

Supporting Information

Cu/Chiral Phosphoric Acid-Catalyzed Radical-Initiated Asymmetric Aminosilylation of Alkene with Hydrosilane

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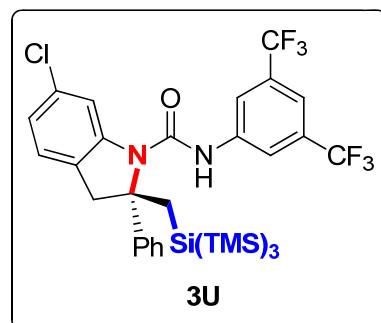
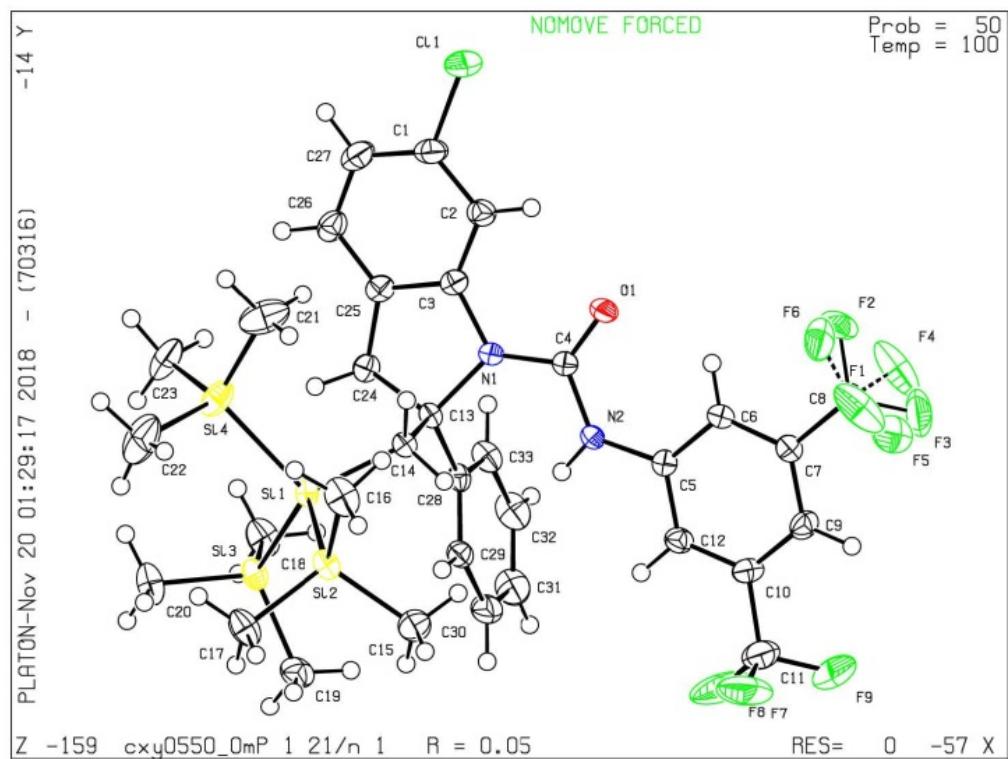
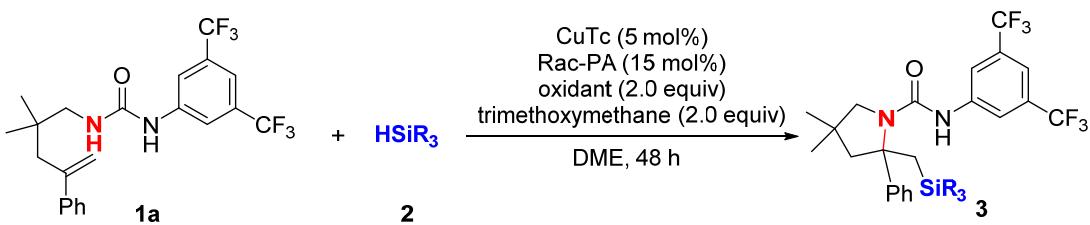


Figure S1. X-ray of chiral compound **3U**

Table S1. Screening of Reaction Conditions for Other Hydrosilanes^{a)}



Entry	Hydrosilane	Oxidant	T (°C)	Result
1	Et ₃ SiH	LPO	RT	No conv. of 1a
2	Ph ₃ SiH	LPO	RT	No conv. of 1a
3	Ph ₂ MeSiH	LPO	RT	No conv. of 1a
4	Et ₃ SiH	DTBP	RT	No conv. of 1a
5	Et ₃ SiH	DCP	RT	No conv. of 1a
6	Et ₃ SiH	TBHP	RT	No conv. of 1a
7	Et ₃ SiH	DTBP	80	Almost no conv. of 1a
8	Et ₃ SiH	DCP	80	Almost no conv. of 1a
9	Et ₃ SiH	TBHP	80	Almost no conv. of 1a
10	Ph ₃ SiH	DTBP	RT	No conv. of 1a
11	Ph ₃ SiH	DCP	RT	No conv. of 1a
12	Ph ₃ SiH	TBHP	RT	No conv. of 1a
13	Ph ₃ SiH	DTBP	80	Almost no conv. of 1a
14	Ph ₃ SiH	DCP	80	Almost no conv. of 1a
15	Ph ₃ SiH	TBHP	80	Almost no conv. of 1a

a) Reaction conditions: **1a** (0.025 mmol), **2** (2 equiv), CuTc (5 mol %), Rac-PA (15 mol %), oxidant (2.0 equiv), trimethoxymethane (2.0 equiv), DME (0.5 mL), 48 h under argon.

Table S2. Screening of Reaction Conditions for the Construction of Indoline^{a)}

1p + (TMS)₃Si-H → CuTc (5 mol%)
 CPA (15 mol%)
 LPO (2.0 equiv)
 DME, 0 °C, 96 h
 additive (1.0 equiv) → 3P

Entry	CPA	Additive	ee (%) ^{b)}
1	(R)-A1	-	70
2	(R)-A2	-	36
3	(R)-A3	-	64
4	(R)-A4	-	42
5	(R)-A5	-	62
6	(R)-A6	-	63
7	(R)-A7	-	3
8	(R)-A1	-	73
9 ^{c)}	(R)-A1	5Å MS	74
10	(R)-A1	methylparaben	87
11	(R)-A1	pivalic anhydride	82
12	(R)-A1	4-(<i>tert</i> -butyl)phenol	80

a) Reaction conditions: **1p** (0.025 mmol), **2** (2 equiv), CuTc (5 mol %), CPA (15 mol %), LPO (2.0 equiv), DME (0.5 mL), Additive (1.0 equiv), 0 °C, 96 h under argon. b) ee value based on HPLC analysis. c) 5Å MS (25 mg). DME, 1,2-dimethoxyethane; LPO, dilauroyl peroxide; CuTc, copper (I) thiophene-2-carboxylate; 5Å MS, 5Å molecular sieves.

General Information

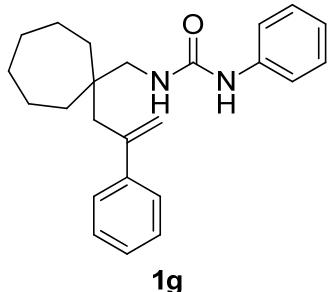
All reactions were carried out under argon using Schlenk techniques. Reagents were purchased at the commercial quality and used without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm), KMnO₄ or iodine stain. NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR and 376 MHz for ¹⁹F NMR in CDCl₃ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). Mass spectrometric data are obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector ($\lambda = 320, 254, 230$ or 214 nm). Column conditions are reported in the experimental section below. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu-K α radiation.

Procedures for synthesis of substrates

Procedures for synthesis of substrates 1a-1o.

The preparation and characterization data of substrates **1a-1f**, **1j-1l** are the same as that reported in literature[1-3].

1-phenyl-3-((1-(2-phenylallyl)cycloheptyl)methyl)urea (**1g**)



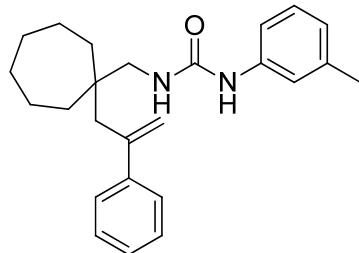
1g

¹H NMR (400 MHz, CDCl₃) δ 7.33 (t, *J* = 7.9 Hz, 2H), 7.26-7.19 (m, 7H), 7.12 (t, *J* = 7.3 Hz, 1H), 6.23 (s, 1H), 5.17 (d, *J* = 1.8 Hz, 1H), 5.00 (d, *J* = 1.4 Hz, 1H), 4.54 (t, *J* = 6.1 Hz, 1H), 2.92 (d, *J* = 6.3 Hz, 2H), 2.42 (s, 2H), 1.52-1.22 (m, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 156.1, 146.8, 143.7, 138.6, 129.4, 128.6, 127.4, 126.4, 124.2, 121.8, 117.8, 47.3, 43.7, 41.6, 36.3, 31.2, 22.7.

HRMS (ESI) m/z calcd. for C₂₄H₃₁N₂O [M + H]⁺ 363.2431, found 363.2430

1-((1-(2-phenylallyl)cycloheptyl)methyl)-3-(m-tolyl)urea (**1h**)



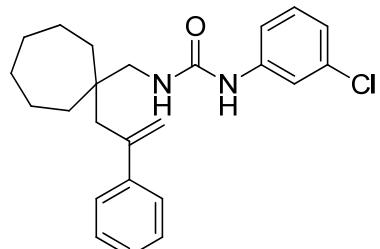
1h

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.14 (m, 6H), 7.10 (s, 1H), 7.02 (d, *J* = 6.1 Hz, 1H), 6.93 (d, *J* = 6.1 Hz, 1H), 6.44 (s, 1H), 5.16 (s, 1H), 5.00 (s, 1H), 4.74 (s, 1H), 2.93 (d, *J* = 4.5 Hz, 2H), 2.42 (s, 2H), 2.33 (s, 3H), 1.51-1.20 (m, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 156.3, 146.9, 143.6, 139.3, 138.5, 129.2, 128.5, 127.4, 126.4, 124.9, 122.4, 118.8, 117.7, 47.3, 43.7, 41.6, 36.3, 31.2, 22.7, 21.5.

HRMS (ESI) m/z calcd. for C₂₅H₃₃N₂O [M + H]⁺ 377.2587, found 377.2586.

1-(3-chlorophenyl)-3-((1-(2-phenylallyl)cycloheptyl)methyl)urea (**1i**)



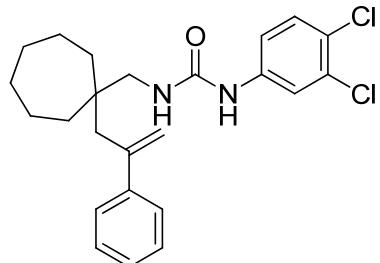
1i

¹H NMR (400 MHz, CDCl₃) δ 7.36-7.21 (m, 6H), 7.20-7.09 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.76 (s, 1H), 5.20 (s, 1H), 5.03 (s, 1H), 4.81 (s, 1H), 2.93 (d, *J* = 6.0 Hz, 2H), 2.43 (s, 2H), 1.49-1.19 (m, 12H).

¹³C NMR (100 MHz, CDCl₃) δ 155.8, 146.6, 143.7, 140.2, 134.8, 130.1, 128.6, 127.5, 126.5, 123.3, 120.3, 118.2, 117.9, 47.5, 43.6, 41.4, 36.3, 31.1, 22.7.

HRMS (ESI) m/z calcd. for C₂₄H₃₀ClN₂O [M + H]⁺ 397.2041, found 397.2039.

1-(3,4-dichlorophenyl)-3-((1-(2-phenylallyl)cycloheptyl)methyl)urea (**1m**)



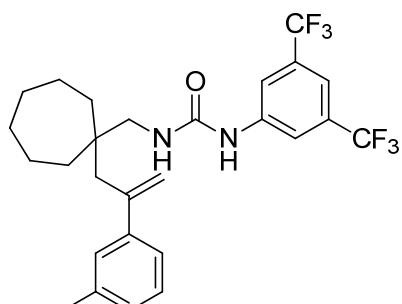
1m

¹H NMR (400 MHz, CDCl₃) δ 7.44 (s, 1H), 7.39-7.28 (m, 6H), 7.07 (d, *J* = 8.2 Hz, 1H), 5.76 (s, 1H), 5.25 (s, 1H), 5.07 (s, 1H), 4.09 (s, 1H), 2.88 (s, 2H), 2.46 (s, 2H), 1.51-1.17 (m, 12H).

¹³C NMR (100 MHz, DMSO) δ 155.0, 146.3, 143.1, 140.8, 131.0, 130.5, 128.3, 127.2, 126.2, 122.1, 118.5, 117.5, 117.4, 46.6, 42.6, 40.9, 35.7, 30.6, 22.4.

HRMS (ESI) m/z calcd. for C₂₄H₂₉Cl₂N₂O [M + H]⁺ 431.1651, found 431.1650.

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1-(2-(m-tolyl)allyl)cycloheptyl)methyl)urea (**1n**)



1n

¹H NMR (400 MHz, CDCl₃) δ 7.72 (s, 2H), 7.45 (s, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.21-7.16 (m, 2H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.38 (s, 1H), 5.25 (d, *J* = 1.7 Hz, 1H),

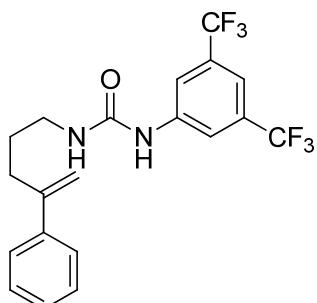
5.06 (d, $J = 1.4$ Hz, 1H), 4.42 (t, $J = 6.1$ Hz, 1H), 2.92 (d, $J = 6.2$ Hz, 2H), 2.46 (s, 2H), 2.34 (s, 3H), 1.50-1.35 (m, 10H), 1.34-1.24 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.7, 146.5, 143.8, 140.5, 138.6, 132.3 (q, $J = 33.3$ Hz), 128.5, 128.5, 127.5, 123.5, 123.2 (q, $J = 272.7$ Hz), 118.5 (d, $J = 3.2$ Hz), 118.1, 116.0-115.7, 47.5, 43.8, 41.4, 36.3, 31.1, 22.6, 21.6.

^{19}F NMR (376 MHz, CDCl_3) δ -63.01 (s, 6F).

HRMS (ESI) m/z calcd. for $\text{C}_{27}\text{H}_{31}\text{F}_6\text{N}_2\text{O} [\text{M} + \text{H}]^+$ 513.2335, found 513.2334.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-phenylpent-4-en-1-yl)urea (1o)



1o

^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 2H), 7.45 (s, 1H), 7.38 – 7.32 (m, 2H), 7.33-7.28 (m, 2H), 7.28-7.25 (m, 1H), 7.08 (s, 1H), 5.28 (s, 1H), 5.07 (d, $J = 5.7$ Hz, 1H), 5.05 (d, $J = 1.0$ Hz, 1H), 3.26 (dd, $J = 13.1, 6.8$ Hz, 2H), 2.55 (t, $J = 7.3$ Hz, 2H), 1.75-1.63 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 147.3, 140.7, 140.4, 132.3 (q, $J = 33.2$ Hz), 128.5, 127.7, 126.1, 123.2 (q, $J = 272.8$ Hz), 118.7 (q, $J = 3.3$ Hz), 113.2, 40.1, 32.6, 28.3.

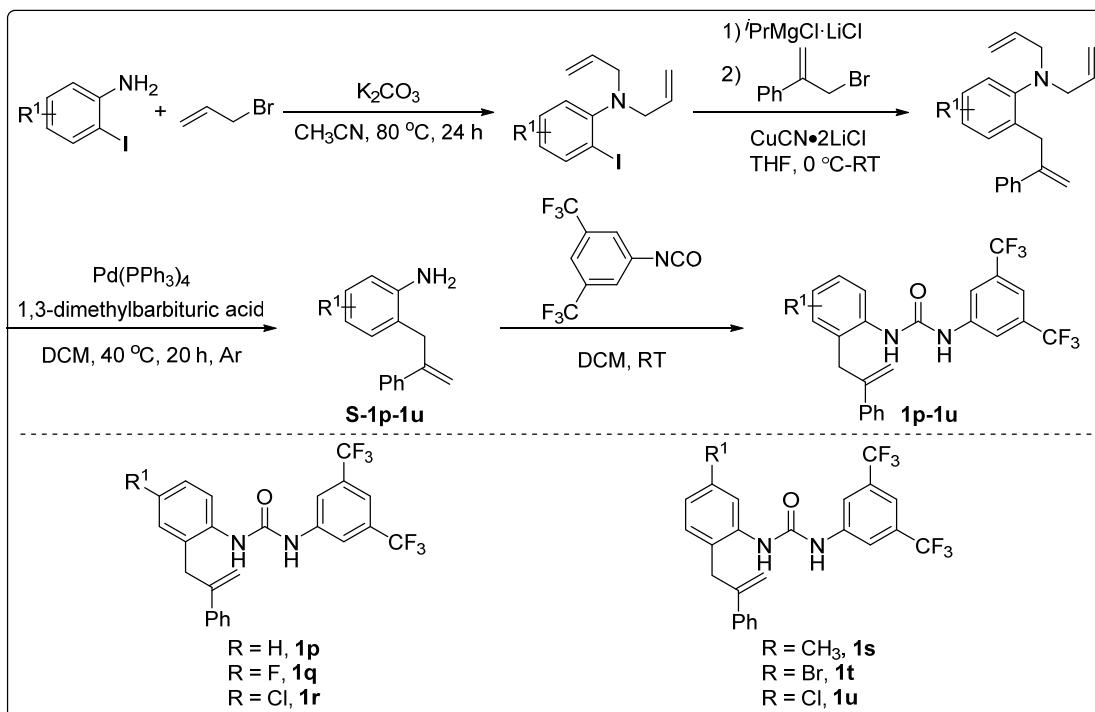
^{19}F NMR (376 MHz, CDCl_3) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_6\text{N}_2\text{O} [\text{M} + \text{H}]^+$ 417.1396, found 417.1393.

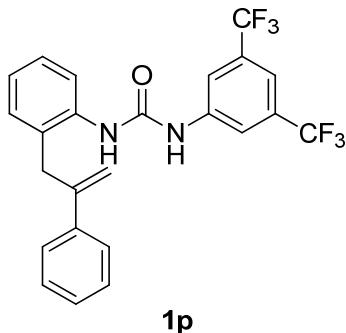
Procedures for synthesis of substrates 1p-1u.

S-1p-1u were synthesized according to the procedures [3].

1p-1u were synthesized according to the procedures [2].



1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2-phenylallyl)phenyl)urea (**1p**)



1p

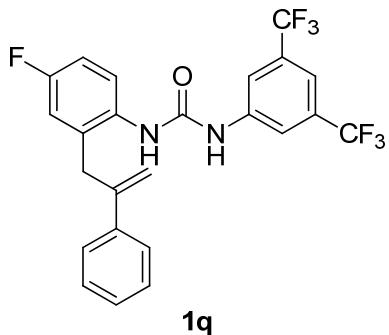
¹H NMR (400 MHz, CDCl₃) δ 7.73 (s, 2H), 7.47 (d, *J* = 10.0 Hz, 2H), 7.39 (d, *J* = 6.5 Hz, 2H), 7.34-7.19 (m, 6H), 6.89 (s, 1H), 6.54 (s, 1H), 5.43 (s, 1H), 4.84 (s, 1H), 3.80 (s, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 153.2, 146.1, 140.4, 139.8, 134.9, 134.2, 132.2 (q, *J* = 33.3 Hz), 131.7, 128.6, 128.2, 128.1, 127.2, 126.2, 126.0, 123.2 (q, *J* = 272.6 Hz), 119.0 (d, *J* = 3.0 Hz), 116.7-116.4 (m), 114.5, 37.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₄H₁₉F₆N₂O [M + H]⁺ 465.1396, found 465.1393.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-fluoro-2-(2-phenylallyl)phenyl)urea (**1q**)



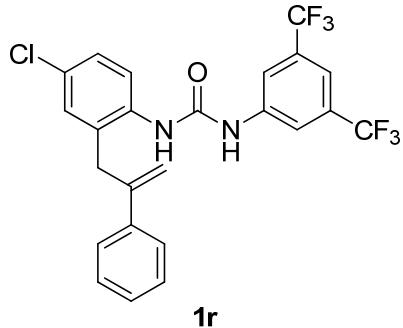
¹H NMR (400 MHz, DMSO) δ 9.60 (s, 1H), 8.24 (s, 1H), 8.12 (s, 2H), 7.64-7.55 (m, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.38-7.23 (m, 3H), 7.04 (td, *J* = 8.5, 3.0 Hz, 1H), 6.96 (dd, *J* = 9.8, 2.9 Hz, 1H), 5.59 (s, 1H), 4.97 (s, 1H), 3.84 (s, 2H).

¹³C NMR (100 MHz, DMSO) δ 159.1 (d, *J* = 241.1 Hz), 153.1, 144.5, 142.0, 139.5, 135.2 (d, *J* = 7.6 Hz), 132.6 (d, *J* = 2.6 Hz), 130.7 (q, *J* = 32.5 Hz), 128.4, 127.8, 126.7 (d, *J* = 8.3 Hz), 125.8, 123.3 (q, *J* = 272.7 Hz), 117.8 (d, *J* = 3.2 Hz), 115.8 (d, *J* = 22.7 Hz), 114.7, 114.4-114.0 (m), 113.2 (d, *J* = 22.1 Hz), 36.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -61.7 (s, 6F), -118.1 (s, 1F).

HRMS (ESI) m/z calcd. for C₂₄H₁₈F₇N₂O [M + H]⁺ 483.1302, found 483.1298.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-chloro-2-(2-phenylallyl)phenyl)urea (1r)



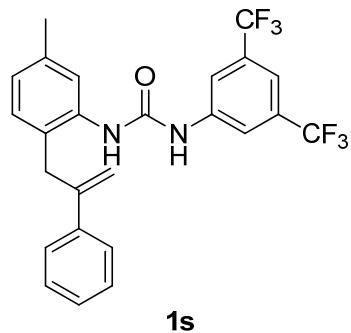
¹H NMR (400 MHz, CDCl₃) δ 7.81 (s, 2H), 7.53 (s, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.43 (dt, *J* = 8.5, 2.3 Hz, 2H), 7.38-7.28 (m, 5H), 6.44 (s, 1H), 6.21 (s, 1H), 5.50 (s, 1H), 4.93 (s, 1H), 3.81 (s, 2H).

¹³C NMR (100 MHz, DMSO) δ 152.8, 144.4, 141.8, 139.5, 135.5, 133.7, 130.8 (q, *J* = 32.3 Hz), 129.2, 128.4, 128.1, 127.9, 126.6, 125.8, 125.4, 123.3 (q, *J* = 272.7 Hz), 117.9 (d, *J* = 3.1 Hz), 114.7, 114.6-114.3 (m), 35.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₄H₁₈ClF₆N₂O [M + H]⁺ 499.1006, found 499.1002.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(5-methyl-2-(2-phenylallyl)phenyl)urea (1s)



1s

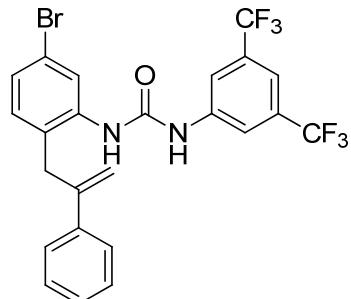
¹H NMR (400 MHz, CDCl₃) δ 7.79 (s, 2H), 7.51 (s, 1H), 7.44-7.38 (m, 2H), 7.32-7.26 (m, 4H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.08 (dd, *J* = 7.8, 0.7 Hz, 1H), 6.53 (s, 1H), 6.24 (s, 1H), 5.43 (d, *J* = 0.7 Hz, 1H), 4.90 (d, *J* = 1.0 Hz, 1H), 3.81 (s, 2H), 2.36 (s, 3H).

¹³C NMR (100 MHz, DMSO) δ 152.9, 145.2, 142.0, 139.9, 136.1, 135.8, 130.8 (q, *J* = 32.7 Hz), 129.6, 128.3, 128.2, 127.7, 125.8, 125.0, 124.7, 124.4, 123.4 (q, *J* = 272.7 Hz), 117.7 (q, *J* = 3.3 Hz), 114.1, 35.7, 20.8.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₅H₂₁F₆N₂O [M + H]⁺ 479.1553, found 479.1552.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(5-bromo-2-(2-phenylallyl)phenyl)urea (**1t**)



1t

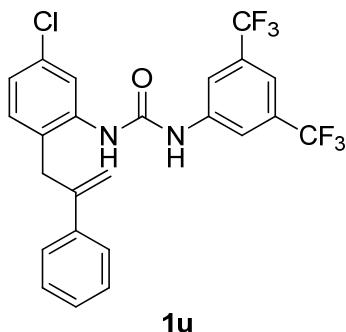
¹H NMR (400 MHz, CDCl₃) δ 7.86-7.78 (m, 3H), 7.53 (s, 1H), 7.43 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.38-7.29 (m, 4H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.57 (s, 1H), 6.35 (s, 1H), 5.49 (s, 1H), 4.91 (s, 1H), 3.78 (s, 2H).

¹³C NMR (100 MHz, DMSO) δ 152.6, 144.4, 141.7, 139.5, 138.1, 131.6, 131.0, 130.6, 129.8, 128.4, 127.8, 126.5, 125.8, 125.2, 123.3 (q, *J* = 272.7 Hz), 119.1, 118.0 (d, *J* = 2.4 Hz), 114.5, 35.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₄H₁₈BrF₆N₂O [M + H]⁺ 543.0501, found 543.0501.

1-(3,5-bis(trifluoromethyl)phenyl)-3-(5-chloro-2-(2-phenylallyl)phenyl)urea (**1u**)



1u

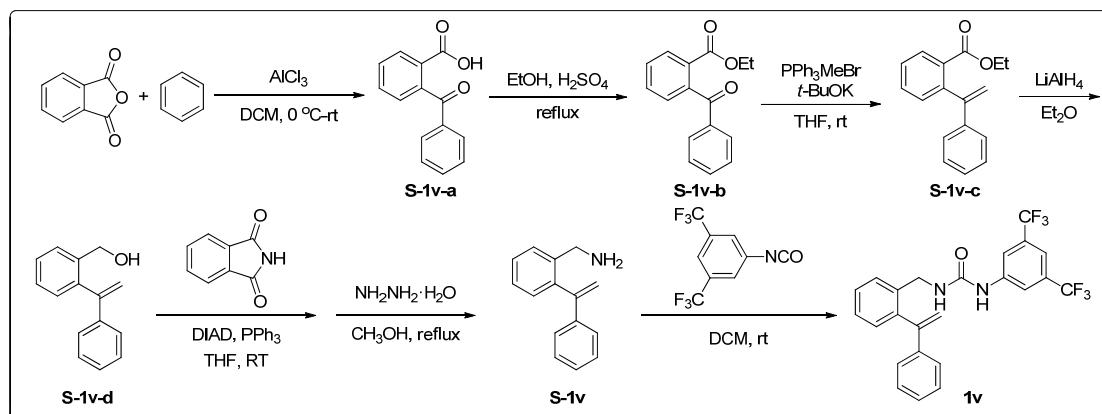
¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 2H), 7.72 (s, 1H), 7.51 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.37-7.30 (m, 3H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.93 (s, 1H), 6.51 (s, 1H), 5.49 (s, 1H), 4.87 (s, 1H), 3.77 (s, 2H).

¹³C NMR (100 MHz, DMSO) δ 152.6, 144.5, 141.7, 139.5, 137.9, 131.3, 131.0, 130.8, 130.6, 129.2, 128.4, 127.8, 125.8, 123.6, 123.3 (q, *J* = 272.7 Hz), 122.3, 118.0 (d, *J* = 2.4 Hz), 114.5, 35.4.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₄H₁₈ClF₆N₂O [M + H]⁺ 499.1006, found 499.1008.

Procedure for synthesis of substrate **1v**.



In a flame-dried flask, benzene (3.51 g, 45 mmol) was added to the solution of isobenzofuran-1,3-dione (4.44 g, 30 mmol) and AlCl₃ (8.00 g, 60 mmol) in anhydrous DCM (60 mL) at 0 °C. The mixture was allowed to stir at room temperature for 12 h, then quenched by addition of ice water at 0 °C, and extracted with DCM (3 × 100 mL). The combined organic extracts were washed with brine (50 mL), dried over Na₂SO₄, filtered and concentrated *in vacuo* to afford the crude product **S-1v-a**, which was used for next step without further purification. Concentrated sulfuric acid (5 mL) was added to the solution of **S-1v-a** in EtOH (30 mL) and the mixture was stirred at reflux for 12 h. The resulting solution was concentrated *in vacuo* and purified by flash column chromatography to give **S-1v-b** (6.33 g, 83% yield over two steps).

In a flame-dried flask, *t*-BuOK (4.21 g, 37.5 mmol) was added to the solution of PPh₃MeBr (13.40 g, 37.5 mmol) in anhydrous THF (50 mL) and the mixture was stirred at room temperature for 2 h, and compound **S-1v-b** (6.33 g, 25 mmol) in THF

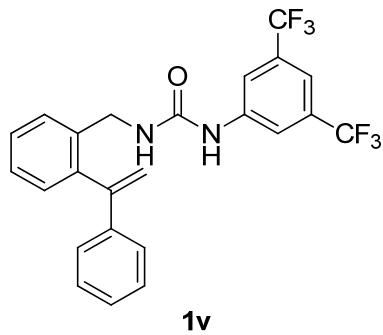
(20 mL) was slowly added. The resulting mixture was stirred overnight, then acidified with saturated aqueous NH₄Cl (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic extracts were dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give **S-1v-c** (3.91 g, 62% yield).

In a flame-dried flask, LiAlH₄ (1.18 g, 31 mmol) was slowly added to the solution of **S-1v-c** (3.91 g, 15.5 mmol) in anhydrous Et₂O (100 mL) at 0 °C and the resulting mixture was allowed to stir at room temperature for 1 h. The resulting mixture was quenched by saturated aqueous NH₄Cl (50 mL) and extracted with EtOAc (3 × 100 mL). The combined organic extracts were dried over Na₂SO₄, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give **S-1v-d** (2.93 g, 90% yield).

In a flame-dried flask, isoindoline-1,3-dione (2.05 g, 13.9 mmol), DIAD (3.11 g, 15.35 mmol) and PPh₃ (4.03 g, 15.35 mmol) were added to the solution of **S-1v-d** (2.93 g, 13.95 mmol) in anhydrous THF (30 mL) and the resulting mixture was allowed to stir at room temperature for 12 h. The resulting mixture was concentrated *in vacuo*. To a solution of crude product in MeOH (30 mL) was added NH₂NH₂•H₂O (1.40 g, 27.9 mmol) and the resulting mixture was stirred at reflux for 12 h. The resulting mixture was concentrated *in vacuo* and purified by flash column chromatography to give **S-1v** (1.98 g, 68% yield).

Substrate **1v** was synthesized according to the procedure [2].

1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(1-phenylvinyl)benzyl)urea (1v)



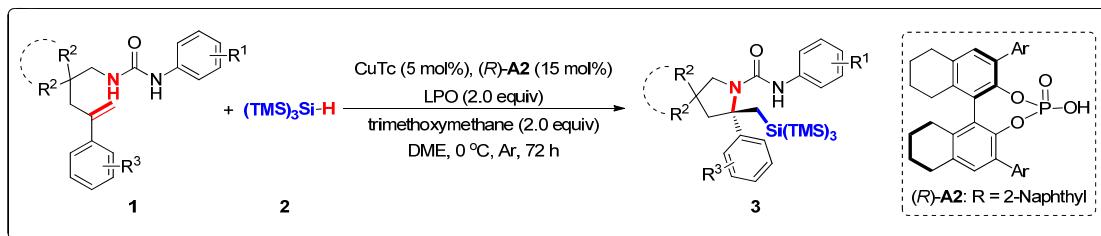
¹H NMR (400 MHz, DMSO) δ 9.34 (s, 1H), 8.05 (s, 2H), 7.53 (s, 1H), 7.42-7.24 (m, 8H), 7.18 (d, *J* = 7.2 Hz, 1H), 6.77 (t, *J* = 5.8 Hz, 1H), 5.91 (d, *J* = 0.9 Hz, 1H), 5.23 (d, *J* = 0.9 Hz, 1H), 4.06 (d, *J* = 5.8 Hz, 2H).

¹³C NMR (100 MHz, DMSO) δ 154.7, 147.5, 142.5, 140.0, 139.8, 137.2, 130.6 (q, *J* = 32.5 Hz), 129.7, 128.6, 128.3, 127.9, 127.8, 126.9, 126.2, 123.4 (q, *J* = 272.6 Hz), 117.3 (d, *J* = 2.7 Hz), 115.8, 113.8-113.4 (m), 40.7.

¹⁹F NMR (376 MHz, CDCl₃) δ -61.8 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₄H₁₉F₆N₂O [M + H]⁺ 465.1396, found 465.1395.

General procedure for 1,2-aminosilylation of alkenes for construction of pyrrolidine



General Procedure A

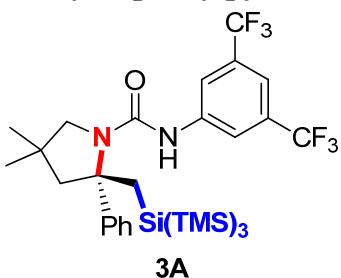
Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1** (0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid (*(R)*-**A2** (9.12 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), $(\text{TMS})_3\text{SiH}$ **2** (49.7 mg, 0.2 mmol, 2.0 equiv), trimethoxymethane (21.2 mg, 0.2 mmol, 2.0 equiv) and 1,2-dimethoxyethane (2.0 mL) at room temperature, and the sealed tube was then stirred at 0 °C for 72 h, the reaction mixture was directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 20/1, using dichloromethane (100%) to remove the solvent (1,2-dimethoxyethane) at first] to afford the desired product **3**.

General Procedure B

Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1** (0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid (*(R)*-**A2** (9.12 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), $(\text{TMS})_3\text{SiH}$ **2** (49.7 mg, 0.2 mmol, 2.0 equiv), trimethoxymethane (21.2 mg, 0.2 mmol, 2.0 equiv) and 1,2-dimethoxyethane (2.0 mL) at room temperature, and the sealed tube was then stirred at room temperature for 48 h, the reaction mixture was directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 20/1, using dichloromethane (100%) to remove the solvent (1,2-dimethoxyethane) at first] to afford the desired product **3**.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-4,4-dimethyl-2-phenylpyrrolidine-1-carboxamide (3A)



According to General Procedure A with **1a** (44.4 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3A** as a white solid (35.2 mg, 51% yield, 93% ee).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99.5/0.5, flow rate 0.18 mL/min, λ = 254 nm), t_R (minor) = 24.40 min, t_R (major) = 26.46 min.

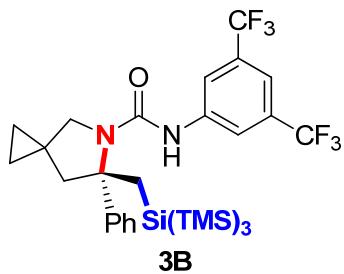
¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 2H), 7.40-7.55 (m, 5H), 7.30-7.39 (m, 1H), 6.41 (s, 1H), 3.64 (d, J = 10.4 Hz, 1H), 3.56 (d, J = 10.4 Hz, 1H), 2.37 (d, J = 13.2 Hz, 1H), 2.32 (d, J = 13.2 Hz, 1H), 2.17 (s, 1H), 1.99 (d, J = 14.8 Hz, 1H), 1.26 (s, 3H), 1.07 (s, 3H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.7, 146.6, 140.6, 132.1 (q, J = 33.2 Hz), 129.2, 127.9, 126.9, 123.3 (q, J = 272.6 Hz), 118.5 (d, J = 3.2 Hz), 115.8 (dt, J = 7.8, 3.8 Hz), 71.0, 60.9, 58.2, 35.6, 29.5, 29.2, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₁H₄₉F₆N₂OSi₄ [M + H]⁺ 691.2821, found 691.2819.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-6-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-6-phenyl-5-azaspiro[2.4]heptane-5-carboxamide (3B)



According to General Procedure A with **1b** (44.2 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3B** as a white solid (39.9 mg, 58% yield, 88% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 99.5/0.5, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 33.03 min, t_R (major) = 35.23 min.

