

Supporting Information

Enantioselective Synthesis of Chiral Acylsilanes by Copper/HZNU-Phos -Catalyzed Asymmetric Conjugate Addition of Diethylzinc to α,β -Unsaturated Acylsilanes

Ji-Yuan Lv^a, Zheng Xu, Zhan-Jiang Zheng, Li Li^{a,*}, Yu-Ming Cui^a, Jian Cao^a, Ke-Fang Yang^a,
and Li-Wen Xu^{a,b,*}

^a Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, No 1378, Wenyi West Road, Science Park of HZNU, Hangzhou 311121, P. R. China.
E-mail: liwenxu@hznu.edu.cn

^b Suzhou Research Institute and State Key Laboratory for Oxo Synthesis and Selective Oxidation Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS), P. R. China.

Table of Contents

1. General Information.....	2
2. General Procedure for the preparation of α,β -unsaturated acylsilanes.....	2
3. General Procedure for Cu(II)/(S,R)-HZNU-Phos-catalyzed enantioselective Cu-catalyzed conjugate addition.....	3
4. Characterization data of 3.....	4
Figure S1-S5. Calculated and Experimental CD spectrum.....	14
Table S1. The reaction results of copper-catalyzed asymmetric conjugate addition of other organometallic reagents to α,β -unsaturated acylsilane 1a.....	16
5. ¹ H, ¹³ C, ¹⁹ F and ²⁹ Si NMR Spectra.....	17
6. HPLC Spectra.....	48

1. General Information.

All reactions were performed in flame- or oven-dried glassware under inert of argon or N₂ and conjugate additions were carried out using standard Schlenk techniques. Unless specifically stated, all reagents were commercially available and purified prior to use. For example, all the aldehydes were recrystallized or distilled prior to use. Dichloromethane and toluene were freshly distilled from CaH₂, and THF was freshly distilled from sodium prior to use. Ether (Et₂O) and 1,4-dioxane were dried and distilled from sodium and benzophenone. Alcohol solvents were dried and distilled from magnesium. Except α,β -unsaturated acylsilanes, other reagents and solvents were commercially available and used directly without purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica (300 - 400 mesh). ¹H, ¹³C, ¹⁹F and ²⁹Si NMR spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer in CDCl₃. Multiplicities were given as: s (singlet); d (doublet); *dd* (doublets of doublet); t (triplet); q (quartet); or m (multiplets). High resolution mass spectra (HRMS) of the products were obtained on a Bruker Daltonics micro TOF-spectrometer. HPLC was carried out with Agilent 1260 infinity using a chiralpak AD-H column, a chiralpak OJ-H column or a chiralcel IC column.

2. General Procedure for the preparation of α,β -unsaturated acylsilanes

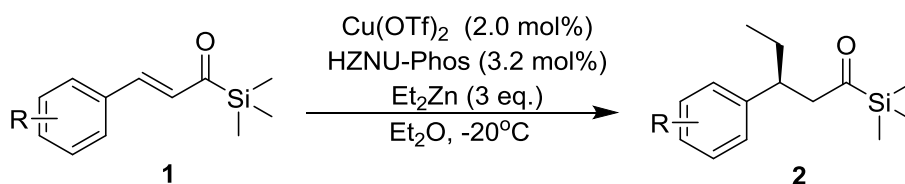
General experimental details for the synthesis of α,β -unsaturated acylsilanes are the same as those previously reported.^[1] To a round-bottomed flask equipped with a stir bar and charged with *n*-Bu₄N•ReO₄ (0.05 eq.), *p*-TsOH•H₂O (0.05 eq.) was added a 0.2 M solution of propargyl alcohol (1.00 eq) in DCM. After overnight stirring at ambient temperature the reaction was diluted with water and the aqueous phase separated. The organic phase was washed with brine, dried with anhydrous MgSO₄, and concentrated in vacuo.

The crude product was purified by flash column chromatography, eluting with the indicated solvent mixture to afford the desired product. For example, when the propargyl alcohol **1a** (0.69 mmol, 1.0 eq.) was converted into α,β -unsaturated acyl silane **2a**, the product was obtained with 72% yield as a red oil after purification by flash column chromatography (EA/PE=1/20).

Reference

[1] A. Nikolaev, A. Orellana, *Org. Lett.* **2015**, *17*, 5796-5799.

3. General Procedure for Cu(II)/(*S,R*)-HZNU-Phos-catalyzed enantioselective Cu-catalyzed conjugate addition of α,β -unsaturated acylsilanes

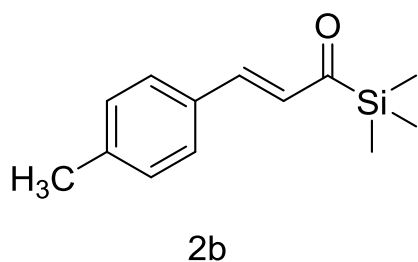


A flame-dried Schlenk tube was charged with $\text{Cu}(\text{OTf})_2$ (3.6 mg, 0.01 mmol, 2.0 mol%) and (*S,R*)-HZNU-Phos (10.0 mg, 0.016 mmol, 3.2 mol%) under an N_2 atmosphere, and the mixture was dissolved in dry Et_2O (3.0 mL). The solution was stirred at room temperature for 30 min and then cooled to -20°C . Diethylzinc (3.0 mmol, 3.0 mL of 1 M toluene solution, 6 eq.) was added dropwise to the above solution. Then α,β -unsaturated acylsilane (0.5 mmol) was added to the clear yellow solution at once. The mixture was stirred at -20°C for 9-12 h before quenched with aqueous saturated NH_4Cl (aq.). The layers were separated and the aqueous layer was extracted with ethyl acetate (5 mL \times 2). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the addition product. The enantiomeric excess of the product was determined by chiral HPLC.

4. Characterization data of 3

(*E*)-3-phenyl-1-(trimethylsilyl)prop-2-en-1-one (α,β -unsaturated acyl silane **2a**), has been reported in ref. [1].

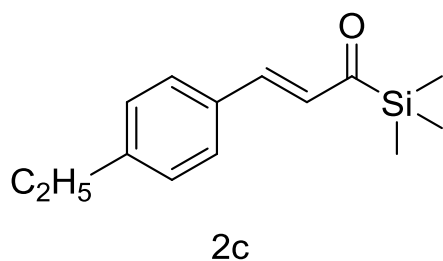
(*E*)-3-(*p*-tolyl)-1-(trimethylsilyl)prop-2-en-1-one (**2b**)



Purification by flash column chromatography (EA/PE = 1/20) yielded the product (65%) as a red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (dd, $J = 12.4, 6.1$ Hz, 3H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.71 (d, $J = 16.4$ Hz, 1H), 2.21 (s, 3H),

0.17 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 236.9, 144.3, 142.1, 133.4, 131.8, 130.9, 129.5, 22.7, -0.74. ^{29}Si NMR (99 MHz, CDCl_3) δ -8.70 (s). HRMS Calculated for $[\text{M}+\text{H}]^+$: $\text{C}_{13}\text{H}_{19}\text{OSi}$: 219.1200; Found: 219.1209

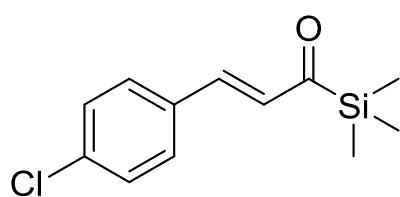
(*E*)-3-(4-ethylphenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2c**)



Purification by flash column chromatography (EA/PE = 1/20) yielded the product (70%) as a red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.23 (m, 3H), 7.08 (d, $J = 7.8$ Hz, 2H), 6.73 (d, $J = 16.4$ Hz, 1H),

2.52 (q, $J = 7.5$ Hz, 2H), 1.10 (t, $J = 7.6$ Hz, 4H), 0.18 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 238.1, 149.3, 145.1, 134.4, 132.6, 130.5, 130.3, 30.8, 17.3, -0.0. ^{29}Si NMR (99 MHz, CDCl_3) δ -8.48 (s). HRMS Calculated for: $\text{C}_{14}\text{H}_{21}\text{OSi}$ $[\text{M}+\text{H}]^+$: 233.1356; Found: 233.1366

(*E*)-3-(4-chlorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2d**)

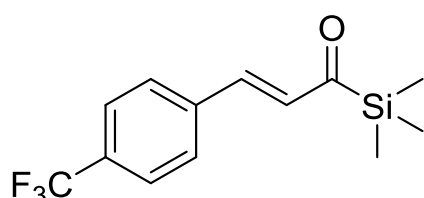


2d

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (80%) as an red oil. ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.6 Hz, 3H), 6.69 (d, J = 16.4 Hz, 1H), 0.14 (s, 9H). ¹³C NMR

(100 MHz, CDCl₃) δ 238.1, 143.0, 133.4, 131.5, 131.3, -0.0. ²⁹Si NMR (99 MHz, CDCl₃) δ -7.86 (s). HRMS Calculated for: C₁₂H₁₄OSi[M+Na]⁺: 295.0083; Found: 295.0093

(*E*)-3-(4-(trifluoromethyl)phenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2e**)

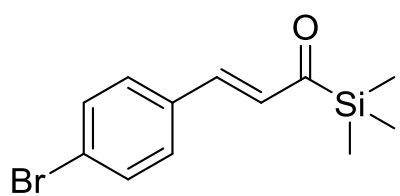


2e

purification by flash column chromatography (EA/PE=1/20) yielded the product (80%) as an red oil. ¹H NMR (400 MHz, CDCl₃) δ 7.45 (s, 5H), 7.23 (d, J = 16.4 Hz, 1H), 6.77 (dd, J = 16.4, 1.9 Hz, 1H), 0.14 (d, J = 3.2 Hz, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 238.5, 142.3, 140.7, 134.8, 130.6, 128.1 (q, J = 3.8 Hz), 0.0. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.86. ²⁹Si NMR (99 MHz, CDCl₃) δ -7.70. HRMS Calculated for C₁₃H₁₆F₃OSi [M+H]⁺: 273.0917, found: 273.0927.

(*E*)-3-(4-bromophenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2f**)

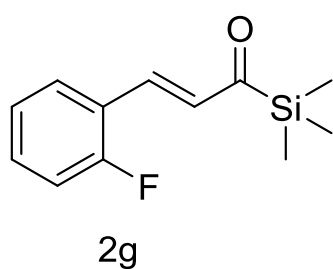


2f

was Purification by flash column chromatography (EA/PE=1/20) yielded the product (75%) as an red oil ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 16.4 Hz, 1H), 1.26

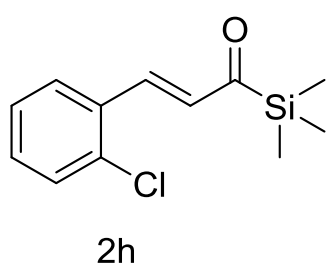
(s, 1H), 0.32 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 238.2, 143.1, 136.0, 134.3, 133.5, 131.7, 126.8, 0.0. ²⁹Si NMR (99 MHz, CDCl₃) δ -8.06 (s). HRMS Calculated for: C₁₂H₁₆FOSi[M+Na]⁺: 285.0138; Found: 283.0148.

(*E*)-3-(2-fluorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2g**)



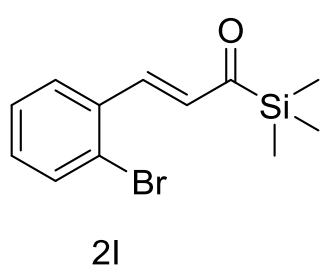
Purification by flash column chromatography (EA/PE = 1/20) yielded the product (73%) as a red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.34 (m, 2H), 7.14 (dd, J = 13.9, 7.0 Hz, 1H), 6.91 (dt, J = 18.9, 8.4 Hz, 2H), 6.68 (d, J = 16.7 Hz, 1H), 0.11 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 238.7, 164.7, 162.2, 137.4 (d, J = 3.9 Hz), 135.2 (d, J = 4.5 Hz), 133.9 (d, J = 8.7 Hz), 130.3 (d, J = 2.7 Hz), 126.7 (d, J = 3.6 Hz), 118.2 (d, J = 22.0 Hz), 0.0. ^{29}Si NMR (99 MHz, CDCl_3) δ -7.98 (s). ^{19}F NMR (471 MHz, CDCl_3) δ -115.26 (s). HRMS Calculated for: $\text{C}_{12}\text{H}_{16}\text{FO}$ $[\text{M}+\text{H}]^+$: 223.0949; Found: 223.0958

(*E*)-3-(2-chlorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2h**)



Purification by flash column chromatography (EA/PE = 1/20) yielded the product (60%) as a red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 16.7 Hz, 1H), 7.41 (dd, J = 7.2, 2.0 Hz, 1H), 7.18 (dd, J = 7.6, 1.6 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.50 (d, J = 16.7 Hz, 1H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 238.5, 142.1, 137.0, 135.9, 134.9, 133.0, 131.9, 131.2, 129.0, 0.0. ^{29}Si NMR (99 MHz, CDCl_3) δ -7.99 (s). HRMS Calculated for: $\text{C}_{12}\text{H}_{15}\text{ClOSi}$ $[\text{M}+\text{Na}]^+$: 261.0473; Found: 261.0482.

(*E*)-3-(2-bromophenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2i**)



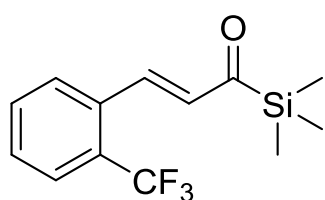
Purification by flash column chromatography (EA/PE=1/20) yielded the product (65%) as a red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 16.6 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.39 – 7.23 (m, 2H), 6.70 (d, J = 16.6 Hz, 1H), 0.39 (s, 9H). ^{13}C NMR (100 MHz,

CDCl₃) δ 238.1, 144.4, 136.1, 135.7, 134.7, 132.6, 129.1, 128.6, 127.1, -0.5.

²⁹Si NMR (99 MHz, CDCl₃) δ -7.75 (s). HRMS Calculated for:

C₁₂H₁₆BrOSi[M+H]⁺: 283.0148; Found: 283.0162

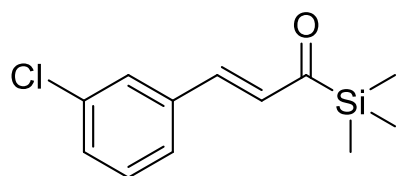
(E)-3-(2-(trifluoromethyl)phenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2j**)



2j

purification by flash column chromatography (EA/PE = 1/20) yielded the product (80%) as a red oil. ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 16.6 Hz, 1H), 7.50 (dd, J = 14.6, 7.9 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 6.47 (d, J = 16.5 Hz, 1H), 0.11 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 238.8, 141.9, 137.8, 135.9, 134.4, 131.9, 129.6, 128.3 (q, J = 5.5 Hz), 127.7, 124.9, -0.0. ²⁹Si NMR (99 MHz, CDCl₃) δ -7.41. ¹⁹F NMR (471 MHz, CDCl₃) δ -58.83. HRMS Calculated for C₁₃H₁₆F₃OSi [M+H]⁺: 273.0917; found: 273.0927.

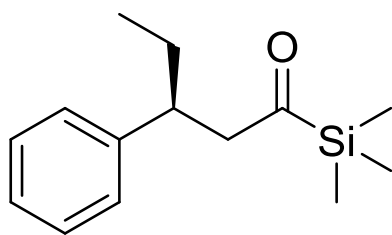
(E)-3-(3-chlorophenyl)-1-(trimethylsilyl)prop-2-en-1-one (**2k**)



2k

was Purification by flash column chromatography (EA/PE = 1/20) yielded the product (50%) as a red oil. ¹H NMR (400 MHz, CDCl₃) δ 7.33 (s, 1H), 7.23 (d, J = 7.0 Hz, 1H), 7.15 (dd, J = 9.2, 7.2 Hz, 3H), 6.69 (d, J = 16.4 Hz, 1H), 0.13 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 142.8, 139.0, 137.2, 134.0, 132.4, 130.1, 128.5, 0.0. ²⁹Si NMR (99 MHz, CDCl₃) δ -7.85 (s) HRMS Calculated for: C₁₂H₁₆FOSi[M+Na]⁺: 261.0482; Found: 261.0473.

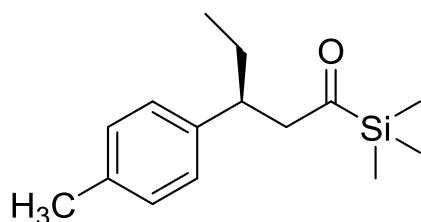
(*R*)-3-phenyl-1-(trimethylsilyl)pentan-1-one (**3a**)



3a

^1H NMR (400 MHz, CDCl_3) δ 7.18 (dd, $J = 9.1, 5.8$ Hz, 1H), 7.11 – 7.04 (m, 3H), 3.03 (ddd, $J = 12.4, 9.1, 6.7$ Hz, 1H), 2.91-2.73 (m, 2H), 1.19 (d, $J = 11.1$ Hz, 2H), 0.67 (t, $J = 7.3$ Hz, 3H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.3, 145.0, 128.3, 127.6, 126.1, 55.0, 41.2, 30.7, 29.3, 12.0, -3.3. ^{29}Si NMR (99 MHz, CDCl_3) δ -10.06 (s). Enantiomeric excess was determined by HPLC with a Chiralpak OJ column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 210 nm); $t_{\text{R}} = 5.65$ min, $t_{\text{R}} = 6.23$ min, 85% ee.

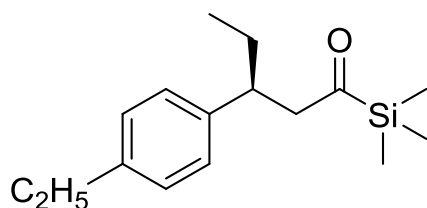
3-(*p*-tolyl)-1-(trimethylsilyl)pentan-1-one (**3b**)



3b

Purification by flash column chromatography (EA/PE=1/20) yielded the product (60%) as a colorless oil [$\alpha_{\text{D}}^{25} = 25$ ($c = 0.1$, CHCl_3)]. ^1H NMR (400 MHz, CDCl_3) δ 6.95 (q, $J = 7.5$ Hz, 4H), 3.02-2.93 (m, 1H), 2.76 (ddd, $J = 24.0, 16.7, 6.9$ Hz, 2H), 2.18 (s, 3H), 1.53-1.33 (m, 2H), 0.63 (t, $J = 7.3$ Hz, 3H), -0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 246.8, 142.1, 129.7, 127.9, 127.1, 126.8, 53.8, 36.8, 28.2, 11.6, -3.3. ^{29}Si NMR (99 MHz, CDCl_3) δ -10.23 (s). HRMS Calculated for: $\text{C}_{15}\text{H}_{24}\text{OSi}$ [$\text{M}+\text{Na}$] $^+$: 271.1489; Found: 271.1498. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.5:0.5, 0.8 mL/min, 210 nm); $t_{\text{R}} = 6.72$ min, $t_{\text{R}} = 7.4$ min, 80% ee

3-(4-ethylphenyl)-1-(trimethylsilyl)pentan-1-one (**3c**)

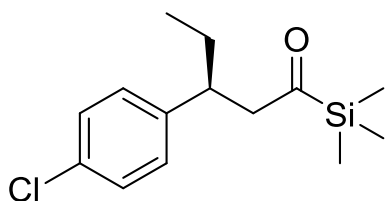


3c

Purification by flash column chromatography

(EA/PE = 1/20) yielded the product (60%) as an colorless oil. $[\alpha]_D^{25} = 15.42$ ($c = 0.11$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.97 (q, $J = 8.1$ Hz, 9H), 3.03-2.94 (m, 1H), 2.77 (ddd, $J = 24.0, 16.6, 6.8$ Hz, 1H), 2.49 (dd, $J = 15.3, 7.6$ Hz, 1H), 1.10 (t, $J = 7.6$ Hz, 1H), 0.64 (t, $J = 7.3$ Hz, 1H), 0.00 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 248.0, 142.3, 142.0, 127.9, 127.5, 55.2, 40.9, 29.4, 28.5, 15.6, 12.1, -3.3. $^{29}\text{Si NMR}$ (99 MHz, CDCl_3) δ -10.18 (s). HRMS Calculated for: $\text{C}_{16}\text{H}_{26}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 285.1645; Found: 285.1655. Enantiomeric excess was determined by HPLC with a Chiralpak AD column(hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_R = 5.10$ min, $t_R = 5.39$ min, 72% ee.

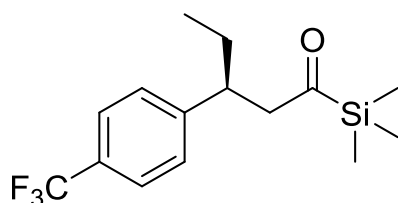
(R)-3-(4-chlorophenyl)-1-(trimethylsilyl)pentan-1-one (**3d**)



3d

$[\alpha]_D^{25} = 11.94$ ($c = 0.1$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.10-6.99 (m, 3H), 6.91 (d, $J = 7.4$ Hz, 1H), 3.04-2.95 (m, 1H), 2.75 (ddd, $J = 42.3, 17.0, 6.8$ Hz, 2H), 1.52-1.33 (m, 2H), 0.63 (t, $J = 7.4$ Hz, 3H), 0.00 (s, 9H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 247.1, 147.4, 134.3, 127.7, 126.4, 54.7, 41.0, 29.3, 12.1, -3.3. $^{29}\text{Si NMR}$ (99 MHz, CDCl_3) δ -7.89 (s). HRMS Calculated for: $\text{C}_{14}\text{H}_{21}\text{ClOSi}$ $[\text{M}+\text{Na}]^+$: 291.0952; Found: 291.0942. Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 14.8$ min, $t_2 = 16.0$ min, 66% ee.

3-(4-(trifluoromethyl)phenyl)-1-(trimethylsilyl)pentan-1-one (**3e**)

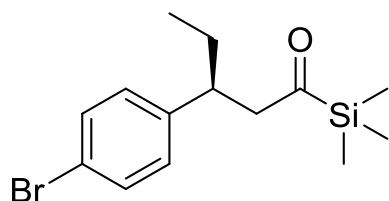


3e

Purification by flash column chromatography

(EA/PE=1/20) yielded the product (60%) as a colorless oil. $[\alpha]_D^{25} = 10.2$ ($c = 0.1$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 2H), 3.08 (dd, $J = 14.9, 6.4$ Hz, 1H), 2.79 (dd, $J = 15.7, 6.8$ Hz, 2H), 1.55-1.37 (m, 2H), 0.63 (t, $J = 7.3$ Hz, 3H), -0.00 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 246.7, 149.3, 127.9, 125.3 (q, $J = 3.8$ Hz), 54.5, 40.8, 29.1, 11.9, -3.5. $^{29}\text{Si NMR}$ (99 MHz, CDCl_3) δ -7.89 (s). HRMS Calculated for: $\text{C}_{15}\text{H}_{21}\text{F}_3\text{OSi}[\text{M}+\text{Na}]^+$: 325.1206; Found: 325.1215. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 5.10$ min, $t_2 = 5.39$ min, 52% ee.

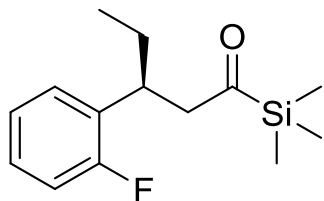
(R)-3-(4-bromophenyl)-1-(trimethylsilyl)pentan-1-one (**3f**)



3f

$[\alpha]_D^{25} = 8.9$ ($c = 0.1$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.30 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.42$ Hz, 1H), 3.01 (ddd, $J = 12.2, 9.4, 6.7$ Hz, 1H), 2.78 (ddd, $J = 37.6, 17.1, 6.8$ Hz, 2H), 1.17 (s, 2H), 0.65 (t, $J = 7.3$ Hz, 3H), 0.03 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 247.1, 144.1, 131.4, 129.4, 119.7, 54.7, 40.5, 29.2, 11.9, -3.4. $^{29}\text{Si NMR}$ (99 MHz, CDCl_3) δ -9.83 (s). HRMS Calculated for: $\text{C}_{14}\text{H}_{21}\text{BrOSi}[\text{M}+\text{Na}]^+$: 337.0427; Found: 335.0437. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 12.97$ min, $t_2 = 14.16$ min, 73 % ee.

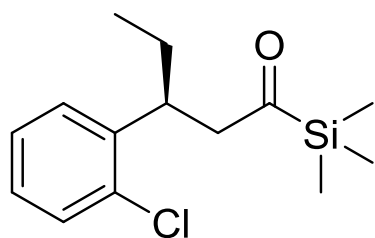
3-(2-fluorophenyl)-1-(trimethylsilyl)pentan-1-one (**3g**)



3g

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (35%) as a colorless oil $[\alpha]_D^{25} = 1.8$ ($c = 0.05$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.01 (dd, $J = 10.5, 4.7$ Hz, 2H), 6.94 – 6.83 (m, 2H), 3.28 (dq, $J = 9.0, 6.8$ Hz, 1H), 2.82 (ddd, $J = 39.5, 17.0, 6.9$ Hz, 2H), 1.51-1.42 (m, 2H), 0.63 (t, $J = 7.4$ Hz, 3H), 0.00 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 246.1, 160.1 (d, $J = 244.9$ Hz), 130.4 (d, $J = 14.2$ Hz), 128.3 (d, $J = 5.5$ Hz), 126.5 (d, $J = 8.4$ Hz), 123.0 (d, $J = 3.4$ Hz), 114.5 (d, $J = 23.0$ Hz), 52.5, 34.2, 27.1, 11.0, -4.4. $^{29}\text{Si NMR}$ (99 MHz, CDCl_3) δ -9.91. $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ -117.49 (s). HRMS Calculated for: $\text{C}_{15}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 275.1238; Found: 275.1247. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 4.74$ min, $t_2 = 5.67$ min, 26% ee.

(R)-3-(2-chlorophenyl)-1-(trimethylsilyl)pentan-1-one (**3h**)

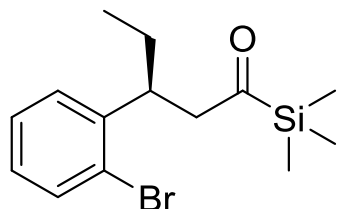


3h

$[\alpha]_D^{25} = 13$ ($c = 0.1$, CHCl_3). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.29-6.98 (m, 4H), 3.79 – 3.55 (m, 1H), 2.95-2.73 (m, 2H), 1.52 (s, 2H), 0.69 (t, $J = 7.4$ Hz, 3H), 0.07 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 246.8, 142.1, 134.2, 129.7, 128.0, 127.1, 126.8, 53.8, 36.8, 28.2, 11.6, -3.2. $^{29}\text{Si NMR}$ (99 MHz, CDCl_3) δ -9.87 (s). HRMS Calculated for: $\text{C}_{14}\text{H}_{21}\text{ClOSi}$ $[\text{M}+\text{H}]^+$: 269.1133; Found: 269.1123. Enantiomeric excess was determined by HPLC

with a Chiralpak AD column(hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 5.30$ min, $t_2 = 5.65$ min, 9% ee.

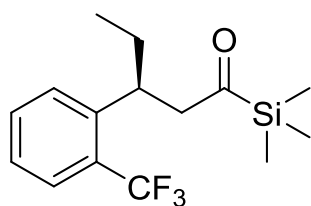
3-(2-bromophenyl)-1-(trimethylsilyl)pentan-1-one (**3i**)



3i

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (70%) as a colorless oil. $[\alpha]_D^{25} = 2.62$ (c = 0.12, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.36 (dd, J = 8.0, 0.8 Hz, 1H), 7.12 – 6.97 (m, 1H), 6.85 (td, J = 8.0, 1.6 Hz, 1H), 3.63 – 3.52 (m, 1H), 2.73 (qd, J = 16.8, 6.9 Hz, 2H), 1.59 – 1.34 (m, 2H), 0.62 (t, J = 7.4 Hz, 3H), -0.00 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 246.6, 143.8, 133.0, 127.9, 127.5, 127.5, 125.2, 55.0, 39.3, 28.4, 11.6, -3.3. ²⁹Si NMR (99 MHz, CDCl₃) δ -9.96 (s). HRMS Calculated for: C₁₄H₂₁BrOSi [M+Na]⁺: 335.0437; Found: 337.0427. Enantiomeric excess was determined by HPLC with a Chiralpak IB column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 5.43$ min, $t_2 = 5.68$ min, 34% ee.

3-(2-(trifluoromethyl)phenyl)-1-(trimethylsilyl)pentan-1-one (**3j**)

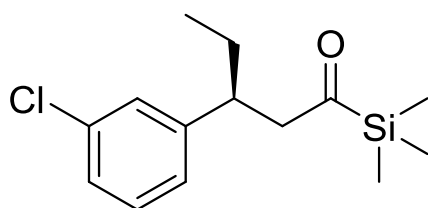


3j

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (40%) as a colorless oil $[\alpha]_D^{25} = -1.24$ (c = 0.06, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 3.48 (dd, J = 8.8, 4.4 Hz, 2H), 2.68 (ddd, J = 21.4, 16.9, 6.6 Hz, 2H), 0.56 (t, J = 7.4 Hz, 3H), 0.00 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 244.4, 130.2, 126.0, 124.2 (dd, J = 12.0,

6.2 Hz), 53.6, 34.0, 27.2, 10.1, -5.1. ^{19}F NMR (471 MHz, CDCl_3) δ -58.45. ^{29}Si NMR (99 MHz, CDCl_3) δ -9.64 (s). HRMS Calculated for: $\text{C}_{15}\text{H}_{21}\text{F}_3\text{OSi}[\text{M}+\text{Na}]^+$: 325.1206; Found: 325.1215. Enantiomeric excess was determined by HPLC with a Chiralpak Phenomenex column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_{\text{R}} = 4.72$ min, $t_{\text{R}} = 5.66$ min, 27% ee.

3-(3-chlorophenyl)-1-(trimethylsilyl)pentan-1-one (**3k**)



3k

Purification by flash column chromatography (EA/PE = 1/20) yielded the product (98%) as a colorless oil. $[\alpha]_{\text{D}}^{25} = 21.86$ ($c = 0.12$, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.07 – 6.99 (m, 3H), 6.91 (dt, $J = 7.4, 1.3$ Hz, 1H), 3.04-2.95 (m, 1H), 2.81 (dd, $J = 17.0, 6.7$ Hz, 1H), 2.70 (dd, $J = 17.0, 6.9$ Hz, 1H), 1.53 – 1.35 (m, 2H), 0.62 (t, $J = 7.4$ Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 247.1, 147.5, 134.4, 129.8, 127.8, 126.5, 126.3, 54.8, 41.1, 29.4, 12.2, -3.2. ^{29}Si NMR (99 MHz, CDCl_3) δ -9.85 (s). HRMS Calculated for: $\text{C}_{14}\text{H}_{21}\text{ClOSi} [\text{M}+\text{Na}]^+$: 291.0952; Found: 291.0942. Enantiomeric excess was determined by HPLC with a Chiralpak AD column (hexanes: 2-propanol = 99.8:0.2, 1 mL/min, 210 nm); $t_1 = 10.36$ min, $t_2 = 10.84$ min, 68 % ee.

