Supporting Information

Pd-Catalyzed C(sp^3)-C(sp^2) Cross-Coupling of $Y(CH_2SiMe_3)_3(THF)_2$ with Vinyl Bromides and Triflates Followed by Subsequent Hosomi-Sakurai Reaction: Development of A Novel Three-Component One-Pot Cascade Reaction

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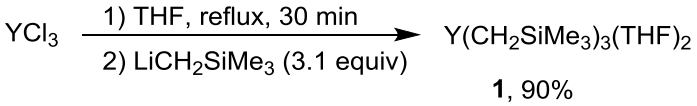
General Information

All reactions were carried out in oven-dried glassware with magnetic stirring and some reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. THF, hexane and toluene were dried and distilled over sodium. Palladium catalysts (>98% purity), phosphine ligands, rare-earth metal trichlorides and $LiCH_2SiMe_3$ are purchased from *J&K Scientic* and used without further purification. The real purity of $Pd_2(dba)_3$ was determined as 92% according to the method in the literature (S. S. Zalesskiy, V. P. Ananikov, *Organometallics*, **2012**, *31*, 2302-2309). Other reagents were purchased from *J&K Scientic* and *Energy Chemical* and used without further purification. Chromatographic purification was conducted with technical grade solvents (petroleum ether, dichloromethane and ethyl acetate) and silica gel 40-63 μm. TLC was performed on Merck silica gel 60 F_{254} TLC aluminium plates and visualized with UV light (254 nm), permanganate stain, CAN stain or PMA stain. ^{1}H NMR spectra were recorded on a Brucker Advance 400 MHz spectrometer in $CDCl_3$ (all signals are reported in ppm with the internal chloroform signal at 7.26 ppm). ^{13}C NMR spectra were recorded with ^{1}H-decoupling on a Brucker Advance 101 MHz and 176 MHz spectrometer in $CDCl_3$ (all signals are reported in ppm with the internal chloroform signal at 77.16 ppm). Infrared spectra were recorded on a micro-FTIR (Nicolet iN10TM) spectrometer with a liquid-nitrogen cooled Mercury Cadmium Telluride (MCT) detector and two ZnSe wafers (Φ20mm×2mm), which could be used to obtain FTIR transmission spectra in the range of 800-4000 cm-1 and were reported as cm^{-1} (w = weak, m = medium, s = strong). High resolution mass spectrometric measurements were performed by the mass spectrometry service of ICCAS and BIT.

Preparation of $Y(CH_2SiMe_3)_3(THF)_2$

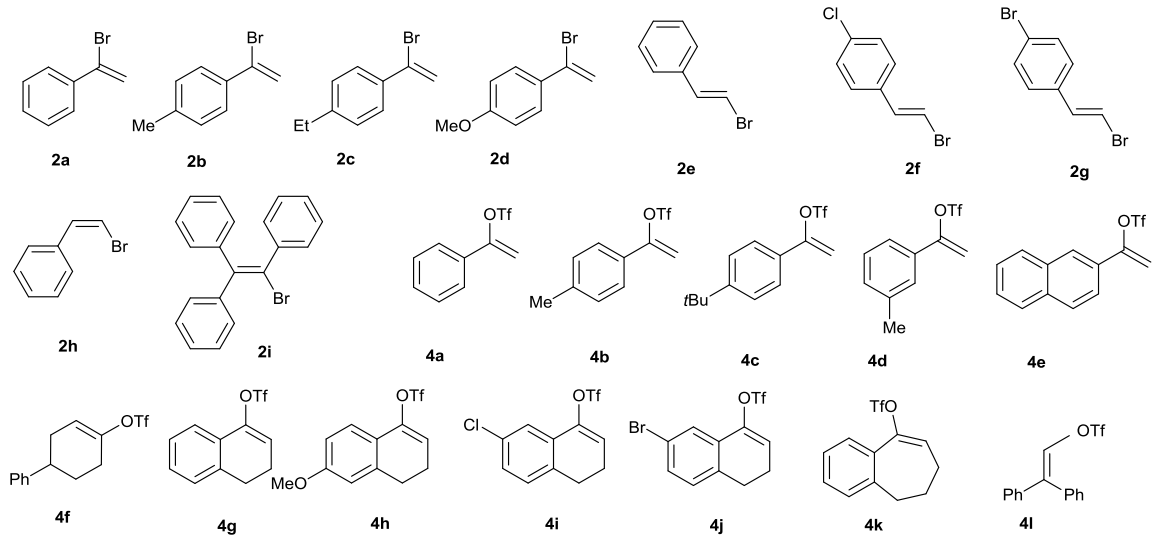


Procedure: Anhydrous YCl_3 (488 mg, 2.5 mmol) was slurried in THF (60 mL) and stirred at 60 ℃ for 7 days. To the resulting suspension of $YCl_3(THF)_x$ was added dropwise a solution of $LiCH_2SiMe_3$ (7.75 mmol) in 10 mL of THF at ambient temperature. The mixture was stirred for 3 h and the solvent was removed under reduced pressure. The resulting residue was extracted with 3×10 mL of hexane. The solvent was evaporated in *vacuo* to give $Y(CH_2SiMe_3)_3(THF)_2$ (**1**, 1100 mg, 90% yield) as a white solid.

^{1}H NMR (400 MHz, toluene-d_8) δ 4.09 (t, *J* = 6.4 Hz, 8H), 1.61-1.33 (m, 8H), 0.18 (s, 27H), -0.38 (s, 6H). The NMR data is in good agreement with that reported in the literature.[1]

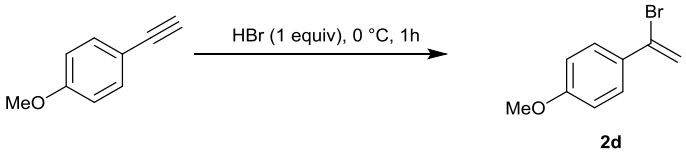
[1] M. F. Lappert, R. Pearce, *J. Chem. Soc., Chem. Commun.*, **1973**, 126-126.

Preparation of Vinyl Bromides and Triflates



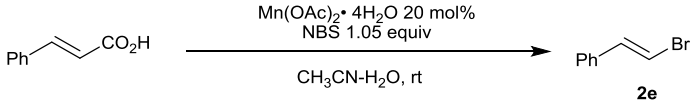
2b-2d were prepared from the corresponding 1-arylethynes using ***Method A***,[2] **2e-2g** are prepared from the corresponding cinnamic acid and its derivatives using ***Method B***,[3] **2h** is prepared from the corresponding cinnamyl acids using ***Method C***,[4] **4a-4i** are prepared from the corresponding ketone or aldehyde using ***Method D***.[5] **2a** and **2i** are commercially available.

Method A:



To cold (0 ℃, ice/water bath) neat 1-ethynyl-4-methoxybenzene (66.5 mg, 0.5 mmol, 1.0 equiv.) was added HBr (38% *w*/*w* in AcOH, 89 μL, 0.5 mmol, 1.0 equiv.) slowly by syringe. The resulting dark-blue solution was then stirred at ambient temperature for 1 h. Upon completion, the reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with methylene chloride. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was rapidly purified by flash chromatography on silica gel (petroleum ether, R_f 0.3) to give the product **2d** as a colorless liquid (86 mg, 81% yield).

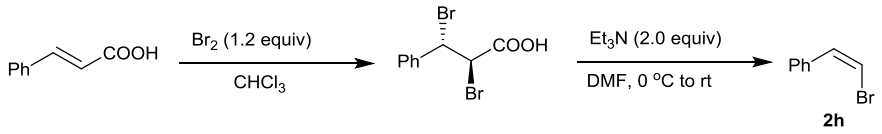
Method B:



A round-bottomed flask was charged with cinnamic acid (148 mg, 1 mmol), *N*-bromosuccinimide (187 mg, 1.05 mmol), $Mn(OAc)_2$ $4H_2O$ (50 mg, 0.2 mmol), 2 mL of H_2O and 2mL of acetonitrile.

The reaction mixture was stirred at room temperature and monitored by TLC analysis. After total conversion of substrates, acetonitrile was evaporated. The mixture was extracted by Et_2O (2 mL×3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by flash chromatography on silica gel (petroleum ether, R_f 0.4) to give the product **2e** as a colorless oil (168 mg, 92% yield).

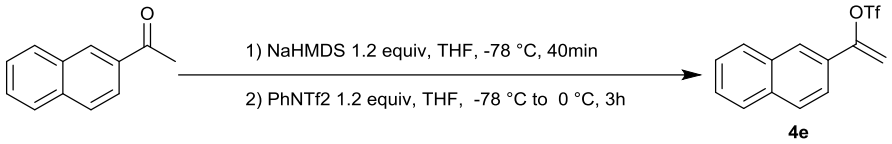
Method C:



To a mixture of *trans*-cinnamic acid (148mg, 1.0 mmol) and chloroform (1 mL) at 0 ℃, was added bromine (60 μL, 1.2 mmol) dropwise. The resulting solution was stirred at this temperature for 20 min. Then the solution was stored in refrigerator overnight. The precipitated sample was collected by filtration and washed twice with cold chloroform to give the crude product 2,3-dibromopropanoic acid, which was used in the next step without further purification.

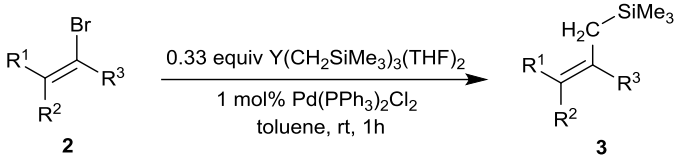
Triethylamine (0.3 mL, 2.0 mmol) in dry DMF (0.5 mL) was added dropwise to 2,3-dibromopropanoic acid in DMF (2 mL) at 0 ℃. The solution was stirred at 0 ℃ for 30 min, then at room temperature for 6 h. Water (5 mL) was added. The mixture was extracted with diethyl ether (5 mL×3). The combined organic layers were washed with saturated potassium carbonate (5 mL×2) and saturated sodium chloride (5 mL×2), dried over magnesium sulfate and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether, R_f 0.4) to give the product **2h** as a colorless oil (119 mg, 65% yield).

Method D:

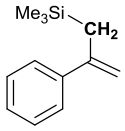


To a solution of 2-acetonaphthone (170 mg, 1 mmol) in THF (5 ml) was added a THF solution of NaHMDS (1 M, 1.2 ml, 1.2 mmol) at -78 ℃. After 40 min, a THF solution of $PhNTf_2$ (0.4 g, 1.2 mmol) was slowly added to the mixture. Then the resulting mixture was gradually warmed to 0 ℃, and stirred for 3 h at this temperature. The reaction mixture was quenched with saturated $NaHCO_3$ and extracted by Et_2O. The organic extracts were washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 40/1 with 0.1% Et_3N) to give 1-(naphthalene-2-yl)vinyltrifluoromethanesulfonate **4e** as a white solid (0.2 g, 66 %, white solid).

Substrate Scope for Vinyl Bromides

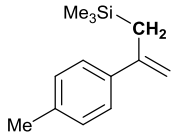


General procedure: In a dry Schlenk flask, to a mixture of $Pd(PPh_3)_2Cl_2$ and vinyl bromides **2** (1.0 equiv, 0.3 mmol) in 3.2 mL of dry toluene was added a solution of (trimethylsilyl)methyl yttrium complex **1** (0.33 equiv) in 0.8 mL of dry toluene dropwise. After being stirred at room temperature for 1 h, the reaction was quenched with saturated NH_4Cl aqueous solution (20 mL). The resulting mixture was extracted by ethyl acetate (3×10 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the product **3**.



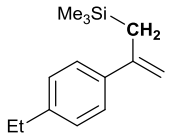
3a, 97%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2a** and **4a**. R_f = 0.45 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.30 – 7.26 (m, 1H), 5.16 (d, *J* = 1.7 Hz, 1H), 4.90 (d, *J* = 1.7 Hz, 1H), 2.06 (d, *J* = 1.1 Hz, 2H), -0.06 (s, 9H). The NMR data is in good agreement with that reported in the literature.[5]



3b, 95%

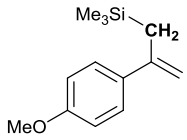
From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2b** and **4b**. R_f = 0.4 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 2H), 7.17 – 7.11 (m, 2H), 5.15 (d, *J* = 1.8 Hz, 1H), 4.86 (d, *J* = 1.7 Hz, 1H), 2.37 (s, 3H), 2.04 (d, *J* = 1.1 Hz, 2H), -0.05 (s, 9H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.5, 139.9, 136.9, 128.8, 126.3, 109.4, 26.1, 21.2, -1.2. The NMR data is in good agreement with that reported in the literature.[6]



3c, 97%

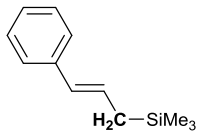
From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2c**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 5.15 (d, *J* = 1.8 Hz, 1H), 4.86 (d, *J* = 1.7 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.04 (d, *J* = 1.1 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H), -0.05 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.5, 143.3, 140.1, 127.6, 126.3, 109.4, 28.6, 26.1, 15.6, -1.2.

IR(neat) 2957 (m), 2924(m), 1730 (m), 1494 (w), 1250(s),1089(m), 1070(m), 946(w), 840(s), 700(m). HRMS (ESI) calcd for $C_{14}H_{23}Si^{+}[M+H]^{+}$ 219.1564; found 219.1561.



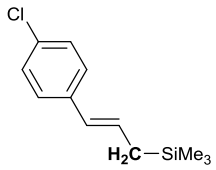
3d, 99%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2d**. R_f = 0.3 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.08 (d, *J* = 1.7 Hz, 1H), 4.80 (d, *J* = 1.5 Hz, 1H), 3.82 (s, 3H), 2.01 (d, *J* = 1.1 Hz, 2H), -0.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 145.9, 135.3, 127.5, 113.5, 108.6, 55.3, 26.2, -1.2. The NMR data is in good agreement with that reported in the literature.[5]



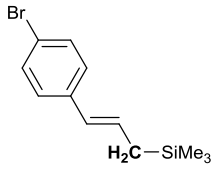
3e, 98%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2e**. R_f = 0.4 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.22 (m, 4H), 7.18 – 7.10 (m, 1H), 6.26 – 6.21 (m, 2H), 1.69 – 1.63 (m, 2H), 0.04 (s, 9H). The NMR data is in good agreement with that reported in the literature.[7]



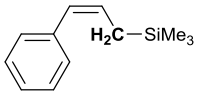
3f, 99%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2g**. R_f = 0.35 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.20 (m, 4H), 6.32 – 6.16 (m, 2H), 1.69 (d, *J* = 7.0 Hz, 2H), 0.08 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.1, 131.7, 128.8, 128.6, 127.1, 126.8, 24.1, -1.7. The NMR data is in good agreement with that reported in the literature.[8]



3g, 99%

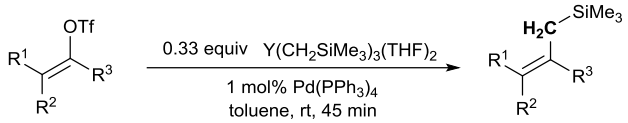
From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2f**. R_f = 0.35 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.33 (m, 2H), 7.22 – 7.10 (m, 2H), 6.43 – 6.11 (m, 2H), 1.68 (dd, *J* = 7.8, 0.8 Hz, 2H), 0.07 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.5, 131.5, 129.0, 127.2, 127.1, 119.8, 24.2, -1.6. The NMR data is in good agreement with that reported in the literature.[9]



3h, 95%

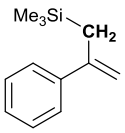
From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **2h**. R_f = 0.5 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (h, *J* = 6.1 Hz, 4H), 7.21 – 7.15 (m, 1H), 6.33 (dt, *J* = 11.7, 1.6 Hz, 1H), 5.72 (dt, *J* = 11.6, 9.1 Hz, 1H), 1.83 (dd, *J* = 9.1, 1.5 Hz, 2H), 0.04 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 129.1, 128.7, 128.2, 126.9, 126.1, 19.7, -1.4. The NMR data is in good agreement with that reported in the literature.[10]

Substrate Scope for Vinyl Triflates



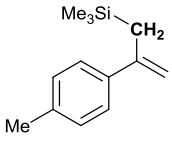
4 **5**

General procedure: In a dry Schlenk flask, to a mixture of vinyl triflates **4** (1.0 equiv, 0.3 mmol) and $Pd(PPh_3)_4$ (1 mol%) in 3.2 mL of dry toluene was added a solution of the (trimethylsilyl)methyl yttrium complex **1** (0.1 mmol, 0.33 equiv) in 0.8 mL of dry toluene dropwise. After being stirred at room temperature for 45 min, the reaction was quenched with saturated NH_4Cl aqueous solution (20 mL). The resulting mixture was extracted by ethyl acetate (3×10 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the product **5**.



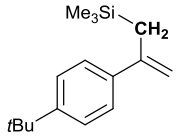
5a, 96%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4a**. The data is the same as **3a**.



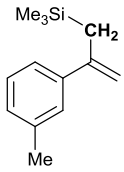
5b, 98%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4b**. The data is the same as **3b**.



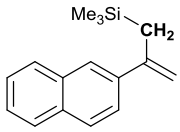
5c, 94%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4c**. R_f = 0.55 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 4H), 5.15 (d, *J* = 1.7 Hz, 1H), 4.84 (dt, *J* = 1.9, 1.1 Hz, 1H), 2.02 (d, *J* = 1.1 Hz, 2H), 1.33 (s, 9H), -0.07 (s, 9H). The NMR data is in good agreement with that reported in the literature.[11]



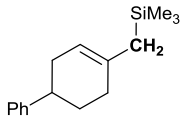
5d, 97%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4d**. R_f = 0.45 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.15 (m, 3H), 7.06 (tdd, *J* = 3.8, 1.8, 0.8 Hz, 1H), 5.11 (d, *J* = 1.7 Hz, 1H), 4.85 (dt, *J* = 2.0, 1.1 Hz, 1H), 2.35 (d, *J* = 0.7 Hz, 3H), 2.01 (d, *J* = 1.0 Hz, 2H), -0.09 (s, 9H). The NMR data is in good agreement with that reported in the literature.[5]



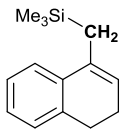
5e, 93%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4e**. R_f = 0.4 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.76 (m, 4H), 7.62 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.53 – 7.42 (m, 2H), 5.32 (d, *J* = 1.6 Hz, 1H), 5.01 (q, *J* = 1.2 Hz, 1H), 2.17 (d, *J* = 1.1 Hz, 2H), -0.05 (s, 9H). The NMR data is in good agreement with that reported in the literature.[5]



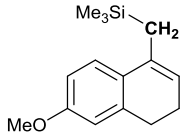
5f, 90%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4f**. R_f = 0.3 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 5.32 – 5.26 (m, 1H), 2.79 – 2.67 (m, 1H), 2.34 – 2.23 (m, 1H), 2.21 – 2.08 (m, 2H), 2.01 – 1.88 (m, 2H), 1.83 – 1.69 (m, 1H), 1.47 (s, 2H), 0.03 (s, 9H).The NMR data is in good agreement with that reported in the literature.[12]



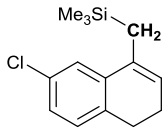
5g, 98%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4g**. R_f = 0.4 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.09 (m, 4H), 5.70 (td, *J* = 4.6, 2.3 Hz, 1H), 2.82 – 2.69 (m, 2H), 2.29 – 2.18 (m, 2H), 1.94 (q, *J* = 1.2 Hz, 2H), -0.01 (s, 9H). The NMR data is in good agreement with that reported in the literature.[13]



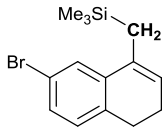
5h, 99%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4h**. R_f = 0.45 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.08 (m, 1H), 6.71 (dq, *J* = 5.5, 2.9 Hz, 2H), 5.57 (t, *J* = 4.6 Hz, 1H), 3.81 (s, 3H), 2.71 (t, *J* = 7.9 Hz, 2H), 2.30 – 2.15 (m, 2H), 1.90 (d, *J* = 1.3 Hz, 2H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.2, 138.7, 133.9, 129.1, 124.7, 120.4, 113.6, 110.5, 55.3, 29.6, 23.3, 22.5, -0.9. IR(neat) 2952 (s), 2926(s), 2832 (m), 1607 (m), 1497(m), 1250(s), 1187(m), 839(s), 847(s), 694(w). HRMS (ESI) calcd for $C_{15}H_{23}OSi^+$ $[M+H]^+$ 247.1513; found 247.1510.



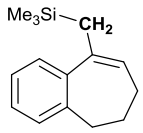
5i, 92%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4i**. R_f = 0.4 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 2.0 Hz, 1H), 7.13 – 6.99 (m, 2H), 5.73 (td, *J* = 4.5, 2.2 Hz, 1H), 2.68 (t, *J* = 7.9 Hz, 2H), 2.22 (dddd, *J* = 9.0, 7.7, 4.6, 1.2 Hz, 2H), 1.88 (d, *J* = 1.2 Hz, 2H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.6, 135.1, 133.6, 131.8, 128.5, 126.1, 124.2, 123.7, 28.3, 23.3, 22.4, -0.9. IR(neat) 2953 (m), 2933(m), 2887 (m), 2832 (w), 1480(m), 1247 (s), 1098(m), 839(s), 809(m), 693(w). HRMS (ESI) calcd for $C_{14}H_{20}ClSi^+$ $[M+H]^+$ 251.1017; found 251.1016.



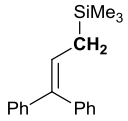
5j, 97%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4j**. R_f = 0.4 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 2.0 Hz, 1H), 7.23 (dd, *J* = 7.9, 2.1 Hz, 1H), 6.98 (dt, *J* = 7.9, 1.0 Hz, 1H), 5.72 (td, *J* = 4.6, 2.4 Hz, 1H), 2.66 (t, *J* = 7.9 Hz, 2H), 2.22 (dddt, *J* = 9.0, 6.0, 4.6, 1.2 Hz, 2H), 1.88 (q, *J* = 1.2 Hz, 2H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.0, 135.6, 133.5, 129.1, 128.9, 126.6, 124.2, 119.8, 28.4, 23.2, 22.5, -0.9. IR(neat) 2952 (m), 2931(m), 1478(m), 1247(s), 1021(m), 851(s). ESI-MS: *m/z* 295.0 for $[M+H]^+$. Anal. Calcd (%) for C14H20BrSi: C, 56.94; H, 6.49; found: C, 56.71; H, 6.20.



5k, 98%

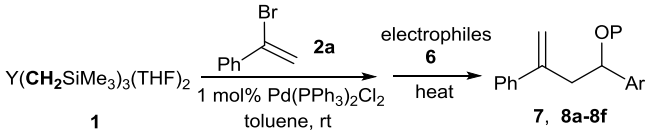
From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4k**. R_f = 0.45 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.12 (m, 4H), 5.79 (tt, *J* = 7.1, 1.2 Hz, 1H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.06 (p, *J* = 7.1 Hz, 2H), 1.97 (d, *J* = 1.0 Hz, 2H), 1.79 (q, *J* = 7.2 Hz, 2H), -0.14 (s, 9H). The NMR data is in good agreement with that reported in the literature.[14]



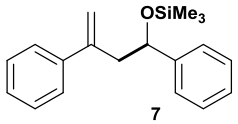
5l, 81%

From the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ **1** with **4l**. R_f = 0.3 (Petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.28 (m, 4H), 7.26 – 7.12 (m, 6H), 6.16 (t, *J* = 8.8 Hz, 1H), 1.63 (d, *J* = 8.8 Hz, 2H), 0.01 (s, 9H). The NMR data is in good agreement with that reported in the literature.[15]

Three-Component Reactions of 2a with 1 and 6

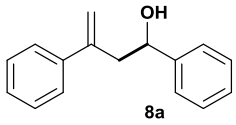


General procedure: In a dry Schlenk flask, to a mixture of vinyl bromide **2a** (1.0 equiv, 0.3 mmol) and $Pd(PPh_3)_2Cl_2$ (1 mol%) in 3.2 mL of dry toluene was added a solution of (trimethylsilyl)methyl yttrium complex **1** (0.33 equiv) in 0.8 mL of dry toluene dropwise. After being stirred at room temperature for 2 h, the reaction mixture was treated with ArCHO (1.1 equiv, 0.33 mmol) and heated at 100 °C for 3 hours. Then the reaction was quenched with saturated $NaHCO_3$ (20 mL) or with aq. HCl (1.0 M, 10 mL). The resulting mixture was extracted by ethyl acetate (3×10 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the product **7**, **8a-8f**.



7 74%

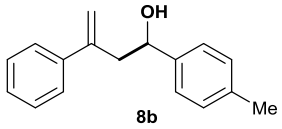
R_f = 0.4 (Petroleum ether/ethyl acetate 20:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.42 (m, 2H), 7.39 – 7.27 (m, 8H), 5.31 (d, *J* = 1.6 Hz, 1H), 5.03 (q, *J* = 1.2 Hz, 1H), 4.68 (dd, *J* = 7.9, 5.2 Hz, 1H), 2.96 – 2.81 (m, 2H), -0.09 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.2, 128.4, 128.1, 127.5, 127.1, 126.5, 126.0, 115.4, 77.3, 47.1, 0.1. IR(neat) 2958 (m), 1731 (w), 1453(w), 1261(s), 1091(s), 947(m), 841(s), 700(s). ESI-MS: *m/z* 297.2 for $[M+H]^+$. Anal. Calcd (%) for C19H24OSi: C, 76.97; H, 8.16; found: C, 76.69; H, 7.98.



74%

8a

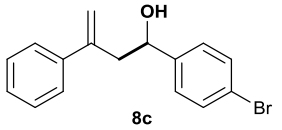
R_f = 0.3 (Petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.26 (m, 10H), 5.42 (d, *J* = 1.4 Hz, 1H), 5.18 (q, *J* = 1.3 Hz, 1H), 4.74 (ddd, *J* = 9.2, 4.2, 1.8 Hz, 1H), 3.16 – 2.76 (m, 2H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 145.1, 140.4, 128.6, 128.5, 127.9, 127.7, 126.4, 125.9, 115.9, 72.1, 46.1. The NMR data is in good agreement with that reported in the literature.[16]



83%

8b

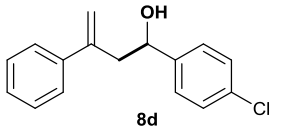
R_f = 0.35 (Petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.27 (m, 5H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.41 (d, *J* = 1.4 Hz, 1H), 5.17 (d, *J* = 1.3 Hz, 1H), 4.79 – 4.60 (m, 1H), 3.09 – 2.72 (m, 2H), 2.34 (s, 3H). The NMR data is in good agreement with that reported in the literature.[17]



78%

8c

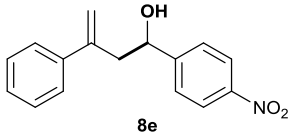
R_f = 0.35 (Petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.28 (m, 7H), 7.25 – 7.19 (m, 2H), 5.42 (d, *J* = 1.4 Hz, 1H), 5.15 (q, *J* = 1.2 Hz, 1H), 4.69 (ddd, *J* = 9.2, 4.5, 2.1 Hz, 1H), 3.12 – 2.68 (m, 2H). The NMR data is in good agreement with that reported in the literature.[16]



81%

8d

R_f = 0.35 (Petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.27 (m, 9H), 5.42 (d, *J* = 1.3 Hz, 1H), 5.15 (q, *J* = 1.2 Hz, 1H), 4.71 (ddd, *J* = 9.0, 4.5, 2.1 Hz, 1H), 3.00 – 2.78 (m, 2H). ^{13}C NMR (176 MHz, Chloroform-*d*) δ 142.4, 133.3, 128.6, 128.0, 127.3, 126.4, 116.2, 71.5, 46.2. IR(neat) 3386 (m), 3082(w), 2924 (s), 2852 (s), 1667(w),1627(w), 1598(w), 1492(s), 1261(s), 1091(s), 1028(s), 1013(s), 902(m), 828(s), 778(s), 706(s). HRMS (ESI) calcd for $C_{16}H_{15}ClONa$ $[M+Na]^+$ 281.0704; found 281.0708.

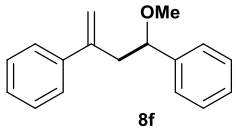


75%

8e

R_f = 0.3 (Petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.07 (m, 2H), 7.68 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.46 – 7.29 (m, 5H), 5.45 (d, *J* = 1.3 Hz,

1H), 5.18 (d, *J* = 1.2 Hz, 1H), 4.83 (ddd, *J* = 8.9, 4.5, 2.7 Hz, 1H), 3.12 – 2.80 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.0, 144.4, 132.0, 129.4, 128.8, 128.2, 126.4, 122.6, 121.0, 116.8, 71.2, 46.3, 29.8. IR(neat) 3361(w), 2920(s), 2850(s), 1659(w), 1632(w), 1529(s), 1470(m), 1349(s), 779(w), 708(w). HRMS (ESI) calcd for $C_{16}H_{16}NO_3^+$ [M+H]$^+$ 270.1125; found 270.1122.

