$ArNMeCH(SiMe_3)_2$: A Useful Precursor of Formal α-Aminoalkyl Diradical in Visible-Light-Mediated Homo- or Hetero- Diaddition with Alkenes

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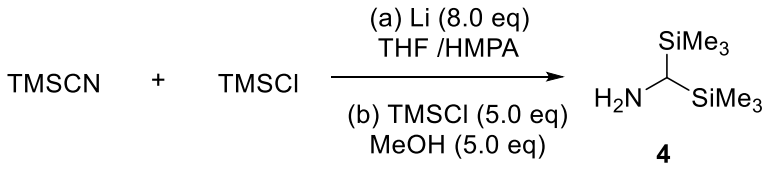
1. General Methods

All reagents purchased from Energy-Chemical, Inno-Chem, JK-chemical, BiDepharm, LaaJoo, Aladdin and TCI without additional purification. Synthesis of substrates were performed using common anhydrous, argon atmosphere with magnetic stirring. Visible-light-induced catalytic reactions were performed in 15 ml Schlenk seal tubes (purchased from Syhthware Glass, Art. No. P260001) at room temperature under an argon atmosphere and under irradiation with 40W blue LEDs lamp Kessil PR160-427nm. Inert atmosphere techniques was carried out through Schlenk system and Standard Glovebox (purchased from Vigor Gas Purification Technologies (Suzhou) Co. Ltd.) Reactions were monitored by TLC which was performed on glass-backed silica plates (purchased from Yantai Jiangyou Silica Gel Development Co. Ltd.) and visualized using UV, $KMnO_4$ stains, $H_3PO_4 \cdot 12MoO_3$/EtOH stains, H_2SO_4 (conc.)/ anisaldehyde/ EtOH stains. Column chromatography was performed using silica gel (200-300 or 300-400 mesh) eluting with EtOAc/petroleum ether. Melting point were recorded at WRX-4 Melting-point Apparatus (purchased from Shanghai Yice Apparatus & Equipments Co. Lit.). ^1H NMR spectra were recorded at 400 MHz (Varian and Bruker) or 600 MHz (Agilent), ^{13}C NMR spectra were recorded at 100 MHz (Bruker) or 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS as standard. NMR standards were used as follows: $CDCl_3$ = 7.26 ppm (^1H NMR), 77.1 ppm (^{13}C NMR). Infrared spectra were obtained using PerkinElmer Spectrum Two FT-IR Spectrometer. High-resolution mass spectral analyses performed on Waters Q-TOF in positive mode. Electrochemical potentials were obtained with a standard set of conditions to main internal consistency. Cyclic voltammograms were collected with a CH Instruments Model 600E Series Electrochemical Analyzer/Workstation containing platinum wire working electrode, platinum wire counter electrode, saturated KCl silver-silver chloride electrode reference electrode (Sweep rate: 20 mV/s). TMSCl were distilled from CaH_2. CH_2Cl_2 were distilled from CaH_2, THF were distilled from Na. All spectral data obtained for new compounds are reported here.

2. Experimental Procedures and Spectral Data of Products

2.1. Synthesis of bis(trimethylsilyl)methylamine (BSMA) 4



4 was synthesized according to this protocol reported by Picard and coworkers.[1]

To a mixture of granular lithium (3.92 g, 564.5 mmol), trimethylsilyl cyanide (8.83 mL, 70.6 mmol) and chlorotrimethylsilane (358 mL, 2.82 mol) in THF (175 mL) was added dropwise the mixture of hexamethylphosphoramide (126 mL) and THF (35 mL) at 0 °C. The mixture was stirred for four days at 0 °C, then concentrated in vacuo. To the residue was added water (400 mL). The resulting mixture was neutralized with sat. aq. NaOH, then extracted with hexane (3 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo to afford crude residue, which was used for next reaction without purification.

To the mixture of the above residue in MeOH (14.5 mL, 352.8 mmol) was added dropwise chlorotrimethylsilane (45 mL, 352.8 mmol) at 0 °C. The mixture was stirred for 30 min at 25 °C, then concentrated in vacuo. To the residue was added water (100 mL). The resulting mixture was filtered and the filtration was alkalized with sat. aq. NaOH, and extracted with Et_2O (4 × 30 mL). The combined organic layers were dried over NaOH, filtered and concentrated in vacuo to afford bis(trimethylsilyl)methylamine **4** (8.4 g, yield: 68 %) as a faint yellow liquid, which was used for next reaction without purification.

Spectral Data of 4

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (s, 1H), 0.97 (s, 2H), 0.04 (s, 18H);

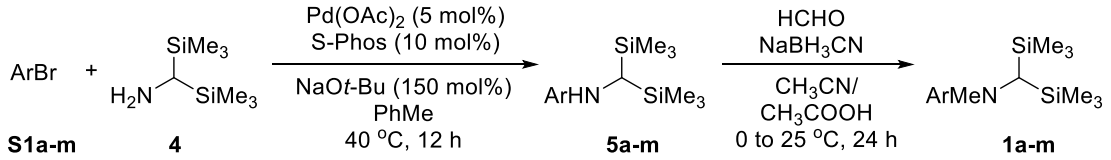
^{13}C NMR (100 MHz, $CDCl_3$) δ 31.5, -1.6;

1. J. P. Picard, S. Grelier, T. Constantieux, and J. Dunogués, *Organometallics*, 1993, **12**, 1378.

IR (neat) cm^{-1} 2955, 1650, 1594, 1249, 841, 751;

HRMS (ESI-TOF, m/z) calcd for $C_7H_{22}NSi_2$ $(M+H)^+$: 176.1285 , found 176.1286.

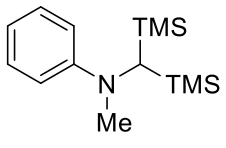
2.2. Synthesis of Geminal Bis(silyl) Amines 1a-m and 8



General procedure A. A dried 15 mL Schlenk seal tube was charged with $Pd(OAc)_2$ (17.5 mg, 0.078 mmol), S-Phos (64 mg, 0.16 mmol) and NaO*t*-Bu (225 mg, 2.34 mmol) in Standard Glovebox. Then to the mixture was added aryl bromides **S1a-m** (1.56 mmol), bis(trimethylsilyl)methylamine **4** (300 mg, 1.72 mmol) and toluene (5 mL) at 25 °C under positive argon pressure. The mixture was stirred for 12 h at 40 °C, then quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The residues were purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 500:1→250:1) to afford geminal bis(silyl) secondary aryl amines **5a-m**.

To a suspension of **5a-m** (1.0 mmol) and sodium cyanoborohydride (630 mg, 10 mmol) in CH_3CN (5 mL) was added 40 % formaldehyde aqueous solution (0.7 mL, 10 mmol) and CH_3CO_2H (0.5 mL) at 0 °C. The mixture was stirred for additional 60 min at 0 °C and warmed to25 °C for 24 h. The reaction was quenched with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The residues were purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 500:1→250:1) to afford geminal bis(silyl) aryl amines **1a-m**.

Preparation of 1a



1a

According to General Procedure A, bromobenzene (**S1a**, 245 mg, 1.56 mmol) was converted to corresponding **5a** (302 mg, 77 % yield) as a colorless liquid. **5a** (252 mg, 1.0 mmol) was converted to **1a** (231 mg, 87 % yield) as a faint yellow liquid.

Spectral Data of 5a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 2H), 6.59-6.52 (m, 3H), 3.28 (s, 1H), 2.41 (s, 1H), 0.07 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 129.1, 115.7, 112.3, 34.3, -1.0;

IR (neat) cm $^{-1}$ 2953, 1599, 1499, 1317, 1251, 843, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{13}H_{26}NSi_2$ $(M+H)^+$: 252.1598, found 252.1600.

Spectral Data of 1a

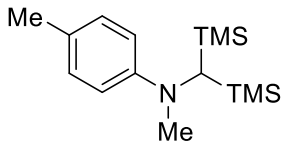
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J_1 = 9.0 Hz, J_2 = 7.2 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 6.56 (t, J = 7.2 Hz, 1H), 2.96 (s, 3H), 2.91 (s, 1H), 0.11 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 129.0, 114.1, 111.0, 43.5, 38.9, 0.6;

IR (neat) cm $^{-1}$ 2953, 2896, 1560, 1502, 1353, 1251, 841;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{28}NSi_2$ $(M+H)^+$: 266.1755 , found 266.1757.

Preparation of 1b



1b

According to the General Procedure A, 1-bromo-4-methylbenzene (**S1b**, 267 mg, 1.56 mmol) was converted to corresponding **5b** (294 mg, 71 % yield, mp: 46-48.5 ºC) as a white solid. **5b** (266 mg, 1 mmol) was converted to **1b** (62 mg, 22 % yield) as a colorless liquid.

Spectral Data of 5b

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 3.19 (s, 1H), 2.37 (s, 1H), 2.23 (s, 3H), 0.07 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 129.6, 124.7, 112.3, 34.5, 20.4, -0.9;

IR (neat) cm^{-1} 2952, 1616, 1514, 1313, 1249, 1013, 839, 763;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{28}NSi_2$ $(M+H)^+$: 266.1755, found 266.1755.

Spectral Data of 1b

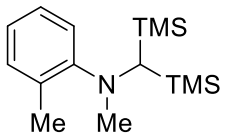
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 2.93 (s, 3H), 2.86 (s, 1H), 2.23 (s, 3H), 0.10 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 129.6, 123.0, 111.1, 43.7, 39.0, 20.2, 0.7;

IR (neat) cm^{-1} 2953, 1616, 1516, 1349, 1250, 1193, 1015, 839, 795, 765;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{30}NSi_2$ $(M+H)^+$: 280.1911 , found 280.1904.

Preparation of 1c



1c

According to the General Procedure A, 1-bromo-2-methylbenzene (**S1c**, 267 mg, 1.56 mmol) was converted to corresponding **5c** (373 mg, 90 % yield) as a faint yellow liquid. Then **5c** (266 mg, 1 mmol) was converted to **1c** (168 mg, 60% yield) as a colorless liquid.

Spectral Data of 5c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.61-6.58 (m, 2H), 3.28 (s, 1H), 2.60 (s, 1H), 2.20 (s, 3H), 0.15 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 129.8, 127.1, 120.7, 115.0, 109.0, 33.9, 17.5, -1.0;

IR (neat) cm^{-1} 2953, 1605, 1509, 1250, 843;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{28}NSi_2$ $(M+H)^+$: 266.1755, found 266.1754.

Spectral Data of 1c

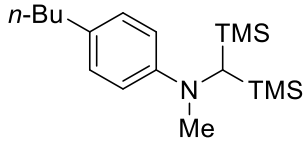
^1H NMR (400 MHz, $CDCl_3$) δ 7.10-7.06 (m, 2H), 7.00-6.98 (m, 1H), 6.79 (td, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 2.90 (s, 3H), 2.64 (s, 1H), 2.29 (s, 3H), 0.12 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 131.7, 129.7, 126.0, 120.3, 119.4, 46.6, 42.1, 20.3, 1.3;

IR (neat) cm^{-1} 2951, 2897, 1596, 1490, 1249, 838, 756;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{30}NSi_2$ $(M+H)^+$: 280.1911 , found 280.1910.

Preparation of 1d



1d

According to the General Procedure A, 1-bromo-4-butylbenzene (**S1d**, 326 mg, 1.56 mmol) was converted to corresponding **5d** (302 mg, 63 % yield) as a colorless liquid. Then **5d** (308 mg, 1 mmol) was converted to **1d** (196 mg, 61 % yield) as a colorless liquid.

Spectral Data of 5d

^1H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 8.4 Hz, 2H), 3.17 (s, 1H), 2.48 (t, J = 8.0 Hz, 2H), 2.36 (s, 1H), 1.58-1.51 (m, 2H), 1.39-1.30 (m, 2H), 0.92 (t, J = 7.2Hz, 3H), 0.06 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 130.1, 128.9, 112.4, 34.8, 34.6, 34.1, 22.5, 14.1, -0.9;

IR (neat) cm^{-1} 2955, 1614, 1514, 1313, 1251, 844;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{34}NSi_2$ $(M+H)^+$: 308.2224 , found 308.2217.

Spectral Data of 1d

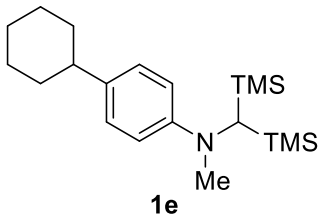
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 2.93 (s, 3H), 2.87 (s, 1H), 2.49 (t, *J* = 7.6 Hz, 2H), 1.59-1.52 (m, 2H), 1.40-1.30 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.10 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 128.8, 128.4, 111.1, 43.7, 39.0, 34.6, 34.1, 22.6, 14.1, 0.7;

IR (neat) cm^{-1} 2954, 1614, 1686, 1515, 1350, 1250, 1015, 839, 767;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{36}NSi_2$ $(M+H)^+$: 322.2381 , found 322.2381.

Preparation of 1e



1e

According to the General Procedure A, 1-bromo-4-cyclohexylbenzene (**S1e**, 373 mg, 1.56 mmol) was converted to corresponding **5e** (224 mg, 43 % yield, mp: 29.5-32 ºC) as a white solid. Then **5e** (334 mg, 1 mmol) was converted to **1e** (174 mg, 50 % yield, mp: 52.5-55 ºC) as a white solid.

Spectral Data of 5e

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 3.16 (s, 1H), 2.40-2.30 (m, 2H), 1.86-1.70 (m, 5H), 1.38-1.22 (m, 5H), 0.06 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 135.5, 127.2, 112.3, 43.5, 34.8, 34.6, 27.2, 26.4, -0.9;

IR (neat) cm^{-1} 2923, 1613, 1513, 1250, 843;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{36}NSi_2$ $(M+H)^+$: 334.2381 , found 334.2381.

Spectral Data of 1e

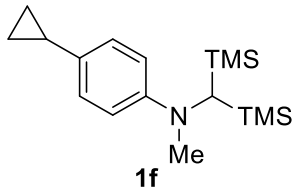
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.4 Hz, 2H), 2.93 (s, 3H), 2.87 (s, 1H), 2.41-2.34 (m, 1H), 1.87-1.70 (m, 5H), 1.42-1.31 (m, 5H), 0.09 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 133.8, 127.1, 111.1, 43.7, 43.3, 39.0, 34.8, 27.2, 26.4, 0.7;

IR (neat) cm^{-1} 2922, 2850, 1613, 1514, 1350, 1249, 1015, 837, 803, 765;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{38}NSi_2$ $(M+H)^+$: 348.2537 , found 348.2531.

Preparation of 1f



1f

According to the General Procedure A, 1-bromo-4-cyclopropylbenzene (**S1f**, 308 mg, 1.56 mmol) was converted to corresponding **5f** (250 mg, 55 % yield, mp: 41-45 ºC) as a white solid. Then **5f** (292 mg, 1 mmol) was converted to **1f** (217 mg, 71 % yield) as a colorless liquid.

Spectral Data of 5f

^{1}H NMR(400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 3.19 (d, *J* = 9.6 Hz, 1H), 2.36 (s, *J* = 9.6 Hz, 1H), 1.82-1.75 (m, 1H), 0.86-0.81 (m, 2H), 0.60-0.56 (m, 2H), 0.07 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 130.6, 126.7, 112.3, 34.5, 14.6, 8.1, -0.9;

IR (neat) cm^{-1} 2953, 1615, 1515, 1250, 842, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{32}NSi_2$ $(M+H)^+$: 294.2068 , found 294.2065.

Spectral Data of 1f

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.4 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 2.93 (s, 3H), 2.85 (s, 1H), 1.83-1.76 (m, 1H), 0.85-0.80 (m, 2H), 0.60-0.56 (m, 2H), 0.09 (s,

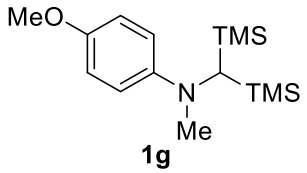
18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 128.9, 126.6, 111.2, 43.6, 39.0, 14.4, 8.1, 0.7;

IR (neat) cm $^{-1}$ 3004, 2953, 2895, 1679, 1614, 1518, 1338, 1251, 1115, 842;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{32}NSi_2$ $(M+H)^+$: 306.2068 , found 306.2075.

Preparation of 1g



1g

According to the General Procedure A, 1-bromo-4-methoxybenzene (**S1g**, 292 mg, 1.56 mmol) was converted to corresponding **5g** (299 mg, 68 % yield, mp: 37.5-43 °C) as a white solid. Then **5g** (282 mg, 1 mmol) was converted to **1g** (142 mg, 48 % yield) as a colorless liquid.

Spectral Data of 5g

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.04 (s, 1H), 2.29 (s, 1H), 0.06 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 144.9, 114.8, 113.3, 55.9, 35.2, -0.9;

IR (neat) cm $^{-1}$ 3408, 2951, 1507, 1247, 1044, 839, 762;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{28}NOSi_2$ $(M+H)^+$: 282.1704 , found 282.1704.

Spectral Data of 1g

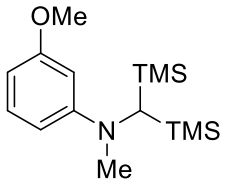
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.8 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 2.92 (s, 3H), 2.80 (s, 1H), 0.09 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 114.8, 113.6, 112.1, 55.9, 44.2, 39.2, 0.7;

IR (neat) cm $^{-1}$ 2953, 1674, 1512, 1342, 1246, 1112, 1033, 833;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{30}NOSi_2$ $(M+H)^+$: 296.1860 , found 296.1851.

Preparation of 1h



1h

According to the General Procedure A, 1-bromo-3-methoxybenzene (**S1h**, 292 mg, 1.56 mmol) was converted to corresponding **5h** (378 mg, 86 % yield, mp: 54-59 ºC) as a white solid. Then **5h** (282 mg, 1 mmol) was converted to **1h** (180.3 mg, 61 % yield) as a colorless liquid.

Spectral Data of 5h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 (t, J = 8.4 Hz, 1H), 6.15 (tdd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, J_3 = 1.2 Hz, 2H), 6.08 (t, J = 2.4 Hz, 1H), 3.77 (s, 3H), 3.33 (d, J = 4.4 Hz, 1H), 2.38 (s, J = 7.2 Hz, 1H), 0.07 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 151.6, 129.7, 105.9, 100.6, 98.1, 55.1, 34.4, -1.0;

IR (neat) cm $^{-1}$ 3408, 2952, 1609, 1505, 1492, 1250, 1208, 1160, 840;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{28}NOSi_2$ $(M+H)^+$: 282.1704 , found 282.1711.

Spectral Data of 1h

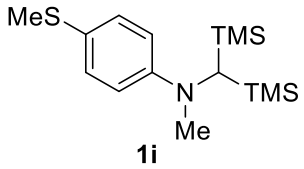
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.07 (m, 1H), 6.27-6.25 (m, 1H), 6.16-6.14 (m, 2H), 3.79 (s, 3H), 2.94 (s, 3H), 2.87 (s, 1H), 0.10 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 152.1, 129.6, 104.7, 98.6, 97.8, 55.1, 43.7, 39.0, 0.6;

IR (neat) cm $^{-1}$ 2952, 2897, 1607, 1572, 1496, 1250, 1167, 839, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{30}NOSi_2$ $(M+H)^+$: 296.1860 , found 296.1855.

Preparation of 1i



1i

According to the General Procedure A, (4-bromophenyl)(methyl)sulfane (**S1i**, 317 mg, 1.56 mmol) was converted to corresponding **5i** (362 mg, 78 % yield, mp: 47-48.2 ºC) as a faint yellow solid. Then **5i** (298 mg, 1 mmol) was converted to **1i** (171 mg, 55 % yield) as a faint yellow liquid.

Spectral Data of 5i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 2H), 6.47 (d, *J* = 8.4 Hz, 2H), 3.35 (s, 1H), 2.40 (s, 3H), 2.38 (s, 1H), 0.06 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 131.9, 121.7, 112.8, 34.5, 19.6, -0.9;

IR (neat) cm^{-1} 3412, 2952, 1594, 1495, 1313, 1249, 841, 757;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{28}NSSi_2$ $(M+H)^+$: 298.1476 , found 298.1480.

Spectral Data of 1i

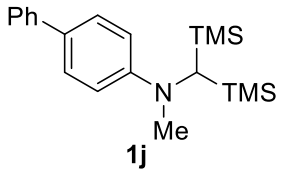
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 8.8 Hz, 2H), 2.94 (s, 3H), 2.86 (s, 1H), 2.40 (s, 3H), 0.10 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 132.0, 120.0, 111.6, 43.7, 39.0, 19.7, 0.6;

IR (neat) cm^{-1} 2952, 1592, 1498, 1356, 1250, 1201, 840, 801;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{30}NSSi_2$ $(M+H)^+$: 312.1632 , found 312.1631.

Preparation of 1j



1j

According to the General Procedure A, 4-bromo-1,1'-biphenyl (**S1j**, 364 mg, 1.56 mmol) was converted to corresponding **5j** (245 mg, 48 % yield, mp: 37-42 ºC) as a white solid.

Then **5j** (323 mg, 1 mmol) was converted to **1j** (113 mg, 33 % yield, mp: 74-79 ºC) as a white solid.

Spectral Data of 5j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.32-7.26 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 2H), 3.33 (d, *J* = 8.0 Hz, 1H), 2.37 (d, *J* = 8.0 Hz, 1H), 0.00 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 141.4, 128.6, 128.4, 127.8, 126.1, 125.7, 112.5, 34.5, -0.9;

IR (neat) cm $^{-1}$ 3418, 3026, 2952, 1610, 1521, 1489, 1250, 844, 760;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{30}NSi_2$ $(M+H)^+$: 328.1911 , found 328.1915.

Spectral Data of 1j

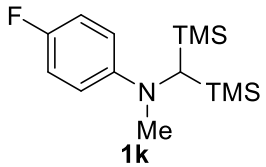
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (m, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.8, 2H), 3.00 (s, 3H), 2.95 (s, 1H), 0.13 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 141.3, 128.6, 127.6, 126.6, 126.0, 125.6, 111.3, 43.7, 39.1, 0.6;

IR (neat) cm $^{-1}$ 2953, 2896, 1607, 1522, 1488, 1359, 1251, 1202, 1013, 840, 759;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{32}NSi_2$ $(M+H)^+$: 342.2068 , found 342.2063.

Preparation of 1k



1k

According to the General Procedure A, 1-bromo-4-fluorobenzene (**S1k**, 273 mg, 1.56 mmol) was converted to corresponding **5k** (177 mg, 42 % yield) as a yellow liquid. Then **5k** (270 mg, 1 mmol) was converted to **1k** (94 mg, 33 % yield) as a yellow liquid.

Spectral Dates of 5k

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (t, *J* = 8.8 Hz, 2H), 6.45 (q, *J* = 4.4 Hz, 2H), 3.18 (d, *J* = 8.8 Hz, 1H), 2.31 (d, *J* = 8.8 Hz, 1H), 0.07 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8 (d, *J* = 154.6 Hz), 146.7, 115.5 (d, *J* = 14.7 Hz), 112.7 (d, *J* = 4.8 Hz), 35.2, -1.0;

IR (neat) cm $^{-1}$ 2954, 1509, 1252, 1226, 842, 764, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{13}H_{25}NFSi_2$ $(M+H)^+$: 270.1504 , found 270.1504.

Spectral Dates of 1k

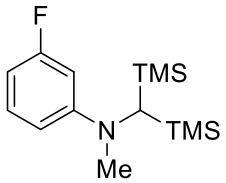
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (t, *J* = 9.2 Hz, 2H), 6.53-6.50 (m, 2H), 2.93 (s, 3H), 2.81 (s, 1H), 0.10 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 (d, *J* = 231.0 Hz), 147.7 (d, *J* = 1.3 Hz), 115.3 (d, *J* = 21.7 Hz), 111.5 (d, *J* = 7.1 Hz), 44.3, 39.2, 0.6;

IR (neat) cm $^{-1}$ 2953, 1679, 1511, 1335, 1227, 1115, 981, 837;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{27}FNSi_2$ $(M+H)^+$: 284.1661 , found 284.1657.

Preparation of 1l



1l

According to the General Procedure A, 1-bromo-3-fluorobenzene (**S1l**, 273 mg, 1.56 mmol) was converted to corresponding **5l** (181 mg, 43 % yield) as a colorless liquid. Then **5l** (270 mg, 1 mmol) was converted to **1l** (136 mg, 48 % yield) as a colorless liquid.

Spectral Dates of 5l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-6.98 (m, 1H), 6.29 (ddd, J_1 = 8.0 Hz, J_2 = 2.0 Hz,

J_3 = 0.8 Hz, 1H), 6.26-6.24 (m, 1H), 6.20 (dt, J_1 = 12.0 Hz, J_2 = 2.4 Hz, 1H), 3.44 (d, J = 8.0 Hz, 1H), 2.35 (d, J = 8.0 Hz, 1H), 0.07 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, J = 240.2 Hz), 151.9 (d, J = 10.8 Hz), 130.0 (d, J = 10.5 Hz), 108.4 (d, J = 2.0 Hz), 102.0 (d, J = 21.6 Hz), 98.4 (d, J = 25.5 Hz), 34.7, -1.0;

IR (neat) cm $^{-1}$ 3428, 2954, 1618, 1587, 1505, 1493, 1251, 1147, 839;

HRMS (ESI-TOF, m/z) calcd for $C_{13}H_{25}NFSi_2$ $(M+H)^+$: 270.1504 , found 270.1505.

Spectral Dates of 1l

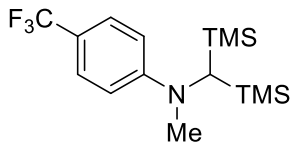
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, J_1 = 15.6 Hz, J_2 = 8.4 Hz, 1H), 6.36 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.31-6.22 (m, 2H), 2.94 (s, 3H), 2.83 (s, 1H), 0.11 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, J = 239.0 Hz), 152.3 (d, J = 10.7 Hz), 129.9 (d, J = 10.6 Hz), 106.7 (d, J = 2.0 Hz), 100.6 (d, J =21.7 Hz), 97.8 (d, J = 26.2 Hz), 44.0, 39.0, 0.5;

IR (neat) cm $^{-1}$ 2954, 2897, 1615, 1575, 1497, 1362, 1251, 1161, 1003, 884, 840;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{27}FNSi_2$ $(M+H)^+$: 284.1661 , found 284.1667.

Preparation of 1m



1m

According to the General Procedure A, 1-bromo-4-(trifluoromethyl)benzene (**S1m**, 351 mg, 1.56 mmol) was converted to corresponding **5m** (448 mg, 90 % yield, mp: 44-47 ^{o}C) as a white solid. Then **5m** (319 mg, 1 mmol) was converted to **1m** (326 mg, 98 % yield) as a colorless liquid.

Spectral Dates of 5m

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 3.68

(d, J = 10.0 Hz, 1H), 2.46 (d, J = 10.0 Hz, 1H), 0.08 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 126.6 (q, J = 2.5 Hz), 125.3 (q, J = 178.9 Hz), 117.0 (q, J = 21.5 Hz), 111.2, 34.4, -1.1;

IR (neat) cm $^{-1}$ 3433, 2955, 1614, 1528, 1327, 1279, 1252, 1184, 1158, 1107, 1067, 844, 763;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{25}F_3NSi_2$ $(M+H)^+$: 320.1472 , found 320.1473.

Spectral Dates of 1m

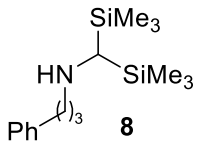
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.8 Hz, 2H), 6.52 (d, J = 8.8 Hz, 2H), 2.98 (s, 3H), 2.92 (s, 1H), 0.11 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 126.4 (q, J = 3.6 Hz), 125.5 (q, J = 268.0 Hz), 115.4 (q, J = 32.4 Hz), 110.1, 44.0, 39.1, 0.5;

IR (neat) cm $^{-1}$ 2955, 2896, 1613, 1527, 1368, 1330, 1264, 1252, 1200, 1162, 840, 808, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{27}F_3NSi_2$ $(M+H)^+$: 334.1629 , found 334.1629.

Preparation of 8



8

According to the reductive amination of General Procedure A, bis(trimethylsilyl)methylamine **4** (176 mg, 1.0 mmol) and phenylpropyl aldehyde (0.15 mL, 1.2 mmol) was converted to **8** (186.5 mg, 64 % yield) as a colorless thick liquid.

Spectral Dates of 8

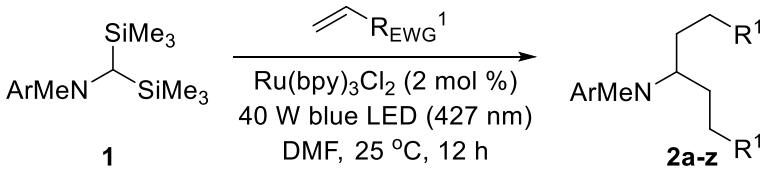
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.22-7.19 (m, 3H), 6.42 (s, 1H), 2.96-2.92 (m, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.22-2.14 (m, 2H), 2.06 (s, 1H), 0.19 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 128.8, 128.5, 126.6, 51.4, 41.5, 32.7, 27.4, -0.1.;

IR (neat) cm^{-1} 2955, 2330, 2178, 1604, 1454, 1257, 1118, 1029, 831;

HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{32}NSi_2$ $(M+H)^+$: 294.2068 , found 294.2077.

2.3. Synthesis of Homo-Diaddition Products 2 and 7

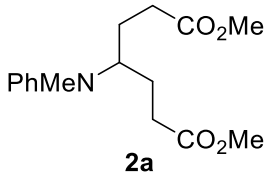


General Procedure B ***(alkenes were added after deoxygenation of DMF).*** A dried 15 mL Schlenk seal tube was charged with $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002mmol) and sealed with rubber plug in Standard Glovebox. Geminal bis(silyl) aryl amines **1** (0.1 mmol) and DMF (2 mL) was added into the tube at 25 °C under positive argon pressure. The solution was allowed to purge with high purity argon gas using a 15 cm syringe needle for at least 10 mins at 25 °C before adding alkene (0.5 mmol) using syringe under positive argon pressure. The rubber plug was changed to polytetrafluoroethylene seal plug under positive argon pressure. The resulting mixture was stirred for 12 h under irradiation with 427 nm blue LED. The reaction was concentrated in vacuo and purified using silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 50:1→10:1) to afford **2**.

General procedure C ***(alkenes were added before deoxygenation of DMF).*** A dried 15 mL Schlenk seal tube was charged with $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002mmol) and sealed with rubber plug in Standard Glovebox. Geminal bis(silyl) aryl amines **1** (0.1 mmol), alkenes (0.5 mmol) and DMF (2 mL) was added into the tube at 25 °C under positive argon pressure. The solution was allowed to purge with high purity argon gas using a 15 cm syringe needle for at least 10 mins at 25 °C. The rubber plug was changed to polytetrafluoroethylene seal plug under positive argon pressure. The solution was stirred for 12 h under irradiation with 427 nm blue LED. The reaction was concentrated

in vacuo and purified using silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 50:1→10:1) to afford **2**.

Preparation of 2a



2a

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding products **2a** (25 mg, 85 % yield) as a colorless liquid.

Spectral Data of 2a

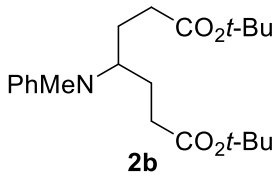
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 4.00-3.93 (m, 1H), 3.58 (s, 6H), 2.67 (s, 3H), 2.28-2.24 (m, 4H), 1.94-1.79 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 150.9, 129.2, 116.7, 112.7, 56.5, 51.6, 31.0, 29.4, 28.1;

IR (neat) cm^{-1} 2951, 1733, 1598, 1504, 1436, 1196, 1170, 1104;

HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{23}NNaO_4$ $(M+Na)^+$: 316.1519 , found 316.1527.

Preparation of 2b



2b

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and *tert*-butyl acrylate (74 μL, 0.5 mmol) were converted to corresponding products **2b** (17 mg, 45 % yield) as a colorless liquid.

Spectral Data of 2b

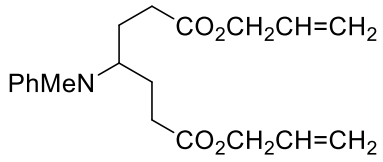
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 6.66 (t, J = 7.2 Hz, 1H), 4.00-3.89 (m, 1H), 2.67 (s, 3H), 2.17 (t, J = 7.6 Hz, 4H), 1.88-1.73 (m, 4H), 1.38 (s, 18H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 151.1, 129.2, 116.4, 112.8, 80.3, 56.8, 32.5, 29.5, 28.2, 28.1;

IR (neat) cm $^{-1}$ 2977, 2929, 1725, 1598, 1505, 1366, 1249, 1147, 849;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{35}NNaO_4$ $(M+Na)^+$: 400.2458 , found 400.2460.

Preparation of 2c



2c

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and allyl acrylate (61 μL, 0.5 mmol) were converted to corresponding products **2c** (26 mg, 74 % yield) as a colorless liquid.

Spectral Data of 2c

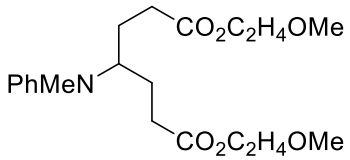
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 8.0 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 5.87-5.77 (m, 2H), 5.27-5.18 (m, 4H), 4.49 (d, J = 5.6 Hz, 4H), 4.02-3.95 (m, 1H), 2.68 (s, 3H), 2.29 (t, J = 7.2 Hz, 4H), 1.96-1.80 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 150.9, 132.2, 129.3, 118.3, 116.7, 112.8, 65.2, 56.6, 31.2, 29.5, 28.1;

IR (neat) cm $^{-1}$ 2931, 1730, 1597, 1504, 1168, 1103, 988, 924;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{27}NNaO_4$ $(M+Na)^+$: 368.1832 , found 368.1840.

Preparation of 2d



2d

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and 2-methoxyethyl acrylate (65 μL, 0.5 mmol) were converted to corresponding products **2d** (32 mg, 83 % yield) as a colorless liquid.

Spectral Data of 2d

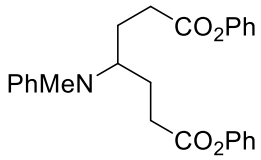
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.66 (t, J = 7.2 Hz, 1H), 4.13 (t , J = 4.8 Hz, 4H), 4.01-3.94 (m, 1H), 3.47 (t, J = 4.8 Hz, 4H), 3.32 (s, 6H), 2.66 (s, 3H), 2.29 (t, J = 8.0 Hz, 4H), 1.95-1.78 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 150.1, 129.2, 116.6, 112.7, 70.4, 63.4, 59.0, 56.5, 31.2, 29.5, 28.0;

IR (neat) cm $^{-1}$ 2927, 2885, 2817, 1729, 1597, 1504, 1452, 1322, 1248, 1197, 1172, 1127, 1100, 1032, 864;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{31}NNaO_6$ $(M+Na)^+$: 404.2044 , found 404.2061.

Preparation of 2e



2e

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and 2-phenoxyethyl acrylate (70 μL, 0.5 mmol) were converted to corresponding products **2e** (34 mg, 80 % yield) as a colorless liquid.

Spectral Data of 2e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 8.0 Hz, 4H), 7.21 (dt, J_1 = 20.8 Hz, J_2 = 8.0 Hz, 4H), 6.93 (d, J = 8.0 Hz, 4H), 6.84 (d, J = 8.0 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H),

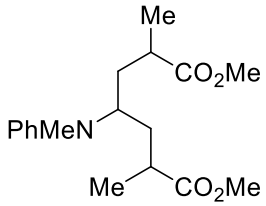
4.20-4.12 (m, 1H), 2.74 (s, 3H), 2.56-2.52 (m, 4H), 2.08-1.93 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 150.9, 150.6, 129.5, 129.4, 125.8, 121.6, 117.0, 112.9, 56.5, 31.3, 29.6, 27.9;

IR (neat) cm $^{-1}$ 2926, 1753, 1596, 1193, 1162, 1131;

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{27}NNaO_4$ $(M+Na)^+$: 440.1832 , found 440.1843.

Preparation of 2f



2f

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and methyl methacrylate (54 μL, 0.5 mmol) were converted to corresponding products **2f** (19.9 mg, 61 % yield, dr = 3:2:1) as a colorless liquid.

Spectral Data of 2f

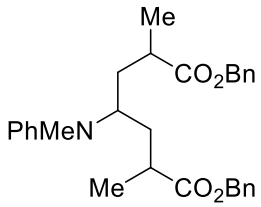
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 4.00-3.93 (m, 1H), 3.54 (s, 6H), 2.64 (s, 3H), 2.46-2.36 (m, 2H), 2.08-2.01 (m, 2H), 1.51-1.44 (m, 2H), 1.12 (s, 3H), 1.10 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 150.4, 129.2, 116.7, 112.8, 53.7, 51.6, 36.8, 36.8, 29.8, 17.4;

IR (neat) cm $^{-1}$ 2924, 1734, 1598, 1504, 1275, 1261, 1167, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{27}NNaO_4$ $(M+Na)^+$: 344.1832 , found 344.1835.

Preparation of 2g



2g

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and benzyl methacrylate (86 μL, 0.5 mmol) were converted to corresponding products **2g** (31 mg, 64 % yield, dr = 5.5:1) as a colorless liquid.

Spectral Data of 2g

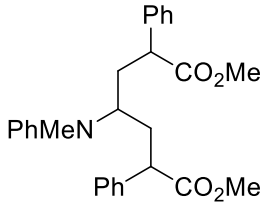
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.08 (m, 12H), 6.72-6.62 (m, 3H), 5.07-4.82 (m, 4H), 4.15-4.05 (m, 1H), 2.65-2.62 (m, 3H), 2.49-2.37 (m, 2H), 2.14-2.05 (m, 1H), 1.94-1.85 (m, 1H), 1.65-1.55 (m, 1H), 1.50-1.44 (m, 1H), 1.16-1.12 (m, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 176.3, 176.3, 150.6, 150.5, 136.1, 136.0, 136.0, 129.2, 129.2, 128.5, 128.5, 128.3, 128.3, 128.2, 128.2, 128.1, 116.7, 116.6, 112.8, 112.7, 66.3, 66.2, 54.2, 54.0, 37.2, 37.1, 37.0, 36.5, 36.4, 36.3, 29.9, 29.7, 18.6, 18.2, 17.6;

IR (neat) cm $^{-1}$ 2971, 1729, 1597, 1504, 1276, 1260, 1163, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{30}H_{35}NNaO_4$ $(M+Na)^+$: 496.2458 , found 496.2463.

Preparation of 2h



2h

According to the General Procedure C, **1a** (27 mg, 0.1 mmol) and methyl 2-phenylacrylate (83 mg, 0.5 mmol, which was prepared according to the procedure described by Loh and coworkers.[2]) were converted to corresponding products **2h** (41.4

[2] B. Jiang, M. zhao, S. S. Li, Y. H. Xu, T. P. Loh, *Angew. Chem. Int. Ed.,* 2018, **57**, 555.

mg, 91 % yield, dr = 1.8:1:1) as a colorless liquid.

Spectral Data of 2h

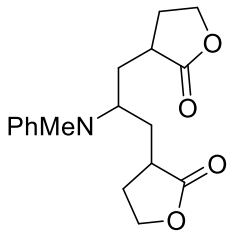
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.22 (m, 10H), 7.14 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 6.52 (d, J = 8.8 Hz, 2H), 4.06-4.00 (m, 1H), 3.55-3.51 (m, 8H), 2.62 (s, 3H), 2.42-2.35 (m, 2H), 1.91-1.84 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 150.4, 139.3, 129.1, 128.8, 127.8, 127.4, 116.8, 112.8, 54.1, 52.0, 48.2, 37.2, 29.8;

IR (neat) cm $^{-1}$ 3028, 2950, 2923, 1730, 1597, 1504, 1454, 1434, 1356, 1253, 1210, 1162;

HRMS (ESI-TOF, m/z) calcd for $C_{28}H_{31}NNaO_4$ $(M+Na)^+$: 468.2145 , found 468.2153.

Preparation of 2i



2i

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and 3-methylenedihydrofuran-2(3H)-one (45 μL, 0.5 mmol) were converted to corresponding products **2i** (33 mg, 95 % yield, dr = 2.5:1.4:1) as a colorless semisolid.

Spectral Data of 2i

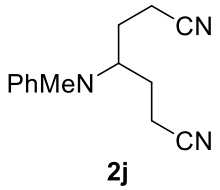
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.72 (t, J = 7.2 Hz, 1H), 4.51-4.44 (m, 1H), 4.32-4.24 (m, 2H), 4.13-3.97 (m, 2H), 2.74 (s, 3H), 2.62-2.53 (m, 1H), 2.37-2.27 (m, 3H), 2.18-2.11 (m, 1H), 2.00-1.79 (m, 4H), 1.52-1.43 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 179.4, 150.6, 129.7, 117.2, 112.6, 66.5, 53.9, 36.8, 36.2, 34.6, 34.0, 29.8, 29.5, 29.2;

IR (neat) cm^{-1} 2921, 1763, 1597, 1505, 1205, 1159, 1022, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{23}NNaO_4$ $(M+Na)^+$: 340.1519 , found 340.1519.

Preparation of 2j



2j

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and acrylonitrile (34 μL, 0.5 mmol) were converted to corresponding products **2j** (11.6 mg, 50 % yield) as a colorless liquid.

Spectral Data of 2j

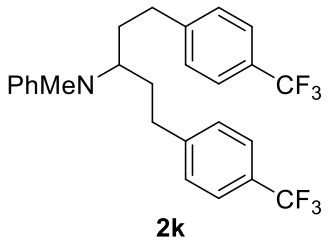
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.80 (t, J = 7.2 Hz, 1H), 4.10-4.03 (m, 1H), 2.71 (s, 3H), 2.36-2.23 (m, 4H), 2.05-1.95 (m, 2H), 1.92-1.83 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 129.7, 119.2, 118.5, 113.6, 56.7, 29.7, 28.7, 14.6;

IR (neat) cm^{-1} 2922, 2851, 2246, 1596, 1503, 1314, 1106, 1033, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{17}N_3Na$ $(M+Na)^+$: 250.1315 , found 250.1307.

Preparation of 2k



2k

According to the General Procedure B, **1a** (27 mg, 0.1 mmol) and 4-(trifluoromethyl)styrene (75 μL, 0.5 mmol) were converted for 24 h to corresponding products **2k** (32 mg, 68 % yield) as a colorless liquid.

Spectral Dates of 2k

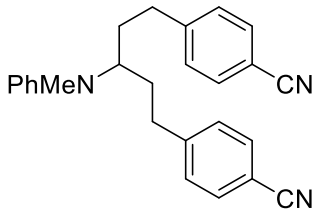
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 4H), 7.21-7.14 (m, 6H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.81-3.75 (m, 1H), 2.78 (s, 3H), 2.68-2.54 (m, 4H), 1.98-1.89 (m, 2H), 1.86-1.77 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 146.0, 129.3, 128.8, 128.4 (q, *J* = 33.0 Hz), 125.3 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.2 Hz), 116.7, 112.9, 56.5, 34.6, 32.9, 29.8;

IR (neat) cm $^{-1}$ 2929, 2860, 1597, 1504, 1323, 1161, 1115, 1067, 1018, 841;

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{26}F_6N$ $(M+H)^+$: 466.1964 , found 466.1964.

Preparation of 2l



2l

According to the General Procedure C, **1a** (27 mg, 0.1 mmol) and 4-vinylbenzonitrile (65.6 mg, 0.5 mmol, which was prepared according to the procedure described by Gilmour and coworkers[3]) were converted to corresponding products **2l** (27 mg, 71 % yield, mp: 125-129.5 ºC) as a white solid.

Spectral Data of 2l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 4H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 4H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.83-3.76 (m, 1H), 2.76 (s, 3H), 2.69-2.53 (m, 4H), 1.98-1.89 (m, 2H), 1.84-1.76 (m, 2H);

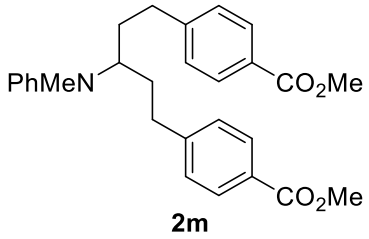
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 147.5, 132.2, 129.3, 129.2, 119.1, 116.9, 112.9, 109.9, 56.7, 34.5, 33.2, 29.7;

IR (neat) cm $^{-1}$ 2924, 2856, 2226, 1596, 1503, 1177, 1093, 840, 822;

3. F. Scheidt, M. Schäfer, J. C. Sarie, C. G. Daniliuc, J. J. Molloy and R. Gilmour, *Angew. Chem. Int. Ed.,* 2018, **57**, 16431.

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{25}N_3Na$ $(M+Na)^+$: 402.1941 , found 402.1924.

Preparation of 2m



2m

According to the General Procedure C, **1a** (27 mg, 0.1 mmol) and methyl 4-vinylbenzoate (82 mg, 0.5 mmol) were converted to corresponding products **2m** (16 mg, 36 % yield) as a white semisolid.

Spectral Data of 2m

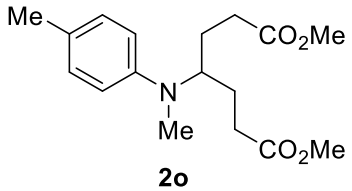
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 4H), 7.20 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 7.13 (d, J = 8.4 Hz, 4H), 6.72-6.66 (m, 3H), 3.90 (s, 6H), 3.85-3.78 (m, 1H), 2.78 (s, 3H), 2.68-2.53 (m, 4H), 1.98-1.89 (m, 2H), 1.86-1.78 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 150.9, 147.5, 129.8, 129.3, 128.5, 127.9, 116.5, 112.9, 56.8, 52.1, 34.6, 33.1, 29.8;

IR (neat) cm^{-1} 2924, 2854, 1716, 1597, 1504, 1434, 1276, 1178, 1107, 1019;

HRMS (ESI-TOF, m/z) calcd for $C_{28}H_{31}NNaO_4$ $(M+Na)^+$: 468.2145 , found 468.2157.

Preparation of 2o



2o

According to the General Procedure B, **1b** (28 mg, 0.1 mmol) and methyl acrylate (45 μL, 0.5 mmol) were converted to corresponding products **2o** (25 mg, 81 % yield) as a colorless liquid.

Spectral Data of 2o

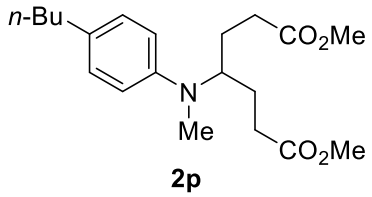
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 3.93-3.86 (m, 1H), 3.59 (s, 6H), 2.65 (s, 3H), 2.28-2.21 (m, 7H), 1.93-1.77 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 148.9, 129.7, 125.8, 113.0, 57.0, 51.6, 31.1, 29.6, 28.0, 20.2;

IR (neat) cm^{-1} 2951, 1735, 1617, 1519, 1436, 1196, 1171, 1103, 805;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{25}NNaO_4$ $(M+Na)^+$: 330.1676, found 330.1674.

Preparation of 2p



2p

According to the General Procedure B, **1d** (33 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding products **2p** (30 mg, 84 % yield) as a colorless liquid.

Spectral Data of 2p

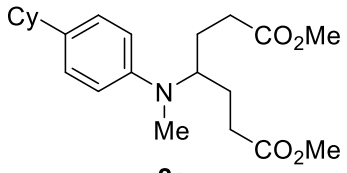
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.94-3.86 (m, 1H), 3.58 (s, 6H), 2.65 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.29-2.24 (m, 4H), 1.93-1.77 (m, 4H), 1.58-1.51 (m, 2H), 1.39-1.30 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.0, 131.1, 129.1, 112.9, 56.9, 51.6, 34.6, 34.0, 31.1, 29.6, 28.0, 22.5, 14.1;

IR (neat) cm^{-1} 2953, 2927, 2856, 1733, 1613, 1516, 1436, 1250, 1194, 1169, 1102, 806;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{31}NNaO_4$ $(M+Na)^+$: 372.2145, found 372.2149.

Preparation of 2q



2q

According to the General Procedure B, **1e** (35 mg, 0.1 mmol) and methyl acrylate (45 μL, 0.5 mmol) were converted to corresponding products **2q** (29.5 mg, 78 % yield, mp: 54.5-57 ºC) as a white solid.

Spectral Data of 2q

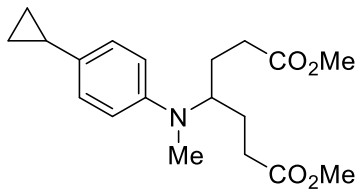
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.94-3.87 (m, 1H), 3.58 (s, 6H), 2.65 (s, 3H), 2.41-2.33 (m, 1H), 2.39-2.25 (m, 4H), 1.93-1.77 (m, 8H), 1.72 (d, *J* = 12.4 Hz, 1H), 1.42-1.31 (m, 4H), 1.27-1.18 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.1, 136.5, 127.4, 113.0, 56.9, 51.5, 43.5, 34.8, 31.2, 29.6, 28.0, 27.1, 26.3;

IR (neat) cm^{-1} 2922, 2850, 1734, 1612, 1517, 1436, 1251, 1194, 1169, 1103, 811;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{33}NNaO_4$ $(M+Na)^+$: 398.2302, found 398.2306.

Preparation of 2r



2r

According to the General Procedure B, **1f** (31 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding products **2r** (26 mg, 77 % yield) as a colorless liquid.

Spectral Data of 2r

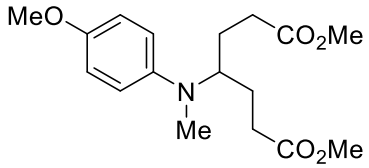
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J*= 8.4 Hz, 2H), 3.92-3.85 (m, 1H), 3.59 (s, 6H), 2.64 (s, 3H), 2.27-2.23 (m, 4H), 1.92-1.76 (m, 5H), 0.87-0.82 (m, 2H), 0.60-0.56 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.0, 131.8, 126.7, 113.0, 57.0, 51.6, 31.1, 29.6, 28.0, 14.4, 8.2;

IR (neat) cm $^{-1}$ 2999, 2950, 1731, 1615, 1518, 1435, 1250, 1196, 1168, 1018, 811;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{27}NNaO_4$ $(M+Na)^+$: 356.1832, found 356.1826.

Preparation of 2s



2s

According to the General Procedure B, **1g** (30 mg, 0.1 mmol) and methyl acrylate (40 μL, 0.5 mmol) were converted to corresponding products **2s** (12 mg, 37 % yield, mp: 36.5-39 °C) as a white solid.

Spectral Data of 2s

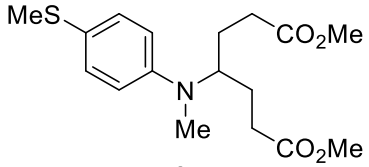
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, J = 9.2 Hz, 2H), 6.70 (d, J = 9.2 Hz, 2H), 3.82-3.73 (m, 4H), 3.59 (s, 6H), 2.62 (s, 3H), 2.33-2.21 (m, 4H), 1.92-1.74 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 151.6, 145.7, 114.7, 114.7, 58.1, 55.8, 51.6, 31.2, 29.9, 27.8;

IR (neat) cm $^{-1}$ 2950, 1731, 1510, 1436, 1242, 1170, 1103, 1036, 816;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{25}NNaO_5$ $(M+Na)^+$: 346.1625, found 346.1618.

Preparation of 2t



2t

According to the General Procedure B, **1i** (32 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding products **2t** (12.4 mg, 36 % yield) as a faint yellow liquid.

Spectral Data of 2t

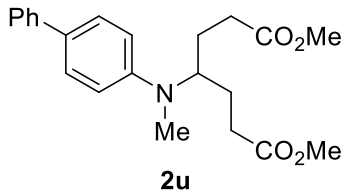
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 3.98-3.97 (m, 1H), 3.58 (s, 6H), 2.66 (s, 3H), 2.41 (s, 3H), 2.24 (t, *J* = 8.0 Hz, 4H), 1.93-1.78 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 149.8, 131.4, 123.6, 113.4, 56.7, 51.6, 31.0, 29.6, 28.0, 19.1;

IR (neat) cm $^{-1}$ 2921, 1731, 1594, 1500, 1485, 1250, 1197, 1170, 1110, 1092, 810;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{25}NNaO_4S$ $(M+Na)^+$: 362.1397, found 362.1395.

Preparation of 2u



2u

According to the General Procedure B, **1j** (35 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding products **2u** (32.3 mg, 85 % yield) as a colorless liquid.

Spectral Data of 2u

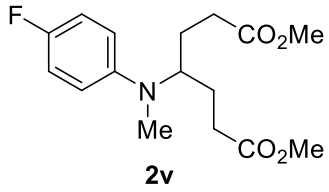
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.53 (m, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.07-4.00 (m, 1H), 3.59 (s, 6H), 2.73 (s, 3H), 2.29 (t, *J* = 8.0 Hz, 4H), 1.97-1.82 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 150.3, 141.1, 129.3, 128.7, 127.8, 126.3, 126.1, 112.9, 56.5, 51.6, 31.0, 29.6, 28.1;

IR (neat) cm $^{-1}$ 2950, 1734, 1609, 1524, 1488, 1436, 1254, 1201, 1172, 1104, 820, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{27}NNaO_4$ $(M+Na)^+$: 392.1832, found 392.1833.

Preparation of 2v



2v

According to the General Procedure B, **1k** (29 mg, 0.1 mmol) and methyl acrylate (40 μL, 0.5 mmol) were converted to corresponding products **2v** (15 mg, 48 % yield) as a colorless liquid.

Spectral Dates of 2v

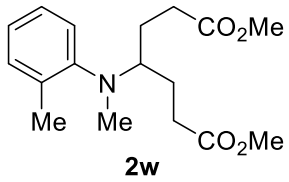
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, J_1 = 9.2 Hz, J_2 = 8.4 Hz, 2H), 6.68-6.64 (m, 2H), 3.89-3.81 (m, 1H), 3.58 (s, 6H), 2.63 (s, 3H), 2.27-2.23 (m, 4H), 1.92-1.76 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 155.4 (d, J = 234.0 Hz), 147.6 (d, J = 1.6 Hz), 115.5 (d, J = 22.0 Hz), 114.0 (d, J = 7.3 Hz), 57.7, 51.6, 31.1, 29.9, 27.9;

IR (neat) cm $^{-1}$ 2952, 1730, 1508, 1436, 1226, 1197, 1167, 1103, 815;

HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{22}FNNaO_4$ $(M+Na)^+$: 334.1425, found 334.1416.

Preparation of 2w



2w

According to the General Procedure B, **1c** (28 mg, 0.1 mmol) and methyl acrylate (45 μL, 0.5 mmol) were converted to corresponding products **2w** (18.6 mg, 61 % yield) as a colorless liquid.

Spectral Data of 2w

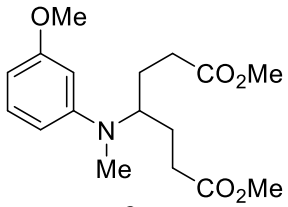
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.11 (m, 2H), 7.04 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 6.4 Hz, 1H), 3.63 (s, 6H), 3.07-3.00 (m, 1H), 2.63 (s, 3H), 2.41-2.36 (m, 4H), 2.24 (s, 3H), 1.94-1.76 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 151.4, 132.3, 131.5, 126.4, 122.7, 121.9, 59.4, 51.6, 33.2, 31.3, 26.0, 19.1;

IR (neat) cm $^{-1}$ 2951, 1733, 1597, 1492, 1436, 1255, 1196, 1167, 1087, 762;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{25}NNaO_4$ $(M+Na)^+$: 330.1676, found 330.1674.

Preparation of 2x



2x

According to the General Procedure B, **1h** (30 mg, 0.1 mmol) and methyl acrylate (45 μL, 0.5 mmol) were converted to corresponding products **2x** (23.3 mg, 71 % yield) as a colorless liquid.

Spectral Data of 2x

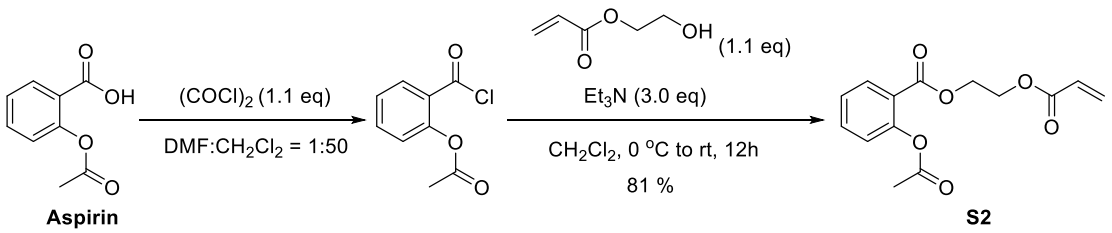
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 8.4 Hz, 1H), 6.36 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 6.29-6.24 (m, 2H), 3.99-3.91 (m, 1H), 3.78 (s, 3H), 3.59 (s, 6H), 2.66 (s, 3H), 2.25 (t, J = 8.0 Hz, 4H), 1.93-1.78 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 160.8, 152.3, 129.8, 105.8, 101.3, 99.3, 56.5, 55.1, 51.6, 31.0, 29.6, 28.1;

IR (neat) cm $^{-1}$ 2951, 1730, 1607, 1573, 1497, 1435, 1231, 1197, 1163, 1104, 1052, 990, 825, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{25}NNaO_5$ $(M+Na)^+$: 346.1625, found 346.1625.

