

Supporting Information

Regio-selective and Stereo-selective Hydrosilylation of Internal Alkynes Catalyzed by Ruthenium Complexes

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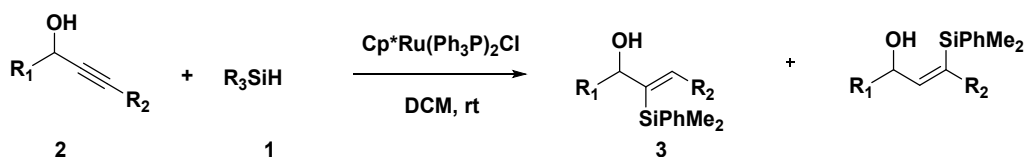
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(A) General Methods

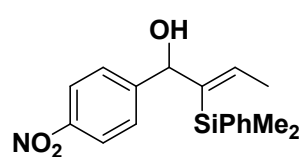
Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). Preparative thin layer chromatography (PTLC) was HSGF 254 (0.4-0.5 mm thickness). The reagents (chemicals) were purchased from commercial sources (J&K, TCI, Sigma-Aldrich, Adamas-beta, TCI, etc.), and used without further purification. Analytical all products were characterized by their NMR and MS spectra. ^1H and ^{13}C NMR spectra were recorded on a 400 MHz, 500 MHz or 600 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet(t), quartet (q), multiplet (m), doublet of doublets (dd) and broad (br). High-resolution mass spectra (HRMS) were measured on Micromass Ultra Q-TOF spectrometer. All propargyl alcohols were prepared by following the same procedure as described in the literature¹.

(B) Typical Synthesis Procedure and Characterization of 3



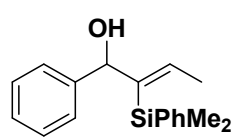
To a reaction tube was added propargyl alcohols **2** (0.2mmol), silanes **1** (0.24mmol), CpRu(Ph₃P)₂Cl (2mol%) and dichloromethane (2.0 mL). Then the reaction tube was evacuated and purged with argon three times. The solution was kept at room temperature for 12h. The crude mixture was purified by silica gel column chromatography (EA/PE=1/20 v/v) to give the corresponding product **3**.

1. Characterization of **3**



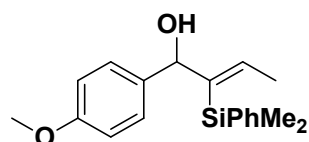
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-nitrophenyl)but-2-en-1-ol (3a)

Following general procedure B, **3a** was obtained as colorless oil (61.4 mg, yield 94%). ¹H NMR (500 MHz, CDCl₃) δ 8.18 – 8.12 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.36 – 7.28 (m, 3H), 6.44 (m, *J* = 7.0, 0.8 Hz, 1H), 5.37 (s, 1H), 2.11 – 1.98 (m, 1H), 1.76 (t, *J* = 6.3 Hz, 3H), 0.33 – 0.28 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 150.8, 147.0, 142.7, 140.9, 138.6, 133.7, 129.0, 127.9, 127.3, 123.2, 79.3, 19.0, -0.7, -0.8. HRMS (ESI) *m/z*: calculated for C₁₈H₂₀NO₃Si⁻ [M - H]⁻: 326.1218, found: 326.1224.



(Z)-2-(dimethyl(phenyl)silyl)-1-phenylbut-2-en-1-ol (3b)

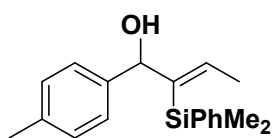
Following general procedure B, **3b** was obtained as colorless oil (49.0 mg, yield 87%). ¹H NMR (500 MHz, CDCl₃) δ 7.39 (dd, *J* = 7.5, 1.7 Hz, 2H), 7.30 – 7.18 (m, 8H), 6.46 – 6.38 (m, 1H), 5.29 (d, *J* = 3.0 Hz, 1H), 1.81 (d, *J* = 4.4 Hz, 1H), 1.66 (d, *J* = 7.0 Hz, 3H), 0.24 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 142.7, 140.3, 139.6, 138.8, 133.3, 128.2, 127.6, 127.2, 126.7, 126.4, 78.4, 17.4, -1.3, -1.4. HRMS (ESI) *m/z*: calculated for C₁₈H₂₂NaOSi⁺ [M+Na]⁺: 305.1332, found: 305.1332



(Z)-2-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)but-2-

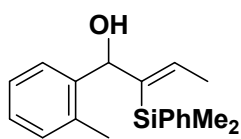
en-1-ol (3c)

Following general procedure B, **3c** was obtained as colorless oil (44.3mg, yield 71%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.44 (dd, *J* = 6.3, 2.9 Hz, 2H), 7.33 – 7.28 (m, 3H), 7.21 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.32 (q, *J* = 6.9 Hz, 1H), 5.33 (d, *J* = 4.4 Hz, 1H), 5.16 (d, *J* = 4.2 Hz, 1H), 3.73 (s, 3H), 1.55 (d, *J* = 7.0 Hz, 3H), 0.17 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 158.4, 142.2, 140.2, 138.1, 137.0, 134.0, 129.0, 128.4, 128.0, 113.5, 77.6, 55.4, 18.0, -0.21, -0.23. HRMS (ESI) *m/z*: calculated for C₁₉H₂₄NaO₂Si⁺ [M+Na]⁺: 335.1438, found: 335.1434.



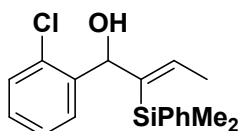
(Z)-2-(dimethyl(phenyl)silyl)-1-(p-tolyl)but-2-en-1-ol (3d)

Following general procedure C, **3d** was obtained as colorless oil (49.7 mg, yield 84%). ¹H NMR (500 MHz, CDCl₃) δ 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 3H), 7.22 – 7.16 (m, 2H), 7.13 (d, *J* = 6.6 Hz, 2H), 6.48 (q, *J* = 6.8 Hz, 1H), 5.31 (s, 1H), 2.35 (d, *J* = 1.5 Hz, 3H), 1.87 – 1.80 (m, 1H), 1.70 (dd, *J* = 7.0, 1.4 Hz, 3H), 0.28 (t, *J* = 2.4 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 140.2, 139.7, 139.1, 138.9, 136.3, 133.3, 128.3, 128.2, 127.2, 126.4, 78.1, 20.6, 17.4, -1.3, -1.4. HRMS (EI) *m/z*: calculated for C₁₉H₂₄O₂Si: 296.1591, found 296.1597.



(Z)-2-(dimethyl(phenyl)silyl)-1-(o-tolyl)but-2-en-1-ol (3e)

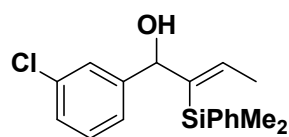
Following general procedure B, **3e** was obtained as colorless oil (45mg, yield 76%). ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.51 – 7.44 (m, 2H), 7.36 (d, *J* = 6.8 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.19 – 7.05 (m, 3H), 6.06 – 5.99 (m, 1H), 5.33 (s, 1H), 2.14 (s, 3H), 1.52 (d, *J* = 7.0 Hz, 3H), 0.34 (d, *J* = 5.5 Hz, 3H), 0.24 (d, *J* = 10.0 Hz, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 142.7, 140.7, 139.8, 137.6, 135.6, 134.0, 130.3, 129.1, 128.1, 127.6, 127.1, 125.7, 72.4, 19.2, 18.0, -0.7, -0.8. HRMS (ESI) *m/z*: calculated for C₁₉H₂₄NaOSi⁺ [M +Na]⁺: 319.1489, found: 319.149.



(Z)-1-(2-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol

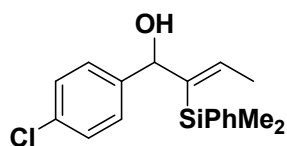
(3f)

Following general procedure B, **3f** was obtained as colorless oil (51.8mg, yield 82%). ¹H NMR (500 MHz, CDCl₃) δ 7.61 – 7.56 (m, 2H), 7.56 – 7.52 (m, 1H), 7.35 (m, *J* = 8.5, 4.7, 2.0 Hz, 4H), 7.30 (m, *J* = 7.4, 1.2 Hz, 1H), 7.25 – 7.20 (m, 1H), 6.16 (qd, *J* = 7.0, 1.1 Hz, 1H), 5.72 (s, 1H), 1.94 (dd, *J* = 15.5, 1.9 Hz, 1H), 1.67 (dd, *J* = 7.1, 0.9 Hz, 3H), 0.49 (d, *J* = 3.3 Hz, 3H), 0.46 (d, *J* = 3.2 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 140.8, 140.2, 139.4, 139.0, 133.9, 133.0, 129.5, 128.9, 128.6, 128.5, 127.8, 126.6, 73.2, 18.1, -1.2, -1.3. HRMS (ESI) *m/z*: calculated for C₁₈H₂₁ClNaOSi⁺ [M + Na]⁺: 339.0942, found: 339.0948.



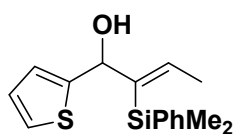
(Z)-1-(3-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3g)

Following general procedure B, **3g** was obtained as colorless oil (53.7mg, yield 85%). ¹H NMR (500 MHz, CDCl₃) δ 7.48 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.32 (s, 1H), 7.29 – 7.26 (m, 2H), 7.22 (dt, *J* = 5.3, 3.8 Hz, 1H), 6.48 (dd, *J* = 6.9, 3.5 Hz, 1H), 5.31 (s, 1H), 2.05 (s, 1H), 1.78 (d, *J* = 7.1 Hz, 3H), 0.36 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 145.4, 141.1, 140.7, 139.0, 134.1, 133.8, 129.4, 128.9, 127.9, 127.2, 127.0, 125.0, 78.8, 18.0, -0.8, -0.9. HRMS (ESI) *m/z*: calculated for C₁₈H₂₀ClOSi⁻ [M - H]⁻: 315.0977, found: 315.0971.



(Z)-1-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3h)

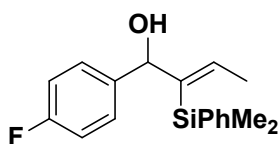
Following general procedure B, **3h** was obtained as colorless oil (56.8mg, yield 90%). ¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.37 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 (t, *J* = 3.5 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.42 (dd, *J* = 7.0, 3.5 Hz, 1H), 5.25 (d, *J* = 4.1 Hz, 1H), 1.85 (d, *J* = 4.5 Hz, 1H), 1.69 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.2, 140.3, 140.2, 138.5, 133.3, 132.4, 128.4, 127.7, 127.7, 127.3, 78.1, 17.4, -1.3, -1.4. HRMS (ESI) *m/z*: calculated for C₁₈H₂₀ClOSi⁻ [M - H]⁻: 315.0977, found: 315.0973.



(Z)-2-(dimethyl(phenyl)silyl)-1-(thiophen-3-yl)but-2-en-1-ol

(3i)

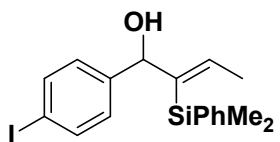
Following general procedure B, **3i** was obtained as colorless oil (52.4mg, yield 91%). ¹H NMR (600 MHz, CDCl₃) δ 7.50 – 7.45 (m, 2H), 7.38 – 7.31 (m, 3H), 7.29 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.98 (d, *J* = 5.0 Hz, 1H), 6.56 – 6.50 (m, 1H), 5.37 (s, 1H), 1.94 (s, 1H), 1.74 (d, *J* = 7.1 Hz, 3H), 0.35 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 145.3, 140.9, 139.6, 139.2, 133.8, 128.8, 127.8, 126.9, 125.6, 121.5, 76.1, 17.9, -0.9, -1.0. HRMS (EI) *m/z*: calculated for C₁₆H₂₀OSSi: 288.0999, found 288.0998.



(Z)-2-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)but-2-en-

1-ol (3j)

Following general procedure B, **3j** was obtained as colorless oil (48mg, yield 80%). ¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 7.26 – 7.22 (m, 2H), 7.03 – 6.96 (m, 2H), 6.48 (qd, *J* = 7.0, 1.1 Hz, 1H), 5.30 (s, 1H), 1.85 – 1.76 (m, 1H), 1.73 (dd, *J* = 7.1, 0.7 Hz, 3H), 0.28 (dd, *J* = 6.3, 3.1 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 161.6 (d, *J* = 252 Hz), 140.4, 139.6, 138.7, 138.5 (d, *J* = 2.5 Hz), 133.4, , 128.4, 128.2 (d, *J* = 7.5 Hz), 127.36, 114.4 (d, *J* = 20 Hz), 78.0, 17.5, -1.3, -1.4. ¹⁹F NMR (471 MHz, CDCl₃) δ -115.78 (s). HRMS (ESI) *m/z*: calculated for C₁₈H₂₁FN₁OSi⁺ [M + Na]⁺: 323.1238, found: 323.1246.

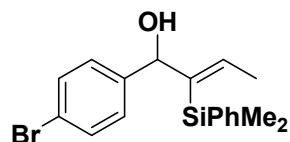


(Z)-2-(dimethyl(phenyl)silyl)-1-(4-iodophenyl)but-2-en-1-ol

(3k)

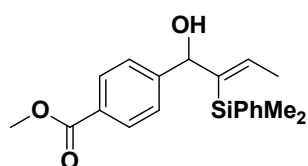
Following general procedure B, **3k** was obtained as white solid (71mg, yield 87%). ¹H NMR (500 MHz, CDCl₃) δ 7.66 – 7.61 (m, 2H), 7.45 – 7.41 (m, 2H), 7.36 – 7.28 (m, 3H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.43 (tt, *J* = 7.0, 3.5 Hz, 1H), 5.25 (s, 1H), 1.90 (m, 1H), 1.72 (d, *J* = 7.0 Hz, 3H), 0.30 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 143.0, 140.9, 140.8, 139.0, 137.1, 133.8, 128.9, 127.8, 92.7, 78.8,

18.0, -0.7, -0.8. HRMS (ESI) m/z : calculated for $C_{18}H_{20}IOSi^-$ [M-H] $^-$: 407.0334, found: 407.0333.



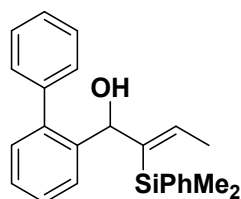
(Z)-1-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3l)

Following general procedure B, **3l** was obtained as colorless oil (57.6mg, yield 80%). 1H NMR (500 MHz, $CDCl_3$) δ 7.42 (ddd, $J = 11.4, 7.0, 5.4$ Hz, 4H), 7.34 – 7.28 (m, 3H), 7.16 (t, $J = 7.4$ Hz, 2H), 6.49 – 6.40 (m, 1H), 5.27 (s, 1H), 1.75 – 1.69 (m, 3H), 0.29 (d, $J = 3.3$ Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 140.8, 140.7, 139.0, 133.8, 131.2, 128.9, 128.6, 127.8, 121.0, 78.7, 17.9, -0.8, -0.9. HRMS (ESI) m/z : calculated for $C_{18}H_{20}BrOSi^-$ [M-H] $^-$: 359.0472, found: 359.0467.



(Z)-methyl 4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)benzoate (3m)

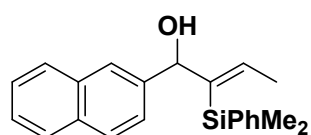
Following general procedure B, **3m** was obtained as white solid (43.5mg, yield 63%). 1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, $J = 8.3$ Hz, 2H), 7.42 (dd, $J = 7.8, 1.5$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.35 – 7.27 (m, 3H), 6.46 – 6.40 (m, 1H), 5.35 (s, 1H), 3.92 (s, 3H), 2.02 (m, 1H), 1.71 (d, $J = 7.0$ Hz, 3H), 0.28 (d, $J = 2.9$ Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 148.1, 141.1, 140.4, 138.5, 133.3, 129.0, 128.4, 128.4, 127.4, 126.2, 78.8, 51.7, 17.5, -1.2, -1.3. HRMS (ESI) m/z : calculated for $C_{20}H_{23}O_3Si^-$ [M-H] $^-$: 339.1422, found: 339.1416.



(Z)-1-([1,1'-biphenyl]-2-yl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3n)

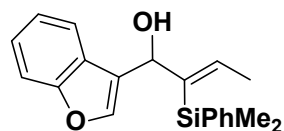
Following general procedure B, **3n** was obtained as colorless oil (56.5mg, yield 79%). 1H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.43 – 7.26 (m, 13H), 6.27 (qd, $J = 7.0, 1.4$ Hz, 1H), 5.41 (s, 1H), 1.80 (m, 1H), 1.69 – 1.64 (m, 3H), 0.26 (d, $J = 3.3$ Hz, 3H), 0.20 (d, $J = 3.2$ Hz, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 141.5, 141.1, 140.8, 140.2, 139.6, 139.3, 133.8, 130.2, 129.4, 128.7, 128.0, 127.7, 127.7, 127.3, 127.2, 127.1, 73.4, 18.1, -1.4, -1.5. HRMS (ESI) m/z : calculated for $\text{C}_{24}\text{H}_{26}\text{NaOSi}^+$ [$\text{M} + \text{Na}$] $^+$: 381.1645, found: 381.1647.



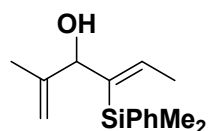
(Z)-2-(dimethyl(phenyl)silyl)-1-(naphthalen-2-yl)but-2-en-1-ol (3o)

Following general procedure B, **3o** was obtained as colorless oil (59.1mg, yield 89%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.90 – 7.84 (m, 3H), 7.82 (s, 1H), 7.54 – 7.44 (m, 5H), 7.34 – 7.26 (m, 3H), 6.42 – 6.34 (m, 1H), 5.63 (d, $J = 4.4$ Hz, 1H), 5.39 (d, $J = 4.3$ Hz, 1H), 1.60 (d, $J = 7.0$ Hz, 3H), 0.19 (dd, $J = 13.9, 3.2$ Hz, 6H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 142.6, 142.0, 140.1, 139.3, 134.0, 133.2, 132.5, 129.0, 128.2, 128.1, 127.9, 127.5, 126.4, 126.1, 125.9, 125.3, 78.3, 18.1, -0.1, -0.2. HRMS (ESI) m/z : calculated for $\text{C}_{22}\text{H}_{24}\text{NaOSi}^+$ [$\text{M} + \text{Na}$] $^+$: 355.1489, found: 355.1499.



(Z)-1-(benzofuran-3-yl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3p)

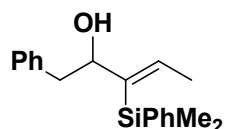
Following general procedure B, **3p** was obtained as colorless oil (52.8mg, yield 82%). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 7.57 (d, $J = 7.4$ Hz, 1H), 7.52 – 7.45 (m, 3H), 7.33 – 7.25 (m, 3H), 7.25 – 7.16 (m, 2H), 6.45 (q, $J = 6.9$ Hz, 1H), 5.79 (d, $J = 5.1$ Hz, 1H), 5.31 (d, $J = 5.0$ Hz, 1H), 1.58 (d, $J = 7.0$ Hz, 3H), 0.30 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 161.2, 154.6, 139.9, 139.6, 138.9, 134.0, 129.1, 128.6, 128.1, 124.2, 123.1, 121.4, 111.4, 103.5, 72.25, 18.1, -0.5, -0.6. HRMS (ESI) m/z : calculated for $\text{C}_{20}\text{H}_{22}\text{NaO}_2\text{Si}^+$ [$\text{M} + \text{Na}$] $^+$: 345.1281, found: 345.1284.



(Z)-4-(dimethyl(phenyl)silyl)-2-methylhexa-1,4-dien-3-ol (3q)

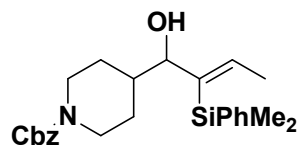
Following general procedure B, **3q** was obtained as colorless oil (36.9mg, yield 75%). ^1H NMR (500 MHz, CDCl_3) δ 7.60 – 7.51 (m,

2H), 7.40 – 7.30 (m, 3H), 6.46 (qd, $J = 7.0, 1.0$ Hz, 1H), 5.02 (s, 1H), 4.94 (d, $J = 1.2$ Hz, 1H), 4.63 (s, 1H), 1.68 (dd, $J = 7.1, 0.6$ Hz, 3H), 1.67 (s, 3H), 1.60 (s, 1H), 0.46 – 0.43 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 146.7, 140.0, 139.5, 138.9, 133.8, 128.8, 127.8, 111.5, 79.3, 19.5, 18.0, -0.8, -0.9. HRMS (ESI) m/z : calculated for $\text{C}_{15}\text{H}_{22}\text{NaOSi}^+ [\text{M}+\text{Na}]^+$: 269.1338, found: 269.1335.



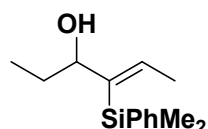
(Z)-3-(dimethyl(phenyl)silyl)-1-phenylpent-3-en-2-ol (3r)

Following general procedure B, **3r** was obtained as colorless oil (50.3mg, yield 85%). ^1H NMR (500 MHz, CDCl_3) δ 7.62 – 7.56 (m, 2H), 7.41 – 7.36 (m, 3H), 7.29 (t, $J = 7.4$ Hz, 2H), 7.22 (t, $J = 7.3$ Hz, 1H), 7.10 (d, $J = 7.3$ Hz, 2H), 6.63 – 6.57 (m, 1H), 4.41 (dd, $J = 9.4, 3.1$ Hz, 1H), 2.91 (dd, $J = 13.7, 3.3$ Hz, 1H), 2.62 (dd, $J = 13.7, 9.5$ Hz, 1H), 1.72 (d, $J = 7.1$ Hz, 3H), 1.57 (s, 1H), 0.52 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.8, 139.3, 139.0, 138.1, 133.9, 129.4, 128.9, 128.5, 127.9, 126.4, 76.7, 45.0, 18.0, -0.5, -0.6. HRMS (ESI) m/z : calculated for $\text{C}_{19}\text{H}_{24}\text{NaOSi}^+ [\text{M}+\text{Na}]^+$: 319.1489, found: 319.1487.



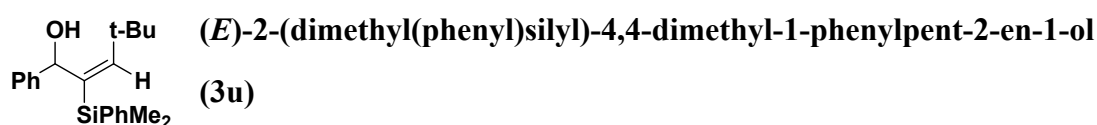
(Z)-benzyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)piperidine-1-carboxylate (3s)

Following general procedure B, **3s** was obtained as colorless oil (71.1mg, yield 84%). ^1H NMR (600 MHz, CDCl_3) δ 7.55 – 7.51 (m, 2H), 7.38 – 7.33 (m, 7H), 7.33 – 7.29 (m, 1H), 6.36 (q, $J = 7.0$ Hz, 1H), 5.12 (s, 2H), 4.20 (s, 2H), 3.89 (d, $J = 7.2$ Hz, 1H), 2.66 (s, 2H), 1.94 – 1.83 (m, 1H), 1.69 (d, $J = 7.1$ Hz, 3H), 1.55 (m, $J = 14.8, 11.0, 7.4, 4.0$ Hz, 2H), 1.45 (s, 1H), 1.17 (d, $J = 10.7$ Hz, 2H), 0.46 (d, $J = 2.2$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 155.2, 140.3, 140.1, 139.3, 137.0, 133.7, 128.9, 128.4, 127.9, 127.8, 81.8, 66.9, 44.1, 44.0, 41.0, 18.0, -0.41, -0.42. HRMS (ESI) m/z : calculated for $\text{C}_{25}\text{H}_{33}\text{NNaO}_3\text{Si}^+ [\text{M}+\text{Na}]^+$: 446.2122, found: 446.2122.

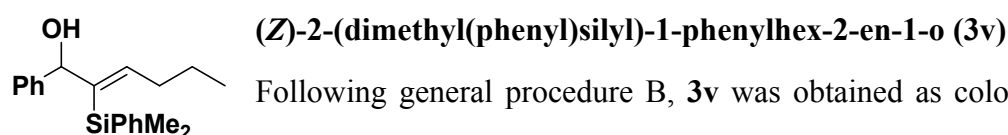


(Z)-4-(dimethyl(phenyl)silyl)hex-4-en-3-ol (3t)

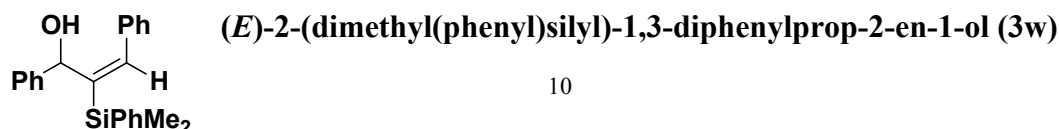
Following general procedure B, **3t** was obtained as colorless oil (33.7mg, yield 72%). ¹H NMR (600 MHz, CDCl₃) δ 7.57 – 7.52 (m, 2H), 7.35 (dd, *J* = 9.3, 6.3 Hz, 3H), 6.44 (qd, *J* = 7.0, 0.8 Hz, 1H), 4.16 – 4.09 (m, 1H), 1.64 (d, *J* = 7.0 Hz, 3H), 1.61 (ddd, *J* = 14.9, 7.0, 5.2 Hz, 1H), 1.51 (m, 2H), 0.90 (q, *J* = 7.4 Hz, 3H), 0.44 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 141.0, 139.1, 137.5, 133.3, 128.3, 127.4, 78.1, 30.2, 17.5, 10.2, -0.9, -1.0. HRMS (ESI) *m/z*: calculated for C₁₄H₂₂NaOSi⁺ [M + Na]⁺: 257.1332, found: 257.1331.



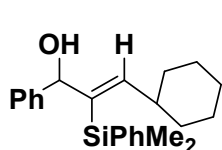
Following general procedure B, **3u** was obtained as colorless oil (57mg, yield 88%). ¹H NMR (500 MHz, CDCl₃) δ 7.45 – 7.41 (m, 2H), 7.37 – 7.20 (m, 8H), 6.20 (d, *J* = 4.5 Hz, 1H), 6.07 (d, *J* = 1.0 Hz, 1H), 1.71 (d, *J* = 4.8 Hz, 1H), 1.18 (s, 9H), 0.20 (d, *J* = 3.1 Hz, 3H), 0.10 – 0.06 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 153.3, 142.4, 140.0, 139.7, 133.4, 128.2, 127.4, 127.3, 126.3, 125.8, 71.0, 34.6, 31.2, -1.1, -1.6. LRMS (APCI) *m/z* calculated for (M-H)⁻[C₂₁H₂₇OSi]⁻: 323.2, found 323.7. HRMS (EI) *m/z*: calculated for C₂₁H₂₈O₂Si: 324.1908, found: 324.1910



Following general procedure B, **3v** was obtained as colorless oil (54mg, yield 87%). ¹H NMR (500 MHz, CDCl₃) δ 7.47 – 7.42 (m, 2H), 7.38 – 7.26 (m, 8H), 6.41 (td, *J* = 7.5, 0.9 Hz, 1H), 5.36 (s, 1H), 2.12 – 2.04 (m, 2H), 1.38 – 1.28 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H), 0.30 (d, *J* = 2.0 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 145.8, 143.1, 139.6, 139.6, 133.8, 128.7, 128.1, 127.7, 127.2, 127.0, 79.0, 34.0, 22.7, 13.8, -0.6, -0.7. LRMS (APCI) *m/z* calculated for (M-H)⁻[C₂₀H₂₅OSi]⁻: 309.2, found 309.0. HRMS (ESI) *m/z*: calculated for C₂₀H₂₆NaOSi⁺ [M + Na]⁺: 333.1645, found: 333.1638

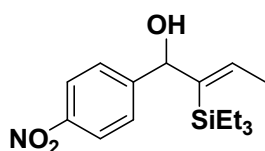


Following general procedure B, **3w** was obtained as colorless oil (46mg, yield 67%). ¹H NMR (500 MHz, CDCl₃) δ 7.59 – 7.54 (m, 2H), 7.43 – 7.39 (m, 2H), 7.39 – 7.33 (m, 5H), 7.33 – 7.25 (m, 6H), 7.13 (s, 1H), 6.02 (s, 1H), 0.33 (d, *J* = 3.3 Hz, 3H), 0.29 (d, *J* = 3.4 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 144.91, 142.75, 141.86, 139.35, 137.26, 134.05, 128.97, 128.61, 128.23, 127.87, 127.46, 127.05, 126.29, 72.75, -1.12, -1.44. HRMS (ESI) *m/z*: calculated for C₂₃H₂₄OSi⁺ [M + H]⁺: 344.1597, found: 344.1596.