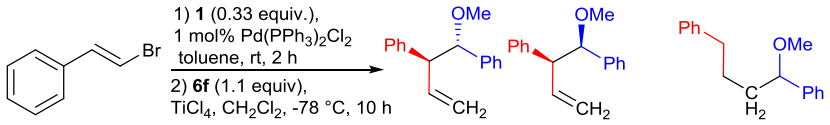


8f 80%

R_f = 0.5 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.15 (m, 10H), 5.24 (d, *J* = 1.5 Hz, 1H), 5.09 – 4.87 (m, 1H), 4.18 (dd, *J* = 7.7, 6.0 Hz, 1H), 3.13 (s, 3H), 3.04 (ddd, *J* = 14.5, 7.7, 1.1 Hz, 1H), 2.78 (ddd, *J* = 14.5, 5.9, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.1, 141.9, 128.4, 128.4, 127.7, 127.5, 126.8, 126.4, 115.2, 82.3, 56.8, 44.6. The NMR data is in good agreement with that reported in the literature.[18]

Three-Component Reactions for Other Vinyl Bromides and Triflates

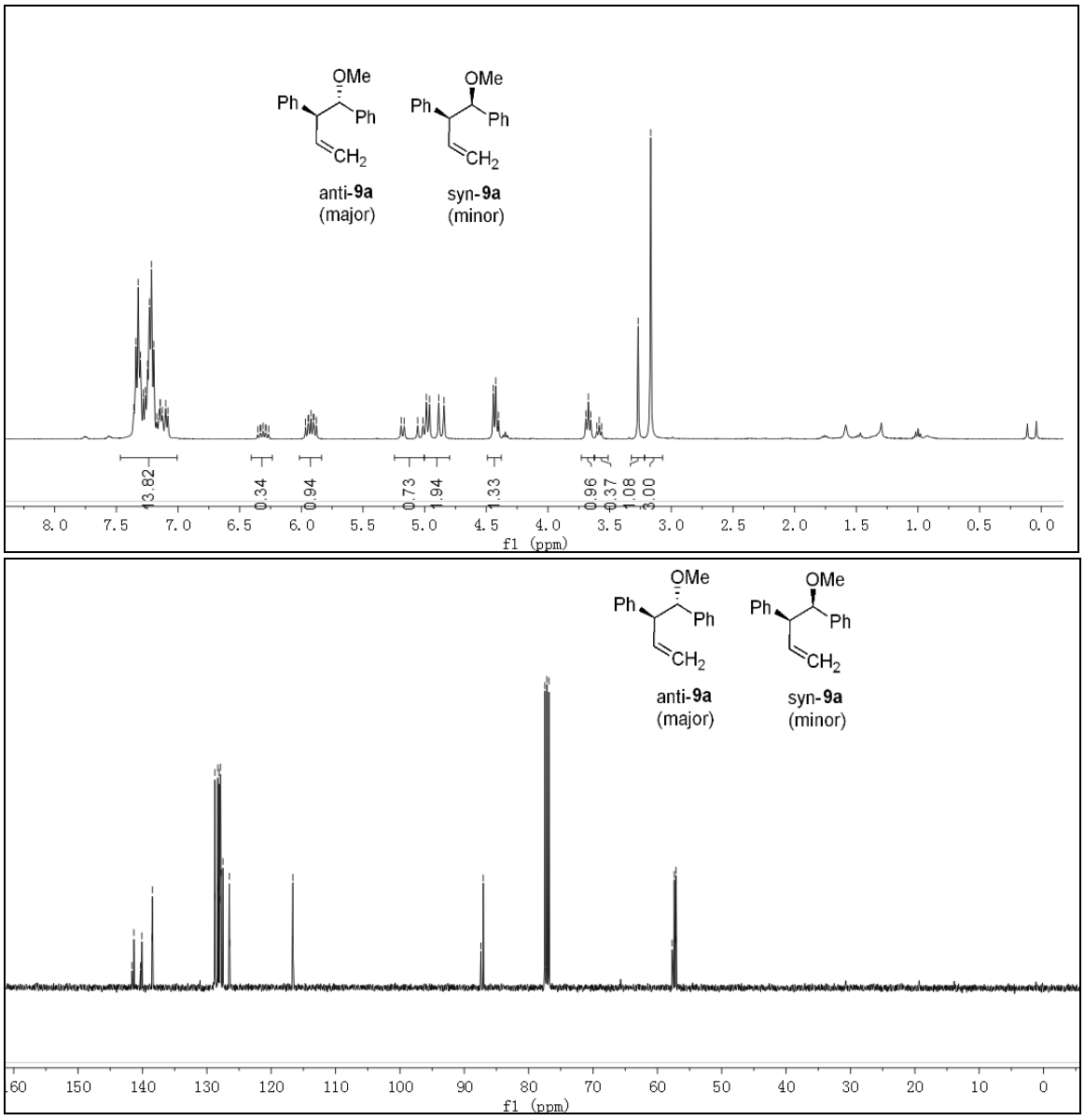
General Procedure: In a dry Schlenk flask, to a mixture of vinyl bromide or triflates (1.0 equiv, 0.3 mmol) and $Pd(PPh_3)_2Cl_2$ (1 mol%) or Pd(PPh3)4 (1 mol%) in 3.2 mL of dry toluene was added a solution of (trimethylsilyl)methyl yttrium complex **1** (0.33 equiv, 0.1 mmol) in 0.8 mL of dry toluene dropwise. After being stirred at room temperature for 2 h, the solvent was evaporated *in vacuo*. To the residue was added a solution of benzadldehyde dimethyl acetal **6f** (1.1 equiv, 0.33 mmol) in 2 mL of dry CH_2Cl_2 and $TiCl_4$ (0.3 equiv) dropwise at -78 ℃, and the mixture was stirred under N_2 at -78 ºC for 10 hours. Then the reaction was quenched with saturated $NaHCO_3$ (20 mL). The resulting mixture was extracted by ethyl acetate (3×10 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the product **9-11**.



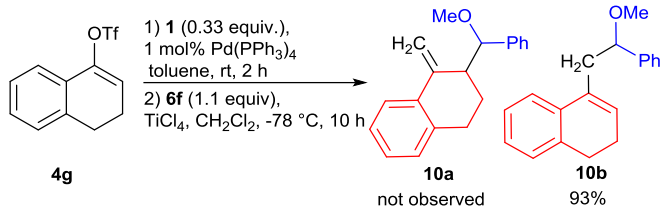
2e

9a 92%, anti : syn = 3 : 1

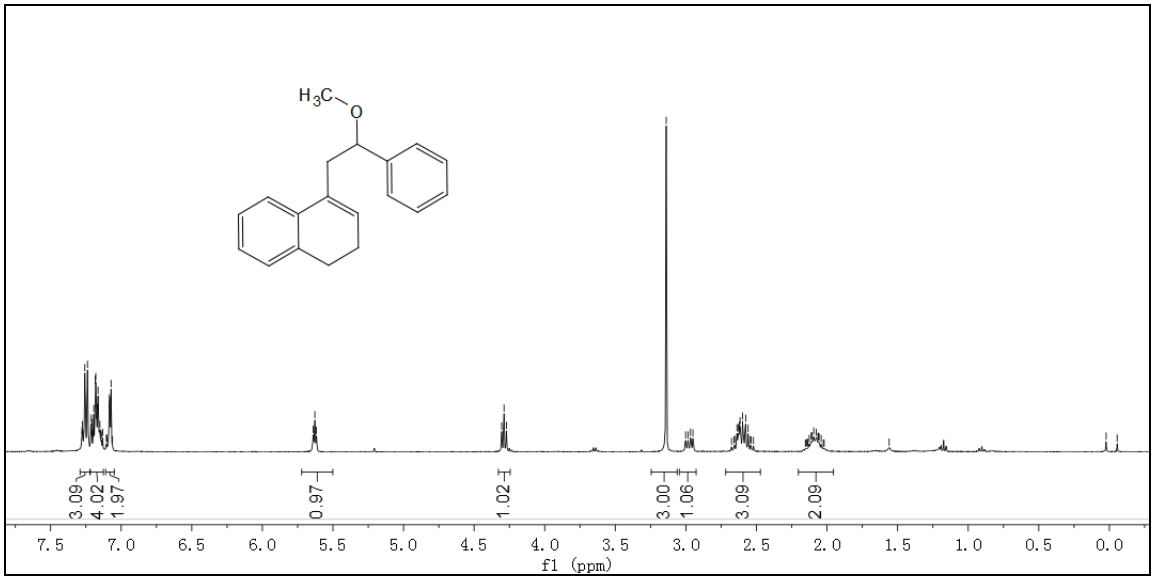
9b not observed

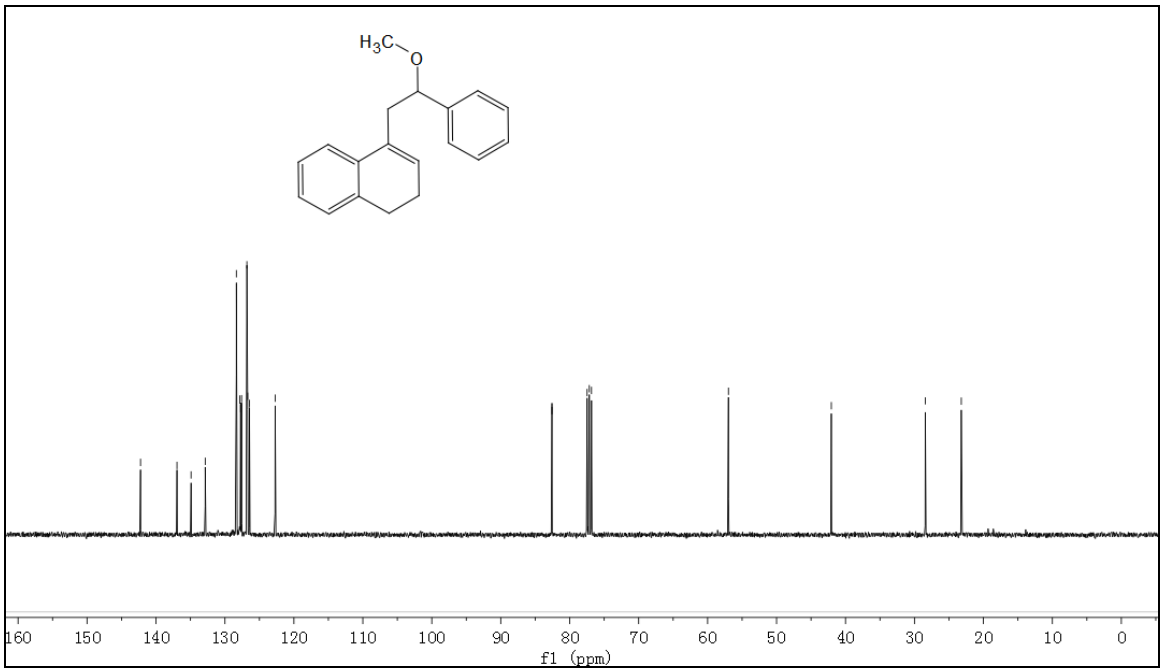


Two diastereoisomers of **9a** (dr 3:1) were inseparable with the anti-isomer as the major one. R_f = 0.4 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 6.01 (m, 13.3H), 6.41 – 6.24 (m, 0.33H), 6.02 – 5.84 (m, 1H), 5.11 (dd, *J* = 57.1, 13.7 Hz, 0.67H), 4.92 (dd, *J* = 43.7, 13.7 Hz, 2H), 4.44-4.37 (m, 1.33H), 3.67 (t, *J* = 7.8 Hz, 1H), 3.58 (t, *J* = 7.5 Hz, 0.33H), 3.27 (s, 1H), 3.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 141.3 (anti), 140.3, 140.1 (anti), 138.49, 138.47 (anti), 128.8 (anti), 128.7, 128.29 (anti), 128.26, 128.1 (anti), 128.0, 127.9 (anti), 127.8, 127.5 (anti), 127.5, 126.5 (anti), 126.4, 116.64 (anti), 116.60, 87.4, 87.1 (anti), 57.7, 57.4 (anti), 57.2, 57.1 (anti). The NMR data is in good agreement with that reported in the literature.[19]



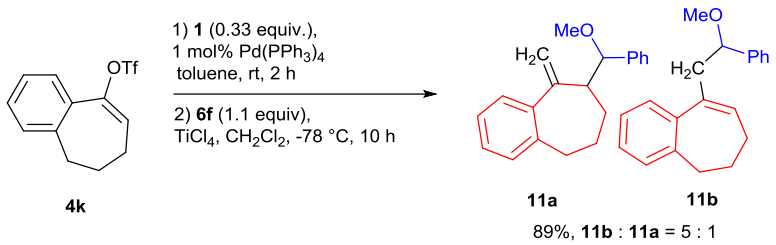
4g **10a** not observed **10b** 93%





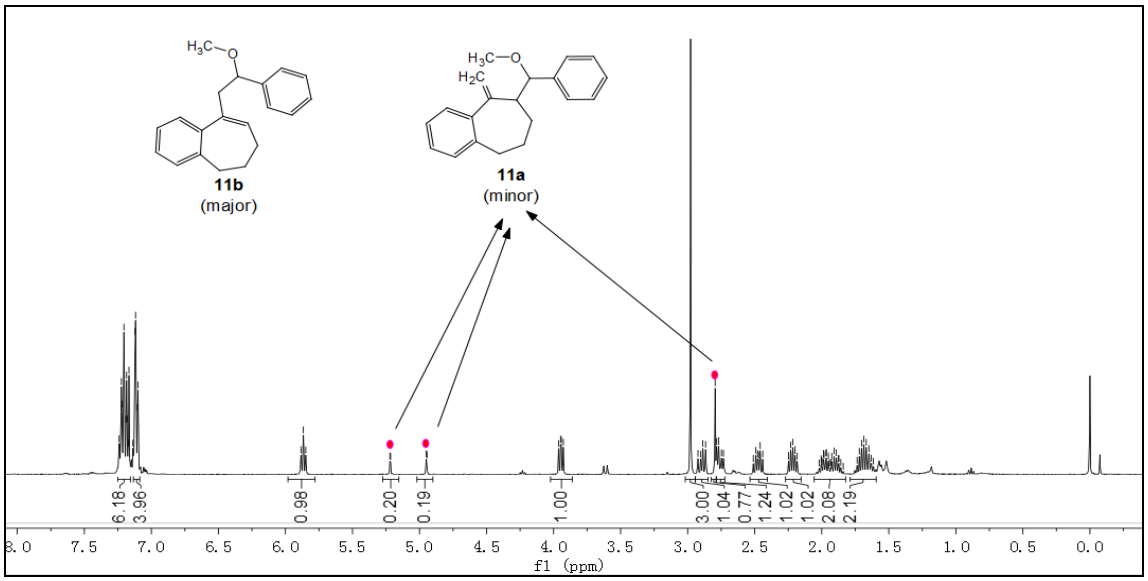
Only **10b** was observed by NMR. R_f = 0.45 (Petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 3H), 7.31 – 7.22 (m, 4H), 7.20 – 7.14 (m, 2H), 5.72 (t, *J* = 4.5 Hz, 1H), 4.38 (t, *J* = 6.7 Hz, 1H), 3.23 (s, 3H), 3.07 (dd, *J* = 14.0, 6.7 Hz, 1H), 2.81 – 2.57 (m, 3H), 2.30 – 2.05 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 137.0, 134.9, 132.9, 128.3, 127.8, 127.7, 127.6,

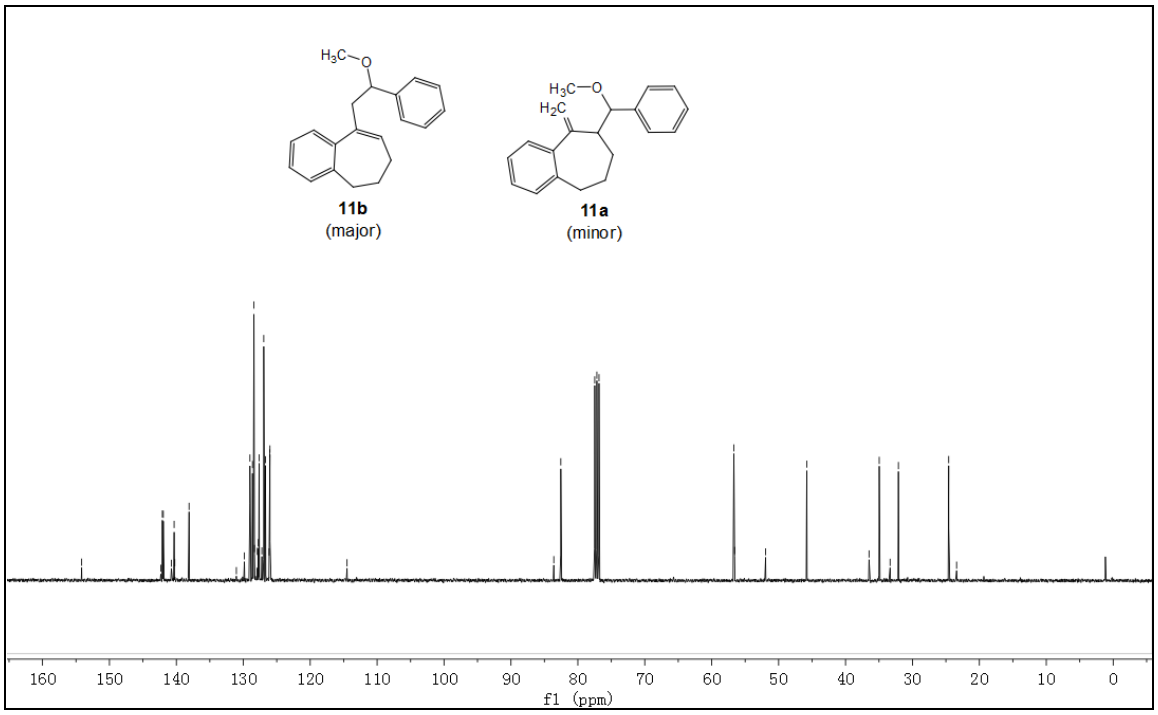
126.8, 126.7, 126.4, 122.7, 82.6, 57.0, 42.1, 28.4, 23.2. IR(neat) 3028(m), 2932(s), 2882(m), 2826(m), 1729(w), 1487(s), 1451(s), 1099(s), 760(s), 736(m), 701(s). HRMS (ESI) calcd for $C_{19}H_{20}ONa^+$ $[M+Na]^+$ 287.1406; found 287.1405.



4k **11a** **11b**

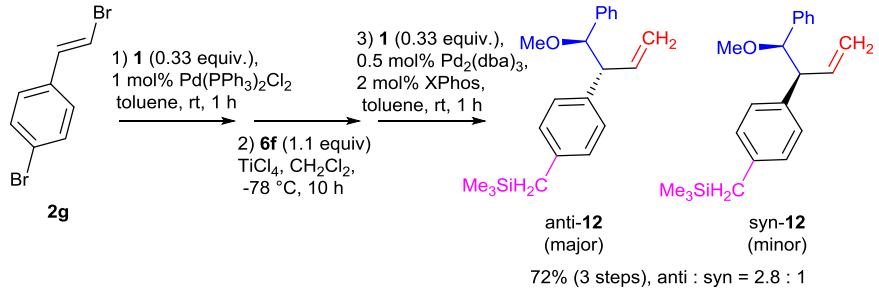
89%, **11b** : **11a** = 5 : 1





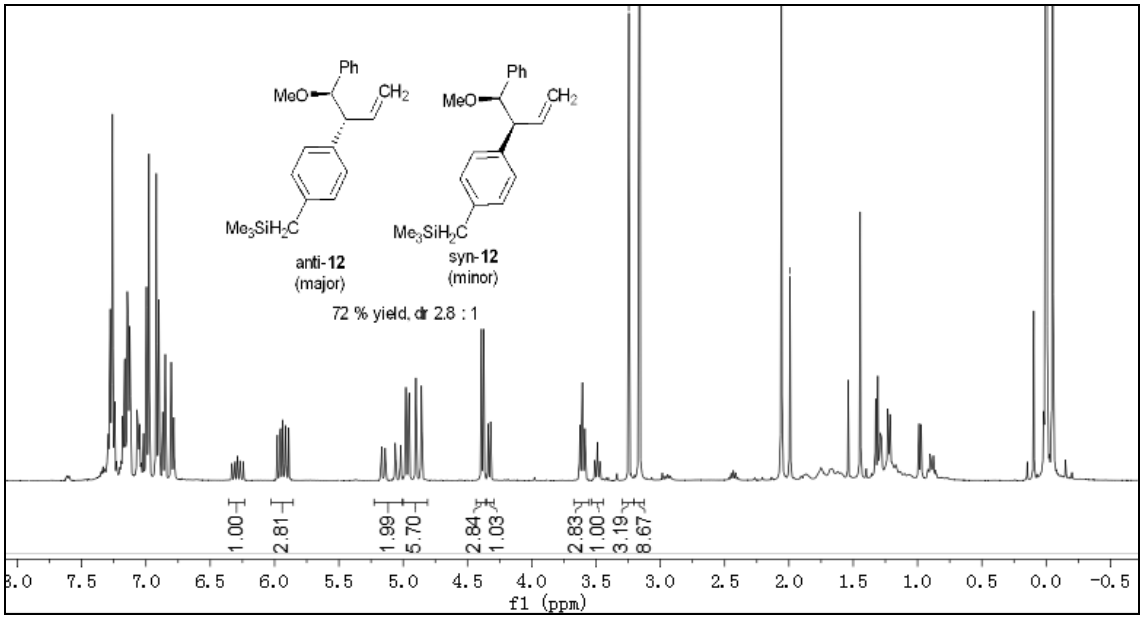
The mixture of **11a** and **11b** was isolated in 89% yield and they were inseparatable. R_f = 0.45 (Petroleum ether/ethyl acetate 50:1).
For the major product **11b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 5H), 7.13 – 7.09 (m, 4H), 5.87 (t, *J* = 7.2 Hz, 1H), 3.94 (dd, *J* = 8.2, 5.8 Hz, 1H), 2.92 (s, 3H), 2.89 (dd, *J* = 14.4, 8.3 Hz, 1H), 2.76 (dd, *J* = 14.4, 5.9 Hz, 1H), 2.48 (dt, *J* = 12.8, 7.6 Hz, 1H), 2.22 (dt, *J* = 12.8, 6.5 Hz, 1H), 2.05 – 1.83 (m, 2H), 1.77 – 1.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 142.0, 140.3, 138.1, 129.0, 128.6, 128.4, 127.6, 126.9, 126.7, 126.0, 126.0, 82.6, 56.7, 45.8, 35.0, 32.1, 24.6.
For the major product **11a**: ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 142.3, 140.7, 140.2, 131.0, 129.8, 128.3, 127.9, 127.8, 127.2, 126.1, 114.5, 83.6, 56.6, 52.0, 36.5, 33.3, 23.4.
IR (neat) 3062(w), 3026(w), 2930(s), 2855(m), 1452(m), 1101(s), 759(s), 700(s). HRMS (ESI) calcd for $C_{20}H_{22}ONa^+$ $[M+Na]^+$ 301.1563; found 301.1567.

Multi-functionalization of Styrenes



Procedure: In a dry Schlenk flask, to a mixture of vinyl bromide **2g** (1.0 equiv, 0.15 mmol) and $Pd(PPh_3)_2Cl_2$ (1 mol%) in 1.6 mL of dry toluene was added a solution of (trimethylsilyl)methyl yttrium complex **1** (0.33 equiv, 0.05 mmol) in 0.4 mL of dry toluene dropwise. After being stirred at room temperature for 1 h, the solvent was evaporated *in vacuo*. To the residue was added a solution of benzaldehyde **6a** (1.1 equiv) in 2 mL of dry CH_2Cl_2 and $TiCl_4$ (0.3 equiv) dropwise at -78 ℃, and the

mixture was stirred under N_2 at -78 °C for 10 hours. Then the solvent was evaporated again *in vacuo* followed by addition of 1.6 mL of dry toluene, $Pd_2(dba)_3$ (0.5 mol%), XPhos(2 mol%), and a solution of (trimethylsilyl)methyl yttrium complex **1** (0.33 equiv) in 2.0 mL of dry toluene successively. After being stirred at room temperature for 1 h, the reaction mixture was treated with with aq HCl (1 M, 10 mL). The resulting mixture was extracted by ethyl acetate (3×10 mL) and the combined extracts were washed by brine, dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the product **12** as a colorless oil (33.5 mg, 72% yield for three steps).



Two diastereoisomers of **12** were inseparable with the anti-isomer as the major one. The ratio of anti-**12** to syn-**12** was determined as 2.8:1 by NMR analysis of the crude sample. R_f = 0.4 (Petroleum ether/ethyl acetate 10:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 6.72 (m, 13.5H), 6.25 (ddd, *J* = 17.7, 10.3, 7.9 Hz, 0.5H), 5.90 (ddd, *J* = 17.8, 10.3, 8.1 Hz, 1H), 5.10 (dd, *J* = 45.6 Hz, *J* = 13.7 Hz, 1H), 4.92 (d, *J* = 35.7 Hz, *J* = 13.7 Hz, 1H), 4.35 (d, *J* = 7.2 Hz, 1H), 4.30 (d, *J* = 7.5 Hz, 0.5H), 3.57 (t, *J* = 7.6 Hz, 1H), 3.46 (t, *J* = 7.7 Hz, 0.5H), 3.22 (s, 1.5H), 3.13 (s, 3H), 2.03 (s, 2H), 1.96 (s, 1H), -0.03 (s, 9H), -0.08 (s, 4.5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.1, 138.9, 138.6, 138.4, 136.4, 128.5, 128.4, 127.9, 127.8, 127.8, 127.8, 127.6, 127.5, 127.3, 116.3, 116.1, 87.6, 87.2, 57.3, 57.1, 57.1, 56.7, 26.6, 26.6, -1.7, -1.8. IR(neat) 3291(w), 2955(m), 1905(m), 1248(s), 1101(s), 851(s), 700(s). HRMS (ESI) calcd for $C_{21}H_{28}OSiNa^+$ $[M+Na]^+$ 347.1802; found 347.1804.

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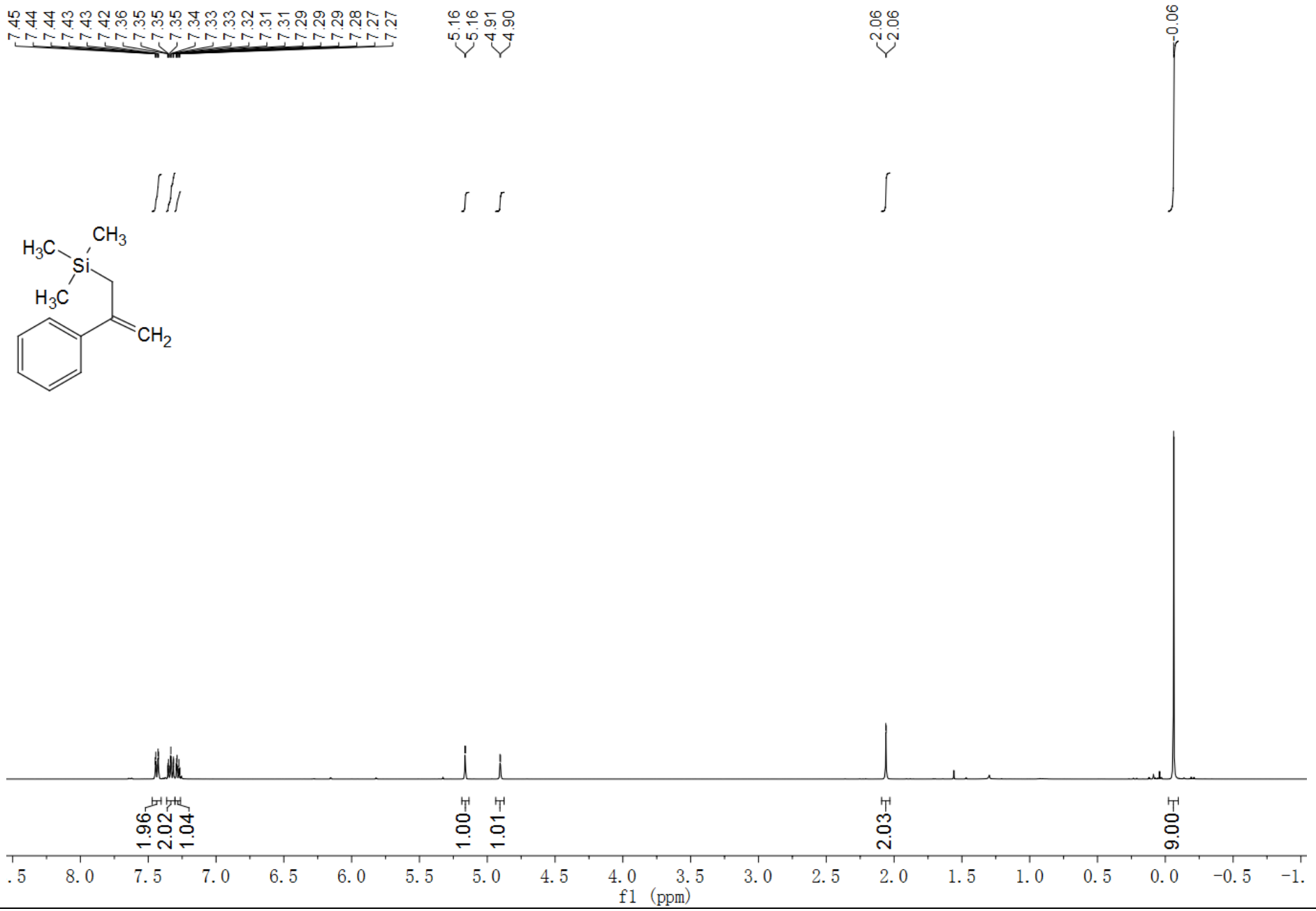
Copies of ^{1}H and ^{13}C NMR Spectra

^{1}H NMR of **3a**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7.31
7.31
7.29
7.29
7.29
7.28
7.27
7.27
5.16
5.16
4.91
4.90
2.06
2.06
0.06
H3C
CH3
Si
H3C
CH2
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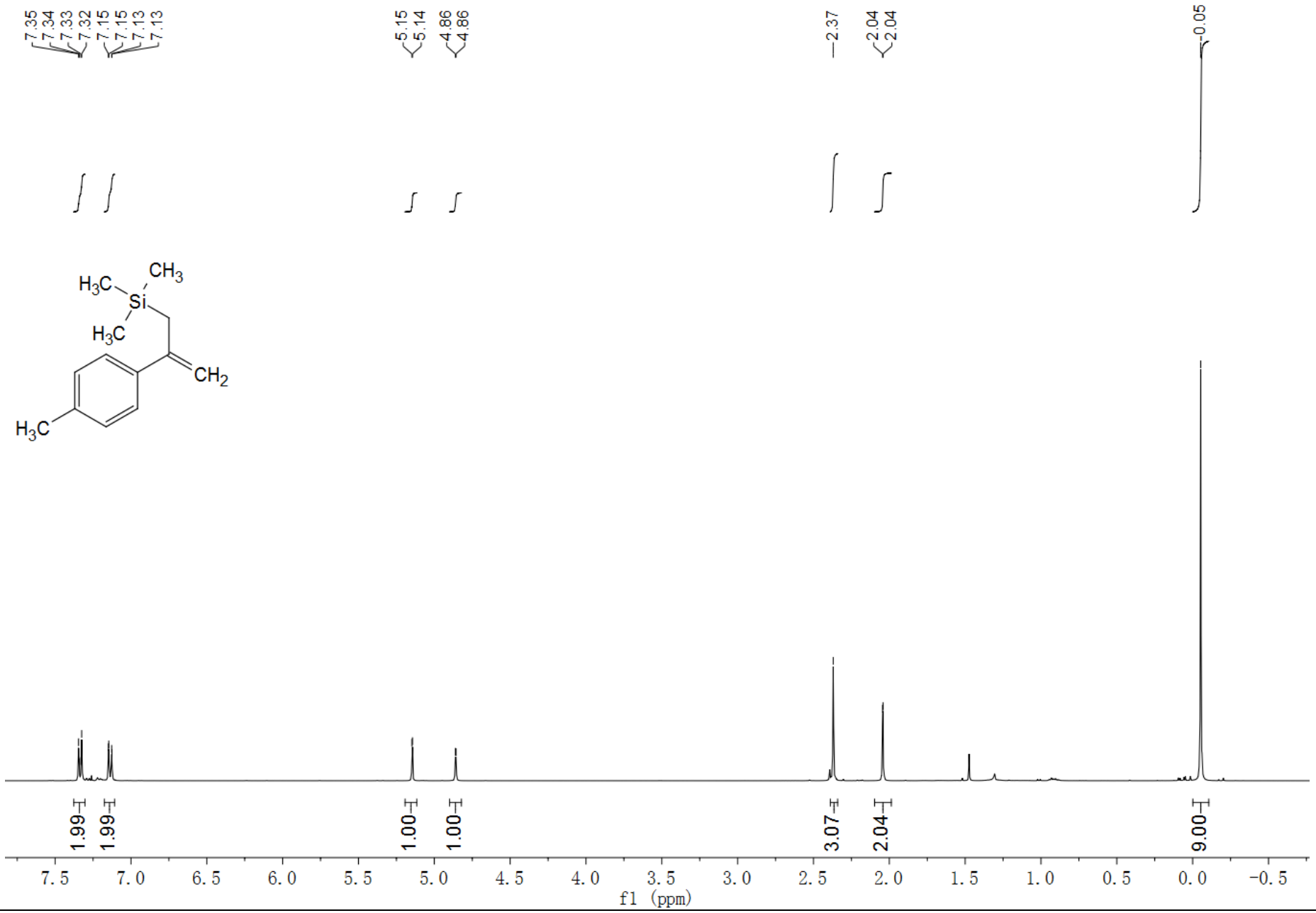
2.02
1.04
1.00
1.01
2.03
9.00
f1 (ppm)