Figure S1. The experimental CD spectra of 4-Pheny-hexan-2-one (*S*-configuration).

1

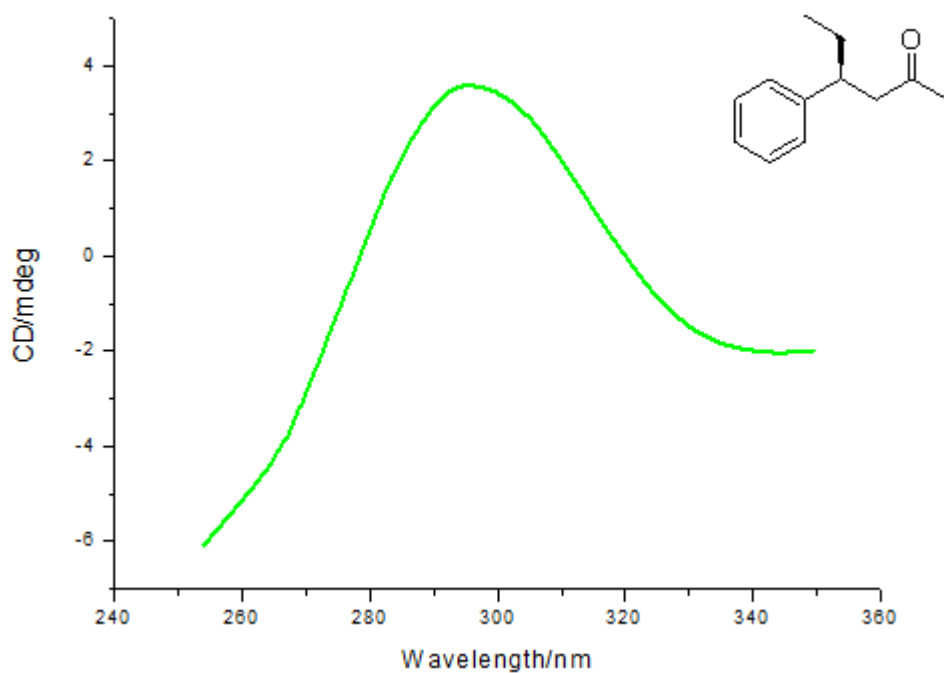


Figure S2. The experimental CD spectra of product **3d**.

1

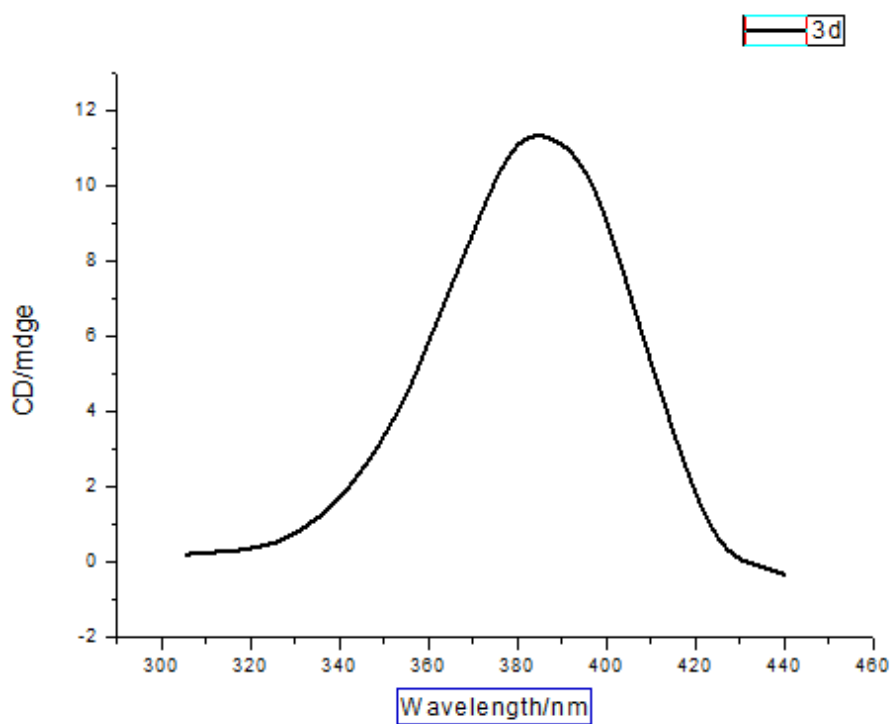


Figure S3. Computed ECD spectra for compound (*S*)-**3d** in with the lowest-energy conformer calculated with TD DFT/CAM-B3LYP/6-31G(d,p)//CAM-B3LYP/6-31G(d,p) using PCM(CH₂Cl₂) model.

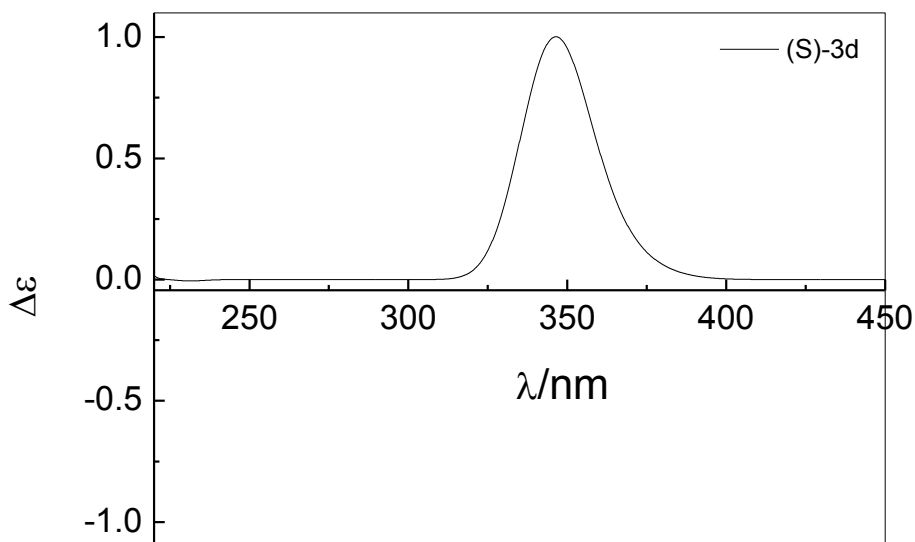
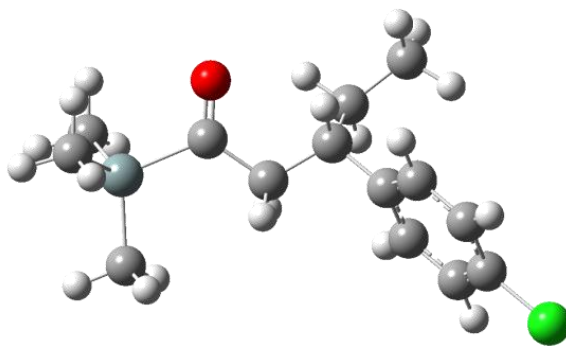


Figure S4. The optimized geometries of compound (*S*)-**3d** calculated at CAM-B3LYP/6-31G(d,p) using PCM model in dichloromethane.



The calculated ECD spectra were obtained from calculated excitation energies and rotational strengths as a sum of Gaussians functions centred at wavelength of each transition with bandwidth $\sigma=0.16$ eV using the SpecDis program.^[1,2] The final spectra were Boltzmann averaged ($T = 298$ K) weighted according to the population percentages of selected representative low-energy conformers based on the relative Gibbs free energies (ΔG).

1. Bruhn, T.; Schaumlöffel, A.; Hemberger, Y.; Bringmann, G. *Chirality* **2013**, *25*, 243–249.
2. T. Bruhn, A. Schaumlöffel, Y. Hemberger, G. Pecitelli, *SpecDis version 1.71*, Berlin, Germany, **2017**, <https://specdis-software.jimdo.com>.

Figure S5. The experimental CD spectra of product **3b**, **3e**, **3h**, **3c**,

3k.

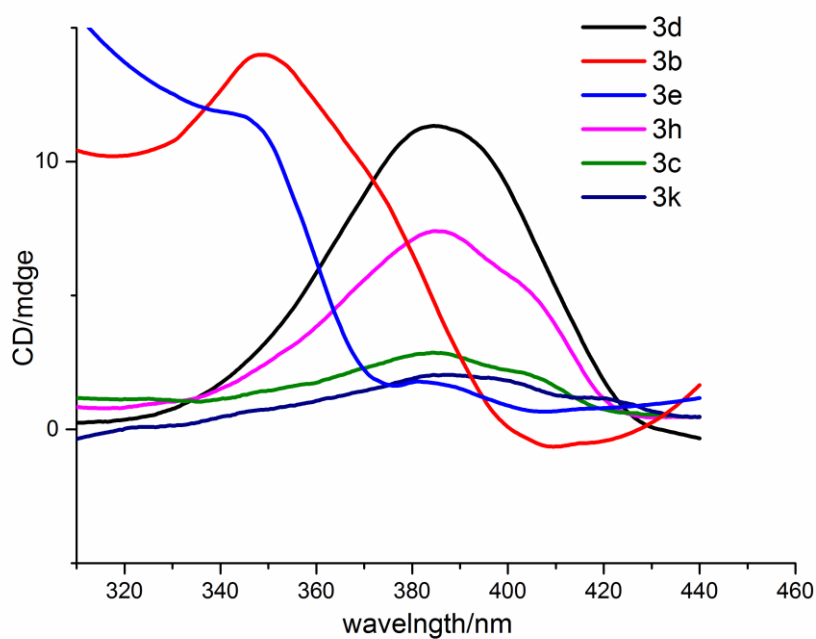
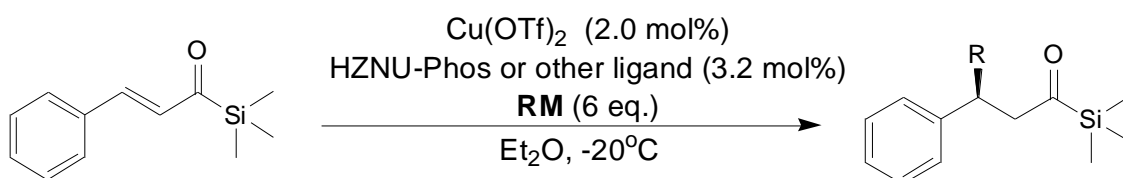


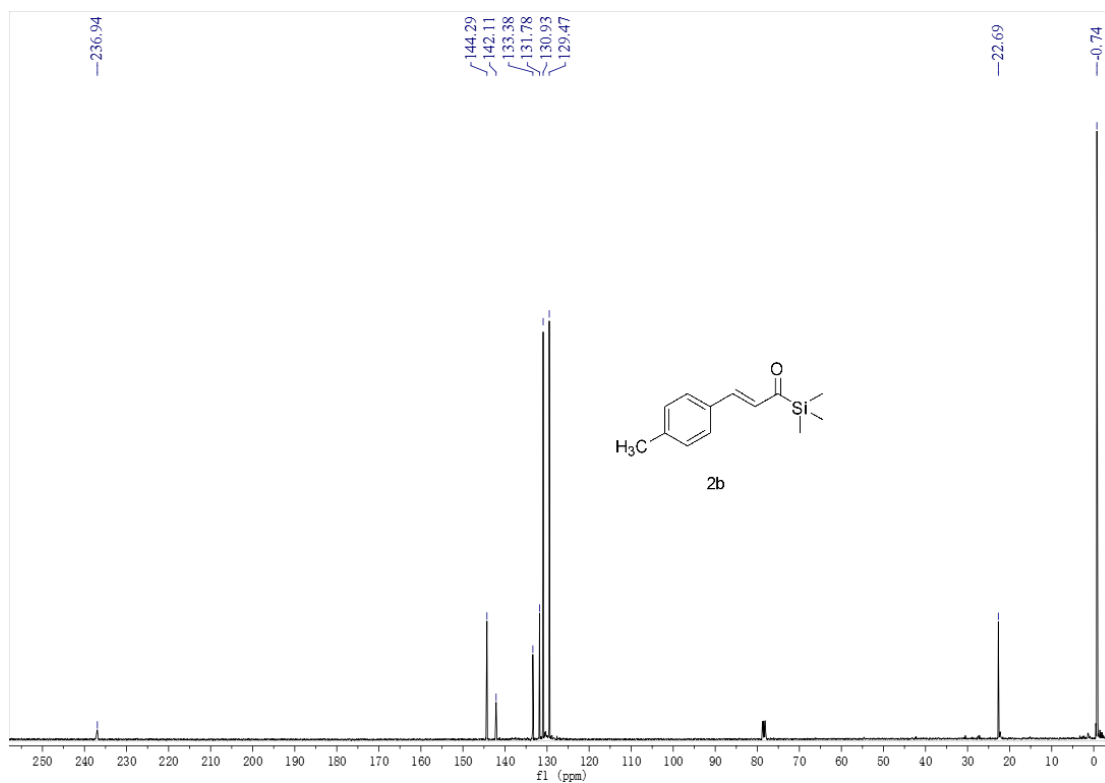
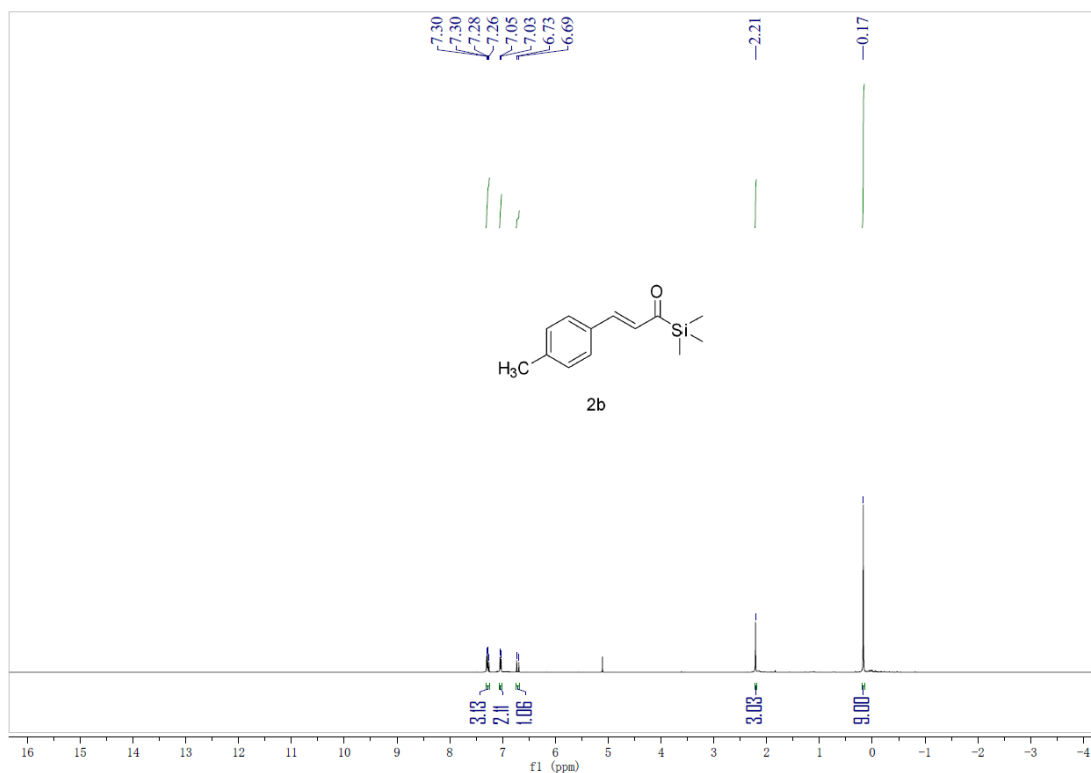
Table S1. The reaction results of copper-catalyzed asymmetric conjugate addition of other organometallic reagents to α,β -unsaturated acylsilane **1a**.

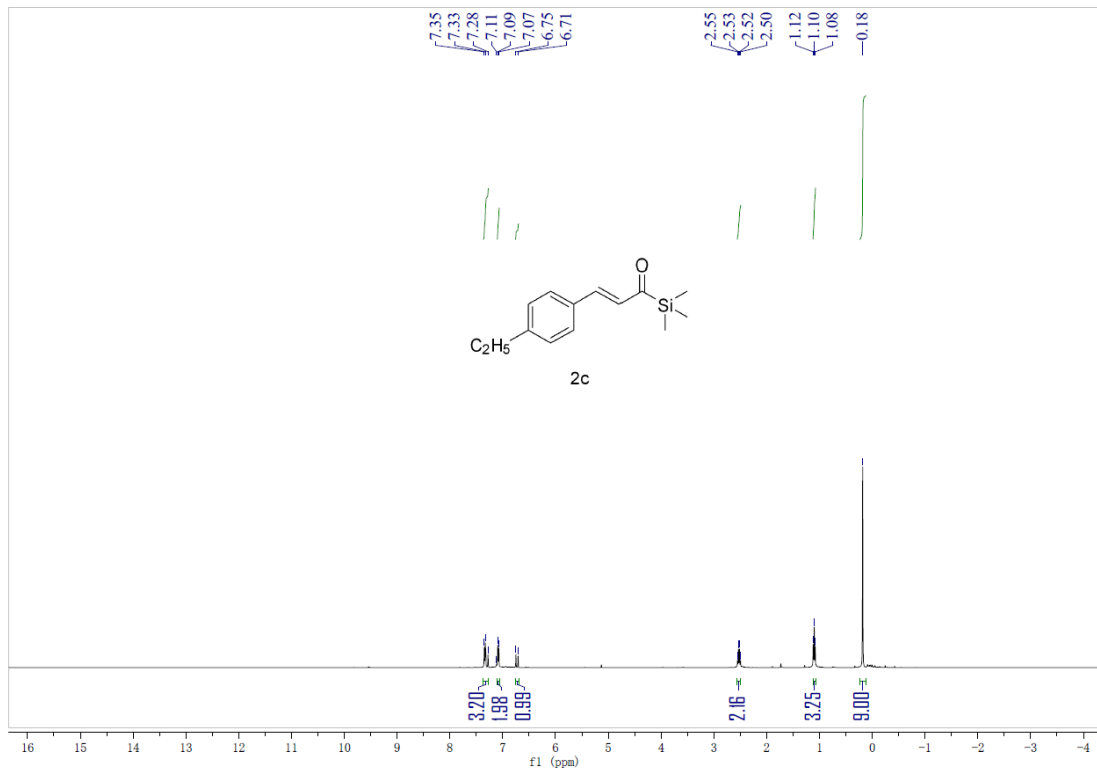
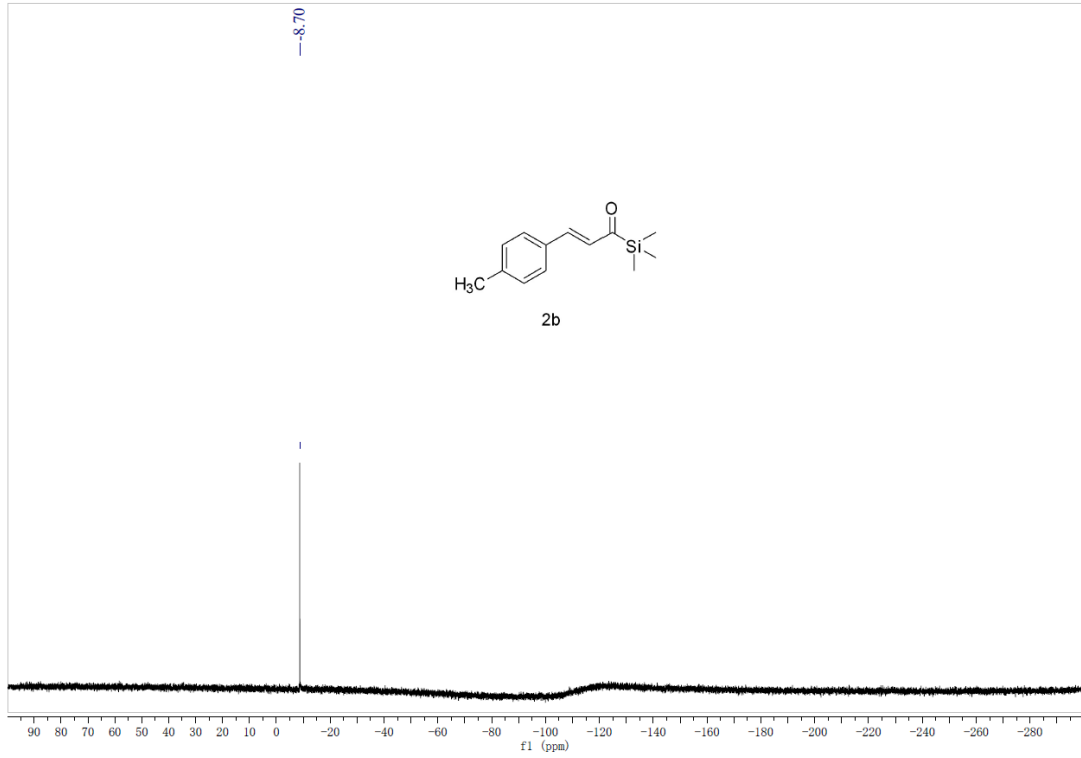


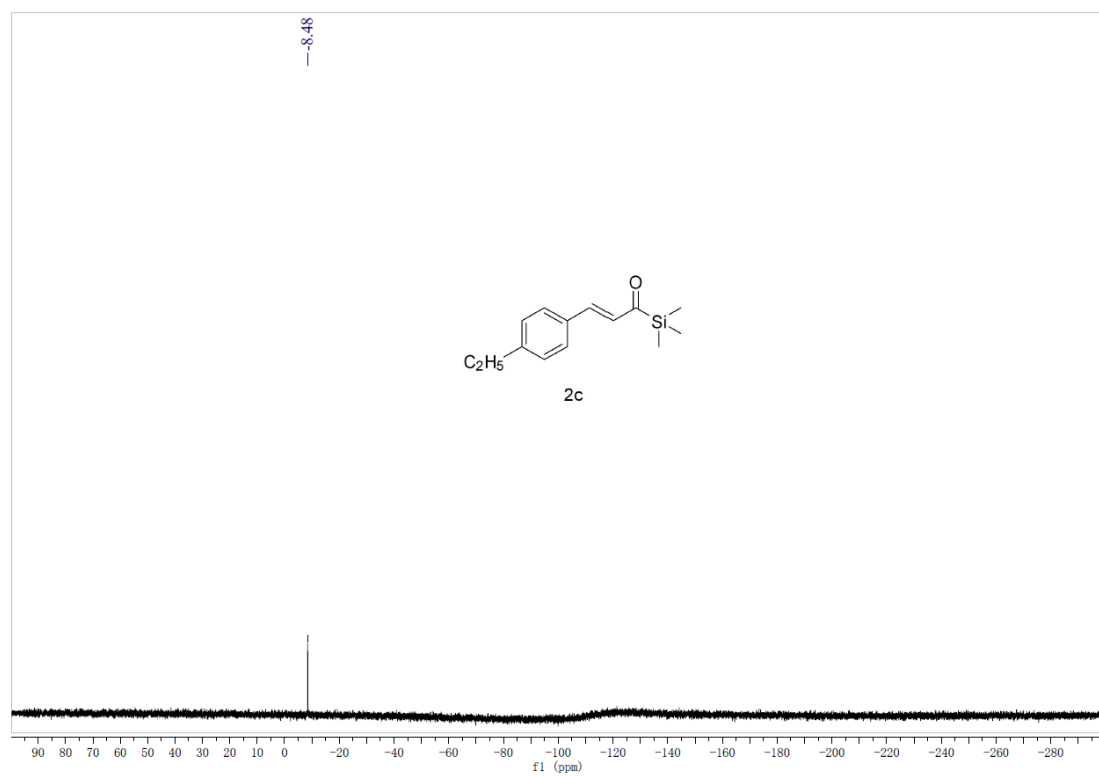
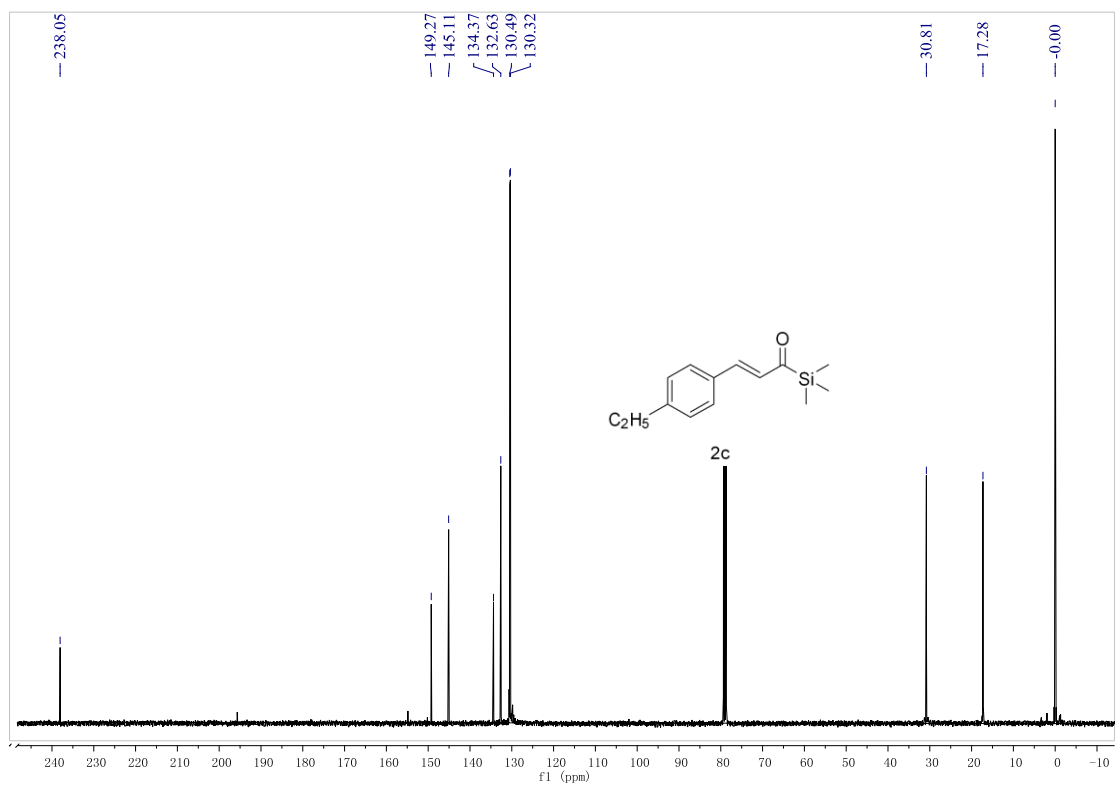
Ligand	Yield (%) of product ^a	Yield (%) of product ^b	Yield (%) of product ^c
L4	Nr ^d	nr	<10%
L5	nr	nr	<10%
L6 (HZNU-Phos)	nr	nr	<10%
L17	nr	nr	<10%

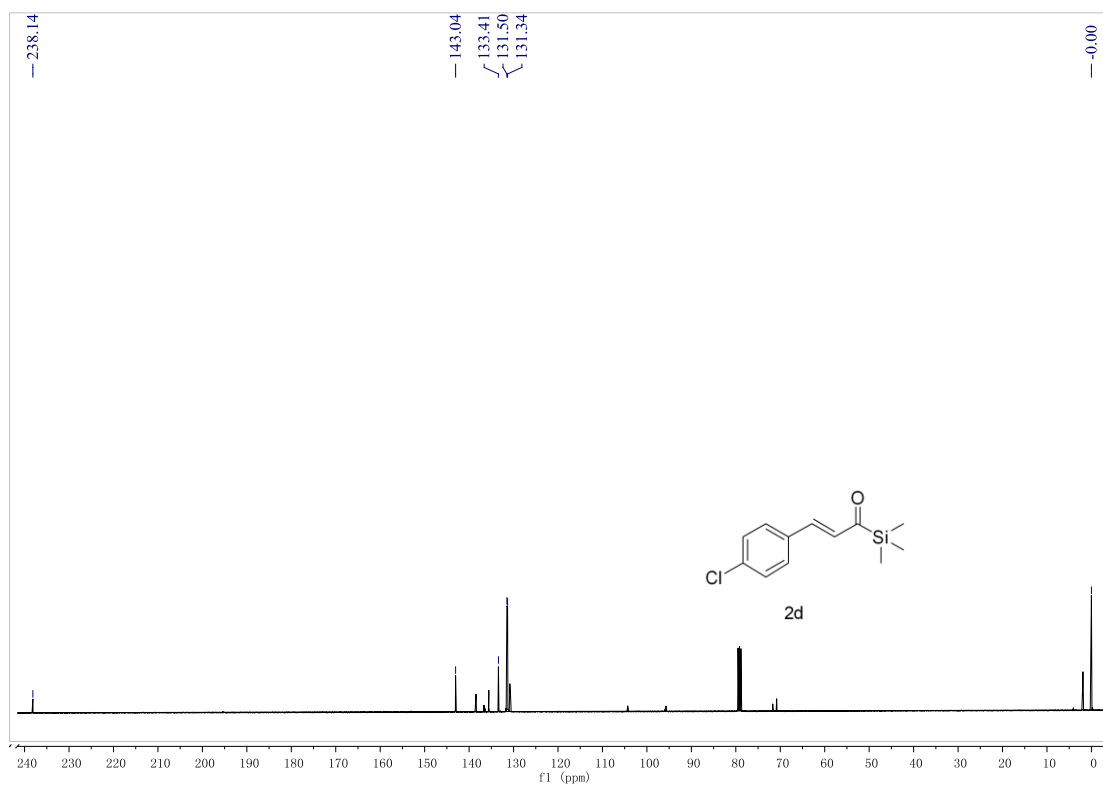
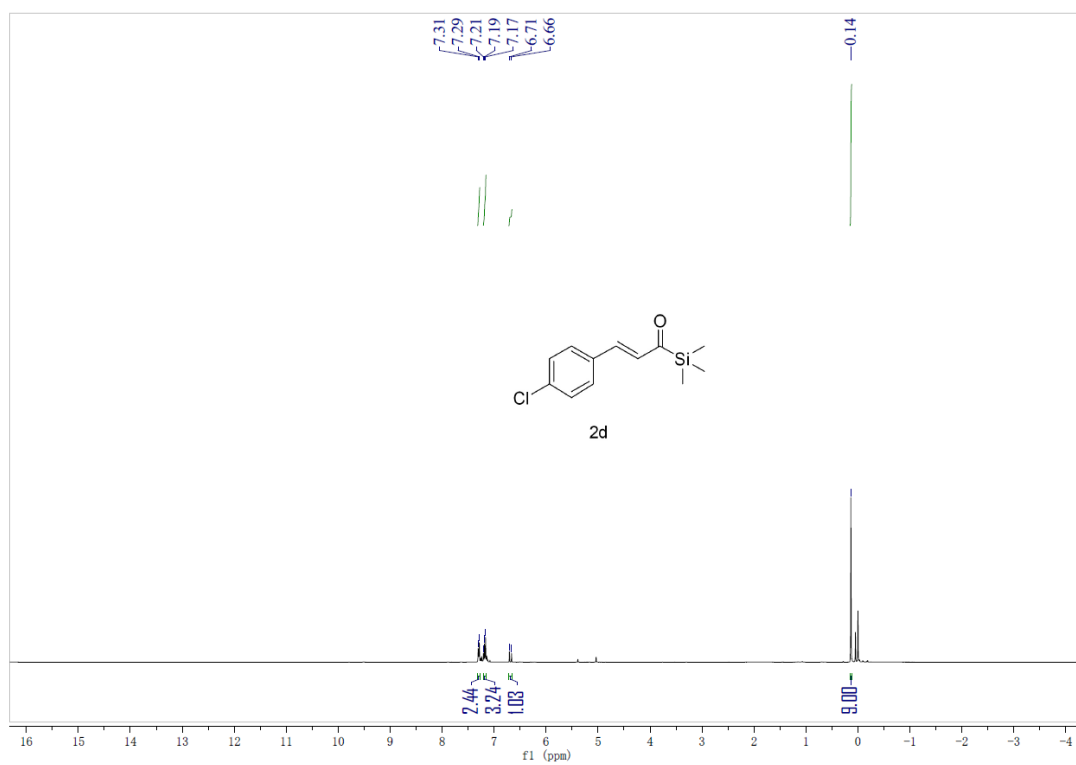
Note: ^a With Me₂Zn as a nucleophile. ^b With Ph₂Zn as a nucleophile. ^c With Et₃Al as a nucleophile. ^d nr is no reaction.

