Supplementary Information

Nickel-Catalyzed Regiodivergent Hydrosilylation of α-(Fluoroalkyl)styrenes without Defluorination

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1. Supplementary Methods

1.1 General Information.

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All the reactions were carried out under argon atmosphere in a argon filled glove box. The ^{1}H NMR spectra were recorded on a 400 MHz or 600 MHz NMR spectrometer. The ^{13}C NMR spectra were recorded at 101 MHz or 150 MHz. The ^{19}F NMR spectra were recorded at 377 MHz or 565 MHz. Chemical shifts were expressed in parts per million(δ) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet), brs (broad singlet), etc. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale. High resolution mass spectra were obtained on a Thermo Fisher Scientific LTQ FTICR-MS. Column chromatography was performed on silica gel (300-400 mesh). Thin layer chromatography was performed on pre-coated glassback plates and visualized with UV light at 254 nm. Flash column chromatography was performed on silica gel. Ph_2SiH_2 and $PhMeSiH_2$ were purchased from commercial sources. The starting materials **1** were prepared according to literature reports.[1]

1.2 General Synthetic Procedures

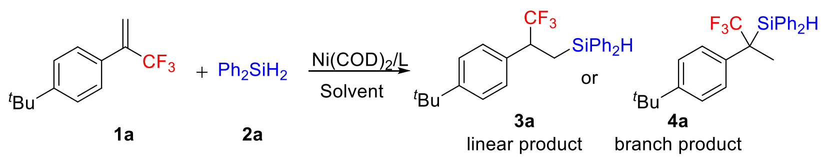
General procedure A：$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and PPh_3 (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol), after stirred for 20 min, **1a** (0.2 mmol, 1.0 equiv) was added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. After stirred for 24 h, the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated and purified by silica gel chromatography (PE) to give the indicated product **3a**.

General procedure B：$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (6.2 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol), after stirred for 20 min, **1a** (0.2 mmol, 1.0 equiv) was added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 °C. After stirred for 24 h, the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated and purified by silica gel chromatography (PE) to give the indicated product **4a**.

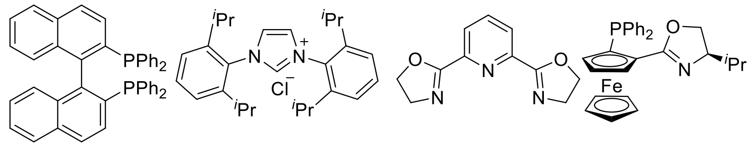
Safety note: Given the hazardous nature of the gaseous products might be formed in the hydrosilylation reacitons, precautions should be taken when using any hydrosilane reagent, particularly if conducted on a large scale.

2. Supplementary Discussion

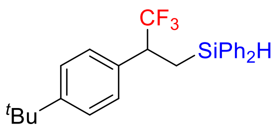
2.1 Supplementary Table 1, Optimization of reaction conditions of **1a** and **2a**. [a]



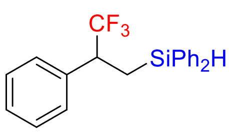
Entry	L	L (%)	Solvent	T/(°C)	Yield(%)	L:B (3a:4a)
1	--	--	toluene	30	18	>20:1
2	PPh_3	10 mol%	toluene	30	17	>20:1
3	PPh_3	5 mol%	toluene	30	96	>20:1
4	PCy_3	5 mol%	toluene	30	38	>20:1
5	BPY	5 mol%	toluene	30	trace	-
6	1,10-phen	5 mol%	toluene	30	trace	7:1
7^{b}	**L1**	5 mol%	toluene	30	81	>20:1
8	**L2**	5 mol%	toluene	30	20	>20:1
9	**L3**	5 mol%	toluene	30	trace	-
10	BINAP	8 mol%	toluene	30	NR	-
11	BINAP	5 mol%	toluene	30	96	>1:20
12	BINAP	4.7 mol%	toluene	30	96	>1:20
13	BINAP	2.5 mol%	toluene	30	90	1:9
14	BINAP	5 mol%	DMA	30	9	>20:1
15	BINAP	5 mol%	^{t}BuOMe	30	59	>1:20
16	BINAP	5 mol%	dioxane	30	95	>1:20
17	BINAP	5 mol%	DCE	30	NR	-
18	BINAP	5 mol%	THF	30	trace	-
19	BINAP	5 mol%	EtOH	30	NR	-
20	BINAP	5 mol%	toluene	0	NR	-
21^{c}	BINAP	5 mol%	toluene	30	60	>1:20
22^{c}	PPh_3	5 mol%	toluene	30	81	>20:1
23^{d}	BINAP	5 mol%	toluene	30	NR	-
24^{d}	PPh_3	5 mol%	toluene	30	NR	-
25^{e}	BINAP	5 mol%	toluene	30	NR	-
26^{e}	PPh_3	5 mol%	toluene	30	NR	-



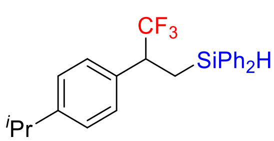
Reaction conditions : **1a** (0.2 mmol), **2a** (0.4 mmol), $Ni(cod)_2$ (5 mol%), L (5 mol%), 30 °C in solvent (2.0 mL) under argon, 24 h, isolated yield. [b]**L1**(5 mol%), CsOAc (20 mol%). [c]**2a** (0.2 mmol). [d]no $Ni(cod)_2$. [e]in air.



Following General procedure A, **3a** was obtained as colorless oil. 81.6 mg, 0.20 mmol, 99% yield. L:B > 20:1.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.40 – 7.35 (m, 4H), 7.34 – 7.30 (m, 2H), 7.30 – 7.27 (m, 1H), 7.27 – 7.22 (m, 2H), 7.24 – 7.21 (m, 1H), 7.10 – 7.03 (m, 2H), 4.59 – 4.57 (m, 1H), 3.40 – 3.25 (m, 1H), 2.22 – 1.58 (m, 2H), 1.30 (s, 9H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.42 (d, J = 8.5 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 136.0, 135.3, 135.1, 133.1, 132.2, 130.0, 129.8, 128.9, 128.3, 128.1, 127.5 (q, J = 280.0 Hz), 125.5, 46.1 (q, J = 27.8 Hz), 34.6, 31.5, 13.1. HRMS (DART, m/z): calcd for $C_{25}H_{31}F_3NSi^+$ $[M + NH_4]^+$: 430.2172, found 430.2173.

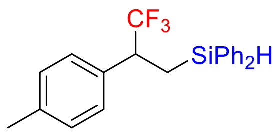


Following General procedure A, **3b** was obtained as colorless oil. 71.2 mg, 0.20 mmol, 99% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.35 – 7.30 (m, 3H), 7.30 – 7.25 (m, 3H), 7.24 – 7.18 (m, 5H), 7.12 – 7.05 (m, 2H), 4.47 – 4.46 (m, 1H), 3.36 – 3.16 (m, 1H), 1.88 – 1.62 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.50 (d, J = 9.0 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 135.0, 133.3, 132.8, 130.2, 129.9, 129.3, 128.6, 128.4, 128.4, 128.2, 127.4 (q, J = 280.4 Hz), 46.5 (q, J = 27.9 Hz), 13.0. HRMS (DART, m/z): calcd for $C_{21}H_{23}F_3NSi^+$ $[M + NH_4]^+$: 374.1546, found 374.1544.

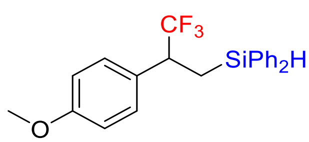


Following General procedure A, **3c** was obtained as colorless oil. 78.8 mg, 0.20 mmol, 99% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.40 – 7.36 (m, 3H), 7.35 – 7.30 (m, 3H), 7.30 – 7.23 (m, 2H), 7.14 – 7.02 (m, 4H), 4.57 (s, 1H), 3.92

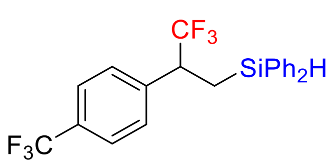
– 3.14 (m, 1H), 2.87 – 2.85 (m, 1H), 2.17 – 1.68 (m, 2H), 1.24 (s , 3H), 1.22 (s , 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.47 (d, *J* = 8.5 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 136.0, 135.3, 135.1, 133.1, 132.6, 130.1, 129.8, 129.2, 128.3, 128.1, 127.5 (q, *J* = 280.4 Hz), 46.1 (q, *J* = 27.7 Hz), 33.9, 24.1, 24.0, 13.1. HRMS (DART, m/z): calcd for $C_{24}H_{29}F_3NSi^+$ [M + NH_4] $^+$: 416.2016, found 416.2017.



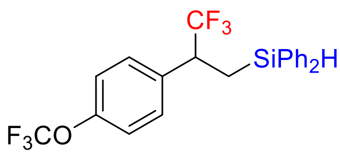
Following General procedure A, **3d** was obtained as colorless oil. 73.7 mg, 0.20 mmol, 99% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.42 – 7.37 (m, 3H), 7.37 – 7.31 (m, 3H), 7.31 – 7.21 (m, 2H), 7.07 – 7.04 (m, 4H), 4.53 (s, 1H), 3.29 – 3.27 (m, 1H), 2.31 (s, 3H), 1.93 – 1.64 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.60 (d, *J* = 8.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 135.3, 135.0, 133.4, 132.9, 132.3, 130.1, 129.8, 129.3, 129.1, 128.3, 128.1, 127.5 (q, *J* = 280.3 Hz), 46.1 (q, *J* = 27.8 Hz), 21.2, 13.0. HRMS (DART, m/z): calcd for $C_{22}H_{25}F_3NSi^+$ [M + NH_4] $^+$: 388.1703, found 388.1704.



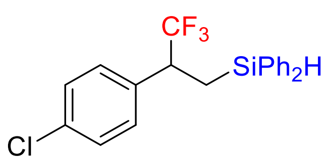
Following General procedure A, **3e** was obtained as colorless oil. 73.8 mg, 0.19 mmol, 96% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.43 – 7.39 (m, 3H), 7.39 – 7.34 (m, 3H), 7.33 – 7.27 (m, 2H), 7.10 – 7.04 (m, 2H), 6.82 – 6.76 (m, 2H), 4.55 – 4.52 (m, 1H), 3.80 (s, 3H), 3.45 – 3.09 (m, 1H), 1.92 – 1.67 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.94 (d, *J* = 8.3 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 135.3, 135.0, 133.4, 132.9, 130.4, 130.1, 129.9, 128.3, 128.2, 127.5 (q, *J* = 280.2 Hz), 114.0, 55.4, 45.6 (q, *J* = 27.7 Hz), 13.0. HRMS (DART, m/z): calcd for $C_{22}H_{25}F_3NOSi^+$ [M + NH_4] $^+$: 404.1652, found 404.1655.



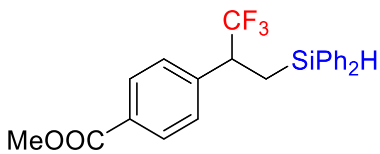
Following General procedure A, **3f** was obtained as colorless oil. 83.7 mg, 0.20 mmol, 99% yield. L:B = 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 2H), 7.45 – 7.41 (m, 2H), 7.39 – 7.32 (m, 5H), 7.31 – 7.21 (m, 5H), 4.56 (d, J = 3.2 Hz, 1H), 3.50 – 3.30 (m, 1H), 1.96 – 1.70 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.76 (s, 3F), -71.41 (d, J = 8.5 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 136.0, 135.2, 135.0, 132.7, 132.4, 130.7 (q, J = 33.3 Hz), 130.3, 130.1, 129.7, 128. 5, 128.3, 125.6 (q, J = 3.8 Hz), 124.1 (q, J = 272.5 Hz), 46.6 (q, J = 28.2 Hz), 12.9. HRMS (ESI, m/z): calcd for $C_{22}H_{22}F_6NSi^+$ [M + NH_4] $^+$: 442.1420, found 442.1406.



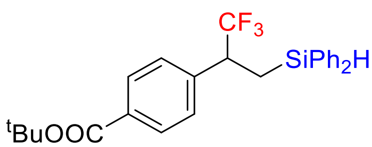
Following General procedure A, **3g** was obtained as colorless oil. 87.0 mg, 0.20 mmol, 99% yield. L:B = 7:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 3H), 7.39 – 7.32 (m, 5H), 7.31 – 7.25 (m, 2H), 7.21 – 7.11 (m, 2H), 7.11 – 7.02 (m, 2H), 4.60 – 4.53 (m, 1H), 3.51 – 3.23 (m, 1H), 1.93 – 1.69 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.80 (s, 3F), -71.72 (d, J = 8.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1 (q, J = 2.0 Hz), 135.2, 135.0, 133.9 (q, J = 1.3 Hz), 132.9, 132.6, 130.7, 130.3, 130.1, 128.4, 128.2, 127.1 (q, J = 280.3 Hz), 120.9, 120.6 (q, J = 257.4 Hz), 46.0 (q, J = 28.0 Hz), 12.9. HRMS (ESI, m/z): calcd for $C_{22}H_{22}F_6NOSi^+$ [M + NH_4] $^+$: 458.1369, found 458.1369.



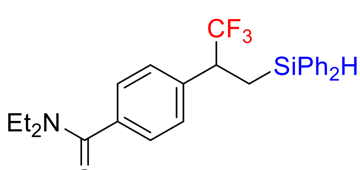
Following General procedure A, **3h** was obtained as colorless oil. 77.8 mg, 0.20 mmol, 99% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.48 – 7.44 (m, 2H), 7.44 – 7.42 (m, 2H), 7.42 – 7.38 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 – 7.25 (m, 2H), 7.15 – 7.07 (m, 2H), 4.66 – 4.53 (m, 1H), 3.45 – 3.29 (m, 1H), 1.97 – 1.73 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.70 (d, J = 8.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 135.0, 134.4, 133.8, 133.0, 132.6, 130.6, 130.3, 130.0, 128.8, 128.4, 128.2, 127.1 (q, J = 280.4 Hz), 46.0 (q, J = 28.0 Hz), 12.9. HRMS (ESI, m/z): calcd for $C_{21}H_{22}ClF_3NSi^+$ [M + NH_4] $^+$: 408.1157, found 408.1148.



Following General procedure A, **3i** was obtained as colorless oil. 82.6 mg, 0.20 mmol, 99% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.84 (m, 2H), 7.51 – 7.42 (m, 3H), 7.42 – 7.34 (m, 5H), 7.32 – 7.26 (m, 2H), 7.26 – 7.17 (m, 2H), 4.51 (s, 1H), 3.91 (s, 3H), 3.57 – 3.29 (m, 1H), 1.98 – 1.73 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.27 (d, *J* = 8.2 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 140.3, 135.2, 135.0, 132.9, 132.4, 130.3, 130.1, 129.9, 129.4, 128.4, 128.2, 127.1 (q, *J* = 280.1 Hz), 52.3, 46.6 (q, *J* = 27.8 Hz), 12.8. HRMS (DART, m/z): calcd for $C_{23}H_{22}F_3O_2Si^+$ [M + H] $^+$: 415.1336, found 415.1336.

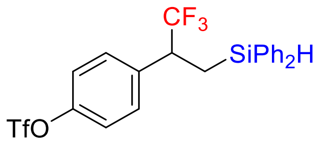


Following General procedure A, **3ii** was obtained as colorless oil. 81.3 mg, 0.18 mmol, 89%. L:B >20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.47 – 7.42 (m, 3H), 7.41 – 7.37 (m, 4H), 7.37 – 7.34 (m, 1H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 2H), 4.50 (dd, *J* = 5.1, 2.4 Hz, 1H), 3.43 – 3.27 (m, 1H), 1.92 – 1.74 (m, 2H), 1.61 (s, 9H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.35 (d, *J* = 9.1 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 139.7, 135.3, 135.0, 133.0, 132.5, 132.2, 130.3, 130.0, 129.7, 129.2, 128.43, 128.2, 127.1 (q, *J* = 280.3 Hz), 81.3, 46.4 (q, *J* = 27.9 Hz), 28.3, 12.9. HRMS (EI, m/z): calcd for $C_{26}H_{27}F_3O_2Si^+$ [M] $^+$: 456.1732, found 456.1728.

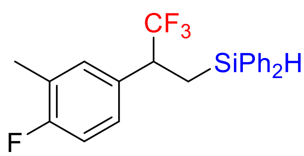


Following General procedure A, 60 °C, **3j** was obtained as colorless oil. 49 mg, 0.11 mmol, 54%. L:B > 20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 5H), 7.40 – 7.34 (m, 3H), 7.34 – 7.28 (m, 4H), 7.22 – 7.16 (m, 2H), 4.59 – 4.50 (m, 1H), 3.55 (s, 2H), 3.34 – 3.31 (m, 1H), 3.23 (s, 2H), 1.91 – 1.74 (m, 2H), 1.26 (s, 3H), 1.12 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.39 (d, *J* = 8.5 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 137.3, 136.4, 135.2, 135.0, 133.0, 132.6, 130.2, 130.0, 129.3, 128.4, 128.2, 127.2 (q, *J* =

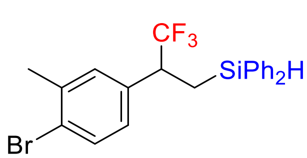
280.2 Hz),126.7, 46.3 (q, J = 28.1 Hz), 43.5, 39.4, 14.4, 13.0, 12.8. HRMS (EI, m/z): calcd for $C_{26}H_{28}F_3NOSi^+$ [M] $^+$: 455.1892, found 455.1881.



Following General procedure A, 60 °C, **3k** was obtained as colorless oil. 42.6 mg, 0.08 mmol, 42%. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 3H), 7.40 – 7.34 (m, 5H), 7.33 – 7.27 (m, 2H), 7.23 – 7.19 (m, 2H), 7.17 – 7.13 (m, 2H), 4.56 (t, J = 3.7 Hz, 1H), 3.45 – 3.32 (m, 1H), 1.80 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.62 (d, J = 8.9 Hz, 3F), -72.84 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 135.8, 135.2, 134.9, 132.6, 132.3, 131.2, 130.4, 130.2, 128.5, 128.3, 126.9 (q, J = 280.2 Hz), 121.5, 118.9 (q, J = 321.1 Hz), 46.1 (q, J = 28.1 Hz), 12.8). HRMS (ESI, m/z): calcd for $C_{22}H_{18}F_6NaO_3SSi^+$ [M + Na] $^+$: 527.0542, found 527.0522.

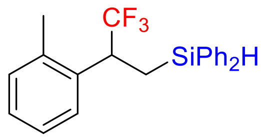


Following General procedure A, **3l** was obtained as colorless oil. 73.2 mg, 0.19 mmol, 94% yield. L:B = 17:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 2H), 7.42 – 7.39 (m, 2H), 7.39 – 7.36 (m, 2H), 7.36 – 7.32 (m, 2H), 7.32 – 7.25 (m, 2H), 7.08 – 6.98 (m, 1H), 6.85 – 6.76 (m, 2H), 4.56 (s, 1H), 3.36 – 3.19 (m, 1H), 2.22 (s, 3H), 1.93 – 1.63 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.66 (d, J = 8.5 Hz, 3F), -116.99 (t, J = 8.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.2 (d, J = 245.0 Hz), 135.3, 135.0, 133.1, 132.7, 131.5 (d, J = 5.3 Hz), 130.2, 129.9, 128.4, 128.2, 127.2 (q, J = 280.1 Hz), 125.0 (d, J = 17.3 Hz), 124.7 (d, J = 3.6 Hz), 115.8 (d, J = 23.2 Hz), 46.0 (q, J = 27.9 Hz), 14.4 (d, J = 3.5 Hz), 13.0. HRMS (ESI, m/z): calcd for $C_{22}H_{21}F_4Si^+$ [M + H] $^+$: 389.1343, found 389.1367.

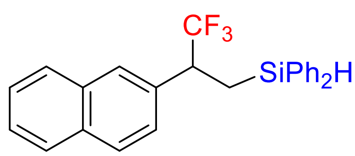


Following General procedure A, 60 °C, **3m** was obtained as colorless oil. 51.6 mg, 0.11 mmol, 57%. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 3H), 7.39 – 7.31

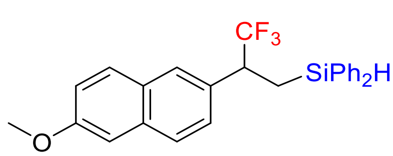
(m, 6H), 7.31 – 7.26 (m, 2H), 6.93 – 6.88 (m, 1H), 6.87 – 6.80 (m, 1H), 4.55 (t, *J* = 3.7 Hz, 1H), 3.33 – 3.21 (m, 1H), 2.28 (s, 3H), 1.90 – 1.64 (m, 2H). ^{19}F NMR (376 MHz, CDCl3) δ -71.62 (d, *J* = 8.9 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.1, 135.2, 134.9, 134.4, 133.0, 132.7, 132.5, 131.7, 130.2, 129.9, 128.3, 128.1, 128.1, 127.6 (q, *J* = 281.3 Hz), 124.9, 46.1 (q, *J* = 28.0 Hz), 23.0, 12.9. HRMS (EI, m/z): calcd for $C_{22}H_{20}BrF_3Si^+$ $[M]^+$: 448.0470, found 448.0470.



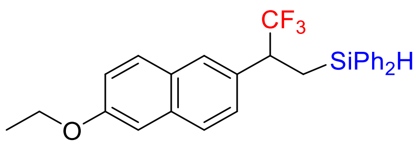
Following General procedure A, 60 °C, **3n** was obtained as colorless oil. 29.6 mg, 0.08 mmol, 40% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 5H), 7.38 – 7.33 (m, 4H), 7.33 – 7.27 (m, 2H), 7.18 – 7.15 (m, 2H), 7.08 – 7.06(m, 1H), 4.50 (dd, *J* = 4.8, 2.9 Hz, 1H), 3.69 – 3.61 (m, 1H), 1.95 – 1.80 (m, 2H), 1.92 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.59 (d, *J* = 8.5 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 135.3, 135.0, 133.4, 132.8, 130.5, 130.2, 129.9, 128.4, 128.2, 128.1, 127.7 (q, *J* = 280.3 Hz), 126.3, 40.5 (q, *J* = 28.2 Hz), 19.6, 12.9. HRMS (DART, m/z): calcd for $C_{22}H_{25}F_3NSi^+$ $[M + NH_4]^+$: 388.1703, found 388.1705.



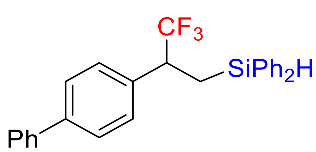
Following General procedure A, **3o** was obtained as colorless oil. 81.0 mg, 0.20 mmol, 99% yield. L:B > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.50 – 7.43 (m, 5H), 7.41 – 7.37 (m, 3H), 7.35 – 7.31 (m, 3H), 7.30 – 7.22 (m, 2H), 7.23 – 7.18 (m, 2H), 4.61 (d, *J* = 2.7 Hz, 1H), 3.38 – 3.31 (m, 1H), 1.99 – 1.74 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.14 (d, *J* = 9.2 Hz, 3F).^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 135.0, 133.3, 133.2, 132.8, 132.7, 130.2, 129.9, 129.0, 128.5, 128.3, 128.1, 127.8, 127.5 (q, *J* = 280.4 Hz), 126.4, 126.4, 126.4, 126.1, 46.6 (q, *J* = 27.7 Hz), 13.0. HRMS (DART, m/z): calcd for $C_{23}H_{22}F_3O_2Si^+$ $[M + H]^+$: 424.1703, found 424.1705.



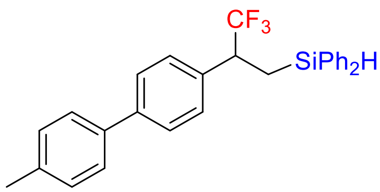
Following General procedure A, **3p** was obtained as colorless oil. 83.8 mg, 0.19 mmol, 96% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 2H), 7.65 – 7.56 (m, 4H), 7.55 – 7.49 (m, 4H), 7.47 – 7.34 (m, 5H), 7.34 – 7.27 (m, 1H), 4.67 (s, 1H), 4.07 (s, 3H), 3.71 – 3.54 (m, 1H), 2.18 – 1.96 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.30 (d, *J* = 8.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 135.3, 135.0, 134.5, 133.3, 132.9, 130.1, 129.9, 129.6, 128.8, 128.7, 128.3, 128.1, 127.6 (q, *J* = 280.5 Hz), 127.3, 127.0, 119.2, 105.7, 55.5, 46.3 (q, *J* = 27.8 Hz), 13.0. HRMS (DART, m/z): calcd for $C_{26}H_{24}F_3OSi^+$ $[M + NH_4]^+$: 437.1543, found 437.1547.



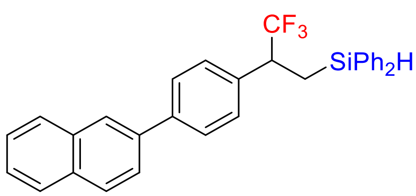
Following General procedure A, **3q** was obtained as colorless oil. 89.0 mg, 0.20 mmol, 99% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 –7.56 (m, 2H), 7.46 – 7.40 (m, 3H), 7.39 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 7.10 – 7.05 (m, 1H), 4.51 (dd, *J* = 4.5, 2.9 Hz, 1H), 4.12 (q, *J* = 7.0 Hz, 2H), 3.54 – 3.36 (m, 1H), 1.98 – 1.81 (m, 2H), 1.46 (t, *J* = 7.0 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.23 (d, *J* = 9.2 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 135.3, 135.0, 134.5, 133.3, 132.9, 130.2, 130.1, 129.8, 128.8, 128.7, 128.3, 128.1, 127.6 (q, *J* = 280.4 Hz), 127.2, 126.9, 119.5, 106.5, 63.7, 46.5 (q, *J* = 27.8 Hz), 14.9, 13.0. HRMS (DART, m/z): calcd for $C_{27}H_{26}F_3OSi^+$ $[M + NH_4]^+$: 451.1700, found 451.1699.



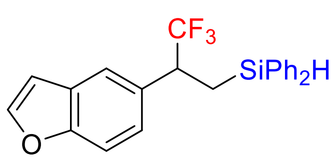
Following General procedure A, **3r** was obtained as white solid, mp: 52~54 °C. 86.4 mg, 0.20 mmol, 99% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.49 – 7.43 (m, 5H), 7.42 – 7.37 (m, 4H), 7.37 – 7.30 (m, 4H), 7.29 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 4.61 (d, *J* = 2.7 Hz, 1H), 3.47 – 3.31 (m, 1H), 1.97 – 1.72 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.34 (d, *J* = 8.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 140.7, 135.3, 135.0, 134.3, 133.2, 132.9, 130.1, 129.9, 129.7, 128.9, 128.3, 128.2, 127.6, 127.4 (q, *J* = 280.4 Hz), 127.3, 127.2, 46.3 (q, *J* = 27.9 Hz), 13.1. HRMS (DART, m/z): calcd for $C_{27}H_{27}F_3NSi^+$ $[M + NH_4]^+$: 450.1859, found 450.1864.



Following General procedure A, **3s** was obtained as white solid, mp: 62~64 °C. 88.2 mg, 0.20 mmol, 99% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.43 (m, 6H), 7.42 – 7.36 (m, 3H), 7.37 – 7.30 (m, 3H), 7.28 – 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 4.60 (s, 1H), 3.50 – 3.24 (m, 1H), 2.39 (s, 3H), 1.96 – 1.71 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.38 (d, *J* = 8.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 137.9, 137.4, 135.6, 135.3, 135.0, 134.0, 133.2, 132.9, 130.1, 129.9, 129.7, 128.3, 128.2, 127.5 (q, *J* = 280.4 Hz), 127.1, 127.1, 46.2 (q, *J* = 27.9 Hz), 21.2, 13.1. HRMS (EI, m/z): calcd for $C_{28}H_{25}F_3Si^+$ [M] $^+$: 446.1678, found 446.1677.

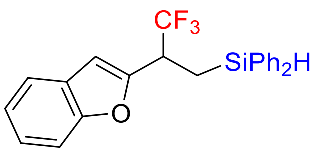


Following General procedure A, **3t** was obtained as white solid, mp: 58~60 °C. 95.7 mg, 0.20 mmol, 99% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.98 – 7.89 (m, 3H), 7.81 – 7.72 (m, 1H), 7.69 – 7.60 (m, 2H), 7.57 – 7.51 (m, 4H), 7.49 – 7.45 (m, 3H), 7.44 – 7.37 (m, 3H), 7.36 – 7.28 (m, 4H), 4.72 – 4.66 (m, 1H), 3.53 – 3.38 (m, 1H), 2.03 – 1.81 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.35 (d, *J* = 9.2 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 138.1, 135.3, 135.0, 134.4, 133.8, 133.2, 132.9, 130.2, 129.9, 129.8, 128.6, 128.4, 128.2, 127.8, 127.6, 127.5 (q, *J* = 280.5 Hz), 127.3, 126.5, 126.2, 126.0, 125.6, 46.3 (q, *J* = 27.9 Hz), 13.1. HRMS (DART, m/z): calcd for $C_{31}H_{29}F_3NSi^+$ [M + NH_4] $^+$: 500.2016, found 500.2017.

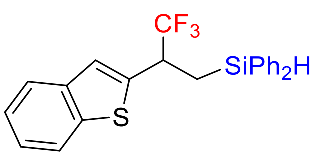


Following General procedure A, **L1**(5 mol%), CsOAc (20 mol%). **3u** was obtained as colorless oil. 78.9 mg, 0.20 mmol, 99 % yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 1H), 7.50 – 7.40 (m, 2H), 7.40 – 7.32 (m, 8H), 7.32 – 7.27 (m, 1H), 7.27

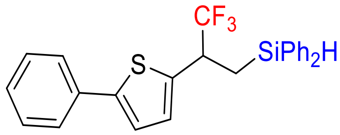
– 7.18 (m, 1H), 7.14 – 7.03 (m, 1H), 6.73 – 6.64 (m, 1H), 4.51 (s, 1H), 3.53 – 3.35 (m, 1H), 1.99 – 1.76 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.60 (d, *J* = 8.7 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 145.6, 135.3, 135.0, 133.3, 132.9, 131.7, 130.1, 129.9, 128.3, 128.1, 127.7, 127.6 (q, *J* = 279.9 Hz), 125.5, 122.1, 111.4, 106.8, 46.4 (q, *J* = 27.8 Hz), 13.5. HRMS (DART, m/z): calcd for $C_{23}H_{23}F_3NOSi^+$ $[M + NH_4]^+$: 414.1496, found 414.1496.



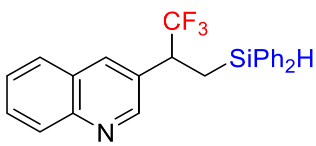
Following General procedure A, **L1** (5 mol%), CsOAc (20 mol%). **3v** was obtained as colorless oil. 62.0 mg, 0.16 mmol, 78% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.45 – 7.41 (m, 2H), 7.41 – 7.38 (m, 1H), 7.38 – 7.30 (m, 3H), 7.30 – 7.26 (m, 2H), 7.26 – 7.22 (m, 2H), 7.22 – 7.18 (m, 1H), 6.54 (s, 1H), 4.70 – 4.63 (m, 1H), 3.70 – 3.56 (m, 1H), 2.00 – 1.82 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -71.35 (d, *J* = 8.3 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.9, 151.2, 135.2, 135.0, 132.6, 132.5, 130.2, 130.0, 128.4, 128.1, 127.9, 126.1 (q, *J* = 280.6 Hz), 124.5, 123.0, 121.1, 111.5, 106.8, 41.0 (q, *J* = 29.8 Hz), 11.0. HRMS (DART, m/z): calcd for $C_{23}H_{20}F_3OSi^+$ $[M + H]^+$: 397.1230, found 397.1233.



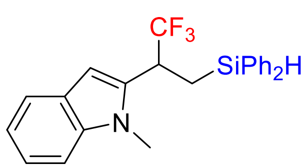
Following General procedure A, **L1** (5 mol%), CsOAc (20 mol%). **3w** was obtained as colorless oil. 46.1 mg, 0.11 mmol, 56% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.71 – 7.66 (m, 1H), 7.54 – 7.50 (m, 2H), 7.47 – 7.42 (m, 3H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 3H), 7.30 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 7.07 (s, 1H), 4.66 (dd, *J* = 4.9, 2.4 Hz, 1H), 3.80 – 3.64 (m, 1H), 1.99 – 1.77 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.05 (d, *J* = 8.3 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 139.2, 138.3, 136.2, 135.3, 135.0, 132.8, 132.5, 130.3, 130.0, 128.4, 128.1, 126.5 (q, *J* = 280.7 Hz), 124.9, 124.5, 123.7, 122.4, 42.9 (q, *J* = 29.5 Hz), 14.2. HRMS (EI, m/z): calcd for $C_{23}H_{19}F_3SSi^+$ $[M]^+$: 412.0929, found 412.0938.



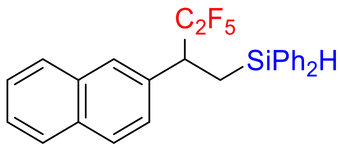
Following General procedure A, **L1** (5 mol%), CsOAc (20 mol%). **3x** was obtained as colorless oil. 49.3 mg, 0.11 mmol, 56% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 4H), 7.51 – 7.46 (m, 2H), 7.44 – 7.35 (m, 6H), 7.34 – 7.27 (m, 3H), 7.15 – 7.06 (m, 1H), 6.87 – 6.79 (m, 1H), 4.72 (s, 1H), 3.72 – 3.57 (m, 1H), 2.01 – 1.71 (m, 2H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -72.53 (d, J = 8.4 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 136.8, 135.3, 135.1, 134.3, 133.0, 132.7, 130.3, 130.0, 129.0, 128.9, 128.4, 128.2, 127.8, 126.6 (q, J = 280.1 Hz), 126.0, 122.7, 42.4 (q, J = 29.7 Hz), 14.5. HRMS (DART, m/z): calcd for $C_{25}H_{22}F_3SSi^+$ [M + H] $^+$: 439.1158, found 439.1160.



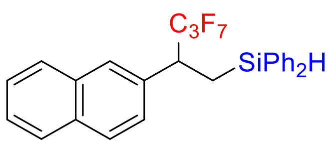
Following General procedure A, 60 ^{o}C**,** **3y** was obtained as colorless oil. 44.7 mg, 0.18 mmol, 55%. L:B = 9:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 – 8.59 (m, 1H), 8.12 – 8.03 (m, 1H), 7.94 – 7.86 (m, 1H), 7.77 – 7.65 (m, 2H), 7.59 – 7.48 (m, 1H), 7.48 – 7.29 (m, 7H), 7.29 – 7.14 (m, 3H), 4.56 (t, J = 3.8 Hz, 1H), 3.62 – 3.48 (m, 1H), 2.06 – 1.82 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.42 (d, J = 8.6 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 148.0, 136.4, 135.2, 134.9, 134.5, 134.5, 132.5, 132.2, 130.4, 130.0, 130.0, 129.4, 128.5, 128.0, 127.6, 127.1, 127.1 (q, J = 280.1 Hz). 44.5 (q, J = 28.5 Hz), 12.8. HRMS (EI, m/z): calcd for $C_{24}H_{20}F_3NSi^+$ [M] $^+$: 407.1317, found 407.1307.



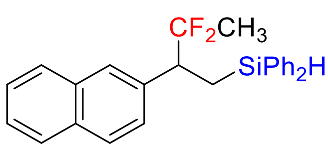
Following General procedure A, **3z** was obtained as colorless oil. 73.2 mg, 0.18 mmol, 89%. L:B = 18:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 1H), 7.45 – 7.41 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.23 (m, 6H), 7.24 – 7.19 (m, 2H), 7.14 – 7.07 (m, 1H), 6.61 (s, 1H), 4.70 (t, J = 3.9 Hz, 1H), 3.57 – 3.44 (m, 1H), 3.16 (s, 3H), 2.00 – 1.91 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.86 (d, J = 7.5 Hz, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.3, 135.3, 135.1, 133.7, 133.0, 132.5, 130.2, 130.1, 128.3, 128.2, 127.4, 126.7 (q, J = 280.3 Hz), 122.0, 120.8, 119.8, 109.5, 102.9, 37.9 (q, J = 29.3 Hz), 29.2, 12.4. HRMS (EI, m/z): calcd for $C_{24}H_{22}F_3NSi^+$ [M] $^+$: 409.1474, found 409.1469.



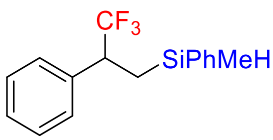
Following General procedure A, **3aa** was obtained as colorless oil. 57.5 mg, 0.13 mmol, 63% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.69 (m, 3H), 7.52 – 7.46 (m, 3H), 7.45 – 7.41 (m, 3H), 7.39 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.27 (m, 1H), 7.22 – 7.16(m, 2H), 4.40 (dd, J = 4.2, 2.8 Hz, 1H), 3.62 – 3.42 (m, 1H), 2.09 – 1.79 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.91 (s, 3F), -114.89 – -122.67 (m, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.2, 135.3, 134.9, 133.3, 133.3, 133.2, 132.8, 132.3, 130.2, 129.8, 129.3, 128.5, 128.3, 128.1, 128.0, 127.8, 126.4, 126.3, 44.4 (t, J = 21.6 Hz), 12.1. HRMS (DART, m/z): calcd $C_{26}H_{25}F_5NSi^+$ [M + NH_4] $^+$: 474.1671, found 474.1673.



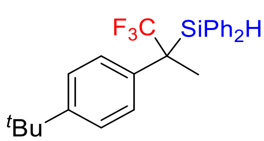
Following General procedure A, **3ab** was obtained as colorless oil. 54.5 mg, 0.11 mmol, 54% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.77 (m, 1H), 7.72 – 7.68 (m, 2H), 7.50 – 7.44 (m, 3H), 7.43 – 7.40 (m, 3H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 3H), 7.26 – 7.24 (m, 1H), 7.21 – 7.15 (m, 2H), 4.37 (dd, J = 4.3, 2.7 Hz, 1H), 3.71 – 3.52 (m, 1H), 2.03 – 1.84 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -80.70 (t, J = 11.0 Hz, 3F), -110.91 – -119.76 (m, 2F), -121.16 – -126.11 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.3, 134.9, 133.3, 133.2, 132.8, 132.3, 130.2, 129.8, 129.4, 128.1, 128.3, 128.1, 128.0, 127.7, 126.6, 126.4, 126.3, 44.7 (t, J = 21.6 Hz), 12.3. HRMS (DART, m/z): calcd for $C_{27}H_{25}F_7NSi^+$ [M + NH_4] $^+$: 524.1639, found 524.1641.



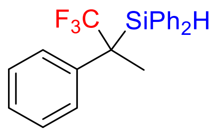
Following General procedure A, **3ac** was obtained as colorless oil. 64.8 mg, 0.16 mmol, 80% yield. L:B >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 1H), 7.75 – 7.68 (m, 2H), 7.50 – 7.43 (m, 5H), 7.42 – 7.34 (m, 4H), 7.33 – 7.26 (m, 3H), 7.23 – 7.16 (m, 2H), 4.46 (d, J = 2.2 Hz, 1H), 3.31 – 3.15 (m, 1H), 2.05 – 2.96 (m, 1H), 1.83 – 1.75 (m, 1H), 1.41 (t, J = 18.6 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.43 – -103.68 (m, 2F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.3, 135.4, 135.0, 134.0, 133.6, 133.3, 133.0, 129.9, 129.6, 128.7, 128.3, 128.2, 128.0, 128.0, 127.7, 126.8, 126.2, 126.1, 124.2 (t, J = 242.0 Hz), 49.8 (t, J = 24.9 Hz), 22.4 (t, J = 28.0 Hz), 12.4. HRMS (DART, m/z): calcd for $C_{26}H_{25}F_2NSi^+$ [M + NH_4] $^+$: 420.1954, found 420.1955.



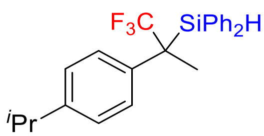
Following General procedure A, **3ad** was obtained as colorless oil. 46.5 mg, 0.16 mmol, 79% yield. L:B > 20:1. dr =1:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ (mixture of isomers) 7.41 – 7.39 (m, 1H), 7.39 – 7.38 (m, 2H), 7.38 – 7.37 (m, 2H), 7.38 – 7.34 (m, 1H), 7.34 – 7.31 (m, 5H), 7.31 – 7.28 (m, 3H), 7.25 – 7.20 (m, 3.6 H), 4.19 – 4.17 (m, 0.78H), 4.13 – 4.11 (m, 1H), 3.33 – 3.28(m, 1.78H), 1.58 – 1.54 (m, 4.48 H), 0.14 (d, J = 3.8 Hz, 2.58H), 0.11 (d, J = 3.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) (mixture of isomers) δ -71.68 (d, J = 2.6 Hz), -71.70 (d, J = 3.1 Hz). ^{13}C NMR (151 MHz, $CDCl_3$) (mixture of isomers) δ 135.7, 135.0, 134.7, 134.4, 134.4, 129.8, 129.7, 129.3, 128.7, 128.4, 128.3, 128.2, 128.1, 126.5, 46.8 (q, J = 27.8 Hz), 46.5 (q, J = 27.7 Hz), 29.9, 14.1, 13.7, -5.3, -5.9. HRMS (DART, m/z): calcd for $C_{16}H_{21}F_3NSi^+$ [M + NH_4] $^+$: 312.1390, found 312.1393.



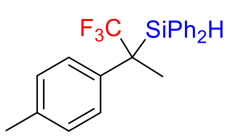
Following General procedure B, **4a** was obtained as colorless solid, mp: 52~54 °C. 79.1 mg, 0.19 mmol, 96% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 3H), 7.37 – 7.33 (m, 3H), 7.33 – 7.30 (m, 2H), 7.30 – 7.28 (m, 2H), 7.28 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 5.08 (s, 1H), 1.69 (s, 3H), 1.33 (s, 9H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.23 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 136.3, 136.3, 133.8, 131.4, 131.3, 130.3, 130.1, 129.3 (q, J = 280.1 Hz), 128.1, 128.0, 127.7, 125.3, 40.1 (q, J = 25.4 Hz), 34.5, 31.5, 16.5 (q, J = 4.1 Hz). HRMS (DART, m/z): calcd for $C_{25}H_{31}F_3NSi^+$ [M + NH_4] $^+$: 430.2172, found 430.2173.



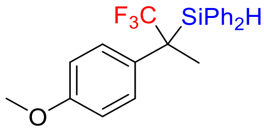
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4b** was obtained as white solid, mp: 45~47 °C. 70.9 mg, 0.20 mmol, 99% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 3H), 7.41 – 7.37 (m, 3H), 7.36 – 7.32 (m, 4H), 7.32 – 7.27 (m, 5H), 5.12 (q, *J* = 1.7 Hz, 1H), 1.71 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.15 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.9, 136.3, 136.2, 131.2, 131.0, 130.4, 130.2, 129.2 (q, *J* = 280.7 Hz), 128.5, 128.4, 128.1, 127.9, 127.2, 40.5 (q, *J* = 25.6 Hz), 16.4 (q, *J* = 3.8 Hz). HRMS (DART, m/z): calcd for $C_{21}H_{23}F_3NSi^+$ [M + NH_4] $^+$: 374.1546, found 374.1547.



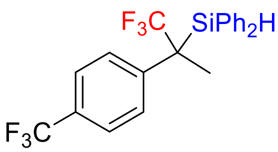
Following General procedure B, **4c** was obtained as white solid, mp: 50~52 °C. 68.5 mg, 0.17 mmol, 86% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 3H), 7.38 – 7.32 (m, 4H), 7.32 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.23 – 7.22 (m, 1H), 7.17 – 7.01 (m, 2H), 5.08 (s, 1H), 2.95 – 2.84 (m, 1H), 1.67 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.27 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 136.3, 136.3, 134.4, 131.4, 131.2, 130.3, 130.1, 129.3 (q, *J* = 280.7 Hz), 128.4, 128.0, 127.9, 126.5, 40.2 (q, *J* = 25.3 Hz), 33.7, 24.1, 24.1, 16.5 (q, *J* = 3.7 Hz). HRMS (DART, m/z): calcd for $C_{24}H_{29}F_3NSi^+$ [M + NH_4] $^+$: 416.2016, found 416.2018.



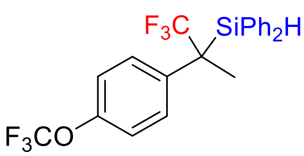
Following General procedure B, **4d** was obtained as white solid, mp: 52~53 °C. 71.1 mg, 0.19 mmol, 97% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.41 – 7.36 (m, 3H), 7.36 – 7.28 (m, 3H), 7.28 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 7.12 – 7.06 (m, 2H), 5.09 (s, 1H), 2.33 (s, 3H), 1.66 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.40 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 136.3, 136.3, 133.8, 131.5, 131.3, 129.3 (q, *J* = 280.4 Hz), 130.4, 130.2, 129.2, 128.4, 128.1, 127.9, 40.1 (q, *J* = 25.4 Hz), 21.1, 16.5 (q, J = 3.8 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{25}F_3NSi^+$ [M + NH_4] $^+$: 388.1703, found 388.1704.



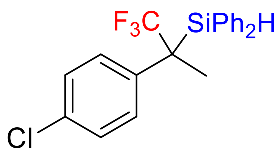
Following General procedure B, **4e** was obtained as white solid, mp: 50~51 ℃. 74.7 mg, 0.19 mmol, 96% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 2H), 7.43 – 7.39 (m, 3H), 7.38 – 7.34 (m, 2H), 7.33 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.25 – 7.23 (m, 1H), 6.84 (d, J = 8.9 Hz, 2H), 5.11 (s, 1H), 3.82 (s, 3H), 1.67 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.78 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 136.3, 136.3, 135.3, 135.0, 131.4, 131.2, 130.4, 129.7, 129.3 (q, J = 280.2 Hz), 128.1, 127.9, 113.8, 55.4, 39.6 (q, J = 25.4 Hz), 16.5 (q, J = 3.9 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{25}F_3NOSi^+$ [M + NH_4] $^+$: 404.1652, found 404.1655.



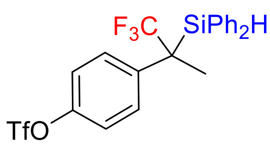
Following General procedure B, **4f** was obtained as colorless oil. 79.2 mg, 0.19 mmol, 94% yield. B:L >20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.45 – 7.42 (m, 4H), 7.42 – 7.38 (m, 4H), 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 2H), 5.08 (s, 1H), 1.72 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.57 (s, 3F), -62.77 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.3, 136.2, 136.1, 130.7, 130.6, 130.3, 129.4 (q, J = 32.9 Hz), 128.9 (q, J = 280.7 Hz), 128.7, 128.3, 128.1, 125.3 (q, J = 3.8 Hz), 124.2 (q, J = 271.9 Hz), 41.2 (q, J = 25.9 Hz), 16.6 (q, J = 3.4 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{19}F_6NSi^+$ [M + NH_4] $^+$: 422.1420, found 422.1442.



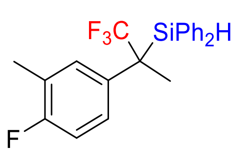
Following General procedure B, **4g** was obtained as colorless oil. 82.7 mg, 0.19 mmol, 95% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 3H), 7.39 – 7.35 (m, 3H), 7.35 – 7.33 (m, 1H), 7.33 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 7.15 – 7.10 (m, 2H), 5.07 (d, J = 1.7 Hz, 1H), 1.69 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87 (s, 3F), -63.18 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4 (q, J = 1.8 Hz), 136.2, 136.1, 135.8 (q, J = 1.5 Hz), 130.6, 130.6 (q, J = 16.2 Hz), 130.5, 129.9, 129.0 (q, J = 280.7 Hz), 128.2, 128.1, 120.7, 120.6 (q, J = 257.1 Hz), 40.5 (q, J = 25.6 Hz), 16.6 (q, J = 4.0 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{19}F_6OSi^+$ $[M + H]^+$: 441.1104, found 441.1076.



Following General procedure B**,** BINAP (5.8 mg, 4.7 mol%). **4h** was obtained as colorless solid, mp: 46~48 °C. 75.5 mg, 0.19 mmol, 97% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.38 (m, 3H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.21 (m, 4H), 5.06 (s, 1H), 1.66 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.25 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 136.2, 133.3, 130.9, 130.7, 130.6, 130.4, 129.8, 129.0 (q, J = 280.5 Hz), 128.6, 128.2, 128.1, 40.4 (q, J = 25.6 Hz), 16.6 (q, J = 3.8 Hz). HRMS (ESI, m/z): calcd for $C_{21}H_{22}ClF_3NSi^+$ $[M + NH_4]^+$: 408.1157, found 408.1156.

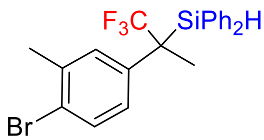


Following General procedure B, BINAP (5.8 mg, 4.7 mol%), 60 °C. **4k** was obtained as colorless oil. 38.5 mg, 0.08 mmol, 38% yield. B:L > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 4H), 7.41 – 7.36 (m, 5H), 7.36 – 7.33 (m, 1H), 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 2H), 5.07 (d, J = 1.3 Hz, 1H), 1.71 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.95 (s, 3F), -72.69 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.6, 137.9, 136.2, 136.1, 134.9, 130.7, 130.6, 130.3, 130.2, 128.9 (q, J = 280.4 Hz), 128.3, 128.2, 121.2, 118.9 (q, J = 320.7 Hz), 40.9 (q, J = 26.2 Hz), 16.6 (q, J = 3.8 Hz). HRMS (ESI, m/z): calcd for $C_{22}H_{18}F_6NaO_3SSi^+$ $[M + Na]^+$: 527.0542, found 527.0556.

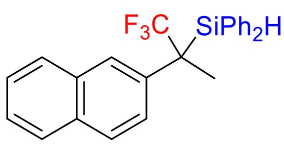


Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4l** was obtained as colorless oil. 76.8 mg, 0.20 mmol, 99% yield. B:L > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 –

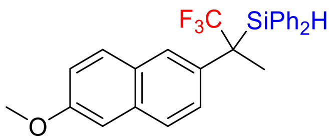
7.44 (m, 2H), 7.44 – 7.40 (m, 3H), 7.40 – 7.33 (m, 3H), 7.33 – 7.31 (m, 1H), 7.30 – 7.27 (m, 1H), 7.13 – 7.07 (m, 1H), 7.03 – 6.95 (m, 2H), 5.09 (s, 1H), 2.28 (s, 3H), 1.67 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.37 (s, 3F), -116.80 – -116.91 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, *J* = 244.1 Hz), 136.3, 136.2, 131.2 (d, *J* = 5.6 Hz), 130.9 (d, *J* = 13.3 Hz), 130.5, 130.4, 129.0 (q, *J* = 280.5 Hz), 128.2, 128.0, 124.0 (d, *J* = 1.1 Hz), 123.7 (d, *J* = 17.0 Hz), 115.3 (d, *J* = 24.1 Hz), 40.3 (q, *J* = 25.9 Hz), 16.5 (q, *J* = 3.5 Hz), 14.3 (d, *J* = 3.0 Hz). HRMS (DART, m/z): calcd for $C_{22}H_{24}F_4NSi^+$ $[M + NH_4]^+$: 406.1609, found 406.1612.



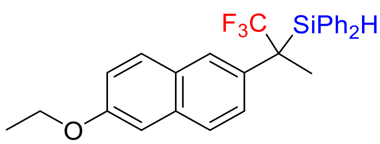
Following General procedure B, BINAP (5.8 mg, 4.7 mol%), 60 °C, 48h. **4m** was obtained as colorless oil. 27.9 mg, 0.06 mmol, 31%. B:L = 9: 1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 3H), 7.38 – 7.35 (m, 3H), 7.33 – 7.29 (m, 2H), 7.30 – 7.26 (m, 1H), 7.21 – 7.16 (m, 1H), 7.13 – 7.08 (m, 3H), 5.08 (s, 1H), 2.26 (s, 3H), 1.67 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.09 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 137.1, 137.1, 136.1, 135.8, 131.2, 131.0, 130.3, 130.1 (q, *J* = 280.4 Hz), 129.1, 128.9, 128.7, 126.3, 41.2 (q, *J* = 25.6 Hz), 22.5, 17.3 (q, *J* = 3.8 Hz). HRMS (EI, m/z): calcd for $C_{22}H_{20}BrF_3Si^+$ $[M]^+$: 448.0470, found 448.0458.



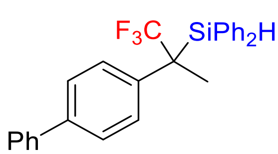
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4o** was obtained as white solid, mp: 80~81 °C. 80.4 mg, 0.20 mmol, 99% yield. B:L > 20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 1H), 7.77 – 7.73 (m, 1H), 7.73 – 7.66 (m, 2H), 7.51 – 7.44 (m, 3H), 7.44 – 7.38 (m, 4H), 7.37 – 7.32 (m, 1H), 7.30 – 7.27 (m, 2H), 7.26 – 7.24 (m, 3H), 5.16 (s, 1H), 1.80 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.84 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 136.3, 134.5, 133.3, 132.4, 131.3, 131.0, 130.4, 130.3, 129.3 (q, *J* = 280.7 Hz), 128.4, 128.1, 128.0, 127.8, 127.7, 127.5, 126.6, 126.3, 126.3, 40.8 (q, *J* = 25.3 Hz), 16.8 (q, *J* = 4.0 Hz). HRMS (DART, m/z): calcd for $C_{25}H_{25}F_3NSi^+$ $[M + NH_4]^+$: 424.1703, found 424.1704.



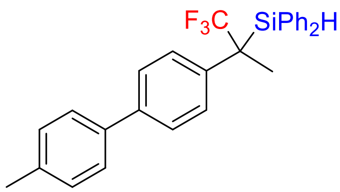
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4p** was obtained as white solid, mp: 86~87 °C. 86.9 mg, 0.20 mmol, 99% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.61 – 7.55 (m, 1H), 7.47 – 7.42 (m, 2H), 7.41 – 7.36 (m, 4H), 7.35 – 7.31 (m, 1H), 7.30 – 7.25 (m, 2H), 7.24 – 7.21 (m, 2H), 7.15 – 7.08 (m, 2H), 5.16 (s, 1H), 3.91 (s, 3H), 1.78 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.03 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 136.3, 136.3, 133.5, 132.0, 131.5, 130.7, 130.4, 129.9, 129.3 (q, J = 280.7 Hz), 128.8, 128.1, 127.9, 127.5, 127.1, 126.7, 119.2, 105.4, 55.5, 40.5 (q, J = 25.4 Hz), 16.7 (q, J = 3.8 Hz). HRMS (EI, m/z): calcd for $C_{26}H_{23}F_3OSi^+$ $[M]^+$: 436.1470, found 436.1475.



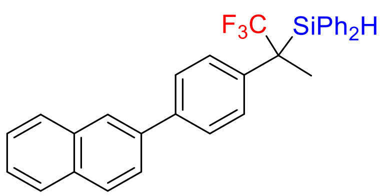
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4q** was obtained as white solid, mp: 86~87 °C, 90.0 mg, 0.20 mmol, 99% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 2H), 7.61 – 7.55 (m, 1H), 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 3H), 7.37 – 7.33 (m, 1H), 7.30 – 7.26 (m, 2H), 7.26 – 7.24 (m, 1H), 7.23 – 7.20 (m, 2H), 7.15 – 7.08 (m, 2H), 5.15 (s, 1H), 4.15 (q, J = 7.0 Hz, 2H), 1.78 (s, 3H), 1.48 (t, J = 7.0 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.06 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 136.3, 136.3, 133.6, 131.9, 131.5, 131.2, 129.3 (q, J = 280.7 Hz), 130.4, 130.2, 129.8, 128.8, 128.1, 127.9, 127.5, 127.0, 126.7, 119.5, 106.2, 63.7, 40.5 (q, J = 25.5 Hz), 16.7 (q, J = 3.8 Hz), 15.0. HRMS (DART, m/z): calcd for $C_{27}H_{29}F_3NOSi^+$ $[M + NH_4]^+$: 451.1700, found 451.1698.



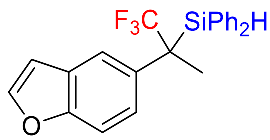
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4r** was obtained as white solid, mp: 59~60 °C. 86.5 mg, 0.20 mmol, 99% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.47 – 7.44 (m, 3H), 7.43 – 7.40 (m, 3H), 7.40 – 7.36 (m, 3H), 7.36 – 7.30 (m, 3H), 7.30 – 7.25 (m, 2H), 7.25 – 7.23 (m, 1H), 5.03 (s, 1H), 1.72 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.02 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 139.9, 136.3, 136.3, 135.3, 131.2, 131.0, 130.5, 130.3, 129.2 (q, *J* = 280.8 Hz), 129.0, 128.9, 128.1, 128.0, 127.6, 127.1, 127.0, 40.5 (q, *J* = 25.7 Hz), 16.6 (q, *J* = 3.8 Hz). HRMS (DART, m/z): calcd for $C_{27}H_{27}F_3NSi^+$ [M + NH_4] $^+$: 450.1859, found 450.1859.



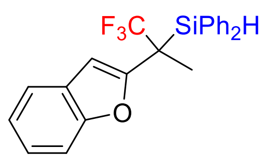
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4s** was obtained as white solid, mp: 88~90 °C. 88.8 mg, 0.20 mmol, 99% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 4H), 7.47 – 7.43 (m, 2H), 7.43 – 7.39 (m, 3H), 7.38 – 7.33 (m, 3H), 7.33 – 7.27 (m, 3H), 7.26 – 7.23 (m, 3H), 5.11 (s, 1H), 2.39 (s, 3H), 1.71 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.05 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.6, 137.4, 136.3, 136.3, 135.7, 131.3, 131.1, 130.4, 130.3, 129.7, 129.3 (q, *J* = 280.8 Hz), 128.8, 128.1, 128.0, 127.0, 126.8, 40.5 (q, *J* = 25.5 Hz), 21.2, 16.5 (q, *J* = 3.6 Hz). HRMS (DART, m/z): calcd for $C_{28}H_{29}F_3NSi^+$ [M + NH_4] $^+$: 464.2016, found 464.2015.



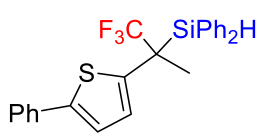
Following General procedure B, **4t** was obtained as white solid, mp: 100~101°C. 96.5 mg, 0.20 mmol, 99% yield. B:L >20:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 1H), 7.96 – 7.86 (m, 3H), 8.00 – 7.76 (m, 1H), 7.78 – 7.66 (m, 2H), 7.55 – 7.49 (m, 4H), 7.48 – 7.44 (m, 4H), 7.44 – 7.38 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 5.16 (s, 1H), 1.77 (s, 3H).^{19}F NMR (377 MHz, $CDCl_3$) δ -63.03 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 137.8, 136.3, 136.3, 136.2, 133.9, 132.9, 131.3, 131.0, 130.5, 130.3, 129.3 (q, *J* = 280.4 Hz), 129.0, 128.6, 128.4, 128.2, 128.0, 127.8, 127.2, 126.5, 126.2, 125.8, 125.5, 40.6 (q, *J* = 25.5 Hz), 16.6 (q, *J* = 3.8 Hz). HRMS (ESI, m/z): calcd for $C_{31}H_{26}F_3Si^+$ [M + H] $^+$: 483.1750, found 483.1753.



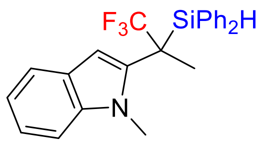
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). **4u** was obtained as colorless oil. 65.5 mg,0.17 mmol, 83% yield. B:L = 5:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 1H), 7.58 – 7.55 (m, 1H), 7.45 – 7.40 (m, 4H), 7.40 – 7.36 (m, 3H), 7.35 – 7.30 (m, 3H), 7.30 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 6.71 – 6.69 (m, 1H), 5.16 (s, 1H), 1.77 (s, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.47 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 145.6, 136.3, 136.3, 135.3, 135.0, 131.4, 131.2, 130.4, 130.2, 129.3 (q, *J* = 279.1 Hz), 128.1, 127.9, 125.1, 121.3, 111.1, 107.0, 40.3 (q, *J* = 25.5 Hz), 16.9 (q, *J* = 4.0 Hz). HRMS (DART, m/z): calcd for $C_{23}H_{23}F_3NOSi^+$ [M + NH_4] $^+$: 414.1496, found 414.1498.



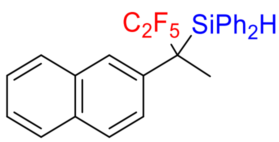
Following General procedure B, BINAP (5.8 mg, 4.7 mol%), 48h. **4v** was obtained as colorless oil. 42.8 mg, 0.11 mmol, 54%. B:L = 7:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 1H), 7.57 – 7.53 (m, 1H), 7.43 – 7.38 (m, 3H), 7.38 – 7.32 (m, 4H), 7.32 – 7.26 (m, 3H), 7.26 – 7.21 (m, 2H), 6.71 – 6.64 (m, 1H), 5.15 (s, 1H), 1.75 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.49 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.1, 145.6, 136.3, 136.3, 135.3, 135.0, 131.4, 131.2, 130.4, 130.2, 129.2 (q, *J* = 281.6 Hz), 127.9, 125.1, 121.3, 111.1, 107.0, 40.2 (q, *J* = 25.5 Hz), 16.9 (q, *J* = 3.5 Hz). HRMS (EI, m/z): calcd for $C_{23}H_{19}F_3OSi^+$ [M] $^+$: 396.1157, found 396.1153.



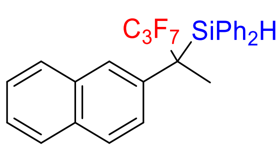
Following General procedure B, BINAP (5.8 mg, 4.7 mol%), 48h, **4x** was obtained as colorless oil. 49.1 mg, 0.11 mmol, 56%. B:L >20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 4H), 7.54 – 7.48 (m, 2H), 7.48 – 7.42 (m, 1H), 7.41 – 7.36 (m, 5H), 7.34 – 7.27 (m, 3H), 7.22 – 7.16 (m, 1H), 6.86 – 6.82 (m, 1H), 5.14 (s, 1H), 1.75 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -65.61 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 140.5, 136.3, 136.3, 134.3, 130.6, 130.6, 130.6, 130.5, 129.0, 128.3 (q, *J* = 279.9 Hz), 128.2, 128.0, 128.0, 127.6, 125.8, 123.2, 39.2 (q, J = 27.0 Hz), 17.9 (q, J = 3.4 Hz). HRMS (ESI, m/z): calcd for $C_{25}H_{21}F_3NaSSi^+$ [M+Na] $^+$: 461.0978, found 461.0986.



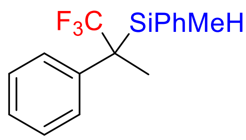
Following General procedure B, BINAP (5.8 mg, 4.7 mol%), 60 ^oC. **4z** was obtained as colorless oil. 36.7 mg, 0.09 mmol, 45%. B:L = 7: 1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 1H), 7.55 – 7.48 (m, 2H), 7.45 – 7.38 (m, 4.3 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.32 – 7.26 (m, 4H), 7.21 – 7.14 (m, 4H), 7.13 – 7.05 (m, 1H), 6.61 (s, 1H), 5.49 (s, 1H), 3.65 (s, 3H), 1.82 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.66 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.1, 136.4, 135.7, 135.3, 135.2, 134.5, 131.4, 130.5, 130.4, 129.3 (q, J = 280.7 Hz), 128.3, 128.2, 122.0, 120.5, 119.8, 109.4, 104.3, 36.3 (q, J = 29.0 Hz), 33.2 (q, J = 3.4 Hz), 19.5 (q, J = 3.9 Hz). HRMS (EI, m/z): calcd for $C_{24}H_{22}F_3NSi^+$ [M] $^+$: 409.1474, found 409.1470.



Following General procedure B, **4aa** was obtained as colorless oil. 43.0 mg, 0.09 mmol, 46% yield. B:L >20:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.78 – 7.74 (m, 1H), 7.73 – 7.67 (m, 2H), 7.55 – 7.45 (m, 3H), 7.43 – 7.37 (m, 5H), 7.37 – 7.28 (m, 3H), 7.25 – 7.18 (m, 2H), 5.22 – 5.18 (m, 1H), 1.86 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.88 (s, 3F), -100.70 – 104.52 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 136.4, 133.2, 132.4, 131.6, 131.4, 130.4, 130.2, 128.4, 128.1, 127.9, 127.8, 127.7, 127.5, 126.9, 126.9, 126.3, 126.3, 39.9 (t, J = 22.0 Hz), 16.2 (m). HRMS (DART, m/z): calcd for $C_{26}H_{25}F_5NSi^+$ [M + NH_4] $^+$: 474.1671, found 474.1674.



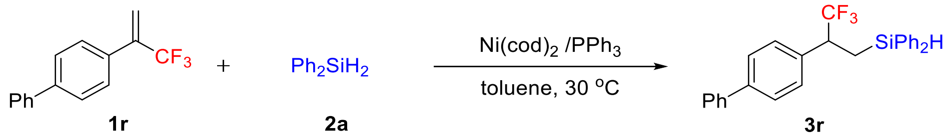
Following General procedure B, **4ab** was obtained as colorless oil. 40.6 mg,0.08 mmol, 40% yield. B:L >20:1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 1H), 7.77– 7.74 (m, 1H), 7.73 – 7.67 (m, 2H), 7.54 – 7.46 (m, 3H), 7.41 – 7.32 (m, 6H), 7.32 – 7.26 (m, 2H), 7.26 – 7.18 (m, 2H), 5.16 (d, *J* = 2.7 Hz, 1H), 1.91 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.03 – -81.15 (m, 3F), -98.64 – -100.00 (m, 2F), -118.83 – -121.61 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 136.4, 136.2, 135.3, 134.8, 133.2, 132.3, 131.6, 131.3, 130.4, 130.2, 128.4, 128.1, 127.9, 127.7, 127.5, 126.3, 126.3, 41.5 (t, *J* = 25.2 Hz), 16.2 (t, *J* = 9.5 Hz). HRMS (DART, m/z): calcd for $C_{27}H_{25}F_7NSi^+$ $[M + NH_4]^+$: 524.1639, found 524.1640.



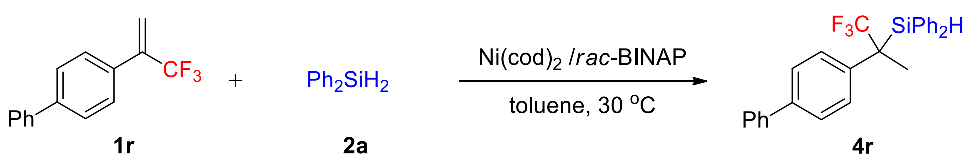
Following General procedure B, BINAP (5.8 mg, 4.7 mol%). 60 °C**. 4ad** was obtained as colorless oil. 30.0mg, 0.10 mmol, 51% yield. L:B =2.3:1. dr of **3ad** =1:1, dr of **4ad** = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of isomers) 7.39 – 7.8 (m, 23H), 7.24 – 7.18 (m, 6H), 4.60 (s, 0.86H), 4.17 – 4.15(m, 1H), 4.13 – 4.10 (m, 1H), 3.33 – 3.25 (m, 2H), 1.59 (s, 1.30 H), 1.56 (s, 1.30H), 1.55 – 1.49 (m, 4H), 0.48 (d, *J* = 3.6 Hz, 1.3 H), 0.30 (d, *J* = 3.7 Hz, 1.3 H), 0.13 (d, *J* = 3.8 Hz, 3H), 0.10 (d, *J* = 3.8 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ Branched products: -63.00 (s), -63.23 (s), linear products: -71.68 (d, *J* = 1.9 Hz, 3F), -71.71(d, *J* = 1.9 Hz, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) (mixture of isomers) δ 135.7, 135.5, 135.0, 134.7, 134.4, 134.4, 132.5, 130.3, 130.2, 129.8, 129.7, 129.3, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 126.9, 126.0, 46.6 (m), 15.9 (q, *J* = 4.0 Hz), 15.6 (q, *J* = 4.0 Hz), 14.1, 13.7, -5.3, -5.9, -6.9. HRMS (DART, m/z): calcd for $C_{16}H_{21}F_3NSi^+$ $[M + NH_4]^+$: 312.1390, found 312.1393.

2.3 Gram-Scale Synthesis and Derivatization Reactions

2.3.1 Scale-up reaction

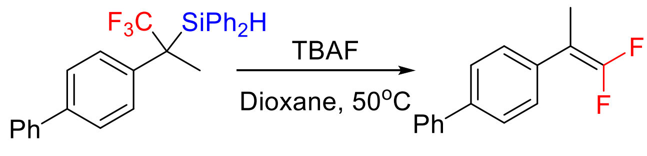


Ni(cod)$_2$ (28 mg, 0.1 mmol) and PPh$_3$ (26 mg, 0.1 mmol) in toluene (20.0 mL) were charged into a 100 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (780 mg, 4 mmol), after stirred for 20 min, **1r** (2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. After the reaction was completed (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **3r** (864.3 mg, yield 99%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.54 (m, 2H), 7.49 – 7.43 (m, 5H), 7.42 – 7.37 (m, 4H), 7.37 – 7.30 (m, 4H), 7.29 – 7.23 (m, 2H), 7.23 – 7.18 (m, 2H), 4.61 (d, *J* = 2.7 Hz, 1H), 3.47 – 3.31 (m, 1H), 1.97 – 1.72 (m, 2H).

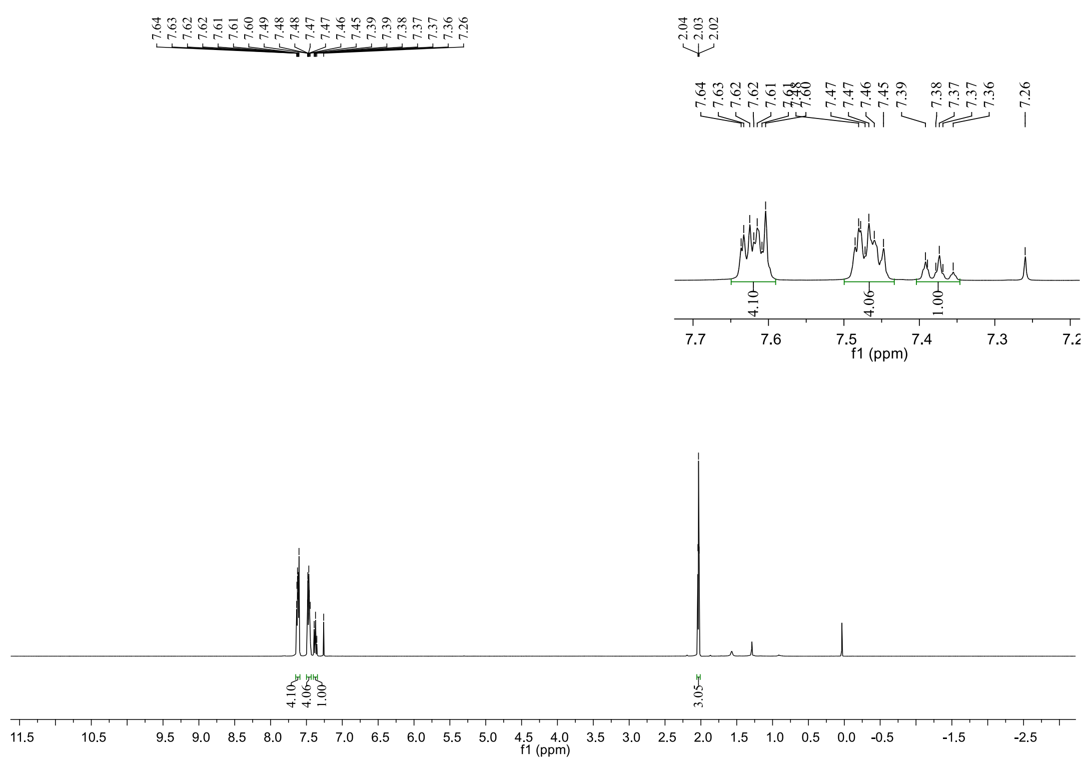


Ni(cod)$_2$ (28 mg, 0.1 mmol) and *rac*-BINAP (58 mg, 0.094 mmol) in toluene (20.0 mL) were charged into a 100 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (780 mg, 4 mmol), after stirred for 20 min, **1r** (2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. After the reaction was completed (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **4r** (864.7mg, yield 99%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.47 – 7.44 (m, 3H), 7.43 – 7.40 (m, 3H), 7.40 – 7.36 (m, 3H), 7.36 – 7.30 (m, 3H), 7.30 – 7.25 (m, 2H), 7.25 – 7.23 (m, 1H), 5.03 (t, *J* = 5.2 Hz, 1H), 1.72 (s, 3H).

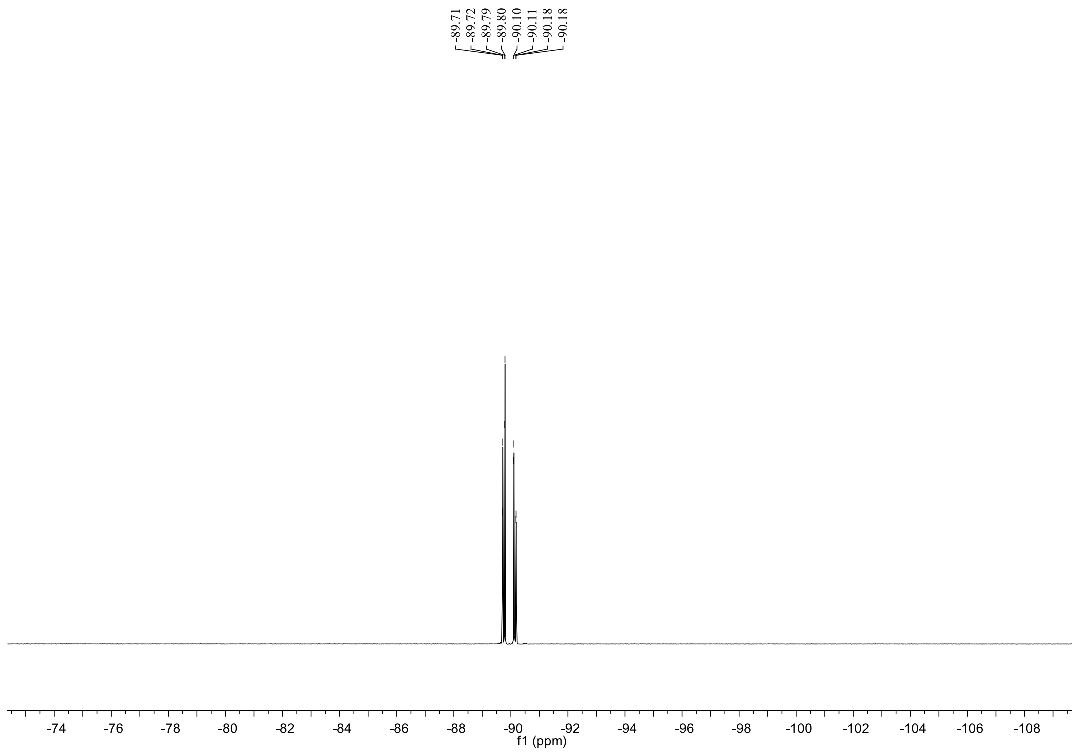
2.3.2 Derivatization Reactions



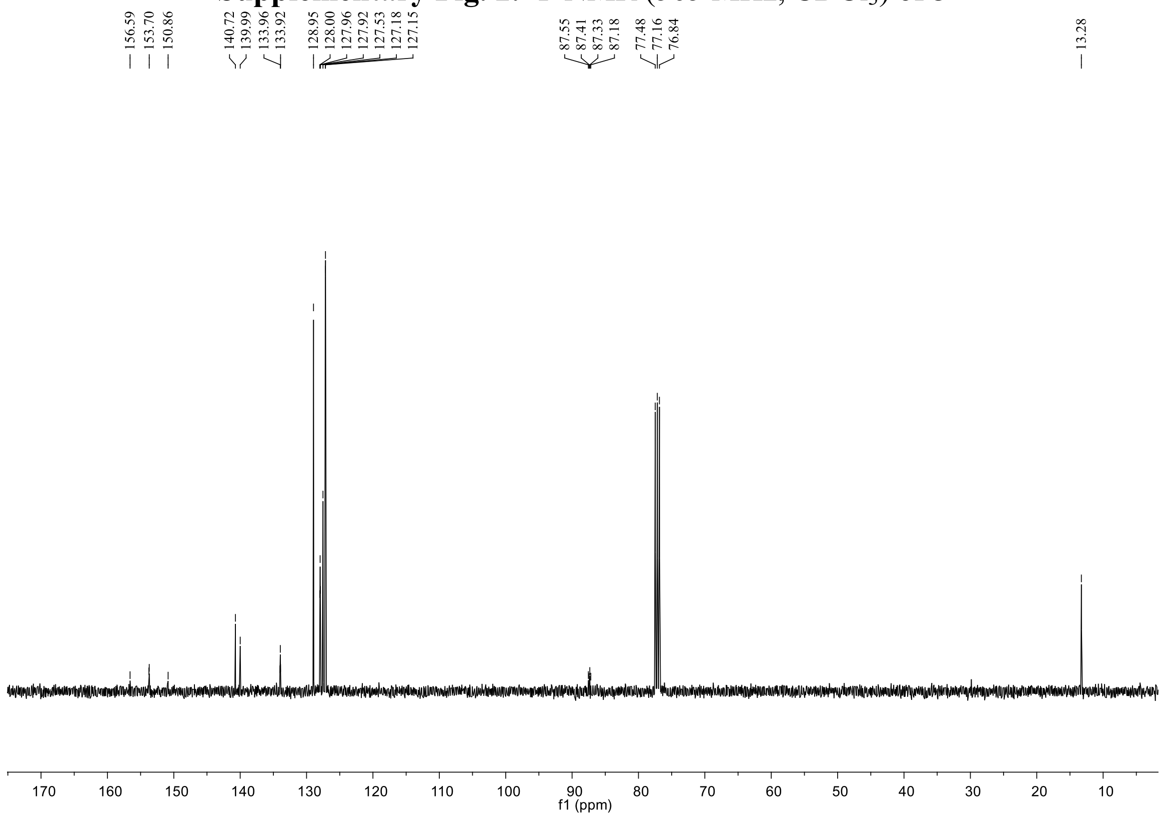
4r (86.5 mg, 0.2 mmol, 1 eq) and TBAF (0.6 mL, 0.6 mmol, 1.0 M in THF) was added in dioxane (2.0 mL), After stirred at 50 °C overnight, the reaction mixture was filtered through a pad of celite eluting with ethyl acetate. The crude mixture was concentrated and purified by silica gel chromatography (PE) to give the indicated product **5** [4] (27.0 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.58 (m, 4H), 7.54 – 7.43 (m, 4H), 7.42 – 7.34 (m, 1H), 2.03 (t, J = 3.4 Hz, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -89.66 – -90.23 (m, 2F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7 (dd, J = 290.6 Hz, 286.3 Hz), 140.7, 140.0, 134.0 (t, J = 4.2 Hz), 129.0, 128.0, 128.0, 127.9, 127.5, 127.2, 127.2, 87.4 (dd, J = 22.7 Hz, 14.0 Hz), 13.3.



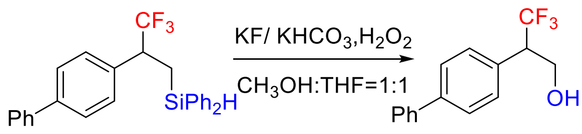
Supplementary Fig. 1. ^{1}H NMR (400 MHz, $CDCl_3$) of **5**



Supplementary Fig. 2. ^{1}F NMR (565 MHz, $CDCl_3$) of **5**

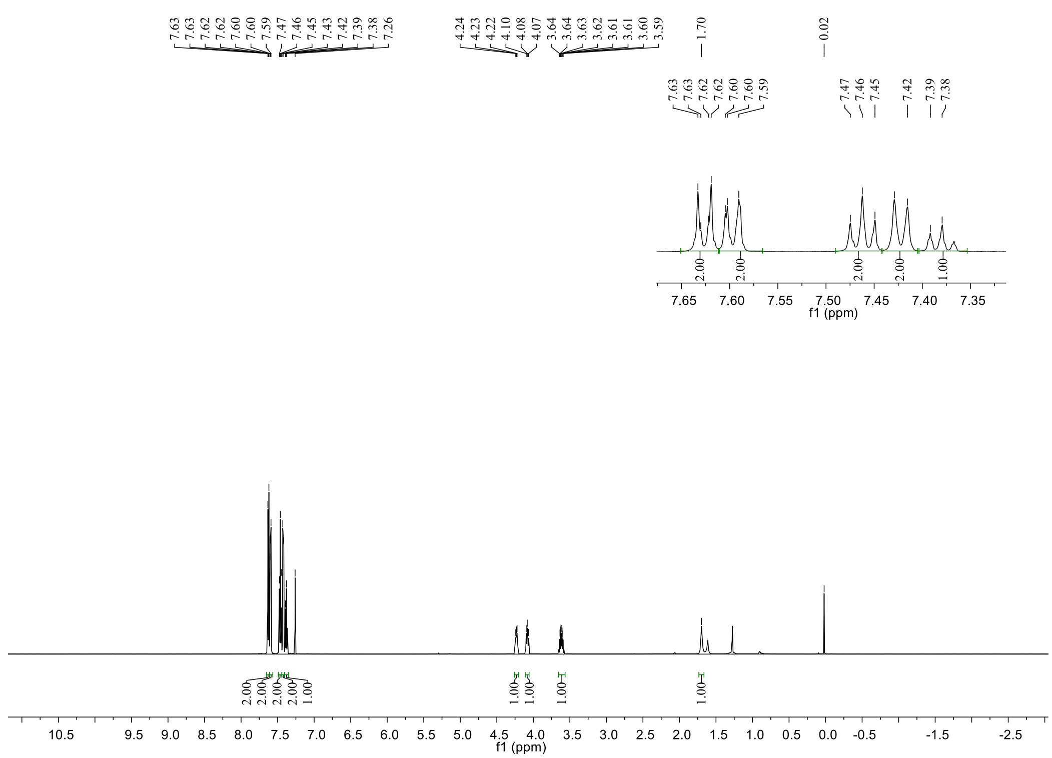


Supplementary Fig. 3. ^{13}C NMR (101 MHz, $CDCl_3$) of **5**

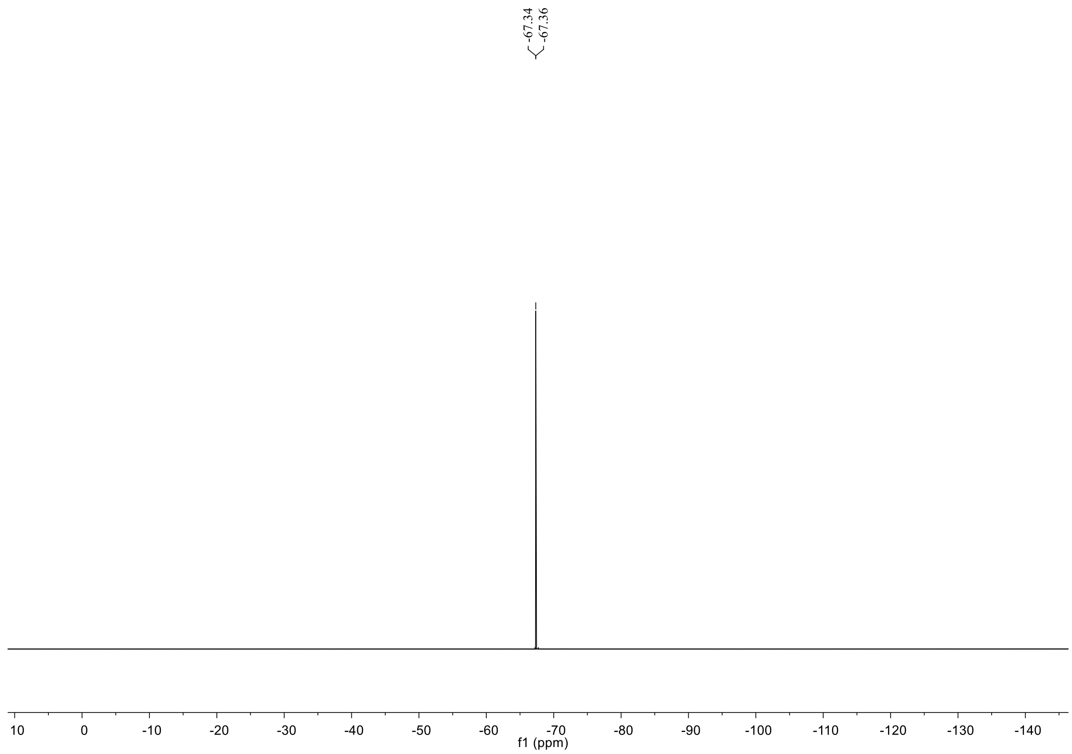


3r **6**

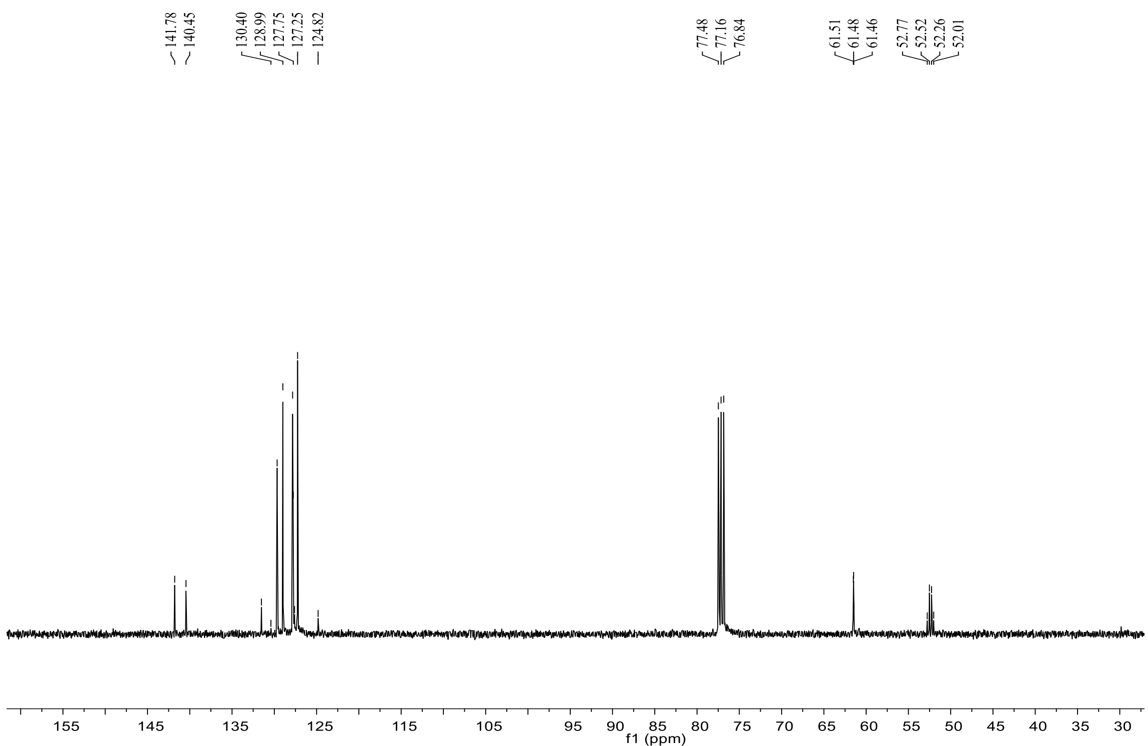
KF (93 mg, 1.6 mmol, 8.0 eq), $KHCO_3$ (100 mg, 10 mmol, 5.0 eq), **3r** (86.5 mg, 0.2 mmol, 1.0 eq) and THF (1.0 mL) were charged into a pressure tube under argon atmosphere, after stirred for 10 min, H_2O_2 (4 mL, 1.2 mmol, 30 wt% in H_2O) were added, then the reaction mixture was stirred at 60 °C overnight. The reaction mixture was filtered through a pad of celite eluting with ethyl acetate. The crude mixture was concentrated and purified by silica gel chromatography (PE: EA = 10:1) to give the indicated product **6** (47.6 mg, 89% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.61 – 7.57 (m, 2H), 7.49 – 7.44 (m, 2H), 7.44 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 4.26 – 4.20 (m, 1H), 4.11 – 4.06 (m, 1H), 3.65 – 3.55 (m, 1H), 1.70 (s, 1H). ^{19}F NMR (565 MHz, $CDCl_3$) δ -67.35 (d, J = 9.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 140.5, 131.5, 129.7, 129.0 (q, J = 280.5 Hz), 129.0, 127.8, 127.6, 127.3, 124.8, 61.5 (d, J = 2.6 Hz), 52.4 (q, J = 25.6 Hz). HRMS (ESI, m/z): calcd for $C_{15}H_{13}F_3NaO^+$ $[M + Na]^+$: 289.0811, found 289.0808.



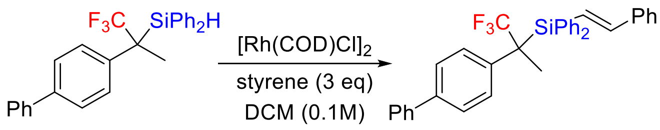
Supplementary Fig. 4. ^{1}H NMR (600 MHz, $CDCl_3$) of **6**



Supplementary Fig. 5. ^{19}F NMR (565 MHz, $CDCl_3$) of **6**



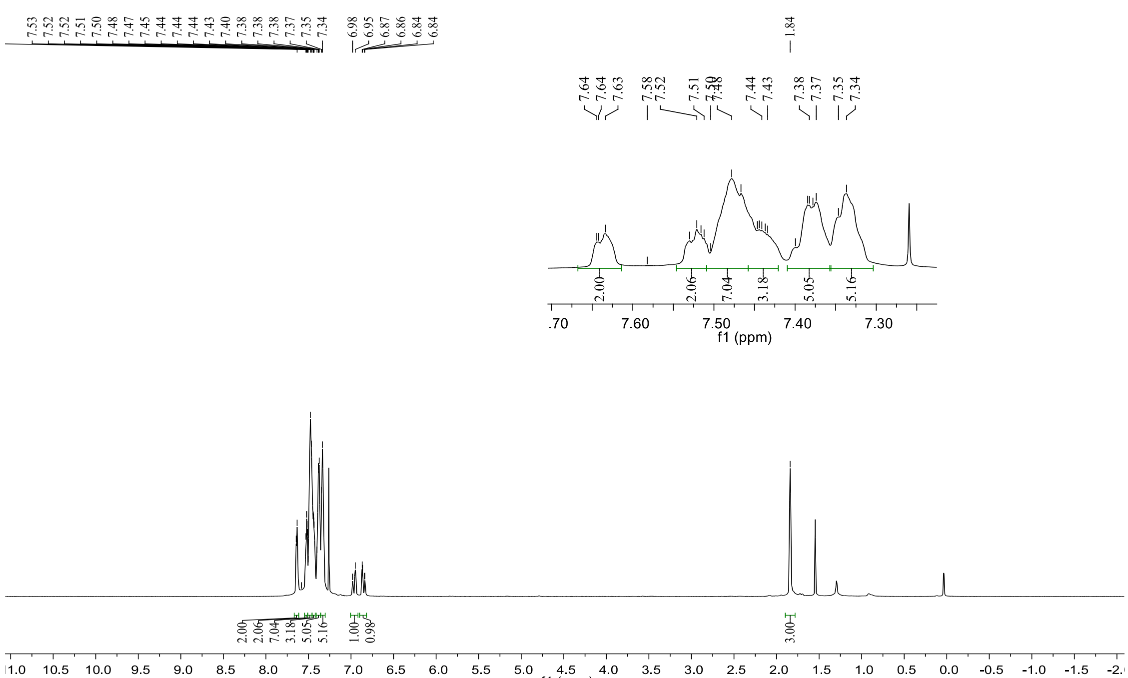
Supplementary Fig. 6. ^{13}C NMR (101 MHz, $CDCl_3$) of **6**



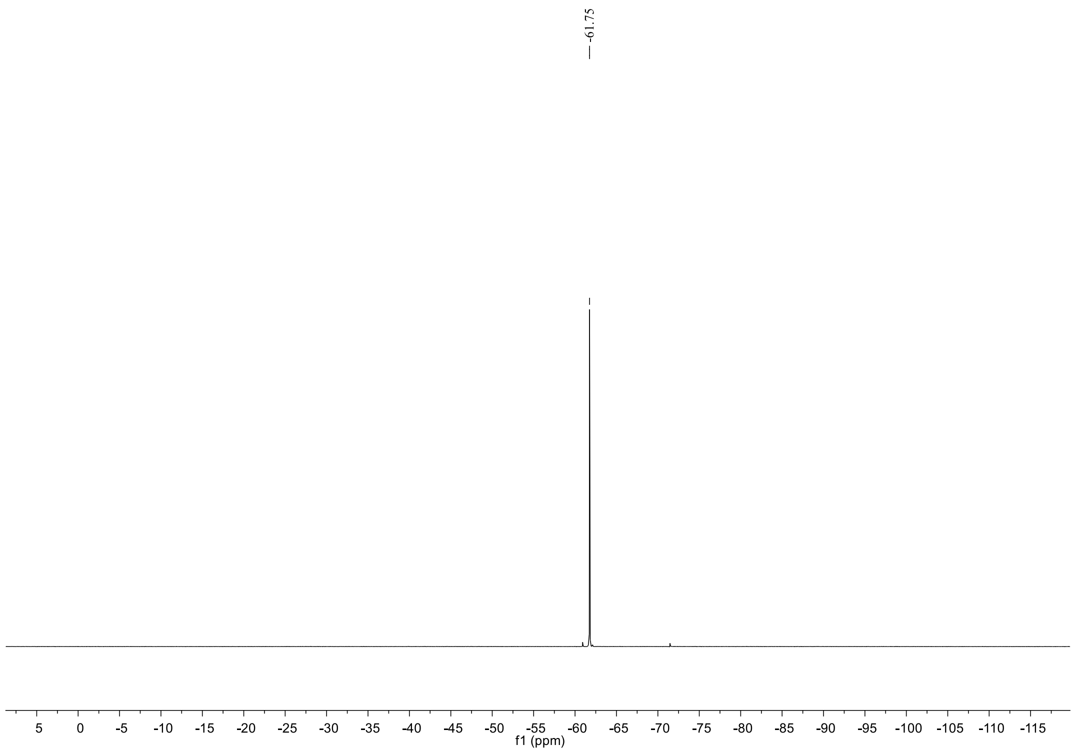
4r

7
75% yield

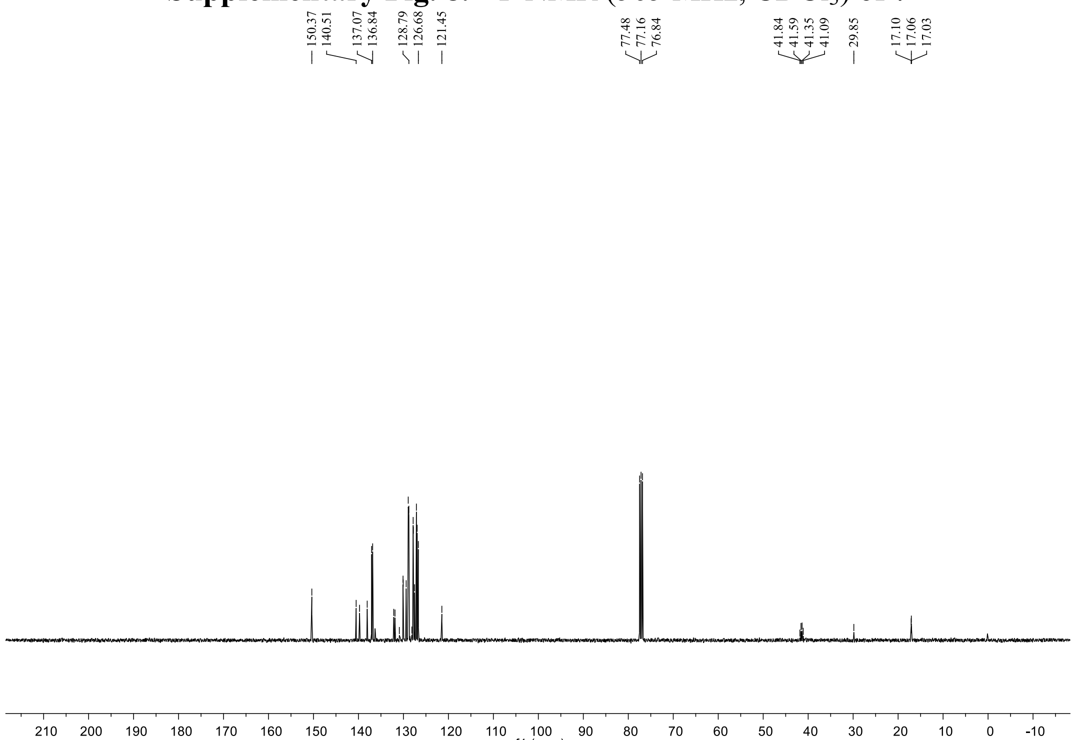
$[Rh(COD)Cl]_2$ (2.5 mg, 2.5 mol%), **4r** (86.5 mg, 0.2 mmol, 1 eq), styrene (62.5 mg, 0.6 mmol) and DCM (2.0 mL) were charged into a pressure tube under argon atmosphere. The tube was sealed and placed into a preheated oil bath and was heated at 40 °C for 16 h. After the reaction was complete, the reaction vial was removed from the oil bath and cooled to ambient temperature. The reaction mixture was filtered through a pad of celite eluting with ethyl acetate. The crude mixture was concentrated and purified by silica gel chromatography (PE:EA = 100:1) to give the indicated product **7** (80.1 mg, 75% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.62 (m, 2H), 7.55 – 7.51 (m, 2H), 7.51 – 7.46 (m, 7H), 7.46 – 7.41 (m, 3H), 7.41 – 7.35 (m, 5H), 7.35 – 7.31(m, 5H), 7.00 – 6.94 (m, 1H), 6.88 – 6.82 (m, 1H), 1.84 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$) -61.75 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) 150.4, 140.5, 139.8, 138.1, 137.1, 136.8, 132.2, 131.9, 130.9, 130.1, 130.1, 129.5 (q, J = 280.7 Hz), 129.4, 128.9, 128.8, 128.1, 127.8, 127.8, 127.5, 127.1, 127.0, 126.7, 121.5, 41.5 (q, J = 25.2 Hz), 17.1 (q, J = 3.7 Hz). HRMS (DART, m/z): calcd for $C_{35}H_{30}F_3Si^+$ $[M + H]^+$: 535.2063, found 535.2061.



