Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of Unsymmetrical Diarylmethanols via C-Si bond Bifunctionalization Enabled by Sequential [1,4]-Csp2 to O-Silyl Migration

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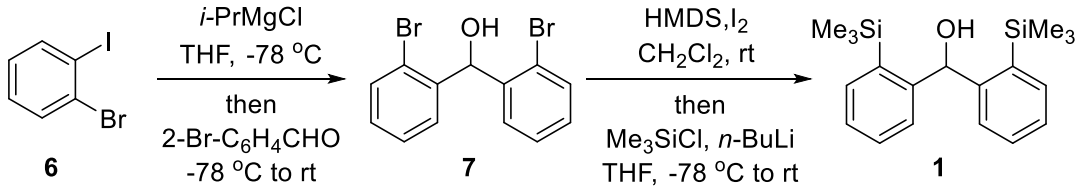
1. General Methods

Commercial reagents were used without any purification. All reactions were performed using common anhydrous, inert atmosphere techniques. Reactions were monitored by TLC which was performed on glass-backed silica plates 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 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian and Bruker) and 600 MHz (Agilent), ^{13}C NMR spectra were recorded at 100 MHz (Bruker) and 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. 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 1



To a solution of 2-bromo-iodobenzene **6** (14 g, 50 mmol, 6.3 mL) in THF (500 mL) at -78 °C under argon was added *i*-PrMgCl (27 mL, 2.0 M in THF). The reaction stirred for 30 min before adding 2-bromobenzaldehyde (9.25 g, 50 mmol, 6.1 mL) at -78 °C. The mixture was warmed to room temperature and reacted overnight. The reaction was quenched with sat. aq. HCl (15 mL, 1 *N*) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford bis(2-bromophenyl)methanol **7** (17 g) as a colorless solid, which was used for the next step without purification.

A solution of bis(2-bromophenyl)methanol **7** (17 g, 50 mmol), hexamethyldisilazane

(7.3 mL, 35 mmol) and ten crystals of iodine in CH_2Cl_2 (100 mL) was stirred at room temperature for 15 min. The reaction was quenched with $Na_2S_2O_3$ (20 g). After stirring for 30 min, the mixture was passed through a short pad of silica and concentrated under reduced pressure to give the crude silyl ether, which was used for the next step without purification.

To a solution of the crude silyl ether and chlorotrimethylsilane（38 mL, 300 mmol) in dry THF (500 mL) was added *n*-butyllithium (2.5 M in hexanes, 60 mL, 150 mmol) over 30 min dropwise at −78 °C. The resulting mixture was warmed to room temperature overnight. The reaction was quenched with H_2O (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 500:1→100:1) to afford **1** as a colorless liquid (10.3 g, 63% from **6**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.31 – 7.25 (m, 4H), 6.99 (d, J = 7.2 Hz, 2H), 6.23 (d, J = 4.8 Hz, 1H), 2.16 (d, J = 4.8 Hz, 1H), 0.32 (s, 18H);

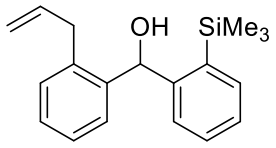
^{13}CNMR (100 MHz, $CDCl_3$) δ 149.0, 139.2, 135.0, 128.9, 127.8, 126.9, 75.1, 0.9;

IR (neat) cm^{-1} 3350, 3054, 2952, 2897, 1433, 1246, 1121, 835;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{28}OSi_2$ $(M+Na)^+$: 351.1576, found 351.1570.

2.2. Preparation of 3a-3f

Preparation of 3a



3a

3a: To a solution of CuI (10 mg, 0.05 mmol) and phenanthroline (12 mg, 0.05 mmol) in DMF (1.0 mL) was slowly added *t*-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. **1**

(33 mg, 0.1 mmol) was added with stirring for 5 min before adding 3-chloroprop-1-ene (15 μL, 0.15 mmol). The mixture was stirred at room temperature for 30 min before quenching with aq. HCl (0.2 mL, 1 *N*) and extracting with EtOAc (3 × 5 mL). The combined organic layers were washed with H_2O (3 × 2 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 300:1→100:1) to afford **3a** (27 mg, 90% yield) as a colorless liquid.

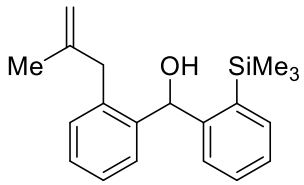
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 4.8 Hz, 1H), 7.35 – 7.20 (m, 6H), 7.13 (t, *J* = 3.6 Hz, 1H), 6.25 (d, *J* = 3.6 Hz, 1H), 5.93 – 5.83 (m, 1H), 5.04 (d, *J* = 10 Hz, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 3.38 (dd, *J* = 6.0, 6.4 Hz, 1H), 3.28 (dd, *J* = 6.0, 6.4 Hz, 1H), 2.08 (d, *J* = 4.4 Hz, 1H), 0.33 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 140.9, 139.0, 137.5, 137.1, 135.2, 129.9, 129.3, 127.7, 127.3, 127.2, 127.1, 126.2, 116.1, 72.5, 36.6, 0.8;

IR (neat) cm^{-1} 3391, 3057, 2953, 1248, 1010, 834, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{24}OSi$ $(M+Na)^+$: 319.1489, found 319.1487.

Preparation of 3b



3b

3b: Using the same procedure as that used for **3a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 0.5 h afforded **3b** (28 mg, 89% yield) as a colorless liquid.

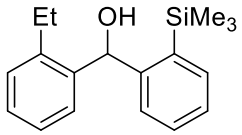
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.59 (m，1H), 7.30 – 7.14 (m, 7H), 6.24 (d, *J* = 4 Hz, 1H), 4.86 (s, 1H), 4.57 (s, 1H), 3.33 (d, *J* = 16 Hz, 1H), 3.24 (d, *J* = 16 Hz, 1H), 2.17 (d, *J* = 4Hz, 1H), 1.67 (s, 3H), 0.31 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 145.2, 141.5, 138.9, 137.1, 135.2, 130.2, 129.2, 127.6, 127.3, 127.1, 126.3, 112.6, 72.5, 40.8, 22.7, 0.7;

IR (neat) cm^{-1} 3436, 3005, 1275, 1260, 837, 764, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{26}OSi$ $(M+Na)^+$: 333.1645, found 333.1647.

Preparation of 3c



3c

3c: Using the same procedure as that used for **3a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), iodoethane (36 μL, 0.15 mmol) at room temperature for 0.5 h afforded **3c** (25 mg, 88% yield) as a colorless liquid.

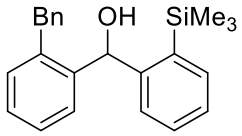
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.60 (m, 1H), 7.45 – 7.43 (m, 1H)，7.30 – 7.20 (m, 5H), 7.08 – 7.06 (m, 1H), 6.26 (d, *J* = 3.6 Hz, 1H), 2.61(ddd, *J* = 7.6, 15.2, 15.2 Hz, 1H), 2.46 (ddd, *J* = 7.6, 15.2, 15.2 Hz, 1H), 2.01 (d, *J* = 4.4 Hz, 1H), 1.11 (t, *J* = 7.6 Hz, 3H), 0.37 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 141.5, 140.5, 139.1, 135.3, 129.3, 128.4, 127.6, 127.3, 127.2, 126.7, 125.7, 72.4, 25.0, 14.7, 0.8;

IR (neat) cm^{-1} 3361, 2962, 1452, 1275, 1249, 837, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{24}OSi$ $(M+Na)^+$: 307.1489, found 307.1485.

Preparation of 3d



3d

3d: Using the same procedure as that used for **3a**: CuI (10 mg, 0.05 mmol),

phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), (bromomethyl)benzene (18 μL, 0.15 mmol) at room temperature for 0.5 h afforded **3d** (27 mg, 77% yield) as a colorless liquid.

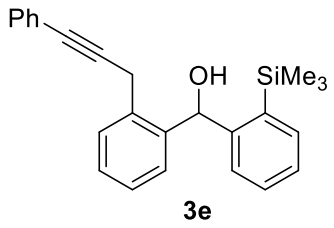
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 1H), 7.38 – 7.35 (m, 1H), 7.31 – 7.28 (m, 2H), 7.25 – 7.14 (m, 6H), 7.06 – 7.03 (m, 3H), 6.23(d, *J* = 3.2 Hz, 1H), 3.97 (d, *J* = 16 Hz, 1H), 3.92 (d, *J* = 16 Hz, 1H), 2.01 (d, *J* = 4.4 Hz, 1H), 0.24 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 141.1, 140.2, 139.3, 138.6, 135.3, 130.5, 129.3, 129.0, 128.5, 127.7, 127.3, 127.3, 127.2, 126.3, 126.1, 72.7, 38.4, 0.7;

IR (neat) cm^{-1} 3403, 3058, 2953, 1723, 1451, 1249, 1009, 837;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{26}OSi$ $(M+Na)^+$: 369.1645, found 369.1642.

Preparation of 3e



3e

3e: Using the same procedure as that used for **3a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 1-(*p*-Tosyloxy)-3-phenyl-2-propyne (43 mg, 0.15 mmol) at room temperature for 0.5 h afforded **3e** (30 mg, 80% yield) as a colorless liquid.

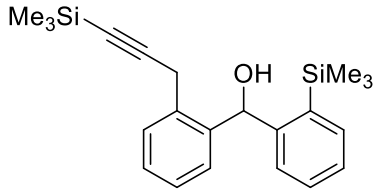
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 2H), 7.40 – 7.26 (m, 10H), 7.16 – 7.14 (m, 1H), 6.31 (d, *J* = 4 Hz, 1H), 3.83 (d, *J* = 18.8 Hz, 1H), 3.65 (d, *J* = 18.8 Hz, 1H), 2.17 (d, *J* = 4.4 Hz, 1H), 0.34 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 140.5, 139.3, 135.3, 134.4, 131.6, 129.5, 129.2, 128.2, 128.0, 127.8, 127.4, 127.2, 126.8, 123.5, 87.2, 83.4, 72.5, 23.3, 0.8;

IR (neat) cm^{-1} 3407, 2920, 2850, 1275, 1260, 764, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{26}OSi$ $(M+Na)^+$: 393.1645, found 393.1649.

Preparation of 3f



3f

3f: Using the same procedure as that used for **3a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-bromo-1-(trimethysilyl)-1-propyne (25 μL, 0.15 mmol) at room temperature for 0.5 h afforded **3f** (27 mg, 70% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54(m, 2H), 7.35 – 7.26 (m, 5H), 7.14 – 7.10 (m, 1H), 6.23 (d, *J* = 4 Hz, 1H), 3.68 (d, *J* = 18.8 Hz, 1H), 3.43 (d, *J* = 19.2 Hz, 1H), 2.21 (d, *J* = 4.4 Hz, 1H), 0.35 (s, 9H), 0.16 (s, 9H);

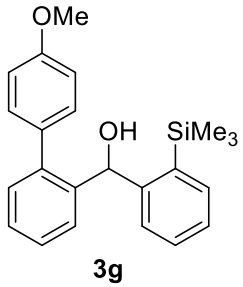
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5 140.6, 139.2, 135.3, 134.0, 129.4, 129.0, 127.9, 127.3, 127.2, 127.1, 126.8, 103.9, 87.8, 72.4, 23.8, 0.9, 0.0;

IR (neat) cm^{-1} 3366, 3056, 2956, 2174, 1248, 1122, 834, 757;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{30}OSi_2$ $(M+Na)^+$: 389.1727, found 389.1725.

2.3. Synthesis of 3g-3i

Preparation of 3g



3g

3g: To a solution of CuI (10 mg, 0.05 mmol) and tetrakis(triphenylphosphine) palladium (6 mg, 5 mol%) in DMF (1.0 mL) was slowly added *t*-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room

temperature for 10 min. **1** (33 mg, 0.1 mmol), 4-iodoanisole (35 mg, 0.15 mmol) was added successively and kept stirring at room temperature for 1 h. The reaction was quenched with aq. HCl (0.2 mL, 1 *N*) solution, extracted with EtOAc (3 × 5 mL) and washed with H_2O (3 × 2 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 300:1→100:1) to afford **3g** (33 mg, 92% yield) as a colorless liquid.

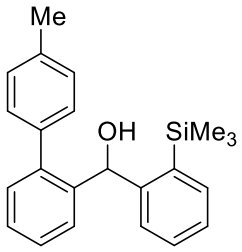
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.35 – 7.32 (m, 4H), 7.29 – 7.23 (m, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8 Hz, 2H), 6.05 (d, *J* = 4.0 Hz, 1H), 3.08 (s, 3H), 2.11 (d, *J* = 4.4 Hz, 1H), 0.06 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 148.6, 141.3, 140.6, 139.0, 135.2, 133.2, 130.7, 130.5, 128.9, 127.8, 127.6, 127.4, 127.2, 126.9, 113.5, 72.3, 55.3, 0.37;

IR (neat) cm^{-1} 3460, 2953, 1611, 1515, 1479, 1244, 1178, 835, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{26}O_2Si$ $(M+Na)^+$: 385.1594, found 385.1601.

Preparation of 3h



3h

3h：Using the same procedure as that used for **3g**: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 4-iodotoluene (33 mg, 0.15 mmol) at room temperature for 1 h afforded **3h** (28 mg, 80% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.27 (m, 8H), 7.14 – 7.08 (m, 4H), 6.05 (d, *J* = 4.0 Hz, 1H), 2.36 (s, 3H), 2.06 (d, *J* = 4.0 Hz, 1H), 0.06 (s, 9H);

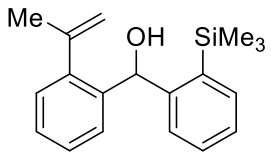
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.6, 140.6, 139.0, 137.9, 136.9, 135.2, 130.5,

129.2, 128.9, 128.7, 127.8, 127.7, 127.4, 127.2, 126.9, 72.3, 21.1, 0.4;

IR (neat) cm^{-1} 3443, 2953, 2853, 1724, 1249, 1006, 837, 821, 759;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{26}OSi$ $(M+Na)^+$: 369.1645, found 369.1649.

Preparation of 3i



3i

3i：Using the same procedure as that used for **3g**: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 2-bromopropene (14 μL , 0.15 mmol) at room temperature for 1 h afforded **3i** (27 mg, 90% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 4.8 Hz, 1H), 7.40 (t, *J* = 4.8 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.16 – 7.11 (m, 2H), 6.28 (d, *J* = 3.6 Hz, 1H), 5.12 (s, 1H), 4.72 (s, 1H), 2.25 (d, *J* = 4.4 Hz, 1H), 1.93 (s, 3H), 0.34 (s, 9H);

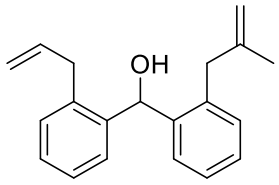
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 144.9, 143.0, 139.8, 139.2, 135.2, 129.1, 128.3, 127.7, 127.6, 127.3, 126.9, 126.8, 115.9, 72.5, 25.2, 0.8;

IR (neat) cm^{-1} 3436, 2954, 1433, 1249, 1121, 1006, 838, 763;

HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{24}OSi$ $(M+Na)^+$: 319.1489, found 319.1488.

2.4. Synthesis of 5a – 5m

Preparation of 5a



5a

5a: To a solution of CuI (10 mg, 0.05 mmol) and phenanthroline (12 mg, 0.05 mmol)

in DMF (1.0 mL) was slowly added *t*-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol) was added successively and kept stirring at room temperature for 0.5 h. Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) were added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H_2O (3 × 3 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→20:1) to afford **5a** (21 mg, 77% yield) as a colorless liquid.

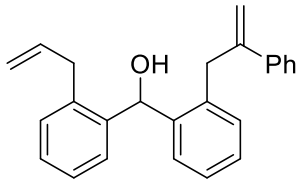
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 1.6, 2 Hz, 1H), 7.26 – 7.17 (m, 7H), 6.25 (d, *J* = 4 Hz, 1H), 5.98 – 5.87 (m, 1H), 5.07 – 5.03 (m, 1H), 5.01 – 4.95 (m, 1H), 4.87 (s, 1H), 4.58 (s, 1H), 3.40 – 3.26 (m, 4H), 2.17 (d, *J* = 4 Hz, 1H), 1.73 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 141.2, 140.7, 137.4, 137.2, 137.1, 130.6, 129.9, 127.7, 127.7, 127.2, 126.9, 126.7, 126.5, 115.9, 112.1, 69.3, 41.0, 36.7, 22.8;

IR (neat) cm^{-1} 3347, 2928, 2850, 1260, 1016, 764, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{22}O$ $(M+Na)^+$: 301.1563, found 301.1560.

Preparation of 5b



5b

5b: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 2-phenylallyl-4-methylbenzenesulfonate (43 mg, 0.15 mmol) at room temperature for

1 h afforded **5b** (24 mg, 70% yield) as a white solid. (mp. 56.9 ºC – 57.6 ºC)

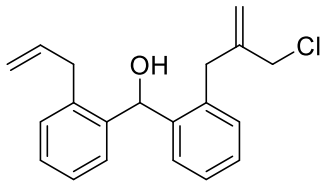
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 8H), 7.25 – 7.18 (m, 5H), 6.26 (s, 1H), 5.97 - 5.83 (m, 1H), 5.49 (s, 1H), 5.00 – 4.92 (m, 2H), 4.82 (s, 1H), 3.77 (s, 2H), 3.41 – 3.25 (m, 2H), 2.12 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 140.9, 140.8, 140.6, 137.7, 137.3, 136.9, 130.5, 130.0, 128.3, 127.9, 127.7, 127.6, 127.2, 127.0, 126.7, 126.6, 125.9, 116.0, 114.4, 69.5, 37.9, 36.7;

IR (neat) cm^{-1} 3336, 3059, 2919, 2850, 1485, 1451, 1260, 1014, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{24}O$ $(M+Na)^+$: 363.1719, found 363.1713.

<u>Preparation of 5c</u>



5c

5c: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloro-2-chloromethyl-1-propene (18 μL, 0.15 mmol) at room temperature for 1 h afforded **5c** (21 mg, 66 % yield) as a colorless liquid.

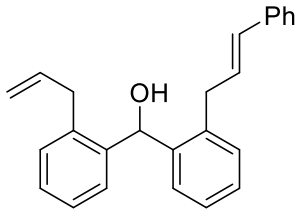
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 3H), 7.24 – 7.17 (m, 5H), 6.26 (d, J = 4 Hz, 1H), 5.98 – 5.87 (m, 1H), 5.22 (s, 1H), 5.07 – 4.96 (m, 2H), 4.81 (s, 1H), 3.99 (d, J = 3.2 Hz, 2H), 3.51 (d, J = 3.2 Hz, 2H), 3.44 – 3.28 (m, 2H), 2.15 (d, J = 4.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 141.1, 140.6, 137.5, 137.3, 135.9, 130.6, 130.0, 127.9, 127.9, 127.4, 127.0, 126.5, 116.6, 116.1, 69.3, 47.9, 36.6, 36.2;

IR (neat) cm^{-1} 3337, 3072, 2922, 1602, 1451, 1260, 1013, 913, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{21}OCl$ $(M+Na)^+$: 335.1179, found 335.1176.

Preparation of 5d



5d

5d: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), cinnamyl chloride (21 μL, 0.15 mmol) at room temperature for 1 h afforded **5d** (20 mg, 60% yield) as a colorless liquid.

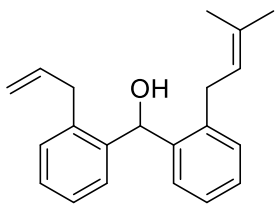
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 5H), 7.25 – 7.17 (m, 8H), 6.36 – 6.21 (m, 3H), 5.98 – 5.87 (m, 1H), 5.06 – 4.93 (m, 2H), 3.57 – 3.34(m, 4H), 2.13 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.7, 137.8, 137.6, 137.3, 137.3, 131.1, 130.1, 128.8, 128.5, 128.4, 127.9, 127.9, 127.2, 127.1, 127.1, 126.6, 126.6, 126.1, 116.1, 69.5, 36.7, 35.9;

IR (neat) cm^{-1} 3337, 3025, 2920, 2850, 1450, 1260, 914,750;

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{24}O$ $(M+Na)^+$:363.1719, found 363.1716.

Preparation of 5e



5e

5e: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 1-chloro-3-methyl-2-butene (17 μL, 0.15mmol) at room temperature for 1 h afforded **5e** (20 mg, 70% yield) as a colorless liquid.

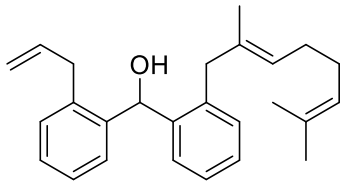
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 8H), 6.27(d, *J* = 2.8 Hz, 1H), 6.00 – 5.88 (m, 1H), 5.23 (t, J = 7.2 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.42 – 3.27 (m, 4H), 2.13 (d, *J* = 4.4 Hz, 1H), 1.72 (s, 3H), 1.66 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.5, 137.4, 137.2, 133.0, 130.0, 129.9, 129.4, 127.9, 127.7, 127.1, 127.0, 126.9, 126.5, 126.2, 123.0, 116.0, 69.3, 36.7, 31.4, 25.7, 17.9;

IR (neat) cm-1 3313, 2918, 2851, 1638, 1451, 1276, 1014, 913, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{24}O$ $(M+Na)^+$: 315.1719, found 315.1715.

Preparation of 5f



5f

5f: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), geranyl chloride (28 μL, 0.15 mmol) at room temperature for 1 h afforded **5f** (22 mg, 60% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.33 (m, 1H), 7.25 – 7.15 (m, 7H), 6.27 (d, *J* = 4.0 Hz, 1H), 5.98 – 5.88 (m, 1H), 5.26 – 5.22 (m, 1H), 5.04 – 4.97 (m, 3H), 3.48 –

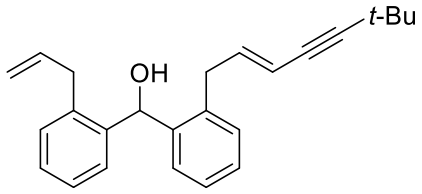
3.25 (m, 4H), 2.13 (d, J = 4.4 Hz, 1H), 2.07 – 1.99 (m, 4H), 1.68 (s, 3H), 1.65 (s, 3H), 1.56 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.5, 137.4, 137.2, 133.0, 130.0, 129.9, 129.4, 127.9, 127.7, 127.0, 126.9, 126.5, 126.2, 123.0, 116.0, 69.3, 36.7, 31.4, 25.7, 17.9;

IR (neat) cm^{-1} 3313, 2966, 2917, 2852, 1638, 1602, 1451, 1014, 913, 751;

HRMS (ESI-TOF, m/z) calcd for: $C_{26}H_{32}O$ $(M+Na)^+$: 383.2345, found 383.2344.

Preparation of 5g



5g

5g: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 1-chloro-6,6-dimethyl-2-heptyene-4-alkyne (25 μL, 0.15 mmol) at room temperature for 1 h afforded **5g** (21 mg, 62% yield) as a colorless liquid.

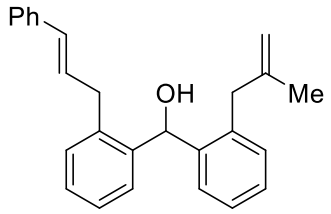
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.24 – 7.16 (m, 6H), 6.22 (d, J = 4.4 Hz, 1H), 6.15 – 6.08 (m, 1H), 6.02 – 5.92 (m, 1H), 5.43 – 5.38 (m, 1H), 5.10 – 4.98 (m, 2H), 3.45 – 3.33 (m, 4H), 2.10 (d, J = 4.8 Hz, 1H), 1.22 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.6, 140.4, 137.5, 137.3, 136.9, 130.1, 130.1, 127.9, 127.9, 127.1, 127.0, 126.7, 126.6, 116.1, 111.5, 98.1, 77.2, 69.4, 36.7, 35.7, 31.0, 27.8;

IR (neat) cm^{-1} 3298, 2968, 2923, 1452, 1266, 1015, 915, 759;

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{28}O$ $(M+Na)^+$: 367.2032, found 367.2031.

Preparation of 5h



5h

5h: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), cinnamyl chloride (14 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 1 h afforded **5h** (30 mg, 84 % yield) as a colorless liquid.

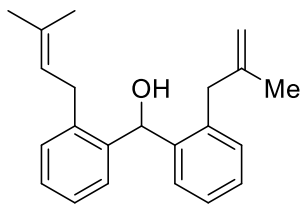
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.33 (d, *J* = 4.0 Hz, 4H）, 7.29 – 7.26 (m, 2H), 7.24 – 7.15 (m, 5H), 6.34 – 6.28 (m, 1H), 6.25 – 6.18 (m, 1H), 6.06 (s, 1H), 4.86 (s, 1H), 4.54 (s, 1H), 3.50 – 3.30 (m, 4H), 2.19 (s, 1H), 1.72 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 143.2, 141.9, 137.3, 136.9, 131.1, 130.6, 129.9, 128.7, 128.4, 128.3, 127.8, 127.7, 127.4, 127.3, 127.1, 126.8, 126.5, 126.1, 112.1, 72.6, 41.0, 35.9, 22.8;

IR (neat) cm^{-1} 3363, 2918, 2154, 1449, 1264, 1013, 893;

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{26}O$ $(M+Na)^+$: 377.1876, found 377.1875.

Preparation of 5i



5i

5i: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 1-chloro-3-methyl-2-butene (12 μL, 0.1 mmol). Then

TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 1 h afforded **5i** (22 mg, 72% yield) as a colorless liquid.

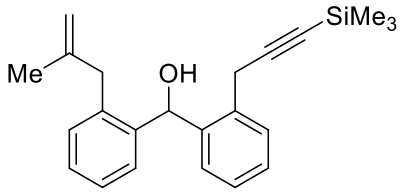
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.12 (m, 8H), 6.25 (d, *J* = 2.4 Hz, 1H), 5.24 – 5.19 (m, 1H)，4.85 (s, 1H), 4.57 (s, 1H)，3.40 – 3.20 (m, 4H), 2.22 (d, *J* = 4.4 Hz, 1H), 1.71 (s, 6H), 1.64 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 141.2, 140.6, 139.3, 137.1, 133.0, 130.5, 129.3, 127.7, 127.6, 127.1, 126.9, 126.6, 126.2, 122.9, 112.1, 69.3, 41.0, 31.3, 25.7, 22.7, 17.8;

IR (neat) cm^{-1} 3345, 2925, 1484, 1260, 1013, 763;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{26}O$ $(M+Na)^+$: 329.1876, found 329.1875.

Preparation of 5j



5j

5j: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloro-2-methylpropene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-bromo-1-(trimethylsilyl)-1-propyne (25 μL, 0.15 mmol)at room temperature for 1 h afforded **5j** (23 mg, 66% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 1H), 7.39 – 7.36 (m, 1H), 7.32 – 7.28 (m, 2H), 7.25 – 7.18 (m, 4H), 6.28 (d, *J*= 4 Hz, 1H), 4.87 (s, 1H), 4.60 (s, 1H), 3.62 (d, *J* = 18.8 Hz, 1H), 3.45 – 3.30 (m, 3H), 2.4 (d, *J* = 4 Hz, 1H), 1.71 (s, 3H), 0.17 (s, 9H);

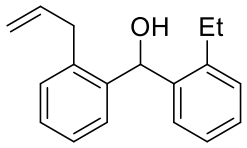
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 140.6, 140.4, 137.3, 133.8, 130.6, 129.0, 127.9,

127.8, 127.1, 126.9, 126.8, 112.3, 104.1, 87.7, 69.1, 41.0, 23.7, 22.7, 0.01;

IR (neat) cm^{-1} 3314, 2921, 2174, 1452, 1250, 1017, 842, 759;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{28}OSi$ $(M+Na)^+$: 371.1802, found 371.1802.

Preparation of 5k



5k

5k: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), iodoethane (36 μL, 0.15 mmol) at room temperature for 1 h afforded **5k** (15 mg, 60% yield) as a colorless liquid.

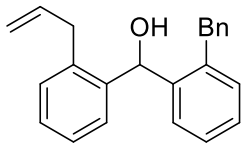
^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 1H), 7.29 – 7.26 (m, 1H), 7.24 – 7.16 (m, 6H), 6.27 (d, J = 4.4 Hz, 1H), 6.02 – 5.92 (m, 1H), 5.10 – 4.98 (m, 2H), 3.45 – 3.43 (m, 2H), 2.68 – 2.50 (m, 2H), 2.03 (d, J = 4.4 Hz, 1H), 1.16 (t, J = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.0, 140.1, 137.5, 137.3, 130.0, 128.6 127.8, 127.8, 127.1, 126.7, 126.6, 125.9, 116.0, 69.3, 36.8, 25.1, 14.9;

IR (neat) cm^{-1} 3289, 2964, 2924, 1638, 1452, 1260, 1016, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{20}O$ $(M+Na)^+$: 275.1406, found 275.1407.

Preparation of 5l



5l

5l: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in

THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), (bromomethyl)benzene (18 μL, 0.15 mmol) at room temperature for 1 h afforded **5l** (20 mg, 59% yield) as a colorless solid. (mp. 64.5 ºC – 65.3 ºC)

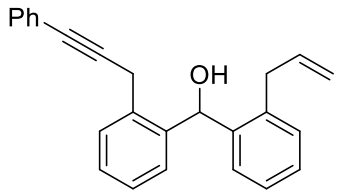
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.23 – 7.09 (m, 9H), 6.27 (d, *J* = 4.0 Hz, 1H), 5.87 – 5.76 (m, 1H), 5.00 – 4.84 (m, 2H), 4.03 (d, *J* = 16 Hz, 1H), 3.98 (d, *J* = 16 Hz, 1H), 3.22 – 3.12 (m, 2H), 1.93 (d, *J* = 4.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.5, 140.3, 138.4, 137.5, 137.1, 130.8, 129.9, 128.7, 128.5, 127.8, 127.8, 127.3, 126.9, 126.8, 126.5, 126.2, 116.0, 69.34, 38.6, 36.5;

IR (neat) cm^{-1} 3335, 2918, 2152, 1452, 1275, 1014, 763;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{22}O$ $(M+Na)^+$: 337.1563, found 337.1560.

Preparation of 5m



5m

5m: Using the same procedure as that used for **5a**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 1-(*p*-Tosyloxy)-3-phenyl-2-propyne (29 mg, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloroprop-1-ene (15 μL, 0.15 mmol) at room temperature for 1 h afforded **5m** (23 mg, 69% yield) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 7H), 7.23 – 7.08 (m, 6H), 6.12 (d, *J* = 3.2 Hz, 1H), 5.79 – 5.69 (m, 1H), 5.07 (d, *J* = 12.8 Hz, 1H), 4.93 – 4.90 (m, 1H), 4.82 – 4.72 (m, 2H), 3.24 – 3.05 (m, 2H), 2.04(d, *J* = 3.6 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 140.8, 137.3, 137.2, 136.0, 134.6, 130.7, 129.5, 128.5, 128.2, 127.9, 127.7, 127.5, 127.1, 127.1, 126.6, 126.4, 115.7, 106.0, 77.8, 69.6,

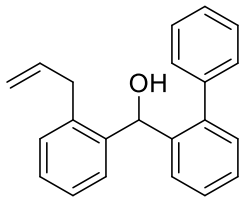
36.6, 29.7;

IR (neat) cm^{-1} 3366, 2923, 2218, 1969, 1260, 915, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{25}H_{22}O$ $(M+Na)^+$: 361.1563, found 361.1561.