^{1}H NMR of **3b**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2.04
2.04
0.05
H3C
CH3
Si
H3C
CH2
H3C
1.99
1.99
1.00
1.00
3.07
2.04
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
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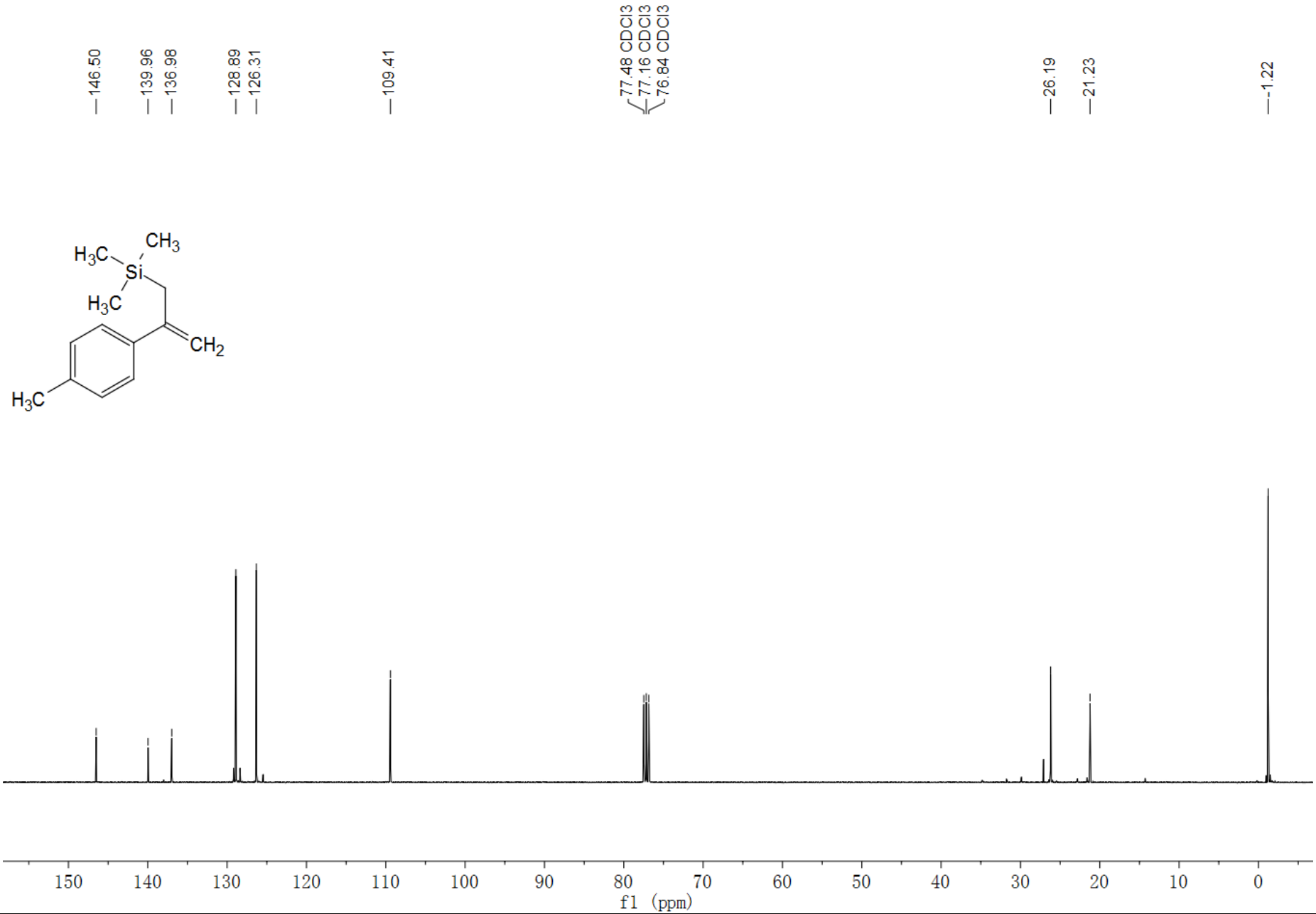
0.0
-0.5
f1 (ppm)

^{13}C NMR of **3b**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136.98
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76.84 CDCl3
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21.23
-1.22
H3C
CH3
Si
H3C
CH2
H3C
150
140
130
120
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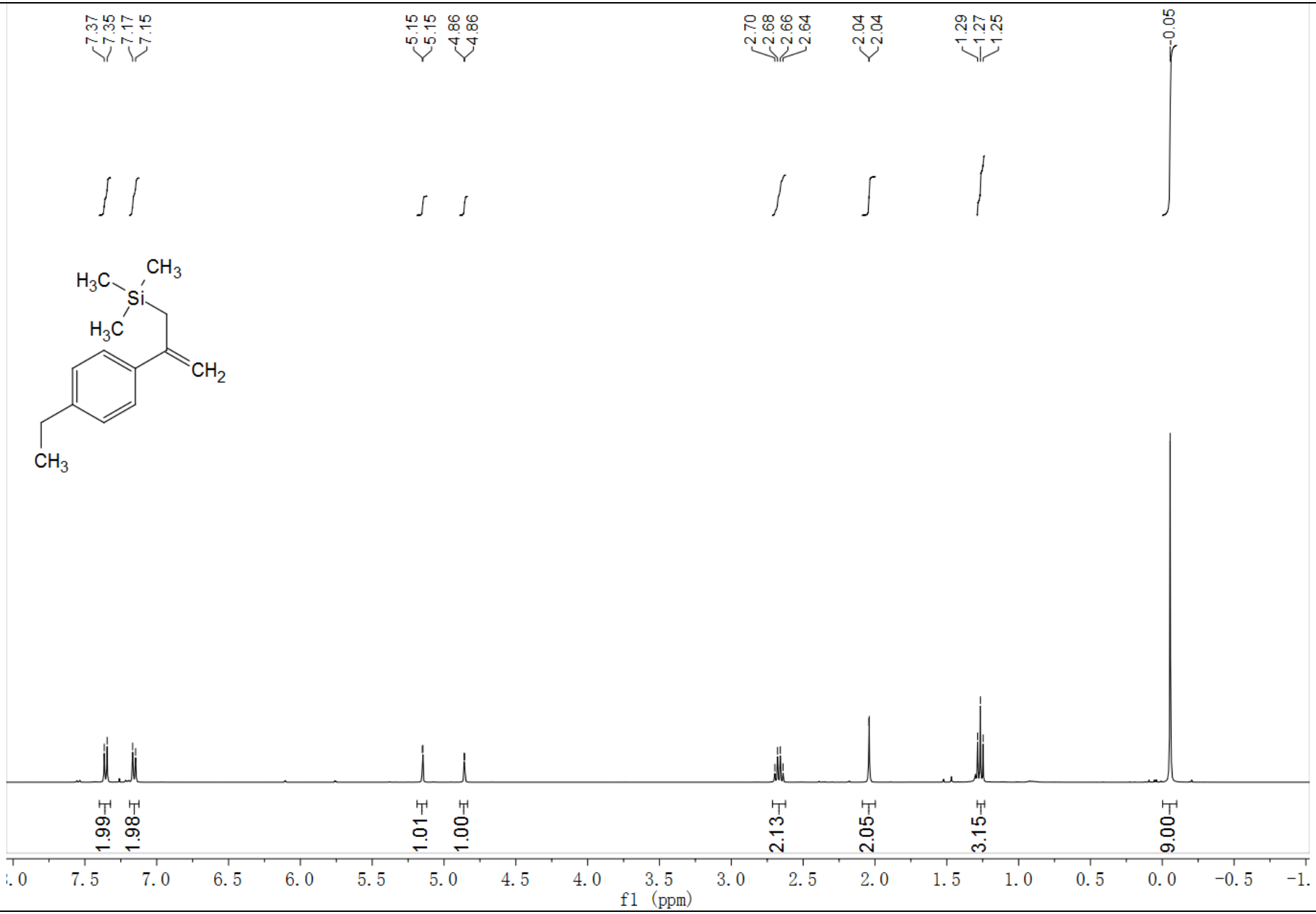
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR of **3c**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4.86
4.86
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2.68
2.66
2.64
2.04
2.04
1.29
1.27
1.25
0.05
H3C
CH3
Si
H3C
CH2
CH3
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1.01
1.00
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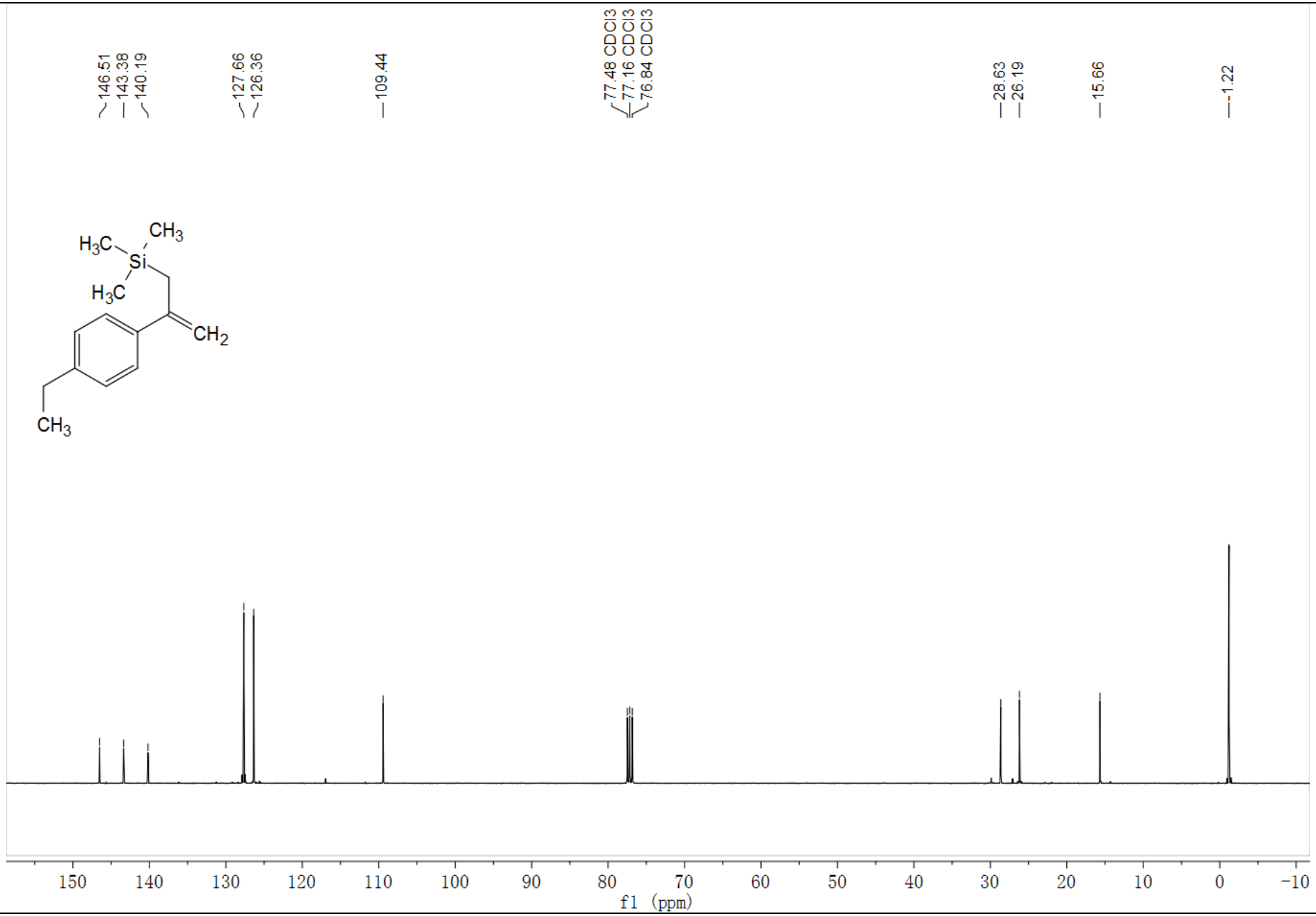
9.00
f1 (ppm)

^{13}C NMR of **3c**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15.66
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CH3
Si
H3C
CH2
CH3
150
140
130
120
110
100
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80
70
60
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40
30
20
10
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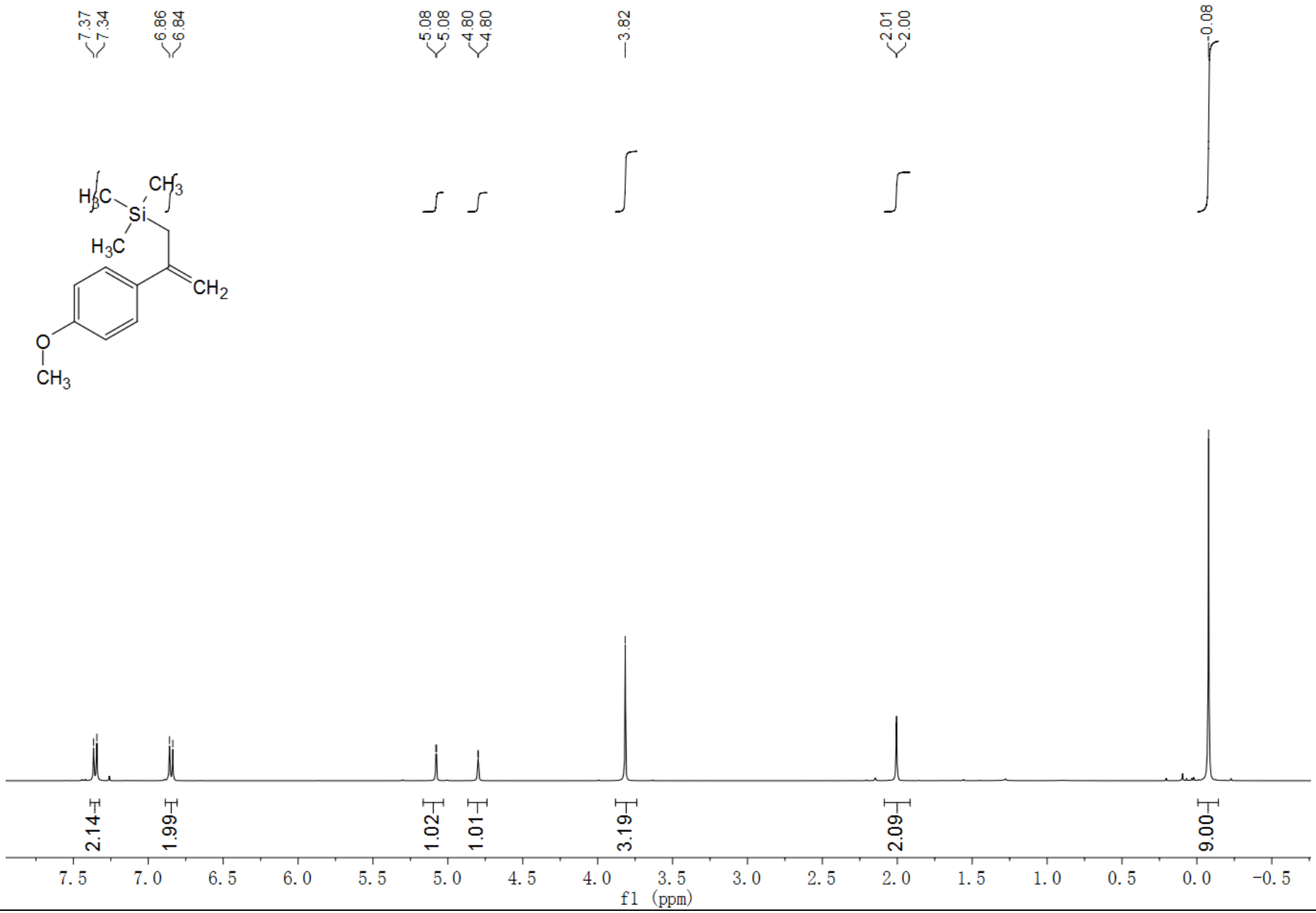
-10
f1 (ppm)

^{1}H NMR of **3d**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2.00
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CH3
Si
H3C
CH2
O
CH3
2.14
1.99
1.02
1.01
3.19
2.09
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.5
1.0
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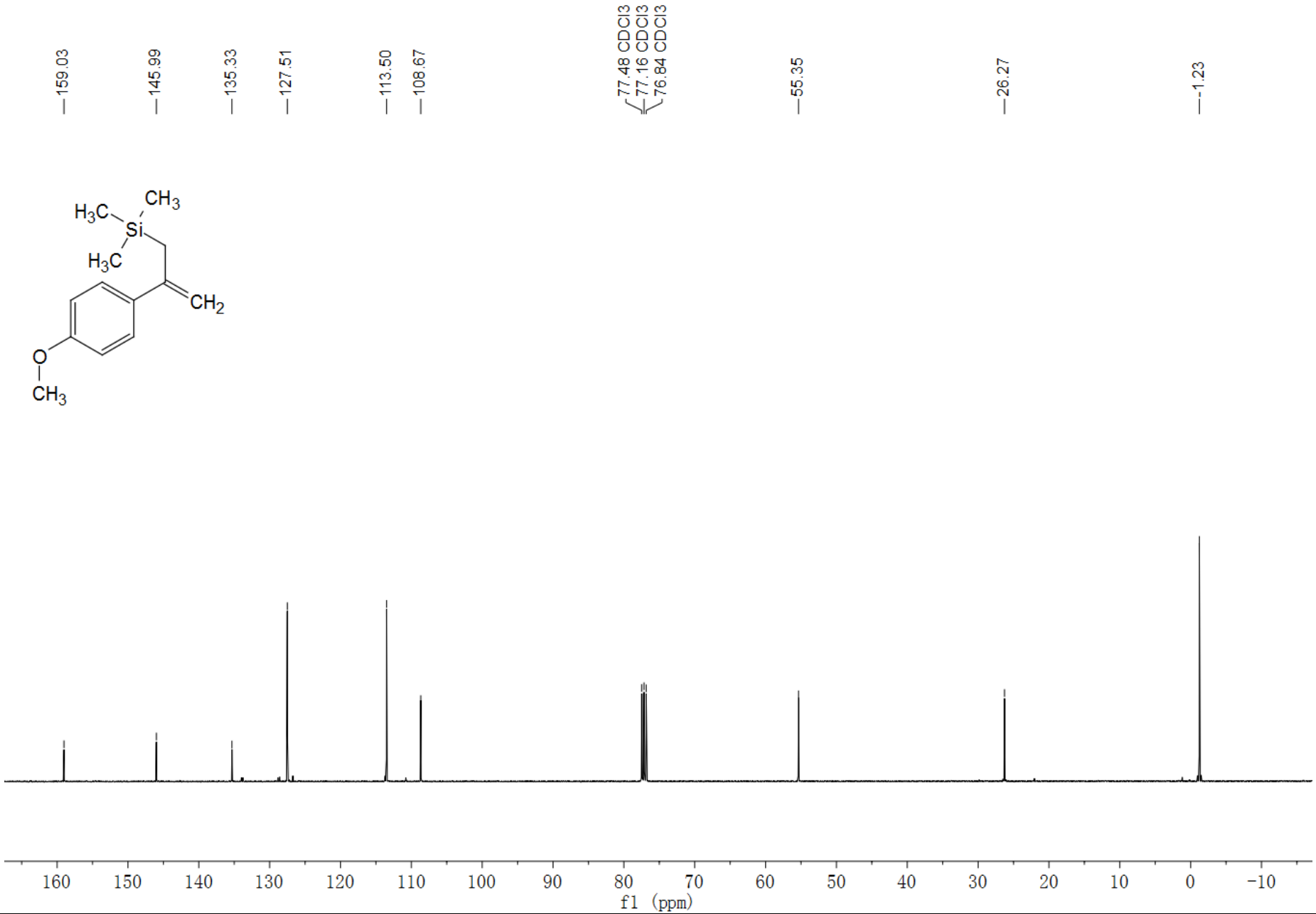
-0.5
f1 (ppm)

^{13}C NMR of **3d**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113.50
108.67
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76.84 CDCl3
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26.27
-1.23
H3C
CH3
Si
H3C
CH2
O
CH3
160
150
140
130
120
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60
50
40
30
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10
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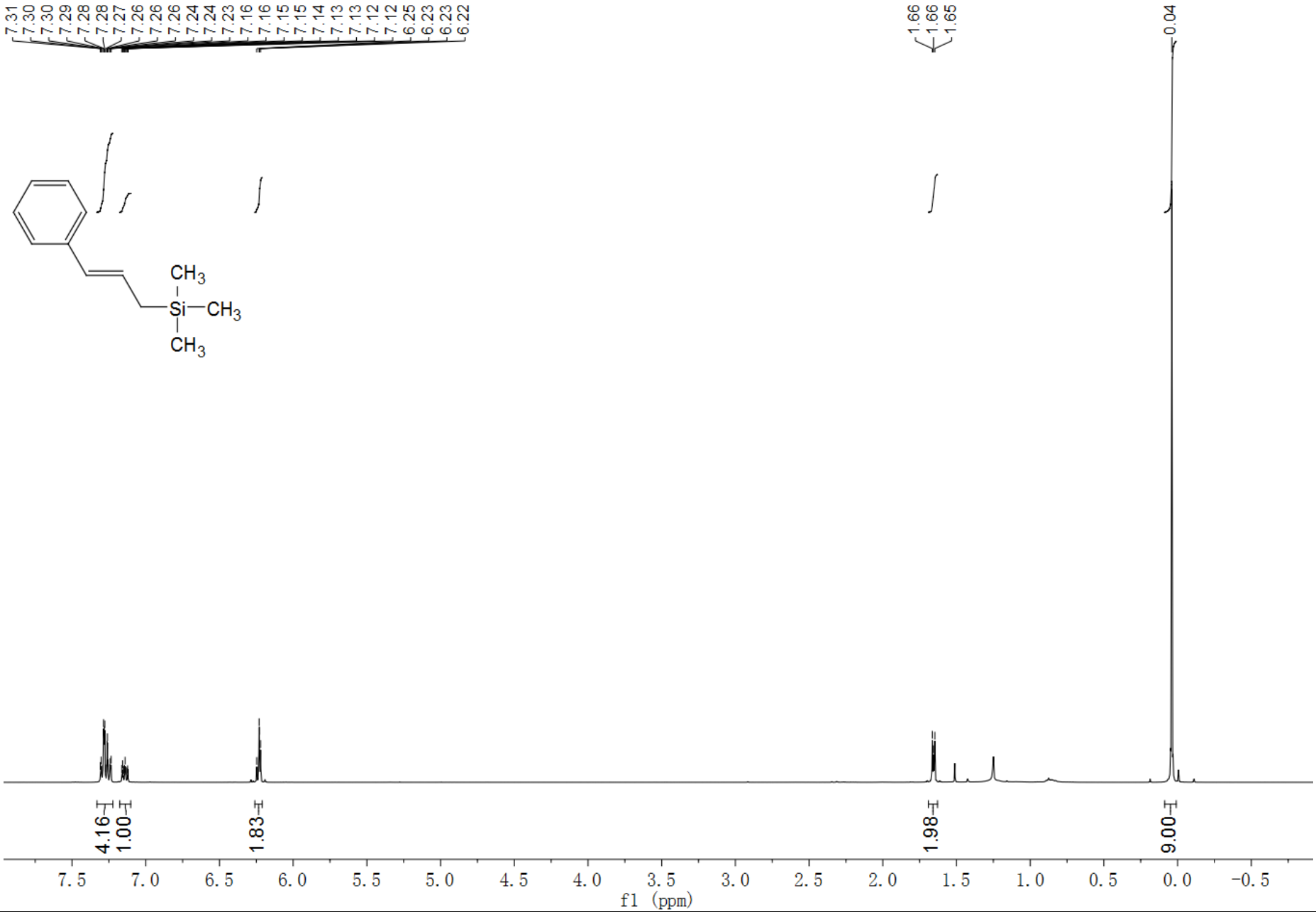
-10
f1 (ppm)

^{1}H NMR of **3e**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6.22
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Si
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CH3
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9.00
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
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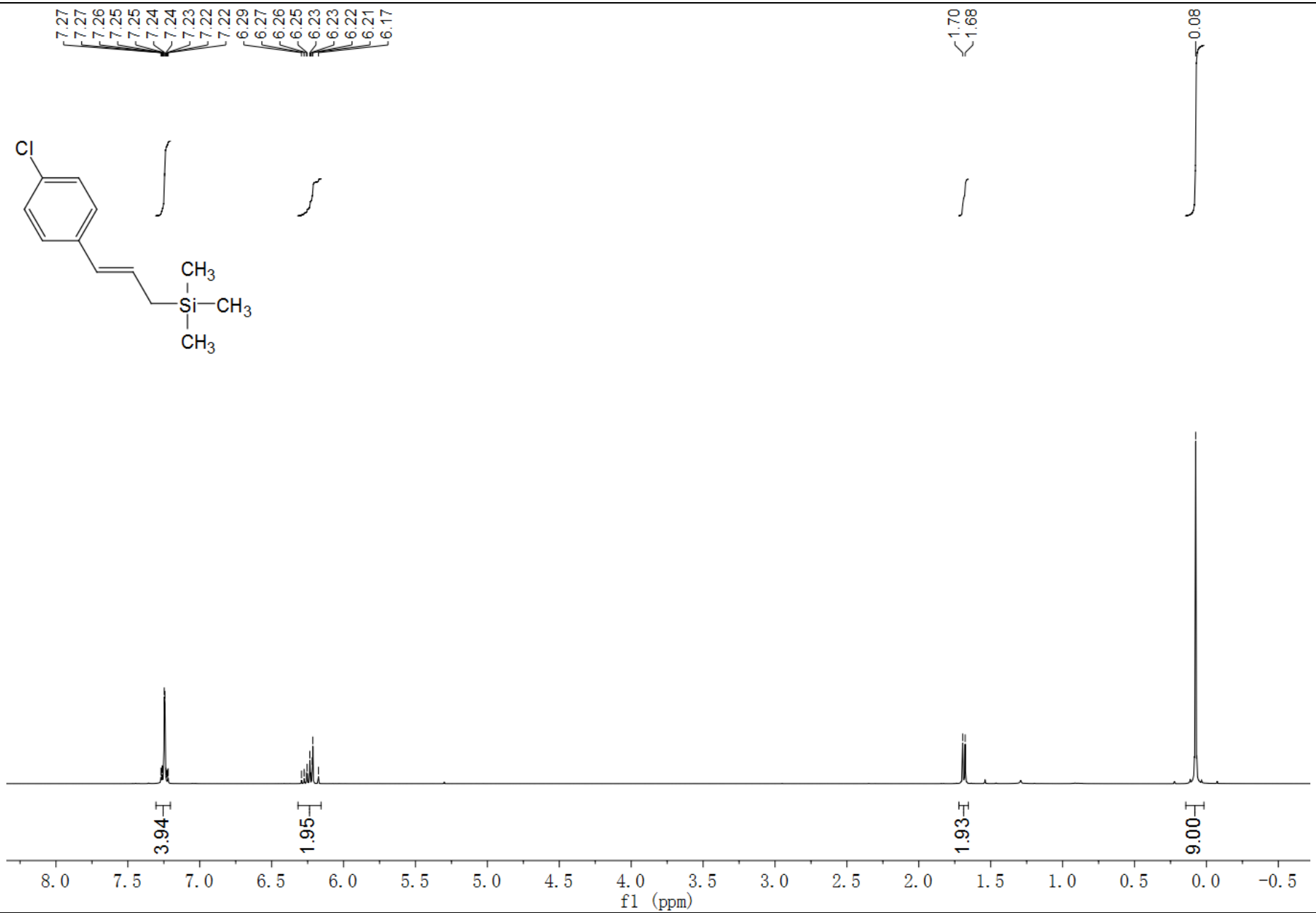
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6.23
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1.68
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Cl
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Si
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1.93
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6.5
6.0
5.5
5.0
4.5
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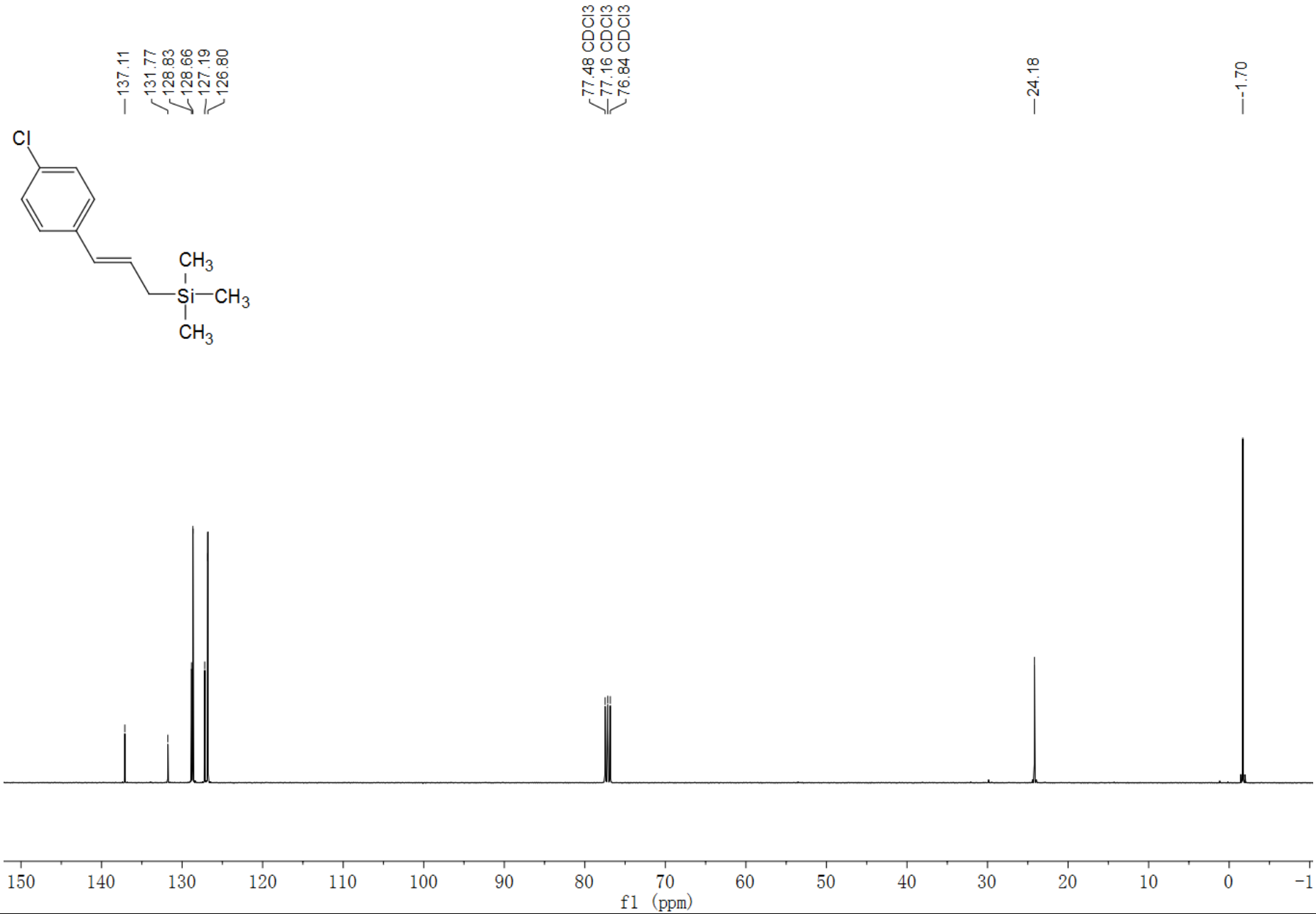
f1 (ppm)