Preparation of 2y



To a solution of aspirin (361 mg, 2.0 mmol) and $(COCl)_2$ (0.19 mL, 2.2 mmol) in CH_2Cl_2 (5 mL) was added DMF (0.1 mL) at 0 °C. After stirring for 5 mins at 0 °C, the reaction was warmed to 25 °C for additional 30 mins. Then the mixture was concentrated in vacuo to afford crude acyl chloride as a white solid.

To a solution of acyl chloride, 2-hydroxyethyl acrylate (0.23 mL, 2.2 mmol) in CH_2Cl_2 (5 mL) was added dropwise Et_3N (0.84 mL, 6.0 mmol) at 0 °C. The reaction was stirred for 12 h at 25 °C before quenching with water (5 mL) and extracting with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 5:1→2:1) to afford **S2** (452 mg, 81 % yield) as a colorless thick liquid.

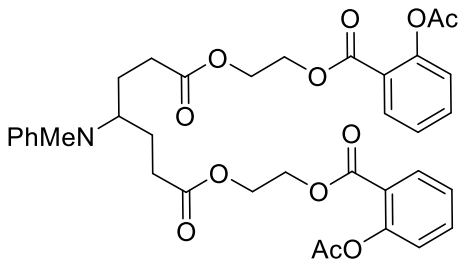
Spectral Data of S2

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.57 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.32 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.11 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.45 (dd, J_1 = 17.6 Hz, J_2 = 1.6 Hz, 1H), 6.15 (dd, J_1 = 17.6 Hz, J_2 = 10.4 Hz, 1H), 5.87 (dd, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 4.53-4.50 (m, 2H), 4.48-4.46 (m, 2H), 2.34 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 166.0, 164.2, 150.9, 134.2, 132.0, 131.6, 128.0, 126.1, 123.9, 122.8, 62.8, 62.2, 21.1;

IR (neat) cm $^{-1}$ 2960, 1766, 1720, 1607, 1452, 1410, 1368, 1290, 1251, 1182, 1135, 1083, 1068, 915, 809, 752;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{14}NaO_6$ $(M+Na)^+$: 301.0683, found 301.0680.



2y

According to the General Procedure C, **1a** (27 mg, 0.1 mmol) and **S2** (85 mg, 0.3 mmol) were converted to corresponding products **2y** (38 mg, 55 % yield) as a colorless semisolid.

Spectral Data of 2y

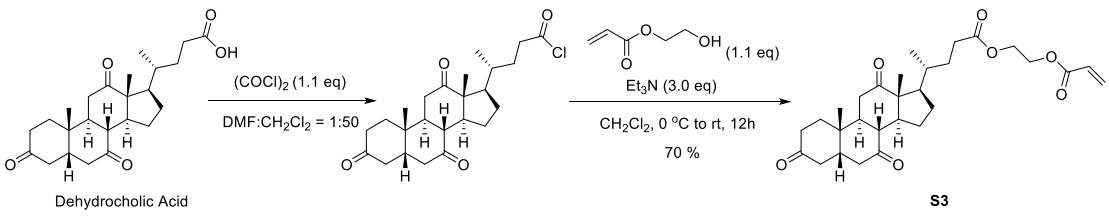
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.56 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.30 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2H), 7.16 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 7.10 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 2H), 6.72 (d, J = 8.0 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 4.38-4.35 (m, 4H), 4.28-4.25 (m, 4H), 4.03-3.94 (m, 1H), 2.64 (s, 3H), 2.33-2.26 (m, 10H), 1.94-1.79 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 169.7, 164.1, 150.8, 150.8, 134.2, 131.9, 129.2, 126.1, 123.9, 123.9, 122.8, 116.8, 112.7, 62.8, 62.1, 56.4, 31.1, 29.4, 28.0, 21.0;

IR (neat) cm $^{-1}$ 2925, 1766, 1723, 1597, 1504, 1452, 1368, 1292, 1251, 1188, 1041, 1081, 1041, 916, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{36}H_{39}NNaO_{12}$ $(M+Na)^+$: 700.2364 , found 700.2358.

Preparation of 2z



Dehydrocholic Acid **S3**

To a solution of dehydrocholic acid (403 mg, 1.0 mmol) and $(COCl)_2$ (0.1 mL, 1.1 mmol) in CH_2Cl_2 (5 mL) was added DMF (0.1 mL) at 0 °C. After stirring for 5 mins at

0 ºC, the reaction was warmed to25 ºC for additional 30 mins. Then the reaction was concentrated in vacuo to afford crude acyl chloride as a white solid.

To a solution of acyl chloride, 2-hydroxyethyl acrylate (0.12 mL, 1.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise Et_3N (0.42 mL, 3.0 mmol) at 0 ºC. The reaction was stirred for 12 h at 25 ºC before quenching with water (5 mL) and extracting with EtOAc (3 × 10 mL). The combined organic layers were washed with sat. aq. NaCl (2 × 10 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 5:1→2:1) to afford **S3** (353 mg, 70 % yield, mp: 157.7-159.1 ºC) as a white soild.

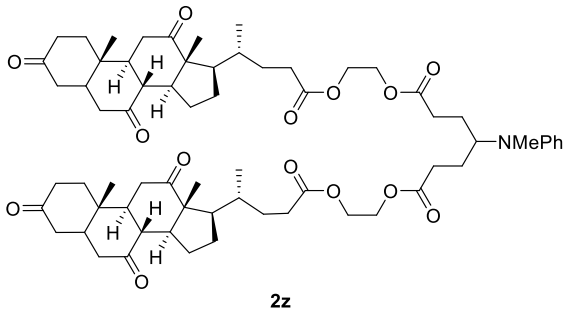
Spectral Data of S3

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (dd, J_1 = 17.2 Hz, J_2 = 1.2 Hz, 1H), 6.13 (dd, J_1 = 17.2 Hz, J_2 = 10.4 Hz, 1H), 5.85 (dd, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.36-4.29 (m, 4H), 2.93-2.80 (m, 3H), 2.45-2.18 (m, 8H), 2.14-2.10 (m, 2H), 2.07-1.92 (m, 4H), 1.87-1.79 (m, 2H), 1.60 (td, J_1 = 14.0 Hz, J_2 = 4.8 Hz, 1H), 1.41-1.24 (m, 7H), 1.05 (s, 3H), 0.83 (d, J = 9.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 209.0, 208.7, 173.8, 165.9, 131.4, 128.1, 62.4, 62.0, 57.0, 51.8, 49.1, 46.9, 45.7, 45.6, 45.0, 42.8, 38.7, 36.5, 36.1, 35.5, 35.3, 31.4, 30.4, 27.7, 25.2, 22.0, 18.7, 11.9;

IR (neat) cm $^{-1}$ 2961, 2870, 1721, 1699, 1446, 1426, 1409, 1385, 1297, 1275, 1184, 1163, 1077, 810;

HRMS (ESI-TOF, m/z) calcd for $C_{29}H_{40}NaO_7$ $(M+Na)^+$: 523.2666, found 523.2662.



2z

According to the General Procedure C, **1a** (27 mg, 0.1 mmol) and **S3** (115 mg, 0.22

mmol) were converted to corresponding products **2z** (71 mg, 63 % yield, mp: 147.5-150.5 °C) as a white solid.

Spectral Data of 2z

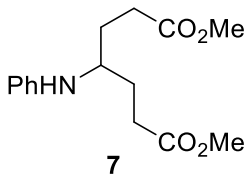
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, J_1 = 8.4 Hz, J_2 = 7.2 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 6.64 (t, J = 7.2 Hz, 1H), 4.12-4.10 (m, 8H), 4.00-3.92 (m, 1H), 2.93-2.79 (m, 7H), 2.65 (s, 3H), 2.40-2.07 (m, 26 H), 2.02-1.76 (m, 18H), 1.63-1.53 (m, 3H), 1.26-1.23 (m, 8H), 1.03 (s, 6H), 0.81 (d, J = 6.8 Hz, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9, 209.1, 208.7, 173.7, 173.1, 150.8, 129.2, 116.7, 112.6, 62.2, 61.9, 56.9, 56.4, 51.7, 49.0, 46.8, 45.6, 45.5, 45.0, 42.8, 38.6, 36.5, 36.0, 35.5, 35.3, 31.2, 31.0, 30.3, 29.7, 29.4, 27.9, 27.6, 25.1, 21.9, 18.6, 11.8;

IR (neat) cm $^{-1}$ 2924, 1732, 1707, 1597, 1505, 1434, 1381, 1268, 1249, 1162, 1103, 954;

HRMS (ESI-TOF, m/z) calcd for $C_{66}H_{91}NNaO_{14}$ $(M+Na)^+$: 1144.6332 , found 1144.6339.

Preparation of 7



7

According to the General Procedure B, **5a** (26 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding products **7** (19.7 mg, 68 % yield) as a colorless liquid.

Spectral Data of 7

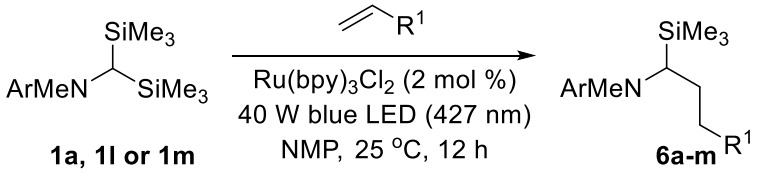
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, J = 5.2 Hz, 2H), 6.66 (t, J = 5.2 Hz, 1H), 6.55 (d, J = 5.2 Hz, 2H), 3.63 (s, 6H), 3.51-3.46 (m, 1H), 3.41 (s, 1H), 2.42 (t, J = 5.2 Hz, 4H), 1.93-1.87 (m, 2H), 1.82-1.76 (m, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 147.6, 129.4, 117.2, 112.9, 52.1, 51.7, 30.7, 30.3.;

IR (neat) cm^{-1} 3388, 2951, 1730, 1602, 1498, 1436, 1319, 1256, 1195, 1173, 1115, 992, 871;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{21}NNaO_4$ $(M+Na)^+$: 302.1363 , found 302.1366.

2.4. Synthesis of Mono-Addition products 6

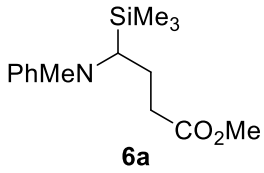


General procedure D <u>(alkenes (0.12 mmol) were added after deoxygenation of NMP)</u>.
A dried 15 mL Schlenk seal tube was charged with $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002mmol) and sealed with rubber plug in Standard Glovebox. Geminal bis(silyl) aryl amines **1a** (0.1 mmol) and NMP (2 mL) were added into the tube at 25 °C under positive argon pressure. The solution was allowed to purge with high purity argon gas using a 15 cm syringe needle for at least 10 mins at 25 °C and charged with alkene (0.12 mmol) using syringe under positive argon pressure. The rubber plug was changed to polytetrafluoroethylene seal plug under positive argon pressure. The solution was stirred for 12 h under irradiation with 427 nm blue LED. The reaction was quenched with water (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→20:1) to afford desired products **6a-g**.

General procedure E <u>(alkenes (0.50 mmol) were added after deoxygenation of DMF)</u>.
A dried 15 mL Schlenk seal tube was charged with $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002mmol) and sealed with rubber plug in Standard Glovebox. Geminal bis(silyl) aryl amines **1a, 1l or 1m** (0.1 mmol) and DMF (2 mL) were added into the tube at 25 °C under positive argon pressure. The solution was allowed to purge with high purity argon gas using a 15 cm syringe needle for at least 10 mins at 25 °C and charged with alkene (0.5 mmol) using syringe under positive argon pressure. The rubber plug was changed to polytetrafluoroethylene seal plug under positive argon pressure. The solution was

stirred for 12 h under irradiation with 427 nm blue LED. The reaction was quenched with water (5 mL), extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (3 × 20 mL), dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→20:1) to afford desired products **6h-m**.

Preparation of 6a



6a

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and methyl acrylate (11 μL, 0.12 mmol) were converted to corresponding product **6a** (17 mg, 60 % yield) as a colorless liquid and by-product **2a** (4.3 mg, 14 % yield).

Spectral Data of 6a

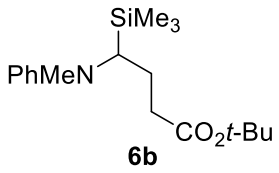
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 6.62 (t, J = 7.2 Hz, 1H), 3.59 (s, 3H), 3.41 (dd, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 1H), 2.80 (s, 3H), 2.39-2.22 (m, 2H), 2.10-2.00 (m, 1H), 1.93-1.84 (m, 1H), 0.07 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 151.2, 129.1, 115.4, 111.8, 51.5, 50.0, 34.0, 32.3, 24.0, -1.7;

IR (neat) cm $^{-1}$ 2951, 1735, 1596, 1503, 1364, 1249, 1201, 837;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{26}NO_2Si$ $(M+H)^+$: 280.1727 , found 280.1725.

Preparation of 6b



6b

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and *tert*-butyl acrylate

(18 μL, 0.12 mmol) were converted to corresponding product **6b** (16.4 mg, 50 % yield) as a colorless liquid and by-product **2b** (3 mg, 7 % yield).

Spectral Data of 6b

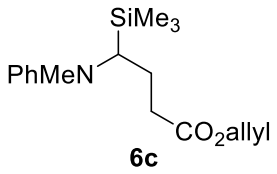
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.70 (d, J = 8.8 Hz, 2H), 6.61 (t, J = 7.2 Hz, 1H), 3.39 (dd, J_1 = 12.0 Hz, J_2 = 3.6 Hz, 1H), 2.79 (s, 3H), 2.30-2.13 (m, 2H), 2.03-1.93 (m, 1H), 1.87-1.79 (m, 1H), 1.40 (s, 9H), 0.05 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 151.3, 129.1, 115.2, 111.9, 80.2, 50.0, 34.0, 33.4, 28.2, 23.8, -1.6;

IR (neat) cm $^{-1}$ 2954, 1725, 1596, 1503, 1366, 1250, 1144, 83;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{32}NO_2Si$ $(M+H)^+$: 322.2197 , found 322.2193.

Preparation of 6c



6c

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and allyl acrylate (15 μL, 0.12 mmol) were converted to corresponding product **6c** (16 mg, 51 % yield) as a colorless liquid and by-product **2c** (7 mg, 21 % yield).

Spectral Data of 6c

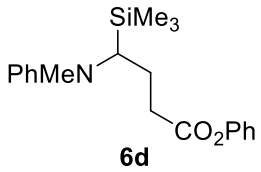
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 6.61 (t, J = 7.2 Hz, 1H), 5.88-5.78 (m, 1H), 5.25 (dq, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 5.19 (dq, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 4.50 (dq, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 2H), 3.41 (dd, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 1H), 2.79 (s, 3H), 2.42-2.24 (m, 2H), 2.10-2.00 (m, 1H), 1.93-1.84 (m, 1H), 0.06 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ173.5, 151.2, 132.3, 129.1, 118.3, 115.4, 111.9, 65.1, 50.0, 34.0, 32.4, 24.0, -1.6;

IR (neat) cm^{-1} 2952, 1733, 1596, 1503, 1371, 1249, 1194, 1144, 987, 836;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{27}NNaO_2Si$ $(M+Na)^+$: 328.1703 , found 328.1701.

Preparation of 6d



6d

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and phenyl acrylate (17 μL, 0.12 mmol) were converted to corresponding product **6d** (14 mg, 40 % yield, mp: 59-62 ºC) as a white solid and by-product **2e** (14 mg, 33 % yield).

Spectral Data of 6d

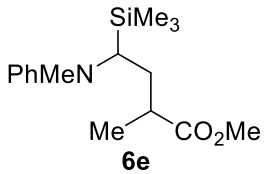
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, J = 8 Hz, 2H), 7.23-7.18 (m, 3H), 6.95 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.0 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 3.51 (dd, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 1H), 2.83 (s, 3H), 2.66-2.49 (m, 2H), 2.19-2.09 (m, 1H), 2.03-1.95 (m, 1H), 0.08 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 151.3, 150.8, 129.4, 129.3, 125.8, 121.7, 115.6, 112.0, 50.0, 34.1, 32.3, 23.8, -1.6;

IR (neat) cm^{-1} 2952, 1756, 1595, 1503, 1493, 1365, 1308, 1250, 1192, 1162, 1125, 837;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{28}NO_2Si$ $(M+H)^+$: 342.1884 , found 342.1882.

Preparation of 6e



6e

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and methyl methacrylate (13 μL, 0.12 mmol) were converted to corresponding product **6e** (16 mg, 54 % yield, dr = 1.1:1) as a colorless liquid.

Spectral Data of 6e

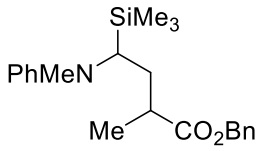
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 8.4 Hz, 2H), 6.70 (d, J = 8.4 Hz, 2H), 6.61 (t, J = 7.2 Hz, 1H), 3.50 (s, 3H), 3.44 (dd, J_1 = 12.4 Hz, J_2 = 3.2 Hz, 1H), 2.76 (s, 3H), 2.43-2.35 (m, 1H), 2.29-2.21 (m, 1H), 1.50-1.44 (m, 1H), 1.11 (d, J = 6.8 Hz, 3H), 0.03 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 150.9, 129.1, 115.4, 111.9, 51.5, 48.0, 37.5, 33.9, 32.9, 16.8, -1.6;

IR (neat) cm $^{-1}$ 2951, 2925, 2855, 1733, 1596, 1503, 1249, 1198, 1160, 857, 837;

HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{27}NNaO_2Si$ $(M+Na)^+$: 316.1703 , found 316.1709.

Preparation of 6f



6f

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and benzyl methacrylate (21 μL, 0.12 mmol) were converted to corresponding products **6f** (30 mg, 78 % yield, dr = 1.5:1) as a colorless liquid.

Spectral Data of 6f

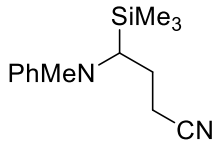
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.29 (m, 3H), 7.20-7.16 (m, 4H), 6.71 (d, J = 8.4 Hz, 2H), 6.62 (t, J = 7.2 Hz, 1H), 5.02 (d, J = 12.4 Hz, 1H), 4.82 (d, J = 12.4 Hz, 1H), 3.45 (dd, J_1 = 12.4 Hz, J_2 = 3.2 Hz, 1H), 2.75 (s, 3H), 2.50-2.41 (m, 1H), 2.33-2.25 (m, 1H), 1.52-1.46 (m, 1H), 1.14 (d, $_J$ = 6.8 Hz, 3H), 0.03 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 150.9, 136.2, 129.2, 128.5, 128.2, 128.1, 115.5, 112.0, 66.2, 48.3, 37.8, 34.0, 32.9, 17.0, -1.6;

IR (neat) cm $^{-1}$ 2927, 1725, 1595, 1502, 1455, 1249, 1152, 835, 857;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{32}NO_2Si$ $(M+H)^+$: 370.2197 , found 370.2196.

Preparation of 6g



6g

According to the General Procedure D, **1a** (27 mg, 0.1 mmol) and acrylonitrile (8 μL, 0.12 mmol) were converted to corresponding products **6g** (12 mg, 47 % yield) as a faint yellow liquid.

Spectral Data of 6g

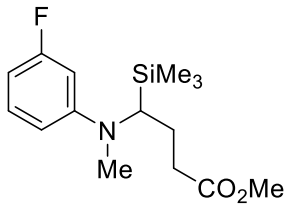
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 3.43 (dd, J_1 = 12.4 Hz, J_2 = 3.2 Hz, 1H), 2.81 (s, 3H), 2.41-2.24 (m, 2H), 2.15-2.05 (m, 1H), 1.95-1.87 (m, 1H), 0.07 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 129.4, 120.0, 116.3, 112.3, 50.1, 34.1, 25.4, 15.6, -1.6;

IR (neat) cm $^{-1}$ 2953, 1596, 1502, 1250, 837, 747, 691;

HRMS (ESI-TOF, m/z) calcd for $C_{14}H_{23}N_2Si$ $(M+H)^+$: 247.1625 , found 247.1622.

Preparation of 6h



6h

According to the General Procedure E, **1l** (29 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding product **6h** (14 mg, 46 % yield) as a colorless liquid and homo-diaddition by-product (8 mg, 25 % yeild).

Spectral Dates of 6h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (q, J = 8.4 Hz, 1H), 6.43 (dd, J_1 = 8.4 Hz, J_2 = 2.8

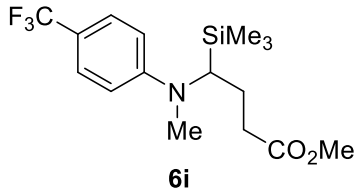
Hz, 1H), 6.35 (dt, J_1 = 13.6 Hz, J_2 = 2.8 Hz, 1H), 6.29 (tdd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, J_3 = 0.8 Hz, 1H), 3.59 (s, 3H), 3.33 (dd, J_1 = 12.4 Hz, J_2 = 3.6 Hz, 1H), 2.77 (s, 3H), 2.36-2.19 (m, 2H), 2.07-1.97 (m, 1H), 1.92-1.84 (m, 1H), 0.06 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 164.4 (d, J = 239.7 Hz), 152.8 (d, J = 10.6 Hz), 130.3 (d, J = 10.5 Hz), 107.3 (d, J = 2.1 Hz), 101.8 (d, J = 21.6 Hz), 98.6 (d, J = 25.9 Hz), 51.6, 50.2, 34.2, 32.1, 23.9, -1.8;

IR (neat) cm $^{-1}$ 2952, 1734, 1615, 1577, 1497, 1250, 1159, 836, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{24}FNNaO_2Si$ $(M+Na)^+$: 320.1453, found 320.1449.

Preparation of 6i



6i

According to the General Procedure E, **1m** (34 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding product **6i** (21 mg, 59 % yield, mp: 49.5-52.5 ºC) as a white solid.

<u>Spectral Dates of 6i</u>

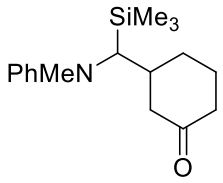
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 3.58 (s, 3H), 3.46 (dd, J_1 = 12.0 Hz, J_2 = 3.6 Hz, 1H), 2.82 (s, 3H), 2.34-2.18 (m, 2H), 2.09-1.99 (m, 1H), 1.95-1.87 (m, 1H), 0.07 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 153.0, 126.5 (q, J = 3.8 Hz), 125.3 (q, J = 268.3 Hz), 116.7 (q, J = 32.5 Hz), 110.7, 51.6, 49.9, 34.1, 32.0, 23.9, -1.8;

IR (neat) cm $^{-1}$ 2953, 1736, 1614, 1528, 1328, 1252, 1201, 1162, 1101, 1070, 839, 814;

HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{25}F_3NO_2Si$ $(M+H)^+$: 348.1601, found 348.1610.

Preparation of 6j



6j

According to the General Procedure E, **1a** (27 mg, 0.1 mmol) and cyclohex-2-en-1-one (49 µL, 0.5 mmol) were converted to corresponding products **6j** (9 mg, 31 % yield, dr = 1:1, mp: 81-84 ºC) as a white solid.

Spectral Data of 6j

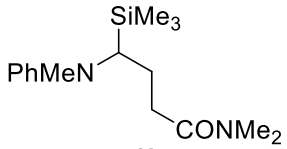
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 2H), 6.64 (d, J = 8.0 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 3.26 (d, J = 10.0 Hz, 1H), 2.82 (s, 3H), 2.40-2.33 (m, 2H), 2.30-2.22 (m, 2H), 2.18-2.11 (m, 1H), 2.00-1.91 (m, 2H), 1.74-1.62 (m, 1H), 1.49-1.39 (m, 1H), 0.11 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 150.7, 129.2, 115.2, 111.3, 56.0, 47.4, 41.6, 40.9, 35.2, 30.5, 25.9, -0.2;

IR (neat) cm $^{-1}$ 2947, 1710, 1596, 1508, 1251, 857, 836;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{27}NNaO_4Si$ $(M+Na)^+$: 312.1754 , found 312.1742.

Preparation of 6k



6k

According to the General Procedure E, **1a** (27 mg, 0.1 mmol) and *N,N*-dimethylacrylamide (52 µL, 0.5 mmol) was converted to corresponding product **6k** (18 mg, 60 % yield) as a colorless liquid after 24 h of stirring time.

Spectral Data of 6k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 6.59 (t, J = 7.2 Hz, 1H), 3.44 (q, J = 5.2 Hz), 2.87 (s, 3H), 2.79 (s, 3H), 2.71

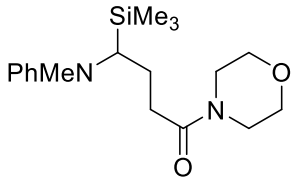
(s, 3H), 2.30-2.18 (m, 2H), 2.05-1.93 (m, 2H), 0.06 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 151.4, 129.1, 115.1, 111.7, 49.8, 37.1, 35.4, 34.0, 30.6, 23.9, -1.6.;

IR (neat) cm $^{-1}$ 2951, 1644, 1595, 1248, 835;

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{28}N_2NaOSi$ $(M+Na)^+$: 315.1863 , found 315.1860.

Preparation of 6l



6l

According to the General Procedure E, **1a** (27 mg, 0.1 mmol) and 1-morpholinoprop-2-en-1-one (64 μL, 0.5 mmol) were converted to corresponding product **6l** (16 mg, 47 % yield, mp: 87.5-91 ºC) as a white solid.

Spectral Data of 6l

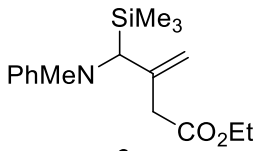
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, 2H), 6.68 (d, J = 8.0 Hz, 2H), 6.61 (t, J = 7.2 Hz, 1H), 3.60-3.35 (m, 7H), 3.24-3.11 (m, 2H), 2.79 (s, 3H), 2.30-2.17 (m, 2H), 2.02-1.97 (m, 2H), 0.06 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 151.4, 129.2, 115.3, 111.7, 66.9, 66.4, 49.8, 45.7, 41.9, 34.1, 30.1, 23.7, -1.7;

IR (neat) cm $^{-1}$ 2954, 2920, 2853, 1647, 1595, 1503, 1432, 1249, 1115, 837;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{30}N_2NaO_2Si$ $(M+Na)^+$: 357.1969 , found 357.1980.

Preparation of 6m



6m

According to the General Procedure E, **1a** (27 mg, 0.1 mmol) and ethyl buta-2,3-dienoate (60 μL, 0.5 mmol) was converted to corresponding product **6m** (17 mg, 54 % yield) as a colorless liquid.

Spectral Data of 6m

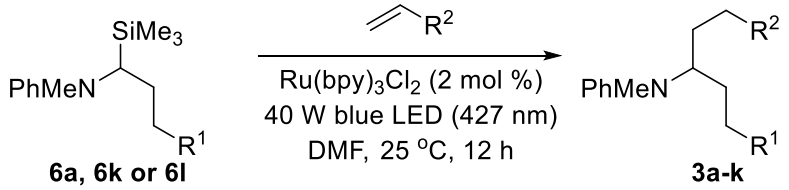
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 5.04 (s, 1H), 5.00 (s, 1H) 4.12 (s, 1H), 4.06-3.89 (m, 2H), 3.00 (d , J = 2.8 Hz, 2H), 2.97 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H), 0.18 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 150.5, 142.2, 129.0, 115.8, 114.1, 111.9, 60.6, 58.4, 40.6, 37.6, 14.2, -0.4;

IR (neat) cm $^{-1}$ 2955, 1733, 1597, 1502, 1252, 839;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{27}NNaO_2Si$ $(M+Na)^+$: 328.1703 , found 328.1700.

2.5. Synthesis of Hetero-Diaddition Products 3



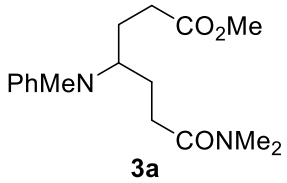
6a, 6k or 6l **3a-k**

General procedure F (alkenes were added after deoxygenation of DMF). A dried 15 mL Schlenk seal tube was charged with $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002mmol) and sealed with rubber plug in Standard Glovebox. **6a**, **6k** or **6l** (0.1 mmol) and DMF (2 mL) were added into the tube at 25 °C under positive argon pressure. The solution was allowed to purge with high purity argon gas using a 15 cm syringe needle for at least 10 mins at 25 °C and charged with alkene (0.5 mmol) using syringe under positive argon pressure. The rubber plug was changed to polytetrafluoroethylene seal plug under positive argon pressure. The solution was stirred for 12 h under irradiation with 427 nm blue LED.

The reaction was concentrated in vacuo and purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 50:1→10:1) to afford **3**.

General procedure G (alkenes were added before deoxygenation of DMF). A dried 15 mL Schlenk seal tube was charged with $Ru(bpy)_3Cl_2$ (1.3 mg, 0.002mmol) and sealed with rubber plug in Standard Glovebox. **6a**, **6k** or **6l** (0.1 mmol), alkenes (0.5 mmol) and DMF (2 mL) were added into the tube at 25 °C under positive argon pressure. The solution was allowed to purge with high purity argon gas using a 15 cm syringe needle for at least 10 mins at 25 °C. The rubber plug was changed to polytetrafluoroethylene seal plug under positive argon pressure. The solution was stirred for 12 h under irradiation with 427 nm blue LED. The reaction was concentrated in vacuo and purified by silica gel chromatography (gradient eluent: petroleum ether/EtOAc = 50:1→10:1) to afford the desired products **3**.

Preparation of 3a



3a

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding product **3a** (24 mg, 79 % yield) as a colorless liquid.

Spectral Data of 3a

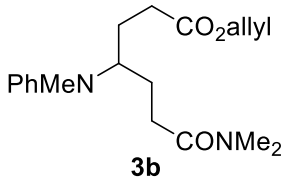
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H), 4.03-3.96 (m, 1H), 3.58 (s, 3H), 2.86 (s, 3H), 2.70 (s, 3H), 2.67 (s, 3H), 2.28-2.16 (m, 4H), 1.97-1.80 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.4, 151.1, 129.2, 116.4, 112.6, 56.5, 51.6, 37.0, 35.4, 31.2, 29.5, 29.5, 28.3, 28.1;

IR (neat) cm^{-1} 2926, 1733, 1640, 1596, 1503, 1396, 1262, 1163, 1101;

HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{26}N_2NaO_3$ $(M+Na)^+$: 329.1836 , found 329.1847.

Preparation of 3b



3b

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and allyl acrylate (62 μL, 0.5 mmol) were converted to corresponding product **3b** (21 mg, 62 % yield) as a colorless liquid.

Spectral Data of 3b

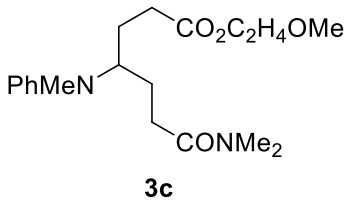
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J_1 = 8.8 Hz, J_2 = 6.8 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.65 (t, J = 6.8 Hz, 1H), 5.87-5.77 (m, 1H), 5.24 (dq, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 5.18 (dq, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 4.48 (d, J = 5.6 Hz, 2H), 4.04-3.97 (m, 1H), 2.86 (s, 3H), 2.70 (s, 3H), 2.68 (s, 3H), 2.30 (t, J = 7.6 Hz, 2H), 2.23-2.14 (m, 2H), 1.97-1.80 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 172.4, 151.1, 132.2, 129.2, 118.3, 116.4, 112.6, 65.2, 56.5, 37.0, 35.4, 31.4, 29.5, 28.2, 28.1;

IR (neat) cm^{-1} 2926, 1732, 1642, 1596, 1504, 1396, 1266, 1158, 1101, 988, 923;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{28}N_2NaO_3$ $(M+Na)^+$: 355.1992 , found 355.1991.

Preparation of 3c



3c

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and 2-methoxyethyl acrylate (66 μL, 0.5 mmol) were converted to corresponding product **3c** (26 mg, 73 % yield) as a colorless liquid.

Spectral Data of 3c

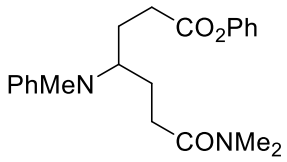
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.45 (t, J = 7.2 Hz, 1H), 4.13 (t, J = 4.8 Hz, 2H), 4.04-3.96 (m, 1H), 3.48 (t, J = 4.8 Hz, 2H), 3.33 (s, 3H), 2.86 (s, 3H), 2.70 (s, 3H), 2.67 (s, 3H), 2.31 (t, J = 7.6 Hz, 2H), 2.23-2.14 (m, 2H), 1.97-1.80 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.4, 151.1, 129.2, 116.4, 112.6, 70.4, 63.4, 59.0, 56.5, 37.0, 35.4, 31.4, 29.5, 29.5, 28.2, 28.1;

IR (neat) cm $^{-1}$ 2924, 1732, 1643, 1597, 1504, 1397, 1129, 1101, 1034;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{30}N_2NaO_4$ $(M+Na)^+$: 373.2098 , found 373.2096.

Preparation of 3d



3d

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and phenyl acrylate (71 μL, 0.5 mmol) were converted to corresponding product **3d** (29 mg, 78 % yield) as a colorless liquid.

Spectral Data of 3d

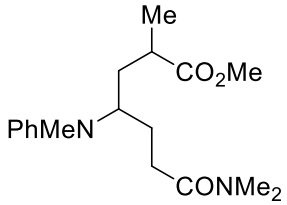
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, J = 7.6 Hz, 2H), 7.23-7.17 (m, 3H), 6.94 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 7.6 Hz, 2H), 6.69 (t, J = 7.2 Hz, 1H), 4.13-4.06 (m, 1H), 2.86 (s, 3H), 2.71 (s, 3H), 2.70 (s, 3H), 2.54 (t, J = 7.2 Hz, 2H), 2.26-2.15 (m, 2H), 2.08-1.84 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 172.1, 151.1, 150.7, 129.3, 129.3, 125.8, 121.6, 116.6, 112.7, 56.6, 37.0, 35.4, 31.5, 29.6, 29.5, 28.1, 28.1;

IR (neat) cm $^{-1}$ 2924, 1755, 1641, 1596, 1504, 1397, 1193, 1162, 1132, 1101;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{28}N_2NaO_3$ $(M+Na)^+$: 391.1992 , found 391.1996.

Preparation of 3e



3e

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and methyl methacrylate (55 μL, 0.5 mmol) were converted to corresponding product **3e** (26 mg, 81 % yield, dr = 1.6:1) as a colorless liquid.

Spectral Data of 3e

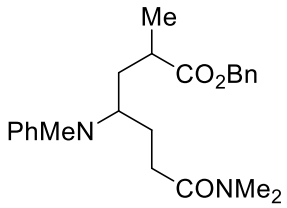
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.75-6.69 (m, 2H), 6.64 (t, J = 7.2 Hz, 1H), 4.08-3.99 (m, 1H), 3.52-3.49 (m, 3H), 2.86-2.85 (m, 3H), 2.73-2.64 (m, 6H), 2.47-2.37 (m, 1H), 2.22-2.04 (m, 3H), 1.95-1.78 (m, 2H), 1.66-1.48 (m, 1H), 1.16-1.11 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 172.4, 172.3, 151.0, 150.9, 129.1, 116.4, 116.3, 112.6, 112.5, 55.3, 54.9, 51.6, 51.5, 37.2, 37.1, 37.1, 37.0, 36.9, 36.4, 35.4, 35.4, 29.8, 29.7, 29.6, 29.4, 28.1, 28.1, 18.2, 17.4;

IR (neat) cm $^{-1}$ 2927, 1731, 1643, 1597, 1504, 1396, 1196, 1165;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{28}N_2NaO_3$ $(M+Na)^+$: 343.1992 , found 343.1990.

Preparation of 3f



3f

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and benzyl methacrylate (87 μL, 0.5 mmol) were converted to corresponding product **3f** (37 mg, 93 % yield, dr = 1.5:1) as a colorless liquid.

Spectral Data of 3f

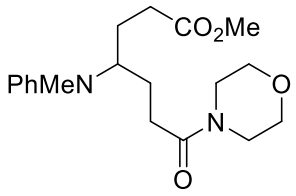
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 3H), 7.23-7.11 (m, 4H), 6.75-6.62 (m, 3H), 5.06-4.83 (m, 2H), 4.08-4.01 (m, 1H), 2.86-2.84 (m, 3H), 2.72-2.63 (m, 6H), 2.53-2.43 (m, 1H), 2.20-1.76 (m, 5H), 1.68-1.50 (m, 1H), 1.18-1.14 (m, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 176.4, 172.4, 172.3, 150.9, 136.1, 136.1, 129.2, 129.2, 128.5, 128.5, 128.3, 128.2, 128.1, 128.1, 116.4, 116.4, 112.6, 112.6, 66.3, 66.2, 55.3, 55.2, 37.3, 37.2, 37.1, 37.0, 36.9, 36.5, 35.4, 35.4, 29.8, 29.7, 29.6, 29.3, 28.2, 28.1, 18.3, 17.6;

IR (neat) cm $^{-1}$ 2928, 1729, 1644, 1597, 1504, 1455, 1396, 1159;

HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{32}N_2NaO_3$ $(M+Na)^+$: 419.2305 , found 419.2305.

Preparation of 3g



3g

According to the General Procedure F, **6l** (34 mg, 0.1 mmol) and methyl acrylate (46 μL, 0.5 mmol) were converted to corresponding product **3g** (28 mg, 80 % yield) as a colorless liquid.

Spectral Data of 3g

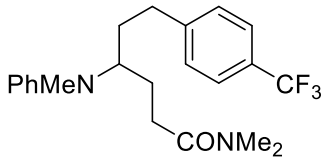
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.73 (d, J = 8.8 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 4.05-3.97 (m, 1H), 3.58-3.34 (m, 9H), 3.23-3.09 (m, 2H), 2.67 (s, 3H), 2.27 (t, J = 7.6 Hz, 2H), 2.21-2.16 (m, 2H), 1.98-1.81 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 171.0, 151.1, 129.3, 116.6, 112.6, 66.8, 66.4, 56.5, 51.6, 45.7, 42.0, 31.2, 29.5, 29.1, 28.3, 27.9;

IR (neat) cm $^{-1}$ 2922, 2854, 1733, 1641, 1596, 1504, 1434, 1228, 1114, 1032, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{28}N_2NaO_4$ $(M+Na)^+$: 371.1941 , found 371.1938.

Preparation of 3h



3h

According to the General Procedure F, **6k** (30 mg, 0.1 mmol) and 4-(trifluoromethyl)styrene (76 μL, 0.5 mmol) were converted to corresponding product **3h** (29 mg, 74 % yield) as a colorless liquid.

Spectral Dates of 3h

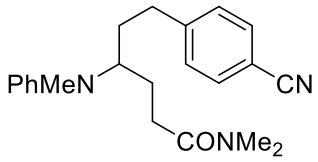
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 4H), 6.70-6.65 (m, 3H), 4.00-3.92 (m, 1H), 2.87 (s, 3H), 2.73 (s, 3H), 2.71 (s, 3H), 2.63-2.59 (m, 2H), 2.24-2.19 (m, 2H), 2.03-1.79 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 151.2, 146.3, 129.2, 128.8, 125.3 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 270.0 Hz), 116.4, 112.7, 56.6, 37.0, 35.4, 35.0, 33.0, 29.6, 29.5, 28.1;

IR (neat) cm $^{-1}$ 2926, 1644, 1597, 1324, 1161, 1120, 1067;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{27}F_3N_2NaO$ $(M+Na)^+$: 415.1968 , found 415.1967.

Preparation of 3i



3i

According to the General Procedure G, **6k** (30 mg, 0.1 mmol) and 4-vinylbenzonitrile (66 mg, 0.5 mmol) were converted to corresponding products **3i** (25 mg, 71 % yield) as a colorless liquid.

Spectral Data of 3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.20-7.15 (m, 4 H), 6.69-6.65 (m, 3H), 3.99-3.91 (m, 1H), 2.87 (s, 3H), 2.71 (s, 3H), 2.70 (s, 3H), 2.64-2.57 (m, 2H),

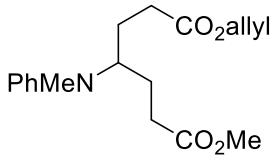
2.25-2.16 (m, 2H), 2.02-1.79 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 151.1, 147.8, 132.2, 129.3, 129.2, 119.2, 116.5, 112.6, 109.7, 56.5, 37.0, 35.4, 34.7, 33.3, 29.6, 29.3, 28.0;

IR (neat) cm $^{-1}$ 2924, 2855, 2226, 1638, 1596, 1503, 1395, 1095;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{27}N_3NaO$ $(M+Na)^+$: 372.2046 , found 372.2050.

Preparation of 3j



3j

According to the General Procedure F, **6a** (28 mg, 0.1 mmol) and allyl acrylate (60 μL, 0.5 mmol) were converted to corresponding product **3j** (28 mg, 89 % yield) as a colorless liquid.

Spectral Data of 3j

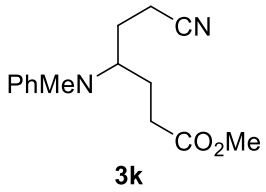
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.74 (d, J = 8.8 Hz, 2H), 6.67 (t, J = 7.2 Hz, 1H), 5.87-5.77 (m, 1H), 5.24 (dq, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 5.19 (dq, J_1 = 10.4 Hz, J_2 = 1.6 Hz, 1H), 4.49 (dt, J_1 = 5.6 Hz, J_2 = 1.6 Hz, 2H), 4.02-3.94 (m, 1H), 3.58 (s, 3H), 2.68 (s, 3H), 2.31-2.24 (m, 4H), 1.96-1.79 (m, 4H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.0, 150.9, 132.2, 129.2, 118.4, 116.7, 112.7, 65.2, 56.5, 51.6, 31.2, 31.1, 29.5, 28.1, 28.0;

IR (neat) cm $^{-1}$ 2926, 1730, 1597, 1504, 1248, 1194, 1169, 1103, 988, 922;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{25}NNaO_4$ $(M+Na)^+$: 342.1676, found 342.1673.

Preparation of 3k



3k

According to the General Procedure F, **6a** (28 mg, 0.1 mmol) and acrylonitrile (34 μL, 0.5 mmol) were converted to corresponding product **3k** (15 mg, 56 % yield) as a colorless liquid.

Spectral Data of 3k

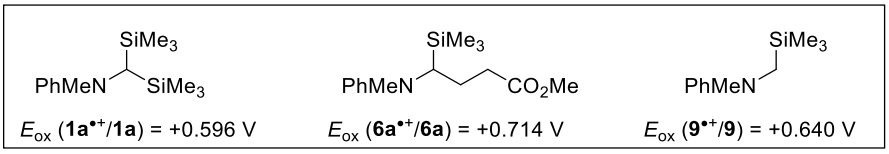
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, J_1 = 8.8 Hz, J_2 = 7.2 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 4.06-3.99 (m, 1H), 3.59 (s, 3H), 2.69 (s, 3H), 2.31-2.24 (m, 4H), 2.00-1.79 (m, 4H);

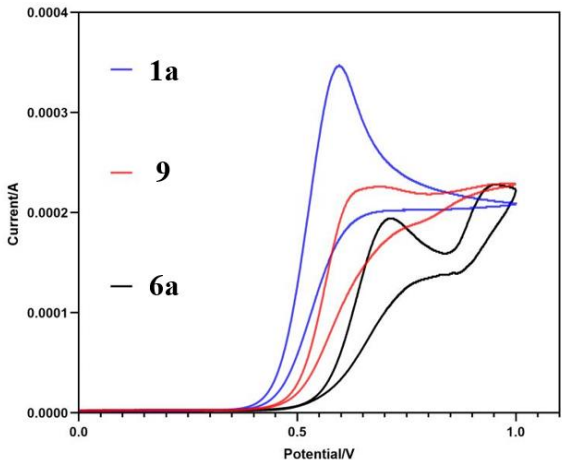
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 150.5, 129.5, 119.6, 117.6, 113.2, 56.5, 51.7, 30.8, 29.6, 28.9, 27.7, 14.6;

IR (neat) cm^{-1} 2951, 2246, 1731, 1596, 1504, 1436, 1319, 1196, 1159, 1105, 1032, 988, 916, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{15}H_{20}N_2NaO_2$ $(M+Na)^+$: 283.1417, found 283.1416.

2.7. Cyclic Voltammetry Analysis



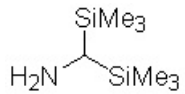


Cyclic Voltammetry experiments were conducted with a computer controlled CH Instruments Model 600E Series Electrochemical Analyzer/Workstation containing platinum wire working electrode, platinum wire counter electrode and saturated KCl silver-silver chloride electrode reference electrode.

Sample were prepared with 0.1 mmol of analyte (**1a**, **6a** and **9**) in 10 mL of 0.05 M *tetra-N*-butylammonium hexafluorophosphate in dry and degassed acetonitrile. Measurements employed a scan rate of 20 mV/s. **9** was prepared according to a published procedure described by Mariano and coworkers.[4]

4. X. M. Zhang and P. S. Mariano, *J. Org. Chem.*, 1991, **56**, 1655.

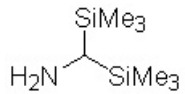
LSF-5-99_H1_CDCl3_2019-12-18.10.fid



4

LSF-5-99_C13_CDCl3_2019-12-18.10.fid

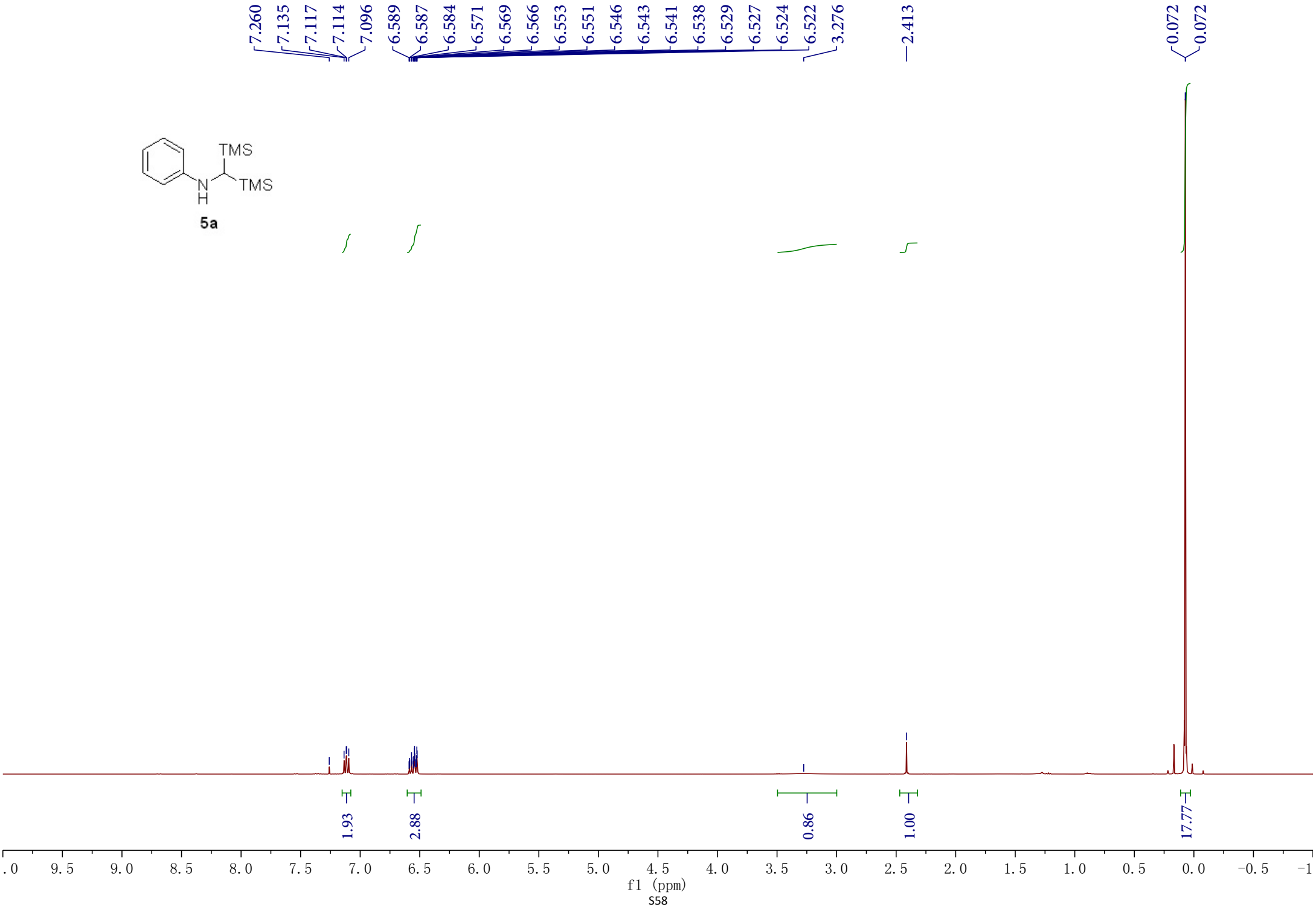
77.417
77.100
76.782
31.510
-1.646



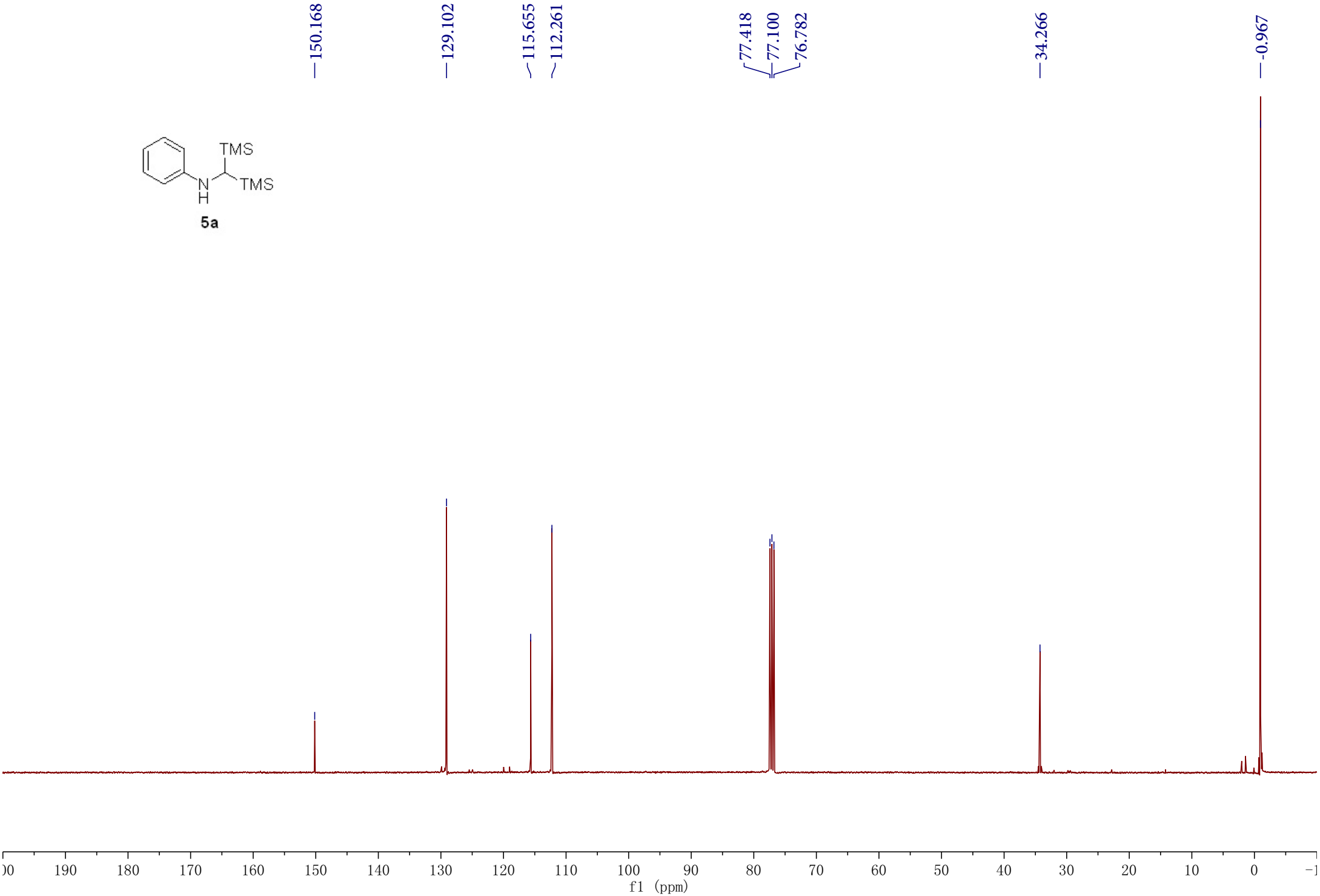
4

f1 (ppm)

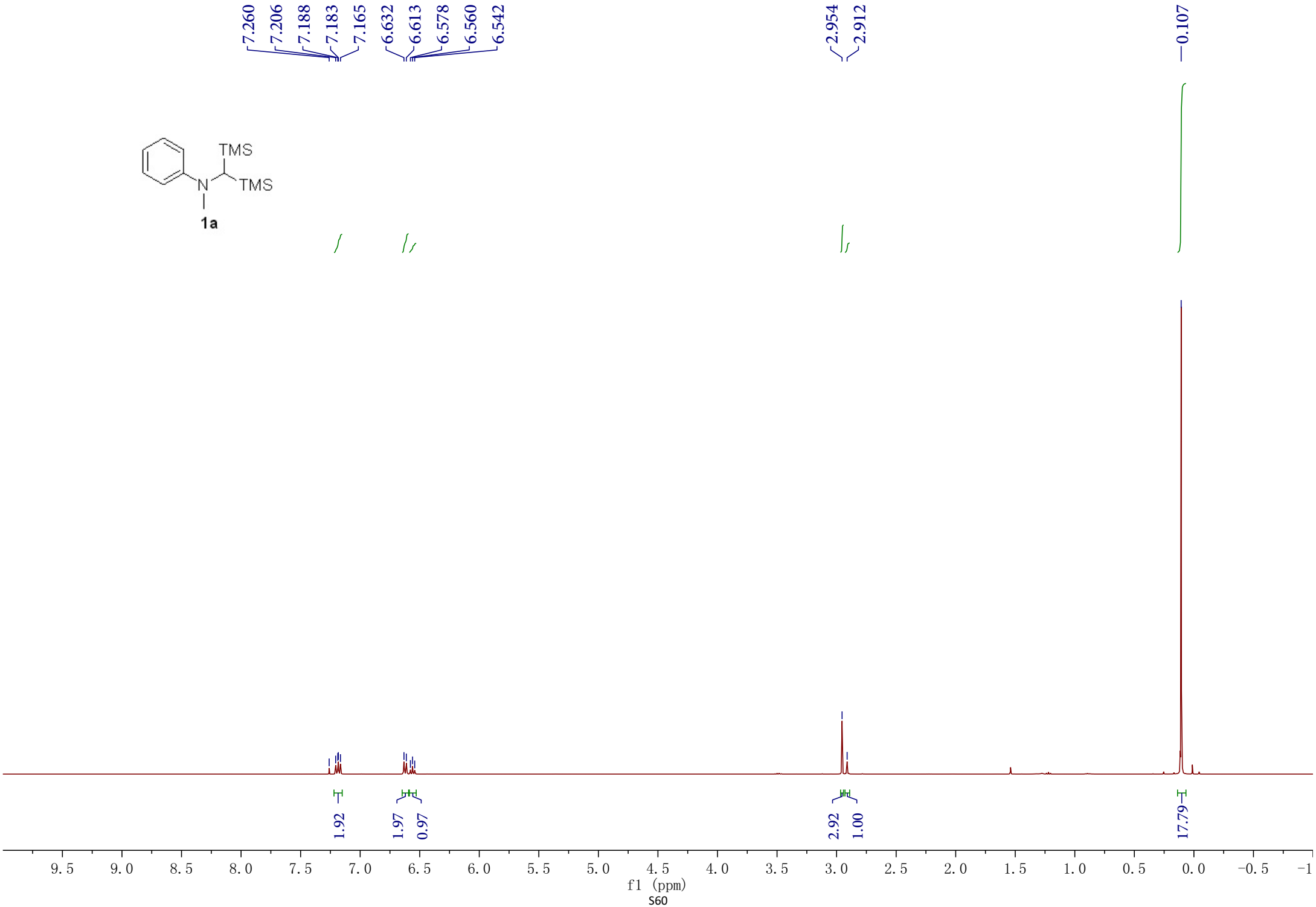
LSF-6-109_H1_CDCl3_2020-2-12.10.fid



LSF-6-109_C13_CDCl3_2020-2-11.10.fid

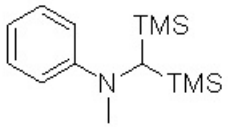


LSF-7-1_H1_CDCl3_2020-2-11.10.fid



LSF-7-1_C13_CDCl3_2020-2-11.10.fid

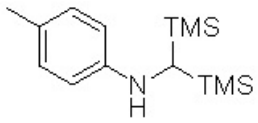
150.729
128.996
114.079
111.030
77.417
77.100
76.783
43.468
38.909
0.603