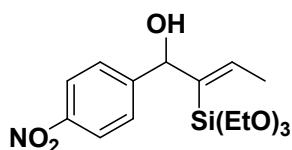
(Z)-3-cyclohexyl-2-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol (3x)

Following general procedure B, **3x** was obtained as colorless oil (67mg, yield 64%). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (m, 2H), 7.35 – 7.26 (m, 8H), 6.18 (d, *J* = 10.0 Hz, 1H), 5.31 (s, 1H), 2.24 – 2.11 (m, 1H), 1.88 (s, 1H), 1.60 (d, *J* = 9.0 Hz, 2H), 1.56 (s, 1H), 1.41 (s, 2H), 1.04 (m, 5H), 0.25 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 150.9, 143.19, 139.89, 137.59, 133.89, 128.7, 128.1, 127.6, 127.2, 127.0, 78.9, 40.8, 32.6, 32.5, 25.9, 25.6, 25.5, -0.59, -0.68. HRMS (ESI) *m/z*: calculated for C₂₃H₃₁OSi⁺ [M + H]⁺: 350.2101, found: 350.2100



(Z)-1-(4-nitrophenyl)-2-(triethylsilyl)but-2-en-1-ol (4a)

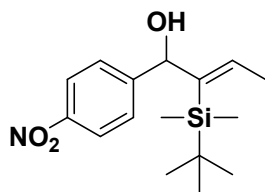
Following general procedure B, **4a** was obtained as colorless oil (57.7mg, yield 94%). ¹H NMR (500 MHz, CDCl₃) δ 8.18 (dd, *J* = 8.5, 6.7 Hz, 2H), 7.53 (t, *J* = 10.1 Hz, 2H), 6.37 (tt, *J* = 7.1, 3.5 Hz, 1H), 5.33 (d, *J* = 3.5 Hz, 1H), 1.89 (d, *J* = 4.1 Hz, 1H), 1.87 (d, *J* = 7.1 Hz, 3H), 0.86 (dd, *J* = 9.5, 6.2 Hz, 9H), 0.69 – 0.50 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 150.6, 146.4, 142.0, 139.9, 126.9, 122.7, 78.3, 17.1, 7.1, 3.6. HRMS (ESI) *m/z*: calculated for C₁₆H₂₅NNaO₃Si⁺ [M + Na]⁺: 330.1496, found: 330.1488.



(Z)-1-(4-nitrophenyl)-2-(triethoxysilyl)but-2-en-1-ol (4b)

Following general procedure B, **4b** was obtained as colorless oil (23.4mg, yield 61%). ¹H NMR (500 MHz, DMSO-*d*₆) δ

8.20 – 8.15 (m, 2H), 7.56 (d, $J = 8.5$ Hz, 2H), 6.61 (m, $J = 7.0, 1.0$ Hz, 1H), 5.59 (d, $J = 4.6$ Hz, 1H), 5.27 (d, $J = 4.5$ Hz, 1H), 3.61 (q, $J = 7.0$ Hz, 6H), 1.90 – 1.85 (m, 3H), 1.05 (t, $J = 7.0$ Hz, 9H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 153.5, 146.6, 142.0, 137.1, 128.3, 123.3, 75.4, 58.0, 18.4, 17.8. HRMS (ESI) m/z : calculated for $\text{C}_{16}\text{H}_{24}\text{NO}_6\text{Si}^-$ [$\text{M} - \text{H}$] $^-$: 354.1378, found: 354.1379.

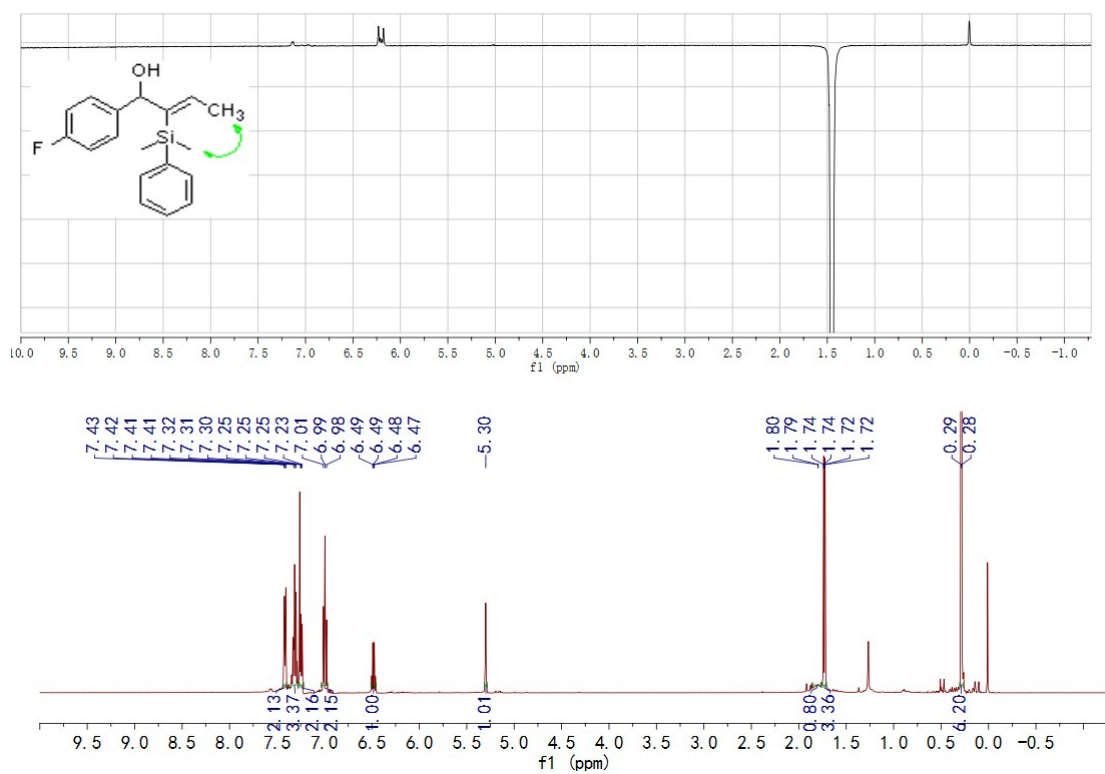


(Z)-2-(tert-butyltrimethylsilyl)-1-(4-nitrophenyl)but-2-en-1-ol (4c)

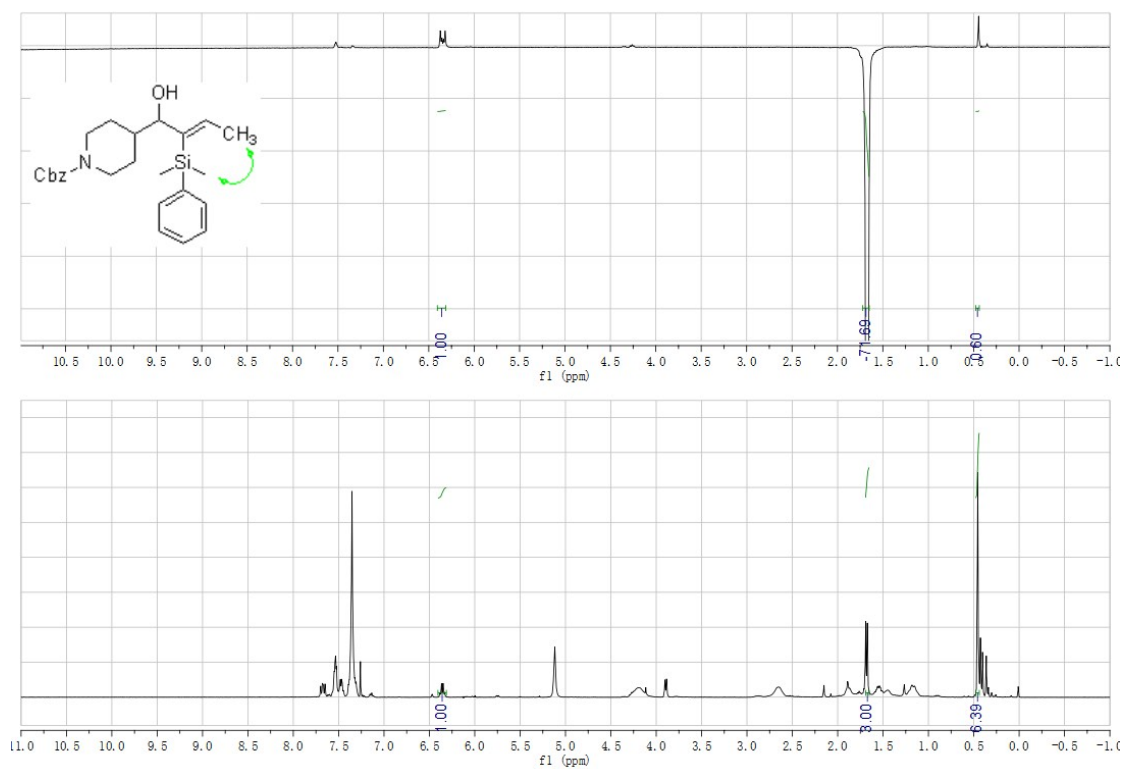
Following general procedure B, **4c** was obtained as colorless oil (36.8mg, yield 60%). ^1H NMR (500 MHz, CDCl_3) δ 8.21 – 8.14 (m, 2H), 7.53 (t, $J = 9.8$ Hz, 2H), 6.36 (tt, $J = 7.0, 3.5$ Hz, 1H), 5.40 (d, $J = 6.6$ Hz, 1H), 1.91 (s, 1H), 1.87 (d, $J = 7.2$ Hz, 3H), 0.93 (d, $J = 3.0$ Hz, 9H), 0.12 (d, $J = 3.1$ Hz, 3H), 0.09 – 0.04 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 151.5, 147.0, 143.4, 141.0, 127.6, 123.3, 77.6, 27.4, 18.9, 18.6, -2.9, -3.3. HRMS (ESI) m/z : calculated for $\text{C}_{16}\text{H}_{24}\text{NO}_3\text{Si}^-$ [$\text{M} - \text{H}$] $^-$: 306.1531, found: 306.1534.

(C) The NOE analysis

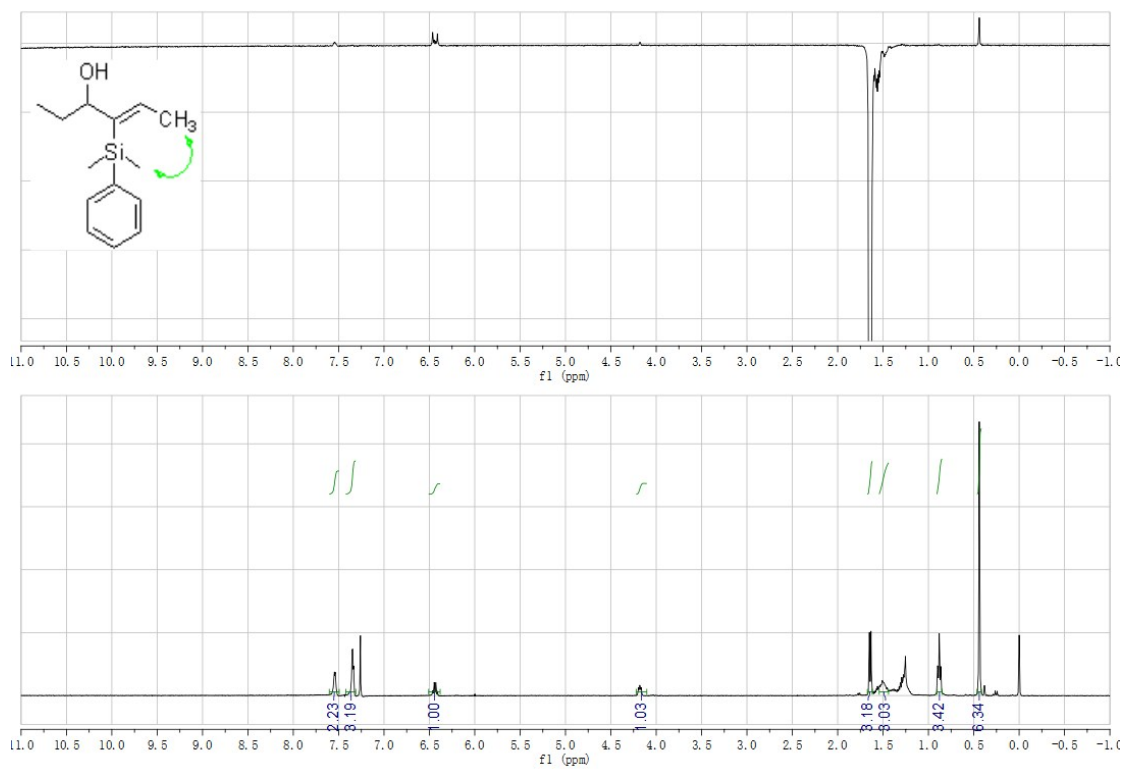
a) The NOE analysis of **3j**



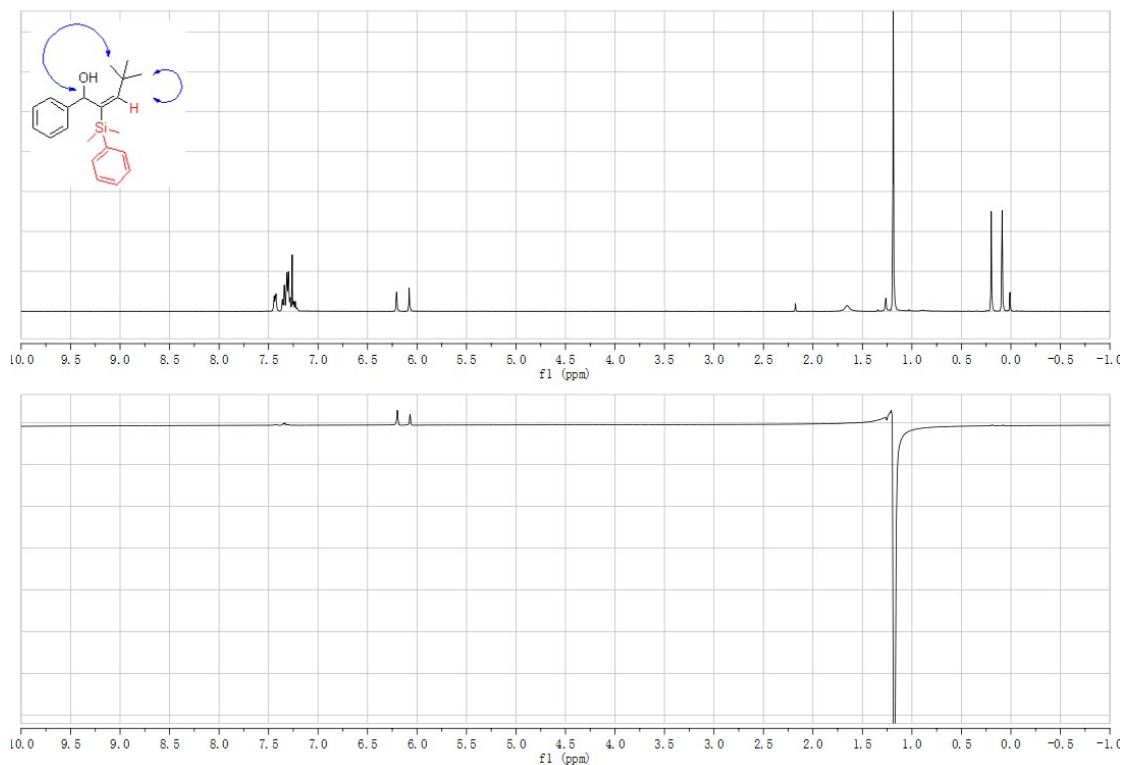
b) The NOE analysis of 3s



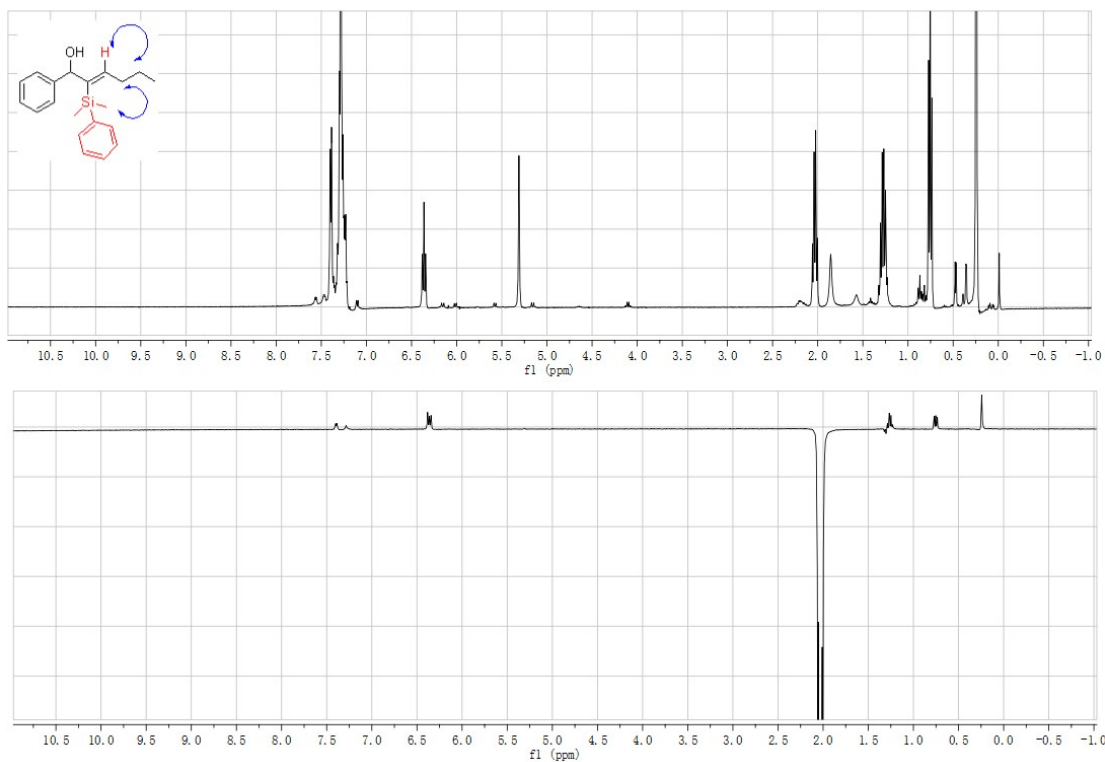
c) The NOE analysis of 3t



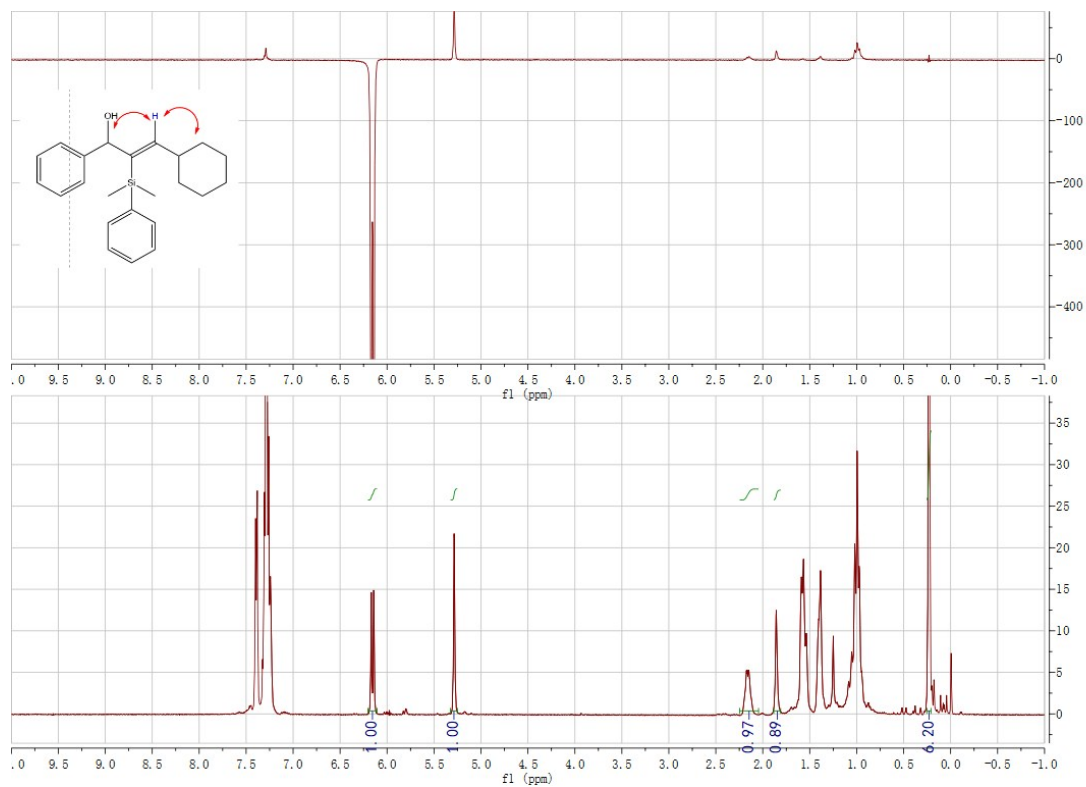
d) The NOE analysis of 3u

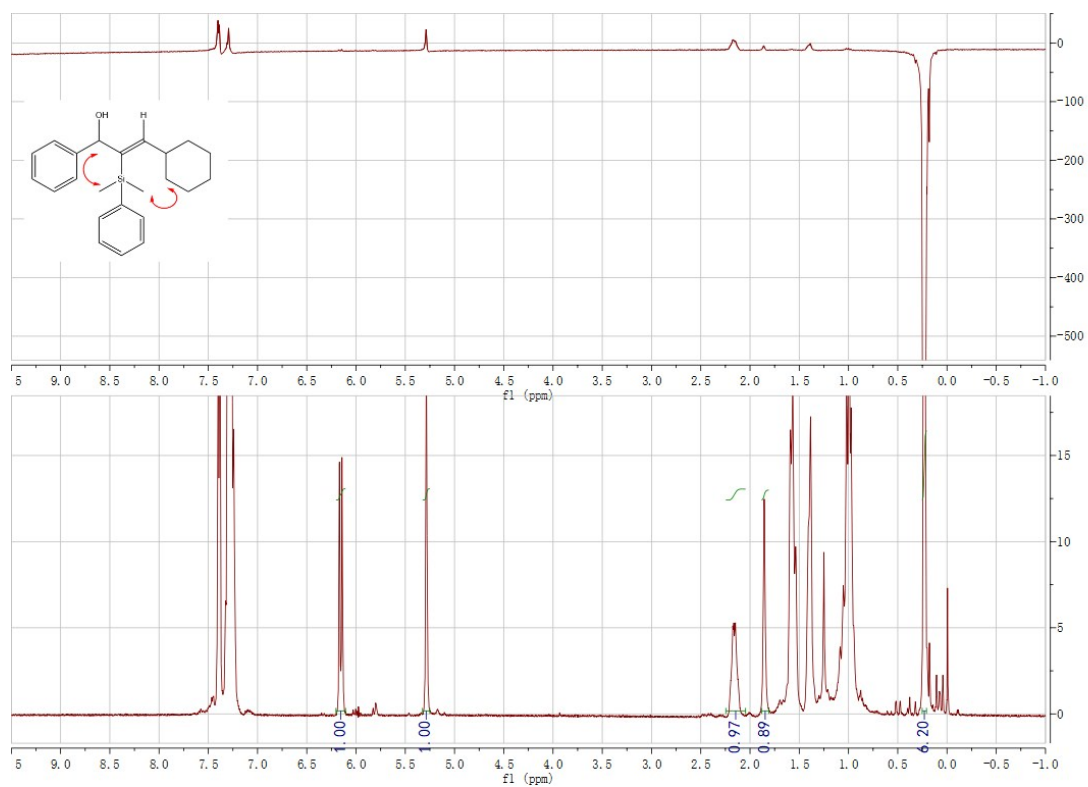


e) The NOE analysis of 3v

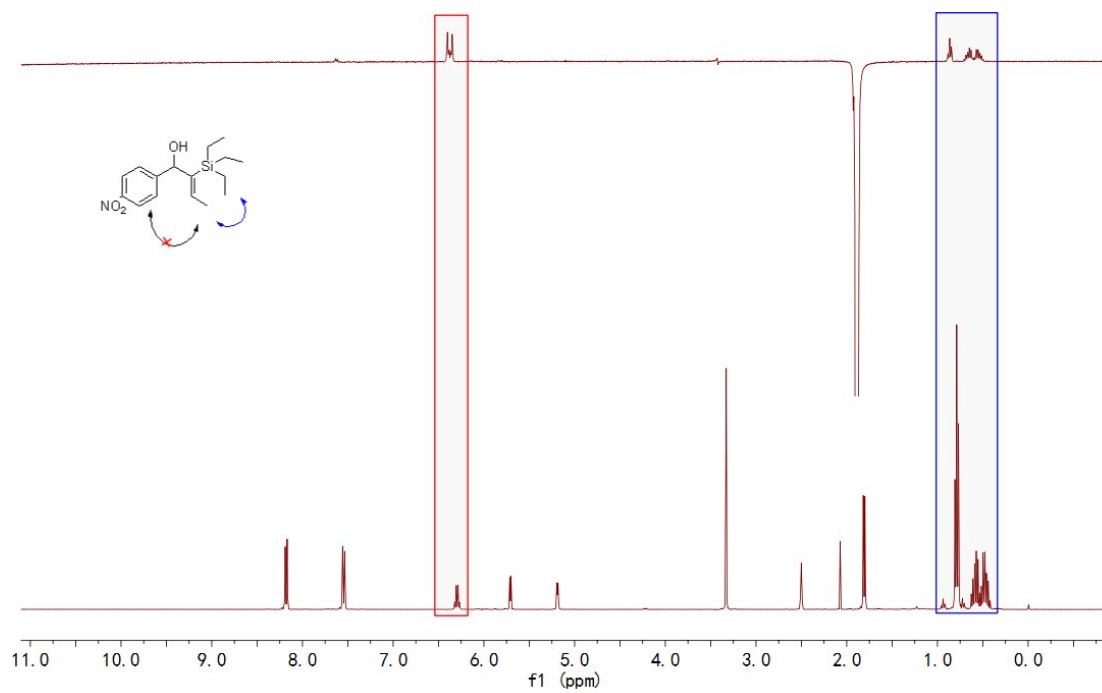


f) The NOE analysis of 3x

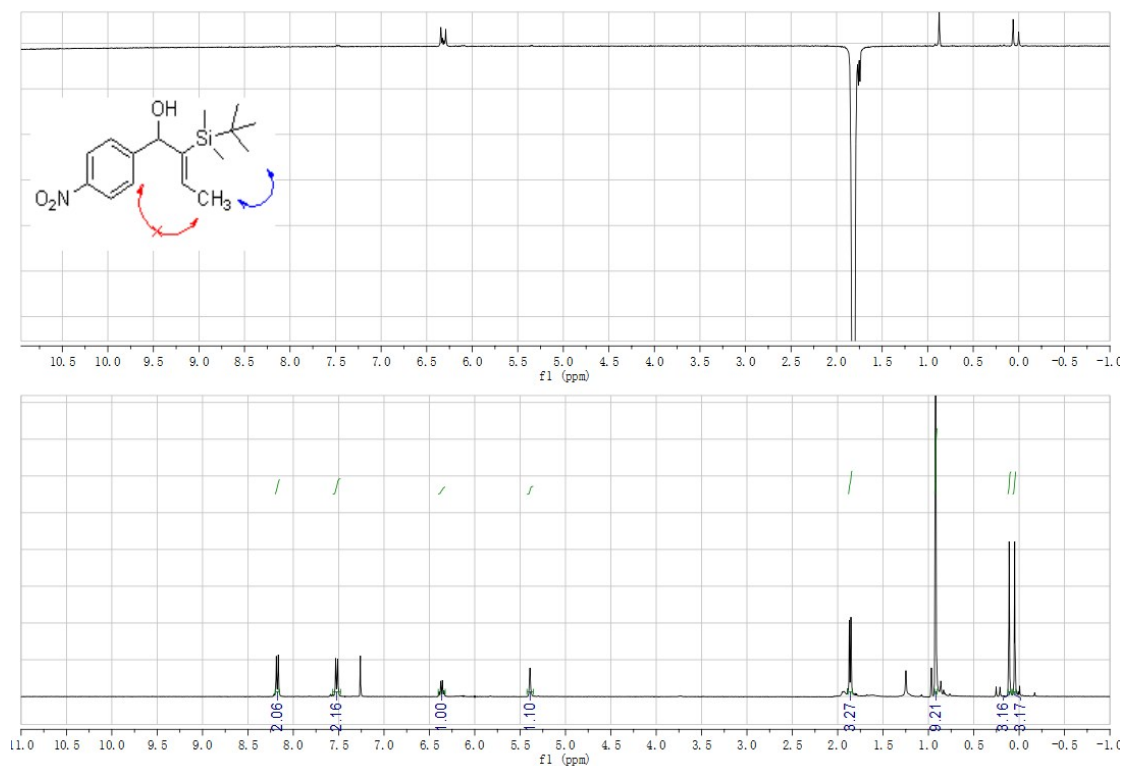




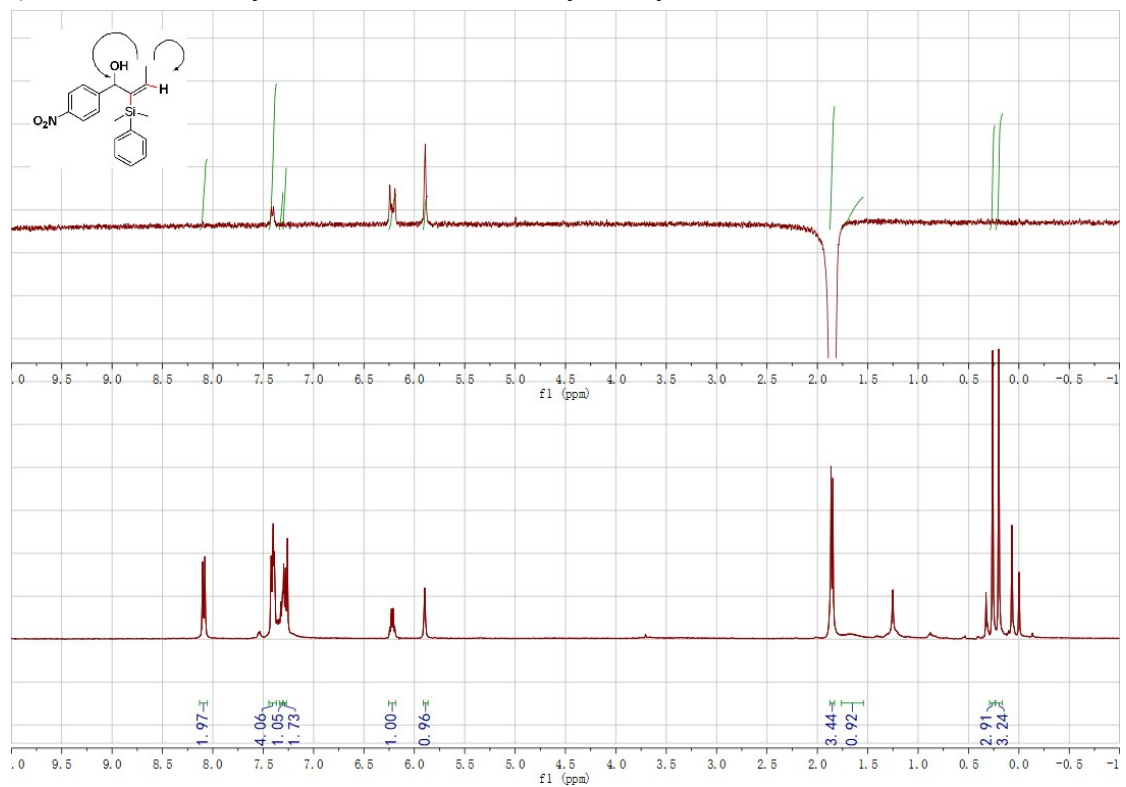
g) The NOE analysis of 4a



h) The NOE analysis of 4c



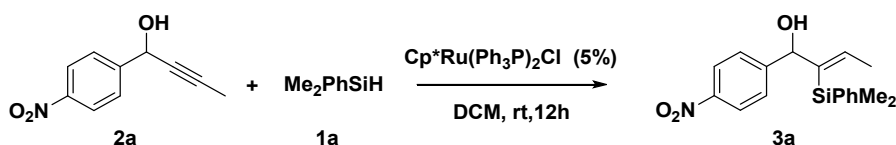
i) The NOE analysis of α -selective *cis*-hydrosilylation



(D) Gram-scale preparation of 3a and synthetic applications of

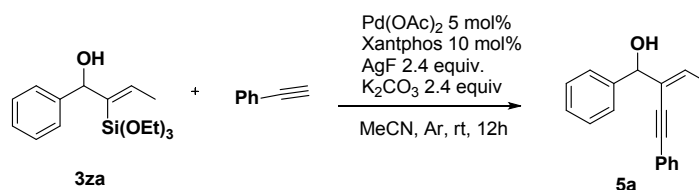
vinylsilane

a) Gram-scale preparation of **3a**

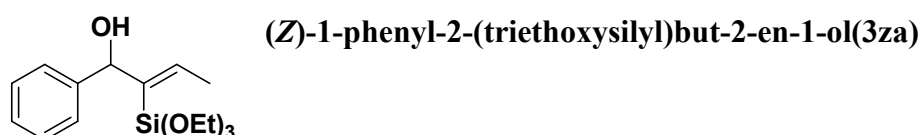


The dry sealed tube was charged with propargyl alcohol **2a** (1g, 5.2mmol, 1 equiv), **1a** (6.2mmol, 1.2 equiv), $\text{CpRu}(\text{Ph}_3\text{P})_2\text{Cl}$ (5mol%) (0.26mmol, 0.05 equiv) and 50 mL dry DCM. The mixture was kept at room temperature for 12h under Argon atmosphere. The resulting mixture was diluted with dichloromethane and washed by water. The combined organic layers were dried with Na_2SO_4 , filtered, concentrated and purified by column chromatography on silica gel (PE/EA = 20/1, v/v) to give the desired product **3a** (1.22 g, 75% yield).