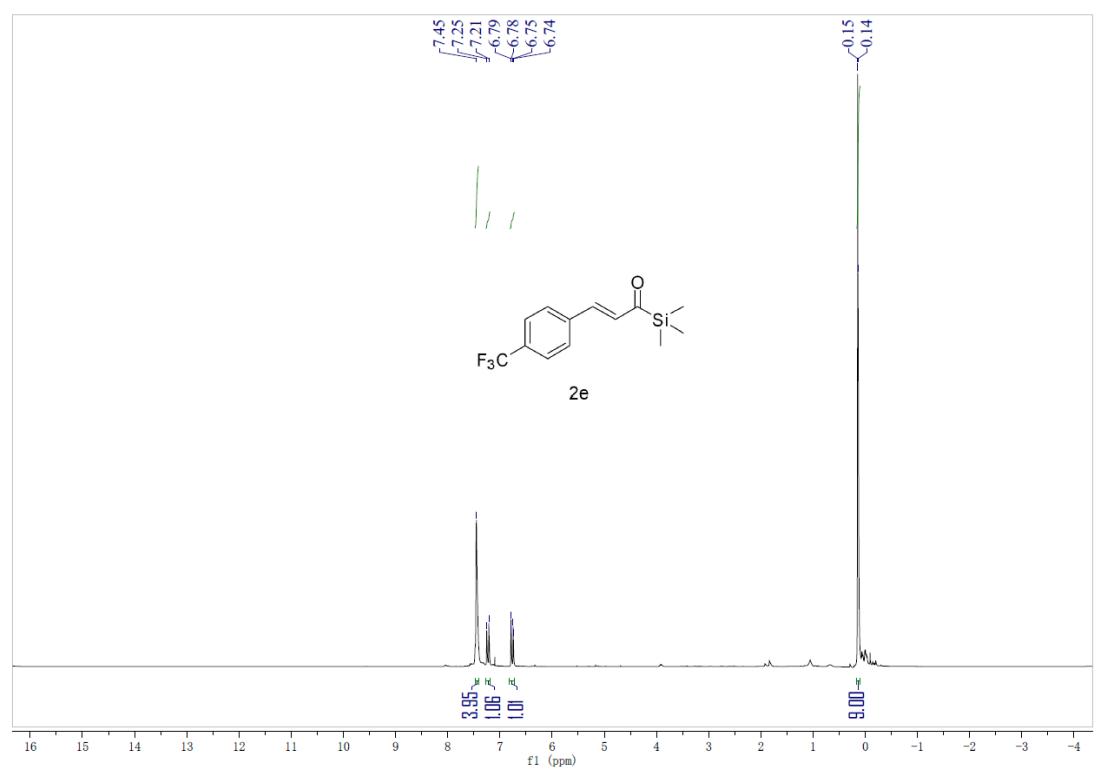
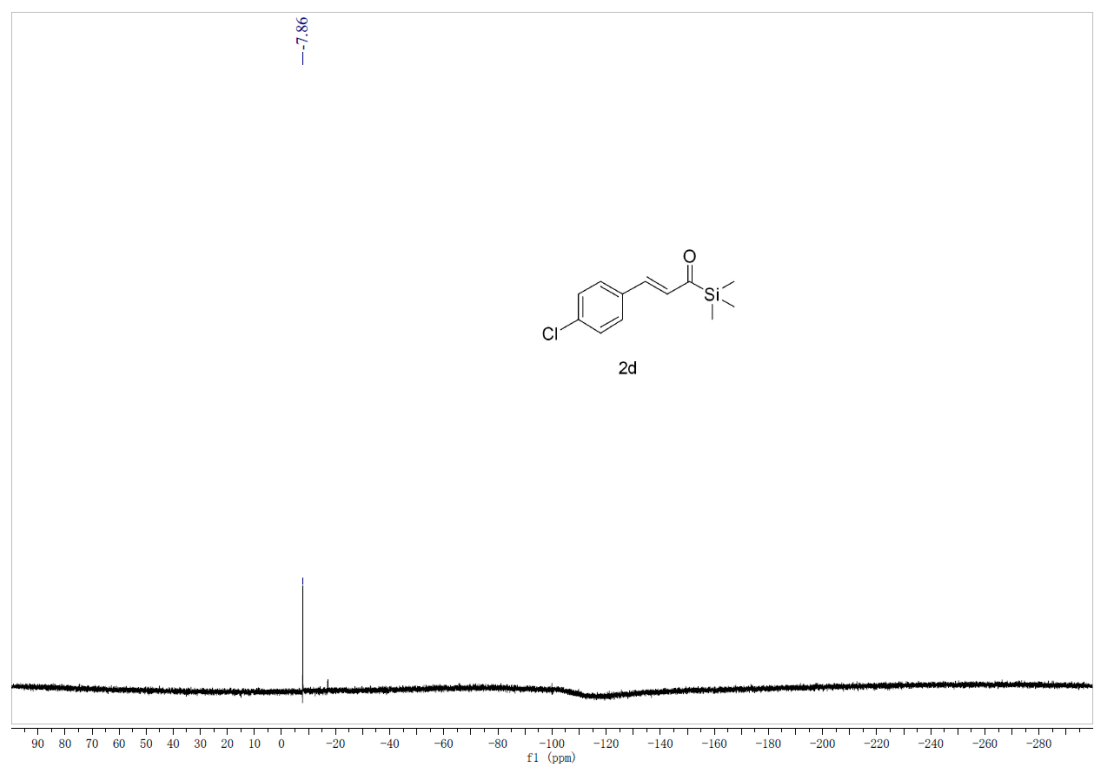
5. NMR Charts of Products (1H , 13C, 19F and 29Si NMR Spectra)

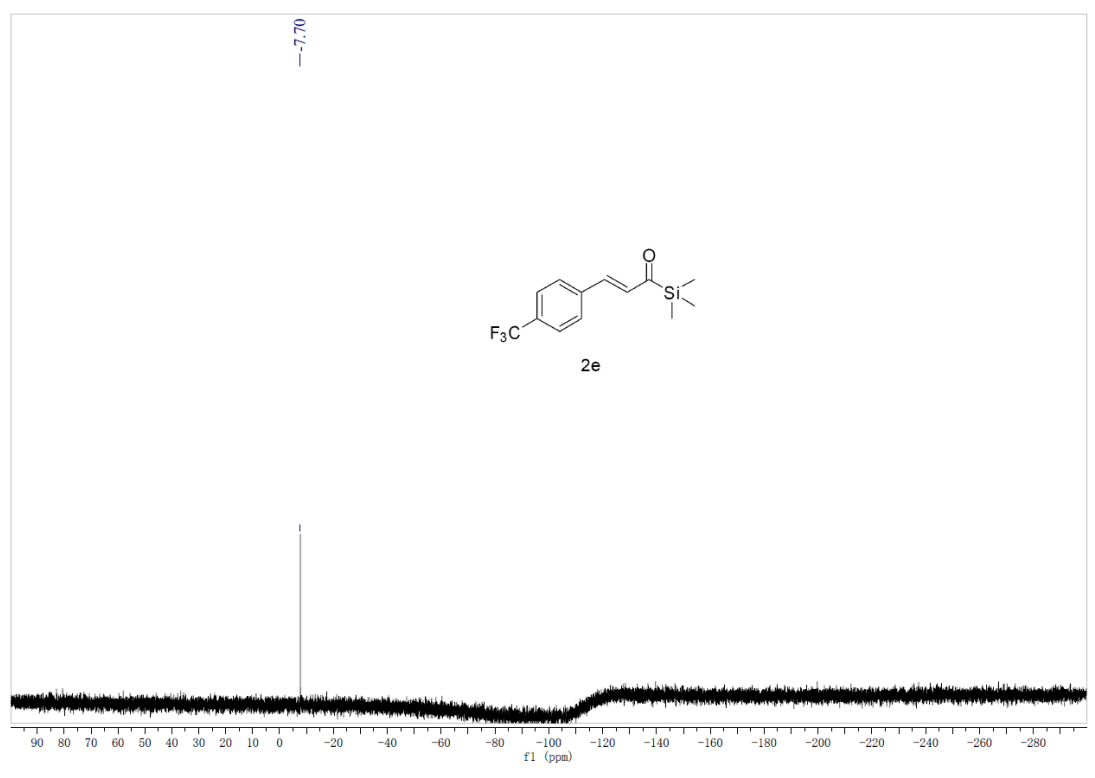
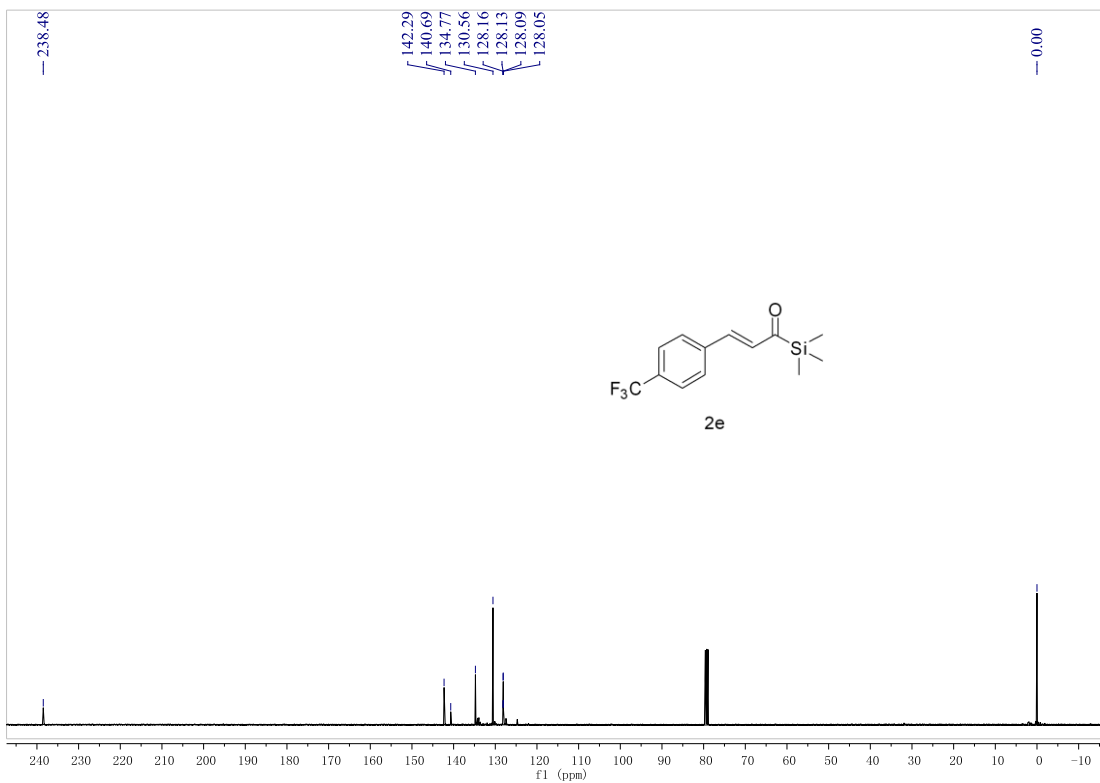


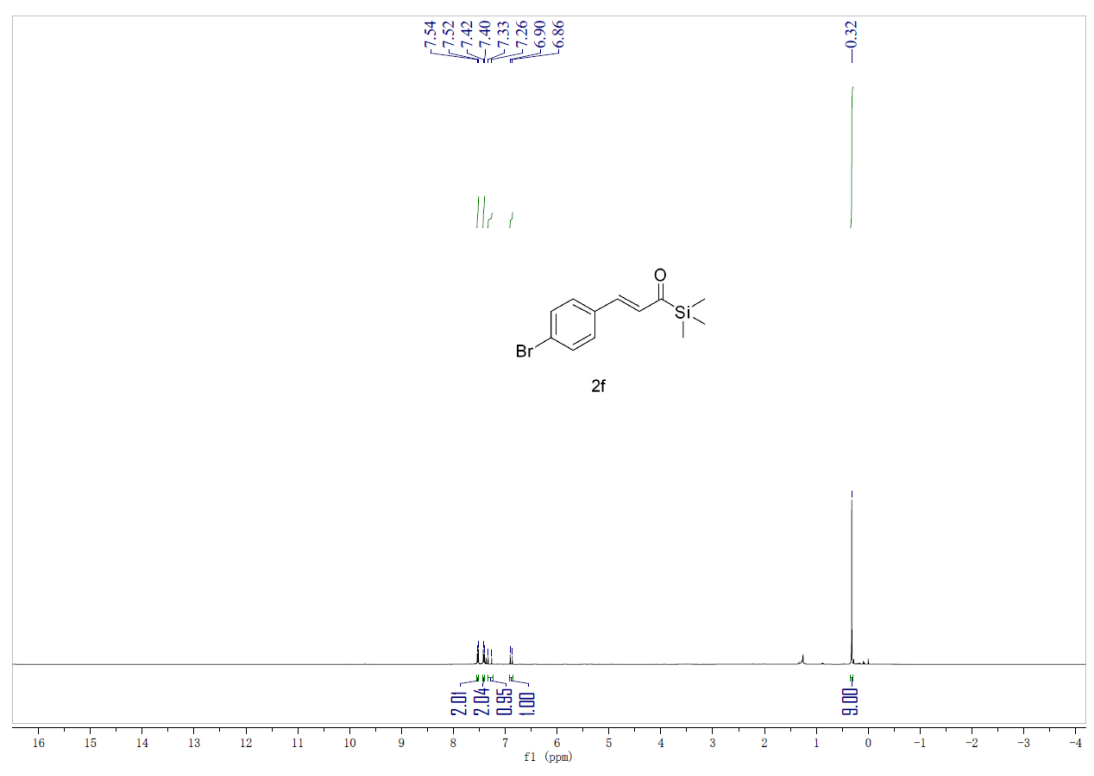
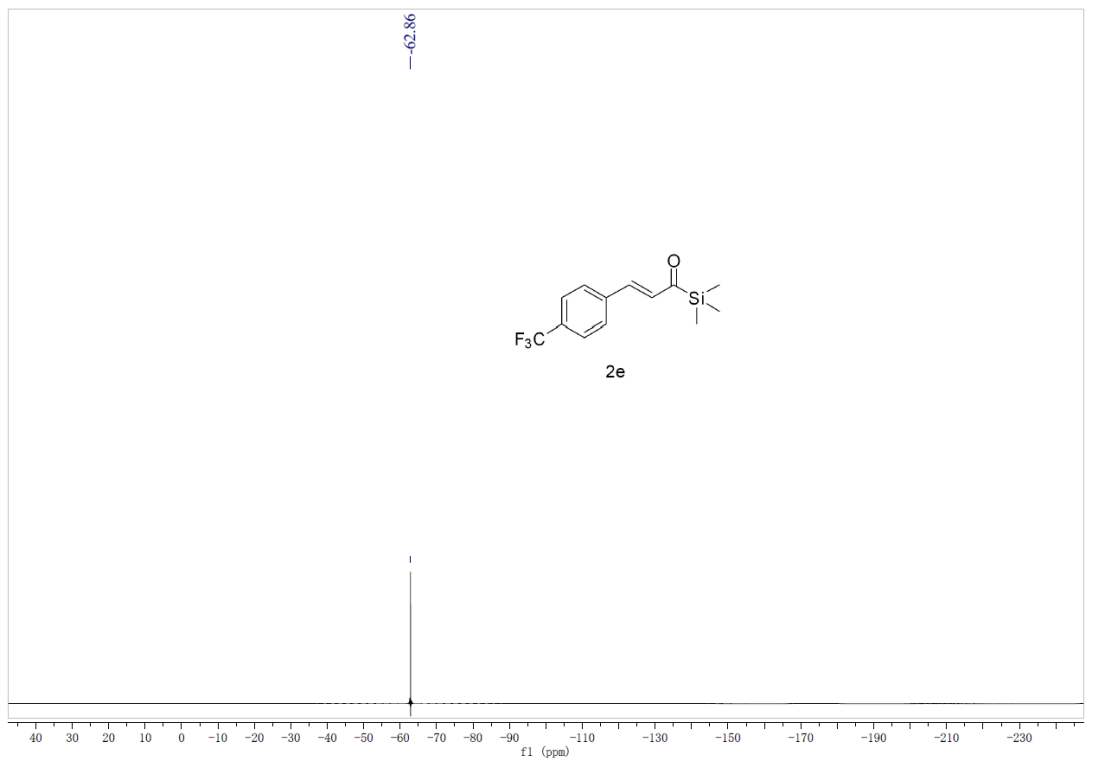


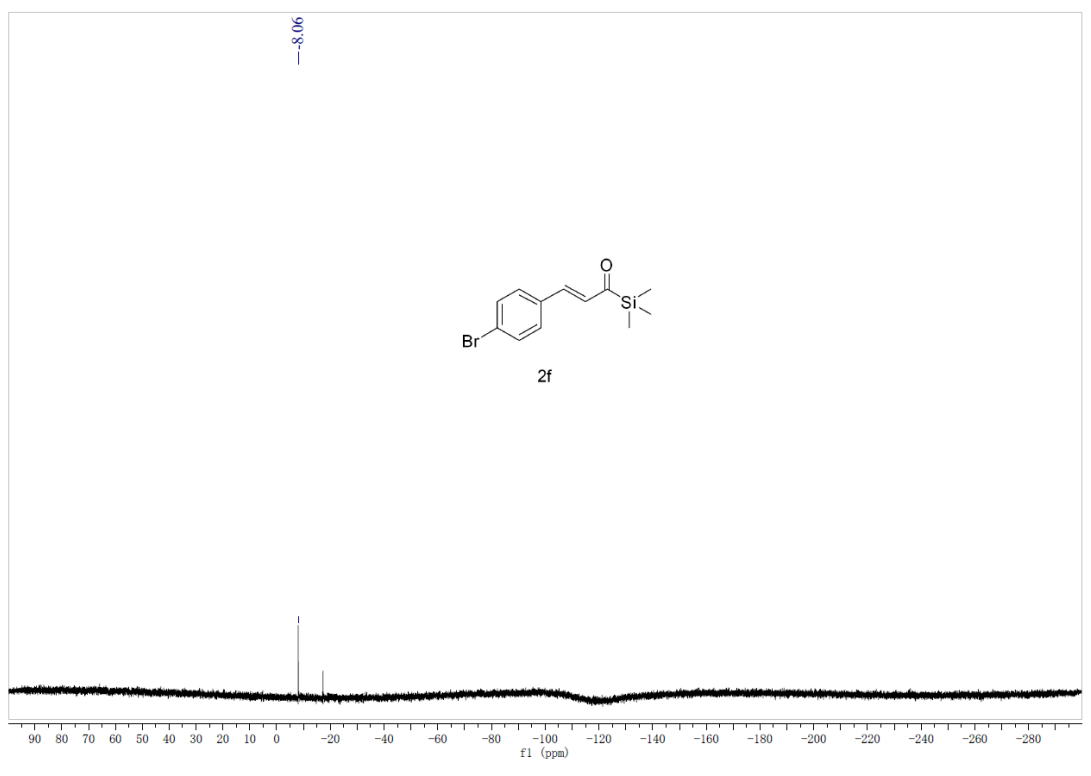
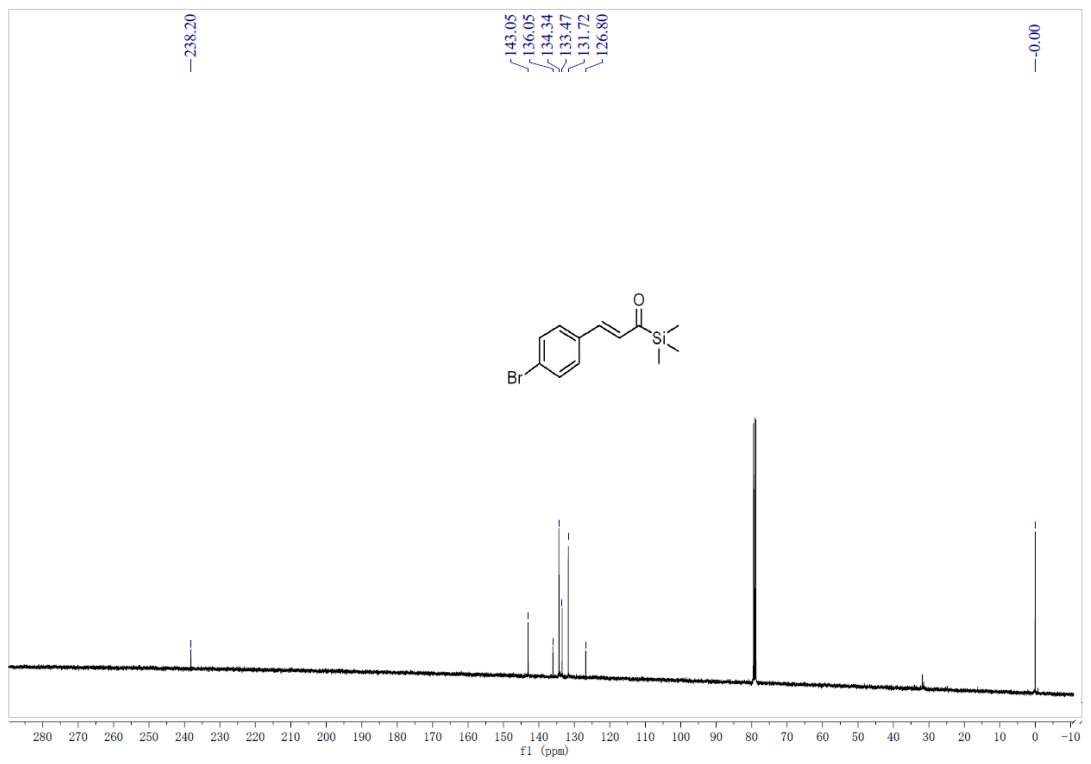


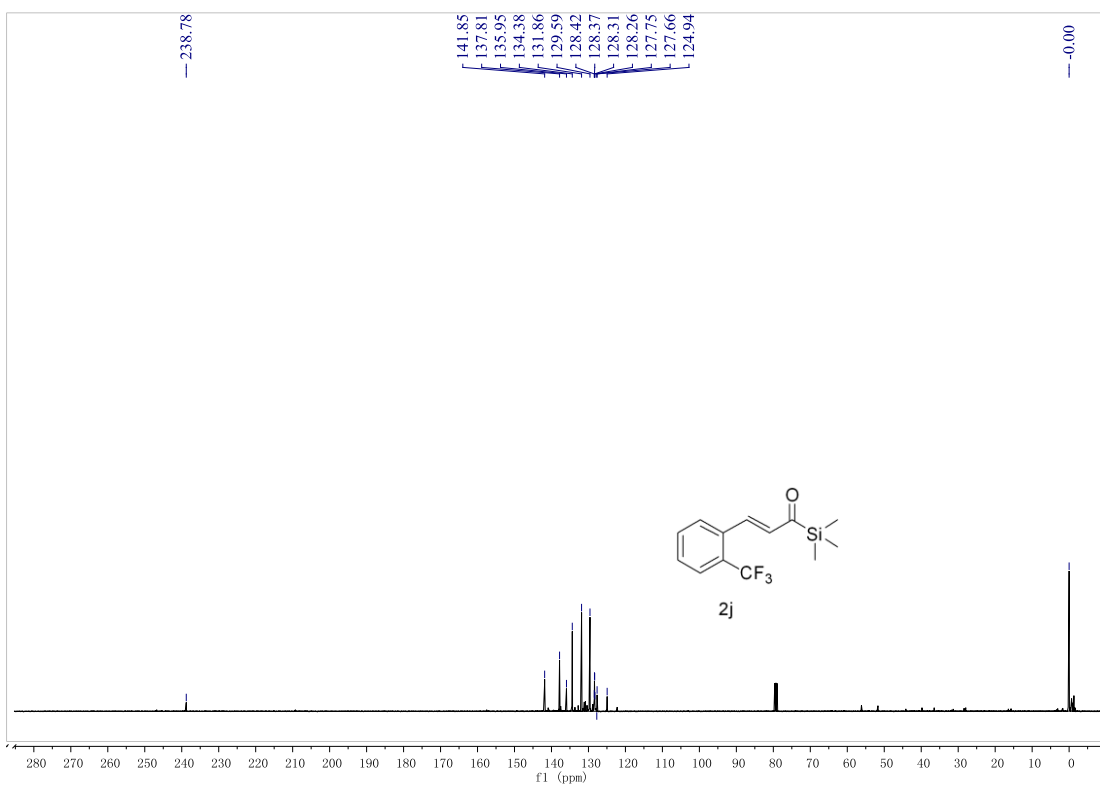
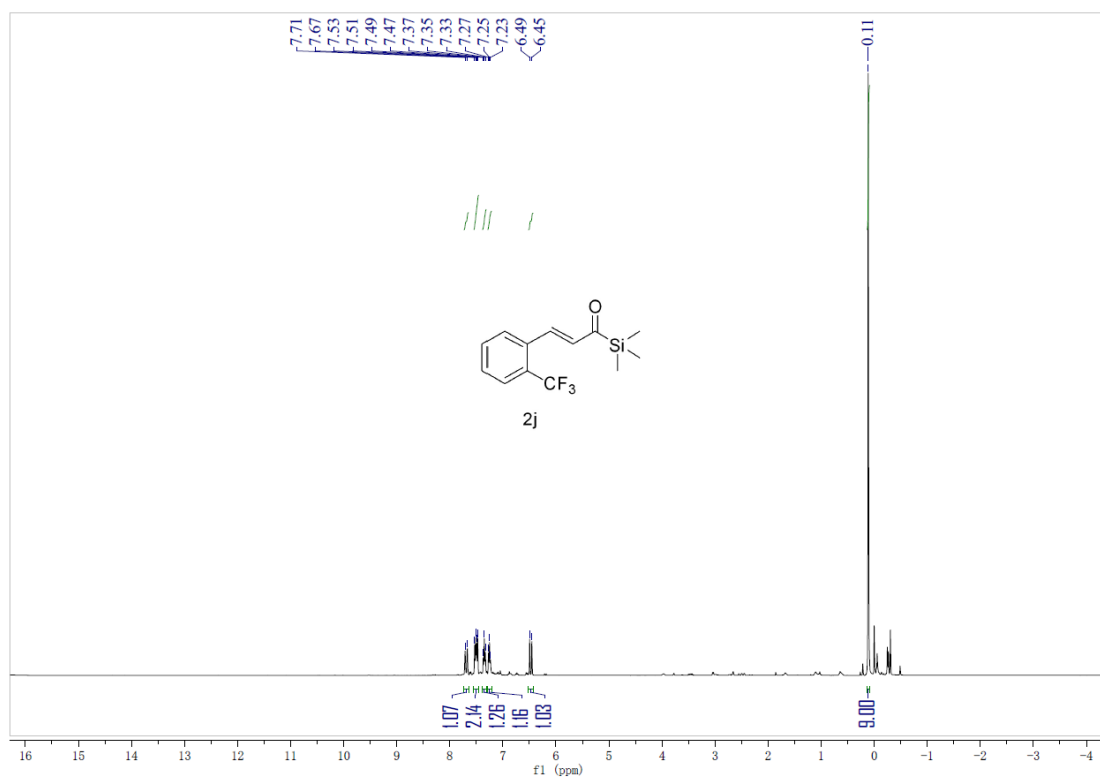