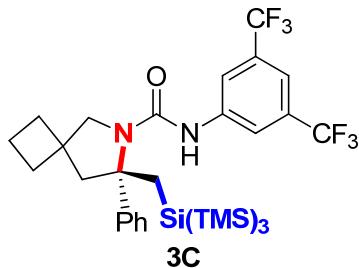
¹H NMR (400 MHz, CDCl₃) δ 7.67-7.31 (m, 8H), 6.29 (s, 1H), 3.94 (d, J = 10.4 Hz, 1H), 3.53 (d, J = 10.2 Hz, 1H), 2.77 (d, J = 12.7 Hz, 1H), 2.16 (d, J = 13.6 Hz, 1H), 1.87 (d, J = 12.6 Hz, 1H), 1.60 (s, 1H), 0.83-0.54 (m, 3H), 0.44 (s, 1H), 0.19 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.1, 146.4, 140.6, 132.1 (q, J = 33.2 Hz), 129.1, 128.1, 126.4, 123.2 (q, J = 272.6 Hz), 118.6, 115.8 (dt, J = 7.7, 3.8 Hz), 70.0, 56.0, 53.1, 20.8, 18.7, 16.7, 6.3, 1.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₁H₄₇F₆N₂OSi₄ [M + H]⁺ 689.2664, found 689.2655.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-7-((1,1,1,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-7-phenyl-6-azaspiro[3.4]octane-6-carboxamide (3C)



According to General Procedure A with **1c** (45.6 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3C** as a white solid (42.8 mg, 61% yield, 91% ee).

HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99.2/0.8, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 24.46 min, t_R (major) = 27.08 min.

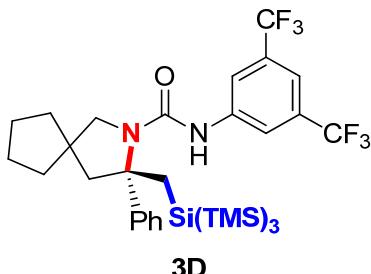
¹H NMR (400 MHz, CDCl₃) δ 7.83-7.28 (m, 8H), 6.36 (s, 1H), 4.07 (s, 1H), 3.66 (d, *J* = 10.5 Hz, 1H), 2.47 (d, *J* = 12.9 Hz, 1H), 2.42 (d, *J* = 12.9 Hz, 1H), 2.16-1.66 (m, 7H), 1.60 (s, 1H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.4, 146.2, 140.6, 132.1 (q, *J* = 33.2 Hz), 129.0, 127.8, 126.5, 123.3 (q, *J* = 272.7 Hz), 118.6, 115.8 (dt, *J* = 7.7, 3.8 Hz), 70.3, 60.1, 57.3, 42.3, 36.6, 30.7, 21.4, 16.4, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₂H₄₉F₆N₂OSi₄ [M + H]⁺ 703.2821, found 703.2804.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-3-((1,1,1,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.4]nonane-2-carboxamide (3D)



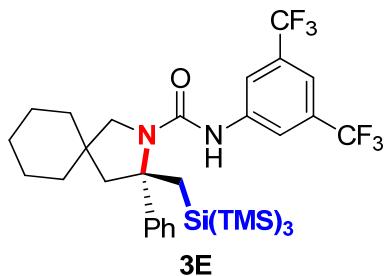
According to General Procedure A with **1d** (47.0 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3D** as a white solid (35.8 mg, 50% yield, 89% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/01, flow rate 0.20 mL/min, λ = 254 nm), t_R (minor) = 20.77 min, t_R (major) = 21.86 min.

¹H NMR (400 MHz, CDCl₃) δ 7.69 (s, 2H), 7.50-7.27 (m, 6H), 6.48 (s, 1H), 3.74 (d, *J* = 9.5 Hz, 1H), 3.56 (d, *J* = 10.3 Hz, 1H), 2.56 (d, *J* = 12.9 Hz, 1H), 2.37 (d, *J* = 12.9

Hz, 1H), 1.99 (d, J = 14.8 Hz, 1H), 1.83-1.48 (m, 8H), 1.23 (s, 1H), 0.20 (s, 27H).
¹³C NMR (100 MHz, CDCl₃) δ 153.6, 146.6, 140.7, 132.1 (q, J = 33.2 Hz), 129.1, 127.8, 126.8, 123.3 (q, J = 272.7 Hz), 118.5, 116.0-115.4 (m), 70.5, 60.0, 56.8, 46.6, 39.7, 39.2, 24.7, 24.2, 21.6, 1.5.
¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).
HRMS (ESI) m/z calcd. for C₃₃H₅₁F₆N₂OSi₄ [M + H]⁺ 717.2977, found 717.2962.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.5]decane-2-carboxamide (3E)



According to General Procedure A with **1e** (48.4 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3E** as a white solid (43.1 mg, 59% yield, 92% ee).

HPLC analysis: Chiralcel IC (hexane/i-PrOH = 99.5/0.5, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 28.65 min, t_R (major) = 30.19 min.

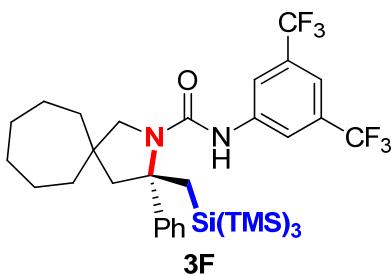
¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 2H), 7.50-7.38 (m, 5H), 7.37-7.29 (m, 1H), 6.44 (s, 1H), 3.76 (d, J = 10.0 Hz, 1H), 3.49 (d, J = 10.7 Hz, 1H), 2.44 (d, J = 13.3 Hz, 1H), 2.22 (d, J = 13.3 Hz, 1H), 1.96 (d, J = 14.7 Hz, 1H), 1.67-1.23 (m, 11H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.8, 146.7, 140.6, 132.1 (q, J = 33.2 Hz), 129.2, 127.9, 126.9, 123.3 (q, J = 272.6 Hz), 118.5, 115.8 (dt, J = 7.4, 3.6 Hz), 70.3, 58.4, 56.4, 39.4, 39.3, 36.8, 25.7, 24.2, 23.0, 21.9, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₄H₅₃F₆N₂OSi₄ [M + H]⁺ 731.3134, found 731.3116.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.6]undecane-2-carboxamide (3F)



According to General Procedure A with **1f** (49.8 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3F** as a white solid (55.1 mg, 74% yield, 96% ee).

HPLC analysis: Chiralcel IC (hexane/*i*-PrOH = 99.5/0.5, flow rate 0.20 mL/min, λ = 254 nm), t_R (minor) = 23.16 min, t_R (major) = 25.15 min.

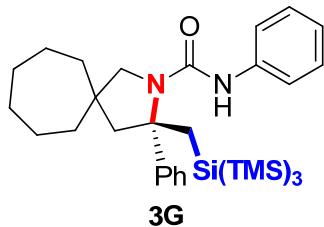
¹H NMR (400 MHz, CDCl₃) δ 7.63-7.48 (m, 4H), 7.43 (dd, J = 13.4, 5.1 Hz, 3H), 7.36 (t, J = 7.2 Hz, 1H), 6.34 (s, 1H), 3.71 (d, J = 10.6 Hz, 1H), 3.45 (d, J = 10.7 Hz, 1H), 2.45 (d, J = 13.3 Hz, 1H), 2.31 (d, J = 13.3 Hz, 1H), 1.97 (d, J = 14.6 Hz, 1H), 1.79-1.36 (m, 12H), 1.25 (s, 1H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.9, 146.6, 140.6, 132.1 (q, J = 33.2 Hz), 129.3, 128.1, 127.2, 123.3 (q, J = 272.7 Hz), 118.4 (d, J = 2.5 Hz), 116.9-115.4 (m), 70.6, 60.3, 58.3, 42.6, 41.9, 40.5, 29.8, 29.7, 29.2, 24.6, 23.4, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₅H₅₅F₆N₂OSi₄ [M + H]⁺ 745.3290, found 745.3276.

(S)-3-((1,1,1,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-N,3-diphenyl-2-azaspiro[4.6]undecane-2-carboxamide (3G)



According to General Procedure B with **1g** (36.2 mg, 0.1 mmol, 1.0 equiv), 48 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3G** as a white solid (54.1 mg, 89% yield, 74% ee).

HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 98/02, flow rate 0.70 mL/min, λ = 254 nm), t_R (minor) = 23.50 min, t_R (major) = 13.75 min.

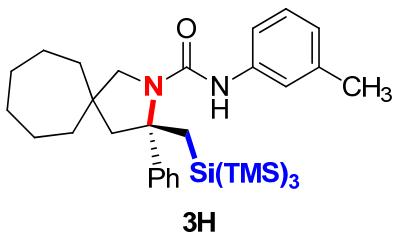
¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.7 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.18 (t, J = 7.7 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 6.93 (t, J = 7.2 Hz, 1H), 6.10 (s, 1H), 3.71 (d, J = 10.6 Hz, 1H), 3.45 (d, J = 10.6 Hz, 1H), 2.43 (d, J = 13.2 Hz, 1H), 2.29 (d, J = 13.2 Hz, 1H), 2.05 (s, 1H), 1.88-1.56 (m, 7H), 1.54-1.35 (m, 6H), 0.19 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 154.6, 147.0, 139.2, 128.9, 128.8, 127.5, 127.2, 122.5, 118.9, 70.0, 60.4, 58.4, 42.4, 42.0, 40.4, 29.7, 29.2, 24.6, 23.4, 21.1, 1.6.

HRMS (ESI) m/z calcd. for C₃₃H₅₇N₂OSi₄ [M + H]⁺ 609.3542, found 609.3533.

(S)-3-((1,1,1,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-N-(

m-tolyl)-2-azaspiro[4.6]undecane-2-carboxamide (3H)



According to General Procedure **B** with **1h** (37.6 mg, 0.1 mmol, 1.0 equiv), 48 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3H** as a white solid (51.0 mg, 82% yield, 71% ee).

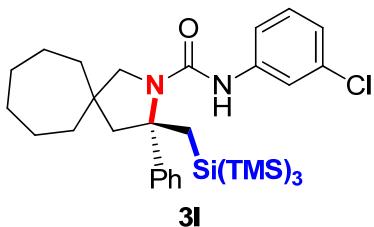
HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 98/02, flow rate 0.70 mL/min, λ = 254 nm), t_R (minor) = 17.50 min, t_R (major) = 12.05 min.

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.29 (dd, J = 14.8, 7.5 Hz, 1H), 7.07 (s, 1H), 7.04 (d, J = 7.8 Hz, 1H), 6.81 (d, J = 7.8 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.05 (s, 1H), 3.69 (d, J = 10.6 Hz, 1H), 3.44 (d, J = 10.6 Hz, 1H), 2.42 (d, J = 13.2 Hz, 1H), 2.28 (d, J = 13.3 Hz, 1H), 2.25 (s, 3H), 2.04 (s, 1H), 1.87-1.56 (m, 7H), 1.52-1.34 (m, 6H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 154.7, 147.1, 139.1, 138.6, 128.9, 128.6, 127.5, 127.2, 123.3, 119.7, 116.0, 70.0, 60.5, 58.4, 42.4, 42.0, 40.4, 29.7, 29.2, 24.7, 23.4, 21.6, 21.1, 1.6.

HRMS (ESI) m/z calcd. for C₃₄H₅₉N₂OSi₄ [M + H]⁺ 623.3699, found 623.3687.

(S)-N-(3-chlorophenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.6]undecane-2-carboxamide (3I)



According to General Procedure **A** with **1i** (39.6 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3I** as a white solid (39.8 mg, 62% yield, 90% ee).

HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 98/02, flow rate 0.70 mL/min, λ = 254 nm), t_R (minor) = 14.14 min, t_R (major) = 9.86 min.

¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.6 Hz, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (dd, J = 14.4, 7.1 Hz, 2H), 7.07 (t, J = 8.1 Hz, 1H), 6.92-6.88 (m, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.09 (s, 1H), 3.68 (d, J = 10.6 Hz, 1H), 3.43 (d, J = 10.7 Hz, 1H), 2.43 (d, J = 13.3 Hz, 1H), 2.28 (d, J = 13.3 Hz, 1H), 2.01 (s, 1H), 1.85-1.58 (m, 7H), 1.53-1.33

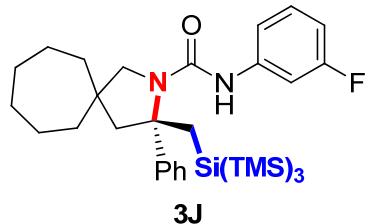
(m, 6H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 154.3, 146.9, 140.4, 134.5, 129.7, 129.1, 127.7, 127.2,

122.5, 118.9, 116.7, 70.2, 60.4, 58.4, 42.5, 42.0, 40.4, 29.7, 29.2, 24.6, 23.4, 21.1, 1.6.

HRMS (ESI) m/z calcd. for C₃₃H₅₆ClN₂OSi₄ [M + H]⁺ 643.3153, found 643.3139.

(S)-N-(3-fluorophenyl)-3-((1,1,1,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.6]undecane-2-carboxamide (3J)



3J

According to General Procedure A with **1j** (38.0 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3J** as a white solid (38.2 mg, 61% yield, 84% ee).

HPLC analysis: Chiralcel AD3 (hexane/i-PrOH = 99/01, flow rate 0.50 mL/min, λ = 254 nm), t_R (minor) = 13.86 min, t_R (major) = 10.44 min.

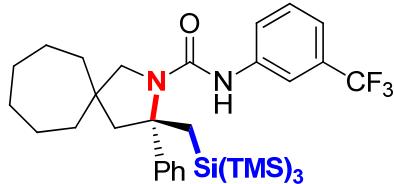
¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.05 (dd, *J* = 8.3, 4.8 Hz, 2H), 6.87 (t, *J* = 8.7 Hz, 2H), 6.04 (s, 1H), 3.68 (d, *J* = 10.5 Hz, 1H), 3.43 (d, *J* = 10.6 Hz, 1H), 2.42 (d, *J* = 13.2 Hz, 1H), 2.28 (d, *J* = 13.3 Hz, 1H), 2.03 (s, 1H), 1.86-1.56 (m, 7H), 1.54-1.33 (m, 6H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 158.5 (d, *J* = 240.9 Hz), 154.7, 147.1, 135.2 (d, *J* = 2.4 Hz), 129.0, 127.6, 127.1, 120.6, 120.6, 115.4, 115.2, 70.1, 60.5, 58.3, 42.5, 42.0, 40.4, 29.7, 29.2, 24.6, 23.4, 21.1, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -120.9 (s, 1F).

HRMS (ESI) m/z calcd. for C₃₃H₅₆FN₂OSi₄ [M + H]⁺ 627.3448, found 627.3434.

(S)-3-((1,1,1,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-N-(3-(trifluoromethyl)phenyl)-2-azaspiro[4.6]undecane-2-carboxamide (3K)



3K

According to General Procedure A with **1k** (43.0 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3K** as a white solid (29.8 mg, 44%

yield, 90% ee).

HPLC analysis: Chiralcel ID (hexane/*i*-PrOH = 99/01, flow rate 0.30 mL/min, λ = 254 nm), t_R (minor) = 38.75 min, t_R (major) = 29.60 min.

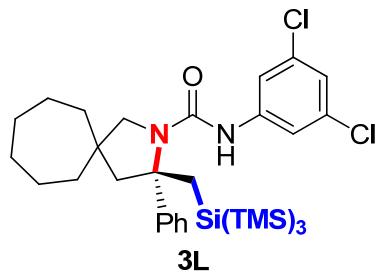
¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 7.6 Hz, 2H), 7.46 (s, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.25-7.12 (m, 3H), 6.21 (s, 1H), 3.68 (d, J = 10.6 Hz, 1H), 3.43 (d, J = 10.7 Hz, 1H), 2.42 (d, J = 13.3 Hz, 1H), 2.28 (d, J = 13.3 Hz, 1H), 2.00 (s, 1H), 1.84-1.55 (m, 7H), 1.50-1.33 (m, 6H), 0.16 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 154.3, 146.8, 139.7, 131.1 (q, J = 32.2 Hz), 129.2, 129.1, 127.88, 127.2, 124.0 (q, J = 272.2 Hz), 121.7, 119.0 (q, J = 3.7 Hz), 115.5 (q, J = 3.7 Hz), 70.3, 60.4, 58.3, 42.5, 41.9, 40.4, 29.7, 29.2, 24.6, 23.4, 21.1, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -62.8 (s, 3F).

HRMS (ESI) m/z calcd. for C₃₄H₅₆F₃N₂OSi₄ [M + H]⁺ 677.3416, found 677.3402.

(S)-N-(3,5-dichlorophenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.6]undecane-2-carboxamide (3L)



According to General Procedure A with **1I** (43.0 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3L** as a white solid (50.0 mg, 74% yield, 97% ee).

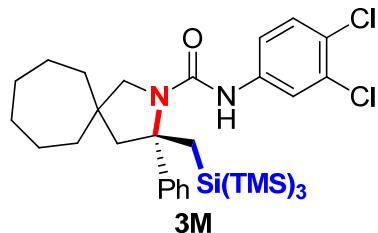
HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/01, flow rate 0.20 mL/min, λ = 254 nm), t_R (minor) = 33.28 min, t_R (major) = 25.25 min.

¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.1 Hz, 1H), 7.05 (s, 2H), 6.91 (t, J = 1.7 Hz, 1H), 6.10 (s, 1H), 3.66 (d, J = 10.6 Hz, 1H), 3.42 (d, J = 10.7 Hz, 1H), 2.43 (d, J = 13.3 Hz, 1H), 2.28 (d, J = 13.3 Hz, 1H), 1.99 (s, 1H), 1.82-1.57 (m, 7H), 1.54-1.34 (m, 6H), 0.18 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.9, 146.7, 141.1, 134.9, 129.2, 127.9, 127.1, 122.4, 117.0, 70.4, 60.4, 58.2, 42.6, 42.0, 40.4, 29.7, 29.2, 24.6, 23.4, 21.3, 1.6.

HRMS (ESI) m/z calcd. for C₃₃H₅₅Cl₂N₂OSi₄ [M + H]⁺ 677.2763, found 677.2751.

(S)-N-(3,4-dichlorophenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-phenyl-2-azaspiro[4.6]undecane-2-carboxamide (3M)

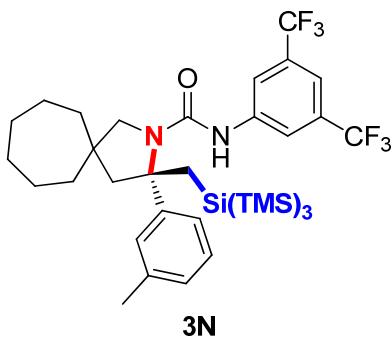


According to General Procedure **A** with **1m** (43.0 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3M** as a white solid (40.6 mg, 60% yield, 88% ee).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/01, flow rate 0.20 mL/min, λ = 254 nm), t_R (minor) = 14.76 min, t_R (major) = 12.18 min.

¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.5 Hz, 3H), 7.32 (t, J = 7.2 Hz, 1H), 7.19 (d, J = 8.7 Hz, 1H), 6.84 (d, J = 7.1 Hz, 1H), 6.10 (s, 1H), 3.67 (d, J = 10.6 Hz, 1H), 3.42 (d, J = 10.7 Hz, 1H), 2.42 (d, J = 13.3 Hz, 1H), 2.28 (d, J = 13.3 Hz, 1H), 1.99 (s, 1H), 1.87-1.54 (m, 7H), 1.53-1.32 (m, 6H), 0.17 (s, 27H).
¹³C NMR (100 MHz, CDCl₃) δ 154.0, 146.7, 138.7, 132.5, 130.2, 129.1, 127.8, 127.1, 125.4, 120.4, 118.0, 70.3, 60.4, 58.2, 42.5, 41.9, 40.4, 29.7, 29.1, 24.6, 23.3, 21.1, 1.6.
HRMS (ESI) m/z calcd. for C₃₃H₅₅Cl₂N₂OSi₄ [M + H]⁺ 677.2763, found 677.2749.

(*S*)-N-(3,5-bis(trifluoromethyl)phenyl)-3-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-3-(m-tolyl)-2-azaspiro[4.6]undecane-2-carboxamide (**3N**)



According to General Procedure **A** with **1n** (51.2 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3N** as a white solid (51.6 mg, 68% yield, 87% ee).

HPLC analysis: Chiralcel IA (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 27.17 min, t_R (major) = 30.77 min.

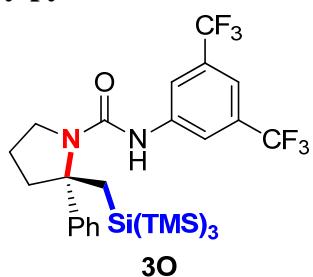
¹H NMR (400 MHz, CDCl₃) δ 7.54 (s, 2H), 7.40 (s, 1H), 7.35 (d, J = 5.6 Hz, 3H), 7.20 (d, J = 5.0 Hz, 1H), 6.42 (s, 1H), 3.73 (d, J = 10.9 Hz, 1H), 3.42 (d, J = 11.0 Hz, 1H), 2.49 (d, J = 13.5 Hz, 1H), 2.41 (s, 3H), 2.31 (d, J = 13.5 Hz, 1H), 2.02-1.85 (m, 3H), 1.77-1.38 (m, 11H), 0.17 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 154.0, 146.3, 140.7, 139.3, 132.1 (q, *J* = 33.2 Hz), 129.2, 129.2, 128.0, 124.5, 123.3 (q, *J* = 272.7 Hz), 118.2 (d, *J* = 2.2 Hz), 115.9-115.4 (m), 70.3, 60.0, 58.4, 42.5, 41.8, 40.6, 29.8, 29.3, 24.6, 23.4, 21.8, 20.4, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₆H₅₇F₆N₂OSi₄ [M + H]⁺ 759.3447, found 759.3446.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylpyrrolidine-1-carboxamide (3O)



According to General Procedure A with **1o** (41.6 mg, 0.1 mmol, 1.0 equiv), 72 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3O** as a white solid (26.5 mg, 40% yield, 66% ee).

HPLC analysis: Chiralcel IB (hexane/i-PrOH = 99/01, flow rate 0.20 mL/min, λ = 254 nm), *t*_R (minor) = 34.02 min, *t*_R (major) = 40.52 min.

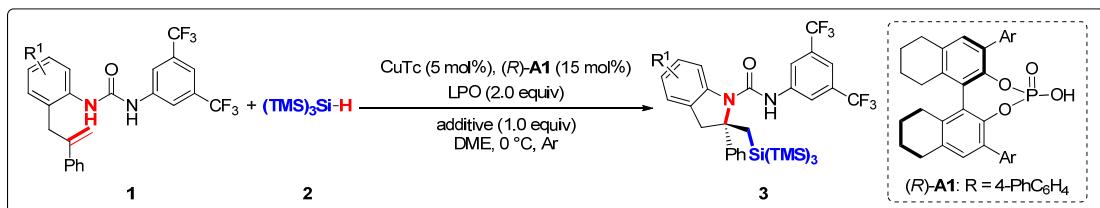
¹H NMR (400 MHz, CDCl₃) δ 7.65-7.29 (m, 8H), 6.24 (s, 1H), 3.95-3.75 (m, 2H), 2.51-2.24 (m, 2H), 2.15 (d, *J* = 14.7 Hz, 1H), 1.85-2.05 (m, 2H), 1.59 (s, 1H), 0.19 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.0, 146.0, 140.6, 132.0 (q, *J* = 33.3 Hz), 129.4, 128.2, 126.6, 123.3 (q, *J* = 272.7 Hz), 118.5, 115.9-115.6 (m), 69.3, 48.3, 44.9, 22.2, 19.7, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for C₂₉H₄₅F₆N₂OSi₄ [M + H]⁺ 663.2508, found 663.2496.

General procedure for 1,2-aminosilylation of alkenes for construction of indoline



General Procedure C

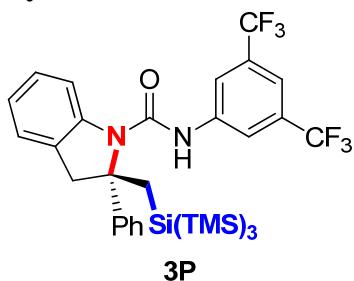
Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1** (0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid ((*R*)-**A1** (9.9 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), ($\text{SiH}_3\text{CH}_2\text{CH}_2\text{SiH}_3$)₃ **2** (49.7 mg, 0.2 mmol, 2.0 equiv), methylparaben (15.2 mg, 0.1 mmol, 1.0 equiv) and 1,2-dimethoxyethane (2.0 mL) at room temperature, and the sealed tube was then stirred at 0 °C for 96 h. The reaction mixture was directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 20/1, using dichloromethane (100%) to remove the solvent (1,2-dimethoxyethane) at first] to afford the desired product **3**.

General Procedure D

Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1** (0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid ((*R*)-**A1** (9.9 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), ($\text{SiH}_3\text{CH}_2\text{CH}_2\text{SiH}_3$)₃ **2** (49.7 mg, 0.2 mmol, 2.0 equiv), pivalic anhydride (18.6 mg, 0.1 mmol, 1.0 equiv) and 1,2-dimethoxyethane (2.0 mL) at room-temperature, and the sealed tube was then stirred at 0 °C for 96 h. The reaction mixture was directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 20/1, using dichloromethane (100%) to remove the solvent (1,2-dimethoxyethane) at first] to afford the desired product **3**.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindoline-1-carboxamide (3P)



According to General Procedure C with **1p** (46.4 mg, 0.1 mmol, 1.0 equiv), 96 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3P** as a white solid (50.4 mg, 71%

yield, 87% ee).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 27.14 min, t_R (major) = 25.14 min.

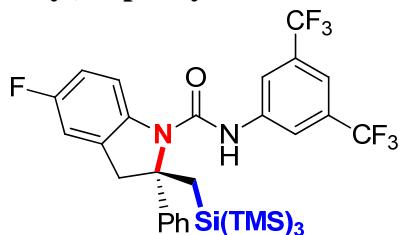
¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, J = 8.2 Hz, 1H), 7.64 (d, J = 6.9 Hz, 2H), 7.55-7.46 (m, 3H), 7.44 (s, 3H), 7.29 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.1 Hz, 1H), 7.07 (td, J = 7.4, 0.6 Hz, 1H), 6.54 (s, 1H), 3.65 (d, J = 16.5 Hz, 1H), 3.59 (d, J = 16.5 Hz, 1H), 2.30 (d, J = 14.7 Hz, 1H), 1.96 (d, J = 14.7 Hz, 1H), 0.13 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 152.1, 145.6, 142.9, 140.0, 132.2 (q, J = 33.4 Hz), 129.9, 129.3, 128.3, 127.5, 126.9, 124.5, 123.4, 123.2 (q, J = 273.4 Hz), 118.7 (d, J = 3.3 Hz), 116.8, 116.5-116.1 (m), 72.5, 48.4, 19.0, 1.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₃H₄₅F₆N₂OSi₄ [M + H]⁺ 711.2508, found 711.2506.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-5-fluoro-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindoline-1-carboxamide (3Q)



3Q

According to General Procedure C with **1q** (48.2 mg, 0.1 mmol, 1.0 equiv), 96 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3Q** as a white solid (49.5 mg, 68% yield, 83% ee).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 28.15 min, t_R (major) = 30.34 min.

¹H NMR (400 MHz, CDCl₃) δ 8.12 (dd, J = 9.0, 4.8 Hz, 1H), 7.63 (d, J = 6.8 Hz, 2H), 7.57-7.48 (m, 3H), 7.44 (s, 1H), 7.41 (s, 2H), 6.98 (td, J = 8.9, 2.6 Hz, 1H), 6.88 (dd, J = 7.8, 2.5 Hz, 1H), 6.47 (s, 1H), 3.63 (d, J = 16.8 Hz, 1H), 3.57 (d, J = 16.9 Hz, 1H), 2.28 (d, J = 14.7 Hz, 1H), 1.93 (d, J = 14.7 Hz, 1H), 0.13 (s, 27H).

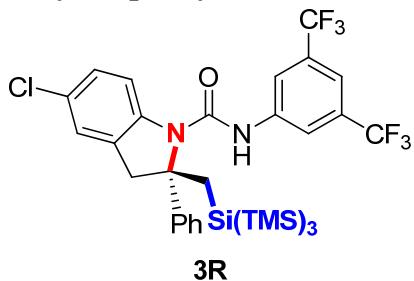
¹³C NMR (100 MHz, CDCl₃) δ 159.2 (d, J = 241.9 Hz), 152.0, 145.2, 139.9, 139.1, 132.2 (q, J = 33.3 Hz), 130.0, 129.6, 129.1 (d, J = 8.3 Hz), 126.9, 123.1 (q, J = 272.7 Hz), 118.7 (d, J = 3.5 Hz), 117.9 (d, J = 7.8 Hz), 116.6-116.0 (m), 114.7 (d, J = 22.5 Hz), 111.5 (d, J = 23.9 Hz), 72.8, 48.2, 19.0, 1.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 6F), -120.1 (s, 1F).

HRMS (ESI) m/z calcd. for C₃₃H₄₄F₇N₂OSi₄ [M + H]⁺ 729.2413, found 729.2412.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-5-chloro-2-((1,1,1,3,3,3-hexamethyl-2-(tri

methylsilyl)trisilan-2-yl)methyl)-2-phenylindoline-1-carboxamide (3R)



According to General Procedure **D** with **1r** (49.8 mg, 0.1 mmol, 1.0 equiv), 96 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3R** as a white solid (46.9 mg, 63% yield, 82% ee).

HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 22.66 min, t_R (major) = 25.02 min.

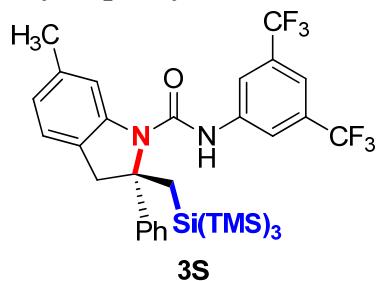
¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.8 Hz, 1H), 7.60 (dd, J = 8.1, 1.5 Hz, 2H), 7.56-7.48 (m, 3H), 7.45 (s, 1H), 7.40 (s, 2H), 7.25 (dd, J = 8.6, 2.2 Hz, 1H), 7.13 (d, J = 2.0 Hz, 1H), 6.48 (s, 1H), 3.62 (d, J = 16.7 Hz, 1H), 3.55 (d, J = 16.9 Hz, 1H), 2.28 (d, J = 14.7 Hz, 1H), 1.92 (d, J = 14.7 Hz, 1H), 0.13 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 151.9, 145.2, 141.7, 139.7, 132.3 (q, J = 33.4 Hz), 130.0, 129.6, 129.3, 128.3, 128.2, 126.8, 124.5, 123.1 (q, J = 272.6 Hz), 118.7 (d, J = 2.9 Hz), 117.9, 116.8-116.4 (m), 72.8, 48.0, 19.1, 1.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₃H₄₄ClF₆N₂OSi₄ [M + H]⁺ 745.2118, found 745.2117.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-6-methyl-2-phenylindoline-1-carboxamide (3S)



According to General Procedure **D** with **1s** (47.8 mg, 0.1 mmol, 1.0 equiv), 96 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3S** as a white solid (43.5 mg, 60% yield, 81% ee).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 26.04 min, t_R (major) = 22.96 min.

¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.61 (d, J = 6.9 Hz, 2H), 7.55-7.44 (m, 3H), 7.43 (d, J = 6.8 Hz, 3H), 7.04 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 7.4 Hz, 1H), 6.52

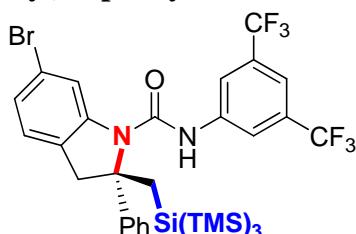
(s, 1H), 3.59 (d, J = 16.3 Hz, 1H), 3.53 (d, J = 16.4 Hz, 1H), 2.39 (s, 3H), 2.27 (d, J = 14.7 Hz, 1H), 1.94 (d, J = 14.7 Hz, 1H), 0.12 (s, 27H).

^{13}C NMR (100 MHz, CDCl_3) δ 152.1, 145.7, 143.0, 140.0, 138.3, 132.2 (q, J = 33.3 Hz), 129.9, 129.3, 126.9, 124.6, 124.2, 124.1, 123.2 (q, J = 272.6 Hz), 118.6 (d, J = 3.2 Hz), 117.4, 116.5-116.1 (m), 72.8, 48.2, 21.9, 19.0, 1.3.

^{19}F NMR (376 MHz, CDCl_3) δ -63.1 (s, 6F).

HRMS (ESI) m/z calcd. for $\text{C}_{34}\text{H}_{47}\text{F}_6\text{N}_2\text{OSi}_4$ [$\text{M} + \text{H}]^+$ 725.2664, found 725.2664.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-6-bromo-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindoline-1-carboxamide (3T)



3T

According to General Procedure **D** with **1t** (54.2 mg, 0.1 mmol, 1.0 equiv), 96 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3T** as a white solid (45.7 mg, 58% yield, 82% ee).

HPLC analysis: Chiralcel OD3 (hexane/i-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_{R} (minor) = 26.59 min, t_{R} (major) = 24.95 min.

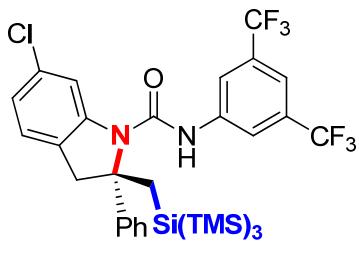
^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, J = 1.7 Hz, 1H), 7.65-7.60 (m, 2H), 7.55-7.49 (m, 3H), 7.44 (d, J = 9.9 Hz, 1H), 7.40 (s, 2H), 7.19 (dd, J = 7.9, 1.8 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.50 (s, 1H), 3.59 (d, J = 16.6 Hz, 1H), 3.52 (d, J = 16.6 Hz, 1H), 2.26 (d, J = 14.7 Hz, 1H), 1.91 (d, J = 14.7 Hz, 1H), 0.13 (s, 27H).

^{13}C NMR (100 MHz, CDCl_3) δ 151.9, 145.1, 144.2, 139.7, 132.3 (q, J = 33.6 Hz), 130.1, 129.7, 127.0, 126.4, 126.3, 125.5, 123.1 (q, J = 273.1 Hz), 121.9, 120.1, 118.7 (d, J = 3.0 Hz), 116.7-116.5 (m), 73.3, 47.9, 19.0, 1.3.

^{19}F NMR (376 MHz, CDCl_3) δ -63.2 (s, 6F).

HRMS (ESI) m/z calcd. for $\text{C}_{33}\text{H}_{44}\text{BrF}_6\text{N}_2\text{OSi}_4$ [$\text{M} + \text{H}]^+$ 789.1613, found 789.1609.

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-6-chloro-2-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-2-phenylindoline-1-carboxamide (3U)



3U

According to General Procedure **D** with **1u** (49.8 mg, 0.1 mmol, 1.0 equiv), 96 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product **3U** as a white solid (46.9 mg, 63% yield, 80% ee).

HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 26.09 min, t_R (major) = 24.87 min.

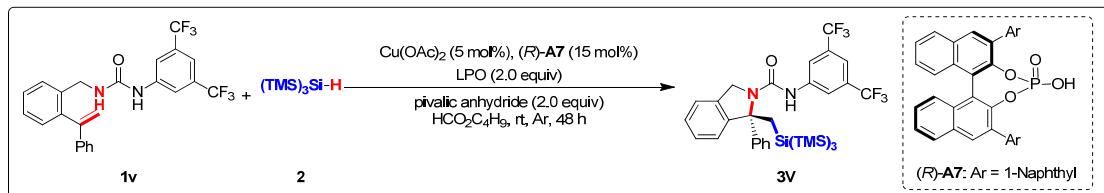
¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 1.6 Hz, 1H), 7.62 (dd, J = 8.0, 1.2 Hz, 2H), 7.57-7.47 (m, 3H), 7.46 (s, 1H), 7.40 (s, 2H), 7.07 (d, J = 8.0 Hz, 1H), 7.04 (dd, J = 8.0, 1.8 Hz, 1H), 6.50 (s, 1H), 3.60 (d, J = 16.6 Hz, 1H), 3.54 (d, J = 16.6 Hz, 1H), 2.26 (d, J = 14.7 Hz, 1H), 1.91 (d, J = 14.7 Hz, 1H), 0.13 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 151.9, 145.1, 144.0, 139.7, 134.0, 132.3 (q, J = 33.4 Hz), 130.1, 129.7, 127.0, 125.9, 125.0, 123.4, 123.1 (q, J = 272.7 Hz), 118.7 (d, J = 3.5 Hz), 117.3, 116.6 (dt, J = 7.7, 3.8 Hz), 73.4, 47.9, 19.0, 1.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.2 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₃H₄₄ClF₆N₂OSi₄ [M + H]⁺ 745.2118, found 745.2116.