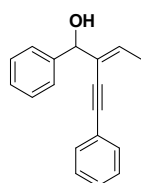
b) The coupling reaction of vinylsilane **3za**



To a 25 mL of Schlenk tube were added $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.01mmol, 5mol%), Xantphos (12 mg, 0.02mmol, 10mol%), K_2CO_3 (66 mg, 0.48 mmol), and AgF (61 mg, 0.48 mmol) under air. The mixture was then evacuated and backfilled with Argon (3 times). **3za** (75 mg, 0.24mmol), Phenylacetylene (20.5 mg, 0.2mmol), and dry MeCN (2 mL) were added subsequently. The Schlenk tube was screw capped and stirred under room temperature for 12h. After this time, the reaction mixture was diluted with EtOAc, filtered through a pad of celite, and concentrated. The residue was purified with silica gel chromatography (PE/EA) to give product **5a** as colorless oil (34 mg, 68% yield).



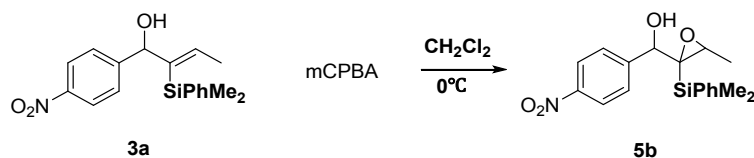
The product **3za** was obtained as colorless oil (55mg, yield 60%). ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.48 – 6.40 (m, 1H), 5.19 (d, *J* = 9.5 Hz, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.69 – 3.60 (m, 6H), 1.93 (d, *J* = 7.0 Hz, 3H), 1.13 (t, *J* = 7.0 Hz, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 144.1, 143.3, 137.0, 127.8, 126.6, 126.0, 79.6, 58.3, 17.9, 17.6. HRMS (EI) *m/z*: calculated for C₁₆H₂₆O₄Si: 310.1595, found: 310.1600



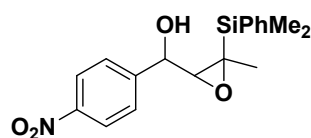
(E)-1-phenyl-2-(phenylethynyl)but-2-en-1-ol (5a)

The product **5a** was a colorless oil (34mg, yield 68%). ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.30 (dd, *J* = 8.2, 5.1 Hz, 4H), 6.21 – 6.13 (m, 1H), 5.30 (d, *J* = 4.2 Hz, 1H), 2.28 (d, *J* = 4.8 Hz, 1H), 1.98 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.6133.1, 130.9, 127.8, 127.8, 127.8, 127.3, 126.8, 126.0, 122.7, 96.0, 84.6, 76.3, 15.6. HRMS (EI) *m/z*: calculated for C₁₈H₁₆O: 248.1196, found: 248.1199

c) The epoxidation reaction of vinylsilane 3a



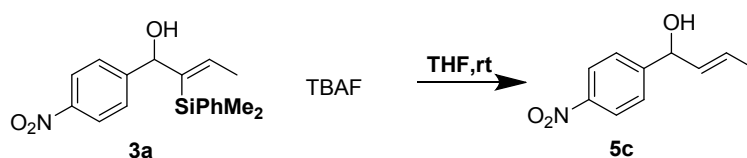
Preparation of silicane epoxide **5b**: Vinylsilane **3a** (65.4 mg, 0.2mmol) was taken up in CH₂Cl₂ (4 mL) and treated with *m*CPBA (662 mg, 3.07 mmol assuming 80% purity) at 0°C. After the reaction mixture had been stirred for 14 h, saturated aqueous sodium bicarbonate (10mL) and solid Na₂S₂O₃ (ca. 2 g) were added. The mixture was extracted with ether (3×30 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Silica gel chromatography (petroleum ether/ethyl acetate(v/v,20/1) as eluent) afforded the desired epoxyalcohol as a single isomer (51.5 mg, 75% yield).



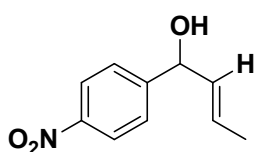
(2-(dimethyl(phenyl)silyl)-3-methyloxiran-2-yl)(4-nitrophenyl)methanol (5b)

The product **5b** was obtained as colorless oil (51.5 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.11 – 8.06 (m, 2H), 7.41 – 7.37 (m, 1H), 7.36 – 7.30 (m, 4H), 7.24 (dd, *J* = 6.4, 4.7 Hz, 2H), 4.76 (s, 1H), 3.54 (q, *J* = 5.7 Hz, 1H), 2.67 (s, 1H), 1.40 (d, *J* = 5.8 Hz, 3H), 0.36 – 0.33 (m, 3H), 0.18 – 0.15 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 147.8, 147.0, 135.8, 134.2, 129.8, 129.0, 128.0, 123.4, 72.5, 58.4, 54.3, 15.8, -1.6, -3.0. HRMS (ESI) *m/z*: calculated for C₁₈H₂₀NO₄Si⁻ [M-H]⁻: 342.1167, found: 342.1165

d) The protodesilylation reaction of vinylsilane 3a



Preparation of protodesilylation **5c**: Vinylsilane **3a** (65.4 mg, 0.2 mmol) was dissolved in THF (4 mL) and treated with TBAF (0.24 mmol, 1m in THF) at room temperature. After the reaction mixture was stirred for 30 min, saturated aqueous sodium bicarbonate was added, the mixture was extracted with ether (3×30 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. Silica gel chromatography (eluent: petroleum ether/ethyl acetate(v/v,20/1) as eluent) afforded the desired product (27.1mg, 70% yield).

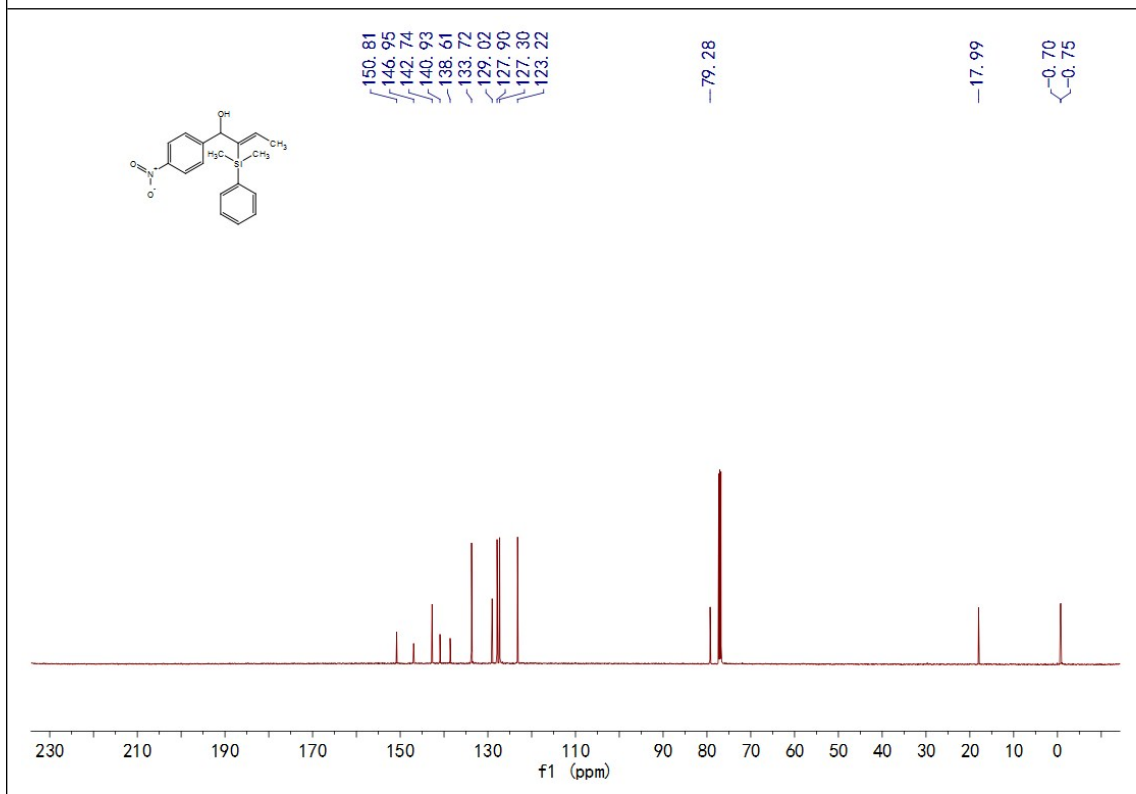
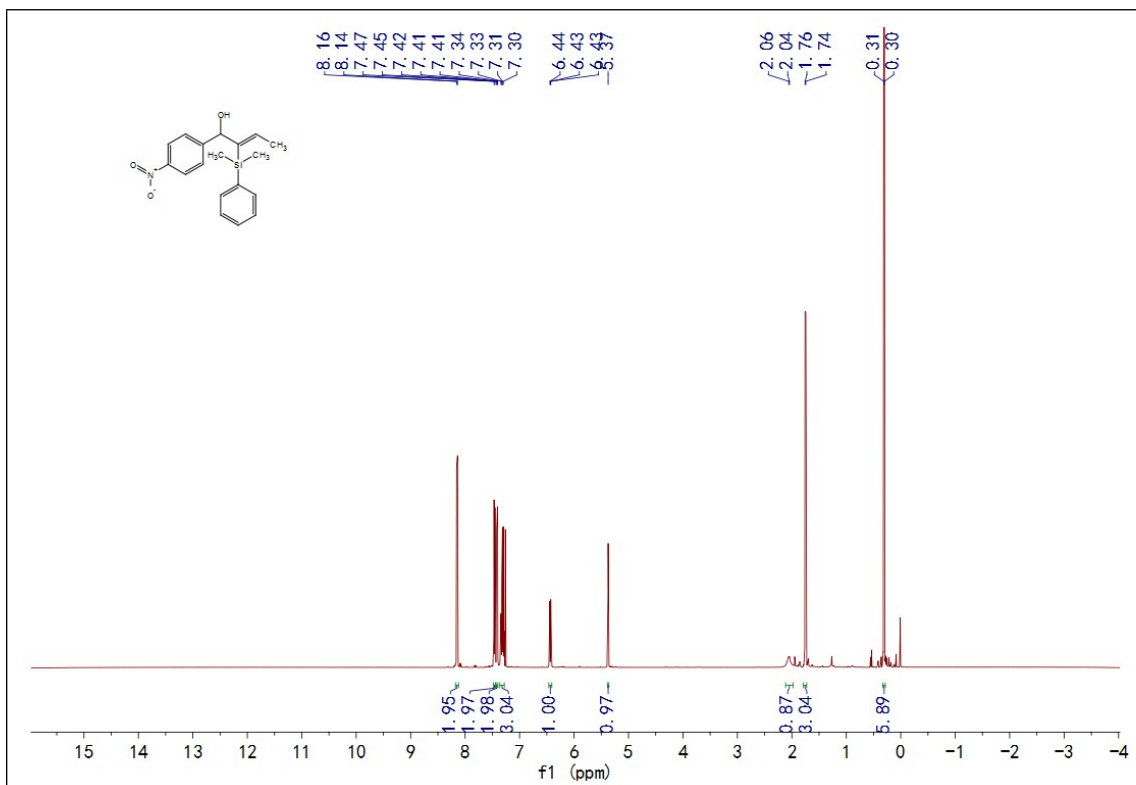


1-hydroxy-1-(4-nitrophenyl)butan-2-one (5c)

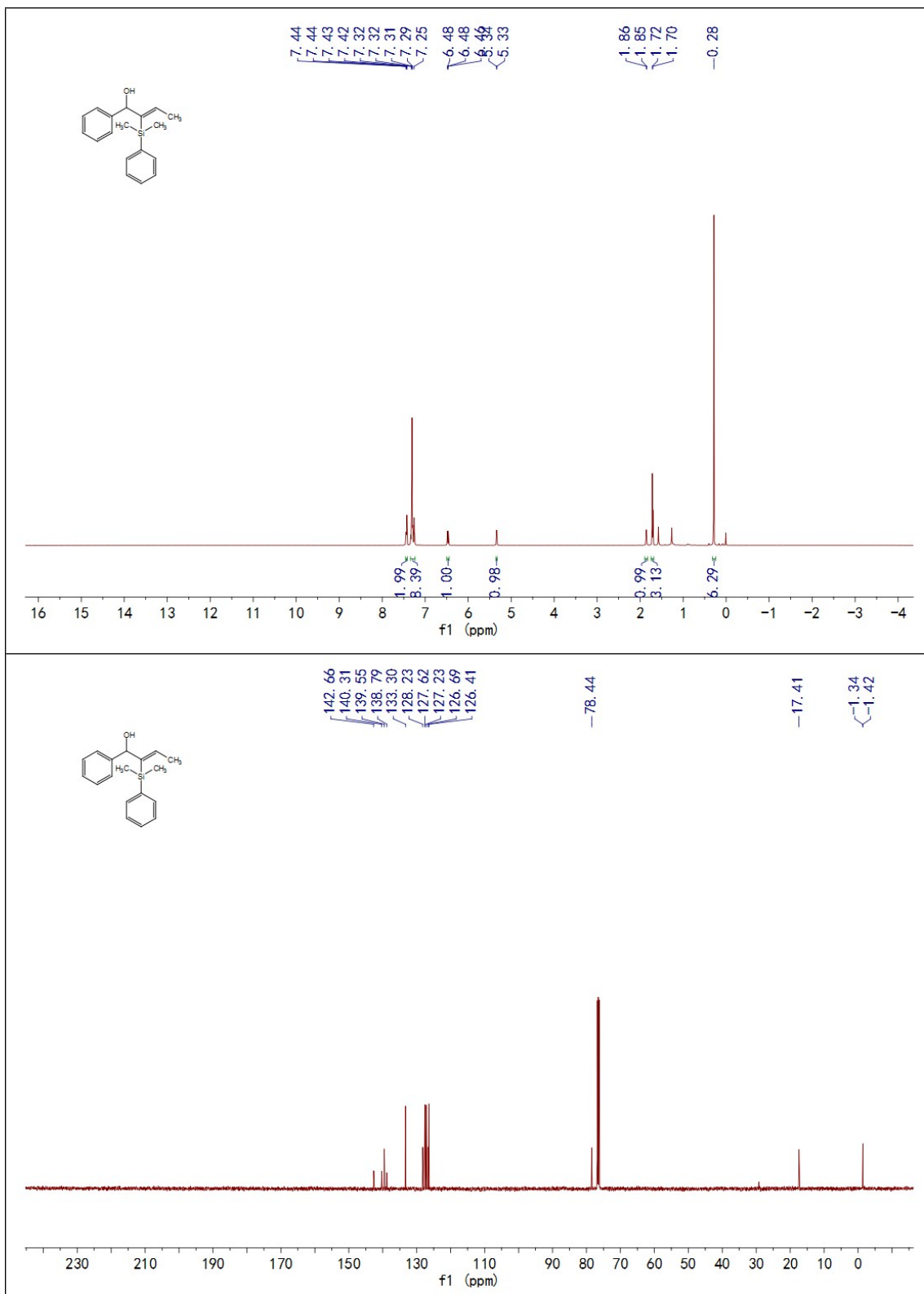
The product **5c** was obtained as colorless oil (27.1mg, 70% yield). ¹H NMR (500 MHz, CDCl₃) δ 8.23 – 8.14 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 5.89 – 5.78 (m, 1H), 5.66 – 5.57 (m, 1H), 5.26 (d, *J* = 7.4 Hz, 1H), 2.03 (s, 1H), 1.74 (dd, *J* = 6.5, 1.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 150.4, 147.2, 132.6, 129.4, 126.8, 123.6, 74.4, 17.7. LRMS (APCI) *m/z* calculated for (M-H)⁻ [C₁₀H₁₁NO₃]⁻: 192.0, found 192.1. HRMS (ESI) *m/z*: calculated for C₁₀H₁₁NNaO₃⁺ [M+Na]⁺: 216.0637, found: 216.0640

(E) Copies of ^1H NMR and ^{13}C NMR Spectra for the Products

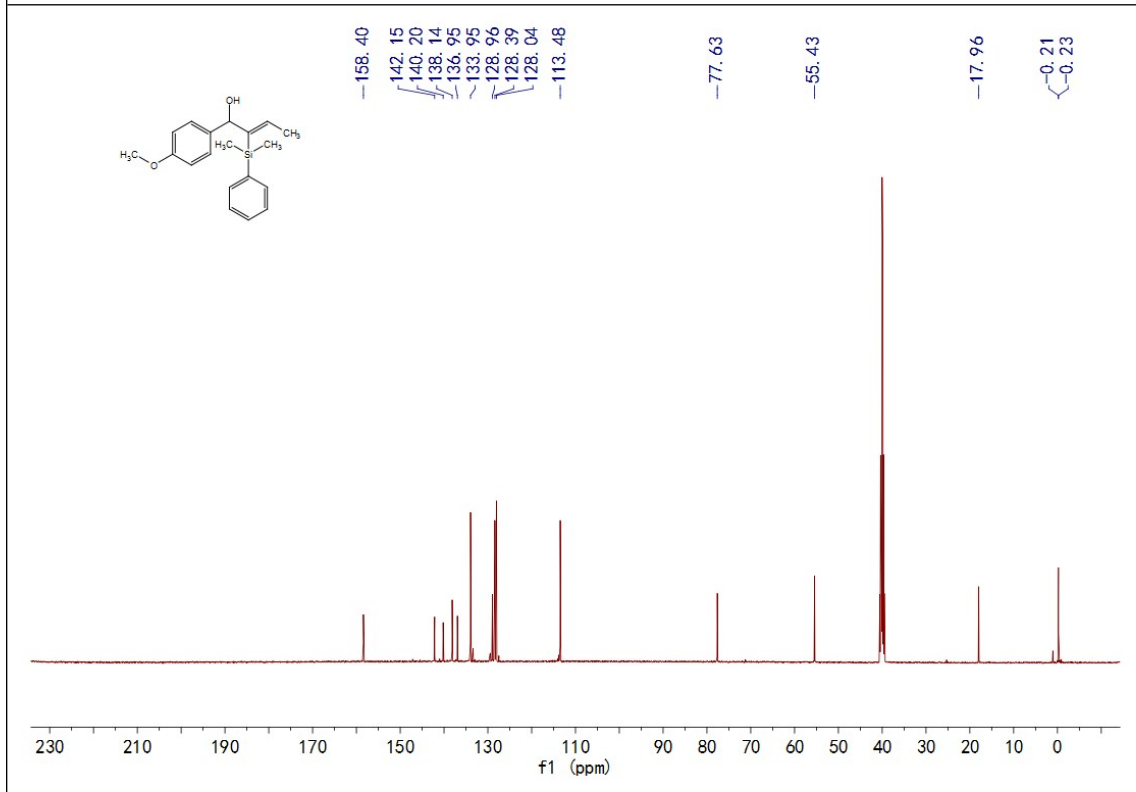
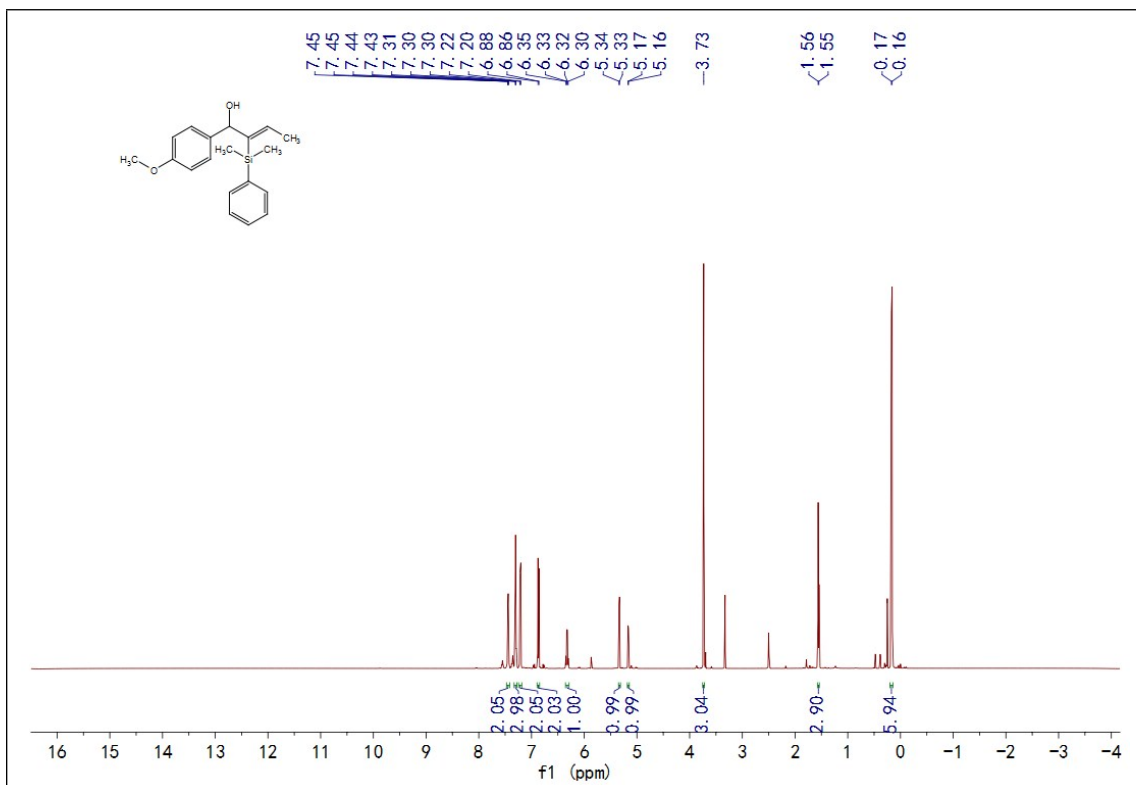
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-nitrophenyl)but-2-en-1-ol (3a)



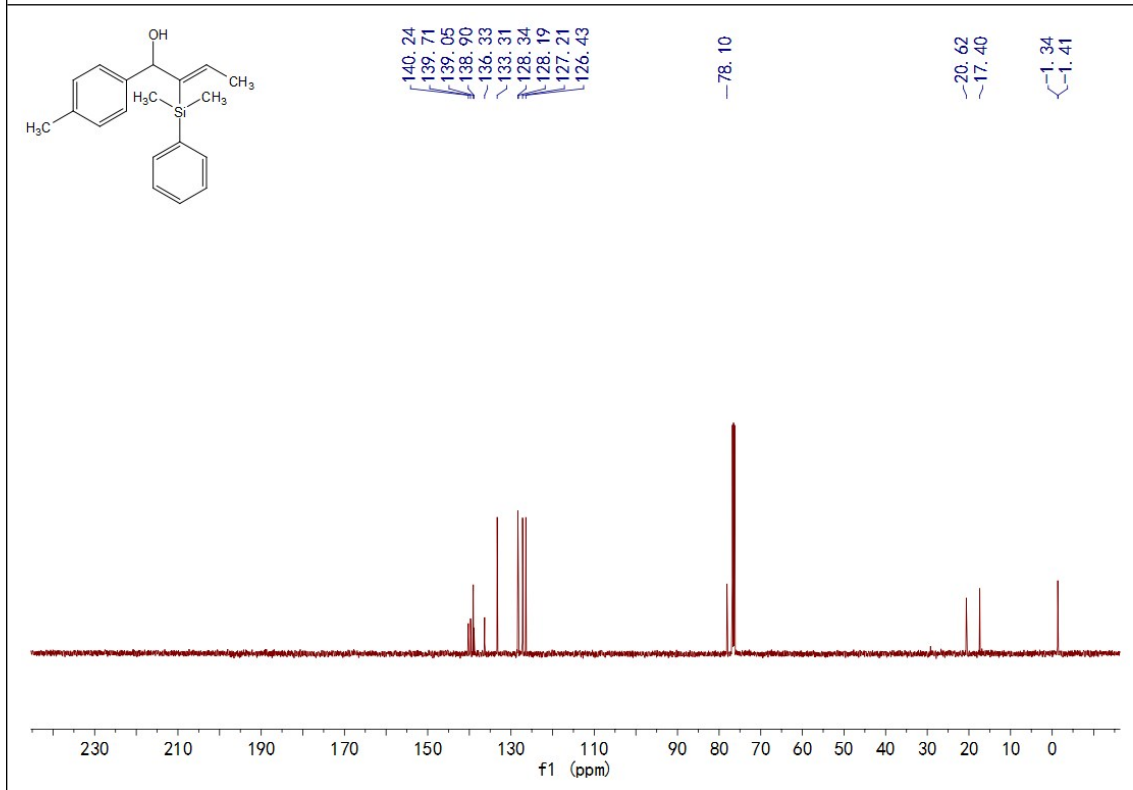
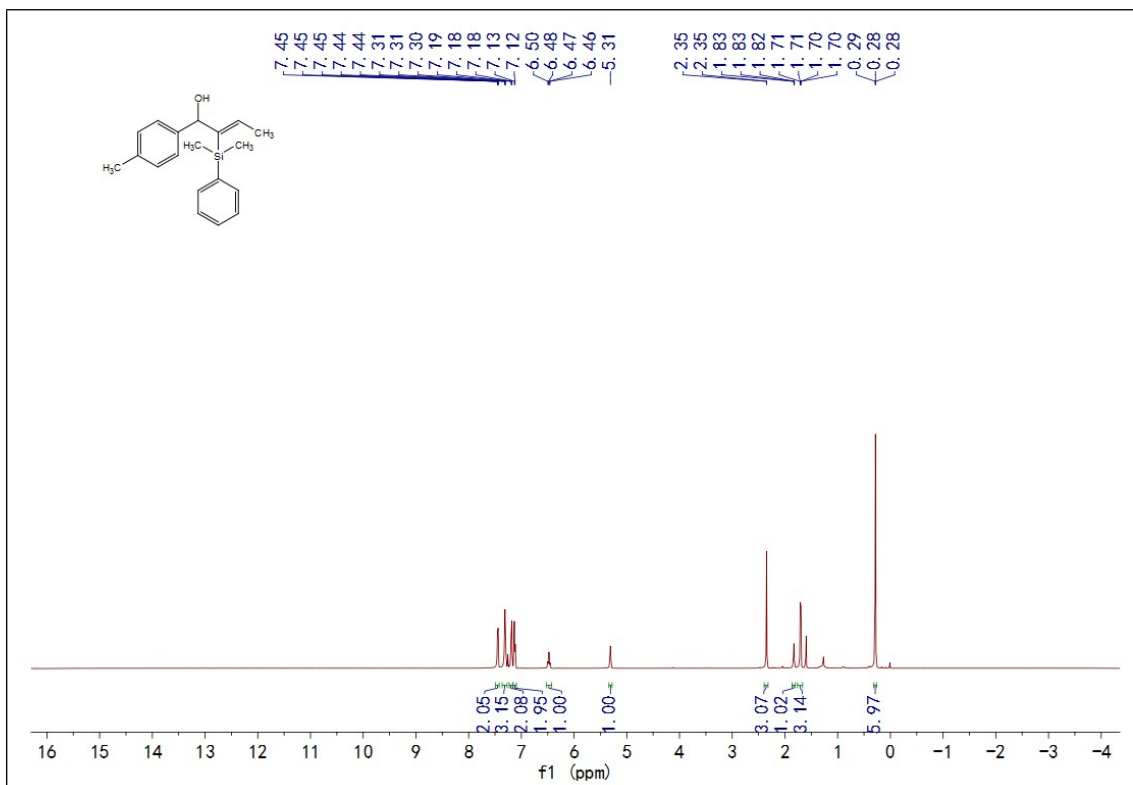
(Z)-2-(dimethyl(phenyl)silyl)-1-phenylbut-2-en-1-ol (3b)