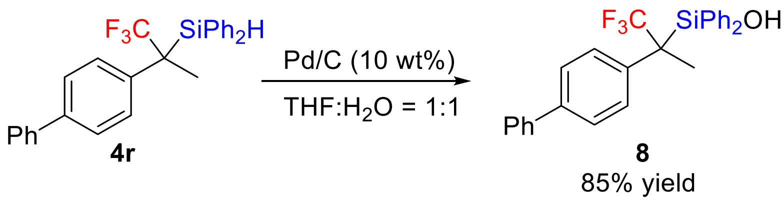
Supplementary Fig. 7. ^{1}H NMR (600 MHz, $CDCl_3$) of **7**



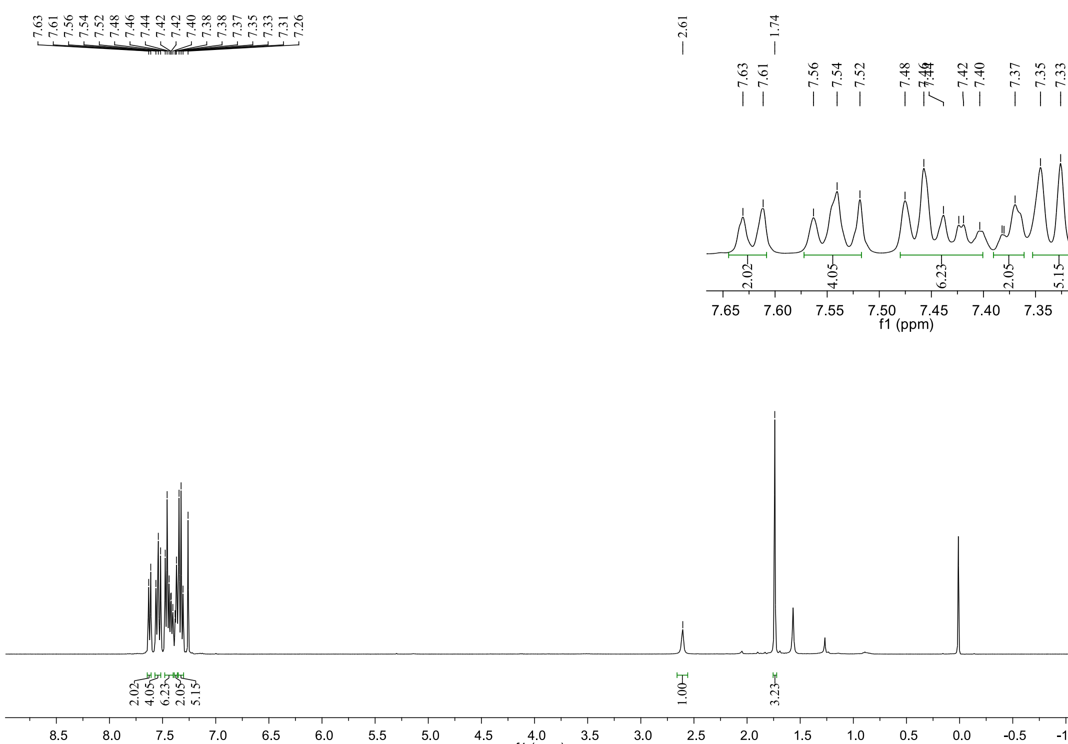
Supplementary Fig. 8. ^{19}F NMR (565 MHz, $CDCl_3$) of **7**



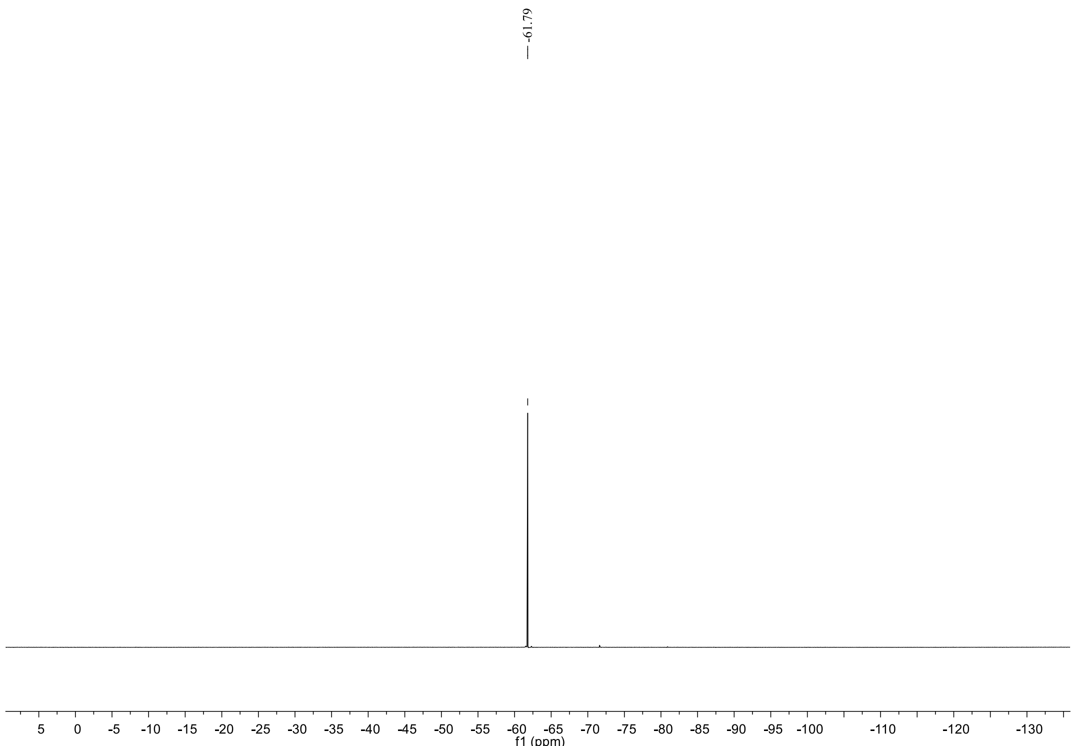
Supplementary Fig. 9. ^{13}C NMR (101 MHz, $CDCl_3$) of **7**



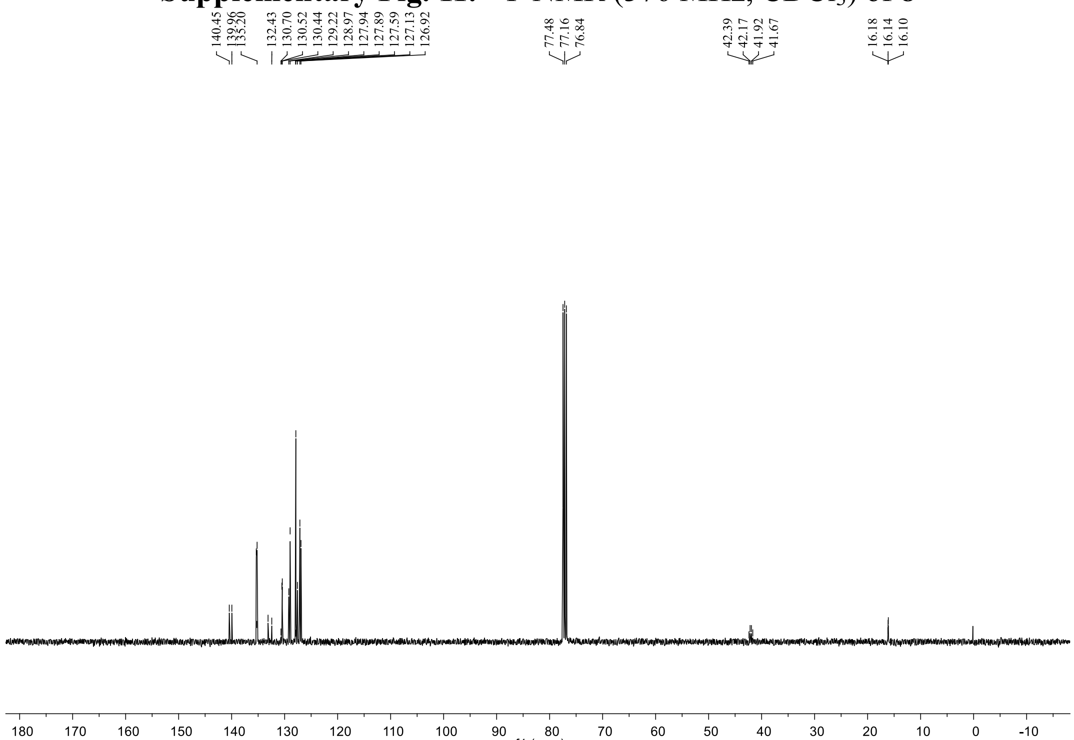
4r (86.5 mg, 0.2 mmol) and THF (2.0 mL, containing 1% v/v H_2O) was added to a flame dried schlenk tube under argon, the Pd/C (15.0 mg, 10 wt%) was added and stirred at room temperature. After the reaction was complete (24 h), DCM (5.0 mL) was added and dried by Na_2SO_4, then the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated in vacuo and purified by silica gel chromatography (PE:EA = 10:1) to give the product **8** (73.7 mg, yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.58 – 7.51 (m, 4H), 7.50 – 7.40 (m, 6H), 7.39 – 7.36 (m, 2H), 7.35 – 7.28 (m, 5H), 2.61 (s, 1H), 1.74 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.79 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 140.0, 135.4, 135.3, 135.2, 133.1, 132.4, 130.5, 130.4, 129.3 (q, J = 277.2 Hz), 129.2, 129.0, 127.9, 127.6, 127.1, 126.9, 42.1 (q, J = 25.2 Hz), 16.1 (q, J = 4.1 Hz). HRMS (DART, m/z): calcd for $C_{27}H_{27}F_3NOSi^+$ [M + NH_4]$^+$: 466.1809, found 466.1807.



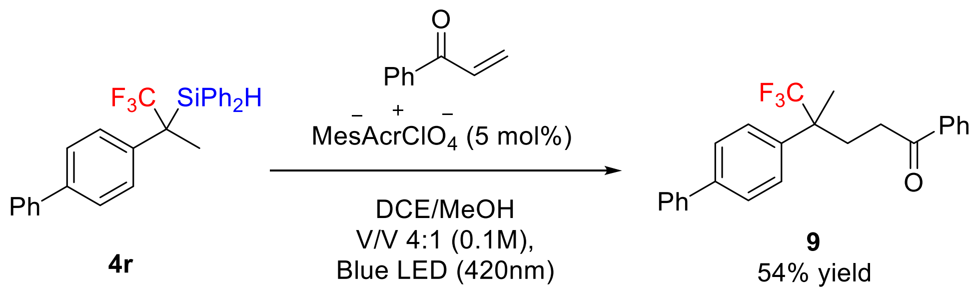
Supplementary Fig. 10. ^{1}H NMR (400 MHz, $CDCl_3$) of **8**



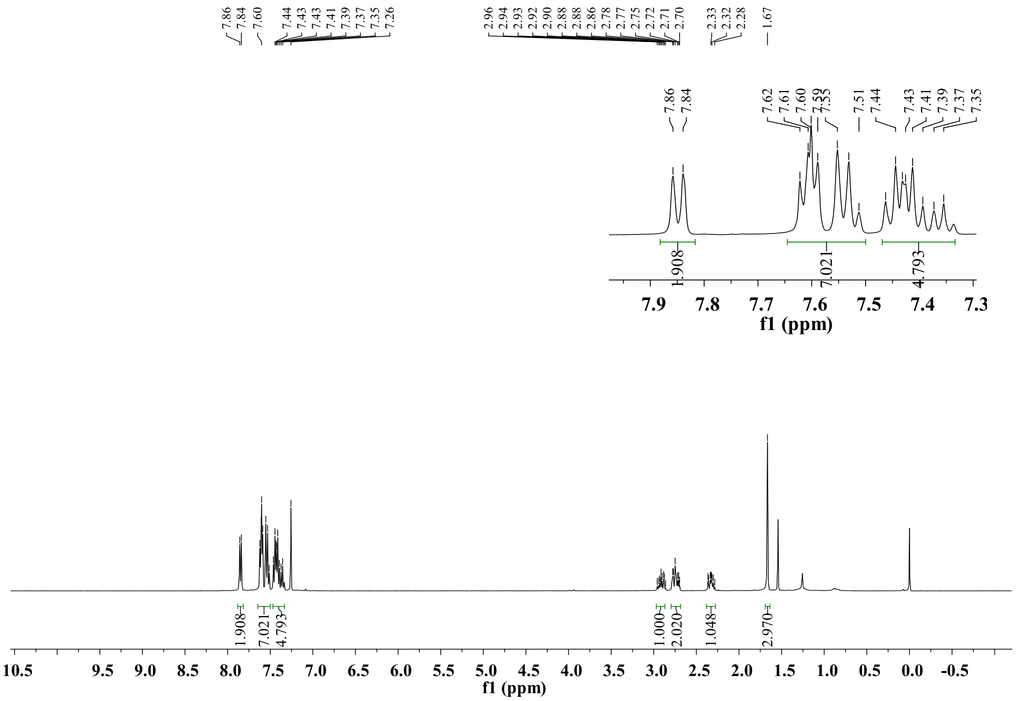
Supplementary Fig. 11. ^{19}F NMR (376 MHz, $CDCl_3$) of **8**



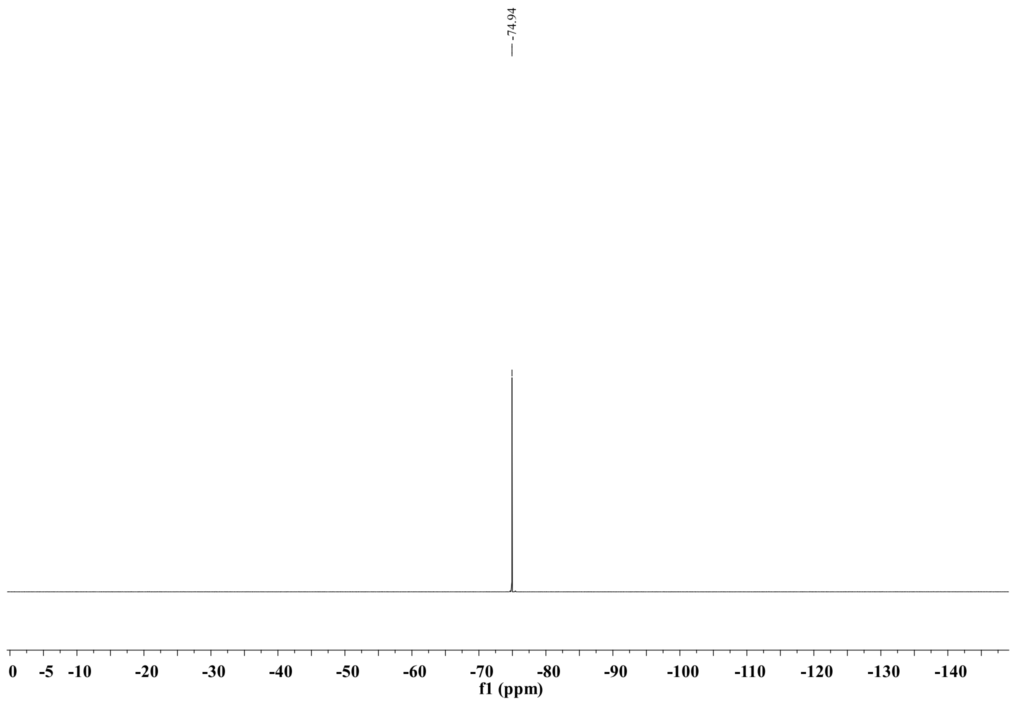
Supplementary Fig. 12. ^{13}C NMR (101 MHz, $CDCl_3$) of **8**



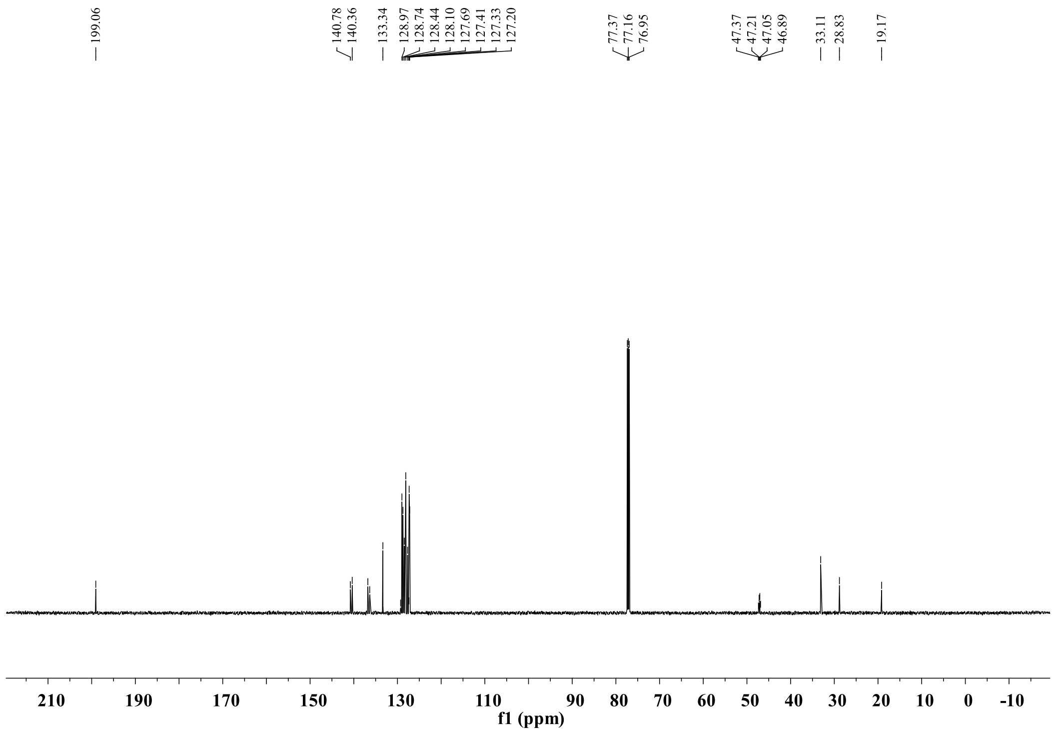
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst $Mes^{-}Acr^{+}ClO_4^{-}$ (2.1 mg, 0.005 mmol), and **4r** (0.1 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequently backfilled with argon for three times. After that, anhydrous DCE and methanol (1.0 mL, V/V 4:1), and 1-Phenyl-2-propen-1-one (0.3 mmol) were added sequentially using a syringe. The reaction setup was placed under blue LED (420 nm) with an argon balloon and irradiated for 24 h. After completion as monitored by TLC, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel via gradient elution (PE:EA = 50:1) give the product **9** (20.5 mg, yield 54%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.65 – 7.50 (m, 7H), 7.48 – 7.33 (m, 5H), 2.97 – 2.87 (m, 1H), 2.80 – 2.69 (m, 2H), 2.39 – 2.27 (m, 1H)，1.67 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.94 (s, 3F). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.1, 140.8, 140.4, 136.8, 136.4, 133.3, 129.0, 128.7, 128.4, 128.2 (q, *J* = 283.4 Hz), 128.1, 127.7, 127.3, 127.2, 47.0 (q, *J* = 24.1 Hz), 33.1, 28.8, 19.1 (q, *J* = 1.4 Hz). HRMS (EI, m/z): calcd for $C_{24}H_{21}F_3O^{+}$ $[M]^{+}$: 382.1544, found 382.1543.



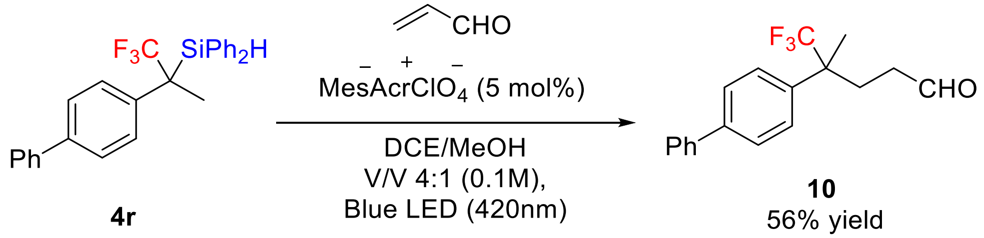
Supplementary Fig. 13. ^{1}H NMR (400 MHz, $CDCl_3$) of **9**



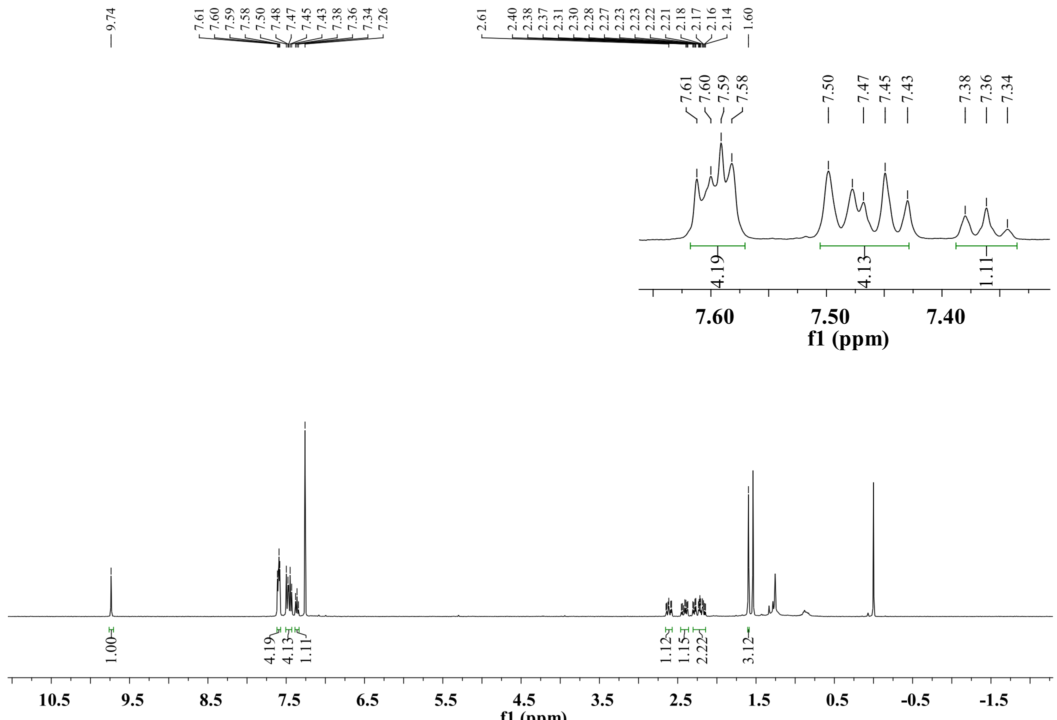
Supplementary Fig. 14. ^{19}F NMR (376 MHz, $CDCl_3$) of **9**



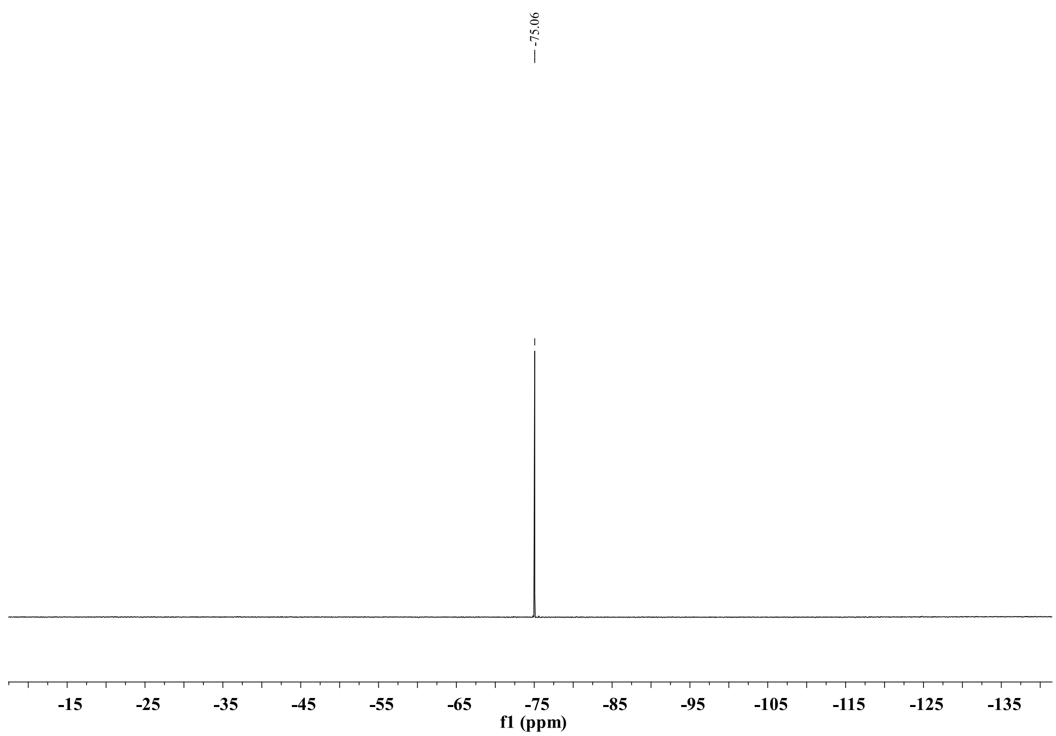
Supplementary Fig. 15. ^{13}C NMR (151 MHz, $CDCl_3$) of **9**



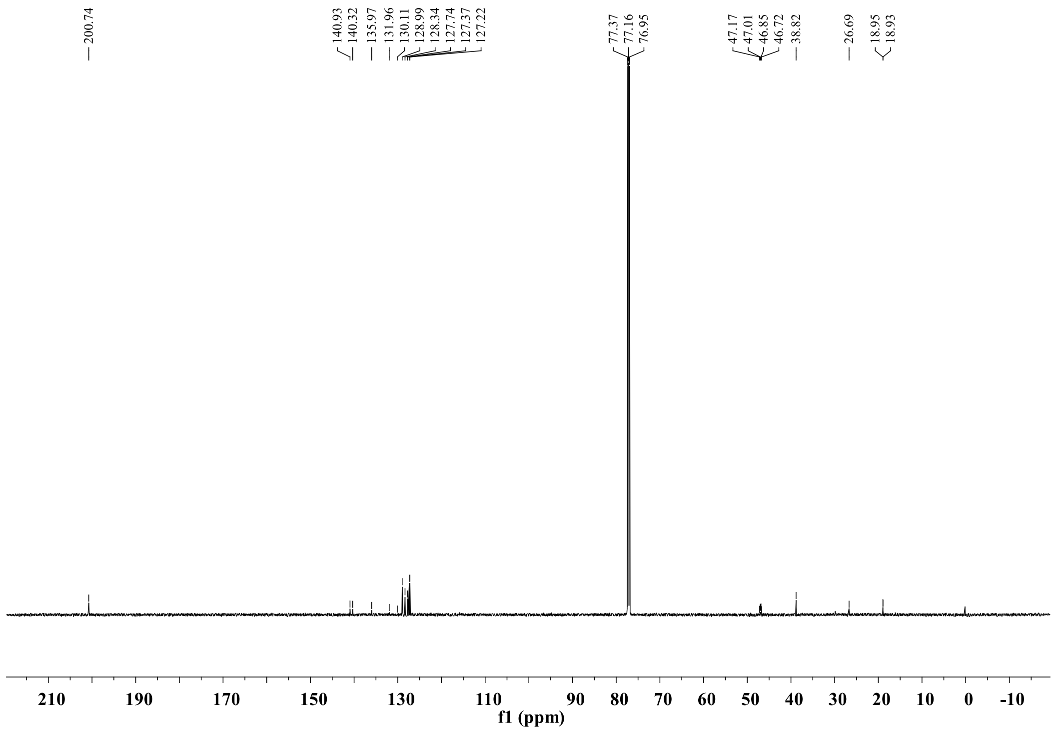
To a 25 mL Schlenk tube equipped with a magnetic stir bar was added the photocatalyst $Mes^-Acr^+ClO_4^-$ (2.1 mg, 0.005 mmol), and **4r** (0.1 mmol). The Schlenk tube was sealed and degassed via vacuum evacuation and subsequently backfilled with argon for three times. After that, anhydrous DCE and methanol (1.0 mL, V/V 4:1), and Acrolein (0.3 mmol) were added sequentially using a syringe. The reaction setup was placed under blue LED (420 nm) with an argon balloon and irradiated for 48 h. After completion as monitored by TLC, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel via gradient elution (PE:Toluene = 10:1) give the product **10** (17.0 mg, yield 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.62 – 7.55 (m, 4H), 7.51 – 7.43 (m, 4H), 7.39 – 7.33 (m, 1H), 2.65 – 2.57 (m, 1H), 2.46 – 7.35 (m, 1H), 2.32 – 7.12 (m, 2 H), 1.60 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.06 (s, 3F). ^{13}C NMR (151 MH z, $CDCl_3$) δ 200.7, 140.9, 140.3, 132.0, 131.03 (q, J = 279.6 Hz) 129.0, 128.3, 127.7, 127.4, 127.2, 46.9 (q, J = 24.0 Hz), 38.8, 26.7, 18.9 (q, J = 1.6 Hz). HRMS (EI, m/z): calcd for $C_{18}H_{17}F_3O^+$ [M] $^+$: 306.1231, found 306.1231.



Supplementary Fig. 16. ^{1}H NMR (400 MHz, $CDCl_3$) of **10**



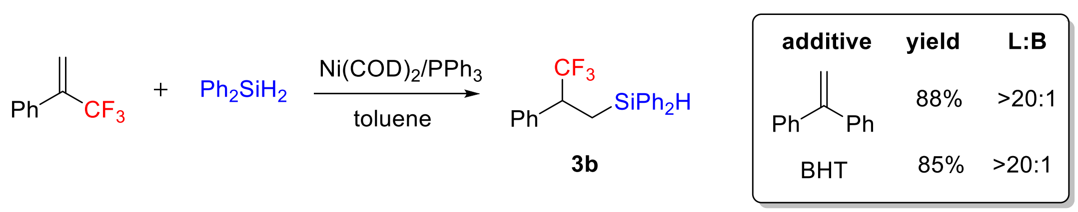
Supplementary Fig. 17. ^{19}F NMR (376 MHz, $CDCl_3$) of **10**



Supplementary Fig. 18. ^{13}C NMR (151 MHz, $CDCl_3$) of **10**

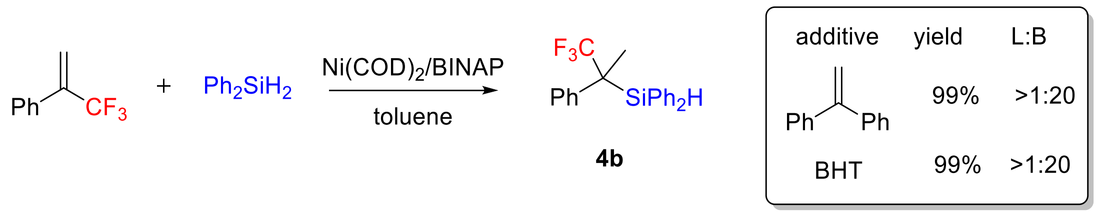
2.4 Mechanistic Studies

2.4.1 Radical inhibitors.



Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$ (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1b** (0.2 mmol, 1.0 equiv) and ethene-1,1-diyldibenzene (0.4 mmol, 2.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **3b** (62.5 mg, yield 88%).

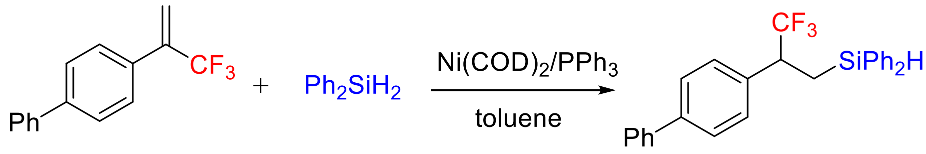
$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and PPh_3 (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1b** (0.2 mmol, 1.0 equiv) and BHT (0.40 mmol) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^oC. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **3b** (60.0 mg, yield 85%).



$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (5.8 mg, 0.0094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1b** (0.2 mmol, 1.0 equiv) and ethene-1,1-diyldibenzene (0.4 mmol, 2.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^oC. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **4b** (70.7 mg, yield 99%).

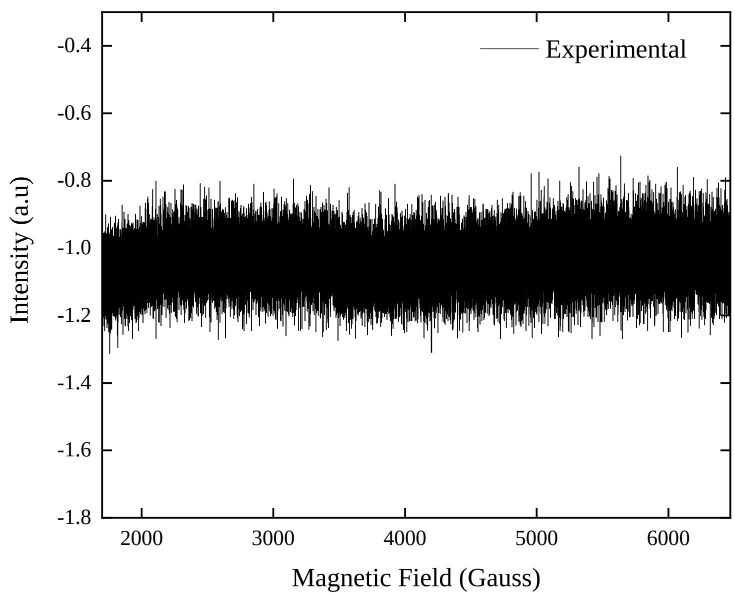
$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and rac-BINAP (5.8 mg, 0.0094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1b** (0.2 mmol, 1.0 equiv) and BHT (0.40 mmol) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^oC. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **4b** (71.2 mg, yield 99%).

2.4.2 EPR experiments.

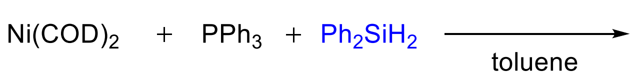


3r

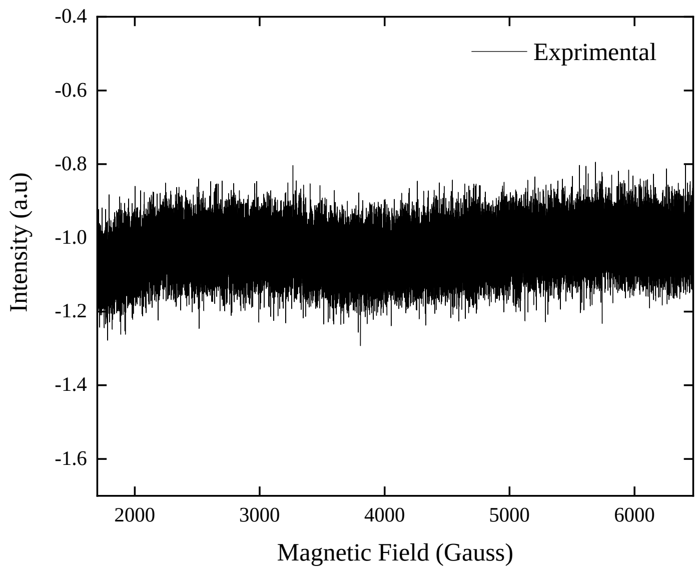
Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$ (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1r** (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The mixture was heated at 30 ^{o}C for 2h. After cooling with liquid nitrogen, this solution was subjected to EPR measurements.



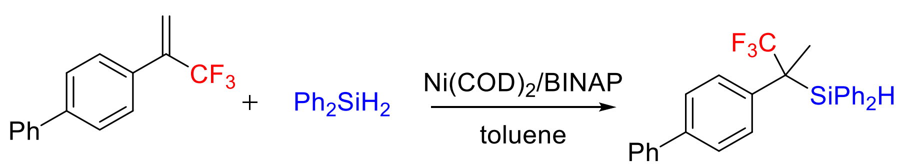
Supplementary Fig. 19 The reaction mixture of synthesis of **3r**



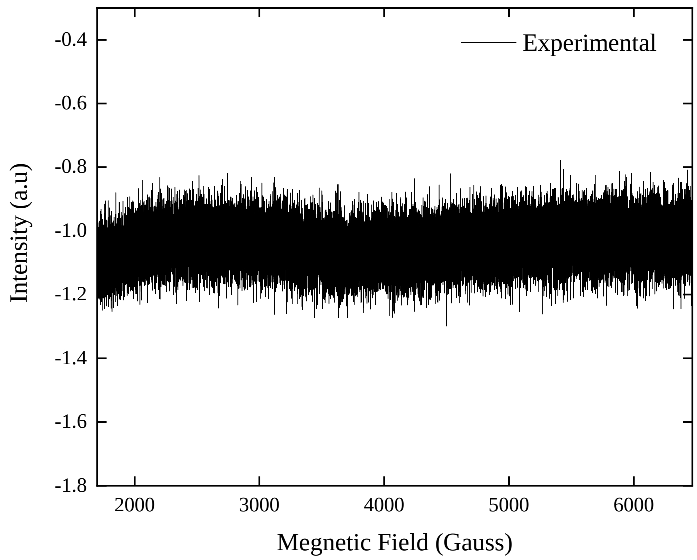
Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$ (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min. After cooling with liquid nitrogen, this solution was subjected to EPR measurements.



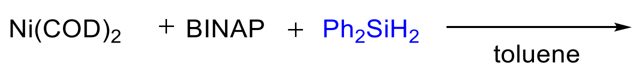
Supplementary Fig. 20 The reaction mixture of synthesis



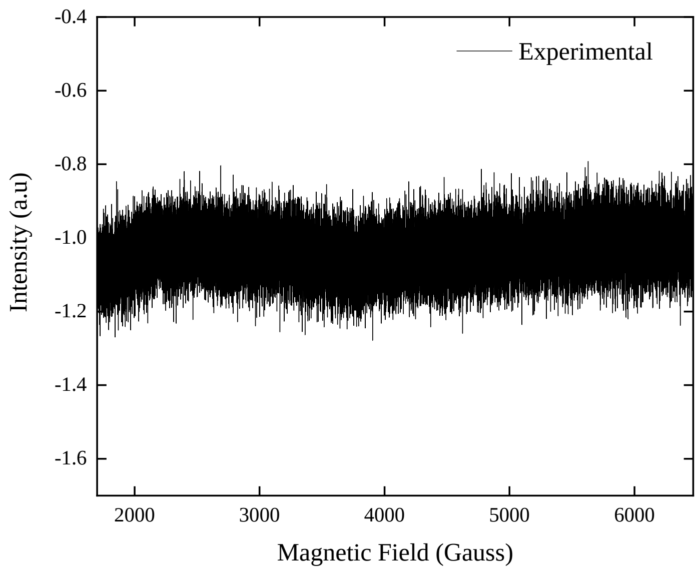
Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (5.8 mg, 0.0094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1r** (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The mixture was heated at 30 ^{o}C for 2h. After cooling with liquid nitrogen, this solution was subjected to EPR measurements.



Supplementary Fig. 21 The reaction mixture of synthesis of **4r**

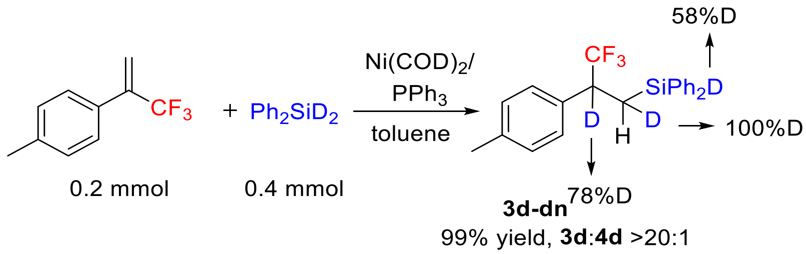


$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (5.8 mg, 0.0094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min. After cooling with liquid nitrogen, this solution was subjected to EPR measurements.

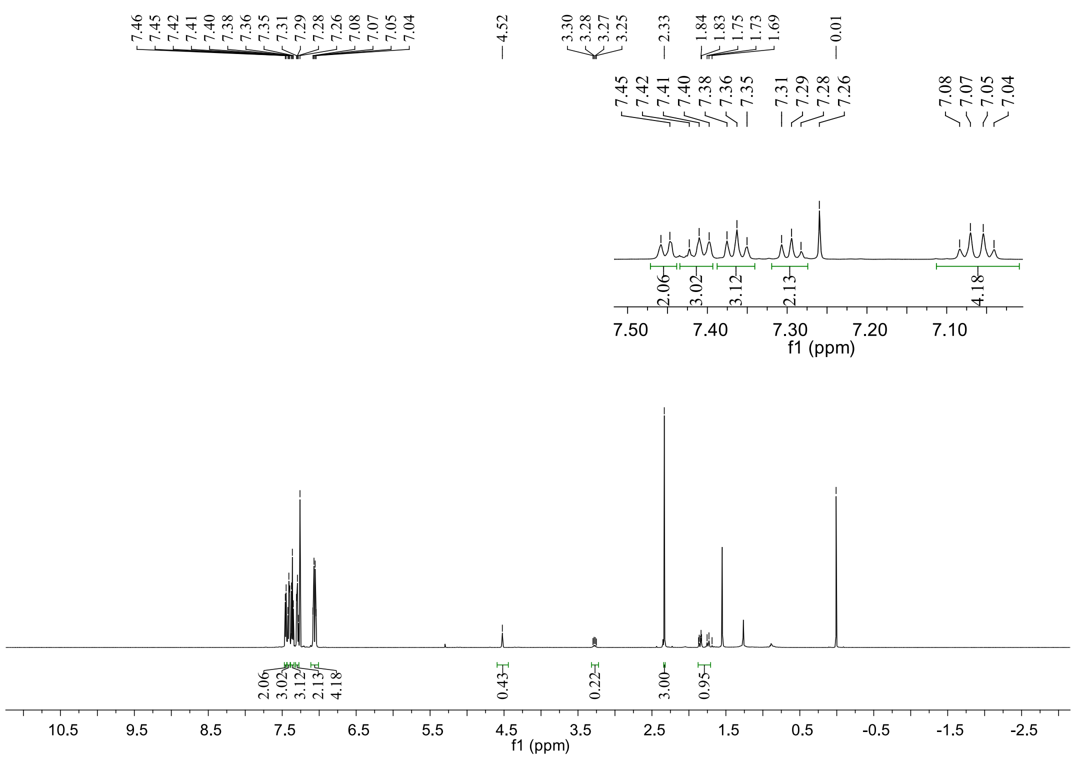


Supplementary Fig. 22 The reaction mixture of synthesis

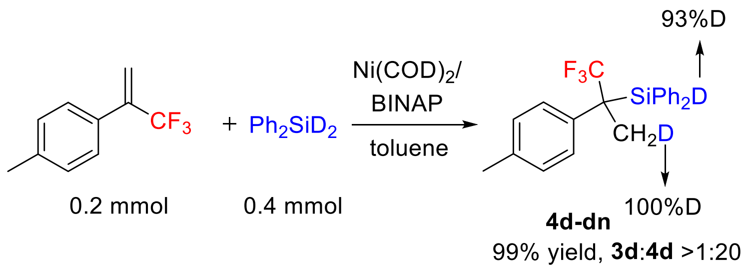
2.4.3 Deuterium labeling experiments



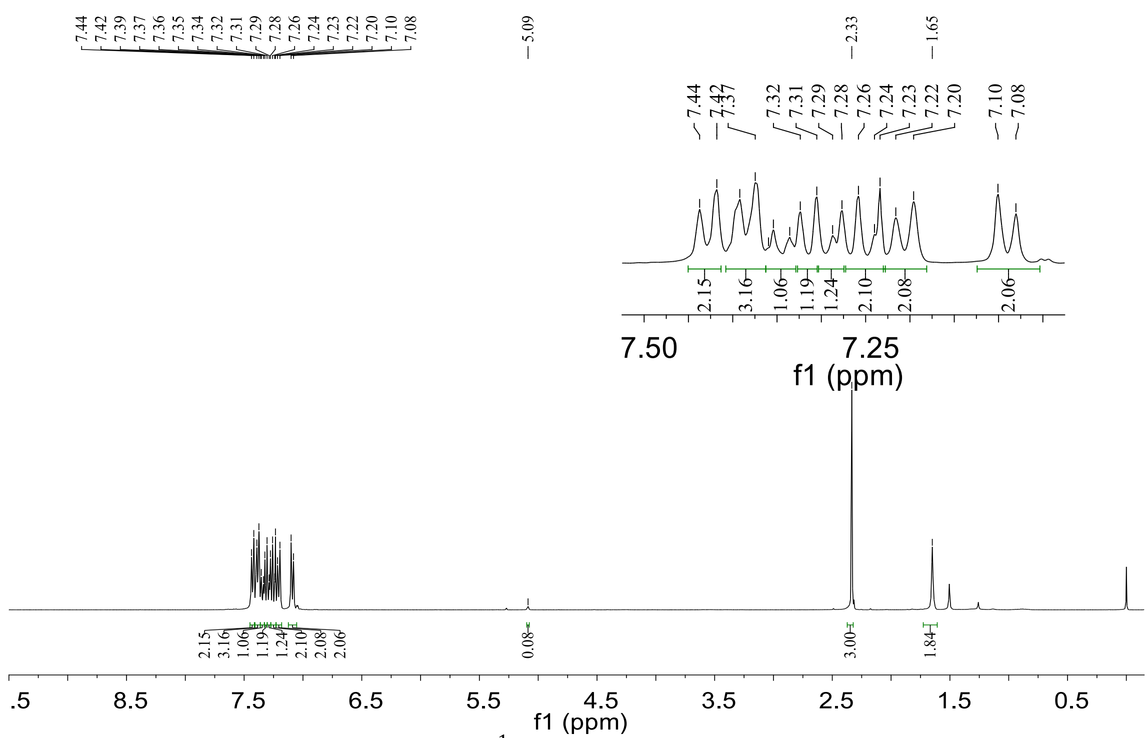
Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$ (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiD$_2$ (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1d** (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **3d-dn** (72.6 mg, yield 99%). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47 – 7.44 (m, 2H), 7.43 – 7.39 (m, 3H), 7.38 – 7.34 (m, 3H), 7.31–7.28 (m, 2H), 7.09 – 7.03 (m, 4H), 4.52 (s, 0.42 H), 3.27 (dd, J = 18.5, 9.2 Hz, 0.22 H), 2.33 (s, 3H), 1.80 (m, 1H).



Supplementary Fig. 23. ^{1}H NMR (600 MHz, CDCl$_3$) of **3d-dn**

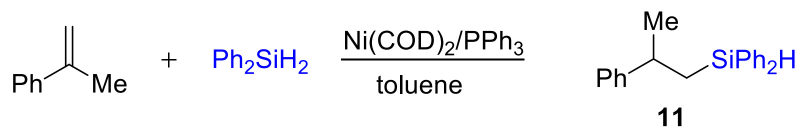


Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (5.8 mg, 0.0094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiD_2 (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, **1d** (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **4d-dn** (74.0 mg, yield 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 3H), 7.37 – 7.33 (m, 1H), 7.33 – 7.31 (m, 1H), 7.31 – 7.27 (m, 1H), 7.27 – 7.21 (m, 1H), 7.21 – 7.18 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.09 (s, 0.07H), 2.33 (s, 3H), 1.65 (s, 1.84H).

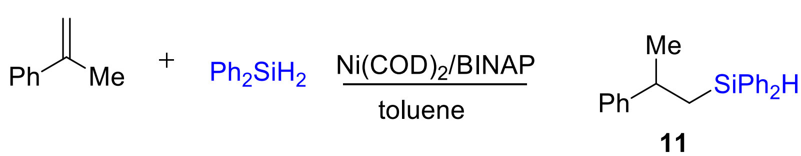


Supplementary Fig. 24. ^{1}H NMR (400 MHz, $CDCl_3$) of 4d-dn

2.4.4 The effect of trifluoromethyl group in the terminal alkene

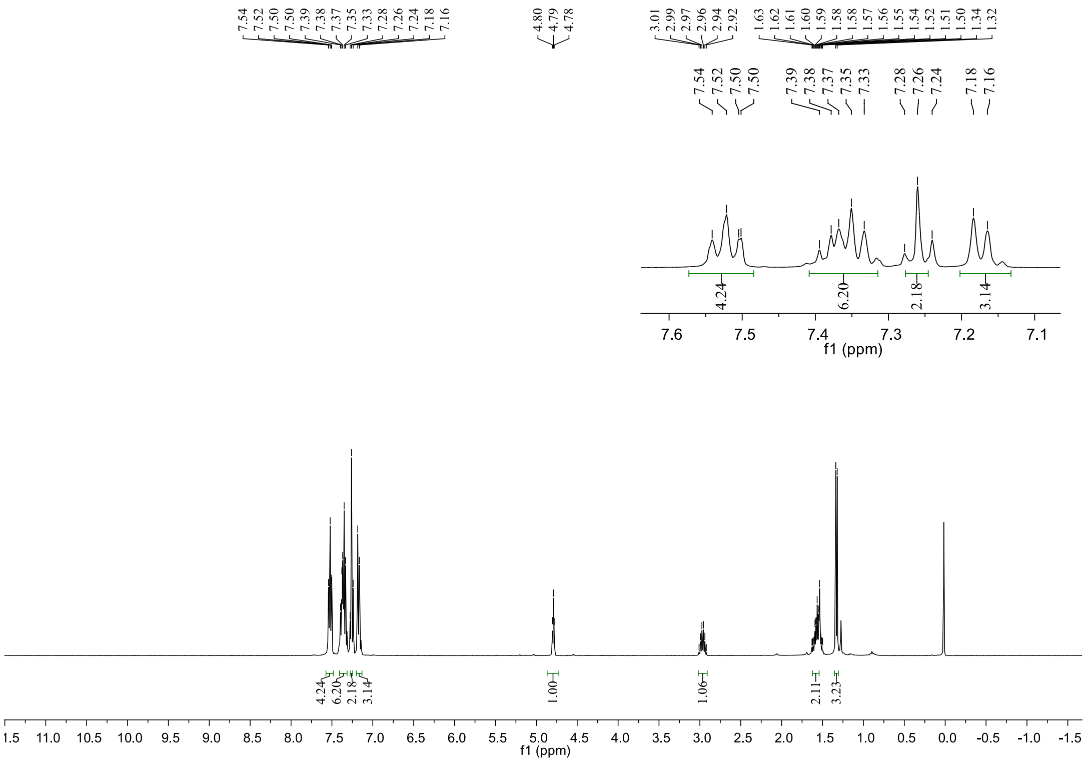


Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$ (2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, 2-Phenyl-1-propene (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 60 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **11**[5] (13.8 mg, yield 23%, L:B >20:1). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.48 (m, 4H), 7.42 – 7.31 (m, 6H), 7.30 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 4.79 (t, *J* = 3.9 Hz, 1H), 3.02 – 2.90 (m, 1H), 1.66 – 1.47 (m, 2H), 1.33 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 149.2, 135.3, 135.2, 134.8, 134.6, 129.7, 129.6, 128.5, 128.1, 128.1, 126.8, 126.1, 36.4, 25.3, 22.8.

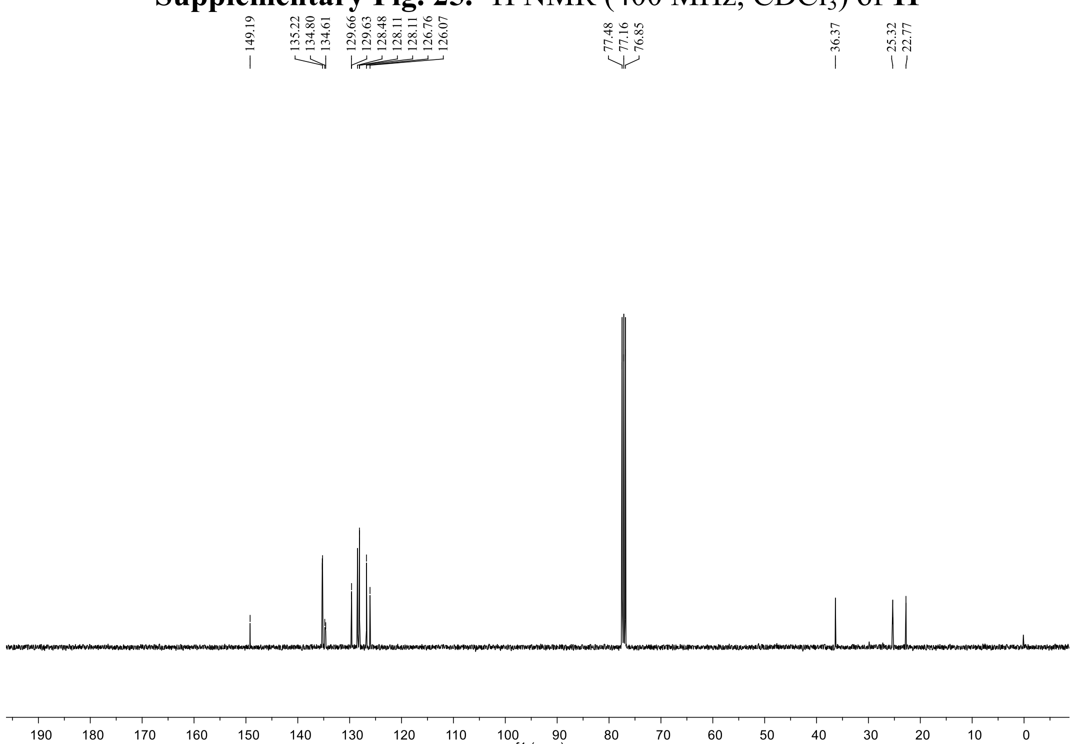


Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (5.8 mg, 0.0094 mmol), in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (78 mg, 0.4 mmol, 2.0 equiv), after stirred for 20 min, 2-Phenyl-1-propene (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 60 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **11**[5] (12.1 mg, yield 11%, L:B > 20:1).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.48 (m, 4H), 7.42 – 7.31 (m, 6H), 7.30 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 4.79 (t, *J* = 3.9 Hz, 1H), 3.02 – 2.90 (m, 1H), 1.66 – 1.47 (m, 2H), 1.33 (d,

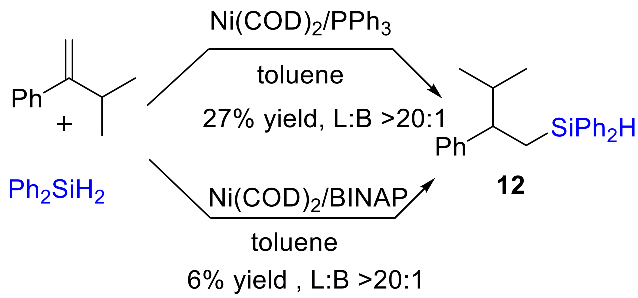
J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 135.3, 135.2, 134.8, 134.6, 129.7, 129.6, 128.5, 128.1, 128.1, 126.8, 126.1, 36.4, 25.3, 22.8.



Supplementary Fig. 25. ^{1}H NMR (400 MHz, $CDCl_3$) of **11**



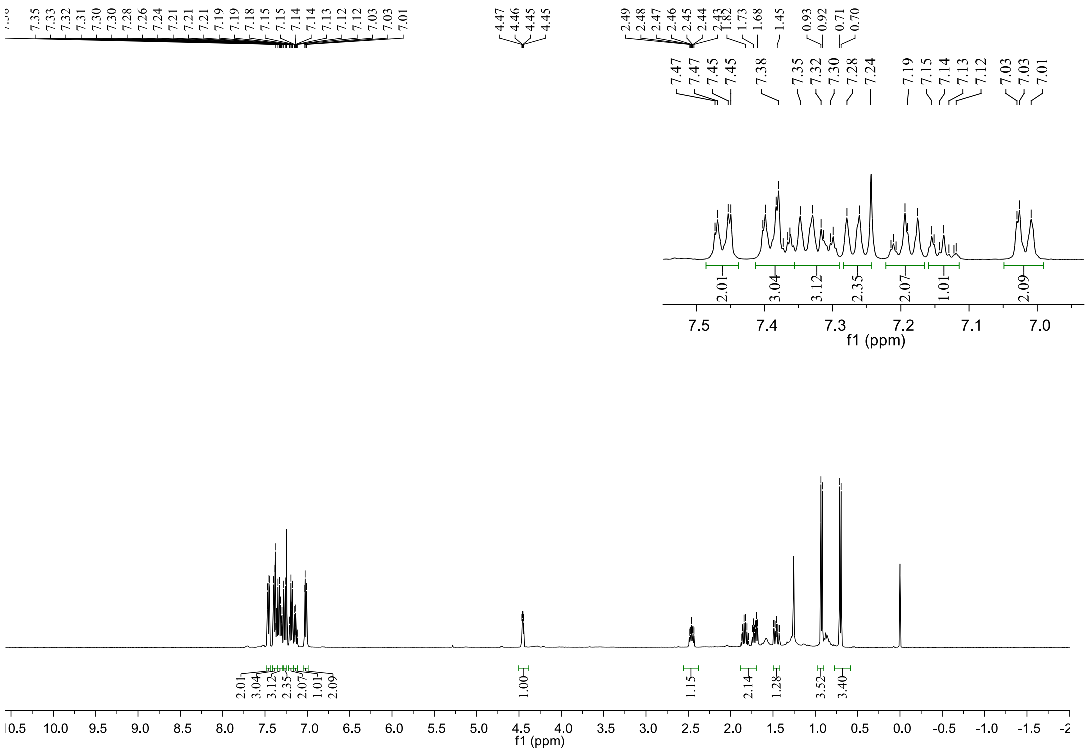
Supplementary Fig. 26. ^{13}C NMR (101 MHz, $CDCl_3$) of **11**



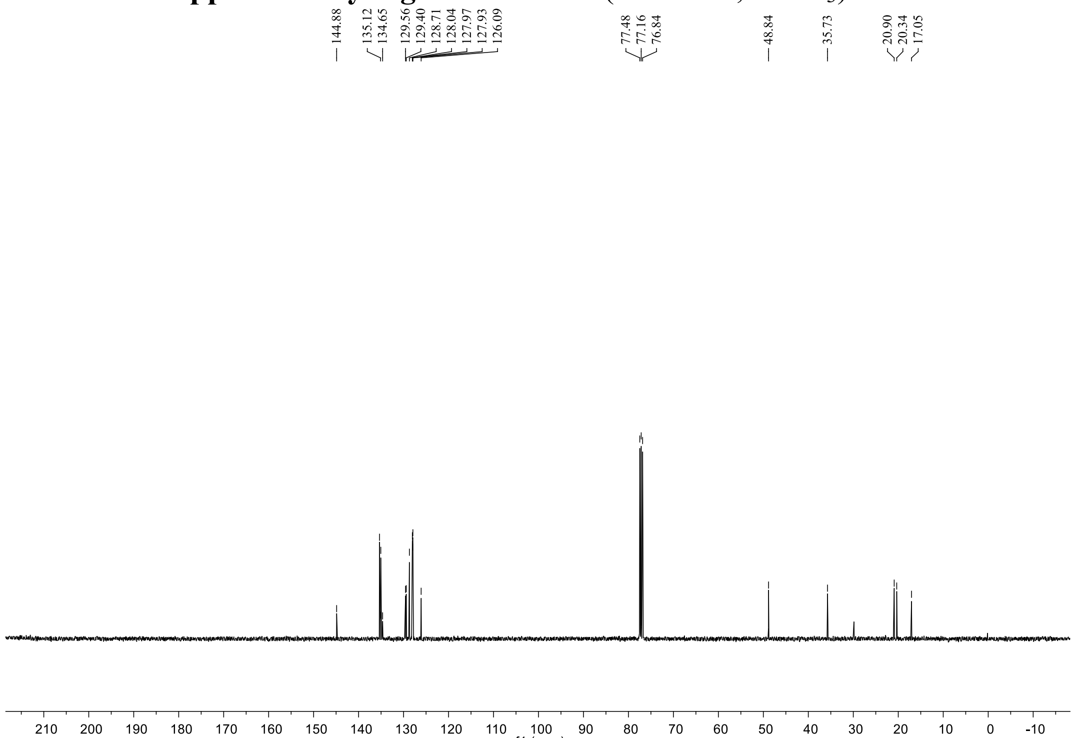
Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$(2.6 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (78 mg, 0.4mmol, 2.0 equiv), after stirred for 20 min, (2-Methyl-1-methylenepropyl)benzene (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 60 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **12**[5] (17.8 mg, yield 27%, L:B > 20:1).

Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP (5.8 mg, 0.0094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (78 mg, 0.4mmol, 2.0 equiv), after stirred for 20 min, (2-Methyl-1-methylenepropyl)benzene (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 60 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **12** [5] (5.2 mg, yield 6%, L:B > 20:1).

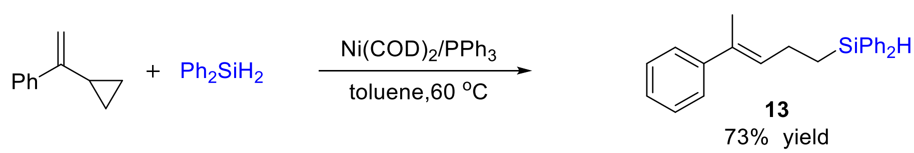
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.44 (m, 2H), 7.41 – 7.35 (m, 3H), 7.35 –7.29 (m, 3H), 7.29 – 7.24 (m, 2H), 7.22 – 7.15 (m, 2H), 7.15 – 7.10 (m, 1H), 7.04 – 7.69 (m, 2H), 4.47 – 4.41 (m, 1H), 2.50 – 2.41 (m, 1H), 1.89 – 1.64 (m, 2H), 1.50 –1.40 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.70 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.9, 135.4, 135.1, 135.1, 134.7, 129.6, 129.4, 128.7, 128.0, 128.0, 127.9, 126.1, 48.8, 35.7, 20.9, 20.3, 17.0.



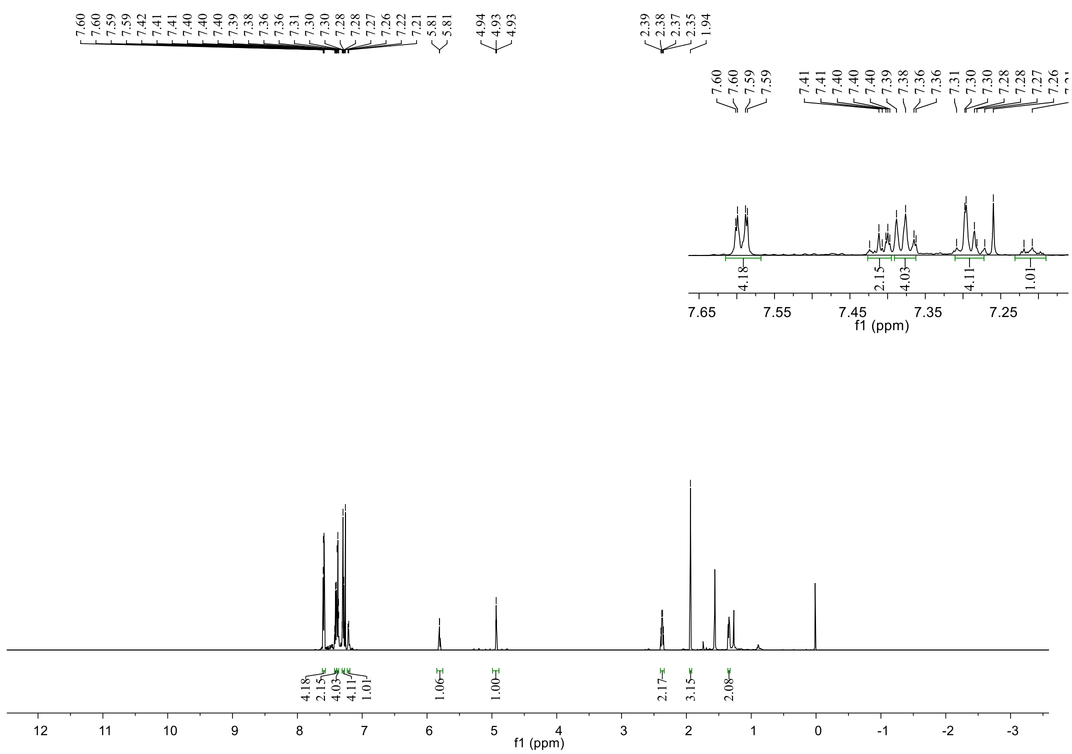
Supplementary Fig. 27. ^{1}H NMR (101 MHz, $CDCl_3$) of **12**



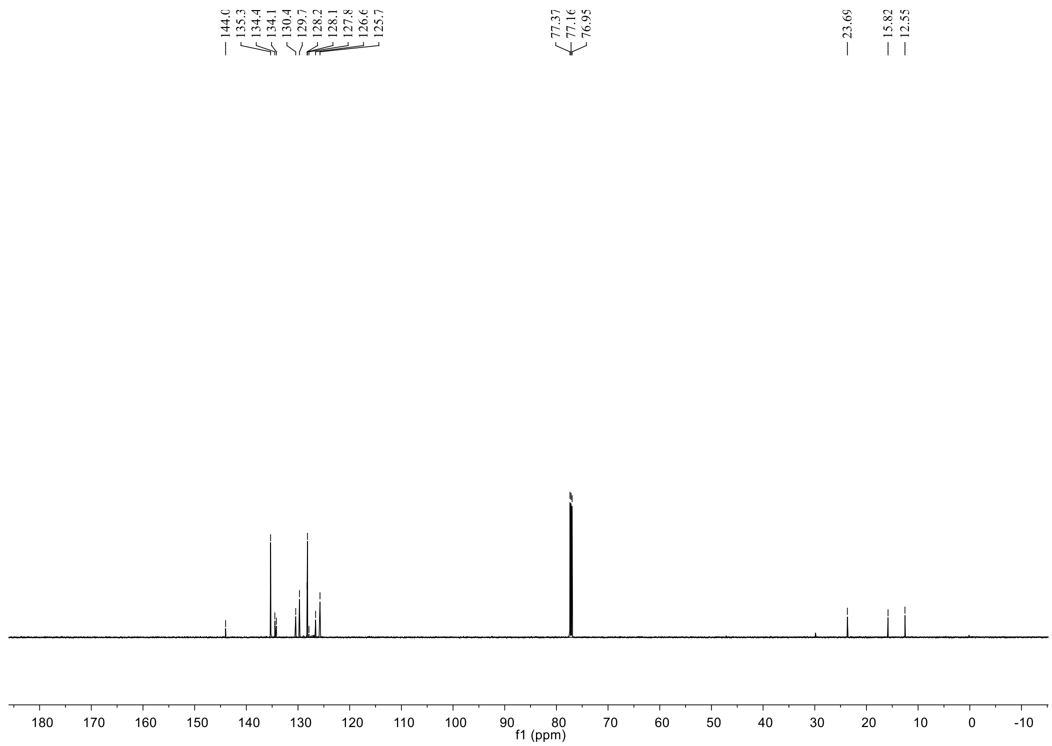
Supplementary Fig. 28. ^{13}C NMR (101 MHz, $CDCl_3$) of **12**



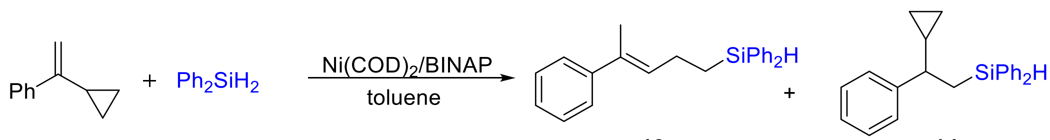
Ni(cod)$_2$ (2.8 mg, 0.01 mmol) and PPh$_3$ (2.6mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (48 mg, 0.2 mmol, 1.0 equiv), after stirred for 20 min, α-cyclopropylstyrene (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 60 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **13**[6] (48.2 mg, yield 73 %). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.62 – 7.58 (m, 4H), 7.43 – 7.39 (m, 2H), 7.39 – 7.36 (m, 4H), 7.31 – 7.27 (m, 4H), 7.23 – 7.18 (m, 1H), 5.81 (d, *J* = 1.2 Hz, 1H), 4.93 (t, *J* = 3.7 Hz, 1H), 2.39 – 2.33 (m, 2H), 1.94 (s, 3H), 1.37 – 1.32 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 144.0, 135.3, 134.5, 134.2, 130.4, 129.7, 128.2, 128.2, 127.9, 126.6, 125.8, 23.7, 15.8, 12.6.



Supplementary Fig. 29. ^{1}H NMR (600 MHz, CDCl$_3$) of **13**



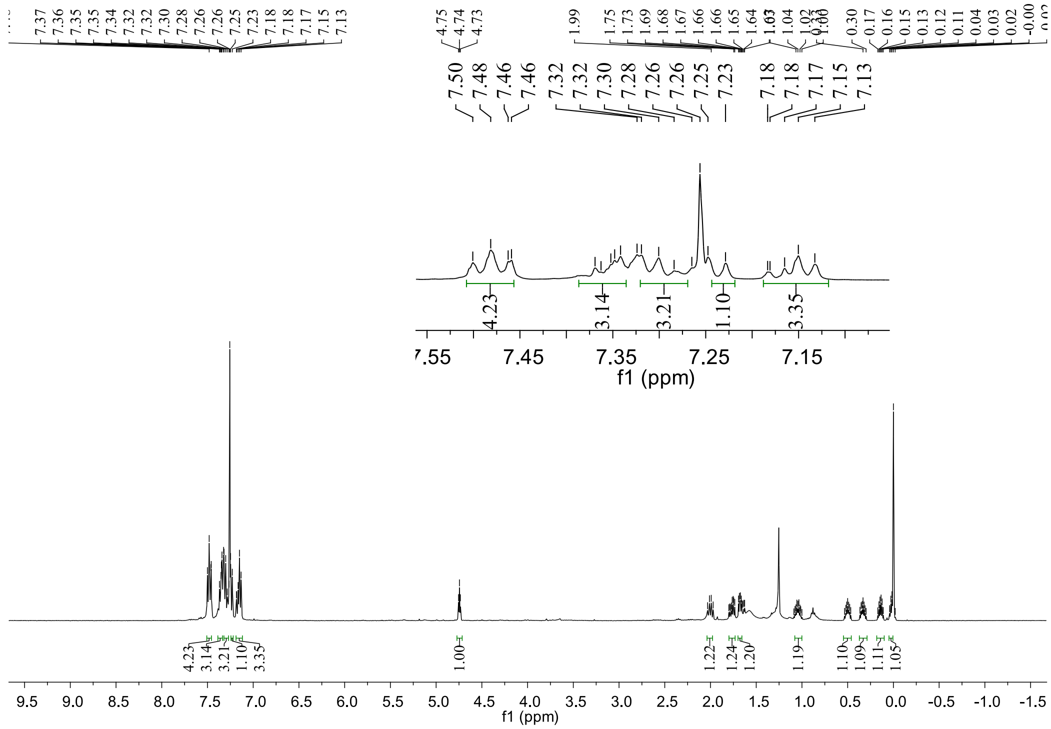
Supplementary Fig. 30. ^{13}C NMR (151 MHz, $CDCl_3$) of **13**



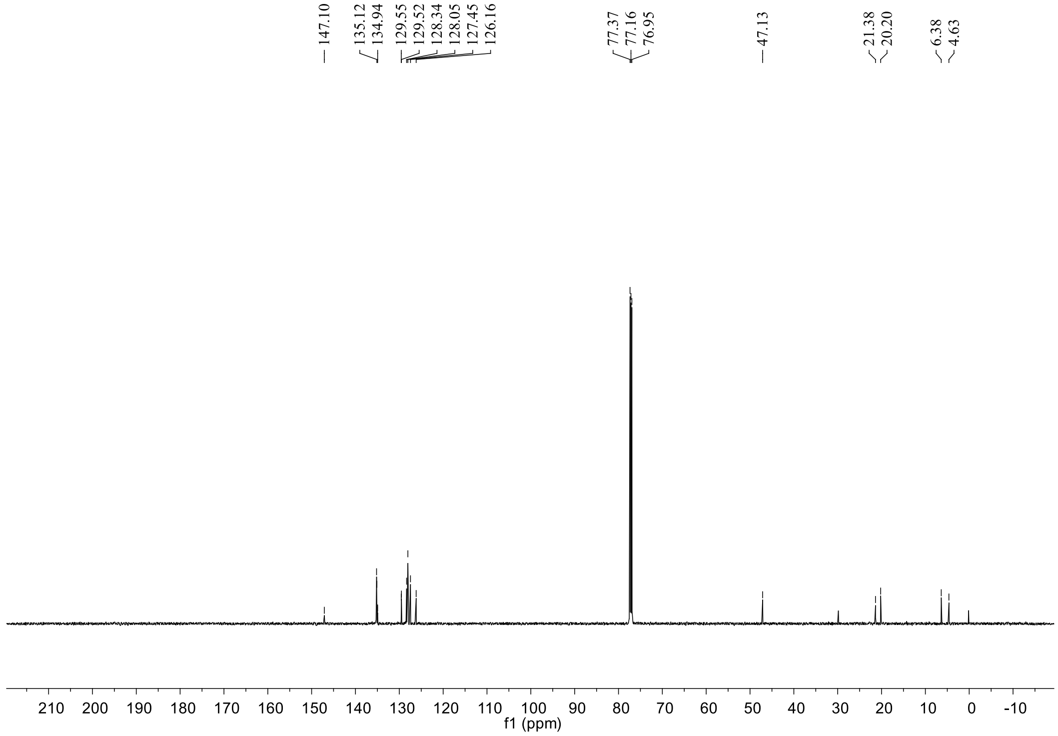
13
8 % yield

14
8 % yield

$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and *rac*-BINAP(5,8 mg, 0.094 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (48 mg, 0.2 mmol, 1.0 equiv), after stirred for 20 min, α-cyclopropylstyrene (0.2 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 60 ^{o}C. After the reaction was complete (24 h), the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated, and purified by silica gel chromatography (PE) to give the indicated product **13**[6] (5.6 mg, yield 8 %) and product **14** (5.6 mg, yield 8 %). product **14:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.44 (m, 4H), 7.39 – 7.27 (m, 7H), 7.25 – 7.21 (m, 1H), 7.19 – 7.12 (m, 3H), 4.75 (t, *J* = 4.0 Hz, 1H), 2.04 – 1.98 (m, 1H), 1.80 – 1.73 (m, 1H), 1.70 – 1.66 (m, 1H), 1.12 – 0.99 (m, 1H), 0.55 – 0.46 (m, 1H), 0.37 – 0.29 (m, 1H), 0.19 – 0.10 (m, 1H), 0.10 – 0.06 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.1, 135.2, 135.1, 135.0, 134.9, 129.6, 129.5, 128.3, 128.1, 127.5, 126.2, 47.1, 21.4, 20.2, 6.4, 4.6.

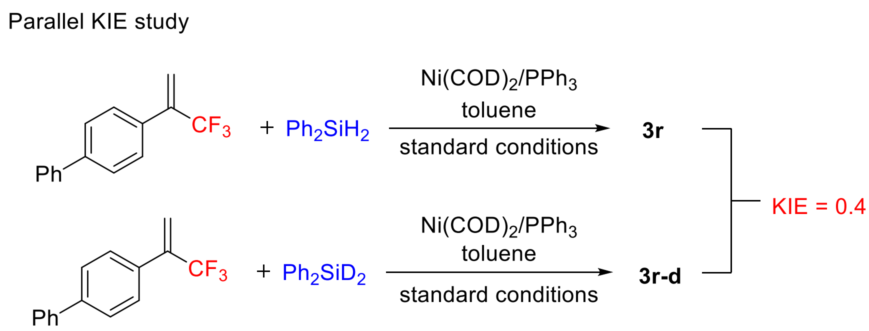


Supplementary Fig. 31 ^{1}H NMR (400 MHz, $CDCl_3$) of **14**



Supplementary Fig. 32. ^{13}C NMR (151 MHz, $CDCl_3$) of **14**

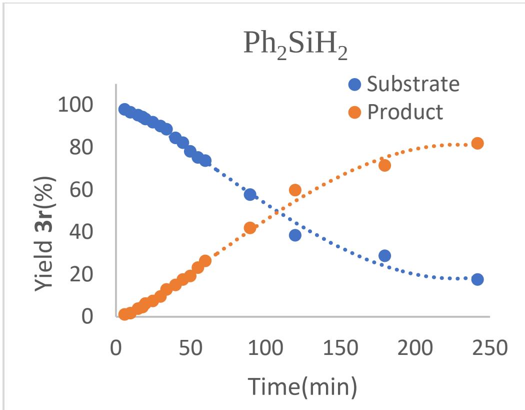
2.4.5 Kinetic isotope effect experiments.

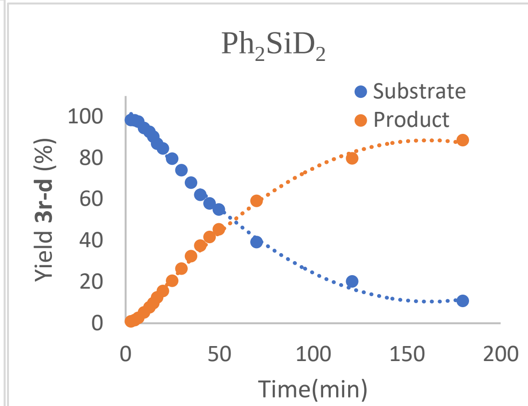


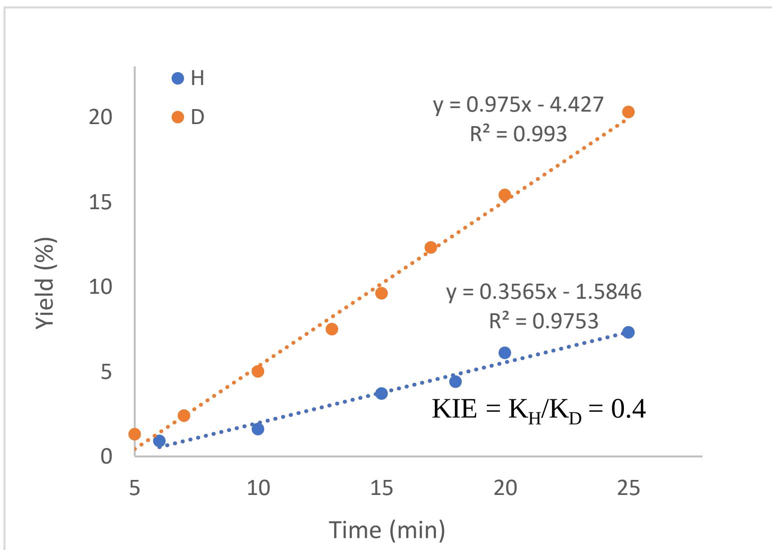
These reactions were conducted with general procedure A. Several oven-dried 25 mL pressure tube were charged with Ni(cod)$_2$ (1.4 mg, 0.005 mmol) and PPh$_3$ (1.3 mg, 0.005 mmol) in toluene (1.0 mL) under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph$_2$SiH$_2$ (39 mg, 0.2mmol, 2.0 equiv), after stirred for 20 min, **1r** (0.1 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 ^{o}C. The reactions were monitored and removed the reactions for yield analysis one by one after the interval of 6 min, 10 min, 15 min, 18 min, 20 min, 25 min, 30 min, 34 min, 40 min, 45 min, 50 min, 55 min 60 min, 90 min, 120 min, 180 min and 242 min. The reaction mixture was filtered through a pad of celite to quench the reaction, All samples were analyzed by ^{19}F NMR spectroscopy to determine the conversion and yields of **3r** with (trifluoromethyl)benzene as an internal standard.

Same set of experiments were repeated with the deuterated substrates Ph$_2$SiD$_2$ and the reactions for yield analysis one by one after the interval of for 3 min, 5 min, 7 min, 10 min, 13 min, 15 min, 17 min, 20 min, 25 min, 30 min, 35 min, 40 min and 45 min, 50 min, 70 min, 121 min and 180 min.

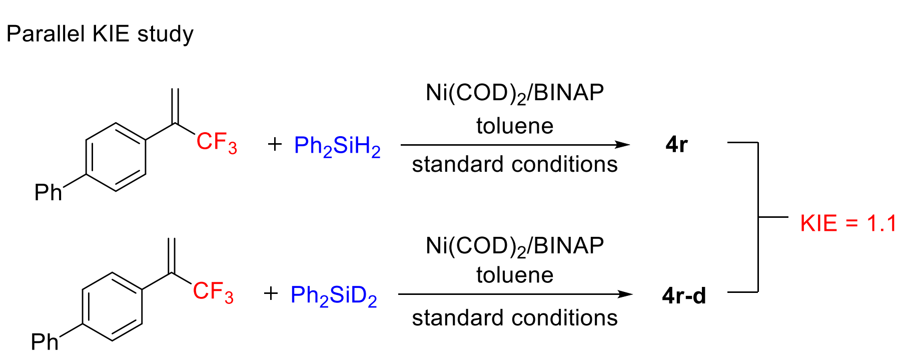
The Ph$_2$SiH$_2$ or Ph$_2$SiD$_2$ reaction was monitored to ~15% conversion, and rate constants were calculated for each reaction using the initial rates method (Supplementary Fig. 33).







Supplementary Fig. 33. kinetic isotope effect experiments of **3r**

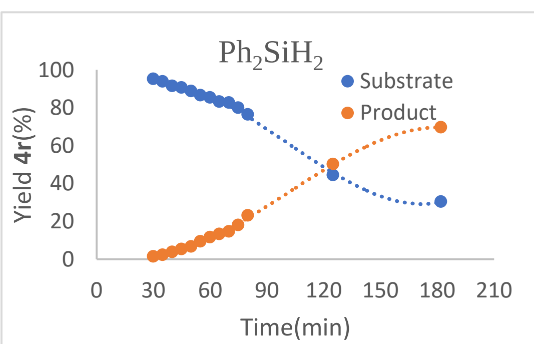


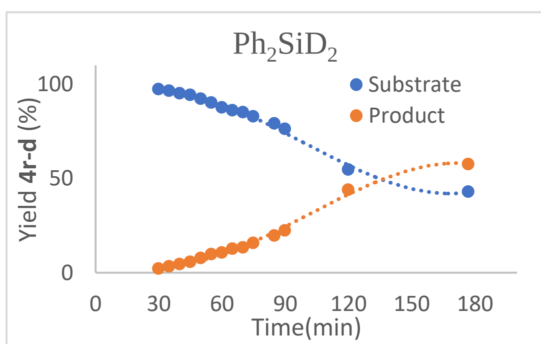
These reactions were conducted with general procedure B, BINAP 4.7 mol%. Several oven-dried pressure tube were charged with $Ni(cod)_2$ (1.4 mg, 0.005 mmol) and BINAP

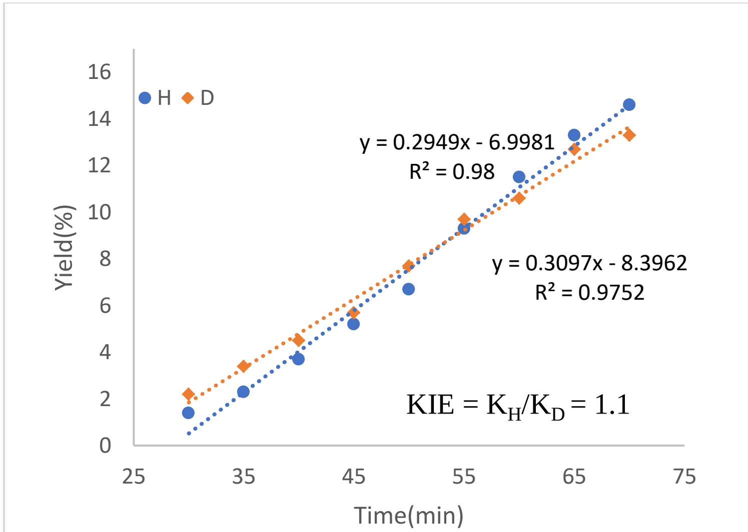
(2.9 mg, 0.0047 mmol) in toluene (1.0 mL) under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (39 mg, 0.1 mmol, 2.0 equiv), after stirred for 20 min, **1r** (0.1 mmol, 1.0 equiv) were added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 °C. The reactions were monitored and removed the reactions for yield analysis one by one after the interval of 30 min, 35 min, 40 min, 45 min, 50 min, 55 min, 60 min, 65 min, 70 min, 75 min, 80 min, 125 min and the processes have been monitored up to 182 min. The reaction mixture was filtered through a pad of celite to quench the reaction, All samples were analyzed by ^{19}F NMR spectroscopy to determine the conversion and yields of **4r** with (trifluoromethyl)benzene as an internal standard. The reaction included an induction period for the generation of active Nickel catalyst. The ^{1}H NMR and ^{19}F NMR showed that no by-products but only starting materials observed in the reaction system during this induction period.

Same set of experiments were repeated with the deuterated substrates Ph_2SiD_2 and the reactions for yield analysis one by one after the interval of for 30 min, 35 min, 40 min, 45 min, 50 min, 55 min, 60 min, 65 min, 70 min, 75 min, 85 min, 90 min, 120 min and 177 min.

The Ph_2SiH_2 or Ph_2SiD_2 reaction was monitored to ~15% conversion, and rate constants were calculated for each reaction using the initial rates method (Supplementary Fig. 34).

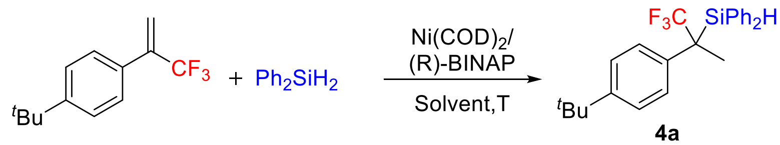






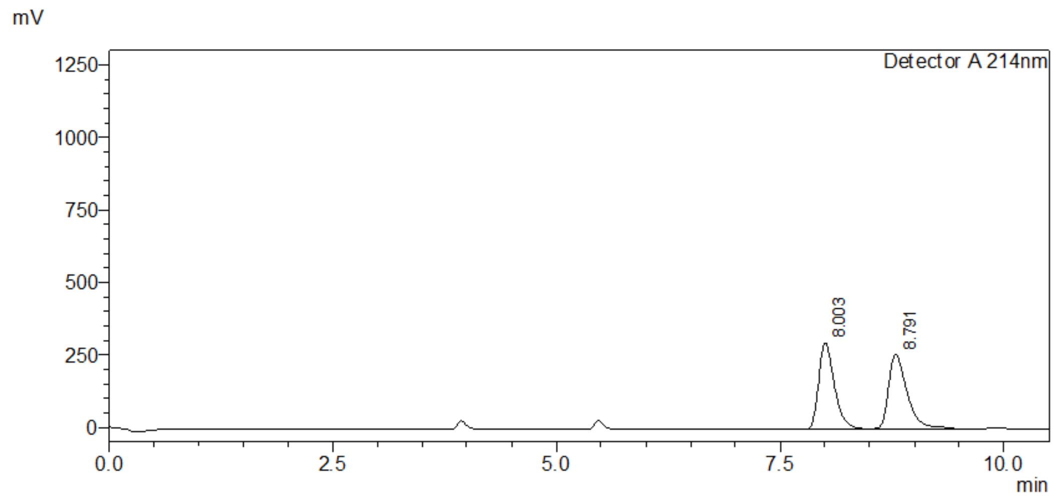
Supplementary Fig. 34. kinetic isotope effect experiments of **4r**

2.5 Supplementary Table 2. Asymmetric investigation.



$Ni(cod)_2$ (2.8 mg, 0.01 mmol) and (R)-BINAP (6.2 mg, 0.01 mmol) in toluene (2.0 mL) were charged into a 25 mL pressure tube under argon. The mixture was stirred for 30 min at room temperature, followed by addition of Ph_2SiH_2 (78 mg, 0.4 mmol), after stirred for 20 min, **1a** (0.2 mmol, 1.0 equiv) was added to the reaction mixture. The reaction tube was then sealed and placed in an oil bath at 30 °C. After stirred for 24 h, the reaction mixture was filtered through a pad of celite, eluted with ethyl acetate, concentrated and purified by silica gel chromatography (PE) to give the indicated product **4a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 3H), 7.37 – 7.33 (m, 3H), 7.33 – 7.30 (m, 2H), 7.30 – 7.28 (m, 2H), 7.28 – 7.26 (m, 2H), 7.25 – 7.22 (m, 2H), 5.08 (s, 1H), 1.69 (s, 3H), 1.33 (s, 9H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.23 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 136.3, 136.3, 133.8, 131.4, 131.3, 130.3, 130.1, 129.3 (q, J = 280.1 Hz), 128.1, 128.0, 127.7, 125.3, 40.1 (q, J = 25.4 Hz), 34.5, 31.5, 16.5 (q, J = 4.1 Hz). HPLC analysis on a Chiralcel OD-H column (hexane 100%, flow rate 0.8 mL/min): t_R = 7.95 min (major), t_R = 8.75 min (minor).

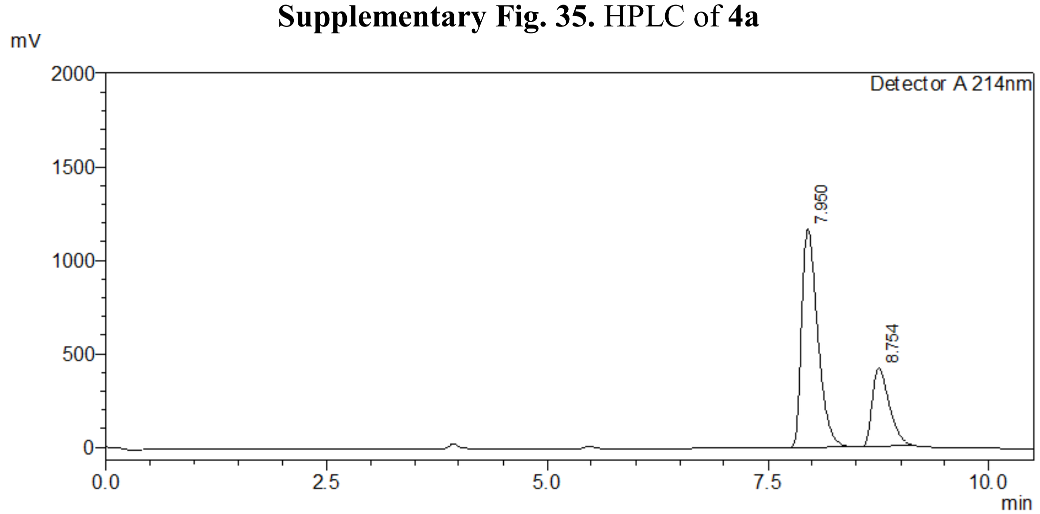
Entry	L	L (%)	Solvent	T/(°C)	Yield(%)	ee (**4a**)	**L:B (3a:4a)**
1	(R)-BINAP	5 mol%	toluene	30	95	45	>1:20
2	(R)-BINAP	4.7 mol%	toluene	30	96	43	>1:20
3	(R)-BINAP	2.5 mol%	toluene	30	84	45	1:8
4	(R)-BINAP	5 mol%	*t*BuOMe	30	59	29	>1:20
5[b]	(R)-BINAP	5 mol%	toluene	30	60	45	>1:20



Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark
1	8.003	3635718	297543	49.320		M
2	8.791	3736034	257969	50.680		V M
Total		7371752	555512			

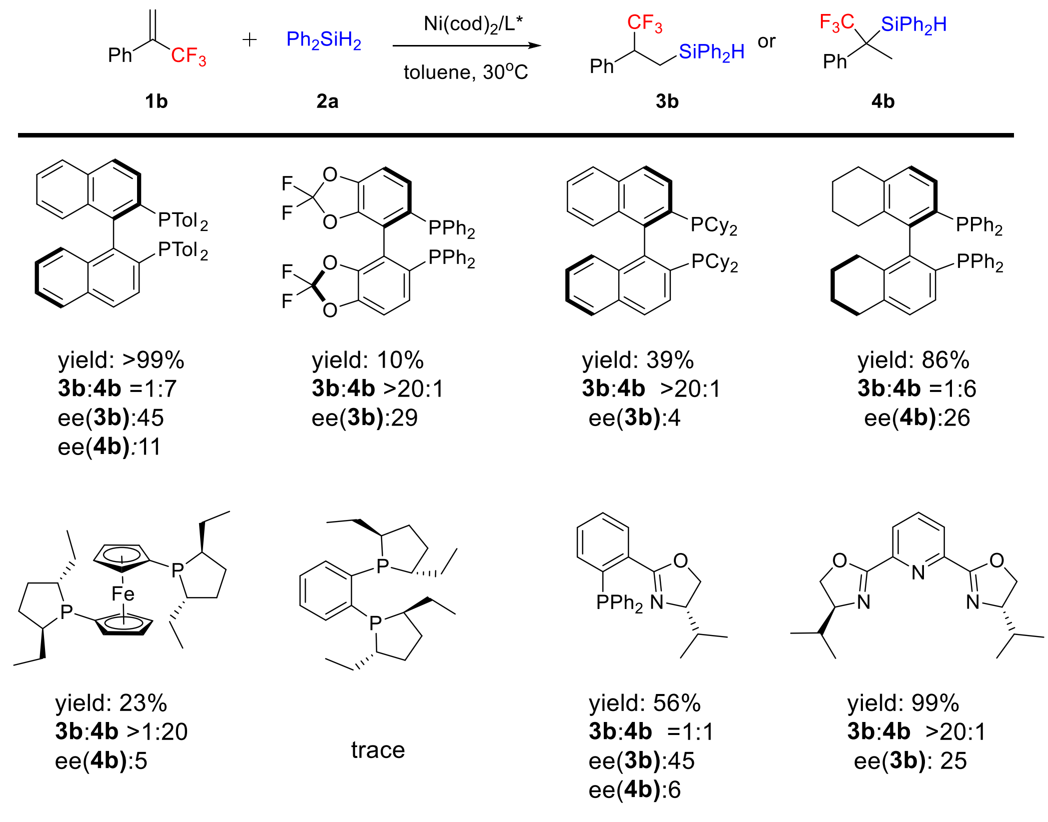
Supplementary Fig. 35. HPLC of **4a**



Detector A 214nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark
1	7.950	14820992	1169784	72.340		M
2	8.754	5667106	417356	27.660		M
Total		20488098	1587140			

Supplementary Fig. 36. HPLC of **4a**



Supplementary Fig. 37. Asymmetric investigation with different chiral ligands. Reaction conditions. **1a** (0.2 mmol), **2a** (0.4 mmol), Ni(cod)$_2$ (5 mol%), **L*** (5 mol%), 30 ^{o}C in toluene (2.0 mL) under argon, 24 h, isolated yield.

2.6. Computational Studies

2.6.1 Complete reference for Gaussian 09

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Men-nucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Ko-bayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyen-gar, J. T omasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cio-slowski, D. J. Fox, Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, **2013**.

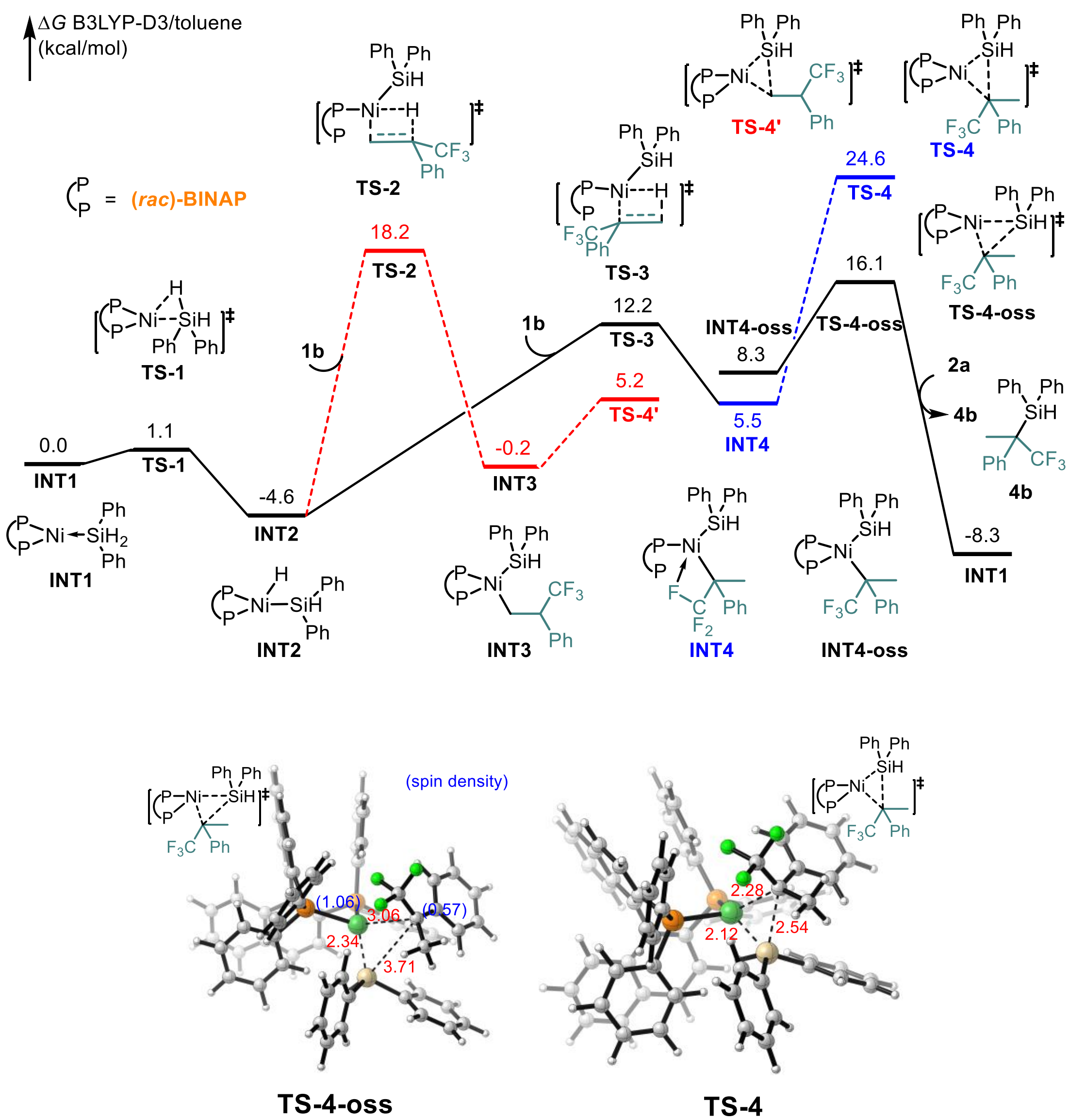
2.6.2 Computational methods

All of the density functional theory (DFT) calculations were performed with the Gaussian 09 series of programs. The B3LYP-D3 functional[7-10] with the standard 6-31G(d) basis set (LANL08 basis set for Ni) was used for the geometry optimizations in the toluene solvent. Harmonic vibrational frequency calculations were performed for all of the stationary points to determine whether they are local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. The B3LYP-D3 functional with the 6-311+G(d,p) basis set (LANL08(f) basis set for Ni) was used to calculate the single-point energies in toluene solvent to provide more accurate energy information. The solvent effect was considered by single-point calculations based on the solution-phase stationary points with the SMD[11,12] continuum solvation model. The Gibbs free energies ($\Delta G_{(toluene)}$) reported in this paper were obtained using Supplementary equation (1),

$$\Delta G_{(toluene)} = \Delta E_{B3LYP\text{-}D3(toluene)} + \Delta G_{B3LYP\text{-}D3(correction)} \qquad (1)$$

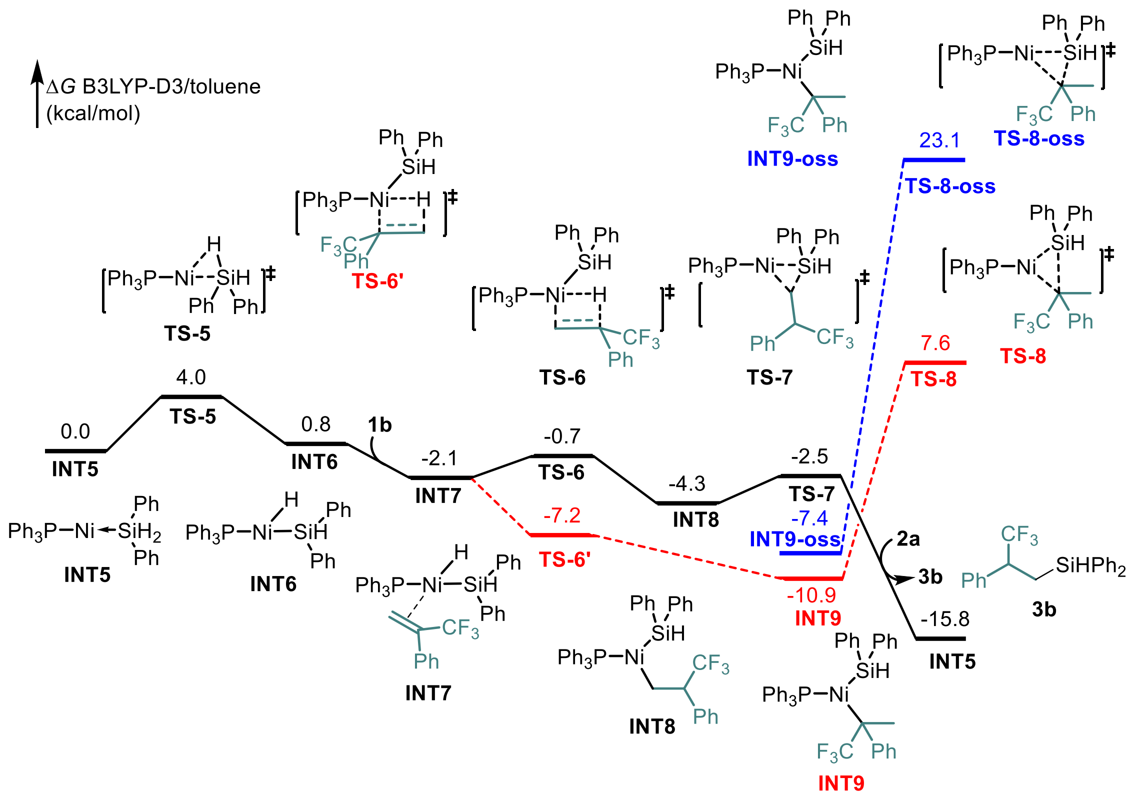
where $\Delta G_{B3LYP\text{-}D3(correction)}$ is the thermochemical correction for the Gibbs free energy calculated at the B3LYP-D3/6-31G(d) (LANL08 basis set for Ni) level in the solution phase (solvent = toluene), and $\Delta E_{B3LYP\text{-}D3(toluene)}$ is the single-point energy calculated at the B3LYP-D3/6-311+G(d,p) (LANL08(f) basis set for Ni) level in toluene solvent relative to stationary points. The $\Delta G_{(toluene)}$ values are used to discuss the energies. The 3D images of the calculated structures were prepared using CYLview[13].

As shown in **Supplementary Figure 38**, for the Ni/BINAP system, both the π-position of alkene **1b** were considered to be attacked by **INT2**, and the calculated results demonstrate that the energy barrier for the formation of Markovnikov addition product via transition state **TS-4-oss** ($\Delta G^{\ddagger}$ =20.7 kcal/mol) is 2.1 kcal/mol lower than that of electrophilic attack on α site of **1a** via transition state TS1′ ($\Delta G^{\ddagger}$ = 22.8 kcal/mol). Therefore, Markovnikov addition product **4b** is the main product in kinetics, which is consistent with the chemoselectivity in experiment.



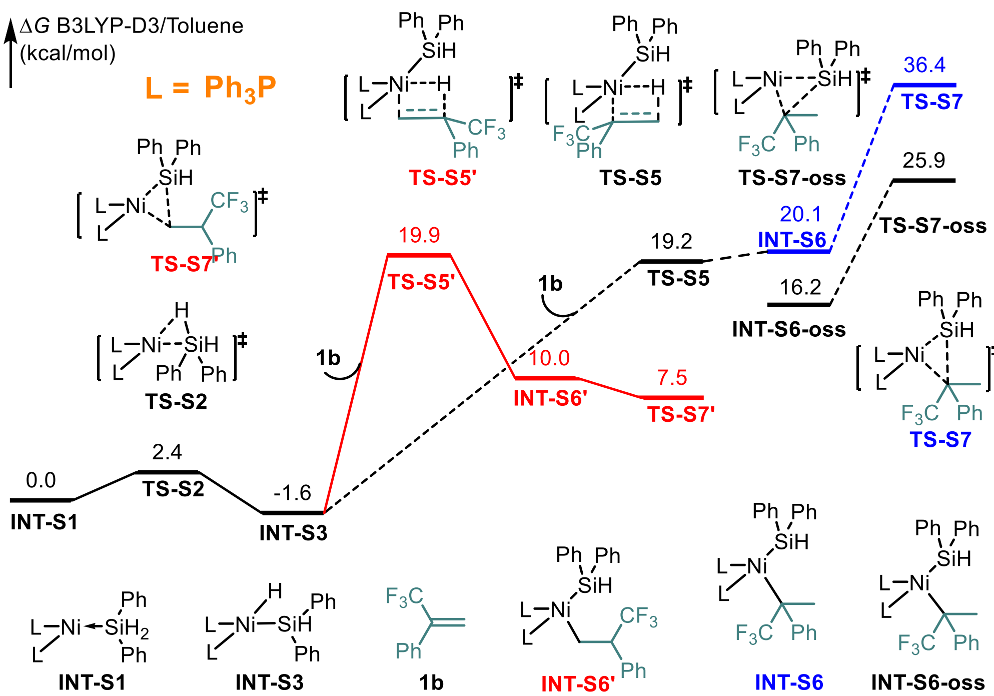
Supplementary Fig. 38. The corresponding energy profiles of the chemoselective pathways for the selected model reaction between alkene **1b** and **2a** in the Ni/BINAP system.

