Chiral Crotyl Geminal Bis(silane): A Useful Reagent for Asymmetric Sakurai Allylation by Selective Desilylation-Enabled Chirality Transfer

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Supporting Information

Table of Contents

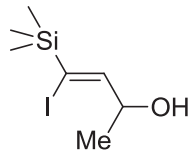
1. General Methods

Commercial reagents were used without any purification. All reactions were performed using common anhydrous, inert atmosphere techniques. Reactions were monitored by thi*n*-layer chromatography (TLC) using aluminium-backed silica gel plates (HSGF-254). TLC spots were viewed under ultraviolet light and by heating the plate after treatment with a staining solution of $KMnO_4$ stains, $H_3PO_4 \cdot 12MoO_3$/EtOH stains, H_2SO_4 (conc.)/anisaldehyde/EtOH stains. Product purifications were performing using Silica Gel (200-300 mesh) for column chromatography. ^1H NMR spectra were recorded at 400 MHz (Varian) and 600 MHz (Agilent), and ^{13}C NMR spectra were recorded at 100 MHz (Varian) and 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. In each case, enantiomeric ratio was determined by HPLC analysis on a chiral column in comparison with racemates, using a Daicel Chiralpak IA Column (250 × 4.6 mm) or Chiralpak IC Column (250 × 4.6 mm), Chiralpak OD-H Column (250 × 4.6 mm). UV detection was monitored at 220 nm or 254 nm. Optical rotation was examined in $CHCl_3$ solution at 20 °C. Pentane, Toluene, CH_2Cl_2, $CHCl_3$, and Et_3N were distilled from CaH_2. Et_2O and THF were distilled from sodium.

2. Experimental Procedures and Spectral Data of Products

2.1. Synthesis of (±)-1a to (±)1e

Preparation of (±)-S1

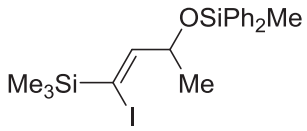


(±)-**S1**

To a solution of **4** (10.0 g, 64.1 mmol) in Et_2O (500 mL) was added Red-Al (19.0 mL, 96.2 mmol) dropwise at 0 ^oC. After stirring for 8 h, I_2 (24.4 g, 96.2 mmol) was added at –20 °C. The resultant mixture was stirred at room temperature overnight before quenching with sat aq NH_4Cl (200 mL)

and extracted with Et_2O (3 × 200 mL). The combined extracts were washed with sat aq $Na_2S_2O_3$ (20 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) afforded (±)-**S1**(15.7 g, 86%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (d, *J* =6.4 Hz, 1H), 4.56 (q, *J* =6.4 Hz, 1H), 2.40 (s, 1H), 1.26 (t, *J* =6.4 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.2, 111.9, 74.0, 21.4, 1.6; IR (liquid film) cm^{-1} 3326m, 2963m, 1249s, 1062m, 888s, 838s, 754m; HRMS (ESI-TOF, m/z) calcd for $C_7H_{15}IOSi$ $(M+Na)^+$: 292.9839, found 292.9838.

***Preparation of* 5**



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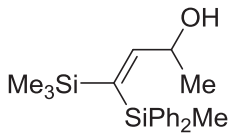
To a solution of (±)-**S1** (15.7 g, 55.1 mmol), Et_3N (23.0 mL, 165.3 mmol) and DMAP (673 mg, 5.5 mmol) in CH_2Cl_2 (200 mL) was added $Ph_2MeSiCl$ (10.3 mL, 60.6mmol) at 0°C. After stirring for 1 h at room temperature, the reaction was quenched with sat aq $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1.0% of EtOAc/petroleum ether) afforded **5** (26.4 g, 99%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* =7.2 Hz, 4H), 7.37-7.43 (m, 6H), 6.21 (d, *J* = 6.8 Hz, 1H), 4.71 (q, *J* = 6.4 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H), 0.69 (s, 3H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 136.3, 136.2, 134.4, 134.0, 129.8, 129.6, 127.8, 127.7, 109.6, 76.1, 22.3, -1.7, -2.4; IR (liquid film) cm^{-1} 2959w, 1428m, 1250m, 1119s, 1076s, 839m, 731s; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{27}IOSi_2$ $(M+Na)^+$:489.0537, found 489.0539.

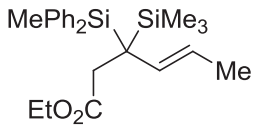
Preparation of 6



6

To a solution of **5** (2.0 g, 4.3 mmol) in dry THF (50 mL) was added *t*-BuLi (6.6 mL of 1.3 M solution in pentane, 8.6 mmol) at -78°C under argon atmosphere. The reaction was allowed to proceed for 30 min at -78°C. The the pale yellow solution was warmed to room temperature and stirred for another 30 min before quenching with sat aq NH_4Cl (60 mL) and extraction with ether (3 × 60 mL). The combined organic layers were dried over anhydrous $NaSO_4$, filtered and concentrated under vacuo. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) afforded **6** (1.38 g, 95%) as a colorless liquid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 4H), 7.39 (m, 6H), 6.72 (d, J = 8.8 Hz, 1H), 4.20 (dq, J_1 =8.8 Hz, J_2 =6.0 Hz, 1H), 1.28 (s, 1H), 0.94 (d, J = 6.0 Hz, 3H), 0.71 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.9, 138.3, 137.9, 137.7, 134.8, 134.7, 129.3, 129.2, 128.0, 127.9, 68.9, 21.5, 0.52, 0.15; IR (liquid film) cm^{-1} 2960m, 1569w, 1428s, 1248s, 1109s, 1052m, 940w, 909s, 858s, 792s; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{28}OSi_2$ $(M+Na)^+$: 363.1571, found 363.1570.

<u>Preparation of (±)-1a</u>

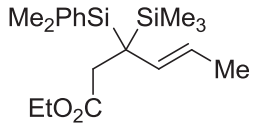


(±)-**1a**

A solution of **6** (2.0 g, 5.88 mmol), 1,1,1-triethoxyethane (4.31 mL, 23.5 mmol), propionic acid (4.8 μL, 0.0647 mmol) in dry toluene (30 mL) was refluxed at 140 °C for 15 h in seal tube. The mixture was concentrated in vacuo at 50 °C to remove toluene. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-0.5% of EtOAc/petroleumether) afforded pure (±)-**1a** (2.29 g, 95%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 6.8 Hz, 2H), 7.63 (d, J = 6.8 Hz, 2H), 7.36 (m, 1H), 7.33 (d, J =6.8 Hz, 4H), 5.8 (d, J = 15.6 Hz, 1H), 5.28 (dq, J_1 =6.4 Hz, J_2 =15.6 Hz, 2H), 3.86 (dq, J_1 =7.2 Hz, J_2 =3.6 Hz, 2H), 2.74 (d, J = 14.8Hz, 1H), 2.64 (d, J = 14.8 Hz, 1H), 1.83 (d, J = 6.4 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H), 0.81 (s, 3H), -0.08 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 137.2, 136.6, 135.6, 135.5, 135.4, 132.2, 128.9, 128.8, 127.4, 127.4, 127.3, 120.6, 60.0, 36.3, 24.7, 18.7, 13.9, -0.7, -2.8; IR (liquid film) cm^{-1} 2927m, 2955m,

1738s, 1428m, 1368w, 1251s, 1176s, 1105m, 840s; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{36}O_2Si_2$ $(M+Na)^+$:433.1990, found 433.1996.

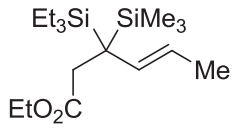
Preparation of (±)-1b



(±)-**1b**

(±)-**1b**: Using the same procedure as that used for (±)-**1a** afforded (±)-**1b** (120 mg, 96%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 6.0 Hz, 2H), 7.33 (m, 1H), 7.32 (d, J =6.0 Hz, 2H), 5.59 (d, J =15.6 Hz, 1H), 5.03 (dq, J_1 =6.0 Hz, J_2 =15.6 Hz, 1H), 4.04 (q, J = 7.2 Hz, 2H), 2.45 (s, 2H), 1.72 (d, J = 6.0 Hz, 3H), 1.22 (t, J = 7.2 Hz , 3H), 0.40 (s, 3H), 0.38 (s, 3H), 0.01 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3, 138.1, 135.0, 132.5, 128.8, 127.2, 119.8, 60.1, 36.3, 24.1, 18.7, 14.1, -0.7, -1.9, -2.6; IR (liquid film) cm^{-1} 2955w, 2917w, 1738m, 1428w, 1368w, 1249m, 1174m, 1109m, 1036m, 989m, 836s, 823s; HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{30}O_2Si_2(M+Na)^+$: 371.1833, found 371.1826.

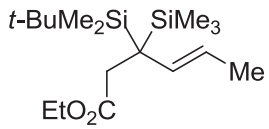
Preparation of (±)-1c



(±)-**1c**

(±)-**1c**: Using the same procedure as that used for (±)-**1a** afforded (±)-**1c** (150 mg, 95%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (d, J = 15.2 Hz, 1H), 5.06 (dq, J_1 =15.2 Hz, J_2 =6.0 Hz, 1H), 4.08 (q, J_1 =4.4 Hz, J_2 =7.2 Hz, 2H), 2.61 (d, J =16.0 Hz, 1H), 2.57, (d, J =16.0 Hz , 1H), 1.68 (d, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H), 0.97 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 8.0 Hz, 6H), 0.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 133.3, 118.5, 60.1, 36.2, 25.0, 18.6, 14.1, 8.5, 3.9, -0.4; IR (liquid film) cm^{-1} 2953m, 2878m, 1739s, 1368w, 1336w, 1247s, 1164s, 1037m, 1009m, 991m, 836s; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{36}O_2Si_2(M+Na)^+$:351.2146, found 351.2146.

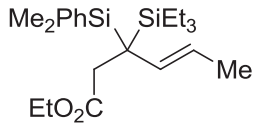
Preparation of (±)-1d



(±)-**1d**

(±)-**1d**:Using the same procedure as that used for (±)-**1a** afforded (±)-**1d** (250 mg, 95%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.68 (d, J = 15.2 Hz, 1H), 5.00 (dq, J_1 =6.4 Hz, J_2 =15.2 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.78 (d, J =15.2 Hz, 1H), 1.69 (d, J = 6.4 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 0.88 (s, 9H), 0.13 (s, 3H), 0.10 (s, 9H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 134.6, 117.2, 60.1, 36.9, 28.4, 25.9, 20.8, 18.6, 14.1, 0.04, -4.0, -4.3; IR (liquid film) cm^{-1} 2932m, 2856m, 1738s, 1474w, 1250s, 1161s, 1068m, 1038w, 986m, 819s, 798s; HRMS (ESI-TOF, m/z) calcd for $C_{13}H_{30}OSi_2$ $(M+Na)^+$:351.2146, found 351.2144.

<u>Preparation of (±)-1e</u>

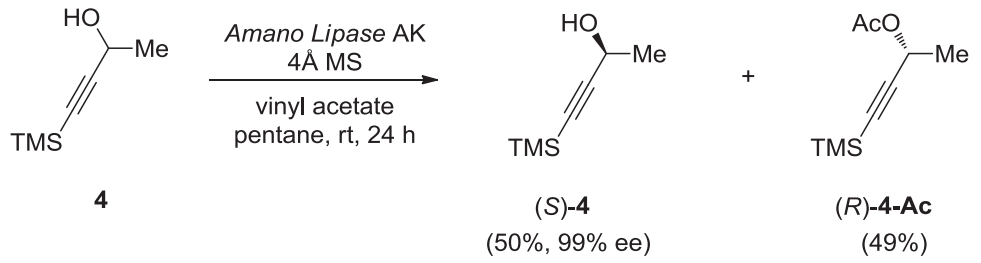


(±)-**1e**

(±)-**1e**:Using the same procedure as that used for (±)-**1a** afforded (±)-**1e** (50mg , 90%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J =6.8, 2H), 7.32 (m, 1H), 7.31 (d, J =6.8 Hz, 2H), 5.64 (d, J =15.6 Hz, 2H), 5.00 (dq, J_1 =6.4 Hz, J_2 =15.6 Hz, 1H), 4.04 (q, J = 7.2 Hz, 2H), 2.54 (d, J =15.6 Hz, 1H), 2.48 (d, J =15.6 Hz, 1H), 1.71 (d, J =6.4 Hz, 3H), 1.22 (d, J =7.2 Hz, 3H), 0.91 (t, J =8.0 Hz, 9H), 0.61 (q, J =8.0 Hz, 6H), 0.41 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.4, 138.5, 135.1, 133.1, 128.7,127.1, 119.0, 60.1, 36.4, 25.5, 18.6, 14.1, 8.5, 4.0, -1.3, -2.1; IR (liquid film) cm^{-1} 2954s, 2877s, 1740s, 1427w, 1248m, 1174s, 1109m, 1037m, 822s, 773m; HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{38}O_2Si_2$ $(M+Na)^+$:413.2303, found 413.2303.

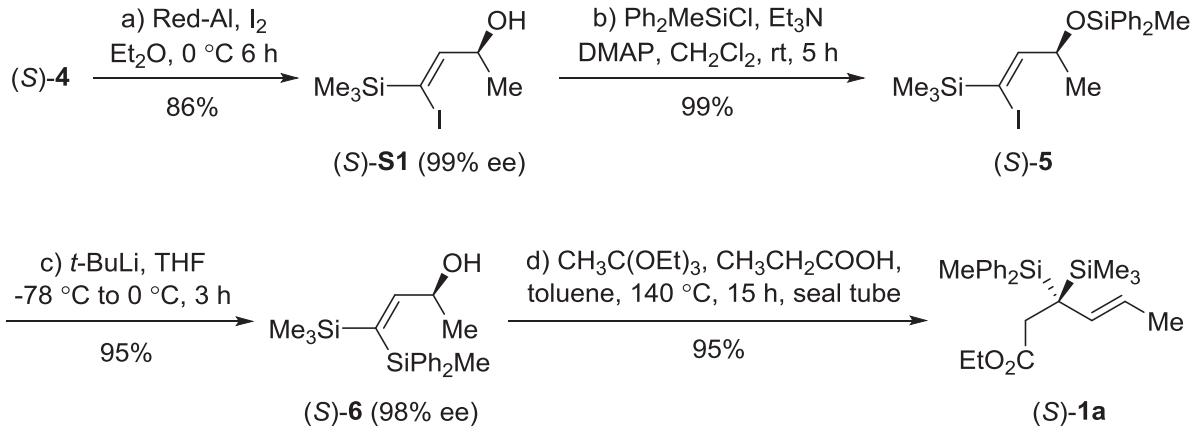
2.2. Synthesis of (S)-1a

<u>Preparation of (S)-4</u>



To a 0.5 M pentane solution of racemic **4**[1] (20.0 g, 140.8 mmol) was added molecular sieve (2.0 g), Amano lipase AK (4.0 g) and vinyl acetate (52 mL, 562.1 mmol). The resulting suspension was stirred at room tempreture for 24 h under argon atomosphere. The mixture was filtered via celite, and the resultant filtration was concentrated and purified by silica gel flash chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) to provide (*S*)-**4** (10.0 g, 50%) as a yellow liquid and (*R*)-**4-Ac** (12.9 g, 49%) as a yellow liquid. (*S*)-**4**: $[\alpha]_D^{20}$ = -17.5 (*c* = 1.0 in $CHCl_3$); {literature reported $[\alpha]_D^{20}$ = -22.3 (*c* = 1.0 in $CHCl_3$)[1]}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (dq, J_1 =5.2 Hz, J_2 =6.8 Hz, 1H), 2.05 (d, *J* =5.2 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H), 0.16 (s, 9H); IR (liquid film) cm^{-1} 3019w, 1372w, 1251w, 1214s, 1114w, 942w, 942w, 866m, 844m; (*R*)-**4**-**Ac**: $[\alpha]_D^{20}$ =+104.3 (*c* = 1.0 in $CHCl_3$). {literature reported $[\alpha]_D^{20}$ = +119 (*c* = 1.0 in $CHCl_3$)[1]}

Preparation of (S)-5, (S)-6, and (S)-1a



(*S*)-**S1**: Using the same procedure as that used for (±)-**S1** afforded (*S*)-**S1** (16.0 g, 86%) as a yellow liquid. The enantiomeric ratio was determined to be 99.5:0.5 by HPLC analysis on Chiralpak IC column (0.66% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 10.58 min, t_{major} = 11.99 min; $[\alpha]_D^{20}$ = -21.3 (*c* = 1.0 in $CHCl_3$).

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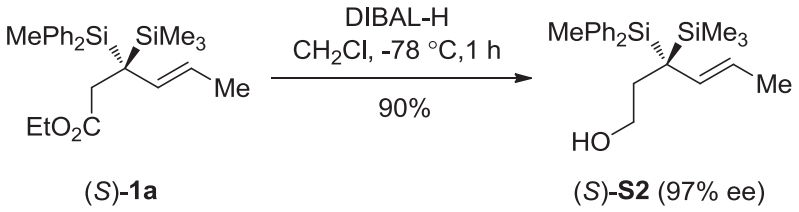
1. S. E. Denmark, N. S. Werner, *J. Am. Chem. Soc.*, **2010**, *132*, 3612.

(*S*)-**5:** Using the same procedure as that used for racemic **5** afforded (*S*)-**5** (28.3 g, 99%) as a colorless liquid. $[\alpha]_D^{20}$ = +6.4 (*c* = 1.0 in $CHCl_3$).

(*S*)-**6:** Using the same procedure as that used for racemic **6** afforded (*S*)-**S6** (19.6 g, 95%) as a colorless liquid. The enantiomeric ratio was determined to be 98.5:1.5 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 6.38 min, t_{major} = 5.84 min; $[\alpha]_D^{20}$ = -3.7 (*c* = 1.0 in $CHCl_3$).

(*S*)-**1a:** Using the same procedure as that used for **(±)-1a** afforded (*S*)-**1a** (22.4 g, 95%) as a colorless liquid. $[\alpha]_D^{20}$ = -13.7 (*c* = 1.0 in $CHCl_3$). The enantiomeric ratio was determined by (*S*)-**S2** as below.



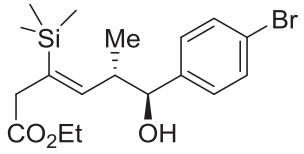
(*S*)-**1a** (*S*)-**S2** (97% ee)

To a solution of (*S*)-**1a** (100 mg, 0.243 mmol) in anhydrous CH_2Cl_2 (2 mL) was added DIBAL-H (0.486 mL of 1.0 M solution in *n*-hexane, 0.486 mmol) at -78 ^oC. After stirring for 1 h at -78 ^oC, the reaction was quenched with sat aq $NaHCO_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) afforded (*S*)-**S2** (80.5 mg, 90% yield) as a colorless oil. The enantiomeric ratio was determined to be 98.6:1.4 by HPLC analysis on Chiralpak OD column (1% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 20.48, t_{major} = 10.04min; $[\alpha]_D^{20}$ = -11.2 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* =7.2 Hz, 2H), 7.59 (d, *J* =7.2 Hz , 2H), 7.36 (s, 1H), 7.35 (d, *J* =7.2 Hz, 2H), 7.32 (s, 1H), 7.31 (d, *J* =7.2 Hz, 2H), 5.96 (d, *J* =15.6 Hz, 1H), 5.25 (dq, J_1 =15.6 Hz, J_2 =6.0 Hz, 1H), 3.62 (t, *J* = 8.0 Hz, 2H), 2.13 (dt, J_1 =16.0 Hz, J_2 =8.0 Hz,, 1H), 2.00 (dt, J_1 =16.0 Hz, J_2 =8.0 Hz, 1H), 1.85 (d, *J* =6.0 Hz, 3H), 0.72 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.4, 137.0, 135.4, 131.6, 129.1, 128.9, 127.6, 127.5, 120.6, 60.7, 34.1, 24.4, 18.7, -0.9, -3.1; IR (liquid film) cm^{-1} 2917m, 1428m, 1251m, 1103m,

1021m, 856s, 786s; HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{32}OSi_2$ $(M+Na)^+$:391.1884, found 391.1884.

2.3. Synthesize of 2a-2j

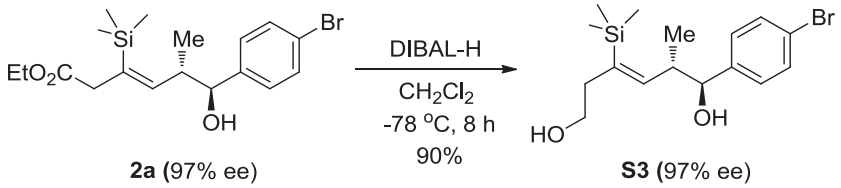
Preparation of 2a



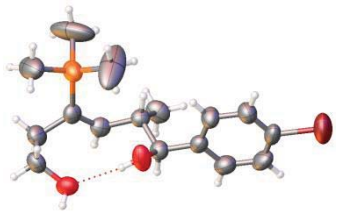
2a

2a: To a solution of (*S*)-**1a** (20.5 mg, 0.05 mmol) and *p*-Br-C_6H_4CHO (9.25 mg, 0.05mmol) in anhydrous $CHCl_3$ (0.5 mL) was added $Ph_3C^+B(C_6F_5)_4^-$ (0.9 mg, 0.001 mmol) at room temperature. After stirring for 2 h, the reaction was quenched with sat aq $NaHCO_3$ (2 mL) and extract with CH_2Cl_2 (3 × 2 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) afforded **2a** (14.9 mg, 75%) as a yellow oil. The enantiomeric ratio was determined to be 98.5:1.5 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 20.69 min, t_{major} = 40.87 min; $[\alpha]_D^{20}$ = +47.8 (*c* = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.90 (d, *J* = 10.8 Hz, 1H), 4.23 (d, *J* = 8.4 Hz, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.19 (d, *J* = 16.0 Hz, 1H), 3.09 (d, *J* = 16.0 Hz, 1H), 2.72 (s, 1H), 2.61 (ddd, J_1 = 6.8 Hz, J_2 = 8.4 Hz, J_3 = 10.8 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 148.7, 141.0, 136.4, 131.1, 128.8, 121.3, 77.7, 60.7, 44.9, 43.5, 16.6, 14.1, 0.16; IR (liquid film) cm^{-1} 3468w, 2962m, 1730s, 1486w, 1249m, 1178w, 1097w, 1011m, 838s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{27}F_3O_3Si$ $(M+Na)^+$: 421.0805, found 421.0805.

Preparation of S3

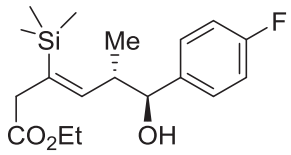


2a (97% ee) **S3** (97% ee)



To a solution of **2a** (100 mg, 0.251 mmol) in anhydrous CH_2Cl_2 (2 mL) was added DIBAL-H (0.502 mL of 1.0 M solution in *n*-hexane, 0.502 mmol) at -78 ^oC. After stirring for 8 h at -78 ^oC, the reaction was quenched with sat aq $NaHCO_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) afforded **S3** (80.5 mg, 90% yield) as a white solid. The enantiomeric ratio was determined to be 97.8:2.1 by HPLC analysis on Chiralpak OD column (5% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 12.54, t_{major} = 10.02 min; m.p.: 94-97 ^oC; $[\alpha]_D^{20}$ = -113.0 (*c* = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* =8.0 Hz, 2H), 7.16 (d, *J* =8.0 Hz , 2H), 5.84 (d, *J* = 10.8 Hz, 1H), 4.14 (d, *J* = 8.8 Hz, 1H), 3.43 (dt, J_1 =4.0 Hz, J_2 = 5.2 Hz, 1H), 3.41 (dt, J_1 = 4.0 Hz, J_2 = 5.2 Hz, 1H), 3.23 (s, 1H), 2.71 (s, 1H), 2.51-2.61 (m, 1H), 2.45 (dt, J_1 =12.8 Hz, J_2 = 4.0 Hz, 1H), 2.25 (dt, J_1 = 12.8 Hz, J_2 = 4.0 Hz, 1H), 0.76 (d, *J* = 6.8 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 141.8, 137.9, 131.3, 128.6, 121.4, 77.8, 60.9, 44.8, 41.2, 16.8, 0.58; IR (liquid film) cm^{-1} 3054w, 2924w, 2370w, 1419w, 1265s, 1010w, 895w; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{25}BrO_2Si$ $(M+Na)^+$:379.0699, found 379.0698. Crystals suitable for *X*-ray diffraction studies (CCDC1528458) were obtained by slow solvents evaporation of a solution of **S3** (25 mg) in a mixture of CH_2Cl_2 (0.2 mL) and *n*-hexane (1.0 mL) at 4°C overnight.

Preparation of 2b

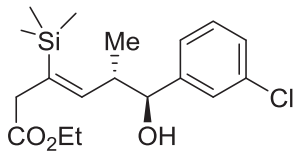


2b

2b: Using the same procedure as that used for **2a** afforded **2b** (10.0 mg, 59%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak IC column (0.67% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 38.16 min, t_{major} = 42.89 min; $[\alpha]_D^{20}$ = -53.6 (*c* = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 6.8 Hz, 1H), 7.30 (d, *J* = 6.8 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.92 (d, *J* = 10.8 Hz, 1H), 4.26 (d, *J* = 8.8 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.20 (d, *J* = 16.0 Hz, 1H), 2.66 (s, 1H), 2.61 (m, 1H), 1.26 (t,

J = 7.2 Hz, 3H), 0.79 (q, J = 6.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 162.3 (CH, d, $J_{C\text{-}F}$ = 244.1 Hz), 149.0, 137.7, 136.8, 128.7 (CH, d, $J_{C\text{-}F}$ = 6.5 Hz), 135.1 (CH, d, $J_{C\text{-}F}$ = 6.5 Hz), 77.9, 60.8, 45.3, 43.6, 16.7, 14.2, 0.28; IR (liquid film) cm^{-1} 2918m, 1731m, 1510m, 1220s, 1029m, 837s, 774s; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{27}FO_3Si$ $(M+Na)^+$: 361.1606, found 361.1609.

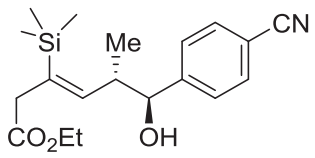
Preparation of 2c



2c

2c: Using the same procedure as that used for **2a** afforded **2c** (12.4 mg, 70%) as a colorless liquid. The enantiomeric ratio was determined to be 98.4:1.6 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 4.12 min, t_{major} = 3.57 min; $[\alpha]_D^{20}$ = -44.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.23-7.26 (m, 3H), 5.90 (d, J = 10.4 Hz, 1H), 4.24 (d, J = 8.4 Hz, 1H), 4.14 (q, J = 6.8 Hz, 2H), 3.19 (d, J = 16.0 Hz, 1H), 3.10 (d, J = 16.0 Hz, 1H), 2.69 (s, 1H), 2.63 (ddd, J_1 = 10.4 Hz, J_2 = 8.4 Hz, J_3 = 6.8 Hz, 1H), 1.26 (t, J = 6.8 Hz, 3H), 0.81 (d, J = 6.4 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9, 148.7, 144.1, 144.0, 137.0, 134.1, 129.5, 127.8, 127.3, 125.4, 77.9, 60.8, 45.1, 43.6, 16.7, 14.2, 0.27, 0.25; IR (liquid film) cm^{-1} 2917w, 1728m, 1249s, 1178m, 1078m, 1028s, 879m, 836s, 786m; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{27}ClO_3Si$ $(M+Na)^+$: 411.1574, found 411.1575.

Preparation of 2d

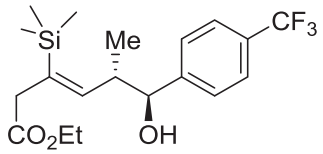


2d

2d: Using the same procedure as that used for **2a** afforded **2d** (15.5 mg, 90%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak OD-H column (5.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 20.64 min, t_{major} = 11.22 min; $[\alpha]_D^{20}$ = -87.2 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0

Hz, 2H), 5.89 (d, J = 10.4 Hz, 1H), 4.32 (d, J = 8.4 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.20 (d, J = 16.0 Hz, 1H), 3.08 (d, J = 16.0 Hz, 1H), 2.88 (s, 1H), 2.60 (ddd, J_1 = 7.2 Hz, J_2 = 8.4 Hz, J_3 = 10.4 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 148.1, 147.4, 137.5, 132.0, 127.9, 118.8, 111.4, 77.8, 60.9, 45.1, 43.5, 16.5, 14.2, 0.2; IR (liquid film) cm^{-1} 2918m, 2228w, 1320w, 1249s, 1176m, 1028m, 836s, 760m; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{27}NO_3Si$ $(M+Na)^+$: 368.1652, found 368.1651.

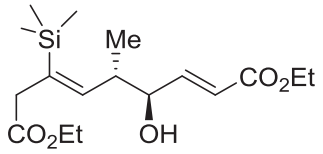
Preparation of 2e



2e

2e: Using the same procedure as that used for **2a** afforded **2e** (13.6 mg, 70%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} =16.02 min, t_{major} = 18.07 min; $[\alpha]_D^{20}$ = -48.4 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 5.92 (d, J = 10.8 Hz, 1H), 4.33 (d, J = 8.4 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.20 (d, J = 16.0 Hz, 1H), 3.10 (d, J = 16.0 Hz, 1H), 2.81 (s, 1H), 2.65 (ddd, J_1 = 6.8 Hz, J_2 = 8.4 Hz, J_3 = 10.8 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 6.8 Hz, 3H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 148.5, 146.0, 137.2, 127.5, 125.1 (CF, d, $J_{C\text{-}F}$ = 3.7 Hz), 125.0, 77.9, 60.8, 45.2, 43.6, 16.6, 14.2, 0.21; IR (liquid film) cm^{-1} 2963w, 1724s, 1325s, 1265m, 1160m, 1125m, 1103m, 840s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{27}F_3O_3Si$ $(M+Na)^+$: 377.1310, found 377.1306.

Preparation of 2g

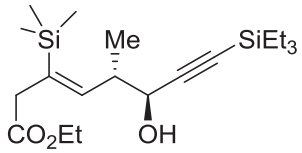


2g

2g: Using the same procedure as that used for **2a** afforded **2g** (12.3 mg, 72%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak IC column (5.0%

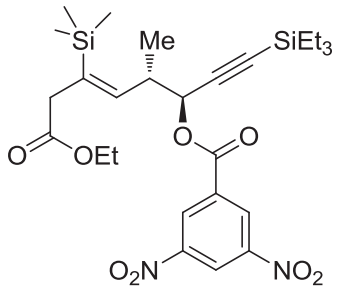
2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 19.43 min, t_{major} = 22.39 min; $[\alpha]_D^{20}$ = -3.2 (*c* = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (dd, J_1 = 15.6 Hz, J_2 = 5.6, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 5.83 (d, *J* = 10.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.95 (dd, J_1 = 6.4 Hz, J_2 = 6.8 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H),1.25 (t, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 166.4, 147.9, 147.2, 137.2, 122.0, 74.5, 60.8, 60.4, 43.5, 43.2, 16.4, 14.2, 14.1, 0.19; IR (liquid film) cm^{-1} 1717w, 1264s, 1177w, 841w; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{30}O_5Si$ $(M+Na)^+$: 365.1755, found 365.1755.

Preparation of 2h



2h

2h: Using the same procedure as that used for **2a** afforded **2h** (13.6 mg, 71%) as a colorless liquid. $[\alpha]_D^{20}$ = +1.2 (*c* = 1.0 in $CHCl_3$); The enantiomeric ratio was determined using **2h-NO_2** (see below) ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (d, *J* = 10.8, 1H), 4.16 (d, *J* = 7.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.11 (d, *J* = 16.4 Hz, 1H), 3.06 (d, *J* = 16.4 Hz, 1H), 2.67-2.72 (m, 1H), 2.17 (s, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.99 (d, *J* = 8.0 Hz, 9H), 0.61 (q, *J* = 8.0 Hz, 6H), 0.18 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 147.7, 135.8, 105.9, 87.9, 66.7, 60.6, 43.7, 43.2, 29.7, 15.8, 14.2, 7.4, 4.3, 0.18; IR (liquid film) cm^{-1} 2916m, 1264m, 1250m, 1178m, 1019m, 839s; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{38}O_3Si_2$ $(M+Na)^+$: 405.2252, found 405.2252.

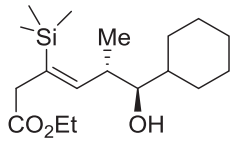


2h-NO_2

To a solution of **2h** (50 mg, 0.131 mmol), Et_3N (55 μL, 0.39 mmol) and DMAP (1.60 mg, 0.013 mmol) in CH_2Cl_2 (1.5 mL) was added 3, 5-dinitrobenzoyl chloride (36.2 mg, 0.157 mmol) at 0°C.

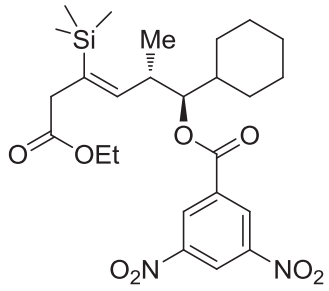
After stirring for 2h at room temperature, the reaction was quenched with sat aq $NaHCO_3$ (2 mL) and extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1.0% of EtOAc/petroleum ether) afforded **2h-NO$_2$** (69.1 mg, 90%) as a colorless liquid. The enantiomeric ratio was determined to be 94:6 by HPLC analysis on ChiralpakODcolumn (0.67% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 18.02 min, t_{major} = 19.71 min; $[\alpha]_D^{20}$ = -23.7 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (m, 1H), 9.15 (d, *J* = 1.2 Hz, 2H), 5.83 (d, *J* = 10.8 Hz, 1H), 5.55 (d, *J* = 8.0 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.05 (d, *J* = 16.0 Hz, 1H), 2.98-3.07 (m, 1H), 2.99 (d, *J* = 16.0 Hz, 1H), 1.23 (d, *J* = 6.8 Hz, 3H), 1.17 (t, *J* = 6.8 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 9H), 0.63 (q, *J* = 7.6 Hz, 6H), 0.19 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 161.4, 148.5, 146.0, 135.8, 133.7, 129.8, 122.3, 100.9, 90.9, 70.1, 60.3, 43.5, 41.5, 16.6, 14.1, 7.4, 4.1, 0.07; IR (liquid film) cm^{-1} 2957m, 1733s, 1548s, 1344s, 1270m, 1164m, 840m; HRMS (ESI-TOF, m/z) calcd for $C_{27}H_{40}N_2O_8Si_2$ $(M+Na)^+$: 599.2215, found 599.2214.

Preparation of 2i



2i

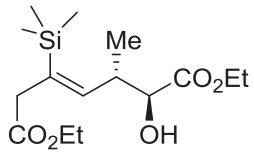
2i: Using the same procedure as that used for **2a** afforded **2i** (9.8 mg, 60%) as a colorless liquid. $[\alpha]_D^{20}$ =-12.4 (*c* = 1.0 in $CHCl_3$); The enantiomeric ratio was determined using **2i-NO$_2$**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (d, *J* = 10.4, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.14 (d, *J* = 16.0 Hz, 1H), 3.11 (m, 1H), 3.04 (d, *J* = 16.0 Hz, 1H), 2.59 (ddd, J_1 = 6.8 Hz, J_2 = 10.4 Hz, J_3 = 6.4 Hz, 1H), 1.41-1.66 (m, 11H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 150.4, 135.3, 78.6, 60.7, 43.6, 39.8, 39.0, 30.9, 26.9, 26.5, 26.4, 24.5, 16.6, 14.2,0.24; IR (liquid film) cm^{-1} 2924s, 2851m, 1731s, 1450m, 1319m, 1249s, 1166m, 1098m, 838s, 760m; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{34}O_3Si$ $(M+Na)^+$: 349.2169, found 349.2168.



2i-NO_2

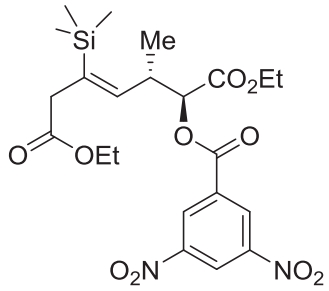
2i-NO_2: Using the same procedure as that used for **2h-NO_2** afforded **2i-NO_2** (58.8 mg, 90%) as a colorless liquid.The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (5.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 11.68 min, t_{major} = 9.94 min; $[\alpha]_D^{20}$ = -15.5 (*c* = 1.0 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (dd, J_1 = 2.0 Hz, J_2 = 2.0 Hz, 1H), 9.09 (d, *J* = 2.0 Hz, 2H), 5.86 (d, *J* = 10.4 Hz, 1H), 5.05 (dd, J_1 = 2.8 Hz, J_2 = 9.2 Hz, 1H), 3.84 (q, *J* = 7.2 Hz, 2H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.92-2.98 (m, 1H), 2.86 (d, *J* = 16.0 Hz, 1H), 1.59-2.01 (m, 10H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 6.8 Hz, 3H), 0.12 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 162.4, 148.4, 148.1, 134.4, 133.7, 129.7, 122.0, 83.2, 60.1, 43.2, 38.7, 38.1, 30.7, 26.2, 26.1, 26.0, 17.3, 14.1, 0.14; IR (liquid film) cm^{-1} 2919s, 1731s, 1547s, 1344s, 1171m, 839m; HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{36}N_2O_8Si$ $(M+Na)^+$:543.2133, found 543.2128.

Preparation of 2j



2j

2j: Using the same procedure as that used for **2a** afforded **2j** (9.5 mg, 60%) as a colorless liquid. $[\alpha]_D^{20}$ = +1.4 (*c* = 1.0 in $CHCl_3$). The enantiomeric ratio was determined using **2j-NO_2**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (d, *J* = 10.8 Hz, 1H), 4.26-4.32 (m, 1H), 4.05-4.19 (m, 4H), 3.07 (d, *J* = 16.0 Hz, 1H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.86 (s, 1H), 2.79-2.85 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz , 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 172.7, 145.6, 134.6, 61.7, 60.4, 43.7, 40.1, 17.2, 14.2, 14.1, 0.11; IR (liquid film) cm^{-1} 2918w, 1728m, 1265m, 1249m, 1177m, 1026m, 839s; HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{28}O_5Si$ $(M+Na)^+$: 339.1598, found 339.1597.

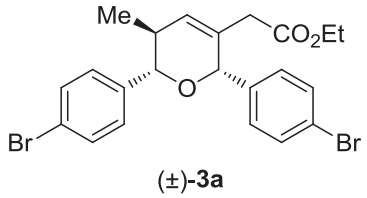


2j-NO_2

2j-NO_2: Using the same procedure as that used for **2i-NO_2** afforded **2j-NO_2** (58.9 mg, 92%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak IC column (0.67% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 46.75 min, t_{major} = 40.73 min; $[\alpha]_D^{20}$ = -4.0 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 2.0, 1H), 9.17 (d, *J* = 2.0 Hz, 1H), 5.98 (d, *J* = 10.8 Hz, 1H), 5.08 (d, *J* = 7.2 Hz, 1H), 4.26 (dq, J_1 = 7.2 Hz, J_2 = 3.2 Hz, 2H), 4.03 (q, *J* = 6.8 Hz, 2H), 3.16-3.24 (m, 1H), 3.12 (d, *J* = 16.0 Hz, 1H), 3.07 (d, *J* = 16.0 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 10.8 Hz, 3H), 1.20 (t, *J* = 6.8 Hz, 3H), 0.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 172.4, 168.3, 162.1, 148.6, 144.9, 135.8, 133.1, 129.8, 122.6, 77.9, 61.9, 60.4, 43.5, 38.2, 17.2, 14.1, 0.1; IR (liquid film) cm^{-1} 2917m, 2849w, 1737w, 1549w, 1215m, 754s; HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{30}N_2O_{10}Si$ $(M+Na)^+$:549.1301, found 549.1300.

2.4. Synthesis of 3a-3j

<u>Preparation of (±)-3a</u>

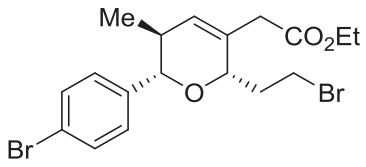


(±)-**3a**

(±)-**3a** was obtained in 36% yield as the by-product in the reaction to form racemic **2a** (Table 1, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 6.0 Hz, 2H), 7.25 (d, *J* = 6.0 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 5.72 (s, 1H), 5.35 (s, 1H), 4.19 (d, *J* = 9.6 Hz, 1H), 4.07 (dq, J_1 = 2.4 Hz, J_2 = 6.8 Hz, 2H), 2.81 (d, *J* = 16.0 Hz, 1H), 2.63 (d, *J* = 16.0 Hz, 3H), 2.57 (s, 1H), 1.23 (t, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 139.5, 138.8, 132.0, 131.6, 131.4, 130.0, 129.0, 122.2, 121.8, 82.6, 79.9, 60.7, 38.9, 36.7, 16.8, 14.1; IR

(liquid film) cm^{-1} 2917m, 2849, 1731, 1487, 1369m, 1260m, 1175m, 1103m, 1070s, 1010s, 850m, 809s; HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{22}Br_2O_3$ $(M+Na)^+$: 514.9828, found 514.9822.

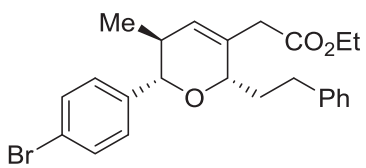
***Preparation of* 3b**



3b

3b: To a solution of **2a** (19.9 mg, 0.05 mmol) in CH_2Cl_2 (1mL) was added $Ph_3C^+B(C_6F_5)_4^-$ (0.922 mg, 0.001 mmol). The mixture was stirred at room temperature for 20 h before quenching with sat aq $NaHCO_3$ (1 mL) and extraction with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-10% of EtOAc/petroleum ether) afforded **3b** (20.4 mg, 92%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak OD column (0.67% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 16.27 min, t_{major} = 11.69 min; $[\alpha]_D^{20}$ = -3.2 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 5.26 (s, 1H), 4.44 (s, 1H), 4.17 (q, *J* = 6.8 Hz, 2H), 3.96 (d, *J* = 9.2 Hz, 3H); 3.46 (t, *J* = 6.8 Hz, 2H), 3.08 (d, *J* = 15.6 Hz, 1H), 3.00 (d, *J* = 15.6 Hz, 1H), 3.32 (m, 1H), 2.02 (m, 2H), 1.91 (d, *J* = 8.8 Hz, 2H), 1.29 (t, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 140.1, 131.9, 131.8, 131.3, 128.9, 121.6, 82.0, 75.6, 60.9, 38.7, 36.8, 34.3, 31.0, 27.7, 16.7, 14.2; IR (liquid film) cm^{-1} 2960w, 2918m, 2850w, 1733m, 1260m, 1175w, 1094m, 1011s, 754s; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{24}Br_2O_3$ $(M+Na)^+$: 480.9984, found 480.9983.

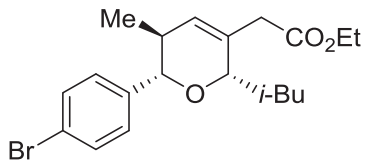
Preparation of 3c



3c

3c: Using the same procedure as that used for **3b** afforded **3c** (15.5 mg, 70%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (0.25% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 30.17 min, t_{major} = 35.48 min; $[\alpha]_D^{20}$ = -8.0 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.19-7.29 (m, 2H), 5.64 (s, 1H), 4.42 (s, 1H), 4.15 (q, *J* = 6.8 Hz, 2H), 3.99 (d, *J* = 9.6 Hz, 1H), 3.09 (d, *J* = 15.6 Hz, 1H), 3.02 (d, *J* = 15.6 Hz, 1H), 2.69-2.82 (m, 2H), 2.36 (m, 1H), 2.10-2.12 (m, 1H), 1.87-1.92 (m, 1H), 1.25 (t, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 142.4, 140.4, 132.1, 131.7, 128.9, 128.5, 128.3, 125.7, 121.5, 82.0, 75.7, 60.8, 38.8, 36.9, 34.3, 16.7, 14.2; IR (liquid film) cm^{-1} 2959m, 2927m, 1732s, 1490m, 1454m, 1369m, 1264m, 1172m, 1098m, 1030s, 1011s, 812m; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{27}BrO_3$ $(M+Na)^+$: 465.1036, found 465.1039.

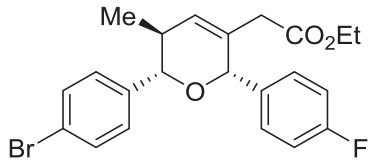
***Preparation of* 3d**



3d

3d: Using the same procedure as that used for **3b** afforded **3d** (19.4 mg, 98%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak IC column (0.25% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 8.79 min, t_{major} = 9.41 min; $[\alpha]_D^{20}$ = -18.5 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 1H), 4.37 (t, *J* = 4.0 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.95 (d, *J* = 9.2 Hz, 1H); 3.09 (d, *J* = 16.0 Hz, 1H), 2.99 (d, *J* = 16.0 Hz, 1H), 2.31 (m, 1H), 1.85-1.95 (dt, J_1 = 6.8 Hz, d, J_2 = 6.8 Hz, 1H), 1.42-1.54 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 6.8 Hz, 6H), 0.80 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 140.5, 133.2, 131.1, 130.8, 128.9, 121.3, 82.0, 60.7, 41.8, 38.9, 36.9, 24.1, 24.0, 21.7, 16.8, 14.2; IR (liquid film) cm^{-1} 2956m, 2927m, 1735s, 1156m, 1094s, 1009s, 912w, 810s; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{27}BrO_3$ $(M+Na)^+$: 417.1036, found 417.1038.

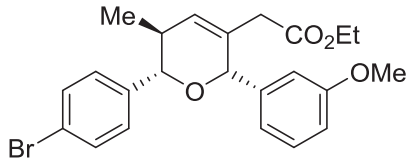
Preparation of 3e



3e

3e: Using the same procedure as that used for **3b** afforded **3e** (19.5 mg, 90%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak OD column (0.67% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 15.81 min, t_{major} =10.32 min; $[\alpha]_D^{20}$ = +21.6 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 5.6 Hz,1H), 7.26-7.30 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.72 (s, 1H), 5.36 (s, 1H), 4.07 (dq, J_1 = 4.8 Hz, J_2 = 7.2 Hz, 2H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.64 (d, *J* =16.0 Hz, 1H), 2.57 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.87 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 163.7 (CH, d, $J_{C\text{-}F}$ = 245.5 Hz), 139.6, 135.6, 132.3, 131.4, 131.2, 130.0 (CH, d, $J_{C\text{-}F}$ = 8.1 Hz), 129.0, 127.9, 127.2, 121.7, 115.4 (CH, d, $J_{C\text{-}F}$ = 21.6 Hz), 82.7, 79.9, 60.7, 38.9, 36.7, 16.8, 14.1; IR (liquid film) cm^{-1} 2926w, 1729w, 1510w, 1261w, 1215m, 1012w, 746s; HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{22}BrFO_3$ $(M+Na)^+$:455.0629, found 455.0636.

Preparation of 3f

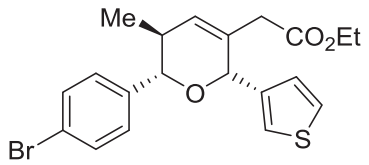


3f

3f: Using the same procedure as that used for **3b** afforded **3f** (21.6 mg, 95%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak OD column (0.25% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 72.38 min, t_{major} = 78.18 min; $[\alpha]_D^{20}$ = +57.6 (c = 1.0 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0, 2H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 5.35 (s, 1H), 4.20 (d, *J* = 9.2 Hz, 1H), 4.09 (dq, J_1 = 4.8 Hz, J_2 = 6.8 Hz, 2H), 3.81 (s, 3H), 2.82 (d, *J* = 16.0 Hz, 1H), 2.68 (d, *J* = 16.0 Hz, 1H), 2.58 (m, 1H), 1.24 (t, *J* = 6.8 Hz,

3H), 0.87 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 159.7, 141.3, 139.7, 132.4, 131.3, 130.8, 129.5, 129.0, 121.6, 120.7, 113.9, 113.6, 82.6, 80.5, 60.6, 55.2, 38.9, 36.7, 14.2, 14.1; IR (liquid film) cm^{-1} 2963w, 1730m, 1488m, 1264s, 1070m, 1012m, 816m, 792m, 732m, 703s; HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{25}BrO_4$ $(M+Na)^+$: 467.0828, found 467.0824.

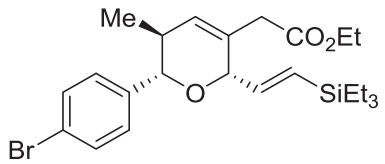
Preparation of 3g



3g

3g: Using the same procedure as that used for **3b** afforded **3g** (20.7 mg, 98%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 12.29 min, t_{major} = 16.51 min; $[\alpha]_D^{20}$ = +11.0 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.24-7.30 (m, 4H), 7.09 (d, J = 4.8 Hz, 1H), 5.68 (s, 1H), 5.52 (s, 1H), 4.18 (d, J = 9.6 Hz,1H), 4.09 (q, J = 6.8 Hz, 2H), 2.84 (d, J = 16.0 Hz, 1H), 2.63 (d, J = 16.0 Hz, 1H), 1.24 (t, J = 6.8 Hz, 3H), 0.86 (t, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 140.6, 139.7, 132.1, 131.1, 130.7, 129.0, 126.6, 126.1, 124.1, 121.7, 82.8, 38.9, 36.7, 16.8, 14.2; IR (liquid film) cm^{-1} 2918w, 1731m, 1489w, 1264m, 1177w, 1071m, 1012m, 788m; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{21}BrO_3S$ $(M+Na)^+$:443.0287, found 443.0290.

Preparation of 3h

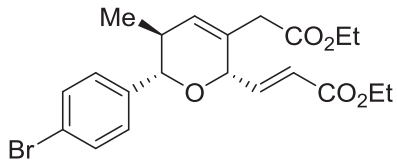


3h

3h: Using the same procedure as that used for **3b** afforded **3h** (21.6 mg, 90%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 4.50 min, t_{major} = 5.78 min; $[\alpha]_D^{20}$ = +3.7 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H),

5.29-5.93 (m, 2H), 5.61 (s, 1H), 4.79 (s, 1H), 4.15 (q, J = 7.2 Hz, 2H), 4.03 (d, J = 9.2 Hz, 1H), 3.05 (d, J = 16.0 Hz, 1H), 2.95 (d, J = 16.0Hz, 1H), 2.40 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 8.0 Hz, 9H), 0.80 (t, J = 7.2 Hz, 3H), 0.58 (q, J = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 144.7, 139.9, 131.9, 131.4, 131.1, 130.9, 129.1, 121.6, 82.1, 82.0, 60.7, 38.7, 36.6, 16.8, 14.2, 7.3, 3.3; IR (liquid film) cm^{-1} 2955m, 2918m, 1737s, 1260m, 1180m, 1070s, 1012s, 991m,; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{35}BrO_3Si$ $(M+Na)^+$: 501.1431, found 501.1425.

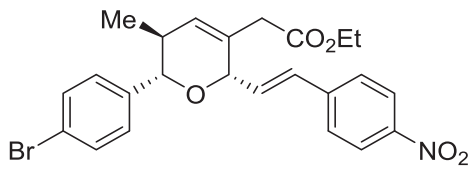
Preparation of 3i



3i

3i: Using the same procedure as that used for **3b** afforded **3i** (15.5 mg, 80%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 55.01 min, t_{major} = 59.21 min; $[\alpha]_D^{20}$ =-3.2° (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.90 (dd, J_1 = 6.8 Hz, J_2 = 6.8 Hz, 1H), 6.14 (d, J = 15.6 Hz, 1H), 5.67 (s, 1H), 5.02 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H),4.15 (q, J = 7.2 Hz, 2H), 4.06 (d, J = 9.2 Hz, 1H), 3.09 (d, J = 16.0 Hz, 1H), 3.01 (d, J = 16.0 Hz, 1H), 2.42 (s, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.27 (t, J = 7.2 Hz, 3H), 0.82 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 166.0, 144.4, 139.4, 132.0, 131.5, 129.8, 129.0, 123.8, 121.9, 82.1, 60.9, 60.5, 38.7, 36.4, 16.6, 14.2, 14.1; IR (liquid film) cm^{-1} 2962w, 2921m, 2851w, 1722s, 1369m, 1261s, 1175s, 1071s, 1031s, 1011s, 981m, 805s; HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{25}BrO_5$ $(M+Na)^+$: 459.0778, found 459.0778.

Preparation of 3j

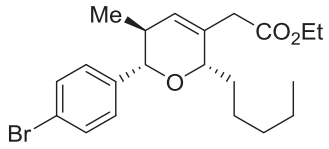


3j

3j: Using the same procedure as that used for **3b** afforded **3j** (21.9 mg, 90%) as a colorless liquid. The enantiomeric ratio was determined to be 98:2 by HPLC analysis on Chiralpak OD column (5.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 18.16 min, t_{major} =14.81 min; $[\alpha]_D^{20}$ = +12.0 (c = 1.0 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.33 (dd, J_1 = 16.0 Hz, J_2 = 8.0 Hz, 1H), 5.71 (s, 1H), 5.00 (d, *J* = 6.0 Hz, 1H), 4.10 (q, *J* = 6.8 Hz, 2H), 4.07 (d, *J* = 6.8 Hz, 1H), 3.08 (d, *J* = 16.0 Hz, 1H), 3.00 (d, *J* = 16.0 Hz, 1H), 2.50 (m, 1H), 1.19 (t, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 147.1, 142.8, 139.4, 132.5, 131.8, 131.5, 130.6, 129.0, 127.1, 123.9, 121.9, 82.3, 78.8, 60.8, 38.7, 36.3, 16.7, 14.1; IR (liquid film) cm^{-1} 2917w, 1730m, 1596m, 1516s, 1341s, 1179m, 1070s, 1011s, 972m, 863m; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{24}BrNO_5$ $(M+Na)^+$: 508.0730, found 508.0731.

2.5. One-pot Synthesis of 3k-3m.

Preparation of 3k

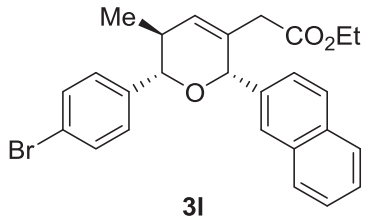


3k

3k: To a solution of (*S*)**-1a** (20.5 mg, 0.05 mmol) and *p*-Br-C_6H_4CHO (9.25 mg, 0.05 mmol) in anhydrous $CHCl_3$ (0.5 mL) was added $Ph_3C^+B(C_6F_5)_4^-$ (0.92 mg, 0.001 mmol) at room temperature. After stirring for 2 h, a solution of *n*-hexanal (14.6 mg, 0.146 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added to the above mixture. The reaction was stirred for 20 h before quenching with sat aq $NaHCO_3$ (2 mL) and extraction with CH_2Cl_2 (3 × 2 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-20% of EtOAc/petroleum ether) afforded **3k** (11.2 mg, 55%) as a yellow oil. The enantiomeric ratio was determined to be 97.5:2.5 by HPLC analysis on Chiralpak IC column (0.5% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220nm, t_{minor} = 8.13 min, t_{major} = 9.09 min; $[\alpha]_D^{20}$ = -3.5 (*c* = 1.0 in $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4Hz, 2H), 5.58 (s, 1H), 4.37 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.95 (d, *J* = 9.6 Hz, 1H), 3.05 (d, *J* = 15.6 Hz, 1H), 2.98 (d, *J* = 15.6 Hz, 1H), 2.31 (m,

1H), 1.70-1.74 (m, 1H), 1.51-1.58 (m, 2H), 1.43-1.50 (m, 1H), 1.28-1.39 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 140.5, 132.5, 131.3, 128.9, 121.5, 81.9, 82.0, 82.0, 76.3, 60.7, 38.9, 36.9, 32.6, 32.0, 23.8, 22.6, 16.8, 14.2, 14.1; IR (liquid film) cm^{-1} 2926s, 2851m, 1736s, 1490m, 1457m, 1369m, 1174m, 1071m, 1011s, 811m; HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{29}BrO_3$ $(M+Na)^+$: 431.1192, found 431.1193.

