Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of Multi-Substituted Vinylsilanes *via* Copper(I)-Catalyzed Hydrosilylation Reactions of Allenes and Propiolate Derivatives with Silylboronate

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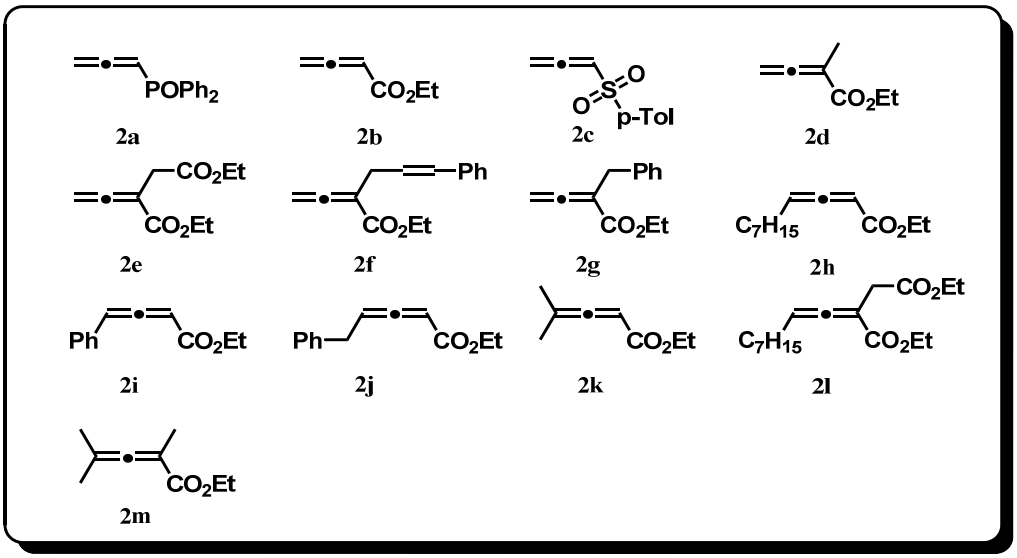
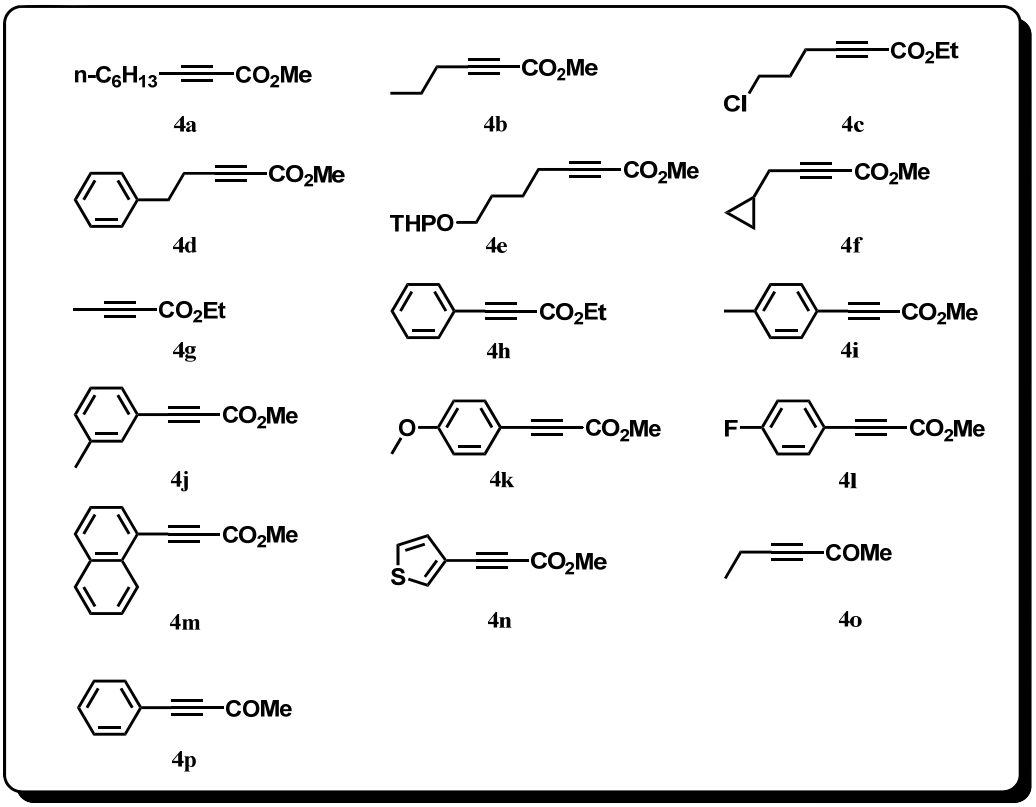
1. General Procedure for the Allenes and alkynes



1b was commercially purchased, 1a[1], 1c[2] and 1d – 1m[3,4,5] were prepared following the reported procedure.



5a was commercially purchased, 5b – 5d[6,7], 5o – 5p[8] were prepared following the reported procedure.

2. General Procedure for the Vinylsilanes

I. General Methods

$Ph(Me)_2SiB(Pin)$, CuBr, NEt_3, Dppe were commercialy purchased.

^1H NMR spectra were performed on a Bruker Advance 400 NMR spectrometer and are relative to a signal of chloroform-d (δ = 7.26 ppm, singlet). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constants in Hz. Proton-decoupled ^{13}C NMR spectra were performed on a Bruker Advance 400 (100 Hz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$, δ = 77.0 ppm). E/Z isomer ratio of the product was determined by NMR analysis of the crude product and NMR 1D NOE. IR spectra were recorded as thin films on KBr plates on a Bruker Tensor 27 spectrometer and were reported in frequency of absorption (cm^{-1}). High resolution mass spectral analysis (HRMS) was performed on Waters Q-Tof Mass spectrometer.

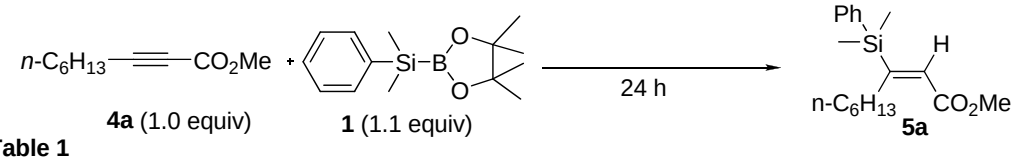
II. Representative experimental procedure for silylation of allenes.

A dry 30 ml glass tube was charged with CuBr (4.3 mg, 0.03 mmol, 10 mol%), Dppe (13.2 mg, 0.033 mmol, 11 mol%) under nitrogen, then mixed with solvent ^{t}BuOH (1 mL) and NEt_3 (3.34 mg, 4.6 μL, 0.033 mmol, 11 mol%) was added into this mixture. Subsequently $Ph(Me)_2SiB(Pin)$ (86.5 mg, 91.1 μL, 0.33 mmol, 1.1 equiv.) was added into the solvent. After that, allene (0.3 mmol, 1.0 equiv) was sequentially added to the mixture. The reaction was stirred at 40 ^{o}C for 24 hours. Then the reaction solution was diluted with dichloromethane, filtered through filter paper and concentrated *in vacuo*. Purification by silica gel column chromatography affords the target product.

III. Representative experimental procedure for silylation of alkynes.

A dry 30 ml glass tube was charged with CuBr (4.3 mg, 0.03 mmol, 10 mol%), under nitrogen, then mixed with solvent MeOH (1 mL) and NEt_3 (3.34 mg, 4.2 μL, 0.033 mmol, 11 mol%) was added into this mixture. Subsequently $Ph(Me)_2SiB(Pin)$ (157.3 mg, 163.6 μL, 0.6 mmol, 2.0 equiv) was added into the solvent. After that, alkyne (0.3 mmol, 1.0 equiv) was sequentially added to the mixture. The reaction was stirred at 28 ^{o}C for 24 hours. Then the reaction solution was diluted with dichloromethane, filtered through filter paper and concentrated *in vacuo*. Purification by silica gel column chromatography affords the target product.

Optimization reaction conditions of silylboronate with internal alkynes

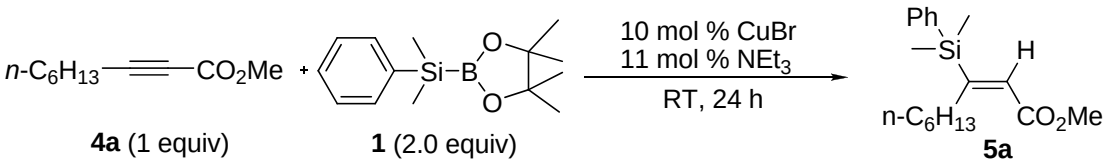


4a (1.0 equiv) **1** (1.1 equiv) **5a**

Table 1

cat (mol %)	additive (mol %)	ligand (mol %)	proton source (equiv)	solvent	T (°C)	yeild (%)[a]
CuCl (10)	NEt_3 (10)	dppe (10)	MeOH (2)	THF	28	42 %
CuCl (10)	NEt_3 (10)	dppe (10)	MeOH (2)	THF	50	56 %
CuBr (10)	NEt_3 (10)	—	—	MeOH	28	65 %
CuBr (10)	NEt_3 (10)	—	—	^{t}BuOH	28	17 %
CuBr (10)	NEt_3 (10)	—	MeOH (2)	THF	28	57 %
CuCl (10)	NEt_3 (10)	—	MeOH (2)	THF	28	65 %
CuBr (10)	NEt_3 (10)	—	—	MeOH	28	92%[b]

a. isolated yield
b.2 equiv $Ph(Me)_2SiB(pin)$ was used



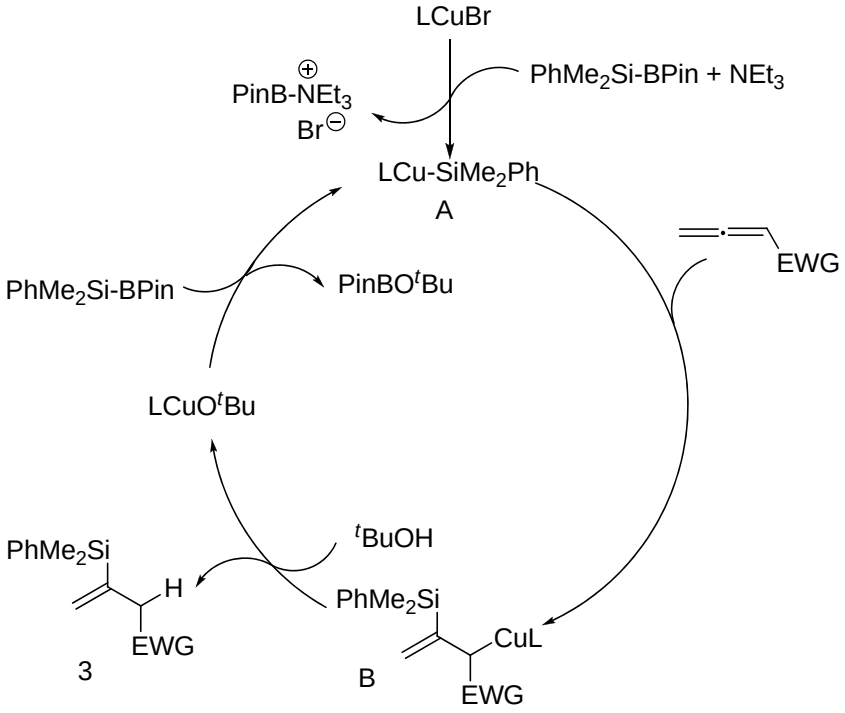
4a (1 equiv) **1** (2.0 equiv) **5a**

Table 2

Contral condition	yield
no change	92 %[a]
no CuBr and NEt_3	NR
no NEt_3	9 %[b]
$FeCl_3$ instead of CuBr	NR
$NiBr_2$ instead of CuBr	NR
CuCl instead of CuBr	84 %[a]
NEt_3 1 equiv	30%[b]

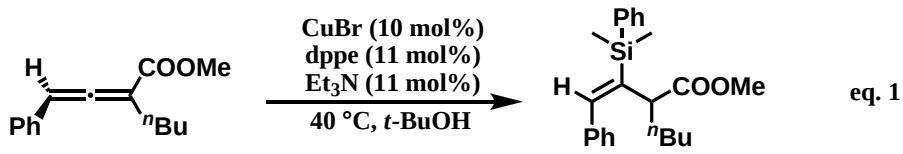
a. isolated yield
b. NMR yield

Proposed mechanism:



Mechanism study:

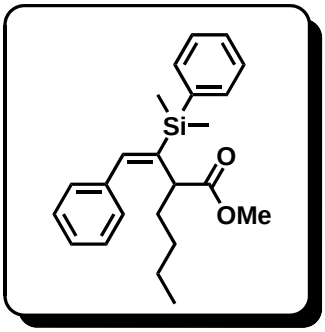
A chiral allene compound **2n** was prepared[9] and applied into the mechanism study of copper-catalyzed hydrosilylation reaction of allene. As depicted in the eq. 1, a racemic product **3n** was resulted from the chiral allene **2n** without any chirality transformation. Therefore, a possible reaction's pathway of an addition of Si-Cu into C=C double bond to afford an allylic copper species **B** which could then undergo protonolysis in the presence of ^{t}BuOH to give the desired product **3** was proposed in the text.