When PPh_3 was used instead of BINAP, the calculated result of one PPh_3 coordinated to nickel center was shown in **Supplementary Figure 39**, indicate that the energy barrier for *anti*-Markovnikov addition product via transition state **TS7** (ΔG‡ = 1.7 kcal/mol) is 16.8 kcal/mol lower than that for Markovnikov addition product **4b** via transition state TS8 (ΔG‡ =18.5 kcal/mol). Thus, *anti*-Markovnikov addition product **3b** should be more energetically favorable, which is in agreement with the experimental result.



Supplementary Fig. 39. The corresponding energy profiles of the chemoselective pathways for the selected model reaction between alkene **1b** and **2a** in the Ni/PPh_3 system (one PPh_3 coordinated to nickel center).

Furthermore, we also considered the reaction pathway with two PPh_3 coordinated to nickel center. As shown in **Supplementary Figure 40**, the activation barrier with two PPh_3 is much higher than one PPh_3 in **Fig. 8** to generate linear product, these results agree with the experimental results in entries 2 and 3 of **Fig. 2**. The energy barrier via open-shell singlet species **TS-S7-oss** for the C(sp^3)-Si bond formation with an activation barrier of 25.9 kcal/mol, which indicated that the branched product formation is also unfavourable with two PPh_3 ligands coordinated to nickel center.



Supplementary Fig. 40. The corresponding energy profiles of the chemoselective pathways for the selected model reaction between alkene **1b** and **2a** in the Ni/PPh_3 system (two PPh_3 coordinated to nickel center).

2.6.3 Supplementary Table 3. B3LYP-D3 calculated absolute energies, enthalpies, and free energies for all structures

Geometry	$E_{(elec\text{-}B3LYP\text{-}D3)}$[1]	$H_{(corr\text{-}B3LYP\text{-}D3)}$[2]	$G_{(cor\text{-}B3LYP\text{-}D3)}$[3]	$E_{(solv\text{-}B3LYP\text{-}D3)}$[4]	IF[5]
INT1	-3302.204552	0.877979	0.739227	-3302.856186	
TS-1	-3302.201212	0.876681	0.735915	-3302.853141	213.2*i*
INT2	-3302.214127	0.878461	0.740378	-3302.864724	
1b	-646.705477	0.150198	0.103443	-646.899563	
TS-2	-3948.909816	1.030072	0.869021	-3949.753053	806.8*i*
INT3	-3948.943707	1.035370	0.873269	-3949.786745	

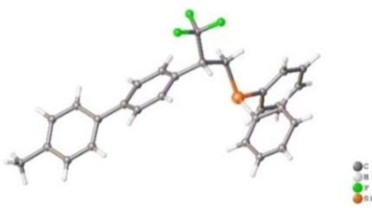
TS-4'	-3948.935961	1.033401	0.873890	-3949.778710	146.9*i*
TS-3	-3948.915450	1.029440	0.866401	-3949.760101	791.8*i*
INT4	-3948.937114	1.033135	0.870508	-3949.774846	
INT4-oss	-3948.930669	1.034798	0.872510	-3949.772284	
TS-4	-3948.911458	1.033727	0.875944	-3949.749753	168.6*i*
TS-4-oss	-3948.915172	1.031396	0.868460	-3949.755897	92.7*i*
2a	-754.034301	0.211856	0.160515	-754.177613	
4b	-1400.789289	0.368421	0.292309	-1401.118691	
INT5	-1959.722763	0.509296	0.411795	-1960.092654	
TS-5	-1959.710363	0.506360	0.409322	-1960.083767	35.8*i*
INT6	-1959.715321	0.507633	0.408238	-1960.087751	
INT7	-2606.457676	0.660463	0.544089	-2607.024377	
TS-6	-2606.452405	0.658801	0.539360	-2607.017486	654.3*i*
TS-6'	-2606.460463	0.658915	0.539444	-2607.027936	781.6*i*
INT8	-2606.454788	0.661803	0.536989	-2607.020873	
TS-7	-2606.457927	0.662922	0.542370	-2607.023375	65.6*i*
INT9	-2606.470377	0.662682	0.541866	-2607.036147	
INT9-oss	-2606.461547	0.661430	0.535957	-2607.024657	
TS-8	-2606.452261	0.663302	0.546509	-2607.011405	111.7*i*
TS-8-oss	-2606.418067	0.661150	0.540484	-2606.980725	74.2*i*
3b	-1400.793688	0.368105	0.289967	-1401.128293	
INT-S1	-2996.069476	0.801936	0.665279	-2996.694276	
TS-S2	-2996.106172	0.800839	0.664807	-2996.690015	15.9*i*
INT-S3	-2996.114788	0.802210	0.666922	-2996.698489	
TS-S5'	-3642.819342	0.953596	0.800840	-3643.594296	899.2*i*
INT-S6'	-3642.840236	0.959162	0.805575	-3643.614774	
TS-S7'	-3642.844085	0.958994	0.805076	-3643.618222	47.4*i*
TS-S5	-3642.820731	0.954210	0.801120	-3643.595697	852.0*i*
INT-S6	-3642.824819	0.957871	0.804922	-3643.59796	

TS-S7	-3642.803012	0.958643	0.804808	-3643.571905	73.8*i*
INT-S6-oss	-3642.834605	0.959121	0.805451	-3643.604738	
TS-S7-oss	-3642.816782	0.958997	0.805091	-3643.588966	162.8*i*

[1]The electronic energy calculated by B3LYP-D3 in solution phase. [2]The thermal correction to enthalpy calculated by B3LYP-D3 in solution phase. [3]The thermal correction to Gibbs free energy calculated by B3LYP-D3 in solution phase. [4]The electronic energy calculated by B3LYP-D3 in toluene solvent. [5]The B3LYP-D3 calculated imaginary frequencies for the transition states.

3. Supplementary Tables and Figures

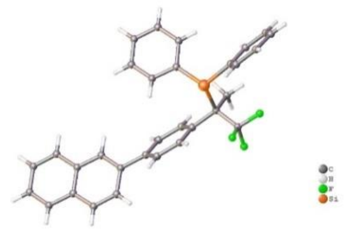
3.1. X-Ray Crystallographic DataCrystal structure details for **3s** (CCDC 2214736). Thermal ellipsoids are shown at 50 % probability level.



Supplementary Table 4 Crystal data and structure refinement for 3s

Identification code	**3s**
Empirical formula	$C_{28}H_{25}F_3Si$
Formula weight	446.57
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4047(3)
b/Å	9.4589(2)
c/Å	24.8272(6)
α/°	90
β/°	91.144(2)
γ/°	90
Volume/Å^3	2442.93(11)
Z	4
ρ_{calc}g/cm^3	1.214
μ/mm^{-1}	1.146
F(000)	936.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/ °	7.122 to 142.978
Index ranges	$-12 \le h \le 12$, $-11 \le k \le 7$, $-24 \le l \le 30$
Reflections collected	14982
Independent reflections	4706 [R_{int} = 0.0456, R_{sigma} = 0.0407]
Data/restraints/parameters	4706/1/290
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0862, wR_2 = 0.2464
Final R indexes [all data]	R_1 = 0.1011, wR_2 = 0.2668
Largest diff. peak/hole / e Å^{-3}	1.05/-0.44

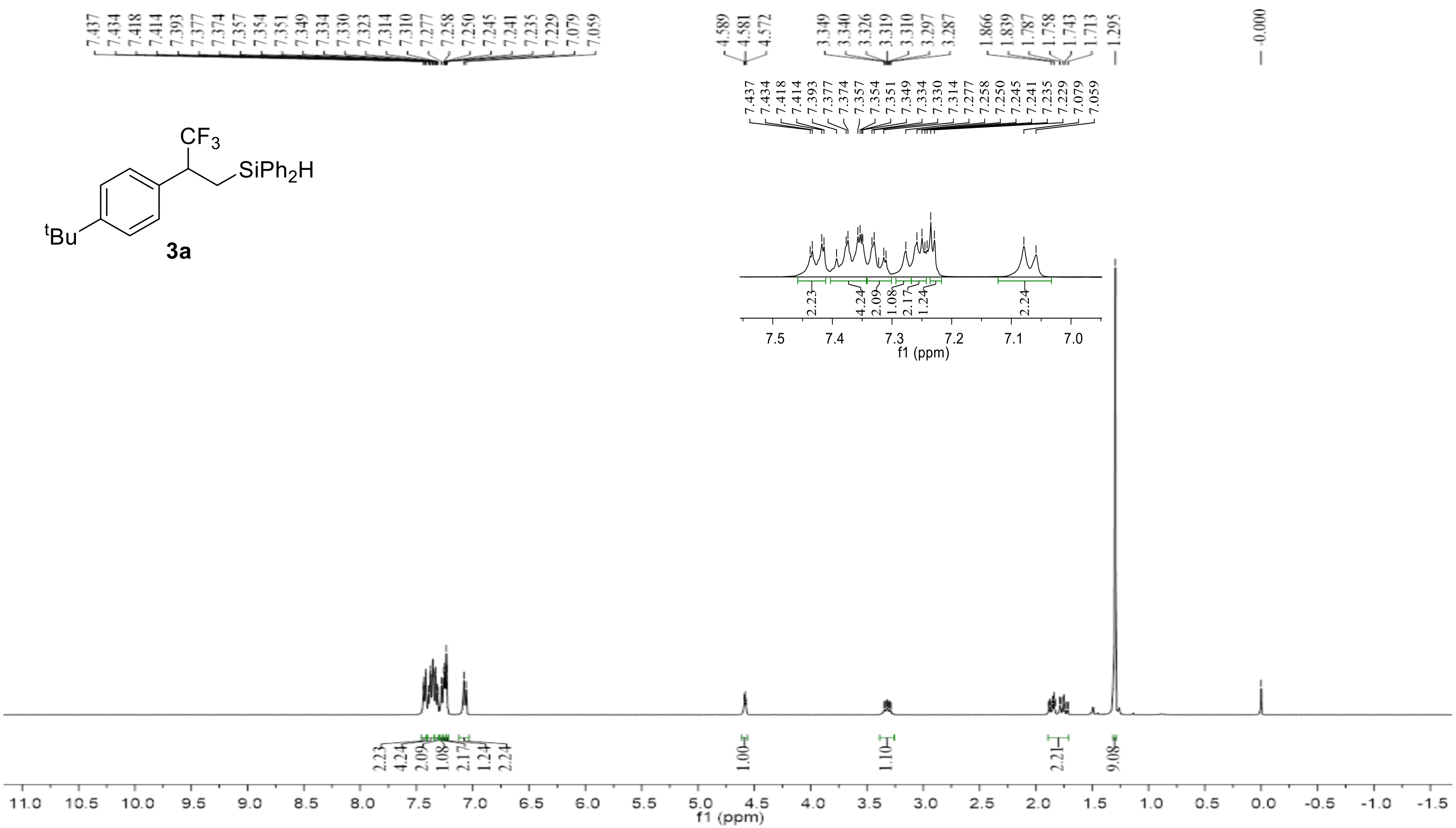
Crystal structure details for **4t** (CCDC 2214737). Thermal ellipsoids are shown at 50 % probability level.



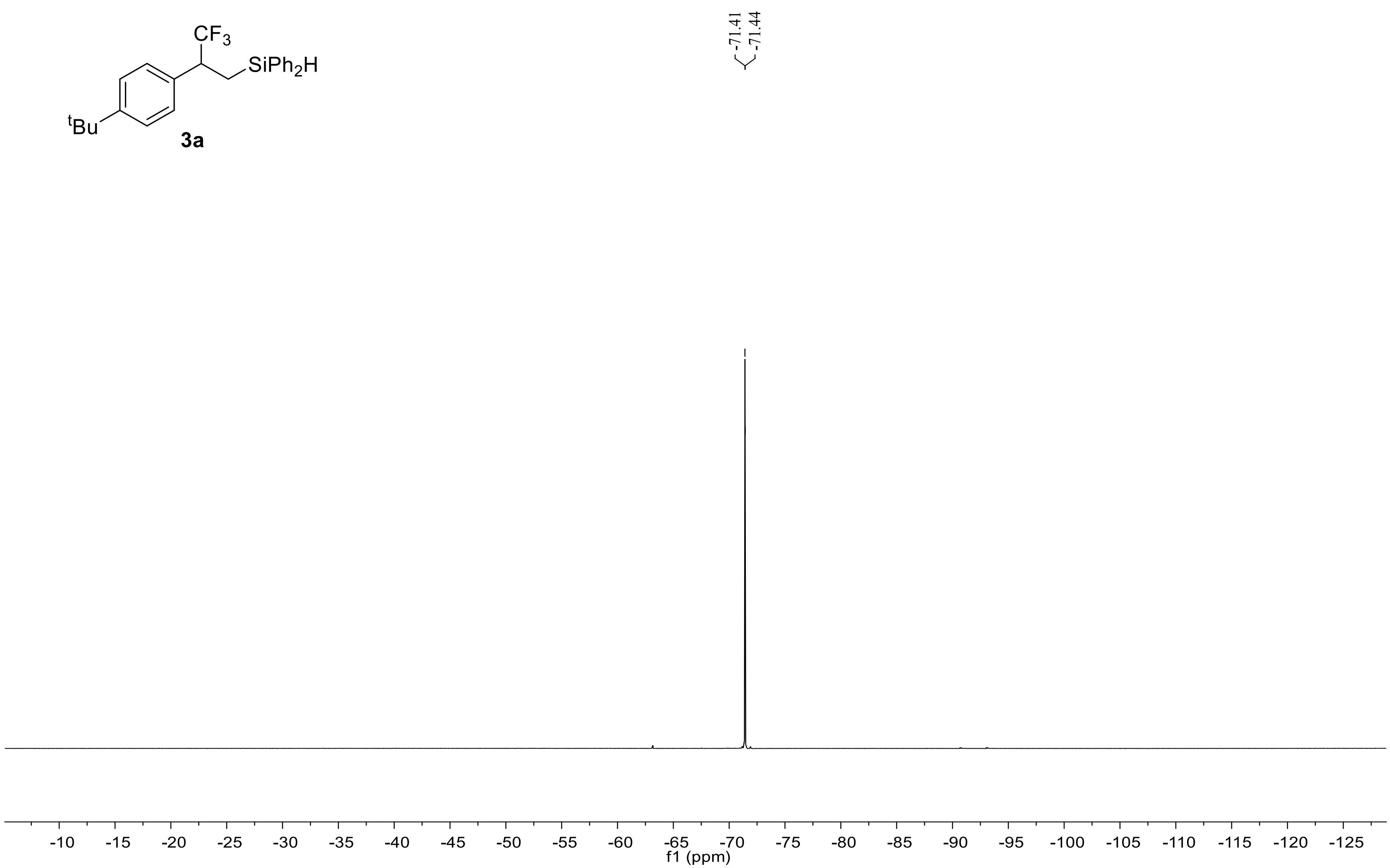
Supplementary Table 5 Crystal data and structure refinement for 4t

Identification code	**4t**
Empirical formula	$C_{31}H_{24}F_3Si$
Formula weight	481.59
Temperature/K	292.66(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	40.8024(7)
b/Å	6.56710(10)
c/Å	18.6566(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4999.10(14)
Z	8
ρ_{calc}g/cm^3	1.280
μ/mm^{-1}	1.163
F(000)	2008.0
Crystal size/mm^3	0.5 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.668 to 143.084
Index ranges	-49 ≤ h ≤ 43, -7 ≤ k ≤ 7, -22 ≤ l ≤ 22
Reflections collected	13470
Independent reflections	4752 [R_{int} = 0.0335, R_{sigma} = 0.0371]
Data/restraints/parameters	4752/0/321
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0592, wR_2 = 0.1790
Final R indexes [all data]	R_1 = 0.0713, wR_2 = 0.1954
Largest diff. peak/hole / e Å^{-3}	0.49/-0.31

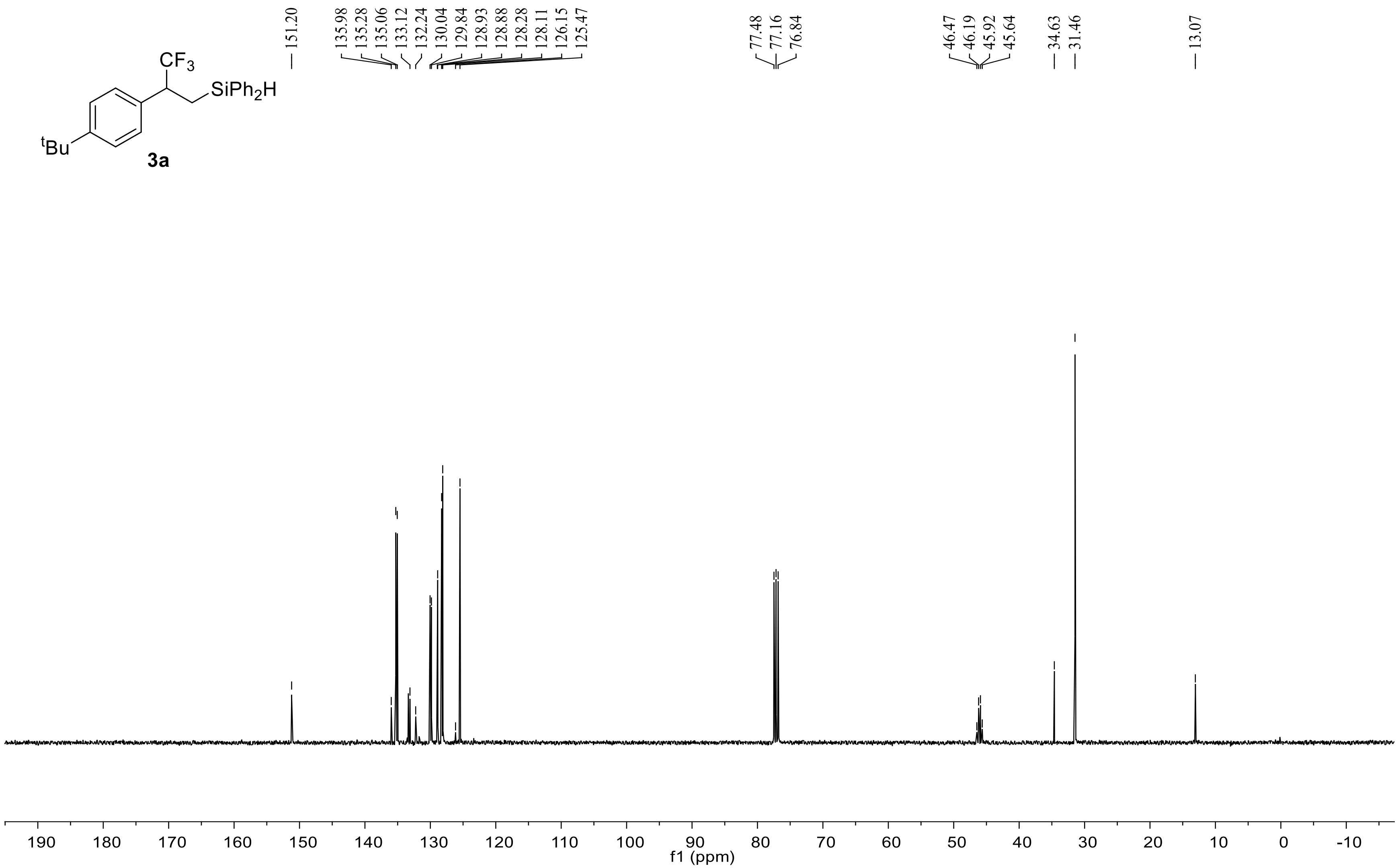
3.2 NMR Spectra.



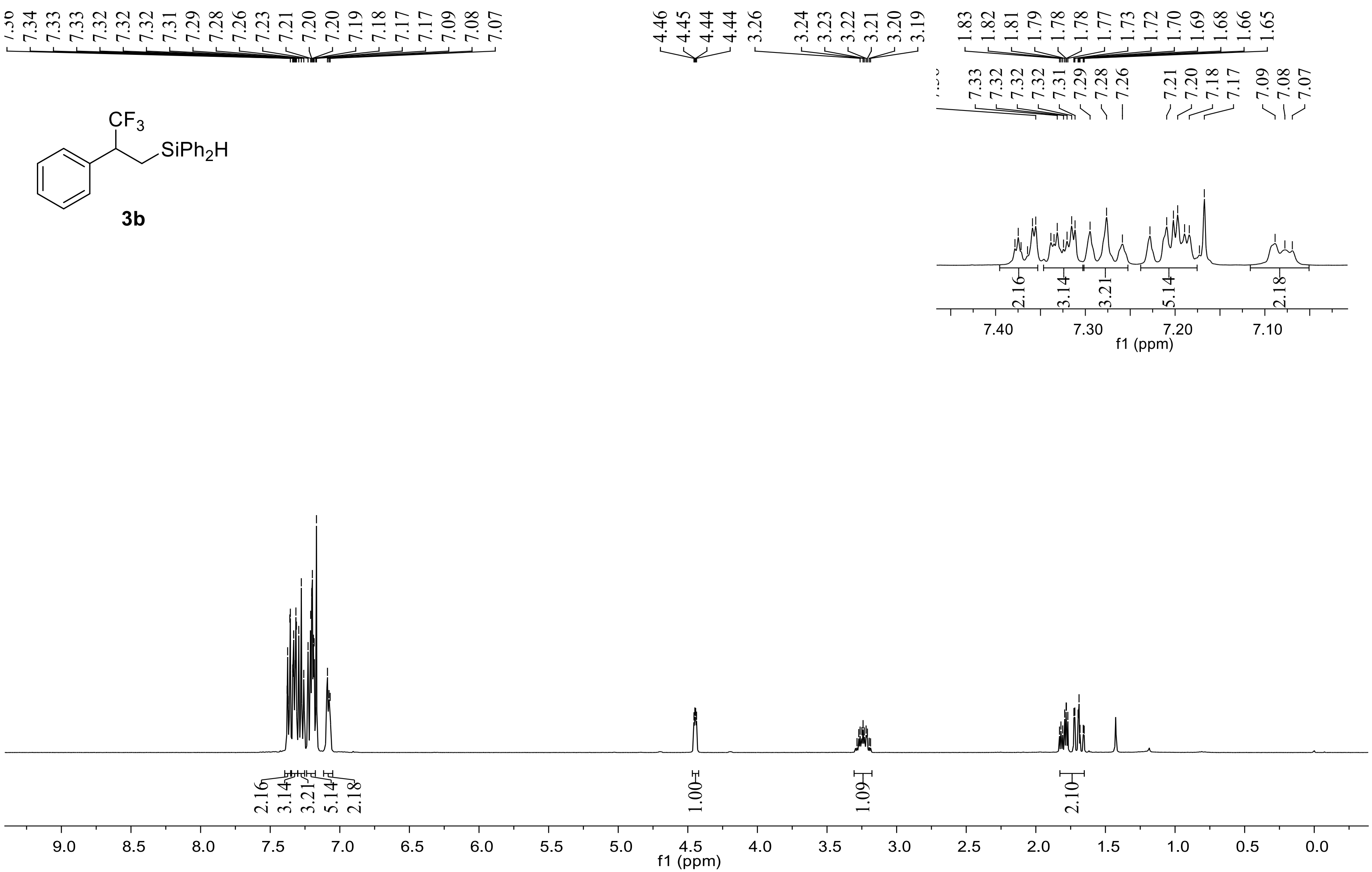
Supplementary Fig. 41. ^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



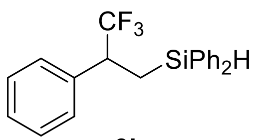
Supplementary Fig. 42. ^{19}F NMR (377 MHz, $CDCl_3$) of **3a**



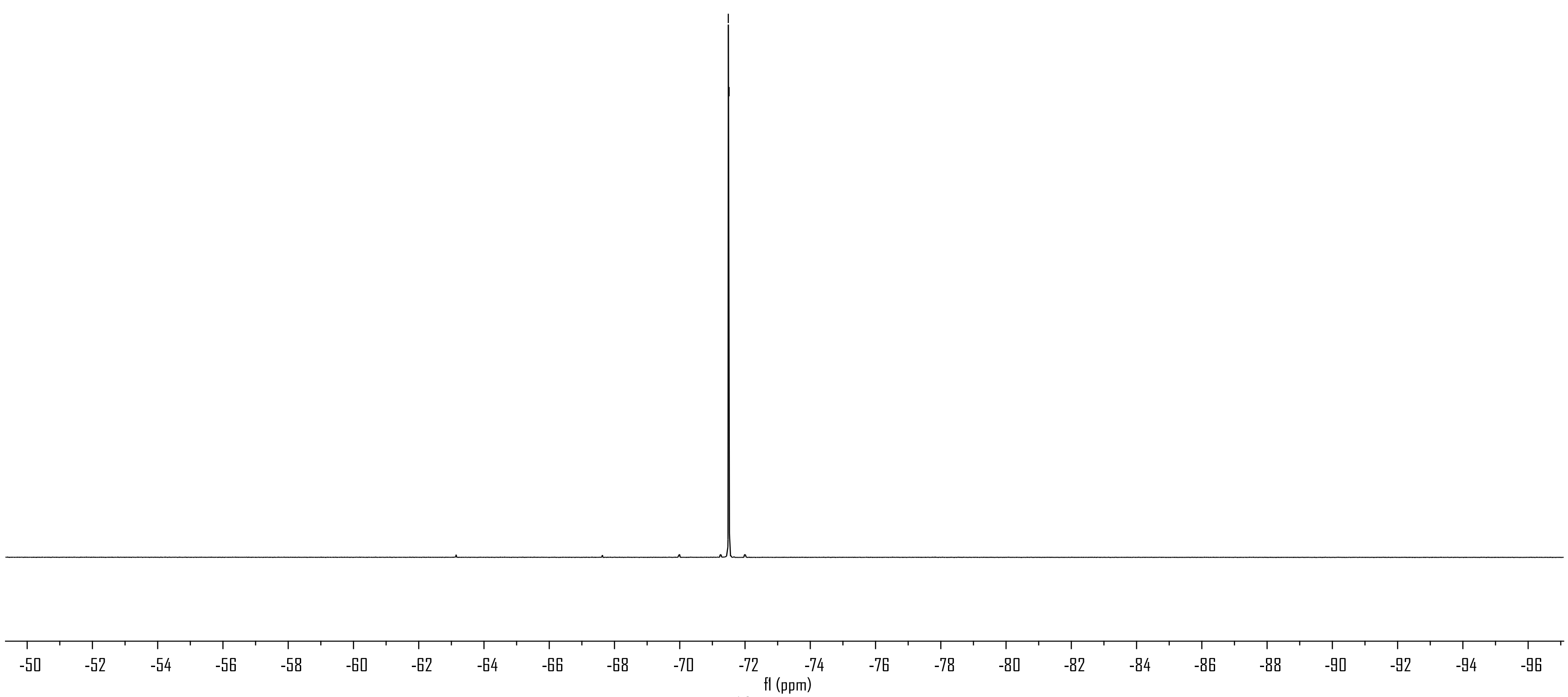
Supplementary Fig. 43. ^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



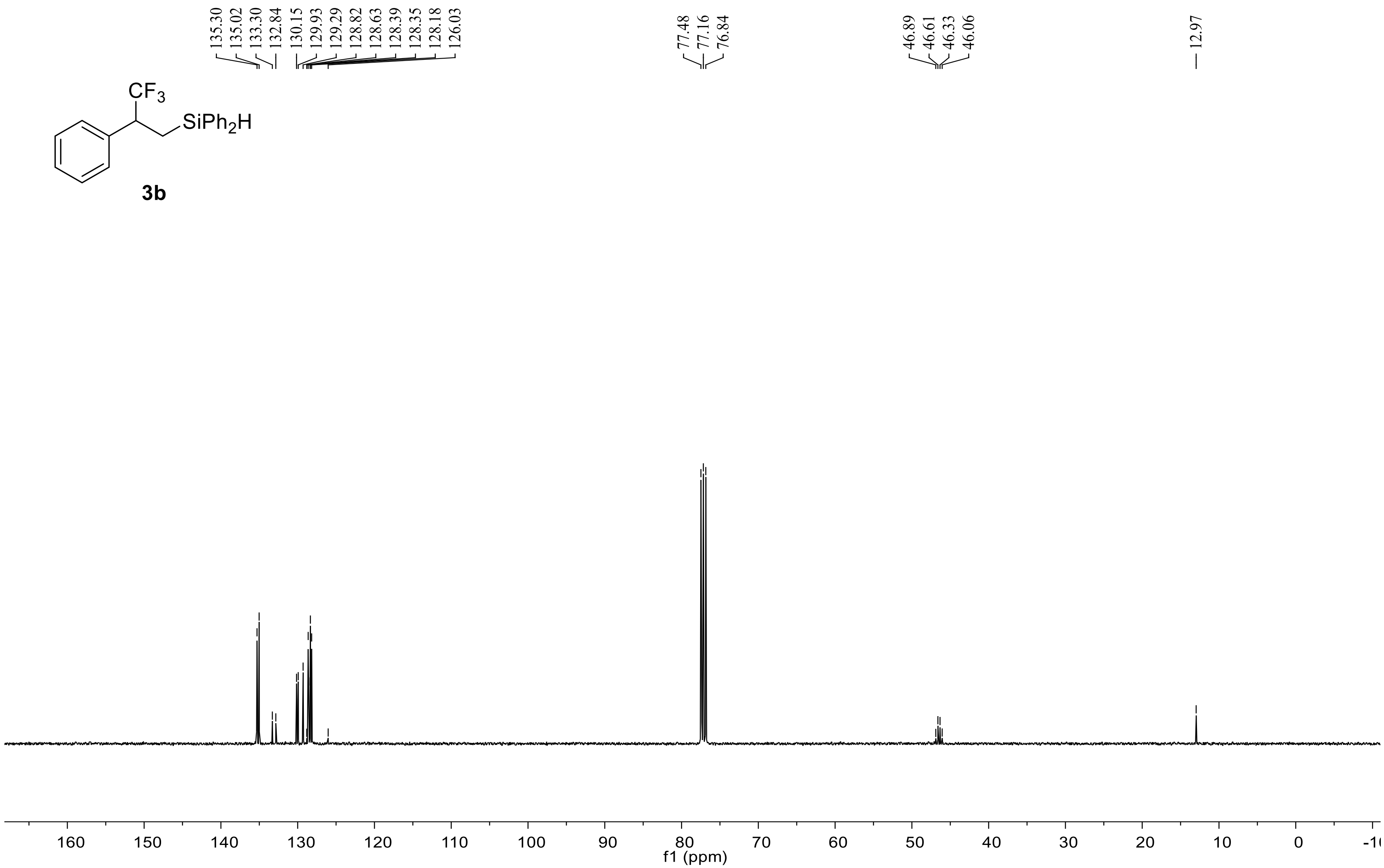
Supplementary Fig. 44. ^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



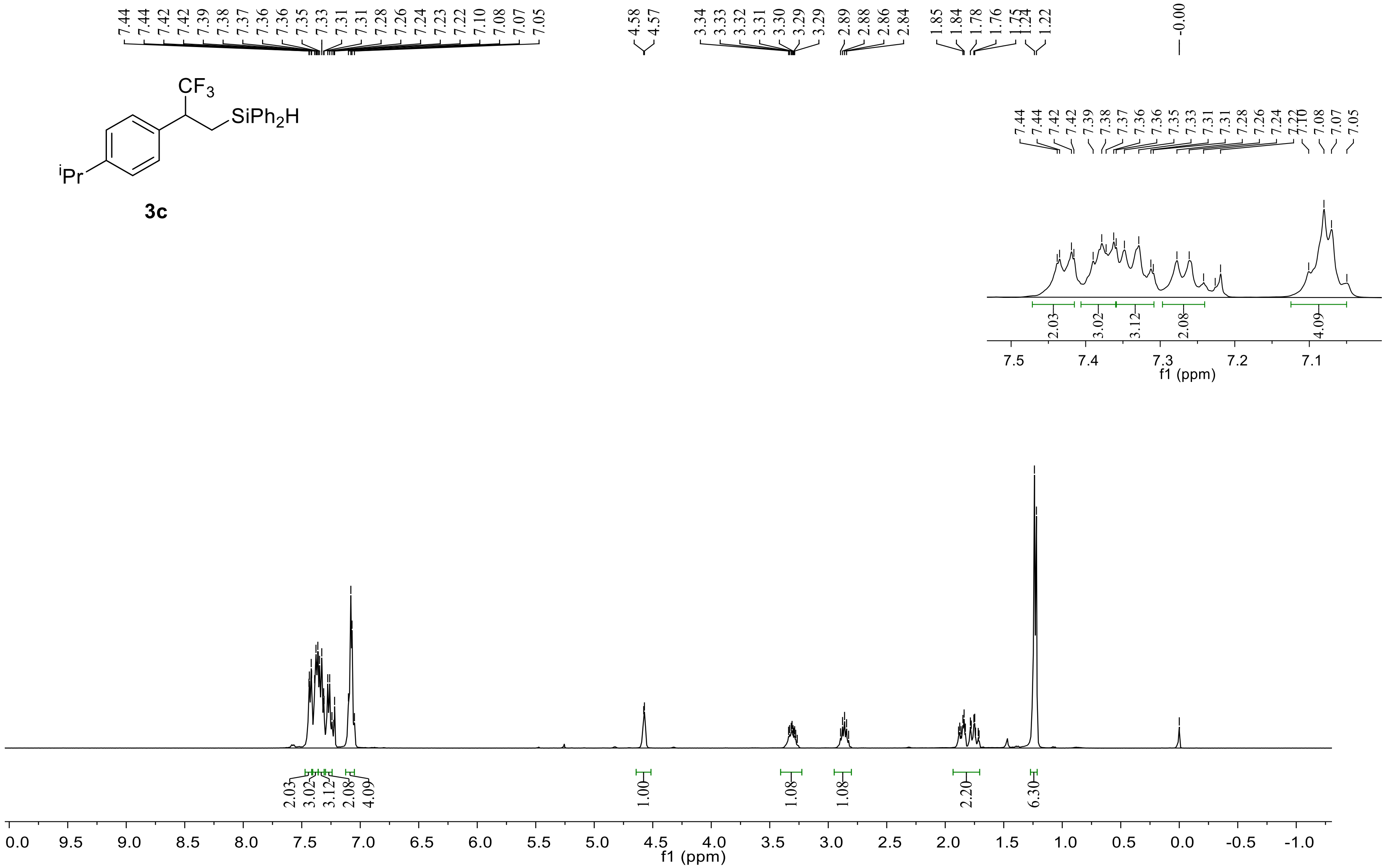
3b



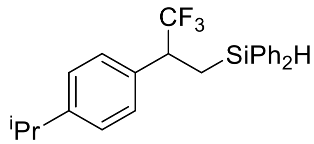
Supplementary Fig. 45. ^{19}F NMR (377 MHz, $CDCl_3$) of **3b**



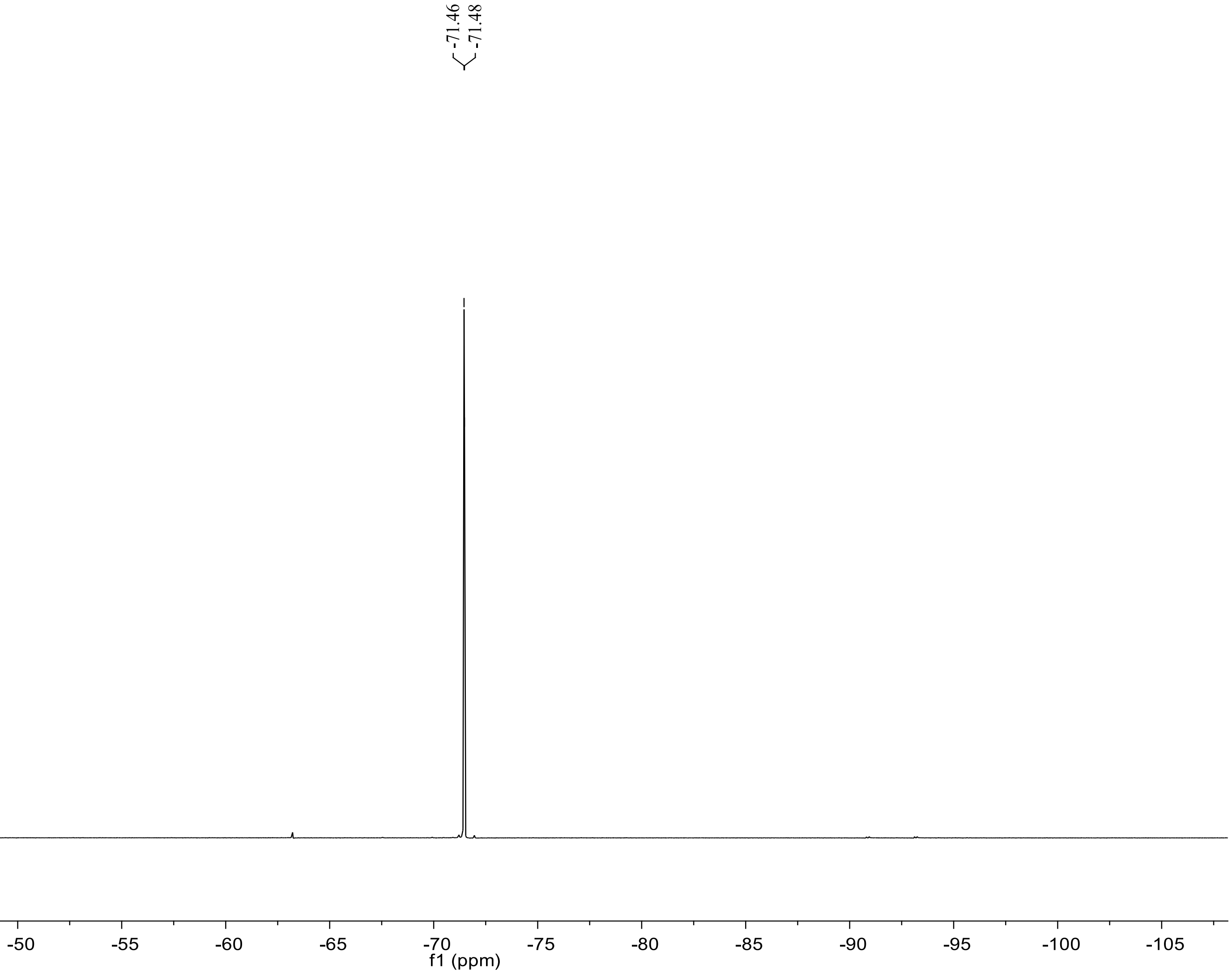
Supplementary Fig. 46. ^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



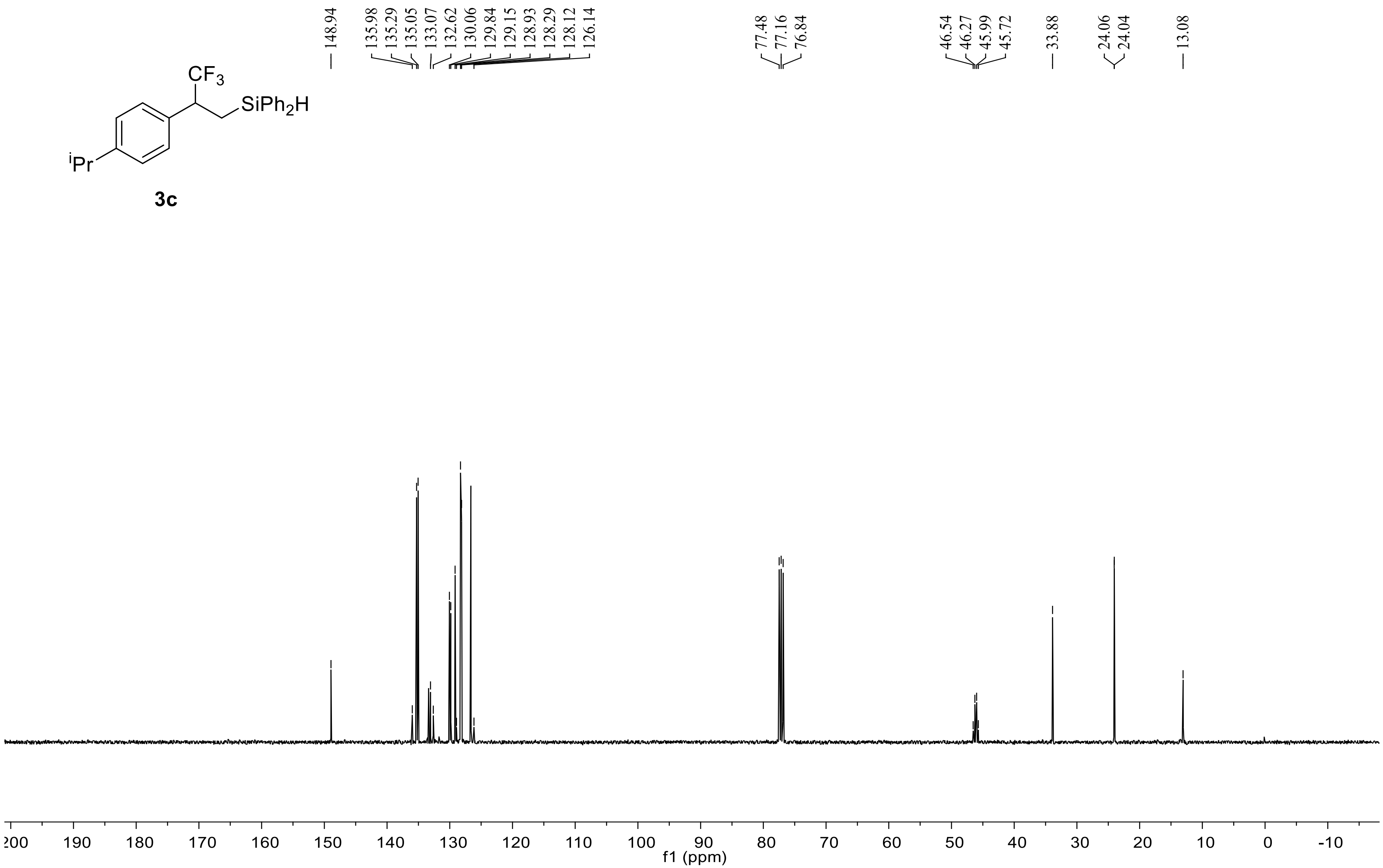
Supplementary Fig. 47. ^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



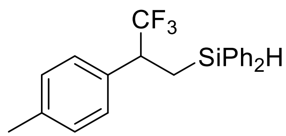
3c



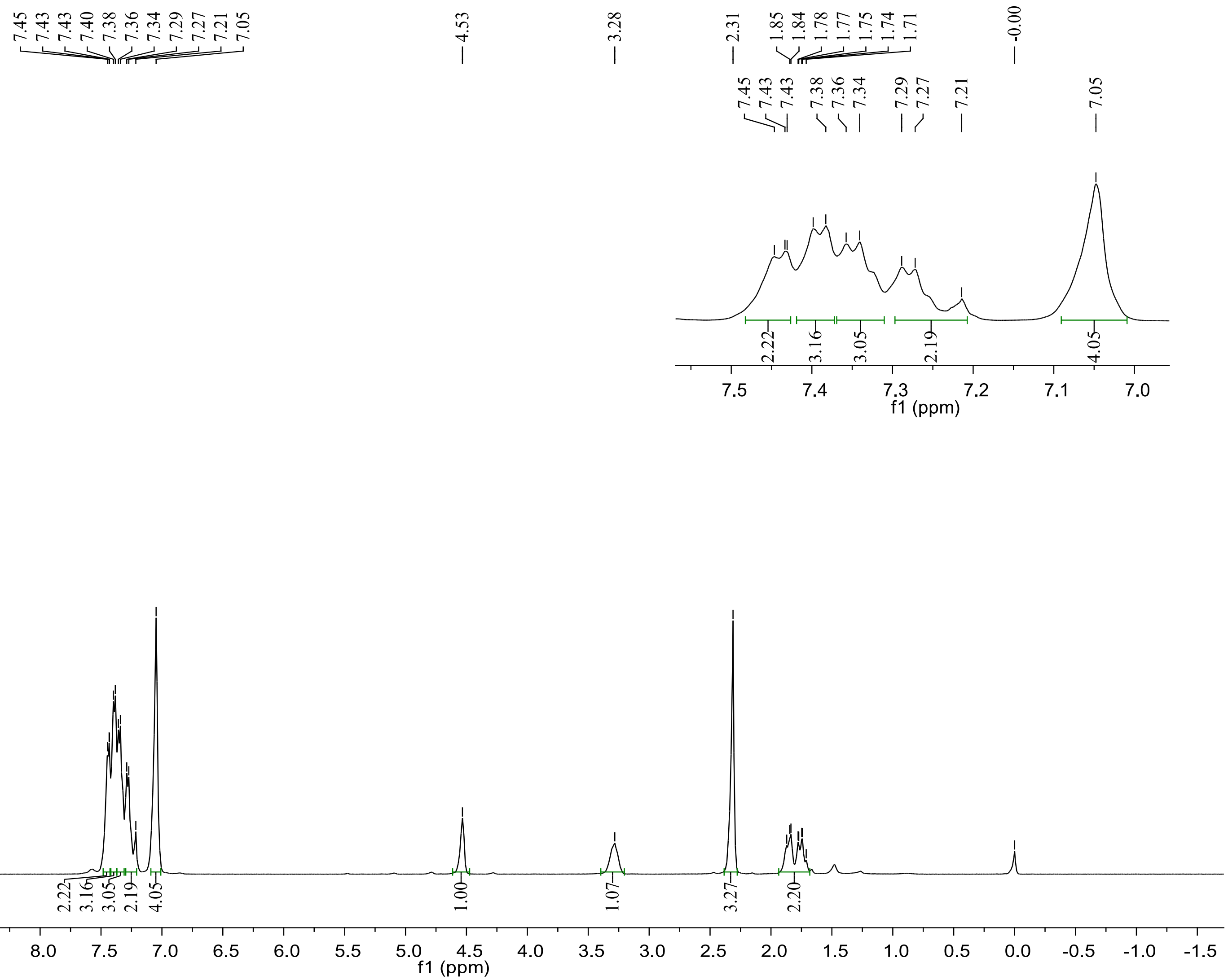
Supplementary Fig. 48. ^{19}F NMR (377 MHz, $CDCl_3$) of **3c**



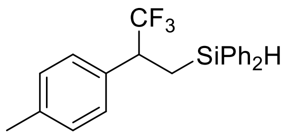
Supplementary Fig. 49. ^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



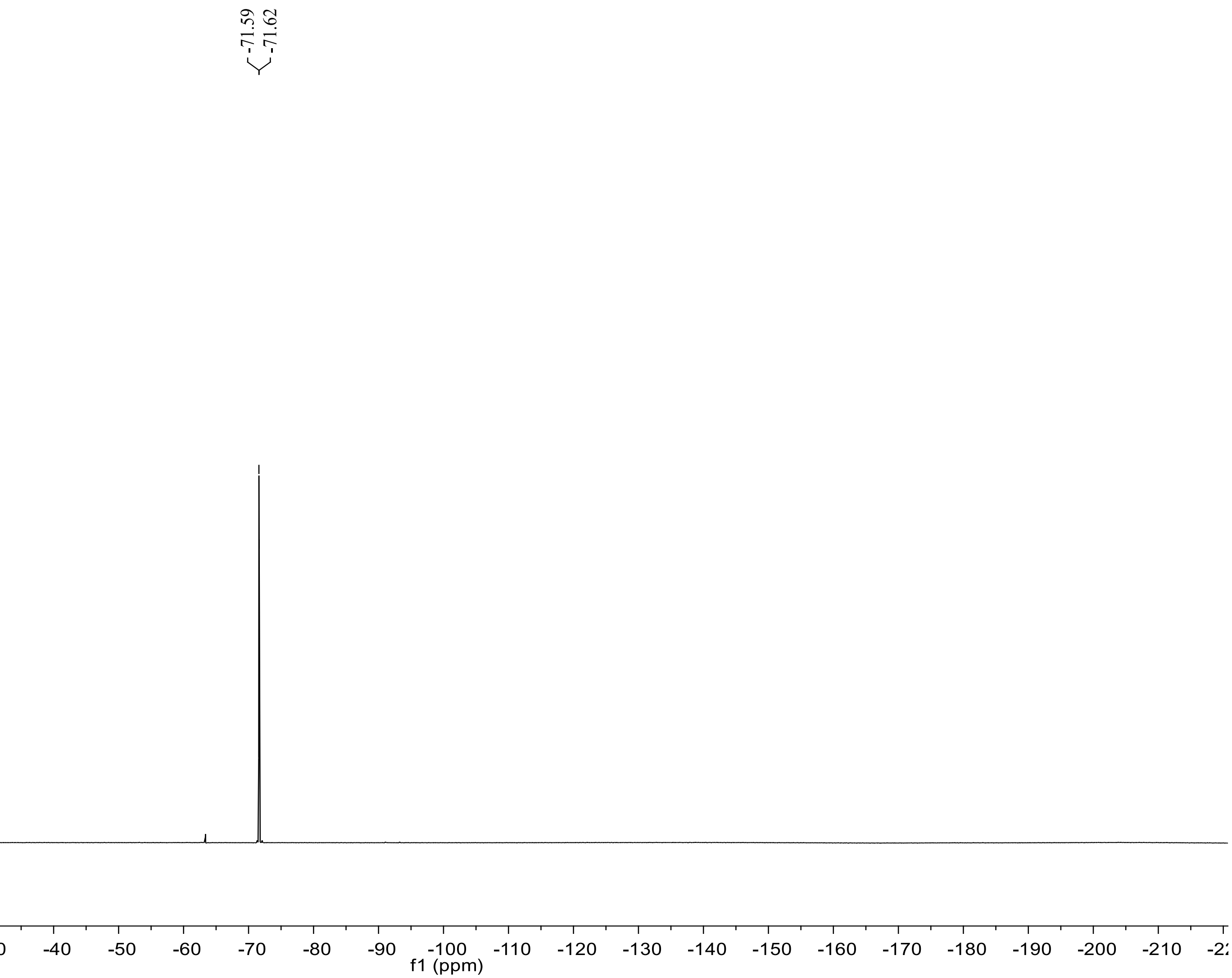
3d



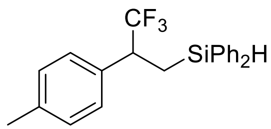
Supplementary Fig. 50. ^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



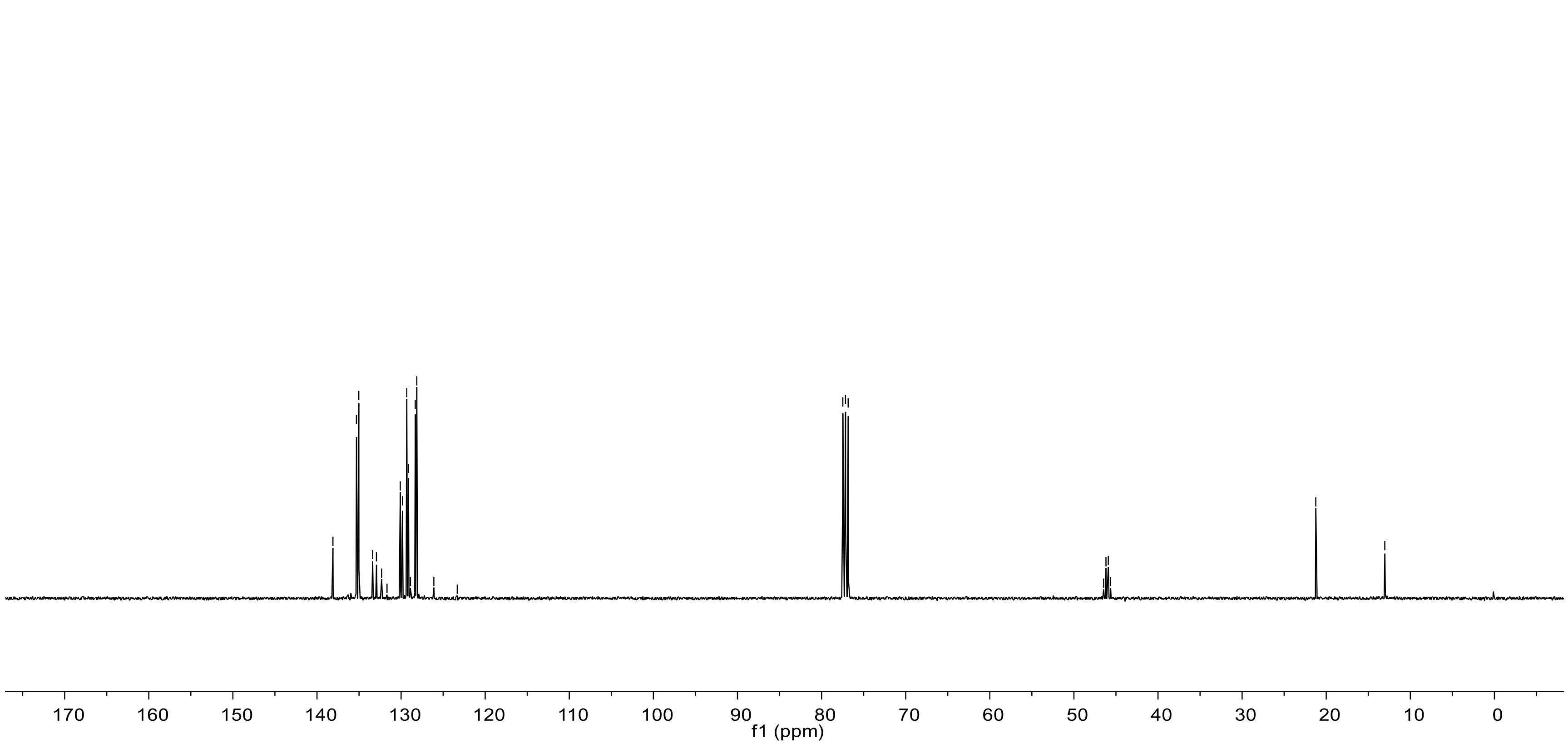
3d



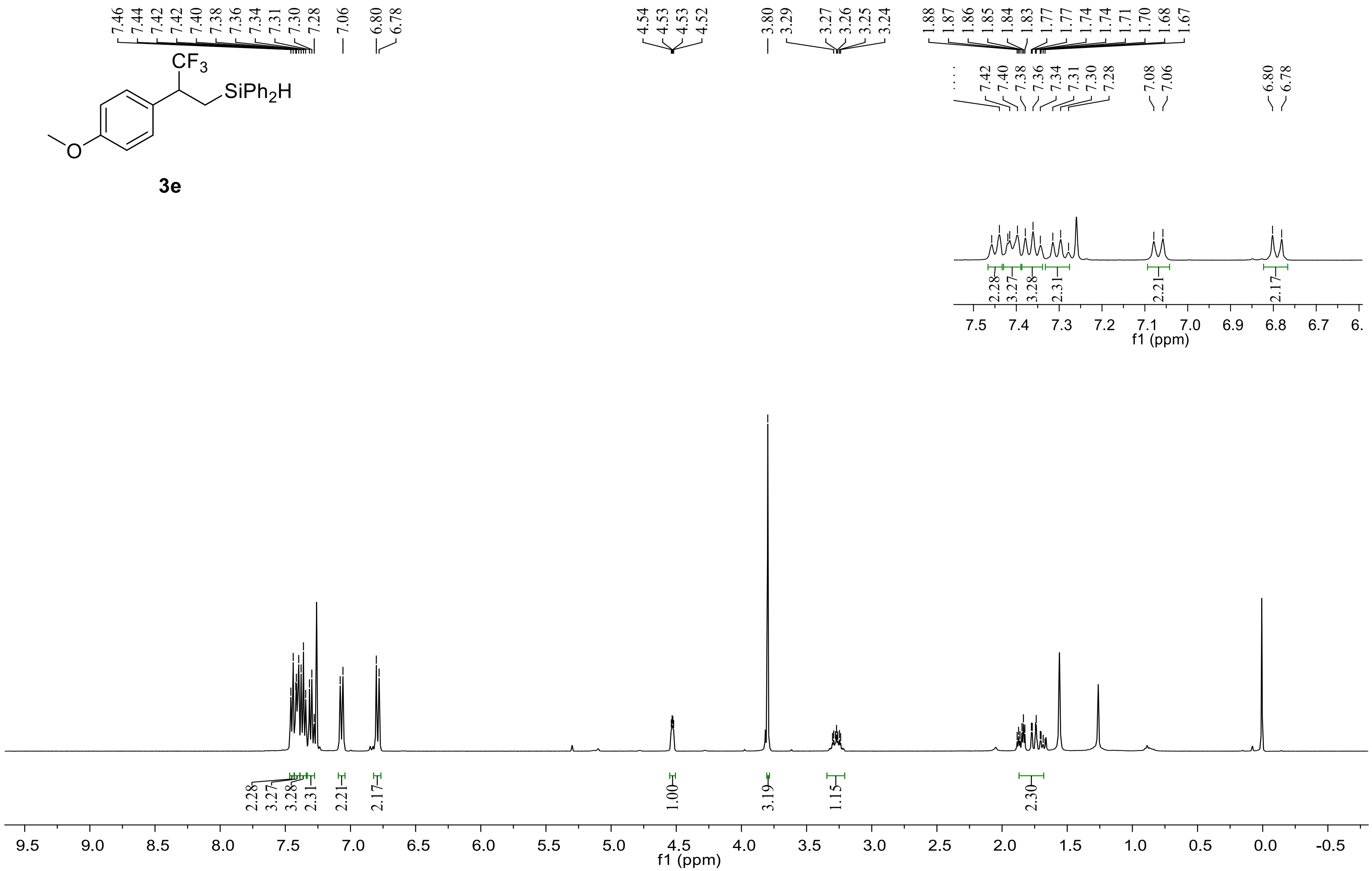
Supplementary Fig. 51. ^{19}F NMR (377 MHz, $CDCl_3$) of **3d**



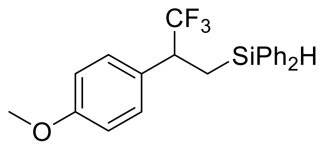
3d



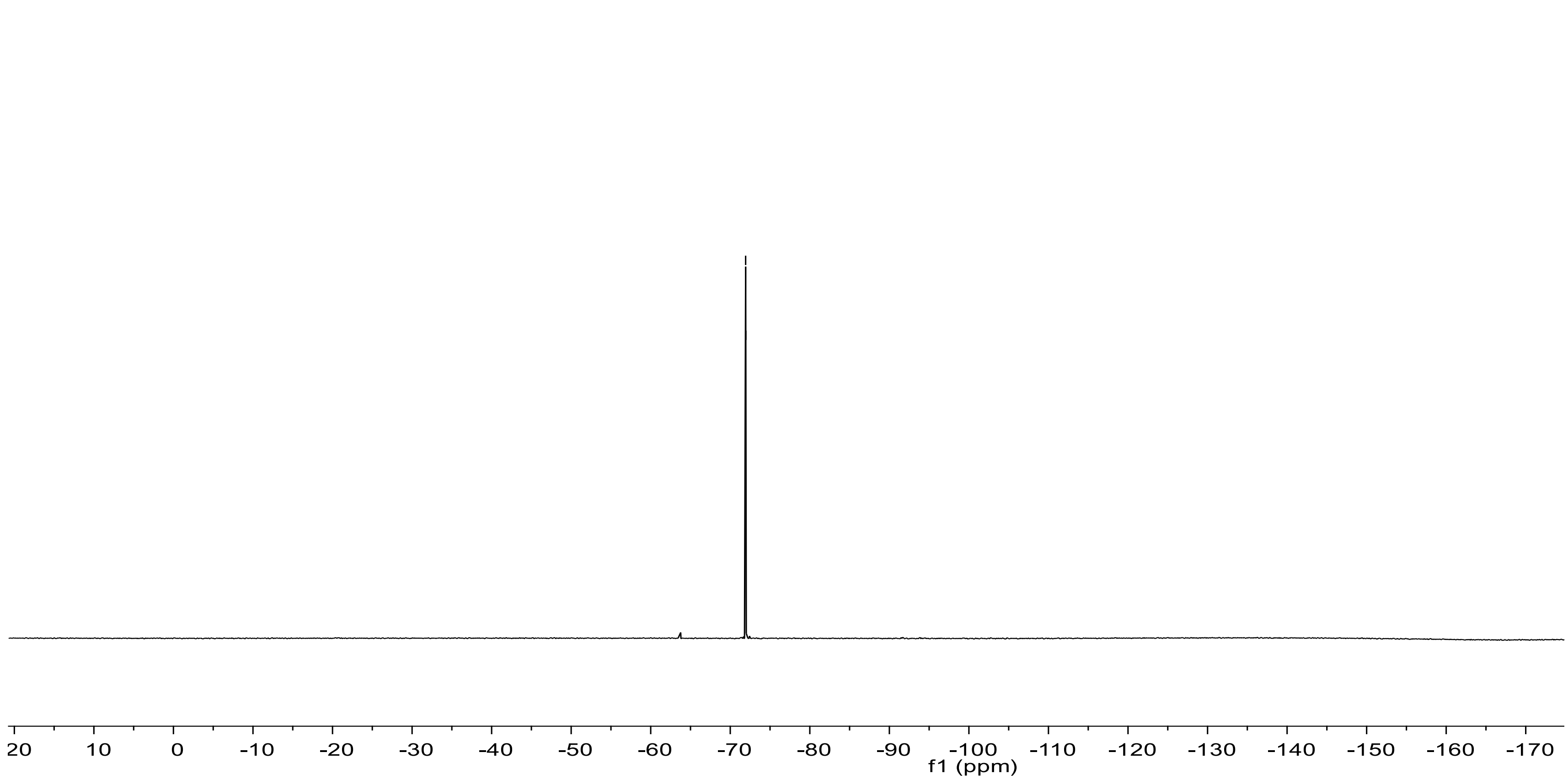
Supplementary Fig. 52. ^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



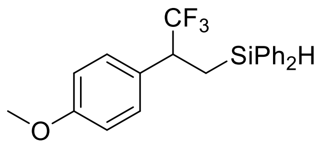
Supplementary Fig. 53. ^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



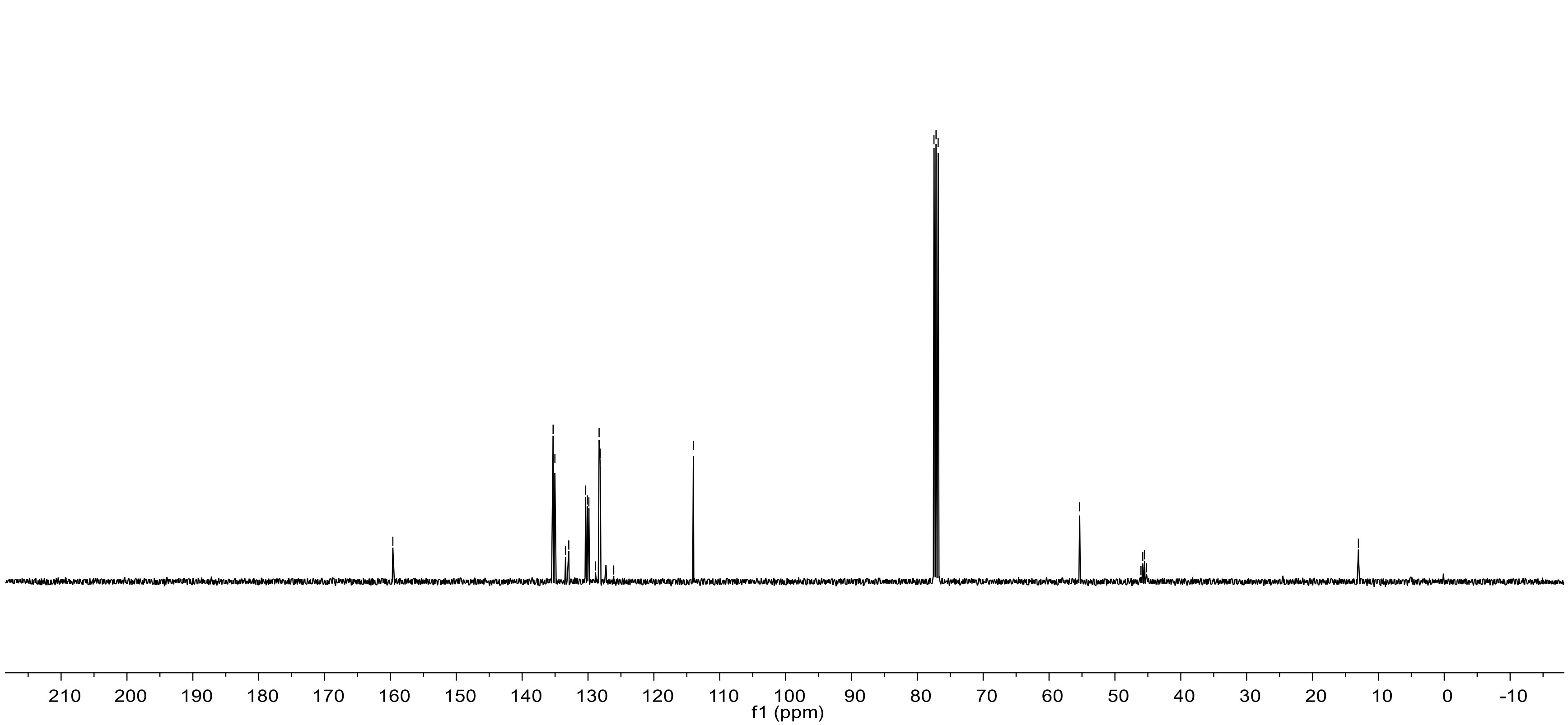
3e



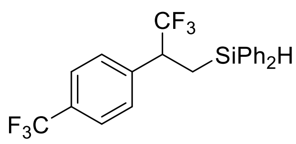
Supplementary Fig. 54. ^{19}F NMR (377 MHz, $CDCl_3$) of **3e**



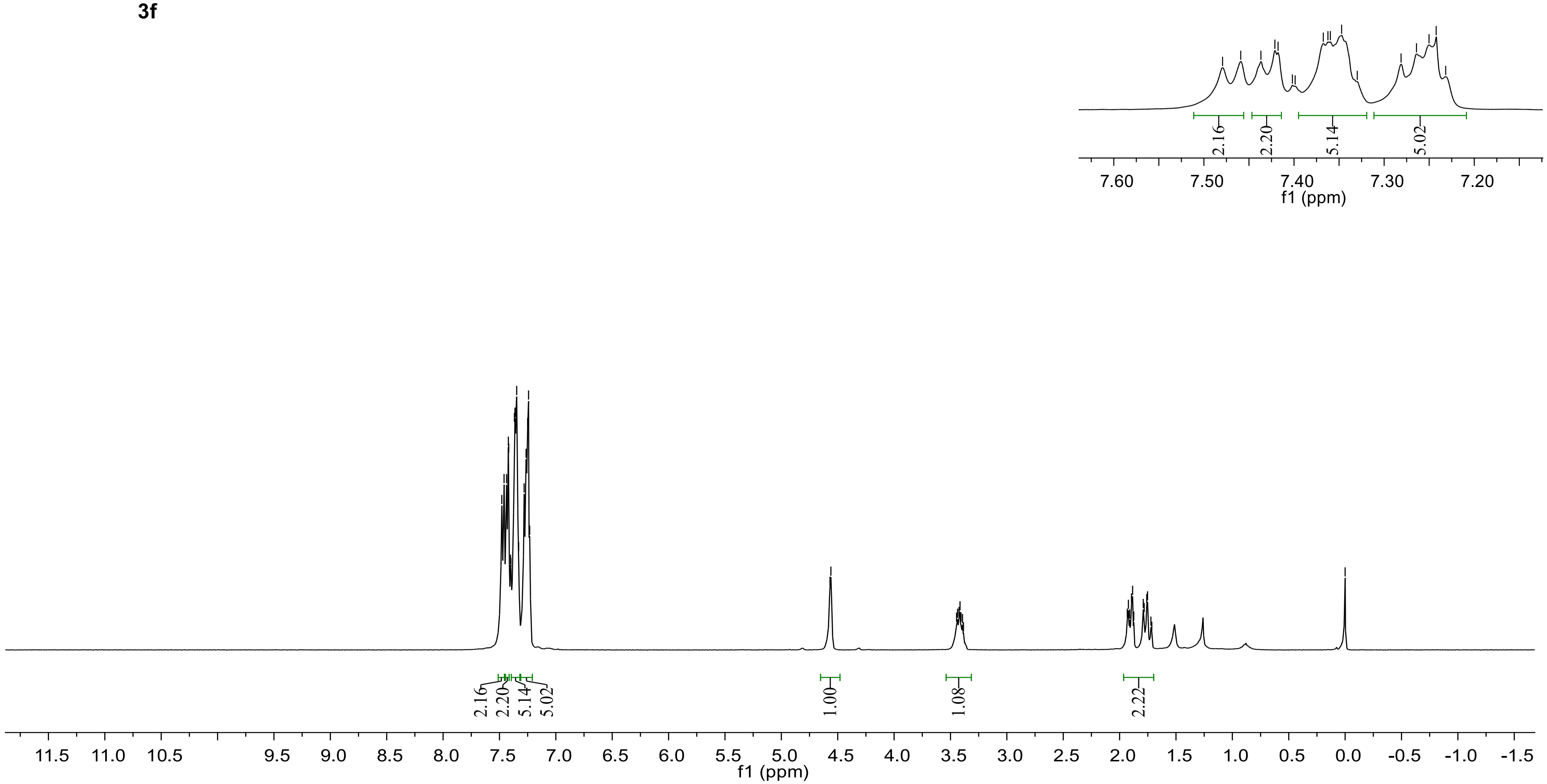
3e



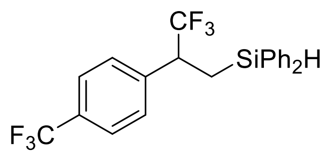
Supplementary Fig. 55. ^{13}C NMR (101 MHz, $CDCl_3$) of **3e**

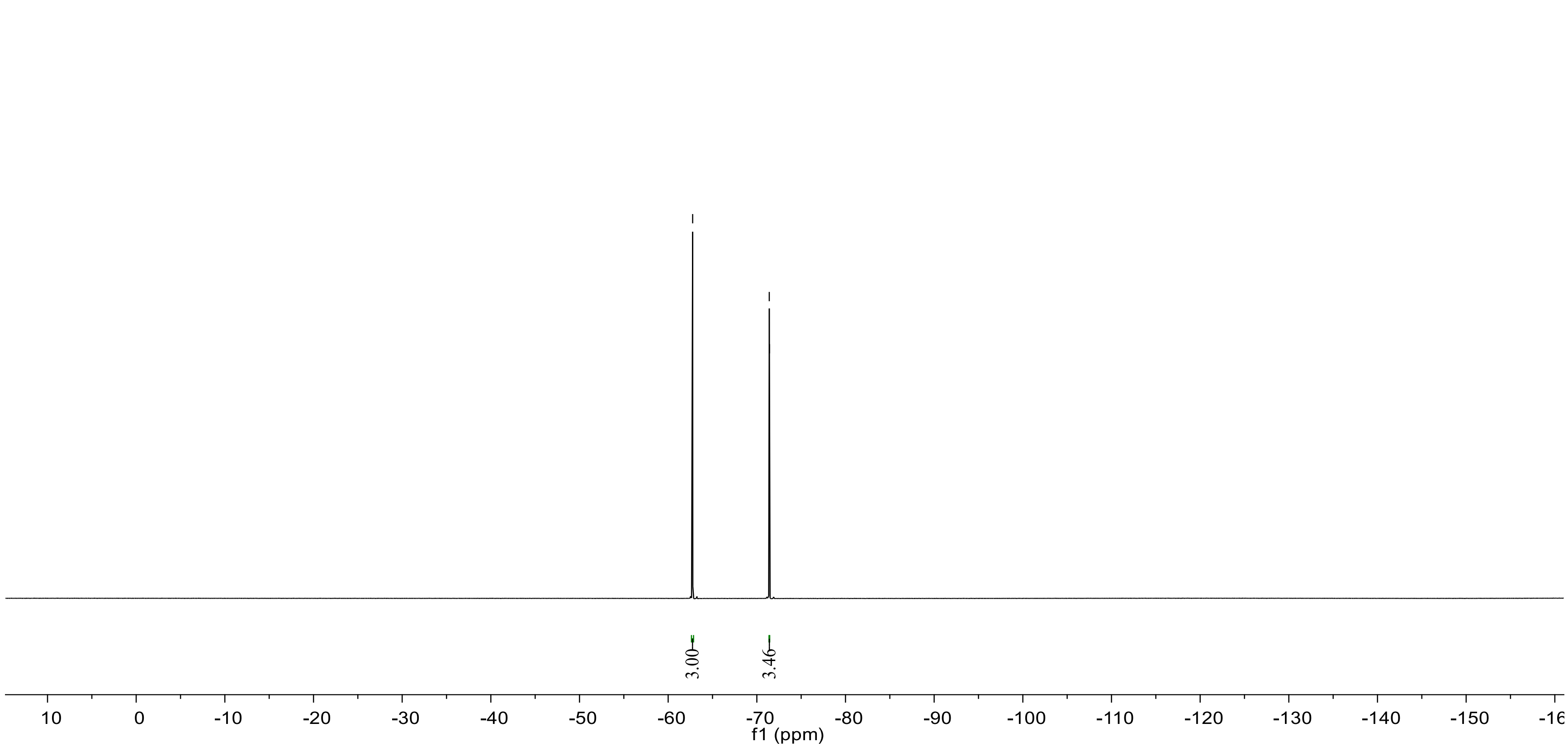


3f

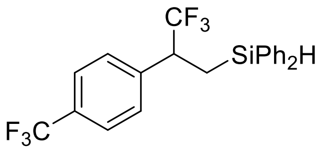


Supplementary Fig. 56. ^{1}H NMR (400 MHz, $CDCl_3$) of **3f**

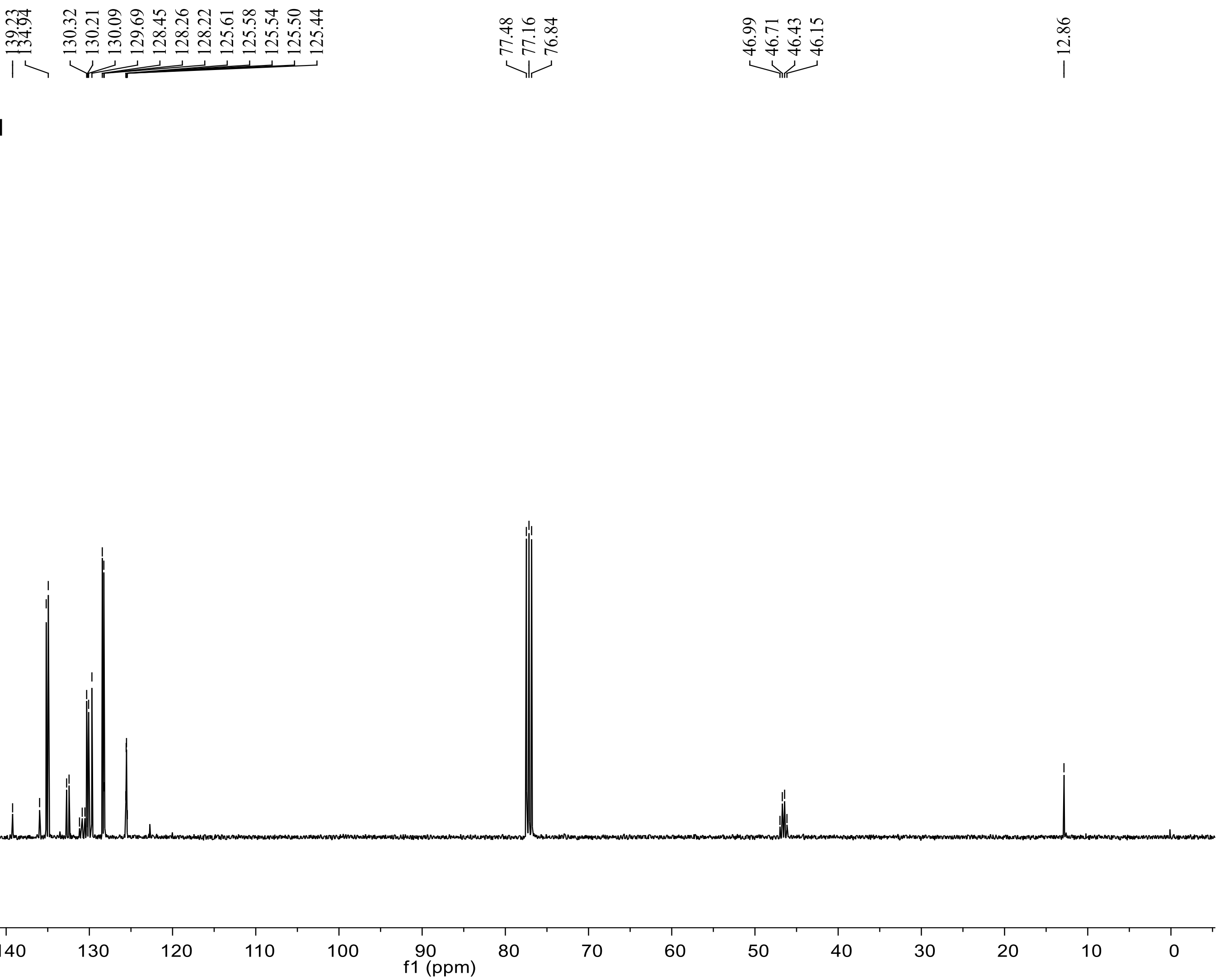




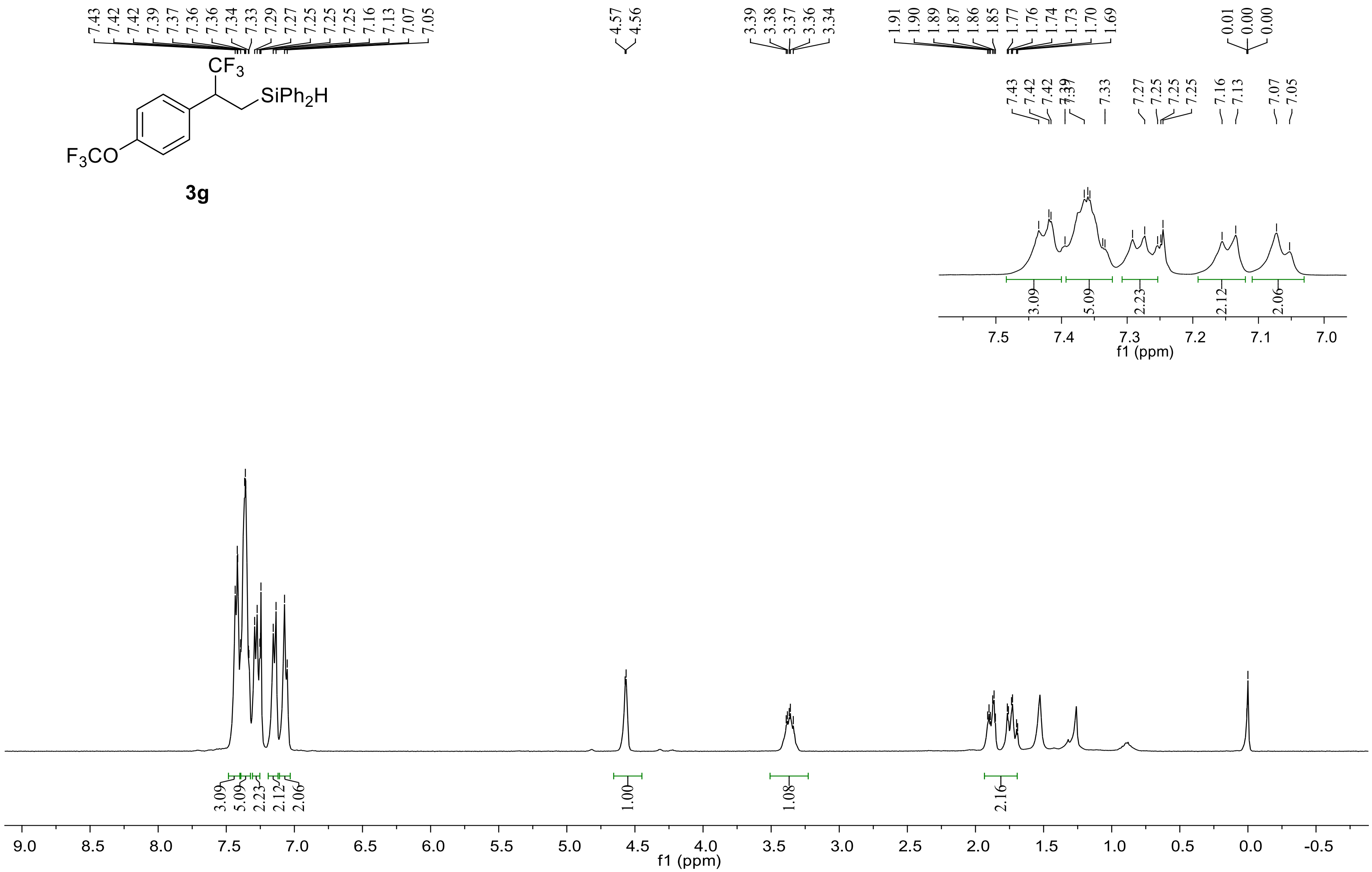
Supplementary Fig. 57. ^{19}F NMR (377 MHz, $CDCl_3$) of **3f**



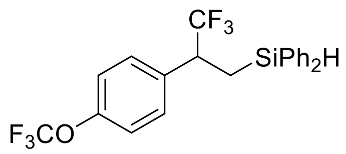
3f



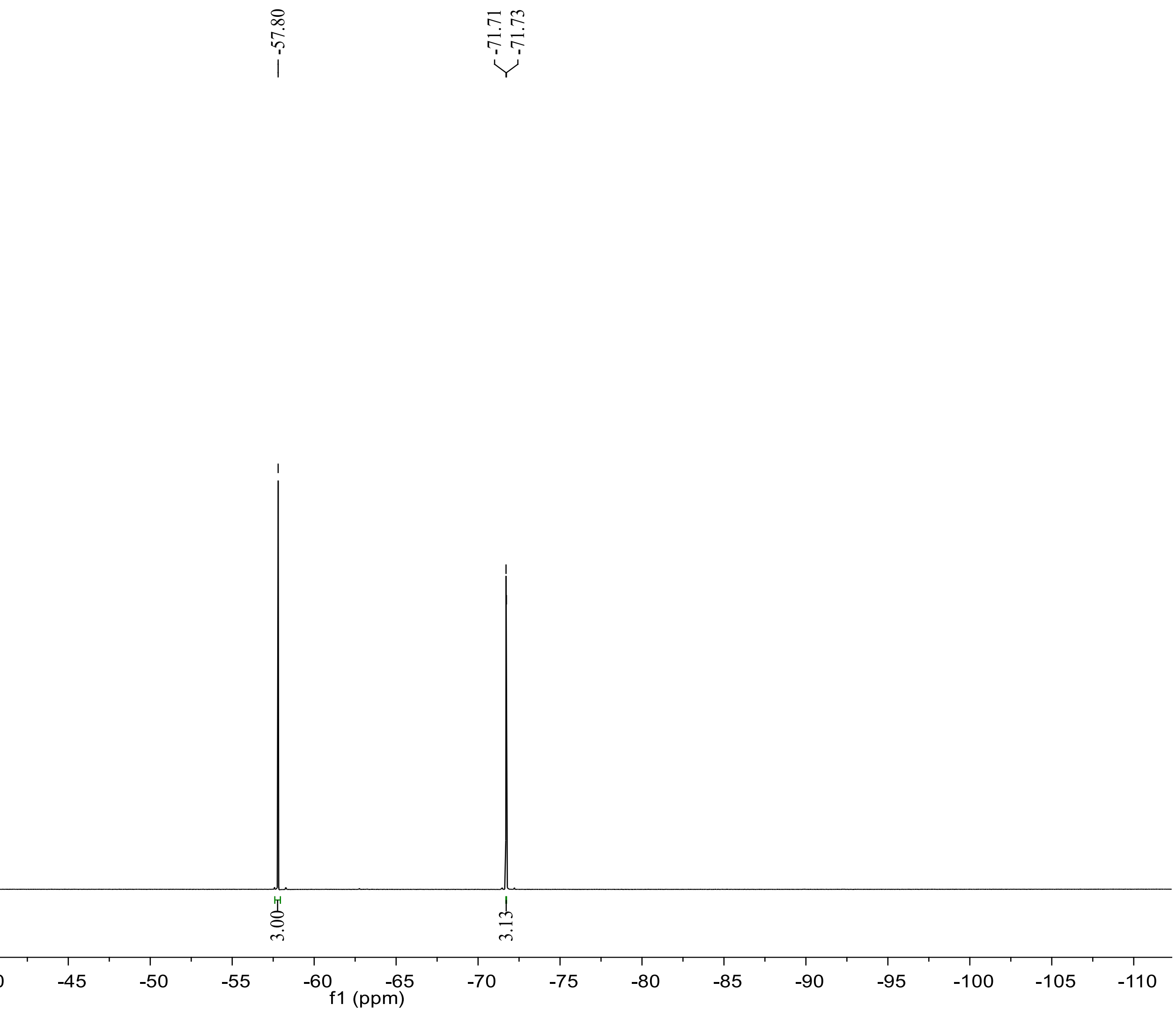
Supplementary Fig. 58. ^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



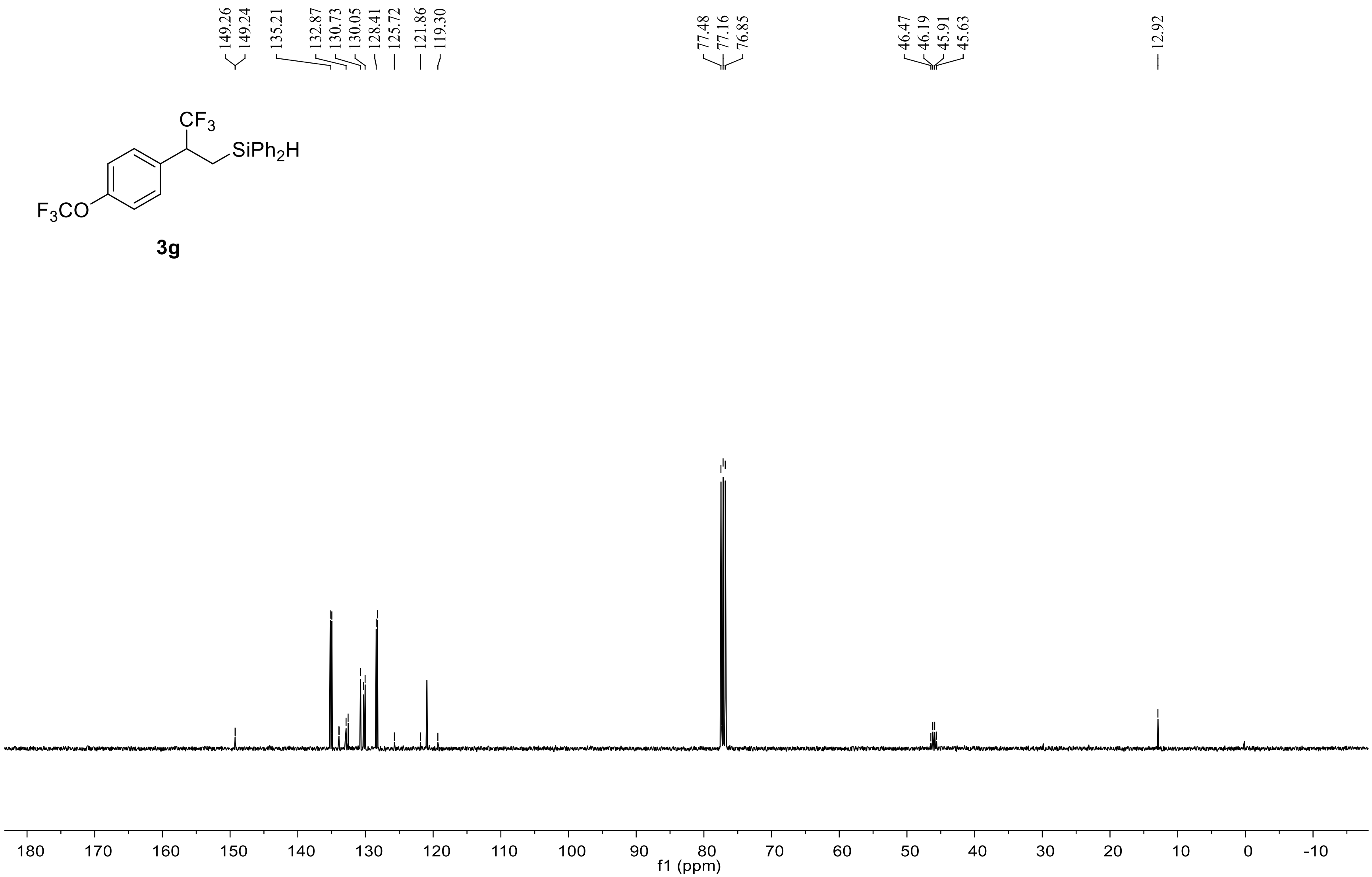
Supplementary Fig. 59. ^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



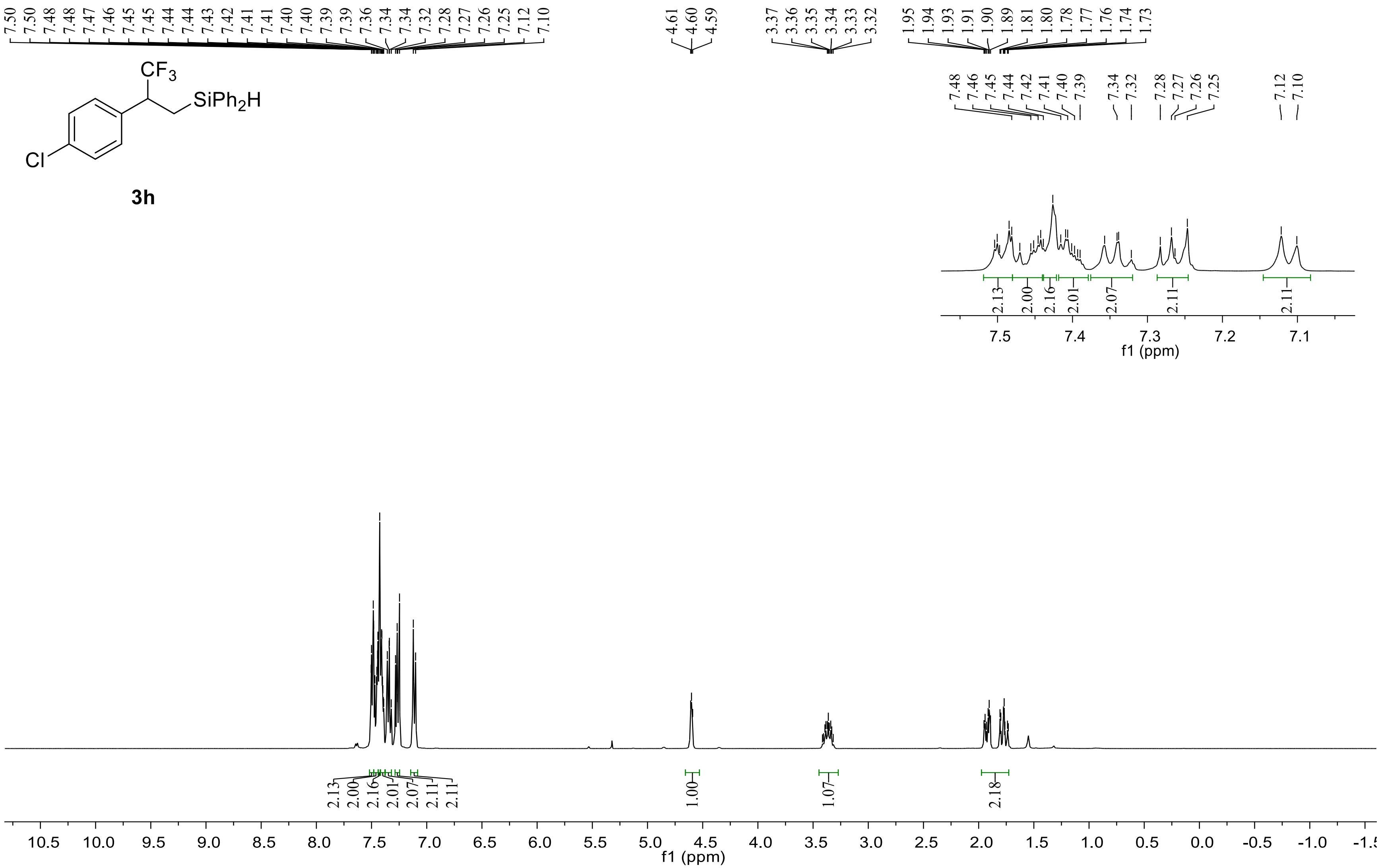
3g



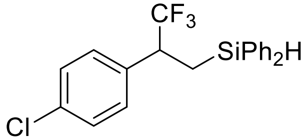
Supplementary Fig. 60. ^{19}F NMR (377 MHz, $CDCl_3$) of **3g**



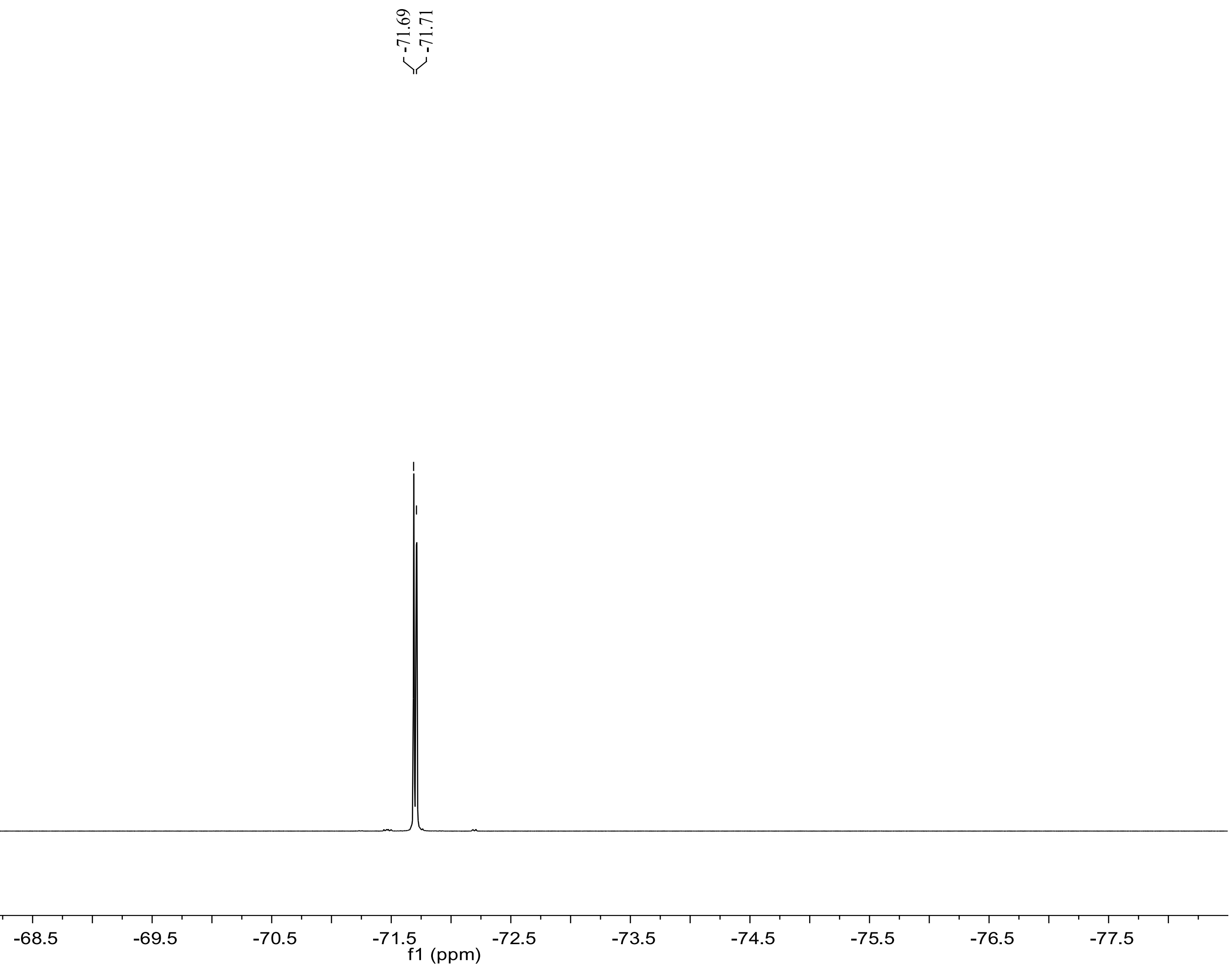
Supplementary Fig. 61. ^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



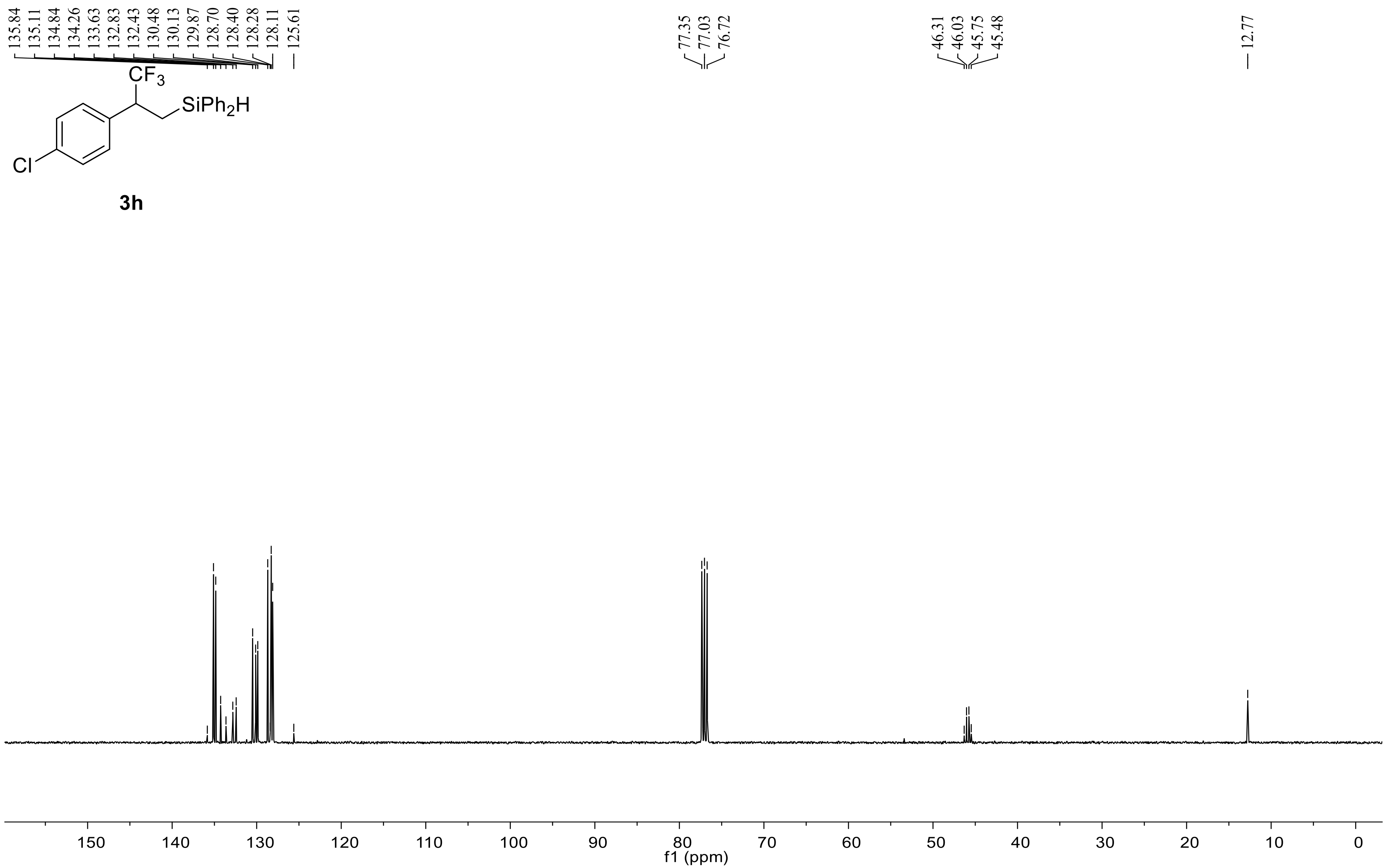
Supplementary Fig. 62. ^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