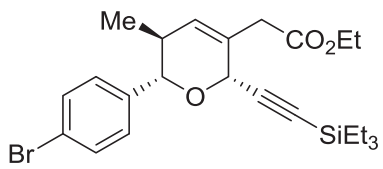
Preparation of 3l



3l

3l: Using the same procedure as that used for **3k** afforded **3l** (11.6 mg, 50%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220nm, t_{minor} = 43.10min, t_{major} = 62.82 min; $[\alpha]_D^{20}$ = +42.5 (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.86 (m, 4H), 7.52 (d, J = 8.0, 1H), 7.48 (d, J = 3.2 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 5.78 (s, 1H), 5.56 (s, 1H), 4.27 (d, J = 6.8 Hz, 1H), 4.02 (dq, J_1 = 3.2 Hz, J_2 = 7.2 Hz, 2H), 2.83 (d, J = 16.0 Hz, 1H), 2.66 (d, J = 16.0 Hz, 1H), 2.64 (m, 1H), 1.16 (t, J = 7.2 Hz, 3H), 0.91 (d, J = 6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 139.8, 132.4, 131.4, 131.2, 129.0, 128.5,128.0, 127.9, 127.6, 126.1, 125.4, 121.7, 82.6, 80.8, 60.6, 38.9, 36.9; IR (liquid film) cm^{-1} 3054w, 1729m, 1264s, 1176w, 1072m, 1012m, 816m; HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{25}BrO_3$ $(M+Na)^+$:487.0879, found 487.0878.

Preparation of 3m

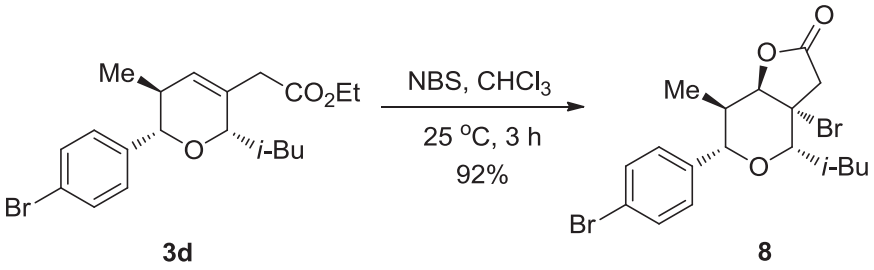


3m

3m: Using the same procedure as that used for **3k** afforded **3m** (15.5 mg, 65%) as a colorless liquid. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (1.0% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220 nm, t_{minor} = 4.61 min, t_{major} = 5.61min; $[\alpha]_D^{20}$ = +9.6 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.62 (s, 1H), 5.29 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.03 (d, *J* = 9.2 Hz, 1H), 3.46 (d, *J* = 16.4 Hz, 1H), 3.13 (d, *J* = 16.4 Hz, 1H), 2.48 (m, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 139.1, 131.4, 131.0, 129.3, 129.2,121.9, 102.5, 88.9, 82.8, 69.1, 60.8, 39.0, 36.2, 16.6, 14.2, 7.4, 4.2; IR (liquid film) cm^{-1} 2958w, 1731w, 1265m, 1088w, 1075w, 1012w; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{33}BrO_3Si$ $(M+Na)^+$:499.1275, found 499.1275.

2.6. Functionalization of 3d

Preparation of 8

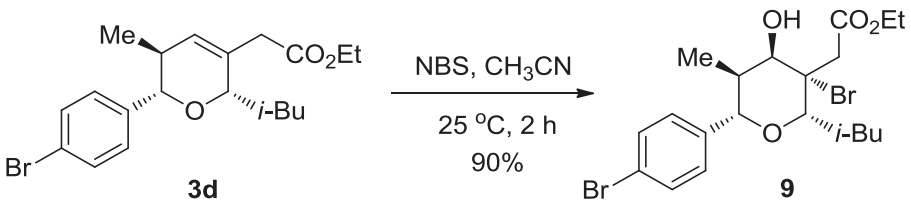


3d **8**

8: To a solution of **3d** (50.0 mg, 0.127 mmol) in anhydrous $CHCl_3$ (1 mL) was added NBS (25 mg, 0.140 mmol) at 25 °C. After stirring for 3 h, the reaction was quenched with sat aq NH_4Cl (1 mL) and extracted with CH_2Cl_2 (3 × 1 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1.0% of EtOAc/petroleum ether) afforded **8** (51.9 mg, 92% yield) as a colorless oil. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak IC column (5% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220nm, t_{minor} = 10.80, t_{major} = 6.99 min;$[\alpha]_D^{20}$ = +1.6 (*c* = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 8.0 Hz , 1H), 4.76 (d, *J* = 2.8 Hz, 1H), 4.21 (d, *J* = 10.4 Hz, 1H), 3.31 (d, *J* = 8.8 Hz, 1H), 3.11 (d, *J* = 17.2 Hz, 1H), 2.88 (d, *J* =17.2 Hz, 1H), 2.36-2.41 (m, 1H), 1.70-1.77 (m, 1H), 1.16-1.25 (m, 1H), 0.87 (q, *J* = 7.2 Hz, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4, 138.3, 131.5, 128.9, 122.2, 87.7, 80.3, 76.7,59.9, 43.6, 41.7, 34.1, 24.7, 23.4,

22.0, 13.0; IR (liquid film) cm^{-1} 2957w, 2917s, 2849s, 1795s, 1462m, 1376w, 1260w, 1073m, 1012m, 808m; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{25}BrO_3$ $(M+Na)^+$:468.9807, found 468.9803.

Preparation of 9

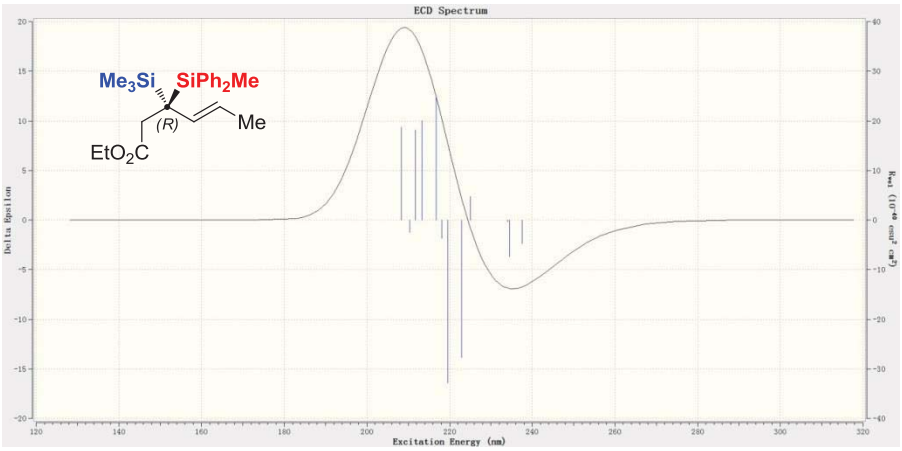


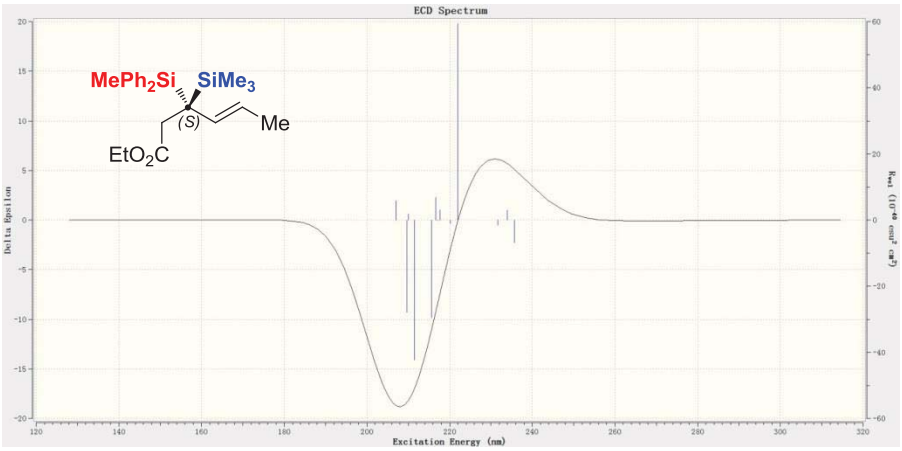
9: To a solution of **3d** (50.0 mg, 0.127 mmol) in anhydrous CH_3CN (1 mL) was added NBS (25 mg, 0.140 mmol) at 25 °C. After stirring for 2 h, the reaction was quenched with sat aq NH_4Cl (1 mL) and extracted with CH_2Cl_2 (3 × 1 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1.0% of EtOAc/petroleum ether) afforded **9** (56.0 mg, 90% yield) as a colorless oil. The enantiomeric ratio was determined to be 97:3 by HPLC analysis on Chiralpak OD column (5% 2-propanol/*n*-hexane, 1.0 mL/min), UV 220nm, t_{minor} = 13.68, t_{major} = 12.58 min; $[\alpha]_D^{20}$ = -28.5 (*c* = 1.0 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz , 2H), 4.25 (dq, J_1 = 3.6 Hz, J_2 = 7.2 Hz, 2H), 4.15 (m, 1H), 3.63 (d, *J* = 8.0 Hz, 1H), 3.62 (s, 1H), 3.03 (d, *J* = 14.4 Hz, 1H), 2.94 (d, *J* = 14.4 Hz, 1H), 2.54-2.59 (m, 1H), 1.67-1.79 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.87 (d, *J* = 6.4Hz, 3H), 0.84 (d, *J* = 6.4Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 140.0, 131.3, 129.1, 121.5, 80.0, 75.9, 74.8, 70.5, 61.6, 42.5, 40.4, 36.7, 24.2, 23.6, 21.8, 14.2, 13.7; IR (liquid film) cm^{-1} 2925w, 2854w, 1710w, 1261m, 1214s, 1093m, 1012m; HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{31}BrO_4$ $(M+Na)^+$:515.0226, found 515.0228.

2.7. Determining the absolute configuration of (S)-1a

DFT Calculation Procedures:

CD spectroscopy is obtained by density functional theory (DFT) calculations. All the DFT calculations of structure of starting material (ground state) and corresponding vibrational frequencies were performed on Gaussian 03 software with B3LYP/6-31G(d) basic set.





Electronic circular dichroism (ECD) spectra provided by quantum chemical calculation with SMD model, at the B3LYP/6-31G (d) level (methanol as solvent) were performed.

Computational data:

R.log

Zero-point correction= 0.523198 (Hartree/Particle)

Thermal correction to Energy= 0.556411

Thermal correction to Enthalpy= 0.557355

Thermal correction to Gibbs Free Energy= 0.458808

E(sov.) = -1664.64809426 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.838595	0.097596	0.160410

2	6	0	-0.596734	0.003863	1.710542
3	1	0	-0.060821	0.907965	2.025080
4	1	0	0.072523	-0.839662	1.911742
5	6	0	-1.651801	1.333179	-0.143060
6	8	0	-1.918052	2.229830	0.638914
7	8	0	-2.085916	1.369980	-1.433993
8	6	0	-2.859536	2.532833	-1.808978
9	1	0	-2.246913	3.427656	-1.657952
10	1	0	-3.724638	2.611387	-1.143359
11	6	0	-3.269989	2.365164	-3.260162
12	1	0	-3.854331	3.234141	-3.582274
13	1	0	-2.392943	2.281144	-3.909998
14	1	0	-3.885510	1.469581	-3.393878
15	6	0	-1.817844	-0.125218	2.588523
16	1	0	-2.589502	0.629626	2.445691
17	6	0	-1.965046	-1.035223	3.557181
18	1	0	-1.176684	-1.775434	3.712241
19	6	0	-3.140088	-1.123063	4.490212
20	1	0	-3.885478	-0.351153	4.270424
21	1	0	-3.633984	-2.102106	4.422583
22	1	0	-2.827780	-1.002304	5.536747
23	14	0	-1.816530	-1.478782	-0.487259
24	6	0	-1.206396	-3.037085	0.398001
25	1	0	-1.373703	-2.981706	1.477996
26	1	0	-1.772340	-3.898843	0.020599
27	1	0	-0.144952	-3.235644	0.222769
28	6	0	-3.665659	-1.275382	-0.111473
29	1	0	-4.094118	-0.398112	-0.607902
30	1	0	-4.208343	-2.157368	-0.475770
31	1	0	-3.854387	-1.188409	0.962639

32	6	0	-1.662612	-1.773554	-2.354011
33	1	0	-0.651372	-2.060347	-2.658337
34	1	0	-2.329513	-2.601752	-2.627168
35	1	0	-1.966203	-0.895420	-2.930803
36	14	0	0.922272	0.307223	-0.682180
37	6	0	1.885140	-1.329091	-0.605474
38	6	0	2.097551	-2.098355	-1.764575
39	6	0	2.427618	-1.818761	0.599637
40	6	0	2.795052	-3.307921	-1.723643
41	1	0	1.717938	-1.749590	-2.721631
42	6	0	3.125086	-3.026569	0.649161
43	1	0	2.319497	-1.241847	1.514665
44	6	0	3.306097	-3.778153	-0.513795
45	1	0	2.941230	-3.879577	-2.636700
46	1	0	3.530471	-3.378798	1.594358
47	1	0	3.848946	-4.719155	-0.477820
48	6	0	1.959964	1.620280	0.224861
49	6	0	1.410505	2.809996	0.744607
50	6	0	3.359460	1.473483	0.291690
51	6	0	2.220286	3.798082	1.307957
52	1	0	0.336886	2.970682	0.726281
53	6	0	4.172957	2.461239	0.850483
54	1	0	3.826728	0.571719	-0.095170
55	6	0	3.604303	3.627524	1.362757
56	1	0	1.766098	4.701677	1.707042
57	1	0	5.249985	2.316641	0.887768
58	1	0	4.234214	4.397025	1.802087
59	6	0	0.807379	0.864313	-2.487189
60	1	0	0.381244	1.870416	-2.547904
61	1	0	1.818370	0.908549	-2.909815

62	1	0	0.198171	0.207299	-3.113429

S.log

Zero-point correction= 0.522797 (Hartree/Particle)

Thermal correction to Energy= 0.556172

Thermal correction to Enthalpy= 0.557116

Thermal correction to Gibbs Free Energy= 0.457638

E(sov.) = -1664.64469774 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.147077	-1.014385	-0.322342
2	6	0	0.983003	-0.651598	-1.609588
3	1	0	0.503864	0.212574	-2.095800
4	1	0	0.873828	-1.475269	-2.321064
5	6	0	-1.128081	-1.690108	-0.793703
6	8	0	-1.316861	-2.183475	-1.890834
7	8	0	-2.085179	-1.711033	0.172801
8	6	0	-3.353025	-2.298494	-0.198207
9	1	0	-3.184419	-3.333857	-0.510832
10	1	0	-3.751187	-1.750977	-1.057957
11	6	0	-4.271479	-2.206812	1.005931
12	1	0	-5.246792	-2.641987	0.761340
13	1	0	-3.856958	-2.752408	1.860033
14	1	0	-4.424835	-1.163669	1.300204
15	6	0	2.447362	-0.331003	-1.444799
16	1	0	2.713277	0.438006	-0.722392
17	6	0	3.418369	-0.873580	-2.187755

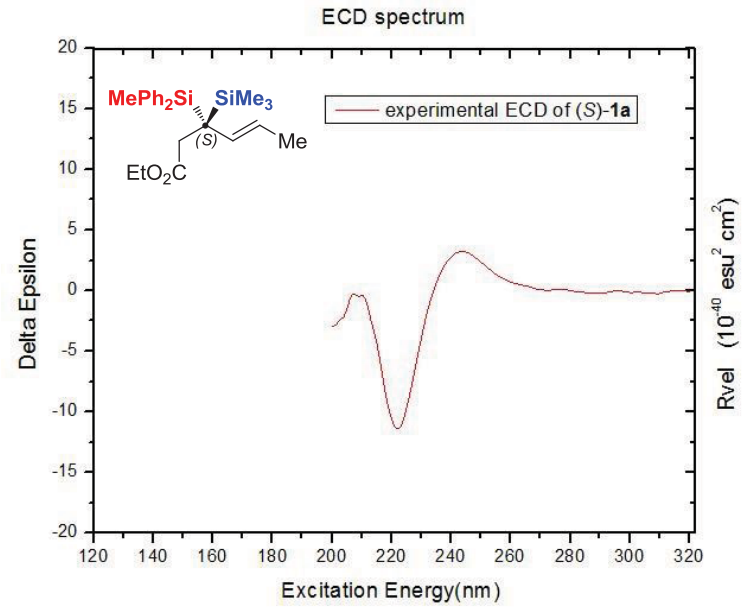
18	1	0	3.154635	-1.631898	-2.928119
19	6	0	4.874191	-0.510552	-2.105267
20	1	0	5.054633	0.254711	-1.342605
21	1	0	5.492718	-1.385842	-1.863913
22	1	0	5.242251	-0.123969	-3.065672
23	14	0	-0.352496	0.576187	0.693925
24	6	0	-0.809097	0.208146	2.495084
25	1	0	0.008459	-0.271752	3.043347
26	1	0	-1.047967	1.138452	3.022983
27	1	0	-1.680611	-0.449713	2.547111
28	14	0	1.070032	-2.427373	0.687525
29	6	0	-0.086164	-3.317355	1.899931
30	1	0	-0.884352	-3.861440	1.384884
31	1	0	0.504752	-4.052668	2.461828
32	1	0	-0.555452	-2.644662	2.622974
33	6	0	-1.826334	1.452773	-0.135417
34	6	0	-2.232453	1.244173	-1.466803
35	6	0	-2.542413	2.410268	0.609504
36	6	0	-3.300772	1.951060	-2.024894
37	1	0	-1.724302	0.512322	-2.087607
38	6	0	-3.611137	3.119348	0.059668
39	1	0	-2.263430	2.613914	1.640858
40	6	0	-3.994458	2.891204	-1.262932
41	1	0	-3.588996	1.764162	-3.056409
42	1	0	-4.143823	3.849515	0.664078
43	1	0	-4.825883	3.441973	-1.695432
44	6	0	1.050258	1.860906	0.723672
45	6	0	1.995516	1.906497	1.765735
46	6	0	1.162904	2.831880	-0.290509
47	6	0	3.016506	2.858845	1.786109

48	1	0	1.940165	1.190291	2.581410
49	6	0	2.181702	3.785529	-0.278686
50	1	0	0.438414	2.848848	-1.100924
51	6	0	3.114896	3.799180	0.759459
52	1	0	3.731997	2.868232	2.604731
53	1	0	2.243913	4.520530	-1.077354
54	1	0	3.908476	4.542016	0.772242
55	6	0	2.542654	-1.784147	1.691800
56	1	0	3.239841	-1.193739	1.091893
57	1	0	2.229706	-1.177505	2.548536
58	1	0	3.092405	-2.646766	2.090452
59	6	0	1.659881	-3.731069	-0.553108
60	1	0	2.481911	-3.364212	-1.174050
61	1	0	2.013948	-4.619034	-0.014299
62	1	0	0.847192	-4.045759	-1.217803

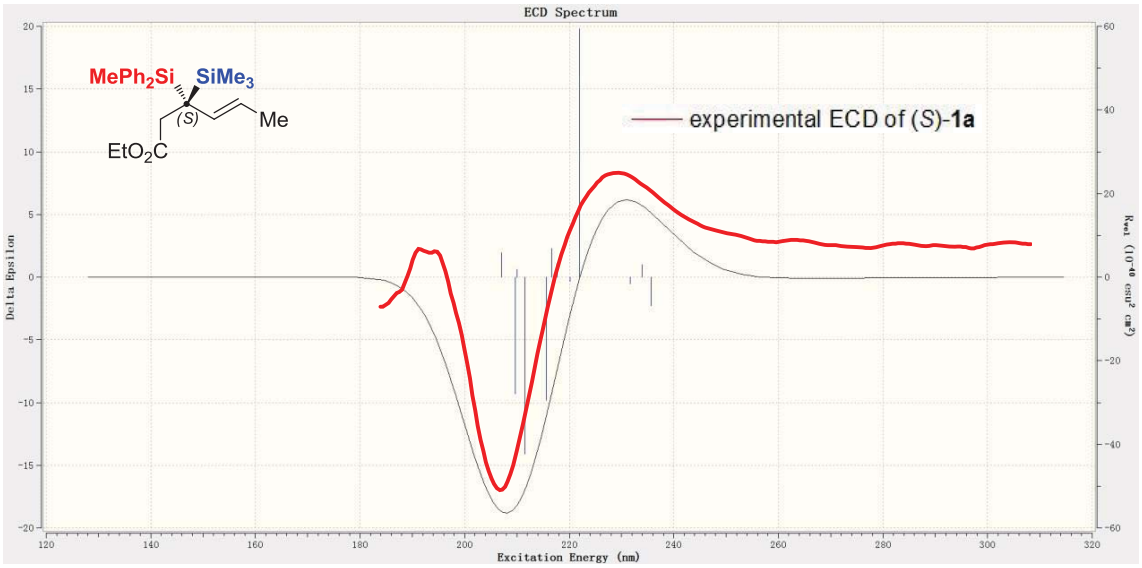
Experiment procedure:

Prior to each use, the CD instrument was purged with nitrogen for 20 min and the chiller was set to equilibrate at 25.0 °C. Spectra were collected between 200 and 520 nm with a standard sensitivity of 100 mdeg, a data pitch of 0.5 nm, a band width of 1 nm, ascanning speed of 500 nm/s^{-1} and a response of 0.5 s using a quartz cuvette (1 cm path length). The data were adjusted through baseline correction and binomial smoothing. The concentration of (*S*)-**1a** was 6.0×10^{-4} M in methanol.

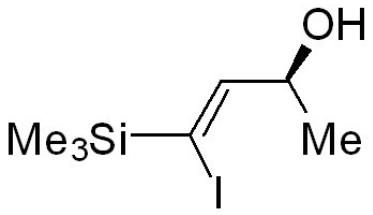
The experimental ECD spectrum of *(S)*-1a



Comparison of experimental ECD spectrum of *(S)*-**1a**in methanol with the calculated ECD spectrum of *(S)*-**1a**.

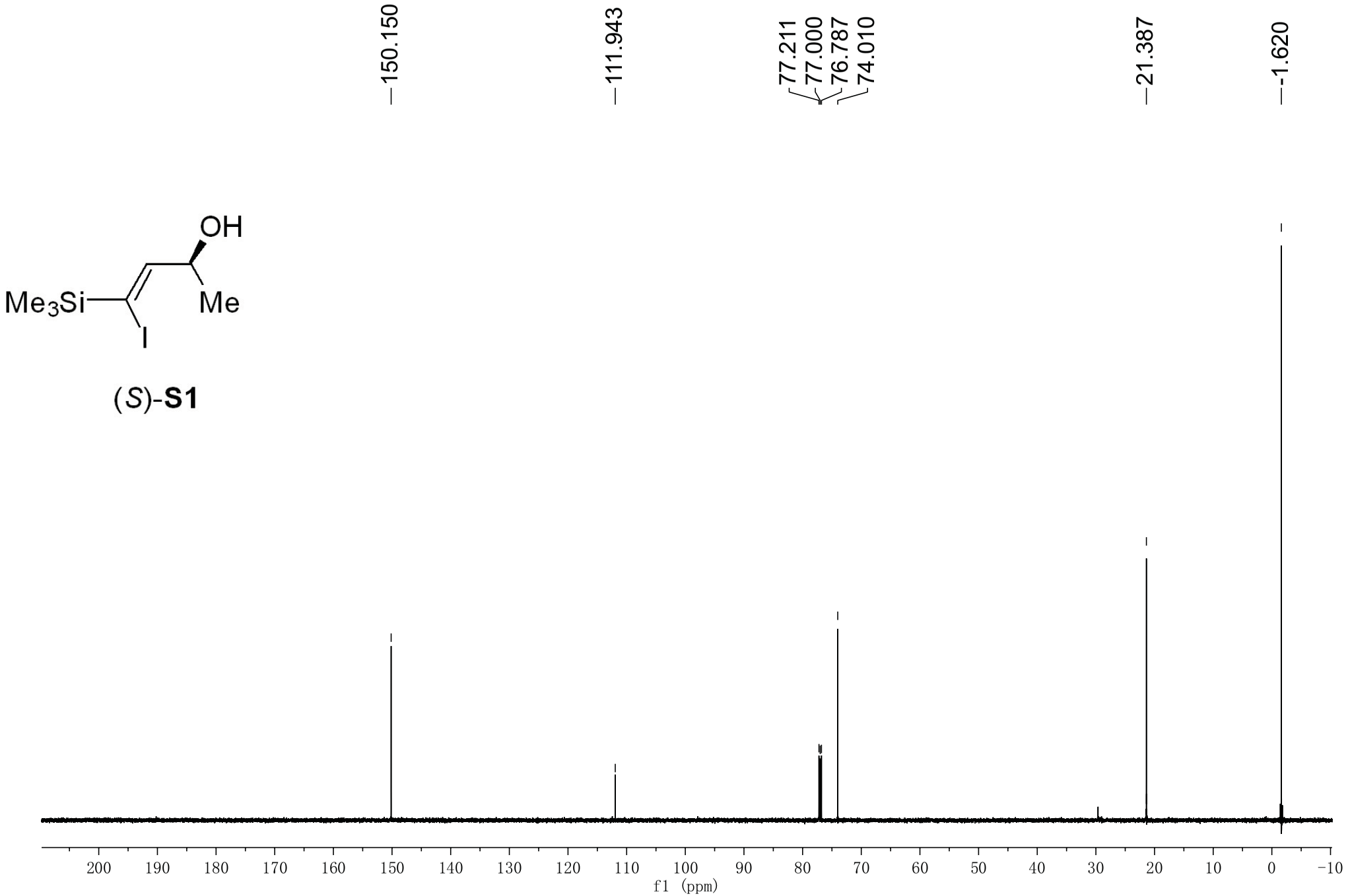


CHU-IV-57 H1 CDCl3 400MHz



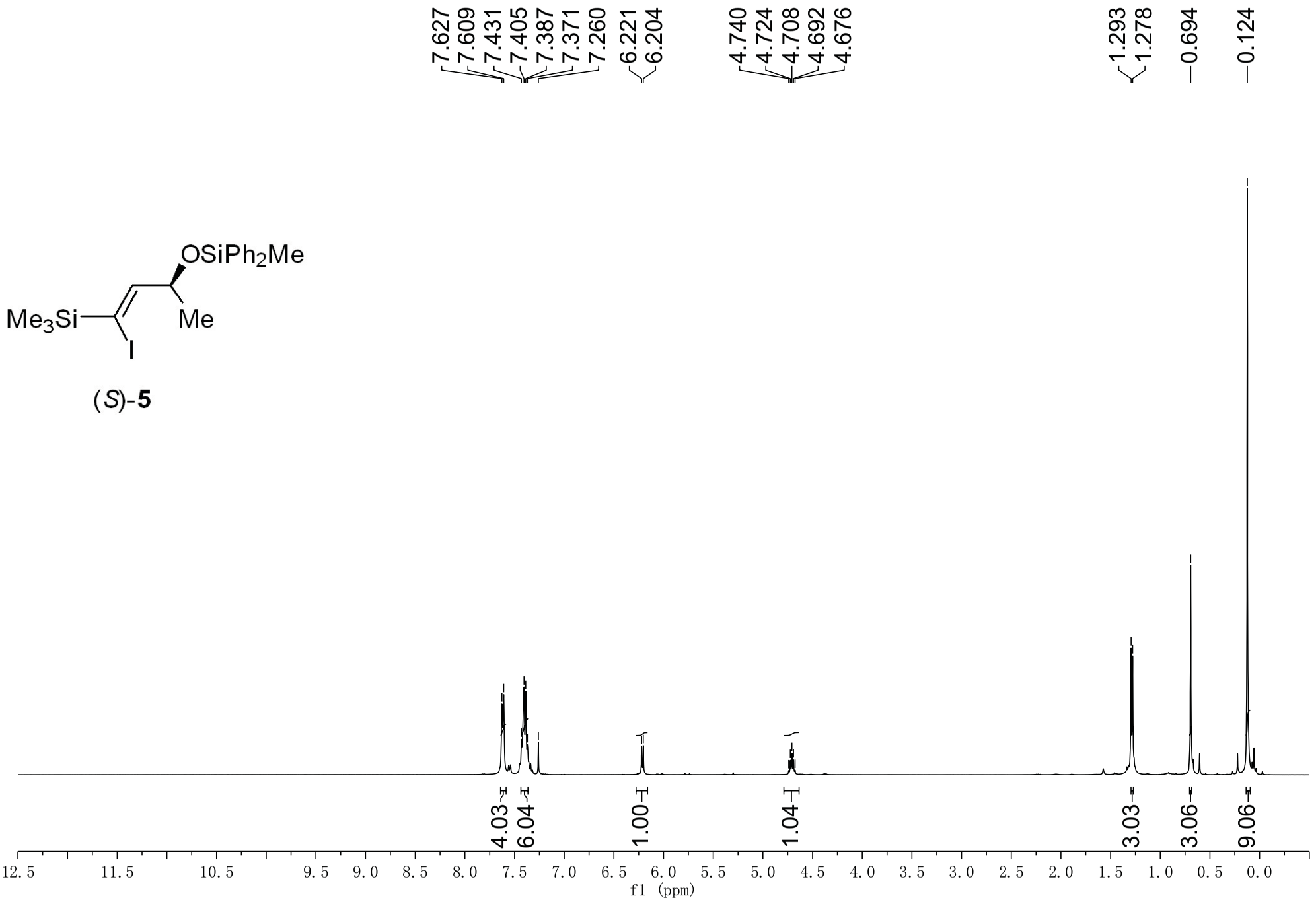
(*S*)-**S1**

WK-I-28C H1 CDCl3 600MHz



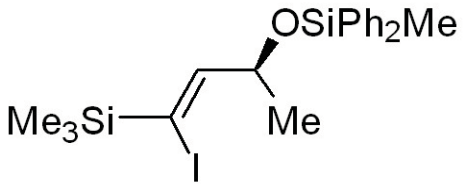
(*S*)-**S1**

WK-I-33M H1 CDCl3 400MHz

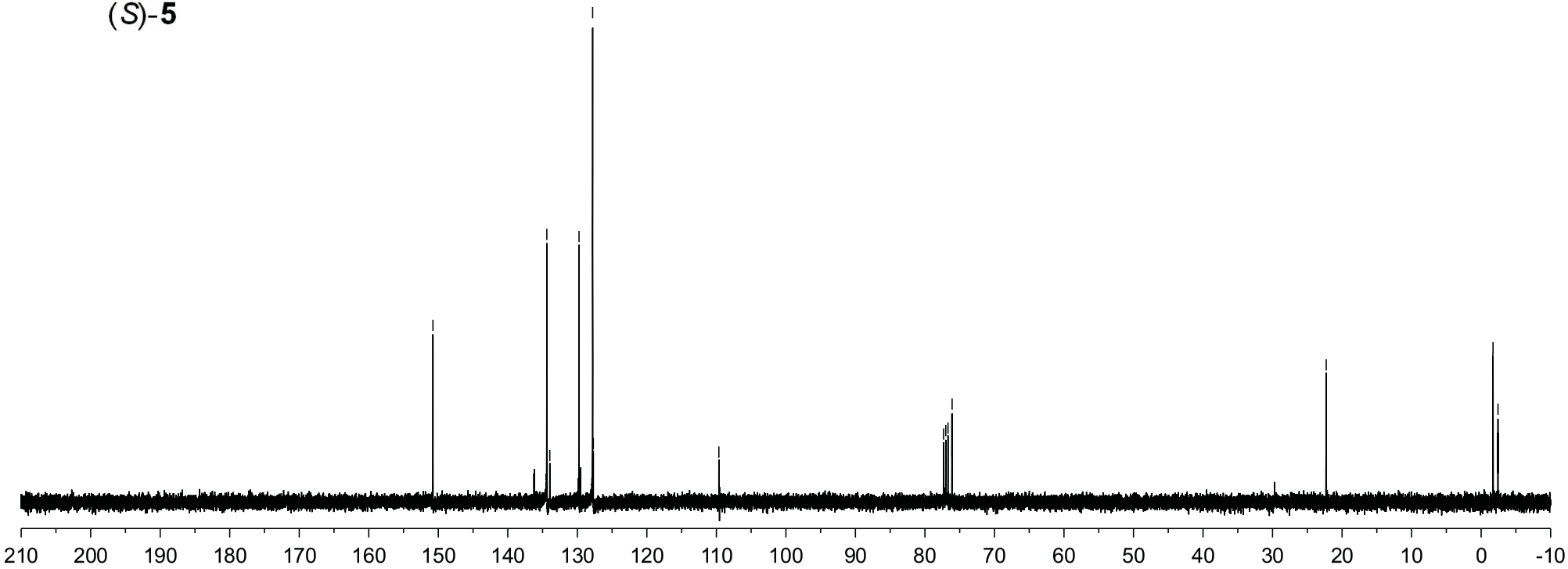


WK-I-33M C13 CDCl3 400MHz

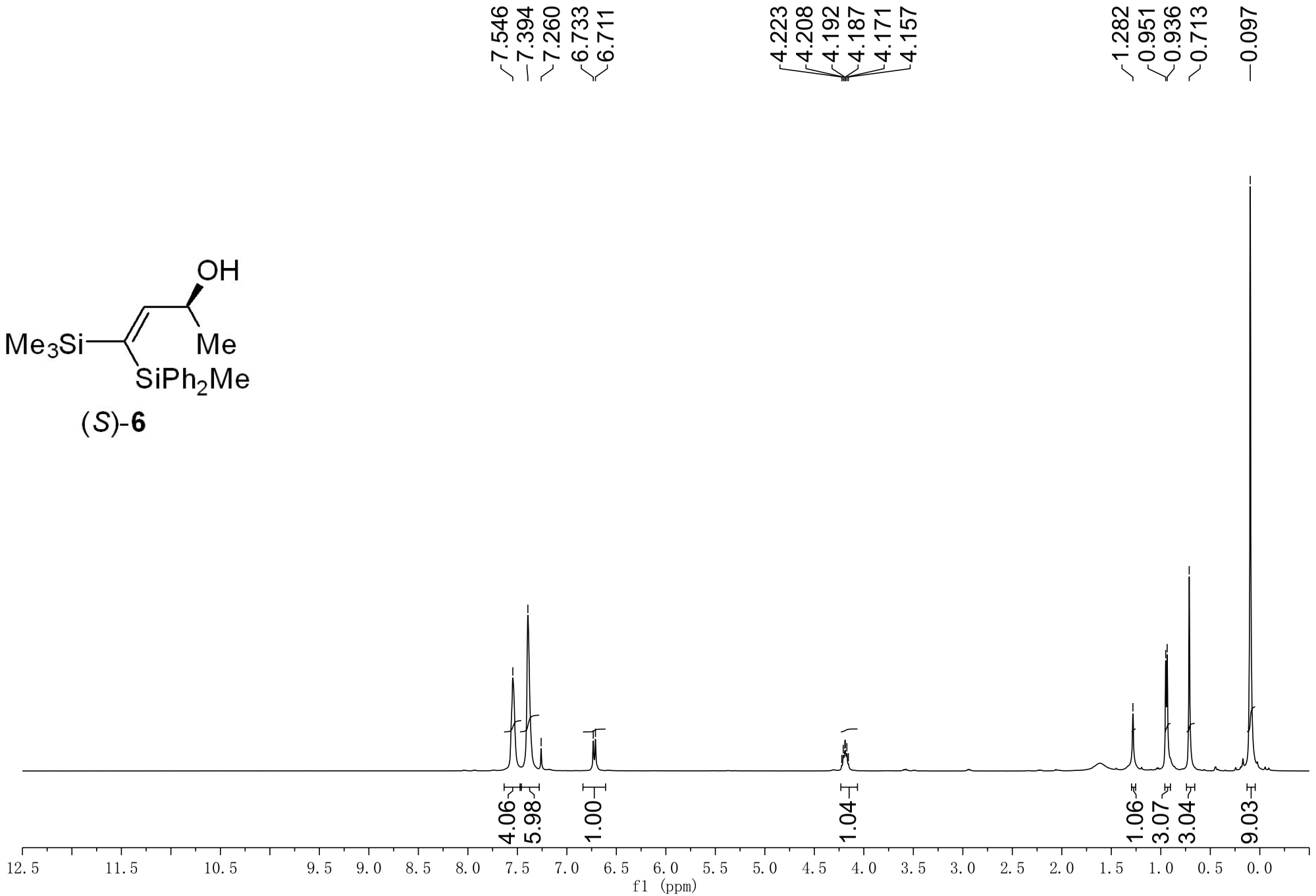
150.767
134.387
134.363
133.962
129.757
127.798
127.700
109.641
77.319
77.000
76.682
76.091
22.283
-1.695
-1.715
-2.428



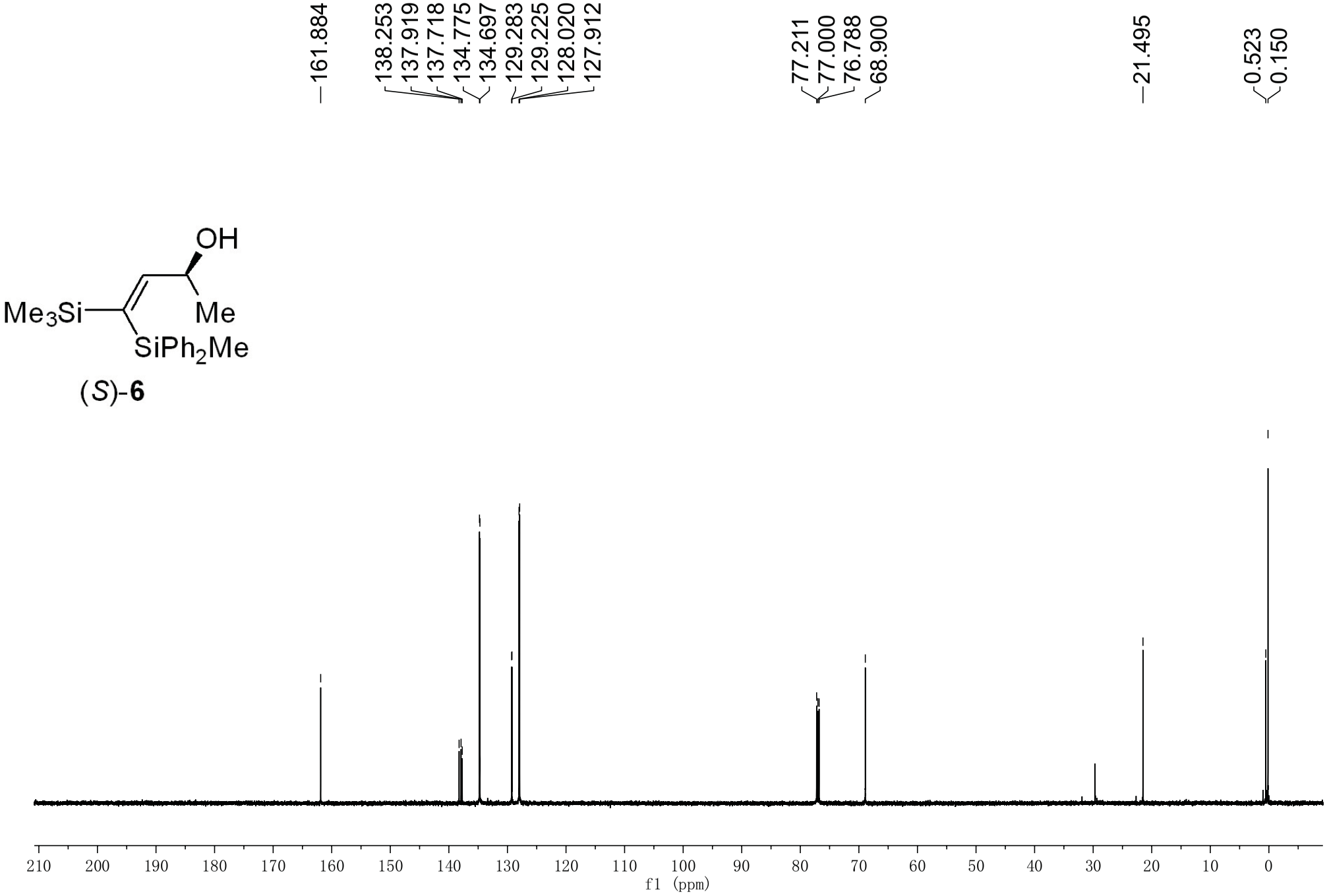
(*S*)-**5**



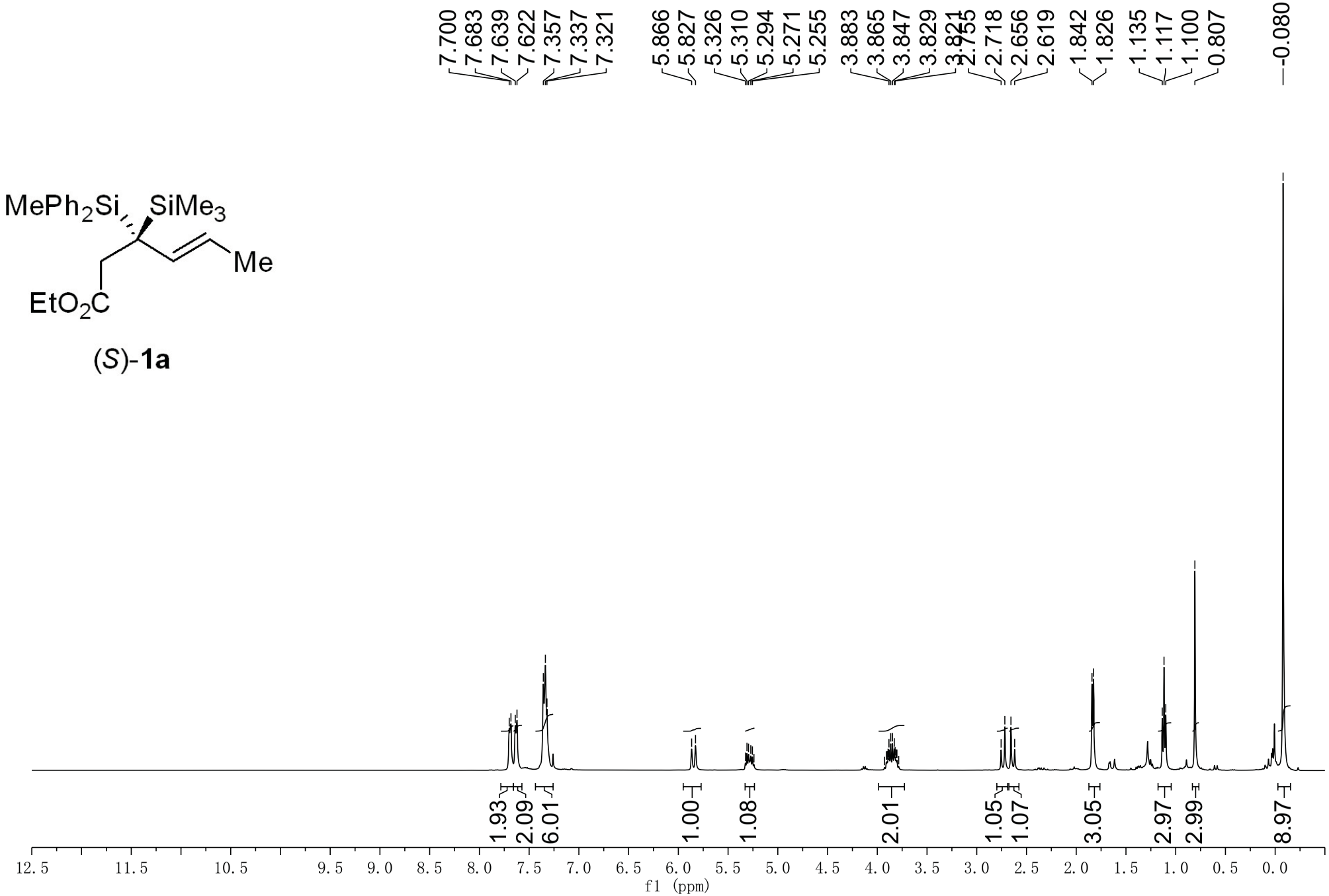
CHU-VII-42S H1 CDCl3 400MHz



CHU-VII-42S C13 CDCl3 600MHz

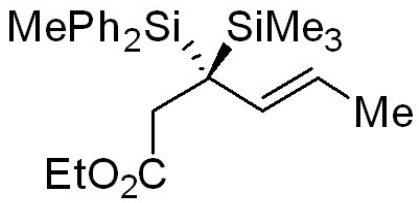


WK-I-25B22 H1 CDCl3 400MHz

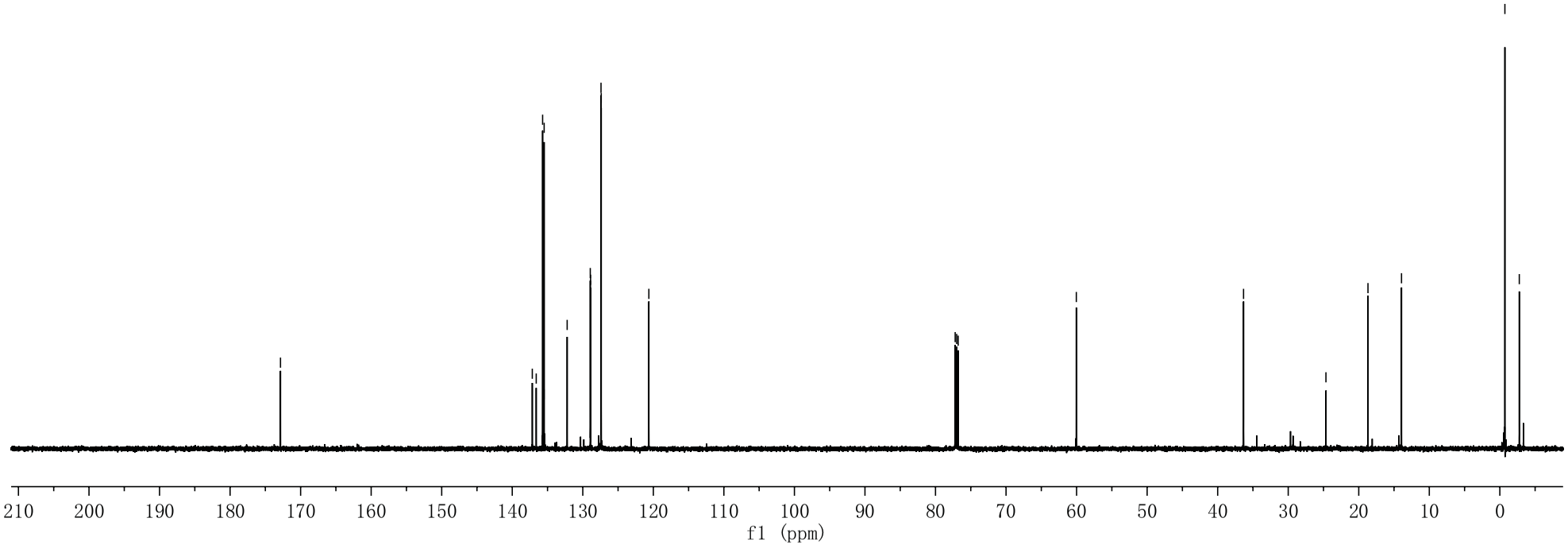


WK-I-25B22 C13 CDCl3 600MHz

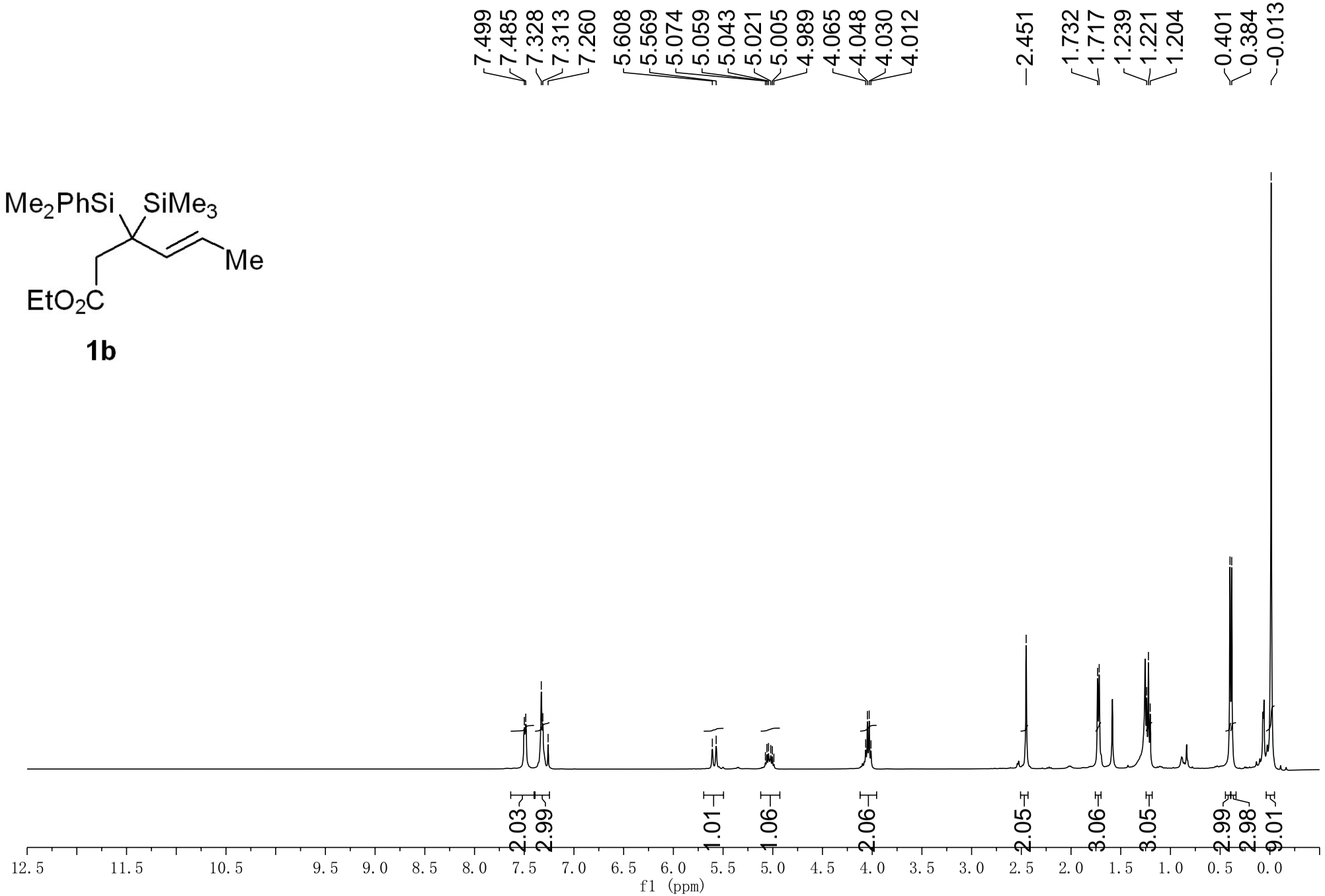
172.853
137.157
136.601
135.695
135.488
135.477
132.215
128.938
128.896
127.417
127.400
127.387
120.634
77.212
77.000
76.789
60.037
36.331
24.652
18.694
13.938
-0.716
-2.757



(*S*)-**1a**

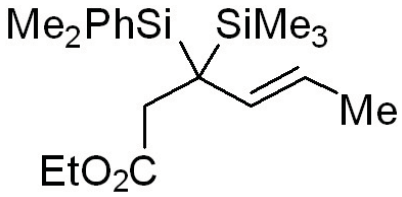


WK-I-25B33 H1 CDCl3 600MHz

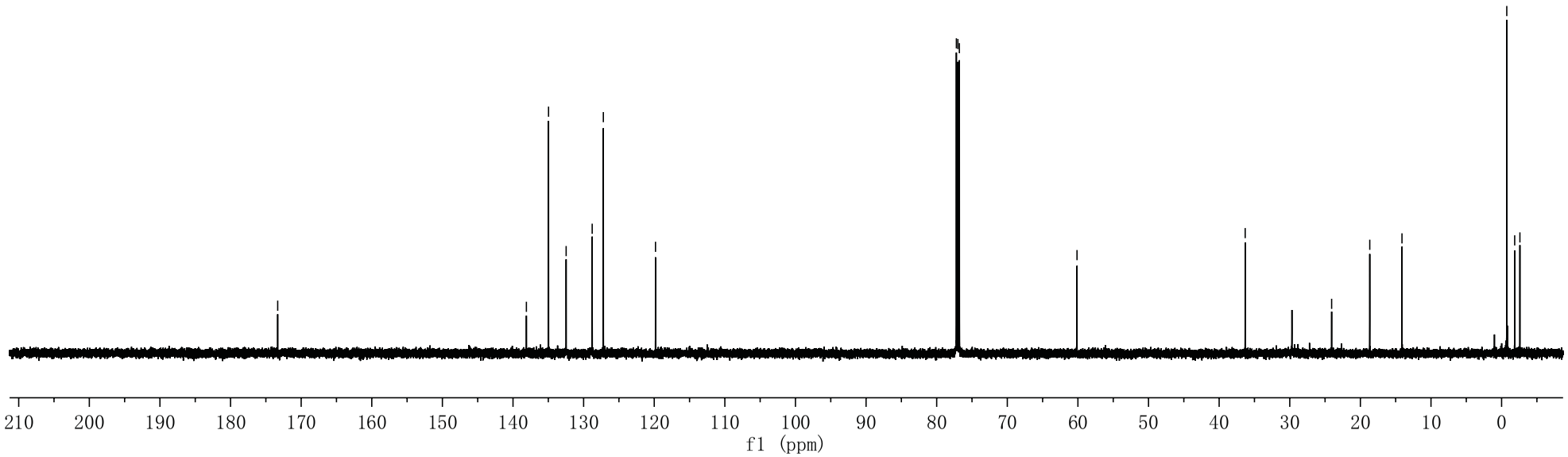


WK-I-25B33 C13 CDCl3 400MHz

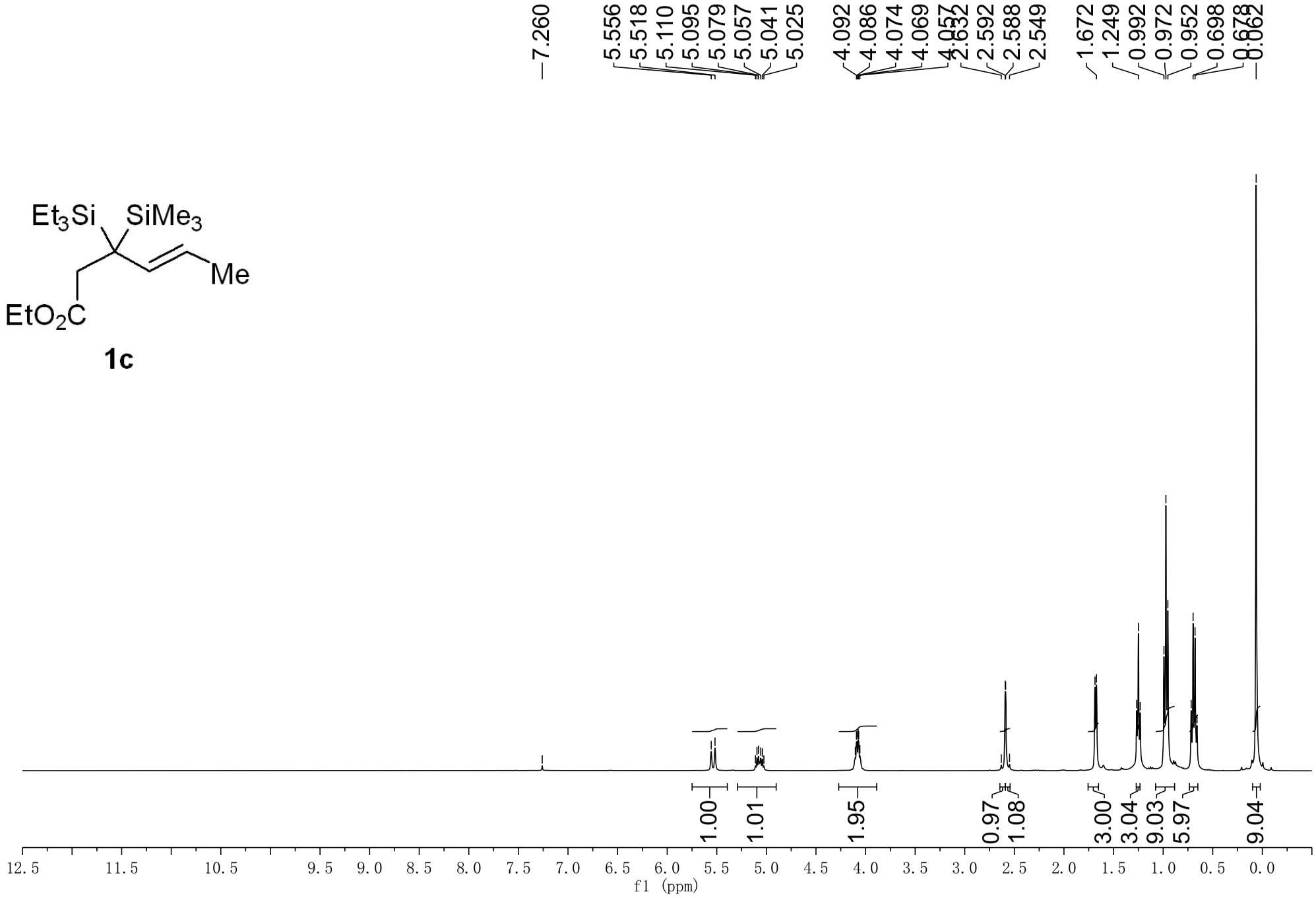
173.322
138.104
134.967
132.475
128.787
127.206
119.820
77.212
77.000
76.788
60.129
36.312
24.069
18.669
14.108
-0.734
-1.854
-2.593