2.4. Synthesis of 5n – 5q

Preparation of 5n



5n

5n: To a solution of CuI (10 mg, 0.05 mmol) and phenanthroline (12 mg, 0.05 mmol) in DMF (1.0 mL) was slowly added *t*-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. Then **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol) was added successively and kept stirring at room temperature for 0.5 h. Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), *t*-BuOLi (0. 2 mL, 1.0 M in THF), iodobenzene (17 μL, 0.15 mmol) were added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H_2O (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→20:1) to afford **5n** (20 mg, 65% yield) as a colorless liquid.

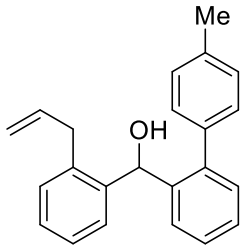
^1H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.29 (m, 9H), 7.23 – 7.05 (m, 4H), 6.01 (s, 1H), 5.60 – 5.50(m, 1H), 4.84 – 4.64(m, 2H), 2.95 – 2.85 (m, 2H), 2.09 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.5, 140.7, 140.1, 137.2, 136.9, 130.1, 129.7, 129.3, 128.1, 127.7, 127.5, 127.5, 127.2, 126.7, 126.3, 115.5, 69.5, 36.4;

IR (neat) cm^{-1} 3330, 2922, 2852, 1450, 1275, 1260, 1007, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{20}O$ $(M+Na)^+$: 323.1406, found 323.1405.

Preparation of 5o



5o

5o: Using the same procedure as that used for **5n**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg ,0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 4-iodotoluene (33 mg, 0.15mmol) at room temperature for 1 h afforded **5o** (22 mg, 70% yield) as a colorless liquid.

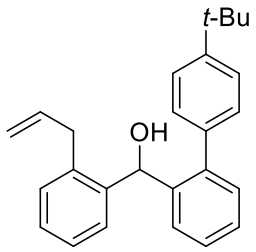
^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 1H), 7.42 – 7.31 (m, 3H), 7.23 – 7.17 (m, 7H), 7.08 – 7.06 (m, 1H), 6.02 (d, *J* = 3.6 Hz, 1H), 5.60 – 5.50 (m, 1H), 4.84 – 4.65 (m, 2H), 2.97 – 2.86 (m, 2H), 2.40 (s, 3H), 2.07 (d, *J* = 4.4 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 141.5, 140.2, 137.8, 137.2, 136.9, 136.9, 130.2, 129.6, 129.1, 128.8, 127.5, 127.5, 127.5, 126.6, 126.3, 115.5, 69.6, 36.4, 21.2;

IR (neat) cm^{-1} 3336, 2922, 2852, 1668, 1450, 1275, 1007, 821, 751;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{22}O$ $(M+Na)^+$:337.1563, found 337.1559.

Preparation of 5p



5p

5p: Using the same procedure as that used for **5n**: CuI (10 mg, 0.05 mmol), phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 1-(tert-butyl)-4-iodobenzene (27 μL, 0.15 mmol) at room temperature for 1 h afforded **5p** (24 mg, 68% yield) as a colorless liquid.

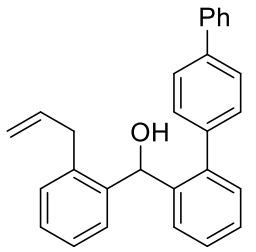
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.28 (m,7H), 7.24 – 7.20 (m,4H), 7.06 – 7.04 (m,1H), 6.02 (s, 1H), 5.58 – 5.48 (m,1H), 4.81 – 4.58 (m, 2H), 2.90 – 2.87 (m,2H), 2.06 (s, 1H), 1.36 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 141.6, 140.3, 137.7, 137.3, 137.0, 130.1, 129.7, 128.9, 127.5, 127.5, 127.5, 126.7, 126.3, 125.0, 115.3, 69.5, 36.5, 34.5, 31.4, 29.7;

IR (neat) cm^{-1} 3337, 3005, 2851, 1363, 1275, 1260, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{28}O$ $(M+Na)^+$: 379.2032, found 379.2030.

<u>Preparation of 5q</u>



5q

5q: Using the same procedure as that used for **5n**: CuI (10 mg, 0.05 mmol),

phenanthroline (12 mg, 0.05 mmol), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 3-chloroprop-1-ene (10 μL, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 4-iodobiphenyl (42 mg, 0.15 mmol) at room temperature for 1 h afforded **5q** (28 mg, 74% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 4H), 7.46 – 7.44 (m, 1H), 7.41 – 7.37 (m, 3H), 7.31 – 7.22 (m, 7H), 7.15 – 7.13 (m, 1H), 7.10 – 6.98 (m, 1H), 5.99 (d, *J*= 4 Hz, 1H), 5.52 – 5.42 (m, 1H), 4.74 – 4.55 (m, 2H), 2.88 – 2.85 (m, 2H), 2.40 (d, *J* = 4.4 Hz, 1H);

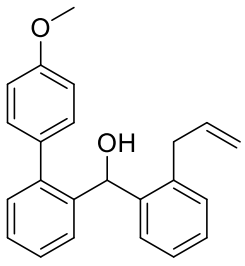
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 141.2, 140.7, 140.2, 140.1, 139.7, 137.3, 136.9, 130.1, 129.7, 129.7, 128.8, 127.8, 127.6, 127.6, 127.4, 127.1, 126.8, 126.7, 126.4, 115.5, 69.6, 36.4;

IR (neat) cm^{-1} 3365, 3006, 2920, 1478, 1006, 1260, 764;

HRMS (ESI-TOF, m/z) calcd for $C_{28}H_{24}O$ $(M+Na)^+$: 399.1719, found 399.1714.

2.6. Synthesis of 5r-5t

Preparation of 5r



5r

5r: To a solution of CuI (10 mg, 0.05 mmol) and tetrakis(triphenylphosphine) palladium (6 mg, 5 mol%) in DMF (1.0 mL) was slowly added *t*-BuOLi (0.15 mL, 1.0 M in THF) at 0 °C under argon atmosphere. The reaction mixture was stirred at room temperature for 10 min. **1** (33 mg, 0.1 mmol), 4-iodoanisole (24 mg, 0.1 mmol) were added successively and kept stirring at room temperature for 1 h. Then TBAF (0.15

mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloroprop-1-ene (15 μL, 0.15mmol) were added successively. The resulted mixture was stirred at room temperature for 1 h. The reaction was quenched with sat. aq. NaCl (2 mL), extracted with EtOAc (3 × 5 mL) and washed with H_2O (3 × 3 mL). The combined organic layers were then dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 100:1→20:1) to afford **5r** (22 mg, 67% yield) as a white solid. (mp. 105.5ºC – 106.3ºC).

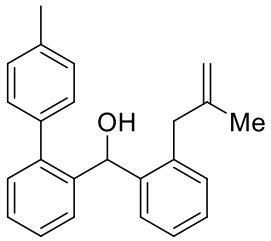
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.31 (t, *J* = 4.8 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8 Hz, 2H), 6.01 (s, 1H), 5.61 – 5.51(m, 5H), 4.38 (d, *J* = 10 Hz, 1H), 4.68 (d, *J* = 16.8 Hz, 1H), 3.84 (s, 3H), 2.98 – 2.87 (m, 2H), 2.12 (s, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 141.5, 141.3, 140.2, 137.2, 136.9, 133.1, 130.4, 130.3, 129.7, 127.6, 127.5, 127.5, 127.4, 126.6, 126.3, 115.5, 113.6, 69.6, 55.3, 36.4;

IR (neat) cm^{-1} 3367, 2917, 1611, 1515, 1480, 1178, 1036, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{22}O_2$ $(M+Na)^+$: 353.1517, found 353.1509.

Preparation of 5s



5s

5s: Using the same procedure as that used for **5r**: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 4-iodotoluene (22 mg, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), 3-chloro-2-methylpropene (15 μL, 0.15 mmol) at room temperature for 1 h afforded **5s** (21 mg, 64% yield) as a colorless liquid.

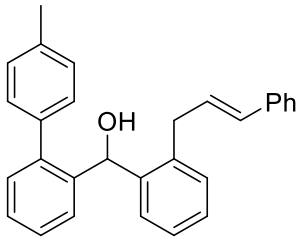
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.17 (m, 11H), 7.06 – 7.03 (m, 1H), 6.01 (d, *J* = 3.6 Hz, 1H), 4.64 (s, 1H), 4.28 (s, 1H), 2.86 (s, 2H), 2.38 (s, 3H), 2.14 (d, *J* = 4 Hz, 1H), 1.44 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 141.9, 141.5, 140.2, 137.8, 136.8, 136.8, 130.2, 130.1, 129.1, 128.8, 127.4, 127.4, 127.3, 126.9, 126.4, 111.8, 69.5, 40.3, 22.3, 21.1.

IR (neat) cm^{-1} 3359, 3061, 3023, 2918, 1649, 1480, 1447, 1006, 750;

HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{24}O$ $(M+Na)^+$: 351.1719, found 351.1720.

Preparation of 5t



5t

5t: Using the same procedure as that used for **5r**: CuI (10 mg, 0.05 mmol), tetrakis(triphenylphosphine)palladium (6 mg, 5 mol%), DMF (1.0 mL); *t*-BuOLi (0.15 mL, 1.0 M in THF); **1** (33 mg, 0.1 mmol), 4-iodotoluene (22 mg, 0.1 mmol). Then TBAF (0.15 mL, 1.0 M in THF), *t*-BuOLi (0. 2 mL, 1.0 M in THF), cinnamyl chloride (21 μL, 0.15 mmol) at room temperature for 1 h afforded **5t** (27 mg, 70% yield) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 1H), 7.38 – 7.22 (m, 8H), 7.20 – 7.10 (m, 8H), 6.07 (d, *J* = 4 Hz, 1H), 5.96 – 5.92 (m, 1H), 5.85 – 5.78 (m, 1H), 3.03 – 3.00 (m, 1H), 2.39 (s, 2H), 2.11 (d, *J* = 4 Hz, 1H);

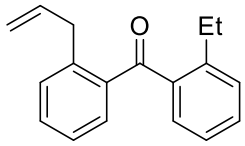
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 141.6, 140.1, 137.8, 137.4, 137.2, 137.0, 130.4, 130.3 129.8, 129.3, 129.0, 128.6, 128.3, 127.9, 127.6, 127.6, 127.5, 126.9, 126.3, 126.3, 126.0, 69.6, 35.6, 21.2;

IR (neat) cm^{-1} 3359, 3024, 2851, 1516, 1480, 1262, 1007, 759;

HRMS (ESI-TOF, m/z) calcd for $C_{29}H_{26}O$ $(M+Na)^+$: 413.1876, found 413.1877.

2.7. Synthesis of Diaryketones 8a-8c

Preparation of 8a



8a

8a: To a solution of **5k** (13 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) was added Dess-Martin periodinane (32 mg, 0.075 mmol) at room temperature. The reaction was stirred for 12 h before extraction with EtOAc (3 × 5 mL) and washing with H_2O (3 × 2 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc = 500:1→300:1) to afford **8a** (12 mg, 94% yield) as a colorless liquid.

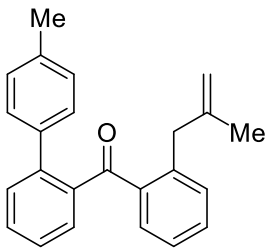
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.28 (m, 5H), 7.24 – 7.17 (m, 3H), 6.03 – 5.92 (m, 1H), 5.05 – 5.00 (m, 2H), 3.64 – 3.62 (m, 2H), 2.86 – 2.80 (m, 2H), 1.23 (t, *J* = 7.6 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 144.6, 140.3, 139.0, 138.7, 137.2, 131.3, 131.2, 130.8, 130.7, 130.4, 129.9, 125.7, 125.2, 116.0, 37.6, 26.6, 15.9;

IR (neat) cm^{-1} 3062, 2965, 2871, 1662, 1572, 1483, 1235, 1255, 924;

HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{18}O$ $(M+Na)^+$: 273.1250, found 273.1240.

Preparation of 8b



8b

8b: Using the same procedure as that used for **8a**: **5s** (17 mg, 0.05 mmol) and

Dess-Martin periodinane (32 mg, 0.075 mmol) in CH_2Cl_2 (1 mL) at room temperature for 12 h afforded **8b** (16 mg, 96% yield) as a colorless liquid.

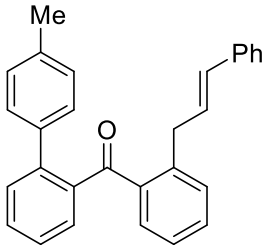
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.10 (m, 12H), 4.81 (s, 1H), 4.51 (s, 1H), 3.54 (s, 2H), 2.27 (s, 3H), 1.68 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 145.1, 141.9, 140.4, 140.1, 138.2, 137.6, 136.8, 131.4, 131.2, 130.7, 130.6, 130.4, 129.6, 128.8, 128.6, 126.7, 125.3, 112.2, 41.0, 22.7, 21.0;

IR (neat) cm^{-1} 3020, 2918, 2849,1661, 1443, 931, 819, 757;

HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{22}O$ $(M+Na)^+$: 349.1568, found 349.1560.

Preparation of 8c



8c

8c: Using the same procedure as that used for **8a**: **5t** (20 mg, 0.05 mmol) and Dess-Martin periodinane (32 mg, 0.075 mmol) in CH_2Cl_2 (1 mL) at room temperature for 12 h afforded **8c** (19 mg, 98% yield) as a colorless liquid.

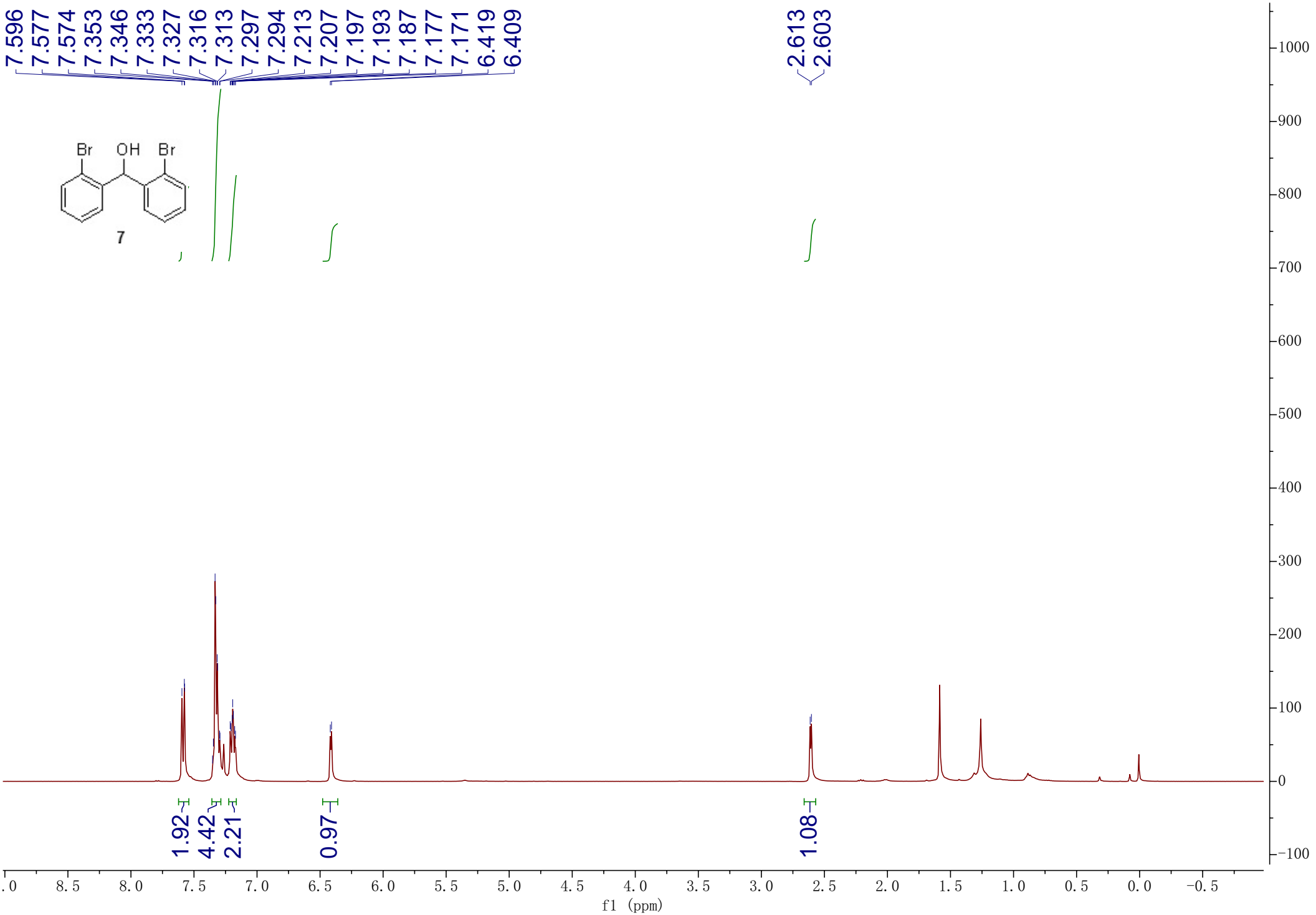
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.42 – 7.39 (m, 2H), 7.35 – 7.27 (m, 4H), 7.22– 7.10 (m, 6H), 7.06 – 7.00 (m, 3H), 6.42 (d, J = 16 Hz, 1H), 6.34 – 6.27 (m, 1H), 3.72 (d, J = 6.8 Hz, 2H), 2.23 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 141.9, 141.0, 140.1, 137.8, 137.6, 137.6, 136.9, 131.4, 131.1, 131.1, 130.7, 130.4, 130.3, 129.6, 129.3, 128.8, 128.7, 128.4, 127.0, 126.8, 126.1, 125.4, 36.8, 21.1;

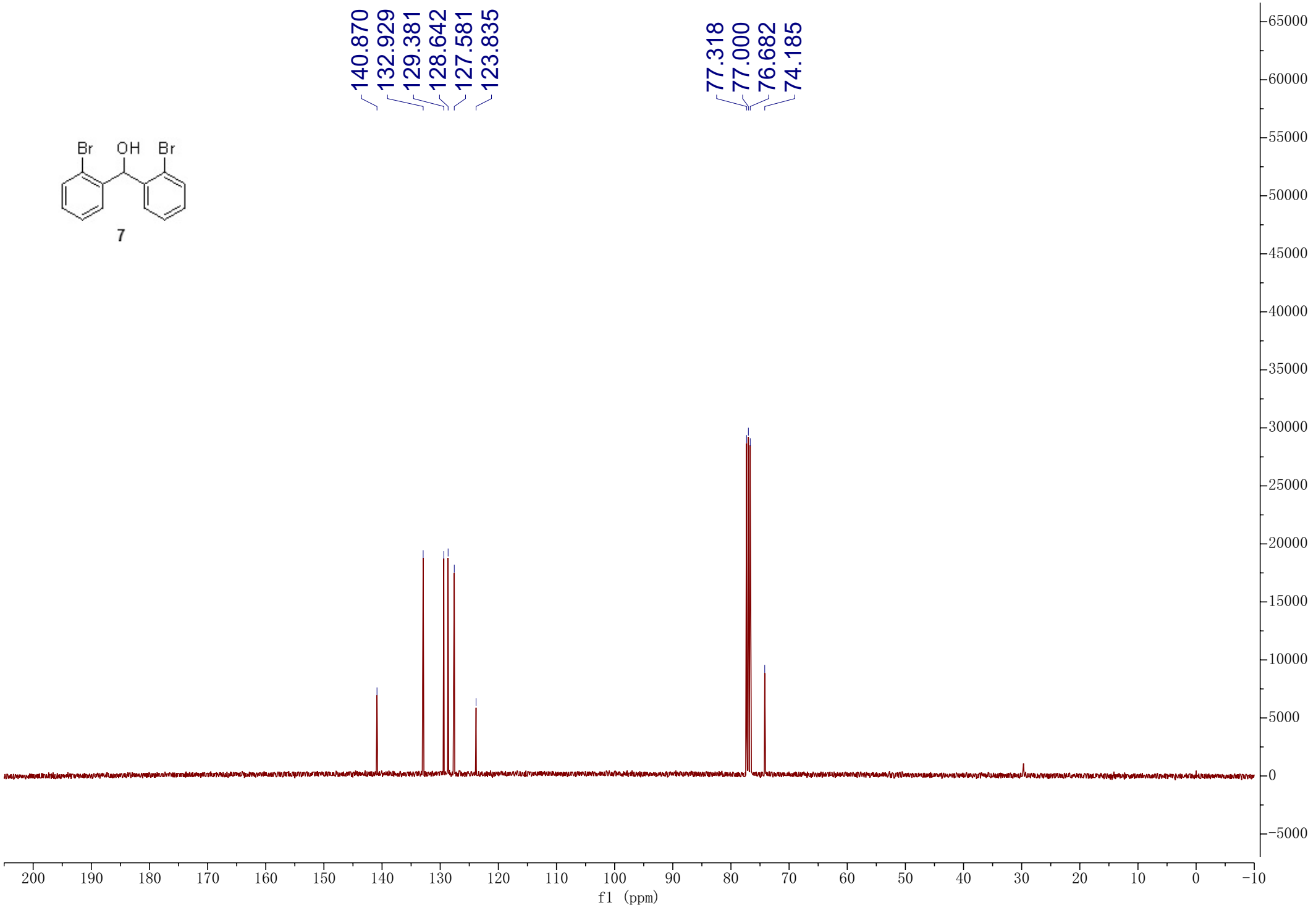
IR (neat) cm^{-1} 3057, 2850, 1660, 1446, 1107, 819,766;

HRMS (ESI-TOF, m/z) calcd for $C_{29}H_{24}O$ $(M+Na)^+$: 411.1725, found 411.1722.

