Supporting Information

Enantioselective Synthesis of Acyclic Monohydrosilanes by Steric Hindrance Assisted C−H Silylation

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1. General information

1.1. Reagents

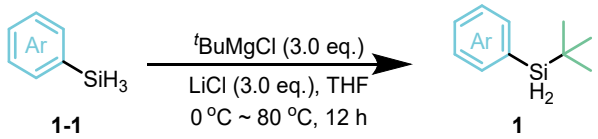
All commercial materials were used as received unless otherwise noted. Anhydrous solvents were obtained from the Inert Pure Solv solvent purification system (THF and toluene). Other solvents were purchased from J&K Chemical and used without further purification. TLC was performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using Silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China. Without specified notes, all reagents were purchased from commercial suppliers (Bide Pharmatech, Energy Chemical, TCI, Aldrich, Alfa and J&K) and directly used without further purification.

1.2. Instruments

NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as an internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. ^{13}C NMR data were reported in chemical shift (δ, ppm). Chiral HPLC chromatograms were obtained from a Thermo Fisher Ultimate 3000 HPLC system. High-resolution mass spectrometry (HRMS) was performed on Agilent Technologies 6230 TOF LC/MS under electrospray ionization (ESI) conditions in a positive mode using CH_2Cl_2 as solvent. Optical rotations were measured on Rudolph Autopol-I Automatic Polarimeter at concentrations of 0.4 g/100 mL in CH_2Cl_2.

2. Preparation of dihydrosilanes

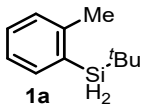
2.1 General procedure of synthesis of ^{t}Bu-tethered dihydrosilanes



Scheme S1. Synthesis of ^{t}Bu-tethered dihydrosilanes

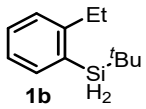
To a solution of **1-1** (10.0 mmol, 1.0 eq.), LiCl (1.27 g, 30 mmol, 3.0 eq.) in THF (20 mL) was added ^{t}BuMgCl (30 mL, 3.0 eq., 1 M) dropwise over 10 min at 0 °C

under argon atmosphere, then reacted at room temperature for 2 h before heated at 80 °C for 12 h. After being cooled to room temperature, the reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc, concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford compound **1**.



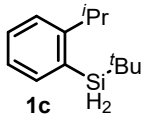
1a

Compound **1a** was isolated in 62% yield (1.1 g, 6.2 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.30 (td, J = 7.5, 1.4 Hz, 1H), 7.20 – 7.14 (m, 2H), 4.22 (s, 2H), 2.47 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.29, 137.66, 131.64, 130.09, 129.75, 124.96, 28.04, 23.53, 17.34; HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{19}Si$ [M+H$^+$]: 179.1251, found: 179.1258.



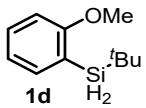
1b

Compound **1b** was isolated in 67% yield (1.28 g, 6.7 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.3, 1.3 Hz, 1H), 7.37 (td, J = 7.5, 1.5 Hz, 1H), 7.26 (d, J = 7.4 Hz, 1H), 7.18 (td, J = 7.3, 1.1 Hz, 1H), 4.25 (s, 2H), 2.79 (q, J = 7.5 Hz, 2H), 1.25 (t, J = 7.5 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.71, 137.76, 130.83, 130.28, 128.07, 125.05, 30.07, 28.10, 17.19, 16.38; HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{21}Si$ [M+H$^+$]: 193.1407, found: 193.1408.



1c

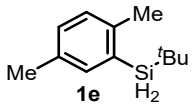
Compound **1c** was isolated in 73% yield (1.50 g, 7.3 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.4, 1.1 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.32 (d, J = 7.0 Hz, 1H), 7.16 (td, J = 7.2, 1.3 Hz, 1H), 4.24 (s, 2H), 3.15 (dt, J = 13.6, 6.8 Hz, 1H), 1.25 (d, J = 6.8 Hz, 6H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.45, 137.81, 130.49, 130.46, 125.21, 124.95, 34.82, 28.09, 24.46, 17.08; HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{23}Si$ [M+H$^+$]: 207.1564, found: 207.1562.



1d

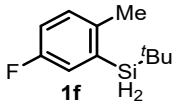
Compound **1d** was isolated in 17% yield (325.0 mg, 1.7 mmol) as pale yellow oil (R_f

= 0.3, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 7.1, 1.7 Hz, 1H), 7.42 – 7.38 (m, 1H), 6.98 – 6.94 (m, 1H), 6.86 (d, J = 8.3 Hz, 1H), 4.14 (s, 2H), 3.81 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.22, 138.48, 131.92, 121.10, 120.70, 109.62, 55.12, 28.25, 16.95; HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{19}OSi$ [M+H$^+$]: 195.1200, found: 195.1200.



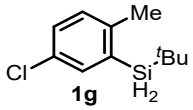
1e

Compound **1e** was isolated in 51% yield (972.0 mg, 5.1 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.13 (dd, J = 7.9, 1.6 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 4.22 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.12, 138.28, 134.11, 131.40, 130.85, 129.68, 28.07, 22.99, 21.08, 17.34; HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{21}Si$ [M+H$^+$]: 193.1407, found: 193.1409.



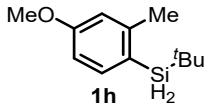
1f

Compound **1f** was isolated in 27% yield (525.0 mg, 2.7 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J = 8.7, 2.9 Hz, 1H), 7.15 (dd, J = 8.4, 5.3 Hz, 1H), 7.00 – 6.94 (m, 1H), 4.20 (s, 2H), 2.42 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.47 (d, J = 246.9 Hz), 139.68 (d, J = 3.1 Hz), 134.00 (d, J = 3.8 Hz), 131.29 (d, J = 6.6 Hz), 123.35 (d, J = 18.9 Hz), 116.73 (d, J = 20.8 Hz), 27.97, 22.59, 17.35; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.00; HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{18}FSi$ [M+H$^+$]: 197.1156, found: 197.1151.



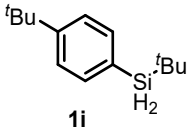
1g

Compound **1g** was isolated in 11% yield (224.4 mg, 1.1 mol) as pale yellow oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 2.3 Hz, 1H), 7.25 (d, J = 2.4 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 4.19 (s, 2H), 2.42 (s, 3H), 1.03 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.39, 136.78, 134.11, 131.23, 131.12, 129.98, 27.98, 22.84, 17.32; HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{18}ClSi$ [M+H$^+$]: 213.0861, found: 213.0859.



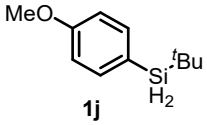
1h

Compound **1h** was isolated in 53% yield (1.10 g, 5.3 mmol) as pale yellow oil (R_f = 0.3, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.1 Hz, 1H), 6.80 – 6.74 (m, 2H), 4.21 (s, 2H), 3.82 (s, 3H), 2.47 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.20, 146.13, 139.05, 122.54, 115.67, 110.54, 55.02, 27.96, 23.75, 17.36; HRMS (ESI, *m*/*z*) calcd for $C_{12}H_{21}OSi$ [M+H$^+$]: 209.1356, found: 209.1357.



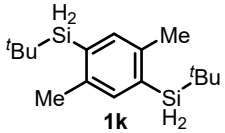
1i

Compound **1i** was isolated in 48% yield (1.05 g, 4.8 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 2H), 7.38 (d, J = 8.2 Hz, 2H), 4.13 (s, 2H), 1.32 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.67, 135.95, 128.72, 124.96, 34.84, 31.35, 27.61, 16.62; HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{25}Si$ [M+H$^+$]: 221.1720, found: 221.1722.



1j

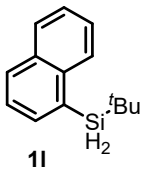
Compound **1j** was isolated in 40% yield (770.0 mg, 4.0 mmol) as pale yellow oil (R_f = 0.3, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 6.92 – 6.90 (m, 2H), 4.12 (s, 2H), 3.82 (s, 3H), 1.00 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.01, 137.50, 123.02, 113.78, 55.07, 27.51, 16.59; HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{19}OSi$ [M+H$^+$]: 195.1200, found: 195.1207.



1k

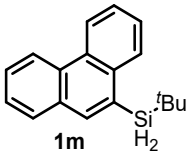
The reaction was carried out on 5 mmol scale using LiCl (1.27 g, 30 mmol, 6.0 eq.), ^{t}BuMgCl (30 mL, 6.0 eq., 1 M). Compound **1k** was isolated in 11% yield (149.0 mg, 1.1 mmol) as pale yellow solid (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 2H), 4.19 (s, 4H), 2.42 (s, 6H), 1.04 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.15, 138.65, 133.64, 28.12, 22.93, 17.38; HRMS (ESI, *m*/*z*) calcd for

$C_{16}H_{30}NaSi_2$ [M+Na$^+$]: 301.1778, found: 301.1782.



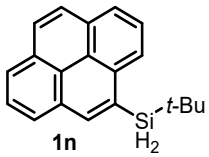
1l

Compound **1l** was isolated in 66% yield (1.4 g, 6.6 mmol) as colorless oil (R_f = 0.8, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.88 – 7.86 (m, 1H), 7.82 – 7.80 (m, 1H), 7.56 – 7.47 (m, 3H), 4.55 (s, 2H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.60, 137.17, 133.33, 131.28, 130.61, 128.89, 128.86, 126.13, 125.80, 125.15, 28.26, 17.50; HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{19}Si$ [M+H$^+$]: 215.1251, found: 215.1253.



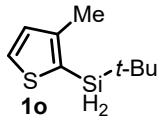
1m

Compound **1m** was isolated in 31% yield (806.8 mg, 3.1 mmol) as white solid (R_f = 0.6, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.0 Hz, 1H), 8.69 (d, J = 8.2 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 8.09 (s, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.71 – 7.60 (m, 4H), 4.59 (s, 2H), 1.09 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.43, 135.30, 131.53, 131.10, 130.27, 130.00, 129.75, 128.95, 127.62, 126.82, 126.58, 126.50, 123.14, 122.66, 28.43, 17.55; HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{21}Si$ [M+H$^+$]: 265.1407, found: 265.1407.



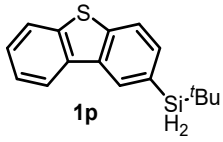
1n

Compound **1n** was isolated in 16% yield (458.0 mg, 1.6 mmol) as yellow solid (R_f = 0.6, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 9.1 Hz, 1H), 8.26 (d, J = 7.5 Hz, 1H), 8.21 (dd, J = 7.6, 4.5 Hz, 2H), 8.16 – 8.11 (m, 3H), 8.08 – 8.01 (m, 2H), 4.75 (s, 2H), 1.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.58, 135.47, 132.78, 131.36, 130.88, 128.48, 128.38, 128.30, 127.62, 126.05, 125.44, 125.42, 124.76, 124.61, 124.12, 28.20, 17.86; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{21}Si$ [M+H$^+$]: 289.1407, found: 289.1411.



1o

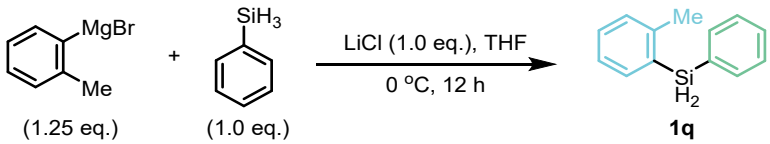
Compound **1o** was isolated in 3% yield (55.4 mg, 0.3 mmol) as pale yellow oil (R_f = 0.7, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 4.6 Hz, 1H), 7.06 (d, J = 4.6 Hz, 1H), 4.28 (s, 2H), 2.40 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.28, 131.29, 131.16, 123.54, 27.58, 17.19, 16.75; HRMS (ESI, *m*/*z*) calcd for $C_9H_{17}SSi$ [M+H$^+$]: 185.0815, found: 185.0813.



1p

Compound **1p** was isolated in 32% yield (873.0 mg, 3.2 mmol) as white solid (R_f = 0.7, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.22 (dd, J = 6.3, 2.7 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.64 (dd, J = 7.9, 0.7 Hz, 1H), 7.49 – 7.47 (m, 2H), 4.32 (s, 2H), 1.08 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.24, 139.27, 135.38, 135.24, 133.63, 129.28, 127.59, 126.97, 124.60, 122.94, 122.46, 121.72, 27.60, 16.72; HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{19}SSi$ [M+H$^+$]: 271.0971, found: 271.0971.

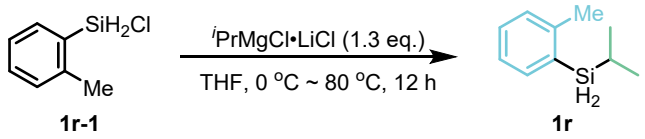
2.2 Procedure of synthesis **1q**, **1r** and **1s**



Scheme S2. Synthesis of **1q**

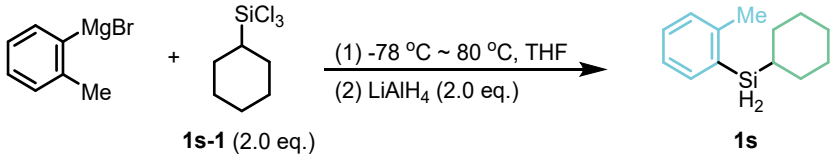
Compound **1q** was prepared according to reported literature.[1] To a solution of phenylsilane (1.08 g, 10.0 mmol, 1.0 eq.), LiCl (423.9 mg, 10 mmol, 1.0 eq.) in THF (20 mL) was added *o*-tolylmagnesium bromide (12.5 mL, 1.25 eq., 1 M) dropwised over 10 min at 0 °C under argon atmosphere, then reacted at the same temperature for 12 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc, concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel to afford compound **1q**. Compound **1q** was isolated in 74% yield (1.47 g, 7.4 mmol) as colorless oil (R_f = 0.7, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.56 (d, J = 7.6 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.35 (m,

3H), 7.21 (t, J = 7.5 Hz, 2H), 4.98 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.58, 137.21, 135.76, 131.62, 130.97, 130.62, 129.88, 129.60, 128.26, 125.41, 22.77.



Scheme S3. Synthesis of **1r**

To a solution of **1r-1** (78.3 mg, 0.5 mmol, 1.0 eq.) in THF (1 mL) was added ^{i}PrMgCl • LiCl (0.5 mL, 0.65 mmol, 1.3 eq., 1.3 M) dropwised over 10 min at 0 °C under argon atmosphere, then reacted at 80 °C for 12 h. After been cooled to room temperature, the reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc, concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel to afford compound **1r**. Compound **1r** was isolated in 14% yield (11.5 mg, 0.07 mmol) as colorless oil (R_f = 0.7, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.50 (m, 1H), 7.31 (td, J = 7.6, 1.4 Hz, 1H), 7.19 – 7.15 (m, 2H), 4.21 (d, J = 3.2 Hz, 2H), 2.44 (s, 3H), 1.31 – 1.26 (m, 1H), 1.08 (d, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.18, 136.93, 131.83, 130.12, 129.51, 125.14, 22.99, 19.33, 10.60; HRMS (ESI, *m/z*) calcd for $C_{10}H_{17}Si$ [M+H$^+$]: 165.1094, found: 165.1092.

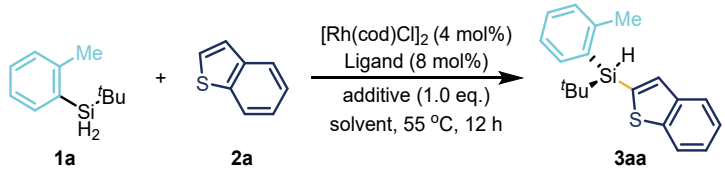


Scheme S4. Synthesis of **1s**

Compound **1s** was prepared according to the similar reported literature.[2] To a solution of **1s-1** (2.18 g, 10.0 mmol, 2.0 eq.) in THF (10 mL) was added *o*-tolylmagnesium bromide (5.0 mL, 5.0 mmol, 1.0 eq., 1 M) dropwised over 10 min at -78 °C under argon atmosphere, reacted at the same temperature for 2 h, then reacted at room temperature for 2 h before heated at 80 °C for 12 h. The reaction mixture was quenched with saturated NH_4Cl and extracted with EtOAc, concentrated *in vacuo*, and the residue was purified by flash chromatography on silica gel to afford compound **1s**. Compound **1s** was isolated in 27% yield (275.9 mg, 1.35 mmol) as colorless oil (R_f =

0.7, petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 7.2, 1.2 Hz, 1H), 7.32 (td, J = 7.5, 1.4 Hz, 1H), 7.21 – 7.16 (m, 2H), 4.22 (d, J = 3.1 Hz, 2H), 2.47 (s, 3H), 1.79 – 1.70 (m, 5H), 1.30 – 1.13 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.19, 137.02, 131.67, 130.07, 129.50, 125.09, 29.34, 27.85, 26.77, 23.07, 22.06; HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{21}Si$ [M+H$^+$]: 205.1407, found: 205.1405.

3. General procedure of optimization of reaction conditions

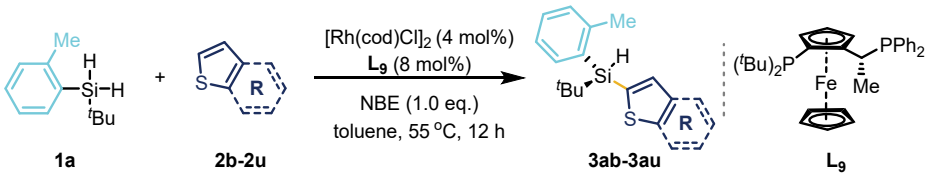


Scheme S5. Optimization of reaction conditions

To a 10 mL vial microwave tube were in order added *tert*-butyl(*o*-tolyl)silane **1a** (17.8 mg, 0.1 mmol, 1.0 eq.), thianaphthene **2a** (26.8 mg, 0.2 mmol, 2.0 eq.), $[Rh(cod)Cl]_2$ (2.0 mg, 4 mol%), Ligand (8 mol%), Additive (0.1 mmol, 1.0 eq.), solvent (1 mL) in glovebox. The tube was capped, removed from the glovebox and stirred in a preheated oil bath at 55 °C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated *in vacuo*; the crude residue was dissolved in 1 mL of deuterated chloroform for ^{1}H NMR analysis. The yields were determined by analysis of crude ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard. The ee value of the desired compound (**3aa**) was determined by the Daicel Chiralpak OD-3 column.

4. Substrate scope

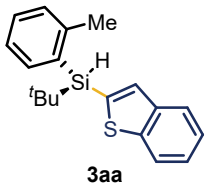
4.1 The substrate scope of heterocyclic compounds



Scheme S6. The substrate scope of heterocyclic compounds

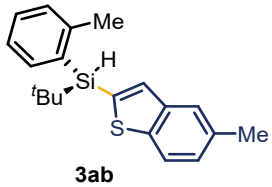
To a 10 mL vial microwave tube were in order added *tert*-butyl(*o*-tolyl)silane **1a** (17.8 mg, 0.1 mmol, 1.0 eq.), heterocyclic compounds (0.2 mmol, 2.0 eq.),

[Rh(cod)Cl]$_2$ (2.0 mg, 4 mol%), **L$_9$** (4.4 mg, 8 mol%), NBE (9.4 mg, 0.1 mmol, 1.0 eq.), toluene (1 mL) in glovebox. The tube was capped, removed from the glovebox and stirred in a preheated oil bath at 55 °C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated *in vacuo*; the residue was purified by flash chromatography on silica gel to afford the desired product. The ee values of desired compounds were determined by the Daicel Chiralpak column.



3aa

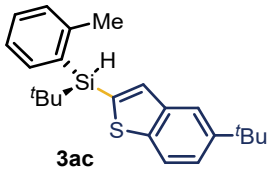
Compound **3aa** was isolated in 90% yield (28.1 mg, 0.090 mmol) as white solid (R_f = 0.6, petroleum ether). ee: 92%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 7.0 min, t (minor) = 7.6 min. [α] $_D^{25}$ = -10 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.6, 3.5 Hz, 1H), 7.81 – 7.79 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 7.35 – 7.30 (m, 3H), 7.22 – 7.18 (m, 2H), 5.06 (s, 1H), 2.48 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.61, 144.13, 140.81, 136.45, 134.67, 131.91, 130.21, 130.12, 124.99, 124.62, 124.19, 123.73, 122.16, 27.76, 23.61, 18.48; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{22}NaSSi$ [M+Na$^+$]: 333.1104, found: 333.1101.



3ab

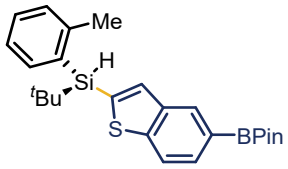
Compound **3ab** was isolated in 83% yield (26.8 mg, 0.083 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 91%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 9.6 min, t (minor) = 10.7 min. [α] $_D^{25}$ = -15.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.62 (s, 1H), 7.55 (s, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.17 (m, 3H), 5.07 (d, *J* = 1.5 Hz, 1H), 2.50 (s, 3H), 2.48 (s, 3H), 1.17 (d, *J* = 1.5 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.60, 141.41, 141.24, 136.45, 134.68, 134.31, 133.91, 132.01, 130.18, 130.07, 126.48, 124.96, 123.56, 121.75, 27.75, 23.60, 21.49, 18.48; HRMS (ESI, *m*/*z*) calcd

for $C_{20}H_{24}NaSSi$ [M+Na$^+$]: 347.1260, found 347.1261.



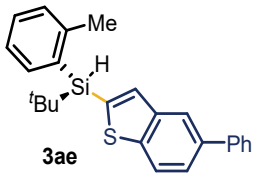
3ac

Compound **3ac** was isolated in 82% yield (30.1 mg, 0.082 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 93%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 5.3 min, t (minor) = 5.9 min. [α] $_D^{25}$ = -15.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.83 (m, 2H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.61 (s, 1H), 7.45 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.24 – 7.21 (m, 2H), 5.08 (s, 1H), 2.51 (s, 3H), 1.41 (s, 9H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.45, 144.60, 141.40, 141.01, 136.44, 134.86, 134.61, 132.03, 130.18, 130.06, 124.95, 123.19, 121.65, 119.72, 34.82, 31.73, 27.78, 23.60, 18.47; HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{30}NaSSi$ [M+Na$^+$]: 389.1730, found 389.1729.



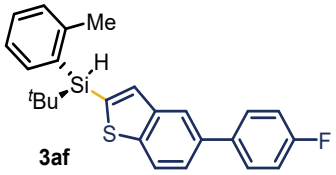
3ad

The reaction was carried out using *tert*-butyl(*o*-tolyl)silane **1a** (35.6 mg, 0.2 mmol, 2.0 eq.), 2-(benzo[b]thiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2d** (26.0 mg, 0.1 mmol, 1.0 eq.). Compound **3ad** was isolated in 90% yield (39.2 mg, 0.090 mmol) as pale yellow oil (R_f = 0.8, toluene/EA = 10/1). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak IF column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 35.8 min, t (minor) = 28.0 min. [α] $_D^{25}$ = -11.8 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.63 (s, 1H), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H), 7.23 – 7.19 (m, 2H), 5.07 (s, 1H), 2.49 (s, 3H), 1.38 (s, 12H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.07, 144.59, 140.45, 136.44, 135.02, 134.42, 131.85, 130.98, 130.21, 130.12, 130.09, 124.97, 121.52, 83.96, 27.73, 25.04, 25.01, 23.59, 18.47; HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{33}BNaO_2SSi$ [M+Na$^+$]: 459.1956, found 459.1954.



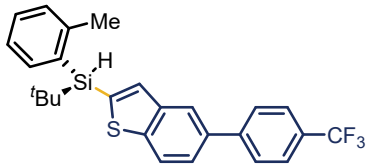
3ae

Compound **3ae** was isolated in 85% yield (32.8 mg, 0.085 mmol) as white solid (R_f = 0.5, petroleum ether). ee: 91%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 30.6 min, t (minor) = 27.7 min. $[\alpha]_D^{25}$ = -15.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 6.7 Hz, 1H), 7.70 – 7.69 (m, 3H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.24 (m, 2H), 5.12 (s, 1H), 2.54 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.62, 143.21, 141.49, 141.44, 137.77, 136.45, 135.63, 134.83, 131.85, 130.25, 130.16, 128.95, 127.54, 127.26, 125.02, 124.39, 122.38, 122.04, 27.78, 23.62, 18.49; HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{26}NaSSi$ [M+Na$^+$]: 409.1417, found: 409.1418.



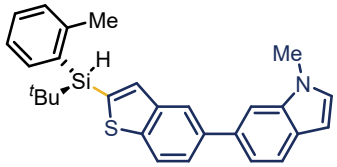
3af

Compound **3af** was isolated in 70% yield (28.3 mg, 0.070 mmol) as pale yellow oil (R_f = 0.7, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 22.7 min, t (minor) = 21.0 min. $[\alpha]_D^{25}$ = -16.4 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 2H), 7.75 (d, *J* = 7.7 Hz, 1H), 7.66 (s, 1H), 7.60 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 6.2 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 2H), 5.09 (s, 1H), 2.52 (s, 3H), 1.19 (d, *J* = 0.9 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.51 (d, *J* = 247.1 Hz), 144.63, 143.17, 141.47, 137.56, 137.53, 136.78, 136.43, 135.89, 134.72, 131.79, 130.22 (d, *J* = 7.5 Hz), 129.03 (d, *J* = 8.0 Hz), 125.02, 124.20, 122.44, 121.90, 115.80 (d, *J* = 21.4 Hz), 27.76, 23.62, 18.49; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.95; HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{25}NaFSSi$ [M+Na$^+$]: 427.1322, found: 427.1323.



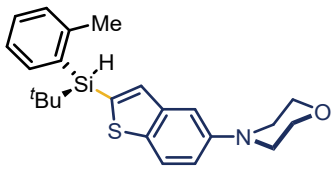
3ag

Compound **3ag** was isolated in 75% yield (34.1 mg, 0.075 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 87%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 28.3 min, t (minor) = 21.6 min. $[\alpha]_D^{25}$ = -11 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.02 (d, *J* = 1.3 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.73 (q, *J* = 8.6 Hz, 5H), 7.68 (s, 1H), 7.57 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.24 – 7.21 (m, 2H), 5.09 (s, 1H), 2.51 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.98, 144.65, 144.03, 141.51, 136.41, 136.38 (d, *J* = 6.2 Hz), 134.72, 131.71, 130.29, 130.23, 129.32 (q, *J* = 32.7 Hz), 127.76, 125.91 (q, *J* = 7.6 Hz), 125.04, 124.48 (q, *J* = 275.8 Hz), 124.11, 122.68, 122.29, 27.76, 23.62, 18.49; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -62.32; HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{25}NaF_3SSi$ [M+Na$^+$]: 477.1291, found: 477.1290.



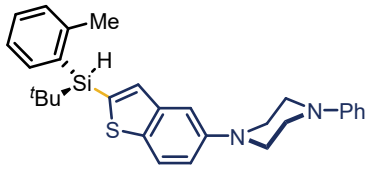
3ah

Compound **3ah** was isolated in 78% yield (34.3 mg, 0.078 mmol) as red-brown solid (R_f = 0.2, petroleum ether). ee: 94%; The enantiomeric excess was determined by Daicel Chiralpak IB column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 18.0 min, t (minor) = 15.3 min. $[\alpha]_D^{25}$ = -12.8 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.09 (d, *J* = 1.3 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.80 – 7.78 (m, 1H), 7.70 – 7.68 (m, 2H), 7.56 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.26 (t, *J* = 5.7 Hz, 2H), 7.11 (d, *J* = 3.1 Hz, 1H), 6.58 (d, *J* = 2.9 Hz, 1H), 5.12 (s, 1H), 3.84 (s, 3H), 2.55 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.62, 142.30, 141.55, 139.19, 136.47, 136.28, 135.13, 134.90, 132.99, 131.96, 130.21, 130.11, 129.64, 129.11, 124.99, 122.16, 122.08, 121.78, 119.75, 109.62, 101.41, 33.06, 27.78, 23.62, 18.50; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{30}NSSi$ [M+H$^+$]: 440.1863, found: 440.1865.



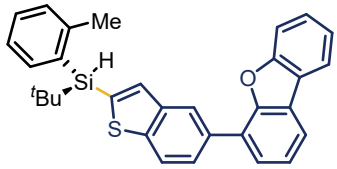
3ai

Compound **3ai** was isolated in 78% yield (30.9 mg, 0.078 mmol) as grey oil (R_f = 0.6, toluene/EA = 10/1). ee: 94%; The enantiomeric excess was determined by Daicel Chiralpak IC column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.9 min, t (minor) = 7.7 min. $[\alpha]_D^{25}$ = -13.4 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.52 (s, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 1.7 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.08 (dd, *J* = 8.8, 2.2 Hz, 1H), 5.05 (s, 1H), 3.92 – 3.89 (m, 4H), 3.19 – 3.17 (m, 4H), 2.50 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.23, 144.59, 141.97, 136.79, 136.43, 135.55, 134.41, 131.99, 130.18, 130.07, 124.95, 122.47, 116.93, 109.26, 67.11, 50.74, 27.75, 23.60, 18.46; HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{29}NNaOSSi$ [M+Na$^+$]: 418.1631, found: 418.1636.



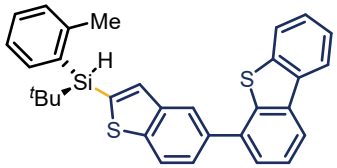
3aj

Compound **3aj** was isolated in 72% yield (34.0 mg, 0.072 mmol) as grey solid (R_f = 0.7, toluene/EA = 10/1). ee: 93%; The enantiomeric excess was determined by Daicel Chiralpak IF column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 9.2 min, t (minor) = 10.5 min. $[\alpha]_D^{25}$ = -9.6 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.73 (d, *J* = 6.8 Hz, 1H), 7.53 (s, 1H), 7.34 – 7.30 (m, 4H), 7.23 – 7.22 (m, 2H), 7.15 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 5.06 (s, 1H), 3.38 (d, *J* = 3.8 Hz, 8H), 2.50 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.35, 149.17, 144.60, 141.98, 136.88, 136.44, 135.48, 134.45, 132.01, 130.18, 130.07, 129.33, 124.95, 122.46, 120.24, 117.63, 116.50, 109.83, 50.80, 49.62, 27.77, 23.61, 18.47; HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{35}N_2SSi$ [M+H$^+$]: 471.2285, found: 471.2285.



3ak

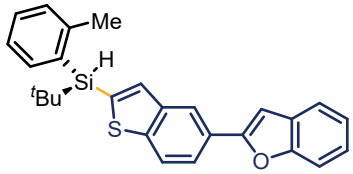
Compound **3ak** was isolated in 88% yield (42.0 mg, 0.088 mmol) as pale yellow oil (R_f = 0.5, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak IB column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 33.1 min, t (minor) =29.9 min. $[\alpha]_D^{25}$ = -7.4 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.05 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.72 (s, 1H), 7.65 – 7.58 (m, 3H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.44 – 7.39 (m, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.28 (s, 1H), 7.25 (s, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 5.15 (s, 1H), 2.56 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 156.55, 156.46, 144.61, 143.70, 141.22, 137.95, 136.48, 136.20, 135.87, 134.84, 131.81, 130.27, 130.20, 127.16, 125.97, 125.05, 124.43, 123.97, 123.83, 122.56, 122.45, 122.15, 122.07, 111.63, 110.59, 27.79, 23.68, 18.53; HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{28}NaOSSi$ [M+Na$^+$]: 499.1522, found: 499.1519.



3al

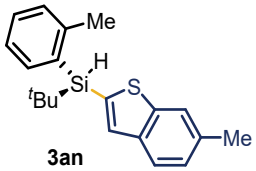
Compound **3al** was isolated in 86% yield (42.3 mg, 0.086 mmol) as pale yellow solid (R_f = 0.6, petroleum ether). ee: 91%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 14.4 min, t (minor) = 8.3 min. $[\alpha]_D^{25}$ = -8.4 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.22 – 8.17 (m, 3H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.84 (dd, *J* = 5.8, 3.0 Hz, 1H), 7.86 – 7.83 (m, 1H), 7.80 – 7.78 (m, 1H), 7.74 – 7.72 (m, 2H), 7.60 – 7.51 (m, 2H), 7.50 – 7.46 (m, 2H), 7.39 – 7.35 (m, 1H), 7.25 (d, *J* = 4.8 Hz, 1H), 5.14 (s, 1H), 2.55 (s, 3H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.62, 143.78, 141.29, 139.70, 138.98, 137.13, 136.94, 136.44, 136.34, 135.97, 135.95, 134.82, 131.78, 130.25, 130.18, 127.28, 126.92, 125.27, 125.13, 125.04, 124.51, 123.24, 122.75, 122.50, 121.88, 120.49, 27.78, 23.64, 18.51; HRMS (ESI, *m*/*z*)

calcd for $C_{31}H_{28}NaS_2Si$ [M+Na^+]: 515.1294, found: 515.1293.



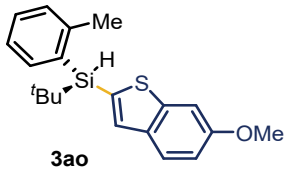
3am

Compound **3am** was isolated in 87% yield (37.1 mg, 0.087 mmol) as white solid (R_f = 0.1, petroleum ether). ee: 87%; The enantiomeric excess was determined by Daicel Chiralpak AD-3 column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.4 min, t (minor) = 7.4 min. $[\alpha]_D^{25}$ = -14.8 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.35 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.83 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.27 – 7.24 (m, 3H), 7.07 (s, 1H), 5.11 (s, 1H), 2.53 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 156.29, 154.98, 144.63, 144.24, 141.22, 136.42, 136.15, 134.83, 131.70, 130.28, 130.22, 129.47, 126.92, 125.04, 124.30, 123.09, 122.47, 121.76, 120.94, 119.95, 111.25, 101.25, 27.76, 23.63, 18.49; HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{26}NaOSSi$ [M+Na^+]: 449.1366, found: 449.1364.



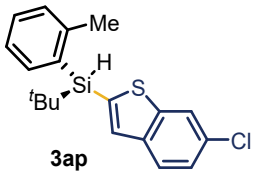
3an

Compound **3an** was isolated in 83% yield (26.8 mg, 0.083 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 93%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.1 min, t (minor) = 11.6 min. $[\alpha]_D^{25}$ = -17.6 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.73 – 7.68 (m, 3H), 7.56 (s, 1H), 7.36 – 7.30 (m, 1H), 7.22 (d, *J* = 6.9 Hz, 2H), 7.19 – 7.16 (m, 1H), 5.05 (s, 1H), 2.49 (s, 3H)), 2.48 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.59, 144.56, 138.71, 136.46, 134.68, 134.48, 133.18, 132.06, 130.18, 130.05, 126.04, 124.95, 123.28, 121.90, 27.76, 23.60, 21.70, 18.48; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{24}NaSSi$ [M+Na^+]: 347.1260, found 347.1260.



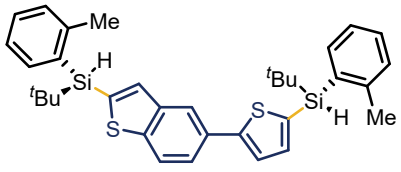
3ao

Compound **3ao** was isolated in 91% yield (31.1 mg, 0.091 mmol) as pale yellow solid (R_f = 0.2, petroleum ether). ee: 95%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 18.5 min, t (minor) = 27.3 min. $[\alpha]_D^{25}$ = -22 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.70 (m, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.51 (s, 1H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.32 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.98 (dd, *J* = 8.7, 2.3 Hz, 1H), 5.04 (s, 1H), 3.88 (s, 3H), 2.49 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.80, 145.80, 144.58, 136.45, 135.08, 134.37, 132.13, 131.58, 130.18, 130.04, 124.94, 124.24, 114.70, 104.17, 55.73, 27.76, 23.61, 18.49; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{24}NaOSSi$ [M+Na$^+$]: 363.1209, found: 363.1211.



3ap

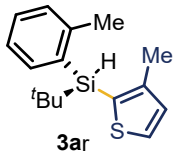
Compound **3ap** was isolated in 66% yield (22.8 mg, 0.066 mmol) as pale yellow solid (R_f = 0.6, petroleum ether). ee: 86%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.7 min, t (minor) = 10.1 min. $[\alpha]_D^{25}$ = -17.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 0.7 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.56 (s, 1H), 7.36 – 7.30 (m, 2H), 7.23 – 7.20 (m, 2H), 5.05 (s, 1H), 2.49 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.16, 144.61, 139.26, 136.36, 135.66, 134.10, 131.57, 130.93, 130.28, 130.24, 125.09, 125.04, 124.37, 121.67, 27.71, 23.60, 18.46; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{21}ClNaSSi$ [M+Na$^+$]: 367.0714, found: 367.0717.



3aq

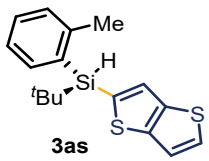
The reaction was carried out using **1a** (71.2 mg, 0.4 mmol, 4.0 eq.), 5-(thiophen-2-

yl)benzo[b]thiophene (21.6 mg, 0.1 mmol, 1.0 eq.), $[Rh(cod)Cl]_2$ (4.0 mg, 8 mol%), **L_9** (8.8 mg, 16 mol%), NBE (18.8 mg, 0.2 mmol，2.0 eq.), toluene (1 mL) at 55 °C for 12 h. Compound **3aq** was isolated in 79% yield (44.8 mg, 0.079 mmol) as pale yellow oil (R_f = 0.5, petroleum ether). d.r. 17:1; ee: 94%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C. For the major isomer, t (major) = 35.9 min, t (minor) = 41.3 min; for the minor isomer, t (major) = 34.3 min, t (minor) = 31.4 min. $[\alpha]_D^{25}$ = -33.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.08 (d, *J* = 1.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.65 – 7.63 (m, 2H), 7.44 (d, *J* = 3.5 Hz, 1H), 7.38 (d, *J* = 3.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.22 (m, 4H), 5.09 (s, 1H), 5.05 (s, 1H), 2.53 (s, 3H), 2.52 (s, 3H), 1.19 (s, 9H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 151.10, 144.62, 144.52, 143.40, 141.42, 138.75, 136.44, 136.42, 135.99, 134.67, 132.31, 131.81, 131.74, 130.67, 130.26, 130.18, 130.17, 129.98, 125.03, 124.95, 124.44, 123.26, 122.45, 120.83, 27.76, 27.71, 23.65, 23.62, 18.50, 18.48; HRMS (ESI, *m*/*z*) calcd for $C_{34}H_{40}NaS_2Si_2$ [M+Na$^+$]: 591.2002, found 591.2006.



3ar

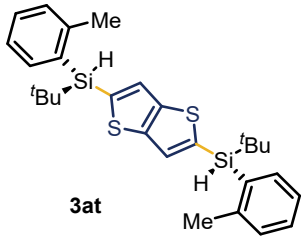
Compound **3ar** was isolated in 71% yield (19.5 mg, 0.071 mmol) as pale yellow oil (R_f = 0.7, petroleum ether). ee: 88%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 5.6 min, t (minor) = 6.5 min. $[\alpha]_D^{25}$ = -4.6 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.66 (d, *J* = 7.0 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.21 – 7.18 (m, 4H), 4.98 (s, 1H), 2.49 (s, 3H), 2.30 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.45, 139.95, 139.04, 136.43, 132.55, 132.20, 130.08, 129.85, 127.40, 124.87, 27.68, 23.61, 18.43, 15.21; HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{22}NaSi$ [M+Na$^+$]: 297.1104, found 297.1106.



3as

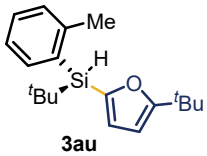
Compound **3as** was isolated in 62% yield (19.6 mg, 0.062 mmol) as colorless oil (R_f =

0.7, petroleum ether). ee: 96%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.8 min, t (minor) = 10.7 min. $[\alpha]_D^{25}$ = -13.2 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.9 Hz, 1H), 7.50 (s, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.26 (d, *J* = 5.2 Hz, 1H), 7.23 – 7.20 (m, 2H), 5.04 (s, 1H), 2.50 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.60, 144.57, 141.36, 136.37, 135.93, 132.01, 130.21, 130.08, 128.94, 128.83, 124.97, 119.27, 27.74, 23.60, 18.51; HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{20}NaSi$ [M+Na$^+$]: 339.0668, found: 339.0667.



3at

The reaction was carried out using **1a** (39.2 mg, 0.22 mmol, 2.2 eq.), thieno[3,2-b]thiophene (14.0 mg, 0.1 mmol, 1.0 eq.), $[Rh(cod)Cl]_2$ (4.0 mg, 8 mol%), $\mathbf{L_9}$ (8.8 mg, 16 mol%), NBE (18.8 mg, 0.2 mmol，2.0 eq.), toluene (1 mL) at 55 °C for 12 h. Compound **3at** was isolated in 85% yield (42.0 mg, 0.085 mmol) as colorless oil (R_f = 0.6, petroleum ether). d.r. >20:1; ee: 92%; The enantiomeric excess was determined by Daicel Chiralpak IF column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 12.6 min, t (minor) = 11.2 min. $[\alpha]_D^{25}$ = -21.4 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.68 (m, 2H), 7.46 (s, 2H), 7.34 – 7.30 (m, 2H), 7.20 (t, *J* = 7.1 Hz, 4H), 5.02 (s, 2H), 2.49 (s, 6H), 1.15 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.39, 144.57, 137.56, 136.37, 131.93, 130.21, 130.09, 128.55, 124.97, 27.75, 23.60, 18.52; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{36}NaSi_2$ [M+Na$^+$]: 515.1689, found: 515.1688.

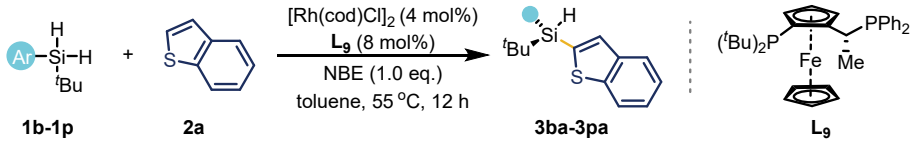


3au

Compound **3au** was isolated in 43% yield (12.9 mg, 0.043 mmol) as pale yellow oil (R_f = 0.7, petroleum ether). ee: 63%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 4.1 min, t (minor) = 4.4 min. $[\alpha]_D^{25}$ = -16.6 (*c* = 0.4, CH_2Cl_2). ^1H

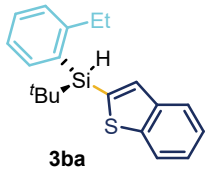
NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.17 (t, J = 7.9 Hz, 2H), 6.69 (d, J = 3.1 Hz, 1H), 6.01 (d, J = 3.1 Hz, 1H), 4.80 (s, 1H), 2.69 (t, J = 7.5 Hz, 2H), 2.47 (s, 3H), 1.70 – 1.62 (m, 2H), 1.41 – 1.33 (m, 2H), 1.08 (s, 9H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.02, 152.25, 144.35, 136.81, 132.23, 129.92, 129.79, 124.80, 124.66, 105.16, 30.36, 28.06, 27.58, 23.50, 22.38, 18.34, 13.98; HRMS (ESI, m/z) calcd for $C_{19}H_{28}NaOSi$[M+Na$^+$]: 323.1802, found: 323.1803.

4.2 The substrate scope of dihydrosilanes



Scheme S7. The substrate scope of dihydrosilanes

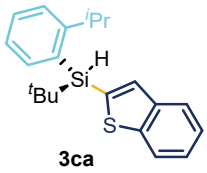
To a 10 mL vial microwave tube were in order added dihydrosilanes **1b-1p** (0.1 mmol, 1.0 eq.), thianaphthene **2a** (26.8 mg, 0.2 mmol, 2.0 eq.), $[Rh(cod)Cl]_2$ (2.0 mg, 4 mol%), **L$_9$** (4.4 mg, 8 mol%), NBE (9.4 mg, 0.1 mmol, 1.0 eq.), toluene (1 mL) in glovebox. The tube was capped, removed from the glovebox and stirred in a preheated oil bath at 55 °C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated *in vacuo*; the residue was purified by flash chromatography on silica gel to afford the desired product. The ee values of desired compounds were determined by the Daicel Chiralpak column.



3ba

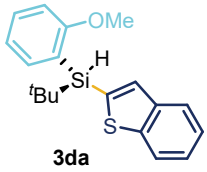
Compound **3ba** was isolated in 79% yield (25.7 mg, 0.079 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 93%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 7.4 min, t (minor) = 8.0 min. $[\alpha]_D^{25}$ = -15.4 (c = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 1H), 7.84 – 7.81 (m, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.63 (s, 1H), 7.42 – 7.32 (m, 3H), 7.28 (d, J = 7.8 Hz, 1H), 7.23 (d, J = 7.4

Hz, 1H), 5.10 (s, 1H), 2.96 – 2.77 (m, 2H), 1.22 (t, J = 7.5 Hz, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.07, 144.12, 140.79, 136.46, 134.98, 134.64, 131.19, 130.29, 128.61, 125.07, 124.60, 124.18, 123.71, 122.15, 29.88, 27.82, 18.37, 16.75; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{24}NaSSi$ [M+Na$^+$]: 347.1260, found: 347.1260.



3ca

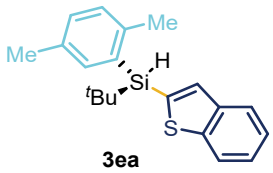
Compound **3ca** was isolated in 73% yield (24.7 mg, 0.073 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 94%; The enantiomeric excess was determined by Daicel Chiralpak IF column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 5.1 min, t (minor) = 5.5 min. [α] $_D^{25}$ = -19.8 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.89 (m, 1H), 7.83 – 7.81 (m, 1H), 7.73 (d, J = 7.4 Hz, 1H), 7.63 (s, 1H), 7.46 – 7.32 (m, 4H), 7.22 (t, J = 6.9 Hz, 1H), 5.12 (s, 1H), 3.37 (dt, J = 13.5, 6.7 Hz, 1H), 1.23 (dd, J = 12.1, 6.8 Hz, 6H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.70, 144.11, 140.79, 136.56, 135.13, 134.68, 130.90, 130.46, 125.27, 125.17, 124.60, 124.17, 123.70, 122.15, 33.98, 27.85, 25.20, 23.81, 18.33; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{26}NaSSi$ [M+Na$^+$]: 361.1417, found: 361.1419.



3da

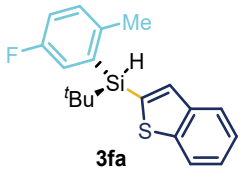
Compound **3da** was isolated in 64% yield (20.8 mg, 0.064 mmol) as white solid (R_f = 0.2, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 16.7 min, t (minor) = 14.9 min. [α] $_D^{25}$ = +7.4 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 1H), 7.89 – 7.82 (m, 1H), 7.70 (s, 1H), 7.62 – 7.60 (m, 1H), 7.44 – 7.40 (m, 1H), 7.36 – 7.31 (m, 2H), 6.98 (t, J = 7.3 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 4.83 (s, 1H), 3.90 (s, 3H), 1.11 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.80, 144.42, 140.80, 138.08, 135.11, 134.71, 132.05, 124.40, 123.95, 123.62, 122.06, 121.68, 120.78, 109.61, 54.81, 27.93, 18.44; HRMS (ESI, *m*/*z*) calcd

for $C_{19}H_{22}NaOSSi$ [M+Na^+]: 349.1053, found: 349.1053.



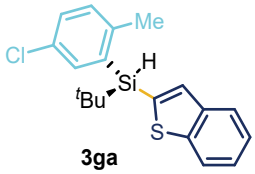
3ea

Compound **3ea** was isolated in 73% yield (23.7 mg, 0.073 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 6.7 min, t (minor) = 8.6 min. [α] $_D^{25}$ = +3.0 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (dd, *J* = 3.9, 3.2 Hz, 1H), 7.84 (dd, *J* = 4.6, 2.7 Hz, 1H), 7.63 (s, 1H), 7.54 (s, 1H), 7.38 – 7.33 (m, 2H), 7.14 (q, *J* = 7.8 Hz, 2H), 5.06 (d, *J* = 1.7 Hz, 1H), 2.46 (s, 3H), 2.35 (s, 3H), 1.19 (d, *J* = 1.6 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.14, 141.42, 140.82, 137.06, 134.85, 134.62, 134.10, 131.63, 130.92, 130.14, 124.58, 124.16, 123.72, 122.16, 27.79, 23.11, 21.27, 18.48; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{24}NaSSi$ [M+Na^+]: 347.1260, found: 347.1259.



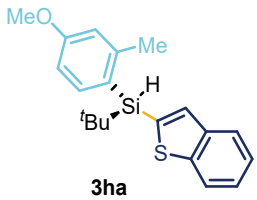
3fa

Compound **3fa** was isolated in 90% yield (29.5 mg, 0.090 mmol) as pale yellow solid (R_f = 0.6, petroleum ether). ee: 91%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 7.1 min, t (minor) = 8.0 min. [α] $_D^{25}$ = -13.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.92 – 7.90 (m, 1H), 7.86 – 7.84 (m, 1H), 7.64 (s, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.34 (m, 2H), 7.19 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.04 – 6.99 (m, 1H), 5.06 (s, 1H), 2.47 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 160.53 (d, *J* = 246.6Hz), 144.10, 140.74, 140.01 (d, *J* = 3.4 Hz), 134.84, 134.35 (d, *J* = 3.8 Hz), 133.70, 131.75 (d, *J* = 6.7 Hz), 124.81, 124.31, 123.81, 122.40 (d, *J* = 19.4 Hz), 122.19, 116.82 (d, *J* = 20.8 Hz), 27.68, 22.72, 18.48; ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -118.23; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{21}NaFSSi$ [M+Na^+]: 351.1009, found: 351.1011.



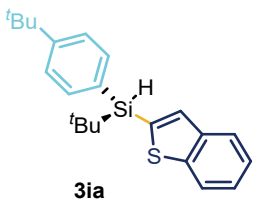
3ga

Compound **3ga** was isolated in 82% yield (28.3 mg, 0.082 mmol) as pale yellow solid (R_f = 0.6, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 6.4 min, t (minor) = 7.1 min. $[\alpha]_D^{25}$ = +14.4 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 1H), 7.86 – 7.83 (m, 1H), 7.66 (d, *J* = 2.2 Hz, 1H), 7.63 (s, 1H), 7.39 – 7.34 (m, 2H), 7.29 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 1H), 5.04 (s, 1H), 2.45 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.12, 142.82, 140.74, 135.74, 134.88, 134.55, 133.58, 131.71, 131.19, 130.03, 124.83, 124.31, 123.83, 122.21, 27.70, 22.99, 18.51; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{21}NaClSSi$ [M+Na^+]: 367.0714, found: 367.0718.



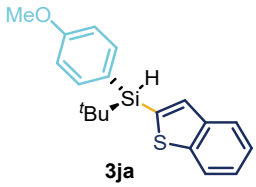
3ha

Compound **3ha** was isolated in 54% yield (18.4 mg, 0.054 mmol) as pale yellow oil (R_f = 0.2, petroleum ether). ee: 91%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 17.3 min, t (minor) = 16.0 min. $[\alpha]_D^{25}$ = -3.8 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 4.5, 3.9 Hz, 1H), 7.83 (dd, *J* = 5.3, 3.7 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.62 (s, 1H), 7.38 – 7.32 (m, 2H), 6.79 (d, *J* = 6.1 Hz, 2H), 5.04 (s, 1H), 3.83 (s, 3H), 2.49 (s, 3H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.11, 146.62, 144.10, 140.84, 137.93, 135.18, 134.47, 124.55, 124.15, 123.69, 122.83, 122.15, 116.11, 110.55, 55.07, 27.75, 23.79, 18.49; HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{24}NaOSSi$ [M+Na^+]: 363.1209, found: 363.1210.



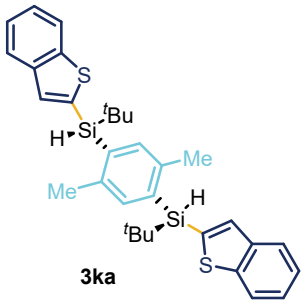
3ia

Compound **3ia** was isolated in 61% yield (21.5 mg, 0.061 mmol) as white solid (R_f = 0.6, petroleum ether). ee: 75%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 6.3 min, t (minor) = 9.6 min. $[\alpha]_D^{25}$ = -1.6 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.89 (m, 1H), 7.86 – 7.82 (m, 1H), 7.66 (d, *J* = 7.6 Hz, 3H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.38 – 7.32 (m, 2H), 4.84 (s, 1H), 1.33 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.94, 144.16, 140.82, 135.64, 134.57, 134.31, 129.27, 125.06, 124.59, 124.18, 123.74, 122.18, 34.87, 31.34, 27.32, 17.99; HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{28}NaSSi$ [M+Na^+]: 375.1573, found: 375.1574.



3ja

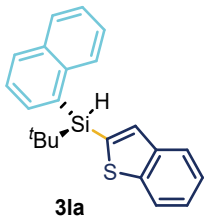
Compound **3ja** was isolated in 52% yield (17.0 mg, 0.052 mmol) as white solid (R_f = 0.2, petroleum ether). ee: 76%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 27.9 min, t (minor) = 20.2 min. $[\alpha]_D^{25}$ = -1.2 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 1H), 7.85 – 7.83 (m, 1H), 7.67 – 7.64 (m, 3H), 7.38 – 7.33 (m, 2H), 6.97 – 6.95 (m, 2H), 4.83 (s, 1H), 3.84 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.14, 144.13, 140.81, 137.27, 134.51, 134.45, 124.62, 124.20, 123.74, 123.67, 122.18, 113.87, 55.16, 27.27, 17.98; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{22}NaOSSi$ [M+Na^+]: 349.1053, found: 349.1053.



3ka

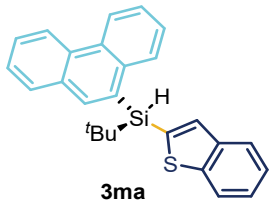
The reaction was carried out on 0.05 mmol scale using $[Rh(cod)Cl]_2$ (2.0 mg, 8 mol%), **L₉** (4.4 mg, 16 mol%), NBE (9.4 mg, 0.1 mmol，2 eq.), toluene (1 mL) at 55 °C for 12 h. Compound **3ka** was isolated in 81% yield (22.1 mg, 0.041 mmol) as

white solid (R_f = 0.6, petroleum ether). d.r. ~ 10:1; ee: 99%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 9.3 min, t (minor) = 12.0 min. $[\alpha]_D^{25}$ = -21.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.85 – 7.80 (m, 2H), 7.61 (s, 2H), 7.53 (s, 2H), 7.37 – 7.31 (m, 4H), 5.03 (s, 2H), 2.46 (s, 6H), 1.17 (s, 16.39H), 1.49 (s, 1.61H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.14, 140.78, 140.32, 137.78, 134.73, 134.51, 133.87, 124.62, 124.18, 123.75, 122.16, 27.81, 27.75, 23.26, 18.52; HRMS (ESI, *m/z*) calcd for $C_{32}H_{38}NaS_2Si_2$ [M+Na$^+$]: 565.1846, found: 565.1844.



3la

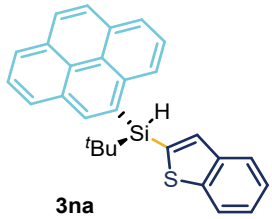
Compound **3ia** was isolated in 95% yield (32.8 mg, 0.095 mmol) as white solid (R_f = 0.6, petroleum ether). ee: 91%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 20.1 min, t (minor) = 17.1 min. $[\alpha]_D^{25}$ = -31.2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.31 (m, 1H), 8.00 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.96-7.87 (m, 3H), 7.84 – 7.80 (m, 1H), 7.70 (s, 1H), 7.53 – 7.49 (m, 3H), 7.38 – 7.33 (m, 2H), 5.43 (s, 1H), 1.23 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.17, 140.81, 137.48, 136.50, 135.02, 134.35, 133.51, 131.50, 130.82, 129.03, 128.73, 126.13, 125.80, 125.10, 124.72, 124.23, 123.81, 122.18, 28.10, 18.79; HRMS (ESI, *m/z*) calcd for $C_{22}H_{22}NaSSi$ [M+Na$^+$]: 369.1104, found: 369.1111.



3ma

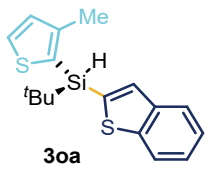
Compound **3ma** was isolated in 80% yield (31.8 mg, 0.080 mmol) as pale yellow oil (R_f = 0.4, petroleum ether). ee: 89%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 10.6 min, t (minor) = 14.9 min. $[\alpha]_D^{25}$ = +4.2 (*c*

= 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.1 Hz, 1H), 8.72 (d, J = 8.3 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 8.29 (s, 1H), 7.92 (dd, J = 5.8, 2.3 Hz, 2H), 7.82 (dd, J = 6.1, 2.9 Hz, 1H), 7.73 (s, 1H), 7.71 – 7.69 (m, 1H), 7.67 – 7.57 (m, 3H), 7.38 – 7.34 (m, 2H), 5.43 (s, 1H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.20, 140.81, 139.09, 135.11, 135.06, 134.27, 131.46, 130.95, 130.52, 130.18, 129.74, 129.21, 127.83, 126.83, 126.53, 124.75, 124.24, 123.84, 123.20, 122.62, 122.20, 28.28, 18.88; HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{24}NaSSi$ [M+Na$^+$]: 419.1260, found: 419.1263.



3na

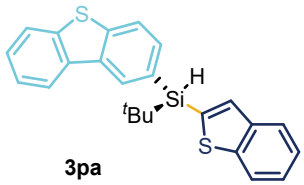
Compound **3na** was isolated in 76% yield (32.1 mg, 0.076 mmol) as pale yellow solid (R_f = 0.3, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 5.5 min, t (minor) = 5.1 min. $[\alpha]_D^{25}$ = -50.4 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 9.2 Hz, 1H), 8.46 (d, J = 7.7 Hz, 1H), 8.21 (dd, J = 7.6, 4.8 Hz, 3H), 8.15 – 8.10 (m, 3H), 8.07 – 8.01 (m, 1H), 7.96 – 7.93 (m, 1H), 7.84 – 7.82 (m, 1H), 7.76 (s, 1H), 7.39 – 7.35 (m, 2H), 5.66 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.21, 140.82, 136.65, 135.20, 134.59, 134.44, 132.79, 131.36, 130.79, 128.66, 128.58, 128.13, 127.63, 127.59, 126.08, 125.50, 124.76, 124.27, 124.18, 123.84, 122.21, 28.09, 19.11; HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{24}NaSSi$ [M+Na$^+$]: 443.1260, found: 443.1263.



3oa

The reaction was carried out at 60 °C for 12 h. Compound **3oa** was isolated in 48% yield (15.2 mg, 0.048 mmol) as grey yellow oil (R_f = 0.5, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.1 min, t (minor)

= 9.2 min. $[\alpha]_D^{25}$ = -9.3 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.87 (m, 1H), 7.83 – 7.81 (m, 1H), 7.62 (s, 1H), 7.59 (d, *J* = 4.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.05 (d, *J* = 4.6 Hz, 1H), 5.06 (s, 1H), 2.37 (s, 3H), 1.16 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.02, 144.25, 140.83, 134.70, 133.96, 131.49, 131.30, 124.71, 124.22, 124.13, 123.83, 122.22, 27.35, 18.31, 16.98; HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{20}NaS_2Si$ [M+Na^+]: 339.0668, found: 339.0670.

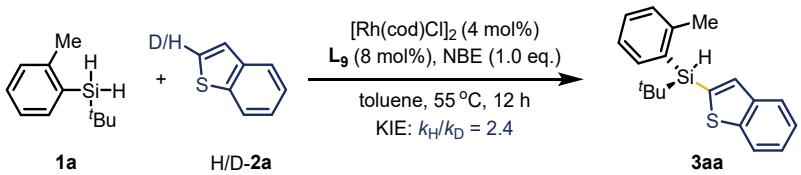


3pa

The reaction was carried out using $[Rh(cod)Cl]_2$ (1.0 mg, 2 mol%), **L₉** (2.2 mg, 4 mol%), NBE (9.4 mg, 0.1 mmol，1 eq.), toluene (1 mL) at 50 °C for 12 h. Compound **3pa** was isolated in 82% yield (33.0 mg, 0.082 mmol) as pale yellow oil (R_f = 0.5, petroleum ether). ee: 90%; The enantiomeric excess was determined by Daicel Chiralpak IF column (*n*-hexane/isopropanol = 99/1, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 5.1 min, t (minor) = 5.6 min. $[\alpha]_D^{25}$ = +3.6 (*c* = 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.9 Hz, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 7.8 Hz, 1H), 8.32 (s, 1H), 7.95 – 7.93 (m, 2H), 7.84 – 7.82 (m, 1H), 7.75 – 7.70 (m, 1H), 7.68 – 7.66 (m, 1H), 7.64 – 7.59 (m, 1H), 7.39 – 7.35 (m, 2H), 5.46 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.22, 140.83, 139.10, 135.12, 134.29, 131.48, 130.97, 130.54, 130.20, 129.75, 129.21, 127.84, 126.84, 126.54, 124.75, 124.25, 123.85, 123.21, 122.63, 122.20, 28.30, 18.88; HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{22}NaS_2Si$ [M+Na^+]: 425.0824, found: 425.0822.

5. Mechanism studies

5.1. Deuterium-labeling experiment study



1a H/D-**2a** **3aa**

Scheme S8. Deuterium-labeling experiment study

To 10 mL vial microwave tube were in order added *tert*-butyl(*o*-tolyl)silane **1a**

(17.8 mg, 0.1 mmol, 1.0 eq.), thianaphthene **2a**-H (26.8 mg, 0.2 mmol, 2.0 eq.) or thianaphthene **2a**-D (27.0 mg, 0.2 mmol, 2.0 eq.), $[Rh(cod)Cl]_2$ (2.0 mg, 4 mol%), $\mathbf{L_9}$ (4.4 mg, 8 mol%), NBE (9.4 mg, 0.1 mmol, 1.0 eq.), toluene (1 mL) in glovebox. The tube was capped, then removed from the glovebox and stirred in a preheated oil bath at 55 °C for 40, 50, 60, and 70 minutes. After being cooled to room temperature, the reaction mixture was concentrated *in vacuo*. The yields were determined by analysis of crude ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

Table S1. Deuterium-labeling experiment study

Time (min)	Yield (H, %)	Yield (D, %)
40	5	3
50	7	4
60	10	5
70	12	6

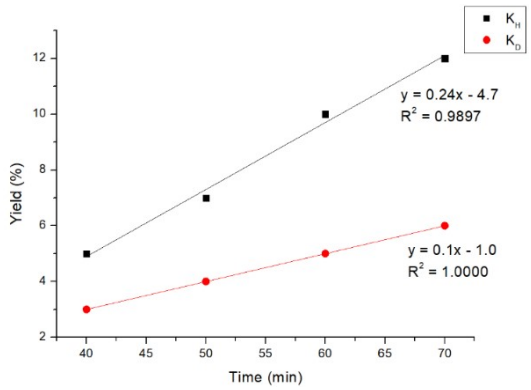
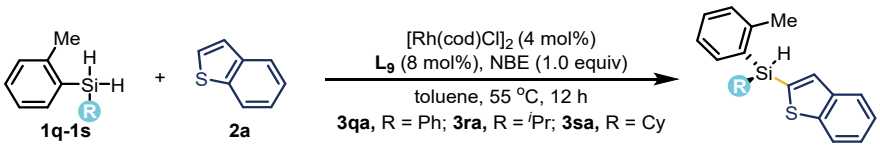


Figure S1. Deuterium-labeling experiment study

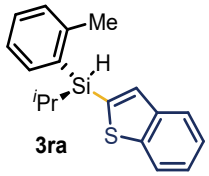
5.2. Evaluation of different R groups



Scheme S9. Evaluation of different R groups

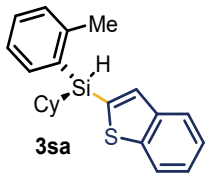
To 10 mL vial microwave tube were in order added dihydrosilane **1q** (19.8 mg, 0.1 mmol, 1.0 eq.) or **1r** (16.4 mg, 0.1 mmol, 1.0 eq.) or **1s** (20.4 mg, 0.1 mmol, 1.0 eq.), thianaphthene (**2a,** 26.8 mg, 0.2 mmol, 2.0 eq.), $[Rh(cod)Cl]_2$ (2.0 mg, 4 mol%), $\mathbf{L_9}$ (4.4 mg, 8 mol%), NBE (9.4 mg, 0.1 mmol, 1.0 eq.), toluene (1 mL) in glovebox. The tube was capped, removed from the glovebox and stirred in a preheated oil bath at 55

°C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated *in vacuo*; the residue was purified by flash chromatography on silica gel to afford the desired product. The ee values of desired compounds were determined by the Daicel Chiralpak OD-3 column.



3ra

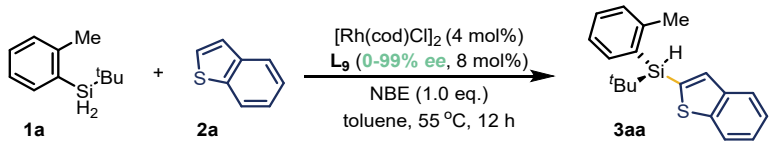
Compound **3ra** was isolated in 3% yield (0.9 mg, 0.003 mmol) as pale yellow oil (R_f = 0.6, petroleum ether). ee: 38%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 8.1 min, t (minor) = 8.5 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.86 (m, 1H), 7.81 – 7.79 (m, 1H), 7.62 – 7.60 (m, 1H), 7.53 (s, 1H), 7.37 – 7.29 (m, 3H), 7.21 (t, J = 7.1 Hz, 2H), 4.98 (d, J = 3.9 Hz, 1H), 2.43 (s, 3H), 1.63 – 1.58 (m, 1H), 1.21 (d, J = 7.3 Hz, 3H), 1.14 (d, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.50, 144.24, 140.99, 136.22, 135.04, 134.08, 132.11, 130.35, 129.99, 125.26, 124.57, 124.18, 123.72, 122.25, 23.07, 18.82, 18.75, 12.22; HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{20}NaSSi$ [M+Na$^+$]: 319.0947, found: 319.0945.