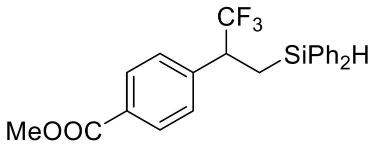
3h



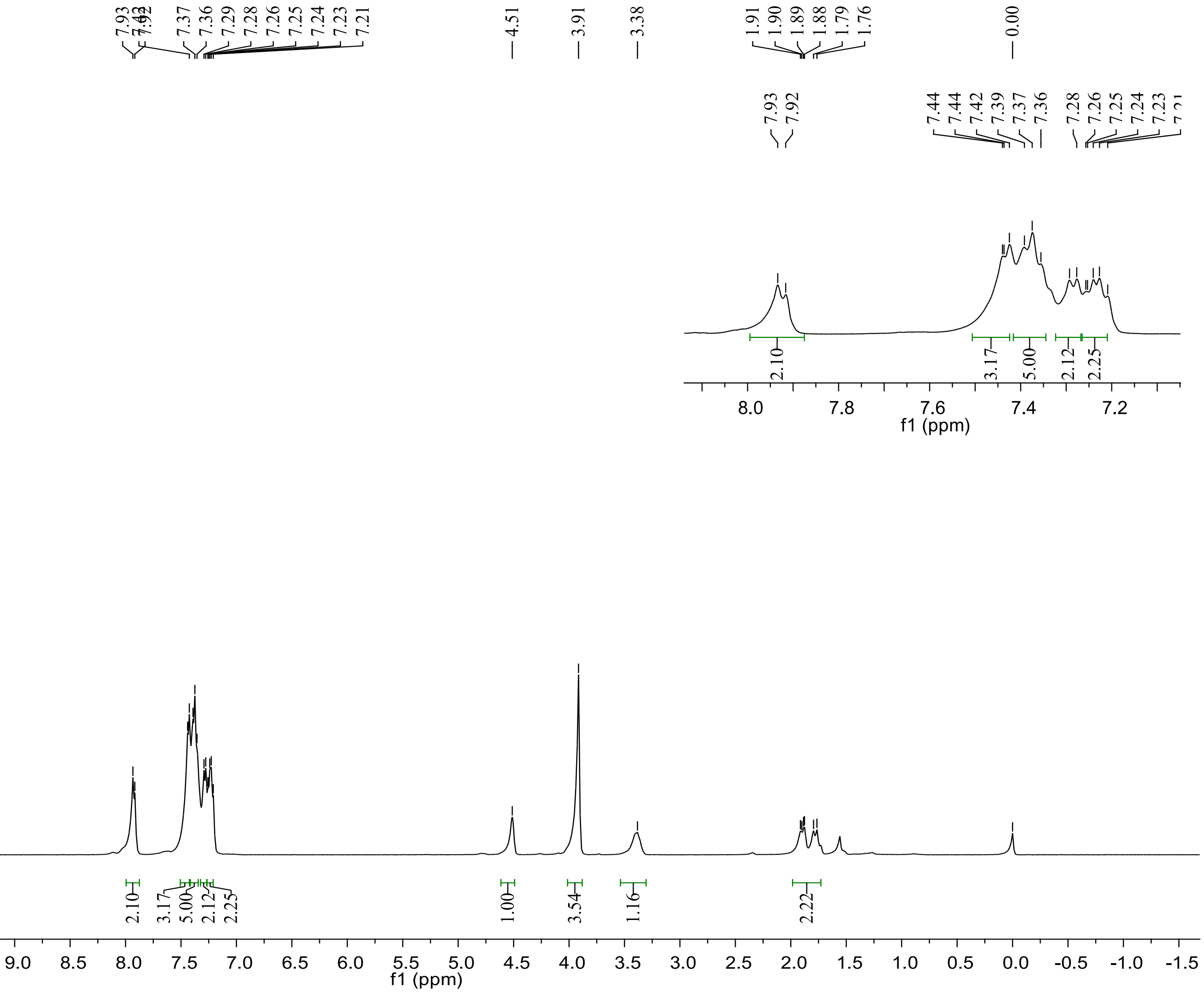
Supplementary Fig. 63. ^{19}F NMR (377 MHz, $CDCl_3$) of **3h**



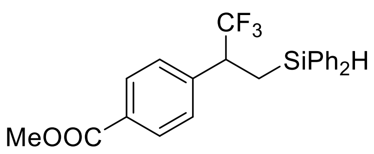
Supplementary Fig. 64. ^{13}C NMR (377 MHz, $CDCl_3$) of **3h**



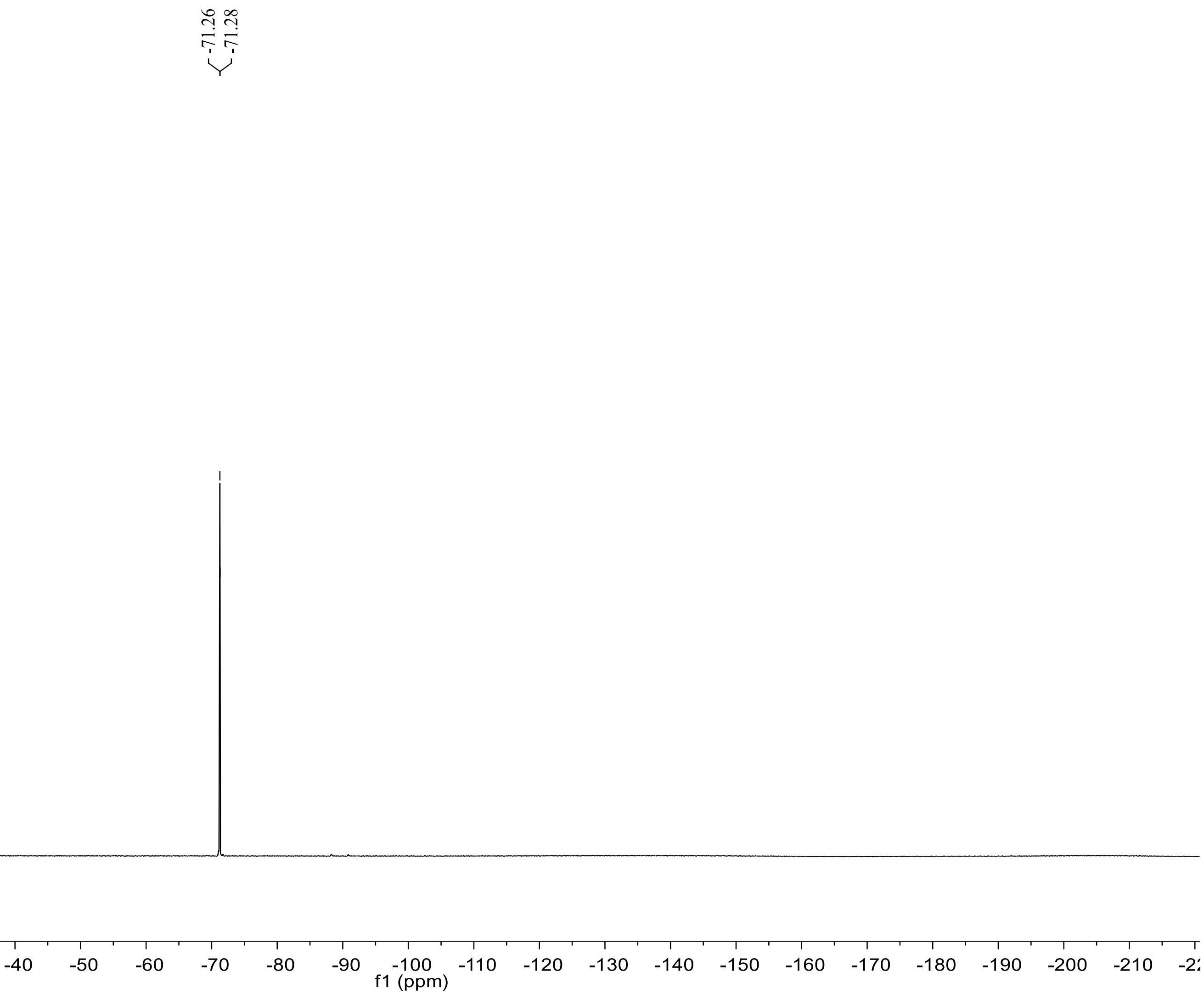
3i



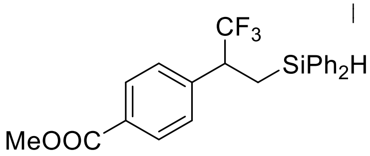
Supplementary Fig. 65. ^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



3i



Supplementary Fig. 66. ^{19}F NMR (377 MHz, $CDCl_3$) of **3i**



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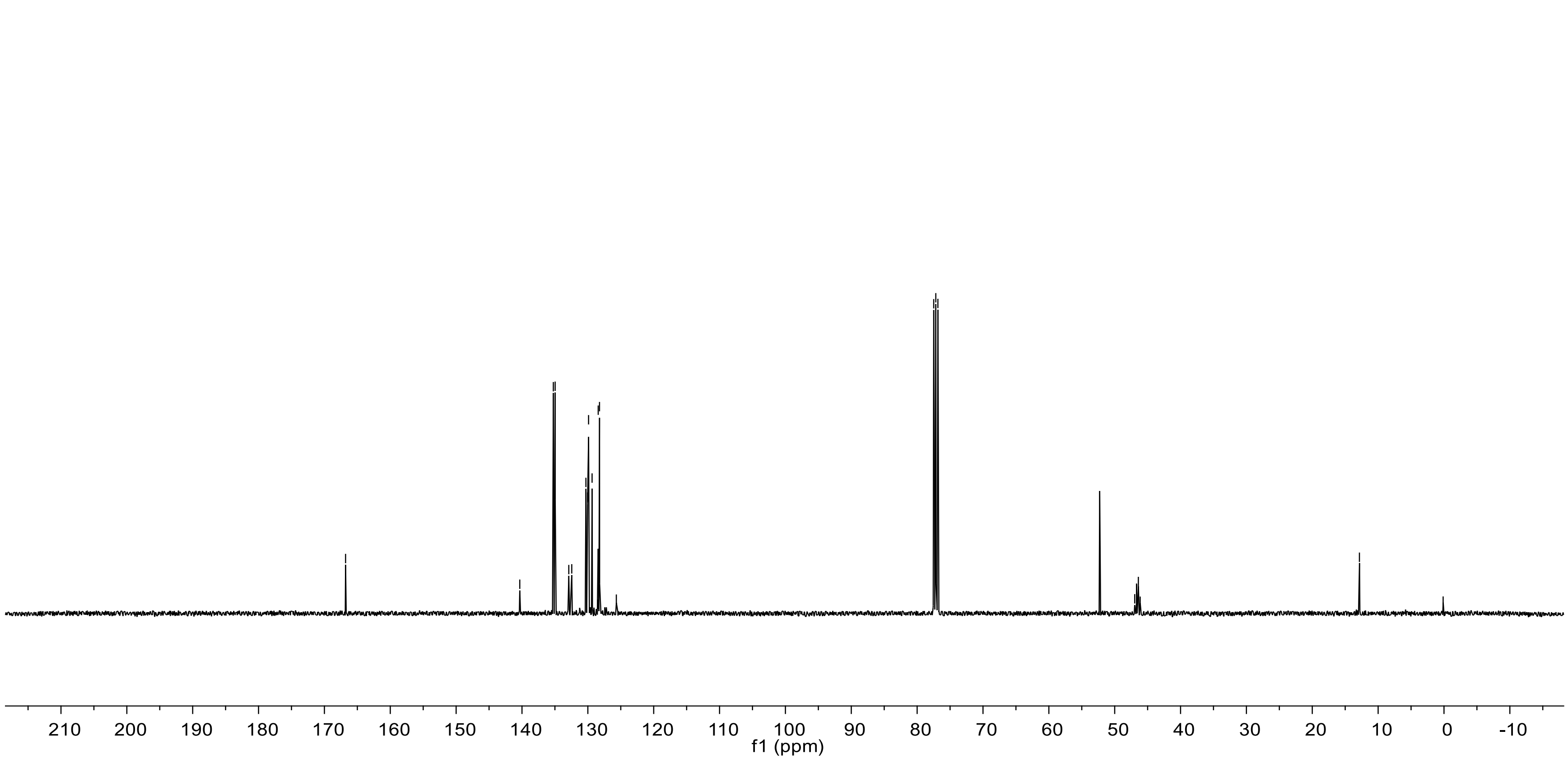
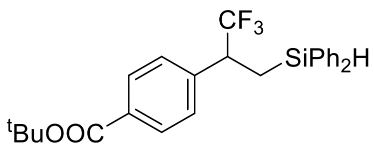
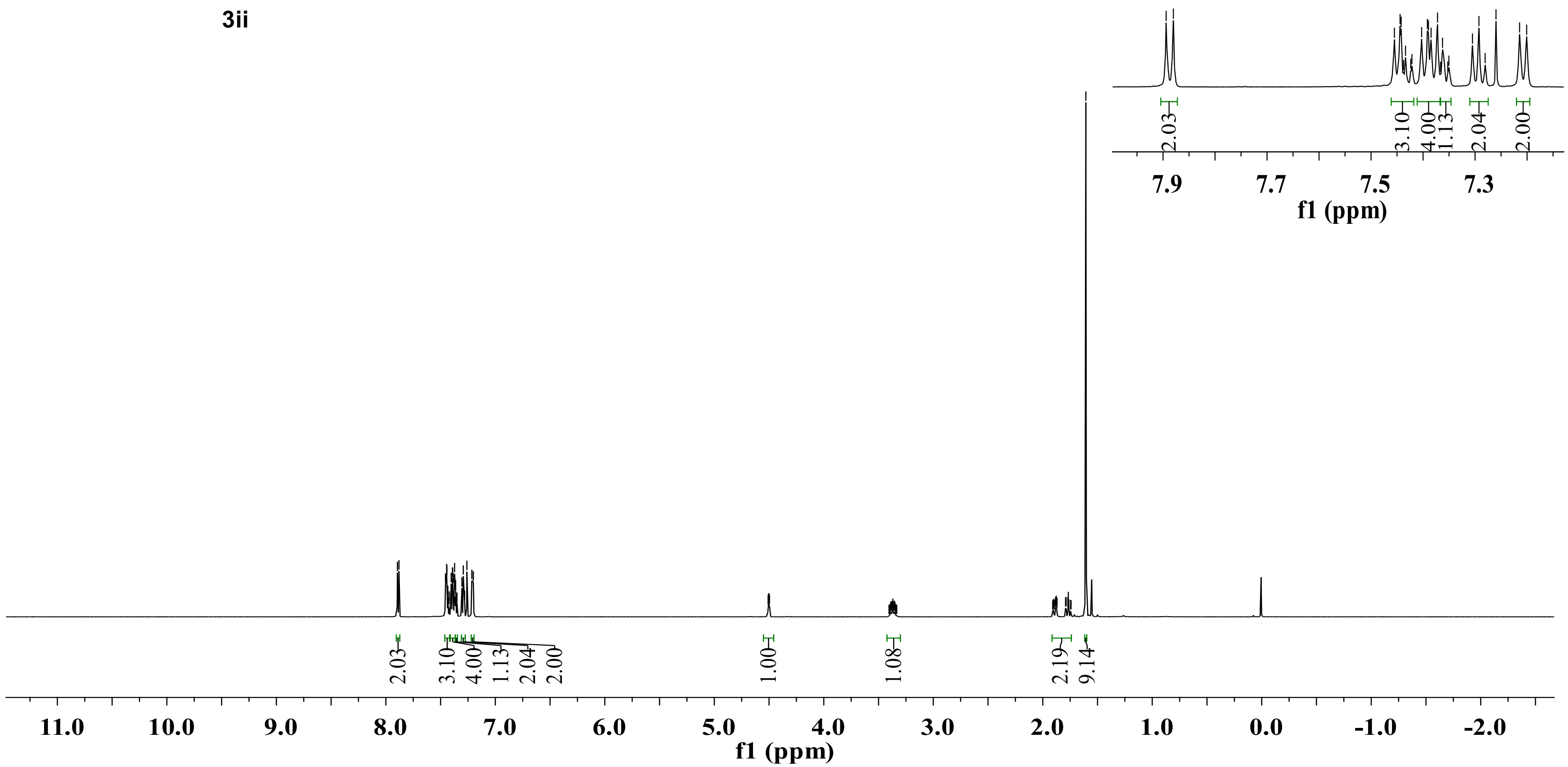


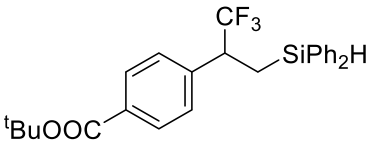
Supplementary Fig. 67. ^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



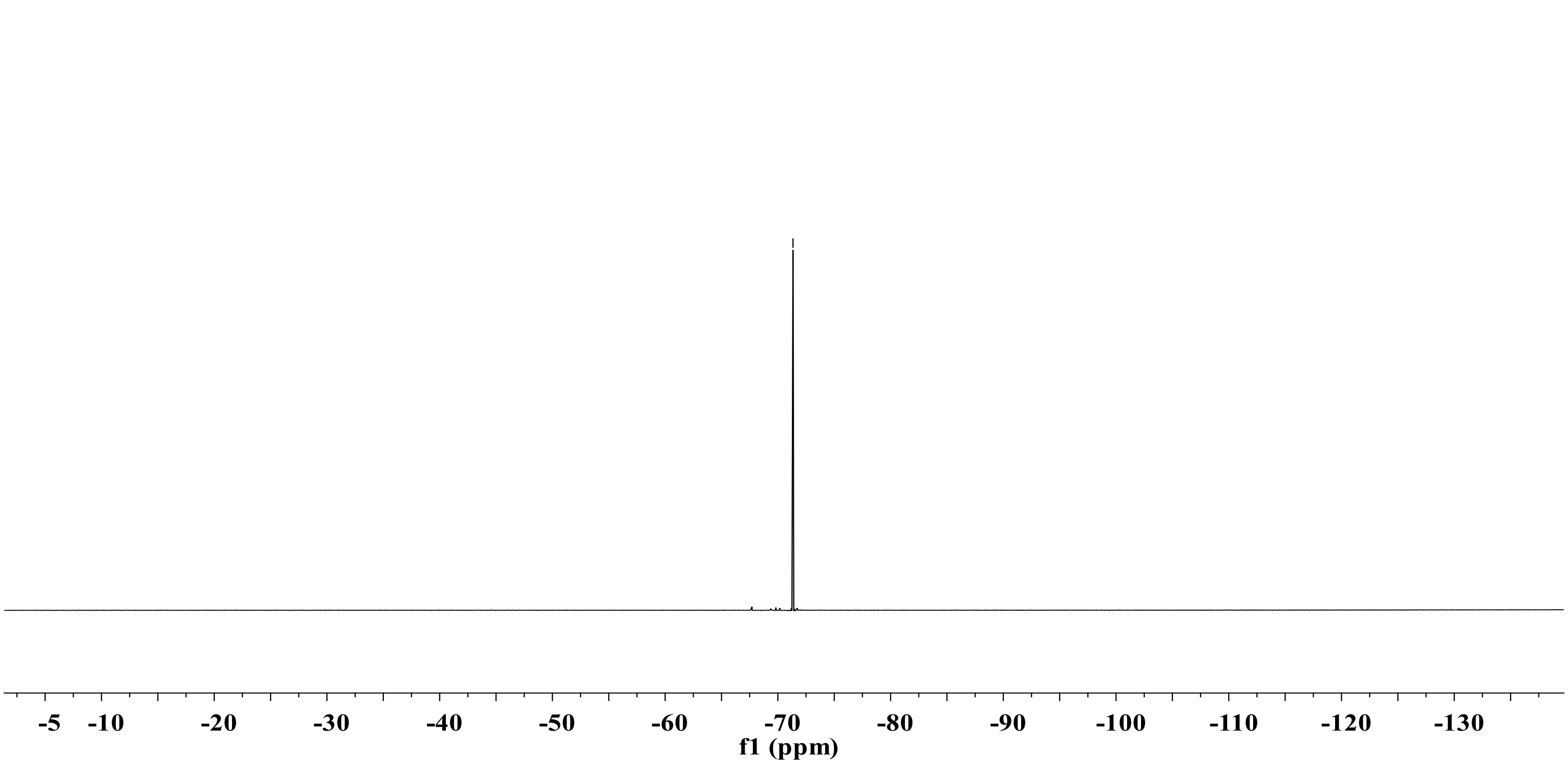
3ii



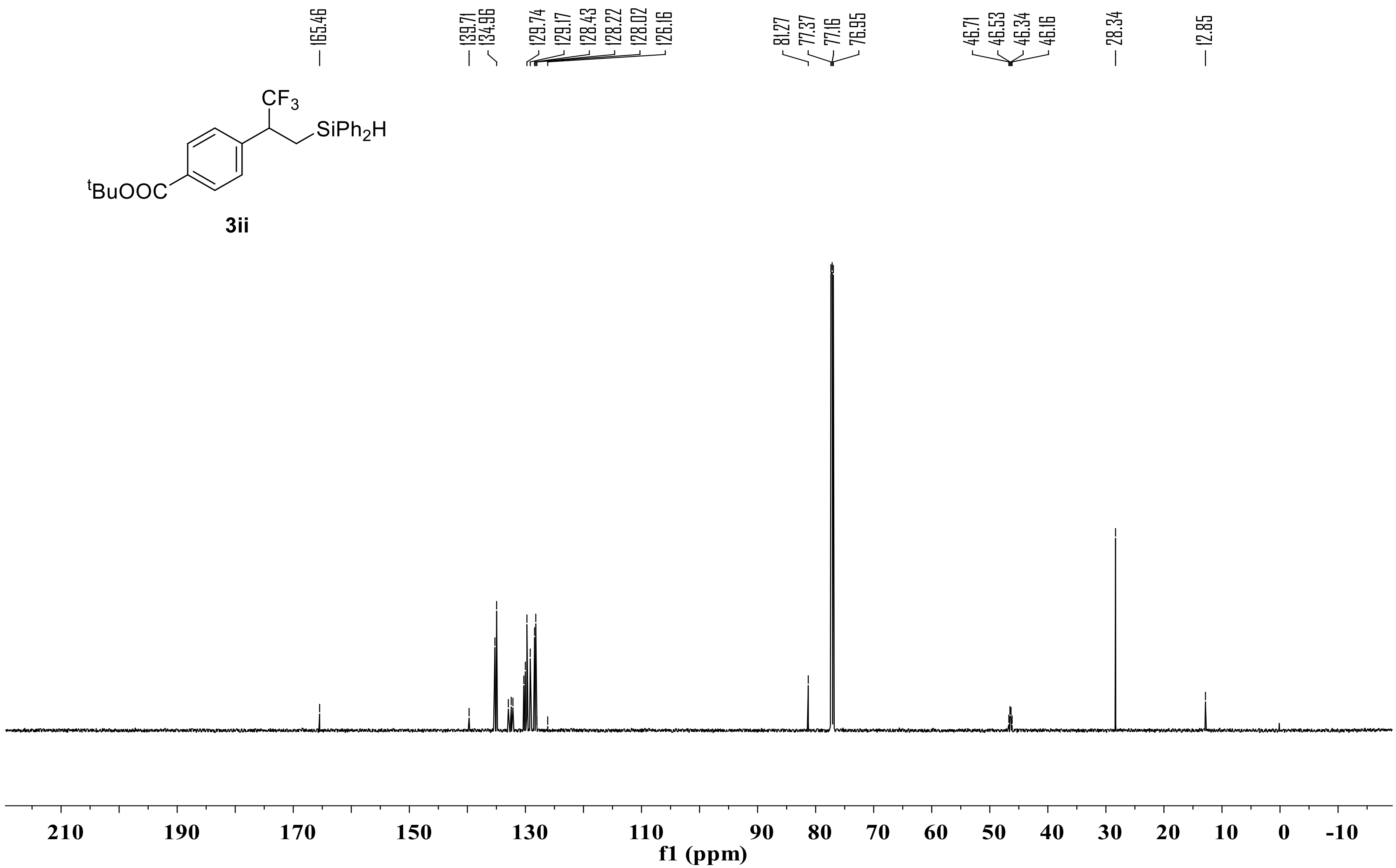
Supplementary Fig. 68. ^{1}H NMR (600 MHz, $CDCl_3$) of **3ii**



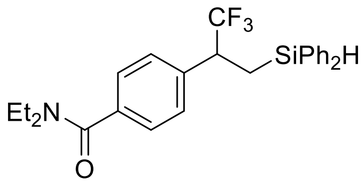
3ii



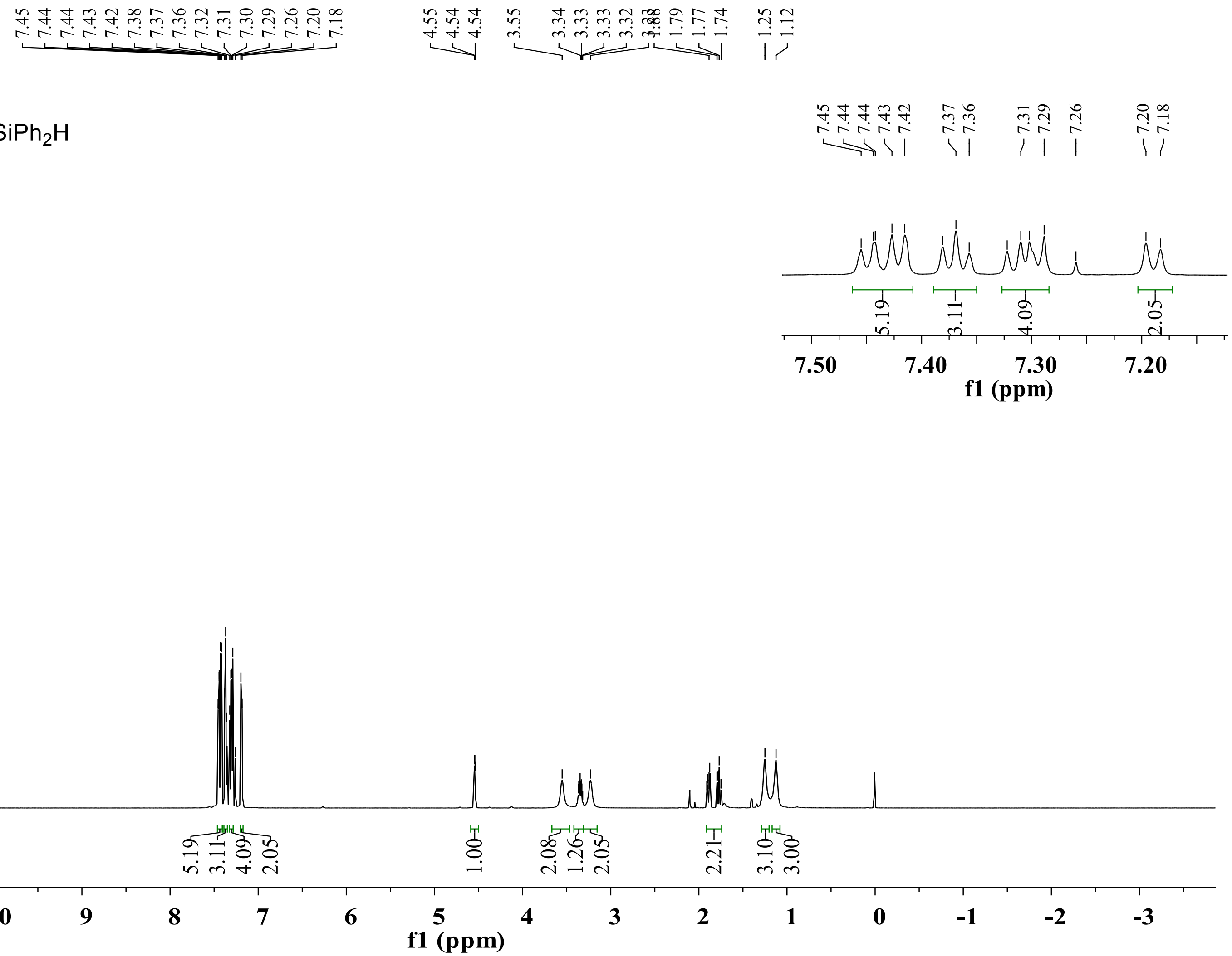
Supplementary Fig. 69. ^{19}F NMR (565 MHz, $CDCl_3$) of **3ii**



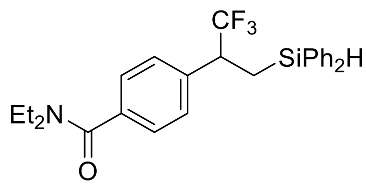
Supplementary Fig. 70. ^{13}C NMR (151 MHz, $CDCl_3$) of **3ii**

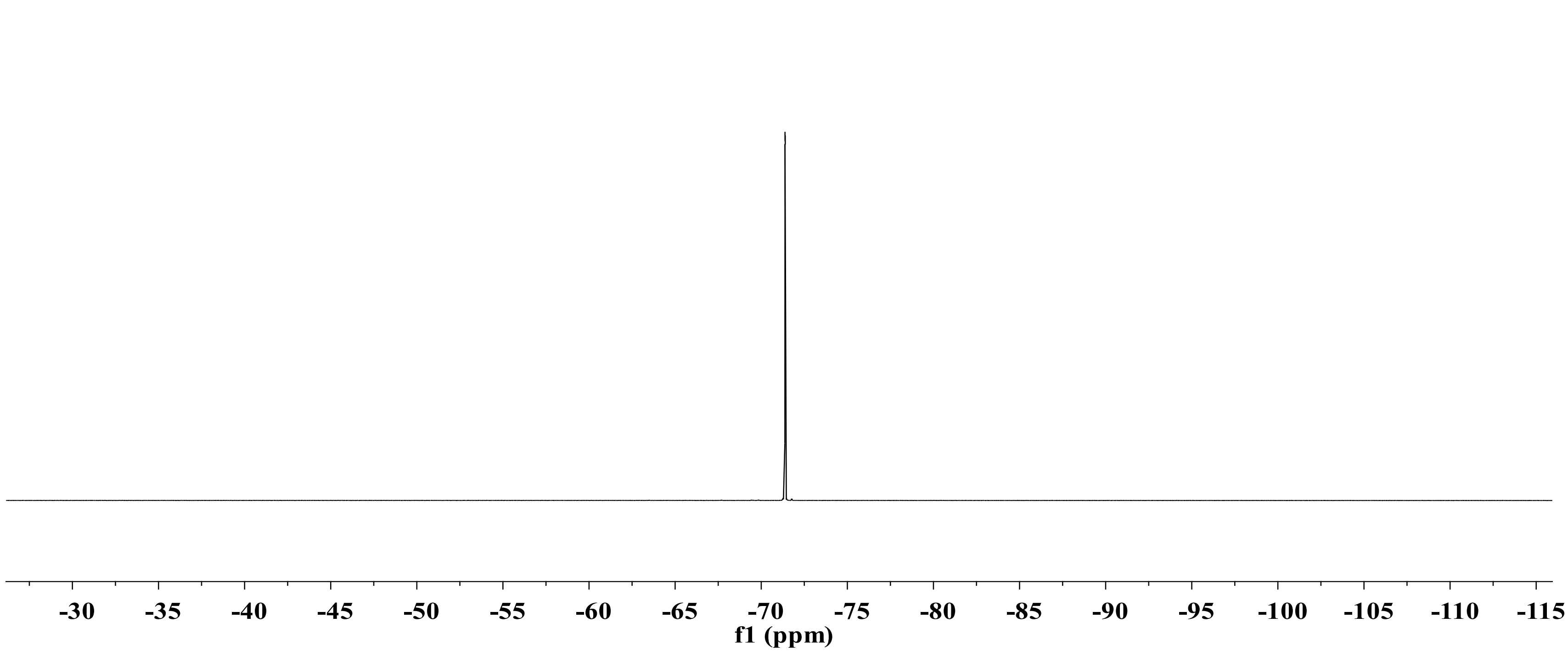


3j

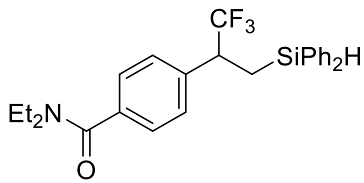


Supplementary Fig. 71. ^{1}H NMR (600 MHz, $CDCl_3$) of **3j**

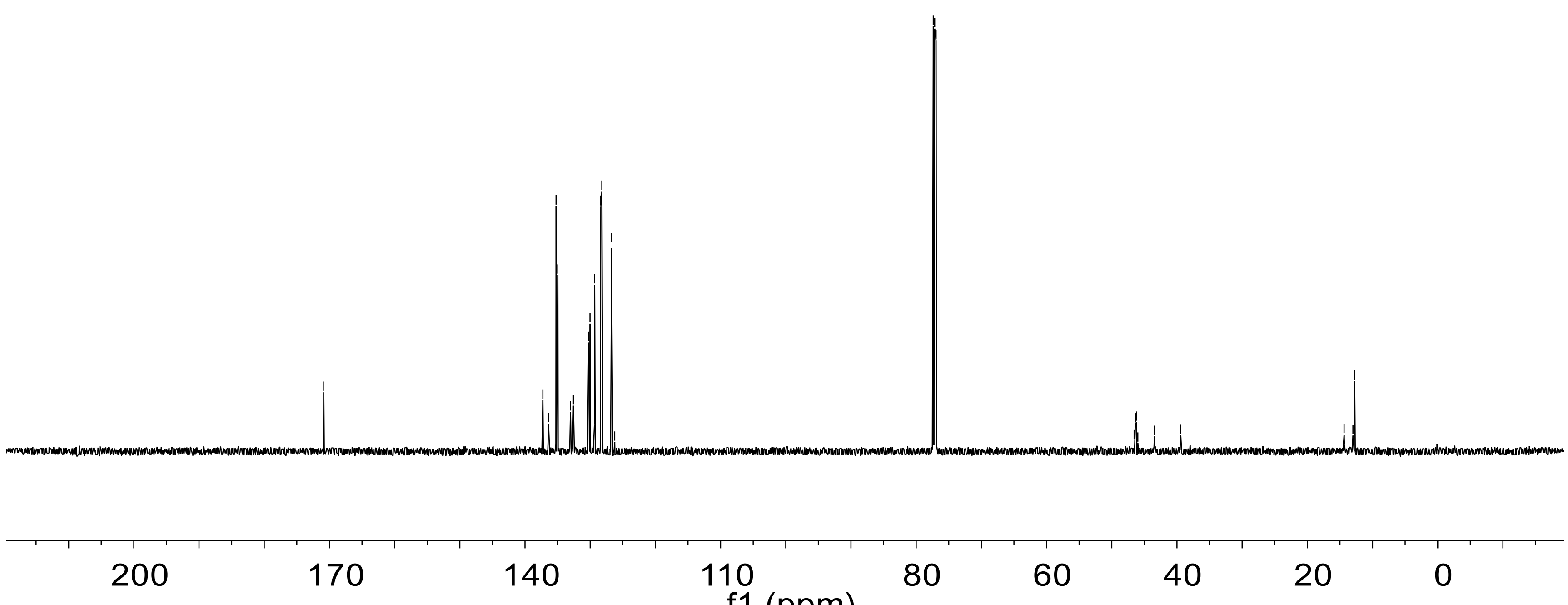




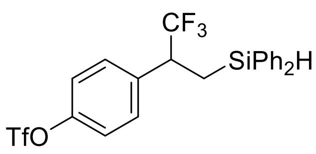
Supplementary Fig. 72. ^{19}F NMR (565 MHz, $CDCl_3$) of **3j**



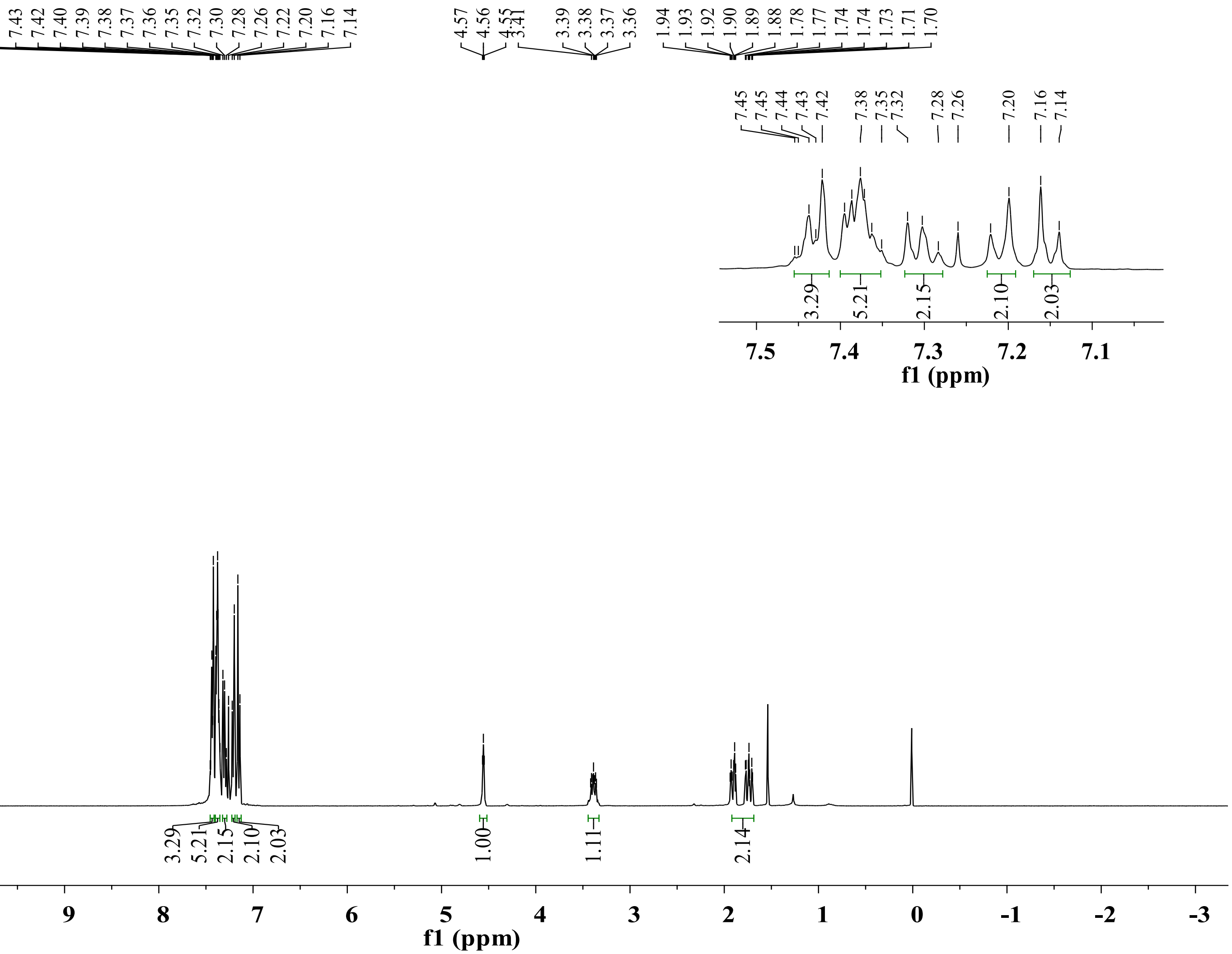
3j



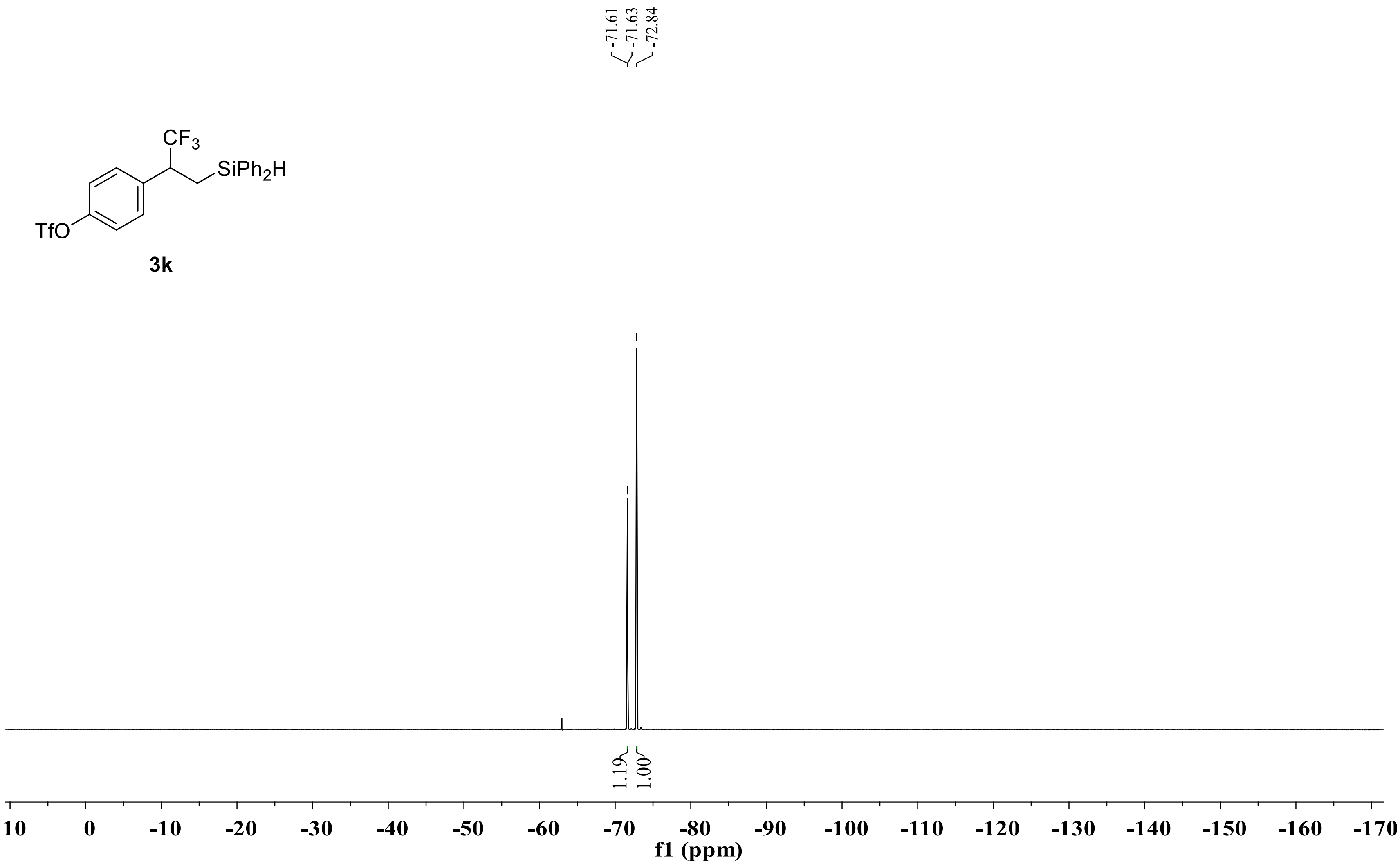
Supplementary Fig. 73. ^{13}C NMR (151 MHz, $CDCl_3$) of **3j**



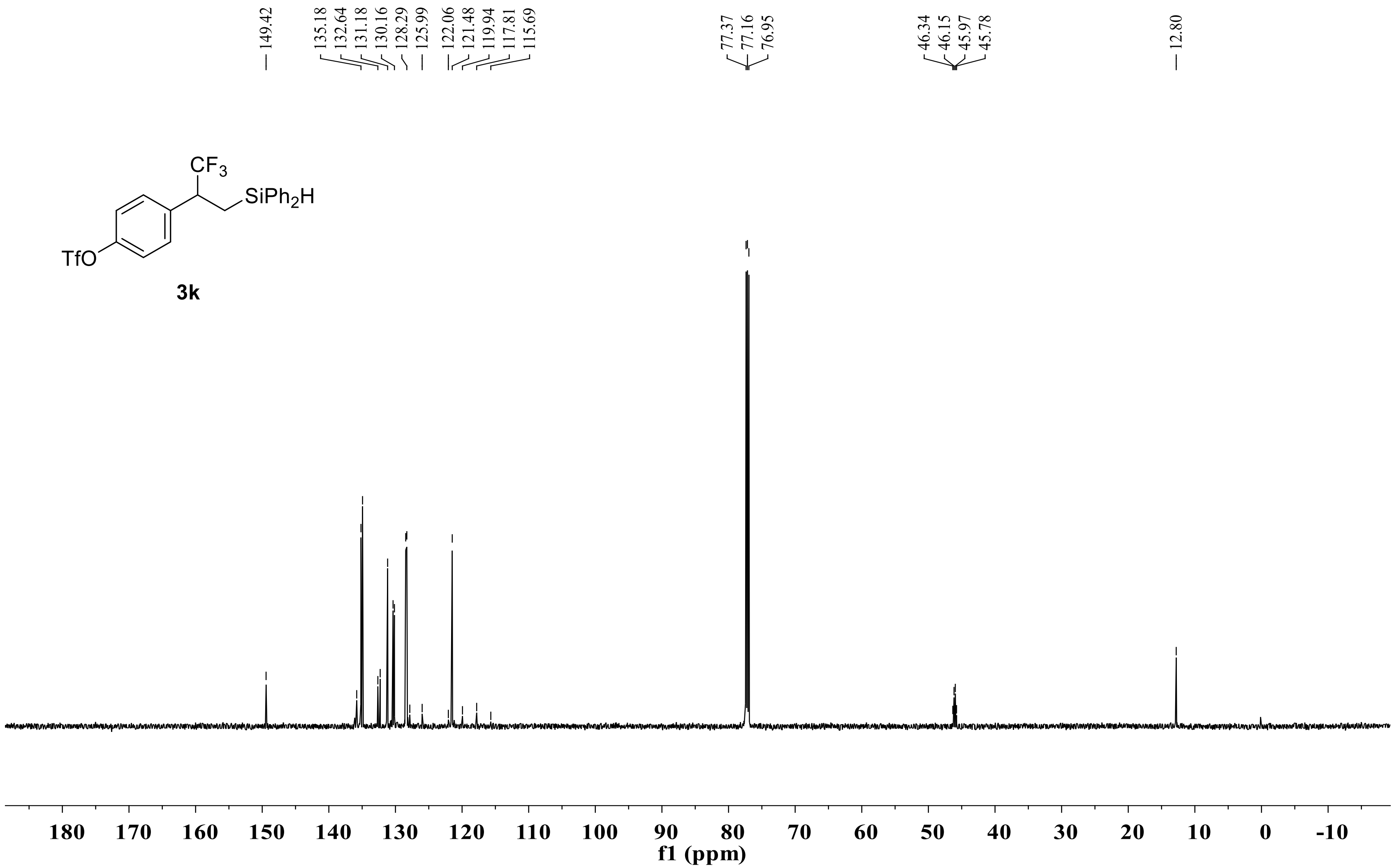
3k



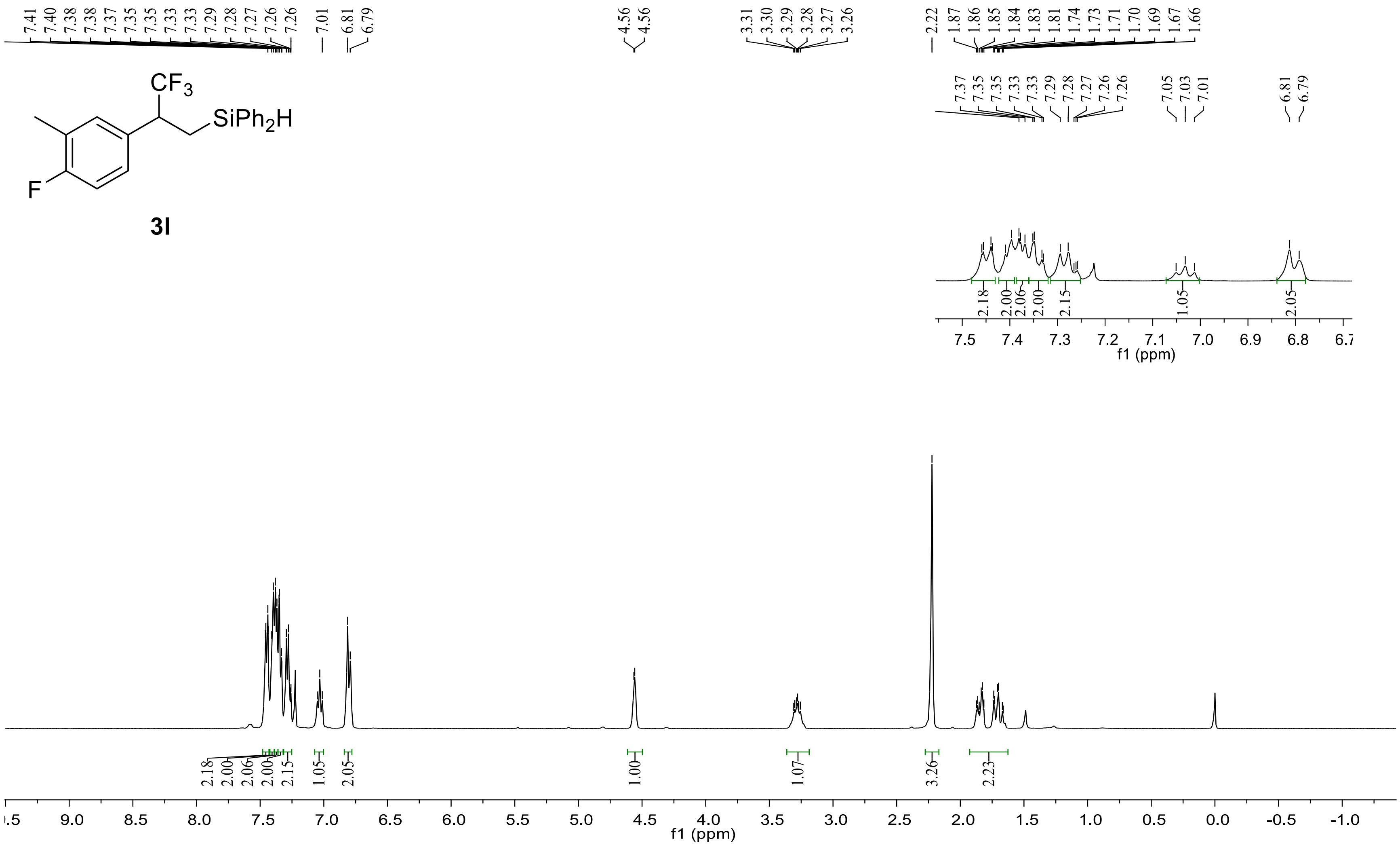
Supplementary Fig. 74. ^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



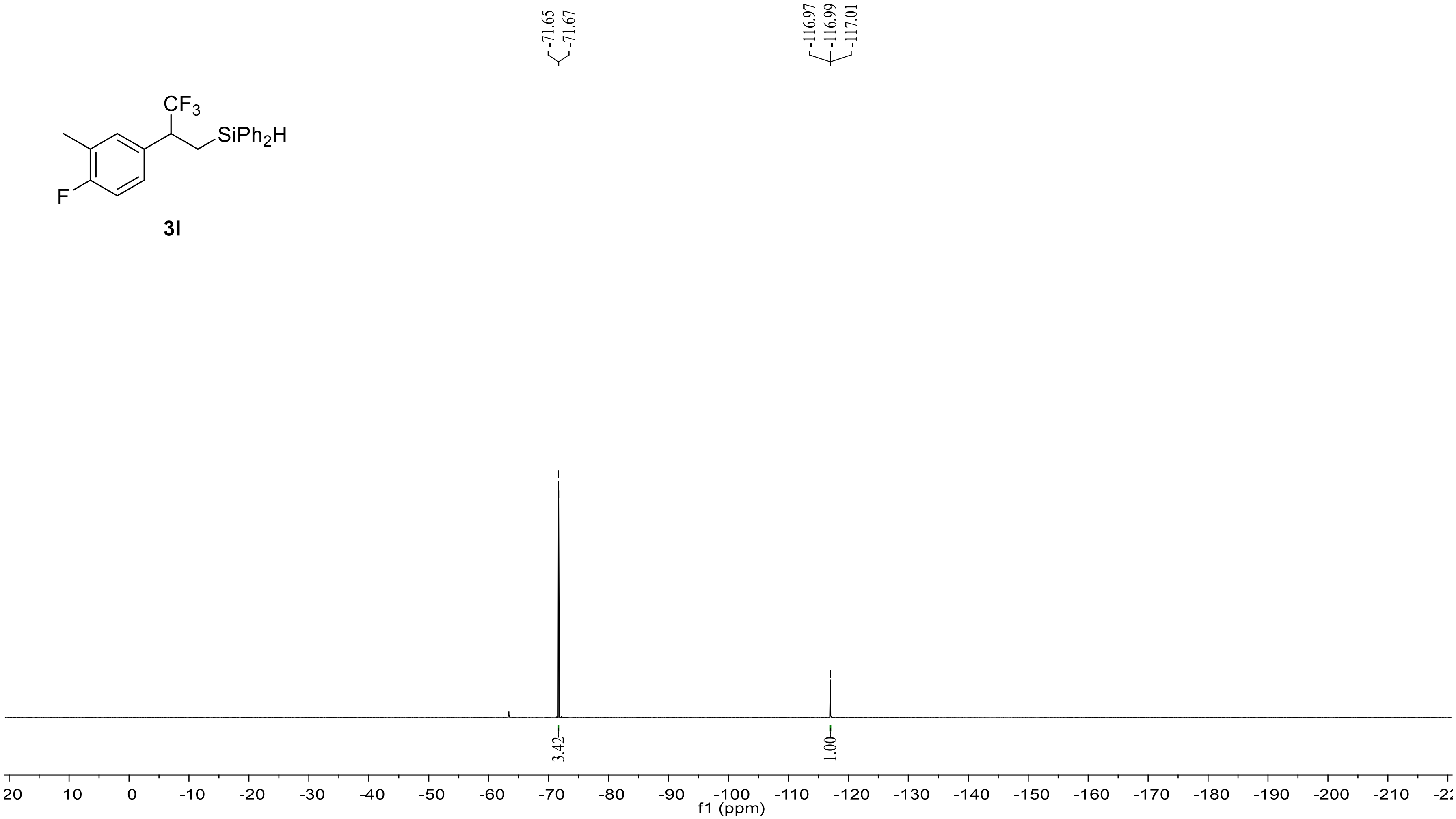
Supplementary Fig. 75. ^{19}F NMR (376 MHz, $CDCl_3$) of **3k**



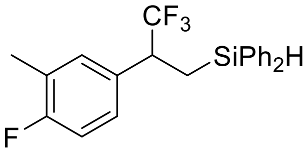
Supplementary Fig. 76. ^{13}C NMR (151 MHz, $CDCl_3$) of **3k**



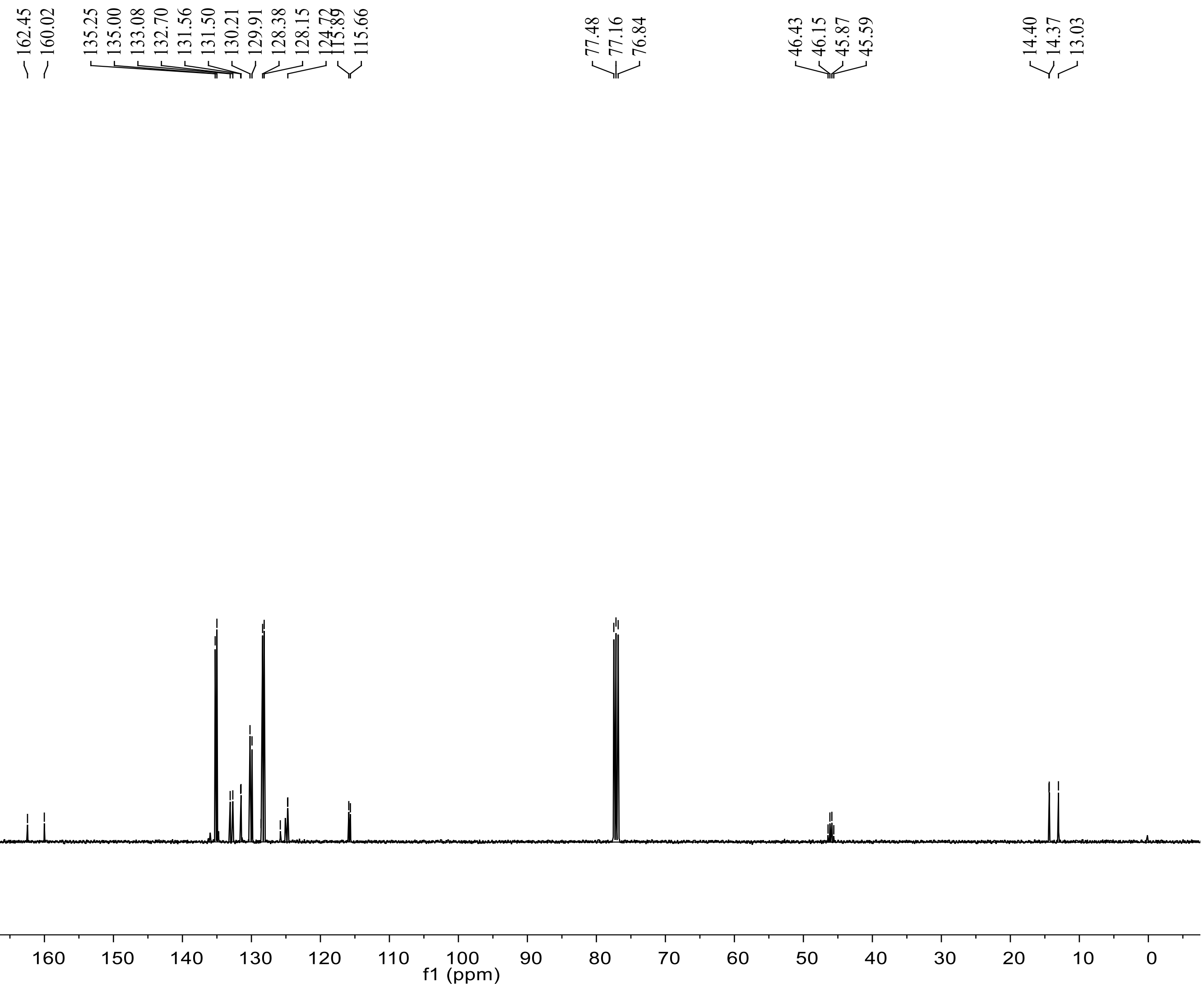
Supplementary Fig. 77. ^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



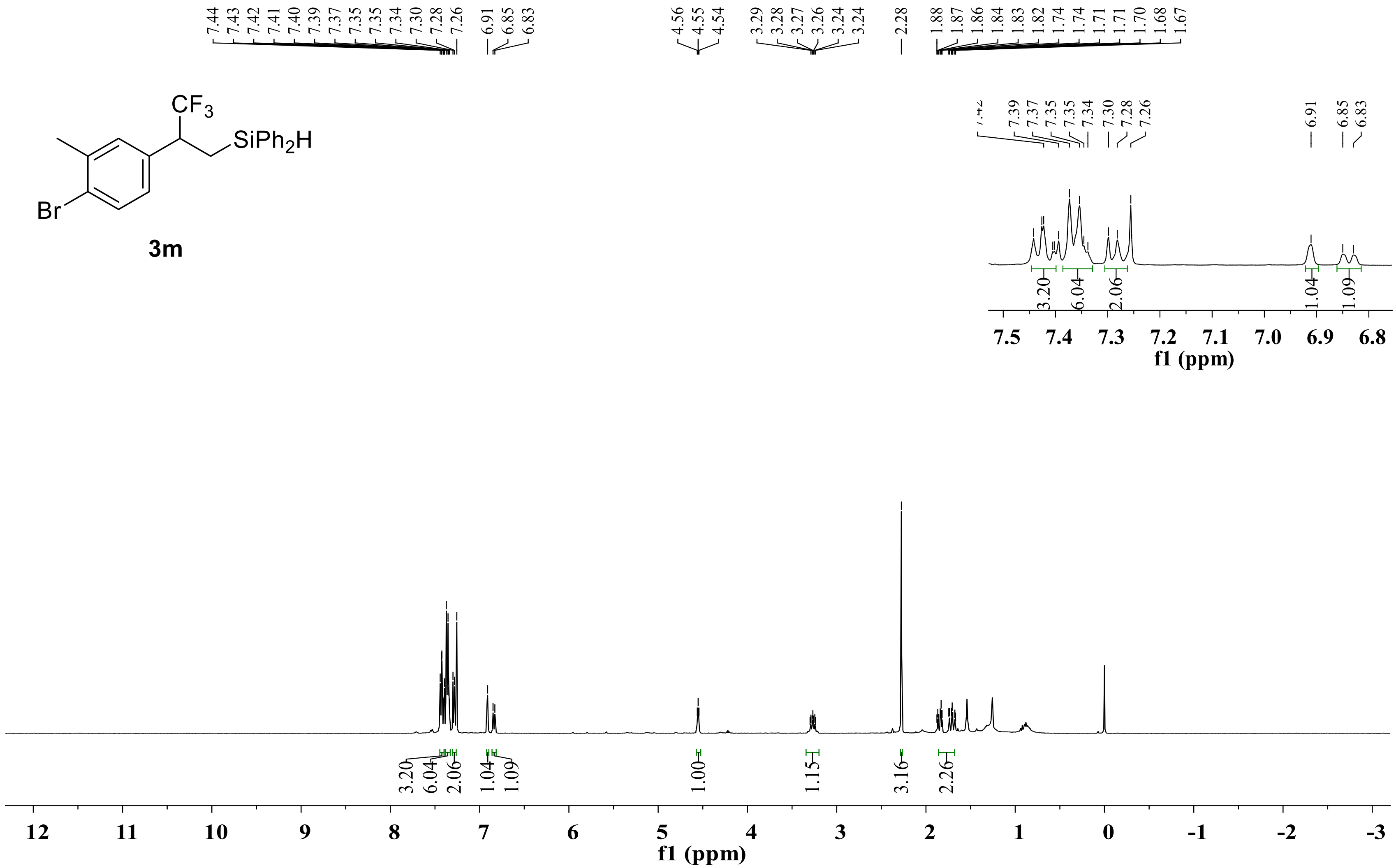
Supplementary Fig. 78. ^{19}F NMR (377 MHz, $CDCl_3$) of **3l**



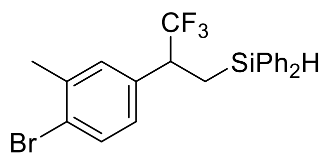
3l



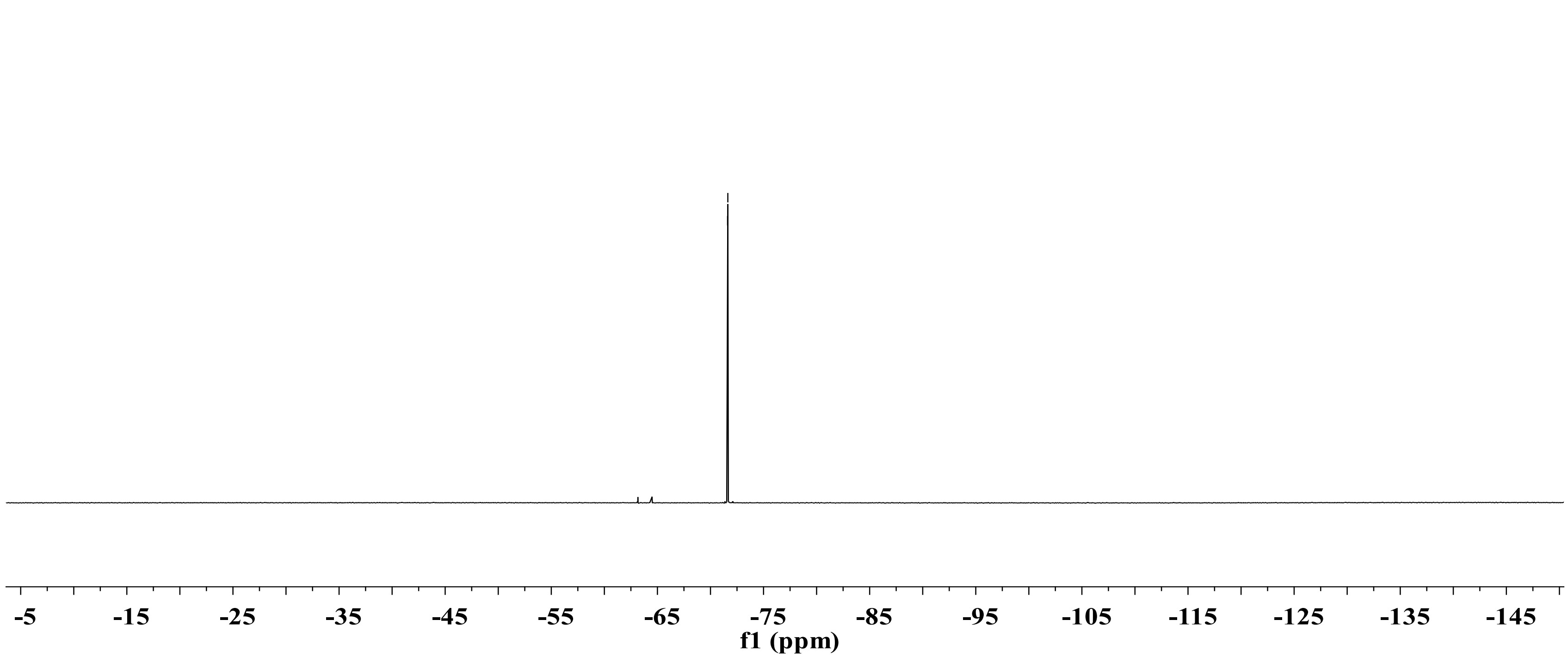
Supplementary Fig. 79. ^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



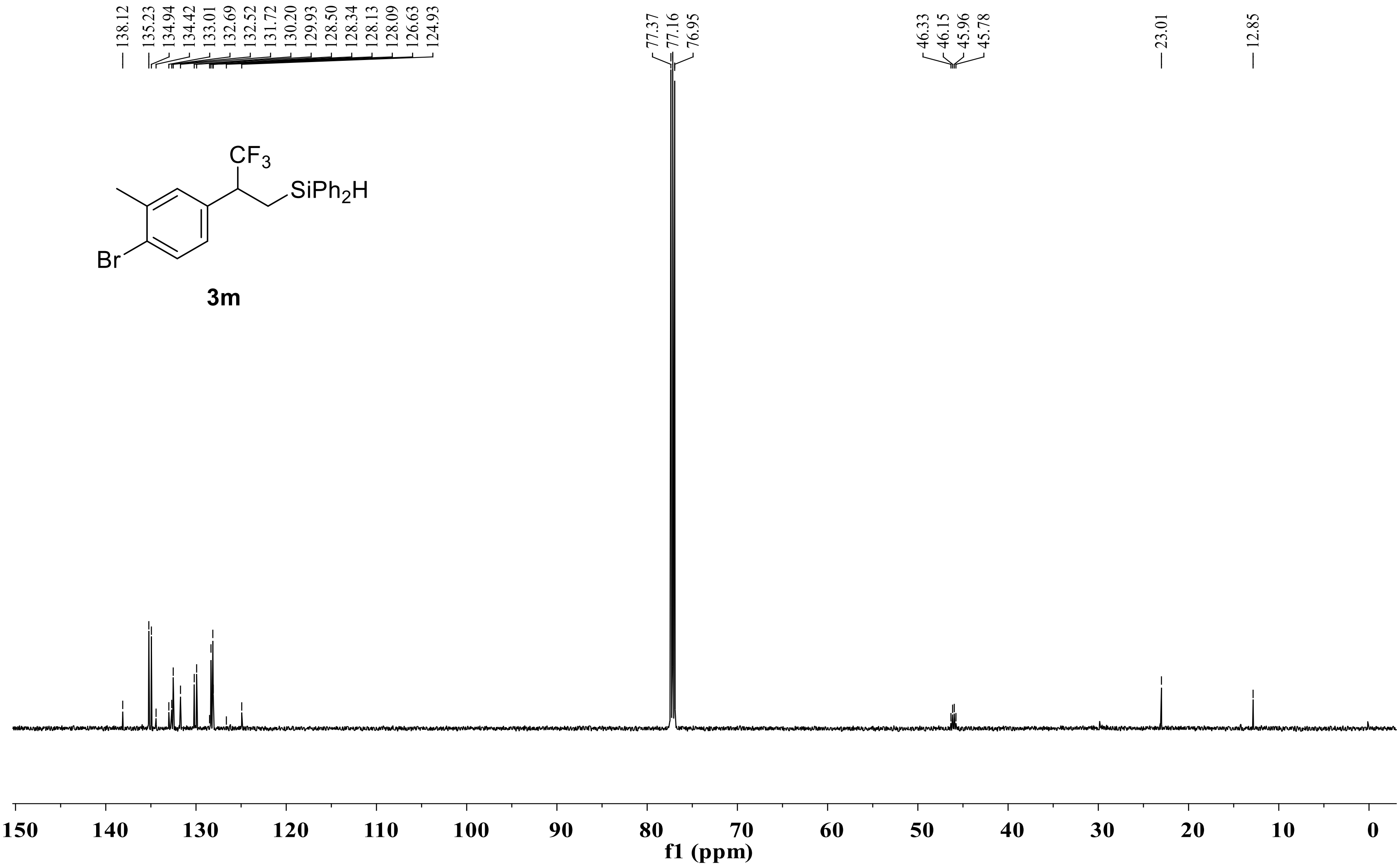
Supplementary Fig. 80. ^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



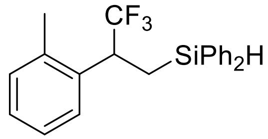
3m



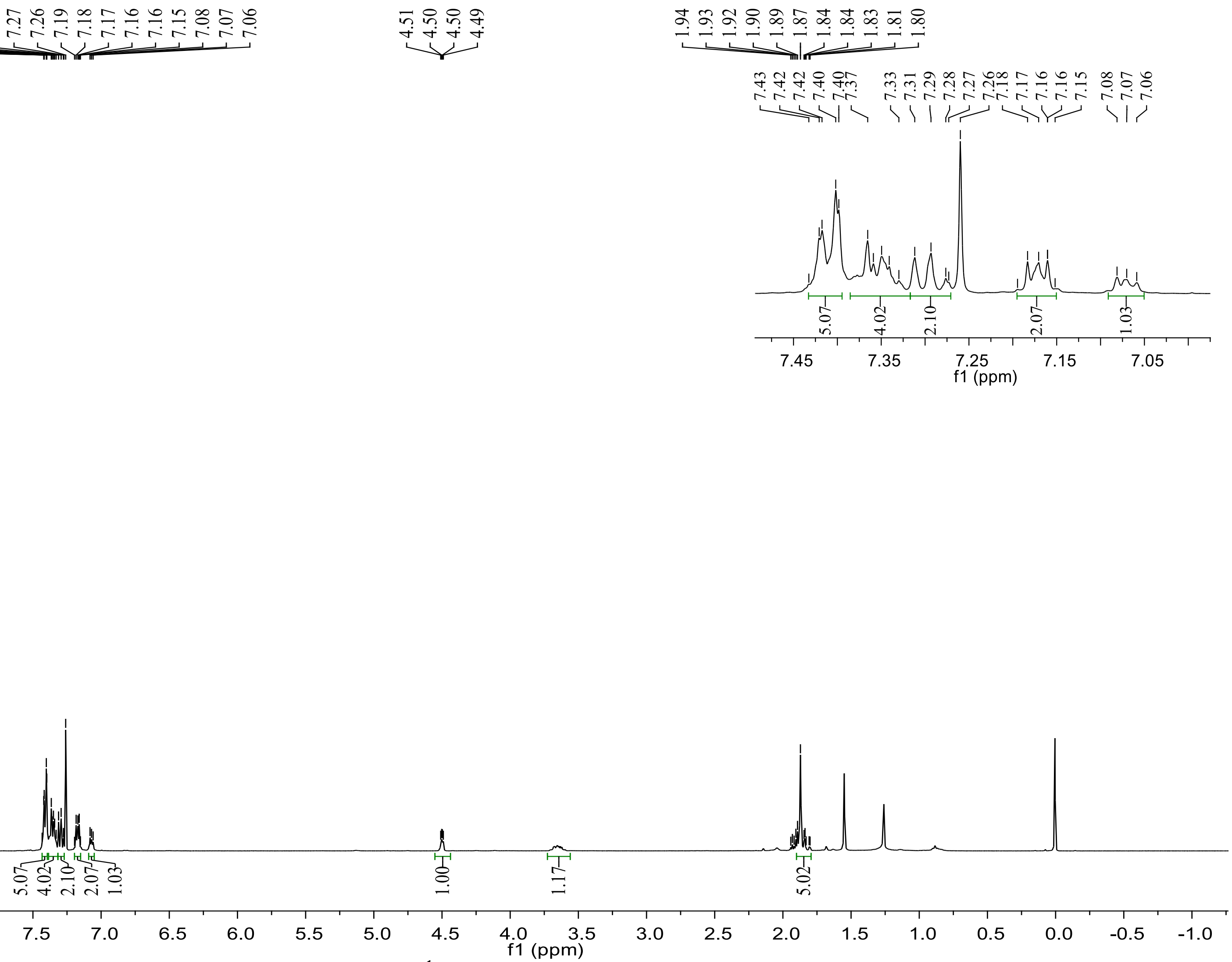
Supplementary Fig. 81. ^{19}F NMR (376 MHz, $CDCl_3$) of **3m**



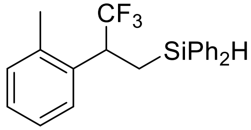
Supplementary Fig. 82. ^{13}C NMR (151 MHz, $CDCl_3$) of **3m**



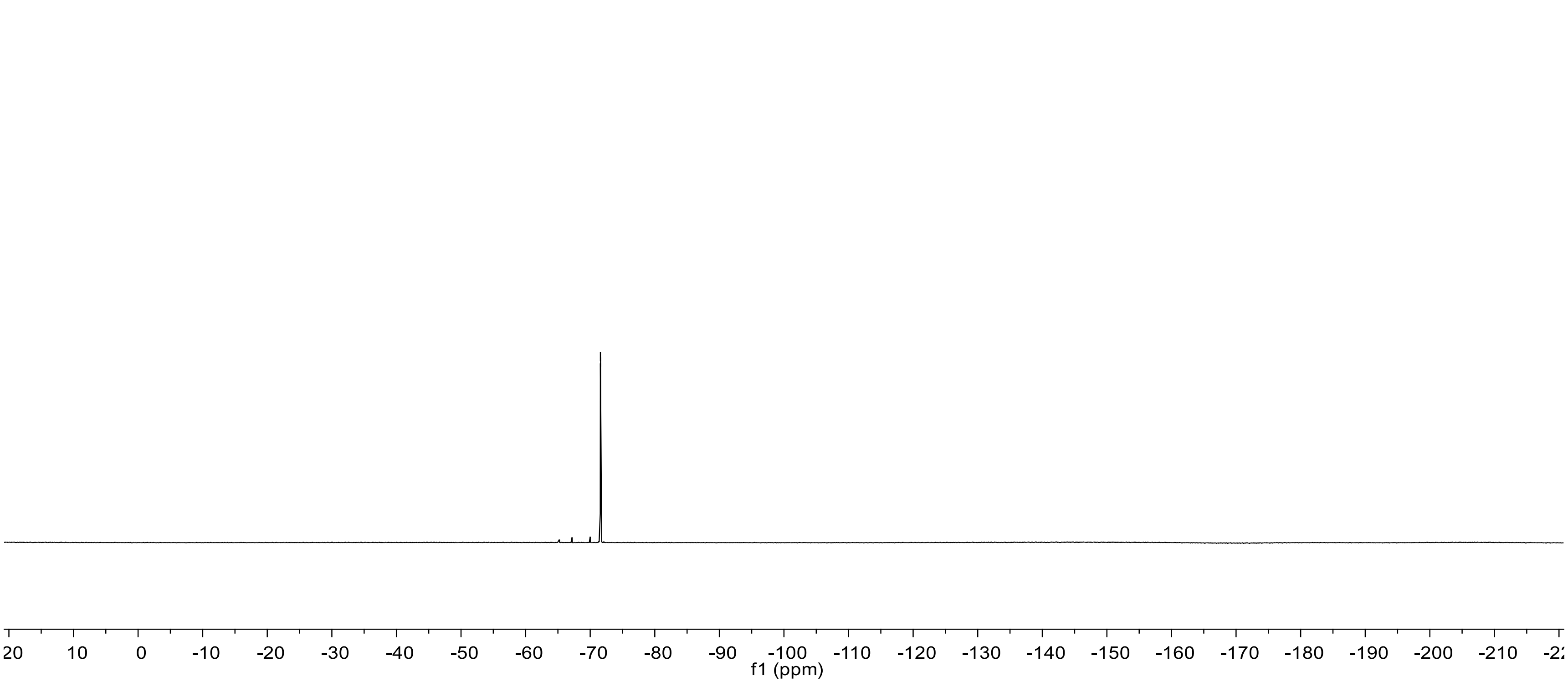
3n



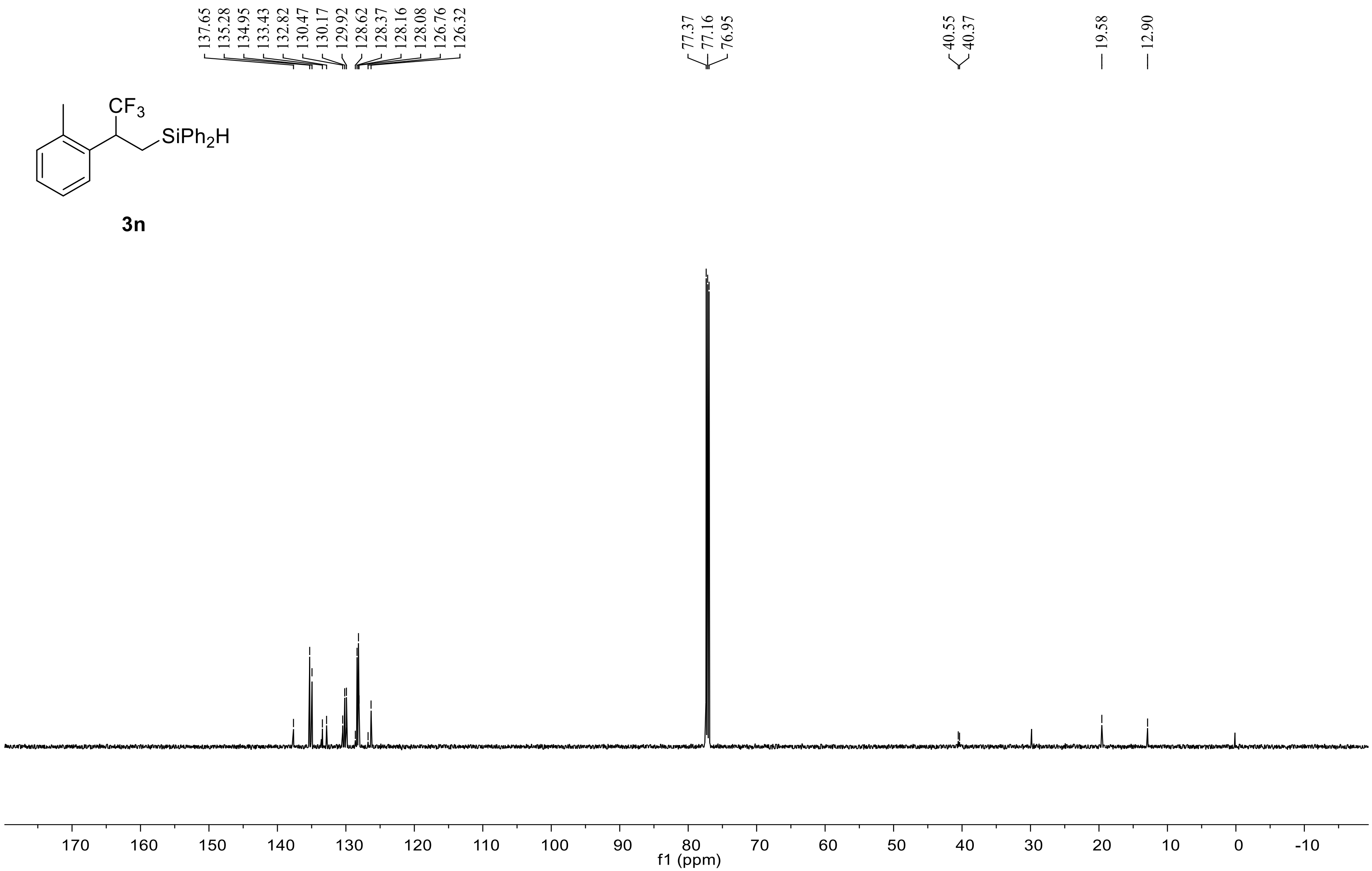
Supplementary Fig. 83. ^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



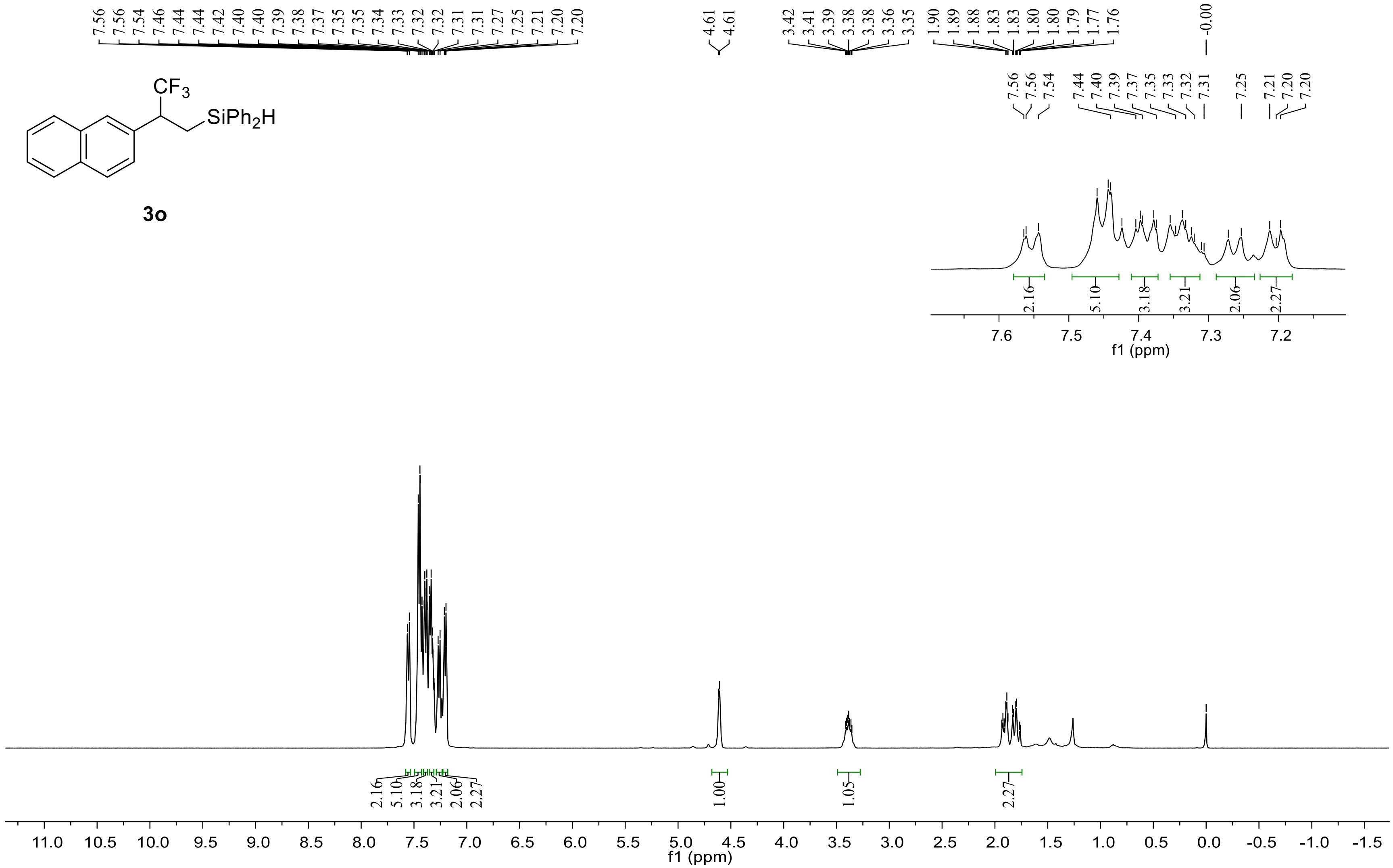
3n



Supplementary Fig. 84. ^{19}F NMR (376 MHz, $CDCl_3$) of **3n**

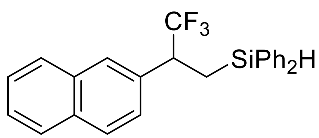


Supplementary Fig. 85. ^{13}C NMR (151 MHz, $CDCl_3$) of **3n**

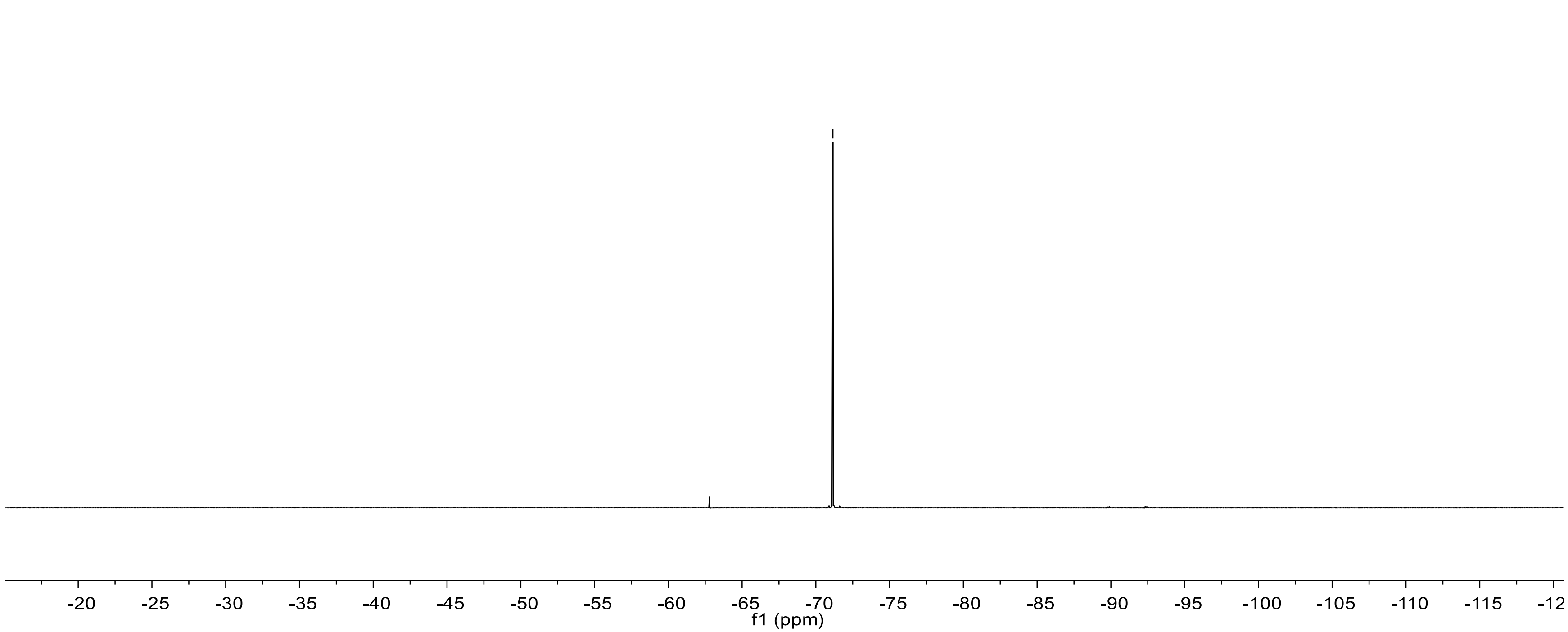


3o

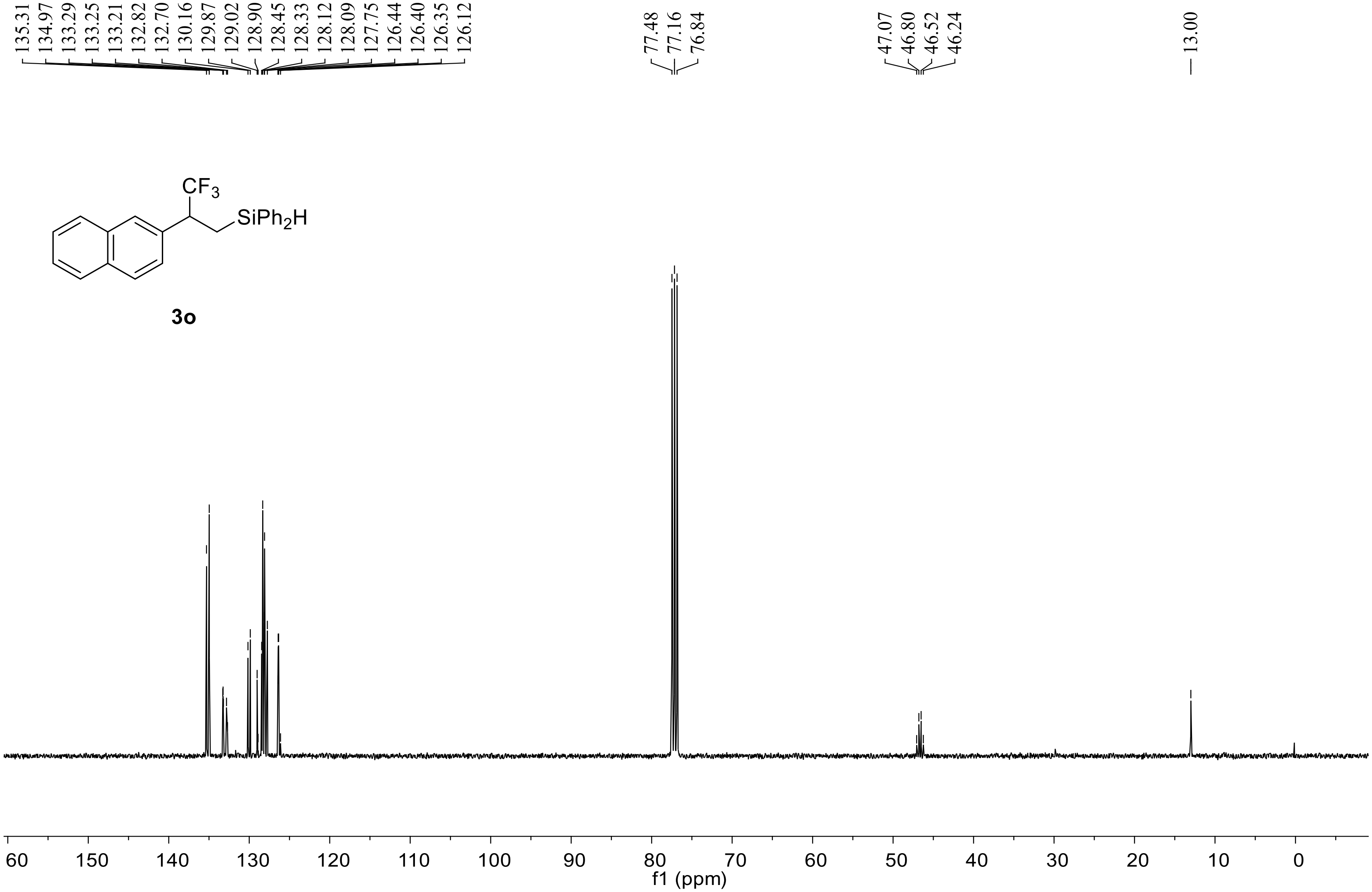
Supplementary Fig. 86. ^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



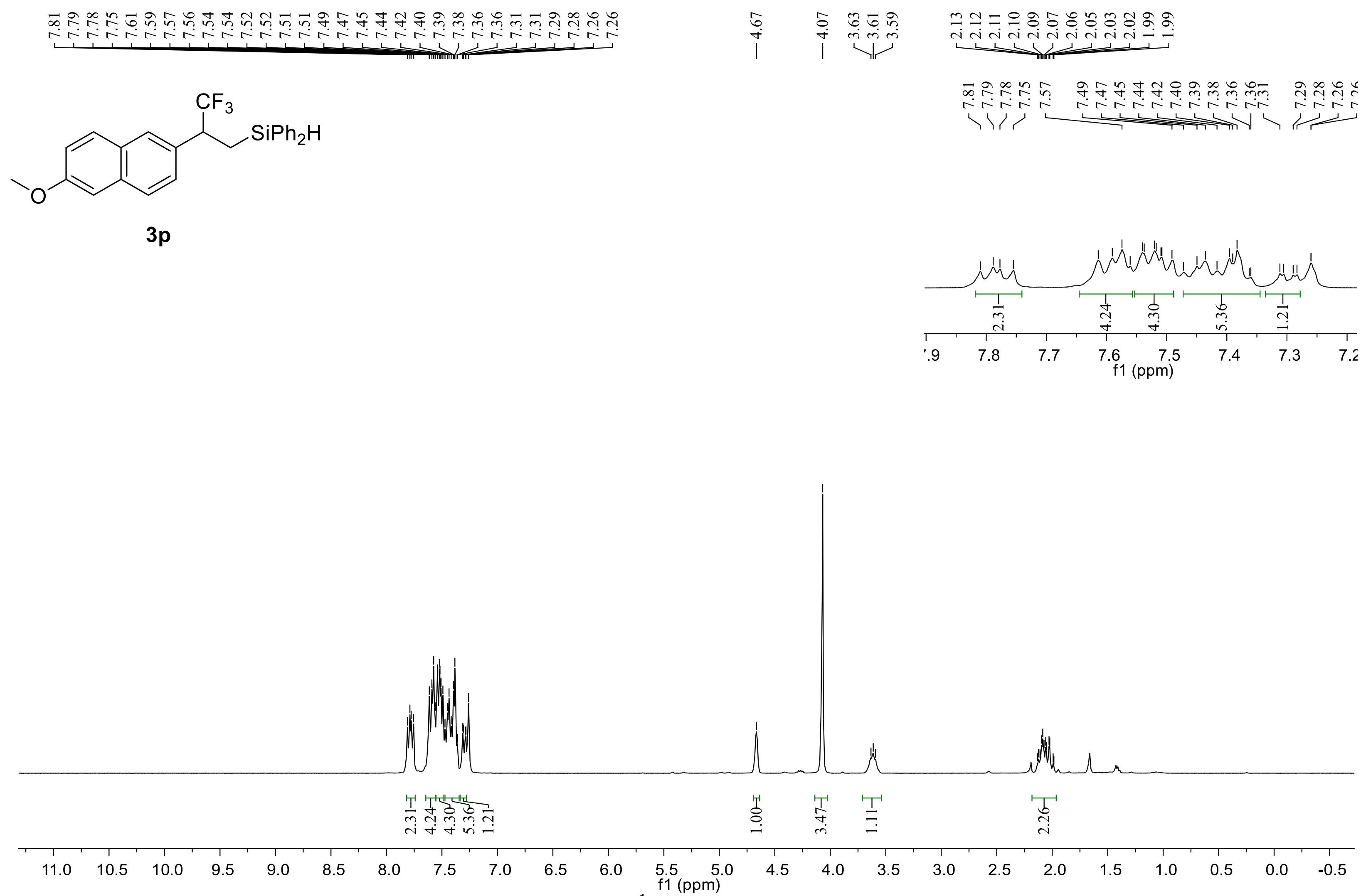
3o



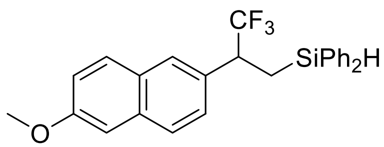
Supplementary Fig. 87. ^{19}F NMR (377 MHz, $CDCl_3$) of **3o**



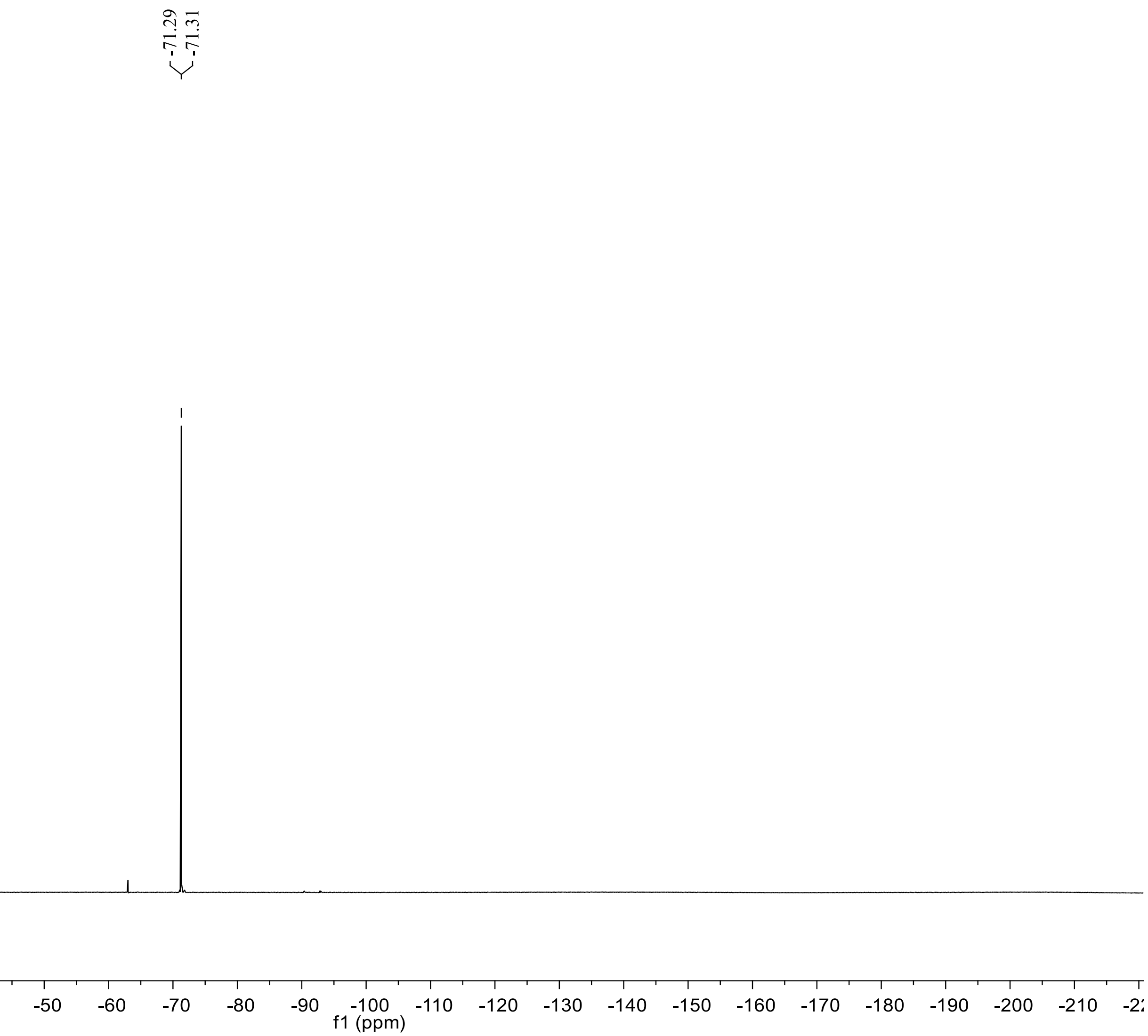
Supplementary Fig. 88. ^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



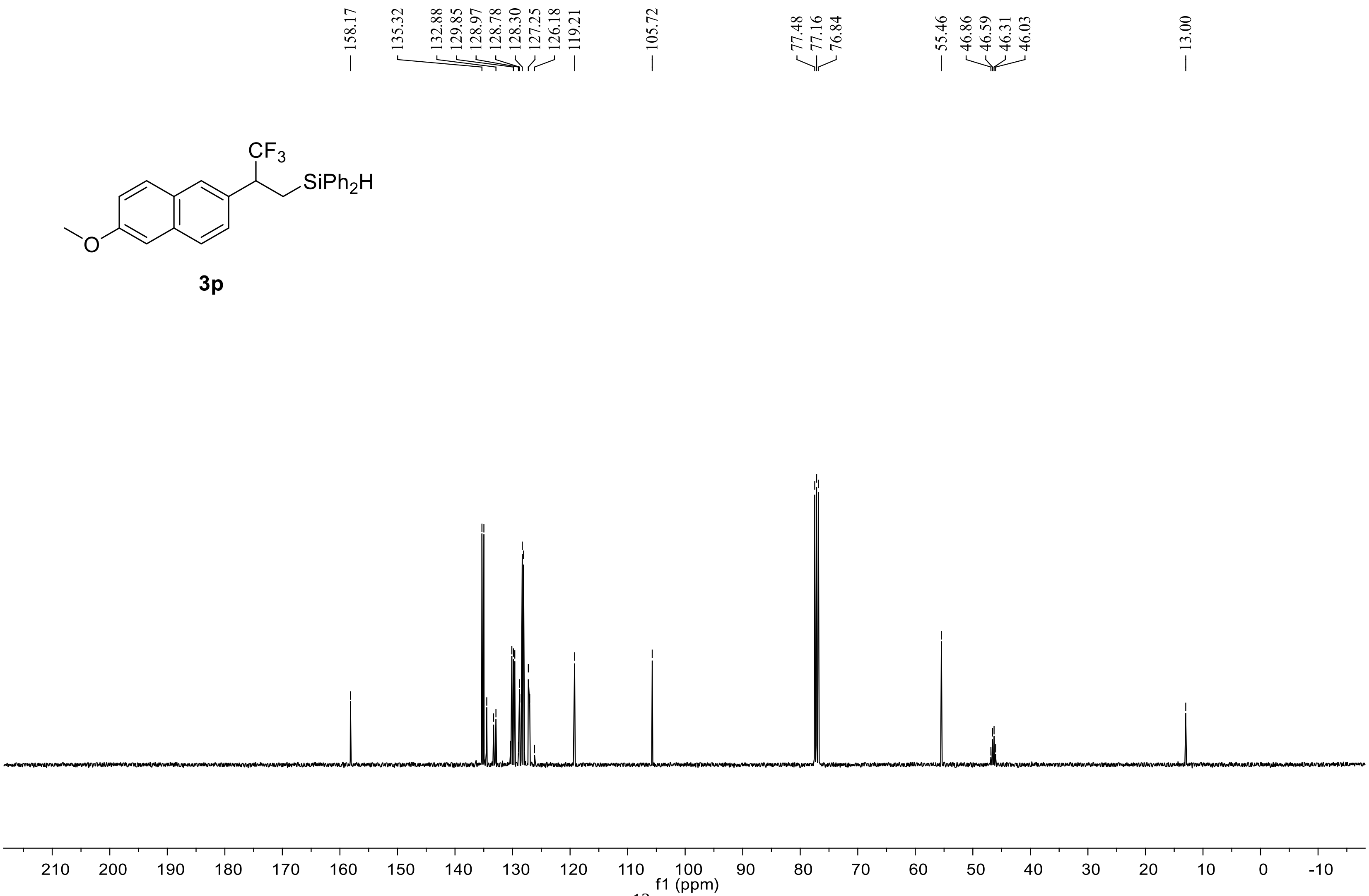
Supplementary Fig. 89. ^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