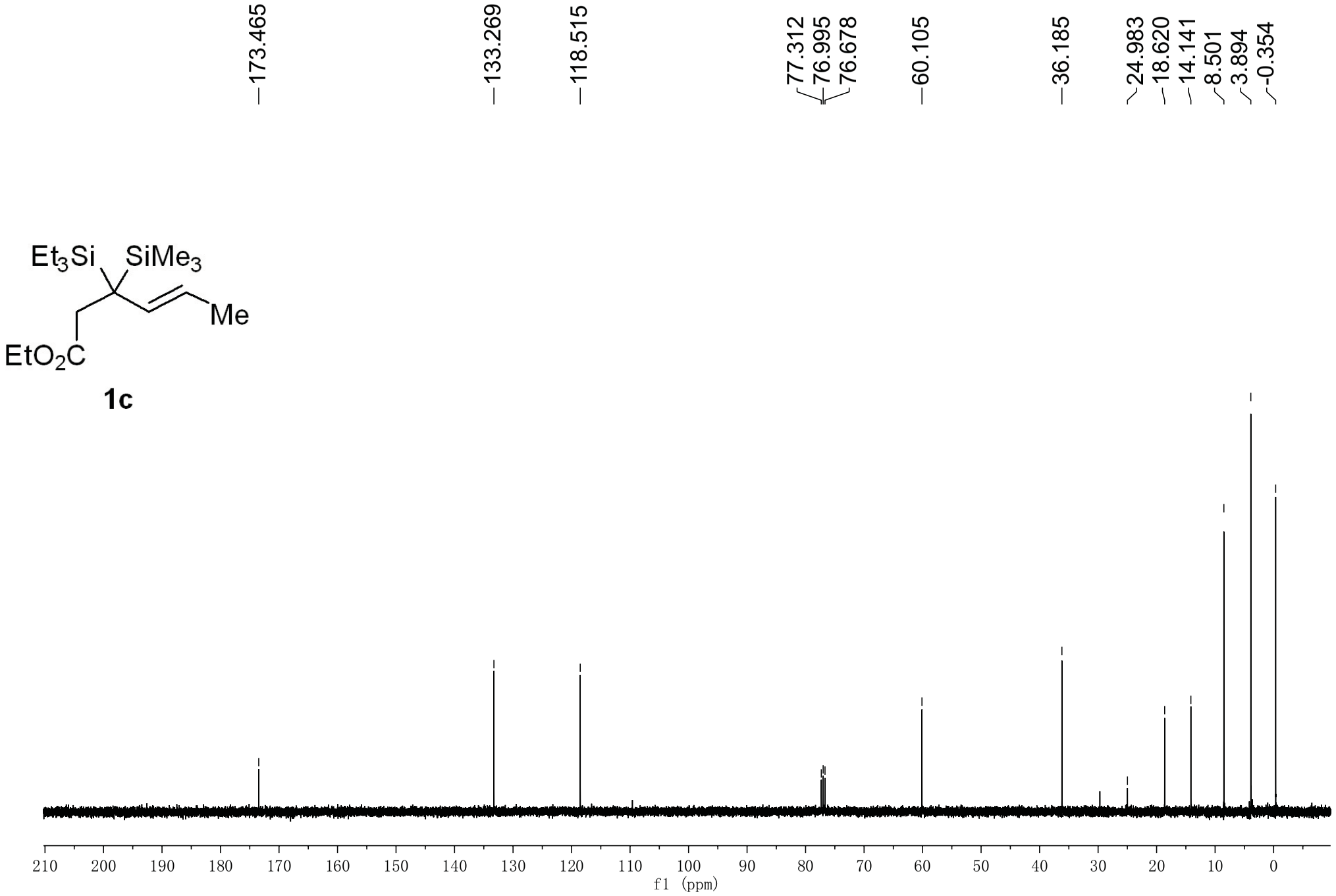
1b



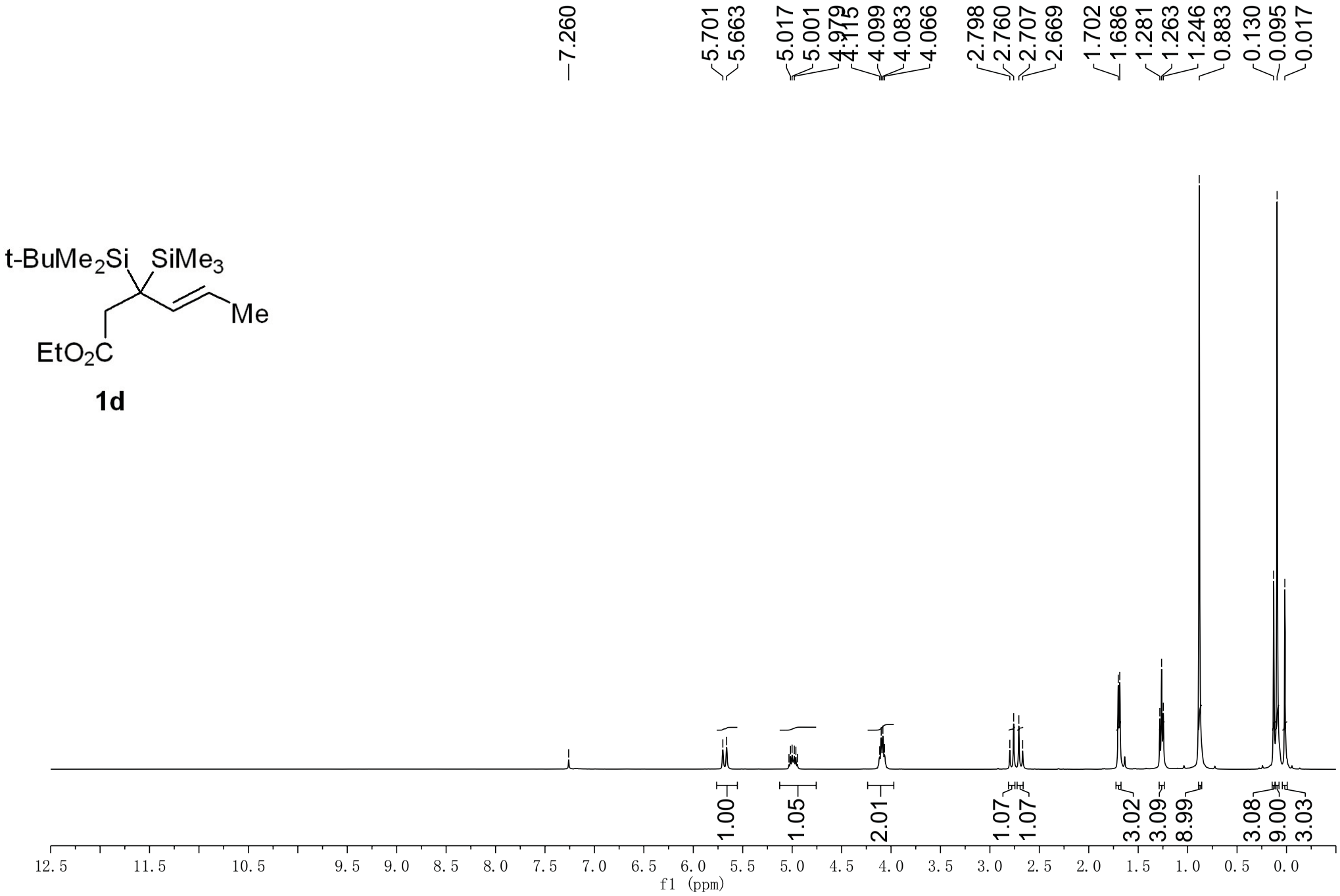
CHU-V-1026F3a H1 CDCl3 400MHz



CHU-V-1026F3a C13 CDCl3 400MHz

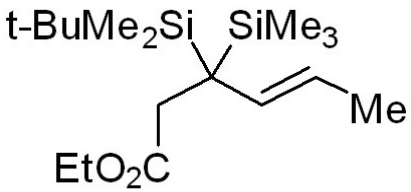


CHU-V-26F2a H1 CDCl3 400MHz

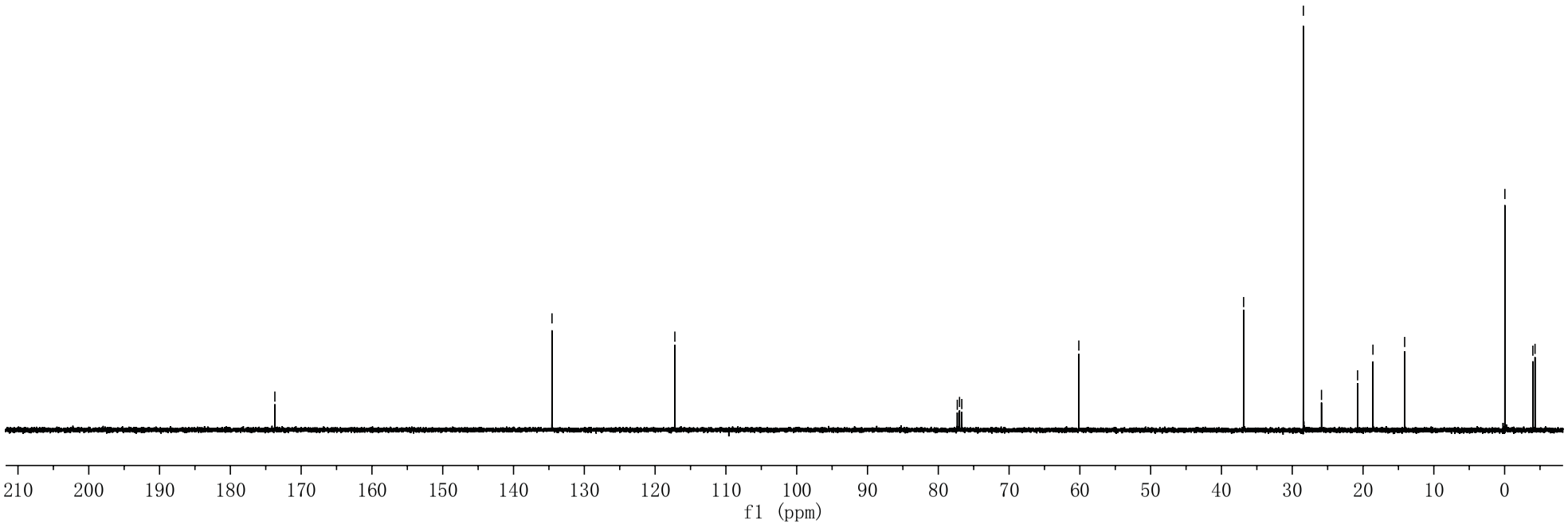


CHU-V-26F2a C13 CDCl3 400MHz

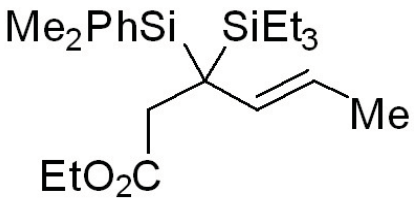
173.714
134.564
117.213
77.317
77.000
76.681
60.149
36.870
28.428
25.870
20.772
18.603
14.124
-0.036
-3.987
-4.294



1d



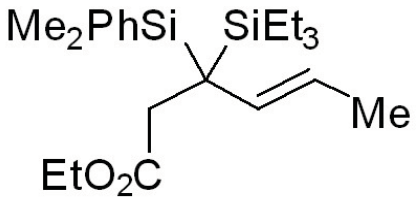
CHU-VII-82F3 H1 CDCl3 400MHz



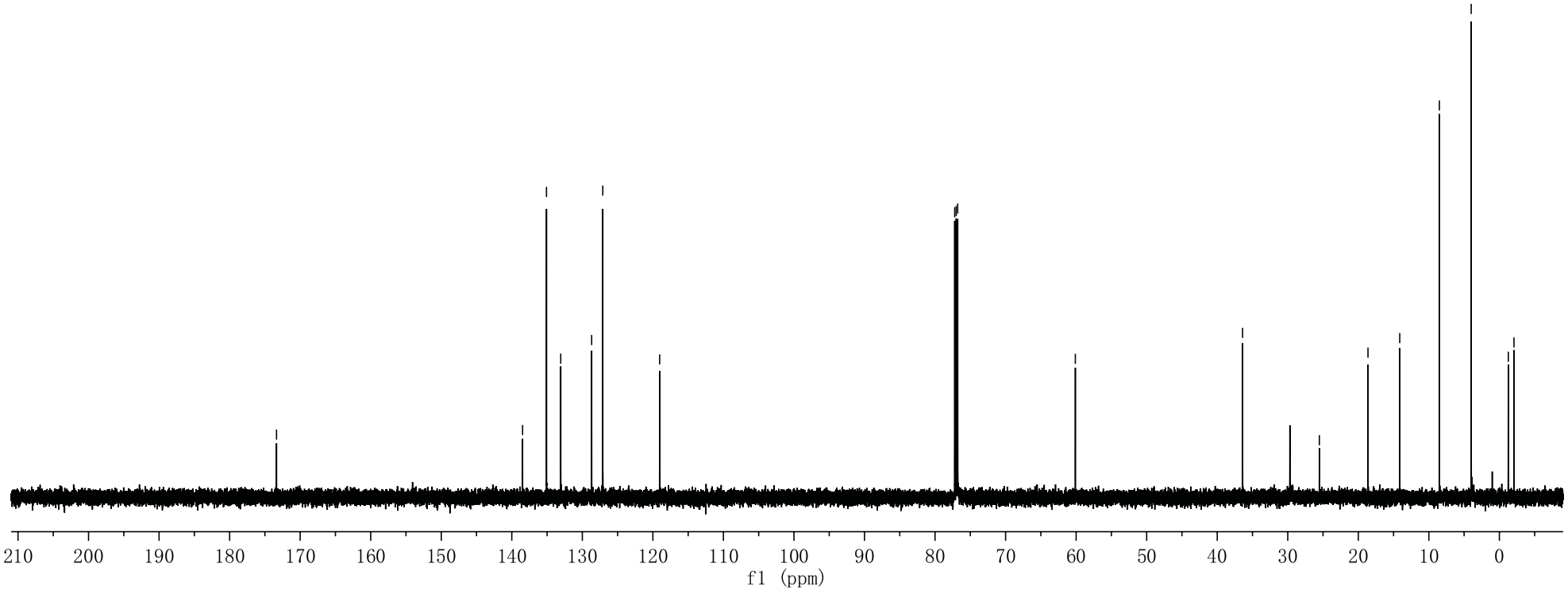
1e

CHU-VII-82F3 C13 CDCl3 600MHz

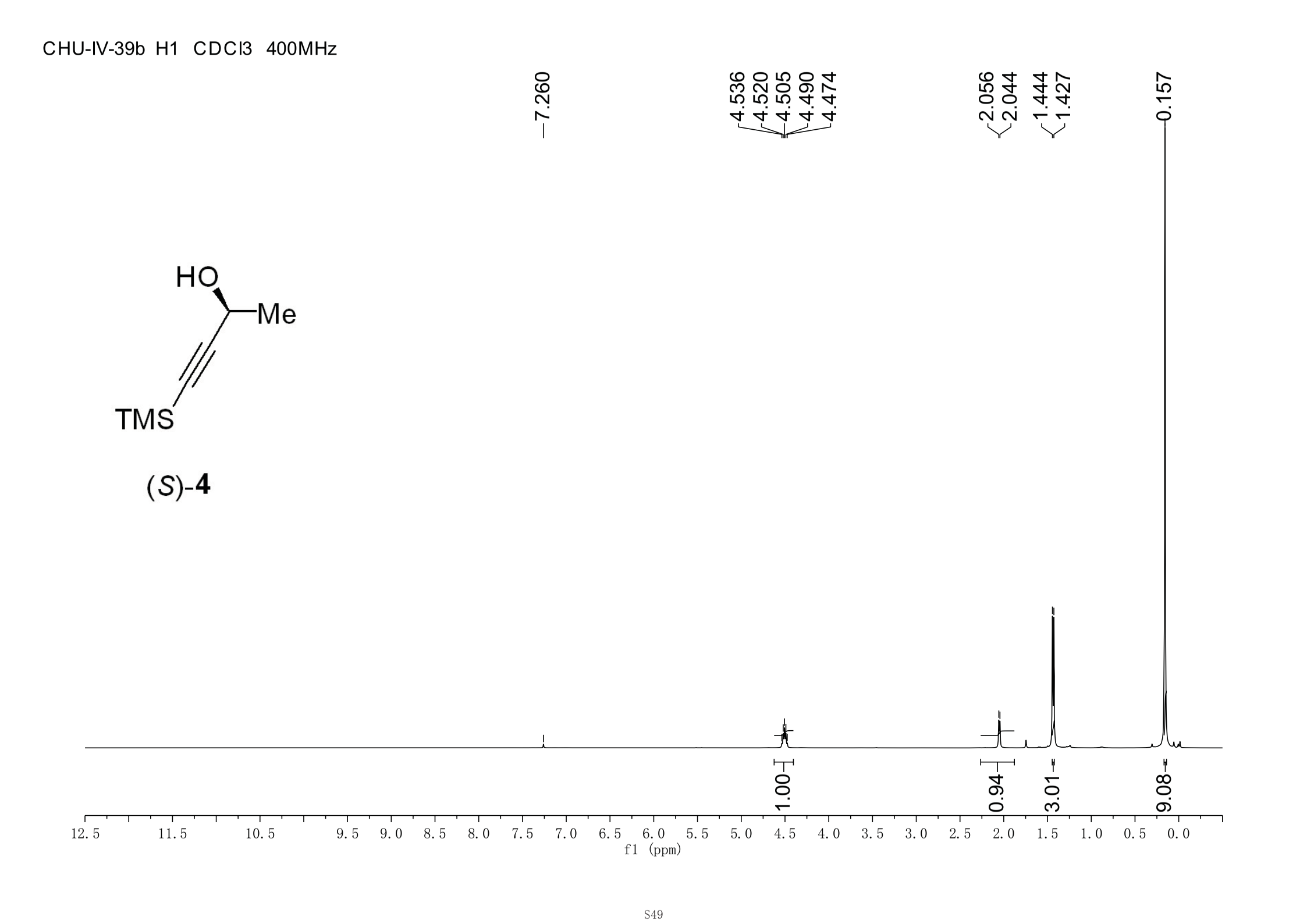
173.350
138.470
135.081
133.061
128.678
127.102
119.039
77.212
77.000
76.789
60.110
36.403
25.518
18.628
14.125
8.505
3.995
-1.266
-2.067



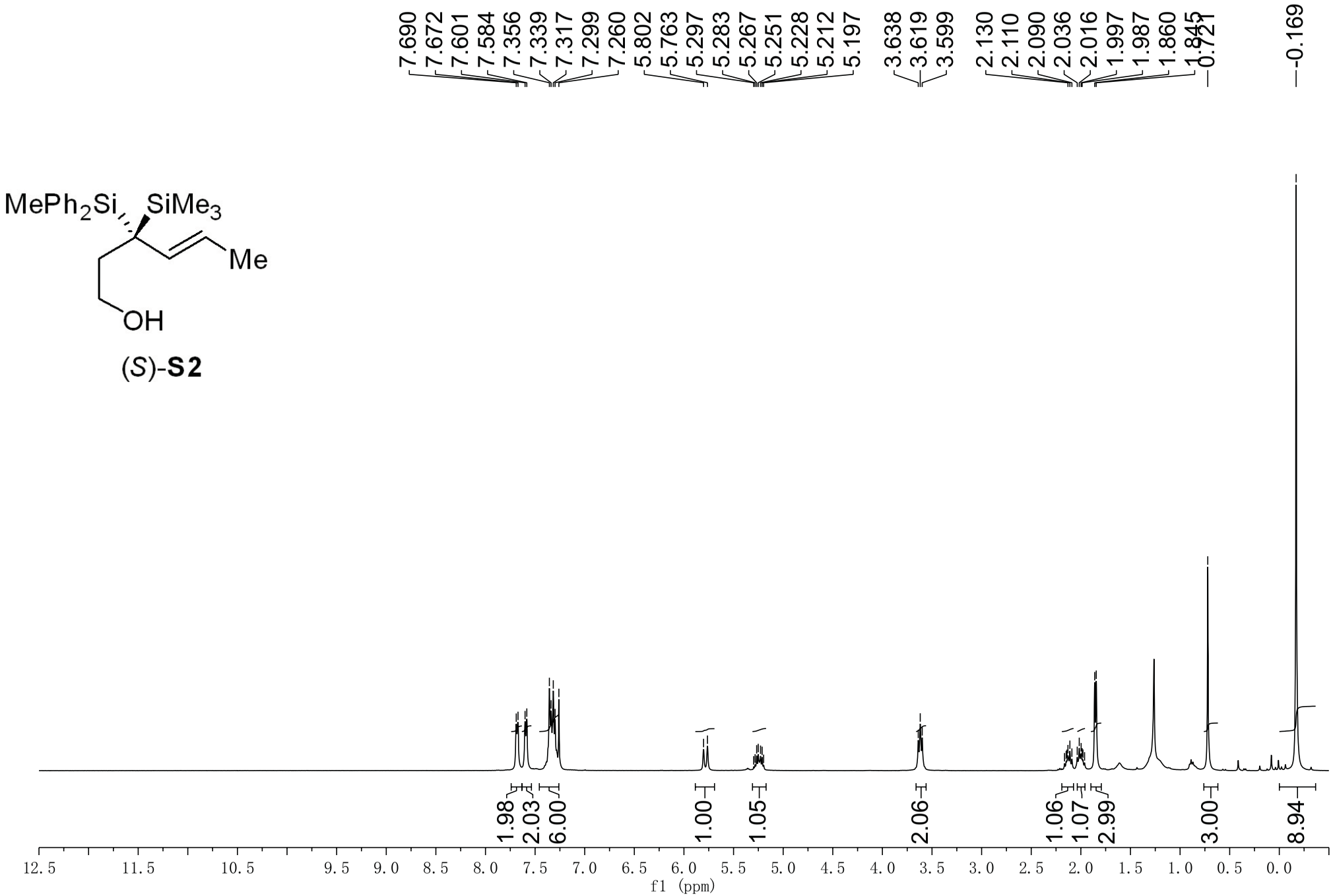
1e



CHU-IV-39b H1 CDCl3 400MHz



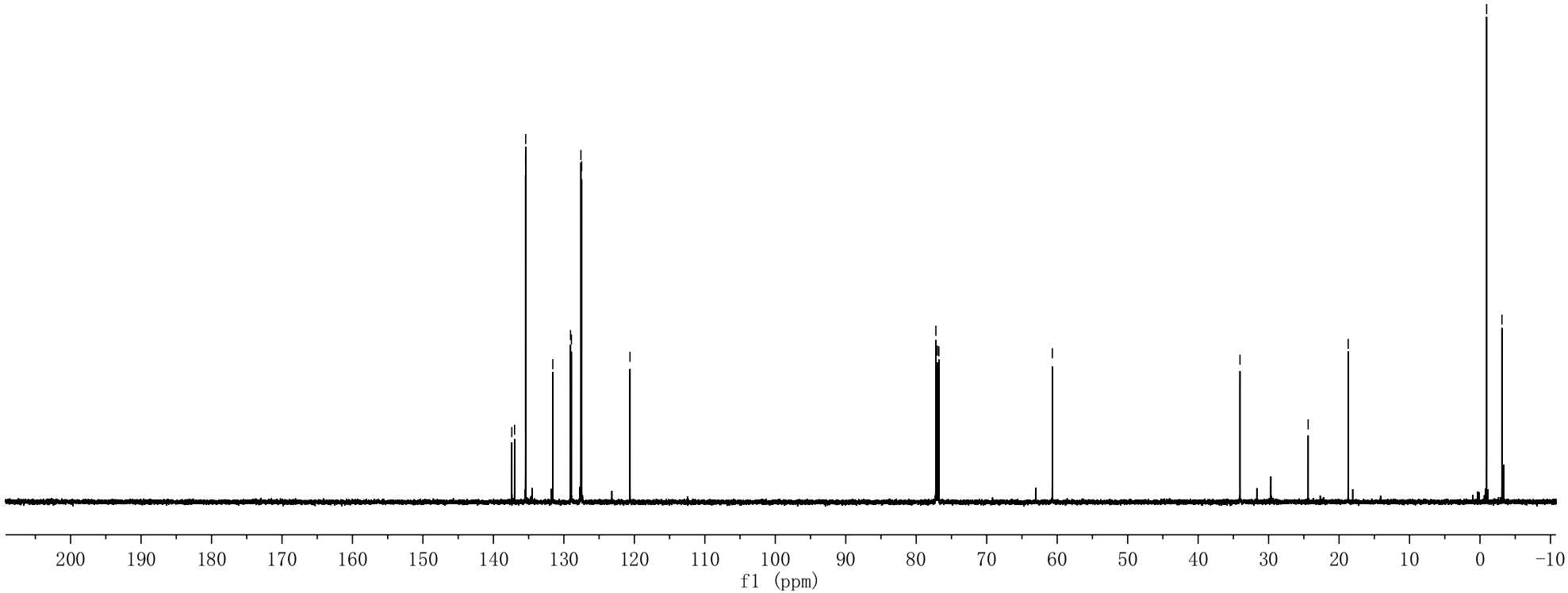
WK-I-31A2 H1 CDCl3 400MHz



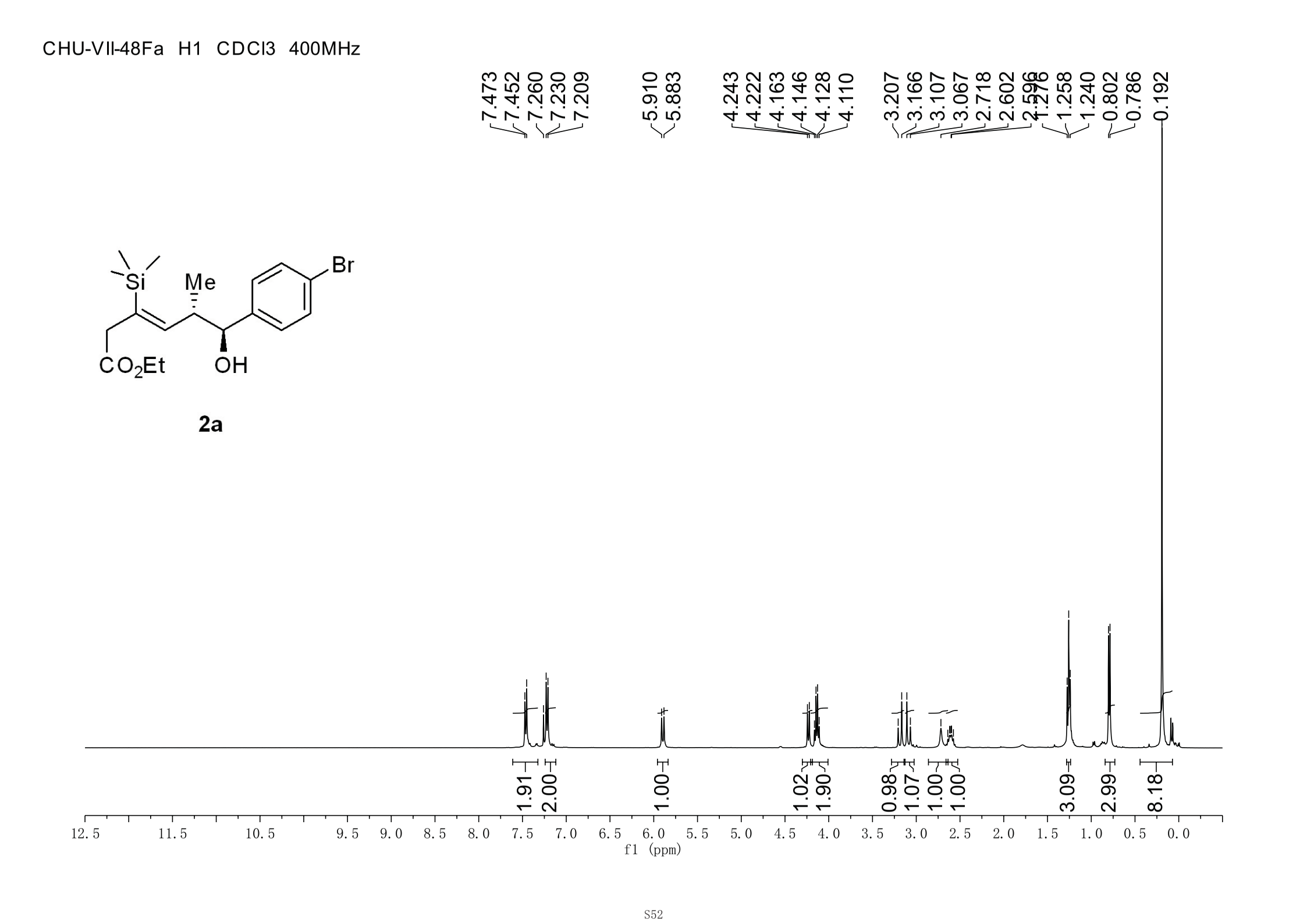
WK-I-28D C13 CDCl3 400MHz

137.391
136.997
135.435
135.415
131.570
129.057
128.933
127.583
127.478
120.618
77.211
77.000
76.788
60.683
34.058
24.388
18.704
-0.940
-3.110

(*S*)-**S2**

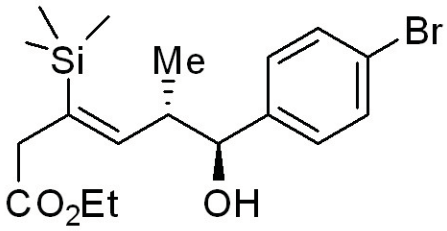


CHU-VII-48Fa H1 CDCl3 400MHz

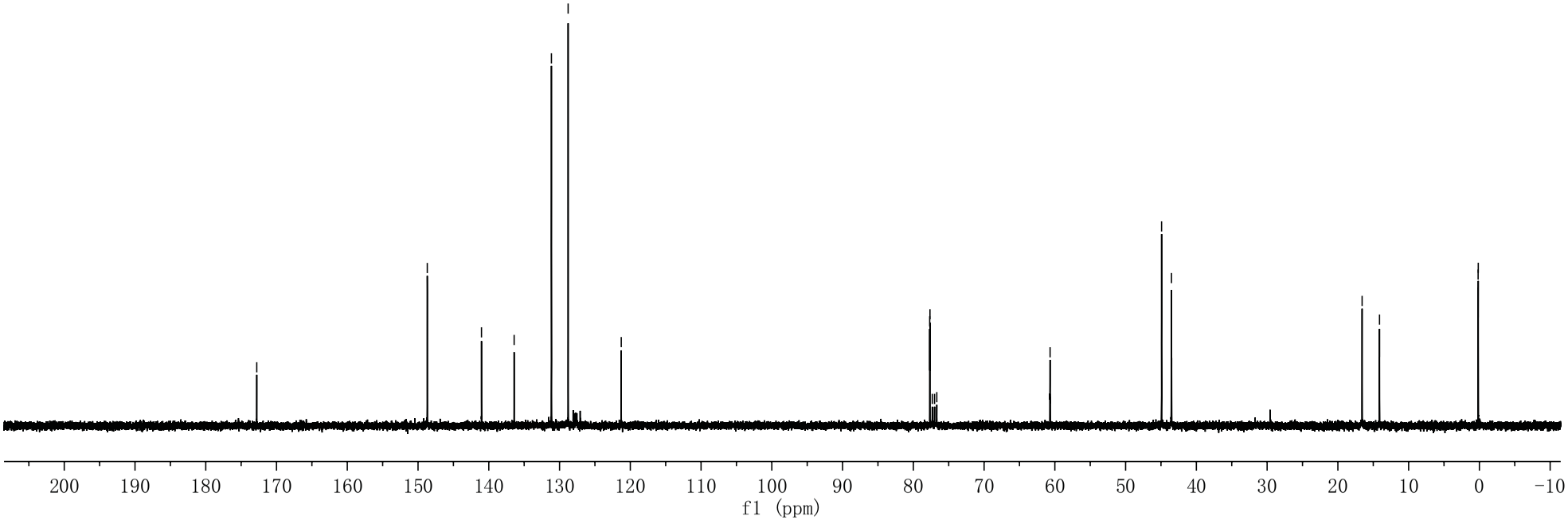


CHU-VII-26Fa C13 CDCl3 600MHz

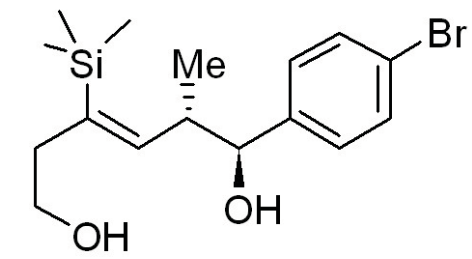
172.792
148.693
141.032
136.417
131.149
128.787
121.280
77.686
77.649
77.321
77.000
76.683
60.673
44.916
43.518
16.575
14.115
0.180
0.159



2a



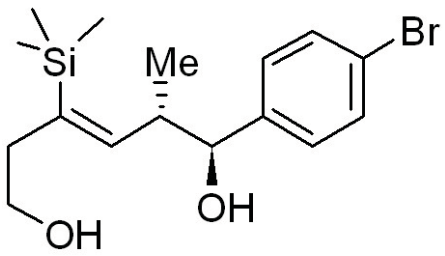
CHU-8-33FPBa H1 CDCl3 400MHz



S3

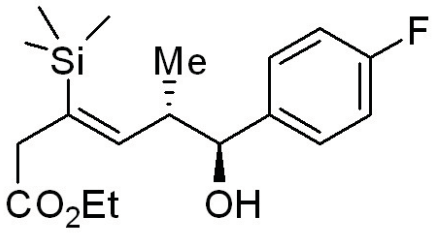
CHU-8-33FPBa C13 CDCl3 400MHz

148.286
141.812
137.936
131.317
128.643
121.414
77.771
77.319
77.000
76.684
60.887
44.846
41.175
16.816
0.578



S3

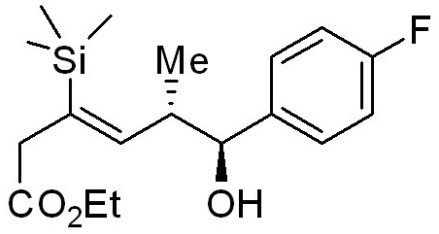
CHU-VII-102F2PB H1 CDCl3 400MHz



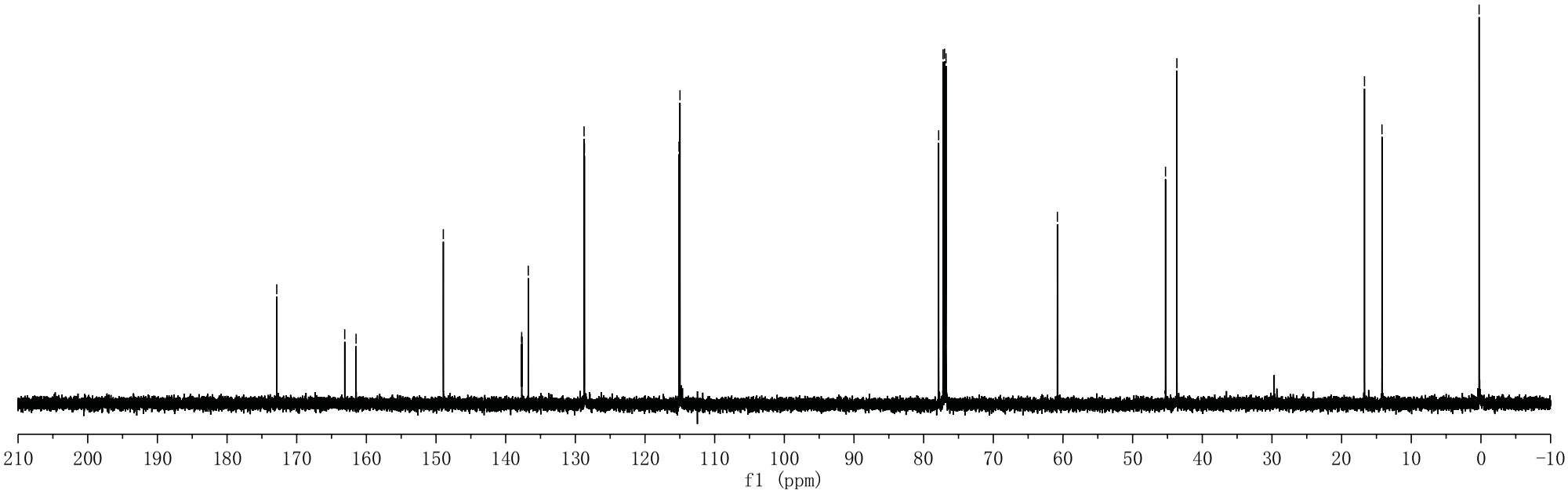
2b

CHU-VII-102F2PB C13 CDCl3 600MHz

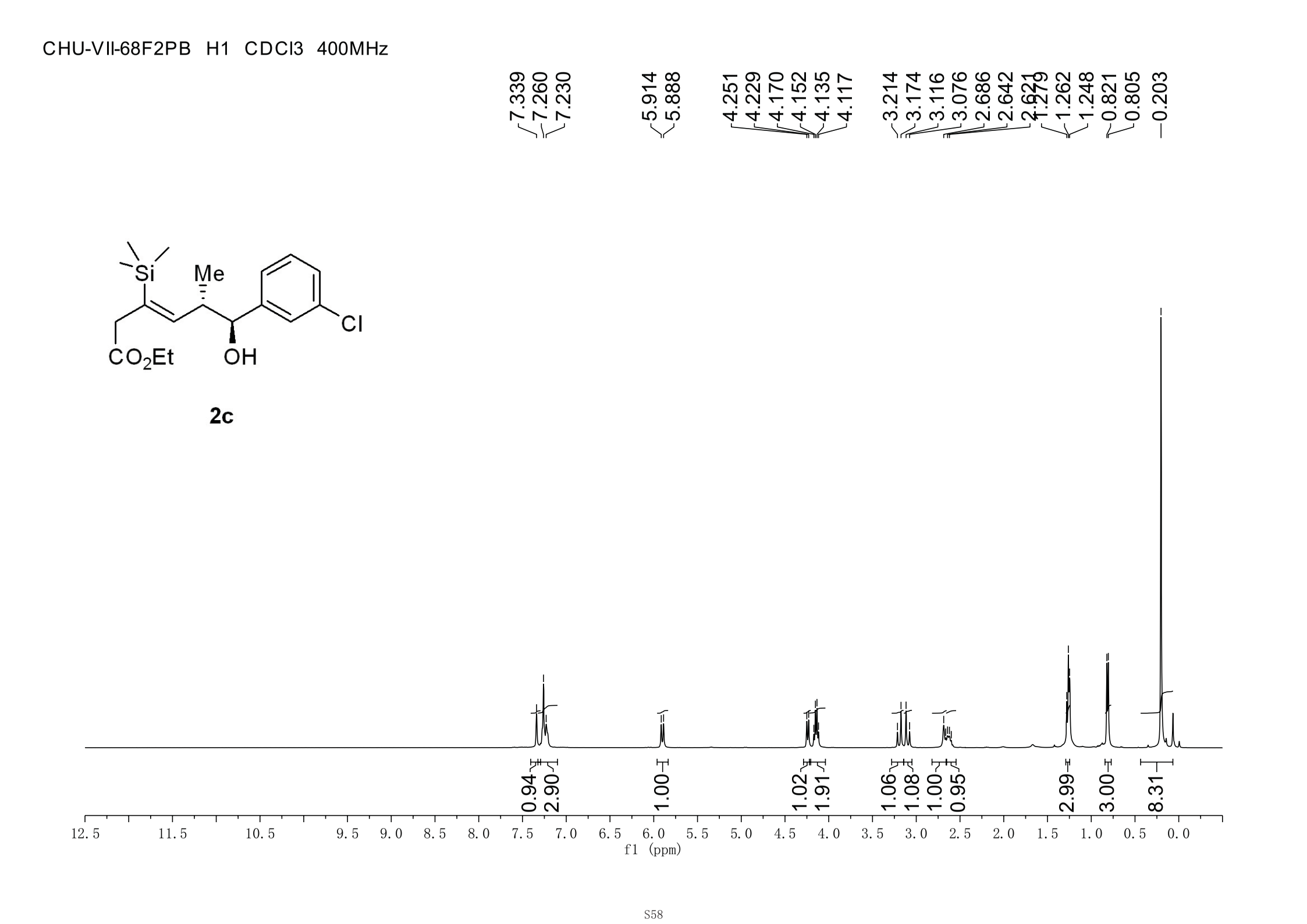
172.866
163.107
161.481
148.954
137.705
136.756
128.748
128.696
115.122
114.980
77.847
77.212
77.000
76.788
60.800
45.279
43.648
16.716
14.205
0.264



2b



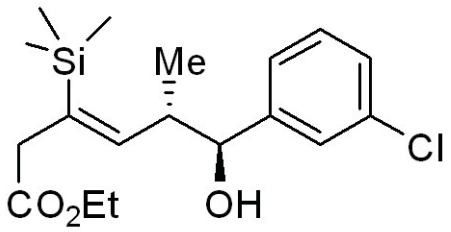
CHU-VII-68F2PB H1 CDCl3 400MHz



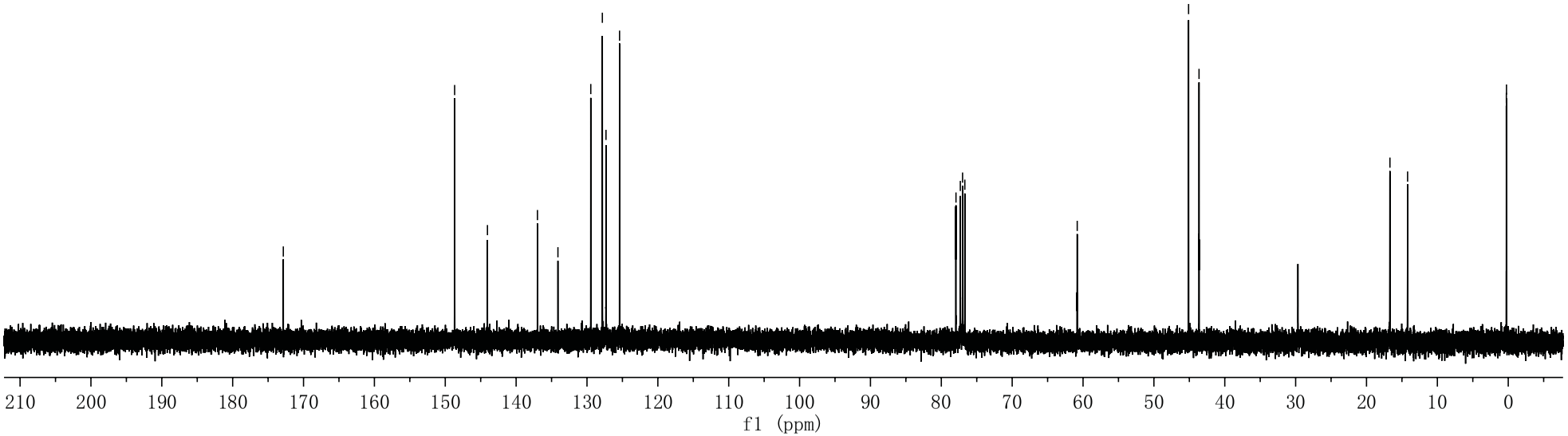
2c

CHU-VII-68F2PB C13 CDCl3 600MHz

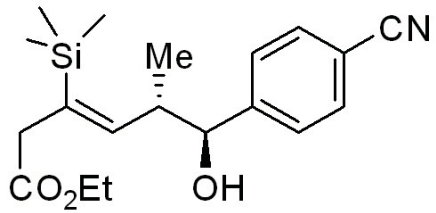
172.853
148.677
144.046
136.991
134.100
129.466
127.833
127.318
125.404
77.931
77.317
77.000
76.682
60.821
45.108
43.633
16.693
14.201
0.266
0.247



2c



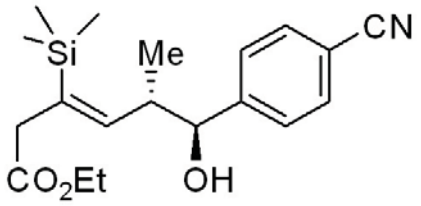
CHU-VII-72F1PB H1 CDCl3 400MHz



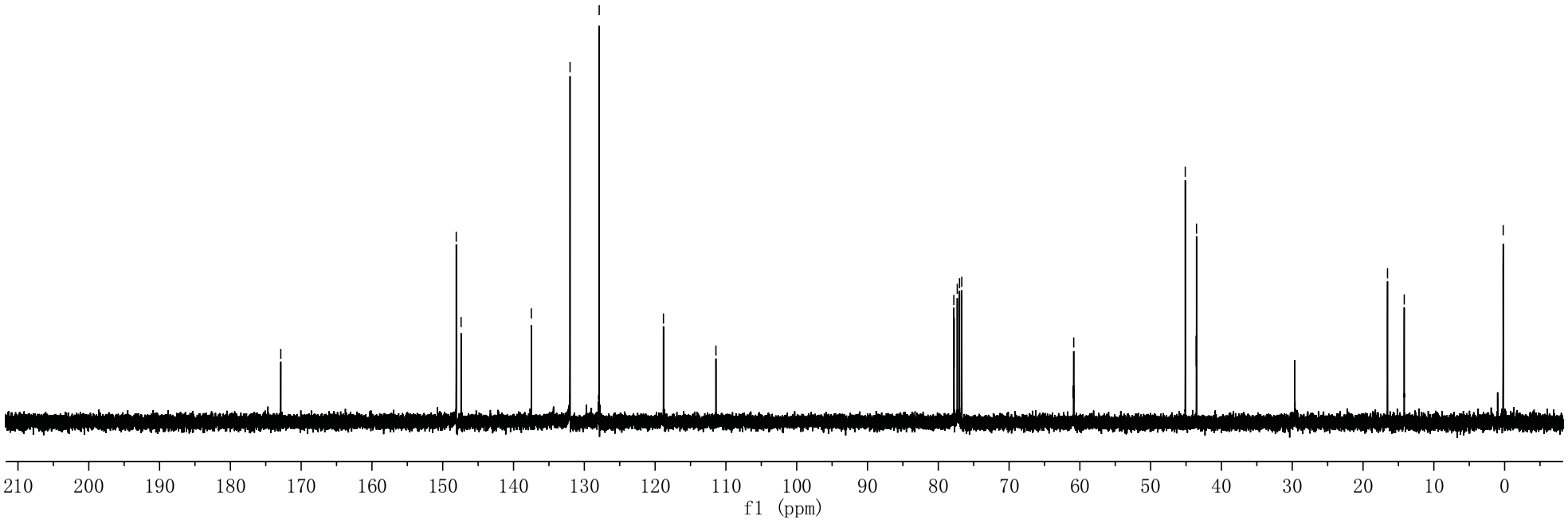
2d

CHU-VII-68F1PB C13 CDCl3 400MHz

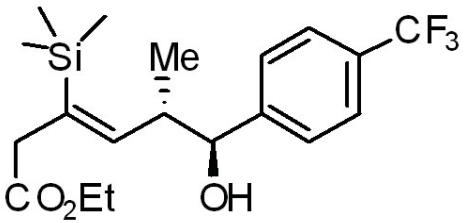
172.877
148.091
147.406
137.484
132.016
127.901
118.822
111.409
77.804
77.318
77.000
76.683
60.869
45.113
43.525
16.545
14.181
0.200



2d



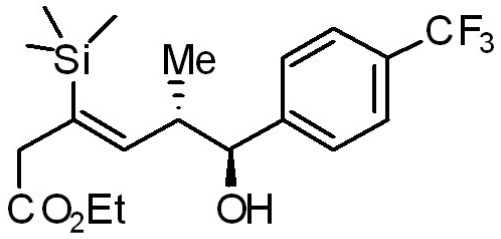
CHU-VII-68F3PB H1 CDCl3 400MHz



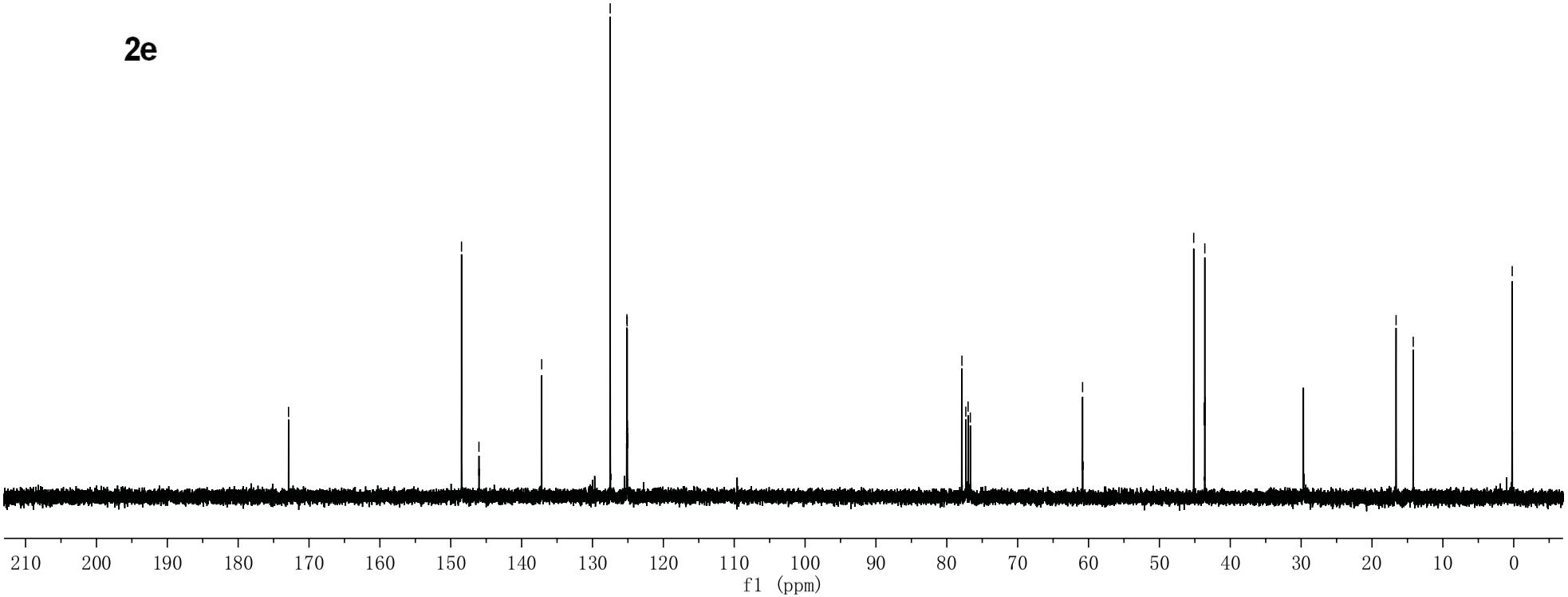
2e

CHU-VII-68F3PB C13 CDCl3 400MHz

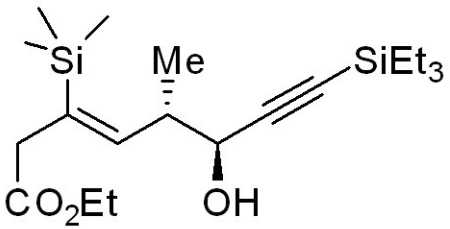
172.891
148.481
146.024
137.162
127.501
125.181
125.143
125.106
125.073
125.063
77.869
77.317
77.000
76.683
60.843
45.161
43.594
16.602
14.179
0.213



2e



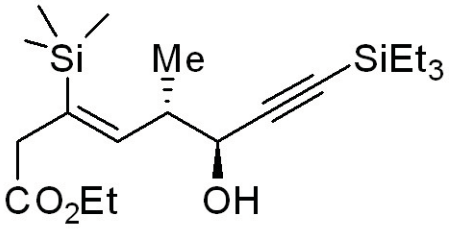
CHU-VII-71F1a4 H1 CDCl3 400MHz



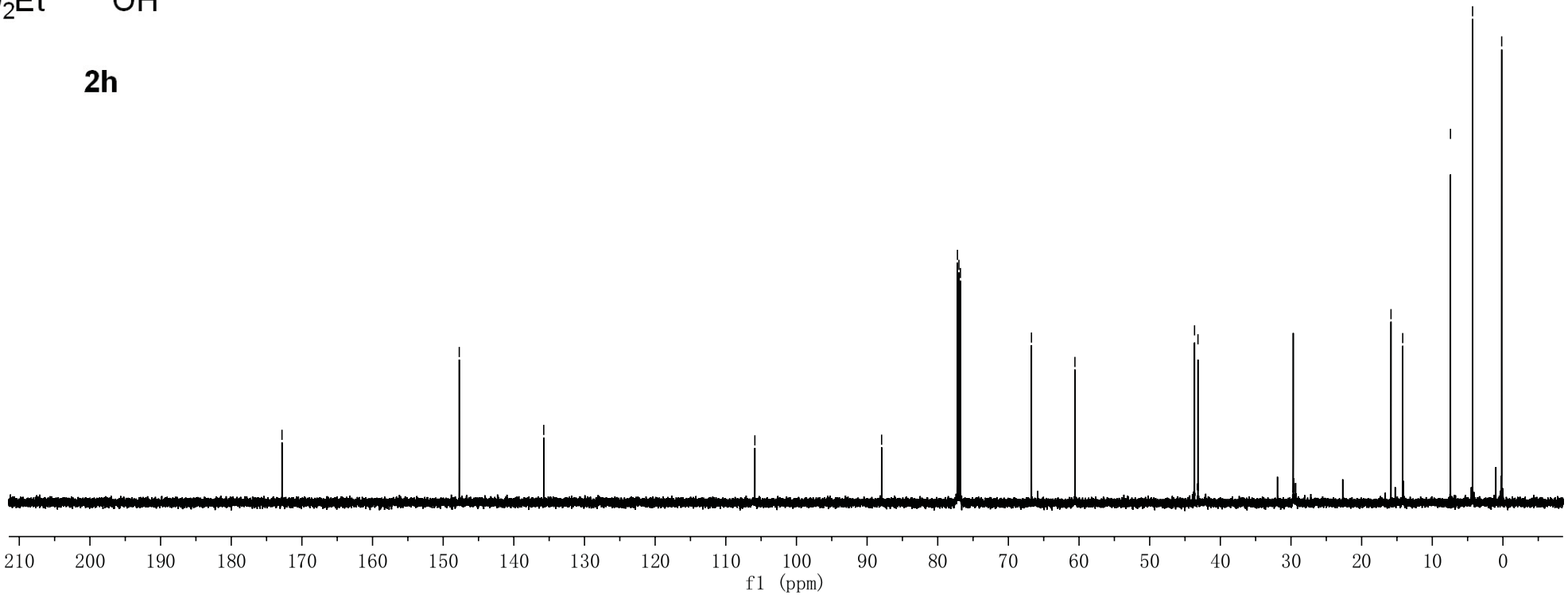
2h

CHU-VII-71F1a4 C13 CDCl3 600MHz

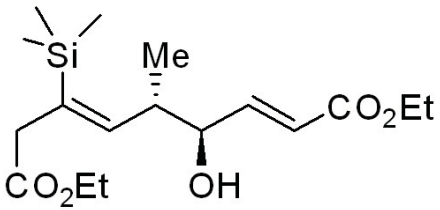
172.816
147.724
135.766
105.886
87.942
77.211
77.000
76.788
66.734
60.582
43.652
43.166
15.844
14.183
7.424
4.294
0.176