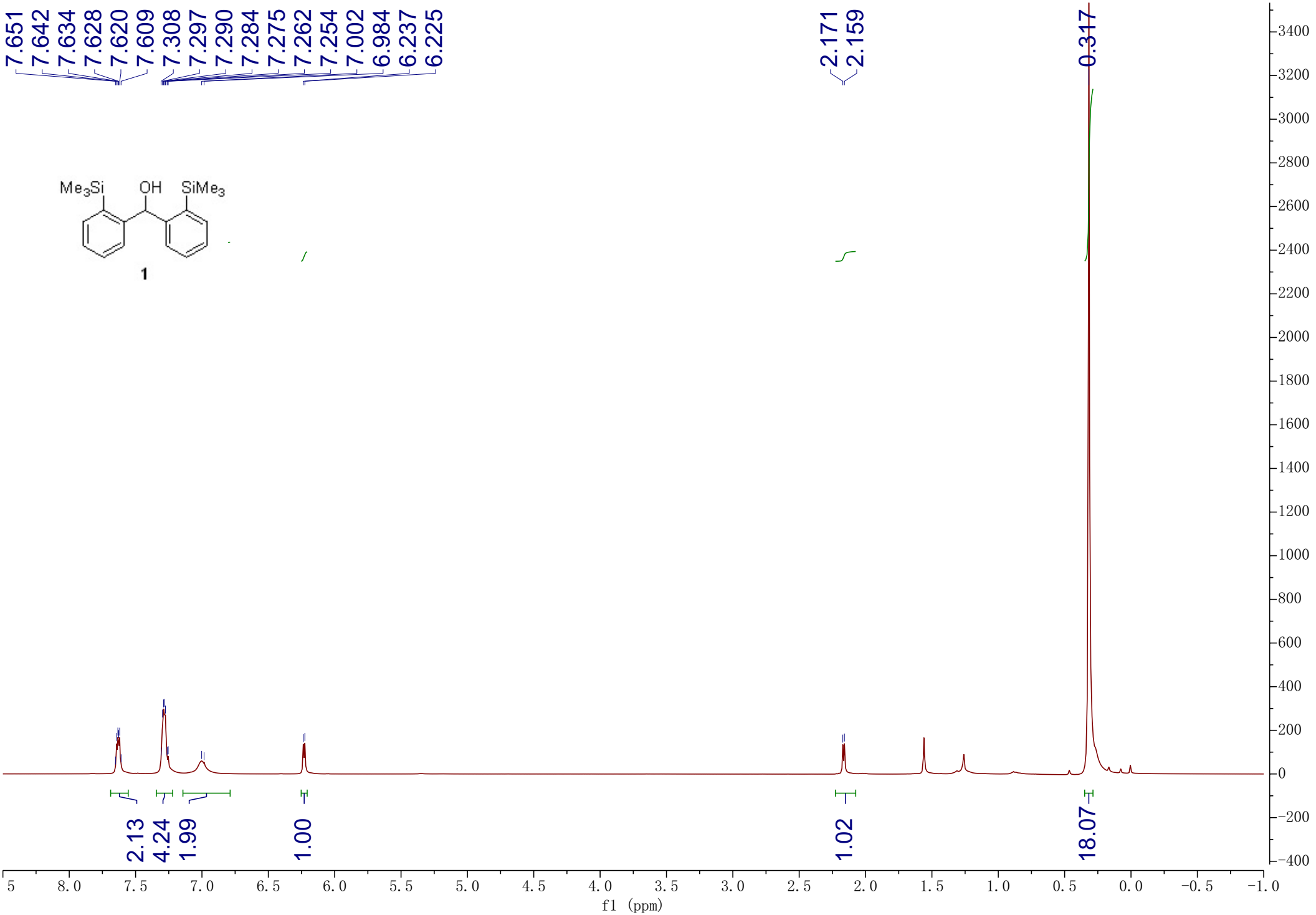
HTB-5-114_CDCl3_H1_2019-5-13



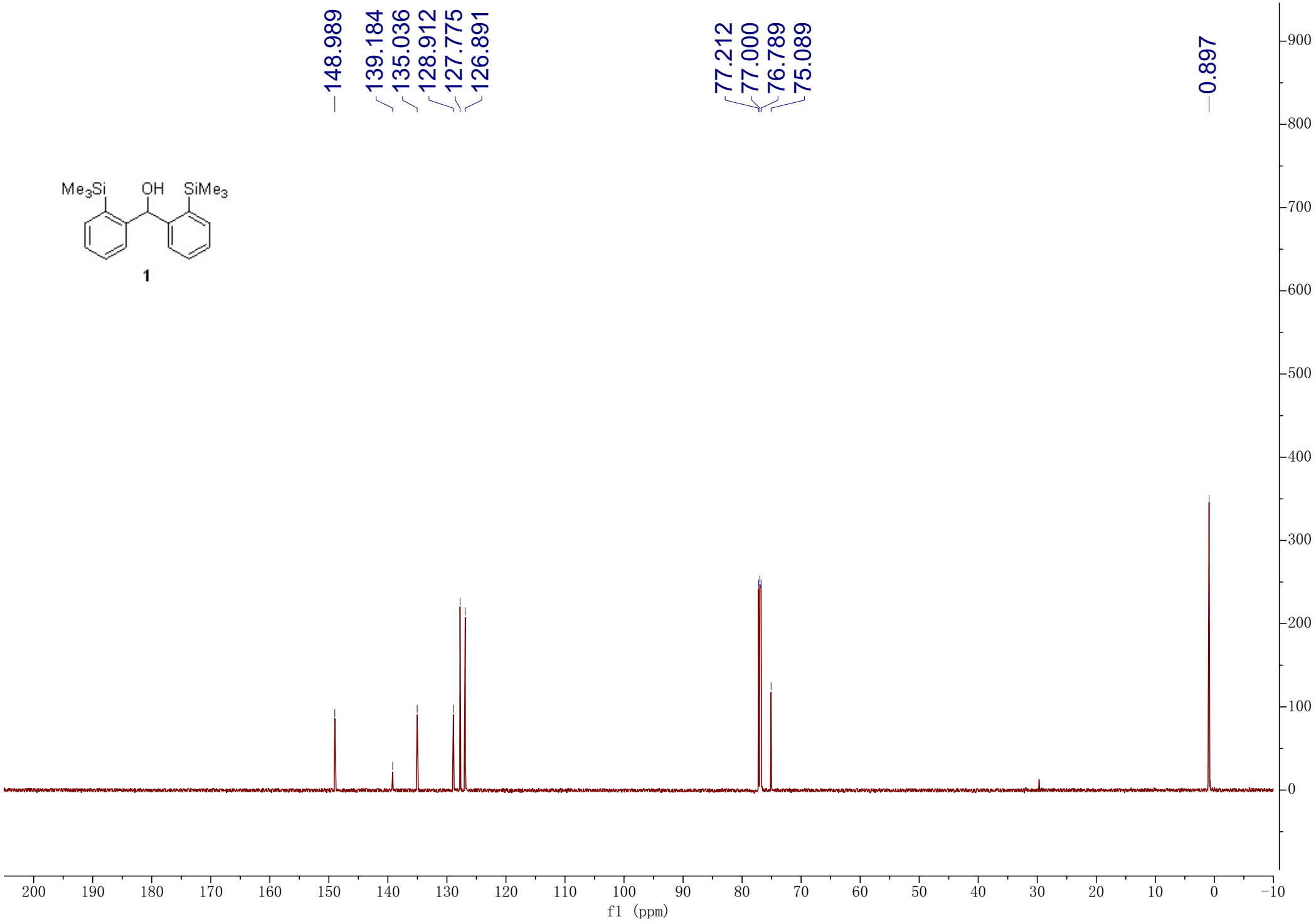
HTB-5-114_CDCl3_13C_2019-5-14



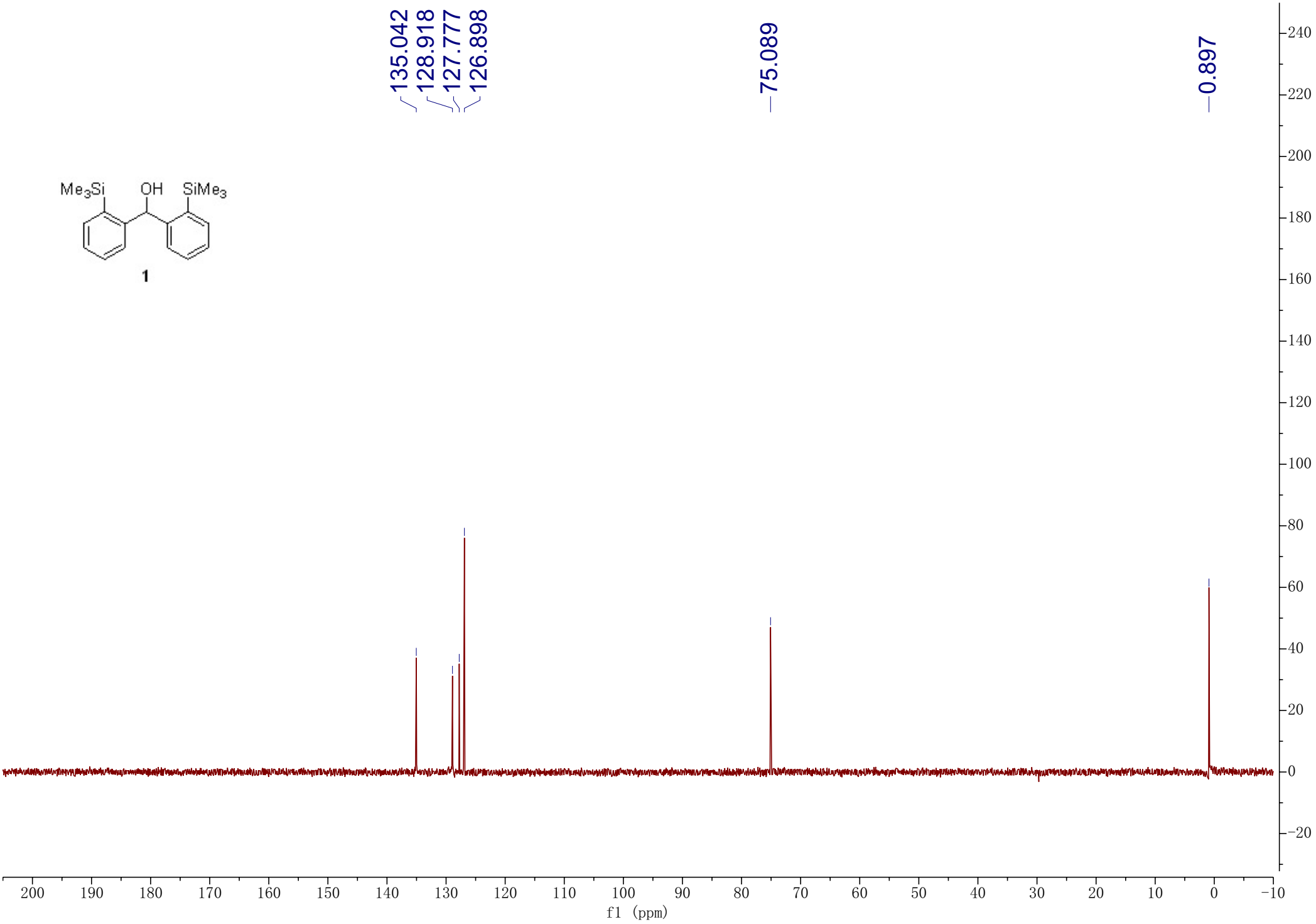
HTB-5-92_CDCl3_H1_2019-5-13



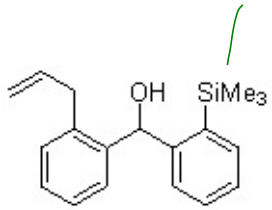
HTB-5-92_13C_CDCl3_2019-5-14



HTB-5-92_CDCl3_DEPT_2019-5-14

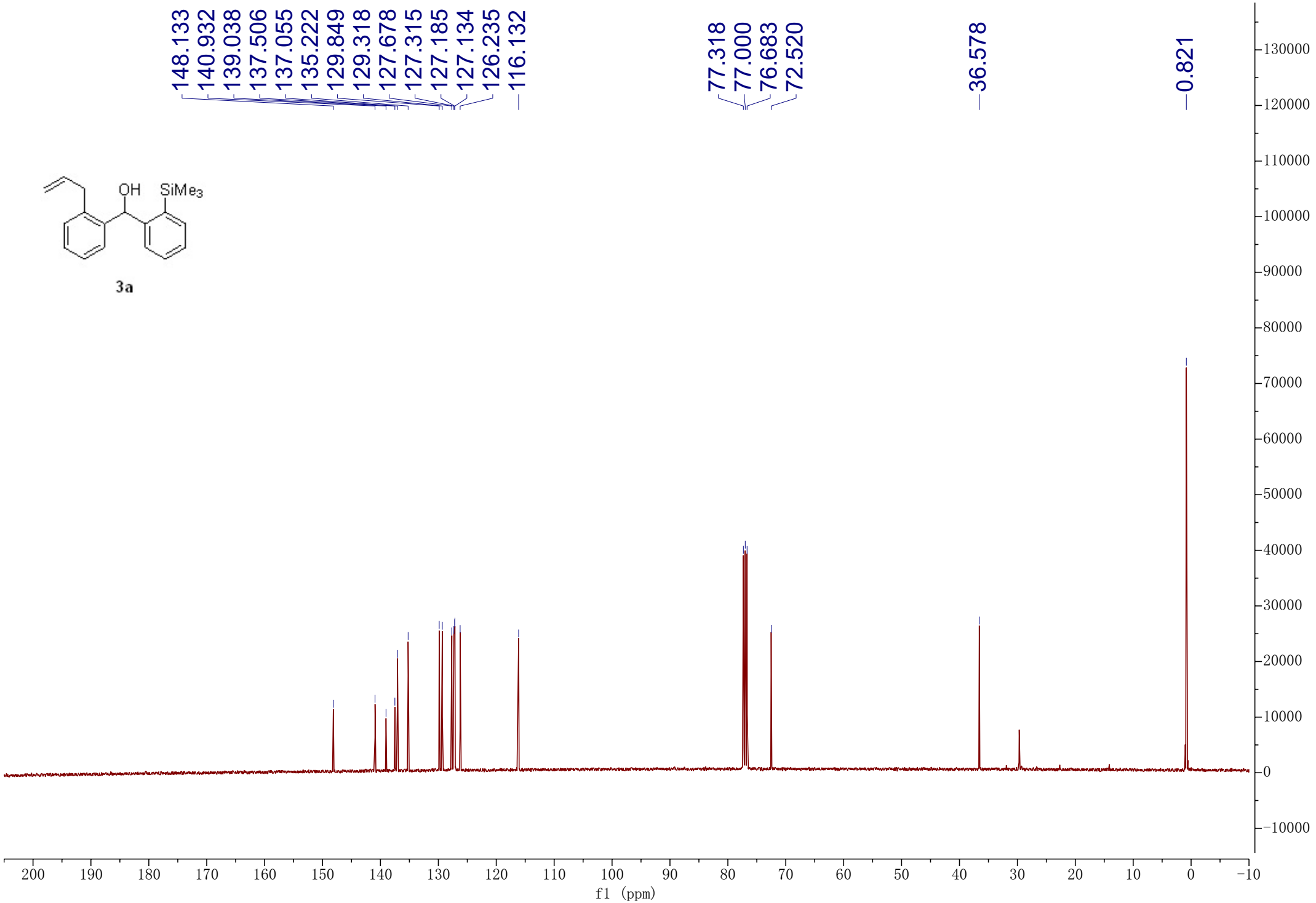


HTB-6-89_CDCl3_H1_2019-5-5

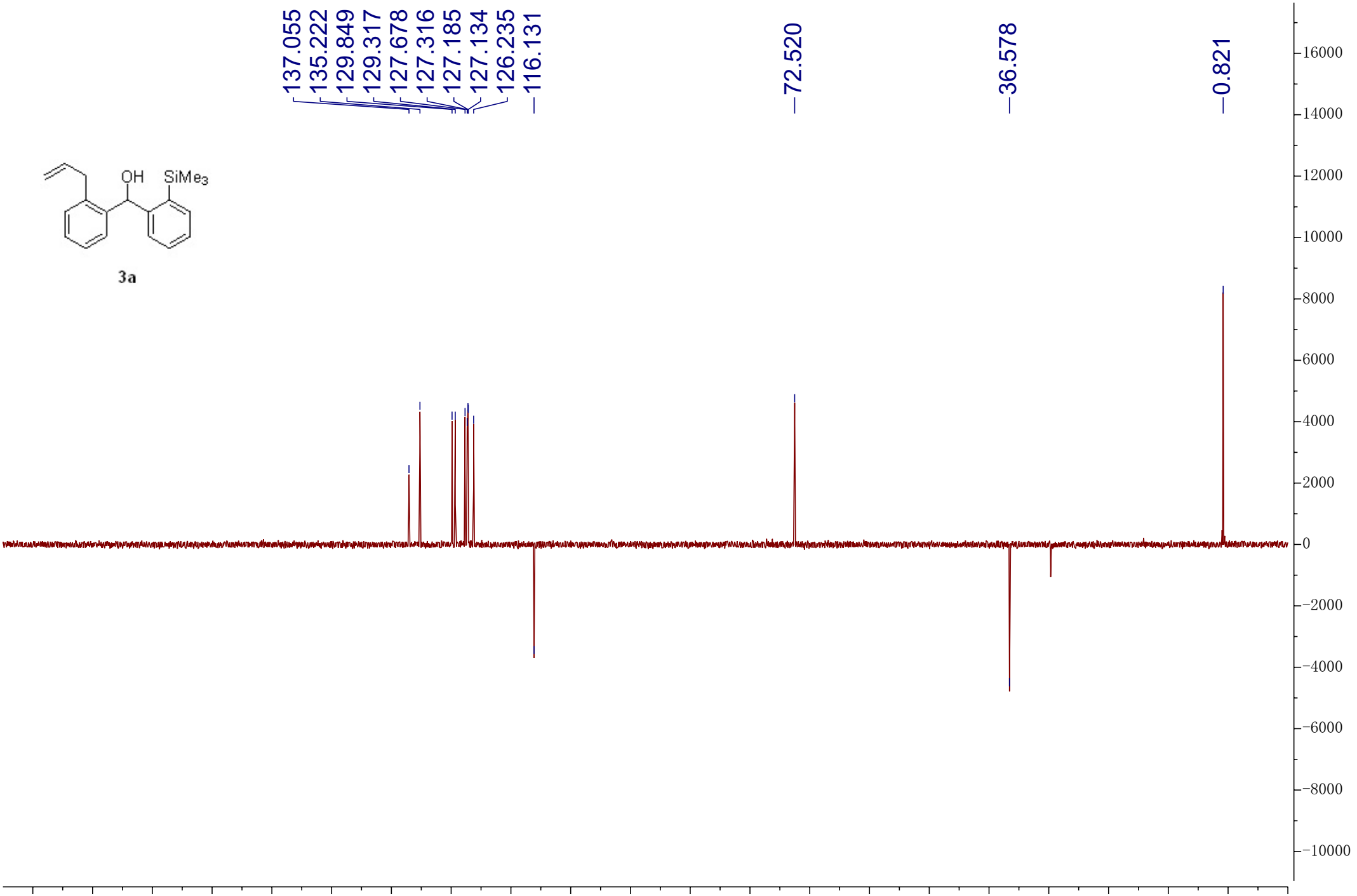


3a

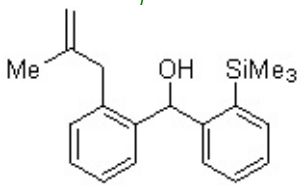
HTB-6-89_CDCl3_13C_2019-7-1



HTB-6-89_CDCl3_DEPT_2019-7-1

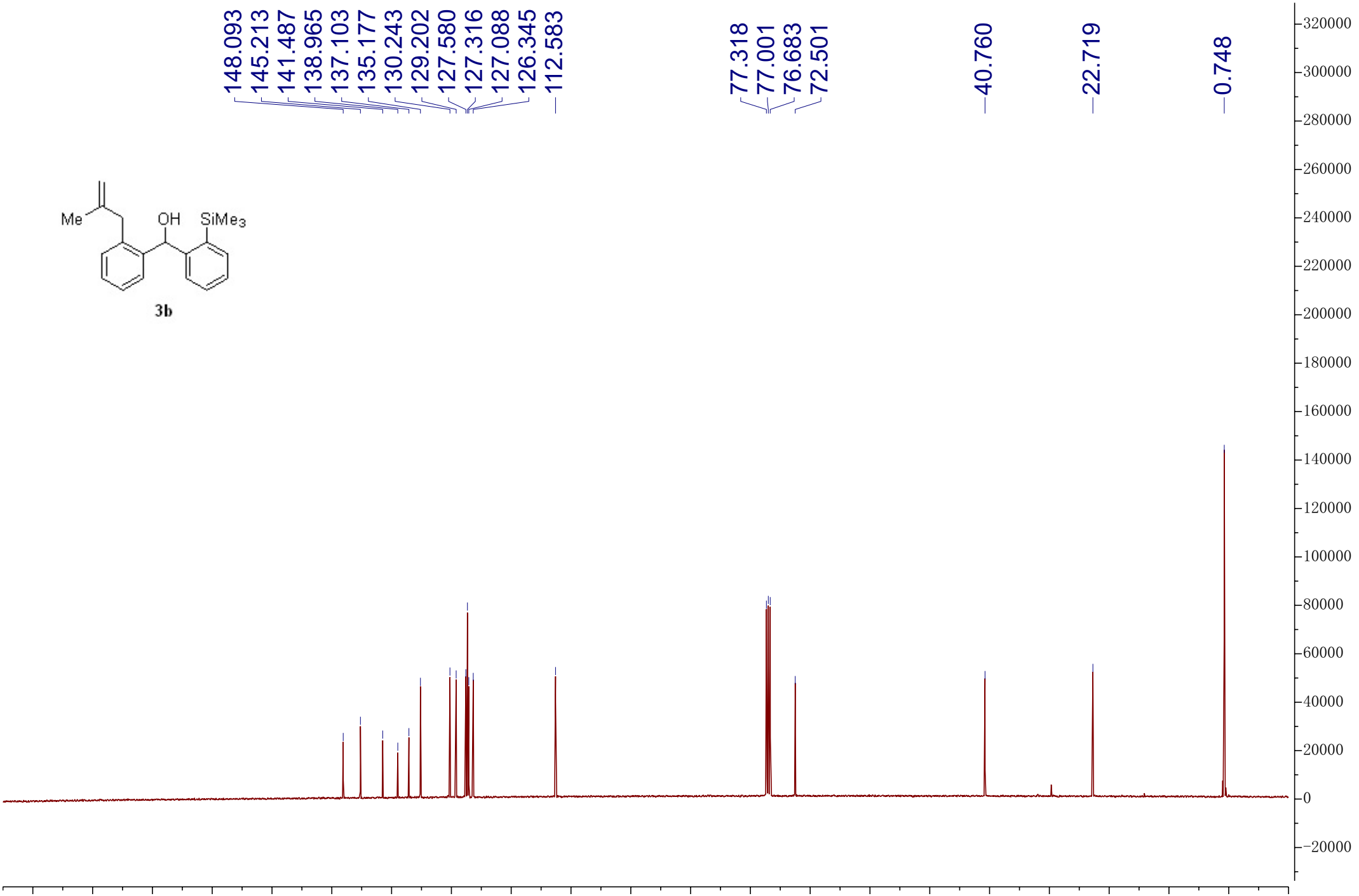


HTB-6-84_CDCl3_H1_2019-7-2

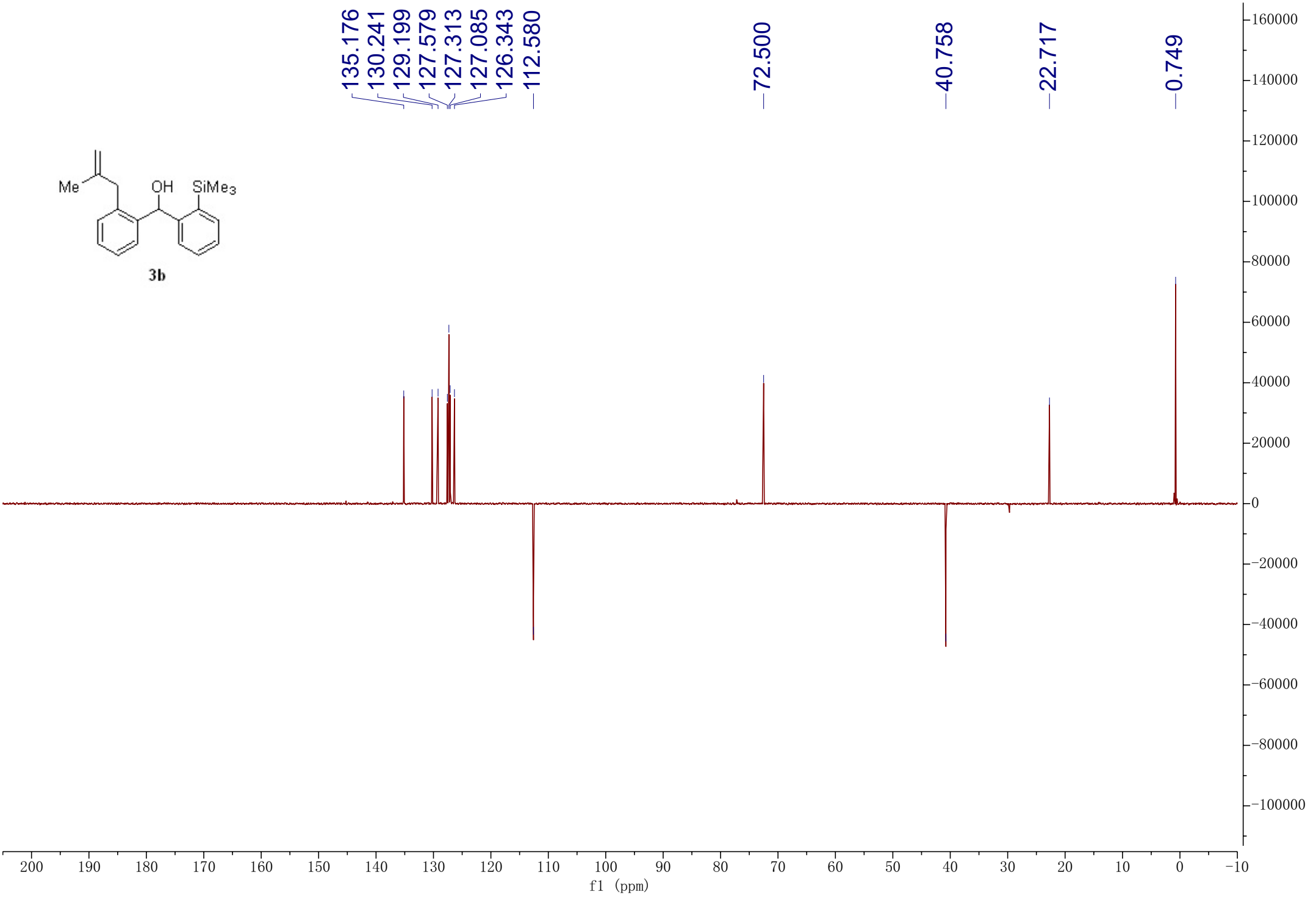


3b

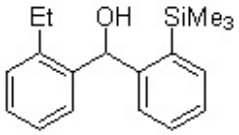
HTB-6-84_CDCl3_13C_2019-7-2



HTB-6-84_CDCl3_DEPT_2019-7-20



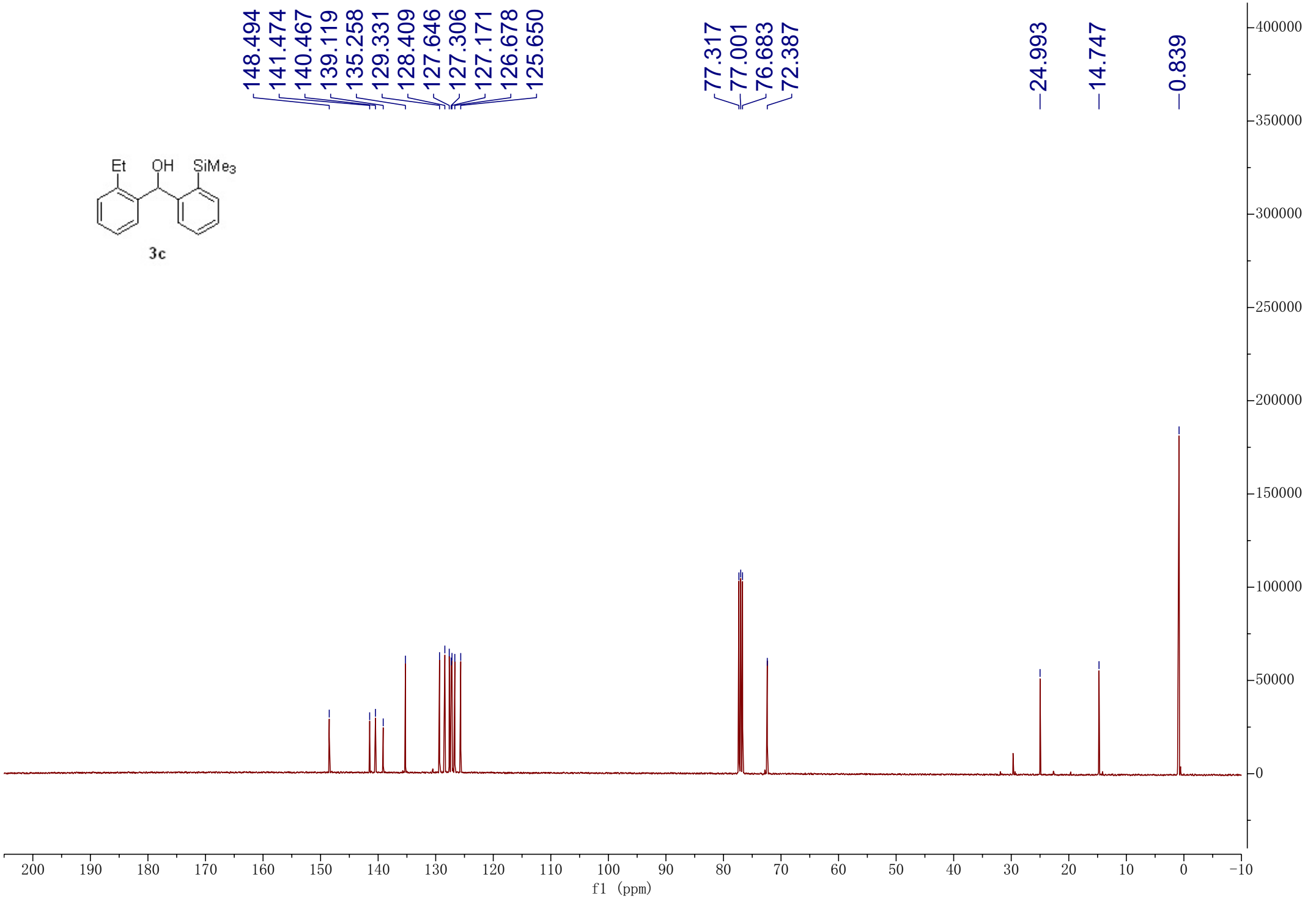
HTB-7-25-2_CDCl3_1H_2019-7-22



3c

f1 (ppm)

HTB-7-25-2_CDCl3_13C_2019-7-23



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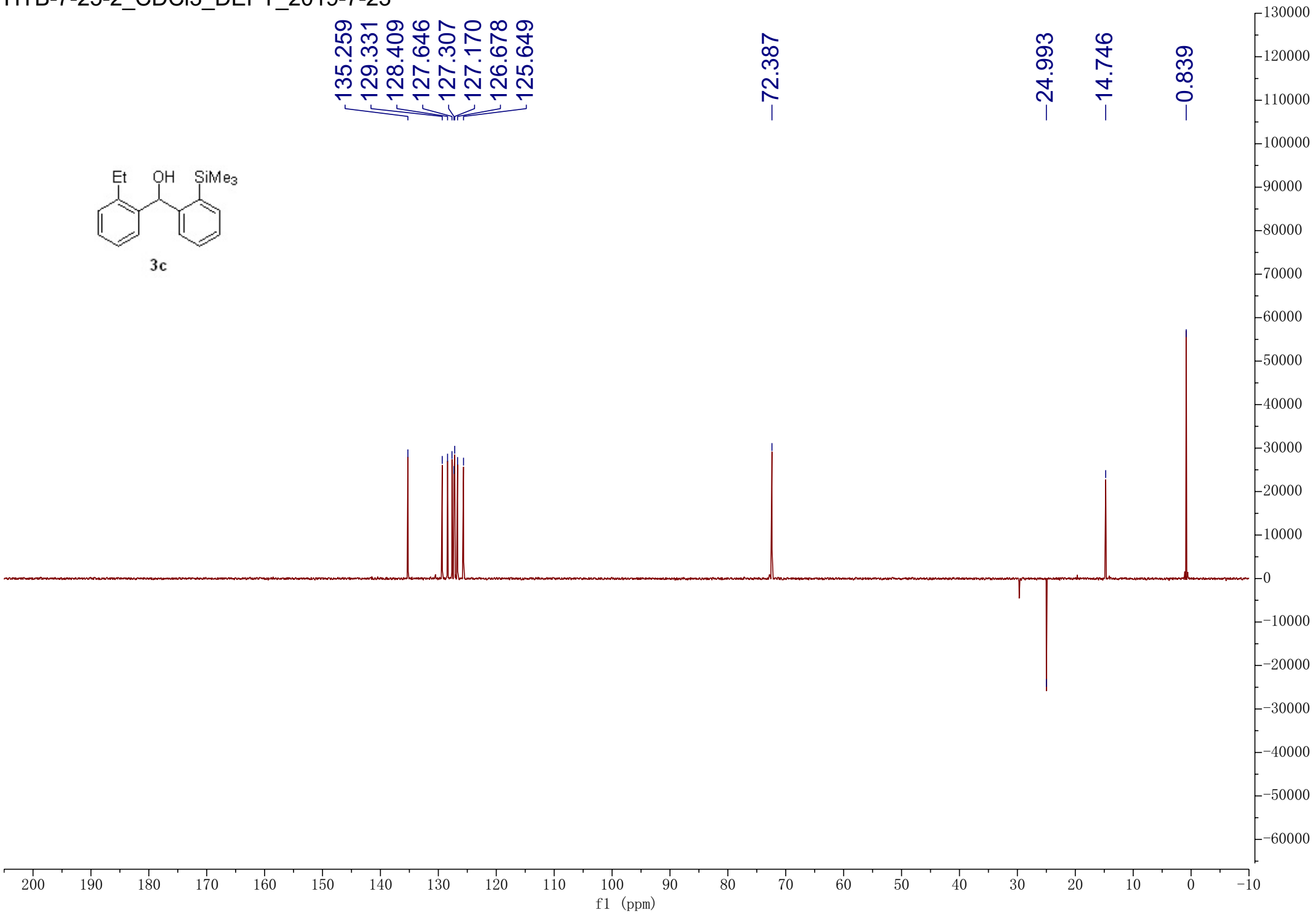
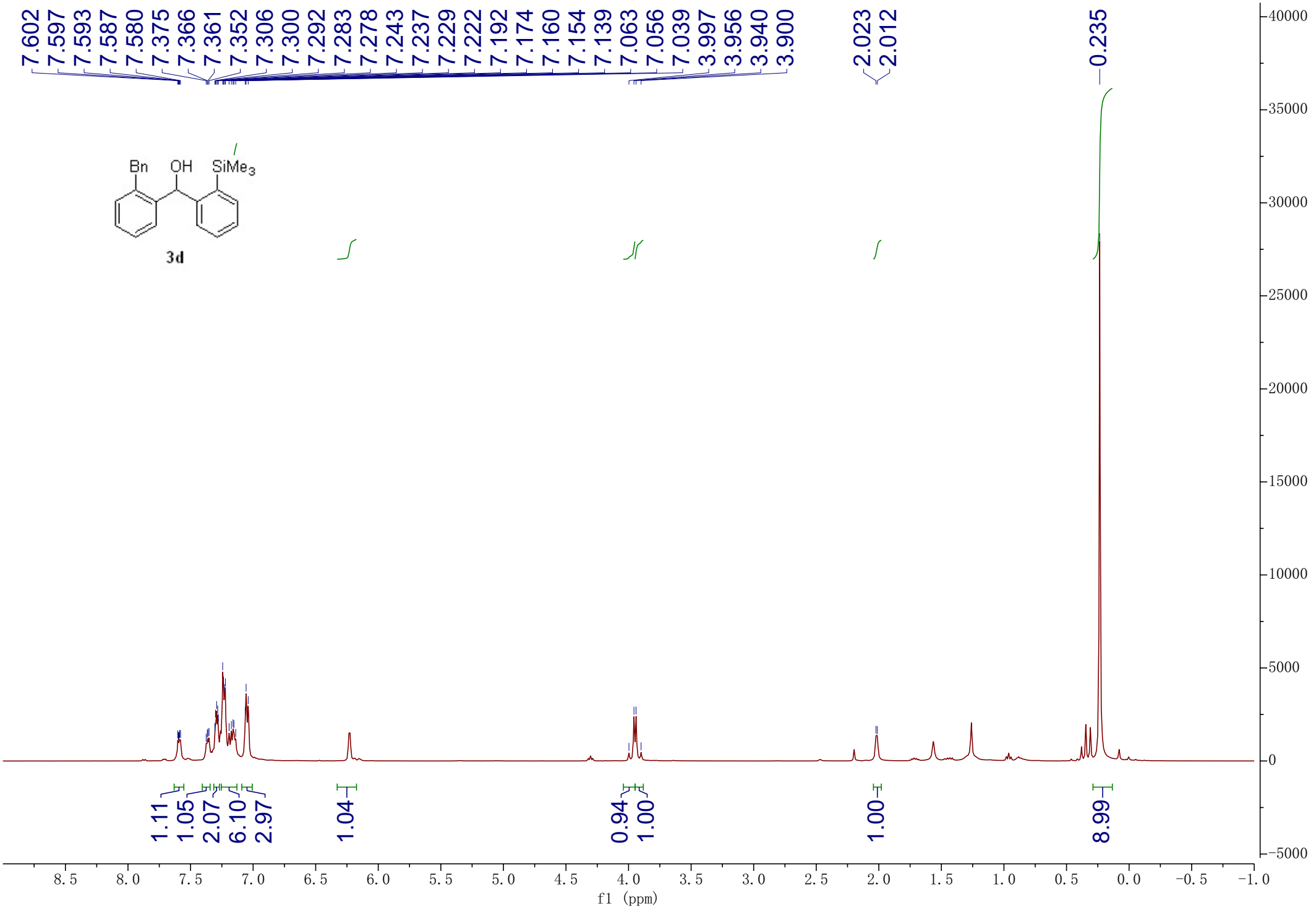