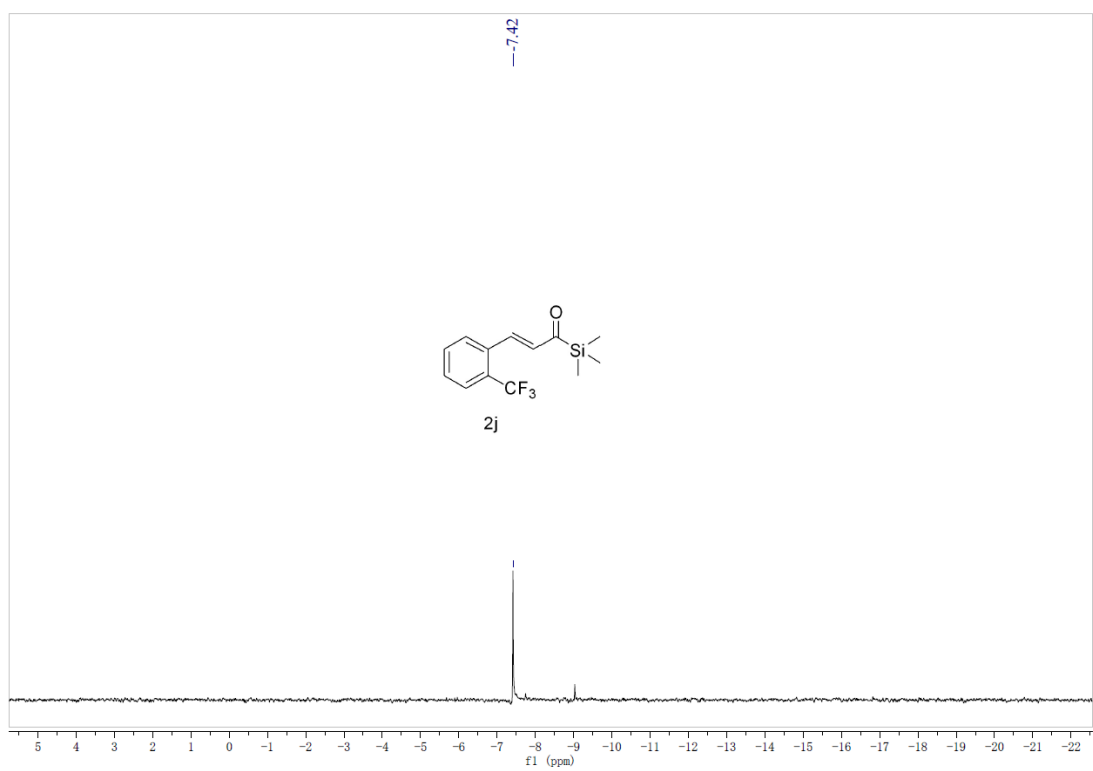
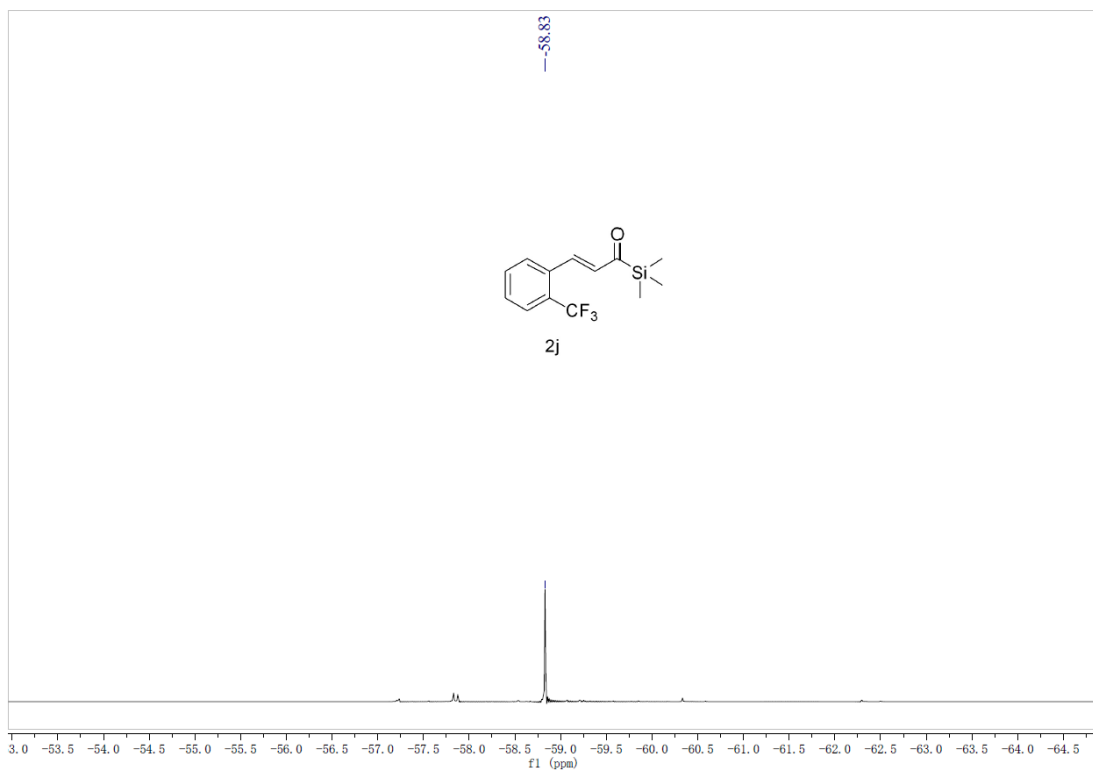


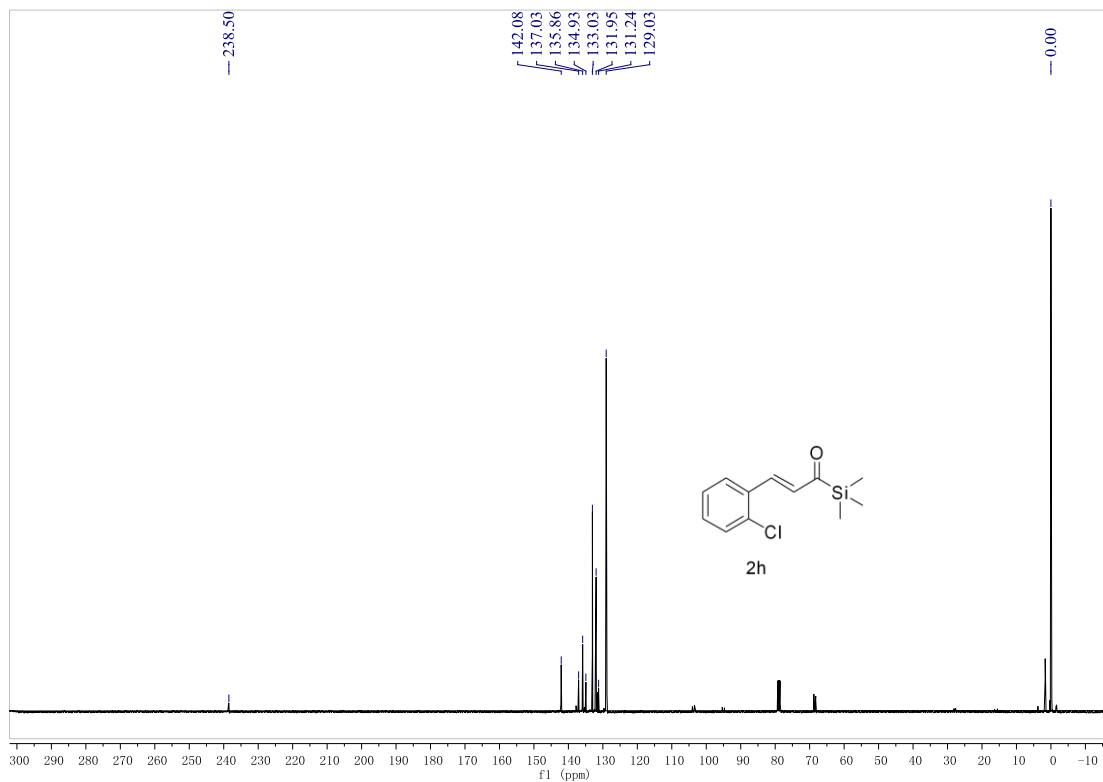
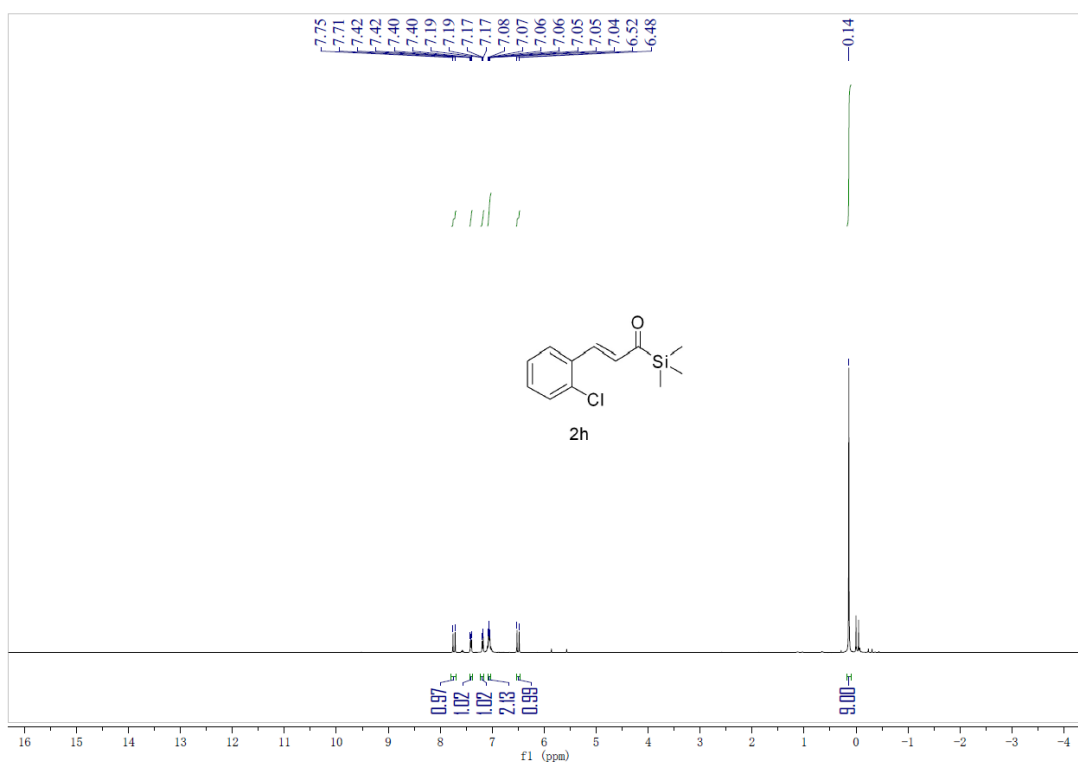


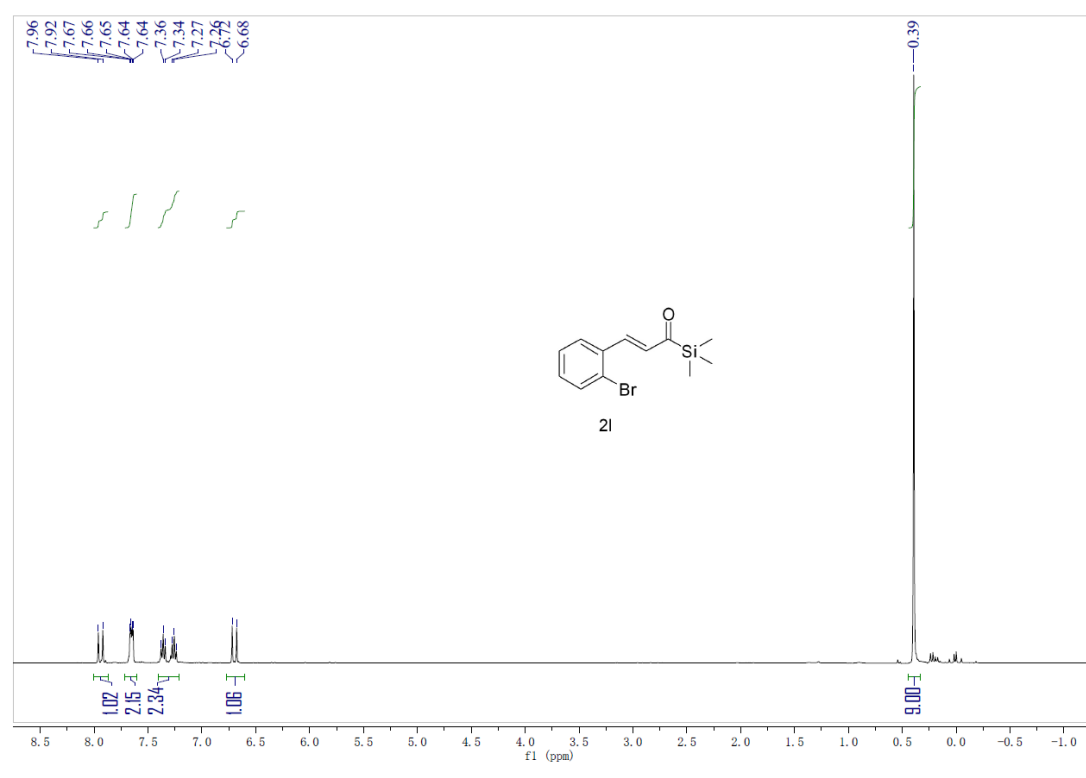
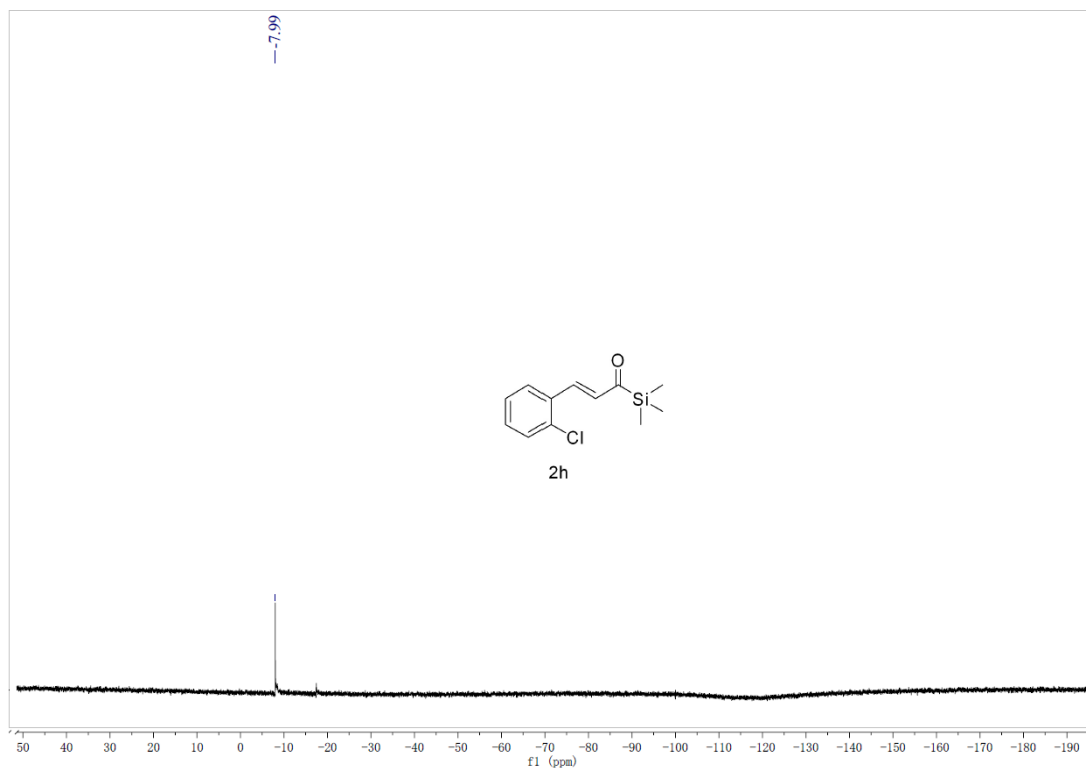


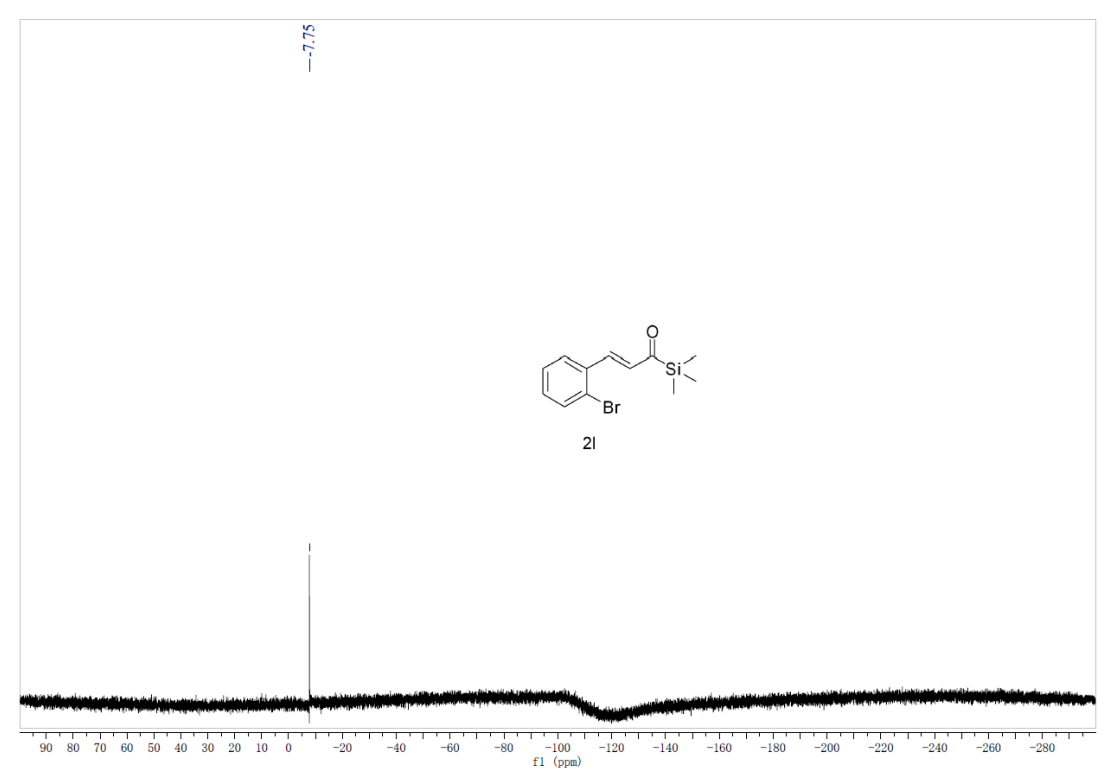
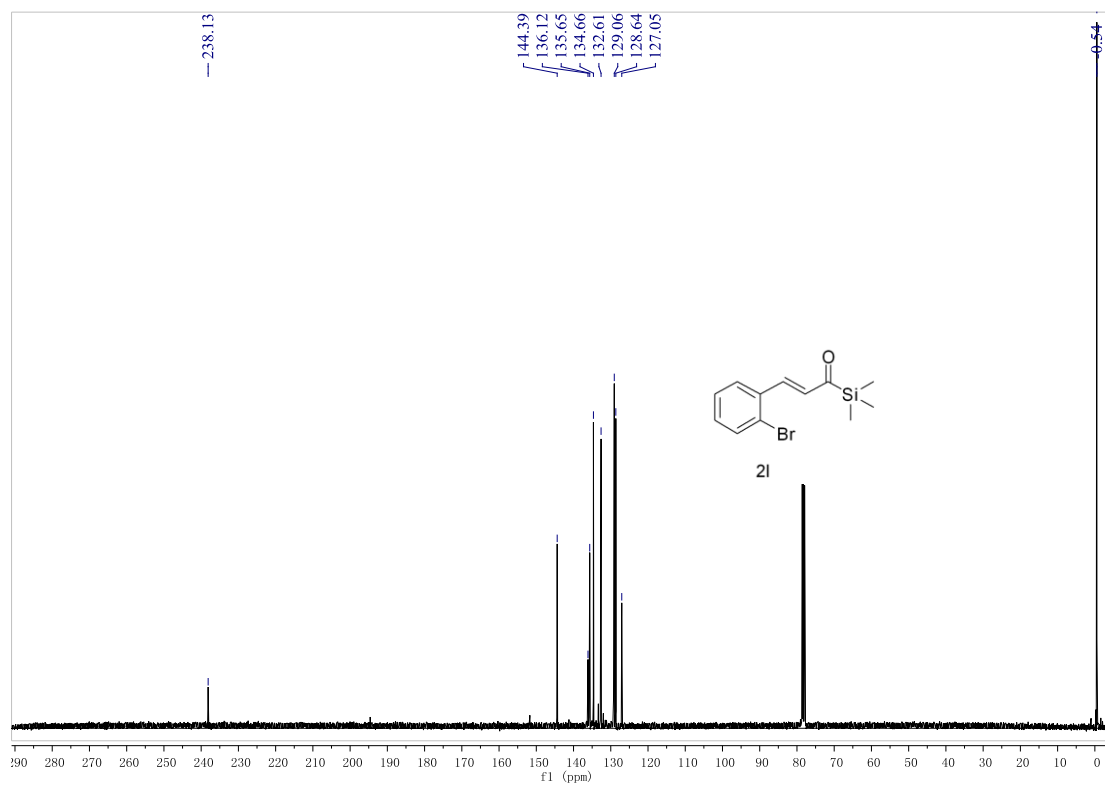


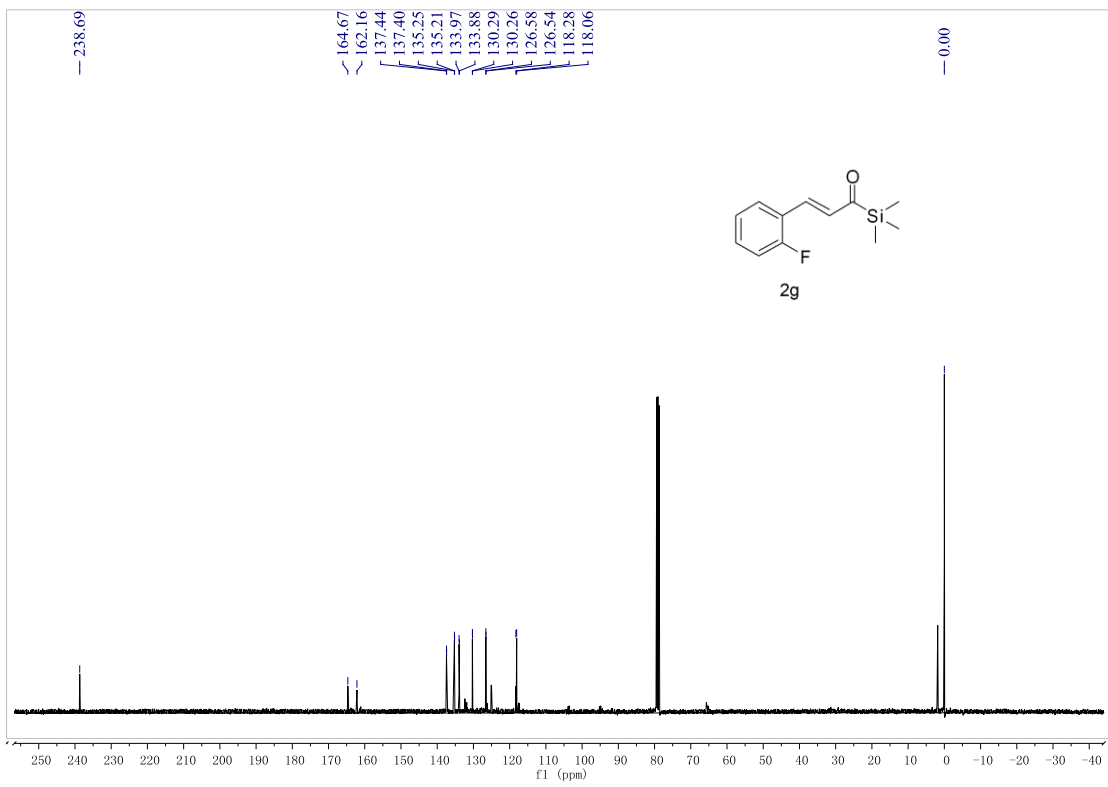
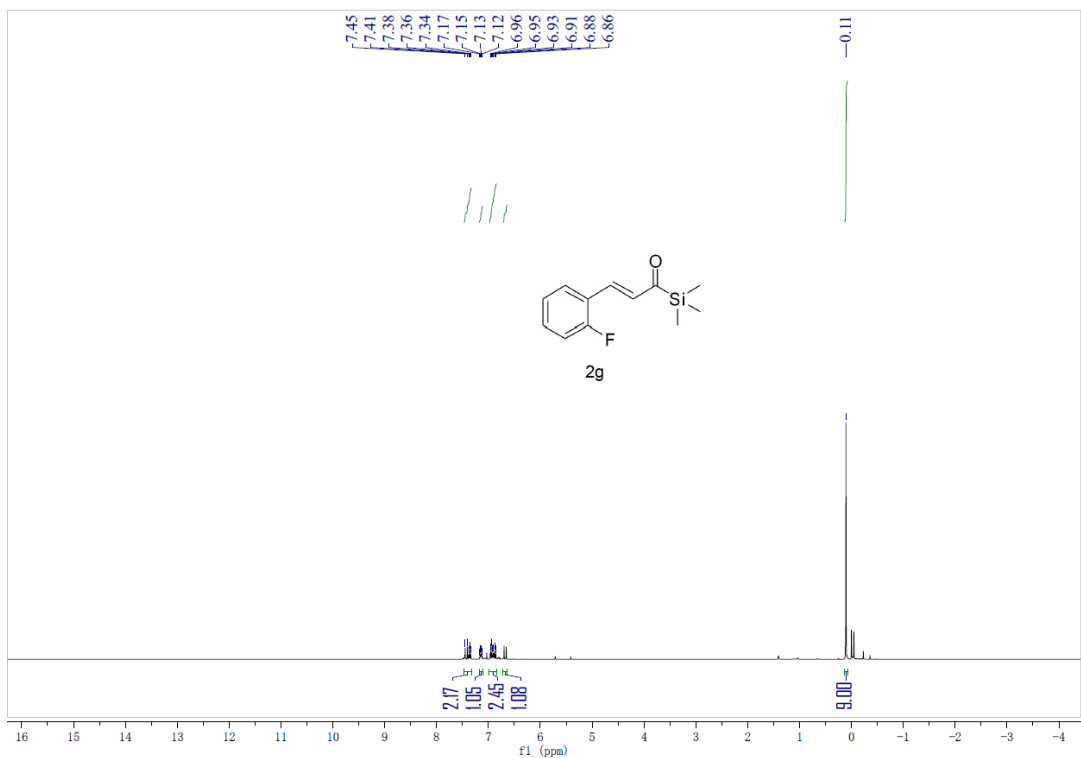


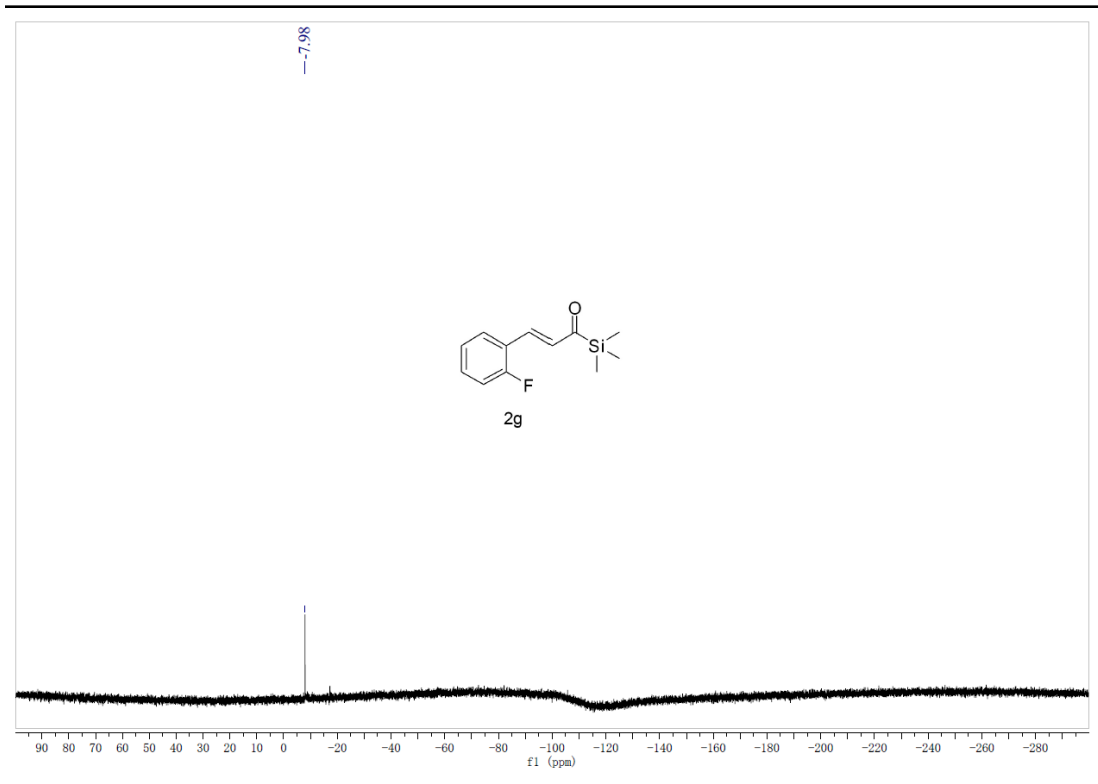
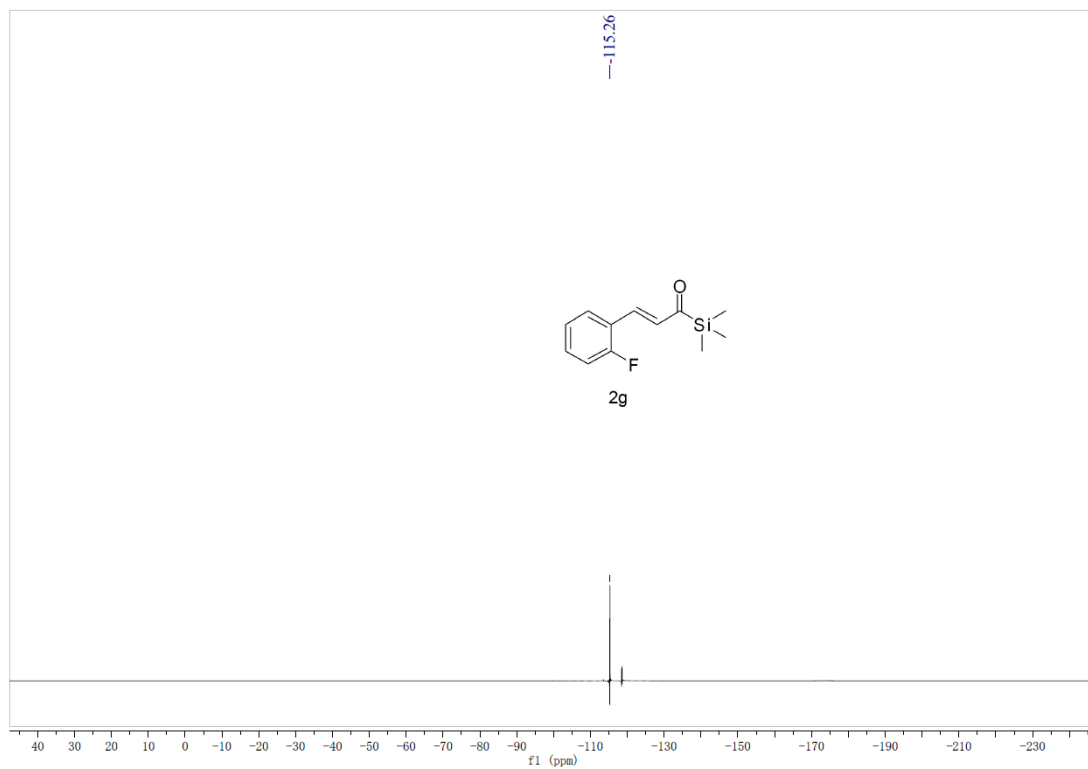