2h



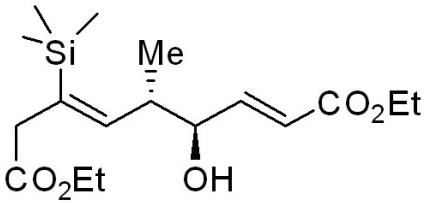
CHU-VII-72F4PB H1 CDCl3 400MHz



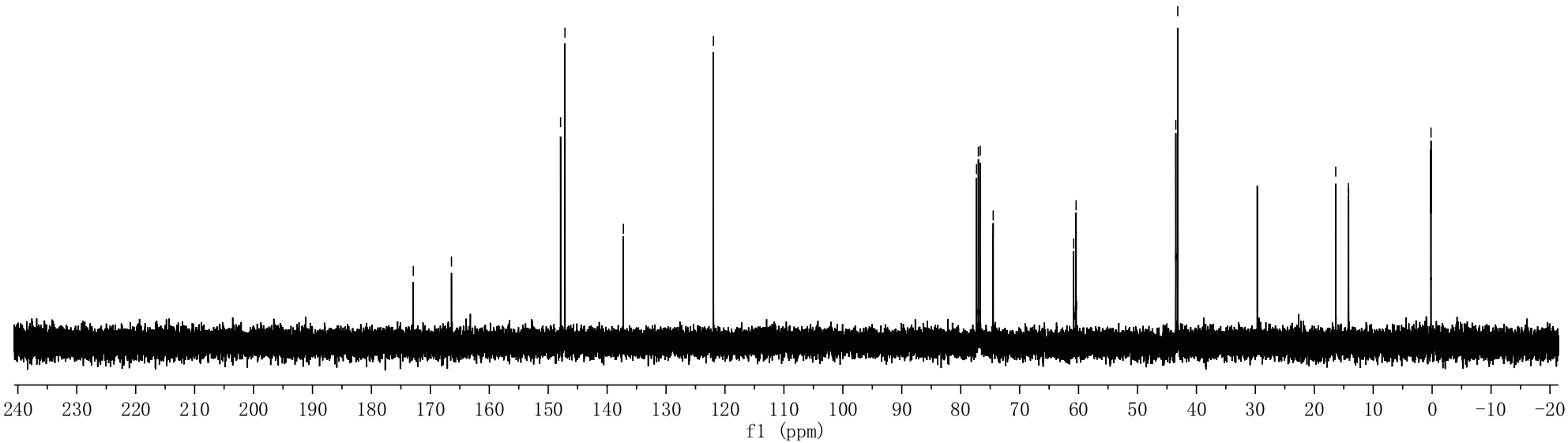
2g

CHU-VII-72F4PB C13 CDCl3 400MHz

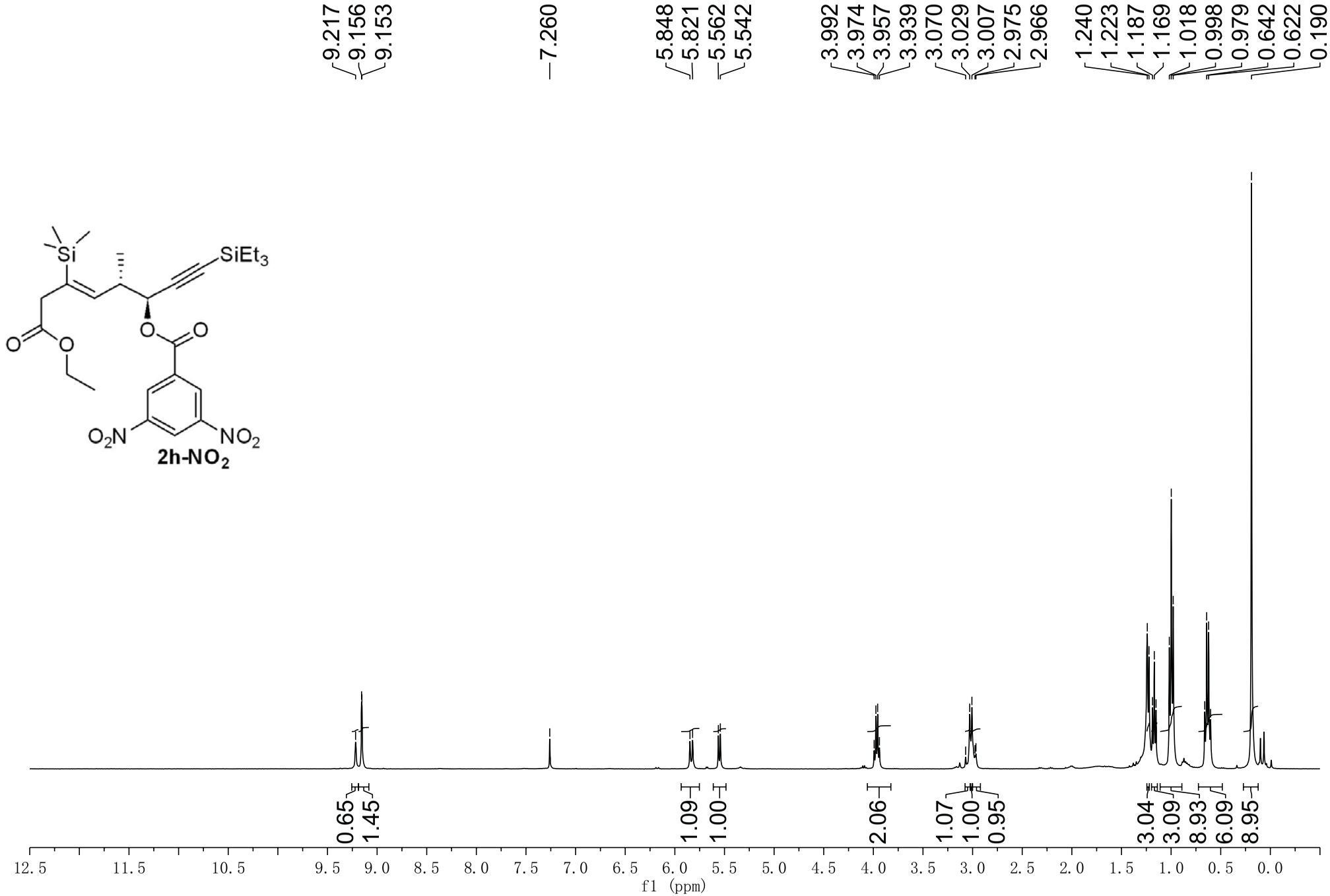
172.892
166.415
147.902
147.159
137.244
121.961
77.317
77.000
76.683
74.482
60.824
60.415
43.495
43.169
16.355
14.221
14.170
0.188



2g

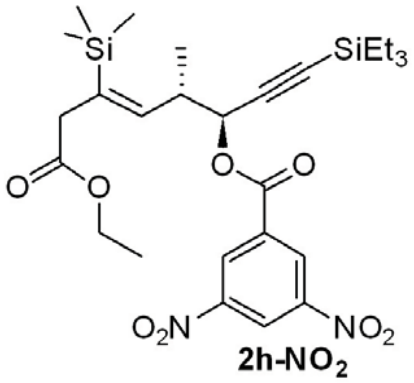


CHU-VII-105F6PB H1 CDCl3 400MHz

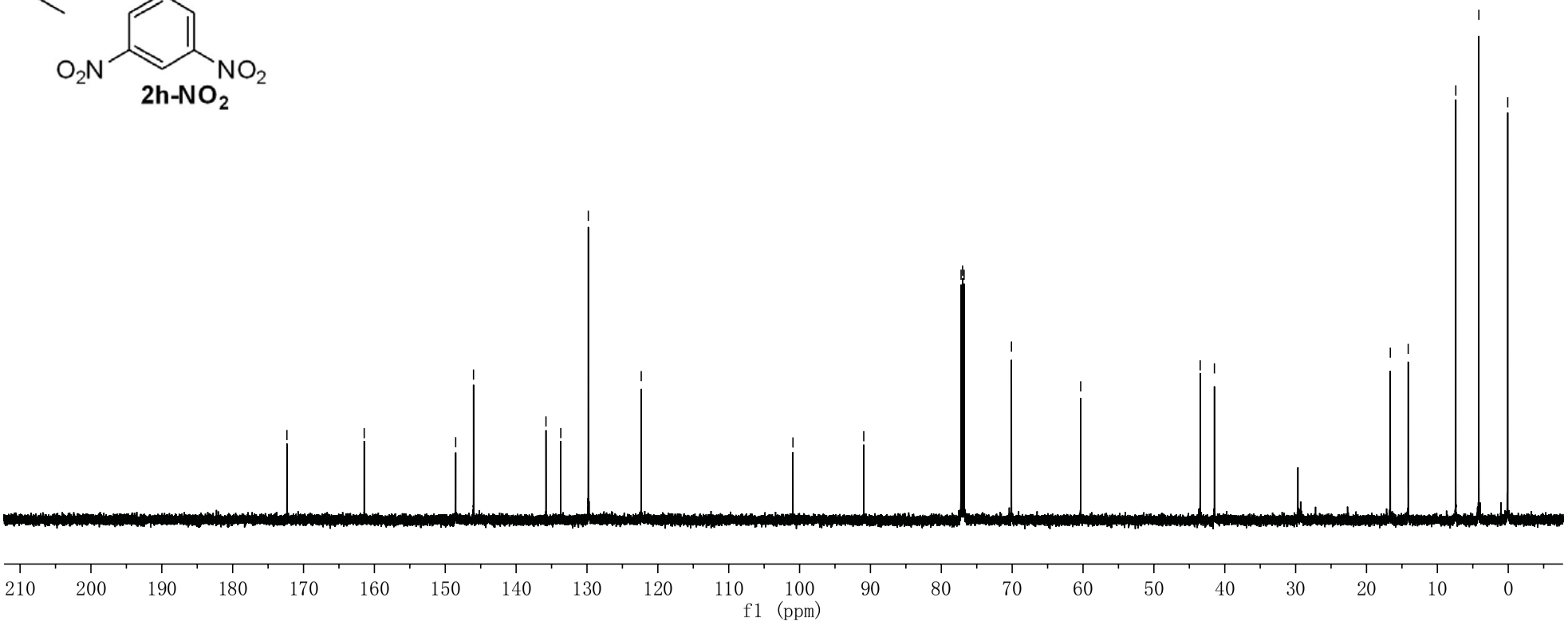


CHU-VII-105F6PB C13 CDCl3 600MHz

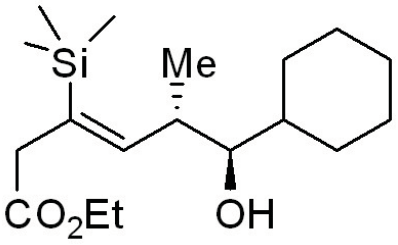
172.343
161.438
148.528
146.013
135.787
133.697
129.815
122.346
100.938
90.944
77.211
77.000
76.788
70.102
60.331
43.466
41.462
16.638
14.116
7.399
4.146
0.070



2h-NO_2



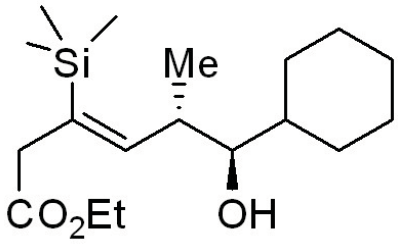
CHU-VII-83P2 H1 CDCl3 400MHz



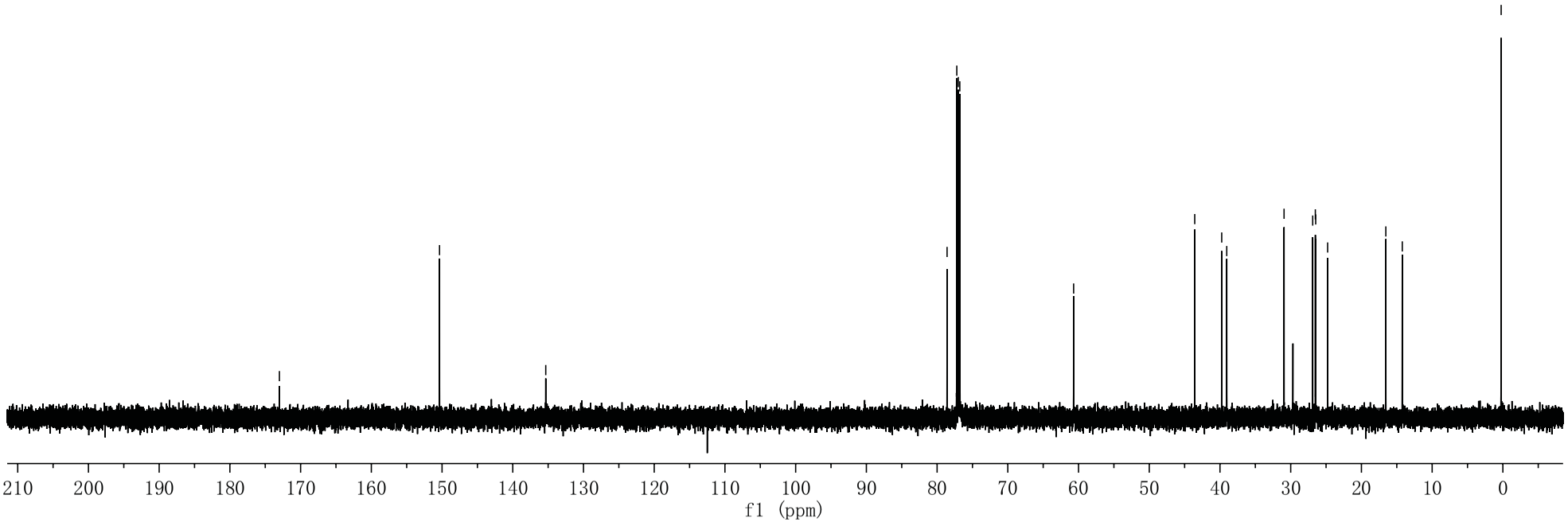
2i

CHU-VII-83P2 C13 CDCl3 600MHz

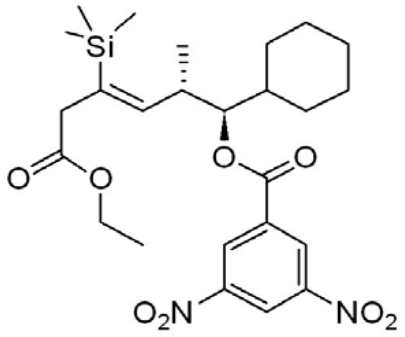
172.996
150.355
135.336
78.590
77.212
77.000
76.789
60.693
43.570
39.754
39.044
30.940
26.889
26.517
26.467
24.777
16.550
14.224
0.243



2i



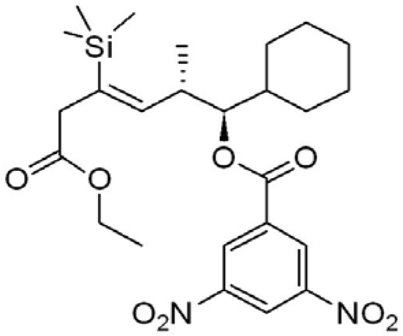
CHU-VII-105F5PB H1 CDCl3 400MHz



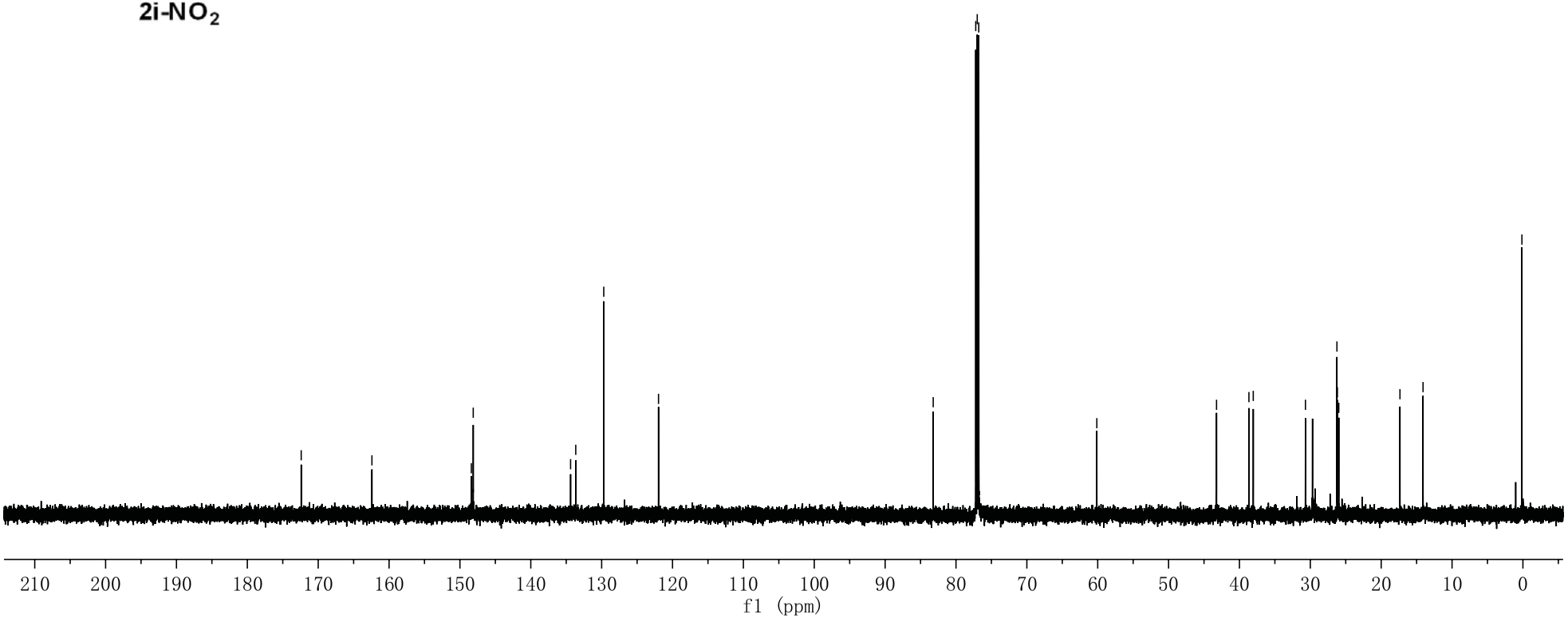
2i-NO_2

CHU-VII-105F5PB C13 CDCl3 600MHz

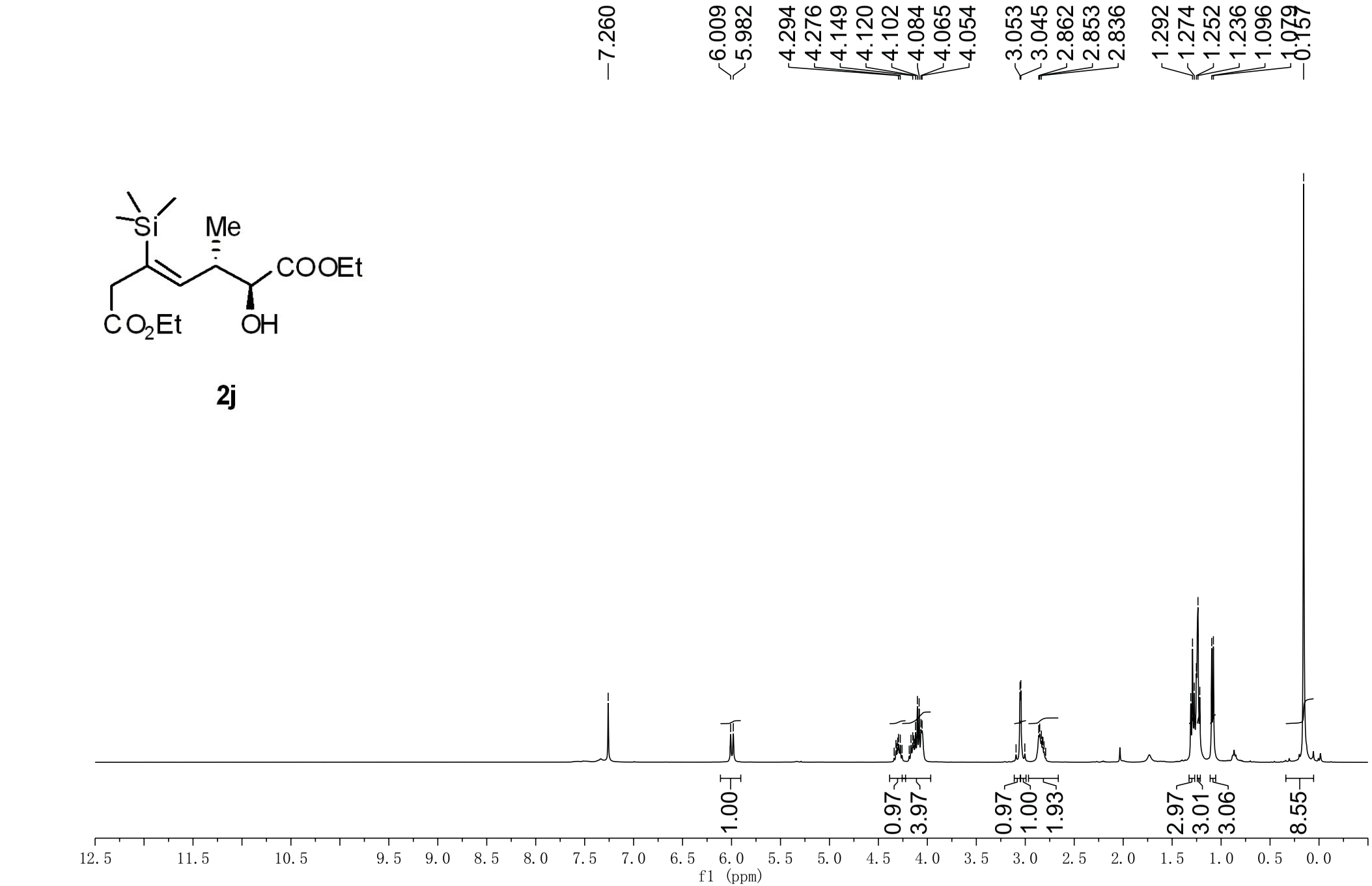
172.397
162.417
148.390
148.121
134.384
133.655
129.703
121.976
83.213
77.211
77.000
76.788
60.124
43.234
38.662
38.050
30.686
26.244
26.182
25.981
17.349
14.092
0.140



2i-NO_2



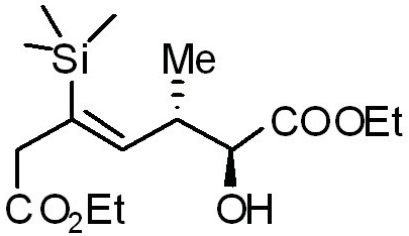
CHU-VII-83P1 H1 CDCl3 400MHz



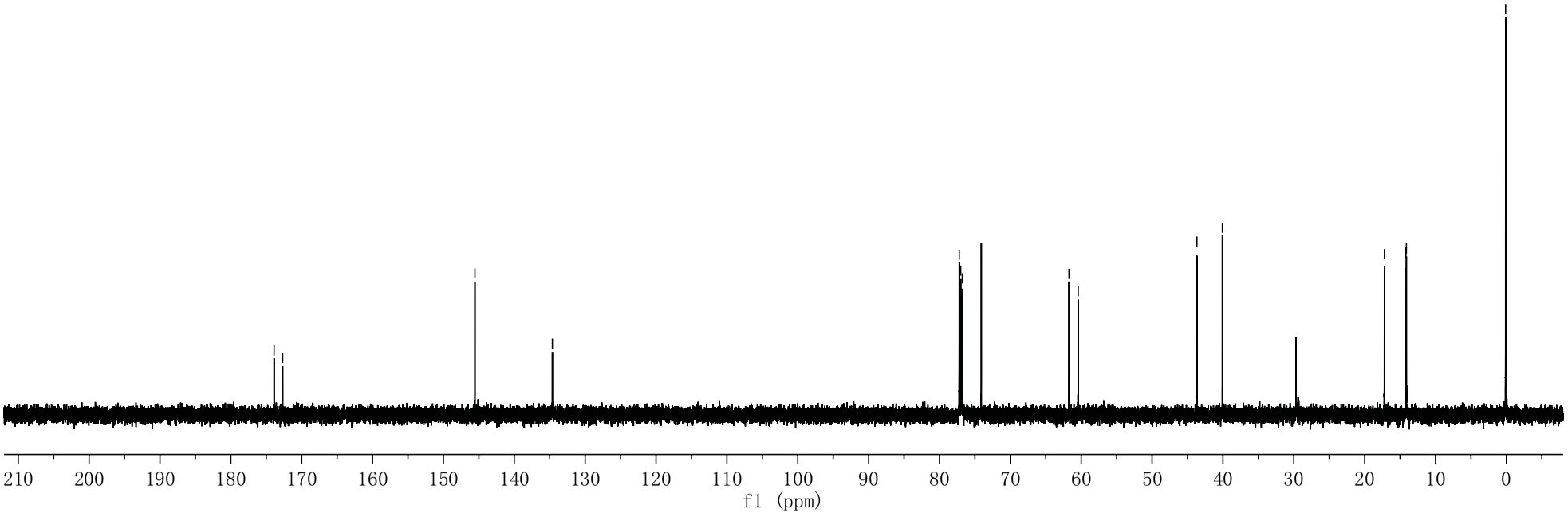
2j

CHU-VII-83P1 C13 CDCl3 600MHz

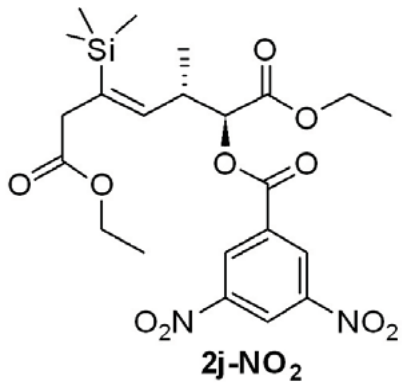
173.895
172.685
145.552
134.625
77.211
77.000
76.788
61.725
60.421
43.672
40.079
17.216
14.178
14.112
0.109



2j



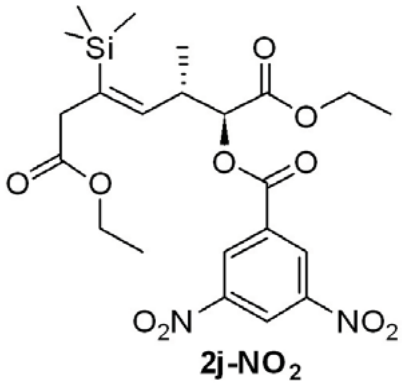
CHU-VII-105F4PB H1 CDCl3 400MHz



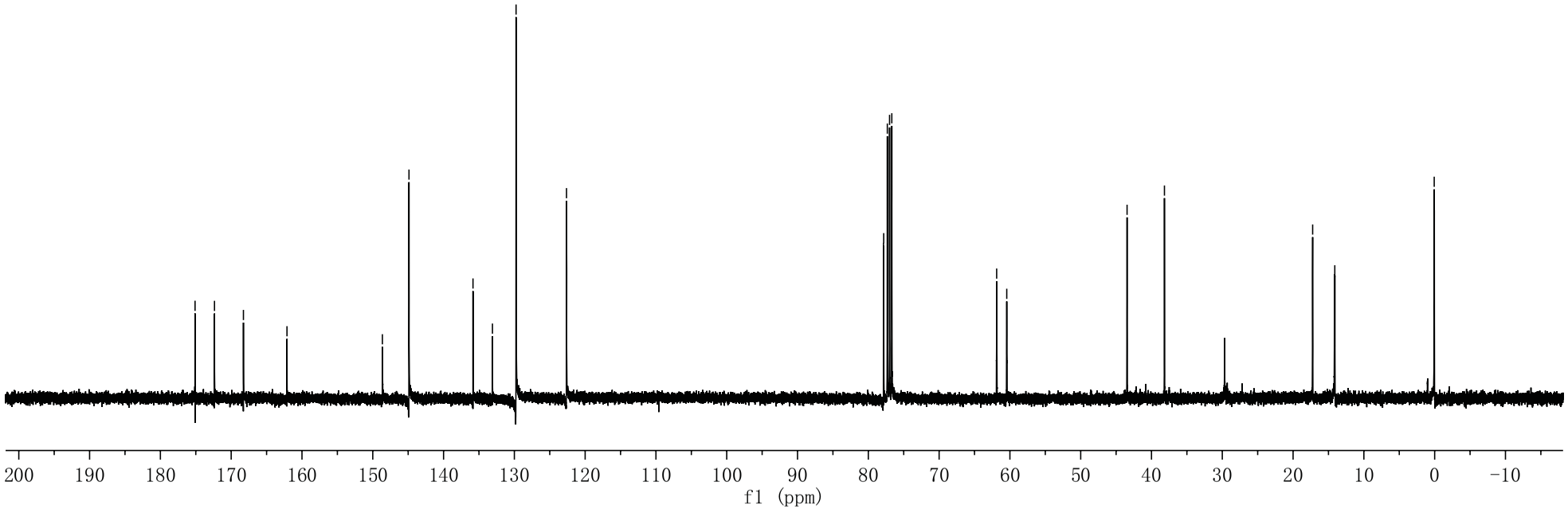
2j-NO_2

CHU-VII-105F1PB C13 CDCl3 400MHz

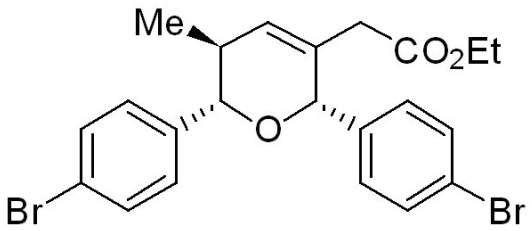
175.102
172.358
168.270
162.119
148.641
144.884
135.843
133.094
129.759
122.633
77.856
77.826
77.317
77.000
76.682
61.870
60.446
43.450
38.171
17.235
14.108
0.065



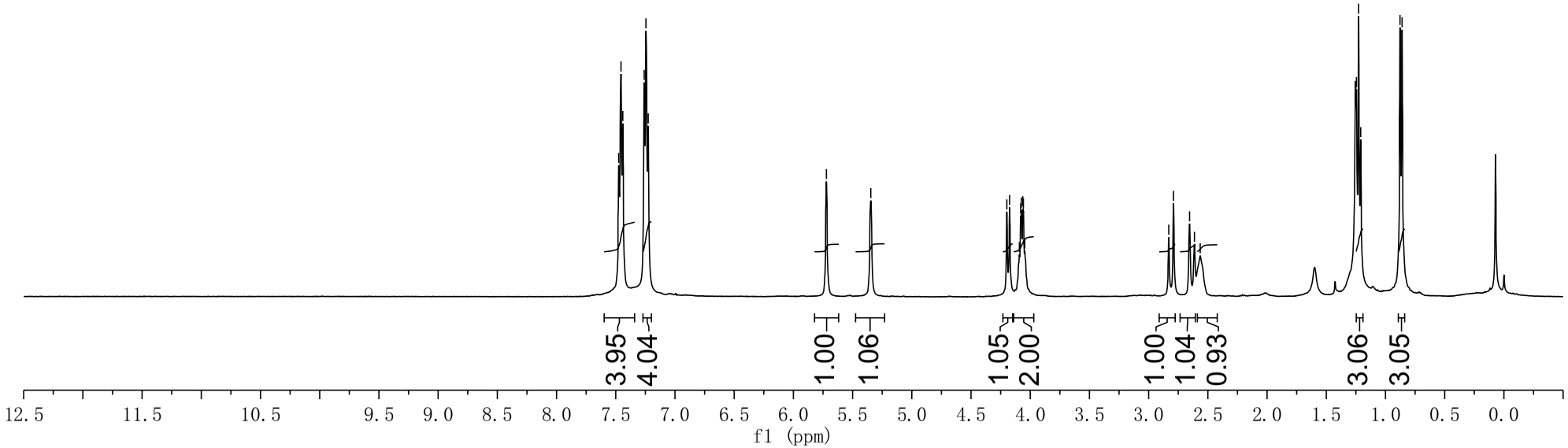
2j-NO_2



CHU-VI-prins-b H1 CDCl3 400MHz

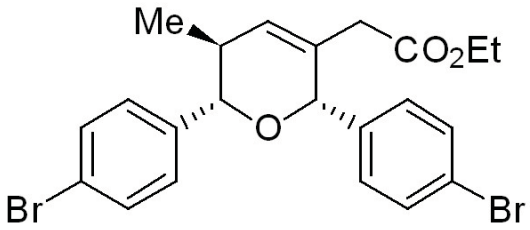


3a

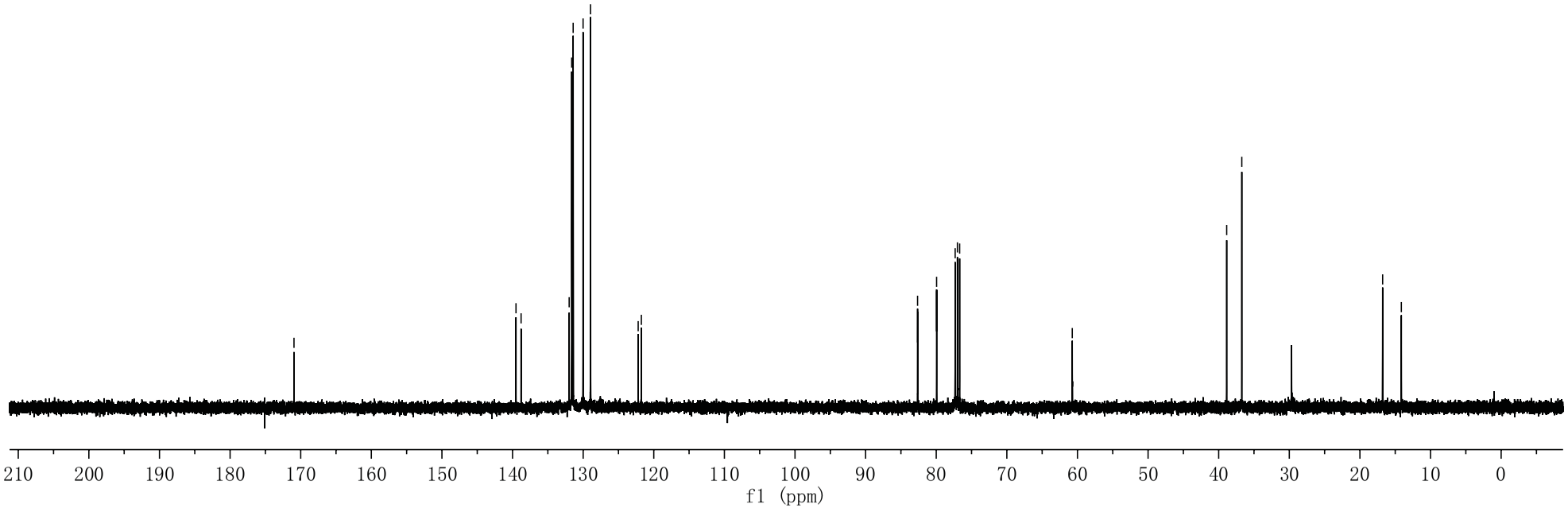


CHU-VI-prins-b C13 CDCl3 400MHz

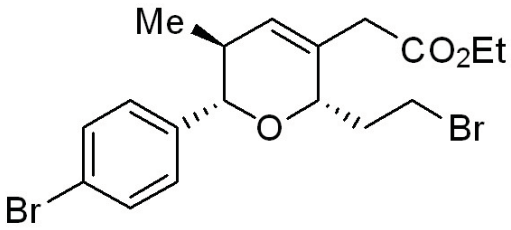
170.950
139.511
138.790
131.982
131.623
131.415
130.012
128.957
122.208
121.759
82.644
79.948
77.319
77.000
76.684
60.736
38.866
36.727
16.780
14.134



3a



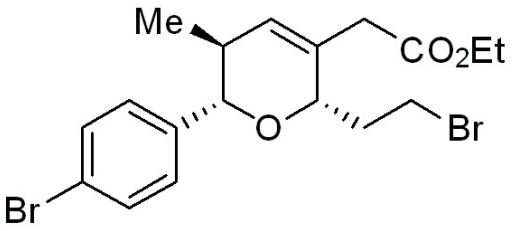
CHU-VII-99F1PB H1 CDCl3 400MHz



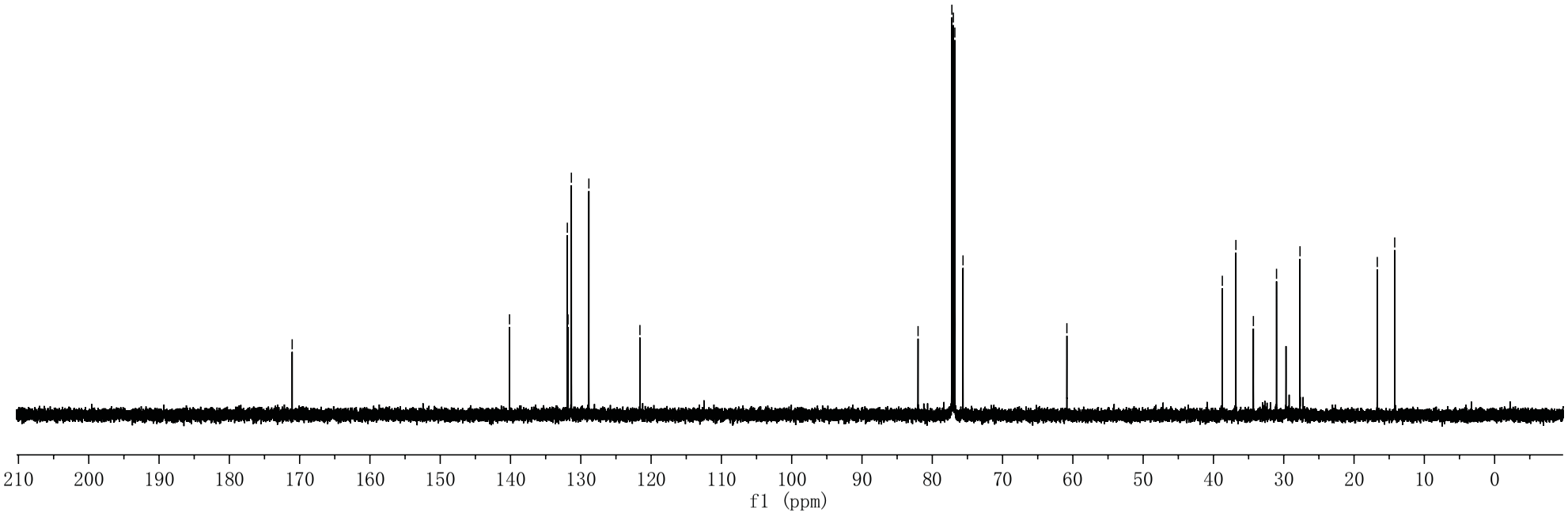
3b

CHU-VII-99F1PB C13 CDCl3 600MHz

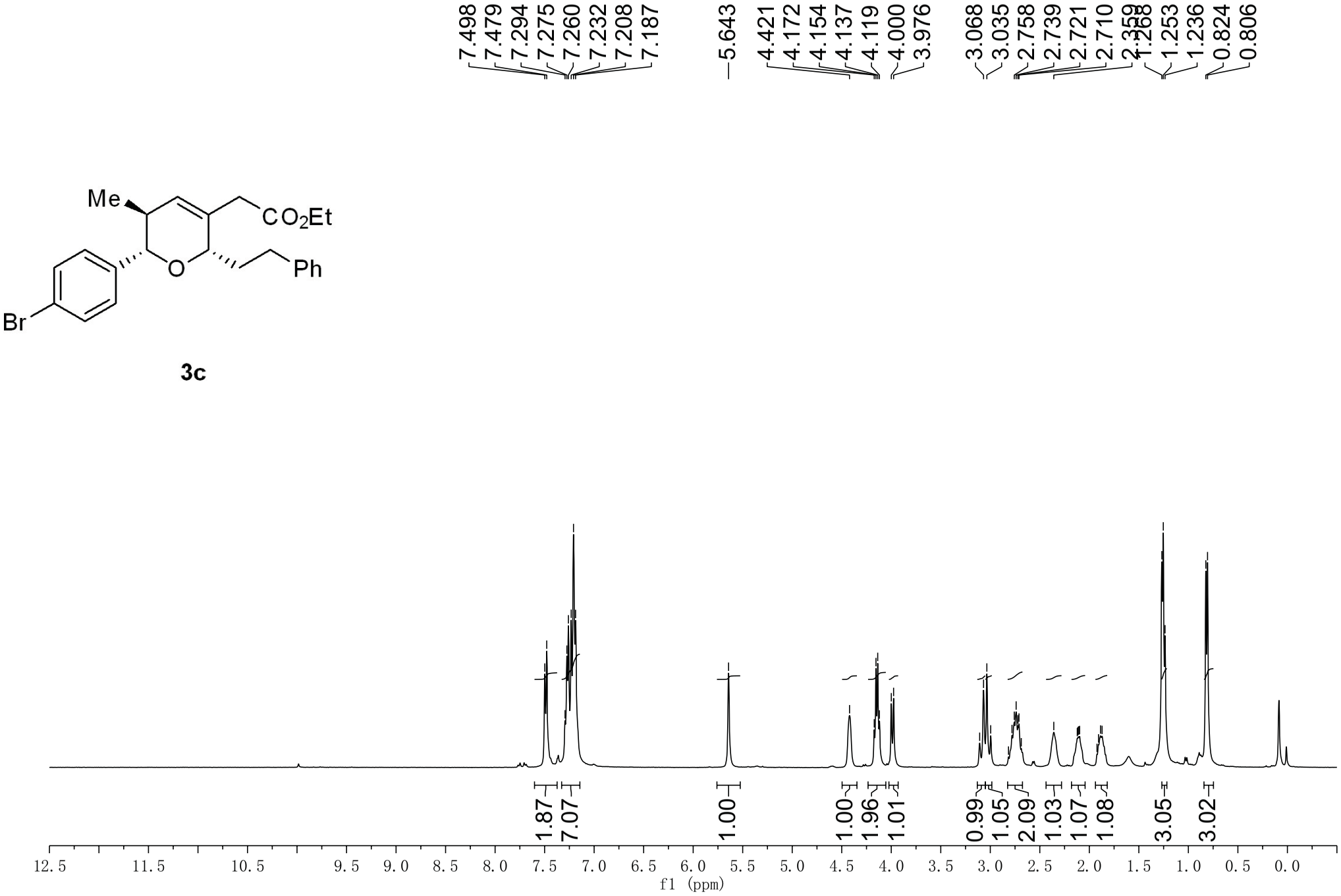
171.061
140.142
131.918
131.816
131.343
128.855
121.590
82.022
77.211
77.000
76.788
75.627
60.851
38.737
36.806
34.318
31.025
27.687
16.691
14.213



3b



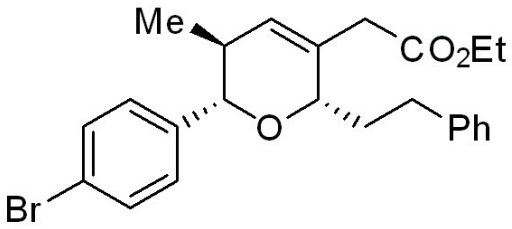
CHU-VII-41F2PB H1 CDCl3 400MHz



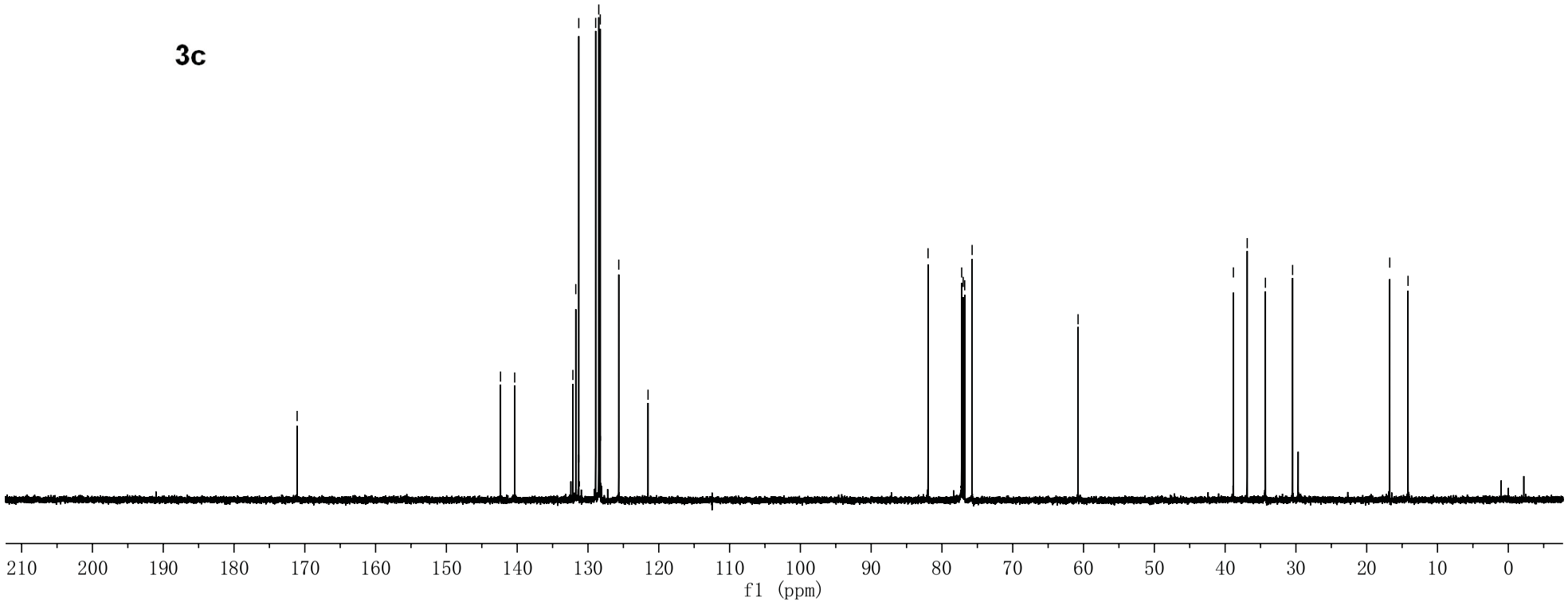
3c

CHU-VII-41F2PB C13 CDCl3 600MHz

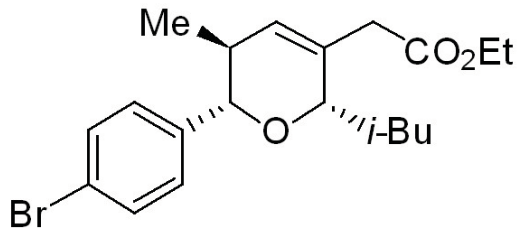
171.084
142.353
140.355
132.134
131.724
131.301
128.914
128.476
128.266
125.651
121.516
81.963
77.212
77.000
76.788
75.738
60.773
38.831
36.880
34.309
30.469
16.747
14.163



3c



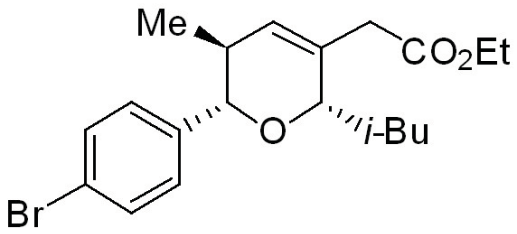
CHU-8-3F1b H1 CDCl3 400MHz



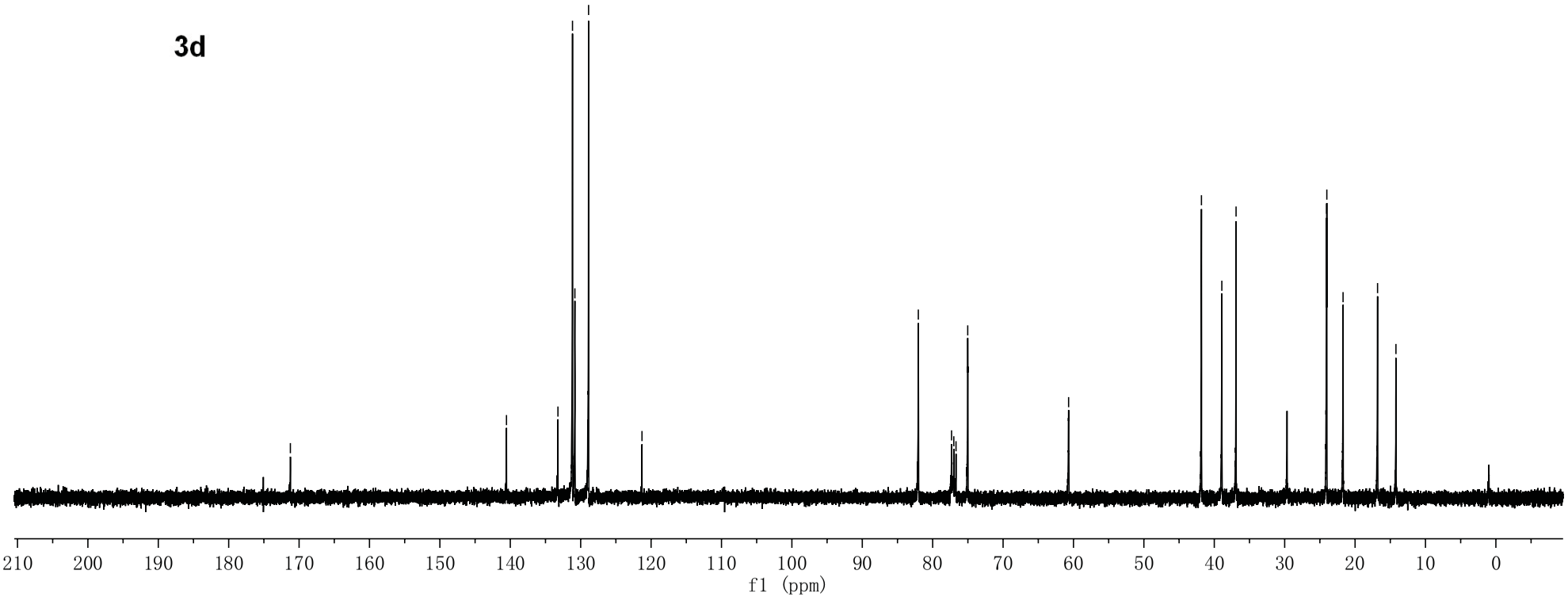
3d

CHU-VII-34F1 C13 CDCl3 400MHz

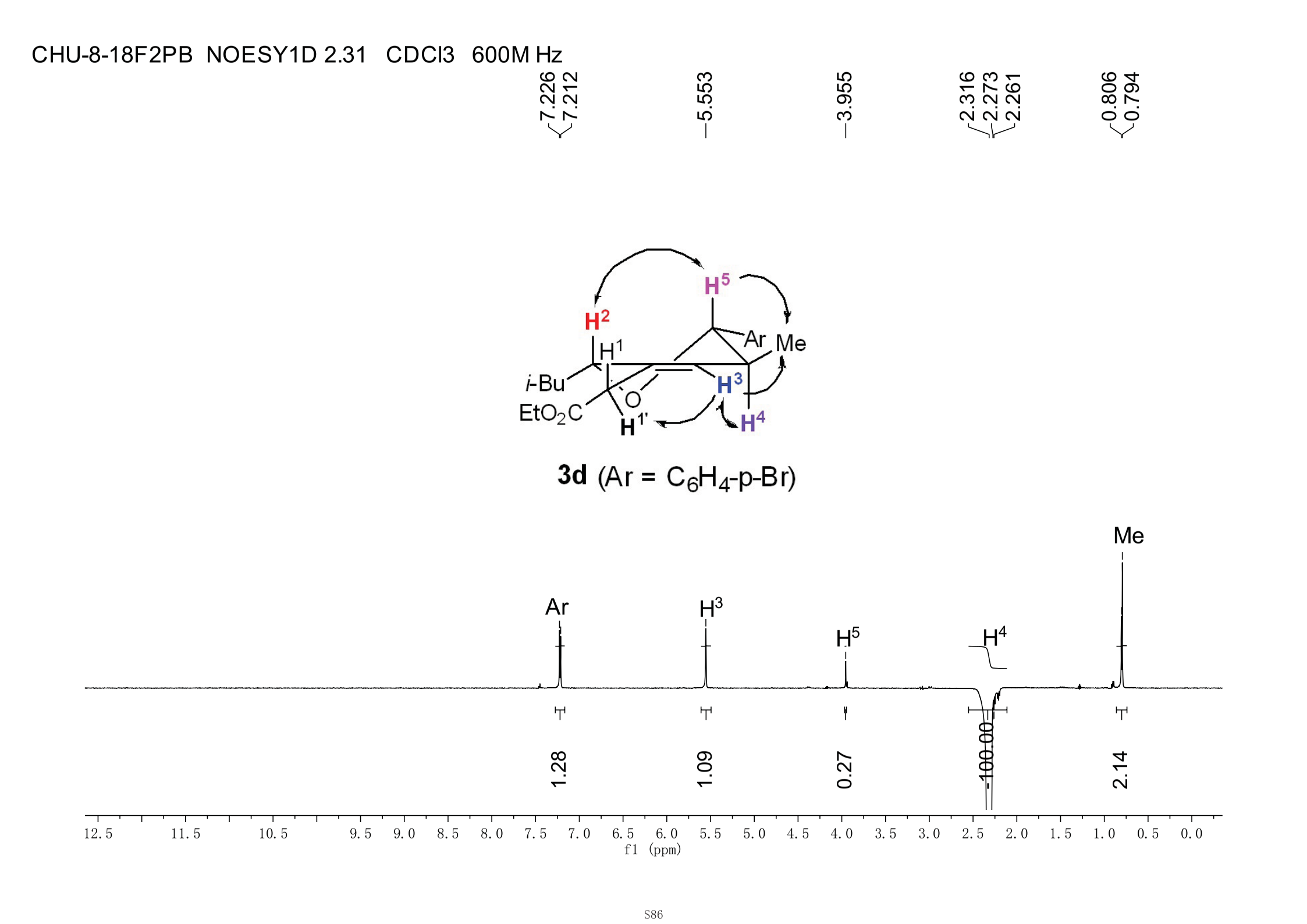
171.237
140.539
133.229
131.163
130.823
128.878
121.292
82.040
77.318
77.000
76.685
75.022
60.692
41.824
38.928
36.906
24.052
24.012
21.708
16.806
14.195