General procedure for 1,2-aminosilylation of alkene **1v for construction of isoindoline**

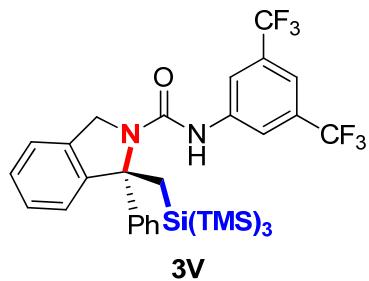


General Procedure E

Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1v** (46.4 mg, 0.1 mmol, 1.0 equiv), Cu(OAc)₂ (0.91 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid ((*R*)-**A7** (9.0 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), (TMS)₃SiH **2** (49.7 mg, 0.2 mmol, 2.0 equiv), pivalic anhydride (37.2 mg, 0.2 mmol, 2.0 equiv) and HCO₂C₄H₉ (2.0 mL) at room temperature, and the sealed tube was then stirred at room temperature for 48 h. The reaction mixture was directly purified by a silica gel chromatography [eluent: petroleum ether/EtOAc = 10/1, using dichloromethane (100%) to remove the solvent (HCO₂C₄H₉) at first] to afford the desired product **3V**.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use.

(*R*)-N-(3,5-bis(trifluoromethyl)phenyl)-1-((1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)methyl)-1-phenylisoindoline-2-carboxamide (3V**)**



According to General Procedure **E** with **1v** (46.4 mg, 0.1 mmol, 1.0 equiv), 48 h later, the reaction mixture was purified by the column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the product **3V** as a white solid (53.3 mg, 75% yield, 74% ee).

HPLC analysis: Chiralcel AD3 (hexane/*i*-PrOH = 99/01, flow rate 0.15 mL/min, λ = 254 nm), t_R (minor) = 31.86 min, t_R (major) = 34.77 min.

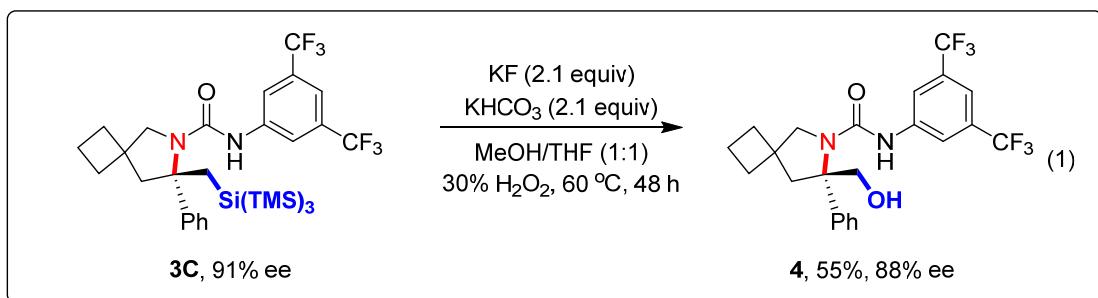
¹H NMR (400 MHz, CDCl₃) δ 7.50-7.16 (m, 11H), 6.88 (d, J = 5.7 Hz, 1H), 6.22 (s, 1H), 5.18 (d, J = 14.8 Hz, 1H), 5.11 (d, J = 14.8 Hz, 1H), 2.56-2.25 (m, 2H), 0.06 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 153.2, 147.6, 146.5, 140.2, 134.1, 132.0 (q, J = 33.3 Hz), 129.5, 128.8, 128.4, 125.9, 123.6, 123.3, 123.2 (q, J = 272.3 Hz), 119.2 (d, J = 3.3 Hz), 116.4-116.1 (m), 73.1, 54.5, 21.5, 1.6.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.1 (s, 6F).

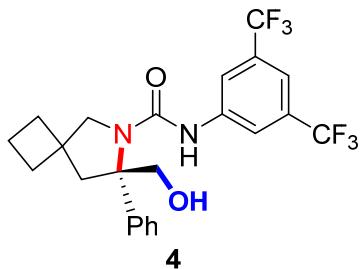
HRMS (ESI) m/z calcd. for C₃₃H₄₅F₆N₂OSi₄ [M + H]⁺ 711.2508, found 711.2507.

Synthetic application



General procedure: To a mixture of KF (12.2 mg, 0.21 mmol, 2.1 equiv) and KHCO_3 (21.0 mg, 0.21 mmol, 2.1 equiv) in MeOH (1 mL) and THF (1 mL) was added **3C** (70.2 mg, 0.1 mmol, 1.0 equiv) and then aqueous 30% H_2O_2 (0.34 g, 3 mmol, 30 equiv). The mixture was stirred at 60 °C for 48 h. [4] After being cooled at room temperature, the reaction mixture was treated with water. The mixture was extracted with EtOAc (3×10 mL), and combined organic phase was washed with 15% aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL). Drying over Na_2SO_4 and subsequent silica gel chromatography (hexane/EtOAc = 5/1) to yield the product **4** as a white solid (26 mg, 55% yield, 88% ee).

(S)-N-(3,5-bis(trifluoromethyl)phenyl)-7-(hydroxymethyl)-7-phenyl-6-azaspiro[3.4]octane-6-carboxamide (4)



HPLC analysis: Chiralcel OD3 (hexane/*i*-PrOH = 85/15, flow rate 0.30 mL/min, $\lambda = 254$ nm), t_{R} (minor) = 15.65 min, t_{R} (major) = 12.65 min.

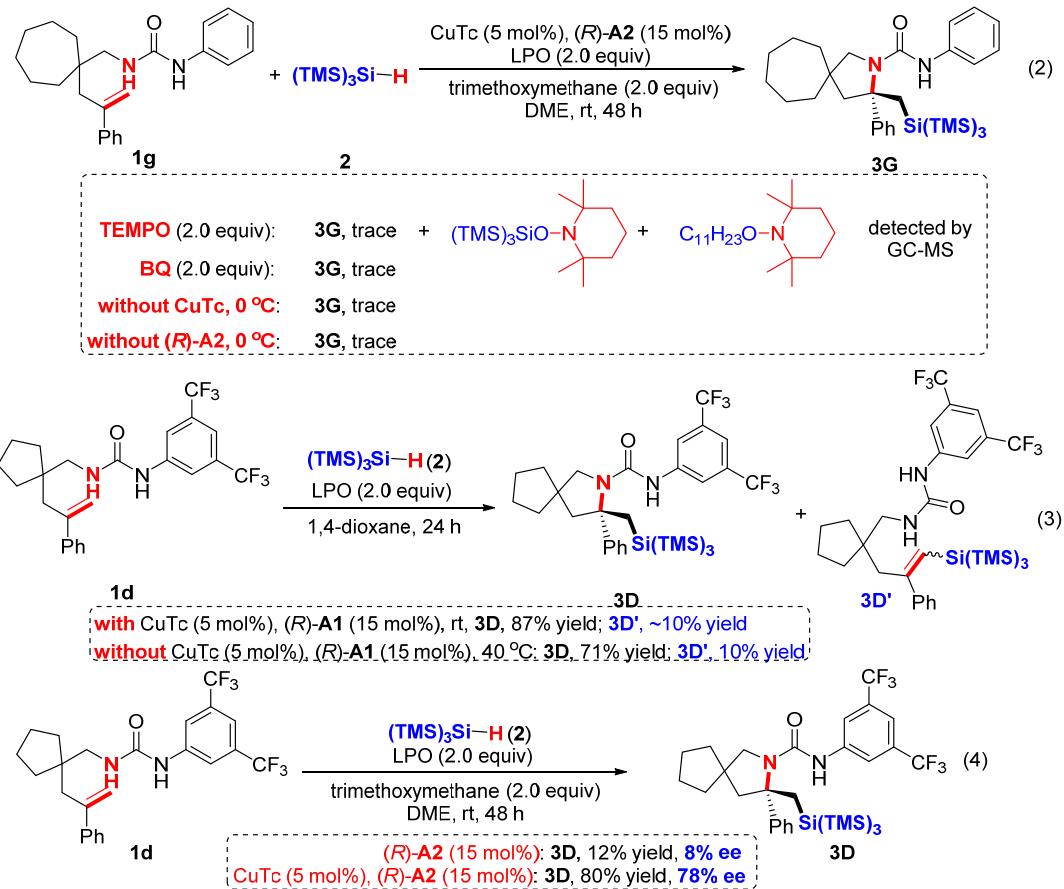
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (s, 2H), 7.43 (s, 1H), 7.36-7.30 (m, 2H), 7.26-7.19 (m, 3H), 4.37 (s, 1H), 4.04 (d, $J = 11.8$ Hz, 1H), 3.95 (d, $J = 8.6$ Hz, 1H), 3.75 (d, $J = 8.6$ Hz, 1H), 2.29 (d, $J = 12.8$ Hz, 1H), 2.11 (d, $J = 12.8$ Hz, 1H), 2.09-1.93 (m, 2H), 1.87-1.40 (m, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 154.7, 141.3, 140.9, 132.0 (q, $J = 33.8$ Hz), 128.9, 127.4, 126.0, 123.3 (q, $J = 272.8$ Hz), 118.9, 115.8, 68.5, 61.6, 41.9, 32.0, 29.8, 29.3, 16.3, 14.2.

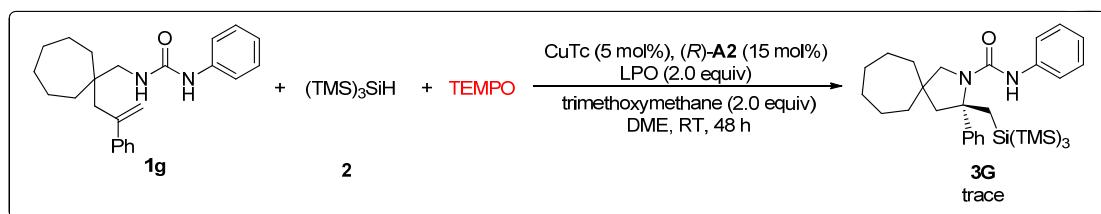
$^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for $\text{C}_{23}\text{H}_{23}\text{F}_6\text{N}_2\text{O}_2 [\text{M} + \text{H}]^+$ 473.1658, found 473.1656.

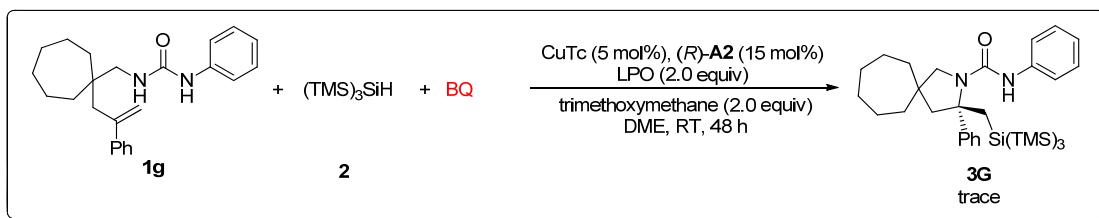
Mechanistic study



a) Trapping with TEMPO or inhibition with BQ

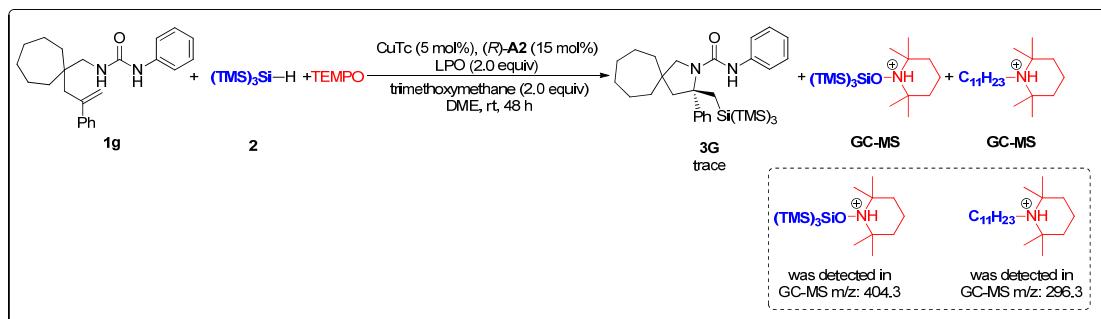


Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1g** (36.2 mg, 0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid ((*R*)-**A2** (9.12 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), (*TMS*)₃SiH **2** (49.7 mg, 0.2 mmol, 2.0 equiv), trimethoxymethane (21.2 mg, 0.2 mmol, 2.0 equiv), DME (2.0 mL) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 31.3 mg, 0.2 mmol, 2.0 equiv) at room temperature, and the sealed tube was then stirred at room-temperature for 48 h. Conversion was based on ¹H NMR/¹⁹F NMR/LC-MS/GC-MS analysis of the crude product.

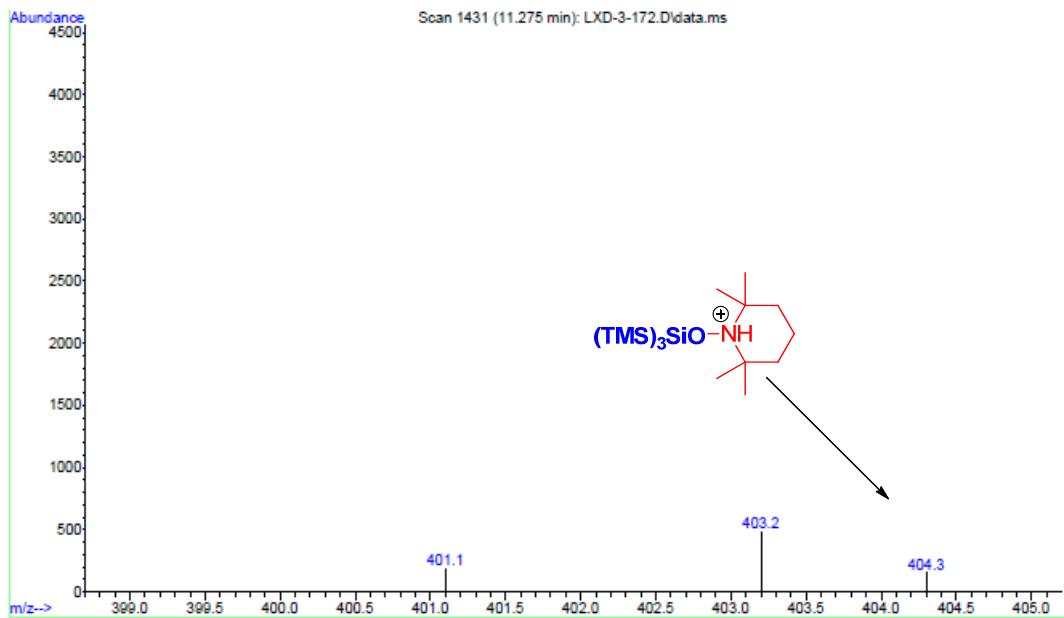
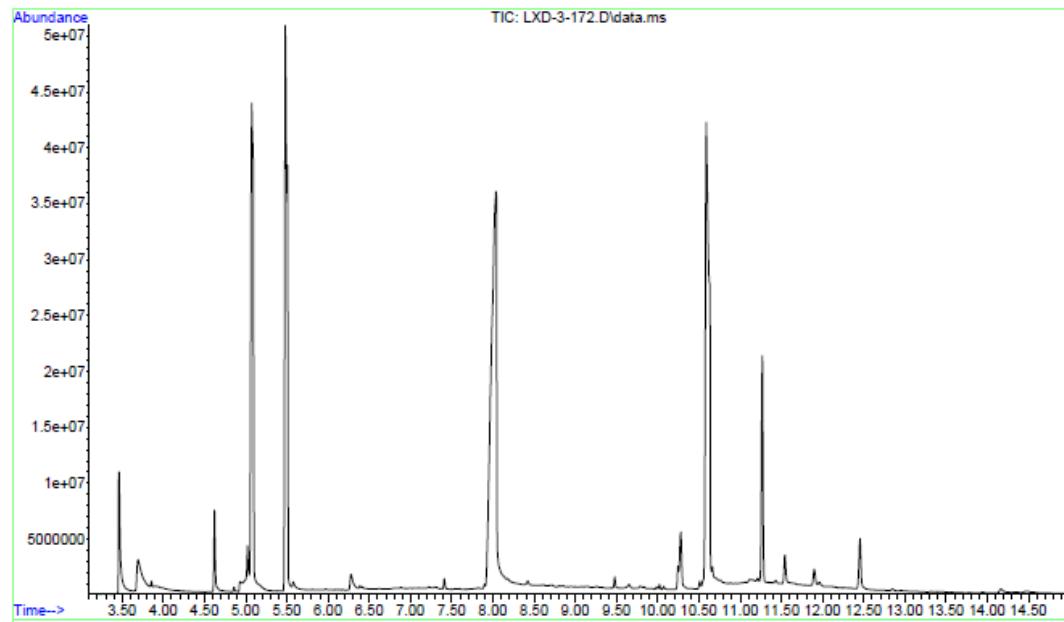


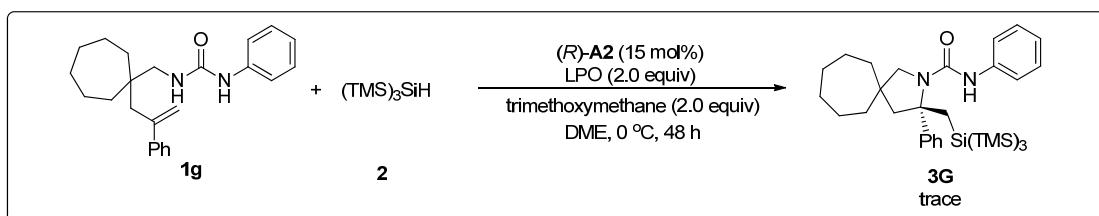
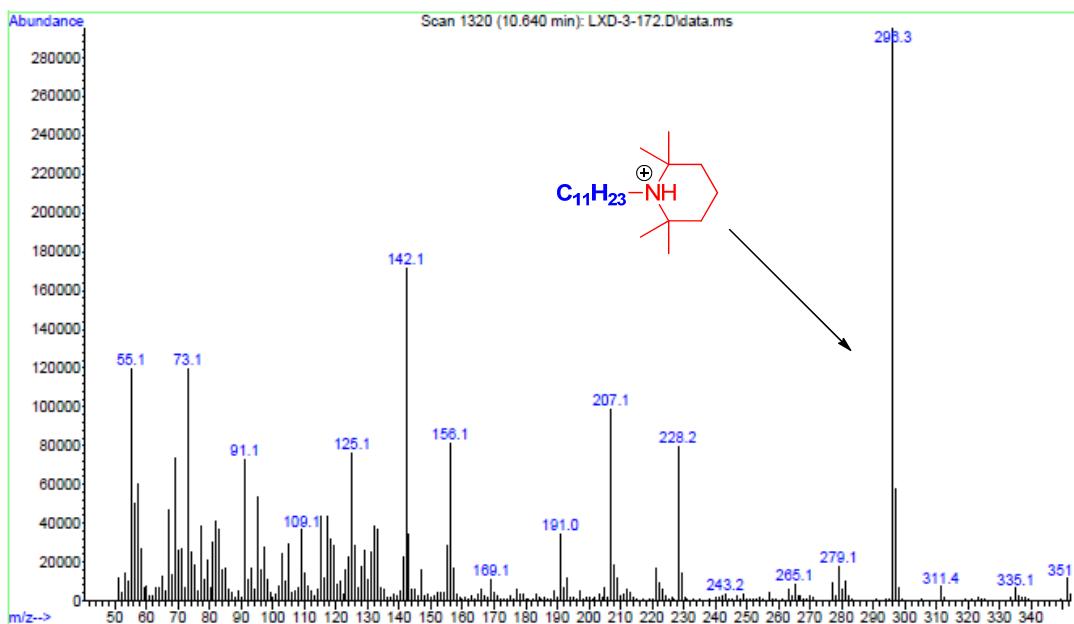
Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1g** (36.2 mg, 0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid ((*R*)-**A2** (9.12 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), (*TMS*)₃SiH **2** (49.7 mg, 0.2 mmol, 2.0 equiv), trimethoxymethane (21.2 mg, 0.2 mmol, 2.0 equiv), DME (2.0 mL) and benzoquinone (BQ, 21.6 mg, 0.2 mmol, 2.0 equiv) at room temperature, and the sealed tube was then stirred at room temperature for 48 h. Conversion was based on ¹H NMR/¹⁹F NMR/LC-MS/GC-MS analysis of the crude product.

Note: Since the reaction is sensitive to water and air, Schlenk tube and the reagents must be dried prior to use.

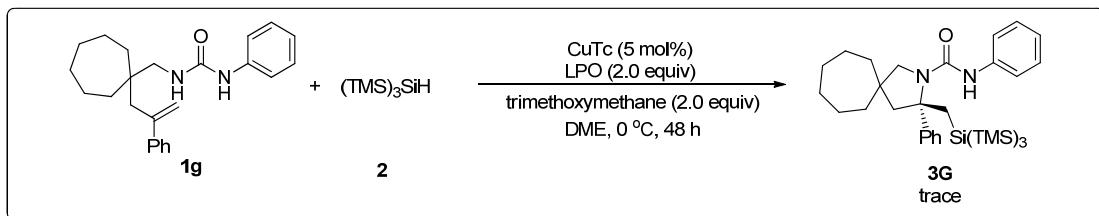


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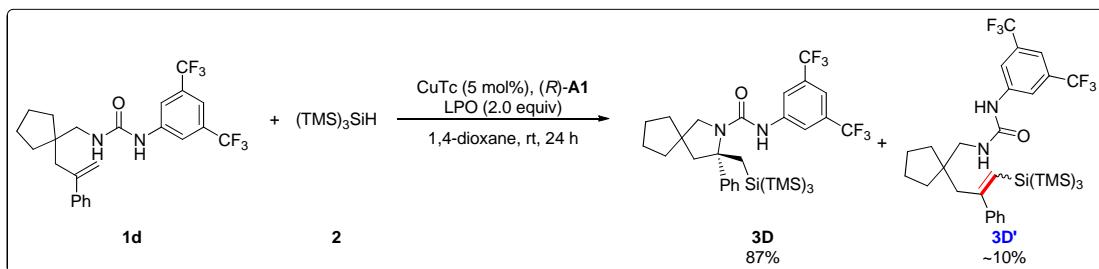


Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1g** (9.06 mg, 0.025 mmol, 1.0 equiv), chiral phosphoric acid ((*R*)-**A2** (2.28 mg, 0.0038 mmol, 15 mol%), LPO (19.90 mg, 0.05 mmol, 2.0 equiv), ($\text{Si}(\text{CH}_3)_3$)₃ (12.40 mg, 0.05 mmol, 2.0 equiv), trimethoxymethane (5.30 mg, 0.05 mmol, 2.0 equiv), DME (0.5 mL) at room temperature, and the sealed tube was then stirred at 0 °C for 48 h. Conversion was based on ¹H NMR/¹⁹F NMR analysis of the crude product.

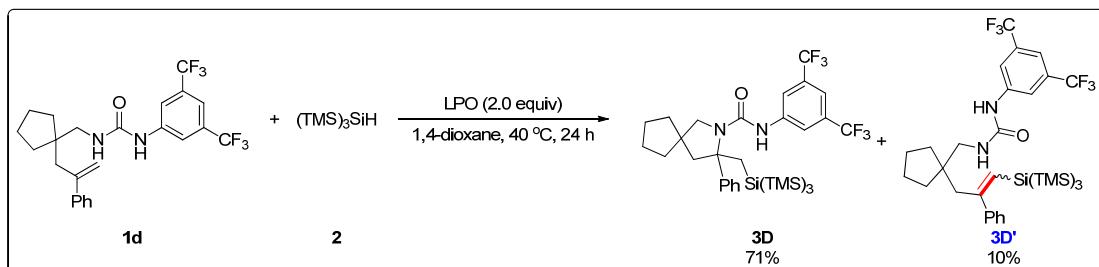


Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1g** (9.06 mg, 0.025 mmol, 1.0 equiv), CuTc (0.24 mg, 0.0013 mmol, 5 mol%), LPO (19.90 mg, 0.05 mmol, 2.0 equiv), ($\text{Si}(\text{CH}_3)_3$)₃ (12.40 mg, 0.05 mmol, 2.0 equiv), trimethoxymethane (5.30 mg, 0.05 mmol, 2.0 equiv), DME (0.5 mL) at room temperature, and the sealed tube was then stirred at 0 °C for 48 h. Conversion was based on ¹H NMR/¹⁹F NMR analysis of the crude product.

b) β -hydride elimination

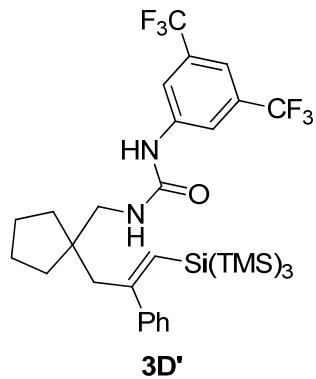


Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1d** (47.0 mg, 0.1 mmol, 1.0 equiv), CuTc (0.95 mg, 0.005 mmol, 5 mol%), chiral phosphoric acid ((*R*)-**A1** (9.90 mg, 0.015 mmol, 15 mol%), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), $(\text{Si}(\text{CH}_3)_3)_3\text{SiH}$ **2** (49.7 mg, 0.2 mmol, 2.0 equiv), 1,4-dioxane (2.0 mL) at room temperature, and the sealed tube was then stirred at room-temperature for 24 h. The product **3D** was obtained in 87% yield and the by-product **3D'** was obtained in about 10% yield purified by the column chromatography on silica gel.



Under argon, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with alkene substrate **1d** (47.0 mg, 0.1 mmol, 1.0 equiv), LPO (79.7 mg, 0.2 mmol, 2.0 equiv), $(\text{Si}(\text{CH}_3)_3)_3\text{SiH}$ **2** (49.7 mg, 0.2 mmol, 2.0 equiv), 1,4-dioxane (2.0 mL) at room temperature, and the sealed tube was then stirred at 40 °C for 24 h. The product **3D** was obtained in 71% yield and the byproduct **3D'** was obtained in 10% yield purified by the column chromatography on silica gel.

1-(3,5-bis(trifluoromethyl)phenyl)-3-((1-(3-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)-2-phenylallyl)cyclopentyl)methyl)urea (3D')



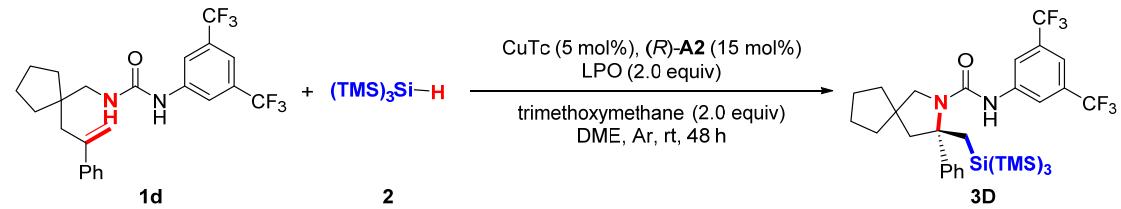
¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 2H), 7.47 (s, 1H), 7.36-7.23 (m, 5H), 6.20 (d, *J* = 12.3 Hz, 1H), 5.68 (s, 1H), 4.05 (s, 1H), 2.91 (d, *J* = 5.9 Hz, 2H), 2.60 (s, 2H), 1.65-1.56 (m, 5H), 1.38-1.26 (m, 3H), 0.04 (s, 27H).

¹³C NMR (100 MHz, CDCl₃) δ 155.3, 154.4, 145.6, 140.5, 132.2 (q, *J* = 33.3 Hz), 128.9, 128.5, 127.5, 124.9, 123.3 (q, *J* = 272.9 Hz), 118.6 (d, *J* = 3.0 Hz), 116.1-115.7 (m), 51.2, 48.1, 46.4, 35.72, 24.2, 1.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.0 (s, 6F).

HRMS (ESI) m/z calcd. for C₃₃H₅₁F₆N₂OSi₄ [M + H]⁺ 717.2977, found 717.2979.

c) Control reaction^{a)}



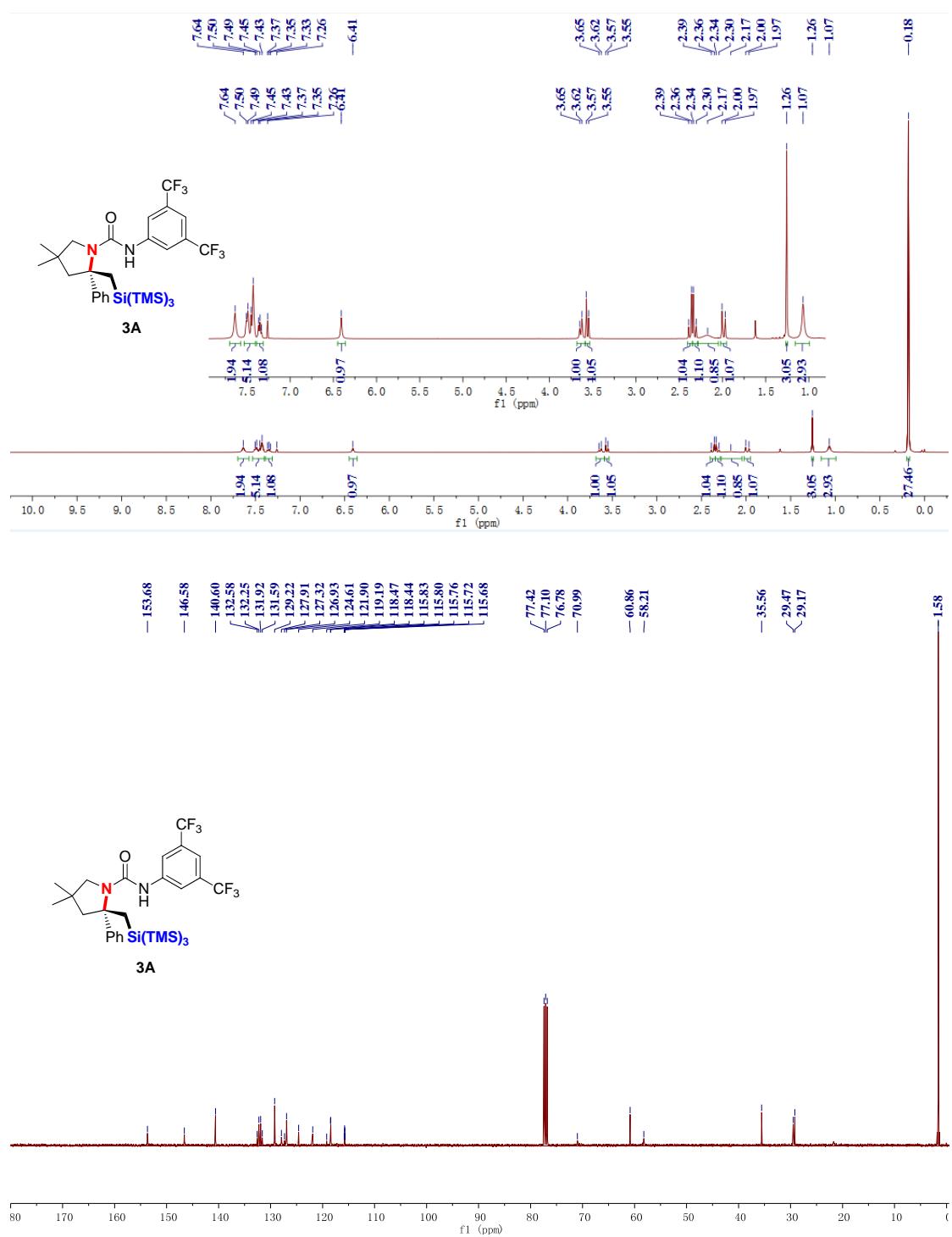
Entry	[Cu]	CPA	Yield (%) ^{b)}	ee (%) ^{c)}
1	-	(R)-A2	12	8
2	CuTc	(R)-A2	80	78

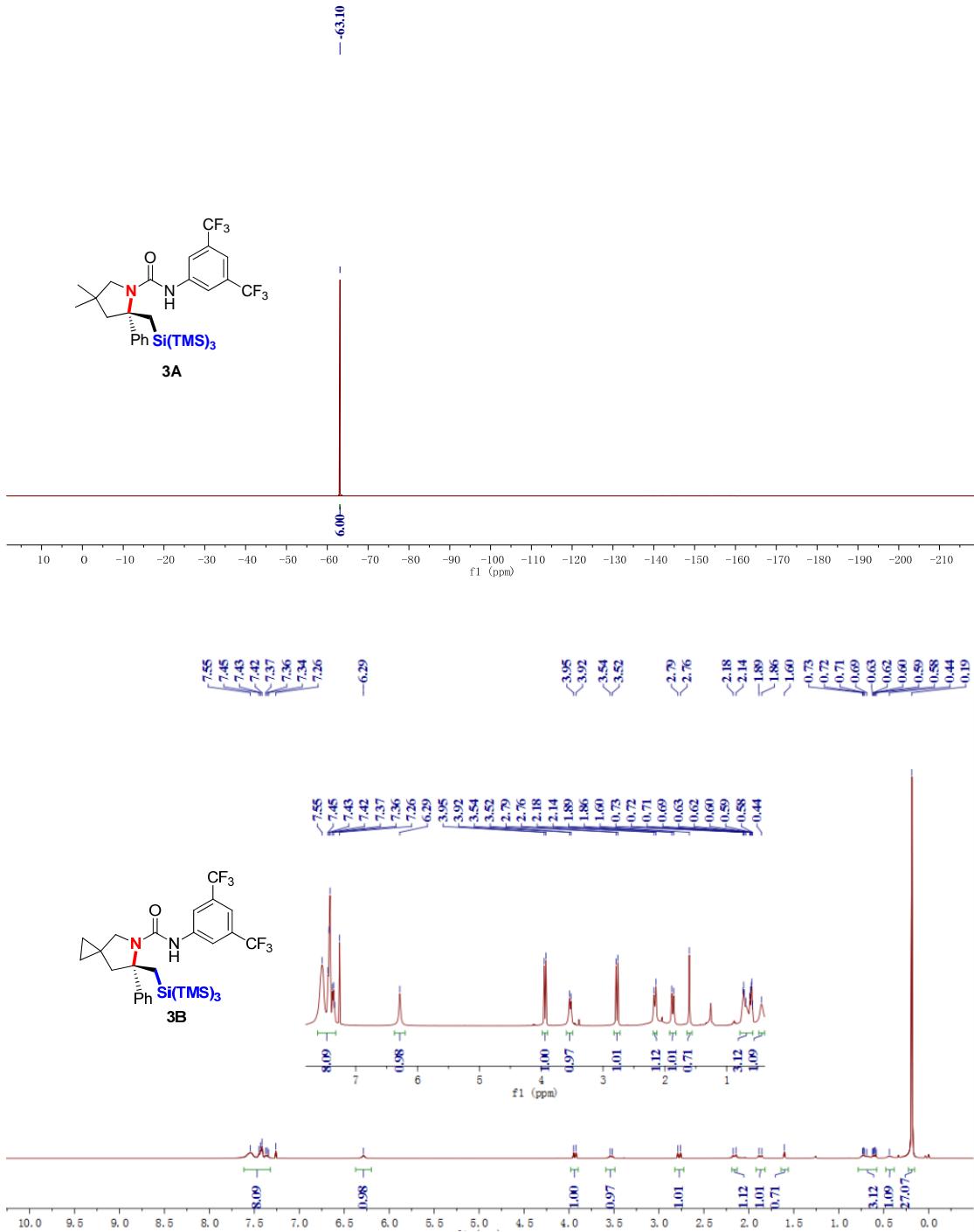
^{a)} Reaction conditions: **1d** (0.025 mmol), **2** (2 equiv), CuTc (5 mol %), (R)-**A2** (15 mol %), LPO (2.0 equiv), trimethoxymethane (2.0 equiv), DME (0.5 mL), rt, 48 h under argon. b) Yield based on ¹H NMR analysis of the crude product with CH₂Br₂ as an internal standard. c) ee value based on HPLC analysis.