HTB-7-25-1_CDCl3_1H_2019-7-22



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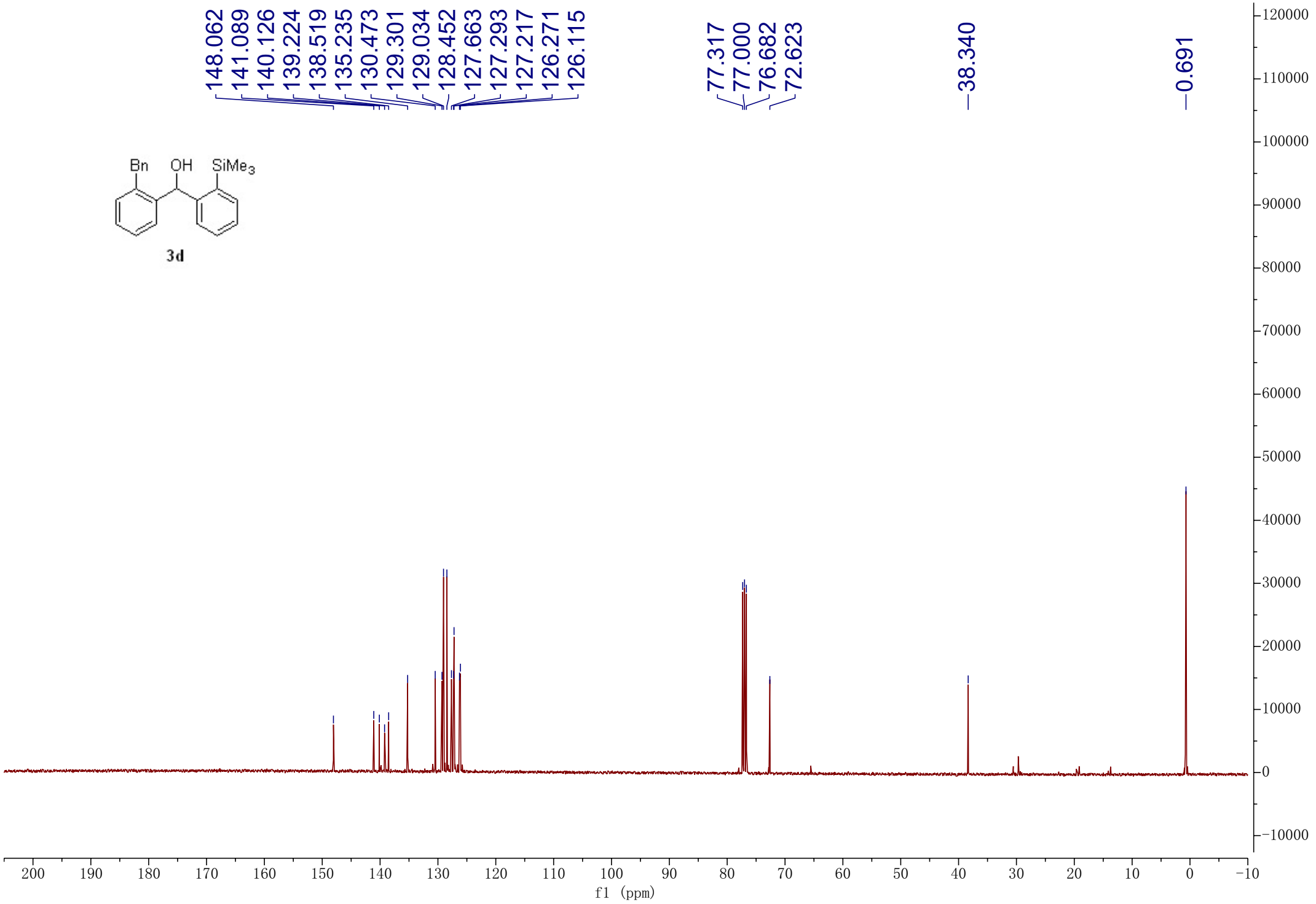

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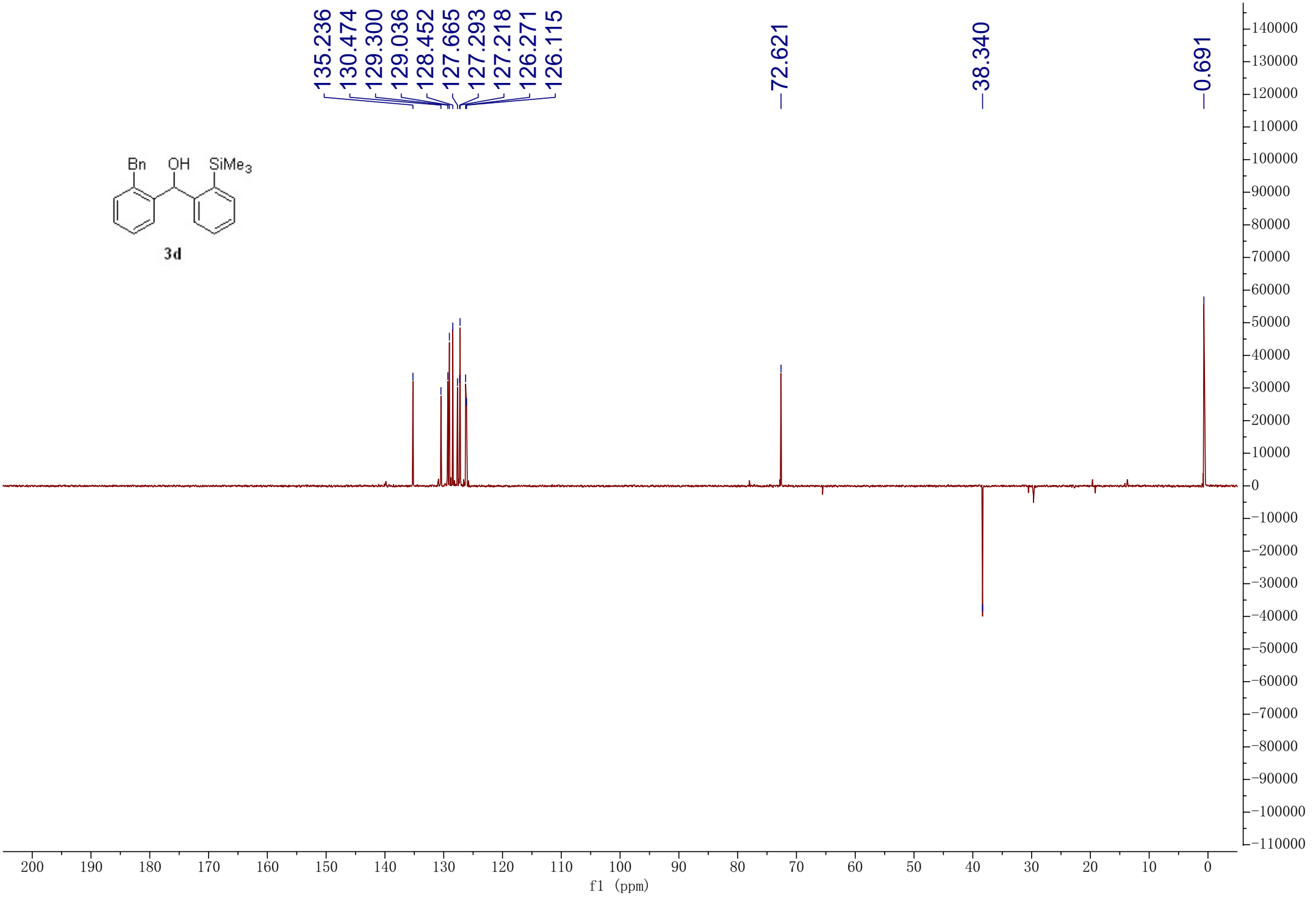
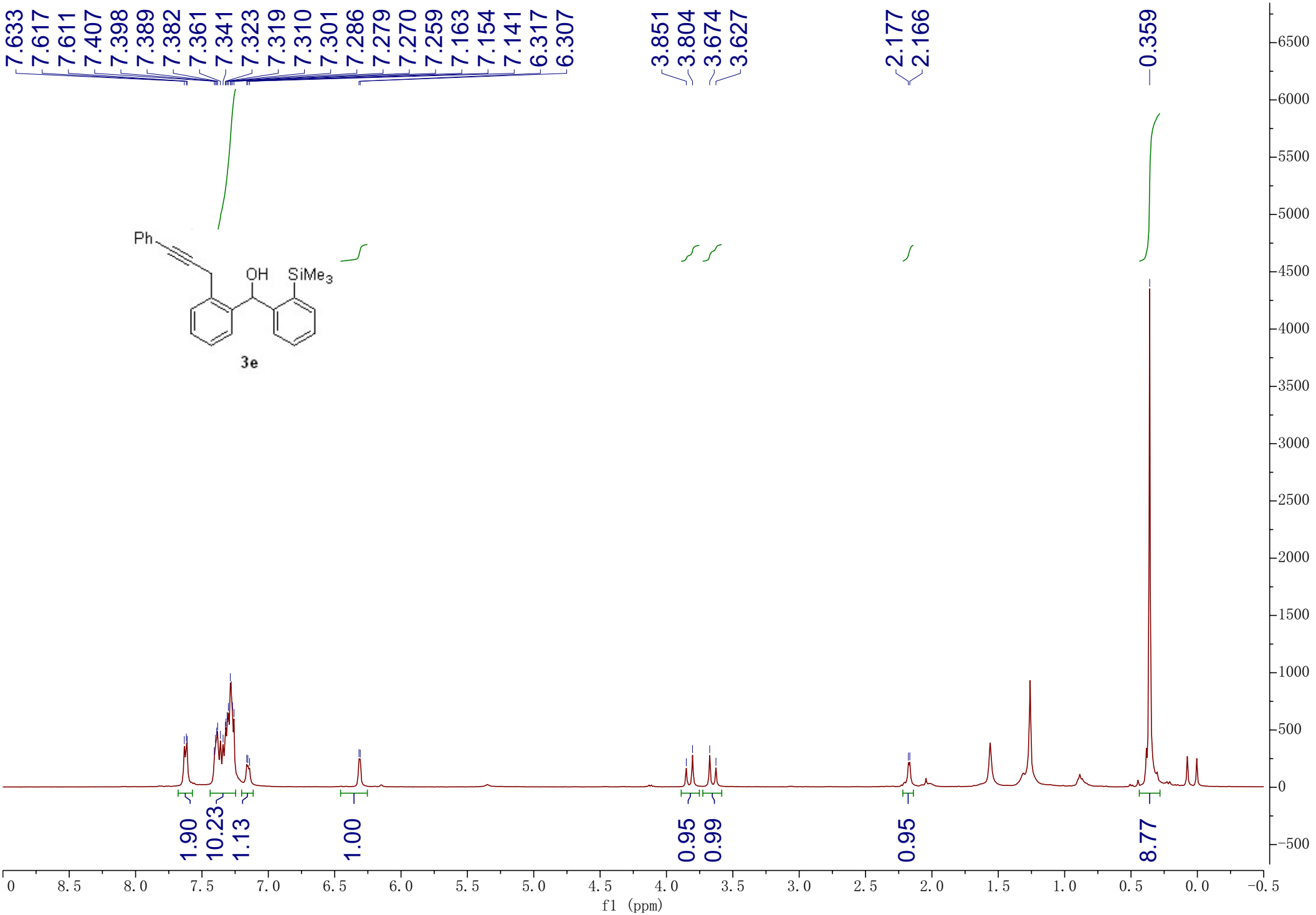
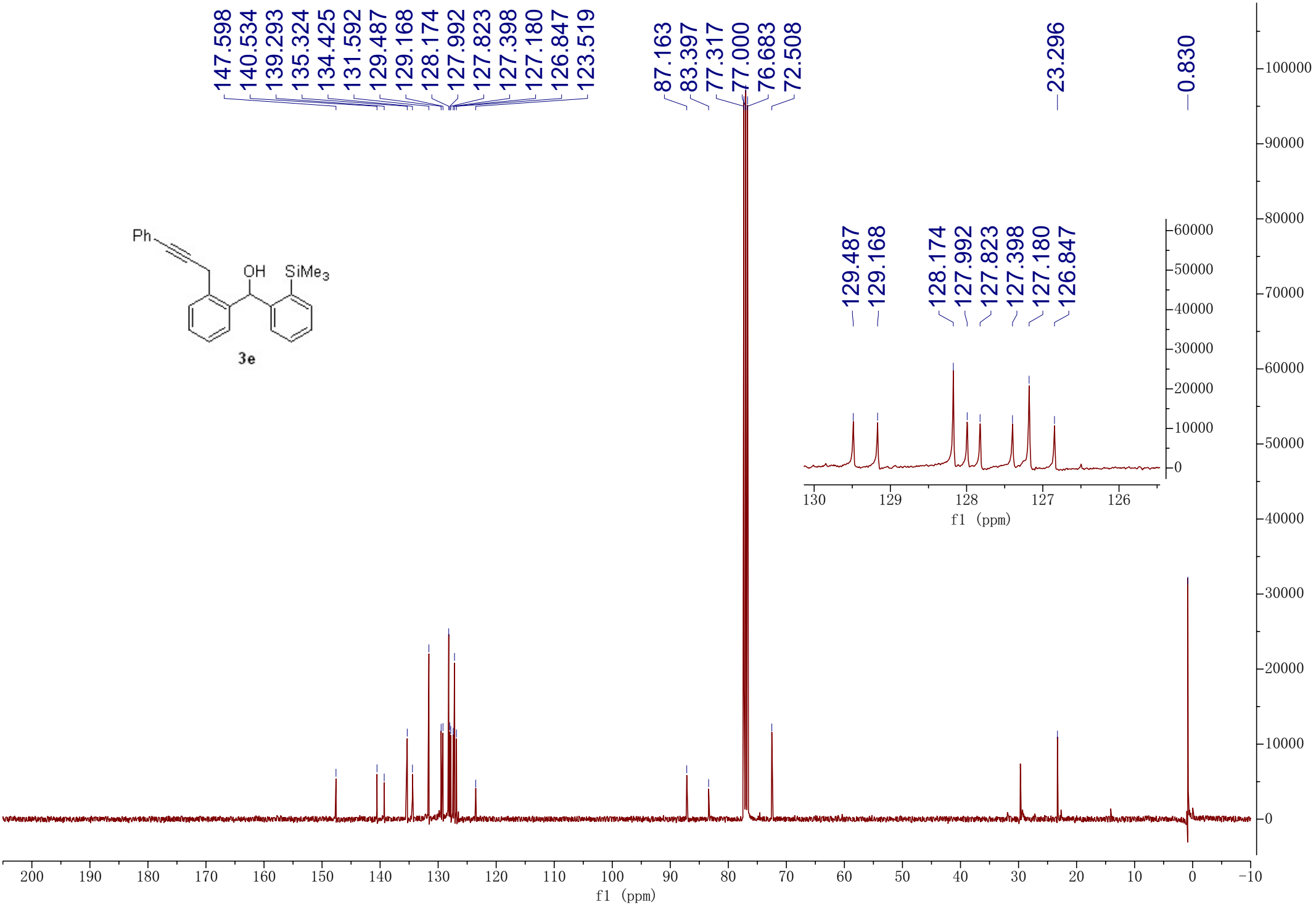


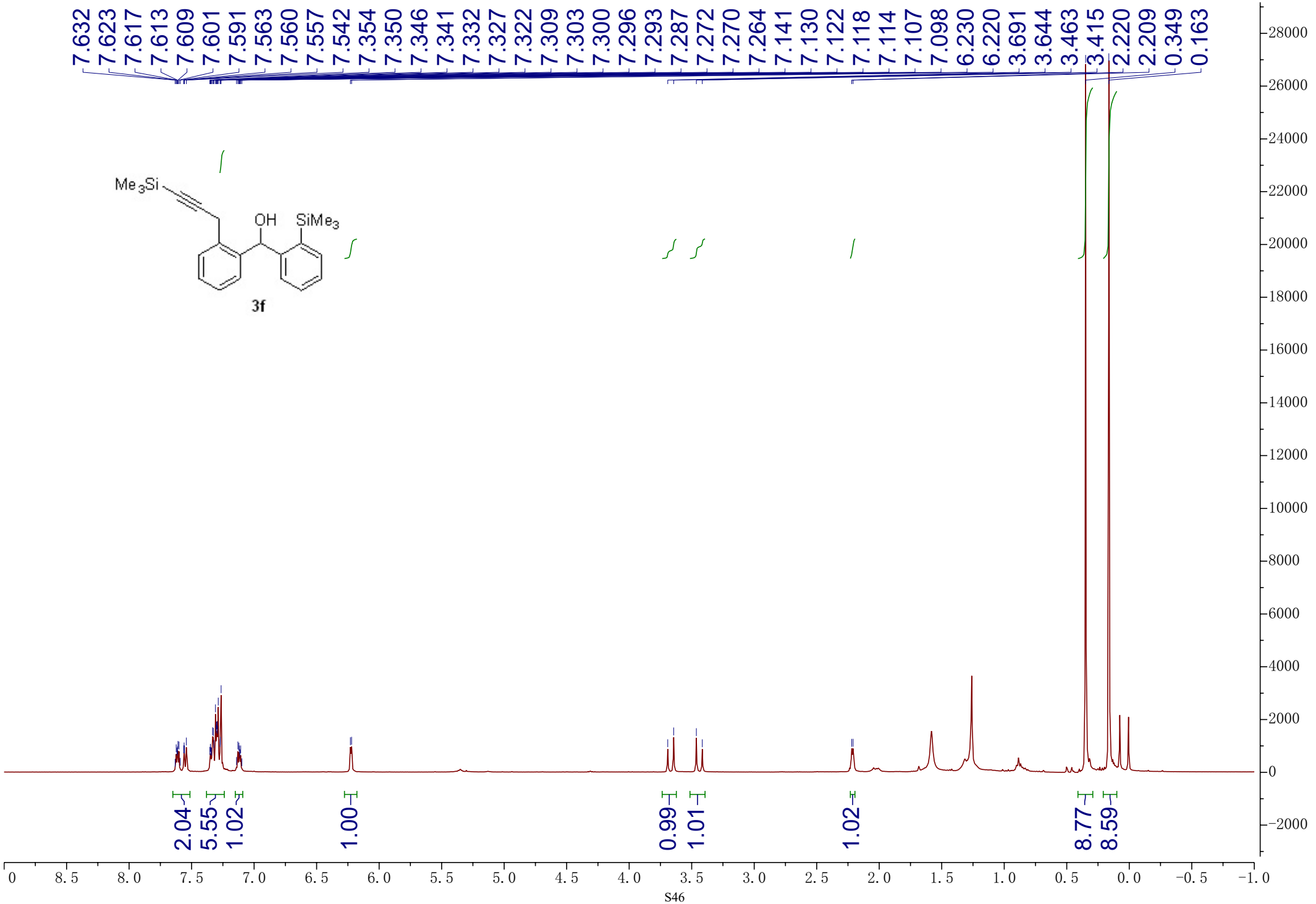
HTB-7-25_CDCl3_1H_2019-11-21



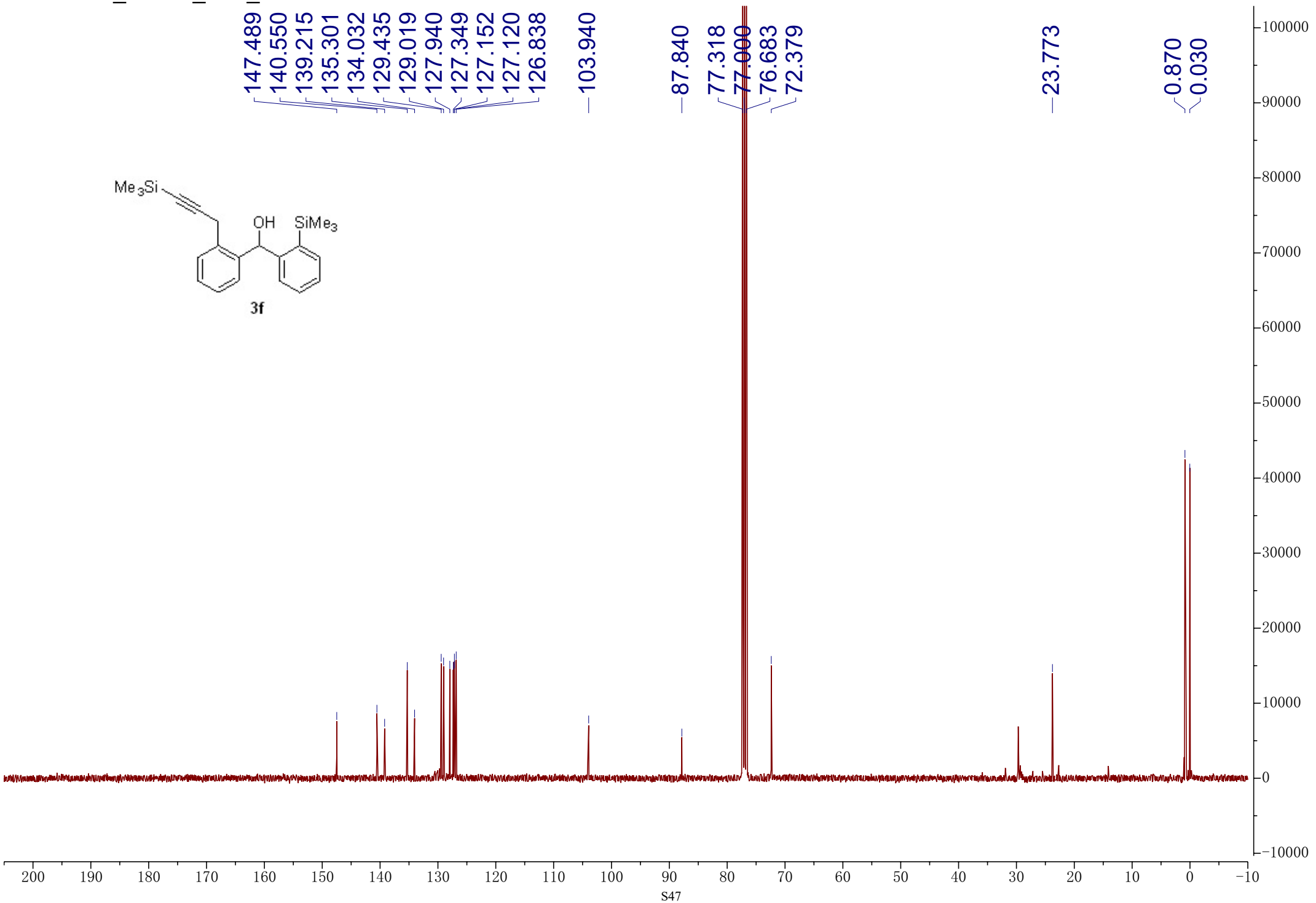
HTB-7-25_CDCl3_1H_2019-10-15



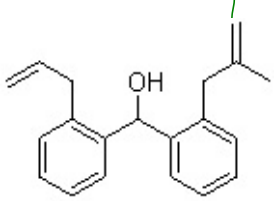
HTB-7-113_CDCl3_1H_2019-7-31



HTB-7-113_CDCl3_13C_2019-8-1



HTB-6-42_CDCl3_1H_2019-6-3



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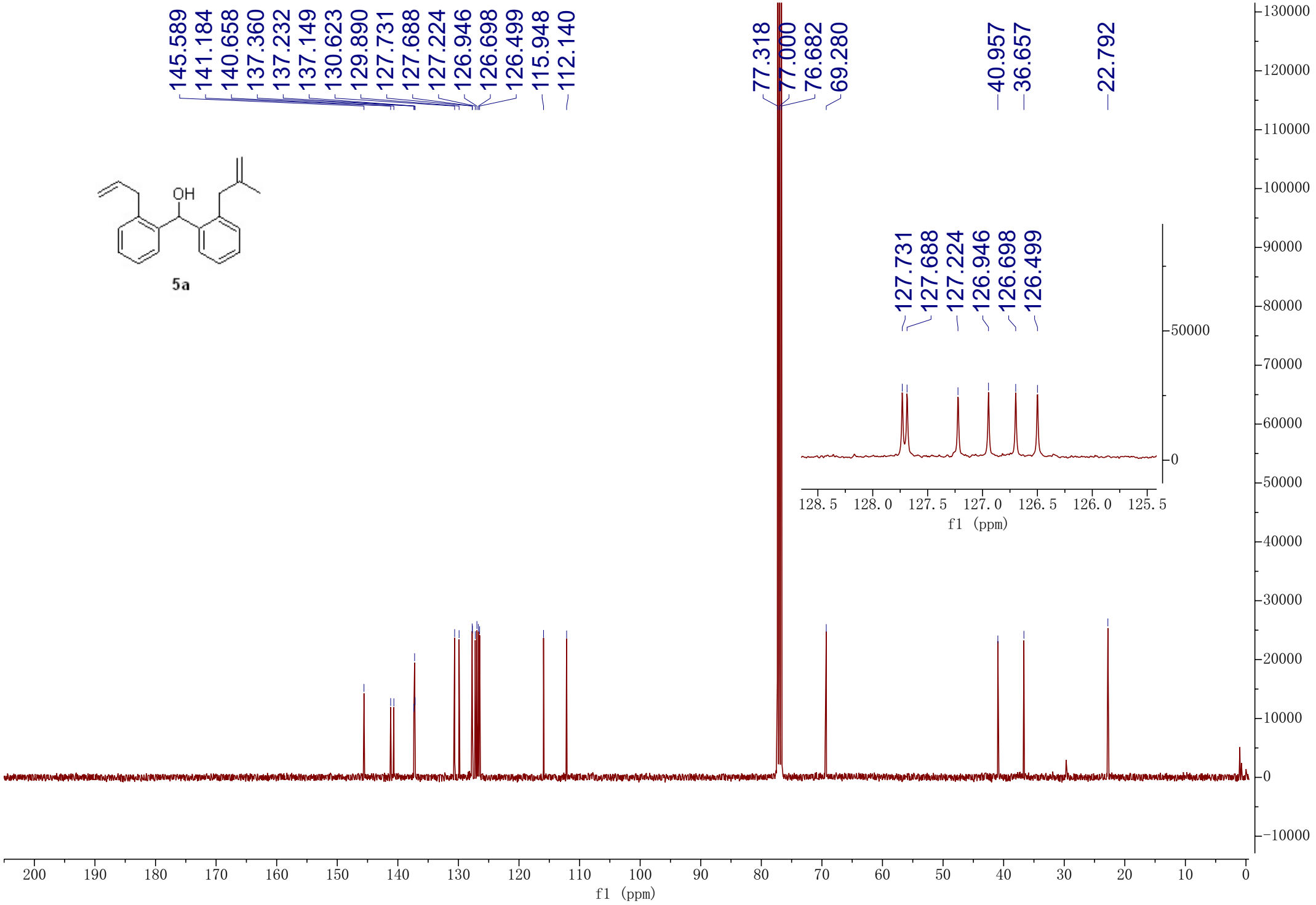
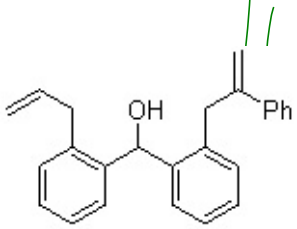
HTB-6-42_CDCl3_13C_2019-6-3



HTB-7-120_CDCl3_1H_2019-7-9



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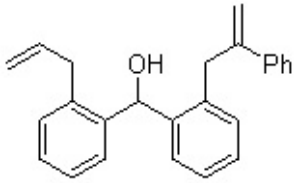
HTB-7-120_CDCl3_13C_2019-7-9



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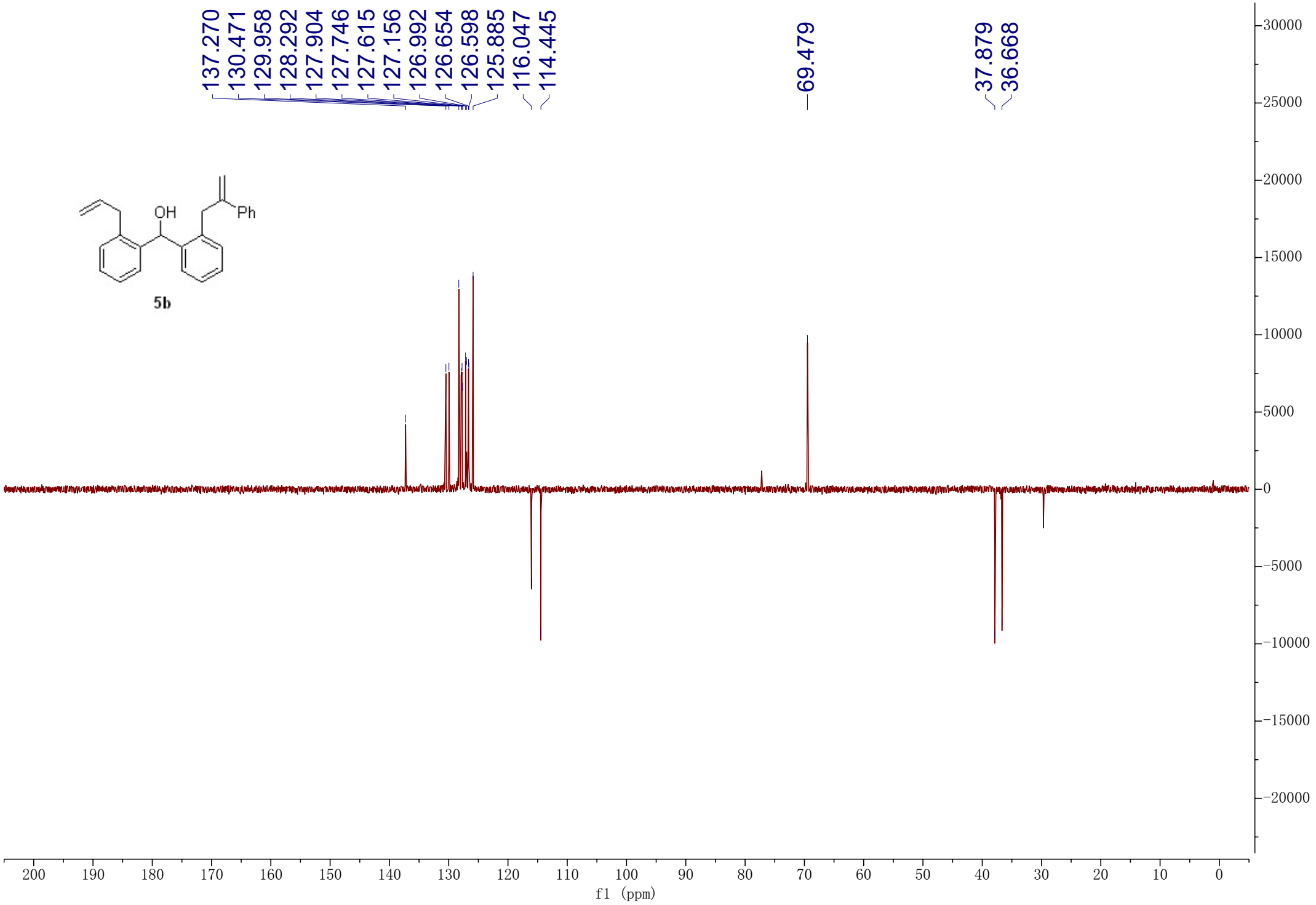
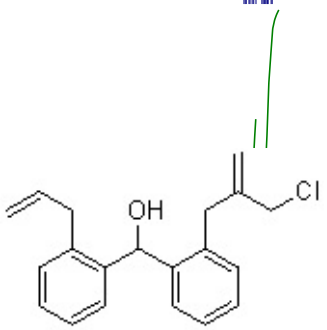
HTB-7-120_CDCl3_DEPT_2019-7-9