1a

f1 (ppm)

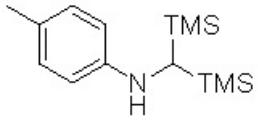
LSF-6-110_H1_CDCl3_2019-12-9.30.fid



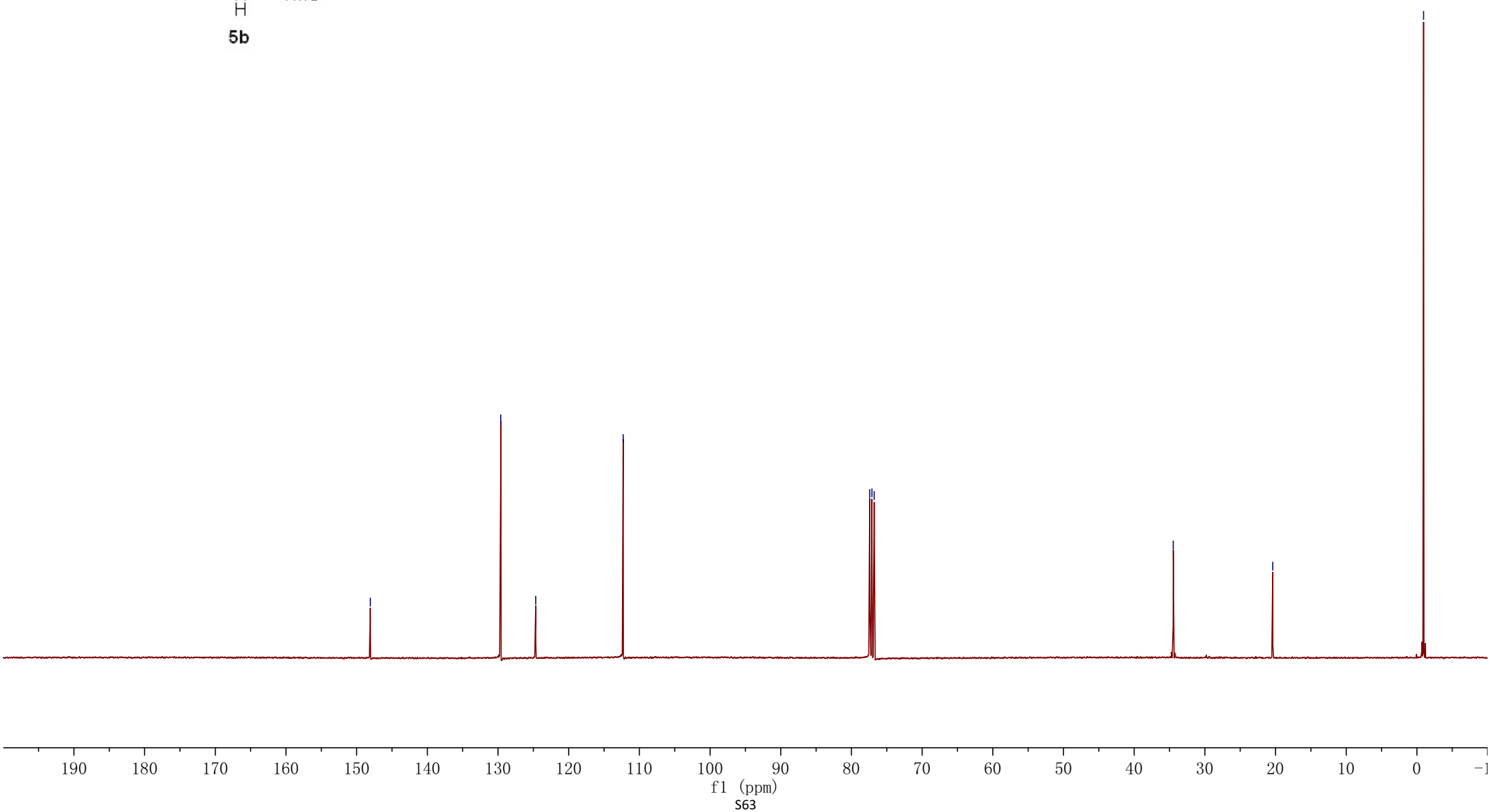
5b

LSF-6-110_C13_CDCl3_2019-12-10.10.fid

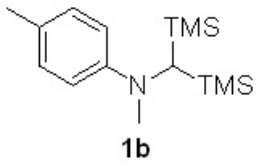
148.061
129.616
124.667
112.296
77.418
77.100
76.784
34.474
20.397
-0.943



5b



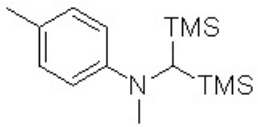
LSF-8-1_H1_CDCl3_2020-3-5.10.fid



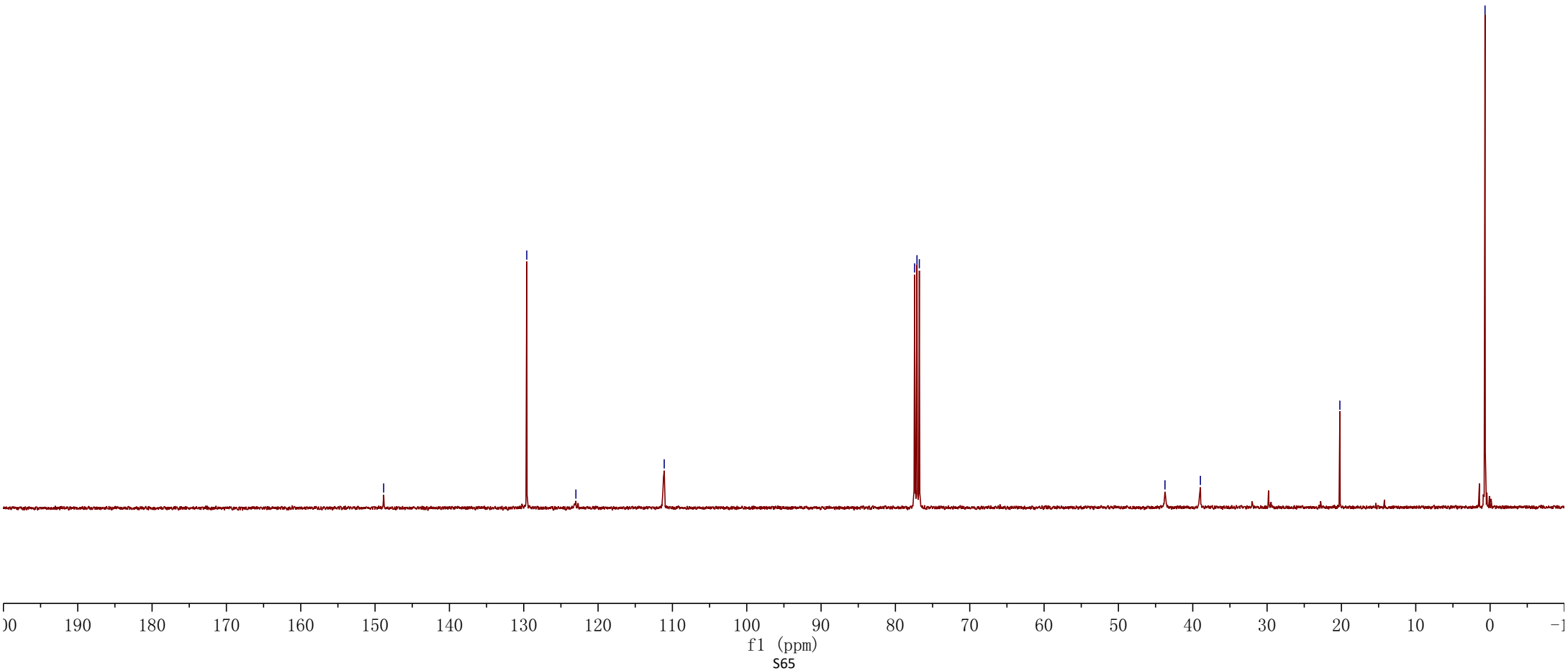
1b

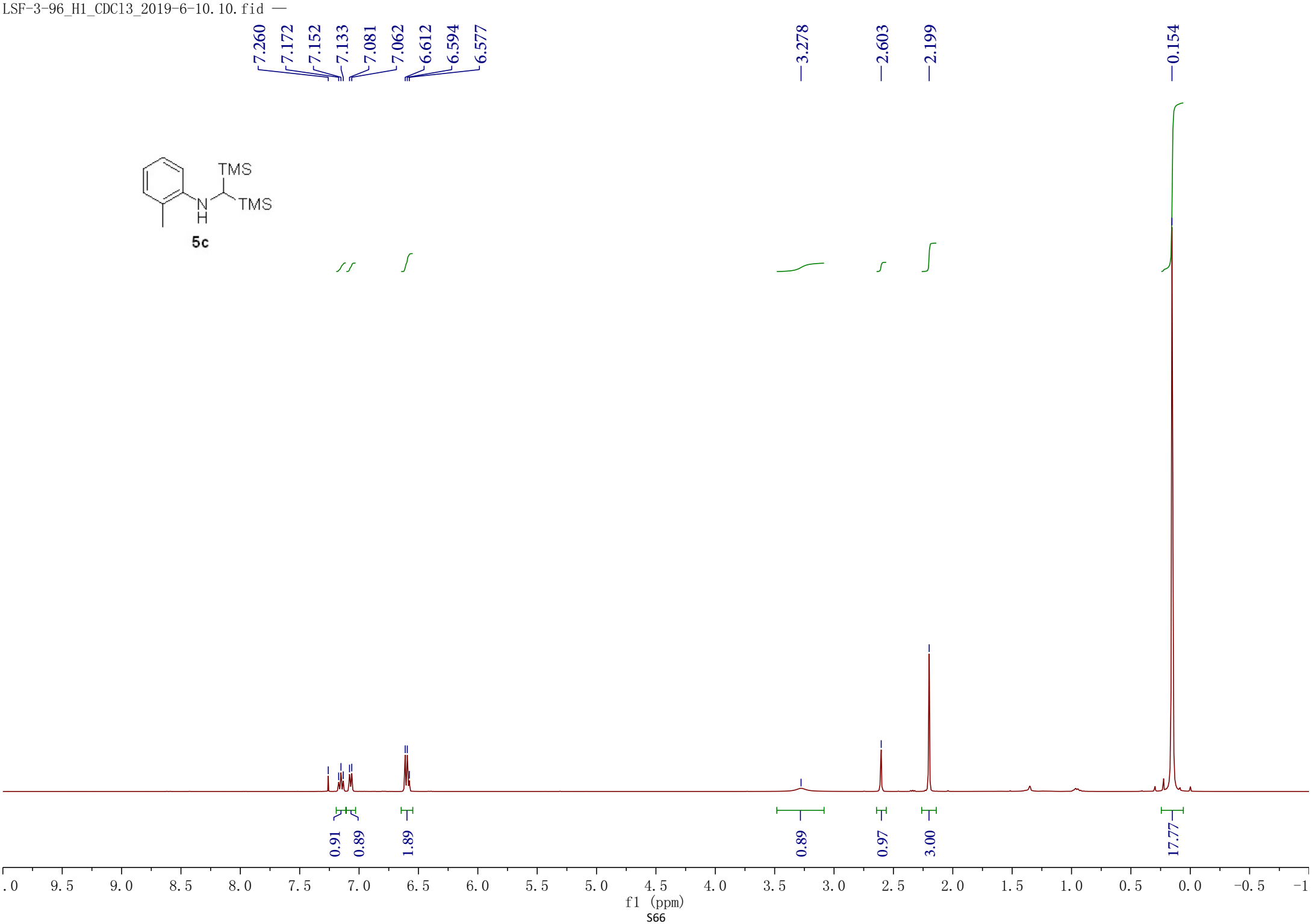
LSF-8-1_C13_CDCl3_2020-3-5.10.fid

148.842
129.595
122.984
111.102
77.419
77.101
76.784
43.737
38.971
20.210
0.680

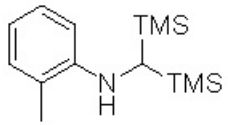


1b

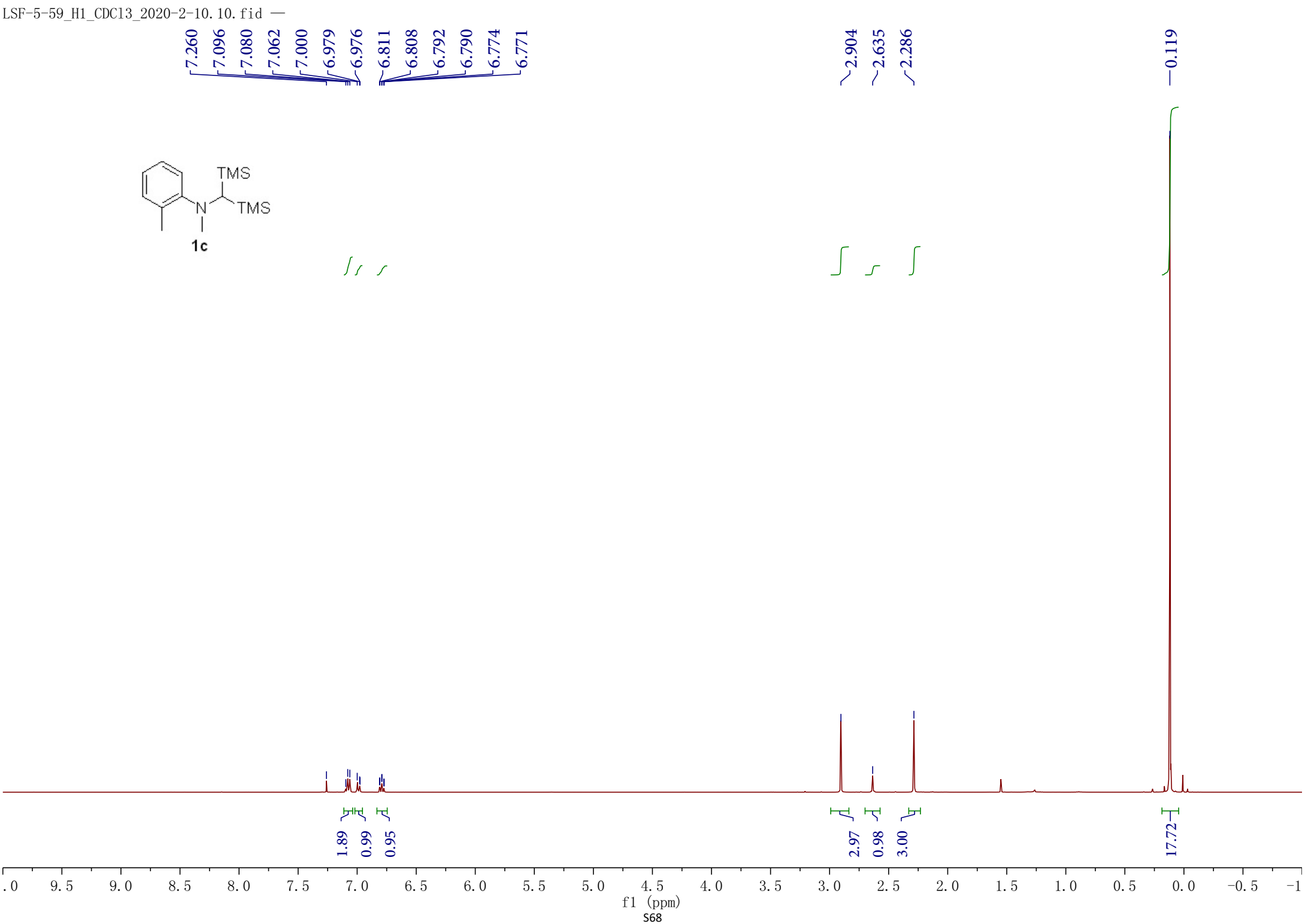



LSF-3-96_H1_CDCl3_2019-6-10.10.fid
7.260
7.172
7.152
7.133
7.081
7.062
6.612
6.594
6.577
3.278
2.603
2.199
0.154
TMS
TMS
N
H
5c
0.91
0.89
1.89
0.89
0.97
3.00
17.77
f1 (ppm)

LSF-3-96_C13_CDCl3_2019-6-6.10.fid

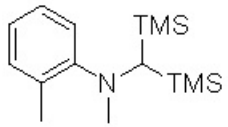


5c


LSF-5-59_H1_CDCl3_2020-2-10.10.fid
7.260
7.096
7.080
7.062
7.000
6.979
6.976
6.811
6.808
6.792
6.790
6.774
6.771
2.904
2.635
2.286
0.119
TMS
TMS
N
1c
1.89
0.99
0.95
2.97
0.98
3.00
17.72
f1 (ppm)

LSF-5-59_C13_CDCl3_2020-2-10.21.fid

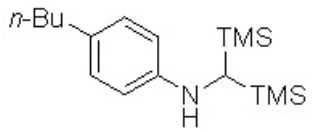
154.244
131.686
129.714
126.029
120.282
119.441
77.417
77.100
76.784
46.622
42.144
20.259
1.287



1c

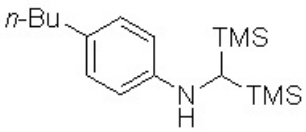
f1 (ppm)

LSF-7-89_H1_CDCl3_2020-1-21.20.fid



5d

LSF-7-89_C13_CDCl3_2020-1-21.20.fid

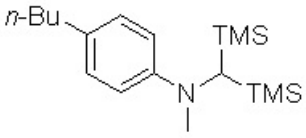


5d

148.281
130.118
128.925
112.356
77.418
77.101
76.783
34.772
34.632
34.062
22.511
14.107
-0.900

f1 (ppm)

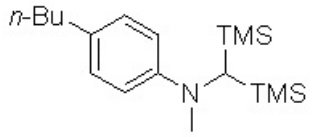
LSF-7-93_H1_CDCl3_2020-2-11.10.fid



1d

LSF-7-93_C13_CDCl3_2020-2-11.21.fid

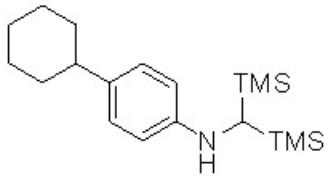
149.044
128.845
128.381
111.106
77.418
77.100
76.783
43.675
38.996
34.596
34.054
22.568
14.139
0.689



1d

f1 (ppm)

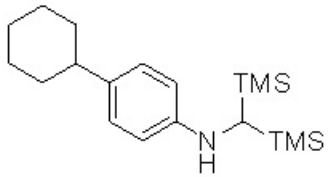
LSF-7-17_H1_CDCl3_2019-12-24.80.fid



5e

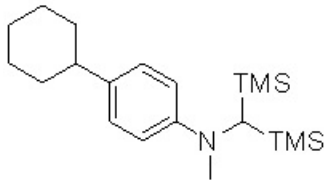
LSF-7-17-CDCL3-C13-2019-12-25.10.fid

148.318
135.530
127.228
112.289
77.417
77.099
76.782
43.514
34.841
34.555
27.156
26.375
-0.885



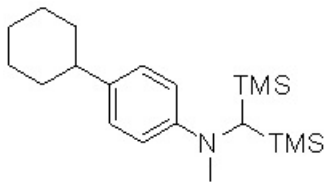
5e

LSF-7-75-CDCL3-H1-2020-1-17.10.fid



1e

LSF-7-75-CDCL3-C13-2020-1-17.10.fid

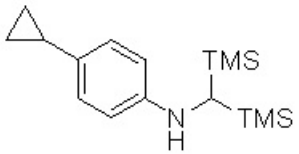


1e

149.150
133.769
127.134
111.088
77.417
77.100
76.782
43.658
43.316
38.964
34.825
27.183
26.402
0.708

f1 (ppm)

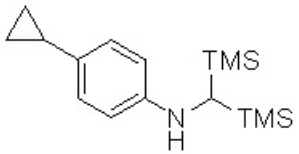
LSF-7-11-CDCL3-H1-2019-12-18 — LSF-7-11-CDCL3-H1-2019-12-18 —



5f

LSF-7-11_C13_CDCl3_2019-12-20.10.fid

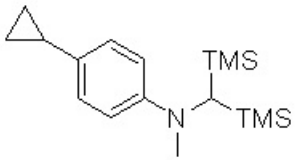
148.247
130.610
126.673
112.328
77.417
77.100
76.782
34.507
14.610
8.114
-0.930



5f

f1 (ppm)

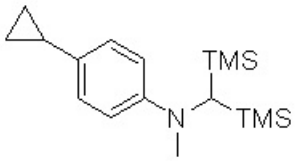
LSF-7-94_H1_CDCl3_2020-2-11.10.fid



1f

LSF-7-94_C13_CDCl3_2020-2-11.21.fid

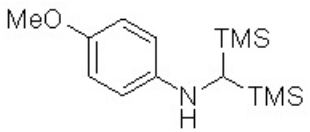
149.035
128.881
126.585
111.150
77.418
77.100
76.782
43.648
38.997
14.444
8.097
0.659



1f

f1 (ppm)

LSF-7-43-CDCL3-H1-2020-2-7.10.fid



5g

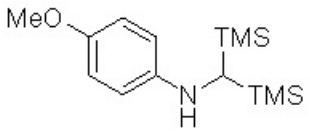
7.260
6.741
6.718
6.501
6.479
3.735
3.043
2.293
0.057

2.01
2.03
3.00
0.96
1.04
18.15

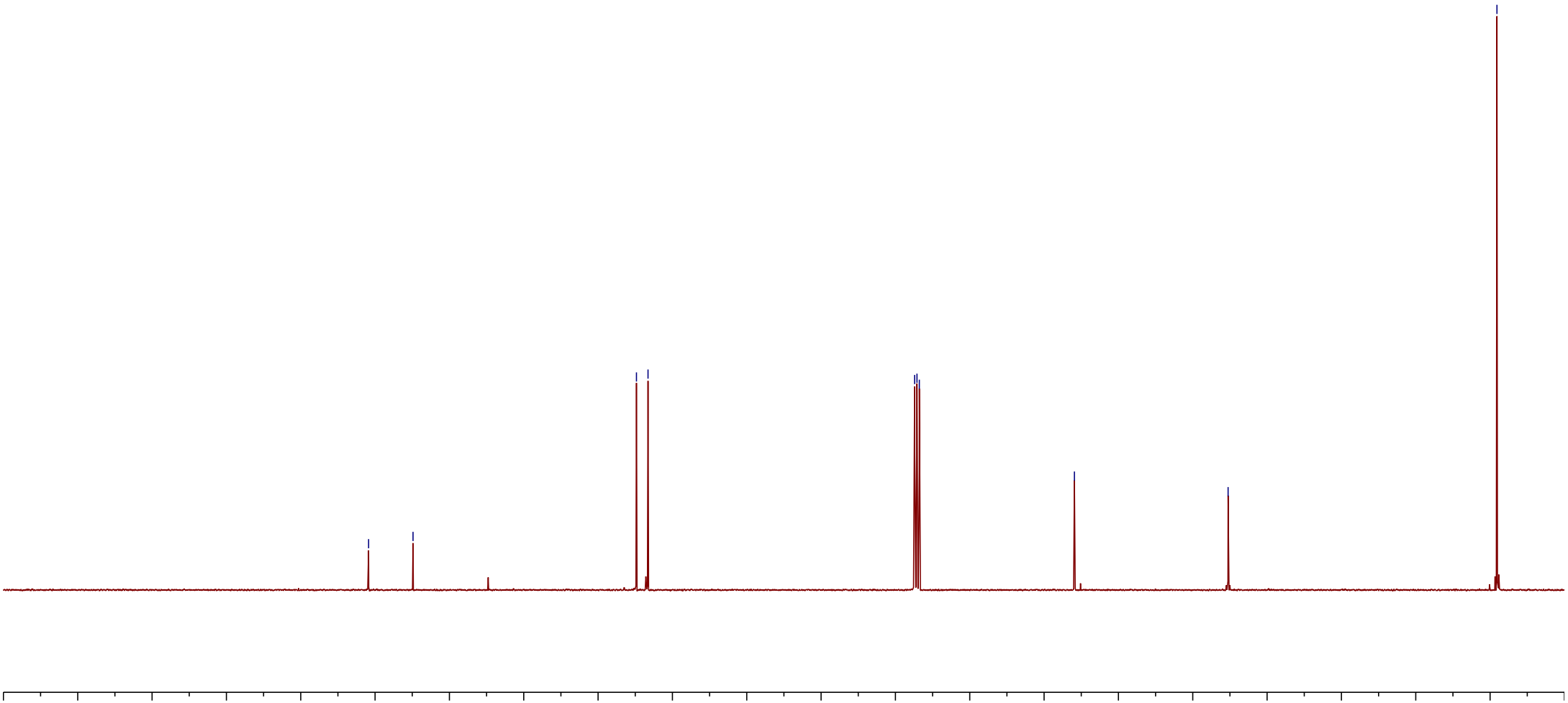
f1 (ppm)

LSF-7-43-CDCL3-C13-2020-2-7.10.fid

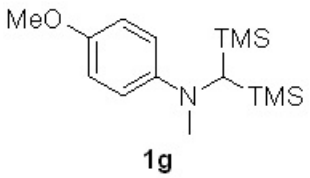
150.870
144.895
114.837
113.282
77.418
77.100
76.783
55.920
35.245
-0.922



5g



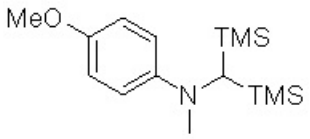
LSF-7-51P-CDCL3-H1-2020-1-8.10.fid



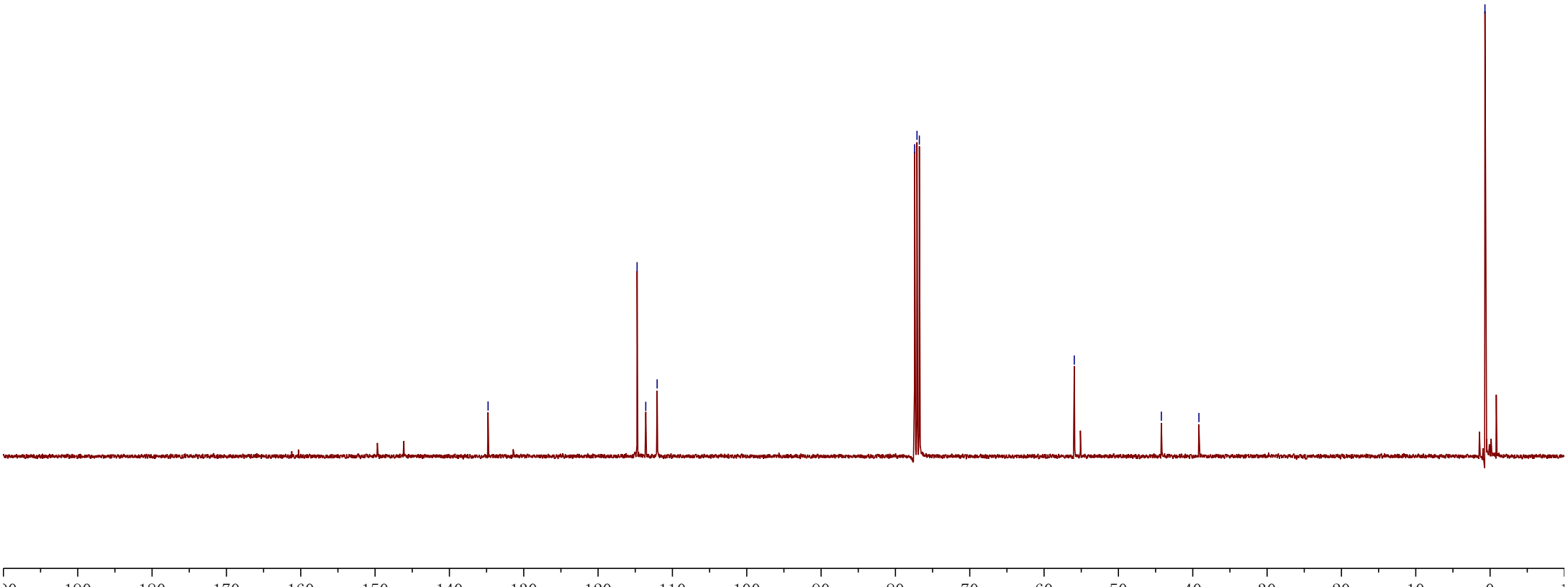
1g

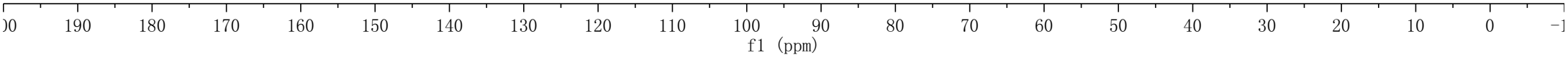
LSF-7-51P-CDCL3-C13-2020-1-8.10.fid

134.799
114.753
113.585
112.057
77.417
77.100
76.782
55.938
44.225
39.171
0.693

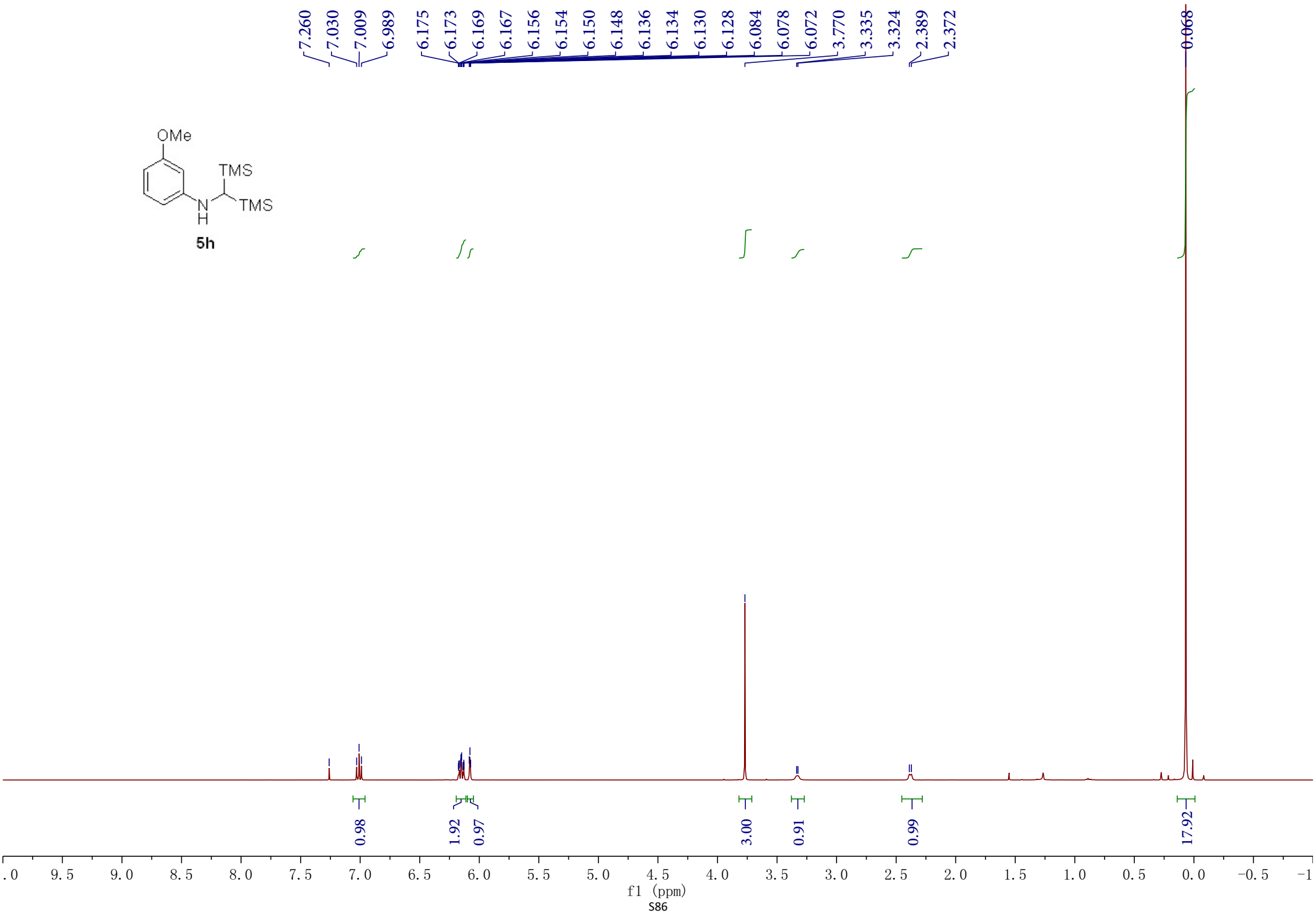


1g



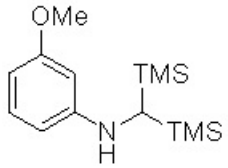


LSF-7-105-CDCL3-H1-2020-2-17.10.fid



LSF-7-105-CDCL3-C13-2020-2-17.10.fid

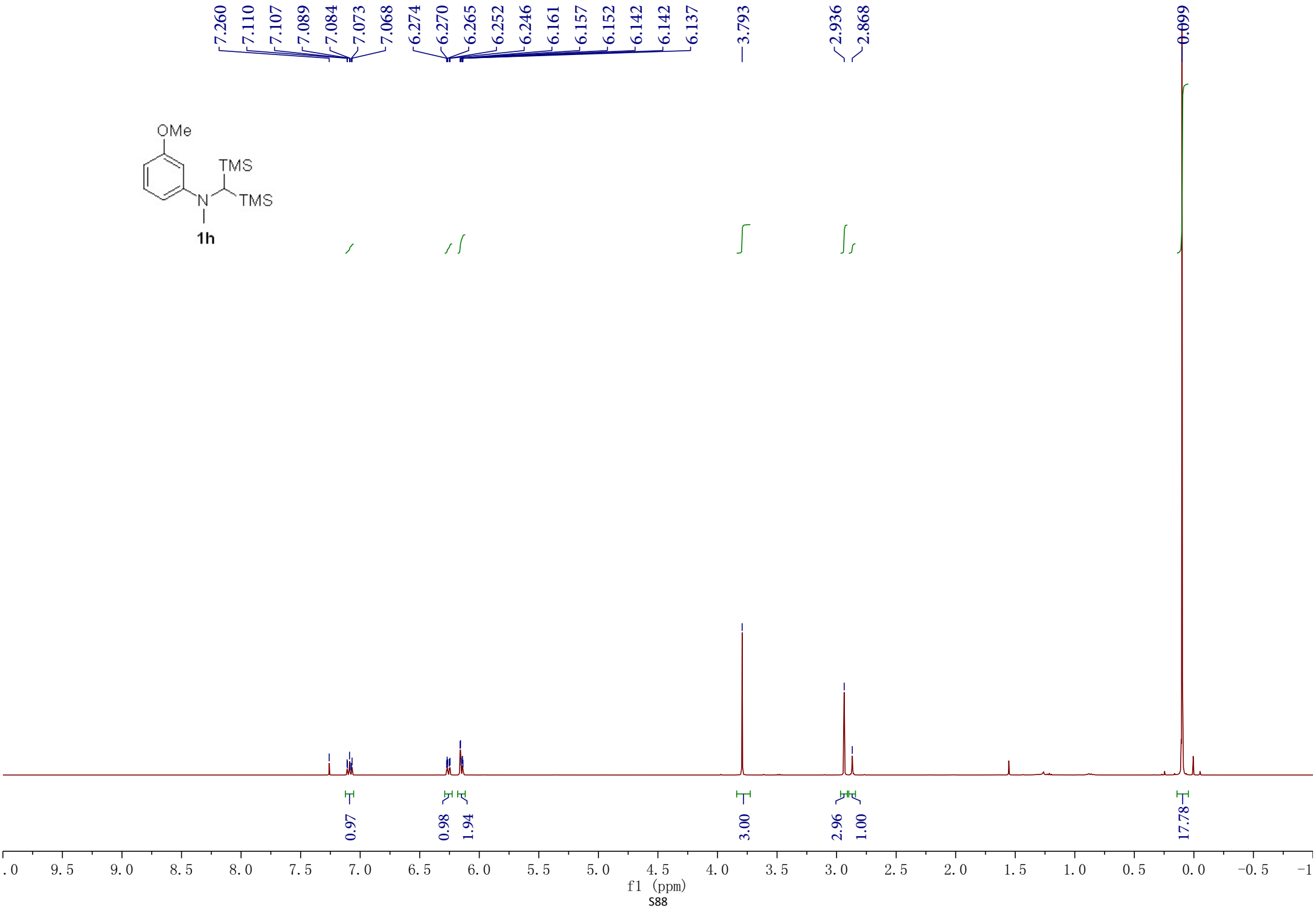
160.878
151.579
129.720
105.878
100.567
98.107
77.418
77.100
76.782
55.084
34.439
-0.981

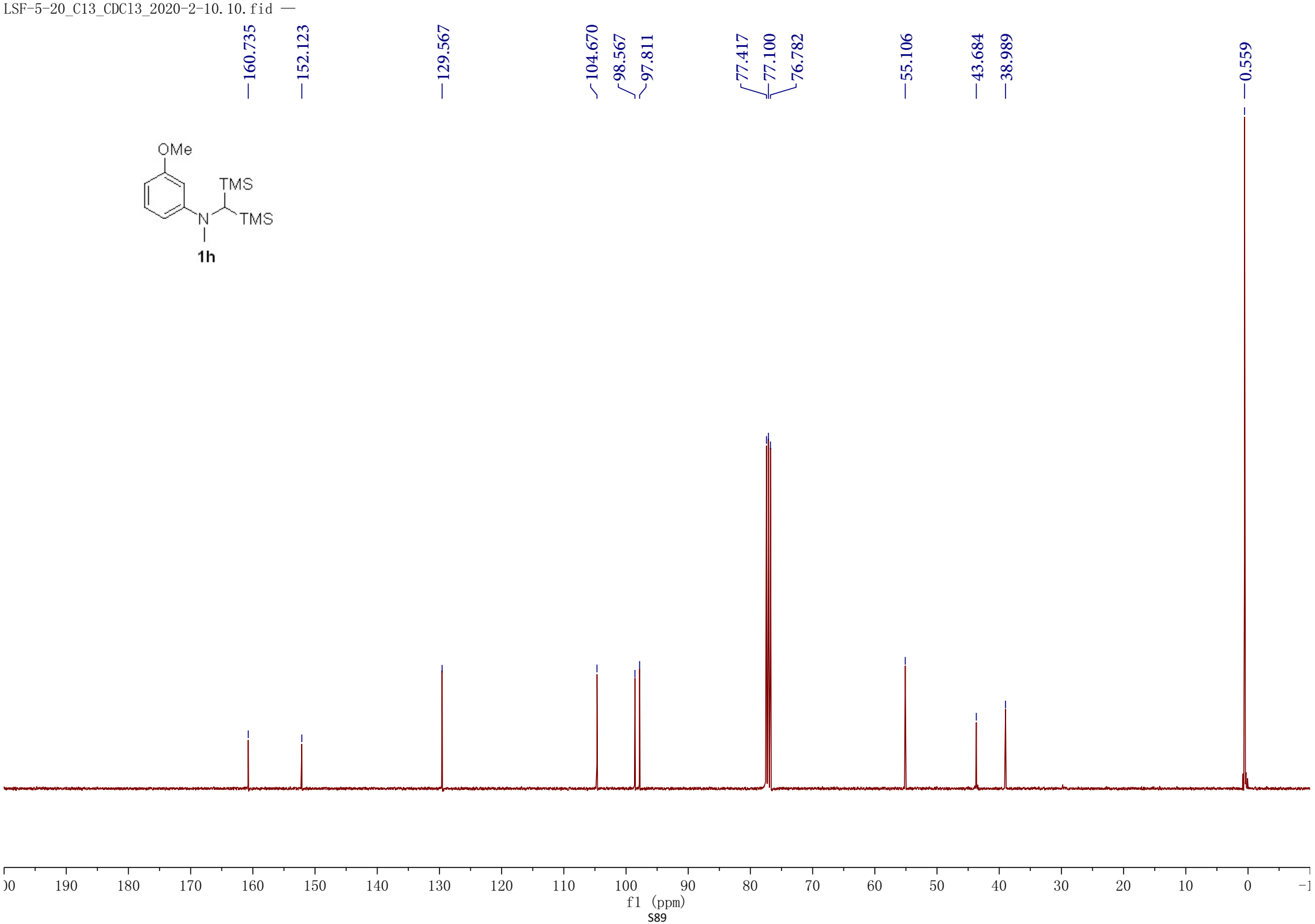


5h

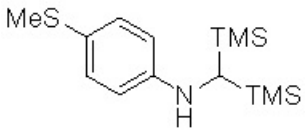
f1 (ppm)

LSF-5-20_H1_CDCl3_2020-2-10.10.fid



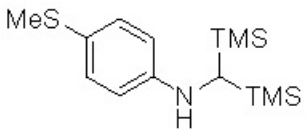

LSF-5-20_C13_CDCl3_2020-2-10.10.fid
160.735
152.123
129.567
104.670
98.567
97.811
77.417
77.100
76.782
55.106
43.684
38.989
0.559
OMe
TMS
TMS
N
1h
f1 (ppm)

LSF-7-10B_H1_CDCl3_2019-12-18.80.fid



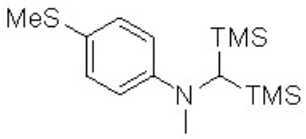
5i

LSF-7-10B_C13_CDCl3_2019-12-20.10.fid



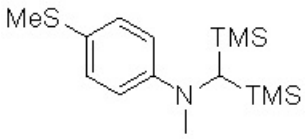
5i

LSF-7-69-CDCL3-H1-2020-1-17.10.fid



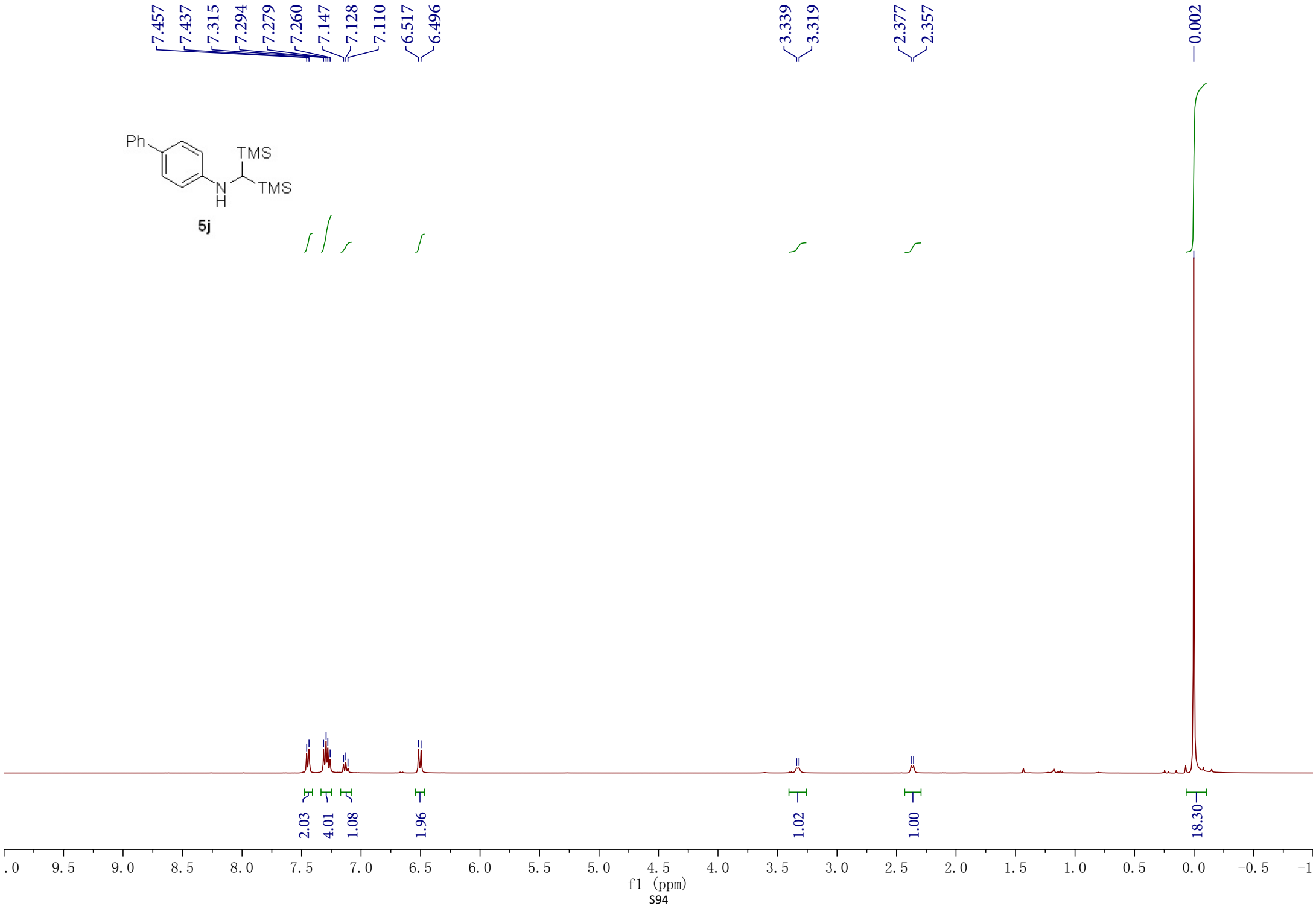
1i

LSF-7-69-CDCL3-C13-2020-1-17.10.fid



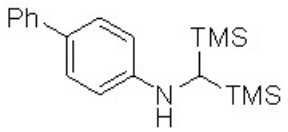
1i

LSF-7-16_H1_CDCl3_2019-12-24.70.fid

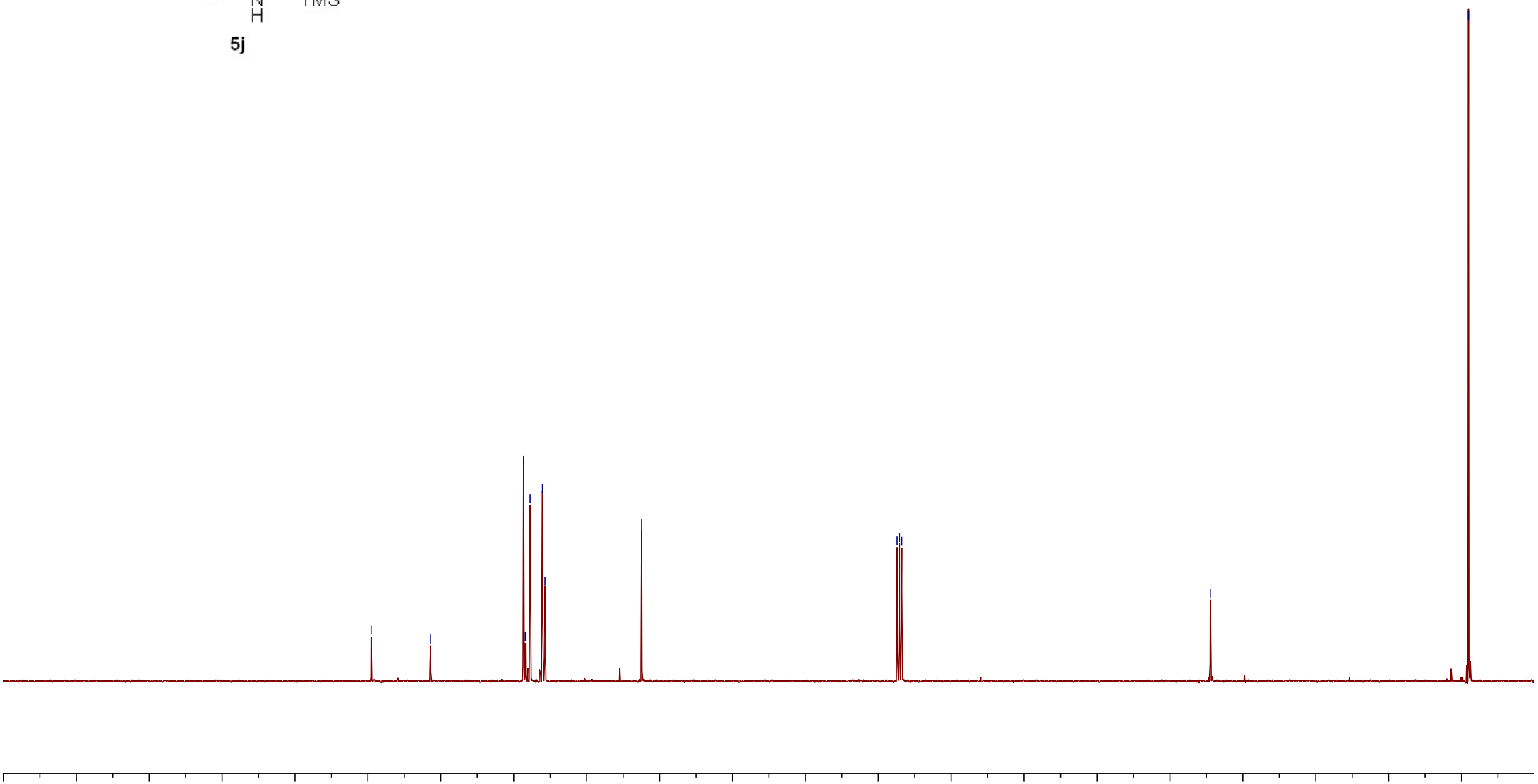


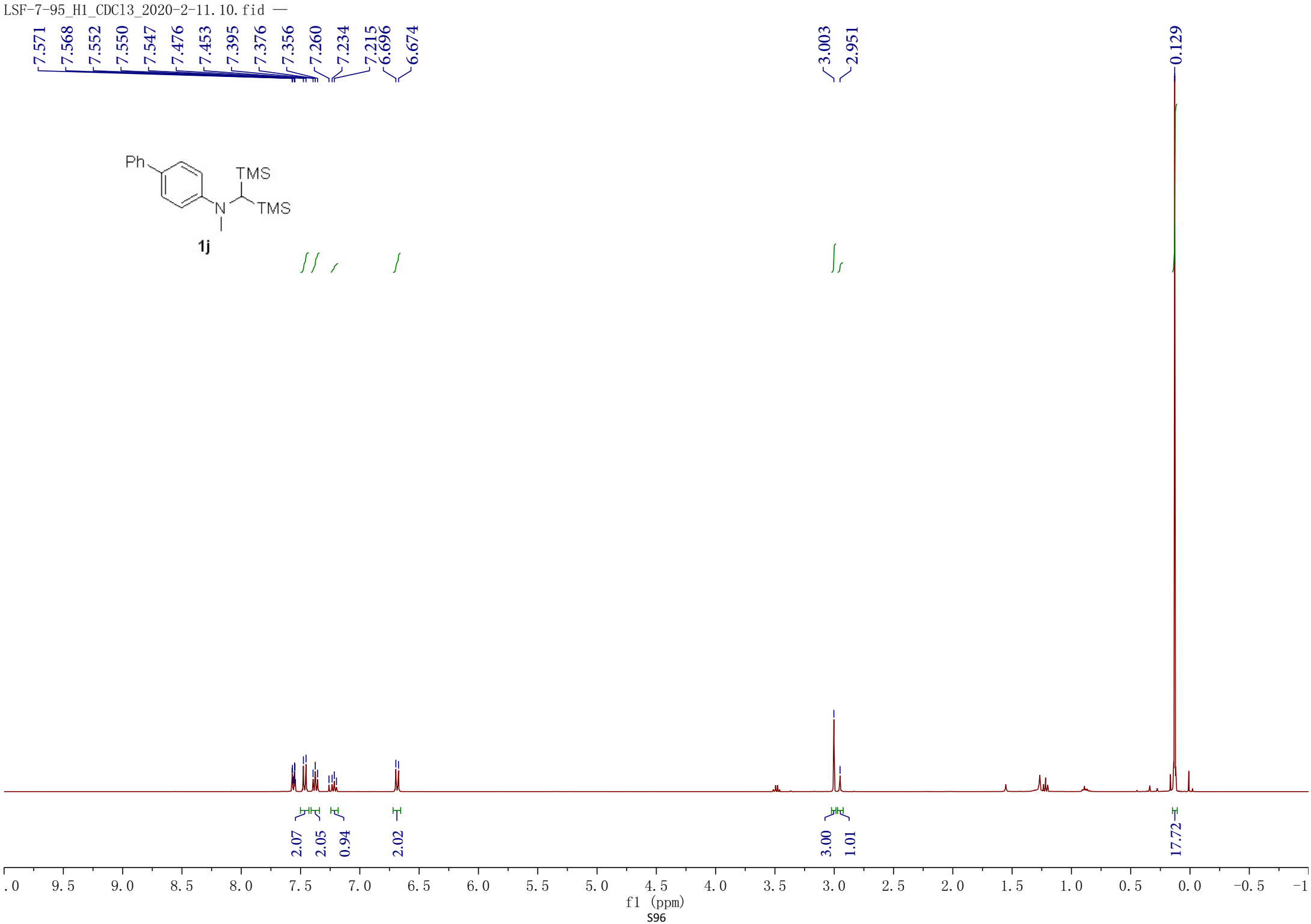
LSF-7-16-CDCL3-C13-2019-12-25.10.fid

149.564
141.400
128.641
128.407
127.751
126.056
125.722
112.460
77.417
77.100
76.783
34.458
-0.941



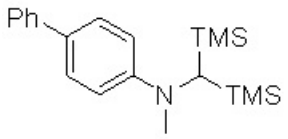
5j




LSF-7-95_H1_CDCl3_2020-2-11.10.fid
7.571
7.568
7.552
7.550
7.547
7.476
7.453
7.395
7.376
7.356
7.260
7.234
7.215
6.696
6.674
3.003
2.951
0.129
Ph
TMS
TMS
N
1j
2.07
2.05
0.94
2.02
3.00
1.01
17.72
f1 (ppm)

LSF-7-95_C13_CDCl3_2020-2-11.10.fid

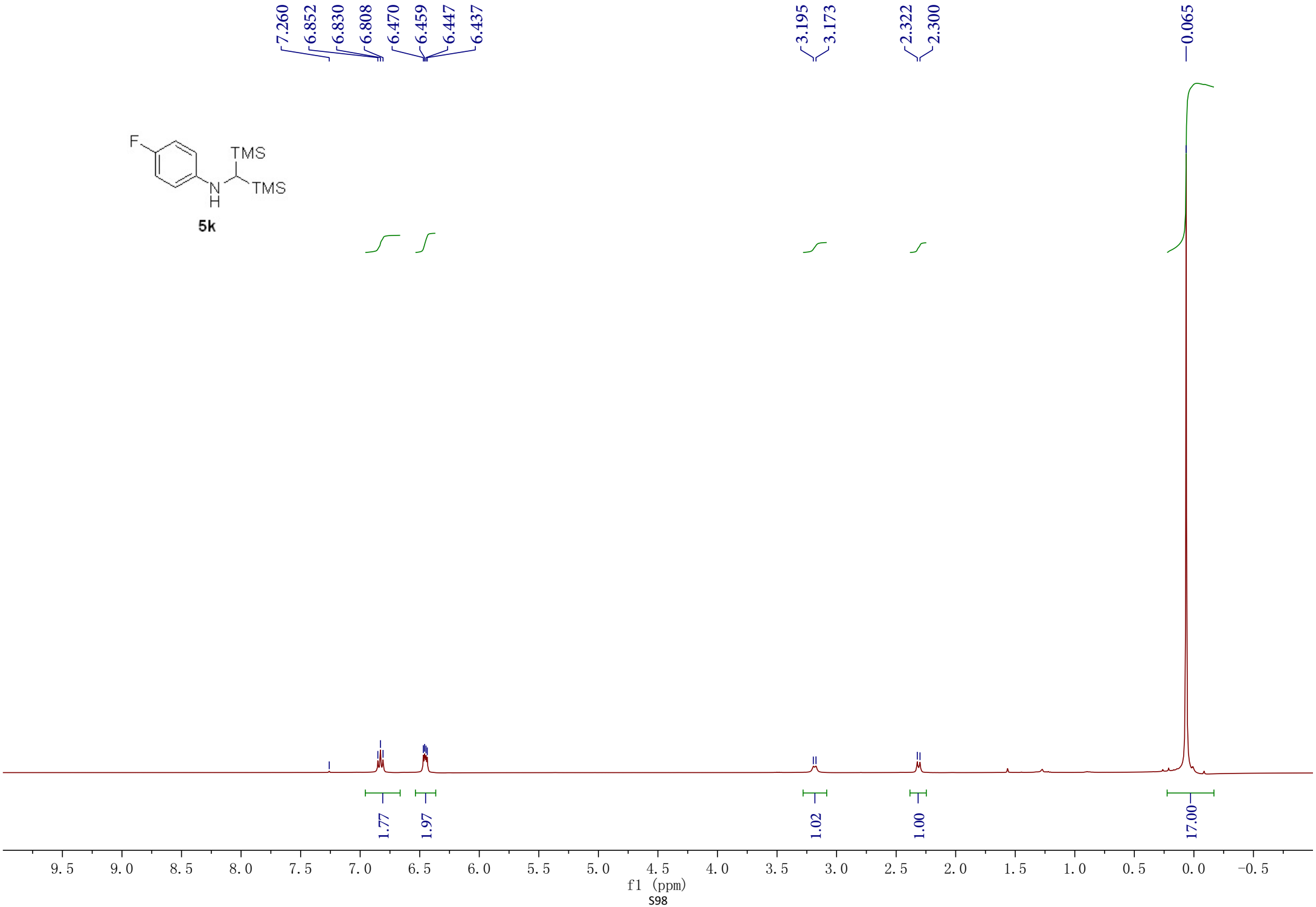
150.085
141.346
128.648
127.565
126.630
125.979
125.578
111.305
77.417
77.100
76.783
43.748
39.074
0.619