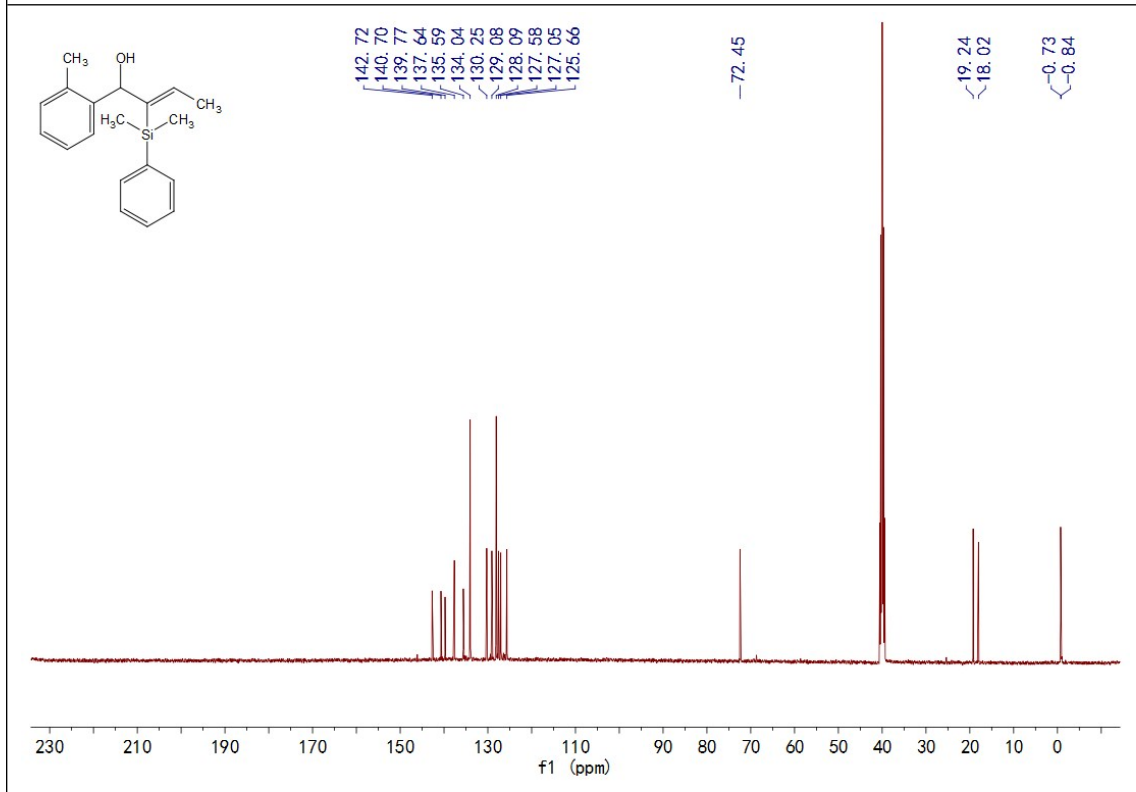
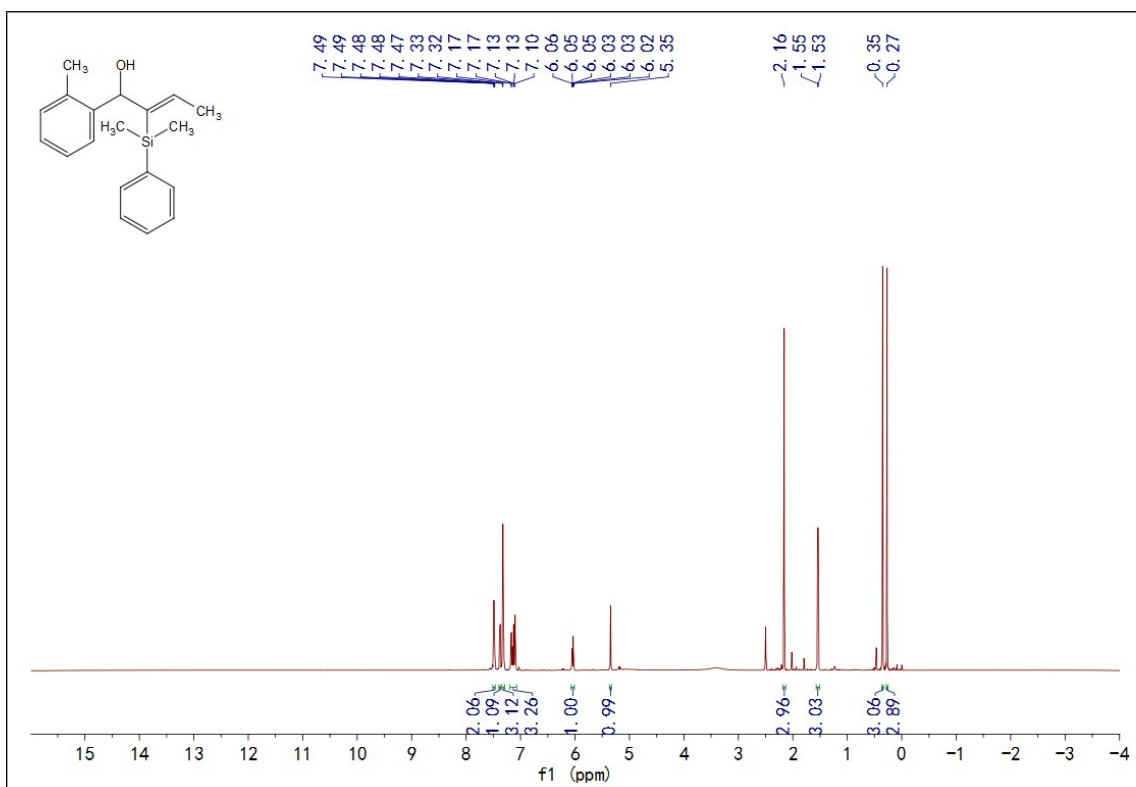
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)but-2-en-1-ol (3c)



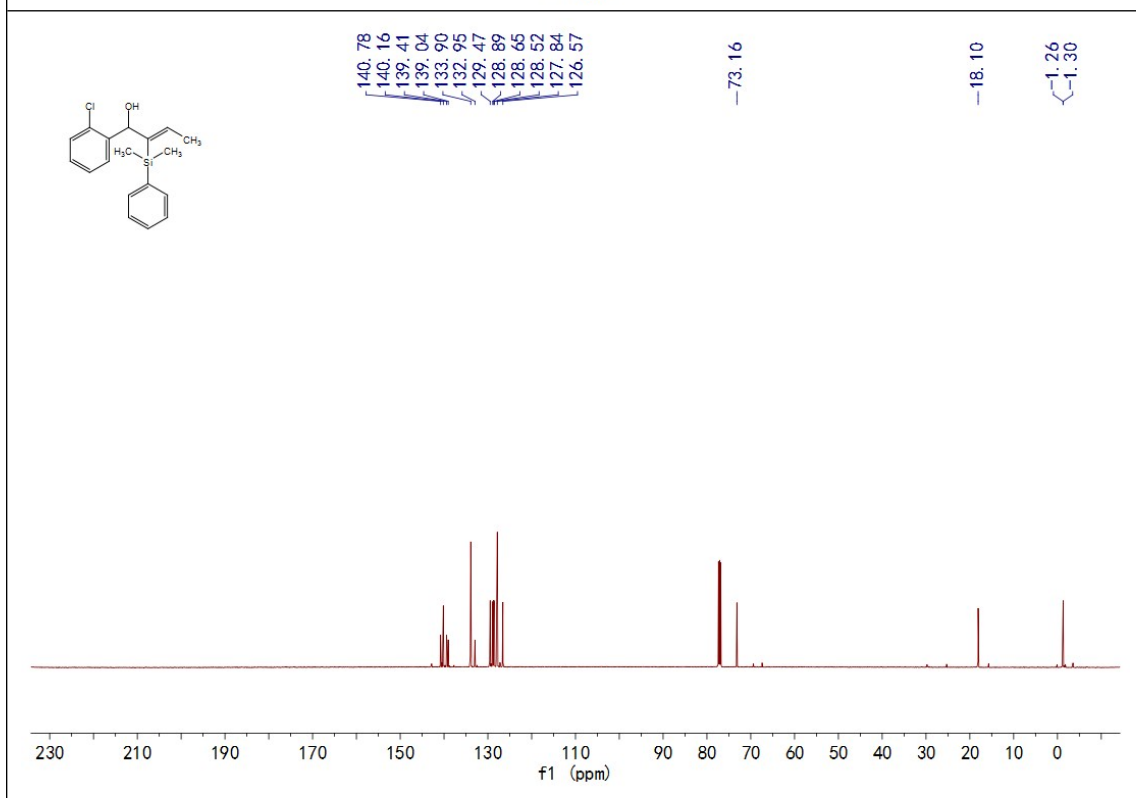
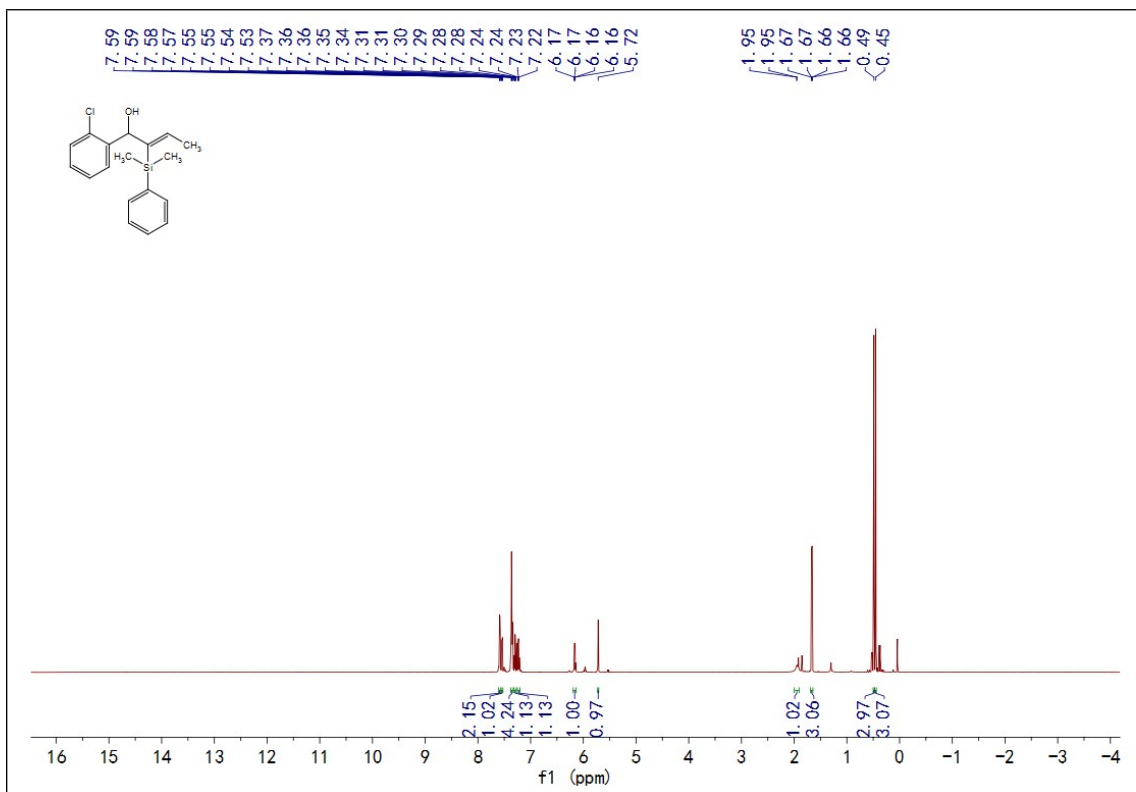
(Z)-2-(dimethyl(phenyl)silyl)-1-(p-tolyl)but-2-en-1-ol (3d)



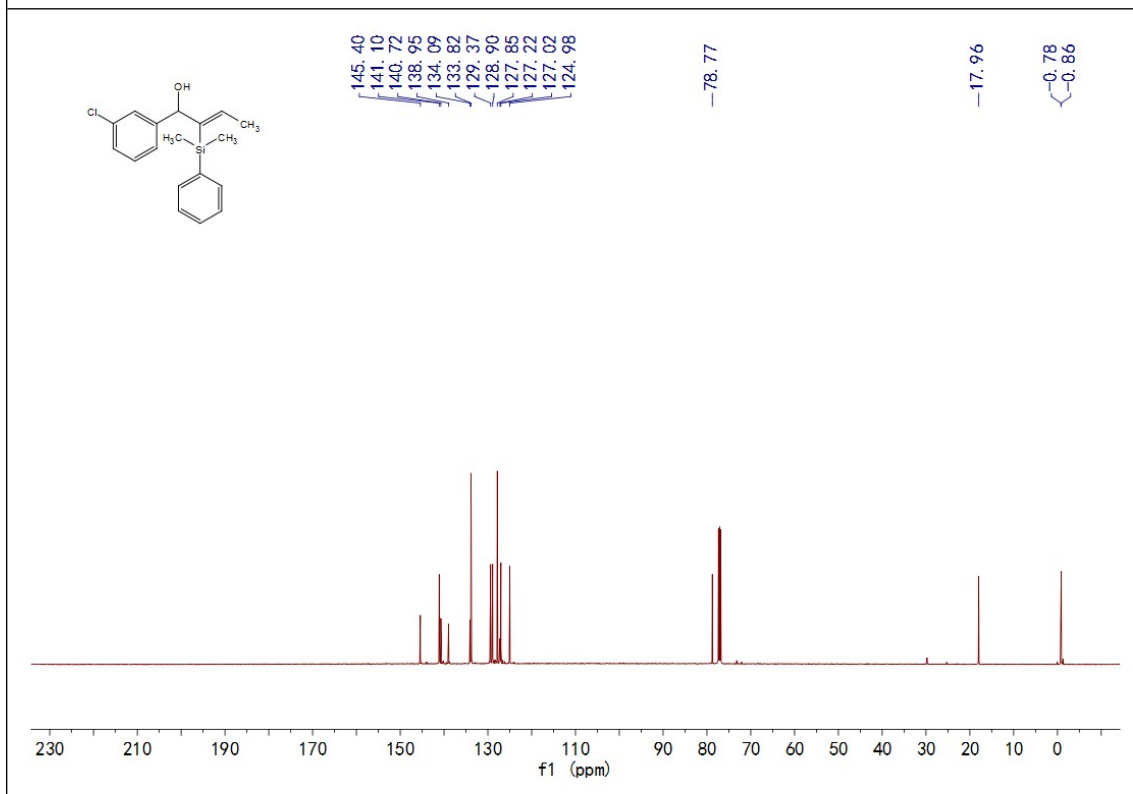
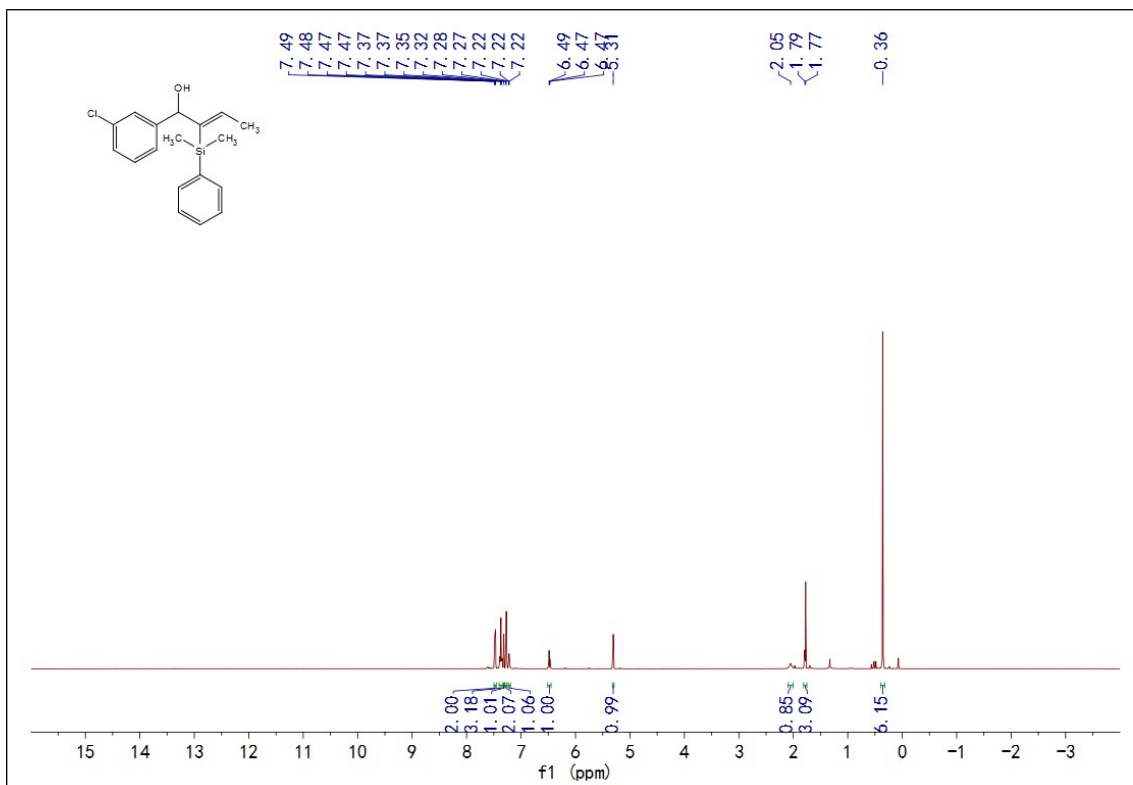
(Z)-2-(dimethyl(phenyl)silyl)-1-(o-tolyl)but-2-en-1-ol (3e)



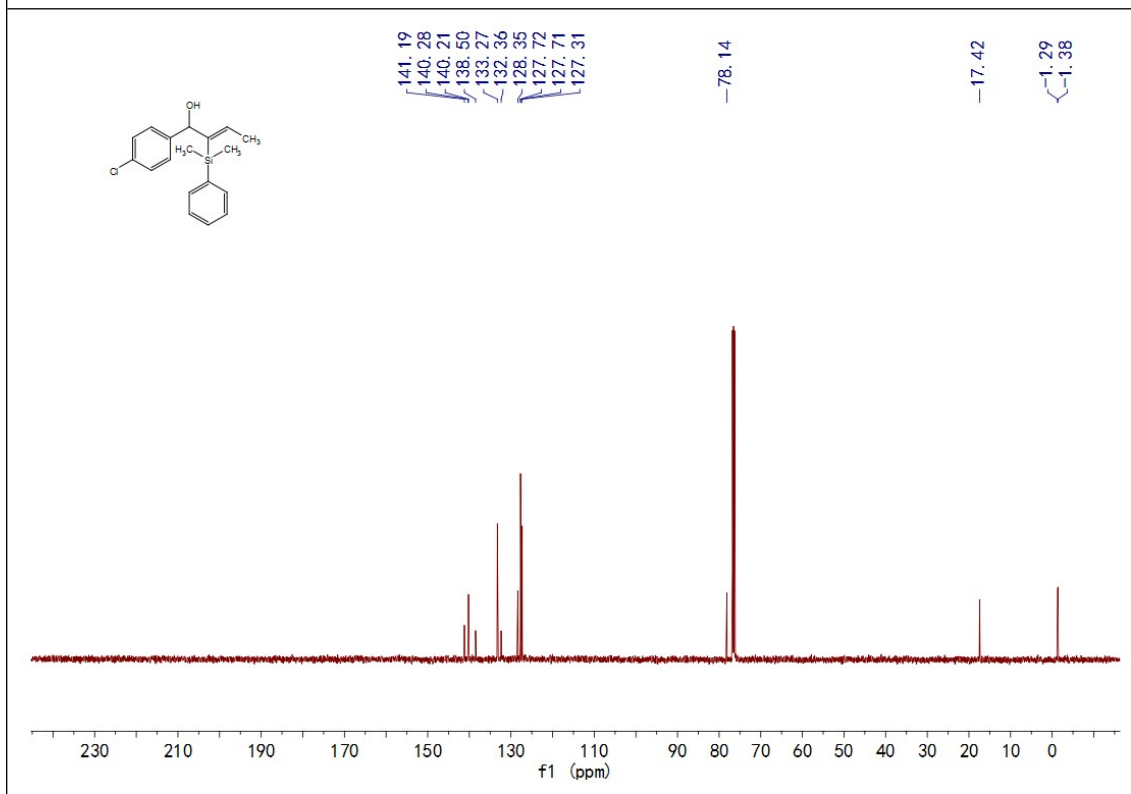
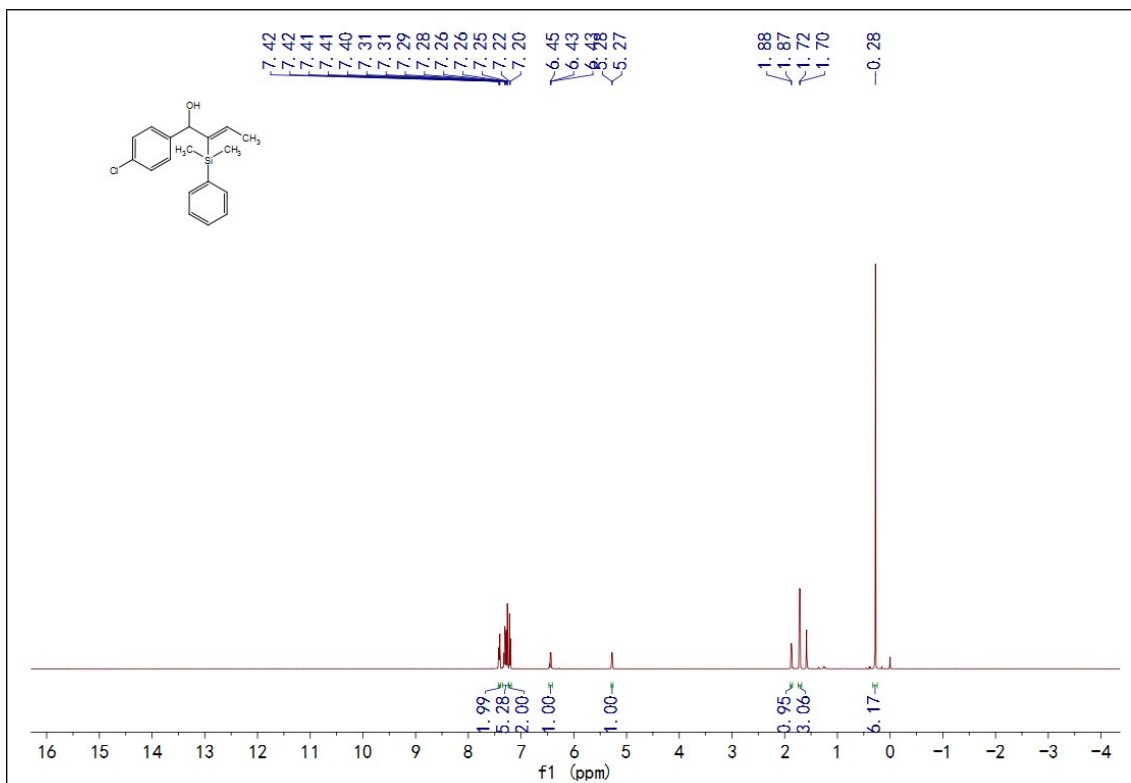
(Z)-1-(2-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3f)



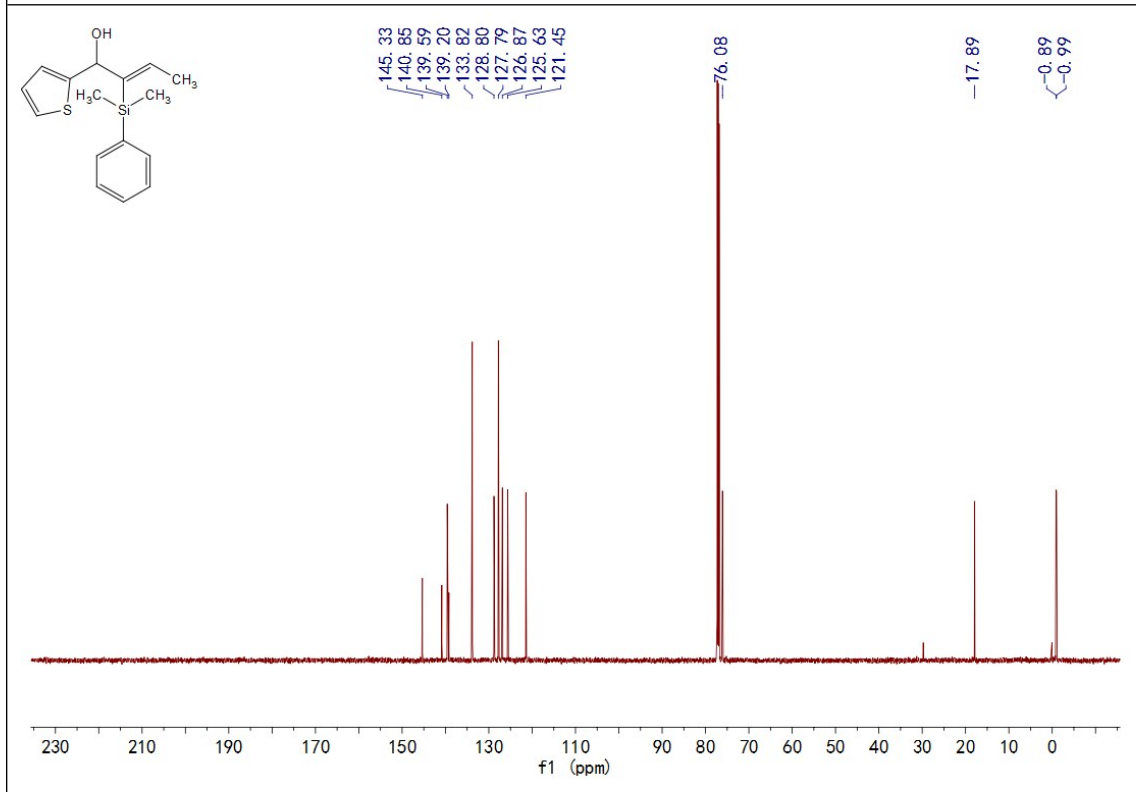
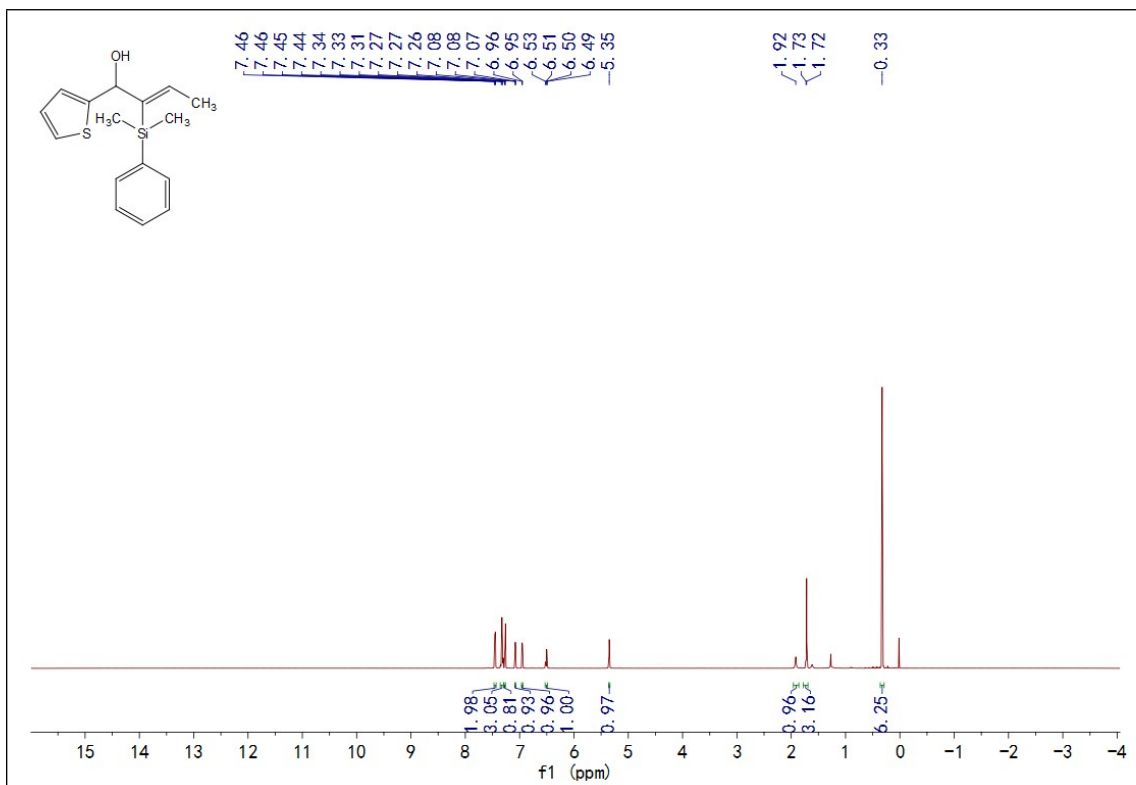
(Z)-1-(3-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3g)