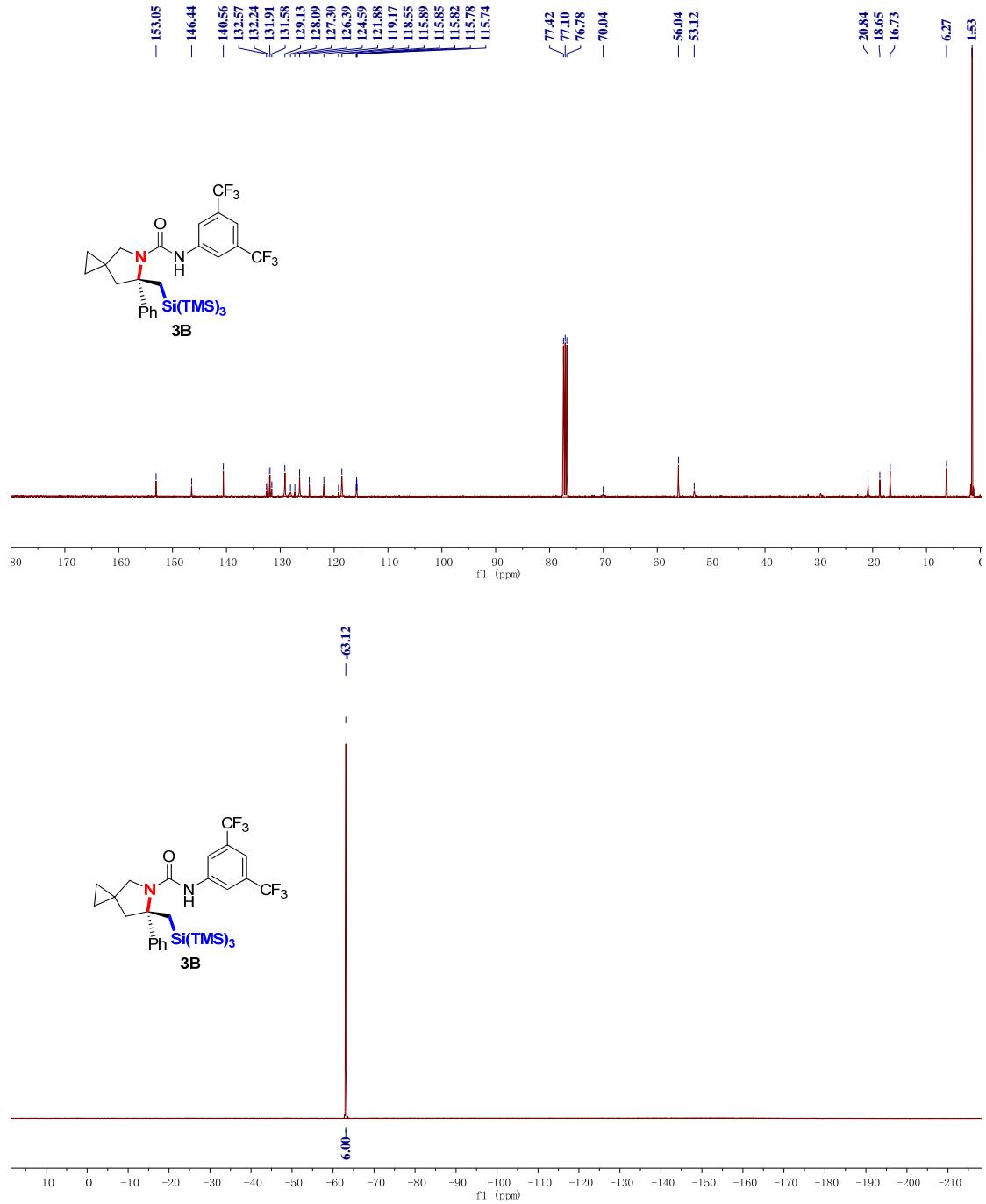
References

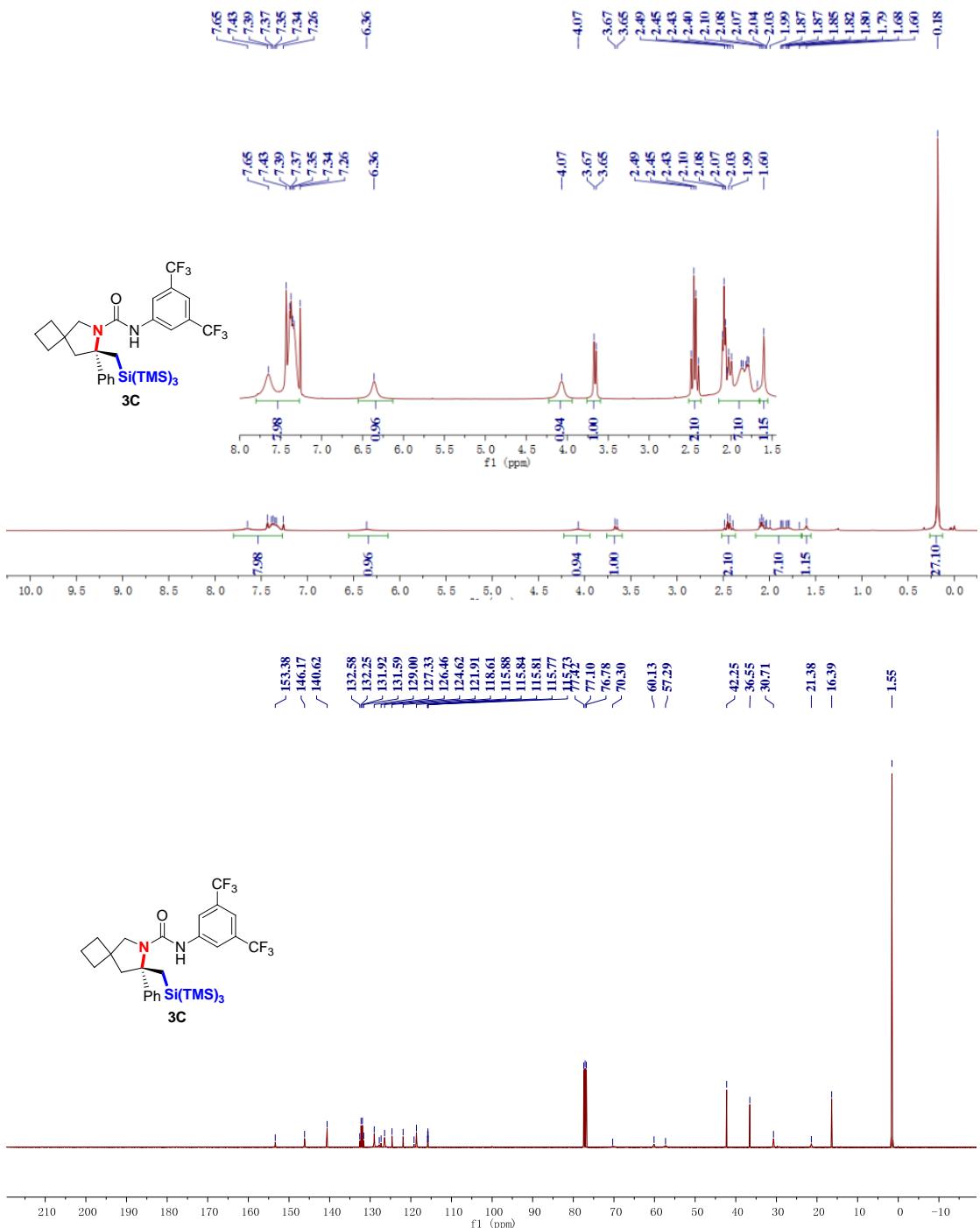
- (1) Lin JS, Yu P, Huang L, Zhang P, Tan B, Liu XY. *Angew Chem Int Ed*, 2015, 54: 7847–7851
- (2) Lin JS, Dong XY, Li TT, Jiang NC, Tan B, Liu XY. *J Am Chem Soc*, 2016, 138: 9357–9360
- (3) Pan Z, Pound SM, Rondla NR, Douglas CJ. *Angew Chem Int Ed*, 2014, 53: 5170–5174
- (4) Itami K, Kamei T, Mitsudo K, Nokami T, Yoshida J. *J Org Chem*, 2001, 66: 3970–3976

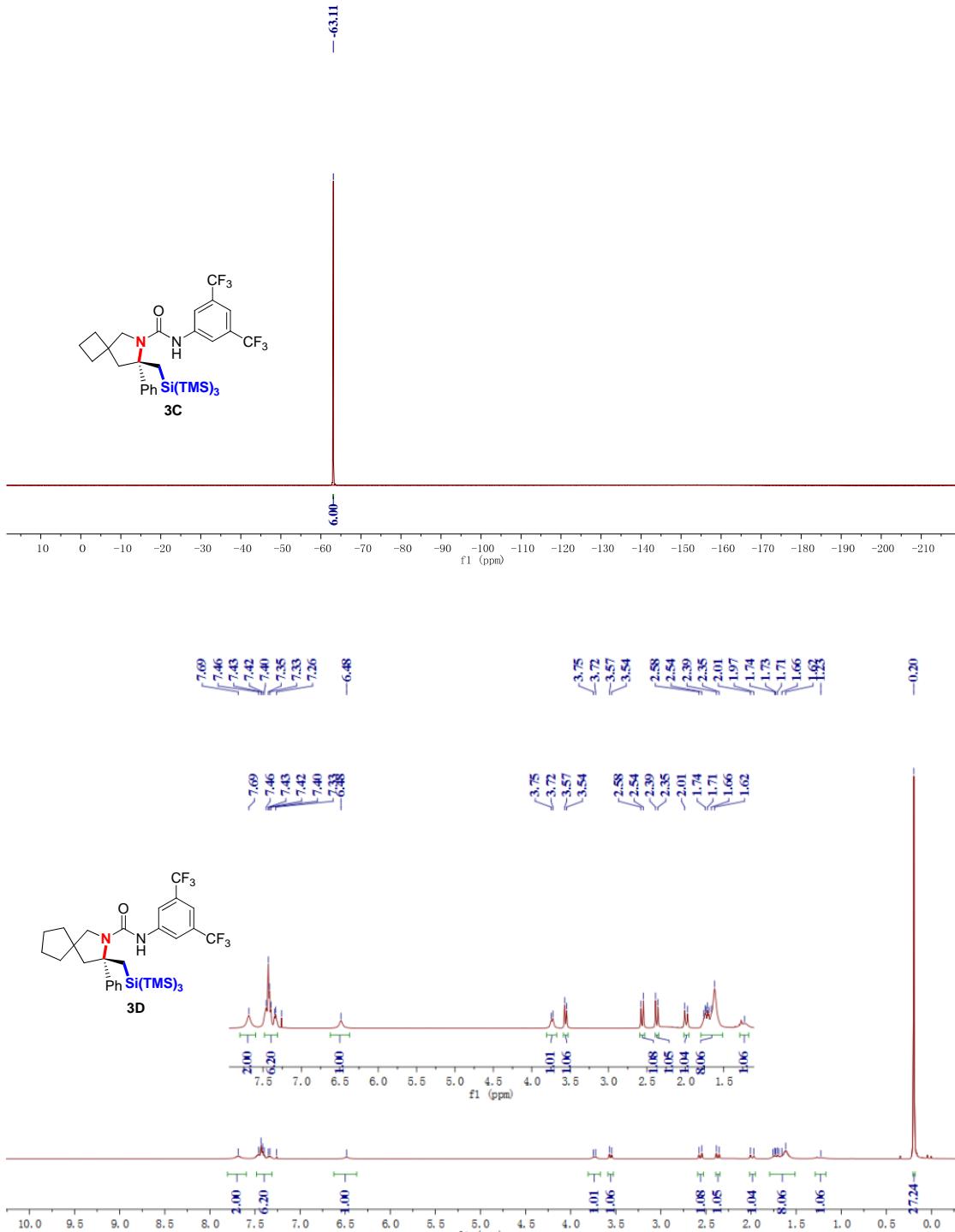
NMR Spectra

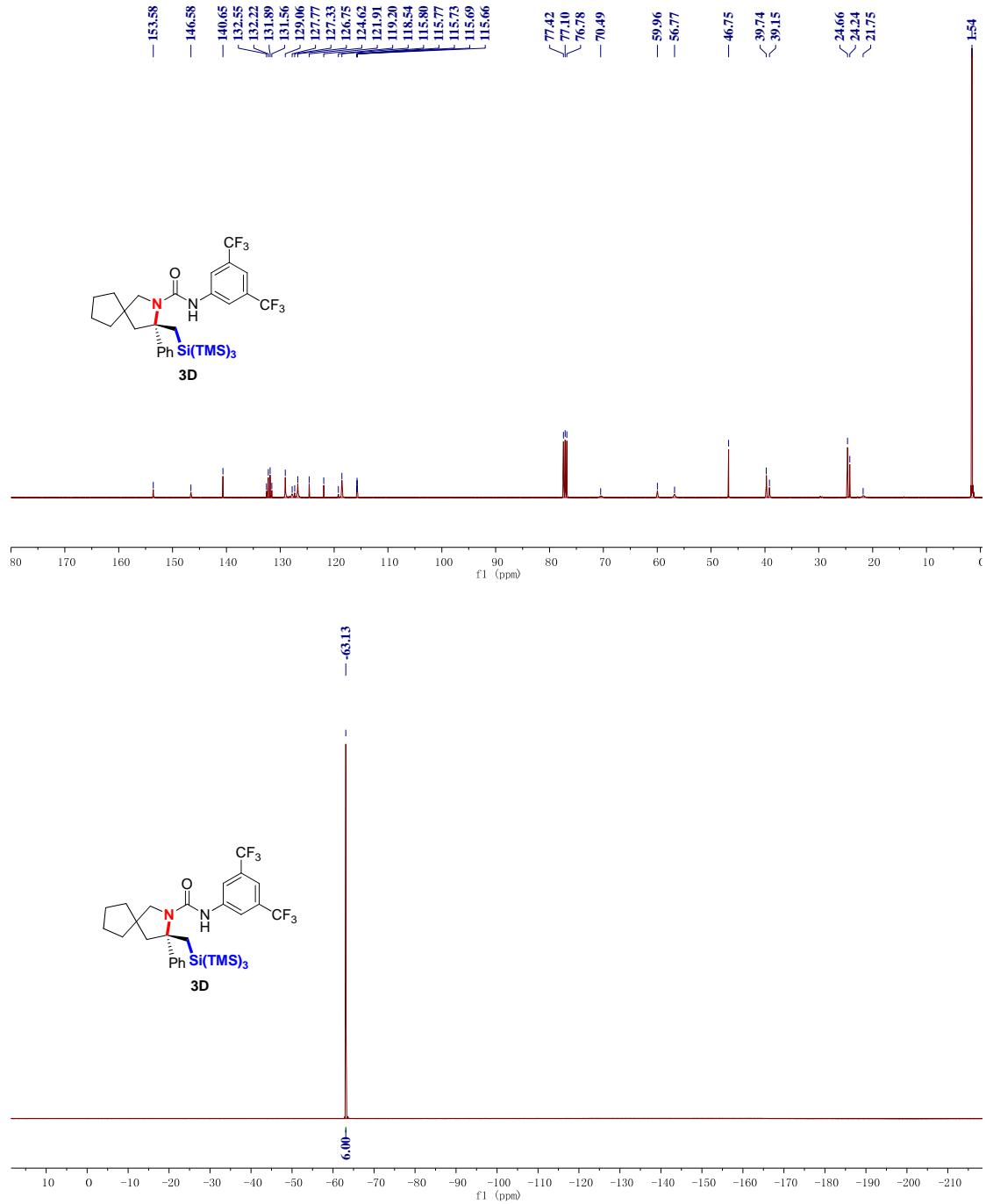


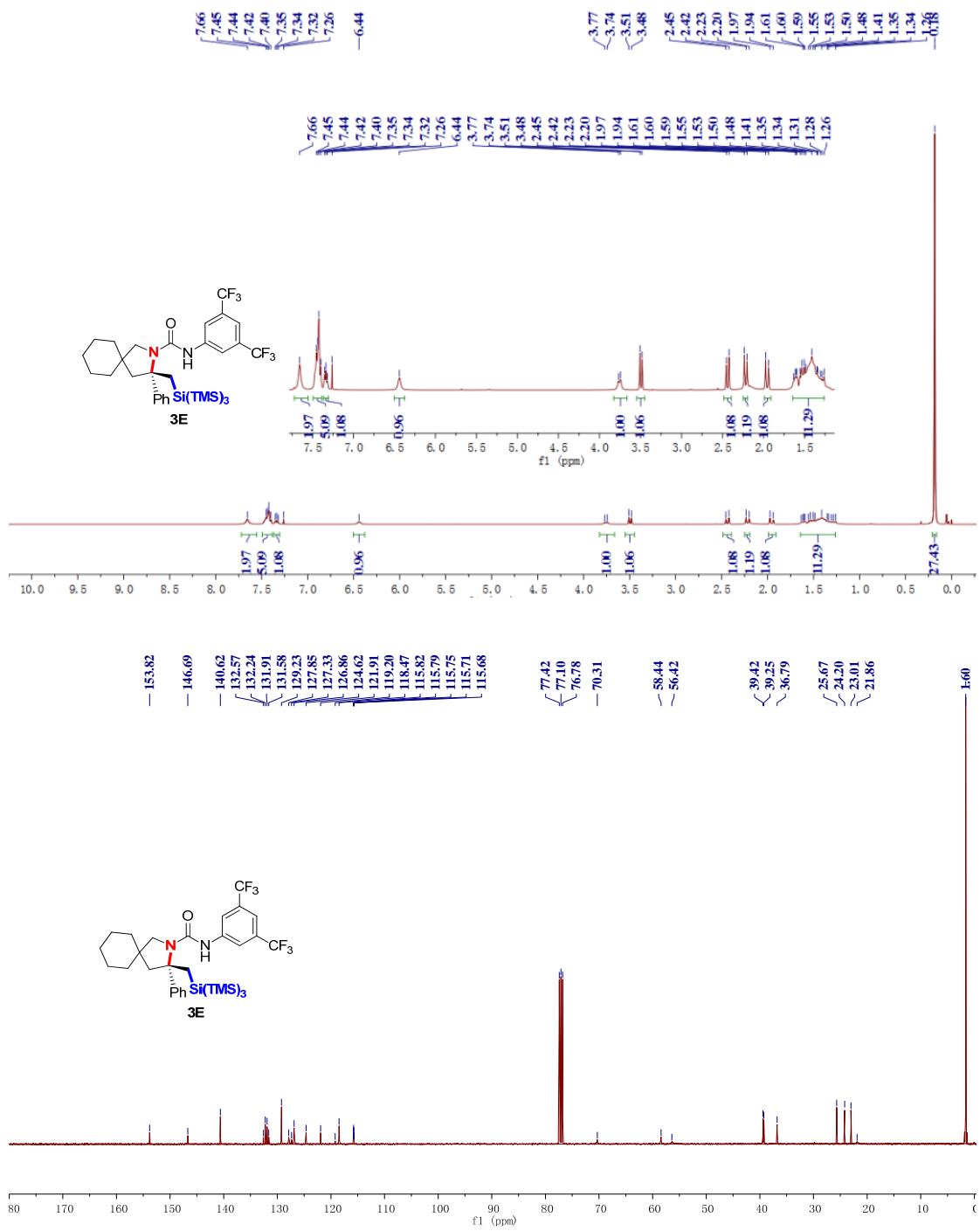


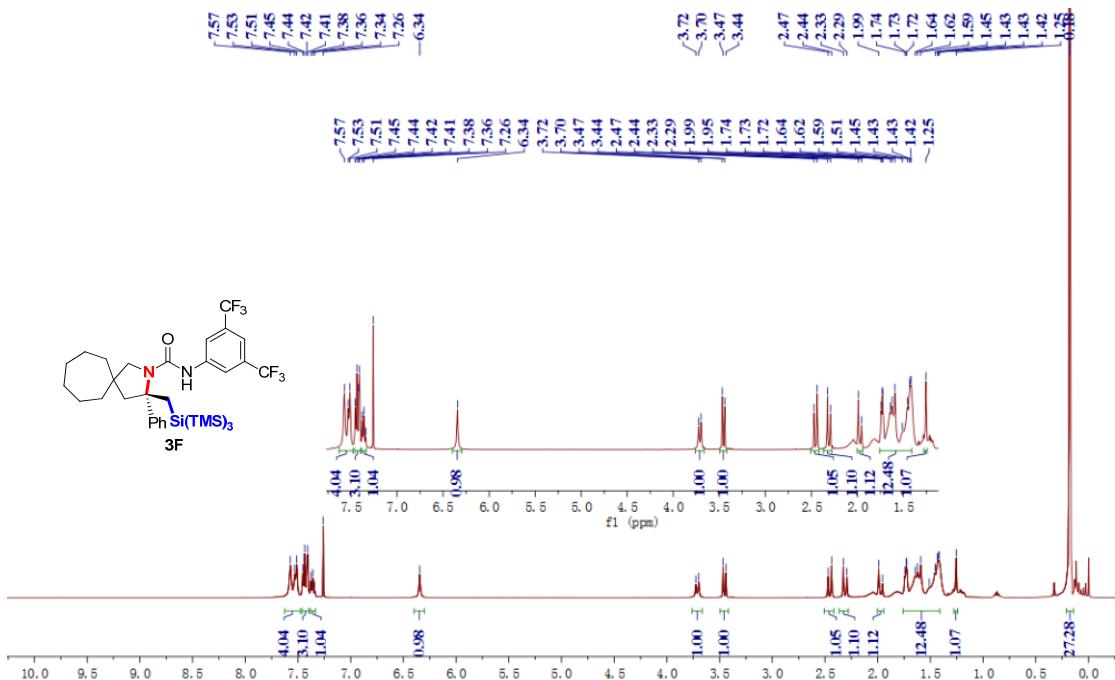
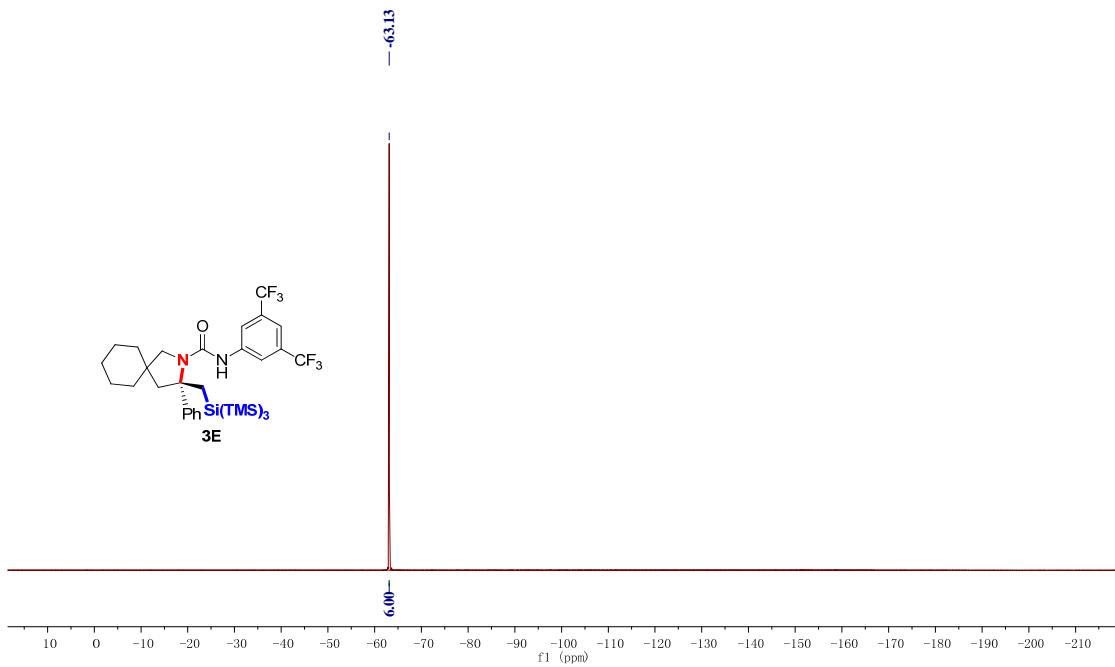