HTB-8-4_CDCl3_1H_2019-10-9



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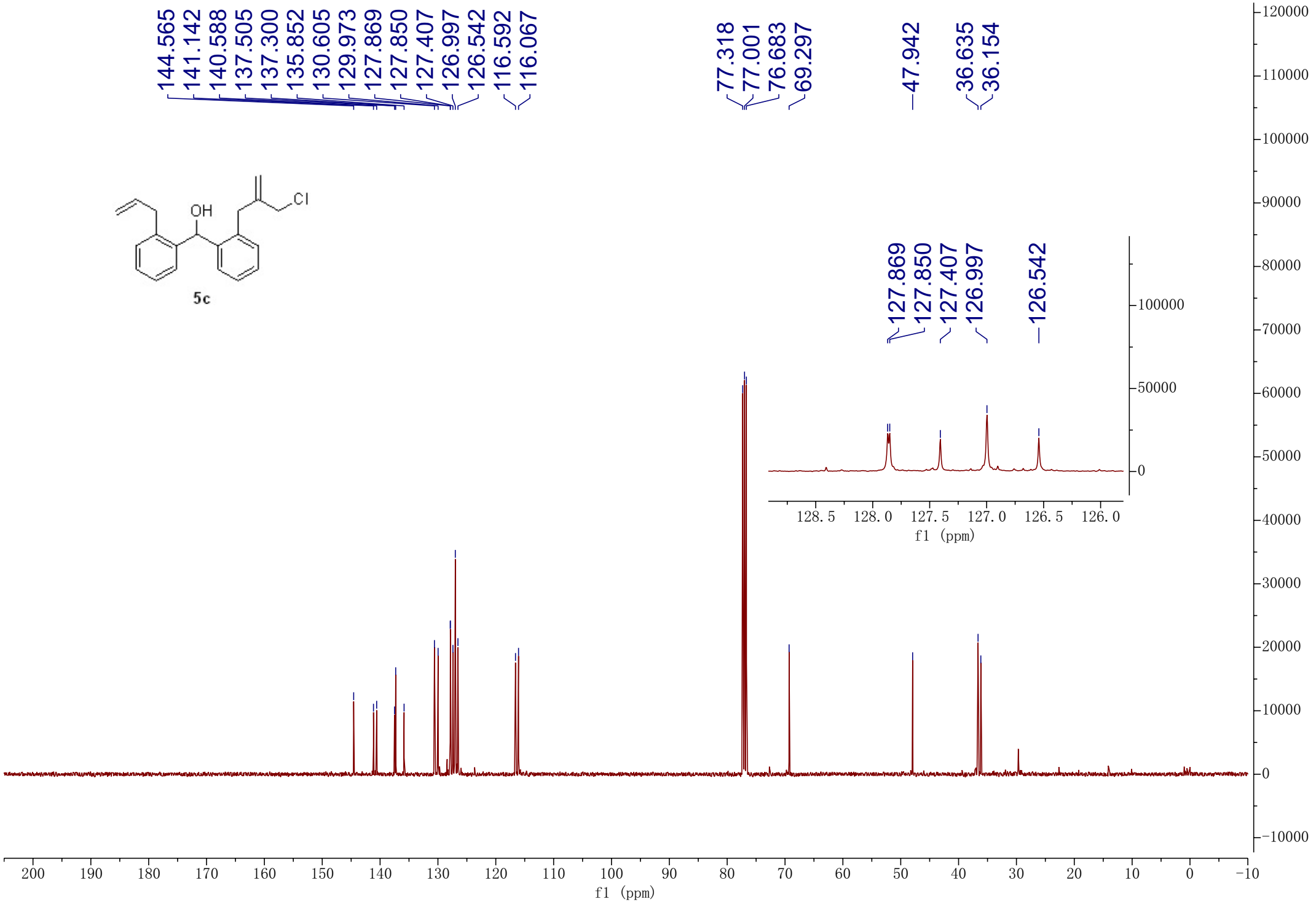
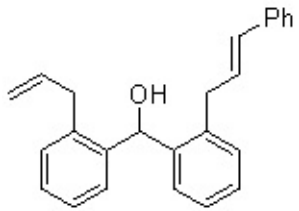
HTB-8-4_CDCl3_13C_2019-10-9



HTB-7-53-D_CDCl3_1H_2019-10-8



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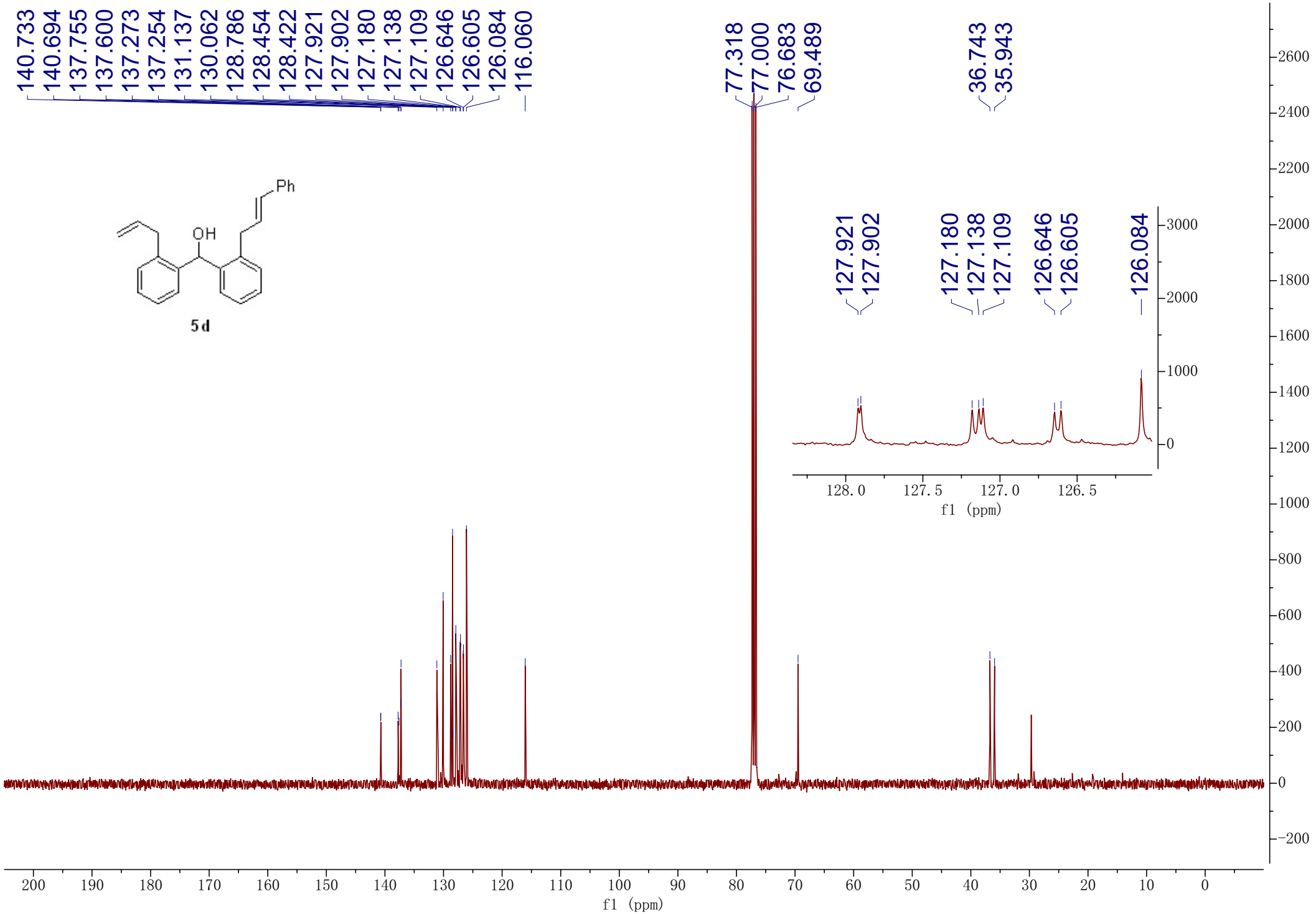
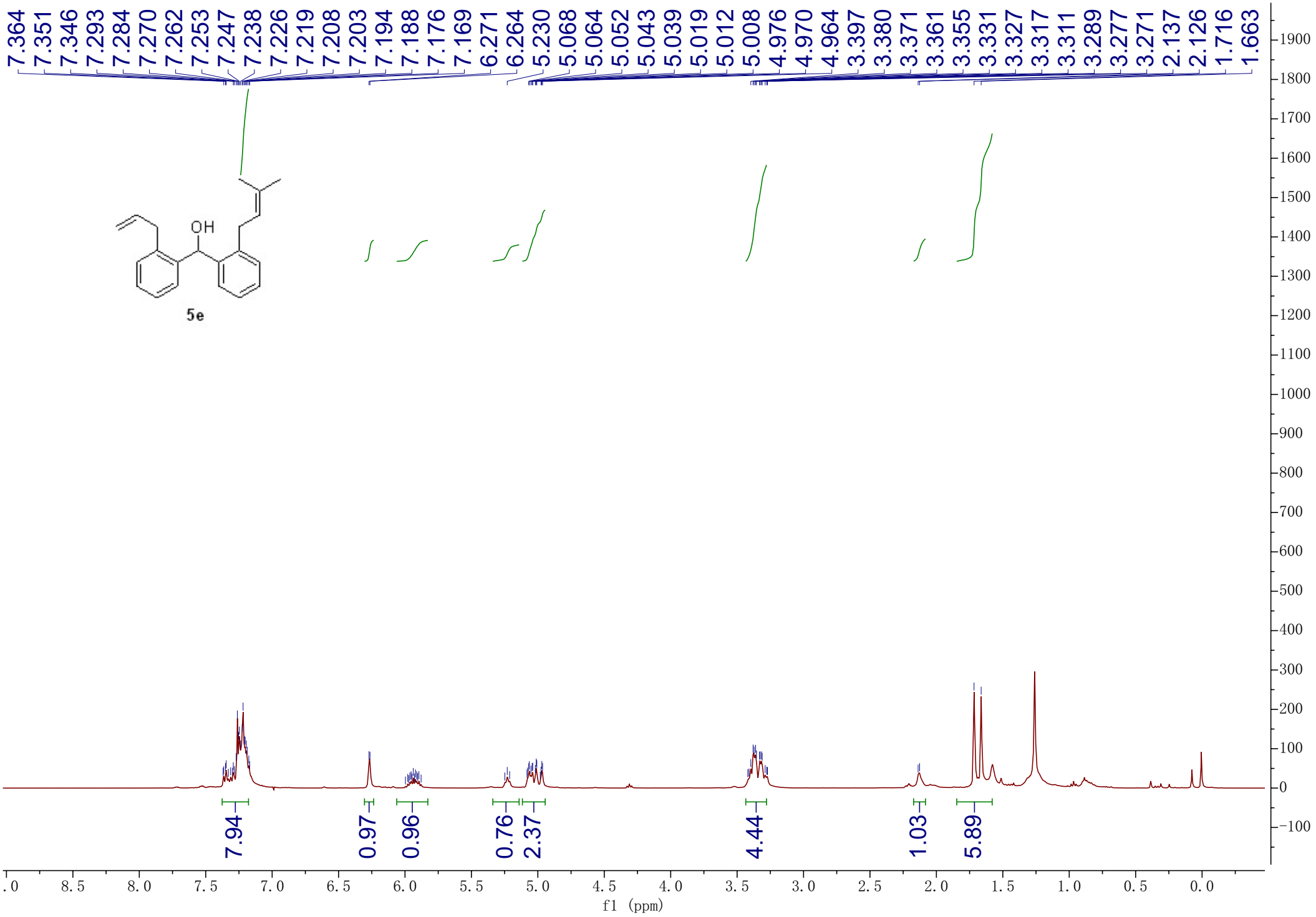
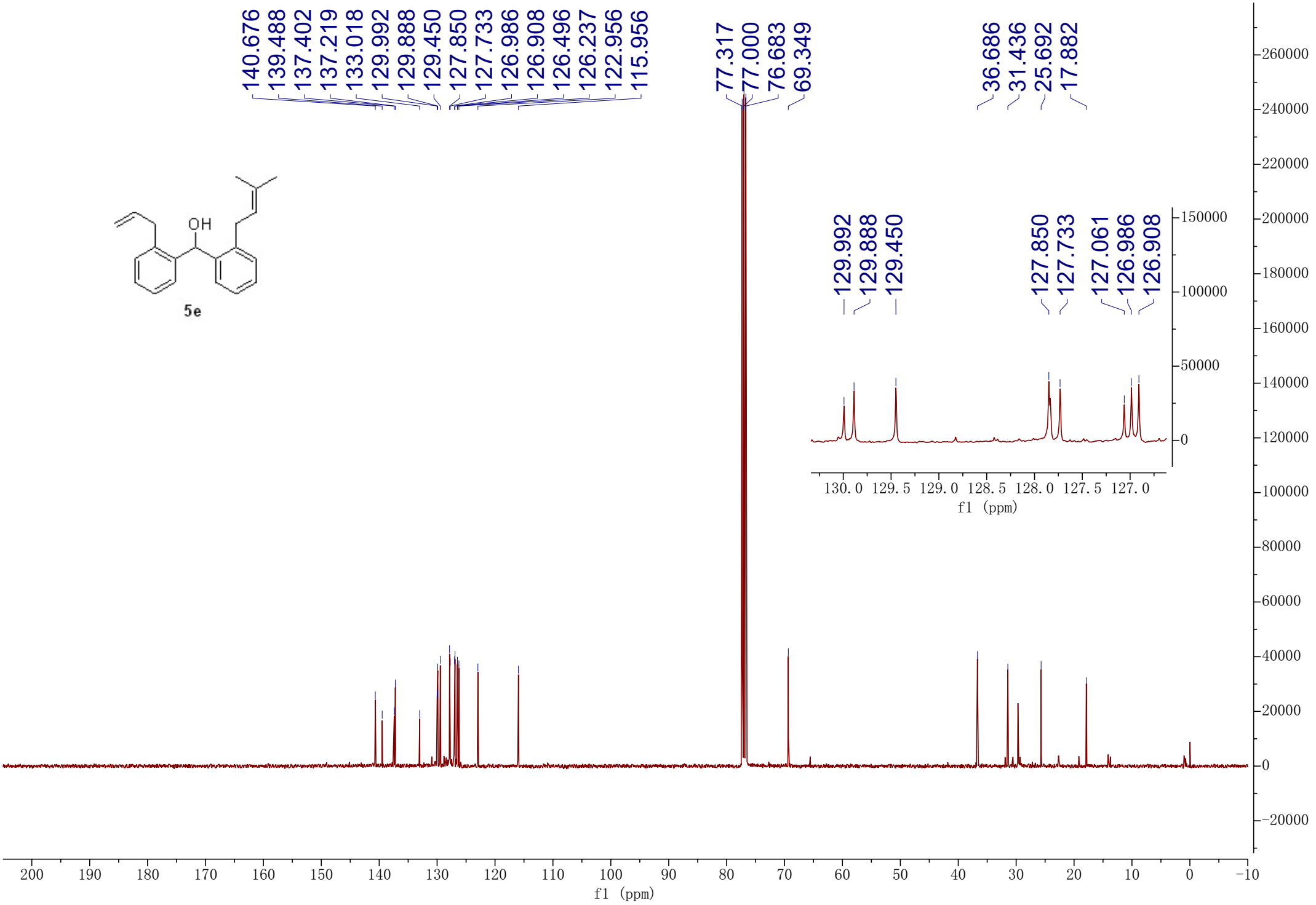
HTB-7-53-D_CDCl3_13C_2019-10-14



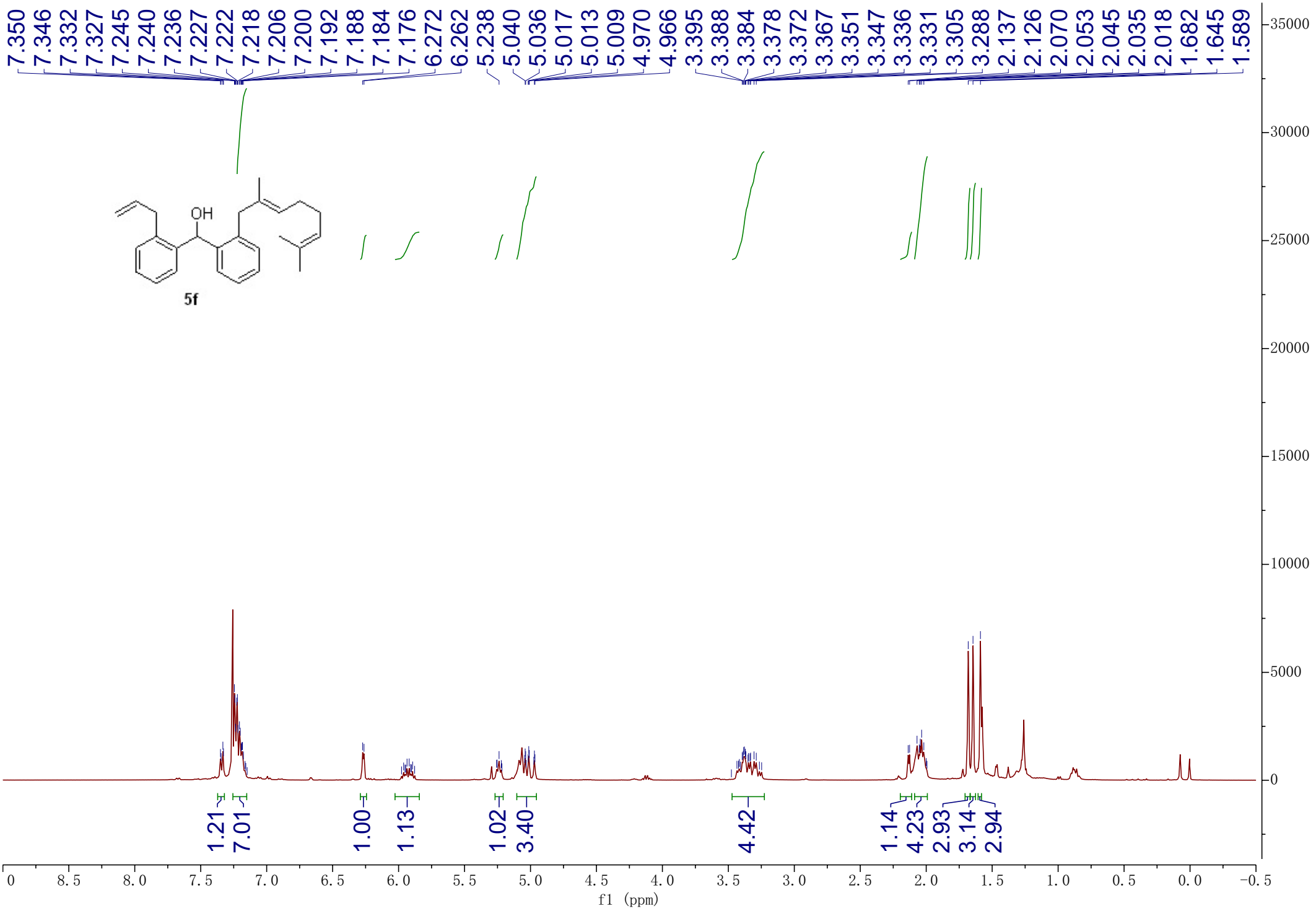
HTB-7-46_CDCl3_1H_2019-9-5



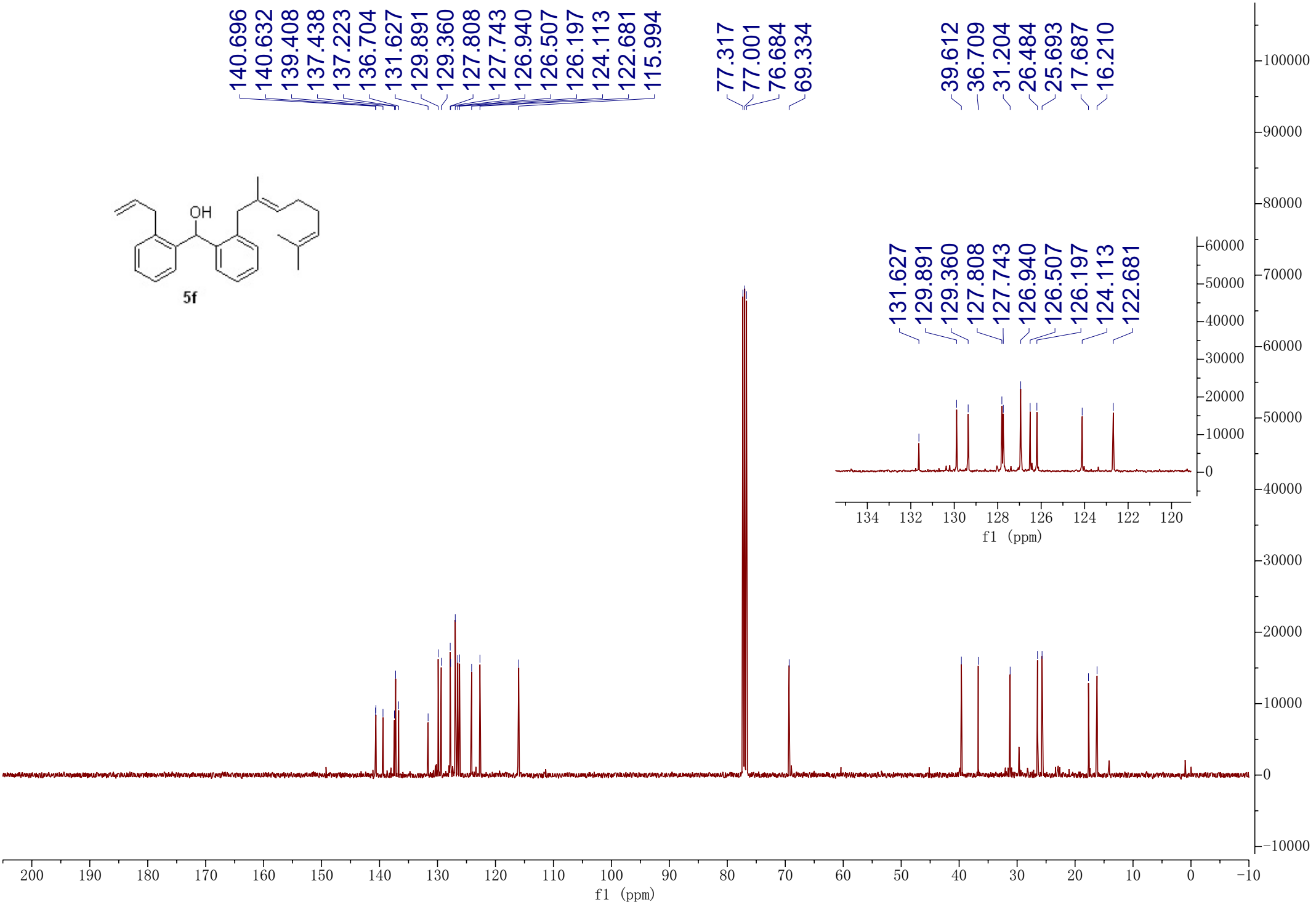
HTB-7-46_CDCl3_13C_2019-9-6



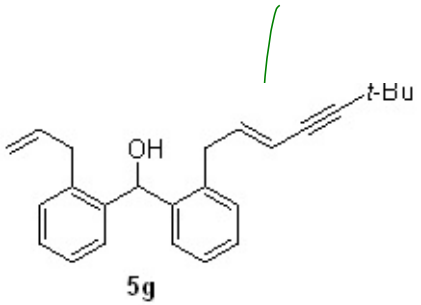
HTB-7-101_CDCl3_1H_2019-10-9



HTB-7-101_CDCl3_13C_2019-10-10



HTB-7-104_CDCl3_1H_2019-10-9



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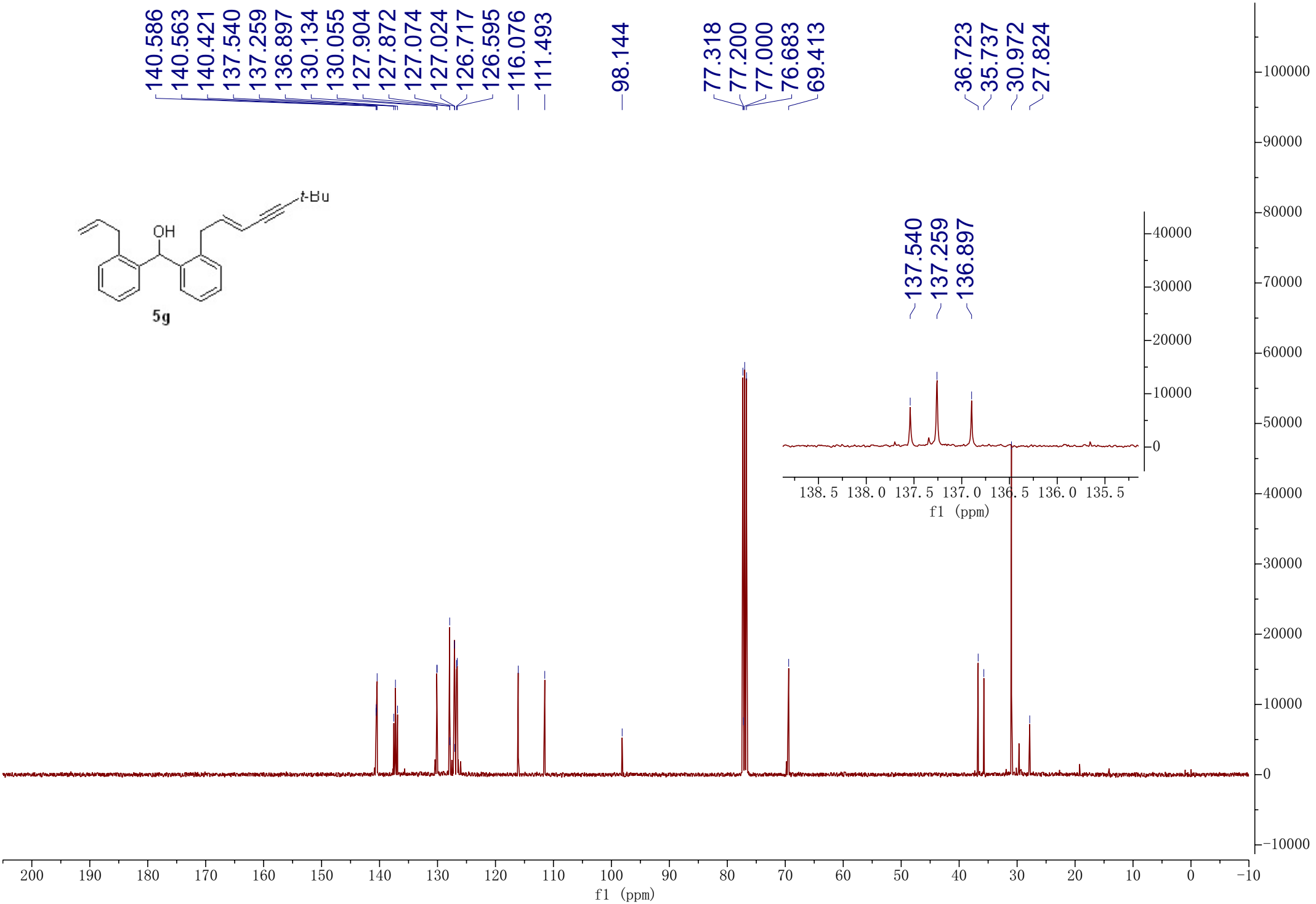
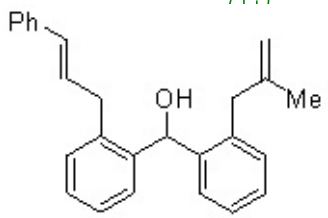
HTB-7-104_CDCl3_13C_2019-10-10



HTB-7-47_CDCl3_1H_2019-9-5



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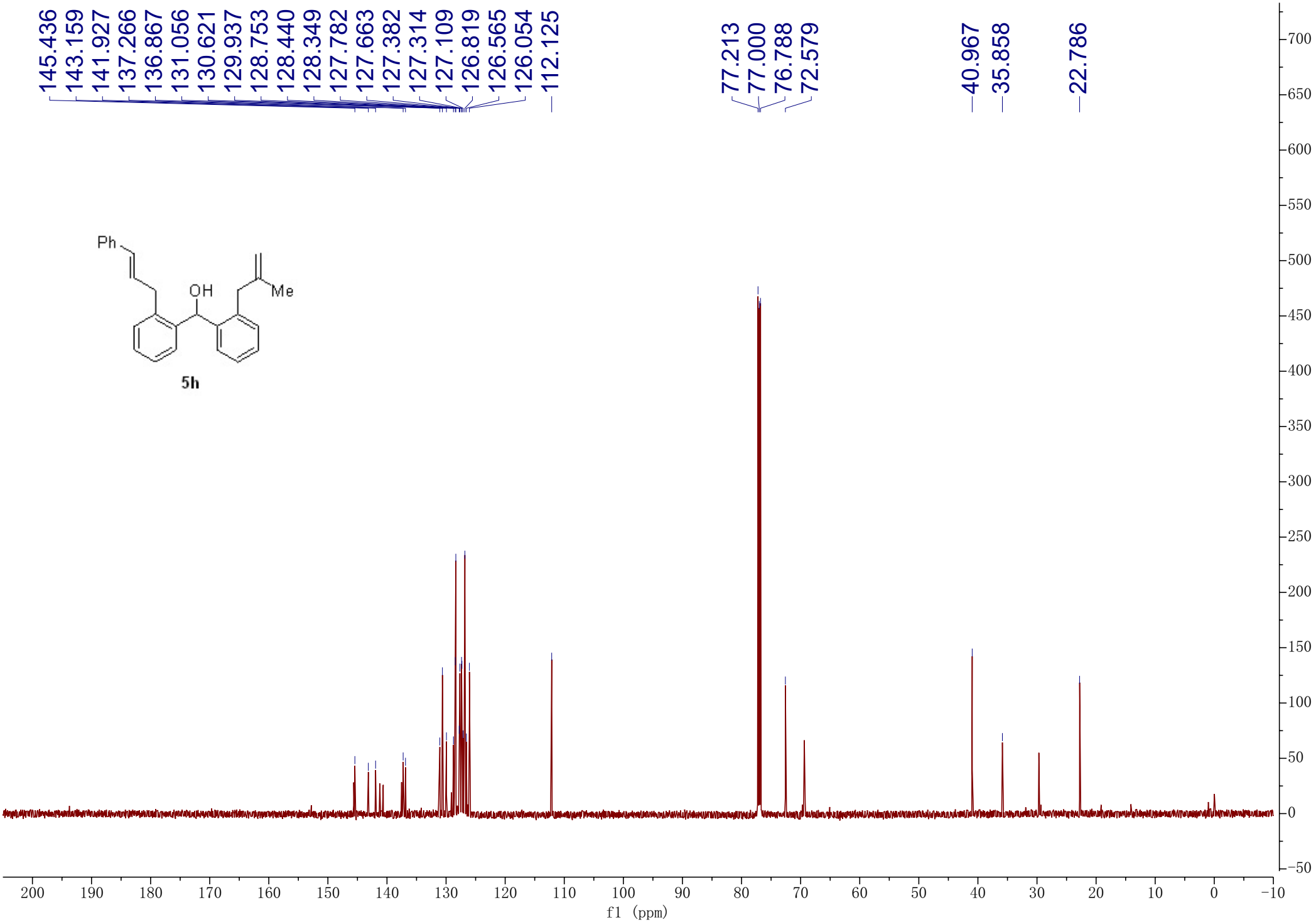
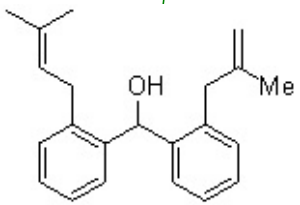
HTB-7-47_CDCl3_13C_2019-9-6