eq. 1

2n

racemic compound
3n



3n (E)-methyl 2-(1-(dimethyl(phenyl)silyl)-2-phenylvinyl)hexanoate
Colorless oil.
Yield = 67 %
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.56 (m, 2H), 7.36 – 7.32 (m, 4H), 7.32 – 7.30 (m, 1H), 7.27 – 7.23 (m, 3H), 7.06 (s, 1H), 3.78 (dd, J_1 = 8.1 Hz, J_2 = 6.6 Hz, 1H), 3.44 (s, 3H), 1.88 – 1.76 (m, 1H), 1.42 – 1.32 (m, 1H), 1.06 – 0.92 (m, 4H), 0.71 (t, J = 6.9 Hz, 3H), 0.47 (s, 3H), 0.46 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm):174.8, 143.6, 140.3, 138.7, 138.1, 128.9, 128.4, 128.1, 127.6, 126.9, 51.4, 46.8, 31.0, 29.4, 22.2, 13.8, -1.2, -1.3.
HPLC conditions: Chiralcel OD-H, isopropanol/hexane = 0.1:99.9, flow: 1.0 mL/min, λ = 254 nm.
FTIR (neat): ν = 3064, 2958, 1732, 1594, 1422, 1252, 919, 813, 772, 740, 691 cm^{-1}
HRMS (ESI, m/z): calcd for $C_{23}H_{30}O_2Si^+$ $[M+H]^+$ 367.2049, found: 367.2093.

```
 File C:\HPCHEM\1\DATA\HYB\14042600.D                    Sample Name: wlh30-3

Hexane: i-PrOH = 99.9:0.1; Flow = 1.0 ml/ min; 23 degre
e;
50 bar; OD-H.
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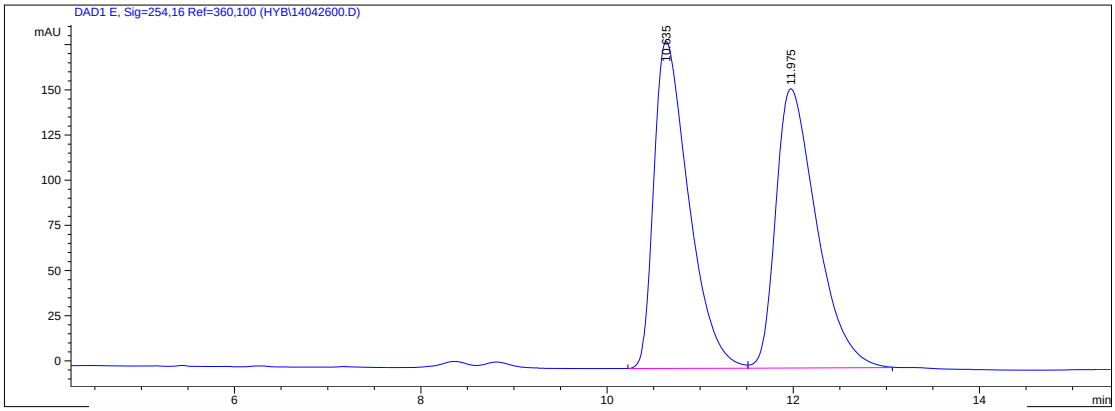


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Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.635 BV    0.3949 4697.53809  180.93880  49.9183
   2  11.975 VB    0.4639 4712.90576  154.50410  50.0817

 File C:\HPCHEM\1\DATA\HYB\14042601.D                    Sample Name: wlh30-4

Hexane: i-PrOH = 99.9:0.1; Flow = 1.0 ml/ min; 23 degre
e;
50 bar; OD-H.
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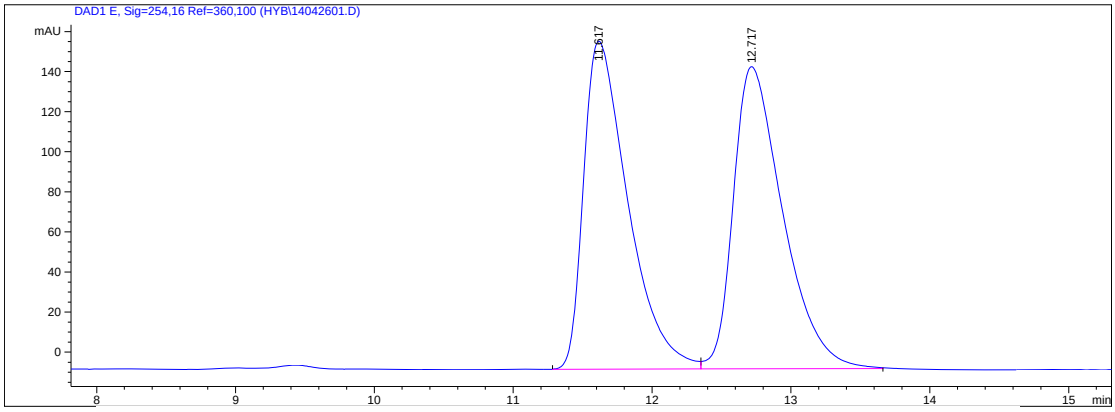
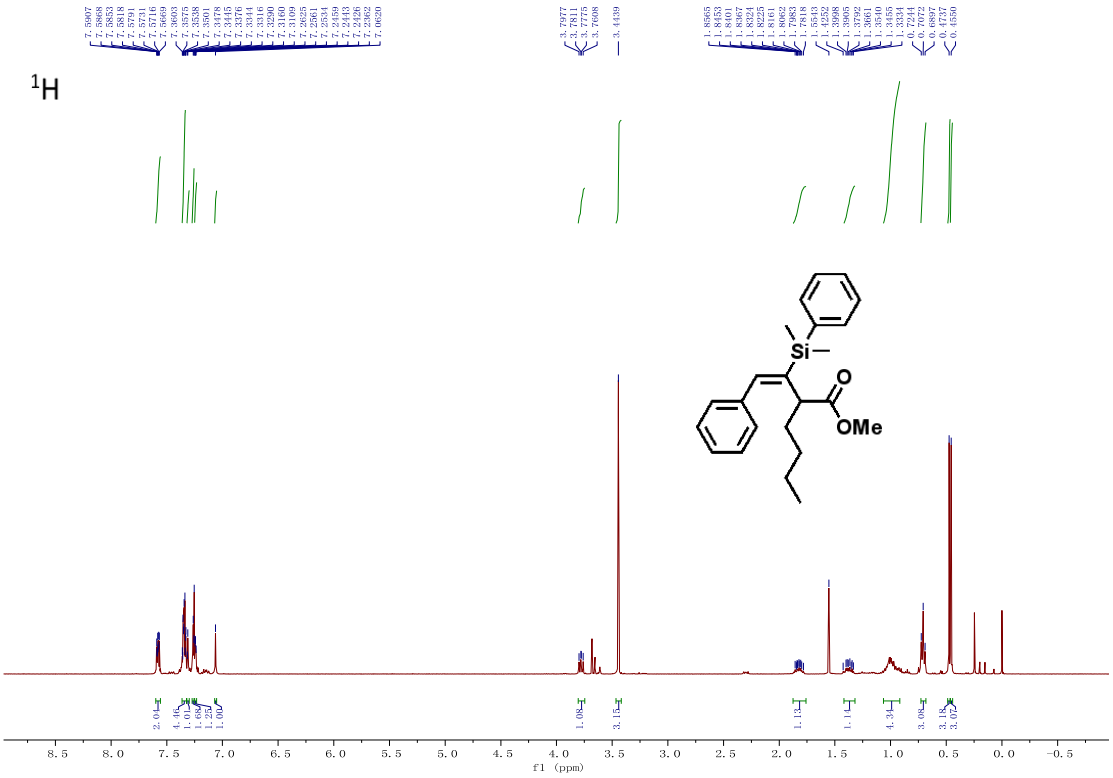
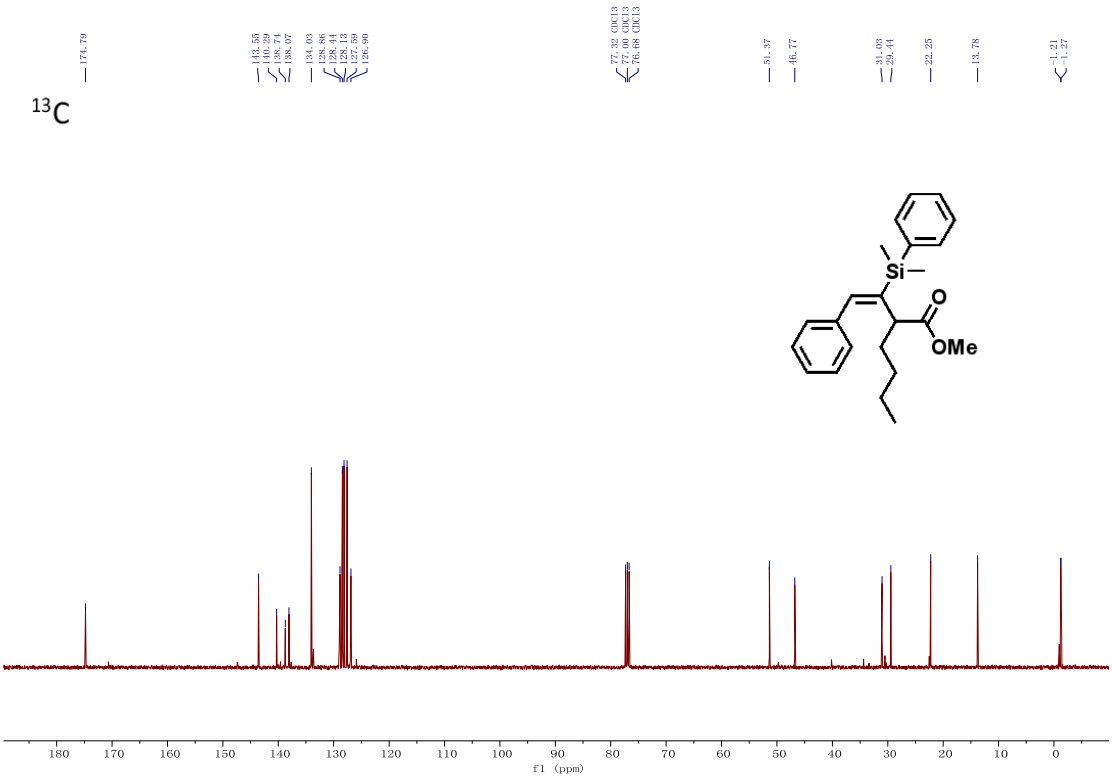


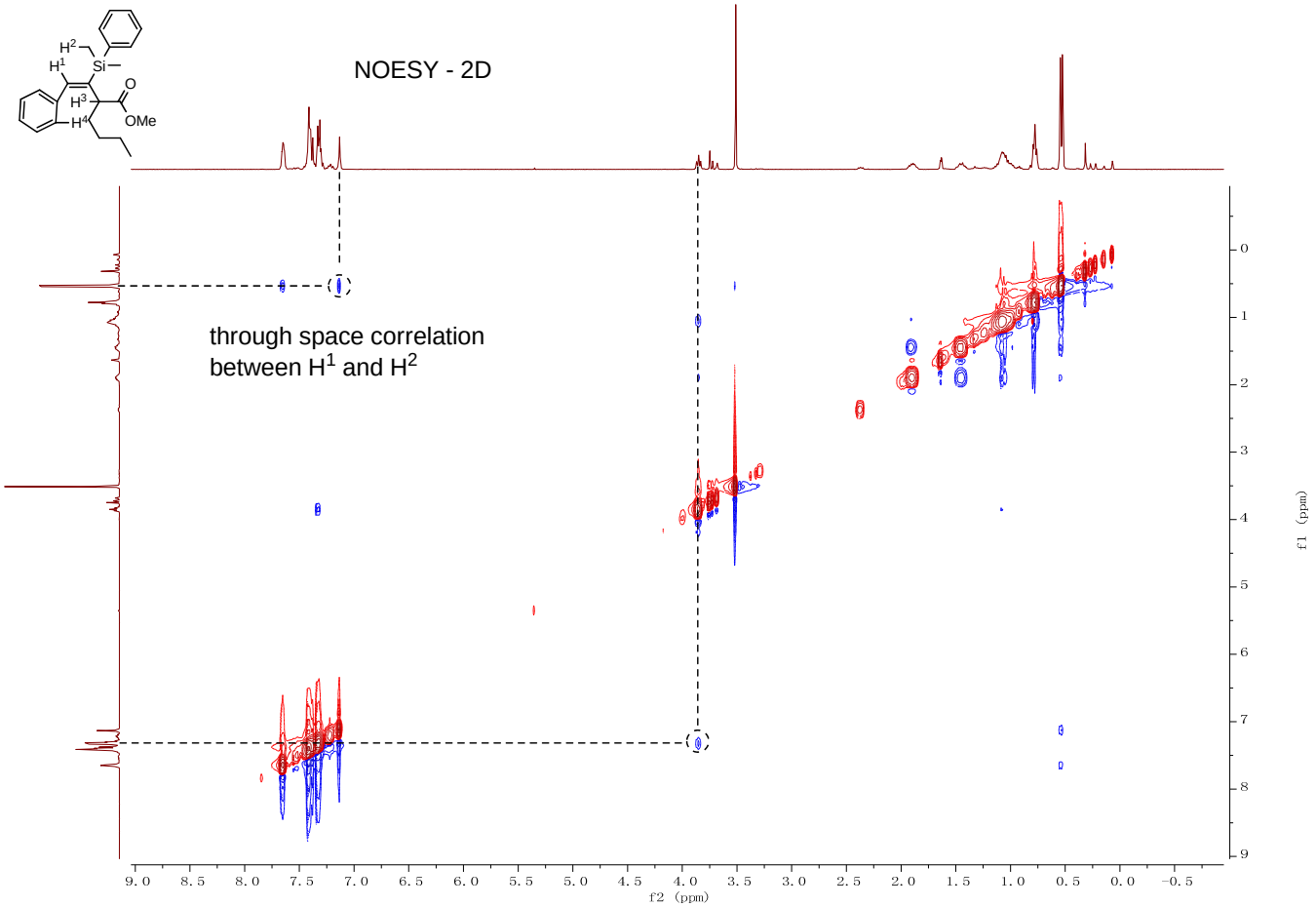
Signal 5: DAD1 E, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.617	BV	0.3348	3630.59424	163.67574	49.2980
2	12.717	VB	0.3750	3733.99170	150.76077	50.7020

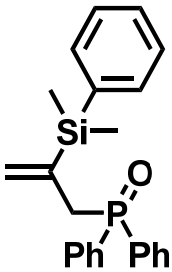


^{13}C

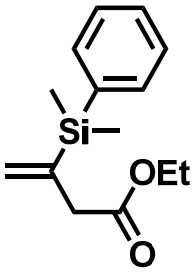

174.79
143.55
140.59
138.74
138.07
134.03
128.86
128.41
128.13
127.89
126.90
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
51.37
46.77
31.03
29.44
22.25
13.78
-1.21
-1.27
Si
O
OMe
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



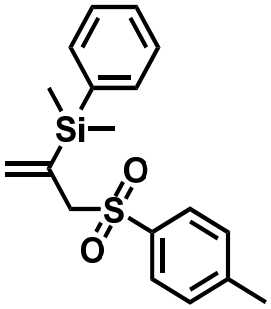
3. Characterization Data for the Vinylsilanes



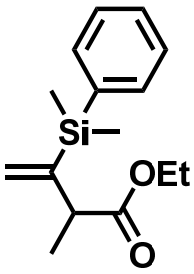
3a diphenyl[2-(dimethyl(phenyl)silyl)- propen-1-yl]- Phosphine oxide
Colorless oil.
Yield = 81%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.69 – 7.60 (m, 4H), 7.52 – 7.44 (m, 4H), 7.44 – 7.38 (m, 4H), 7.38 – 7.30 (m, 3H), 6.00 (dt, J_1 = 5.1 Hz, J_2 = 1.4 Hz, 1H), 5.60 – 5.56 (m, 1H), 3.10 (d, J = 13.6 Hz, 2H), 0.30 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 139.4 (d, J = 9.1 Hz), 137.3, 134.0, 133.1 (d, J = 97.6 Hz), 132.6 (d, J = 10.2 Hz), 131.4 (d, J = 2.6 Hz), 130.9 (d, J = 9.0 Hz), 129.0, 128.3 (d, J = 11.5 Hz), 127.7, 35.2 (d, J = 66.0 Hz), -3.4.
^{31}P NMR ($CDCl_3$) δ (ppm): 29.6.
FTIR (neat): ν = 3061, 2952, 1588, 1433, 1192, 931, 816, 696 cm^{-1}
HRMS (ESI, m/z): calcd for $C_{23}H_{26}OPSi^+$ $[M+H]^+$ 377.1491, found: 377.1491.



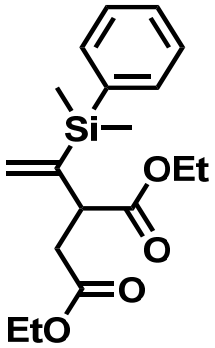
3b ethyl 3-(dimethyl(phenyl)silyl)but-3-enoate
Light yellow oil.
Yield = 83%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 - 7.46 (m, 2H), 7.40 - 7.29 (m, 3H), 5.85 (dt, J_1 = 2.4 Hz, J_2 = 1.1 Hz, 1H), 5.61 - 5.55 (m, 1H), 4.00 (q, J = 7.2 Hz, 2H), 3.09 (t, J = 1.1 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H), 0.40 (s, 6H);
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.7, 142.8, 137.3, 133.8, 130.2, 129.0, 127.6, 60.4, 41.6, 14.0, -3.2.
FTIR (neat): ν = 3057, 2956, 1732, 1567, 1031, 931, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{14}H_{21}O_2Si^+$ $[M+H]^+$ 249.1311, found: 249.1313.



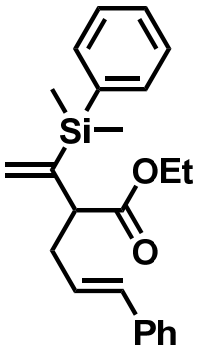
3c dimethyl(phenyl)(3-tosylprop-1-en-2-yl)silane
Colorless oil.
Yield = 68%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.65 – 7.59 (m, 2H), 7.50 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 7.30 – 7.26 (m, 2H), 5.86 (dt, J_1 = 2.0 Hz, J_2 = 0.9 Hz, 1H), 5.73 (d, J = 2.0 Hz, 1H), 3.79 (d, J = 0.9 Hz, 2H), 2.43 (s, 3H), 0.41 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 144.3, 137.4, 136.8, 136.7, 135.8, 133.9, 129.4, 129.2, 128.5, 127.7, 61.6, 21.5, -3.0.
FTIR (neat): ν = 3067, 2952, 1588, 1433, 1313, 1151 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{18}H_{23}O_2SSi^+$ $[M+H]^+$ 331.1188, found: 331.1188.



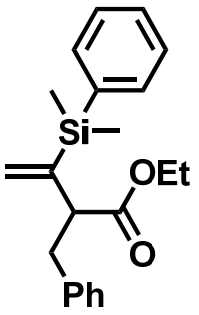
3d ethyl 3-(dimethyl(phenyl)silyl)-2-methylbut-3-enoate
Light yellow oil.
Yield = 81%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 – 7.47 (m, 2H), 7.40 – 7.30 (m, 3H), 5.90 (dd, J_1 = 1.9 Hz, J_2 = 1.1 Hz, 1H), 5.67 (d, J = 1.9 Hz, 1H), 4.05 – 3.88 (m, 2H), 3.23 (qd, J_1 = 7.1 Hz, J_2 = 1.1 Hz, 1H), 1.18 (d, J = 6.6 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H), 0.40 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.6, 149.1, 137.6, 133.9, 129.0, 127.8, 127.6, 60.2, 43.7, 17.6, 13.9, -2.8, -2.8.
FTIR (neat): ν = 3057, 2956, 1732, 1567, 1031, 931, 816, 776, 736, 701 cm^{-1}