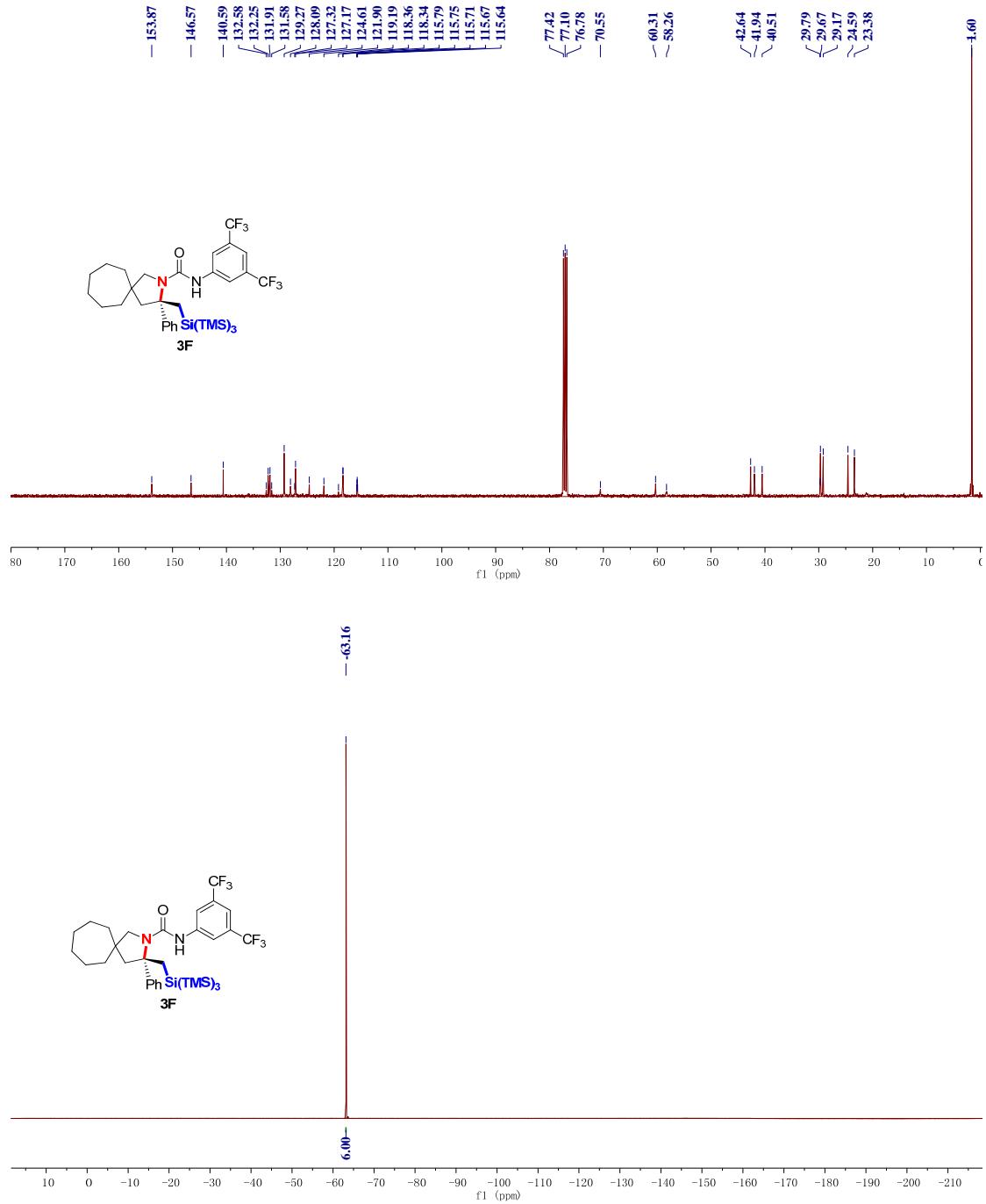


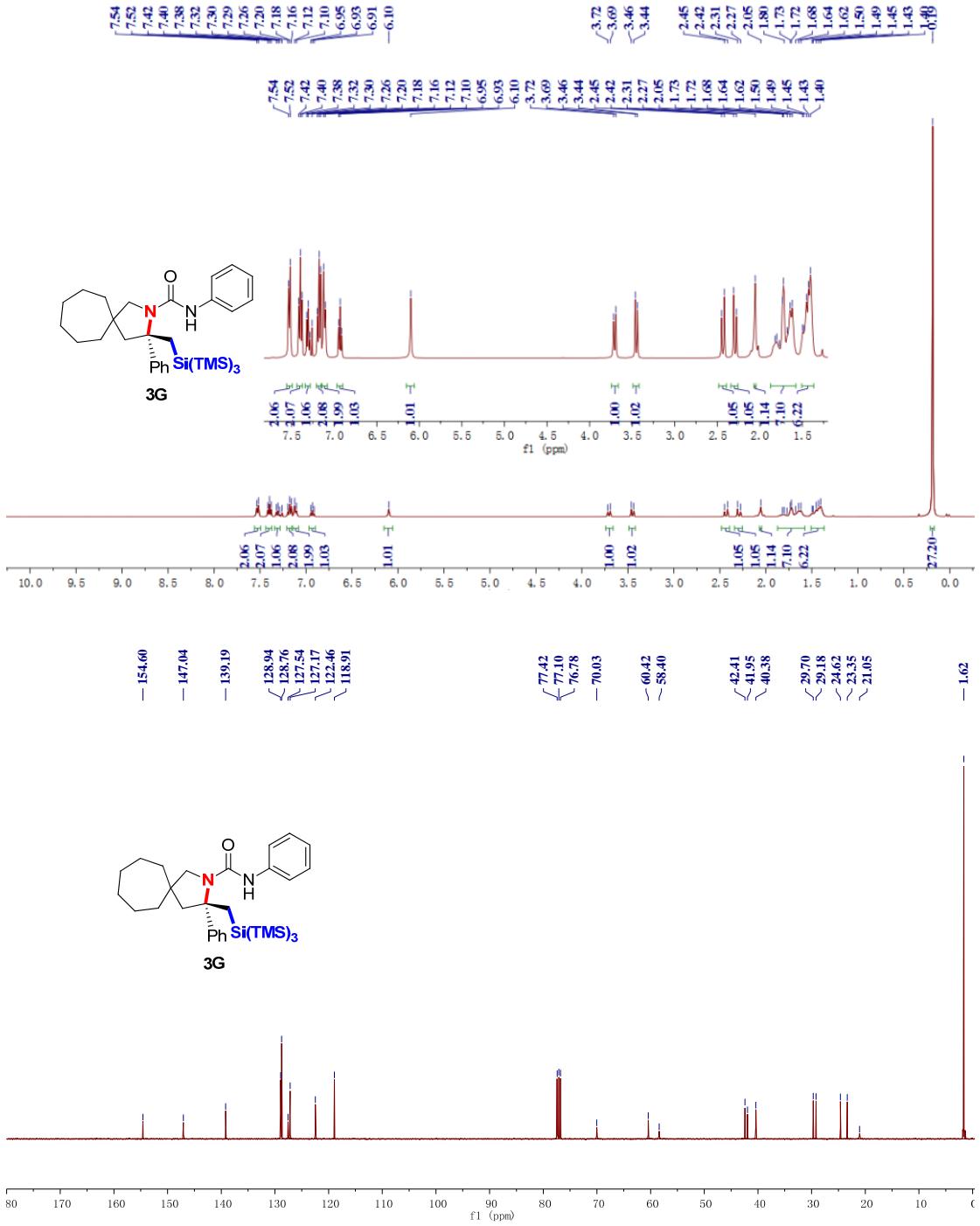




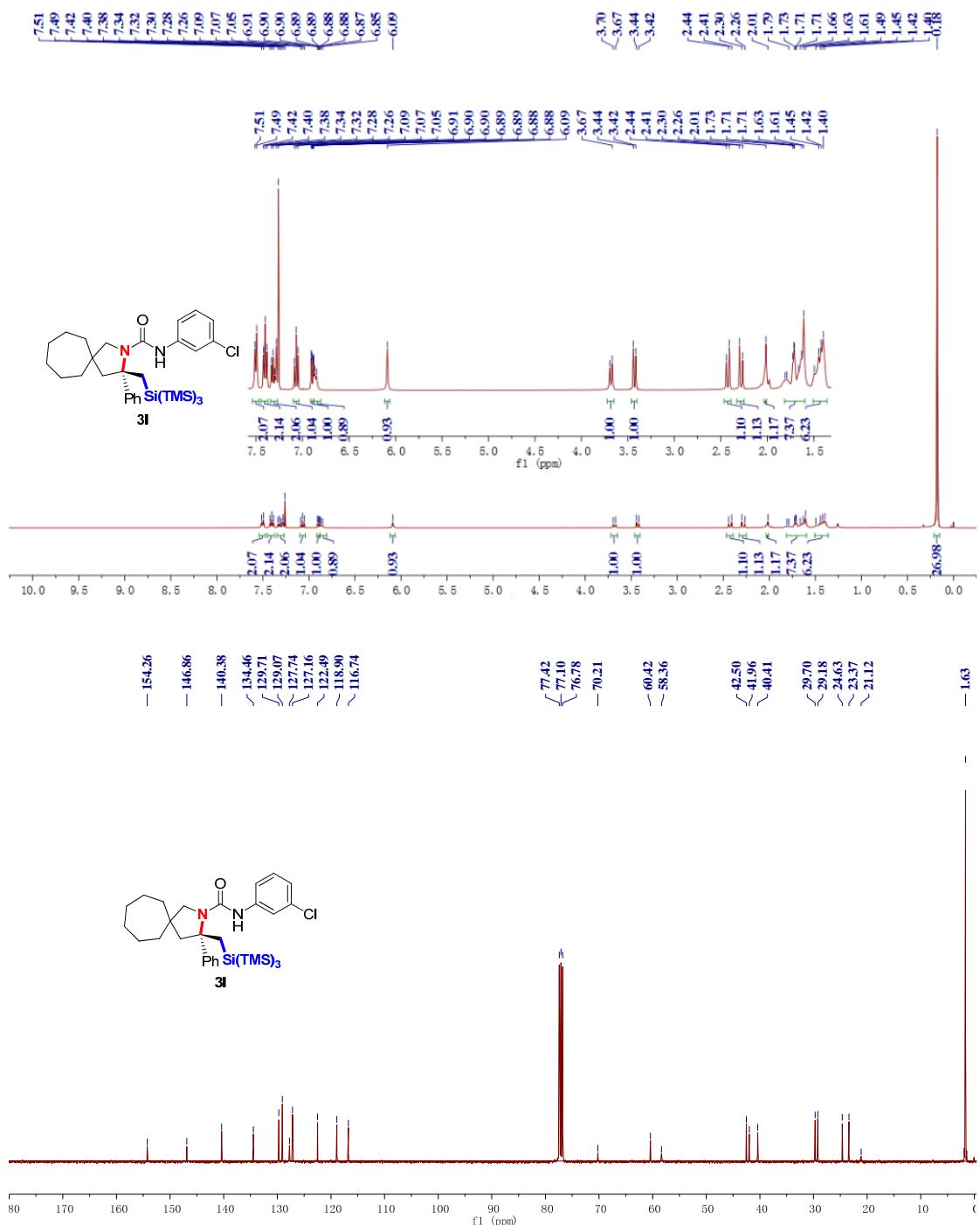


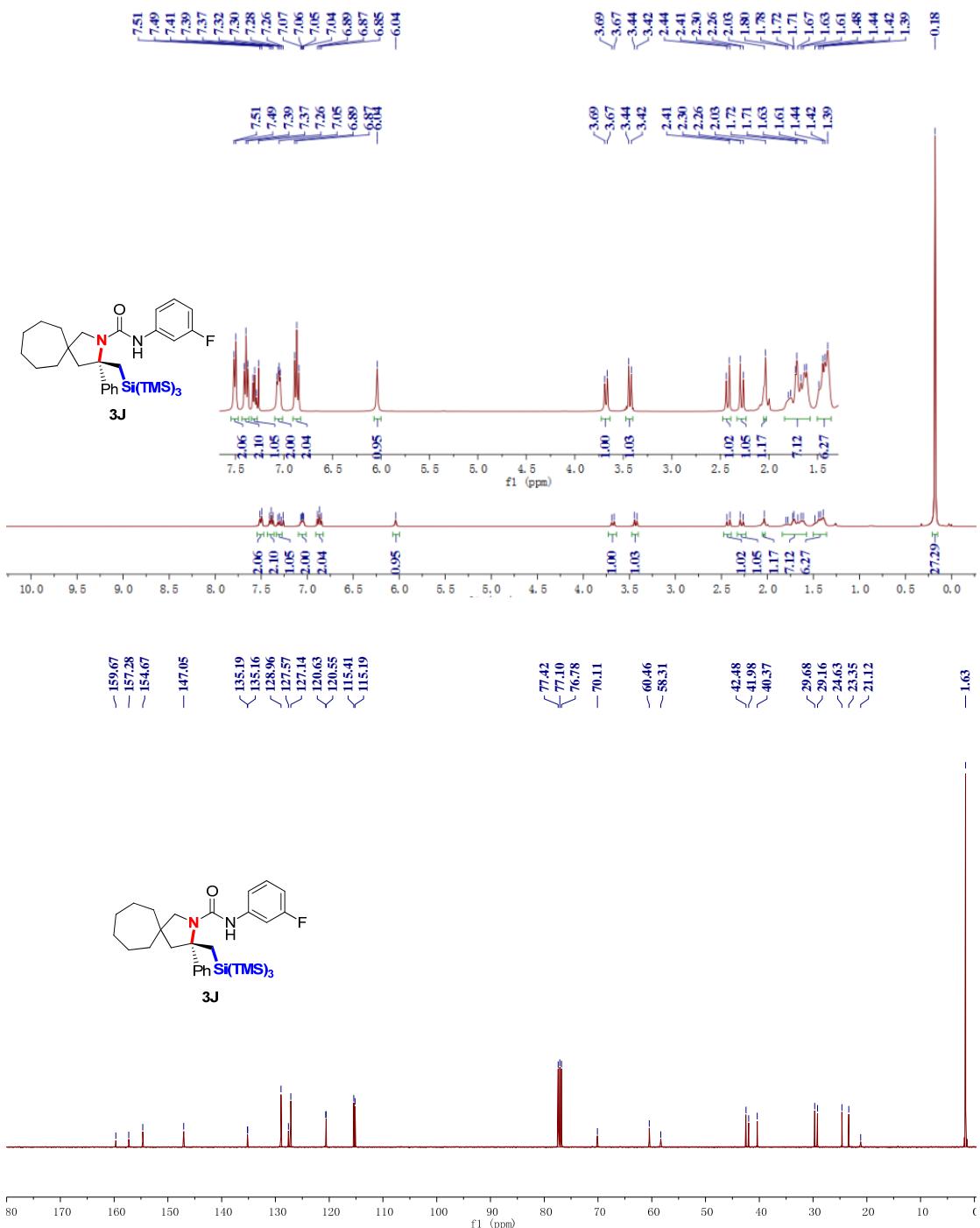


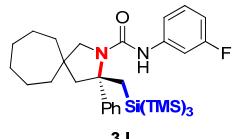




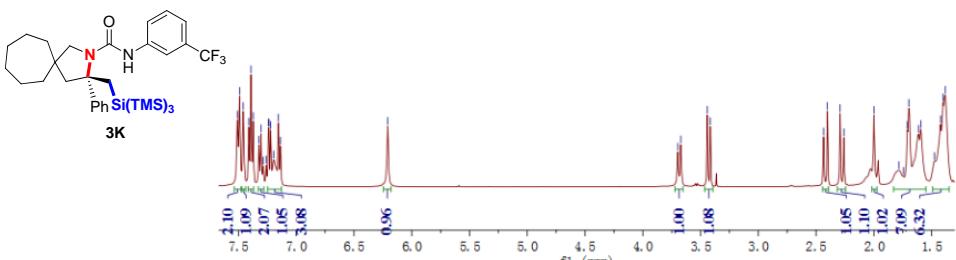
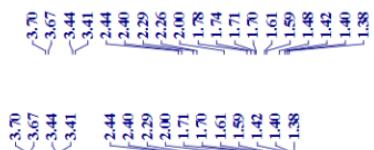
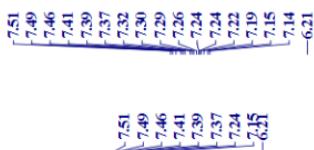
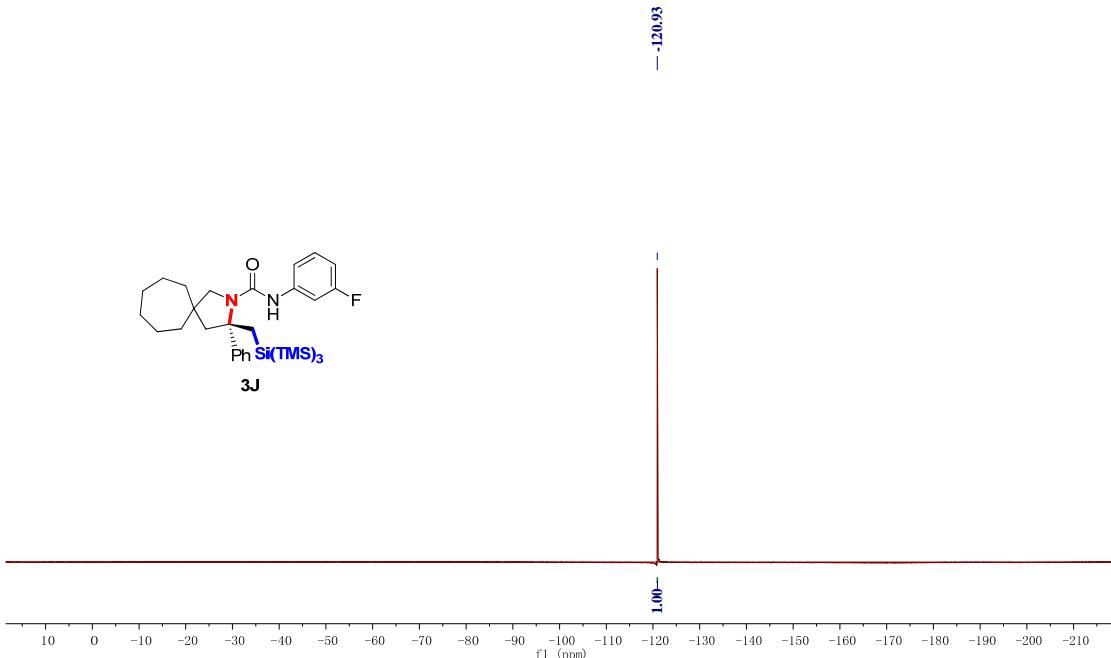




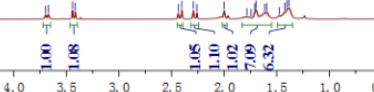
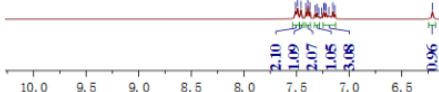


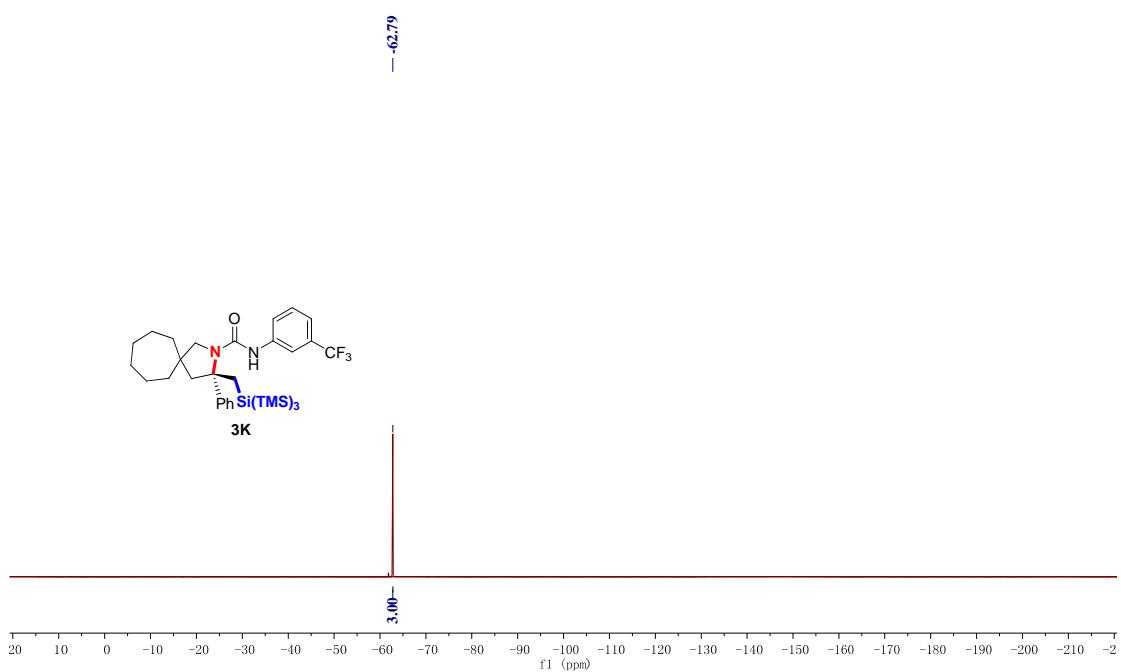
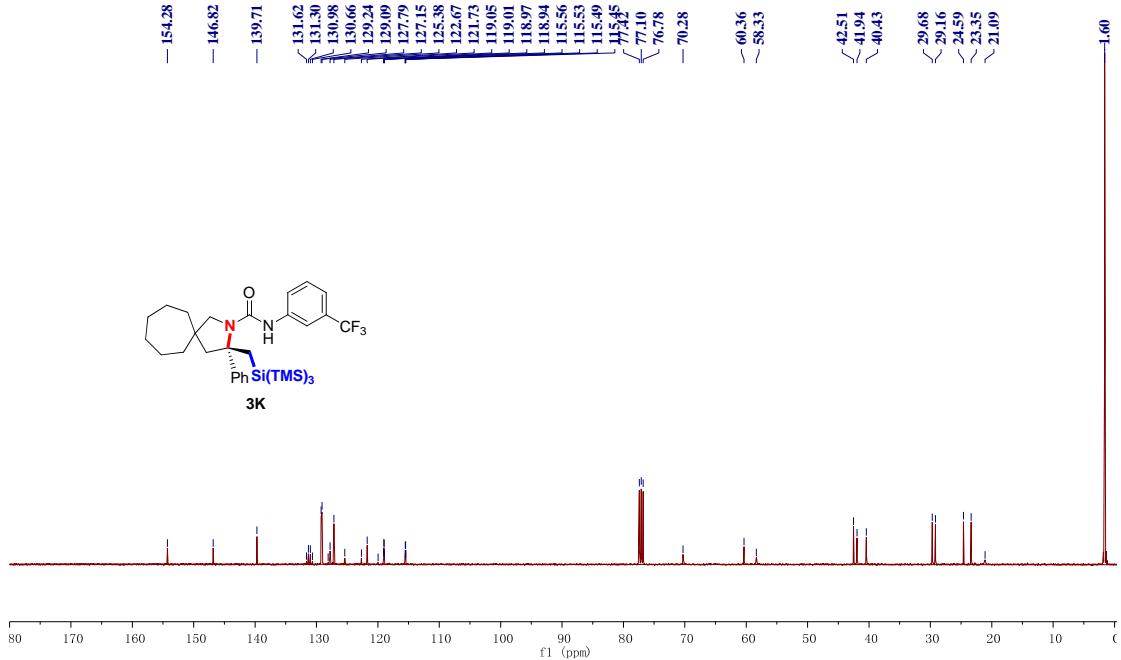


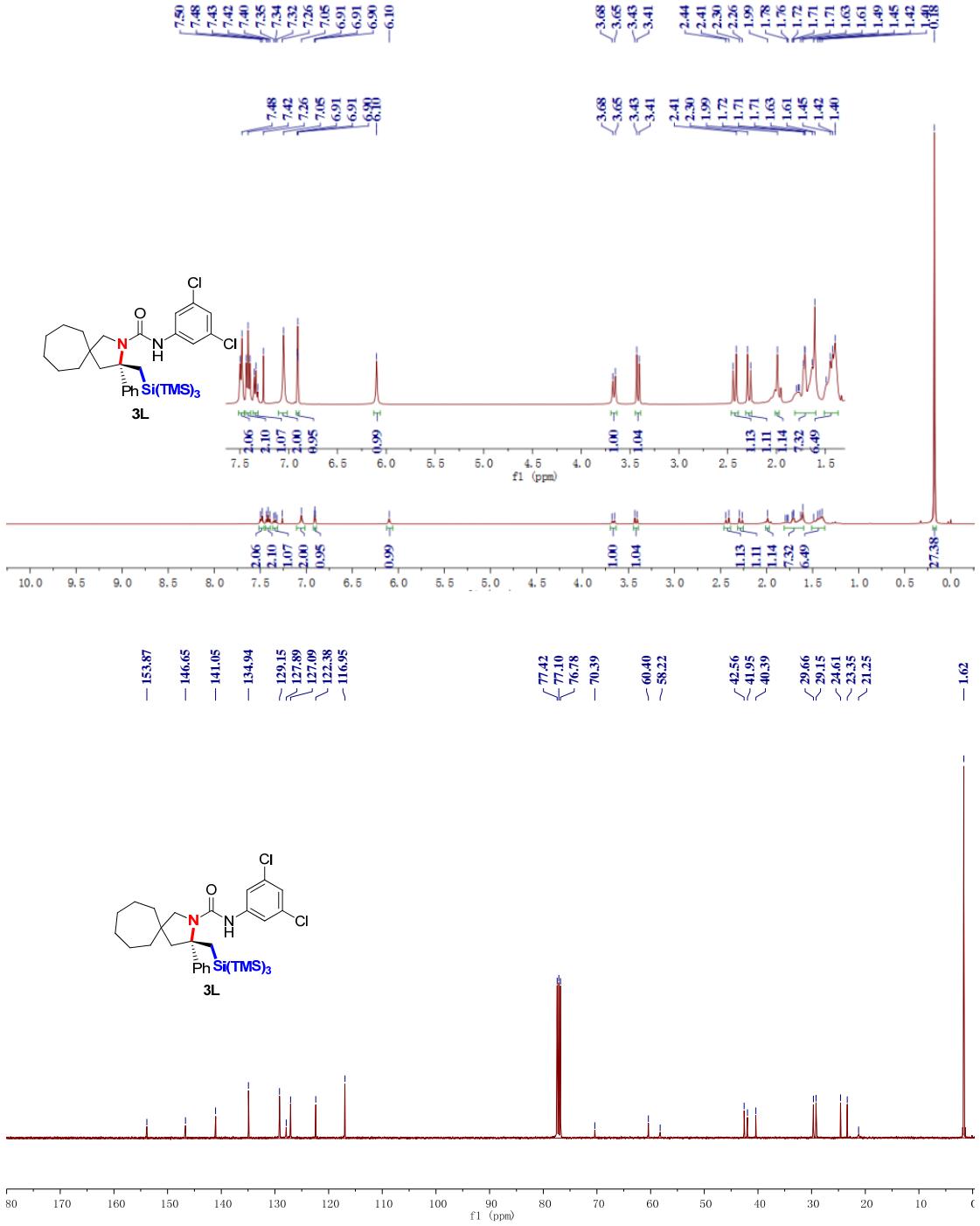
3J

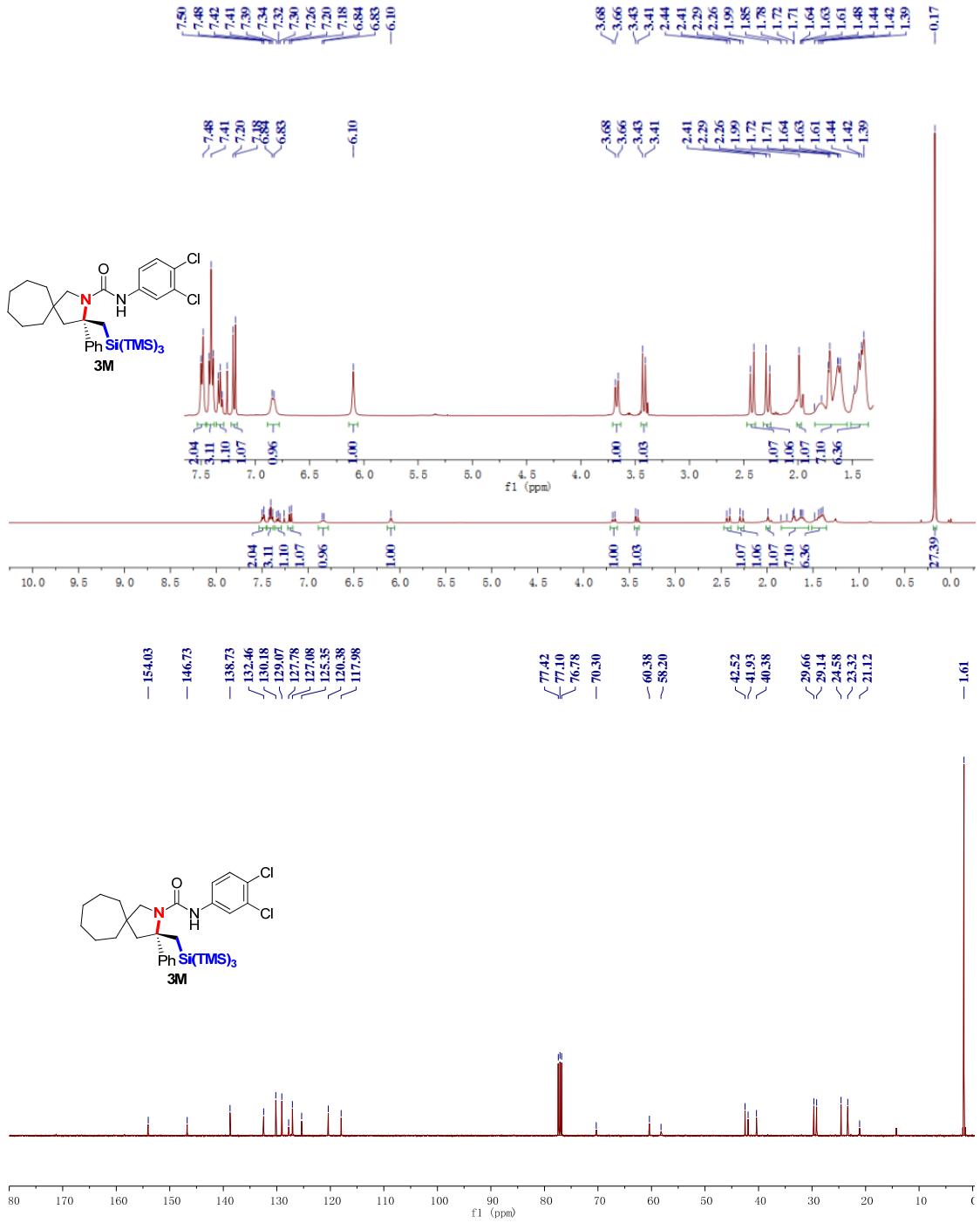


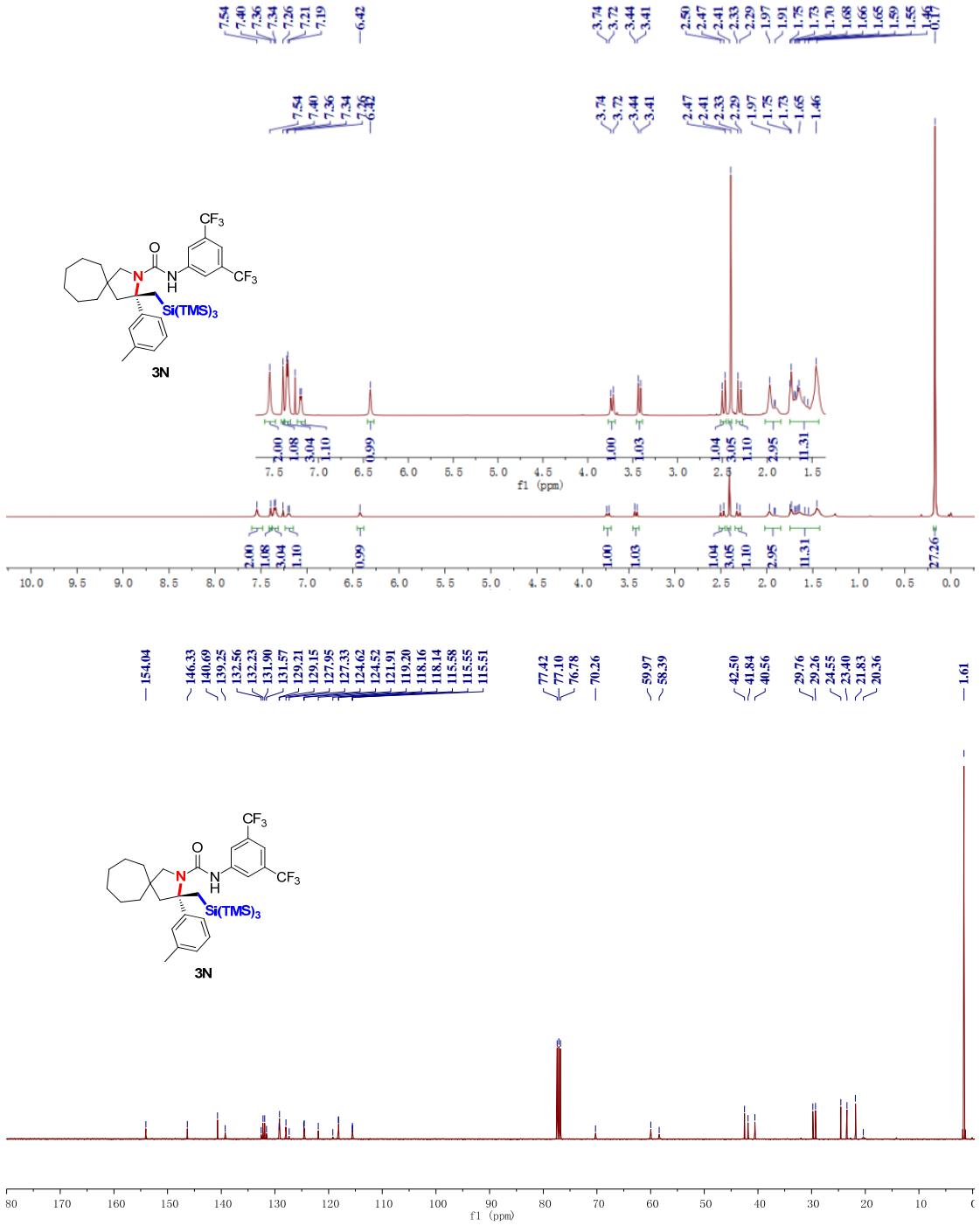
3K

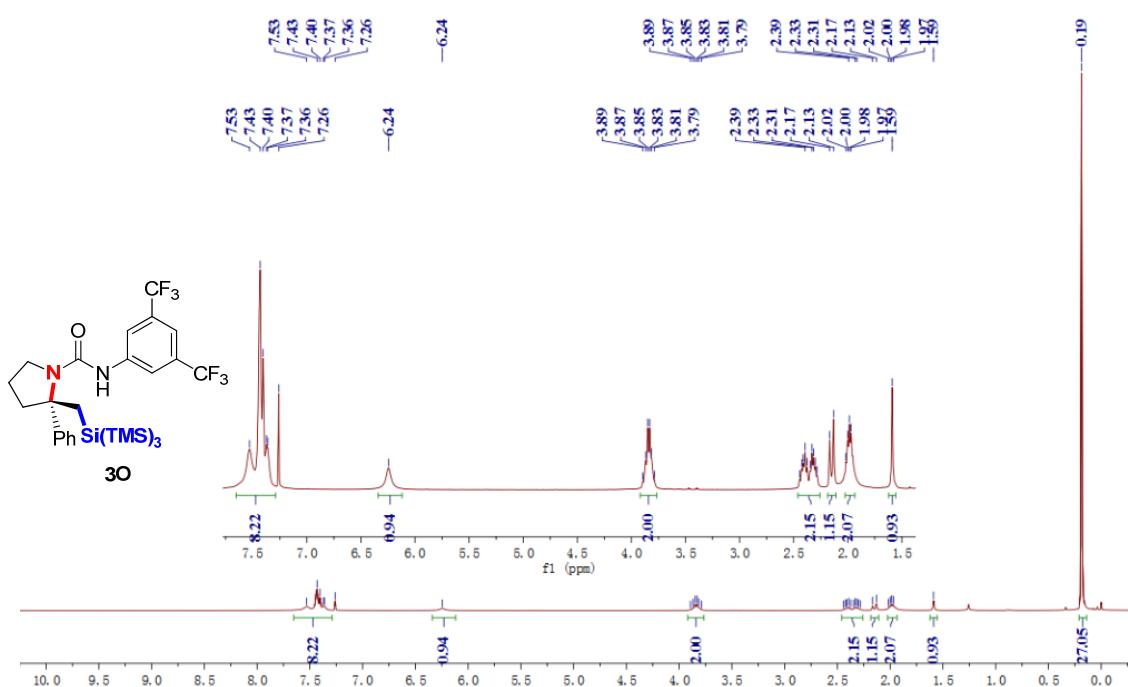
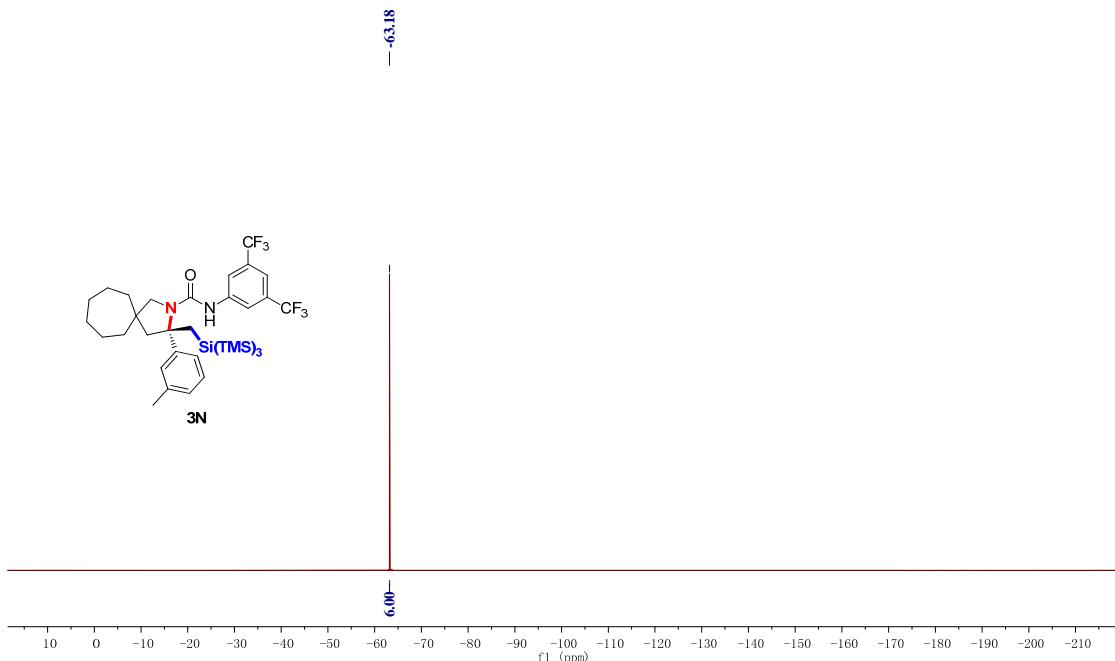


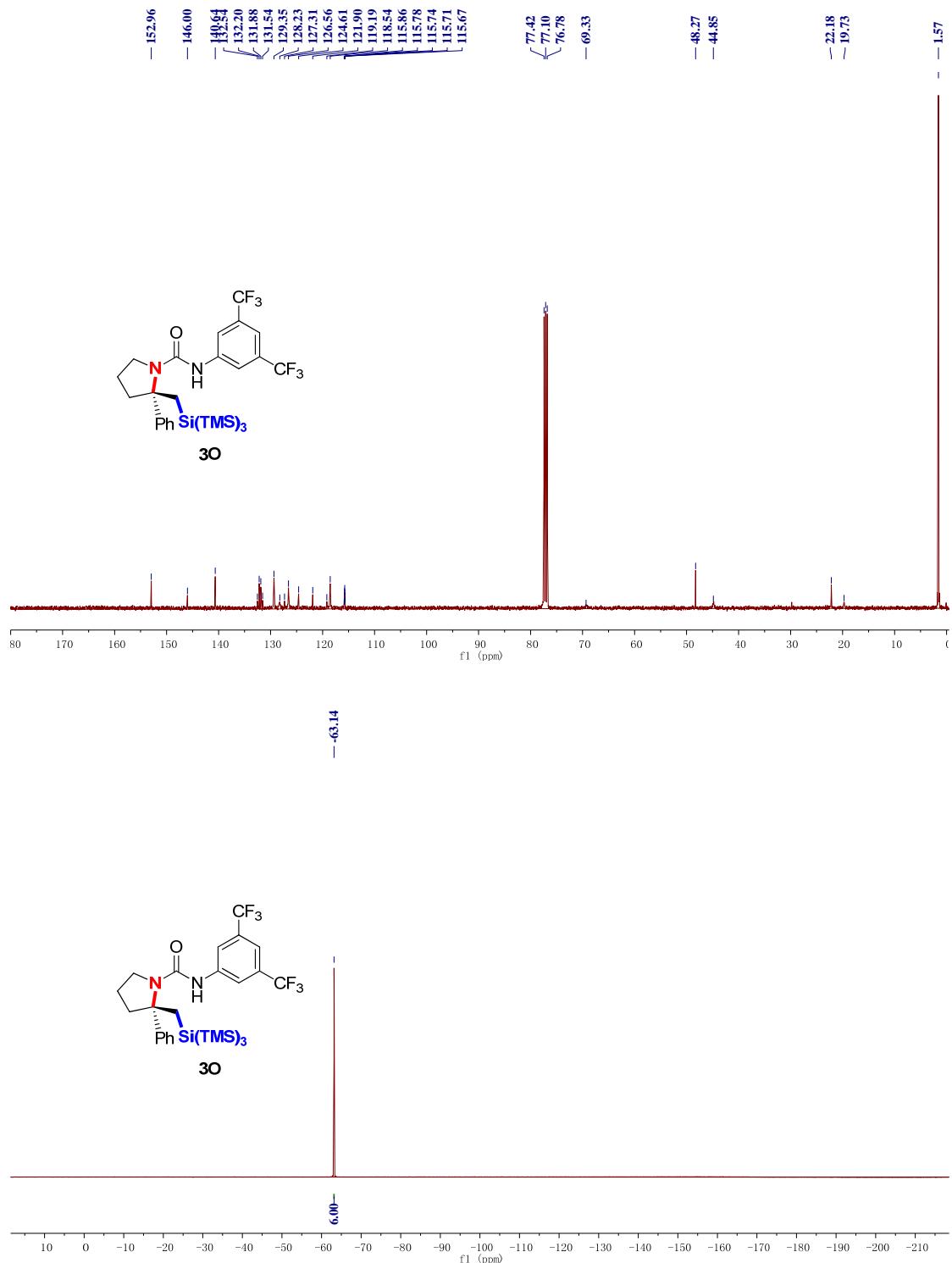


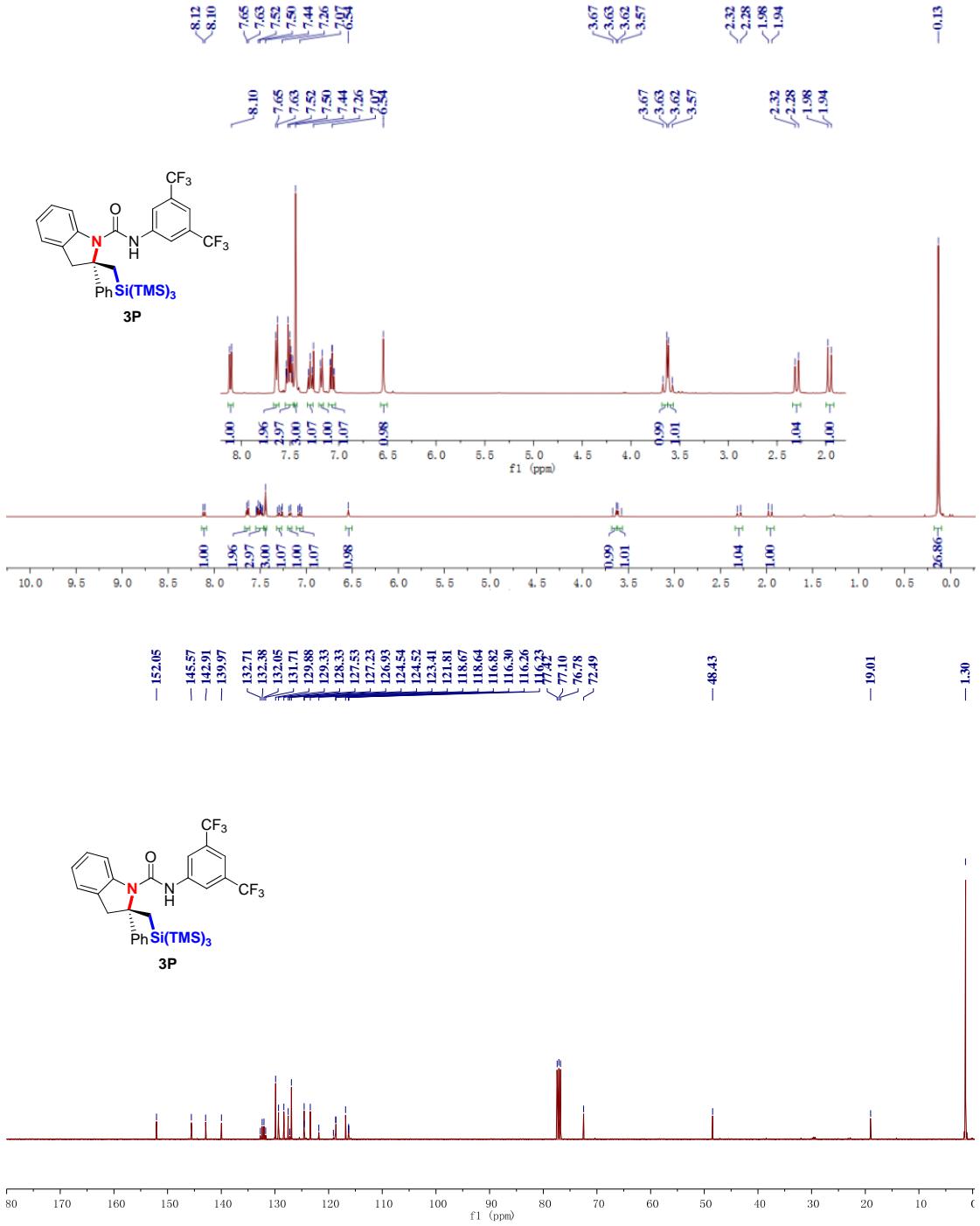


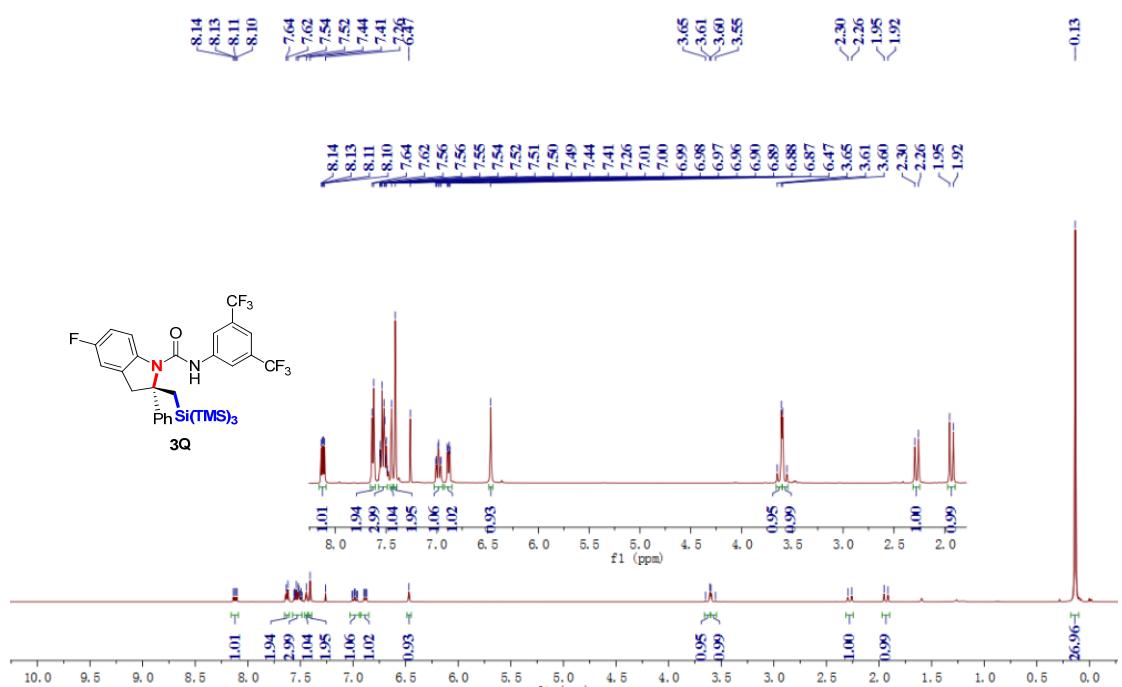
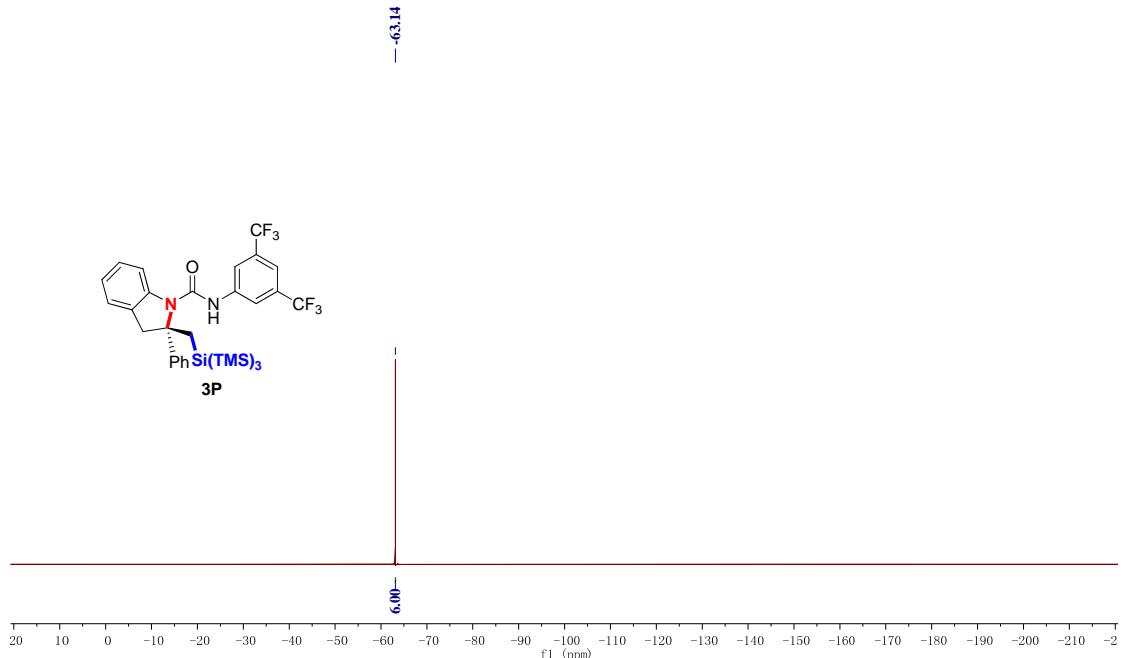