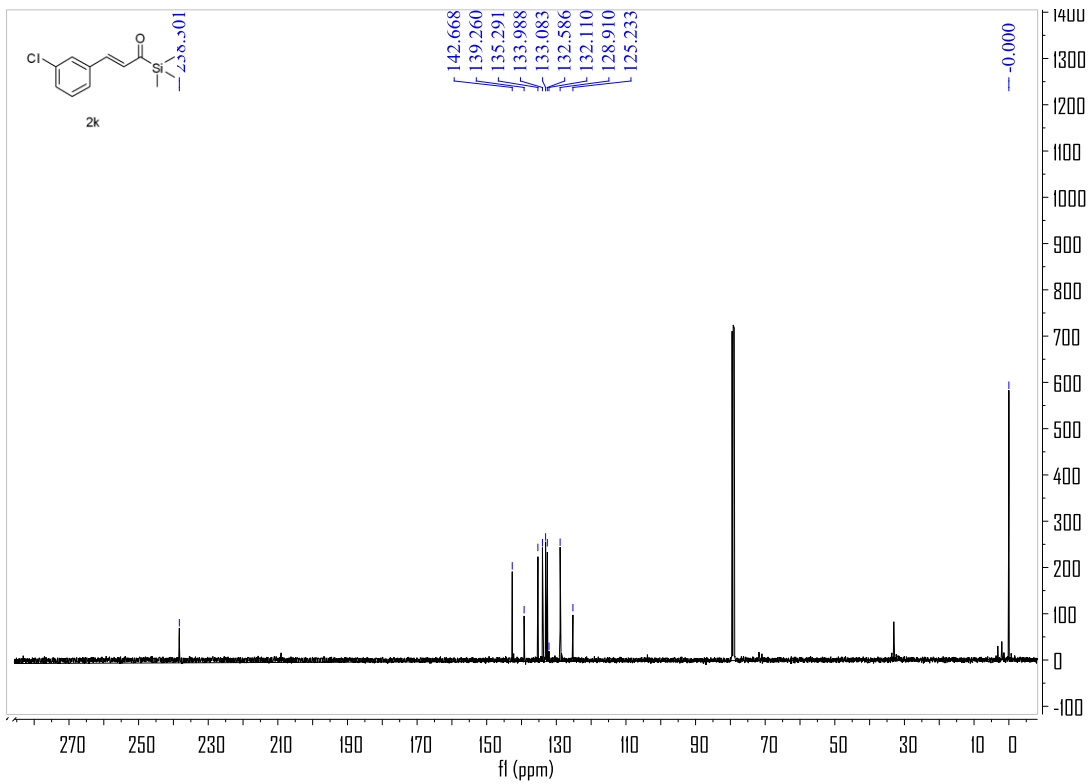
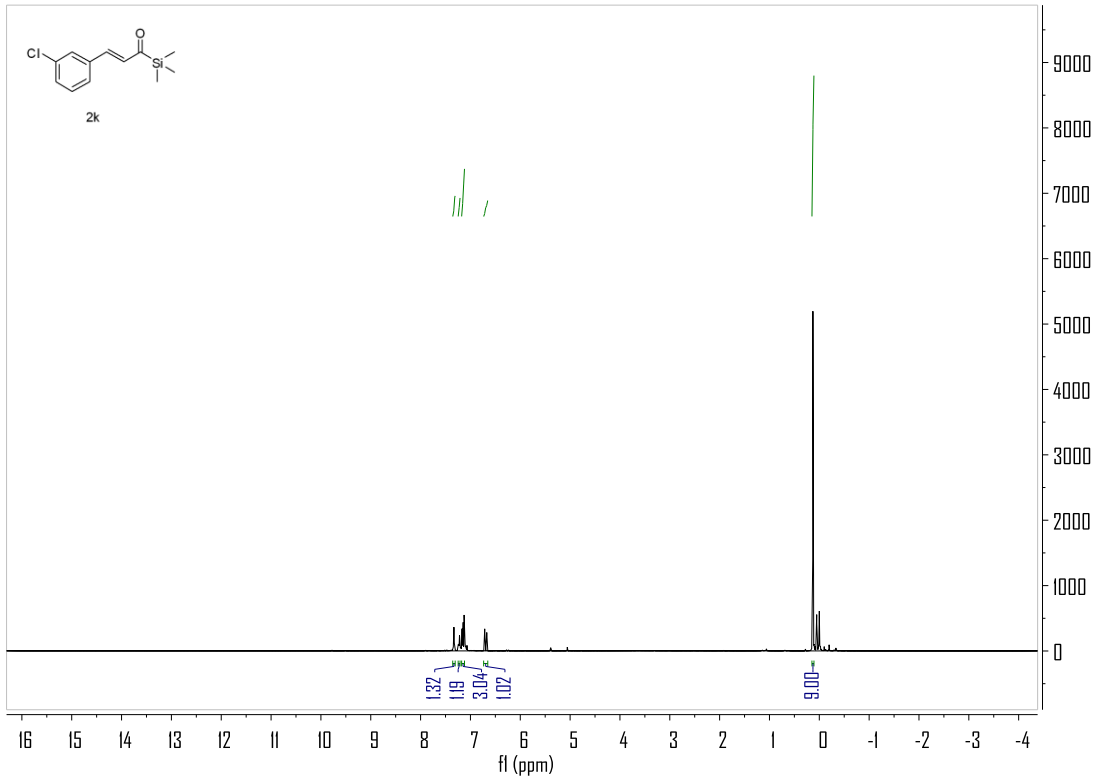


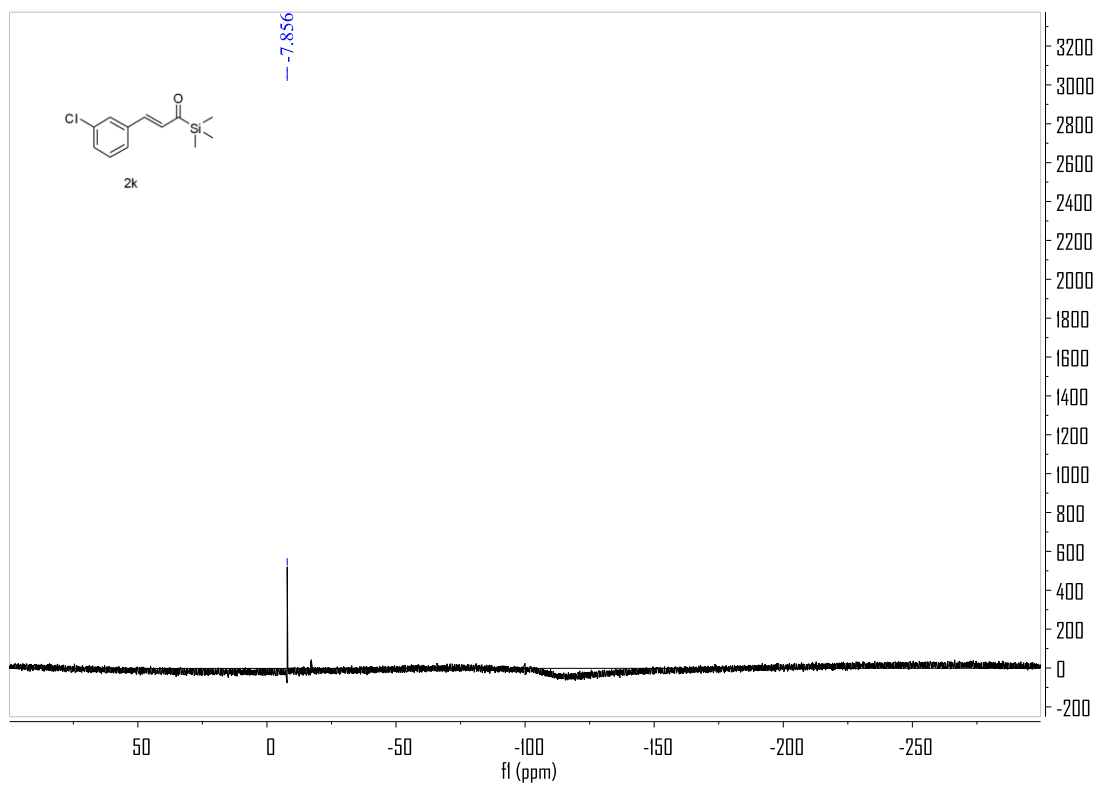


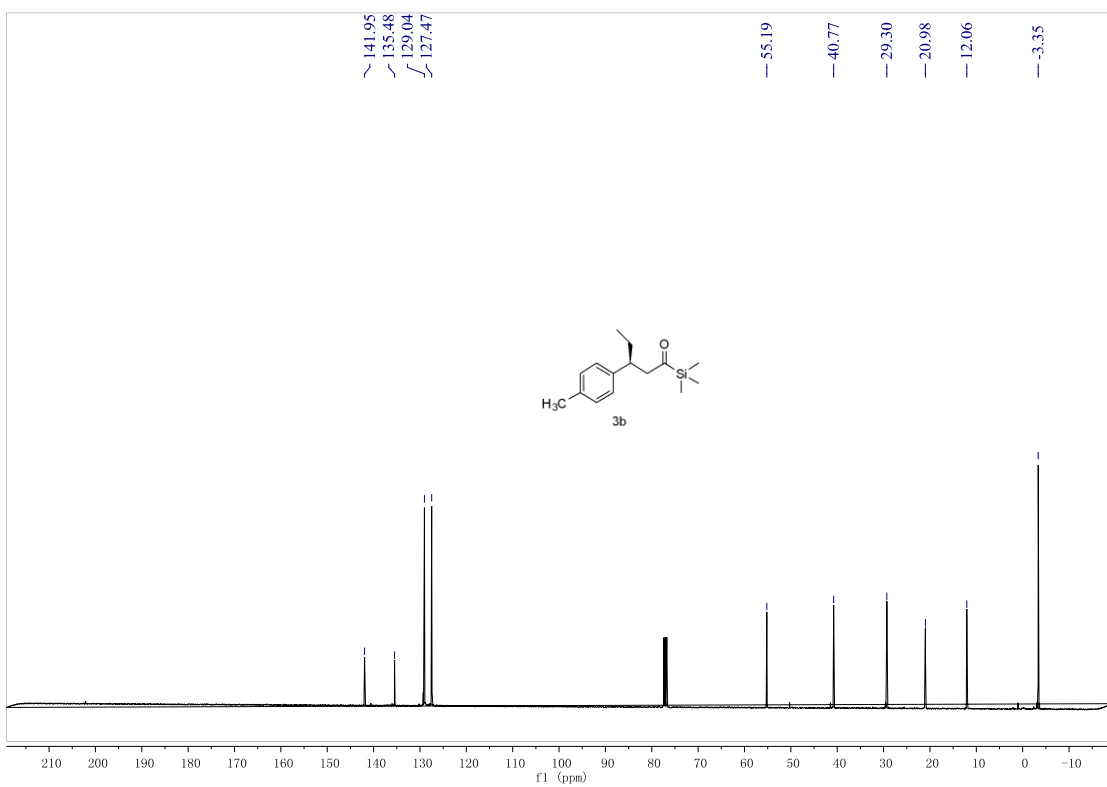
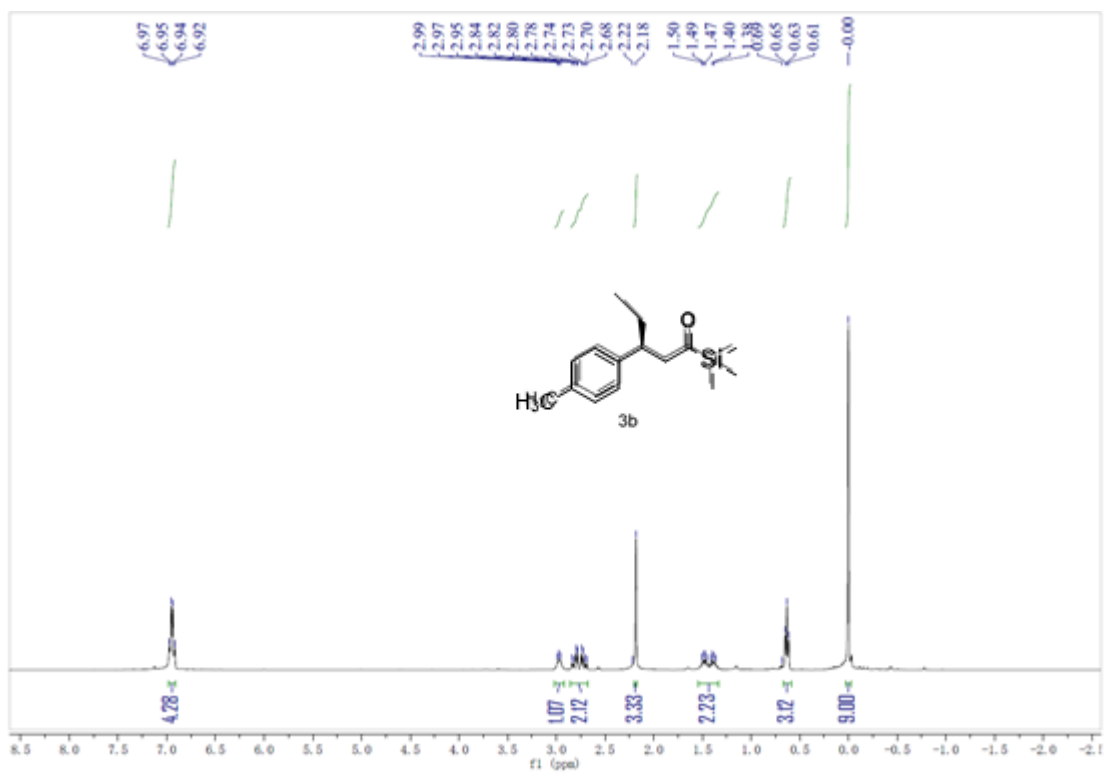


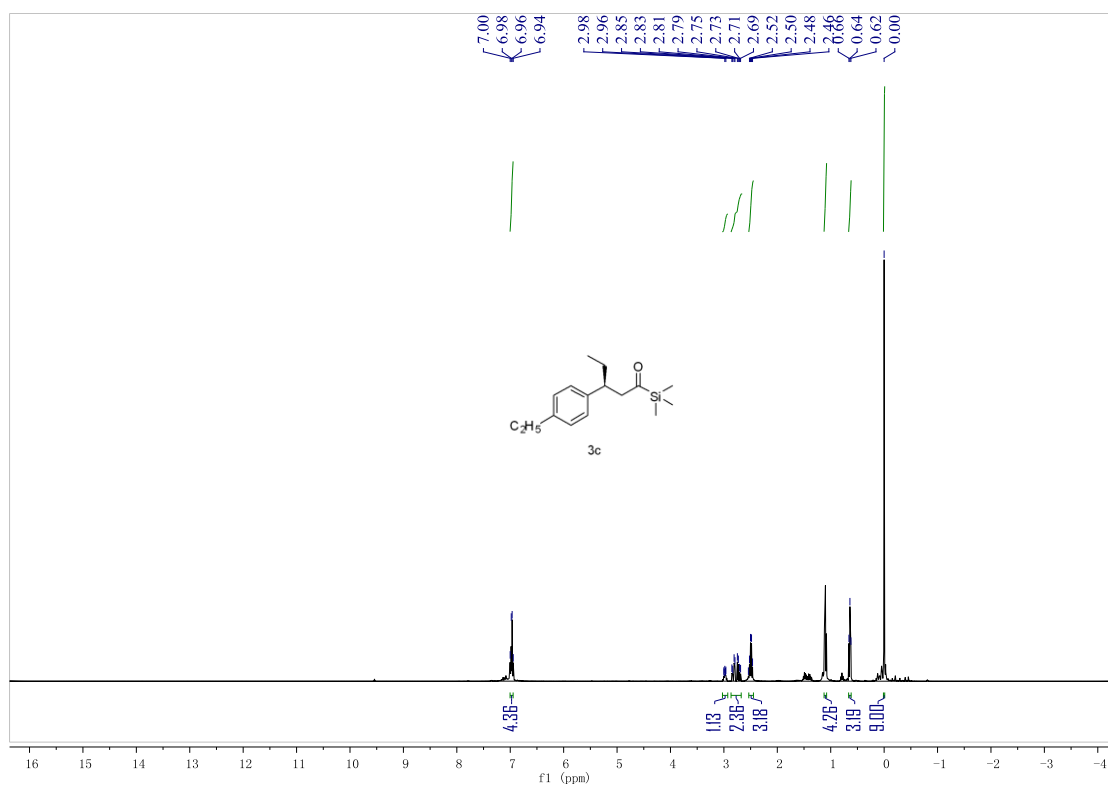
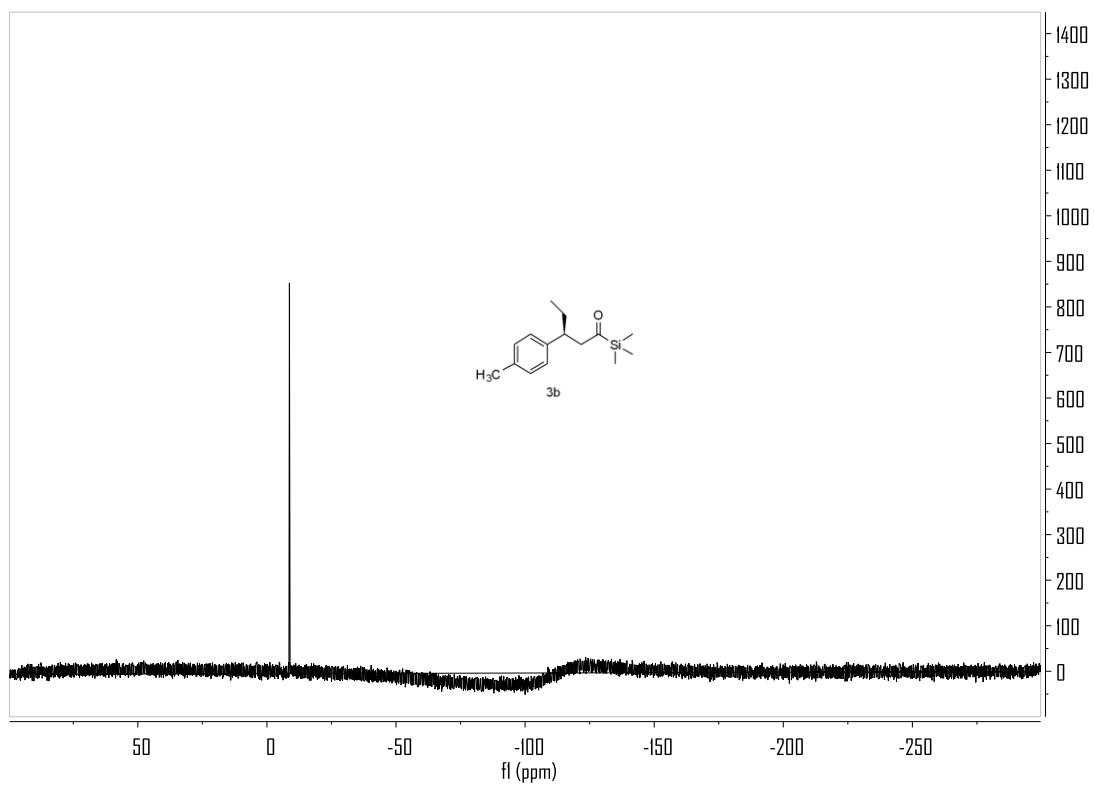


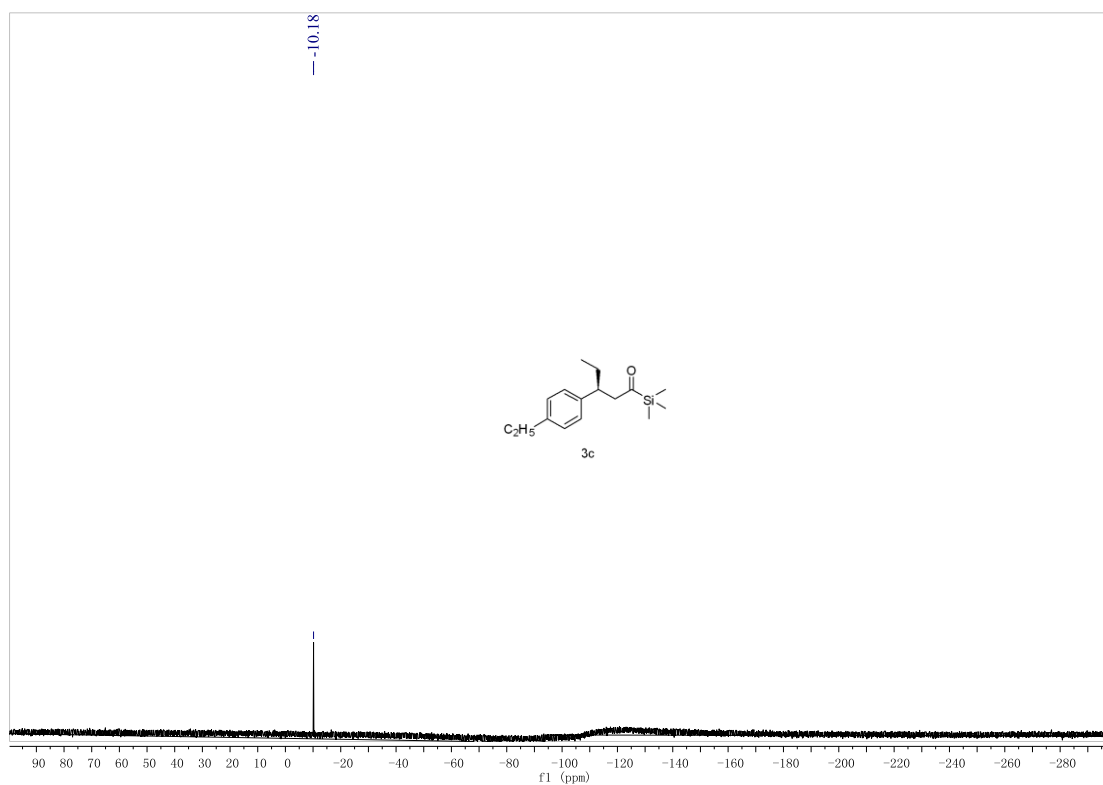
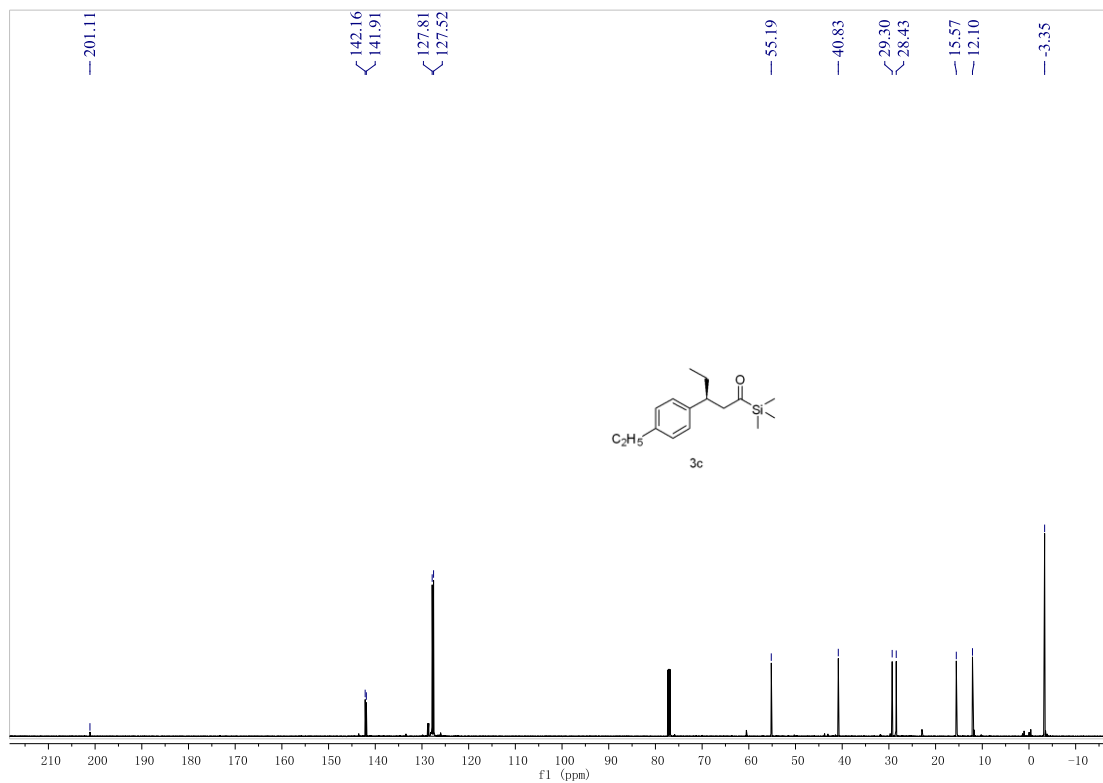


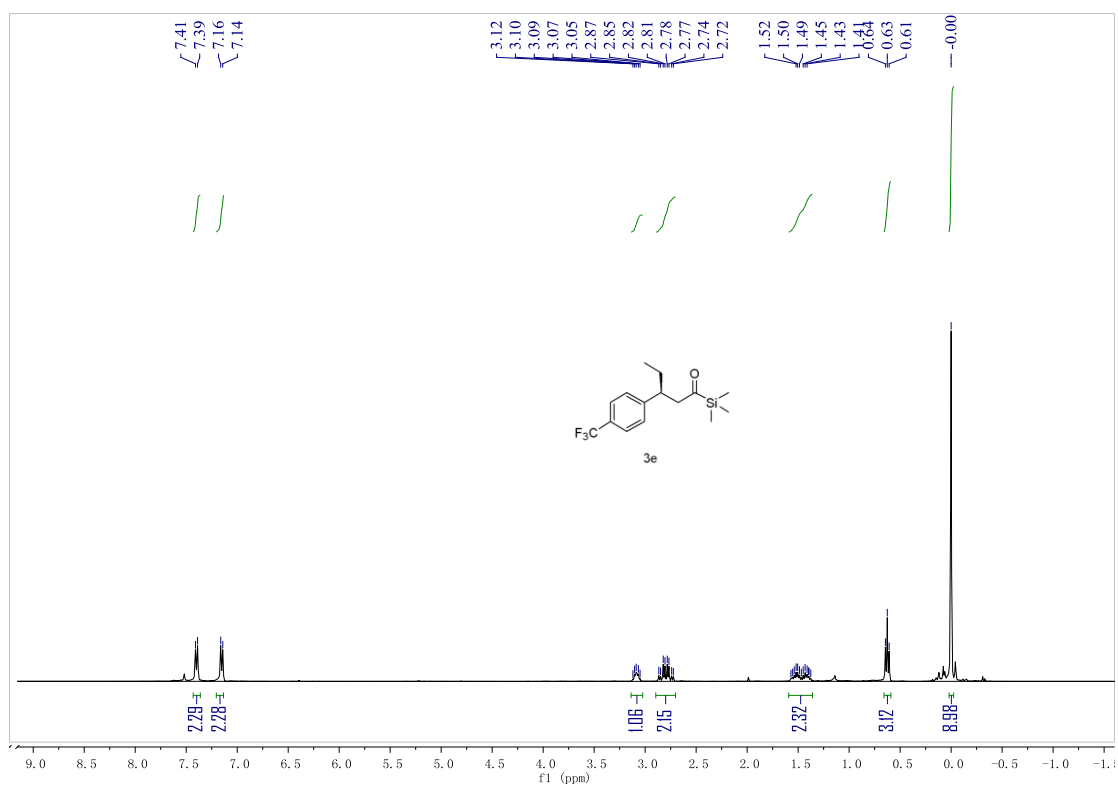
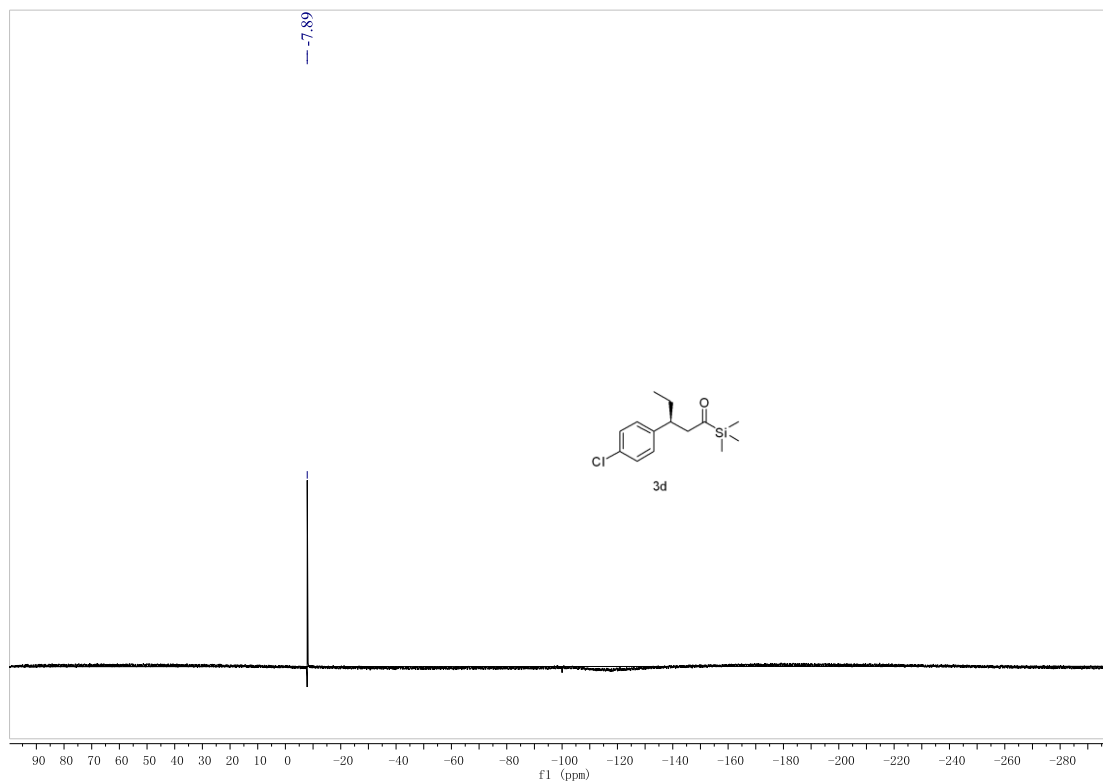


