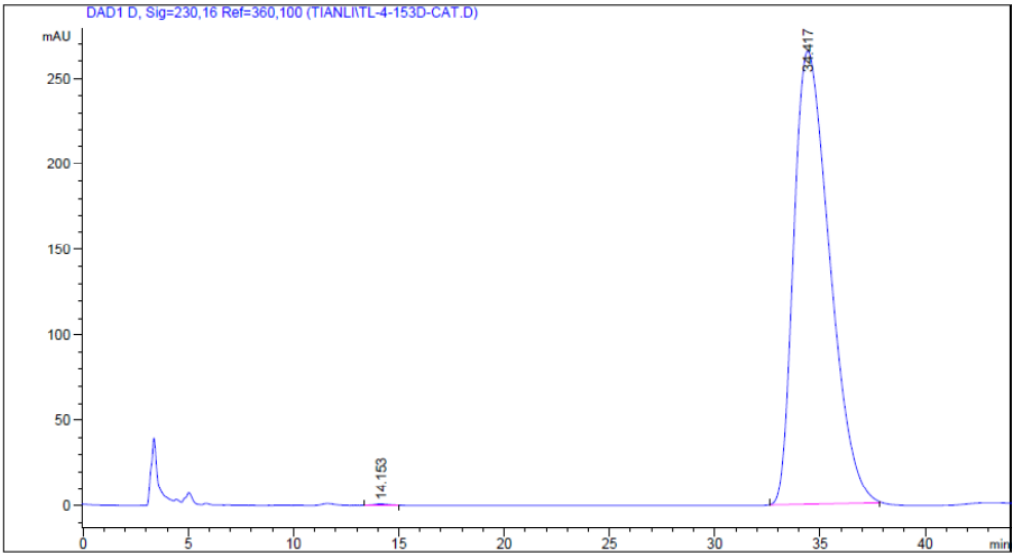


Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	13.307	94.95272	1.95824	0.4820
2	DAD 230.16 nm	32.148	1.96035e4	180.42715	99.5180

3w:HPLC analysis using chiral AD-H Column (*n*-hexane:*i*-PrOH =70:30, 1.0 mL/min)



Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	13.995	6.12049e4	1198.13342	50.0643
2	DAD 230.16 nm	34.215	6.10477e4	508.87573	49.9357



Peak	Processed Channel	Retention Time (min)	Peak Area (mAU*s)	Peak Height (mAU)	Peak Area (%)
1	DAD 230.16 nm	14.153	47.37370	8.79817e-1	0.1508
2	DAD 230.16 nm	34.417	3.13618e4	264.83795	99.8492