^{13}C NMR of **3f**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CH3
Si
CH3
CH3
150
140
130
120
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80
70
60
50
40
30
20
10
0
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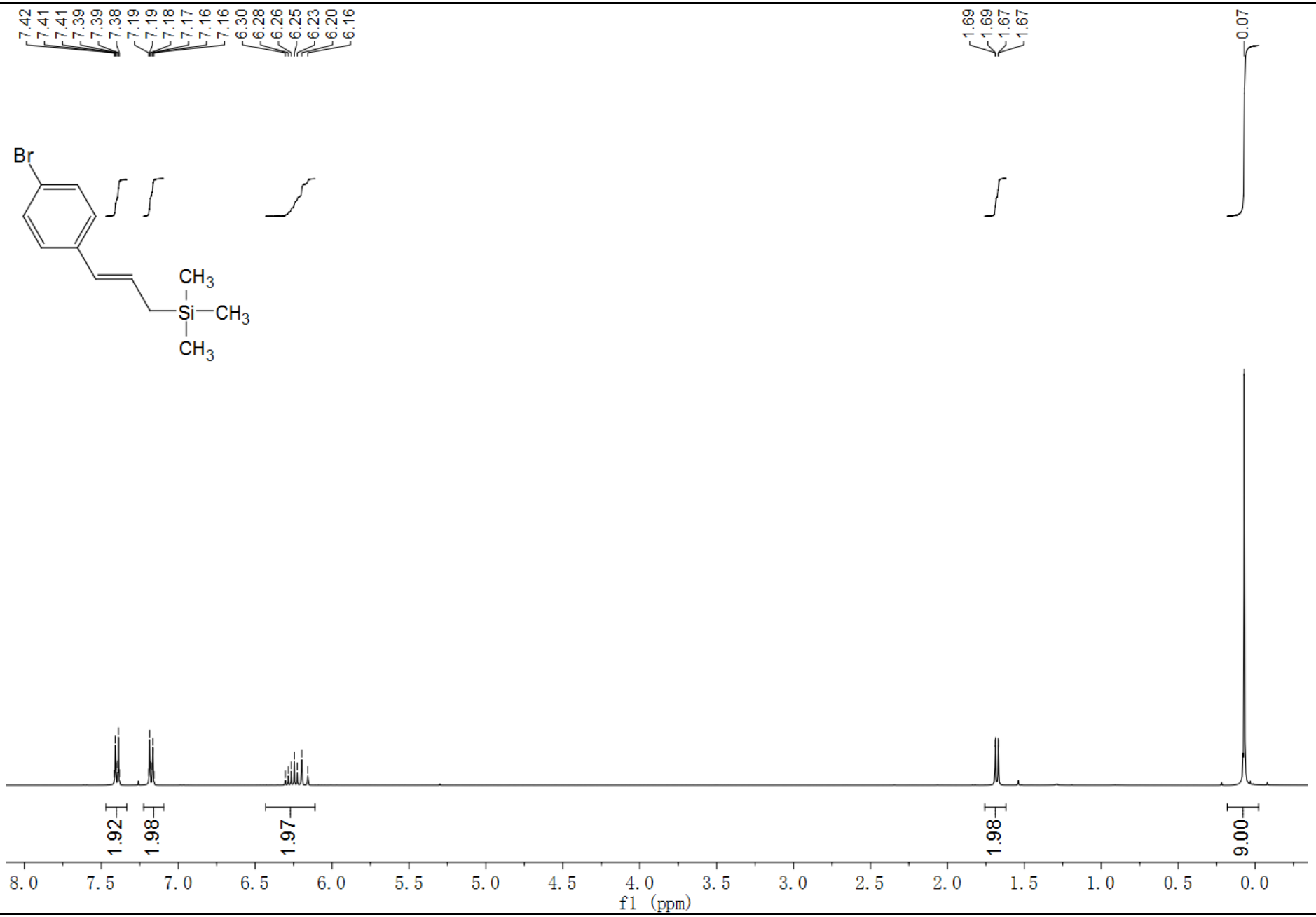
f1 (ppm)

^{1}H NMR of **3g**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6.26
6.25
6.23
6.20
6.16
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Si
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5.0
4.5
4.0
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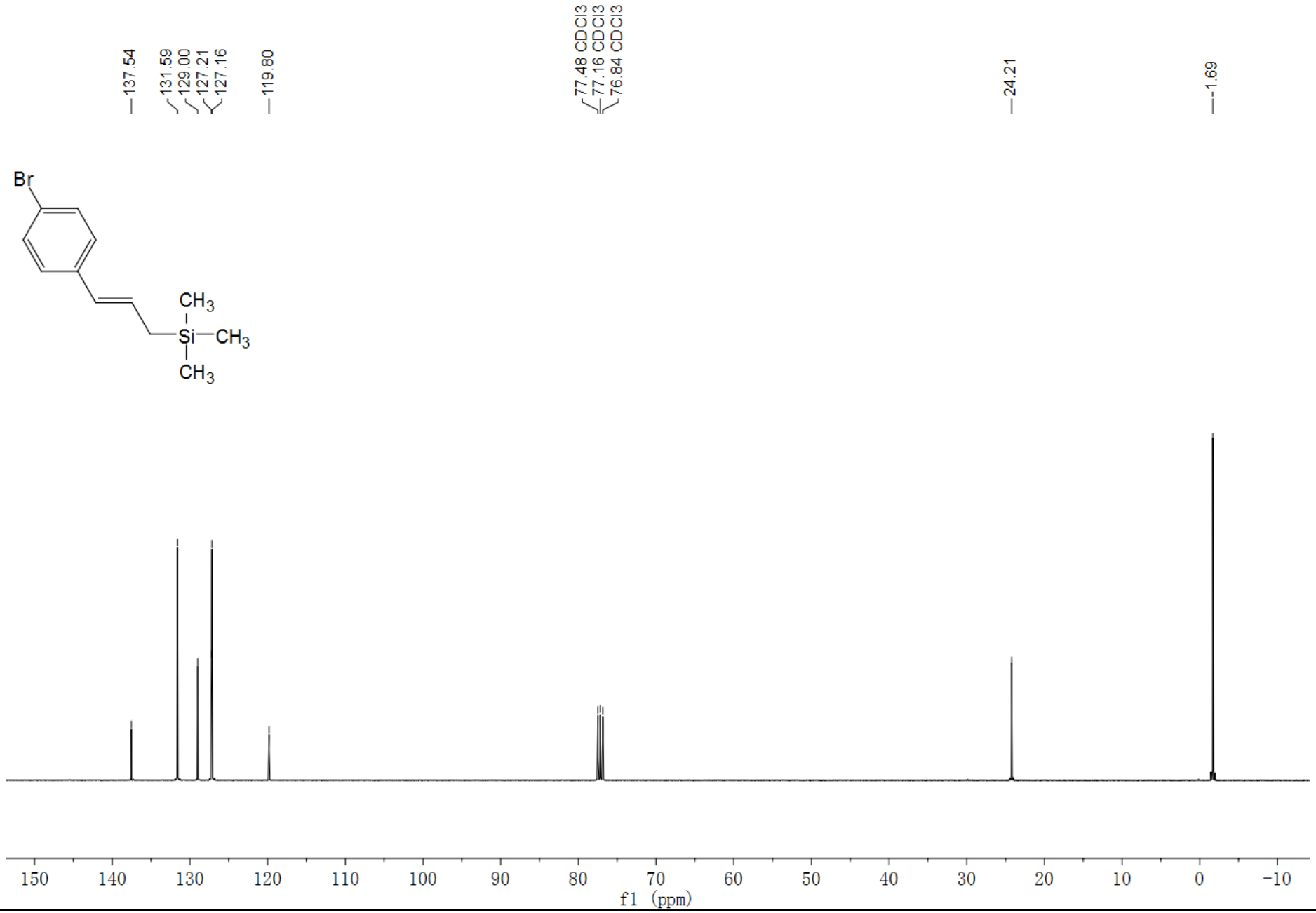
f1 (ppm)

^{13}C NMR of **3g**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150
140
130
120
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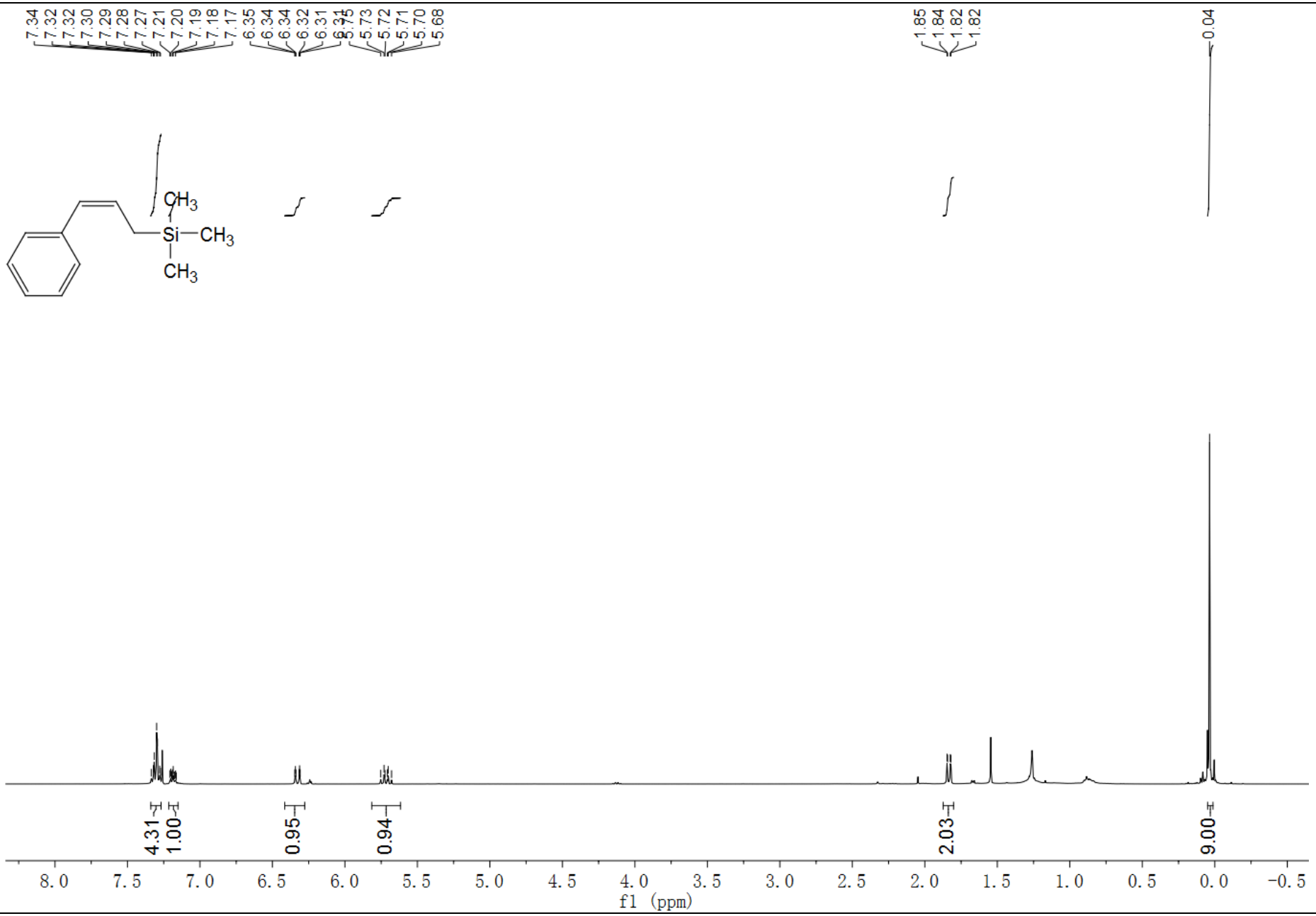
f1 (ppm)

^{1}H NMR of **3h**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6.32
6.31
5.75
5.73
5.72
5.71
5.70
5.68
1.85
1.84
1.82
1.82
0.04
CH3
Si
CH3
CH3
4.31
1.00
0.95
0.94
2.03
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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0.0
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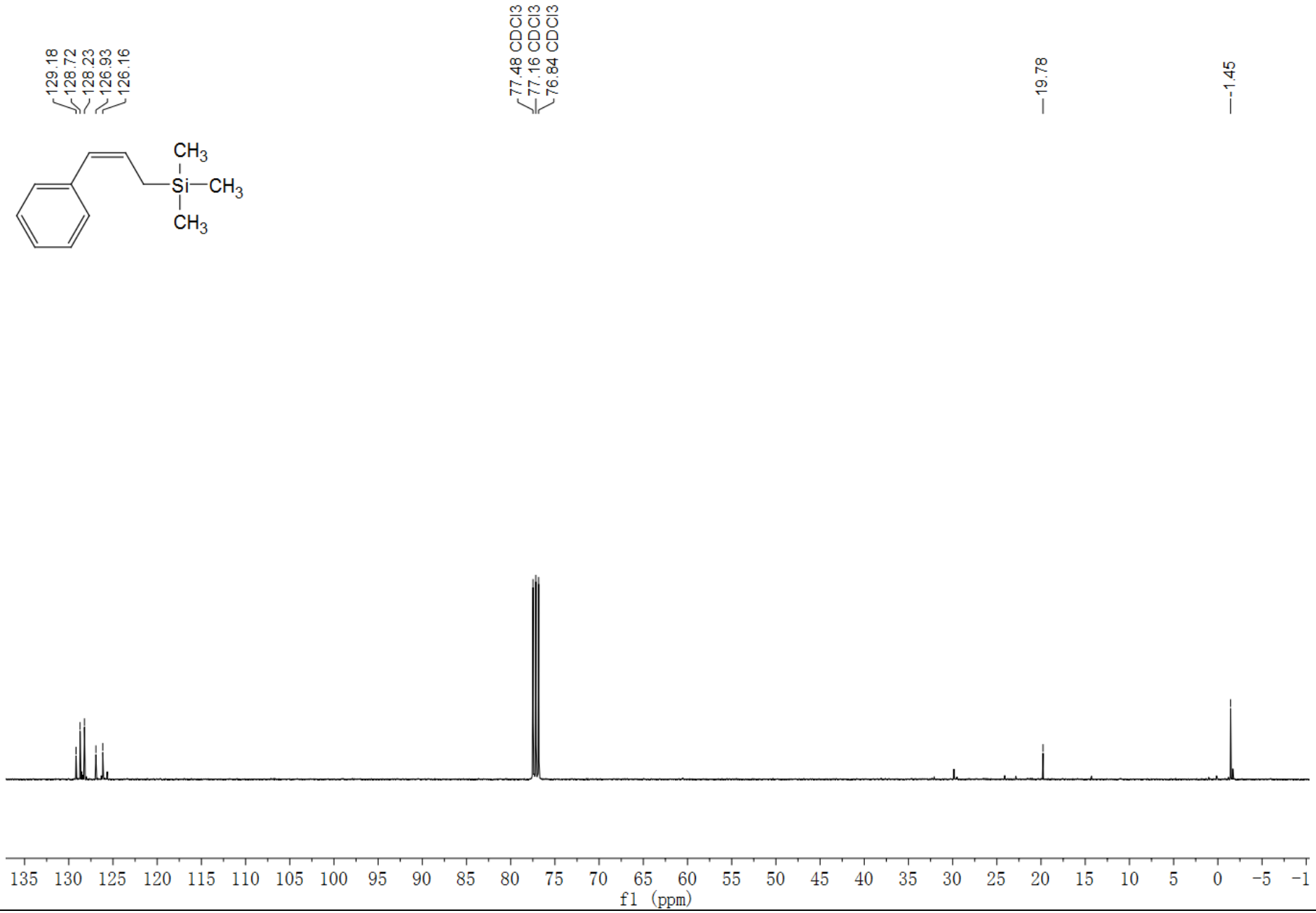
f1 (ppm)

^{13}C NMR of **3h**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Si
CH3
CH3
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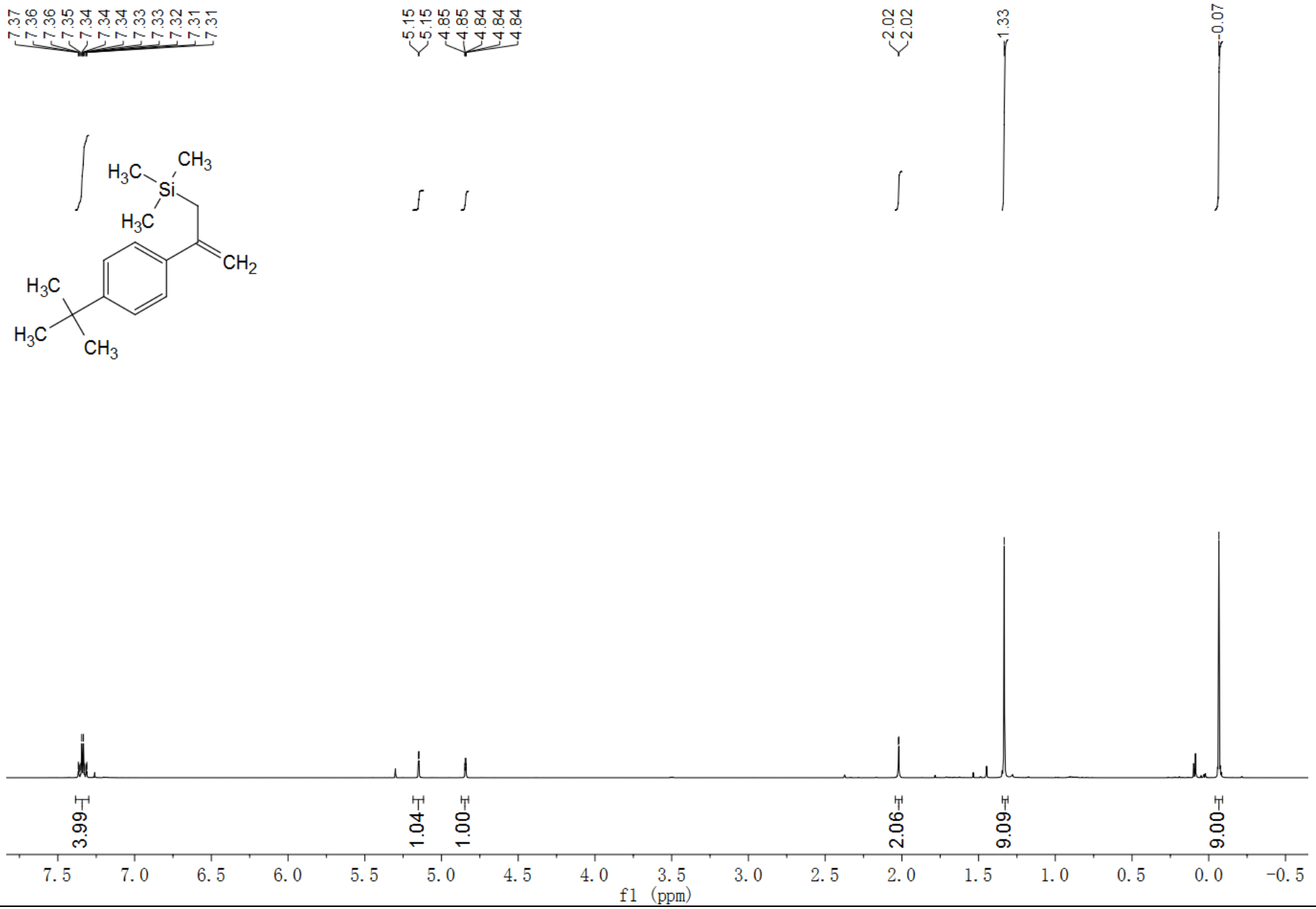
f1 (ppm)

^{1}H NMR of **5c**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5.15
4.85
4.85
4.84
4.84
4.84
2.02
2.02
1.33
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H3C
CH3
Si
H3C
CH2
H3C
H3C
CH3
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1.04
1.00
2.06
9.09
9.00
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7.0
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5.0
4.5
4.0
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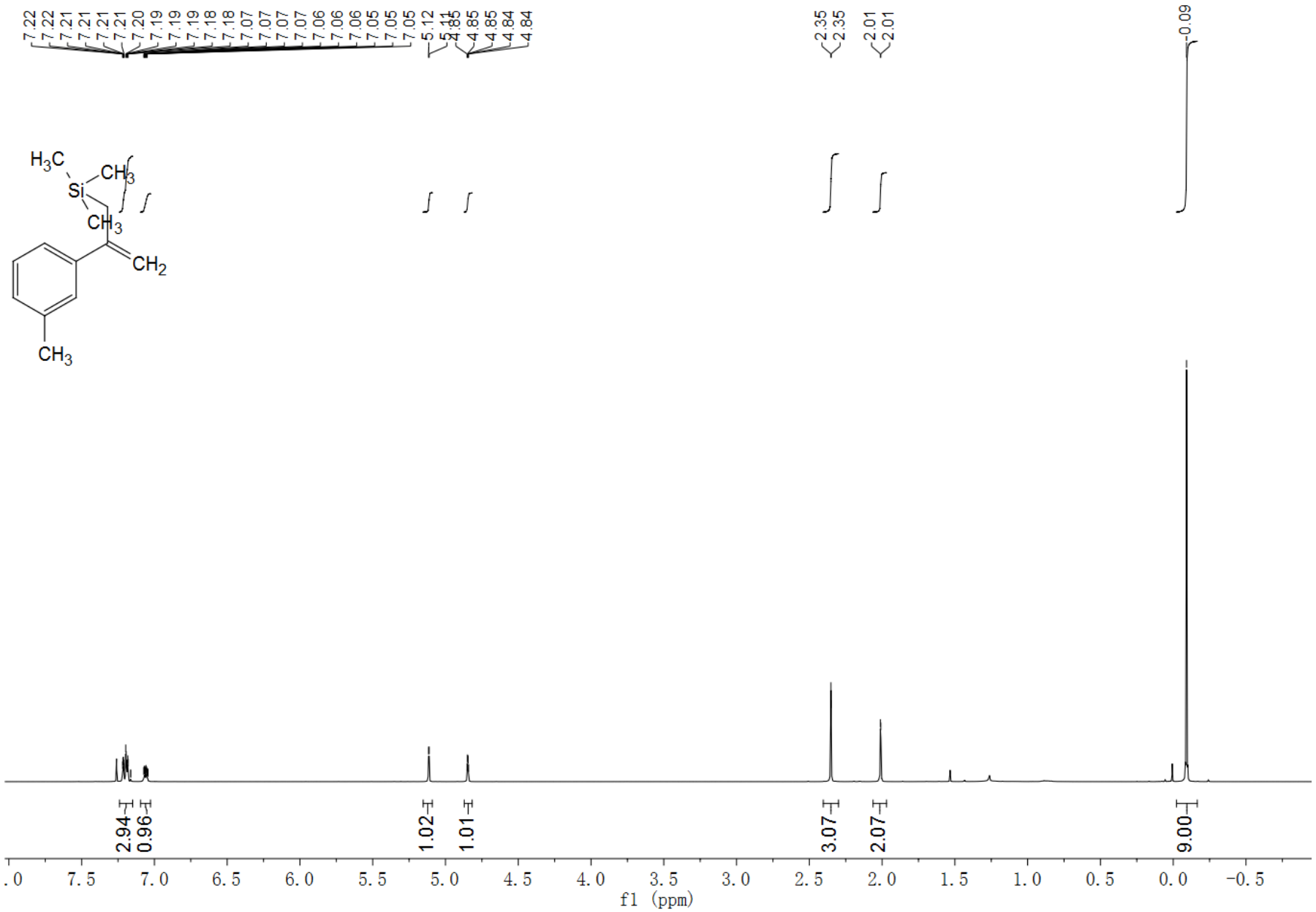
f1 (ppm)

^{1}H NMR of **5d**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5.11
4.85
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4.85
4.84
4.84
4.84
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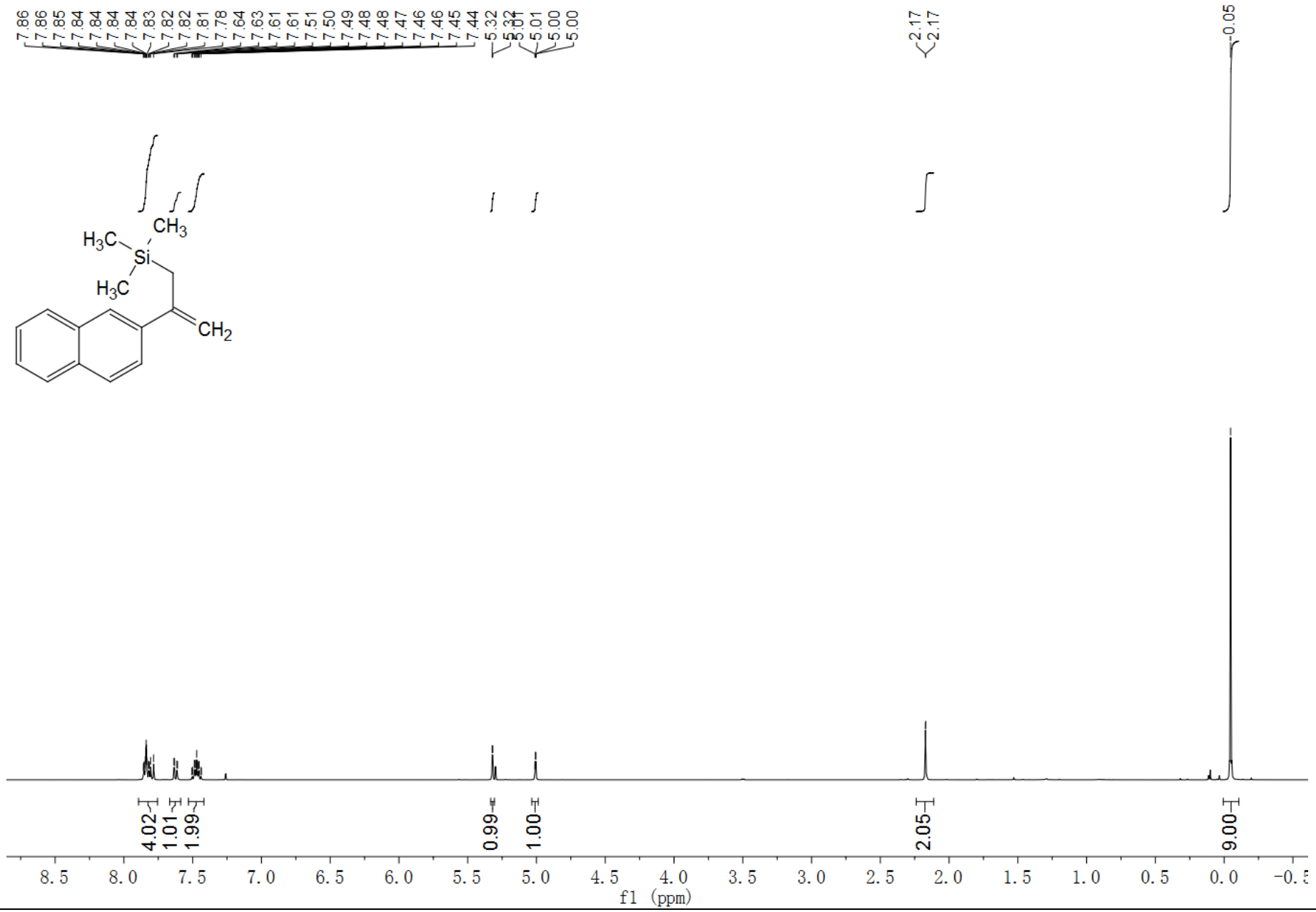
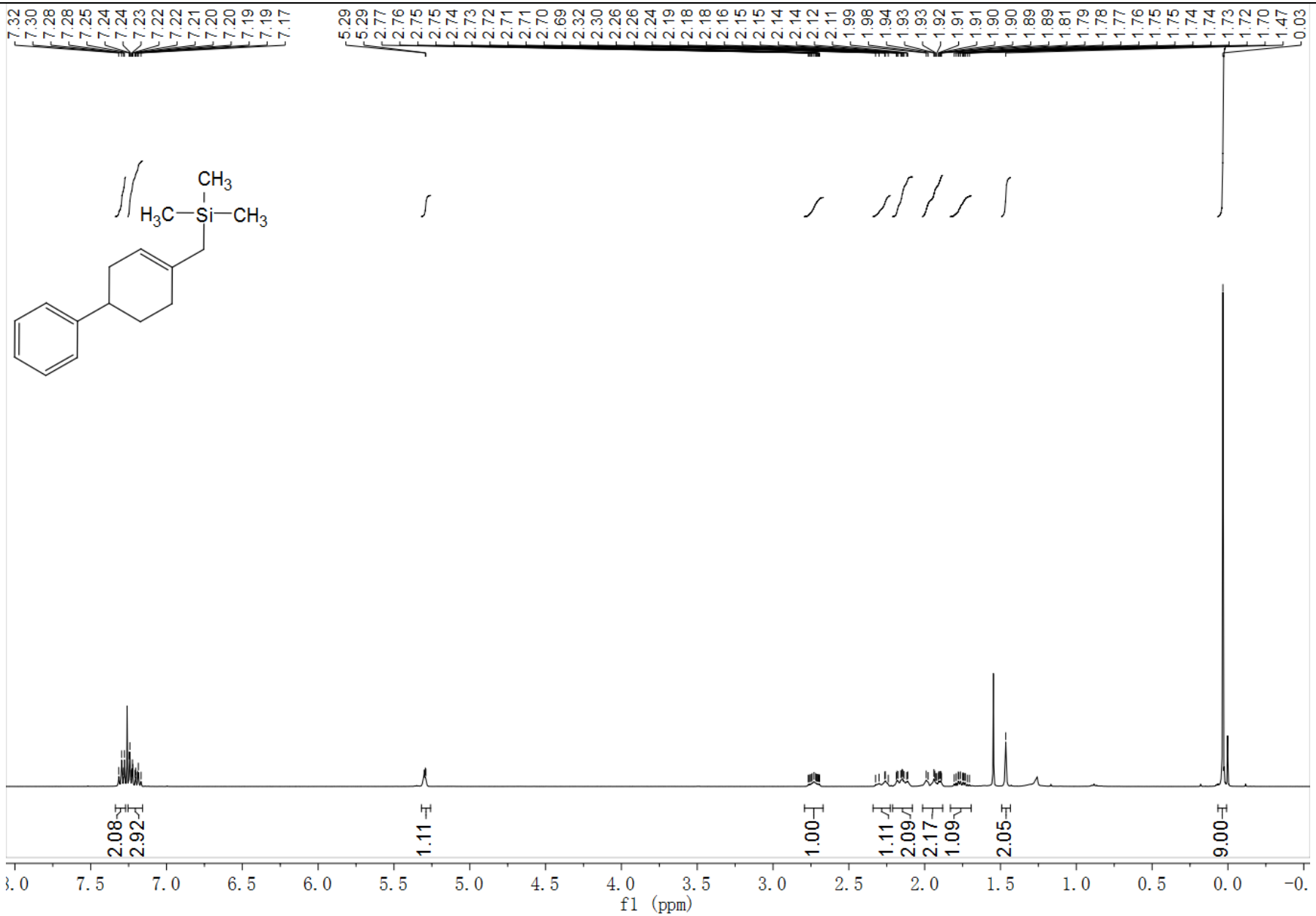
2.35
2.01
2.01
0.09
H3C
CH3
Si
CH3
CH2
CH3
2.94
0.96
1.02
1.01
3.07
2.07
9.00
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