3sa

Compound **3sa** was isolated in 27% yield (9.0 mg, 0.027 mmol) as colorless oil (R_f = 0.6, petroleum ether). ee: 39%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 10.2 min, t (minor) = 8.9 min. $[\alpha]_D^{25}$ = -2 (*c* = 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 1H), 7.83 – 7.79 (m, 1H), 7.62 (d, J = 7.0 Hz, 1H), 7.54 (s, 1H), 7.36 – 7.30 (m, 3H), 7.21 (t, J = 7.3 Hz, 2H), 4.99 (d, J = 3.4 Hz, 1H), 2.44 (s, 3H), 1.96 – 1.72 (m, 5H), 1.43 – 1.27 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.52, 144.23, 141.00, 136.30, 135.05, 134.04, 131.94, 130.30, 129.97, 125.23, 124.54, 124.17, 123.70, 122.24, 28.69, 27.97, 27.92, 26.82, 23.83, 23.13; HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{24}NaSSi$ [M+Na$^+$]: 359.1260, found: 359.1258.

5.3 Observation of non-linear effect



Scheme S10. Observation of non-linear effect

According to the principle of non-linear effect, the reaction was performed 11 times with different ee values of $\mathbf{L_9}$. To 10 mL vial microwave tube were in order added *tert*-butyl(*o*-tolyl)silane **1a** (17.8 mg, 0.1 mmol, 1.0 eq.), thianaphthene **2a** (26.8 mg, 0.2 mmol, 2.0 eq.), $[Rh(cod)Cl]_2$ (2.0 mg, 4 mol%), $\mathbf{L_9}$ (0~99% ee, 4.4 mg, 8 mol%), NBE (9.4 mg, 0.1 mmol, 1.0 eq.), toluene (1 mL) in glovebox respectively. The tube was capped, removed from the glovebox and stirred in a preheated oil bath at 55 °C for 12 h. After being cooled to room temperature, the reaction mixture was concentrated *in vacuo*; the residue was purified by flash chromatography on silica gel to afford the desired product. The ee value of compound **3aa** was determined by the Daicel Chiralpak OD-3 column.

Table S2. Observation of non-linear effect

Entry	ee of $\mathbf{L_9}$ (%)	ee of **3aa** (%)
1	0	0
2	10	11
3	20	20
4	30	29
5	40	38
6	50	48
7	60	57

8	70	66
9	80	80
10	90	87
11	99	92

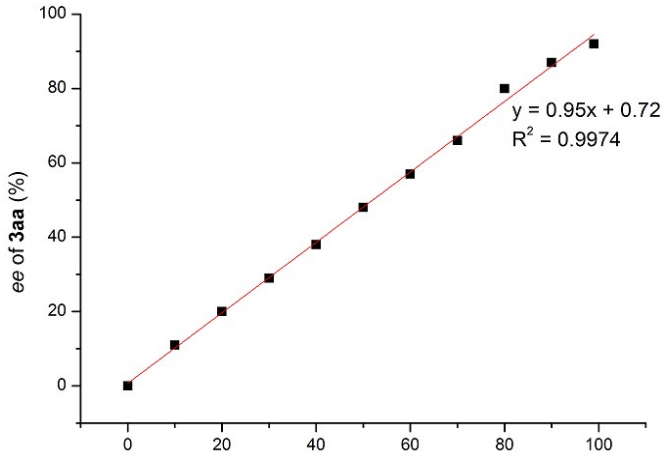
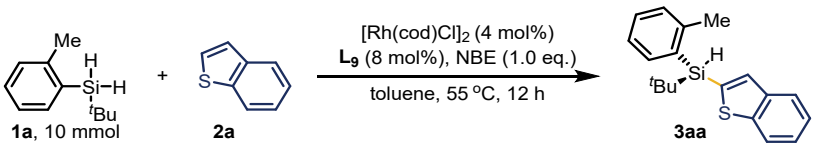


Figure S2. Observation of non-linear effect

6. Gram-scale synthesis and further transformation

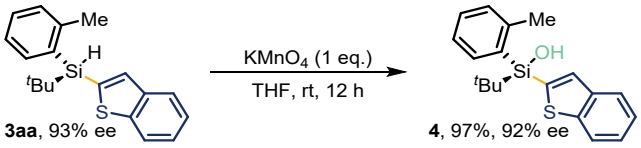
6.1 Gram-scale synthesis



Scheme S11. Gram-scale synthesis

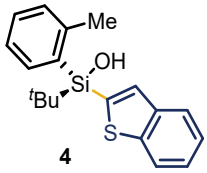
To 100 mL vial microwave tube were in order added *tert*-butyl(*o*-tolyl)silane **1a** (1.78 g, 10.0 mmol, 1.0 eq.), thianaphthene **2a** (2.68 g, 20.0 mmol, 2.0 eq.), $[Rh(cod)Cl]_2$ (200.0 mg, 0.4 mmol, 4 mol%), $\mathbf{L_9}$ (440.0 mg, 0.8 mmol, 8 mol%), NBE (941.0 mg, 10.0 mmol, 1.0 eq.), toluene (20 mL) in glovebox. The tube was capped, then removed from the glovebox and stirred in preheated oil bath at 55 °C for 12 h. After been cooled to room temperature, the reaction mixture was concentrated *in vacuo*, the residue was purified by flash chromatography on silica gel to afford the desired product. ee: 93%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 7.0 min, t (minor) = 7.6 min.

6.2 Further transformation [3]



Scheme S12. Further transformation

To 10 mL vial microwave tube were in order added **3aa** (31.1 mg, 0.1 mmol, 1.0 eq.), $KMnO_4$ (15.8 mg, 0.1 mmol, 1.0 eq.), THF (1 mL) under air. The tube was capped and stirred at room temperature for 12 h. When the reaction was completed, the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated *in vacuo*; the residue was purified by flash chromatography on silica gel to afford compound **4**.



Compound **4** was isolated in 97% yield (31.6 mg, 0.097 mmol) as colorless oil (R_f = 0.3, petroleum ether/EA = 10/1). ee: 92%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane/isopropanol = 98/2, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, t (major) = 15.0 min, t (minor) = 12.5 min. $[\alpha]_D^{25}$ = -15.6 (*c* = 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 7.95 – 7.92 (m, 1H), 7.89 – 7.86 (m, 1H), 7.68 (d, *J* = 0.5 Hz, 1H), 7.59 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.24 (td, *J* = 7.5, 1.4 Hz, 1H), 7.13 – 7.09 (m, 2H), 6.87 (s, 1H), 2.36 (s, 3H), 1.01 (s, 9H); ^{13}C NMR (101 MHz, DMSO) δ 144.21, 142.83, 140.36, 138.63, 135.61, 133.52, 133.36, 130.35, 129.67, 124.63, 124.31, 124.17, 123.86, 122.12, 26.59, 23.19, 19.52; HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{23}OSSi$ [M+H$^+$]: 327.1233, found: 327.1233.

7. Single-crystal X-ray diffraction

Single crystal X-ray diffraction of compound **3la** was obtained by slow evaporation of a solution of compound **3la** in dichloromethane at room temperature. The X-ray crystal structure is deposited in the Cambridge Crystallographic Data Centre with a number of CCDC 2158719. Diffraction Data were collected at 100.2 K on a BrukerD8 venture micro source diffractometer employing Mo-Kα radiation (λ = 0.83 Å). The crystal structure is shown in **Figure S3**. The detailed information is listed in **Tables S3**.

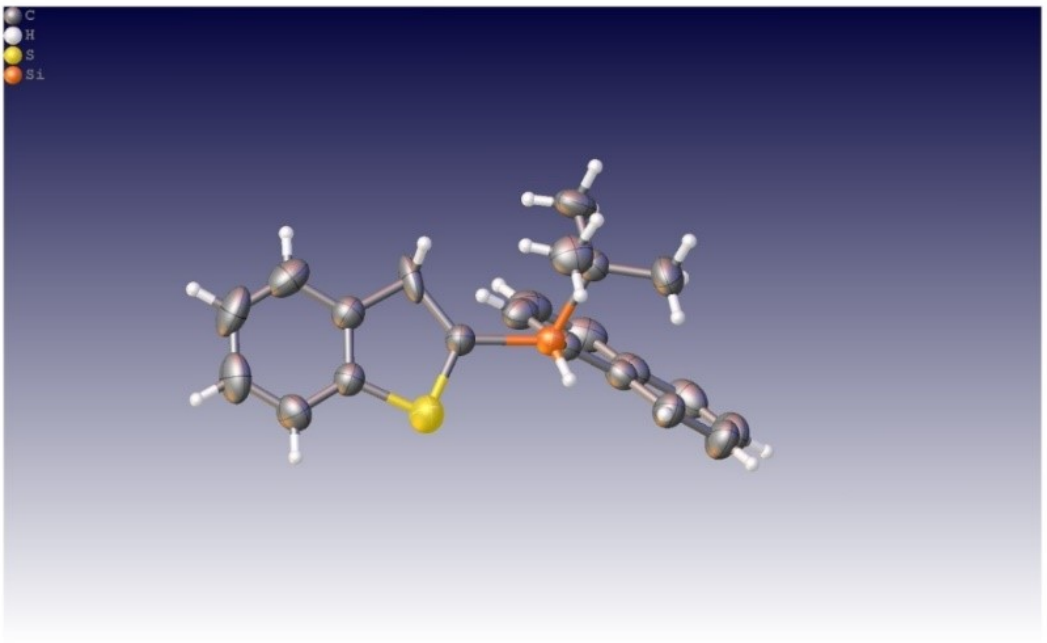


Figure S3. Crystal structure of compound **3la** (CCDC 2158719)

Table S3. Crystallographic data and structure refinement of compound **3la**

Compound	**compound 3la**
CCDC deposition No.	2158719
Empirical formula	$C_{22}H_{22}S_2Si_{0.25}$
Formula weight	357.54
Temperature	100 (2) K
Crystal system, space group	orthorhombic, $P2_12_12_1$
Unit cell dimensions	a = 6.21480(10) Å alpha = 90° b = 7.6293(2) Å beta = 90° c = 38.5427(4) Å gamma = 90°

Volume	1827.49(6) $Å^3$
Z, Z'; Calculated density	4, 1; 1.3000 g cm^{-3}
Crystal size	0.30×0.20×0.20 mm^3
Radiation	MoKα (λ = 1.54184 Å)
2Θ range for data collection	2.293 to 76.900°
Reflections collected	9046
Independent reflections	3650 [R_{int} = 0.0168]
Restaints / parameters	0 / 221
Goodness-of-fit on F^2	1.087
R indices (all data)	R_1 = 0.0521, wR_2 = 0.1482
Largest diff. peak/hole	1.350 and -0.819 e $Å^{-3}$
Flack parameter	0.034(8)

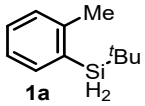
8. References

[1] N. Hirone, H. Sanjiki, R. Tanaka, T. Hata, H. Urabe, *Angew. Chem. Int. Ed.* **2010**, *49*, 7762–7764.

[2] W. Ma, L. Liu, K. An, T. He, W. He, *Angew. Chem. Int. Ed.* **2021**, *60*, 4245–4251.

[3] P. Lickiss, R. Lucas, *J. Organomet. Chem.* **1995**, *521*, 229–234.

9. NMR spectra



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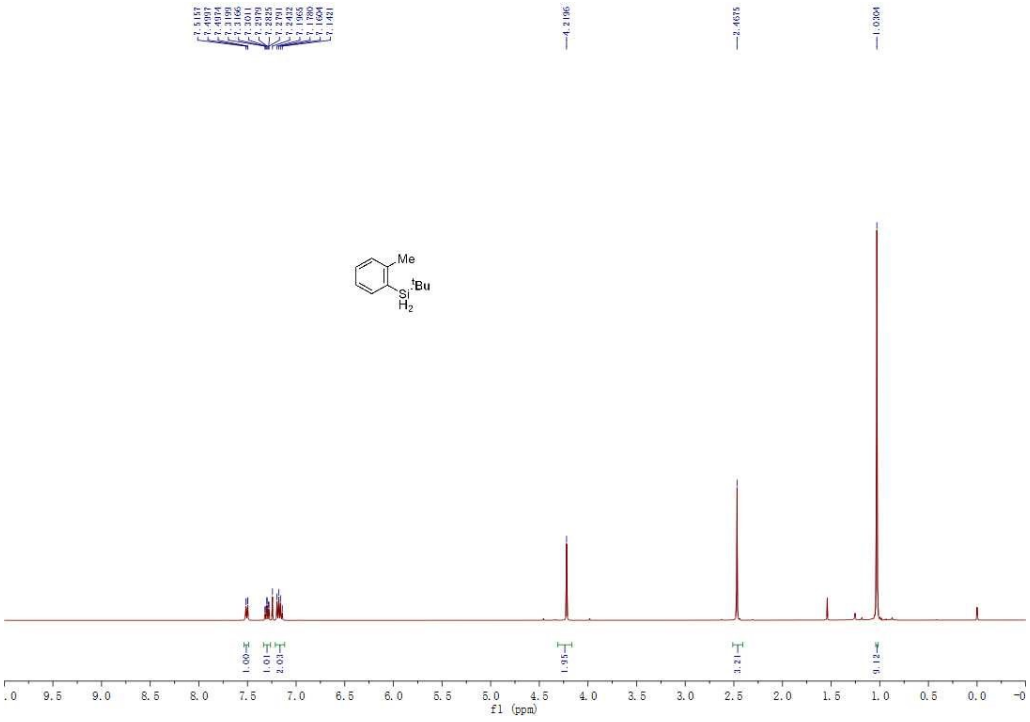

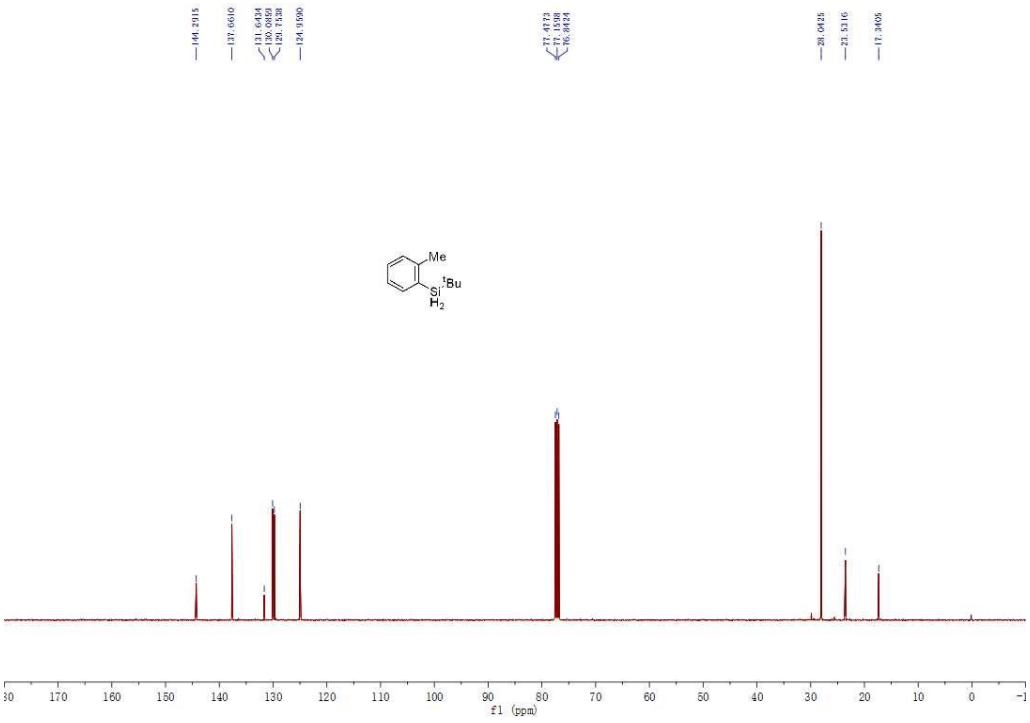

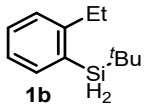

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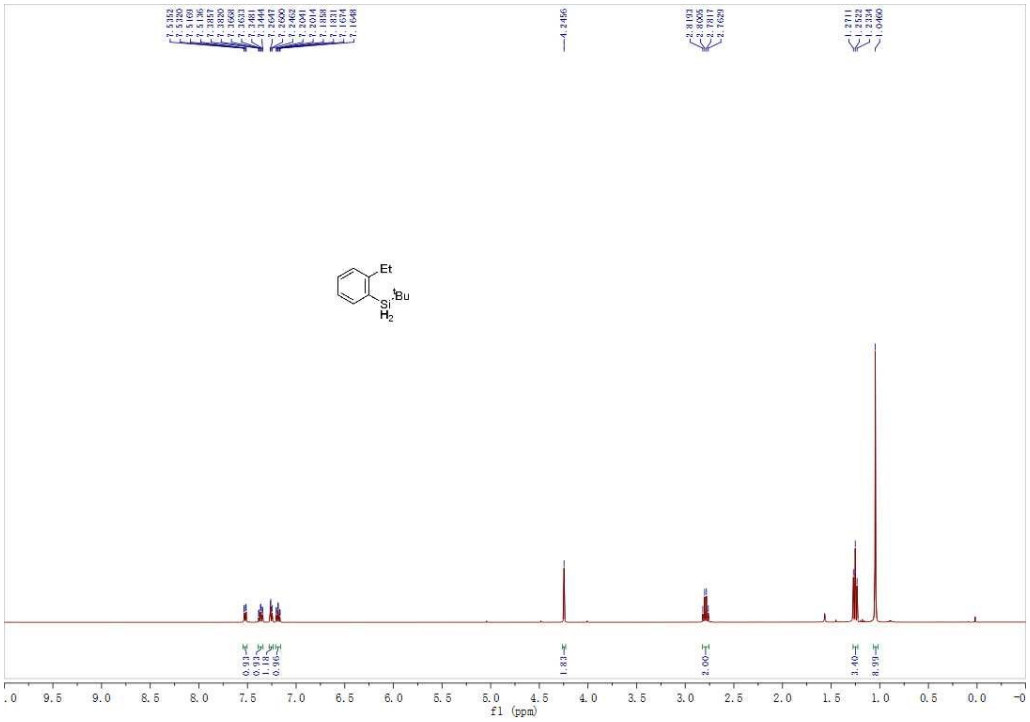

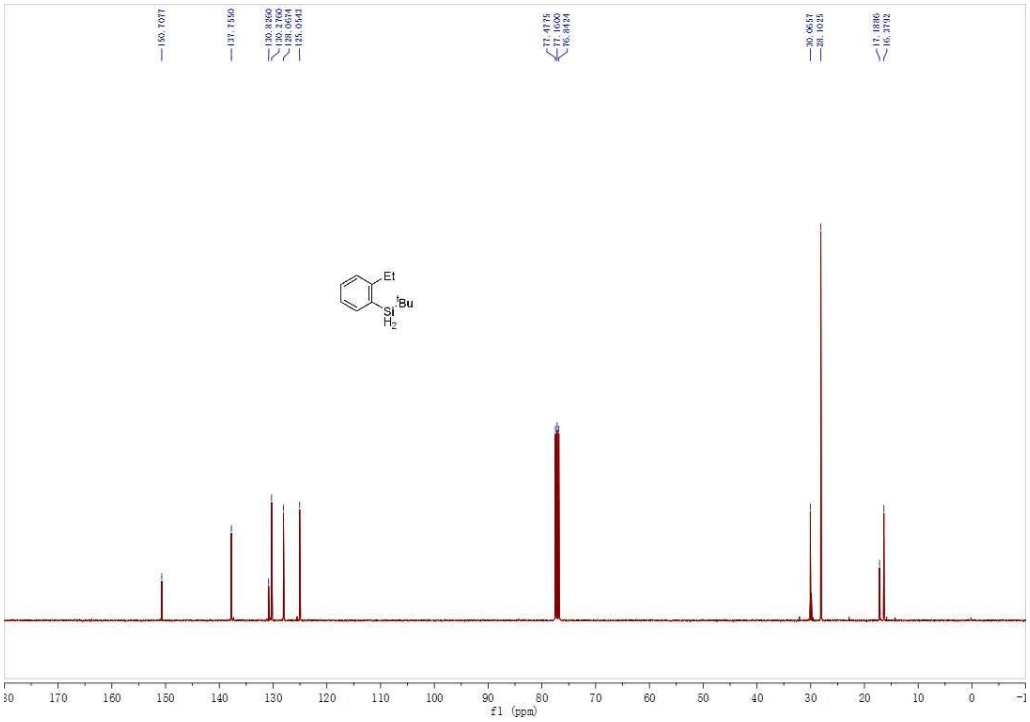

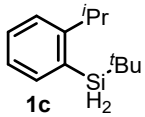

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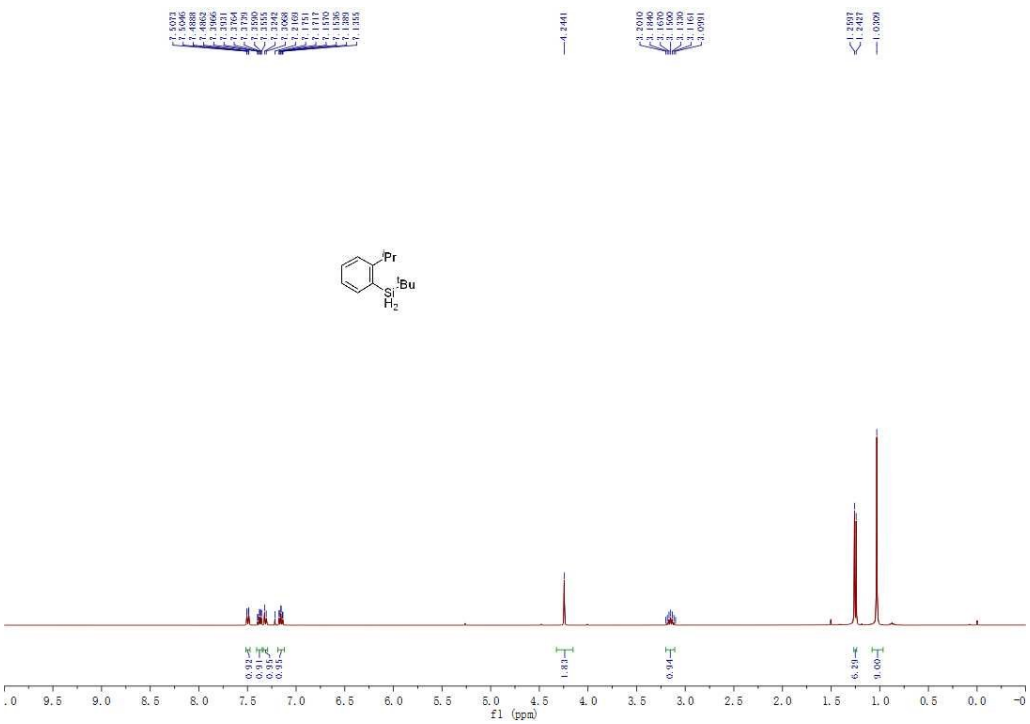

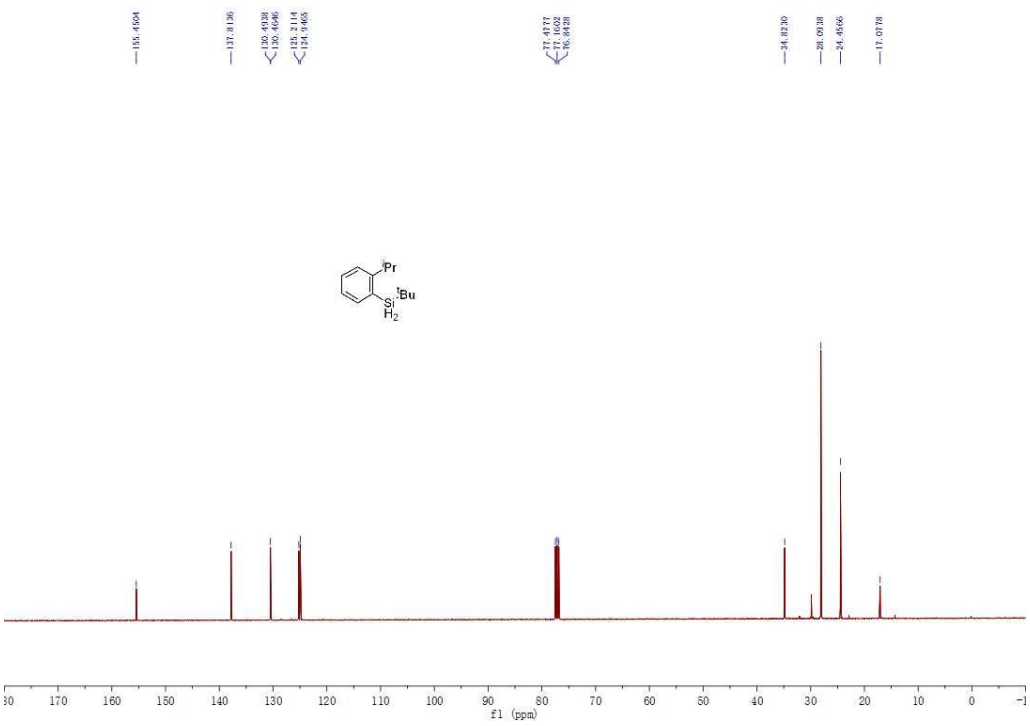

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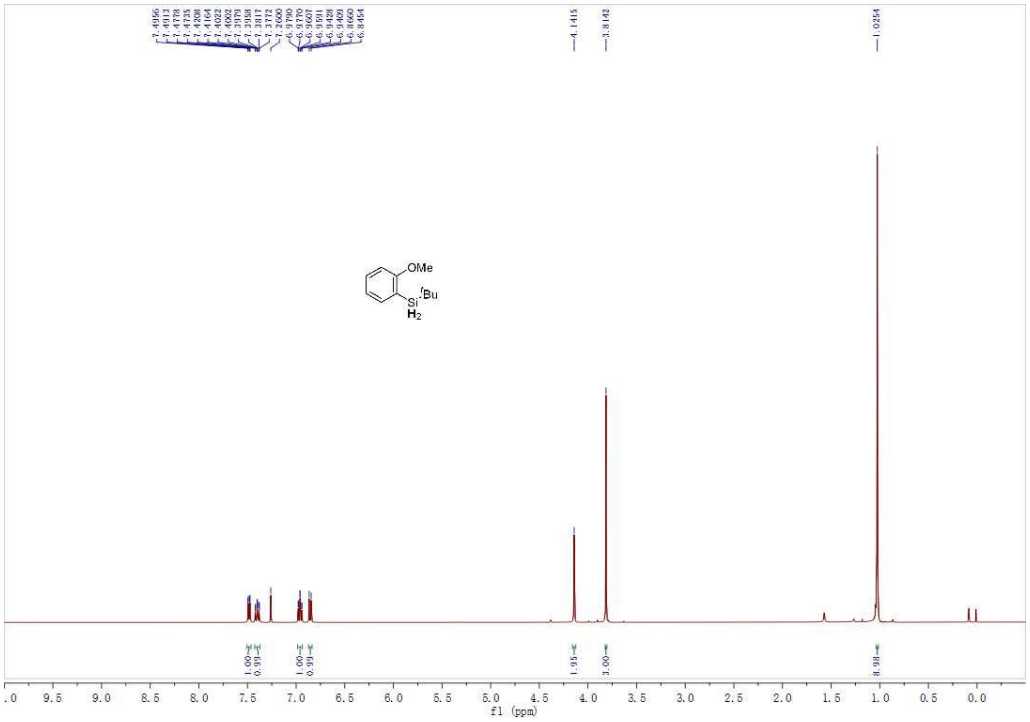

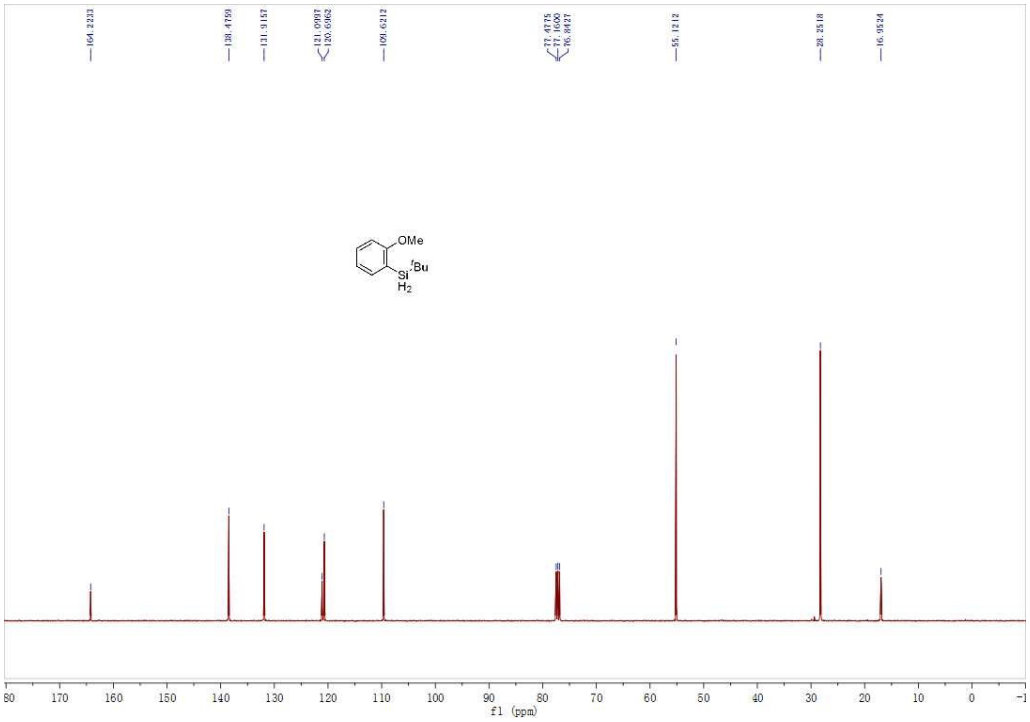

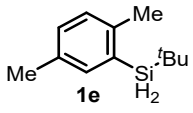

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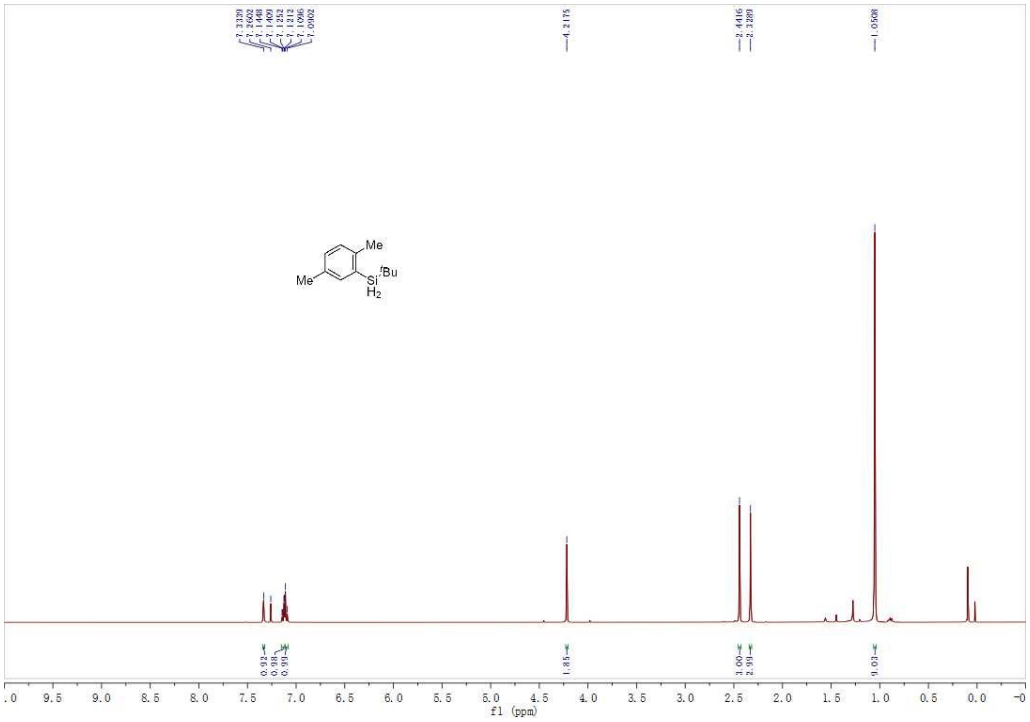

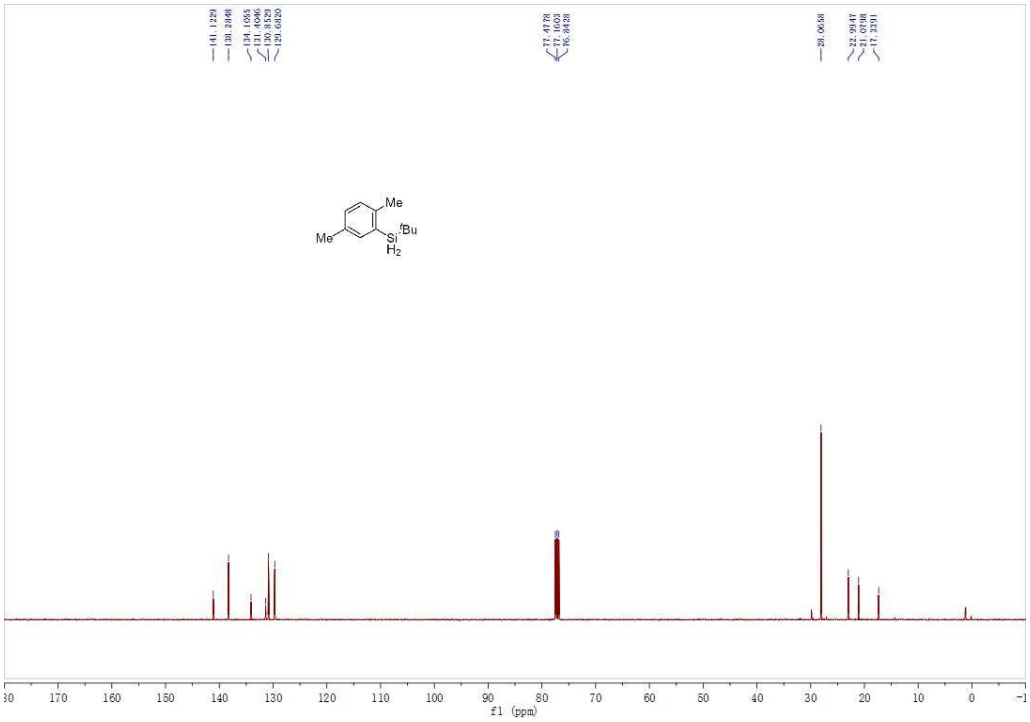

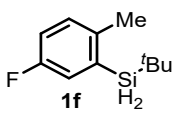

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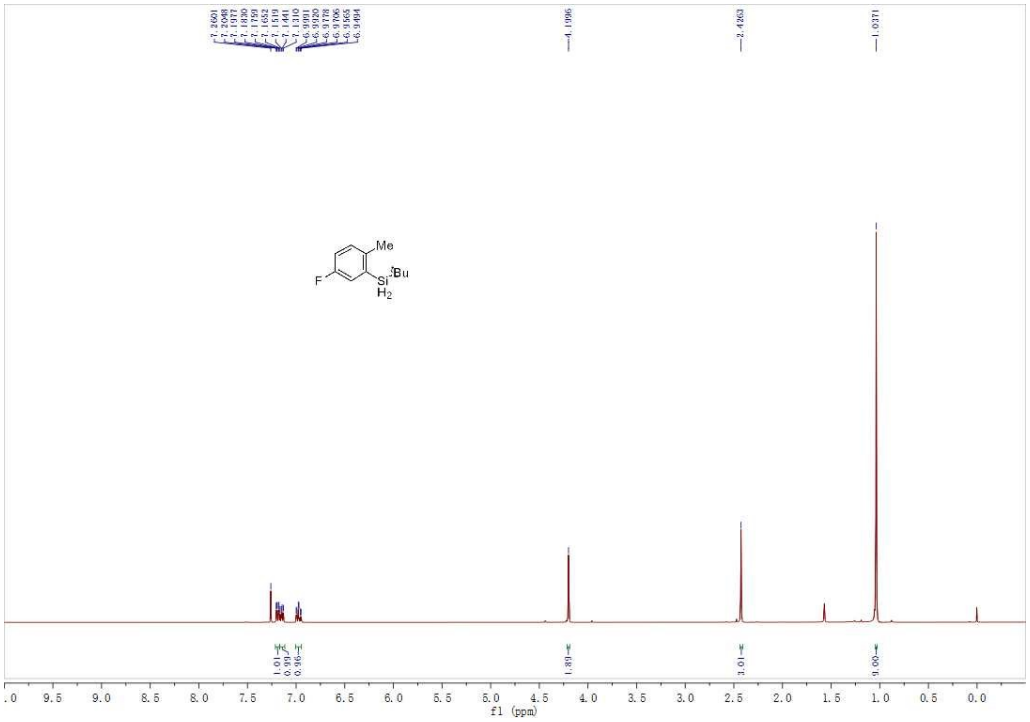
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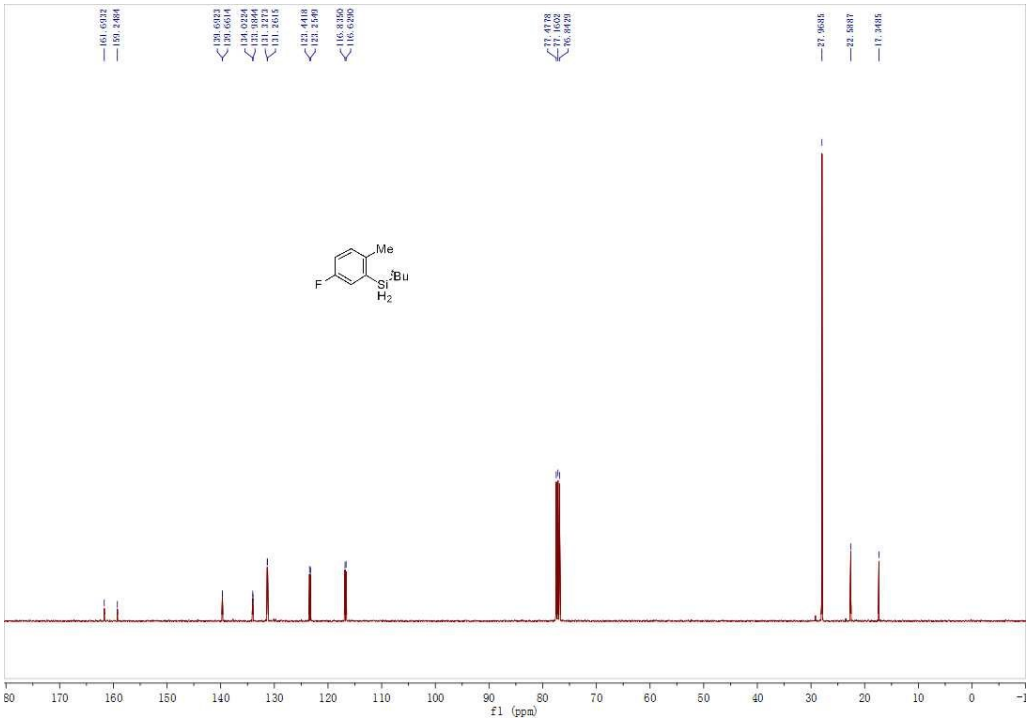
F
tBu
Si
H2
f1 (ppm)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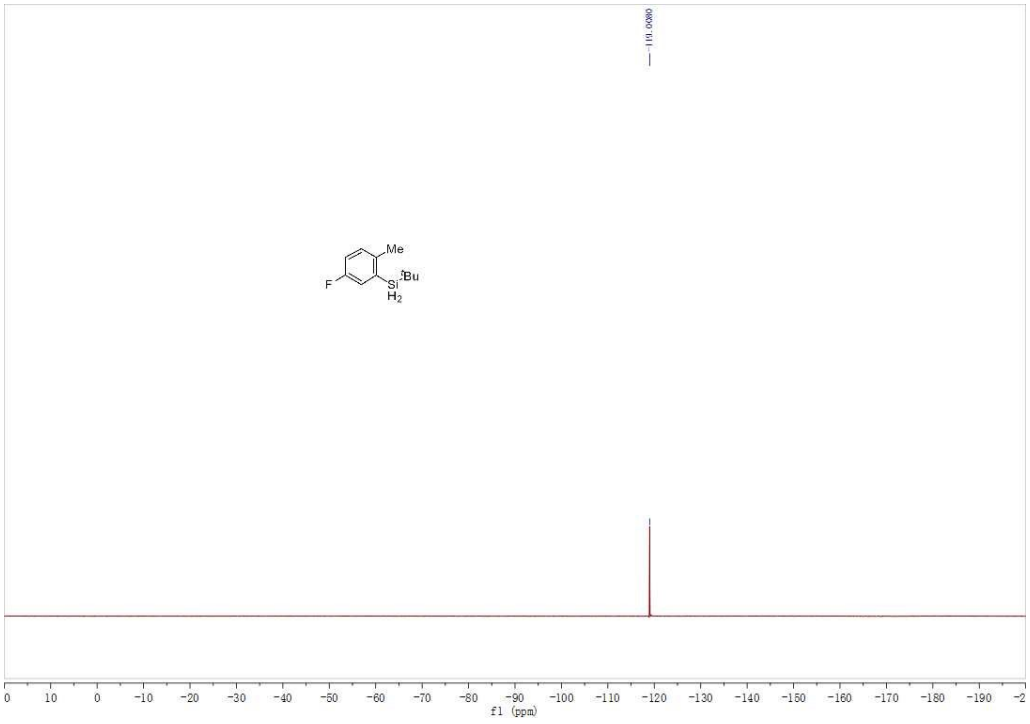
F
tBu
Si
H2
f1 (ppm)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H2
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-40
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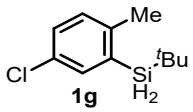
-160
-170
-180
-190
-2
f1 (ppm)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Cl
tBu
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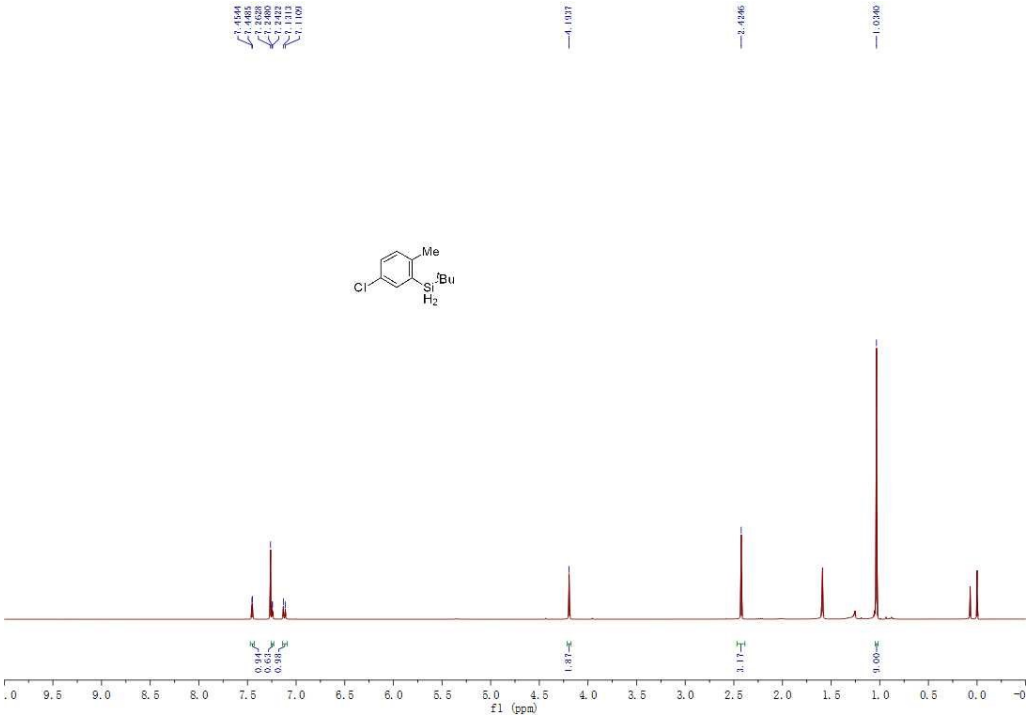
H2

1g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9.00
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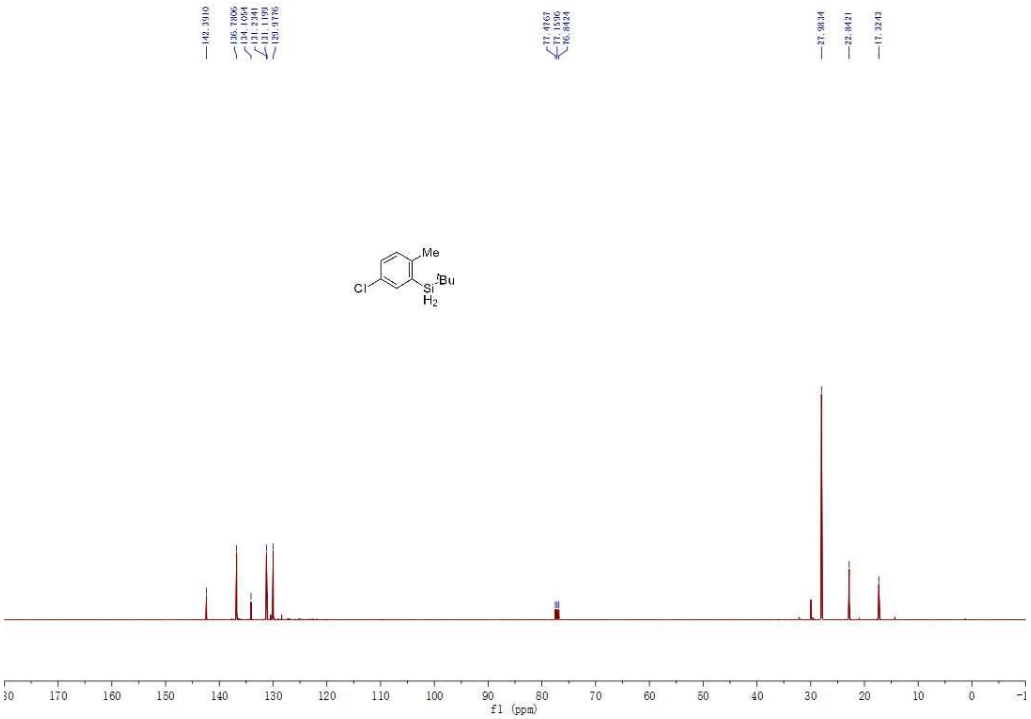
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Si
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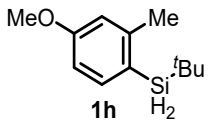
f1 (ppm)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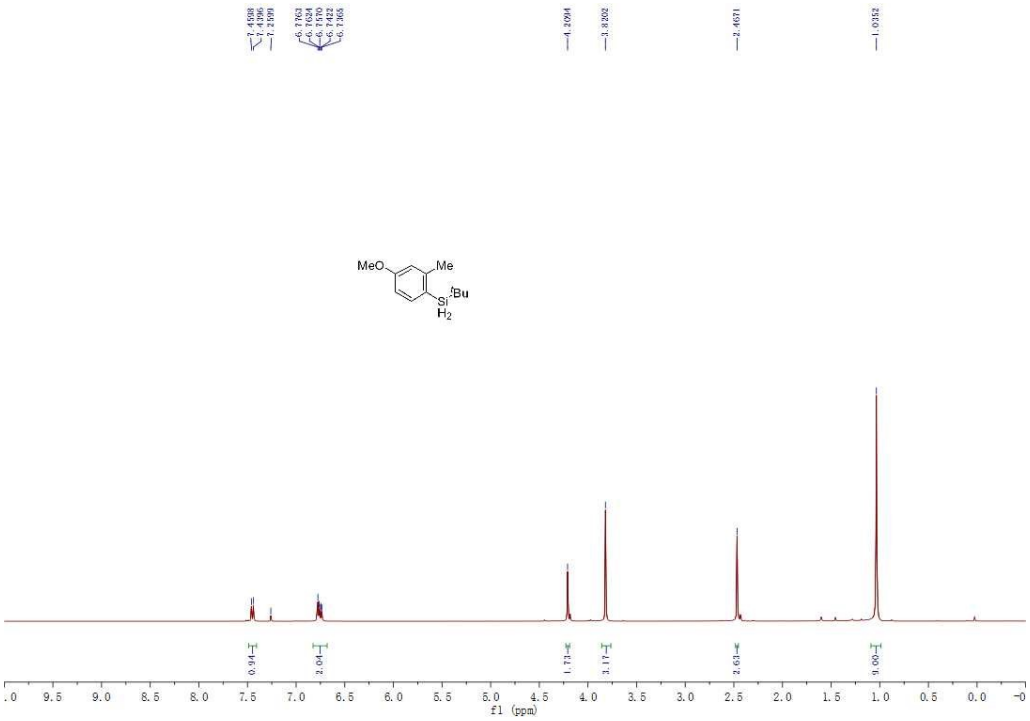
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3.8202
2.4671
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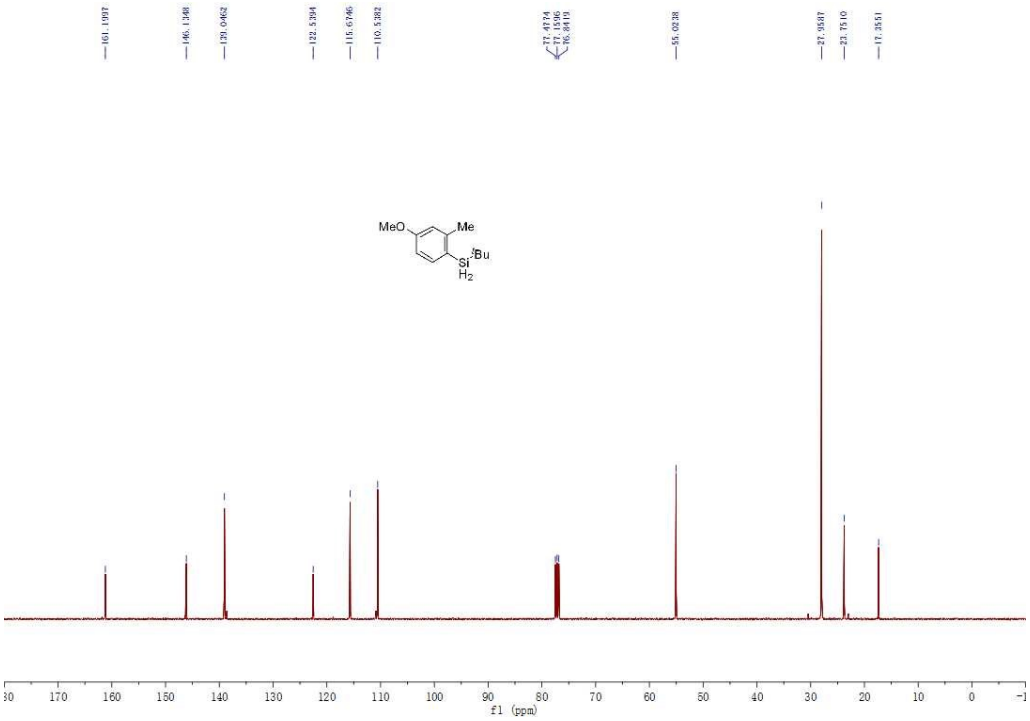
MeO
Me
tBu
Si
H2
0.94
2.04
1.73
3.17
2.63
9.00
f1 (ppm)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110.5382
77.4874
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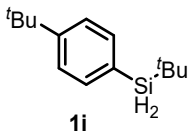
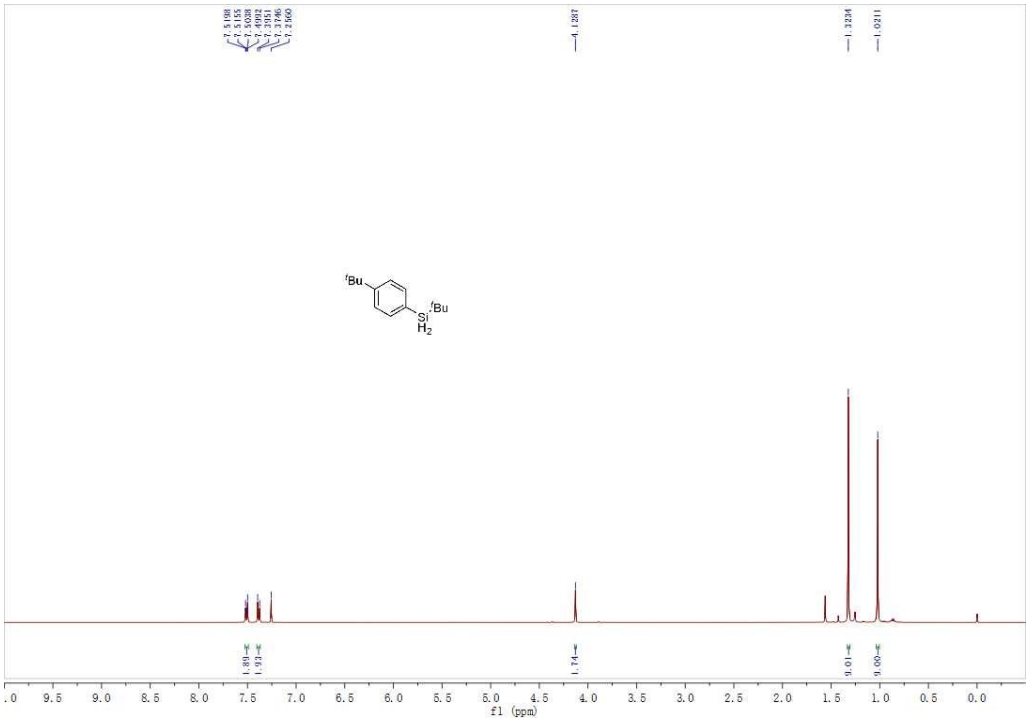
55.0238
27.9587
23.7510
17.2551
MeO
Me
tBu
Si
H2
f1 (ppm)


tBu
tBu
Si
H2

1i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7.3791
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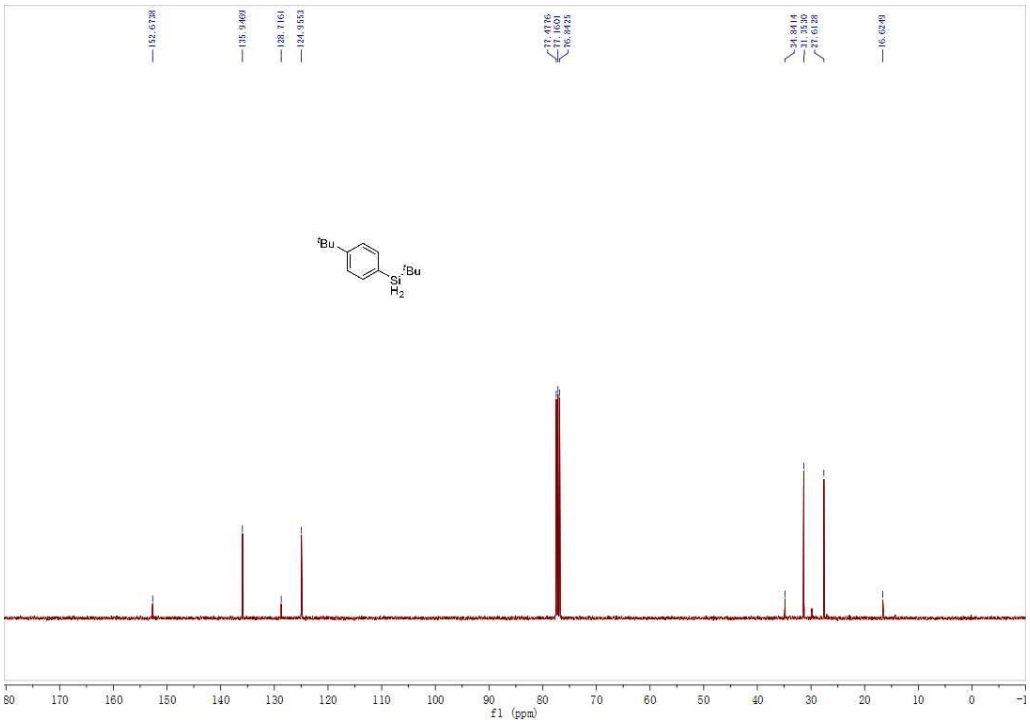
7.2960
1.1287
1.3234
1.0311
1.89
1.93
1.74
9.01
9.00
f1 (ppm)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34.8414
31.3530
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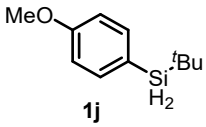
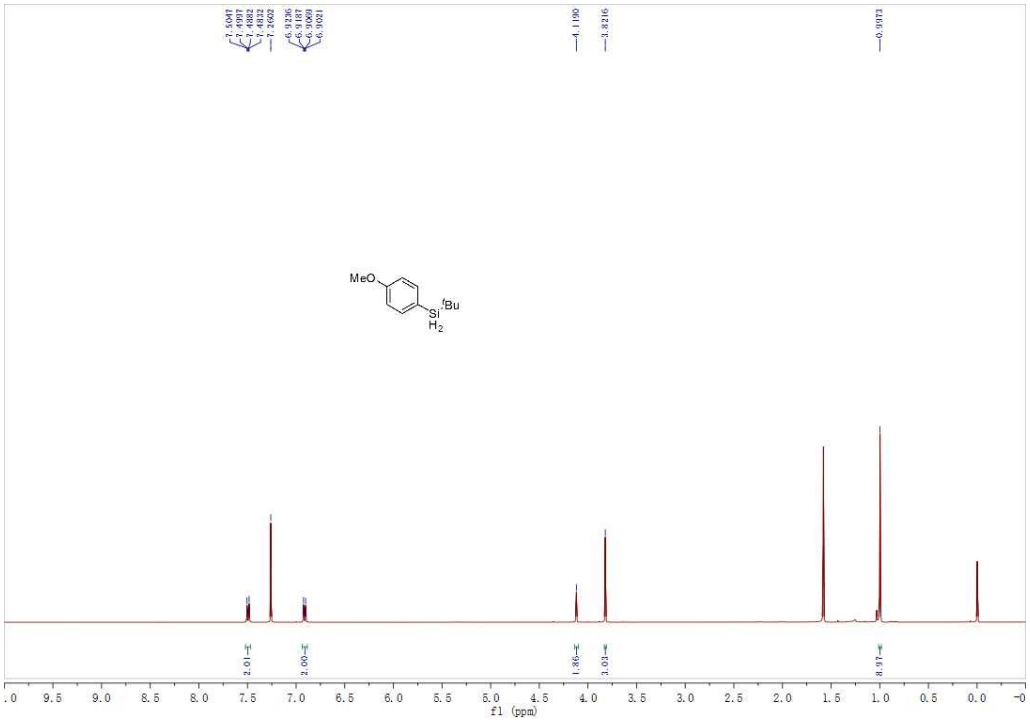
16.6249
f1 (ppm)


MeO
tBu
Si
H2

1j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7.2602
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6.9187
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6.9031
4.1190
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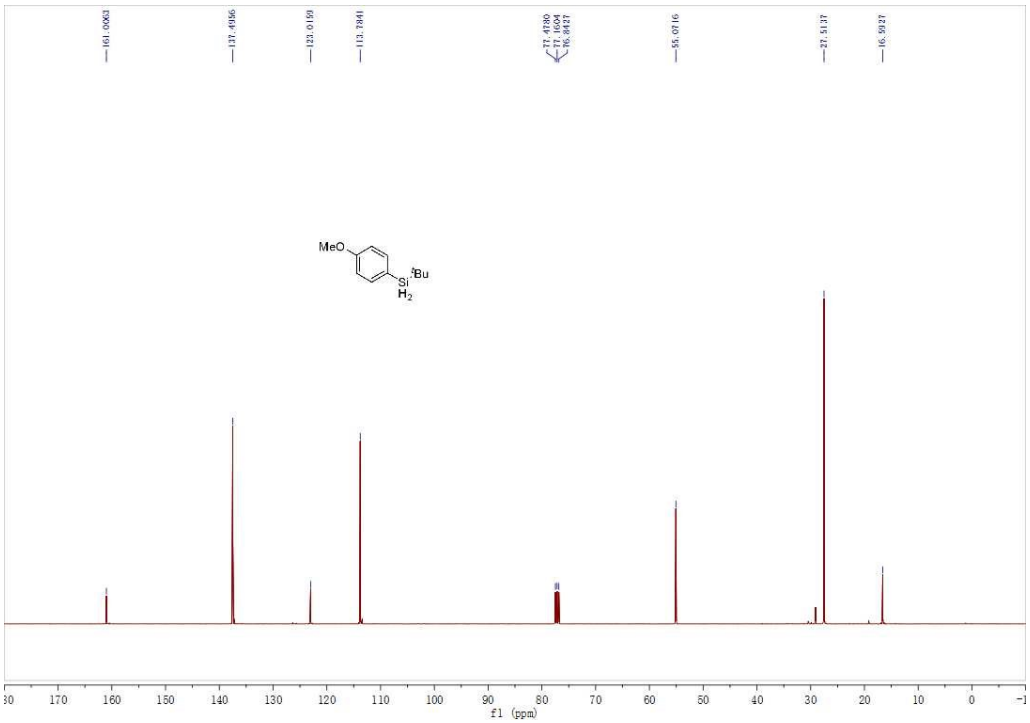
MeO
tBu
Si
H2
2.01
2.00
1.86
3.03
8.97
f1 (ppm)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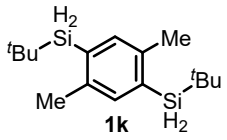
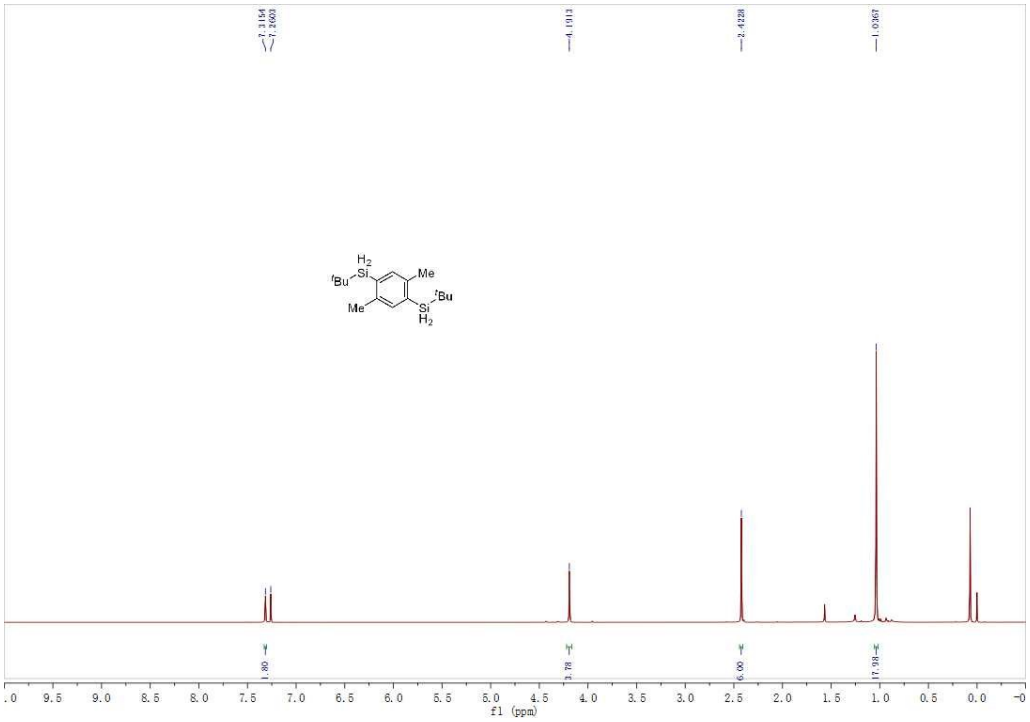
MeO
tBu
Si
H2
f1 (ppm)


H2
Si
tBu
Me
Me
tBu
Si
H2

1k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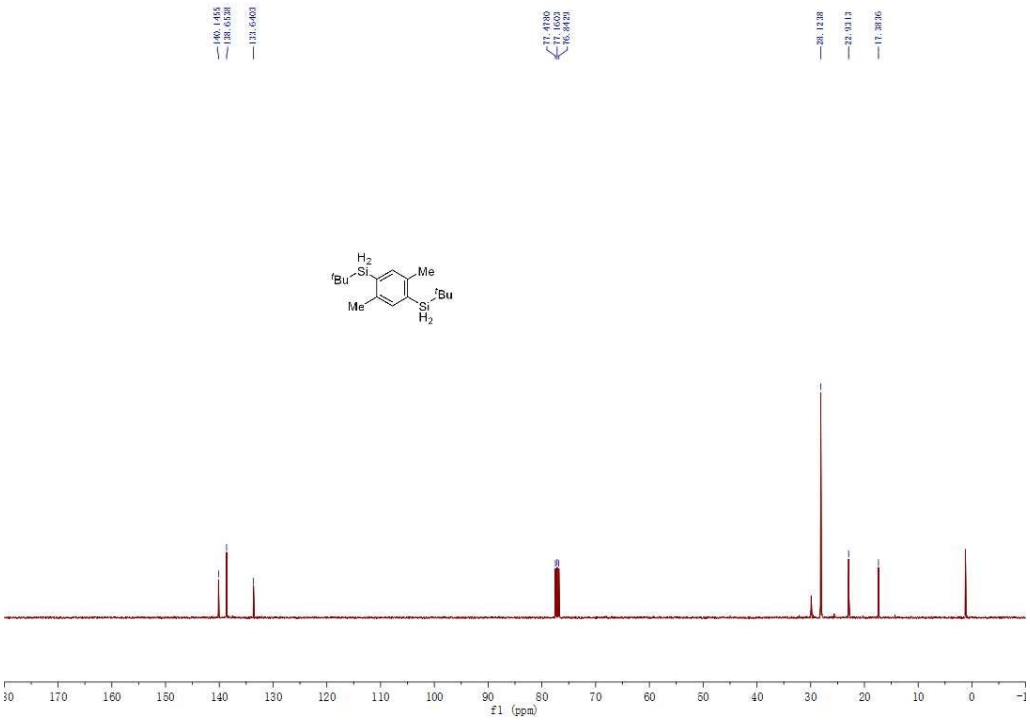
17.98
f1 (ppm)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76.8429
26.1238
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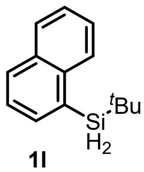
17.2836
f1 (ppm)