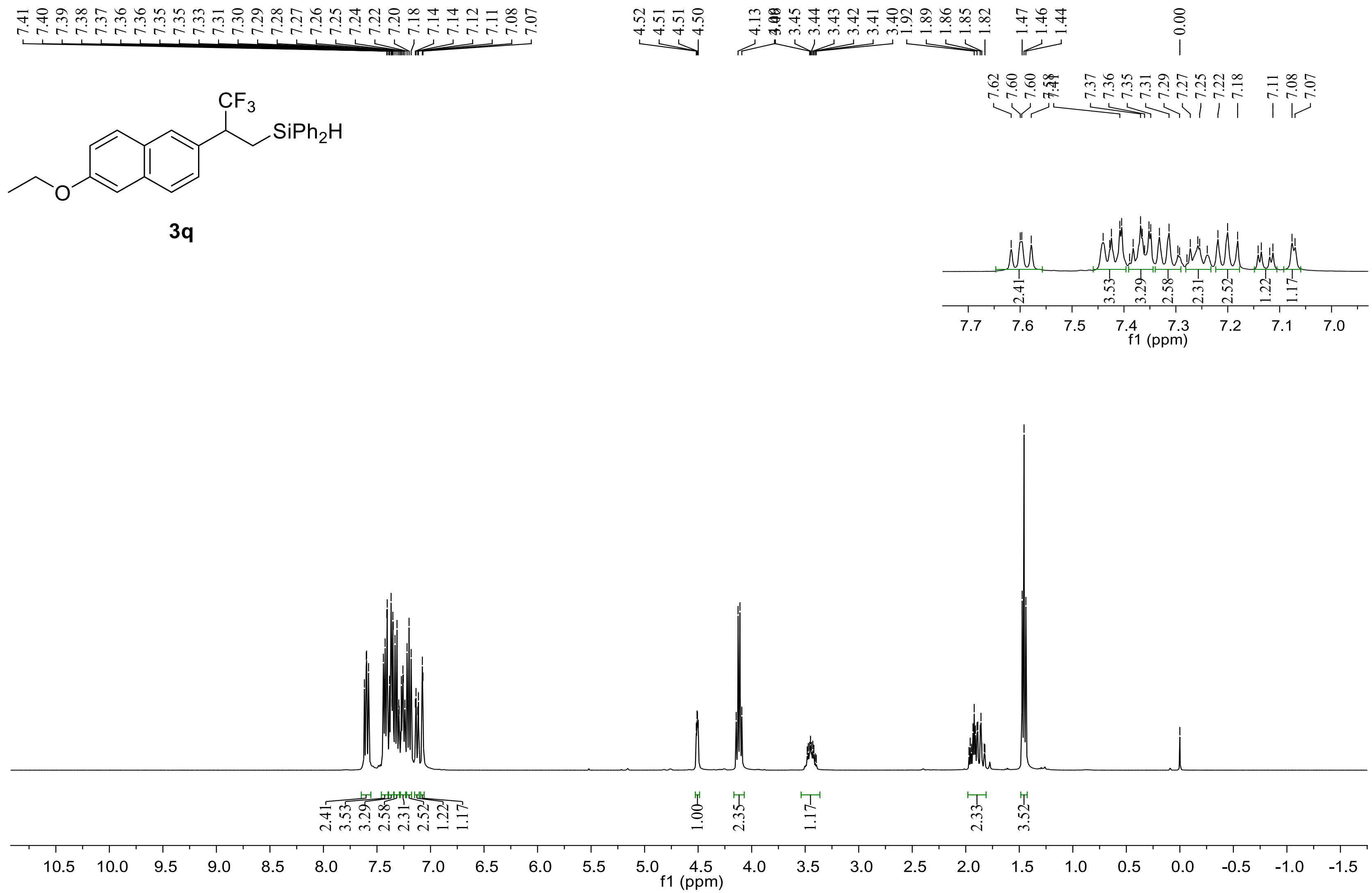
3p



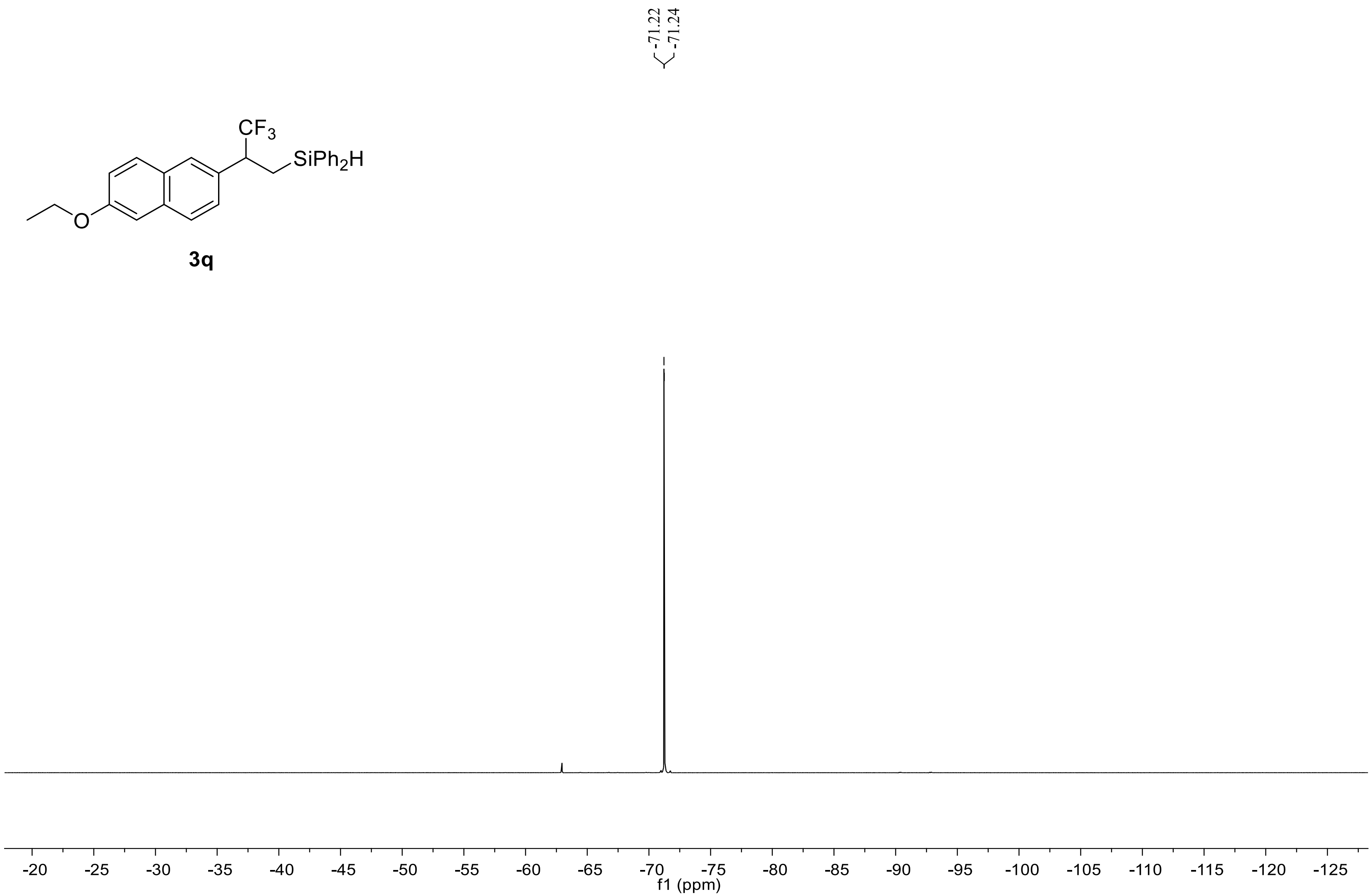
Supplementary Fig. 90. ^{19}F NMR (377 MHz, $CDCl_3$) of **3p**



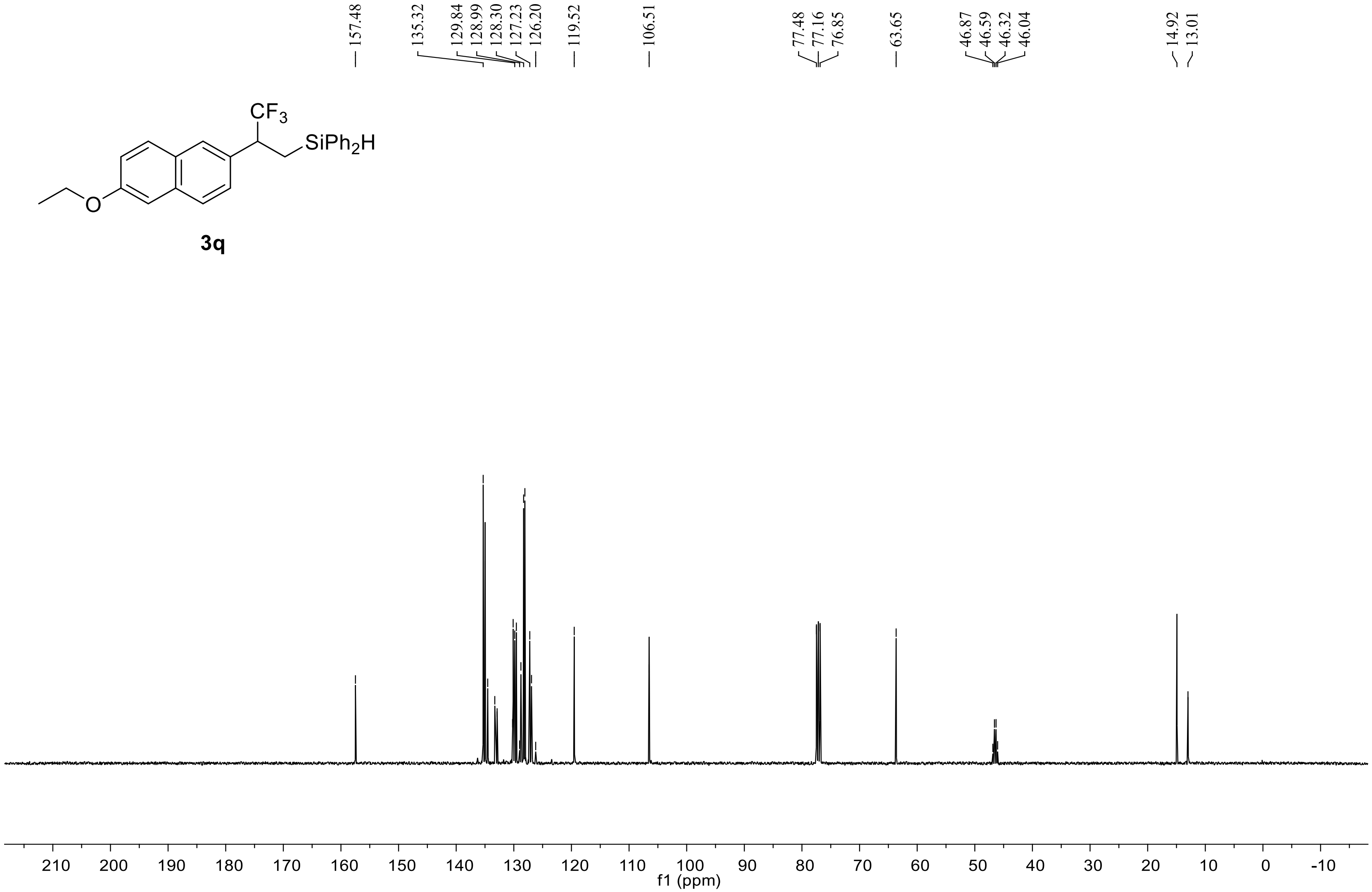
Supplementary Fig. 91. ^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



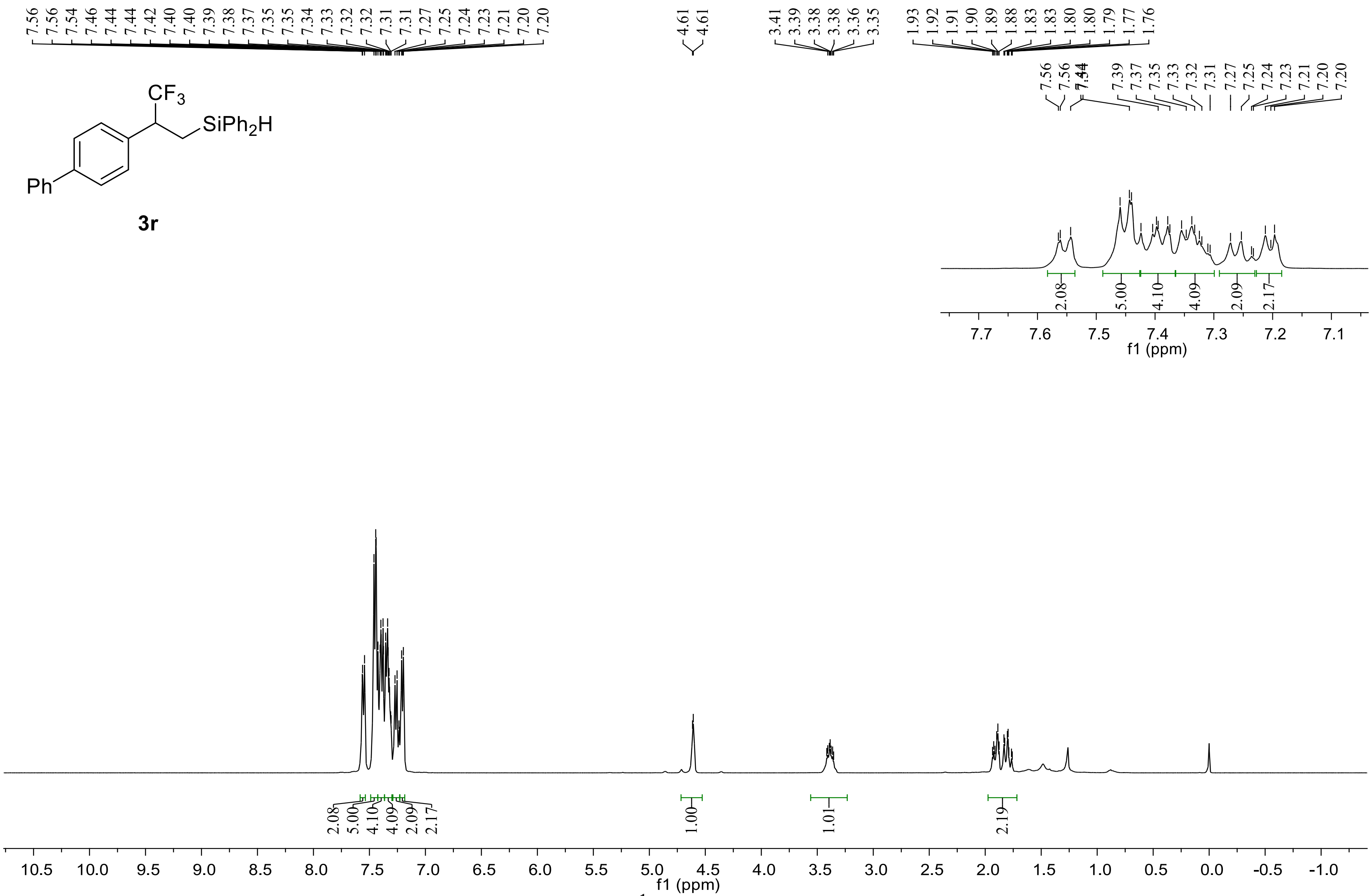
Supplementary Fig. 92. ^{1}H NMR (377 MHz, $CDCl_3$) of **3q**



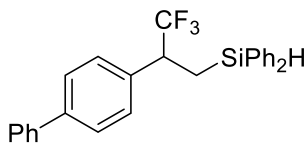
Supplementary Fig. 93. ^{19}F NMR (377 MHz, $CDCl_3$) of **3q**



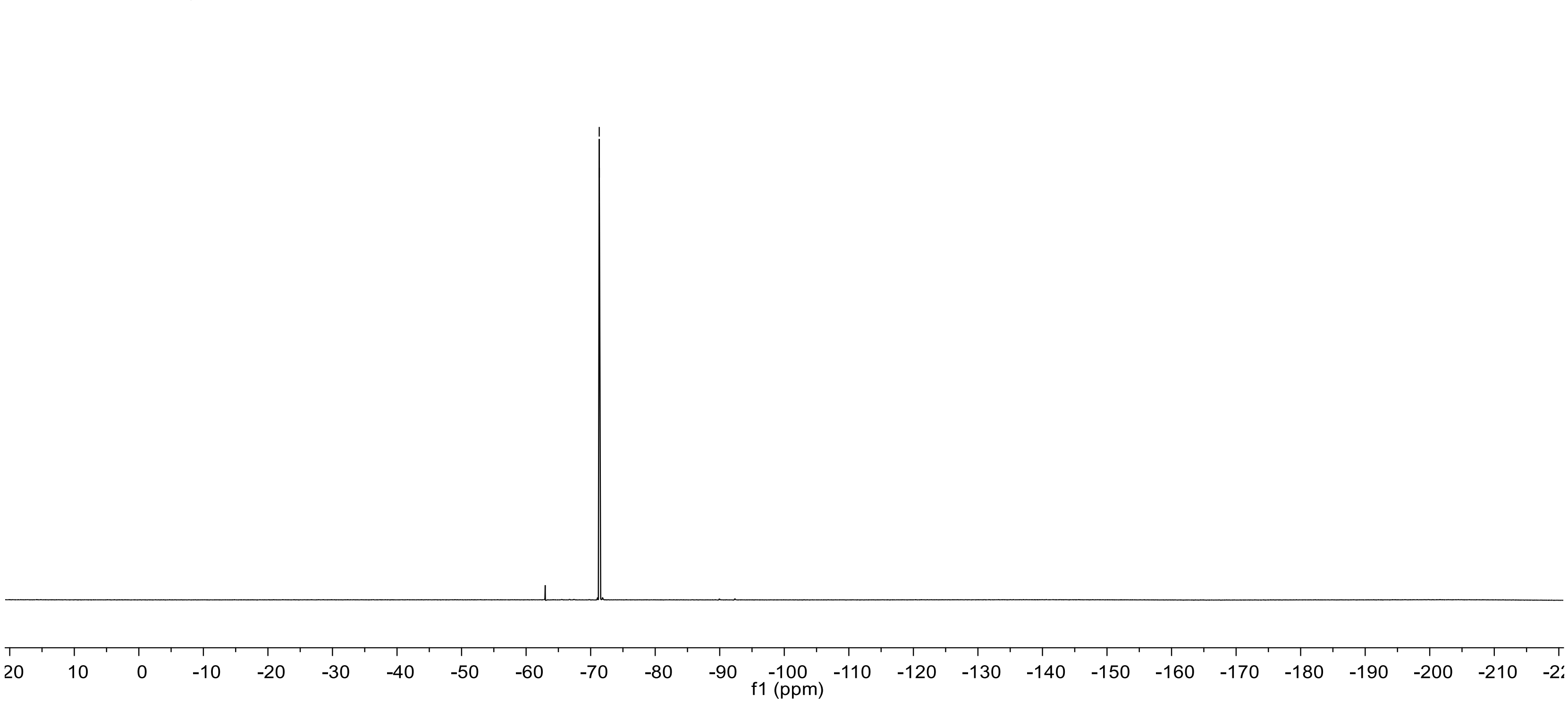
Supplementary Fig. 94. ^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



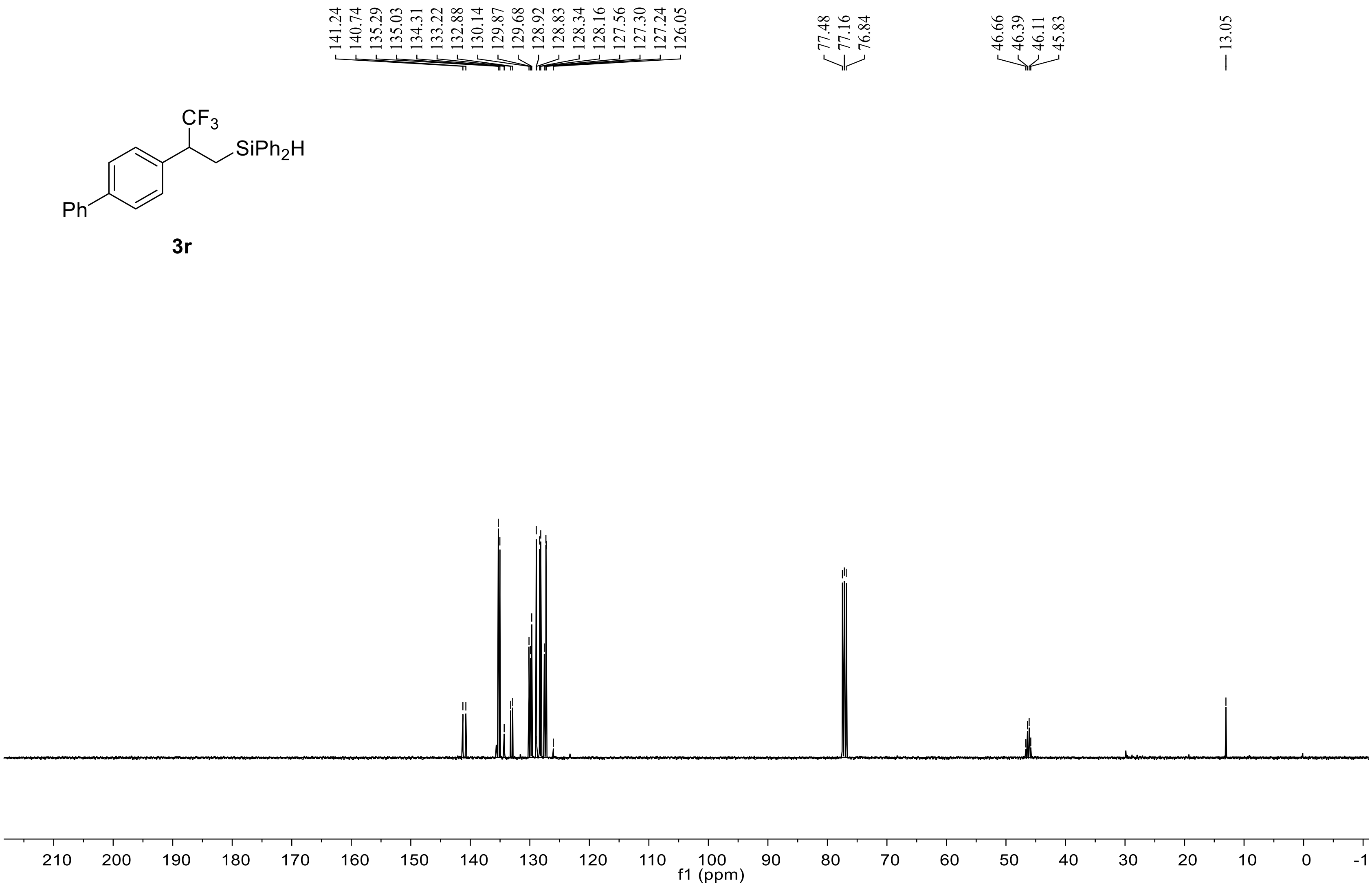
Supplementary Fig. 95. ^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



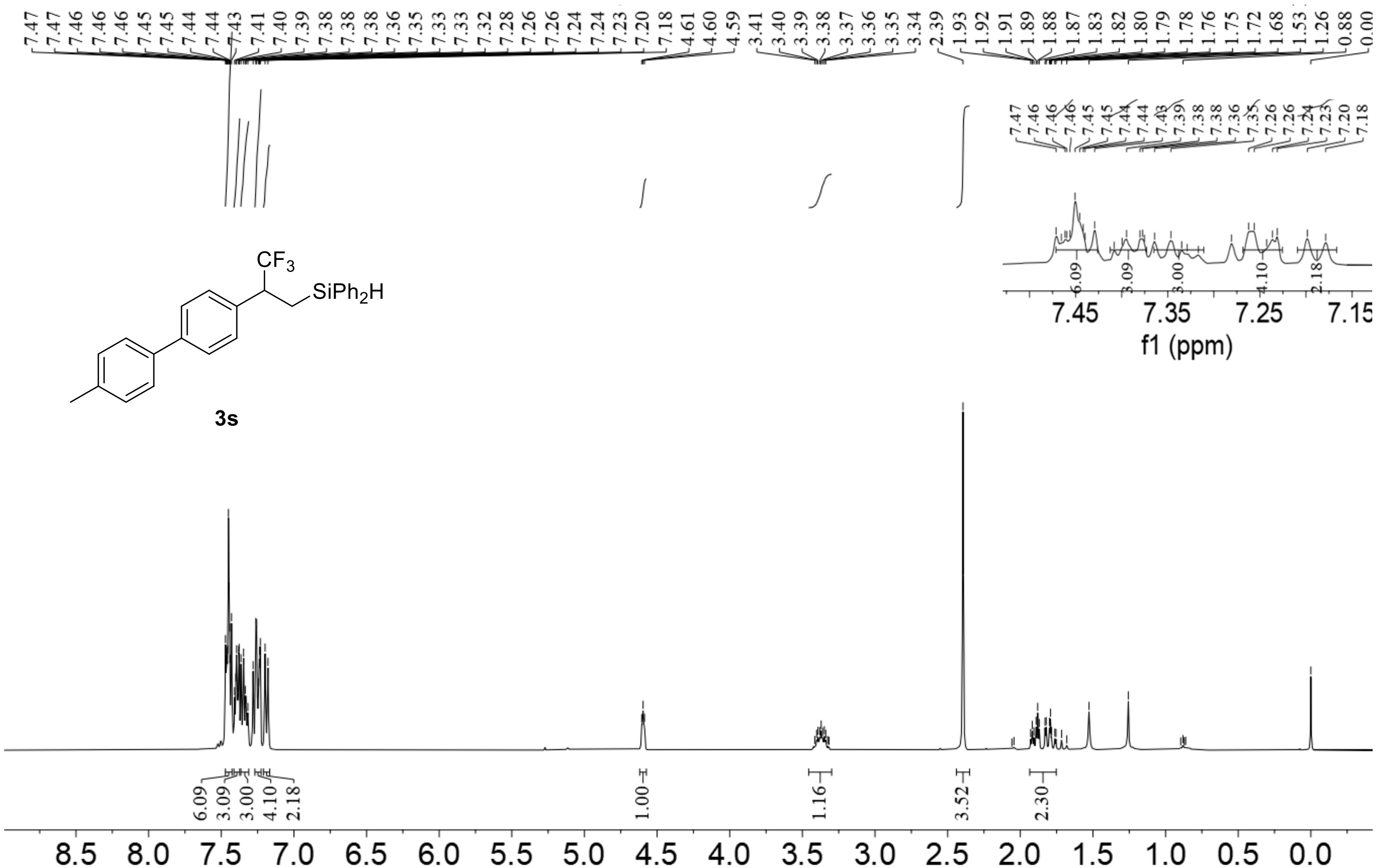
3r



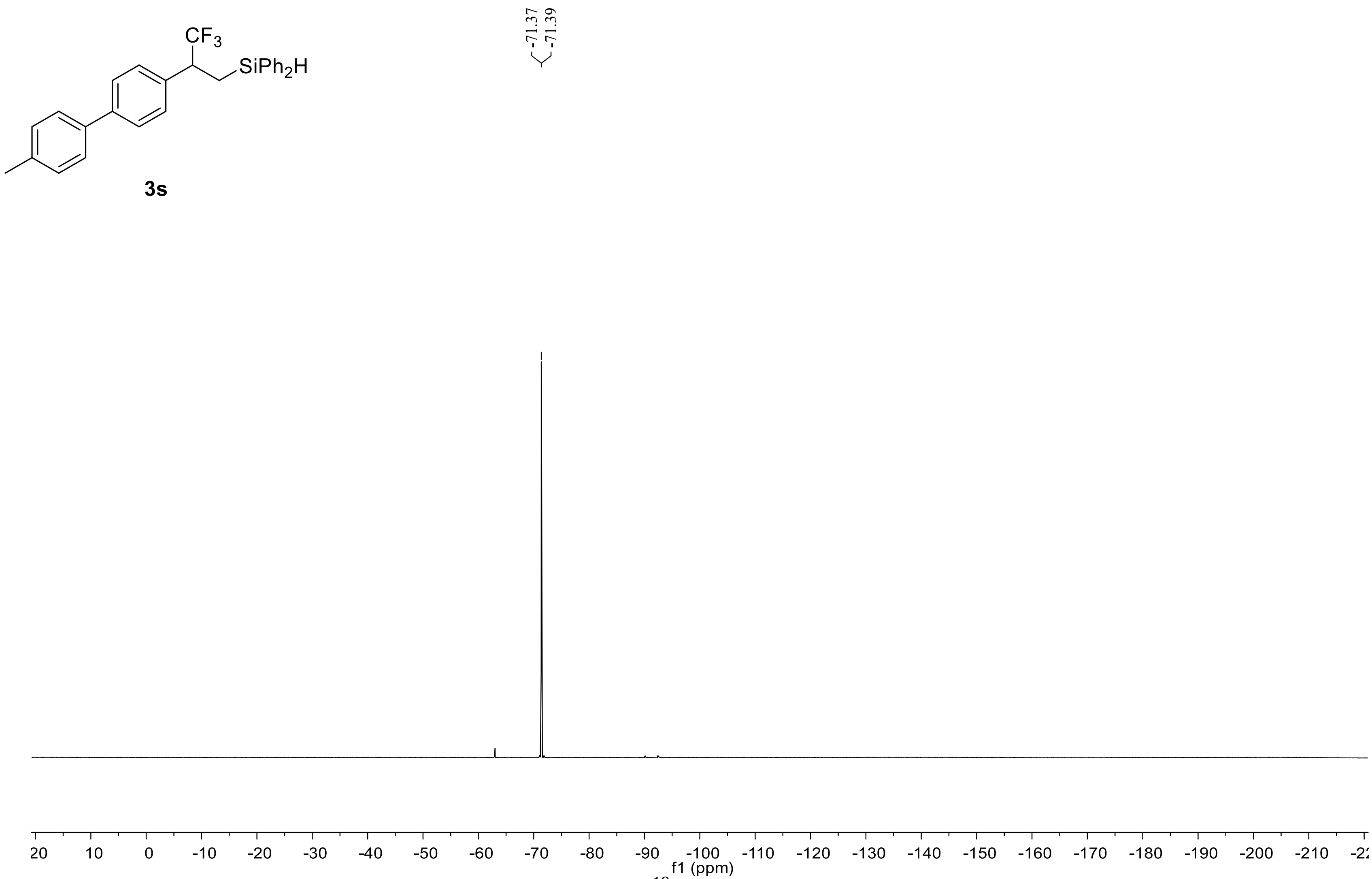
Supplementary Fig. 96. ^{19}F NMR (377 MHz, $CDCl_3$) of **3r**



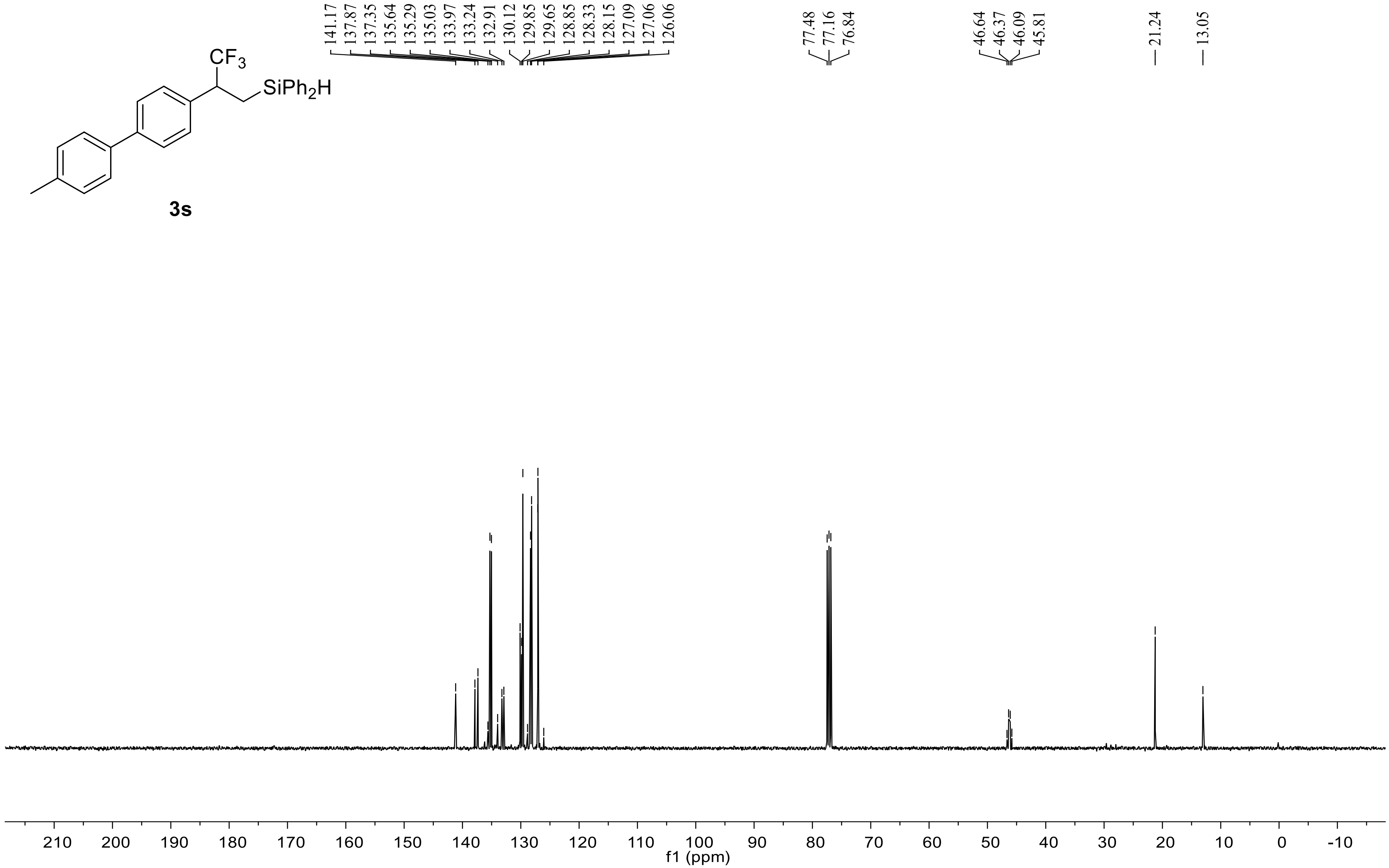
Supplementary Fig. 97. ^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



Supplementary Fig. 98. ^{1}H NMR (400 MHz, $CDCl_3$) of **3s**

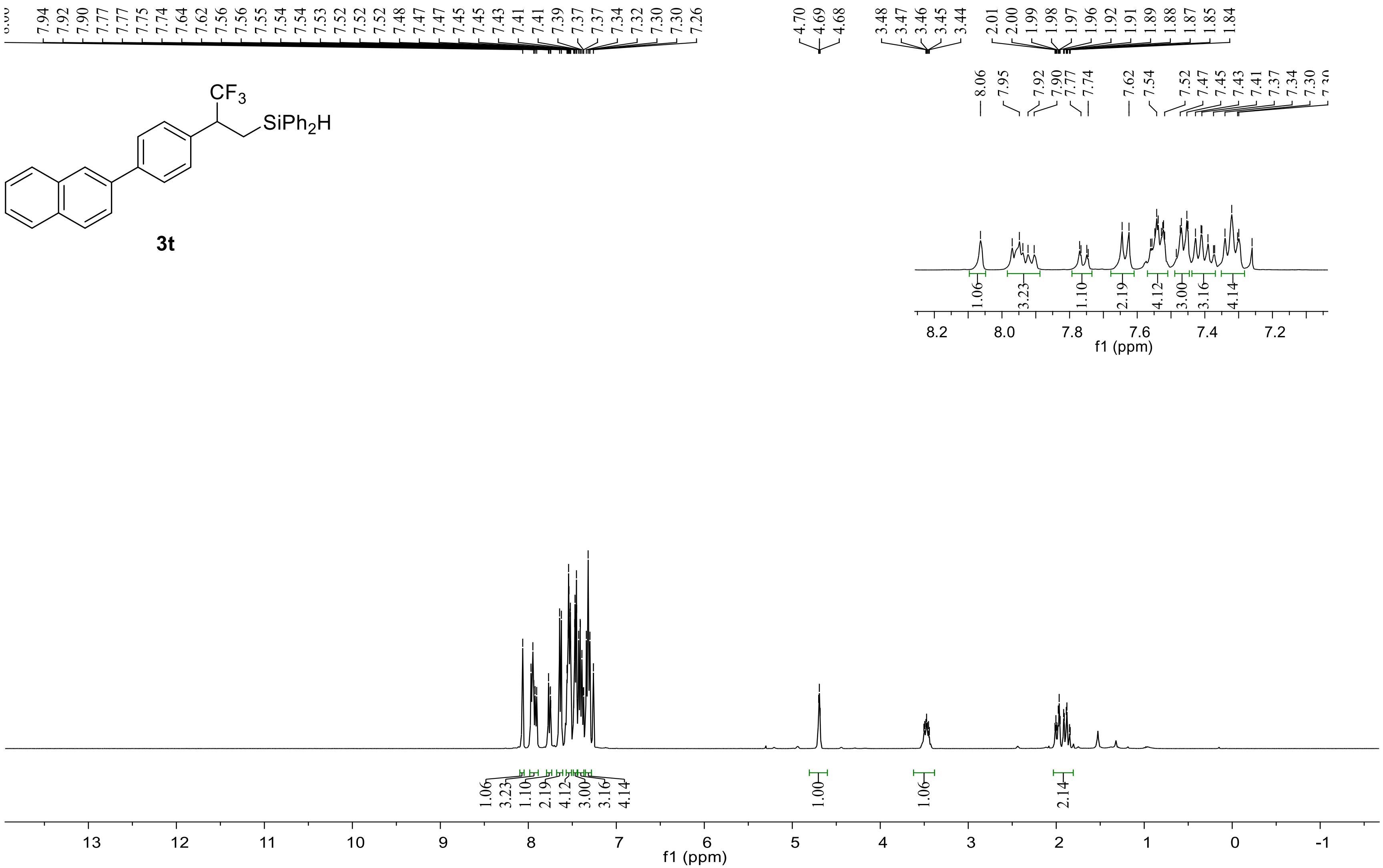


Supplementary Fig. 99. ^{19}F NMR (377 MHz, $CDCl_3$) of **3s**

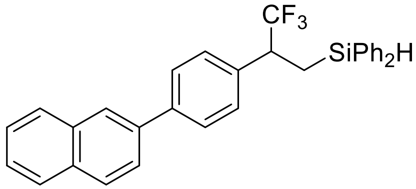


3s

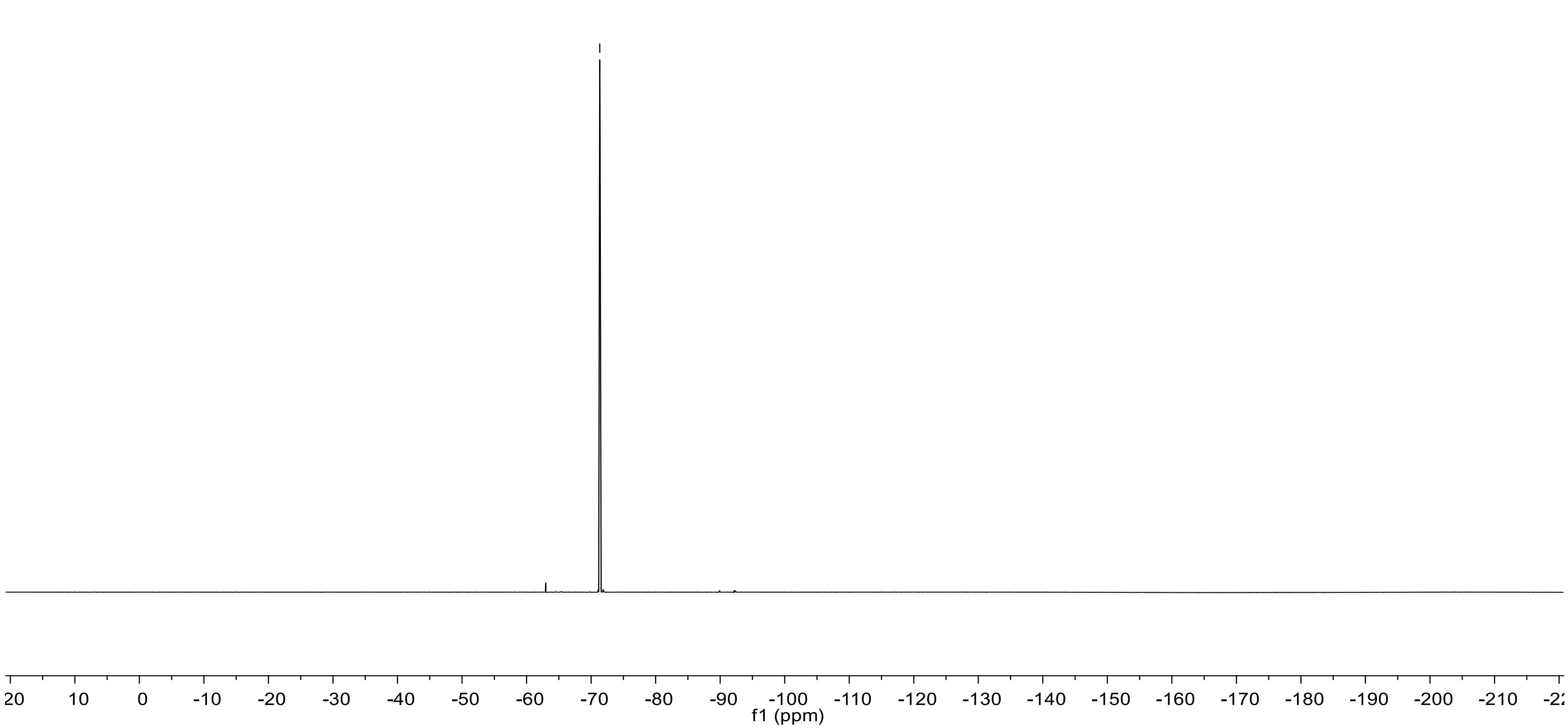
Supplementary Fig. 100. ^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



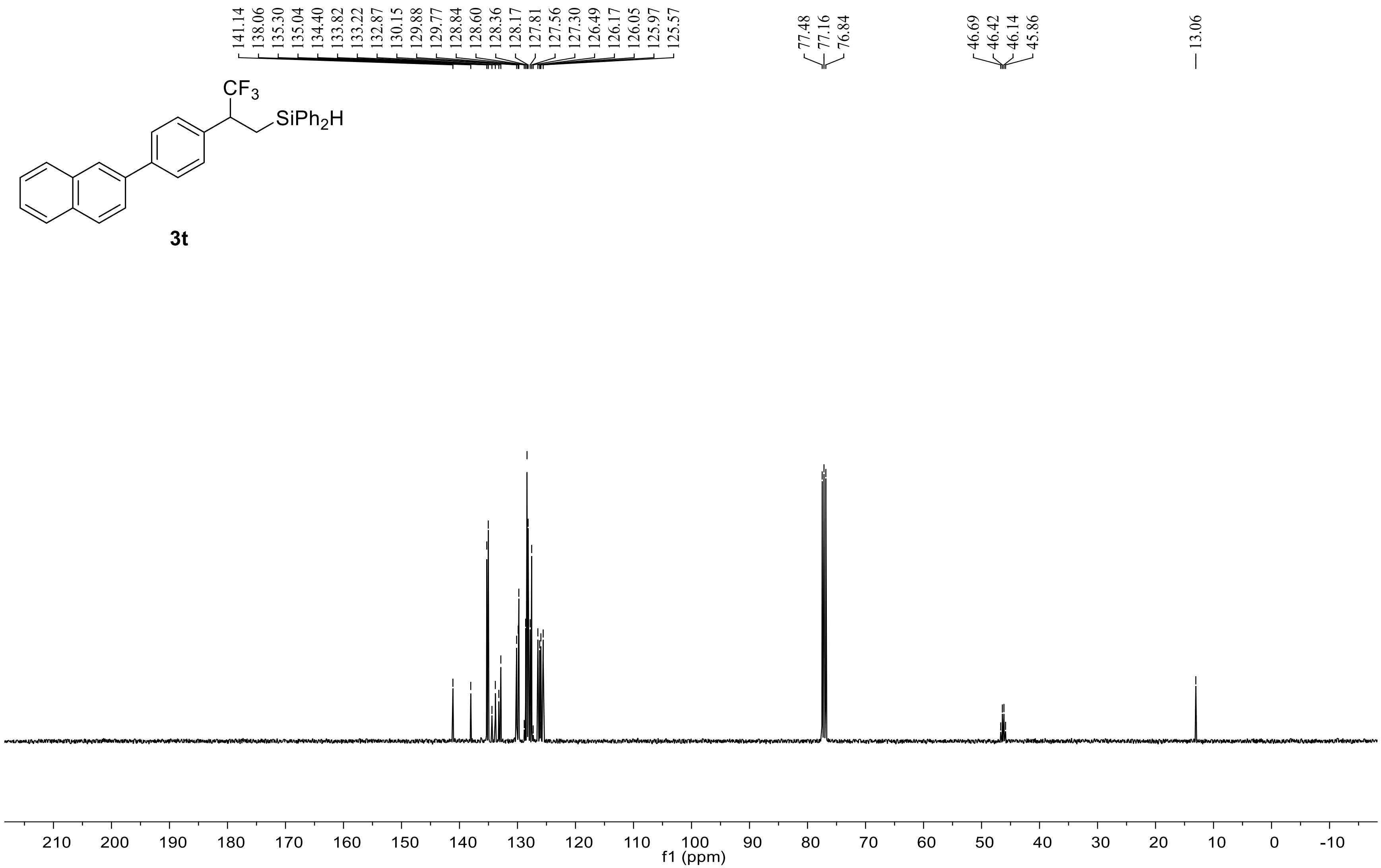
Supplementary Fig. 101. ^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



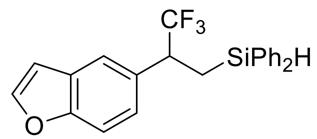
3t



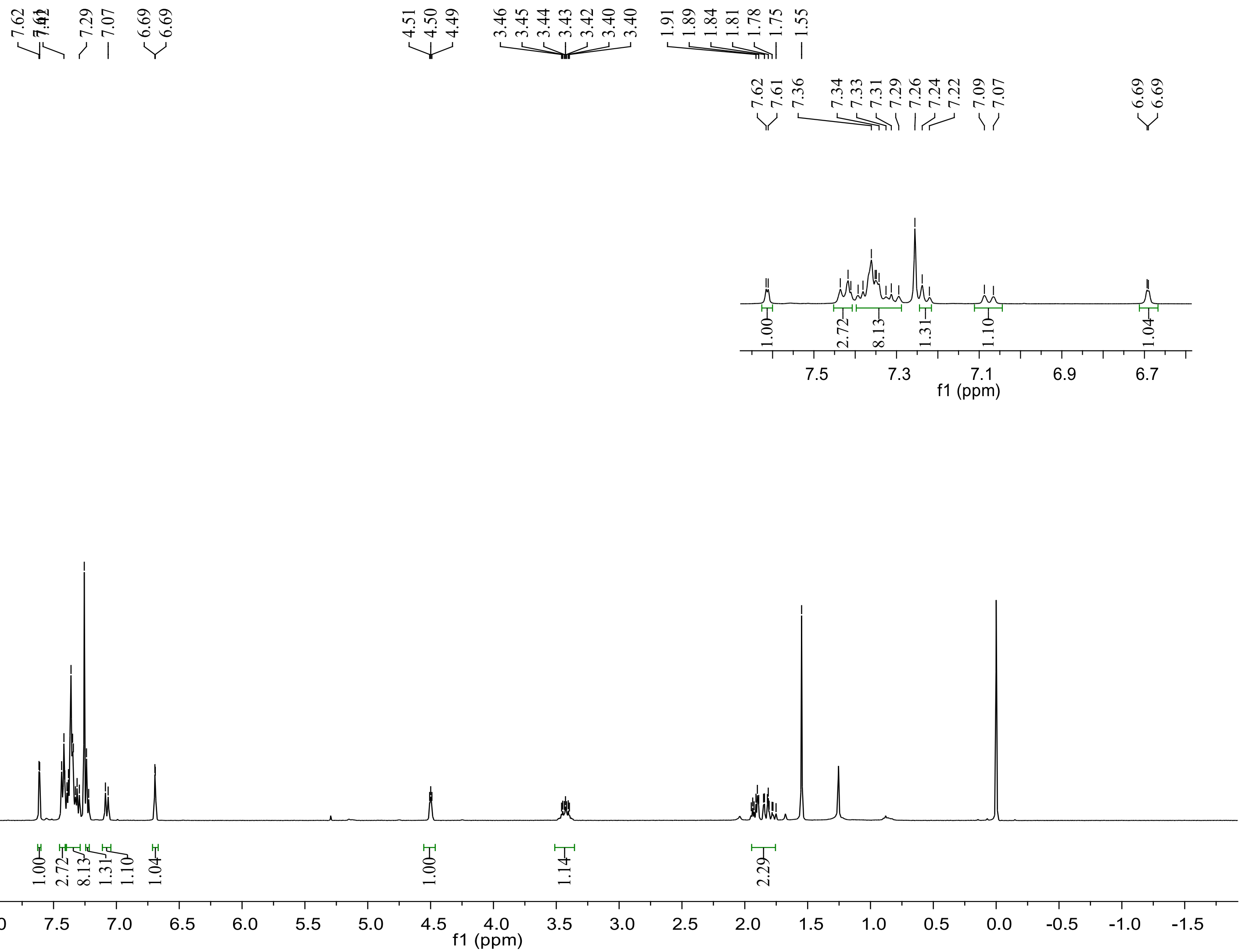
Supplementary Fig. 102. ^{19}F NMR (377 MHz, $CDCl_3$) of **3t**



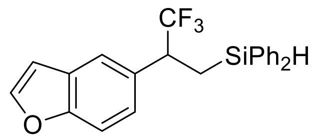
Supplementary Fig. 103. ^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



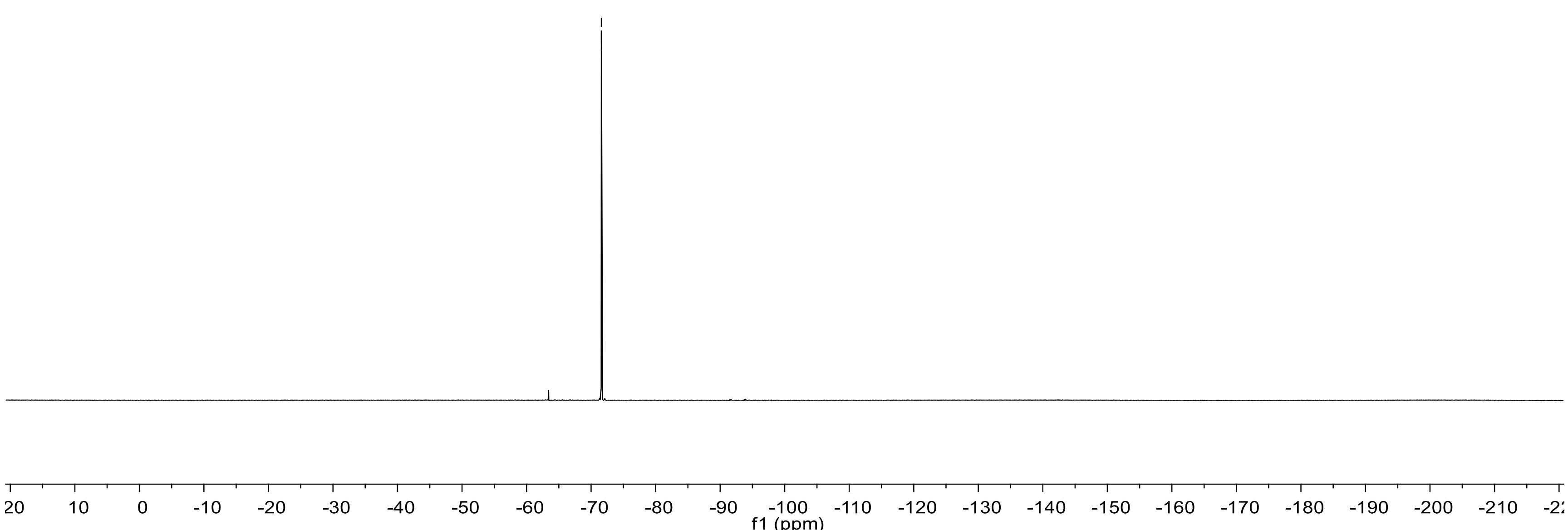
3u



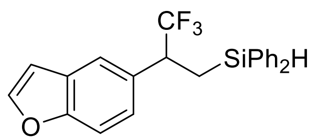
Supplementary Fig. 104. ^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



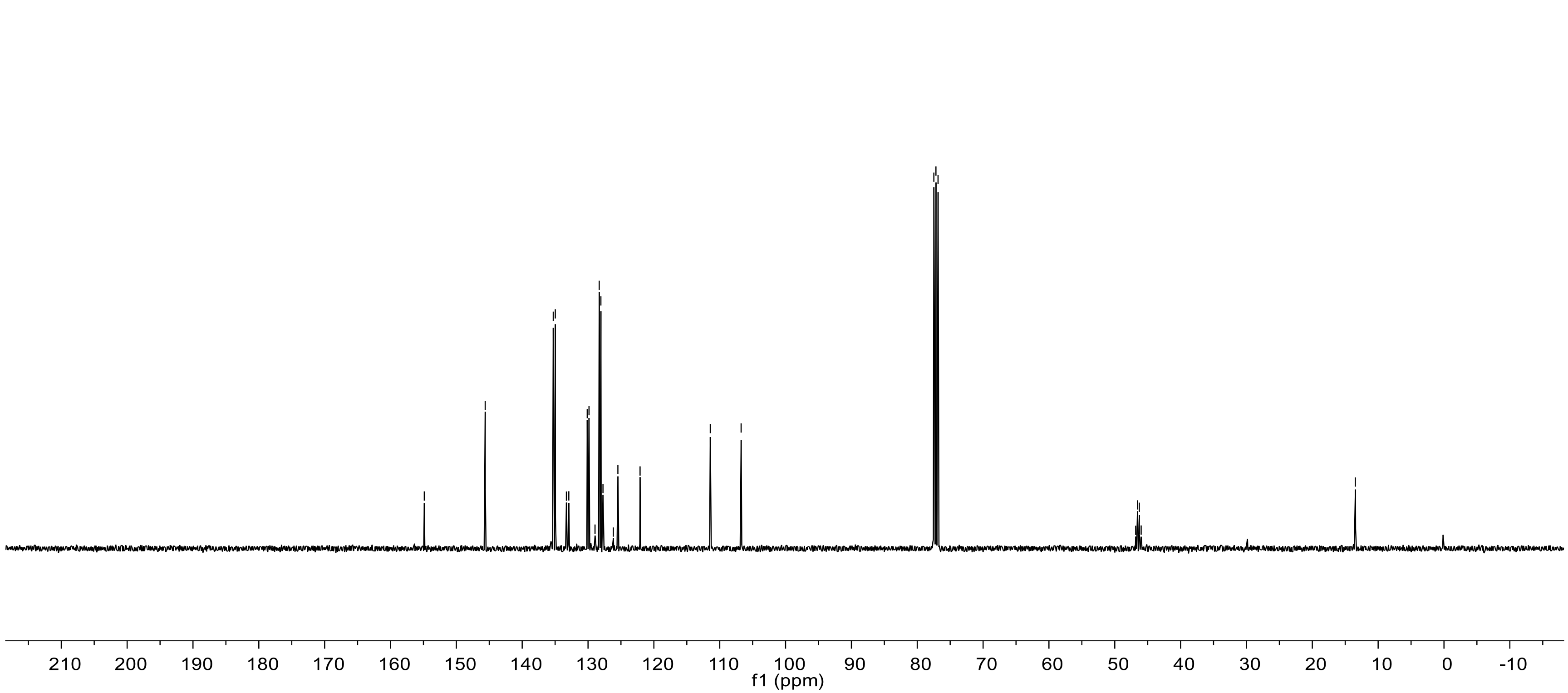
3u



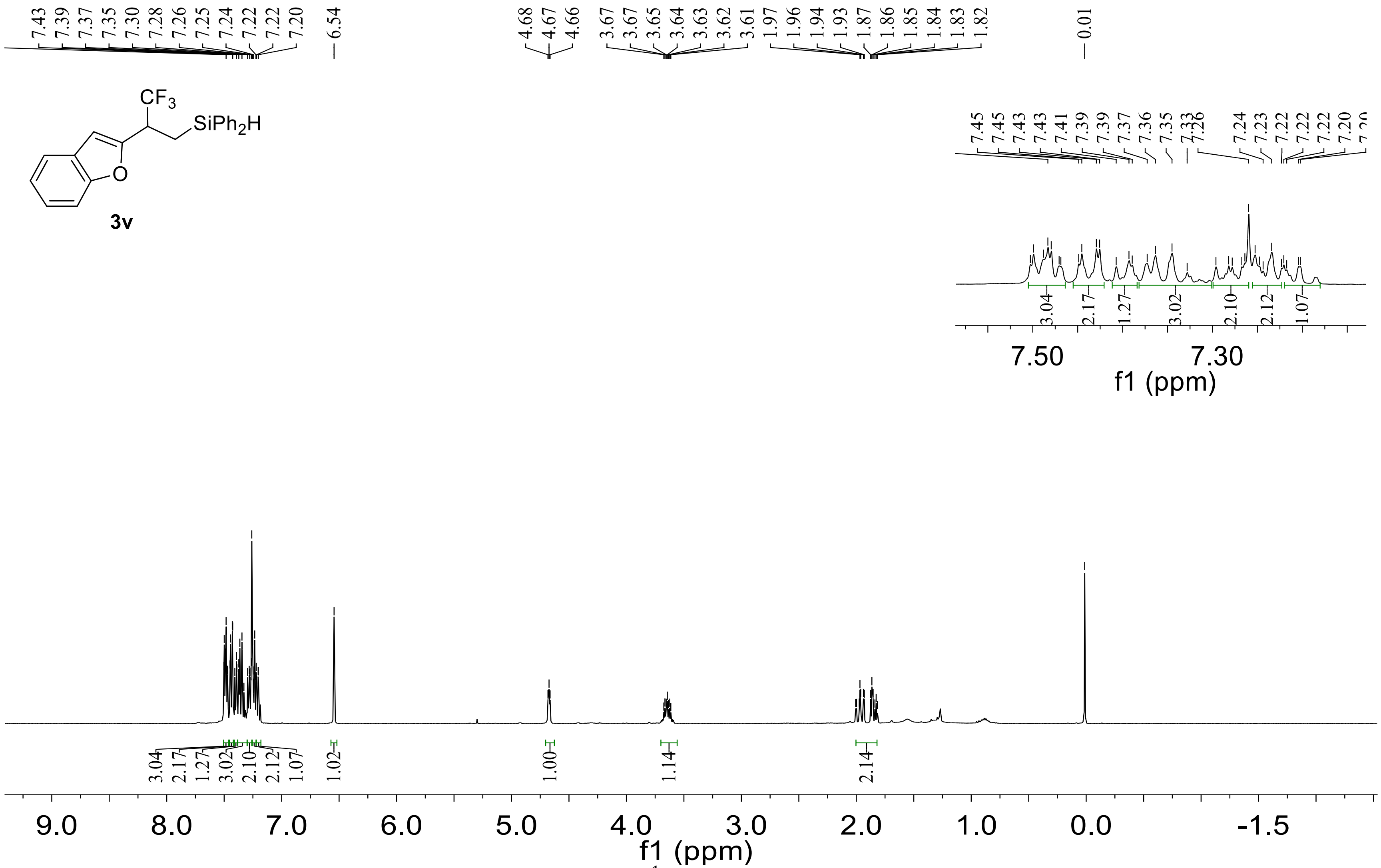
Supplementary Fig. 105. ^{19}F NMR (400 MHz, $CDCl_3$) of **3u**



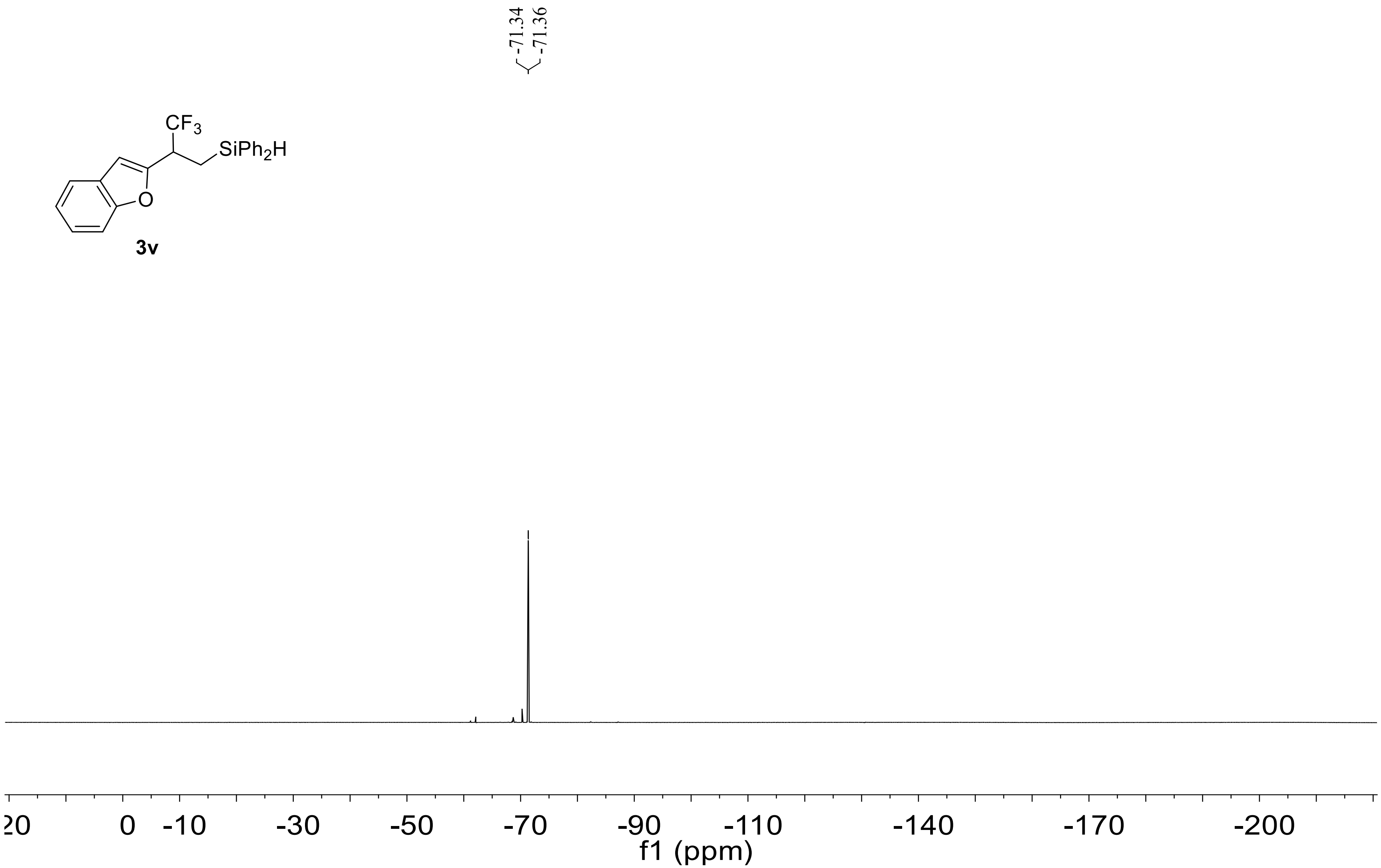
3u



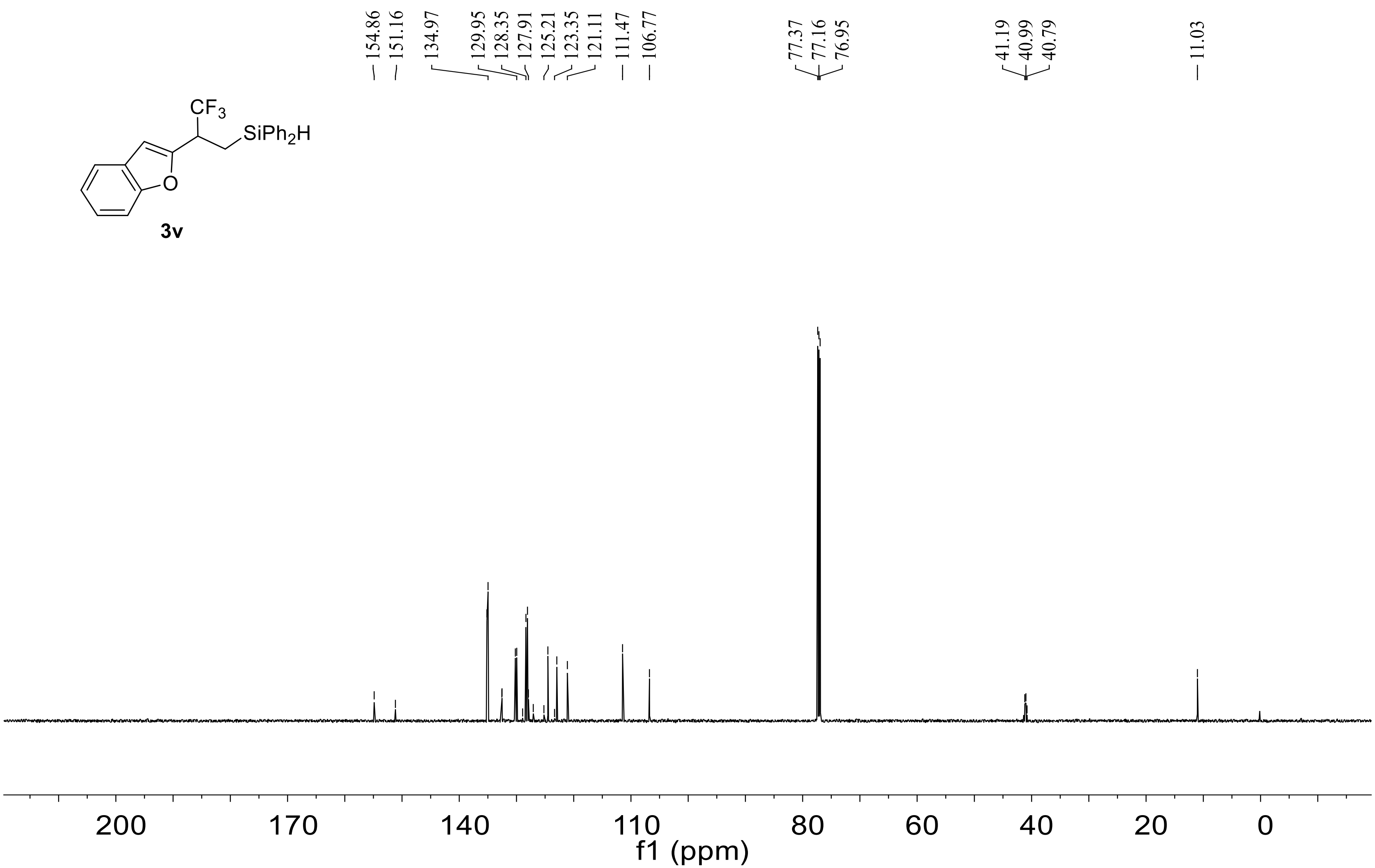
Supplementary Fig. 106. ^{13}C NMR (400 MHz, $CDCl_3$) of **3u**



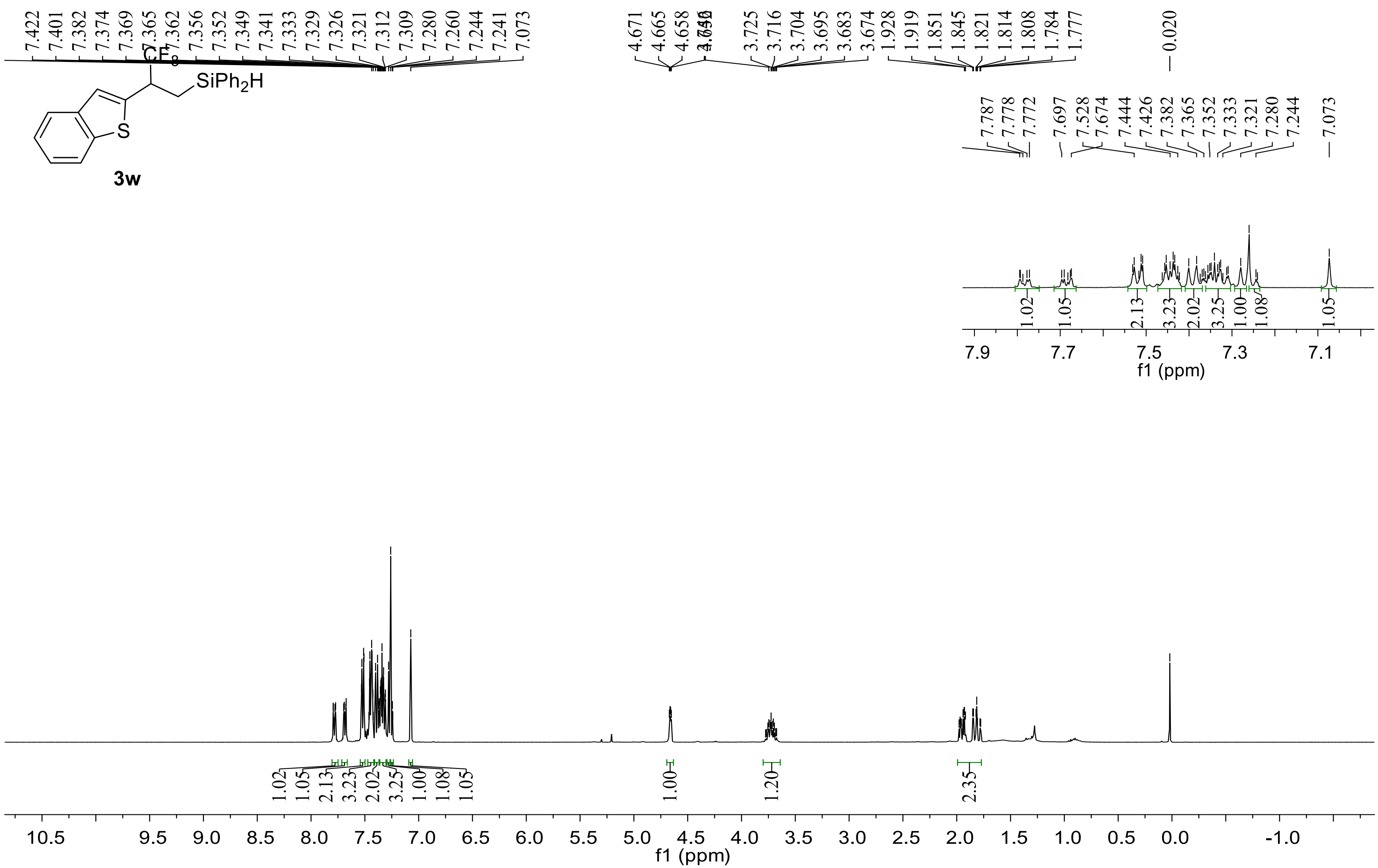
Supplementary Fig. 107. ^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



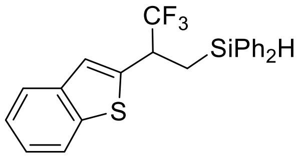
Supplementary Fig. 108. ^{19}F NMR (377 MHz, $CDCl_3$) of **3v**



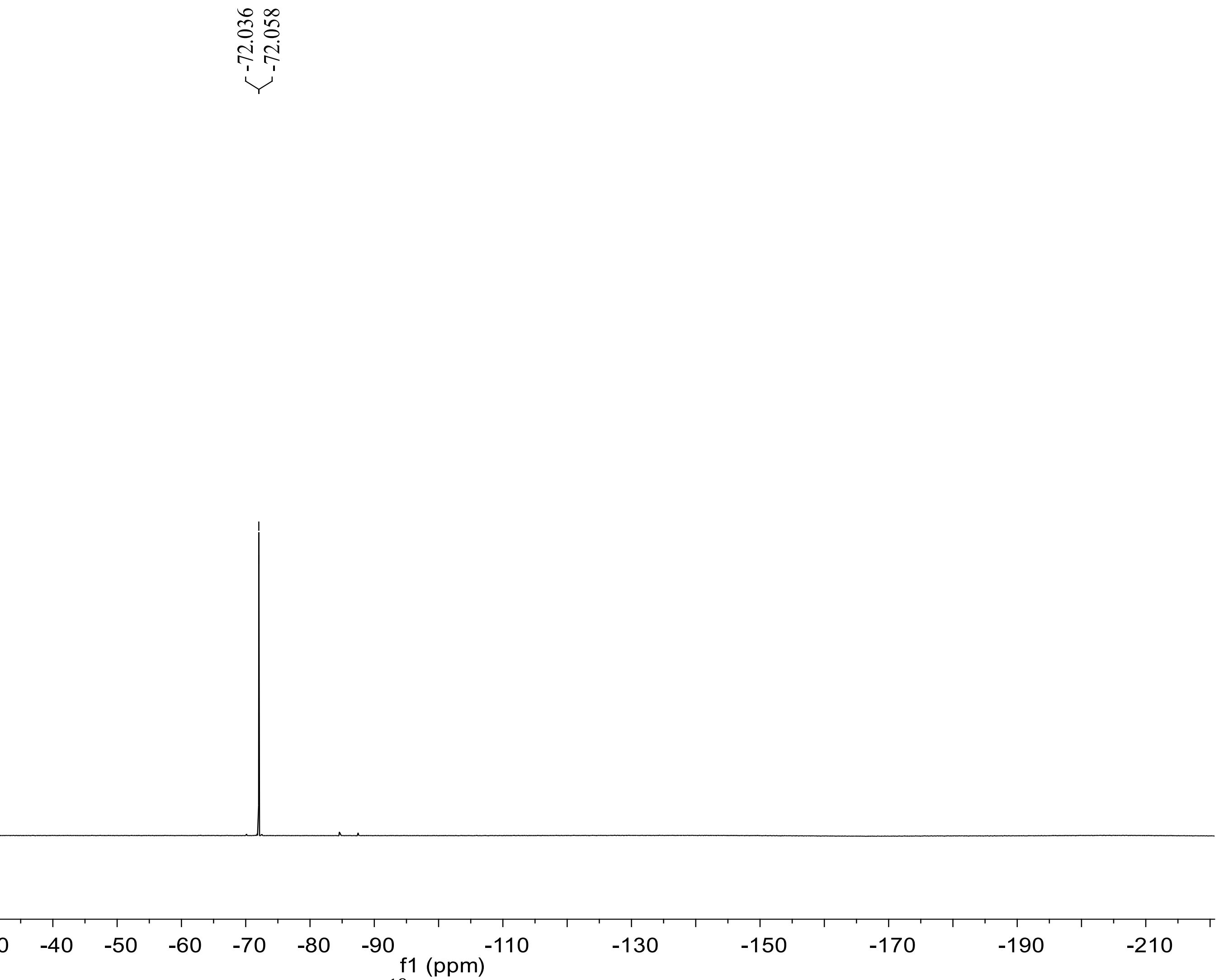
Supplementary Fig. 109. ^{13}C NMR (151 MHz, $CDCl_3$) of **3v**



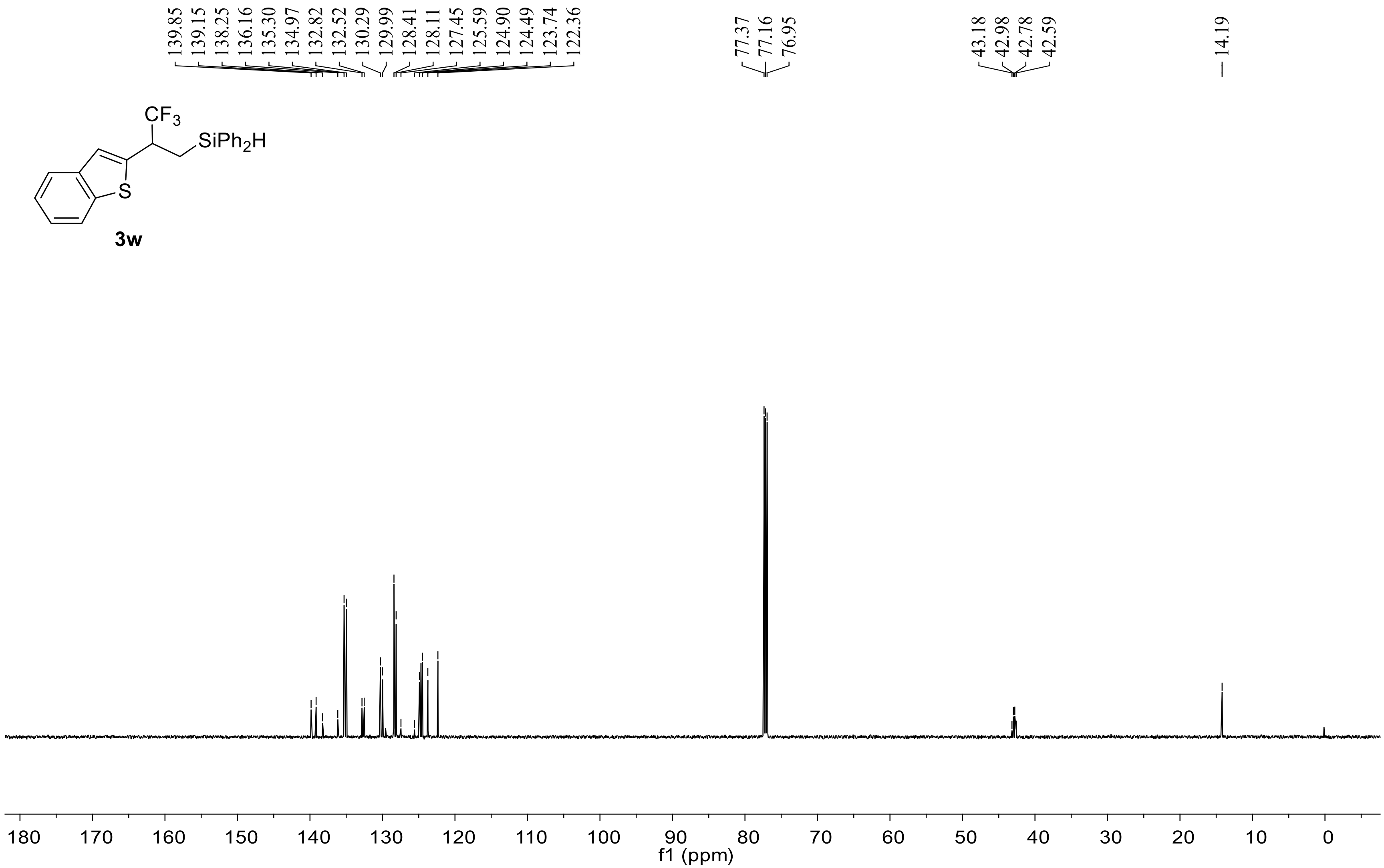
Supplementary Fig. 110. ^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



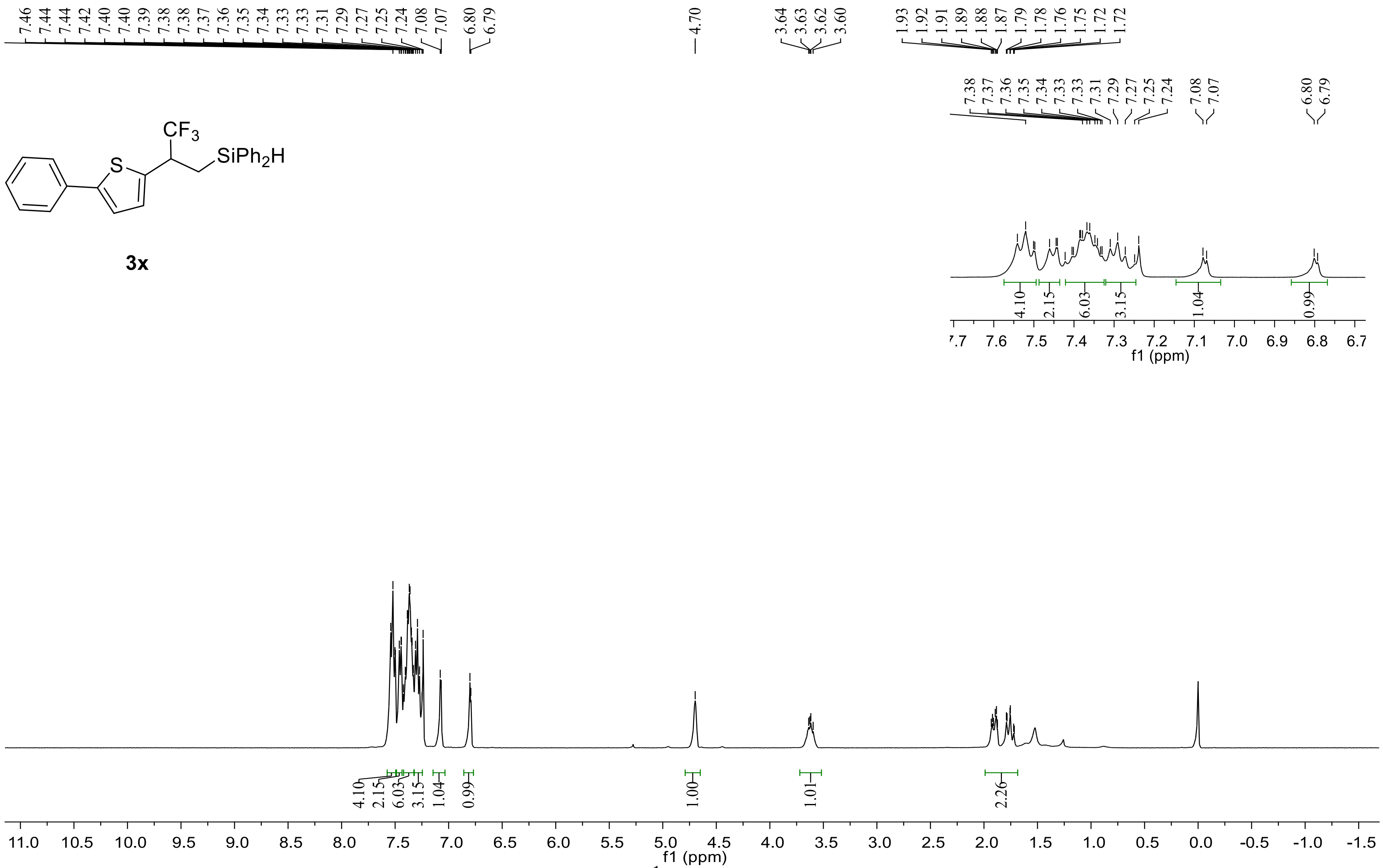
3w



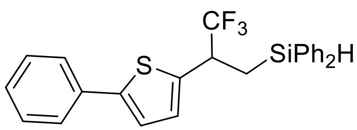
Supplementary Fig. 111. ^{19}F NMR (377 MHz, $CDCl_3$) of **3w**



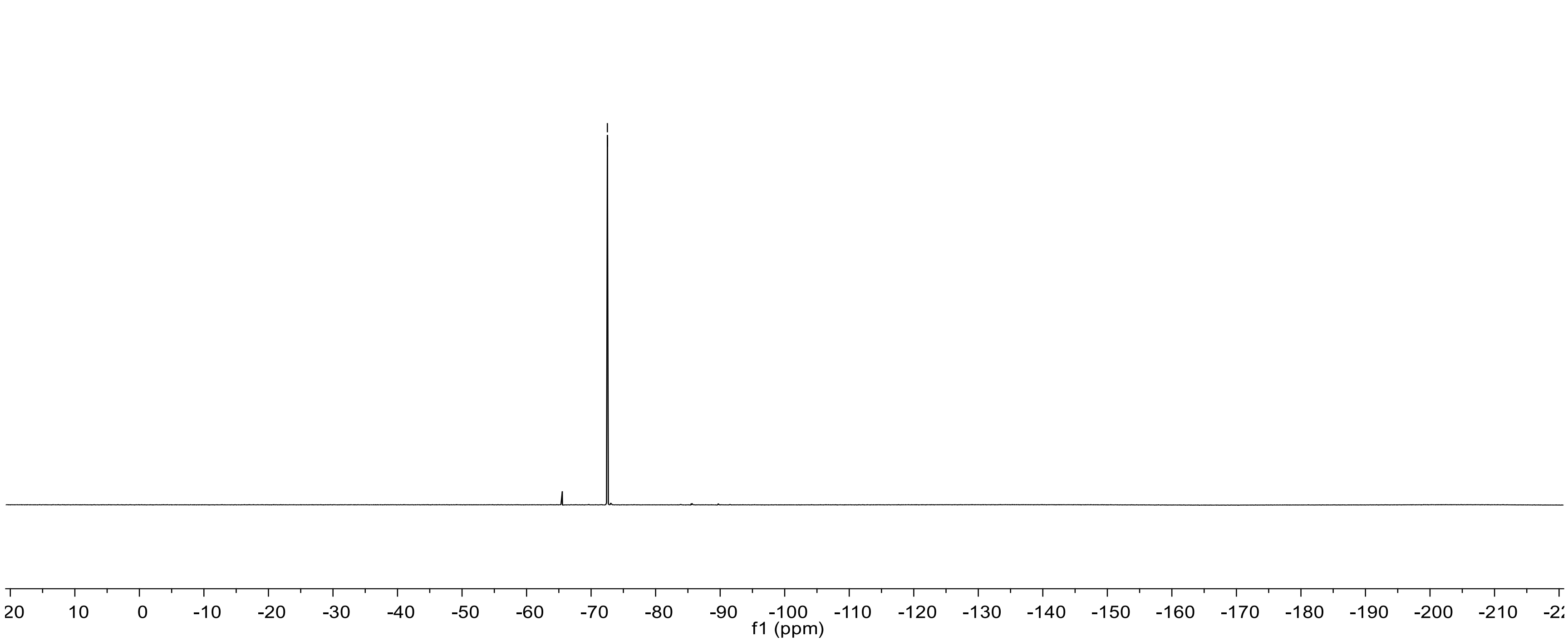
Supplementary Fig. 112. ^{13}C NMR (151 MHz, $CDCl_3$) of **3w**



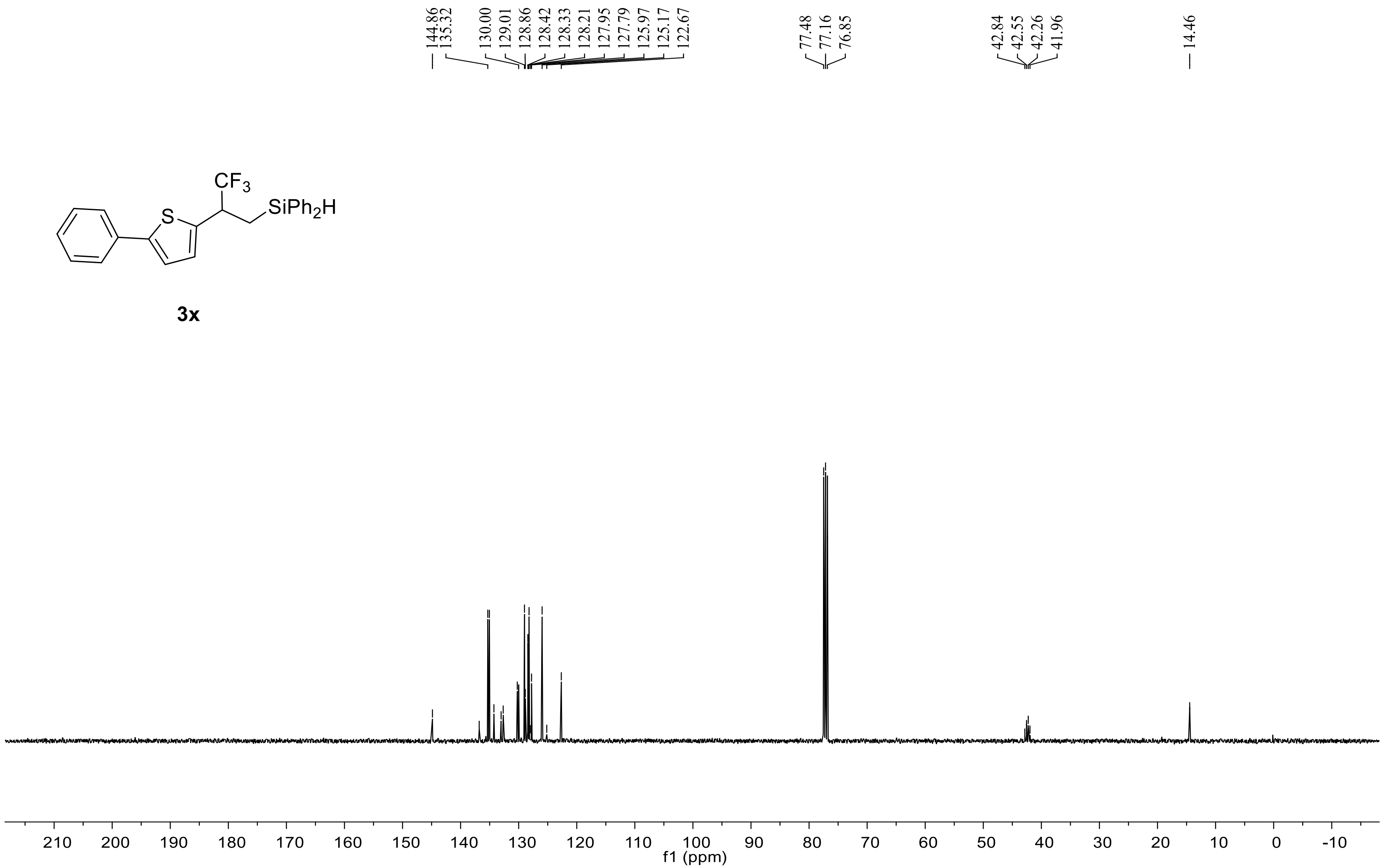
Supplementary Fig. 113. ^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



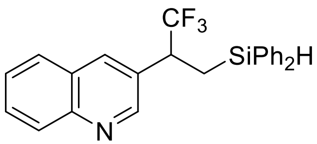
3x



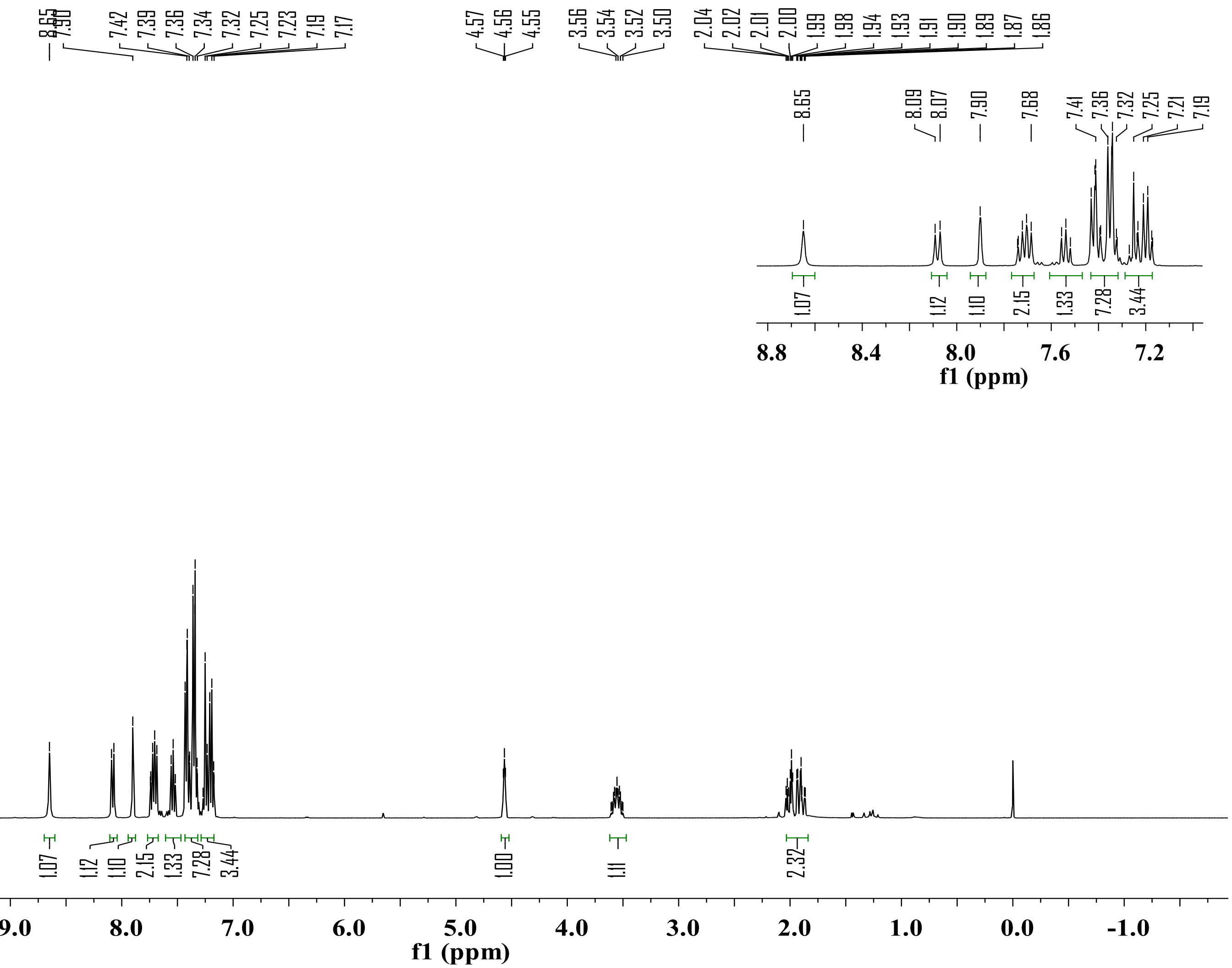
Supplementary Fig. 114. ^{19}F NMR (377 MHz, $CDCl_3$) of **3x**



Supplementary Fig. 115. ^{19}C NMR (400 MHz, $CDCl_3$) of **3x**

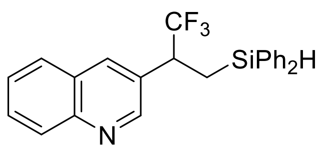


3y

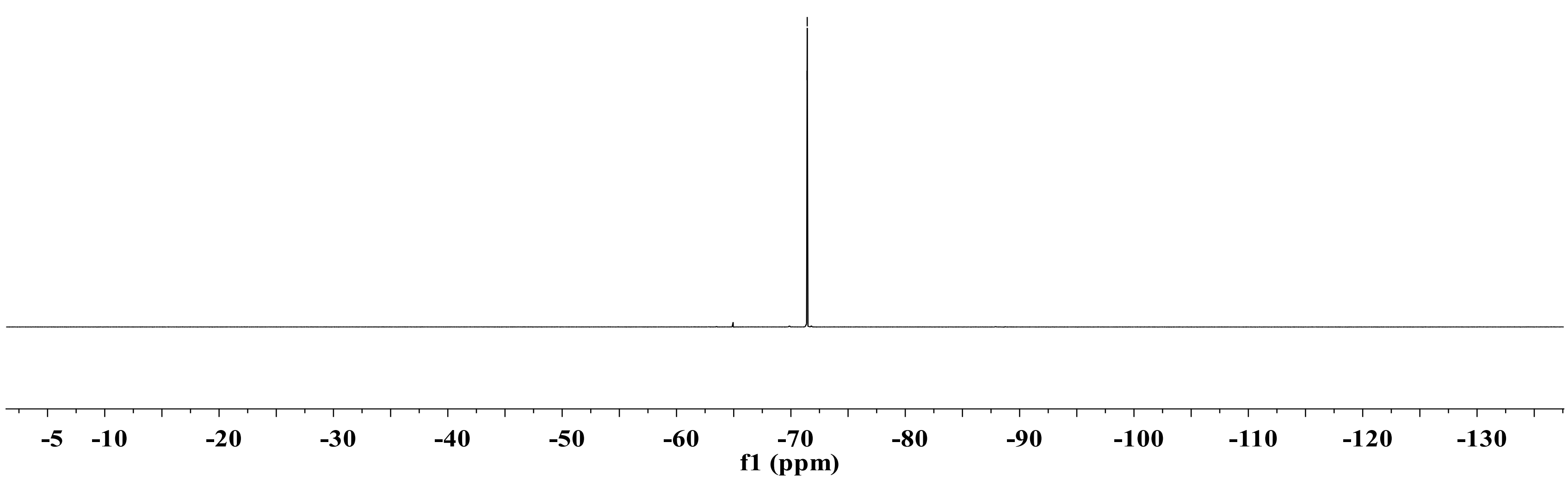


Supplementary Fig. 116. ^{1}H NMR (400 MHz, $CDCl_3$) of **3y**

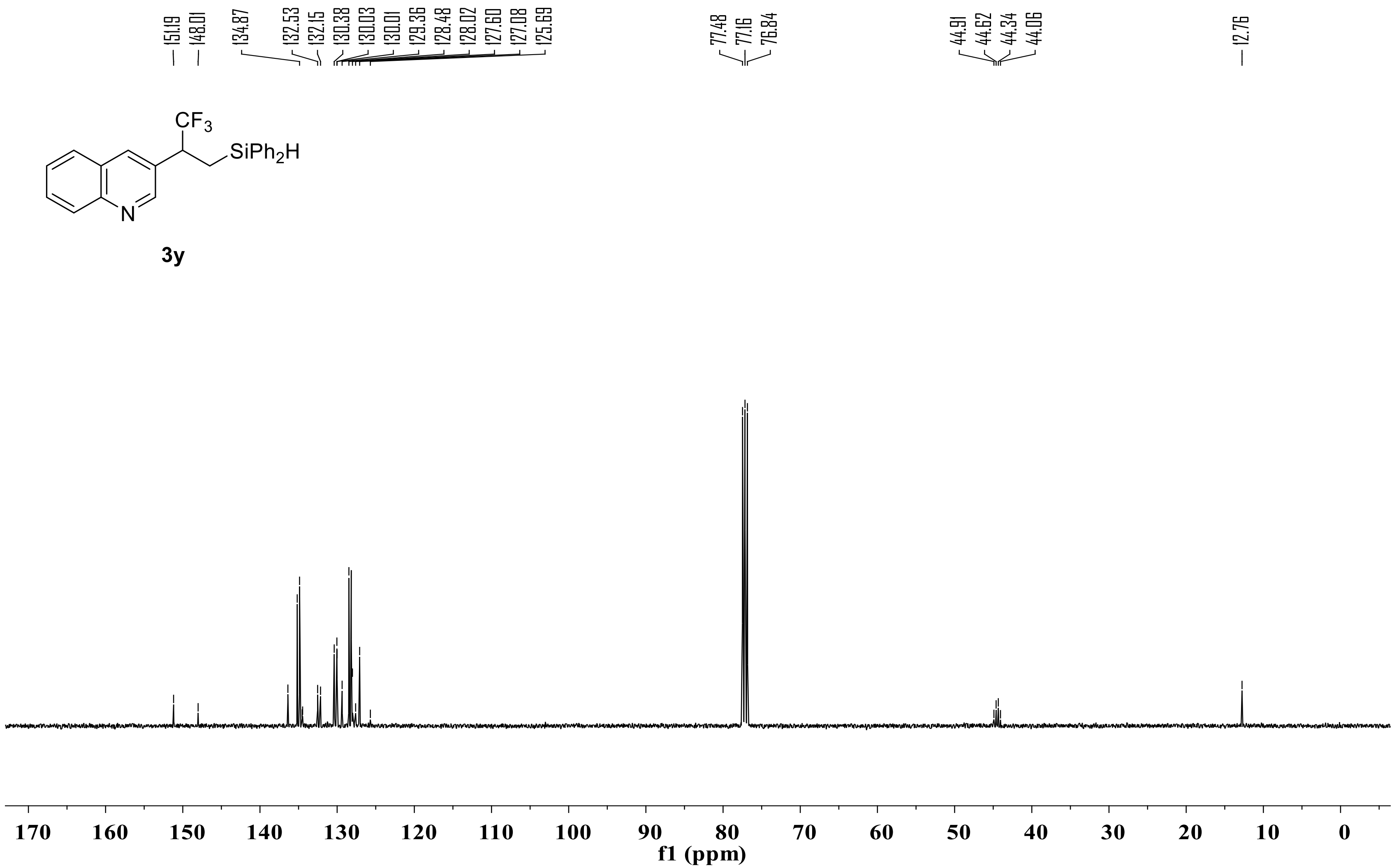
-71.41
-71.43



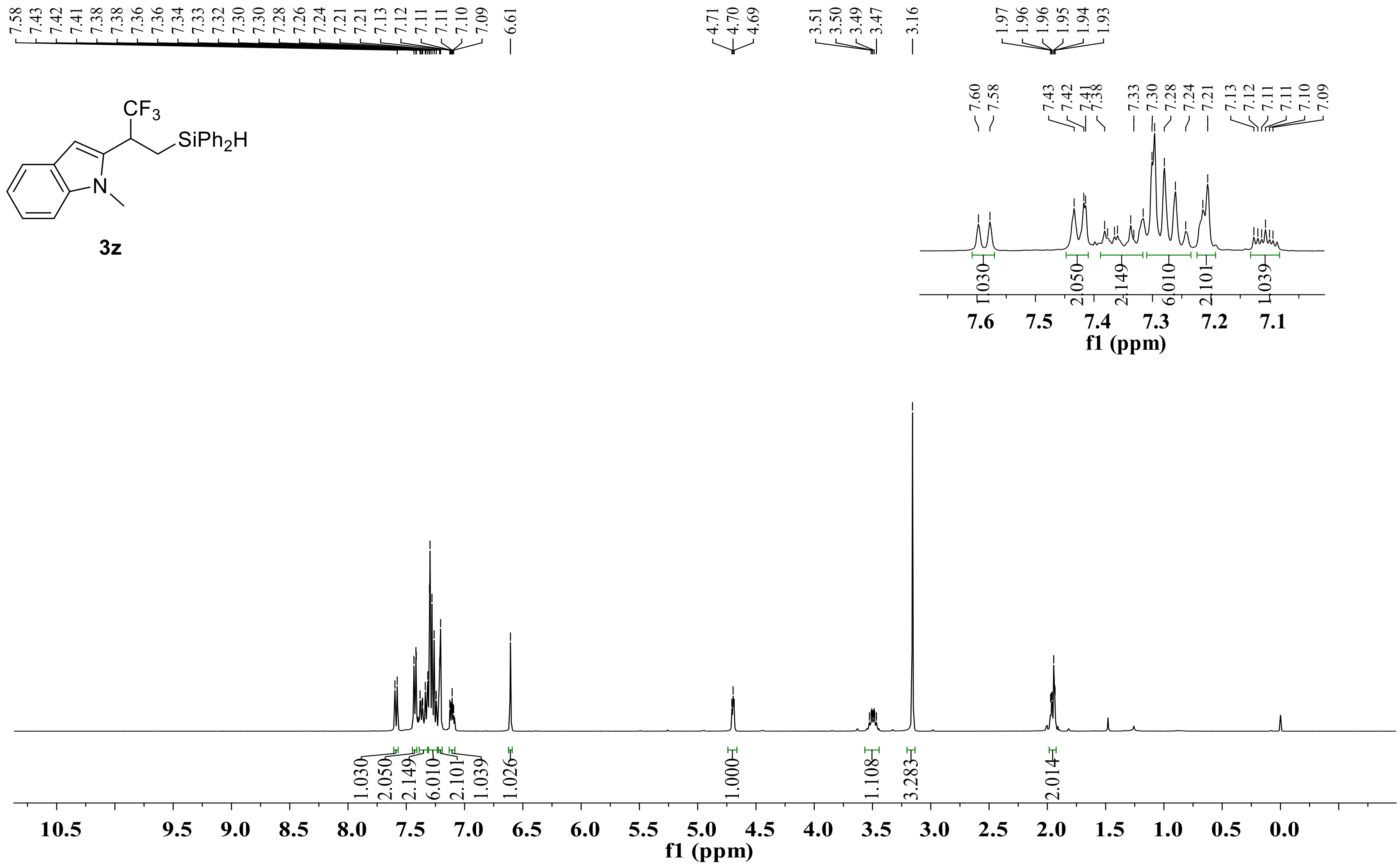
3y



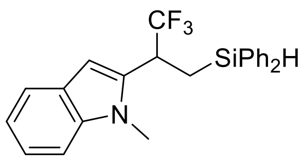
Supplementary Fig. 117. ^{19}F NMR (565 MHz, $CDCl_3$) of **3y**