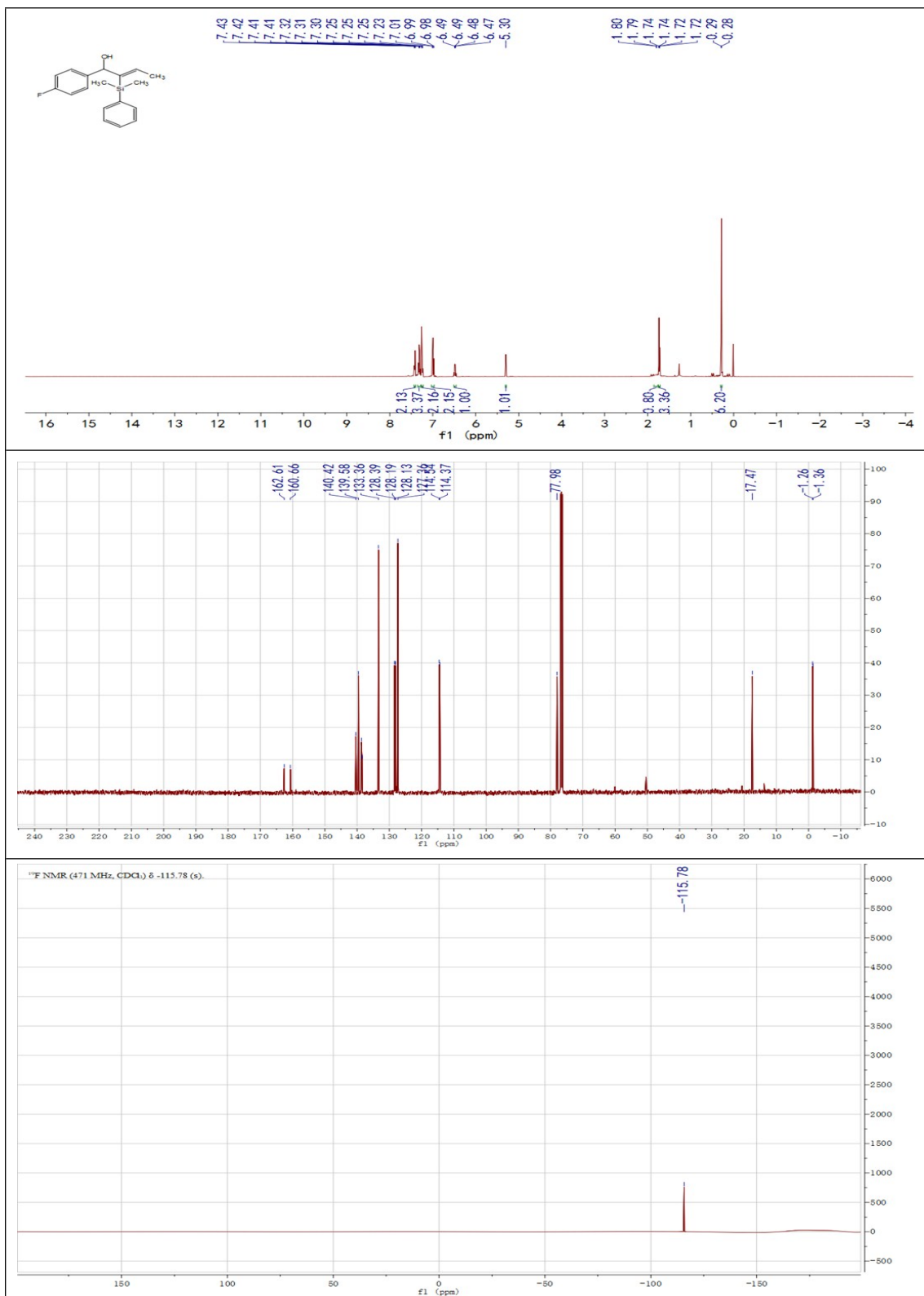
(Z)-1-(4-chlorophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3h)



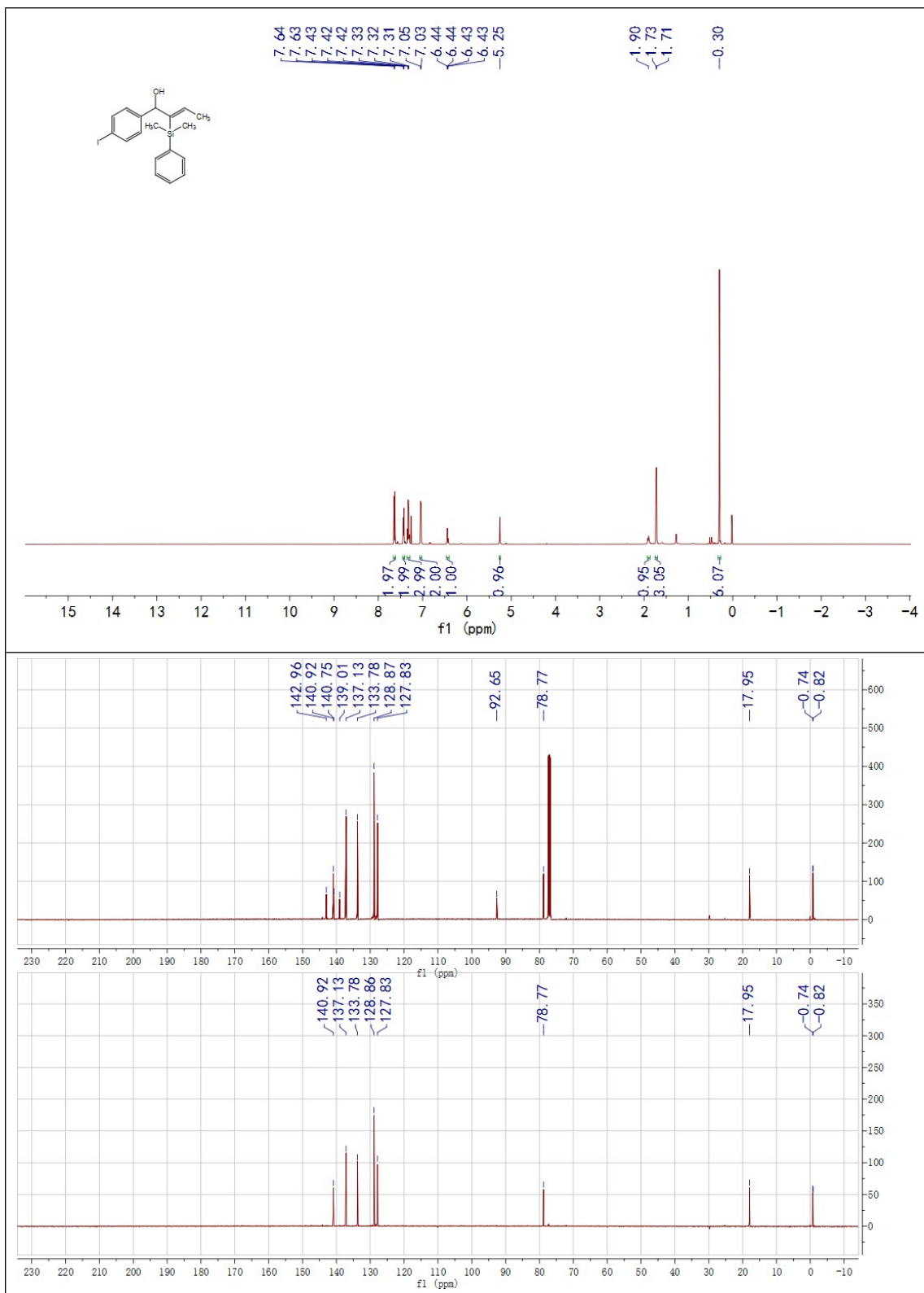
(Z)-2-(dimethyl(phenyl)silyl)-1-(thiophen-3-yl)but-2-en-1-ol (3i)



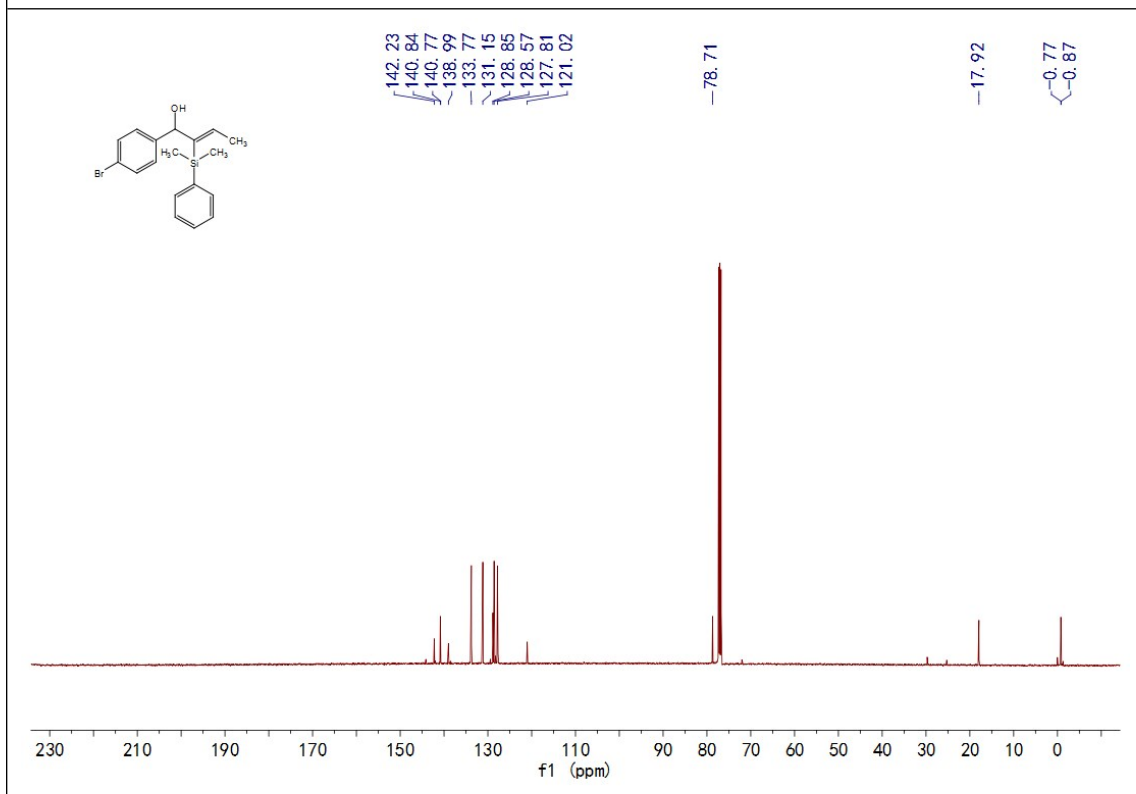
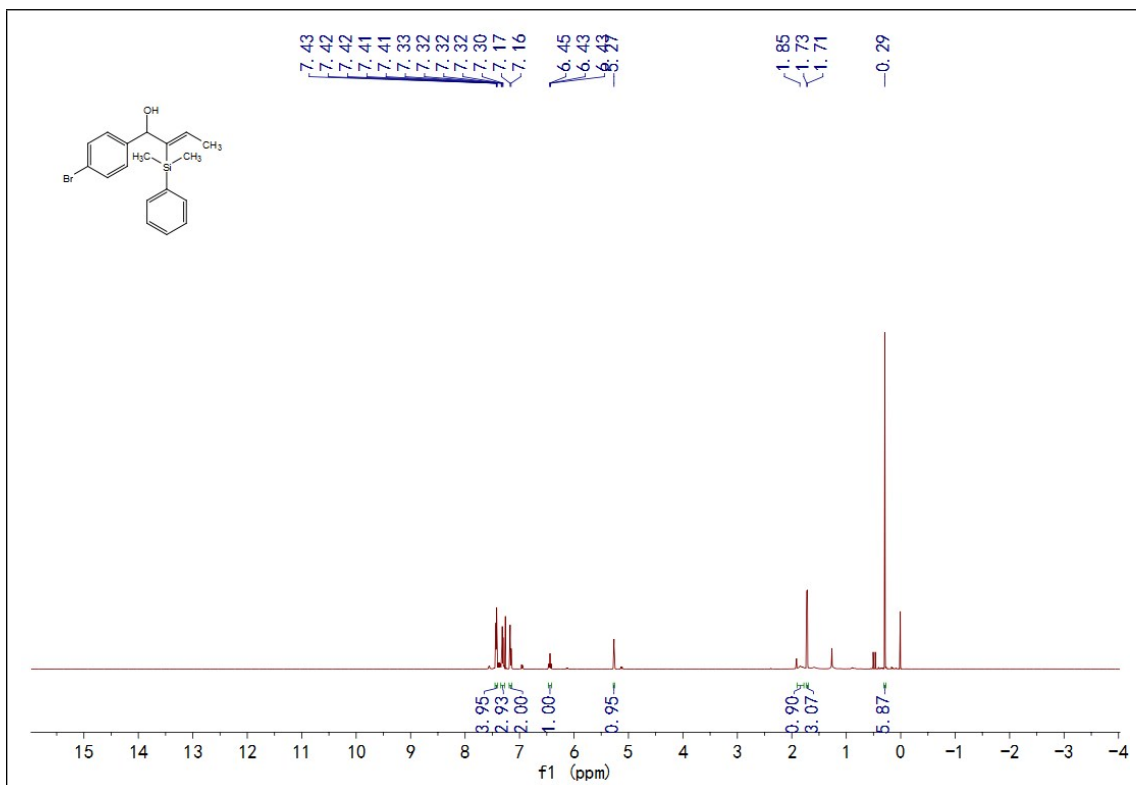
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-fluorophenyl)but-2-en-1-ol (3j)



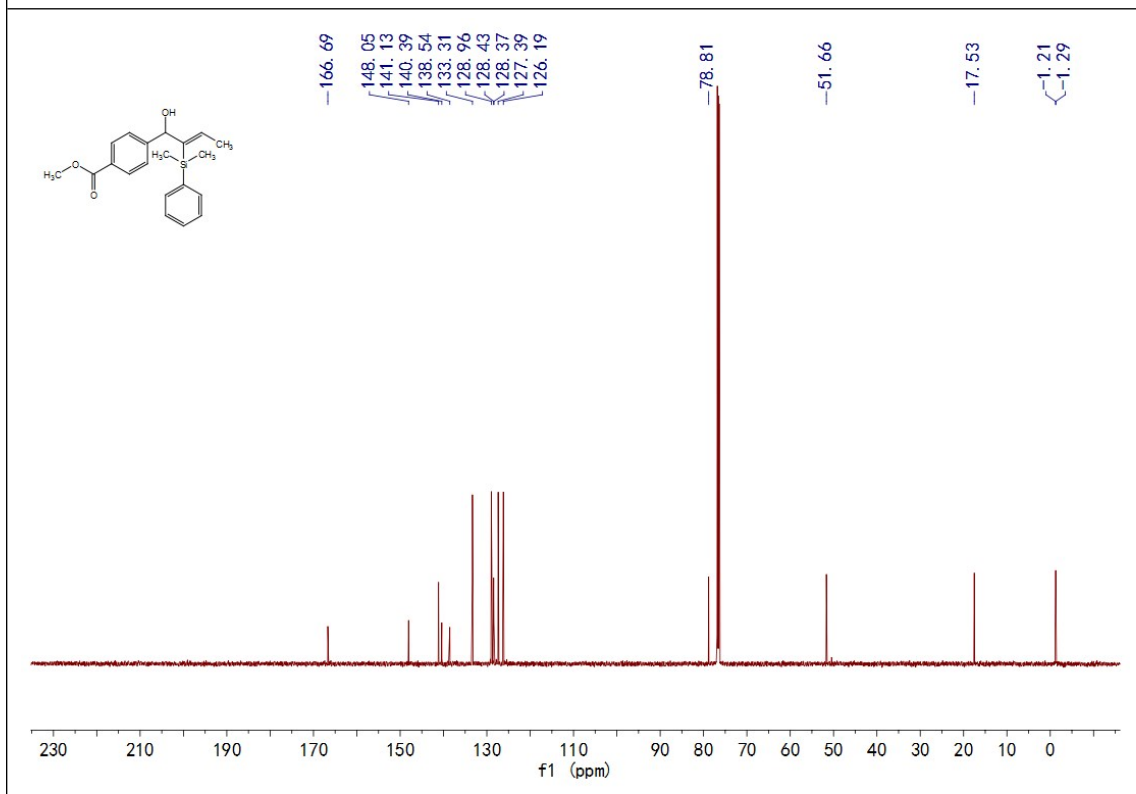
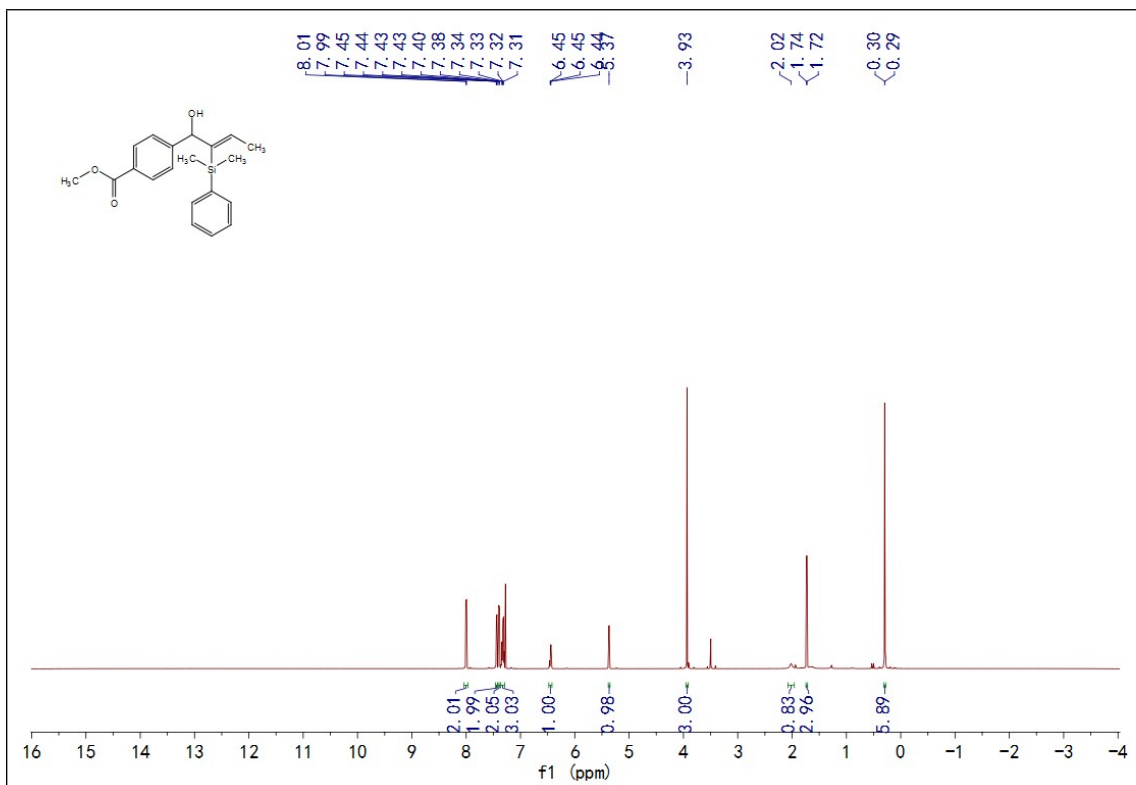
(Z)-2-(dimethyl(phenyl)silyl)-1-(4-iodophenyl)but-2-en-1-ol (3k)



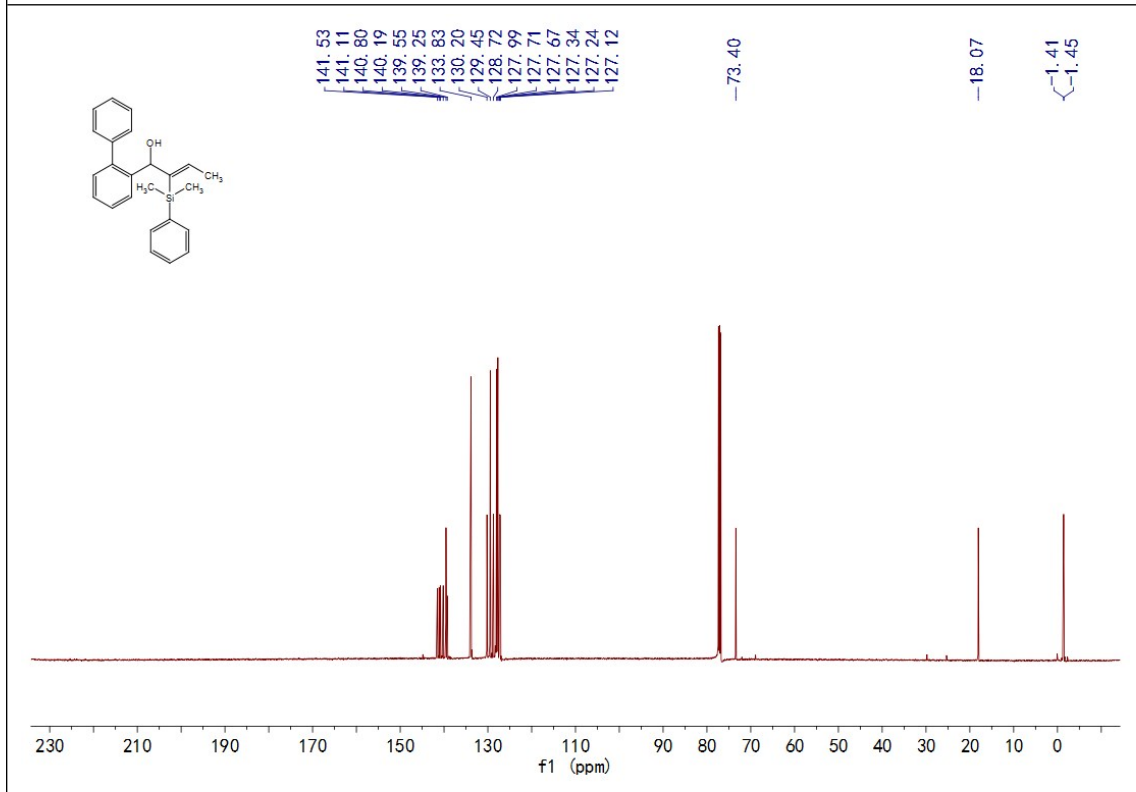
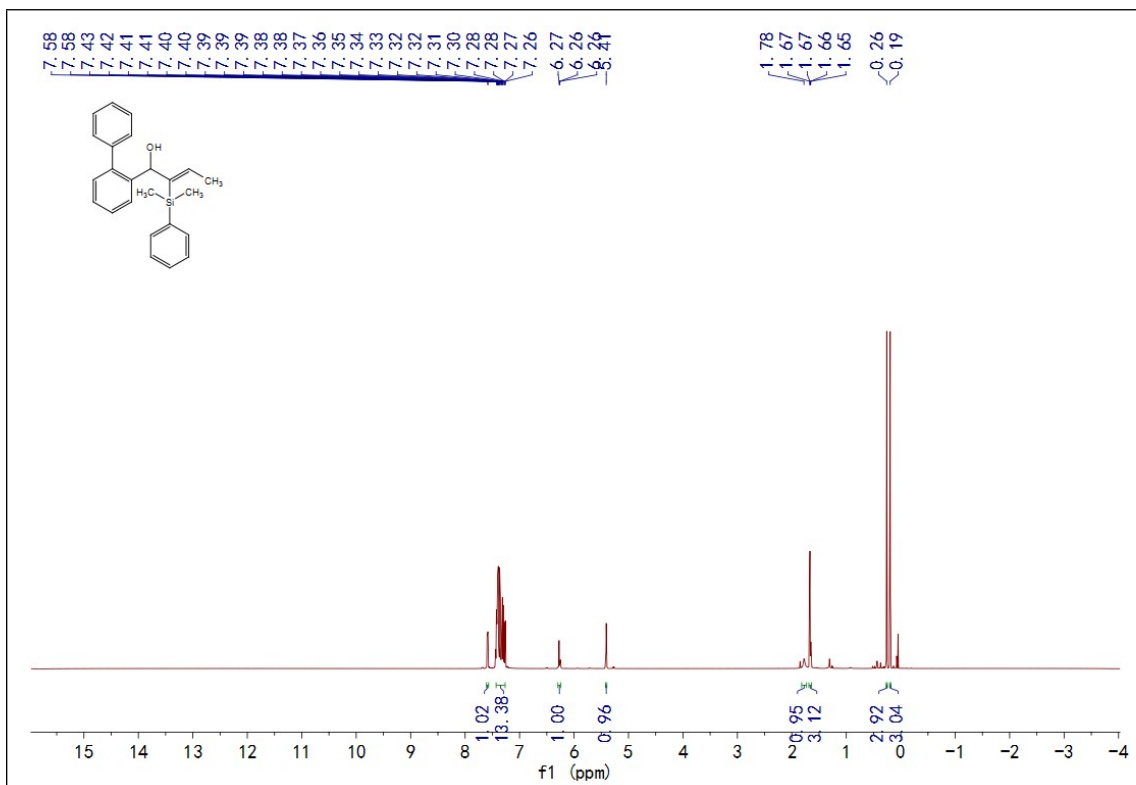
(Z)-1-(4-bromophenyl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (31)