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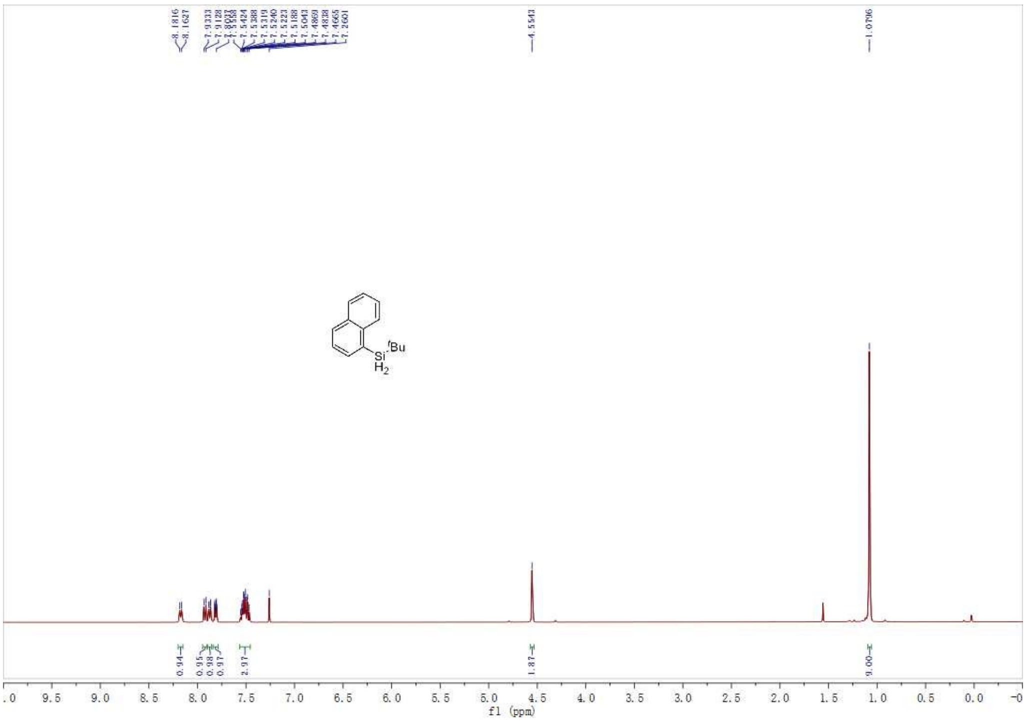
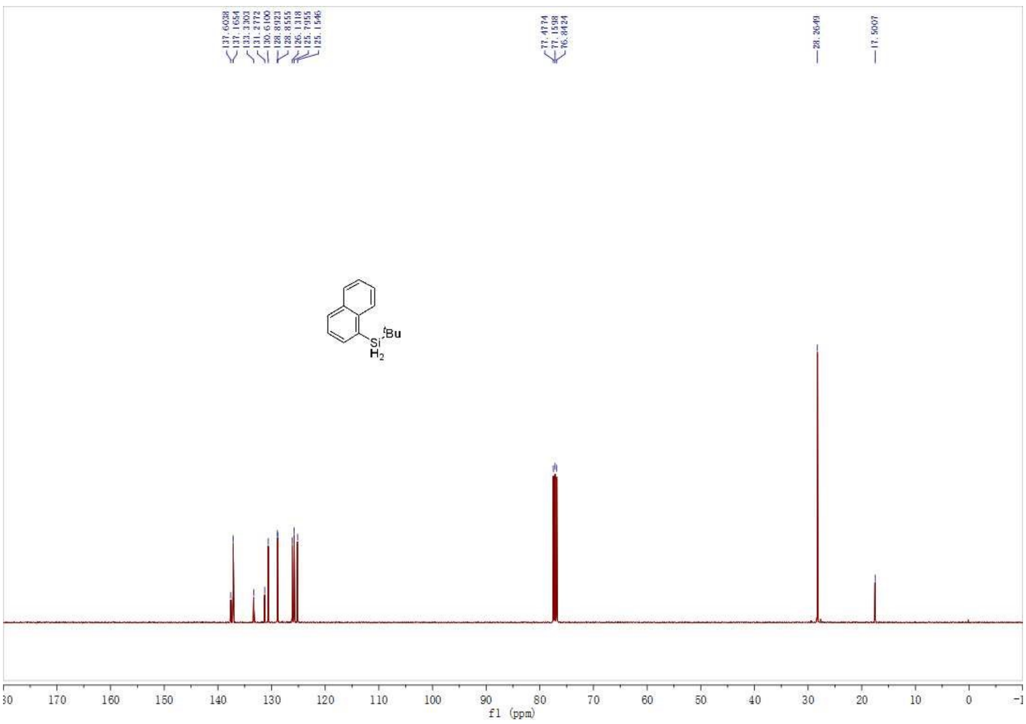
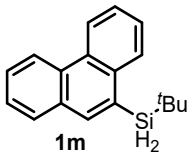
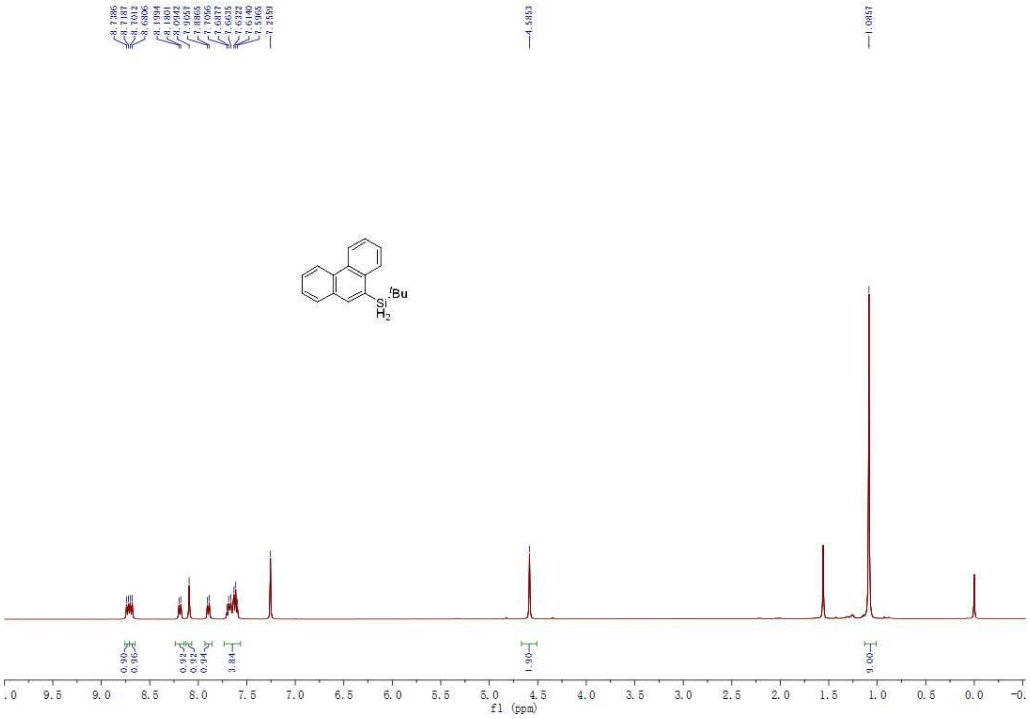
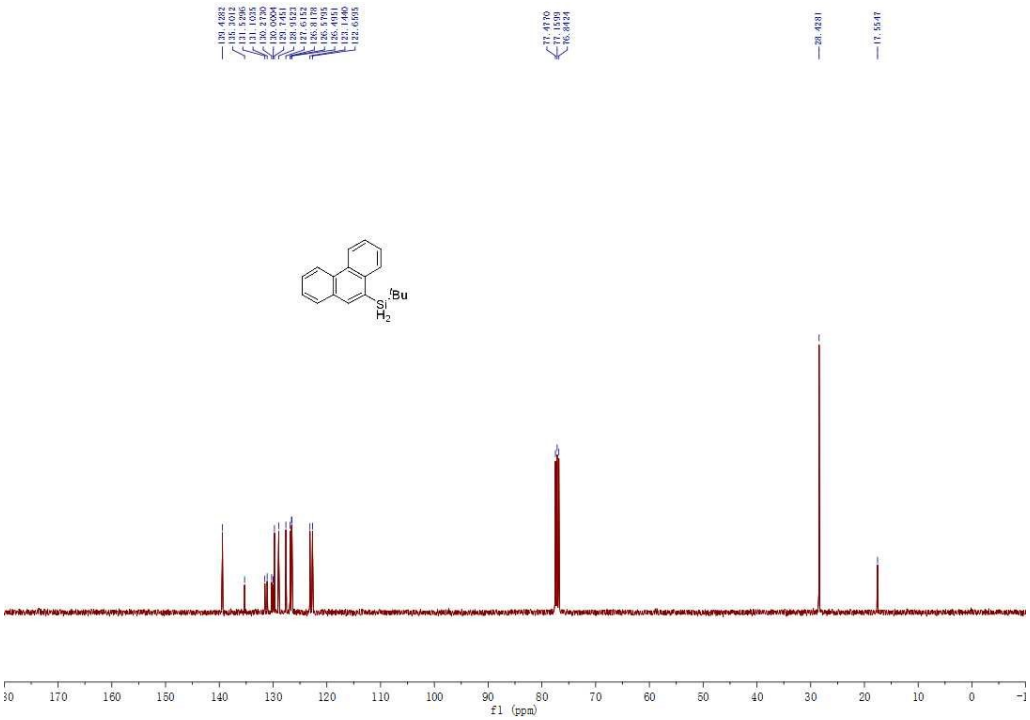


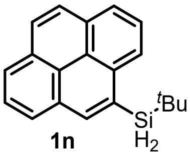




1m







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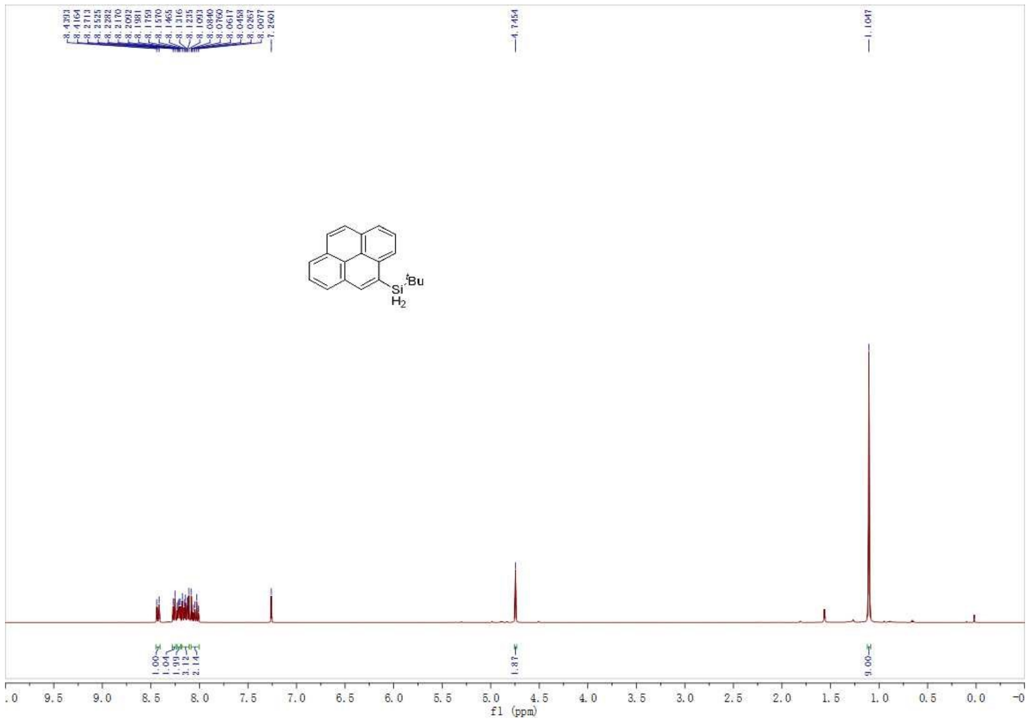
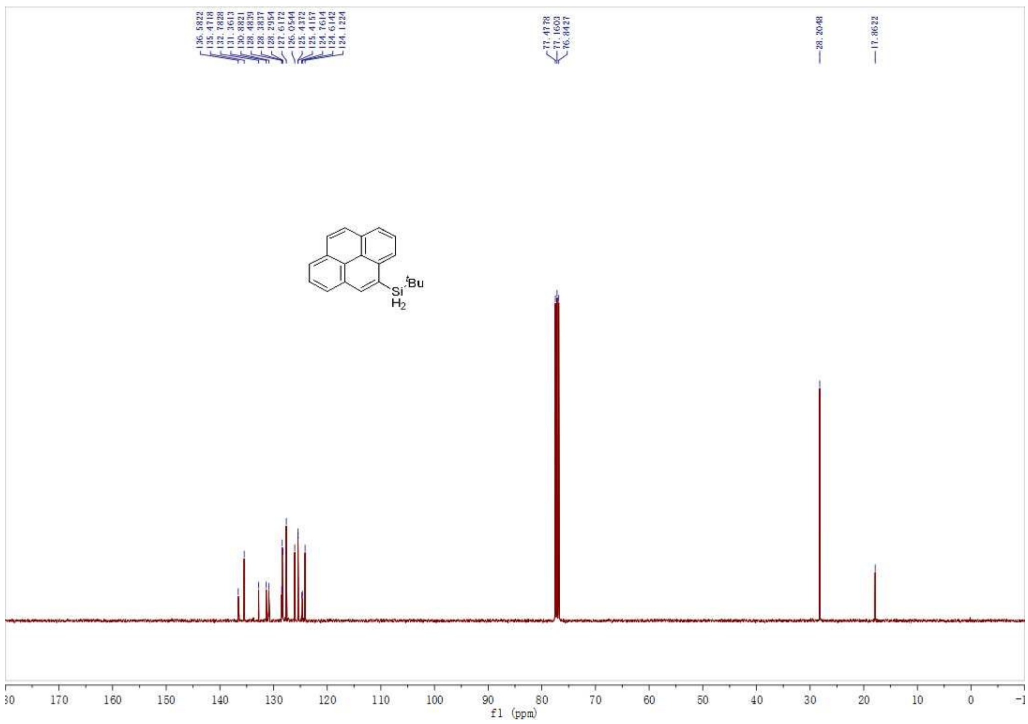
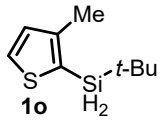
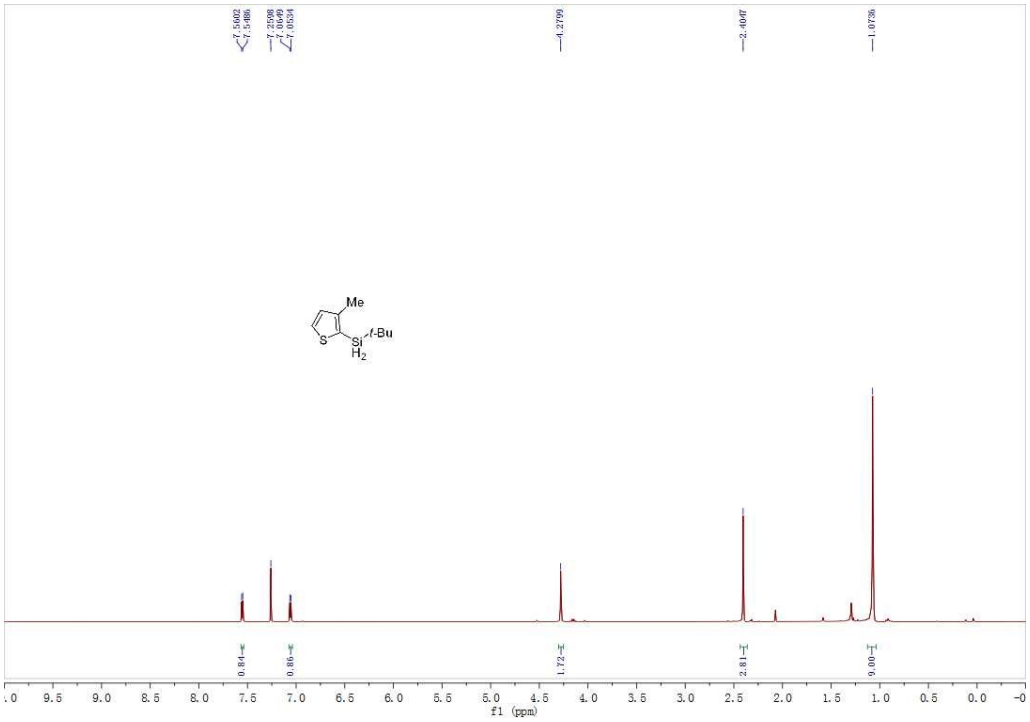





Me
S
Si
t-Bu
H2

1o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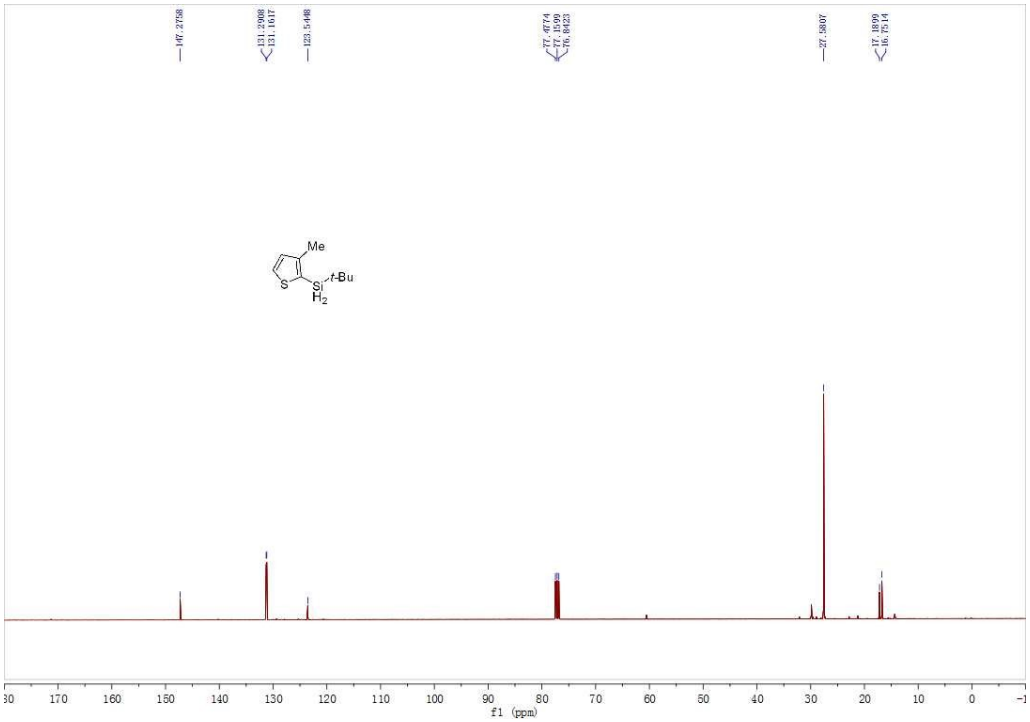
9.00
f1 (ppm)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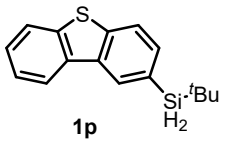
27.5807
17.1899
16.7514
f1 (ppm)



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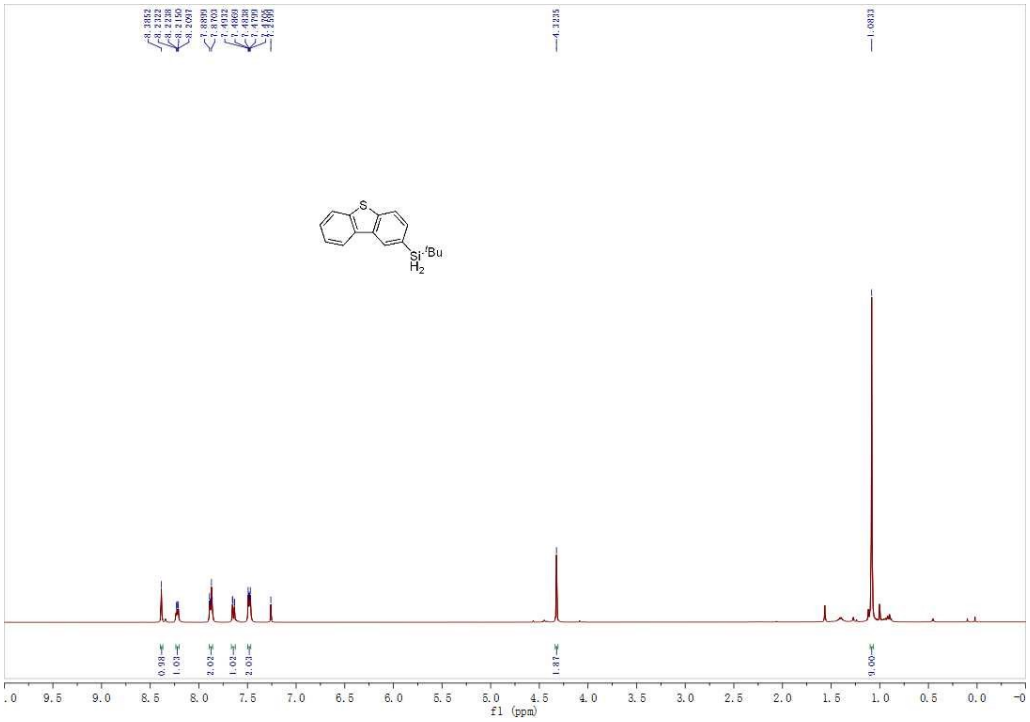

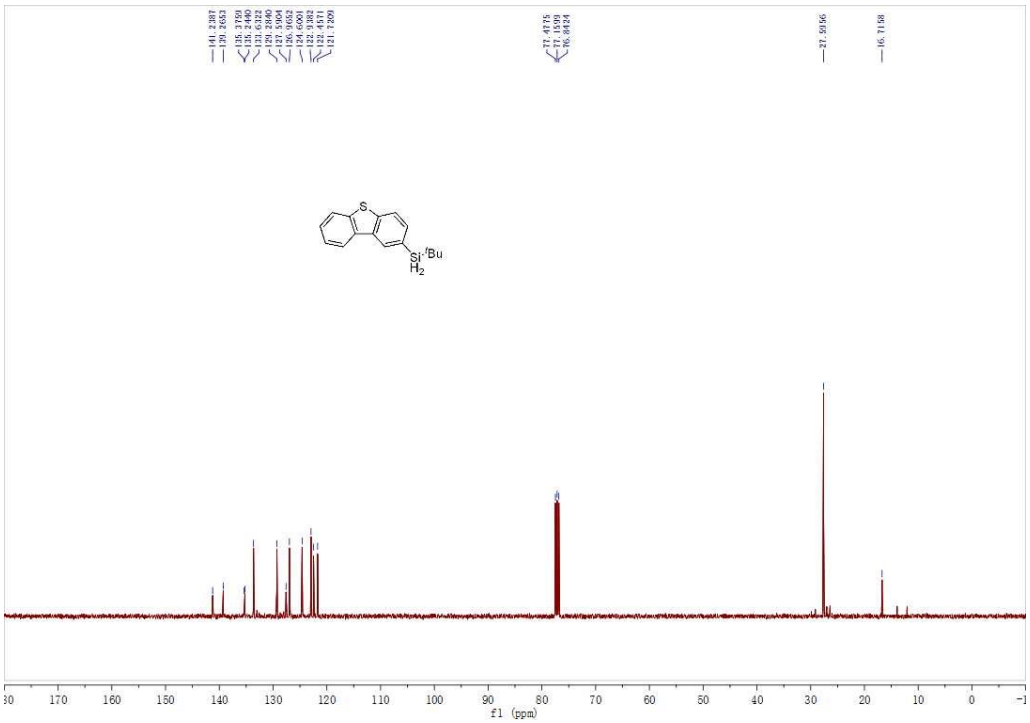

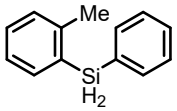

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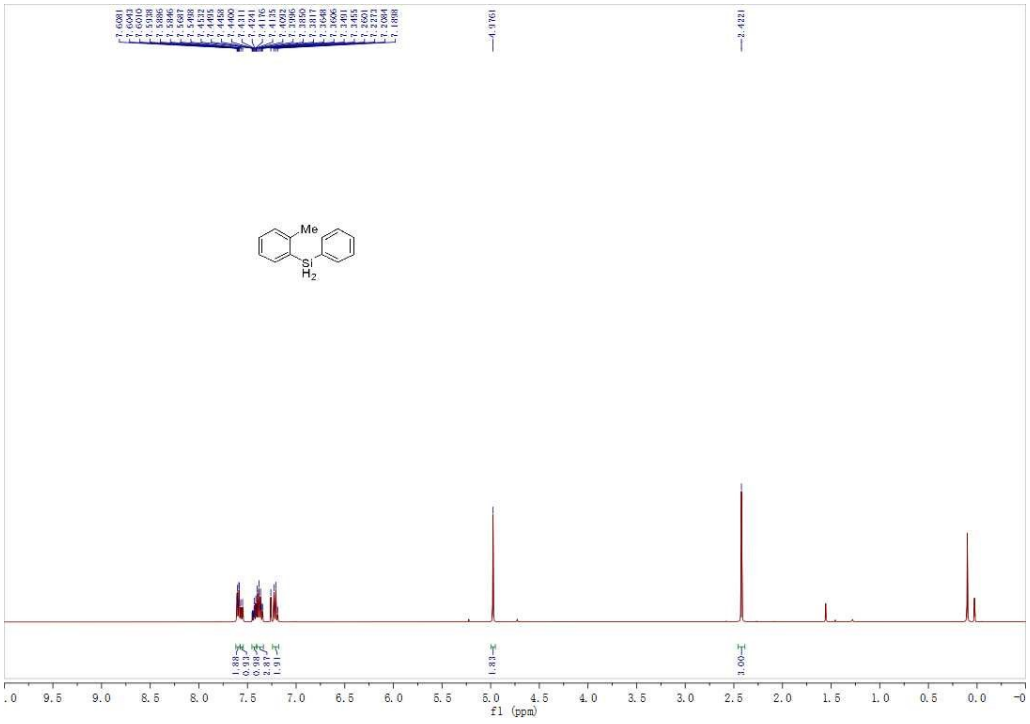
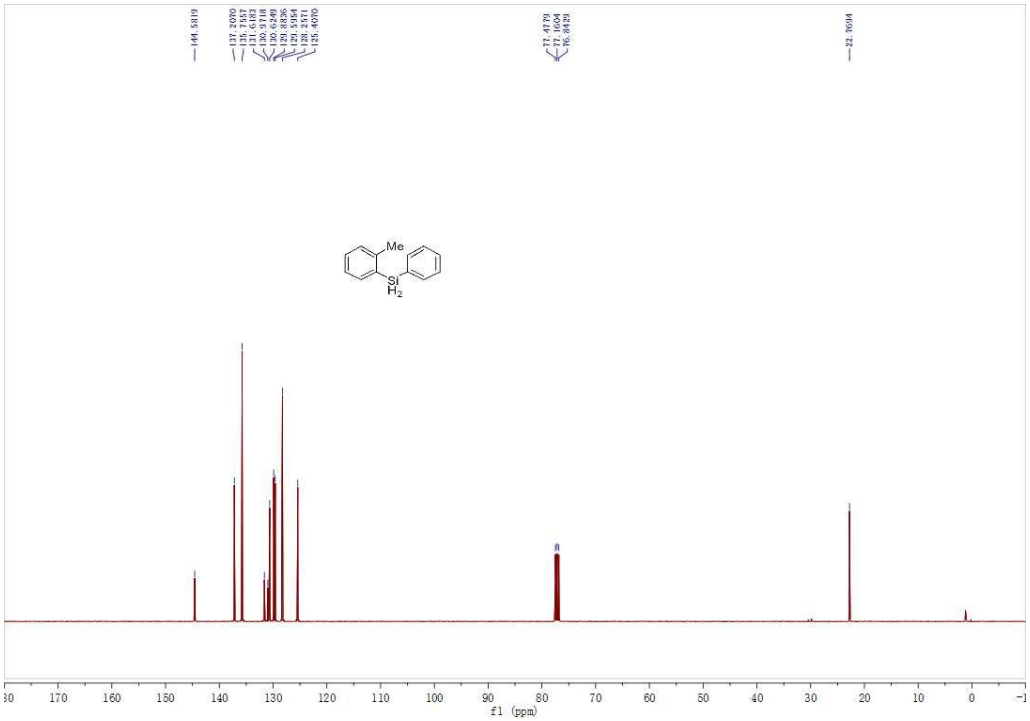
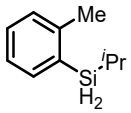
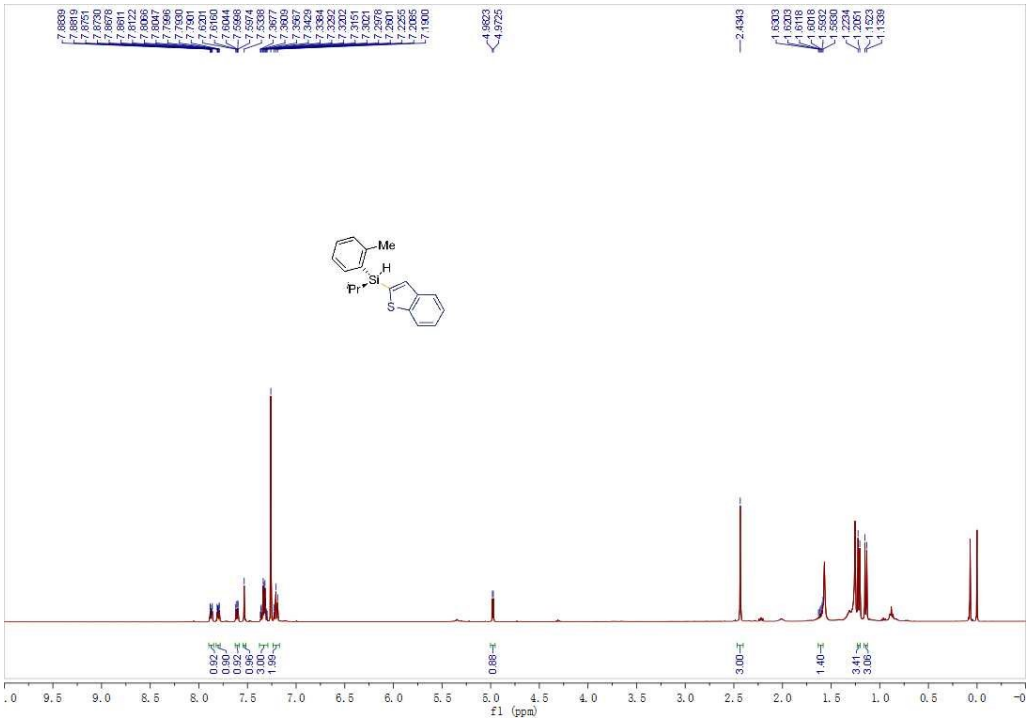
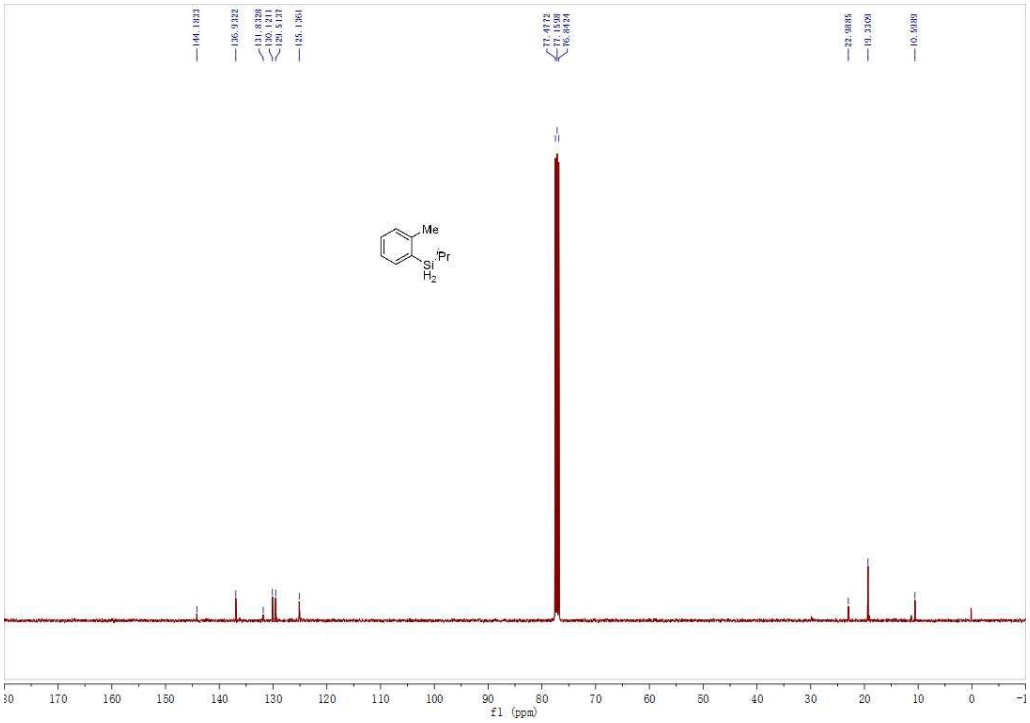


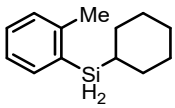




1r







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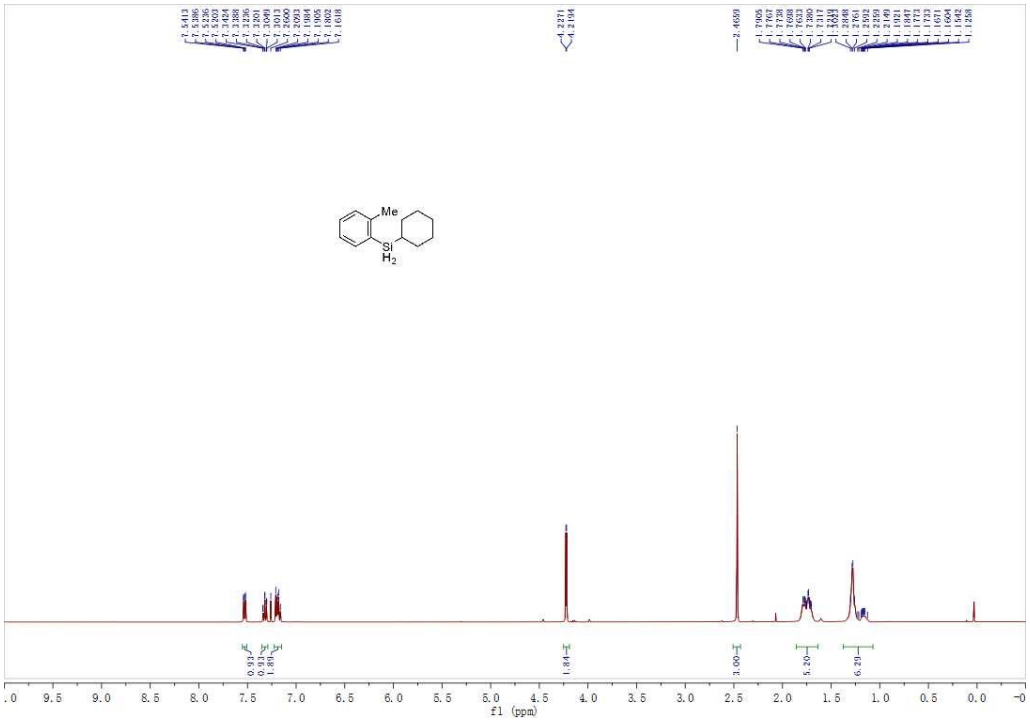

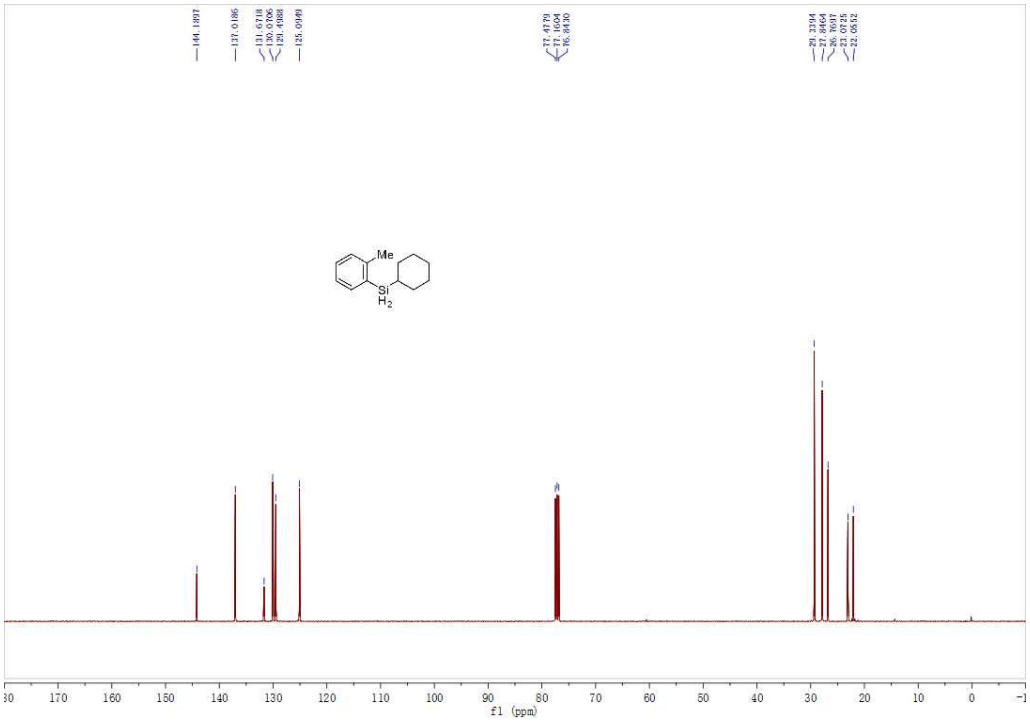

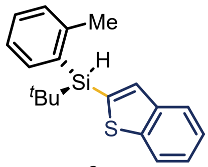
Me
H
tBu
Si
S

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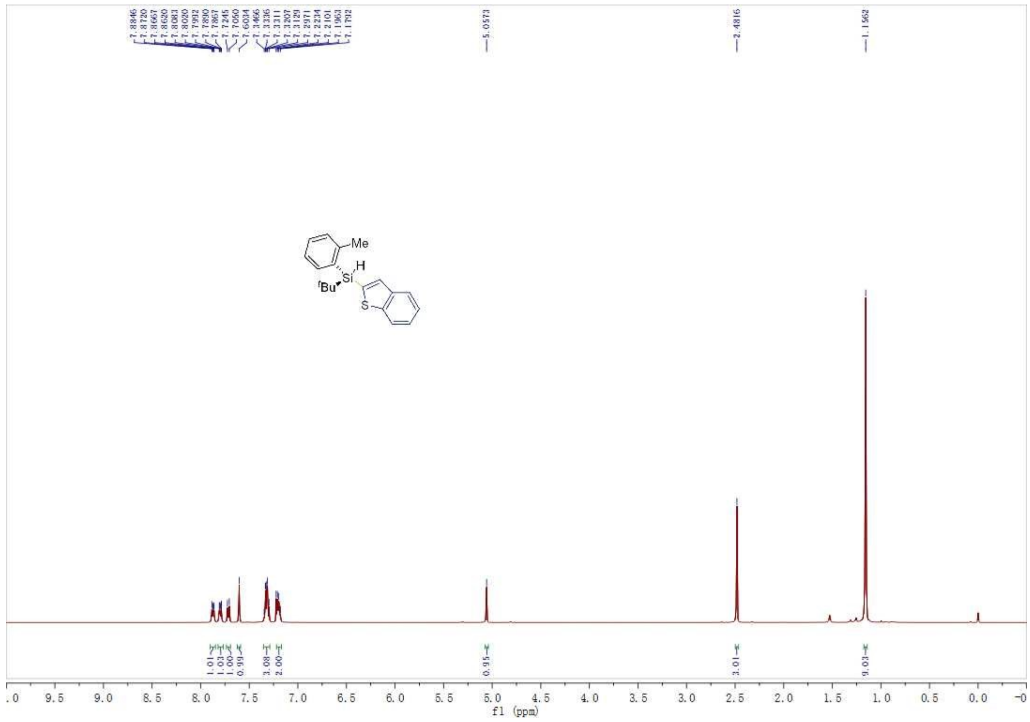
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7.1792
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Me
H
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Si
S
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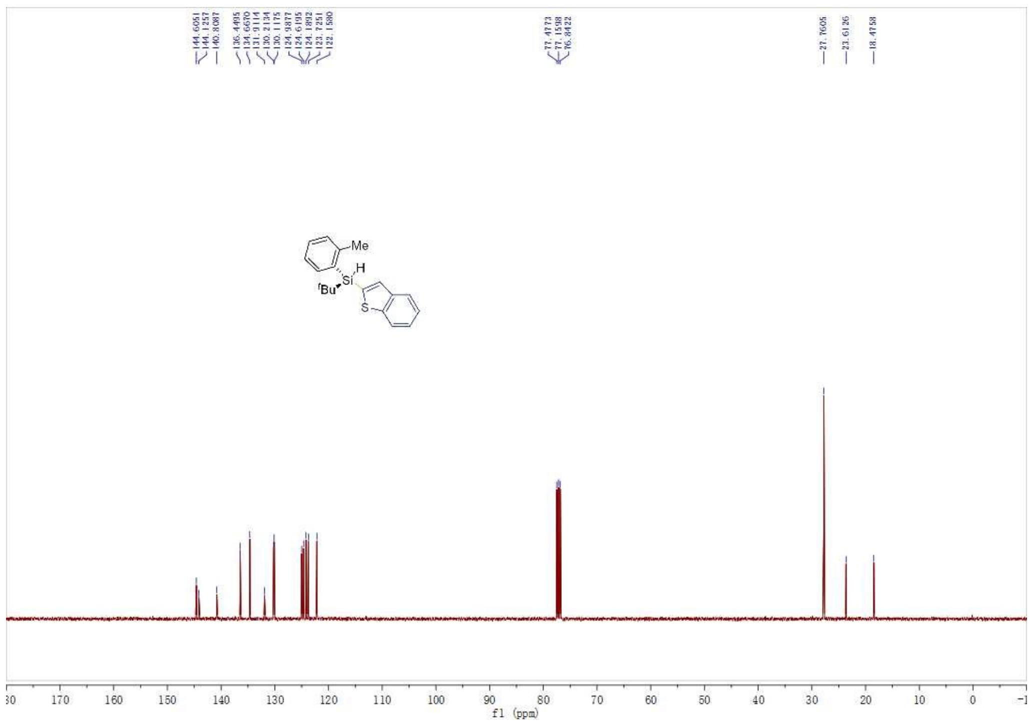
9.03
f1 (ppm)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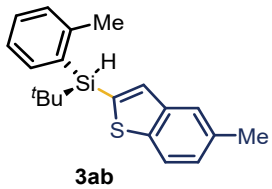
tBu
Si
S
f1 (ppm)



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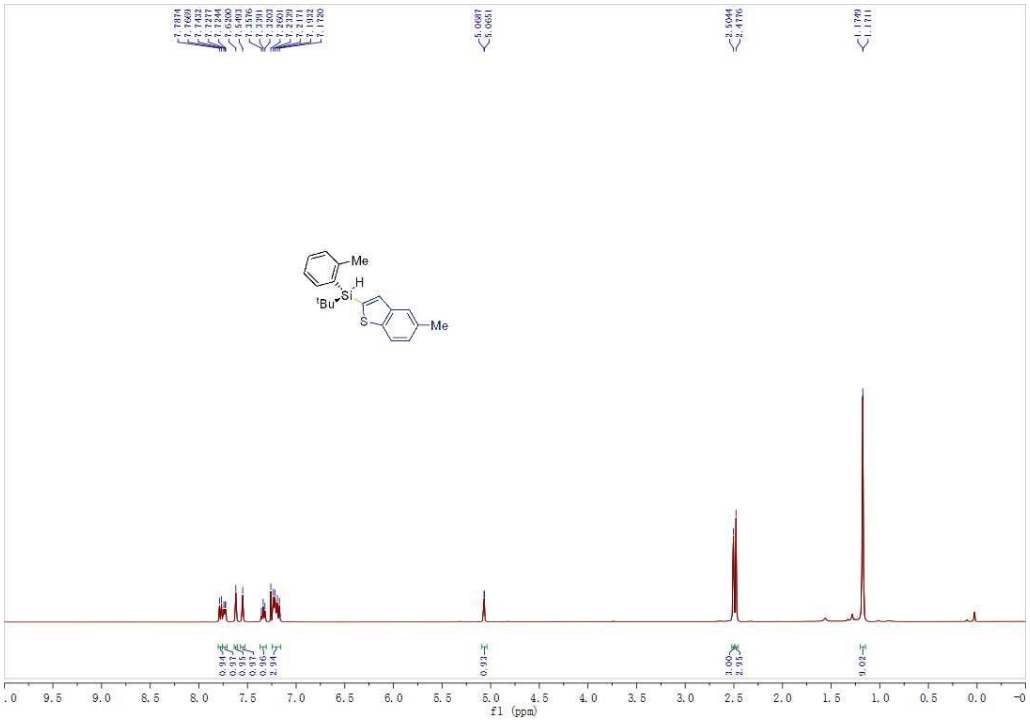

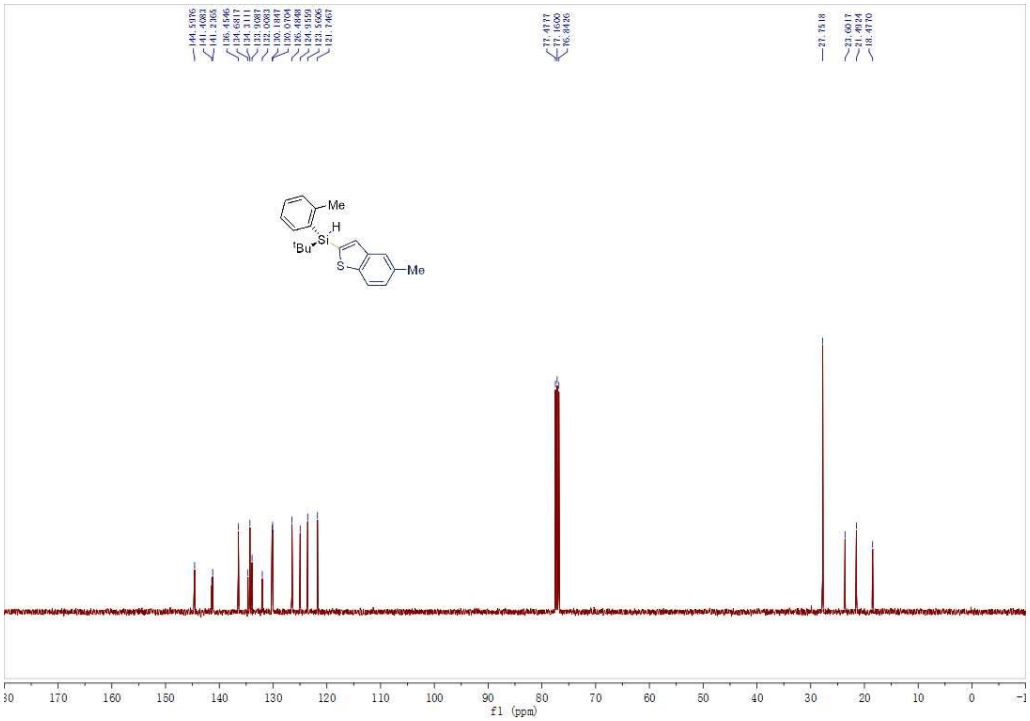

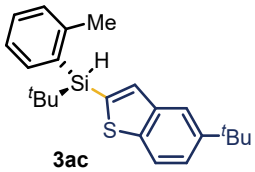

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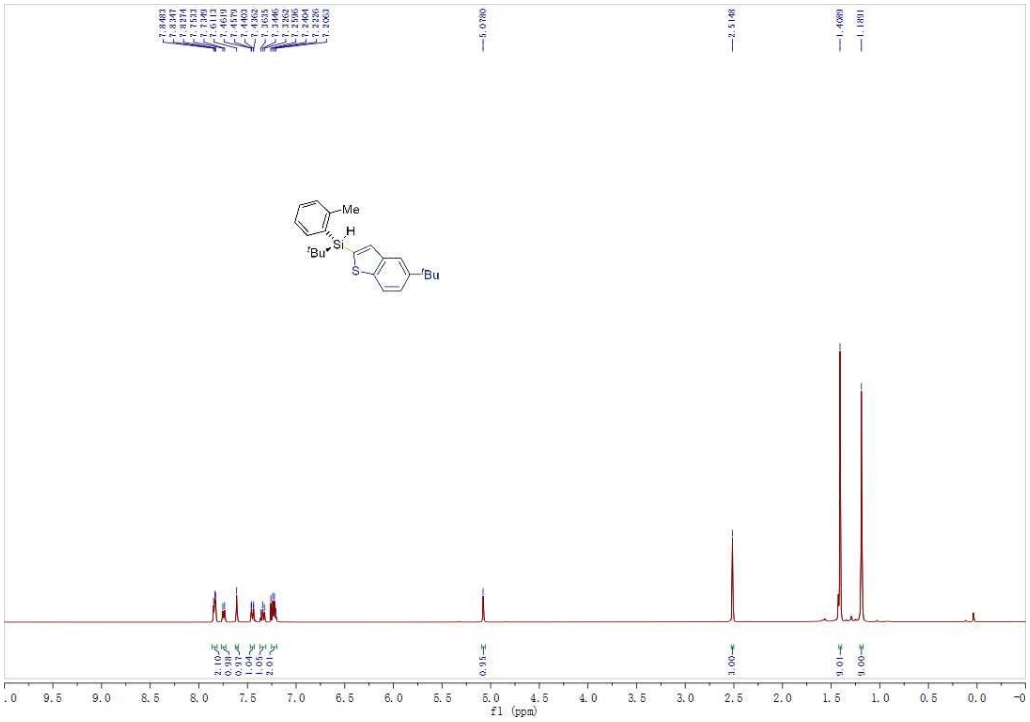

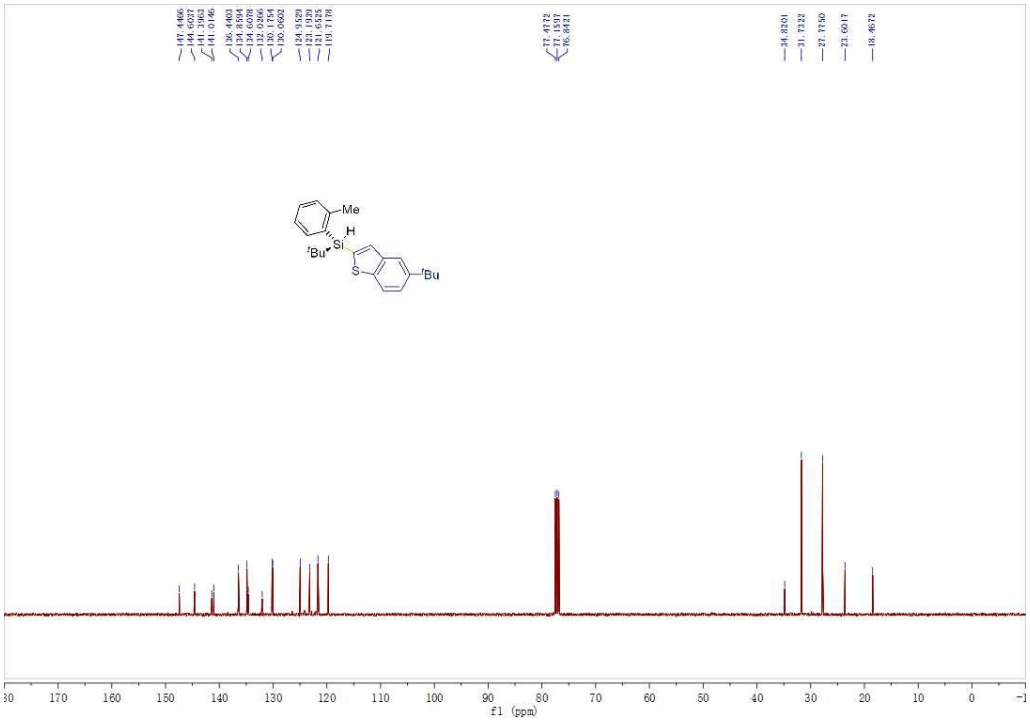

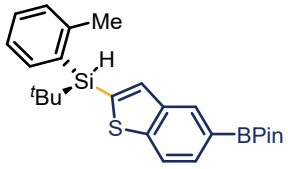
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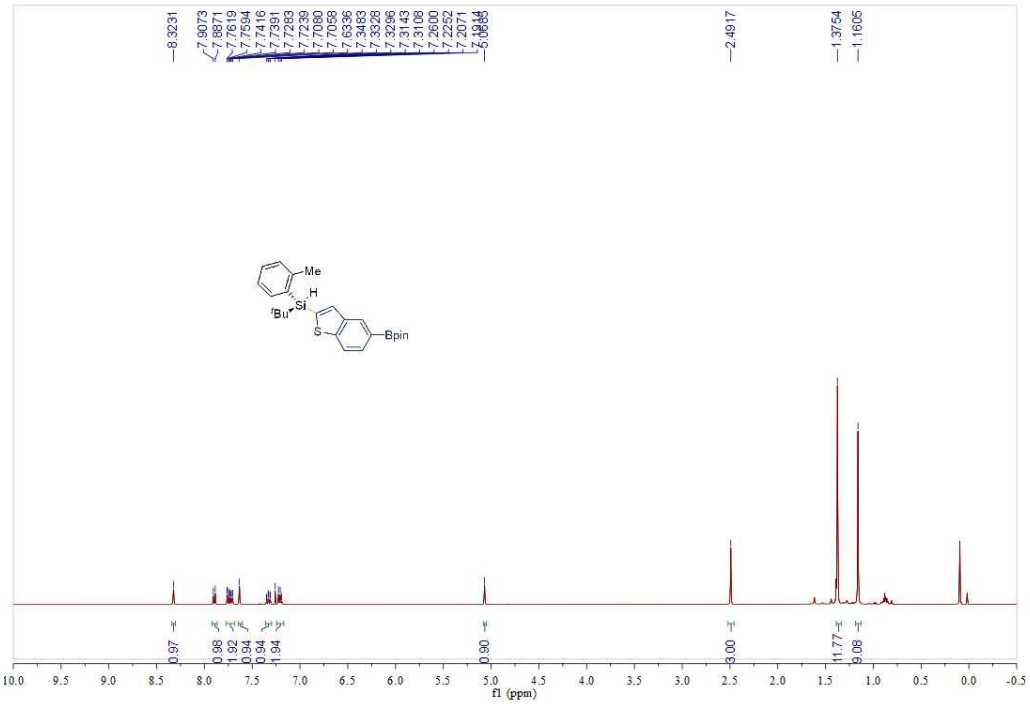
Si
tBu
S
BPin

3ad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1.1605
Me
H
Si
tBu
S
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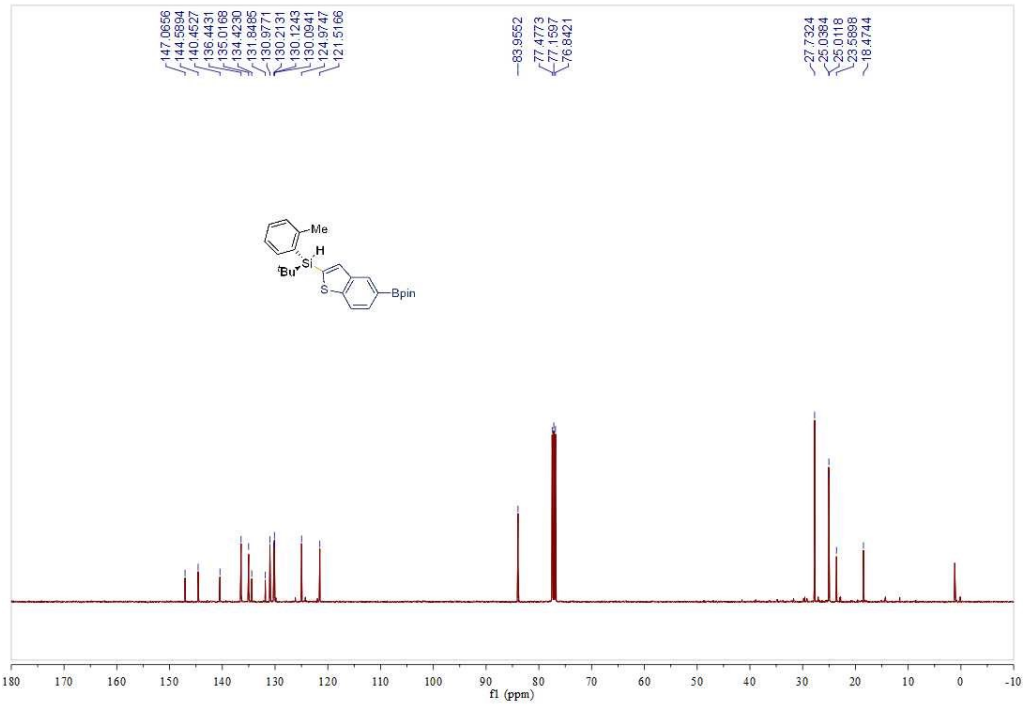
f1 (ppm)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77.4773
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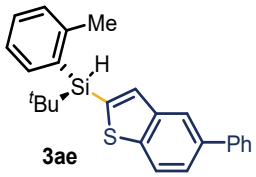
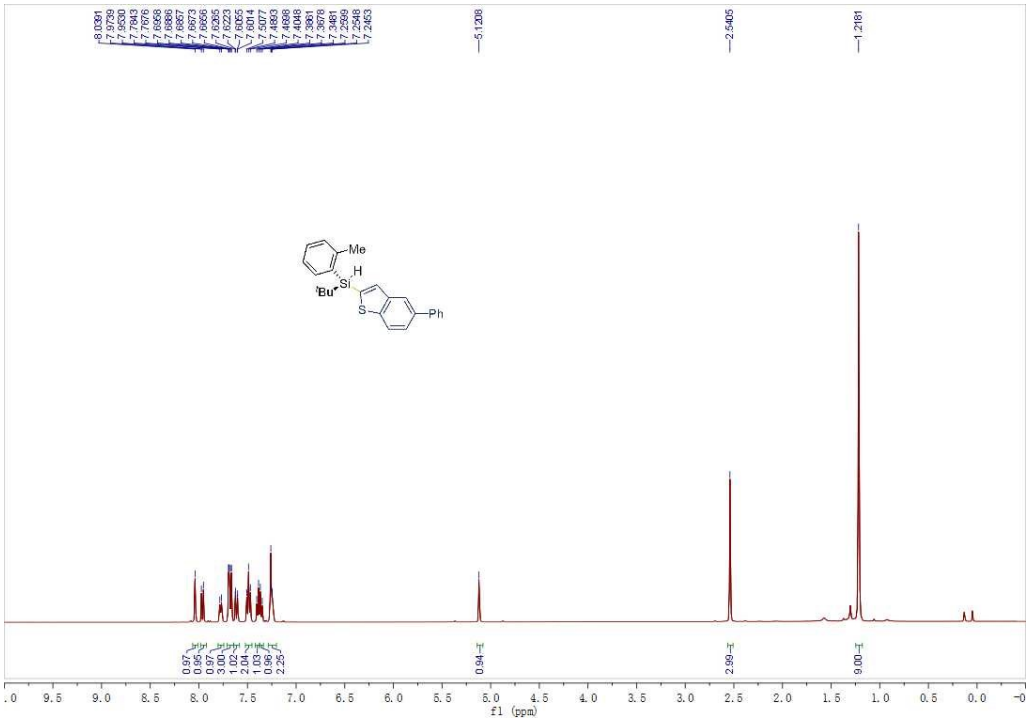
H
Si
tBu
S
Bpin
f1 (ppm)


Me
H
Si
tBu
S
Ph

3ae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7.4048
7.3991
7.3976
7.3461
7.2599
7.2548
7.2463
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2.5405
1.2161
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0.95
0.97
3.00
1.02
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1.03
0.96
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0.94
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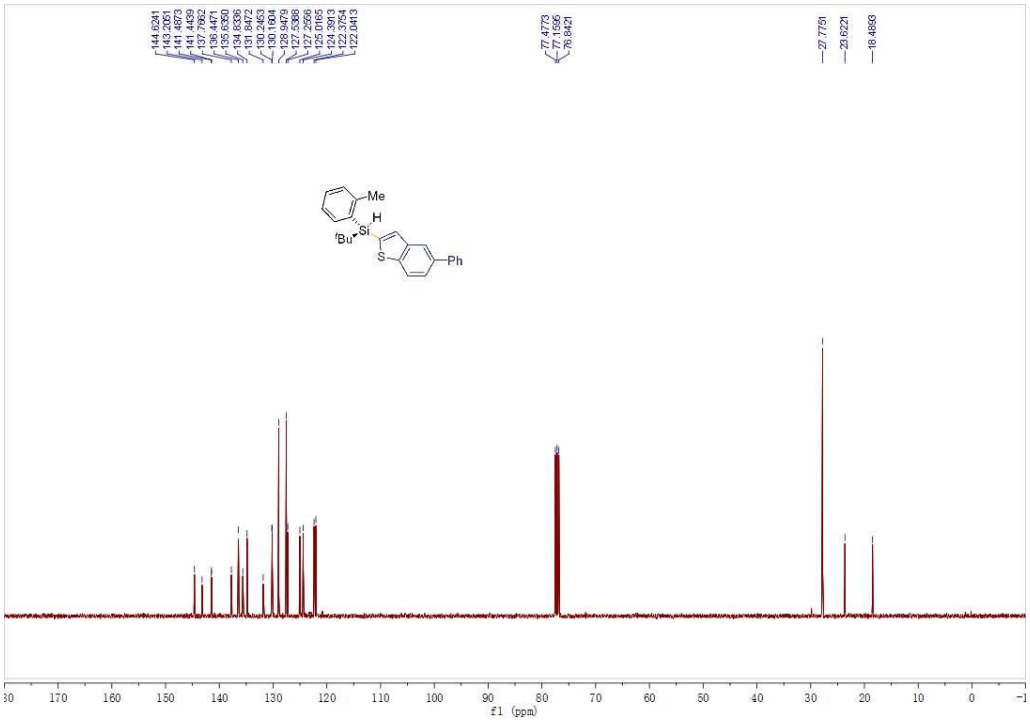
9.00
f1 (ppm)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127.2366
125.0165
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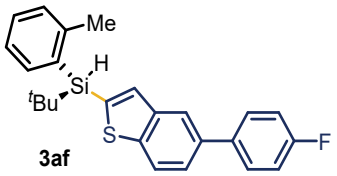
f1 (ppm)



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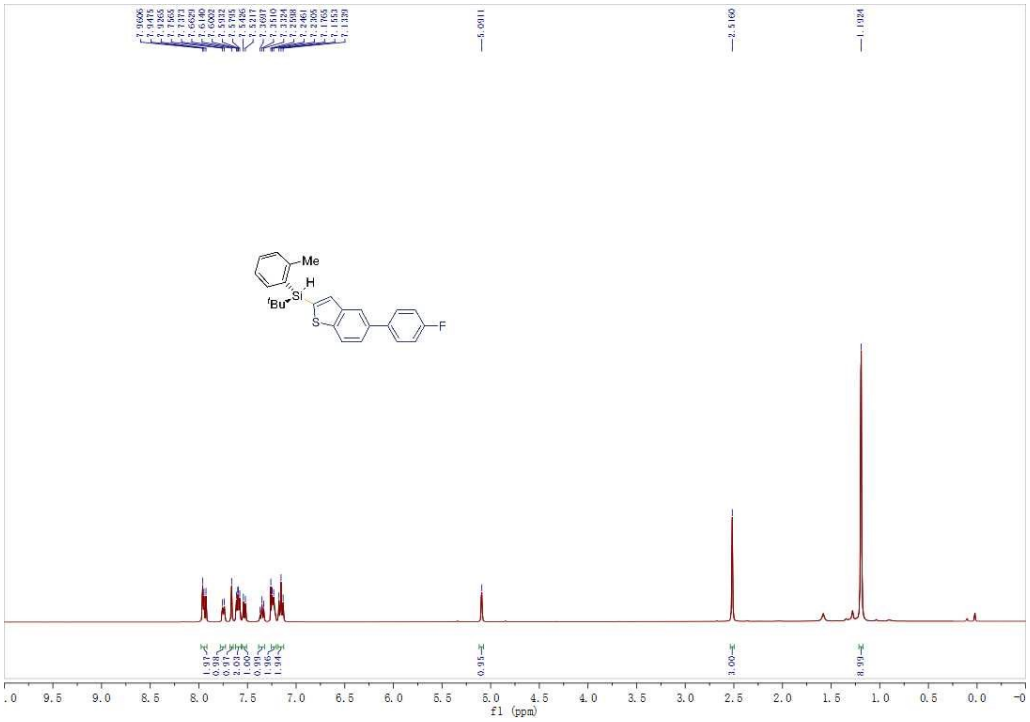