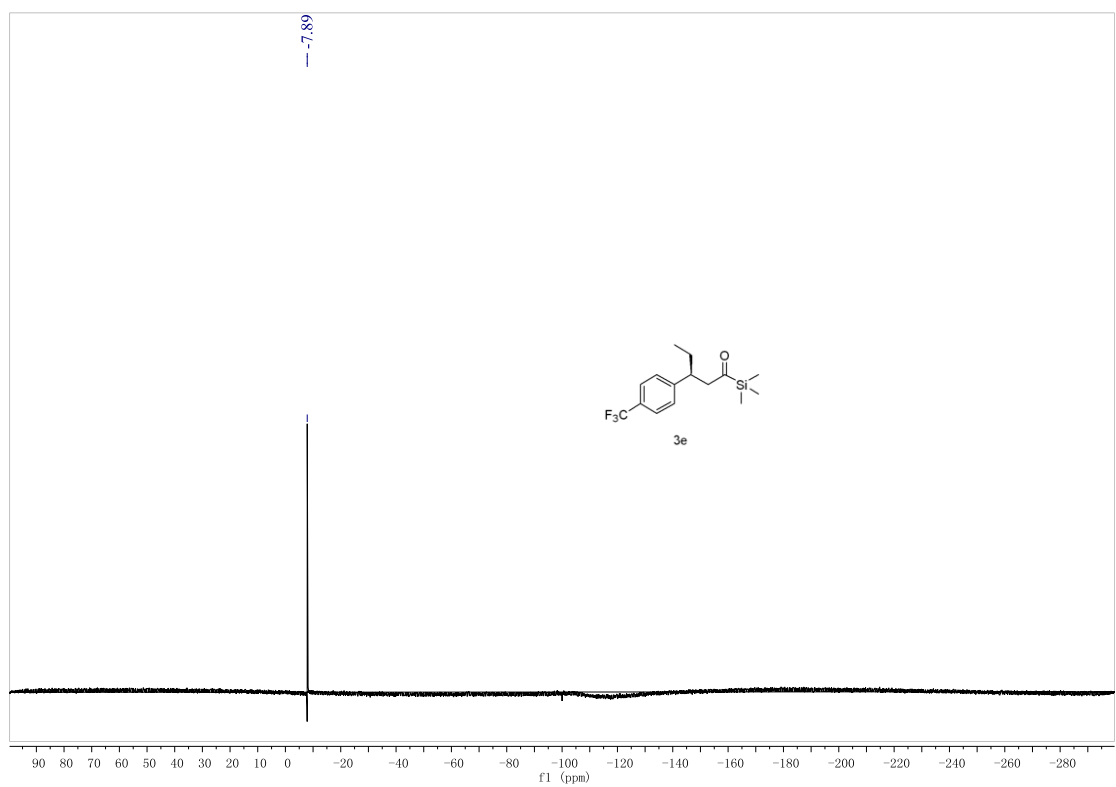
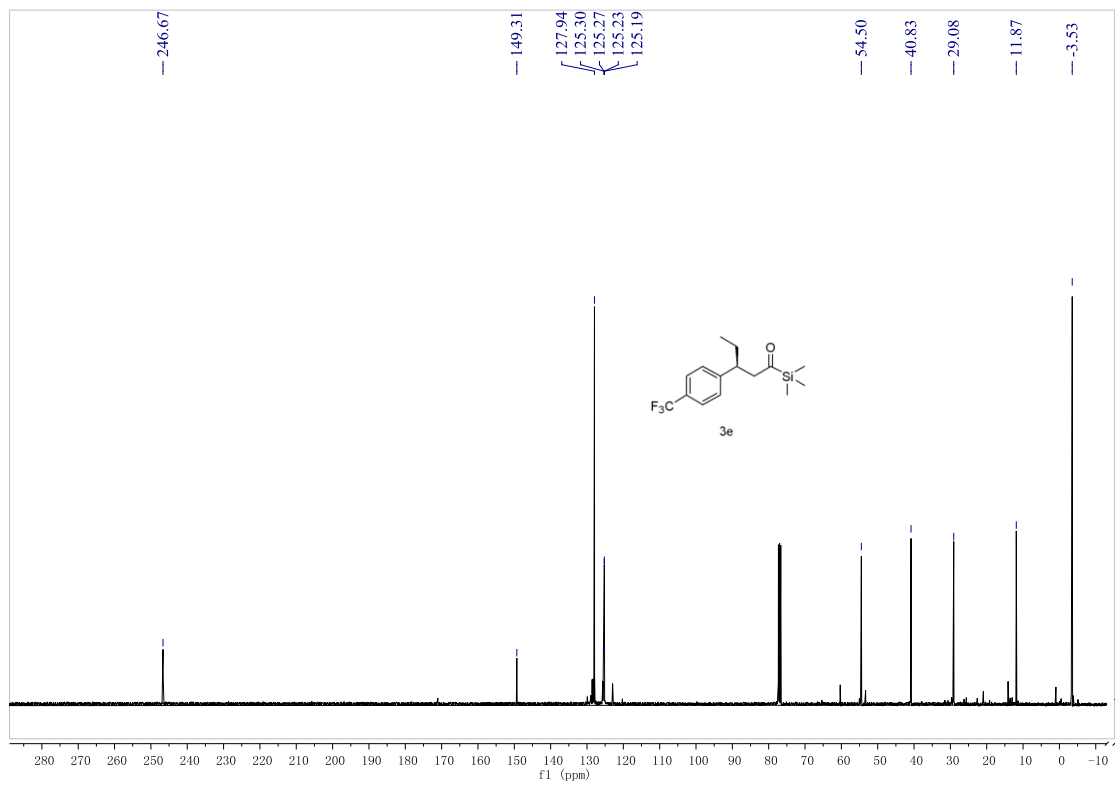


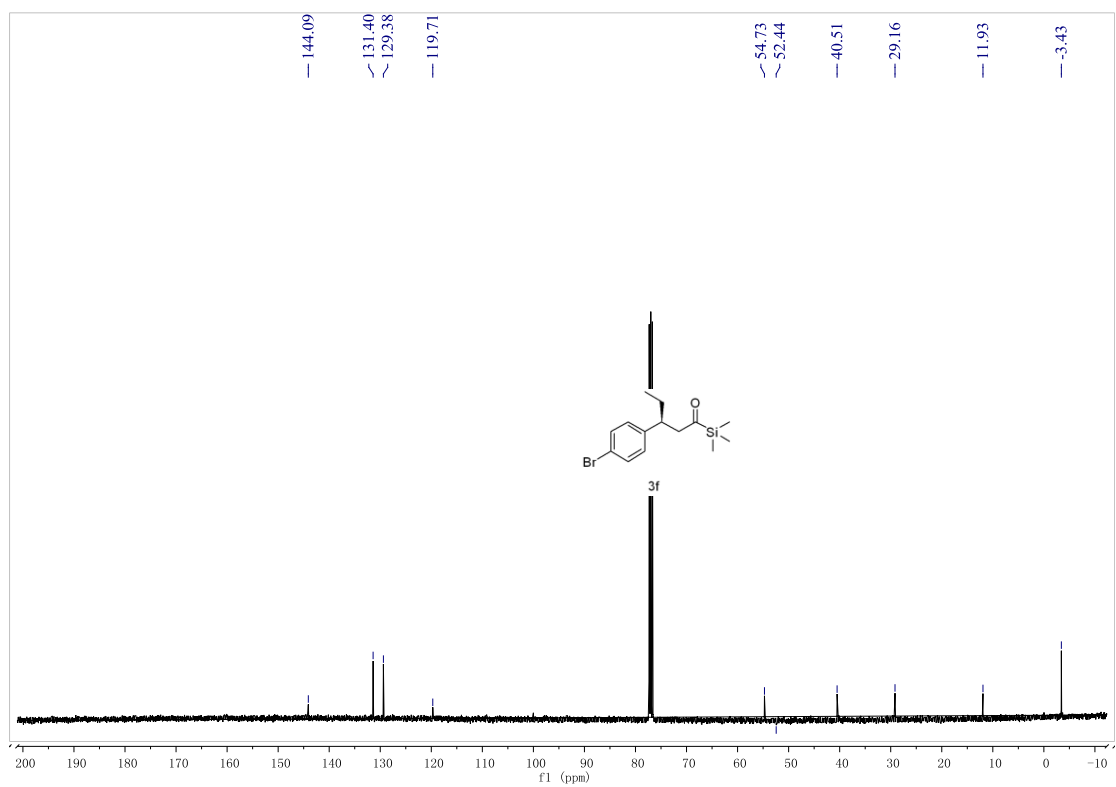
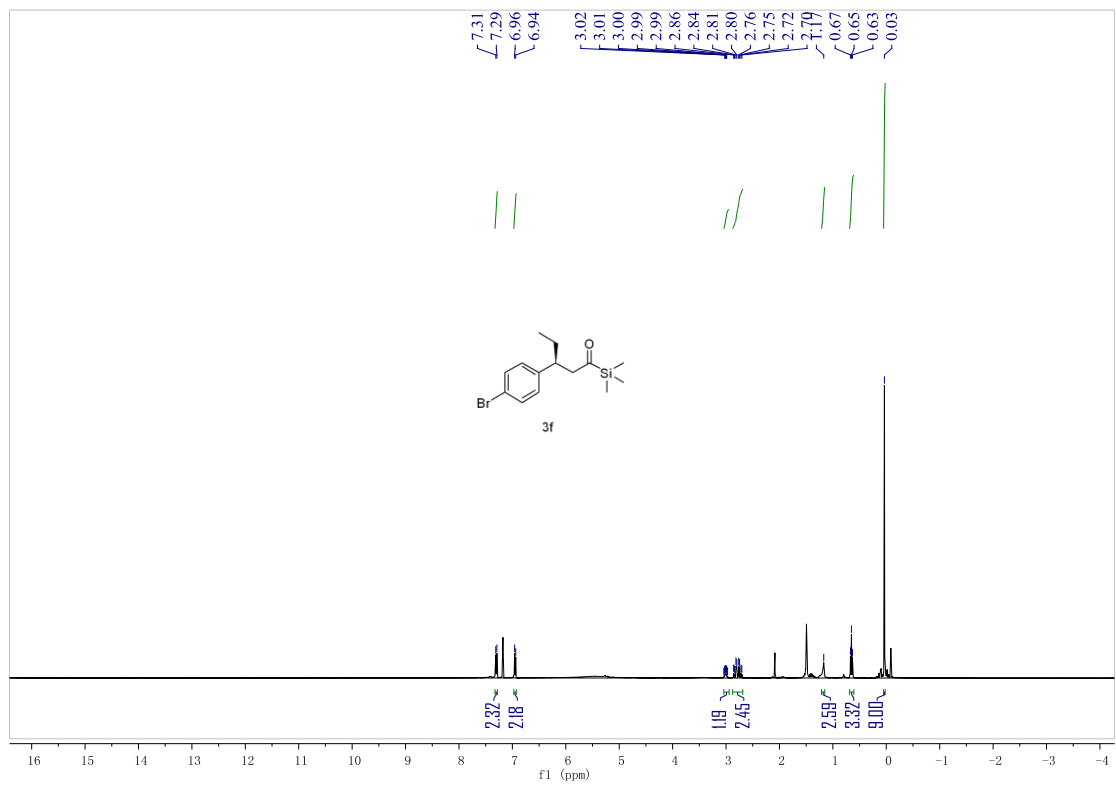


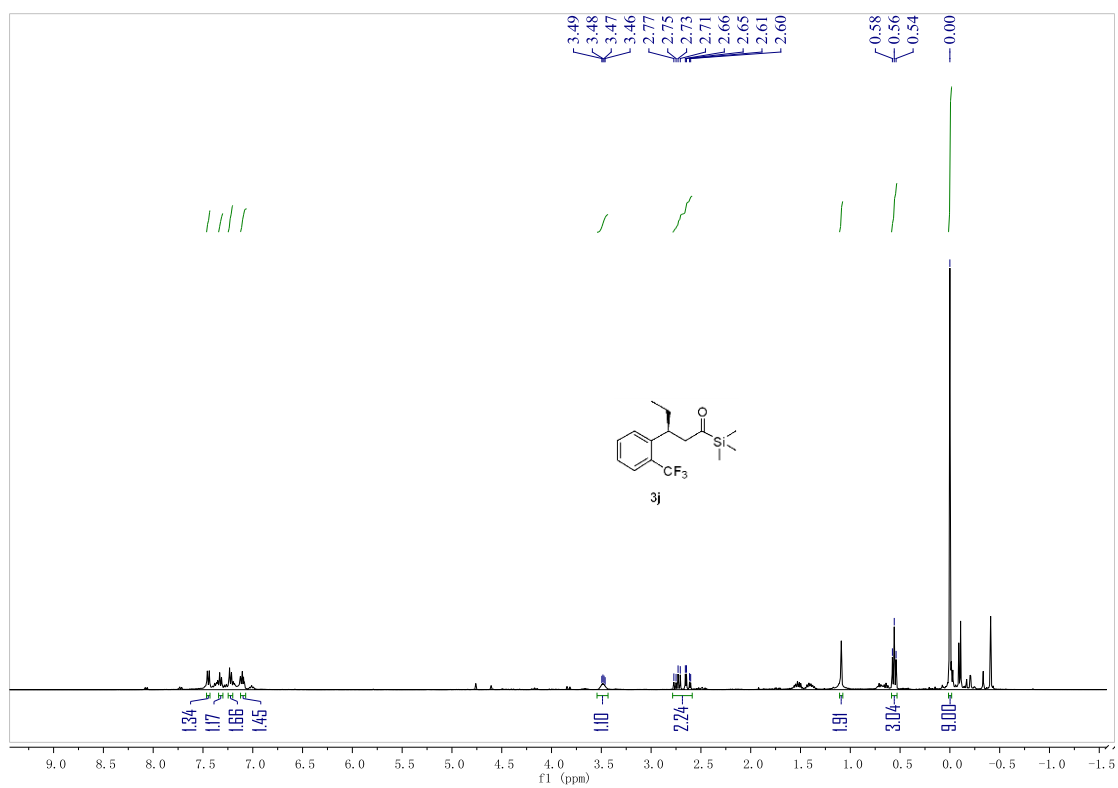
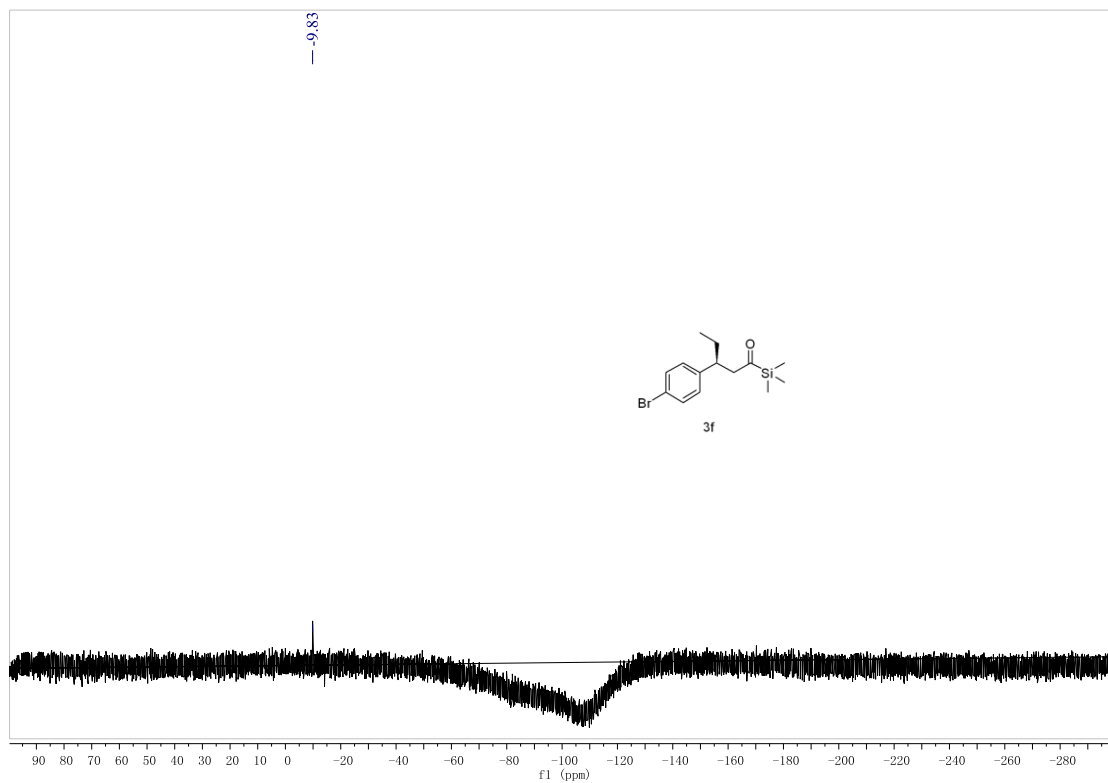


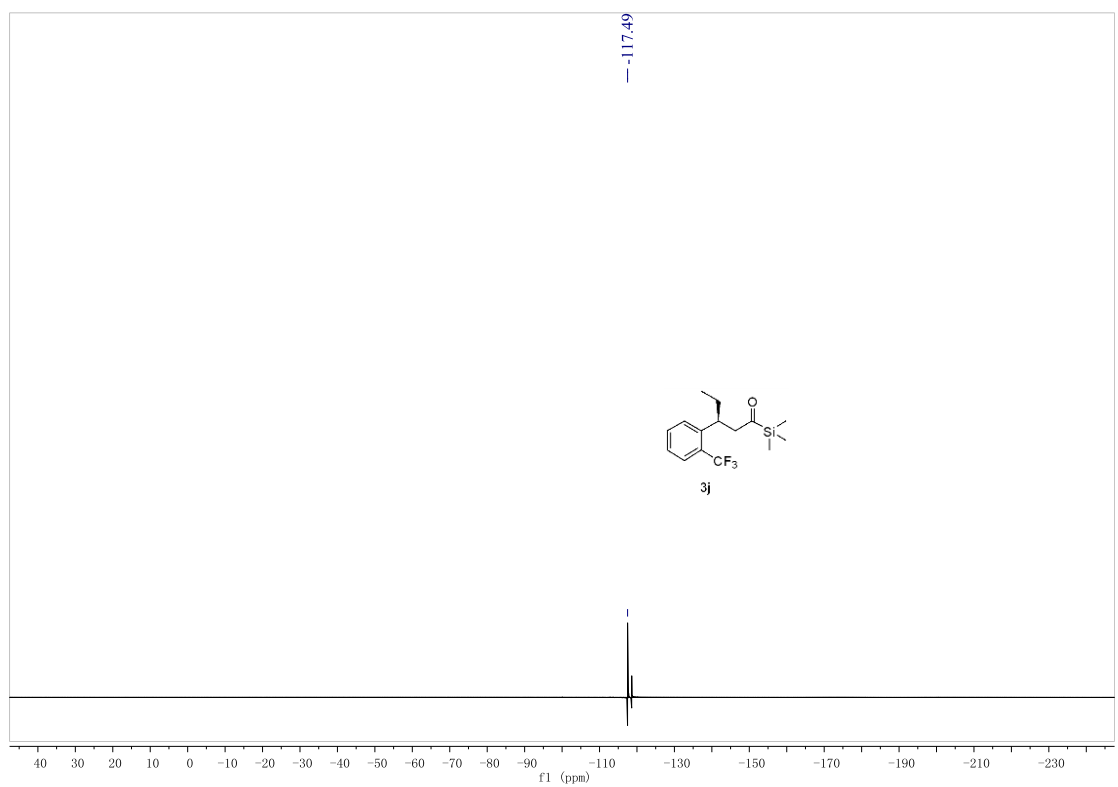
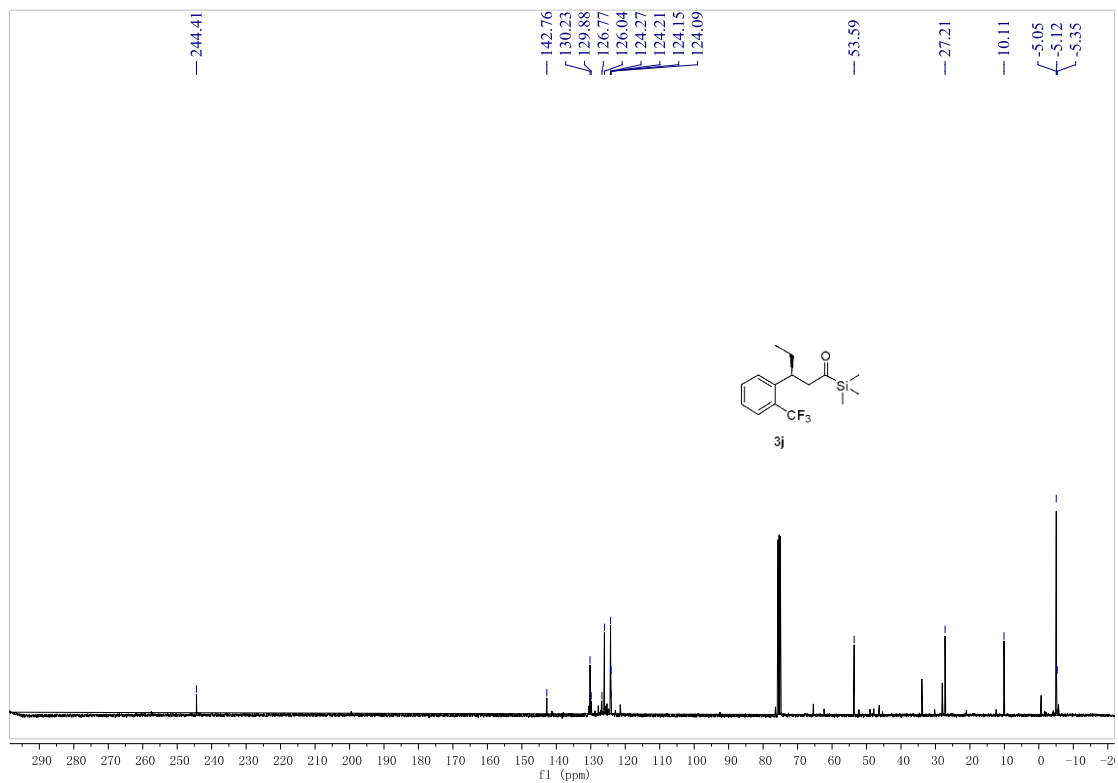


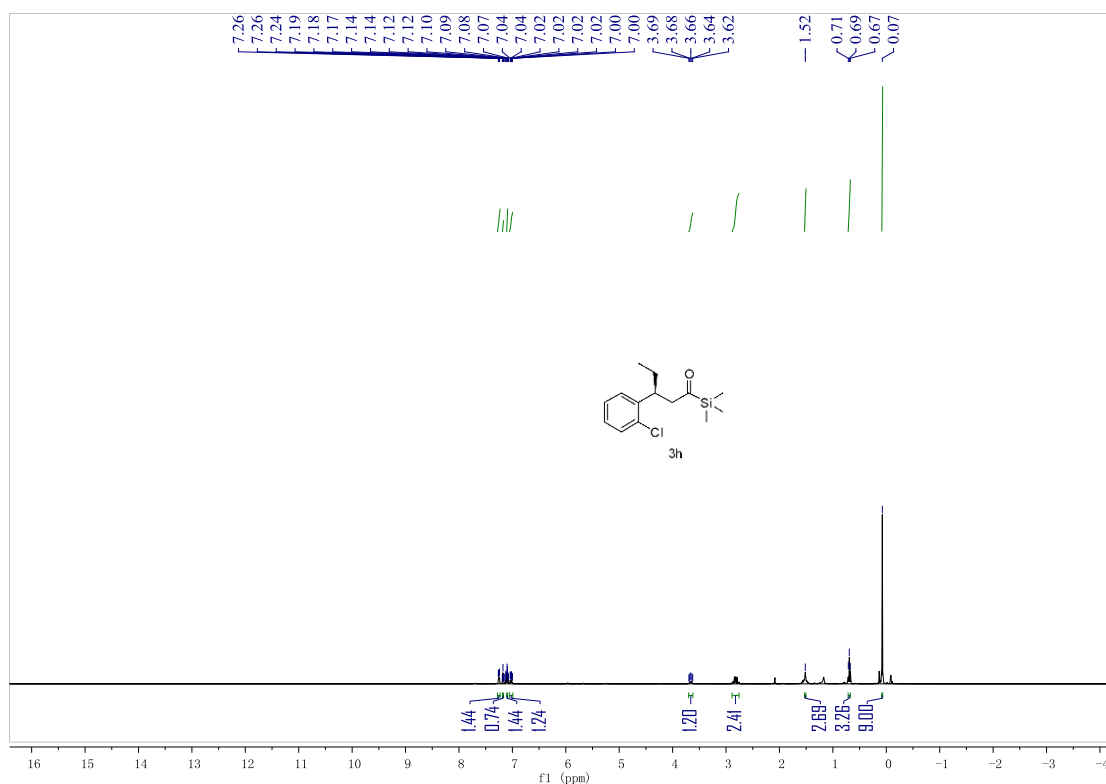
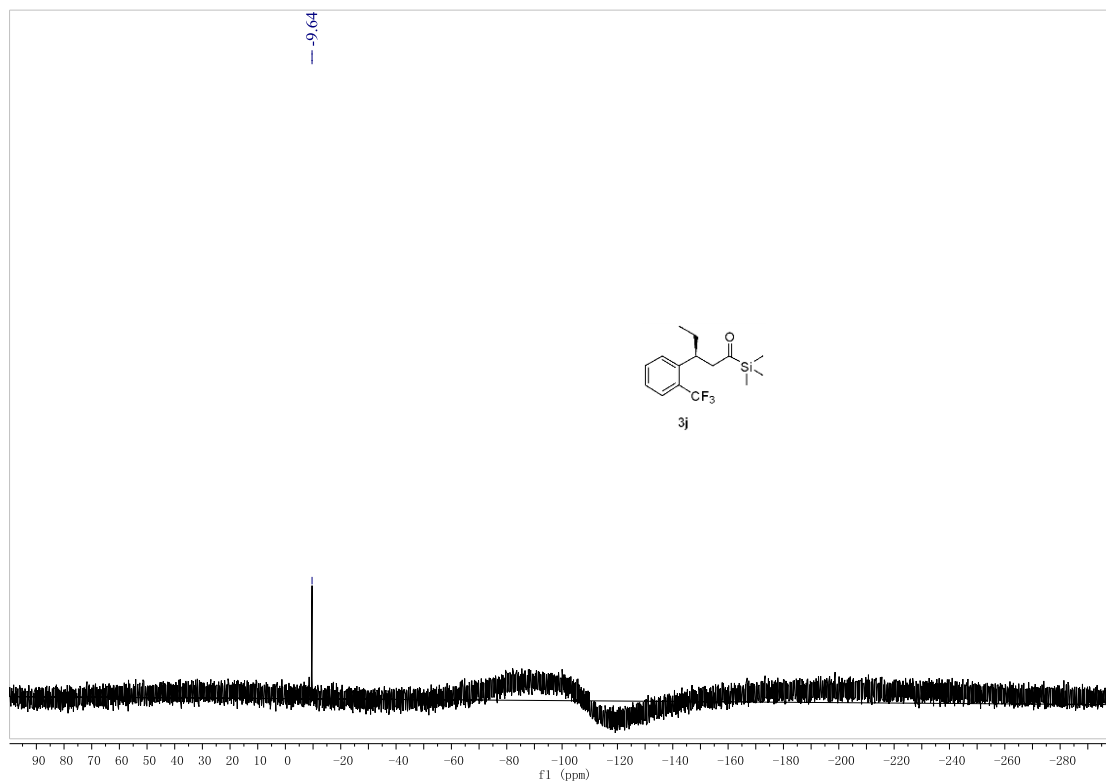


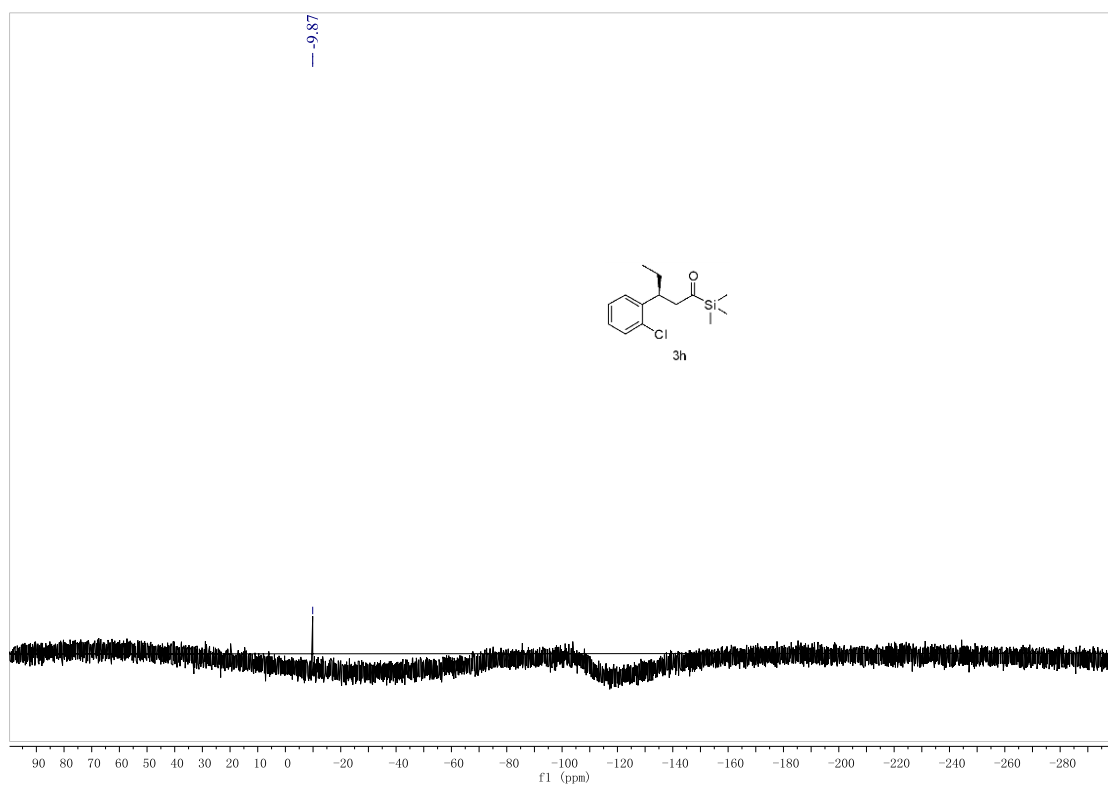
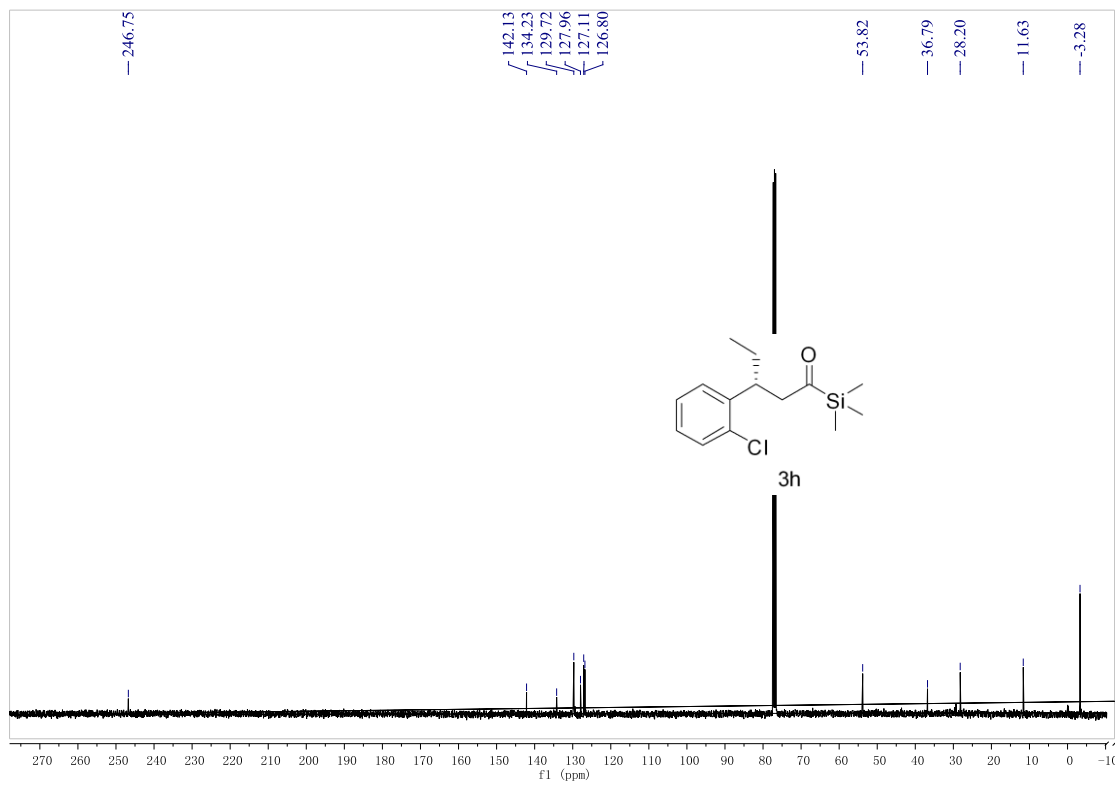