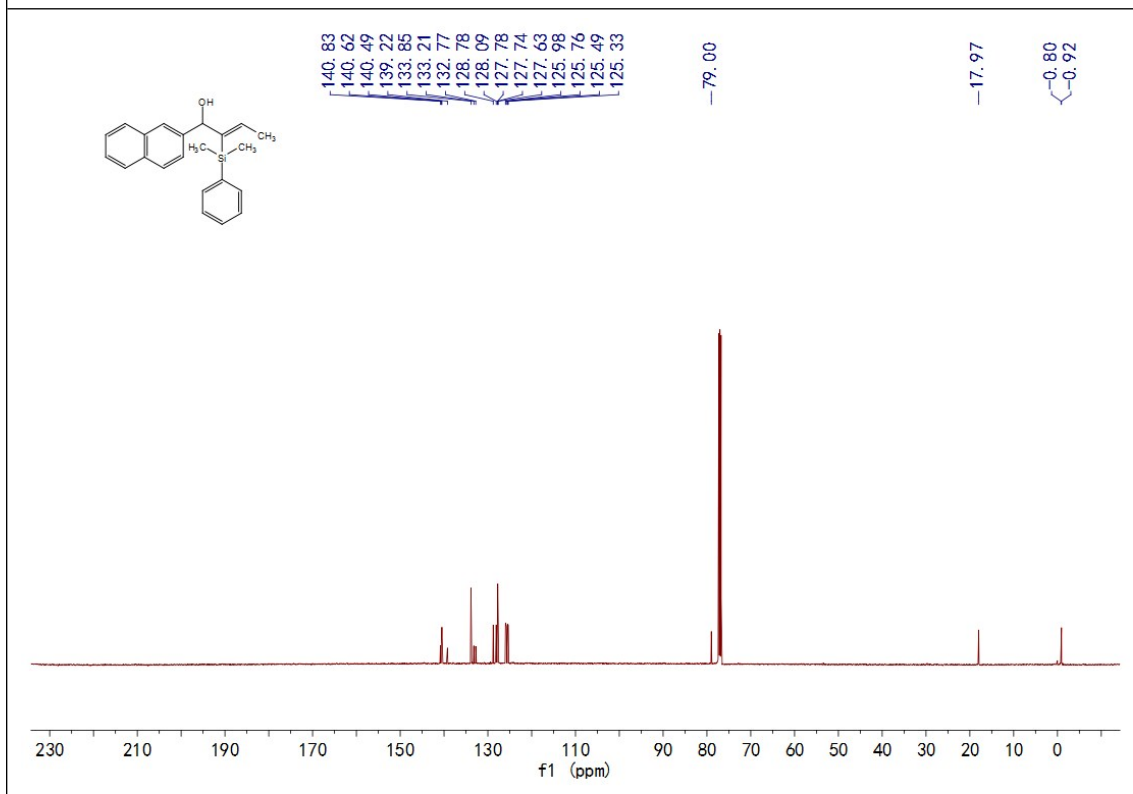
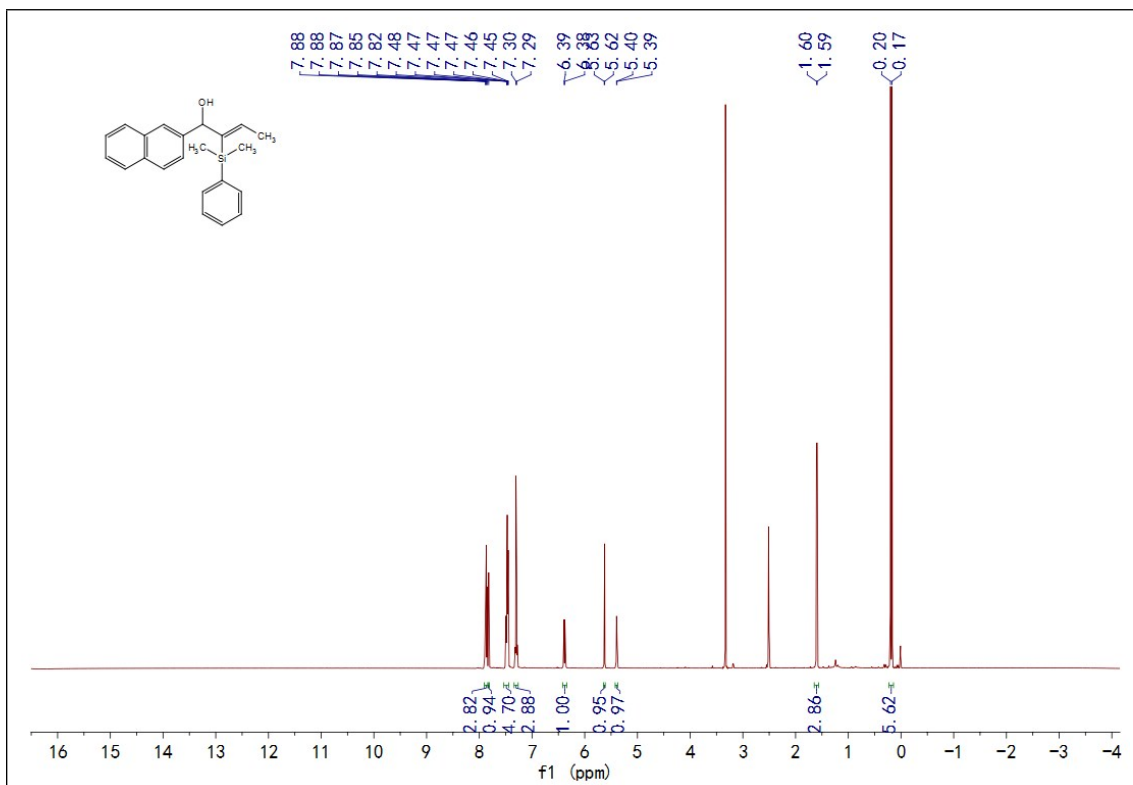
(Z)-methyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)benzoate (3m)



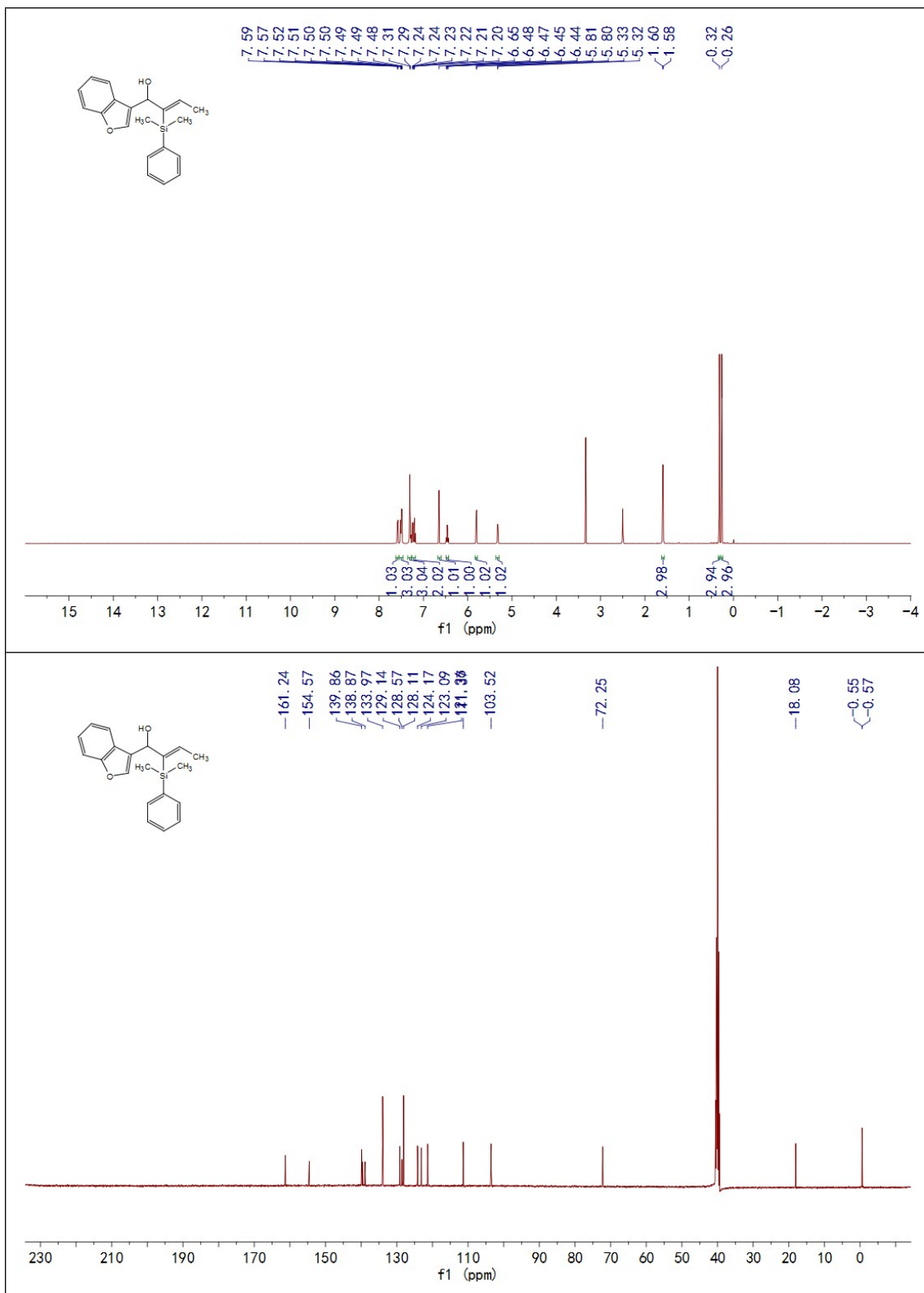
(Z)-1-([1,1'-biphenyl]-2-yl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3n)



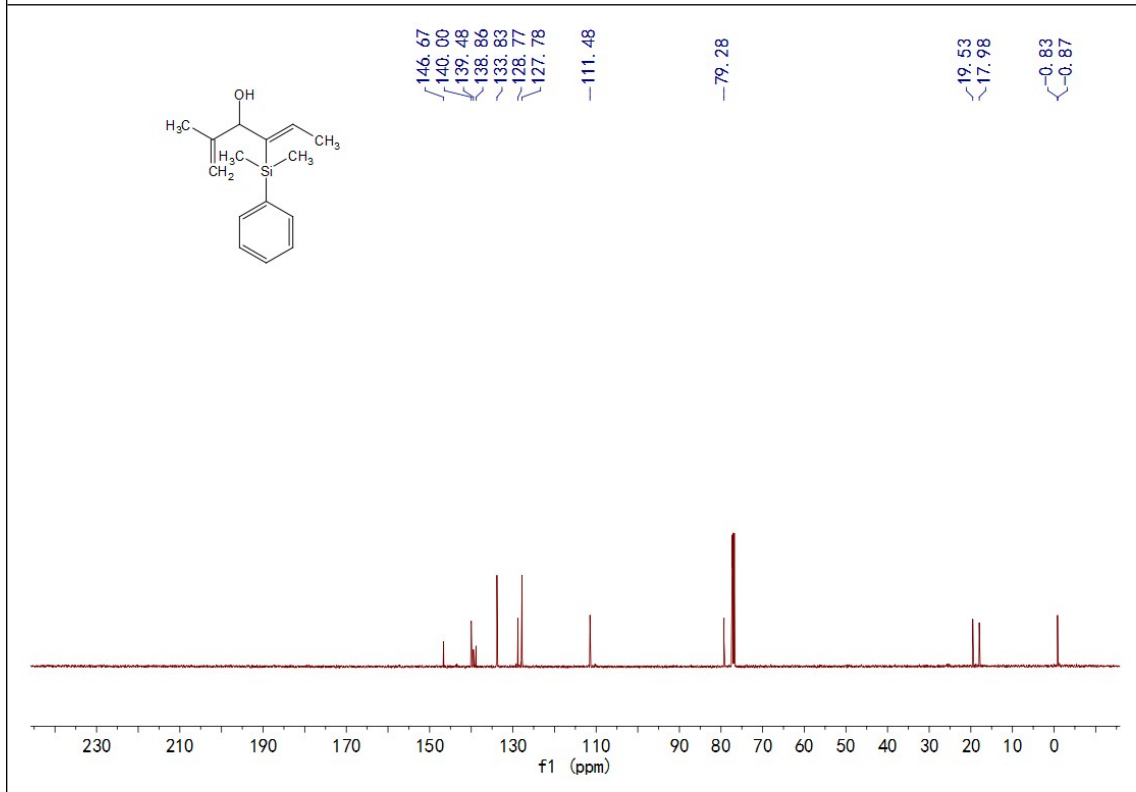
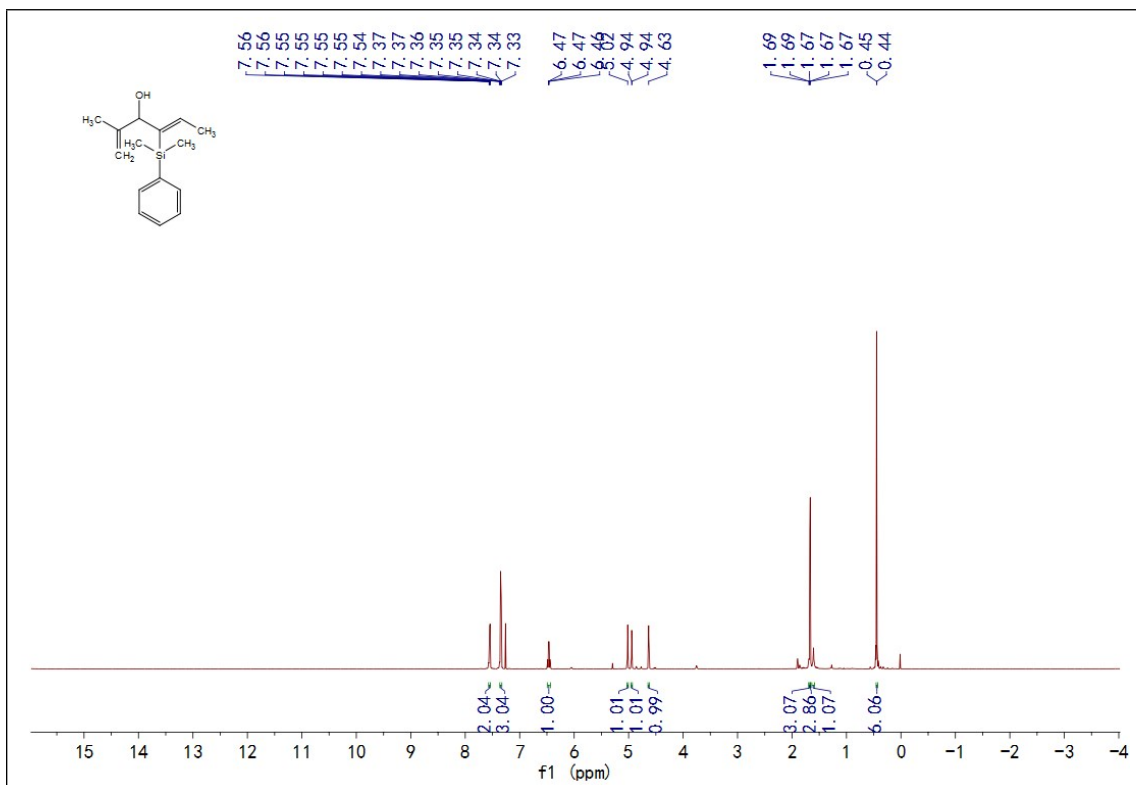
(Z)-2-(dimethyl(phenyl)silyl)-1-(naphthalen-2-yl)but-2-en-1-ol (3o)



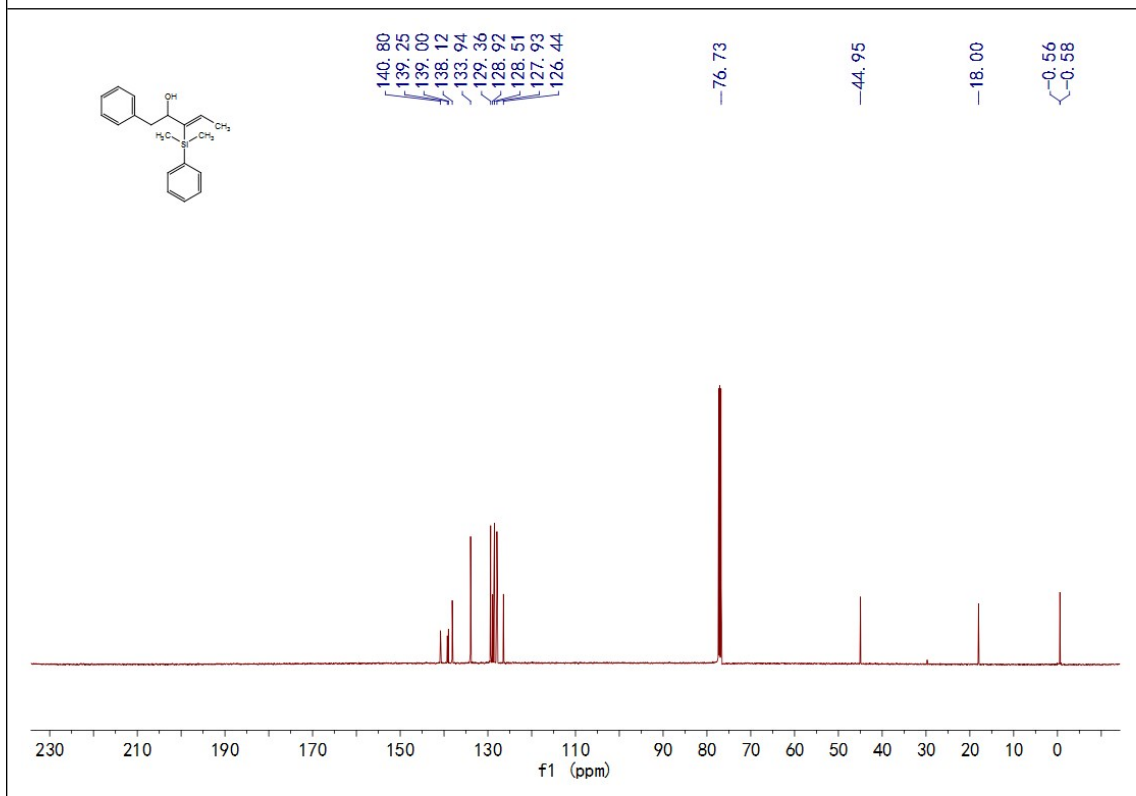
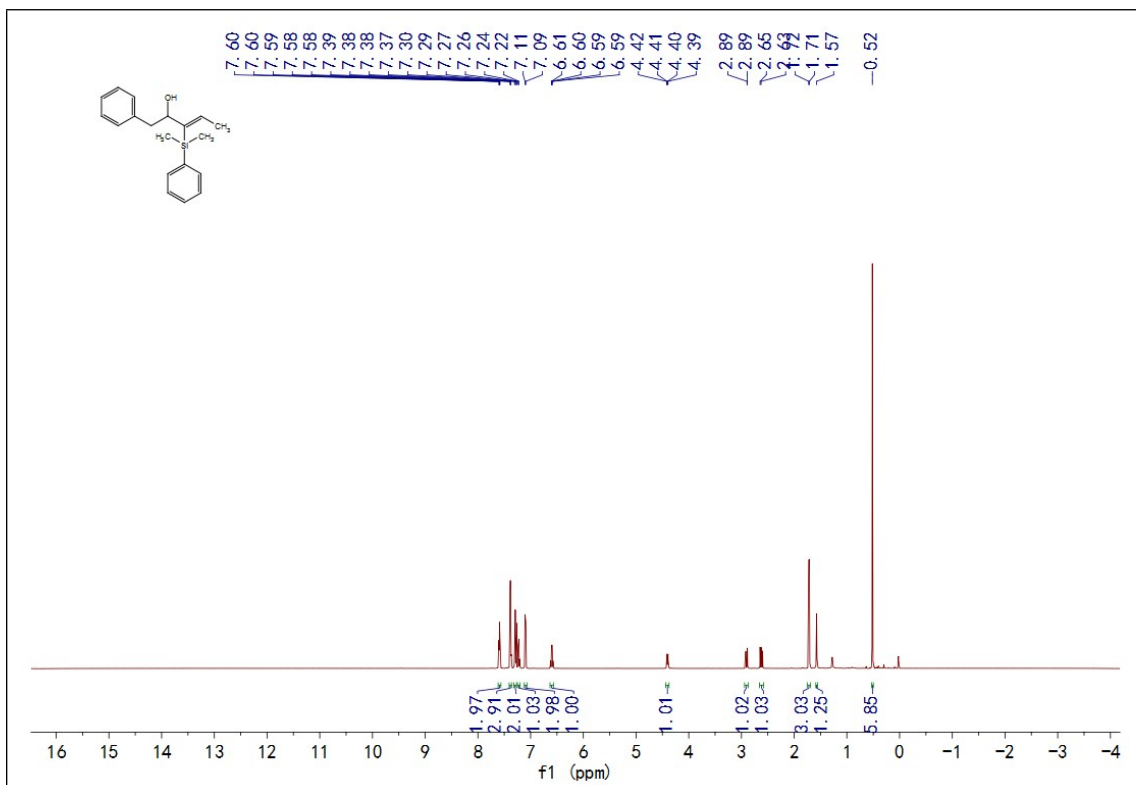
(Z)-1-(benzofuran-3-yl)-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (3p)



(Z)-4-(dimethyl(phenyl)silyl)-2-methylhexa-1,4-dien-3-ol (3q)

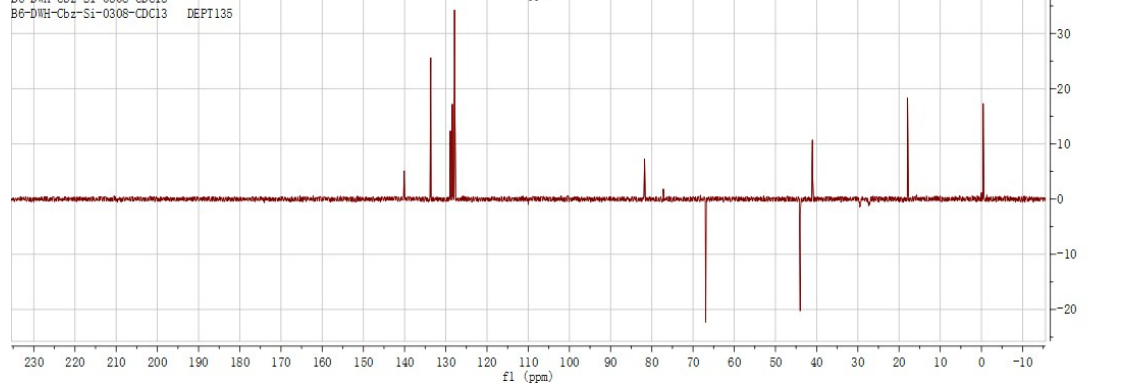
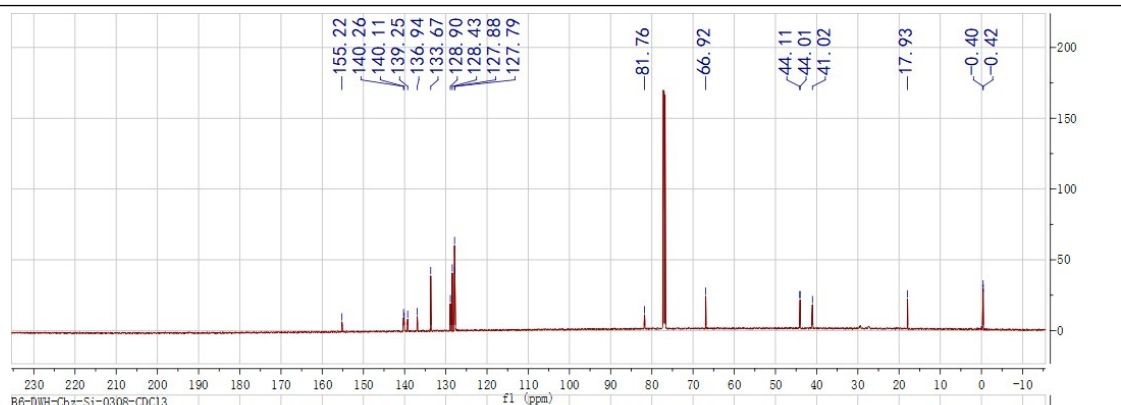
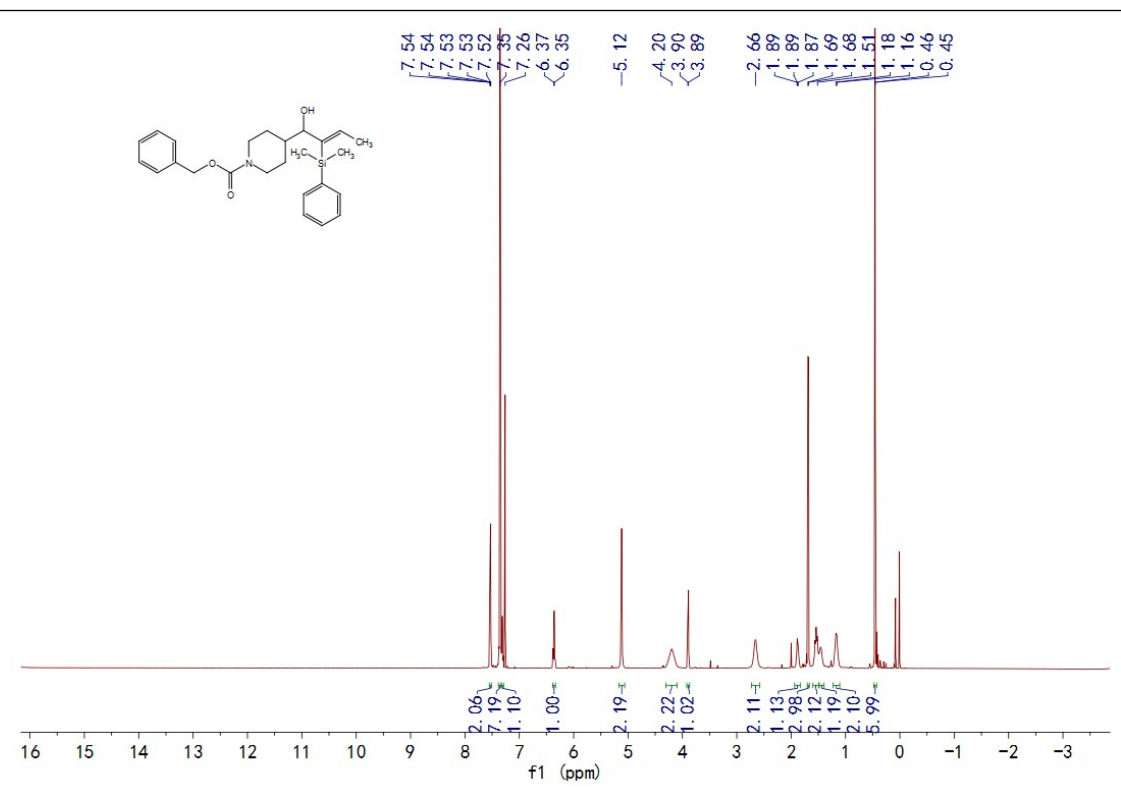


(Z)-3-(dimethyl(phenyl)silyl)-1-phenylpent-3-en-2-ol (3r)

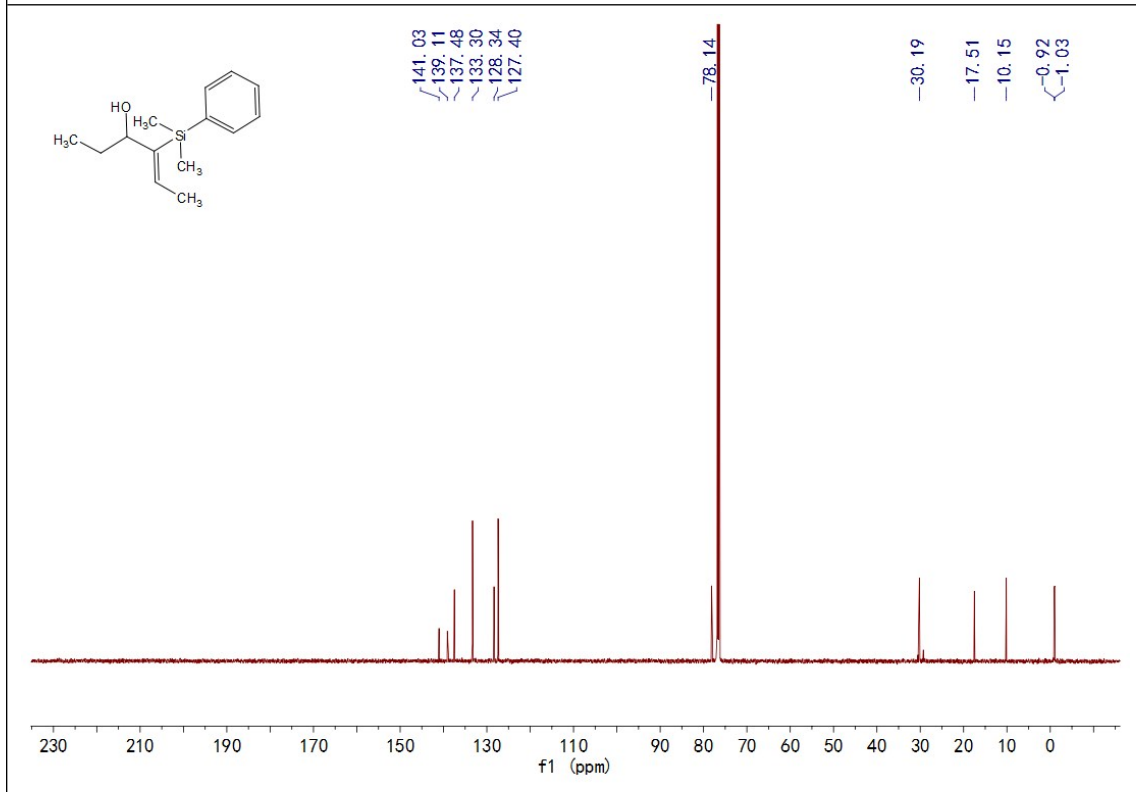
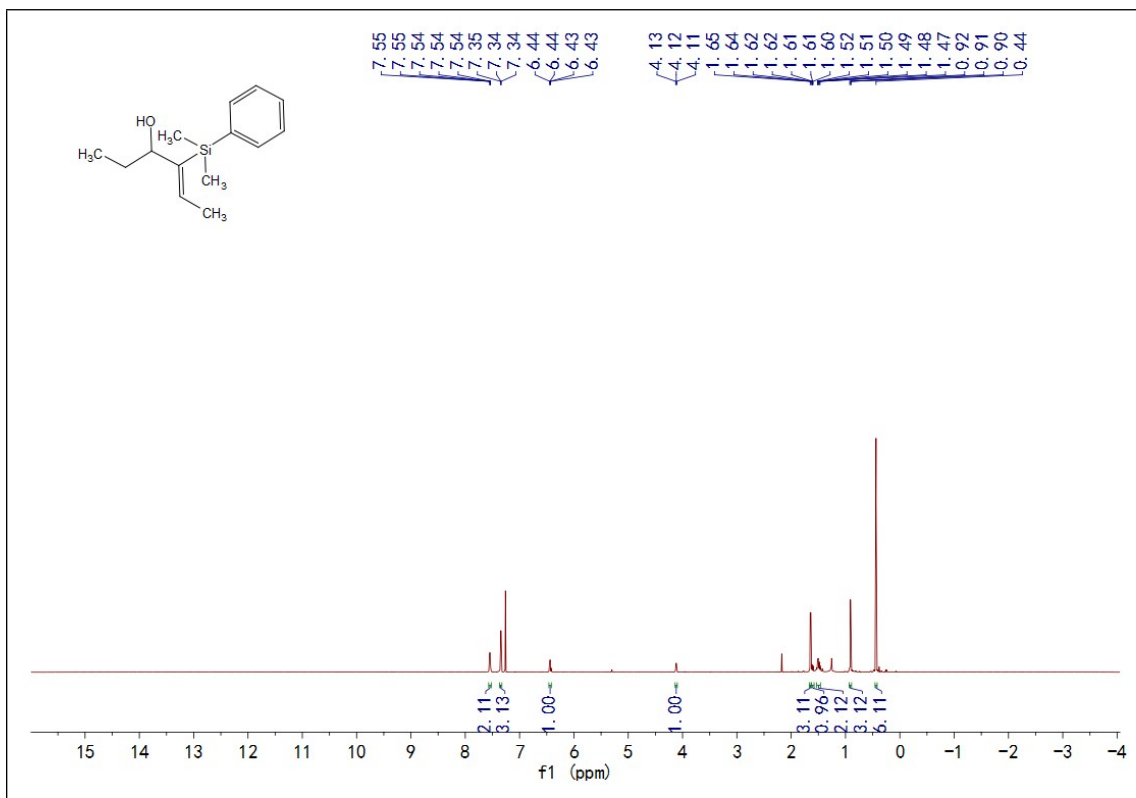