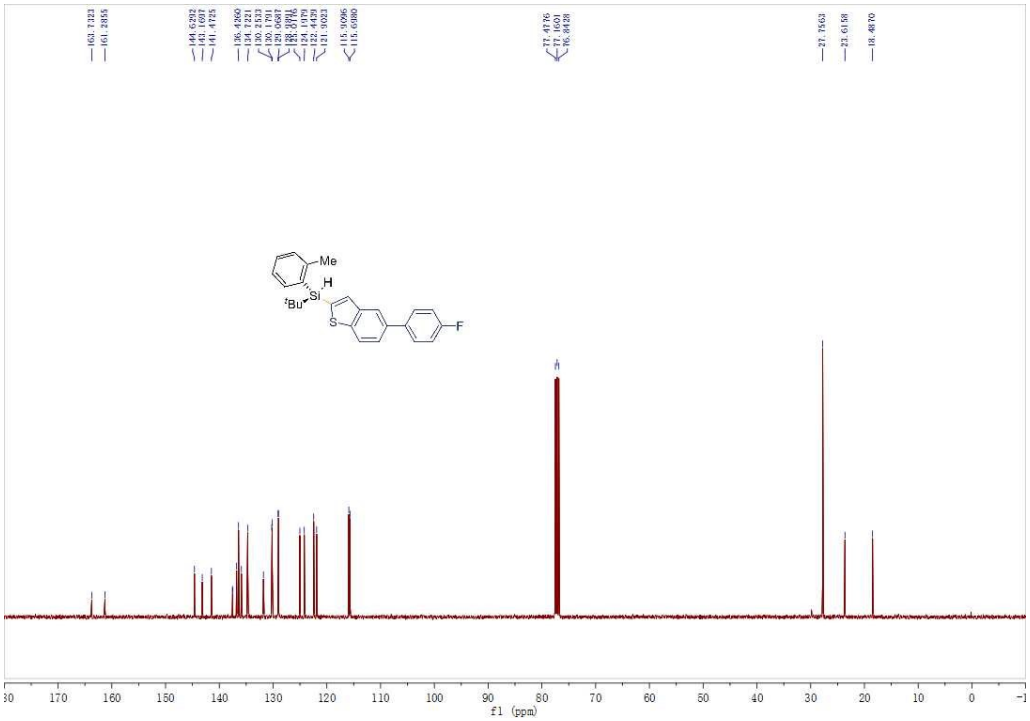

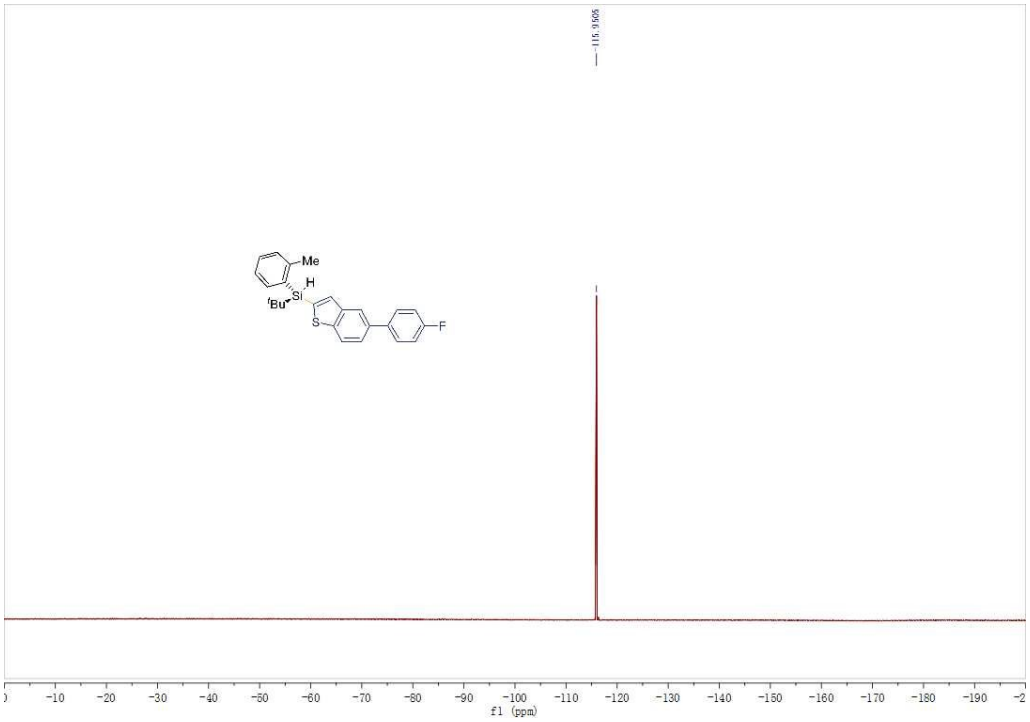
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Me
H
Si
tBu
S
F
-10
-20
-30
-40
-50
-60
-70
-80
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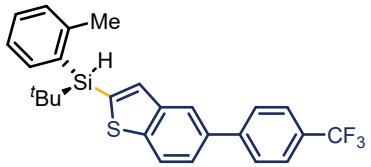
-150
-160
-170
-180
-190
f1 (ppm)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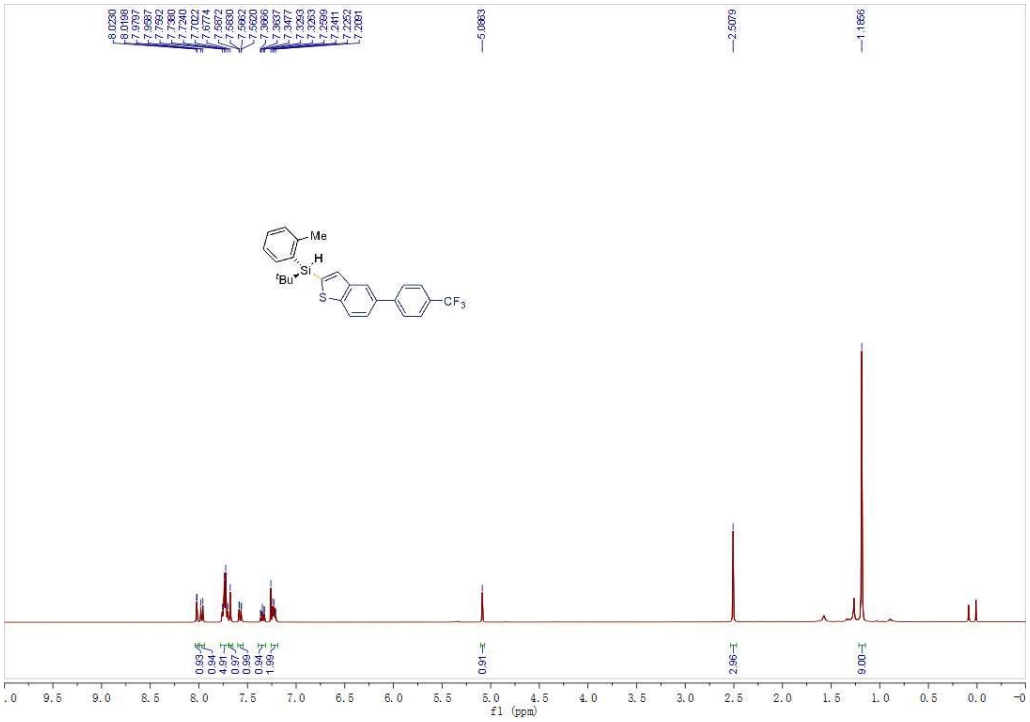
Si
tBu
S
CF3

3ag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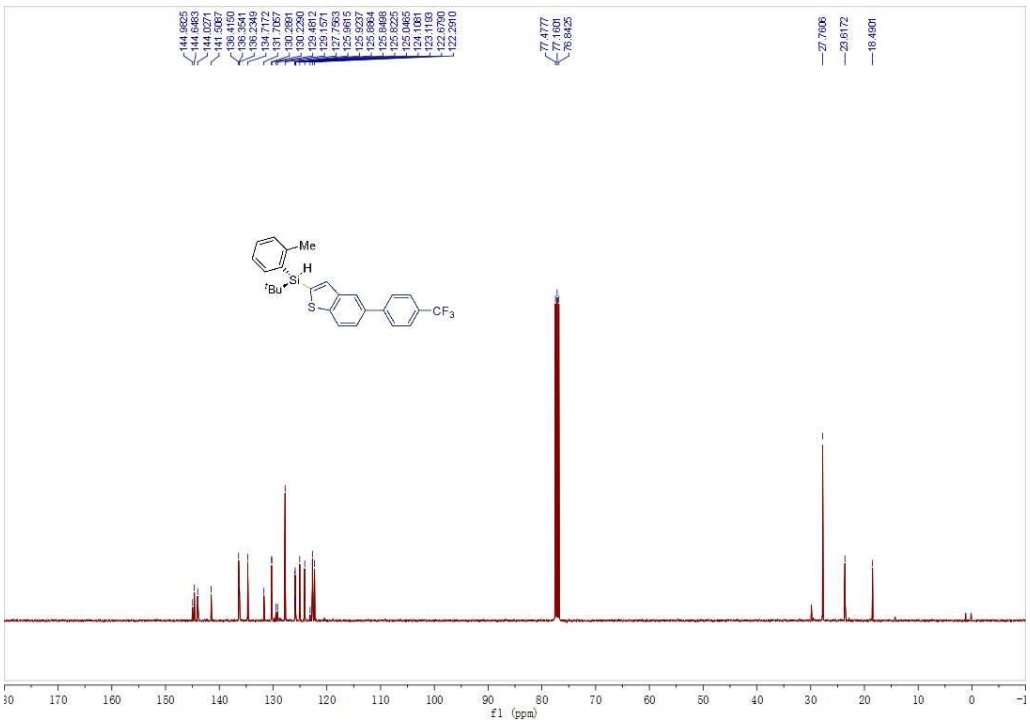
7.5830
7.5662
7.5620
7.3666
7.3637
7.3477
7.3293
7.3269
7.2411
7.2252
7.2091
5.0863
2.5079
1.1856
0.93
0.94
4.05
0.97
0.99
0.94
1.99
0.91
2.96
9.00
f1 (ppm)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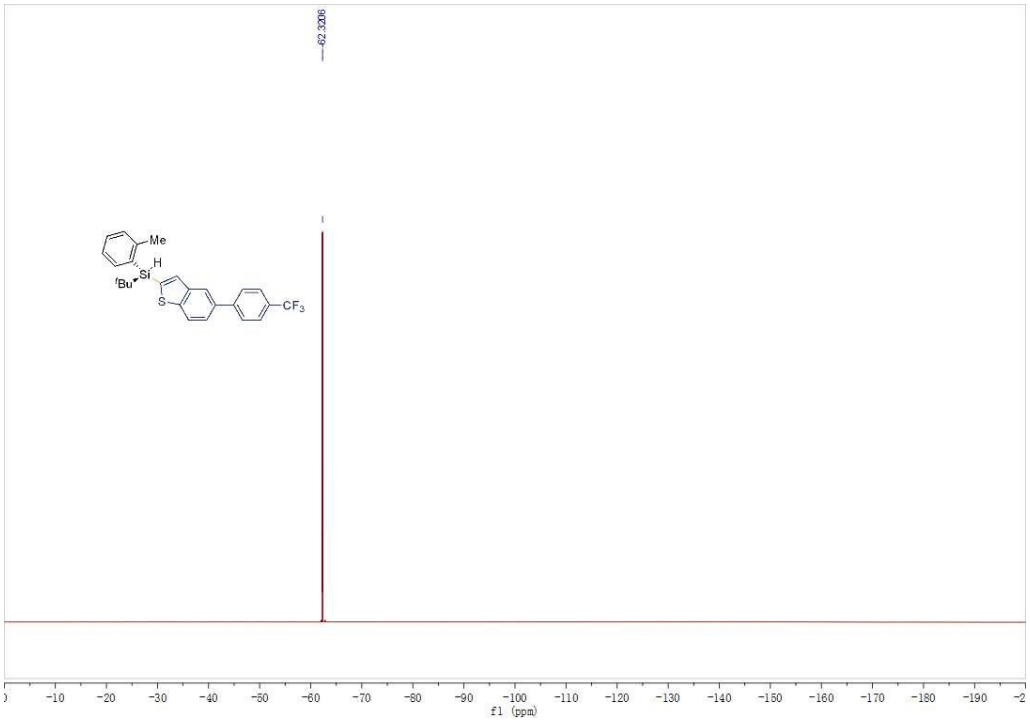
76.8425
27.7606
23.6172
18.4901
f1 (ppm)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Si
tBu
S
CF3
-10
-20
-30
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-50
-60
-70
-80
-90
-100
-110
-120
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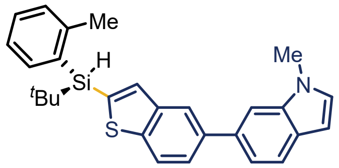
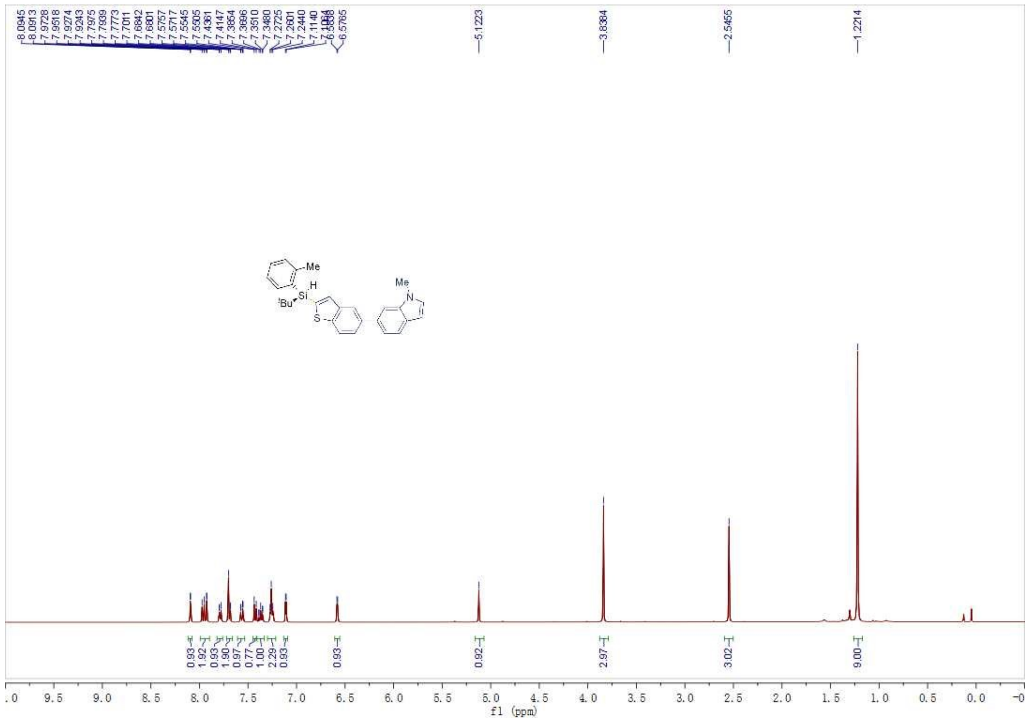
-140
-150
-160
-170
-180
-190
f1 (ppm)



Me
H
Si
tBu
S
Me
N

3ah



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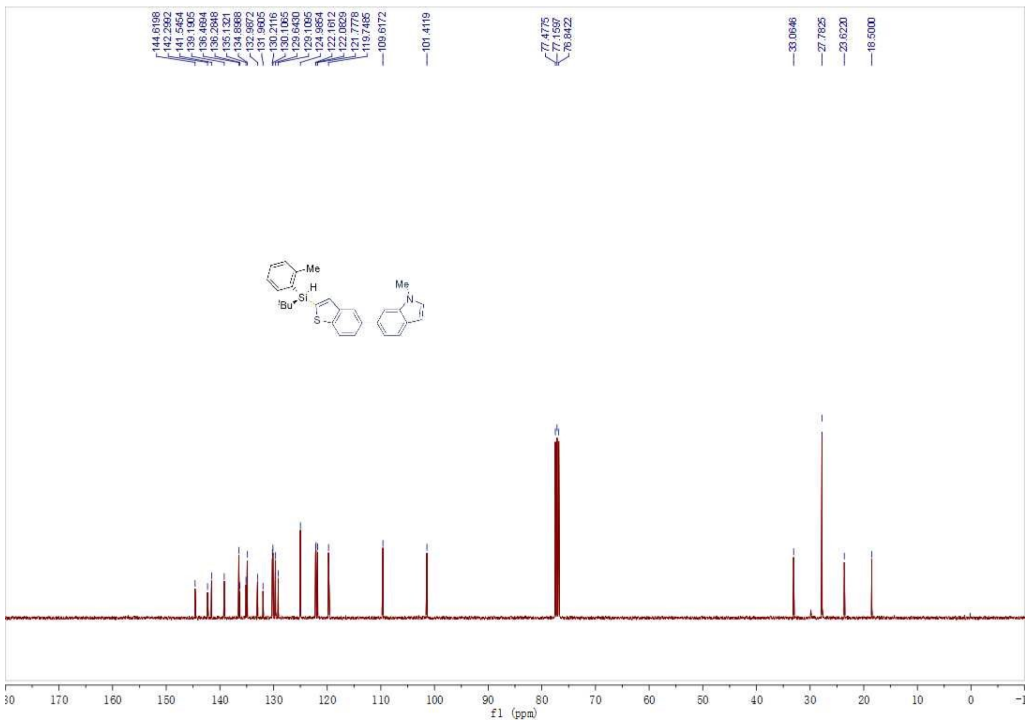
7.9518
7.9274
7.9243
7.7975
7.7939
7.7773
7.7011
7.6842
7.6801
7.5757
7.5717
7.5545
7.5505
7.4361
7.4147
7.3854
7.3996
7.3510
7.3480
7.2725
7.2601
7.2440
7.1140
6.5765
5.1223
3.8384
2.5455
1.2214
0.93
1.92
0.93
1.90
0.97
0.77
1.00
2.29
0.93
0.93
0.92
2.97
3.02
9.00
f1 (ppm)



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134.8988
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130.2116
130.1065
129.6430
129.1095
124.9854
122.1612
122.0829
121.7778
119.7485
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77.1597
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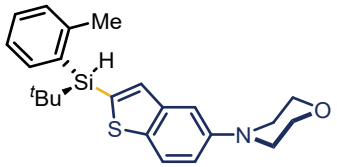
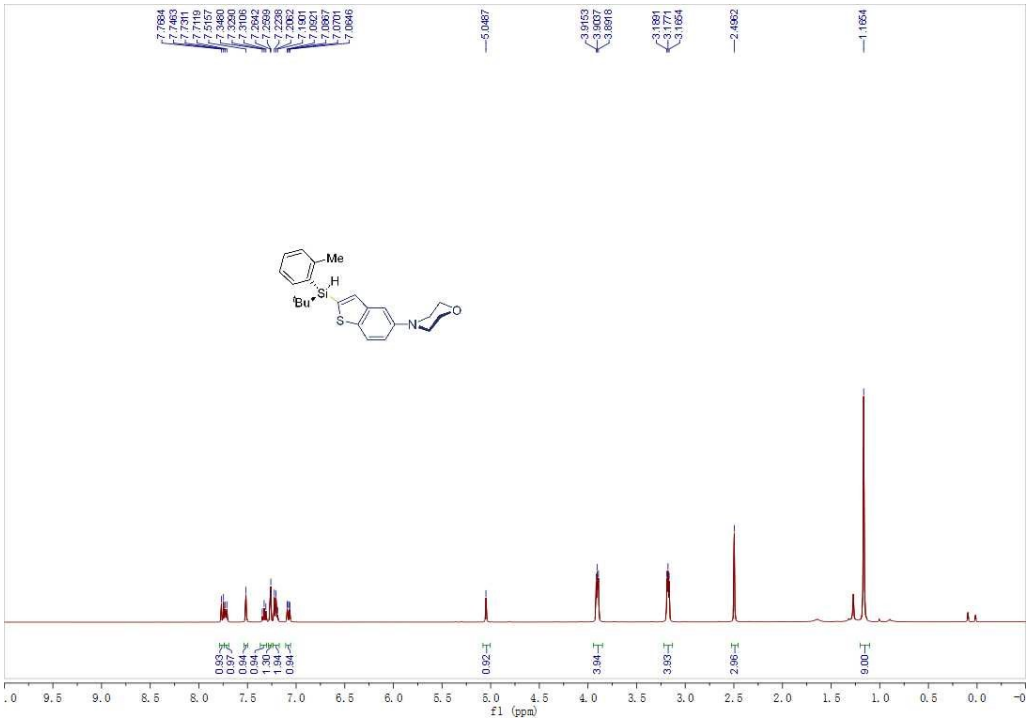
33.0646
27.7825
23.6220
18.5000
f1 (ppm)


Me
H
Si
tBu
S
N
O

3ai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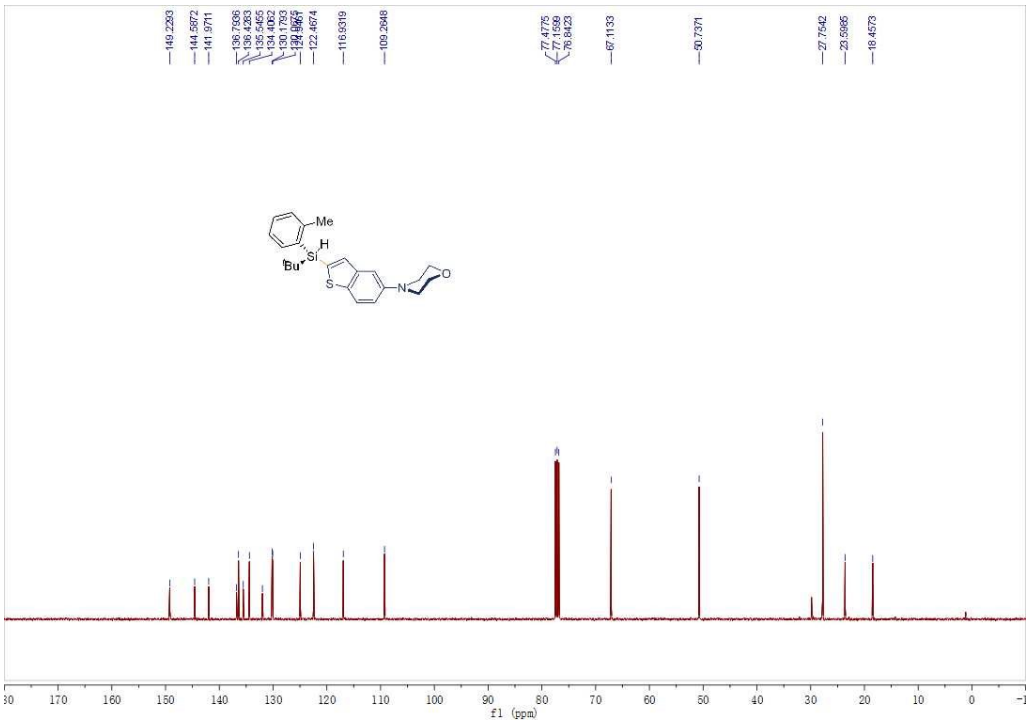
7.3290
7.3106
7.2942
7.2769
7.2238
7.2062
7.1901
7.0921
7.0867
7.0701
7.0648
5.0487
3.9153
3.9037
3.8918
3.1891
3.1771
3.1654
2.4962
1.1654
0.93
0.97
0.84
0.94
1.00
1.94
0.94
0.92
3.94
3.93
2.96
9.00
f1 (ppm)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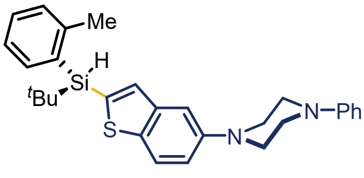
27.7542
23.5965
18.4573
f1 (ppm)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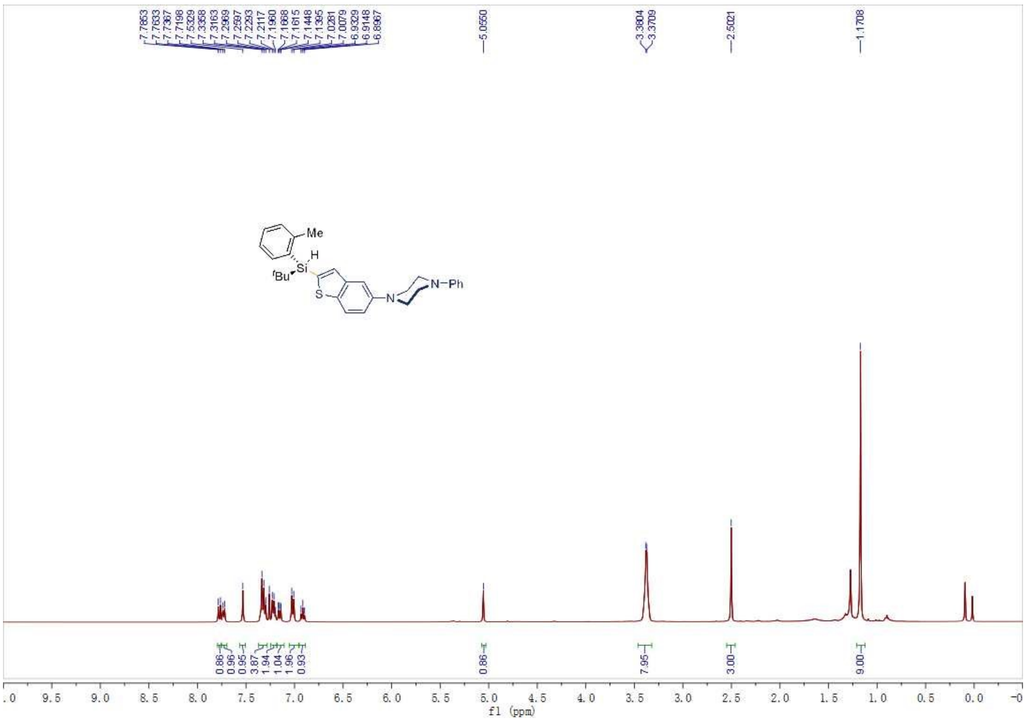
H
Si
tBu
S
N
N–Ph

3aj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7.5329
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7.3163
7.2969
7.2597
7.2293
7.2117
7.1960
7.1668
7.1615
7.1446
7.1395
7.0281
7.0079
6.9329
6.9148
6.8967
5.0550
3.3804
3.3709
2.5021
1.1708
0.86
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0.95
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1.94
1.04
1.96
0.93
0.86
7.95
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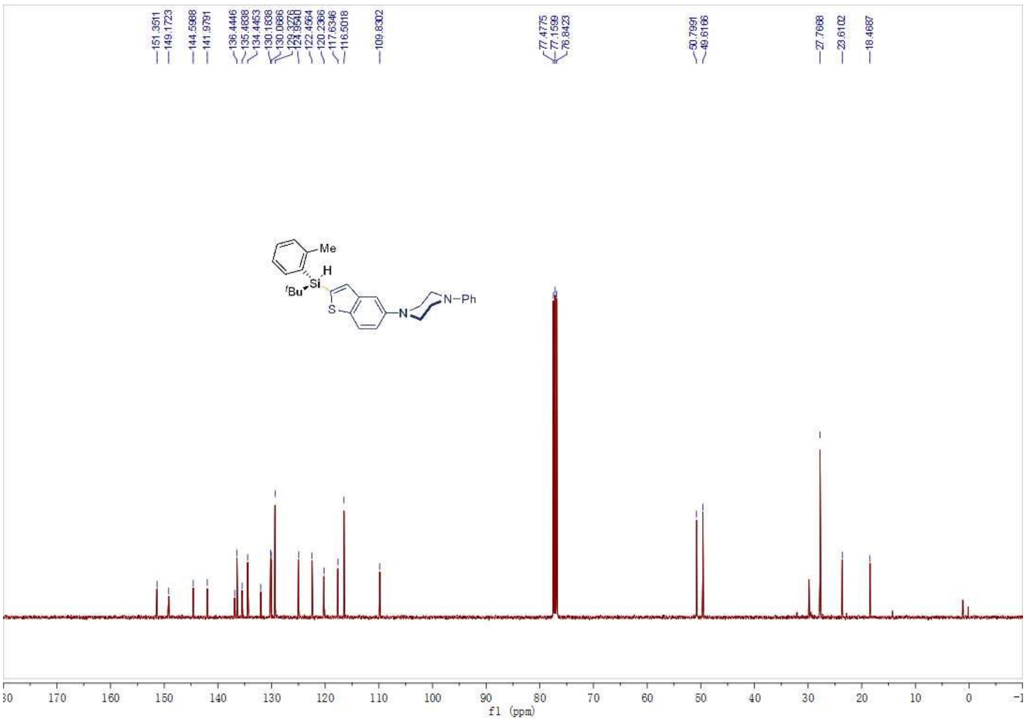
9.00
f1 (ppm)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122.4564
120.2386
117.6346
116.5018
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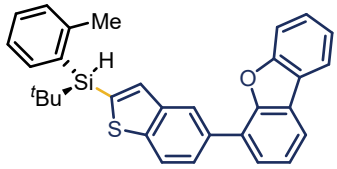
f1 (ppm)



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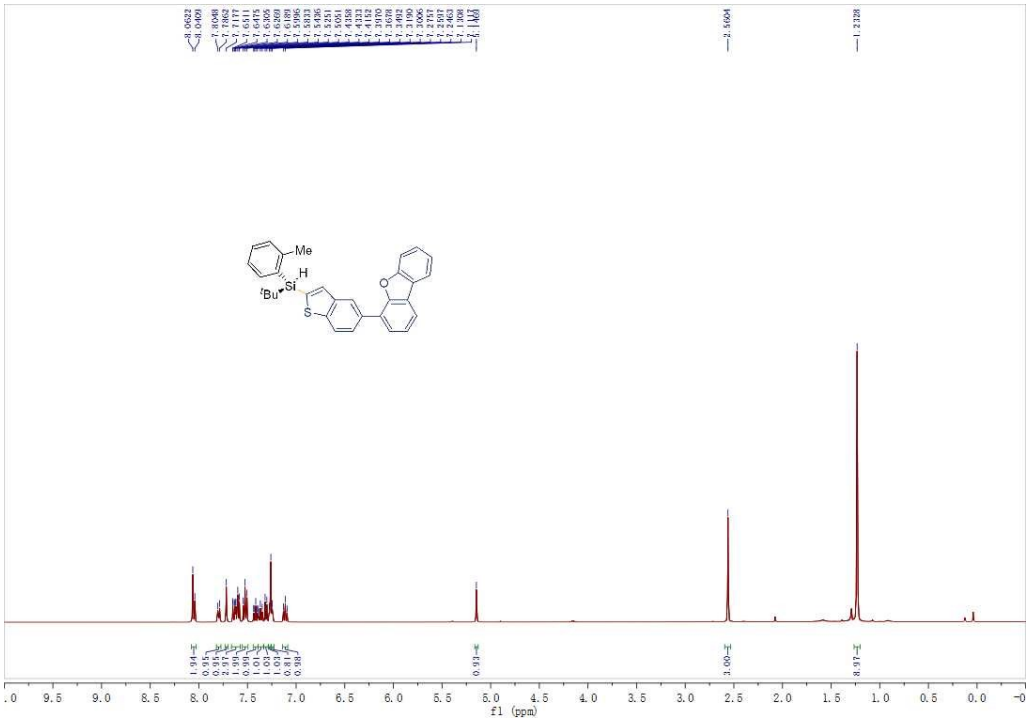

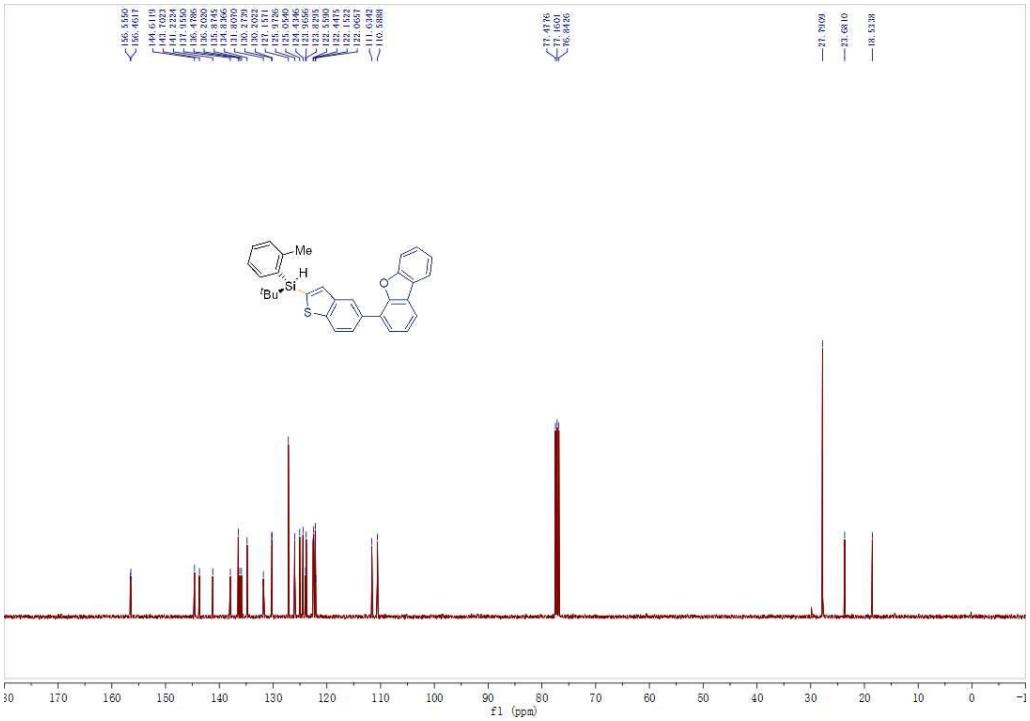

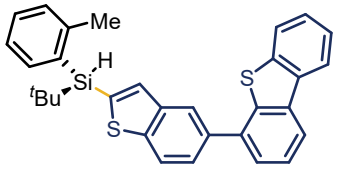

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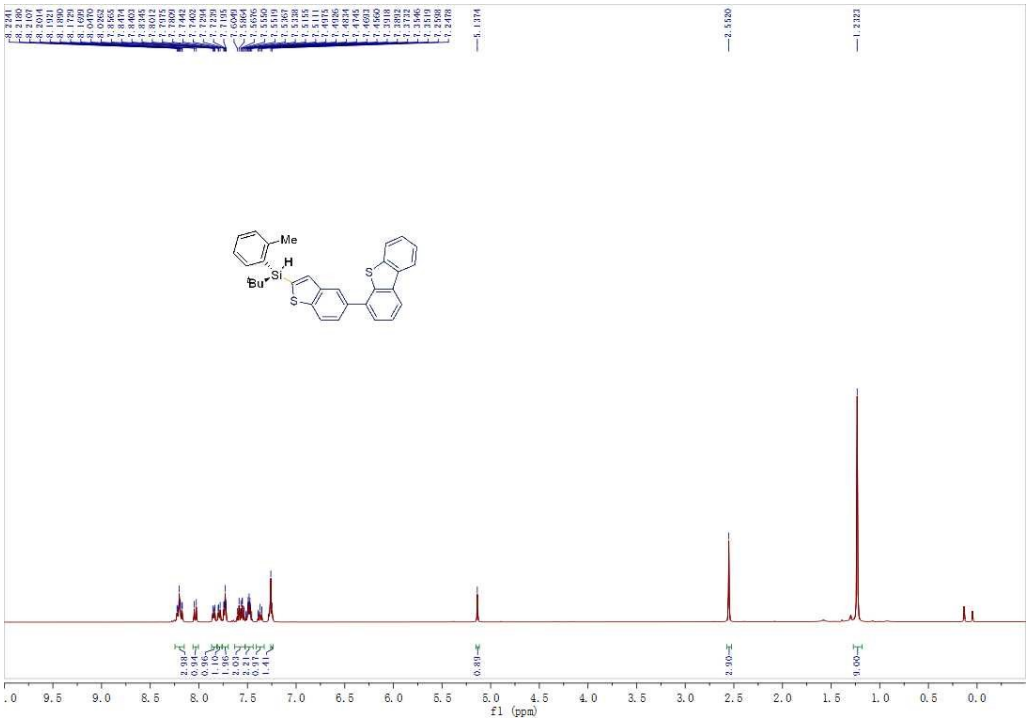

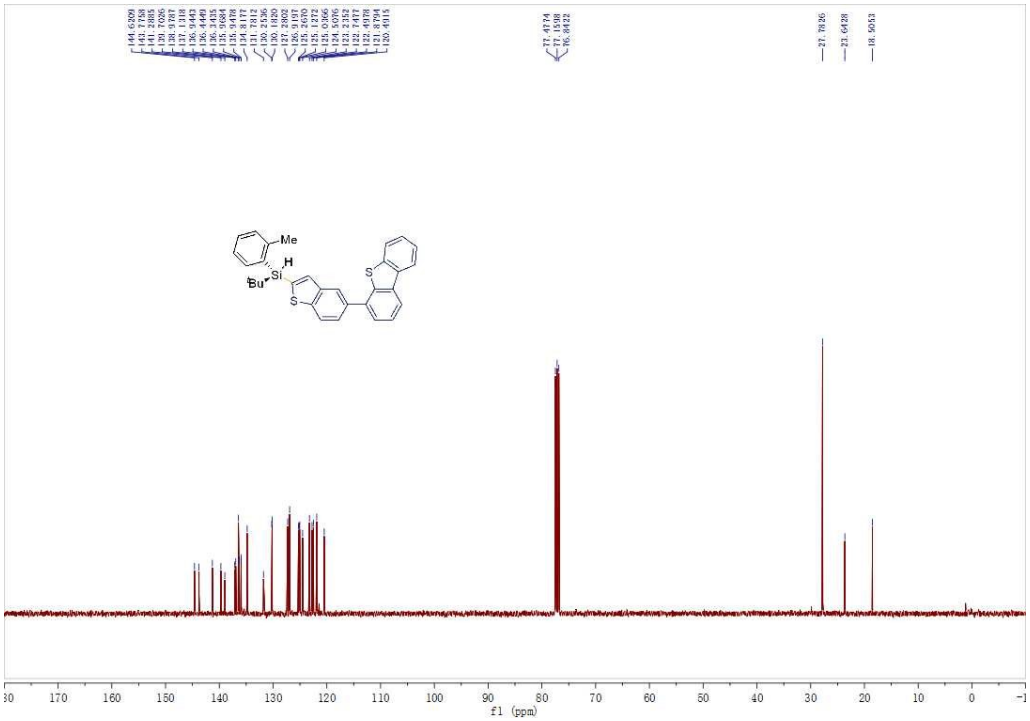

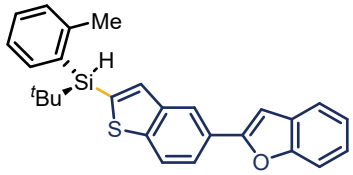

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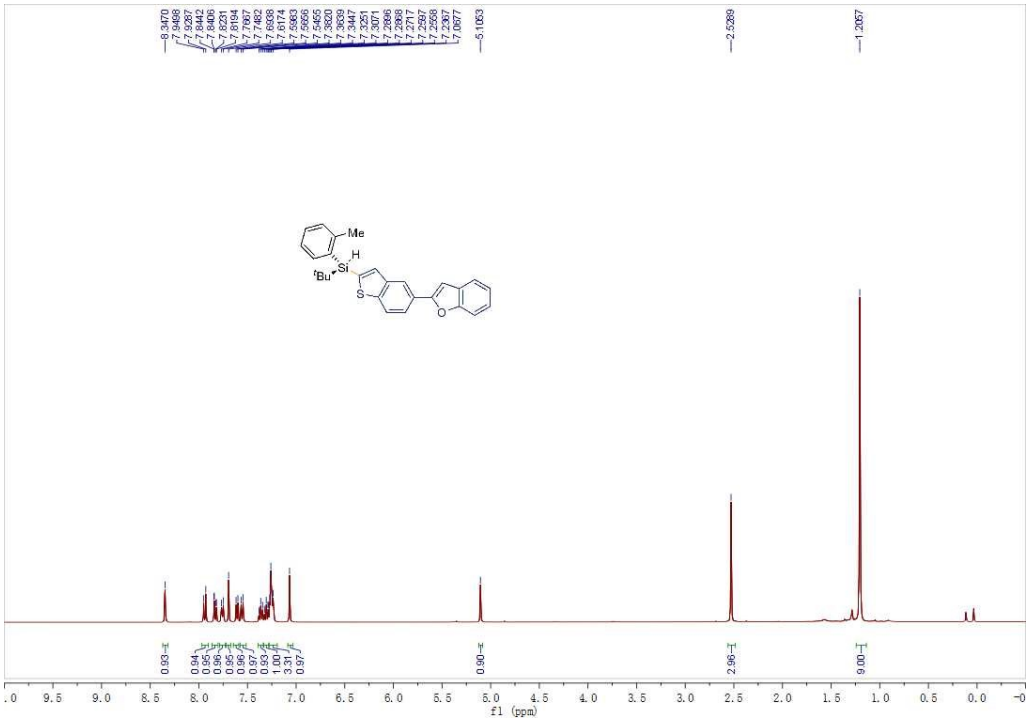

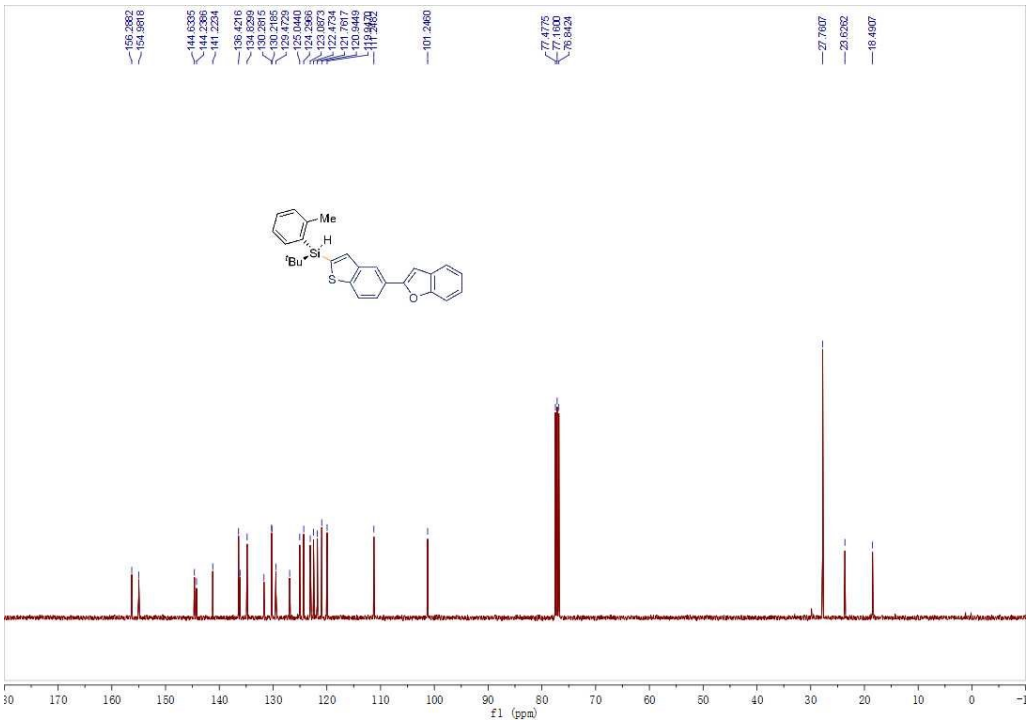

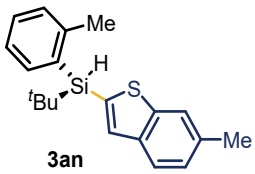

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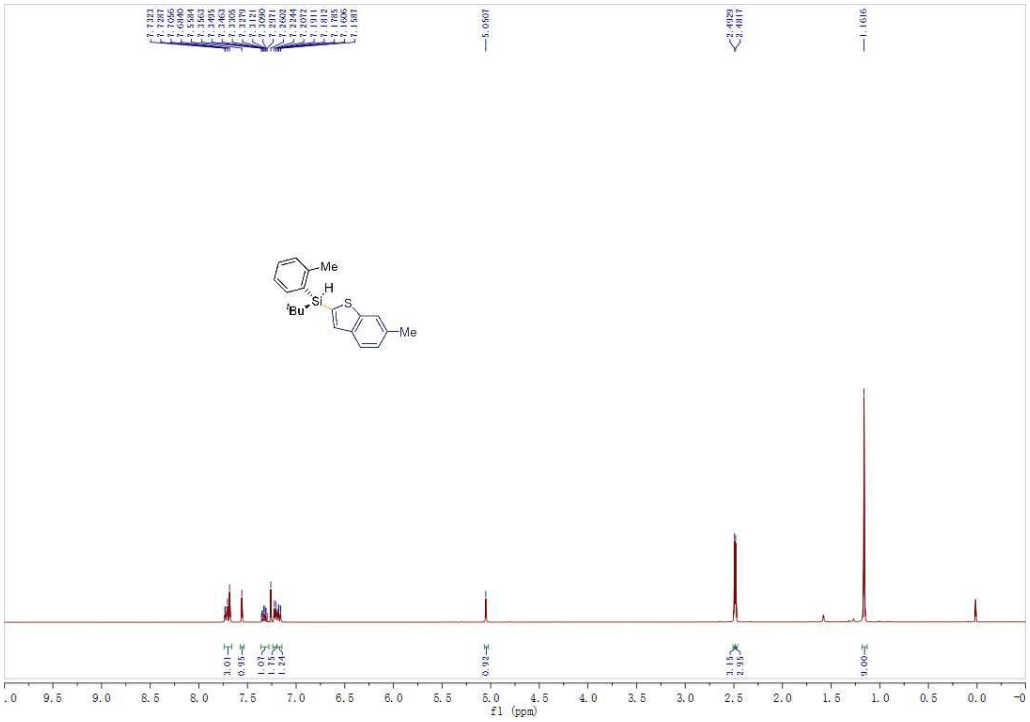

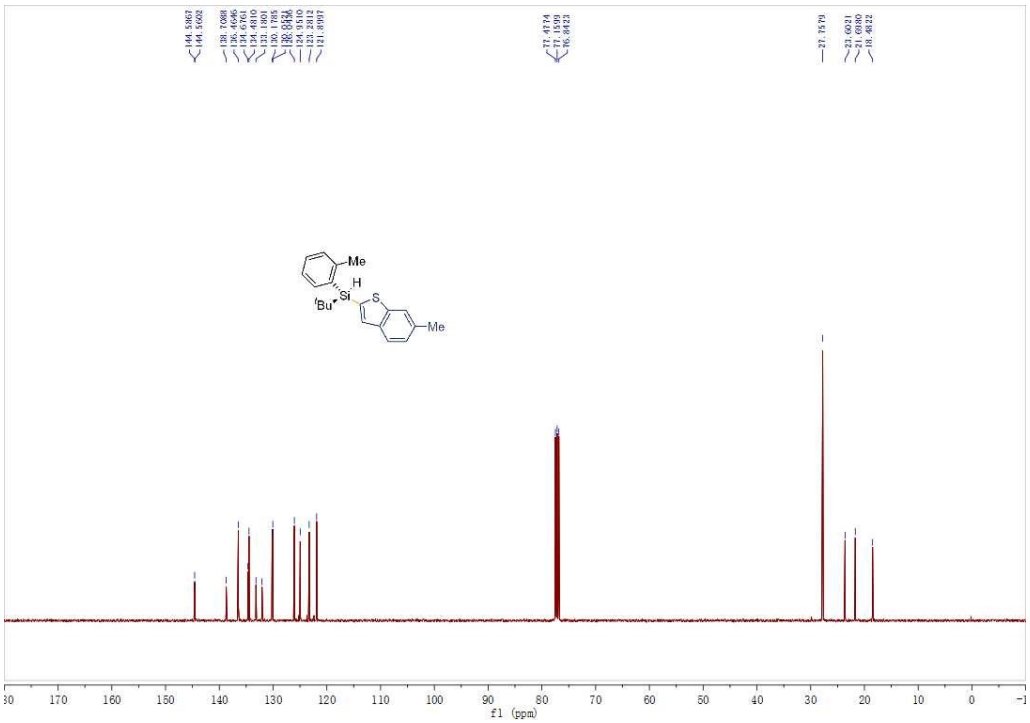

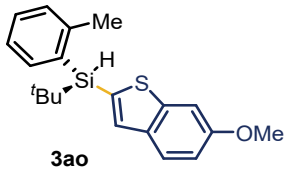

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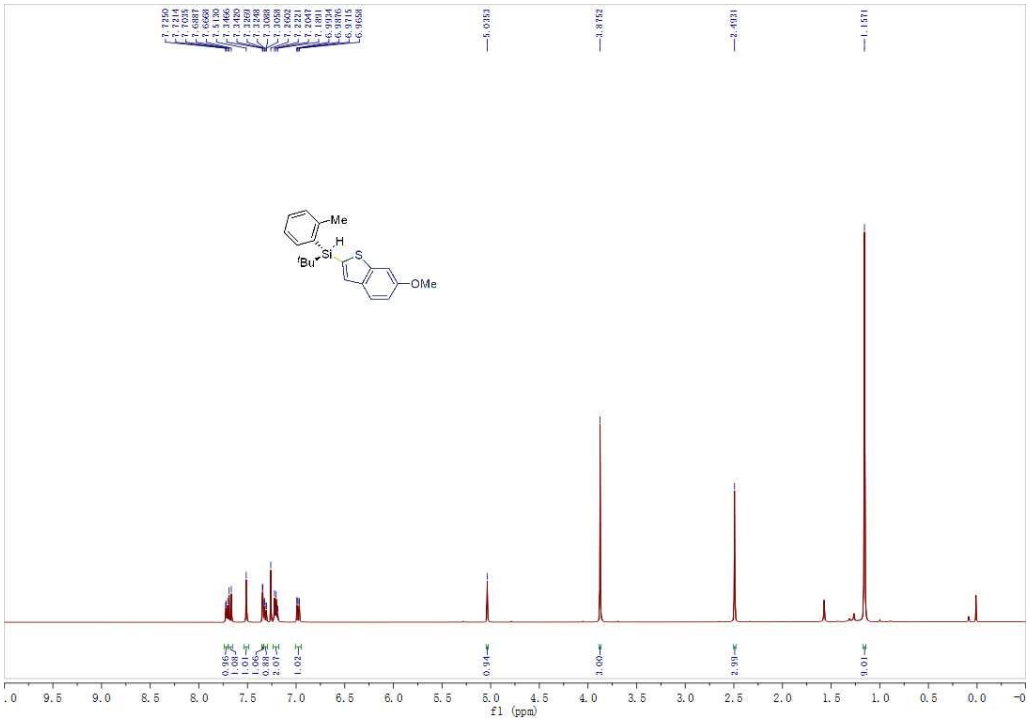

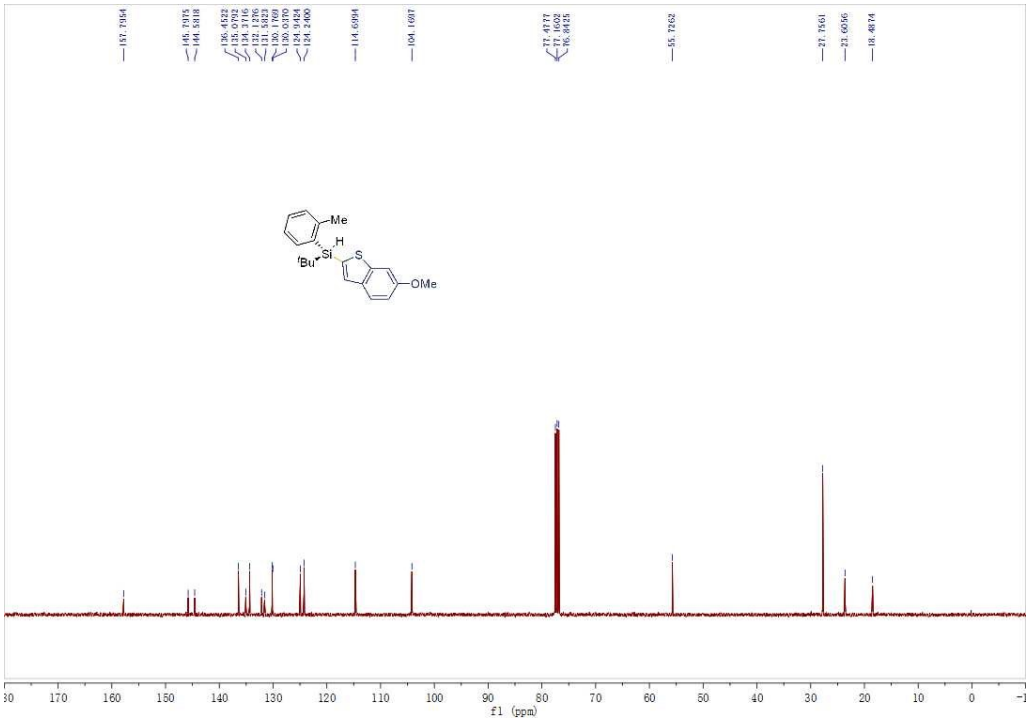

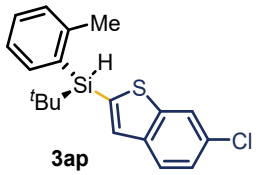

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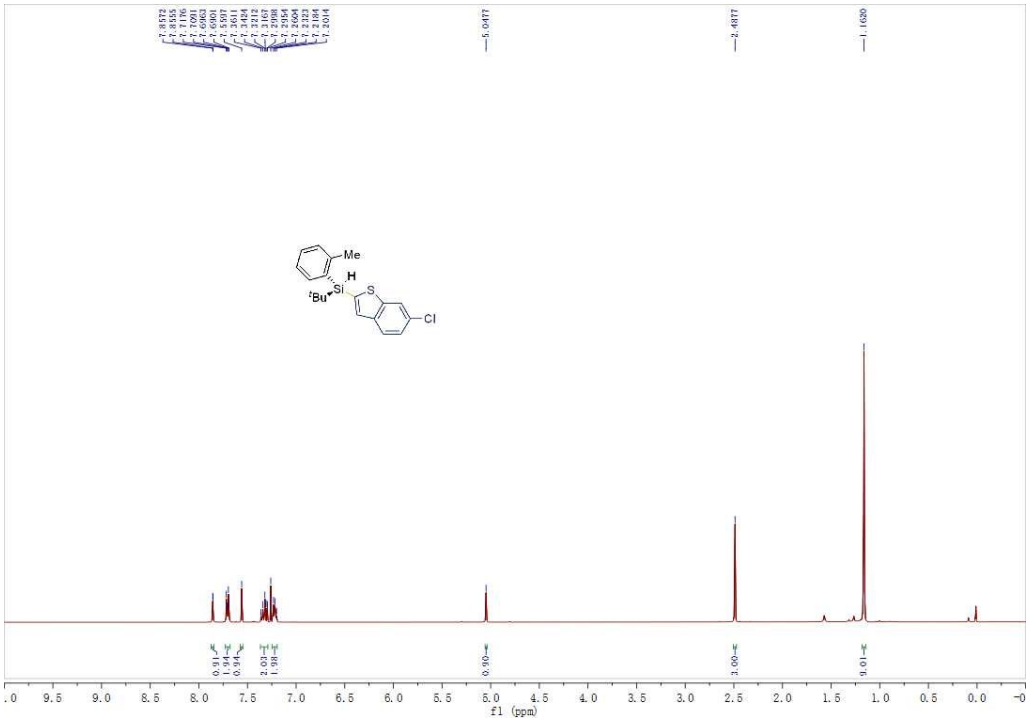

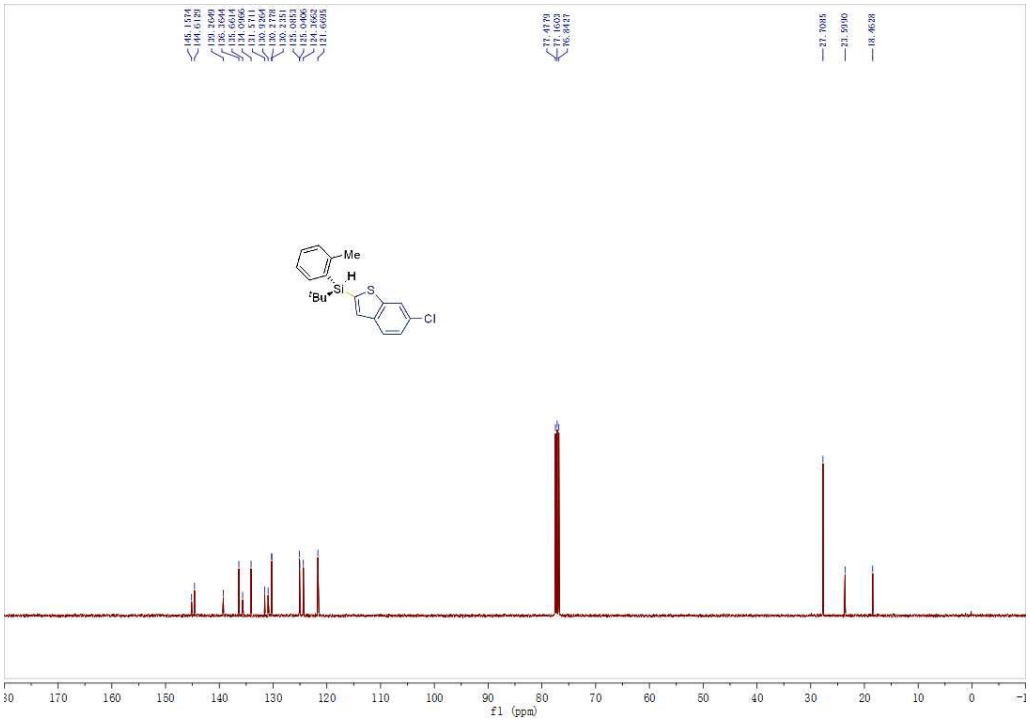

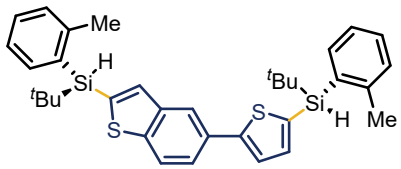

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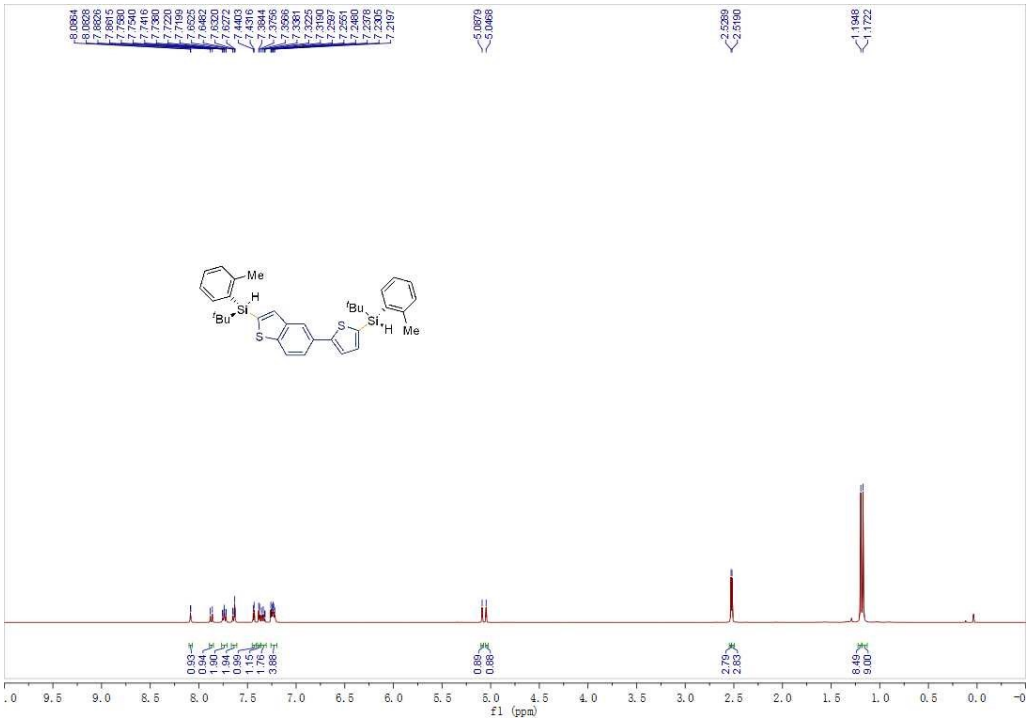
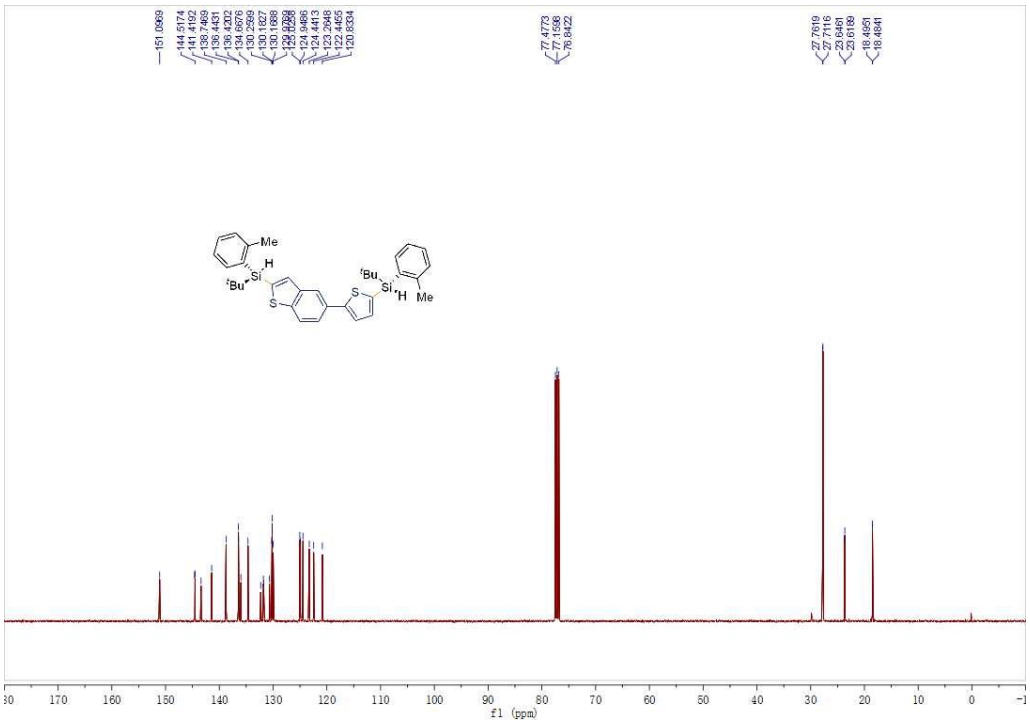
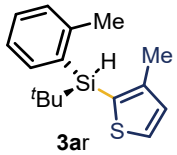
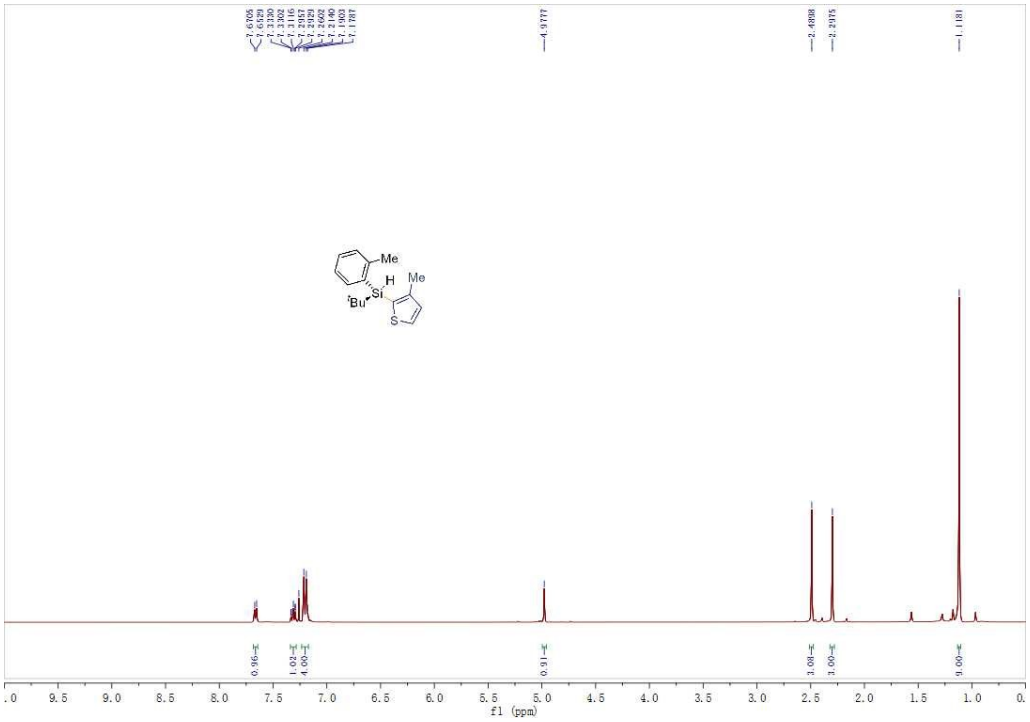





Me
H
Me
tBu
Si
S

3ar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7.2929
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7.1787
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1.02
4.00
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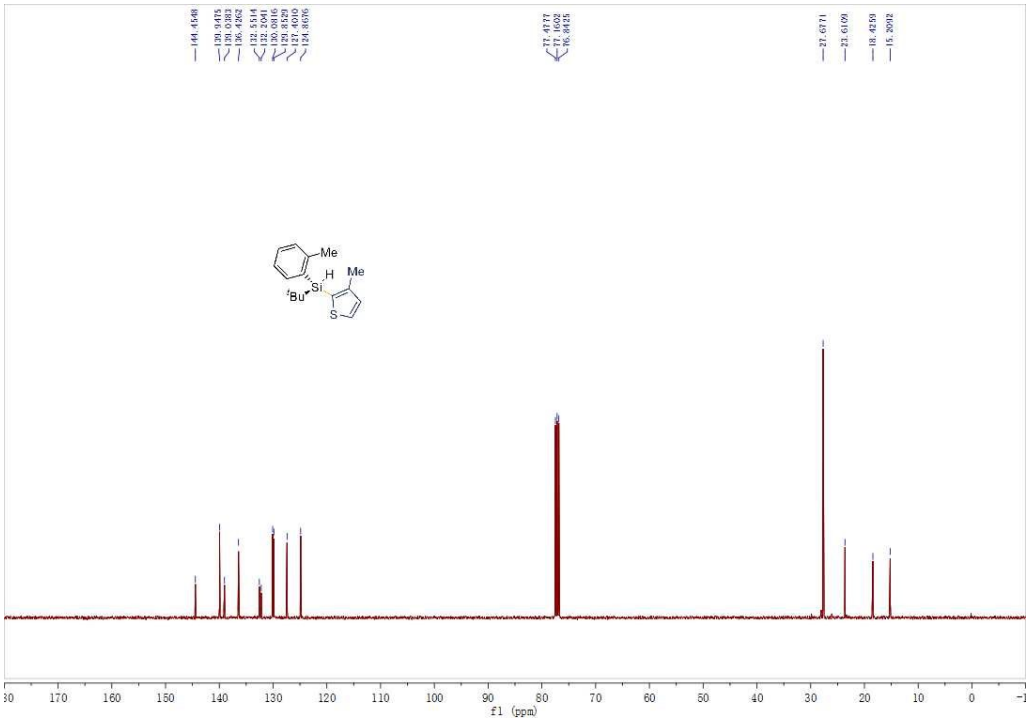
3.08
3.00
9.00
f1 (ppm)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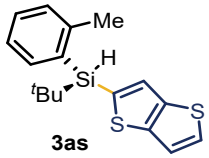
25.6109
18.4259
15.2092
f1 (ppm)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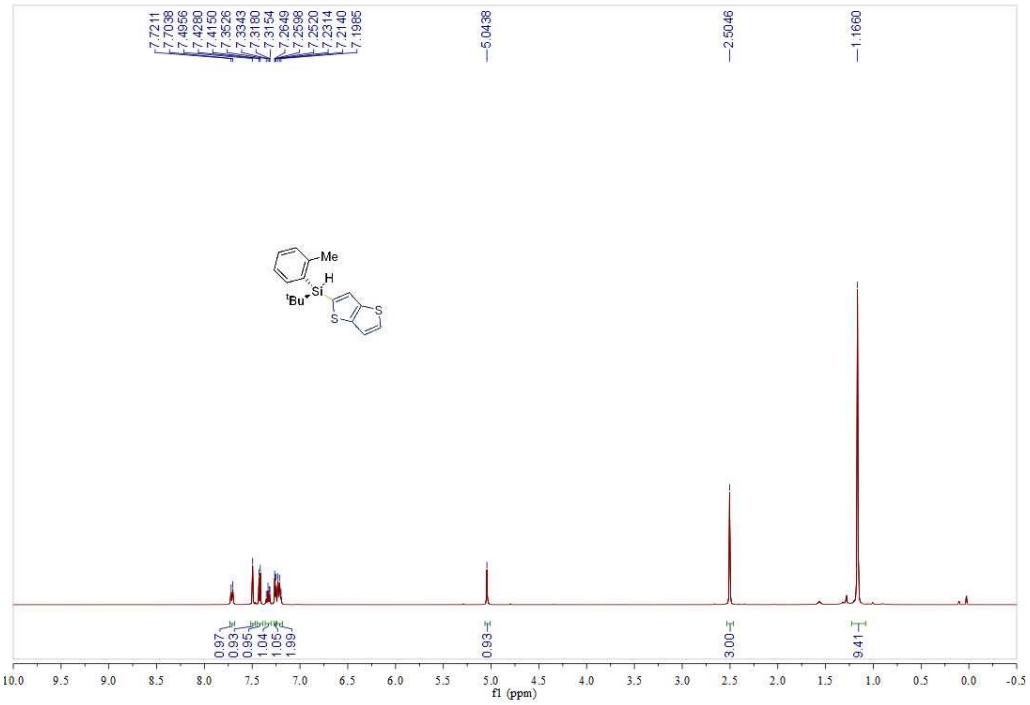
H
Si
tBu
S
S