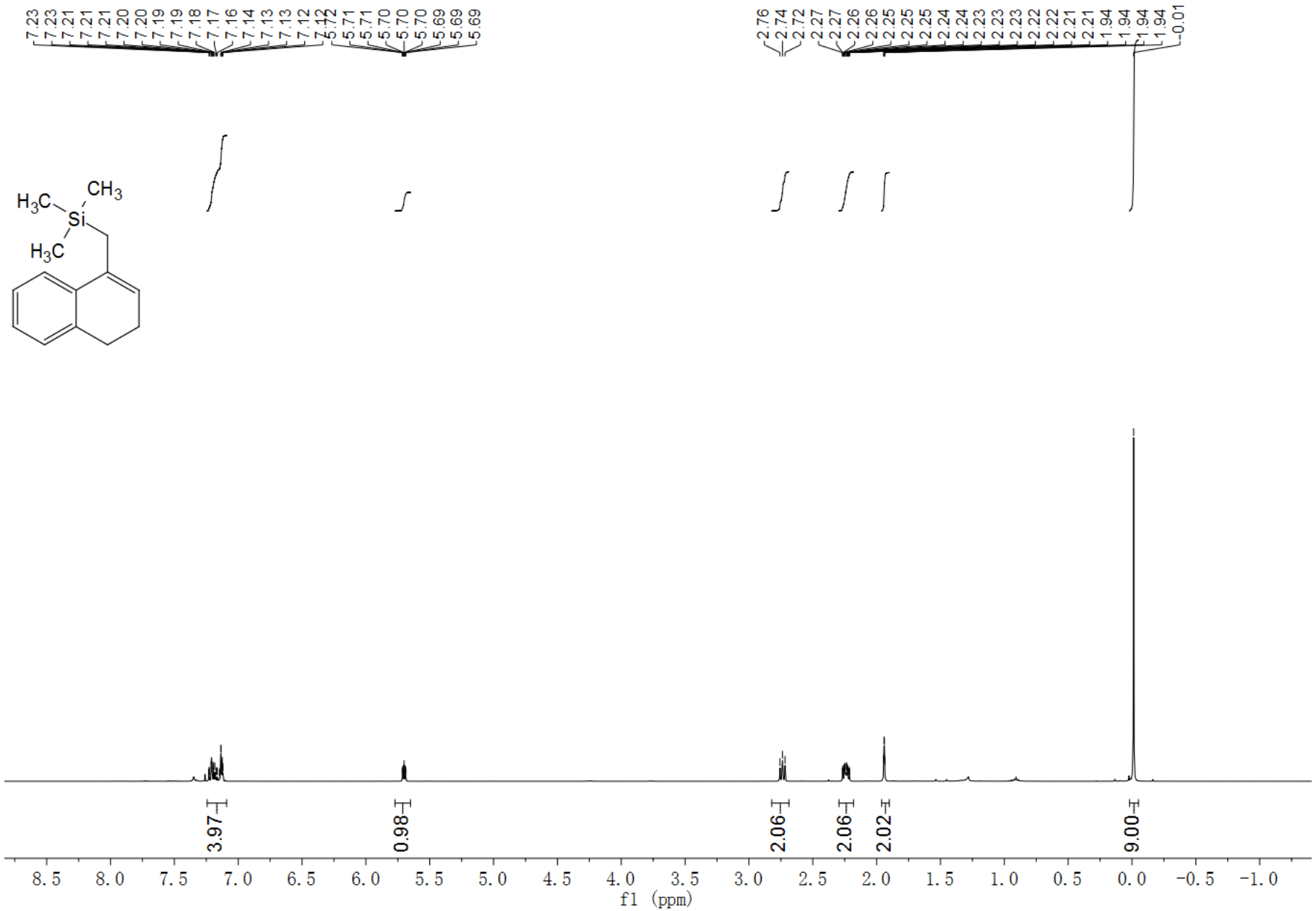
^{1}H NMR of **5e**


7.86
7.86
7.85
7.84
7.84
7.84
7.84
7.83
7.82
7.82
7.81
7.78
7.64
7.63
7.61
7.61
7.51
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
5.32
5.32
5.01
5.00
5.00
2.17
2.17
0.05
H3C
CH3
Si
H3C
CH2
4.02
1.01
1.99
0.99
1.00
2.05
9.00
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
f1 (ppm)

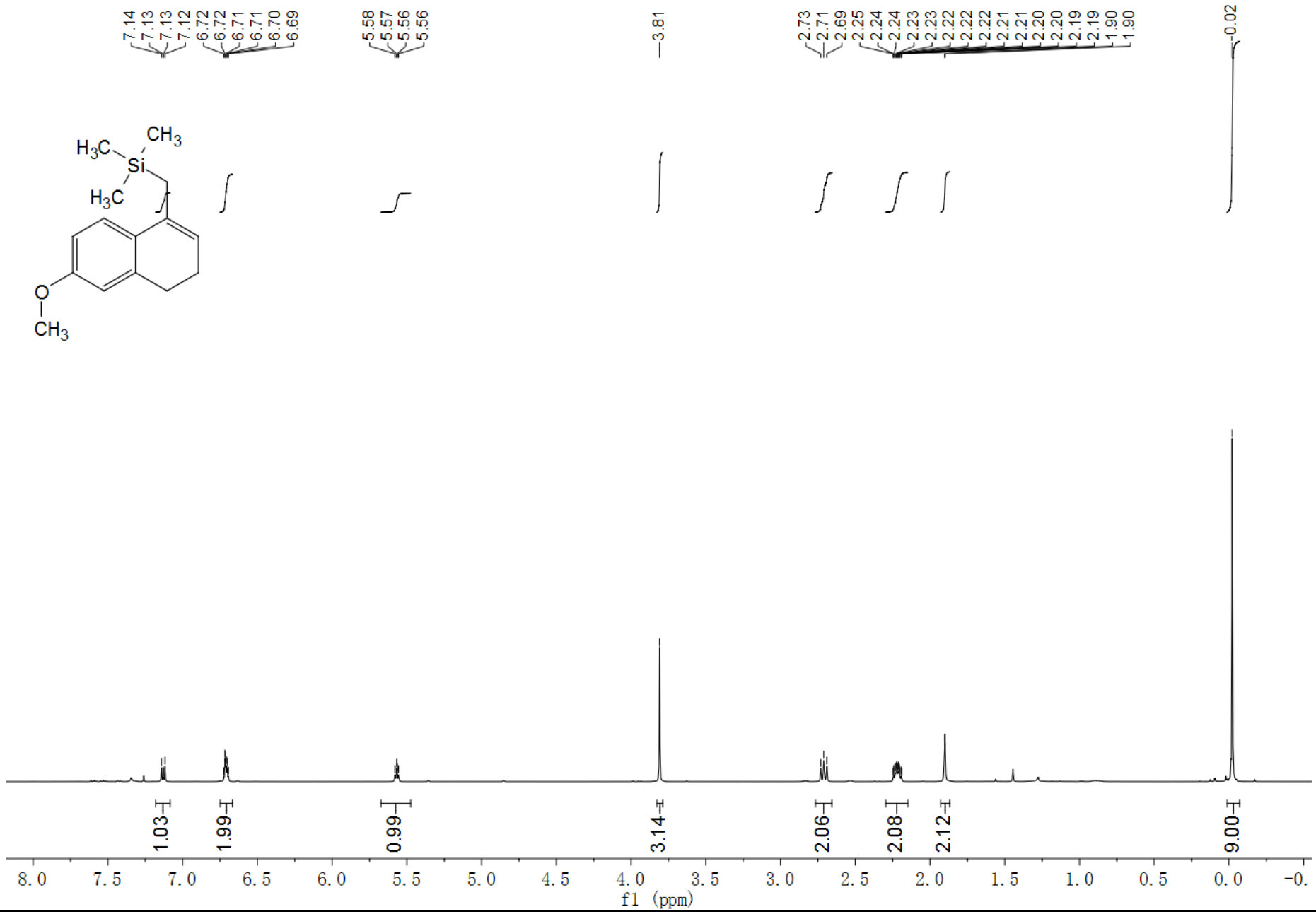
^{1}H NMR of **5f**


7.32 7.30 7.28 7.28 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.17
5.29 5.29 2.77 2.76 2.75 2.75 2.74 2.73 2.72 2.71 2.71 2.70 2.69 2.32 2.30 2.26 2.26 2.24 2.19 2.18 2.18 2.16 2.15 2.15 2.14 2.14 2.12 2.11 1.99 1.98 1.94 1.93 1.93 1.92 1.91 1.91 1.90 1.90 1.89 1.89 1.81 1.79 1.78 1.77 1.76 1.75 1.75 1.74 1.74 1.73 1.72 1.70 1.47 0.03
CH3
H3C—Si—CH3
2.08
2.92
1.11
1.00
1.11
2.09
2.17
1.09
2.05
9.00
f1 (ppm)

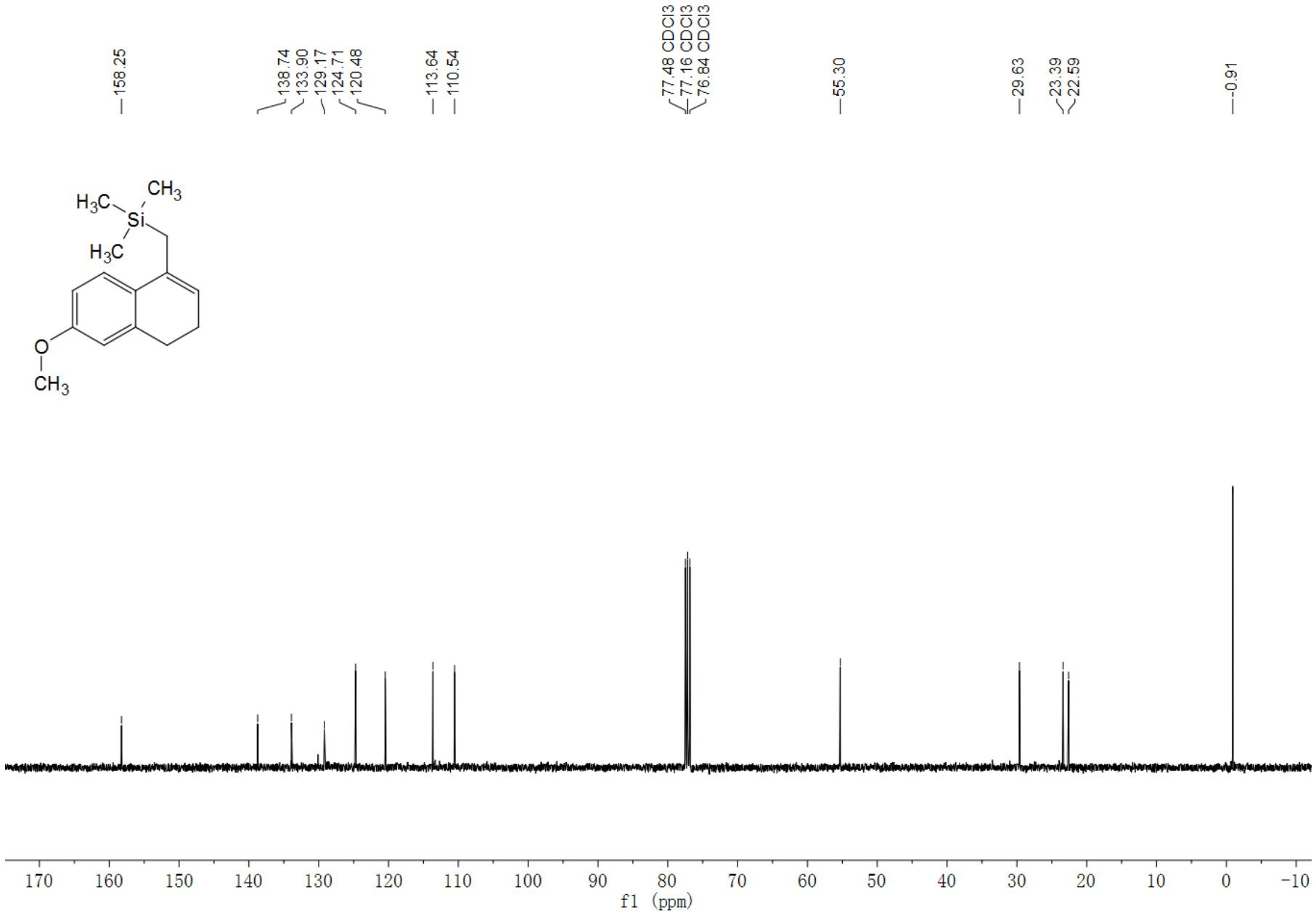
^{1}H NMR of **5g**


7.23
7.23
7.21
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.16
7.14
7.13
7.13
7.12
7.12
5.72
5.71
5.71
5.70
5.70
5.70
5.69
5.69
5.69
2.76
2.74
2.72
2.27
2.27
2.26
2.25
2.25
2.25
2.24
2.24
2.23
2.23
2.23
2.22
2.22
2.21
2.21
1.94
1.94
1.94
1.94
0.01
H3C
CH3
Si
H3C
3.97
0.98
2.06
2.06
2.02
9.00
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
-1.0
f1 (ppm)

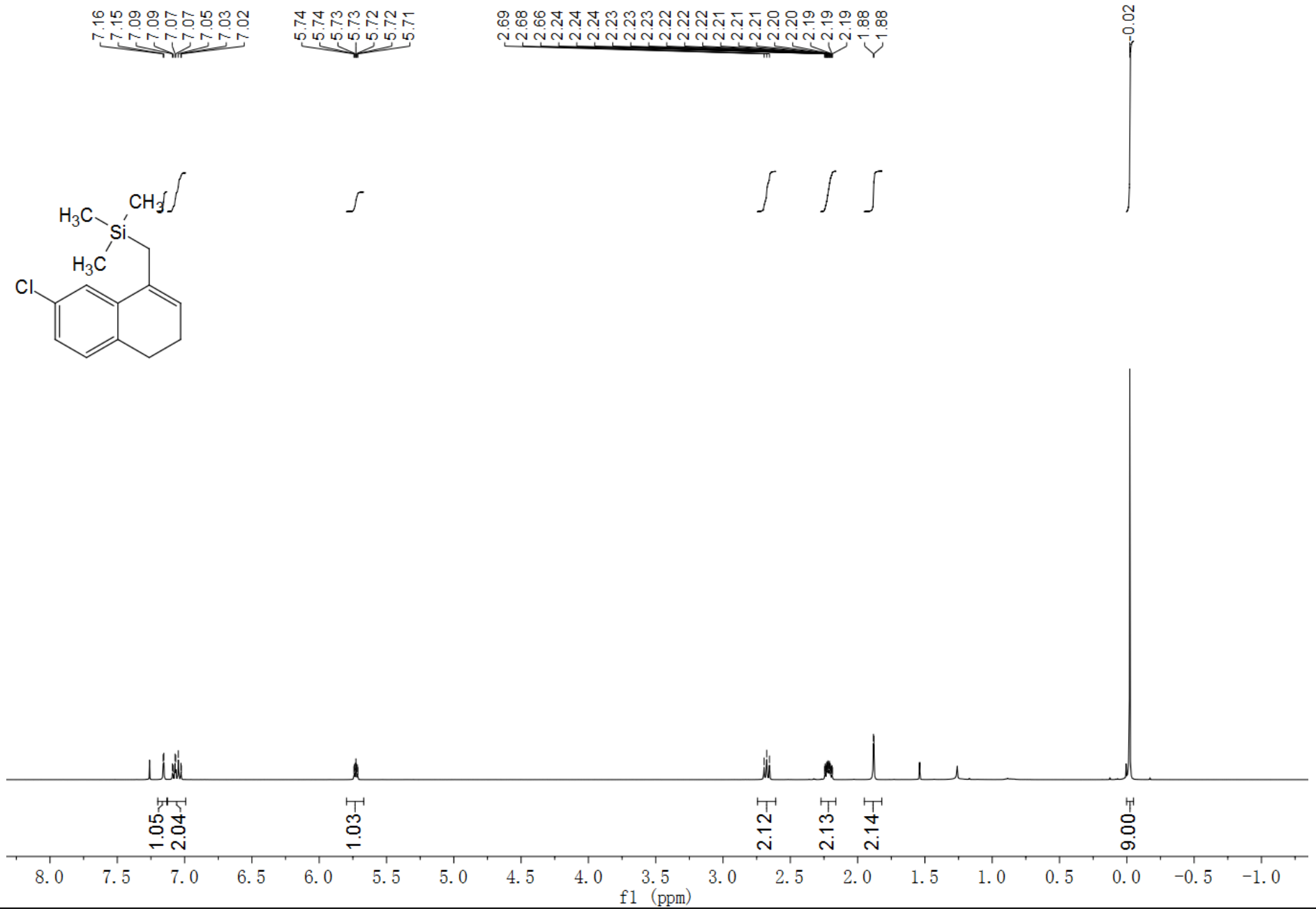
^{1}H NMR of **5h**


7.14
7.13
7.13
7.12
6.72
6.72
6.71
6.71
6.70
6.69
5.58
5.57
5.56
5.56
3.81
2.73
2.71
2.69
2.25
2.24
2.24
2.23
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.20
2.19
2.19
1.90
1.90
0.02
H3C
CH3
Si
H3C
O
CH3
1.03
1.99
0.99
3.14
2.06
2.08
2.12
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

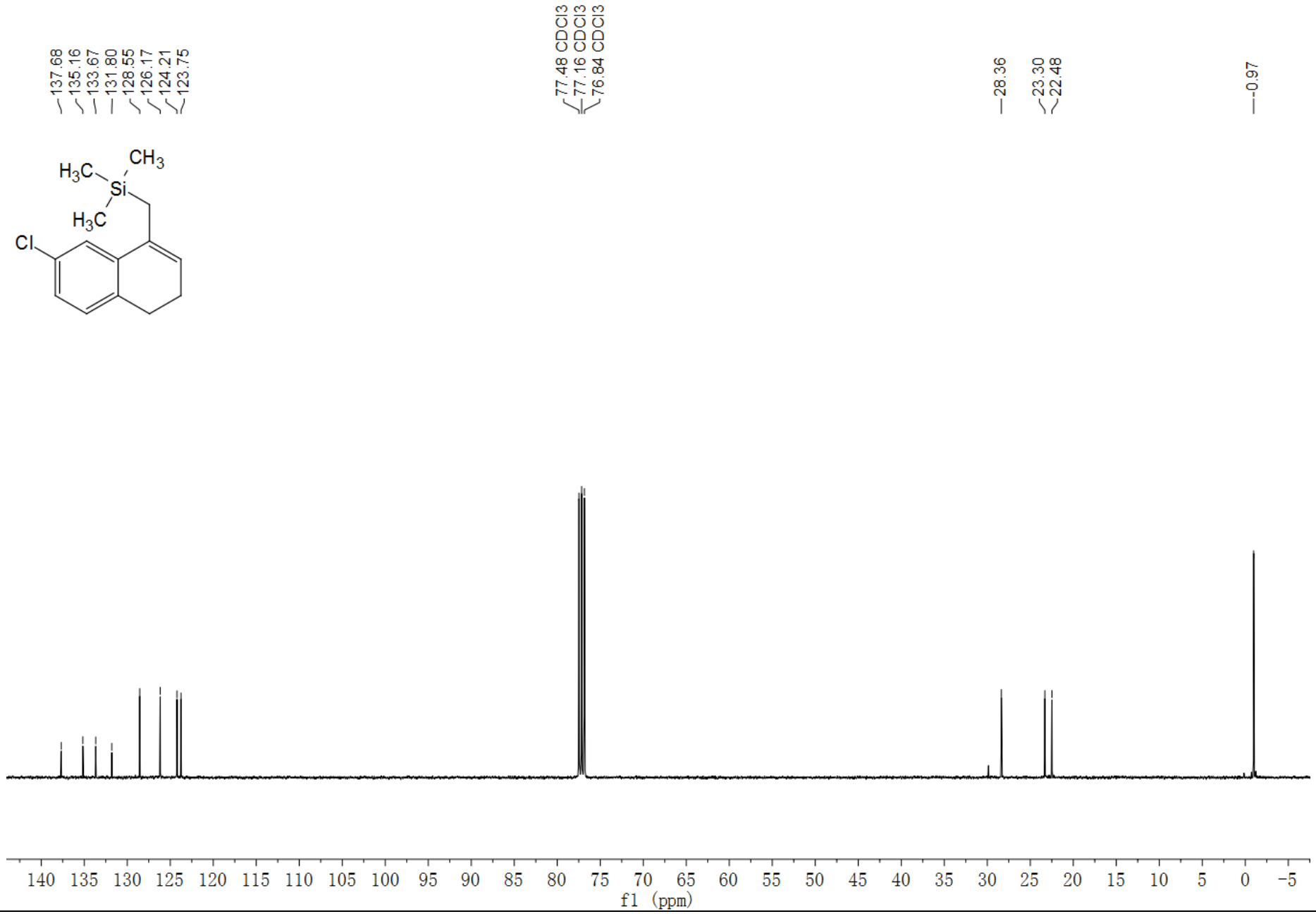
^{13}C NMR of **5h**


158.25
138.74
133.90
129.17
124.71
120.48
113.64
110.54
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.30
29.63
23.39
22.59
-0.91
H3C
CH3
Si
H3C
O
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

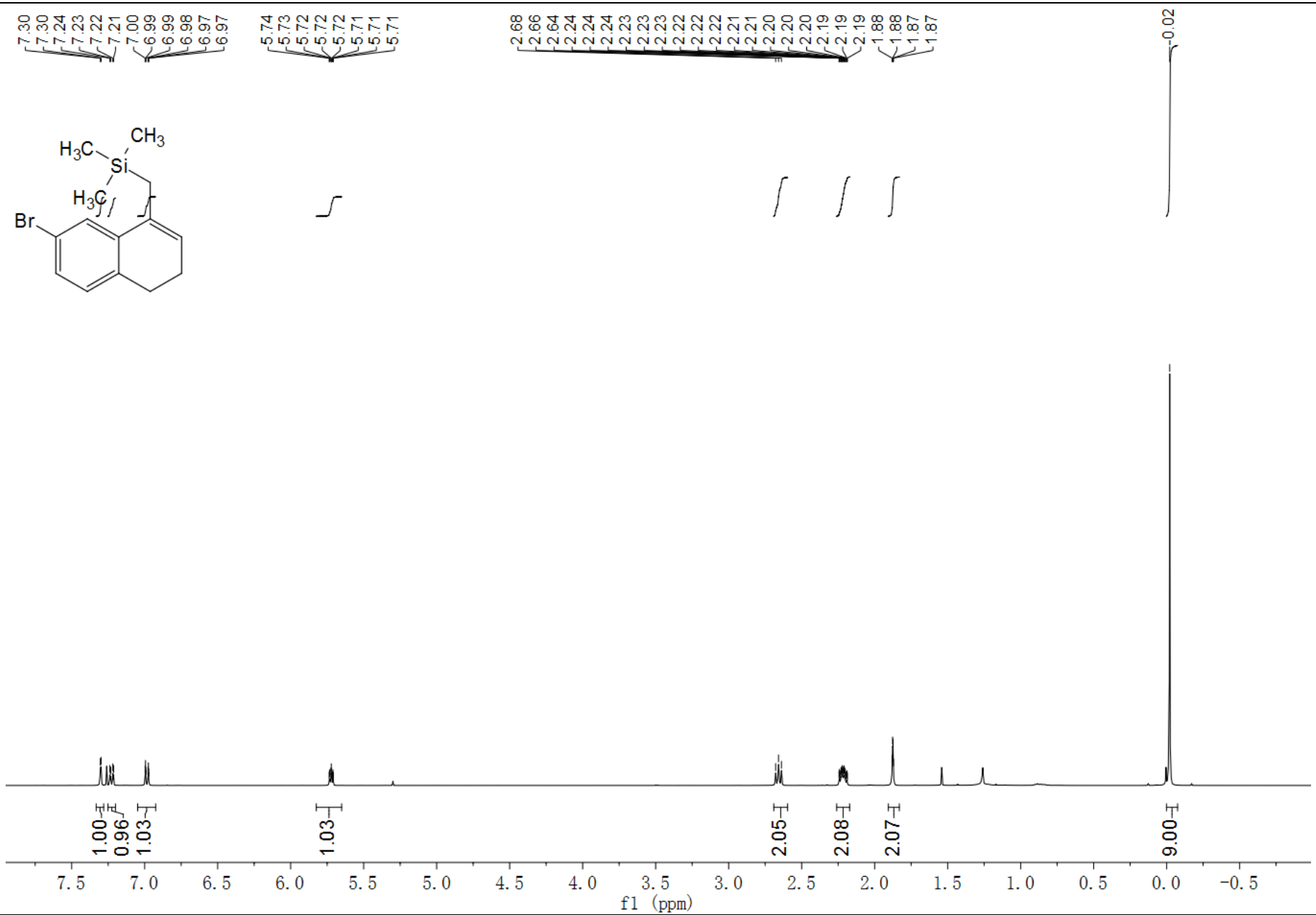
^{1}H NMR of **5i**


7.16
7.15
7.09
7.09
7.07
7.07
7.05
7.03
7.02
5.74
5.74
5.73
5.73
5.72
5.72
5.71
2.69
2.68
2.66
2.24
2.24
2.24
2.23
2.23
2.22
2.22
2.22
2.21
2.21
2.21
2.20
2.20
2.19
2.19
2.19
1.88
1.88
0.02
H3C
CH3
Si
H3C
Cl
1.05
2.04
1.03
2.12
2.13
2.14
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

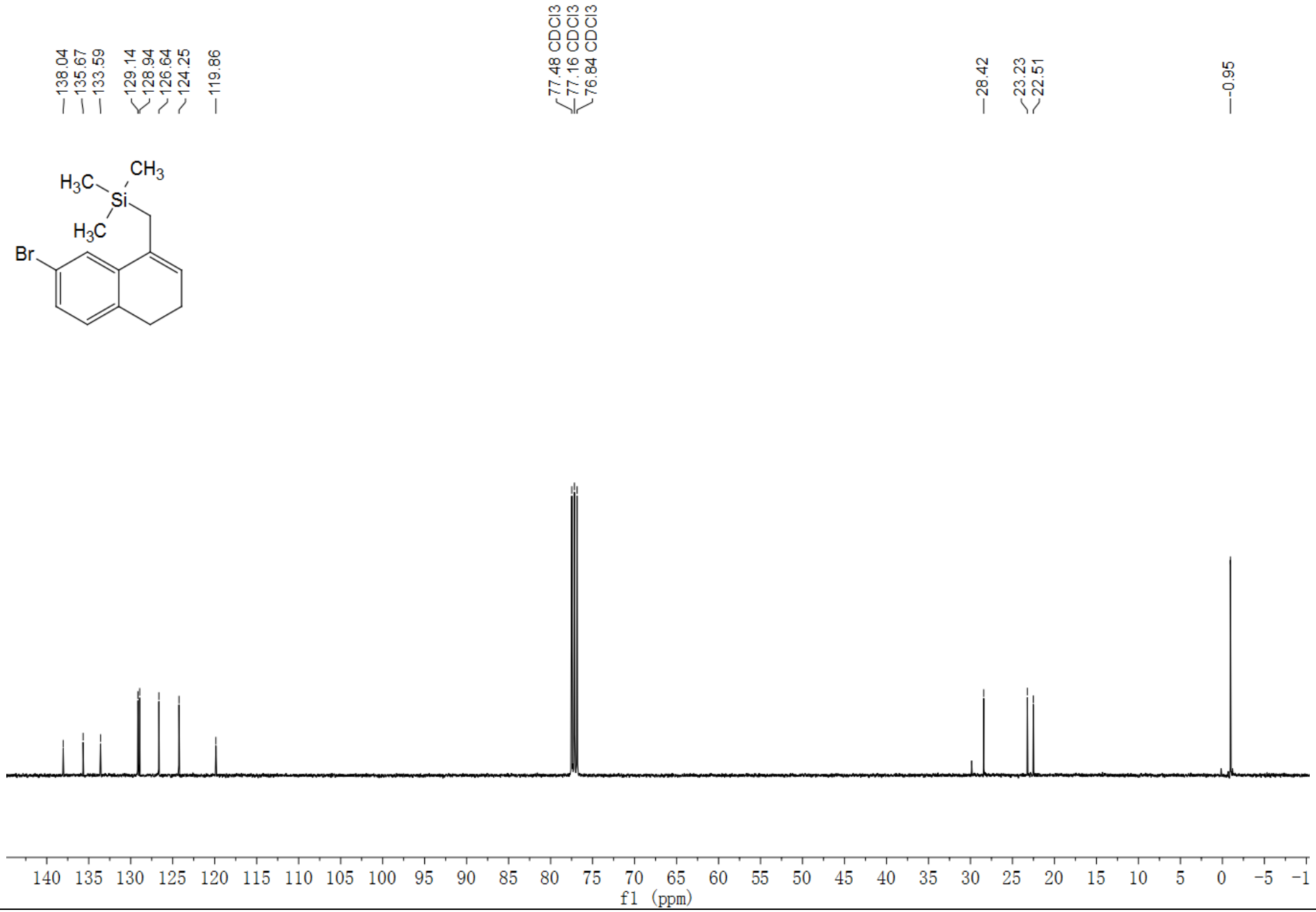
^{13}C NMR of **5i**


137.68
135.16
133.67
131.80
128.55
126.17
124.21
123.75
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
28.36
23.30
22.48
-0.97
H3C
CH3
Si
H3C
Cl
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