HTB-7-32_CDCl3_1H_2019-9-2



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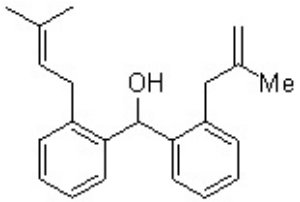
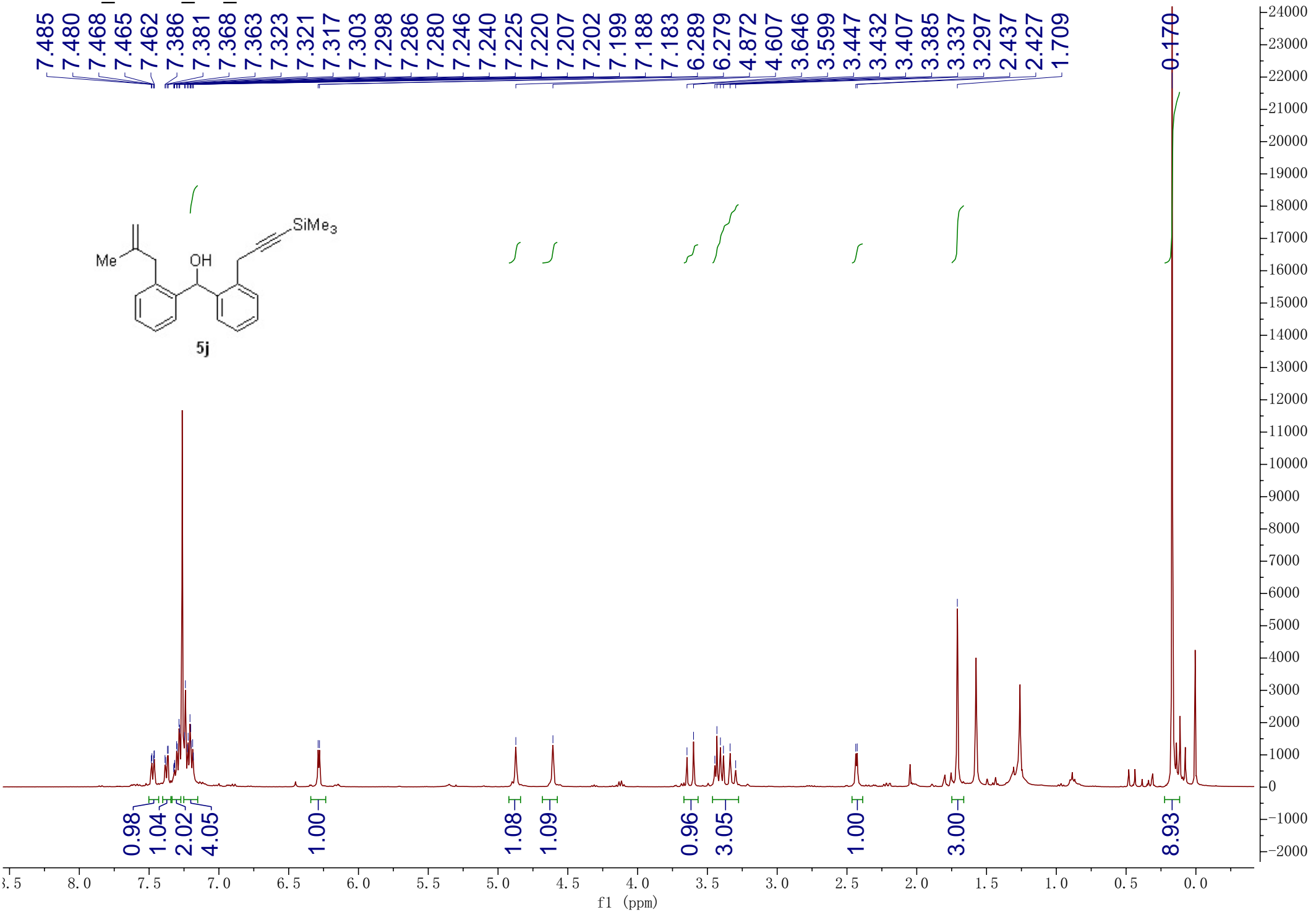
HTB-7-32_CDCl3_13C_2019-9-3

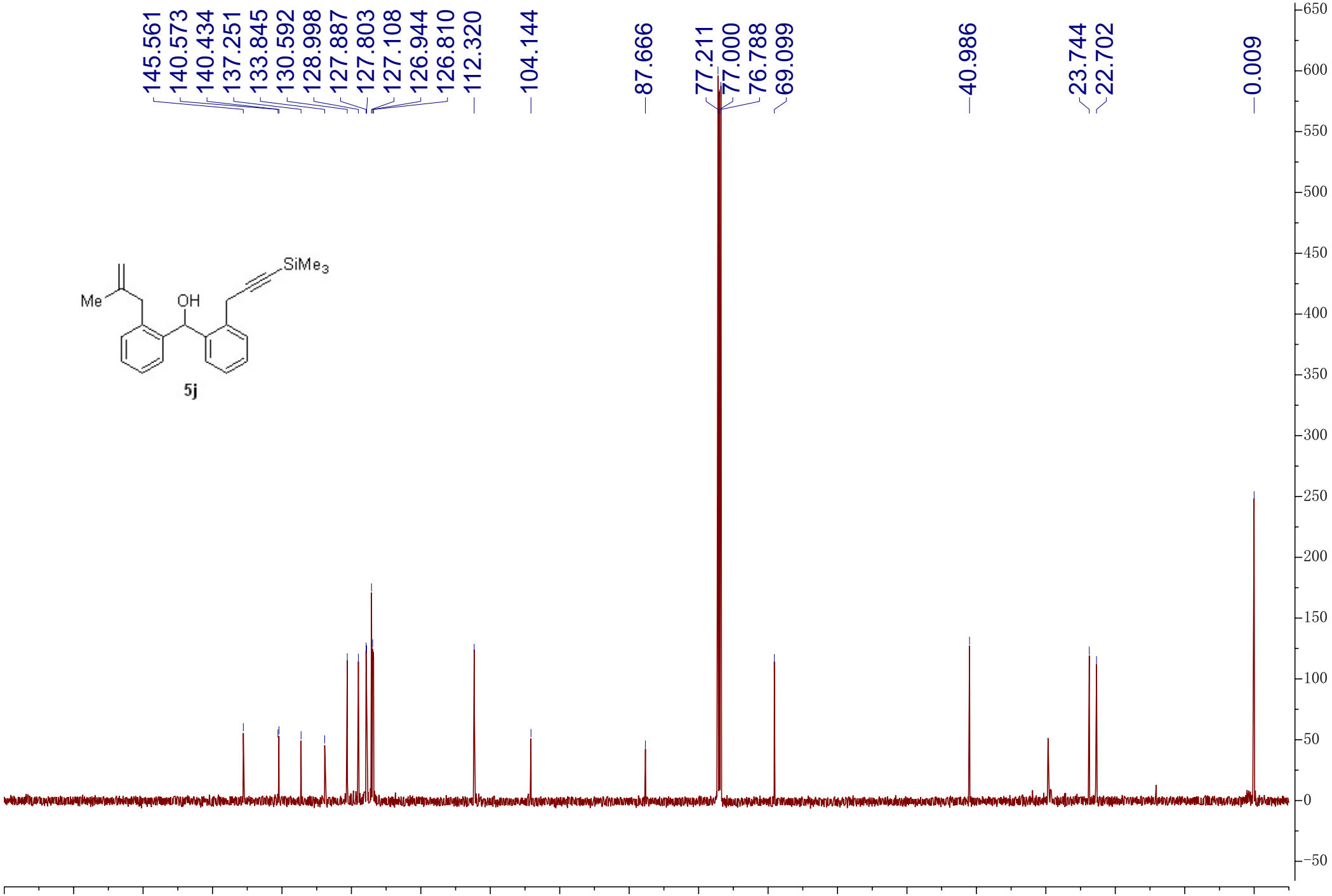


5i

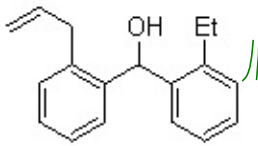
HTB-7-73_CDCl3_1H_2019-9-25



HTB-7-73_CDCl3_13C_2019-10-15



HTB-7-81_CDCl3_1H_2019-10-18



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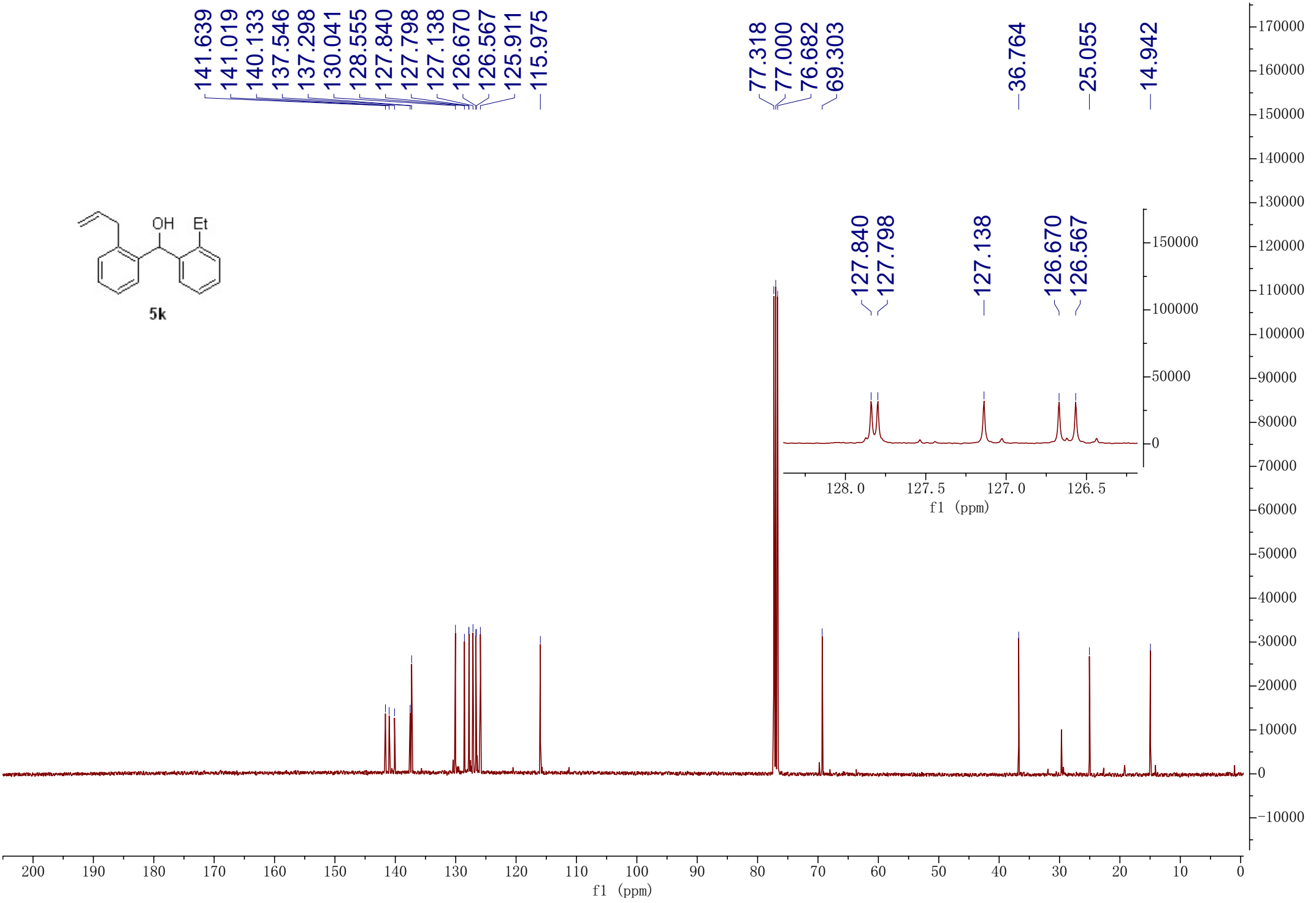
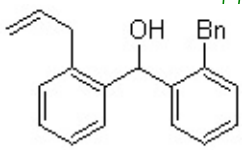
HTB-7-81_CDCl3_13C_2019-10-21



HTB-7-82_CDCl3_1H_2019-10-15



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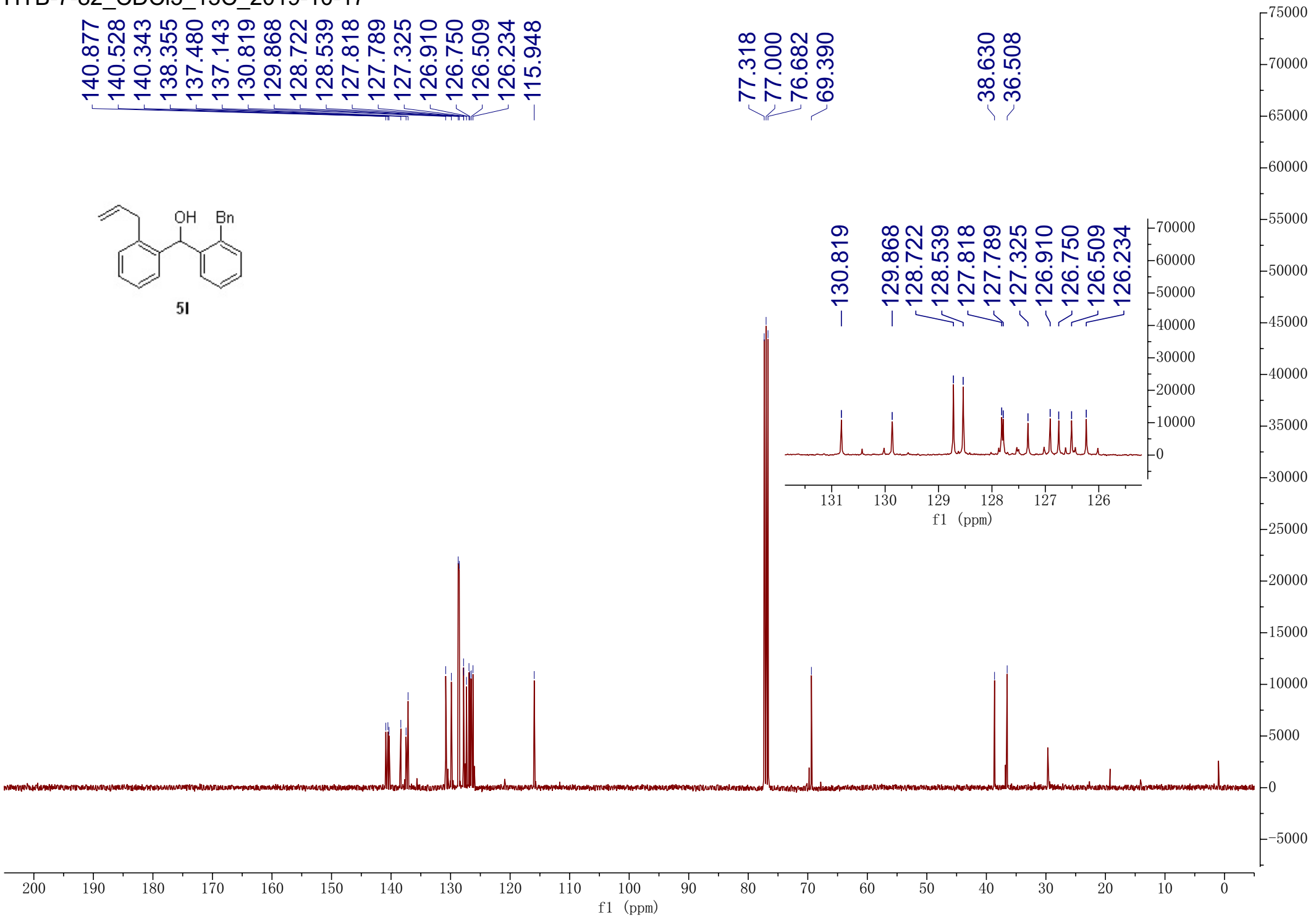
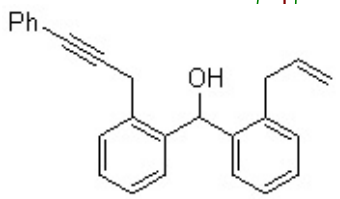
HTB-7-82_CDCl3_13C_2019-10-17



HTB-7-69_CDCl3_1H_2019-9-24



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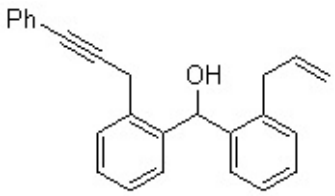
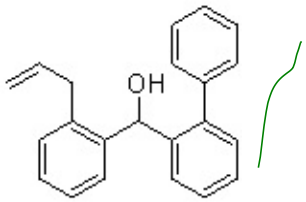
HTB-7-69_CDCl3_13C_2019-10-24



5m

HTB-7-95_CDCl3_1H_2019-10-15



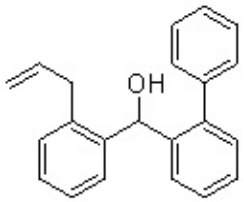
5n

7.537 7.532 7.518 7.513 7.457 7.451 7.447 7.440 7.434 7.384 7.374 7.370 7.360 7.355 7.344 7.337 7.332 7.319 7.294 7.287 7.265 7.246 7.242 7.226 7.220 7.212 7.206 7.202 7.188 7.184 7.069 7.065 7.051 7.047 6.011 4.839 4.834 4.813 4.809 4.682 4.678 4.640 4.635 2.907 2.902 2.891 2.886 2.087

8.70 3.99 0.87 0.73 1.62 1.66 0.79

f1 (ppm)

HTB-7-95_CDCl3_13C_2019-10-17



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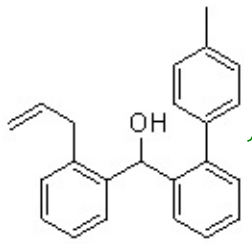
HTB-7-94_CDCl3_1H_2019-10-17



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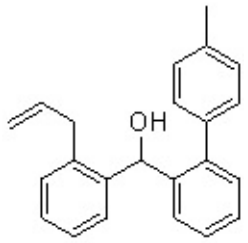
HTB-7-94_CDCl3_13C_2019-10-18



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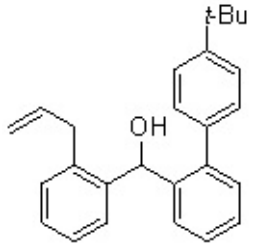
HTB-7-92_CDCl3_1H_2019-10-9



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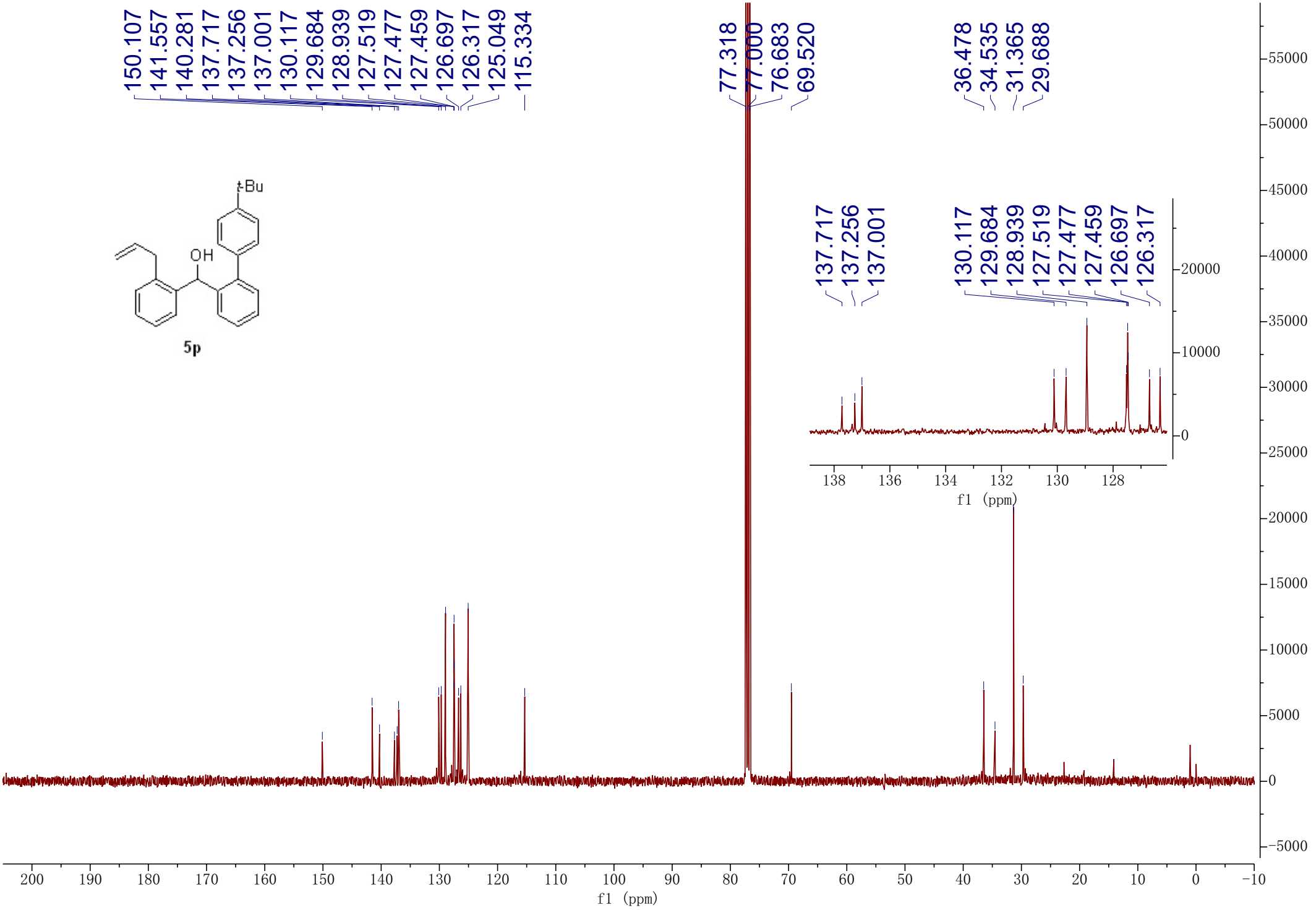
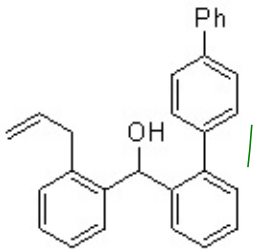
HTB-7-92_CDCl3_13C_2019-10-9



HTB-7-89_CDCl3_1H_2019-10-18



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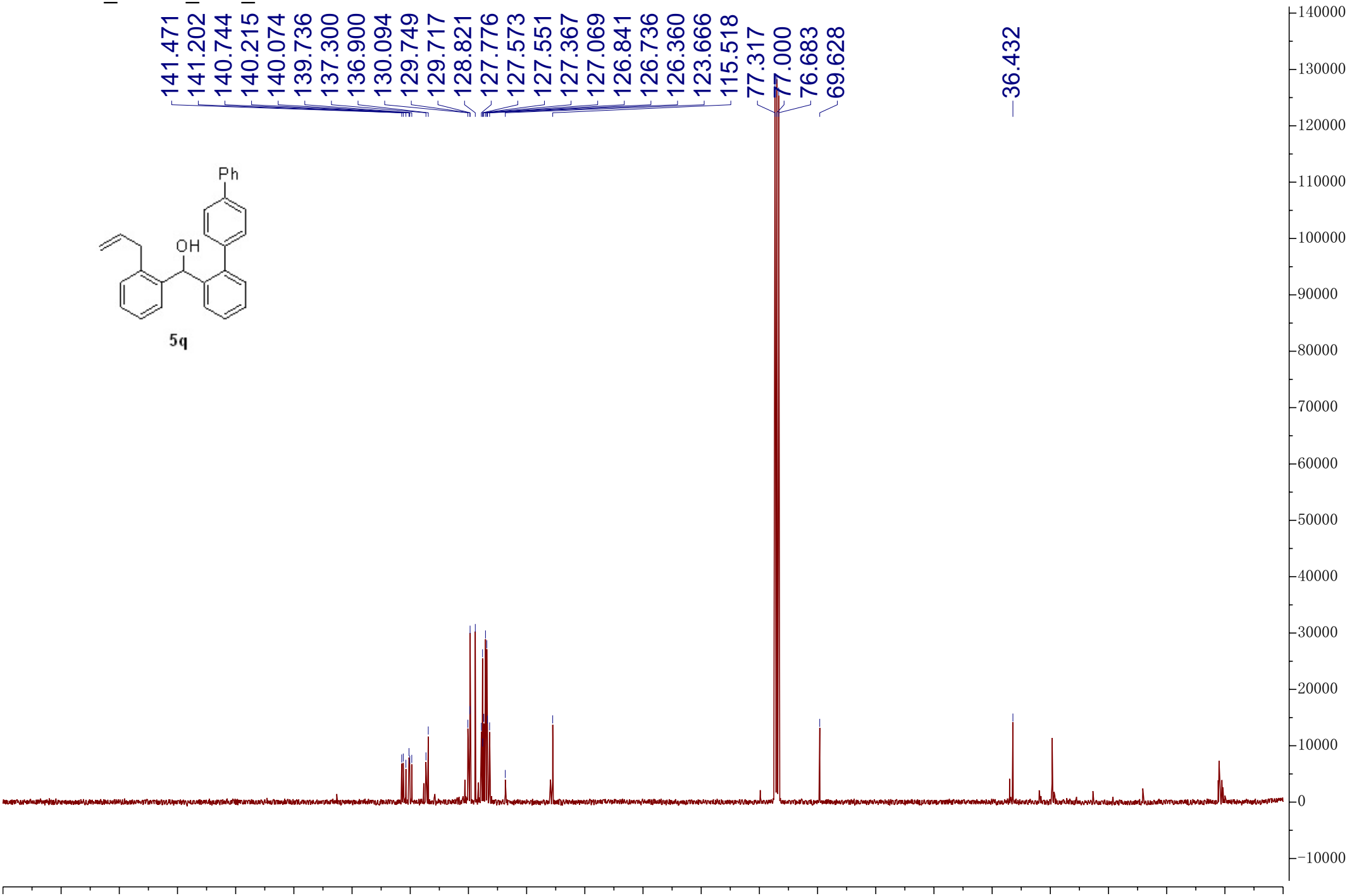
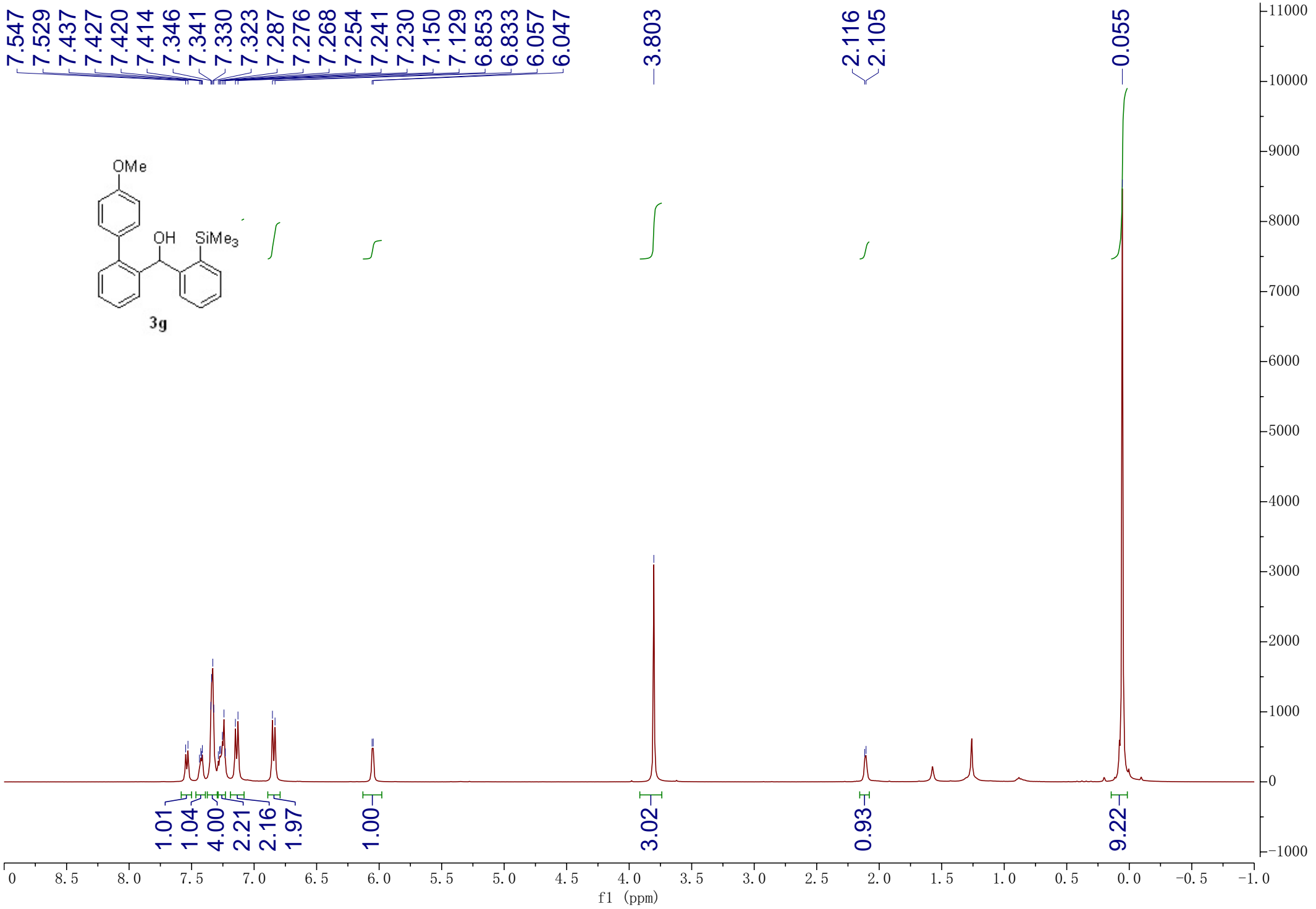
HTB-7-89_CDCl3_13C_2019-10-18