HRMS (ESI, m/z): calcd for $C_{15}H_{23}O_2Si^+$ $[M+H]^+$ 263.1467, found: 263.1467.



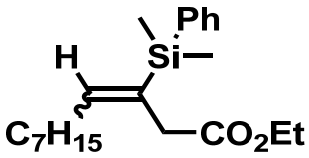
3e diethyl 2-(1-(dimethyl(phenyl)silyl)vinyl)succinate
Light yellow oil.
Yield = 77%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.47 (m, 2H), 7.39 – 7.30 (m, 3H), 5.90 (s, 1H), 5.59 (s, 1H), 4.11 – 3.89 (m, 4H), 3.61 (dd, J_1 = 10.5 Hz, J_2 = 4.8 Hz, 1H), 2.85 (dd, J_1 = 16.8 Hz, J_2 = 10.5 Hz, 1H), 2.30 (dd, J_1 = 16.8 Hz, J_2 = 4.8 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H), 0.43 (s, 3H), 0.42 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.0, 171.6, 146.7, 137.0, 133.9, 129.3, 129.1, 127.7, 60.6, 60.4, 45.2, 36.9, 14.0, 13.8, -2.9, -3.0.
FTIR (neat): ν = 3061, 2956, 1732, 1567, 1031, 931, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{18}H_{27}O_4Si^+$ $[M+H]^+$ 335.1679, found: 335.1679.



3f (E)-ethyl 2-(1-(dimethyl(phenyl)silyl)vinyl)-5-phenylpent-4-enoate
Light yellow oil.
Yield = 93%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 – 7.49 (m, 2H), 7.41 – 7.31 (m, 3H), 7.29 – 7.24 (m, 4H), 7.23 – 7.16 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 6.08 – 6.00 (m, 2H), 5.69 – 5.61 (m, 1H), 4.07 – 3.92 (m, 2H), 3.24 (dd, J_1 = 9.2 Hz, J_2 = 5.8 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.37 – 2.26 (m, 1H), 1.15 (tt, J_1 = 7.2 Hz, J_2 = 0.72 Hz, 3H), 0.43 (s, 3H), 0.43 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.3, 147.2, 137.3, 137.2, 134.0, 131.6, 129.0, 128.7, 128.3, 127.6, 127.4, 126.9, 125.9, 60.3, 49.6, 36.0, 13.9, -3.0, -3.1.
FTIR (neat): ν = 3061, 2956, 1732, 1583, 1031, 931, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{23}H_{29}O_2Si^+$ $[M+H]^+$ 365.1937, found: 365.1937.

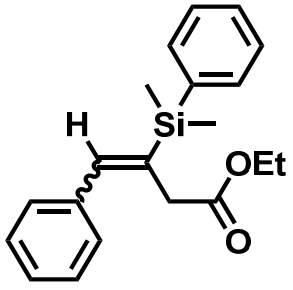


3g ethyl 2-benzyl-3-(dimethyl(phenyl)silyl)but-3-enoate
Light yellow oil.
Yield = 79%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 – 7.46 (m, 2H), 7.43 – 7.30 (m, 3H), 7.23 – 7.09 (m, 3H), 7.04 – 6.95 (m, 2H), 6.05 (dd, J_1 = 1.8 Hz, J_2 = 1.8 Hz, 1H), 5.64 (d, J = 1.8 Hz, 1H), 3.91 (qd, J_1 = 7.2 Hz, J_2 = 1.0 Hz, 2H), 3.36 (qd, J_1 = 5.0 Hz, J_2 = 0.8 Hz, 1H), 3.07 (dd, J_1 = 13.6 Hz, J_2 = 9.9 Hz, 1H), 2.64 (dd, J_1 = 13.6 Hz, J_2 = 5.1 Hz, 1H), 1.06 (t, J = 7.2 Hz, 3H), 0.39 (s, 3H), 0.38 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.4, 147.7, 139.7, 137.2, 134.1, 129.2, 128.9, 128.7, 128.2, 127.8, 126.1, 60.3, 51.2, 38.9, 13.9, -3.1.
FTIR (neat): ν = 3061, 2956, 2927, 1732, 1583, 1207, 1157, 931, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{21}H_{27}O_2Si^+$ $[M+H]^+$ 339.1780, found: 339.1779.



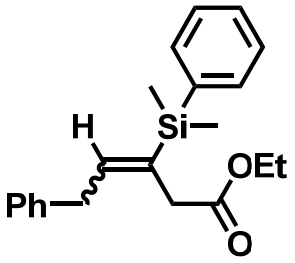
E/Z

3h ethyl 3-(dimethyl(phenyl)silyl)undec-3-enoate
Light yellow oil.
Yield = 63%
E / **Z** = 84:16 (**E** was determined by NMR 1D NOE)
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.46 (m, 2H), 7.36 – 7.32 (m, 3H), 6.02 (tt, J_1 = 6.9 Hz, J_2 = 1.0 Hz, 1H), 3.97 (q, J = 7.2 Hz, 2H), 3.1 (d, J = 1.0 Hz, 2H), 2.16 (q, J = 7.2 Hz, 2H), 1.32 – 1.24 (m, 10H), 1.15 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H), 0.36 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.8, 146.6, 138.2, 133.9, 130.9, 128.8, 127.5, 60.2, 34.8, 31.7, 29.2, 29.1, 29.0, 28.9, 22.5, 14.0, 13.9, -3.0.
FTIR (neat): ν = 3061, 2956, 2927, 2856, 1732, 1567, 1162, 1031, 931, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{21}H_{35}O_2Si^+$ $[M+H]^+$ 347.2406, found: 347.2405.



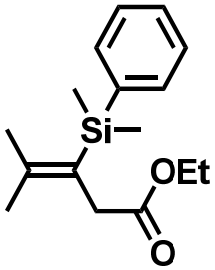
E/Z

3i ethyl 3-(dimethyl(phenyl)silyl)-4-phenylbut-3-enoate
Light yellow oil.
Yield = 68%
E / **Z** = 83:17 (**E** was determined by NMR 1D NOE)
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62 – 7.53 (m, 2H), 7.39 – 7.30 (m, 7H), 7.30 -7.22 (m, 1H), 7.05 (s, 1H), 3.98 (q, J = 7.2 Hz, 2H), 3.30 (d, J = 1.0 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H), 0.47 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.0, 143.1, 139.1, 137.3, 134.6, 134.0, 129.0, 128.4, 128.1, 127.6, 127.1, 60.5, 36.1, 13.9, -2.9.
FTIR (neat): ν = 3061, 2956, 2927, 1732, 1598, 1252, 1162, 1106, 1032, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{20}H_{25}O_2Si^+$ $[M+H]^+$ 325.1624, found: 325.1626.

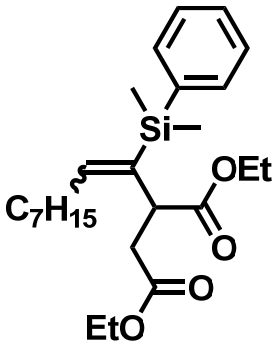


E/Z

3j ethyl 3-(dimethyl(phenyl)silyl)-5-phenylpent-3-enoate
Light yellow oil.
Yield = 59%
E / Z = 80:20 (**E** was determined by NMR 1D NOE)
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.46 (m, 2H), 7.37 – 7.27 (m, 5H), 7.23 – 7.17 (m, 3H), 6.20 (tt, J_1 = 6.9 Hz, J_2 = 1.0 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 3.55 (d, J = 6.9 Hz, 2H), 3.21 (d, J = 1.0 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H), 0.38 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.6, 144.0, 140.1, 137.8, 134.0, 132.4, 128.9, 128.4, 128.3, 127.6, 125.9, 60.4, 35.2, 34.9, 14.0, -3.1.
FTIR (neat): ν = 3057, 2956, 2927, 1732, 1598, 1252, 1162, 1106, 1032, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{21}H_{27}O_2Si^+$ $[M+H]^+$ 339.1780, found: 339.1783.



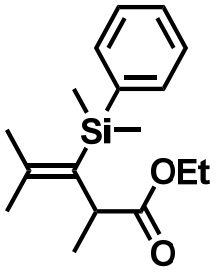
3k ethyl 3-(dimethyl(phenyl)silyl)-4-methylpent-3-enoate
Light yellow oil.