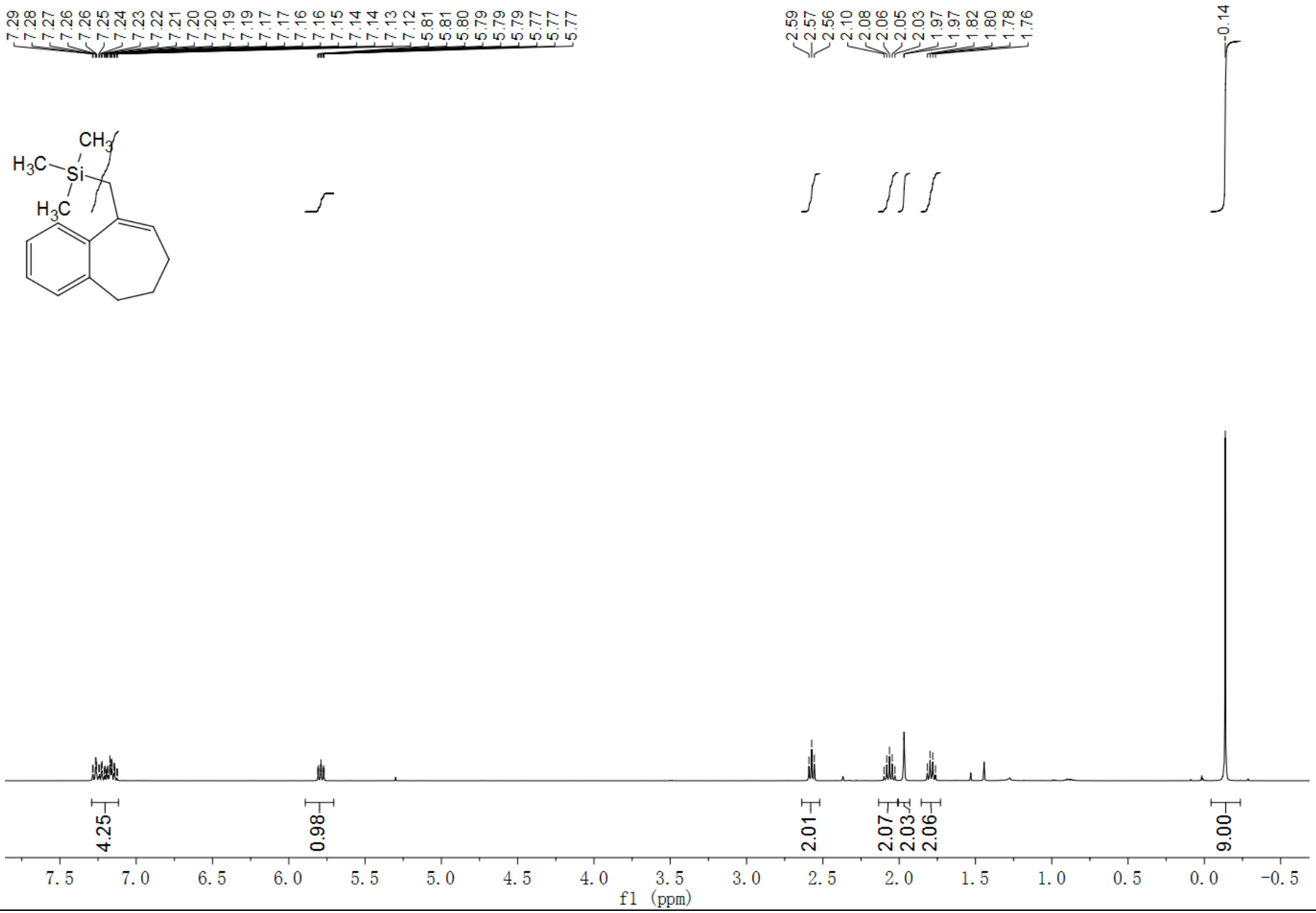
^{1}H NMR of **5j**


7.30
7.30
7.24
7.23
7.22
7.21
7.00
6.99
6.99
6.98
6.97
6.97
5.74
5.73
5.72
5.72
5.72
5.71
5.71
5.71
2.68
2.66
2.64
2.24
2.24
2.23
2.23
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.20
2.20
2.19
2.19
2.19
1.88
1.88
1.87
1.87
-0.02
H3C
CH3
Si
H3C
Br
1.00
0.96
1.03
1.03
2.05
2.08
2.07
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

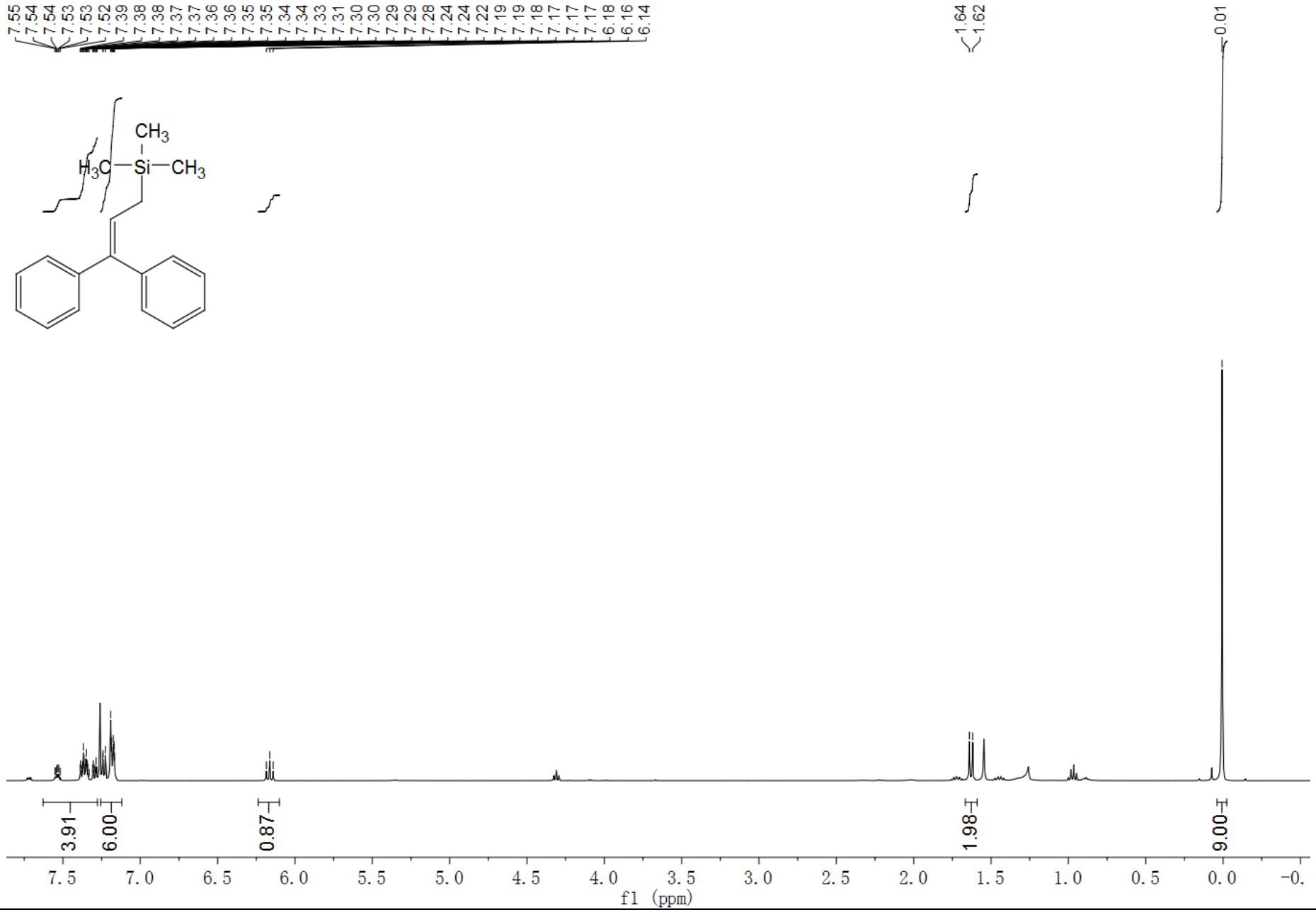
^{13}C NMR of **5j**


138.04
135.67
133.59
129.14
128.94
126.64
124.25
119.86
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
28.42
23.23
22.51
-0.95
H3C
CH3
Si
H3C
Br
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -1
f1 (ppm)

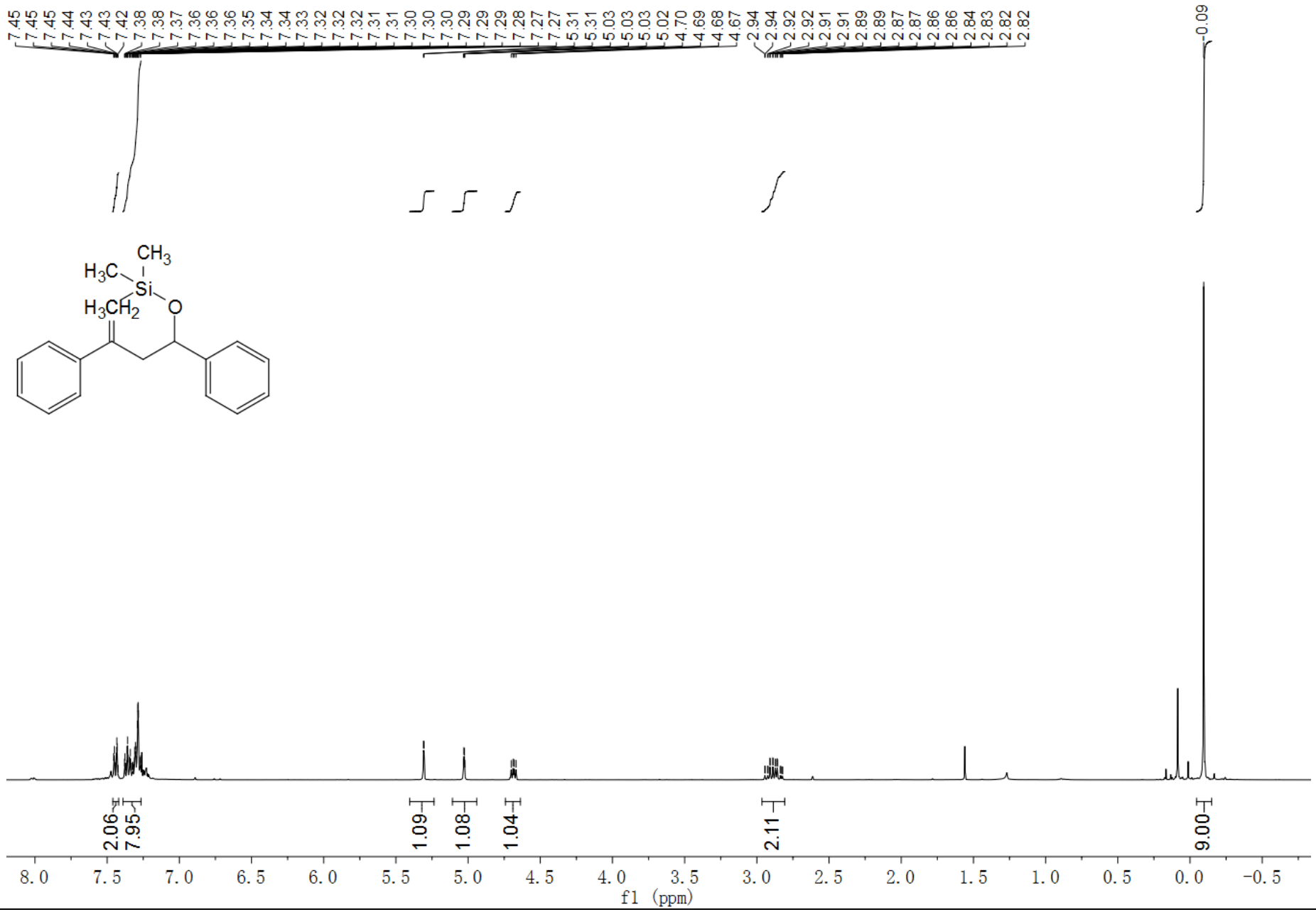
^{1}H NMR of **5k**


7.29 7.28 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.21 7.20 7.20 7.19 7.19 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.13 7.12 5.81 5.81 5.80 5.79 5.79 5.79 5.77 5.77 5.77
2.59 2.57 2.56 2.10 2.08 2.06 2.05 2.03 1.97 1.97 1.82 1.80 1.78 1.76
0.14
CH3
H3C
Si
H3C
4.25
0.98
2.01
2.07
2.03
2.06
9.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

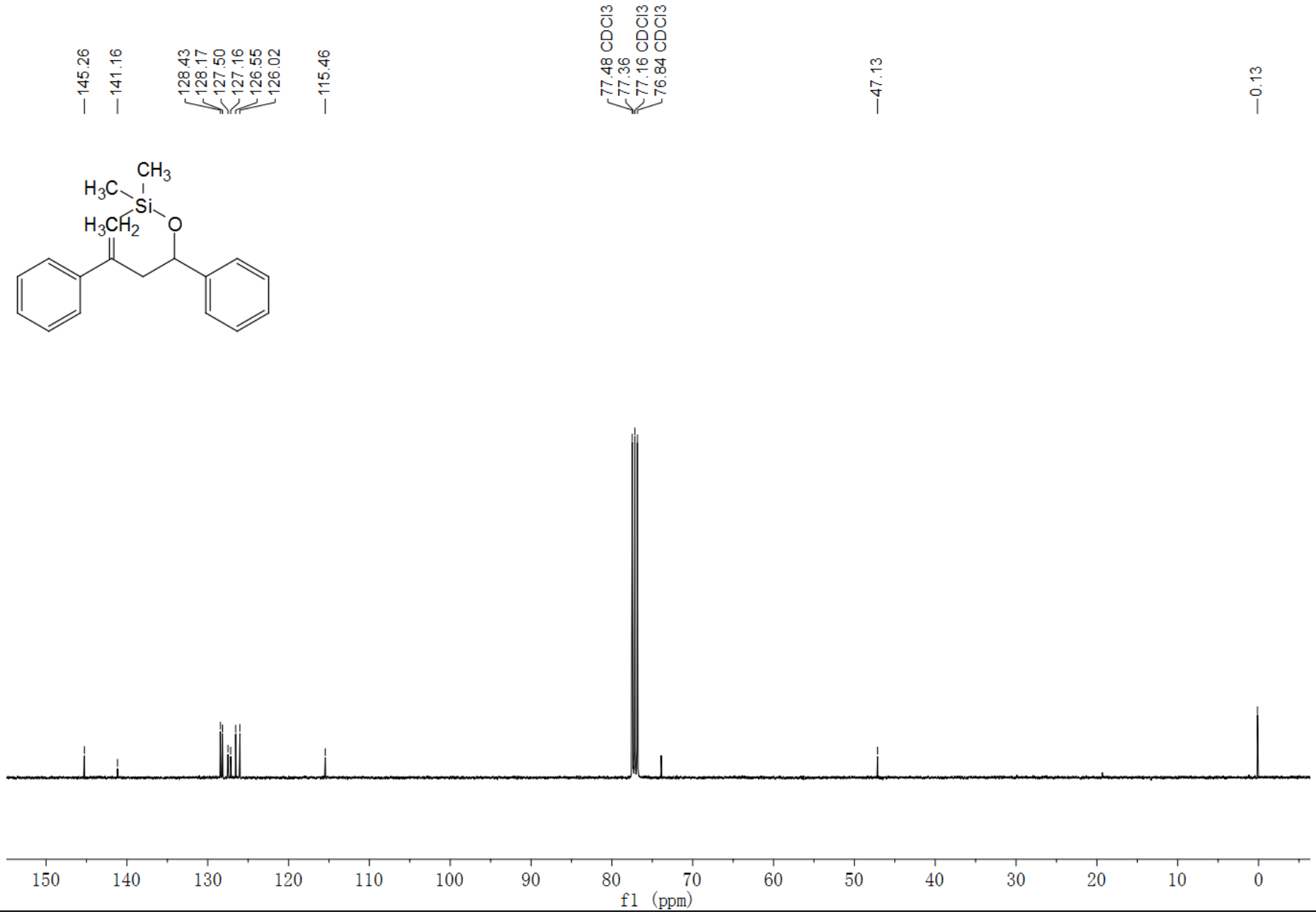
^{1}H NMR of **5l**


7.55
7.54
7.54
7.53
7.53
7.52
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.31
7.30
7.30
7.29
7.29
7.28
7.24
7.24
7.22
7.19
7.19
7.18
7.17
7.17
7.17
6.18
6.16
6.14
1.64
1.62
0.01
CH3
H3C
Si
CH3
3.91
6.00
0.87
1.98
9.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

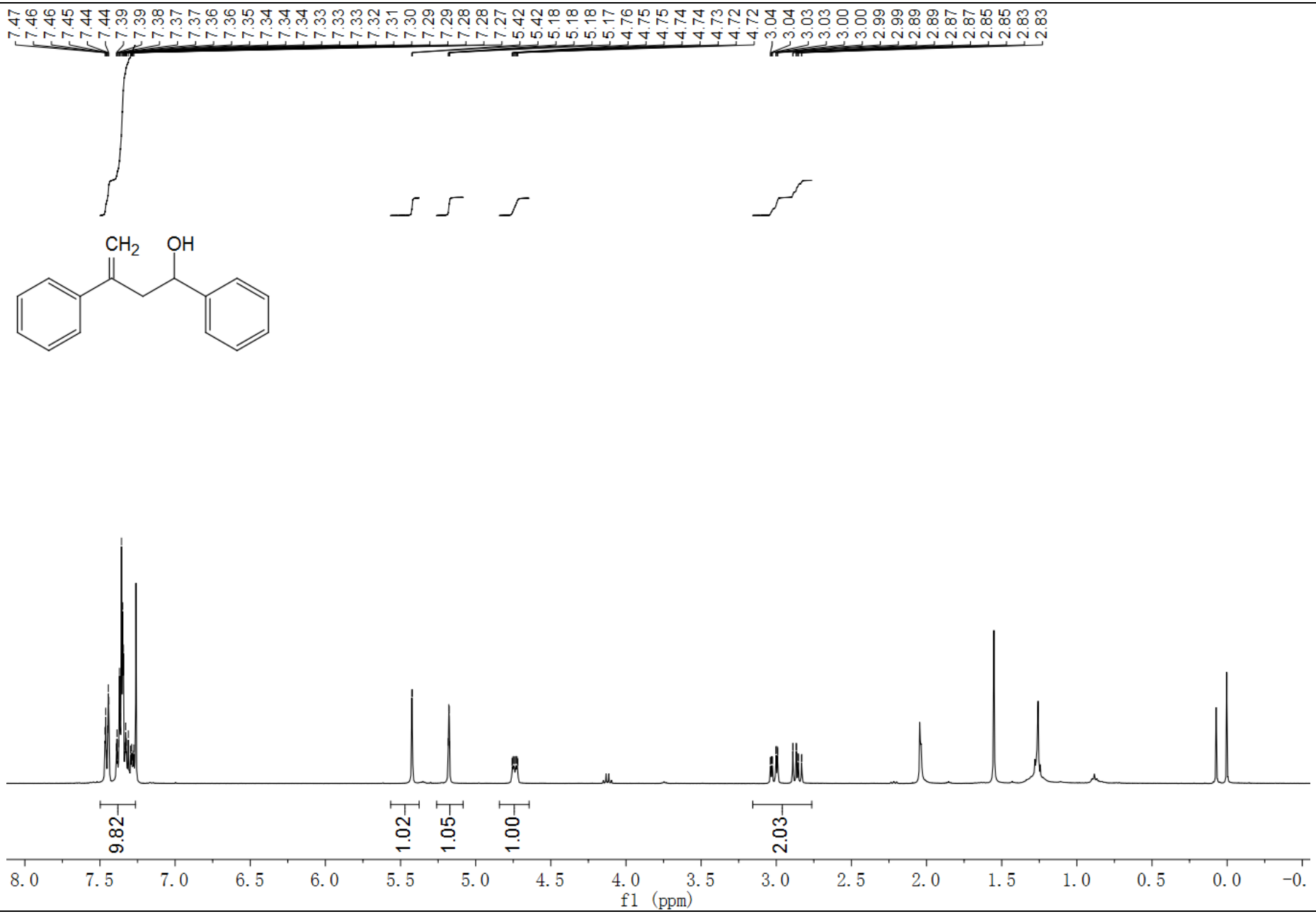
^{1}H NMR of **7**


7.45 7.45 7.45 7.44 7.43 7.43 7.42 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.27 7.27 5.31 5.31 5.03 5.03 5.03 5.02 4.70 4.69 4.68 4.67 2.94 2.94 2.92 2.92 2.91 2.91 2.89 2.89 2.87 2.87 2.86 2.86 2.84 2.83 2.82 2.82
0.09
CH3
H3C
Si
H3CH2
O
2.06
7.95
1.09
1.08
1.04
2.11
9.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

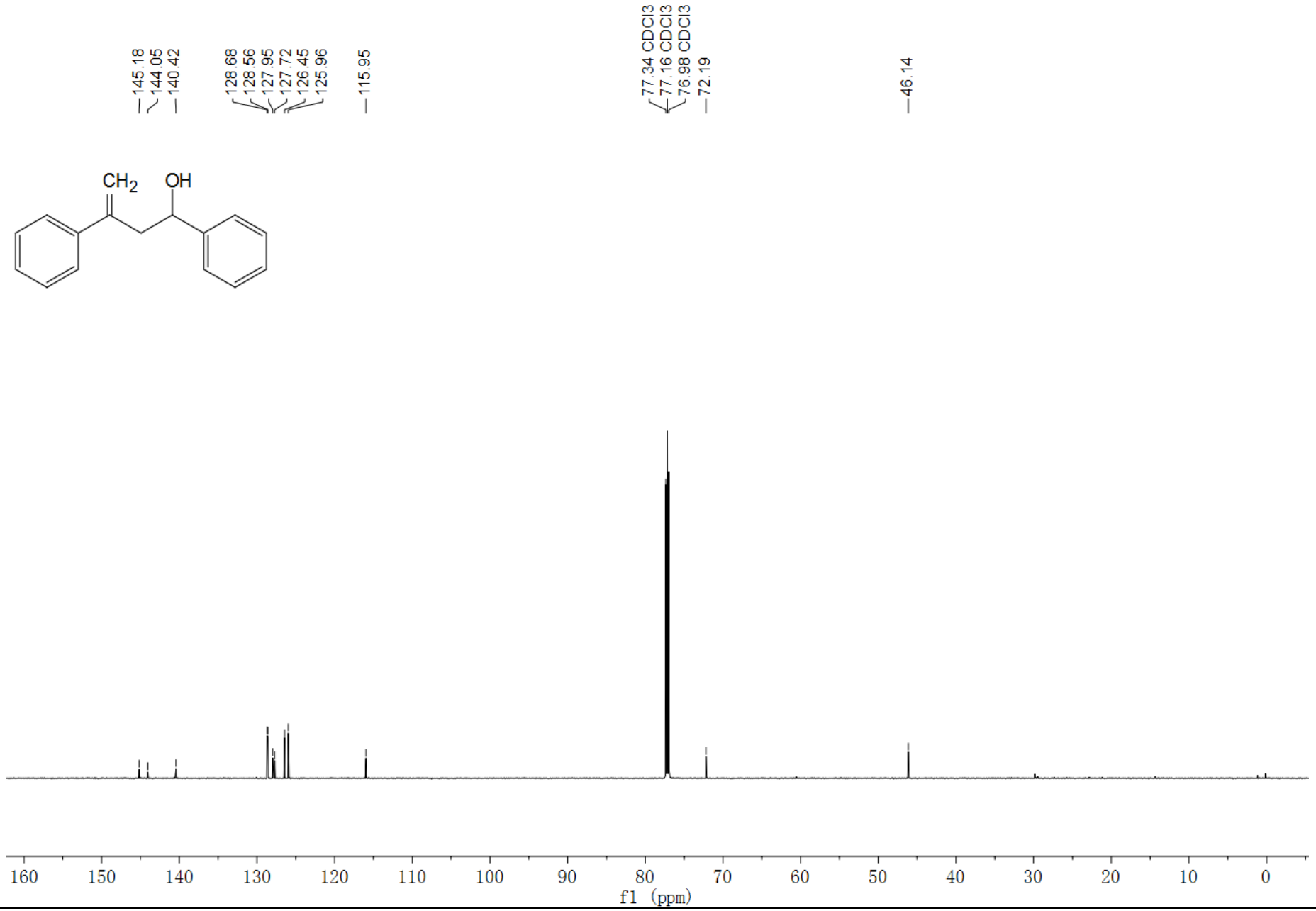
^{13}C NMR of **7**


145.26
141.16
128.43
128.17
127.50
127.16
126.55
126.02
115.46
77.48 CDCl3
77.36
77.16 CDCl3
76.84 CDCl3
47.13
0.13
CH3
H3C
Si
H3CH2
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

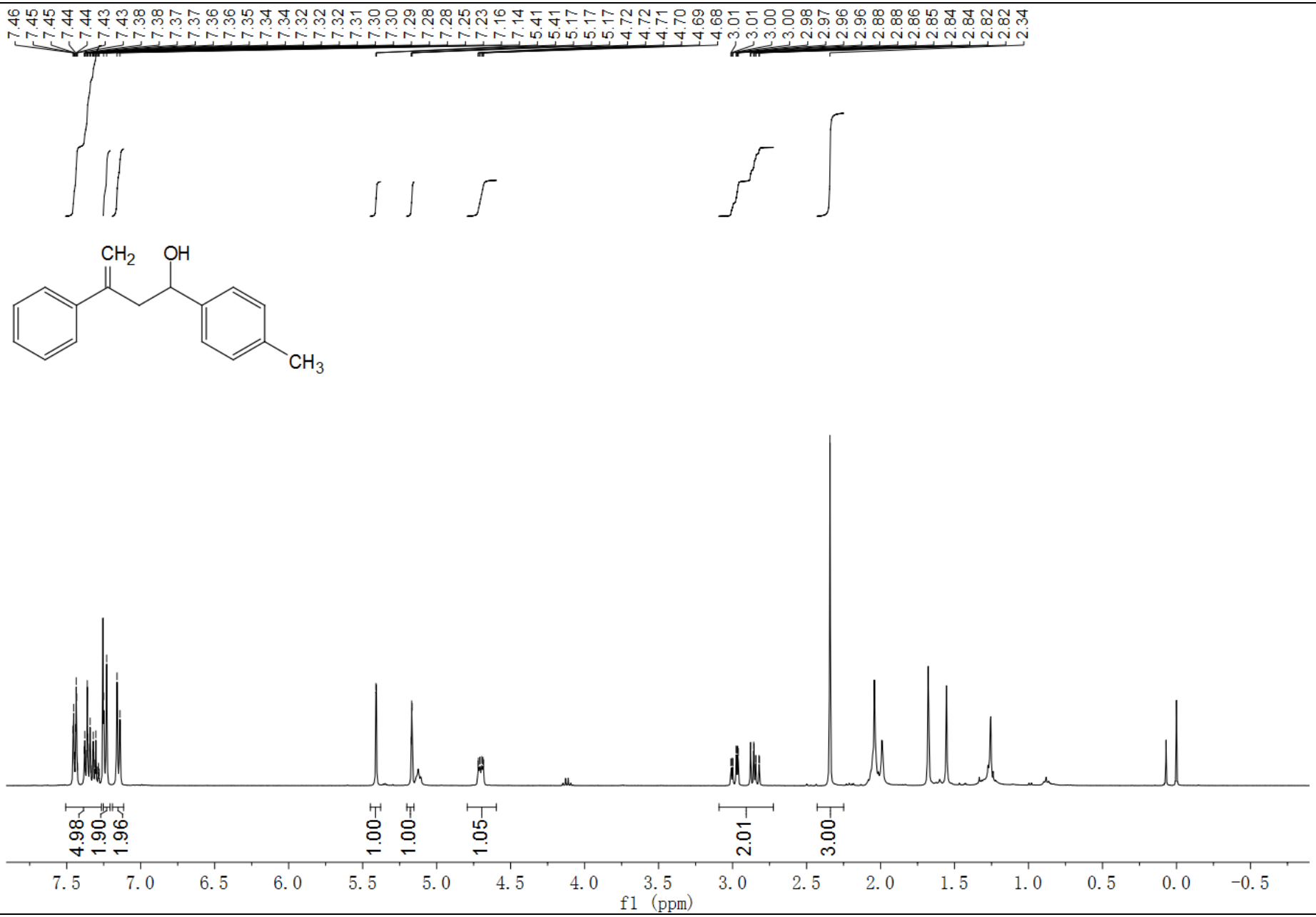
^{1}H NMR of **8a**


7.47 7.46 7.46 7.45 7.44 7.44 7.39 7.39 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 5.42 5.42 5.18 5.18 5.17 4.76 4.75 4.75 4.74 4.74 4.73 4.72 4.72 3.04 3.04 3.03 3.03 3.00 3.00 2.99 2.99 2.89 2.89 2.87 2.87 2.85 2.85 2.83 2.83
CH2
OH
9.82
1.02
1.05
1.00
2.03
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.
f1 (ppm)