HTB-6-71_CDCl3_1H_2019-7-2



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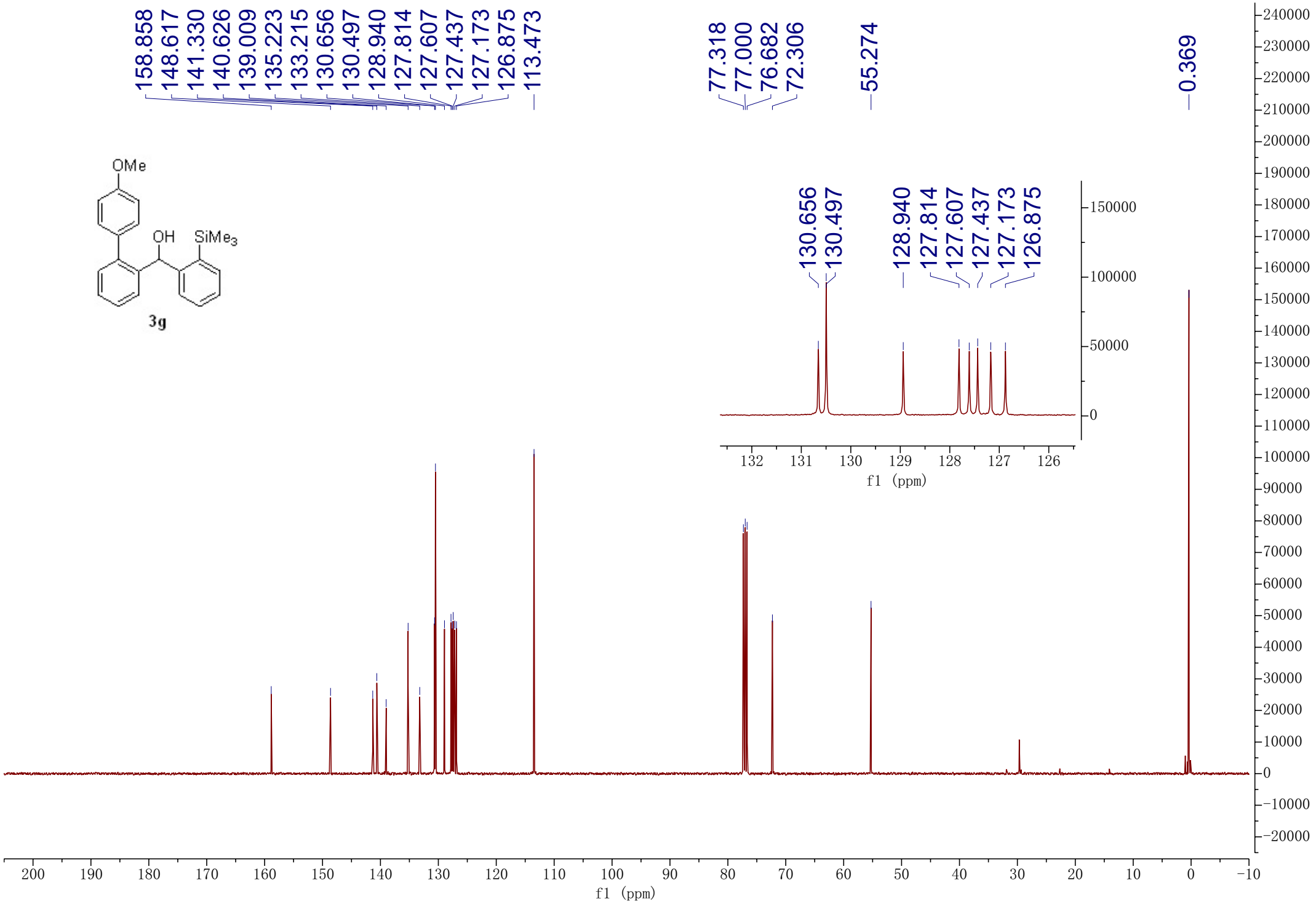
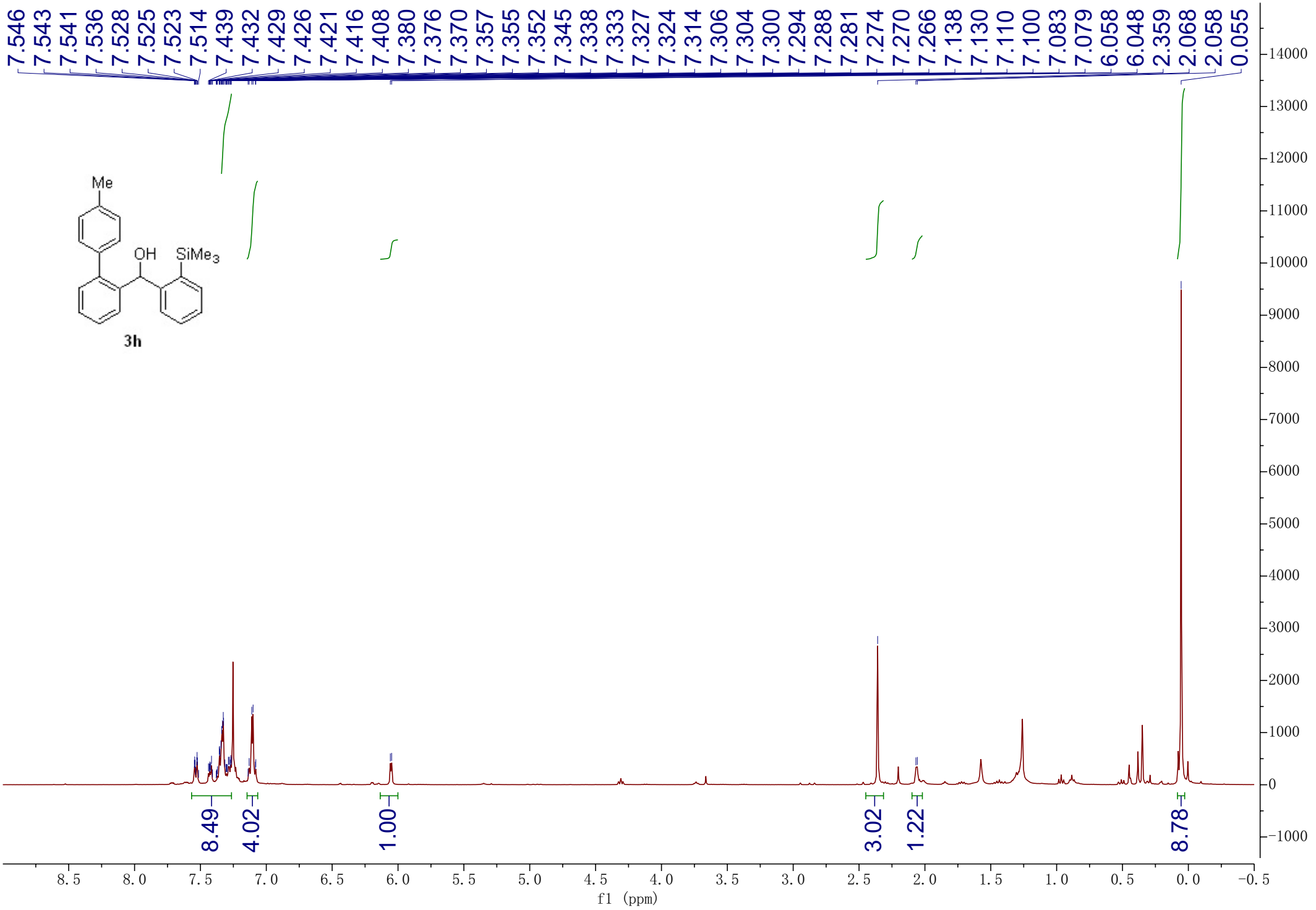
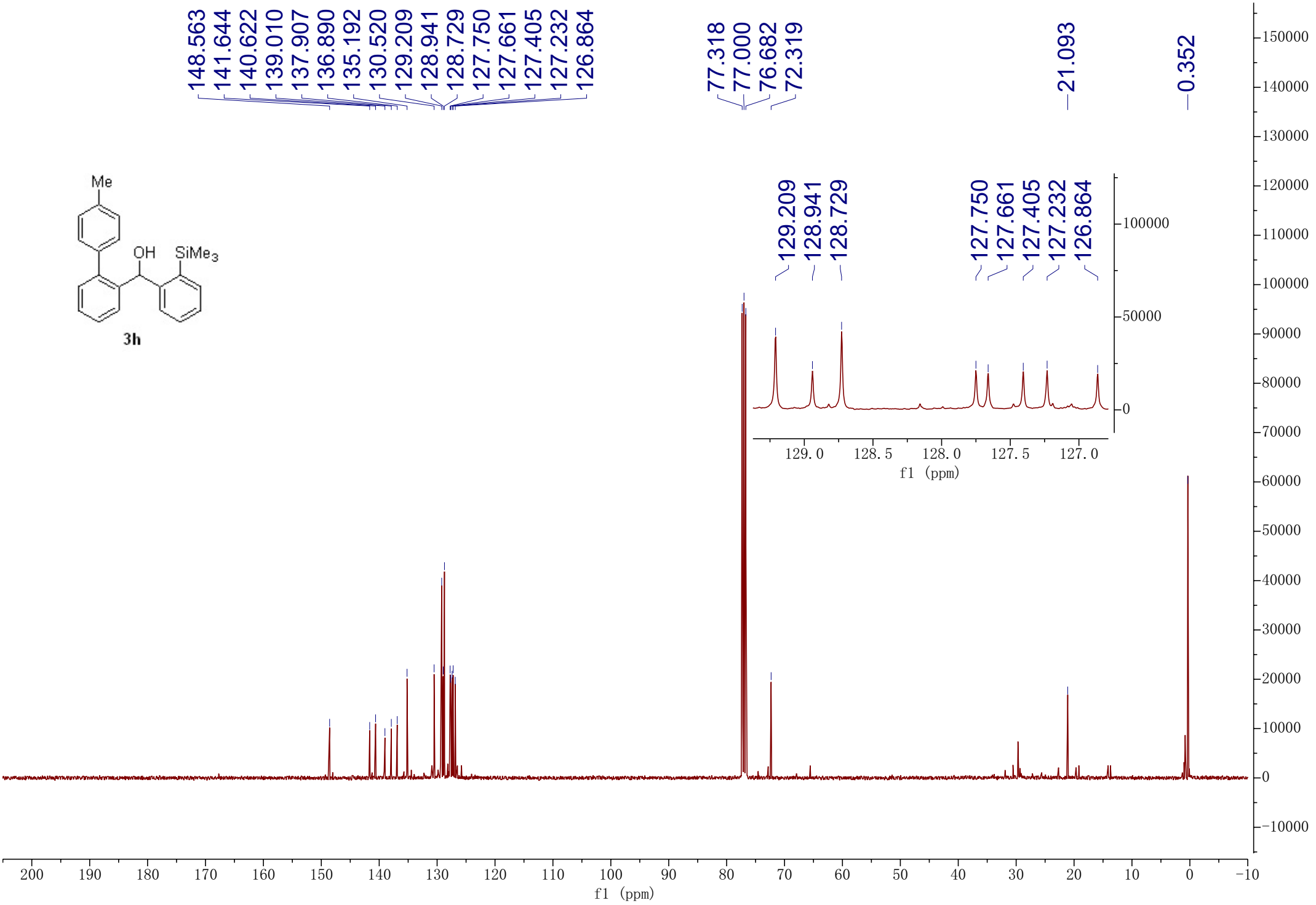


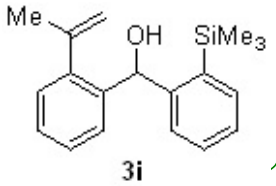
HTB-7-88_CDCl3_1H_2019-10-9



HTB-7-88_CDCl3_13C_2019-10-9



HTB-7-3_CDCl3_1H_2019-7-12



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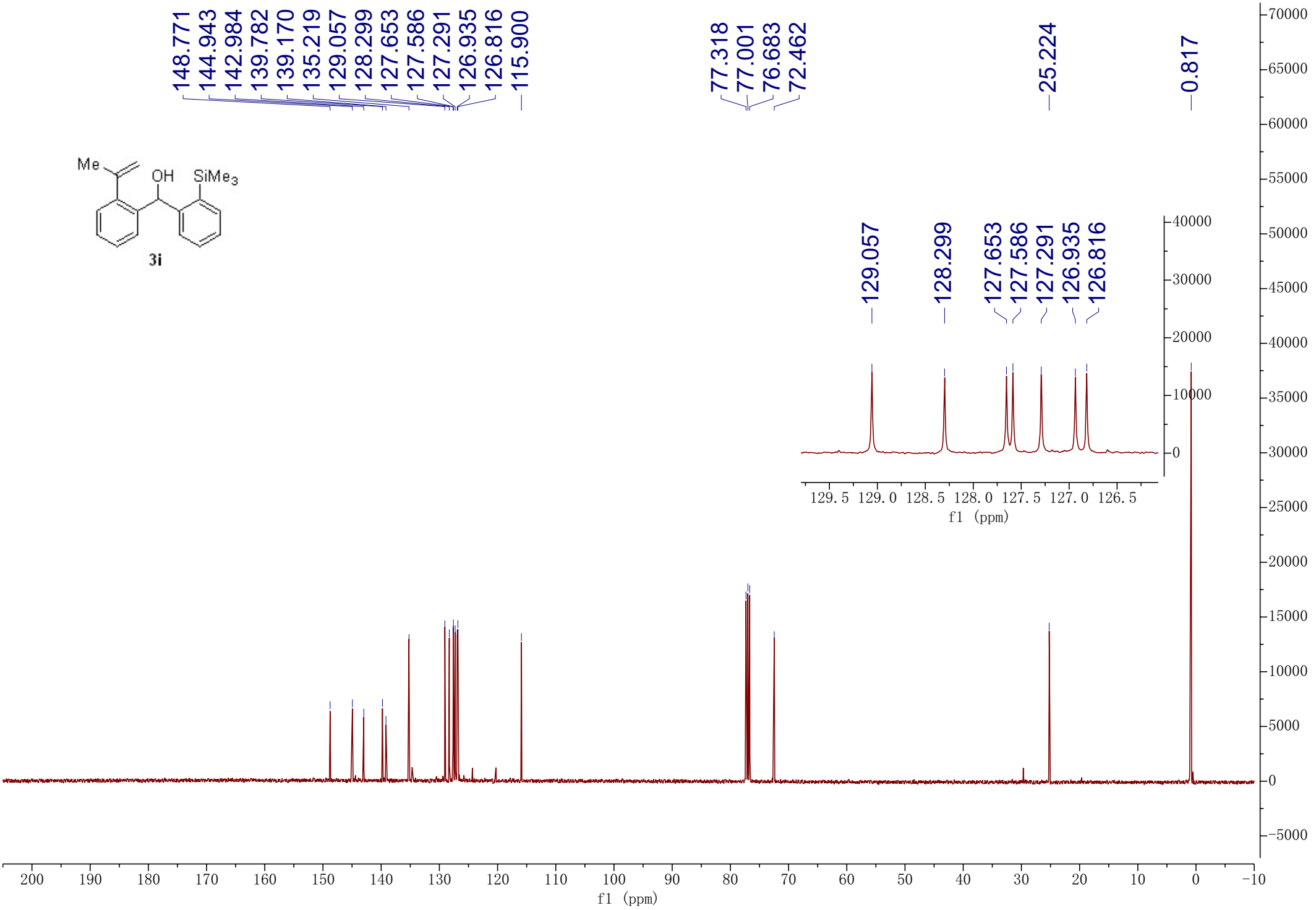
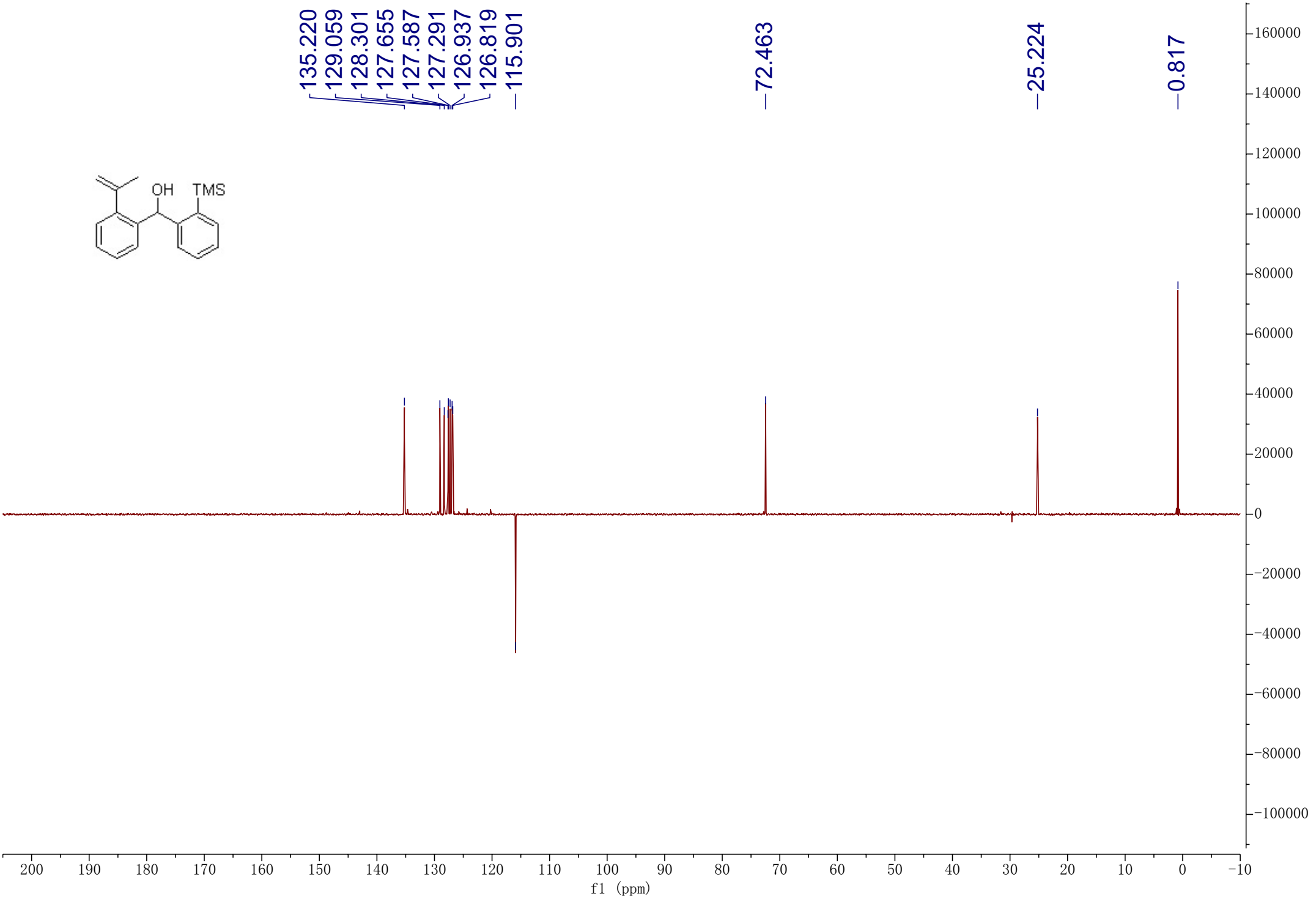
HTB-7-3_CDCl3_13C_2019-7-15



HTB-7-3_CDCl3_DEPT_2019-7-15



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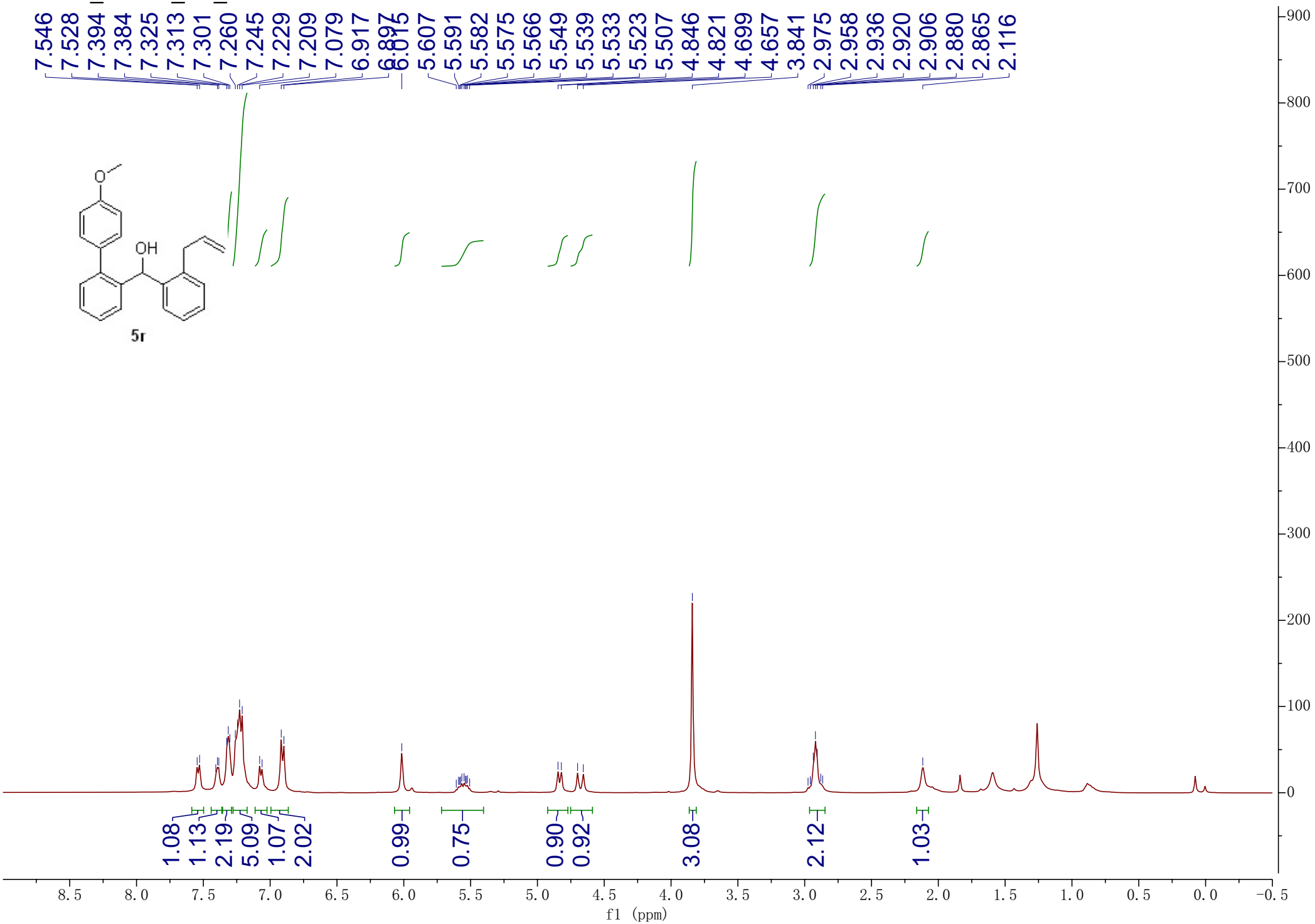

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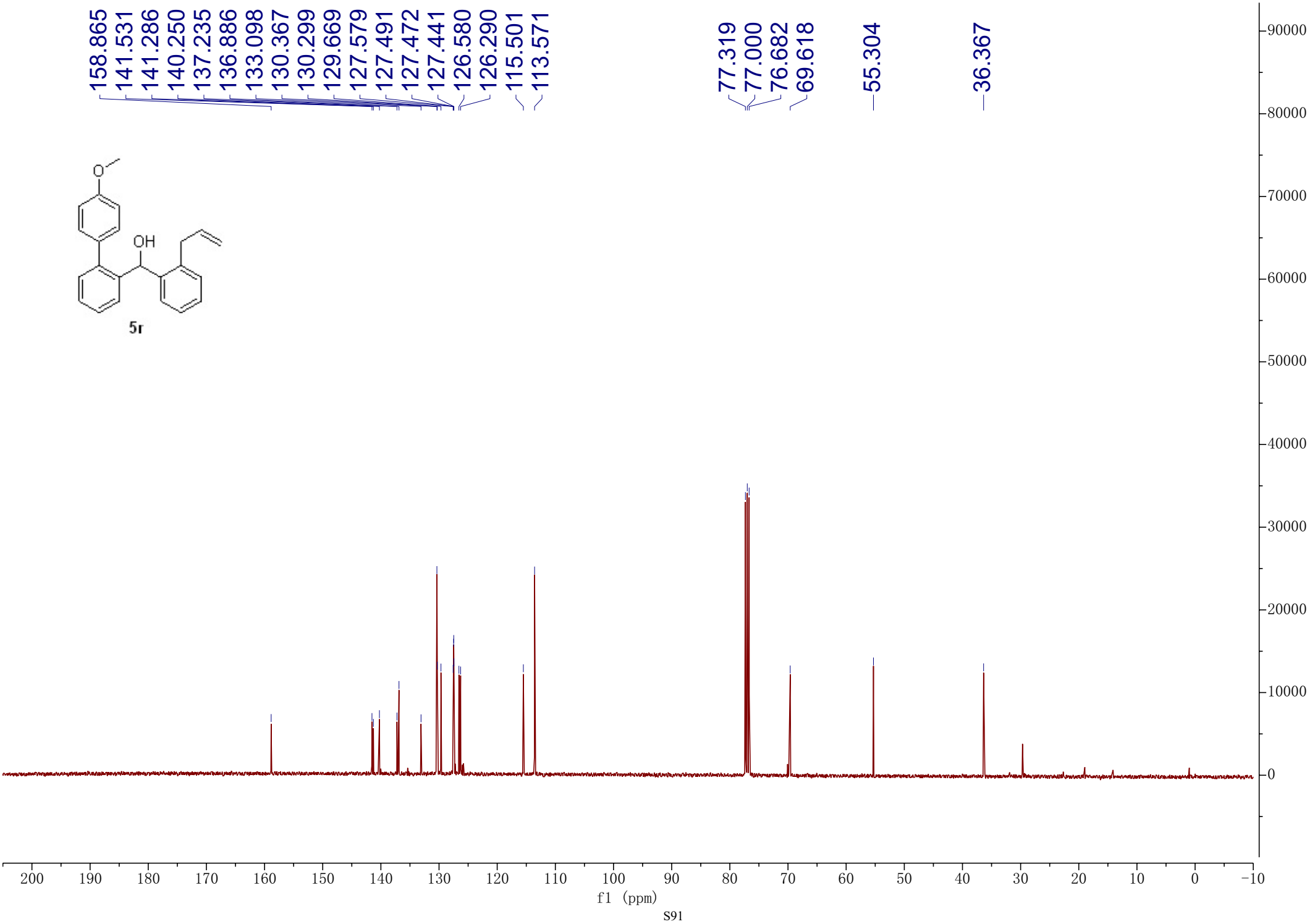