Yield = 90%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.50 (m, 2H), 7.37 – 7.33 (m, 3H), 4.09 (q, J = 7.2 Hz, 2H), 3.20 (s, 2H), 1.80 (s, 3H), 1.72 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 0.40 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 172.6, 149.1, 140.0, 133.7, 128.4, 127.5, 123.1, 60.2, 37.4, 26.0, 21.6, 14.1, -0.90.
FTIR (neat): ν = 3061, 2956, 2927, 1732, 1567, 1252, 1162, 1106, 1032, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{16}H_{25}O_2Si^+$ $[M+H]^+$ 277.1624, found: 277.1626.



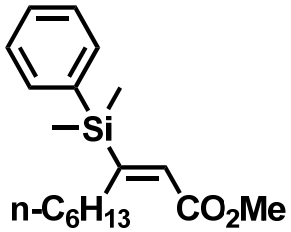
E/Z

3l diethyl 2-(1-(dimethyl(phenyl)silyl)non-1-enyl)succinate
Light yellow oil.
Yield = 68%
E / Z = 81:19 (**E** was determined by NMR 1D NOE)

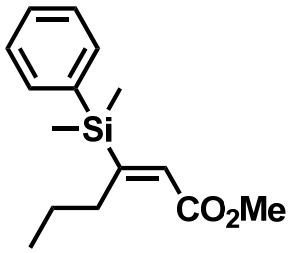
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 – 7.45 (m, 2H), 7.34 – 7.31 (m, 3H), 5.95 (t, *J* = 7.0 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 4.02 – 3.91 (m, 2H), 3.84 – 3.76 (m, 1H), 2.93 (dd, J_1 = 16.6 Hz, J_2 = 9.9 Hz, 1H), 2.29 – 2.19 (m, 1H), 2.19 – 2.09 (m, 2H), 1.34 – 1.23 (m, 10H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.39 (s, 3H), 0.36 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 173.5, 171.8, 147.0, 138.4, 135.1, 133.9, 128.8, 127.5, 60.5, 60.4, 42.2, 36.0, 31.7, 29.3, 29.2, 29.1, 29.0, 22.5, 14.0, 13.9, 13.8, -1.9, -2.0.
FTIR (neat): ν = 3061, 2956, 2927, 1732, 1567, 1252, 1162, 1106, 1032, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{25}H_{41}O_4Si^+$ $[M+H]^+$ 433.2774, found: 433.2776.



3m ethyl 3-(dimethyl(phenyl)silyl)-2,4-dimethylpent-3-enoate
Colorless oil.
Yield = 74%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.51 (m, 2H), 7.38 – 7.28 (m, 3H), 4.20 – 4.03 (m, 2H), 3.57 (q, *J* = 7.2 Hz, 1H), 1.76 (s, 3H), 1.63 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.37 (s, 3H), 0.32 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.0, 146.2, 140.8, 133.5, 130.5, 128.3, 127.5, 60.4, 42.2, 26.4, 21.5, 16.7, 14.1, -0.3, -0.2.
FTIR (neat): ν = 3057, 2956, 2927, 1732, 1602, 1252, 1201, 1101, 816, 776, 736, 701 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{17}H_{27}O_2Si^+$ $[M+H]^+$ 291.1780, found: 291.1779.

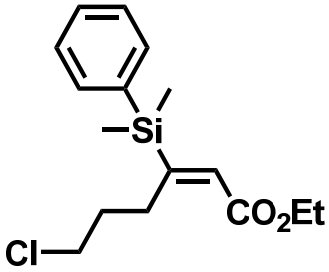


5a (E)-methyl 3-(dimethyl(phenyl)silyl)non-2-enoate
Light yellow oil.
Yield = 92%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 6.06 (t, *J* = 0.8 Hz, 1H), 3.69 (S, 3H), 2.62 (t, *J* = 7.4 Hz, 2H), 1.30 – 1.17 (m, 8H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.42 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.6, 165.2, 136.6, 134.0, 129.4, 127.9, 127.3, 50.9, 31.7, 31.5, 29.8, 29.6, 22.5, 14.0, -3.3.
FTIR (neat): ν = 3072, 2949, 2857, 1728, 1591, 1431, 1248, 1198, 1170, 807, 756, 730, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{18}H_{29}O_2Si^+$ $[M+H]^+$ 305.1937, found: 305.1940.

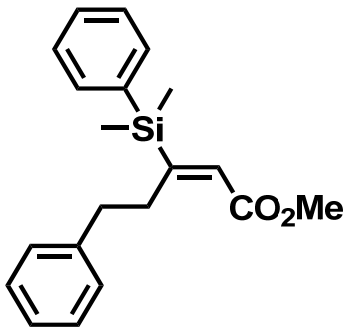


5b (E)-methyl 3-(dimethyl(phenyl)silyl)hex-2-enoate

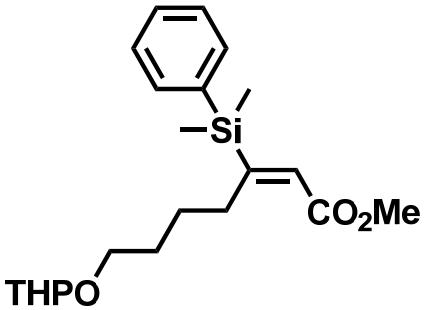
Light yellow oil.
Yield = 75%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.47 (m, 2H), 7.39 – 7.33 (m, 3H), 6.07 (t, *J* = 0.8 Hz, 1H), 3.69 (s, 3H), 2.66 – 2.58 (m, 2H), 1.38 – 1.30 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.42 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 165.0, 136.6, 134.0, 129.4, 127.9, 127.5, 50.9, 33.7, 23.1, 14.5, -3.3.
FTIR (neat): ν = 3077, 2966, 2865, 1714, 1591, 1419, 1248, 1187, 1106, 832, 770, 740, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{15}H_{23}O_2Si^+$ $[M+H]^+$ 263.1467, found: 263.1469.



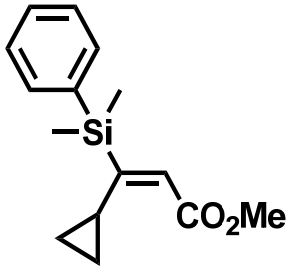
5c (E)-ethyl 6-chloro-3-(dimethyl(phenyl)silyl)hex-2-enoate
Light yellow oil.
Yield = 93%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.48 (m, 2H), 7.41 – 7.34 (m, 2H), 6.12 (t, *J* = 0.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.47 (t, *J* = 6.6 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.45 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.1, 162.8, 136.1, 134.0, 129.6, 128.9, 128.0, 59.9, 45.2, 32.4, 29.0, 14.3, -3.4.
FTIR (neat): ν = 3068, 2966, 2854, 1706, 1594, 1431, 1258, 1177, 1146, 1106, 811, 770, 740, 689 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{16}H_{24}ClO_2Si^+$ $[M+H]^+$ 311.1234, found: 311.1236.



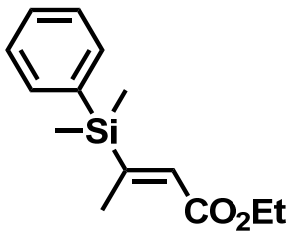
5d (E)-methyl 3-(dimethyl(phenyl)silyl)-5-phenylpent-2-enoate
Light yellow oil.
Yield = 89%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 – 7.52 (m, 2H), 7.42 – 7.37 (m, 3H), 7.27 – 7.22 (m, 2H), 7.18 – 7.10 (m, 3H), 6.16 (t, *J* = 0.8 Hz, 1H), 3.73 (s, 3H), 2.92 – 2.84 (m, 2H), 2.56 – 2.48 (m, 2H), 0.47 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.4, 164.1, 142.1, 136.2, 134.1, 129.6, 128.4, 128.3, 128.0, 127.9, 125.8, 51.0, 35.8, 34.2, -3.5.
FTIR (neat): ν = 3068, 3028, 2956, 2854, 1952, 1887, 1716, 1594, 1432, 1340, 1248, 1197, 1157, 1106, 830, 781, 732, 692 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{20}H_{25}O_2Si^+$ $[M+H]^+$ 325.1624, found: 325.1625.



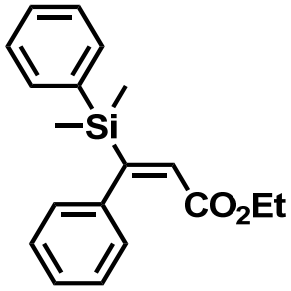
5e (E)-methyl 3-(dimethyl(phenyl)silyl)-7-(tetrahydro-2H-pyran-2-yloxy)hept-2-enoate
Light yellow oil.