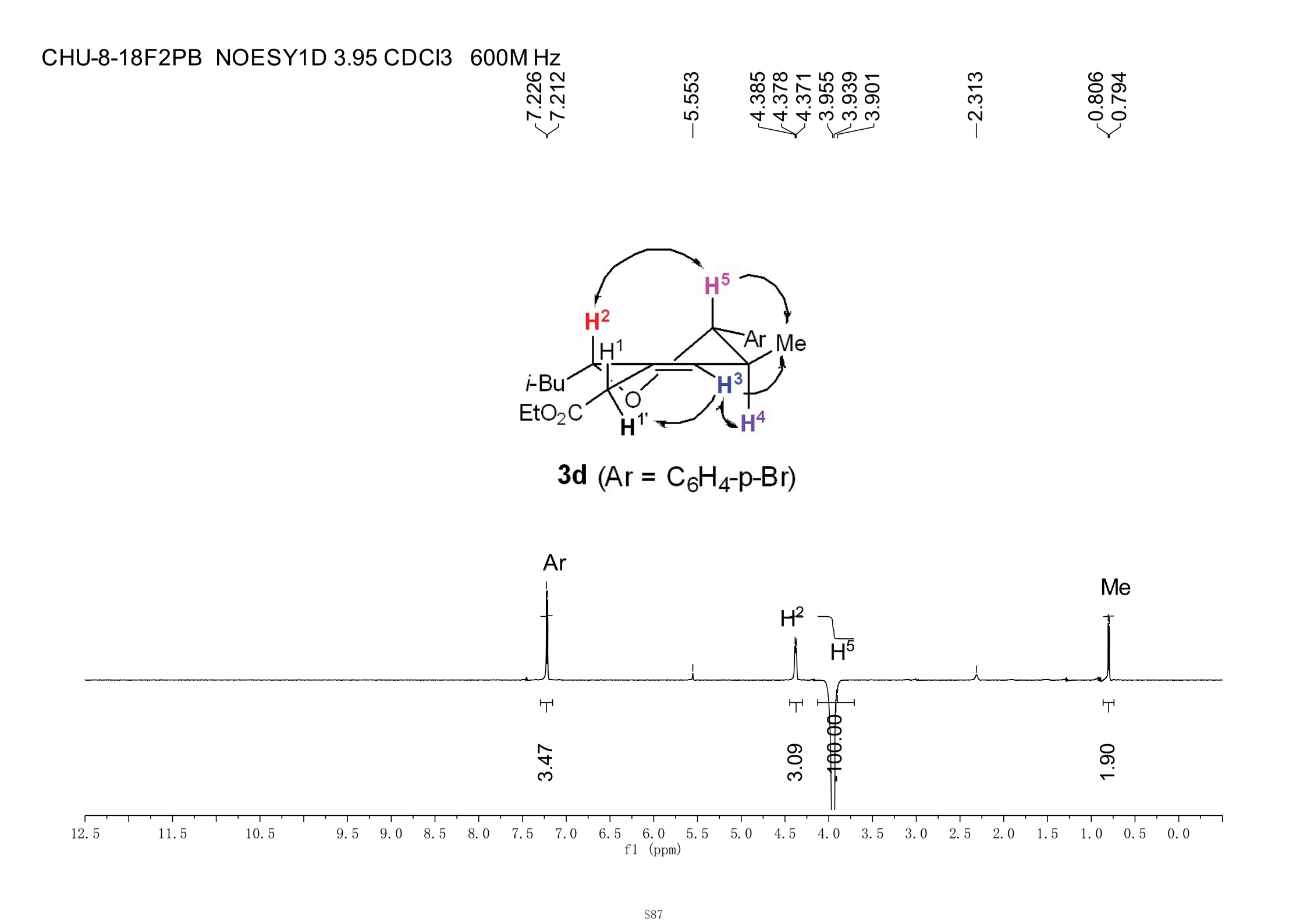
3d



CHU-8-18F2PB NOESY1D 2.31 CDCl3 600M Hz



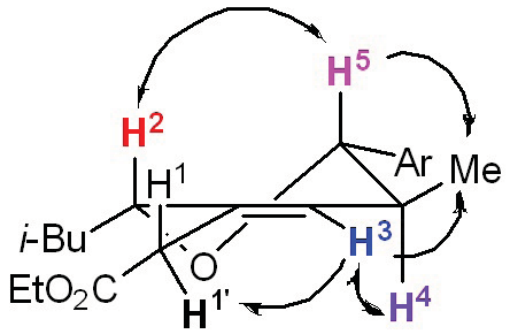
CHU-8-18F2PB NOESY1D 3.95 CDCl3 600M Hz



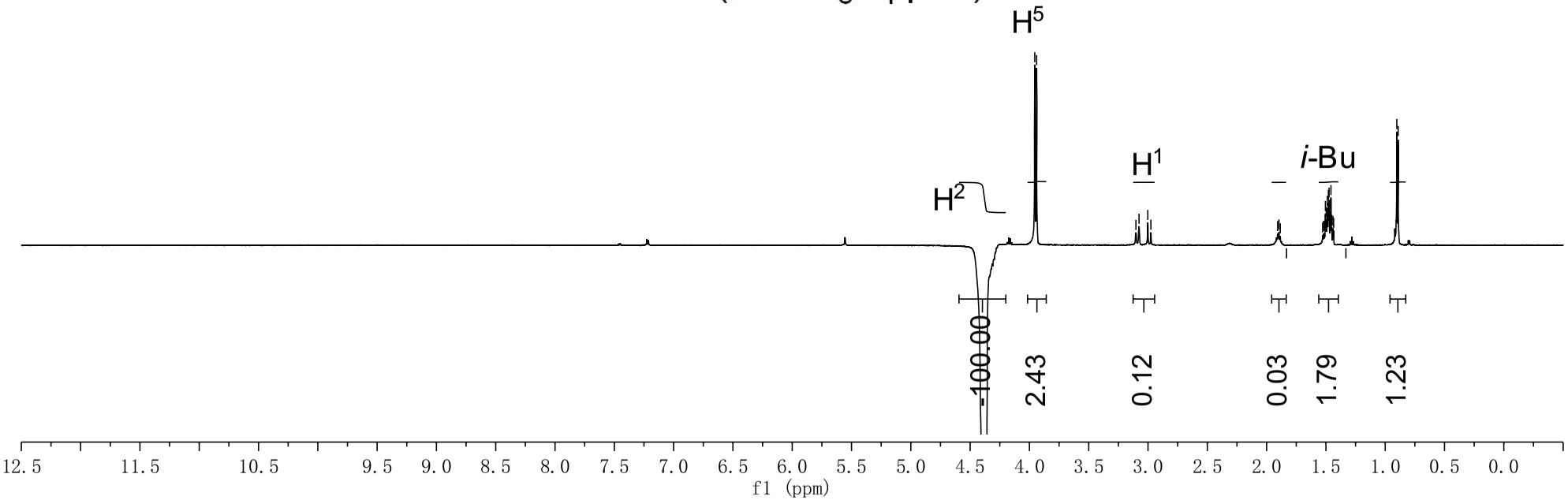
3d (Ar = C_6H_4-p-Br)

CHU-8-18F2PB NOESY1D 4.38 CDCl3 600M Hz

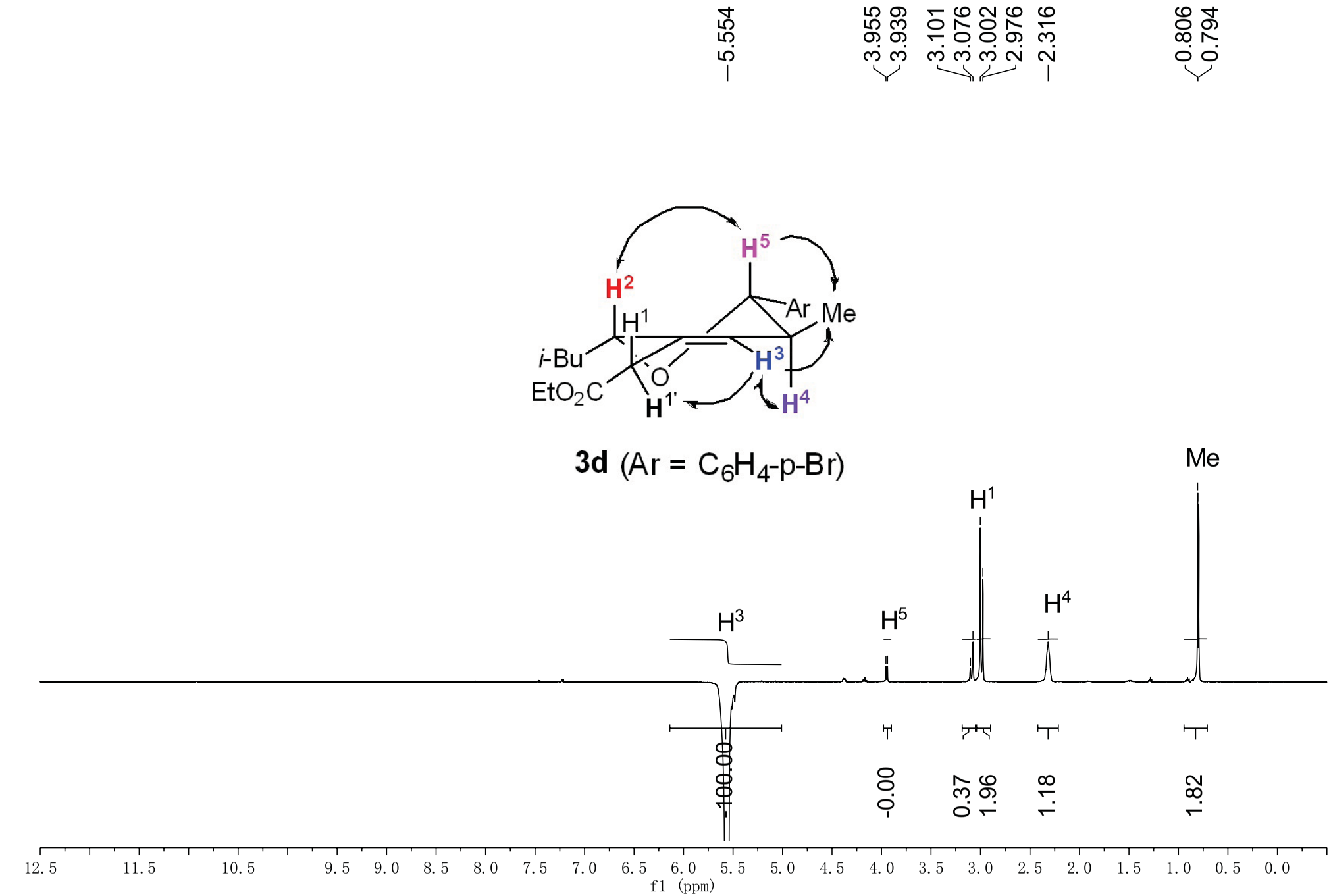
4.385 4.378 4.371 3.955 3.939 3.102 3.076 3.002 2.975 1.504 1.497 1.489 1.479 1.473 1.463 1.458 1.451 1.440 0.902 0.891



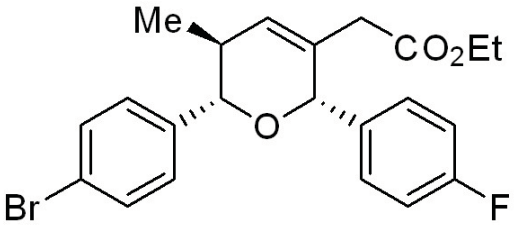
3d (Ar = C_6H_4-p-Br)



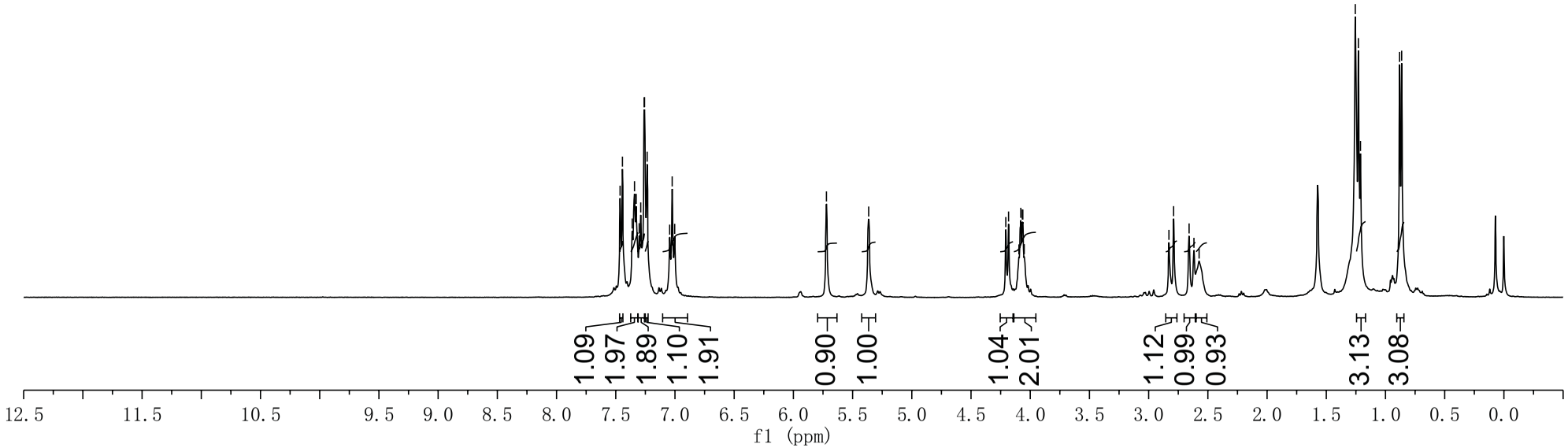
CHU-8-18F2PB NOESY1D 2.31 CDCl3 600M Hz



CHU-VII-99F2PB H1 CDCl3 400MHz

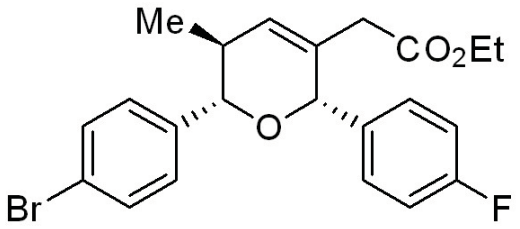


3e

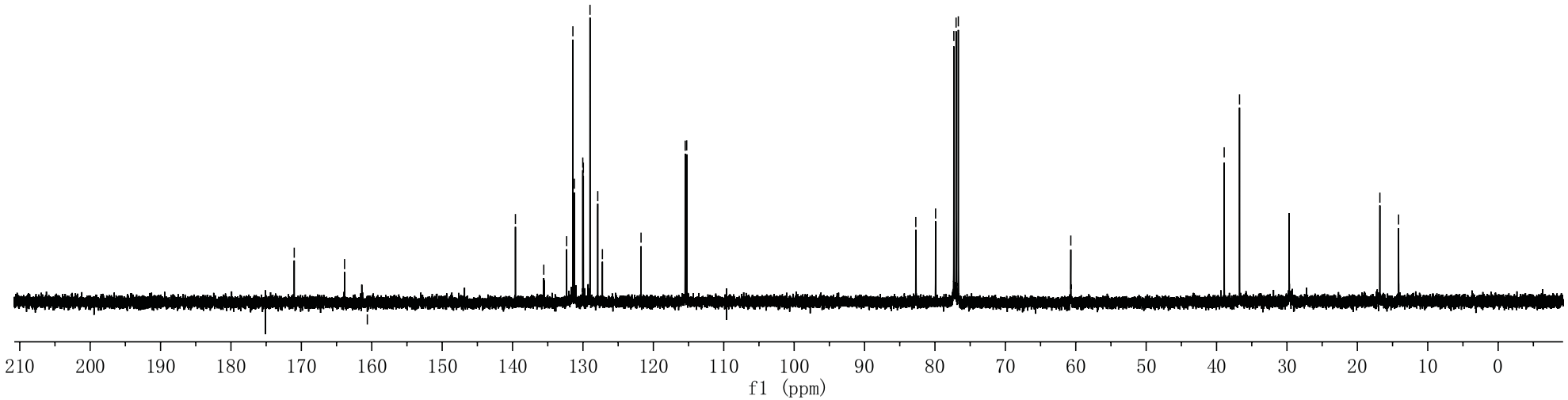


CHU-VII-99F2PB C13 CDCl3 400MHz

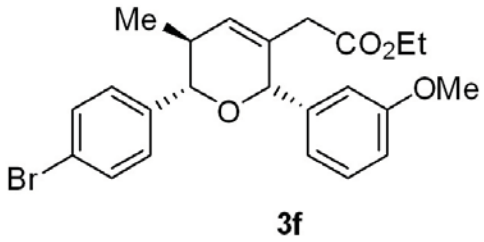
171.012
163.864
160.629
139.593
135.566
132.315
131.430
131.219
130.026
129.945
128.998
127.898
127.238
121.748
115.476
115.262
82.721
79.908
77.317
77.000
76.682
60.703
38.917
36.739
16.800
14.143



3e



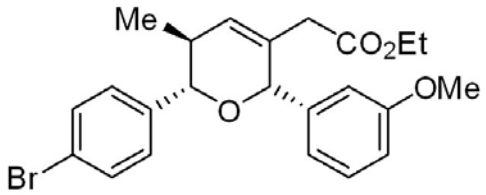
CHU-VII-34F2PB2 H1 CDCl3 400MHz



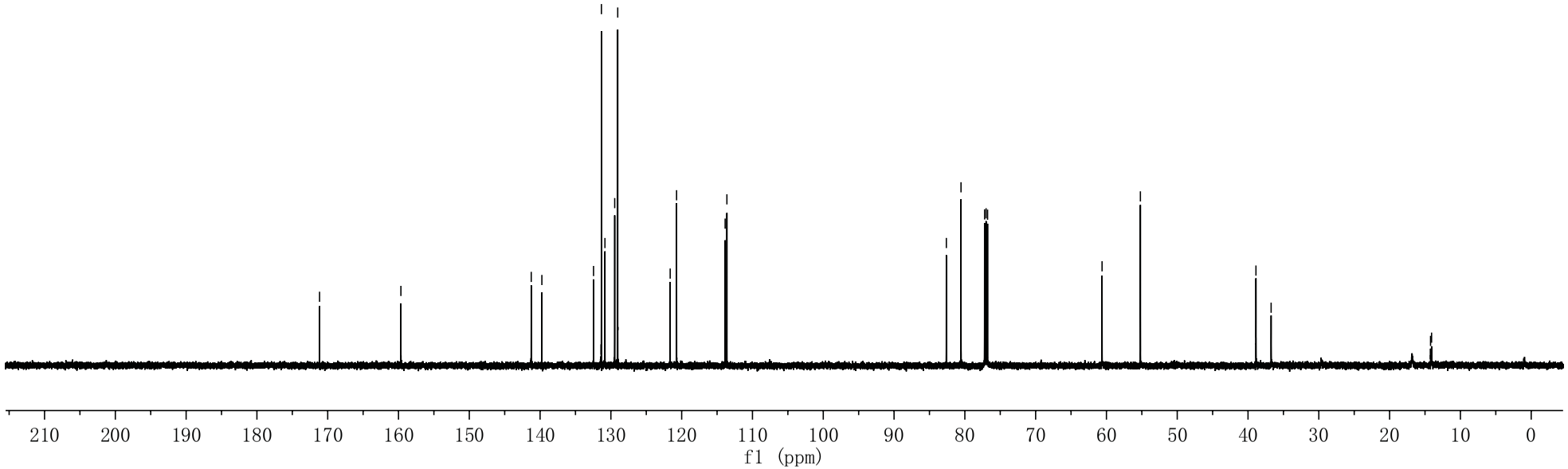
3f

CHU-VII-34F2PB2 C13 CDCl3 600MHz

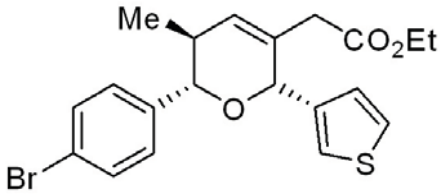
171.151
159.661
141.251
139.748
132.449
131.337
130.839
129.459
129.033
121.623
120.721
113.861
113.612
82.613
80.542
77.212
77.000
76.788
60.618
55.203
38.880
36.737
14.218
14.071



3f



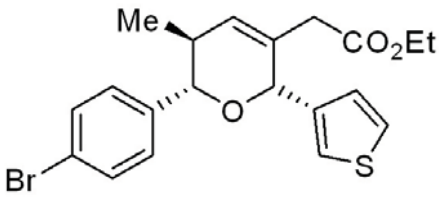
CHU-VII-41F1b2 H1 CDCl3 400MHz



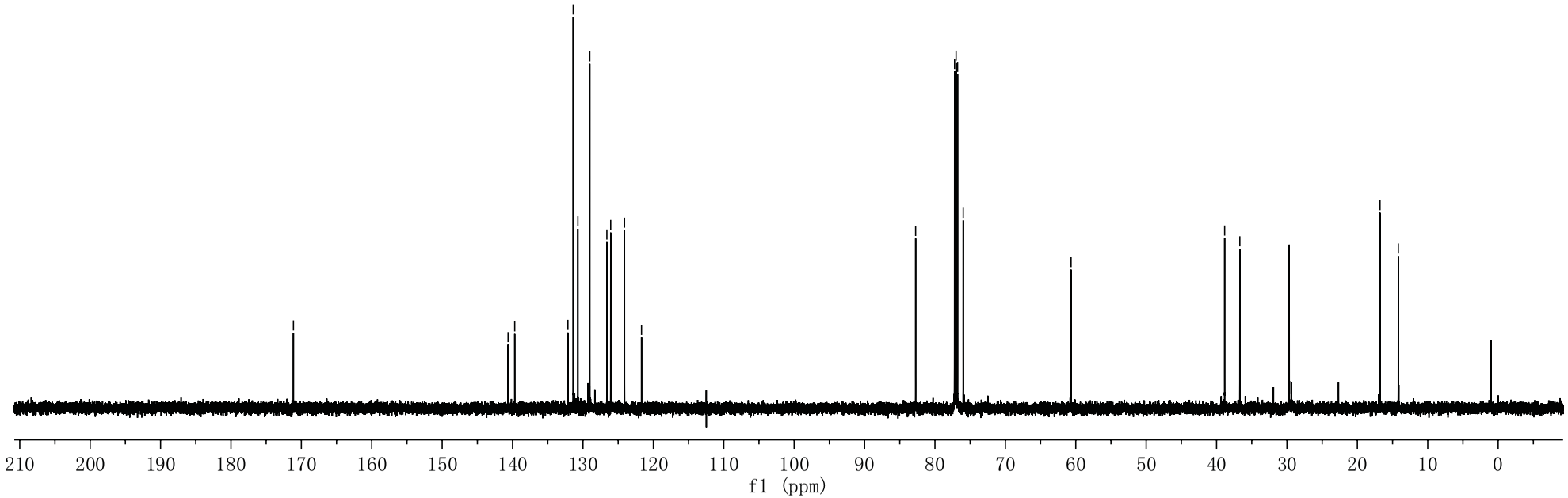
3g

CHU-VII-41F1b2 C13 CDCl3 600MHz

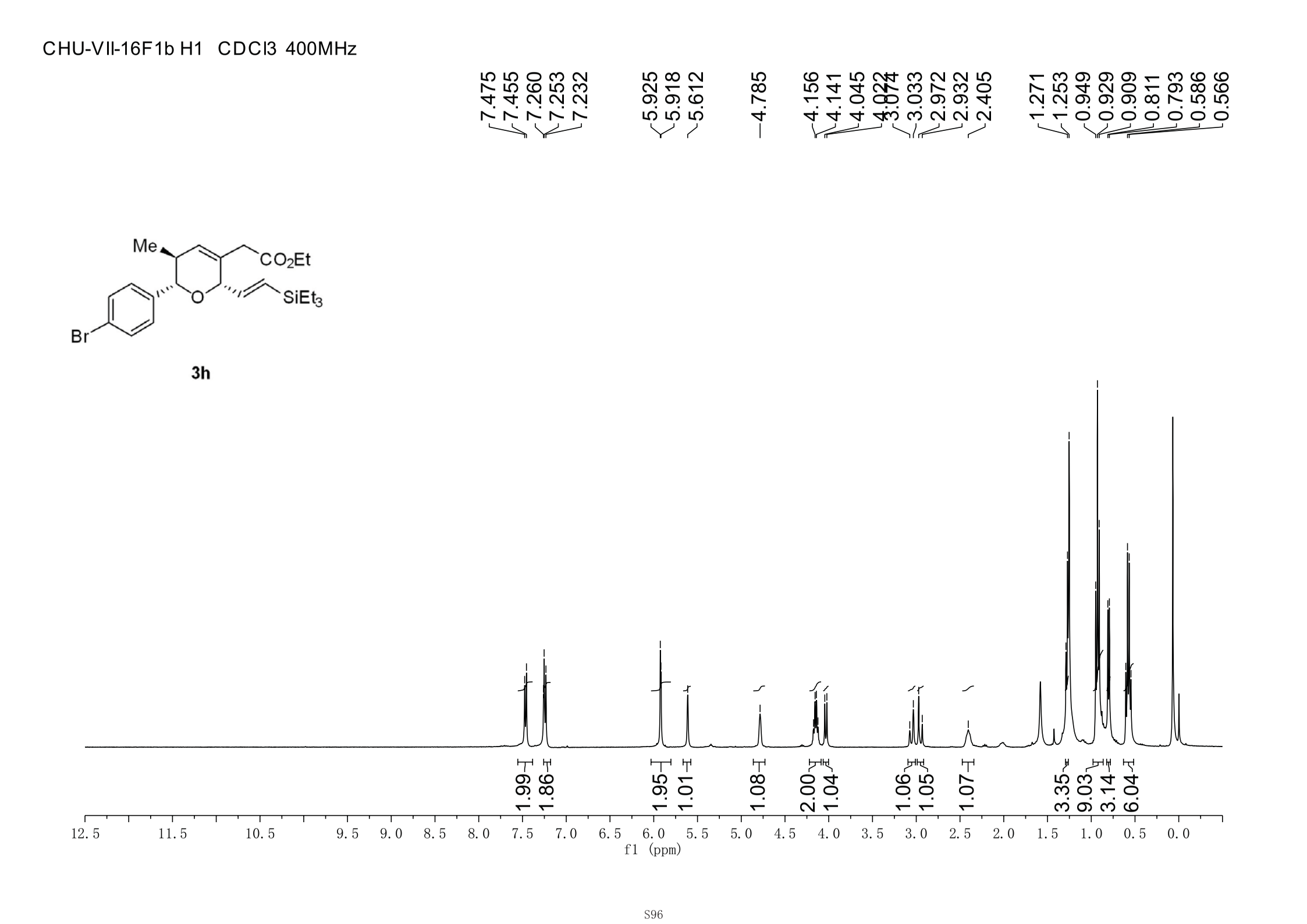
171.125
140.635
139.694
132.136
131.386
130.719
129.029
126.605
126.058
124.098
121.682
82.747
77.211
77.000
76.788
75.988
60.666
38.854
36.695
16.779
14.181



3g

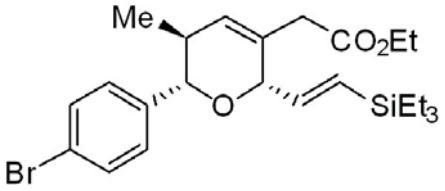


CHU-VII-16F1b H1 CDCl3 400MHz

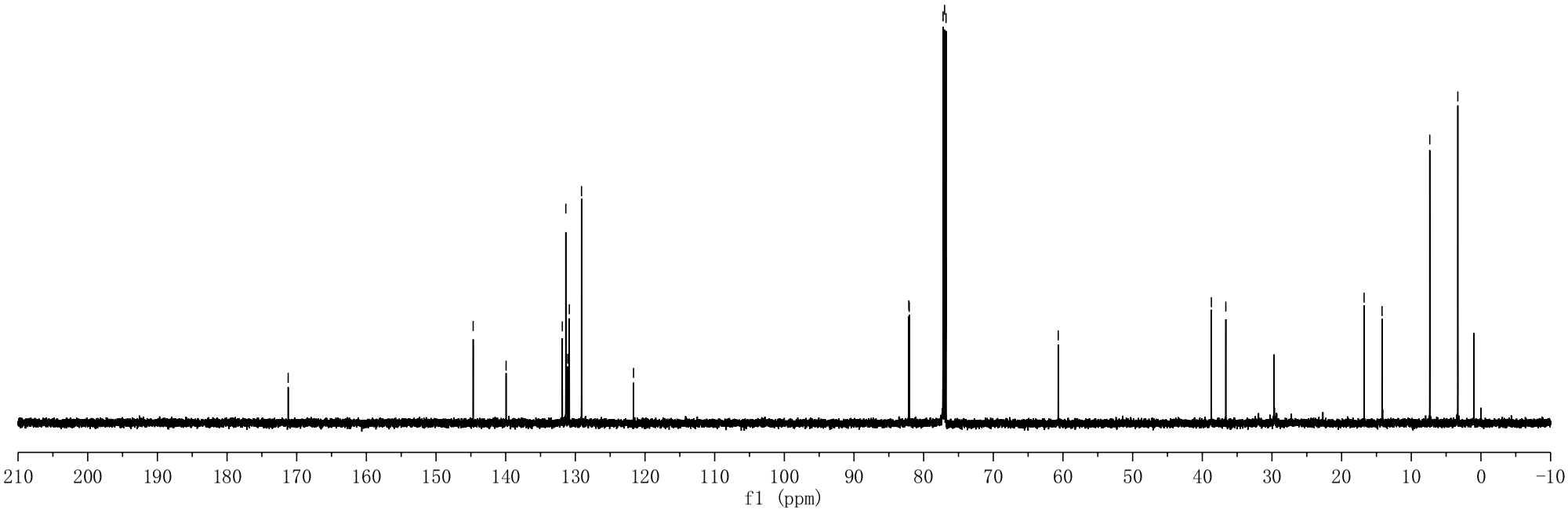


CHU-VII-16F1b C13 CDCl3 600MHz

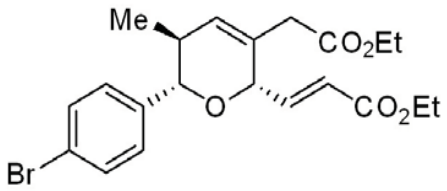
171.225
144.669
139.941
131.871
131.369
131.097
130.862
129.112
121.645
82.139
82.064
77.211
77.000
76.788
60.683
38.696
36.624
16.773
14.196
7.346
3.317



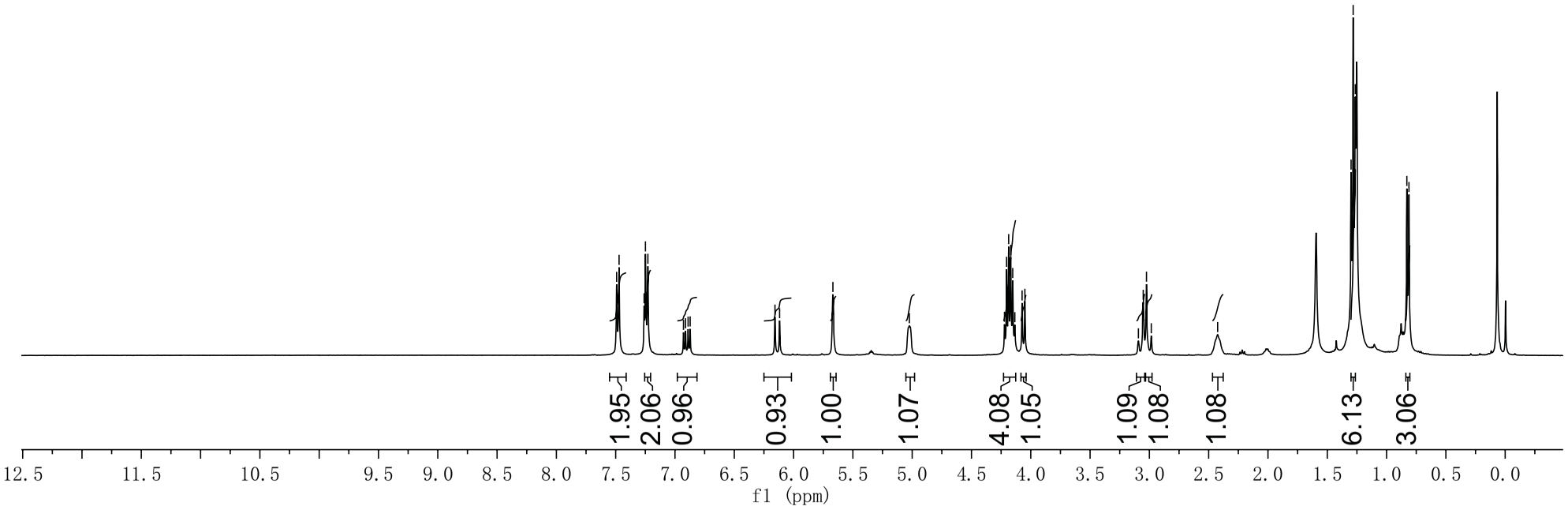
3h



CHU-VII-11b2 H1 CDCl3 400MHz

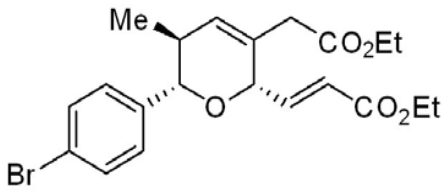


3i

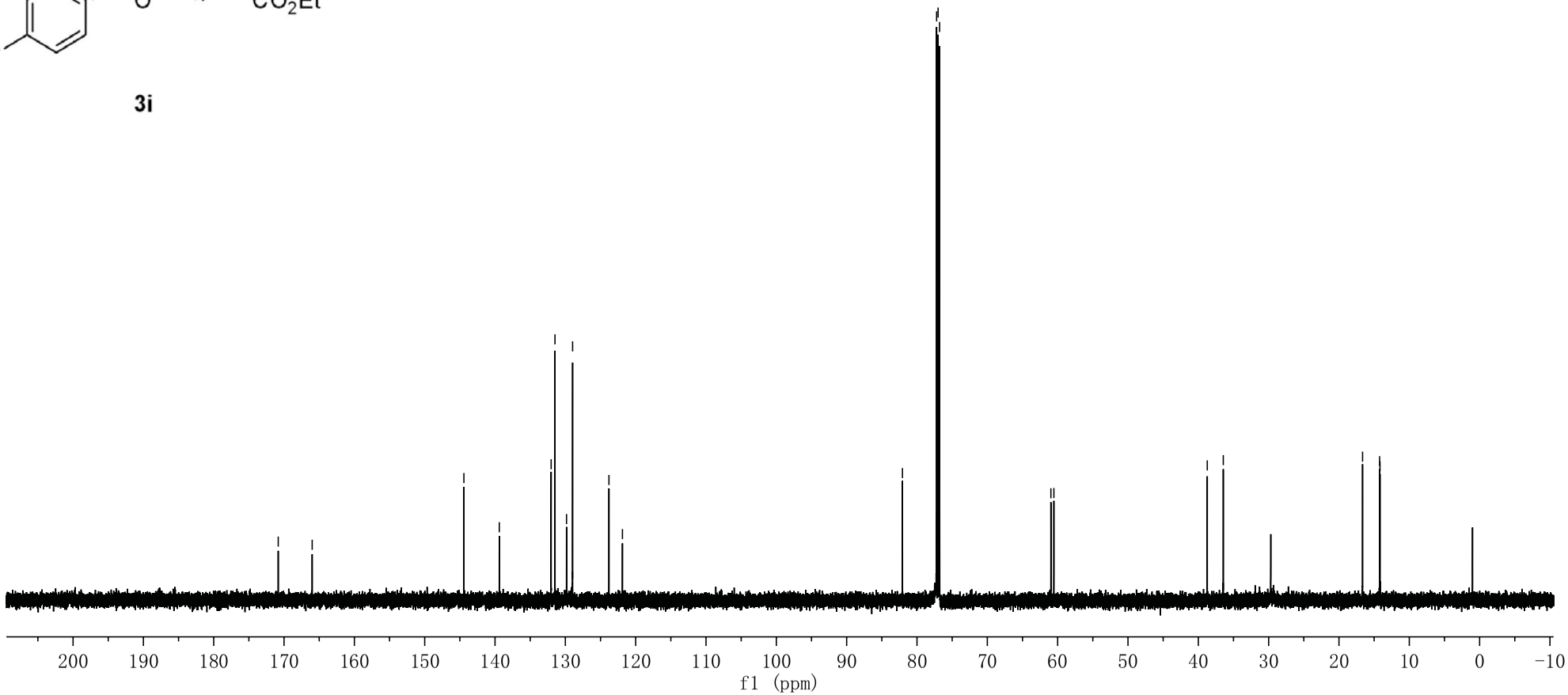


CHU-VII-11b2 C13 CDCl3 600MHz

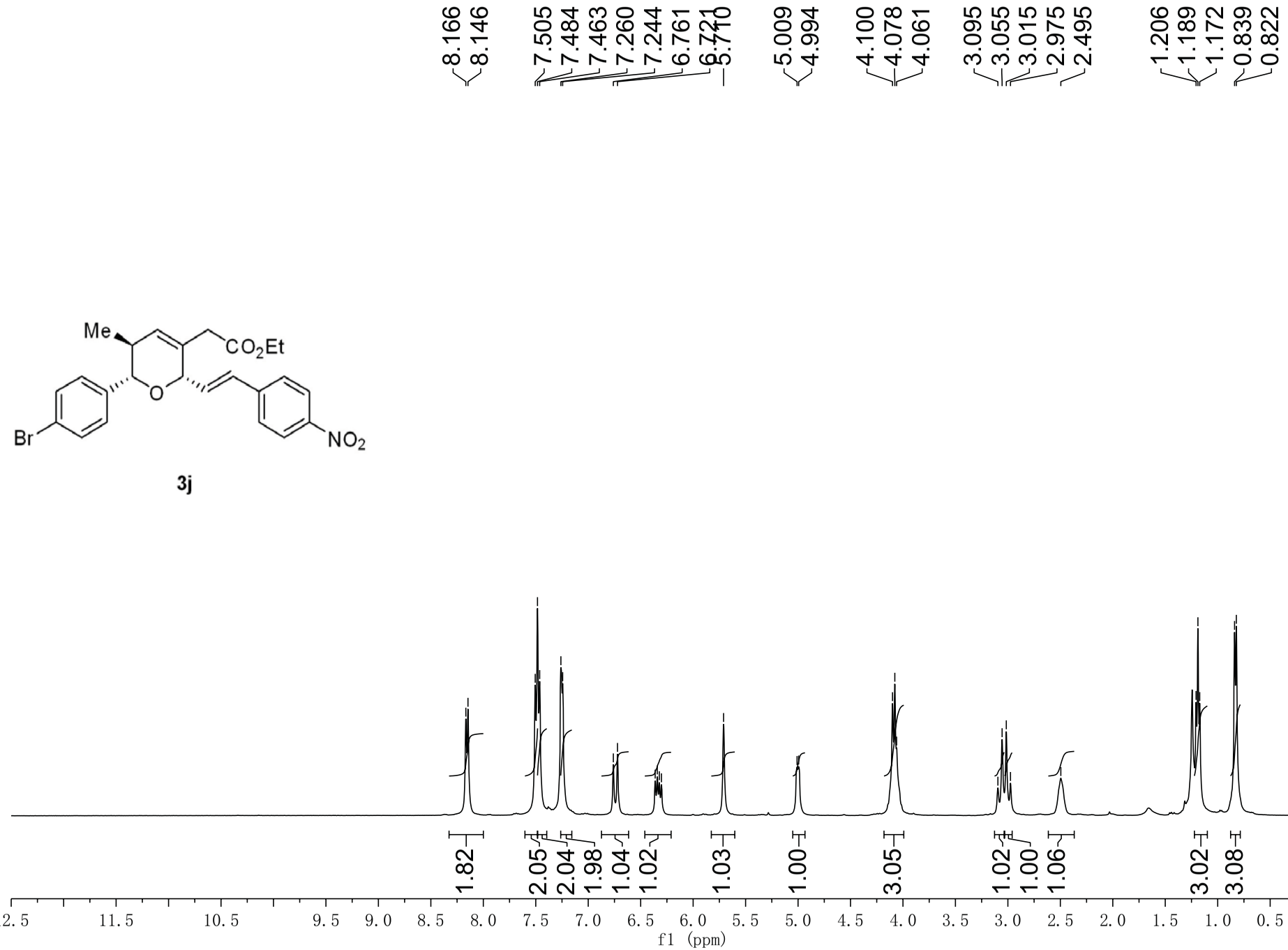
170.828
165.999
144.427
139.392
132.020
131.476
129.833
128.970
123.800
121.883
82.069
77.212
77.000
76.825
76.788
60.961
60.536
38.727
36.450
16.646
14.222
14.168



3i

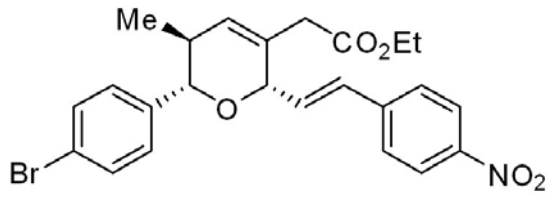


CHU-VII-41F3PB H1 CDCl3 400MHz

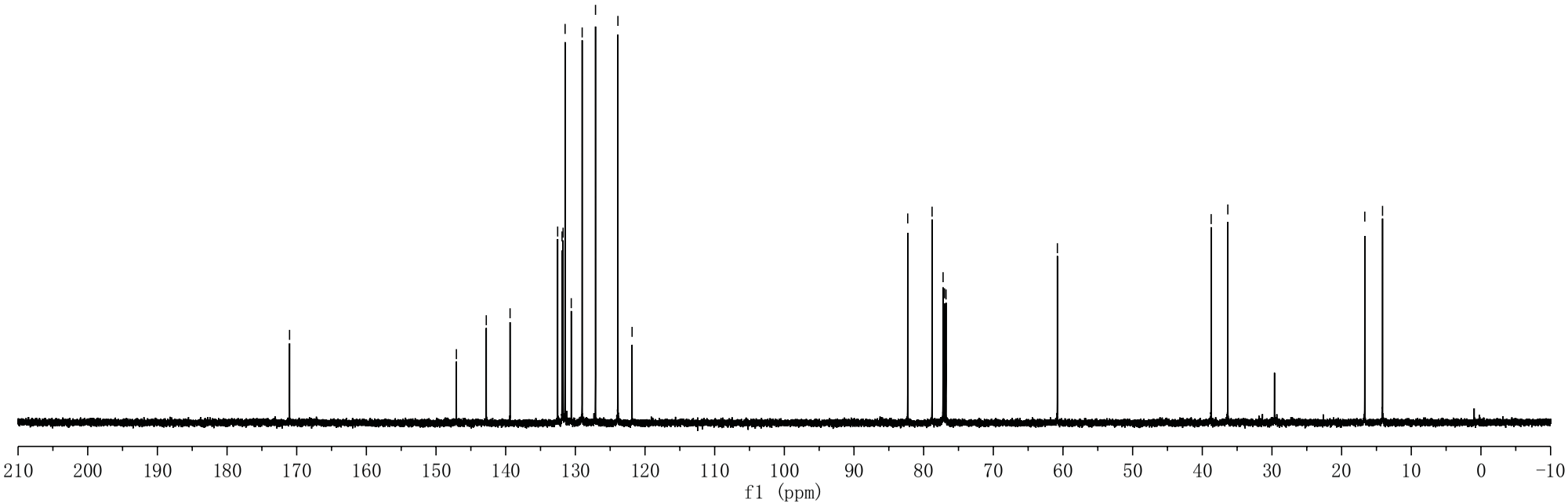


CHU-VII-41F3PB C13 CDCl3 600MHz

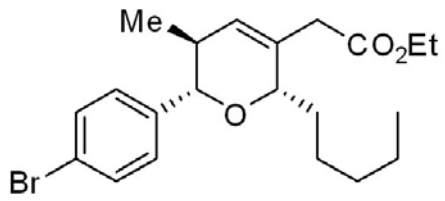
171.026
147.078
142.787
139.372
132.539
131.910
131.759
131.472
130.587
129.019
127.105
123.890
121.856
82.287
78.789
77.210
77.000
76.788
60.802
38.726
36.337
16.674
14.126



3j



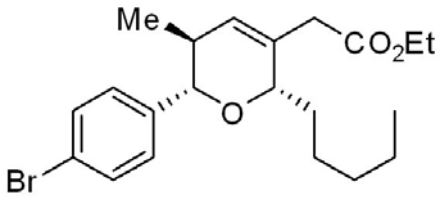
CHU-VII-6F1b H1 CDCl3 400MHz



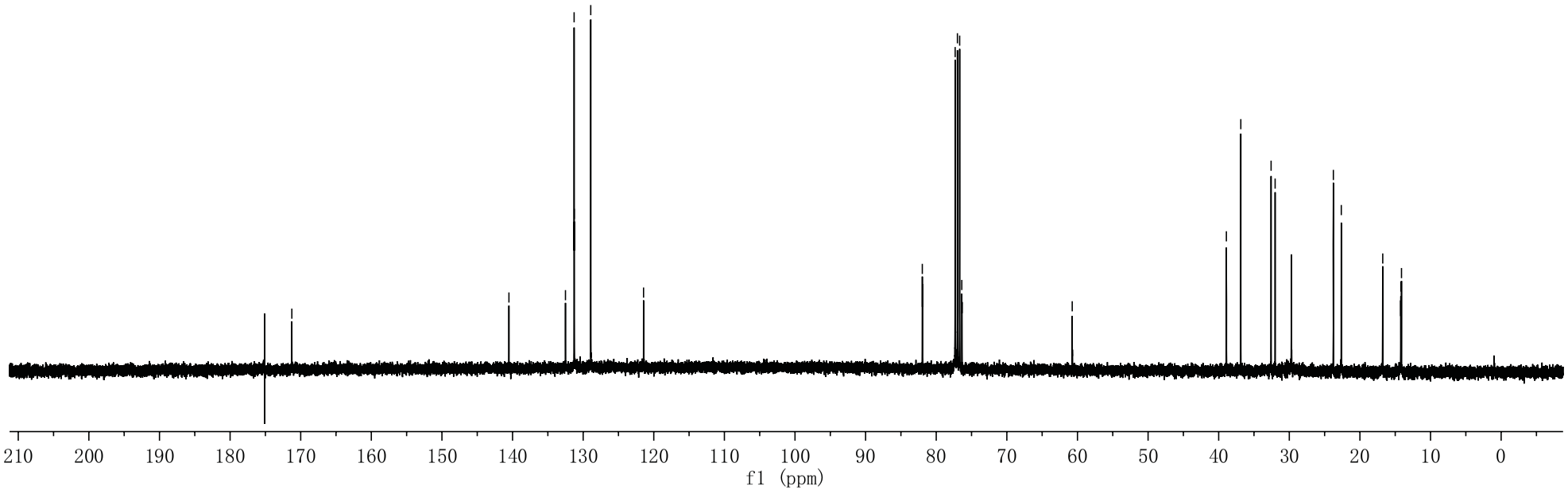
3k

CHU-VII-6F1b C13 CDCl3 400MHz

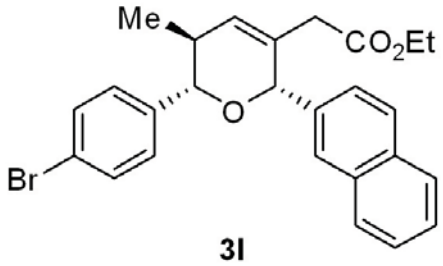
171.255
140.511
132.507
131.281
131.251
128.925
121.447
81.972
77.318
77.000
76.682
76.379
60.742
38.911
36.866
32.578
32.007
23.759
22.637
16.767
14.201
14.112



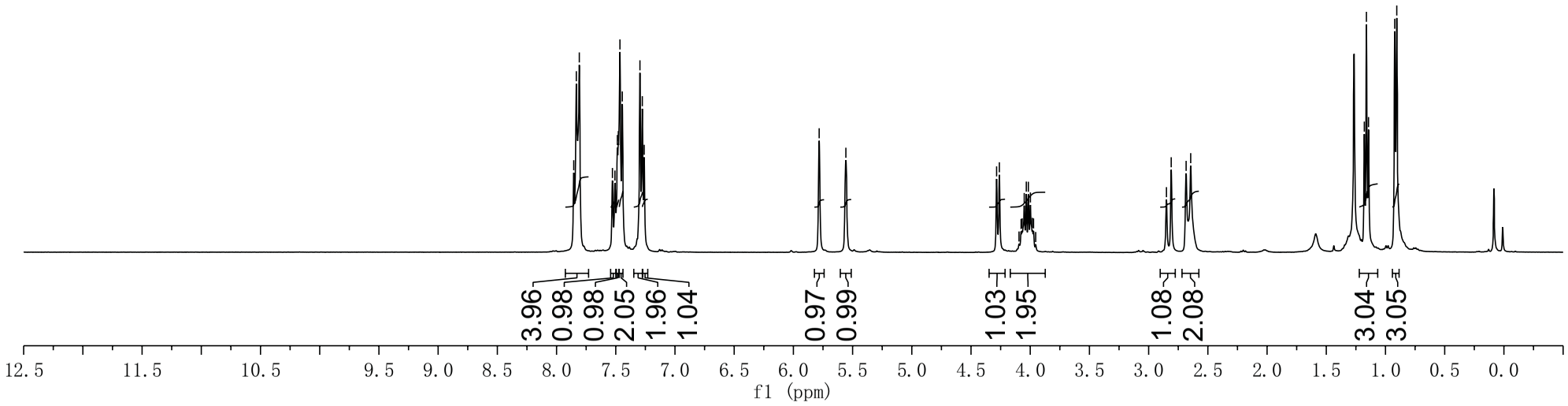
3k



CHU-VII-34F4PB2 H1 CDCl3 400MHz

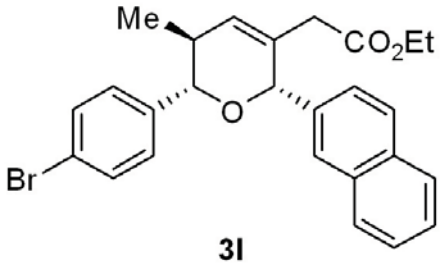


3l

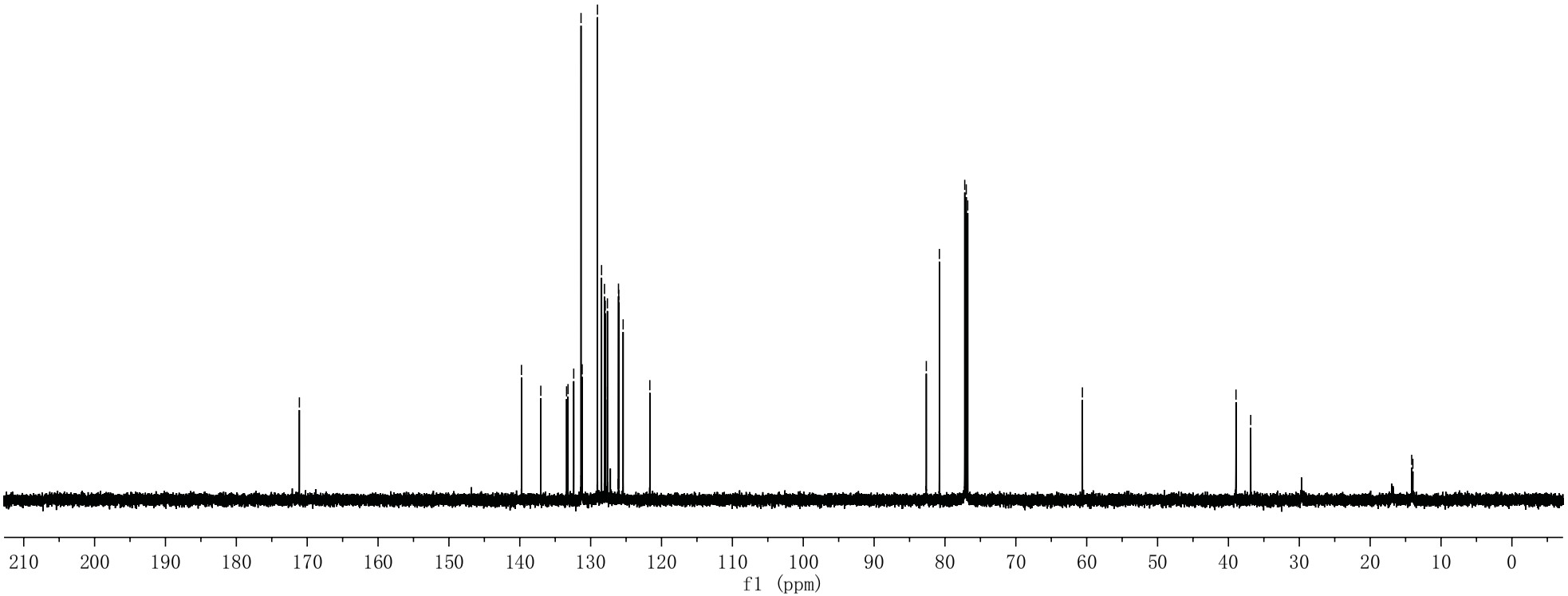


CHU-VII-34F4PB2 C13 CDCl3 600MHz

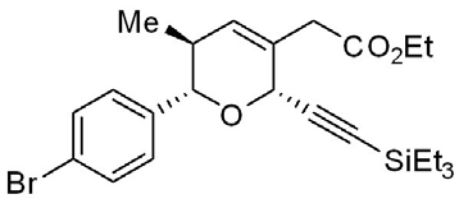
171.103
139.763
137.034
133.398
133.194
132.389
131.358
131.197
129.039
128.461
128.049
127.936
127.888
127.633
126.072
126.039
125.415
121.650
82.634
80.790
77.211
77.000
76.788
60.609
38.934
36.856
14.142
13.978