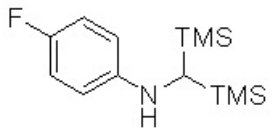
1j

f1 (ppm)

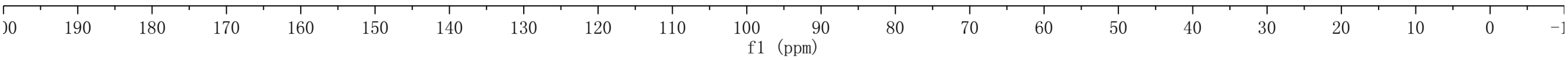
LSF-6-116-CDCL3-H1-2019-12-11 — LSF-6-116-CDCL3-H1-2019-12-11 —



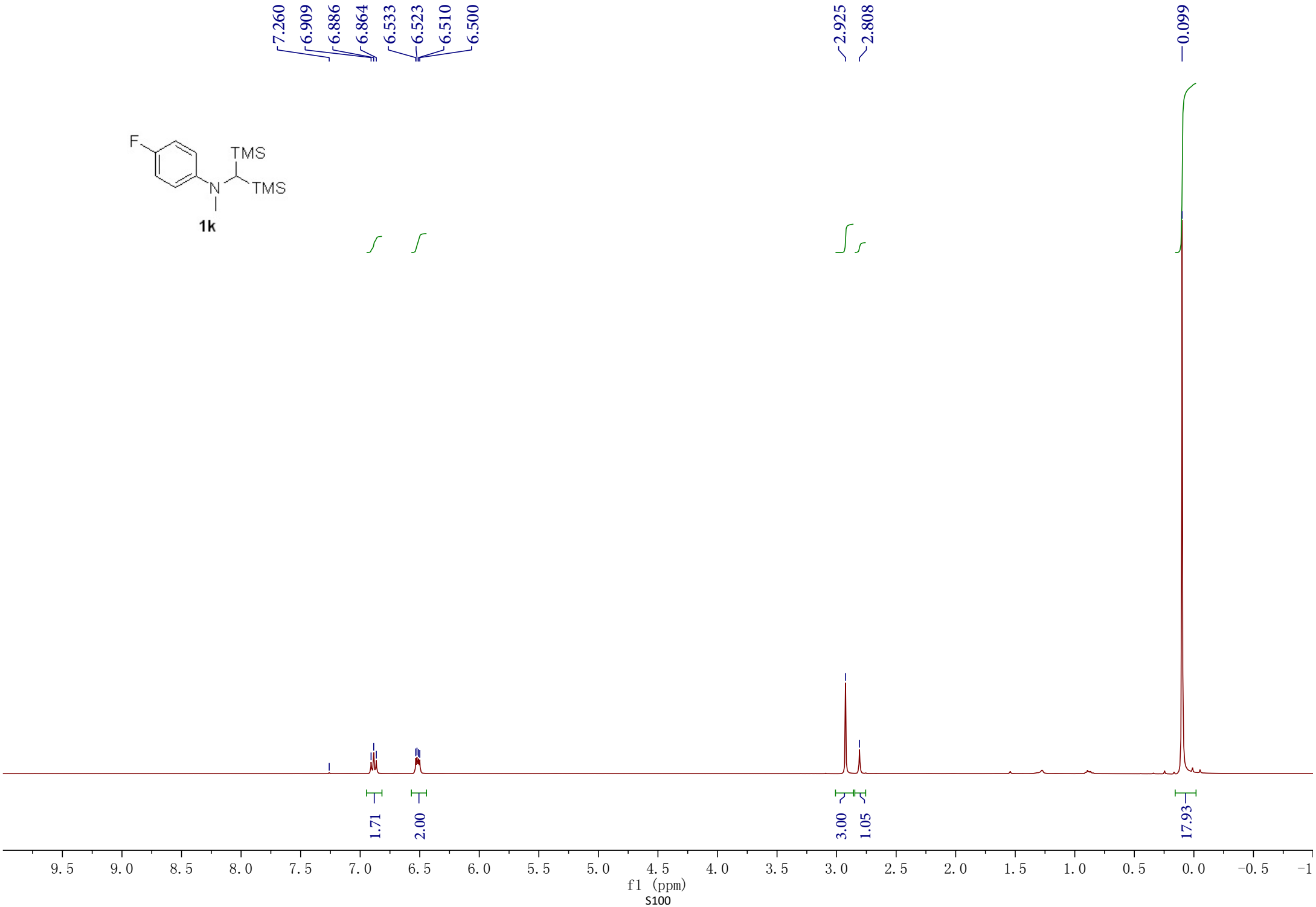
155.549
154.003
146.719
115.551
115.404
112.769
112.721
77.311
77.100
76.887
35.213
-0.970



5k

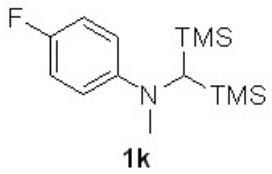


LSF-7-41_H1_CDCl3_2020-1-2.20.fid

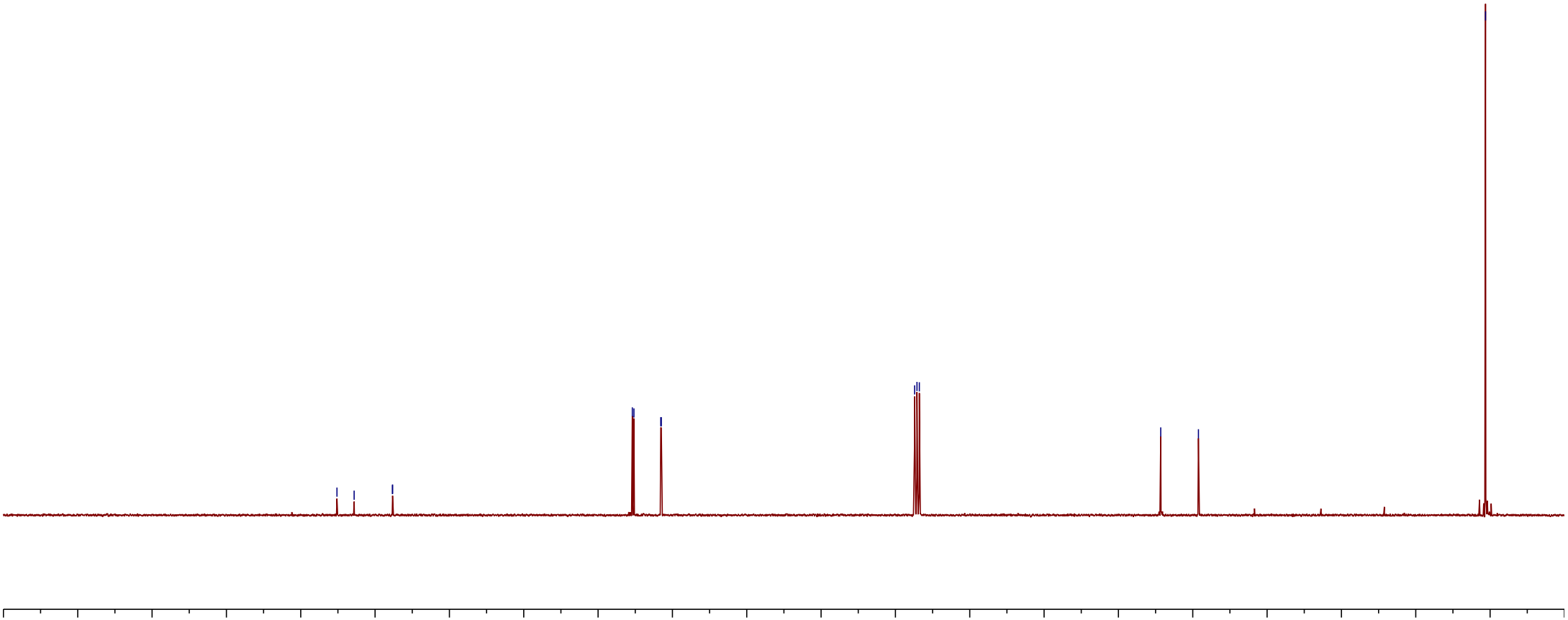


LSF-7-41-CDCL3-C13-2020-1-6.10.fid

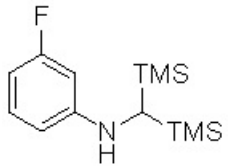
155.127
152.817
147.661
147.648
115.393
115.176
111.567
111.496
77.417
77.100
76.782
44.308
39.236
0.614



1k



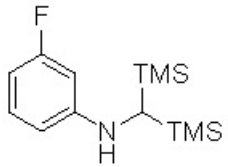
LSF-5-56_H1_CDCl3_2020-2-10.10.fid



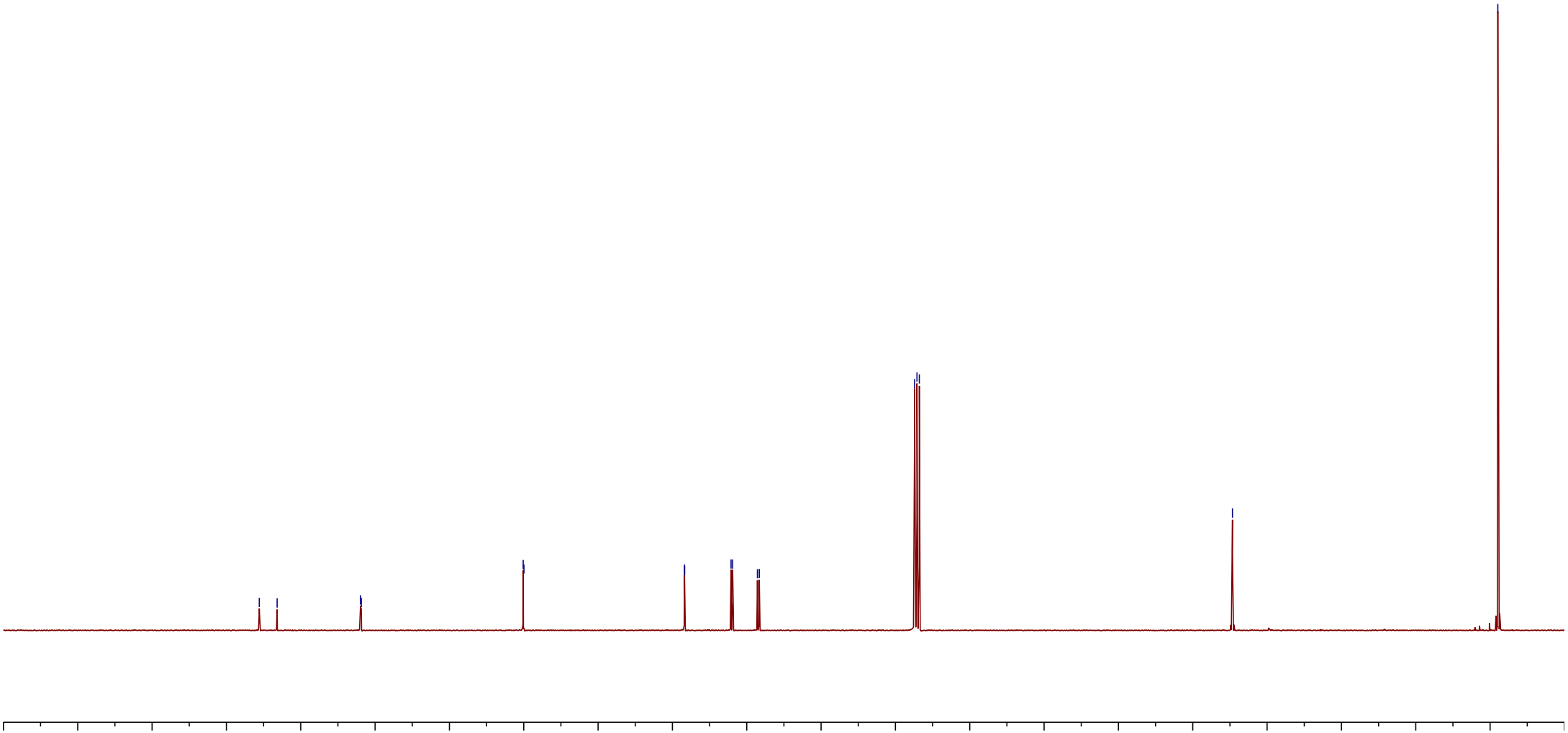
5l

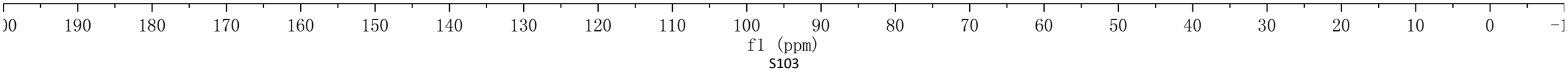
LSF-5-56_C13_CDCl3_2020-2-10.10.fid

165.579
163.177
151.965
151.857
130.075
129.970
108.374
108.354
102.111
101.895
98.567
98.312
77.418
77.101
76.783
34.661
-1.041

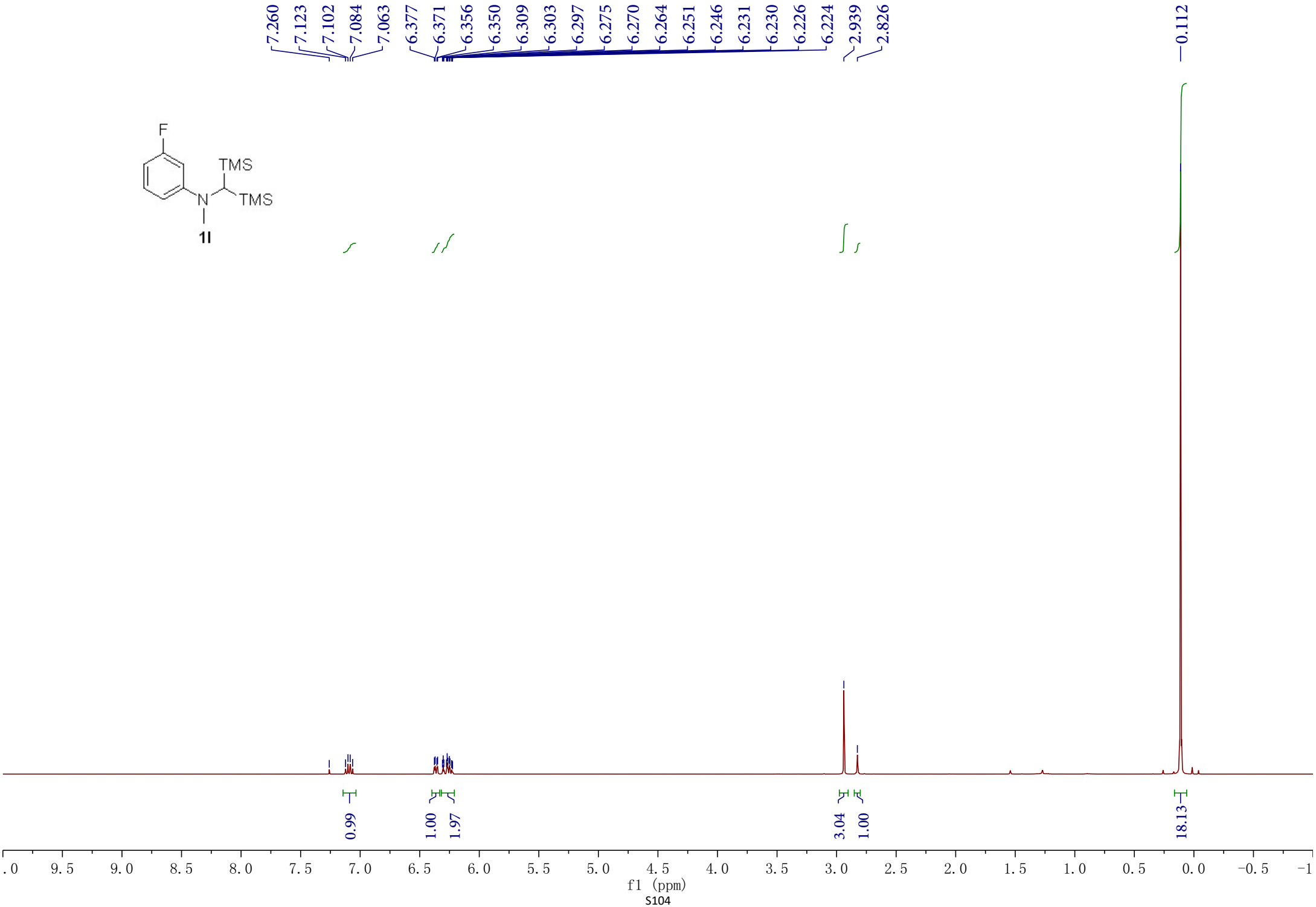


5l

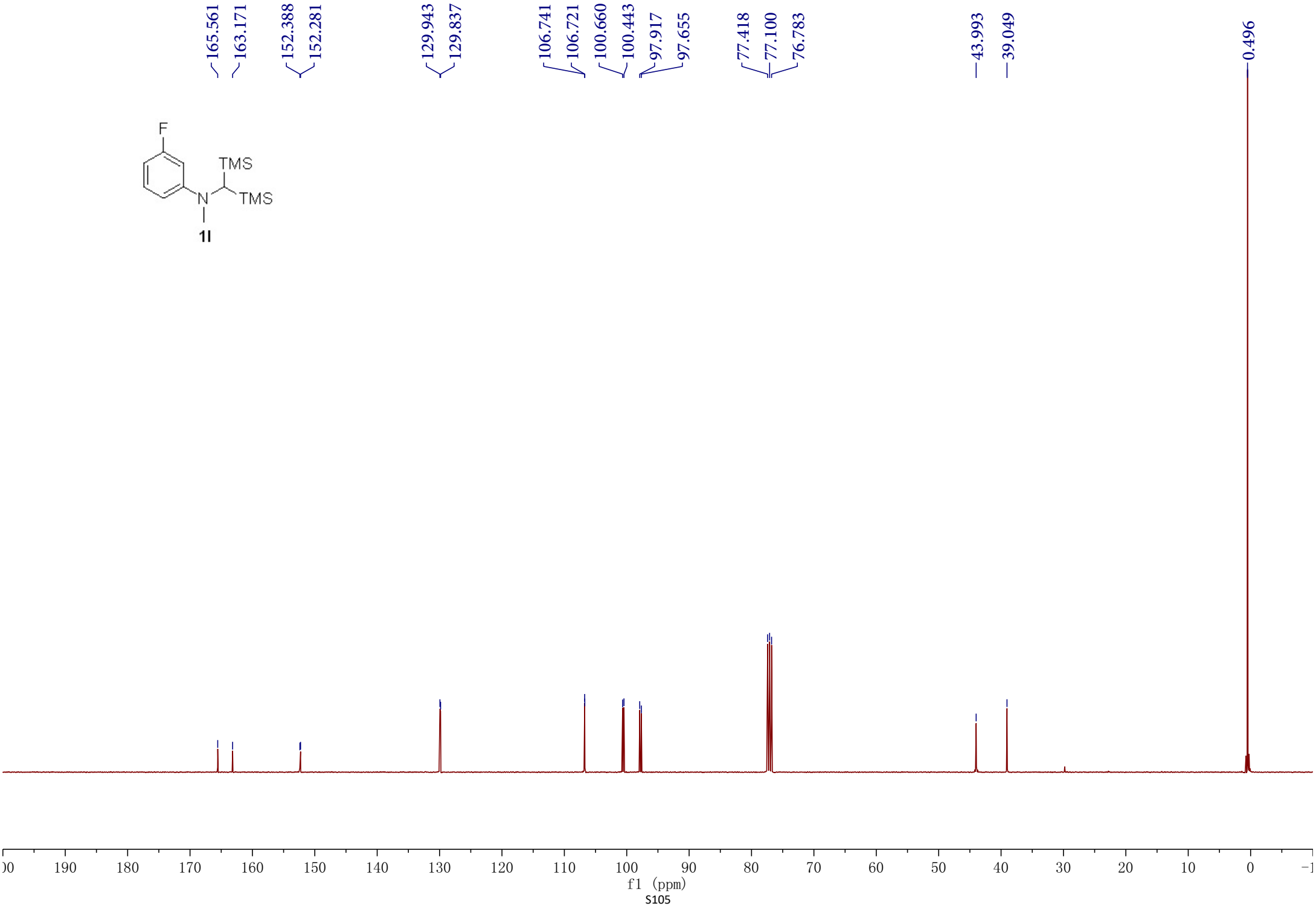




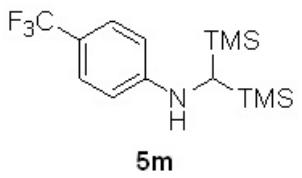
LSF-5-60_H1_CDCl3_2020-2-10.10.fid



LSF-5-60_C13_CDCl3_2020-2-10.10.fid



LSF-6-117-CDCL3-H1-2019-12-11 — LSF-6-117-CDCL3-H1-2019-12-11 —

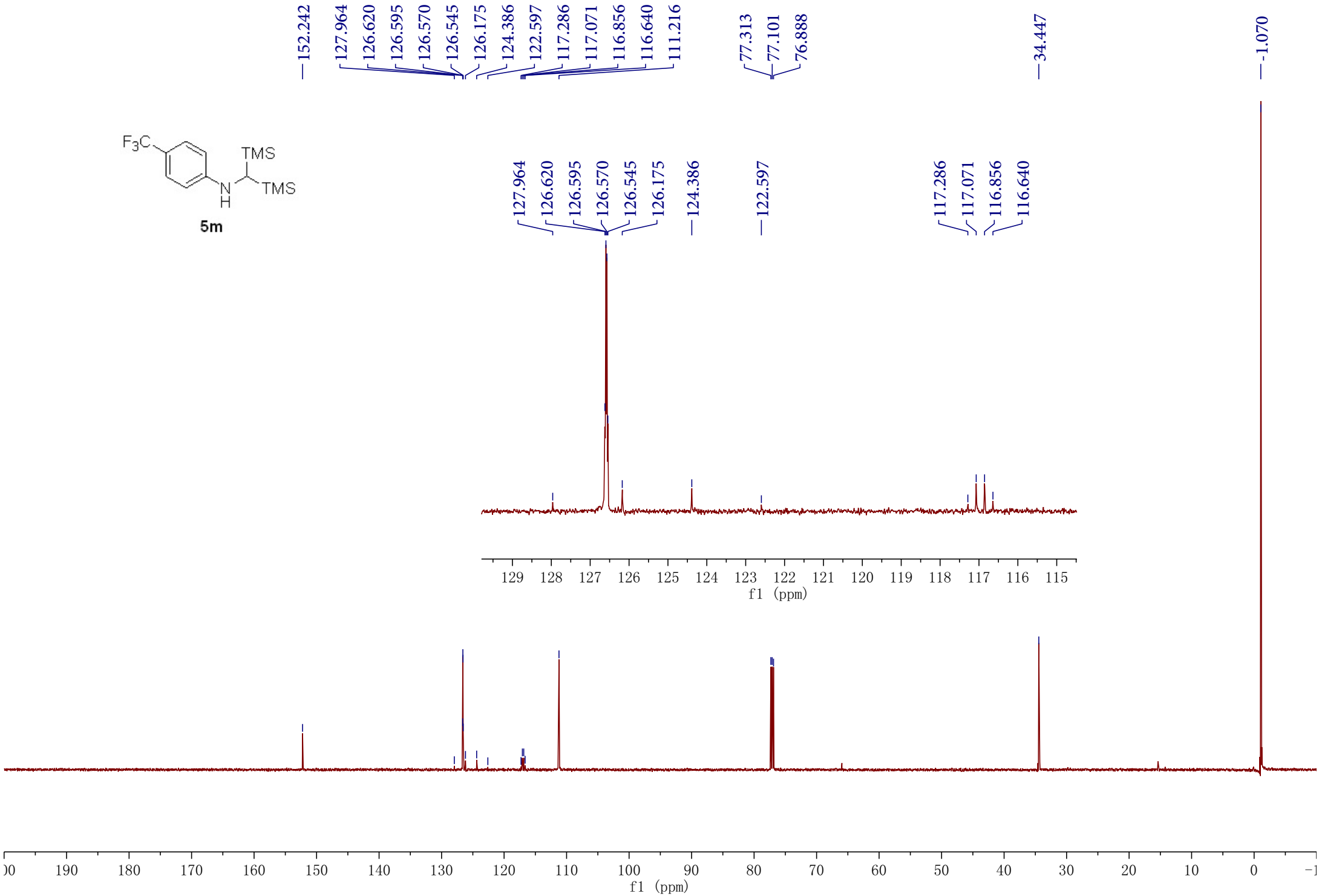


5m

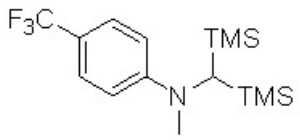
7.342
7.321
7.260
6.532
6.510
3.691
3.665
2.472
2.447
0.078

1.74
2.02
0.98
1.00

f1 (ppm)


152.242
127.964
126.620
126.595
126.570
126.545
126.175
124.386
122.597
117.286
117.071
116.856
116.640
111.216
77.313
77.101
76.888
34.447
-1.070
F3C
TMS
TMS
N
H
5m
f1 (ppm)
f1 (ppm)

LSF-7-92-CDCL3-H1-2020-2-28.10.fid



1m

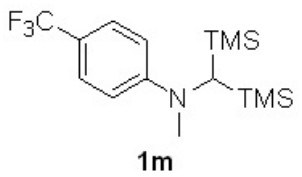
7.392
7.370
7.260
6.607
6.585
2.981
2.923
0.111

2.01
2.12
3.00
1.04
17.85

f1 (ppm)

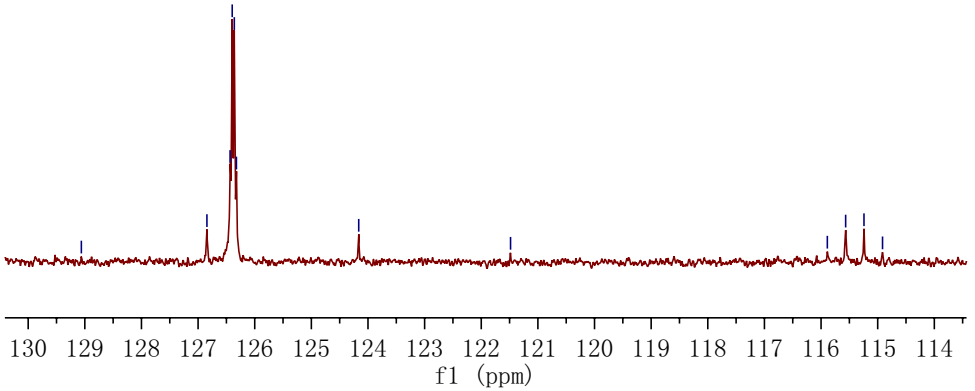
LSF-7-92-CDCL3-C13-2020-2-28.10.fid

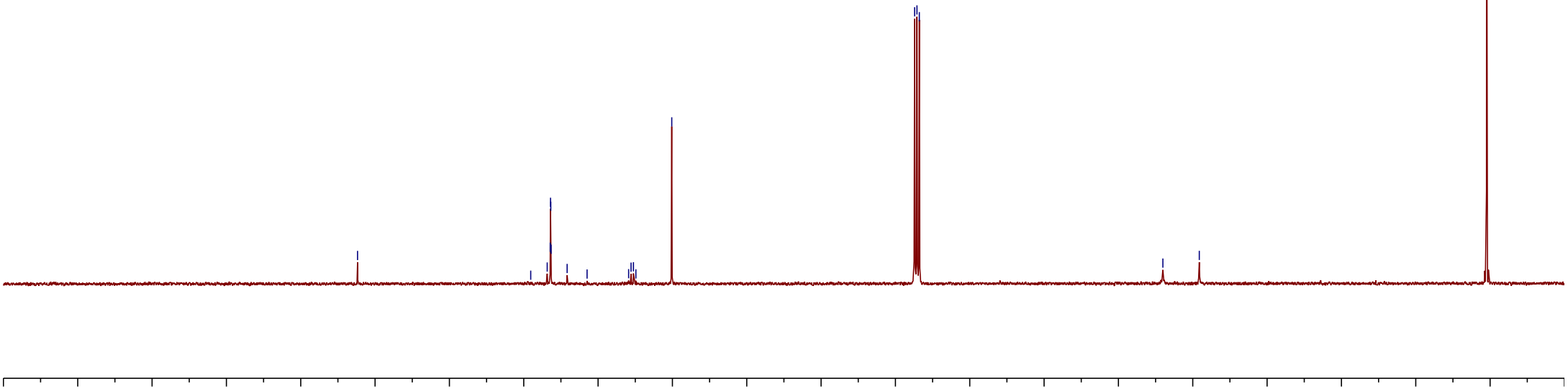
152.358 129.061 126.844 126.435 126.397 126.361 126.323 124.164 121.483 115.889 115.566 115.242 114.914 110.087 77.417 77.101 76.783 44.019 39.120 0.470



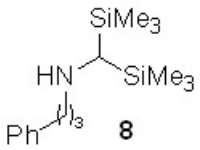
1m

129.061 126.844 126.435 126.397 126.361 126.323 124.164 121.483 115.889 115.566 115.242 114.914





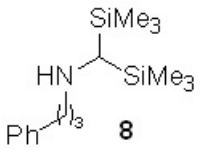
LSF-8-58-CDCL3-H1-2020-5-9.10.fid —



8

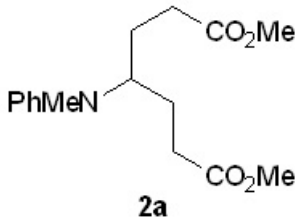
f1 (ppm)

139.627
128.830
128.485
126.621
77.313
77.101
76.889
51.448
41.535
32.705
27.417
-0.115



8

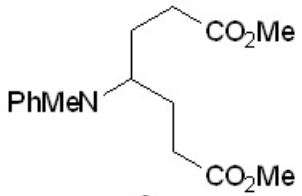
LSF-6-9P-CDCL3-H1-2019-10-28.20.fid



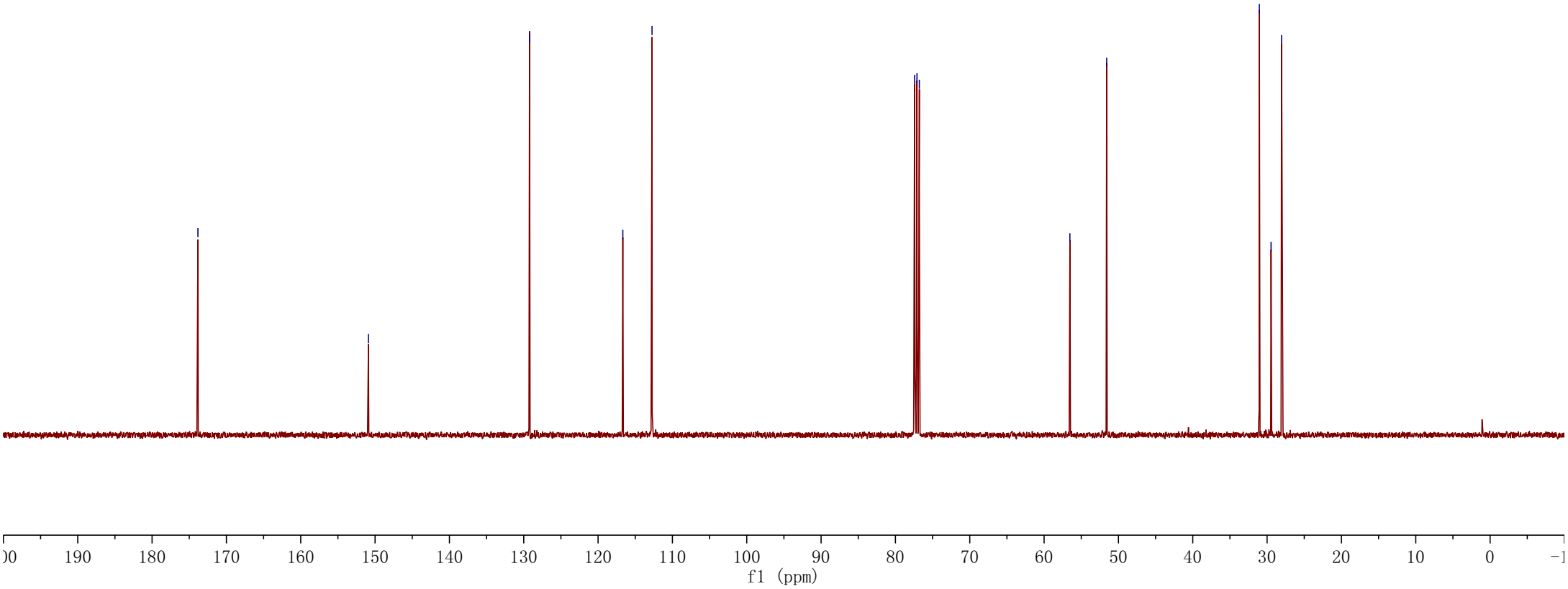
2a

LSF-6-9P-CDCL3-C13-2019-10-28.20.fid

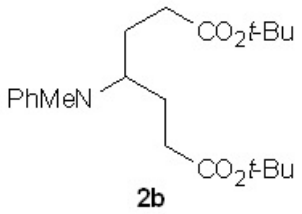
173.832
150.893
129.220
116.672
112.743
77.417
77.100
76.783
56.529
51.578
31.044
29.466
28.054



2a



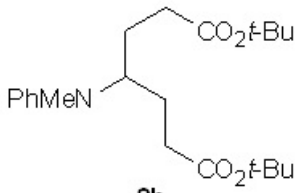
LSF-6-98BP_H1_CDCl3_2019-12-4.10.fid



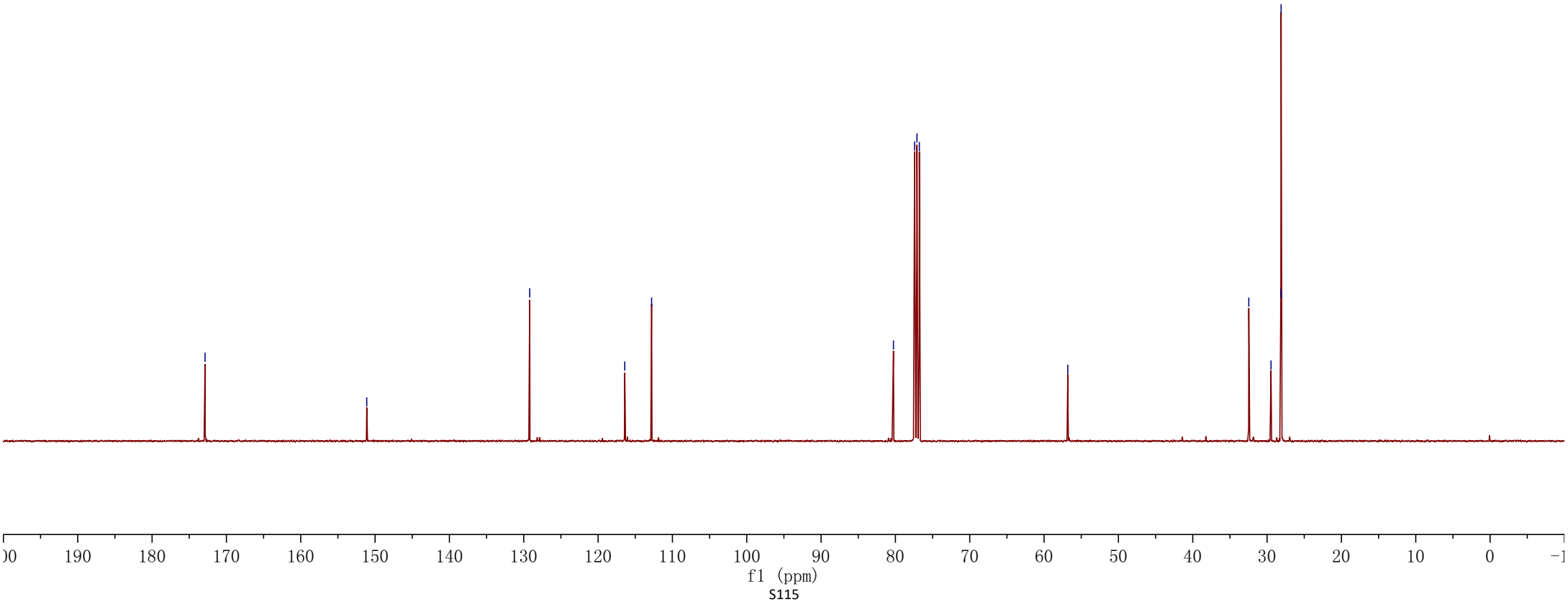
2b

LSF-6-98BP_C13_CDCl3_2019-12-4.10.fid

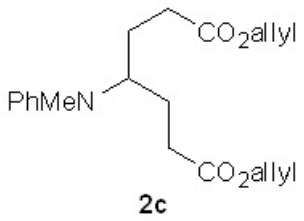
172.871
151.120
129.201
116.410
112.801
80.263
77.419
77.100
76.783
56.810
32.462
29.474
28.154
28.116



2b



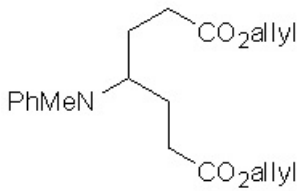
LSF-6-34P-CDCL3-H1-2019-11-1.60.fid —



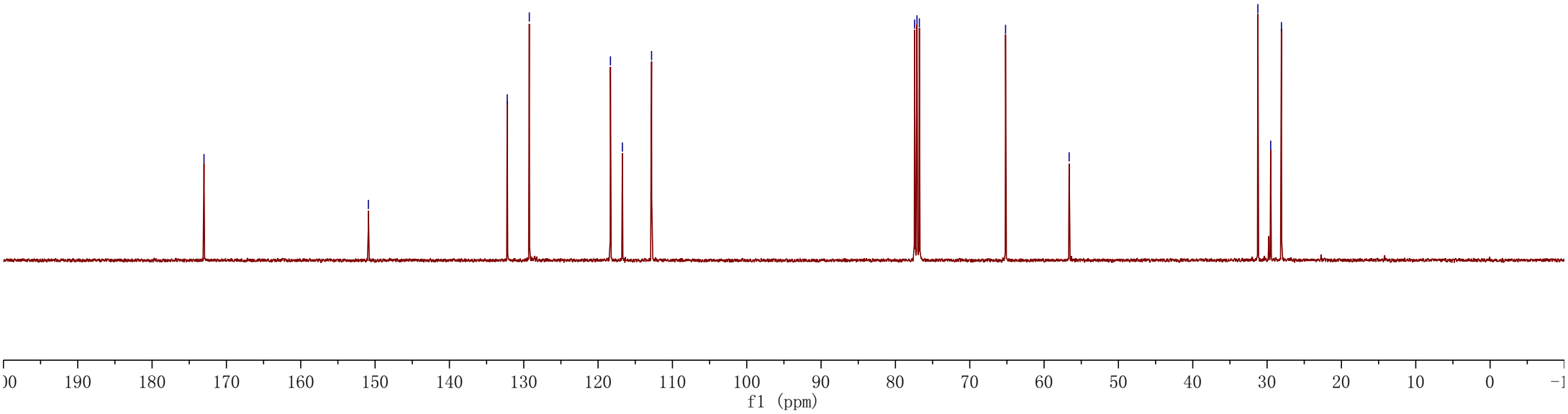
2c

LSF-6-34P-CDCL3-C13-2019-11-1.60.fid

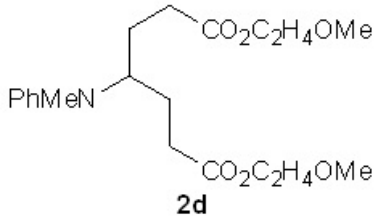
173.014
150.902
132.225
129.252
118.336
116.727
112.805
77.418
77.100
76.783
65.183
56.629
31.241
29.518
28.072



2c



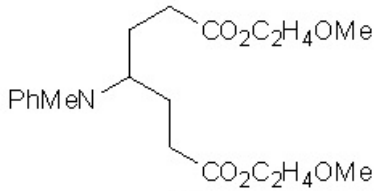
LSF-6-61P-CDCL3-H1-2019-11-15.10.fid



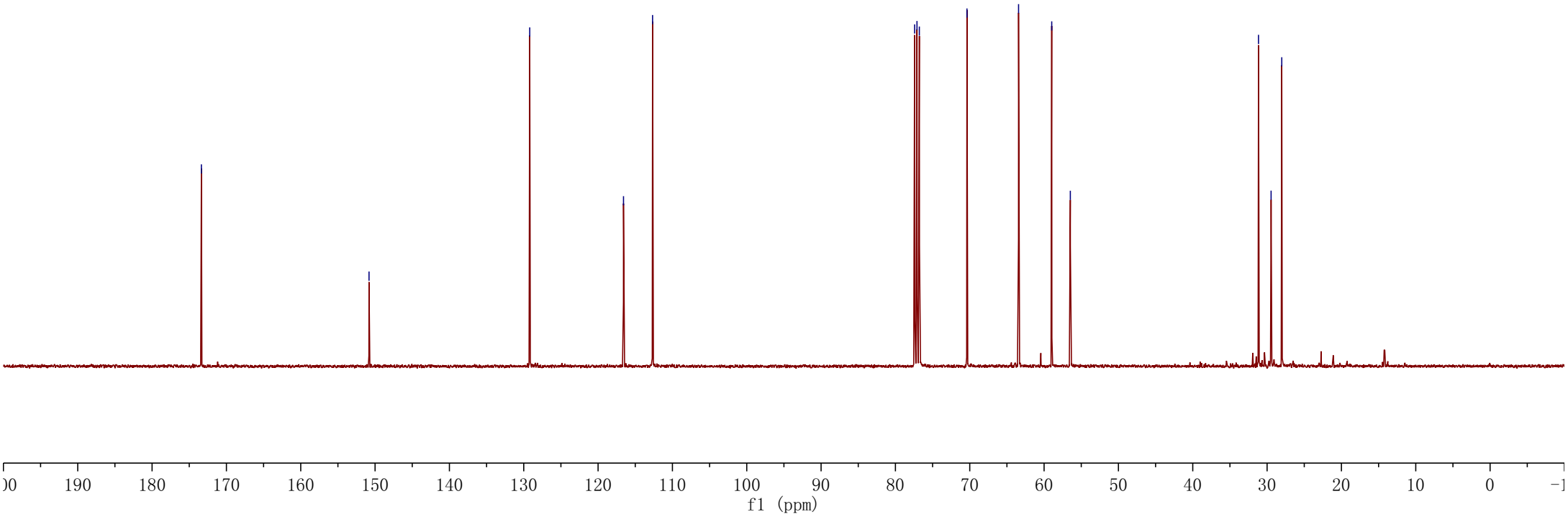
2d

LSF-6-61P_C13_CDCl3_2019-11-15.10.fid

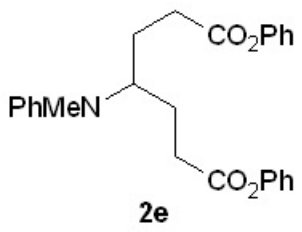
173.366
150.814
129.195
116.580
112.669
77.417
77.100
76.782
70.376
63.434
58.972
56.470
31.155
29.462
28.025



2d



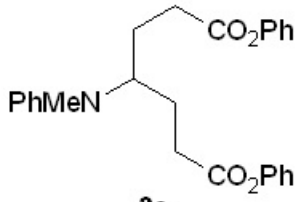
LSF-6-71P_H1_CDCl3_2019-11-22.20.fid —



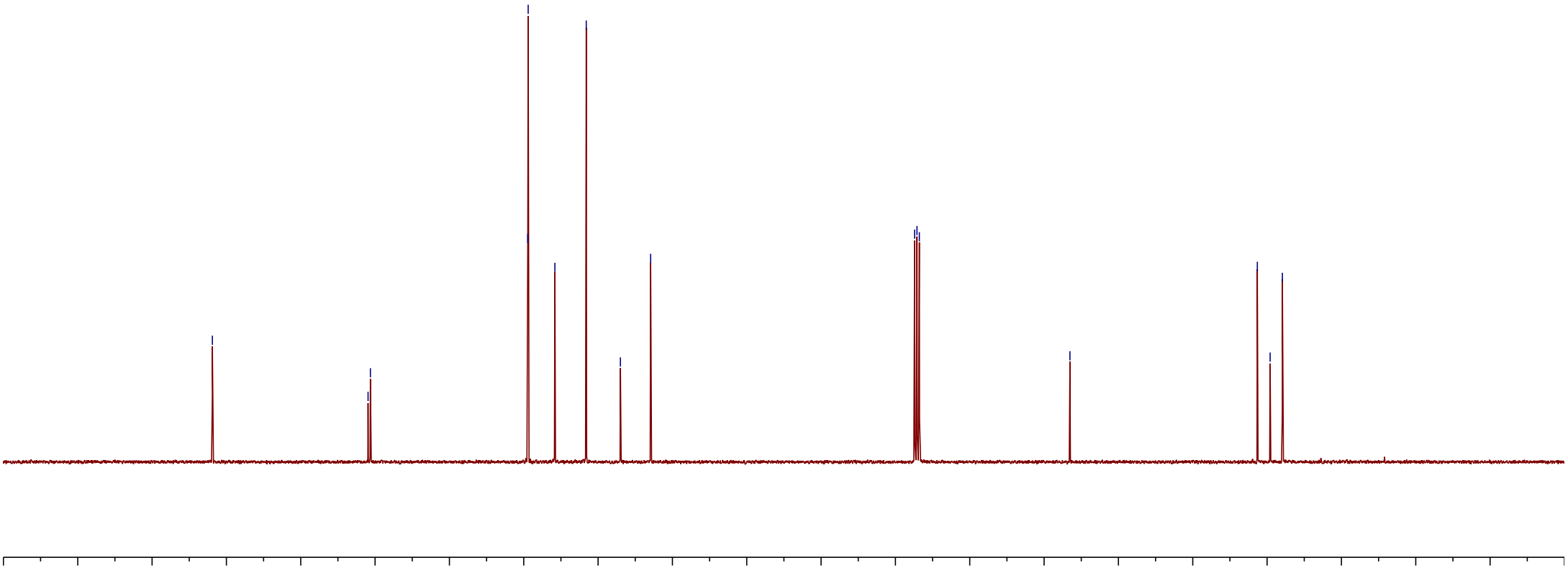
2e

LSF-6-71P_C13_CDCl3_2019-11-22.20.fid

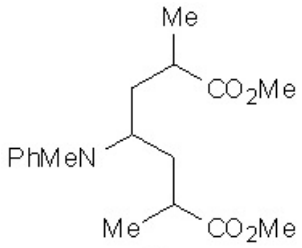
171.887
150.944
150.629
129.459
129.404
125.811
121.590
116.995
112.927
77.417
77.099
76.782
56.524
31.314
29.591
27.943



2e

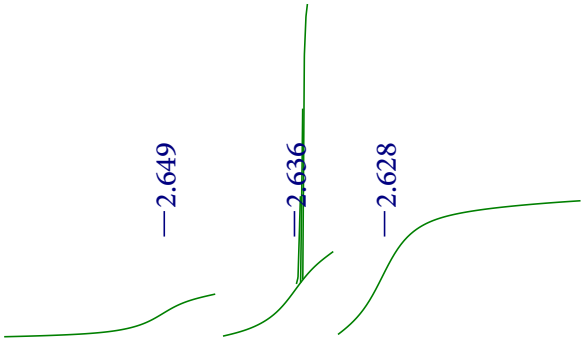


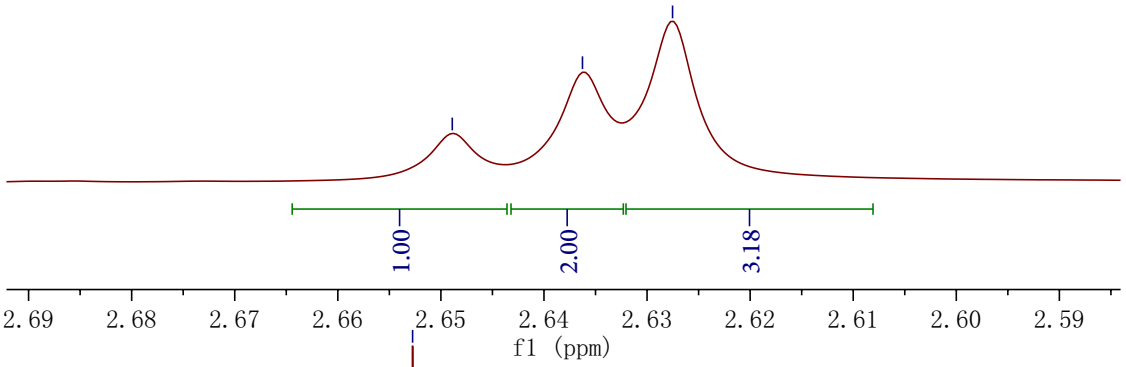
LSF-7-97-CDCL3-H1-2020-2-9.10.fid

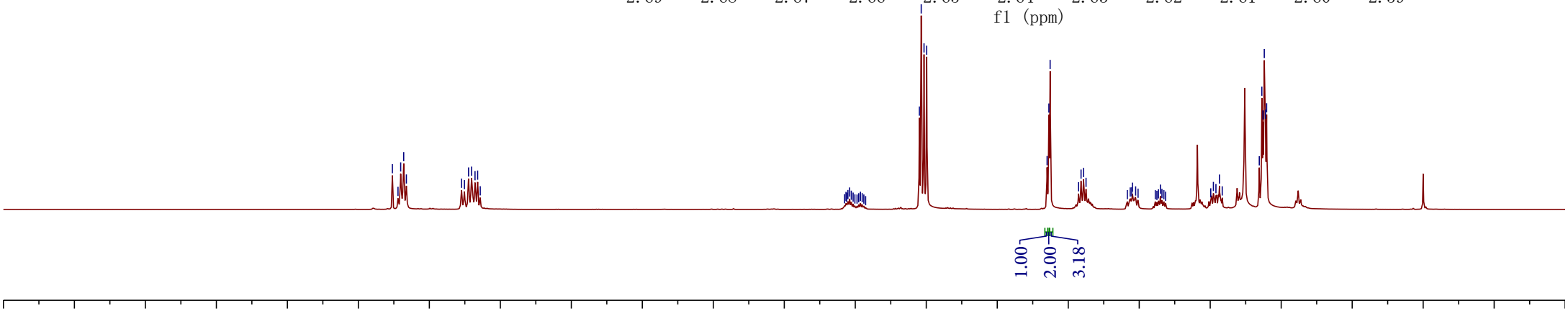


2f

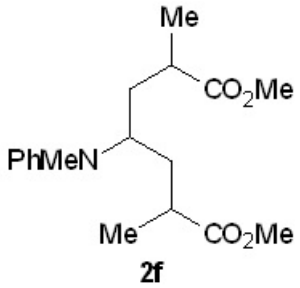
(*dr* = 3.2:2:1)





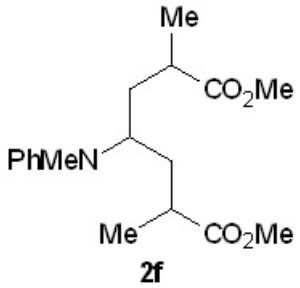


LSF-6-56BP-CDCL3-H1-2019-11-14.10.fid



2f

LSF-6-56BP-CDCL3-C13-2019-11-14.10.fid



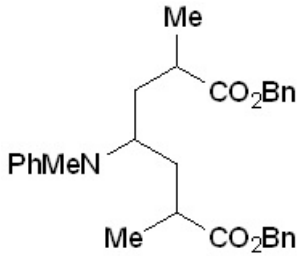
2f

176.875
150.392
129.198
116.701
112.845
77.418
77.100
76.782
53.728
51.581
36.812
36.771
29.797
17.392

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)

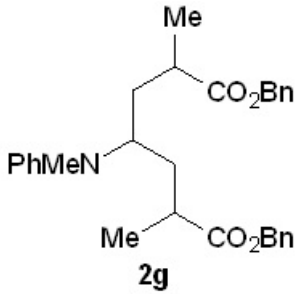
LSF-7-102_H1_CDCl3_2020-2-14.10.fid



2g

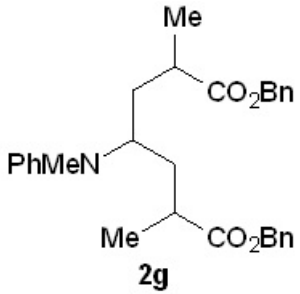
(*dr* = 5.5:1)

LSF-6-69AP_H1_CDCl3_2019-11-22.10.fid



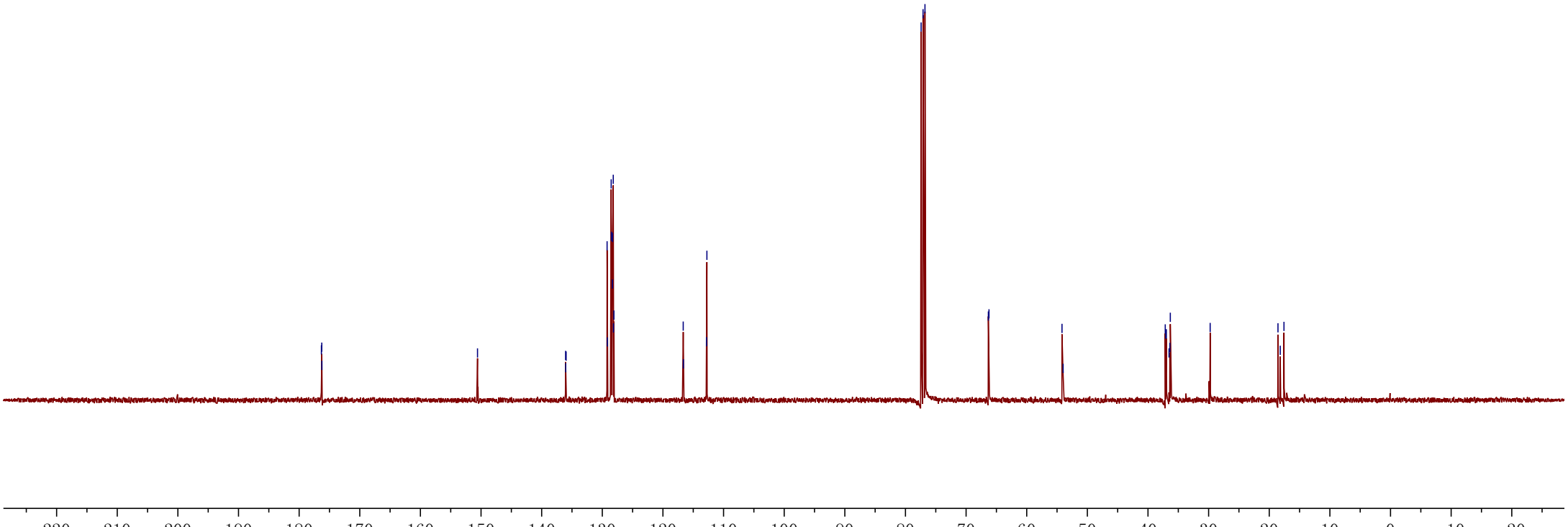
2g

LSF-6-69AP_C13_CDCl3_2019-11-22.10.fid



2g

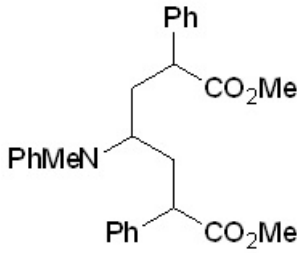
176.330 176.265 176.251 150.582 136.053 136.034 135.967 129.210 129.154 128.534 128.495 128.333 128.306 128.192 128.157 128.082 116.654 116.627 112.817 112.748 77.417 77.100 76.782 66.328 66.223 54.181 37.154 37.071 36.973 36.530 36.396 36.318 29.745 18.561 18.186



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

f1 (ppm)