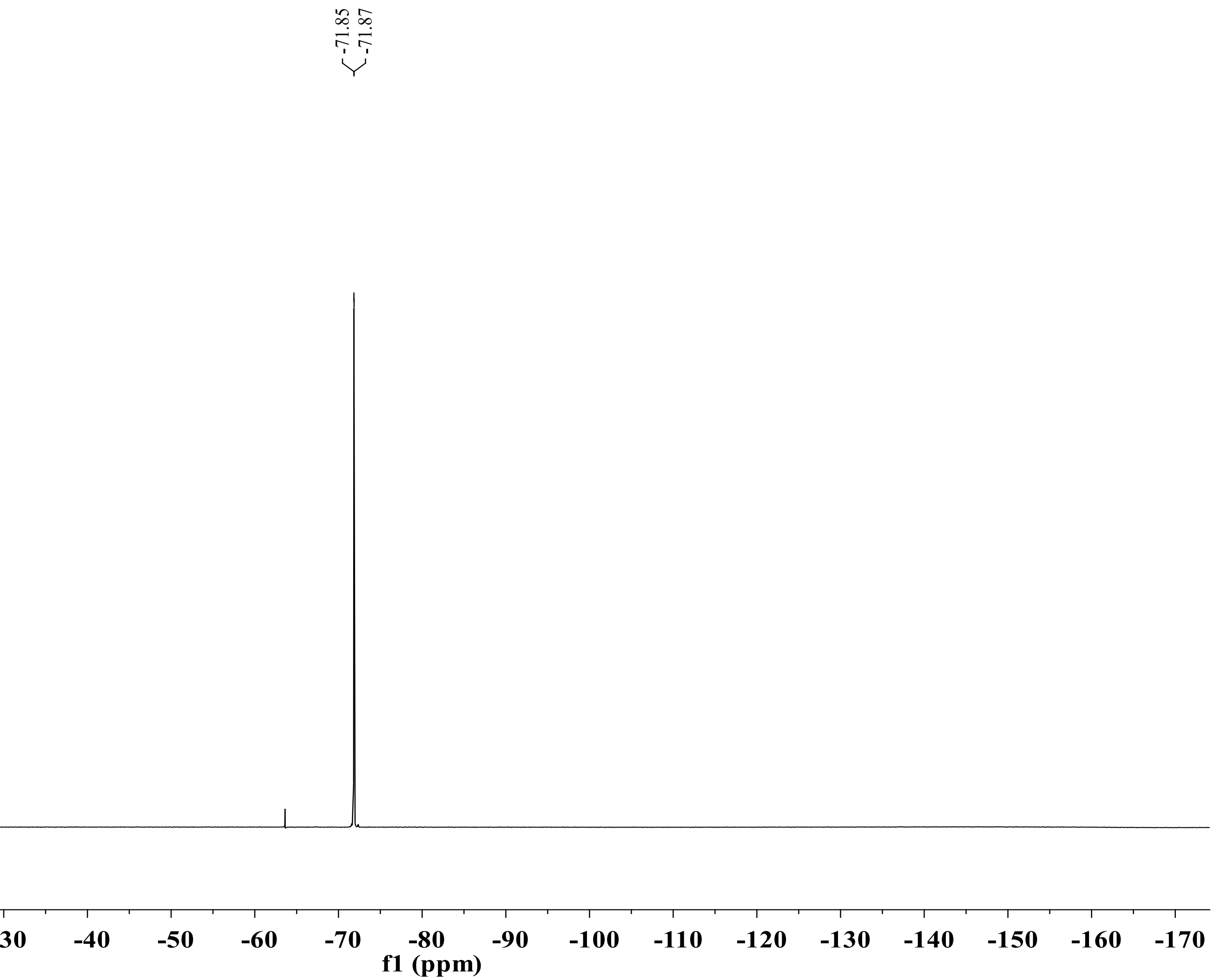
Supplementary Fig. 118. ^{13}C NMR (101 MHz, $CDCl_3$) of **3y**



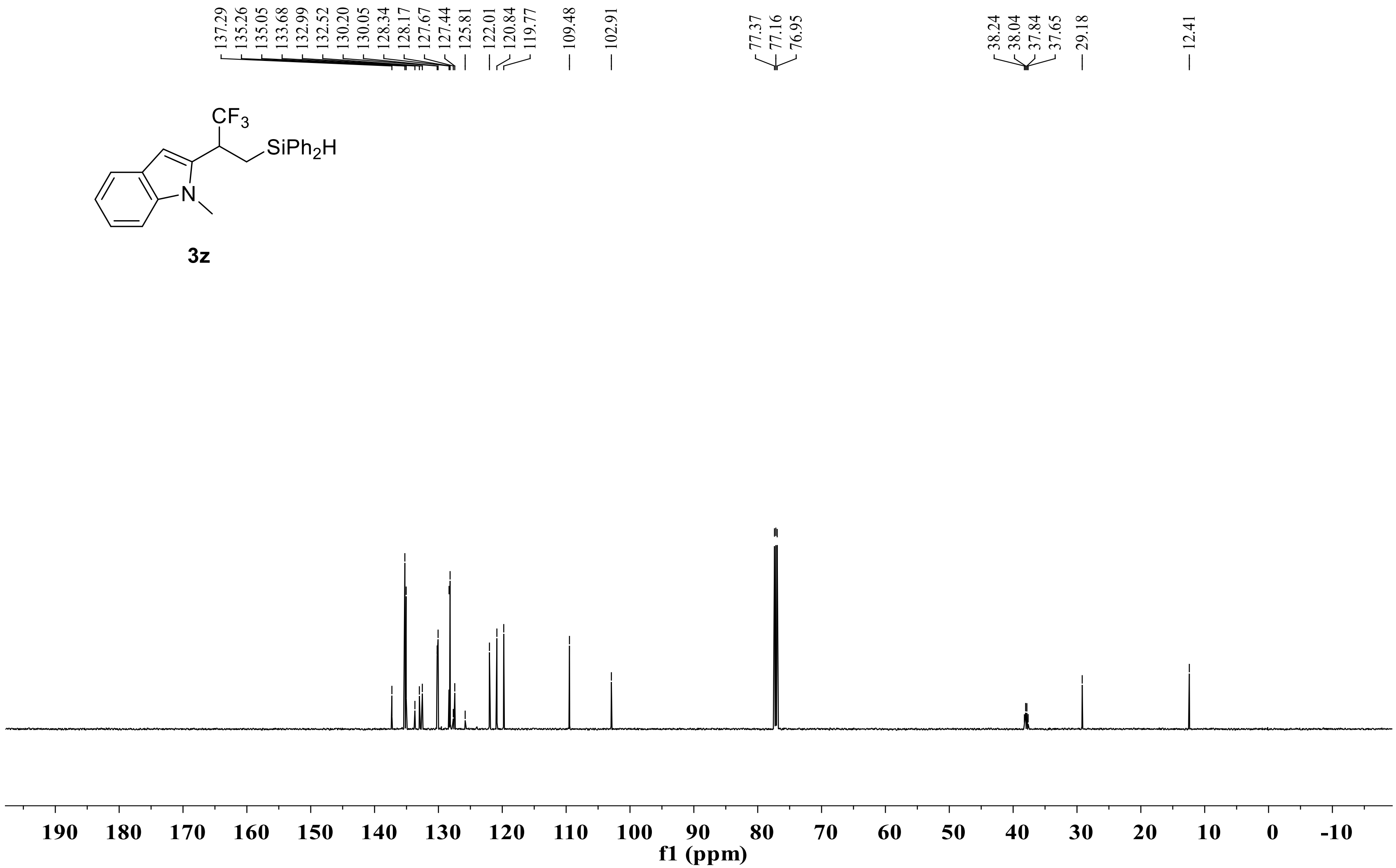
Supplementary Fig. 119. ^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



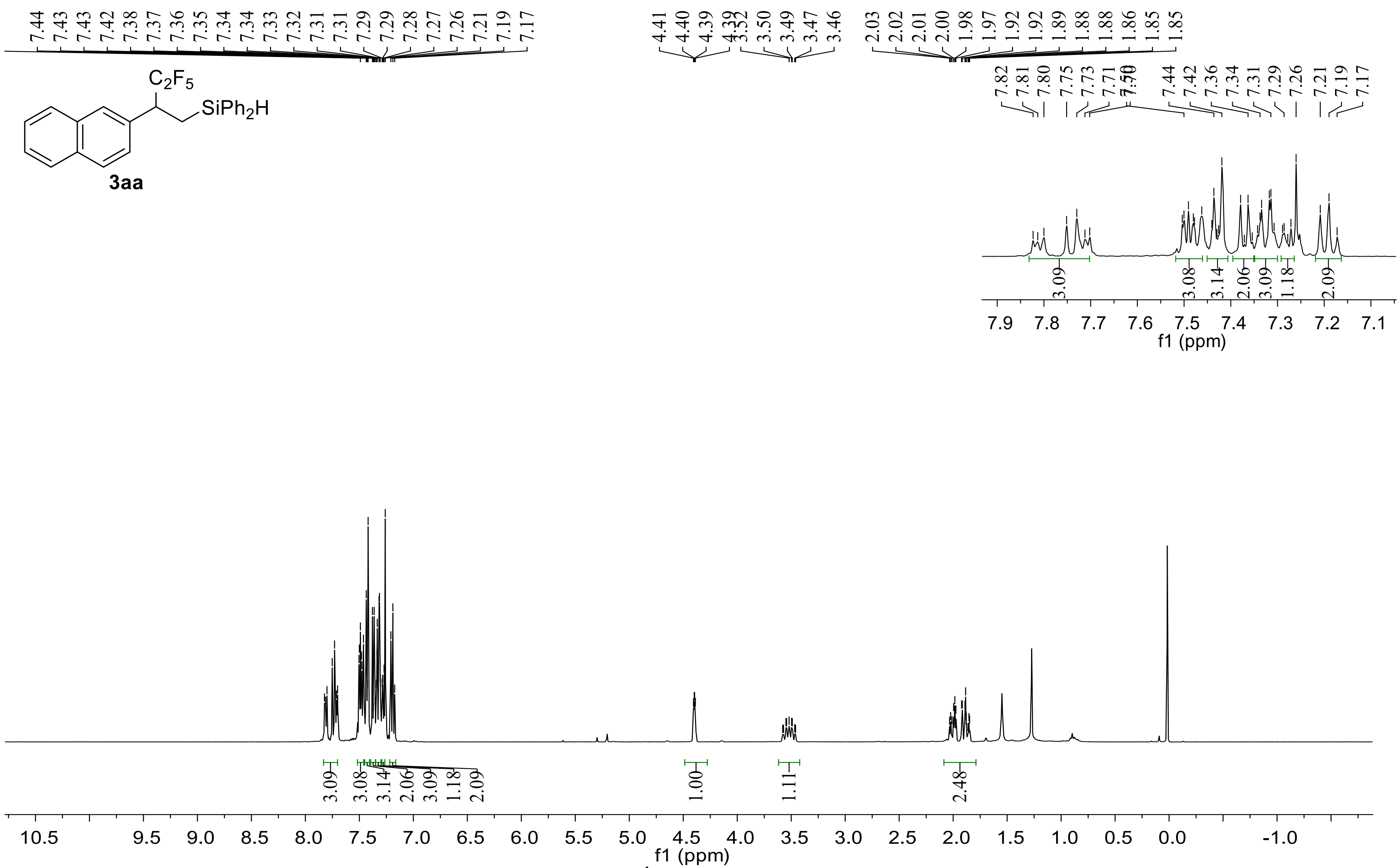
3z



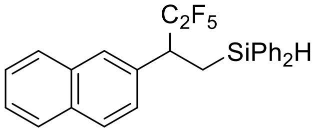
Supplementary Fig. 120. ^{19}F NMR (376 MHz, $CDCl_3$) of **3z**



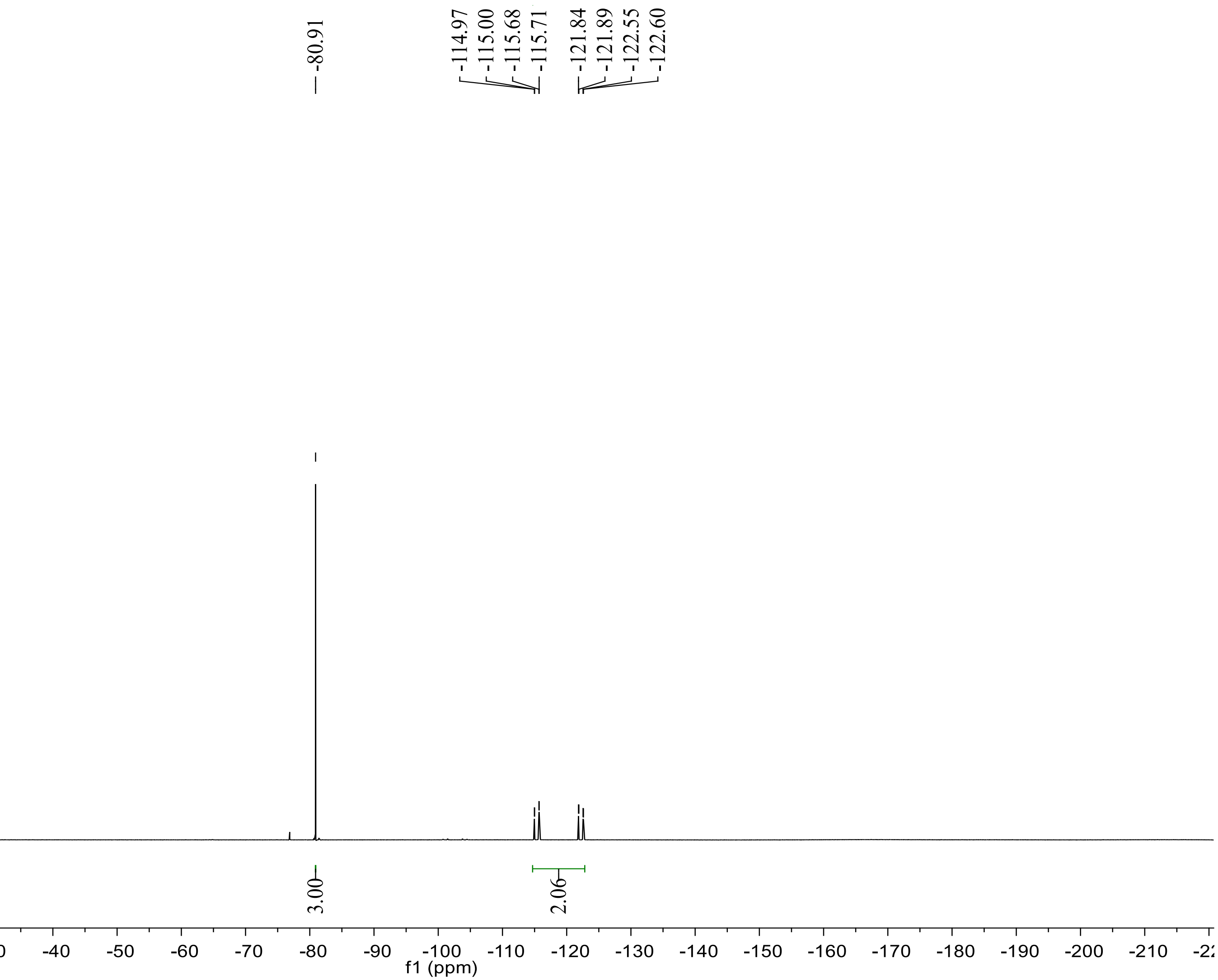
Supplementary Fig. 121. ^{13}C NMR (151 MHz, $CDCl_3$) of **3z**



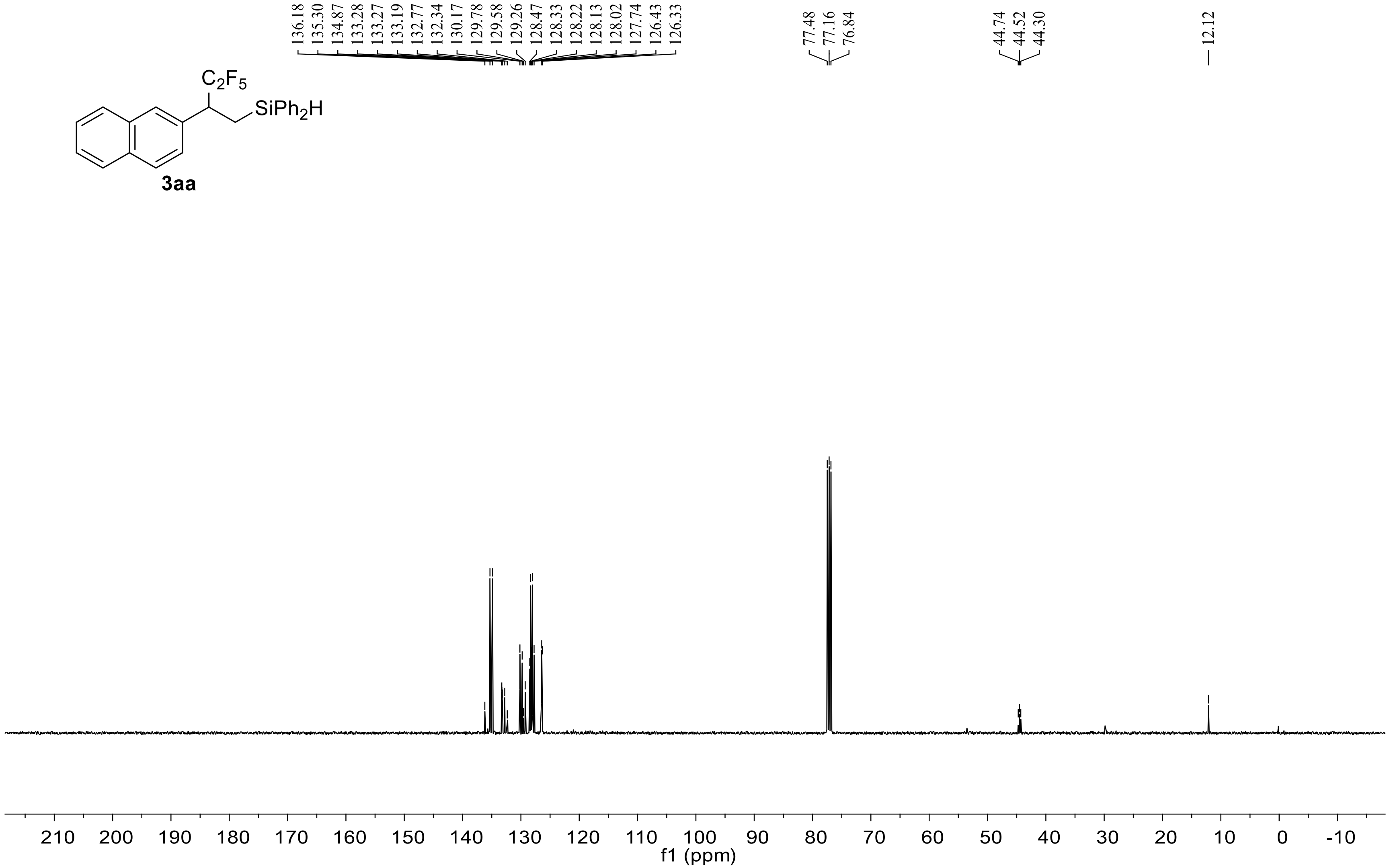
Supplementary Fig. 122. ^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



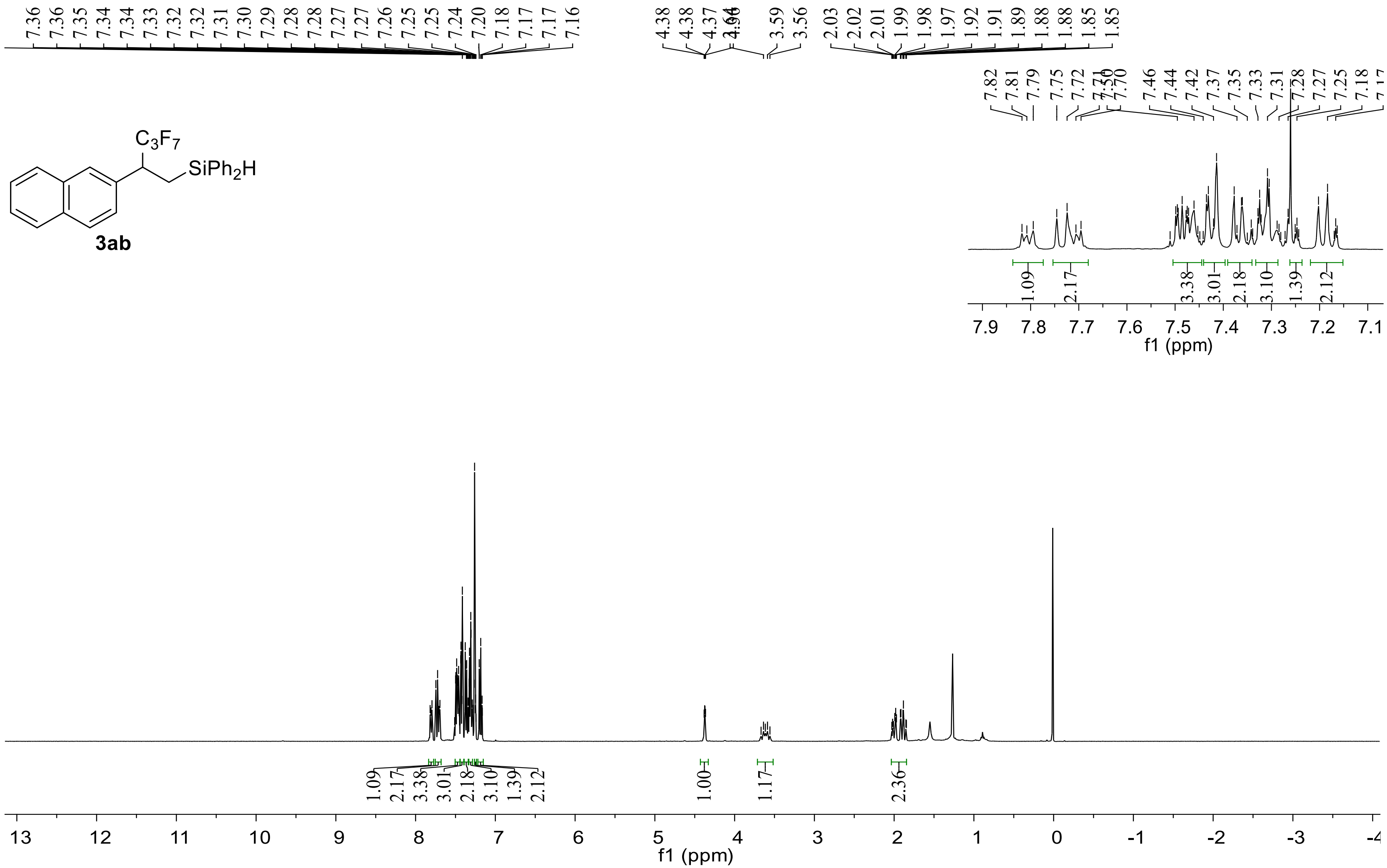
3aa



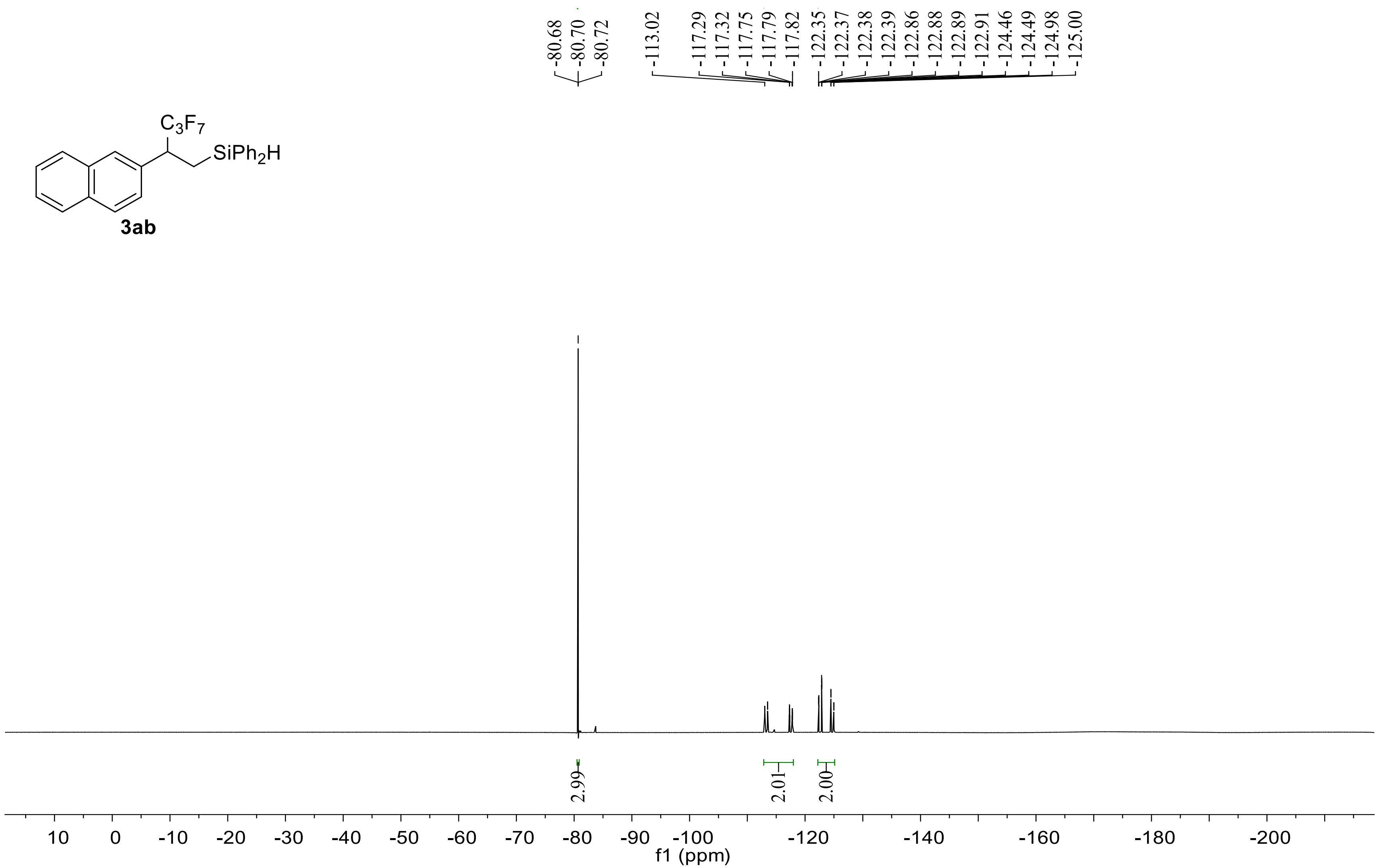
Supplementary Fig. 123. ^{19}F NMR (376 MHz, $CDCl_3$) of **3aa**



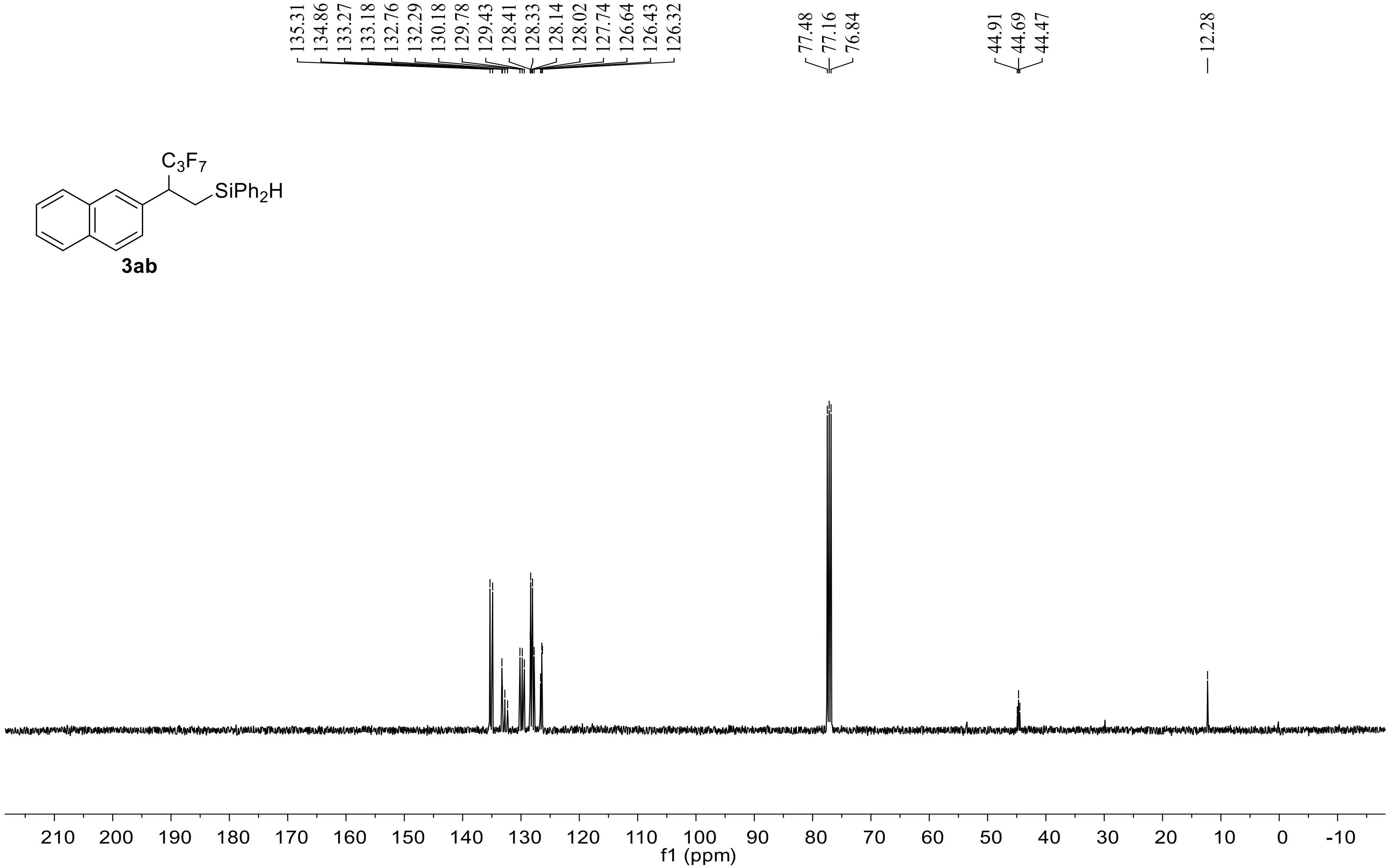
Supplementary Fig. 124. ^{13}C NMR (151 MHz, $CDCl_3$) of **3aa**



Supplementary Fig. 125. ^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**

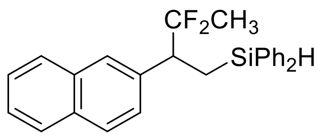


Supplementary Fig. 126. ^{19}F NMR (565 MHz, $CDCl_3$) of **3ab**

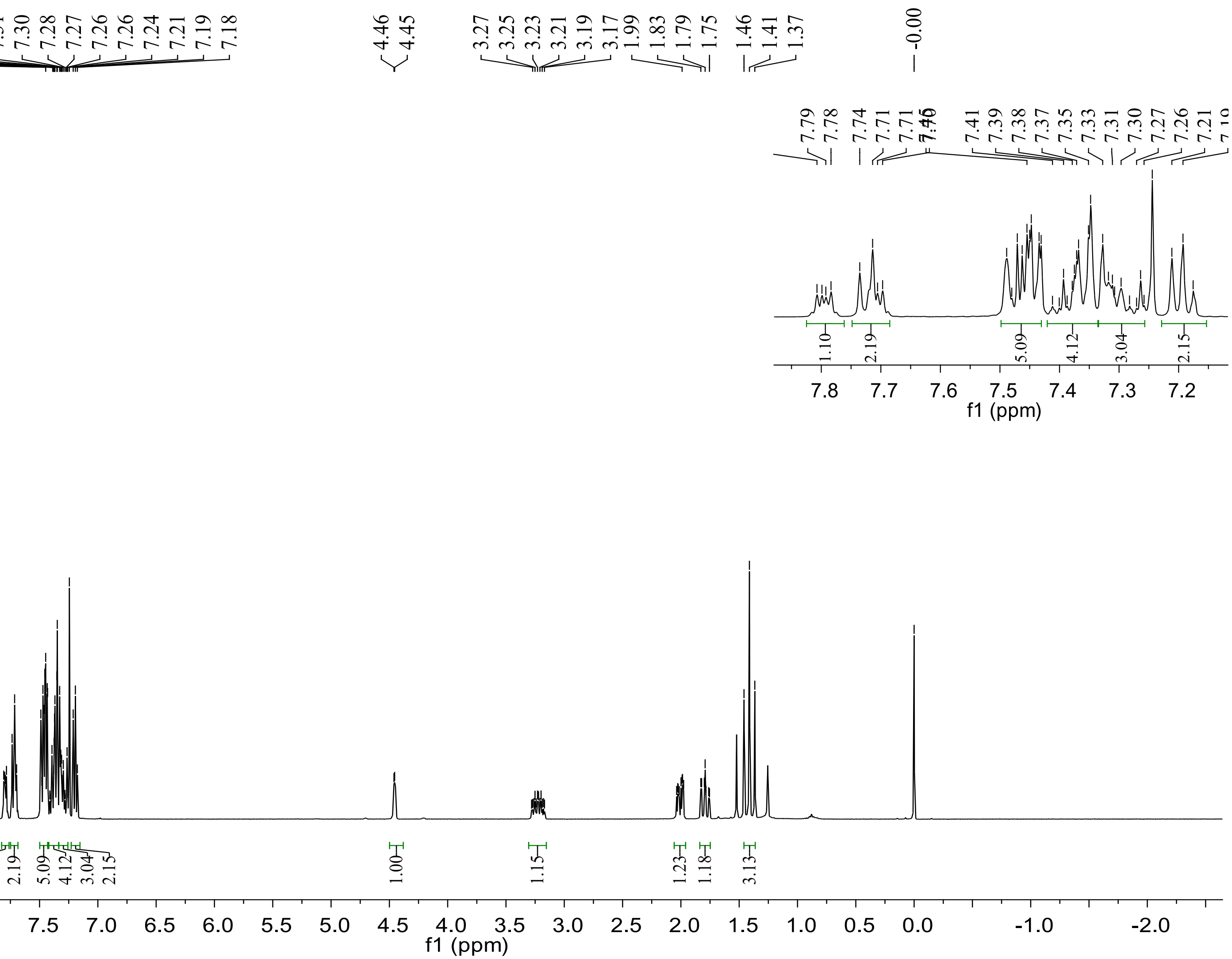


3ab

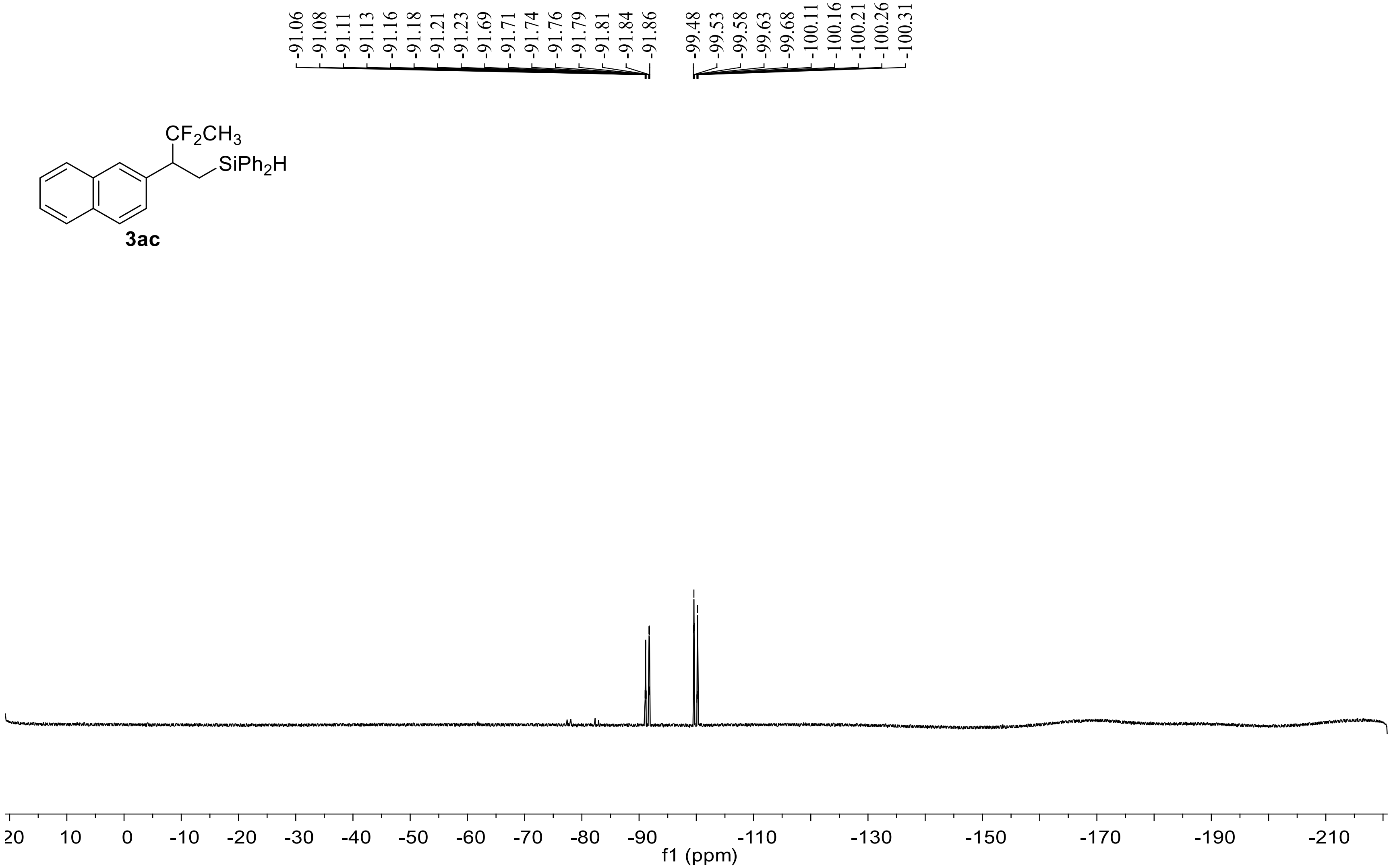
Supplementary Fig. 127. ^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



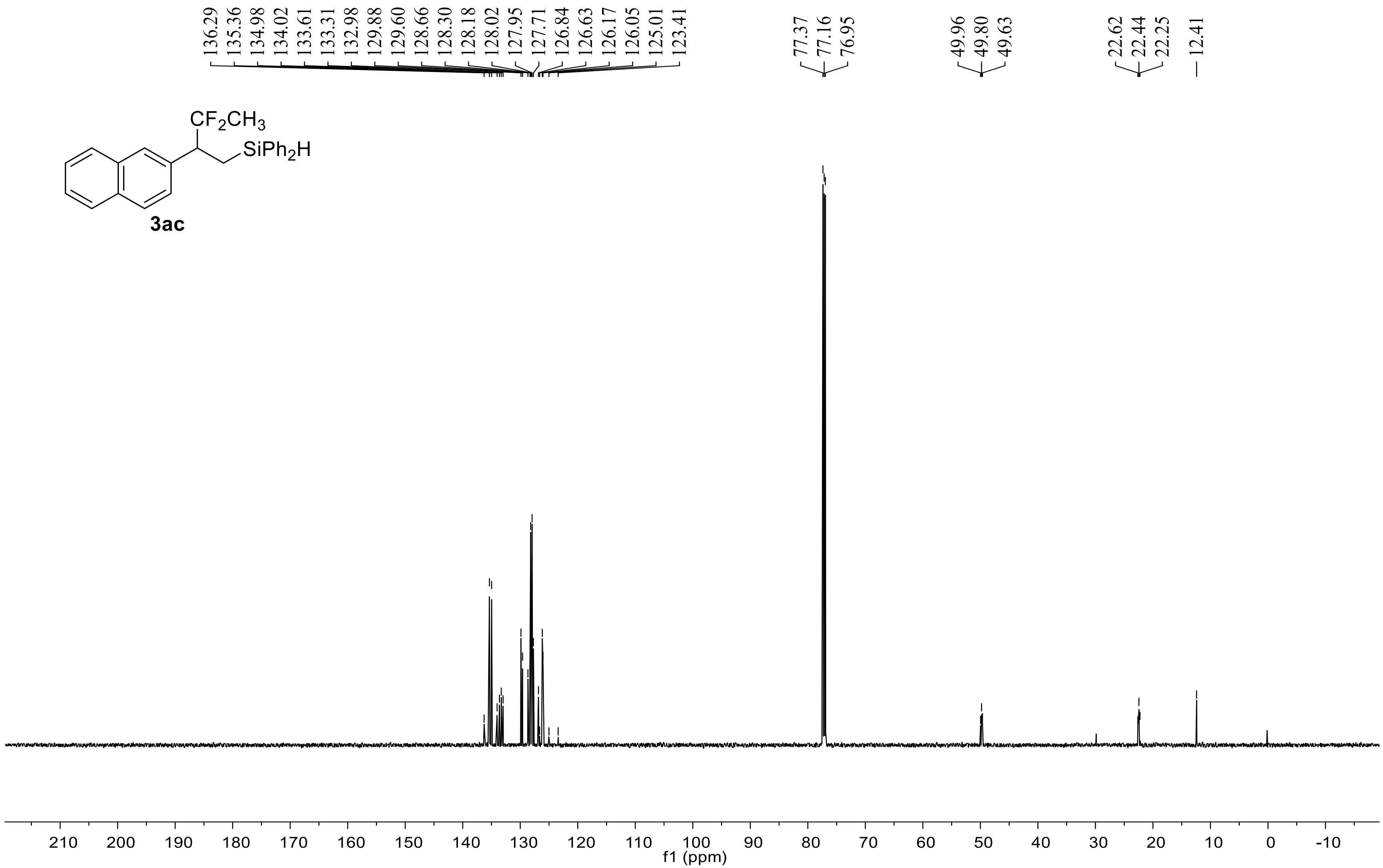
3ac



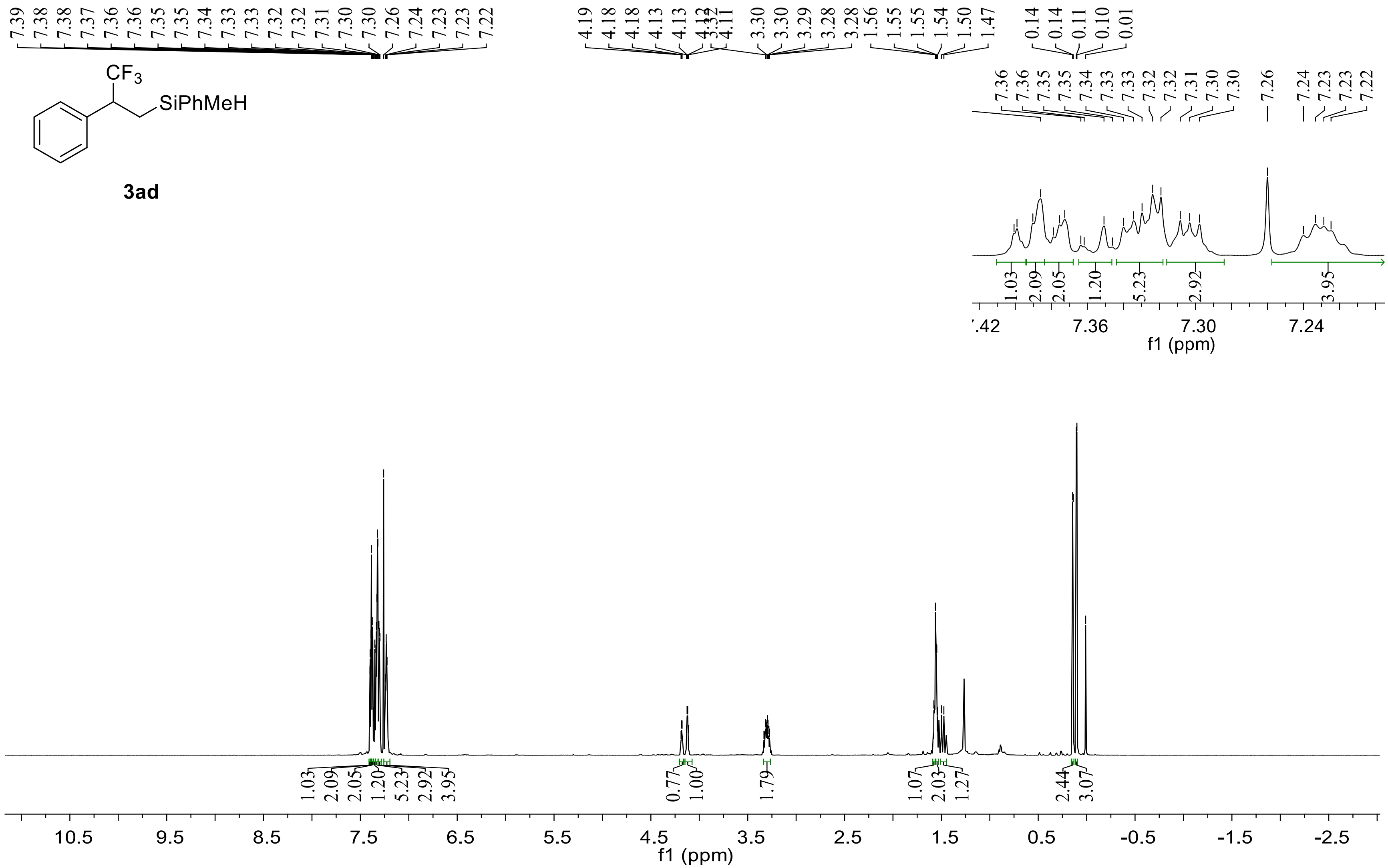
Supplementary Fig. 128. ^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



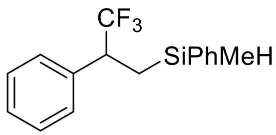
Supplementary Fig. 129. ^{19}F NMR (376 MHz, $CDCl_3$) of **3ac**



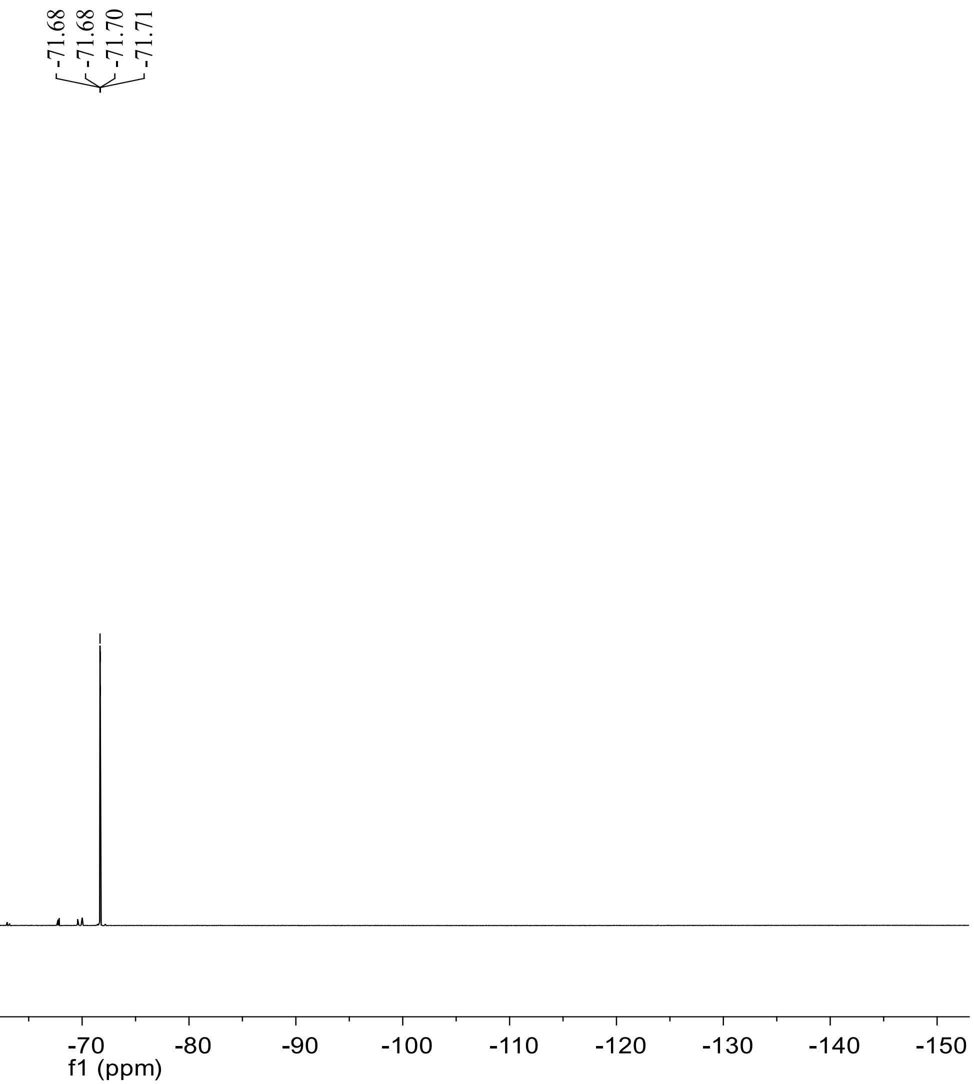
Supplementary Fig. 130. ^{13}C NMR (151 MHz, $CDCl_3$) of **3ac**



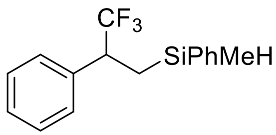
Supplementary Fig. 131. ^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



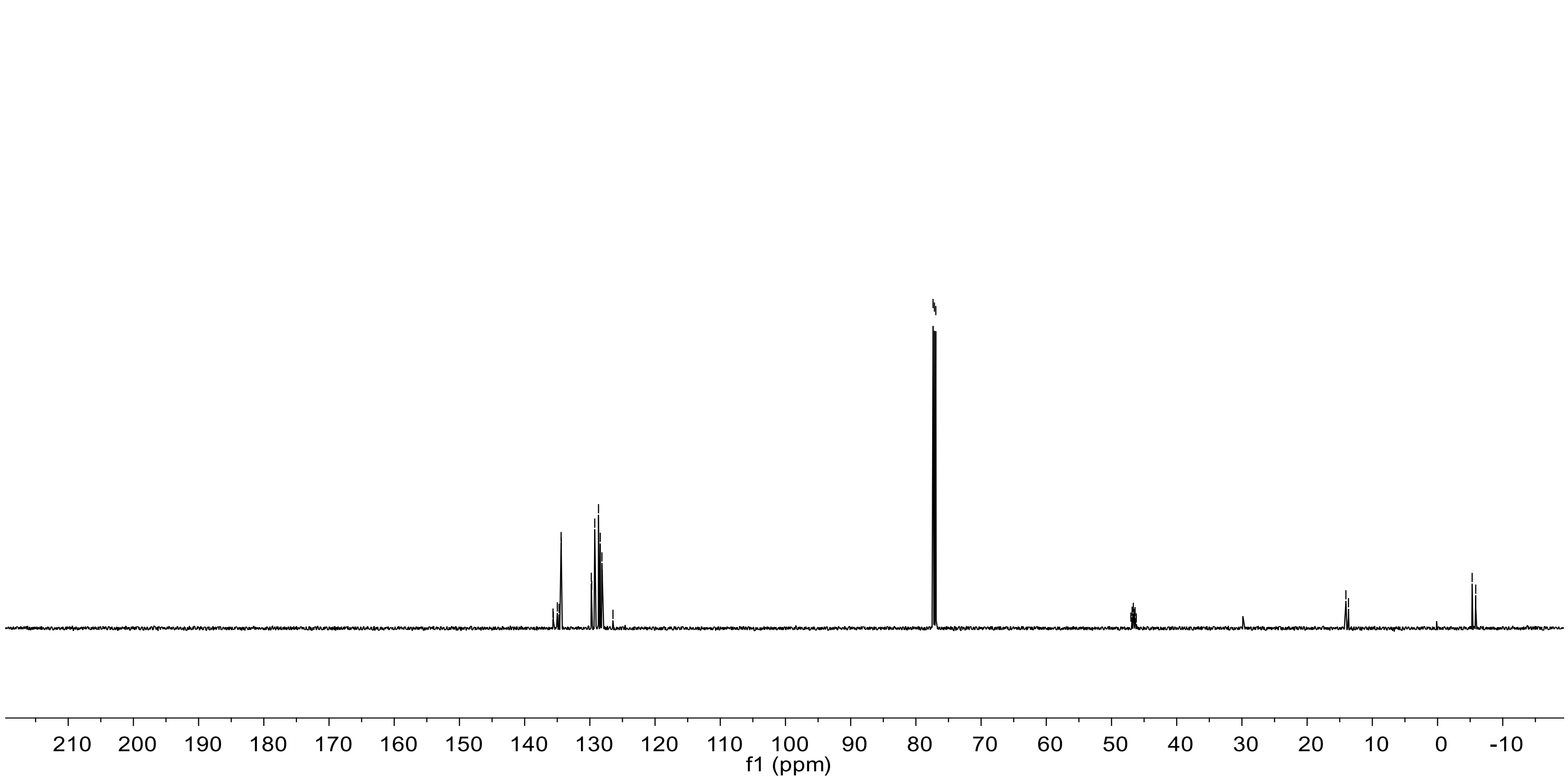
3ad



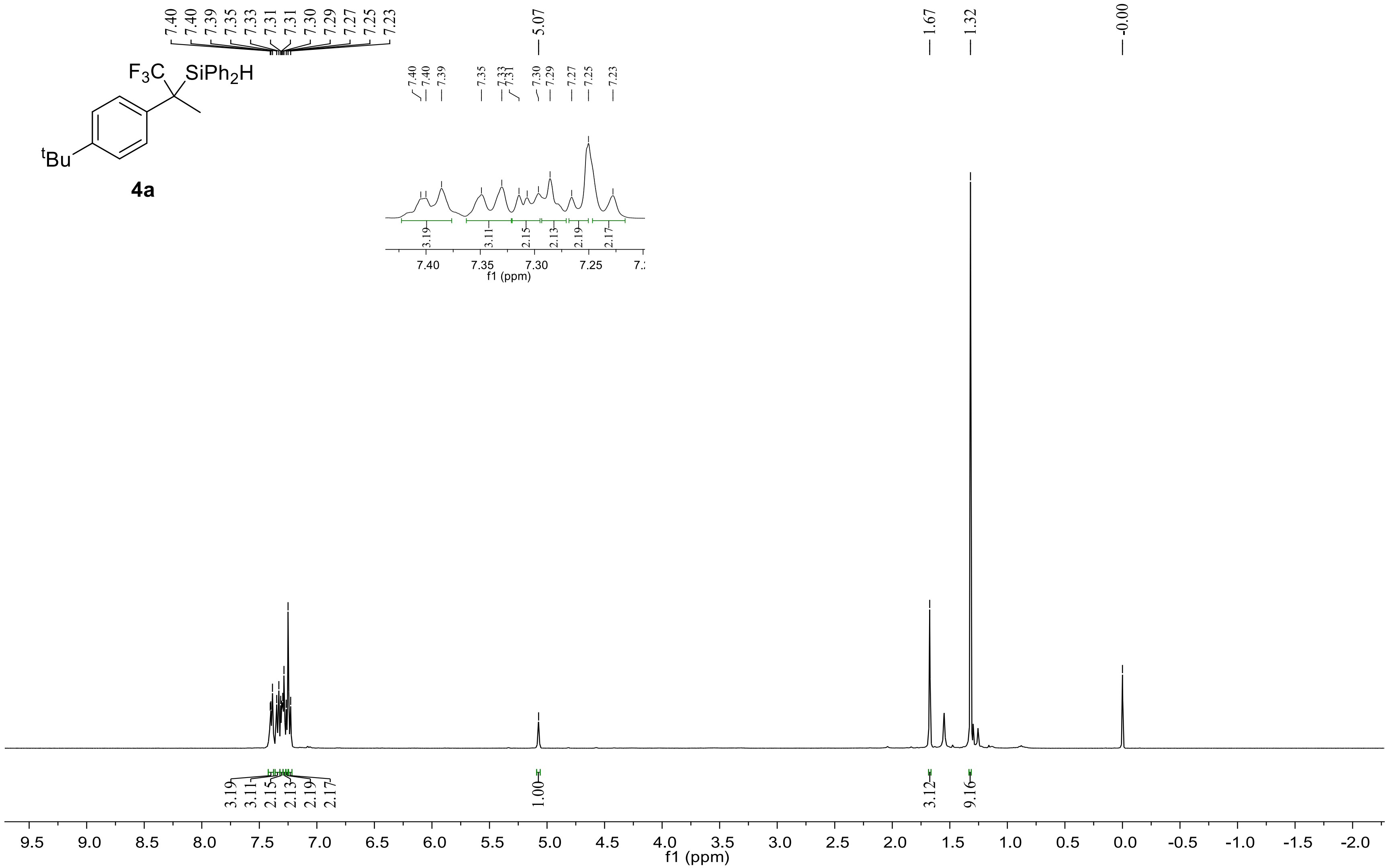
Supplementary Fig. 132. ^{19}F NMR (376 MHz, $CDCl_3$) of **3ad**



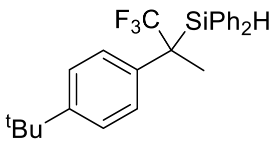
3ad



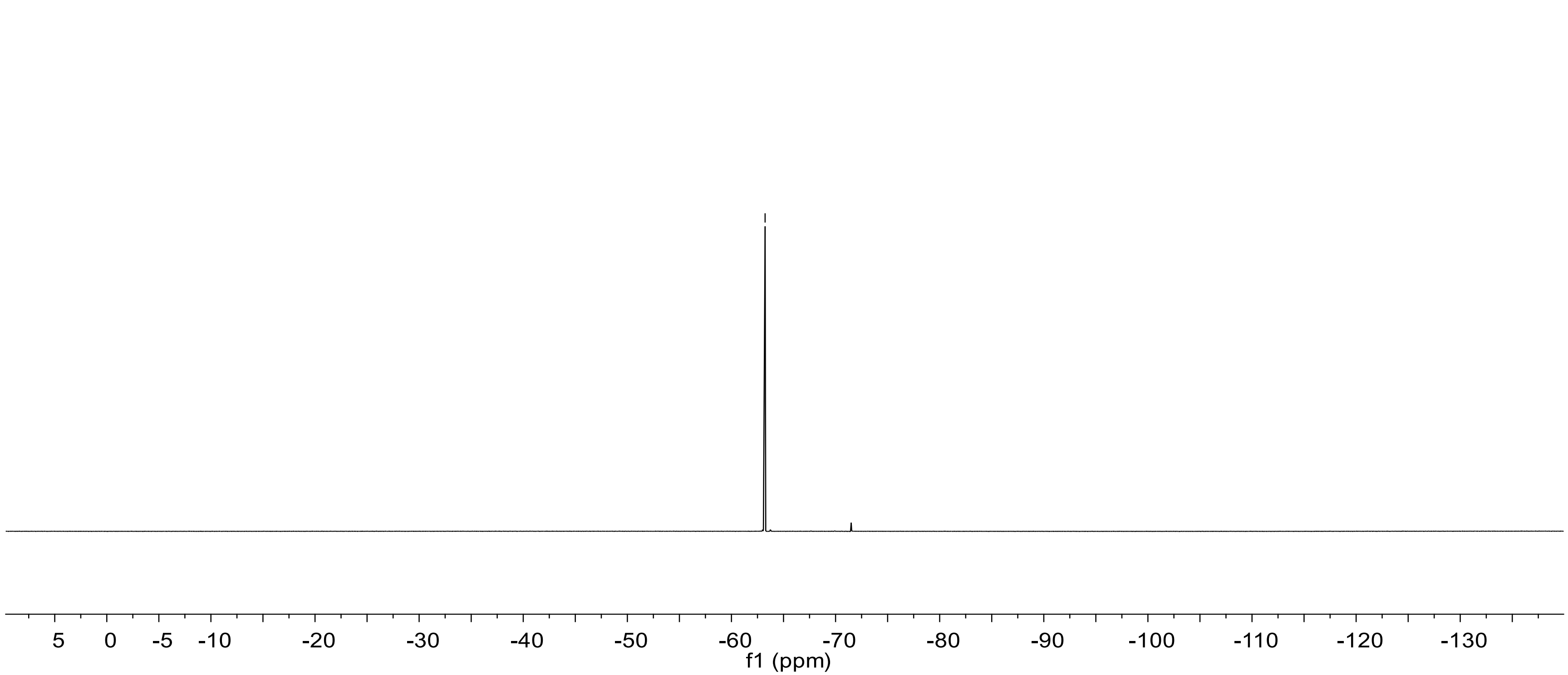
Supplementary Fig. 133. ^{13}C NMR (151 MHz, $CDCl_3$) of **3ad**



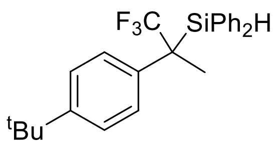
Supplementary Fig. 134. ^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



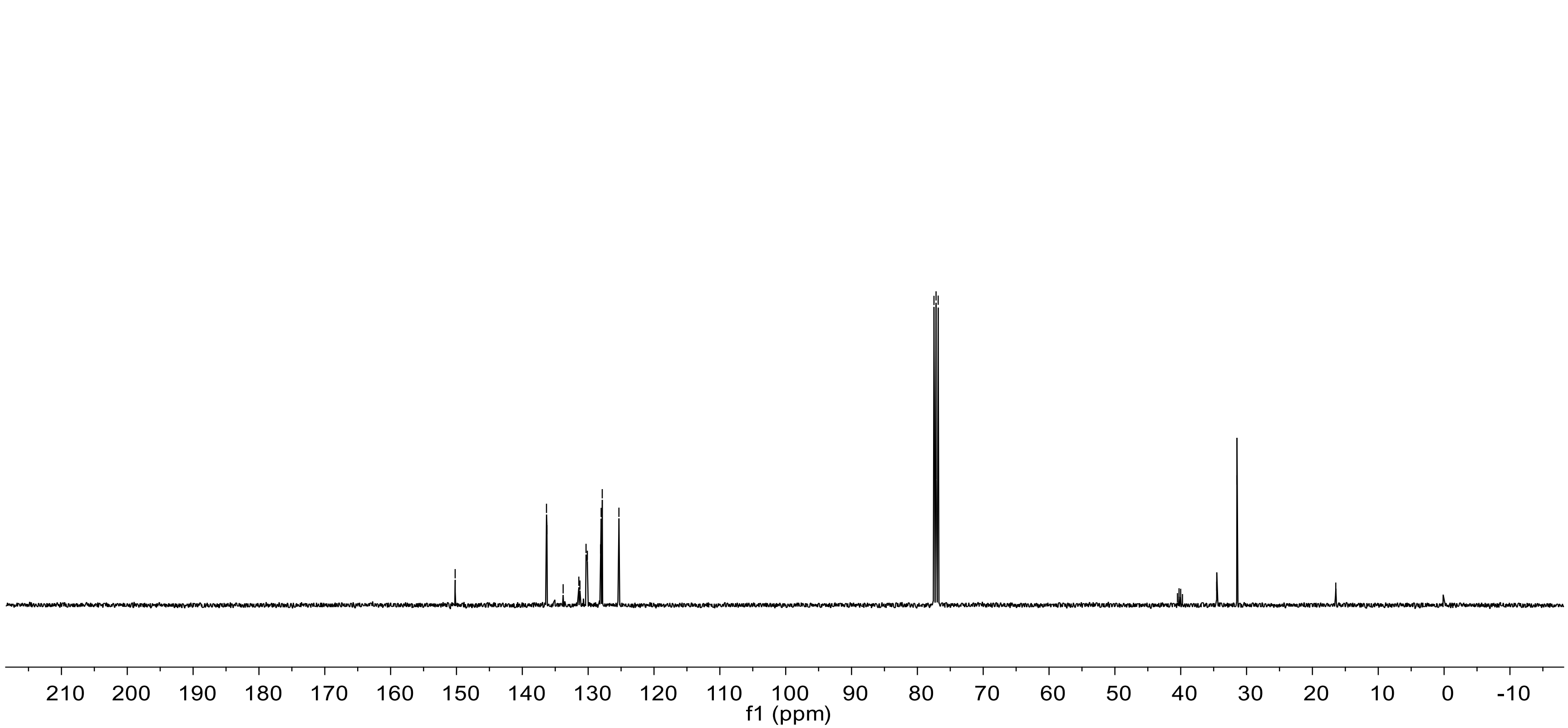
4a



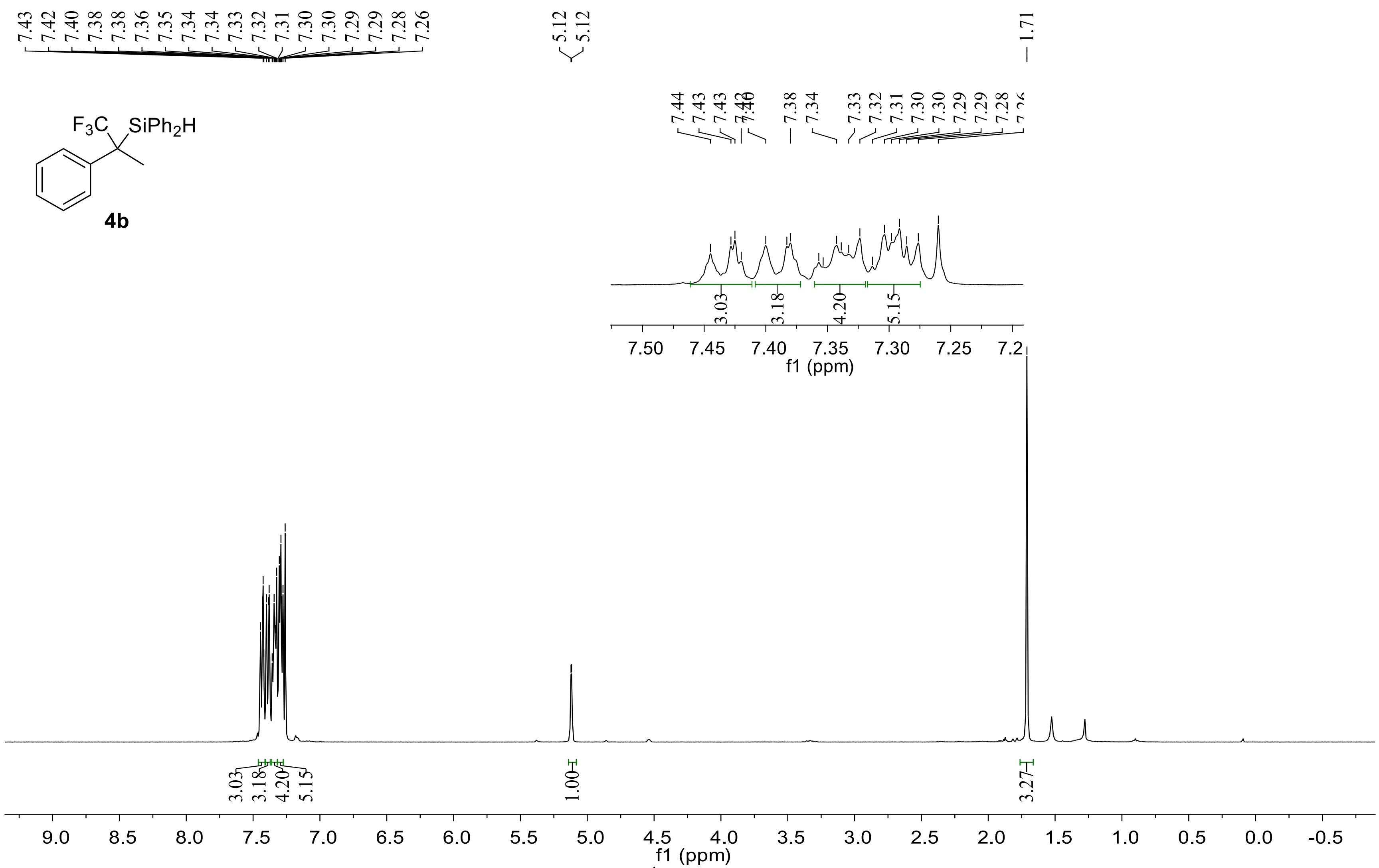
Supplementary Fig. 135. ^{19}F NMR (377 MHz, $CDCl_3$) of **4a**



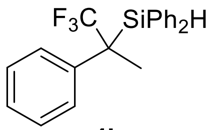
4a



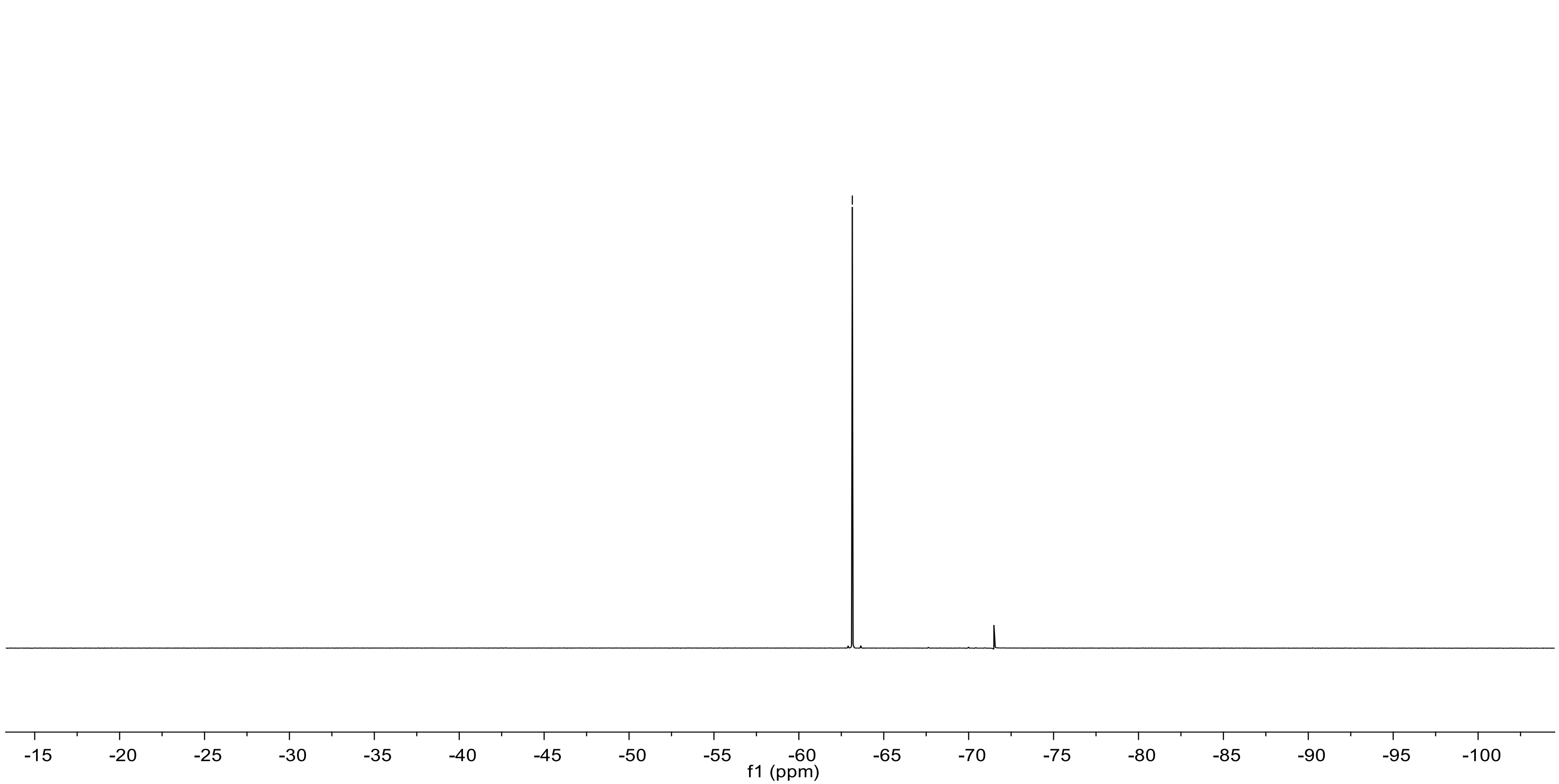
Supplementary Fig. 136. ^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



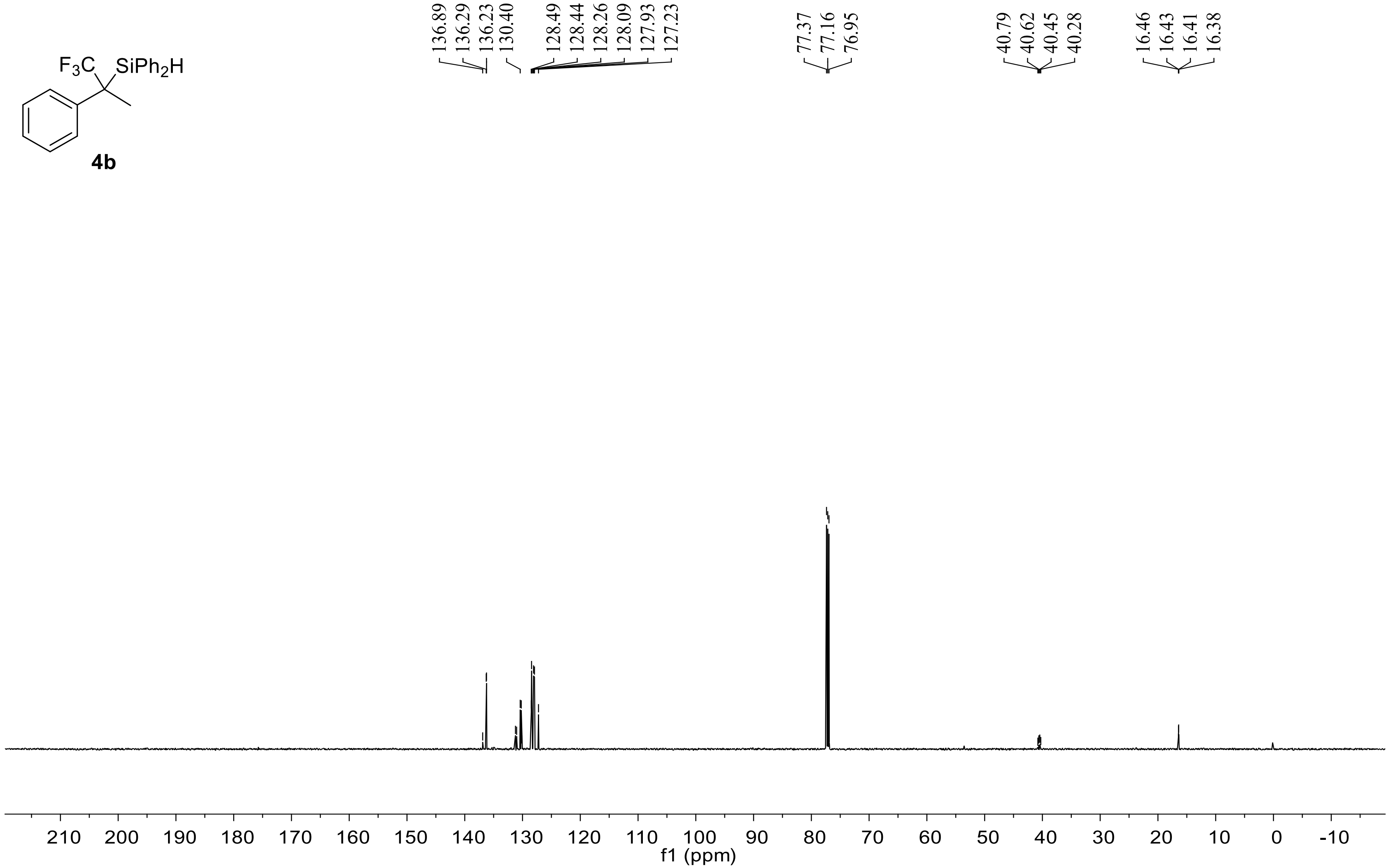
Supplementary Fig. 137. ^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



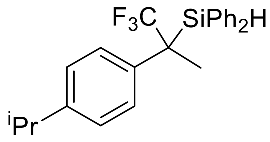
4b



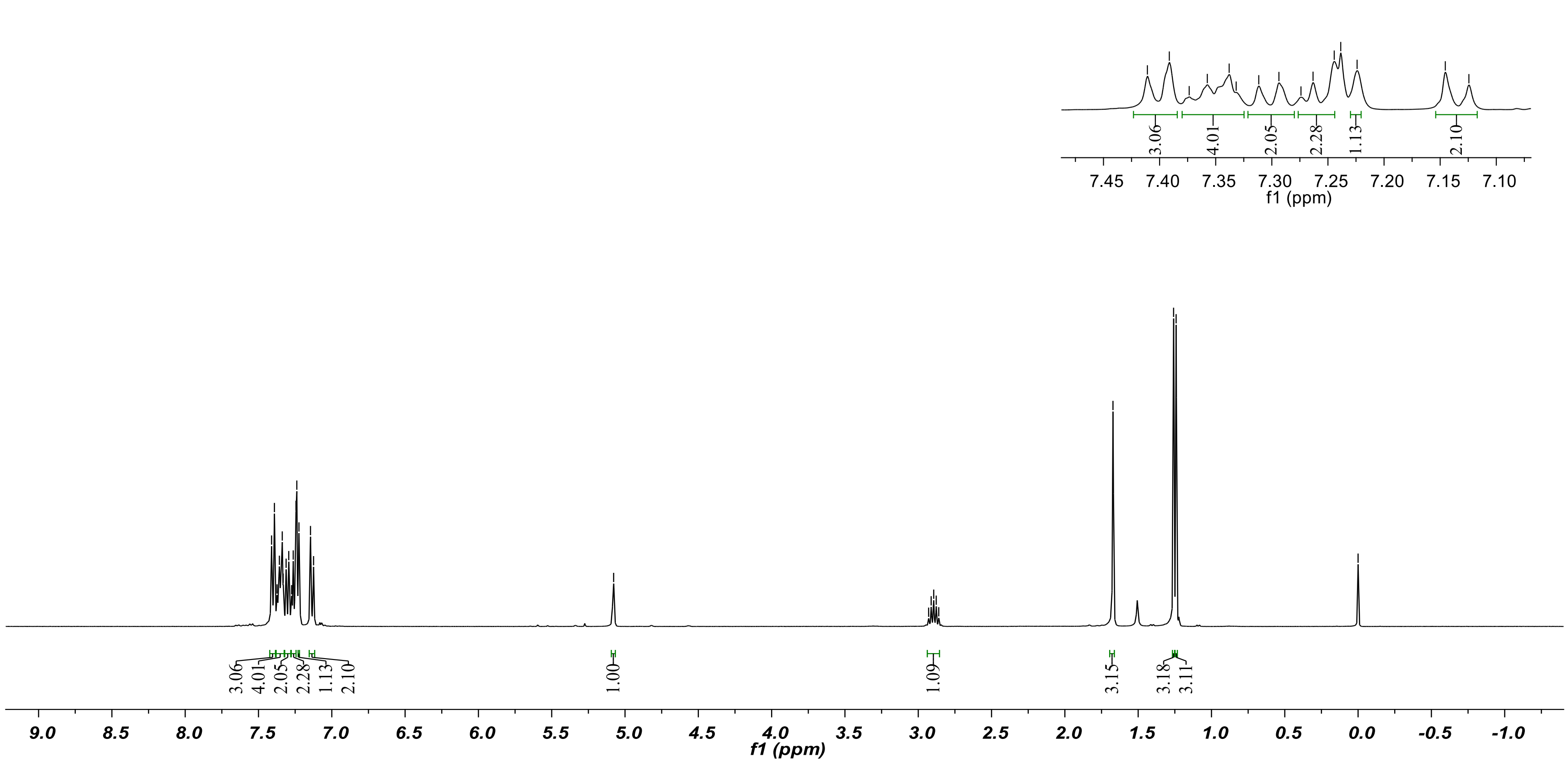
Supplementary Fig. 138. ^{19}F NMR (377 MHz, $CDCl_3$) of **4b**



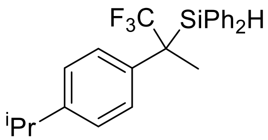
Supplementary Fig. 139. ^{13}C NMR (377 MHz, $CDCl_3$) of **4b**



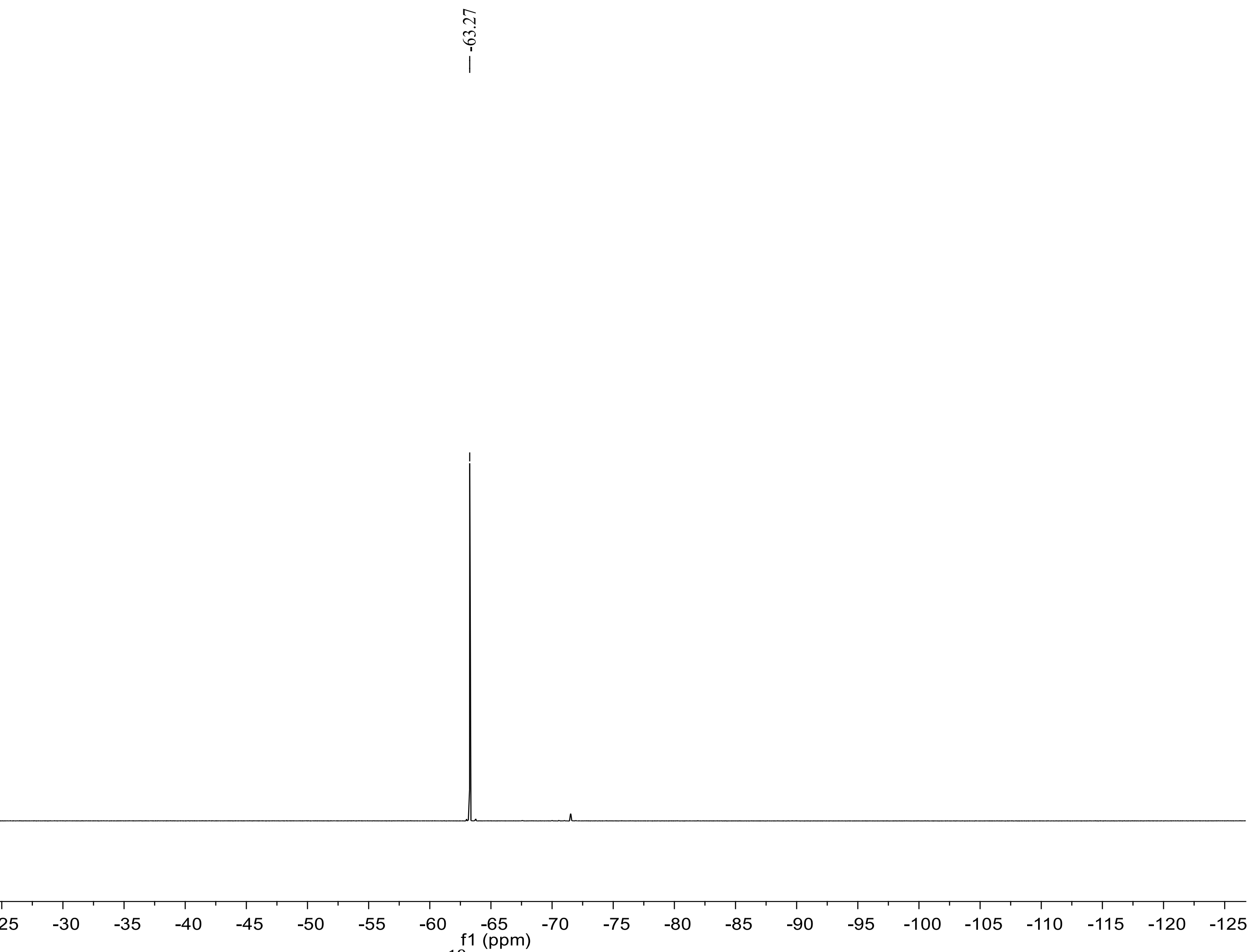
4c



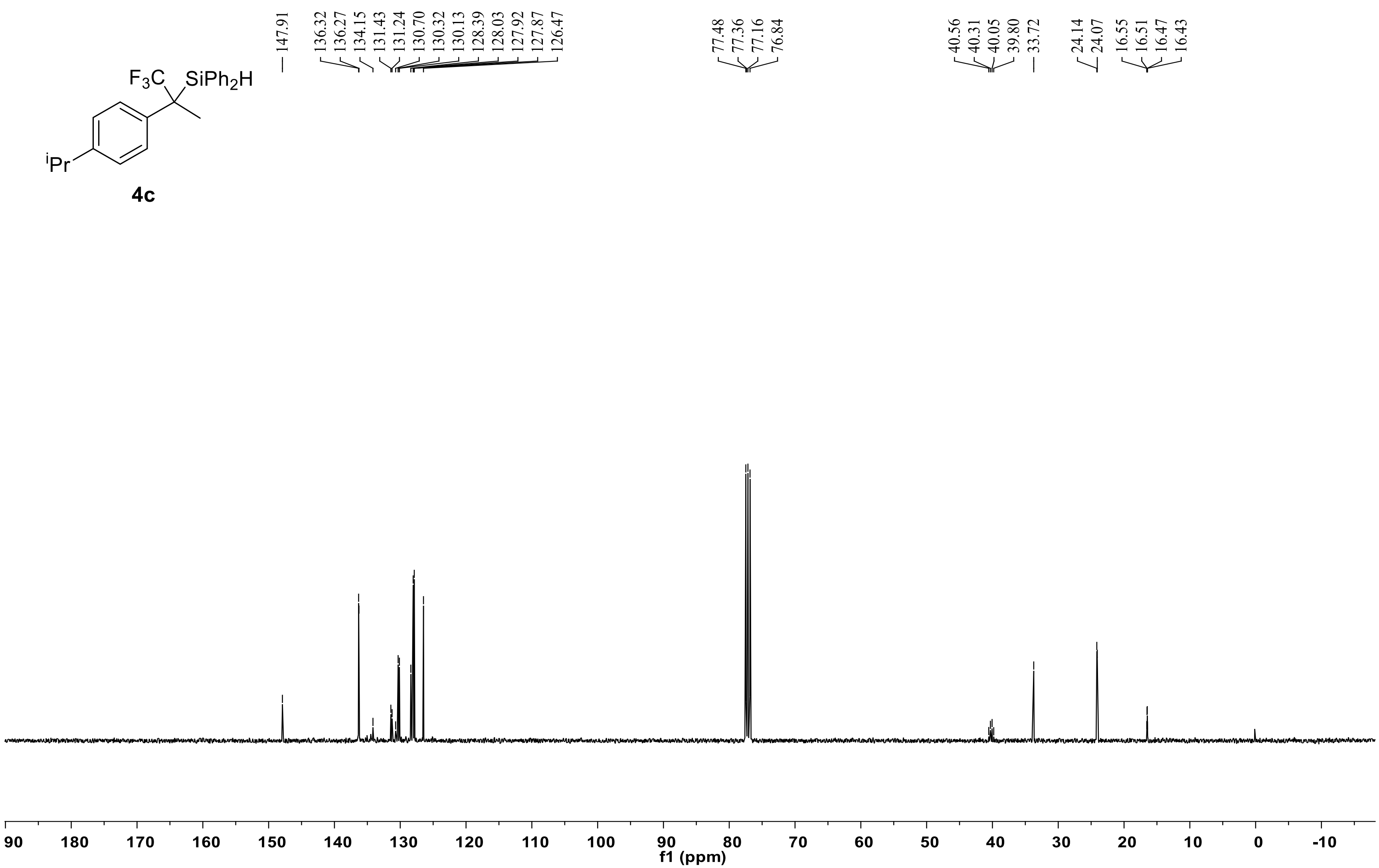
Supplementary Fig. 140. ¹H NMR (400 MHz, $CDCl_3$) of **4c**



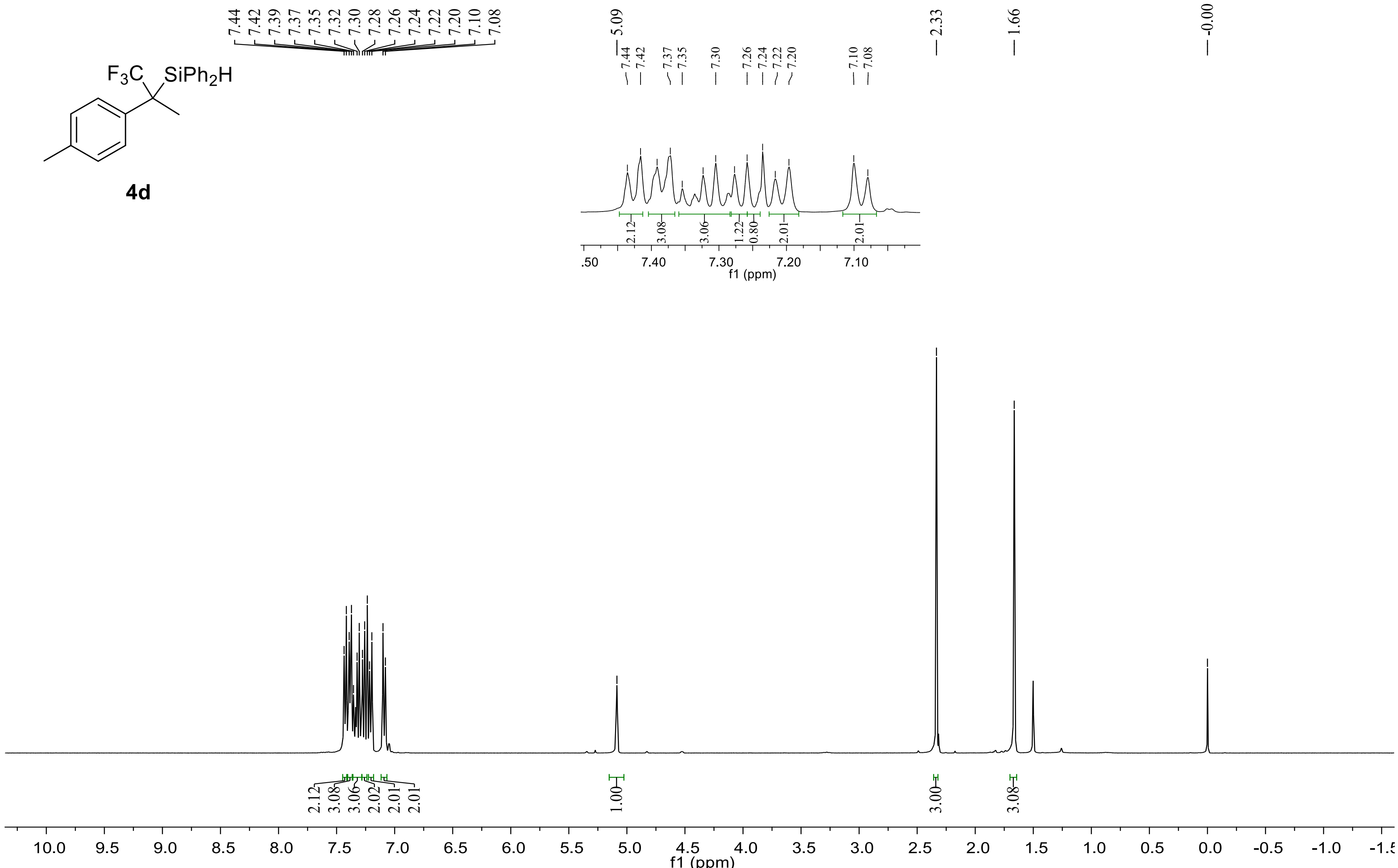
4c



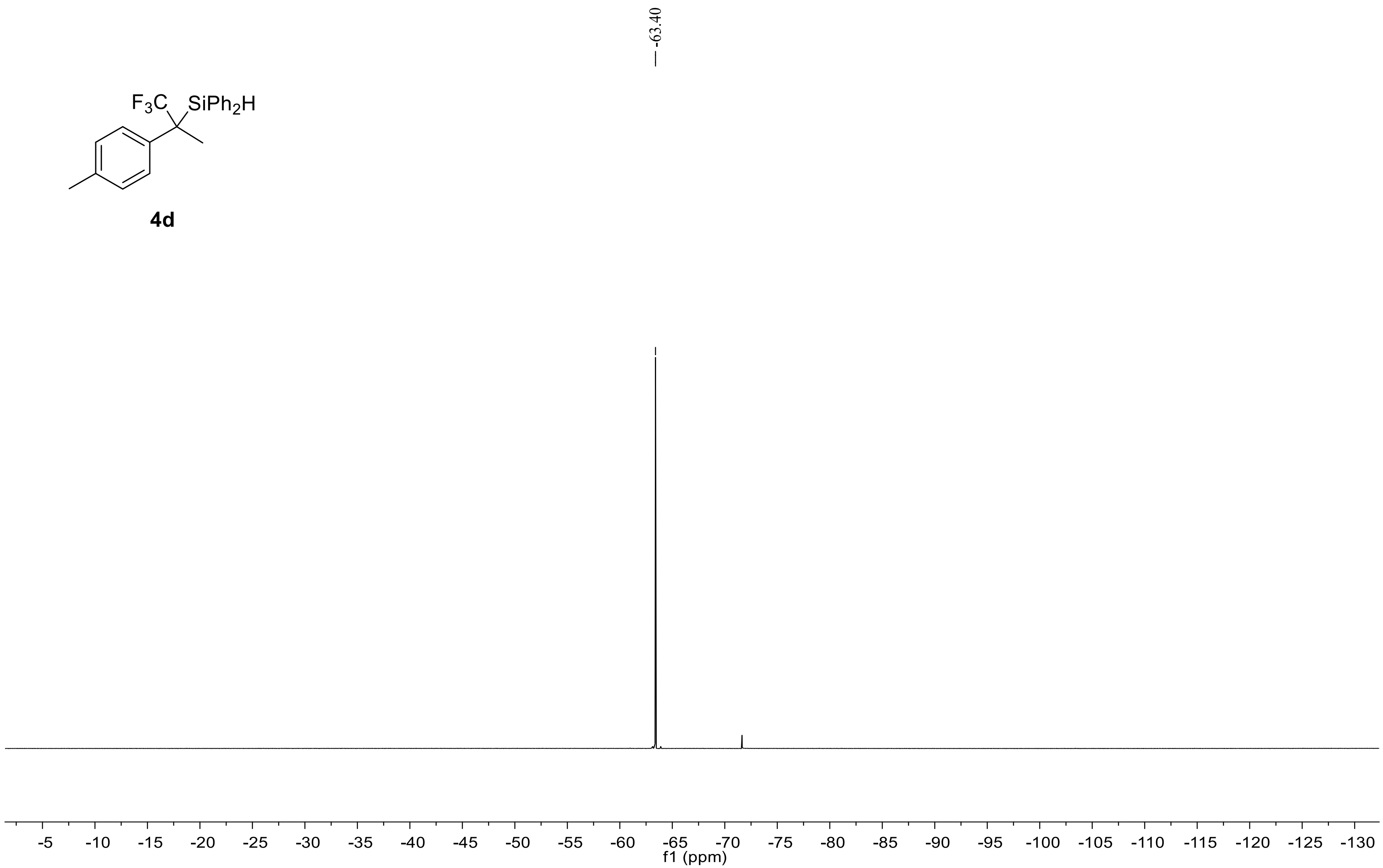
Supplementary Fig. 141. ^{19}F NMR (377 MHz, $CDCl_3$) of **4c**



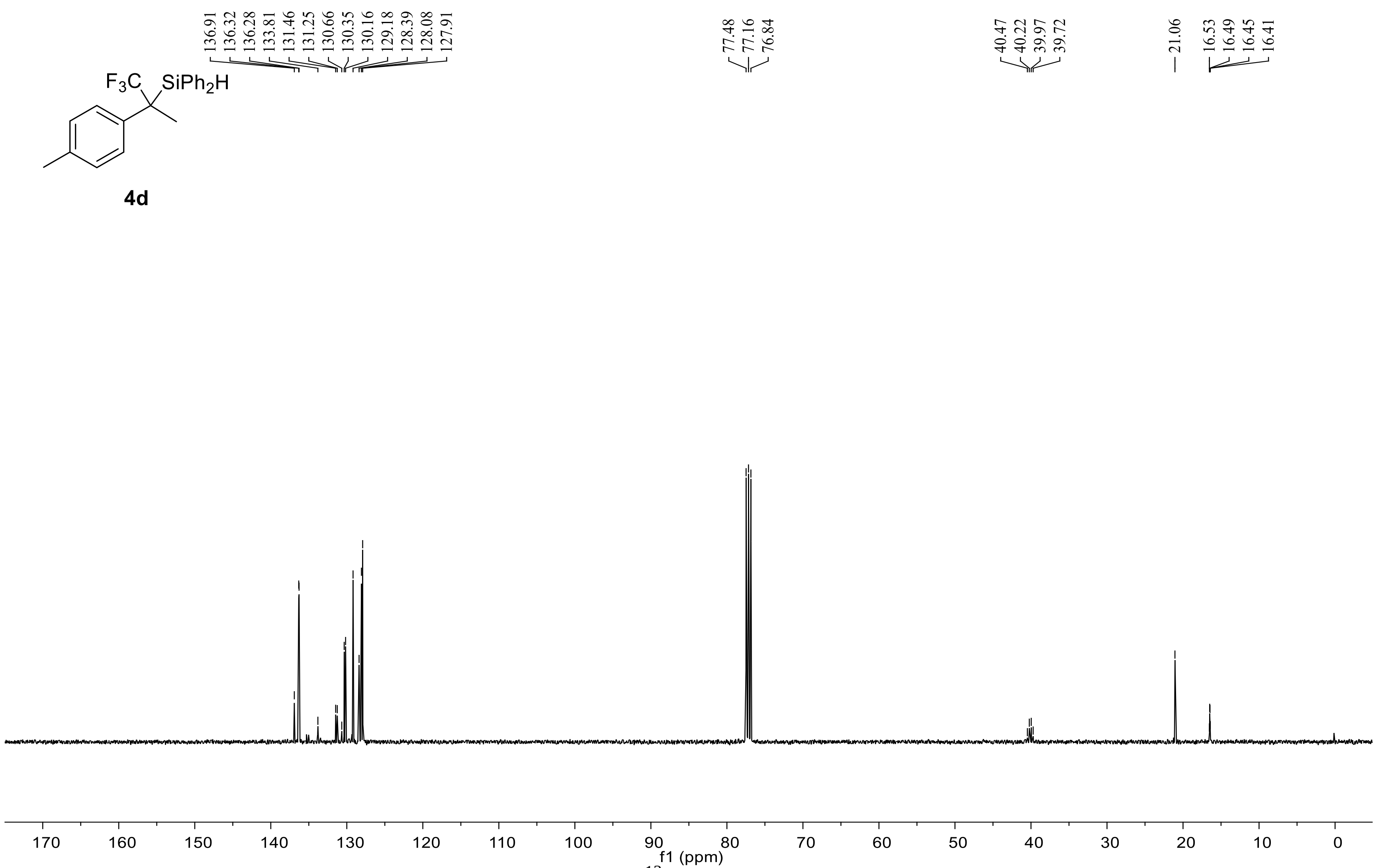
Supplementary Fig. 142. ^{13}H NMR (101 MHz, $CDCl_3$) of **4c**