Yield = 83%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.46 (m, 2H), 7.41 – 7.32 (m, 3H), 6.07 (t, *J* = 0.8 Hz, 1H), 4.53 (t, *J* = 2.8 Hz, 1H), 3.88 – 3.77 (m, 1H), 3.71 – 3.68 (m, 3H), 3.68 – 3.61 (m, 1H), 3.51 – 3.43 (m, 1H), 3.35 – 3.26 (m, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 1.86 – 1.74 (m, 1H), 1.70 – 1.47 (m, 7H), 1.43 – 1.27 (m, 2H), 0.42 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.6, 164.8, 136.5, 134.0, 129.4, 127.9, 127.7, 98.6, 67.1, 62.2, 50.9, 31.3, 30.7, 30.1, 26.3, 25.5, 19.6, -3.3.
FTIR (neat): ν = 3072, 2942, 2868, 1723, 1602, 1422, 1350, 1252, 1204, 1196, 1162, 1114, 1173, 1037, 813, 773, 737, 704 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{21}H_{33}O_4Si^+$ $[M+H]^+$ 377.2148, found: 377.2146.



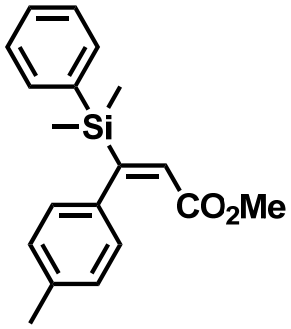
5f (E)-methyl 3-cyclopropyl-3-(dimethyl(phenyl)silyl)acrylate
Light yellow oil.
Yield = 85%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 – 7.46 (m, 2H), 7.39 – 7.32 (m, 3H), 6.14 (d, *J* = 1.4 Hz, 1H), 3.72 (s, 3H), 2.75 – 2.65 (m, 1H), 0.82 – 0.73 (m, 2H), 0.53 – 0.48 (m, 2H), 0.41 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.4, 164.6, 137.2, 133.8, 129.4, 129.0, 127.9, 51.0, 15.3, 7.9, -1.7.
FTIR (neat): ν = 3072, 3016, 2956, 1716, 1578, 1432, 1256, 1187, 1114, 1017, 813, 772, 733, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{15}H_{21}O_2Si^+$ $[M+H]^+$ 261.1311, found: 261.1317.



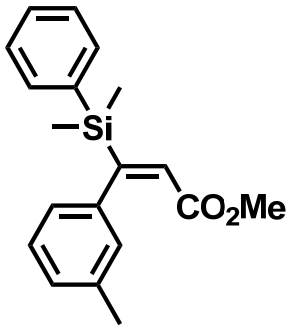
5g (E)-ethyl 3-(dimethyl(phenyl)silyl)but-2-enoate
Light yellow oil.
Yield = 94%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.46 (m, 2H), 7.41 – 7.33 (m, 3H), 6.09 (q, *J* = 1.8 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.19 (d, *J* = 1.8 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.41 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 159.9, 136.2, 134.0, 129.4, 127.9, 127.8, 59.7, 17.5, 14.3, -4.0.
FTIR (neat): ν = 3072, 3048, 2958, 1716, 1617, 1422, 1342, 1249, 1179, 1114, 1033, 838, 813, 773, 732, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{14}H_{21}O_2Si^+$ $[M+H]^+$ 249.1311, found: 249.1308.



5h (E)-ethyl 3-(dimethyl(phenyl)silyl)-3-phenylacrylate
Light yellow oil.
Yield = 91%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.34 – 7.28 (m, 2H), 7.23 – 7.15 (m, 3H), 7.08 – 6.98 (m, 3H), 6.07 – 6.03 (m, 2H), 6.05 (s, 1H), 3.76 (q, *J* = 7.1 Hz, 2H), 0.81 (t, *J* = 7.1 Hz, 3H), 0.21 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.3, 161.2, 141.1, 135.6, 134.2, 129.5, 129.4, 127.9, 127.6, 126.0, 125.9, 59.9, 13.8, -3.7.
FTIR (neat): ν = 3072, 3024, 2968, 2893, 1951, 1878, 1723, 1602, 1488, 1431, 1366, 1252, 1187, 1162, 1114, 1033, 838, 806, 781, 732, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{19}H_{23}O_2Si^+$ $[M+H]^+$ 311.1467, found: 311.1469.

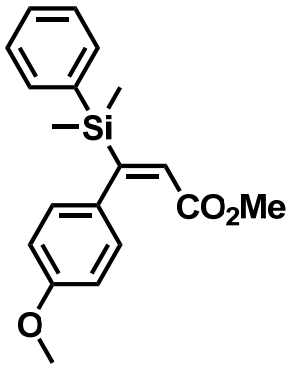


5i (E)-methyl 3-(dimethyl(phenyl)silyl)-3-p-tolylacrylate
Light yellow oil.
Yield = 71%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 – 7.46 (m, 2H), 7.43 – 7.33 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 6.22 (s, 1H), 3.54 (s, 3H), 2.33 (s, 3H), 0.39 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.5, 162.3, 137.8, 135.8, 135.6, 134.2, 129.5, 128.6, 128.5, 127.9, 125.8, 51.0, 21.2, -3.7.
FTIR (neat): ν = 3072, 3016, 2951, 1736, 1602, 1432, 1252, 1204, 1163, 1114, 1032, 871, 814, 773, 741, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{19}H_{23}O_2Si^+$ $[M+H]^+$ 311.1467, found: 311.1463.

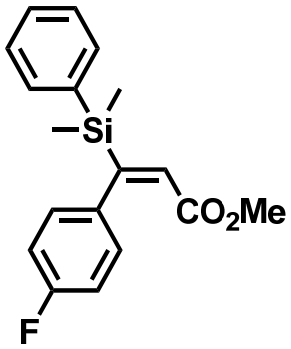


5j (E)-methyl 3-(dimethyl(phenyl)silyl)-3-m-tolylacrylate
Light yellow oil.
Yield = 72%

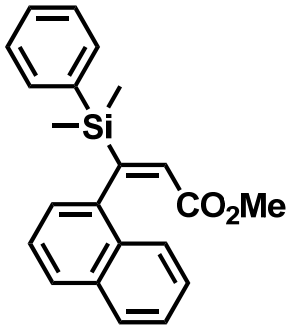
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.44 (m, 2H), 7.40 – 7.33 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.02 – 6.97 (m, 1H), 6.66 – 6.59 (m, 2H), 6.19 (s, 1H), 3.51 (s, 3H), 2.27 (s, 3H), 0.37 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.5, 162.2, 140.8, 137.1, 135.7, 134.2, 129.6, 128.5, 127.9, 127.6, 126.9, 126.5, 123.0, 51.1, 21.5, -3.7.
FTIR (neat): ν = 3056, 3016, 2951, 1732, 1601, 1488, 1432, 1350, 1252, 1163, 1114, 1034, 830, 805, 781, 740, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{19}H_{23}O_2Si^+$ $[M+H]^+$ 311.1467, found: 311.1461.



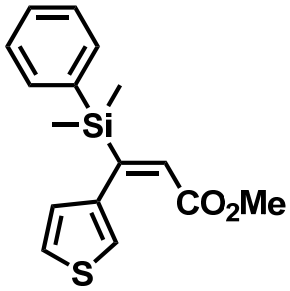
5k (E)-methyl 3-(dimethyl(phenyl)silyl)-3-(4-methoxyphenyl)acrylate
Light yellow oil.
Yield = 70%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.50 – 7.46 (m, 2H), 7.42 – 7.33 (m, 3H), 6.82 – 6.75 (m, 4H), 6.22 (s, 1H), 3.79 (s, 3H), 3.53 (s, 3H), 0.38 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.7, 161.6, 158.1, 135.9, 134.2, 133.0, 129.5, 128.8, 127.9, 127.3, 113.3, 55.1, 51.1, -3.6.
FTIR (neat): ν = 3064, 3000, 2951, 2836, 1724, 1610, 1504, 1456, 1432, 1350, 1253, 1172, 1106, 1033, 875, 822, 773, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{19}H_{23}O_3Si^+$ $[M+H]^+$ 327.1416, found: 327.1417.



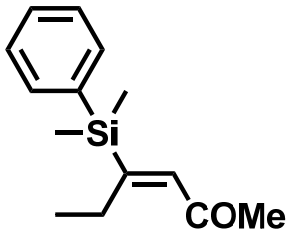
5l (E)-methyl 3-(dimethyl(phenyl)silyl)-3-(4-fluorophenyl)acrylate
Light yellow oil.