3as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7.1985
5.0438
2.5046
1.1660
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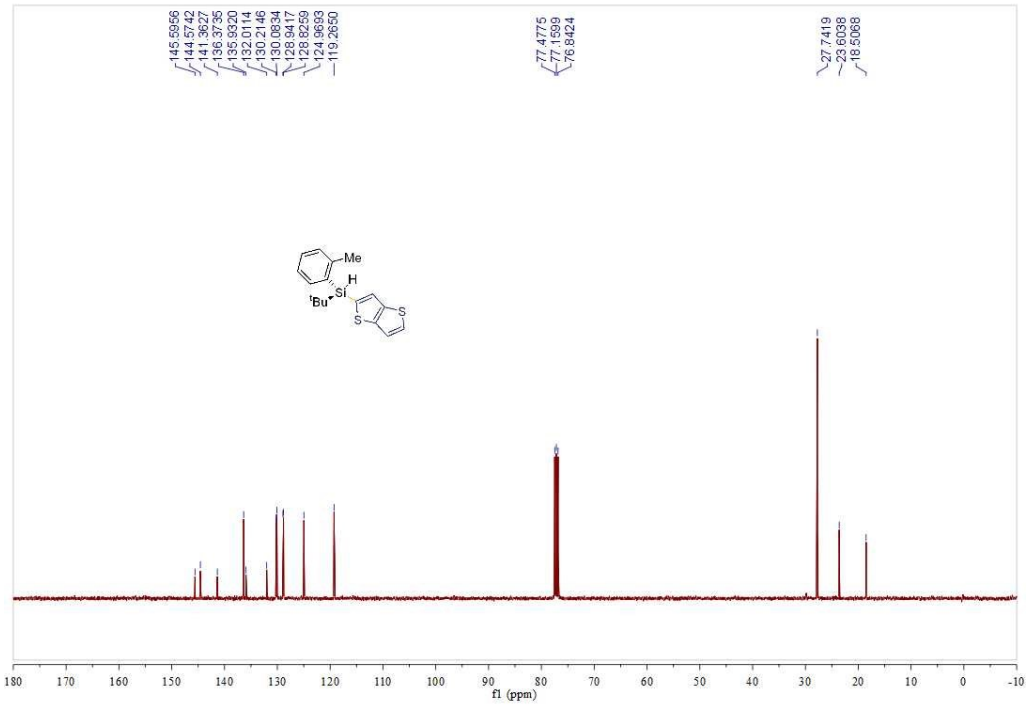
0.93
0.95
1.04
1.05
1.99
0.93
3.00
9.41
f1 (ppm)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130.2146
130.0834
128.9417
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119.2650
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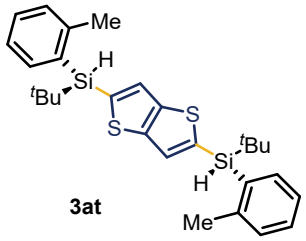
77.1599
76.8424
27.7419
23.6038
18.5068
f1 (ppm)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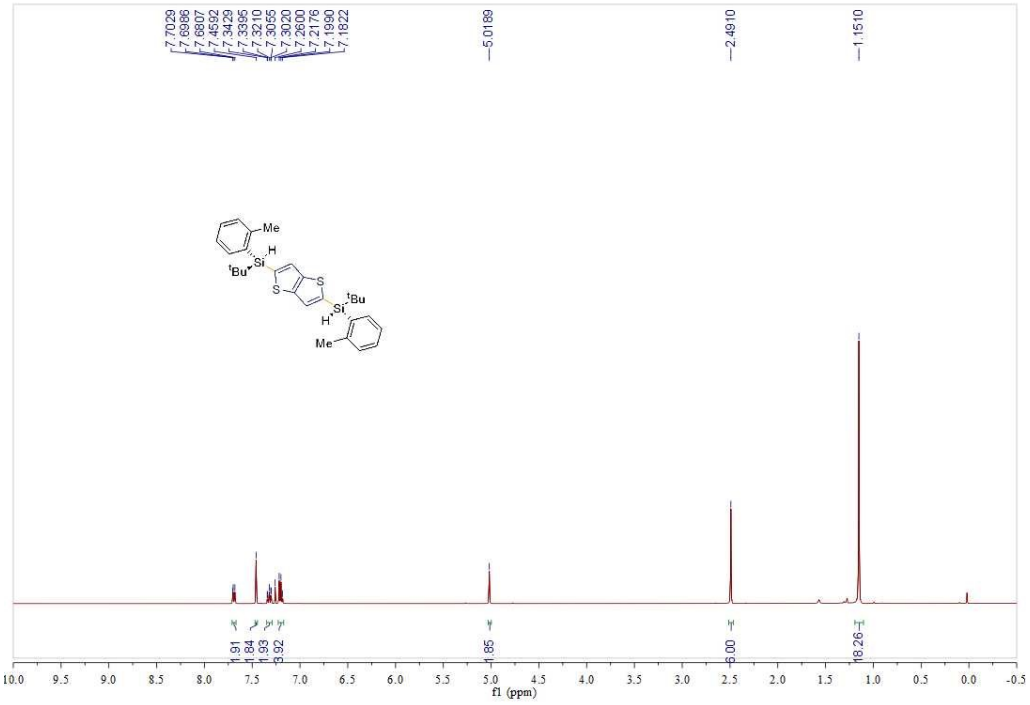
Si
tBu
S
S
Si
tBu
H
Me

3at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7.3429
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7.3210
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7.3020
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7.2176
7.1990
7.1822
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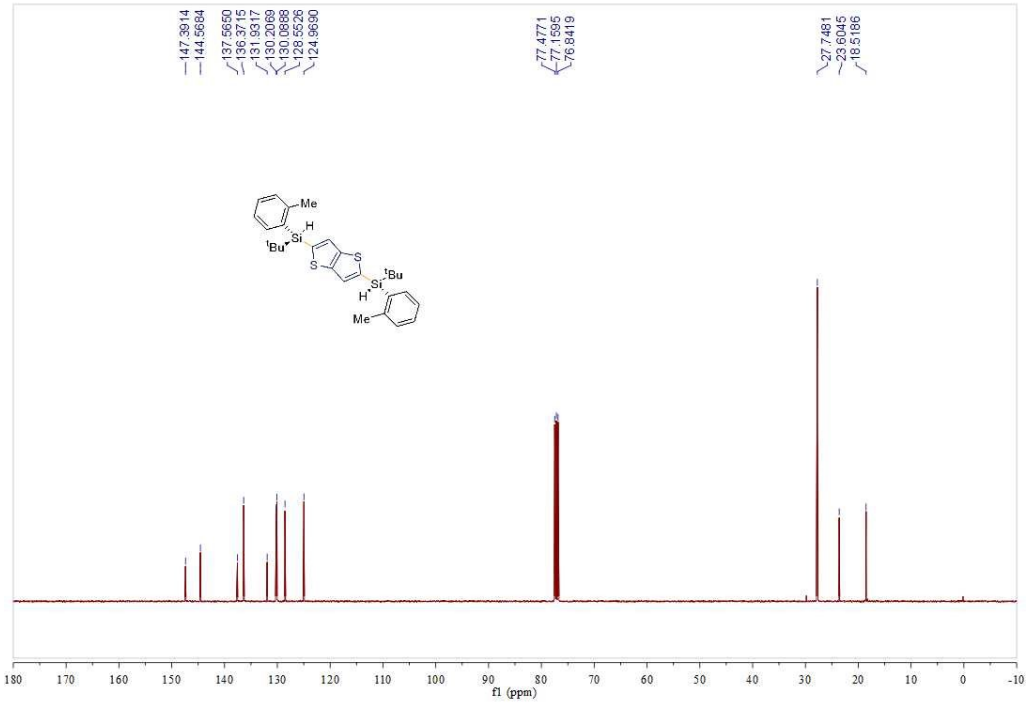
1.91
1.84
1.93
3.92
1.85
6.00
18.26
f1 (ppm)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131.9317
130.2069
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27.7481
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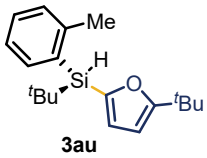
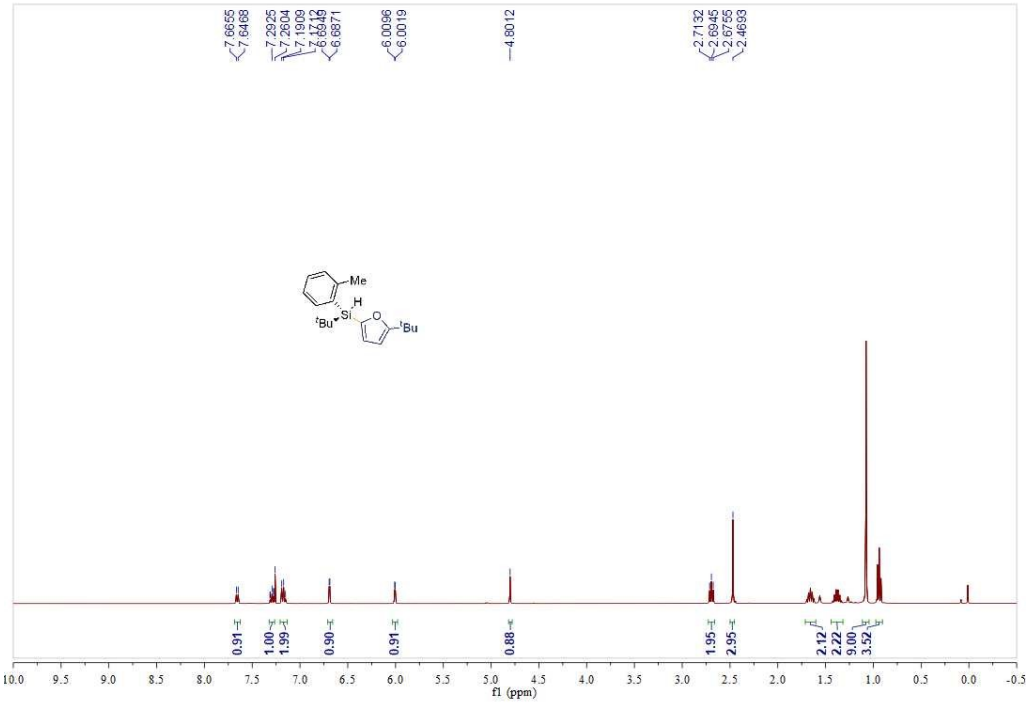
18.5186
f1 (ppm)


Me
H
Si
O
tBu
tBu

3au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6.0096
6.0019
4.8012
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2.6945
2.6755
2.4693
0.91
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0.91
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2.22
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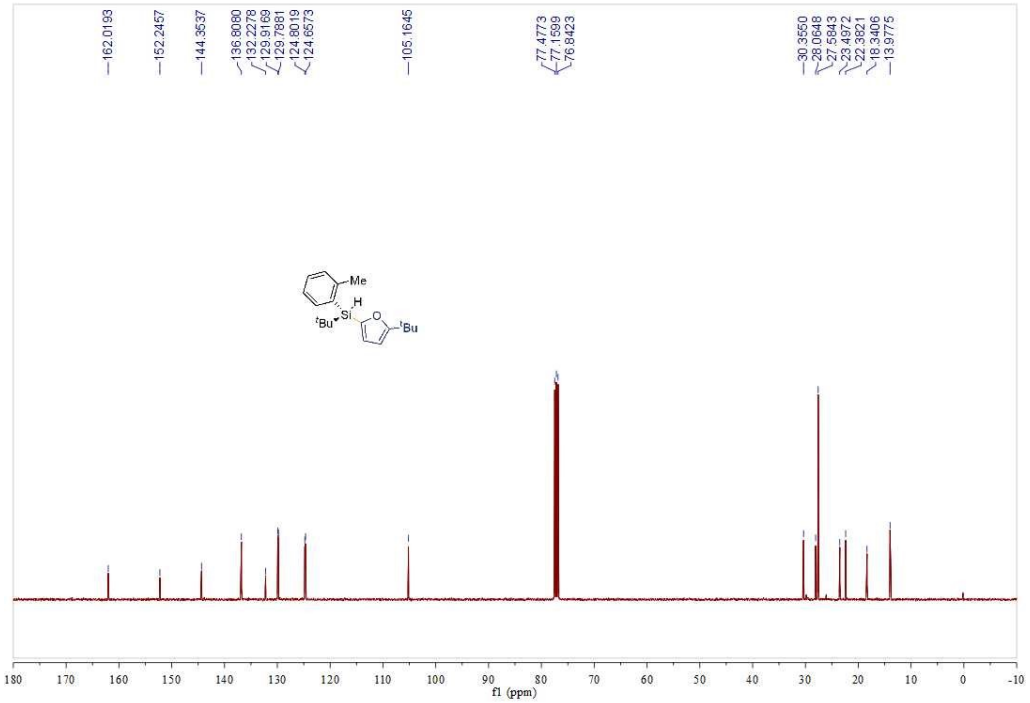
f1 (ppm)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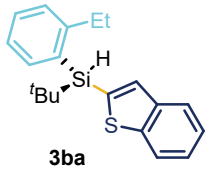
f1 (ppm)



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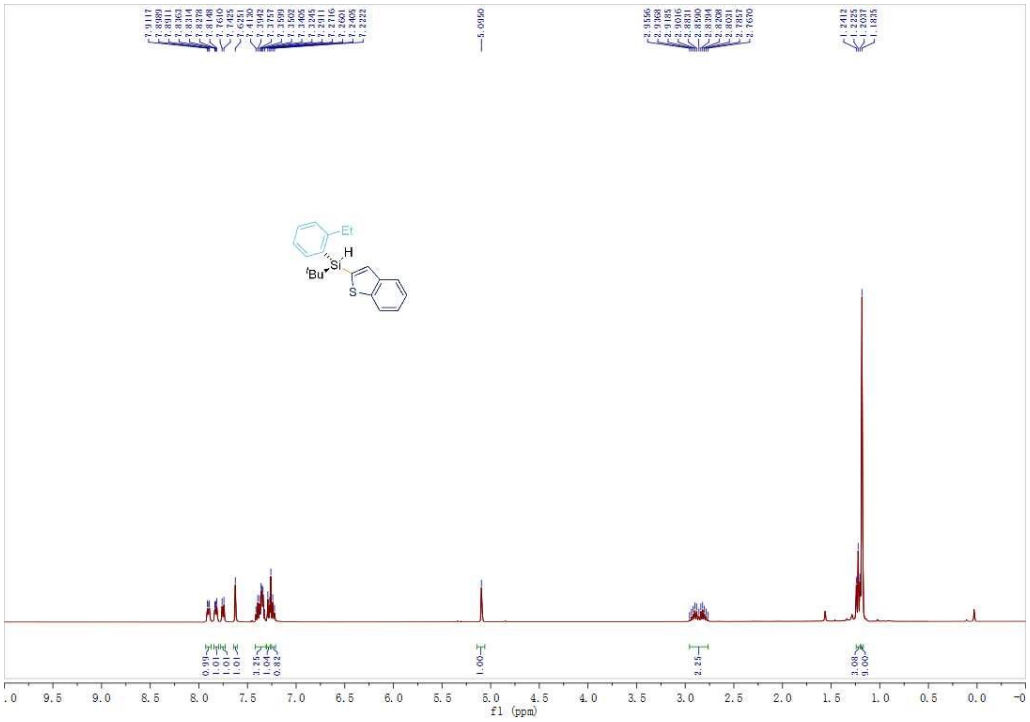

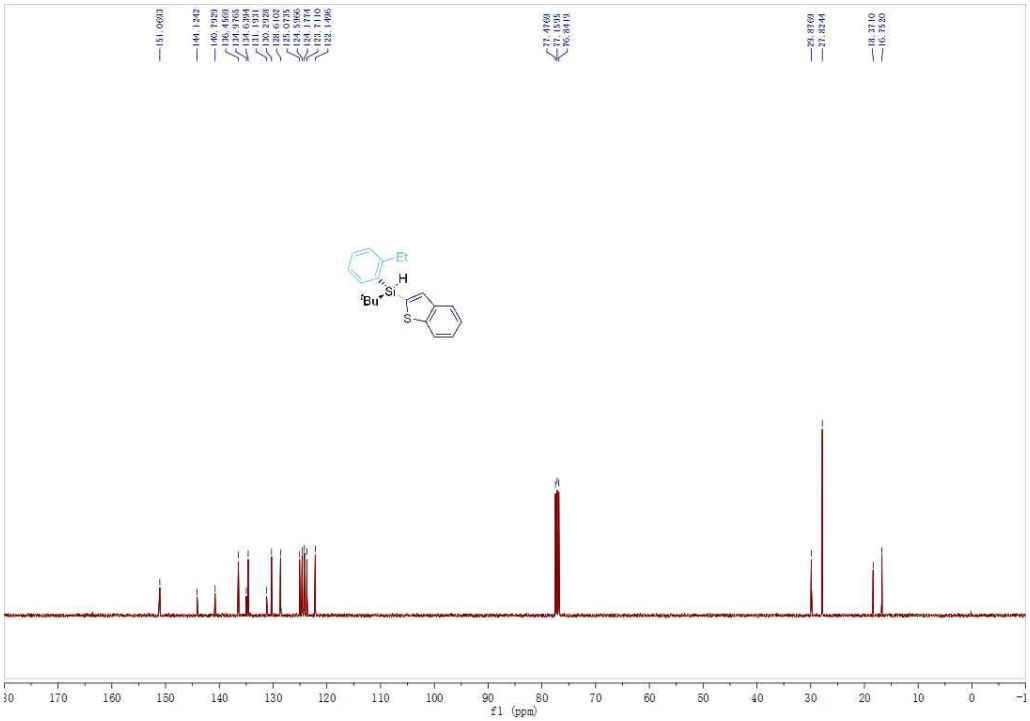

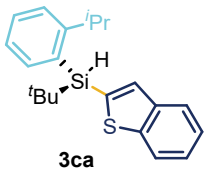

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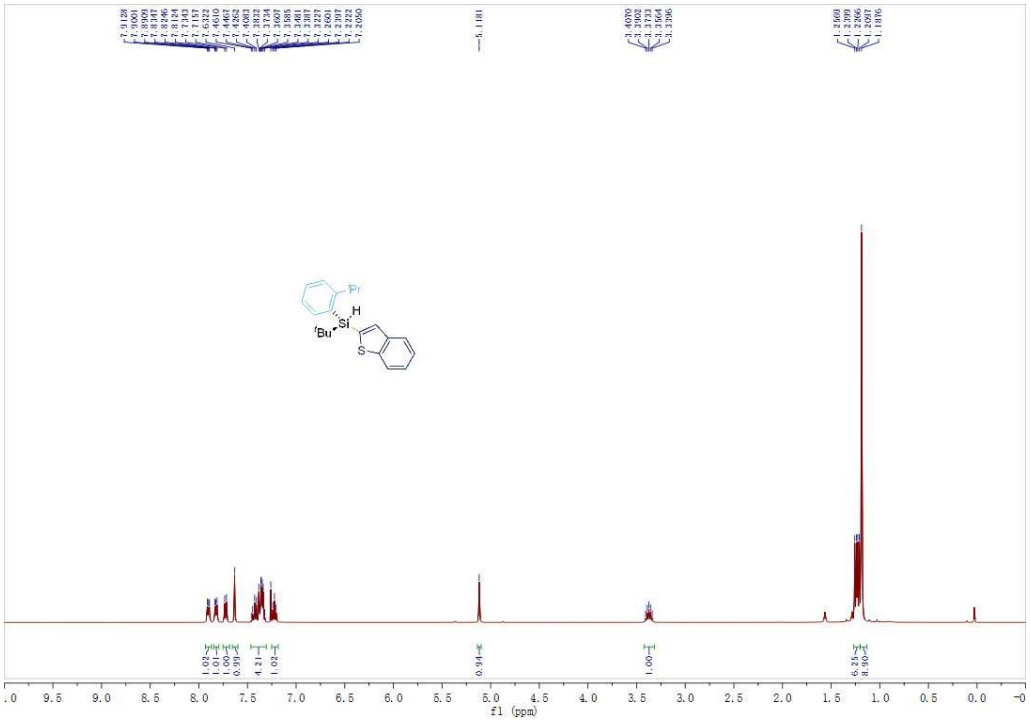

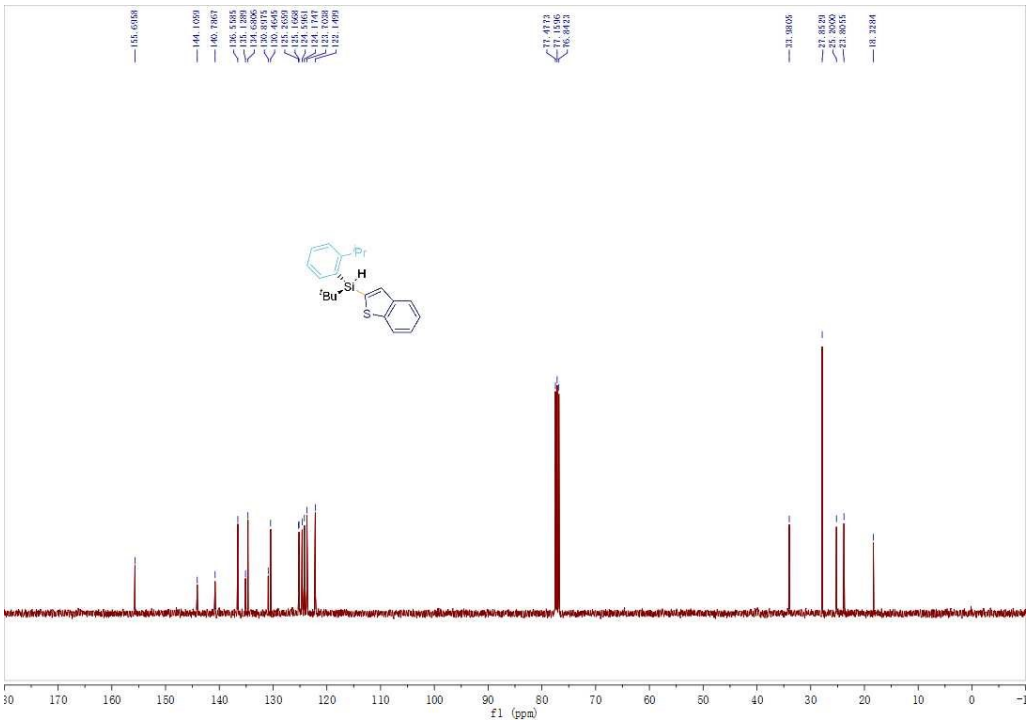

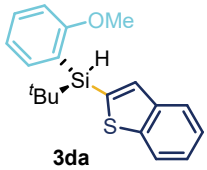

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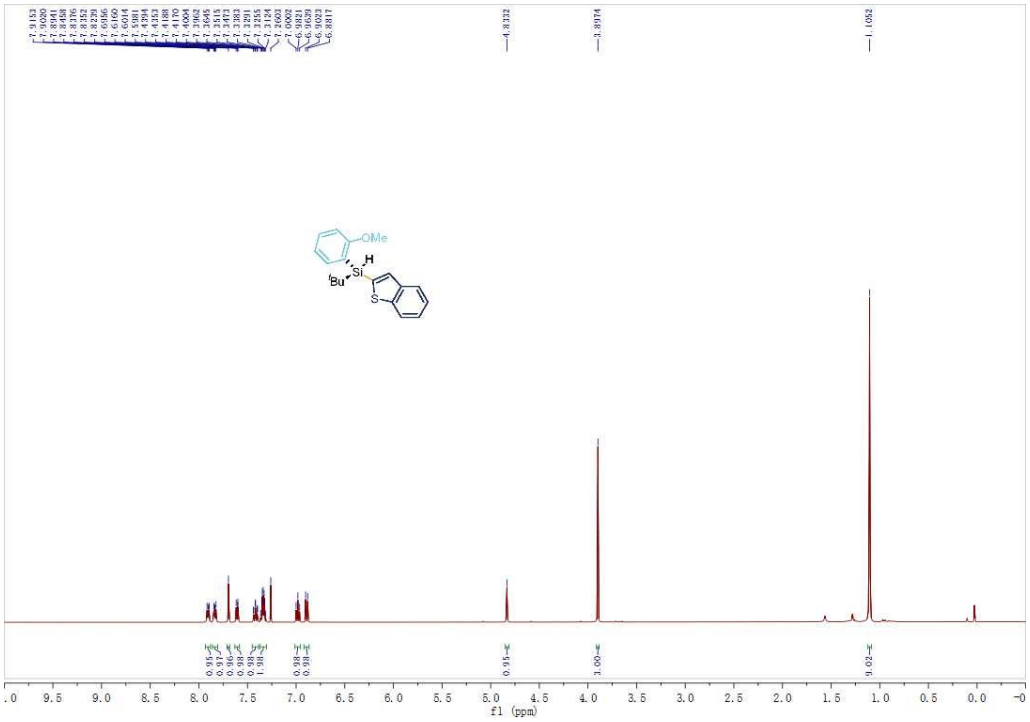

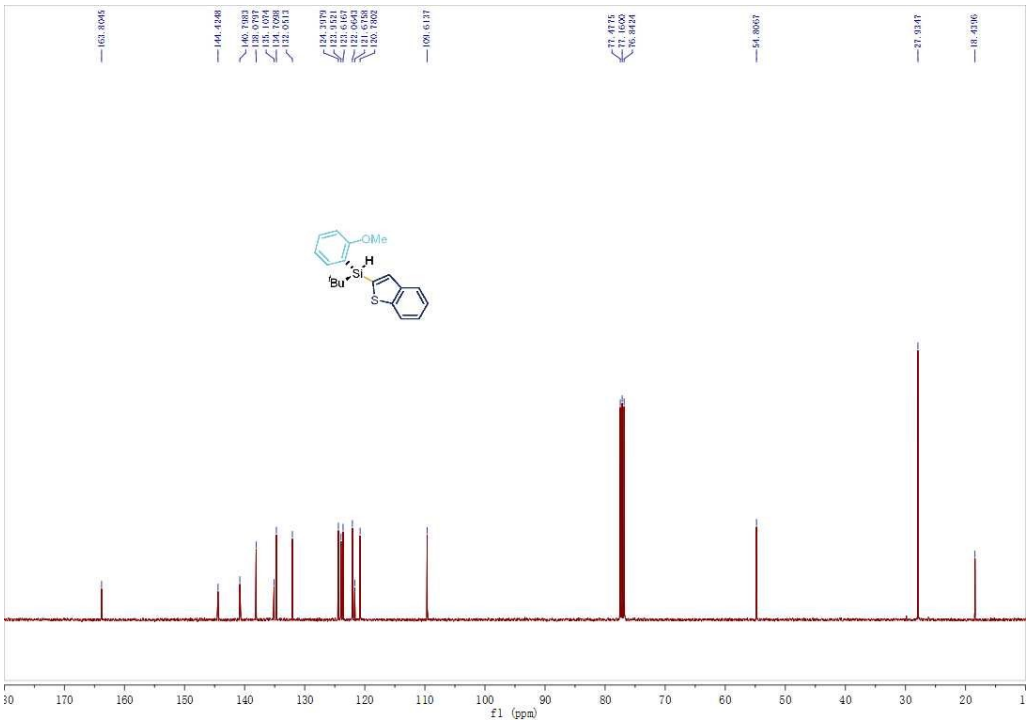

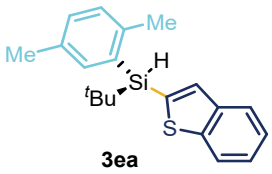

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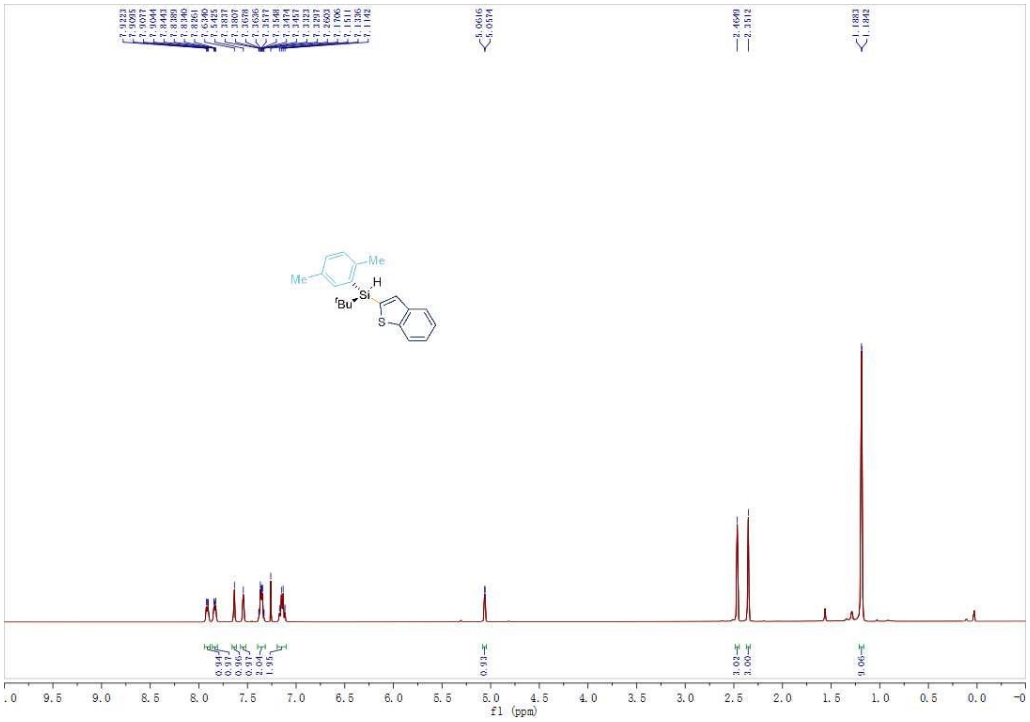

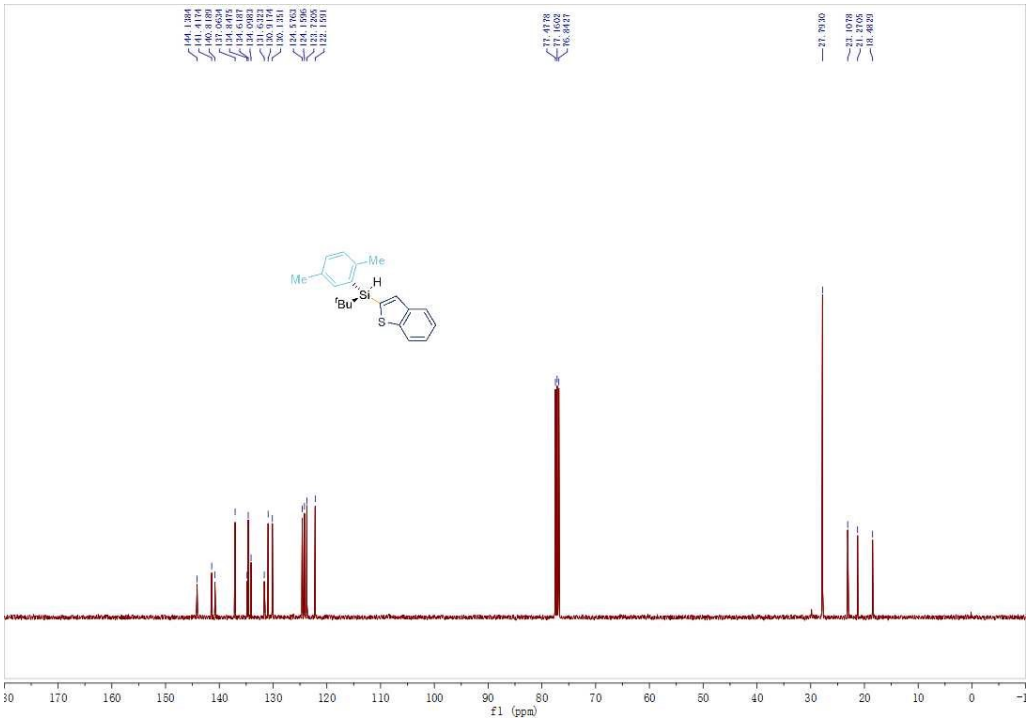

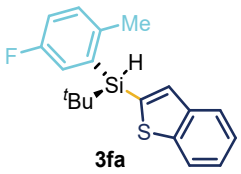

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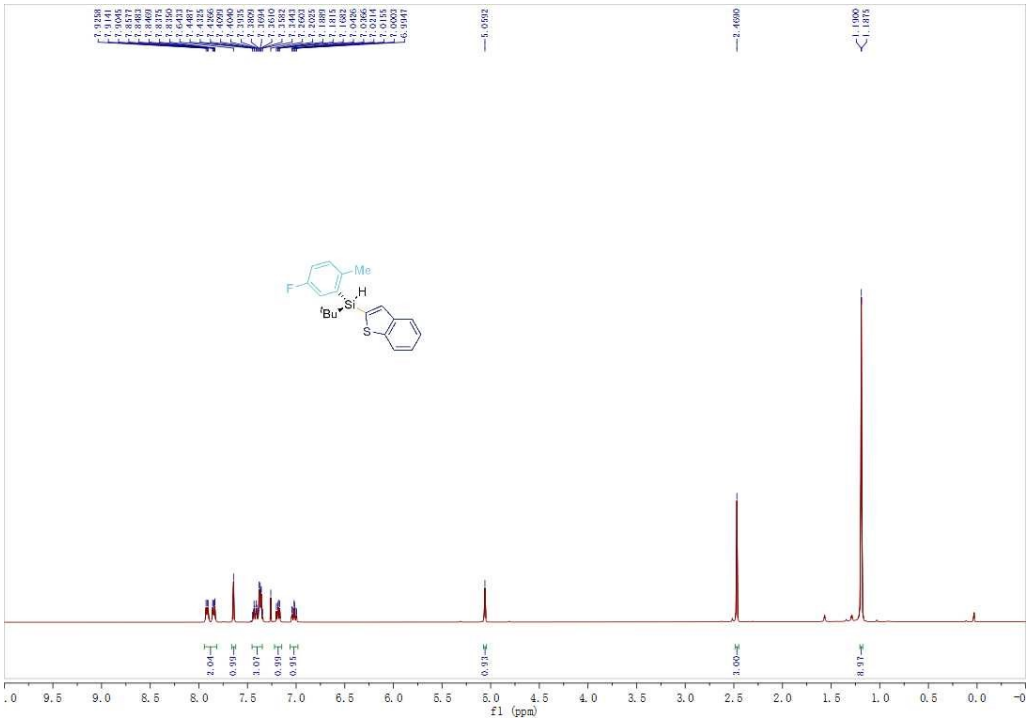

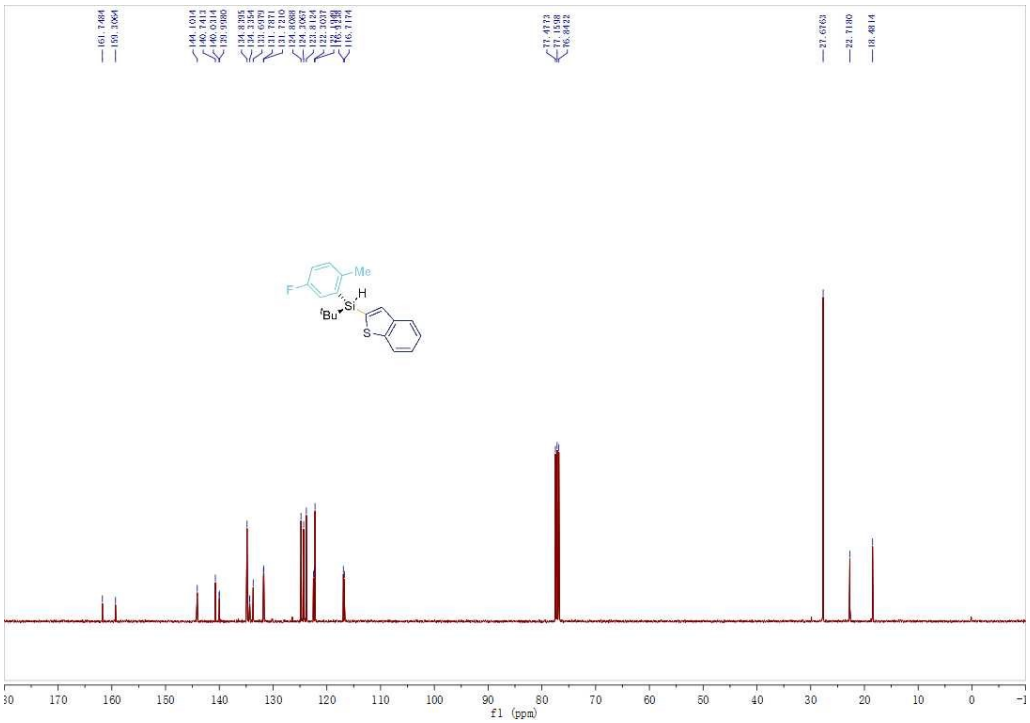

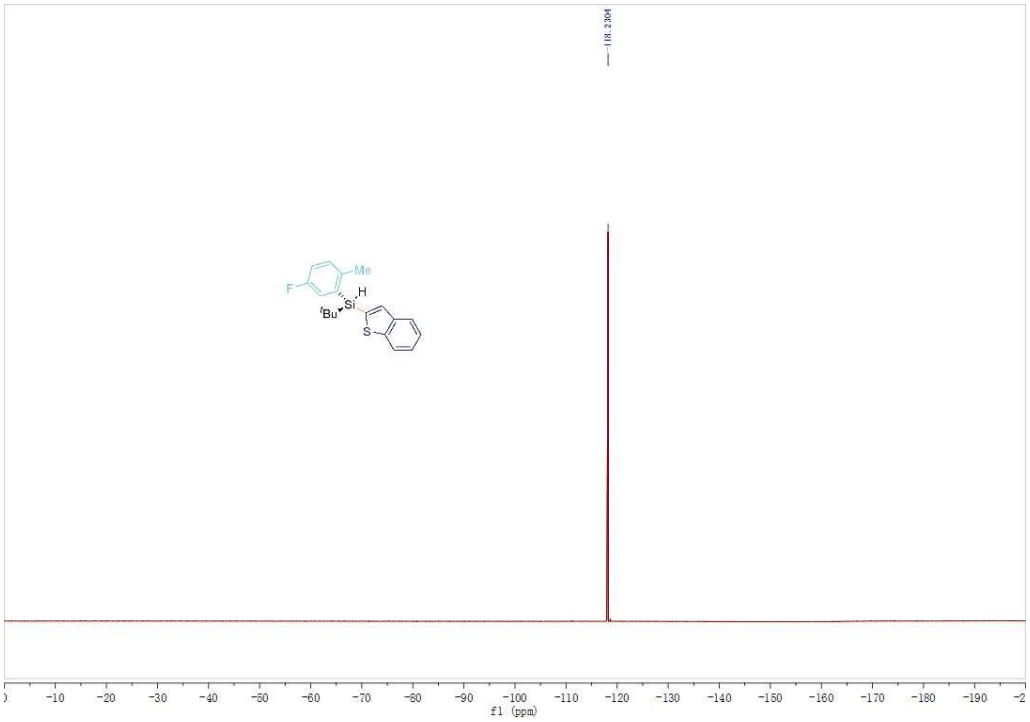
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F
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H
Si
tBu
S
-10
-20
-30
-40
-50
-60
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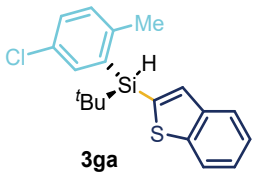
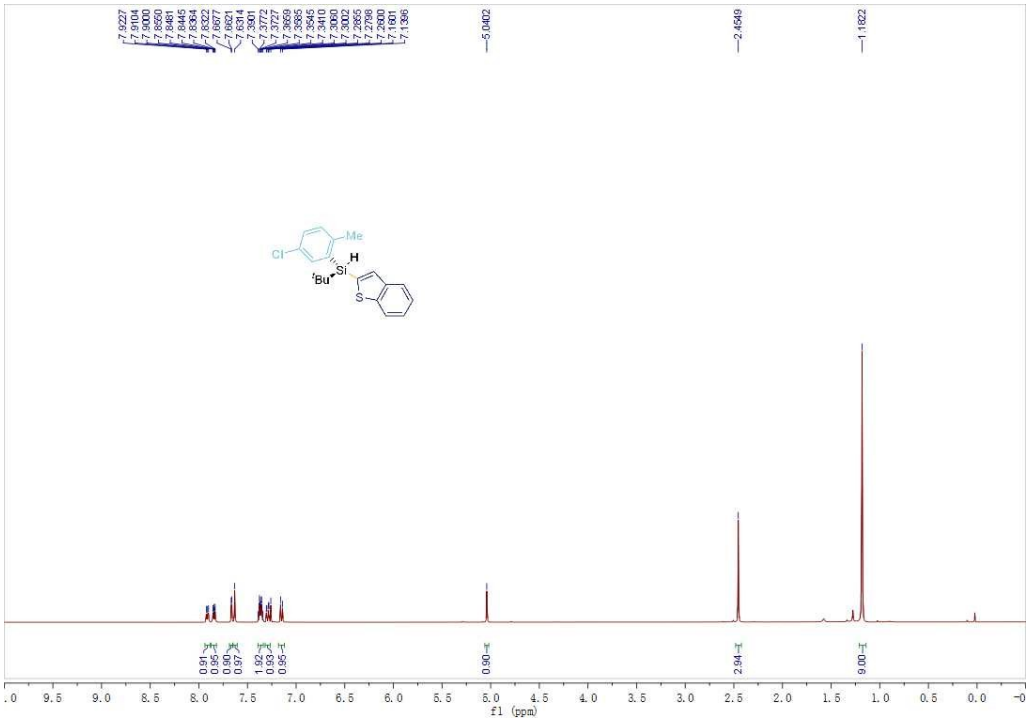
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


Me
Cl
H
Si
tBu
S

3ga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7.3901
7.3772
7.3727
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7.3585
7.3545
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7.2865
7.2798
7.2600
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5.0402
2.4549
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1.92
0.93
0.95
0.90
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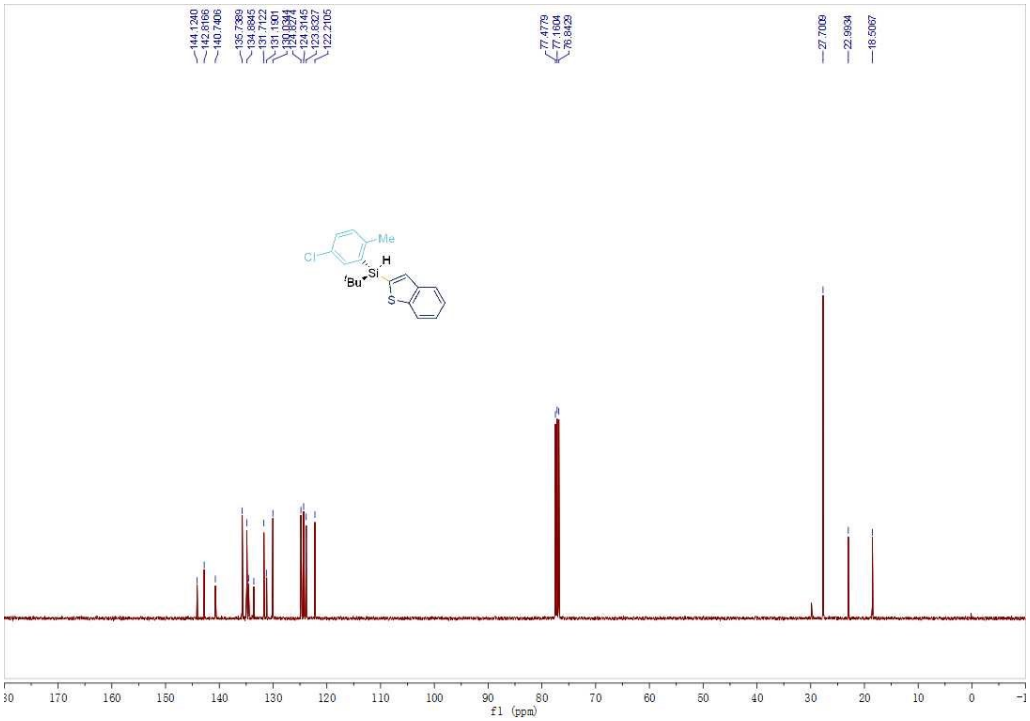
9.00
f1 (ppm)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131.1001
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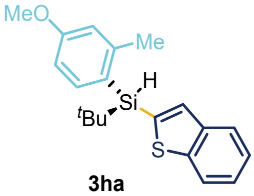
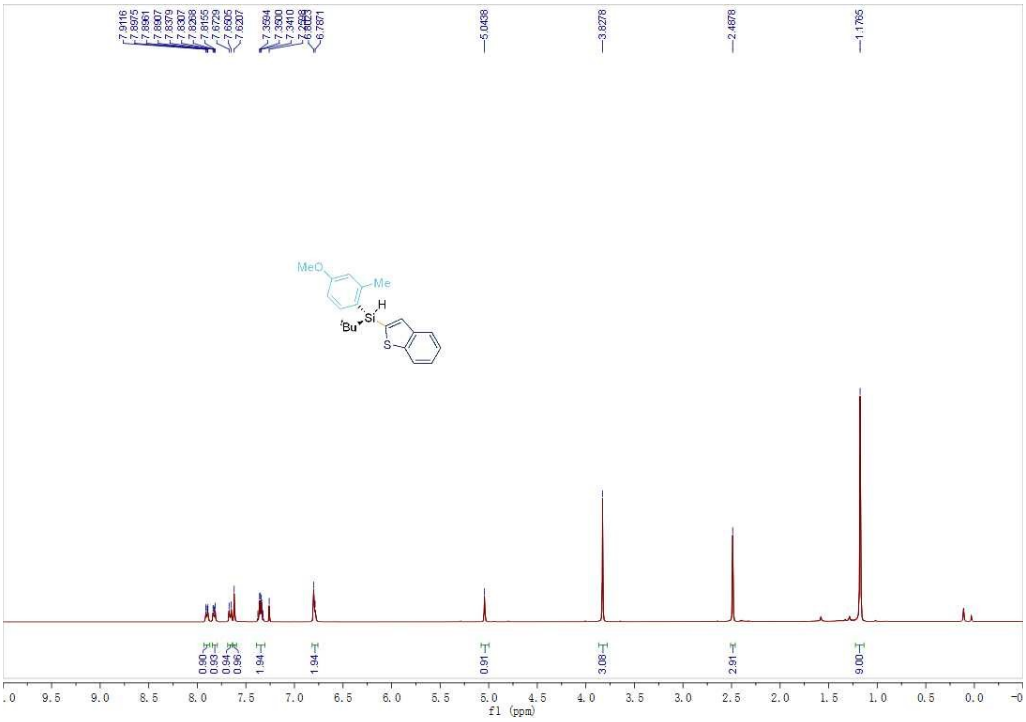
76.8429
27.7009
22.9934
18.5067
f1 (ppm)


MeO
Me
H
Si
tBu
S

3ha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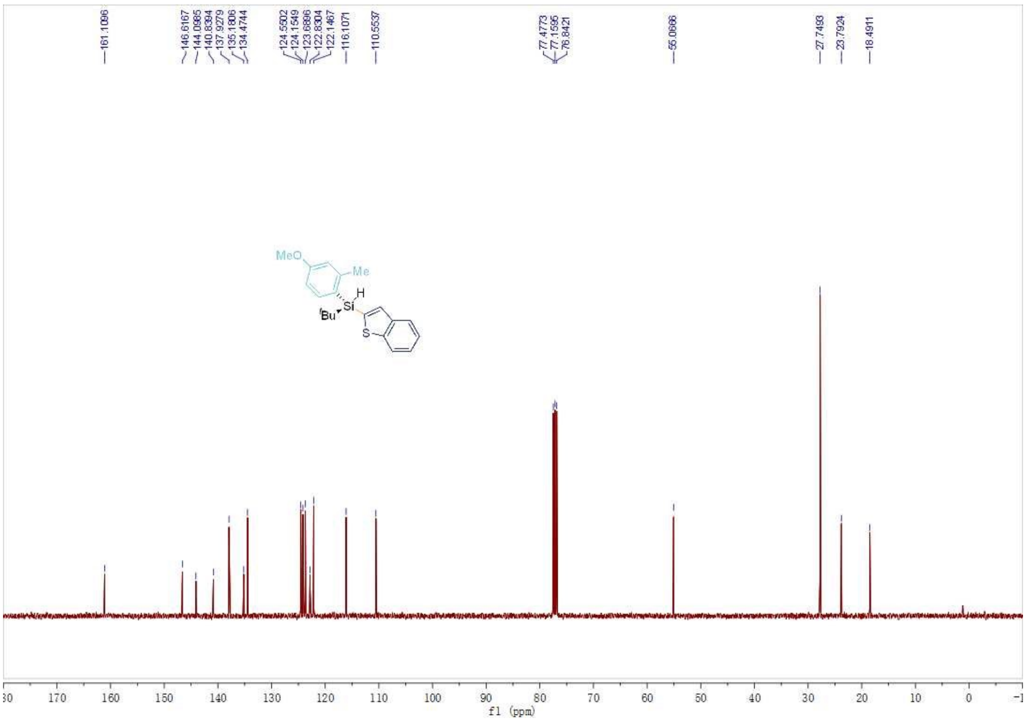
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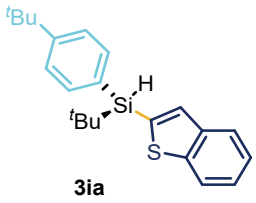
f1 (ppm)



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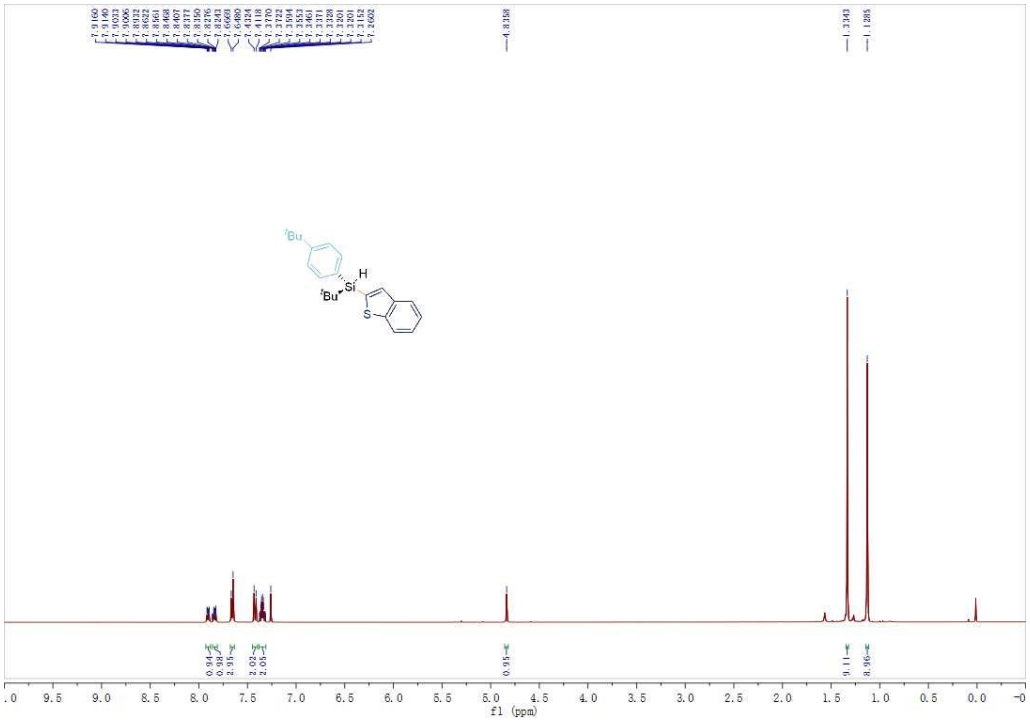

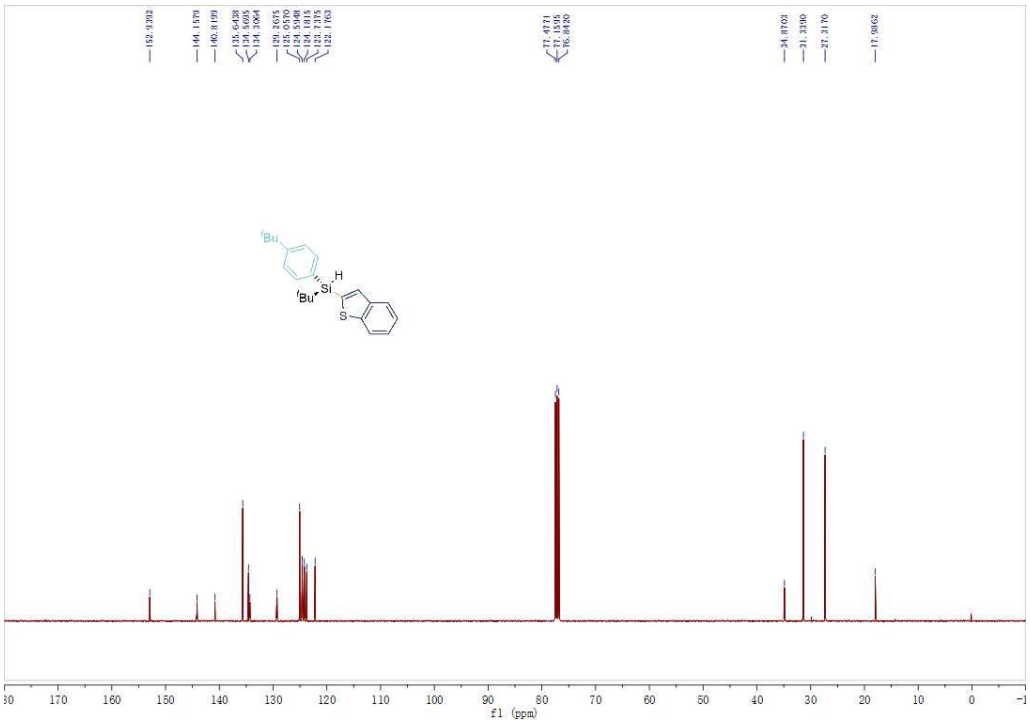

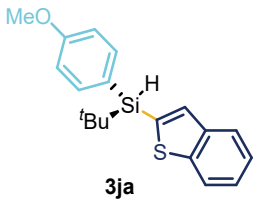

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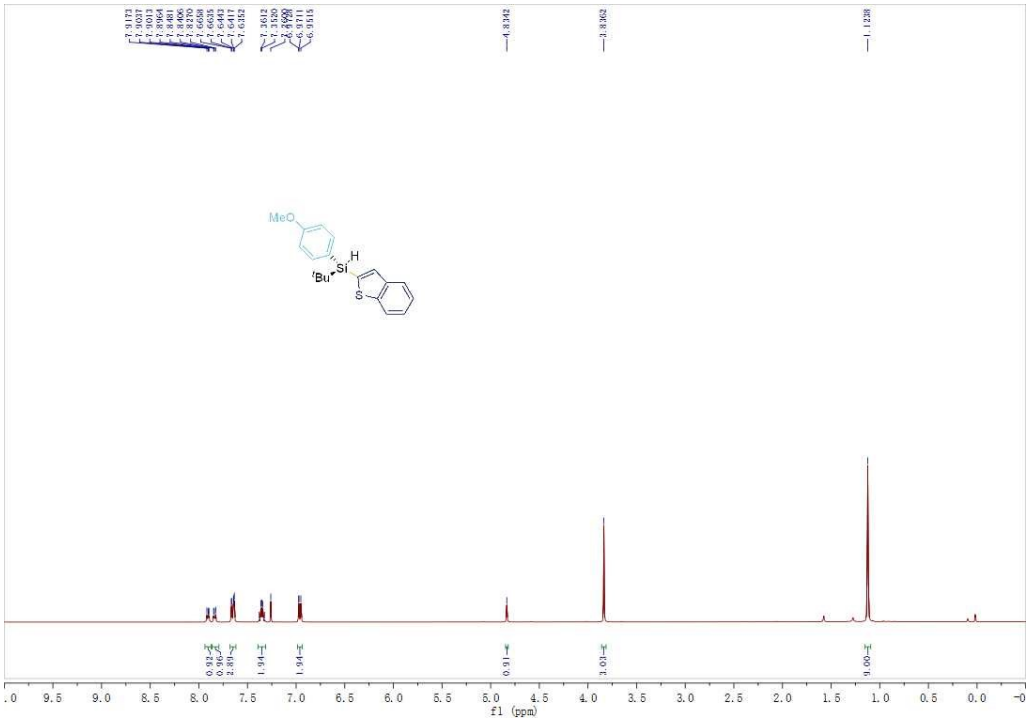

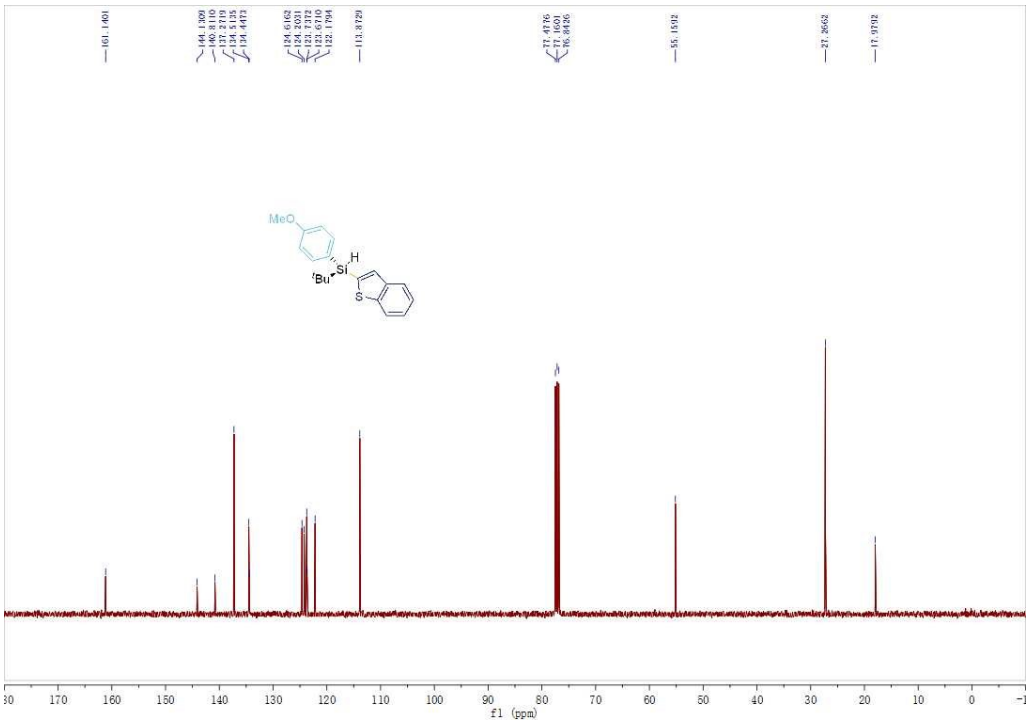

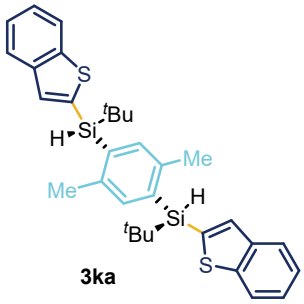

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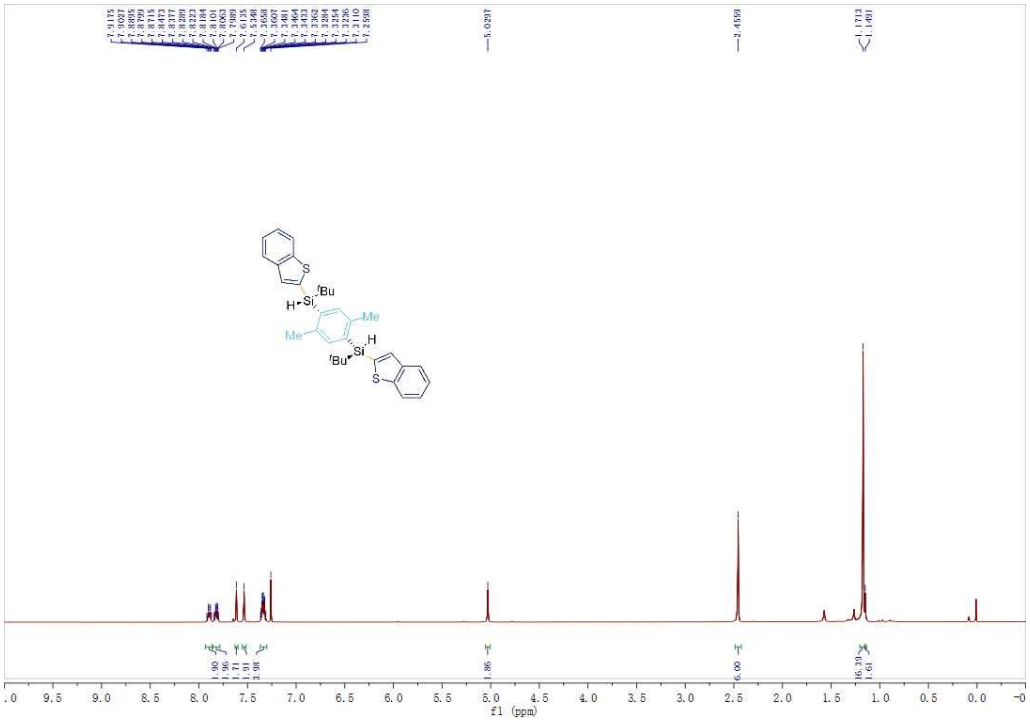

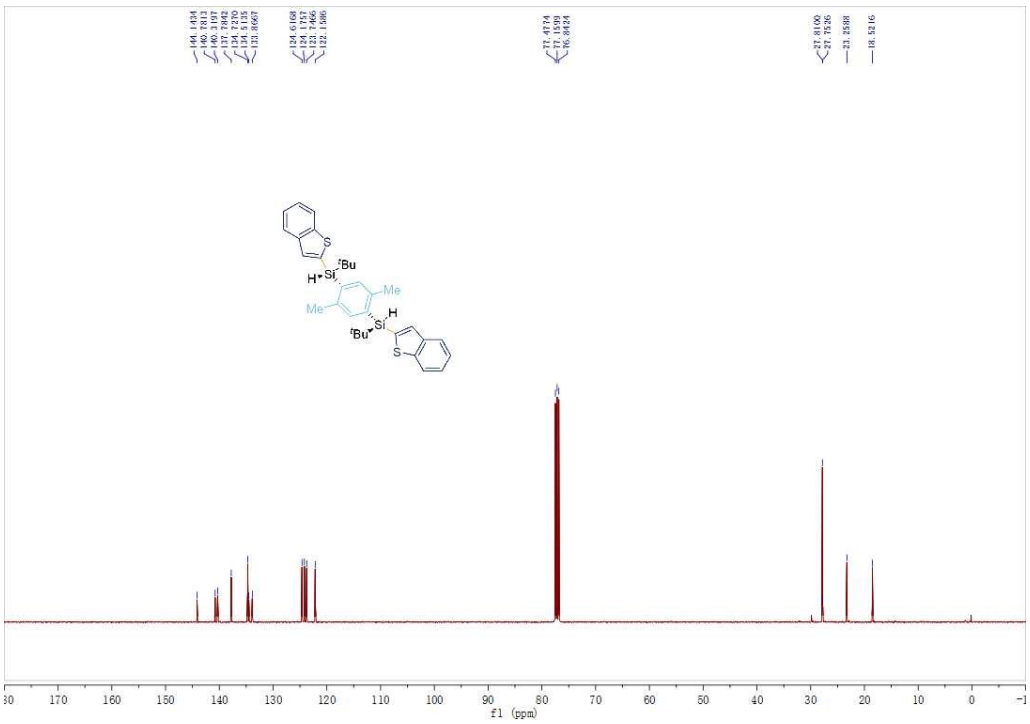

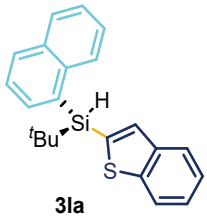

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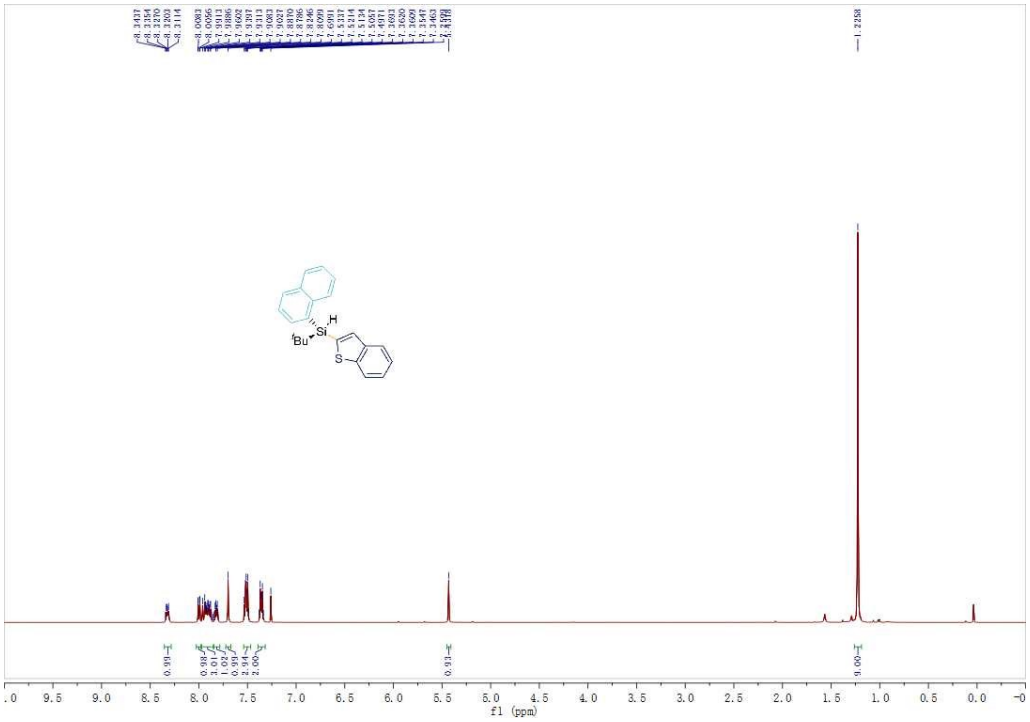