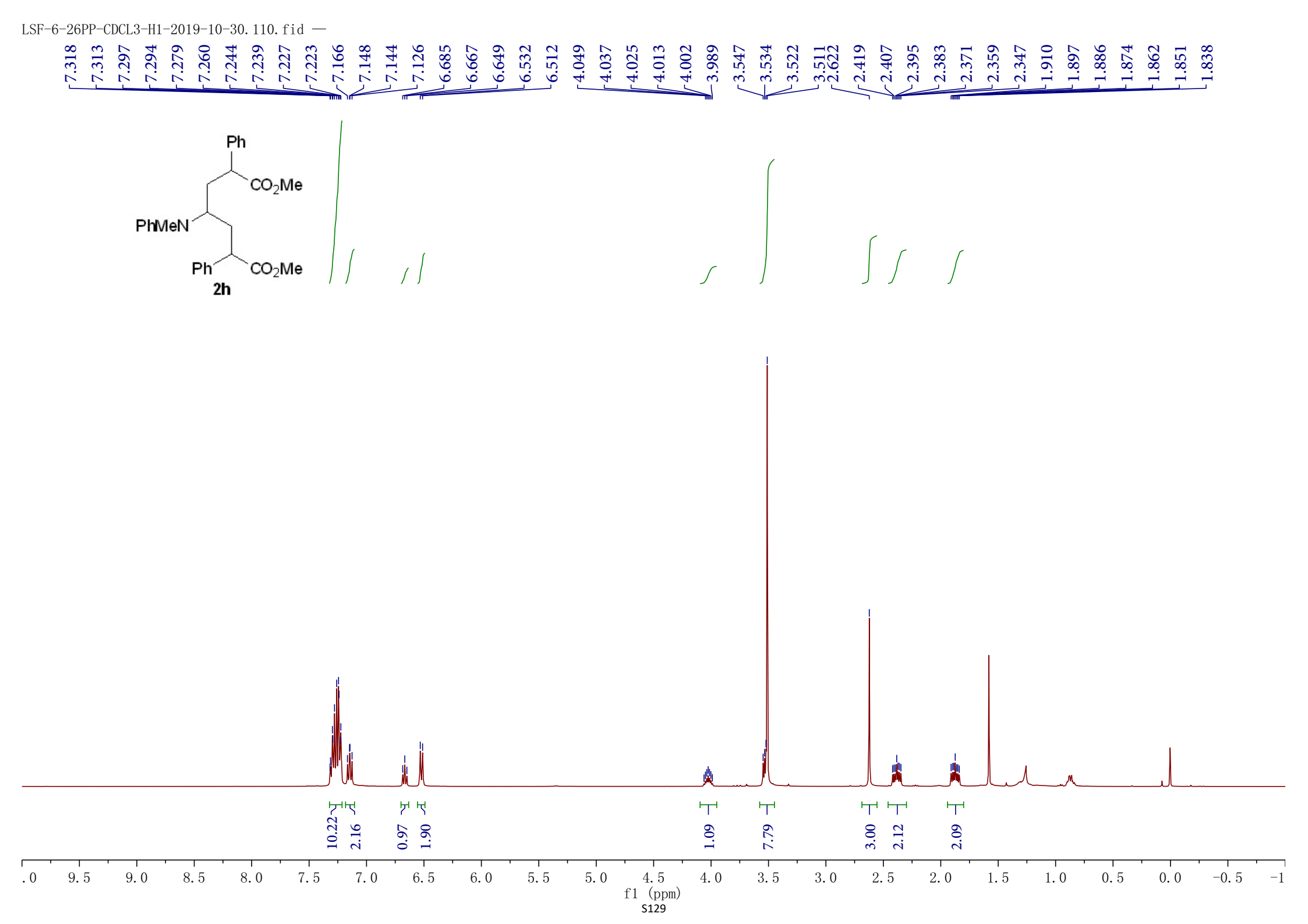
LSF-8-6_H1_CDCl3_2020-2-25.10.fid



2h

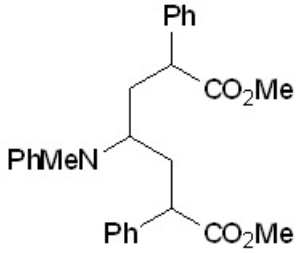
(*dr* = 1.9:1:1)

LSF-6-26PP-CDCL3-H1-2019-10-30.110.fid —

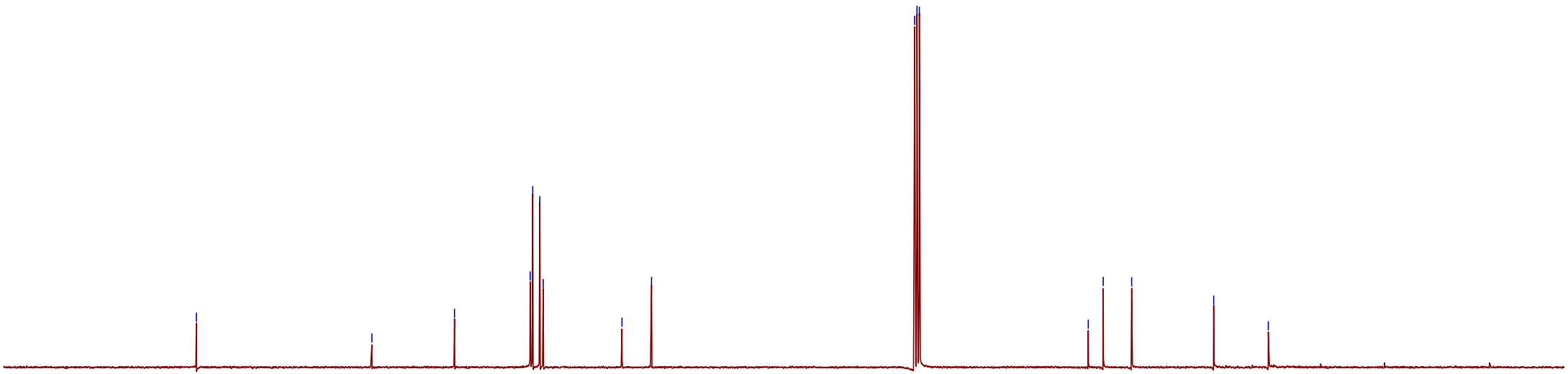


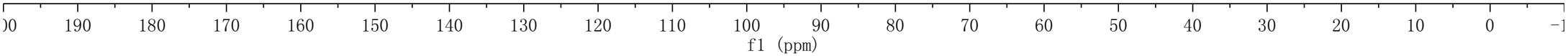
LSF-6-26PP_C13_CDCl3_2019-10-31.10.fid

174.044
150.432
139.312
129.136
128.790
127.841
127.380
116.787
112.809
77.417
77.100
76.782
54.060
52.046
48.219
37.182
29.835

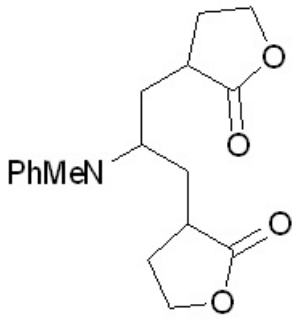


2h



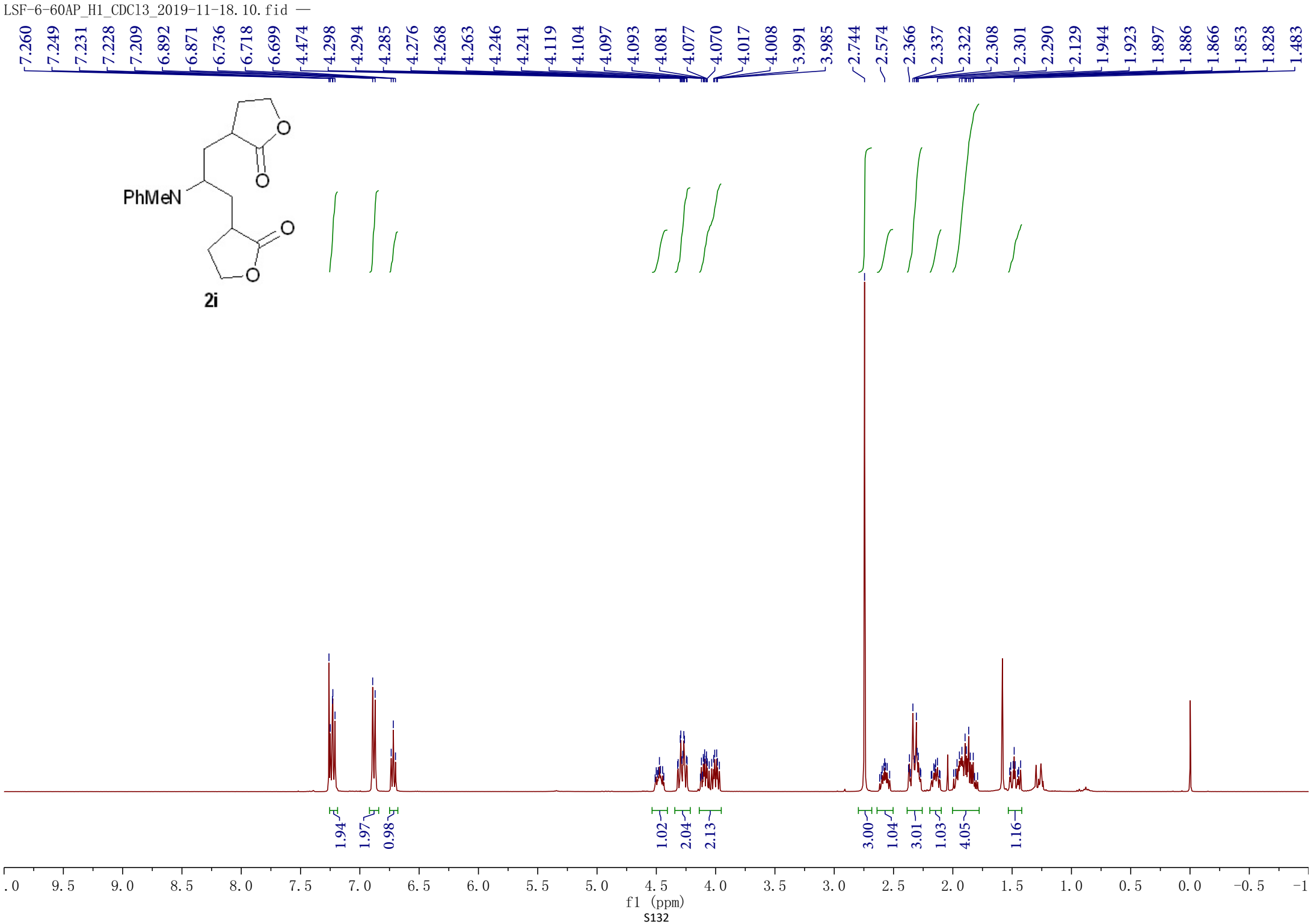


LSF-7-104_H1_CDCl3_2020-2-14.30.fid

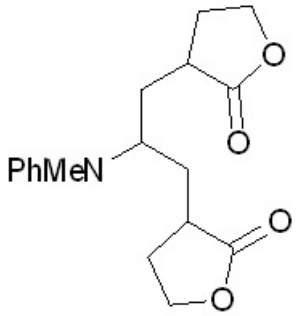


2i

(*dr* = 2.5:1.4:1)


LSF-6-60AP_H1_CDCl3_2019-11-18.10.fid
7.260
7.249
7.231
7.228
7.209
6.892
6.871
6.736
6.718
6.699
4.474
4.298
4.294
4.285
4.276
4.268
4.263
4.246
4.241
4.119
4.104
4.097
4.093
4.081
4.077
4.070
4.017
4.008
3.991
3.985
2.744
2.574
2.366
2.337
2.322
2.308
2.301
2.290
2.129
1.944
1.923
1.897
1.886
1.866
1.853
1.828
1.483
PhMeN
O
O
O
O
2i
1.94
1.97
0.98
1.02
2.04
2.13
3.00
1.04
3.01
1.03
4.05
1.16
f1 (ppm)

LSF-6-60AP_C13_CDCl3_2019-11-18.10.fid

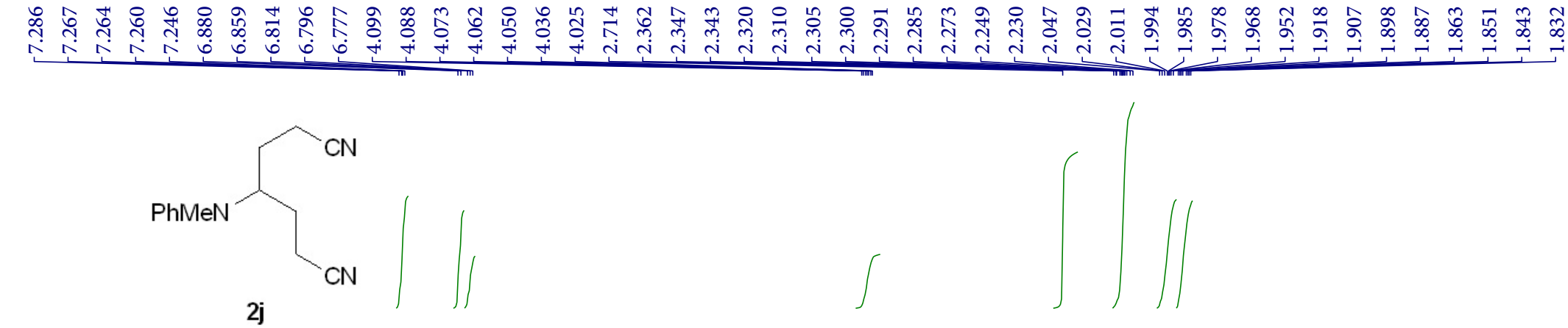


2i

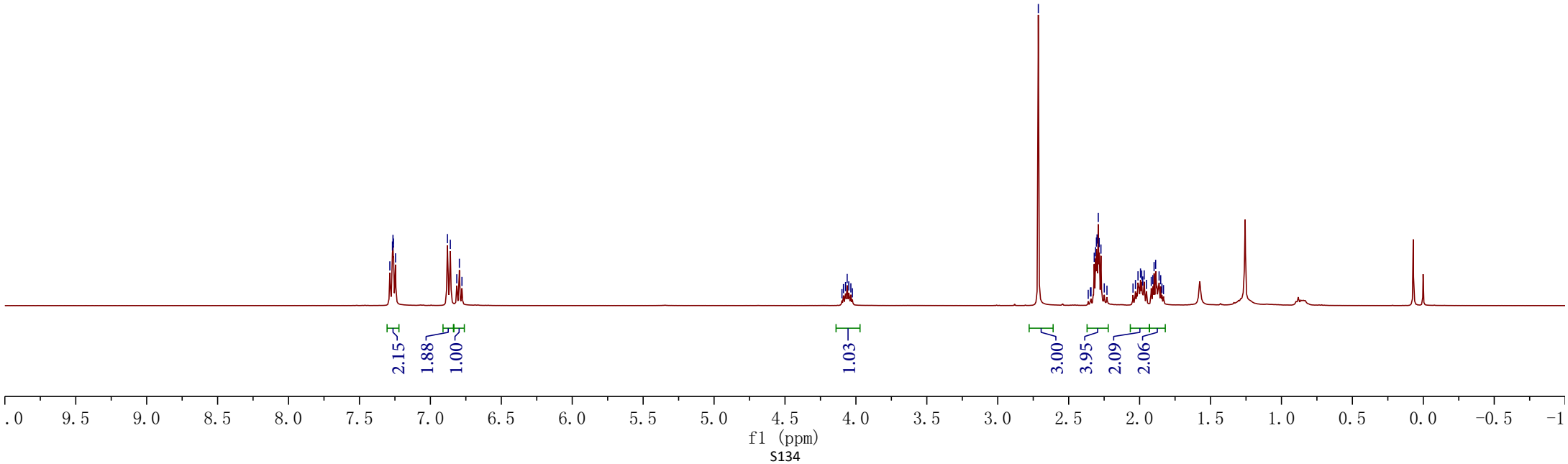
179.669
179.437
150.623
129.654
117.223
112.593
77.417
77.100
76.782
66.549
53.899
36.794
36.150
34.625
34.049
29.841
29.504
29.187

f1 (ppm)

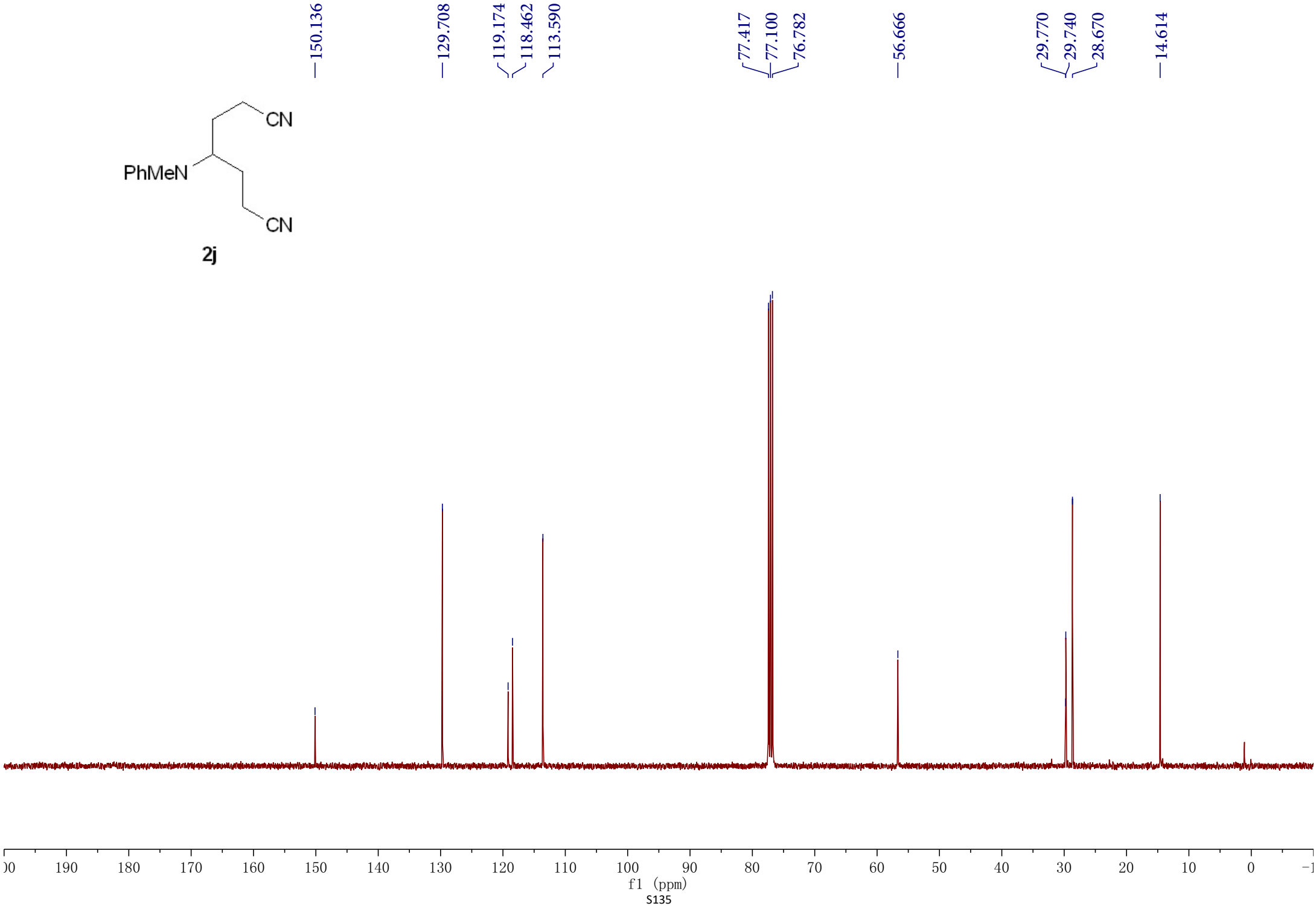
LSF-6-6p-CDCL3-H1-2019-10-16.10.fid



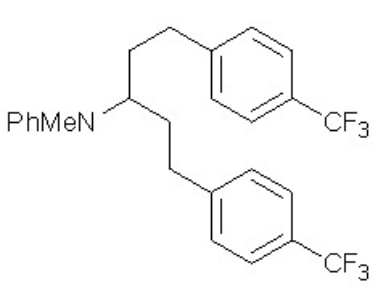
2j



LSF-6-6P-CDCL3-C13-2019-10-16.10.fid

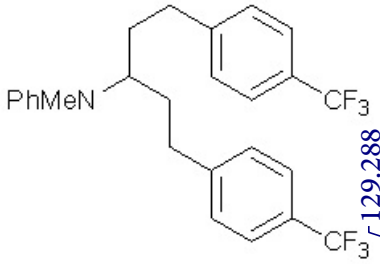


LSF-6-86BP_H1_CDCl3_2019-12-2.10.fid



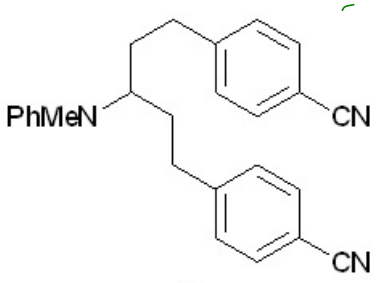
2k

LSF-6-86BP_C13_CDCl3_2019-12-2.10.fid



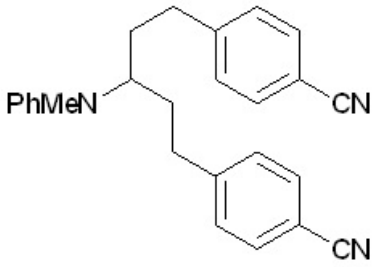
2k

LSF-6-99P_H1_CDCl3_2019-12-6.30.fid



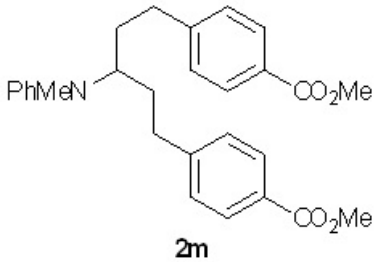
2l

LSF-6-99P_C13_CDCl3_2019-12-6.30.fid



2l

LSF-6-97BP_H1_CDCl3_2019-12-5.10.fid



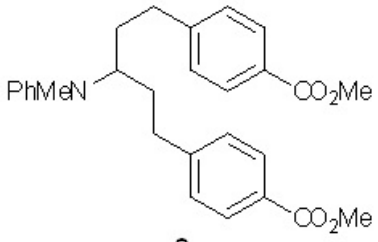
2m

7.913 7.892 7.260 7.220 7.201 7.198 7.180 7.135 7.115 6.719 6.701 6.684 6.664 3.903 3.824 3.812 3.800 2.783 2.663 2.642 2.619 2.605 2.583 2.566 2.549 2.531 1.961 1.948 1.935 1.926 1.911 1.903 1.888 1.863 1.846 1.833 1.827 1.810

3.91 2.00 3.95 2.93 5.94 1.02 3.00 4.01 2.03 2.01

f1 (ppm)

LSF-6-97BP_C13_CDCl3_2019-12-5.10.fid

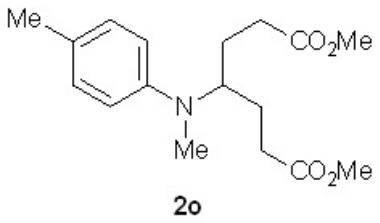


2m

167.168
150.886
147.516
129.758
129.272
128.483
127.916
116.535
112.856
77.418
77.101
76.783
56.752
52.077
34.554
33.078
29.805

f1 (ppm)

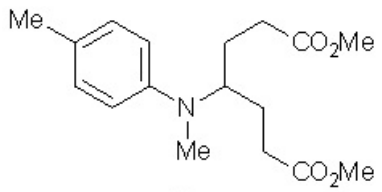
LSF-8-23_H1_CDCl3_2020-3-9.10.fid



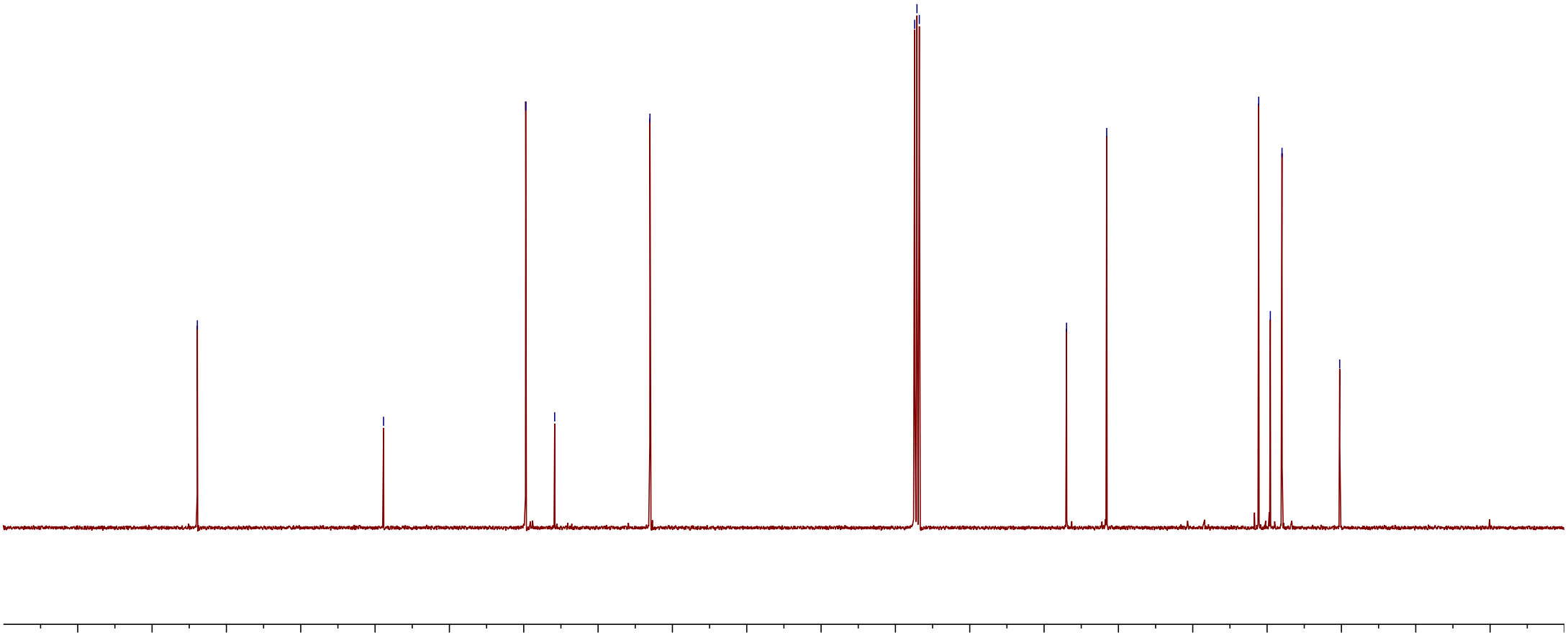
2o

LSF-8-23_C13_CDCl3_2020-3-9.10.fid

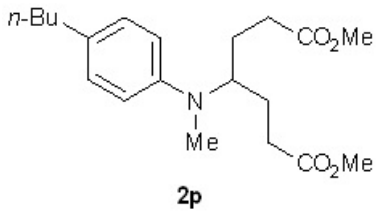
173.909
148.860
129.736
125.838
113.023
77.418
77.100
76.782
56.979
51.576
31.127
29.564
27.991
20.233



2o



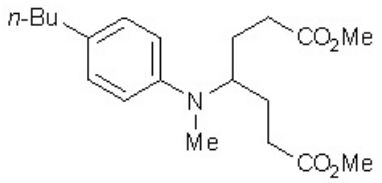
LSF-7-112-CDCL3-H1-2020-2-20.10.fid



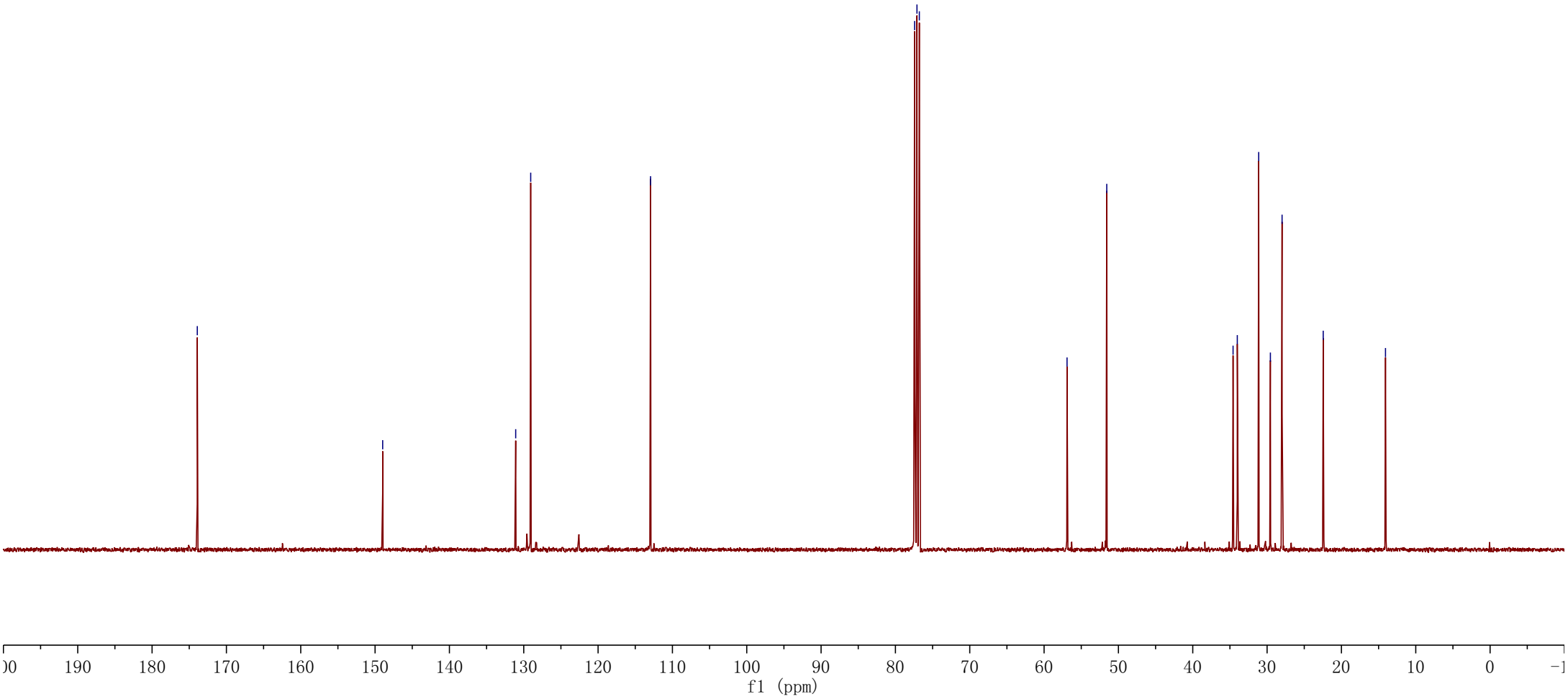
2p

LSF-7-112-CDCL3-C13-2020-2-20.10.fid

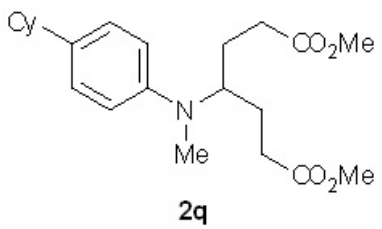
173.917
148.978
131.084
129.064
112.938
77.418
77.101
76.783
56.912
51.569
34.578
34.008
31.129
29.557
27.984
22.450
14.072



2p



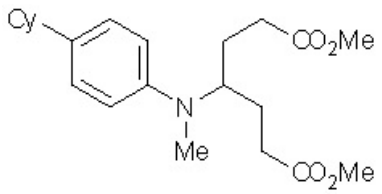
LSF-7-82P_H1_CDCl3_2020-1-21.10.fid



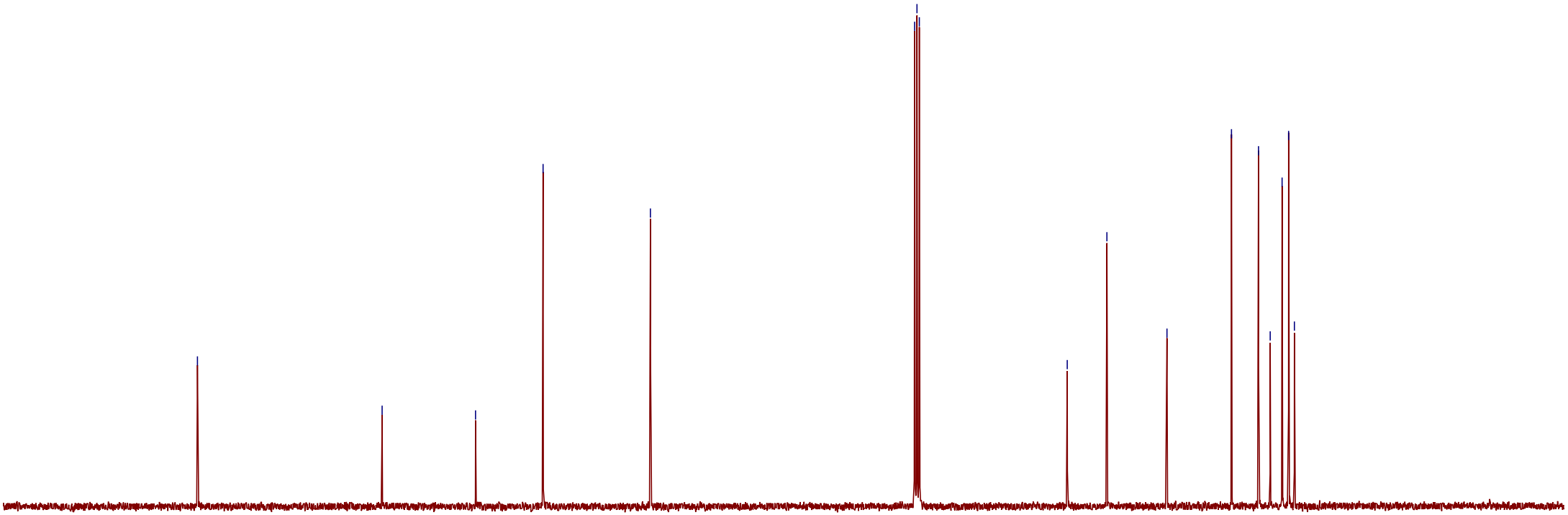
2q

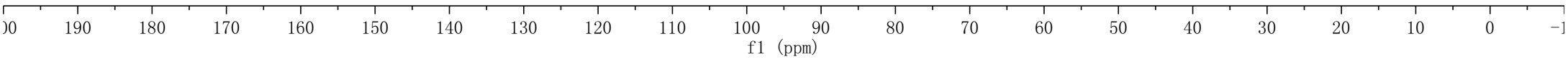
LSF-7-82P_C13_CDCl3_2020-1-21.10.fid

173.897
149.053
136.486
127.400
112.960
77.418
77.100
76.784
56.885
51.549
43.468
34.791
31.152
29.581
27.982
27.104
26.327

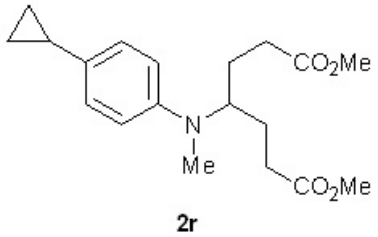


2q



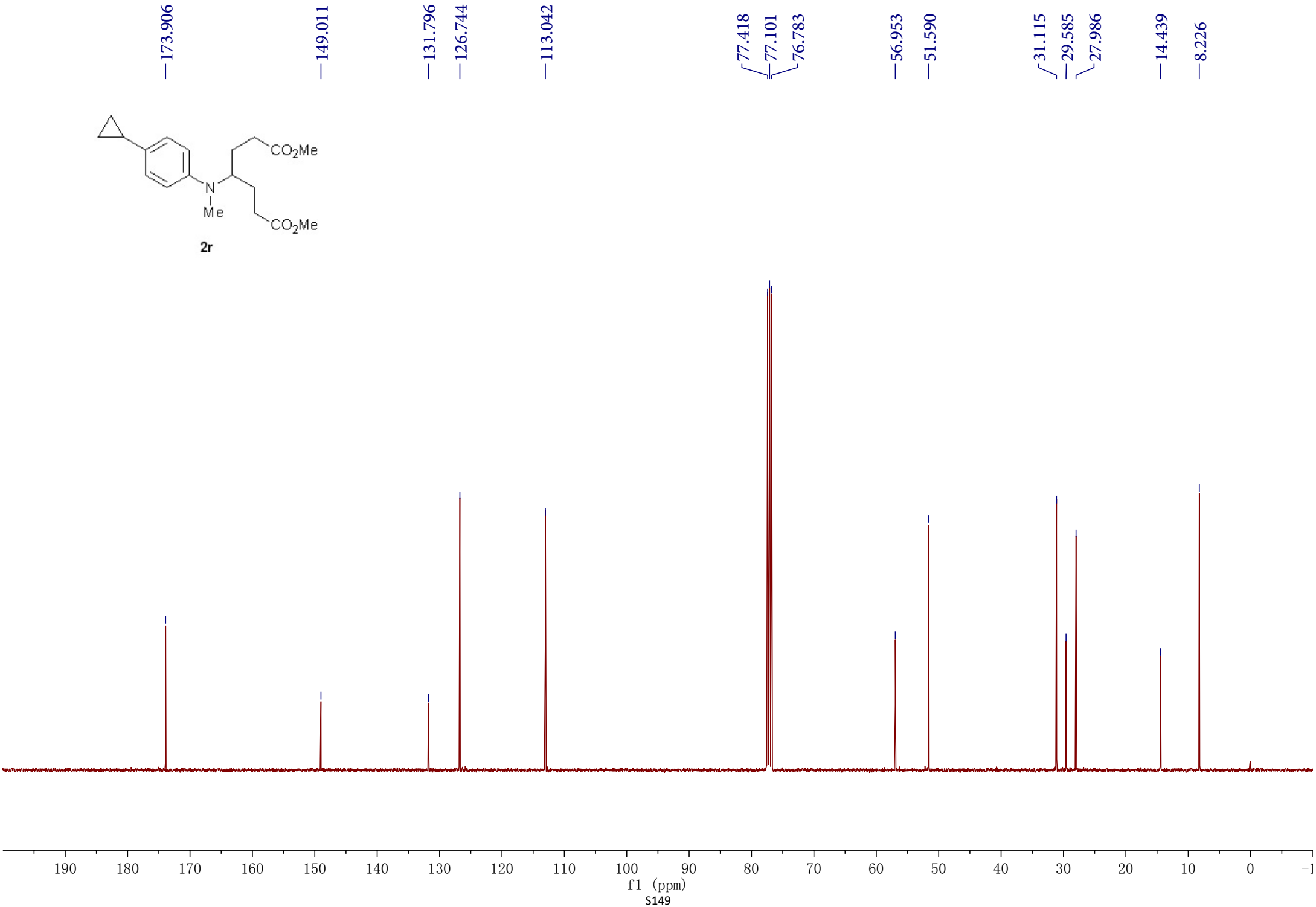


LSF-7-111-CDCL3-H1-2020-2-20.10.fid

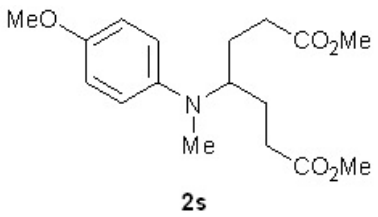


2r

LSF-7-111-CDCL3-C13-2020-2-20.10.fid



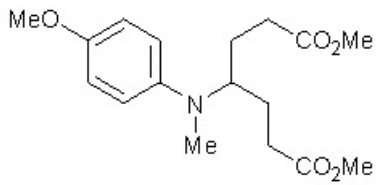
LSF-7-56BP-CDCL3-H1-2020-1-9.10.fid



2s

LSF-7-56BP-CDCL3-C13-2020-1-9.10.fid

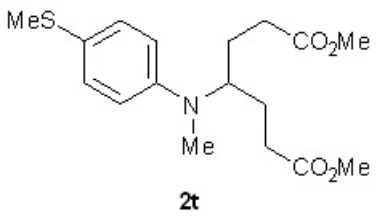
173.938
151.601
145.671
114.738
114.721
77.417
77.100
76.782
58.094
55.828
51.598
31.216
29.887
27.817



2s

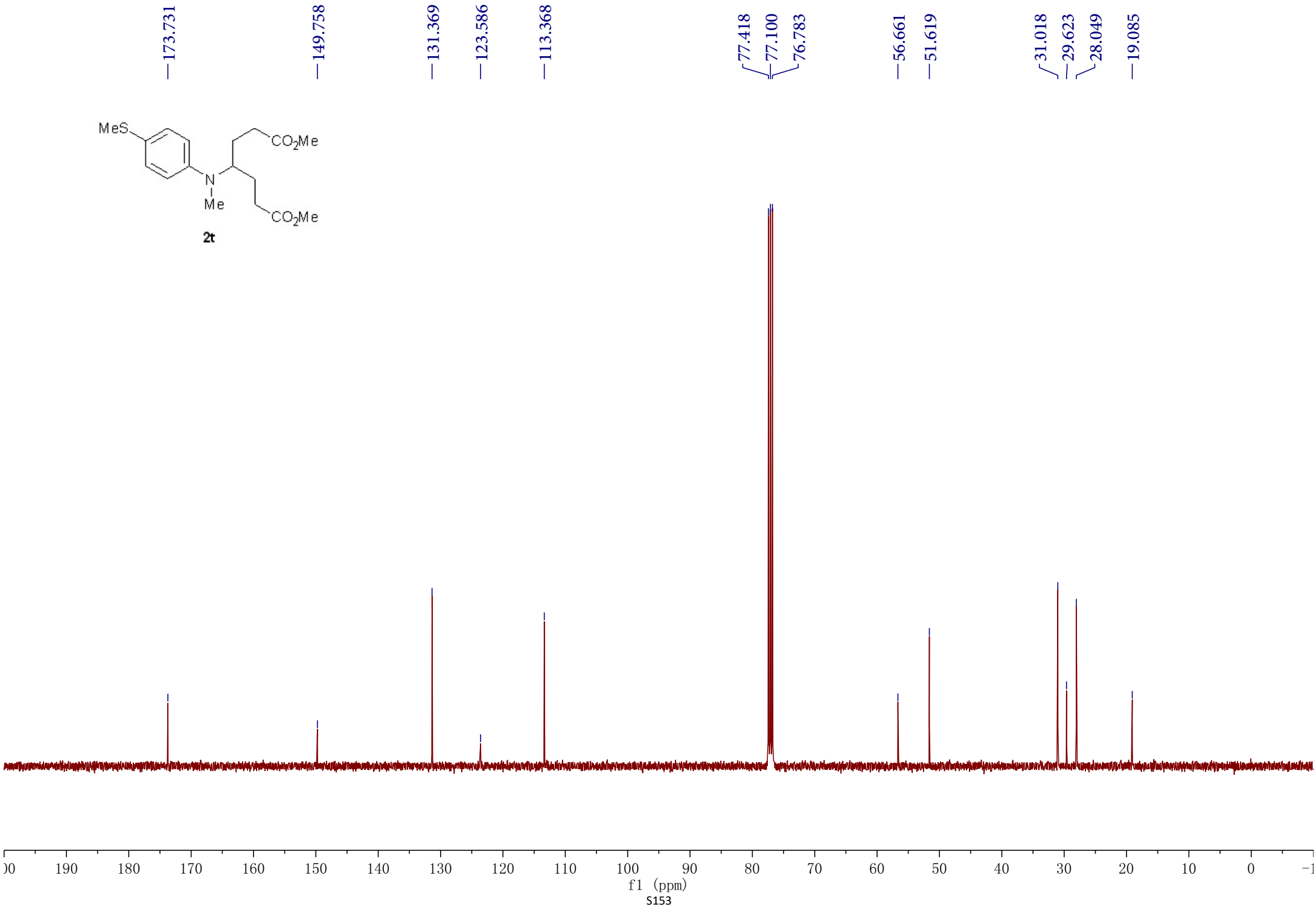
f1 (ppm)

LSF-7-81BP_H1_CDCl3_2020-1-21.20.fid

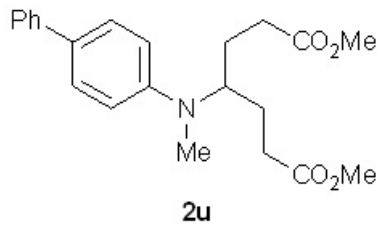


2t

LSF-7-81BP_C13_CDCl3_2020-1-21.10.fid



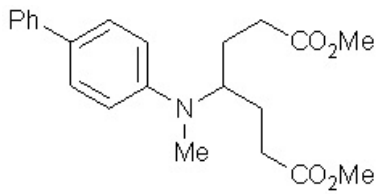
LSF-7-113-CDCL3-H1-2020-2-20.10.fid



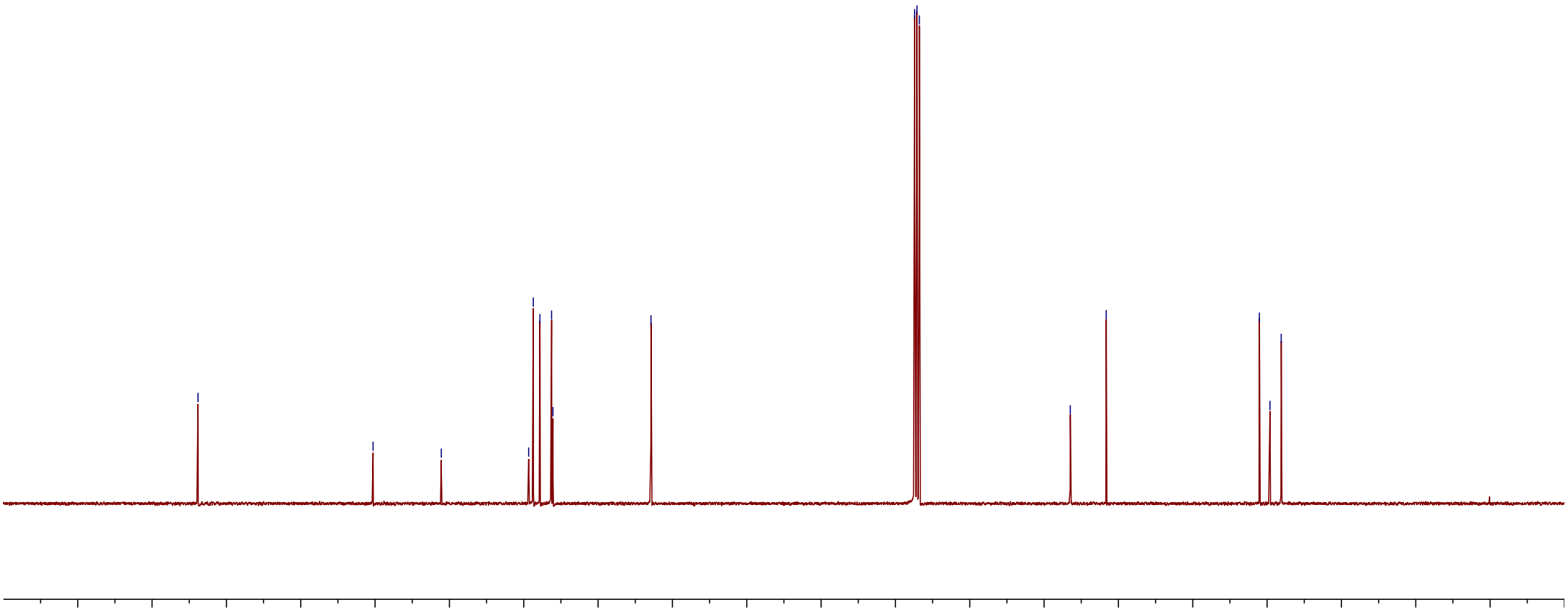
2u

LSF-7-113-CDCL3-C13-2020-2-20.10.fid

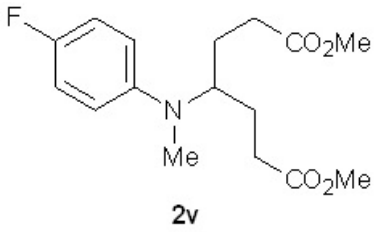
173.820
150.272
141.091
129.341
128.716
127.829
126.256
126.072
112.880
77.417
77.100
76.783
56.474
51.641
31.037
29.613
28.102



2u



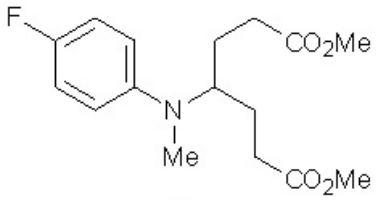
LSF-7-57BP-CDCL3-H1-2020-1-9.10.fid



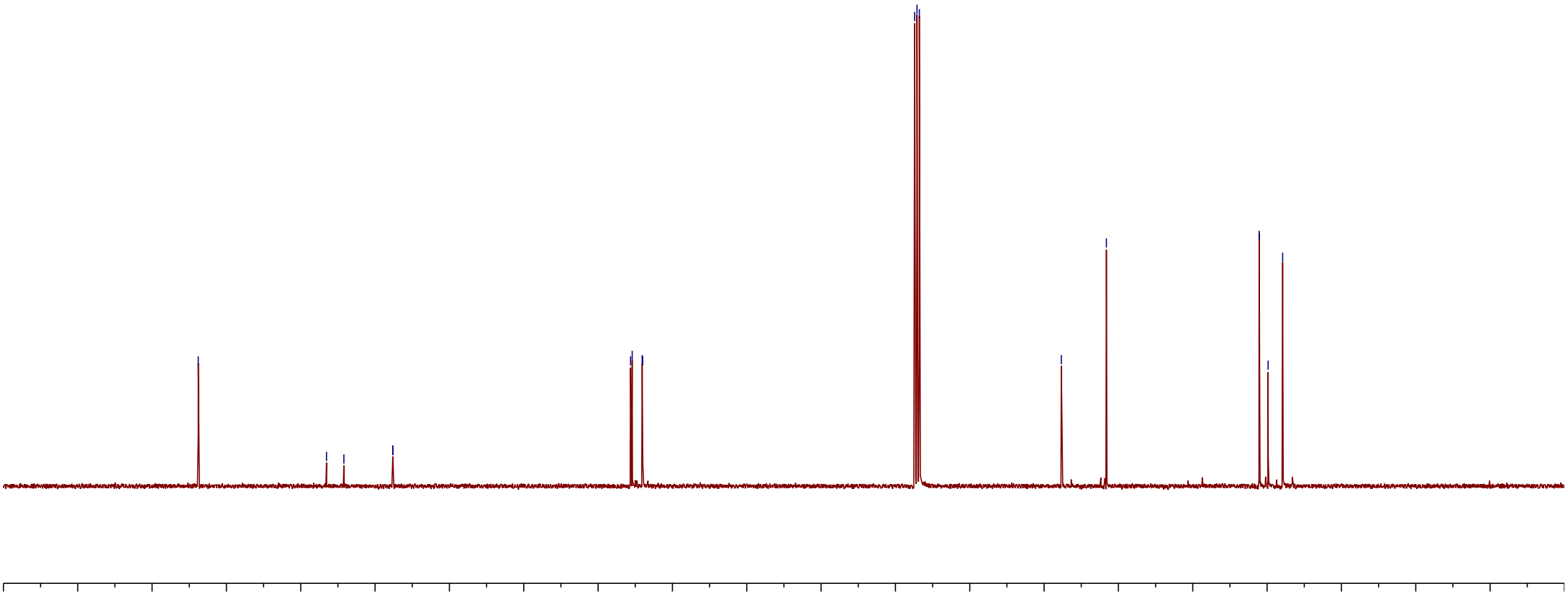
2v

LSF-7-57BP-CDCL3-C13-2020-1-9.10.fid —

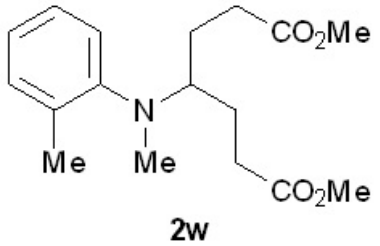
173.786
156.535
154.196
147.621
147.605
115.630
115.410
114.069
113.996
77.417
77.100
76.782
57.683
51.622
31.070
29.865
27.907



2v



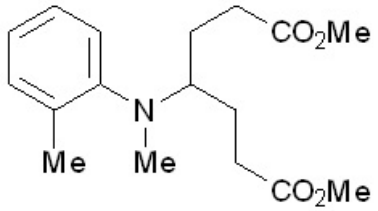
LSF-8-7_H1_CDCl3_2020-2-26.10.fid



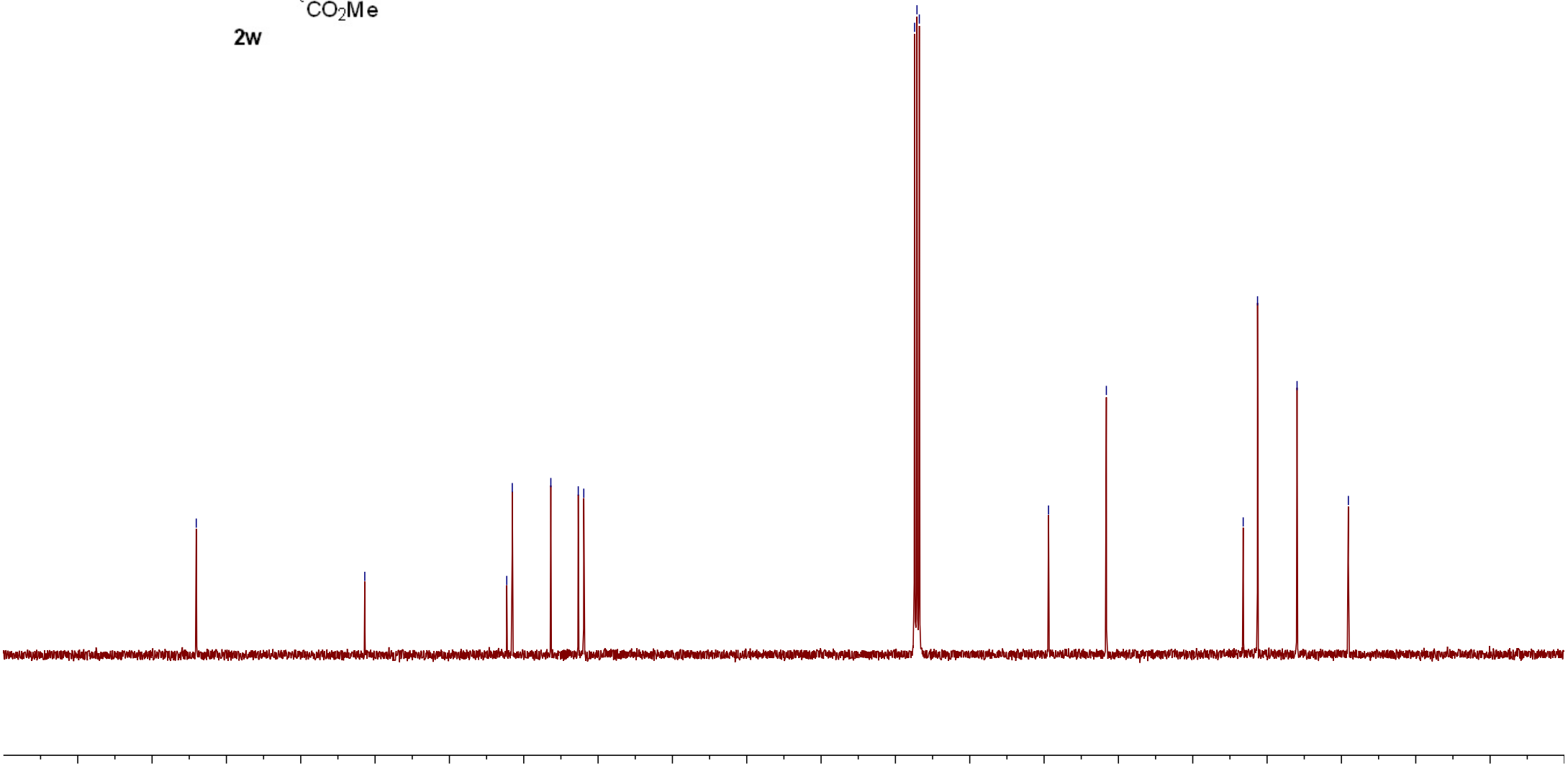
2w

LSF-8-7_C13_CDCl3_2020-2-26.10.fid

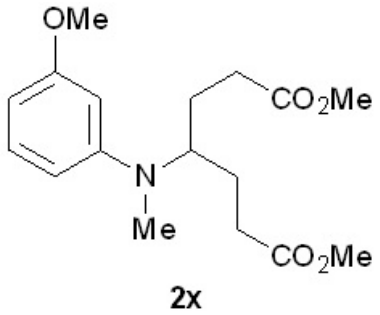
174.056
151.386
132.285
131.543
126.355
122.666
121.923
77.419
77.099
76.783
59.403
51.624
33.214
31.285
25.969
19.067