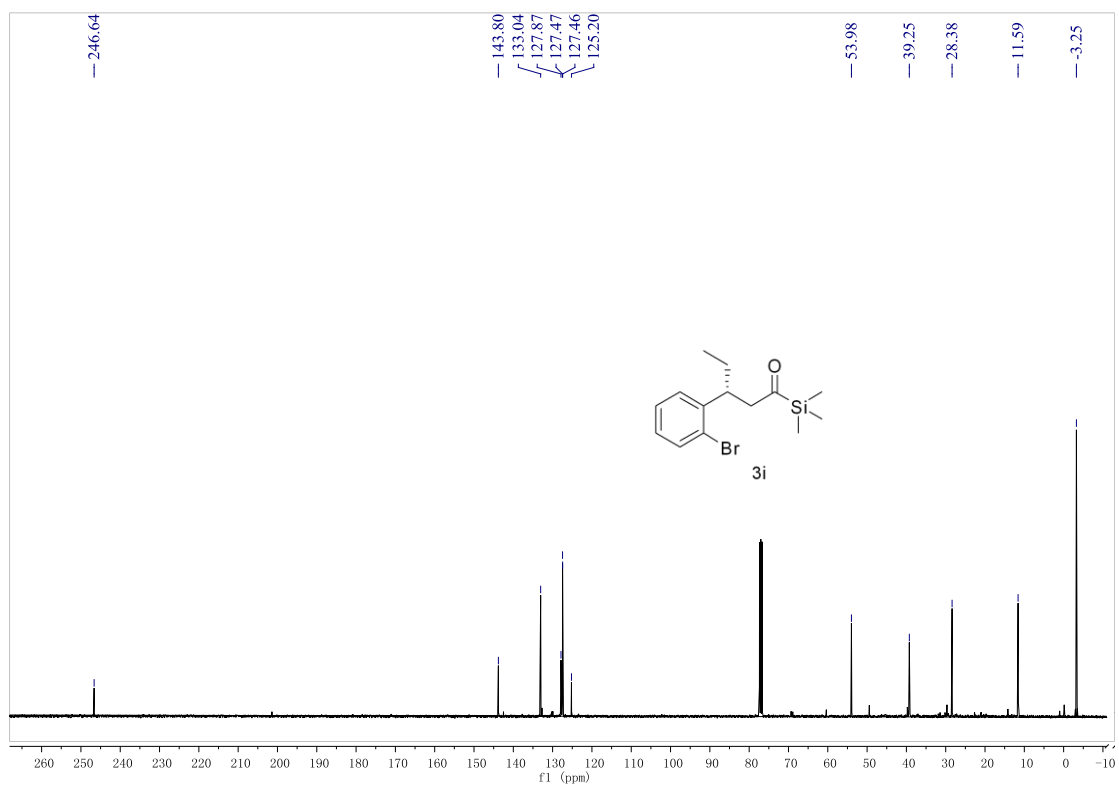
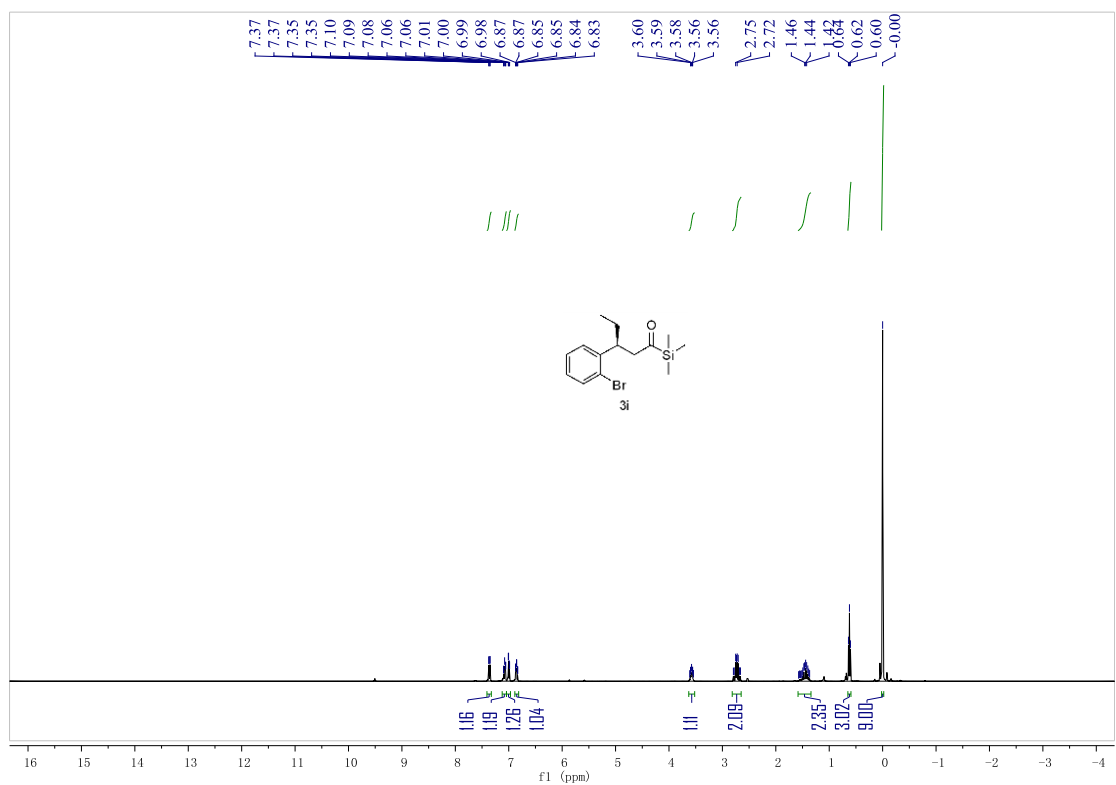


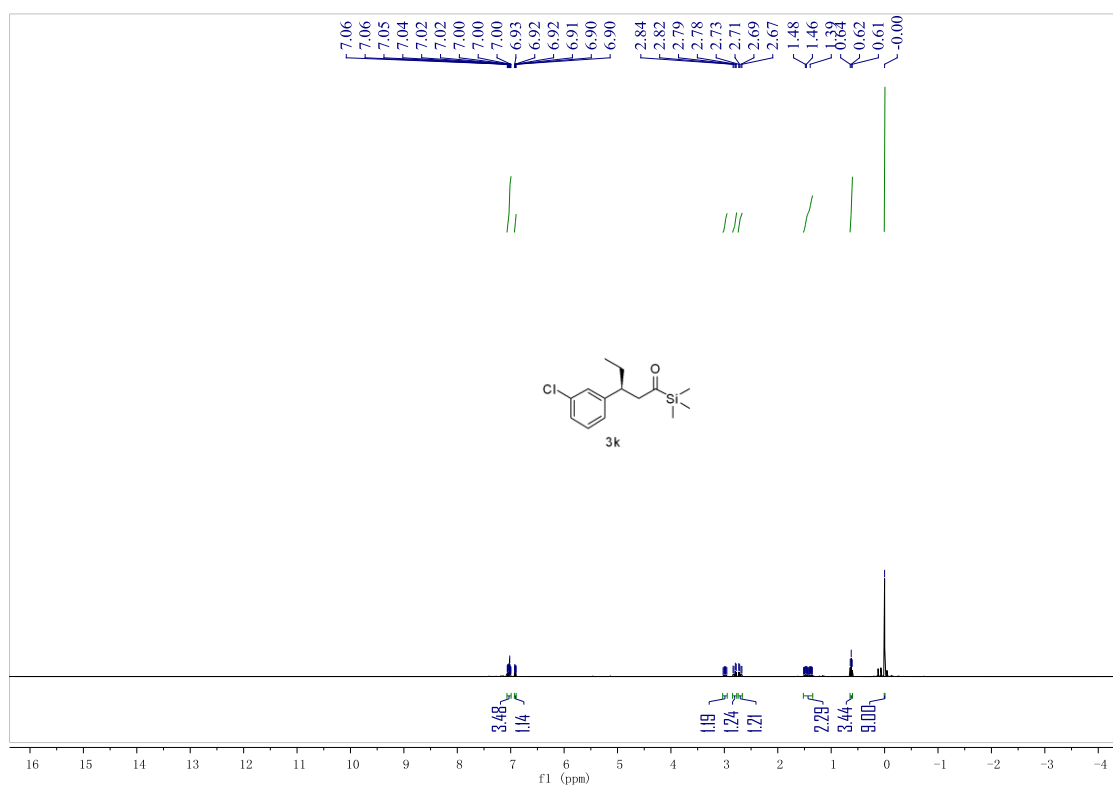
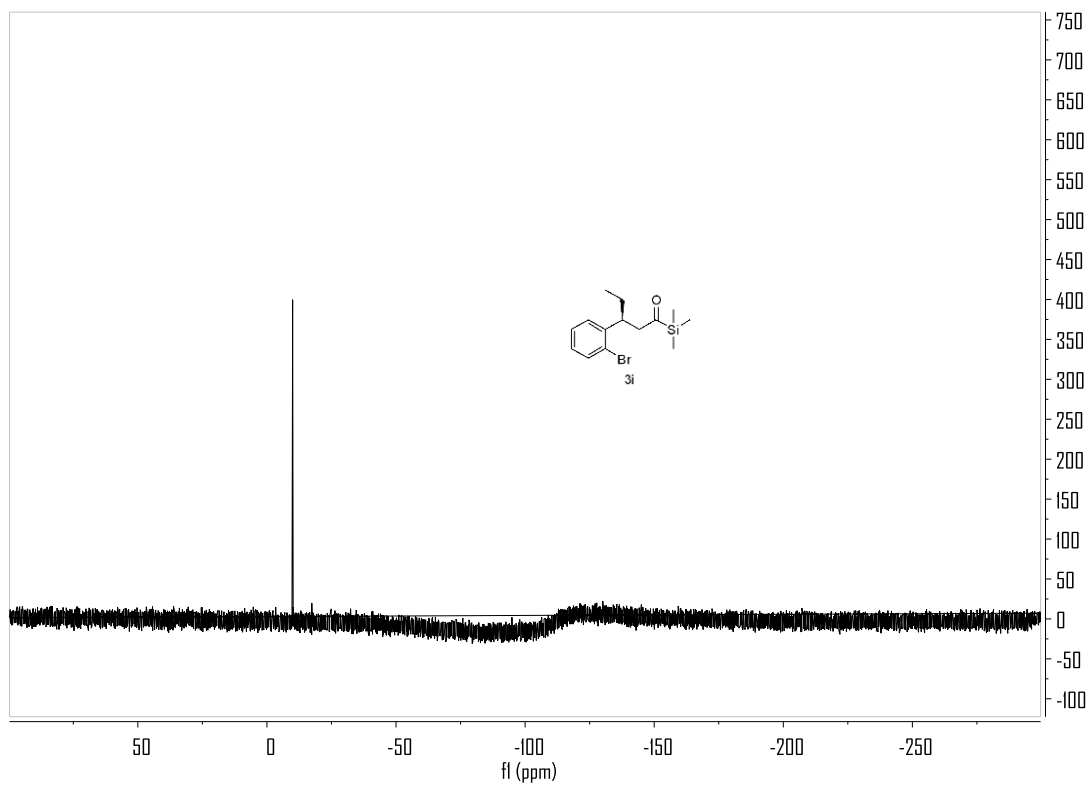


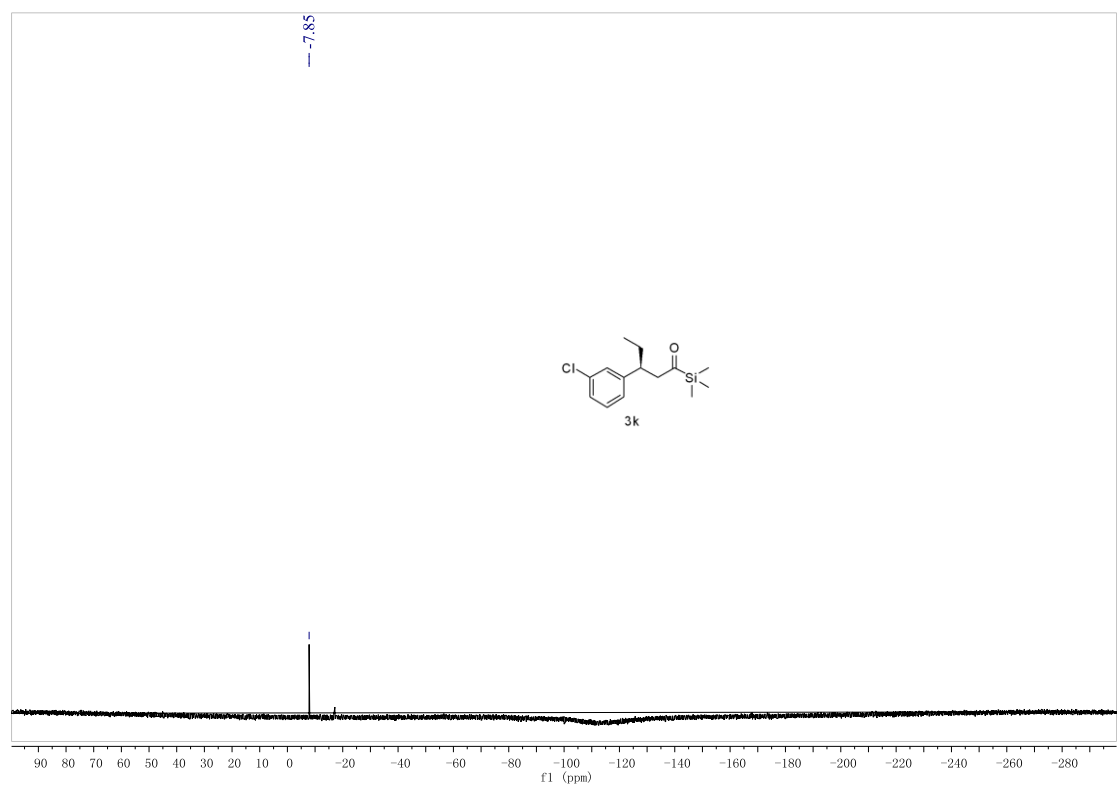
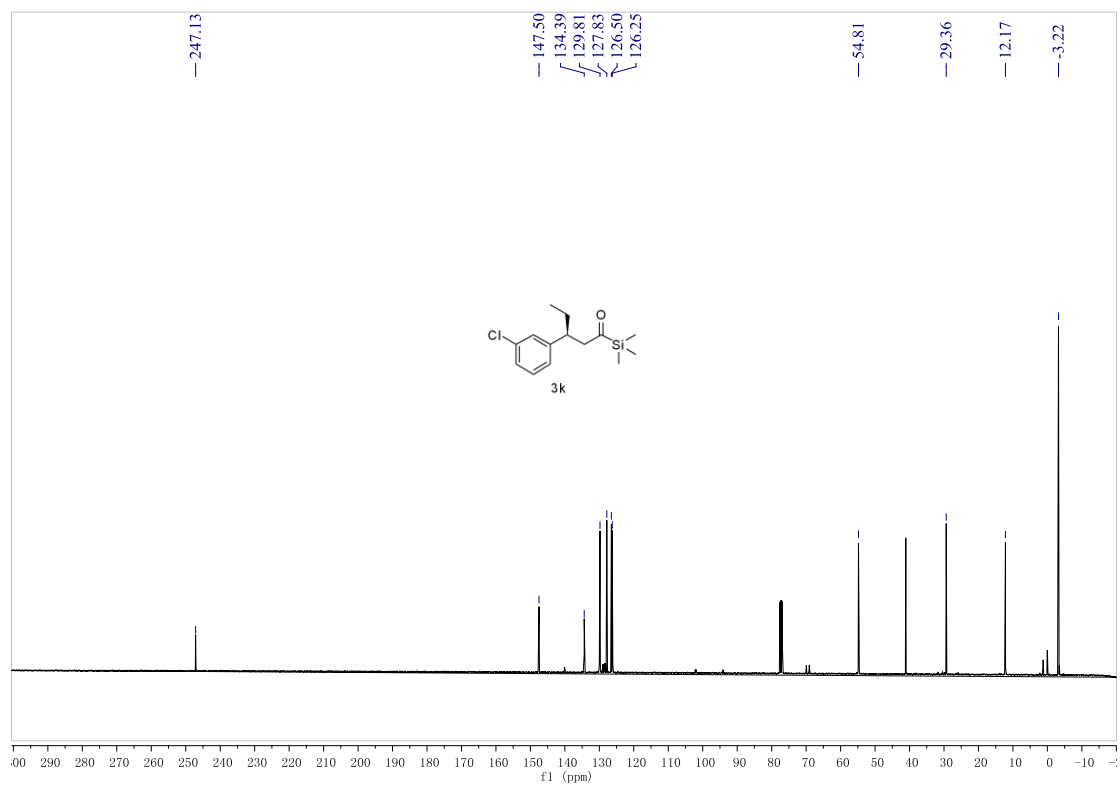




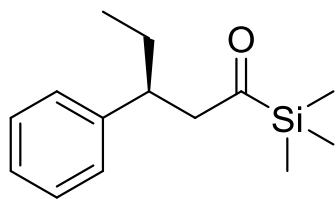




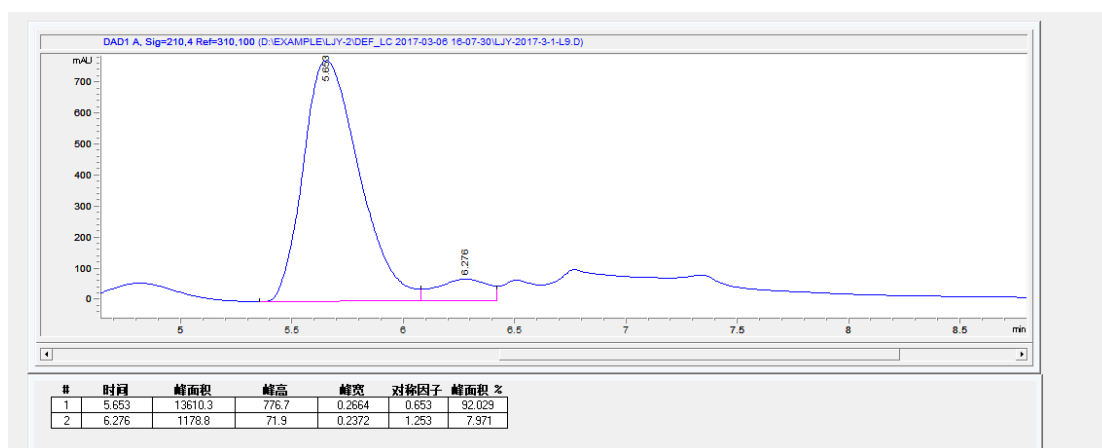
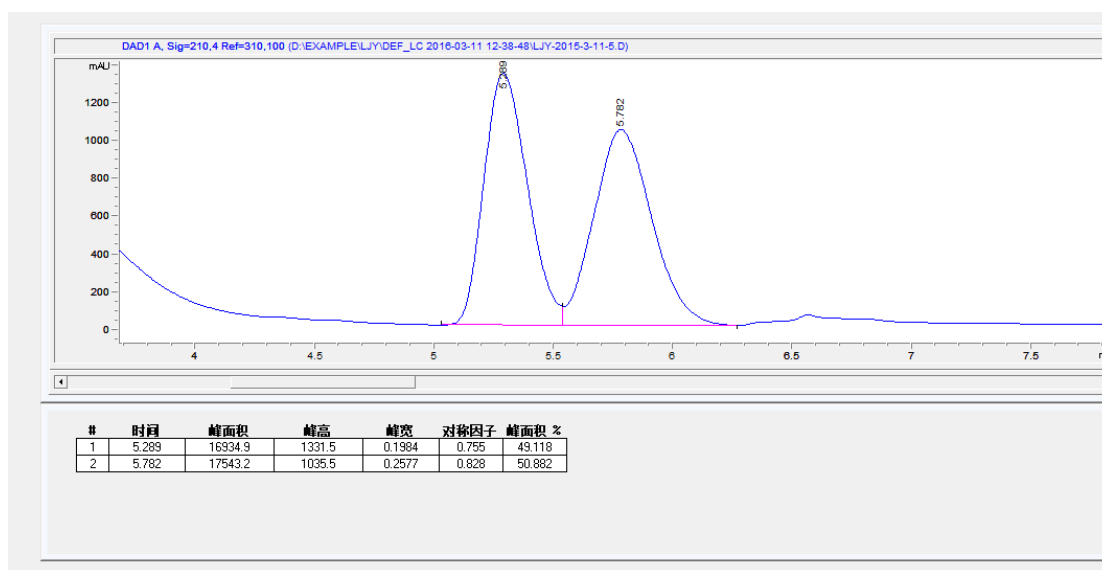




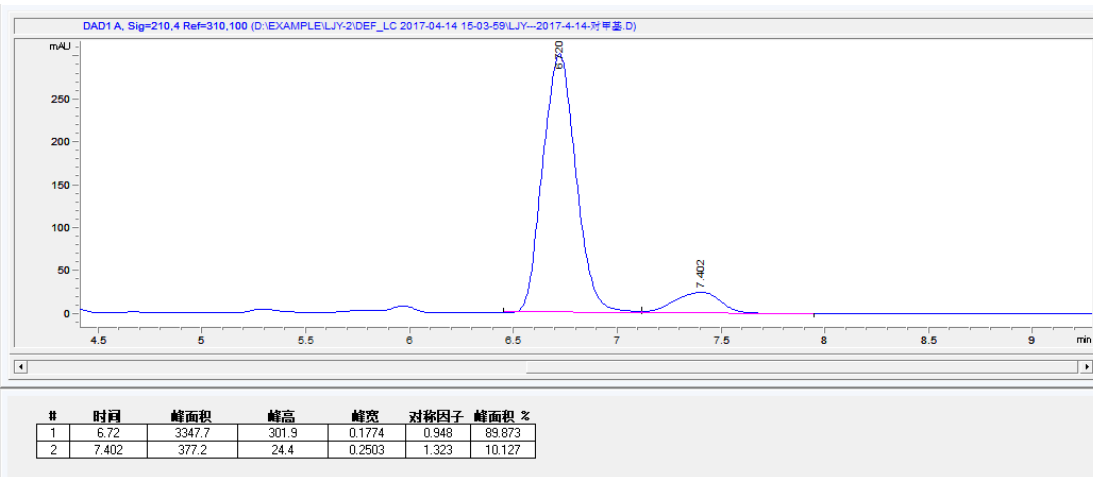
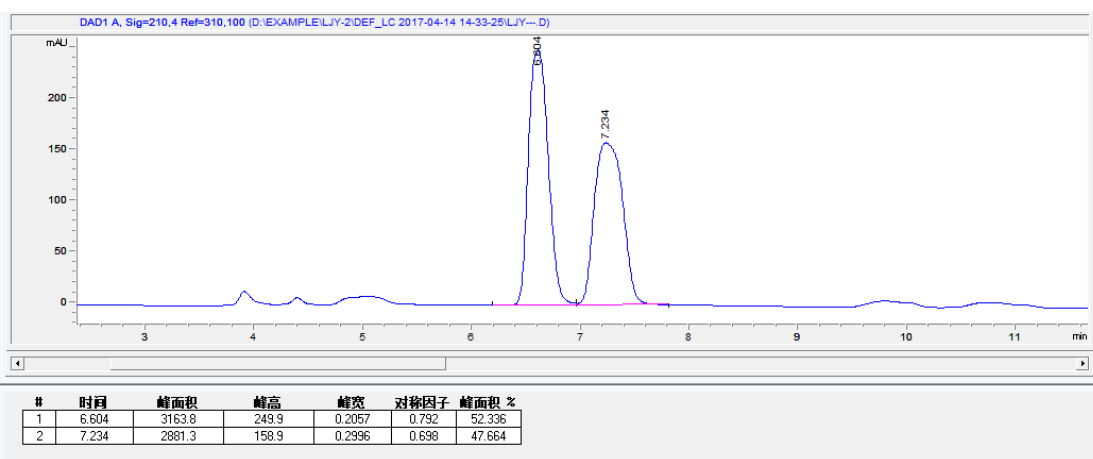
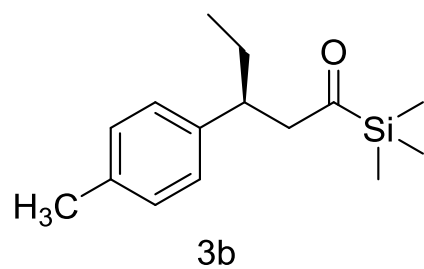
6. HPLC spectra of addition products.



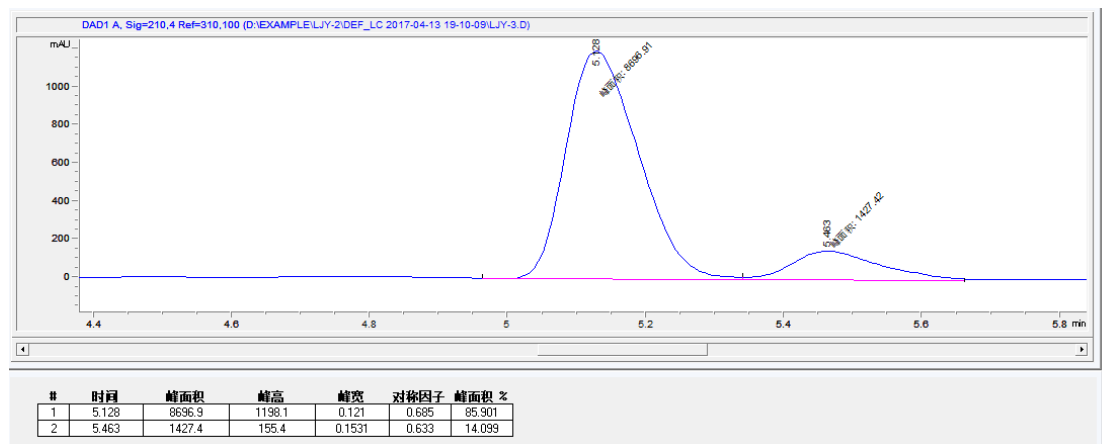
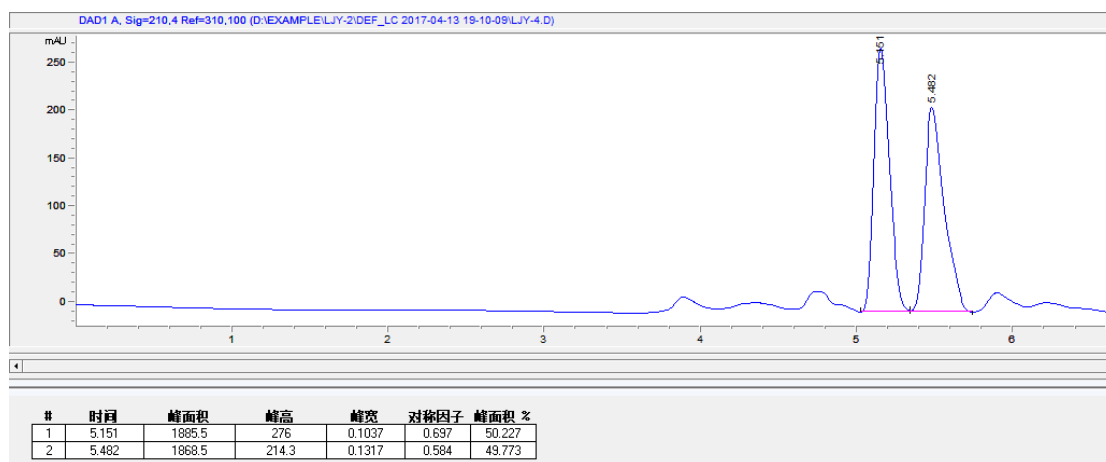
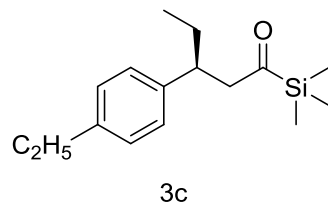
3a



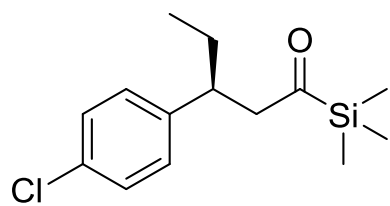
Time/min	Area	Height	Area(%)
5.653	13610.3	776.7	92.03
6.276	1178.8	1.252	7.97