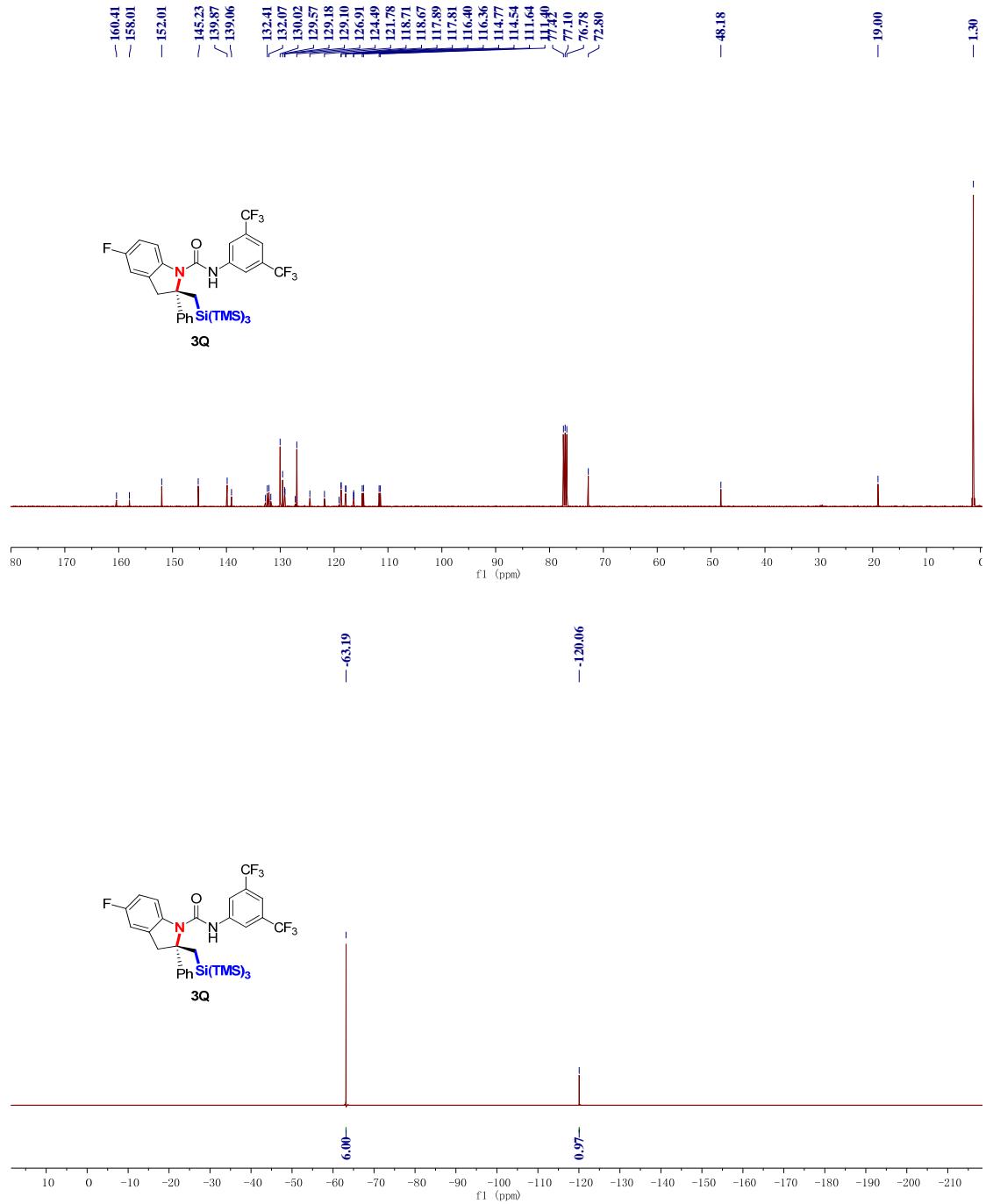


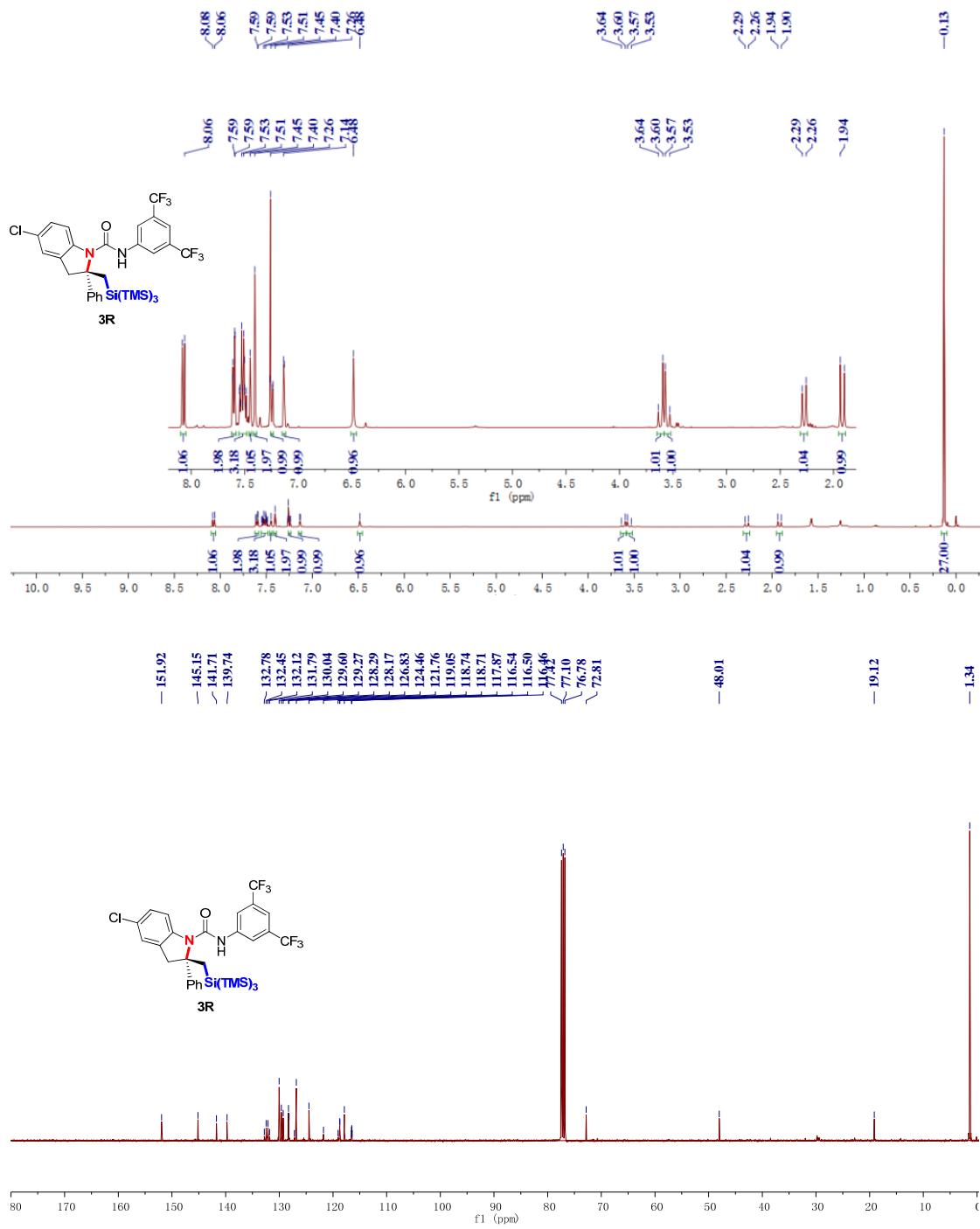


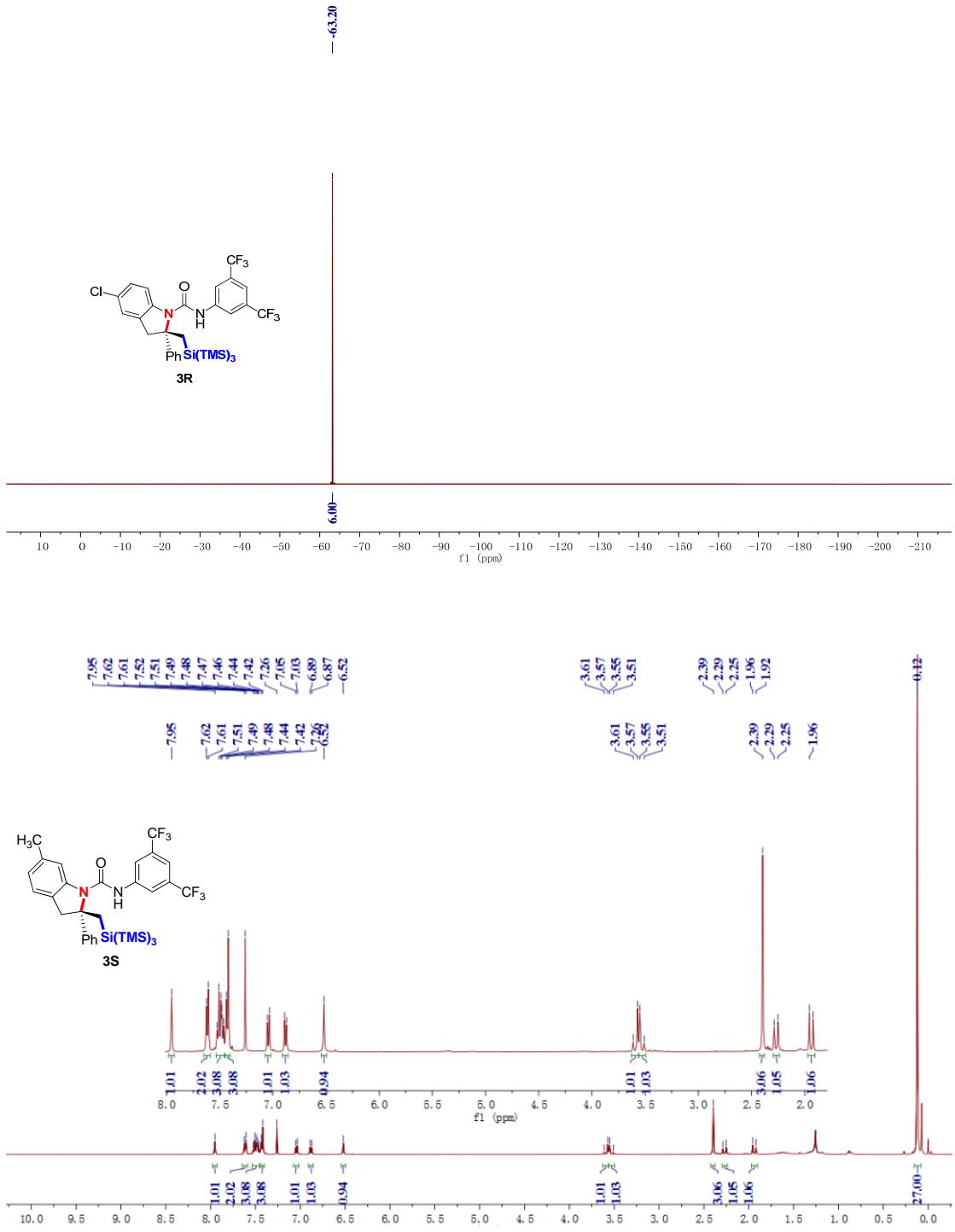


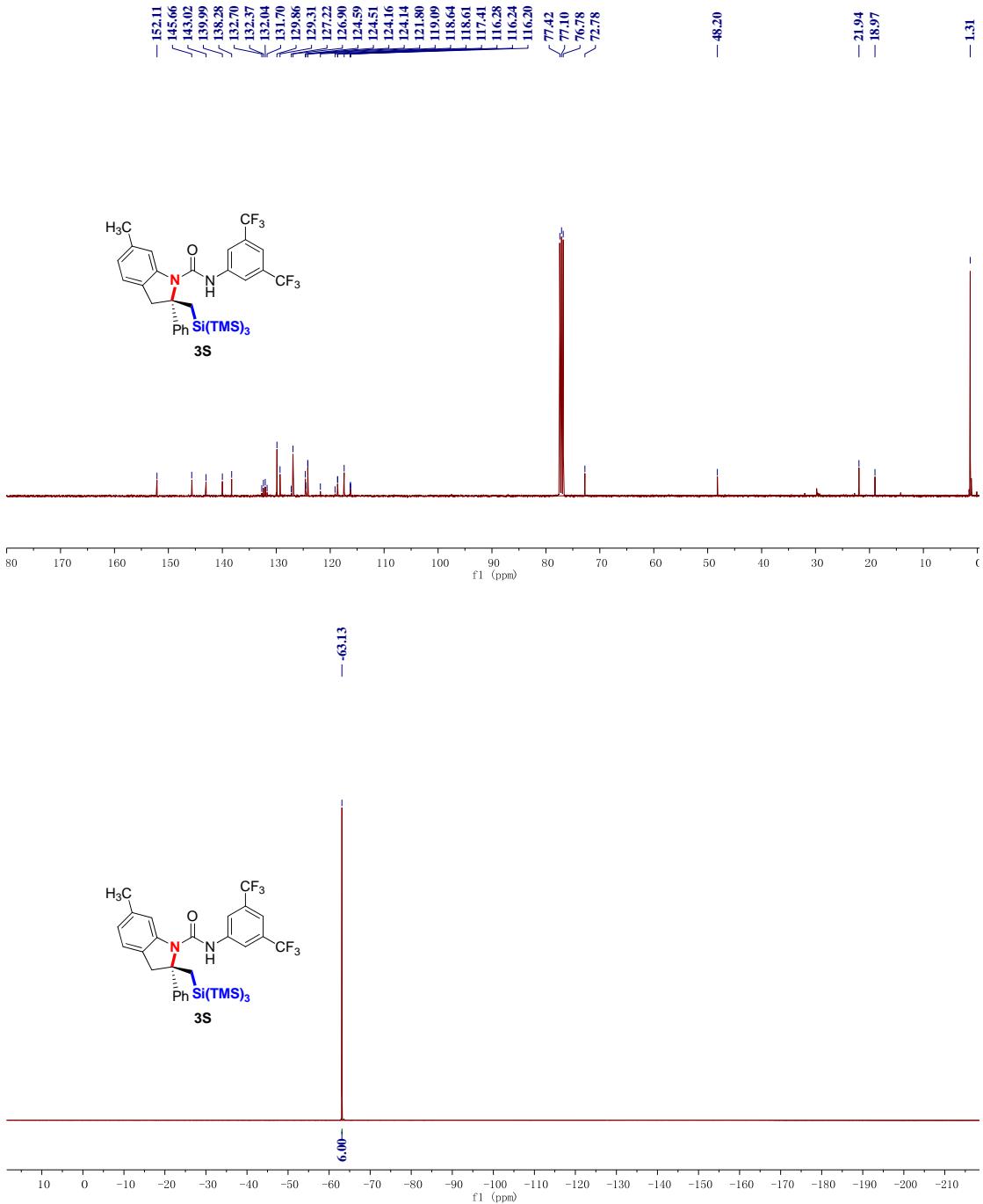


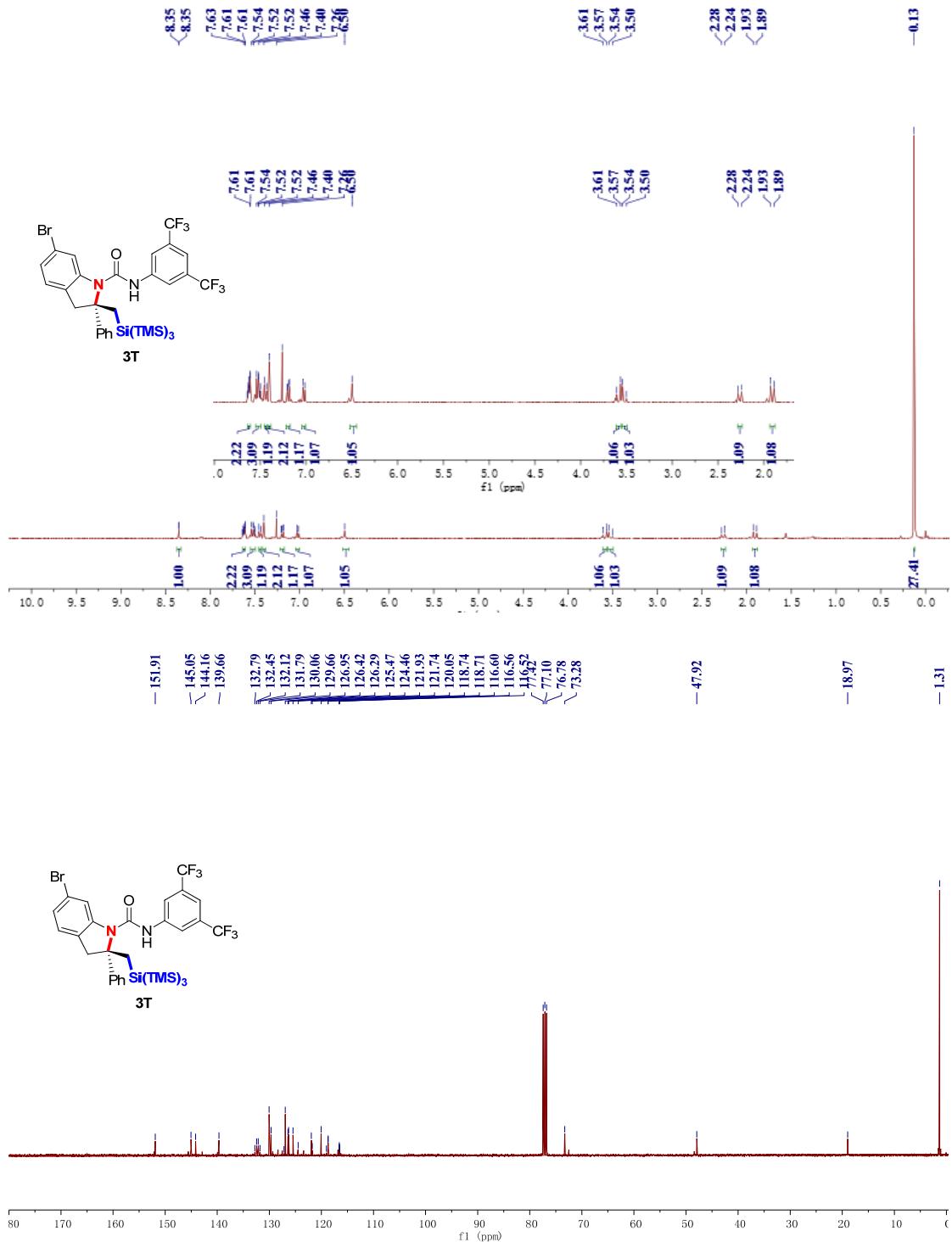


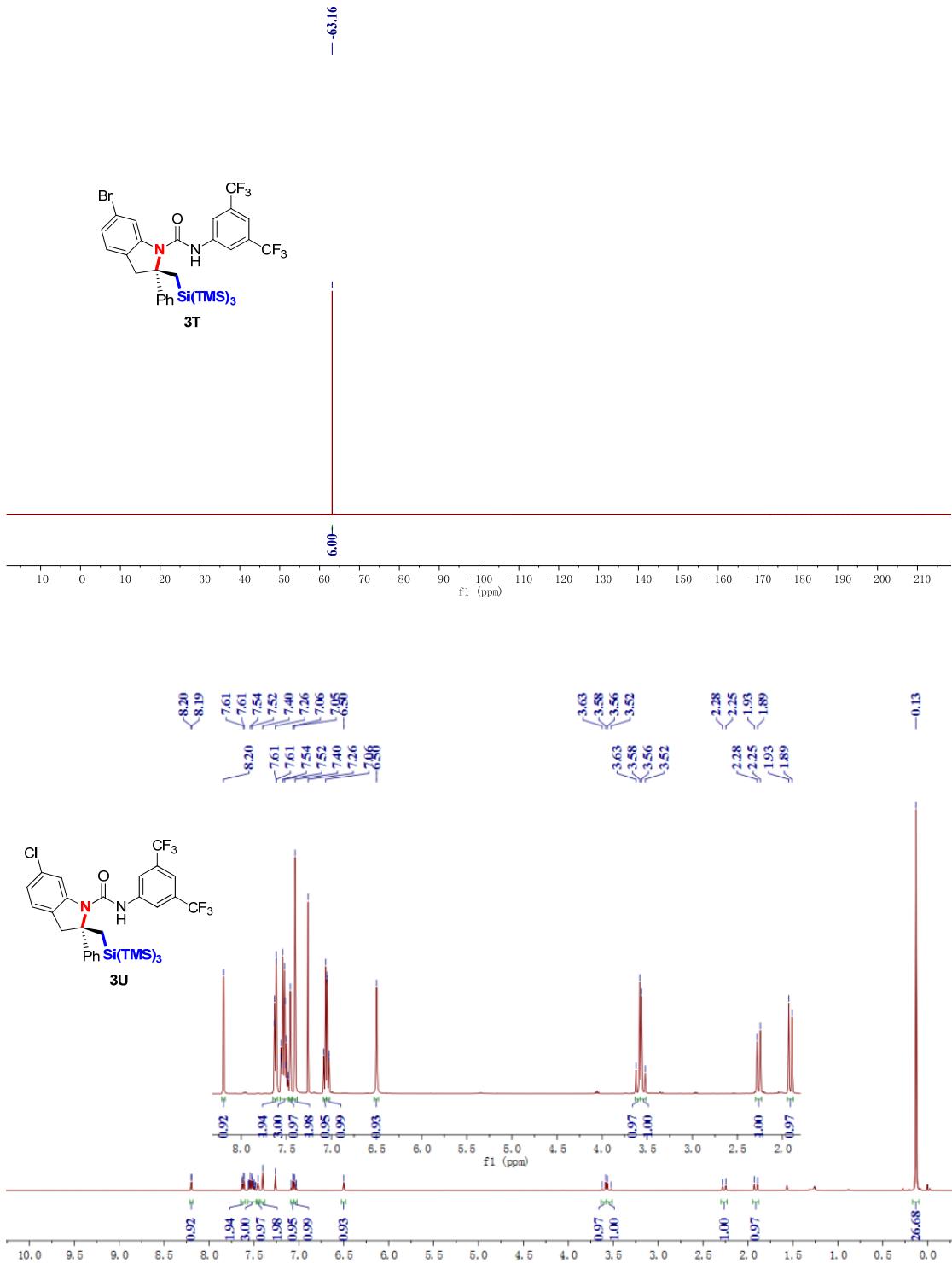


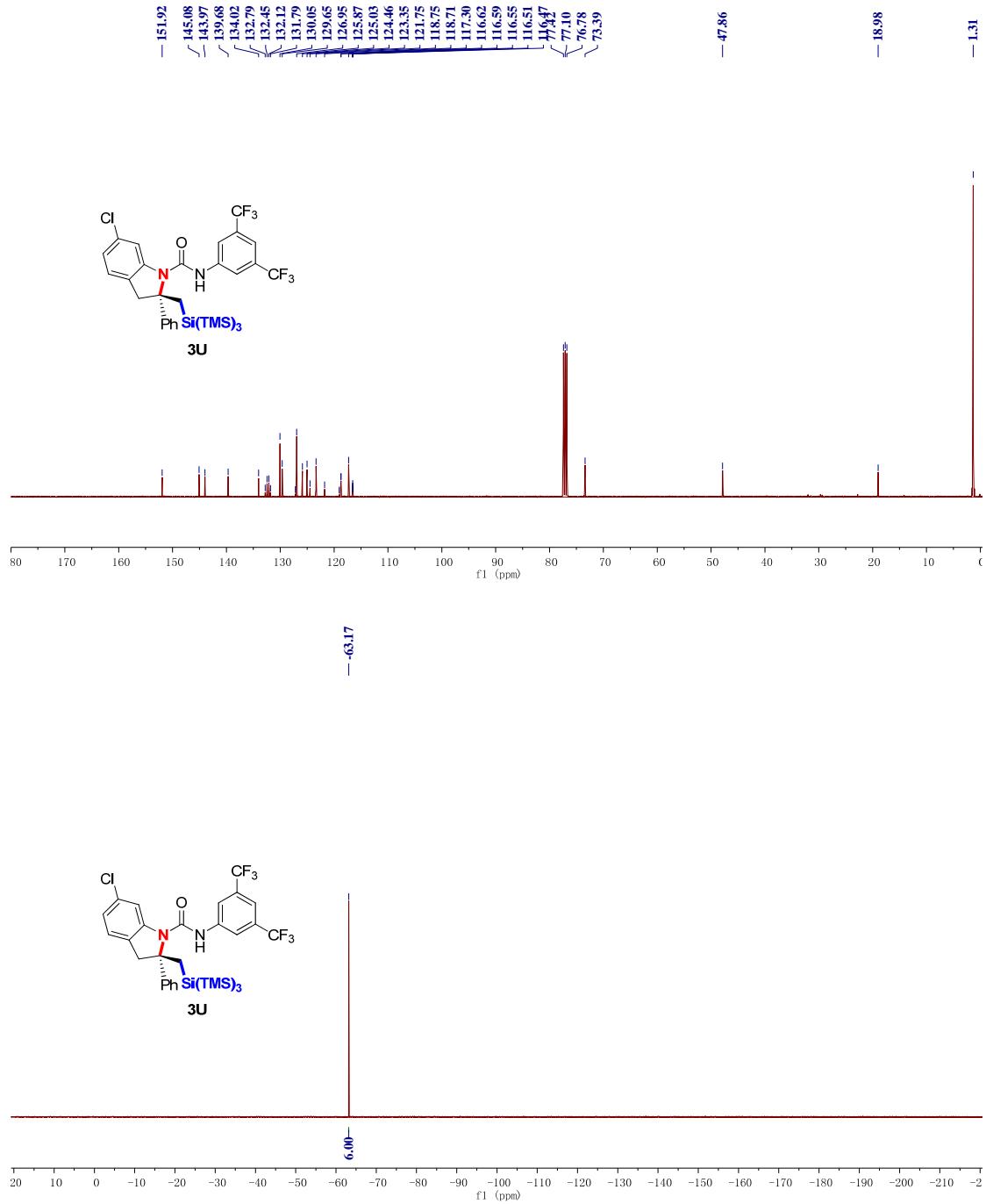


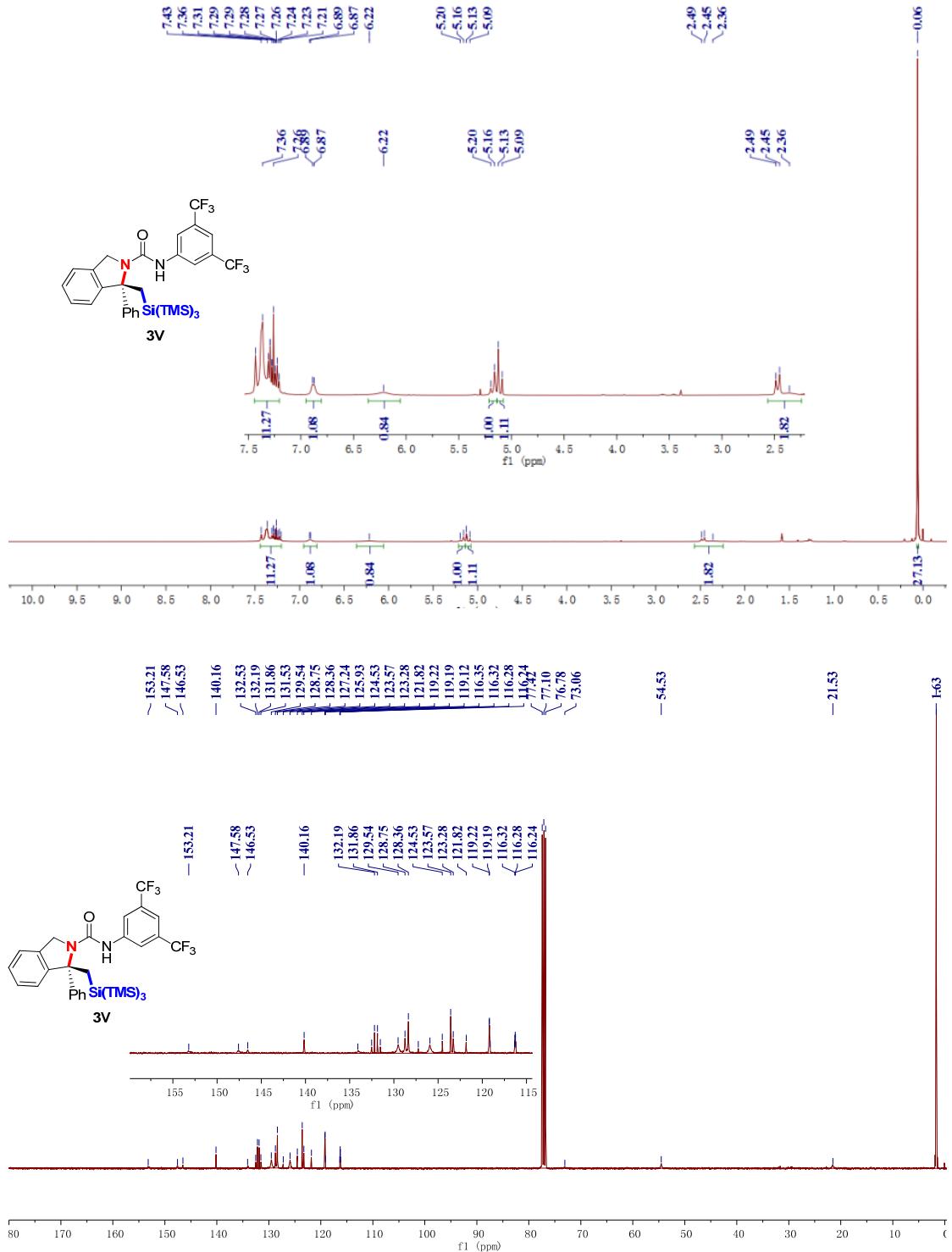


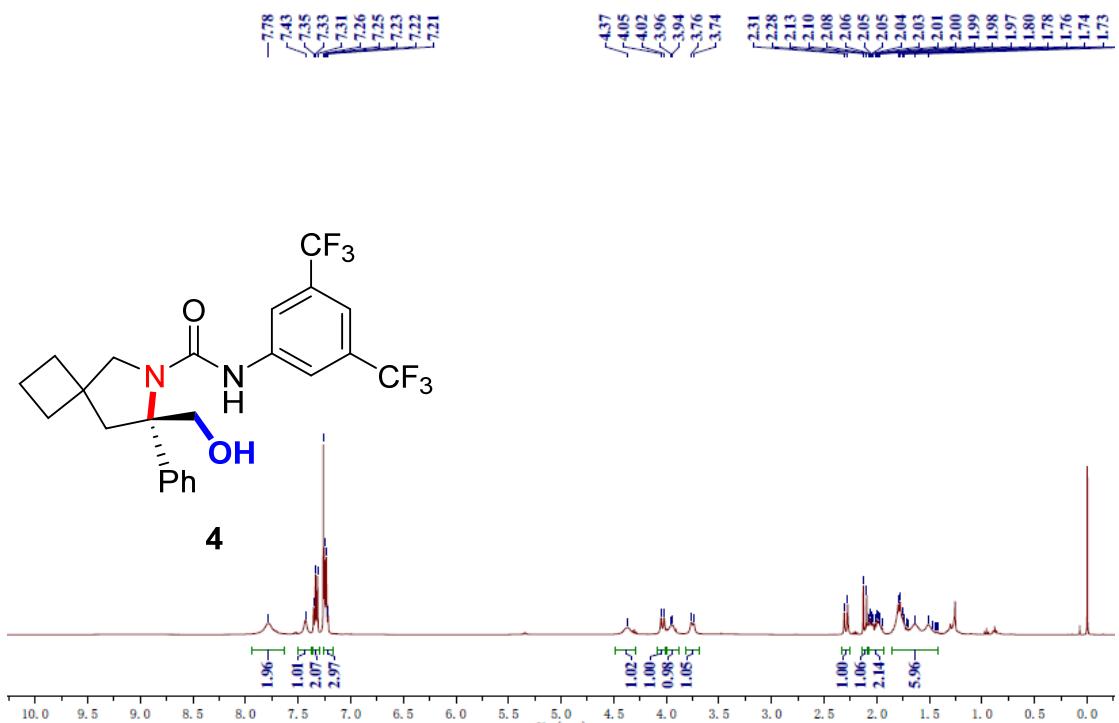
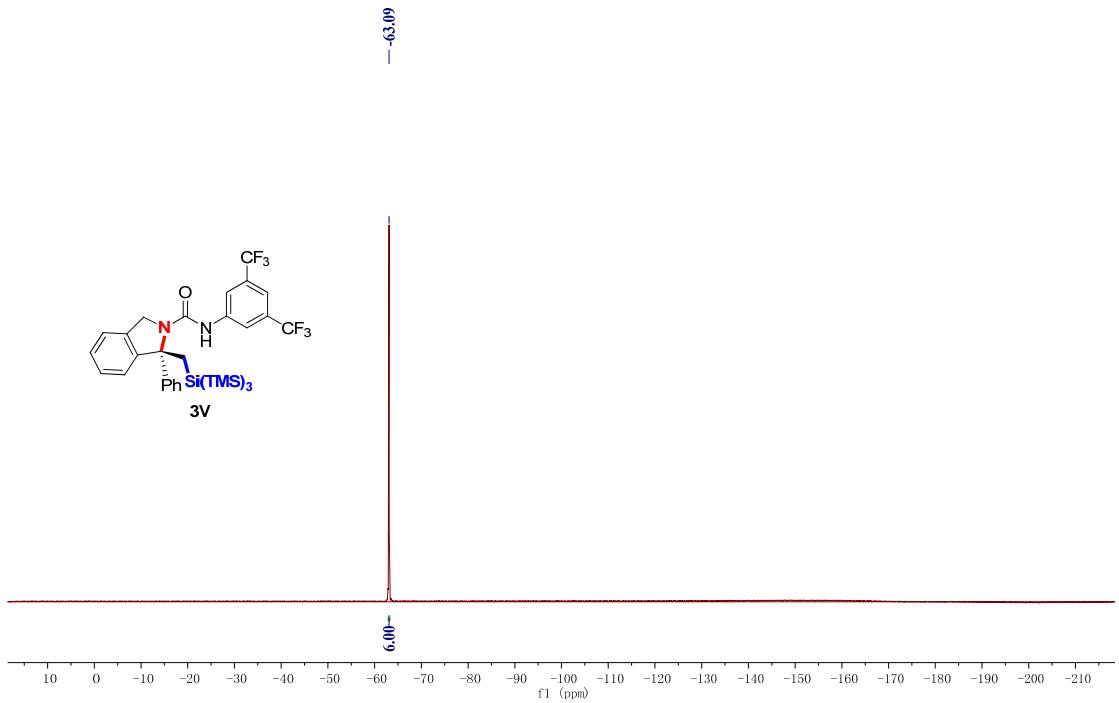