2w

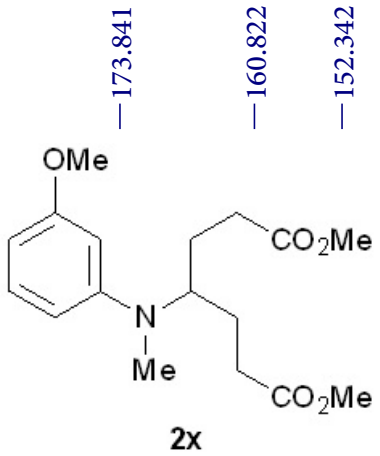


LSF-7-101_H1_CDCl3_2020-2-14.10.fid



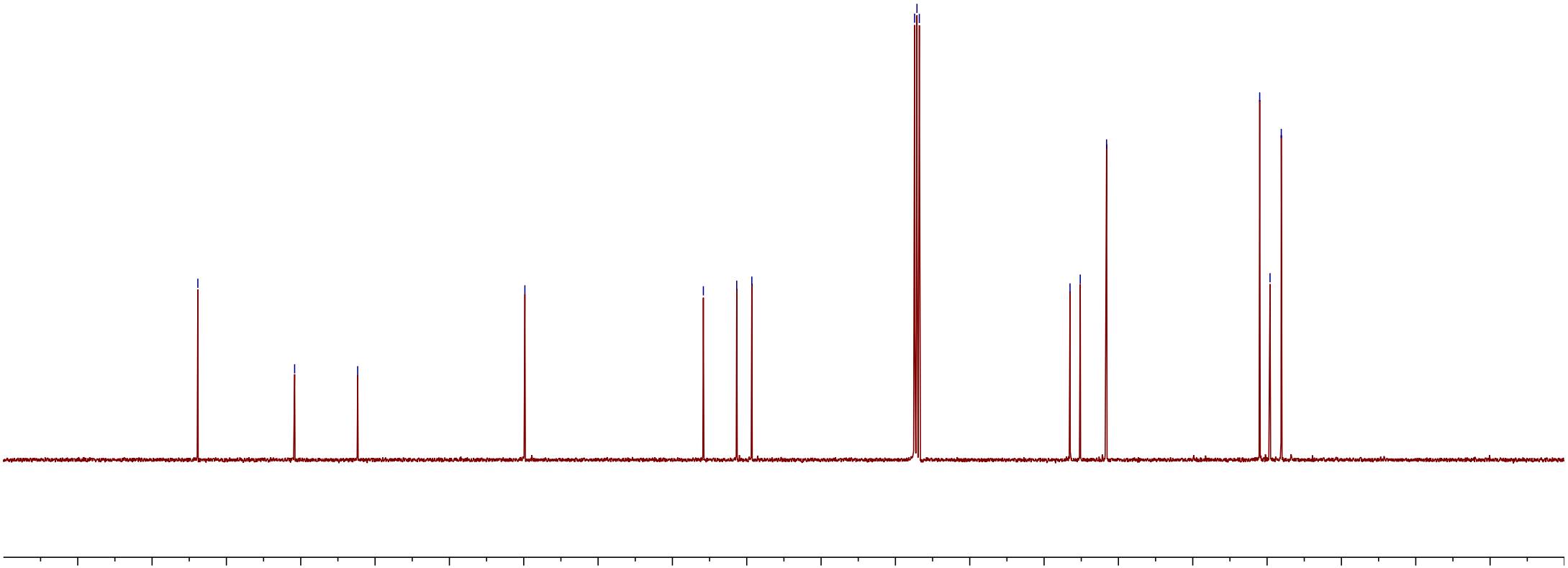
2x

LSF-7-101_C13_CDCl3_2020-2-14.10.fid



2x

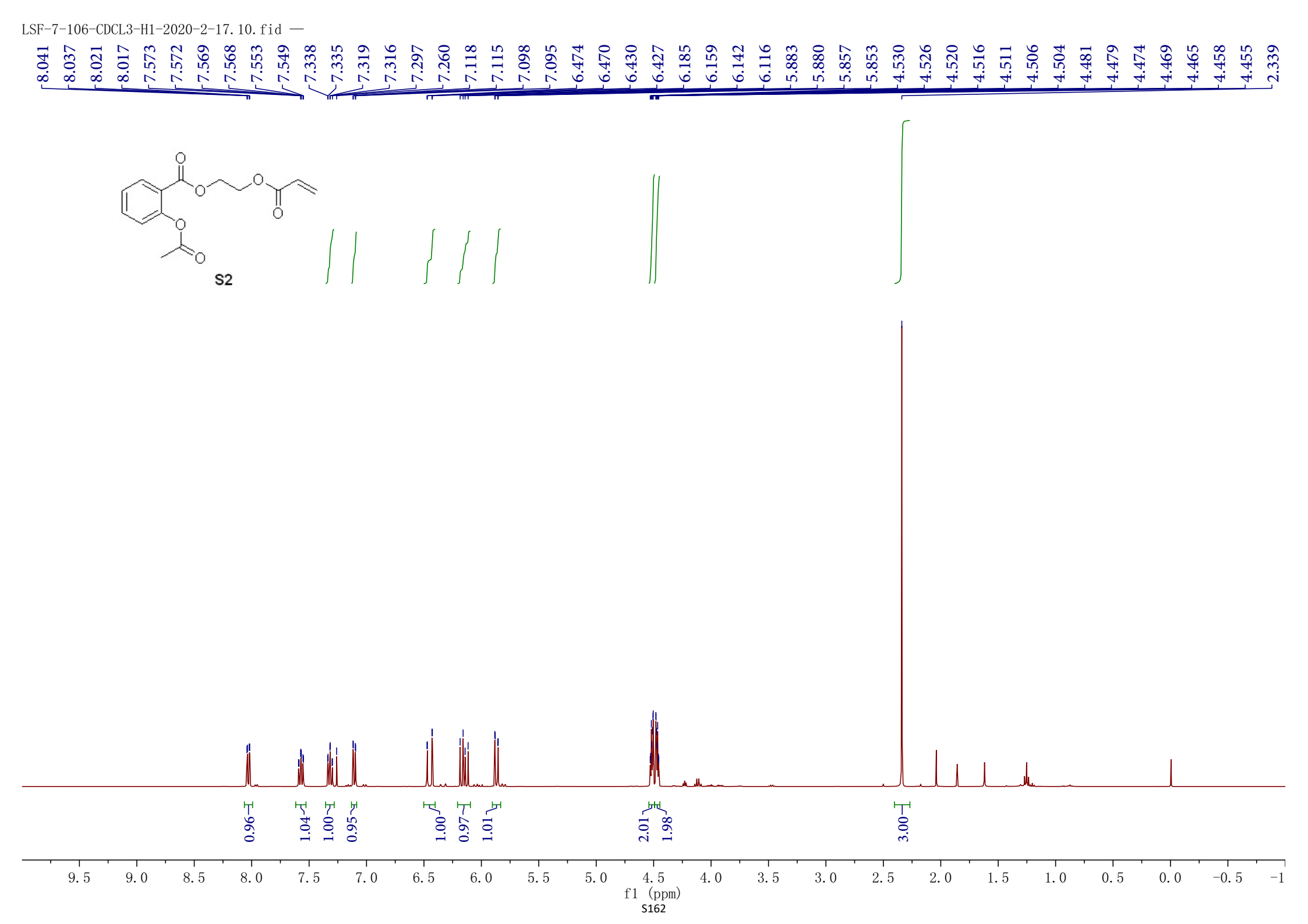
173.841
160.822
152.342
129.848
105.837
101.348
99.317
77.418
77.100
76.782
56.511
55.138
51.594
30.994
29.603
28.091



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

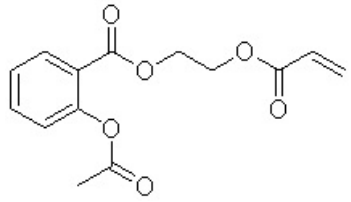
f1 (ppm)

LSF-7-106-CDCL3-H1-2020-2-17.10.fid

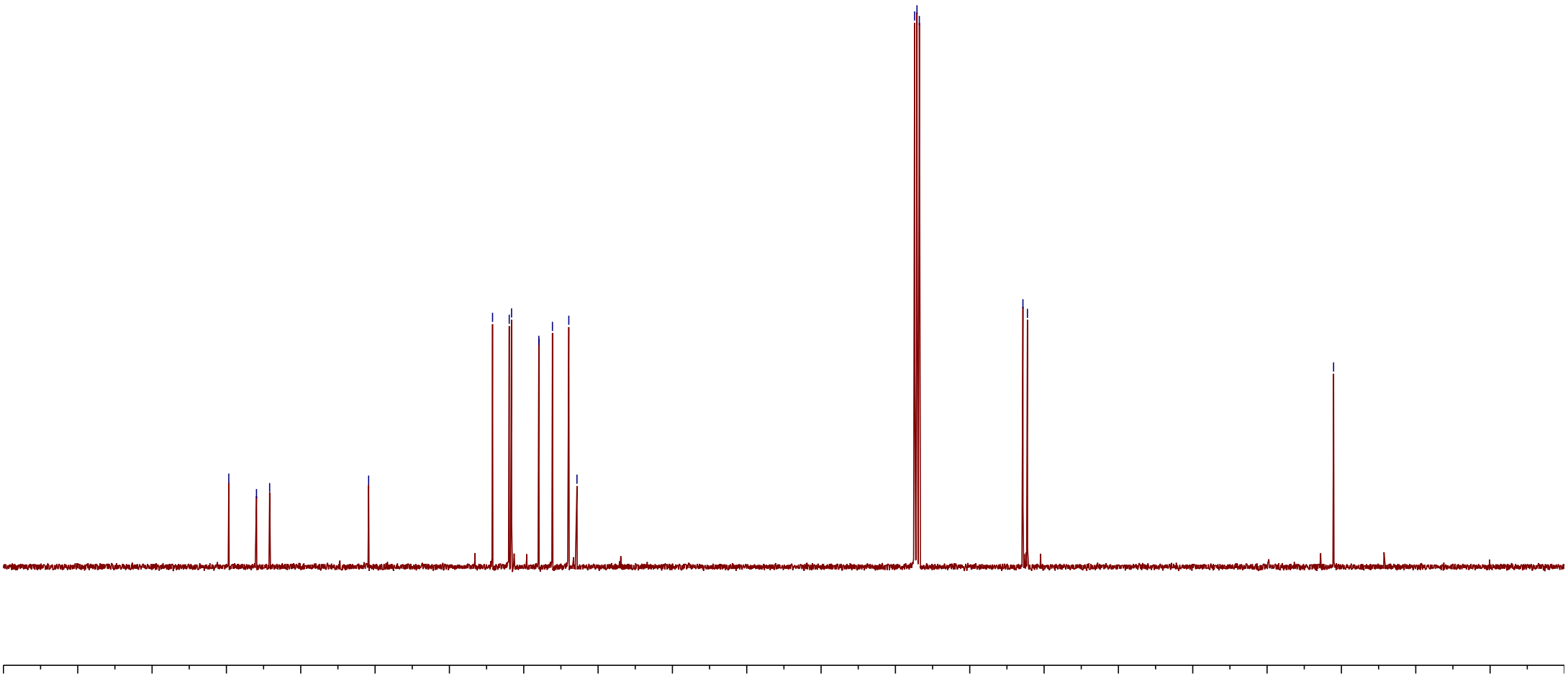


LSF-7-106-CDCL3-C13-2020-2-17.10.fid

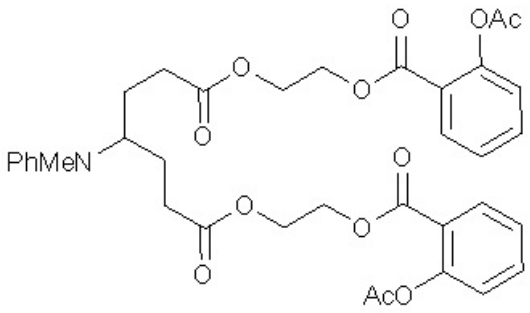
169.681
165.955
164.185
150.867
134.197
131.954
131.640
127.971
126.140
123.940
122.840
77.417
77.100
76.782
62.846
62.241
21.054



S2

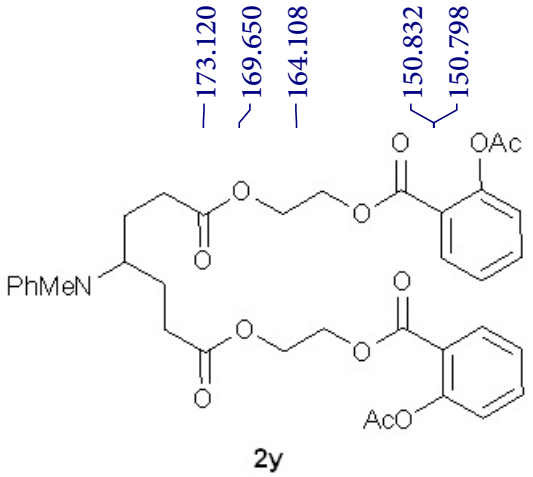


LSF-8-2_H1_CDCl3_2020-2-25.10.fid



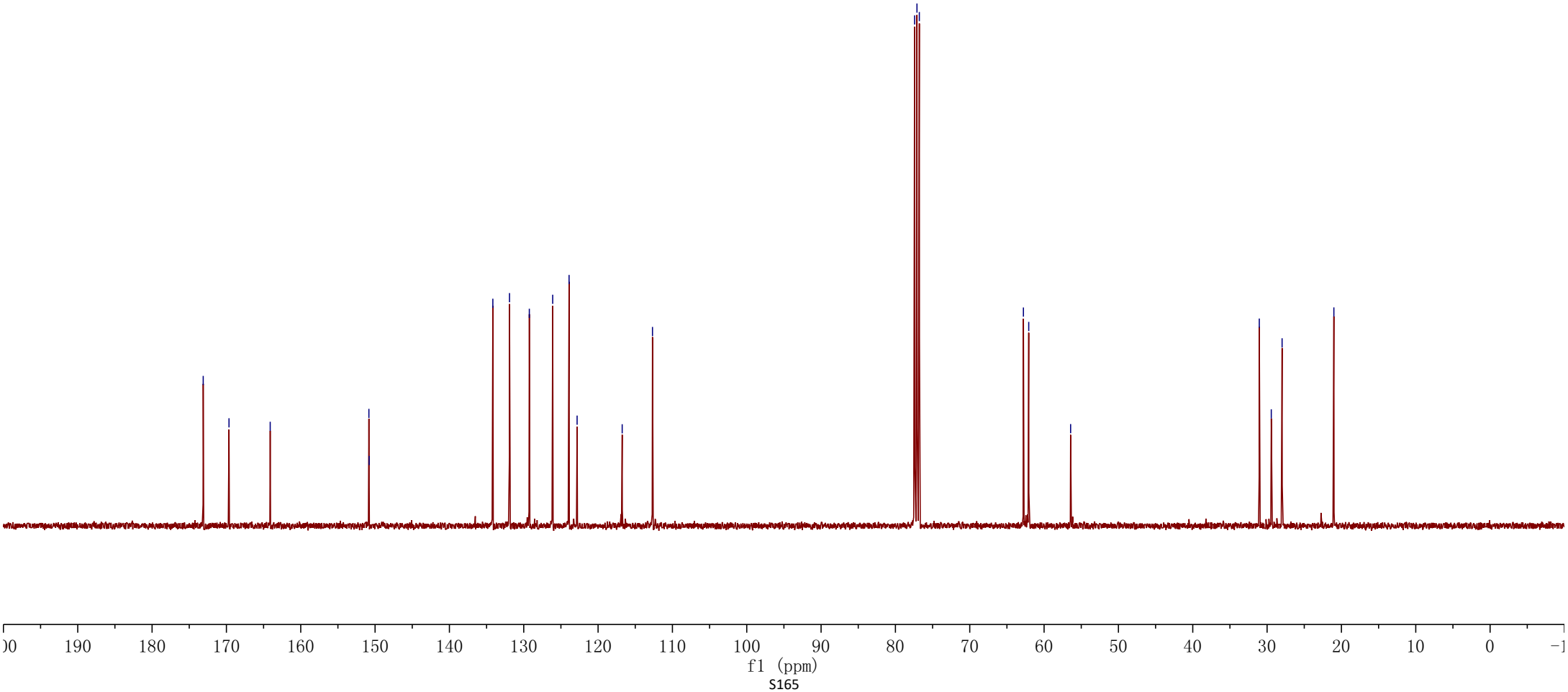
2y

LSF-8-2_C13_CDCl3_2020-2-25.10.fid



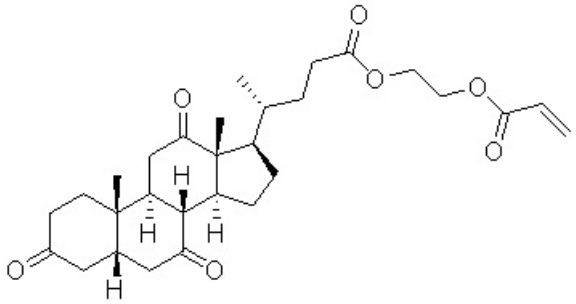
2y

173.120
169.650
164.108
150.832
150.798
134.158
131.916
129.250
126.105
123.903
122.822
116.756
112.681
77.419
77.101
76.783
62.781
62.066
56.431
31.051
29.437
27.982
21.016

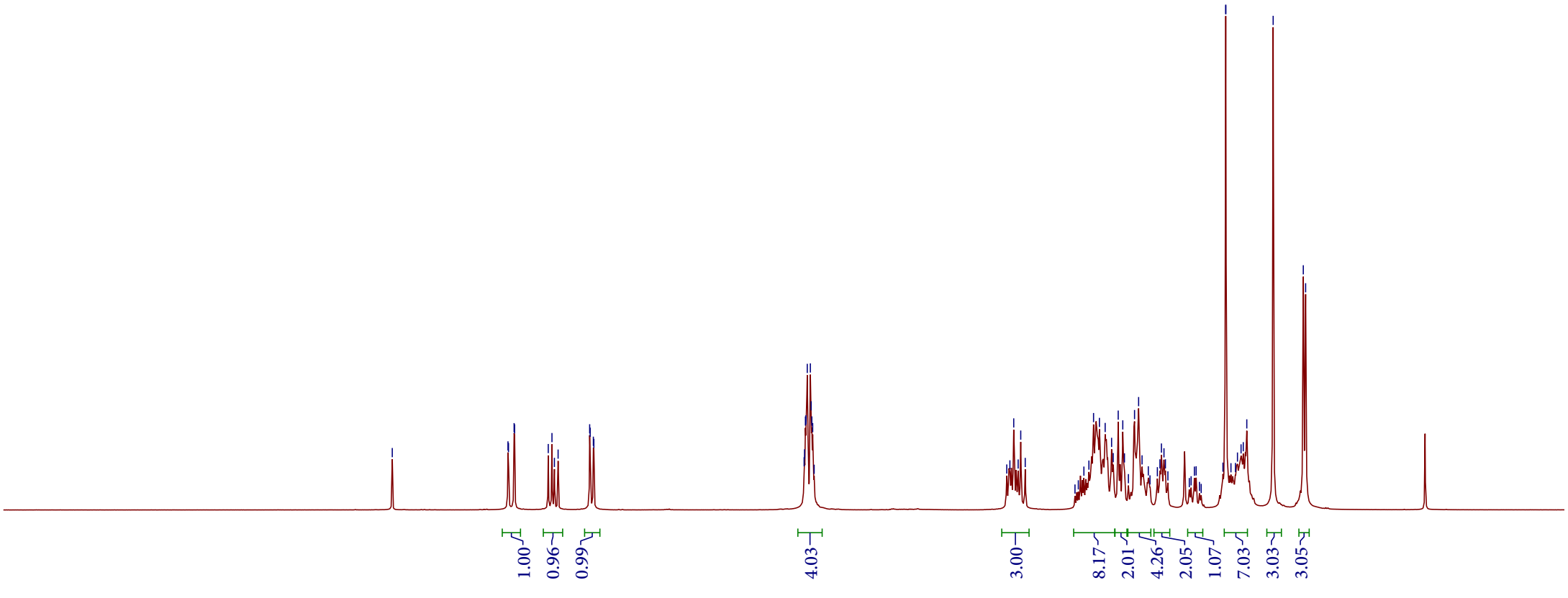


LSF-8-18-CDCL3-H1-2020--3-9.10.fid —

7.260 6.444 6.441 6.401 6.398 6.161 6.135 6.117 6.091 5.869 5.865 5.843 5.839 4.358 4.355 4.348 4.344 4.335 4.314 4.308 4.303 4.297 2.881 2.831 2.800 2.318 2.277 2.236 2.191 2.180 2.144 2.112 2.100 2.029 2.001 1.976 1.840 1.822 1.386 1.386 1.304 1.279 1.263 1.238 1.052 0.840 0.824



S3

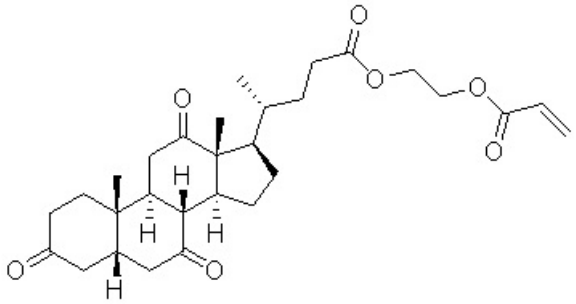


9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1

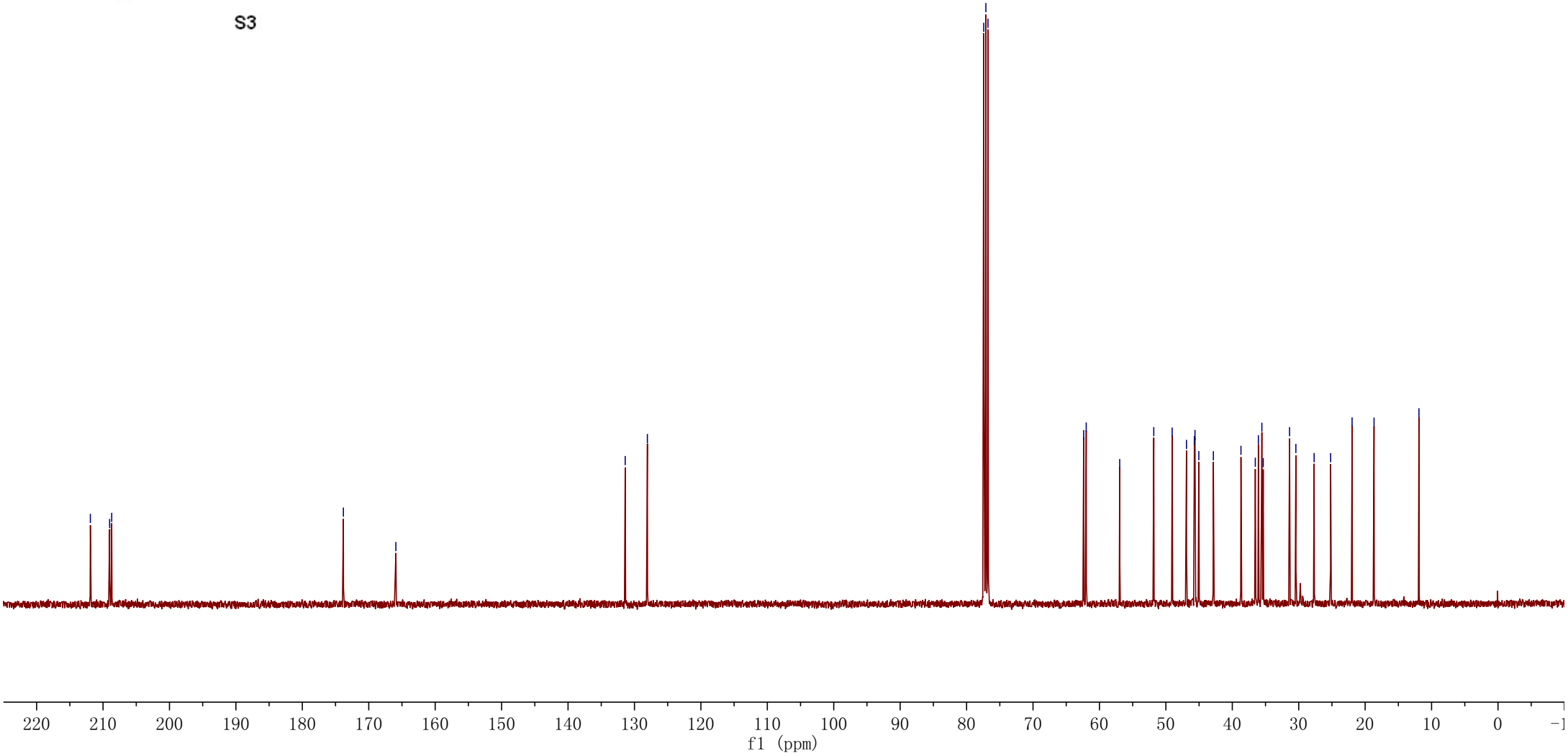
f1 (ppm)

LSF-8-18-CDCL3-C13-2020--3-9.10.fid

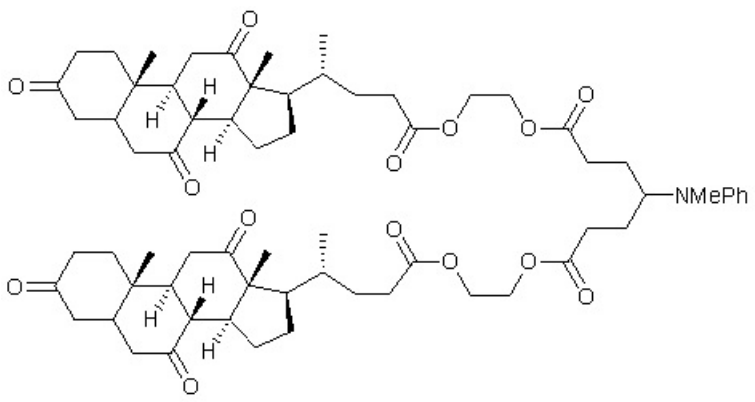
211.908
209.010
208.694
173.818
165.917
131.395
128.054
77.418
77.099
76.783
62.374
61.991
56.950
51.821
49.051
46.896
45.713
45.615
45.040
42.849
38.695
36.539
36.073
35.547
35.342
31.381
30.429
27.681
25.192
21.967
18.662
11.901



S3



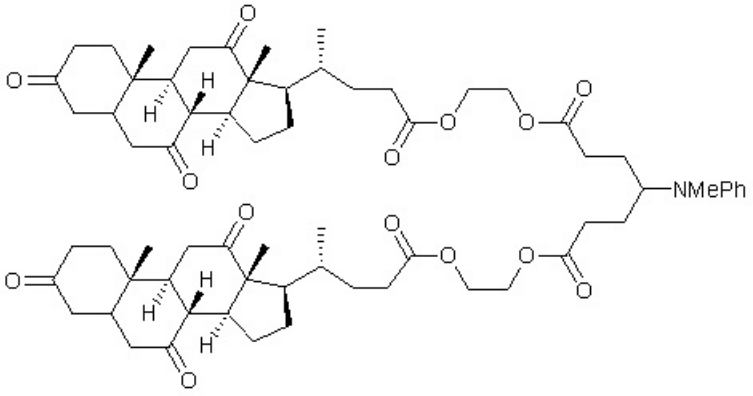
LSF-8-26_H1_CDCl3_2020-3-12.10.fid



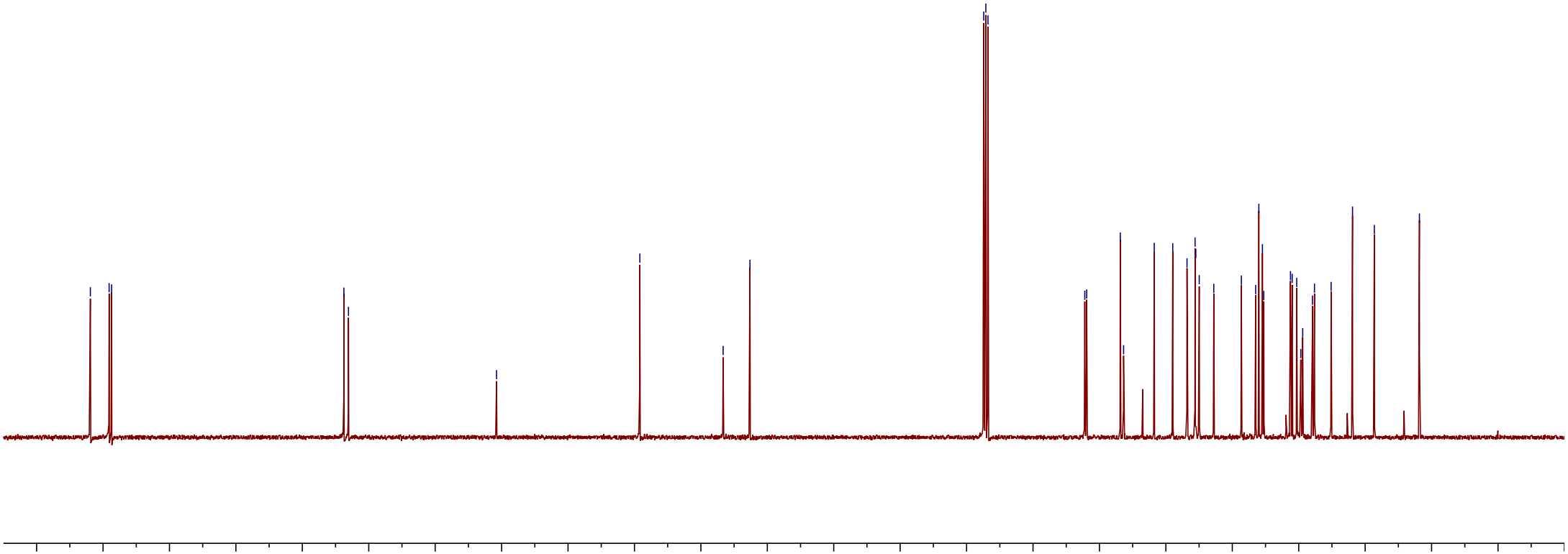
2z

LSF-8-26_C13_CDCl3_2020-3-12.10.fid

211.910 209.084 208.710 173.744 173.051 150.765 129.189 116.653 112.616 77.418 77.100 76.782 62.207 61.923 56.862 56.365 51.748 48.962 46.819 45.605 45.494 44.978 42.785 38.635 36.482 36.004 35.464 35.258 31.241 30.985 30.298 29.689 29.402 27.938 27.628 25.122 21.899 18.619 11.830

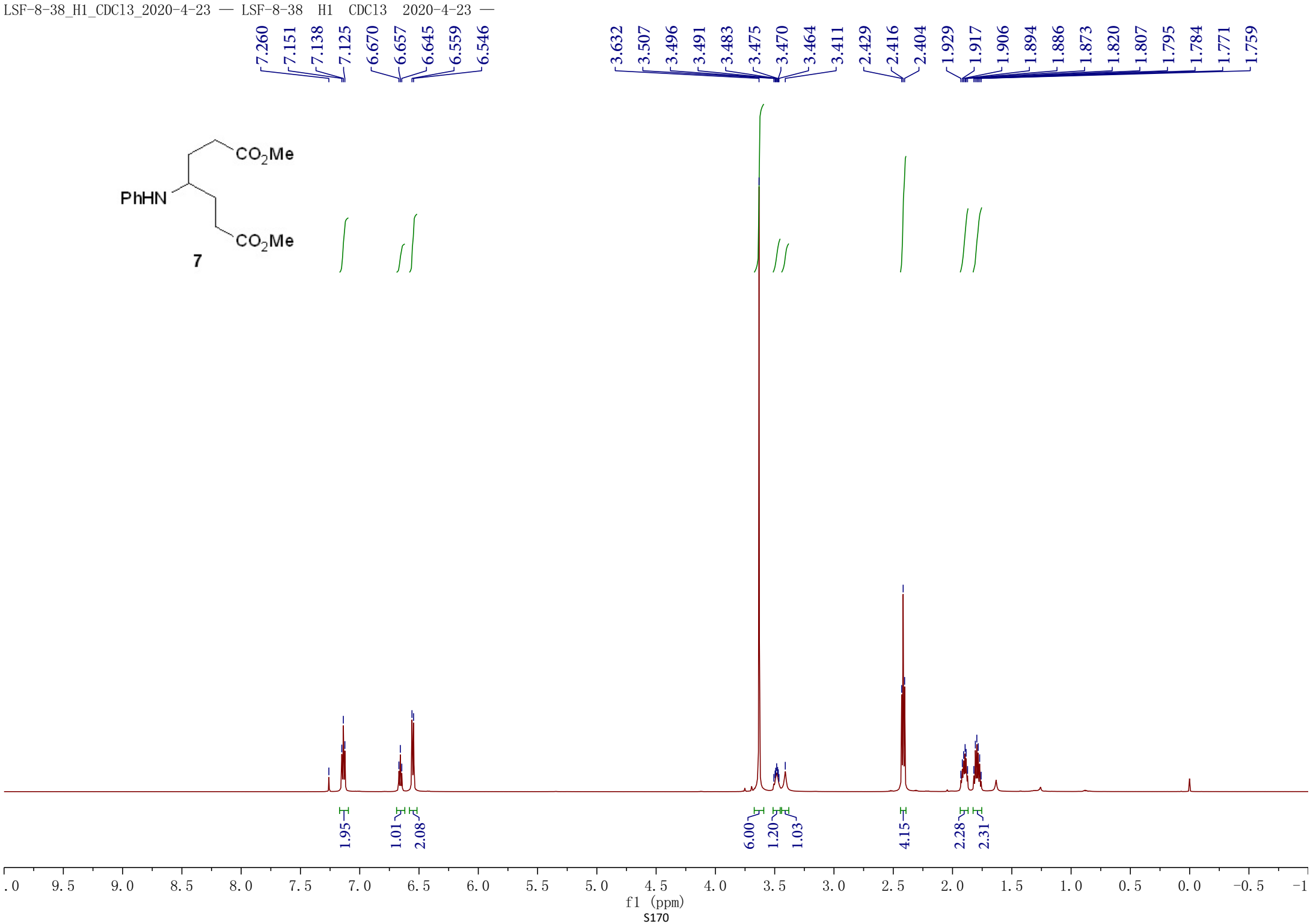


2z

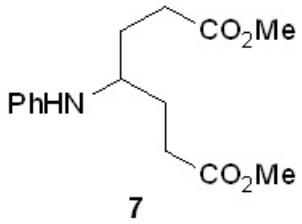


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)

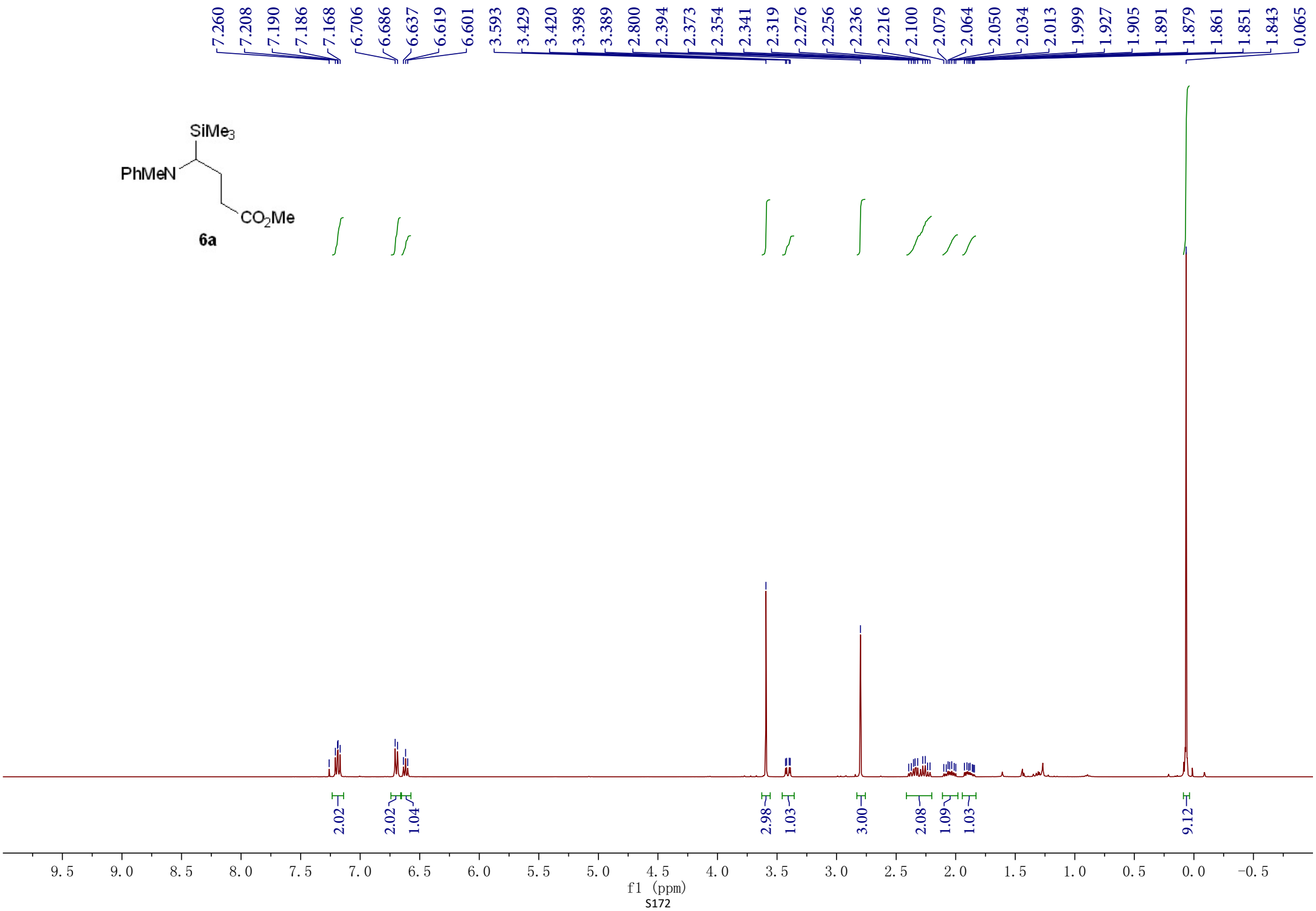

LSF-8-38_H1_CDCl3_2020-4-23 — LSF-8-38 H1 CDCl3 2020-4-23 —
7.260
7.151
7.138
7.125
6.670
6.657
6.645
6.559
6.546
3.632
3.507
3.496
3.491
3.483
3.475
3.470
3.464
3.411
2.429
2.416
2.404
1.929
1.917
1.906
1.894
1.886
1.873
1.820
1.807
1.795
1.784
1.771
1.759
CO2Me
PhHN
CO2Me
7
1.95
1.01
2.08
6.00
1.20
1.03
4.15
2.28
2.31
f1 (ppm)

LSF-8-38_C13_CDCl3_2020-4-23 — LSF-8-38 C13 CDCl3 2020-4-23 —



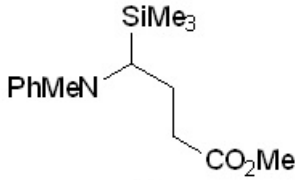
7

LSF-5-107AP-CDCL3-H1-2020-2-7.10.fid —

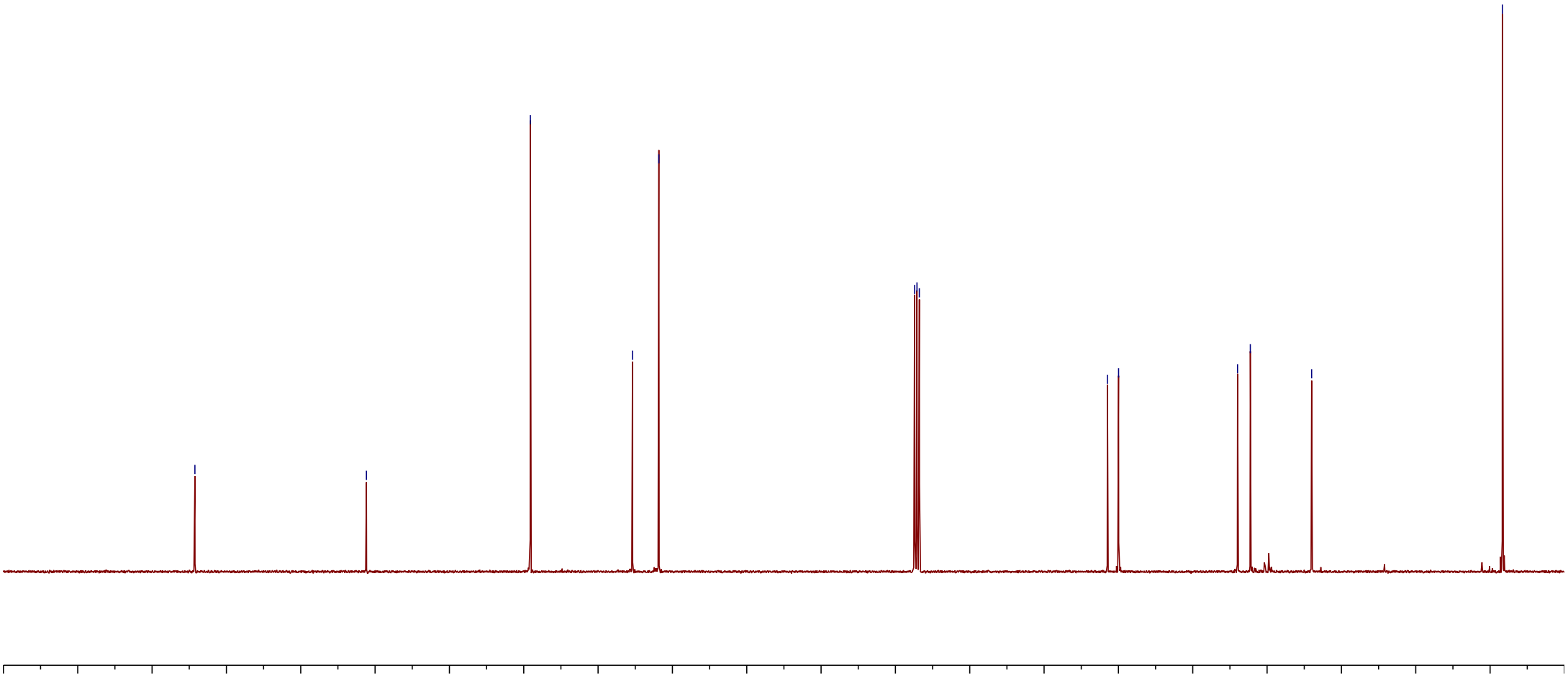


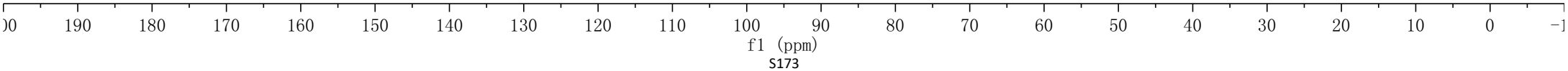
LSF-5-107AP-CDCL3-C13-2020-2-7.10.fid

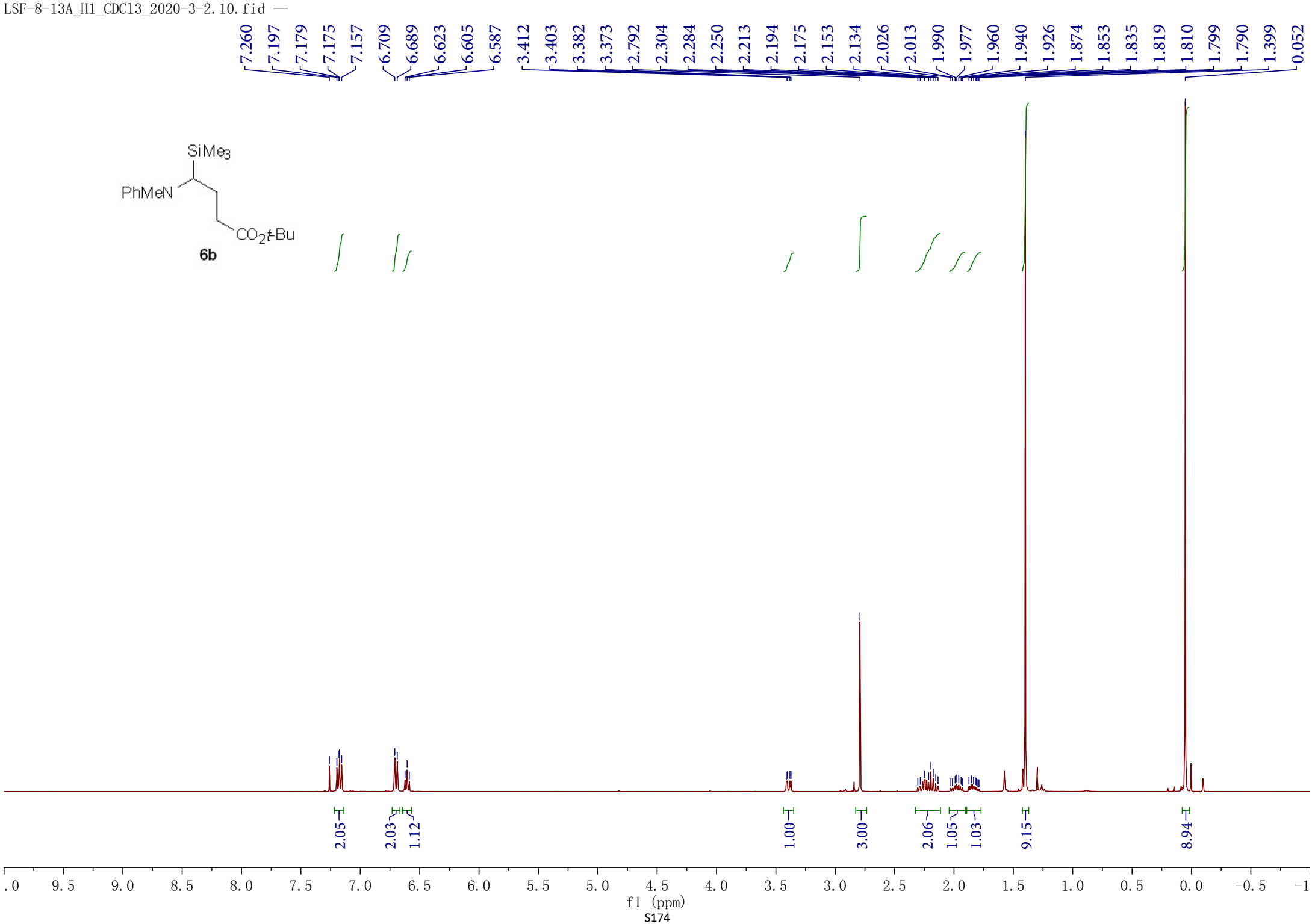
174.237
151.164
129.109
115.371
111.825
77.417
77.100
76.783
51.479
49.979
33.974
32.257
24.008
-1.651



6a

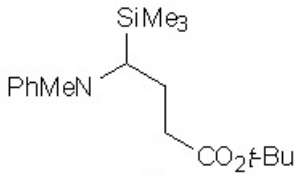




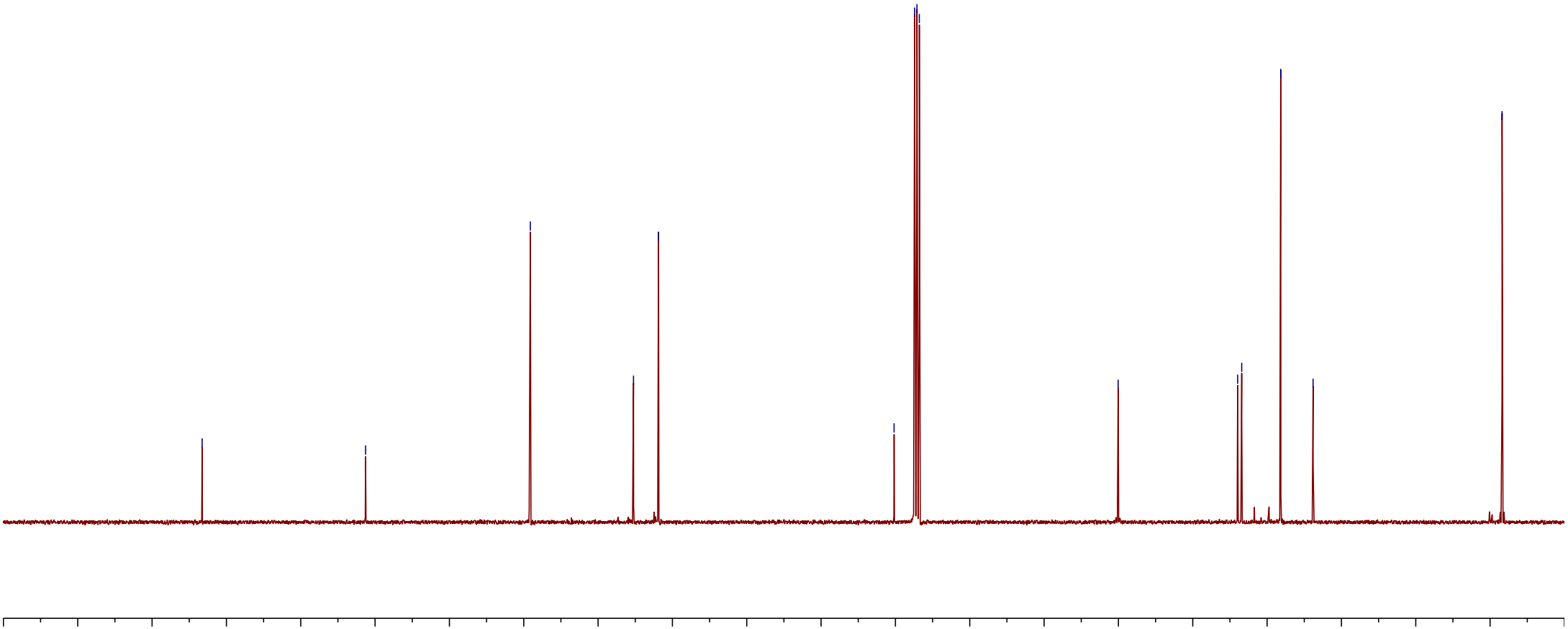

LSF-8-13A_H1_CDCl3_2020-3-2.10.fid
7.260
7.197
7.179
7.175
7.157
6.709
6.689
6.623
6.605
6.587
3.412
3.403
3.382
3.373
2.792
2.304
2.284
2.250
2.213
2.194
2.175
2.153
2.134
2.026
2.013
1.990
1.977
1.960
1.940
1.926
1.874
1.853
1.835
1.819
1.810
1.799
1.790
1.399
0.052
SiMe3
PhMeN
CO2t-Bu
6b
2.05
2.03
1.12
1.00
3.00
2.06
1.05
1.03
9.15
8.94
f1 (ppm)

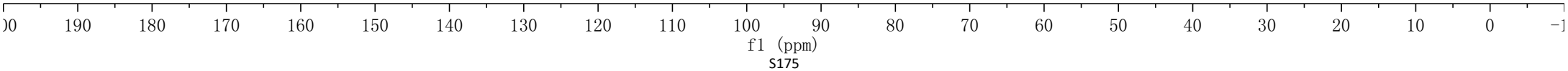
LSF-8-13A_C13_CDCl3_2020-3-2.21.fid

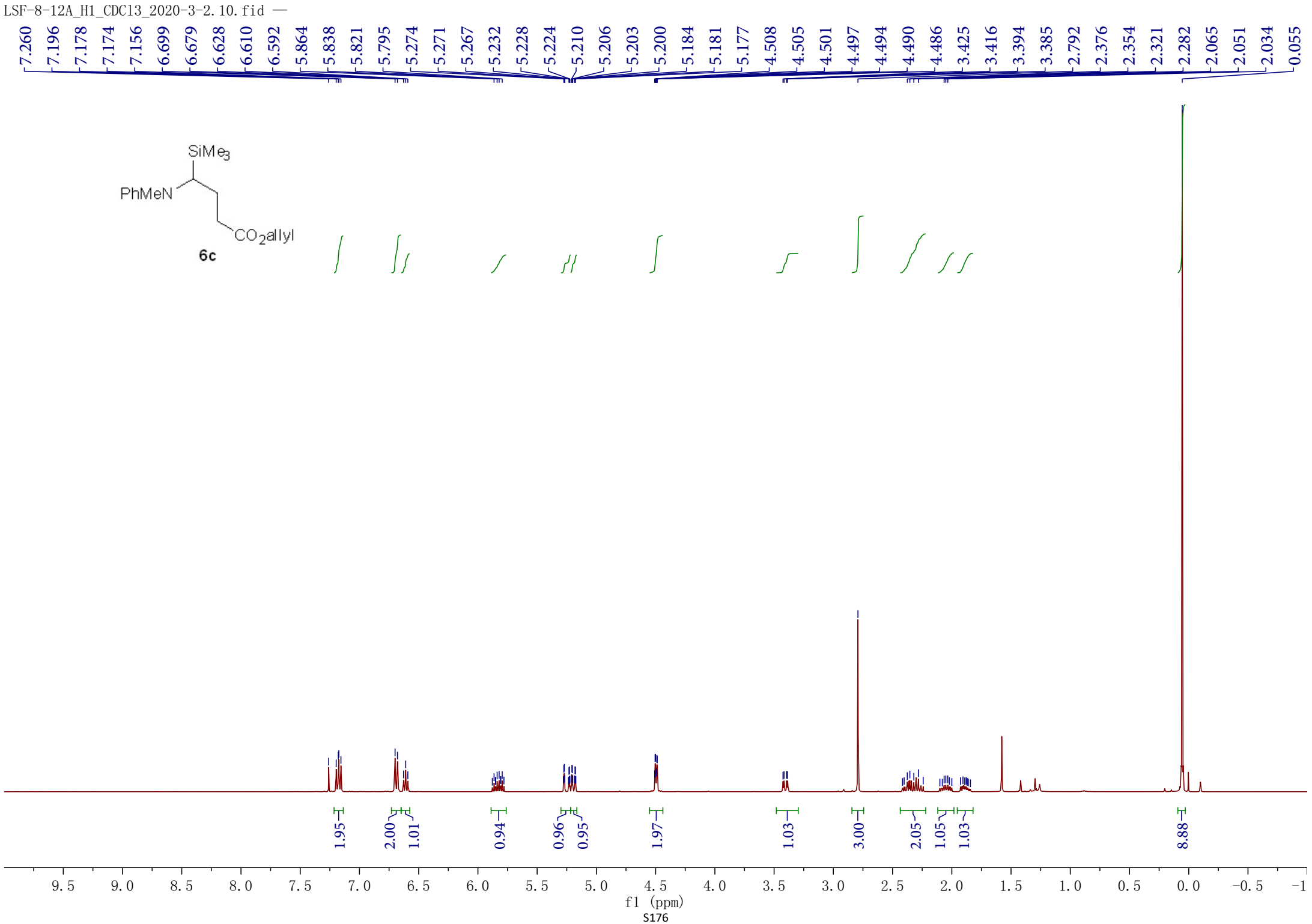
173.264
151.278
129.113
115.236
111.868
80.179
77.418
77.101
76.783
50.036
33.959
33.413
28.166
23.813
-1.611