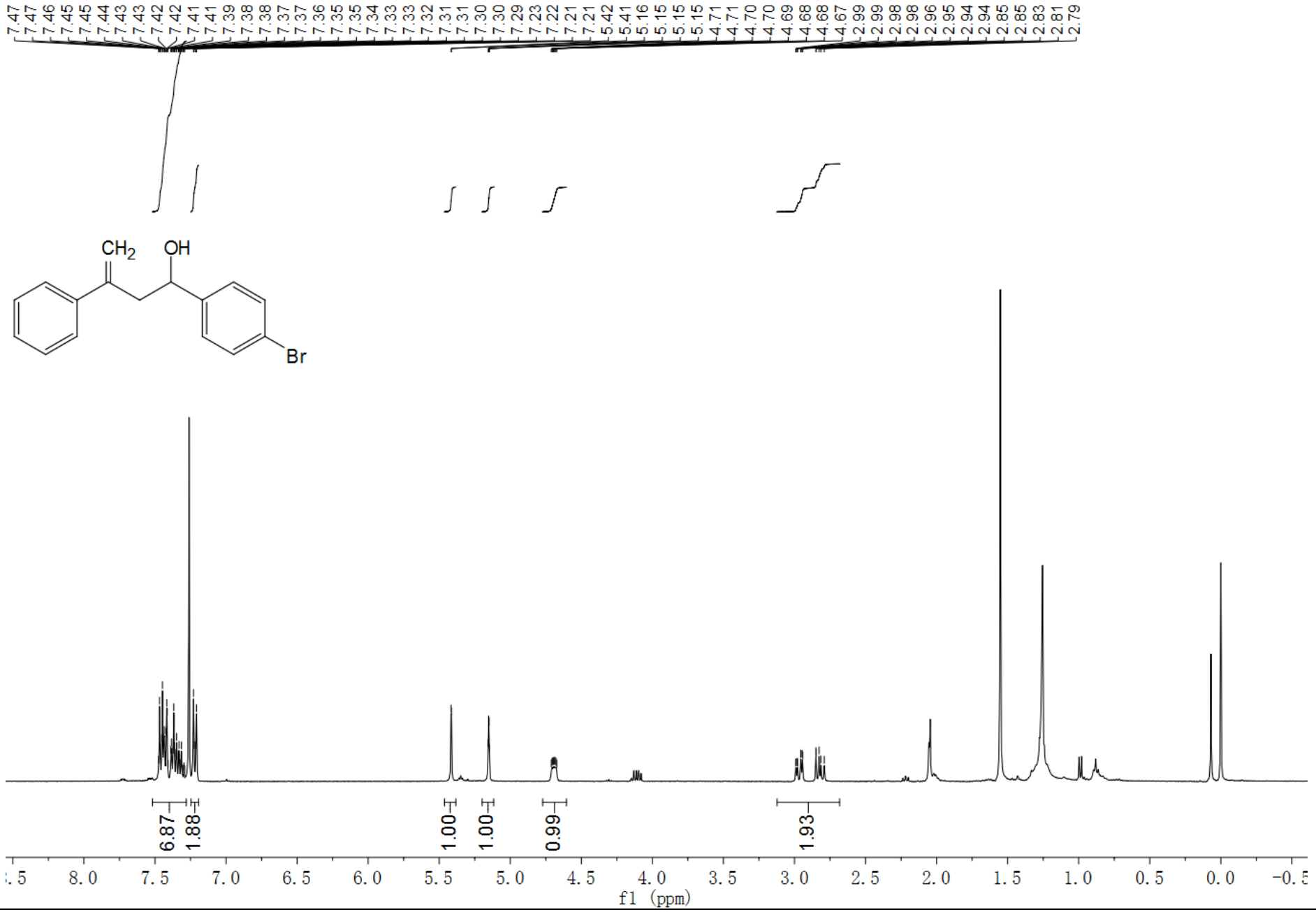
^{13}C NMR of **8a**


145.18
144.05
140.42
128.68
128.56
127.95
127.72
126.45
125.96
115.95
77.34 CDCl3
77.16 CDCl3
76.98 CDCl3
72.19
46.14
CH2
OH
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

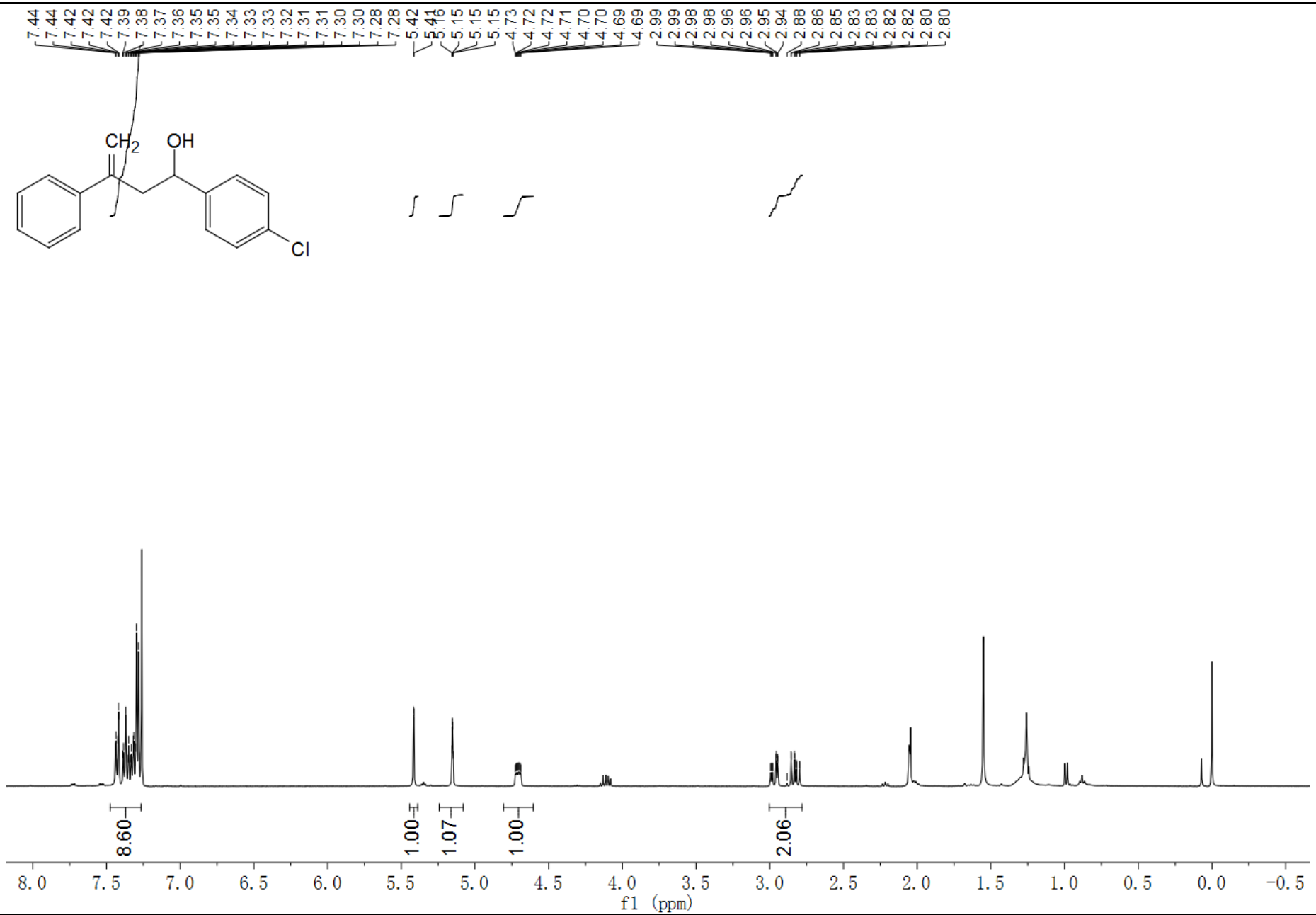
^{1}H NMR of **8b**


7.46 7.45 7.45 7.44 7.44 7.43 7.43 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.32 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.28 7.25 7.23 7.16 7.14 5.41 5.41 5.17 5.17 5.17 4.72 4.72 4.71 4.70 4.69 4.68 3.01 3.01 3.00 3.00 2.98 2.97 2.96 2.96 2.88 2.88 2.86 2.85 2.84 2.84 2.82 2.82 2.34
CH2
OH
CH3
4.98
1.90
1.96
1.00
1.00
1.05
2.01
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

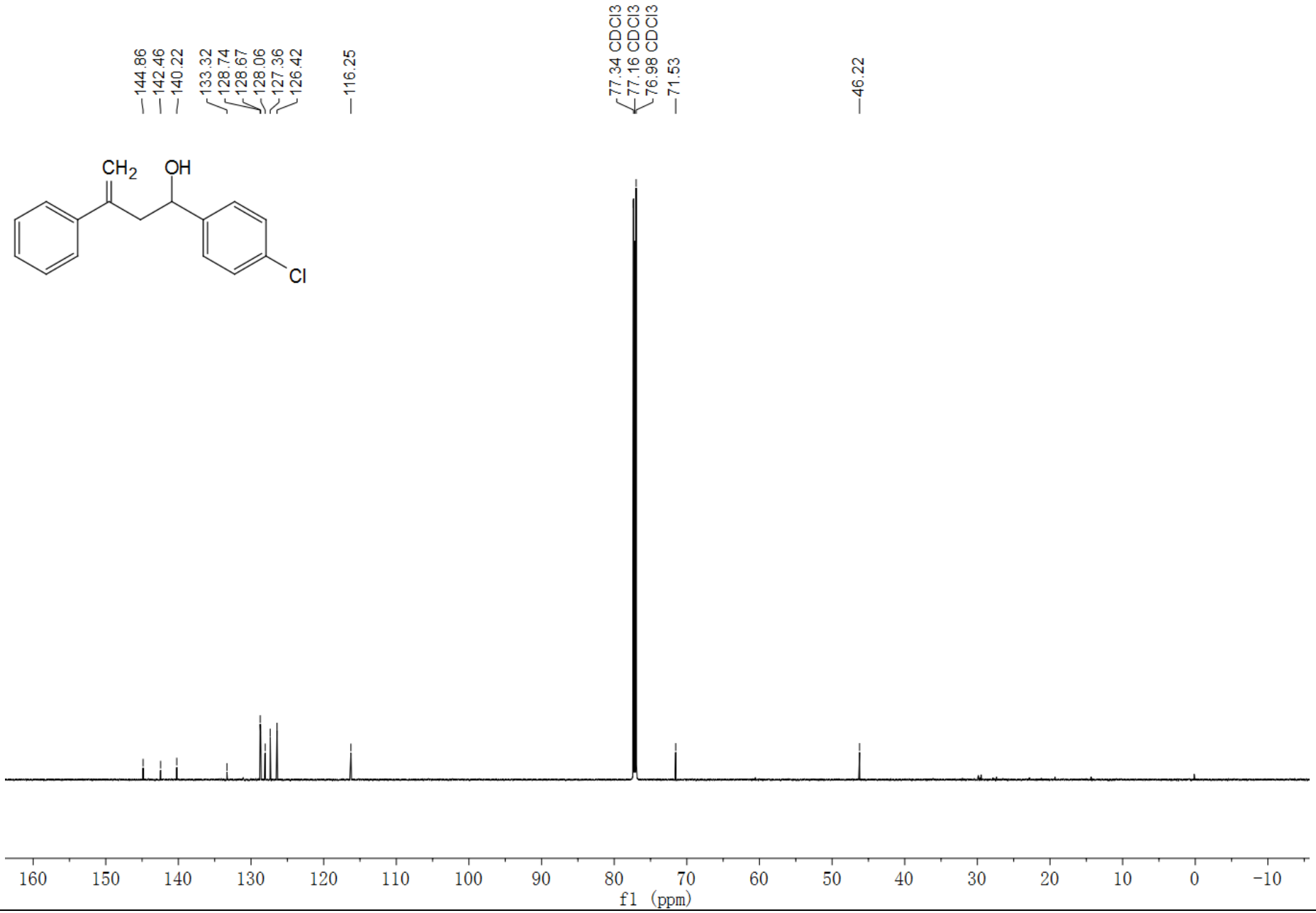
^{1}H NMR of **8c**


7.47 7.47 7.46 7.45 7.45 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.23 7.22 7.21 7.21 5.42 5.41 5.16 5.15 5.15 5.15 4.71 4.71 4.70 4.70 4.69 4.68 4.68 4.67 2.99 2.99 2.98 2.98 2.96 2.95 2.94 2.94 2.85 2.85 2.83 2.81 2.79
CH2
OH
Br
6.87
1.88
1.00
1.00
0.99
1.93
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

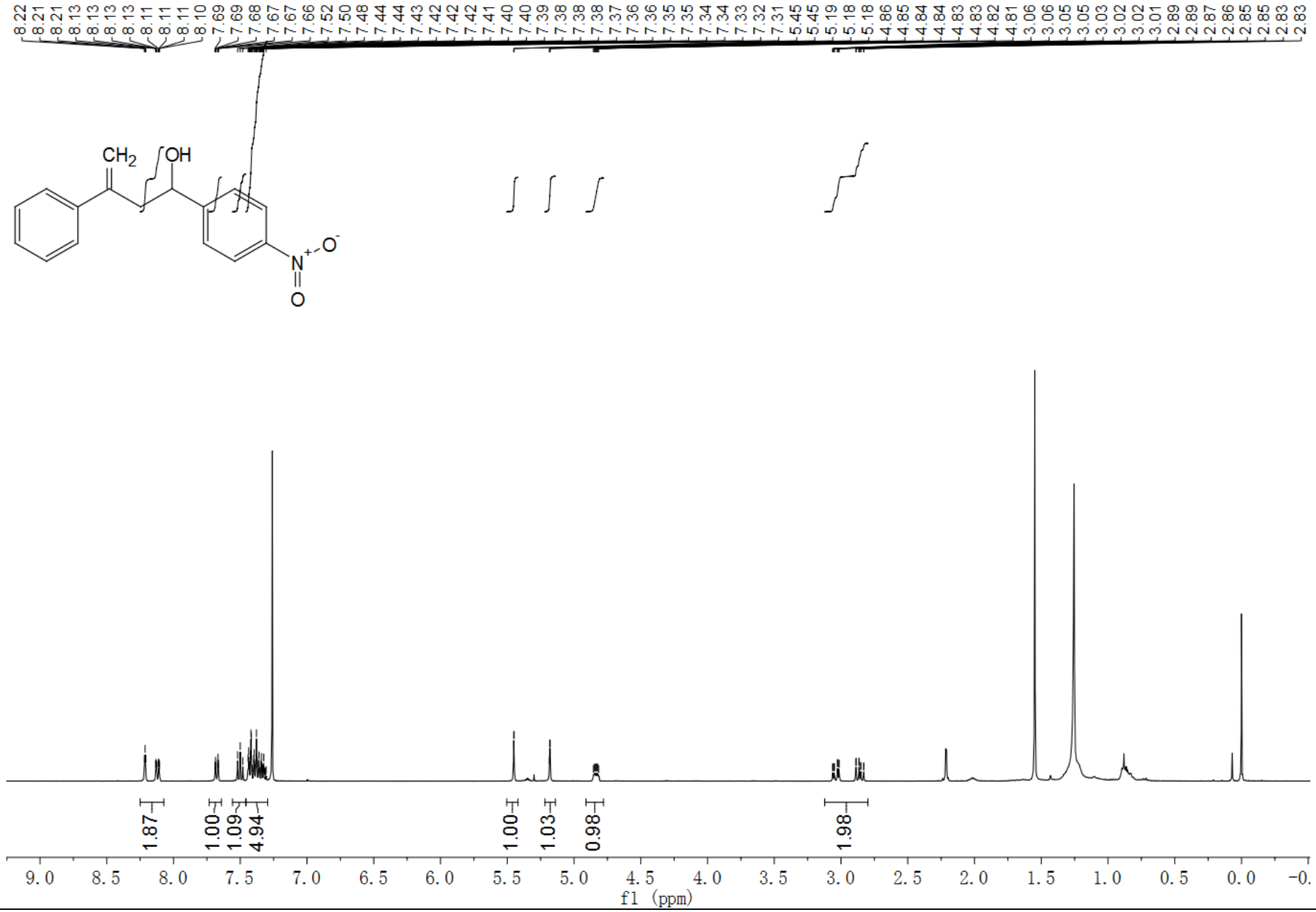
^{1}H NMR of **8d**


7.44 7.44 7.42 7.42 7.42 7.39 7.38 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.28 7.28
5.42 5.41 5.16 5.15 5.15 5.15
4.73 4.72 4.72 4.71 4.70 4.70 4.69 4.69
2.99 2.99 2.98 2.98 2.96 2.95 2.94
2.88 2.86 2.85 2.83 2.83 2.82 2.82 2.80 2.80
CH2
OH
Cl
8.60
1.00
1.07
1.00
2.06
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
f1 (ppm)

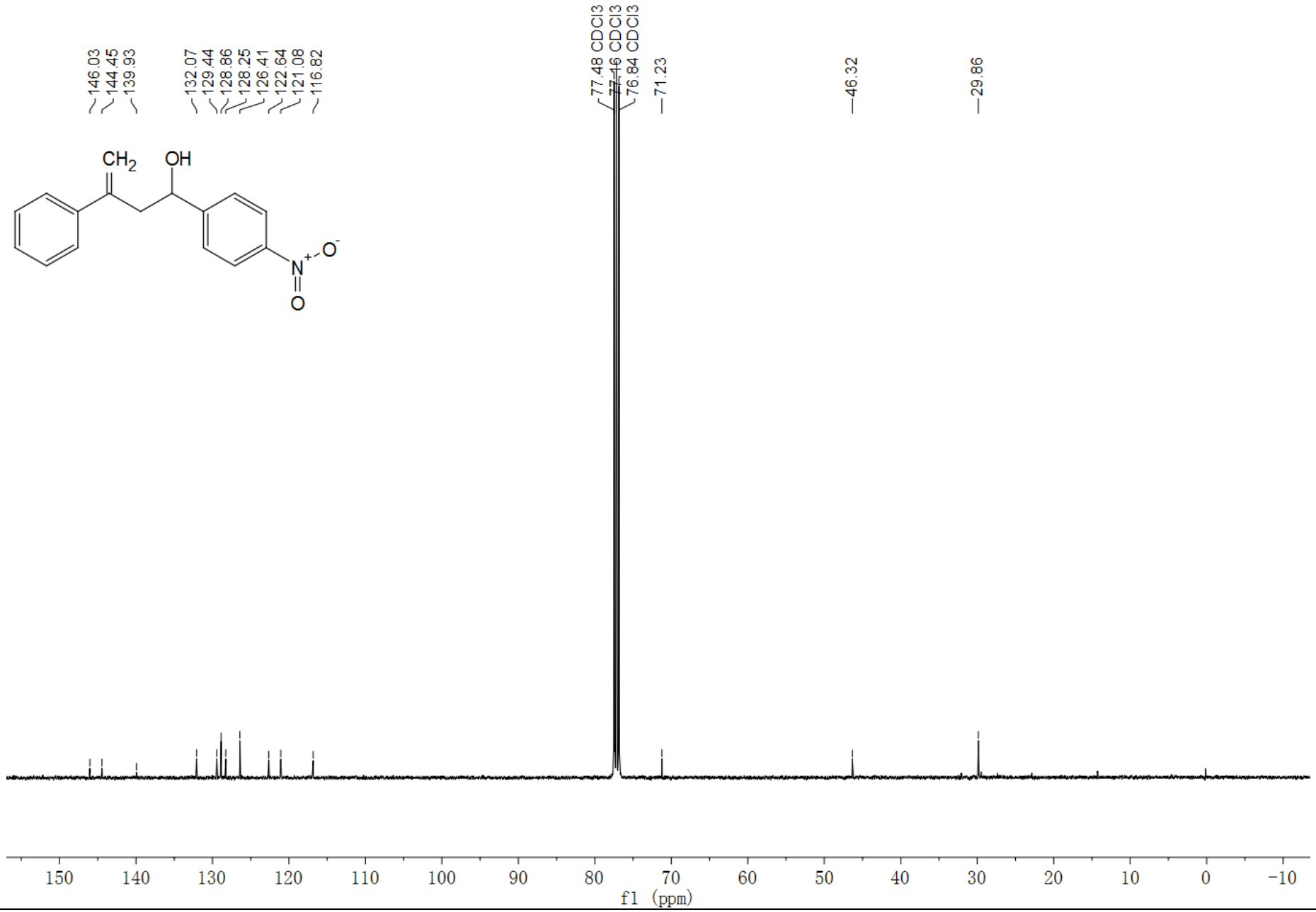
^{13}C NMR of **8d**


144.86
142.46
140.22
133.32
128.74
128.67
128.06
127.36
126.42
116.25
77.34 CDCl3
77.16 CDCl3
76.98 CDCl3
71.53
46.22
CH2
OH
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

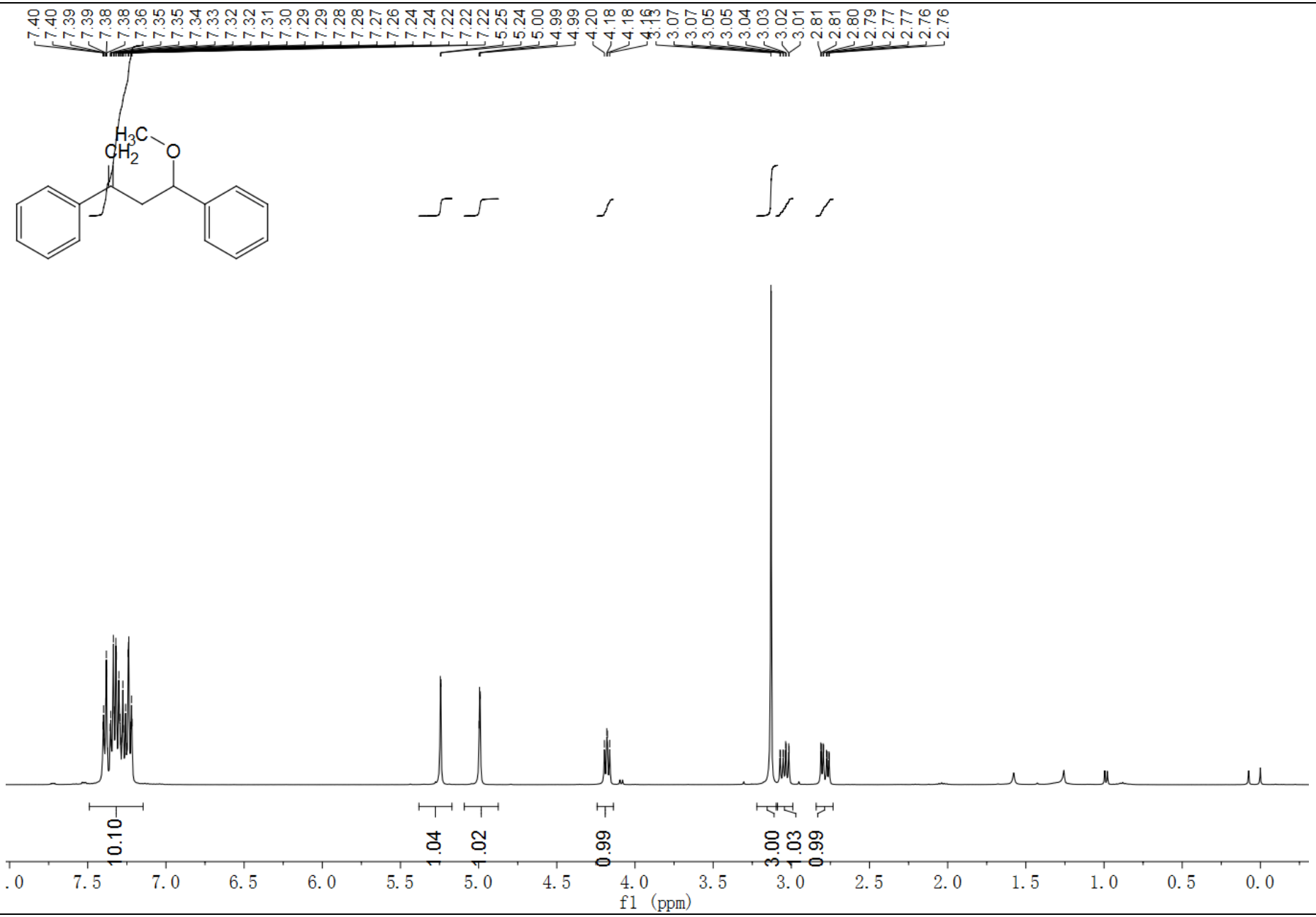
^{1}H NMR of **8e**


8.22 8.21 8.21 8.13 8.13 8.13 8.11 8.11 8.11 8.10
7.69 7.69 7.68 7.67 7.67 7.66 7.52 7.50 7.48 7.44 7.44 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.31
5.45 5.45 5.19 5.18 5.18
4.86 4.85 4.84 4.84 4.83 4.83 4.82 4.81
3.06 3.06 3.05 3.05 3.03 3.02 3.02 3.01
2.89 2.89 2.87 2.86 2.85 2.85 2.83 2.83
CH2
OH
N+
O-
O
1.87
1.00
1.09
4.94
1.00
1.03
0.98
1.98
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.
f1 (ppm)

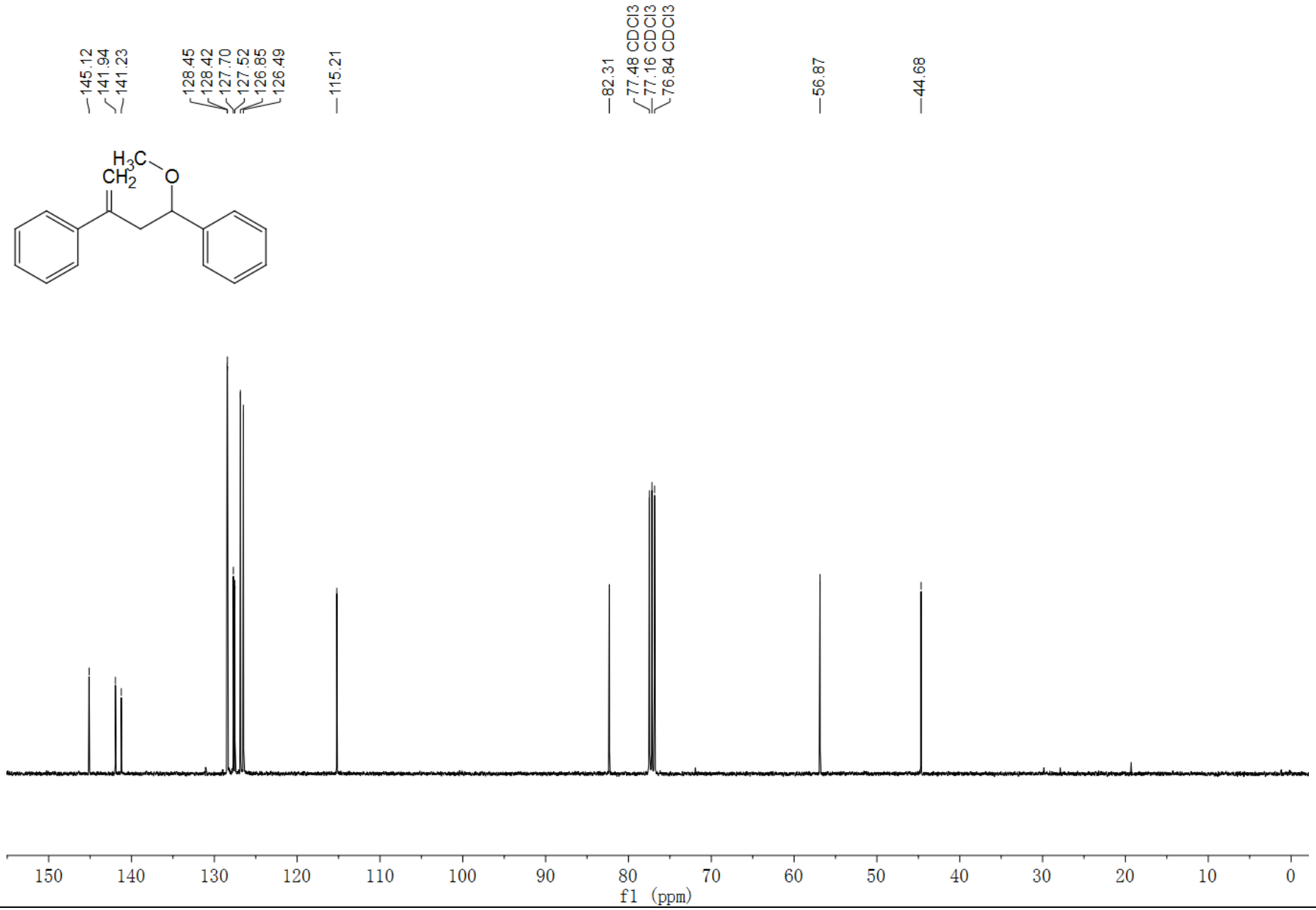
^{13}C NMR of **8e**


146.03
144.45
139.93
132.07
129.44
128.86
128.25
126.41
122.64
121.08
116.82
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.23
46.32
29.86
CH2
OH
N+
O-
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

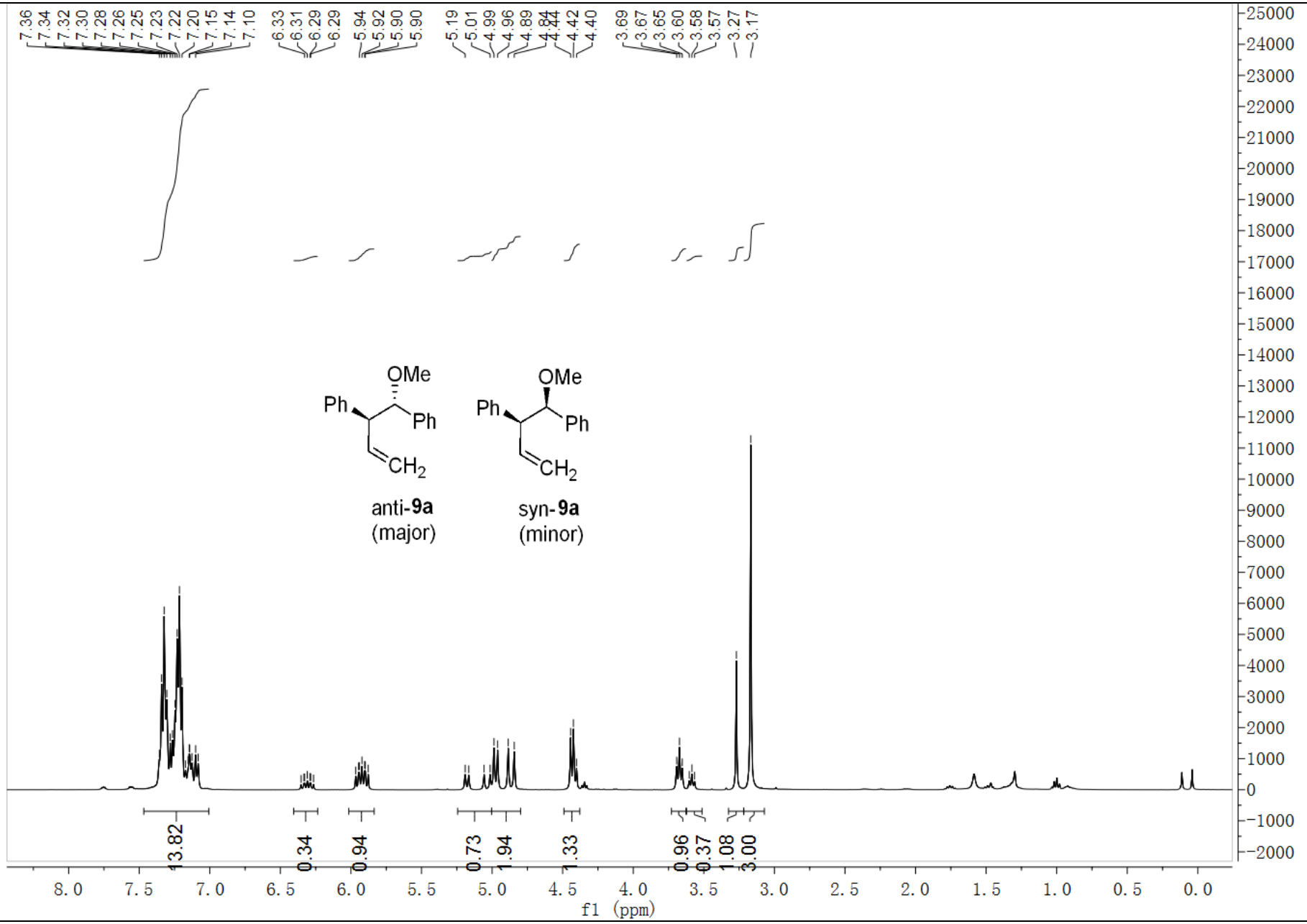
^{1}H NMR of **8f**


7.40 7.40 7.39 7.39 7.38 7.38 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.24 7.24 7.22 7.22 7.22 5.25 5.24 5.00 4.99 4.99 4.20 4.18 4.18 4.16 4.13 3.07 3.07 3.05 3.04 3.03 3.02 3.01 2.81 2.81 2.80 2.79 2.77 2.76 2.76
H3C
CH2
O
10.10
1.04
1.02
0.99
3.00
1.03
0.99
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