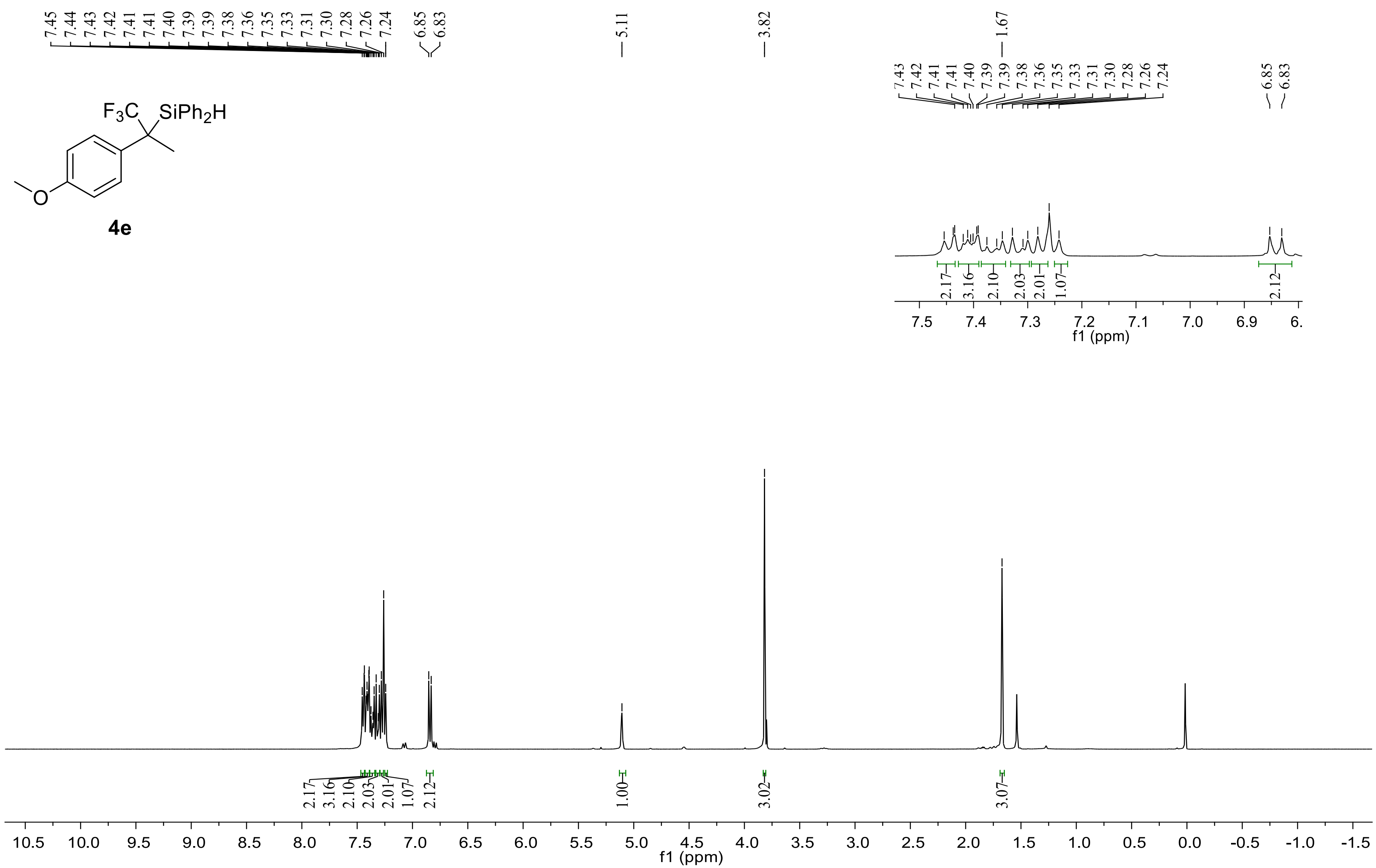
Supplementary Fig. 143. ^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



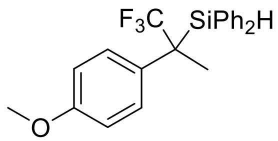
Supplementary Fig. 144. ^{19}F NMR (377 MHz, $CDCl_3$) of **4d**



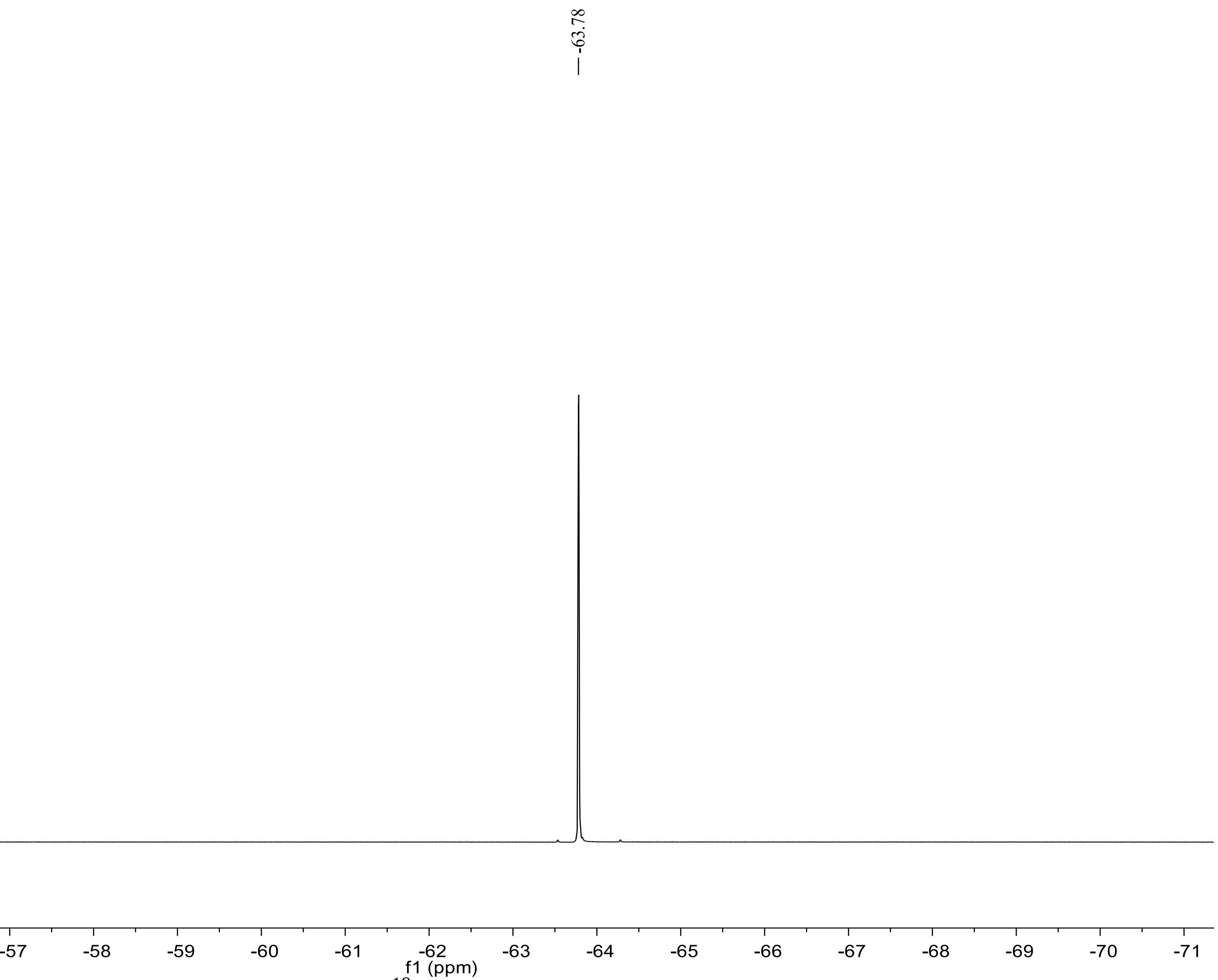
Supplementary Fig. 145. ^{13}C NMR (101 MHz, $CDCl_3$) of **4d**



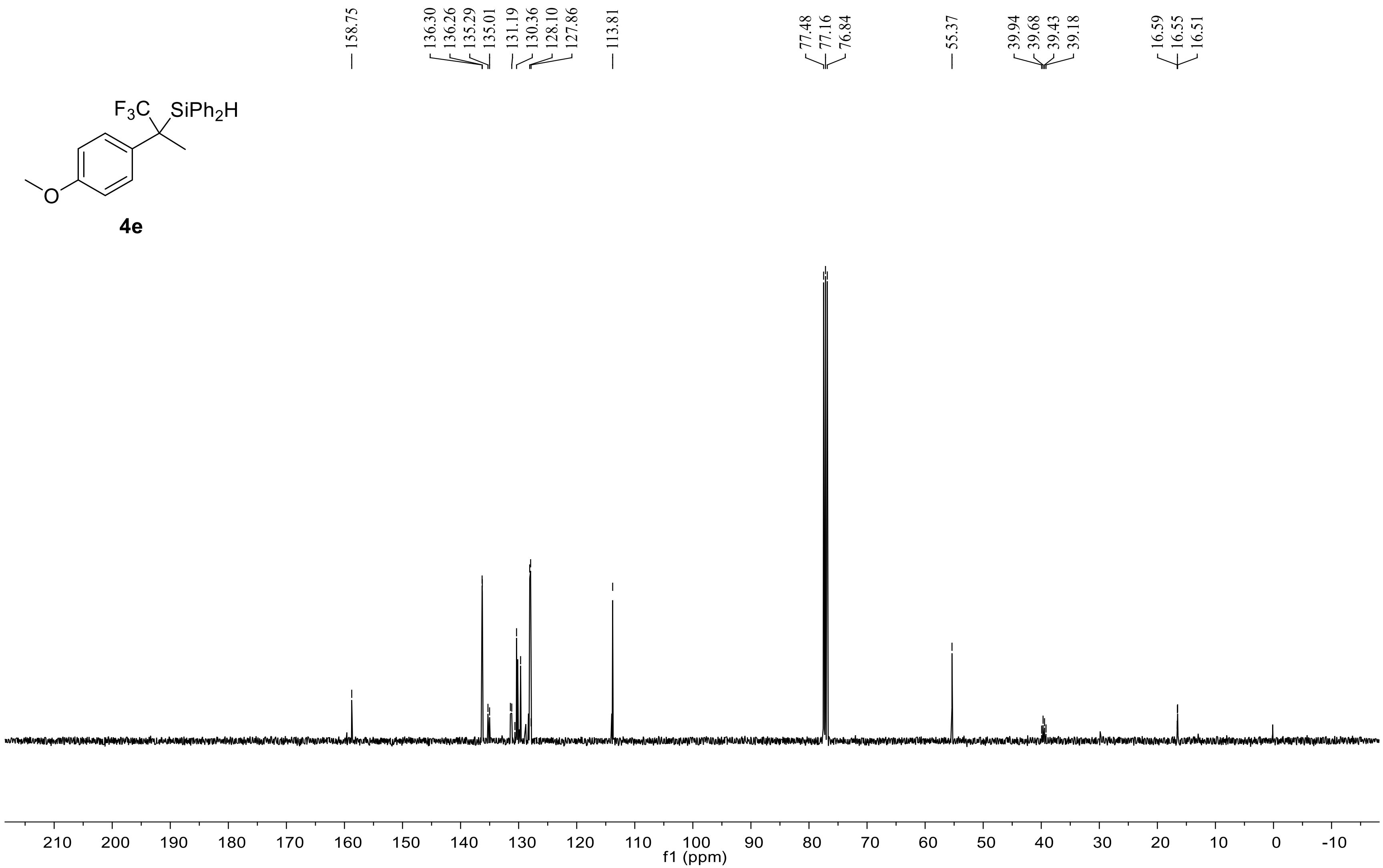
Supplementary Fig. 146. ^{1}H NMR (101 MHz, $CDCl_3$) of **4d**



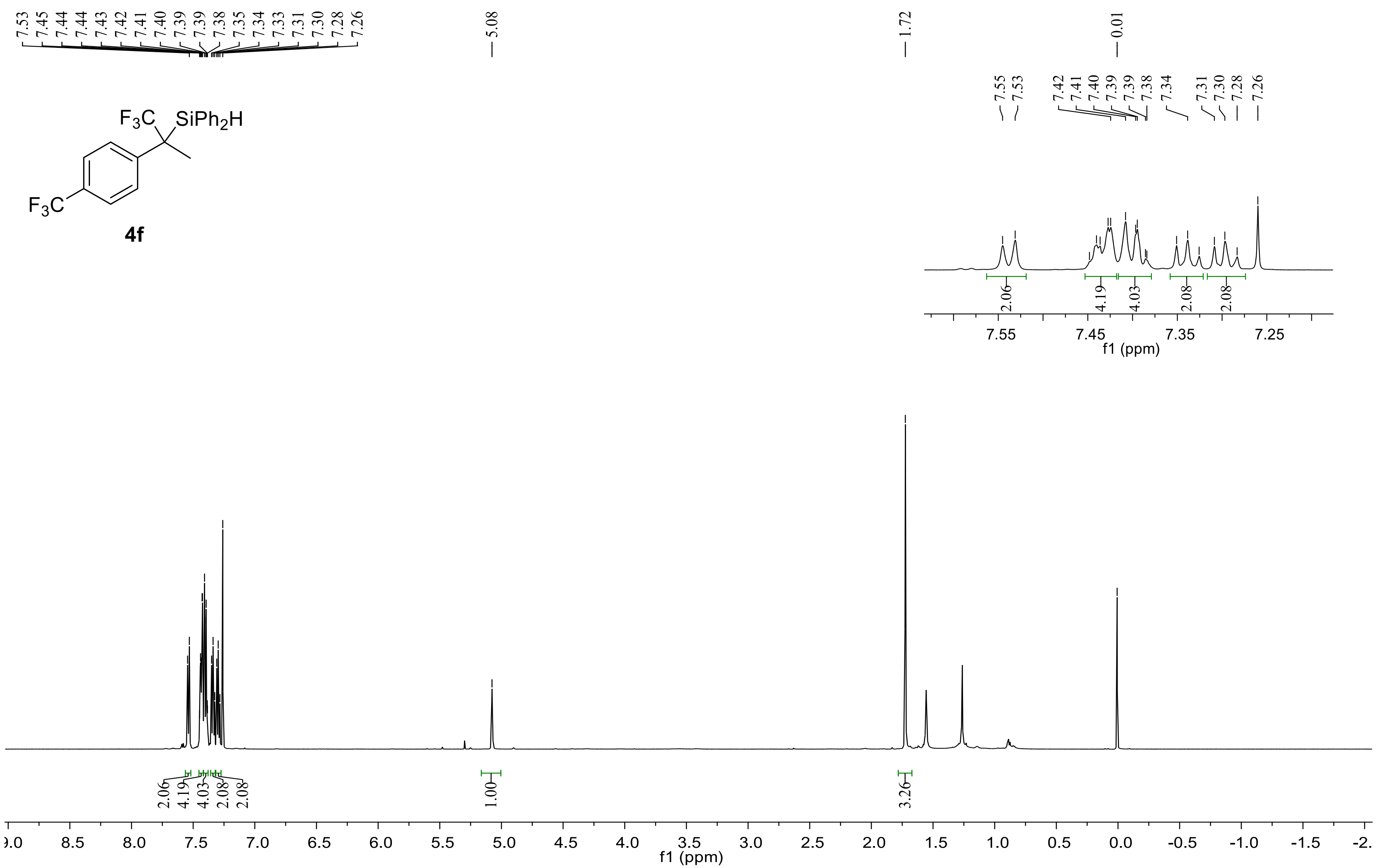
4e



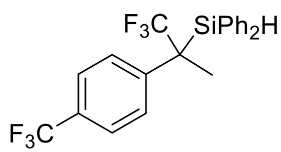
Supplementary Fig. 147. ^{19}F NMR (376 MHz, $CDCl_3$) of **4e**



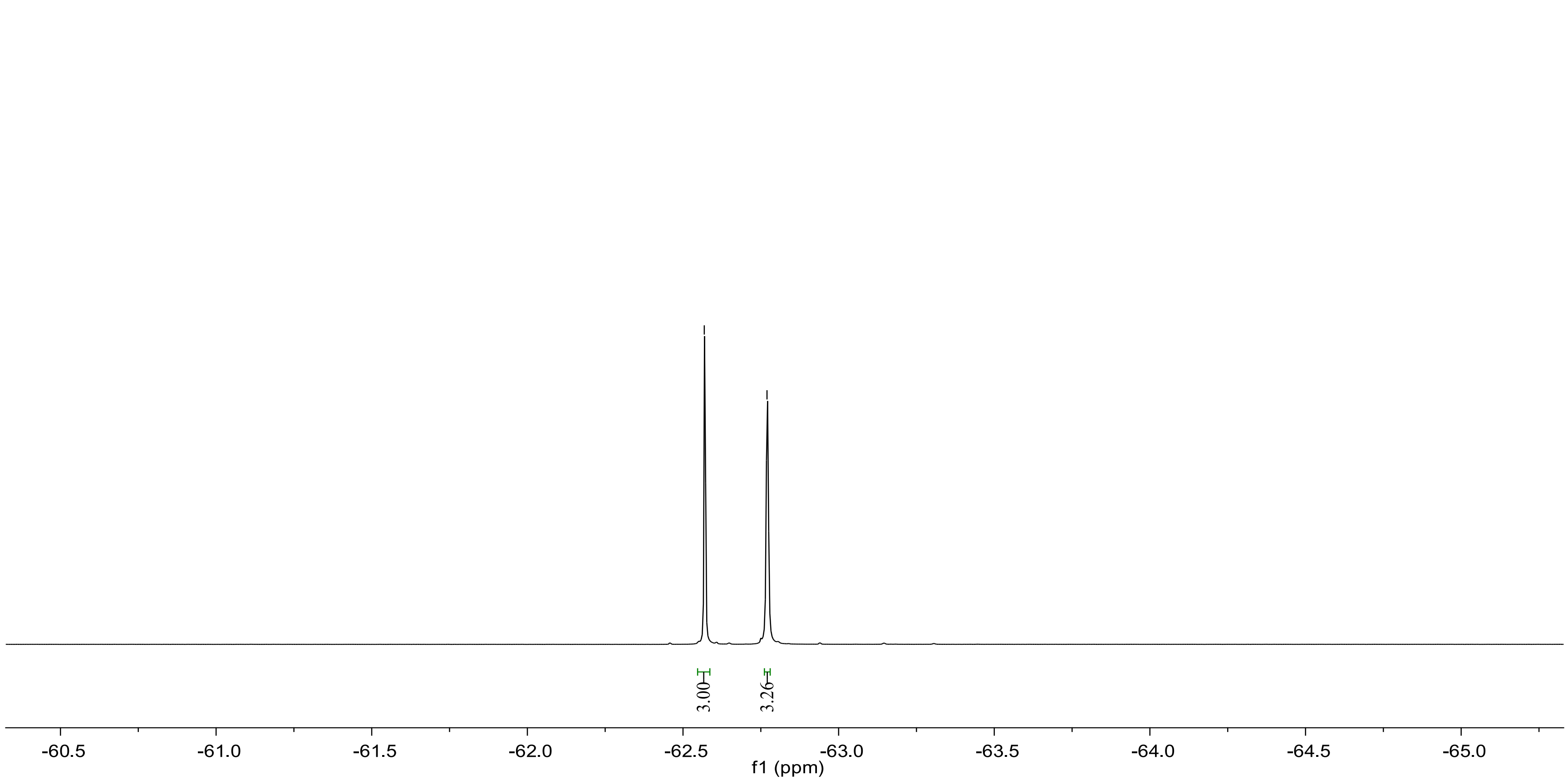
Supplementary Fig. 148. ^{13}C NMR (101 MHz, $CDCl_3$) of **4e**



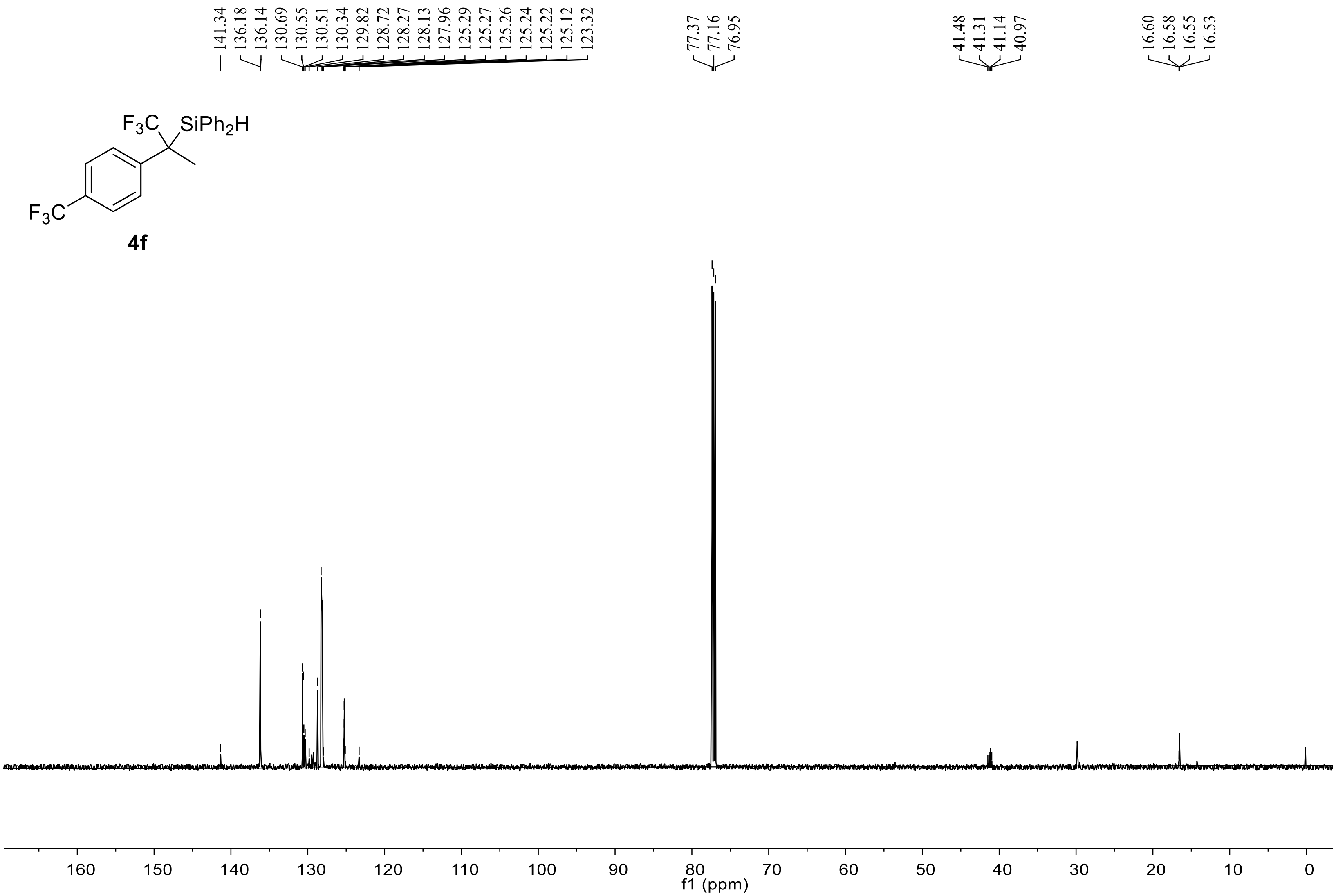
Supplementary Fig. 149. ^{1}H NMR (600 MHz, $CDCl_3$) of **4f**



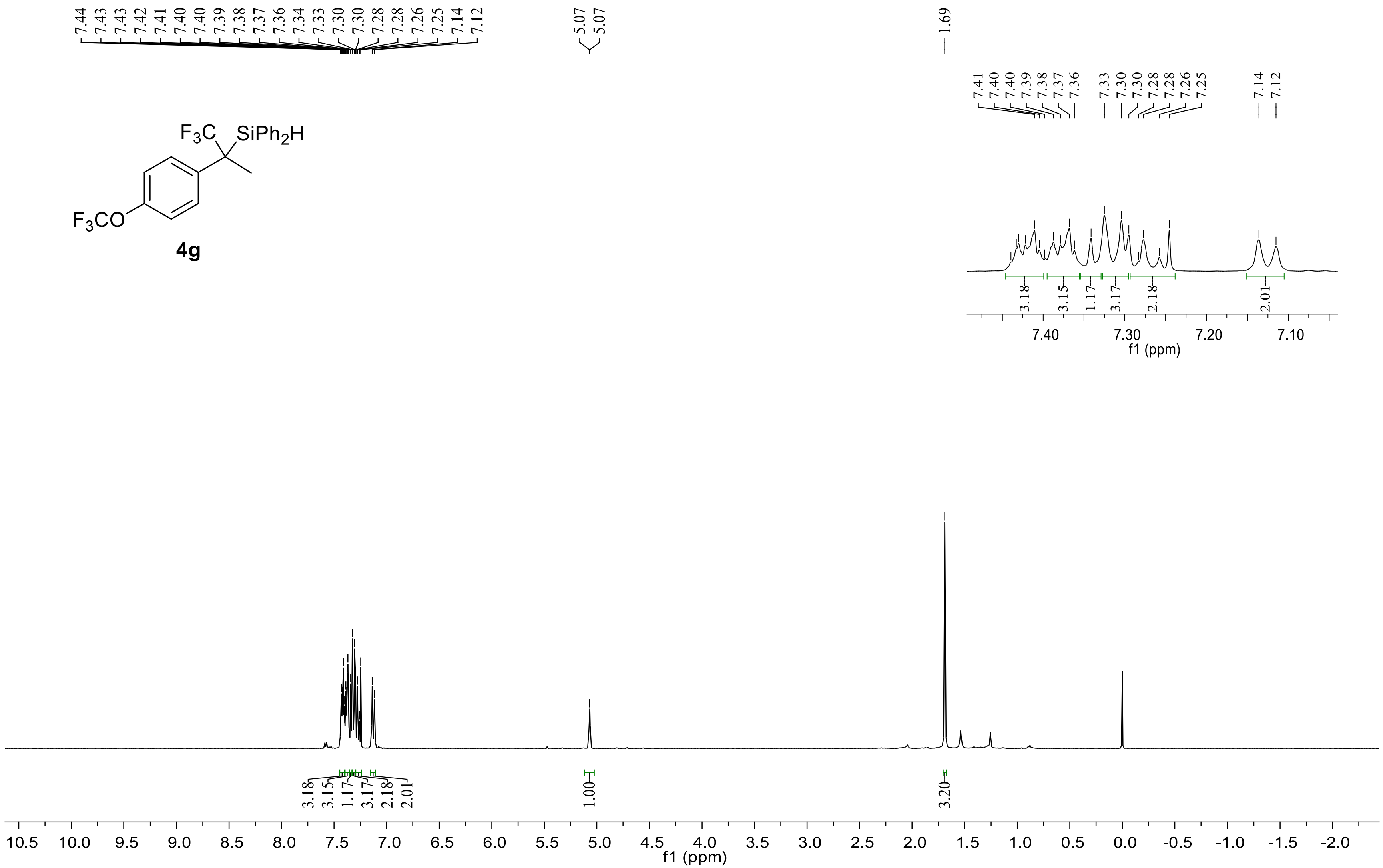
4f



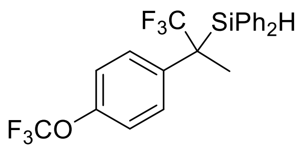
Supplementary Fig. 150. ^{19}F NMR (565 MHz, $CDCl_3$) of **4f**



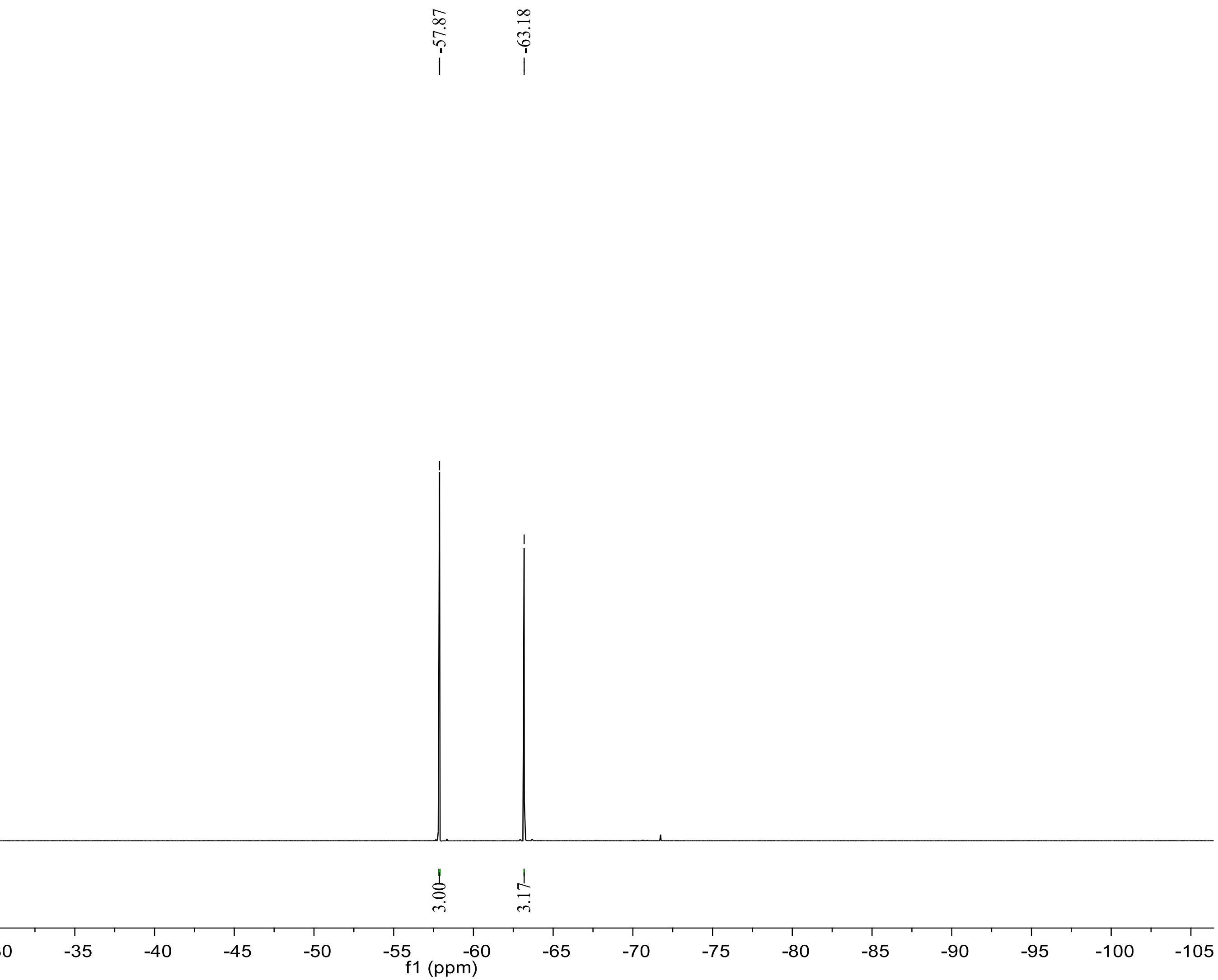
Supplementary Fig. 151. ^{13}C NMR (151 MHz, $CDCl_3$) of **4f**



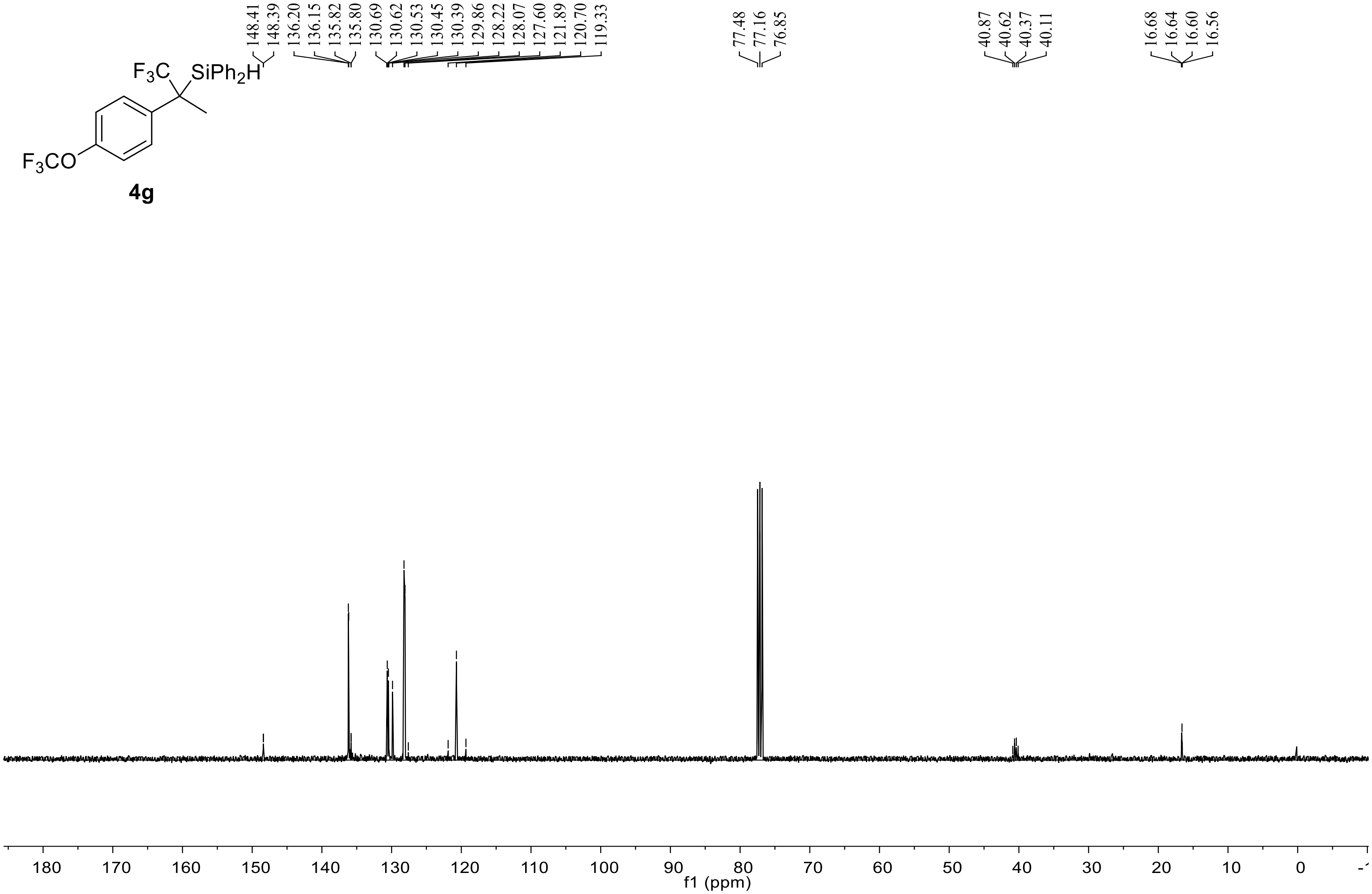
Supplementary Fig. 152. ^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



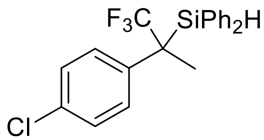
4g



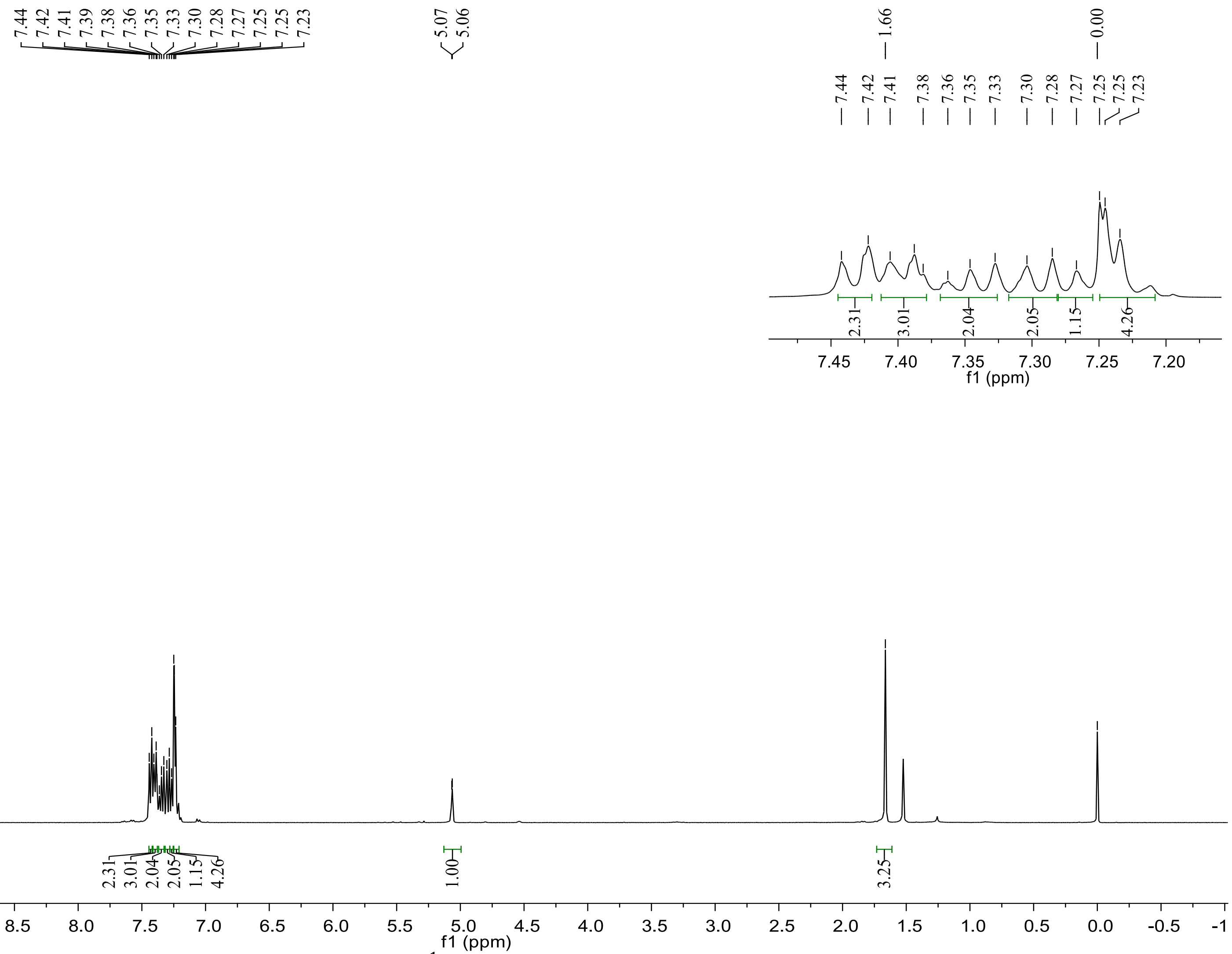
Supplementary Fig. 153. ^{19}F NMR (376 MHz, $CDCl_3$) of **4g**



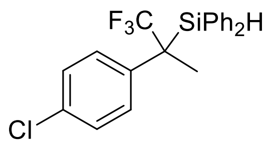
Supplementary Fig. 154. ^{13}C NMR (101 MHz, $CDCl_3$) of **4g**



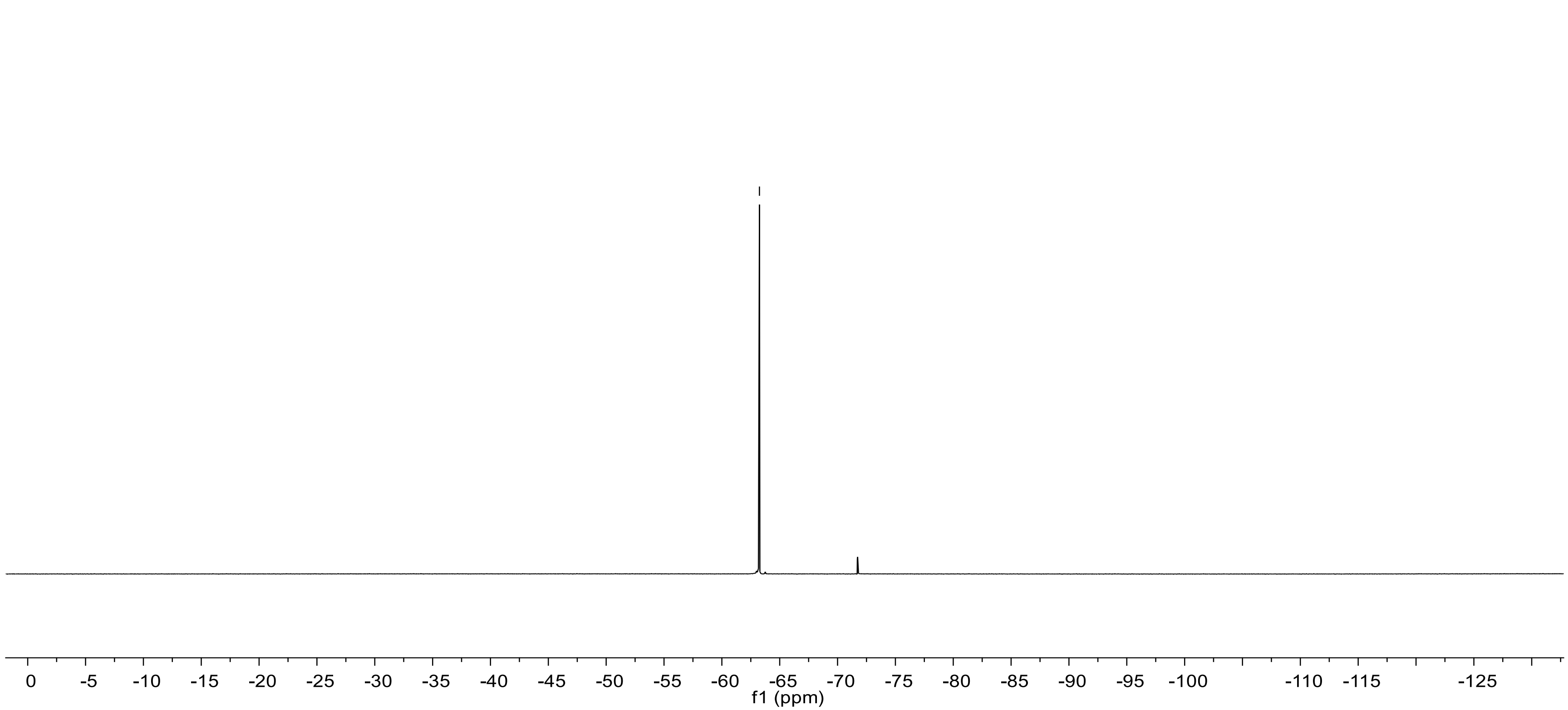
4h



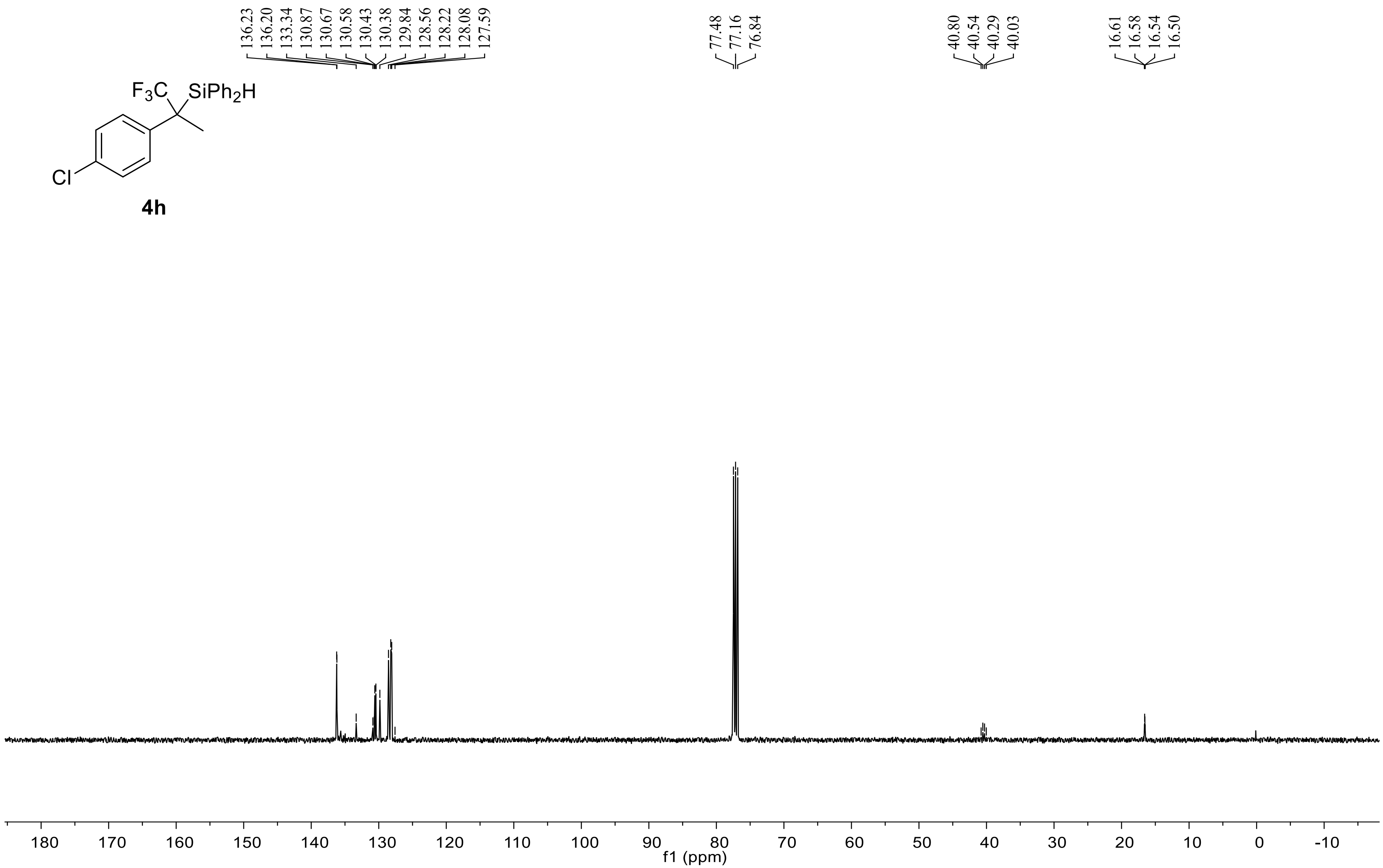
Supplementary Fig. 155. ^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



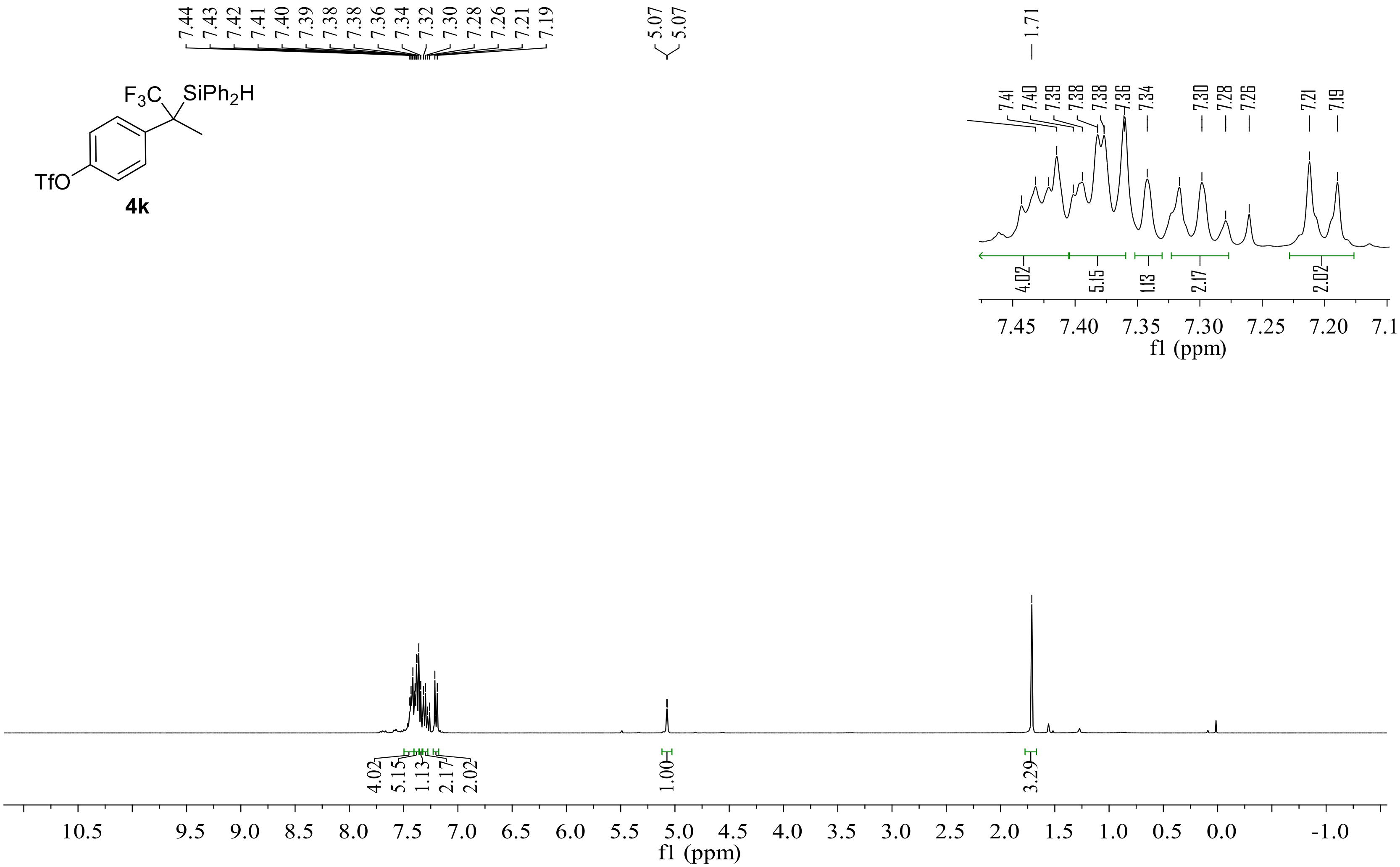
4h



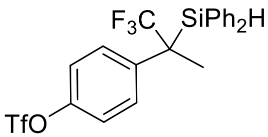
Supplementary Fig. 156. ^{19}F NMR (377 MHz, $CDCl_3$) of **4h**



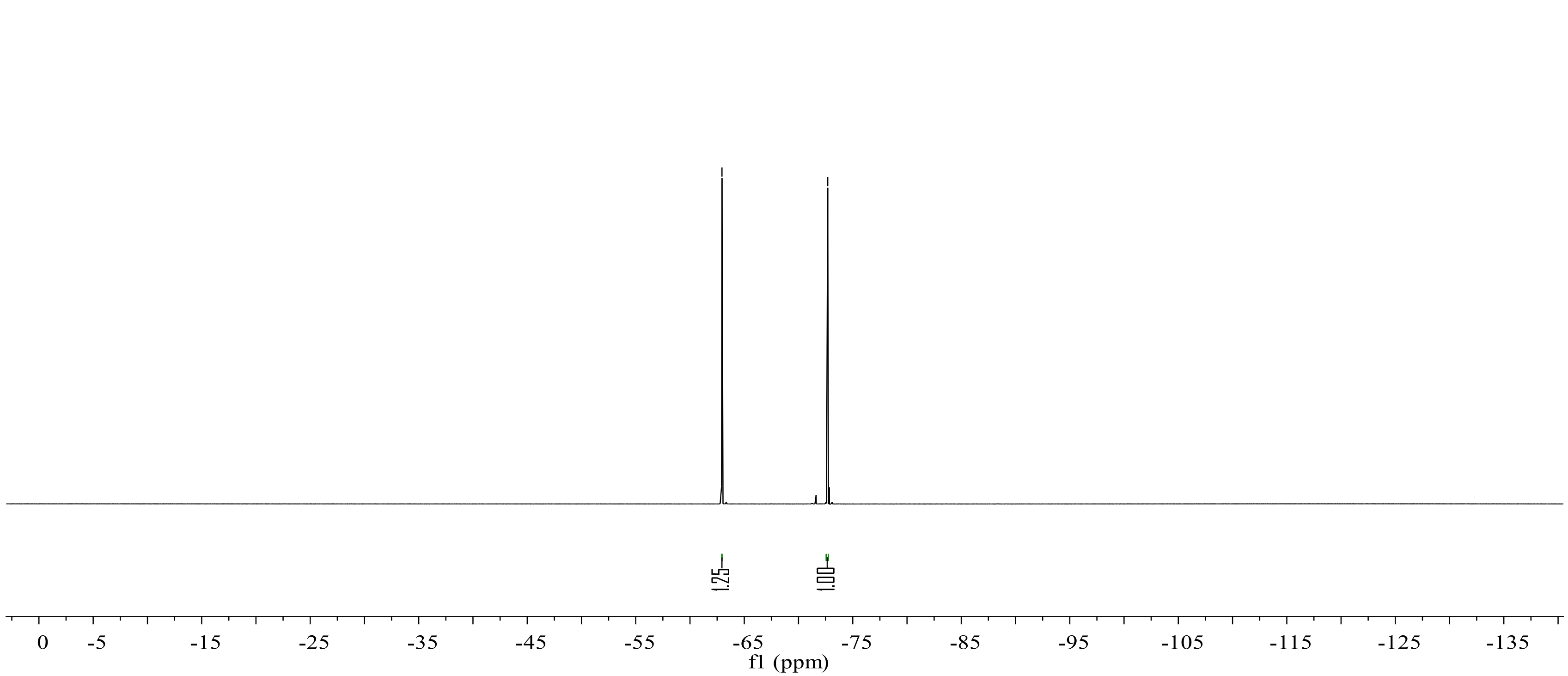
Supplementary Fig. 157. ^{19}F NMR (101 MHz, $CDCl_3$) of **4h**



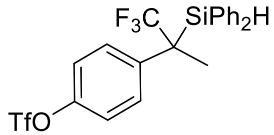
Supplementary Fig. 158. ^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



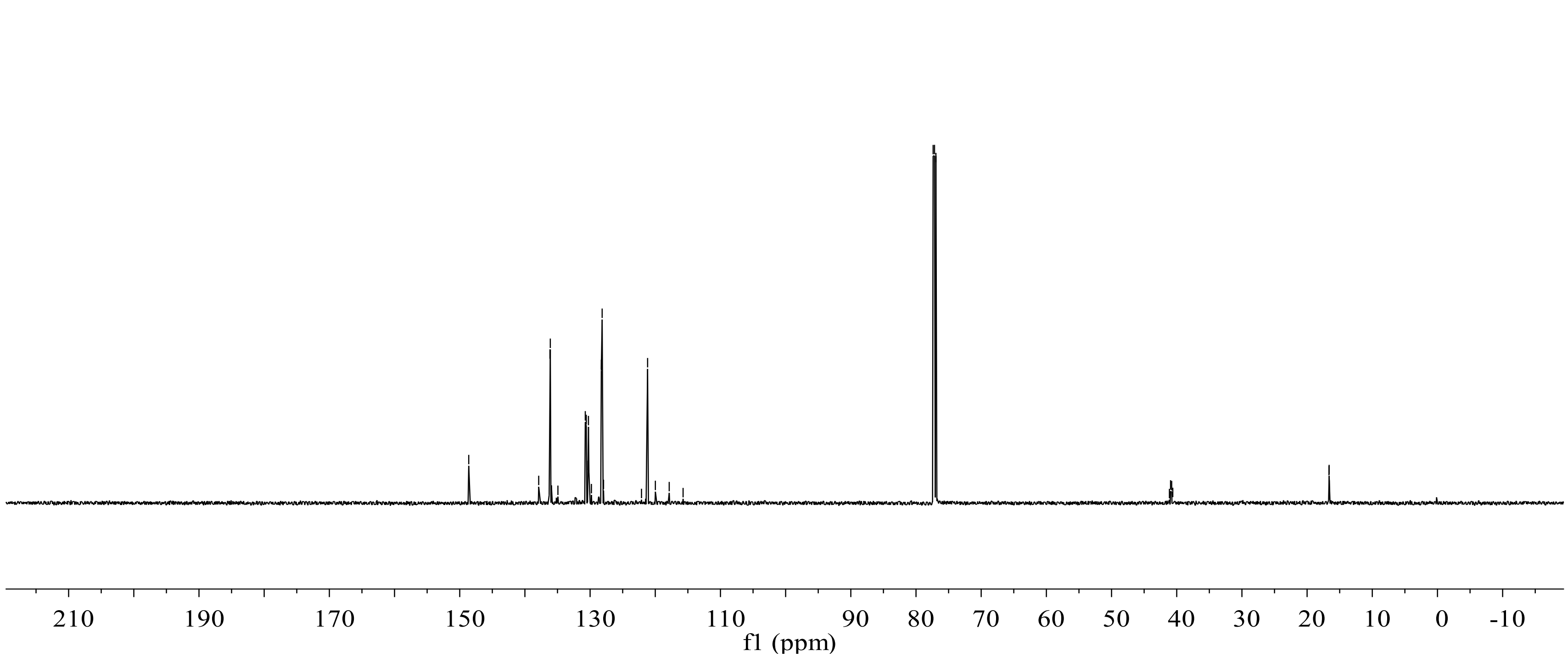
4k



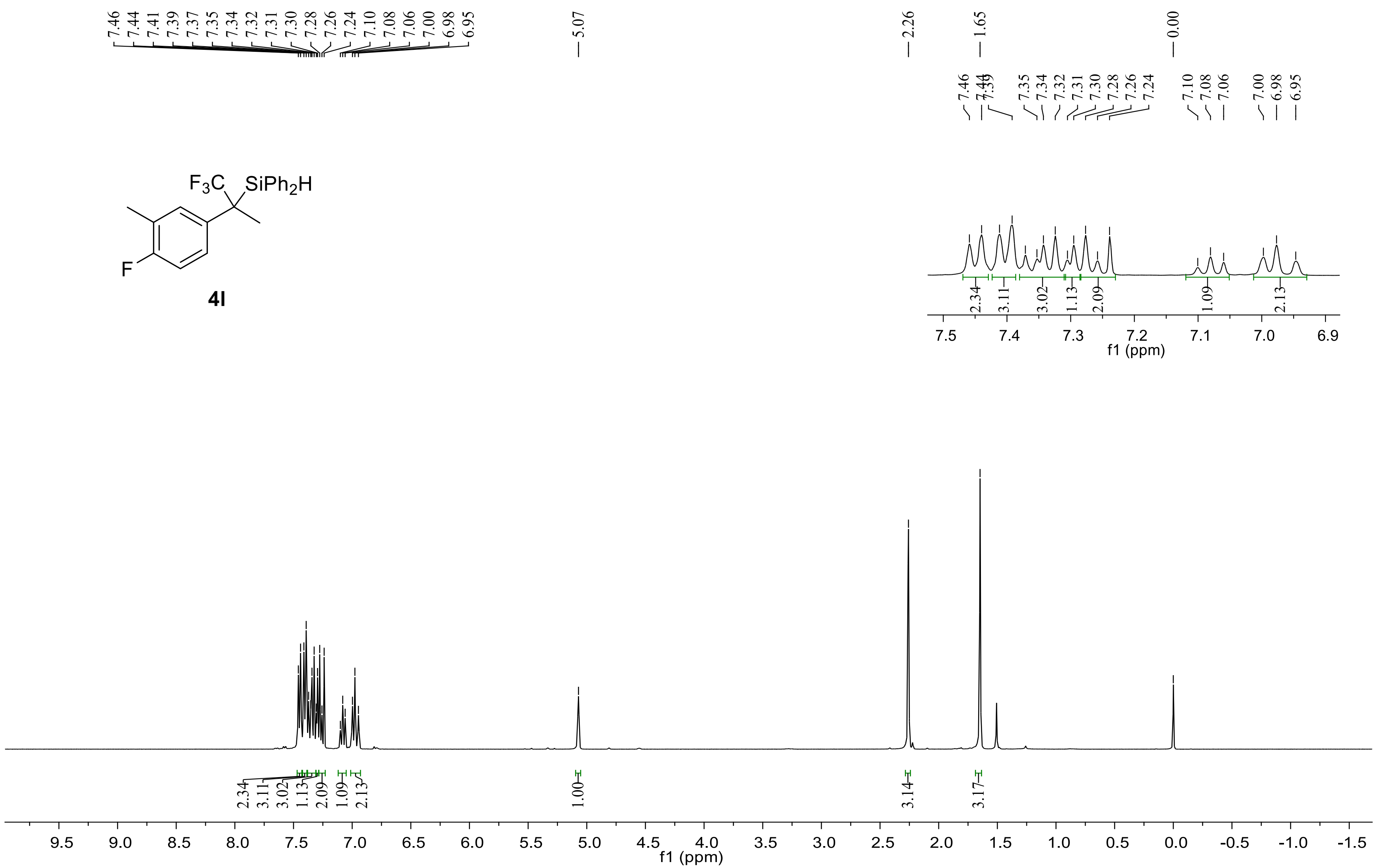
Supplementary Fig. 159. ^{19}F NMR (565 MHz, $CDCl_3$) of **4k**



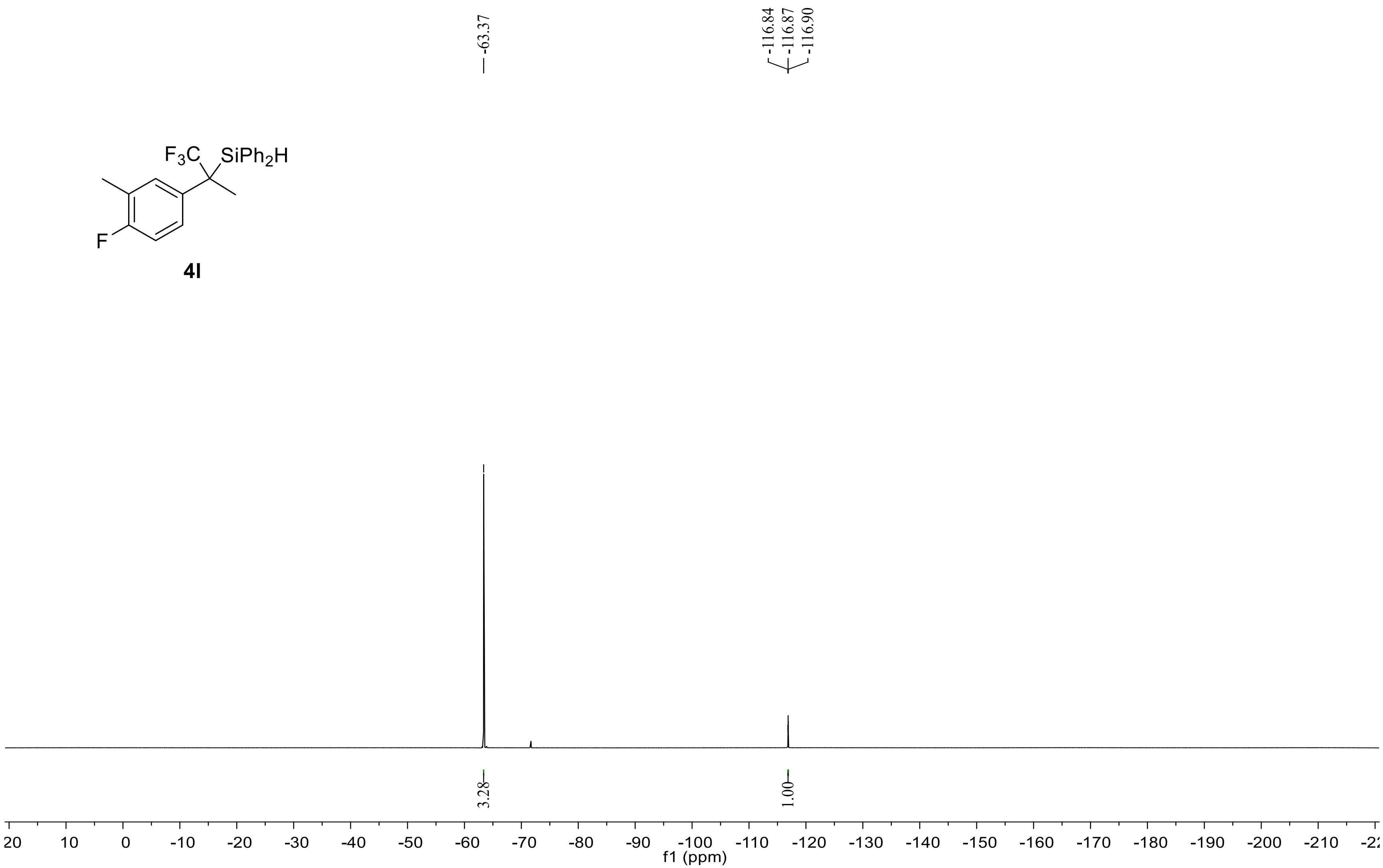
4k



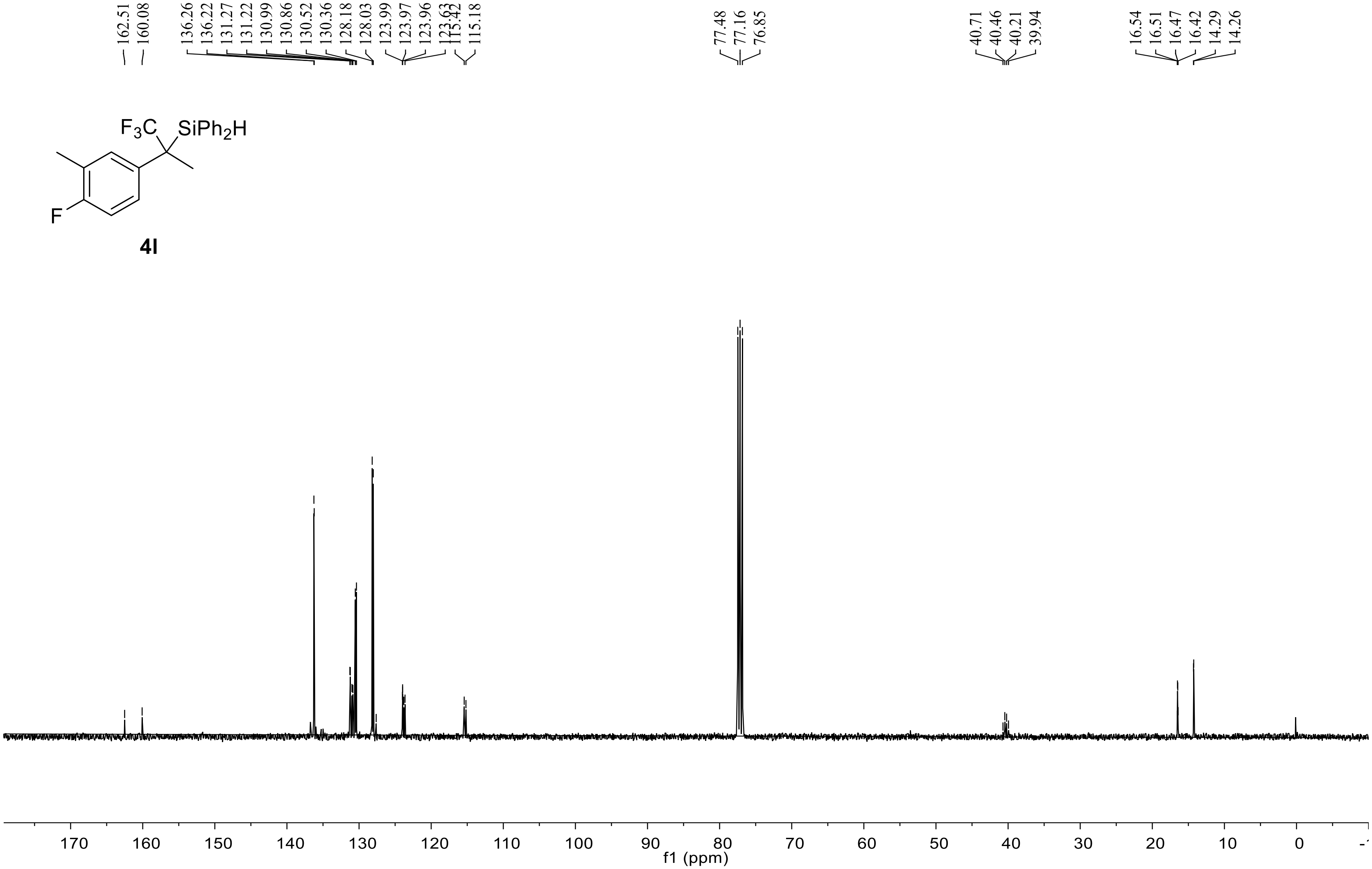
Supplementary Fig. 160. ^{13}C NMR (151 MHz, $CDCl_3$) of **4k**



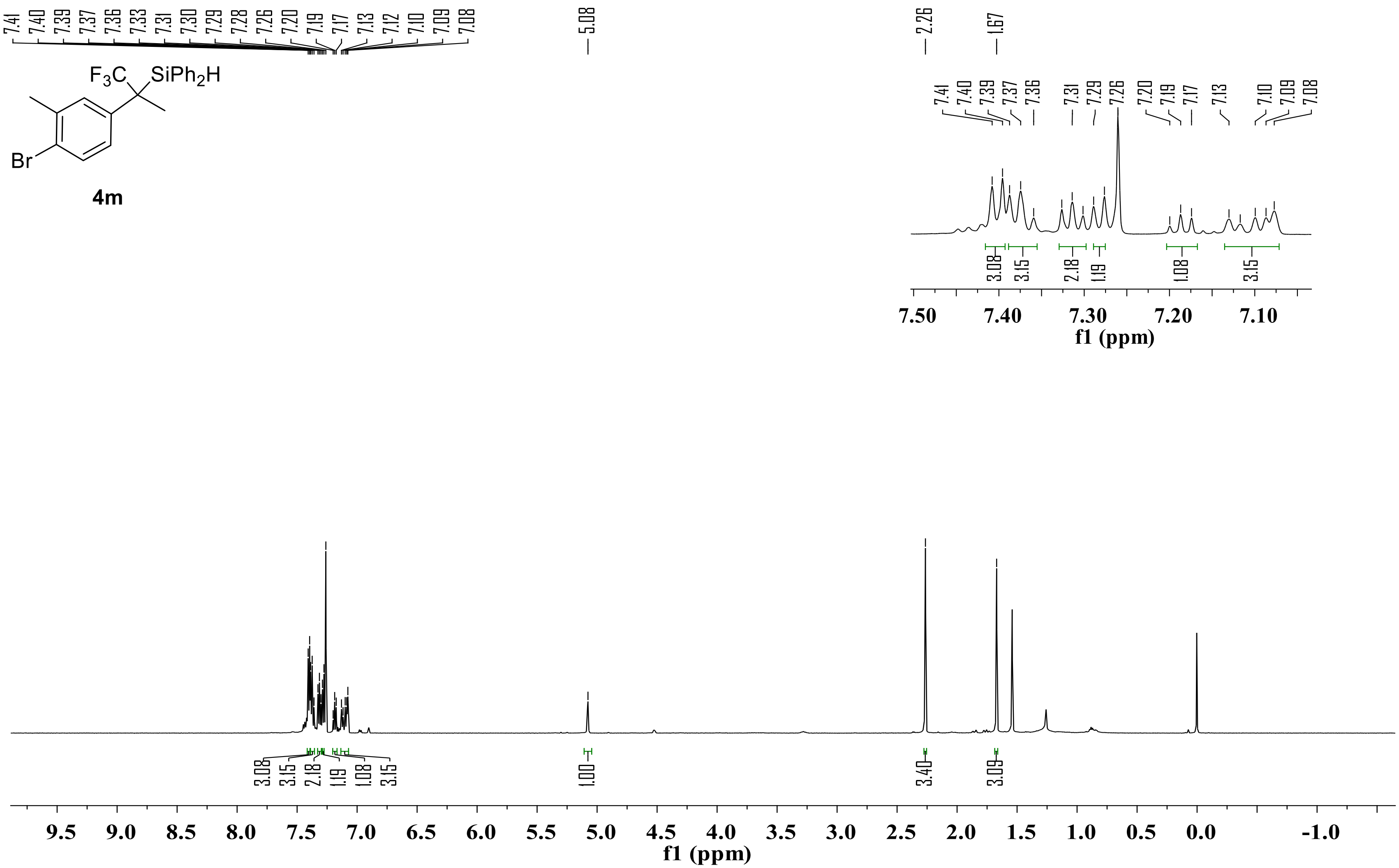
Supplementary Fig. 161. ^{1}H NMR (400 MHz, $CDCl_3$) of **4l**



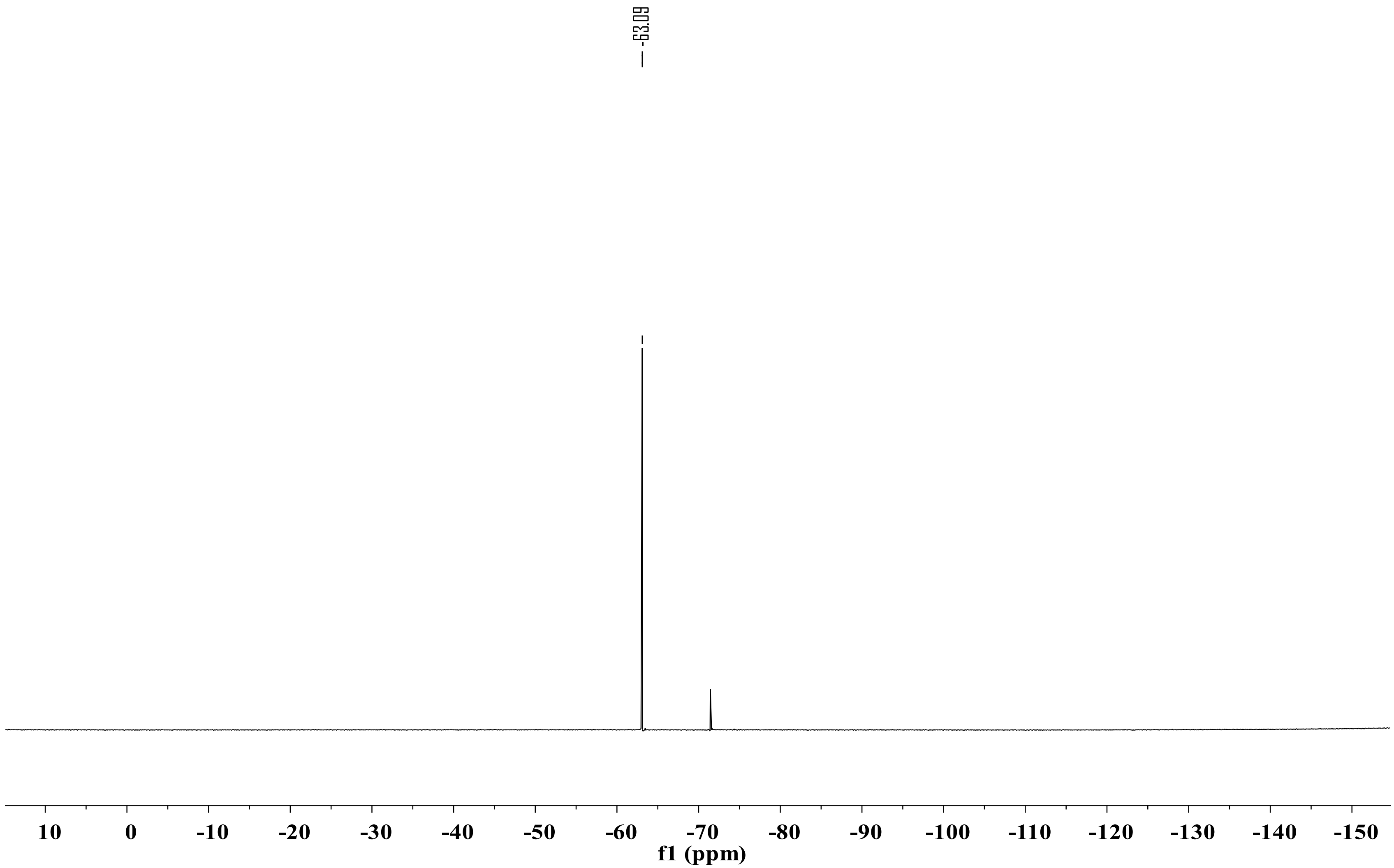
Supplementary Fig. 162. ^{19}F NMR (377 MHz, $CDCl_3$) of **4l**



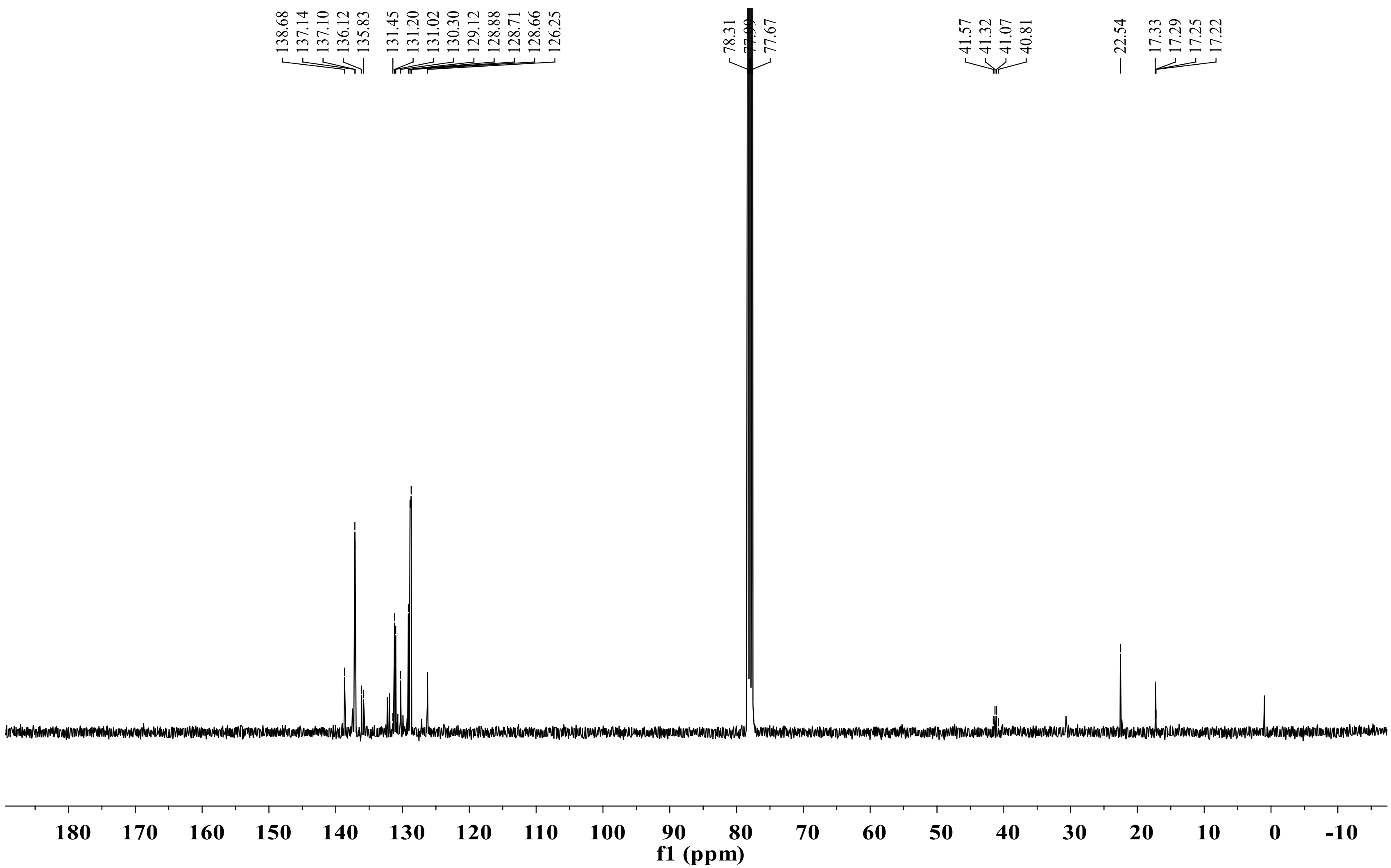
Supplementary Fig. 163. ^{13}C NMR (101 MHz, $CDCl_3$) of **4l**



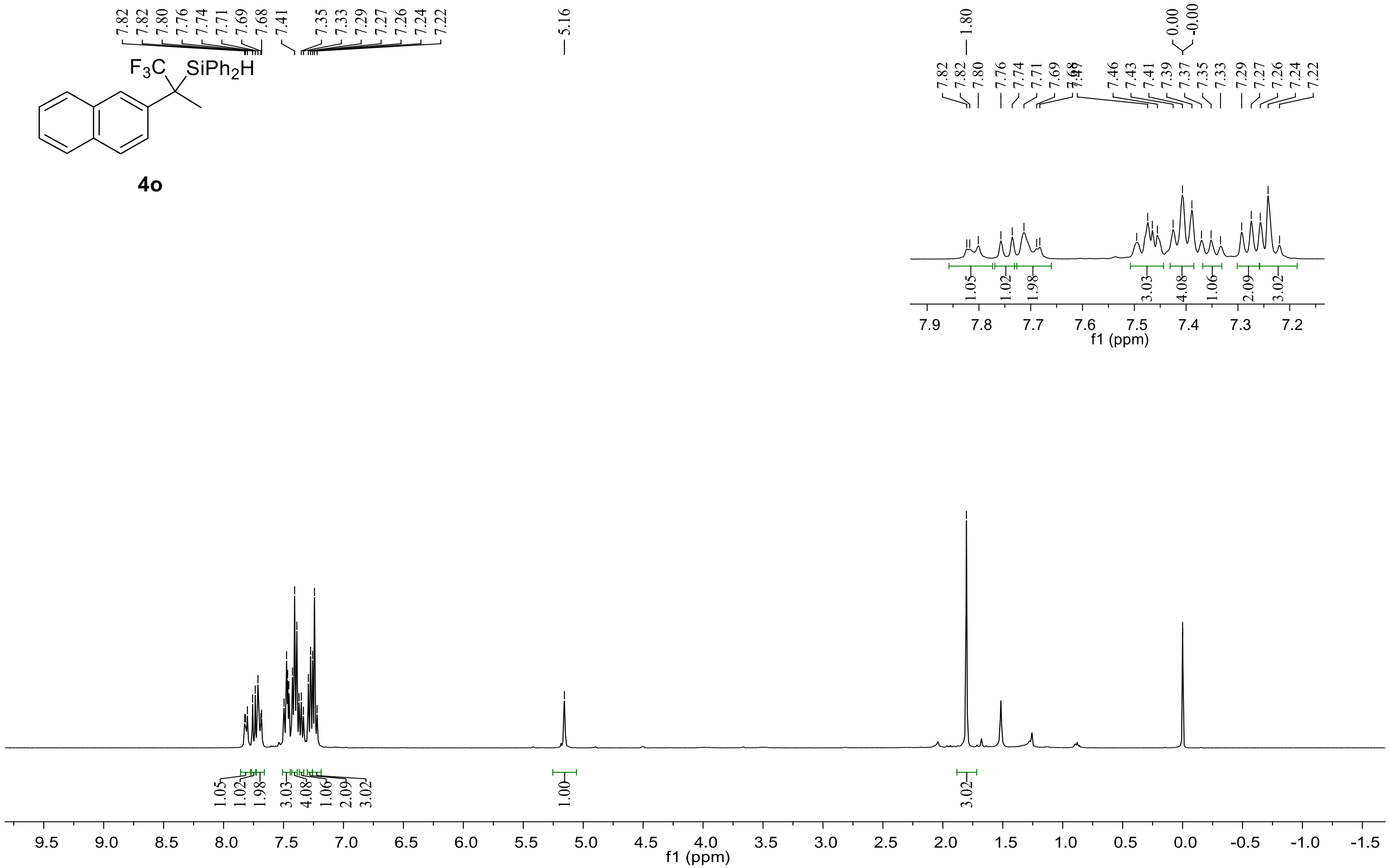
Supplementary Fig. 164. ^{1}H NMR (600 MHz, $CDCl_3$) of **4m**



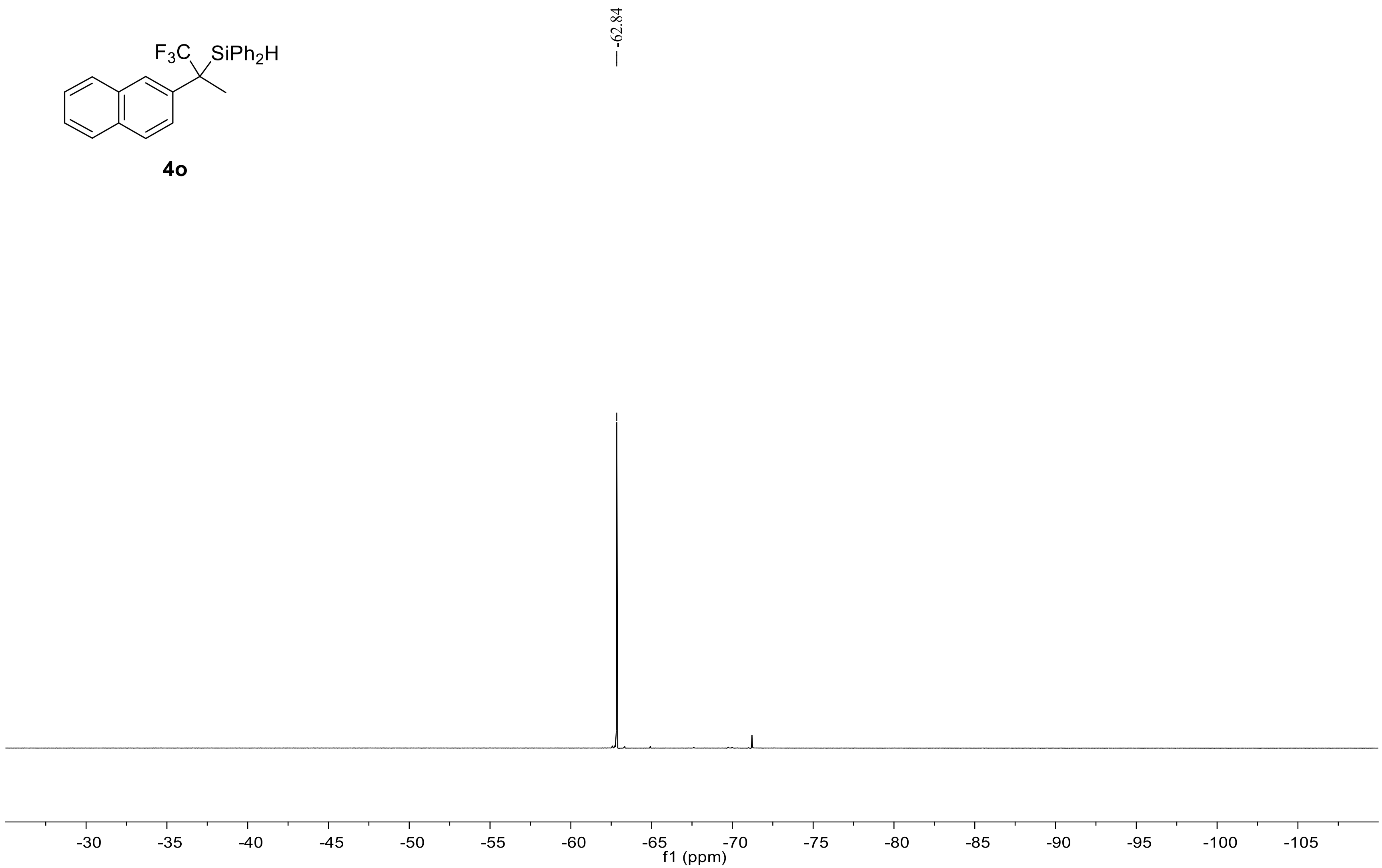
Supplementary Fig. 165. ^{19}F NMR (565 MHz, $CDCl_3$) of **4m**



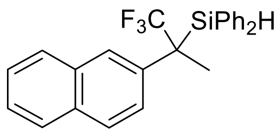
Supplementary Fig. 166. ^{13}C NMR (101 MHz, $CDCl_3$) of **4m**



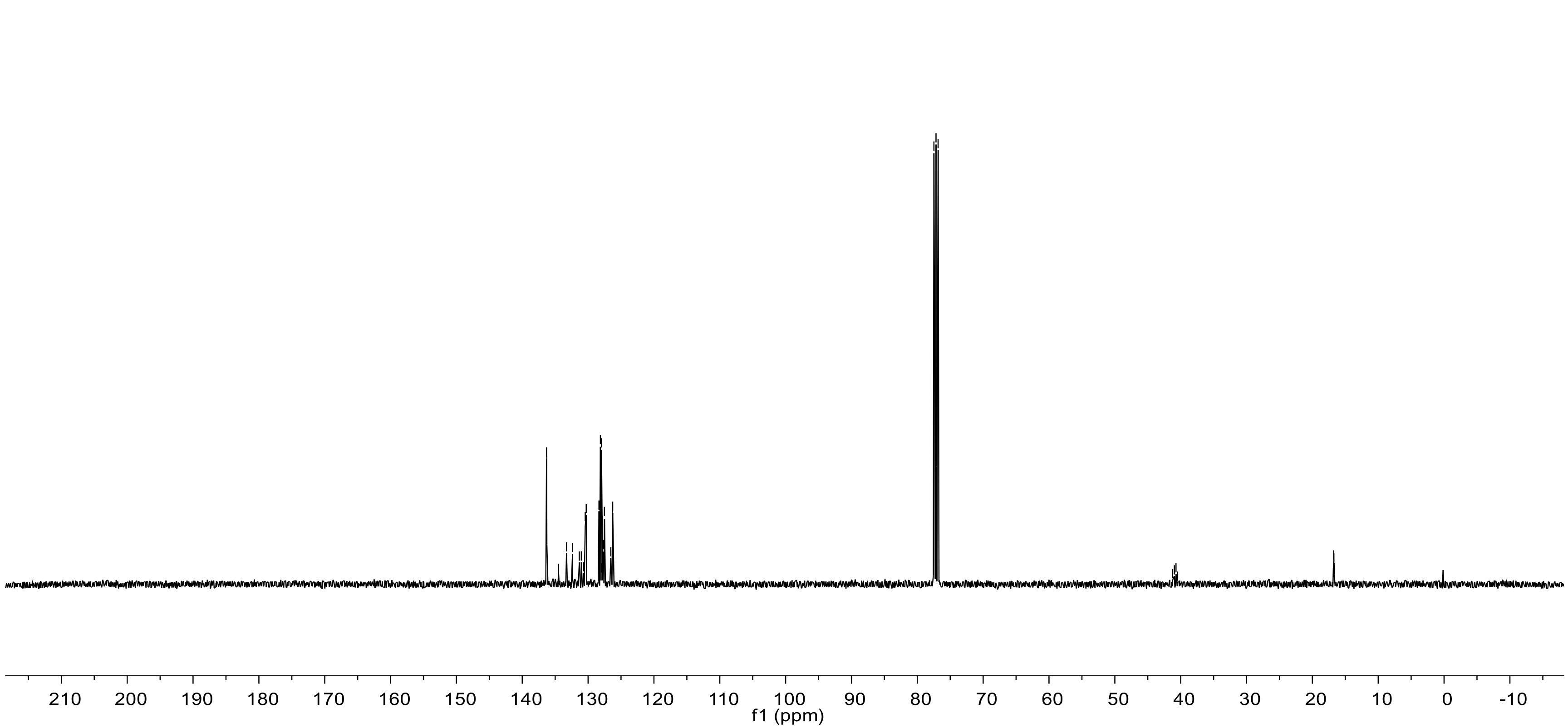
Supplementary Fig. 167. ^{1}H NMR (400 MHz, $CDCl_3$) of **4o**



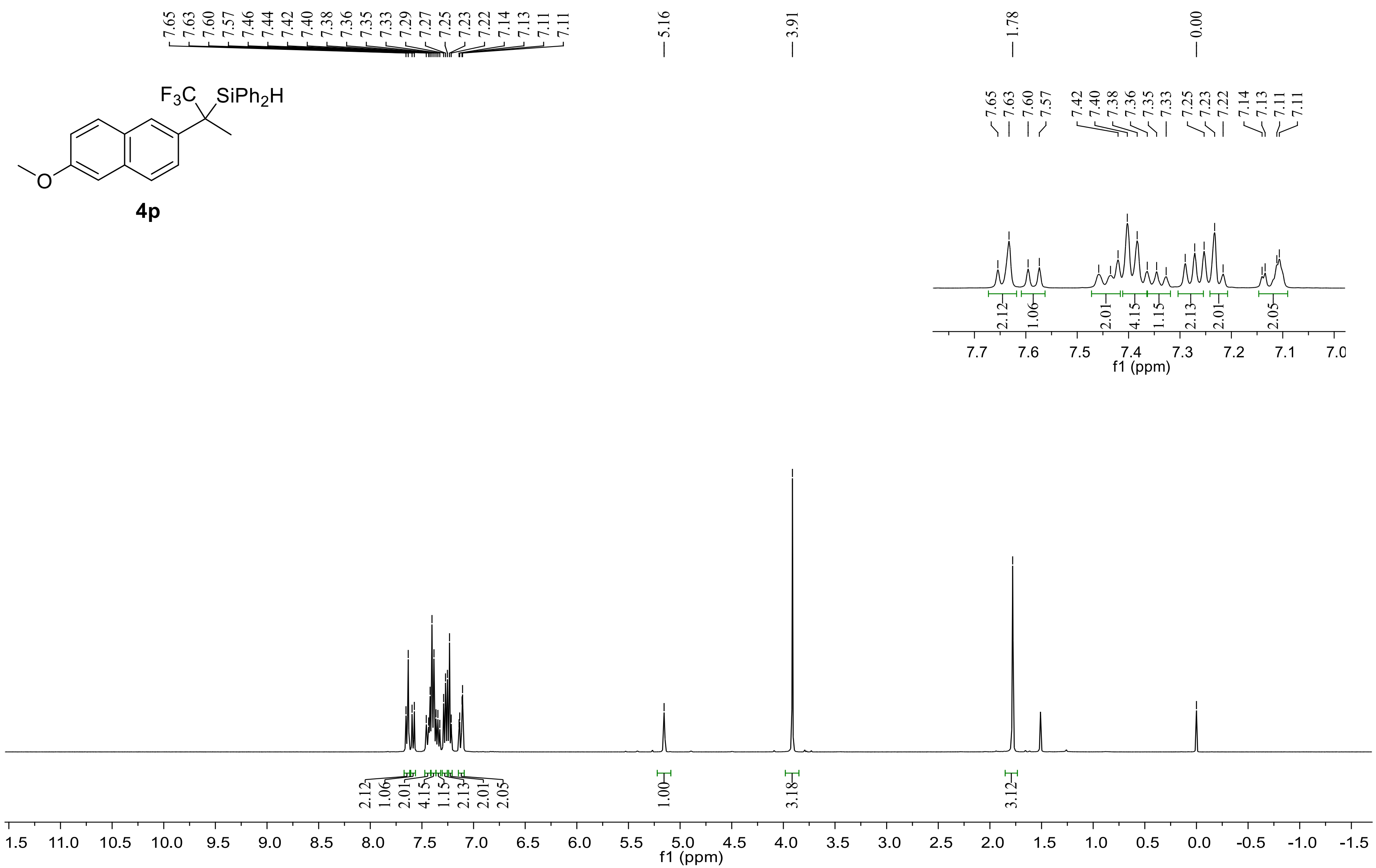
Supplementary Fig. 168. ^{19}F NMR (377 MHz, $CDCl_3$) of **4o**



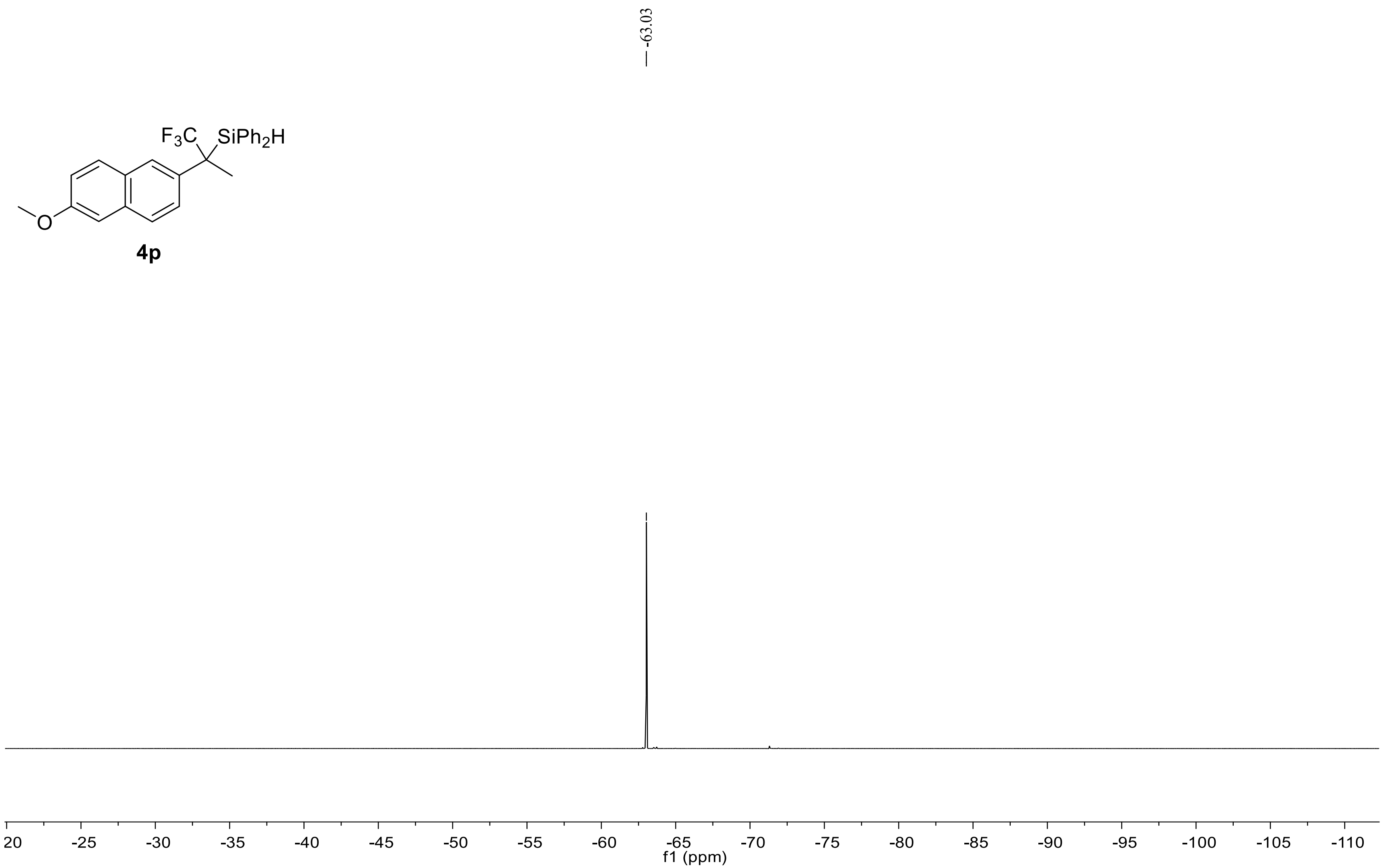
4o



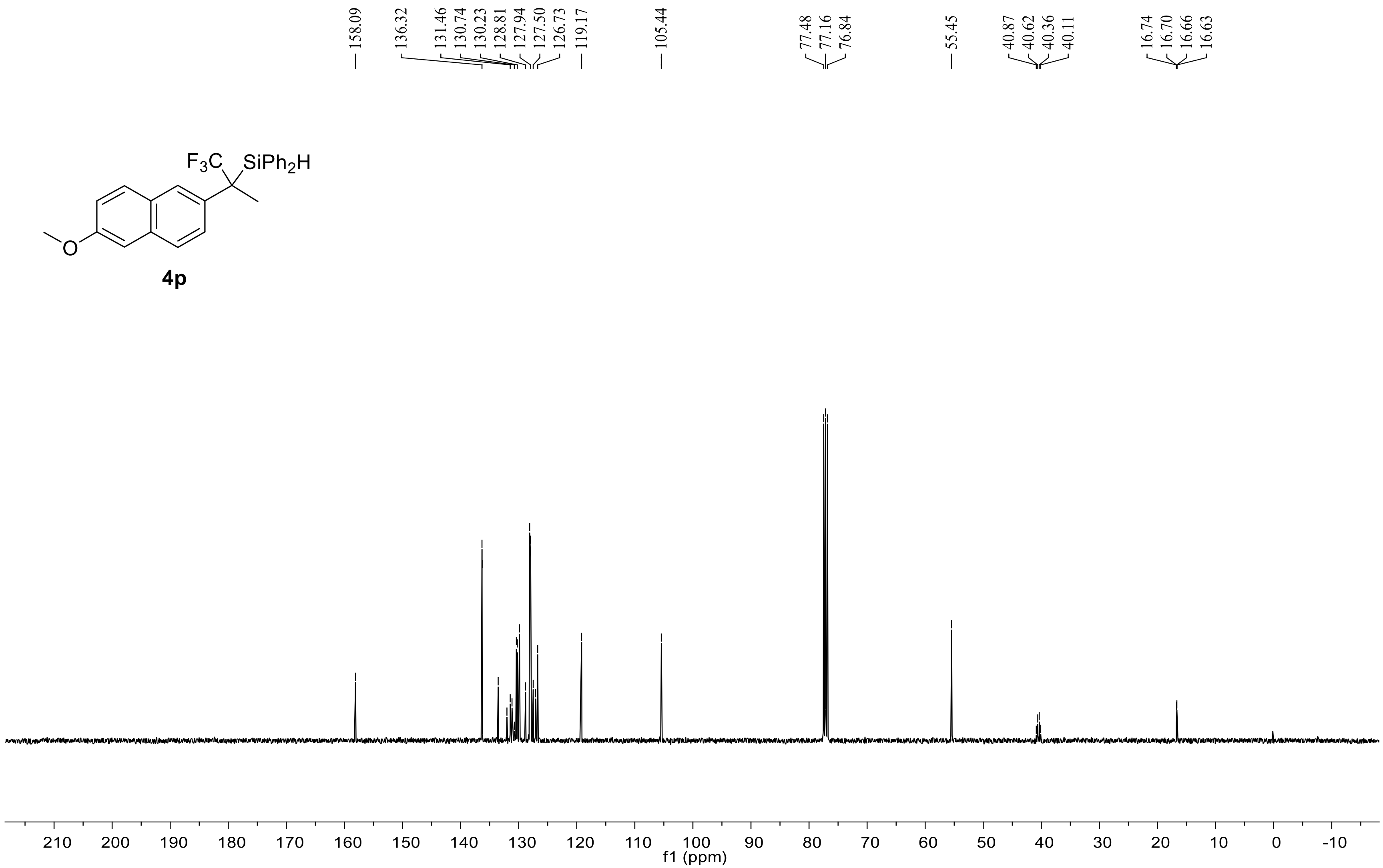
Supplementary Fig. 167. ^{13}C NMR (101 MHz, $CDCl_3$) of **4o**