(Z)-benzyl-4-(2-(dimethyl(phenyl)silyl)-1-hydroxybut-2-en-1-yl)piperidine-1-

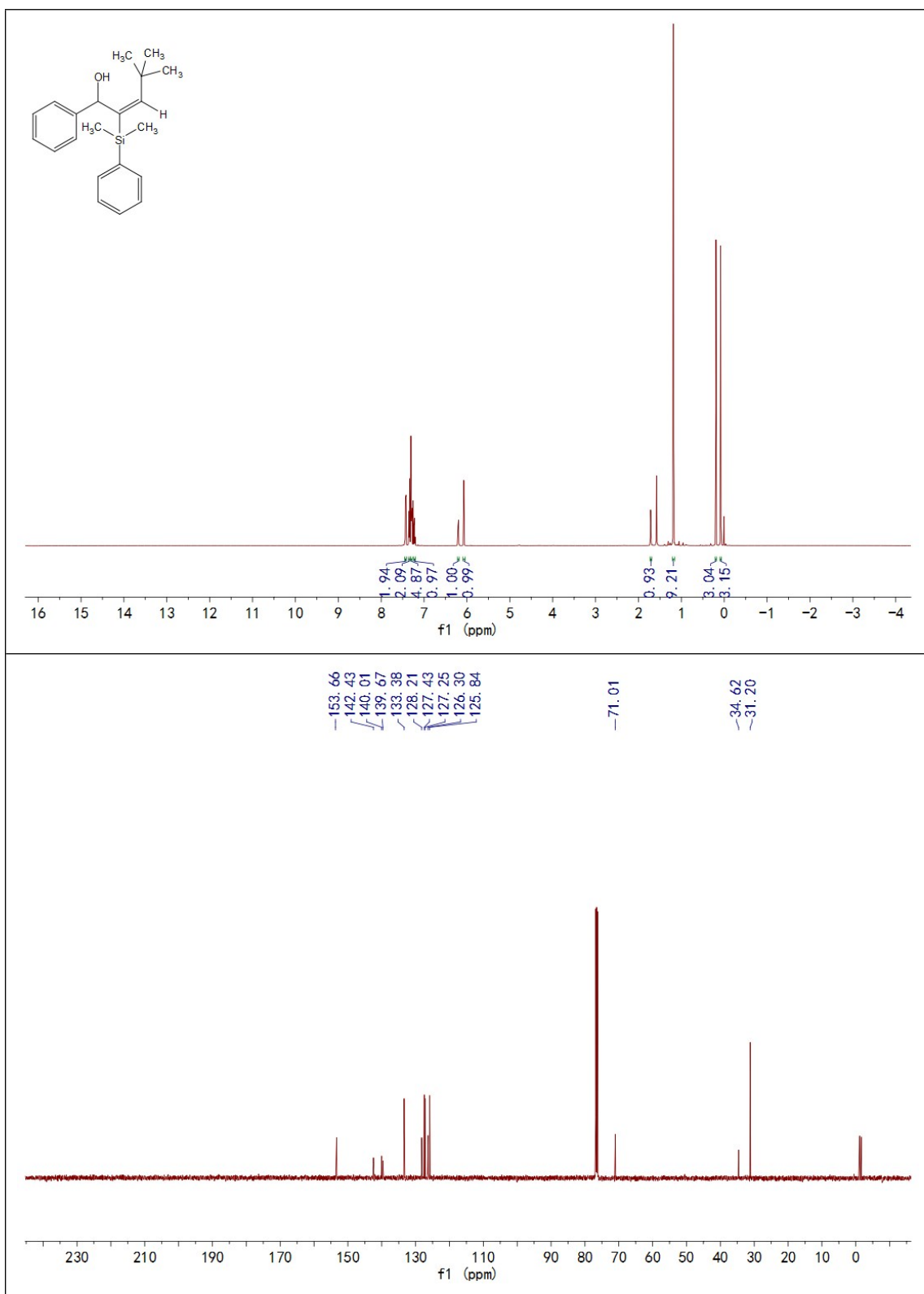
carboxylate (3s)



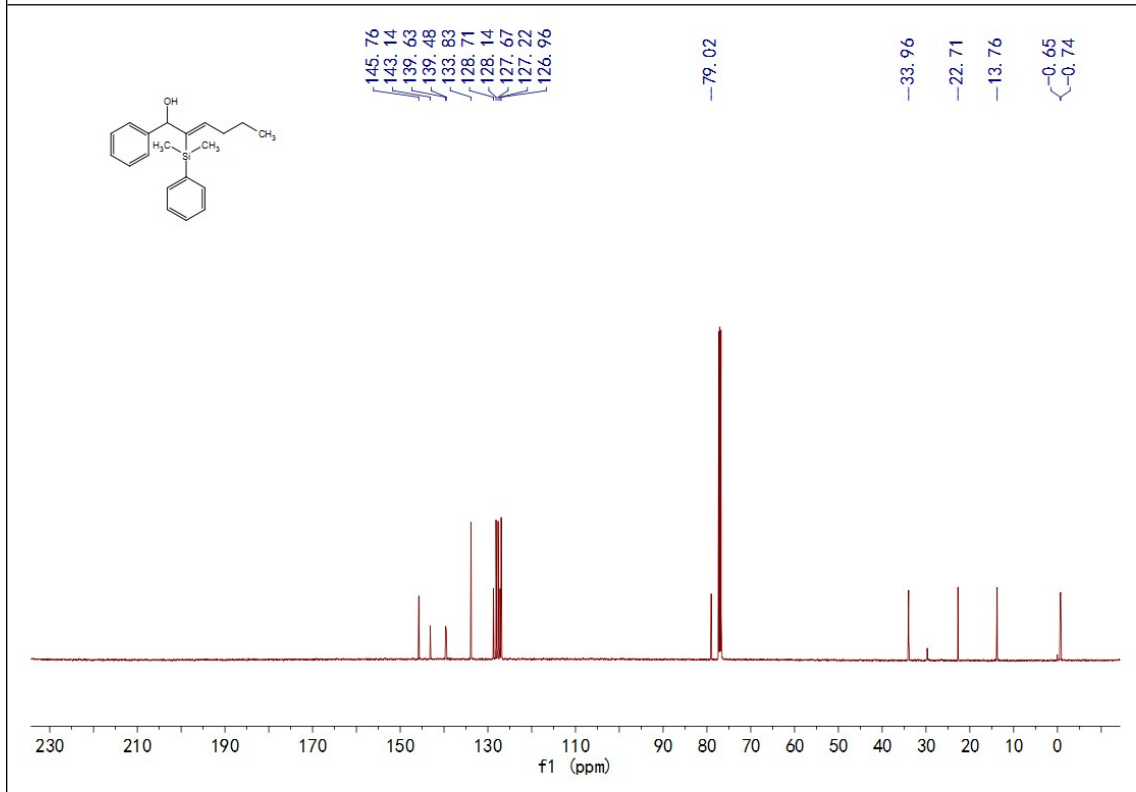
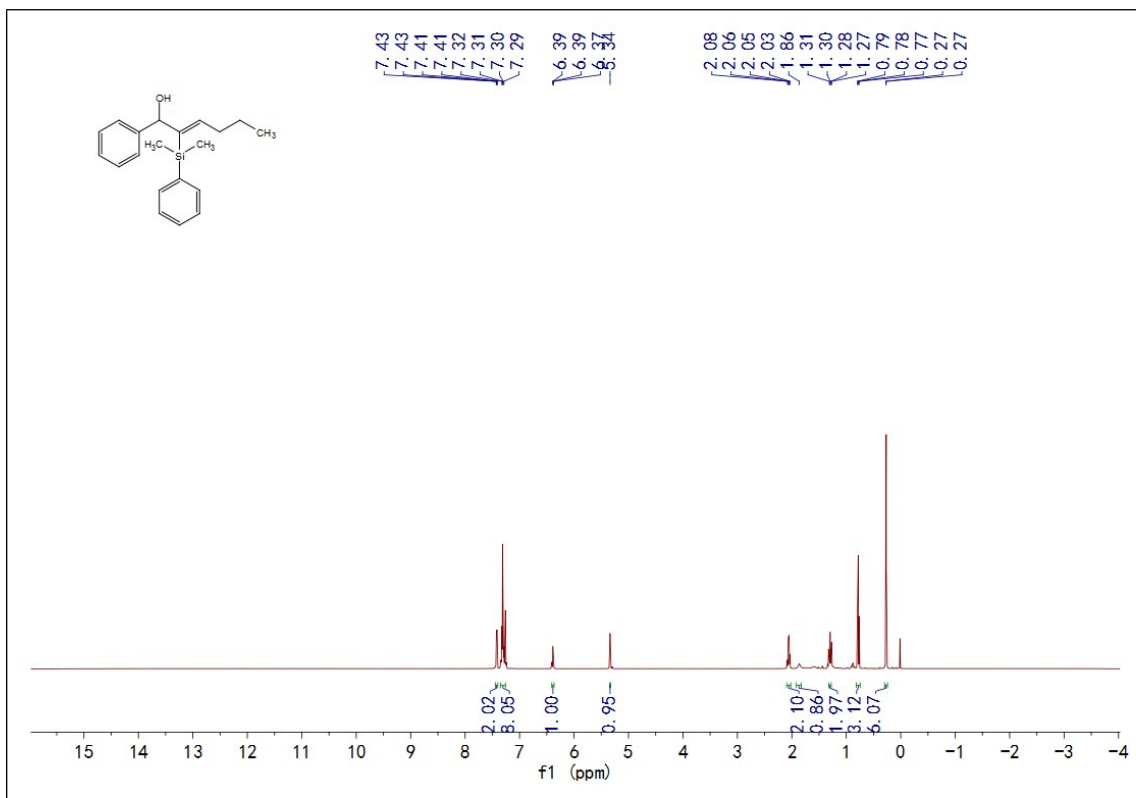
(Z)-4-(dimethyl(phenyl)silyl)hex-4-en-3-ol (3t)



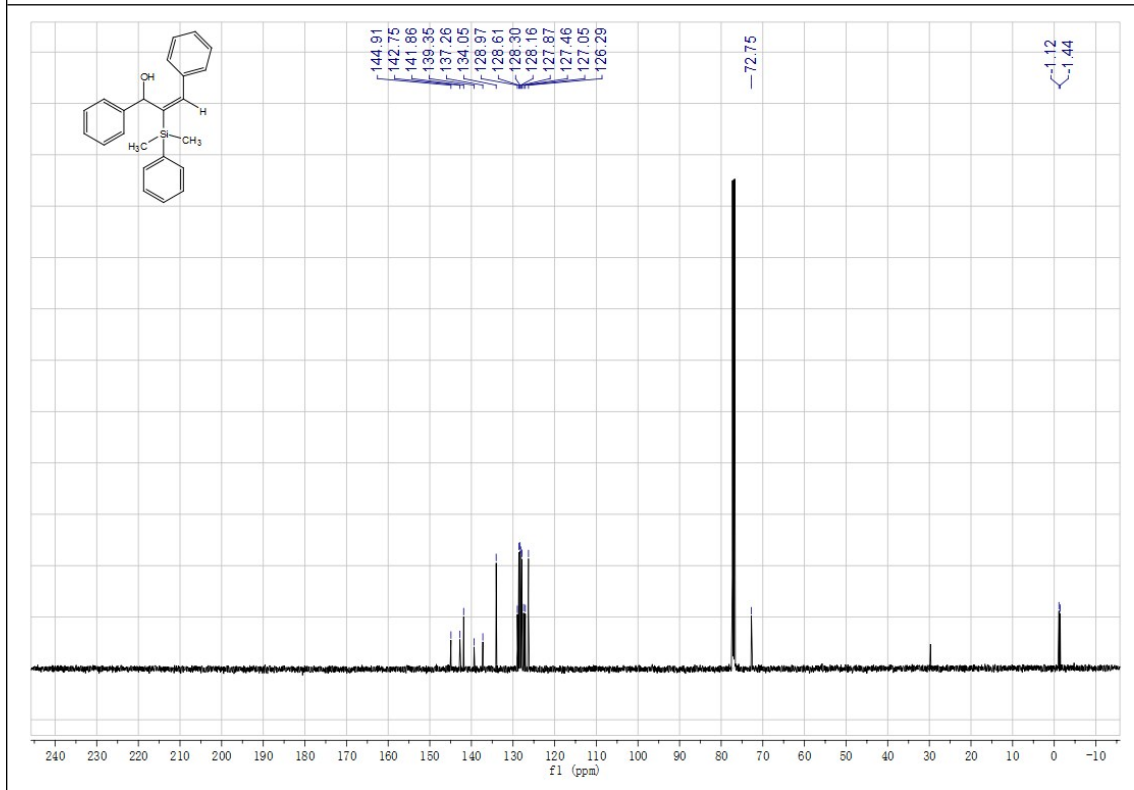
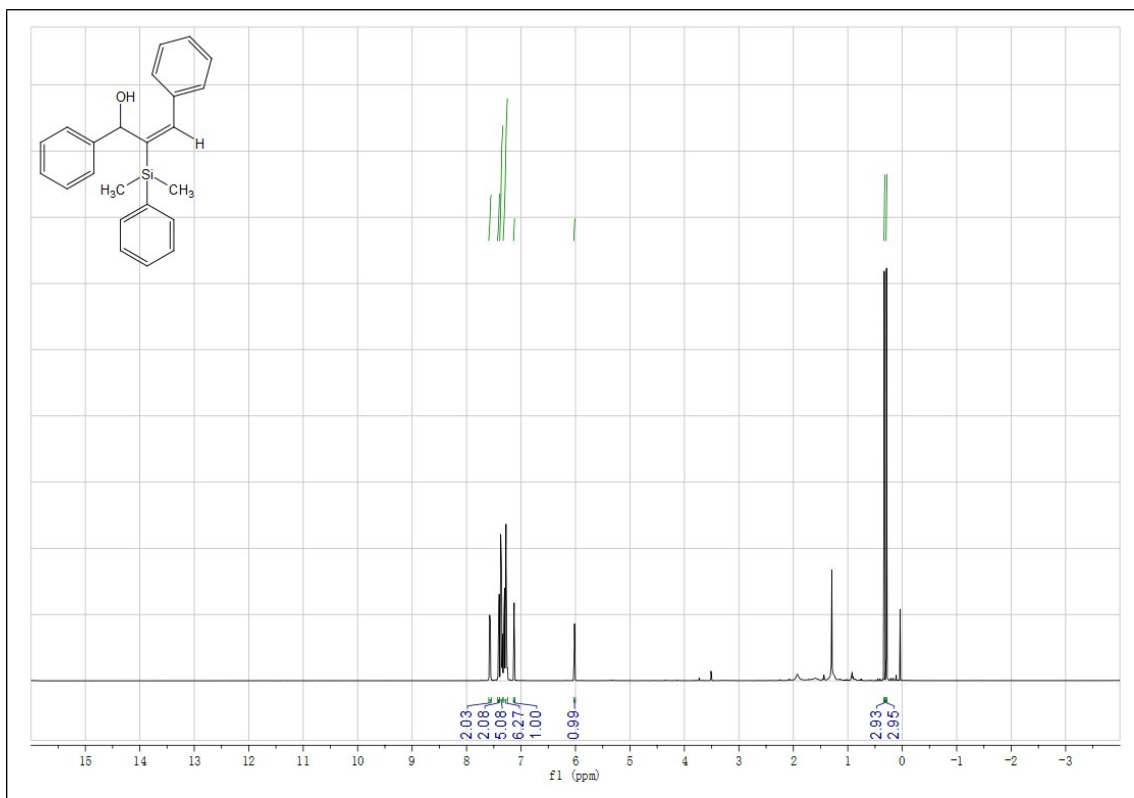
(E)-2-(dimethyl(phenyl)silyl)-4,4-dimethyl-1-phenylpent-2-en-1-ol (3u)



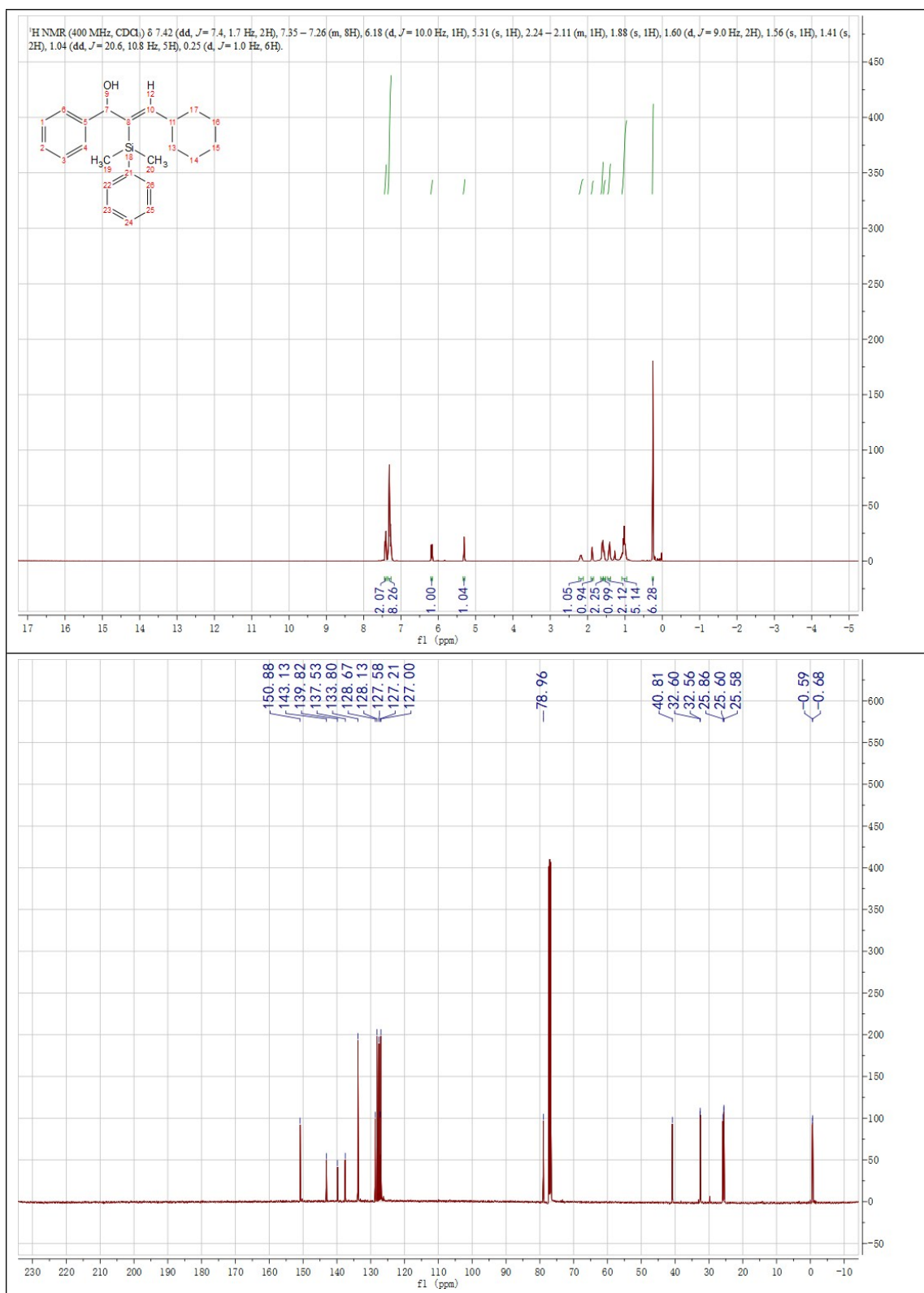
(Z)-2-(dimethyl(phenyl)silyl)-1-phenylhex-2-en-1-ol (3v)



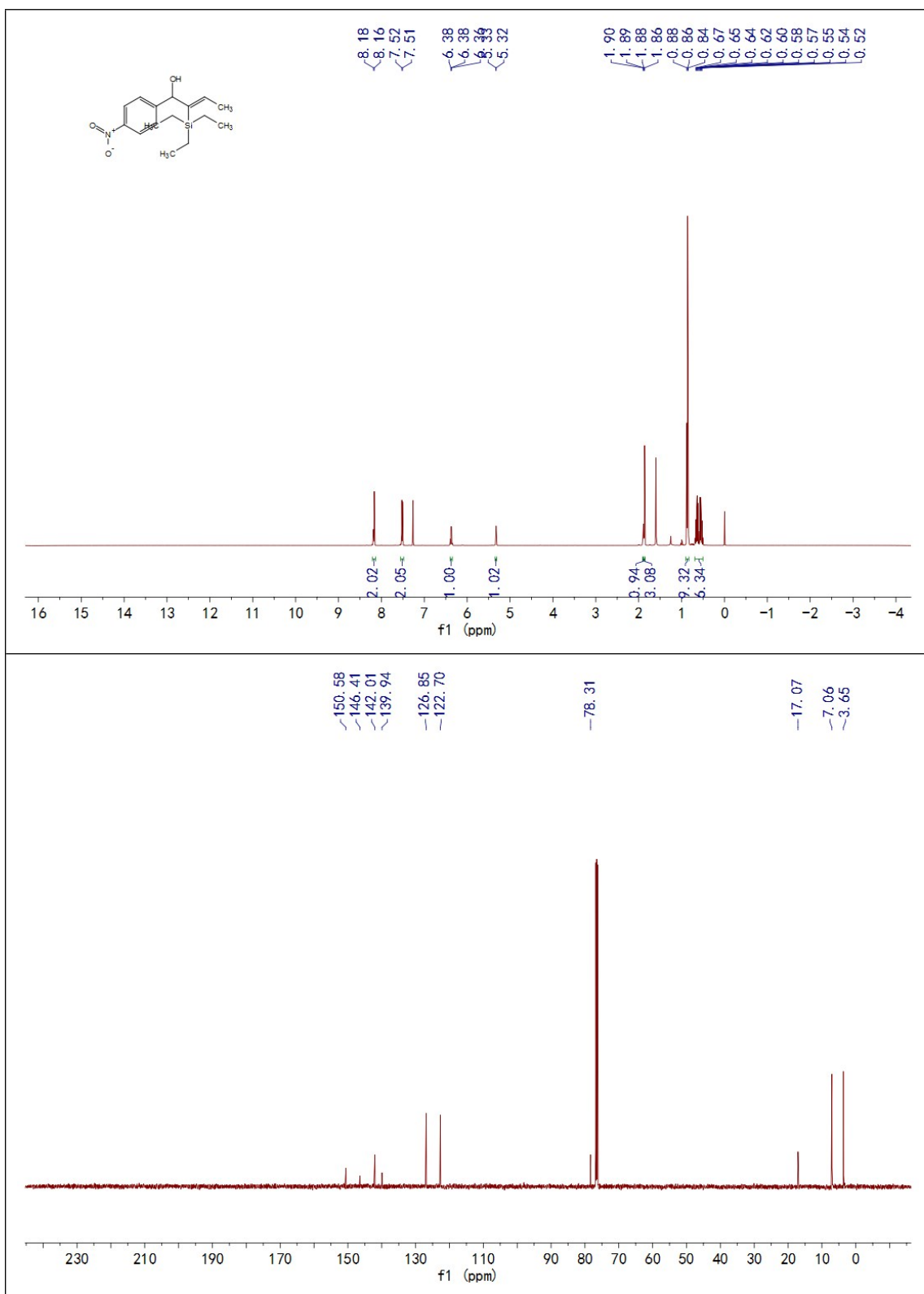
***(E)*-2-(dimethyl(phenyl)silyl)-1,3-diphenylprop-2-en-1-ol (3w)**



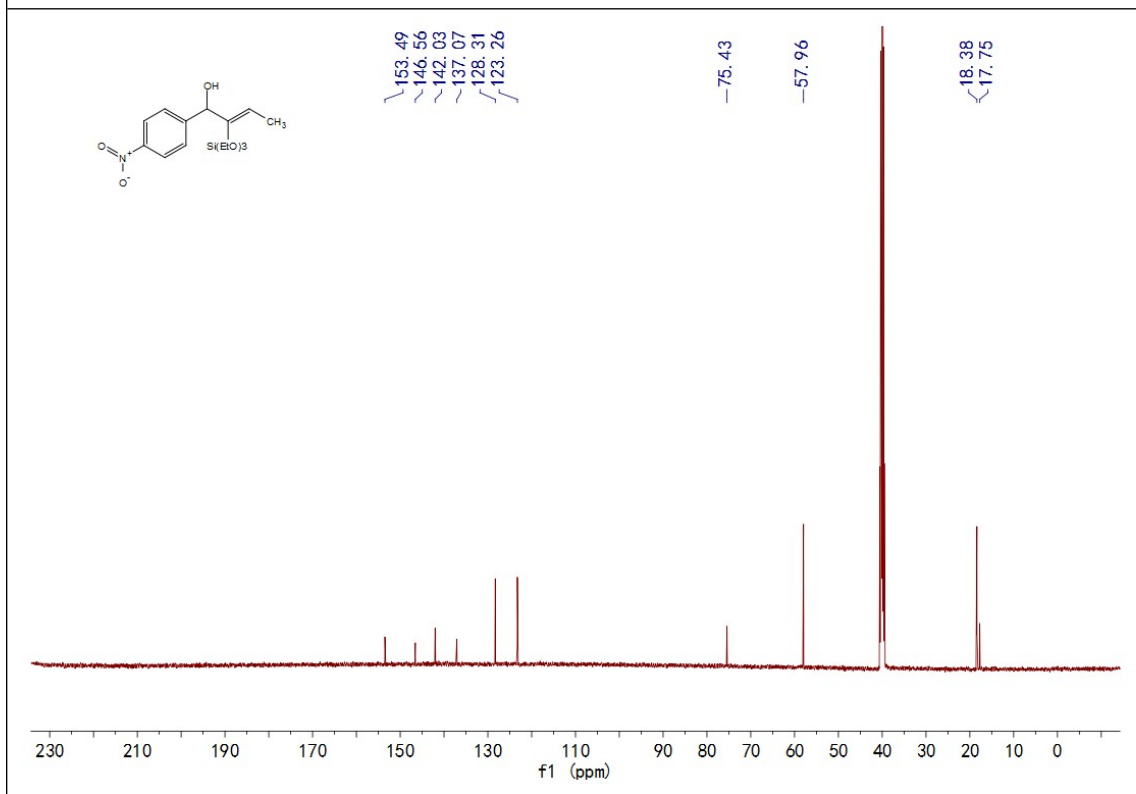
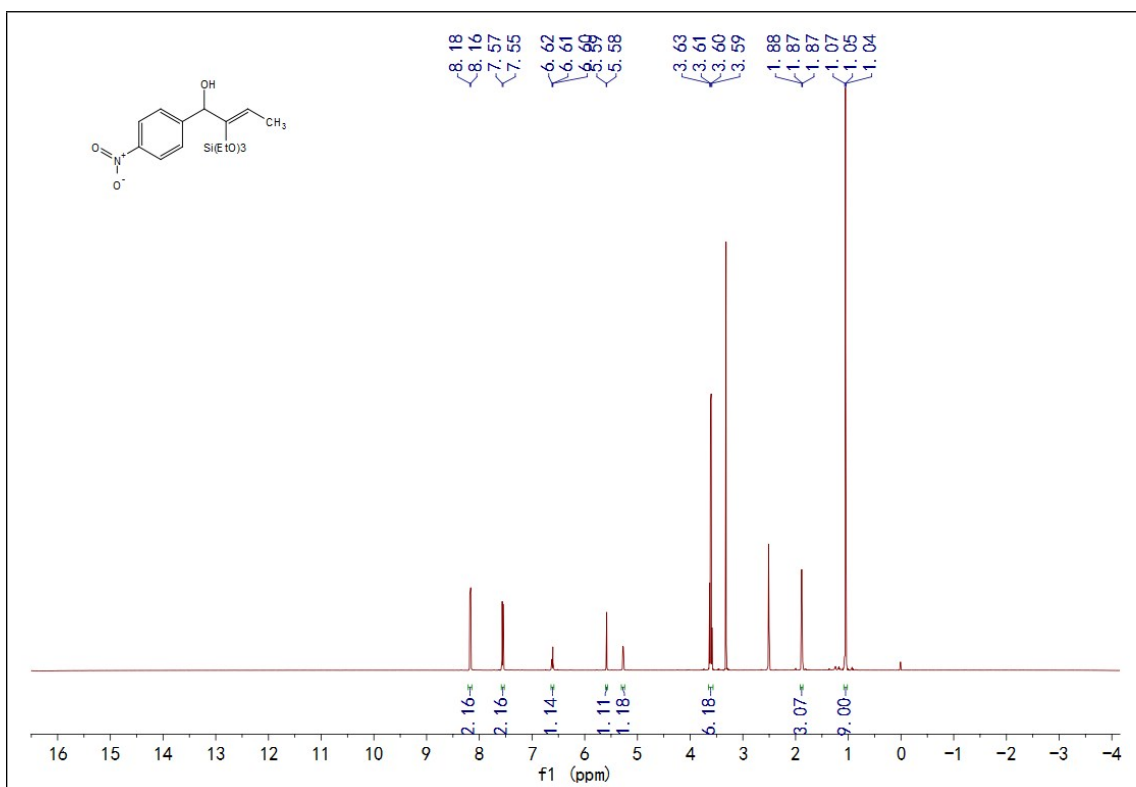
(Z)-3-cyclohexyl-2-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol (3x)