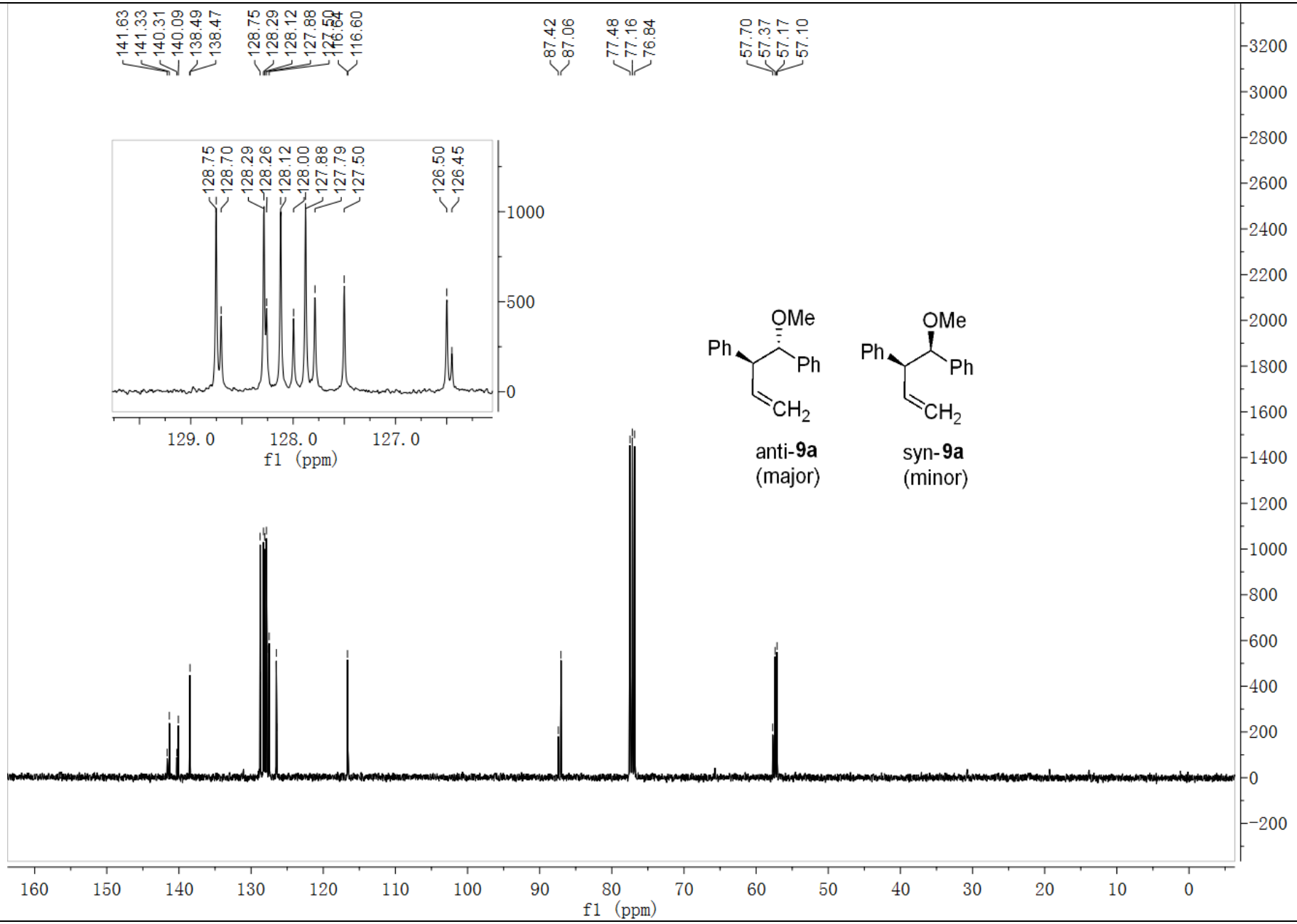
^{13}C NMR of **8f**


145.12
141.94
141.23
128.45
128.42
127.70
127.52
126.85
126.49
115.21
82.31
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
56.87
44.68
H3C
CH2
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

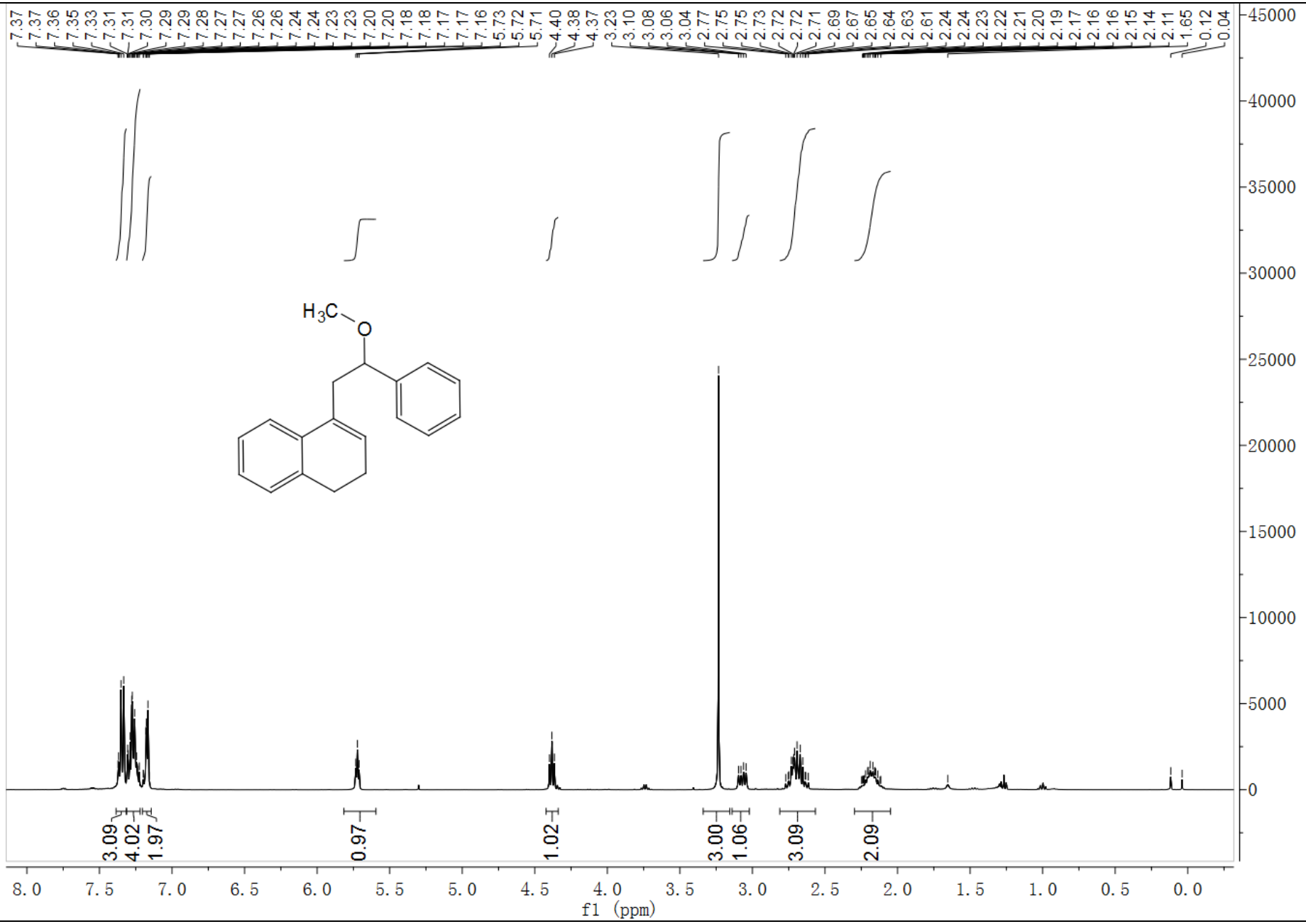
^{1}H NMR of **9a**


7.36
7.34
7.32
7.30
7.28
7.26
7.25
7.23
7.22
7.20
7.15
7.14
7.10
6.33
6.31
6.29
6.29
5.94
5.92
5.90
5.90
5.19
5.01
4.99
4.96
4.89
4.84
4.44
4.42
4.40
3.69
3.67
3.65
3.60
3.58
3.57
3.27
3.17
OMe
Ph
Ph
CH2
anti-9a
(major)
OMe
Ph
Ph
CH2
syn-9a
(minor)
13.82
0.34
0.94
0.73
1.94
1.33
0.96
0.37
1.08
3.00
f1 (ppm)

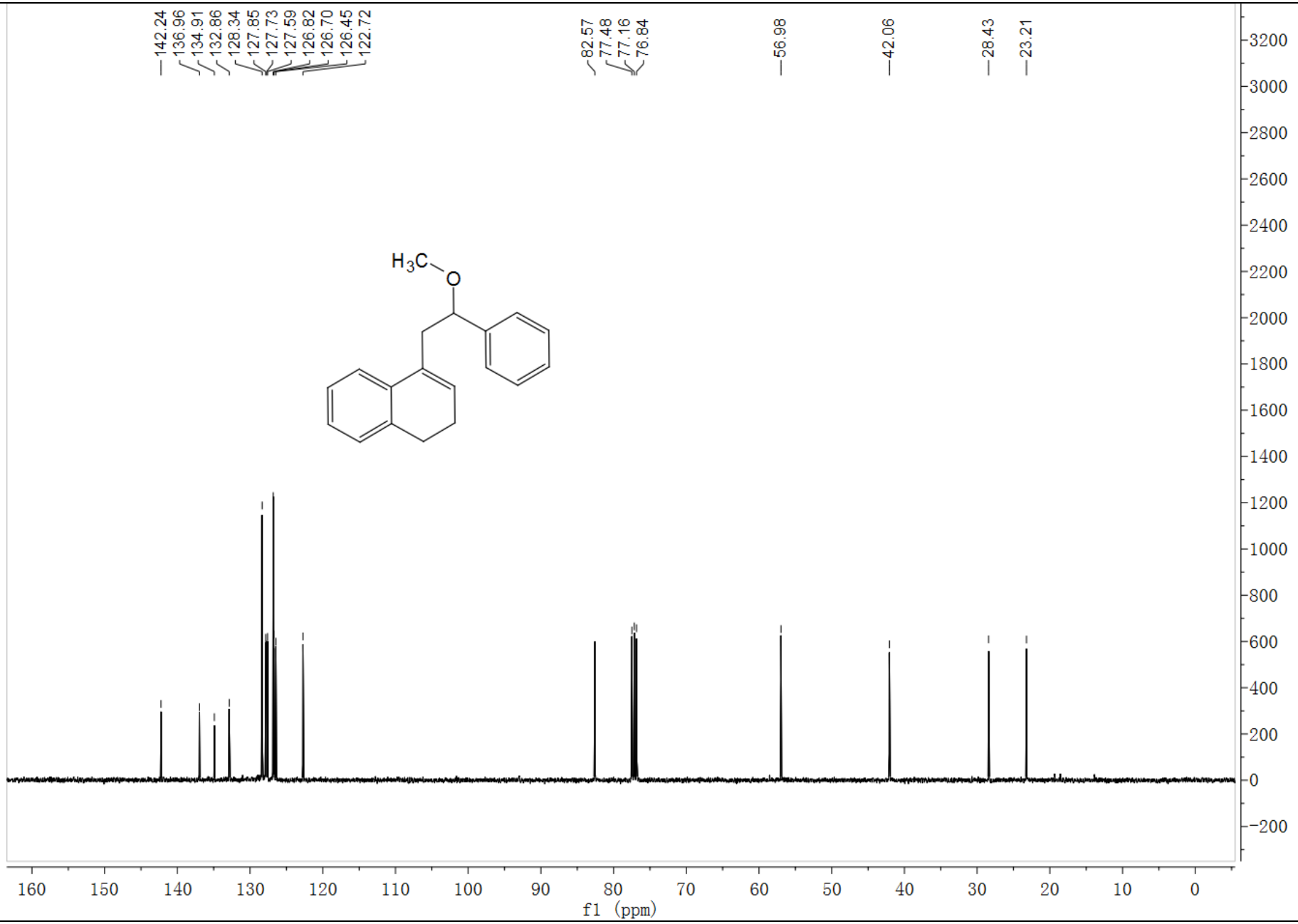
^{13}C NMR of **9a**


141.63
141.33
140.31
140.09
138.49
138.47
128.75
128.29
128.12
127.88
116.60
87.42
87.06
77.48
77.16
76.84
57.70
57.37
57.17
57.10
128.75
128.70
128.29
128.26
128.12
128.00
127.88
127.79
127.50
126.50
126.45
1000
500
0
129.0
128.0
127.0
f1 (ppm)
OMe
Ph
Ph
CH2
anti-9a
(major)
syn-9a
(minor)
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
−200
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

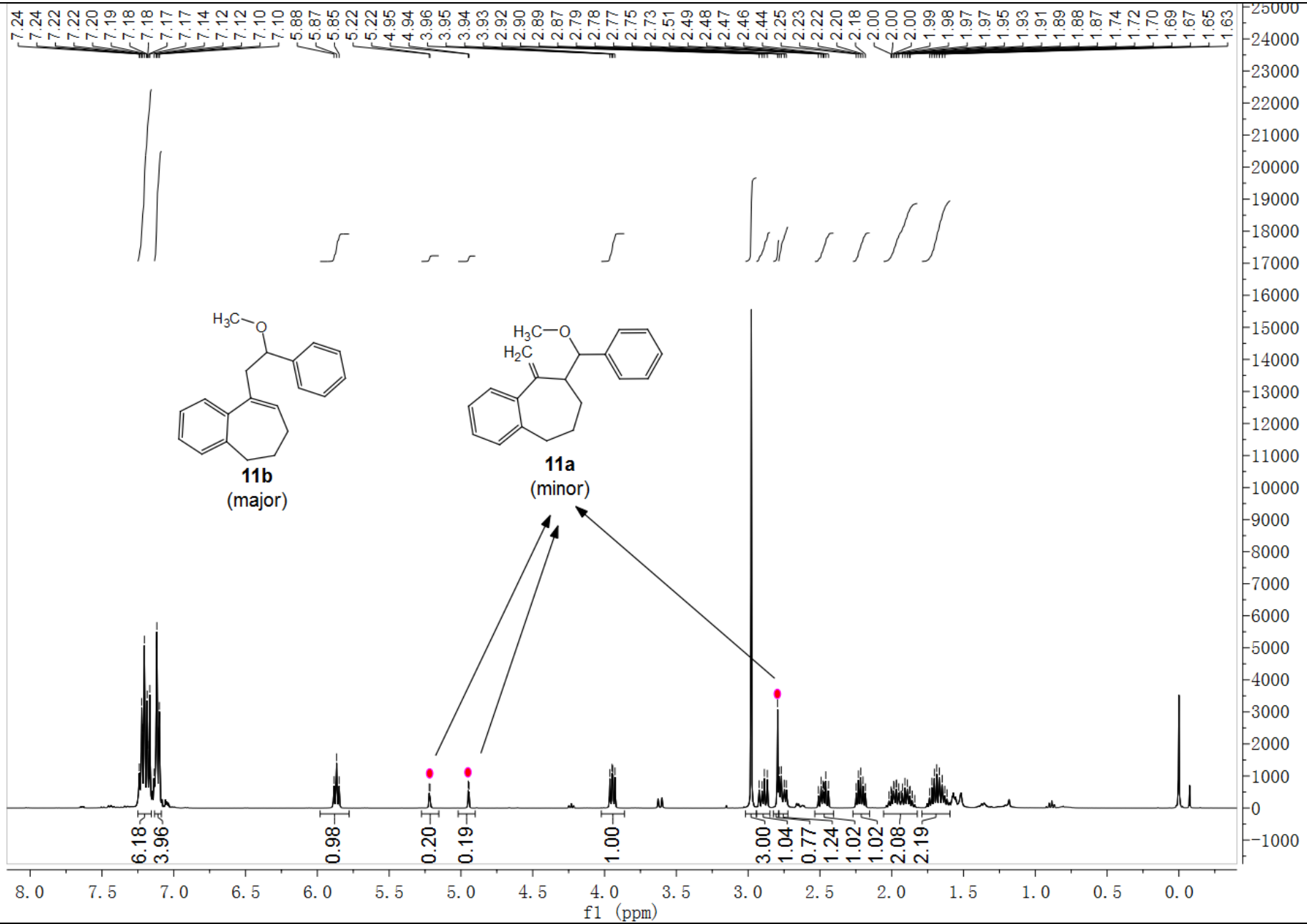
^{1}H NMR of **10b**


7.37 7.37 7.36 7.35 7.33 7.31 7.31 7.30 7.29 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.24 7.23 7.23 7.20 7.20 7.18 7.18 7.17 7.17 7.16 5.73 5.72 5.71 4.40 4.38 4.37 3.23 3.10 3.08 3.06 3.04 2.77 2.75 2.75 2.73 2.72 2.72 2.71 2.69 2.67 2.65 2.64 2.63 2.61 2.24 2.24 2.23 2.22 2.21 2.20 2.19 2.17 2.16 2.16 2.15 2.14 2.11 1.65 0.12 0.04
H3C
O
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
3.09
4.02
1.97
0.97
1.02
3.00
1.06
3.09
2.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

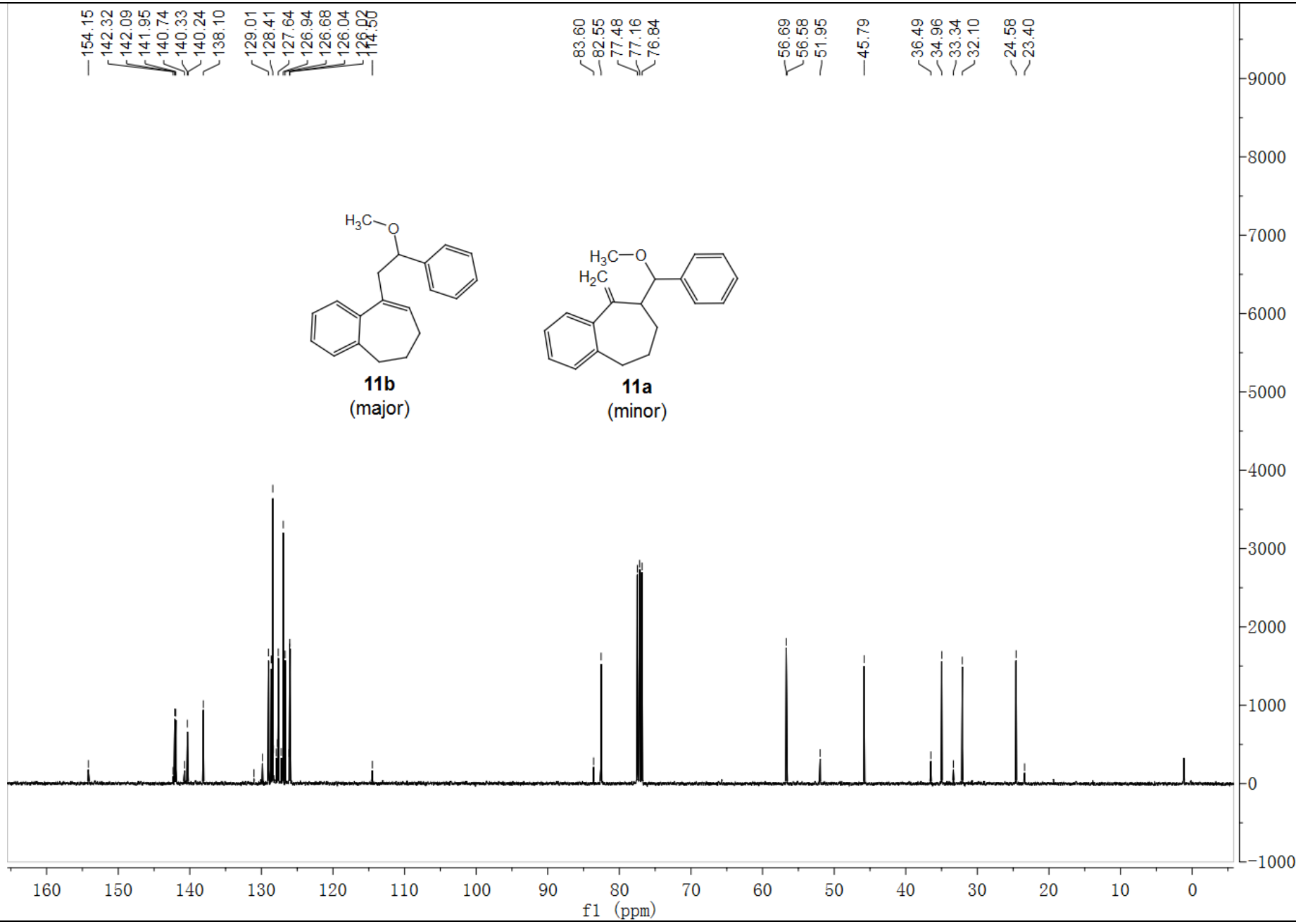
^{13}C NMR of **10b**



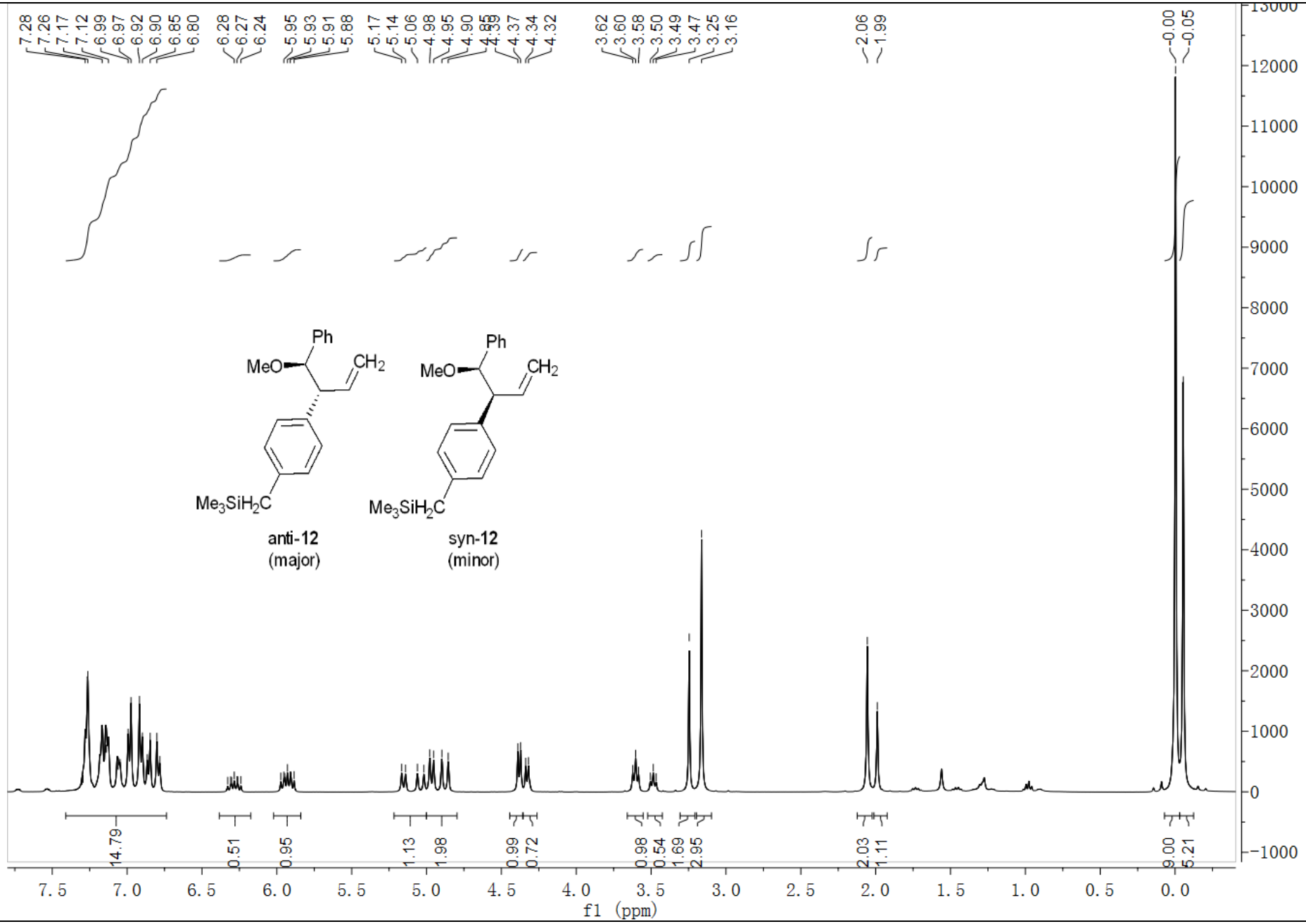
^{1}H NMR of **11a** + **11b**



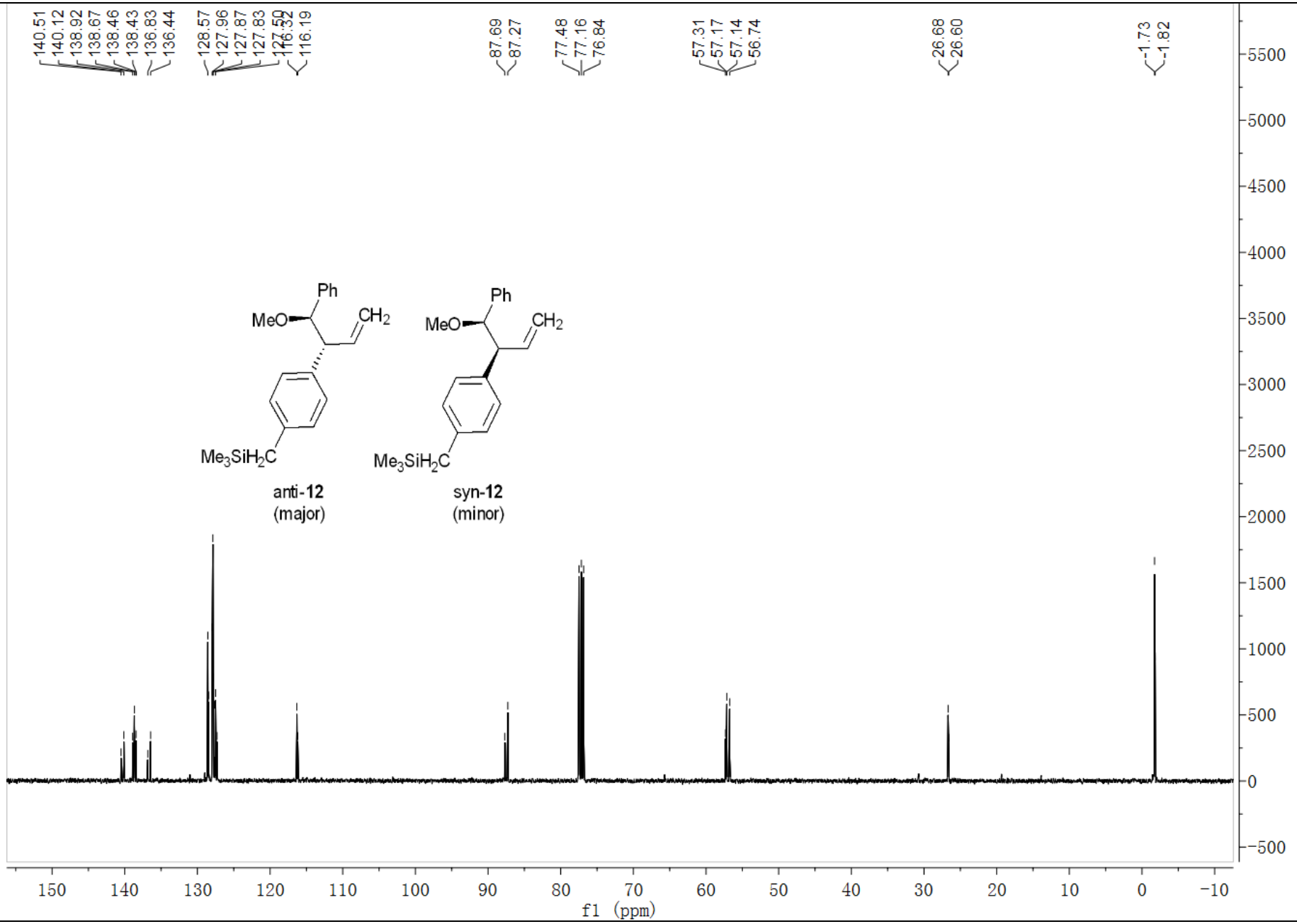
^{13}C NMR of **11a**+**11b**



^{1}H NMR of **12**


7.28
7.26
7.17
7.12
6.99
6.97
6.92
6.90
6.85
6.80
6.28
6.27
6.24
5.95
5.93
5.91
5.88
5.17
5.14
5.06
4.98
4.95
4.90
4.37
4.34
4.32
3.62
3.60
3.58
3.50
3.49
3.47
3.25
3.16
2.06
1.99
0.00
-0.05
Ph
MeO
CH2
Me3SiH2C
anti-12
(major)
Ph
MeO
CH2
Me3SiH2C
syn-12
(minor)
14.79
0.51
0.95
1.13
1.98
0.99
0.72
0.98
0.54
1.69
2.95
2.03
1.11
9.00
5.21
f1 (ppm)

^{13}C NMR of **12**


140.51
140.12
138.92
138.67
138.46
138.43
136.83
136.44
128.57
127.96
127.87
127.83
116.32
116.19
87.69
87.27
77.48
77.16
76.84
57.31
57.17
57.14
56.74
26.68
26.60
-1.73
-1.82
Ph
MeO
CH2
Me3SiH2C
anti-12
(major)
Ph
MeO
CH2
Me3SiH2C
syn-12
(minor)
f1 (ppm)