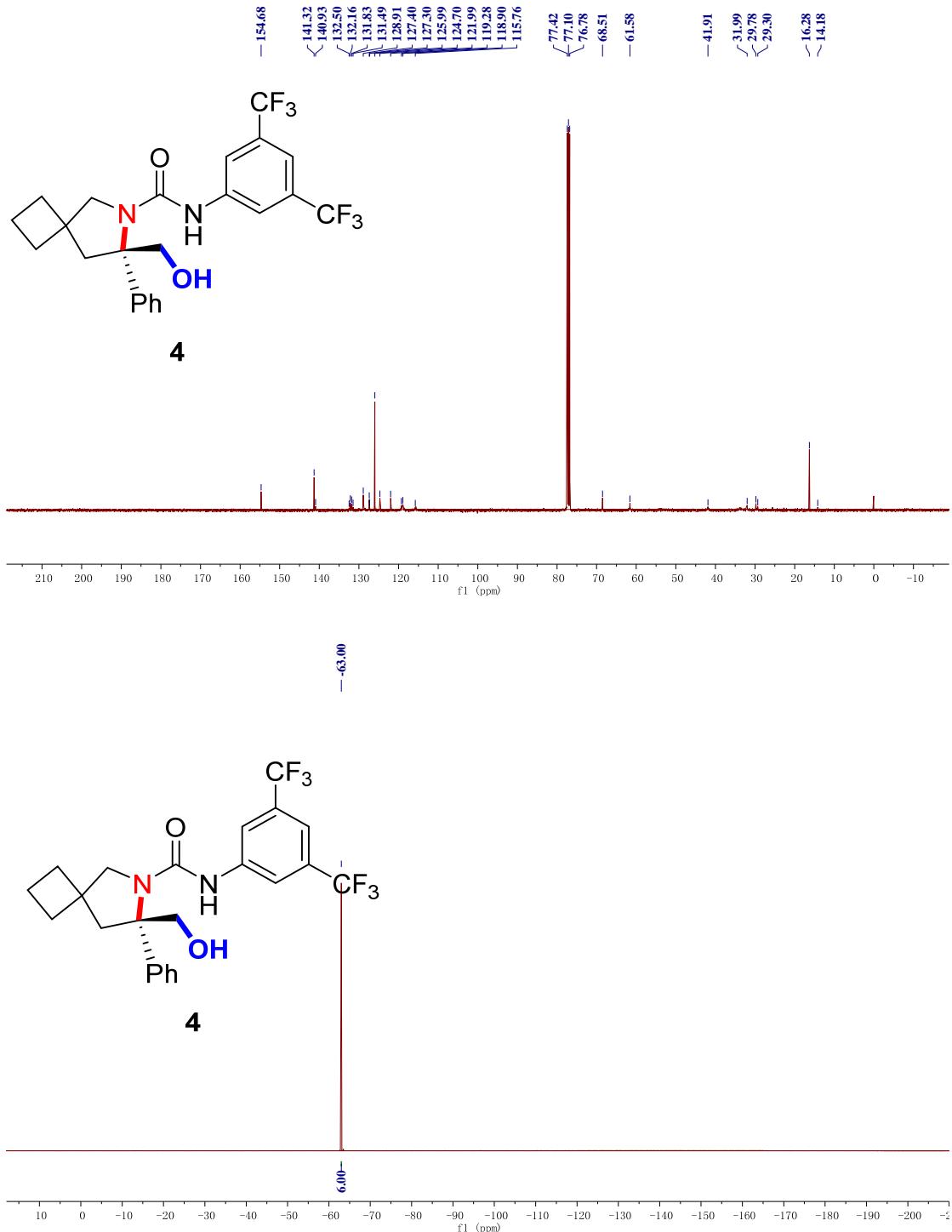


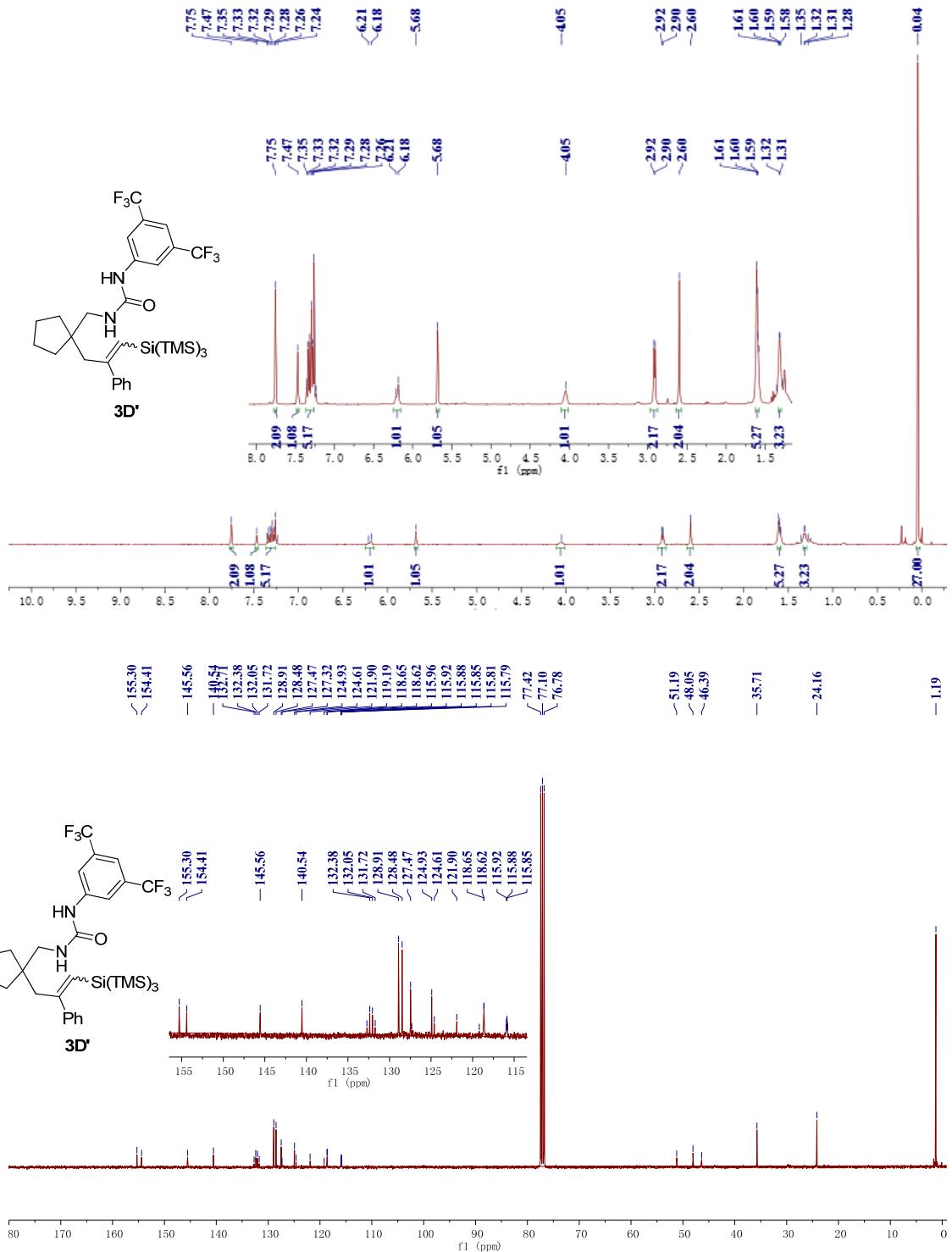


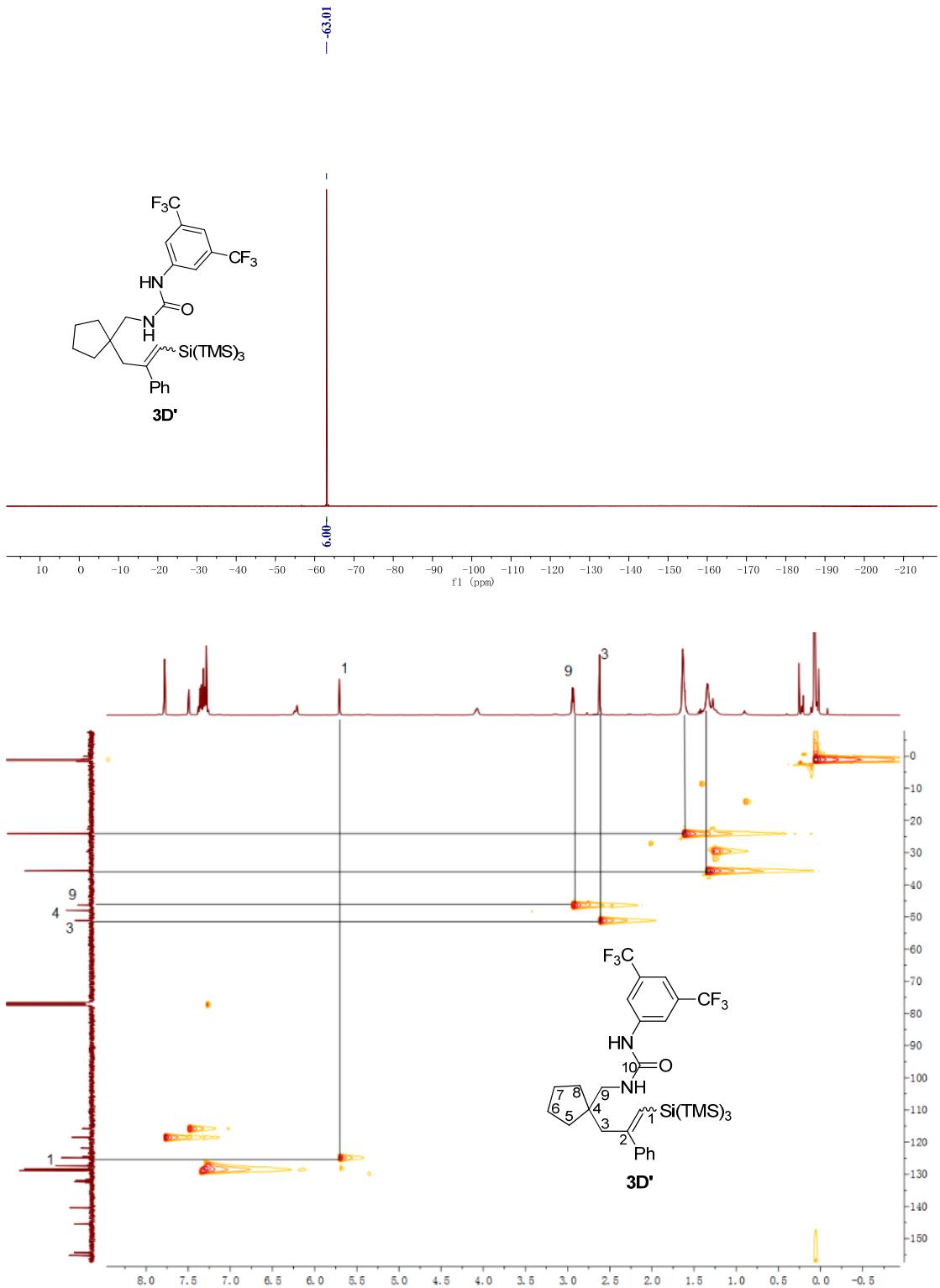


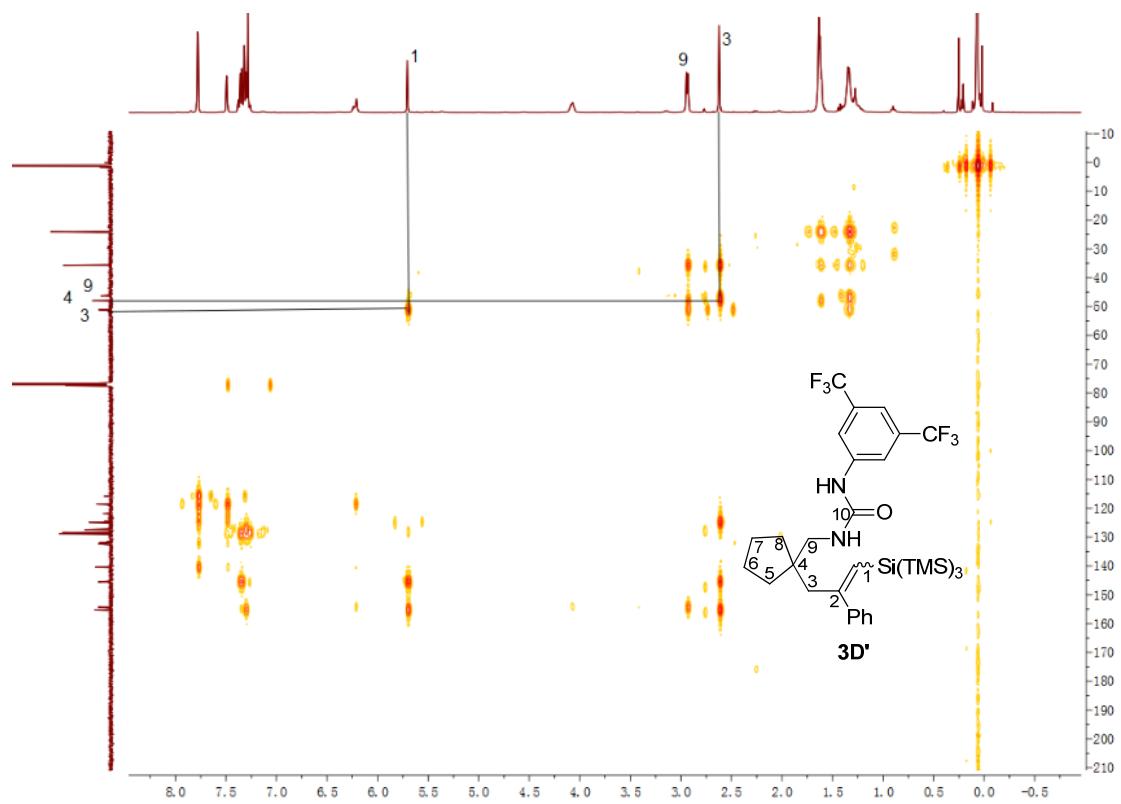




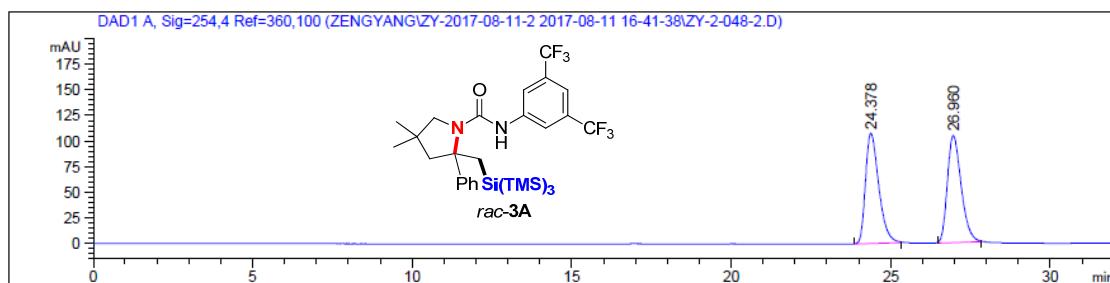








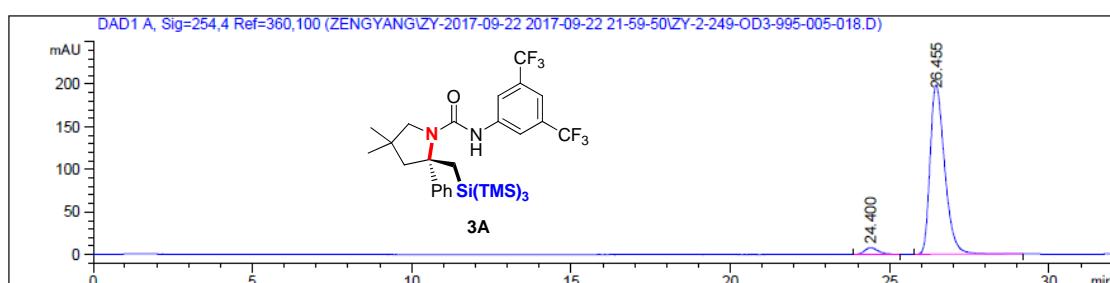
HPLC Spectra



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.378	MM R	0.4810	3105.92505	107.62045	49.6747
2	26.960	MM R	0.5018	3146.60913	104.50945	50.3253

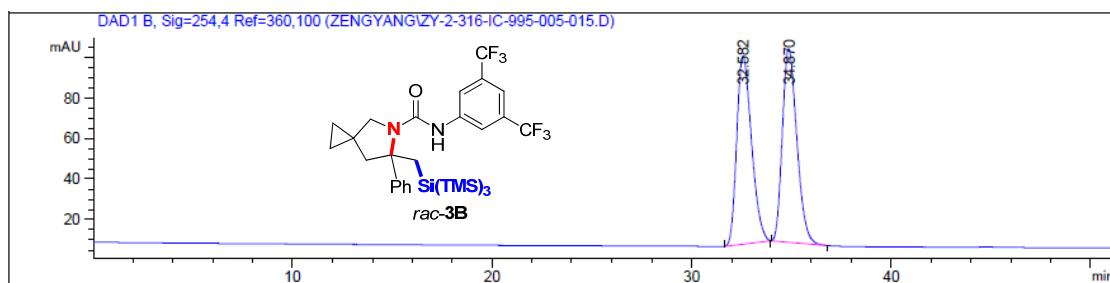
Totals : 6252.53418 212.12990



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	24.400	BB	0.4367	227.98178	7.80599	3.4794
2	26.455	BB	0.4889	6324.39404	198.95967	96.5206

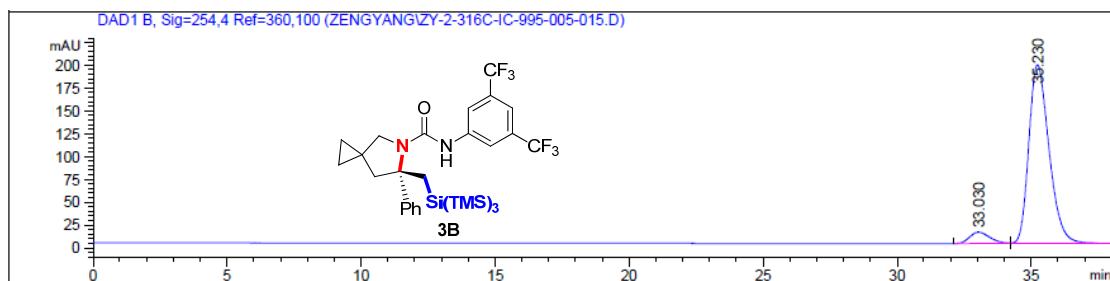
Totals : 6552.37582 206.76566



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.582	BB	0.7766	4772.11914	92.69942	49.7355
2	34.870	BB	0.7654	4822.87744	95.47039	50.2645

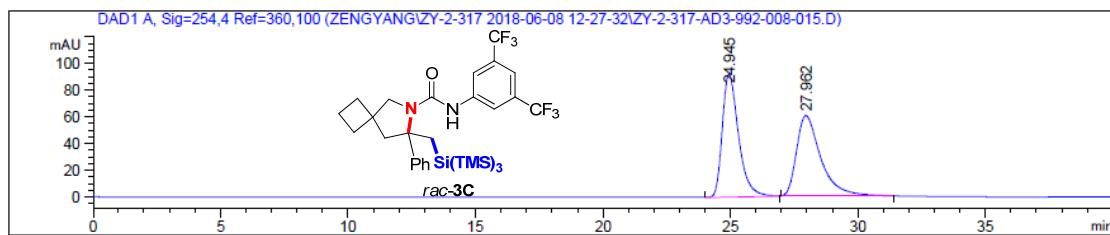
Totals : 9594.99658 188.16981



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.030	BB	0.7488	627.61761	12.26927	5.7777
2	35.230	BB	0.7895	1.02350e4	195.27679	94.2223

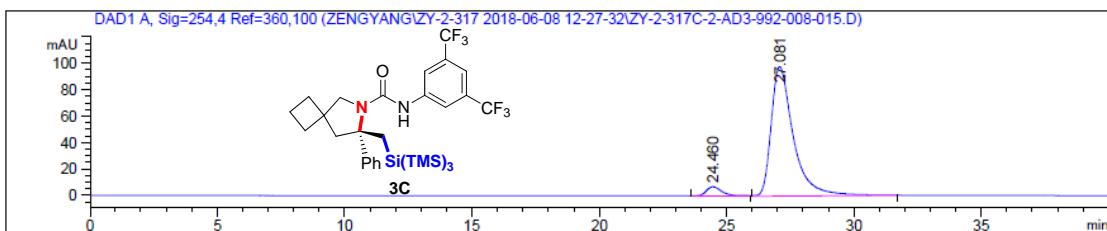
Totals : 1.08627e4 207.54606



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.945	MM R	0.7377	4083.31836	92.24979	50.3265
2	27.962	MM R	1.1120	4030.33765	60.40905	49.6735

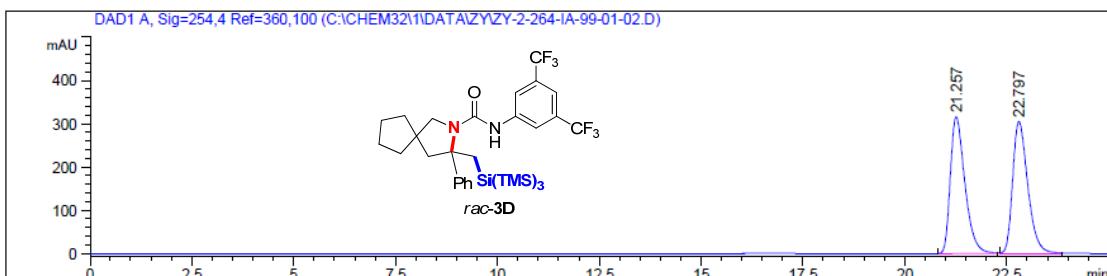
Totals : 8113.65601 152.65884



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.460	BV	0.6300	277.98111	6.78499	4.4810
2	27.081	MM R	1.0117	5925.57227	97.61593	95.5190

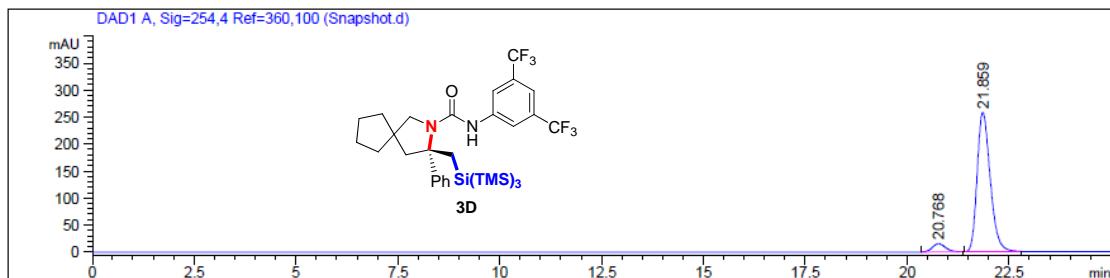
Totals : 6203.55338 104.40092



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.257	BB	0.3827	7864.90186	315.59232	50.0895
2	22.797	BB	0.3963	7836.80176	304.48499	49.9105

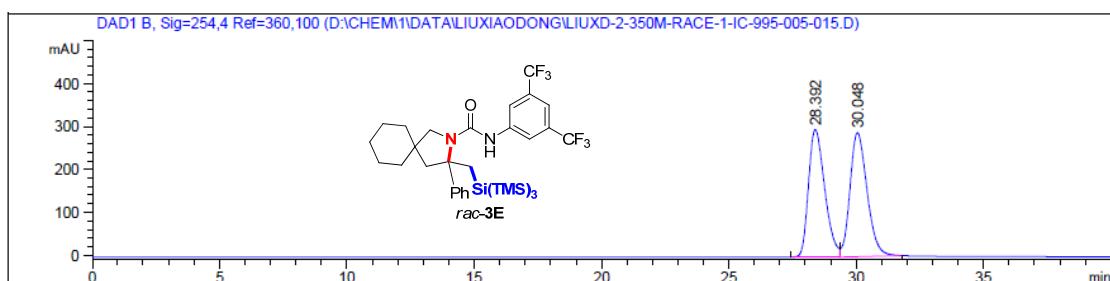
Totals : 1.57017e4 620.07730



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.768	BB	0.3502	340.84579	15.16444	5.5782
2	21.859	BB	0.3468	5769.47656	258.05911	94.4218

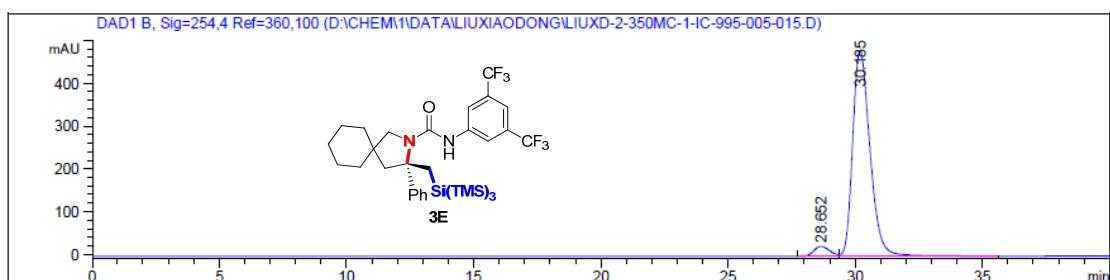
Totals : 6110.32236 273.22356



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

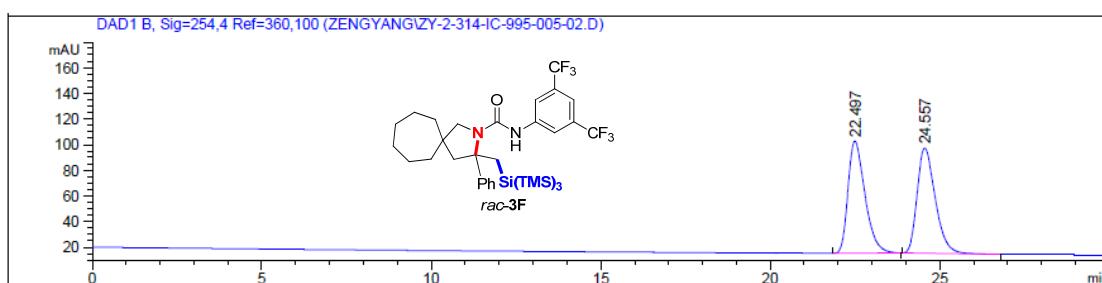
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.392	BV	0.6873	1.30752e4	296.05612	49.3343
2	30.048	MM R	0.7773	1.34281e4	287.92062	50.6657

Totals : 2.65033e4 583.97675



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

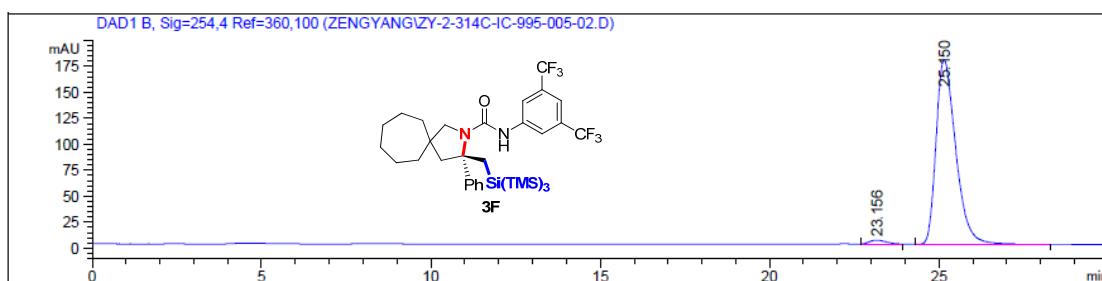
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.652	BV	0.6584	981.57251	22.88684	4.1504
2	30.185	VB	0.7265	2.26683e4	480.41513	95.8496
Totals :				2.36499e4	503.30197	



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.497	BB	0.5321	3038.14136	87.28475	49.8869
2	24.557	BB	0.5741	3051.91553	82.02641	50.1131

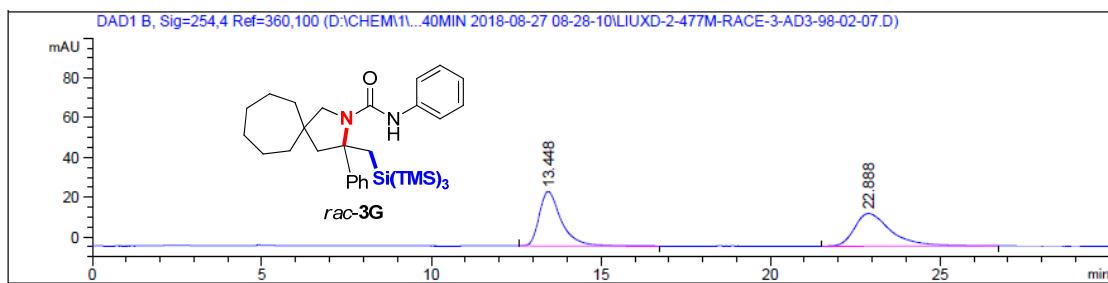
Totals : 6090.05688 169.31116



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.156	MM R	0.5679	127.71933	3.74823	1.7514
2	25.150	BB	0.6278	7164.79395	177.16504	98.2486

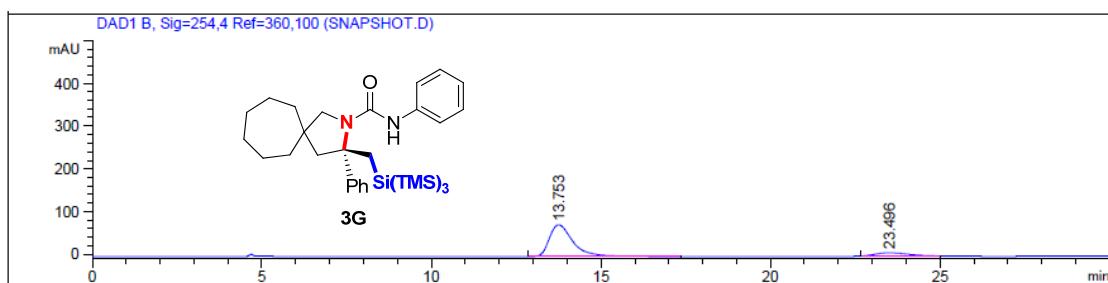
Totals : 7292.51328 180.91327



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.448	BB	0.6751	1228.18420	27.39041	50.0612
2	22.888	BB	1.1227	1225.18347	16.41721	49.9388

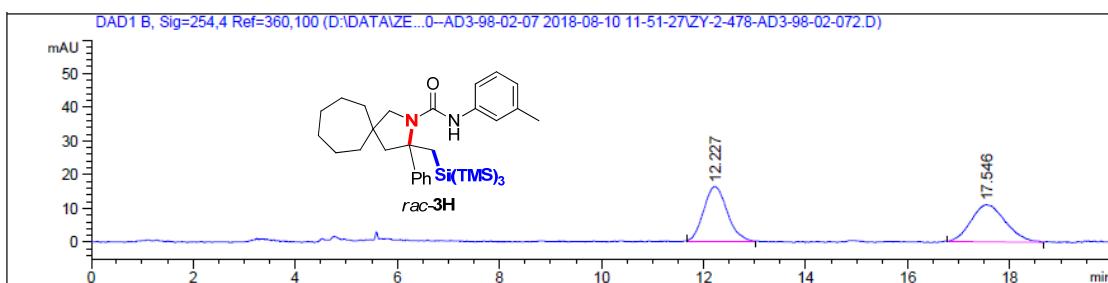
Totals : 2453.36768 43.80762



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

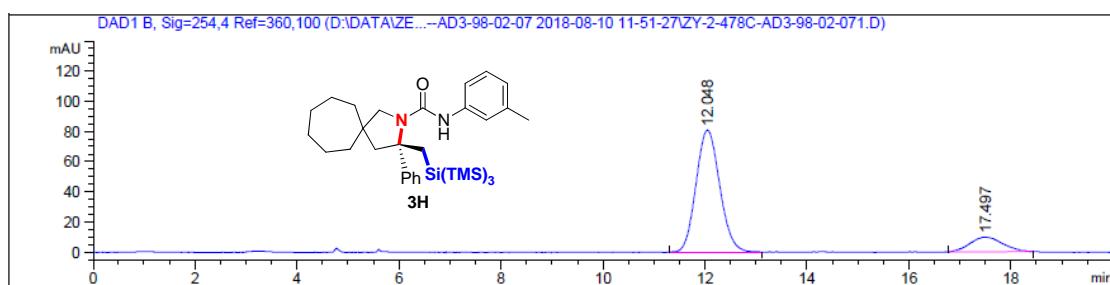
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.753	BB	0.7343	3525.42017	73.40710	87.2125
2	23.496	MM R	1.1338	516.91559	7.59848	12.7875