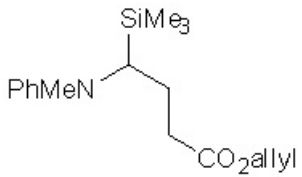
6b



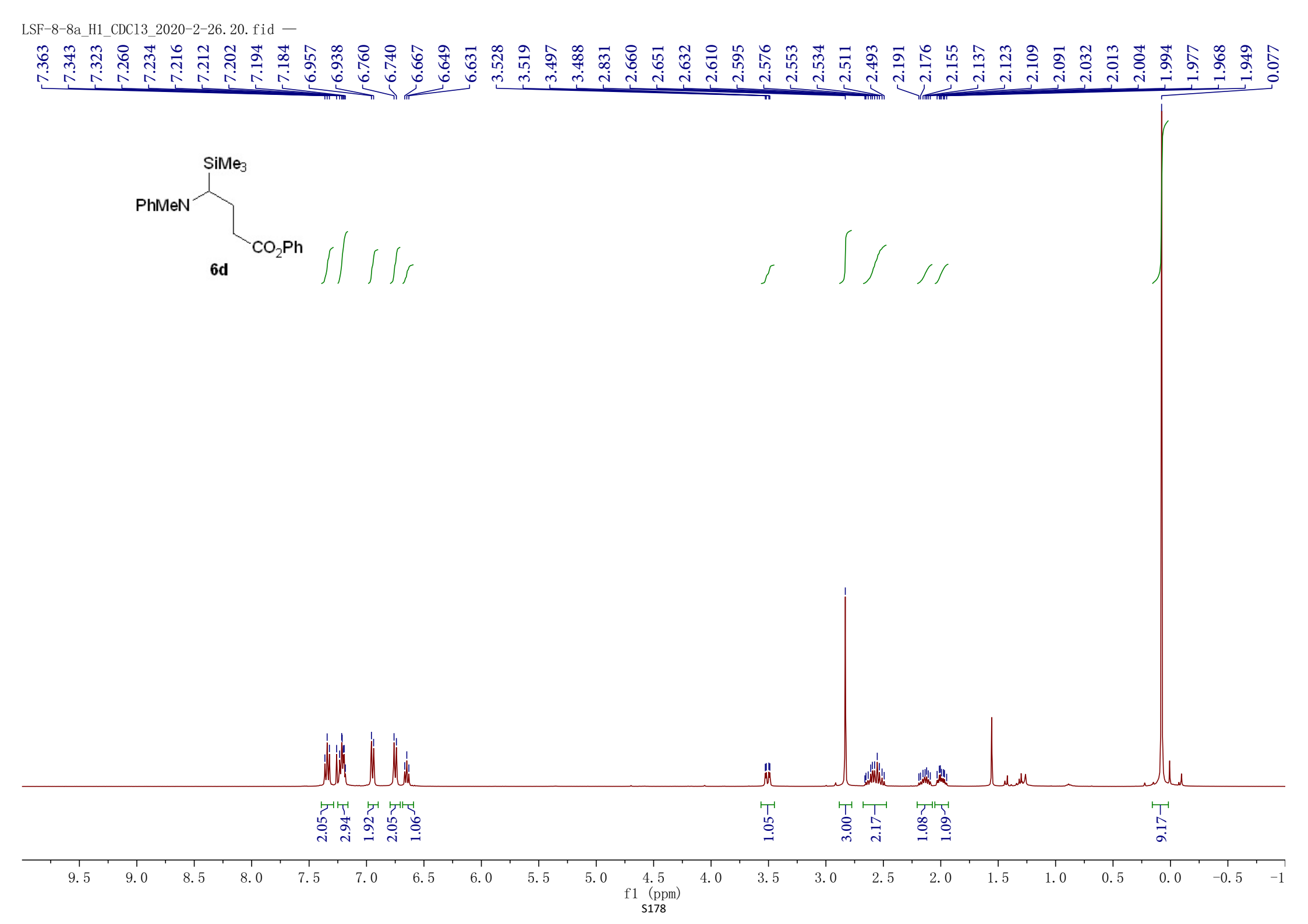



LSF-8-12A_H1_CDCl3_2020-3-2.10.fid
7.260
7.196
7.178
7.174
7.156
6.699
6.679
6.628
6.610
6.592
5.864
5.838
5.821
5.795
5.274
5.271
5.267
5.232
5.228
5.224
5.210
5.206
5.203
5.200
5.184
5.181
5.177
4.508
4.505
4.501
4.497
4.494
4.490
4.486
3.425
3.416
3.394
3.385
2.792
2.376
2.354
2.321
2.282
2.065
2.051
2.034
0.055
SiMe3
PhMeN
CO2allyl
6c
1.95
2.00
1.01
0.94
0.96
0.95
1.97
1.03
3.00
2.05
1.05
1.03
8.88
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

LSF-8-12A_C13_CDCl3_2020-3-2.10.fid

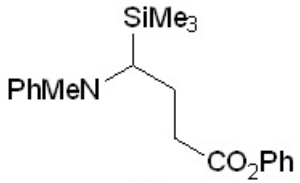


6c

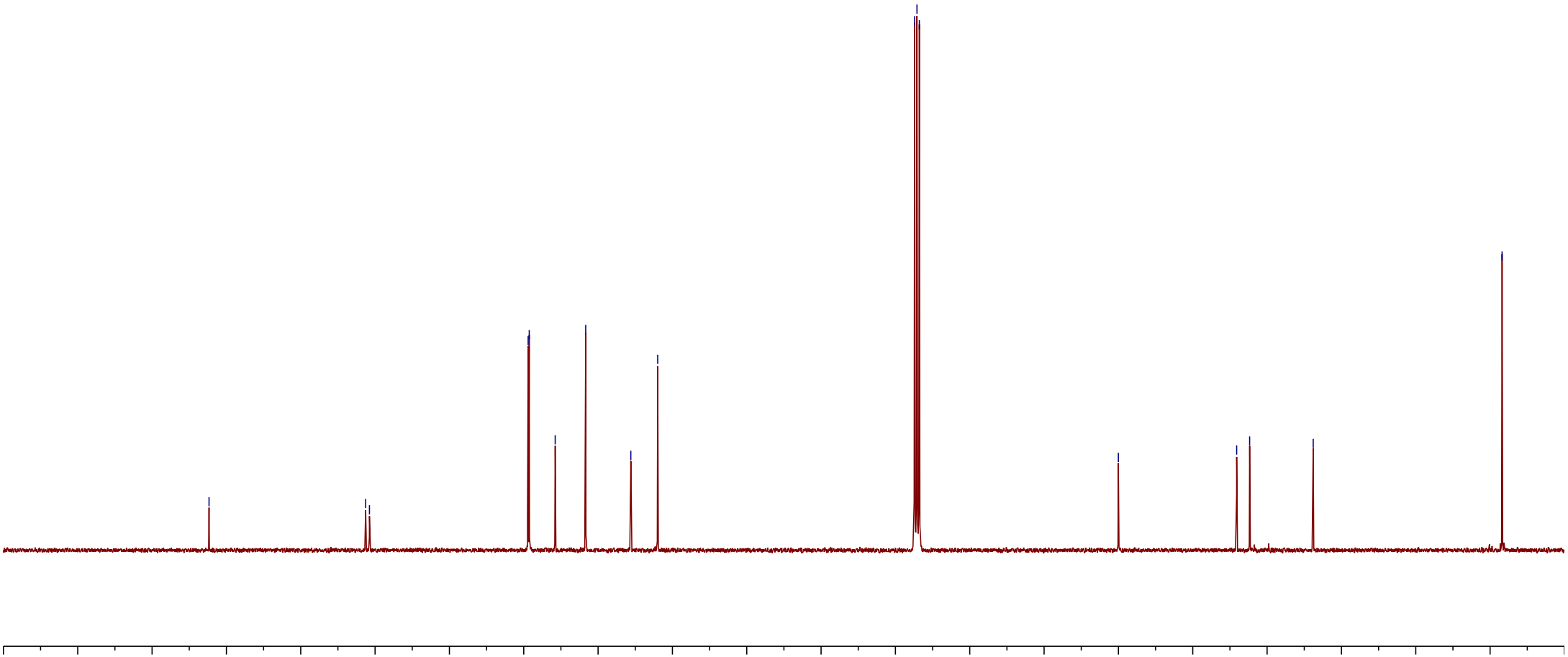

LSF-8-8a_H1_CDCl3_2020-2-26.20.fid
7.363
7.343
7.323
7.260
7.234
7.216
7.212
7.202
7.194
7.184
6.957
6.938
6.760
6.740
6.667
6.649
6.631
3.528
3.519
3.497
3.488
2.831
2.660
2.651
2.632
2.610
2.595
2.576
2.553
2.534
2.511
2.493
2.191
2.176
2.155
2.137
2.123
2.109
2.091
2.032
2.013
2.004
1.994
1.977
1.968
1.949
0.077
SiMe3
PhMeN
CO2Ph
6d
2.05
2.94
1.92
2.05
1.06
1.05
3.00
2.17
1.08
1.09
9.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

LSF-8-8a_C13_CDCl3_2020-2-26.10.fid

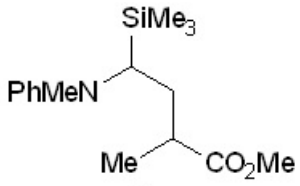
172.337
151.267
150.757
129.409
129.261
125.770
121.663
115.595
111.978
77.418
77.101
76.784
50.010
34.092
32.349
23.796
-1.614



6d



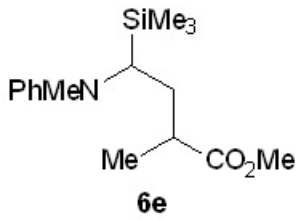
LSF-8-14_H1_CDCl3_2020-3-4.10.fid



6e

(*dr* = 1.1:1)

LSF-8-14B_H1_CDCl3_2020-3-3.10.fid

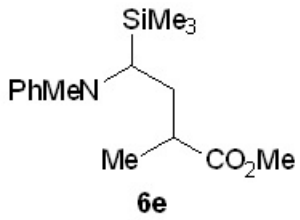


6e

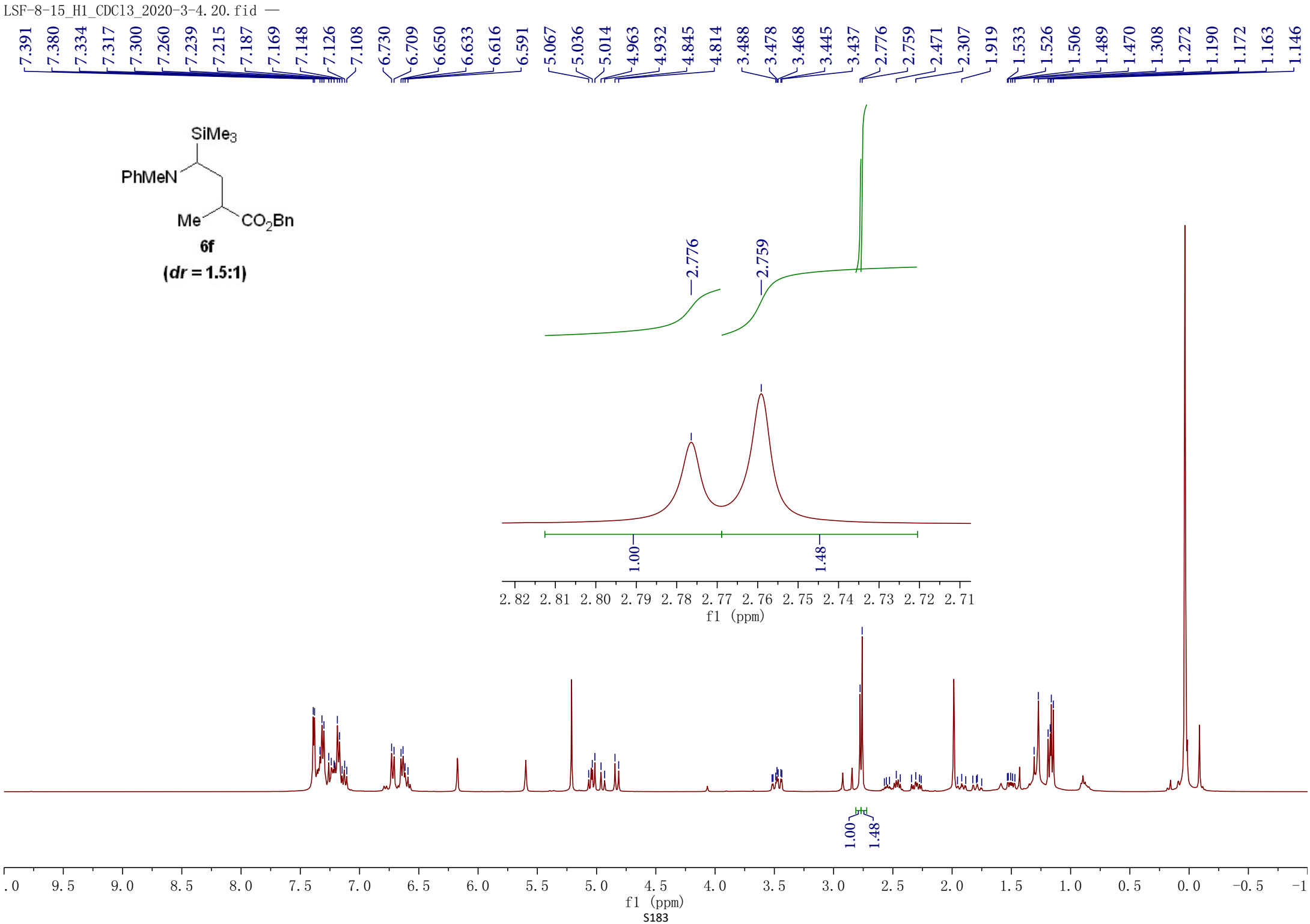
f1 (ppm)

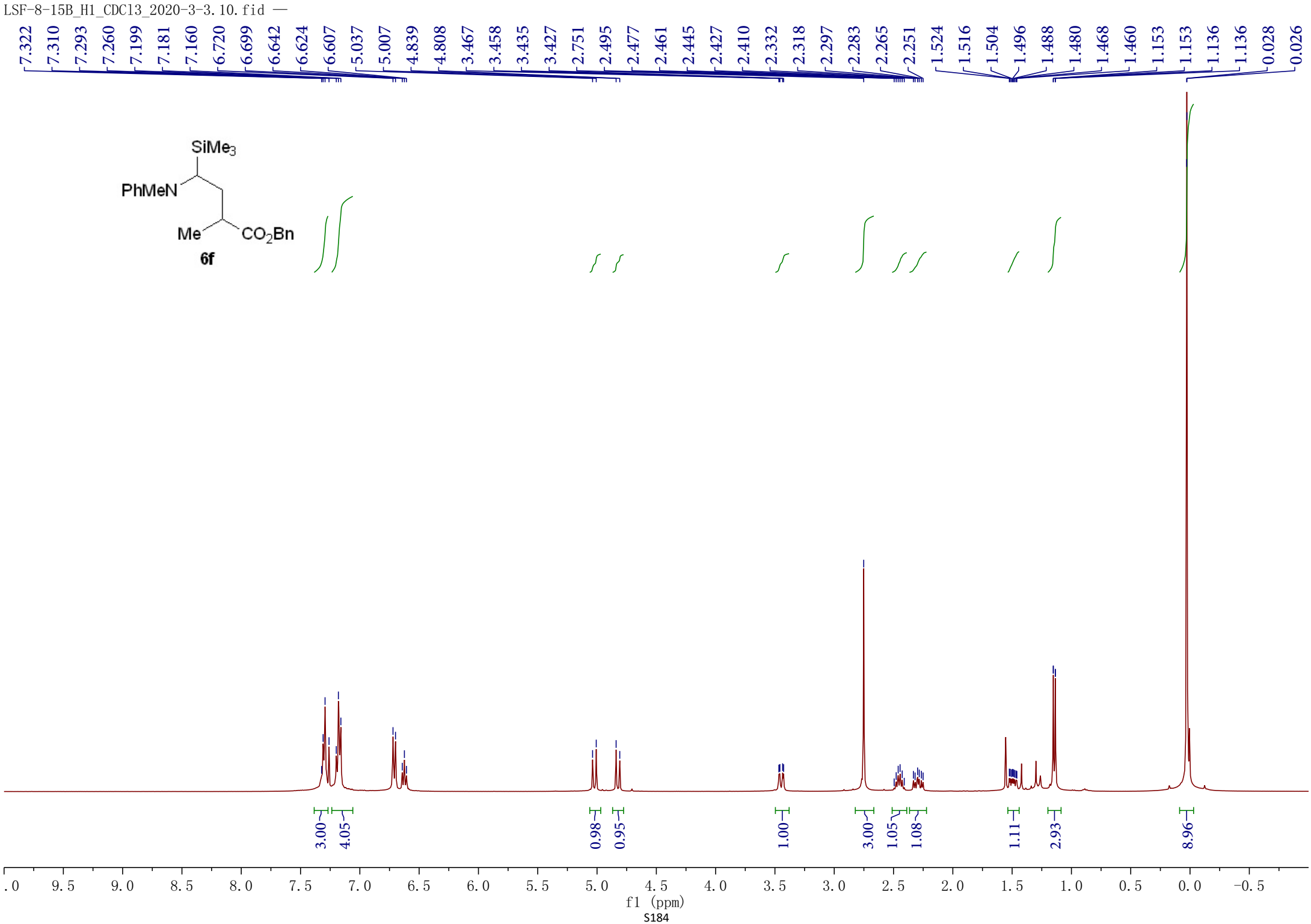
LSF-8-14B_C13_CDCl3_2020-3-3.10.fid

177.406
150.876
129.101
115.397
111.899
77.418
77.100
76.784
51.461
47.963
37.483
33.889
32.900
16.780
-1.607



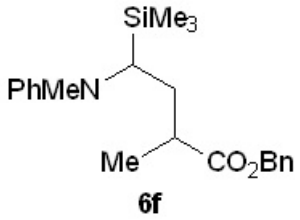
6e


LSF-8-15_H1_CDCl3_2020-3-4.20.fid
7.391 7.380 7.334 7.317 7.300 7.260 7.239 7.215 7.187 7.169 7.148 7.126 7.108 6.730 6.709 6.650 6.633 6.616 6.591 5.067 5.036 5.014 4.963 4.932 4.845 4.814 3.488 3.478 3.468 3.445 3.437 2.776 2.759 2.471 2.307 1.919 1.533 1.526 1.506 1.489 1.470 1.308 1.272 1.190 1.172 1.163 1.146
SiMe3
PhMeN
Me
CO2Bn
6f
(dr = 1.5:1)
2.776
2.759
1.00
1.48
2.82 2.81 2.80 2.79 2.78 2.77 2.76 2.75 2.74 2.73 2.72 2.71
f1 (ppm)
1.00
1.48
.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

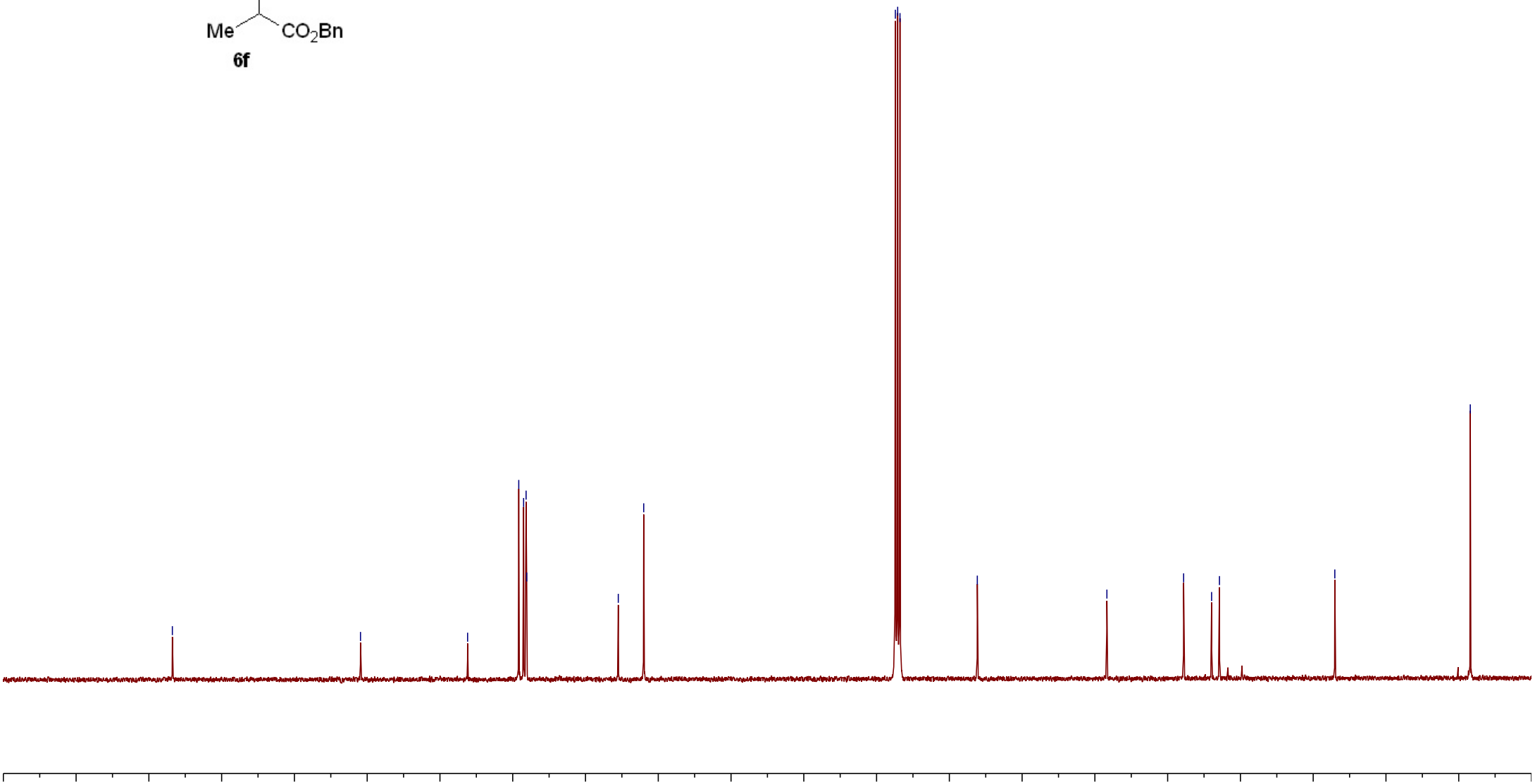

LSF-8-15B_H1_CDCl3_2020-3-3.10.fid
7.322 7.310 7.293 7.260 7.199 7.181 7.160 6.720 6.699 6.642 6.624 6.607 5.037 5.007 4.839 4.808 3.467 3.458 3.435 3.427 2.751 2.495 2.477 2.461 2.445 2.427 2.410 2.332 2.318 2.297 2.283 2.265 2.251 1.524 1.516 1.504 1.496 1.488 1.480 1.468 1.460 1.153 1.153 1.136 1.136 0.028 0.026
SiMe3
PhMeN
Me
CO2Bn
6f
3.00 4.05 0.98 0.95 1.00 3.00 1.05 1.08 1.11 2.93 8.96
f1 (ppm)

LSF-8-15B_C13_CDCl3_2020-3-3.10.fid

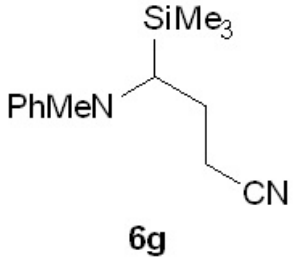
176.772
150.918
136.200
129.170
128.502
128.163
128.075
115.494
112.000
77.418
77.101
76.783
66.157
48.349
37.805
33.960
32.881
17.030
-1.587



6f



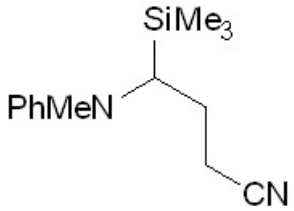
LSF-8-17_H1_CDCl3_2020-3-3.10.fid



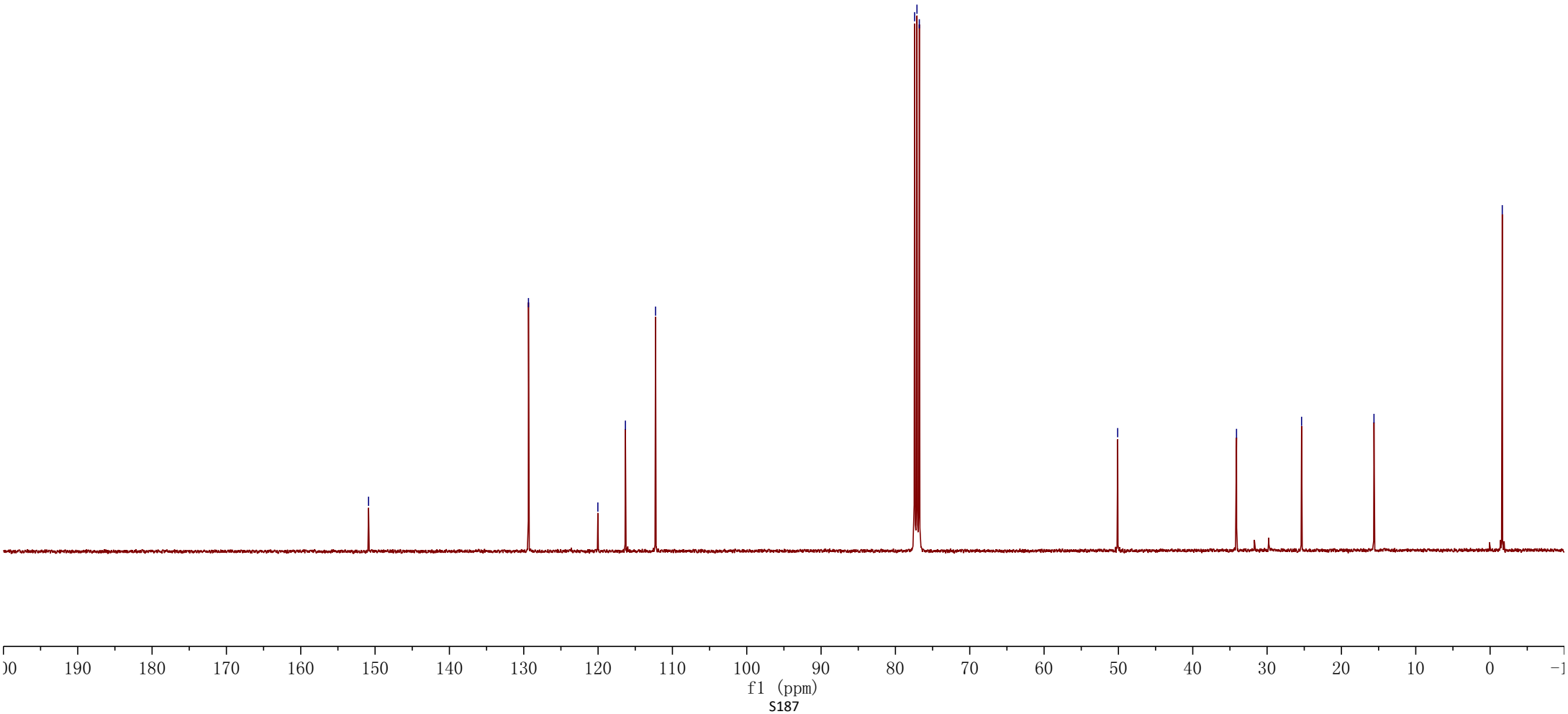
6g

LSF-8-17_C13_CDCl3_2020-3-3.10.fid

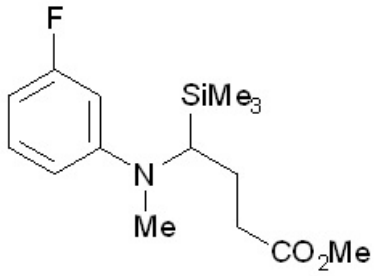
150.877
129.365
120.029
116.324
112.270
77.417
77.101
76.783
50.098
34.114
25.360
15.620
-1.639



6g

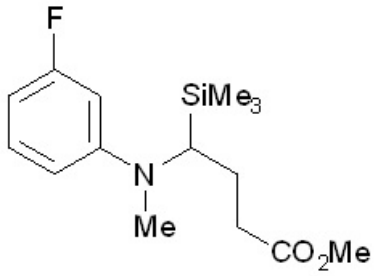


LSF-7-114A-CDCL3-H1-2020-2-20.10.fid



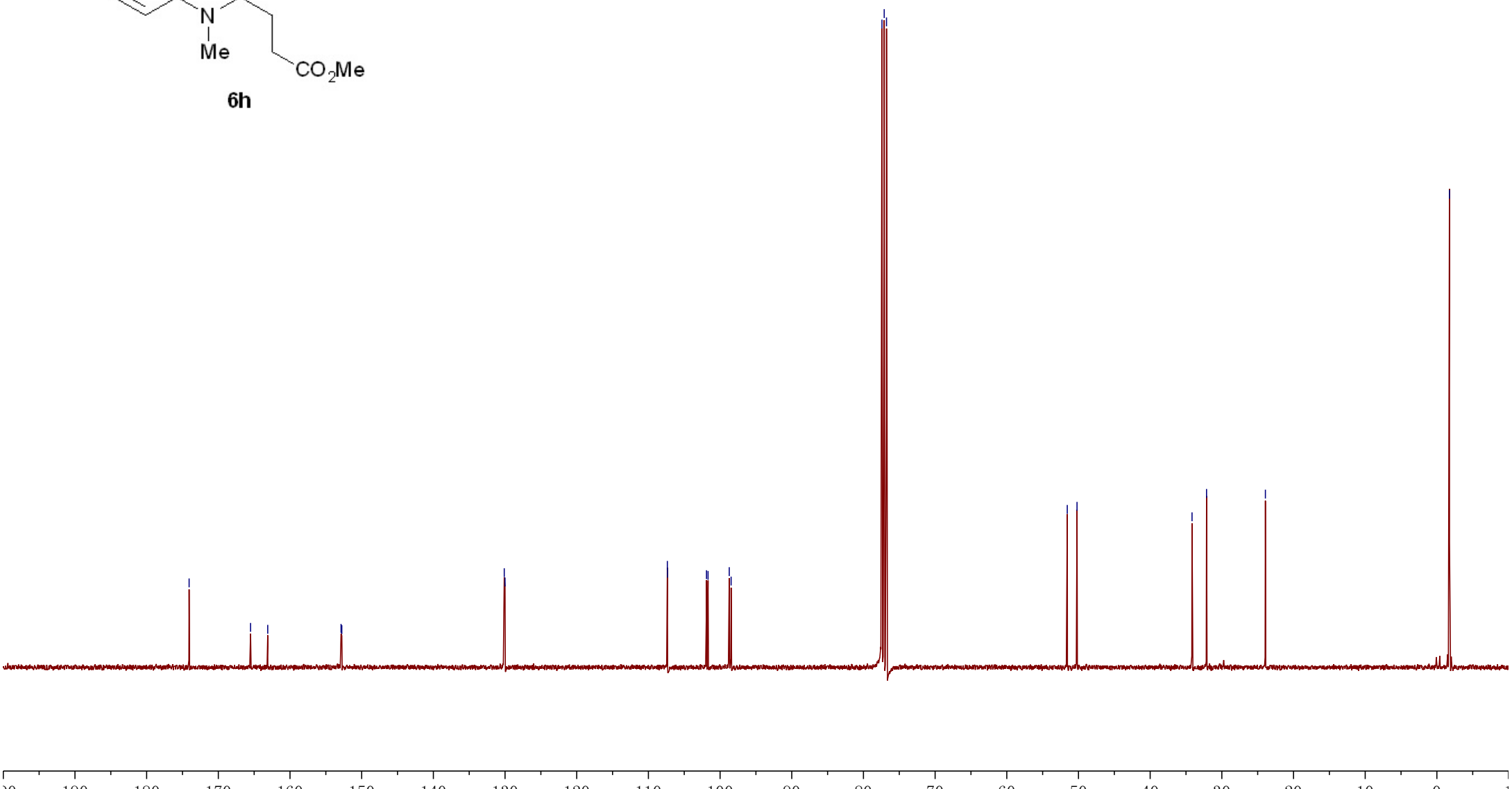
6h

LSF-7-114A-CDCL3-C13-2020-2-20.10.fid

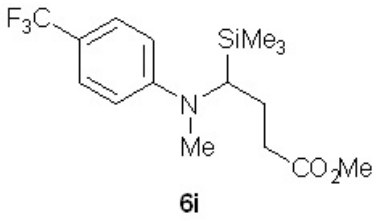


6h

174.075
165.503
163.106
152.878
152.772
130.110
130.005
107.357
107.336
101.895
101.679
98.720
98.461
77.417
77.101
76.783
51.564
50.203
34.158
32.133
23.924
-1.751



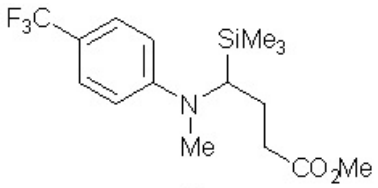
LSF-7-66P-CDCL3-H1-2020-1-14.10.fid



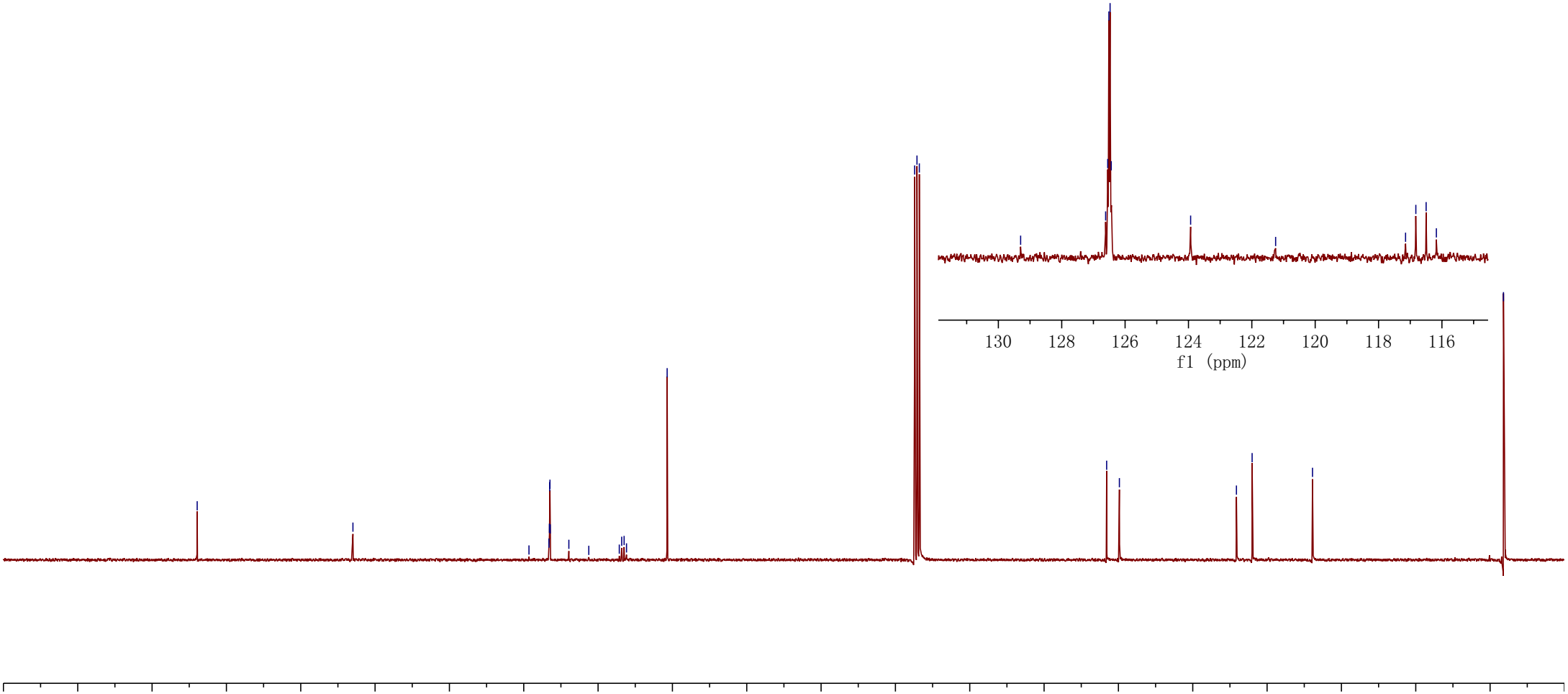
6i

LSF-7-66P-CDCL3-C13-2020-1-14.10.fid

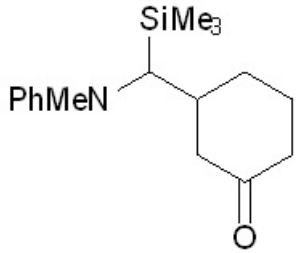
173.931 152.980 129.297 126.614 126.548 126.512 126.474 126.437 123.931 121.249 117.147 116.823 116.498 116.175 110.709 77.417 77.099 76.782 51.583 49.870 34.124 32.014 23.890 -1.800



6i

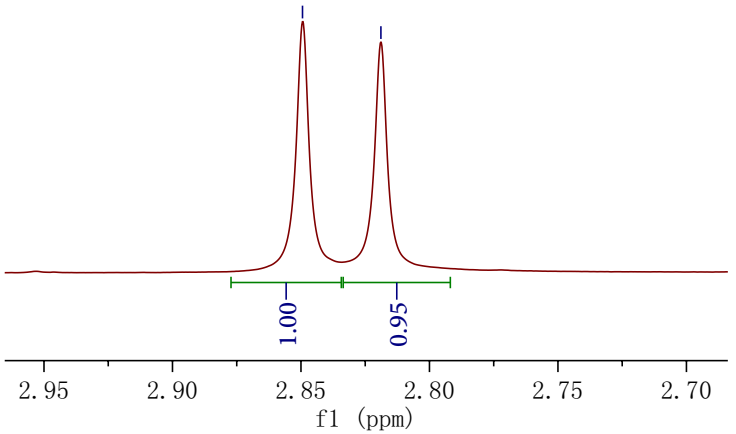


LSF-7-103_H1_CDCl3_2020-2-14.20.fid

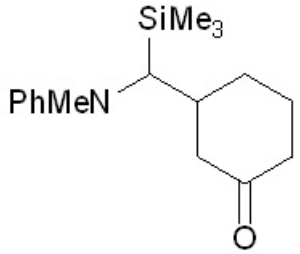


6j

(*dr* = 1:1)

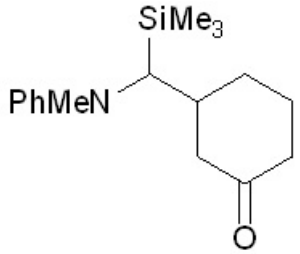


LSF-6-79DP_H1_CDCl3_2019-11-29.30.fid



6j

LSF-6-79DP_C13_CDCl3_2019-11-29.70.fid

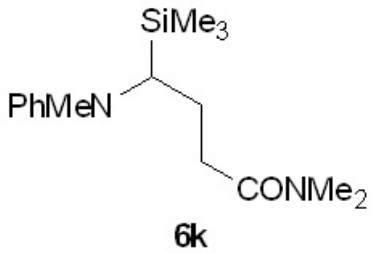


6j

150.664
129.234
115.241
111.336
77.418
77.101
76.783
56.042
47.385
41.573
40.892
35.200
30.543
25.913
-0.229

f1 (ppm)

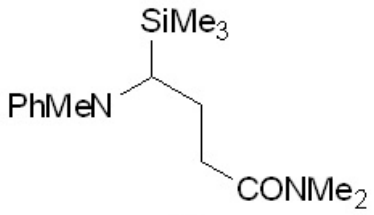
LSF-6-8P_H1_CDCl3_2019-10-19.10.fid



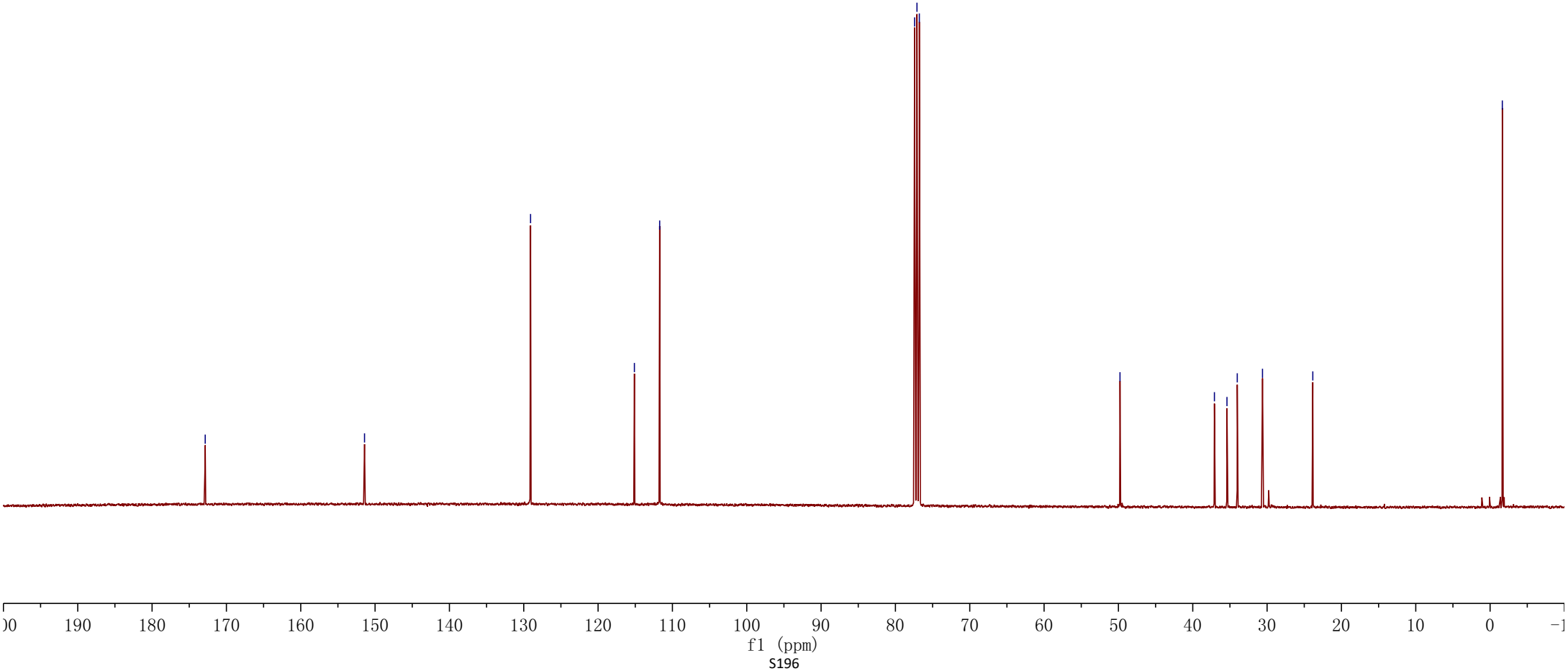
6k

LSF-6-8P_C13_CDCl3_2019-10-19.10.fid

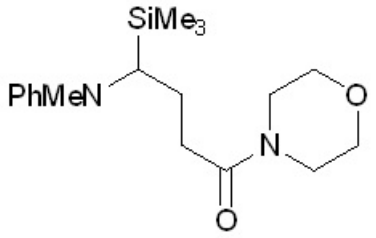
172.852
151.421
129.083
115.115
111.714
77.418
77.100
76.782
49.790
37.087
35.398
34.014
30.619
23.851
-1.645



6k



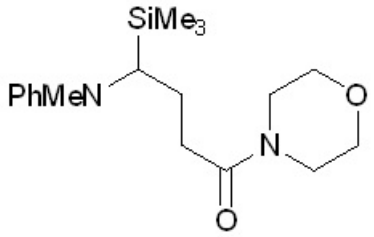
LSF-6-49P-CDCL3-H1-2019-11-12.10.fid



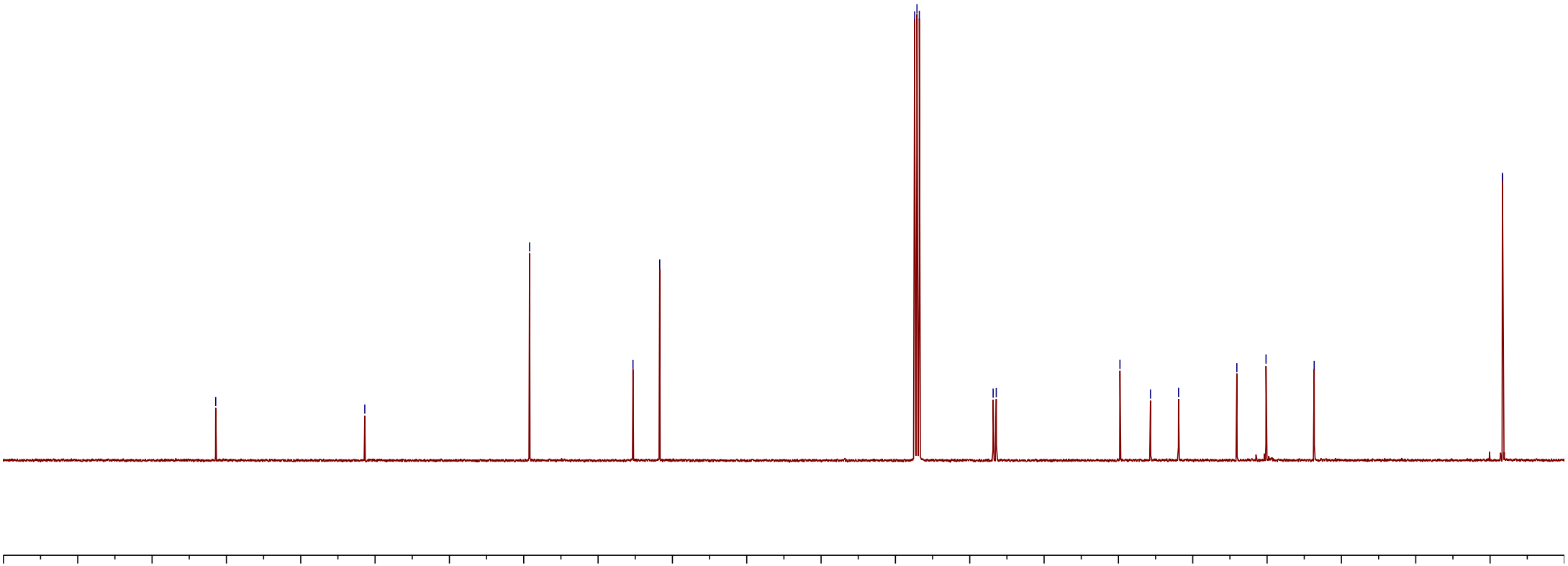
6l

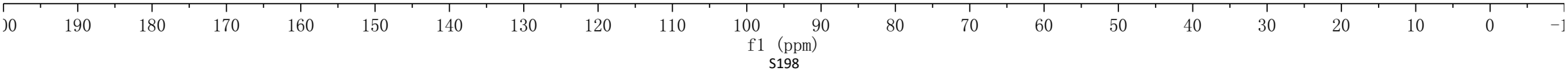
LSF-6-49P-CDCL3-C13-2019-11-12.10.fid

171.438
151.383
129.215
115.305
111.708
77.417
77.100
76.782
66.853
66.435
49.794
45.691
41.910
34.069
30.143
23.664
-1.659

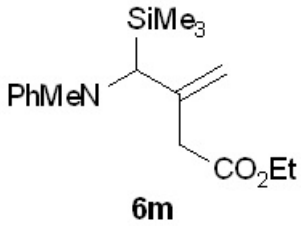


6l





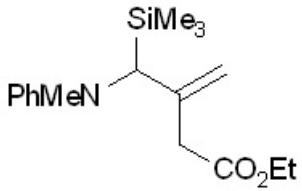
LSF-6-70P_H1_CDCl3_2020-1-21.10.fid



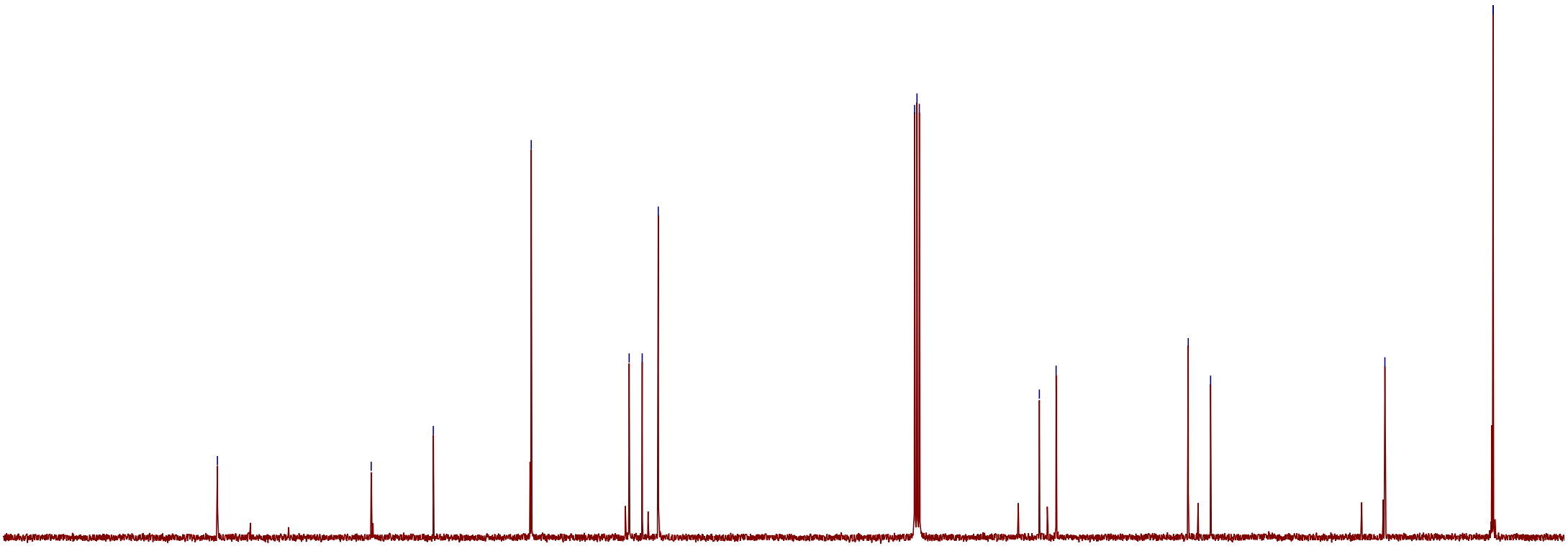
6m

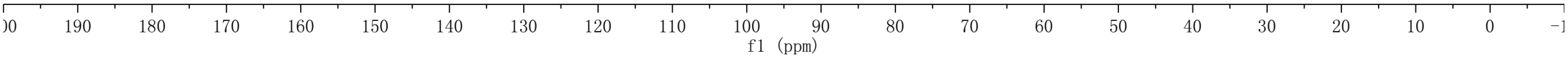
LSF-6-70P_C13_CDCl3_2020-1-21.10.fid

171.211
150.523
142.168
128.995
115.821
114.065
111.903
77.418
77.100
76.783
60.639
58.384
40.607
37.601
14.153
-0.397

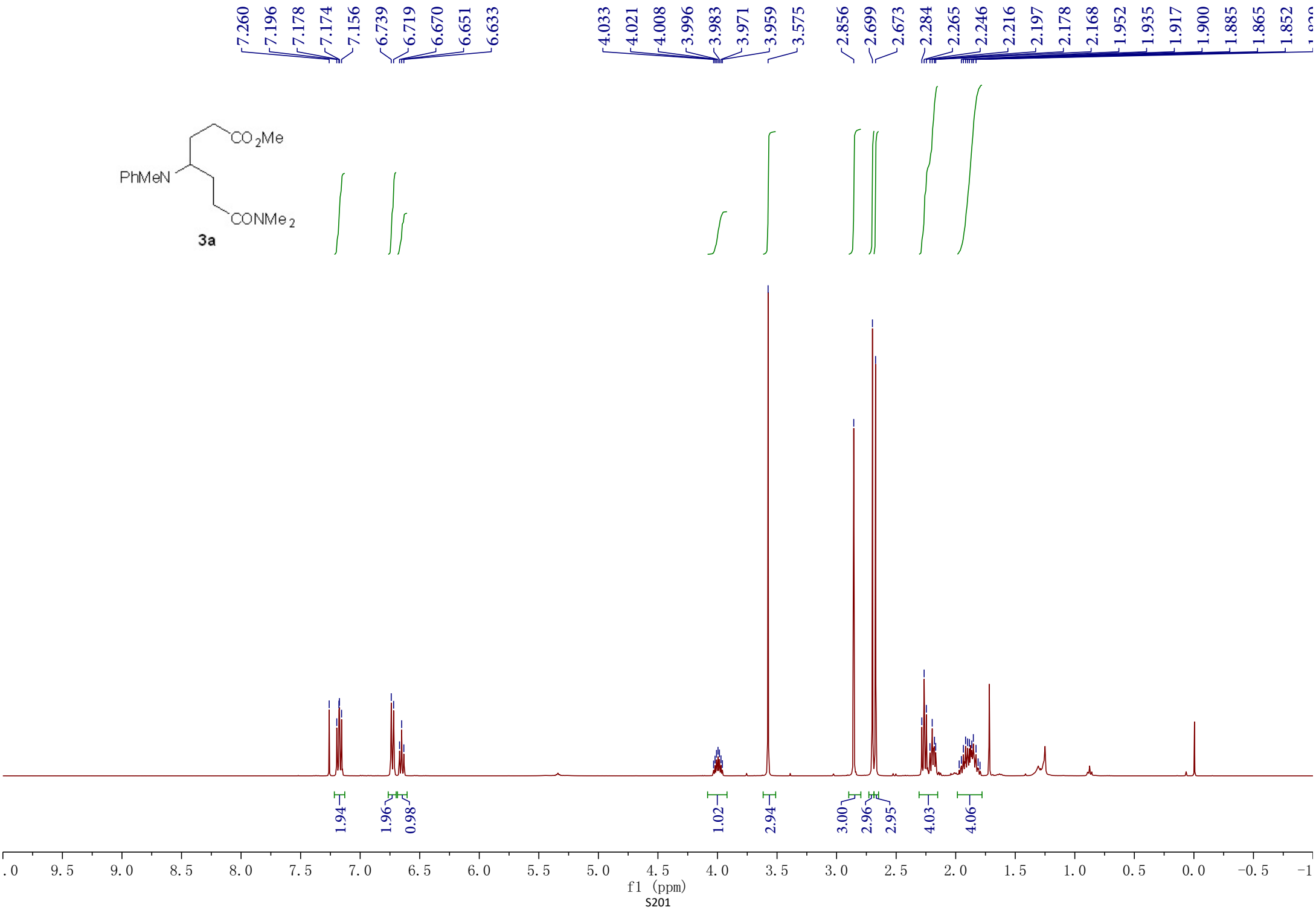


6m



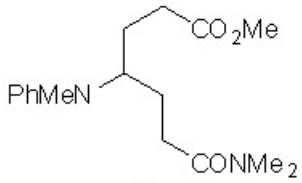


LSF-6-42P-CDCL3-H1-2019-11-7.10.fid —

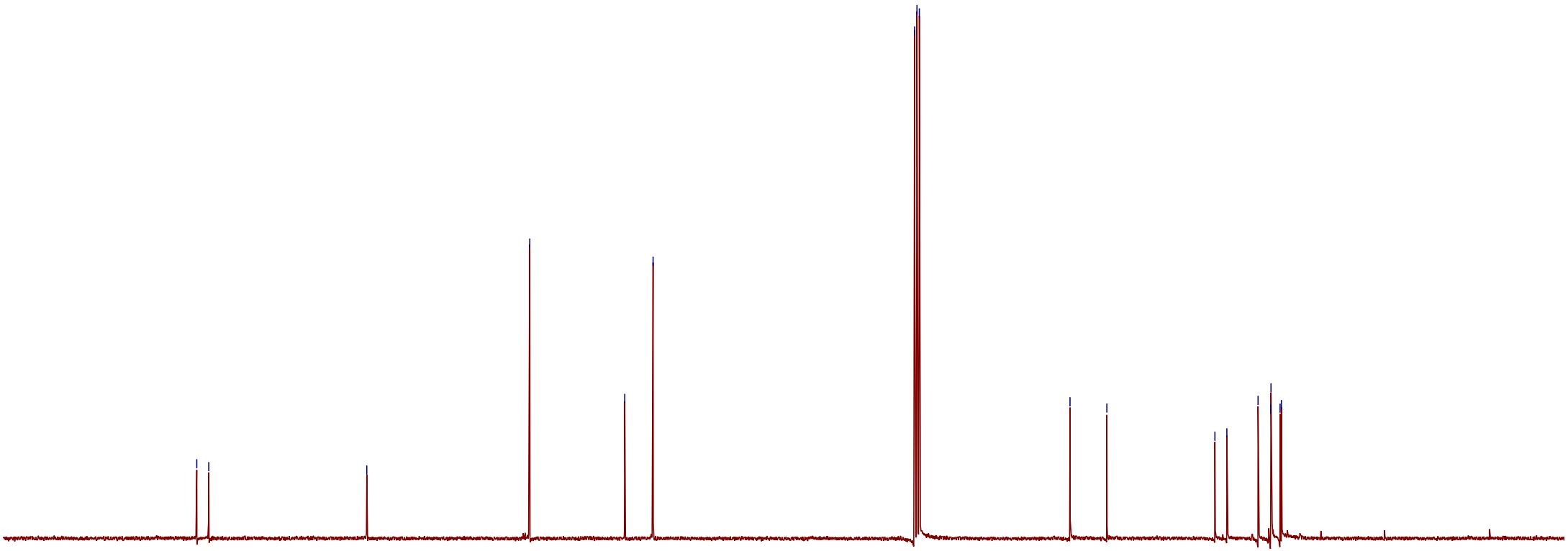


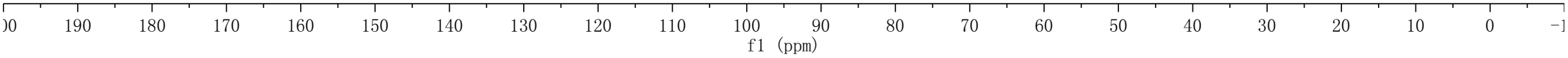
LSF-6-42P-CDCL3-C13-2019-11-7.10.fid

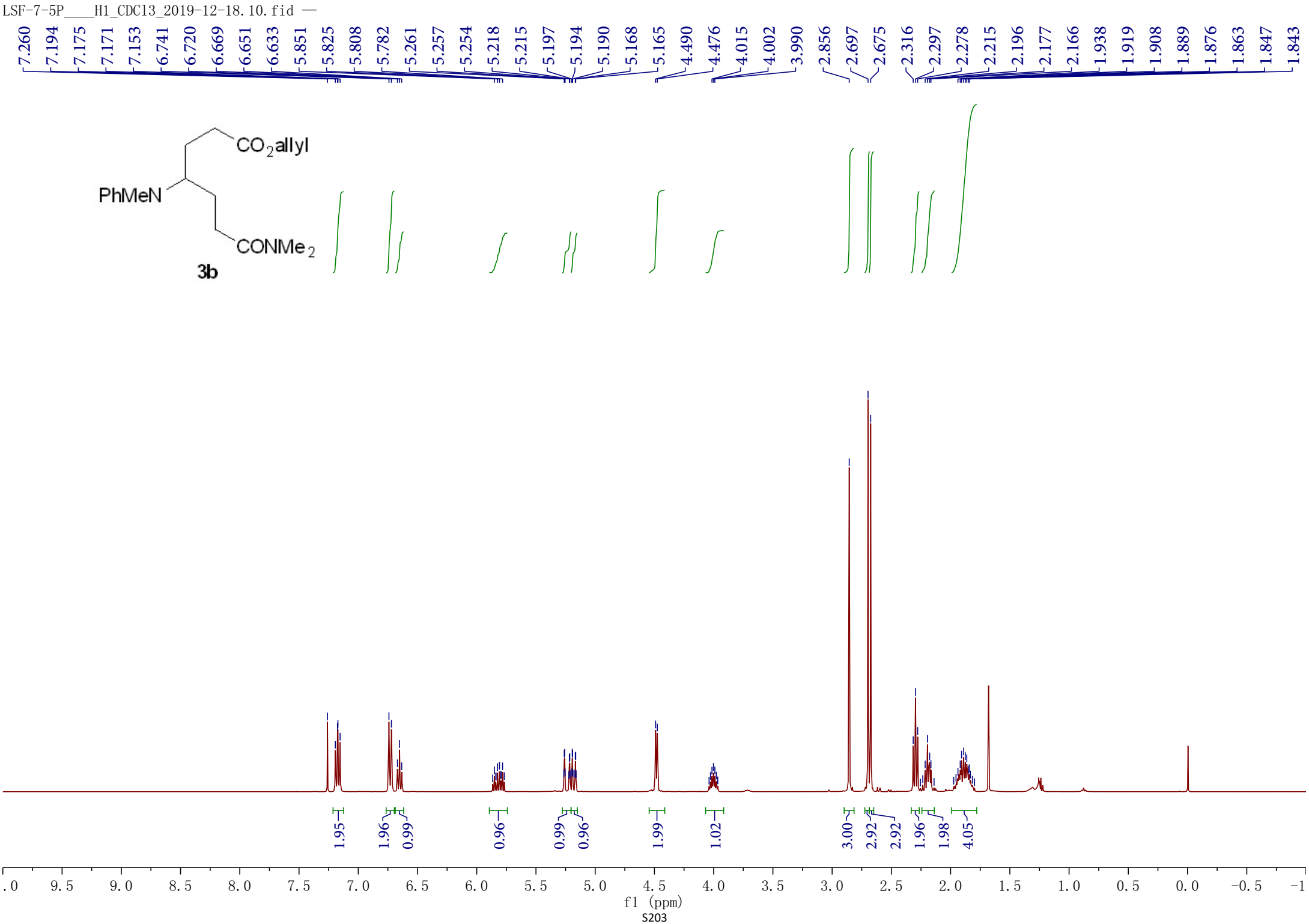
173.987
172.373
151.115
129.190
116.411
112.601
77.417
77.100
76.782
56.511
51.557
37.019
35.413
31.215
29.516
29.474
28.253
28.074