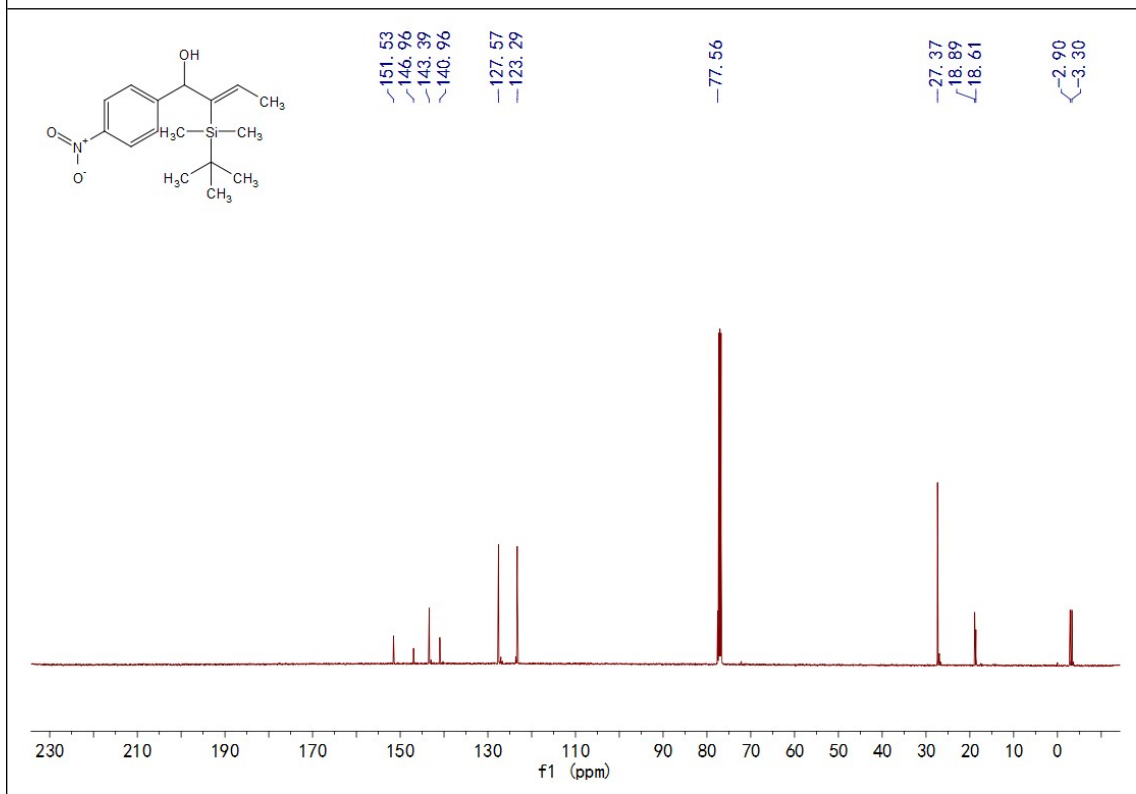
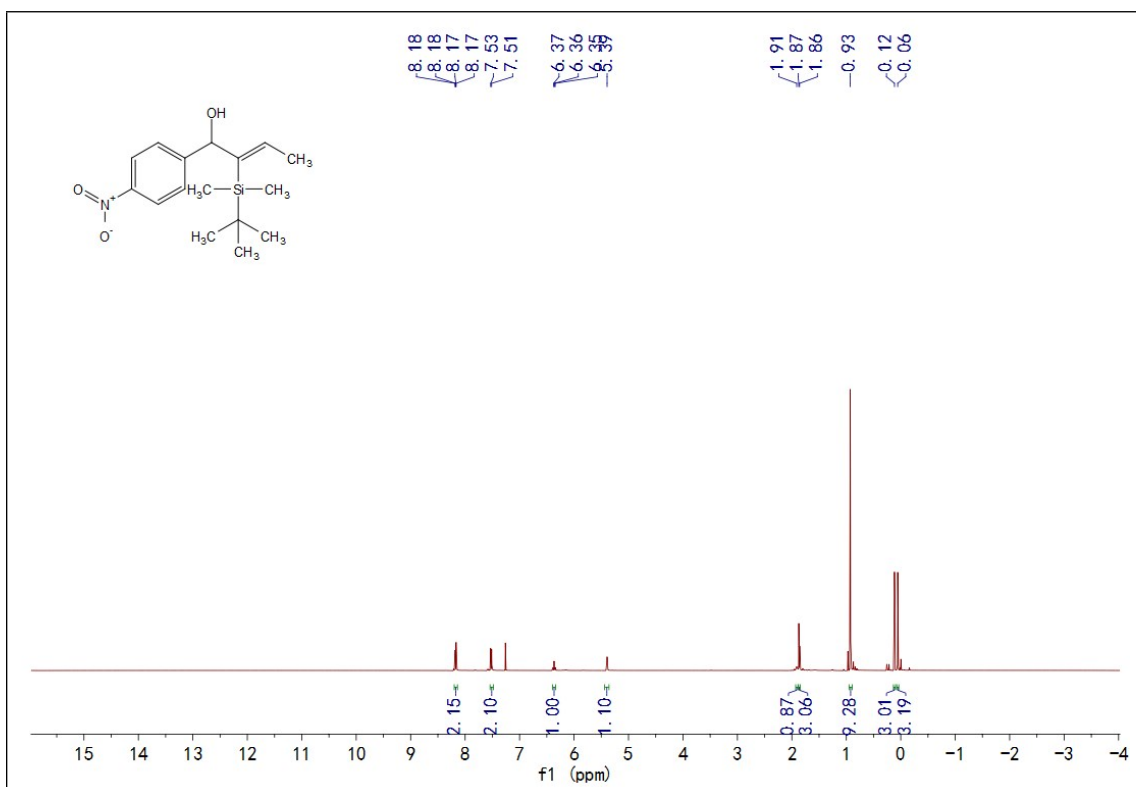
(*Z*)-1-(4-nitrophenyl)-2-(triethylsilyl)but-2-en-1-ol (4a)



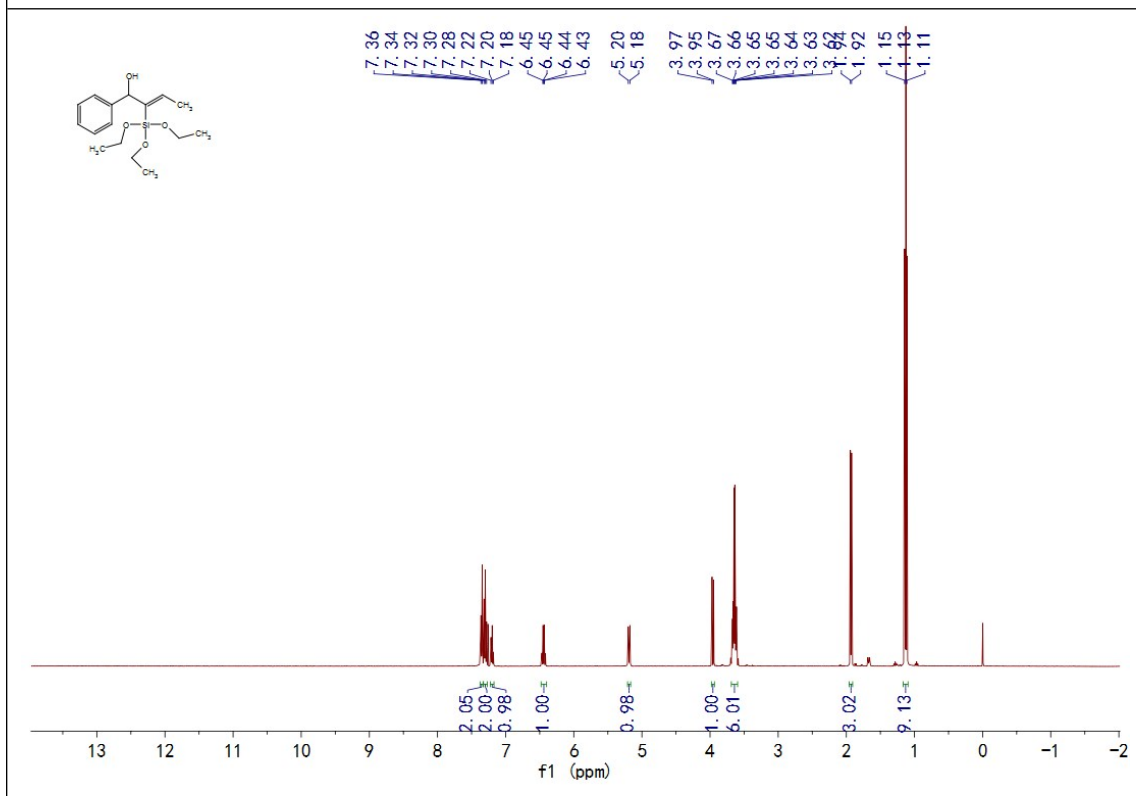
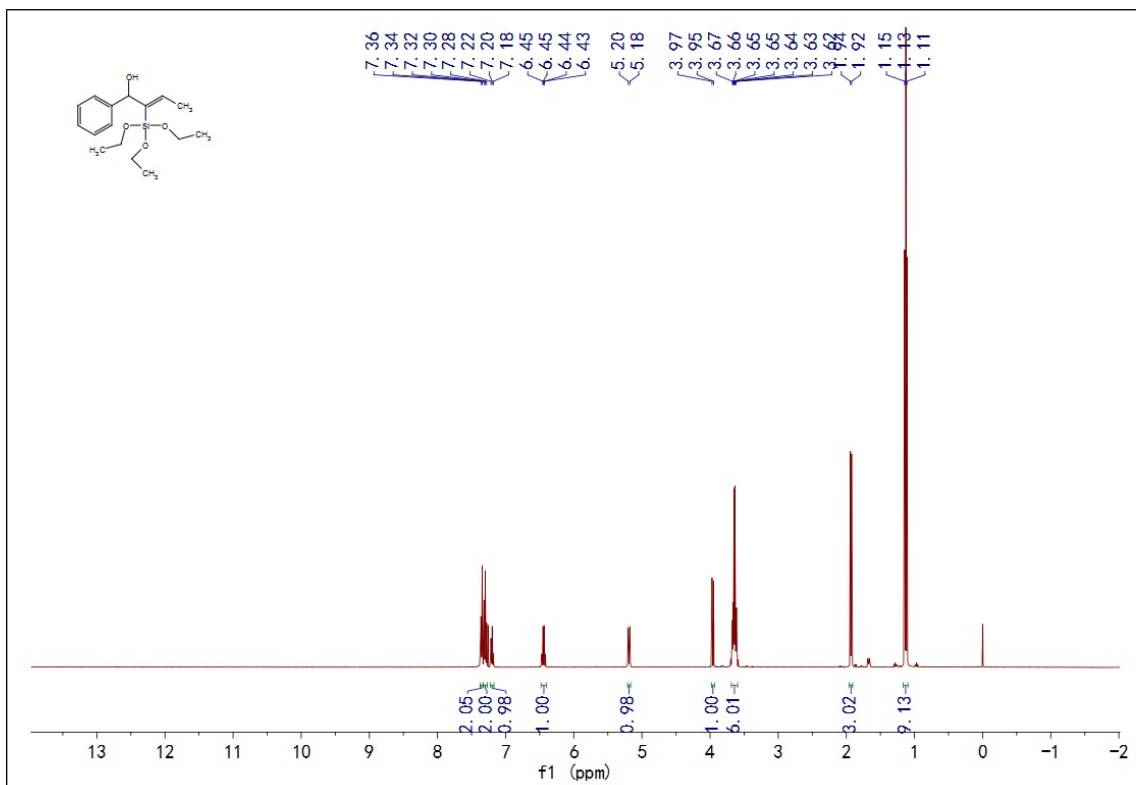
(Z)-1-(4-nitrophenyl)-2-(triethoxysilyl)but-2-en-1-ol (4b)



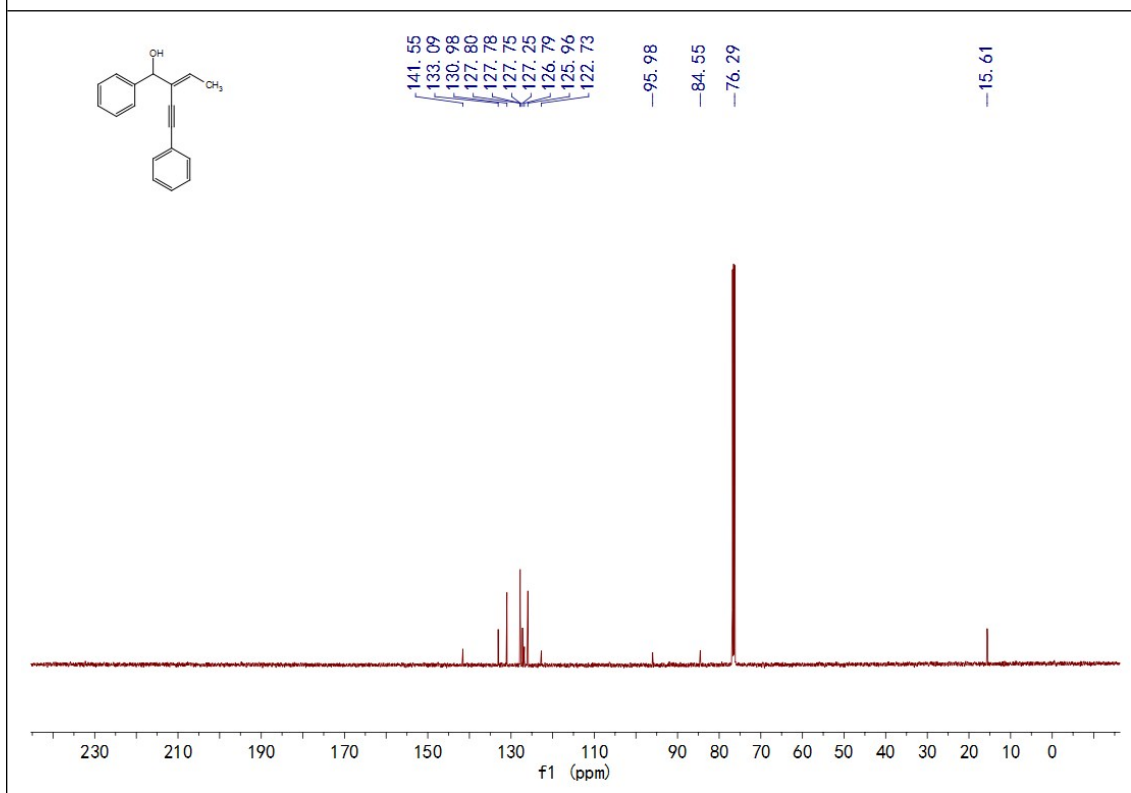
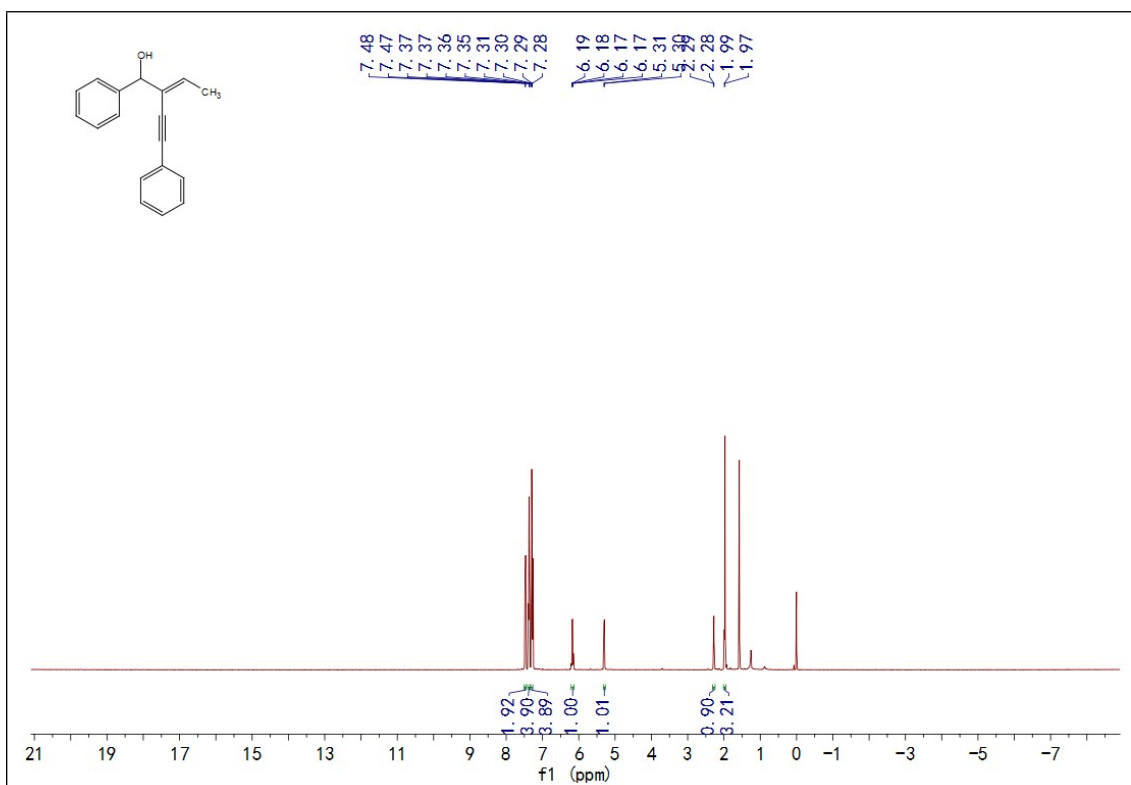
(Z)-2-(tert-butyldimethylsilyl)-1-(4-nitrophenyl)but-2-en-1-ol (4c)



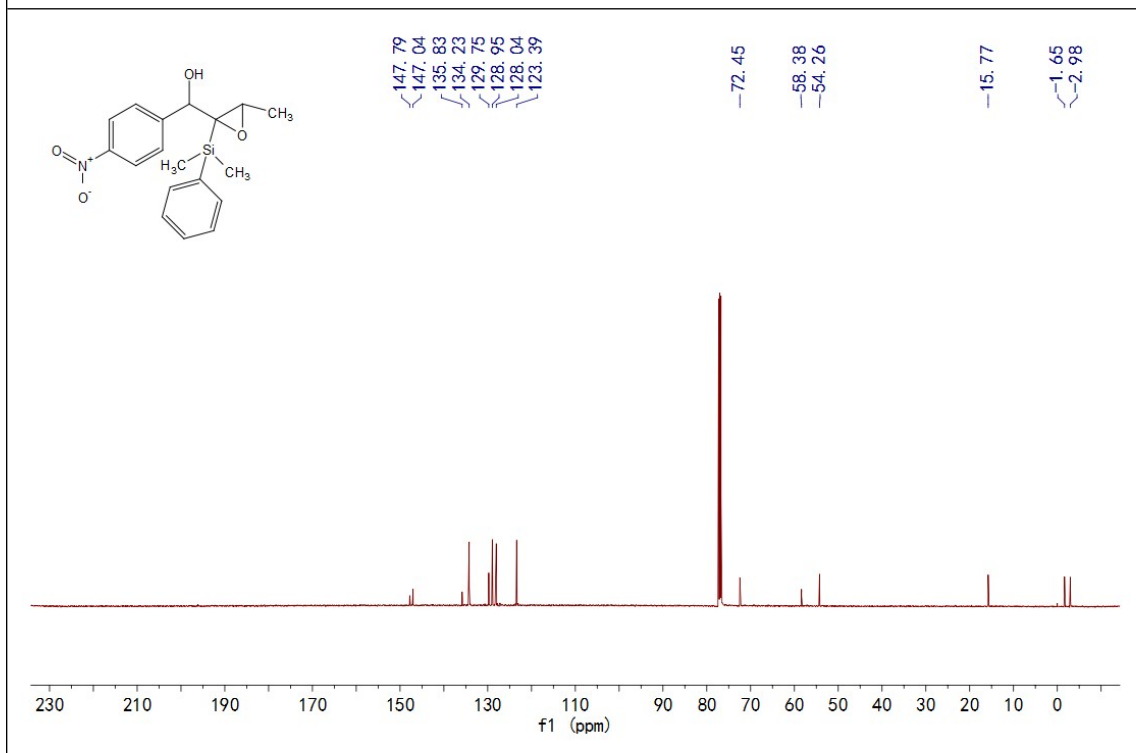
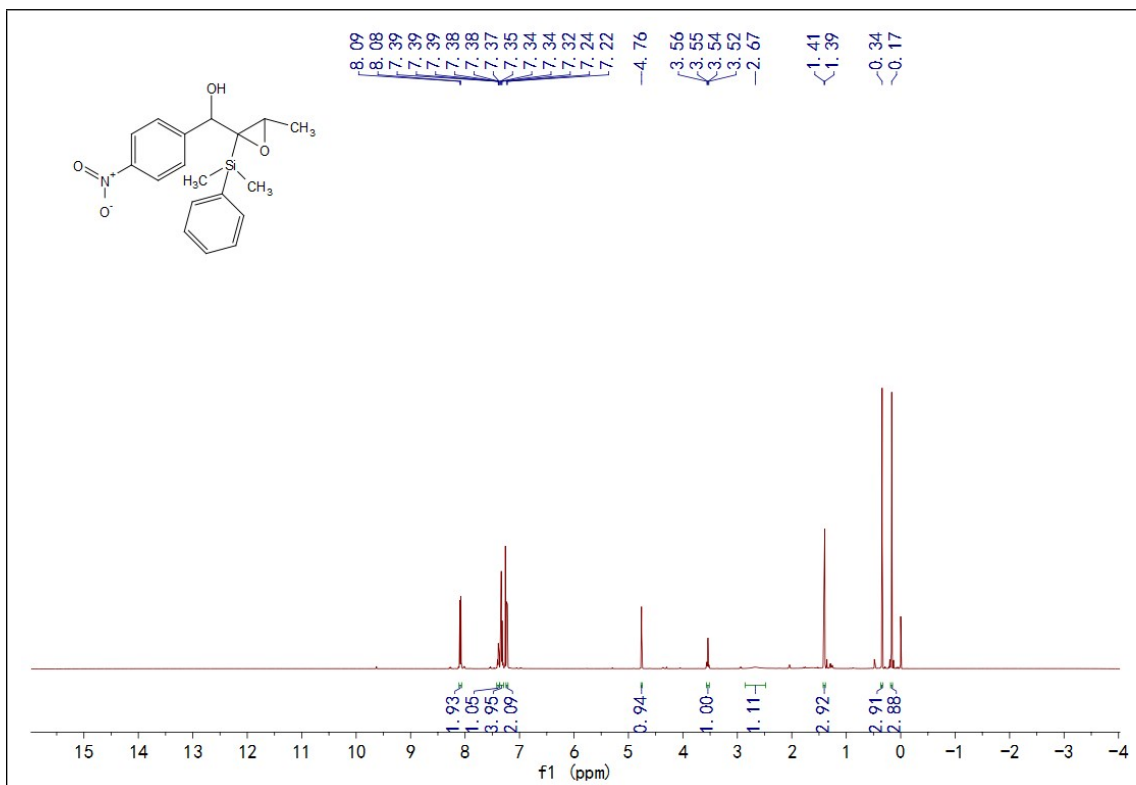
(Z)-1-phenyl-2-(triethoxysilyl)but-2-en-1-ol (3za)



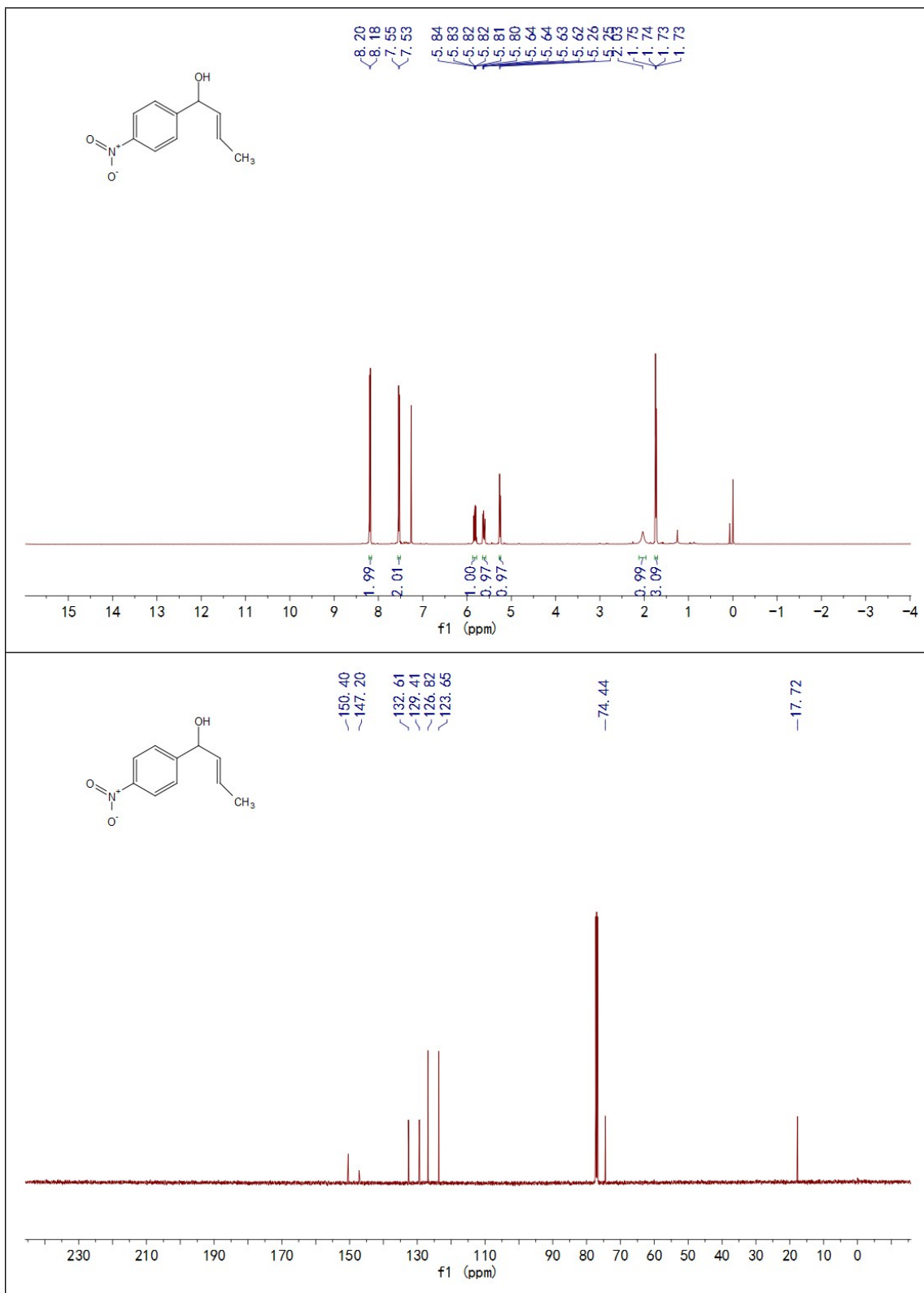
(E)-1-phenyl-2-(phenylethynyl)but-2-en-1-ol (5a)



(2-(dimethyl(phenyl)silyl)-3-methoxiran-2-yl)(4-nitrophenyl)methanol (5b)



1-hydroxy-1-(4-nitrophenyl)butan-2-one (5c)



(F) References

- [1] a) X. W. Wu, B. Wang, S. B. Zhou, Y. Zhou and H. Liu, *ACS Catalysis.*, 2017, **7**, 2494. b) X. W. Wu, B. Wang, Y. Zhou and H. Liu, *Org Lett* 2017, **19**, 1294. c) E. Mattia, A. Porta, V. Merlini, G. Zanoni and G. Vidari, *Chemistry.*, 2012, **18**, 11894. d) M. Stefanoni, M. Luparia, A. Porta, G. Zanoni and G. Vidari, *Chemistry.*, 2009, **15**, 3940. e) Y. N. Xie, X. W. Wu, C. P. Li, J. Wang, J. Li and H. Liu, *J Org Chem.*, 2017, **82**, 5263. f) M. Jha, S. Dhiman, T. S. Cameron, D. Kumar and A. Kumar, *Org Lett.*, 2017, **19**, 2038. g) B. Gonzalo, F. Isabel, M. A. Ali'cia and R. P. Jose', *J. Org. Chem.*, 2006, **71**, 6674.