Yield = 77%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48 – 7.44 (m, 2H), 7.41 – 7.34 (m, 3H), 6.97 – 6.91 (m, 2H), 6.81 – 6.74 (m, 2H), 6.24 (s, 1H), 3.52 (s, 3H), 0.38 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.4, 161.5 (d, *J* = 243.2 Hz), 161.2, 136.6 (d, *J* = 3.3 Hz), 135.3, 134.2, 129.7, 129.2, 128.0, 127.5 (d, *J* = 7.8 Hz), 114.8 (d, *J* = 21.3 Hz), 51.2, -3.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -116.8.
FTIR (neat): ν = 3072, 3048, 2958, 1724, 1594, 1504, 1432, 1350, 1252, 1204, 1172, 1114, 1017, 985, 871, 830, 773, 733, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{18}H_{20}FO_2Si^+$ $[M+H]^+$ 315.1217, found: 315.1216.



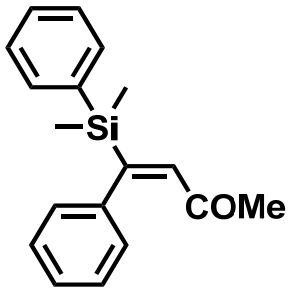
5m (E)-methyl 3-(dimethyl(phenyl)silyl)-3-(naphthalen-1-yl)acrylate
Light yellow oil.
Yield = 64%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.51 – 7.47 (m, 2H), 7.44 – 7.29 (m, 6H), 6.82 (dd, J_1 = 7.1 Hz, J_2 = 1.0 Hz, 1H), 6.47 (s, 1H), 3.34 (s, 3H), 0.34 (s, 3H), 0.30 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.9, 161.7, 138.9, 135.6, 134.2, 133.3, 130.7, 130.1, 129.6, 128.2, 127.9, 126.3, 125.5, 125.4, 125.3, 125.0, 122.1, 51.1, -3.3, -3.9.
FTIR (neat): ν = 3048, 2951, 1732, 1594, 1504, 1432, 1390, 1350, 1252, 1172, 1114, 830, 781, 733, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{22}H_{23}O_2Si^+$ $[M+H]^+$ 347.1467, found:347.1459.



5n (E)-methyl 3-(dimethyl(phenyl)silyl)-3-(thiophen-3-yl)acrylate
Light yellow oil.
Yield = 87%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.51 – 7.46 (m, 2H), 7.41 – 7.33 (m, 3H), 7.24 – 7.20 (m, 1H), 6.76 – 6.66 (m, 2H), 6.24 (s, 1H), 3.57 (s, 3H), 0.39 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.8, 156.0, 140.0, 135.8, 134.2, 129.6, 129.4, 128.0, 127.4, 124.5, 119.9, 51.3, -3.6.
FTIR (neat): ν = 3072, 3007, 2951, 1732, 1585, 1432, 1325, 1252, 1172, 1114, 1034, 830, 781, 740, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{16}H_{19}O_2SSi^+$ $[M+H]^+$ 303.0875, found: 303.0880.



5o (E)-4-(dimethyl(phenyl)silyl)hex-3-en-2-one
Light yellow oil.
Yield = 85%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.55 – 7.50 (m, 2H), 7.33 – 7.28 (m, 3H), 6.74 (t, J = 1.6 Hz, 1H), 2.28 (qd, J_1 = 7.3 Hz, J_2 = 1.6 Hz, 2H), 2.14 (s, 3H), 1.01 (t, J = 7.3 Hz, 3H), 0.44 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.7, 165.4, 139.3, 137.0, 133.8, 128.4, 127.4, 31.9, 30.2, 13.7, -2.0.
FTIR (neat): ν = 3072, 3007, 2951, 1691, 1570, 1488, 1423, 1358, 1245, 1172, 1106, 847, 814, 781, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{14}H_{21}OSi^+$ $[M+H]^+$ 233.1362, found: 233.1358.

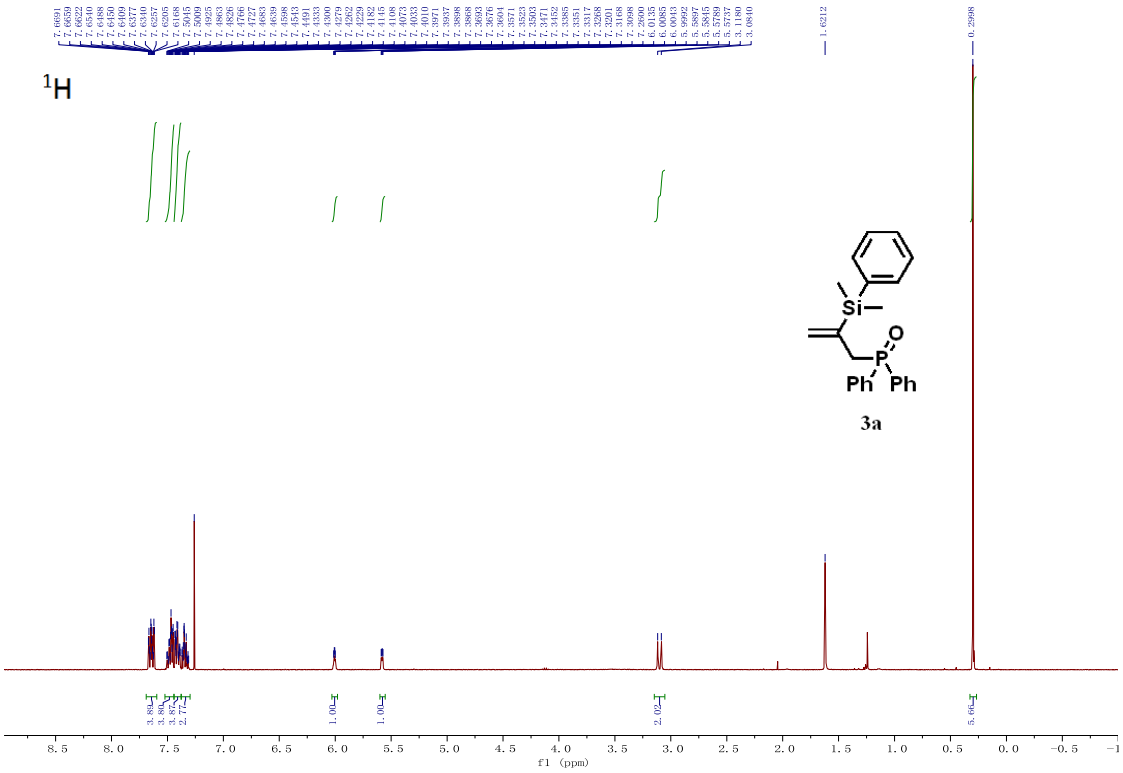


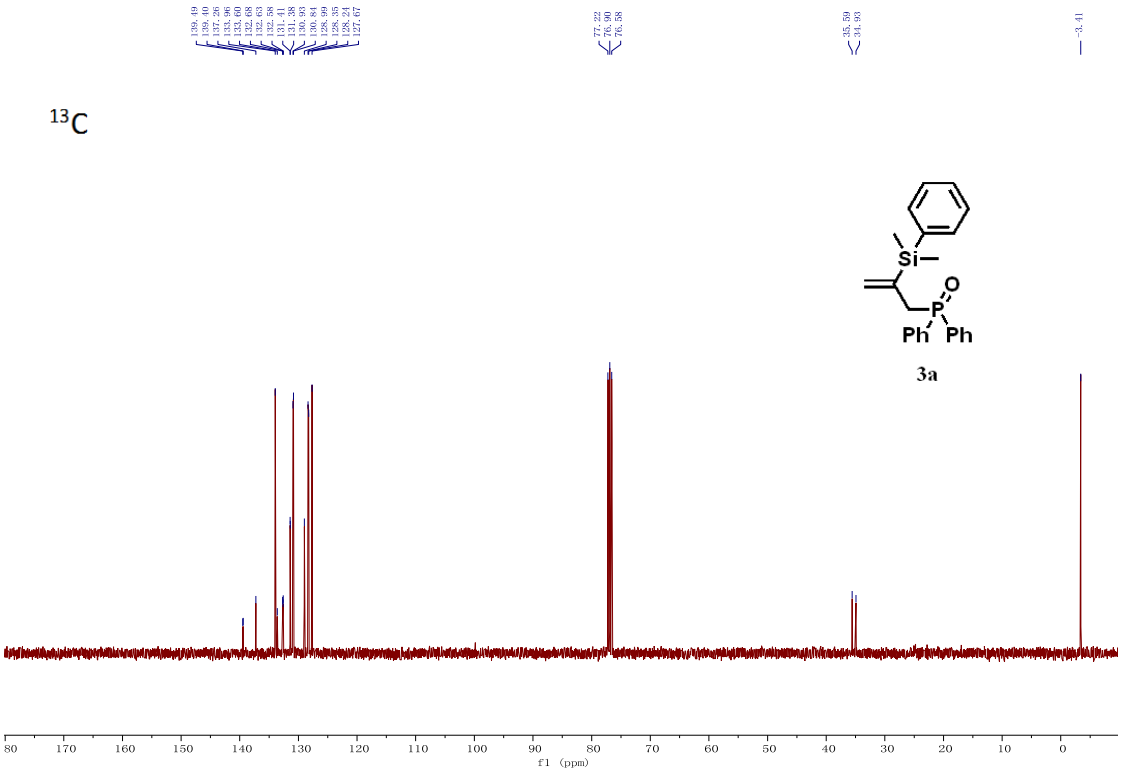
5p (E)-4-(dimethyl(phenyl)silyl)-4-phenylbut-3-en-2-one
Light yellow oil.
Yield = 57%
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.54 (m ,2H), 7.34 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.13 – 7.06 (m, 2H), 6.82 (s, 1H), 2.19 (s, 3H), 0.38 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 197.9, 162.5, 145.2, 140.7, 138.6, 133.8, 128.5, 127.9, 127.4, 126.7, 126.6, 30.4, -0.9.
FTIR (neat): ν = 3072, 2958, 2934, 1691, 1577, 1422, 1358, 1244, 1196, 1106, 968, 822, 772, 732, 700 cm^{-1}.
HRMS (ESI, m/z): calcd for $C_{18}H_{21}OSi^{+}$ $[M+H]^{+}$ 281.1362, found: 281.1367.

4. References

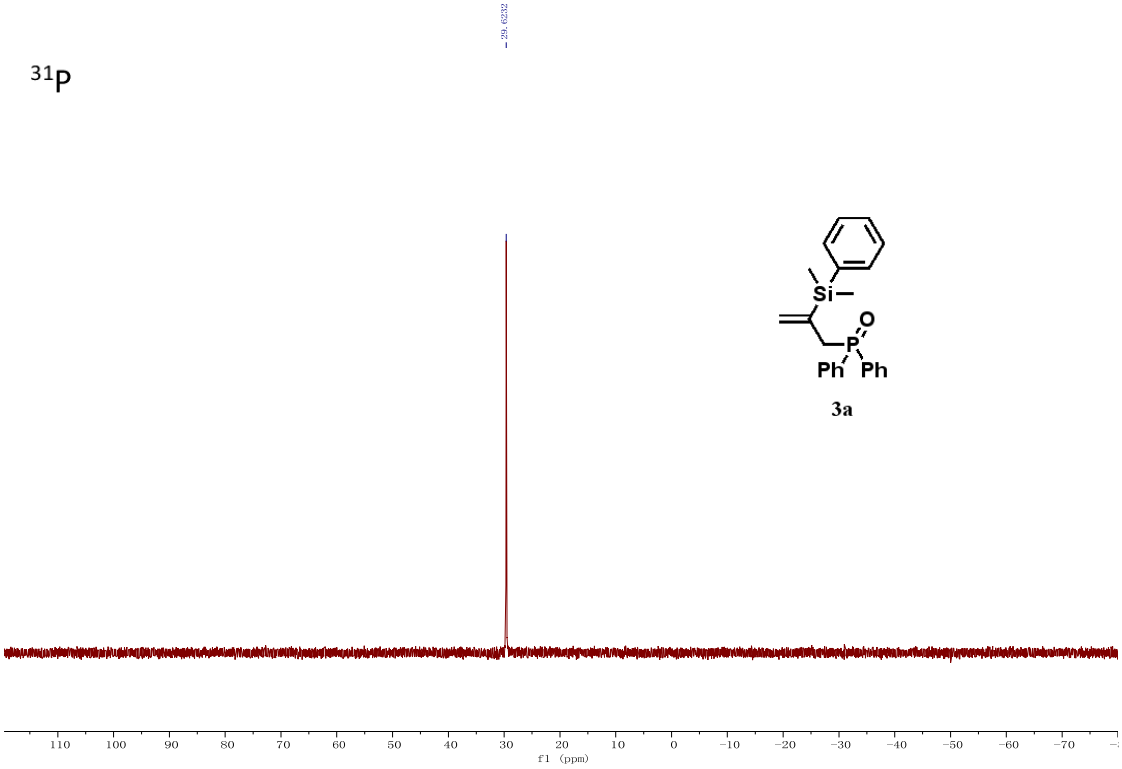
(1) T. Nishimura, S. Hirabayashi, T. Hayashi, *J. Am. Chem. Soc.* **2006**, *128*, 2556 – 2557.
(2) M. Harmata, C. F. Huang, *Adr. Synth. Catal.* **2008**, *350*, 972 – 974.
(3) S. Y. Chow, H. J. Williams, Q. Huang, S. Nanda, A. I. Scott, *J. Org. Chem.* **2005**, *70*, 9997 – 10003.
(4) T. M. Werkhoven, R. V. Nispen, J. Lugtenburg, *Eur. J. Org. Chem.* **1999**, *11*, 2909 – 2914.
(5) E. K. Gary, L. G. Robert, *J. Org. Chem.* **2008**, *73*, 9675 – 9691.
(6) L. G. Beholz, P. Benovsky, D. L. Ward, N. S. Barta, J. R. Stille, *J. Org. Chem.* **1997**, *62*, 1033 – 1042.
(7) D. Patrick, L. I. Quen, *J. Org. Chem.* **1992**, *57*, 1952 – 1954.
(8) R. J. Cox, D. J. Ritson, T. A. Dane, J. Berg, J. Charmant, A. Kantacha, *Chem. Comm*. **2005**, *8*, 1037 – 1039.
(9) Y. Wang, W. Zhang, S. Ma, *J. Am. Chem. Soc.* **2013**, *135*, 11517 – 11520.

5. ^{1}H, ^{13}C spectra





^{31}P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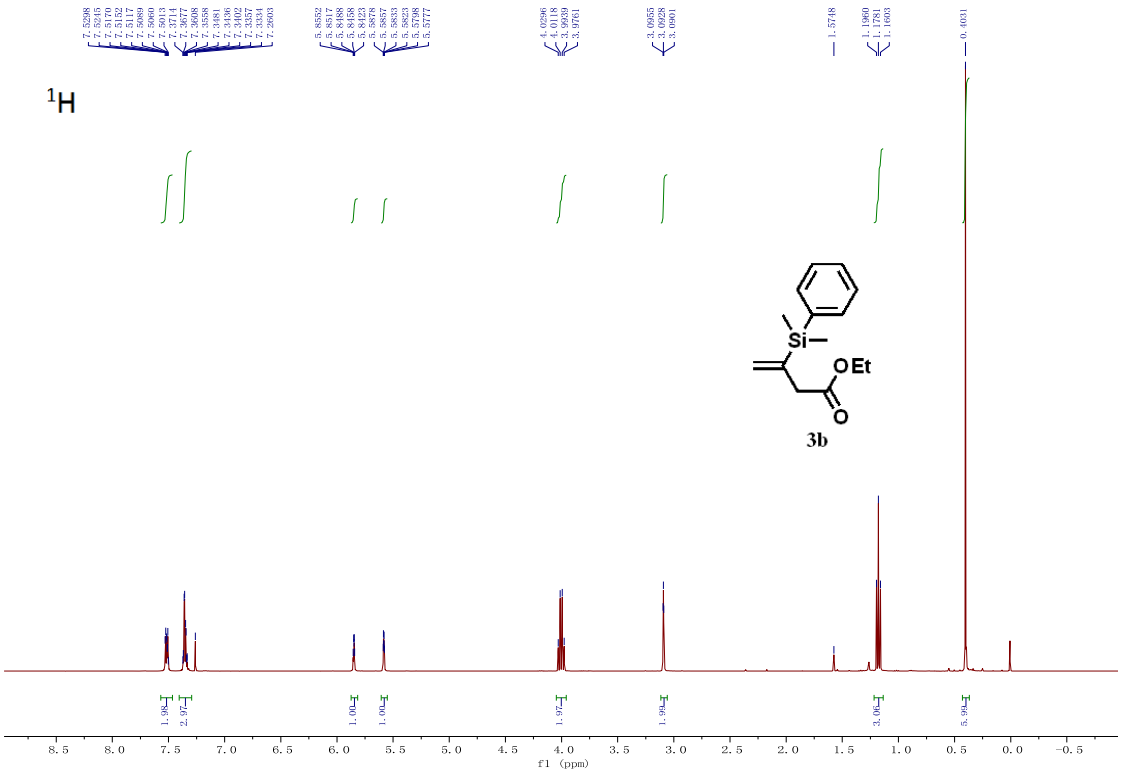
110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70
f1 (ppm)

Si
O
P
Ph
Ph

3a

^{1}H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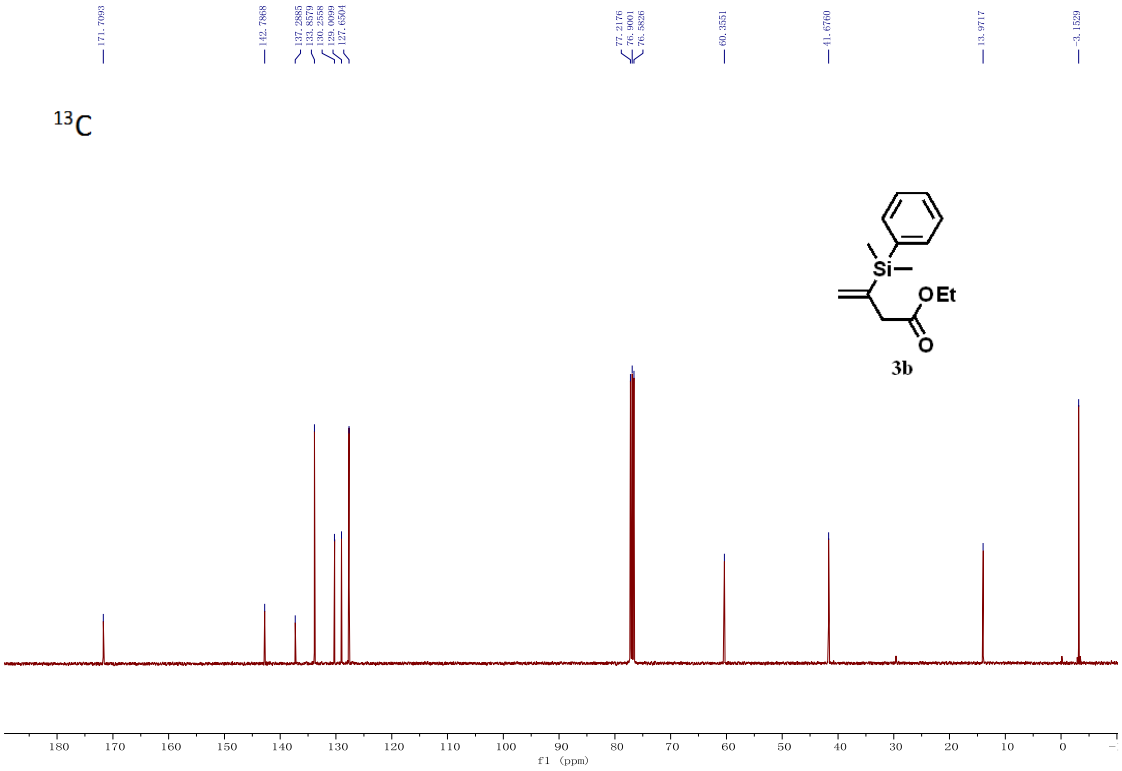
7.3608
7.3558
7.3481
7.3436
7.3402
7.3357
7.3334
7.2883
5.8532
5.8517
5.8488
5.8458
5.8423
5.8378
5.8357
5.8323
5.5798
5.5777
4.0296
4.0118
3.9939
3.9761
3.0955
3.0936
3.0901
1.5748
1.1960
1.1781
1.1603
0.4031
1.98
2.97
1.00
1.00
1.97
1.99
3.00
5.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

Si
OEt
O

3b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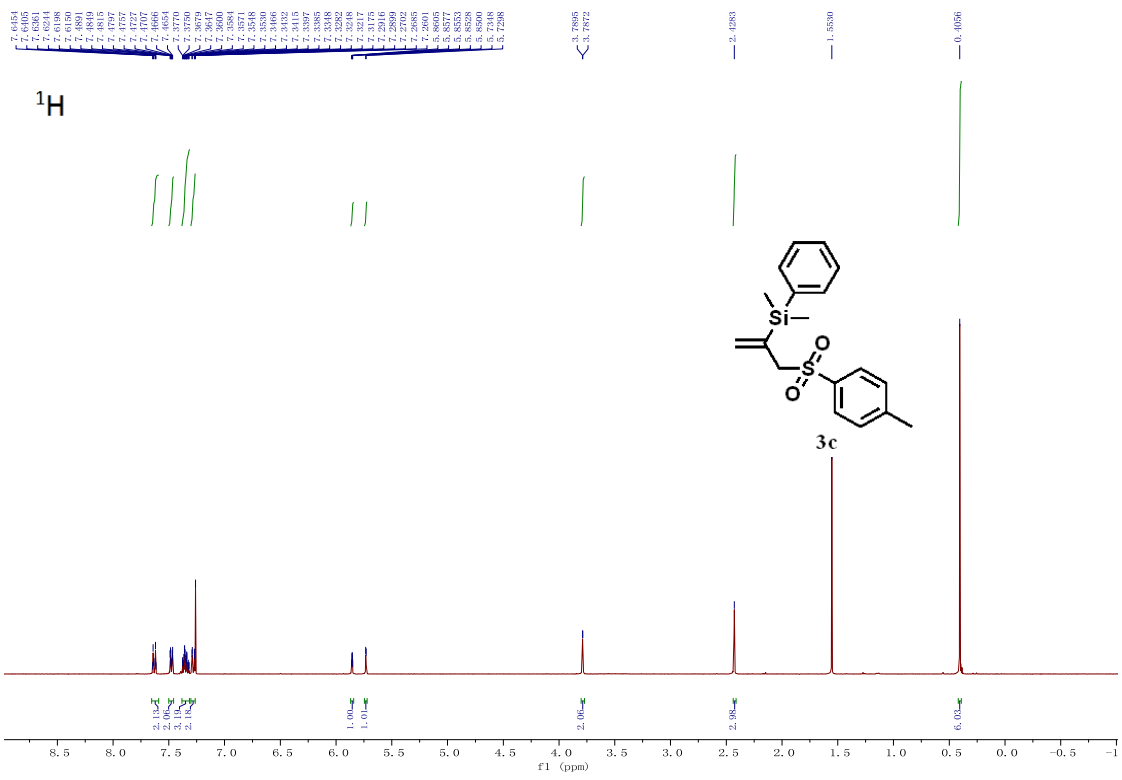
60.3551
41.6760
13.9717
-3.1529
13C
Si
OEt
O
O
3b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.4891
7.4844
7.4815
7.4797
7.4757
7.4737
7.4717
7.4666
7.4654
7.3779
7.3759
7.3679
7.3647
7.3600
7.3594
7.3571
7.3548
7.3530
7.3496
7.3472
7.3415
7.3397
7.3385
7.3348
7.3282
7.3248
7.3217
7.3175