3a

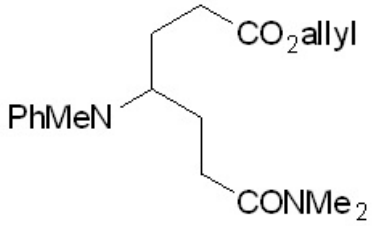




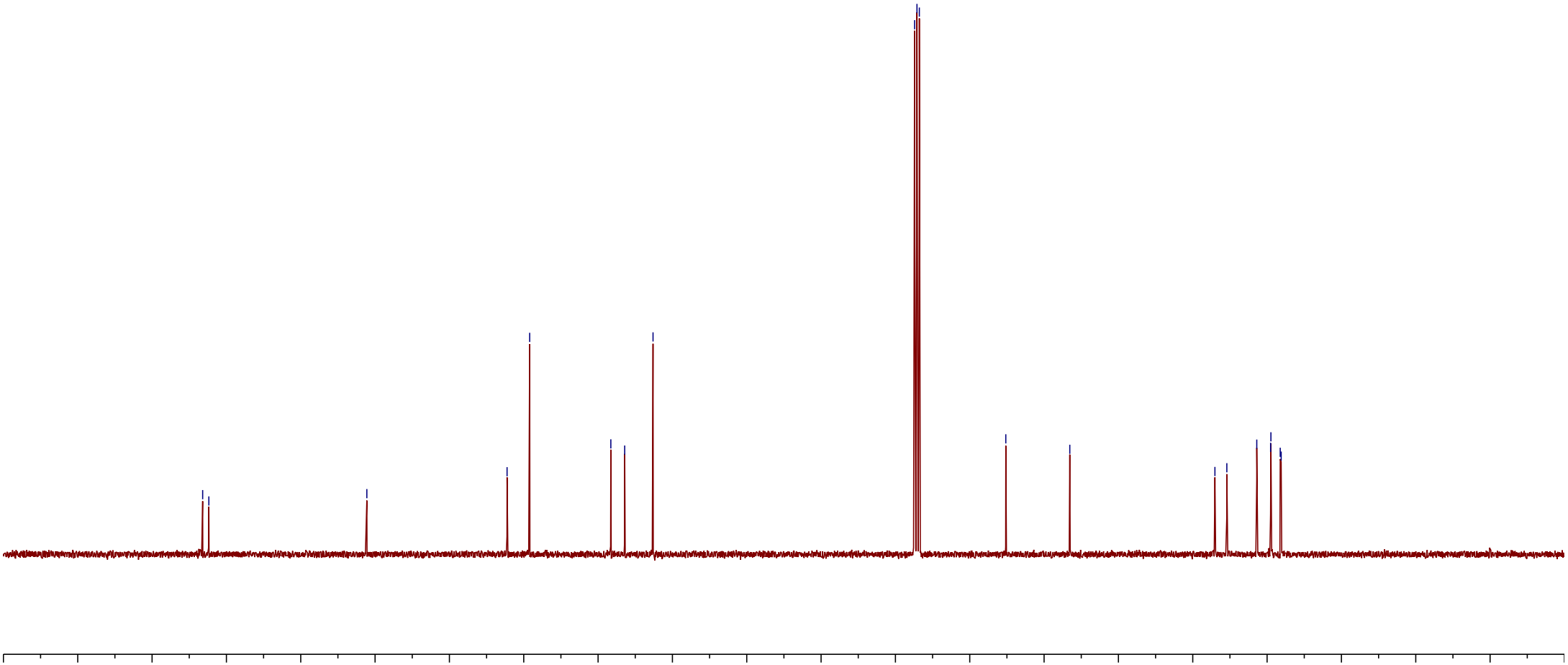

LSF-7-5P____H1_CDCl3_2019-12-18.10.fid
7.260
7.194
7.175
7.171
7.153
6.741
6.720
6.669
6.651
6.633
5.851
5.825
5.808
5.782
5.261
5.257
5.254
5.218
5.215
5.197
5.194
5.190
5.168
5.165
4.490
4.476
4.015
4.002
3.990
2.856
2.697
2.675
2.316
2.297
2.278
2.215
2.196
2.177
2.166
1.938
1.919
1.908
1.889
1.876
1.863
1.847
1.843
CO2allyl
PhMeN
CONMe2
3b
1.95
1.96
0.99
0.96
0.99
0.96
1.99
1.02
3.00
2.92
2.92
1.96
1.98
4.05
f1 (ppm)

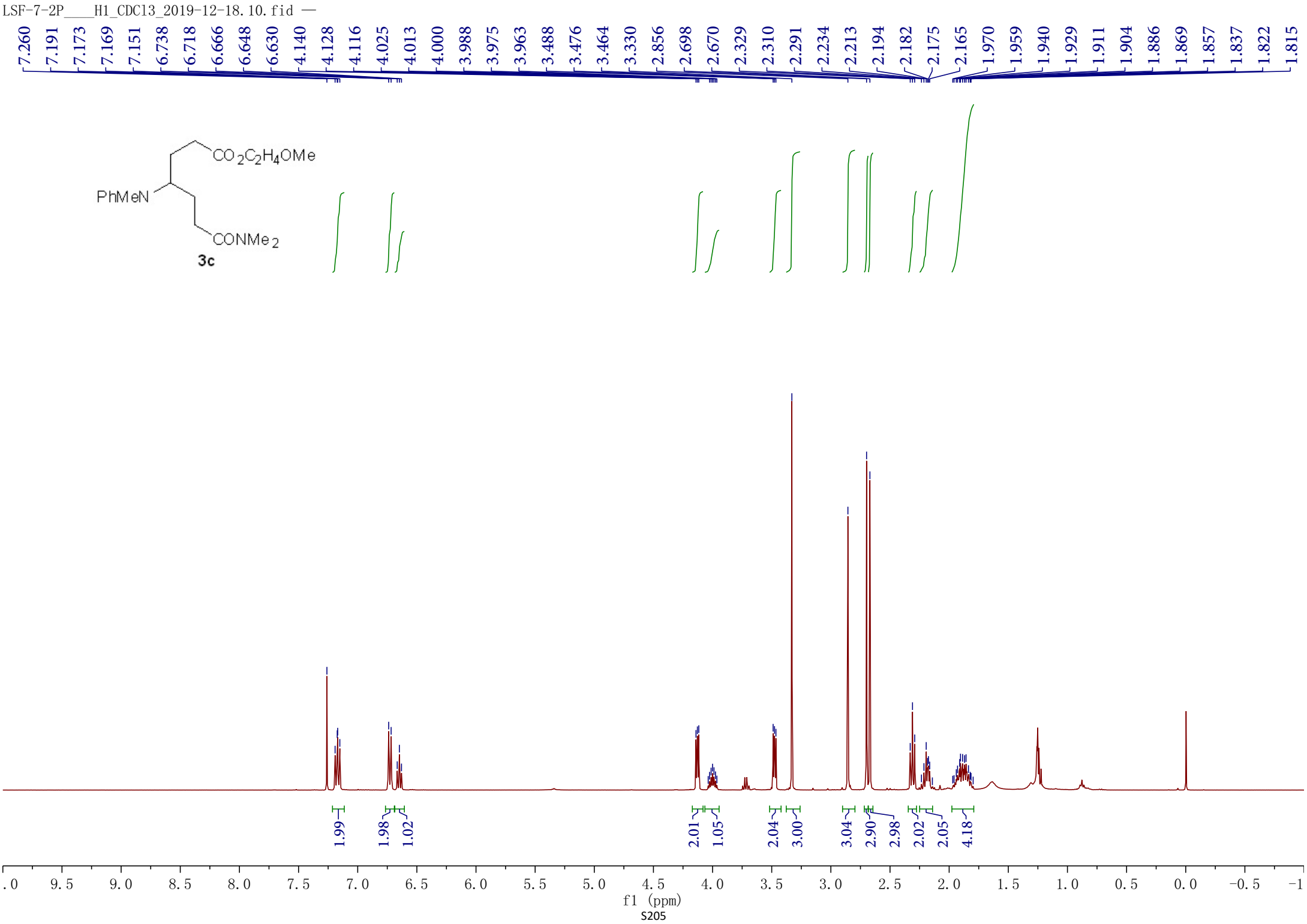
LSF-7-5P____C13_CDCl3_2019-12-18.21.fid

173.194
172.362
151.108
132.243
129.202
118.285
116.420
112.608
77.418
77.101
76.783
65.150
56.541
37.018
35.415
31.387
29.526
29.487
28.234
28.106

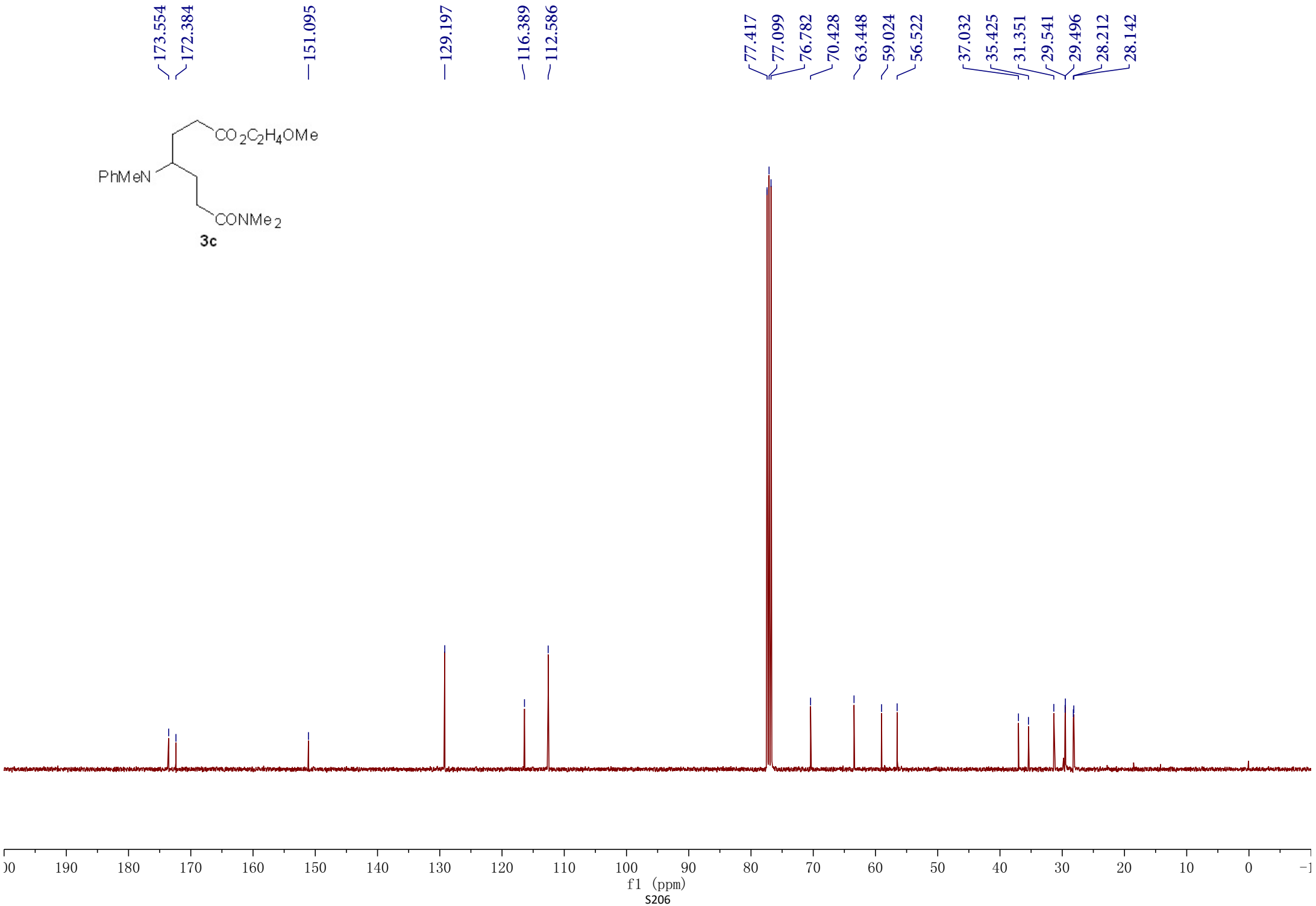


3b

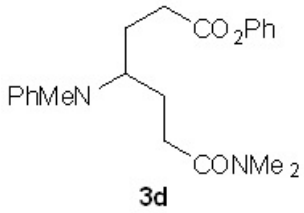



LSF-7-2P____H1_CDCl3_2019-12-18.10.fid
7.260
7.191
7.173
7.169
7.151
6.738
6.718
6.666
6.648
6.630
4.140
4.128
4.116
4.025
4.013
4.000
3.988
3.975
3.963
3.488
3.476
3.464
3.330
2.856
2.698
2.670
2.329
2.310
2.291
2.234
2.213
2.194
2.182
2.175
2.165
1.970
1.959
1.940
1.929
1.911
1.904
1.886
1.869
1.857
1.837
1.822
1.815
CO2C2H4OMe
PhMeN
CONMe2
3c
1.99
1.98
1.02
2.01
1.05
2.04
3.00
3.04
2.90
2.98
2.02
2.05
4.18
f1 (ppm)

LSF-7-2P____C13_CDCl3_2019-12-18.10.fid



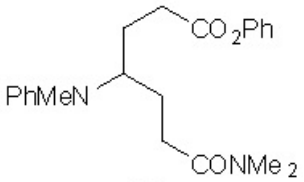
LSF-7-4P_H1_CDCl3_2019-12-19.90.fid



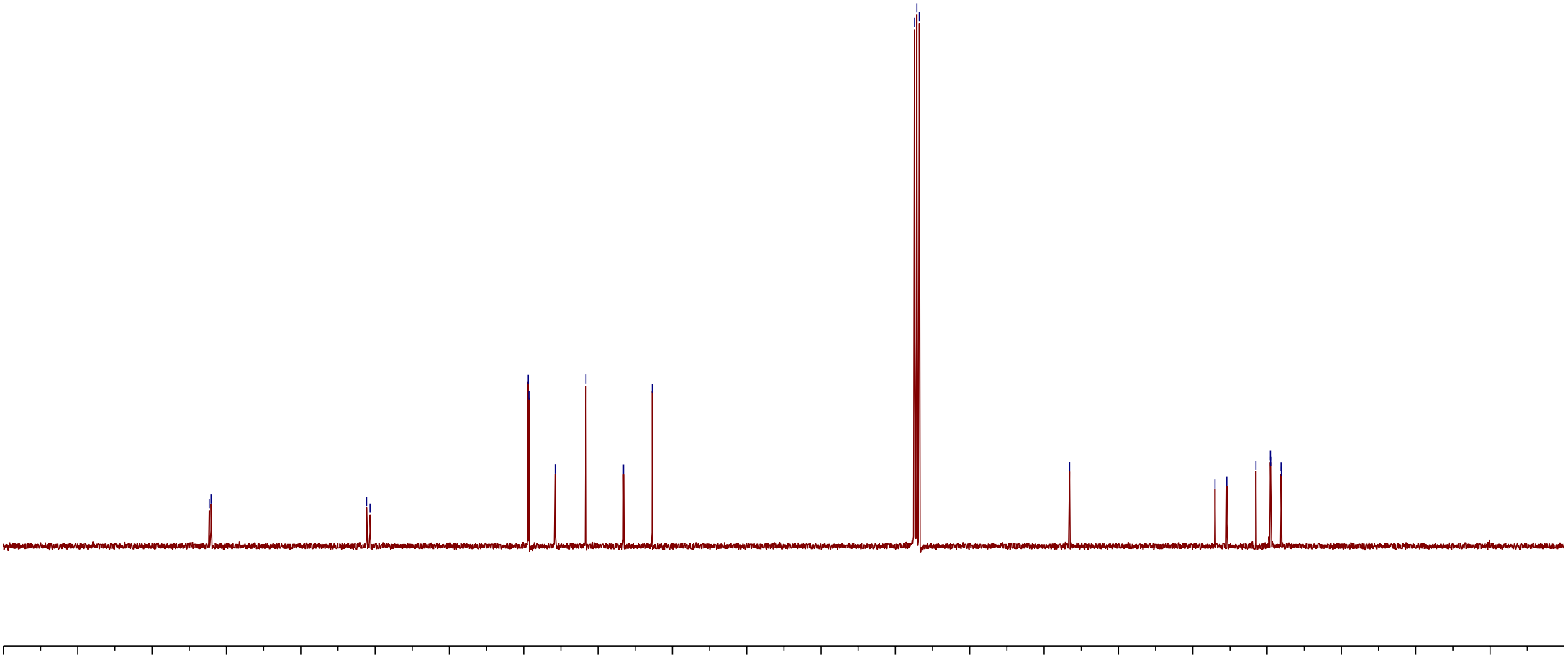
3d

LSF-7-4P_C13_CDCl3_2019-12-18.10.fid

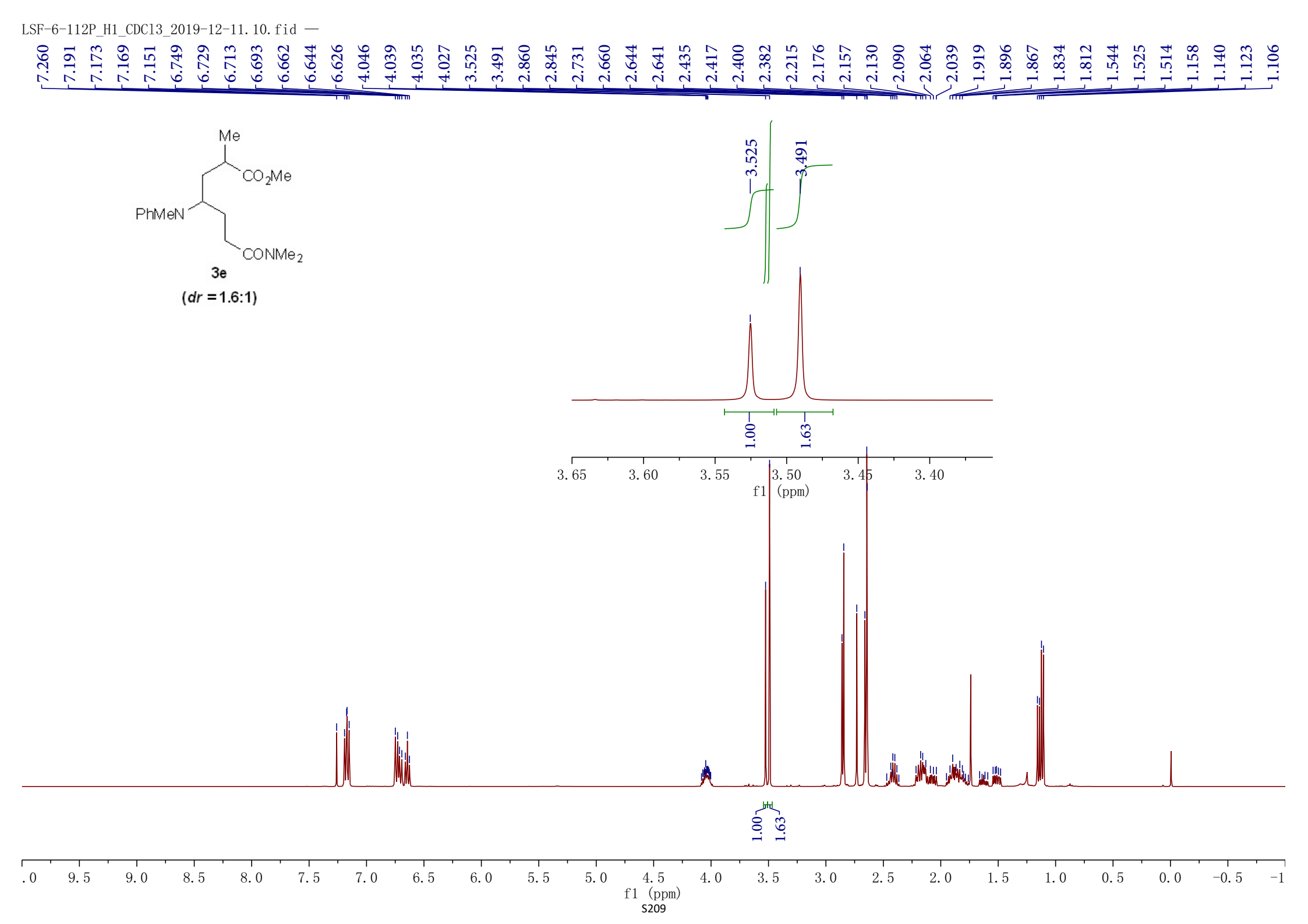
172.310
172.065
151.144
150.684
129.383
129.298
125.758
121.628
116.577
112.702
77.419
77.101
76.783
56.571
37.011
35.424
31.502
29.557
29.529
28.127
28.082



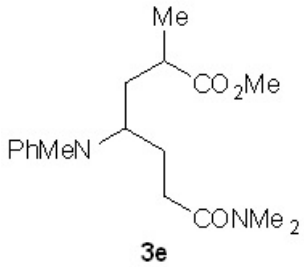
3d



LSF-6-112P_H1_CDCl3_2019-12-11.10.fid



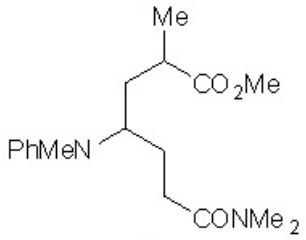
LSF-6-112P_H1_CDCl3_2019-12-11.10.fid



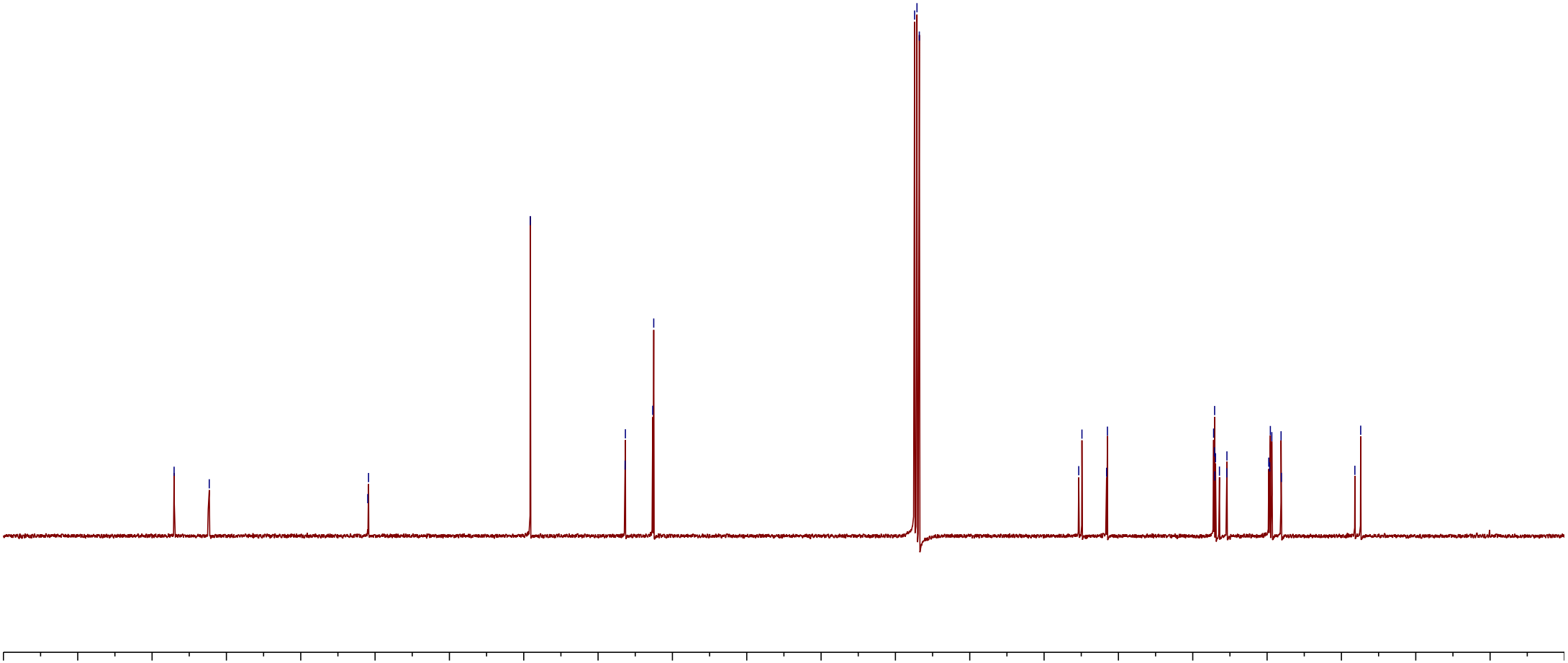
3e

LSF-6-112P_C13_CDCl3_2019-12-11.10.fid

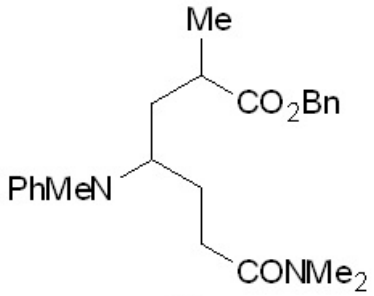
177.037
172.308
150.986
150.879
129.116
116.365
116.326
112.650
112.512
77.418
77.100
76.783
55.340
54.907
51.593
51.478
37.194
37.076
37.060
36.942
35.404
29.776
29.655
29.561
29.365
28.120
18.191



3e



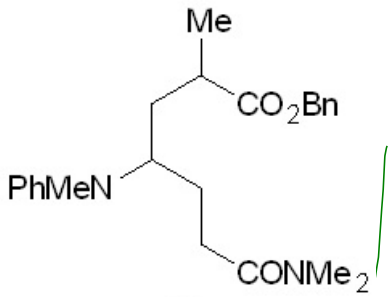
LSF-7-3P_H1_CDCl3_2019-12-18.20.fid



3f

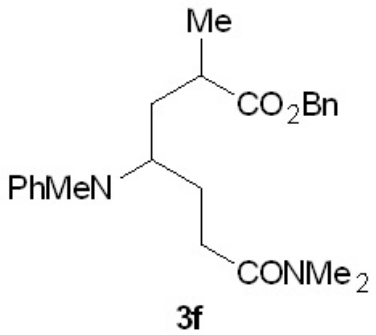
(*dr* = 1.5:1)

LSF-7-3P_H1_CDCl3_2019-12-18.20.fid



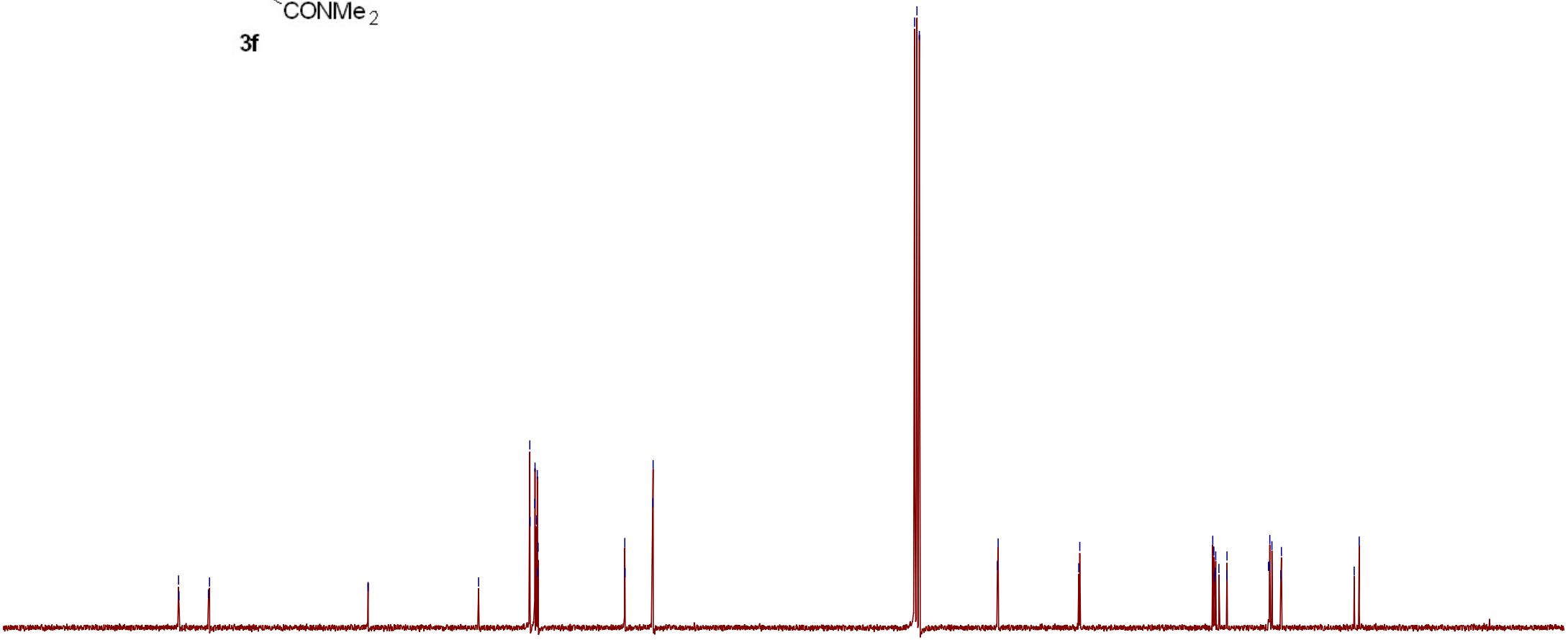
3f

LSF-7-3P_C13_CDCl3_2019-12-18.20.fid



3f

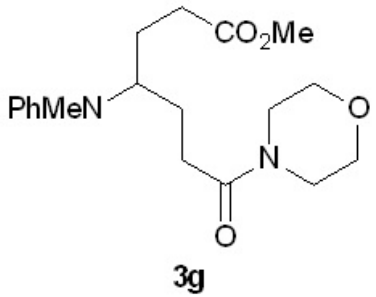
176.438 176.391 172.417 172.271 150.942 136.076 129.185 129.156 128.512 128.483 128.289 128.177 128.124 128.065 116.407 116.377 112.625 112.595 77.418 77.100 76.783 66.283 66.180 55.335 55.197 37.310 37.162 36.954 36.912 36.483 35.394 29.816 29.686 29.634 29.349 28.074 18.280



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

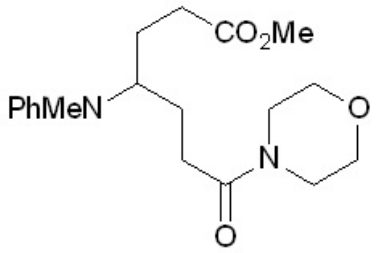
f1 (ppm)

LSF-7-49P_H1_CDCl3_2020-1-7.20.fid



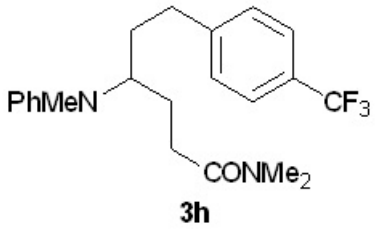
3g

LSF-7-49P_C13_CDCl3_2020-1-7.20.fid



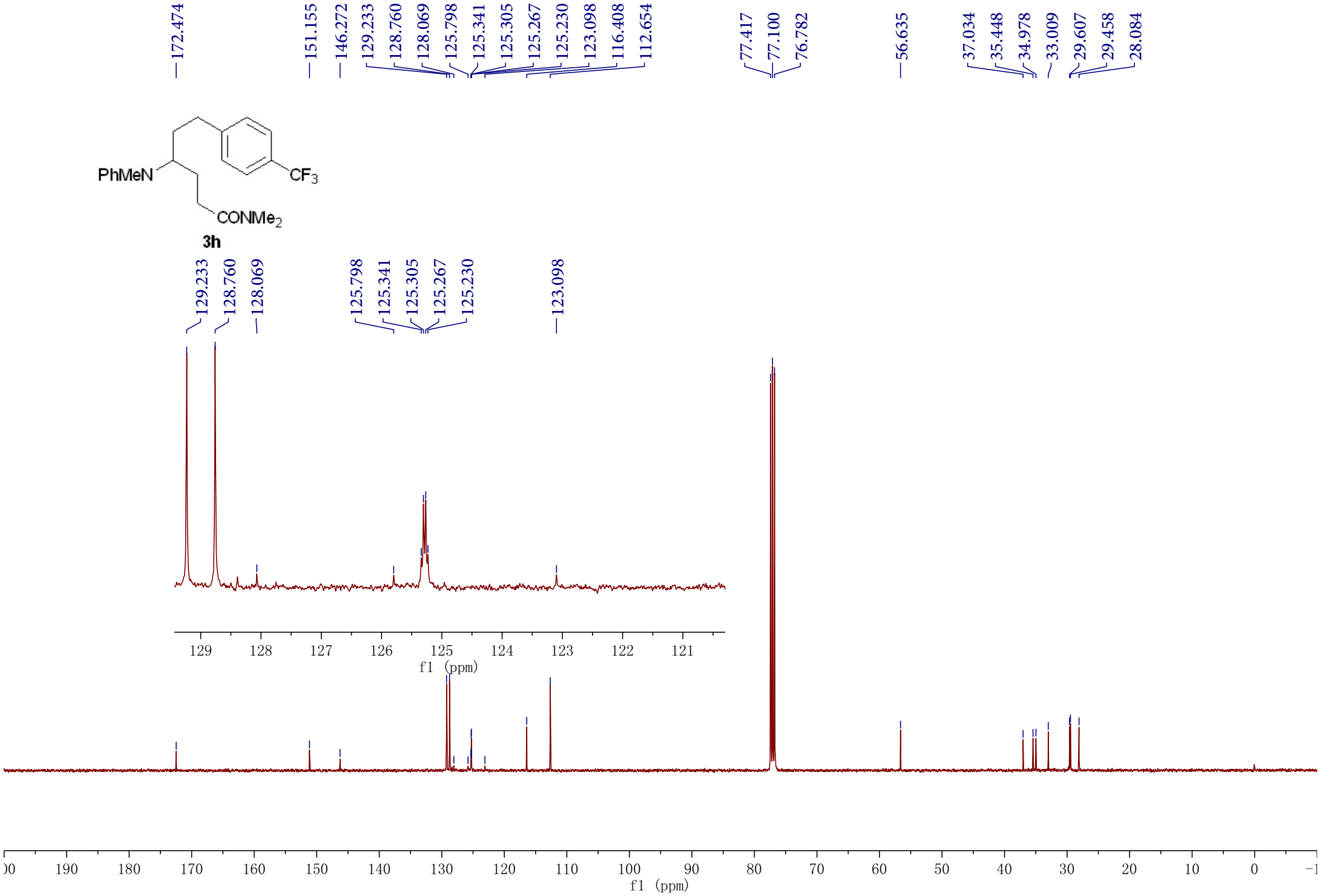
3g

LSF-7-34P_H1_CDCl3_2020-1-7.10.fid

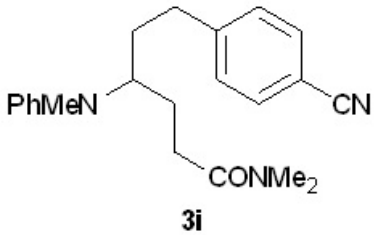


3h

LSF-7-34P_C13_CDCl3_2020-1-7.10.fid



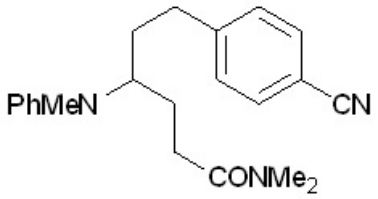
LSF-7-33P_H1_CDCl3_2020-1-1.10.fid



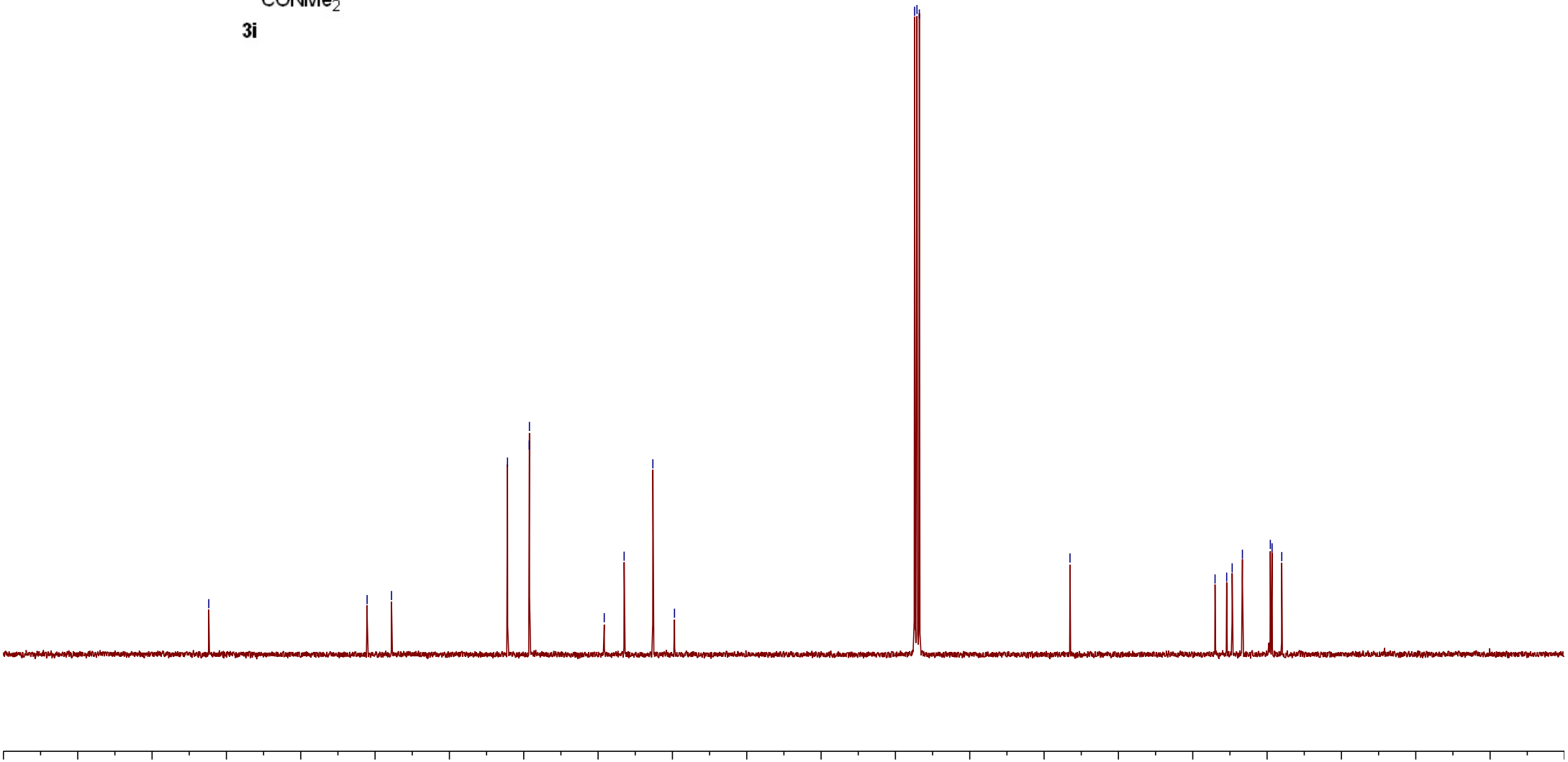
3i

LSF-7-33P_C13_CDCl3_2020-1-1.10.fid

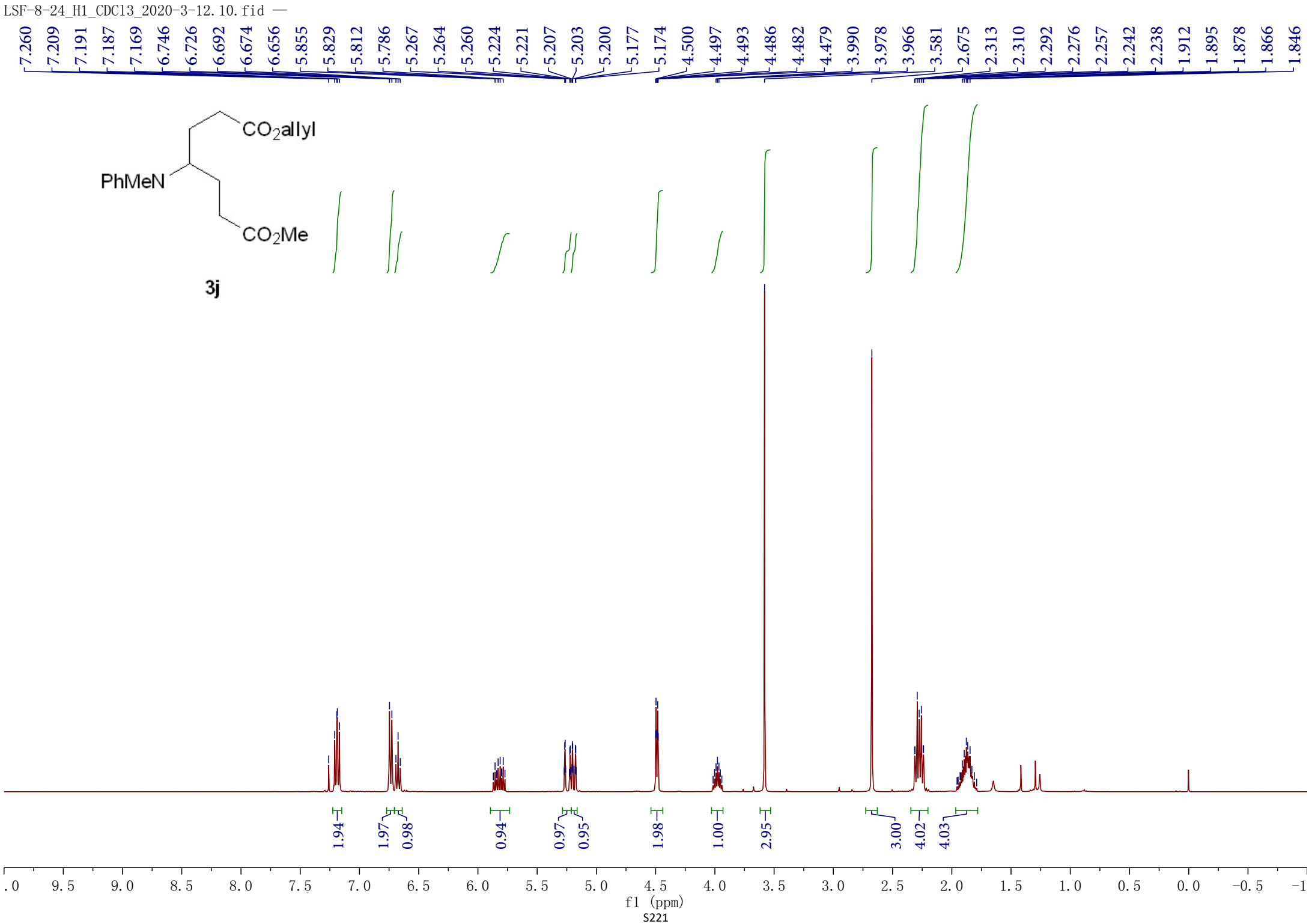
172.372
151.072
147.790
132.186
129.262
129.238
119.171
116.495
112.629
109.721
77.418
77.101
76.783
56.514
37.001
35.437
34.699
33.320
29.564
29.328
28.026



3i

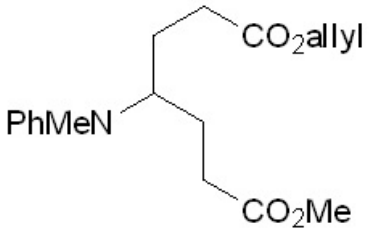


f1 (ppm)

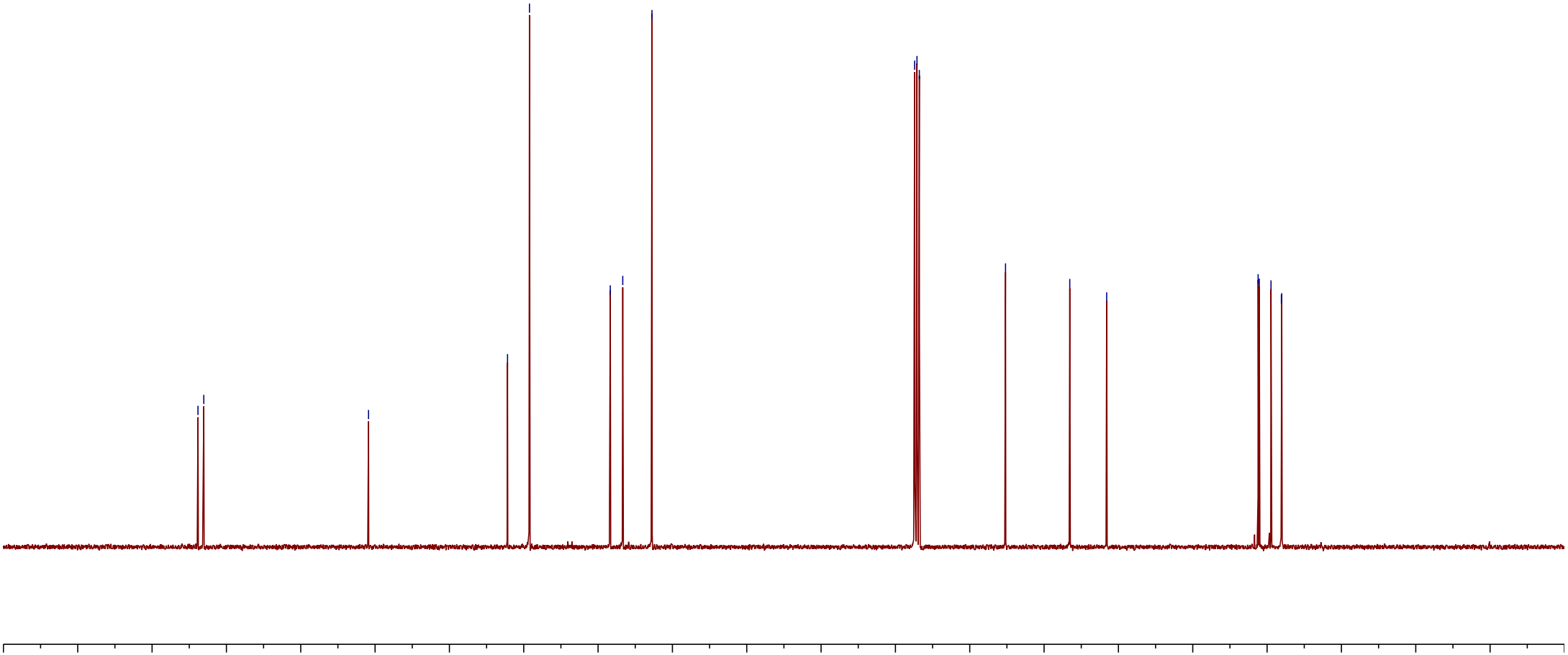

LSF-8-24_H1_CDCl3_2020-3-12.10.fid
7.260
7.209
7.191
7.187
7.169
6.746
6.726
6.692
6.674
6.656
5.855
5.829
5.812
5.786
5.267
5.264
5.260
5.224
5.221
5.207
5.203
5.200
5.177
5.174
4.500
4.497
4.493
4.486
4.482
4.479
3.990
3.978
3.966
3.581
2.675
2.313
2.310
2.292
2.276
2.257
2.242
2.238
1.912
1.895
1.878
1.866
1.846
CO2allyl
PhMeN
CO2Me
3j
1.94
1.97
0.98
0.94
0.97
0.95
1.98
1.00
2.95
3.00
4.02
4.03
f1 (ppm)

LSF-8-24_C13_CDCl3_2020-3-12.10.fid

173.825
173.043
150.882
132.182
129.231
118.357
116.679
112.747
77.417
77.100
76.782
65.188
56.545
51.579
31.206
31.051
29.473
28.079
28.026

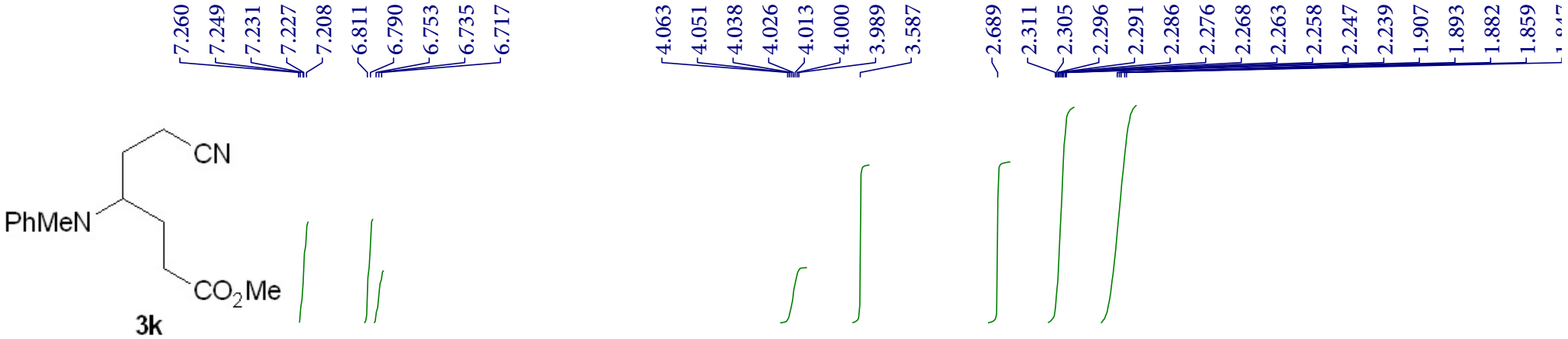


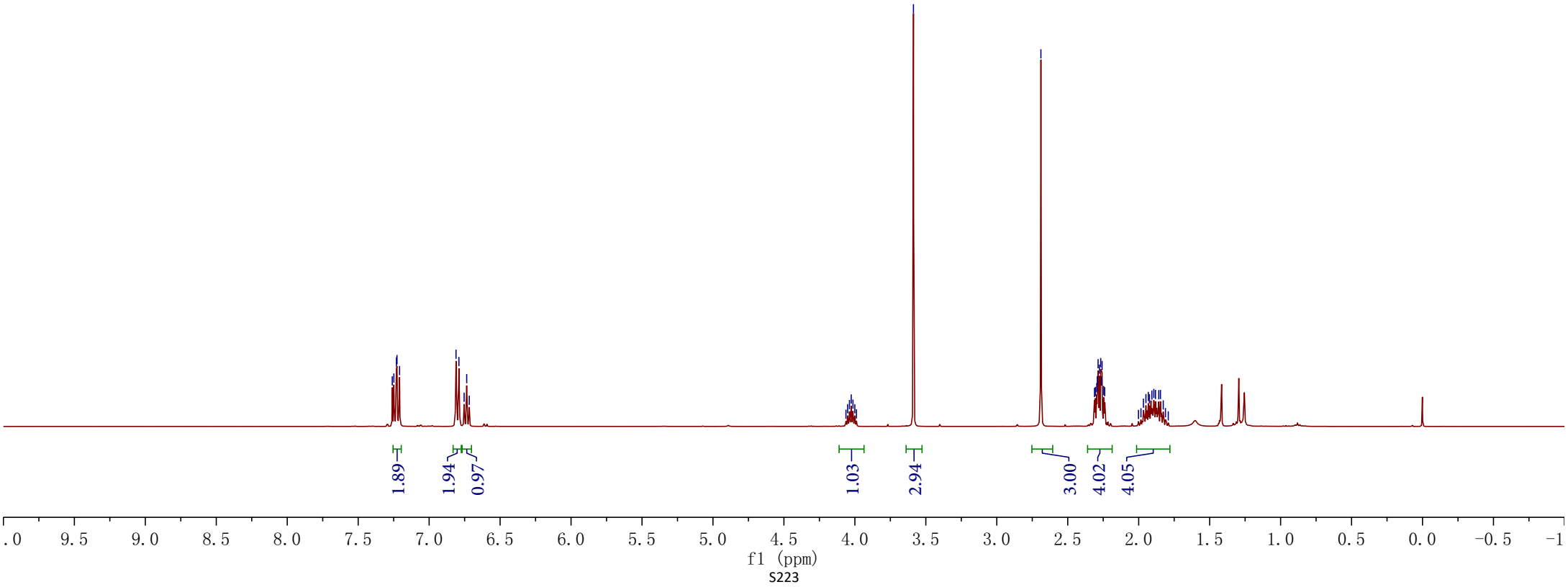
3j



f1 (ppm)

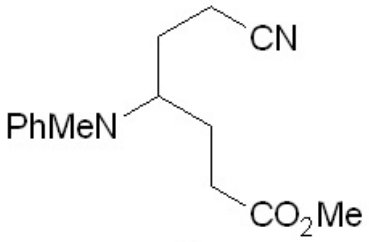
LSF-8-25_H1_CDCl3_2020-3-12.10.fid —





LSF-8-25_C13_CDCl3_2020-3-12.10.fid

173.515
150.540
129.455
119.590
117.556
113.156
77.418
77.100
76.783
56.511
51.697
30.793
29.575
28.901
27.700
14.625



3k