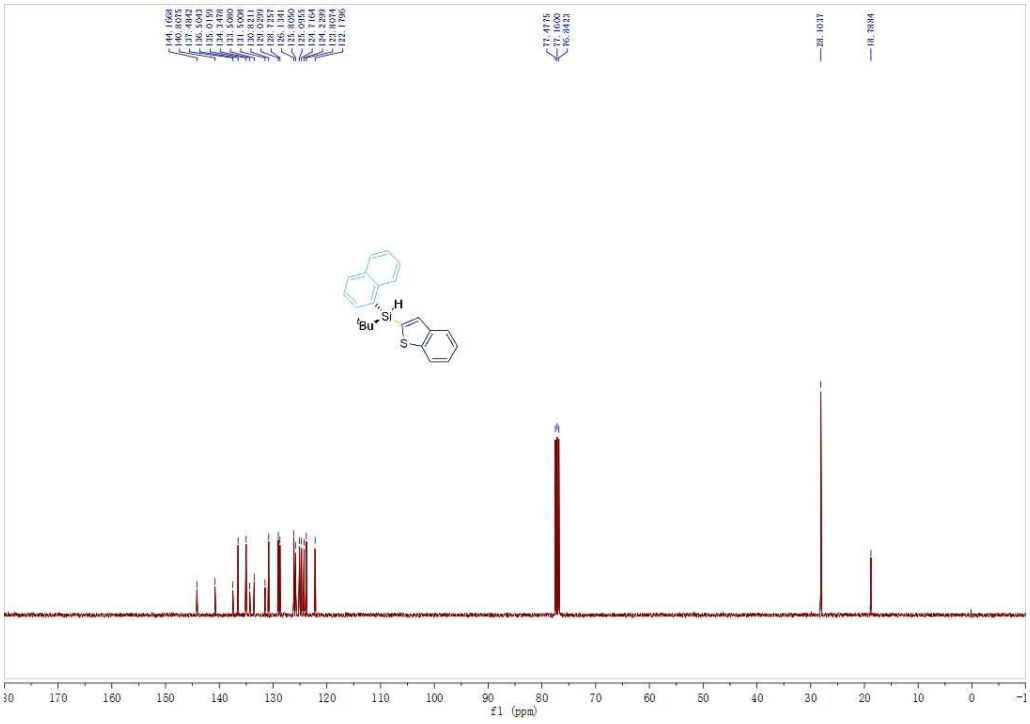

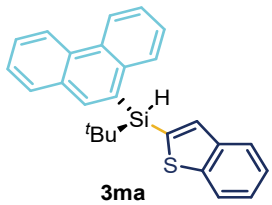

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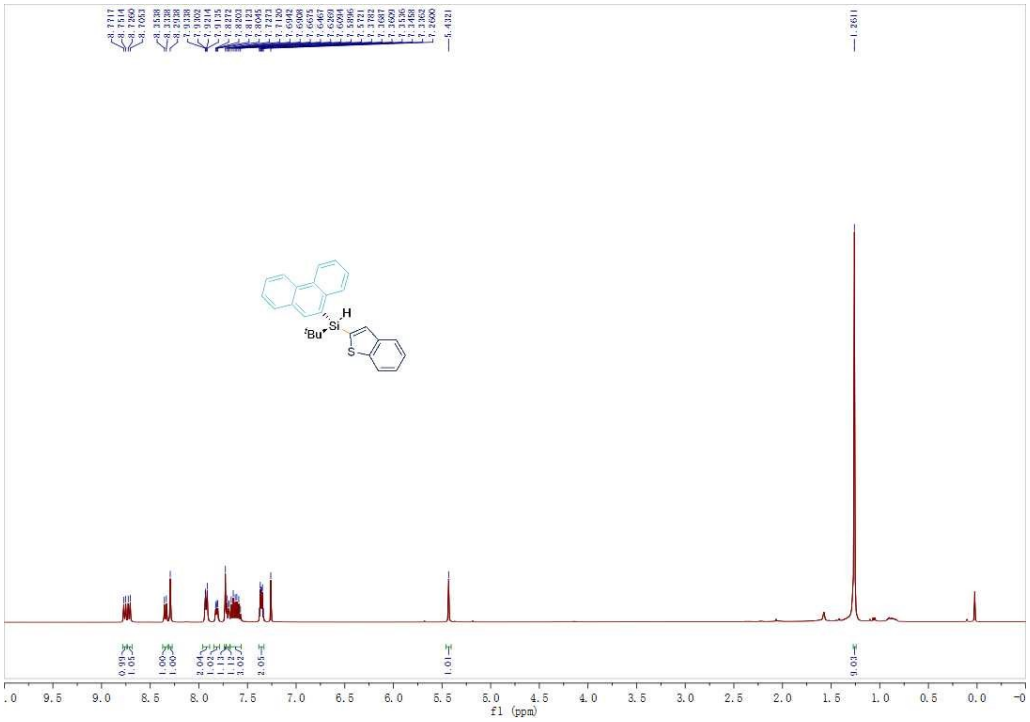

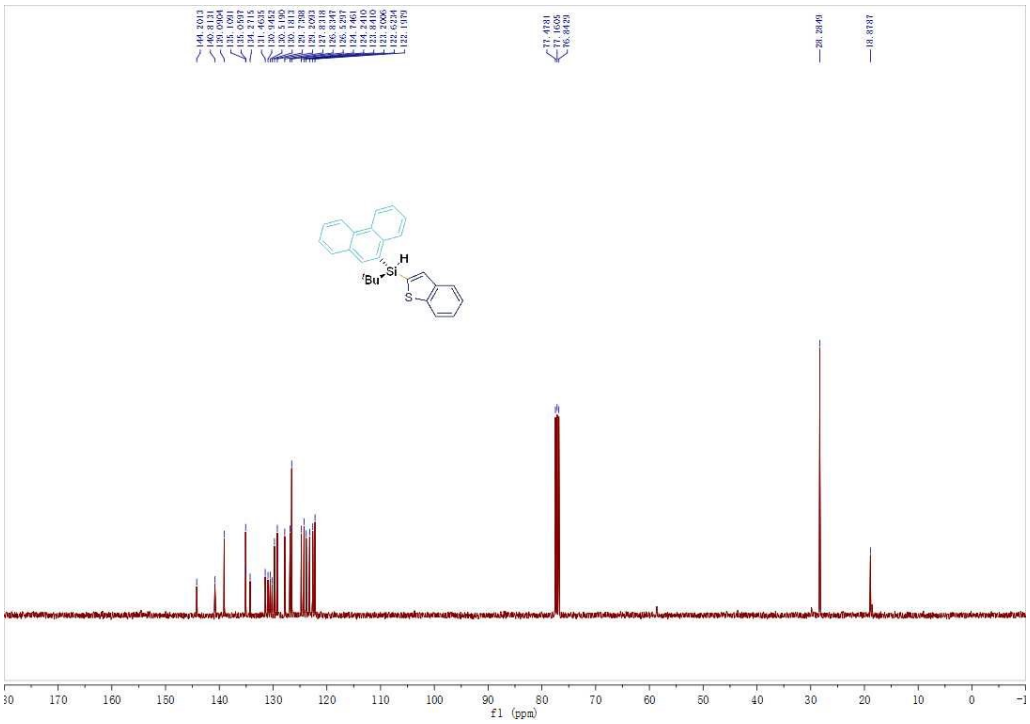

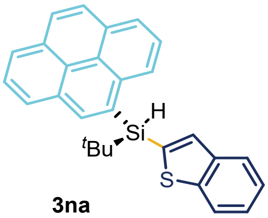

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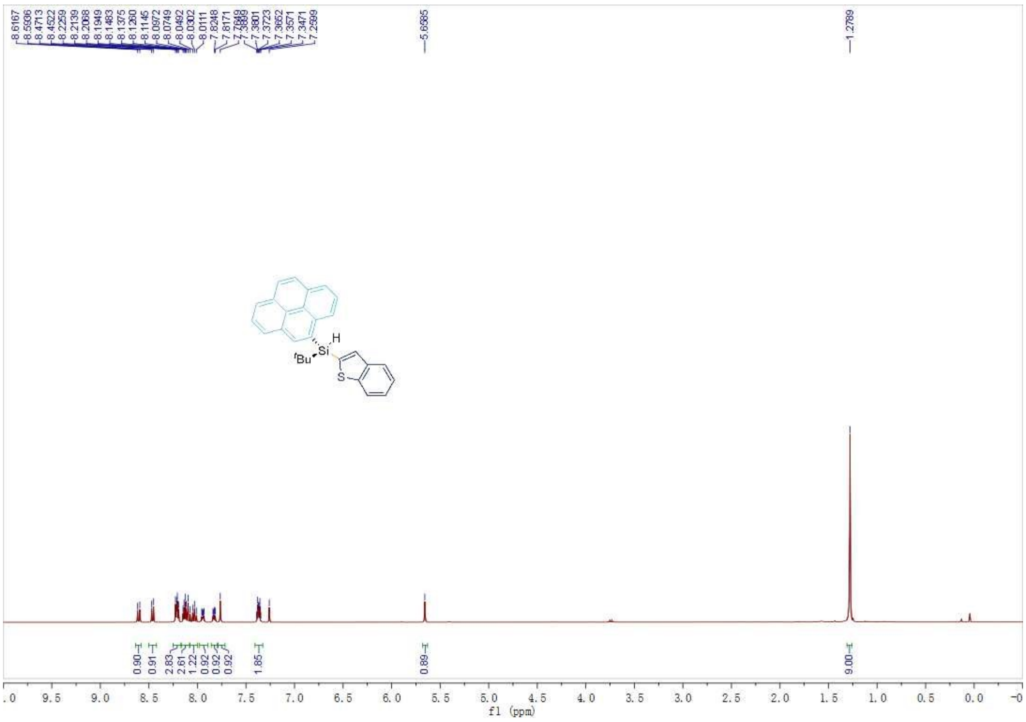

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tBu
S
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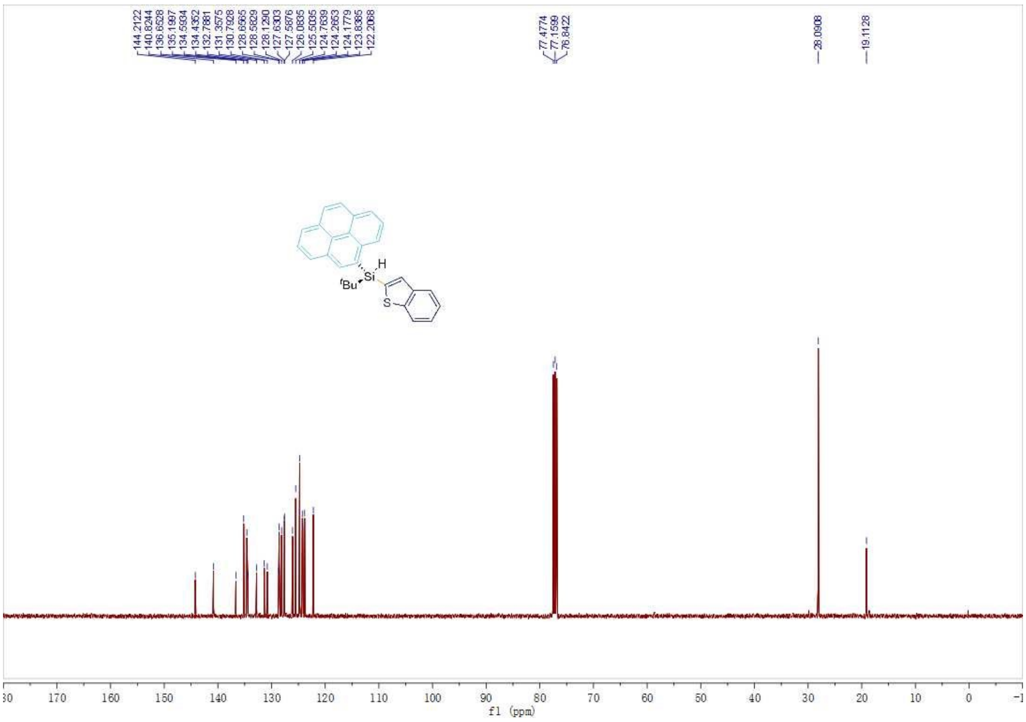

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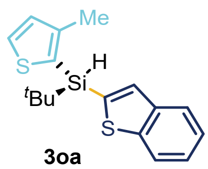
f1 (ppm)



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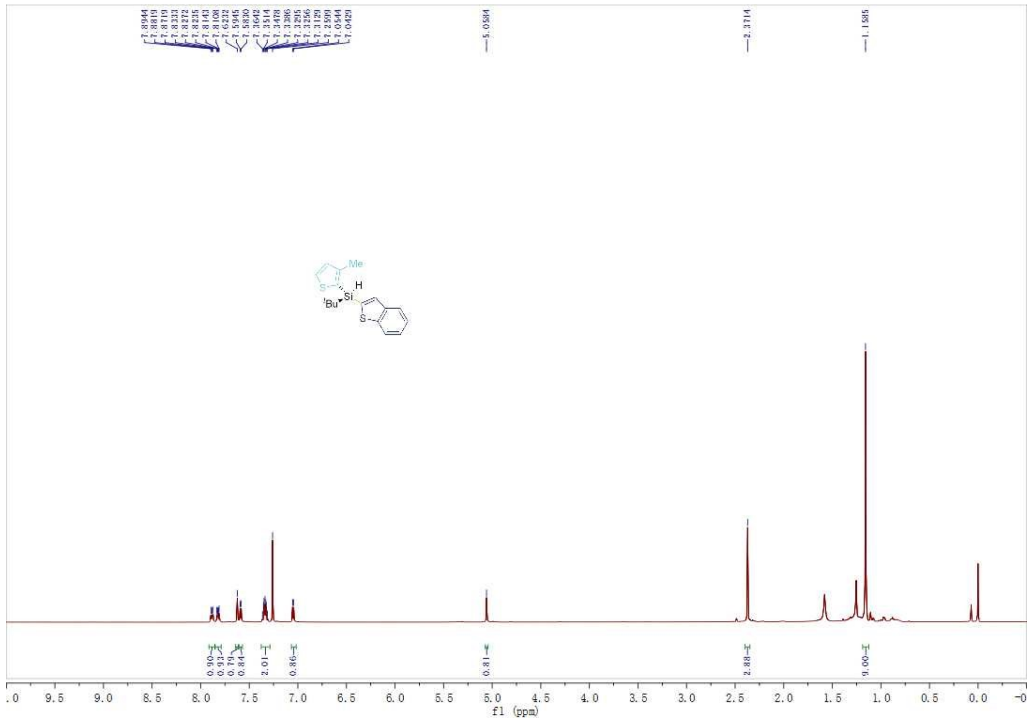

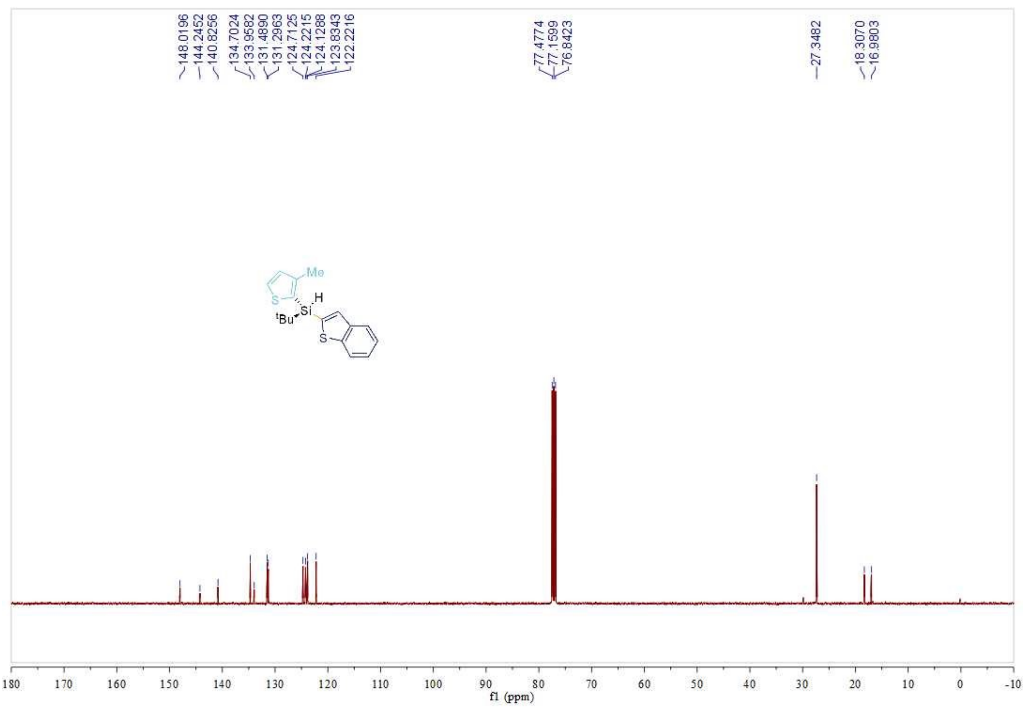

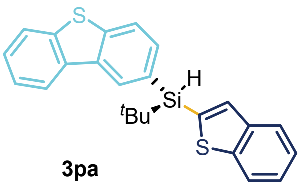

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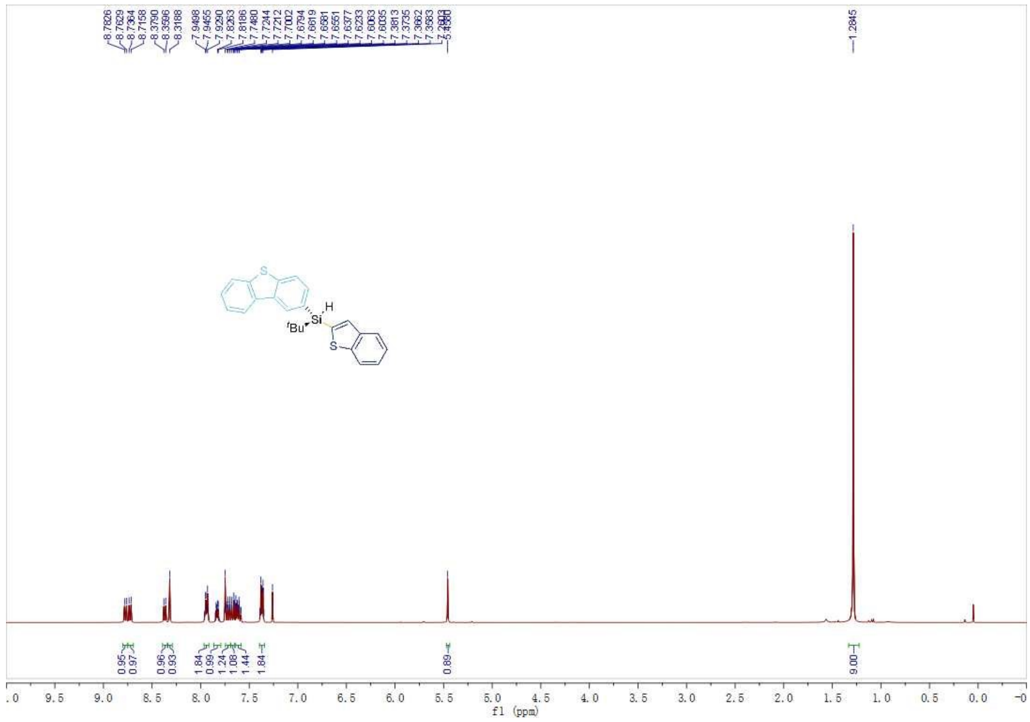

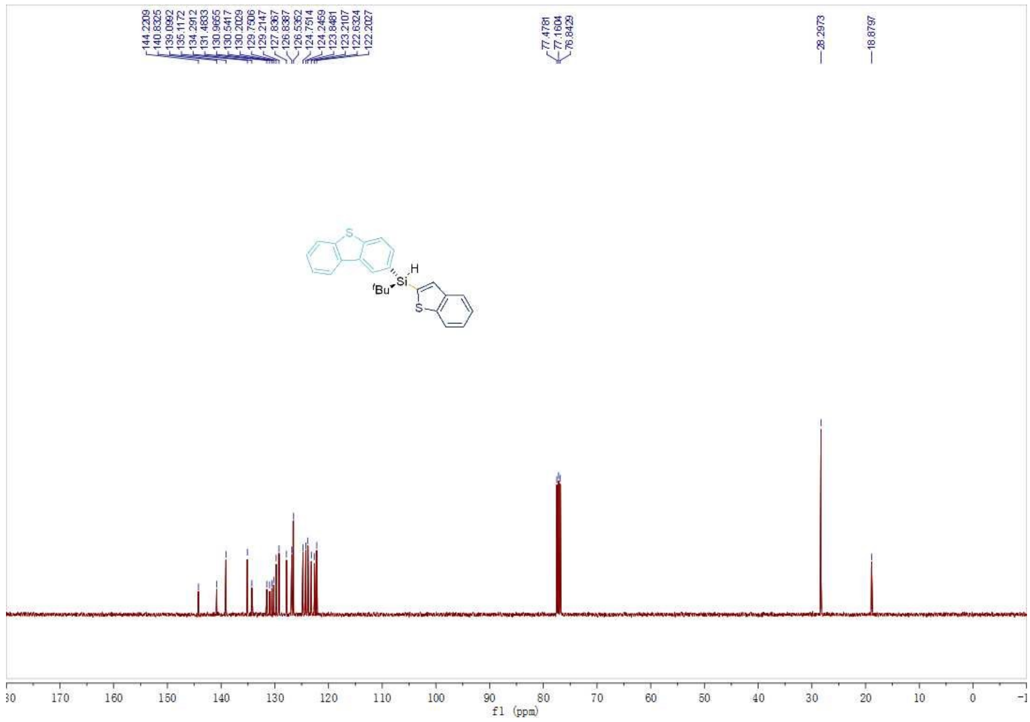

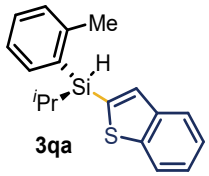

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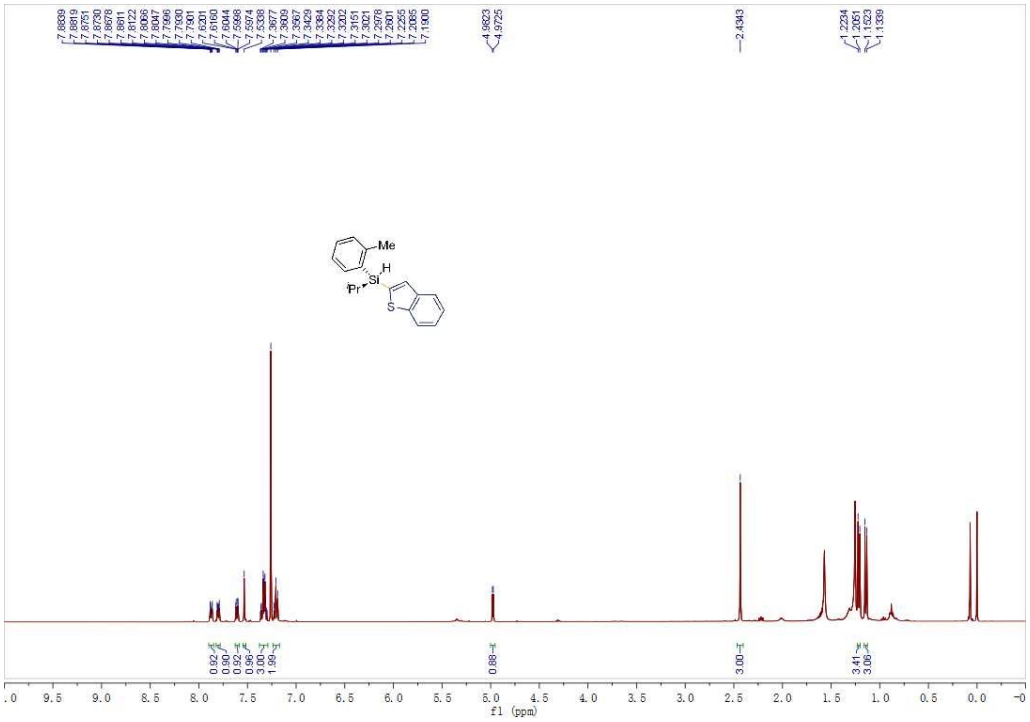

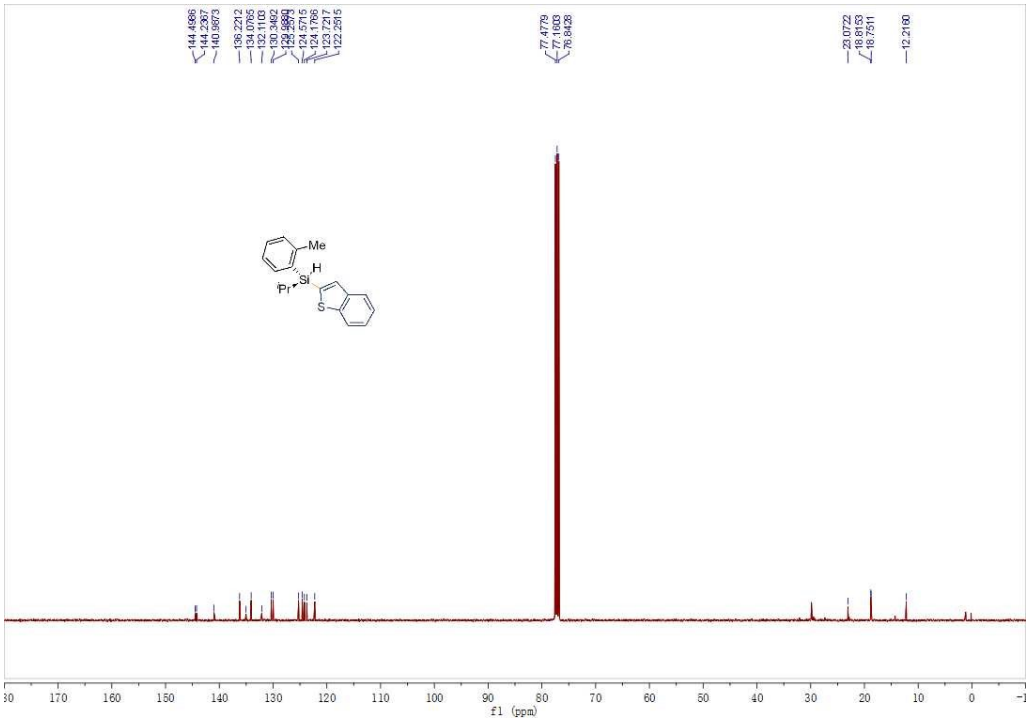

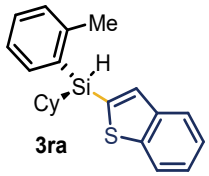

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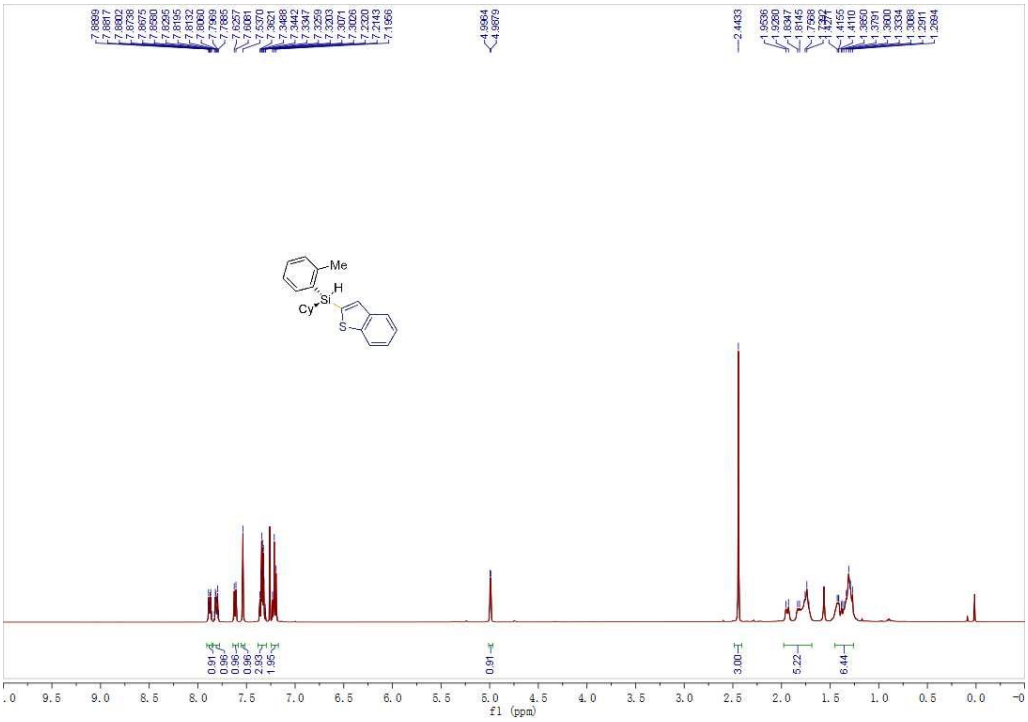

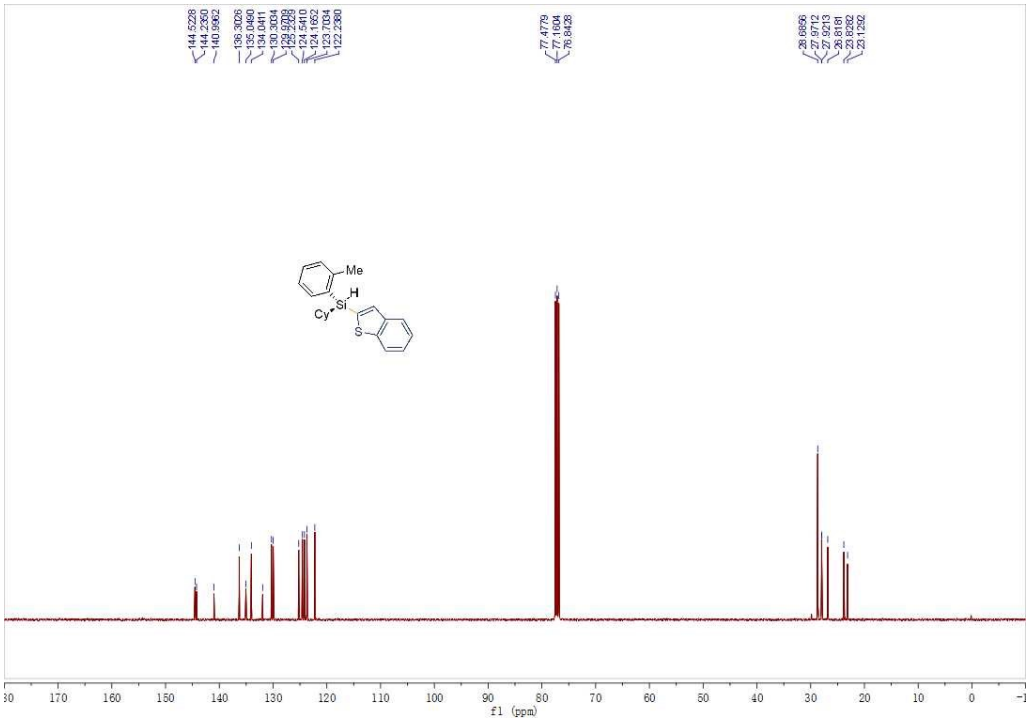

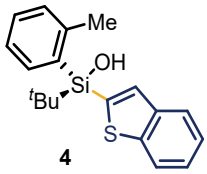
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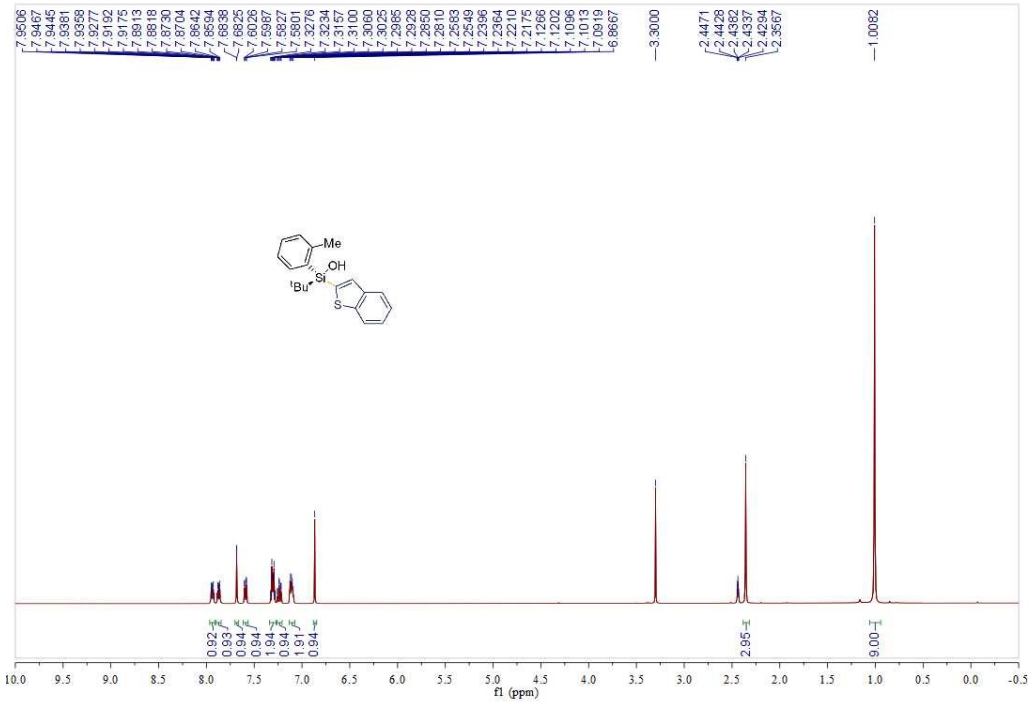
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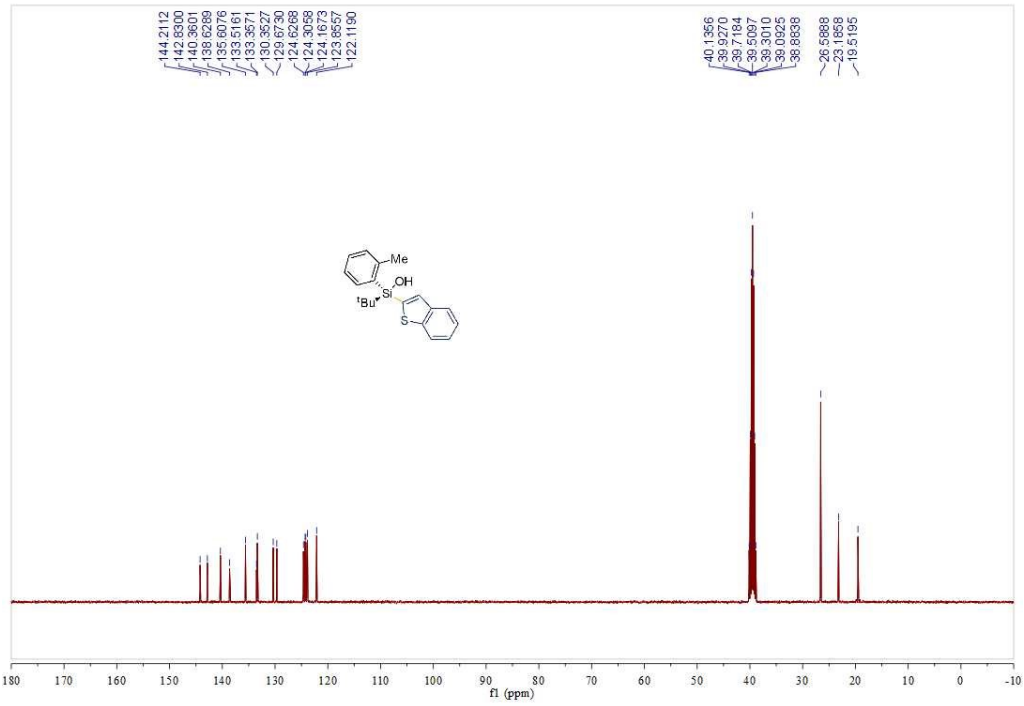
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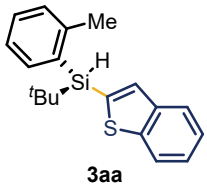
10. HPLC spectra



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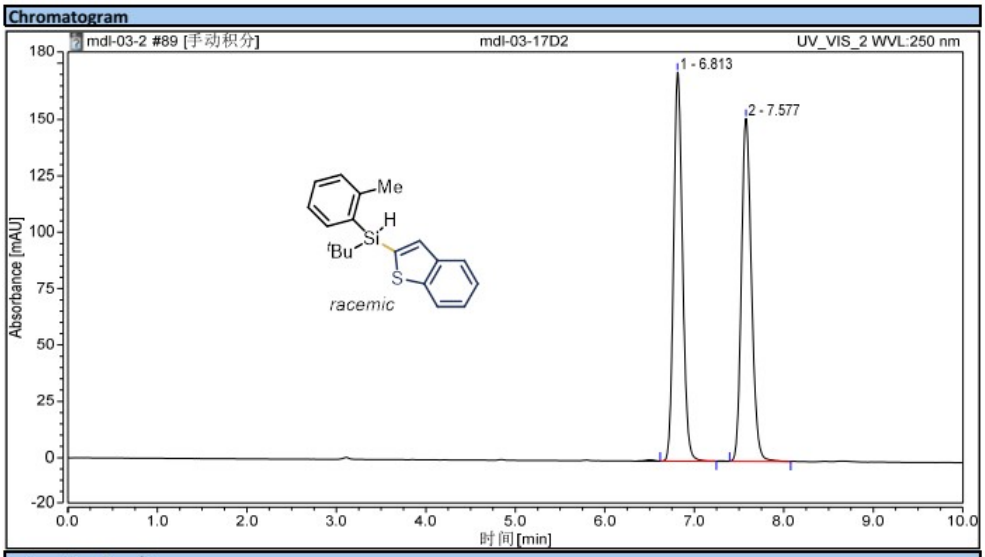
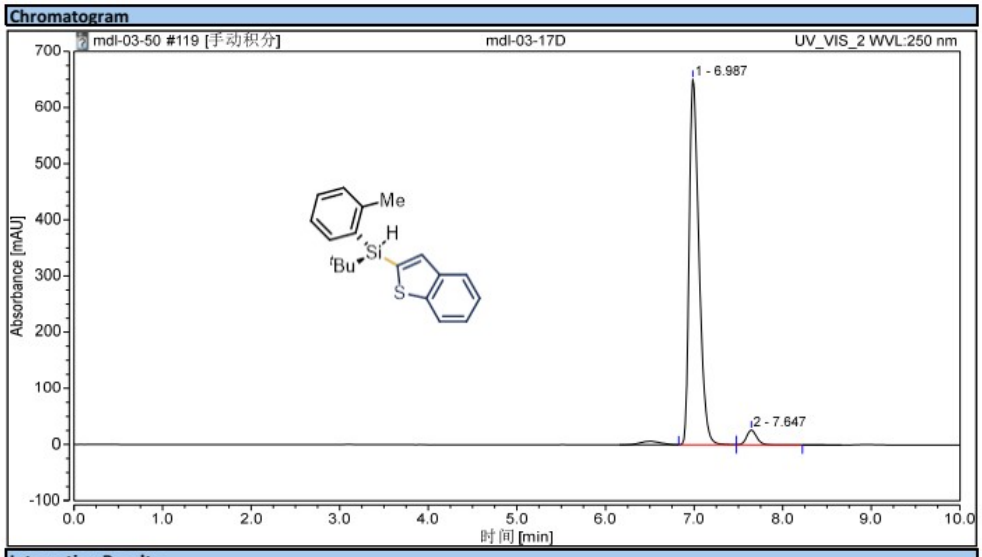


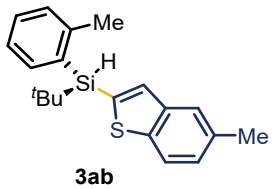
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.813	19.984	172.564	50.29	53.15	n.a.
2		7.577	19.756	152.136	49.71	46.85	n.a.
Total:			**39.740**	**324.700**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.987	82.960	651.093	95.84	96.08	n.a.
2		7.647	3.599	26.576	4.16	3.92	n.a.
Total:			**86.559**	**677.670**	**100.00**	**100.00**	



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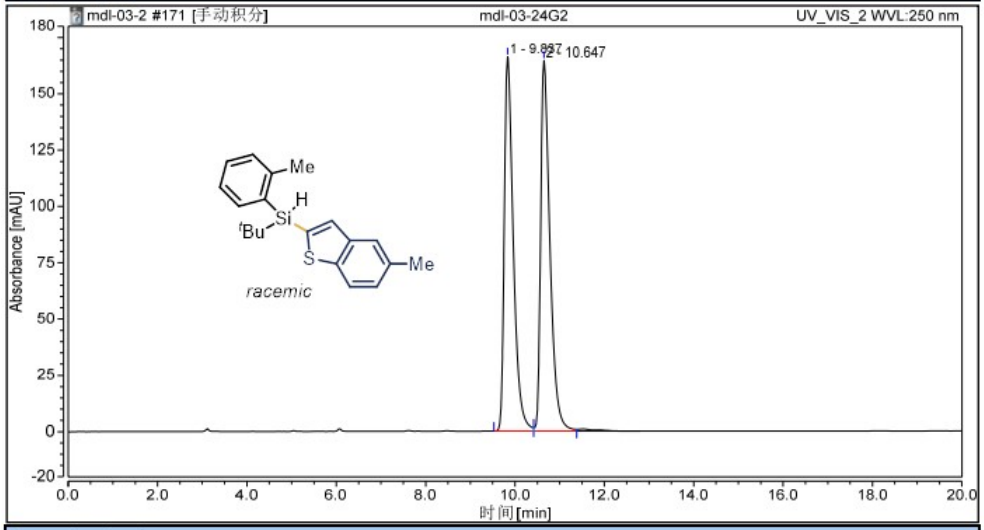
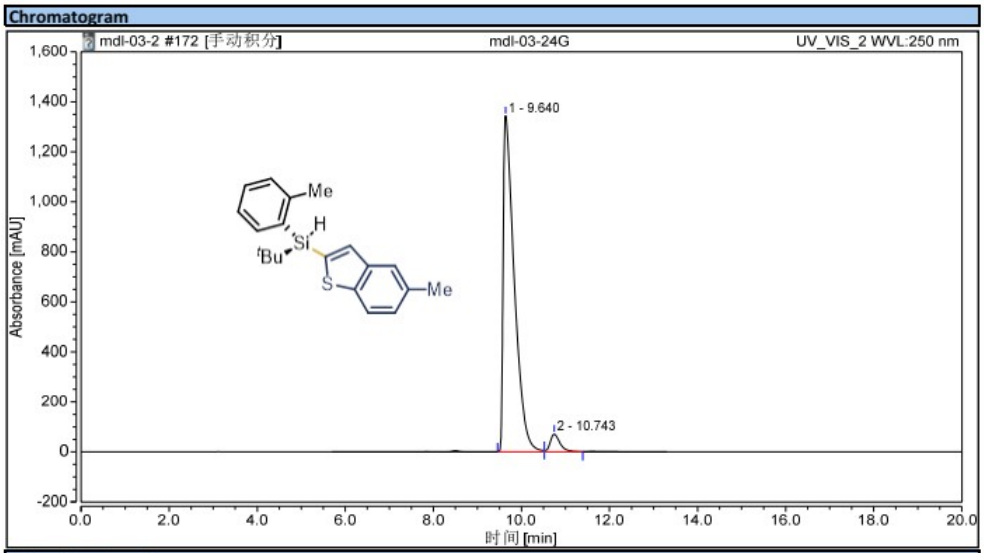
Chromatogram



Integration Results

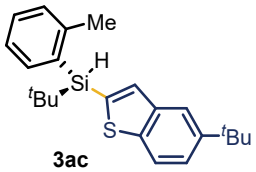
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.837	38.958	166.227	49.36	50.24	n.a.
2		10.647	39.965	164.632	50.64	49.76	n.a.
Total:			**78.923**	**330.859**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.640	392.098	1344.744	95.52	94.99	n.a.
2		10.743	18.397	70.903	4.48	5.01	n.a.
Total:			**410.495**	**1415.648**	**100.00**	**100.00**	



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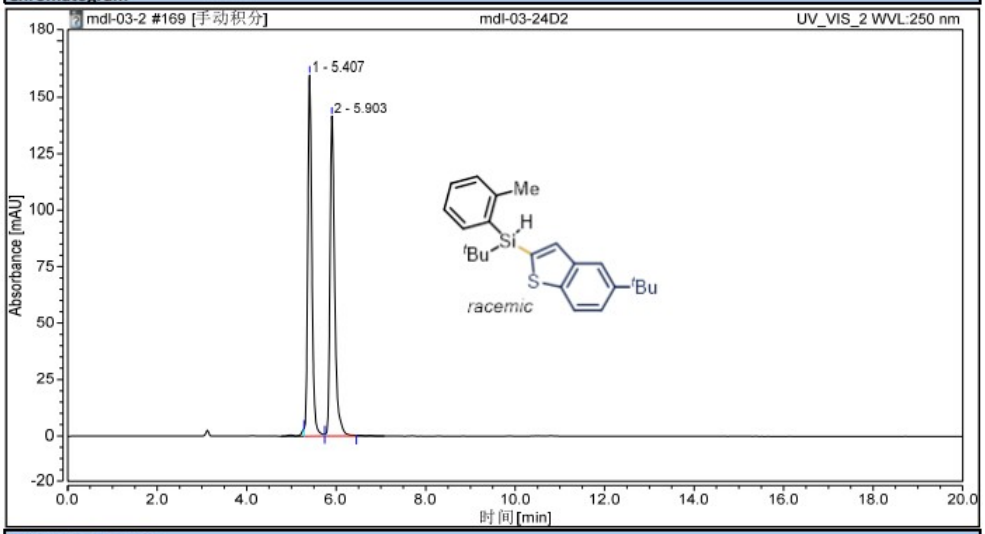
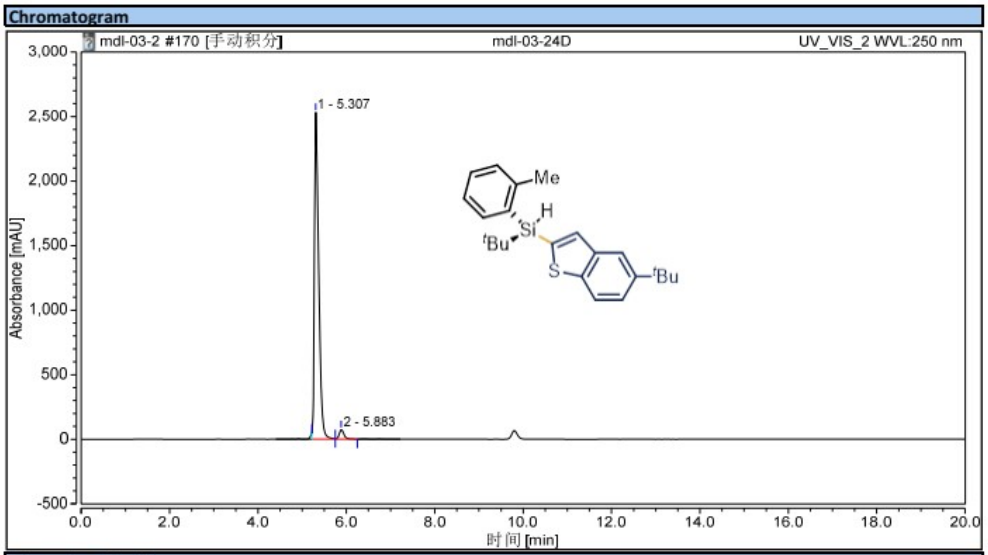
Chromatogram



Integration Results

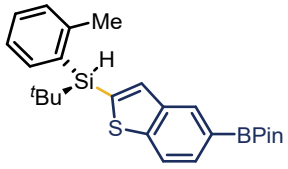
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.407	16.858	159.930	49.25	53.02	n.a.
2		5.903	17.372	141.728	50.75	46.98	n.a.
Total:			**34.230**	**301.658**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.307	283.126	2532.360	96.72	97.13	n.a.
2		5.883	9.615	74.869	3.28	2.87	n.a.
Total:			**292.741**	**2607.229**	**100.00**	**100.00**	



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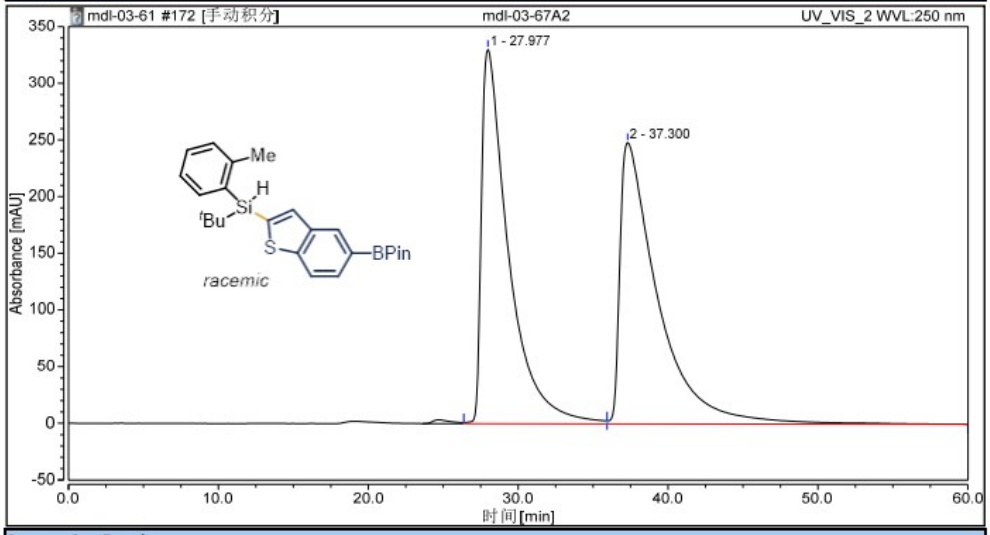
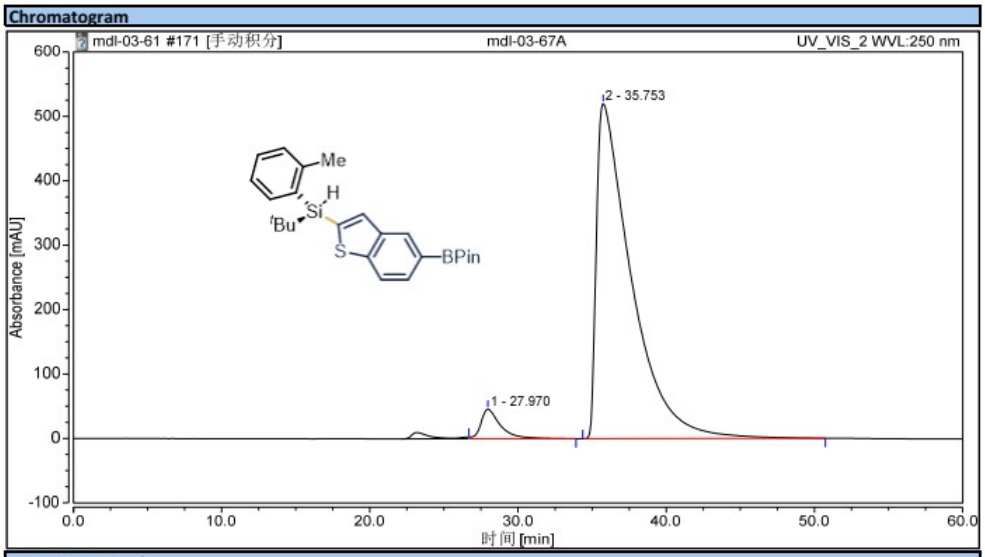
Chromatogram



Integration Results

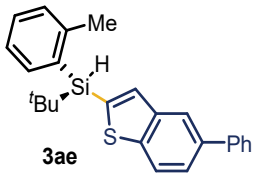
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.977	689.827	330.355	48.72	57.09	n.a.
2		37.300	725.951	248.270	51.28	42.91	n.a.
Total:			**1415.777**	**578.625**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.970	70.213	45.777	4.72	8.09	n.a.
2		35.753	1418.879	520.386	95.28	91.91	n.a.
Total:			**1489.091**	**566.163**	**100.00**	**100.00**	



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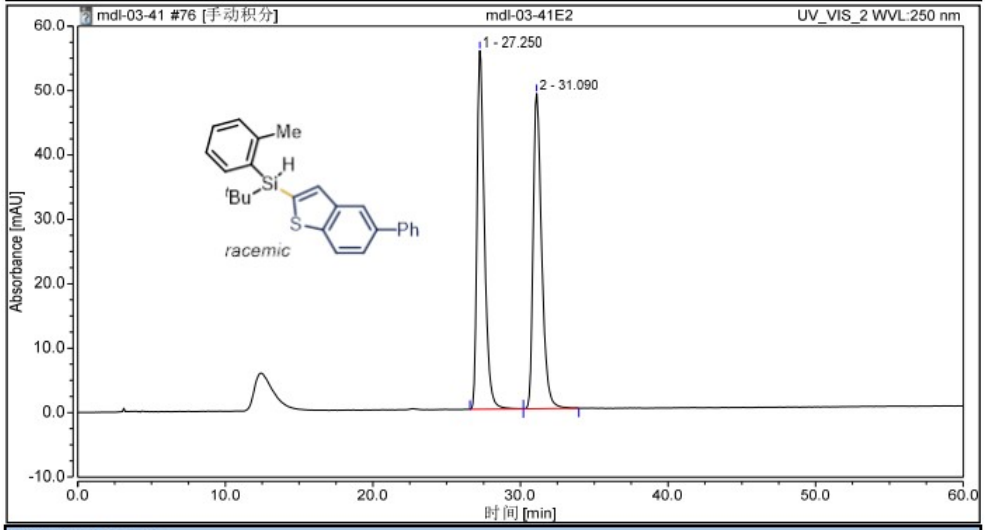
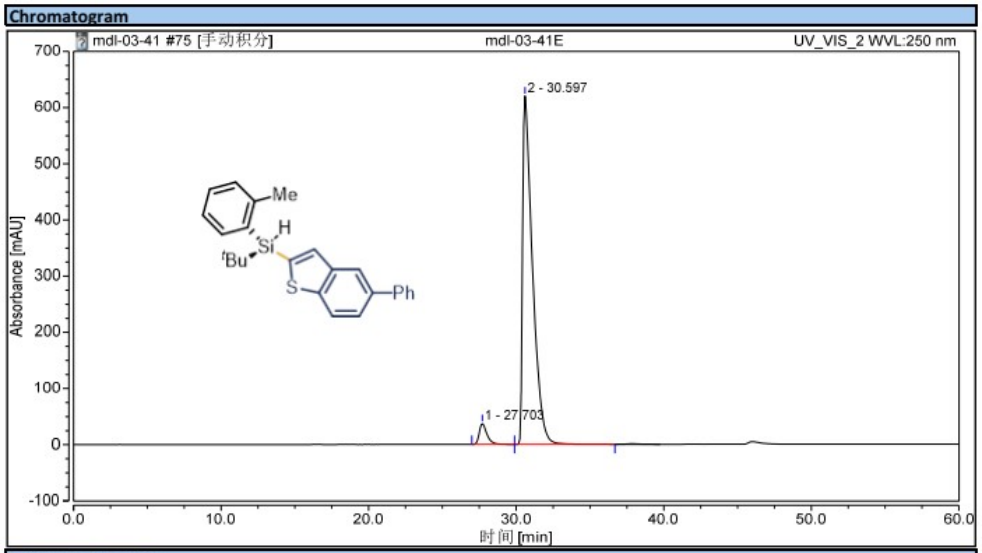
Chromatogram



Integration Results

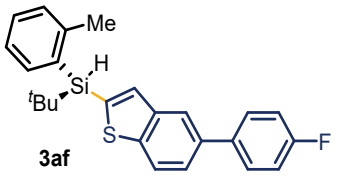
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.250	32.635	55.697	49.98	53.23	n.a.
2		31.090	32.655	48.942	50.02	46.77	n.a.
Total:			**65.290**	**104.639**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.703	22.642	36.977	4.48	5.63	n.a.
2		30.597	482.239	620.125	95.52	94.37	n.a.
Total:			**504.880**	**657.102**	**100.00**	**100.00**	



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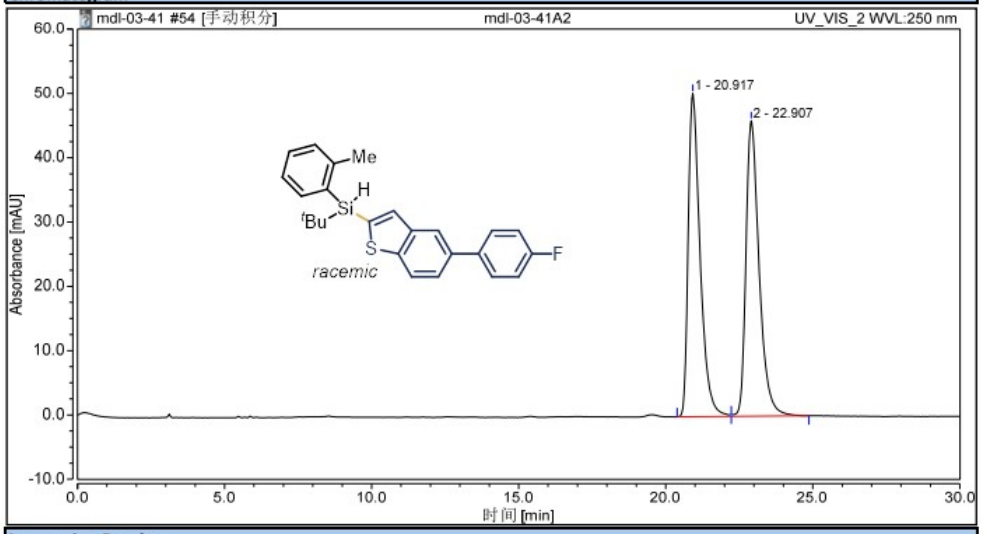
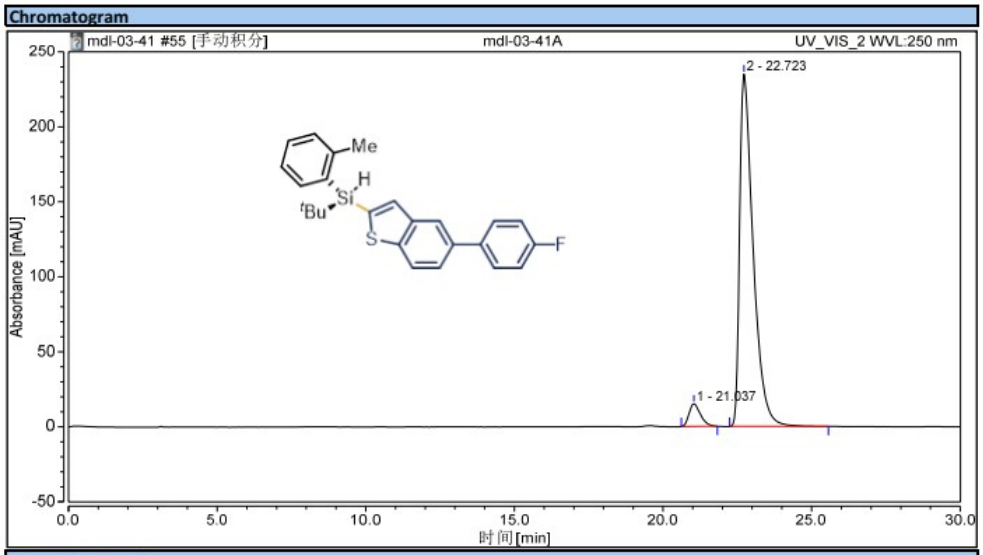


Integration Results

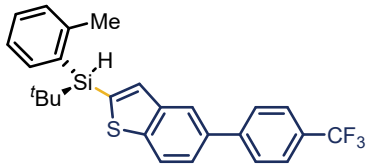
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.917	23.458	50.268	49.54	52.25	n.a.
2		22.907	23.890	45.944	50.46	47.75	n.a.
Total:			**47.348**	**96.212**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.037	6.719	15.056	5.14	6.02	n.a.
2		22.723	123.997	234.982	94.86	93.98	n.a.
Total:			**130.716**	**250.038**	**100.00**	**100.00**	



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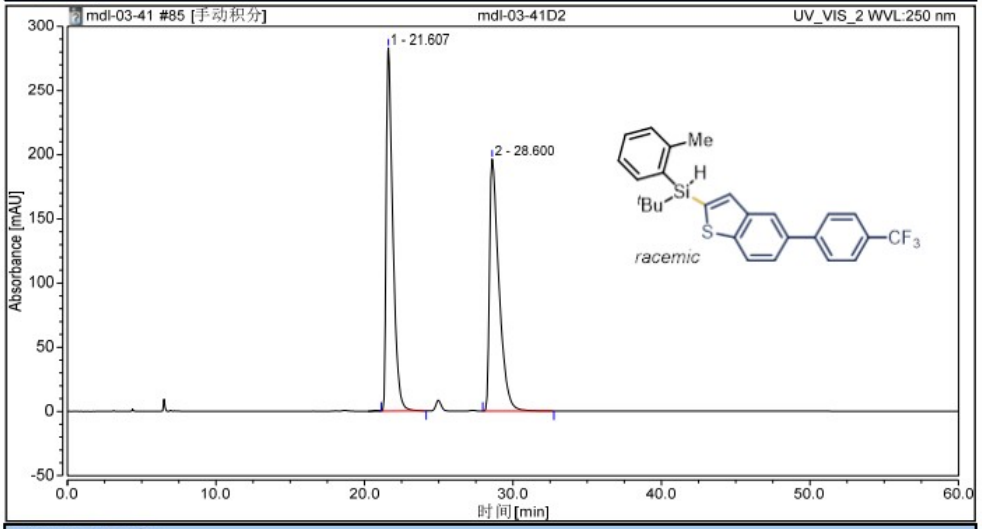
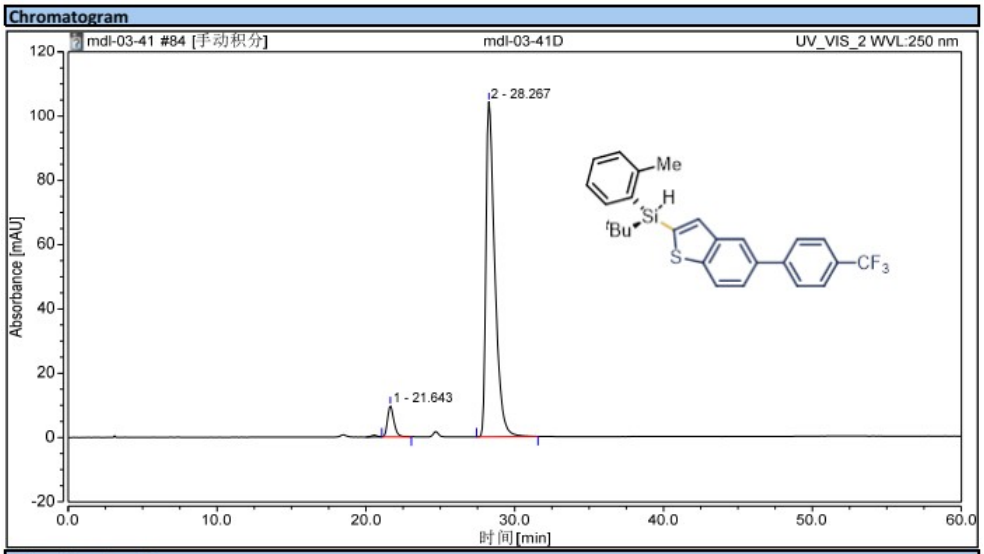


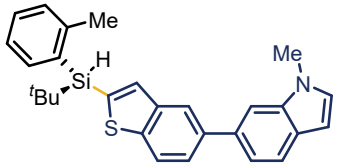
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.607	146.381	283.075	50.18	59.04	n.a.
2		28.600	145.346	196.393	49.82	40.96	n.a.
Total:			**291.727**	**479.468**	**100.00**	**100.00**	