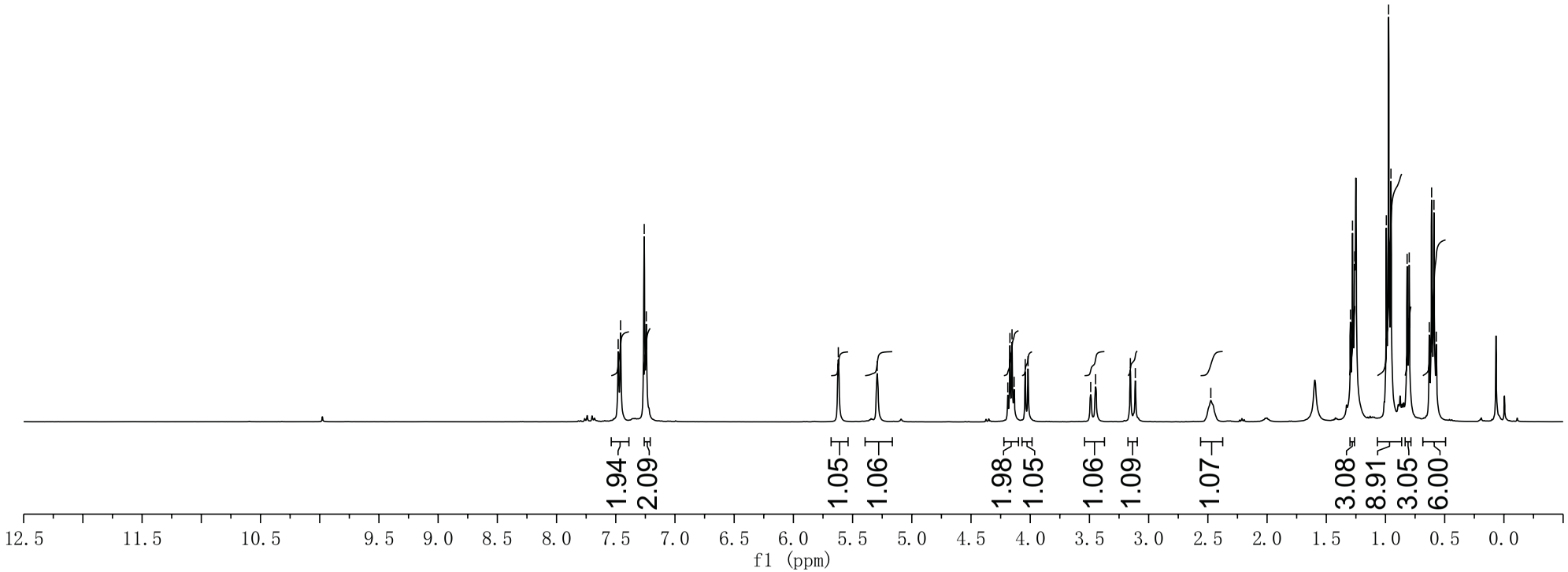
3l



CHU-VII-74F1PB H1 CDCl3 400MHz

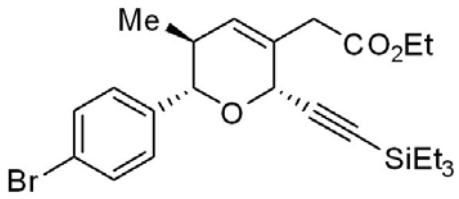


3m

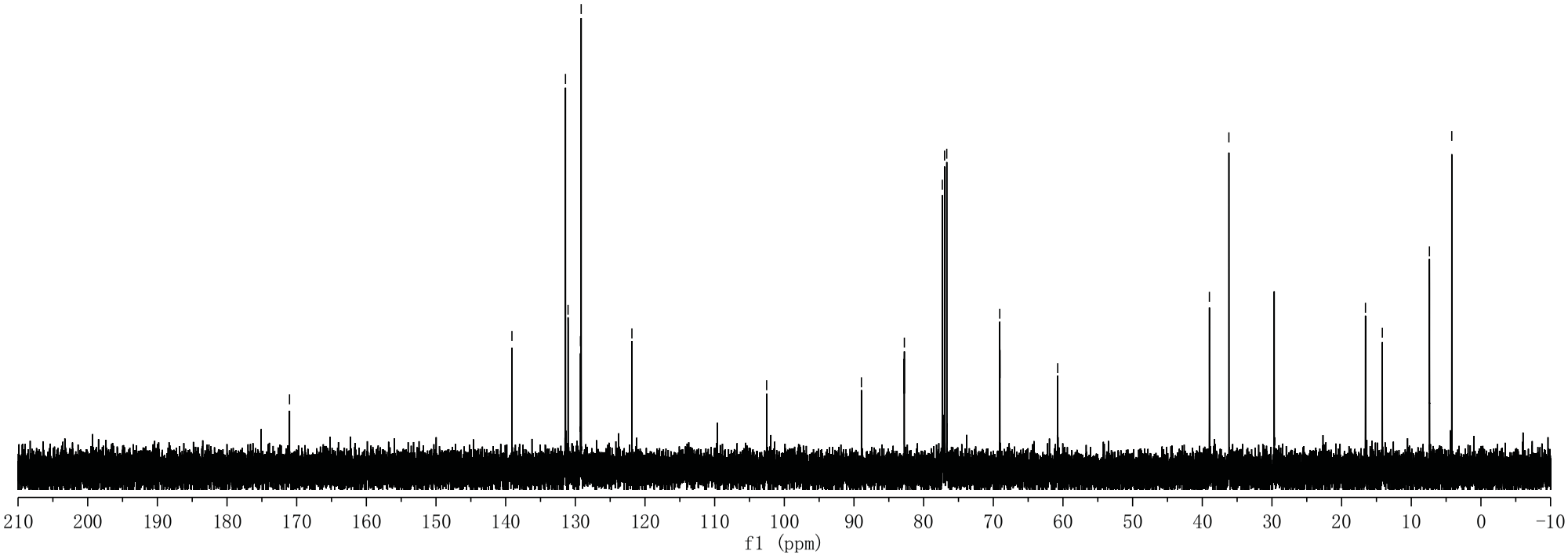


CHU-VII-74F1PB C13 CDCl3 400MHz

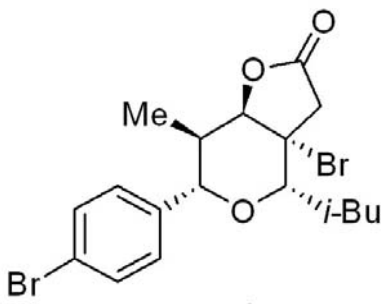
171.031
139.103
131.417
131.045
129.267
129.162
121.881
102.539
88.934
82.769
77.317
77.000
76.682
69.074
60.757
38.981
36.182
16.576
14.157
7.395
4.186



3m



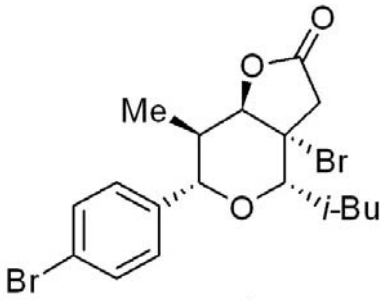
CHU-8-16Fa H1 CDCl3 400MHz



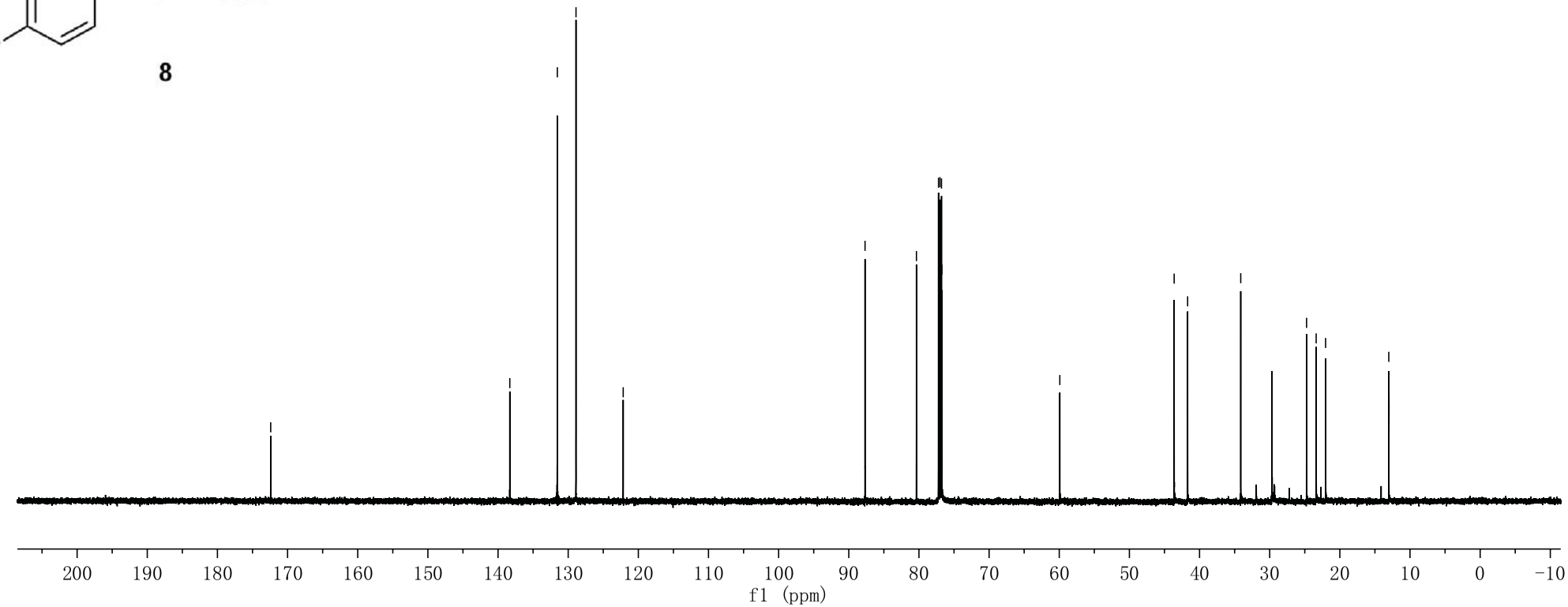
8

CHU-8-16Fa C13 CDCl3 600MHz

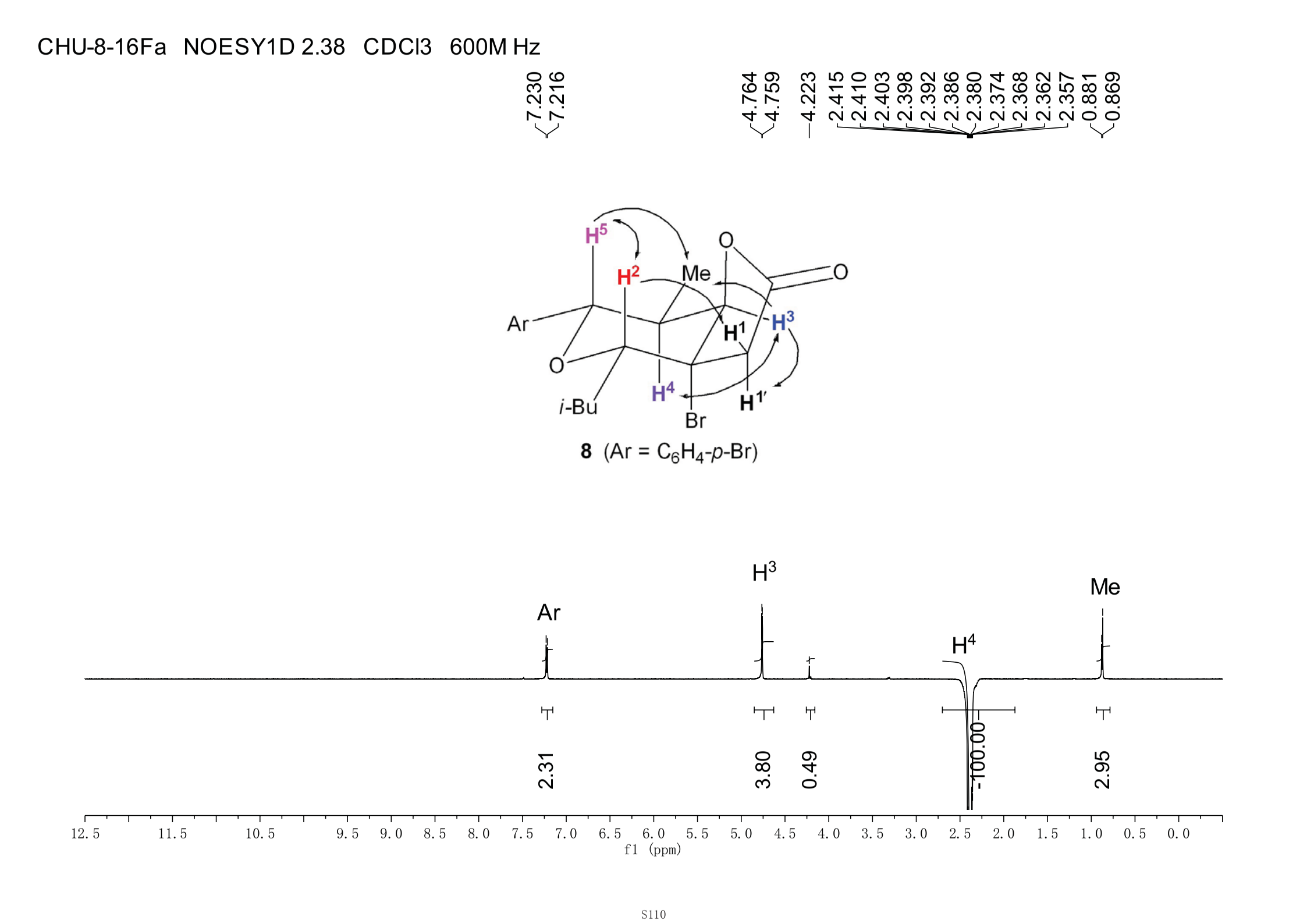
172.404
138.323
131.546
128.884
122.156
87.682
80.356
77.211
77.000
76.788
76.726
59.920
43.618
41.699
34.128
24.743
23.374
22.032
13.023



8



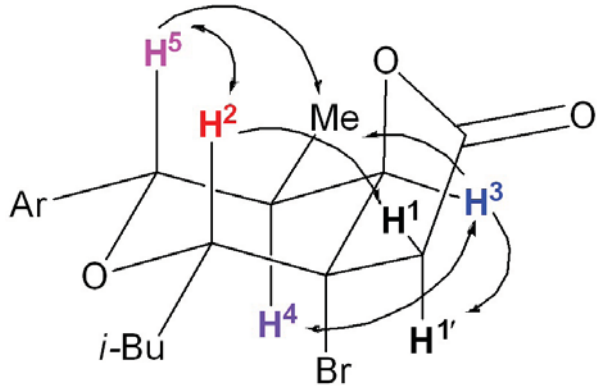
CHU-8-16Fa NOESY1D 2.38 CDCl3 600M Hz



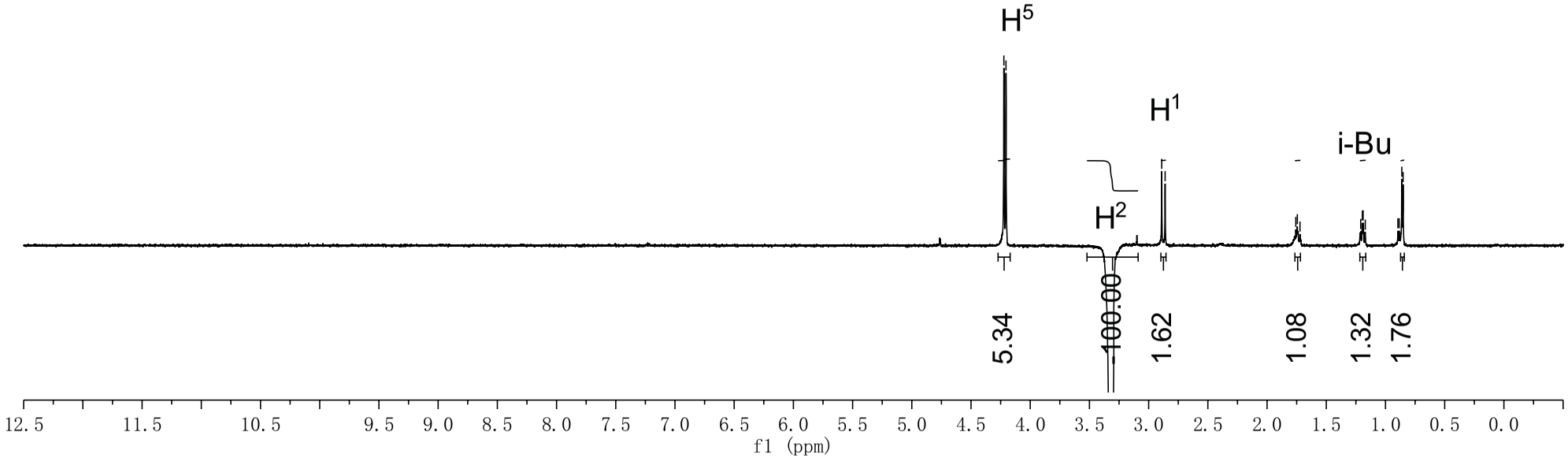
8 (Ar = C_6H_4-*p*-Br)

CHU-8-16Fa NOESY1D 3.31 CDCl3 600M Hz

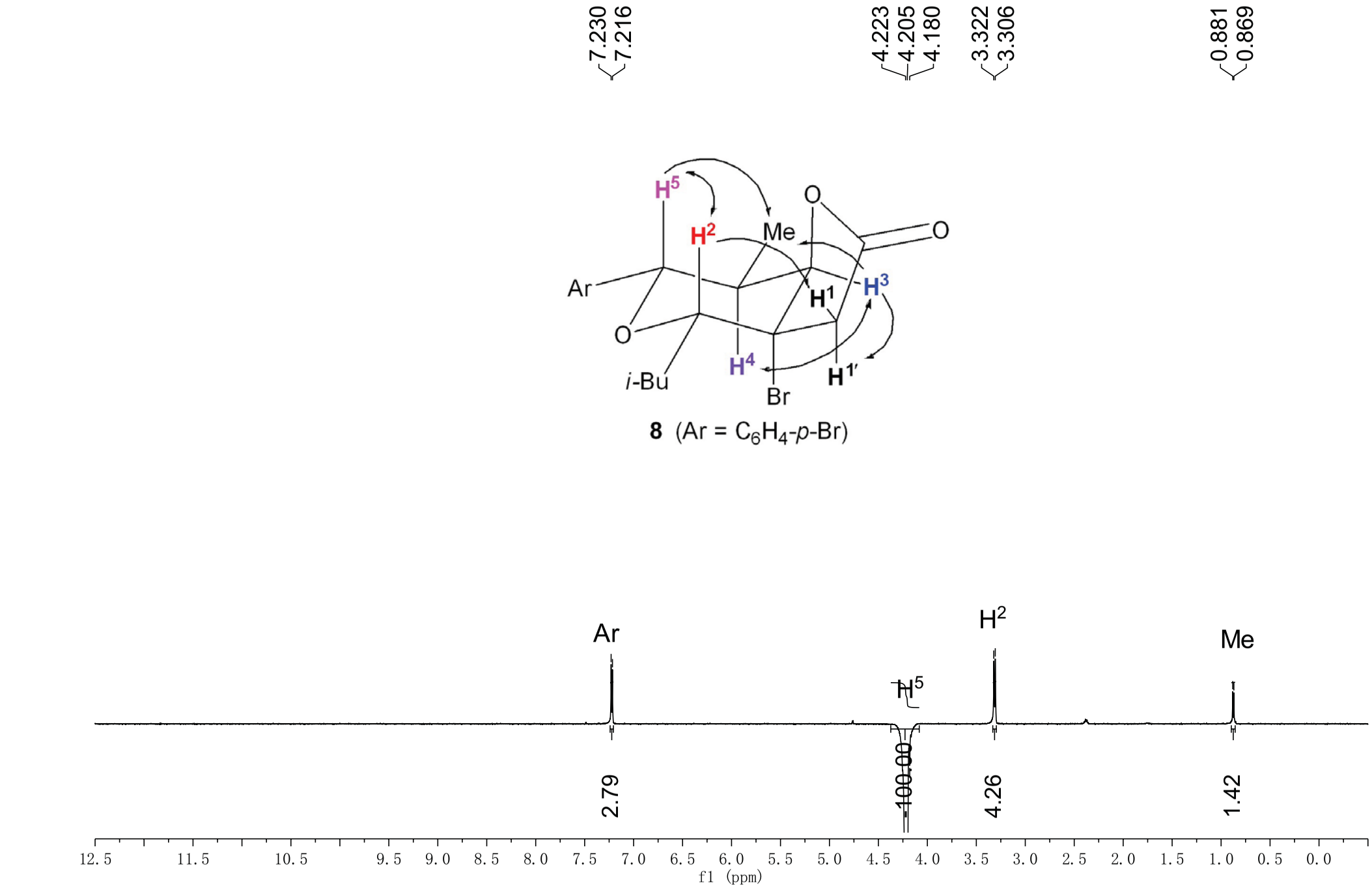
4.223 4.205 3.322 3.307 2.890 2.861 1.757 1.744 1.722 1.209 1.195 1.189 1.171 0.895 0.884 0.862 0.851



8 (Ar = C_6H_4-*p*-Br)

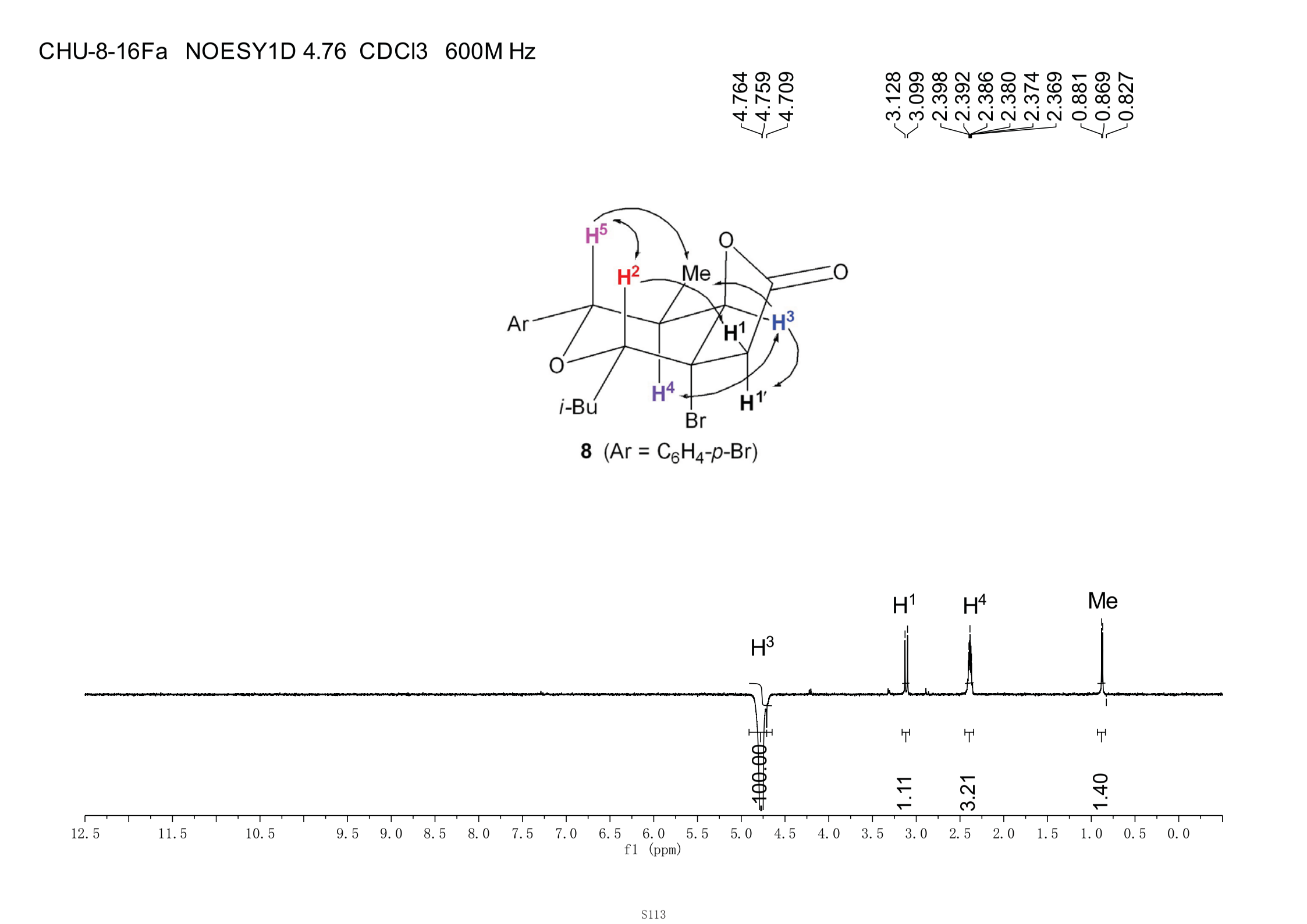


CHU-8-16Fa NOESY1D 4.21 CDCl3 600M Hz

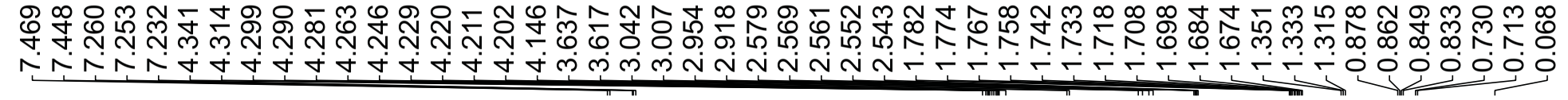


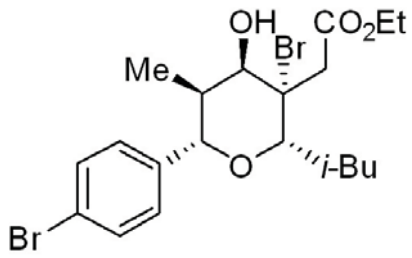
8 (Ar = C_6H_4-*p*-Br)

CHU-8-16Fa NOESY1D 4.76 CDCl3 600M Hz

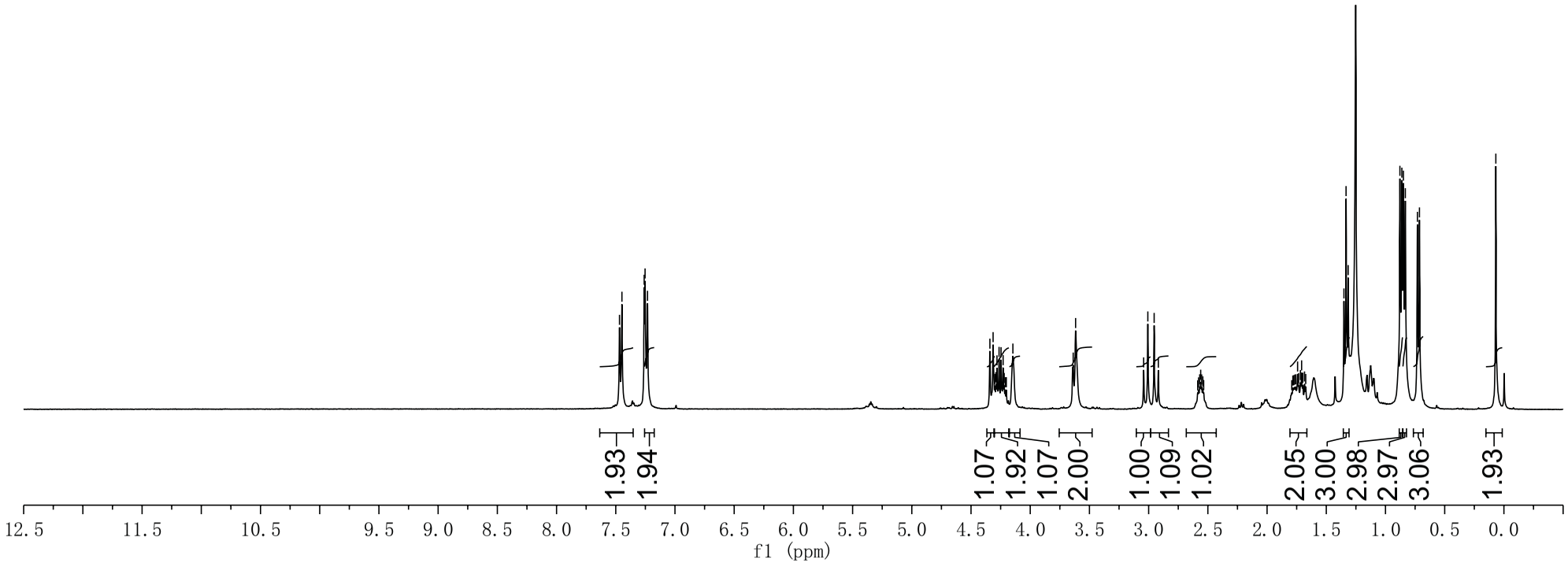


CHU-8-9F1PB H1 CDCl3 400MHz

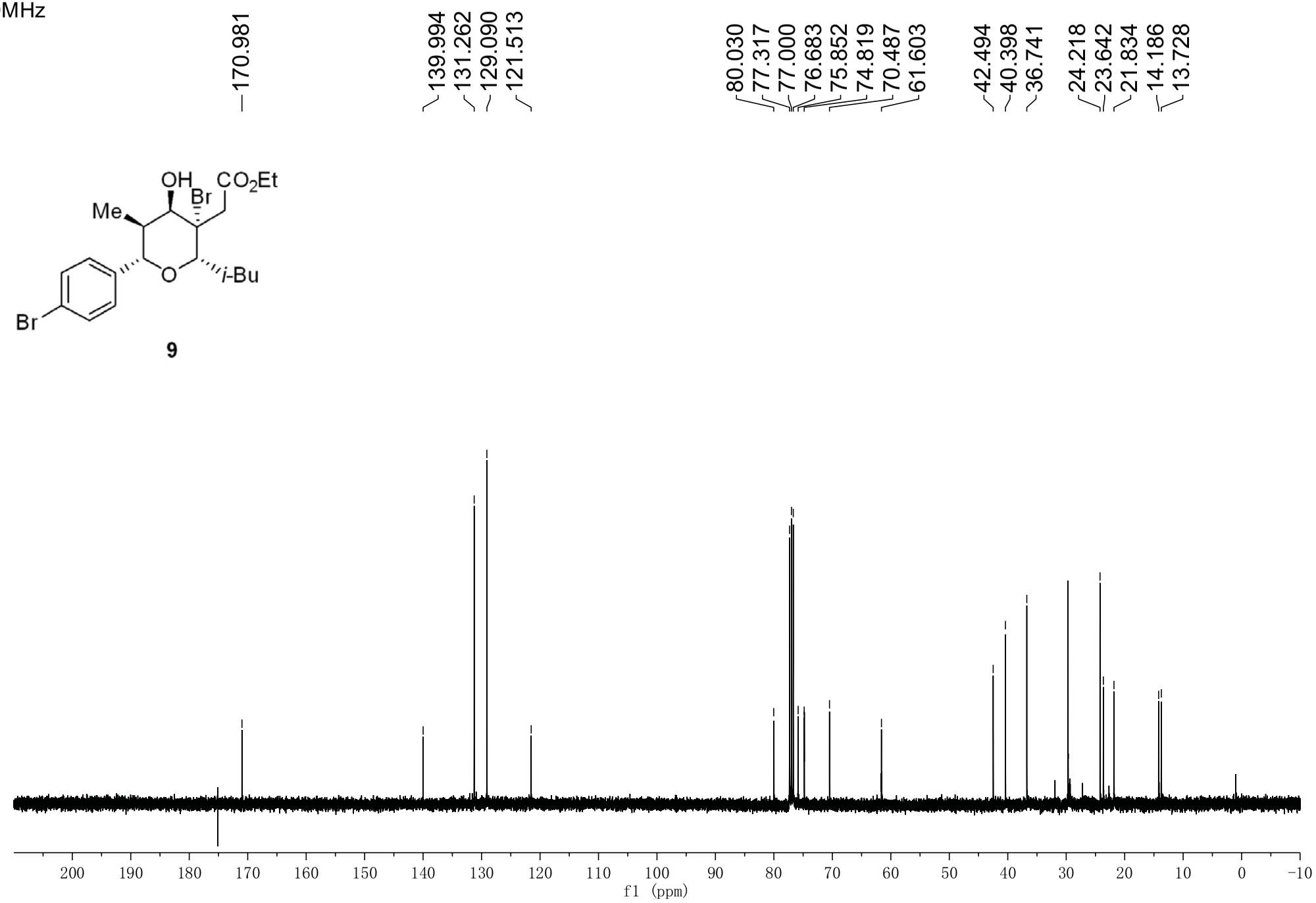




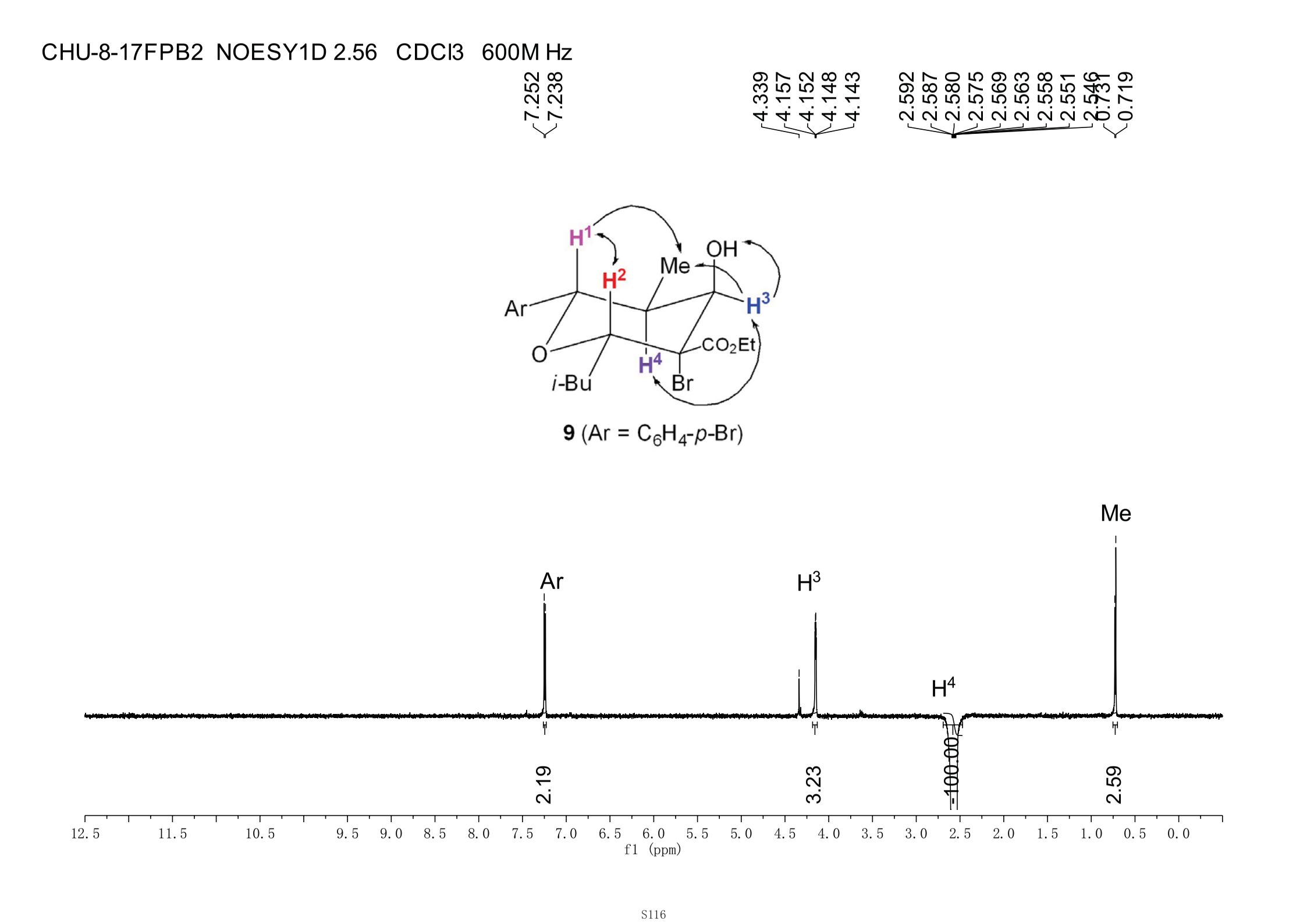
9



CHU-8-17FPB C13 CDCl3
400MHz

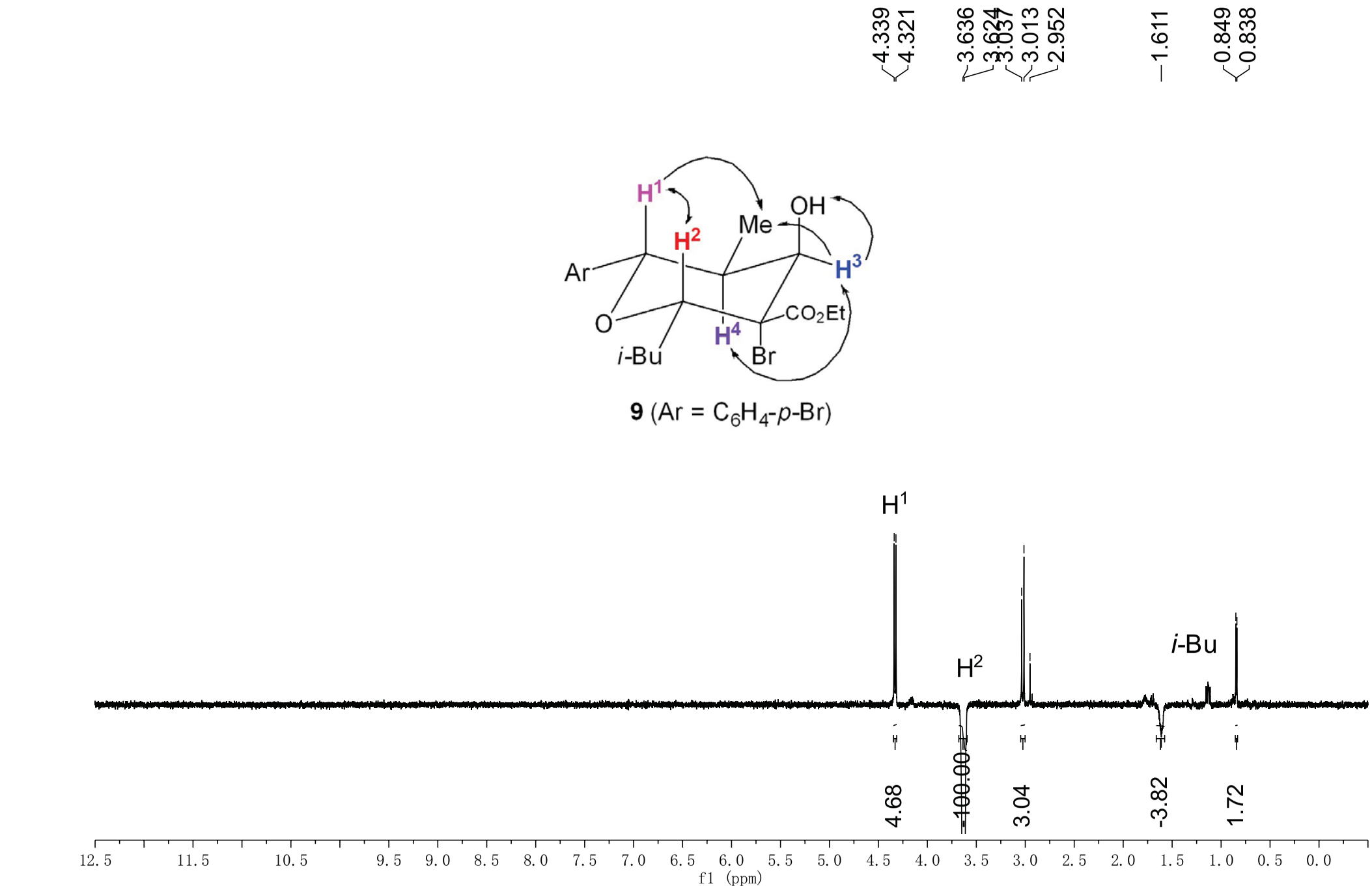


CHU-8-17FPB2 NOESY1D 2.56 CDCl3 600M Hz



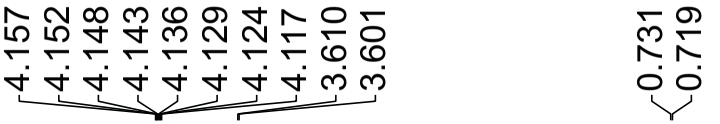
9 (Ar = C_6H_4-*p*-Br)

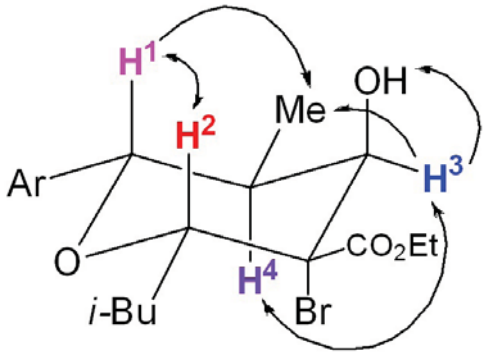
CHU-8-17FPB2 NOESY1D 3.63 CDCl3 600M Hz



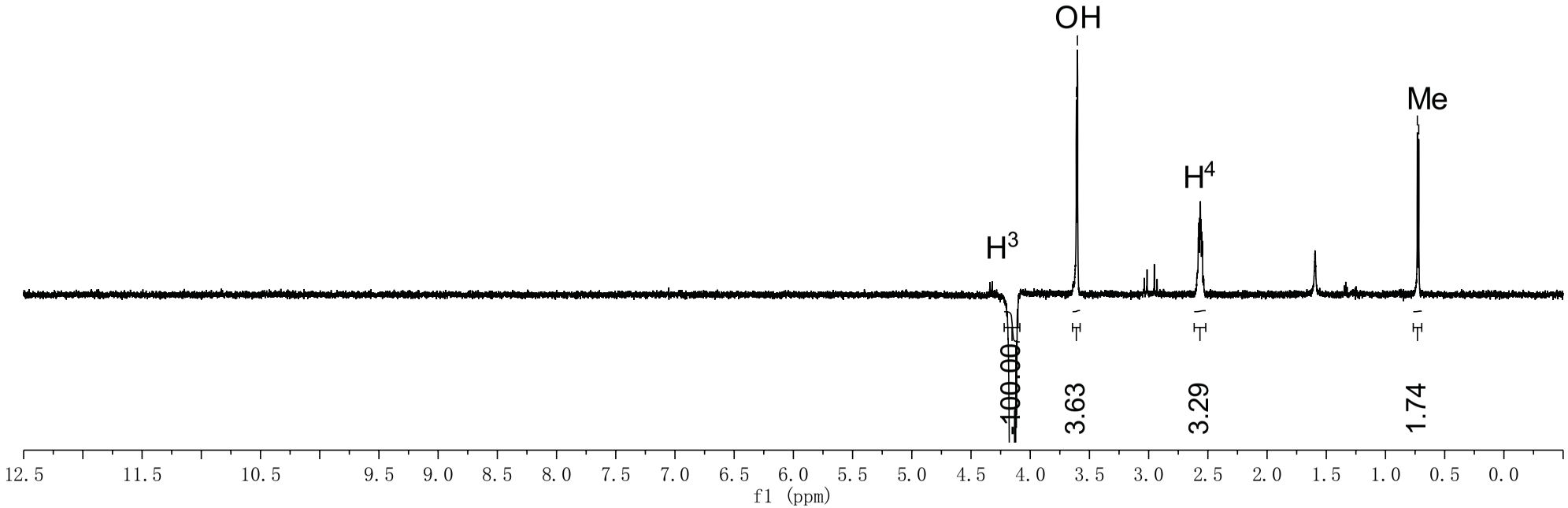
9 (Ar = C_6H_4-*p*-Br)

CHU-8-17FPB2 NOESY1D 4.15 CDCl3 600M Hz

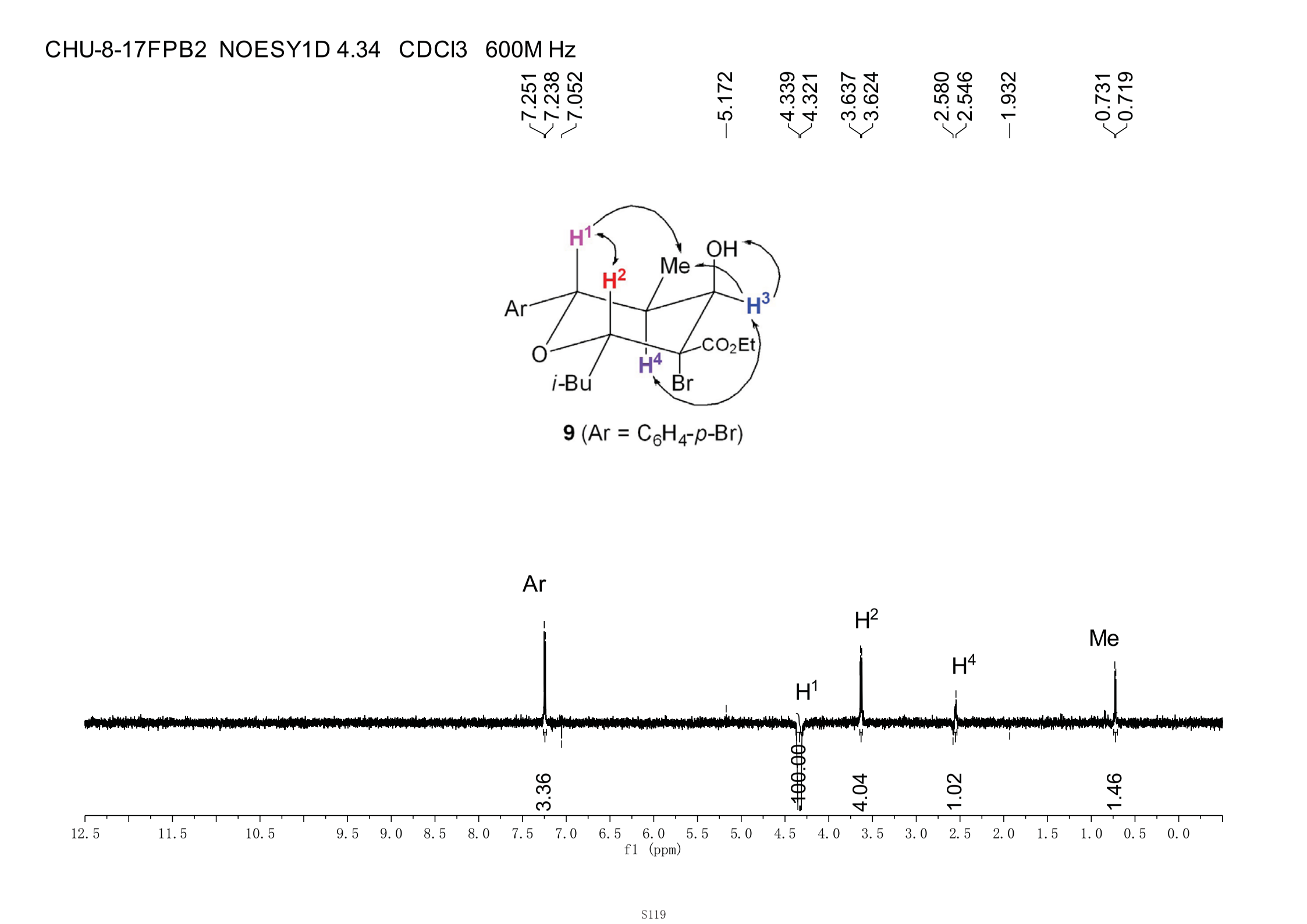




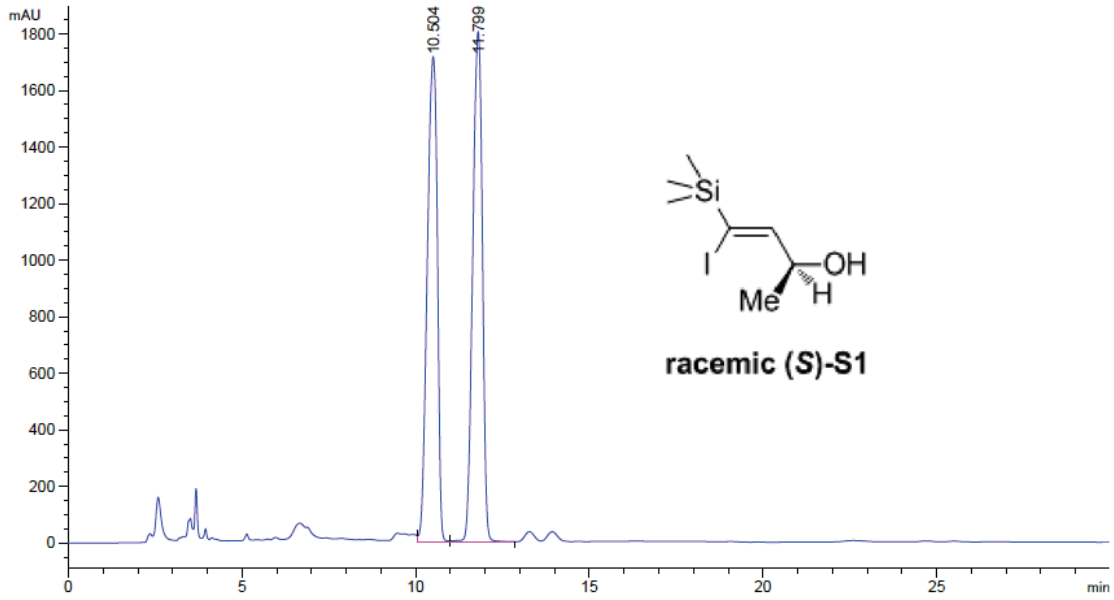
9 (Ar = C_6H_4-*p*-Br)



CHU-8-17FPB2 NOESY1D 4.34 CDCl3 600M Hz

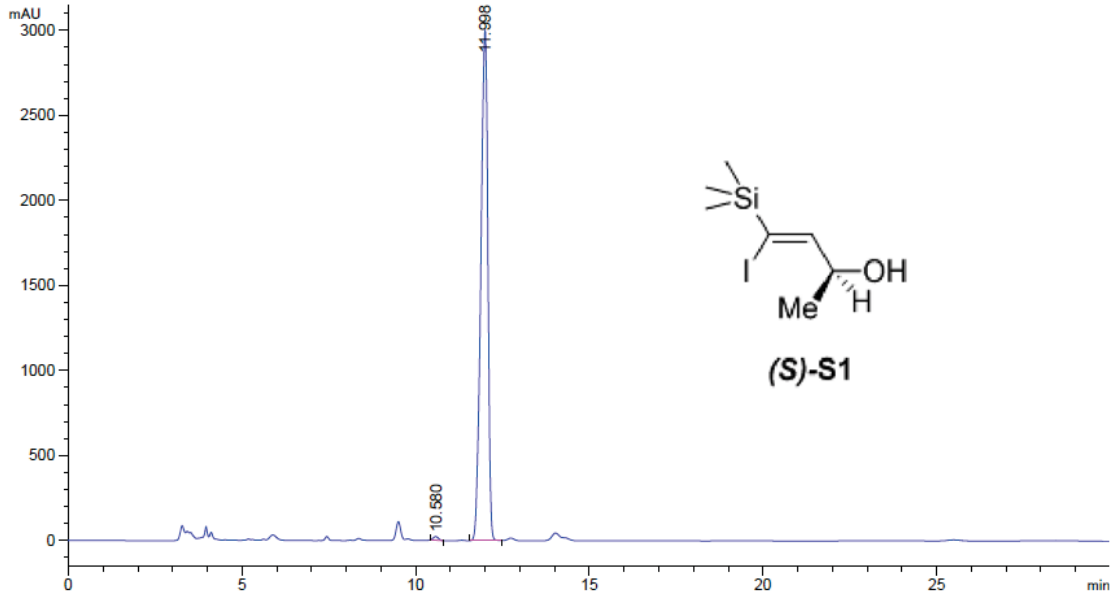


9 (Ar = C_6H_4-*p*-Br)



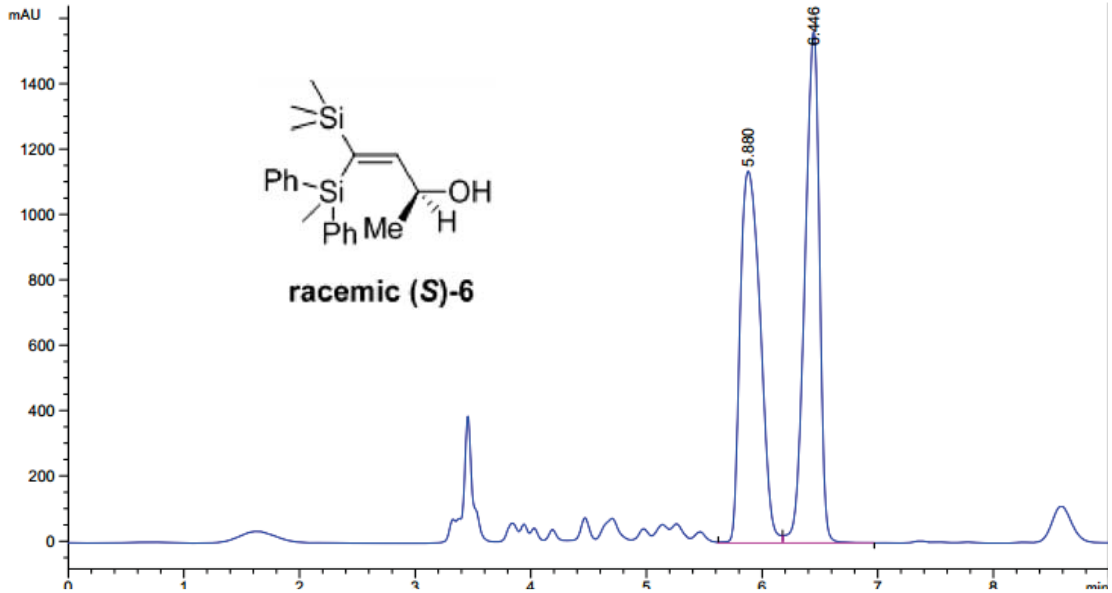
racemic (*S*)-S1

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	10.504	VV	0.3328	3.46118e4		49.7797
2	11.799	VV	0.3146	3.49182e4		50.2203

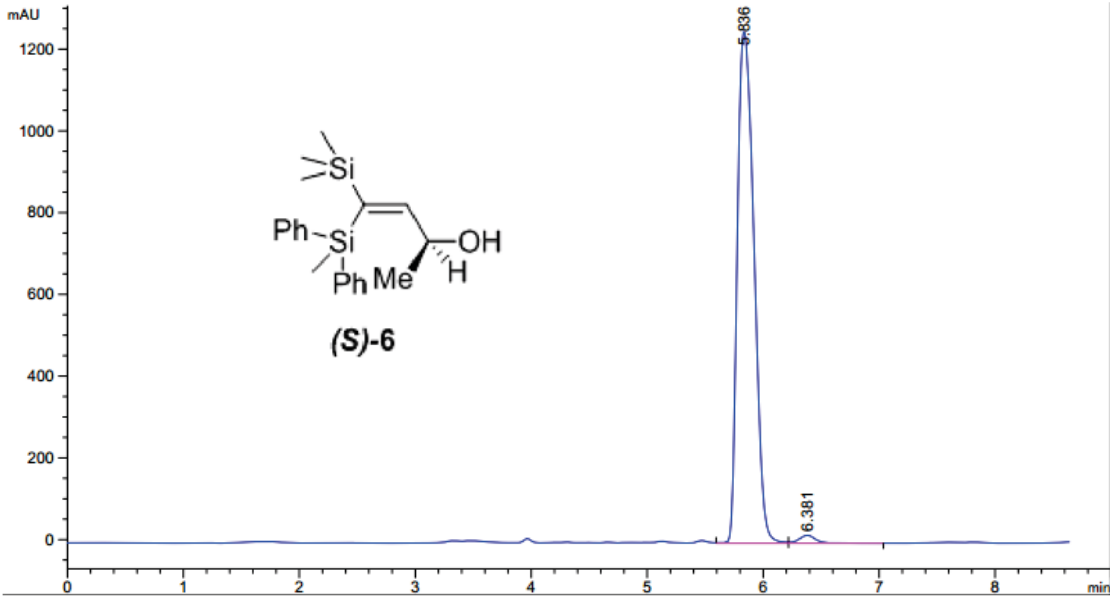


***(S)*-S1**

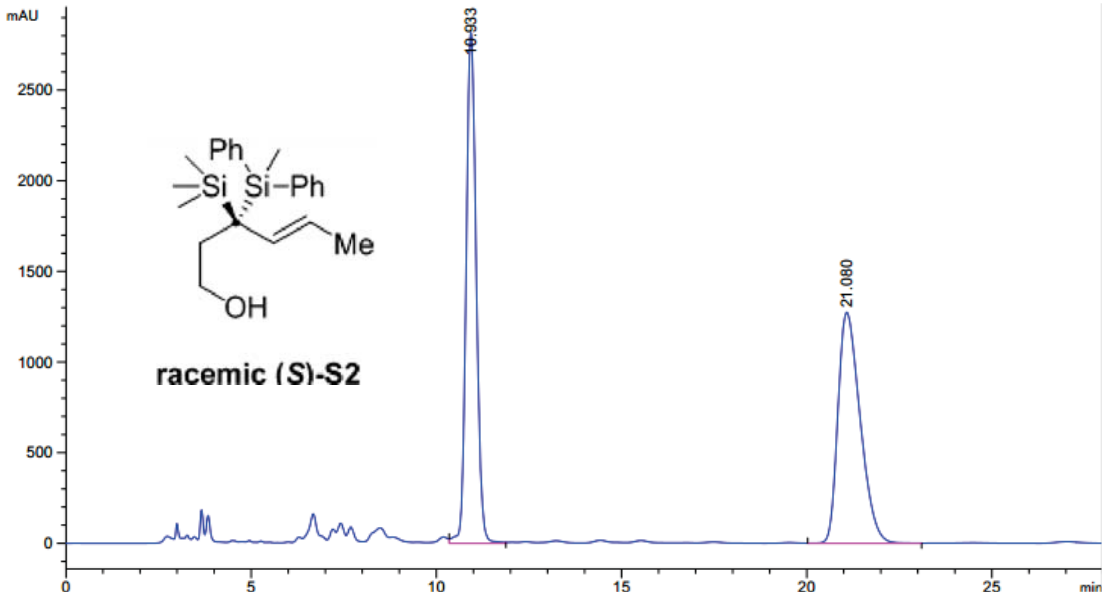
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	10.580	MM	0.1738	218.00398		0.5150
2	11.998	VV	0.2204	4.21143e4		99.4850