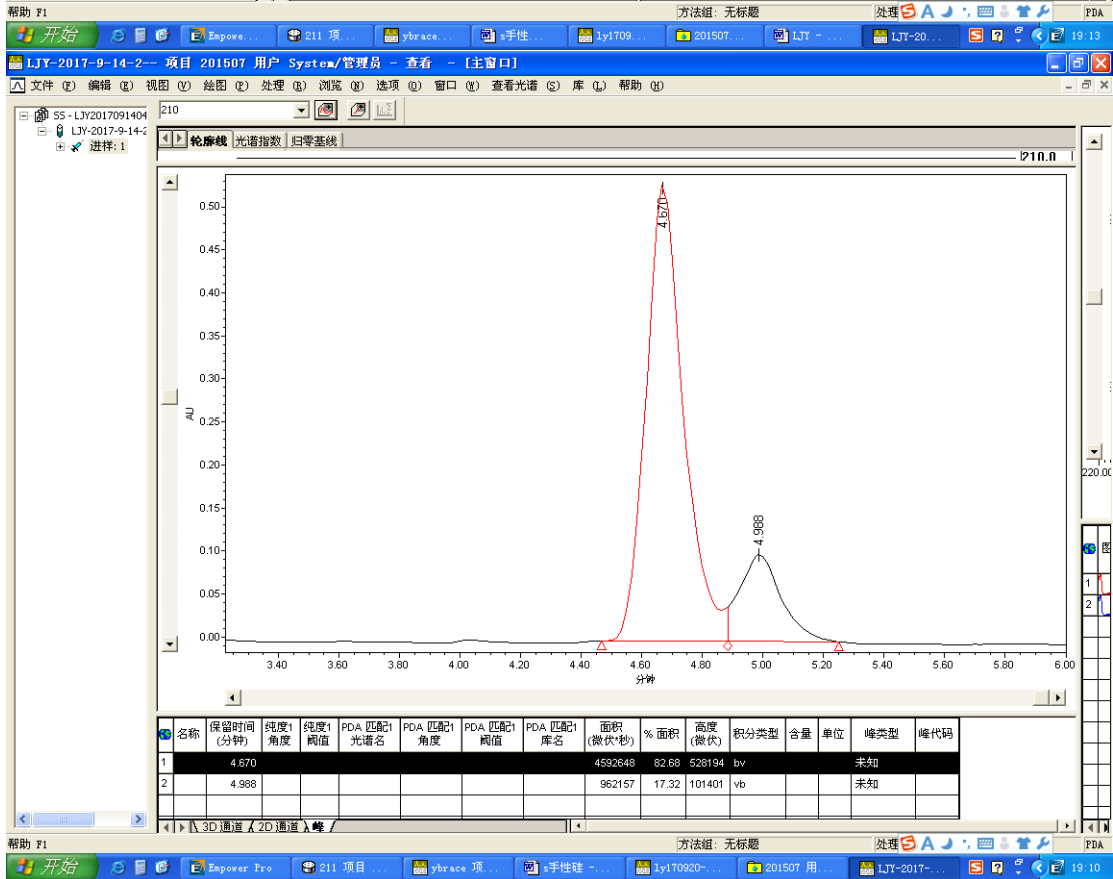
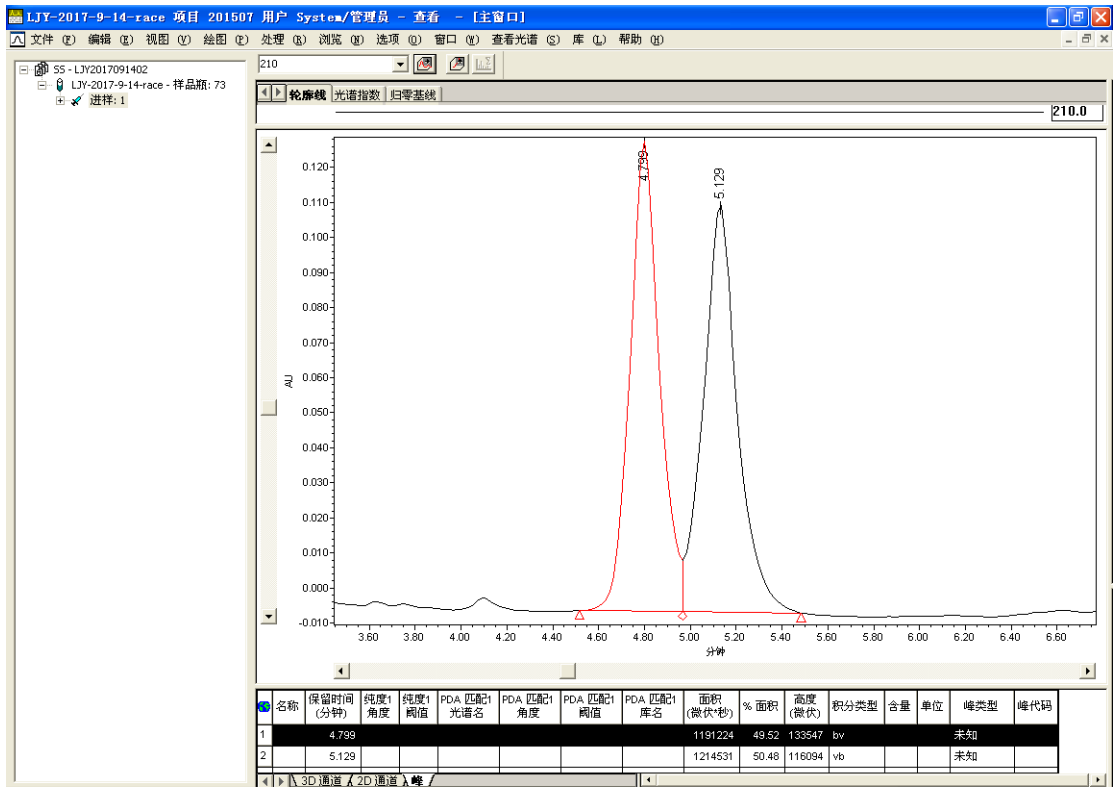
Time/min	Area	Height	Area(%)
6.72	3347.7	301.9	89.9
7.402	377.2	24.4	10.12



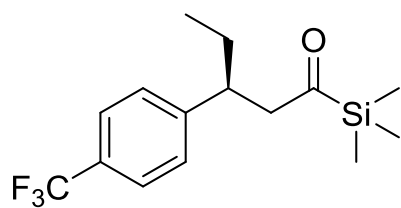
Time/min	Area	Height	Area(%)
5.128	8696.9	1198.1	85.901
5.463	1427.4	155.4	14.099



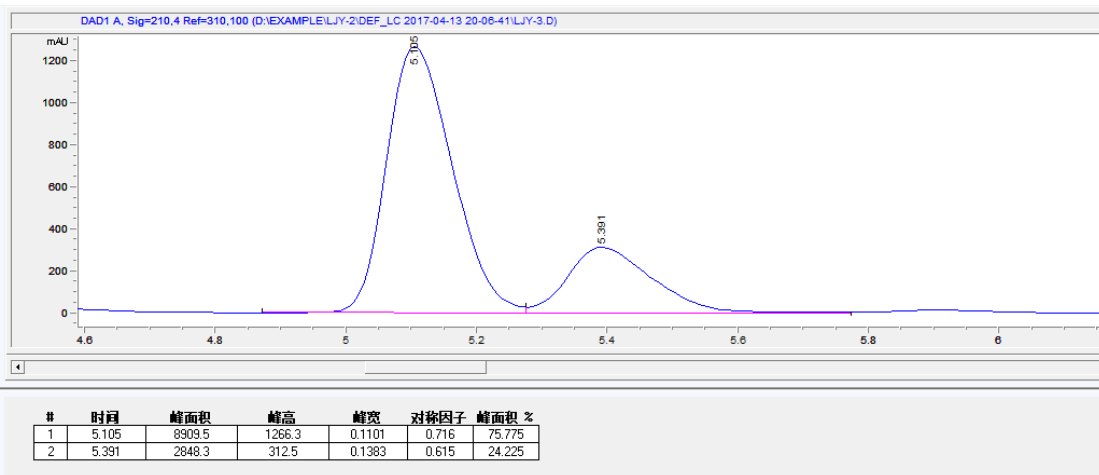
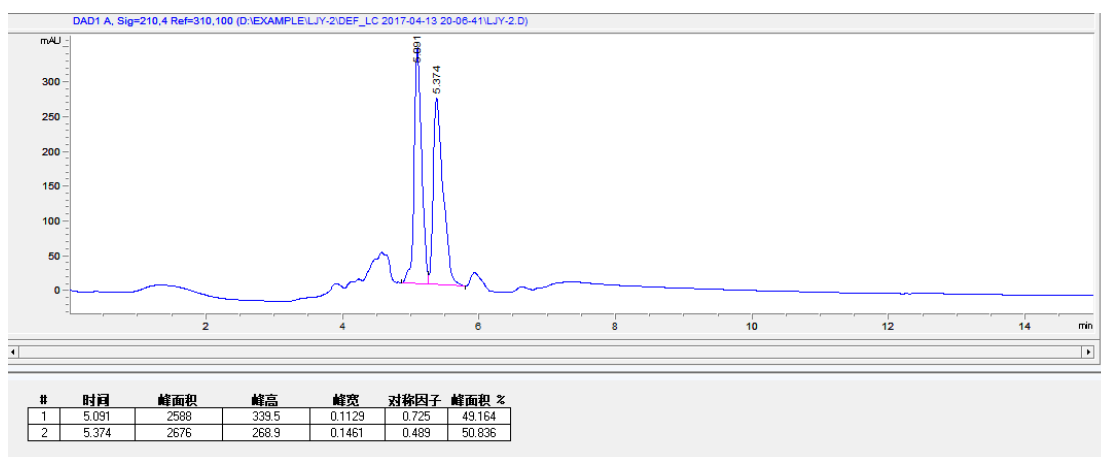
3d



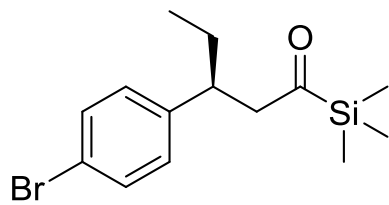
Time/min	Area	Height	Area(%)
4.670	82.69	528194	82.69
4.988	17.32	101401	17.32



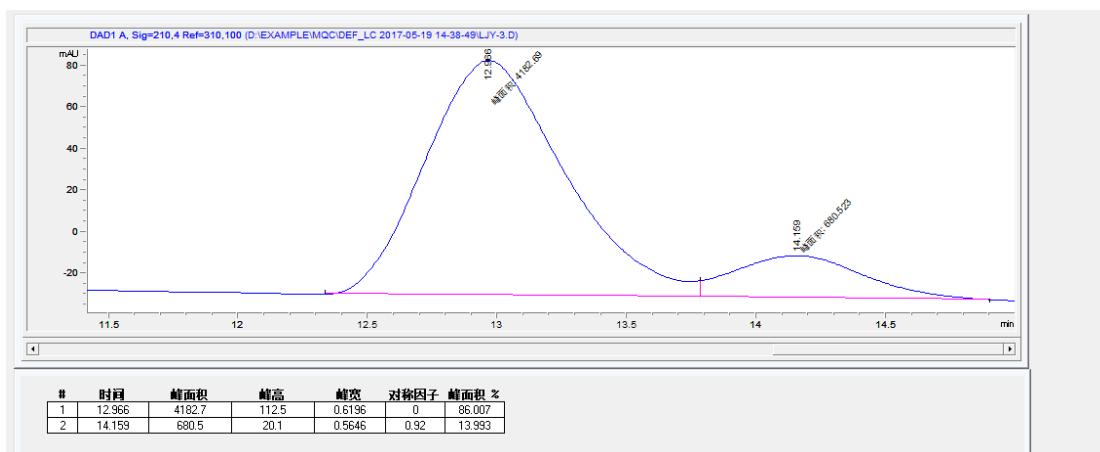
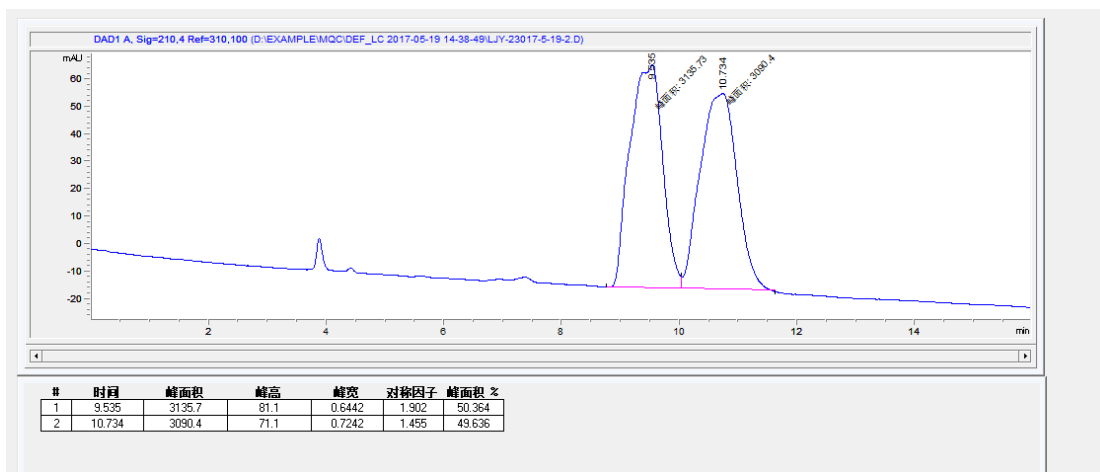
3e



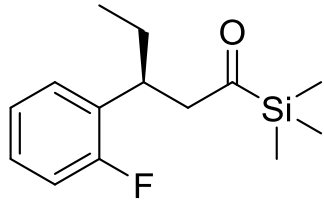
Time/min	Area	Height	Area(%)
5.105	8909.5	1266.3	75.775
5.391	2848.3	312.5	24.225



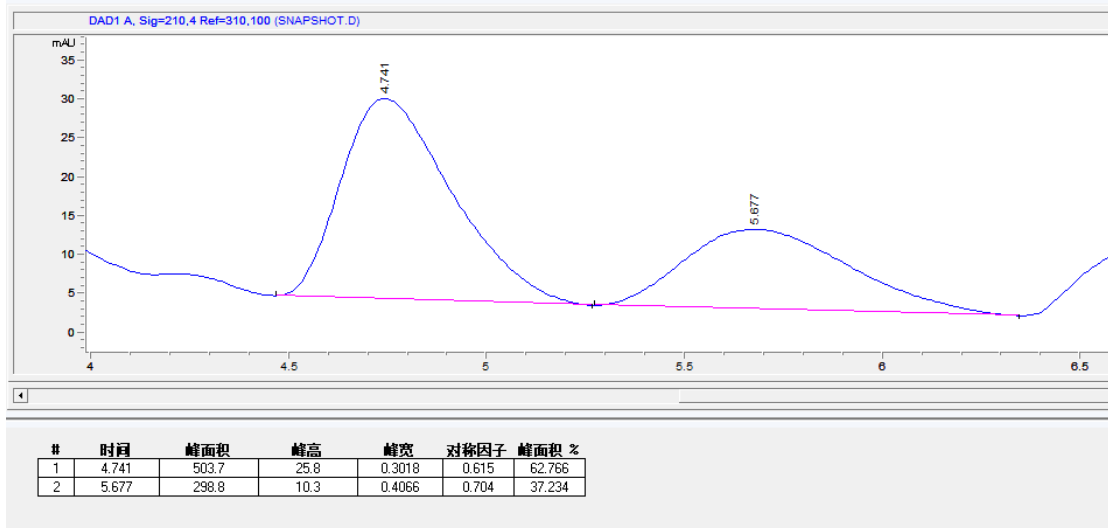
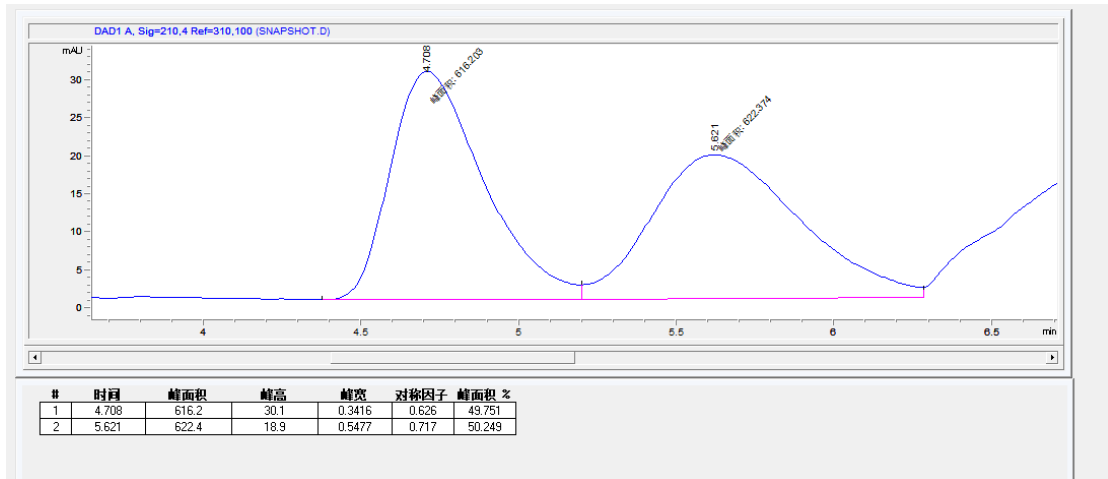
3f



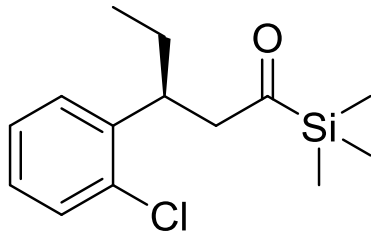
Time/min	Area	Height	Area(%)
12.966	4182.7	112.5	86.007
14.159	680.5	320.1	13.993



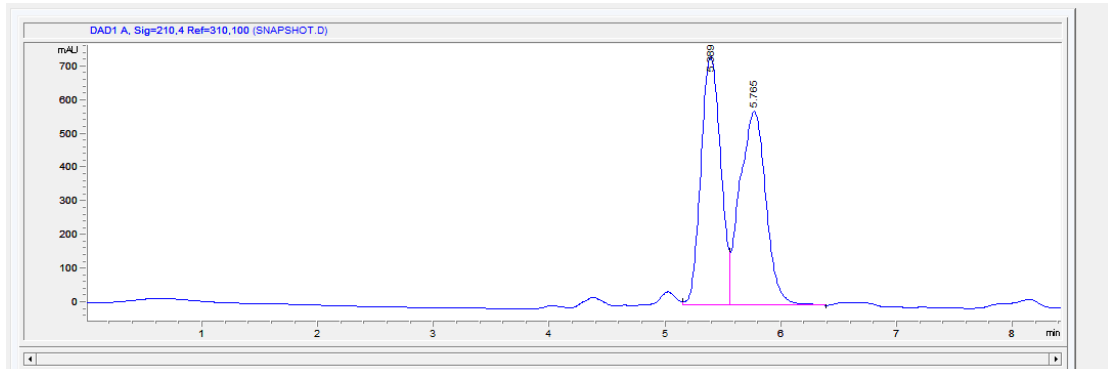
3g



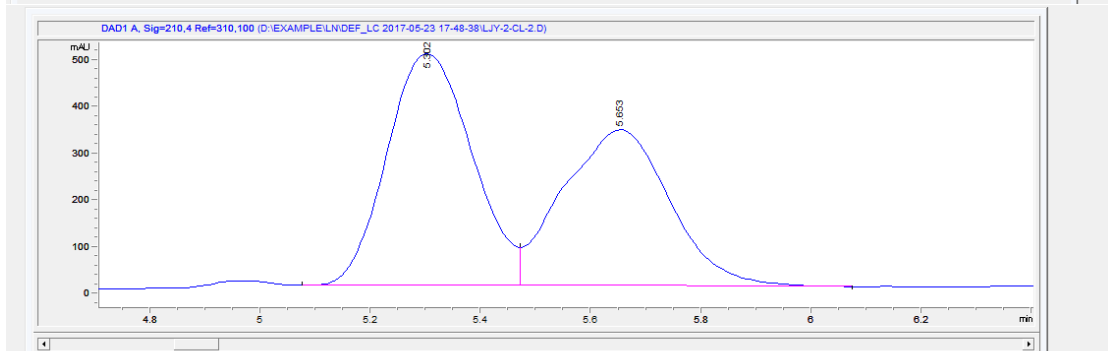
Time/min	Area	Height	Area(%)
4.741	503.7	25.8	62.766
5.677	298.8	10.3	37.234



3h

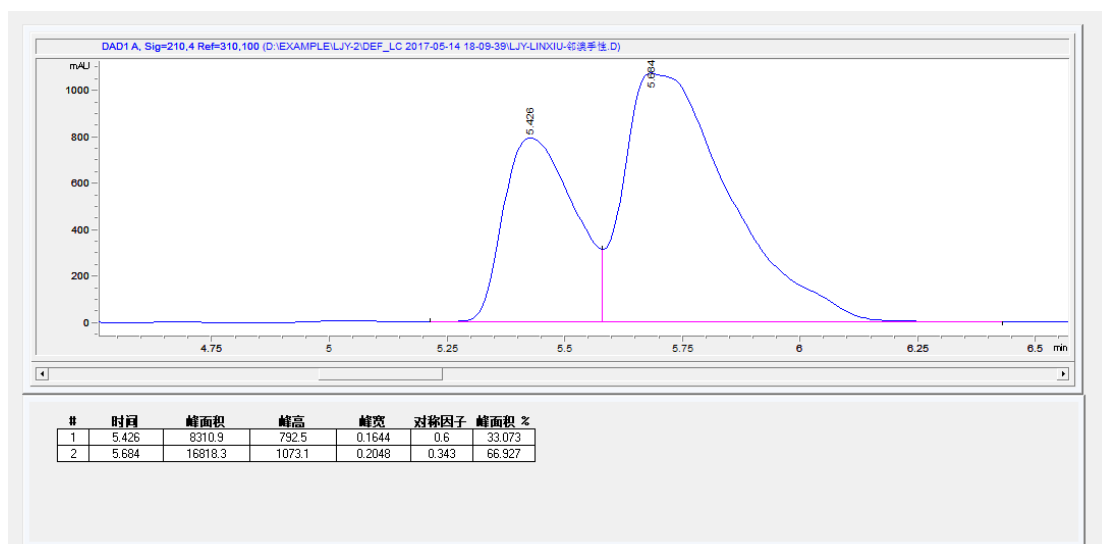
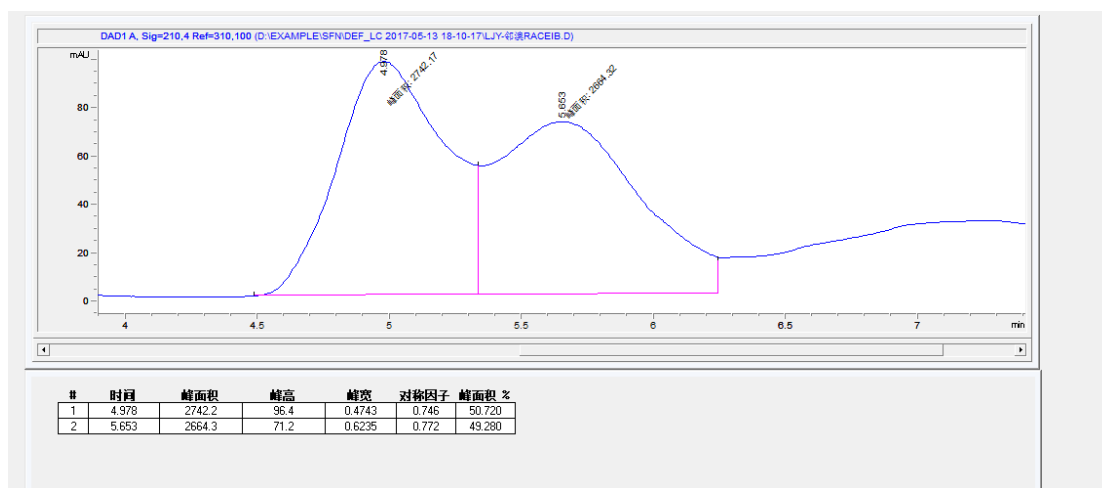
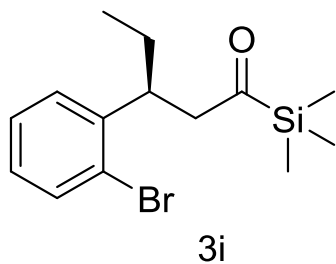


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	5.389	8756.1	737.1	0.1846	0.9	49.359
2	5.765	8983.4	575.1	0.2262	1.108	50.641

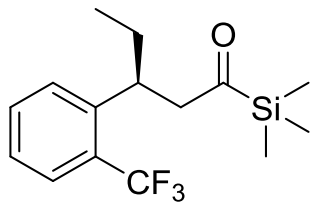


#	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	5.302	5332.1	495.1	0.1636	0.851	51.134
2	5.653	4517.7	334	0.1978	1.078	45.666

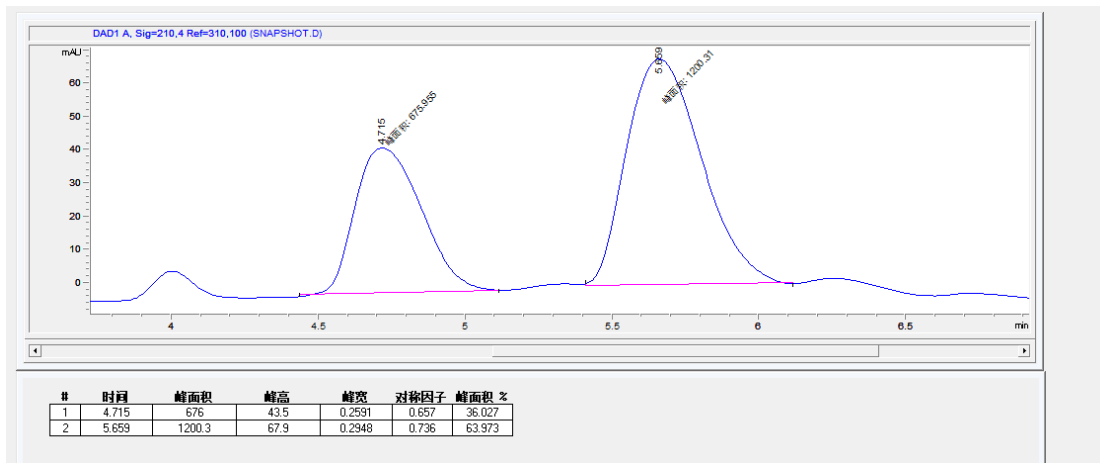
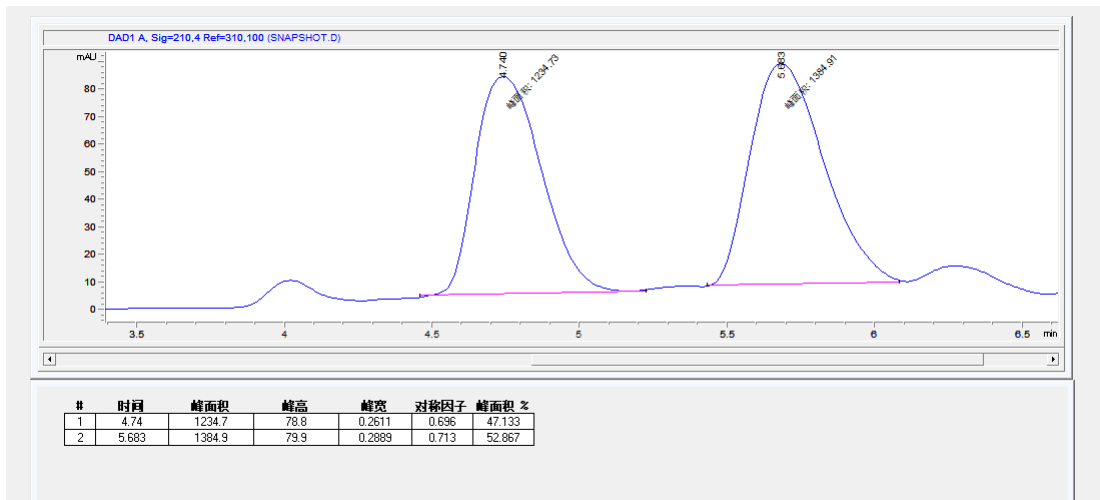
Time/min	Area	Height	Area(%)
5.302	5332.1	495.1	51.134
5.653	4517.7	334	45.666



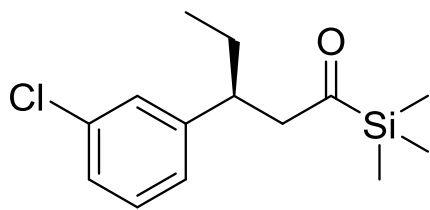
Time/min	Area	Height	Area(%)
5.426	8310.9	792.5	33.073
5.684	16818.3	1073.1	66.927



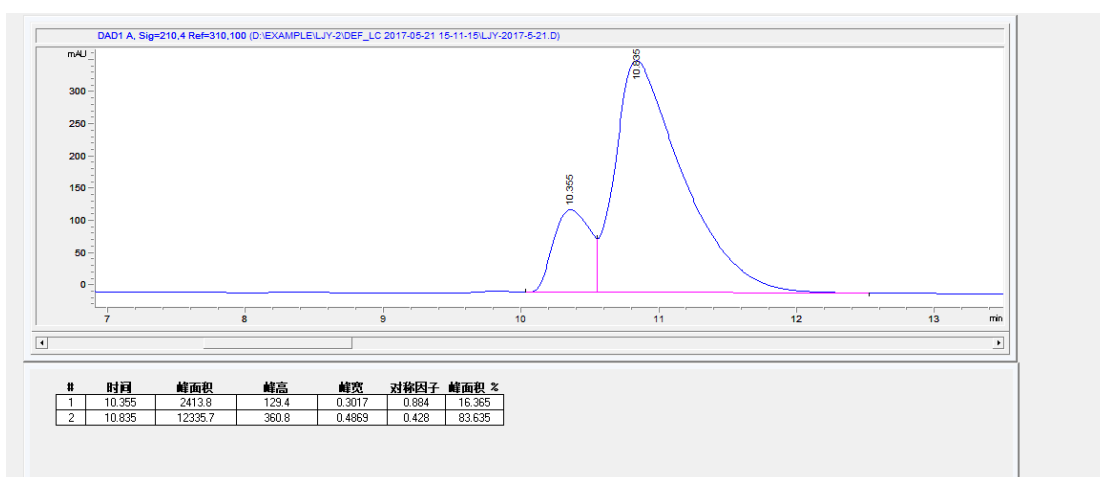
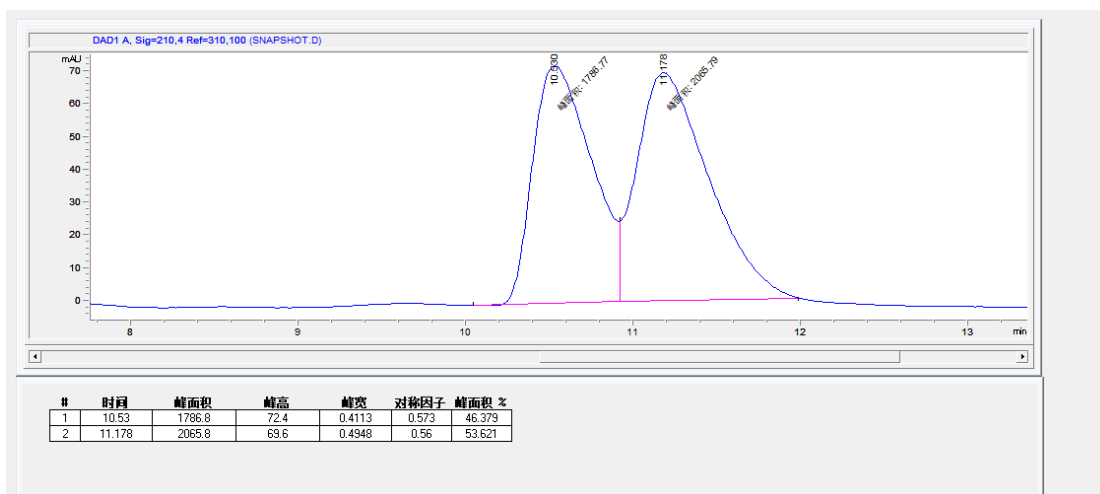
3j



Time/min	Area	Height	Area(%)
7.355	1156.9	57.2	36.027
7.938	2443.5	79.2	63.973



3k



Time/min	Area	Height	Area(%)
10.355	2413.8	0.3017	16.365
10.835	12335.7	0.4669	83.635