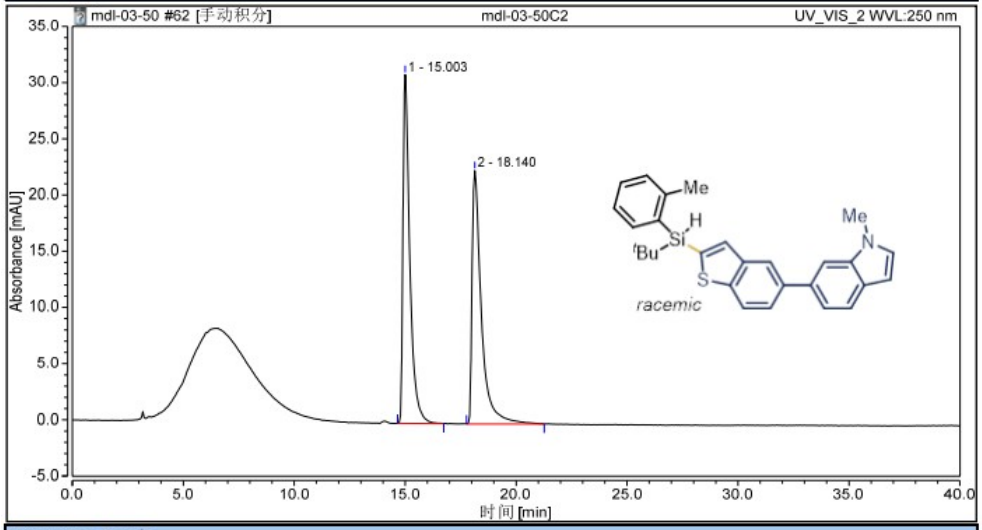
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.643	4.840	9.714	6.29	8.52	n.a.
2		28.267	72.166	104.266	93.71	91.48	n.a.
Total:			**77.006**	**113.980**	**100.00**	**100.00**	



3ah

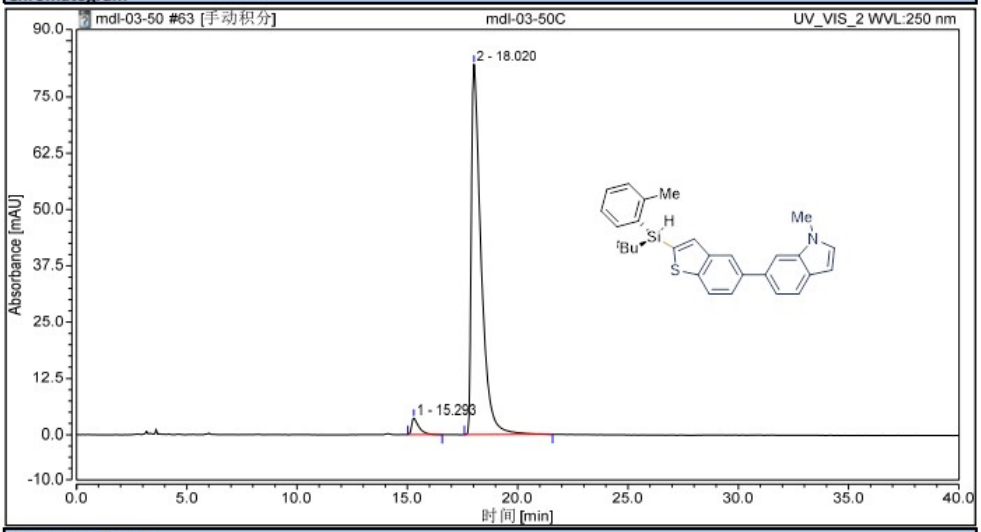
Chromatogram



Integration Results

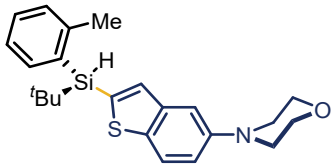
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.003	11.137	31.027	50.37	57.92	n.a.
2		18.140	10.974	22.537	49.63	42.08	n.a.
Total:			**22.111**	**53.564**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.293	1.385	3.625	3.18	4.22	n.a.
2		18.020	42.130	82.242	96.82	95.78	n.a.
Total:			**43.516**	**85.866**	**100.00**	**100.00**	



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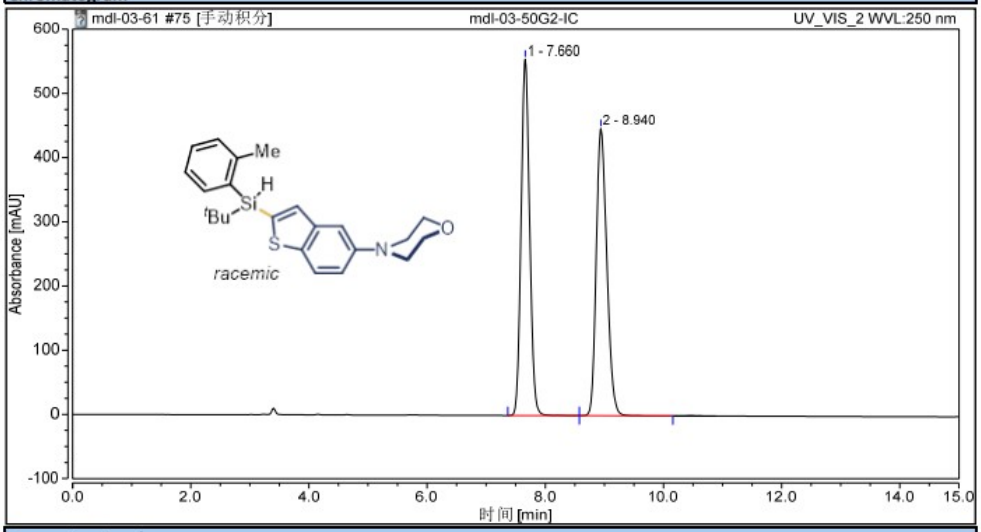
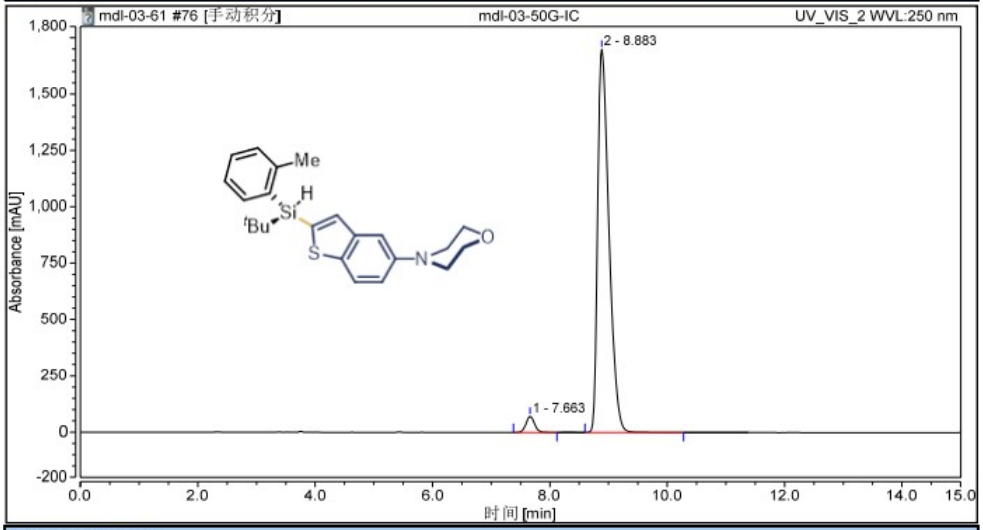
Chromatogram



Integration Results

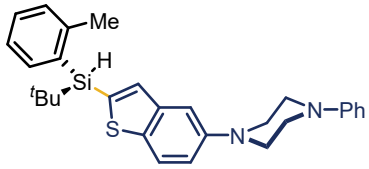
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.660	92.718	555.079	50.05	55.38	n.a.
2		8.940	92.536	447.317	49.95	44.62	n.a.
Total:			**185.254**	**1002.397**	**100.00**	**100.00**	

Chromatogram



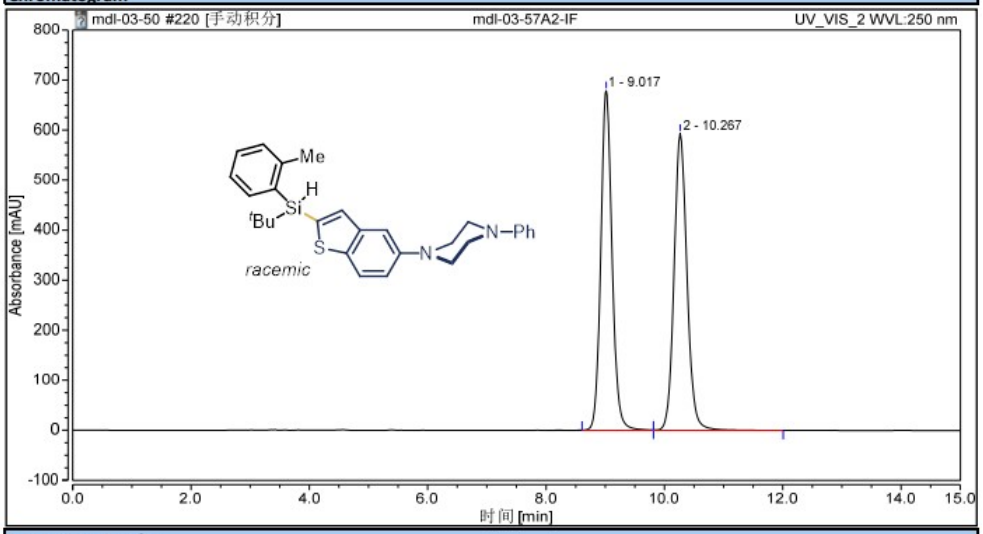
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.663	12.230	71.507	3.13	4.03	n.a.
2		8.883	378.737	1701.105	96.87	95.97	n.a.
Total:			**390.968**	**1772.611**	**100.00**	**100.00**	



3aj

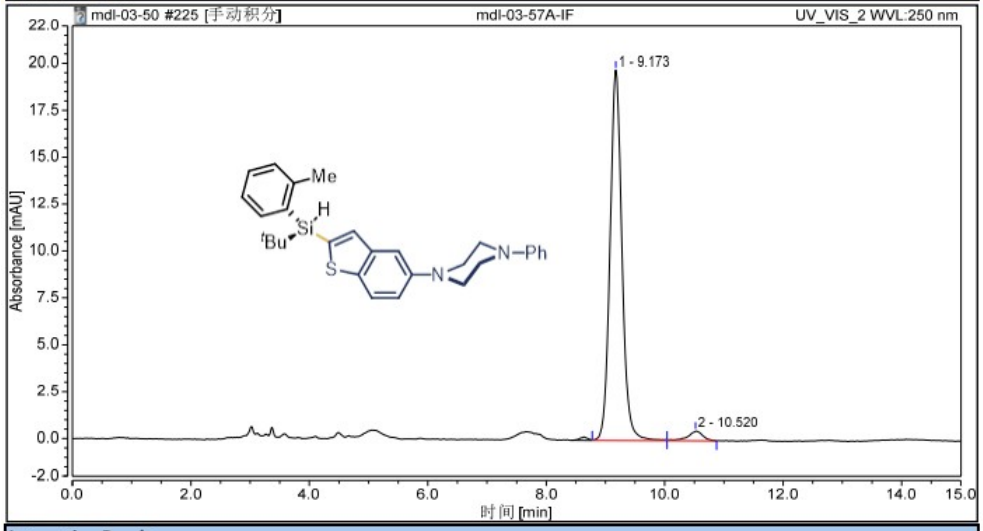
Chromatogram



Integration Results

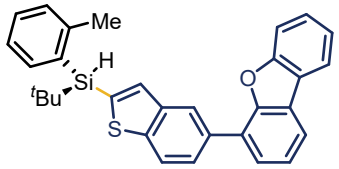
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.017	150.320	679.520	49.95	53.34	n.a.
2		10.267	150.637	594.424	50.05	46.66	n.a.
Total:			**300.957**	**1273.943**	**100.00**	**100.00**	

Chromatogram

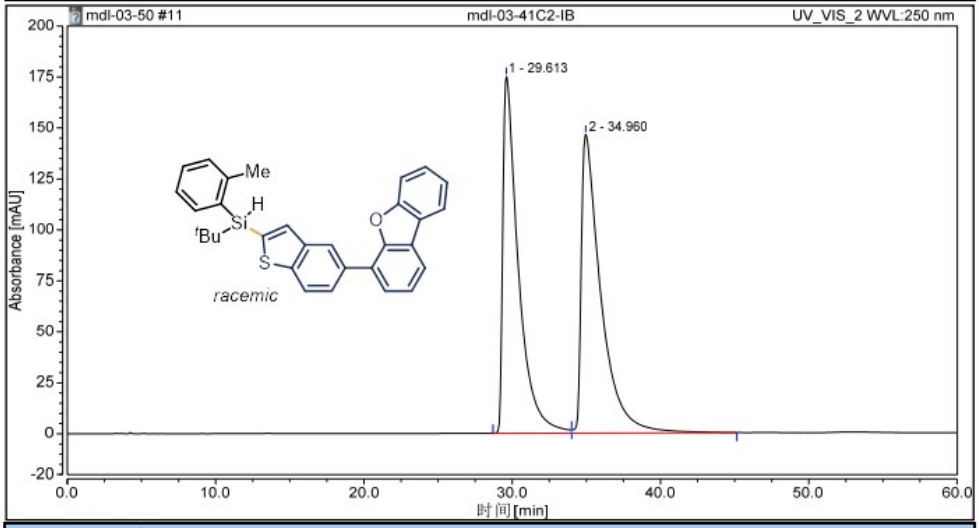


Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.173	4.599	19.758	96.73	97.44	n.a.
2		10.520	0.156	0.519	3.27	2.56	n.a.
Total:			**4.755**	**20.277**	**100.00**	**100.00**	

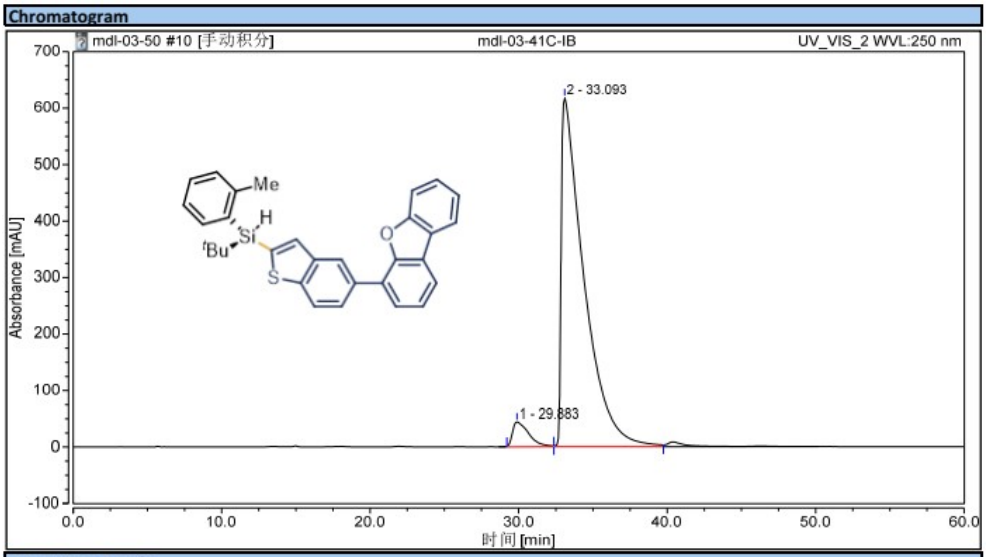


3ak



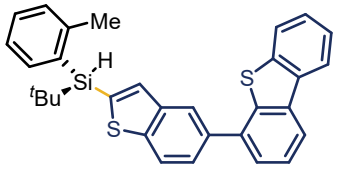
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.613	212.142	175.054	48.63	54.44	n.a.
2		34.960	224.055	146.491	51.37	45.56	n.a.
Total:			**436.197**	**321.545**	**100.00**	**100.00**	



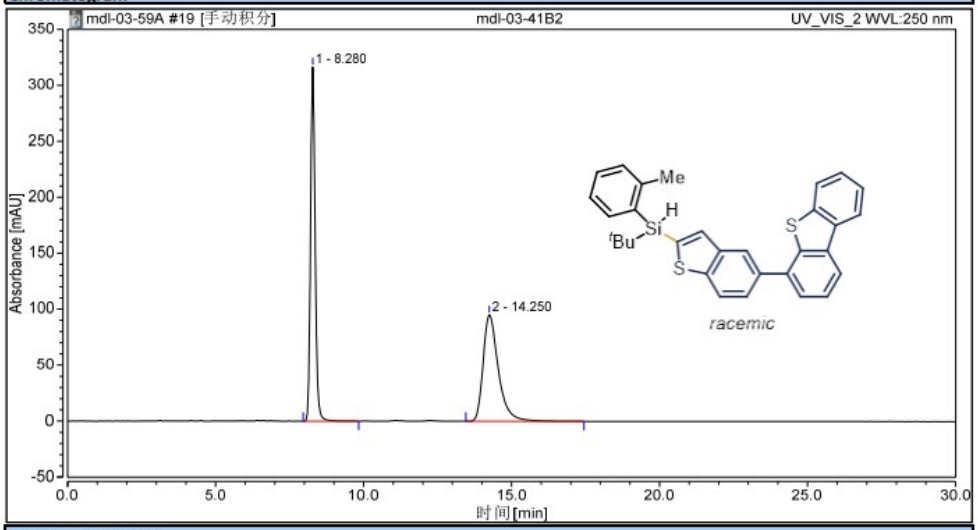
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.883	56.109	44.146	4.91	6.67	n.a.
2		33.093	1086.687	617.923	95.09	93.33	n.a.
Total:			**1142.795**	**662.069**	**100.00**	**100.00**	



3al

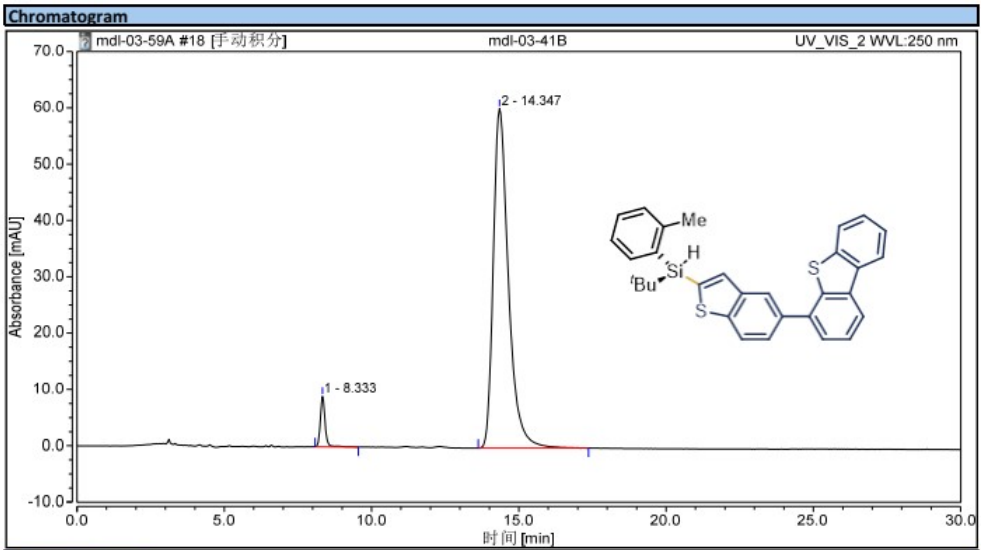
Chromatogram



Integration Results

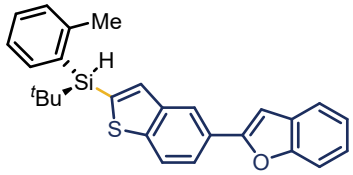
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.280	57.078	316.525	50.11	76.86	n.a.
2		14.250	56.825	95.280	49.89	23.14	n.a.
Total:			**113.903**	**411.804**	**100.00**	**100.00**	

Chromatogram



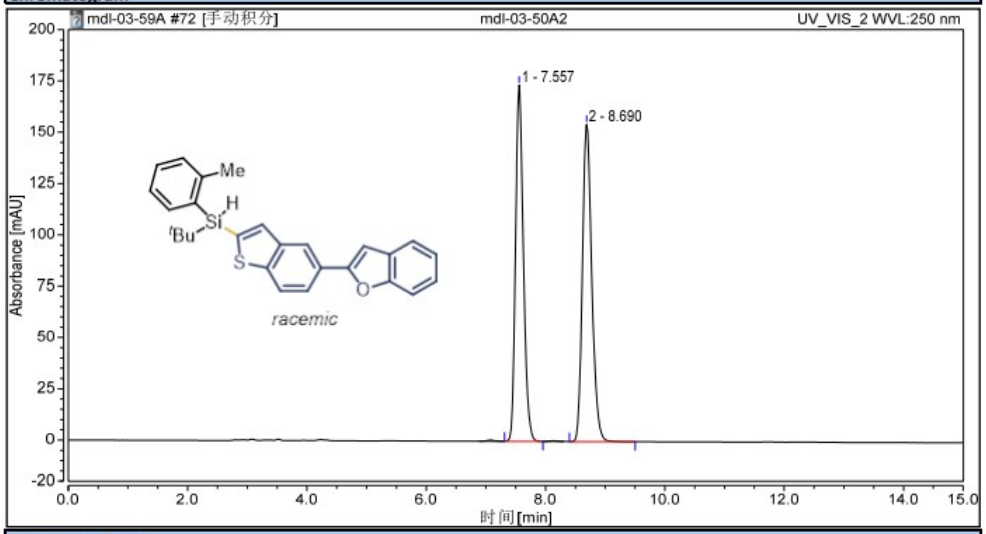
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.333	1.683	8.972	4.47	12.95	n.a.
2		14.347	36.000	60.310	95.53	87.05	n.a.
Total:			**37.682**	**69.282**	**100.00**	**100.00**	



3am

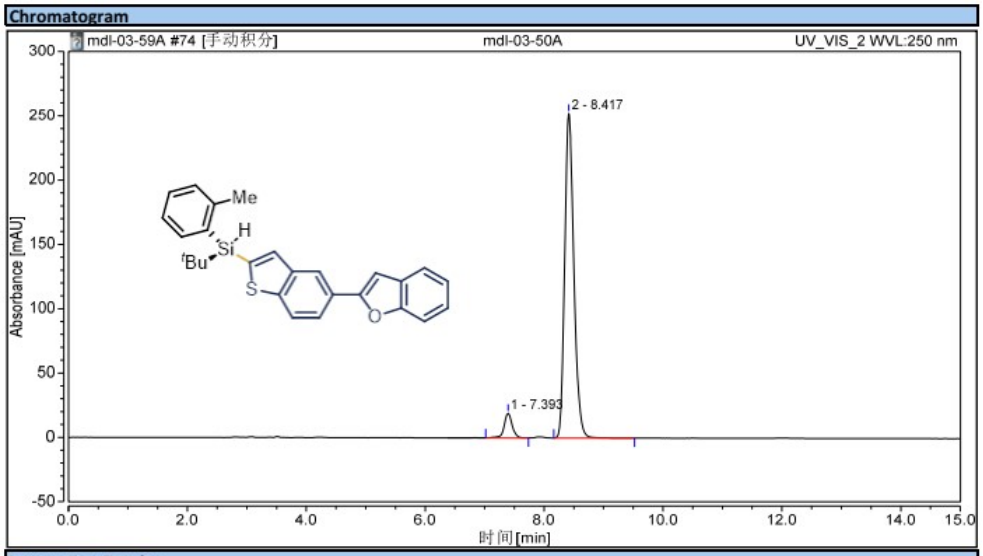
Chromatogram



Integration Results

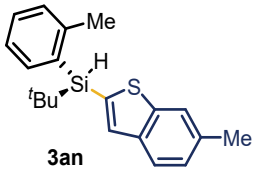
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.557	26.299	173.595	48.37	52.88	n.a.
2		8.690	28.075	154.681	51.63	47.12	n.a.
Total:			**54.374**	**328.276**	**100.00**	**100.00**	

Chromatogram



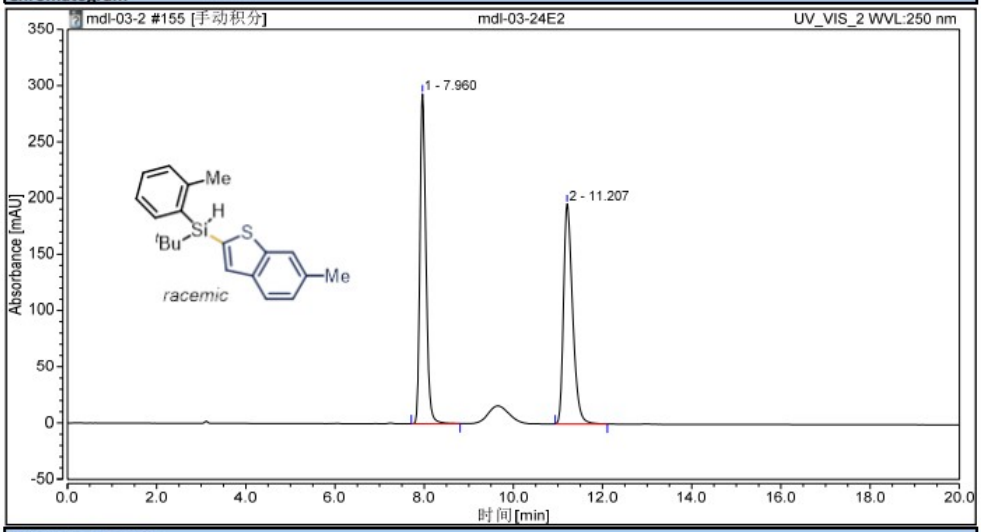
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.393	3.014	19.239	6.29	7.08	n.a.
2		8.417	44.919	252.533	93.71	92.92	n.a.
Total:			**47.932**	**271.772**	**100.00**	**100.00**	



3an

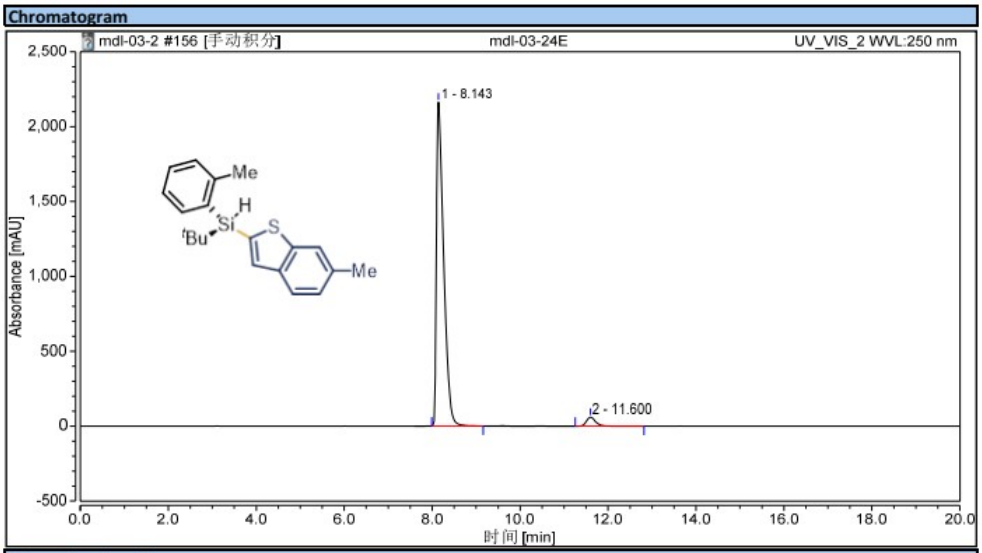
Chromatogram



Integration Results

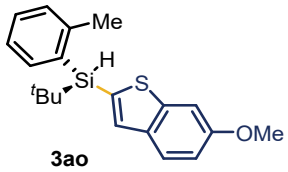
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.960	45.748	293.227	49.90	59.98	n.a.
2		11.207	45.940	195.640	50.10	40.02	n.a.
Total:			**91.688**	**488.868**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.143	411.038	2163.663	96.54	97.29	n.a.
2		11.600	14.752	60.270	3.46	2.71	n.a.
Total:			**425.790**	**2223.933**	**100.00**	**100.00**	



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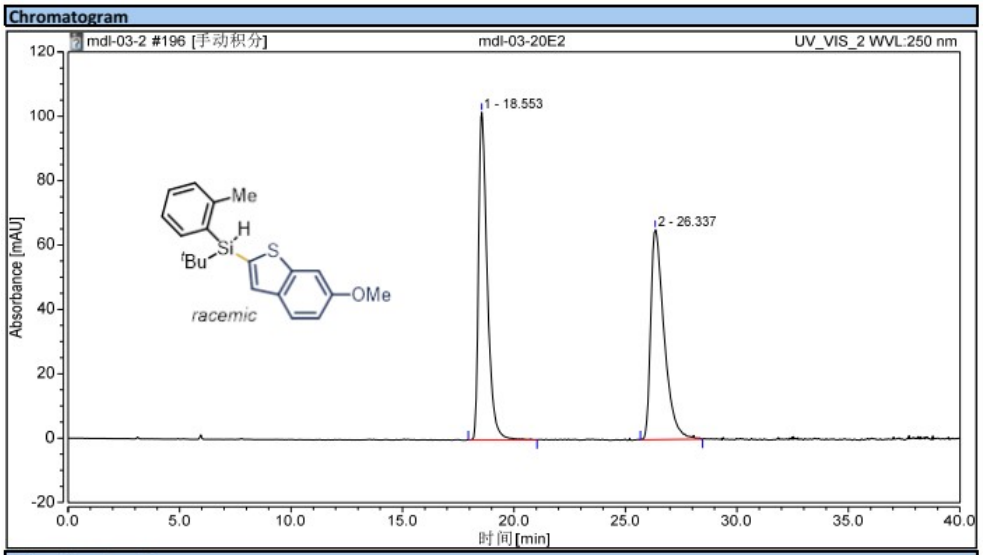
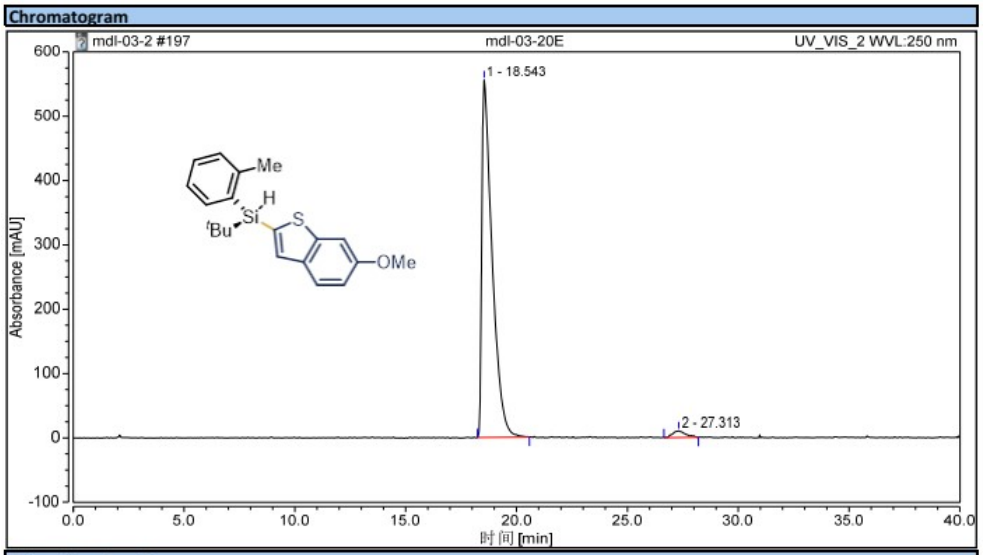


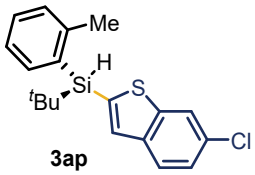
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.553	46.049	101.727	50.22	60.91	n.a.
2		26.337	45.643	65.283	49.78	39.09	n.a.
Total:			**91.693**	**167.010**	**100.00**	**100.00**	



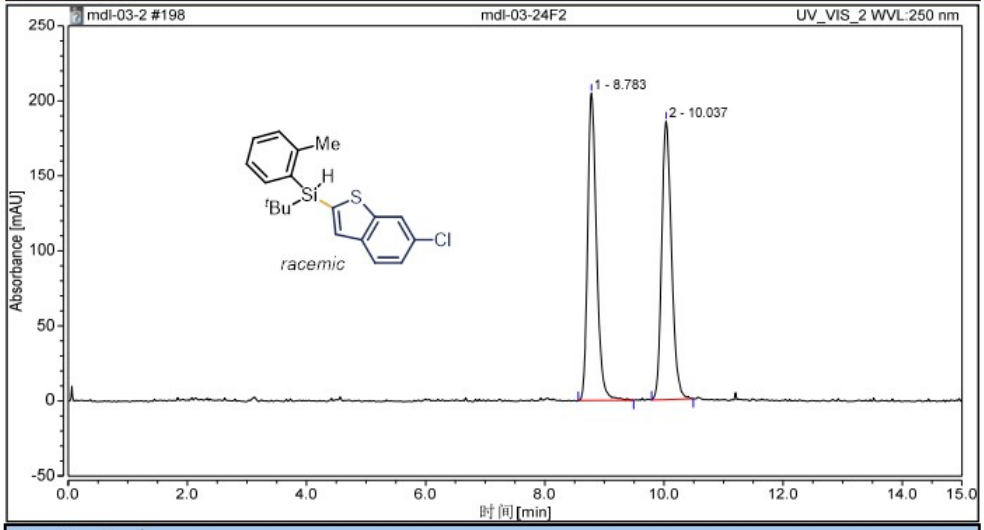
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.543	300.654	555.994	97.73	98.12	n.a.
2		27.313	6.976	10.628	2.27	1.88	n.a.
Total:			**307.630**	**566.622**	**100.00**	**100.00**	



3ap

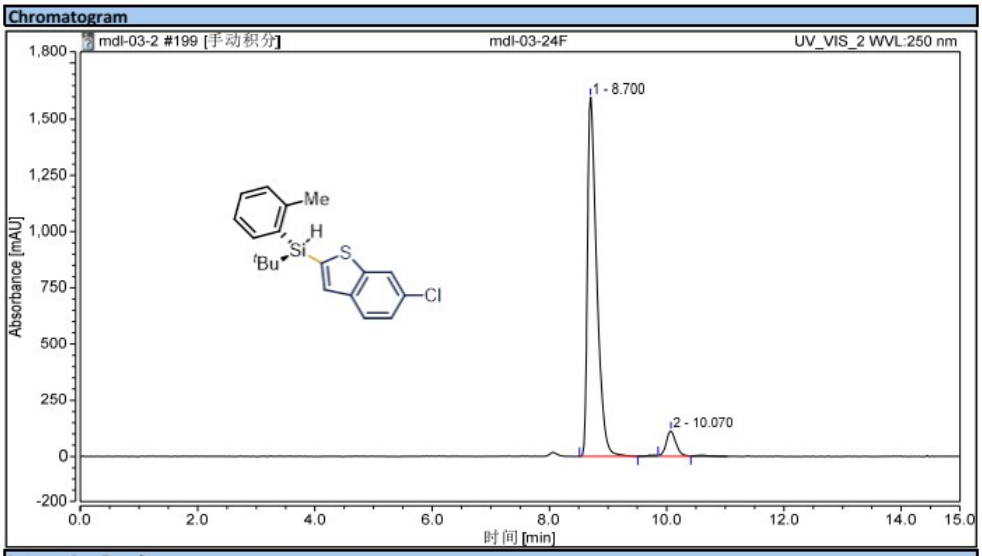
Chromatogram



Integration Results

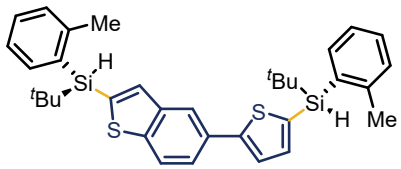
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.783	35.457	204.940	50.03	52.47	n.a.
2		10.037	35.416	185.640	49.97	47.53	n.a.
Total:			**70.873**	**390.580**	**100.00**	**100.00**	

Chromatogram



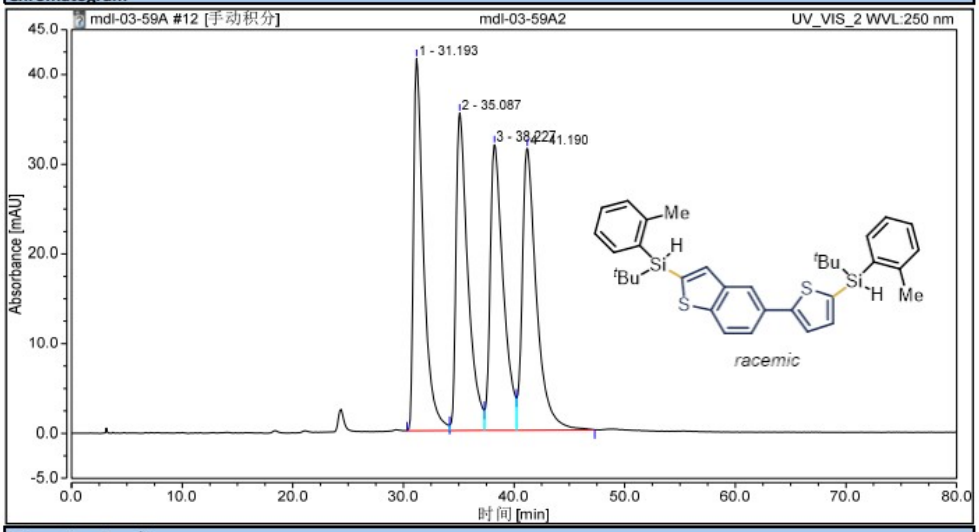
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.700	293.087	1597.705	92.94	93.35	n.a.
2		10.070	22.266	113.735	7.06	6.65	n.a.
Total:			**315.353**	**1711.440**	**100.00**	**100.00**	



3aq

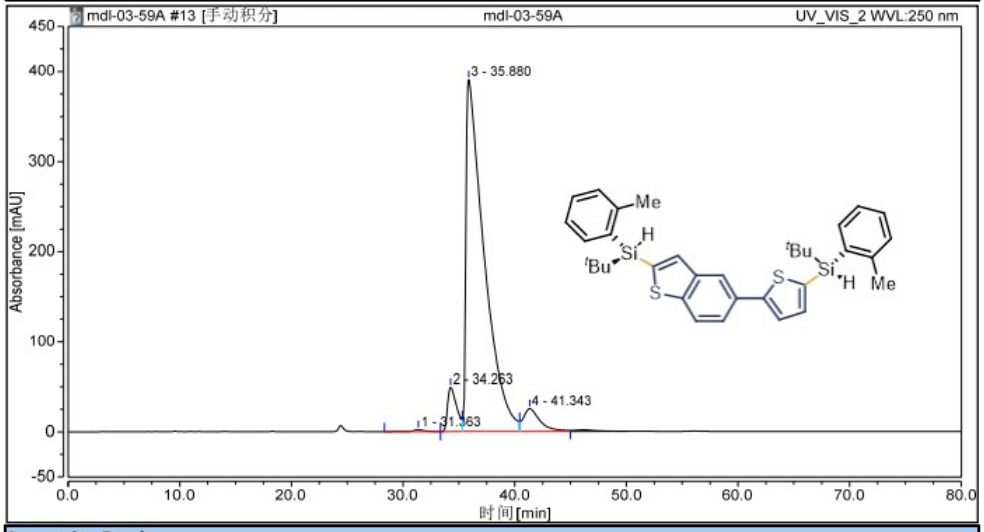
Chromatogram



Integration Results

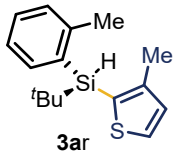
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		31.193	44.019	41.482	24.61	29.60	n.a.
2		35.087	44.027	35.395	24.61	25.25	n.a.
3		38.227	43.837	31.849	24.51	22.72	n.a.
4		41.190	46.994	31.434	26.27	22.43	n.a.
Total:			**178.877**	**140.160**	**100.00**	**100.00**	

Chromatogram

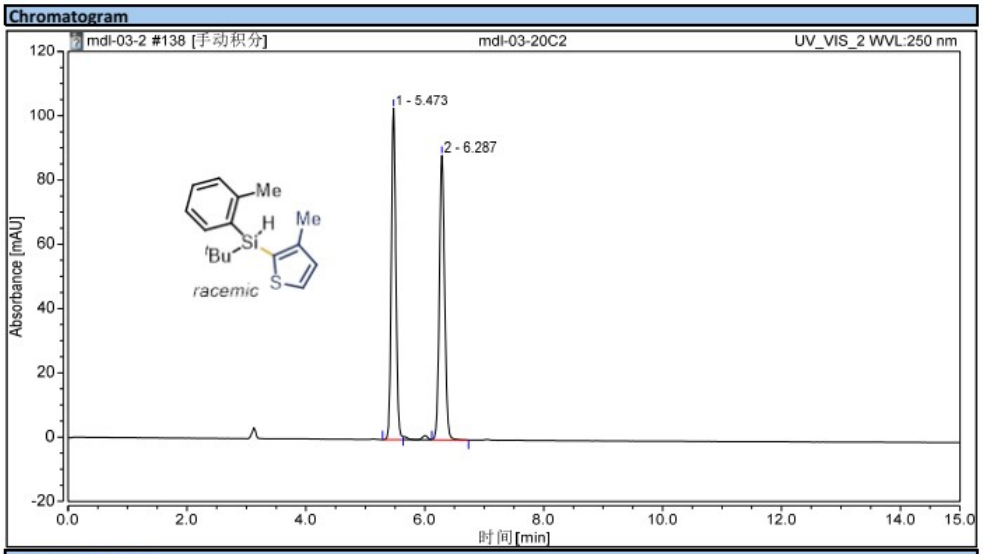


Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		31.363	2.748	2.154	0.33	0.46	n.a.
2		34.263	47.127	49.242	5.67	10.54	n.a.
3		35.880	736.343	390.601	88.66	83.58	n.a.
4		41.343	44.324	25.349	5.34	5.42	n.a.
Total:			**830.542**	**467.345**	**100.00**	**100.00**	

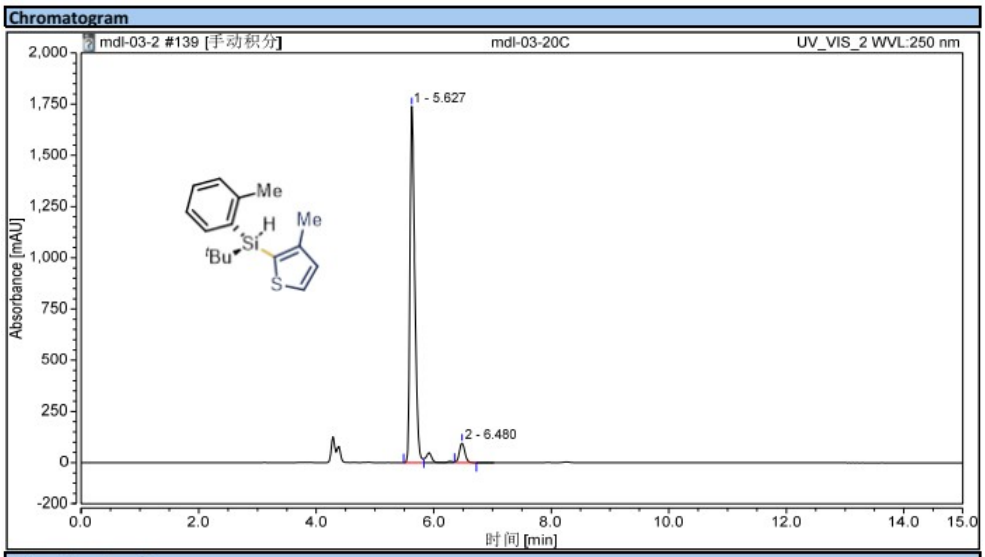


3ar



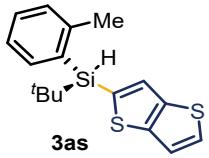
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.473	9.071	103.119	49.89	53.81	n.a.
2		6.287	9.111	88.505	50.11	46.19	n.a.
Total:			**18.182**	**191.623**	**100.00**	**100.00**	



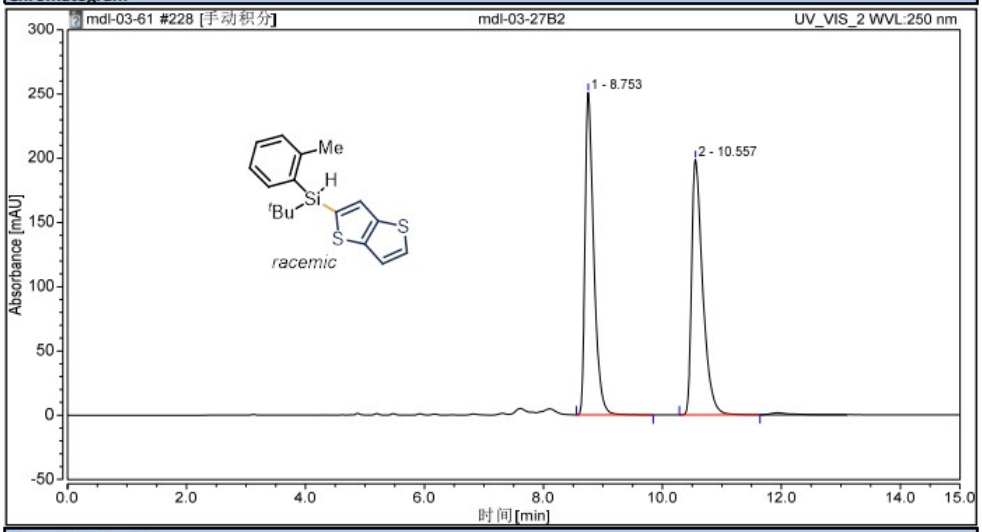
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.627	163.244	1738.950	94.10	94.74	n.a.
2		6.480	10.235	96.498	5.90	5.26	n.a.
Total:			**173.479**	**1835.448**	**100.00**	**100.00**	



3as

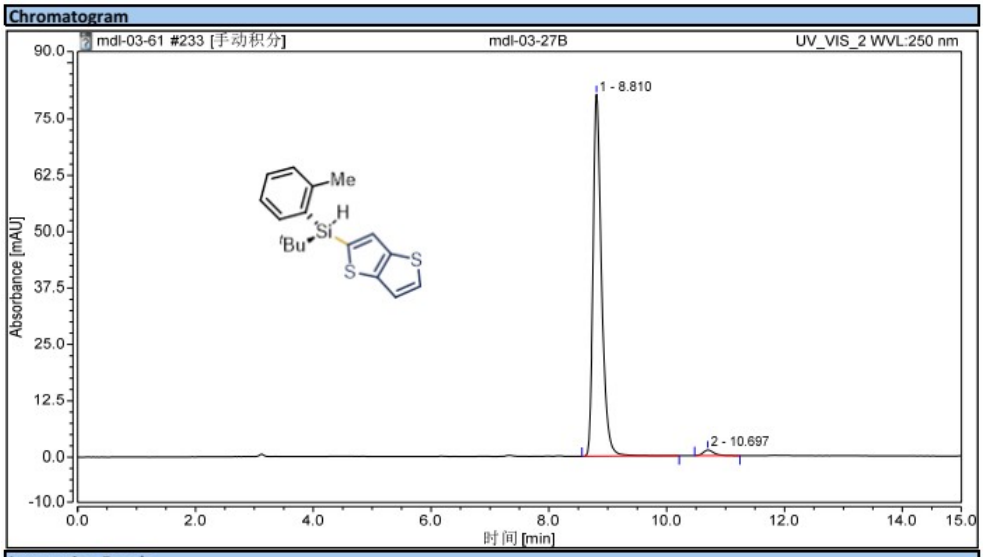
Chromatogram



Integration Results

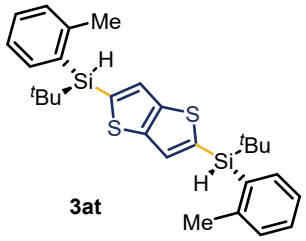
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.753	42.718	250.977	49.89	55.82	n.a.
2		10.557	42.907	198.641	50.11	44.18	n.a.
Total:			**85.625**	**449.617**	**100.00**	**100.00**	

Chromatogram



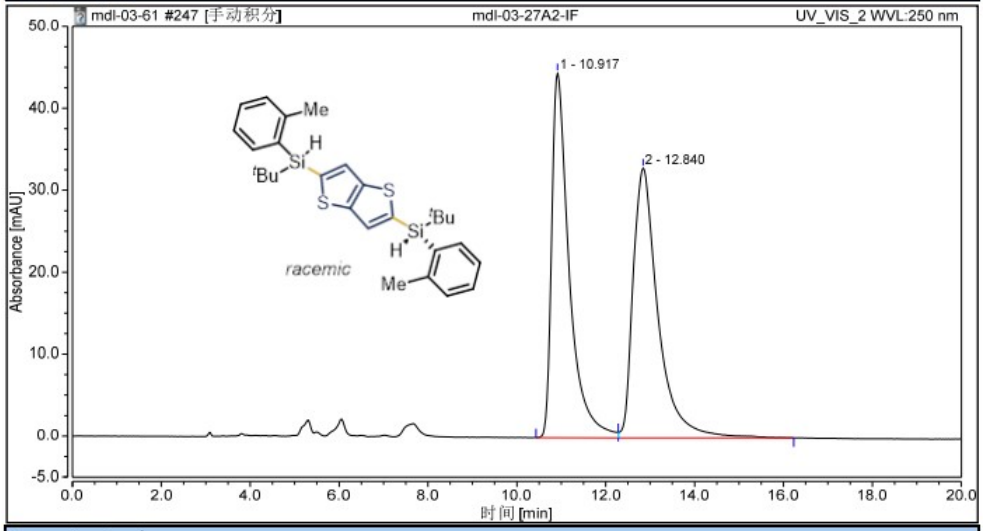
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.810	13.506	80.259	98.03	98.48	n.a.
2		10.697	0.271	1.243	1.97	1.52	n.a.
Total:			**13.778**	**81.501**	**100.00**	**100.00**	



3at

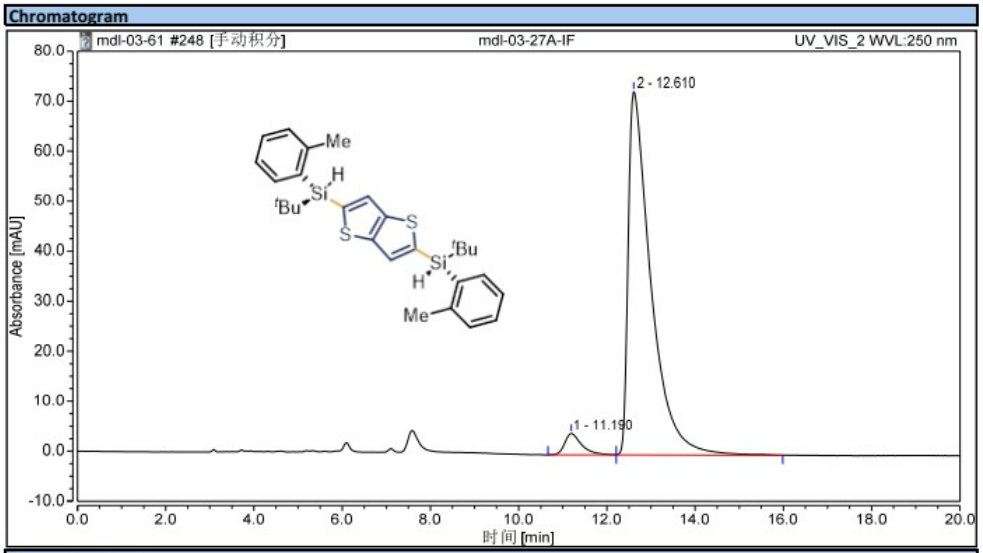
Chromatogram



Integration Results

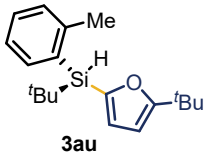
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.917	20.264	44.569	48.59	57.50	n.a.
2		12.840	21.436	32.940	51.41	42.50	n.a.
Total:			**41.700**	**77.508**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.190	1.918	4.296	4.25	5.57	n.a.
2		12.610	43.229	72.802	95.75	94.43	n.a.
Total:			**45.147**	**77.098**	**100.00**	**100.00**	



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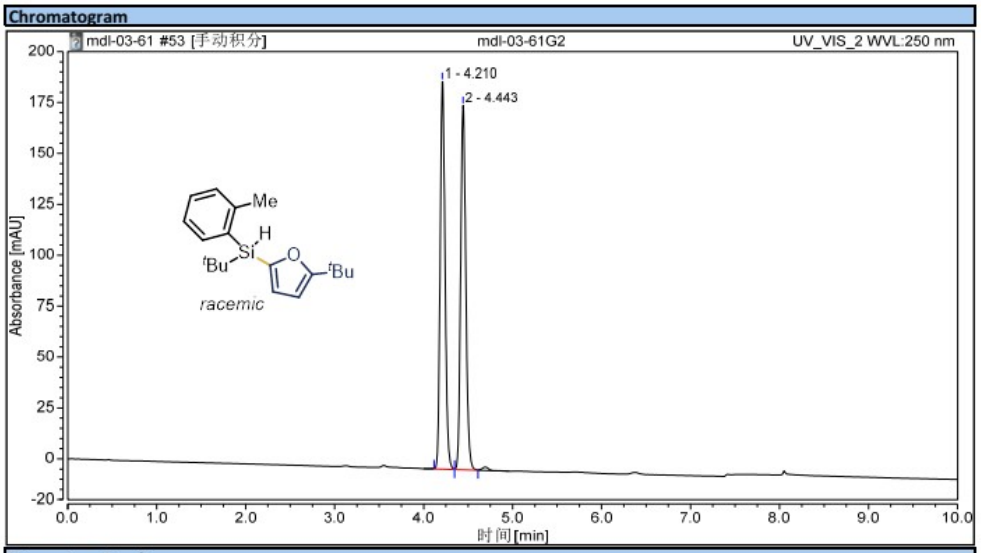
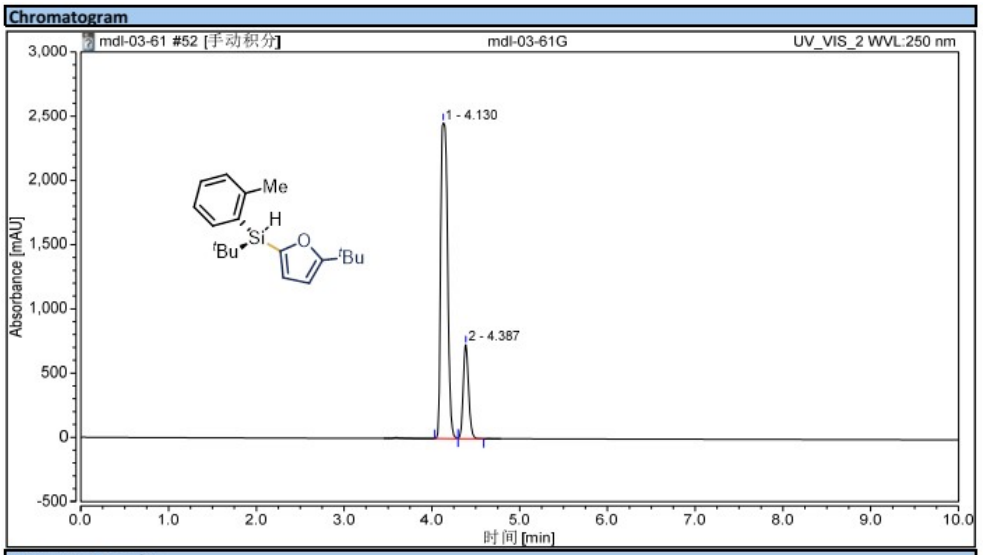


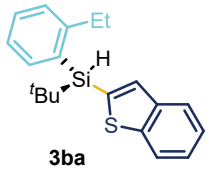
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.210	12.125	190.425	50.10	51.56	n.a.
2		4.443	12.078	178.896	49.90	48.44	n.a.
Total:			**24.202**	**369.321**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.130	223.898	2460.330	81.48	77.08	n.a.
2		4.387	50.890	731.563	18.52	22.92	n.a.
Total:			**274.788**	**3191.893**	**100.00**	**100.00**	



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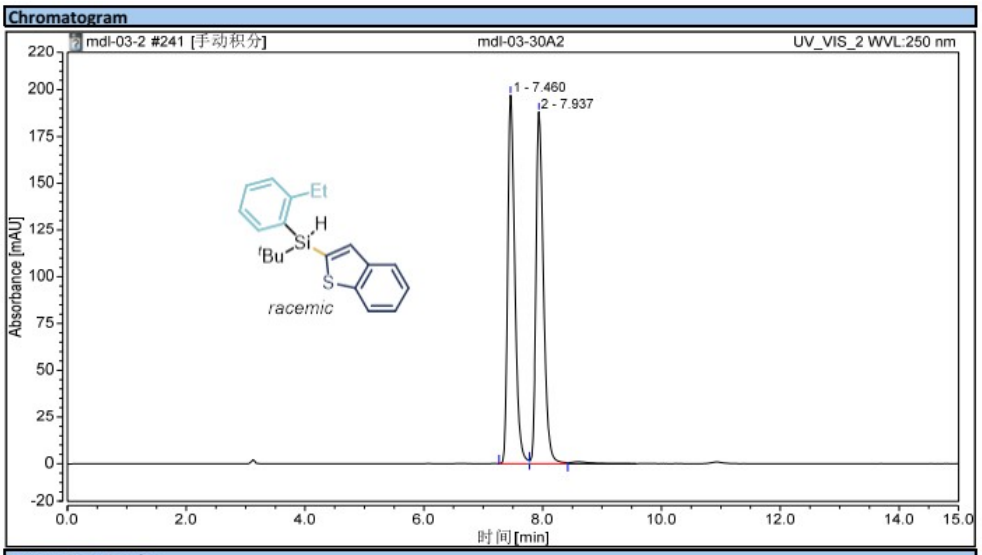
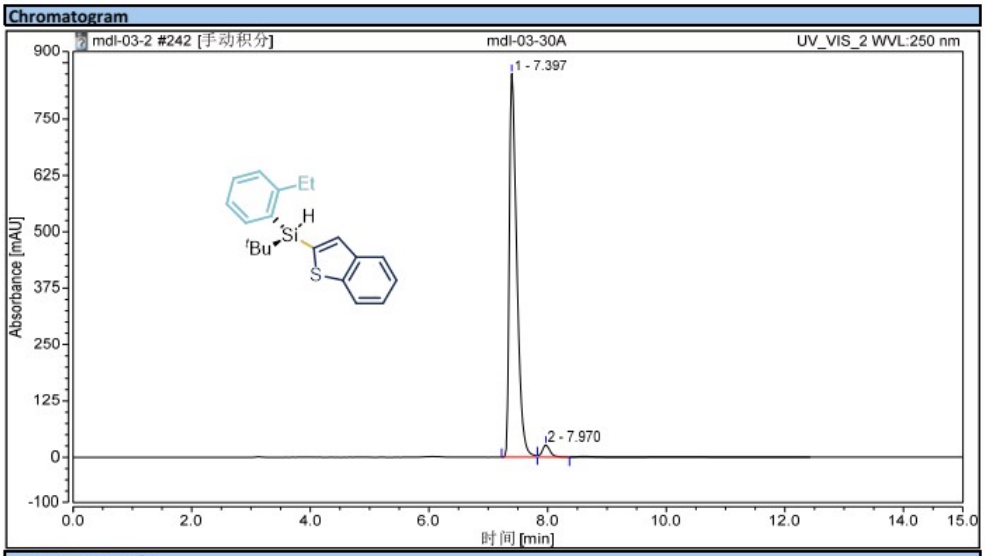


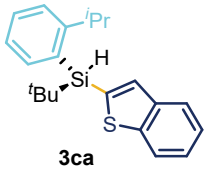
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.460	27.318	197.054	49.88	51.15	n.a.
2		7.937	27.448	188.201	50.12	48.85	n.a.
Total:			**54.766**	**385.256**	**100.00**	**100.00**	



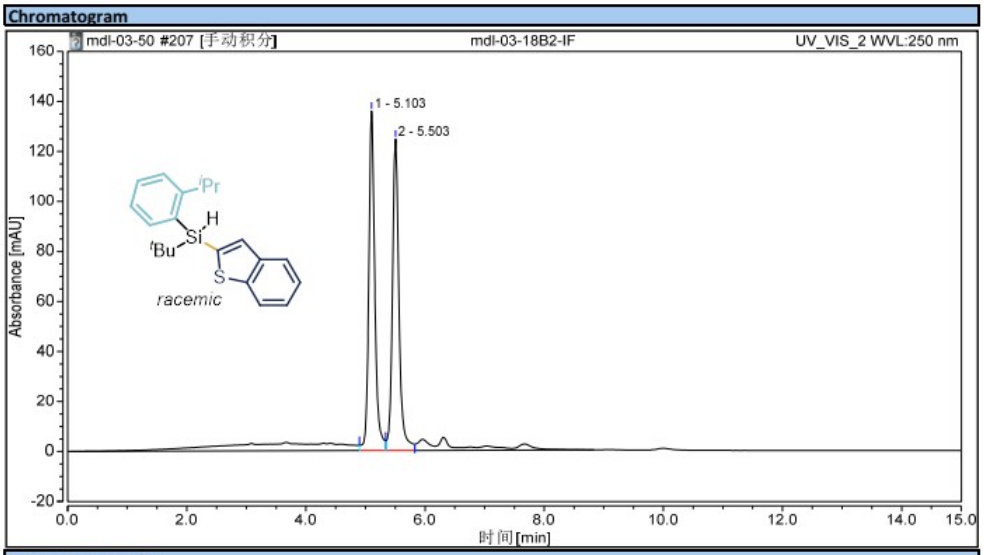
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.397	124.660	850.907	96.68	96.90	n.a.
2		7.970	4.275	27.180	3.32	3.10	n.a.
Total:			**128.935**	**878.087**	**100.00**	**100.00**	



3ca

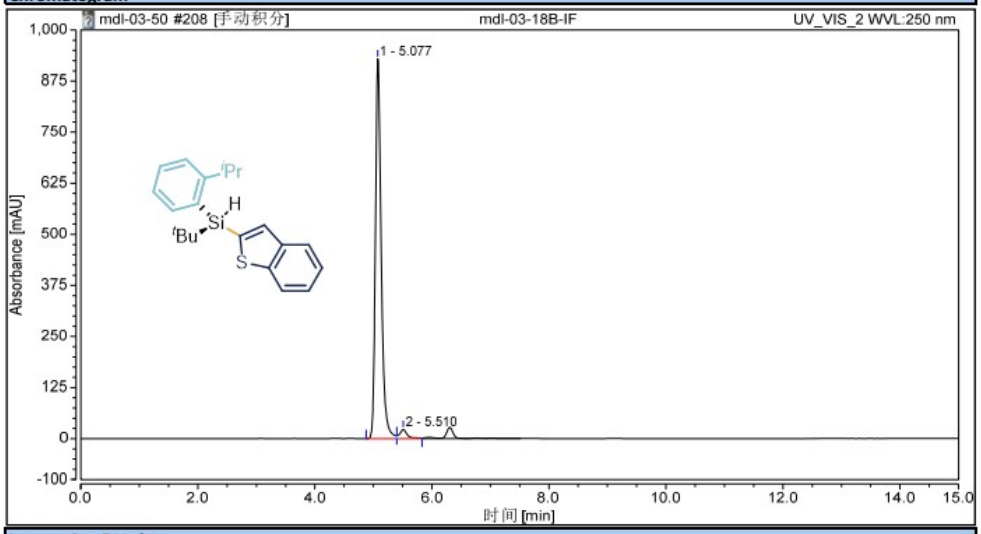
Chromatogram



Integration Results

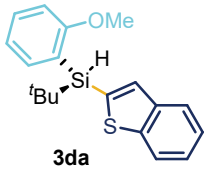
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.103	15.969	135.780	50.26	52.15	n.a.
2		5.503	15.803	124.582	49.74	47.85	n.a.
Total:			**31.772**	**260.362**	**100.00**	**100.00**	

Chromatogram



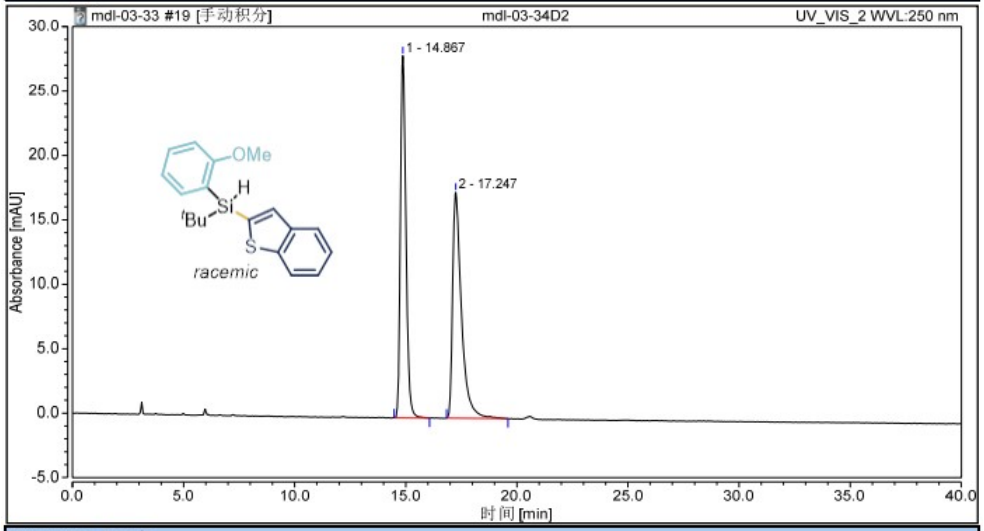
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.077	106.954	929.148	96.94	97.63	n.a.
2		5.510	3.371	22.518	3.06	2.37	n.a.
Total:			**110.325**	**951.666**	**100.00**	**100.00**	