7.2916
7.2916
7.2899
7.2702
7.2685
7.2669
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5.8577
5.8553
5.8538
5.8524
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5.7348
5.7298
3.7895
3.7872
2.4283
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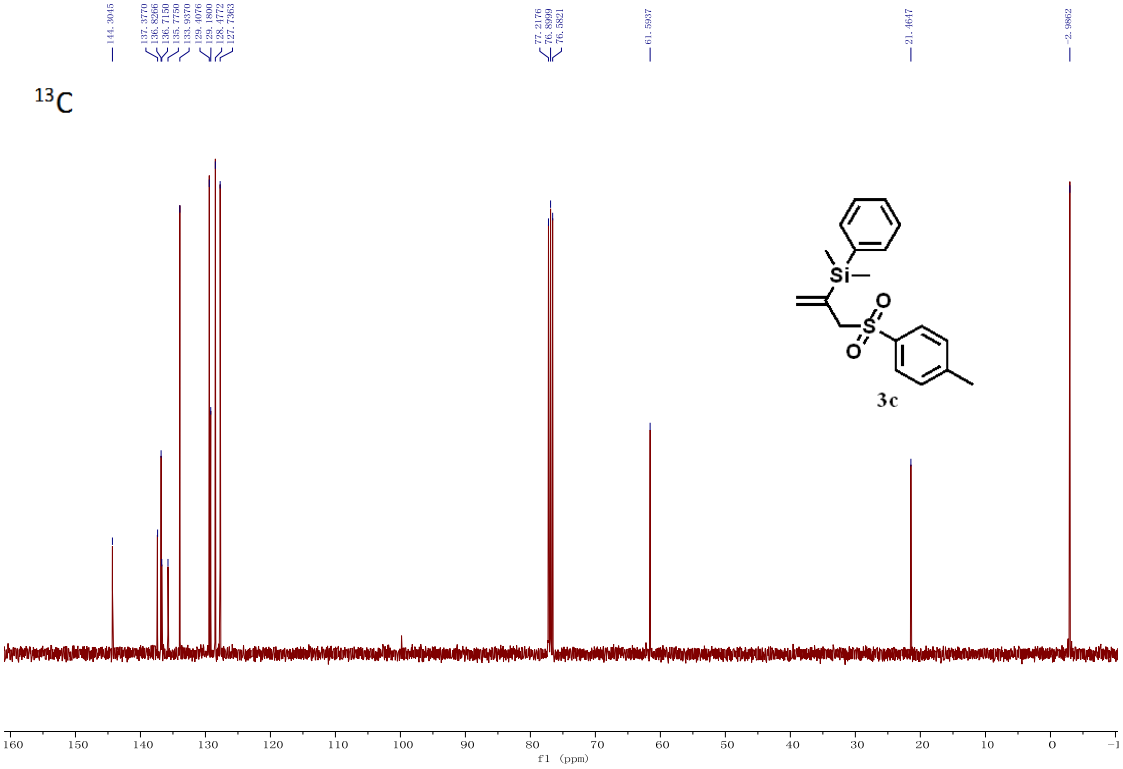
0.4056
1H
Si
S
O
O
3c
2.13
2.00
3.13
2.10
1.00
1.01
2.06
2.08
6.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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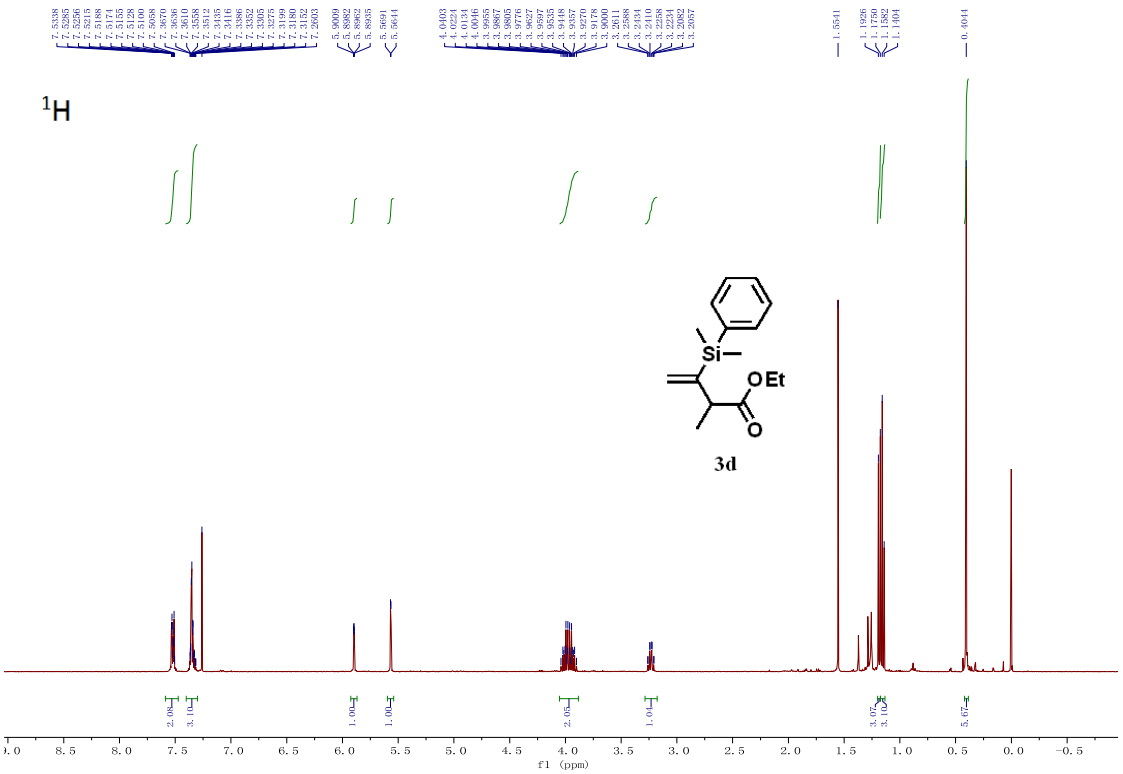
Si
O
S
O
O
3c
f1 (ppm)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7.3636
7.3610
7.3558
7.3512
7.3455
7.3414
7.3386
7.3352
7.3305
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7.3180
7.3152
7.2903
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5.8982
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5.8935
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4.0254
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3.9867
3.9805
3.9776
3.9627
3.9597
3.9555
3.9448
3.9357
3.9270
3.9178
3.9040
3.2611
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3.2410
3.2258
3.2234
3.2082
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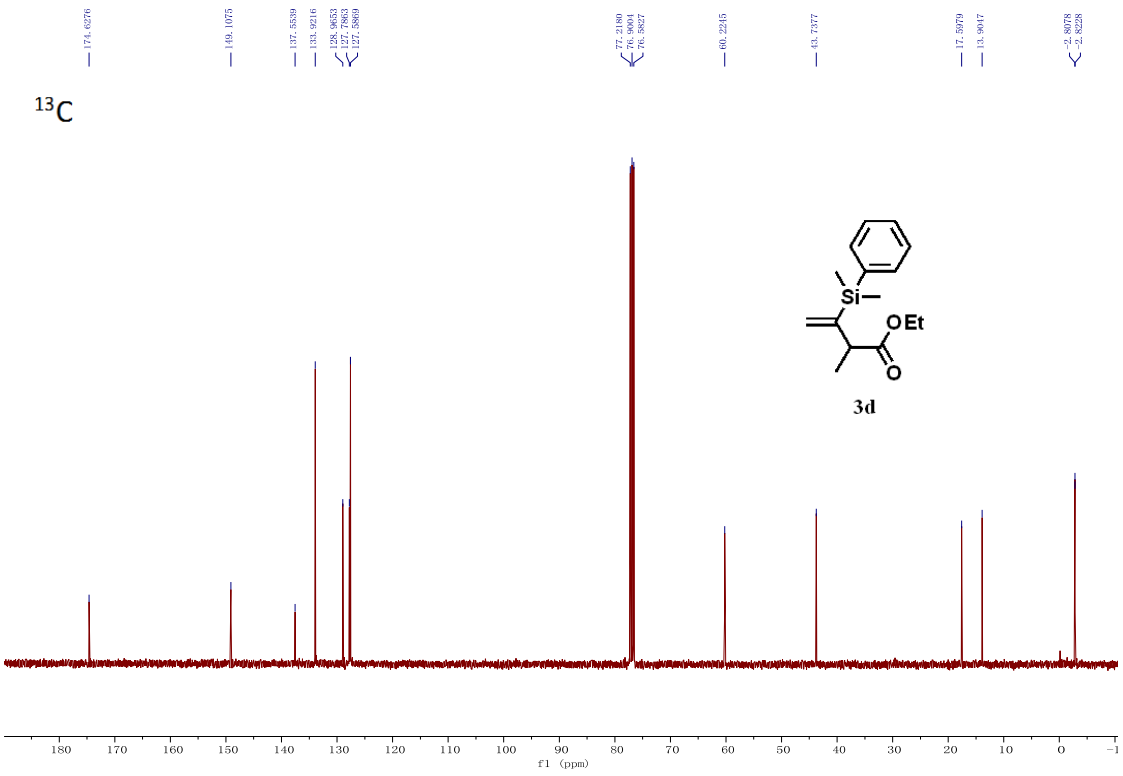
Si
OEt
O
O
3d
f1 (ppm)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OEt
O
Si
3d
180
170
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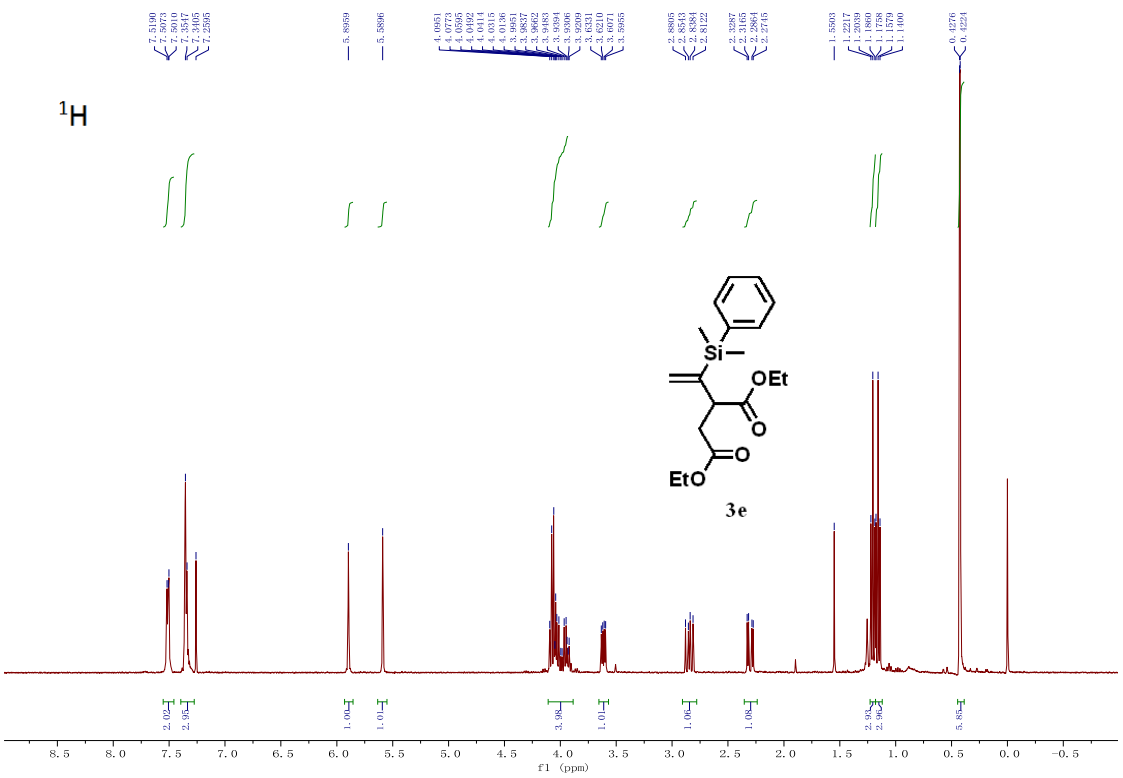
f1 (ppm)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3.9483
3.9394
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EtO
O
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3e
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2.05
1.04
1.01
3.98
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1.06
1.08
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8.5
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7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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2.0
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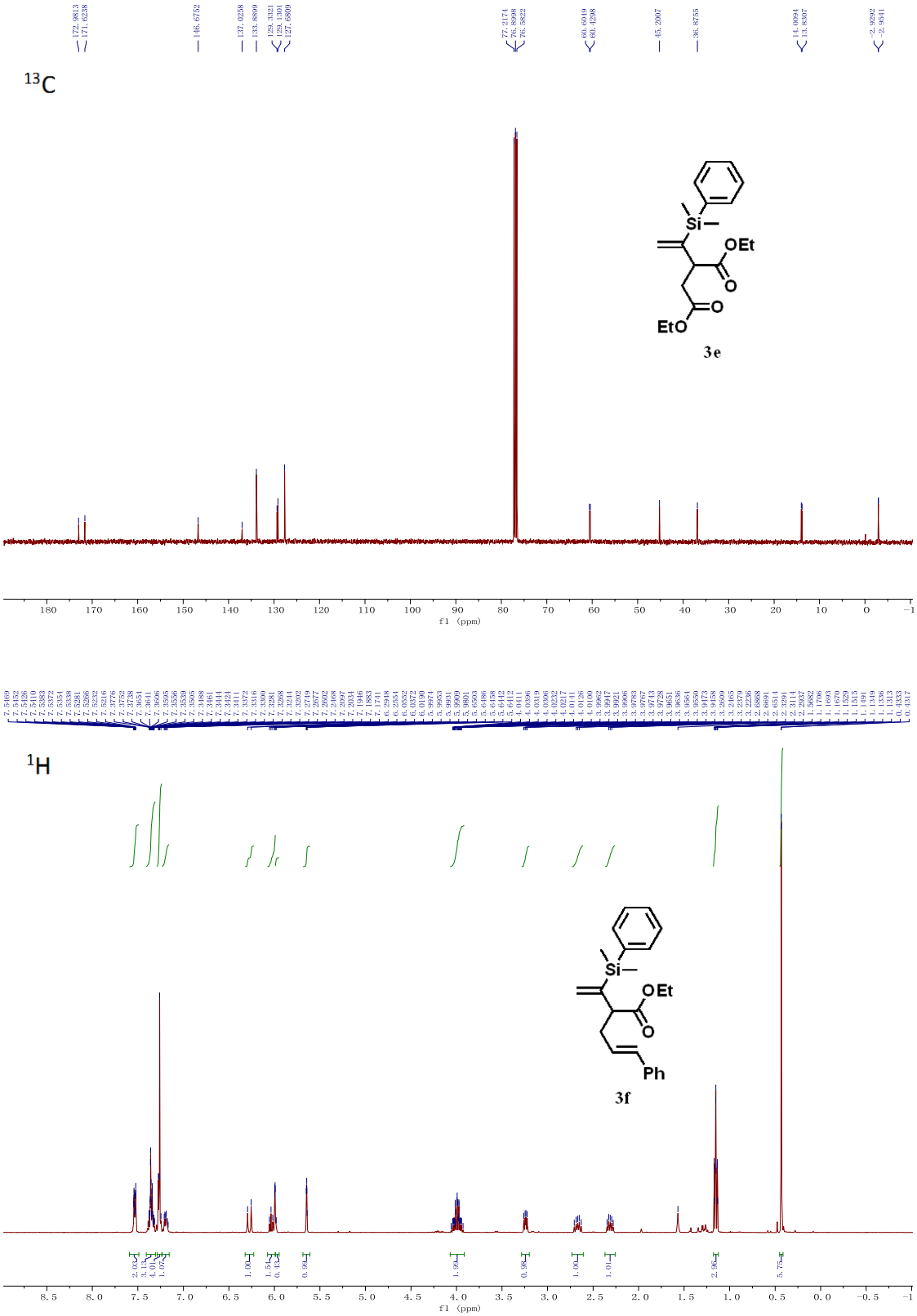
−0.5
f1 (ppm)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O
EtO
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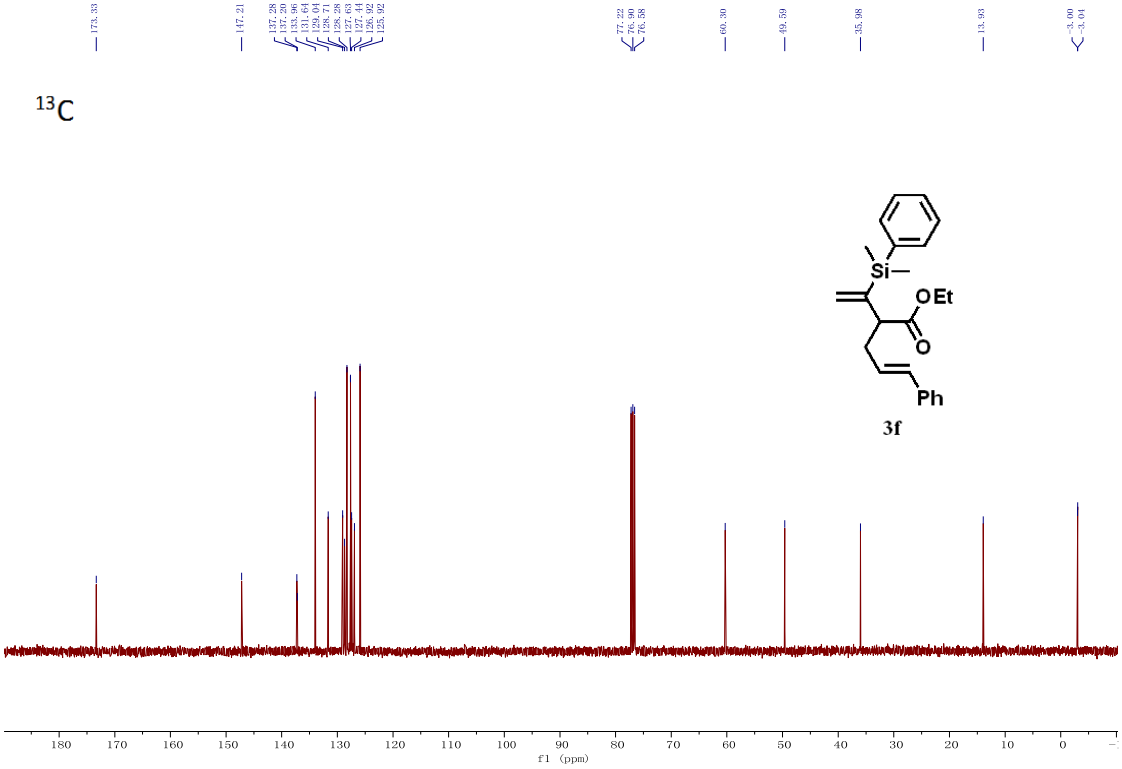
Ph
3f
f1 (ppm)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76.58
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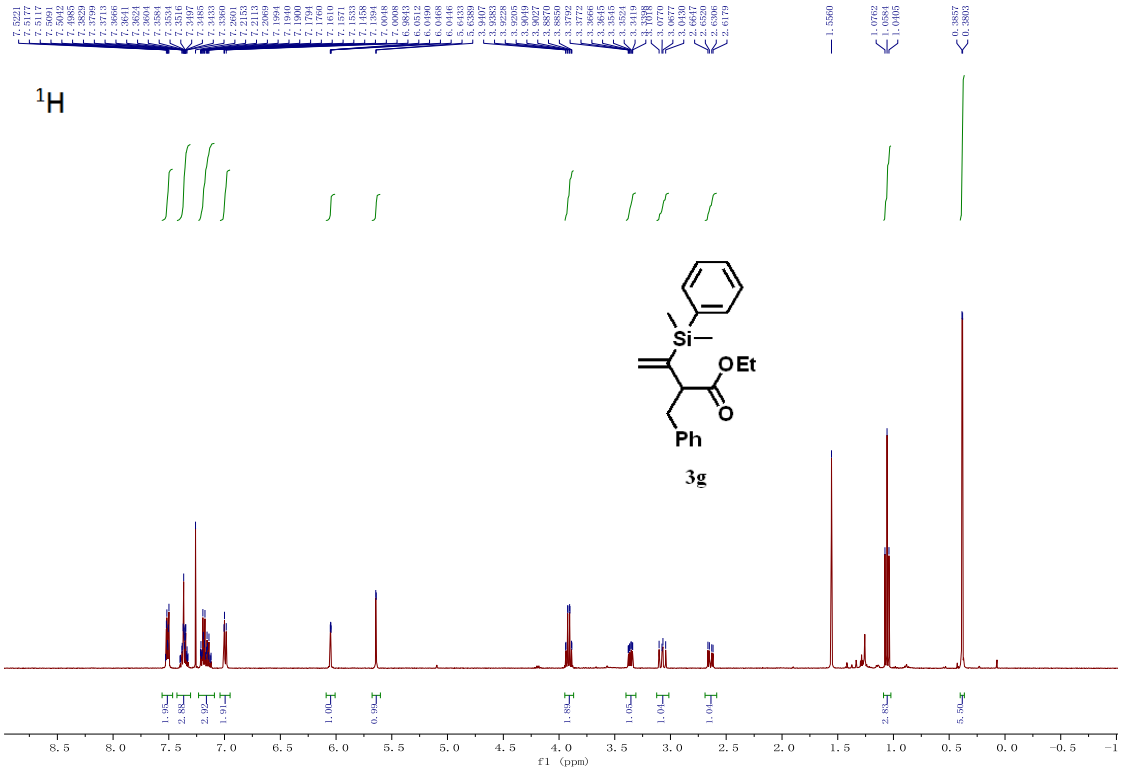
Si
OEt
O
Ph
3f
f1 (ppm)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Si
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O
Ph
3g
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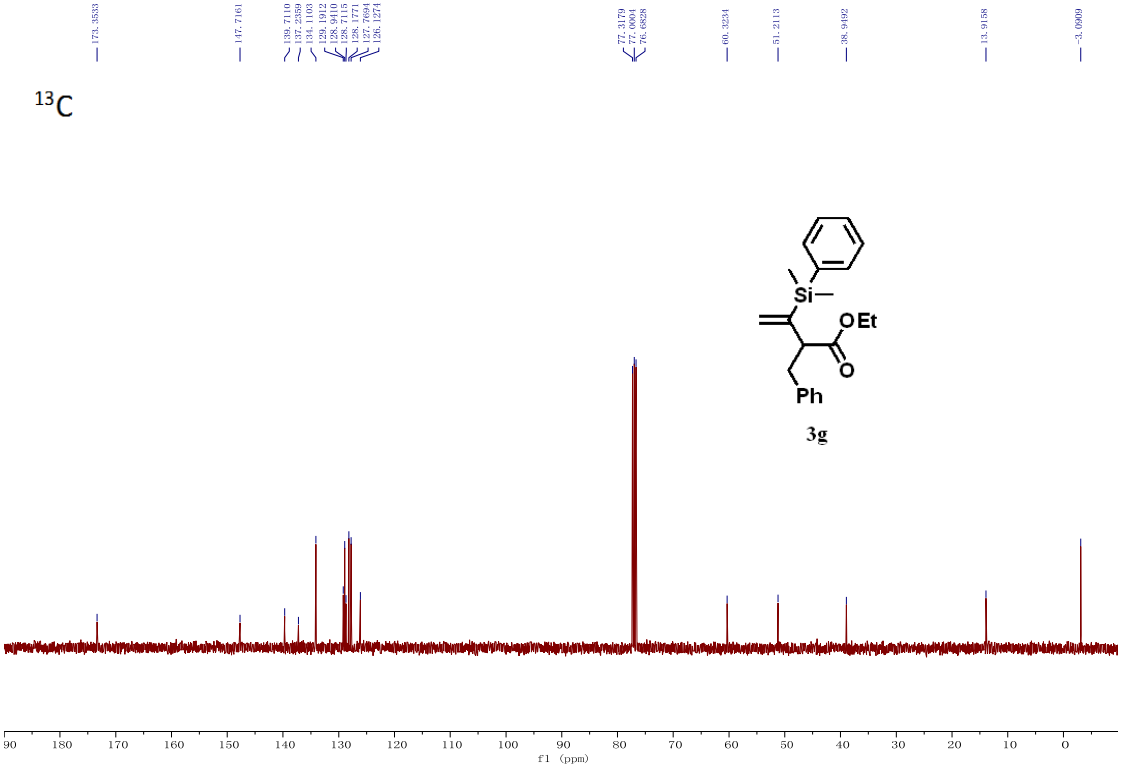
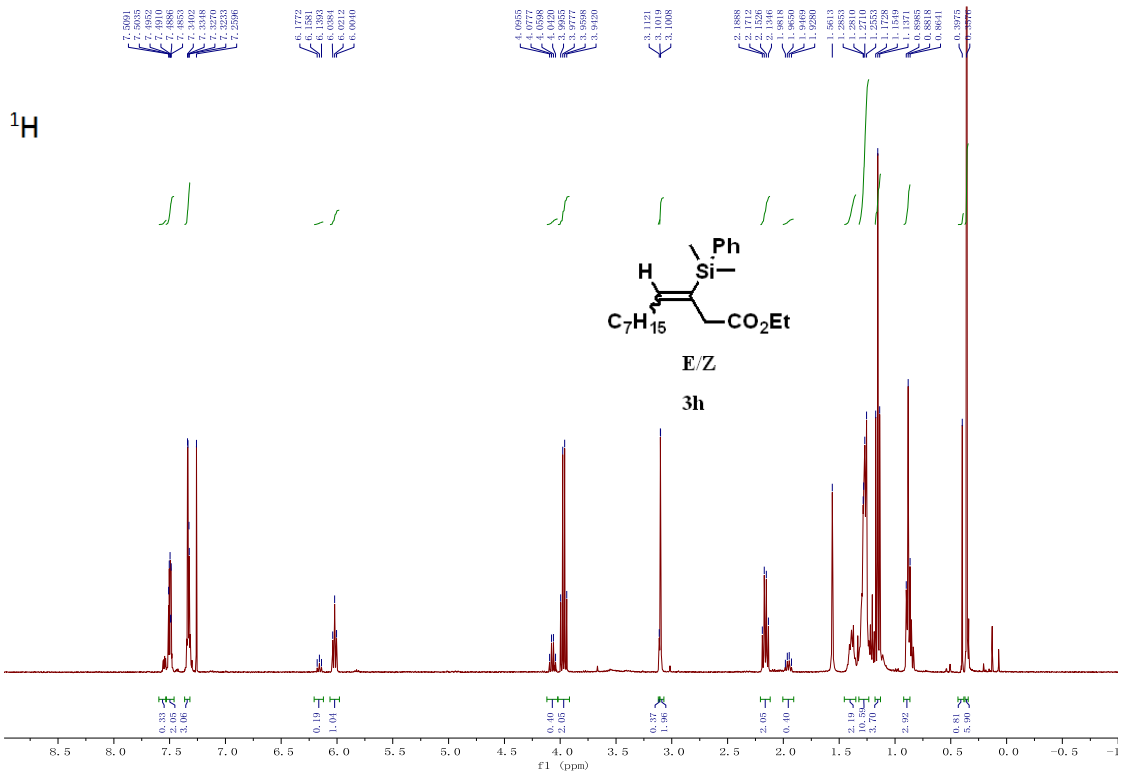
2.88
2.92
1.91
1.00
0.99
1.88
1.05
1.04
1.04
2.83
5.50
f1 (ppm)

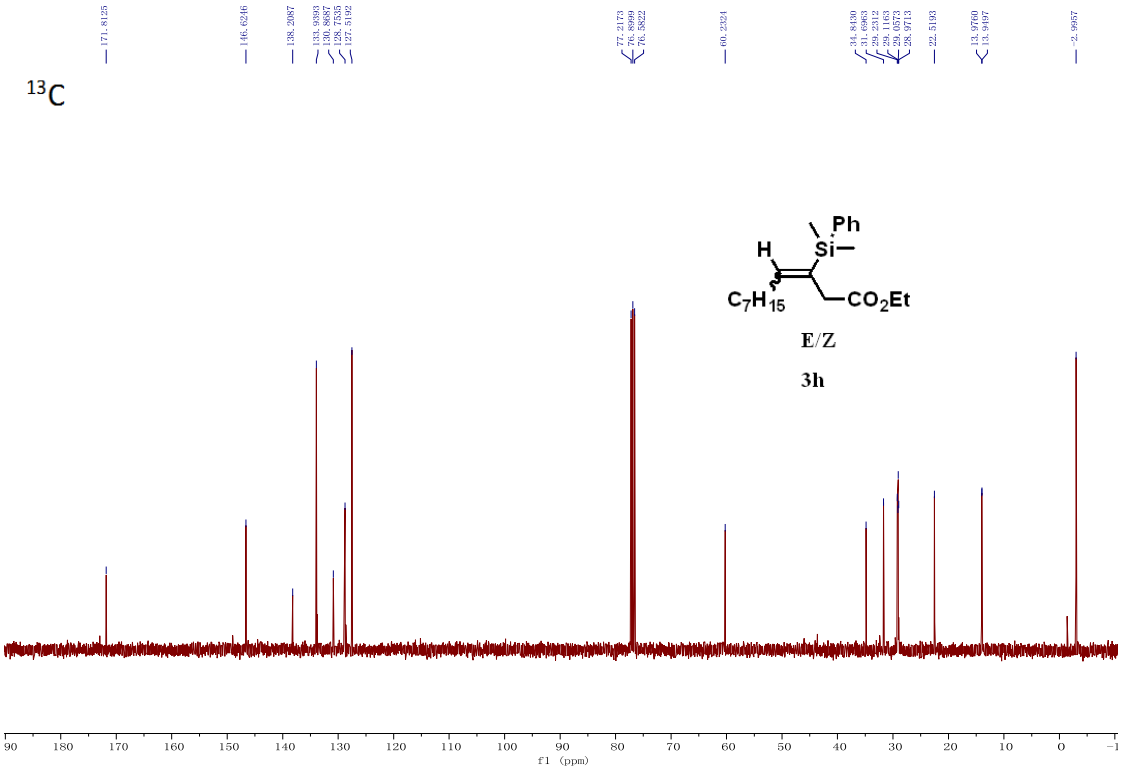
^{13}C



^{1}H



^{13}C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29.1165
29.0573
28.9713
22.5193
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Si
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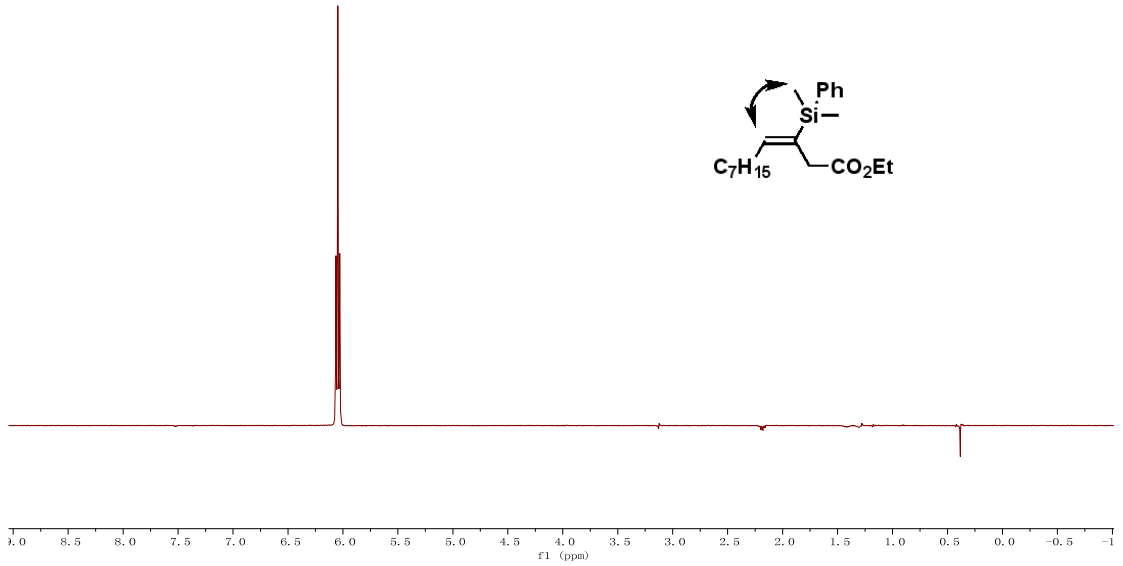
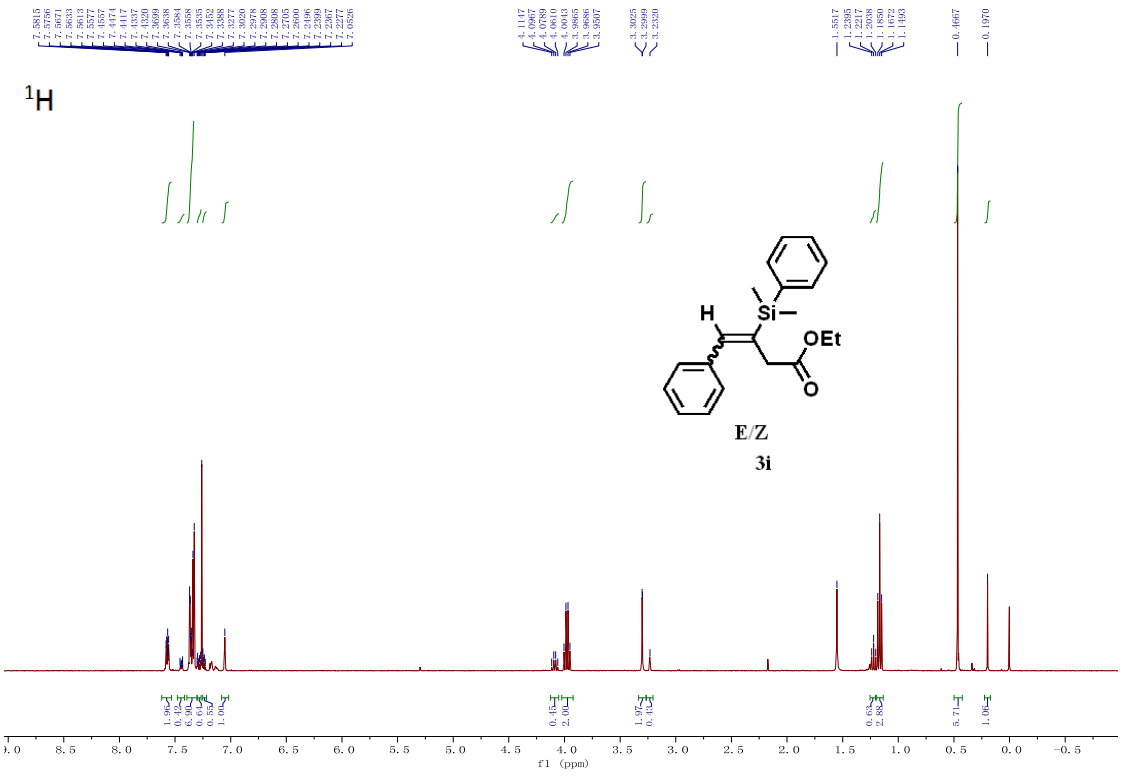
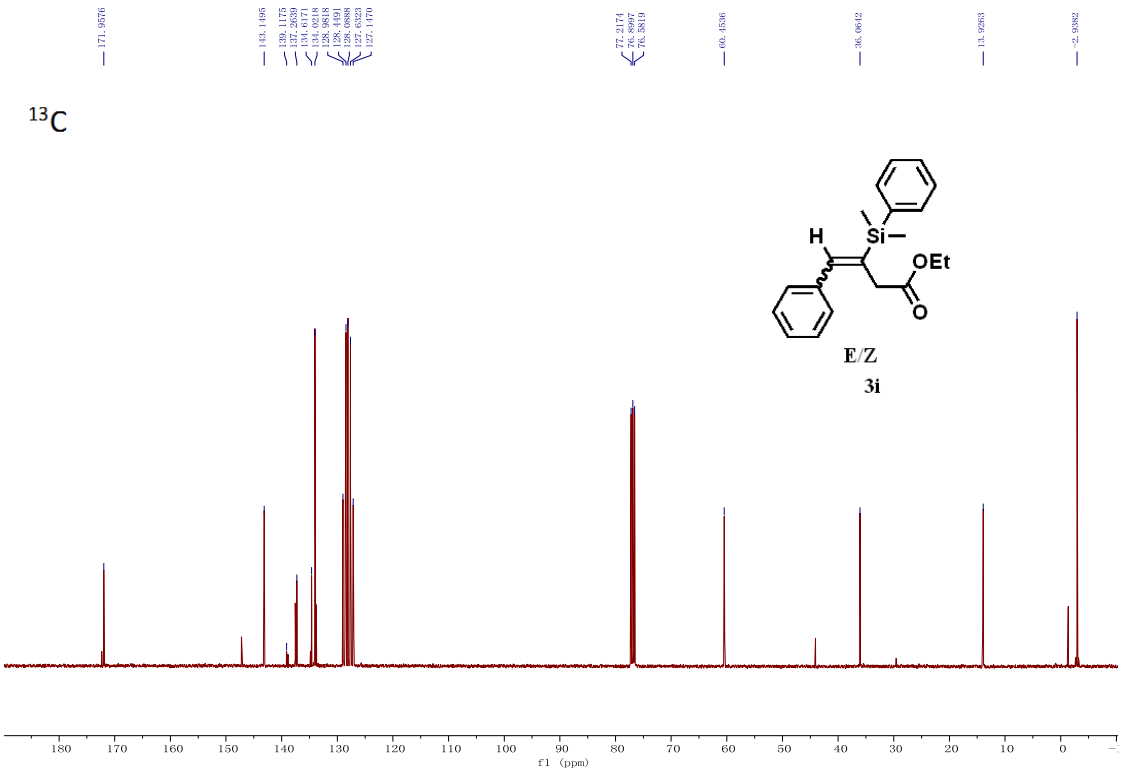
CO2Et
E/Z
3h
f1 (ppm)

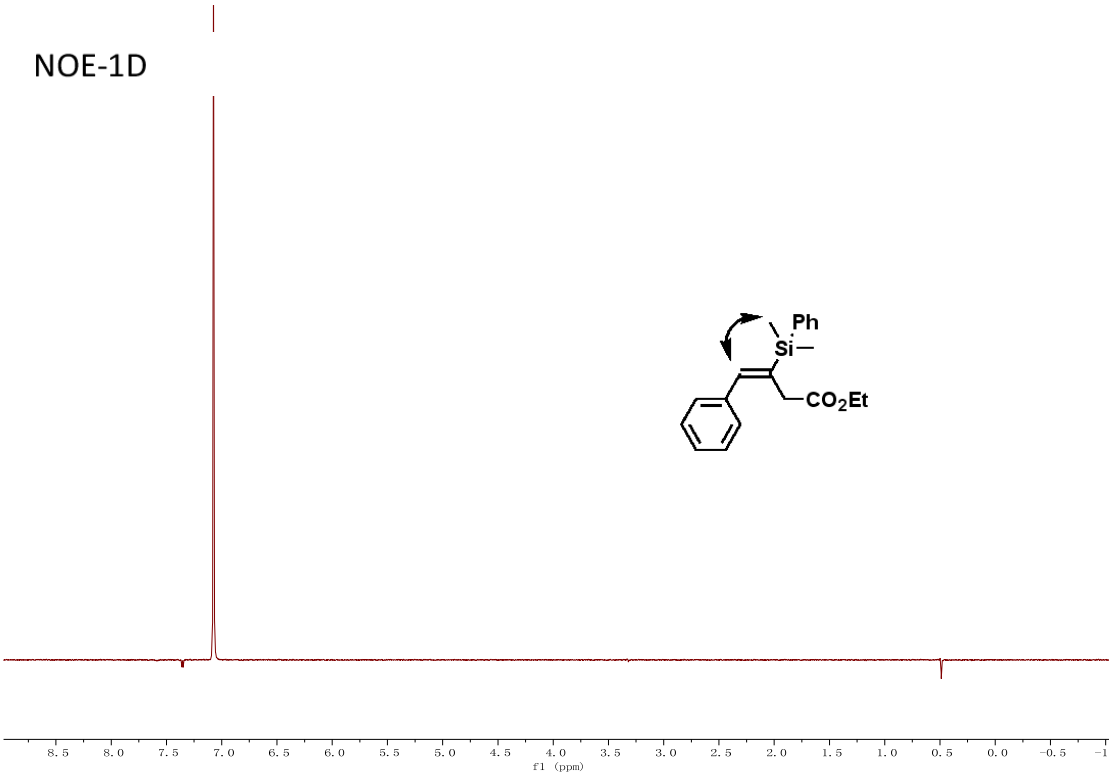
NOE-1D


Ph
Si
C7H15
CO2Et
f1 (ppm)

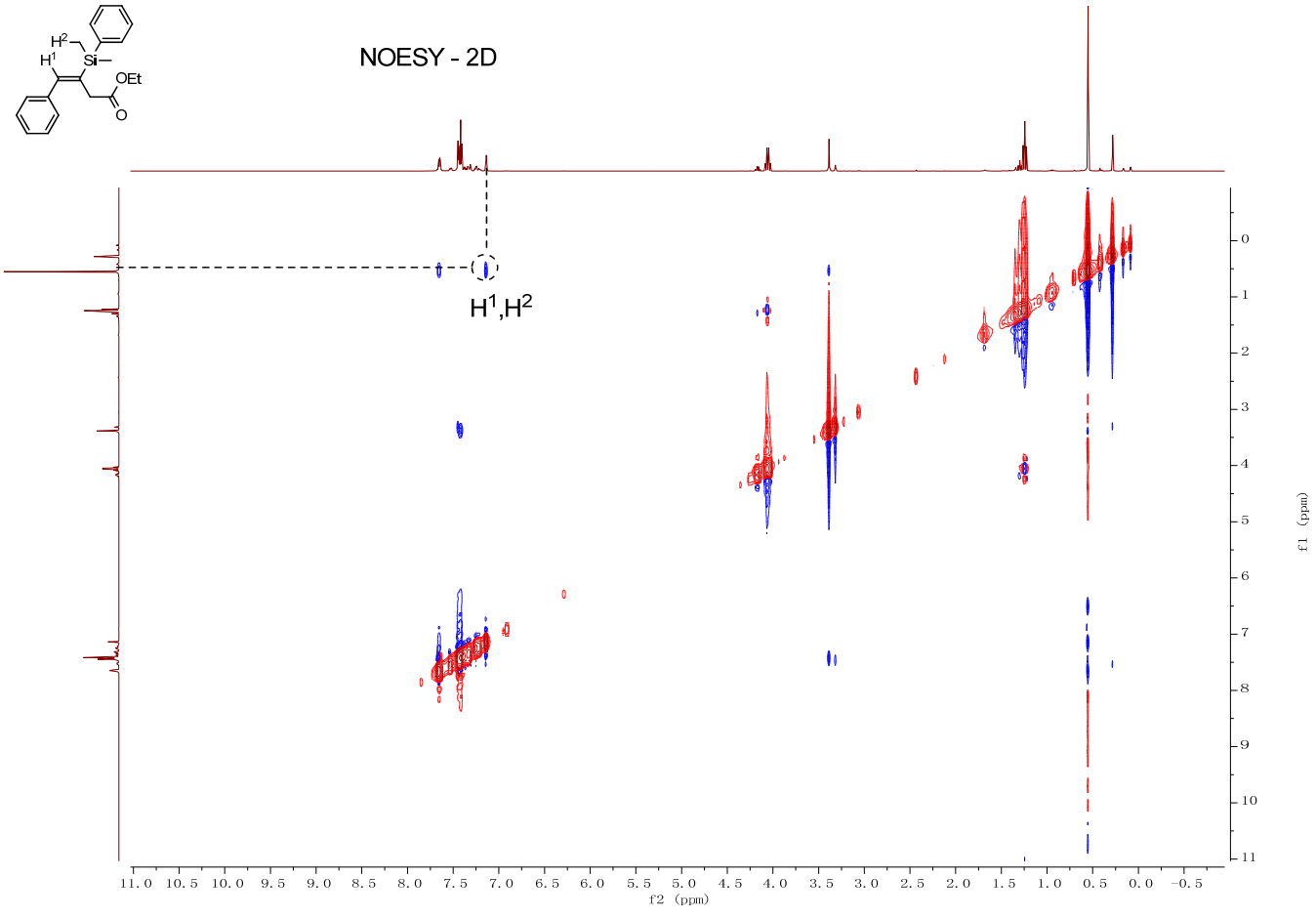

1H
H
Si
OEt
O
E/Z
3i
f1 (ppm)

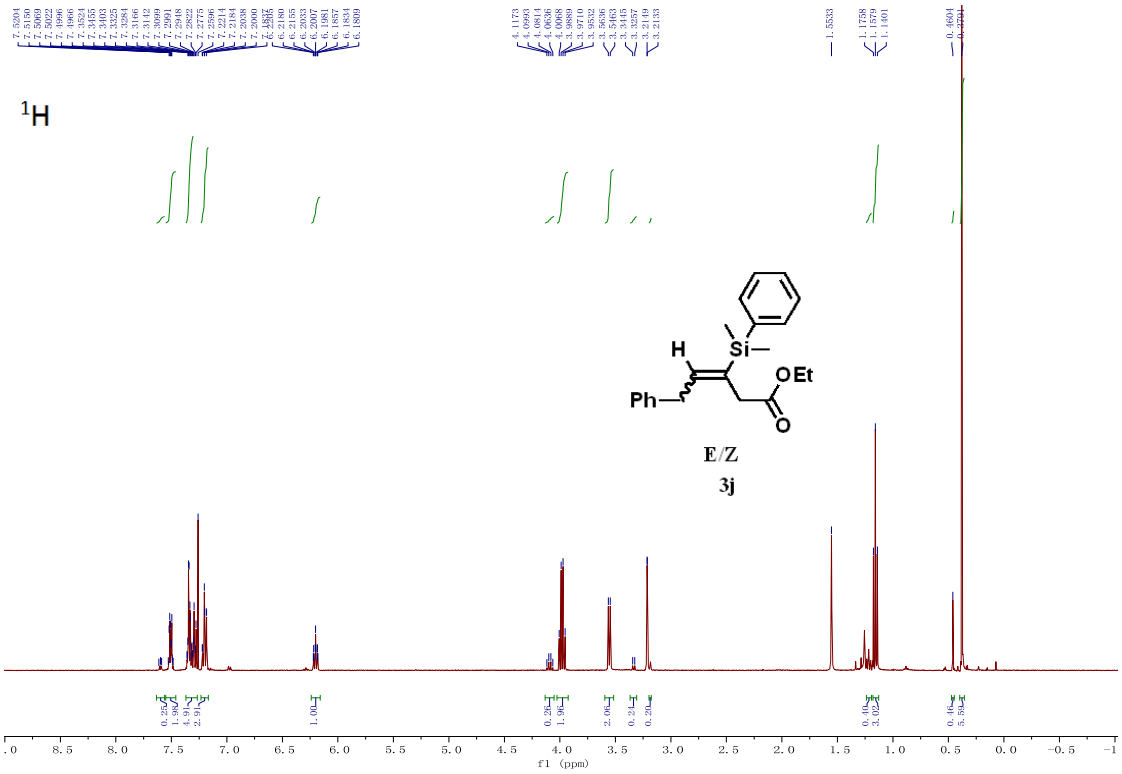

13C
H
Si
OEt
O
E/Z
3i
f1 (ppm)

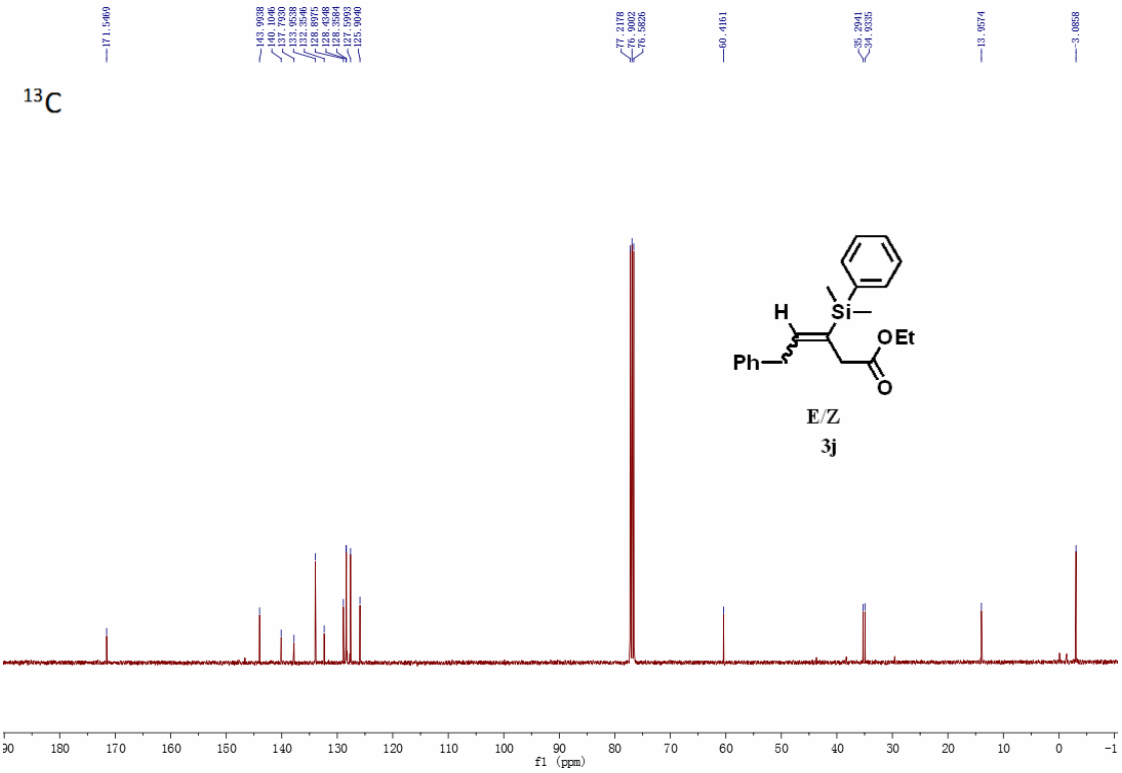
NOE-1D

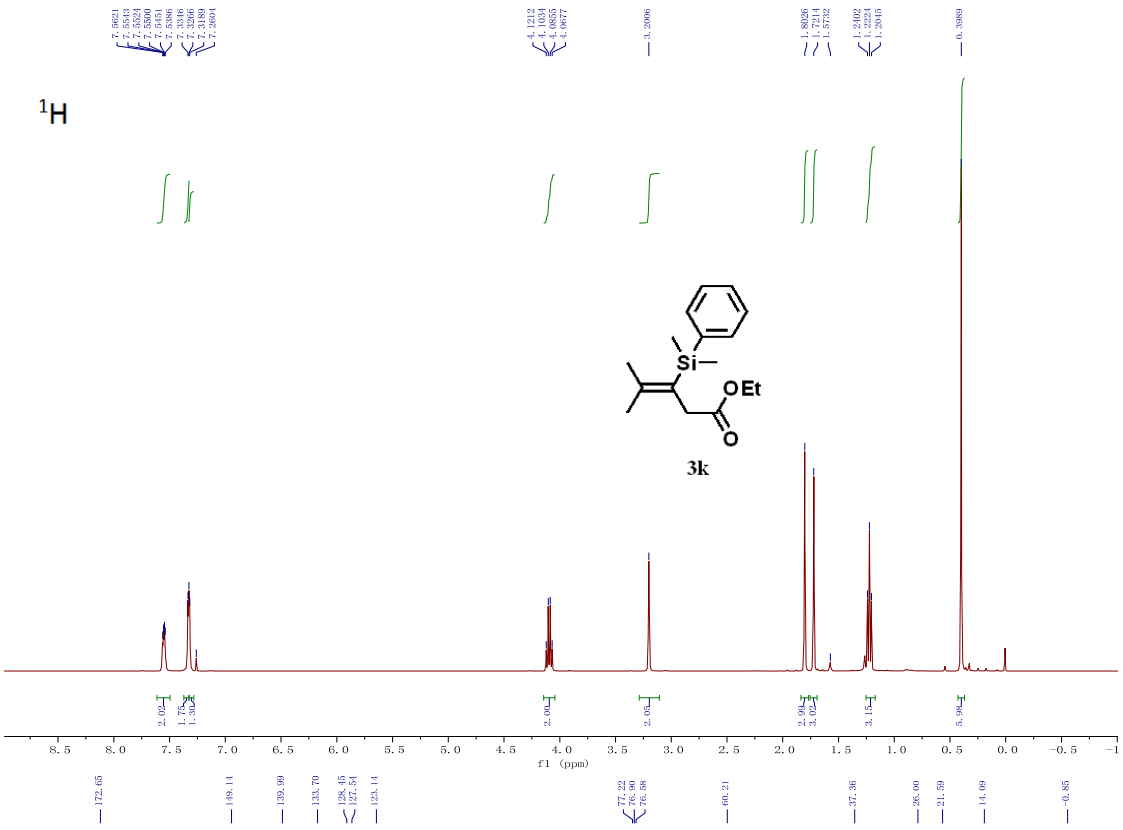


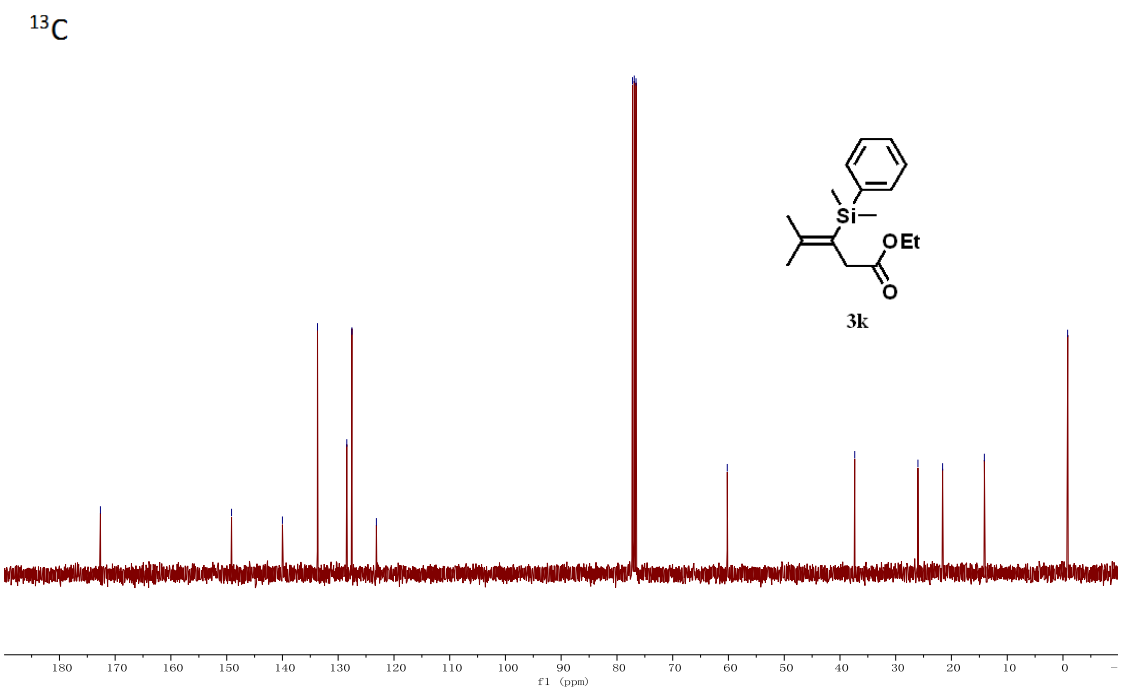
NOESY - 2D



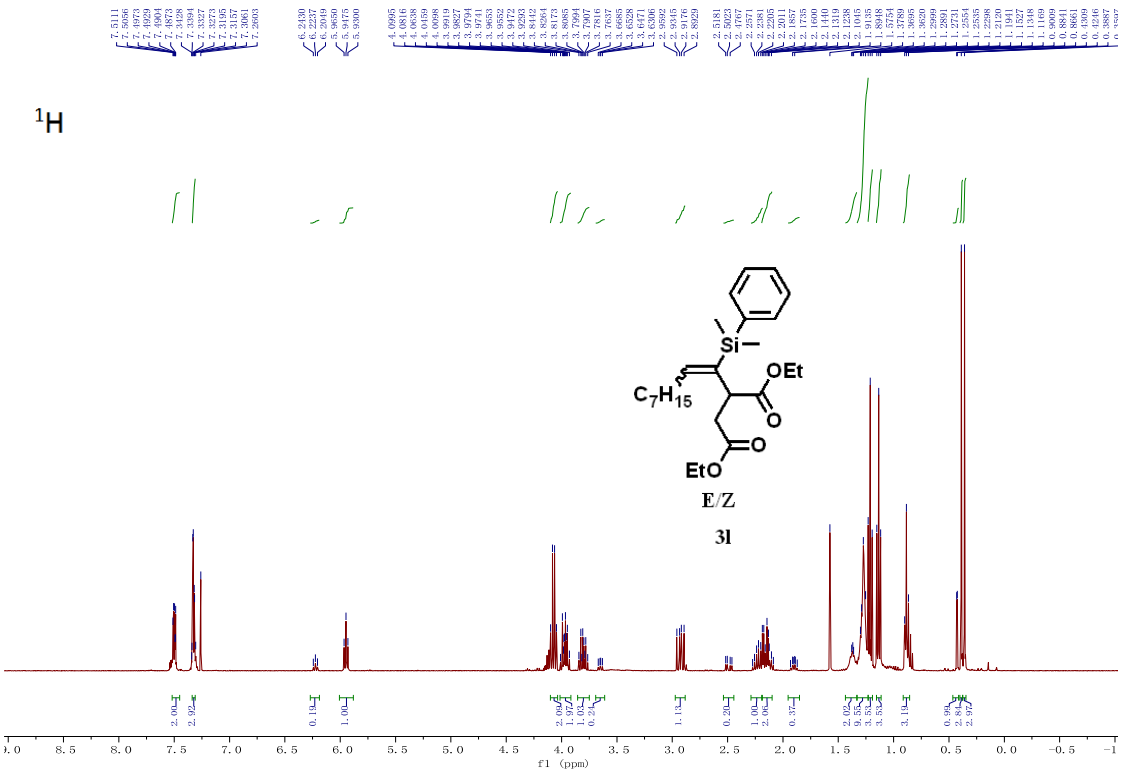

1H
H
Si
OEt
Ph
O
E/Z
3j
f1 (ppm)


13C
H
Si
OEt
Ph
O
E/Z
3j
f1 (ppm)

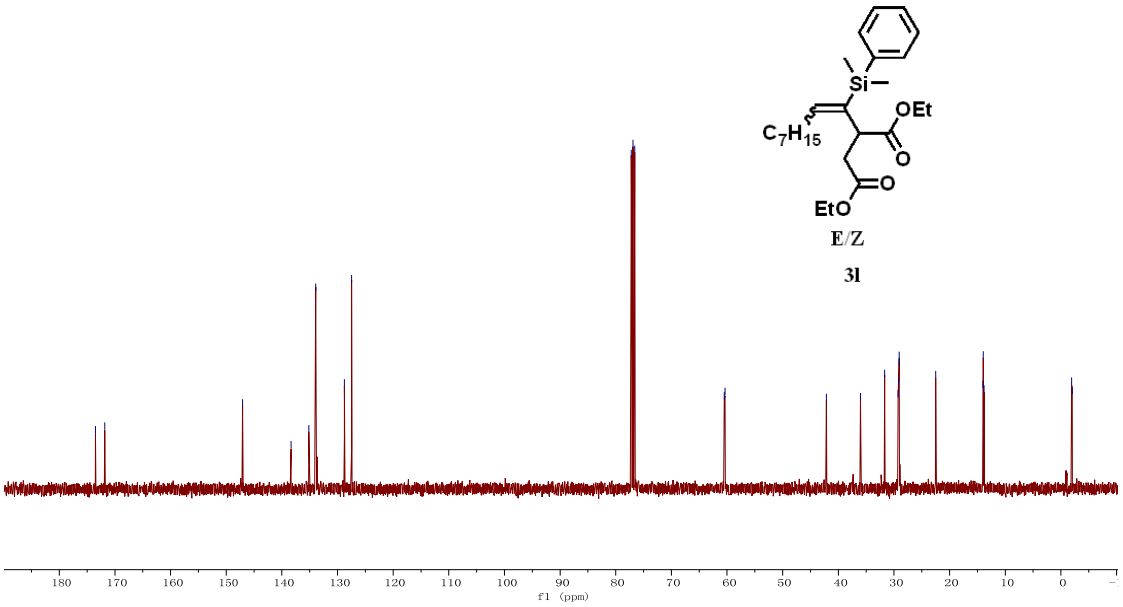

1H
OEt
O
3k


13C
OEt
O
3k

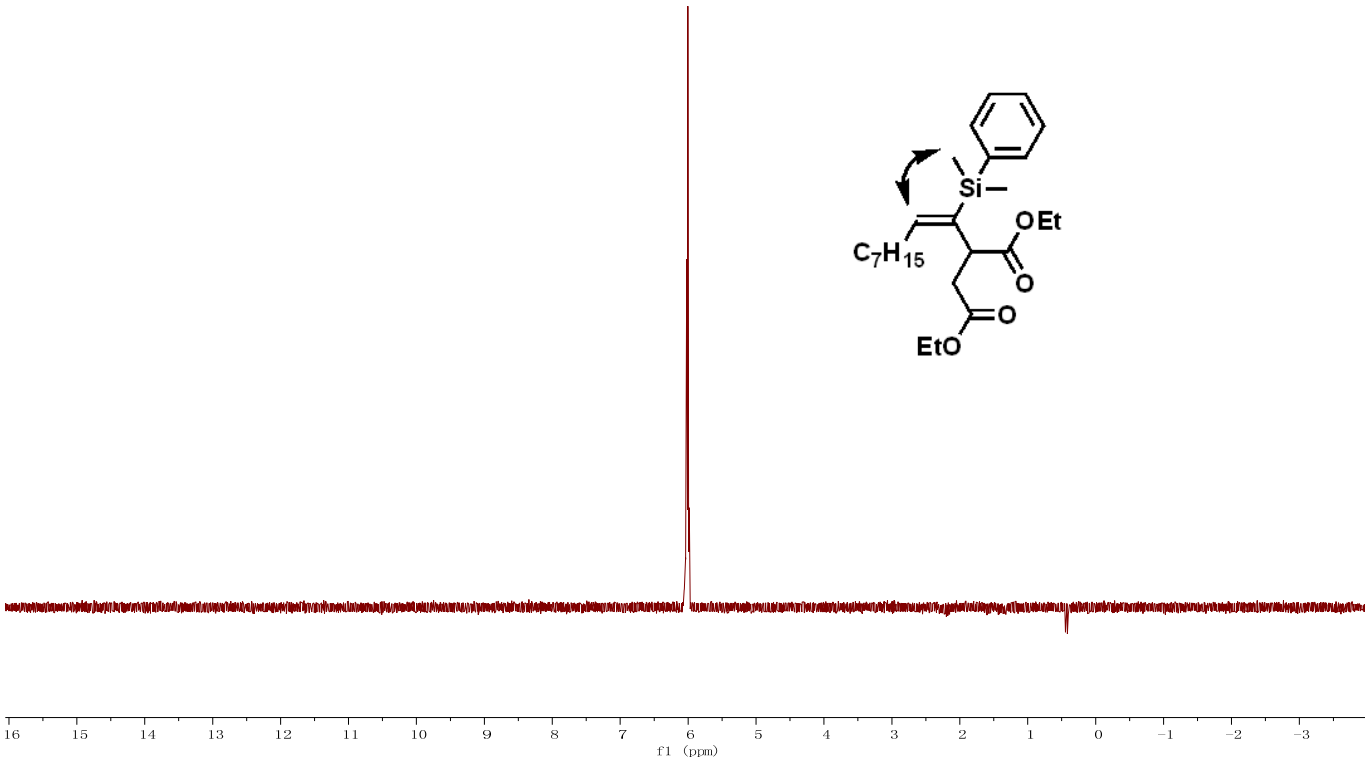
^{1}H



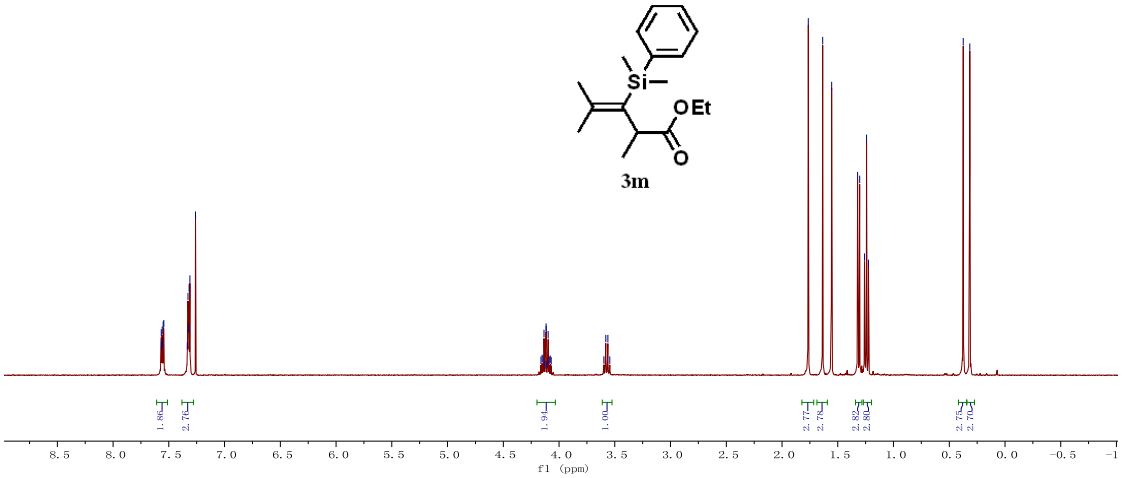
^{13}C

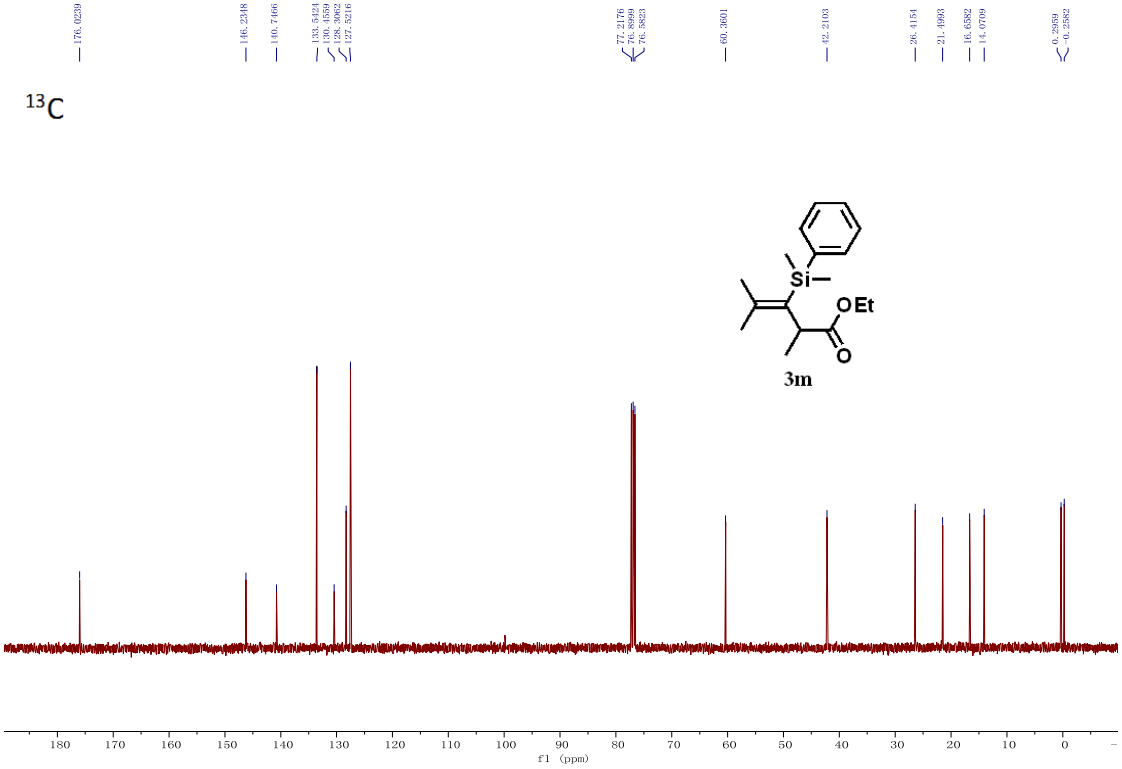


NOE-1D



^1H




176.0259
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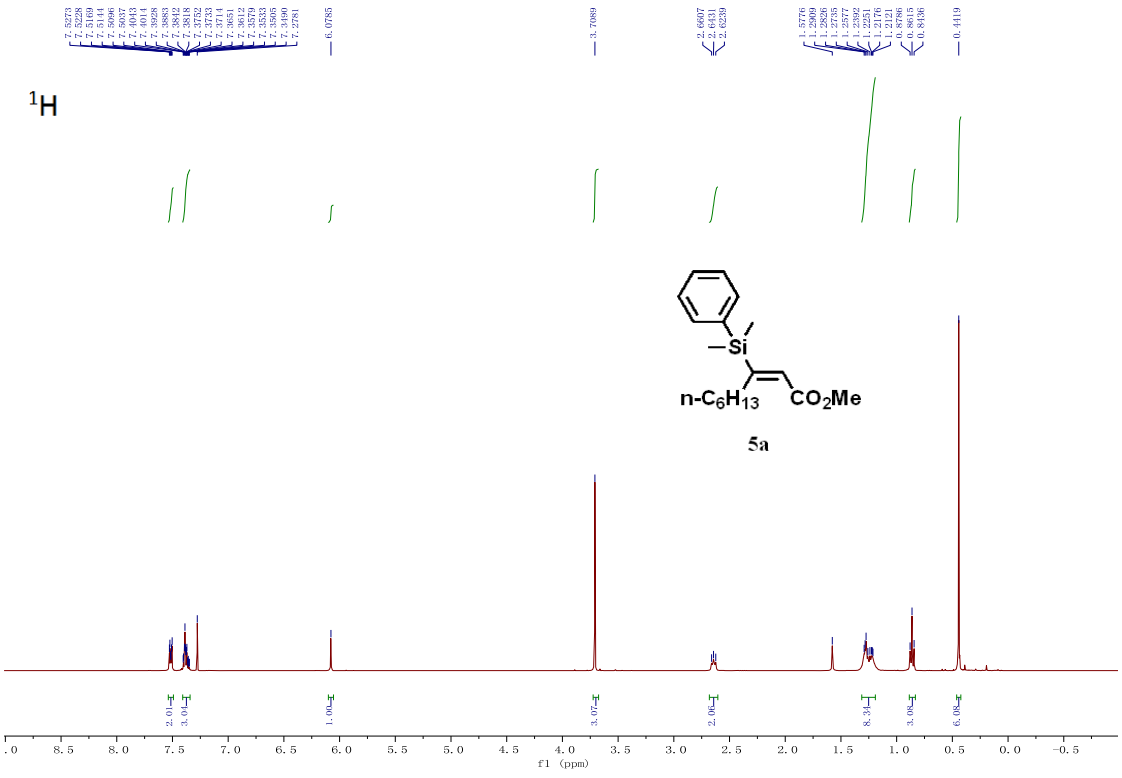
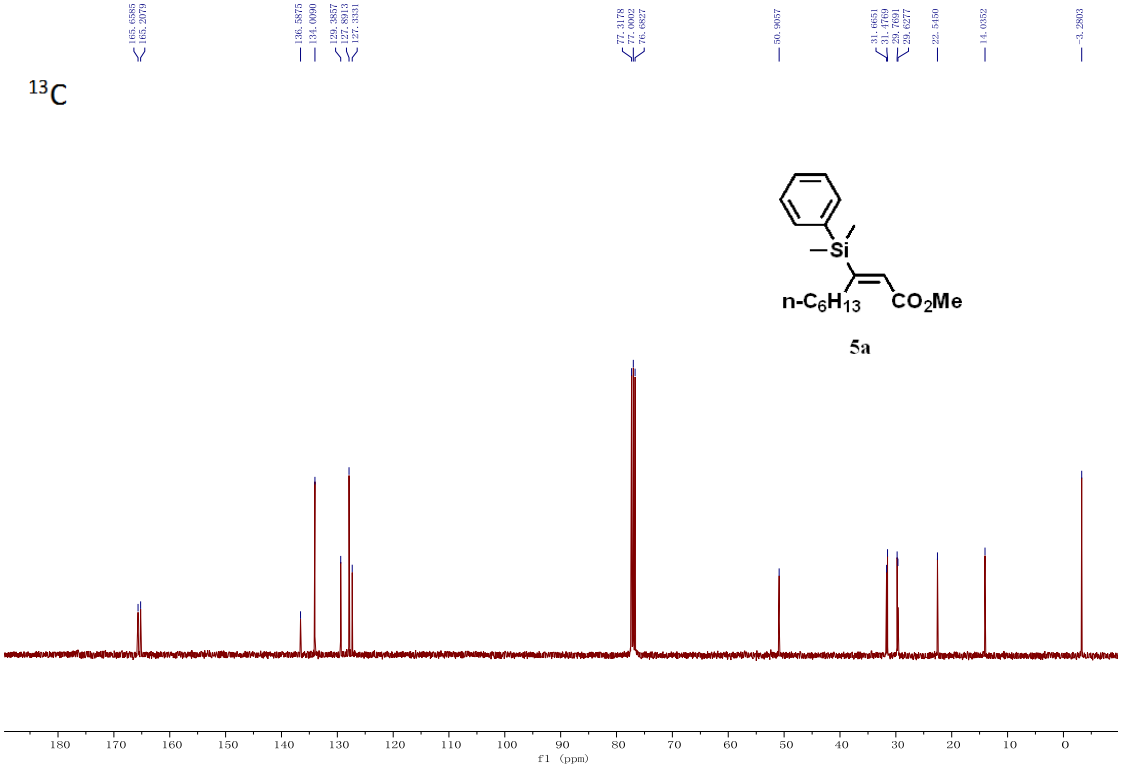
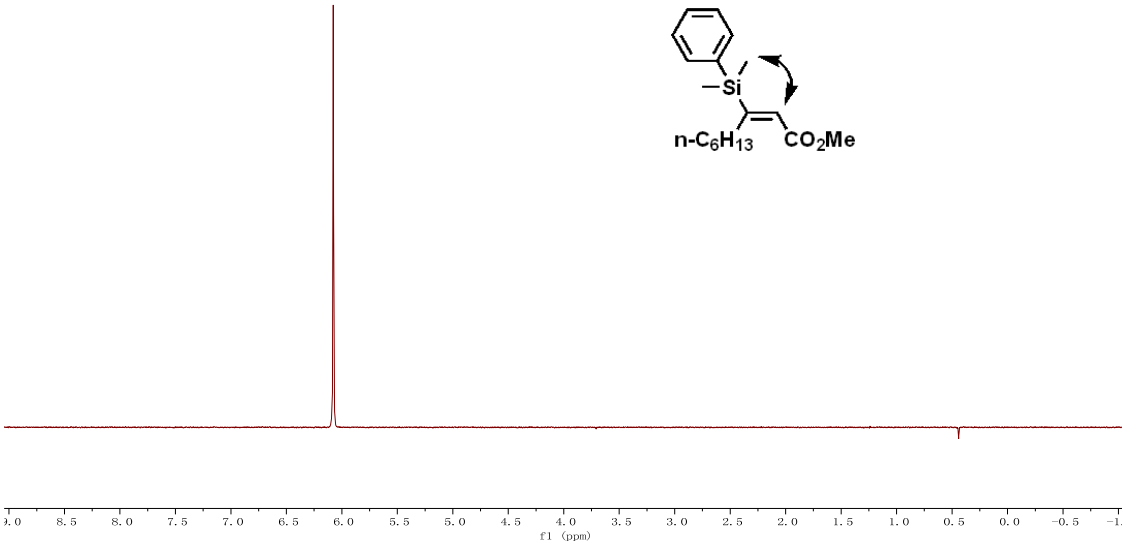
140.7466
133.5424
130.0558
128.3062
127.5216
77.2176
76.8999
76.5823
60.3601
42.2103
26.4154
21.4983
16.6582
14.0709
0.2959
0.2582
13C
Si
OEt
O
3m
f1 (ppm)

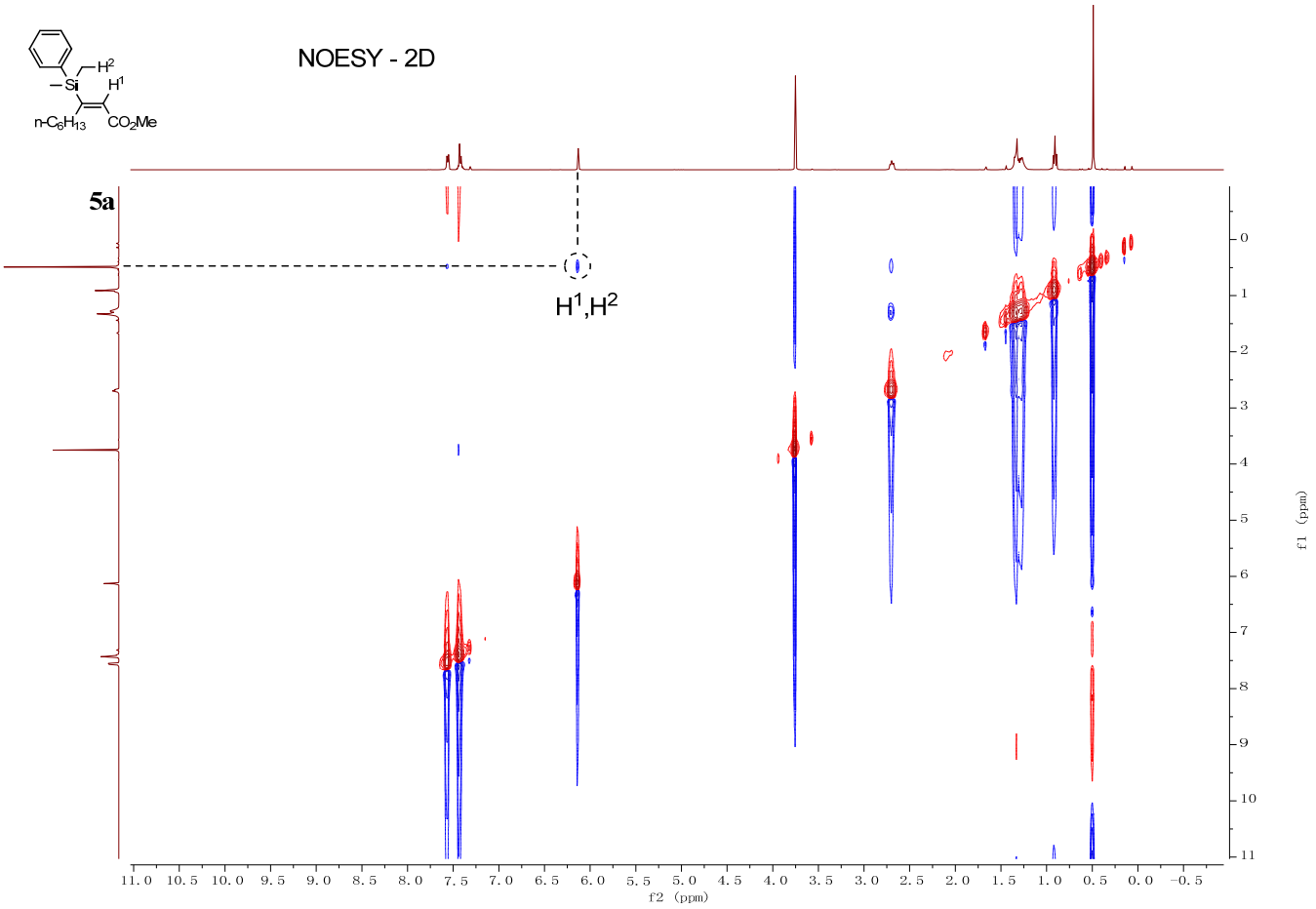

7.5273
7.5228
7.5149
7.5114
7.5096
7.5037
7.4013
7.4014
7.3928
7.3883
7.3842
7.3793
7.3752
7.3733
7.3714
7.3651
7.3632
7.3579
7.3533
7.3505
7.3490
7.2781
6.0785
3.7089
2.6607
2.6431
2.6259
1.5776
1.2909
1.2826
1.2735
1.2577
1.2392
1.2251
1.2176
1.2121
0.8796
0.8615
0.8436
0.4419
1H
Si
n-C6H13
CO2Me
5a
2.01
3.04
1.00
3.07
2.06
8.34
3.08
6.08
f1 (ppm)

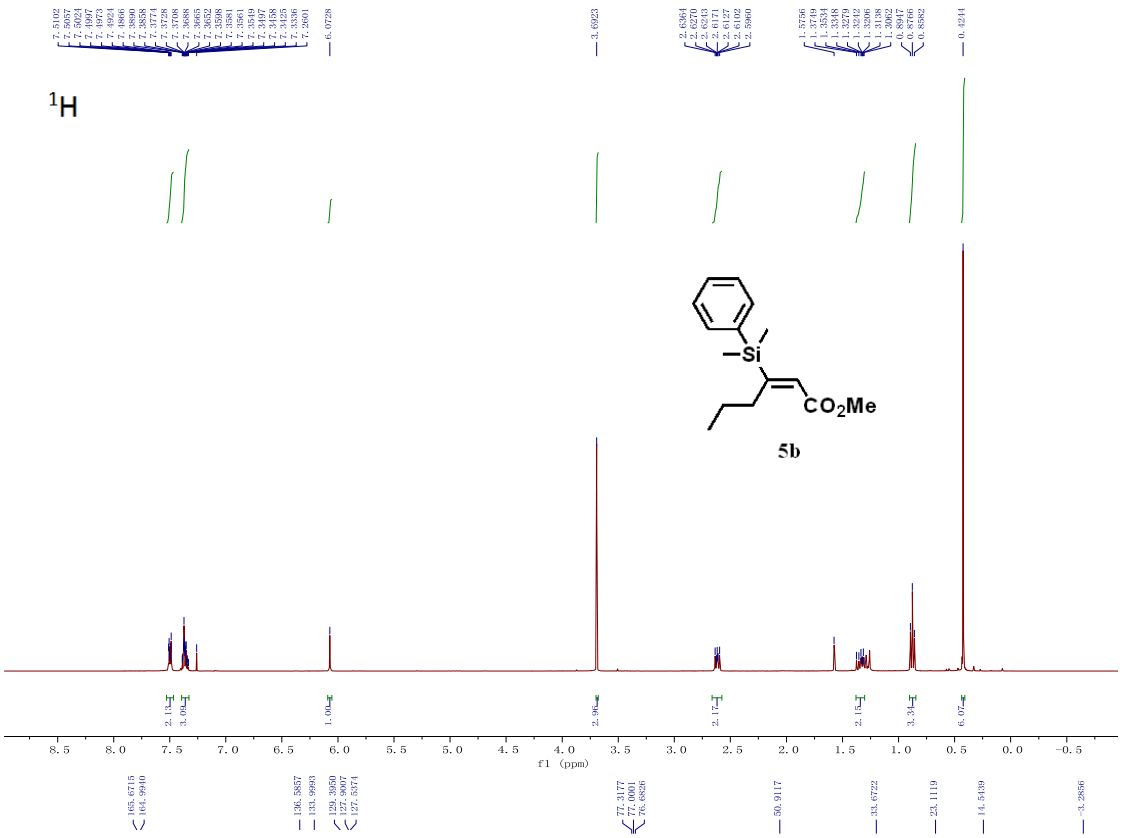
^{13}C

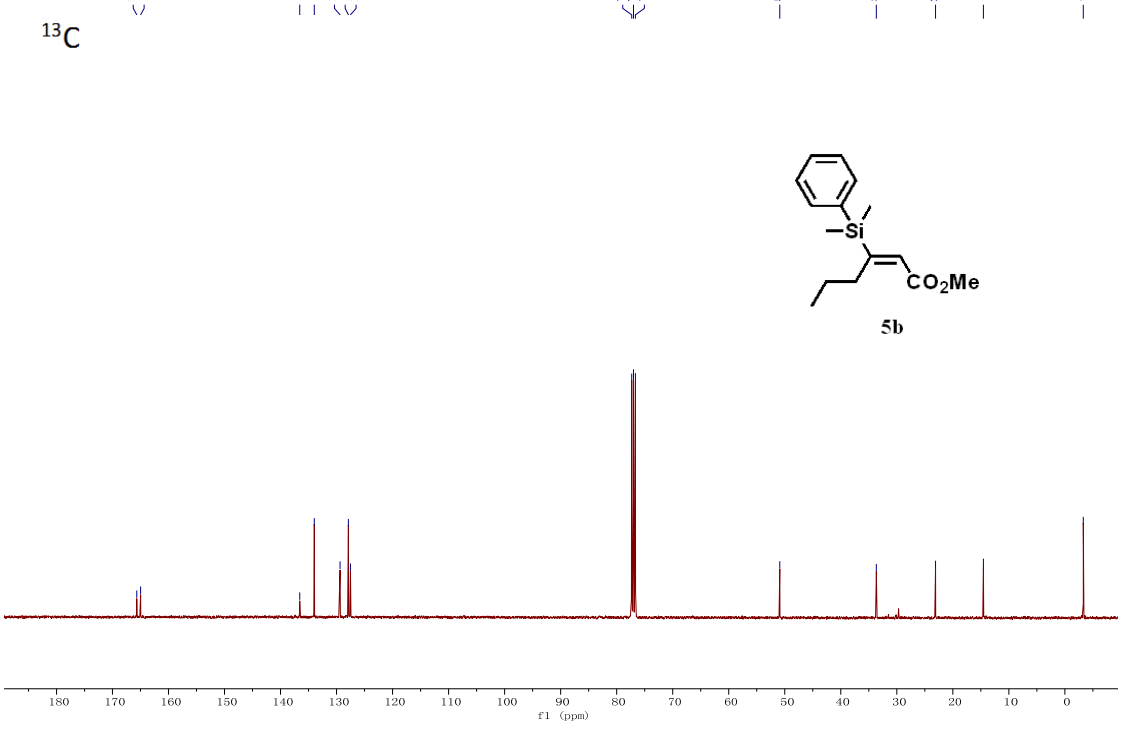

165.65865
165.23709
136.59675
134.06960
129.38557
127.89913
127.13331
77.31178
77.00002
76.68827
50.96057
31.69651
31.47591
29.76911
29.62277
22.54160
14.03582
-0.29803
n-C6H13
CO2Me
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

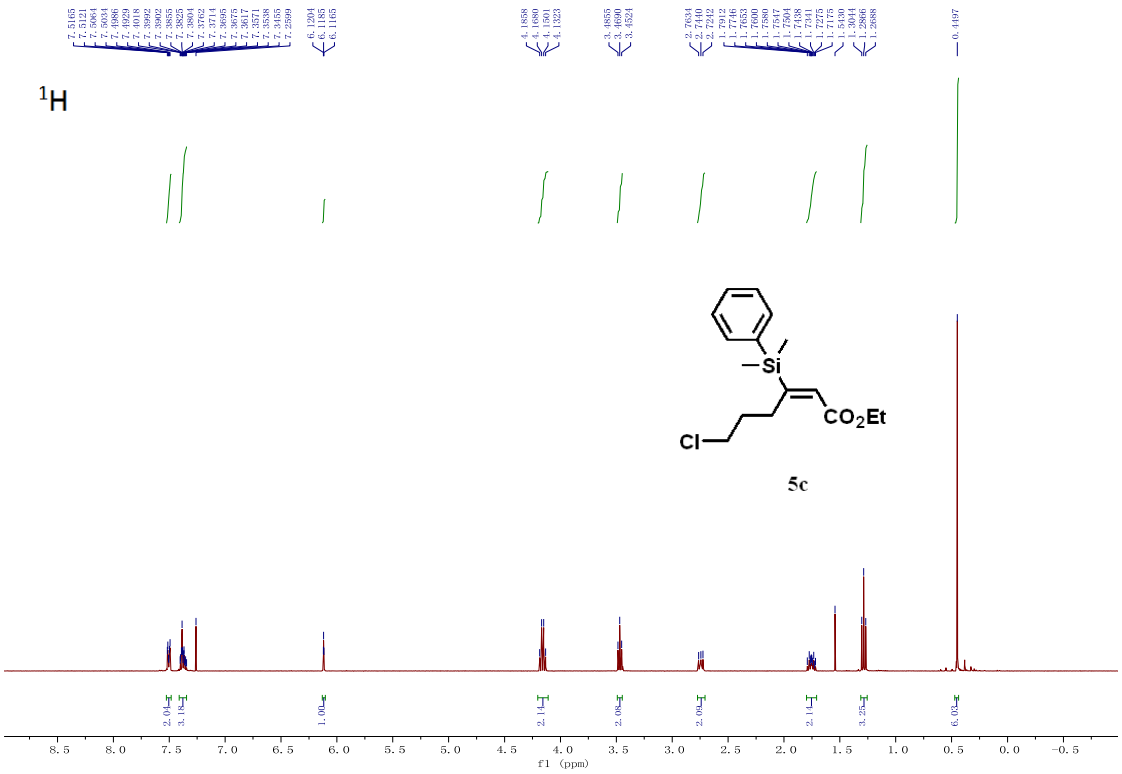
NOE-1D

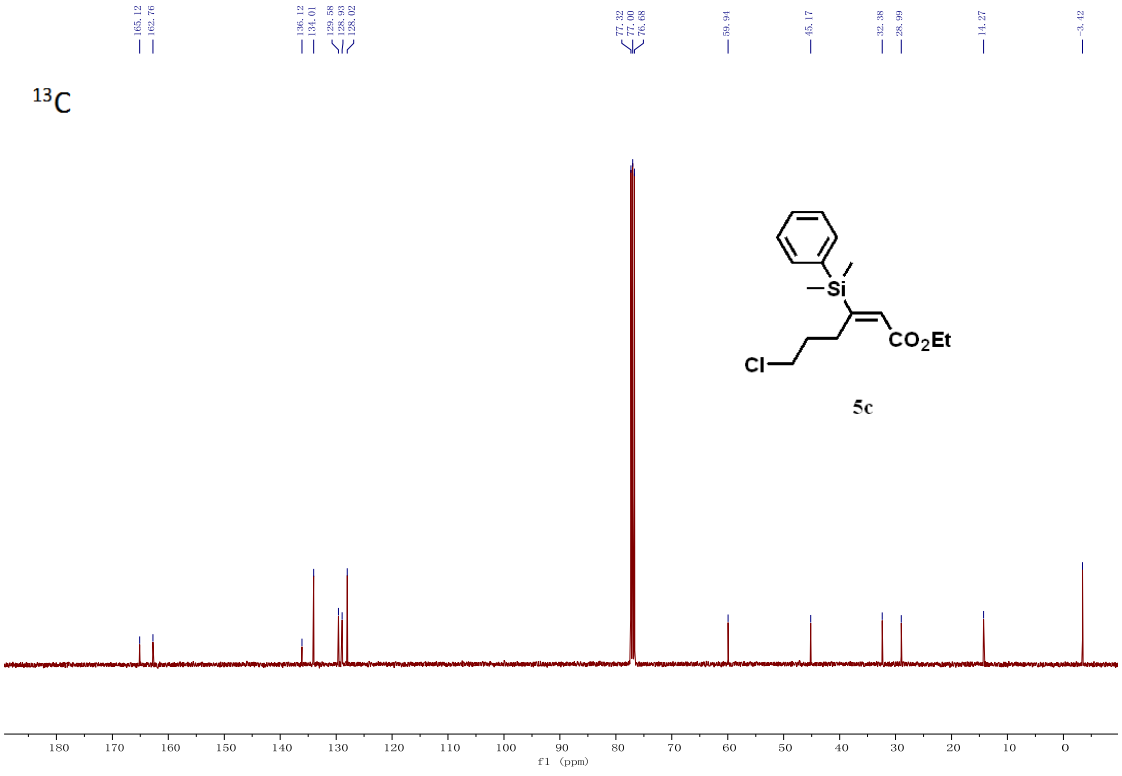

n-C6H13
CO2Me
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

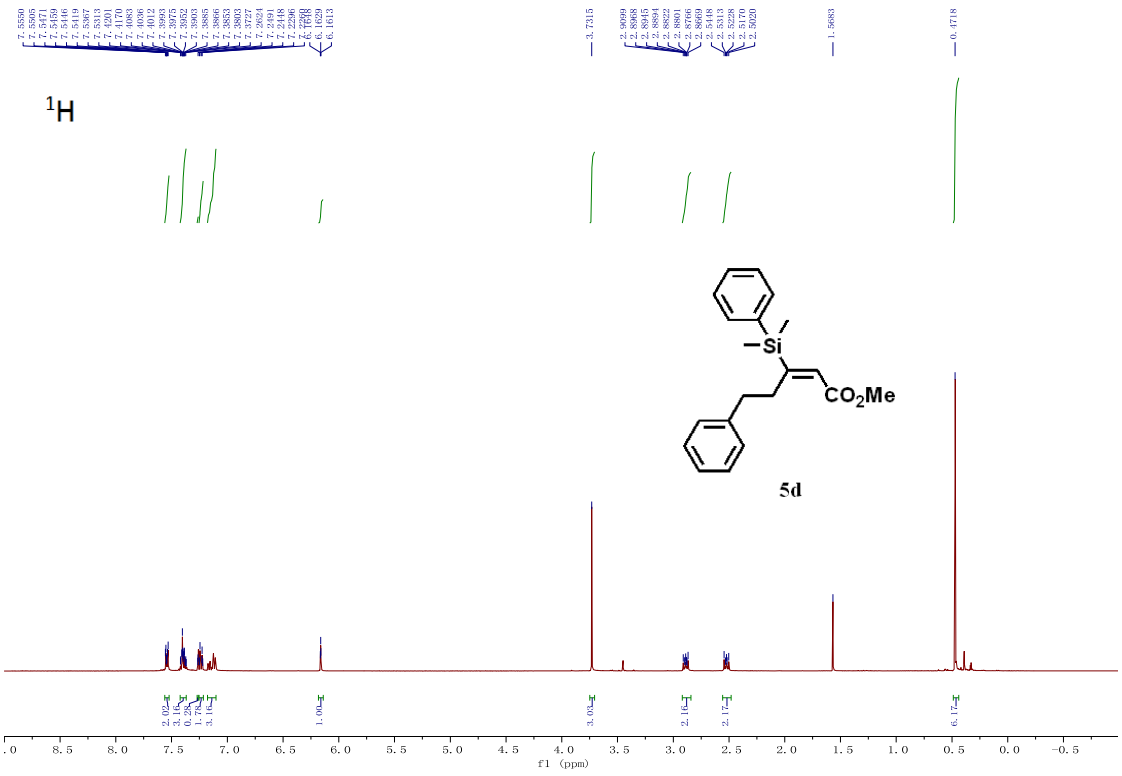

NOESY - 2D
5a
H1,H2