Totals : 4042.33575 81.00558



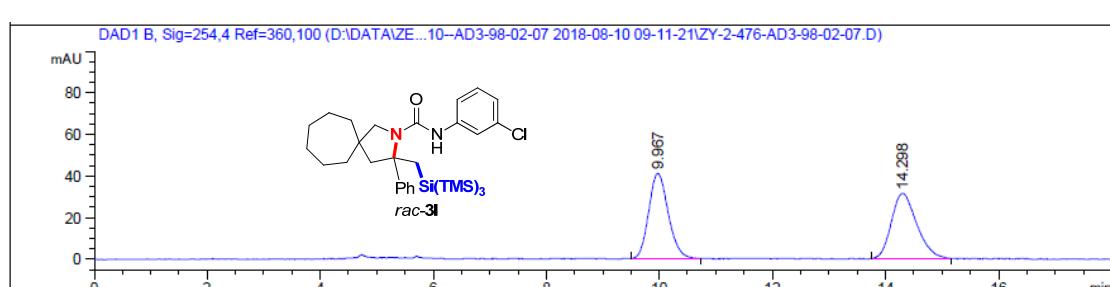
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.227	BB	0.3922	515.49780	16.24663	49.9225
2	17.546	BB	0.5656	517.09882	10.97689	50.0775
Totals :					1032.59662	27.22352



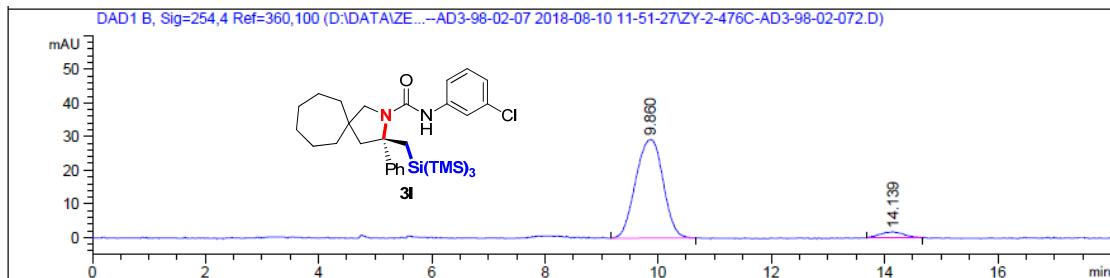
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.048	BB	0.4965	2605.75830	80.74287	85.6732
2	17.497	BB	0.5218	435.75159	9.85655	14.3268
Totals :					3041.50989	90.59942



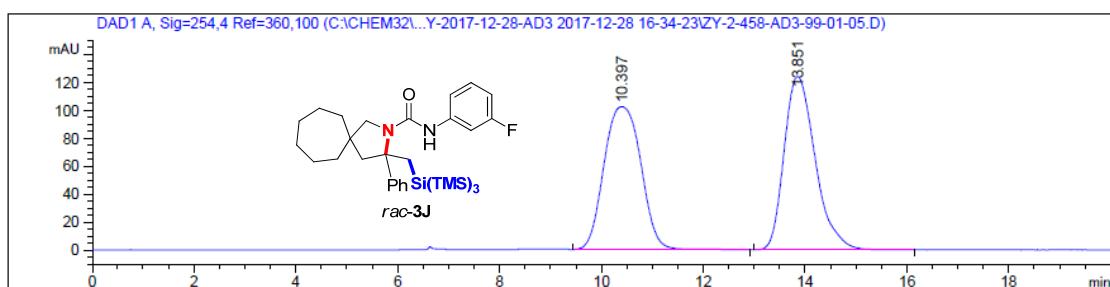
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.967	BB	0.3691	976.72272	40.82310	50.0893
2	14.298	BB	0.4330	973.24072	31.28032	49.9107
Totals :					1949.96344	72.10342



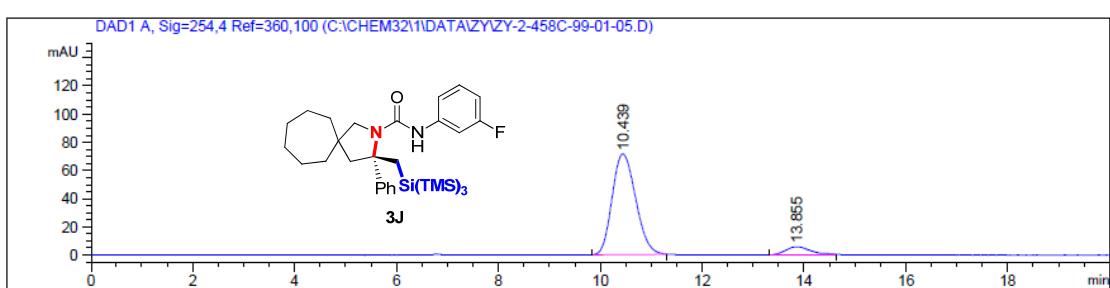
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.860	BB	0.4095	985.97034	29.23462	95.0243
2	14.139	BB	0.3486	51.62785	1.74786	4.9757
Totals :					1037.59819	30.98248



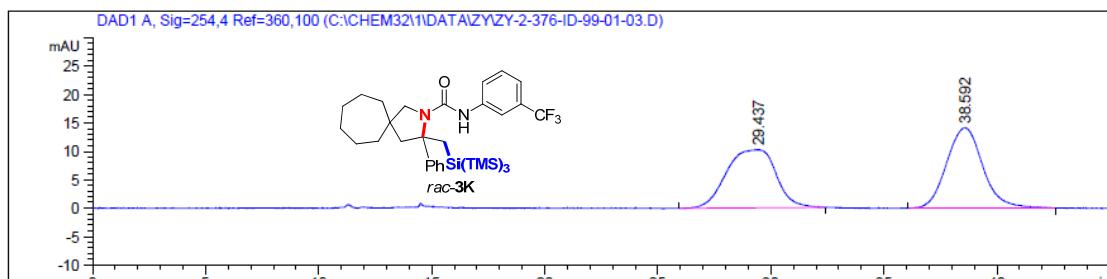
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.397	BB	0.8236	5163.28369	102.52237	49.4624
2	13.851	BB	0.6669	5275.51904	124.36225	50.5376
Totals :					1.04388e4	226.88462



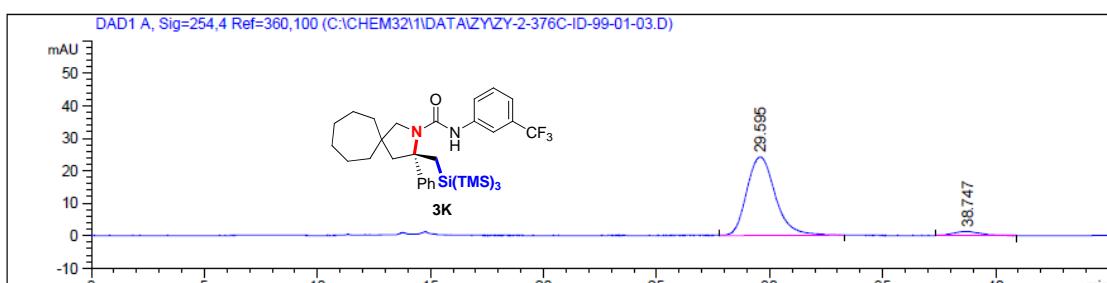
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.439	BB	0.5047	2300.13062	71.61303	92.1745
2	13.855	BB	0.4173	195.27914	5.73467	7.8255
Totals :				2495.40976	77.34770	



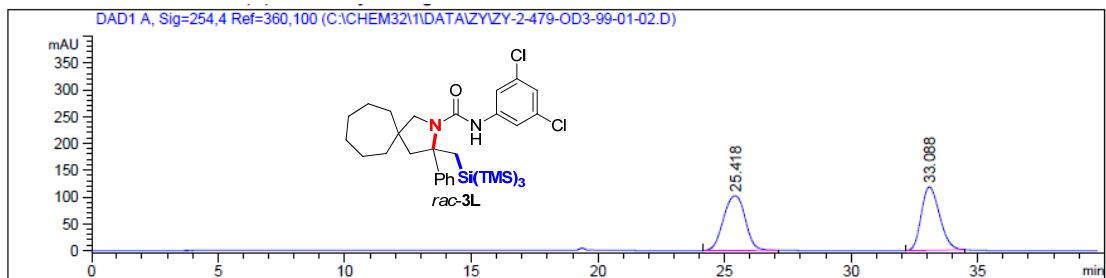
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.437	BB	1.8007	1566.51257	10.24044	49.7368
2	38.592	BB	1.4888	1583.09387	14.15536	50.2632



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

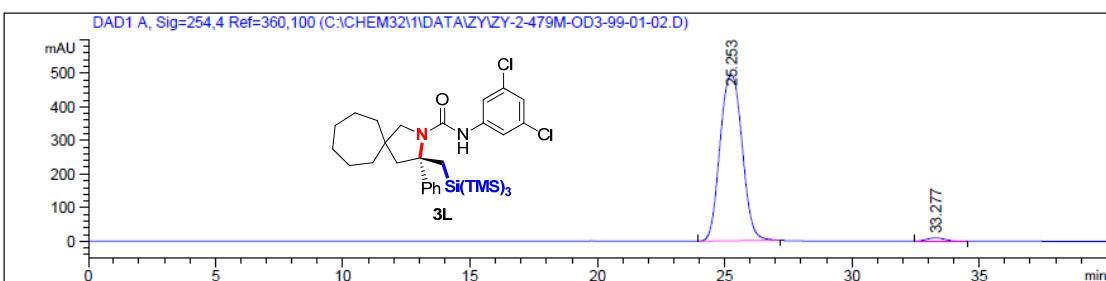
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.595	BB	1.3336	2111.62866	24.11465	95.2216
2	38.747	BB	0.9827	105.96600	1.27889	4.7784



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.418	BB	0.9587	6087.22998	101.64815	50.5827
2	33.088	BB	0.7831	5946.97168	118.17153	49.4173

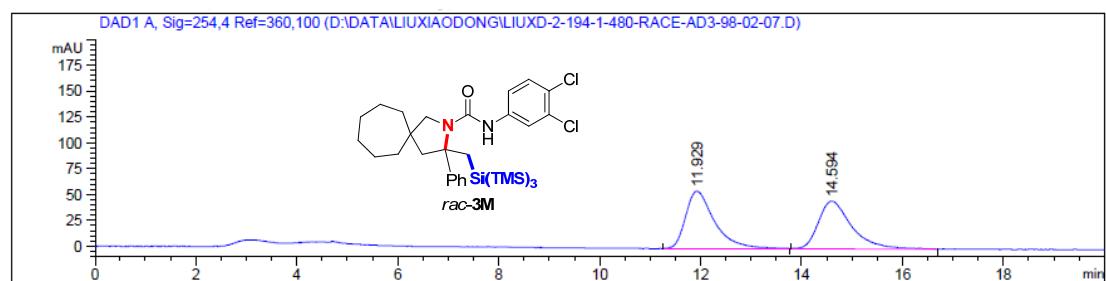
Totals : 1.20342e4 219.81968



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.253	BB	0.9769	2.98133e4	494.86295	98.3730
2	33.277	BB	0.7404	493.10059	9.91173	1.6270

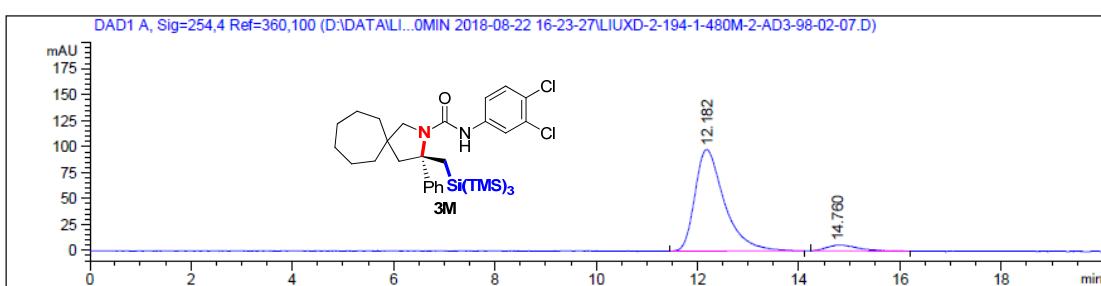
Totals : 3.03064e4 504.77468



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.929	BB	0.5890	2207.39380	55.61713	51.1291
2	14.594	BB	0.6593	2109.90381	46.15851	48.8709

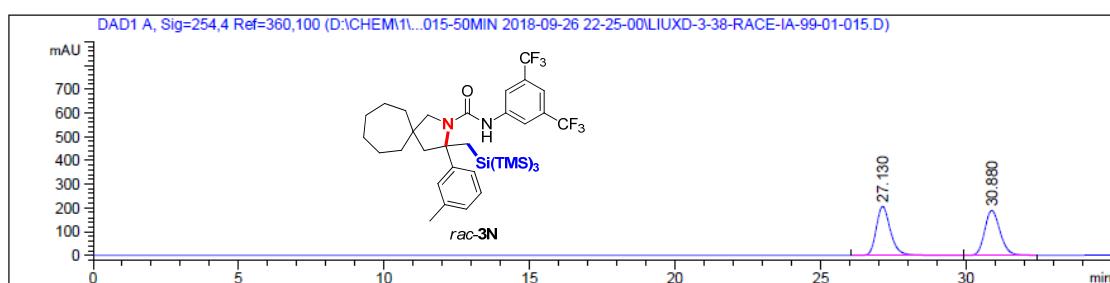
Totals : 4317.29761 101.77564



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

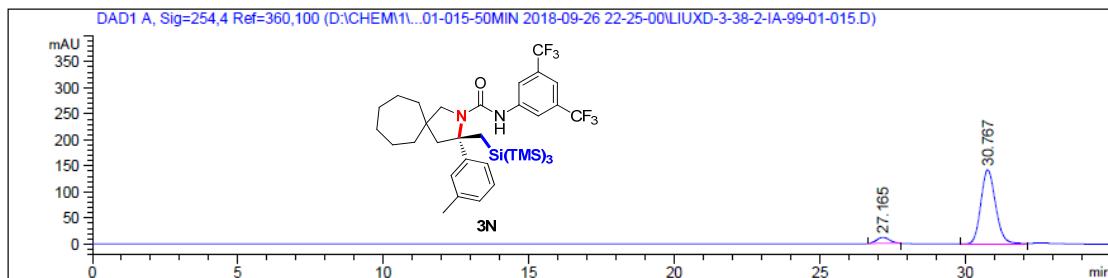
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.182	BB	0.6107	3950.54272	97.92069	94.1067
2	14.760	BB	0.5279	247.39568	5.68291	5.8933

Totals : 4197.93840 103.60360



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

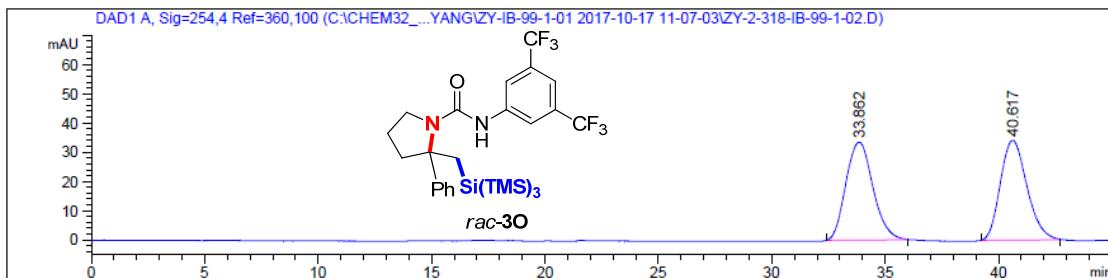
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.130	BB	0.5217	7031.41113	206.25945	50.1230
2	30.880	BV	0.5761	6996.91260	188.91048	49.8770
Totals :				1.40283e4	395.16992	



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.165	MM R	0.5079	352.58975	11.57123	6.5808
2	30.767	BV	0.5468	5005.28613	142.16365	93.4192

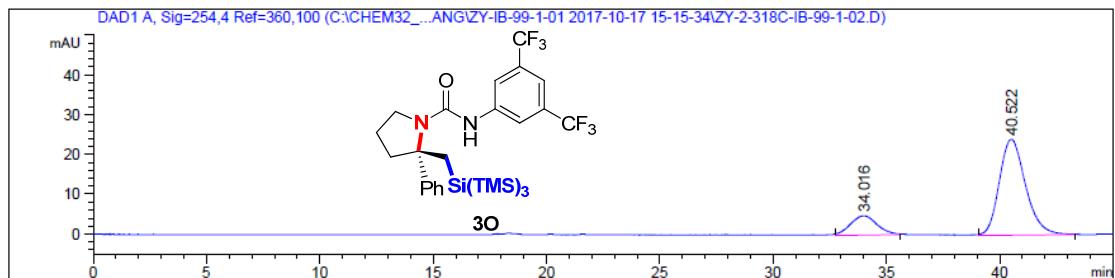
Totals : 5357.87589 153.73488



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

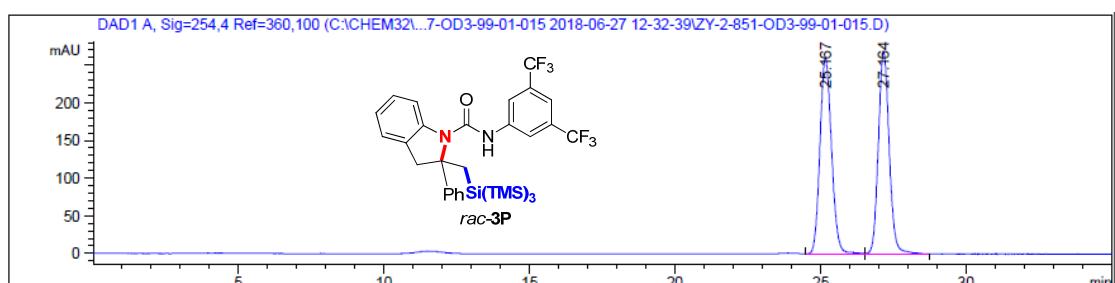
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.862	BB	1.0271	2775.87695	33.48772	50.0626
2	40.617	BB	0.9855	2768.93726	34.09581	49.9374

Totals : 5544.81421 67,58353



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

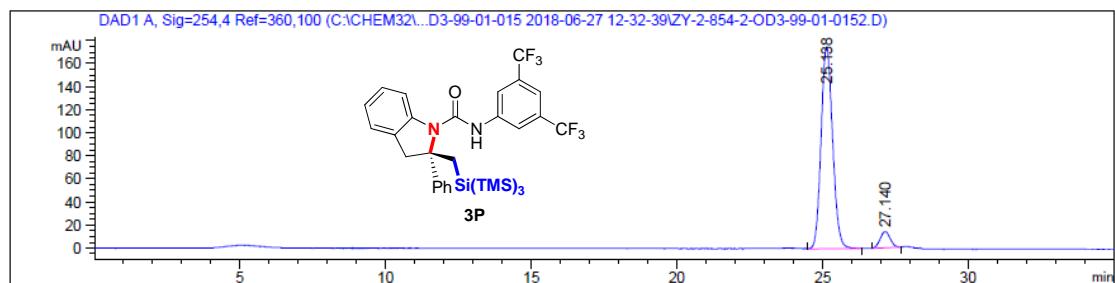
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.016	MM	R	1.3740	397.68863	4.82414 17.0148
2	40.522	MM	R	1.3429	1939.62537	24.07229 82.9852
Totals :					2337.31400	28.89644



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

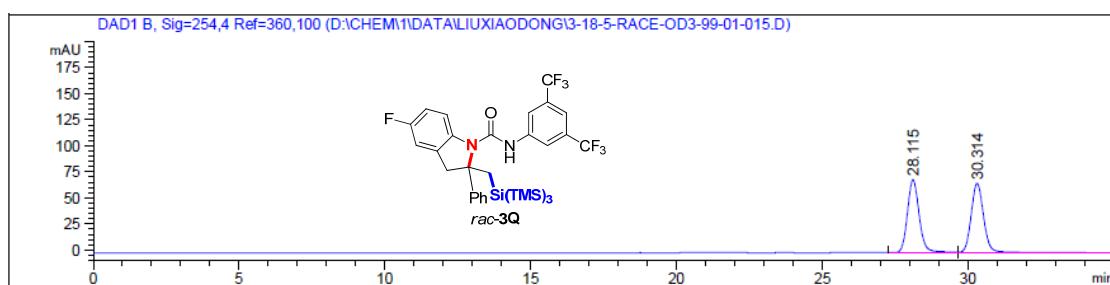
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.167	VW	0.4307	7200.58057	260.30338	50.8283
2	27.164	VB	0.4026	6965.89209	268.58215	49.1717

Totals : 1.41665e4 528.88553



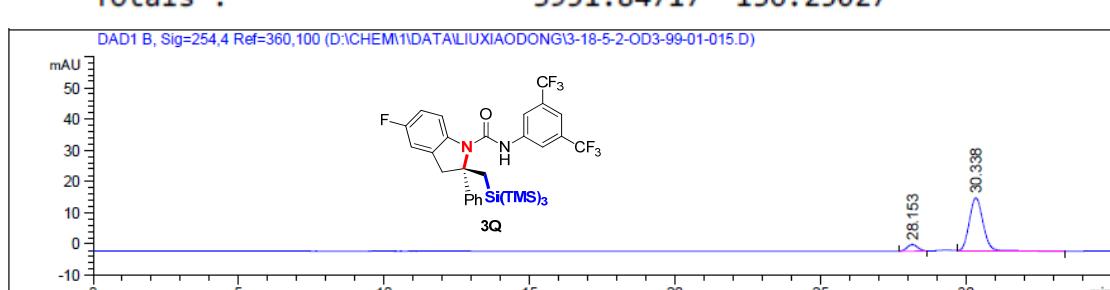
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.138	BB	0.4303	4799.44385	174.78868	93.4629
2	27.140	MM R	0.3987	335.69080	14.03443	6.5371
Totals :					5135.13464	188.82311



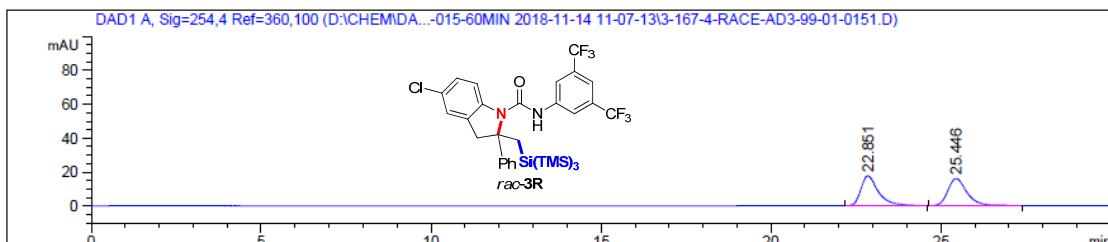
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.115	BV	0.4332	1969.88843	69.80579	49.8473
2	30.314	VBA	0.4640	1981.95874	66.44449	50.1527
Totals :					3951.84717	136.25027



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

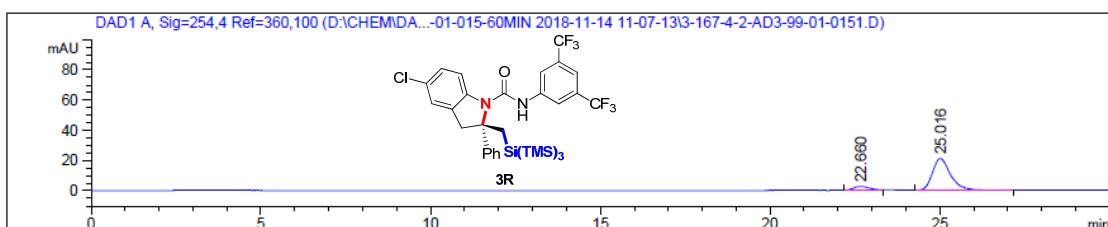
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.153	MM R	0.4238	53.54969	2.10599	8.3950
2	30.338	VB	0.5257	584.32654	17.14060	91.6050
Totals :					637.87623	19.24659



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.851	BB	0.5325	628.68469	17.60877	50.0646
2	25.446	BB	0.5877	627.06219	16.05362	49.9354

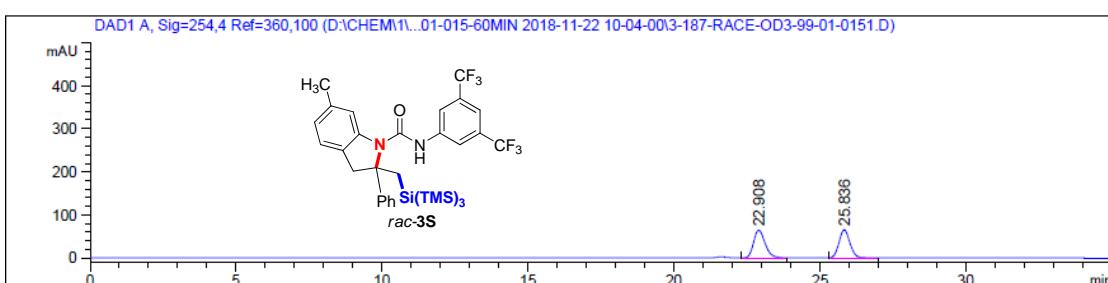
Totals : 1255.74689 33.66239



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.660	MM R	0.5124	78.55956	2.55538	9.0933
2	25.016	VB	0.5653	785.36810	21.14494	90.9067

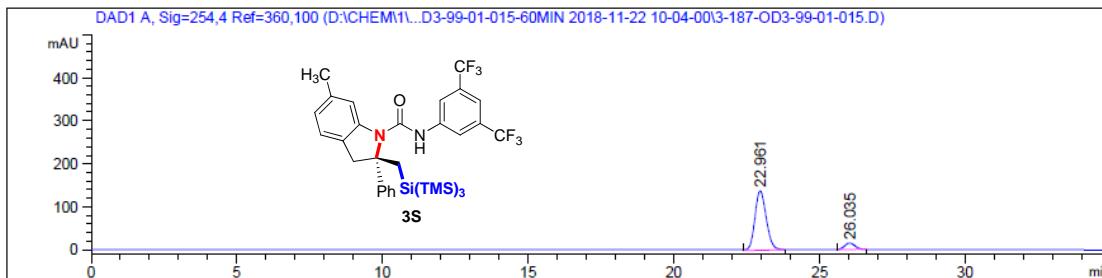
Totals : 863.92766 23.70032



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.908	MM R	0.4550	1759.99487	64.46854	50.5834
2	25.836	MM R	0.4395	1719.39648	65.21011	49.4166

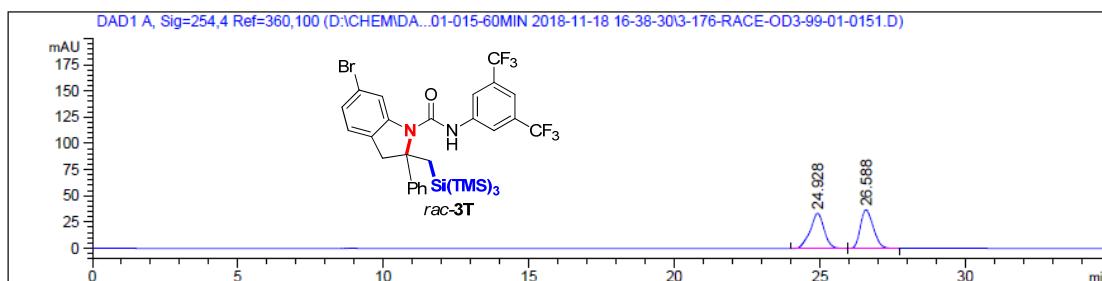
Totals : 3479.39136 129.67864



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.961	MM R	0.4526	3741.23462	137.76720	90.5637
2	26.035	MM R	0.4211	389.81985	15.42861	9.4363

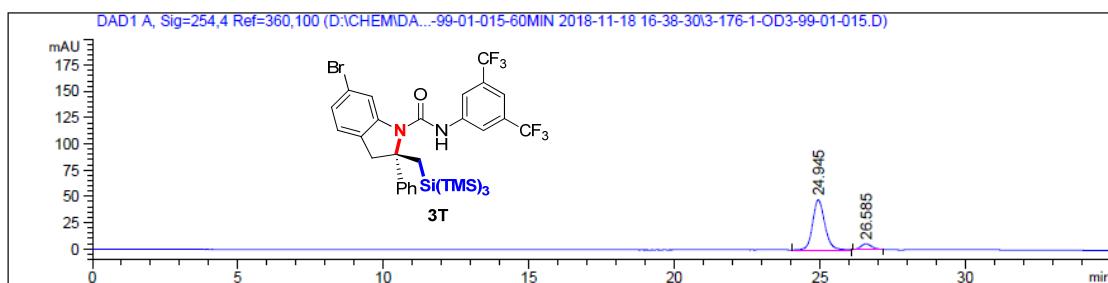
Totals : 4131.05447 153.19581



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

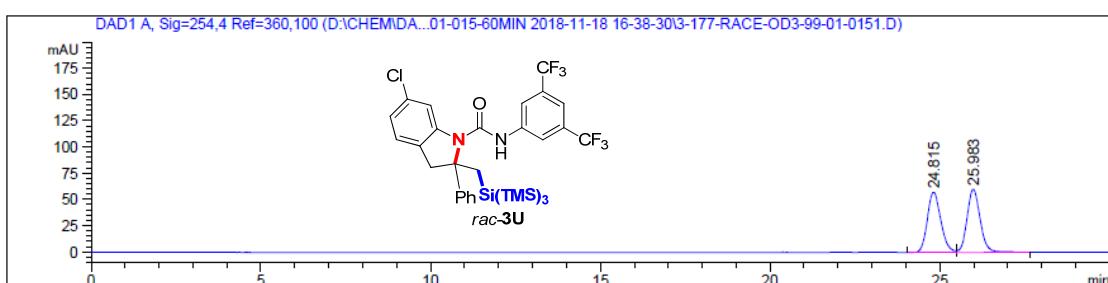
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.928	BV	0.4969	1135.02063	33.70488	49.9346
2	26.588	BV	0.4825	1137.99329	36.82647	50.0654

Totals : 2273.01392 70.53135



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

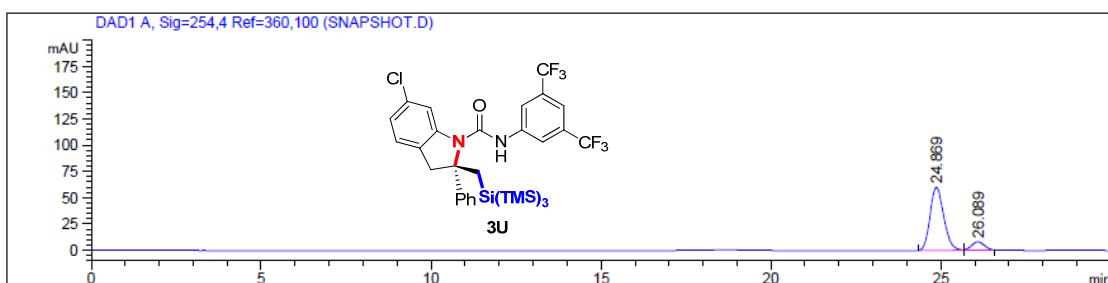
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.945	BV	0.4452	1373.83203	47.53037	91.1496
2	26.585	MM R	0.4273	133.39557	5.20352	8.8504
Totals :					1507.22760	52.73389



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

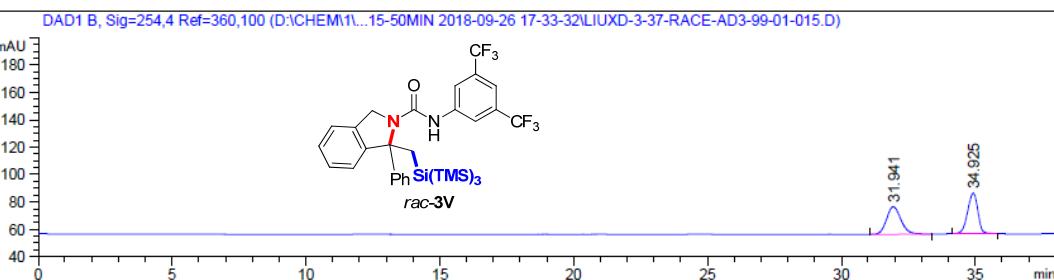
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.815	BV	0.4289	1571.78564	57.15018	49.3935
2	25.983	VB	0.4143	1610.38708	60.15856	50.6065

Totals : 3182.17273 117.30873



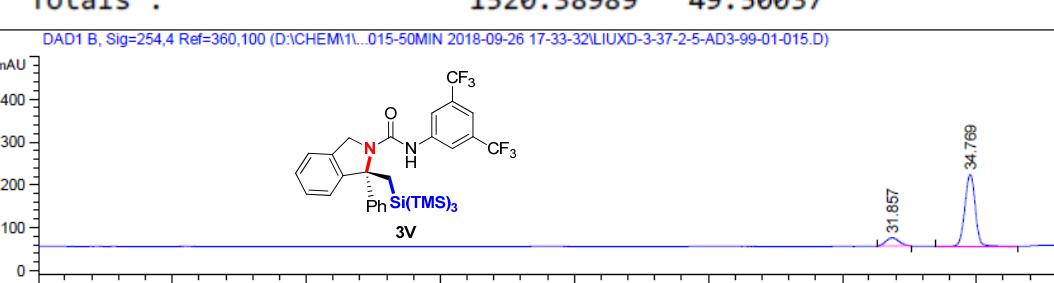
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.869	MM R	0.4662	1681.94568	60.12774	90.1373
2	26.089	MM R	0.4063	184.03568	7.54875	9.8627
Totals :					1865.98135	67.67649



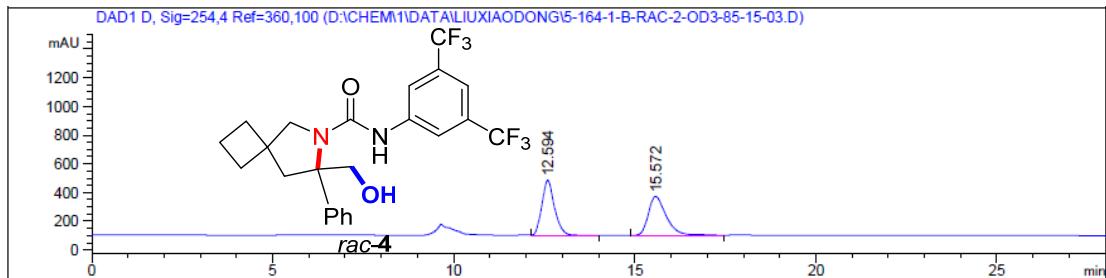
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.941	BB	0.5718	747.76959	20.10867	49.1828
2	34.925	MM R	0.4381	772.62030	29.39170	50.8172
Totals :					1520.38989	49.50037



Signal 2: DAD1 B, Sig=254,4 Ref=360,100

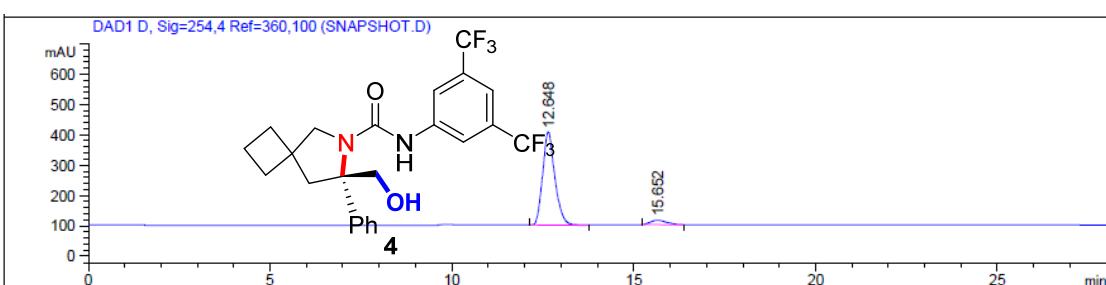
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.857	MM R	0.5725	660.46344	19.22672	12.7969
2	34.769	BB	0.4271	4500.64551	167.70924	87.2031
Totals :					5161.10895	186.93597



Signal 4: DAD1 D, Sig=254,4 Ref=360,100

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.594	VB	0.3568	9281.96484	382.87515	49.9556
2	15.572	BB	0.5154	9298.47266	271.63275	50.0444

Totals : 1.85804e4 654.50790



Signal 4: DAD1 D, Sig=254,4 Ref=360,100

Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.648	MM R	0.3896	7168.04395	306.65359	93.8050
2	15.652	MM R	0.5289	473.39035	14.91725	6.1950

Totals : 7641.43430 321.57085