3da

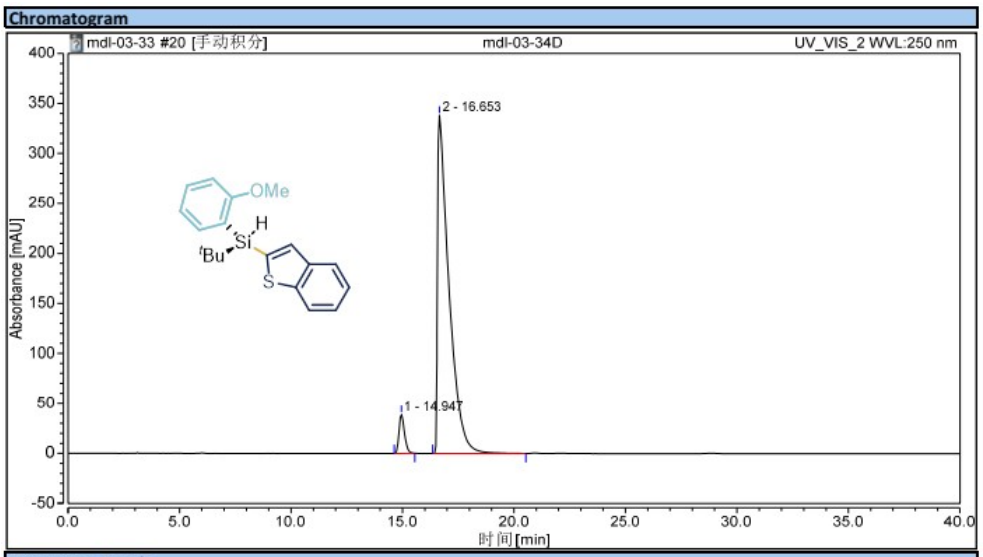
Chromatogram



Integration Results

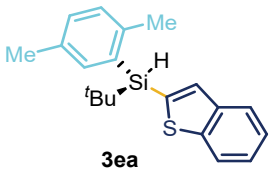
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.867	8.083	28.116	49.87	61.58	n.a.
2		17.247	8.125	17.545	50.13	38.42	n.a.
Total:			**16.207**	**45.662**	**100.00**	**100.00**	

Chromatogram



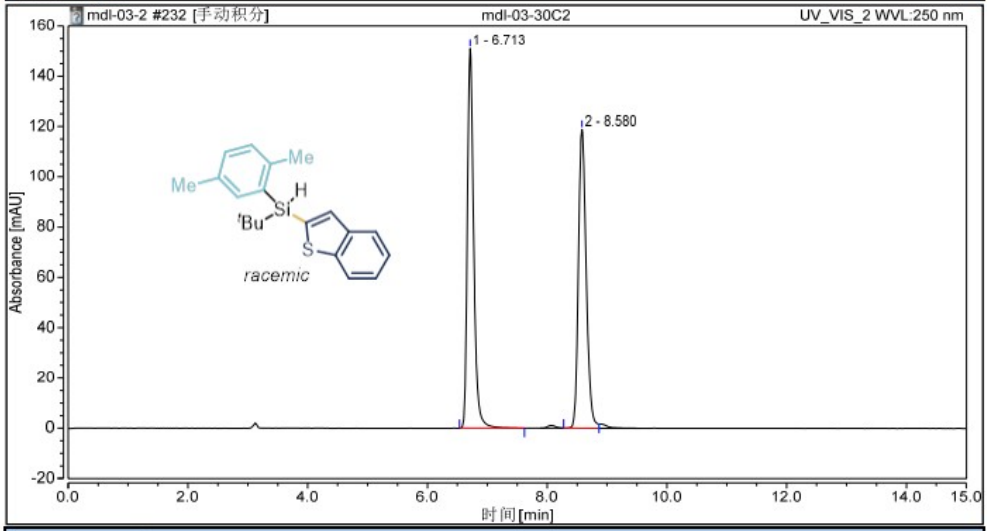
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.947	11.090	39.145	5.23	10.37	n.a.
2		16.653	200.759	338.283	94.77	89.63	n.a.
Total:			**211.849**	**377.428**	**100.00**	**100.00**	



3ea

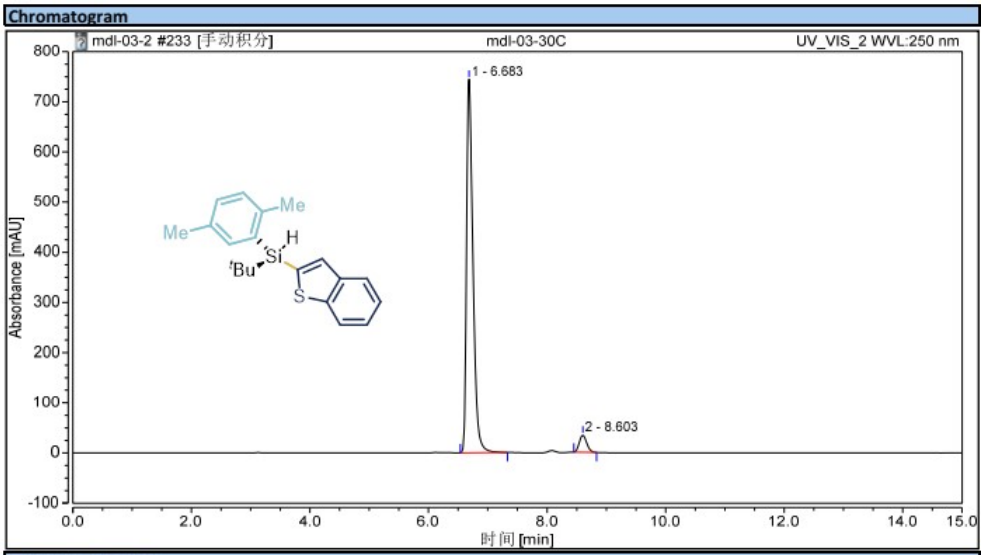
Chromatogram



Integration Results

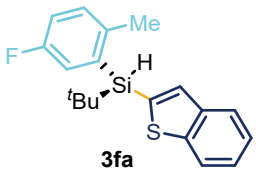
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.713	18.500	151.051	50.77	55.96	n.a.
2		8.580	17.940	118.887	49.23	44.04	n.a.
Total:			**36.440**	**269.938**	**100.00**	**100.00**	

Chromatogram



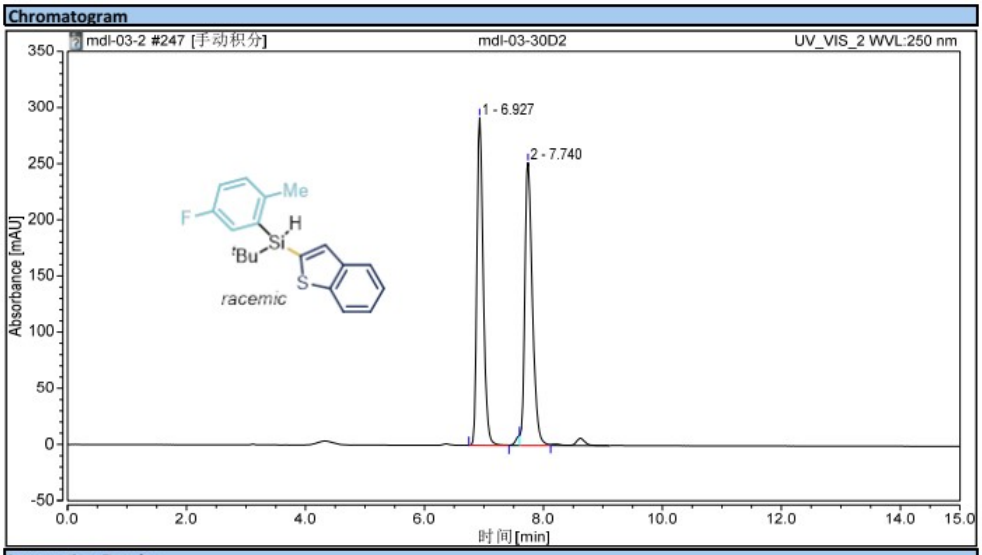
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.683	93.521	744.677	95.00	95.62	n.a.
2		8.603	4.921	34.142	5.00	4.38	n.a.
Total:			**98.442**	**778.819**	**100.00**	**100.00**	



3fa

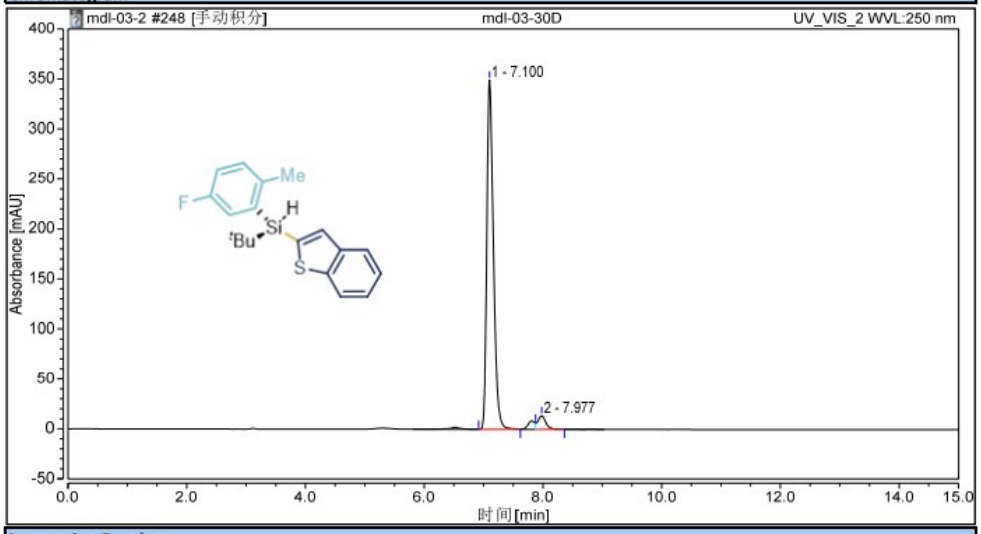
Chromatogram



Integration Results

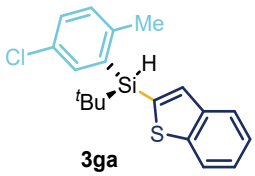
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.927	35.970	291.916	49.28	53.67	n.a.
2		7.740	37.022	252.003	50.72	46.33	n.a.
Total:			**72.992**	**543.918**	**100.00**	**100.00**	

Chromatogram



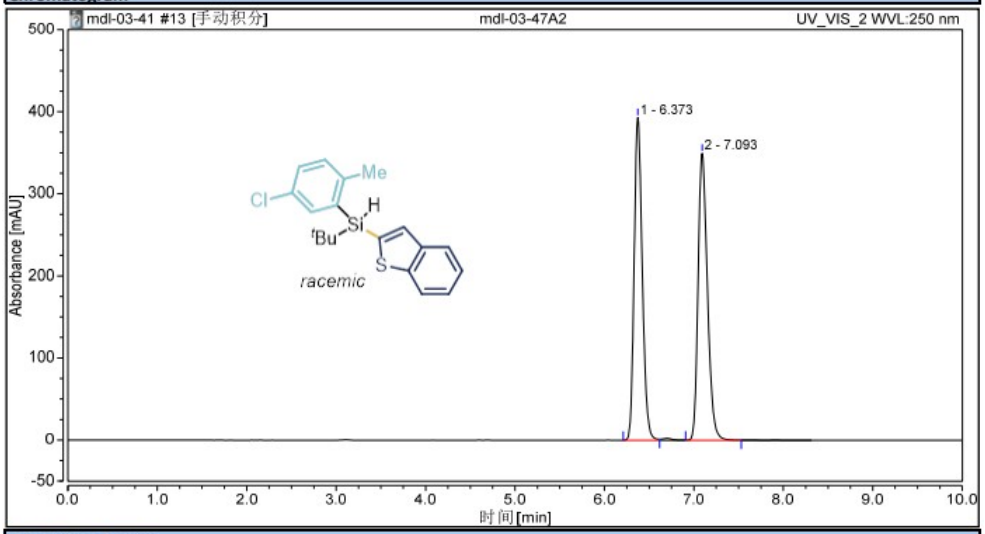
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.100	44.936	349.469	95.47	96.26	n.a.
2		7.977	2.132	13.586	4.53	3.74	n.a.
Total:			**47.067**	**363.055**	**100.00**	**100.00**	



3ga

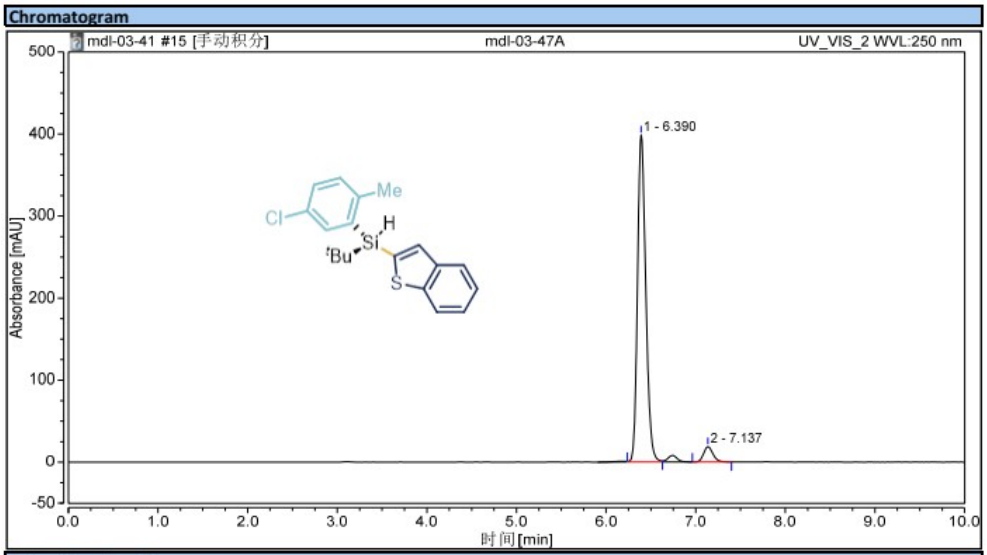
Chromatogram



Integration Results

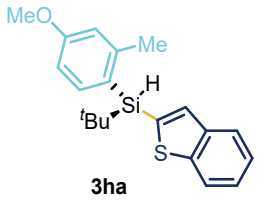
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.373	41.434	393.019	49.48	52.93	n.a.
2		7.093	42.298	349.533	50.52	47.07	n.a.
Total:			**83.731**	**742.552**	**100.00**	**100.00**	

Chromatogram



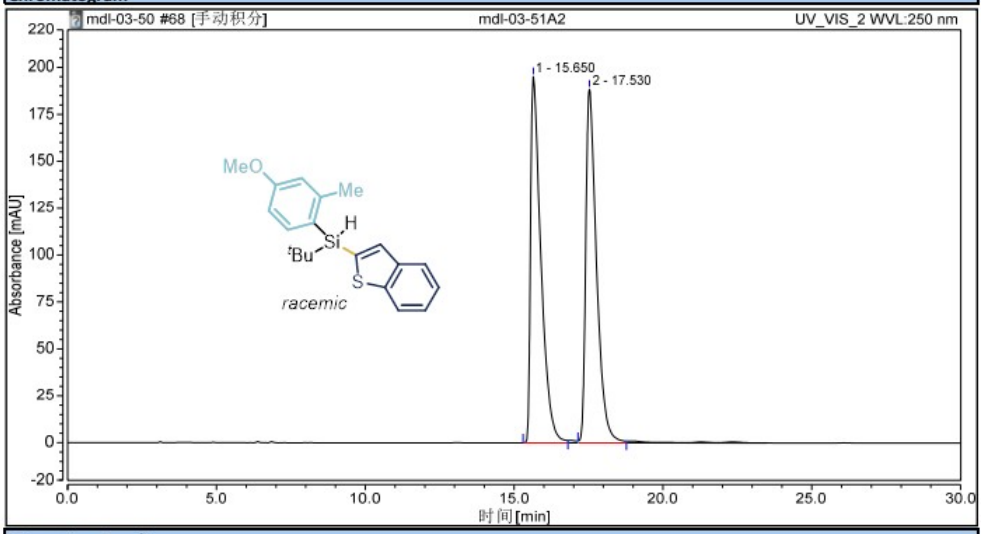
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.390	42.700	398.727	94.97	95.50	n.a.
2		7.137	2.264	18.803	5.03	4.50	n.a.
Total:			**44.964**	**417.530**	**100.00**	**100.00**	



3ha

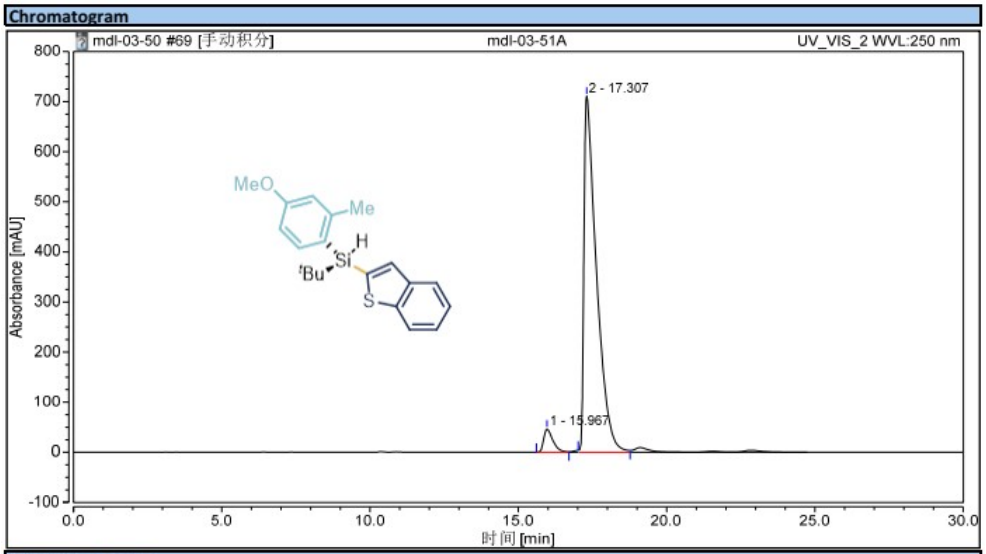
Chromatogram



Integration Results

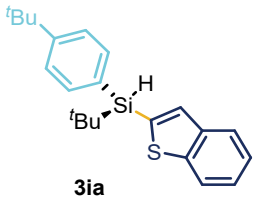
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.650	78.986	195.289	50.00	50.87	n.a.
2		17.530	78.991	188.586	50.00	49.13	n.a.
Total:			**157.977**	**383.875**	**100.00**	**100.00**	

Chromatogram



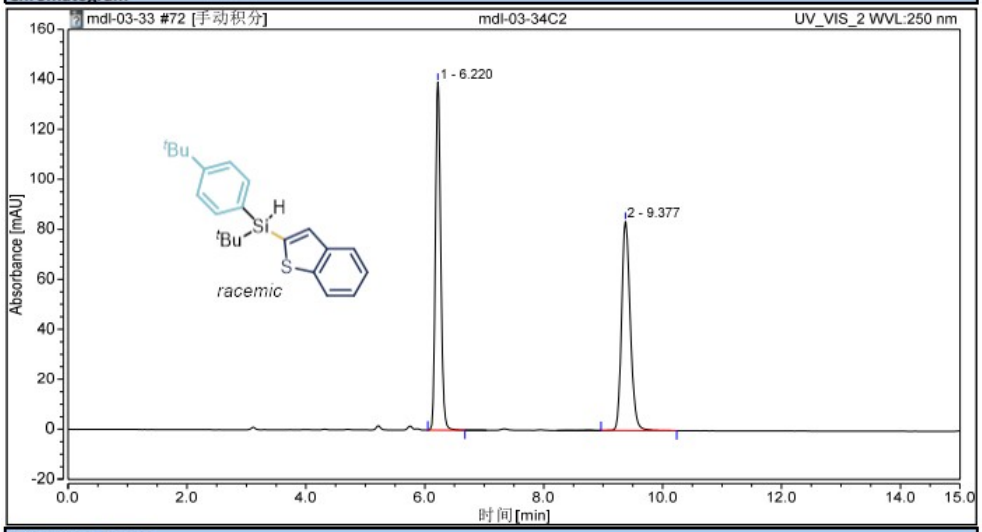
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.967	16.701	46.198	4.58	6.10	n.a.
2		17.307	347.712	710.720	95.42	93.90	n.a.
Total:			**364.413**	**756.917**	**100.00**	**100.00**	



3ia

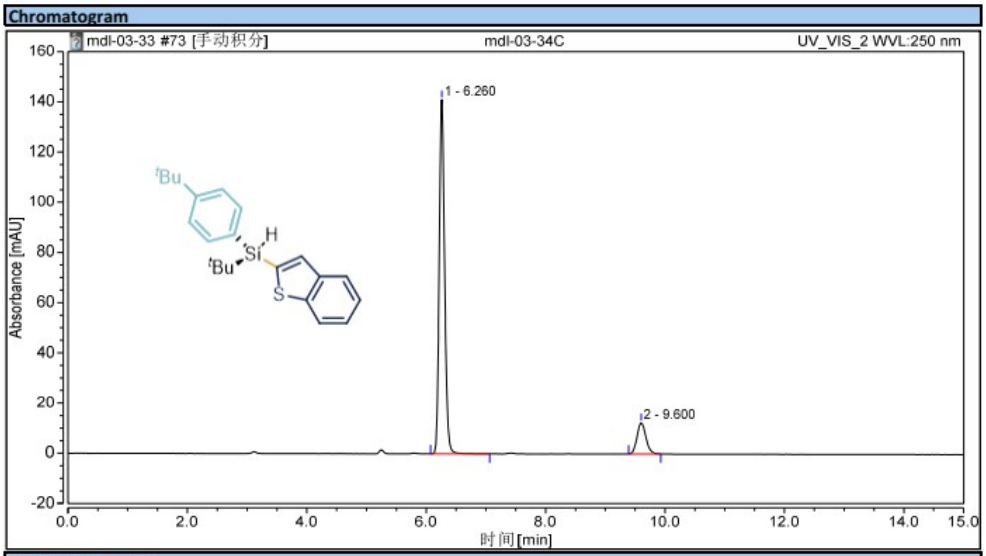
Chromatogram



Integration Results

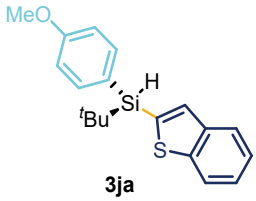
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.220	14.318	139.254	50.22	62.45	n.a.
2		9.377	14.193	83.736	49.78	37.55	n.a.
Total:			**28.512**	**222.990**	**100.00**	**100.00**	

Chromatogram



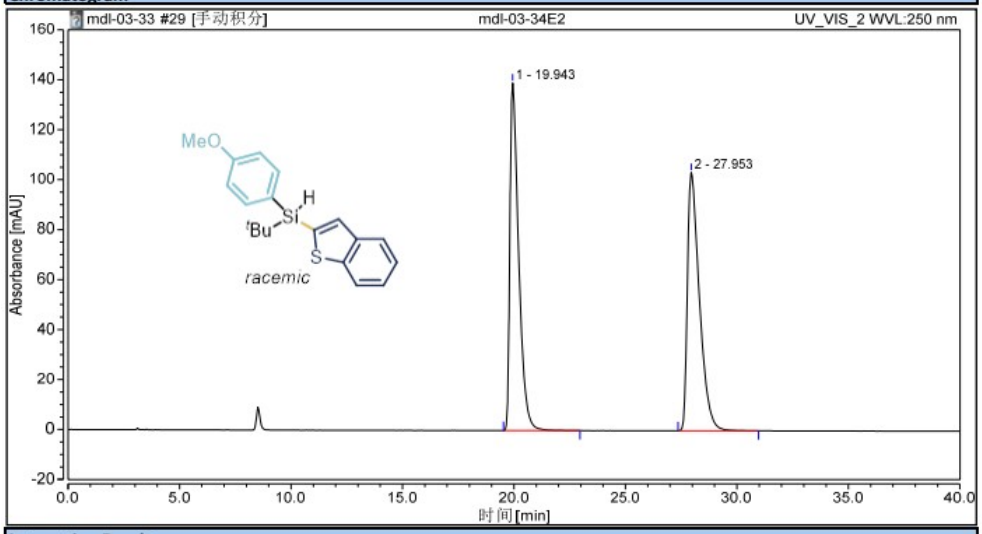
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.260	14.746	141.169	87.32	91.86	n.a.
2		9.600	2.141	12.510	12.68	8.14	n.a.
Total:			**16.887**	**153.679**	**100.00**	**100.00**	



3ja

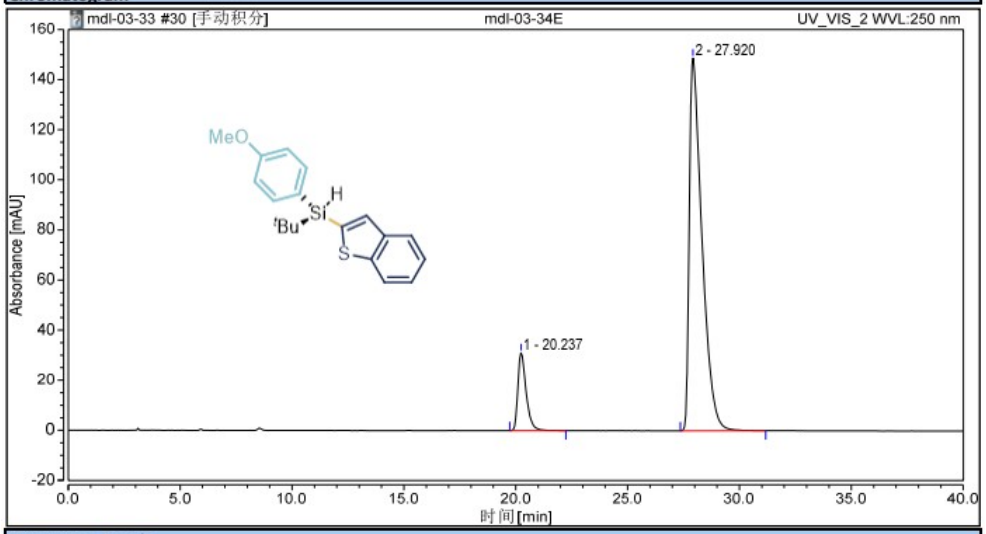
Chromatogram



Integration Results

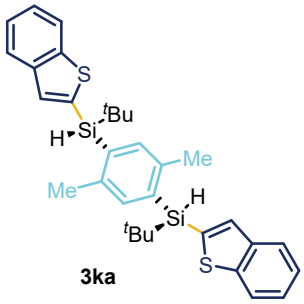
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.943	63.399	139.199	49.54	57.37	n.a.
2		27.953	64.573	103.426	50.46	42.63	n.a.
Total:			**127.972**	**242.626**	**100.00**	**100.00**	

Chromatogram



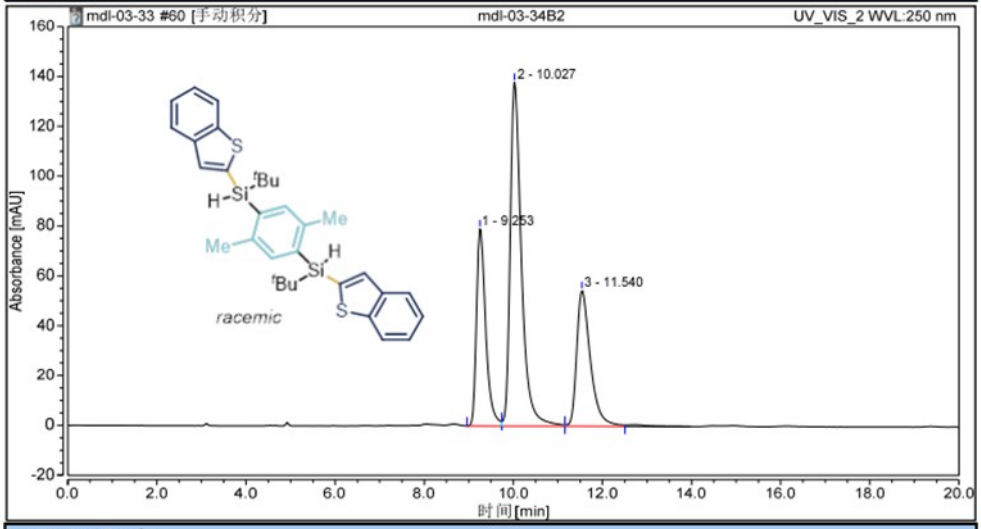
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.237	13.403	31.140	12.01	17.30	n.a.
2		27.920	98.233	148.867	87.99	82.70	n.a.
Total:			**111.636**	**180.007**	**100.00**	**100.00**	



3ka

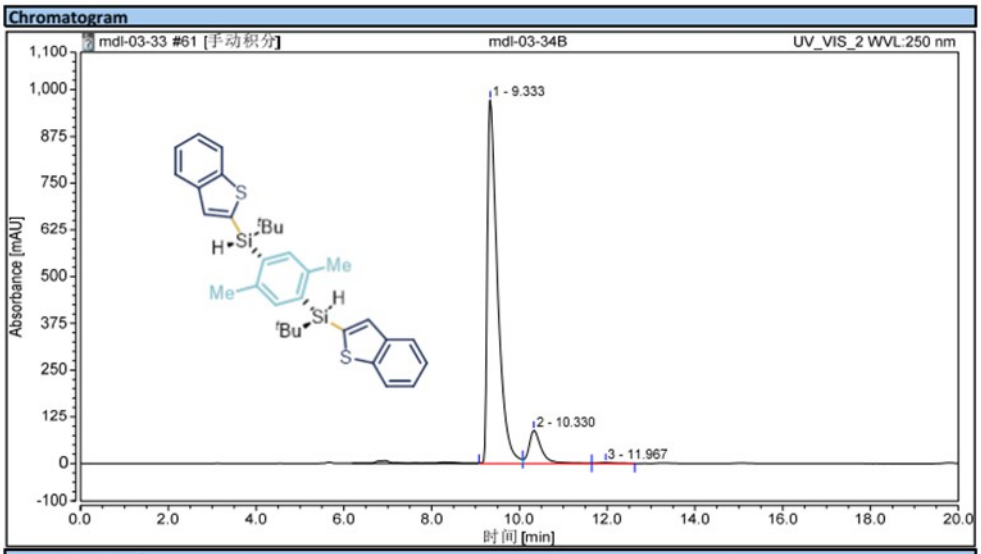
Chromatogram



Integration Results

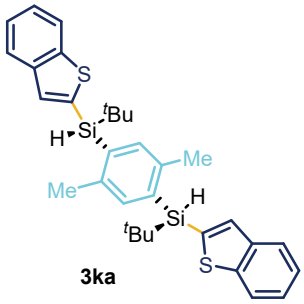
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.253	19.051	79.195	24.26	29.15	n.a.
2		10.027	40.097	137.947	51.06	50.78	n.a.
3		11.540	19.383	54.495	24.68	20.06	n.a.
Total:			**78.532**	**271.638**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.333	262.040	972.594	89.87	91.45	n.a.
2		10.330	28.647	88.780	9.82	8.35	n.a.
3		11.967	0.892	2.179	0.31	0.20	n.a.
Total:			**291.580**	**1063.553**	**100.00**	**100.00**	



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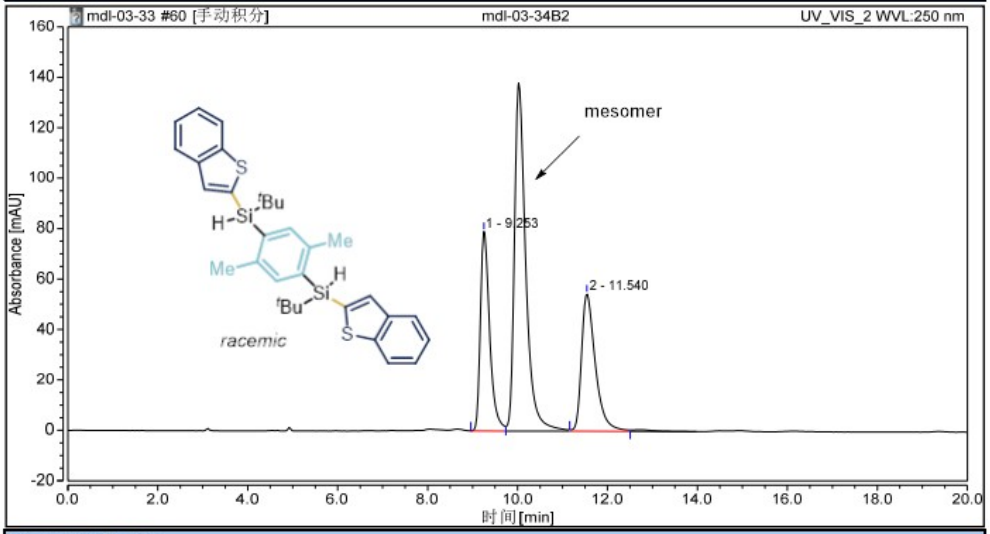
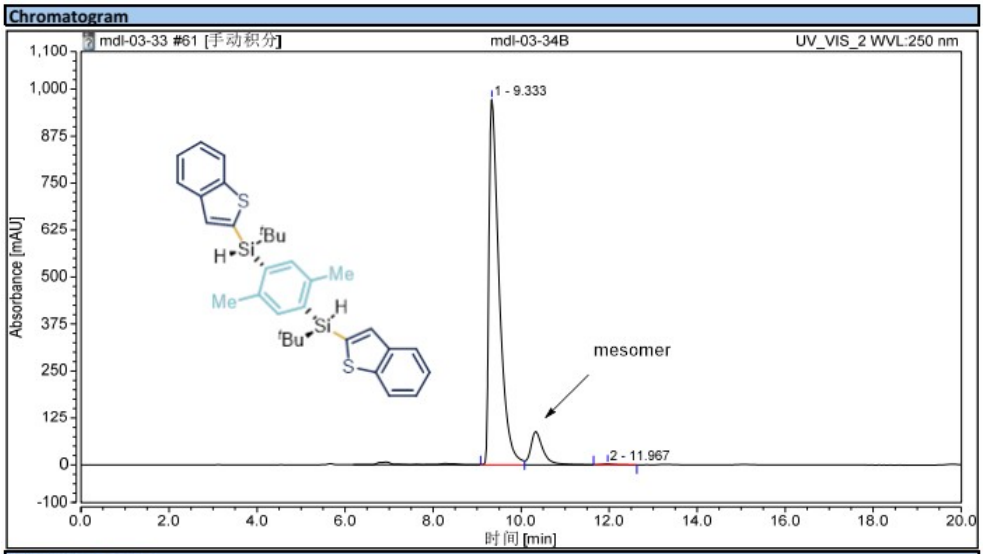


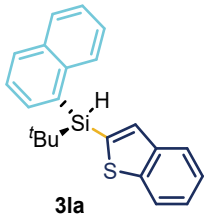
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.253	19.051	79.195	49.57	59.24	n.a.
2		11.540	19.383	54.495	50.43	40.76	n.a.
Total:			**38.435**	**133.690**	**100.00**	**100.00**	



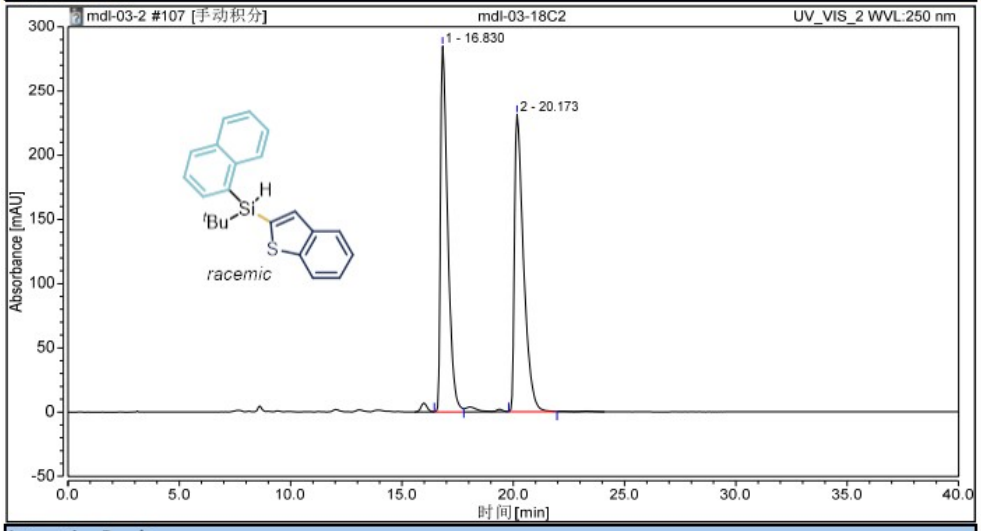
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.333	262.040	972.594	99.66	99.78	n.a.
2		11.967	0.892	2.179	0.34	0.22	n.a.
Total:			**262.933**	**974.773**	**100.00**	**100.00**	



3la

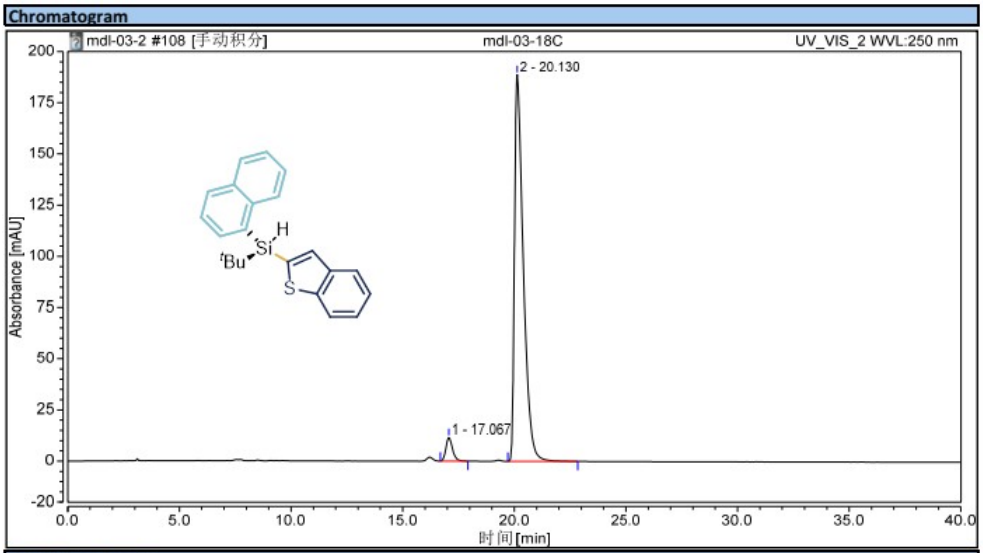
Chromatogram



Integration Results

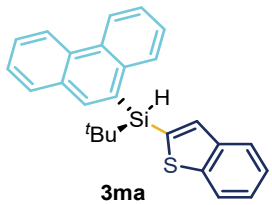
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.830	107.144	284.838	49.37	55.15	n.a.
2		20.173	109.882	231.618	50.63	44.85	n.a.
Total:			**217.026**	**516.456**	**100.00**	**100.00**	

Chromatogram



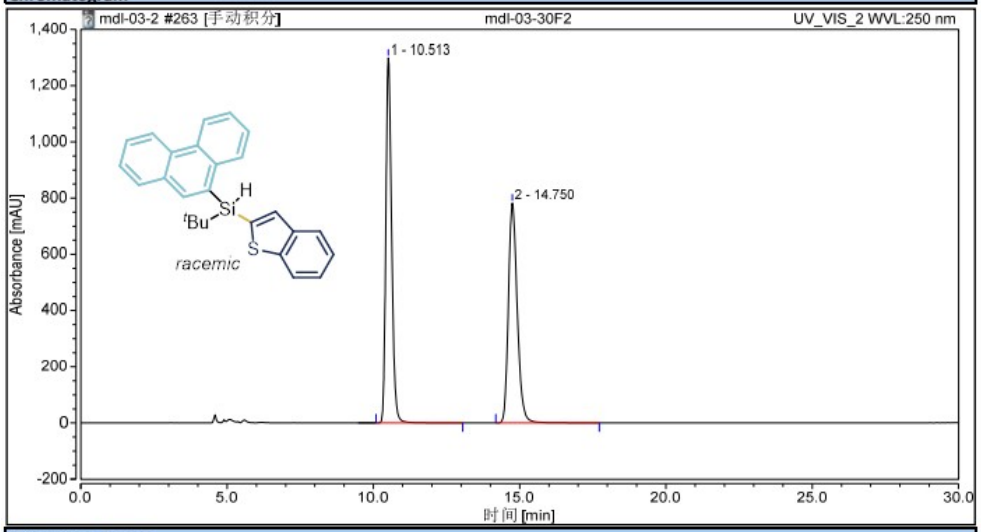
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		17.067	3.978	11.530	4.40	5.75	n.a.
2		20.130	86.482	188.814	95.60	94.25	n.a.
Total:			**90.459**	**200.344**	**100.00**	**100.00**	



3ma

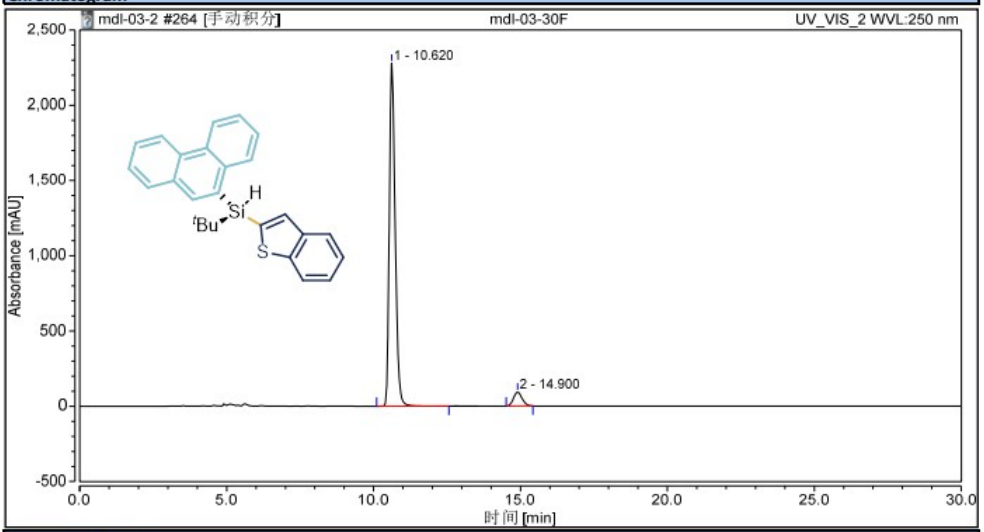
Chromatogram



Integration Results

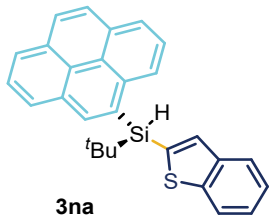
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.513	295.918	1298.139	51.93	62.39	n.a.
2		14.750	273.943	782.545	48.07	37.61	n.a.
Total:			**569.862**	**2080.684**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.620	527.714	2279.386	94.35	96.09	n.a.
2		14.900	31.608	92.793	5.65	3.91	n.a.
Total:			**559.323**	**2372.178**	**100.00**	**100.00**	



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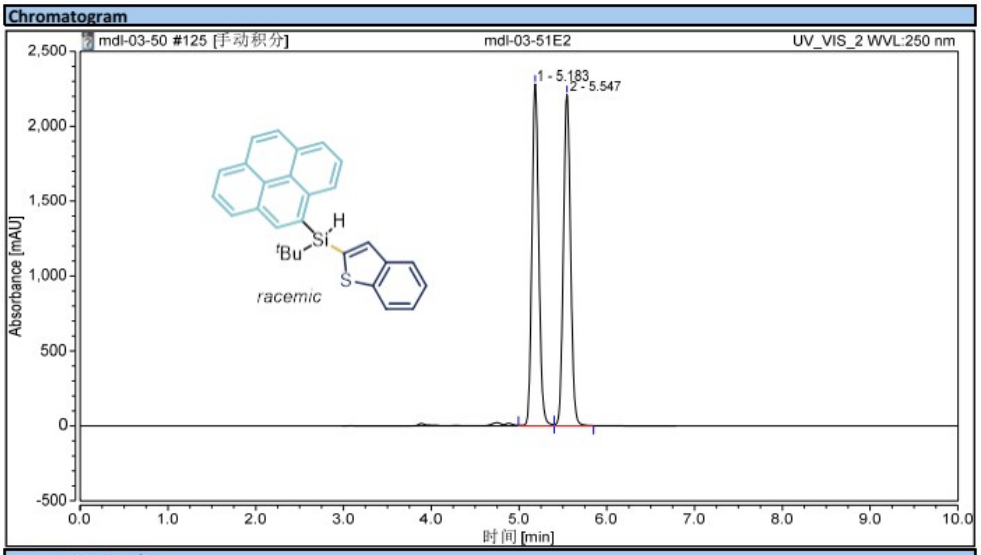
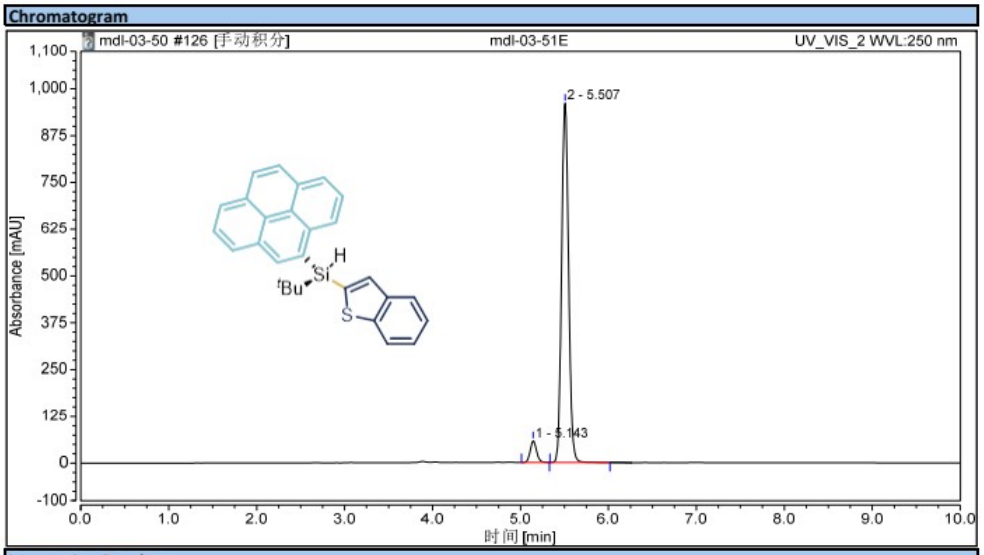


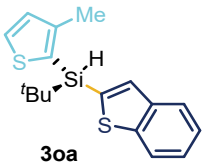
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.183	205.944	2282.427	49.58	50.78	n.a.
2		5.547	209.414	2212.098	50.42	49.22	n.a.
Total:			**415.359**	**4494.526**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.143	4.872	58.412	5.22	5.73	n.a.
2		5.507	88.398	960.274	94.78	94.27	n.a.
Total:			**93.270**	**1018.686**	**100.00**	**100.00**	



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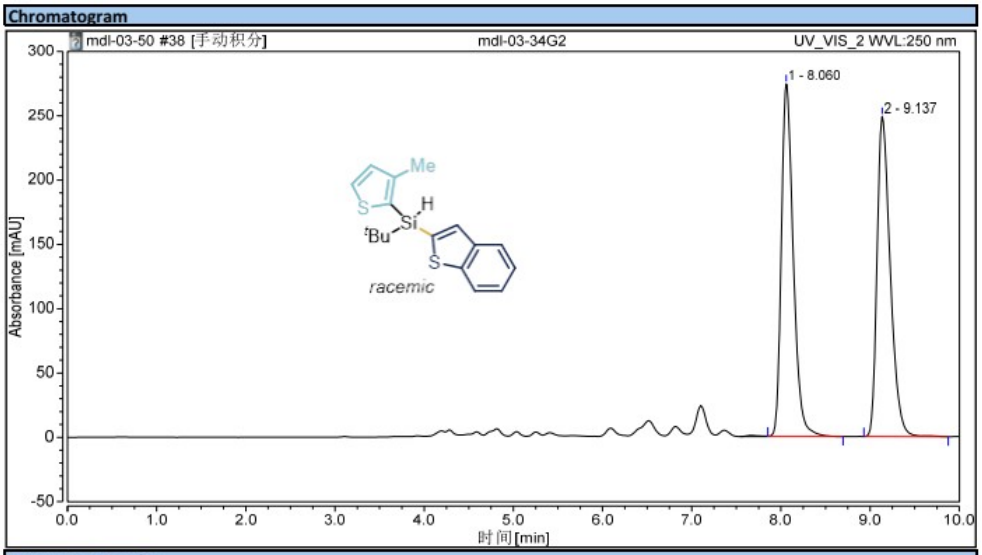
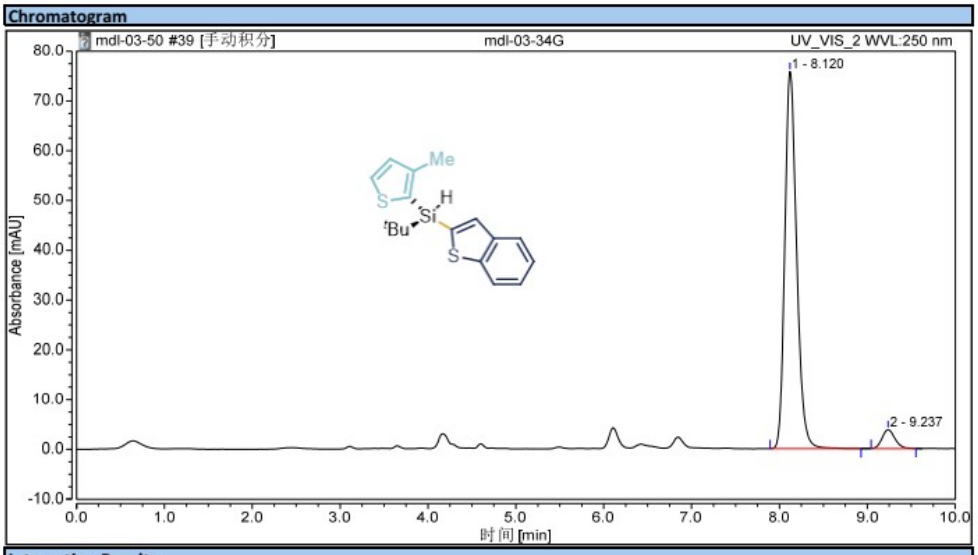


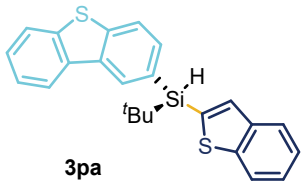
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.060	42.492	274.305	49.88	52.42	n.a.
2		9.137	42.697	248.938	50.12	47.58	n.a.
Total:			**85.189**	**523.242**	**100.00**	**100.00**	



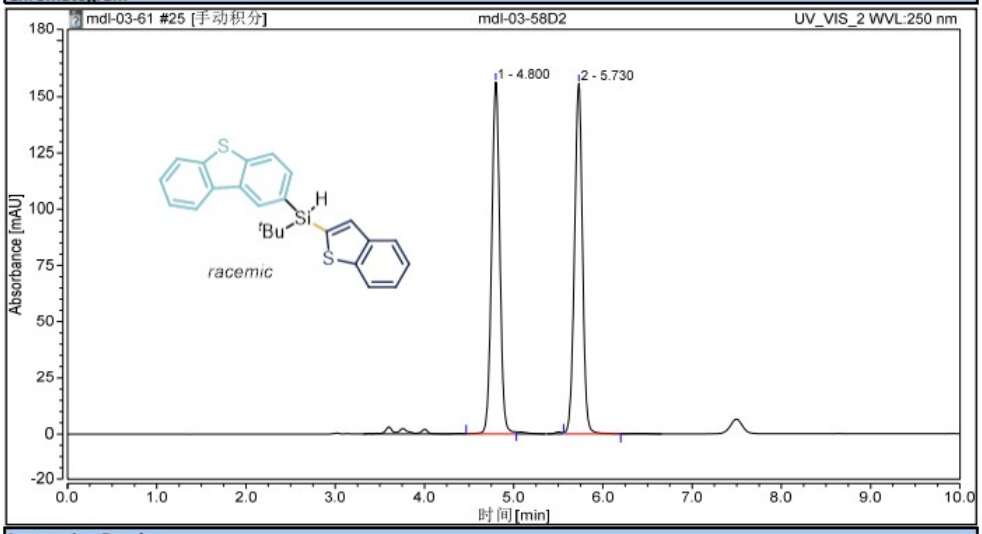
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.120	11.761	75.766	94.80	95.22	n.a.
2		9.237	0.645	3.806	5.20	4.78	n.a.
Total:			**12.406**	**79.571**	**100.00**	**100.00**	



3pa

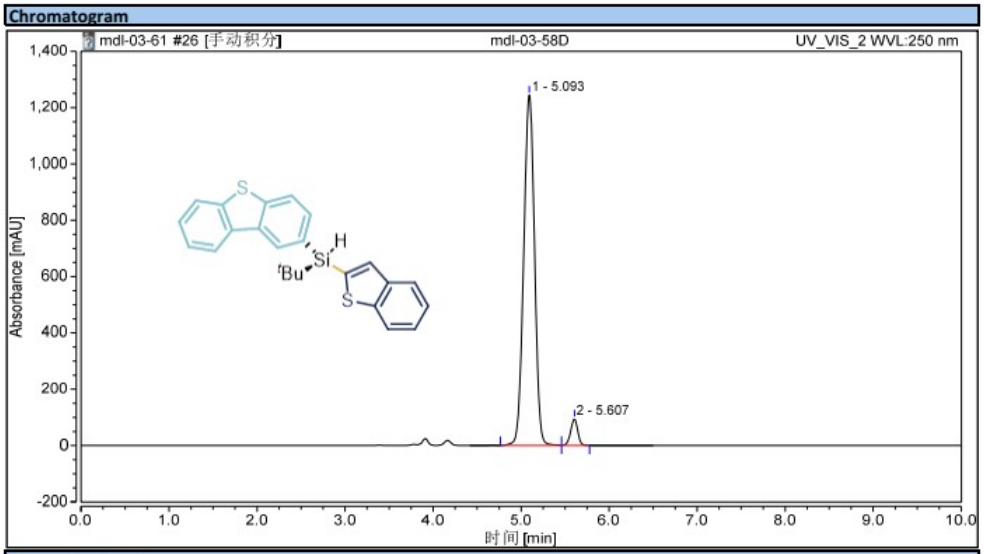
Chromatogram



Integration Results

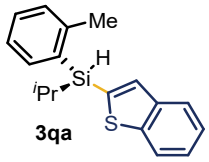
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		4.800	16.481	156.536	50.39	50.11	n.a.
2		5.730	16.227	155.855	49.61	49.89	n.a.
Total:			**32.707**	**312.390**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.093	176.851	1245.532	95.24	92.94	n.a.
2		5.607	8.846	94.572	4.76	7.06	n.a.
Total:			**185.697**	**1340.104**	**100.00**	**100.00**	



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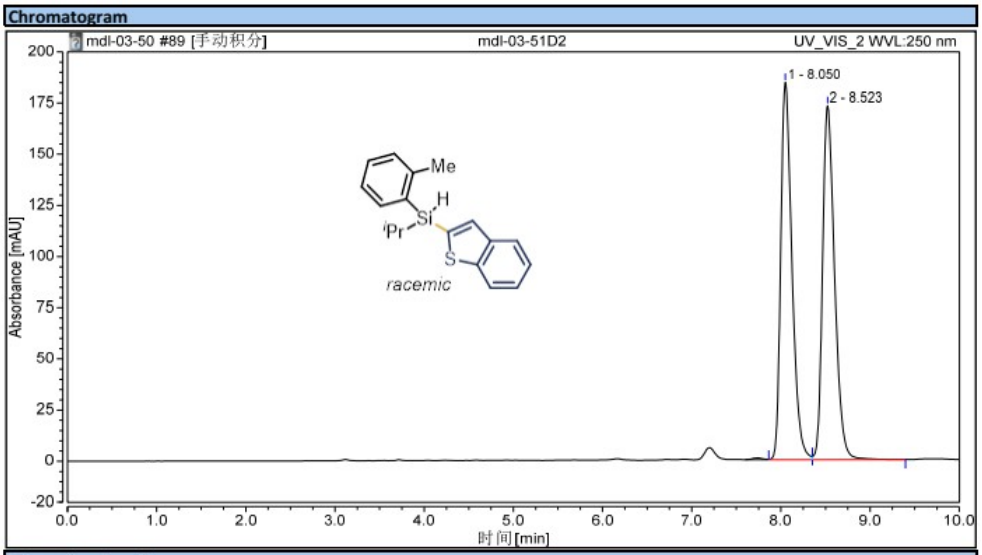
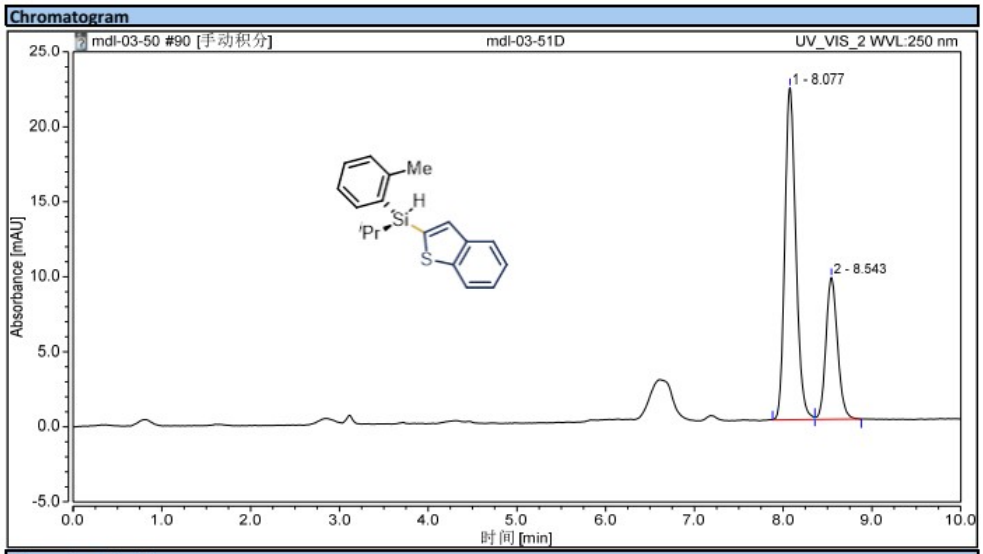


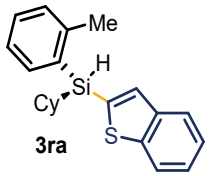
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.050	26.772	184.350	49.75	51.60	n.a.
2		8.523	27.039	172.933	50.25	48.40	n.a.
Total:			**53.811**	**357.283**	**100.00**	**100.00**	



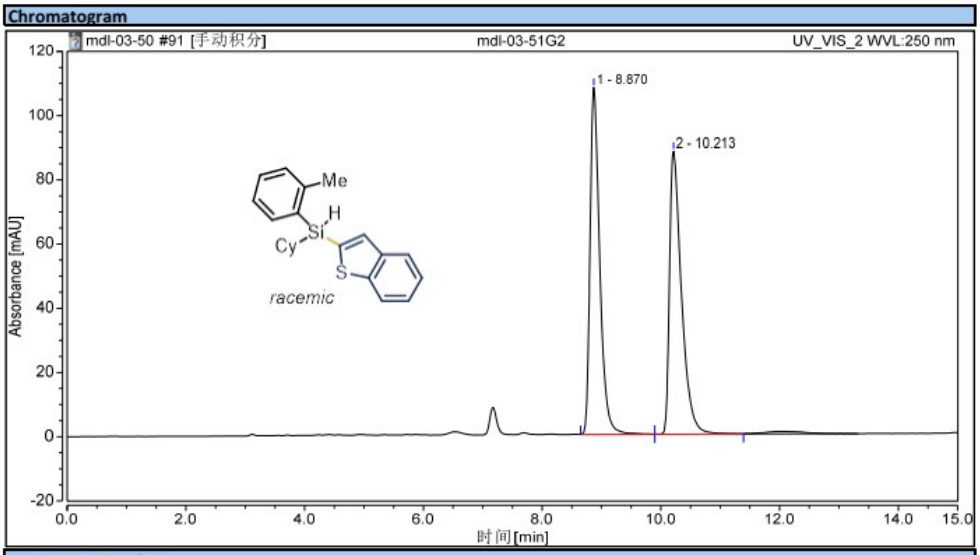
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.077	3.188	22.153	68.88	70.06	n.a.
2		8.543	1.440	9.469	31.12	29.94	n.a.
Total:			**4.628**	**31.622**	**100.00**	**100.00**	



3ra

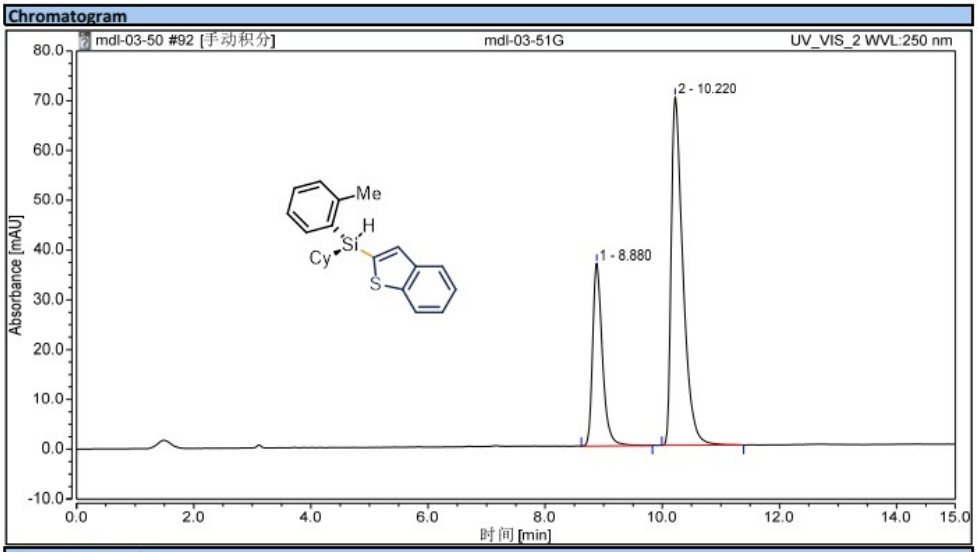
Chromatogram



Integration Results

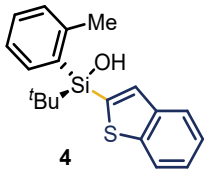
No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.870	20.457	108.096	49.84	55.09	n.a.
2		10.213	20.584	88.130	50.16	44.91	n.a.
Total:			**41.041**	**196.226**	**100.00**	**100.00**	

Chromatogram



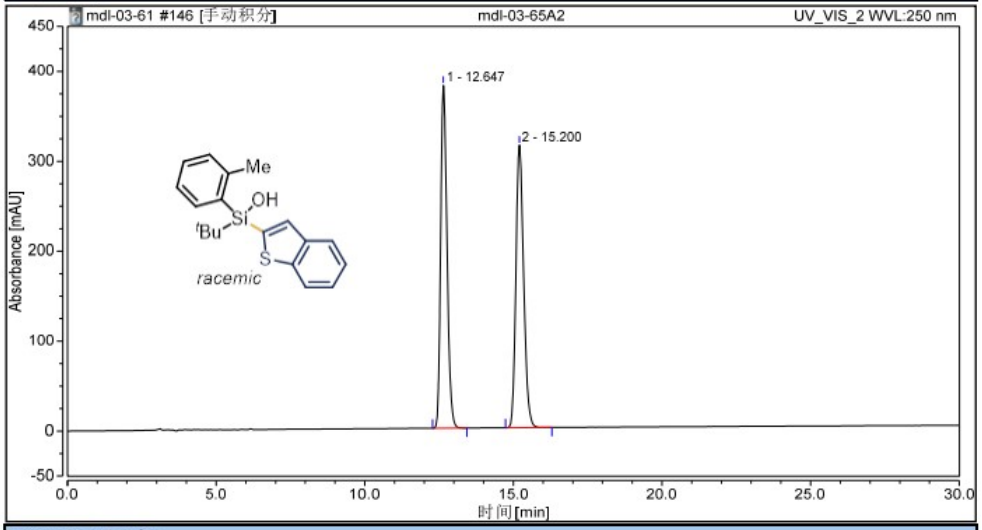
Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.880	7.096	36.726	30.43	34.42	n.a.
2		10.220	16.224	69.969	69.57	65.58	n.a.
Total:			**23.320**	**106.695**	**100.00**	**100.00**	



4

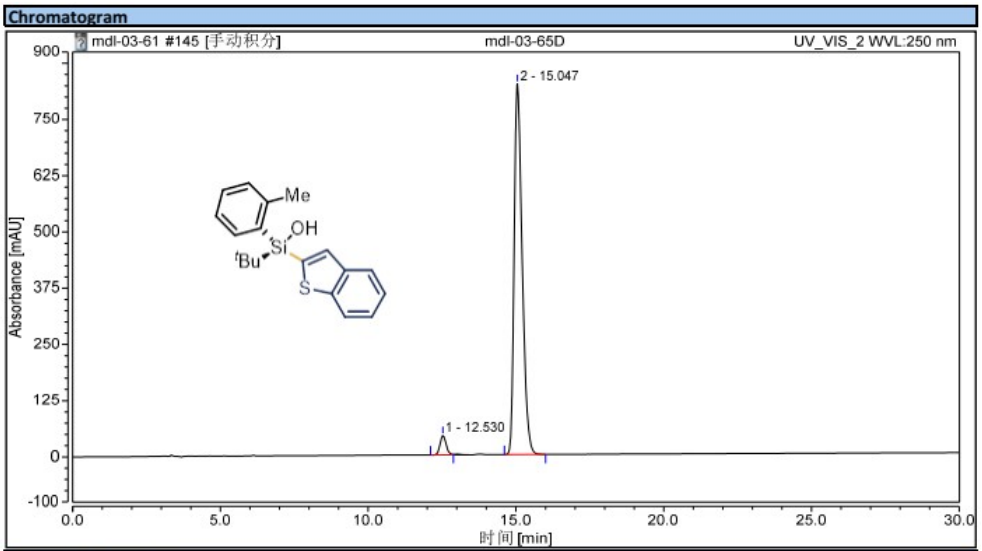
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.647	94.269	381.334	49.85	54.83	n.a.
2		15.200	94.830	314.178	50.15	45.17	n.a.
Total:			**189.099**	**695.513**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAu*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.530	10.262	43.205	3.82	4.98	n.a.
2		15.047	258.696	824.454	96.18	95.02	n.a.
Total:			**268.957**	**867.659**	**100.00**	**100.00**	