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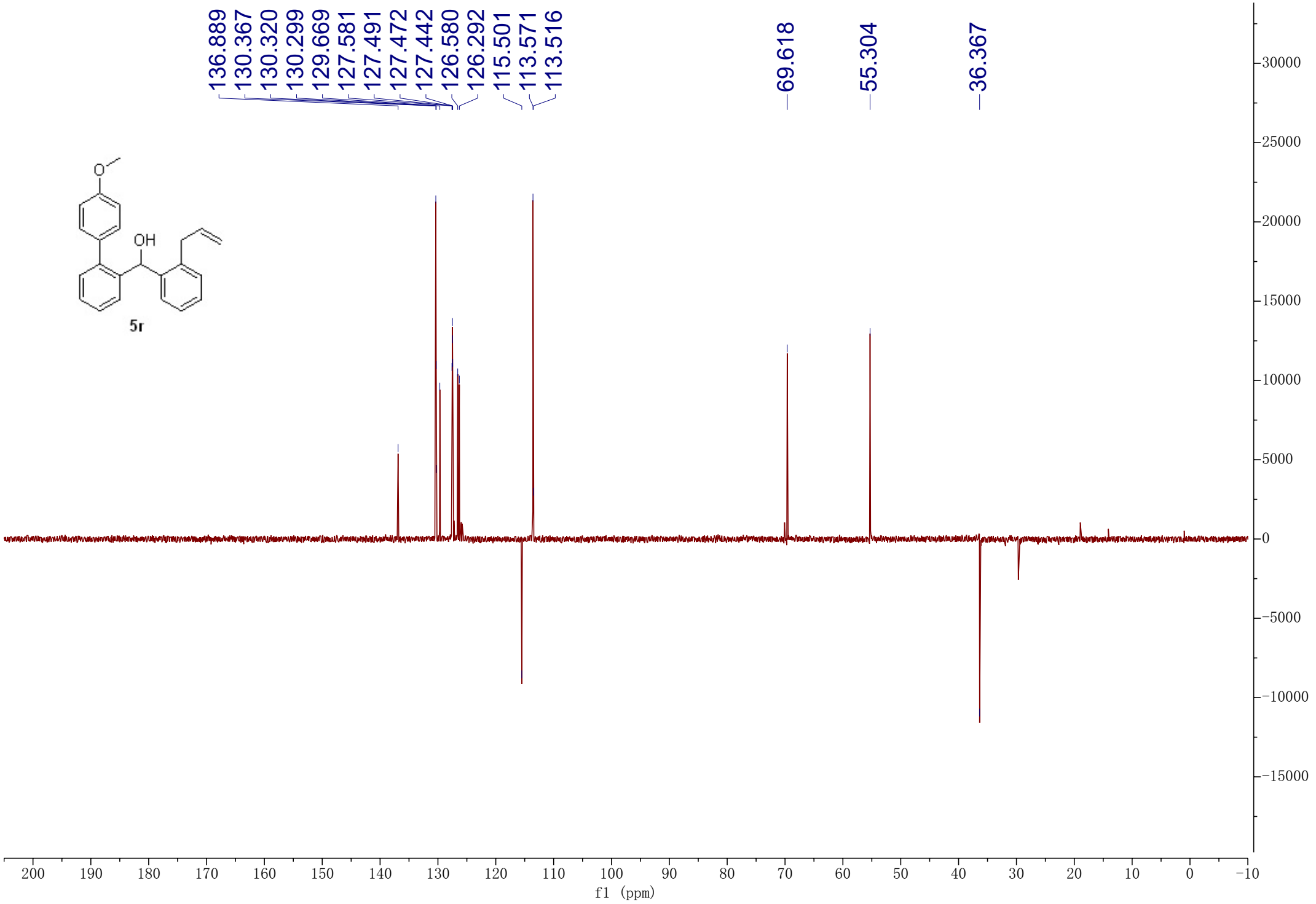
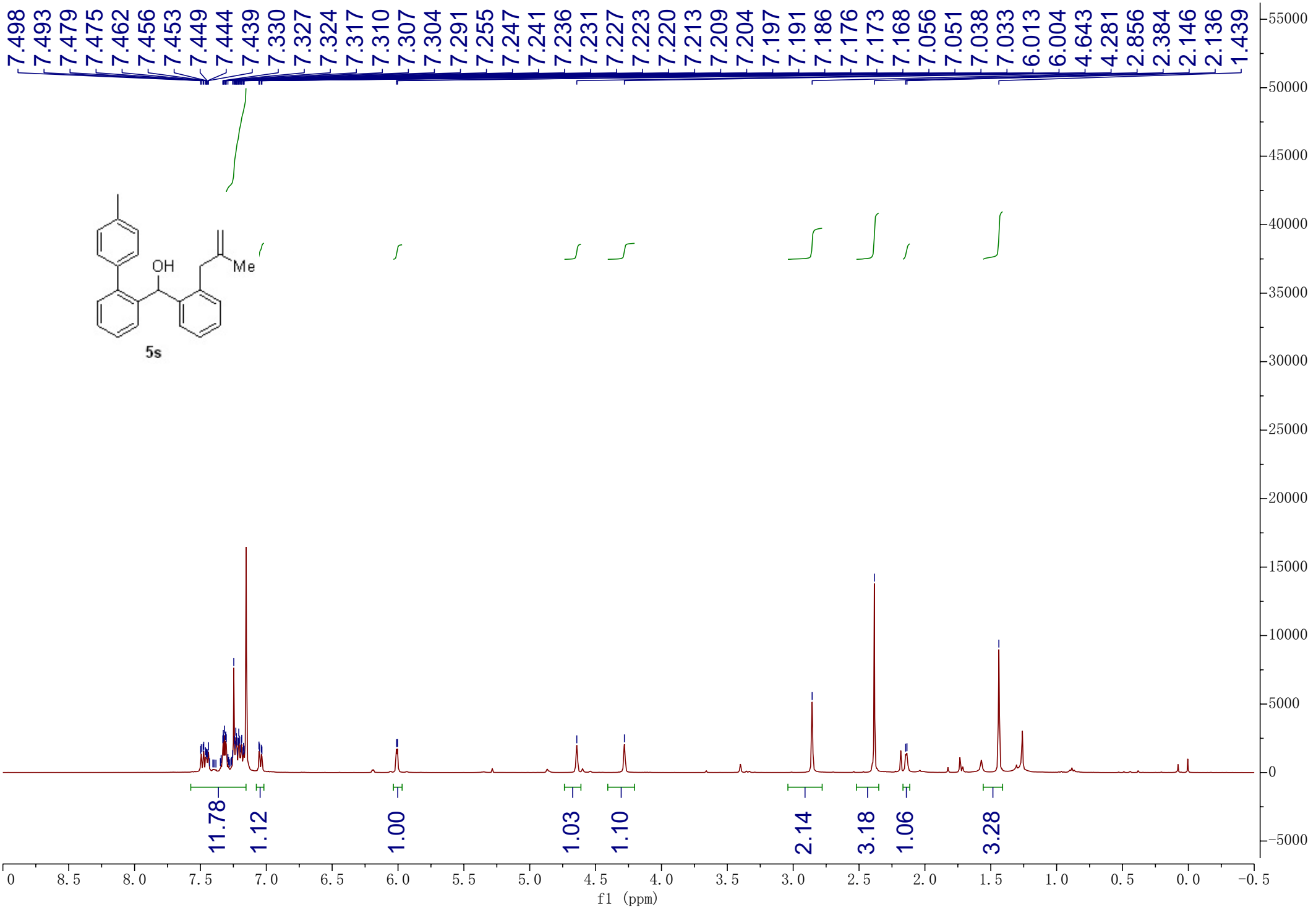


HTB-7-83_CDCl3_1H_2019-10-9



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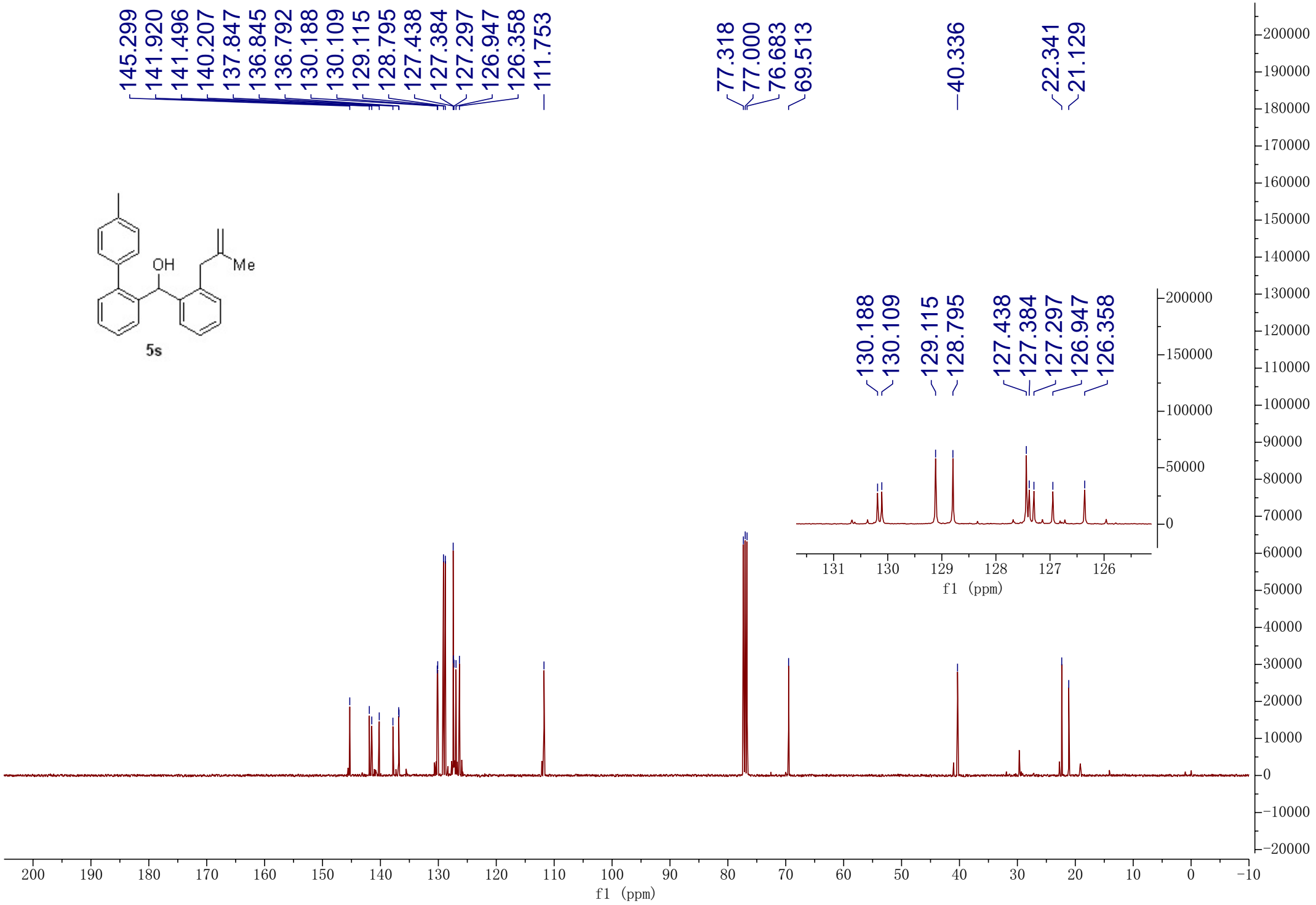

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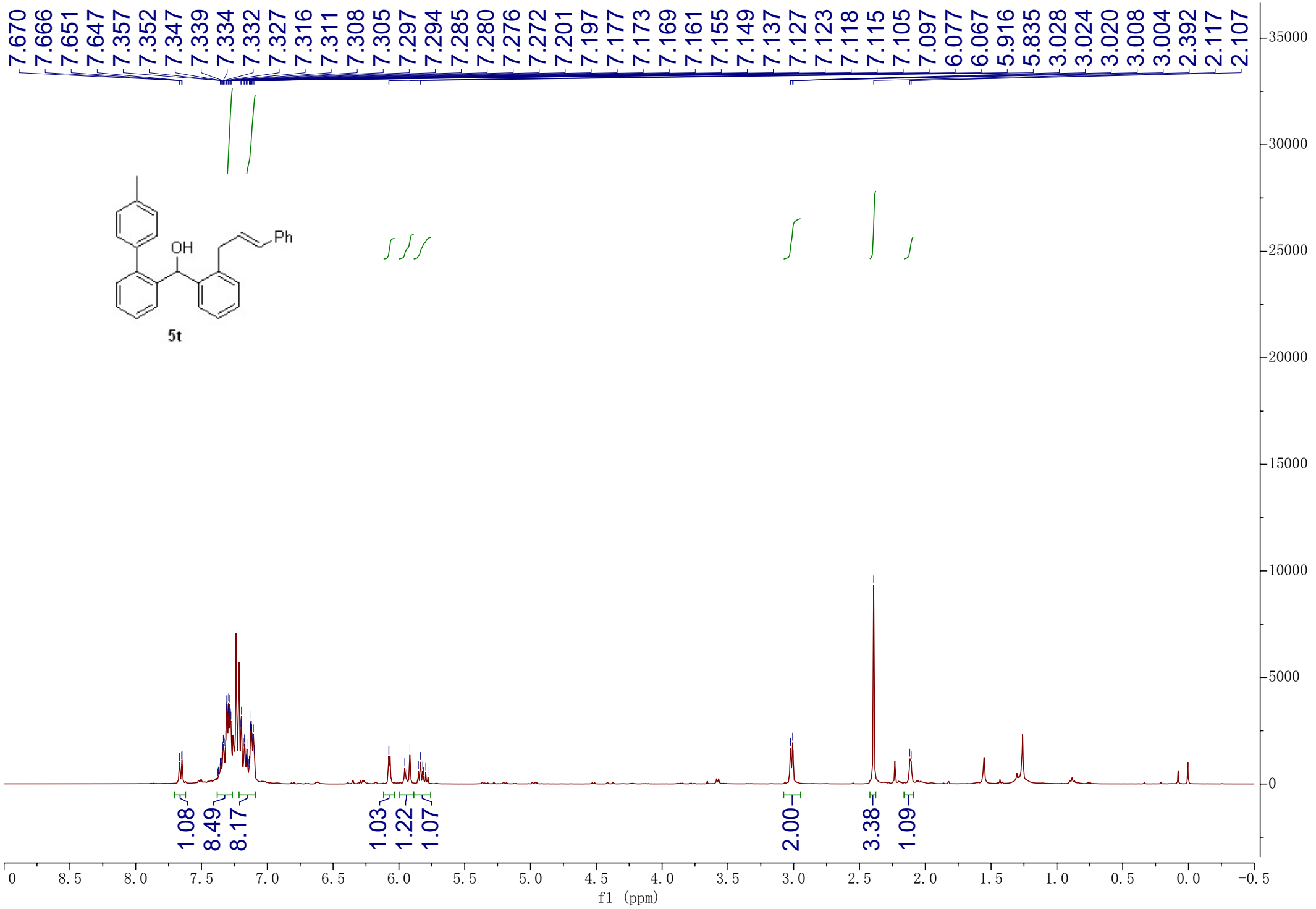

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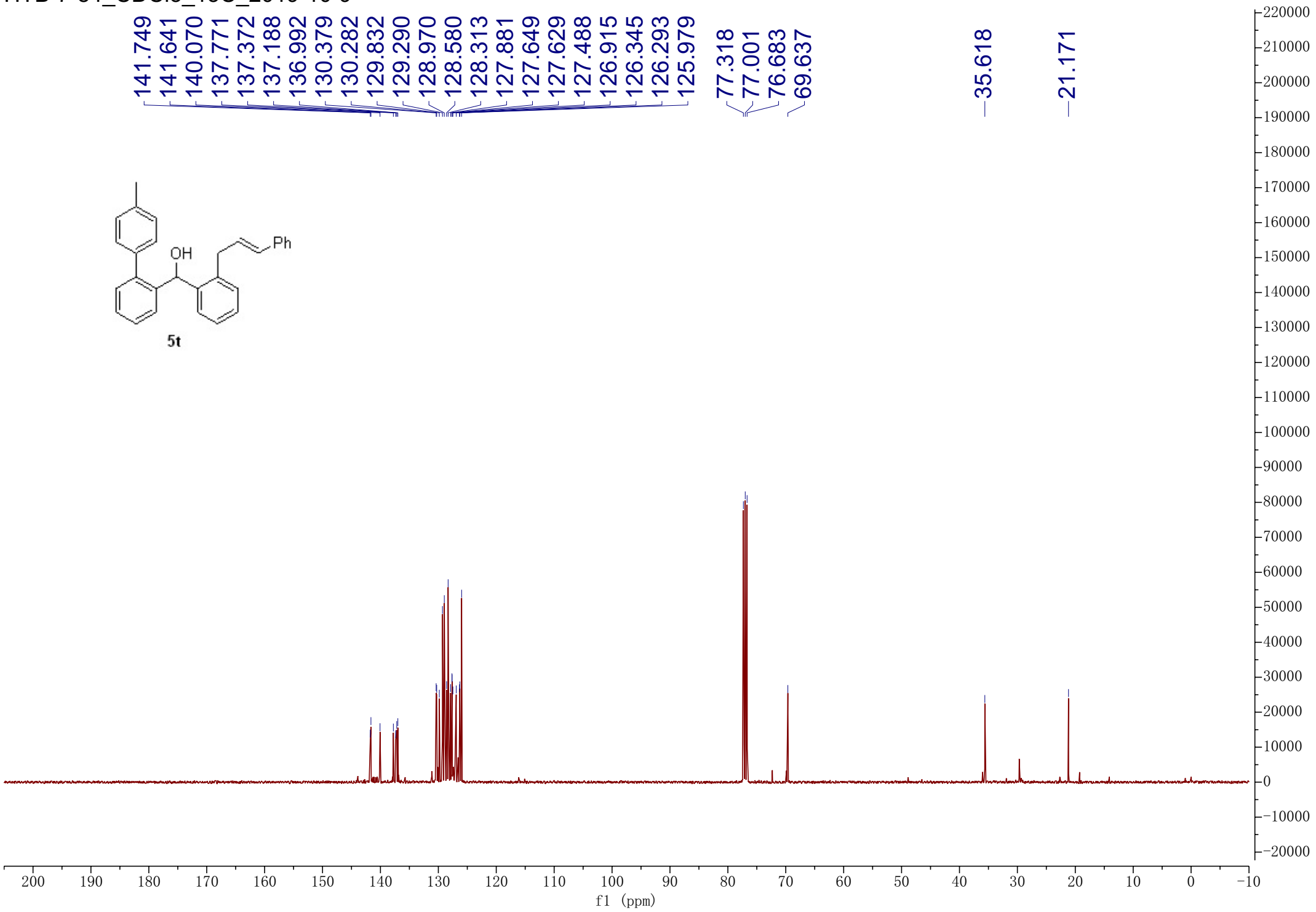
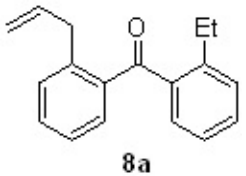
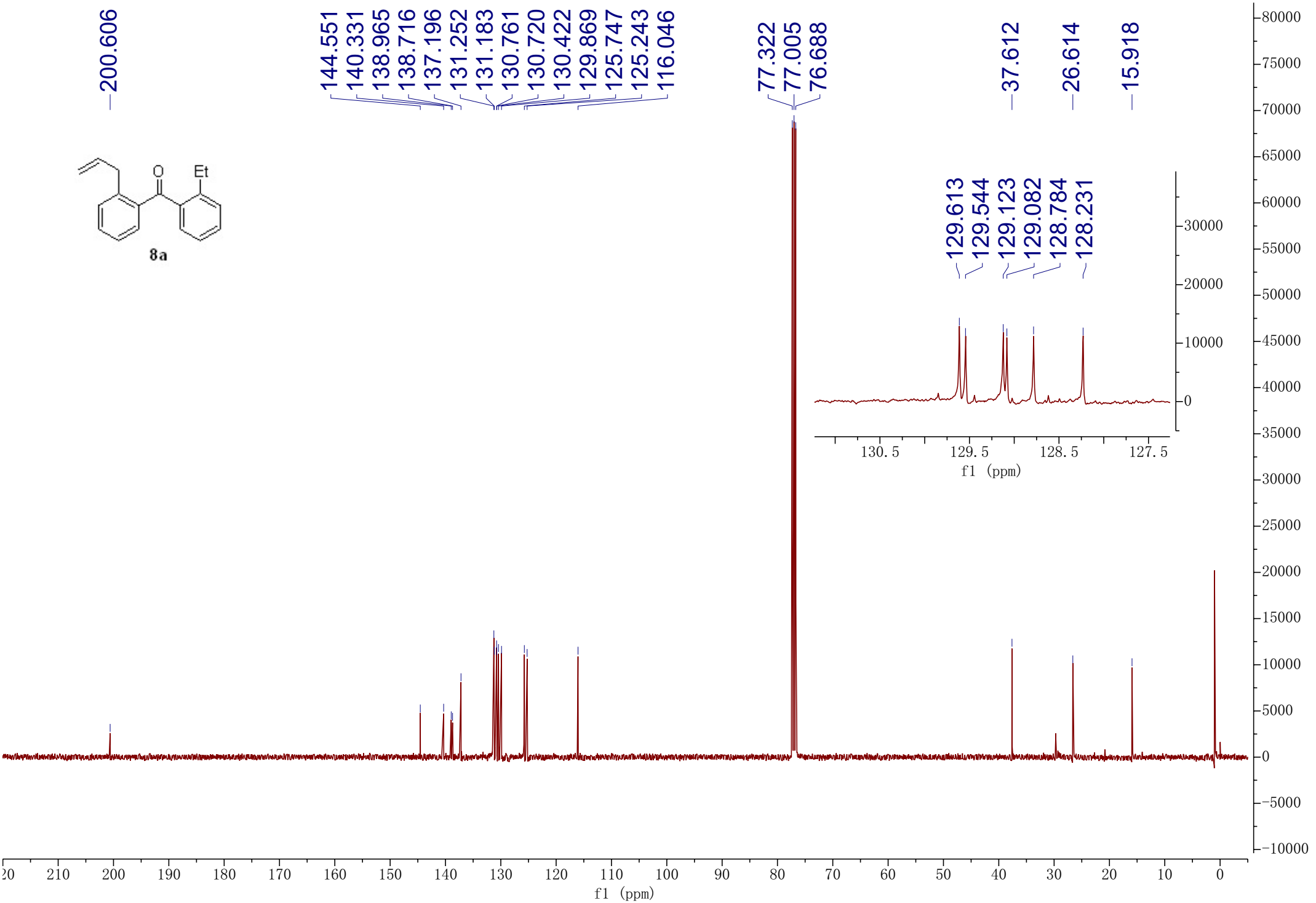


HLY-2-86_CDCl3_1H_2019-11-4

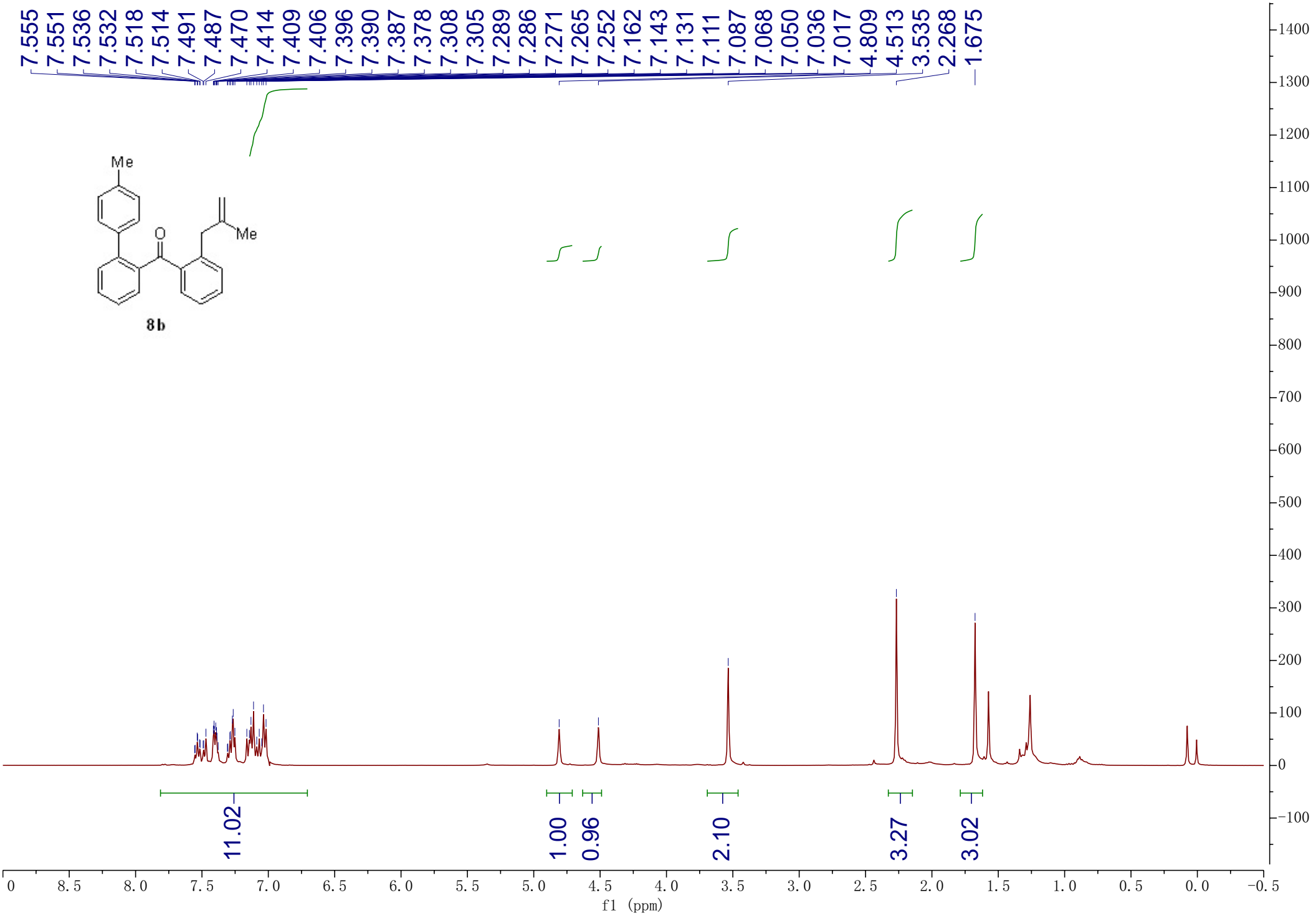


8a

HLY-2-86_CDCl3_13C_2019-10-18



HLY-2-89T_CDCl3_1H_2019-11-5



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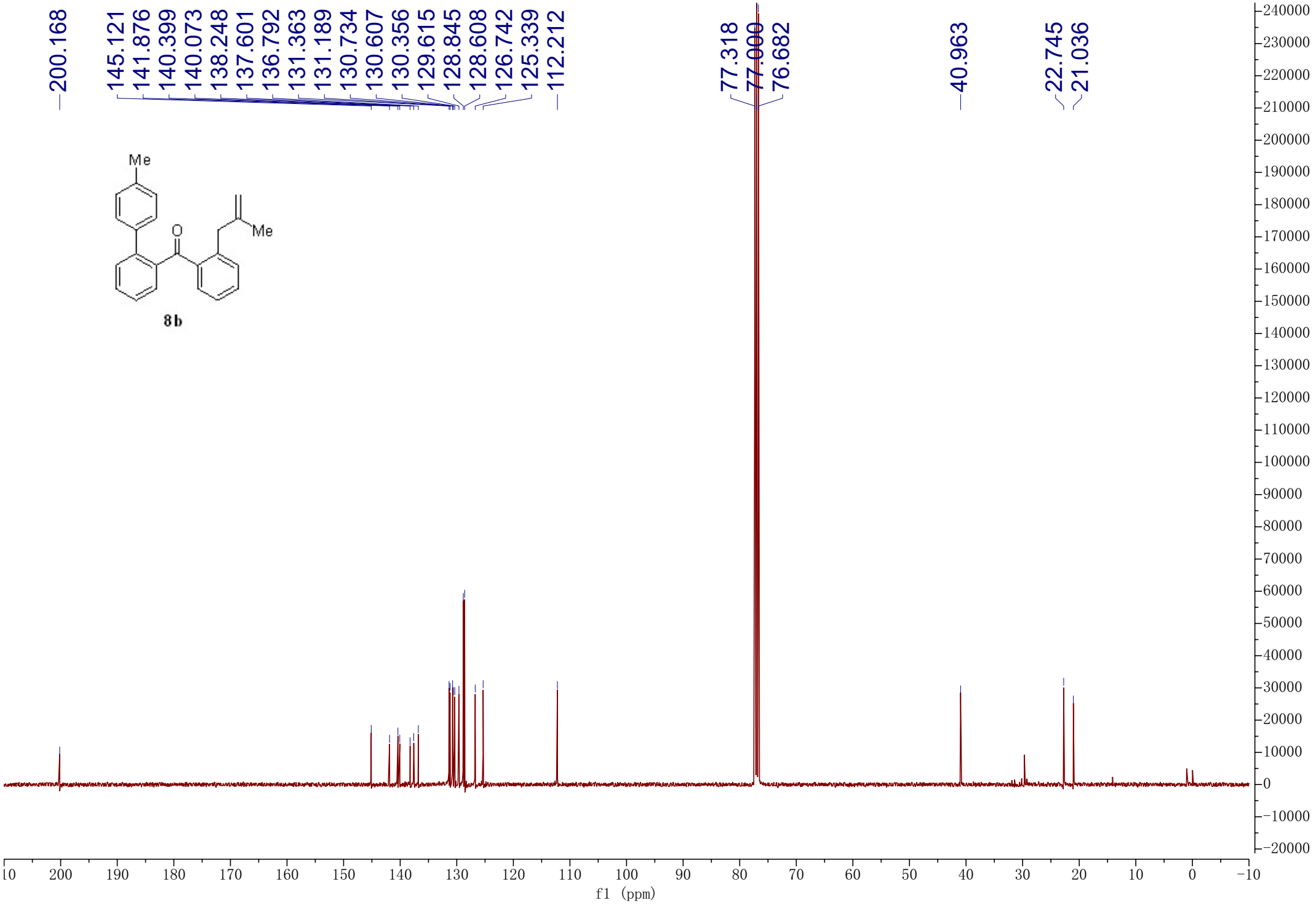
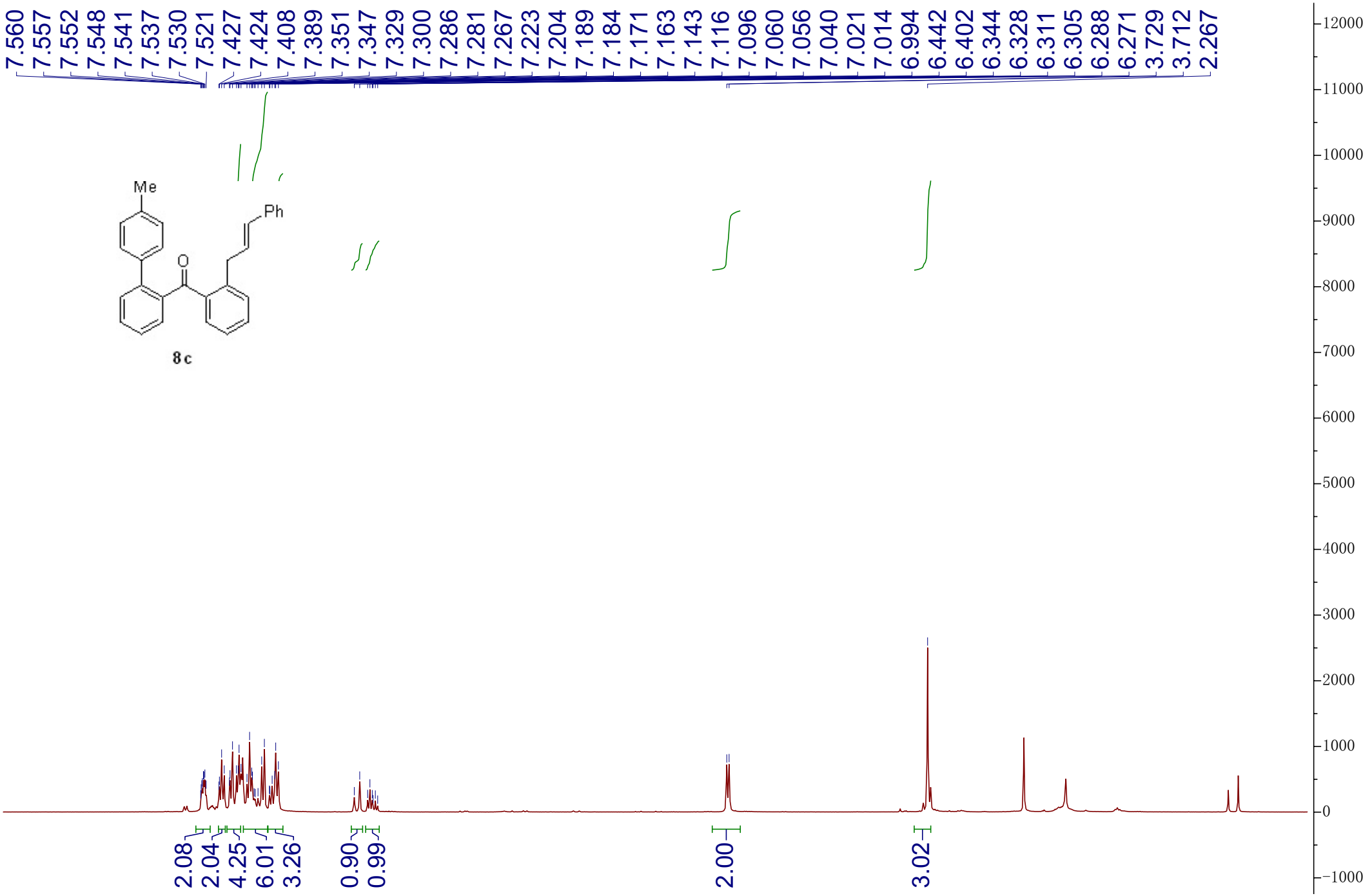


HTB-8-17_CDCl3_1H_2019-11-4



HTB-8-17_CDCl3_13C_2019-11-4

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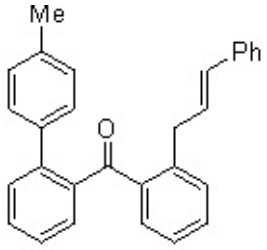

8c