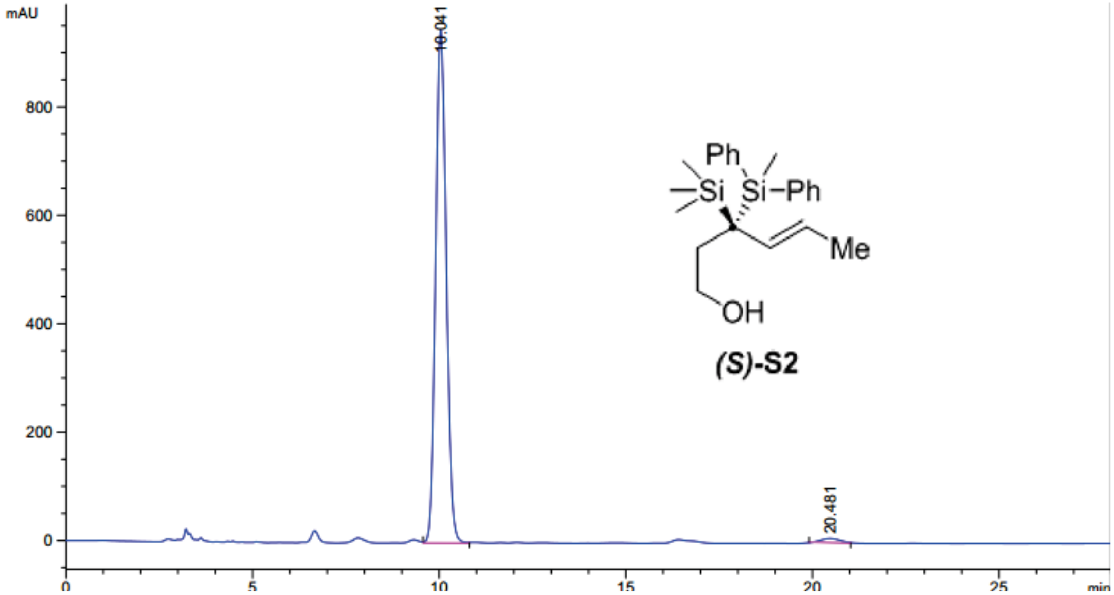
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	5.880	VV	0.2037	1.37563e4	50.1700
2	6.446	VB	0.1368	1.36631e4	49.8300



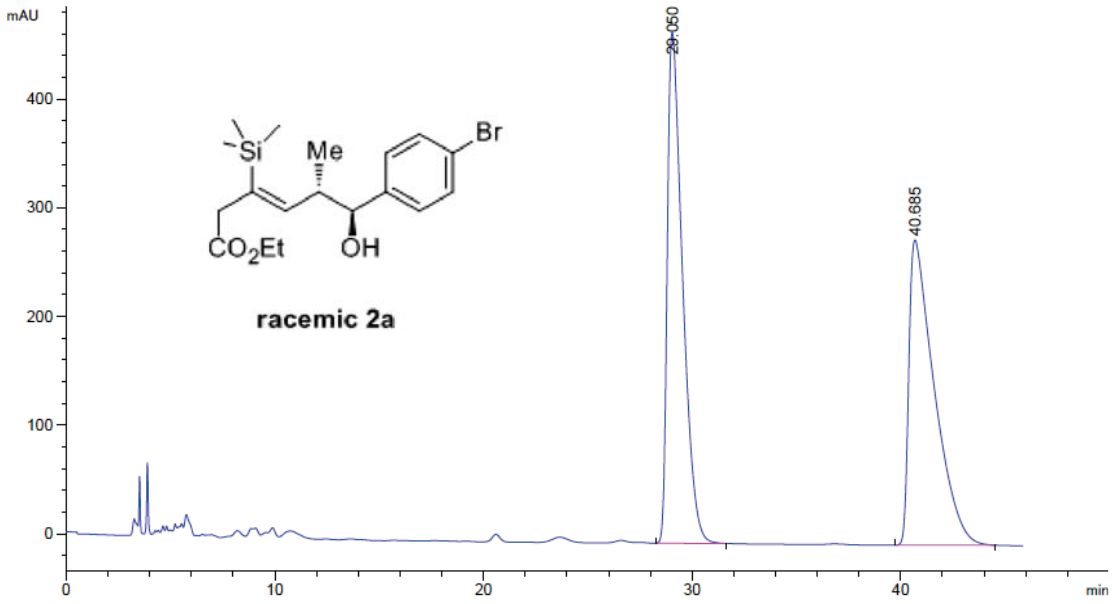
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	5.836	VV	0.1655	1.24497e4	98.4946
2	6.381	VB	0.1520	190.27803	1.5054



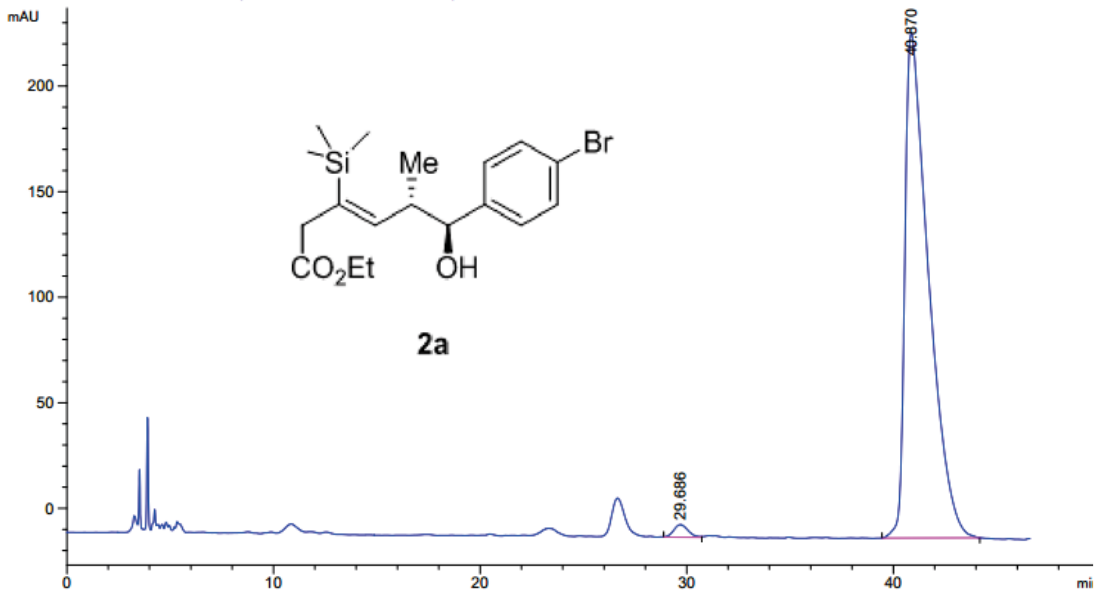
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.933	VV	0.2952	5.33617e4	50.1110
2	21.080	VB	0.6466	5.31253e4	49.8890



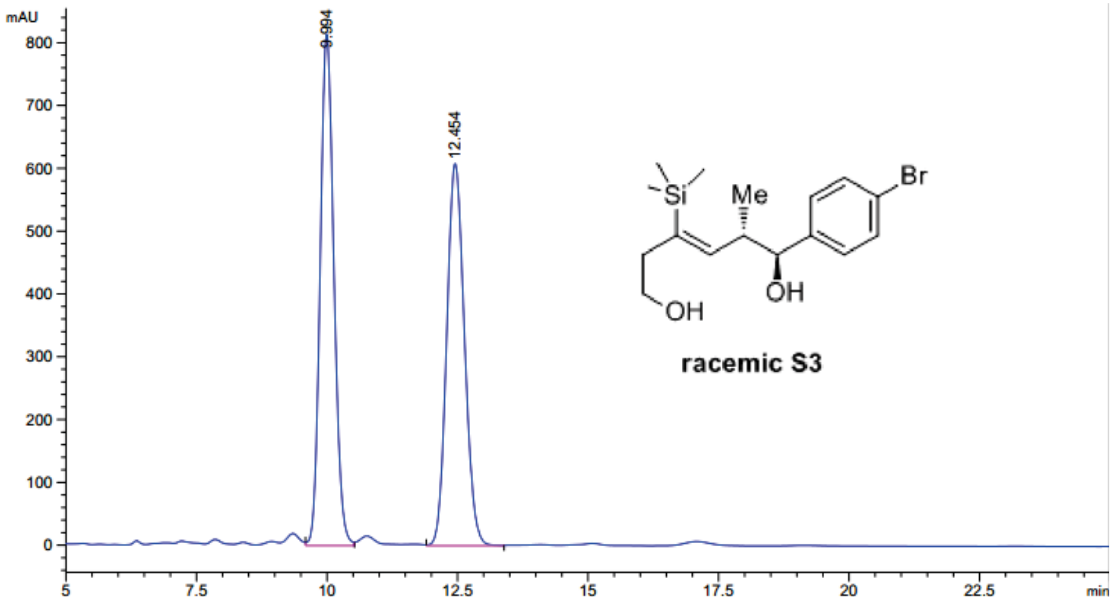
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.041	VV	0.3068	1.86208e4	98.6136
2	20.481	MM	0.5789	261.79694	1.3864



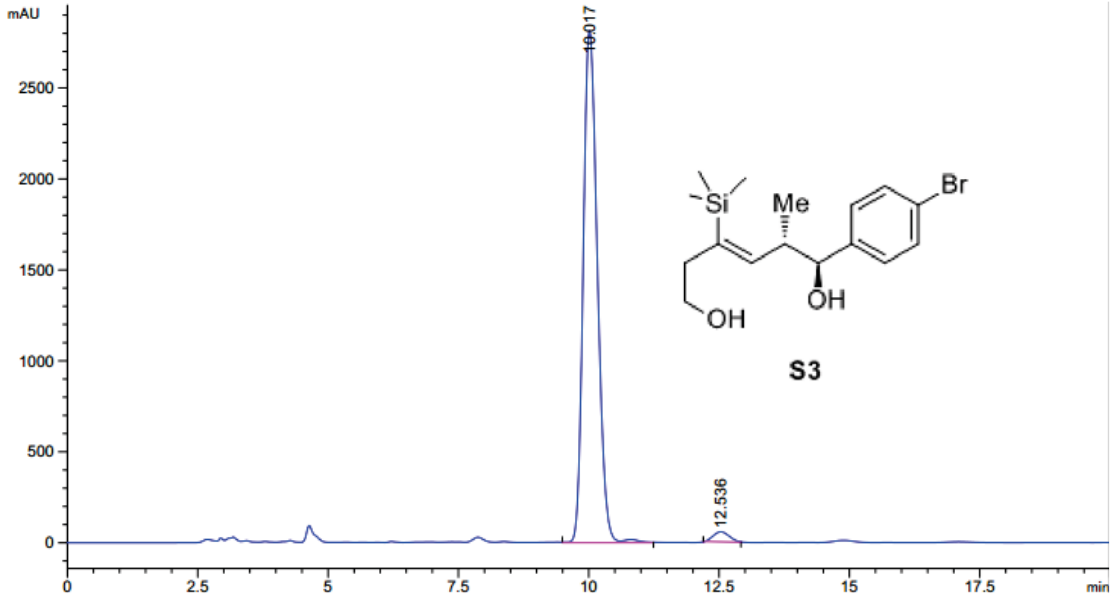
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	29.050	BB	0.7564	2.37971e4	50.1296
2	40.685	BB	1.2183	2.36740e4	49.8704



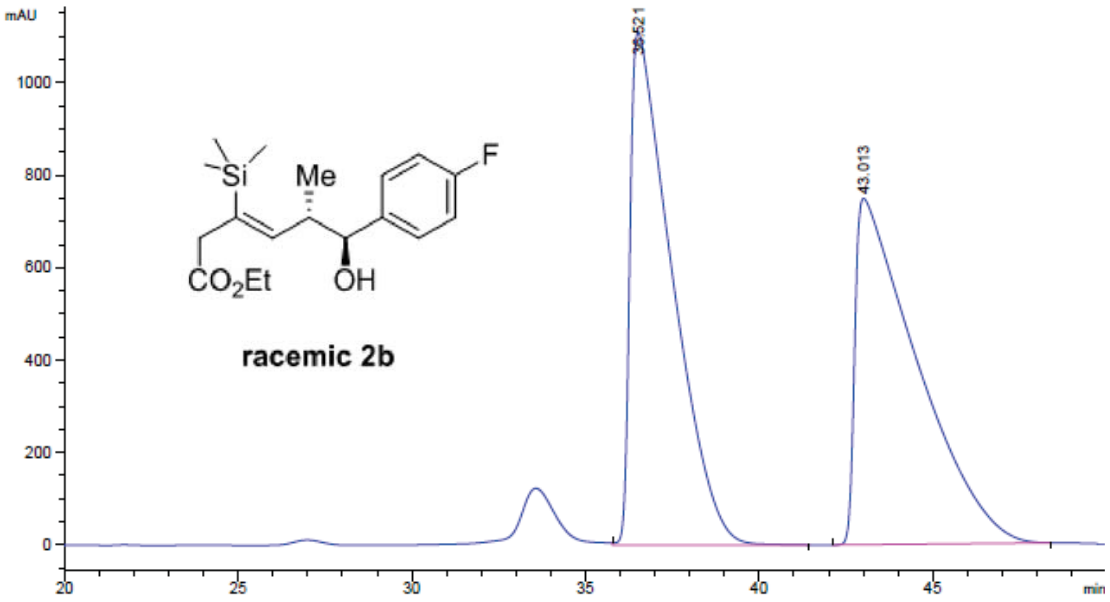
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	29.686	BV	0.7531	285.48019	1.4747
2	40.870	BB	1.1595	1.90737e4	98.5253



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	9.994	VV	0.2826	1.48409e4	50.8366
2	12.454	VB	0.3685	1.43524e4	49.1634

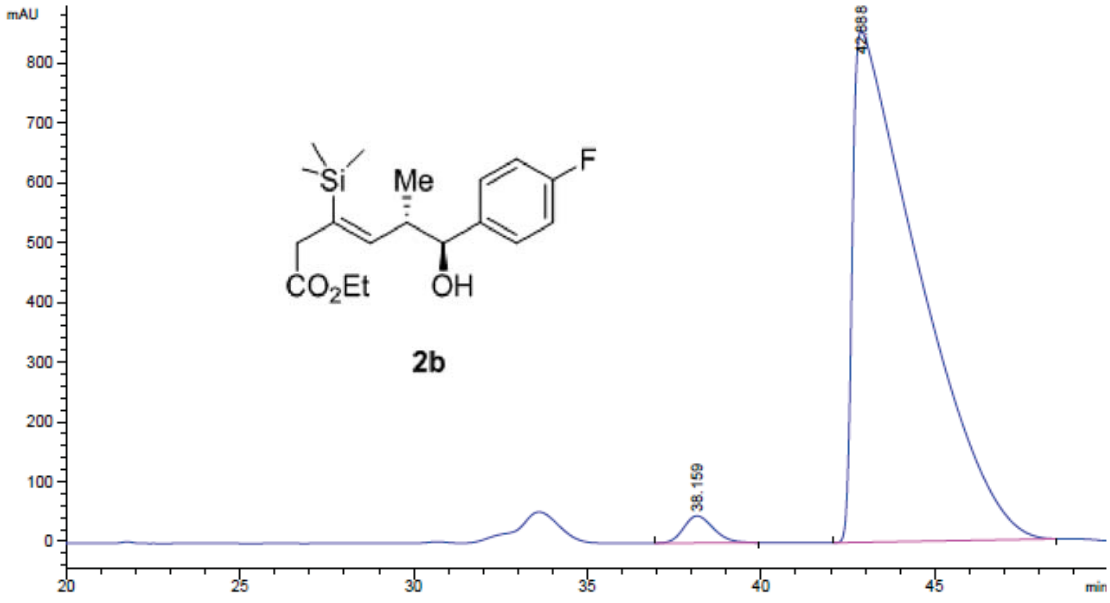


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.017	MM	0.3142	5.30518e4	97.8469
2	12.536	MM	0.3549	1167.37891	2.1531



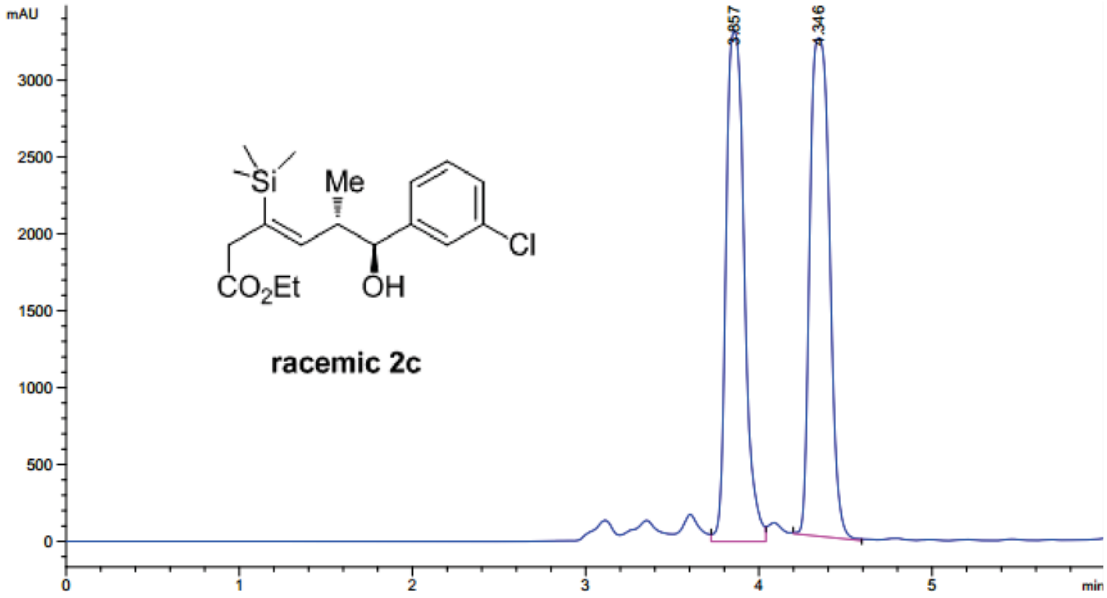
racemic 2b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	36.521	VB	1.2136	9.30604e4	49.9835
2	43.013	BB	1.7053	9.31219e4	50.0165

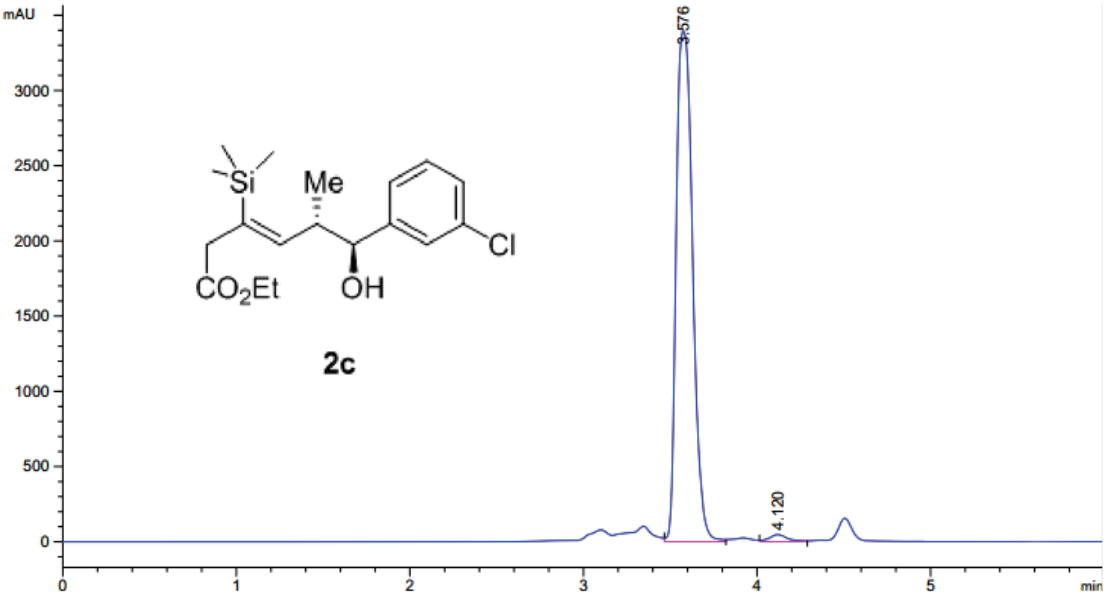


2b

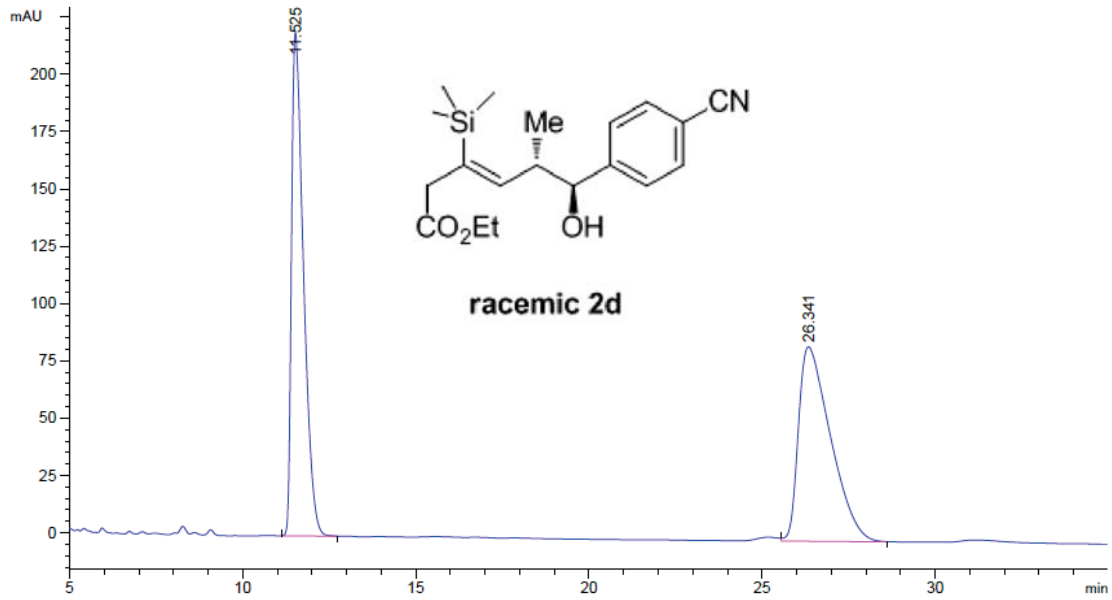
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	38.159	BB	0.9235	2704.07227	2.3186
2	42.888	BB	1.8291	1.13921e5	97.6814



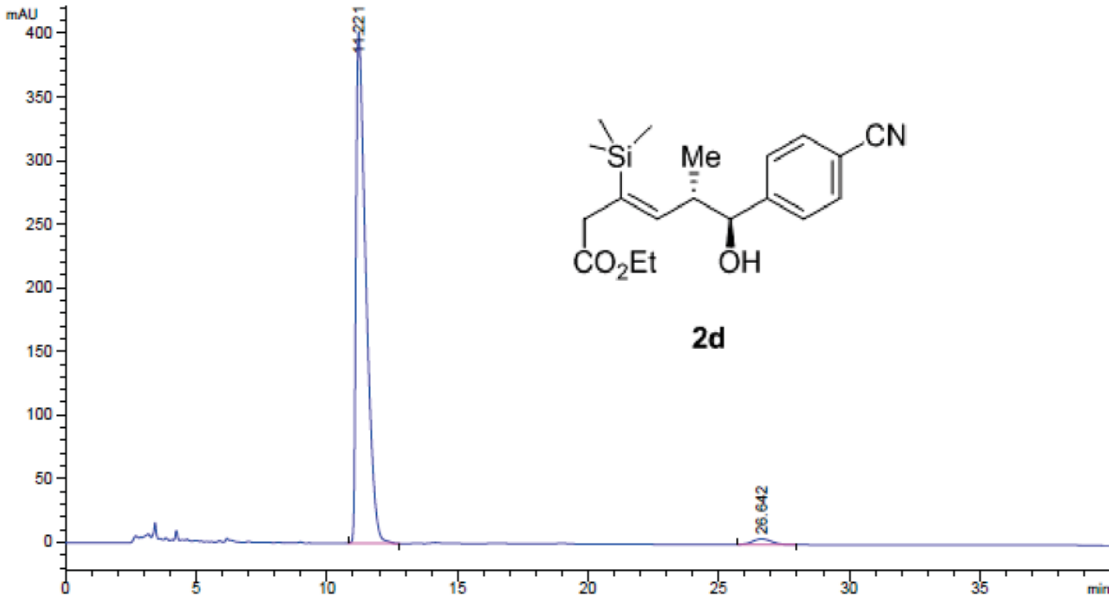
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	3.857	VV	0.1174	2.42958e4		48.0060
2	4.346	VV	0.1301	2.63141e4		51.9940



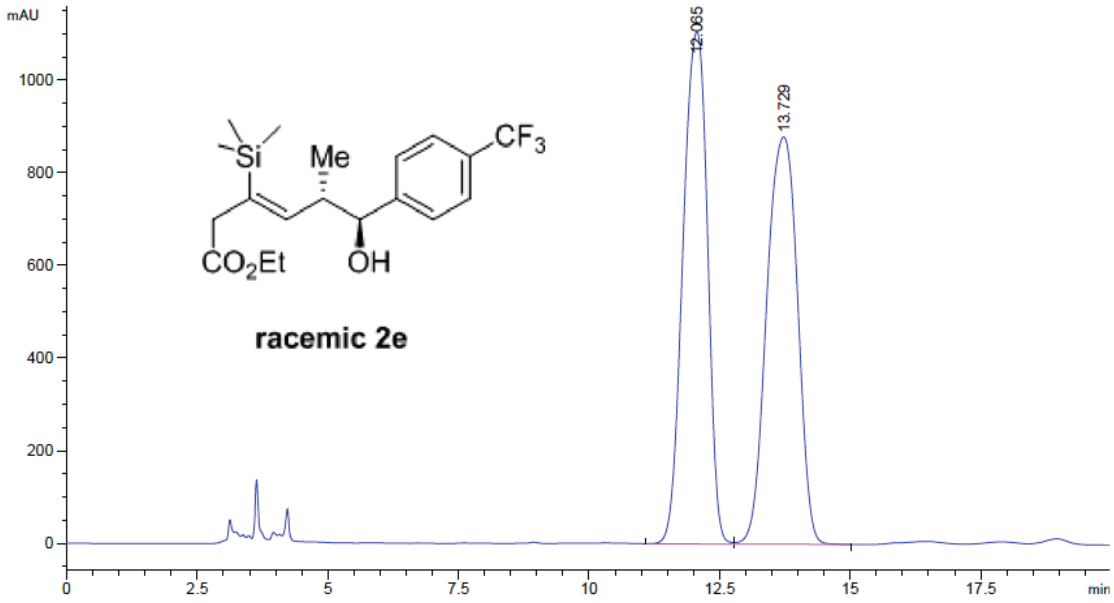
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	3.576	VV	0.1058	2.23189e4		98.4016
2	4.120	VV	0.1104	362.54346		1.5984



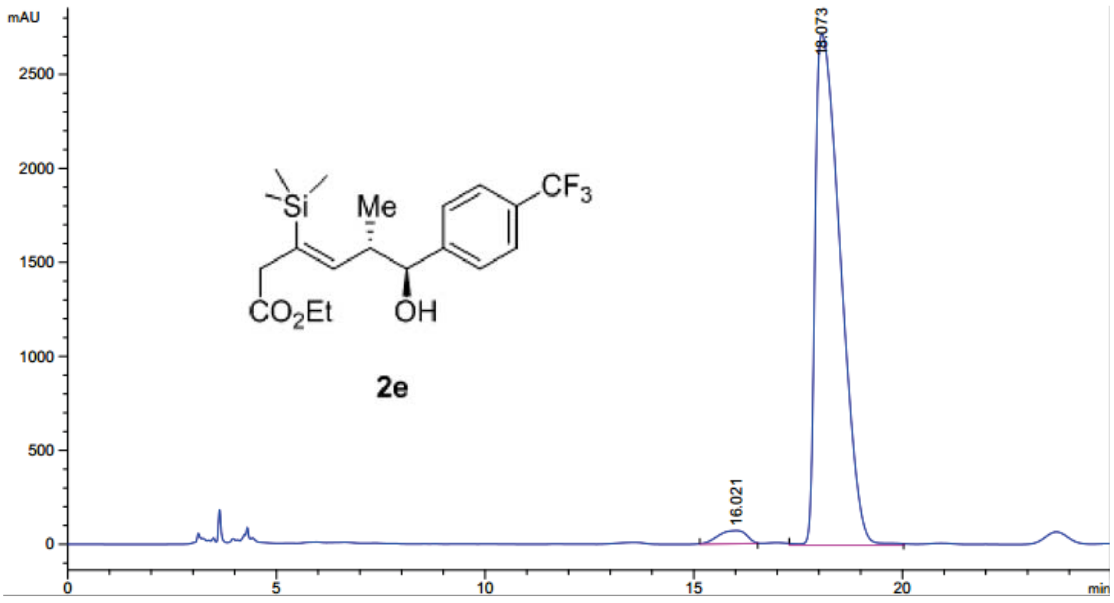
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	11.525	BB	0.3652	5286.09180	49.1807
2	26.341	VB	0.9721	5462.22314	50.8193



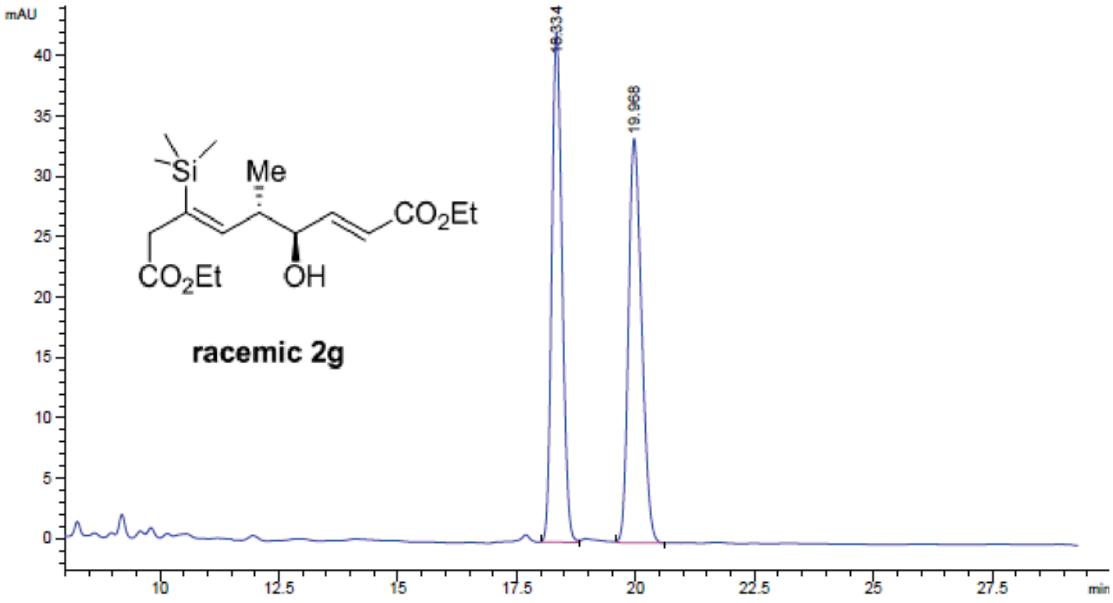
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	11.221	BB	0.3923	1.06097e4	97.9215
2	26.642	BB	0.7748	225.20332	2.0785



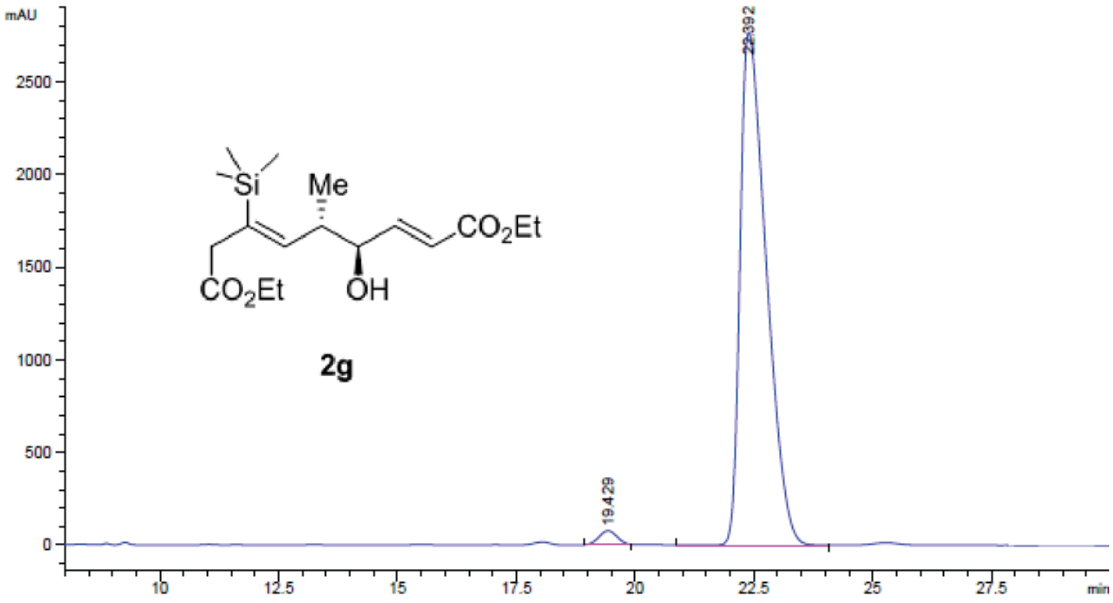
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	12.065	VV	0.5330	3.60496e4	49.9517
2	13.729	VB	0.6728	3.61193e4	50.0483



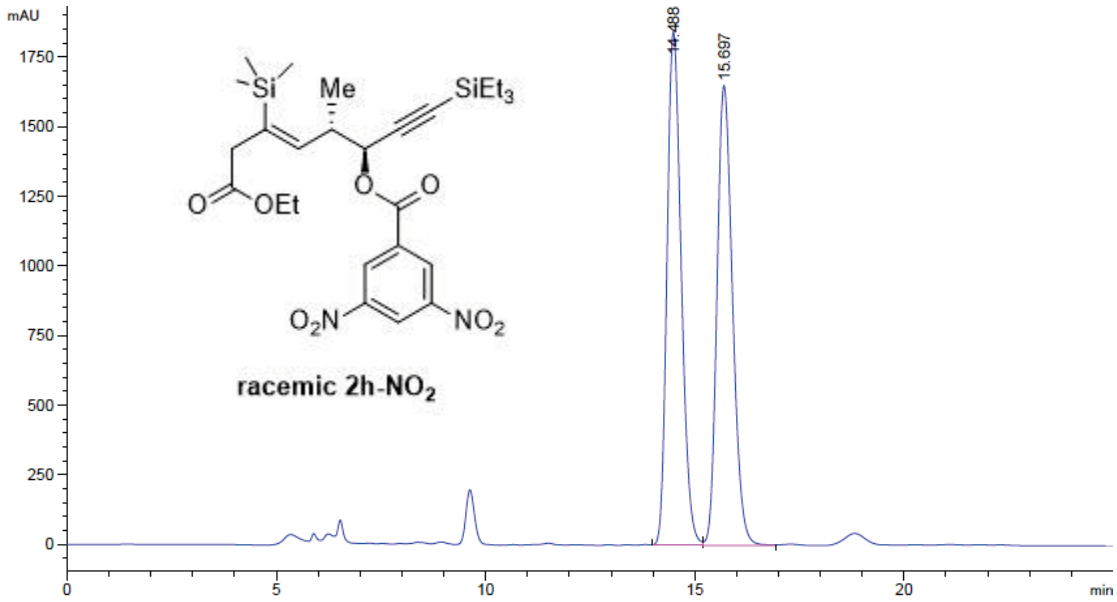
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	16.021	MM	0.7940	3325.87158	2.8250
2	18.073	MM	0.7004	1.14403e5	97.1750



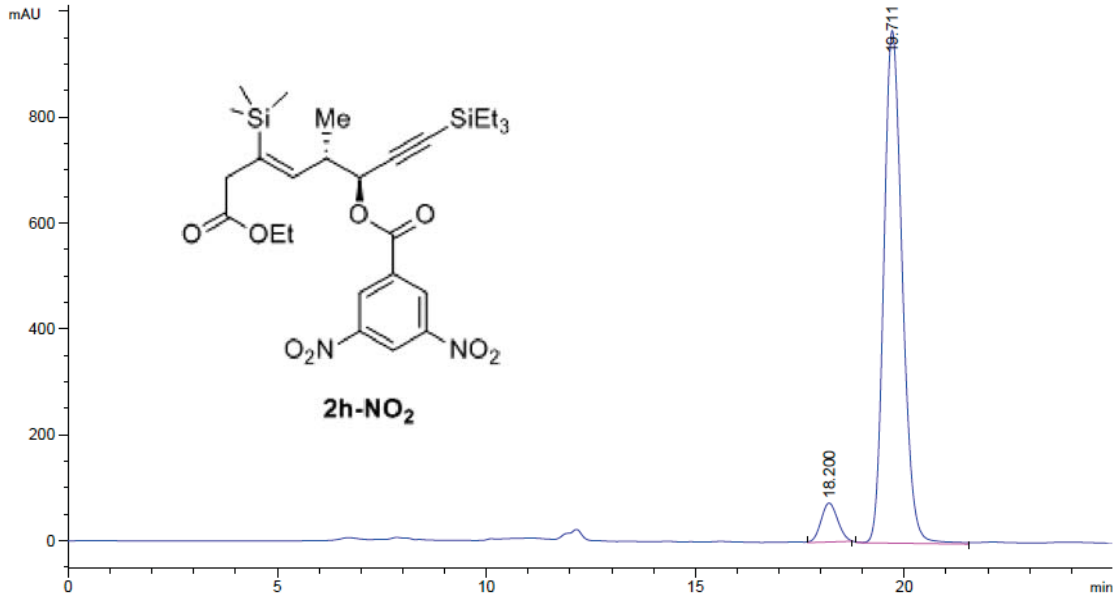
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	18.334	BB	0.2332	634.45331	49.6892
2	19.968	BB	0.2967	642.39093	50.3108



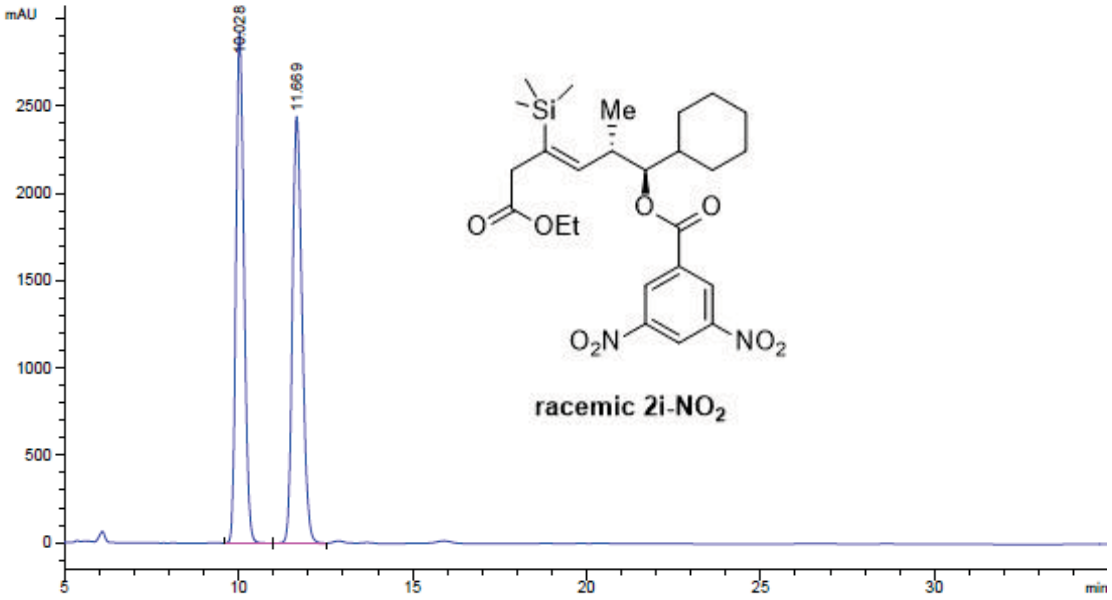
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	19.429	MM	0.4400	1988.66541	1.8421
2	22.392	VV	0.5891	1.05965e5	98.1579



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	14.494	VV	0.3816	4.35291e4	50.5225
2	15.703	VV	0.4066	4.26287e4	49.4775

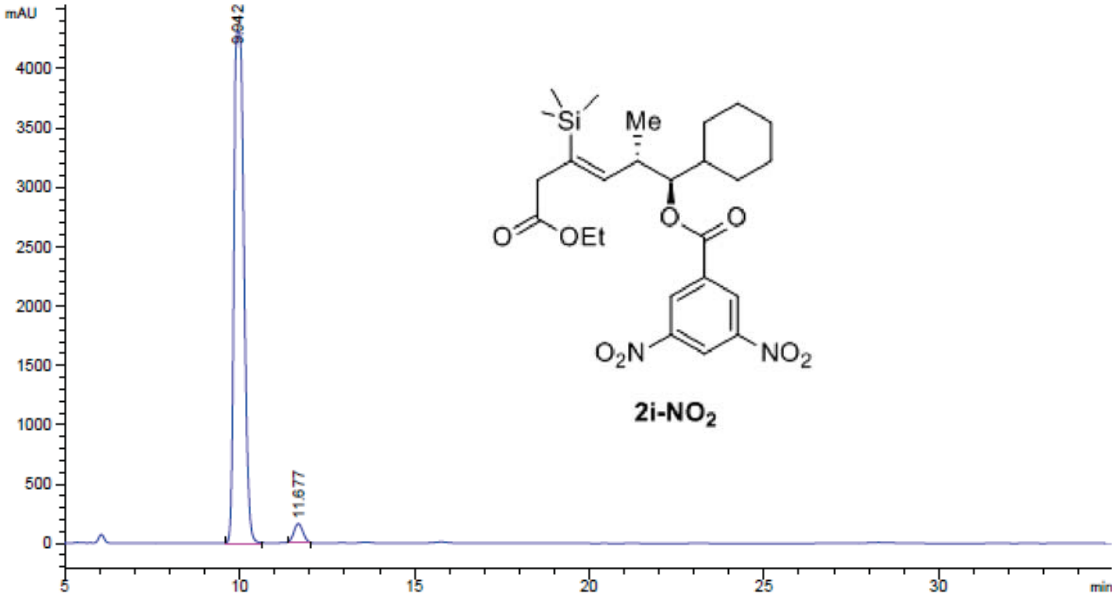


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	18.200	MM	0.4620	2038.15515	6.4359
2	19.711	MM	0.5104	2.96302e4	93.5641



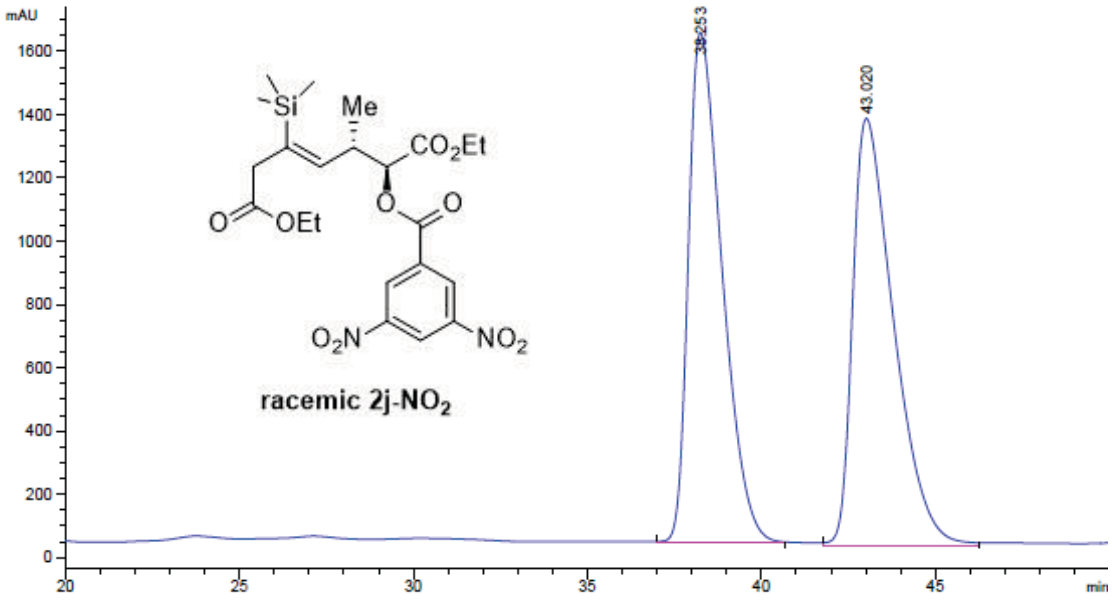
racemic **2i-NO_2**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.028	VV	0.2503	4.71212e4	49.9241
2	11.669	VV	0.3014	4.72645e4	50.0759



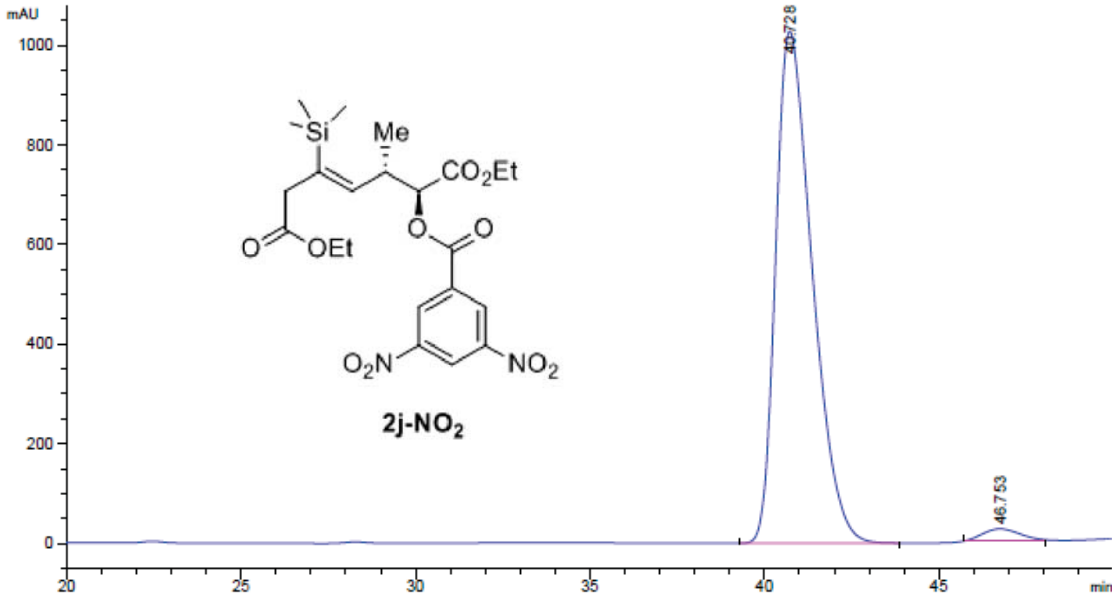
2i-NO_2

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	9.942	MM	0.3302	8.57055e4	96.6194
2	11.677	MM	0.3084	2998.77637	3.3806



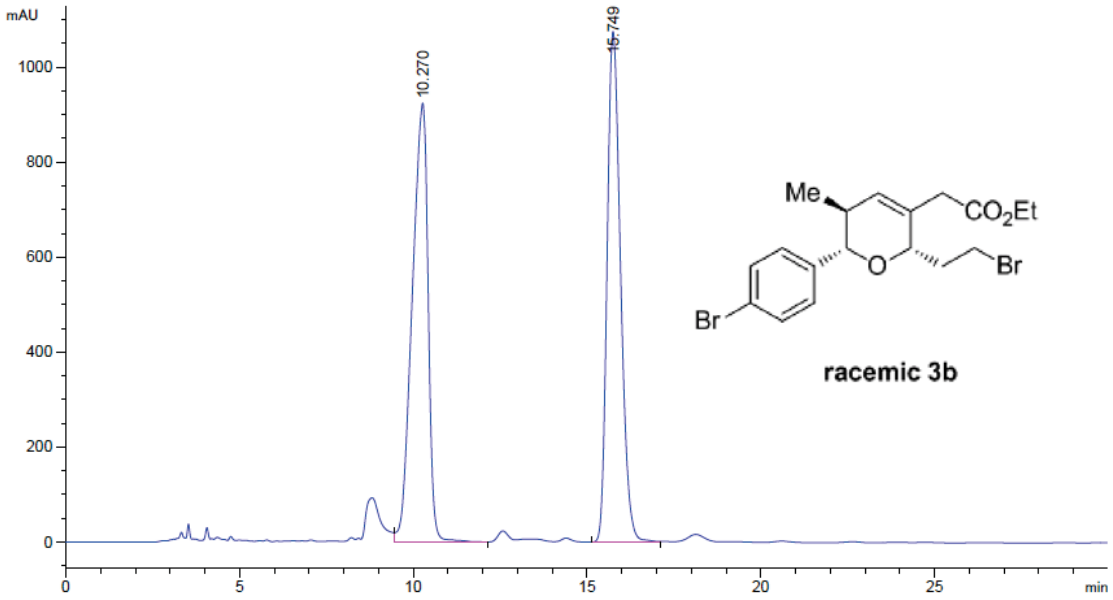
racemic 2j-NO_2

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	38.253	MM	1.1209	1.08389e5	49.5487
2	43.020	MM	1.3617	1.10364e5	50.4513



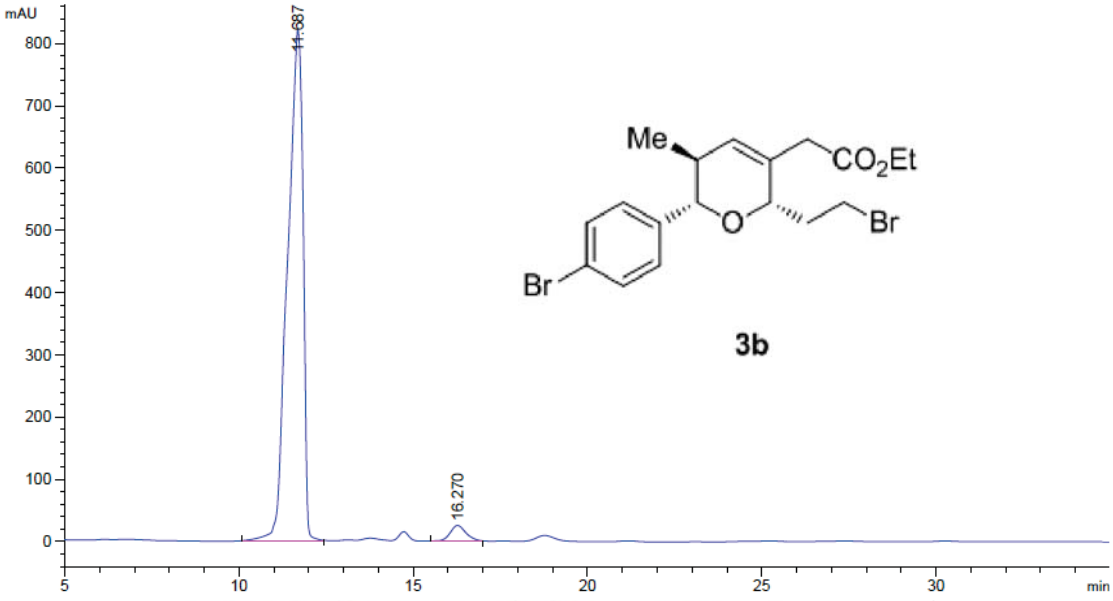
2j-NO_2

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	40.728	BB	1.1155	7.46788e4	97.8075
2	46.753	MM	1.2068	1674.00049	2.1925



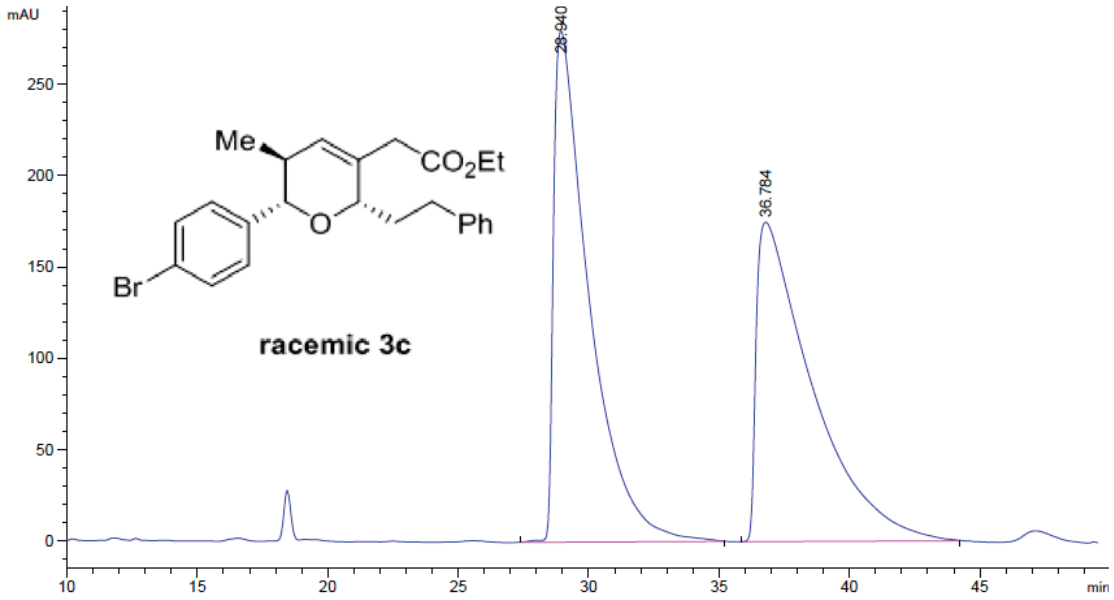
racemic 3b

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.270	VB	0.5180	2.93856e4	50.4694
2	15.749	BB	0.4164	2.88390e4	49.5306