f2 (ppm)
f1 (ppm)

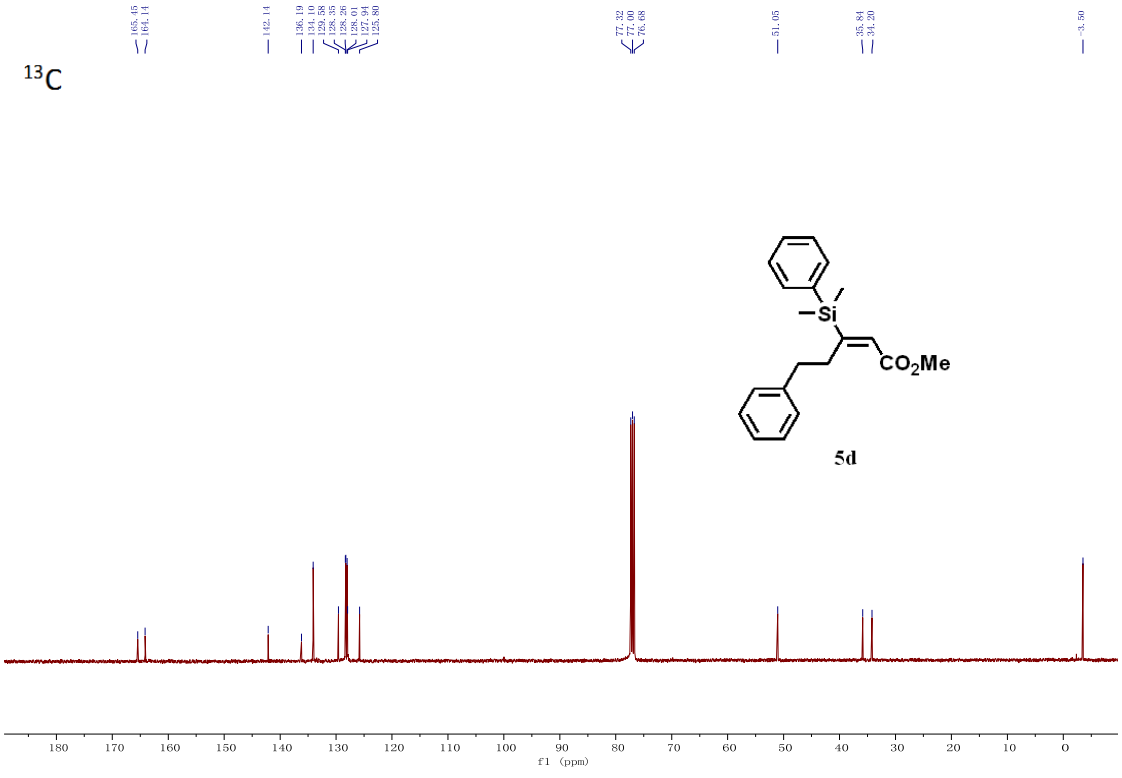

1H
Si
CO2Me
5b
f1 (ppm)


13C
Si
CO2Me
5b
f1 (ppm)

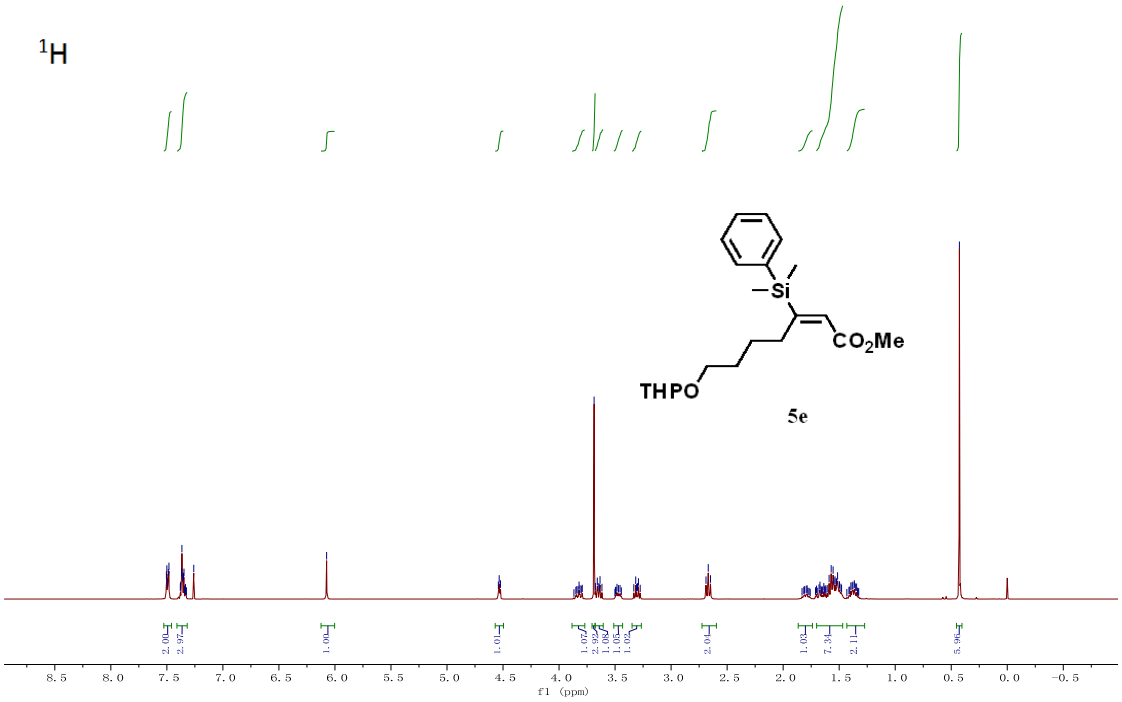

1H
Si
CO2Et
Cl
5c
f1 (ppm)


13C
Si
CO2Et
Cl
5c
f1 (ppm)

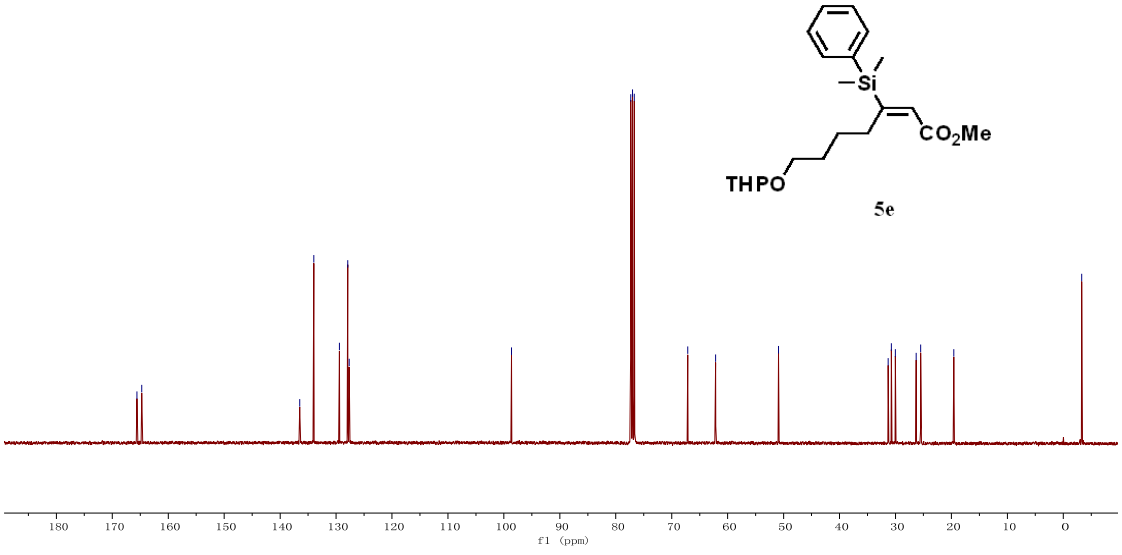

1H
Si
CO2Me
5d
f1 (ppm)


13C
Si
CO2Me
5d
f1 (ppm)

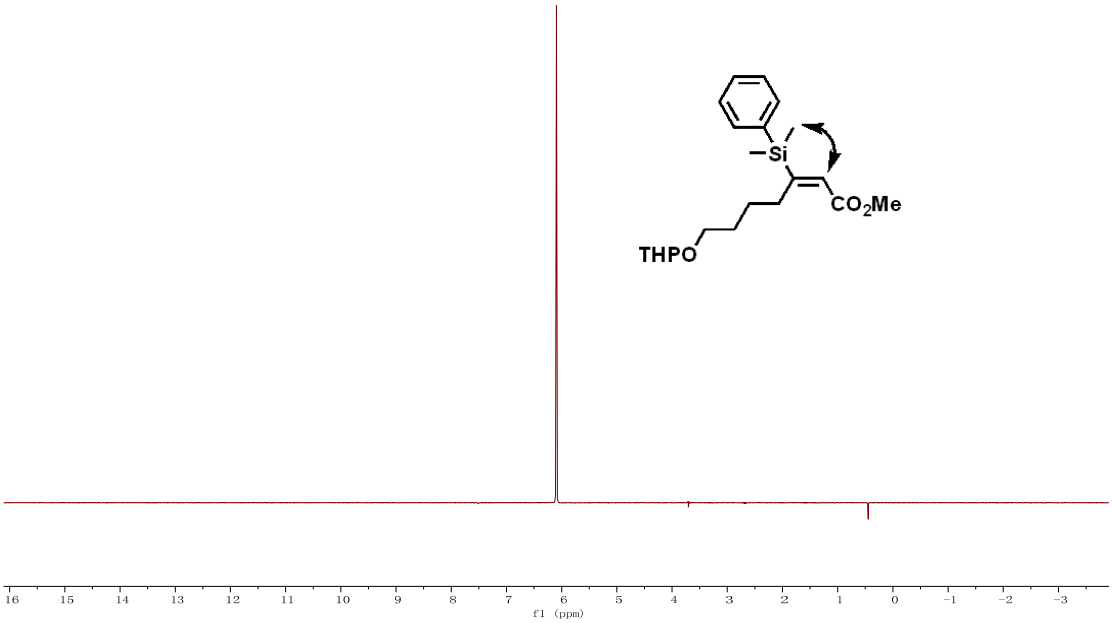
^{1}H

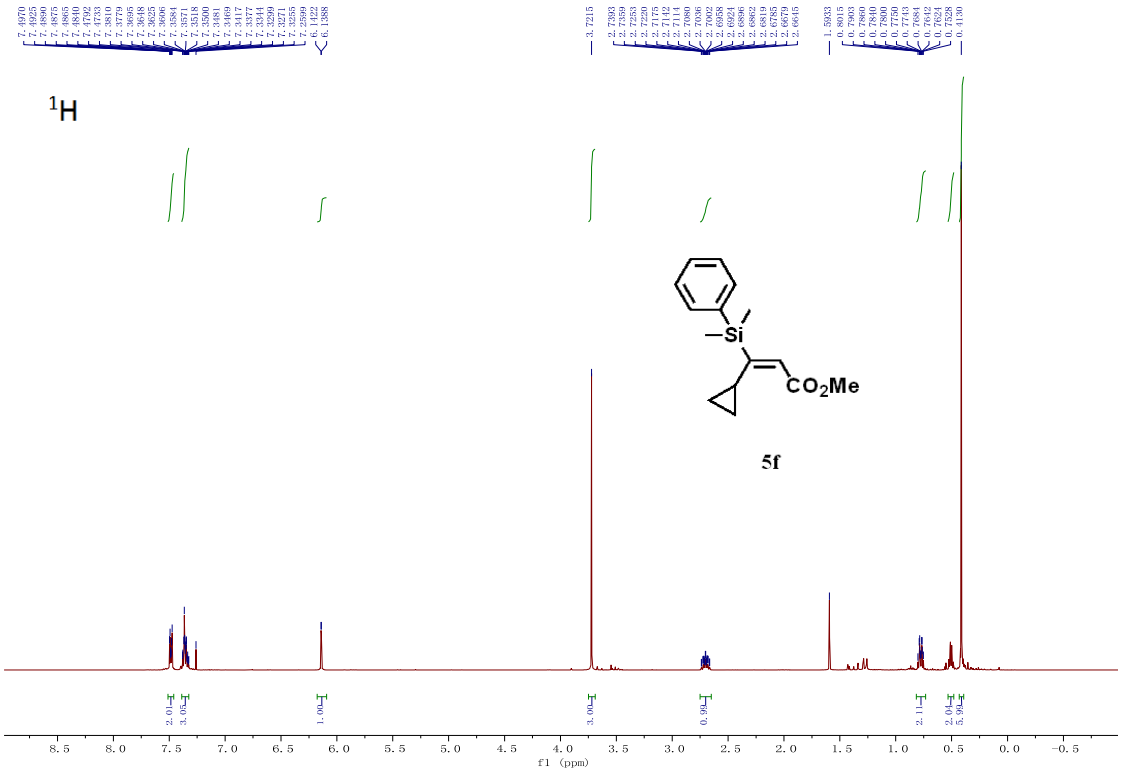


^{13}C

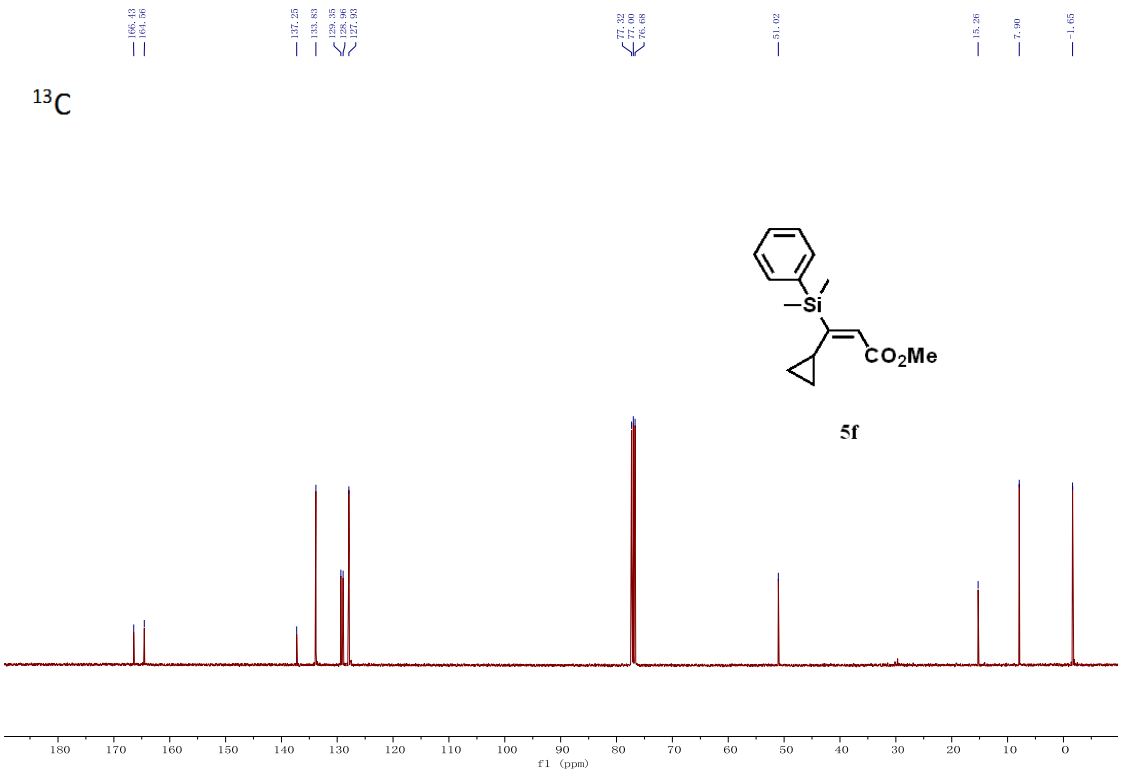


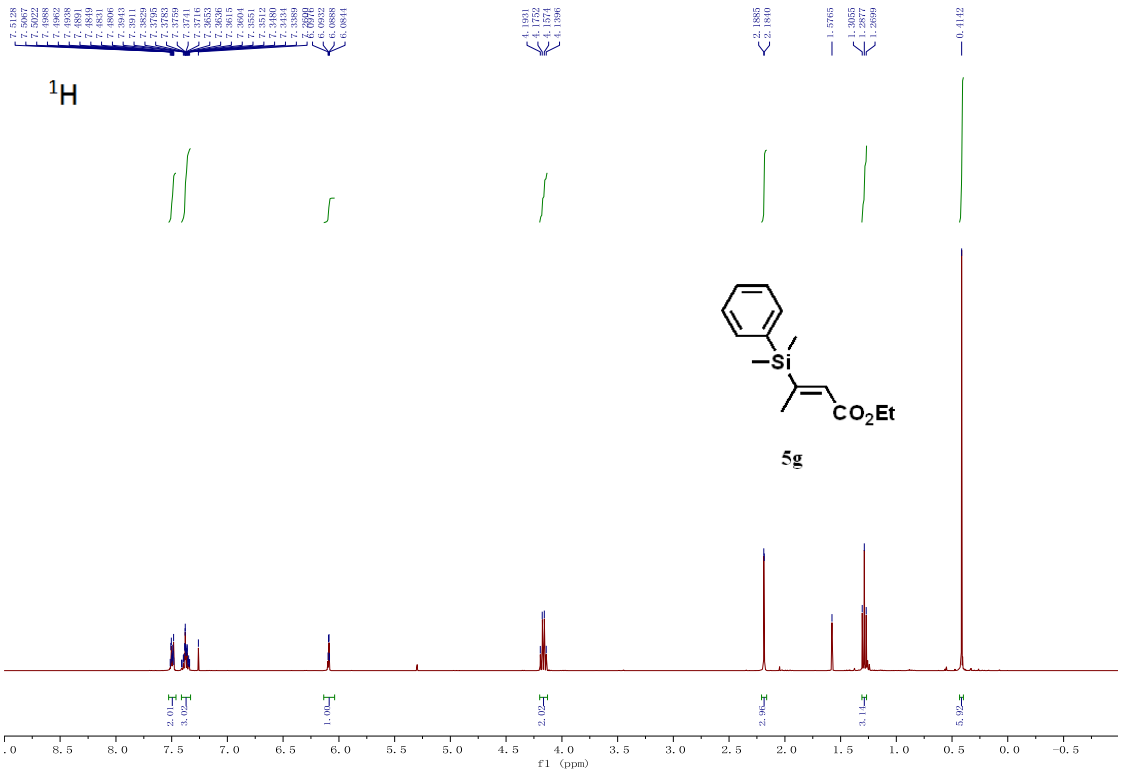
NOE-1D





5f


168.43
166.86
137.25
133.83
129.35
128.96
127.83
77.32
77.00
76.68
51.02
15.26
7.90
-1.65
13C
Si
CO2Me
5f
f1 (ppm)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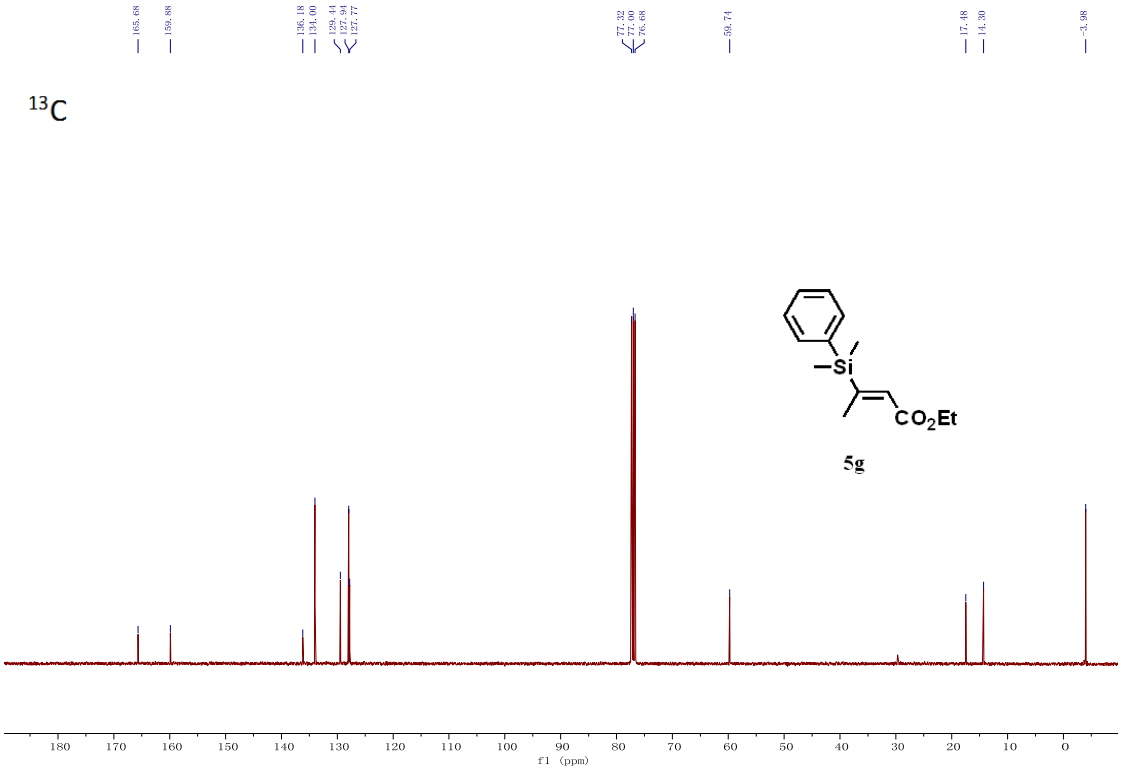
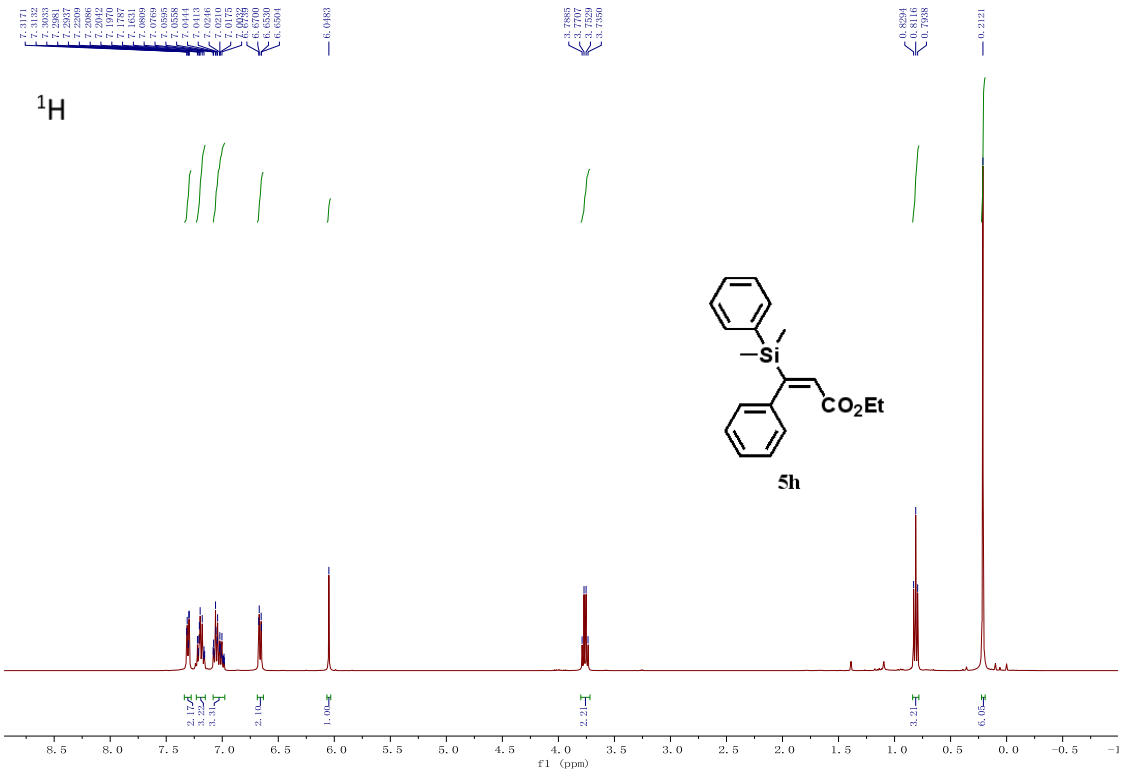
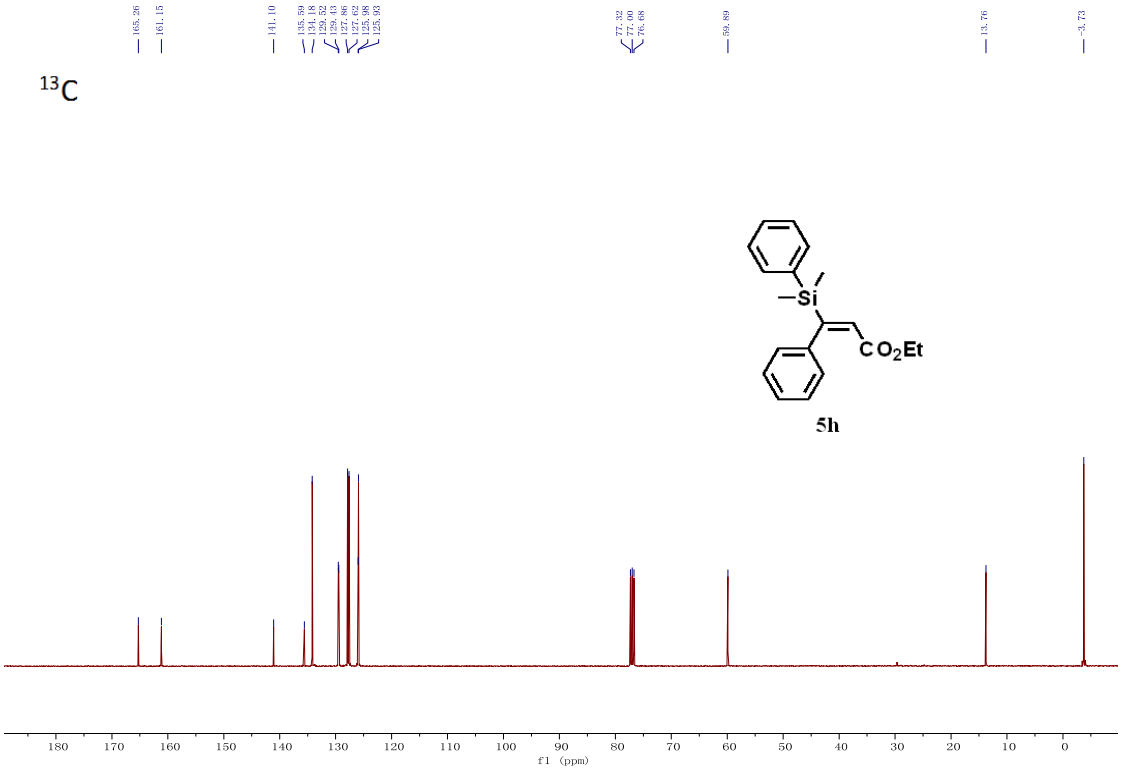
7.5022
7.4988
7.4962
7.4938
7.4891
7.4849
7.4831
7.4806
7.3943
7.3911
7.3859
7.3795
7.3783
7.3759
7.3741
7.3716
7.3653
7.3636
7.3615
7.3604
7.3551
7.3512
7.3480
7.3434
7.3389
6.8898
6.8866
6.6932
6.6888
6.6844
4.1791
4.1752
4.1574
4.1396
2.1885
2.1840
1.5765
1.3055
1.2877
1.2699
0.4142
1H
Si
CO2Et
5g
2.01
3.02
1.00
2.02
2.96
3.11
5.92
f1 (ppm)


165.68
159.88
136.18
134.60
129.44
127.94
127.77
77.32
77.00
76.68
59.74
17.48
14.30
-3.98
13C
Si
CO2Et
5g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.3171
7.3132
7.3033
7.2981
7.2937
7.2299
7.2066
7.2042
7.1970
7.1787
7.1681
7.1649
7.0769
7.0595
6.6538
6.6414
7.6346
7.6210
7.6175
7.6032
6.6738
6.6700
6.6530
6.6504
6.6483
3.7885
3.7707
3.7577
3.7529
3.7350
0.8294
0.8114
0.7938
0.2121
1H
Si
CO2Et
5h
2.17
2.32
3.31
2.10
1.00
2.21
3.21
6.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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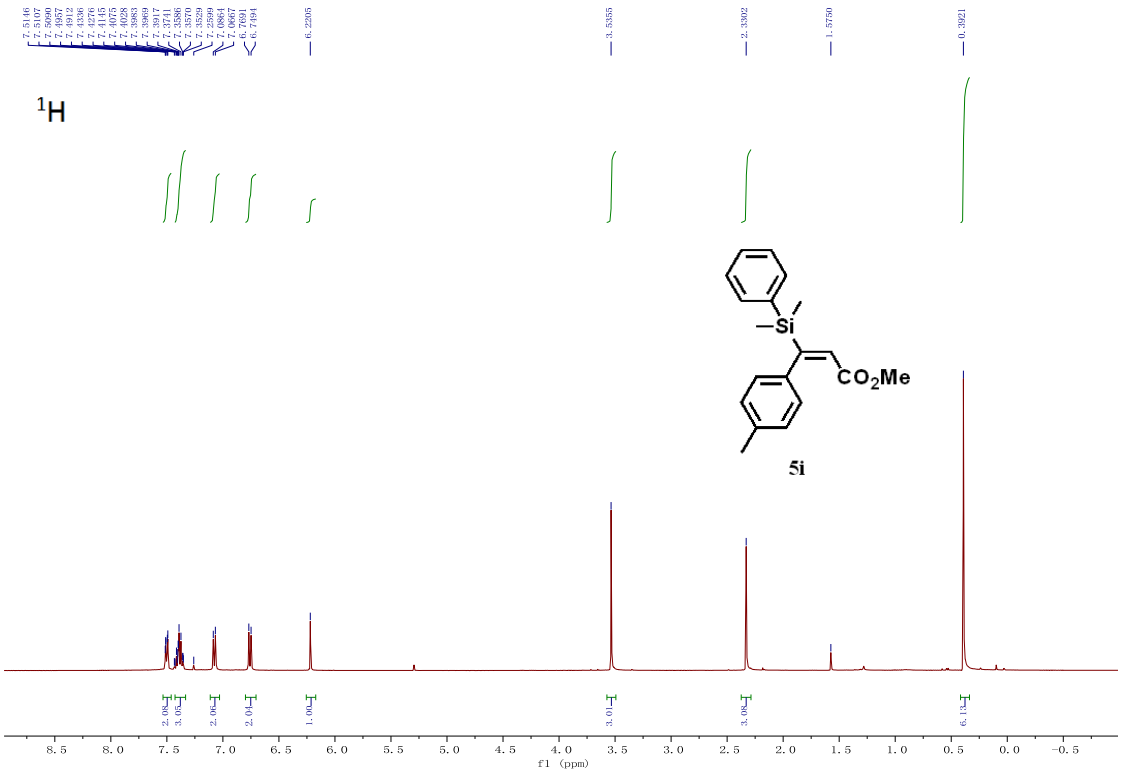
161.15
141.10
135.59
134.18
129.52
129.43
127.86
127.62
125.98
125.93
77.32
77.00
76.68
59.89
13.76
-3.73
13C
Si
CO2Et
5h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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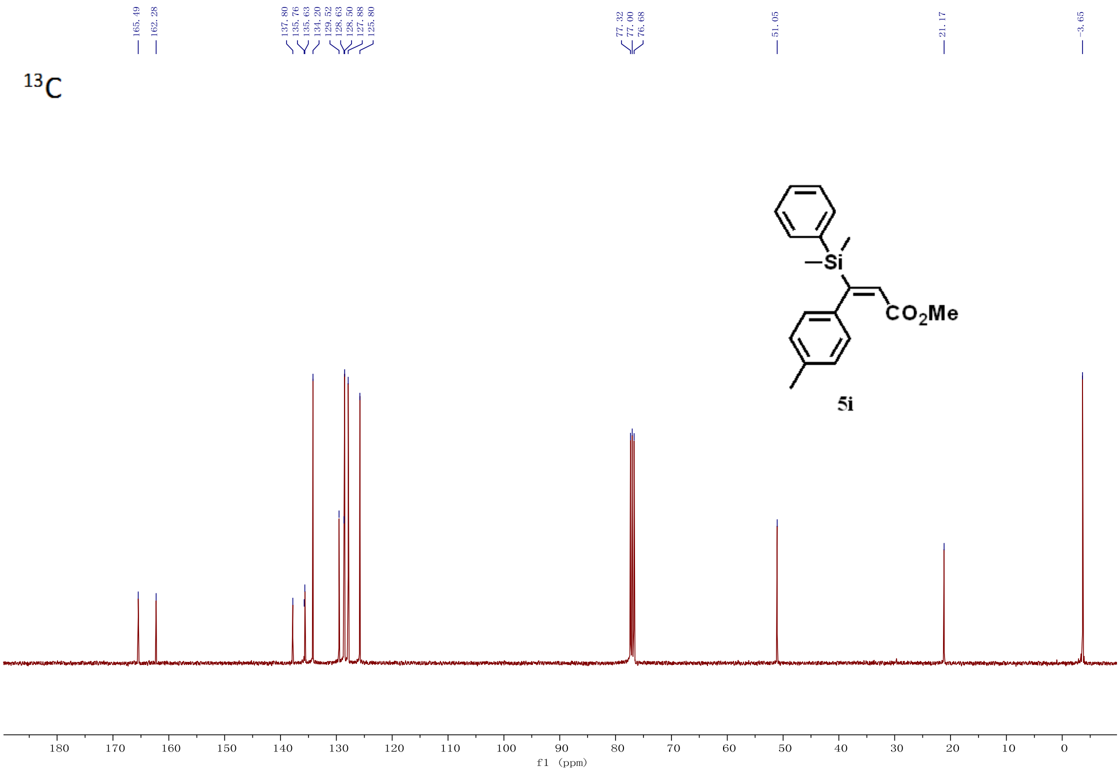
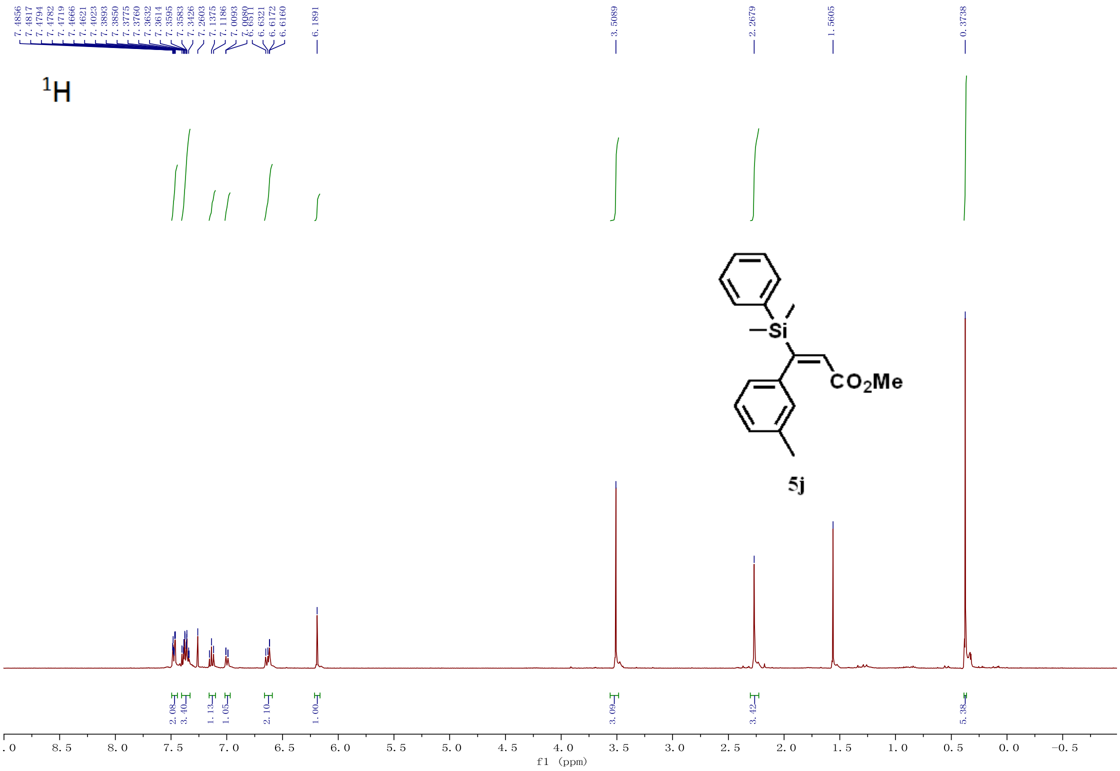
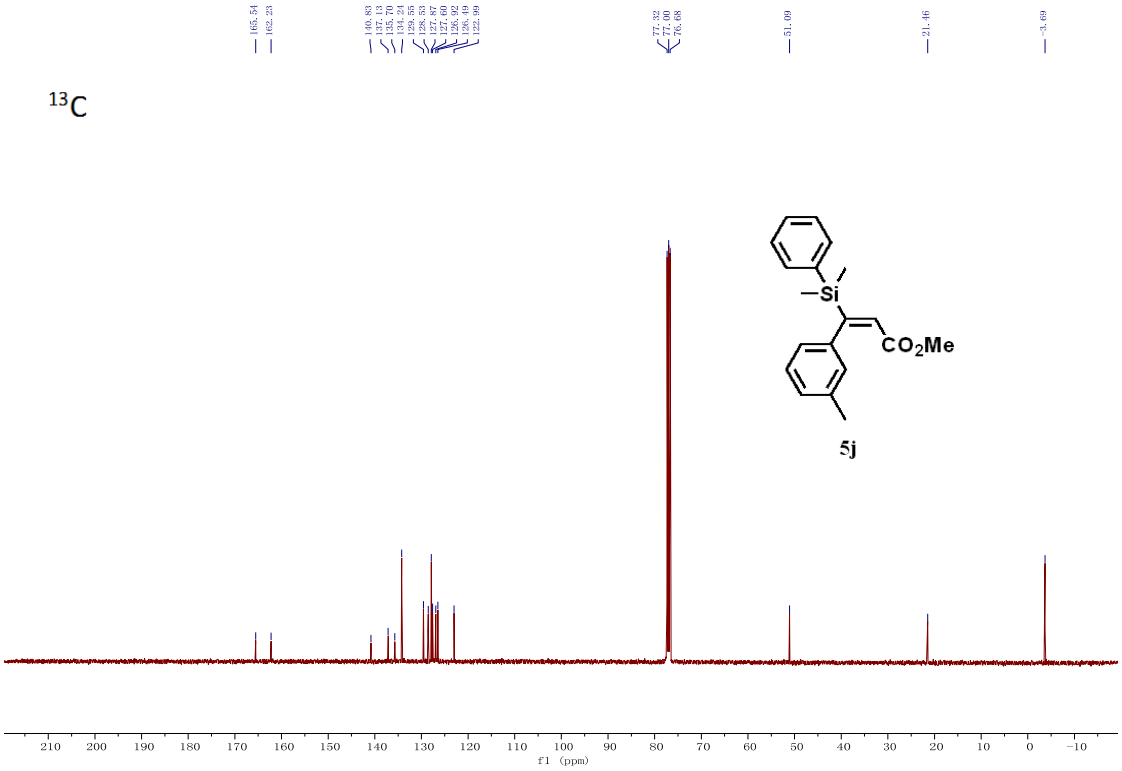
7.5107
7.5060
7.4957
7.4912
7.4336
7.4276
7.4145
7.4075
7.4028
7.3983
7.3969
7.3917
7.3741
7.3586
7.3570
7.3529
7.2599
7.0864
7.0667
6.7991
6.7194
6.2205
3.5355
2.3302
1.5750
0.3921
1H
Si
CO2Me
5i
2.00
3.01
2.00
2.04
1.00
3.01
3.08
6.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


13C
165.49
162.28
137.80
135.76
135.63
134.20
129.52
128.63
128.50
127.88
125.80
77.32
77.00
76.68
51.05
21.17
-3.65
Si
CO2Me
5i
f1 (ppm)


1H
6.1891
3.5089
2.2679
1.5605
0.3738
Si
CO2Me
5j
2.08
3.40
1.13
1.05
2.10
1.00
3.09
3.42
5.38
f1 (ppm)

^{13}C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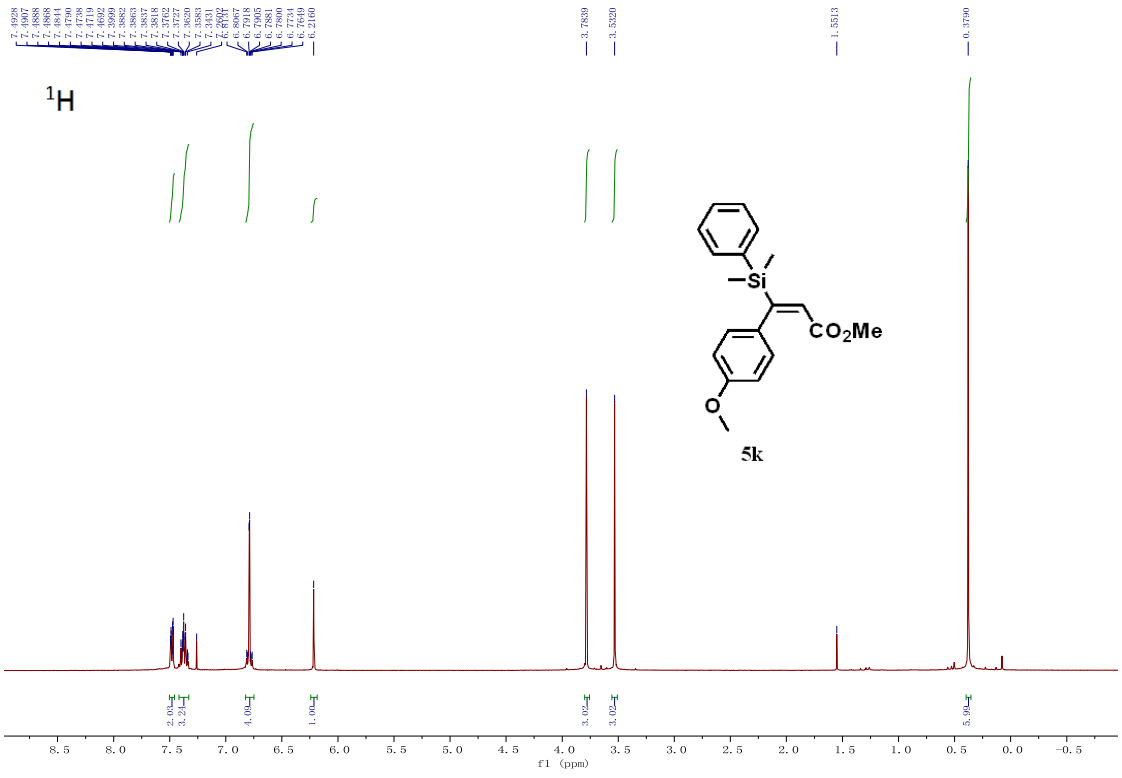
162.23
140.83
137.13
135.70
134.24
128.55
128.53
127.87
127.60
126.92
126.84
122.99
77.32
77.00
76.68
51.09
21.46
-3.69
Si
CO2Me
5j
f1 (ppm)

^{1}H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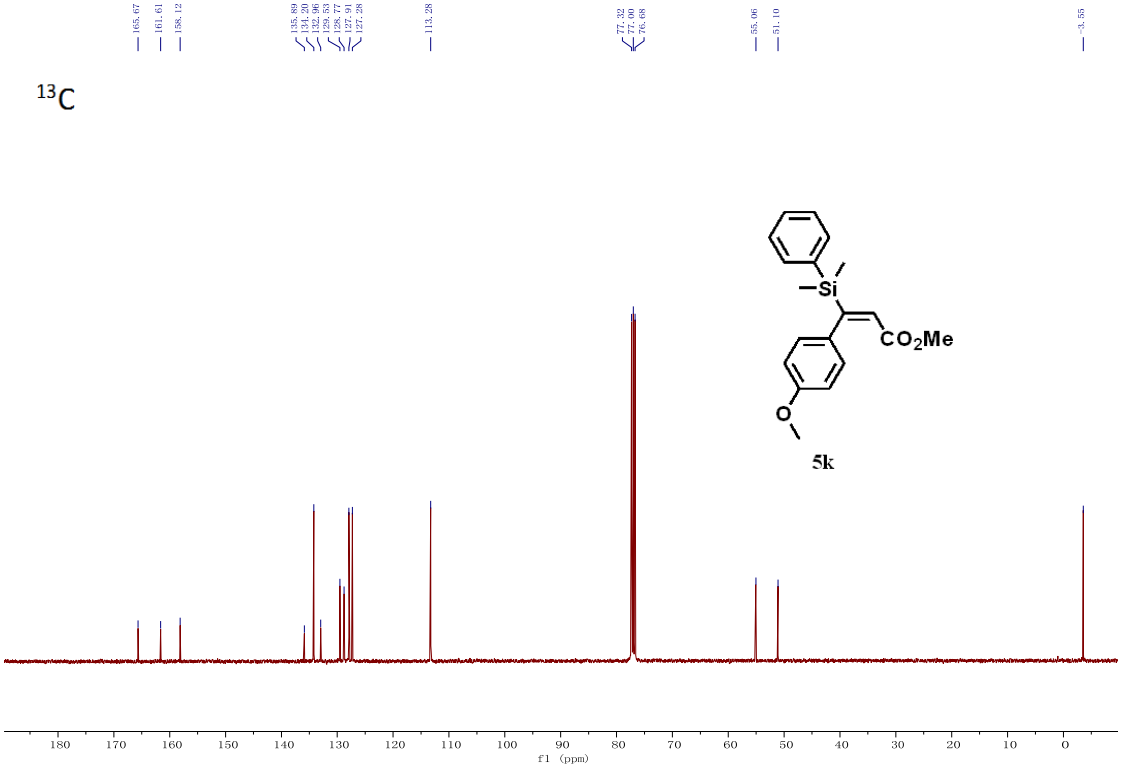
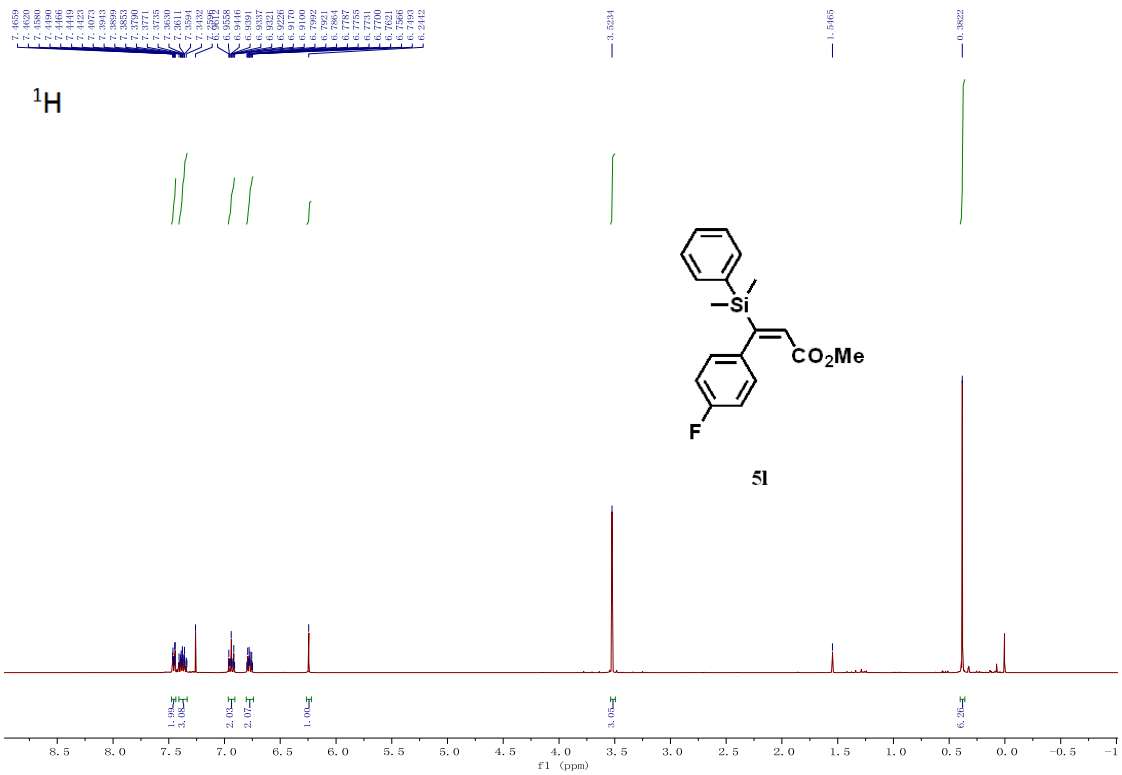
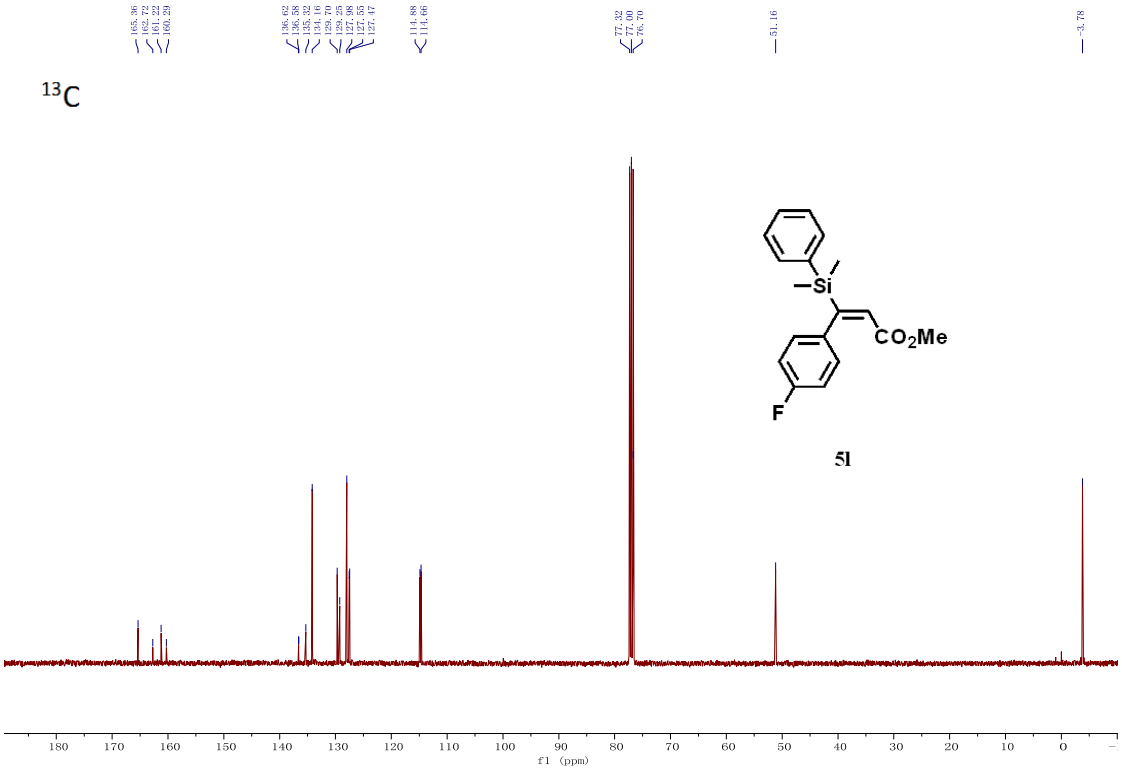
7.4907
7.4888
7.4866
7.4841
7.4790
7.4738
7.4719
7.4692
7.4492
7.3999
7.3882
7.3863
7.3837
7.3818
7.3762
7.3727
7.3699
7.3583
7.3431
7.3407
7.3387
6.8067
6.7918
6.7905
6.7881
6.7800
6.7734
6.7649
6.2160
3.7839
3.5320
1.5513
0.3790
Si
CO2Me
O
5k
2.05
3.24
4.00
1.00
3.02
3.02
5.90
f1 (ppm)


165.67
161.61
158.12
135.89
134.20
132.96
129.53
128.77
127.91
127.28
113.28
77.32
77.00
76.68
55.06
51.10
-3.55
13C
Si
CO2Me
O
5k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

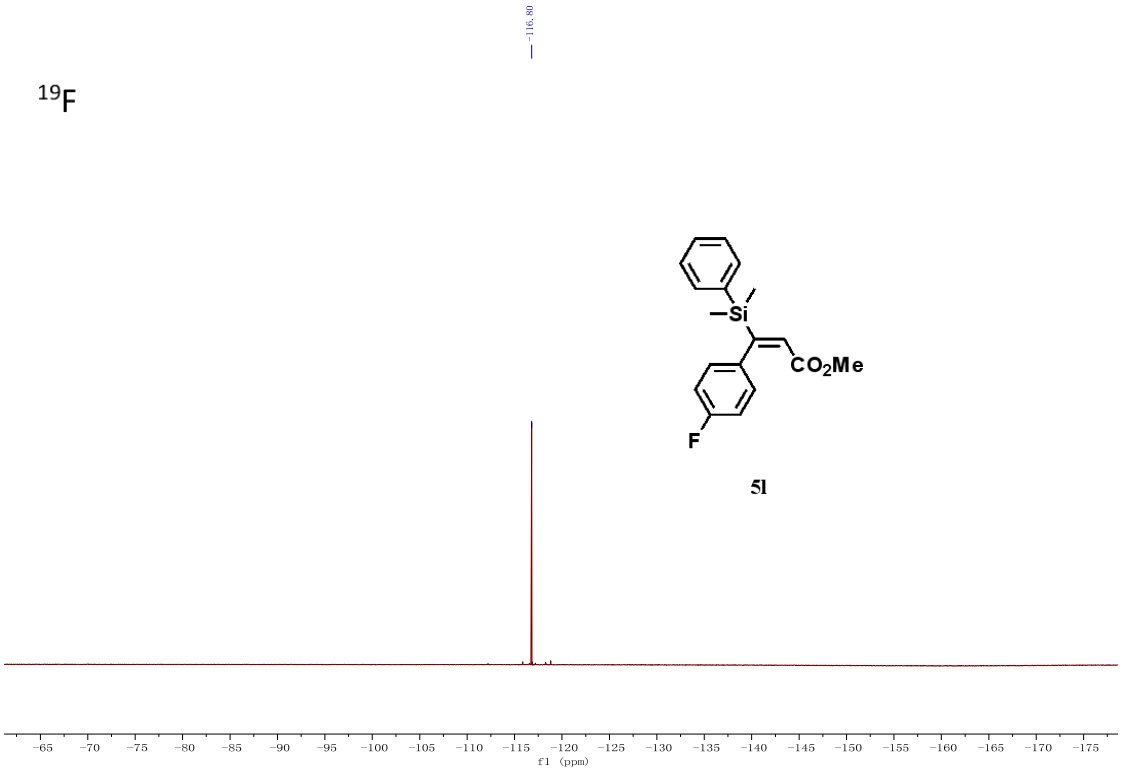

3.8234
1.5465
0.8822
1H
Si
CO2Me
F
5l
1.94
3.08
2.03
2.07
1.00
3.05
6.20
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

^{13}C

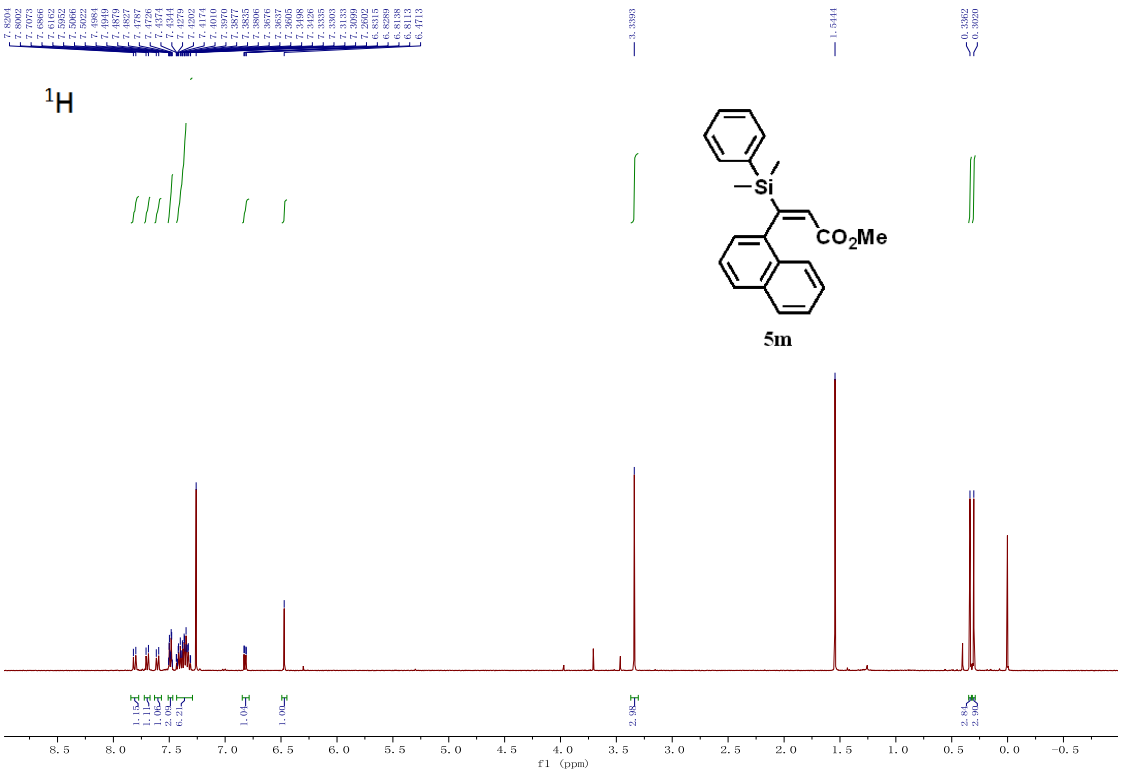

165.36
162.72
161.22
160.29
136.62
136.58
135.32
134.16
129.70
129.35
127.98
127.55
127.47
114.88
114.66
77.32
77.00
76.70
51.16
-3.78
Si
CO2Me
F
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

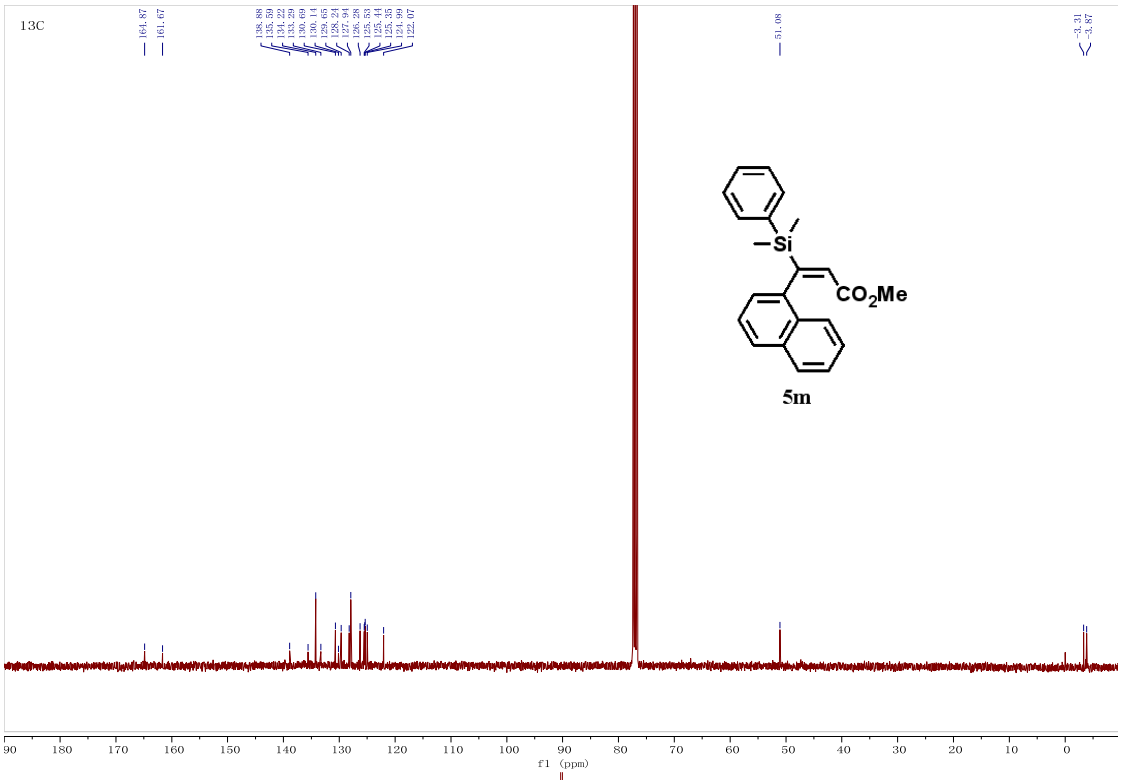
5l

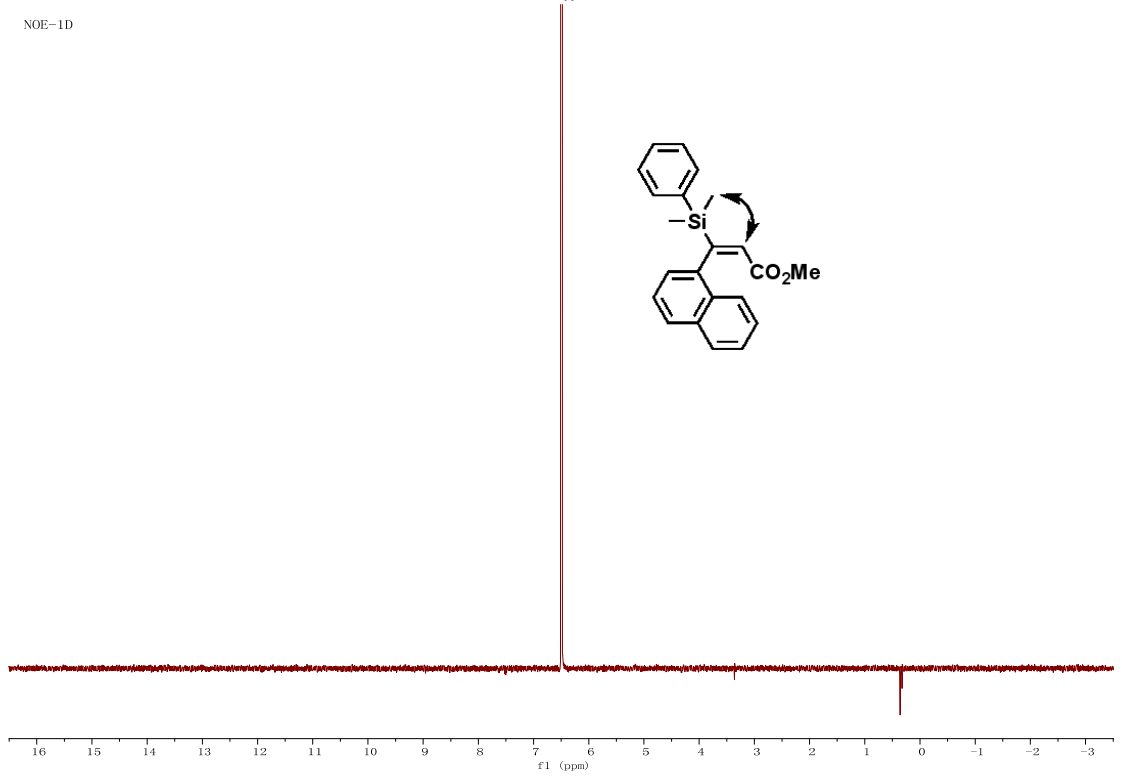
^{19}F

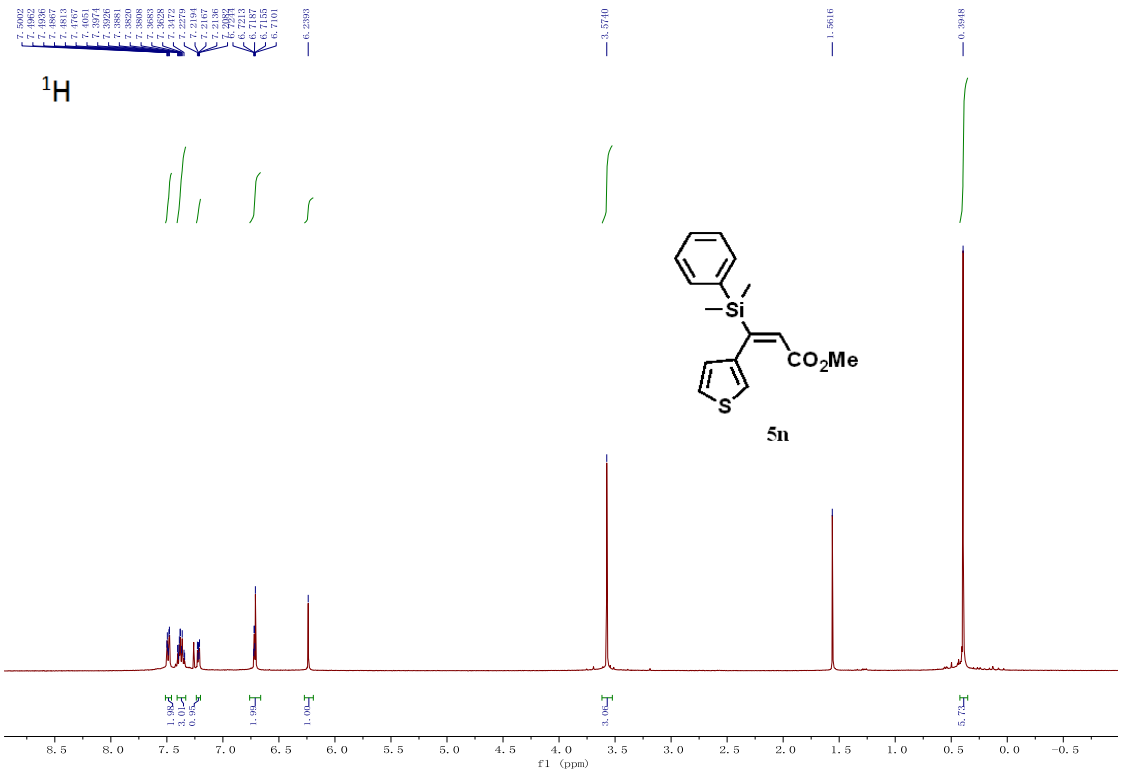

-116.80
Si
CO2Me
F
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175
f1 (ppm)

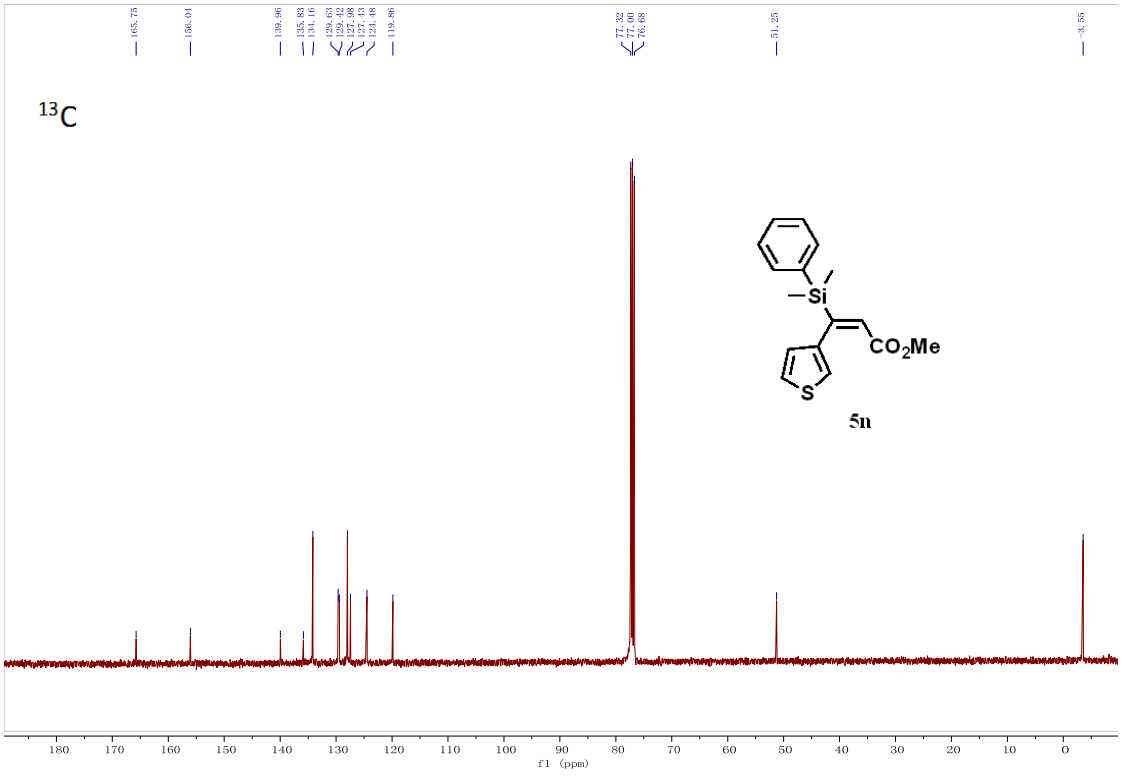
5l

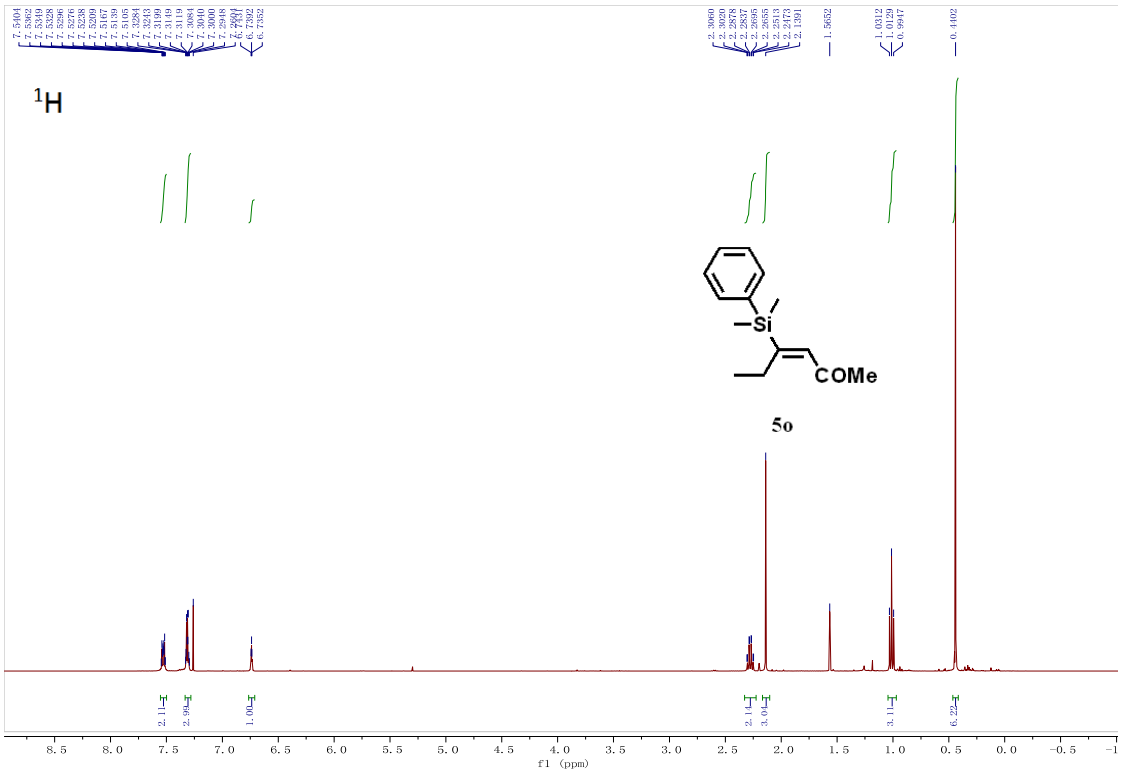

7.8204
7.8065
7.7973
7.6866
7.6162
7.5982
7.5866
7.5022
7.4984
7.4949
7.4859
7.4827
7.4787
7.4726
7.4714
7.4314
7.4279
7.4202
7.4174
7.4010
7.3970
7.3877
7.3835
7.3806
7.3676
7.3637
7.3605
7.3198
7.3168
7.3335
7.3303
7.3133
7.3094
7.2902
6.8289
6.8198
6.8113
6.4713
3.3393
1.5444
0.3362
0.3020
1H
Si
CO2Me
5m
1.15
1.11
1.04
2.00
6.24
1.04
1.00
2.98
2.84
2.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

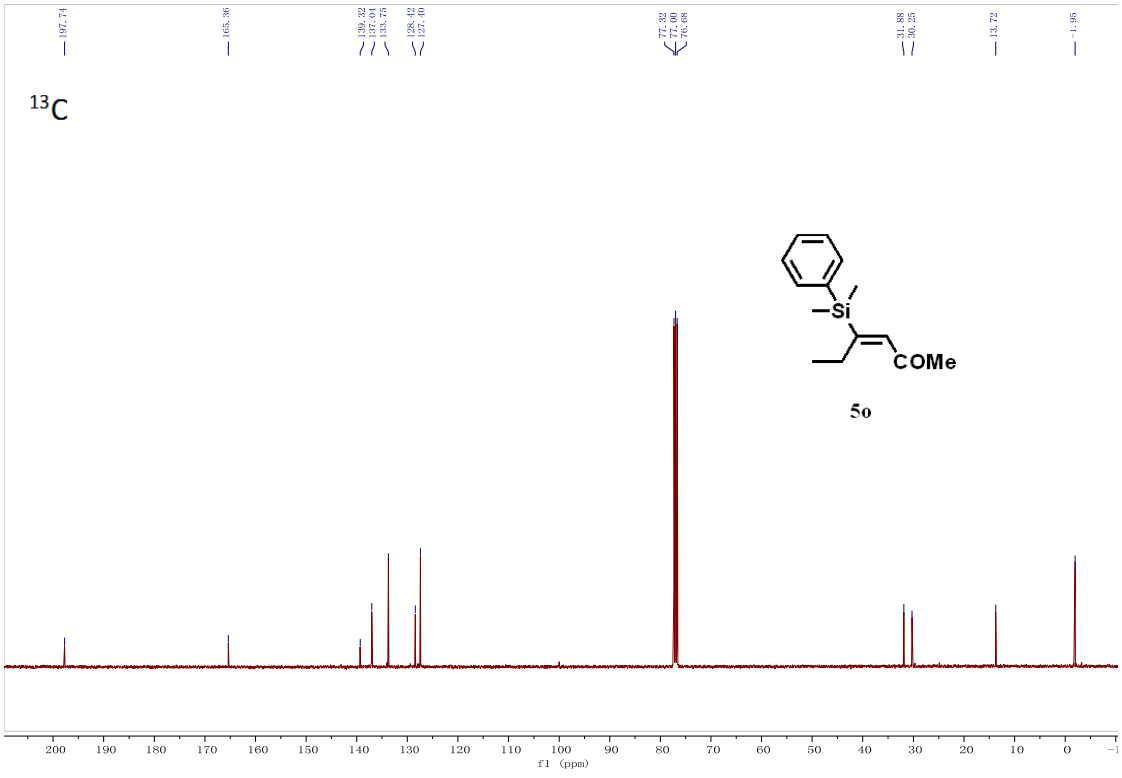

13C
164.87
161.67
138.88
133.59
131.22
133.29
130.69
129.14
129.15
128.24
127.94
125.28
125.53
125.44
125.35
124.99
122.67
51.08
-3.31
-3.87
Si
CO2Me
5m
f1 (ppm)

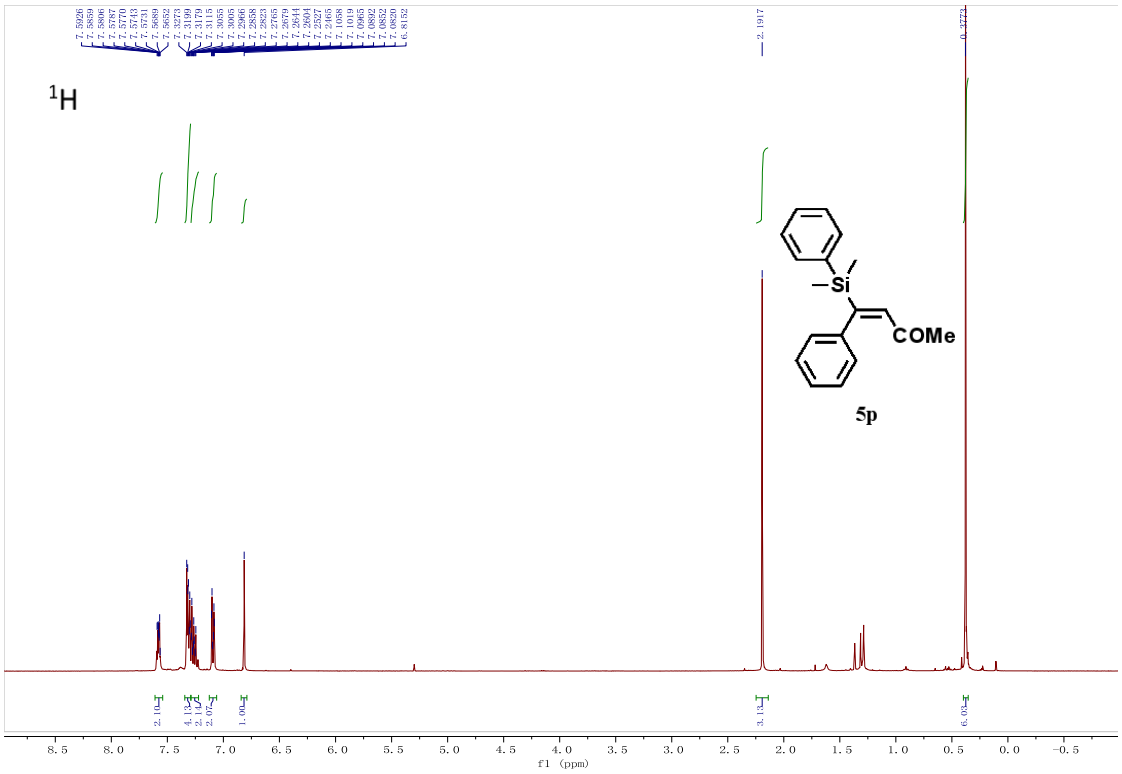

NOE-1D
Si
CO2Me
f1 (ppm)

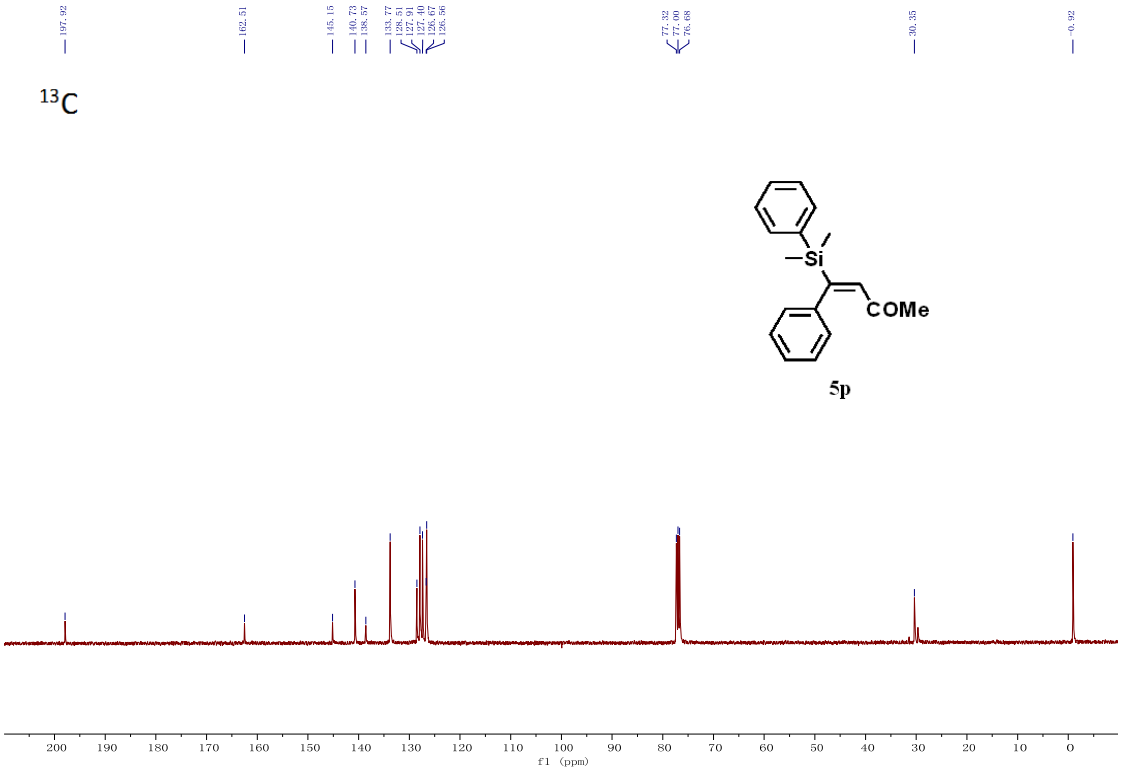

1H
Si
CO2Me
S
5n
f1 (ppm)


13C
Si
CO2Me
S
5n
f1 (ppm)


1H
Si
COMe
5o
f1 (ppm)


13C
Si
COMe
5o
f1 (ppm)


1H
Si
COMe
5p
f1 (ppm)


13C
Si
COMe
5p
f1 (ppm)