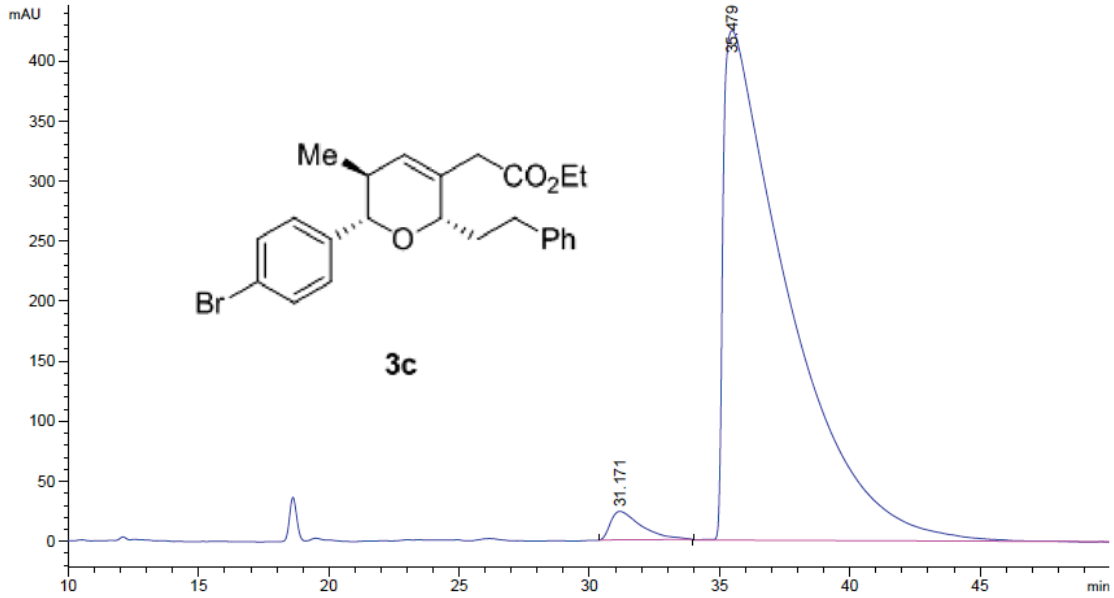


3b

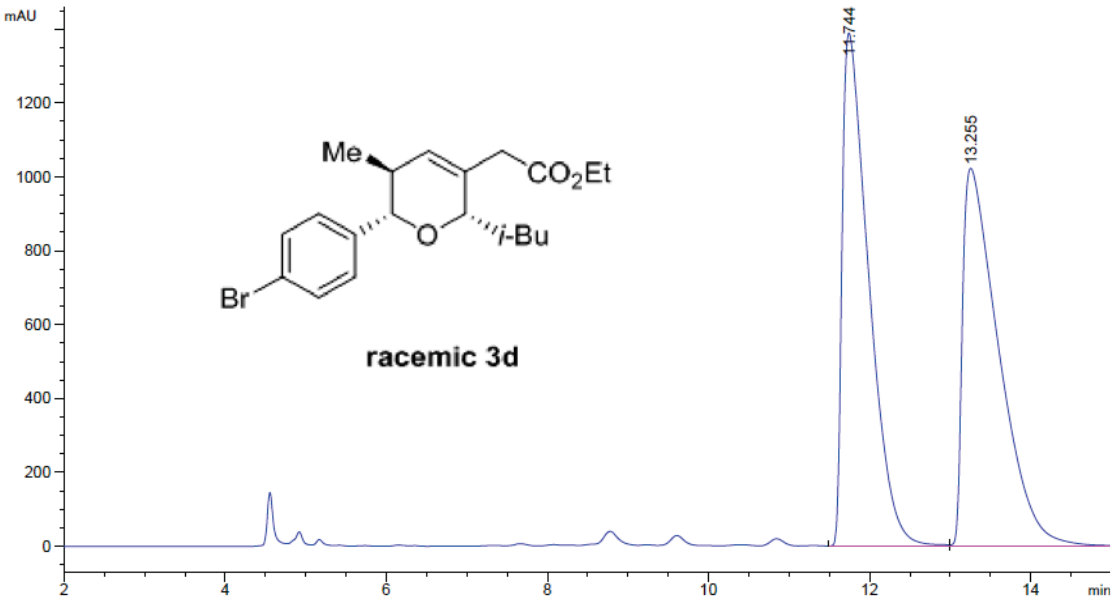
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	11.687	MM	0.5137	2.53156e4	97.2439
2	16.270	MM	0.4948	717.50879	2.7561



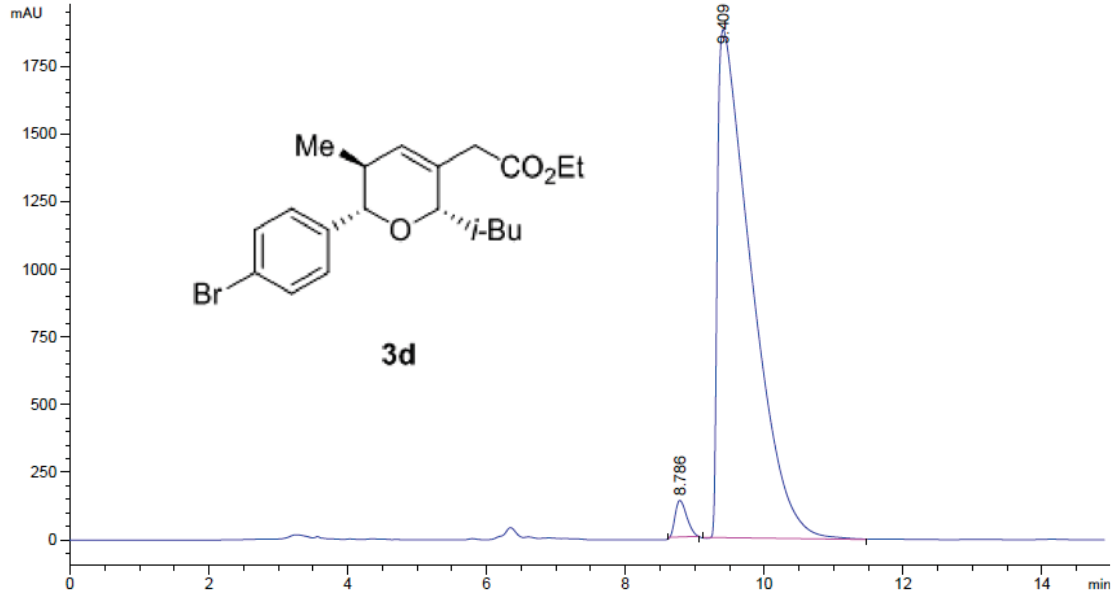
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	28.940	BB	1.3684	2.65703e4	50.5705
2	36.784	BB	2.0256	2.59709e4	49.4295



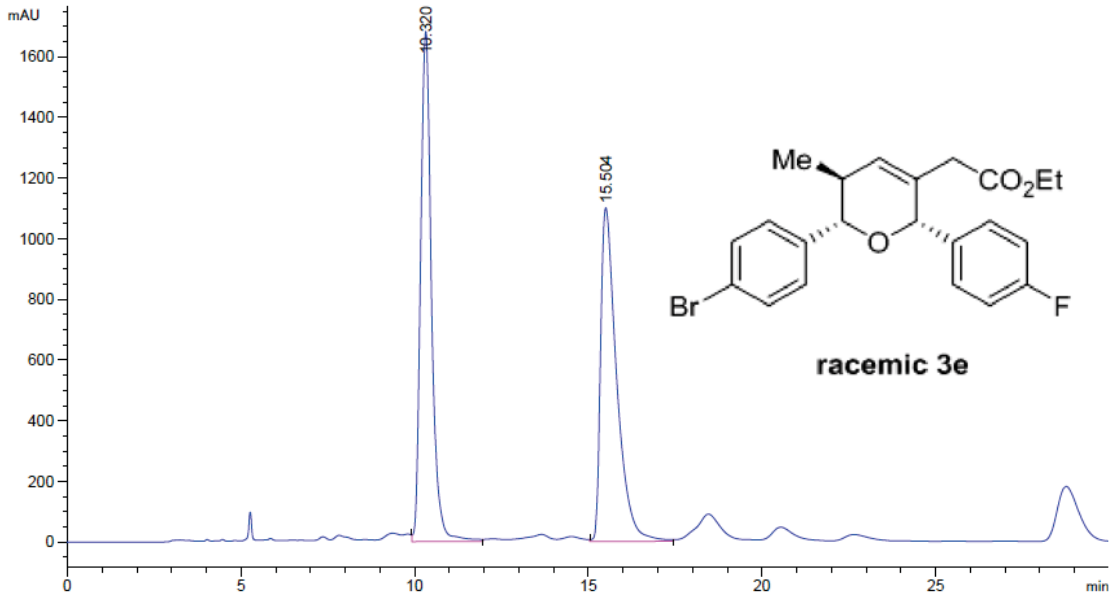
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	31.171	MM	1.3689	1950.72742	2.5838
2	35.479	MM	2.8878	7.35491e4	97.4162



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	11.744	VV	0.3462	3.18740e4		49.8839
2	13.255	VV	0.4683	3.20224e4		50.1161

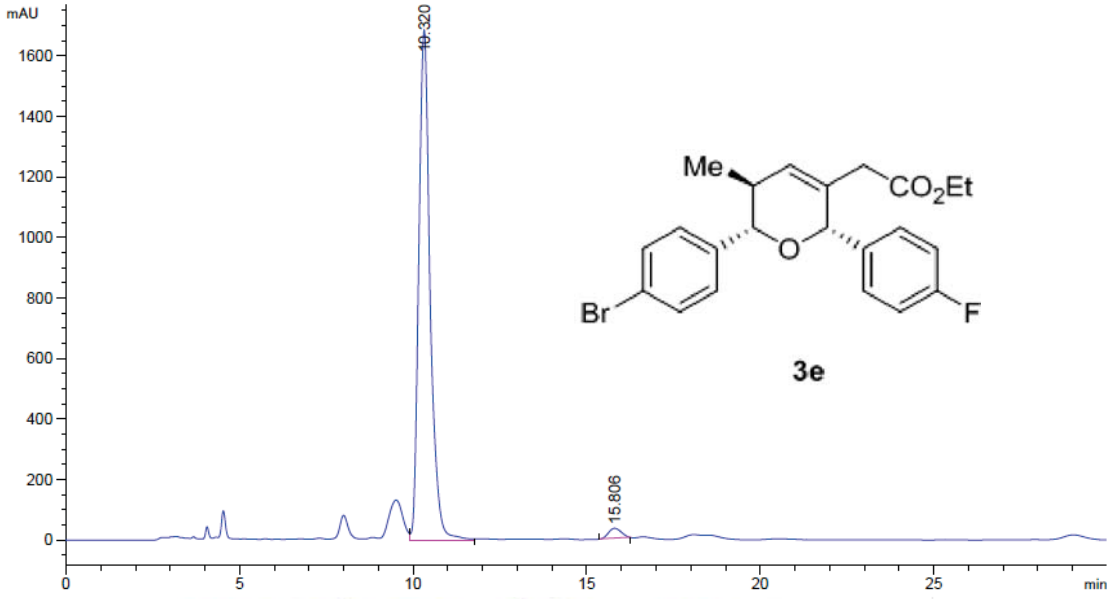


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	8.786	MM	0.1934	1568.10657		2.4020
2	9.409	MM	0.5655	6.37158e4		97.5980



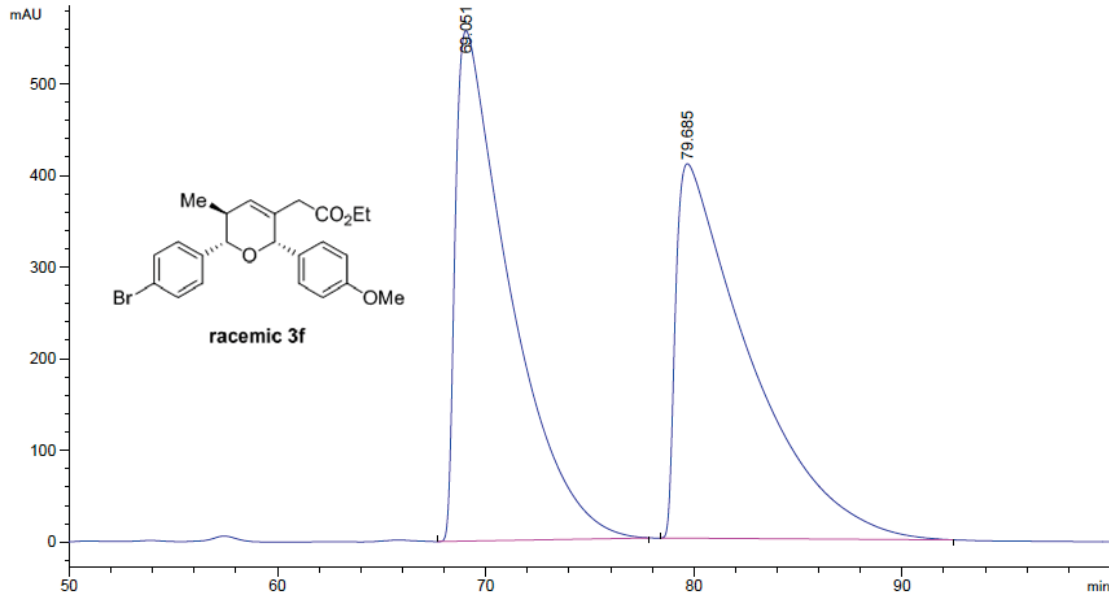
racemic 3e

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.320	VV	0.3396	3.67871e4	50.9656
2	15.504	VV	0.4788	3.53933e4	49.0344

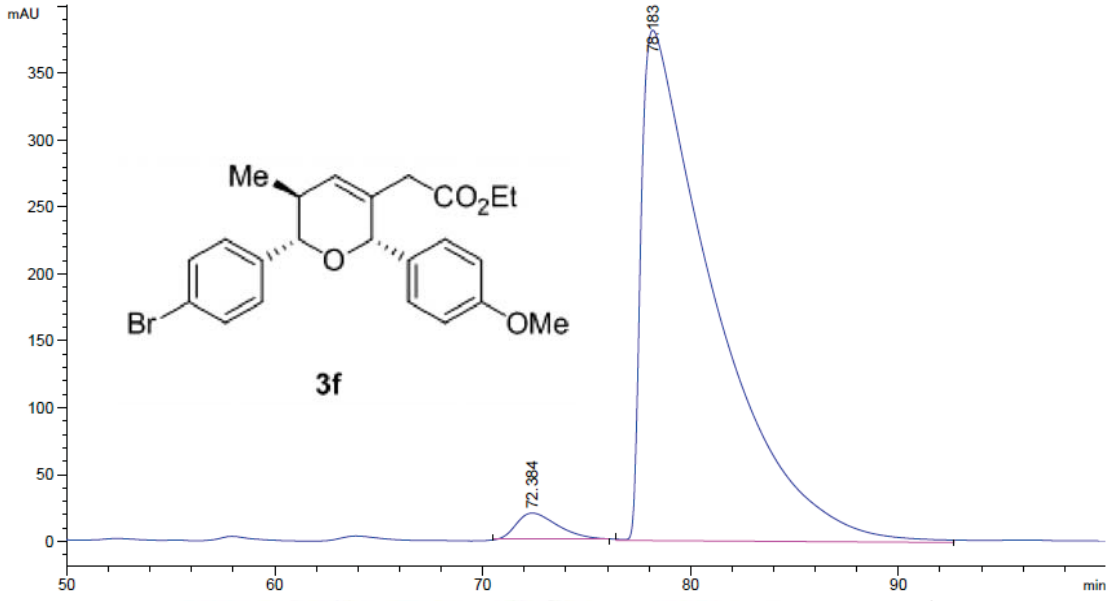


3e

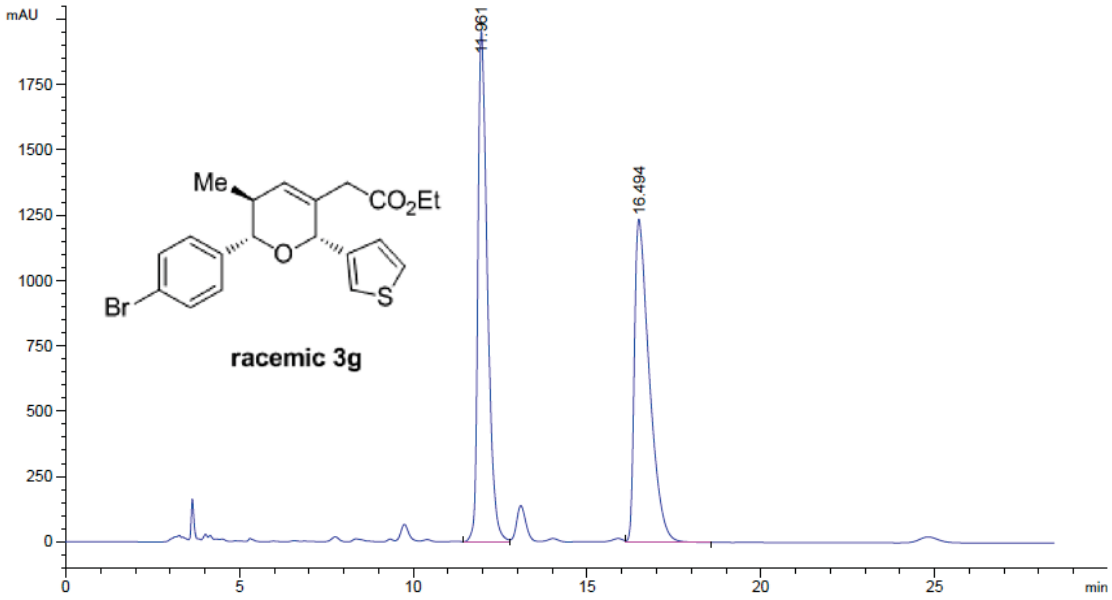
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	10.320	VB	0.3495	3.83149e4	97.9648
2	15.806	MM	0.4119	795.99261	2.0352



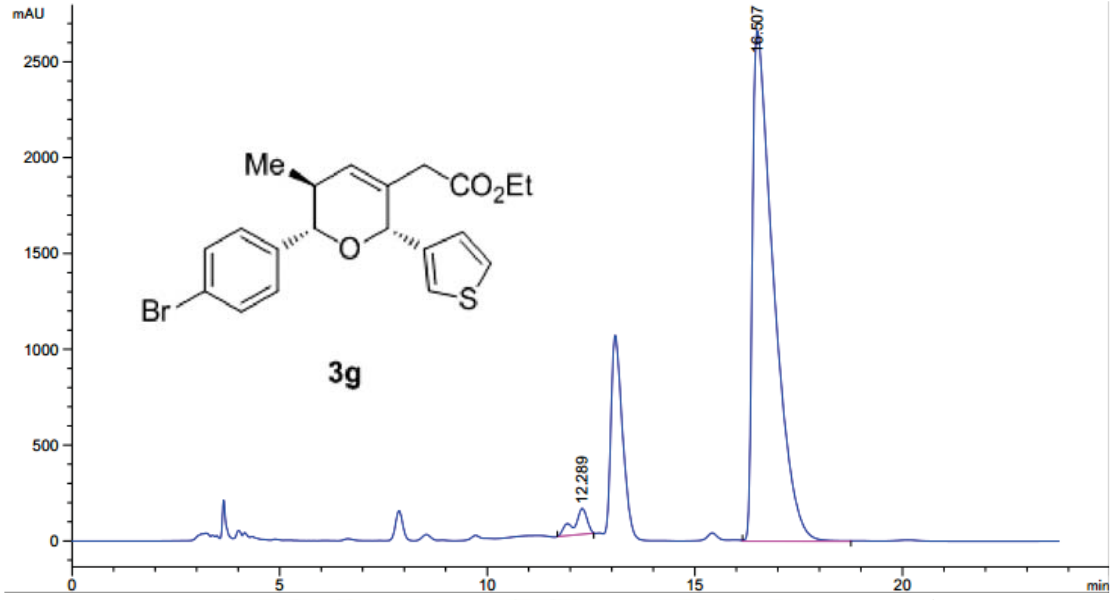
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	69.051	VB	2.4654	1.00832e5		50.1163
2	79.685	BB	3.2389	1.00364e5		49.8837



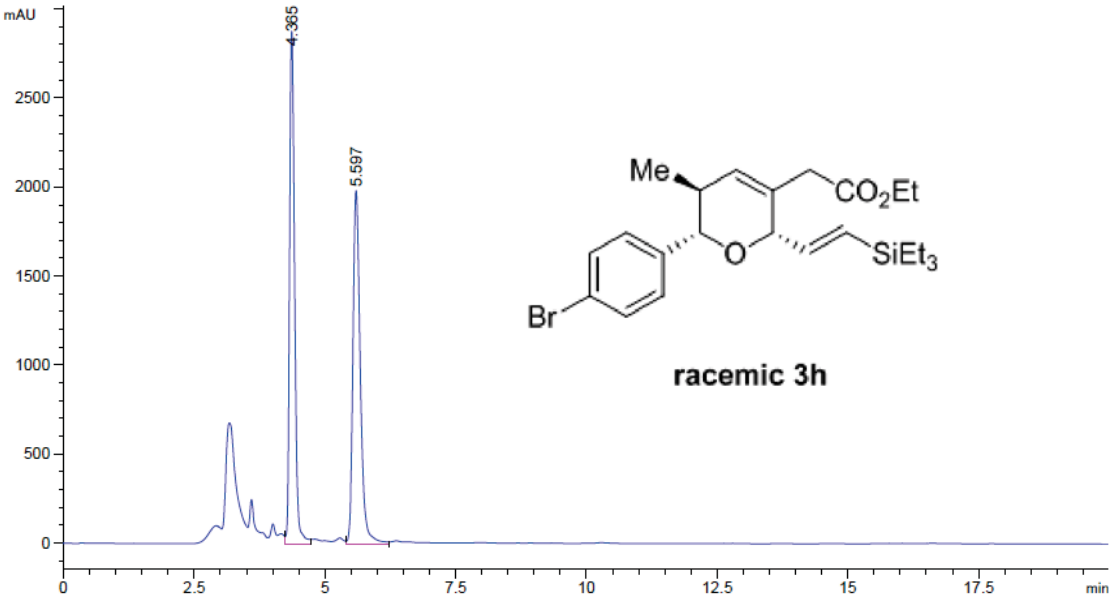
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	72.384	MM	2.1917	2482.89893		2.6015
2	78.183	MM	4.0595	9.29575e4		97.3985



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	11.961	VV	0.2906	3.75103e4		50.2515
2	16.494	VB	0.4462	3.71348e4		49.7485

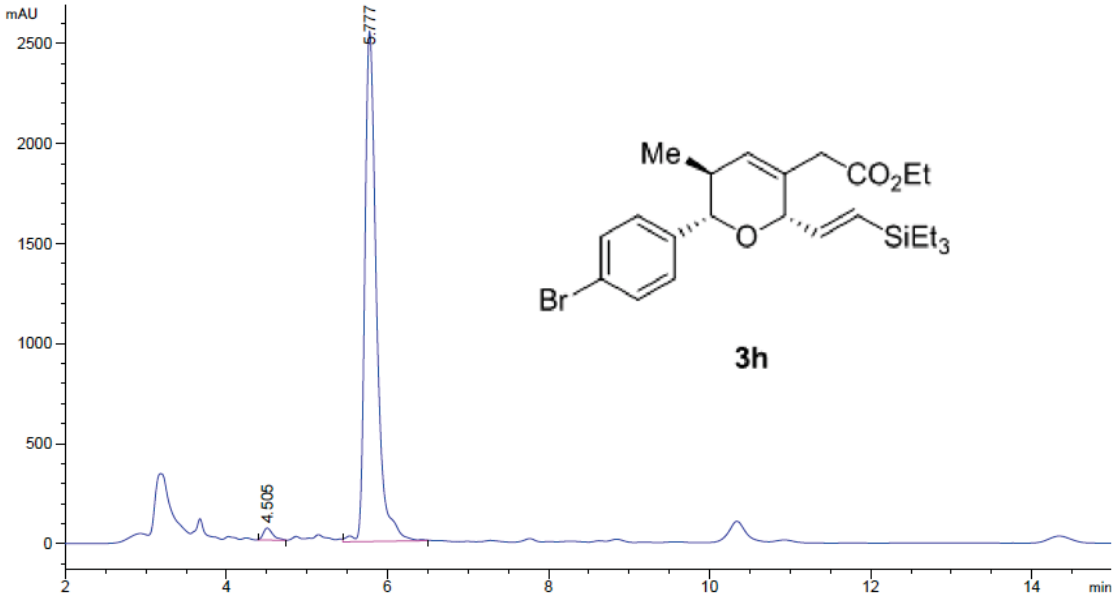


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	12.289	MM	0.3794	3064.22607		3.1511
2	16.507	VV	0.5172	9.41774e4		96.8489



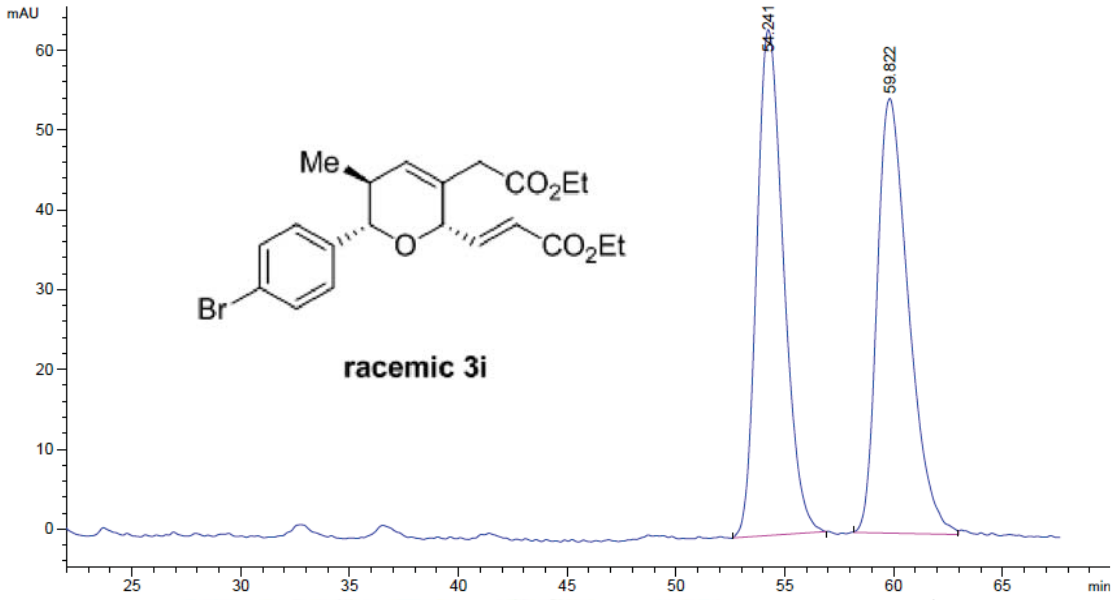
racemic 3h

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	4.365	VV	0.1063	1.94334e4	50.0931
2	5.597	VV	0.1488	1.93612e4	49.9069

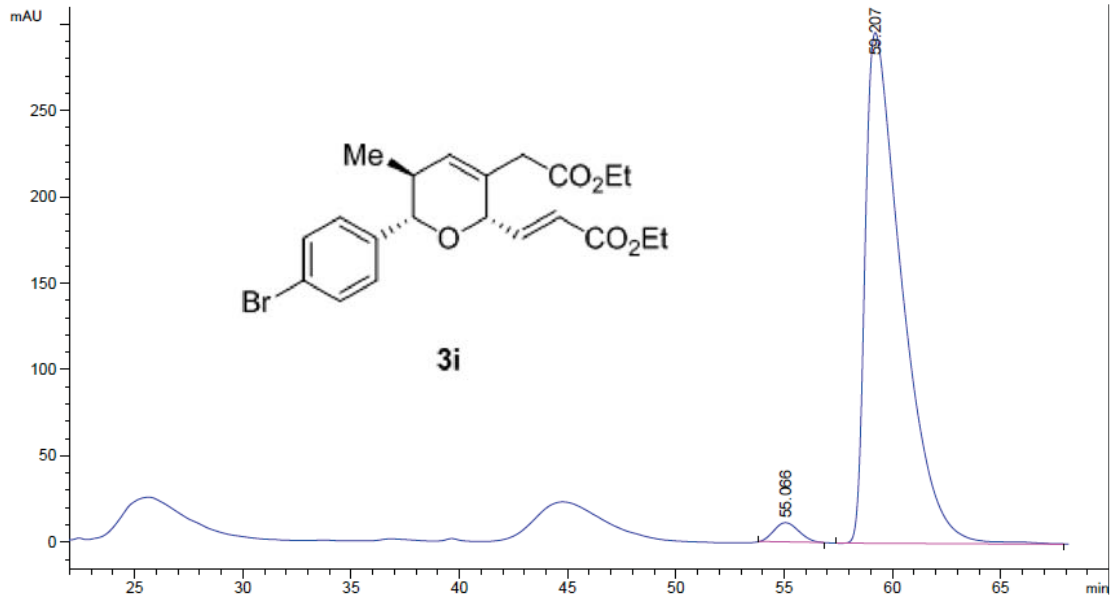


3h

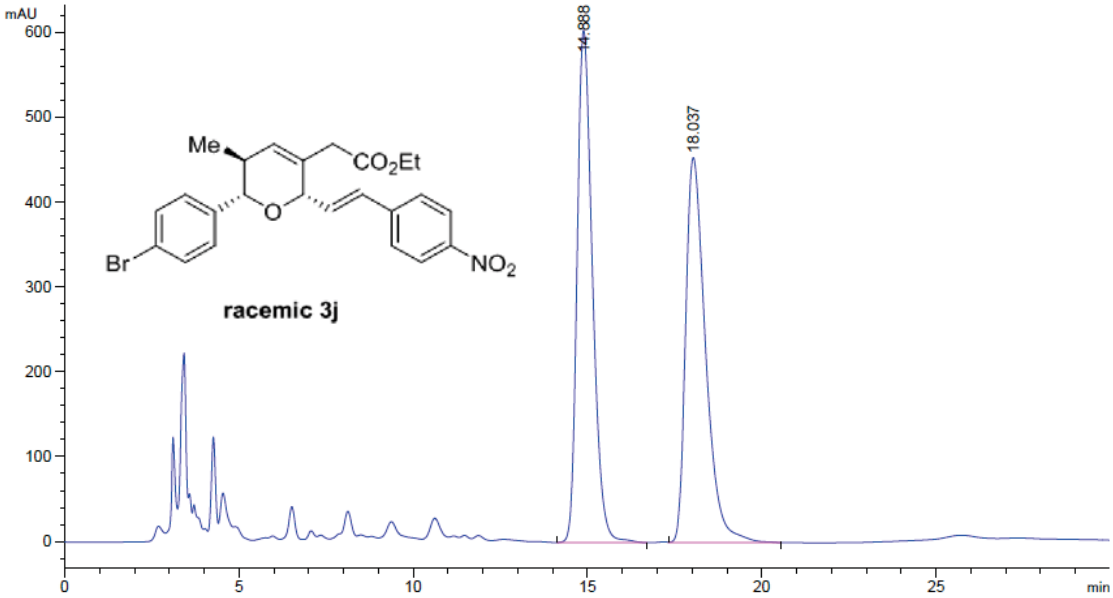
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	4.505	MM	0.1386	500.07956	1.9061
2	5.777	MM	0.1680	2.57350e4	98.0939



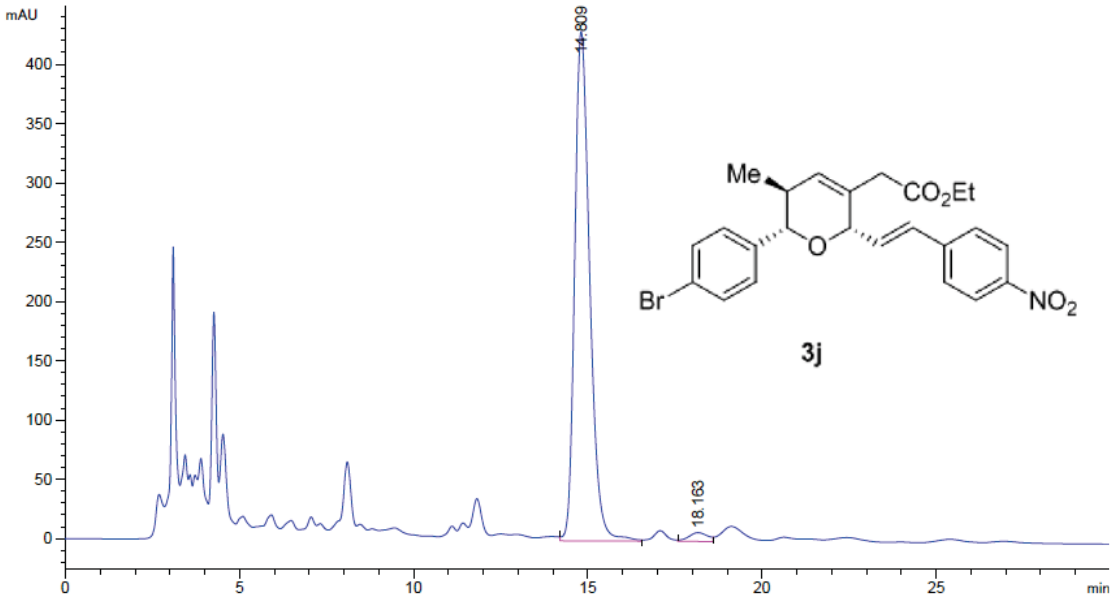
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	54.241	BB	1.3262	5422.08643	49.7356
2	59.822	BV	1.5050	5479.72949	50.2644



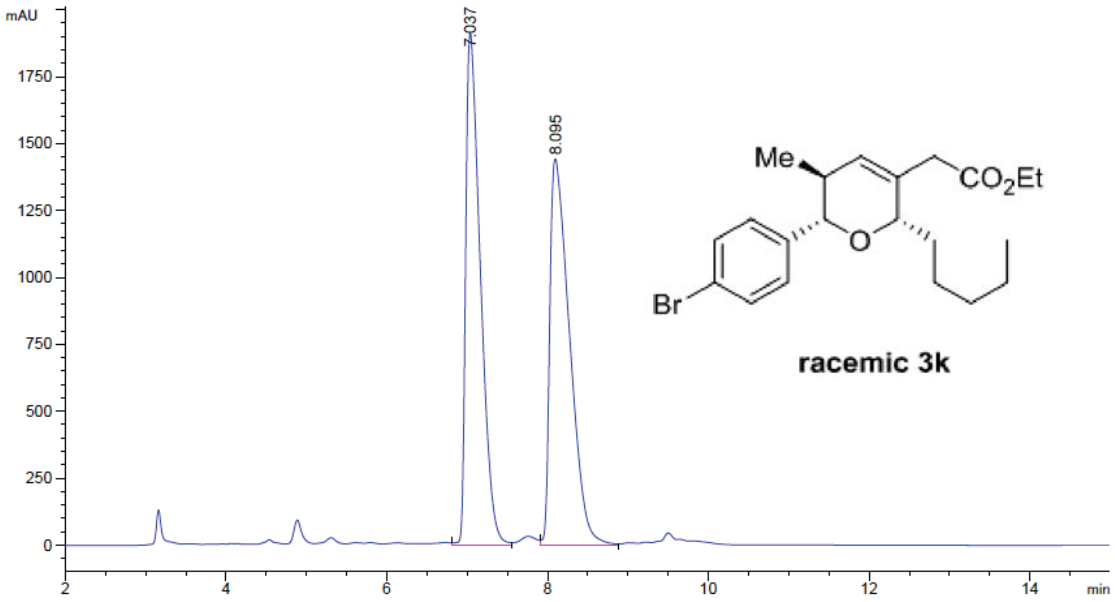
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	55.066	MM	1.3351	890.27448	2.4886
2	59.207	MM	1.9652	3.48832e4	97.5114



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	14.888	BB	0.4696	1.84225e4		50.5891
2	18.037	VB	0.6053	1.79934e4		49.4109

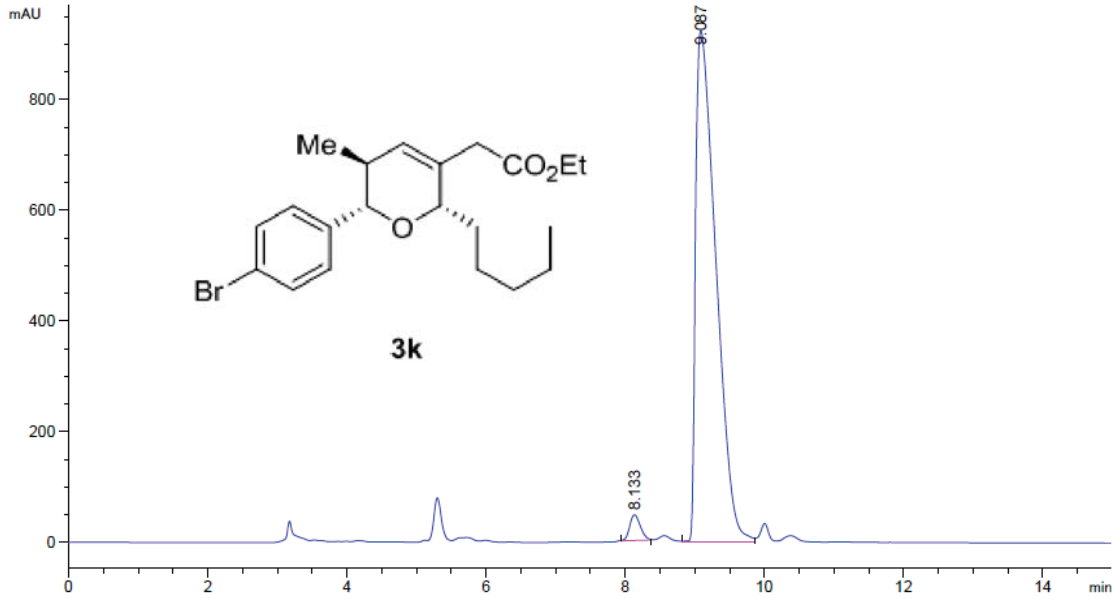


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	14.809	VB	0.4621	1.28927e4		97.8683
2	18.163	VV	0.5766	280.82120		2.1317



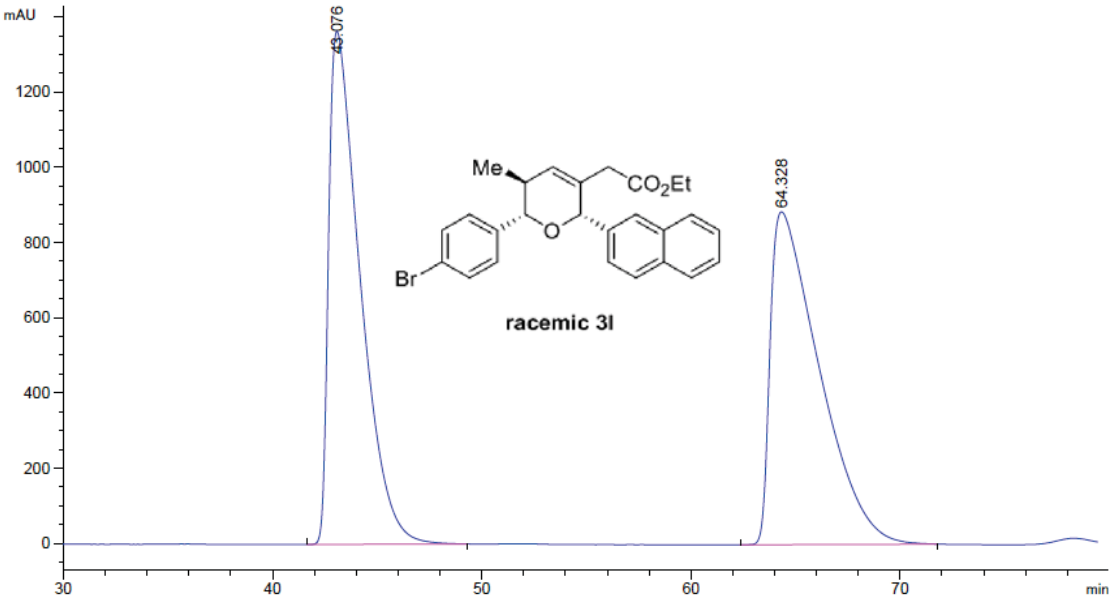
racemic 3k

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	7.037	VV	0.1931	2.42882e4	49.6434
2	8.095	VV	0.2662	2.46372e4	50.3566



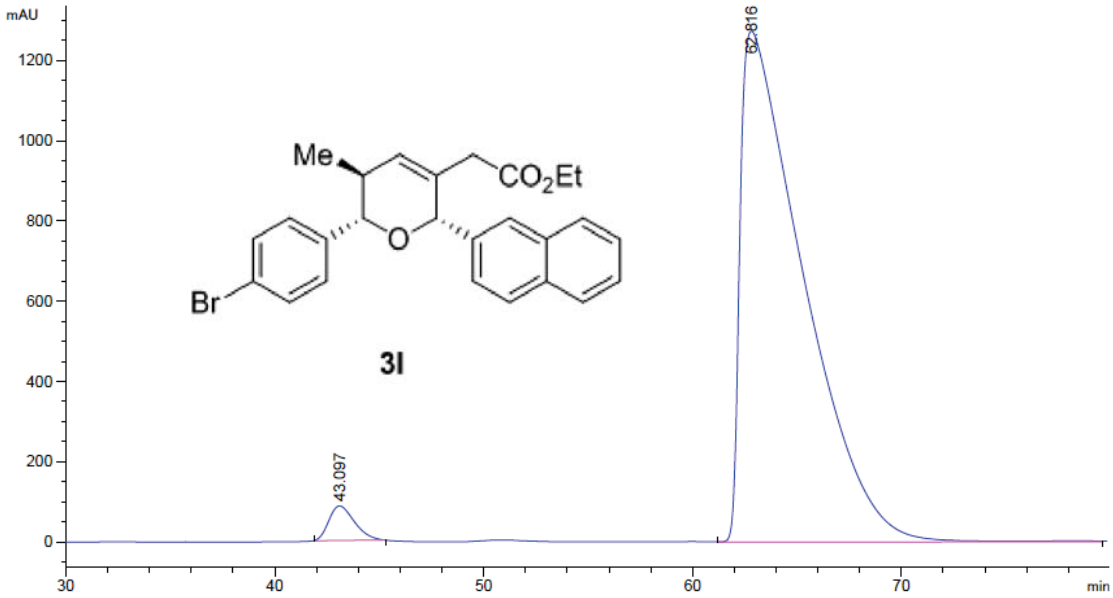
3k

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	8.133	MM	0.1783	496.41330	2.5884
2	9.087	VV	0.3157	1.86820e4	97.4116



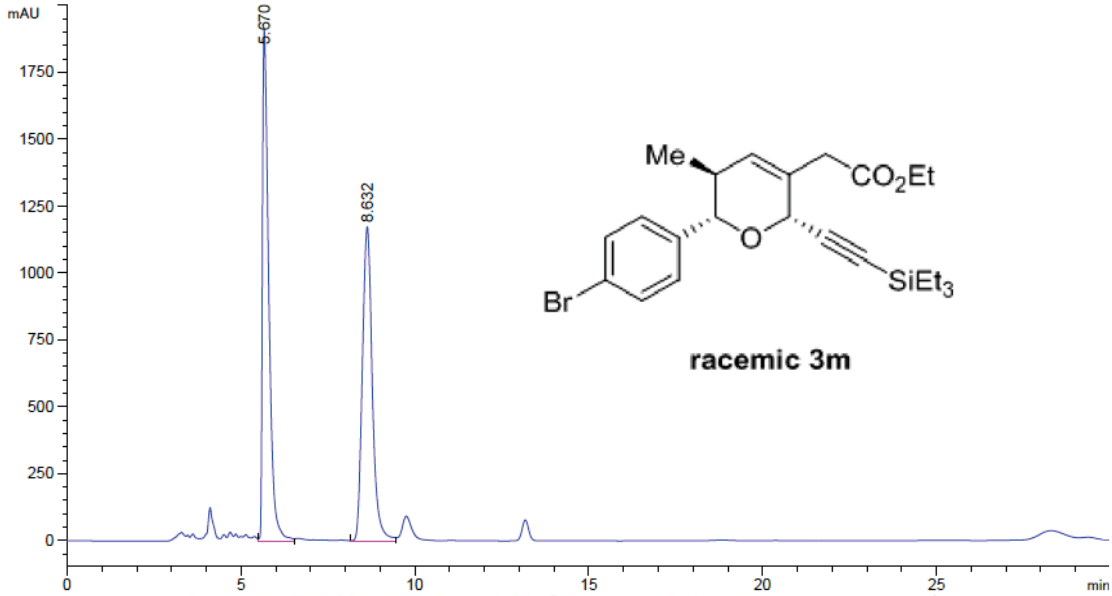
racemic 3l

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	43.076	VB	1.5450	1.42529e5		49.7376
2	64.328	BB	2.3063	1.44033e5		50.2624



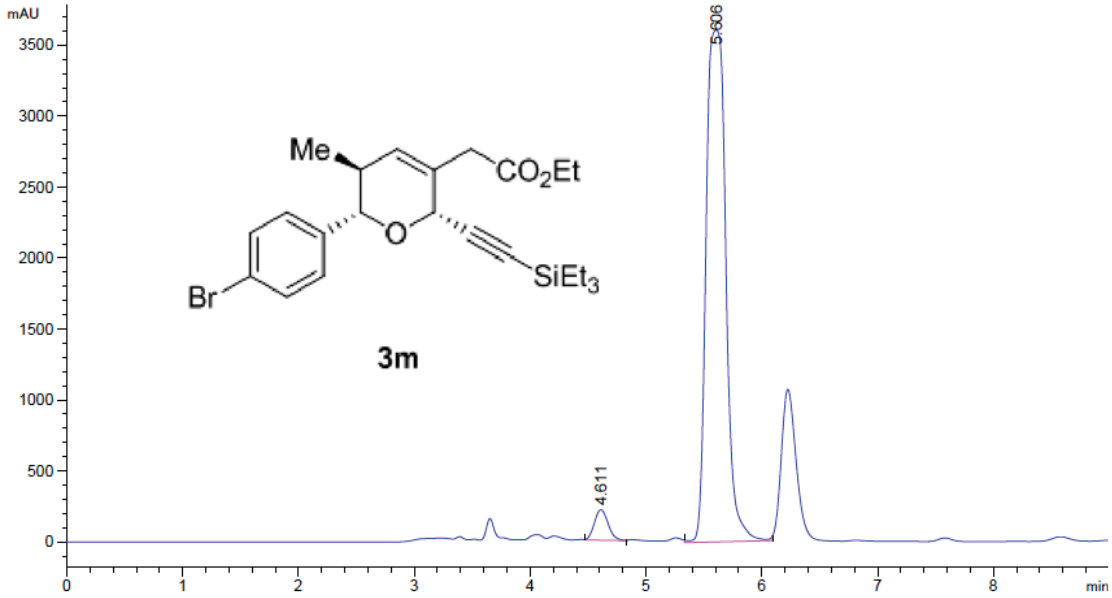
3l

Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Area %
1	43.097	MM	1.4150	7327.45947		2.6702
2	62.816	MM	3.4956	2.67087e5		97.3298



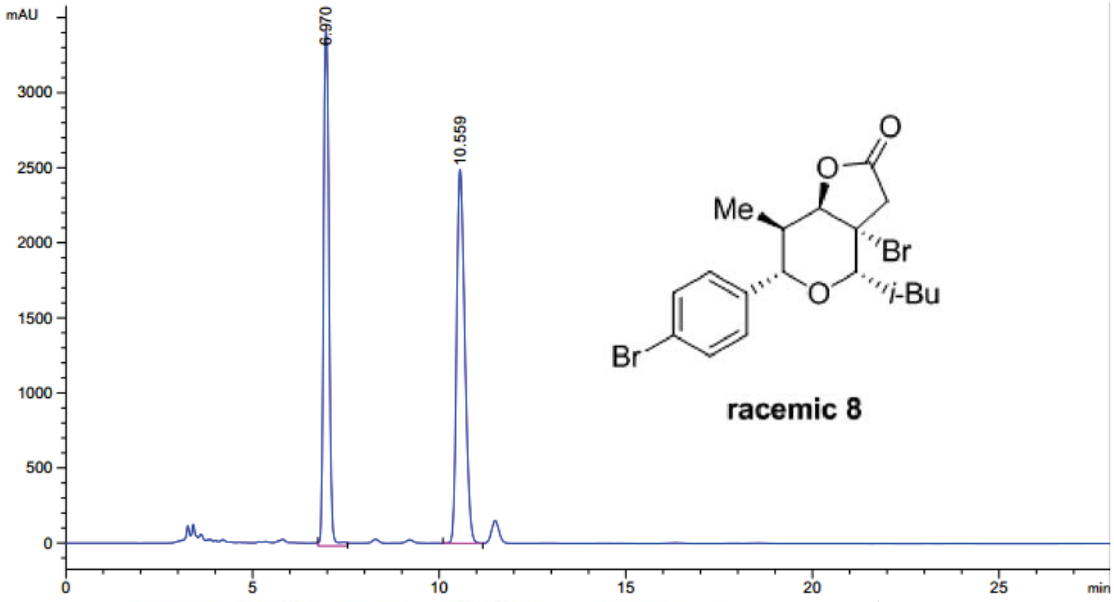
racemic 3m

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	5.670	VV	0.1920	2.42842e4	50.9861
2	8.632	VV	0.3091	2.33448e4	49.0139

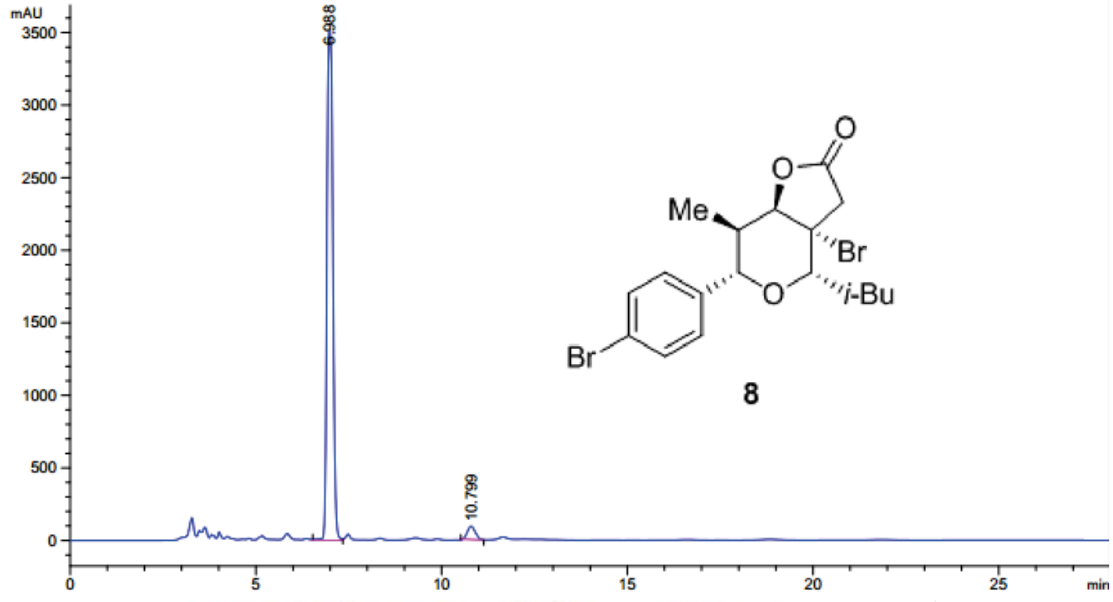


3m

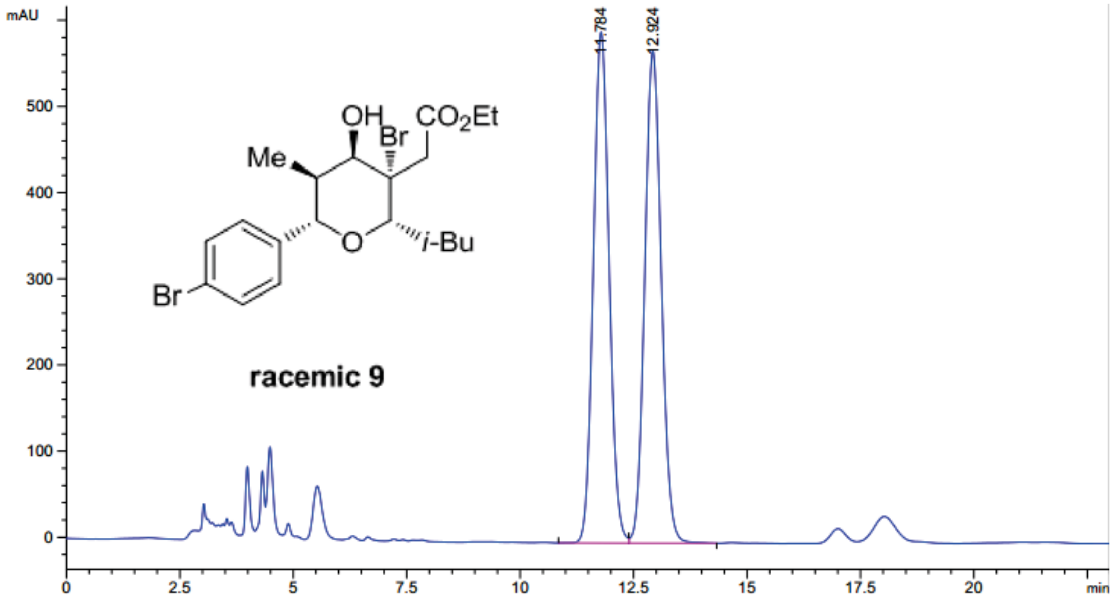
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	5.945	MM	0.1544	1705.52100	2.7031
2	8.995	MM	0.4551	6.13894e4	97.2969



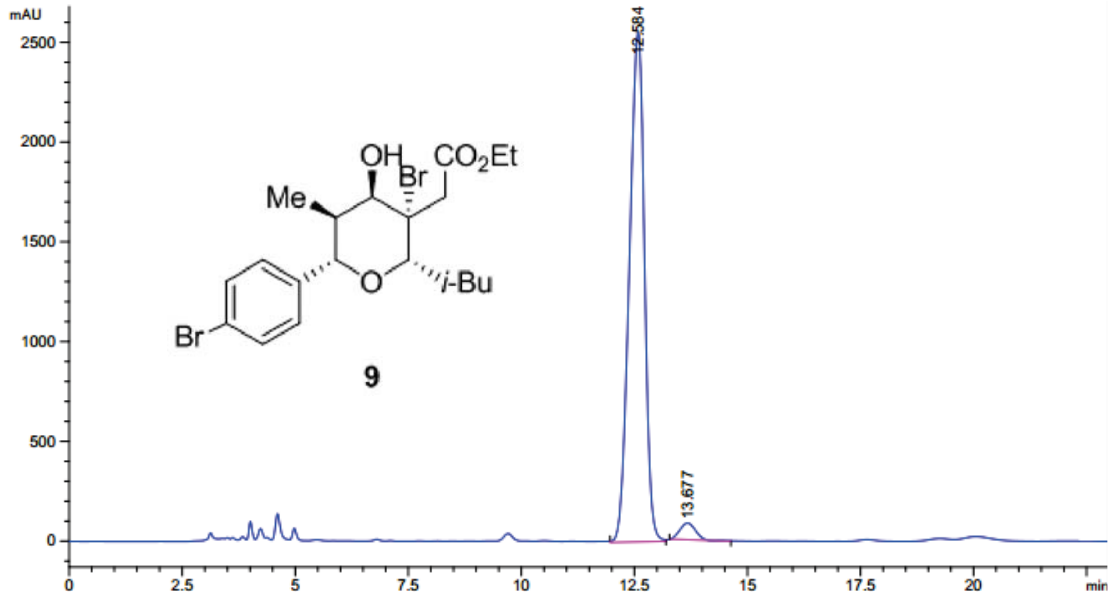
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	6.970	MM	0.1699	3.49374e4	47.9657
2	10.559	VV	0.2372	3.79008e4	52.0343



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	6.988	VV	0.1753	3.87657e4	96.6169
2	10.799	MM	0.2493	1357.40552	3.3831



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	11.784	VV	0.3757	1.42849e4	49.7248
2	12.924	VB	0.3940	1.44430e4	50.2752



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Area %
1	12.584	MM	0.3847	5.90315e4	96.6669
2	13.677	MM	0.4077	2035.44019	3.3331