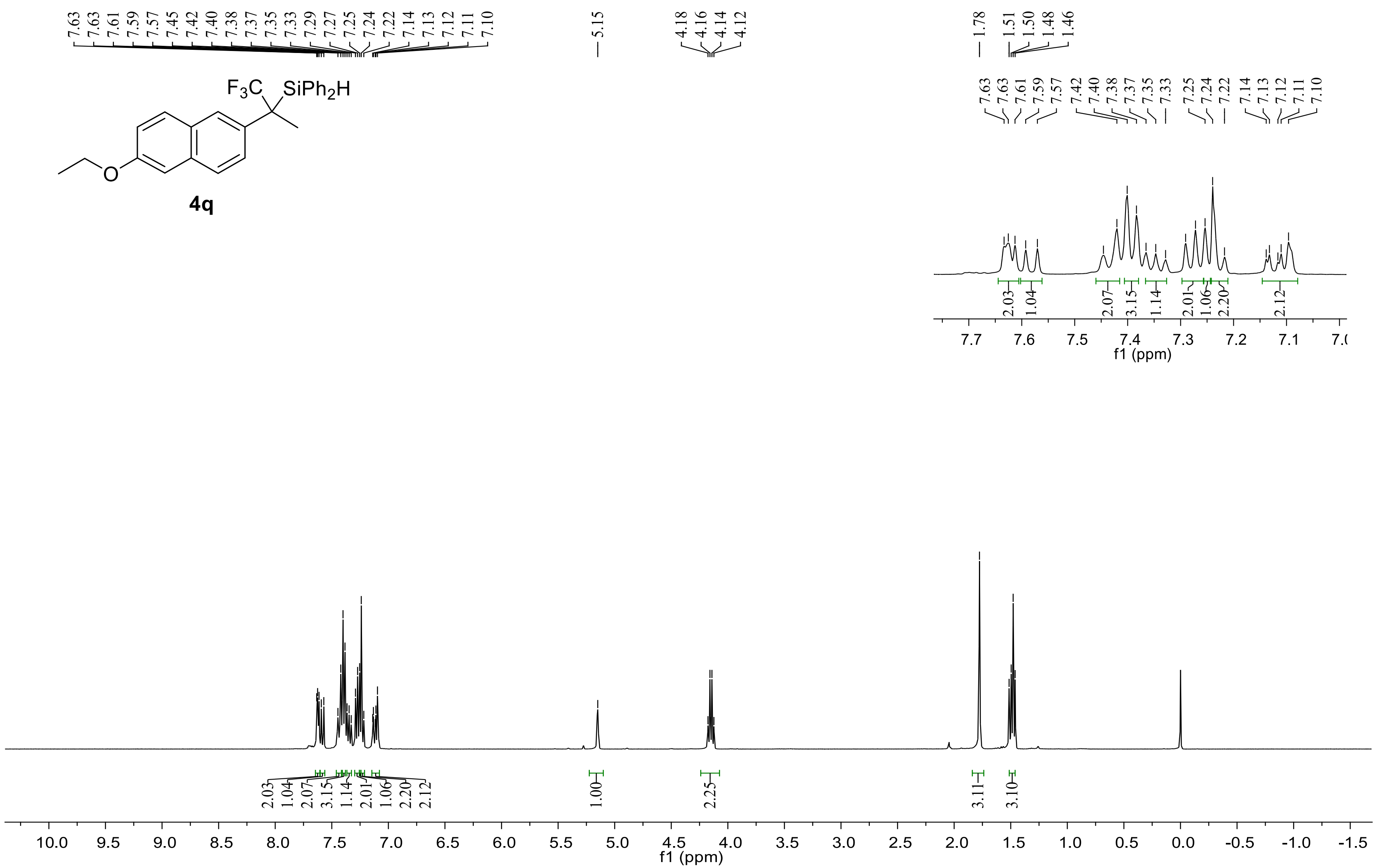
Supplementary Fig. 170. ^{1}H NMR (400 MHz, $CDCl_3$) of **4p**



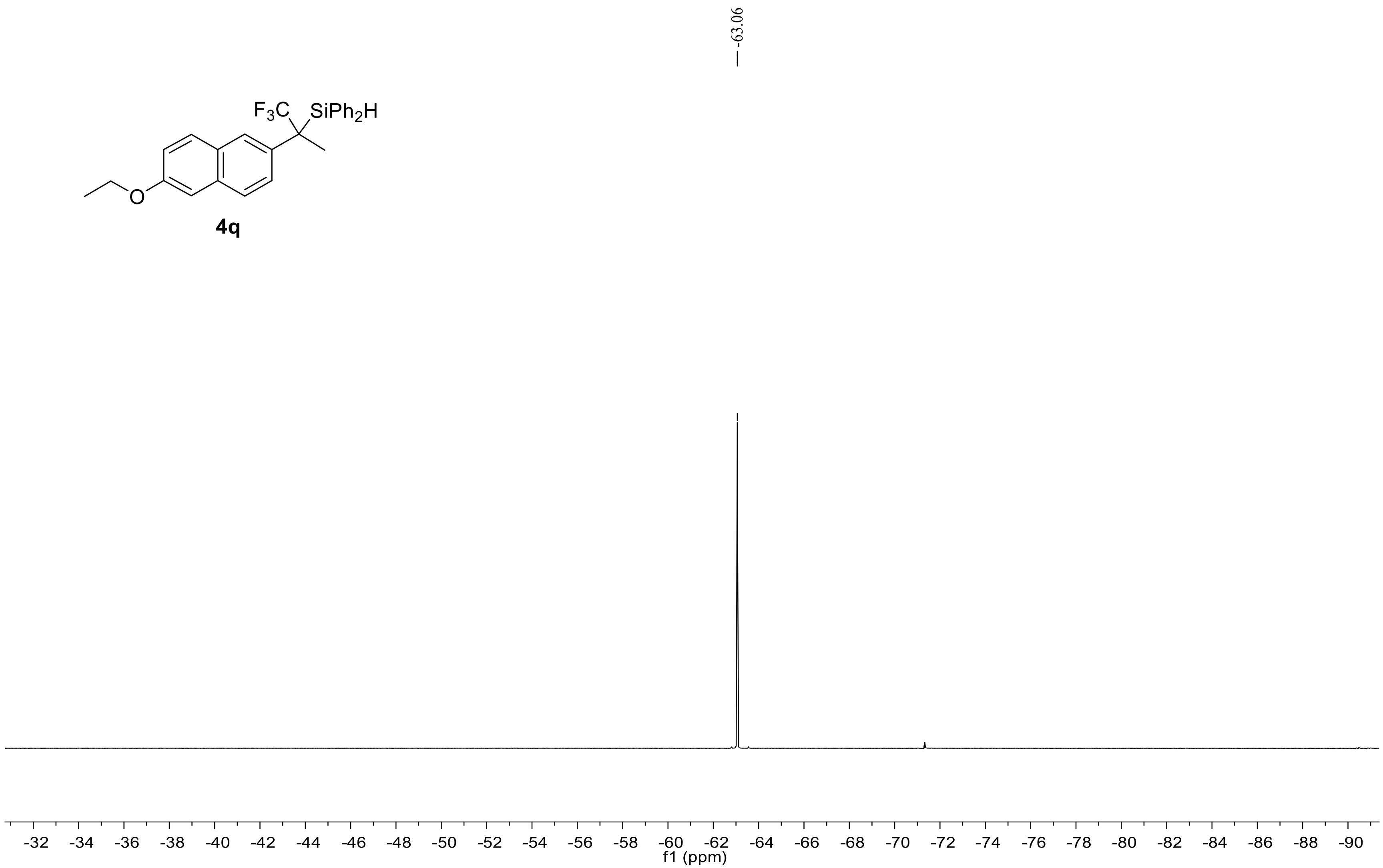
Supplementary Fig. 171. ^{19}F NMR (377 MHz, $CDCl_3$) of **4p**



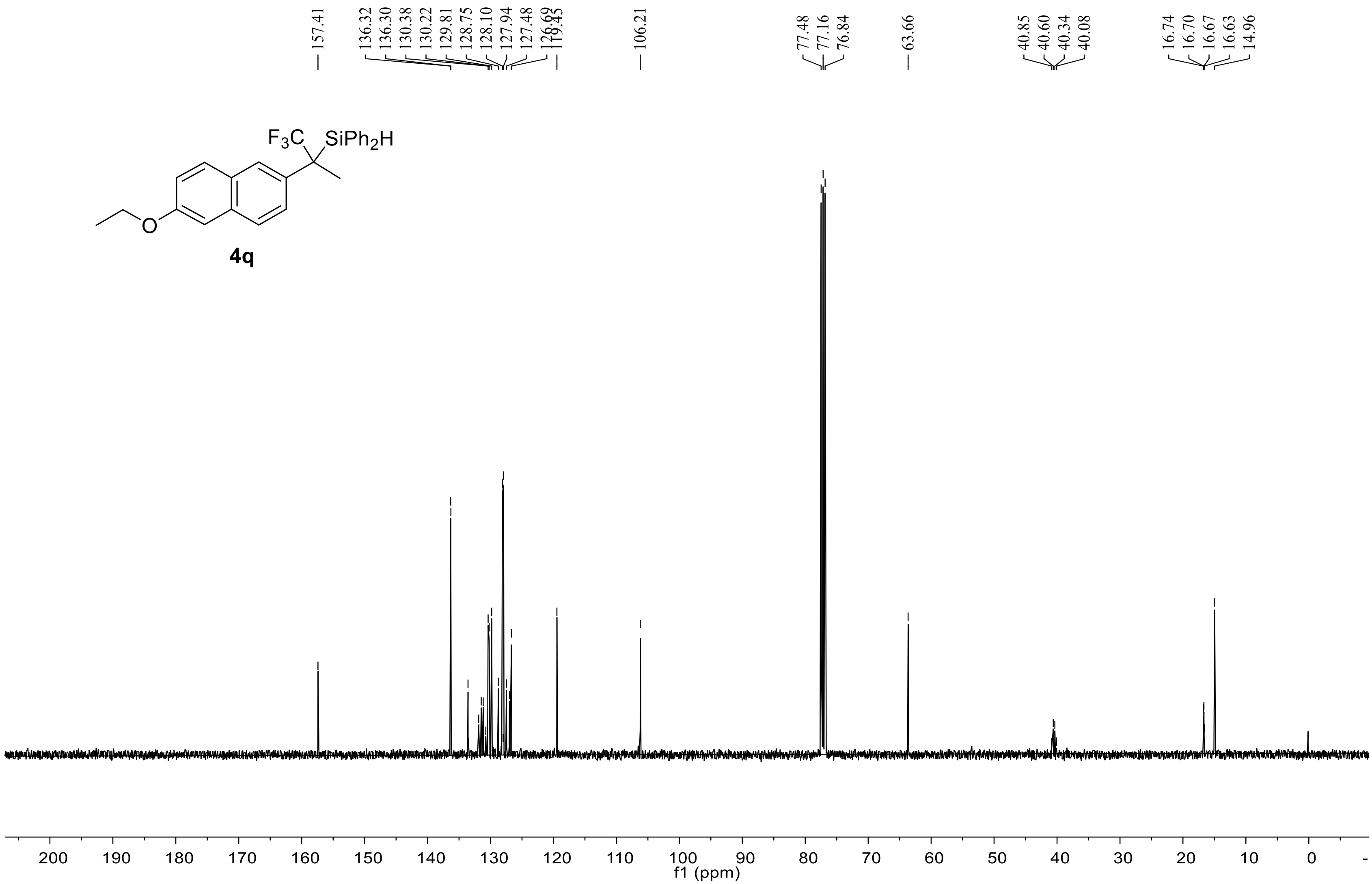
Supplementary Fig. 172. ^{13}C NMR (101 MHz, $CDCl_3$) of **4p**



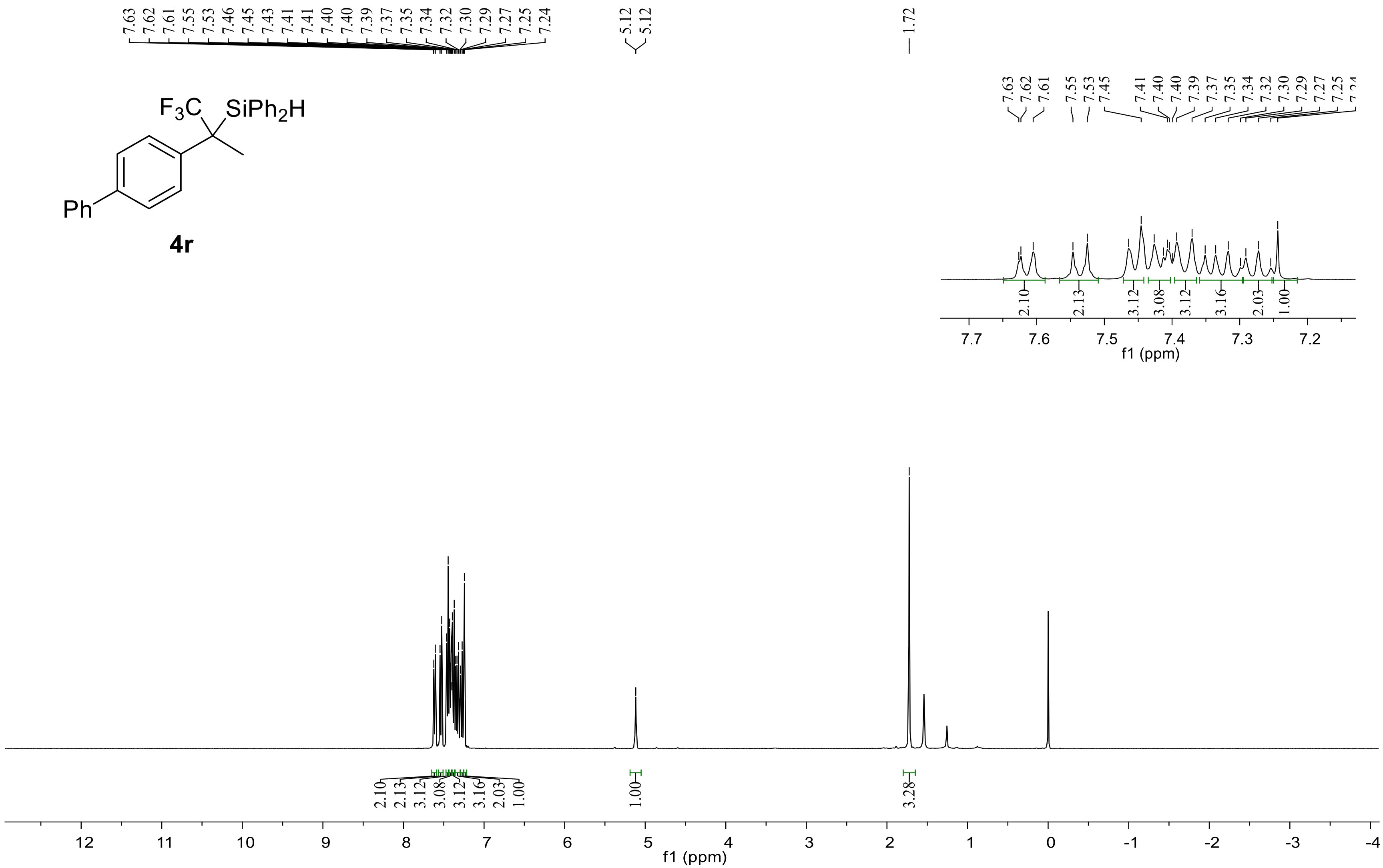
Supplementary Fig. 173. ^{1}H NMR (400 MHz, $CDCl_3$) of **4q**



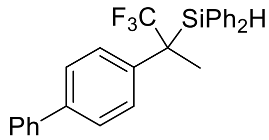
Supplementary Fig. 174. ^{19}F NMR (377 MHz, $CDCl_3$) of **4q**



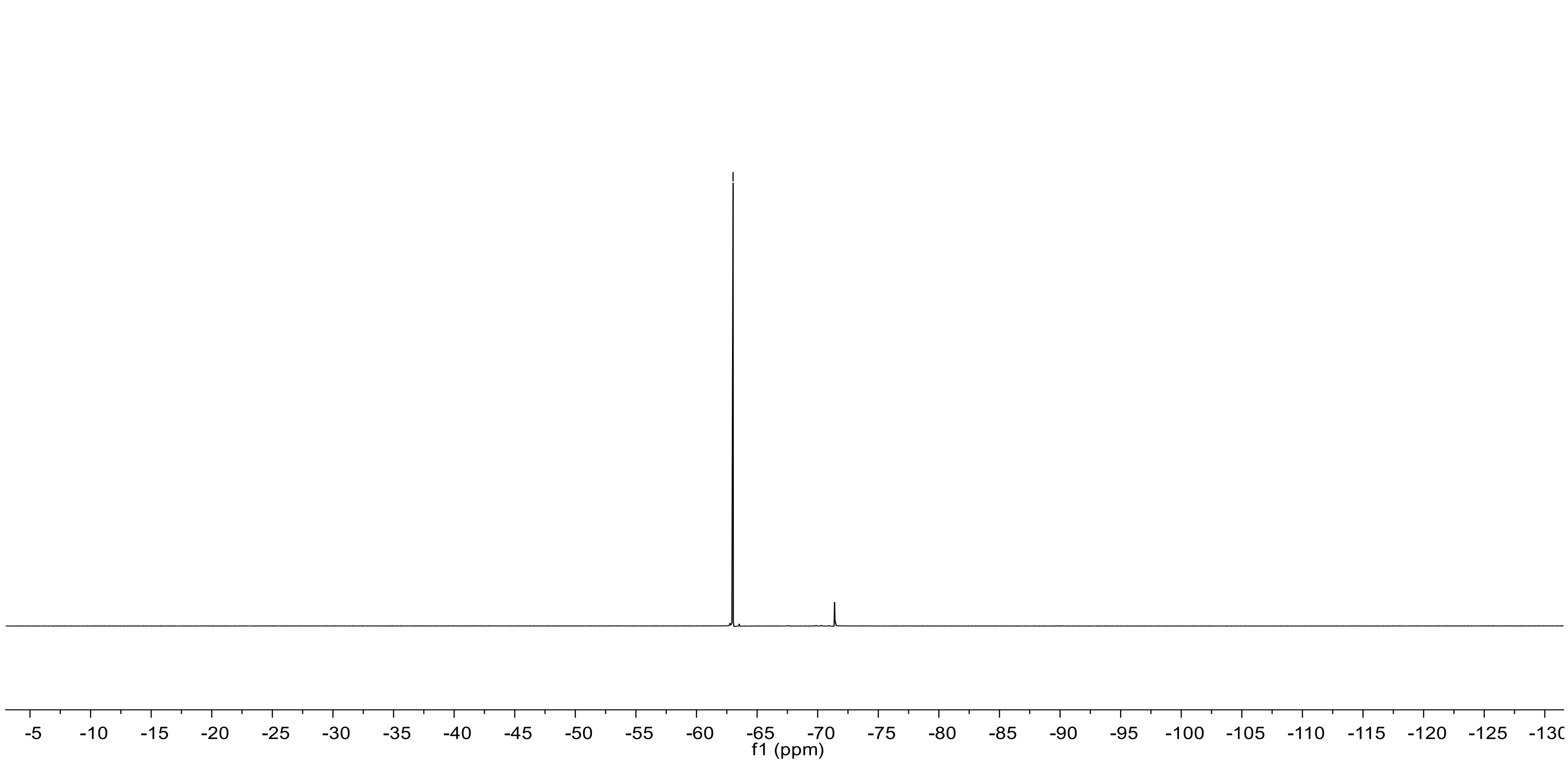
Supplementary Fig. 175. ^{13}C NMR (101 MHz, $CDCl_3$) of **4q**



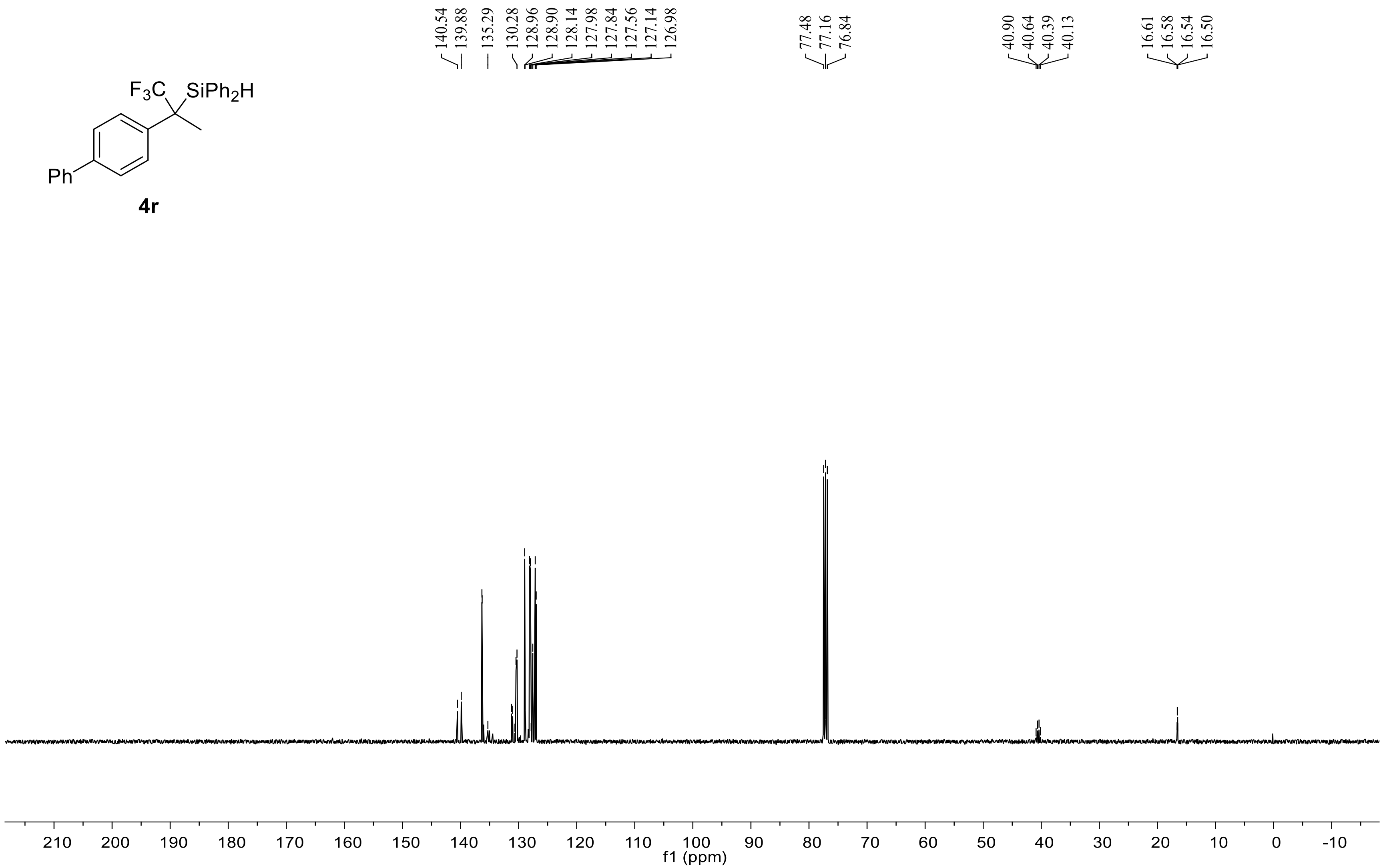
Supplementary Fig. 176. ^{1}H NMR (400 MHz, $CDCl_3$) of **4r**



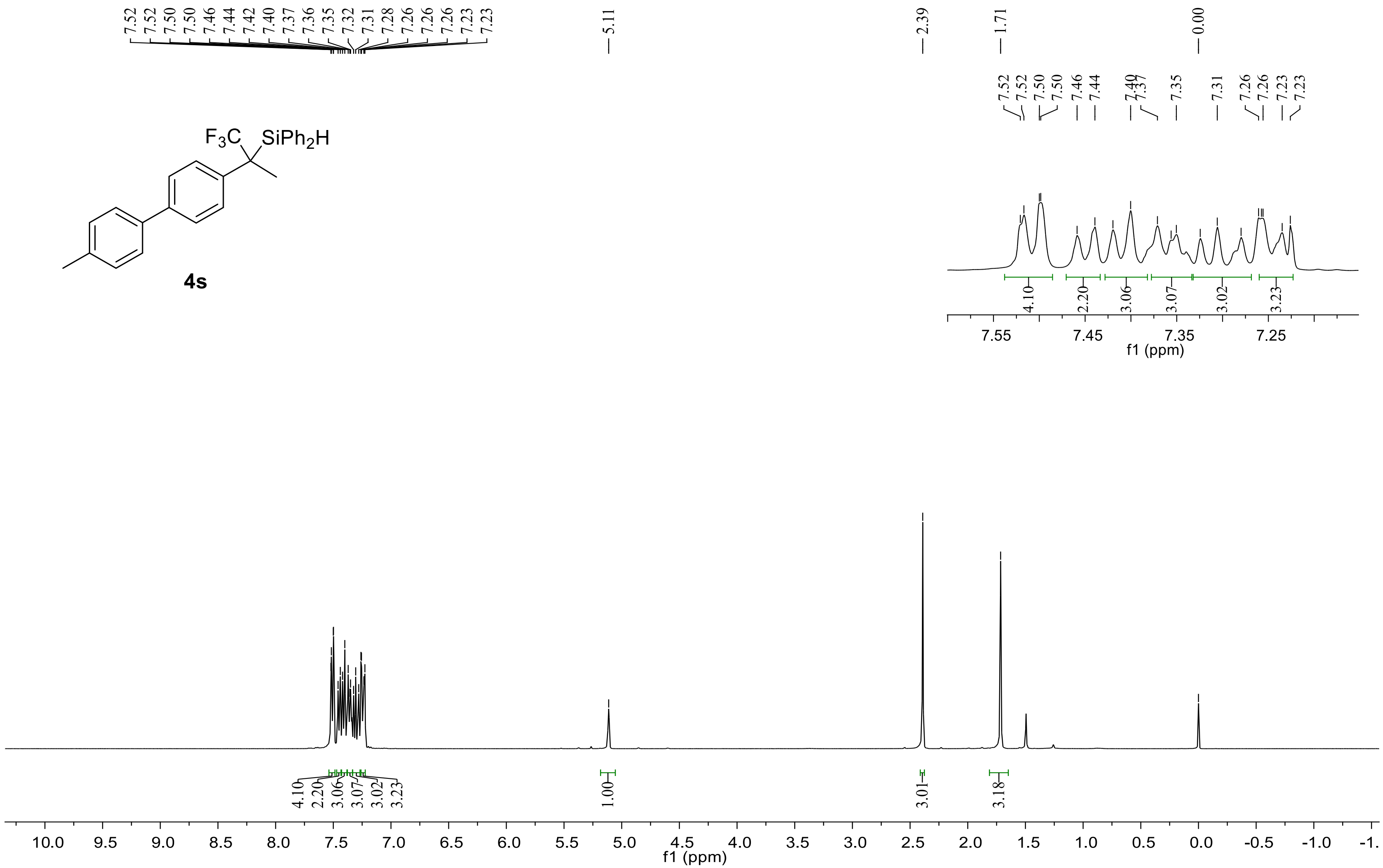
4r



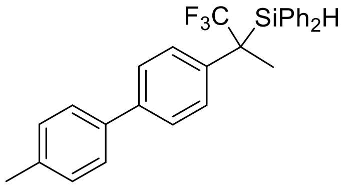
Supplementary Fig. 177. ^{19}F NMR (377 MHz, $CDCl_3$) of **4r**



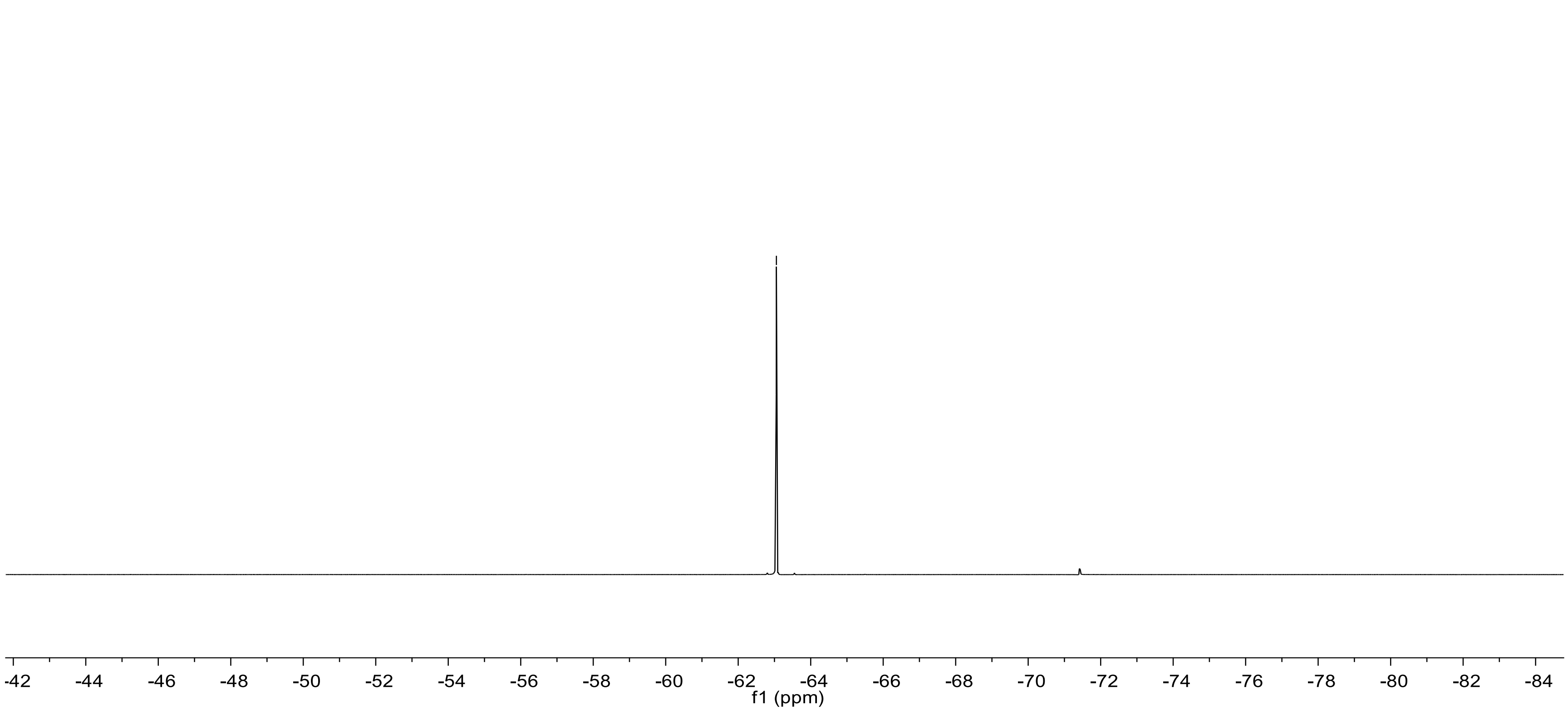
Supplementary Fig. 178. ^{13}C NMR (101 MHz, $CDCl_3$) of **4r**



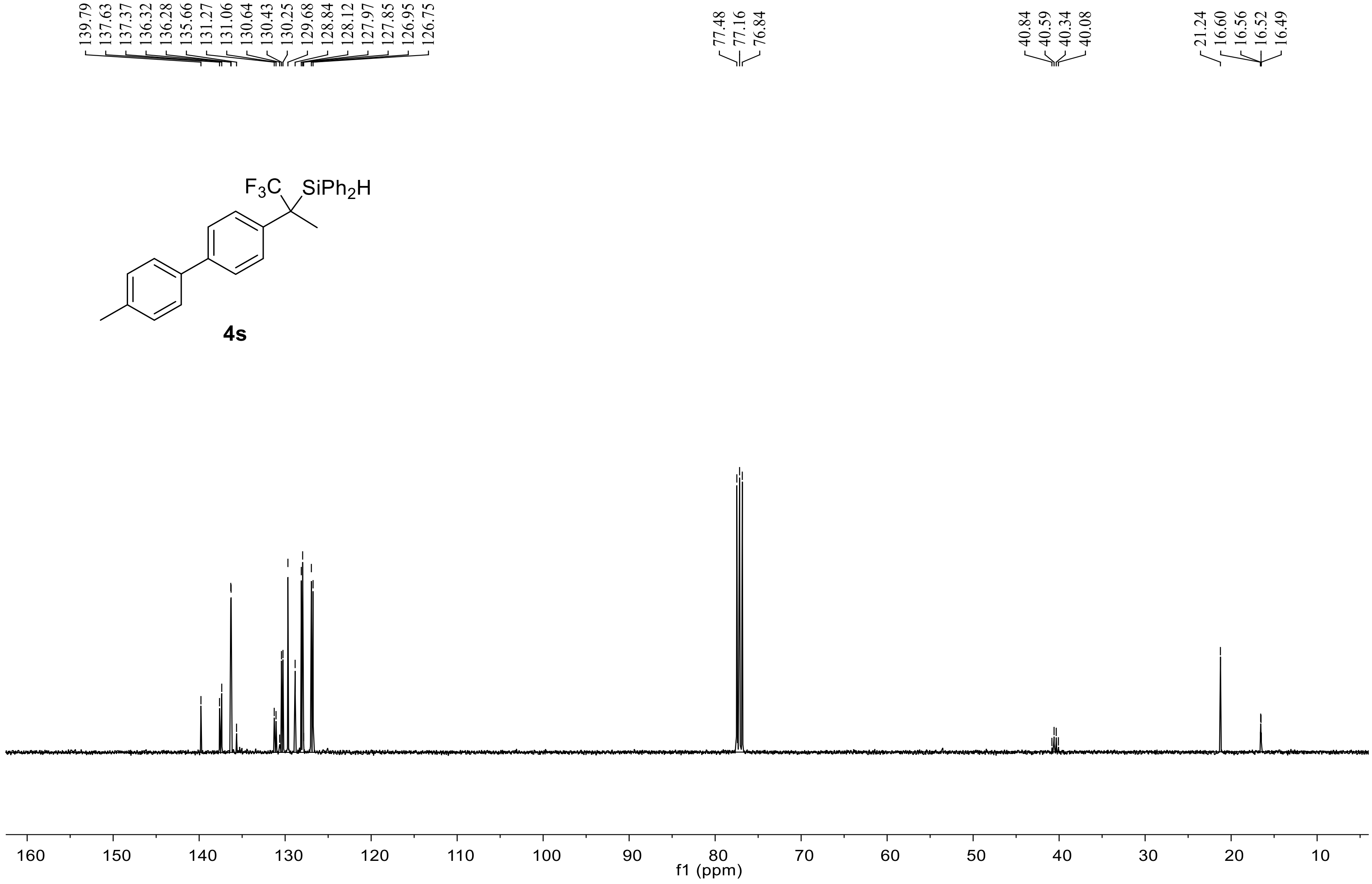
Supplementary Fig. 179. ^{1}H NMR (400 MHz, $CDCl_3$) of **4s**



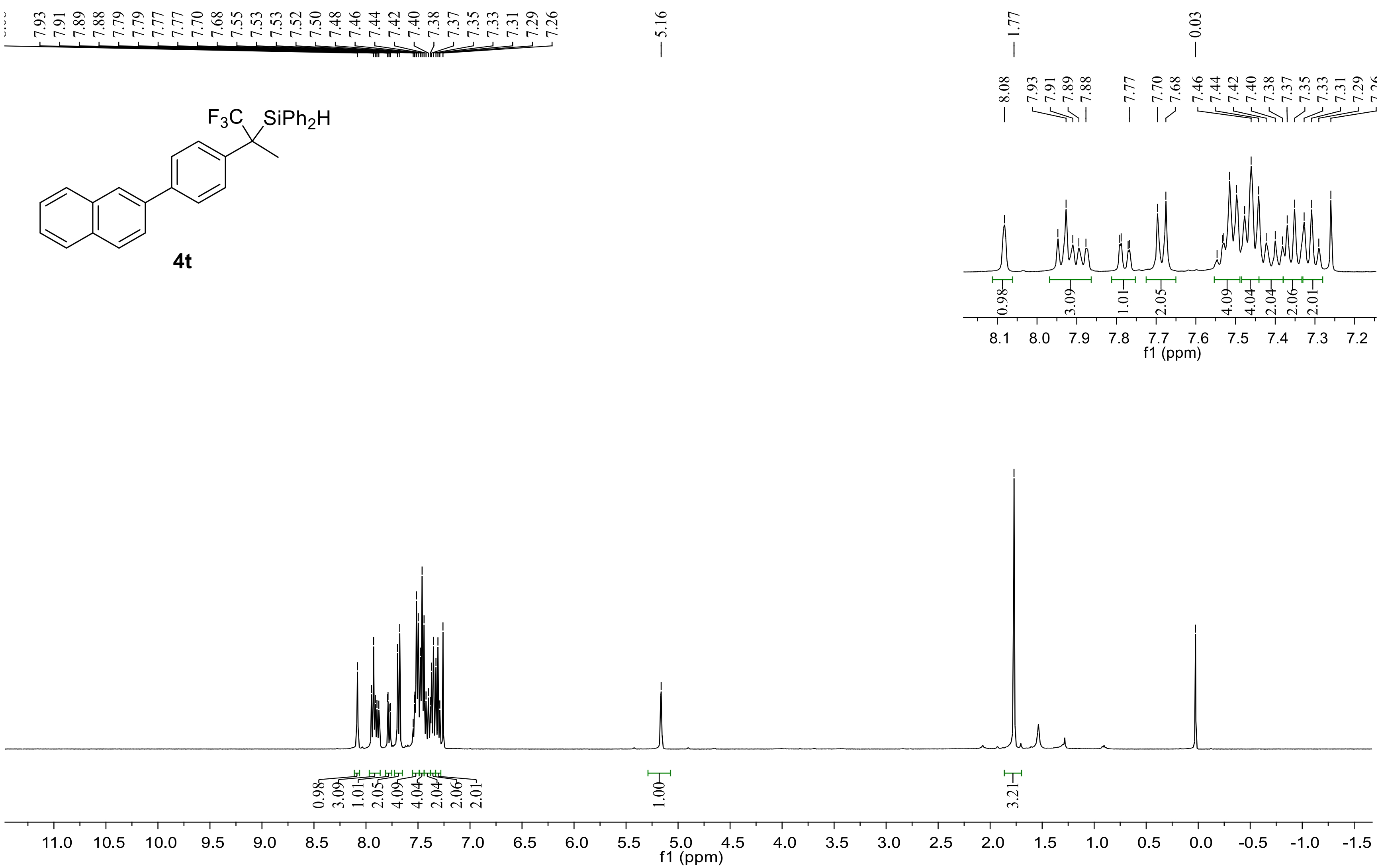
4s



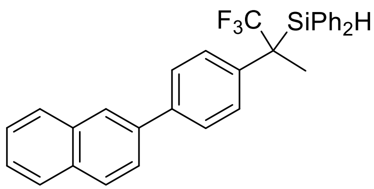
Supplementary Fig. 180. ^{19}F NMR (377 MHz, $CDCl_3$) of **4s**



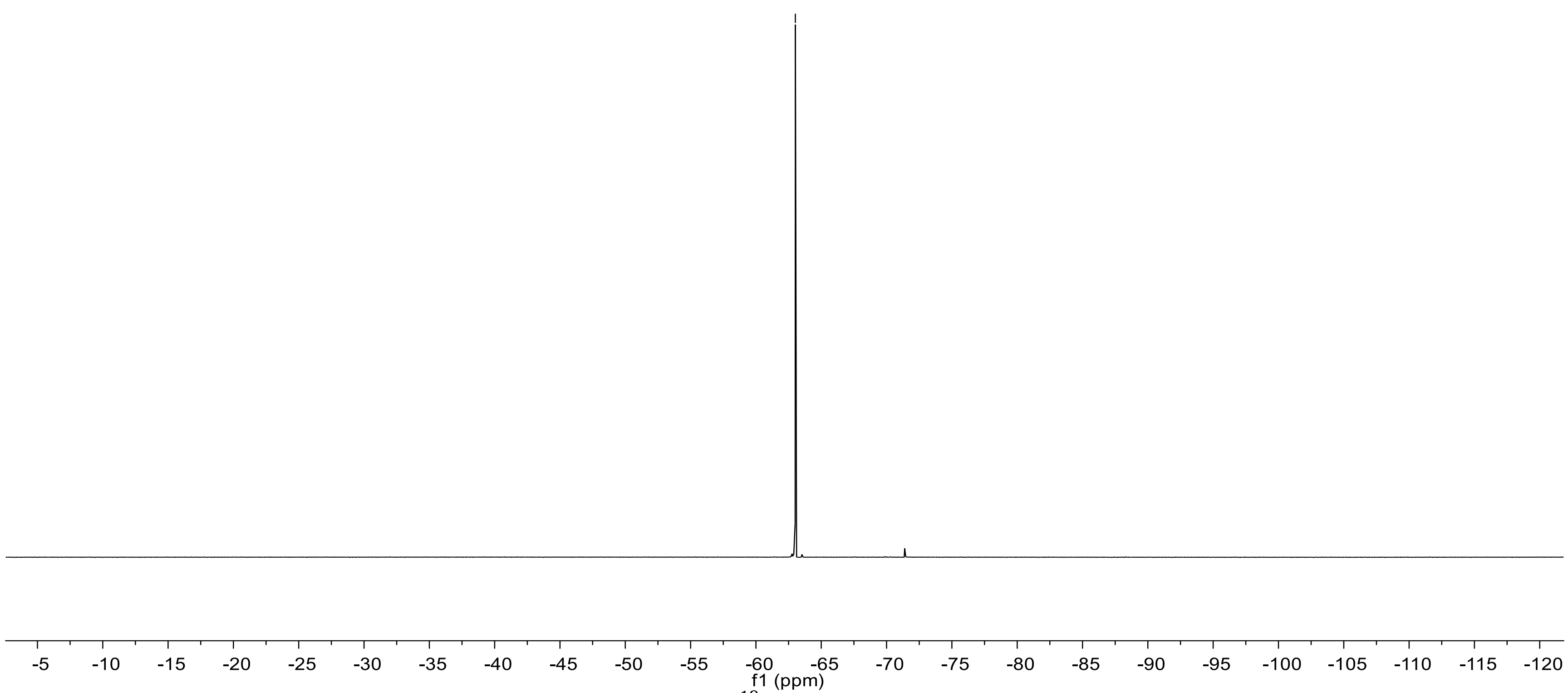
Supplementary Fig. 181. ^{13}C NMR (101 MHz, $CDCl_3$) of **4s**



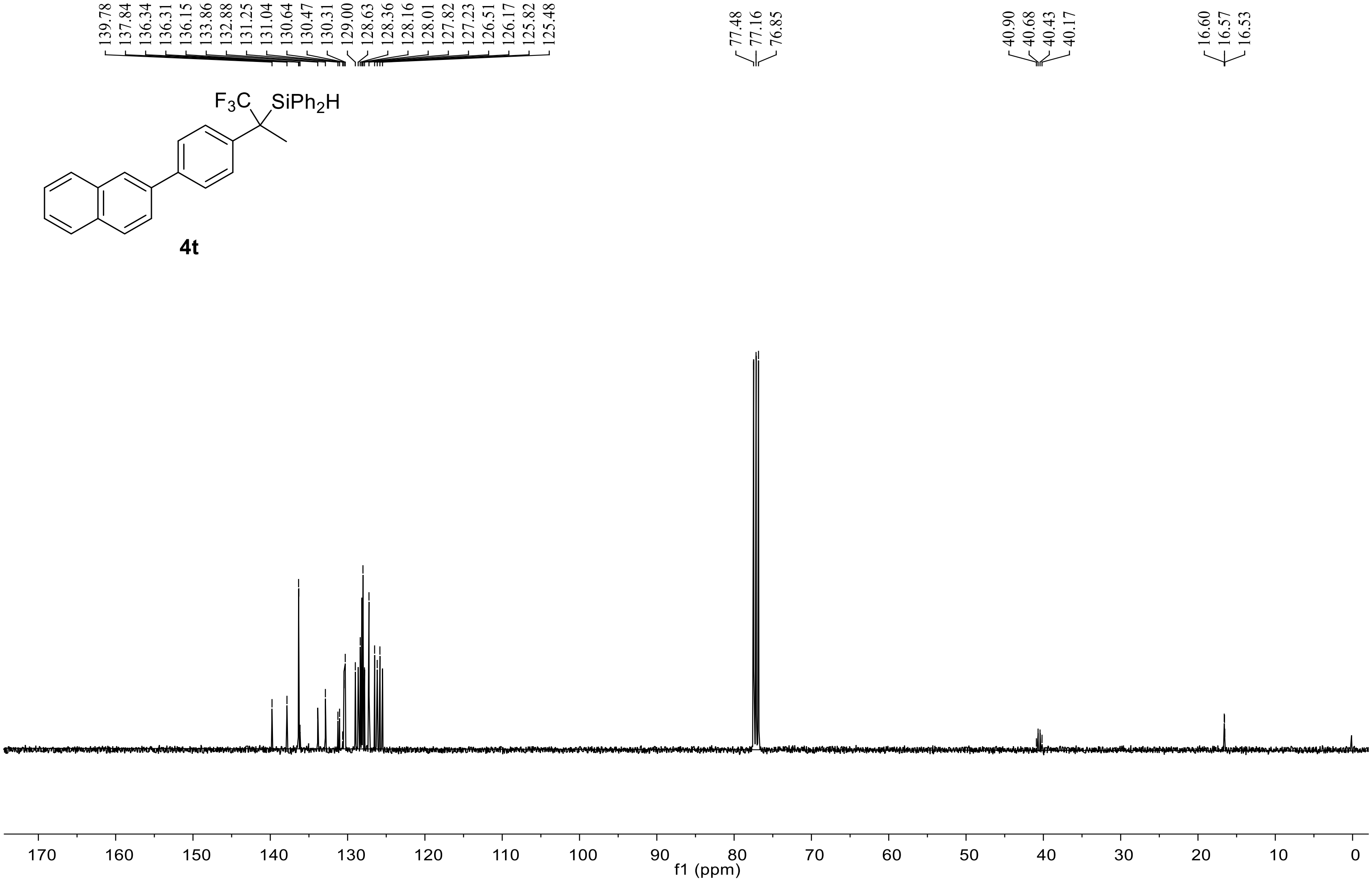
Supplementary Fig. 182. ^{1}H NMR (400 MHz, $CDCl_3$) of **4t**



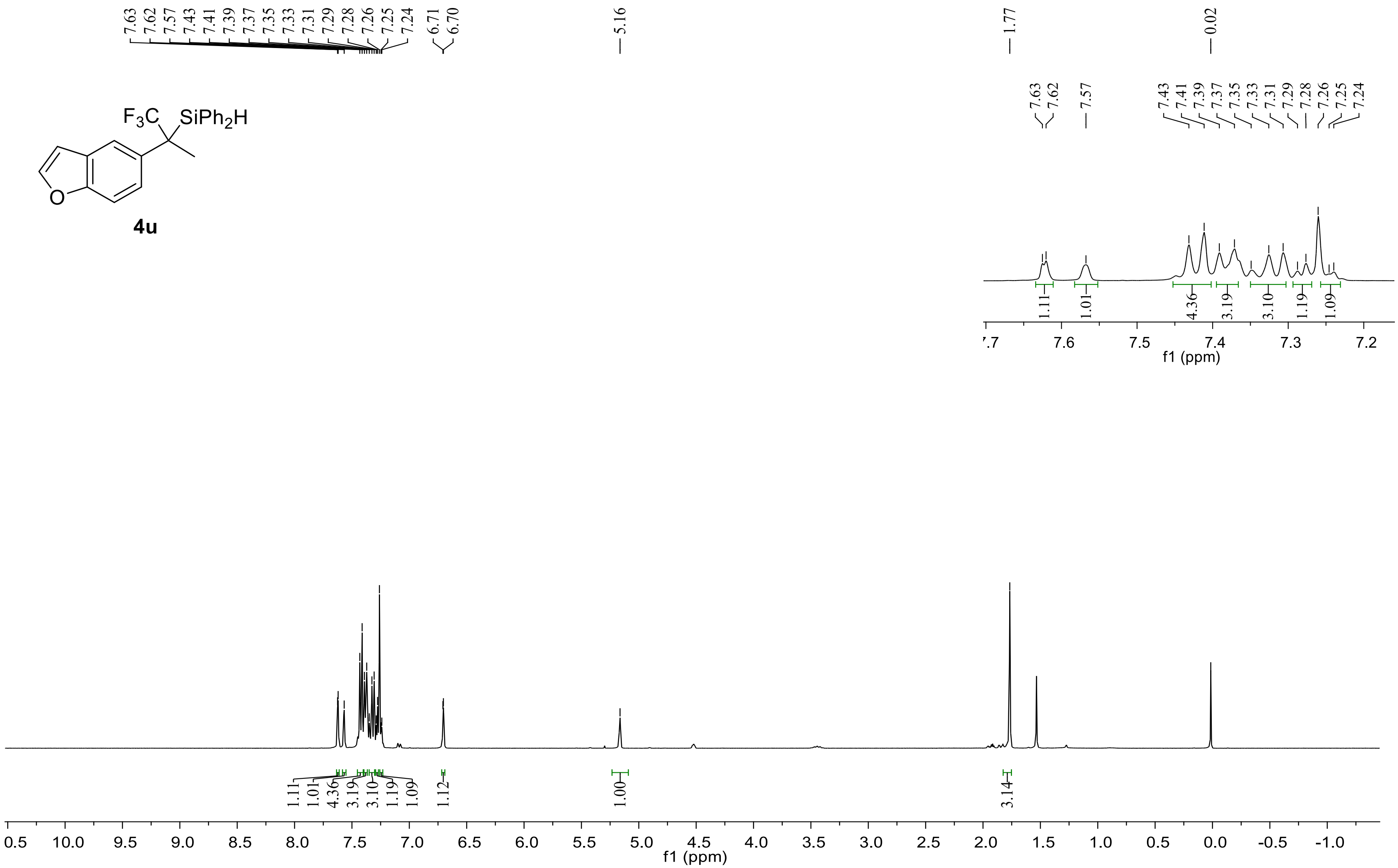
4t



Supplementary Fig. 183. ^{19}F NMR (377 MHz, $CDCl_3$) of **4t**

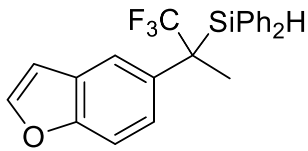


Supplementary Fig. 184. ^{13}C NMR (101 MHz, $CDCl_3$) of **4t**

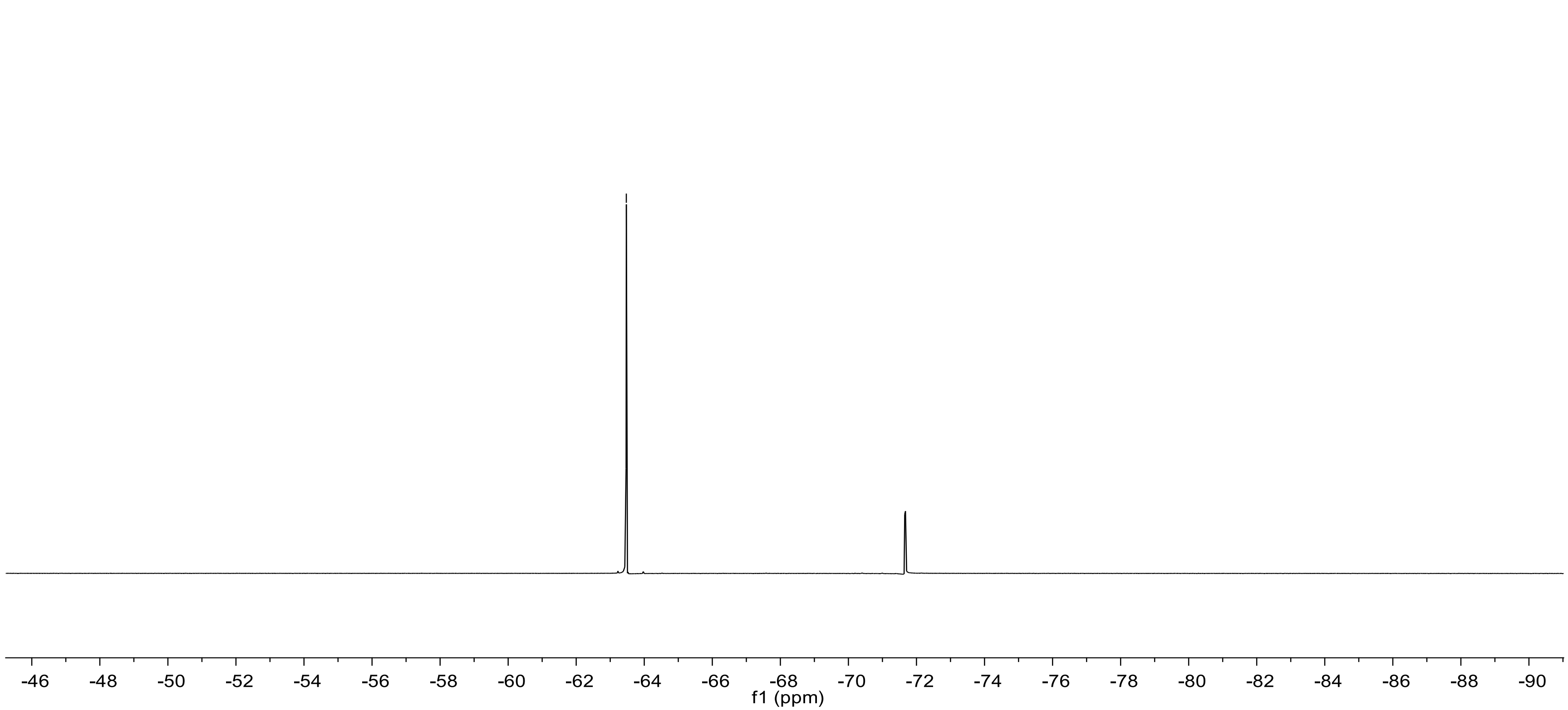


4u

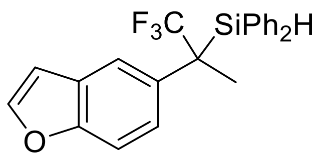
Supplementary Fig. 185. ^{1}H NMR (400 MHz, $CDCl_3$) of **4u**



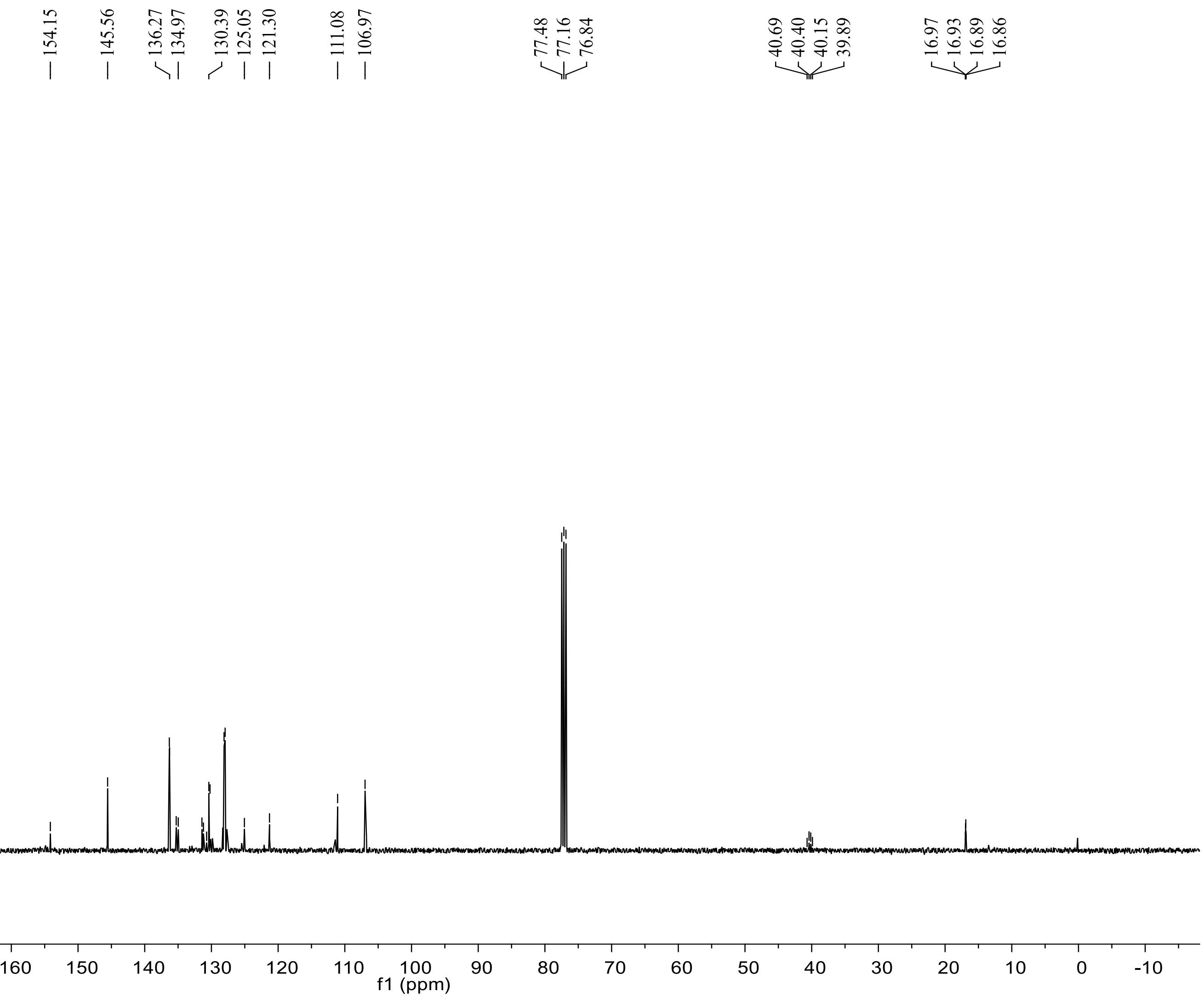
4u



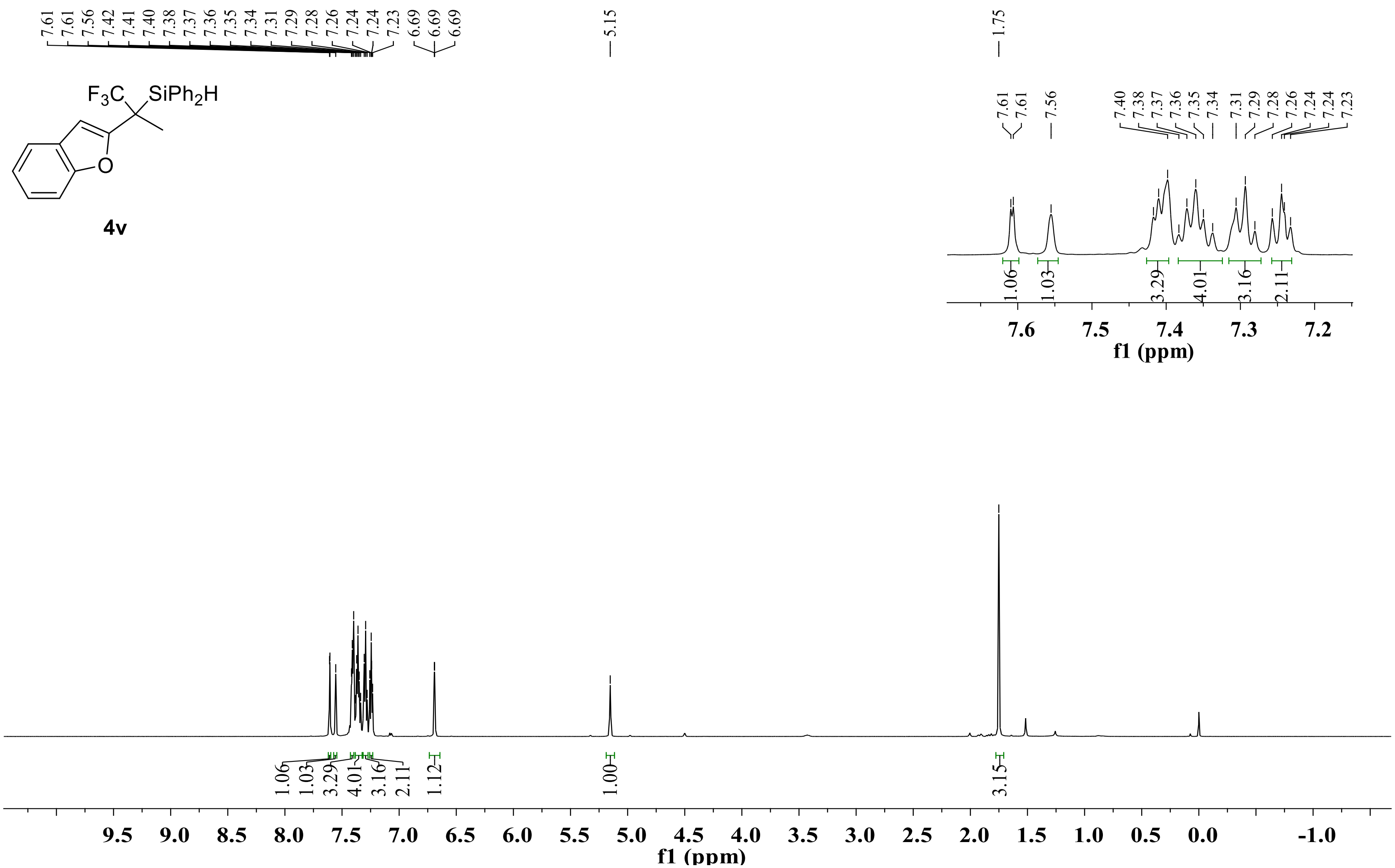
Supplementary Fig. 186. ^{19}F NMR (377 MHz, $CDCl_3$) of **4u**



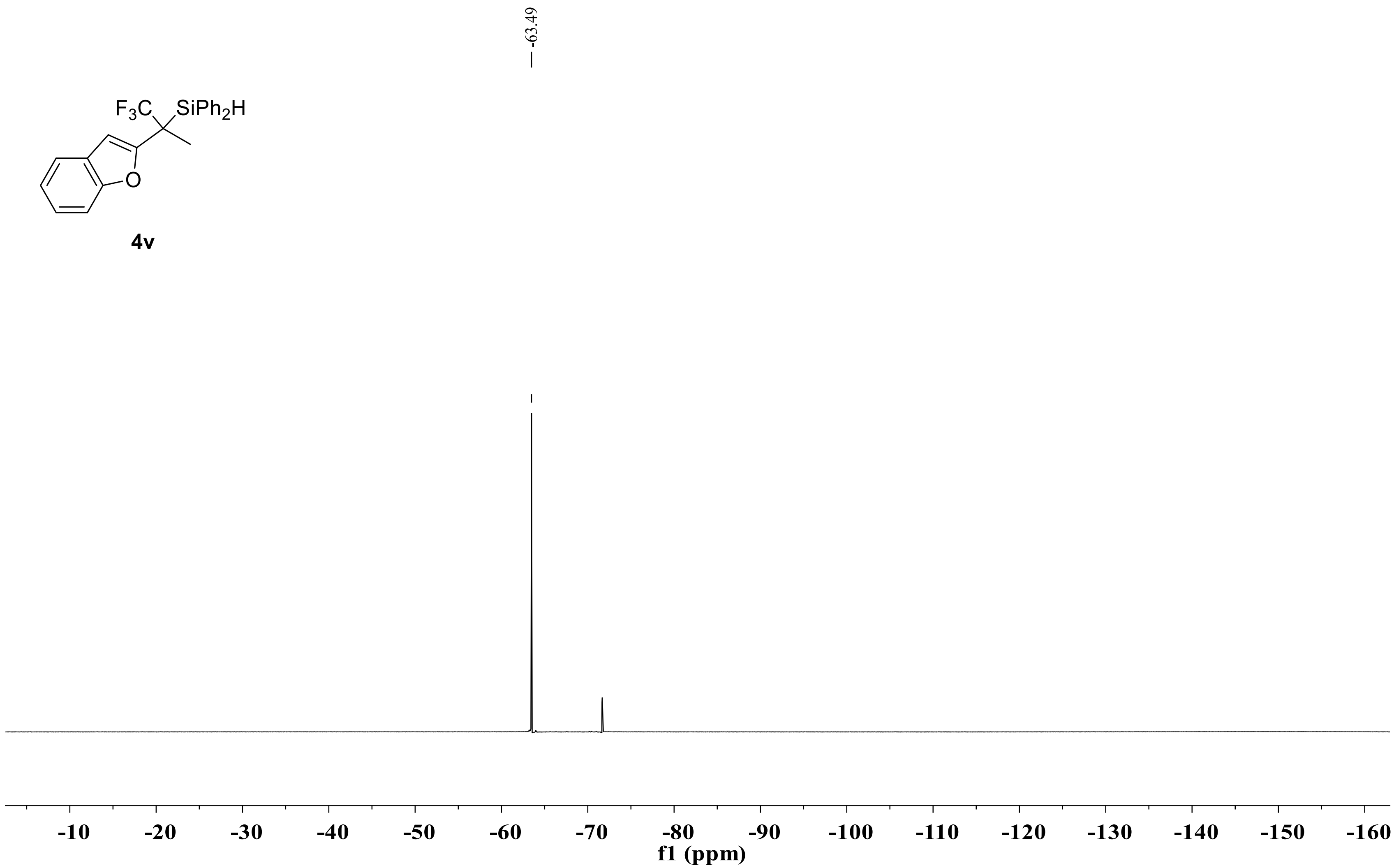
4u



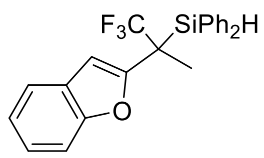
Supplementary Fig. 187. ^{13}C NMR (101 MHz, $CDCl_3$) of **4u**



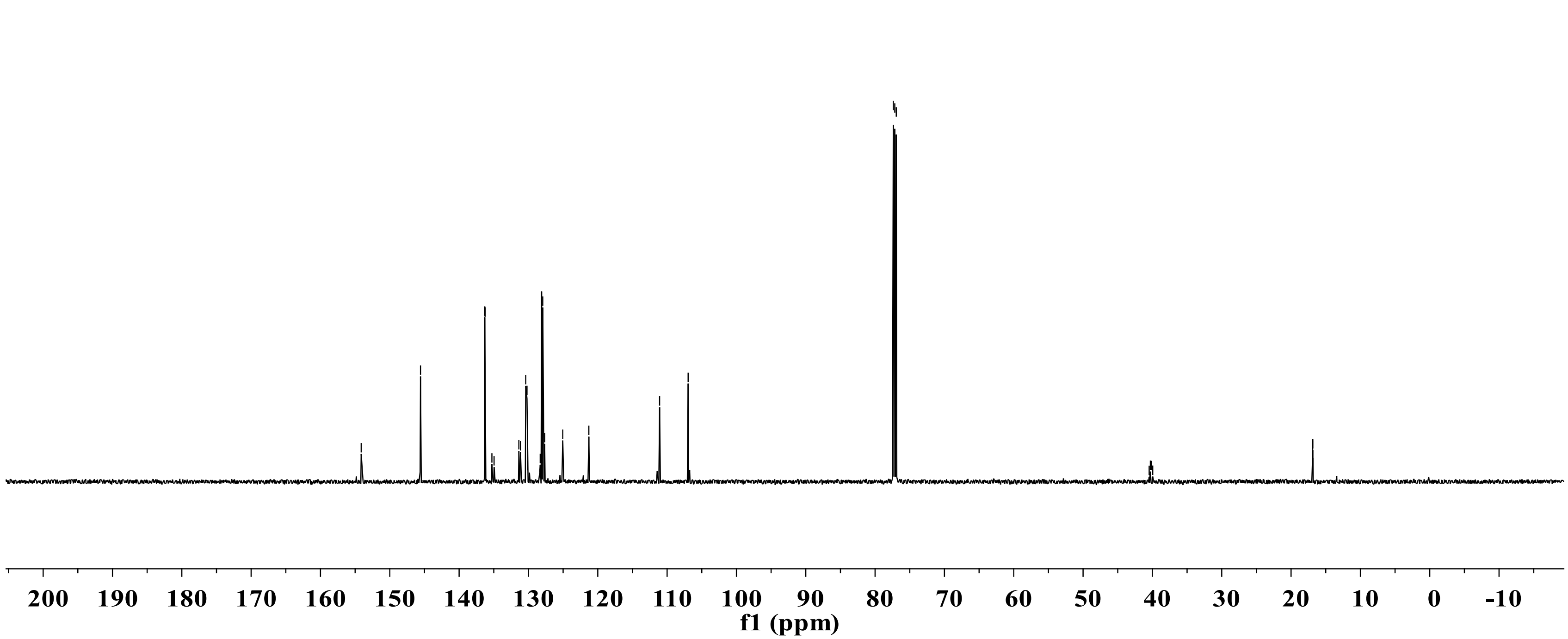
Supplementary Fig. 188. ^{1}H NMR (600 MHz, $CDCl_3$) of **4v**



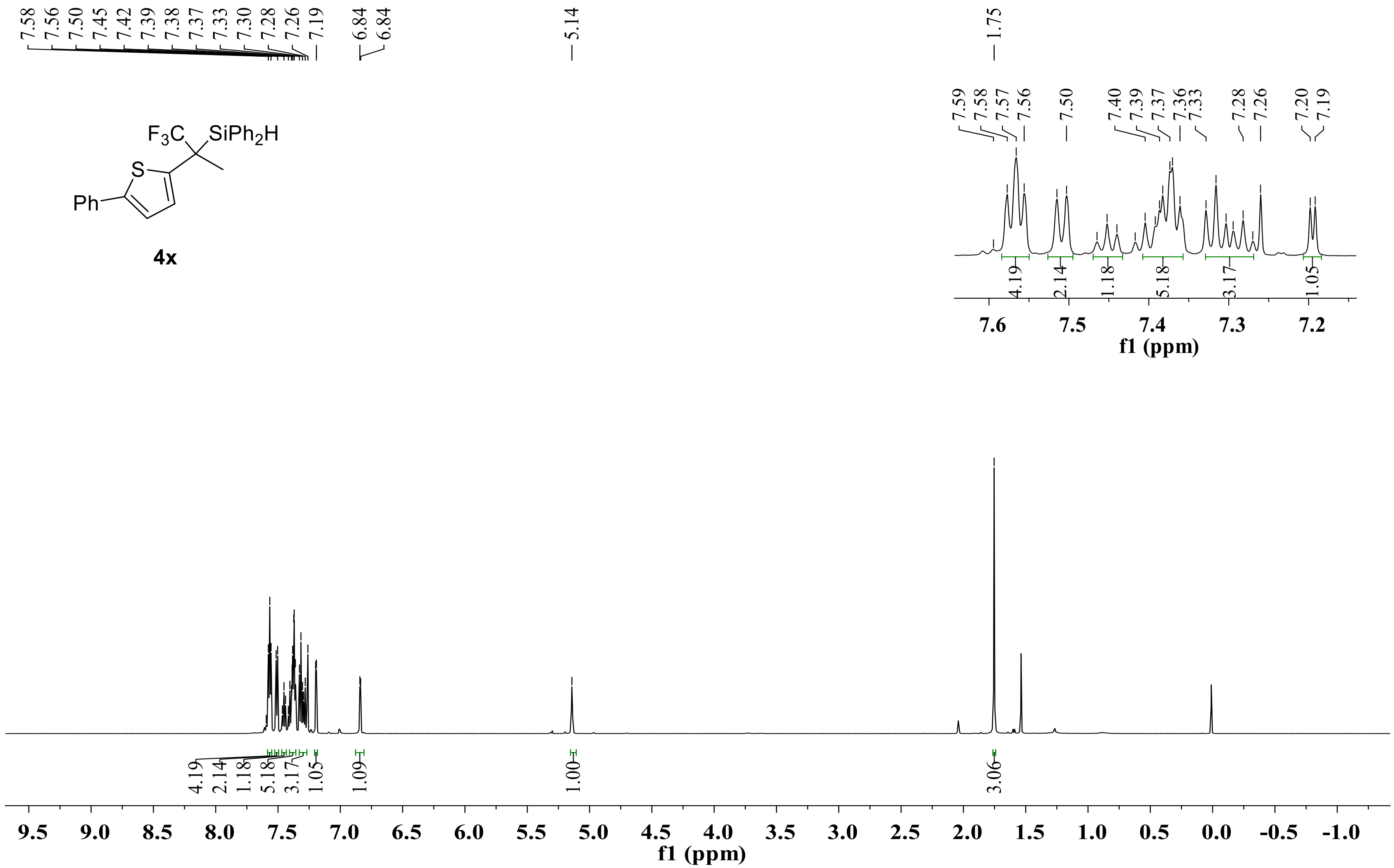
Supplementary Fig. 189. ^{19}F NMR (376 MHz, $CDCl_3$) of **4v**



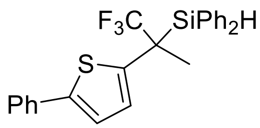
4v



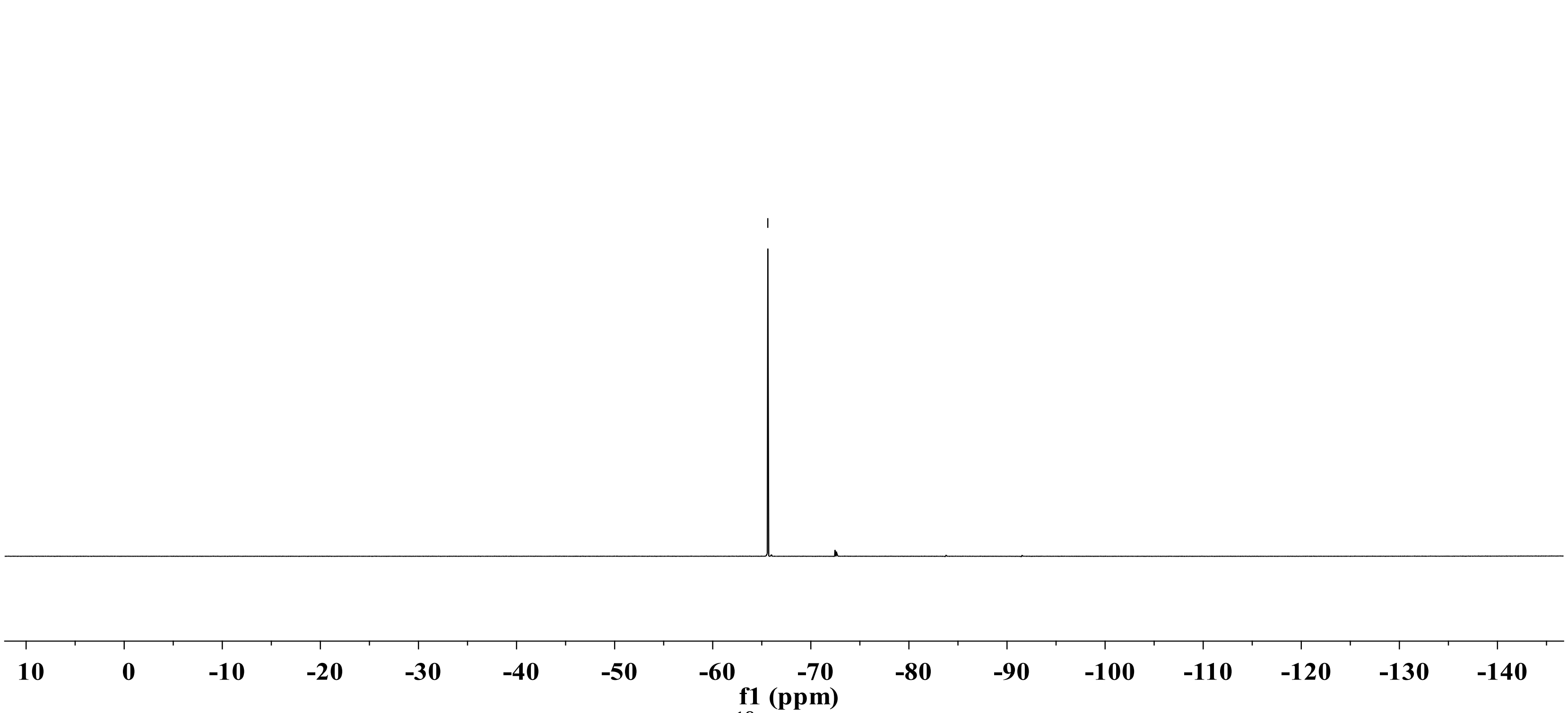
Supplementary Fig. 190. ^{13}C NMR (151 MHz, $CDCl_3$) of **4v**



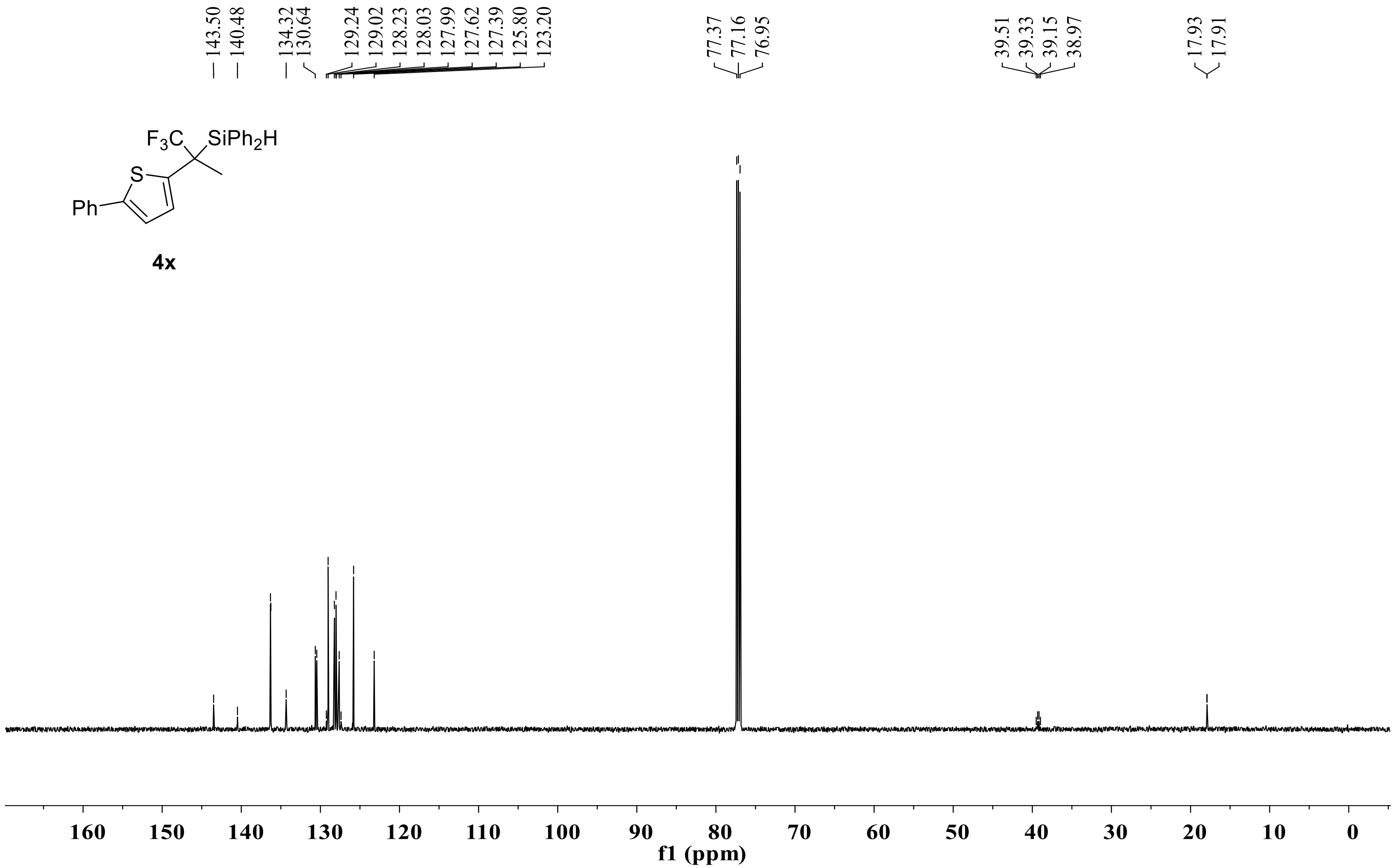
Supplementary Fig. 191. ^{1}H NMR (600 MHz, $CDCl_3$) of **4x**



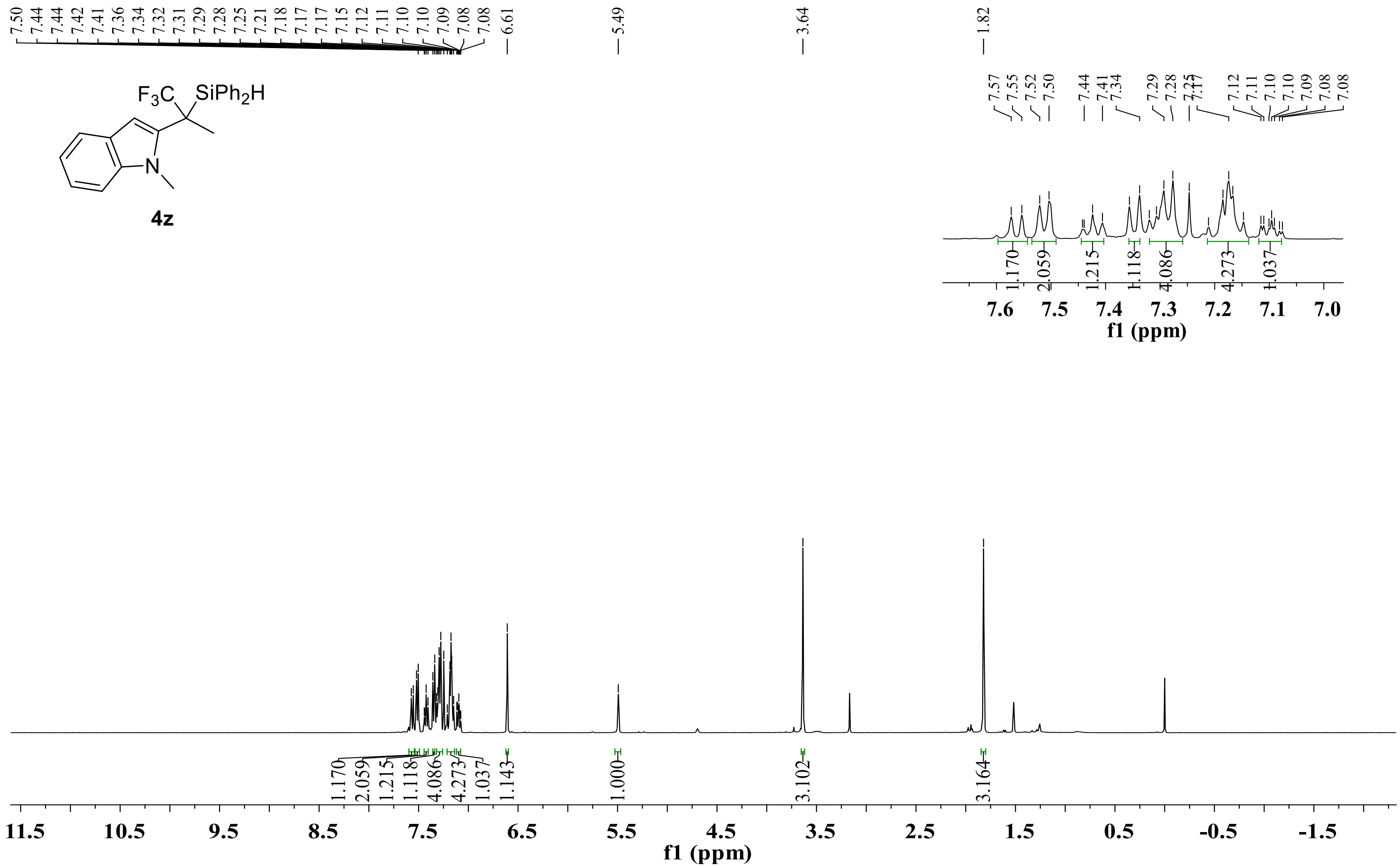
4x



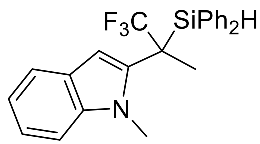
Supplementary Fig. 192. ^{19}F NMR (565 MHz, $CDCl_3$) of **4x**



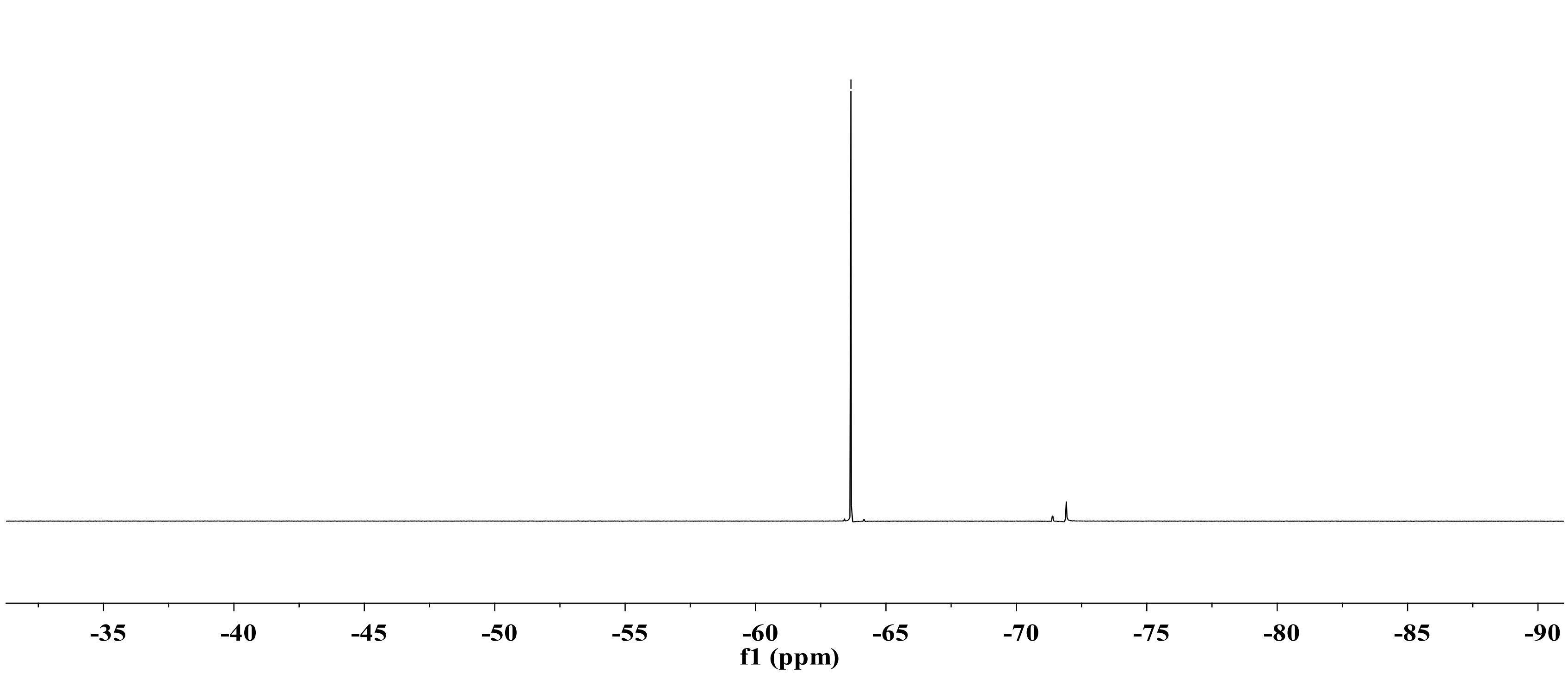
Supplementary Fig. 193. ^{13}C NMR (151 MHz, $CDCl_3$) of **4x**



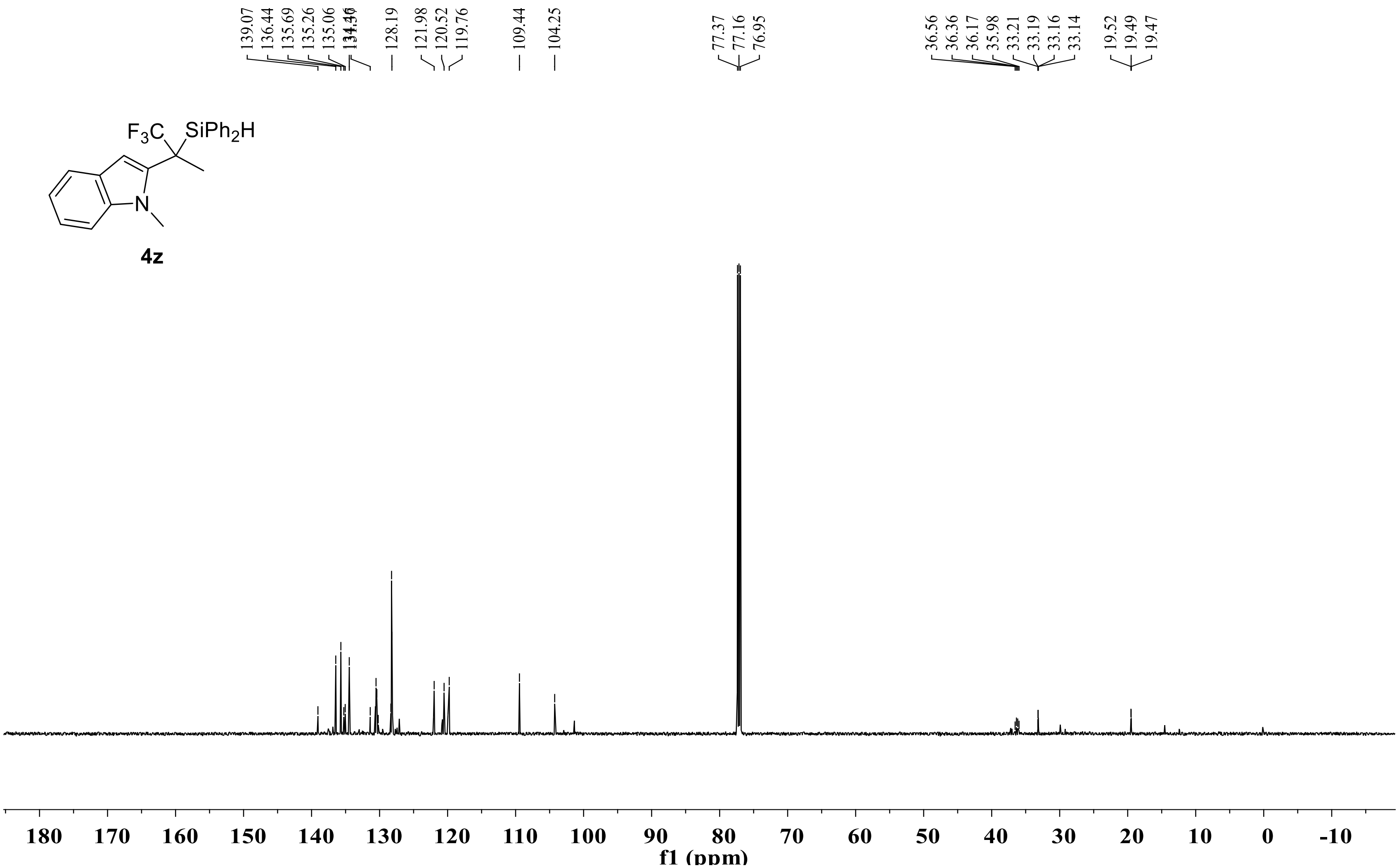
Supplementary Fig. 194. ^{1}H NMR (400 MHz, $CDCl_3$) of **4z**



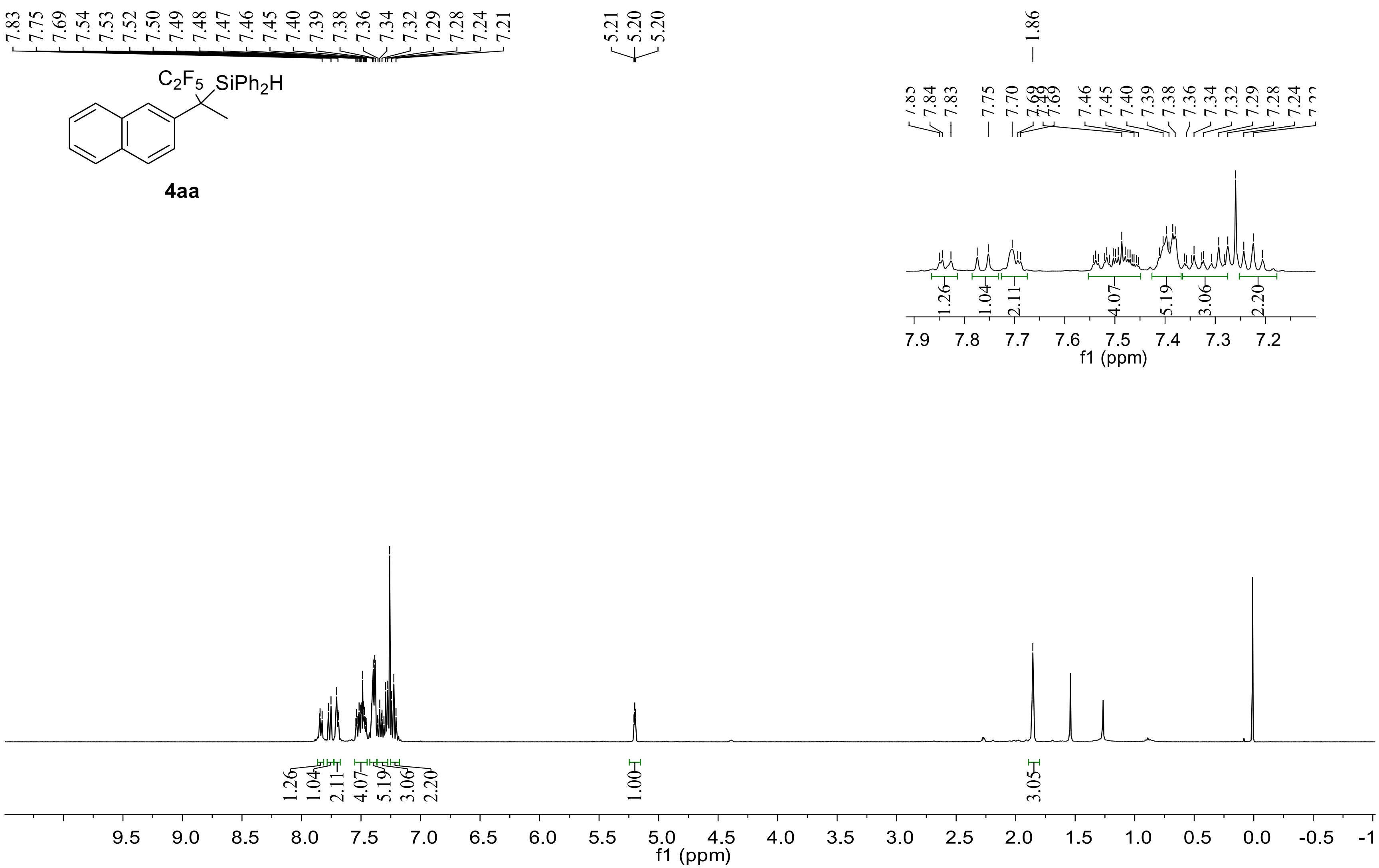
4z



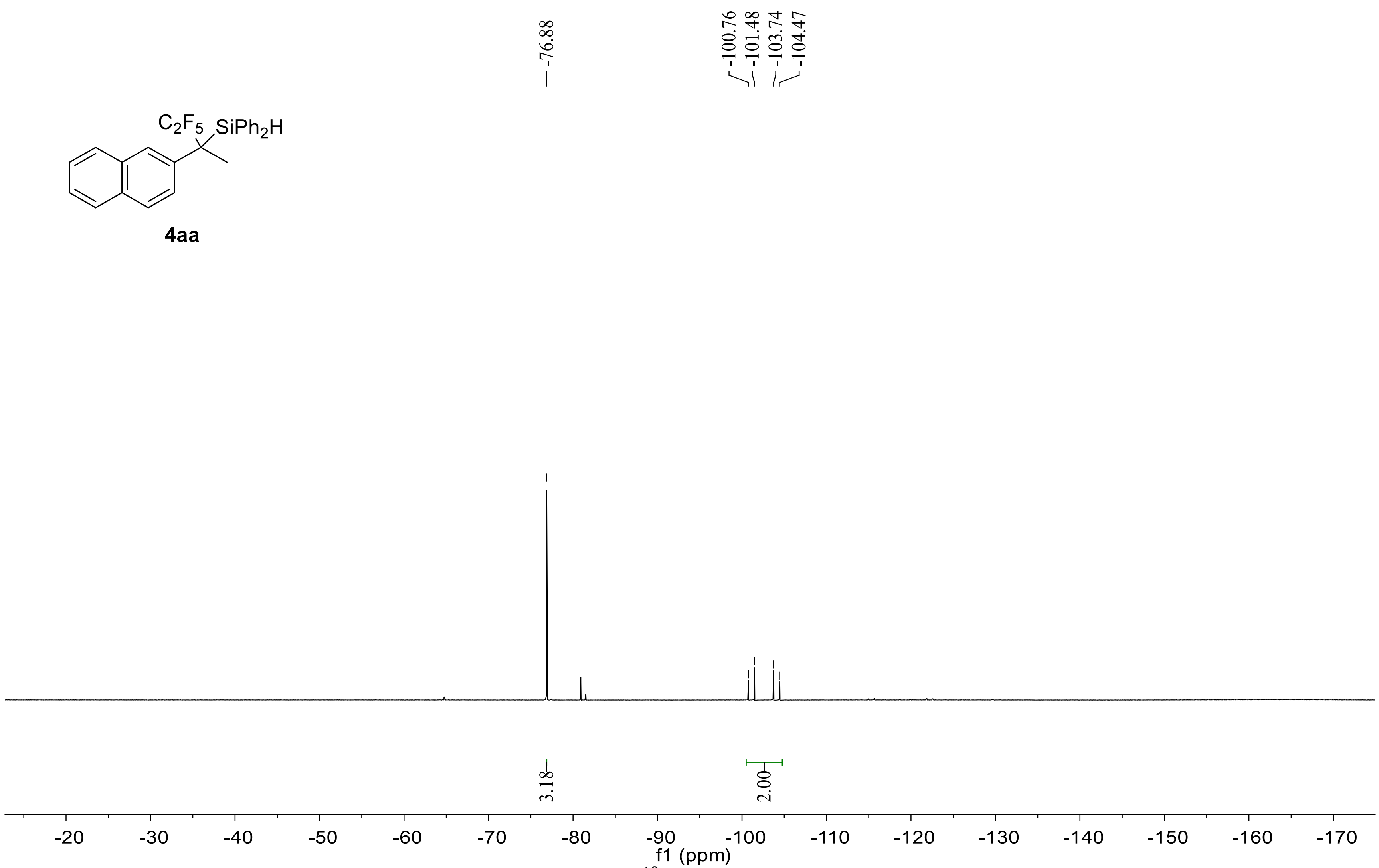
Supplementary Fig. 195. ^{19}F NMR (376 MHz, $CDCl_3$) of **4z**



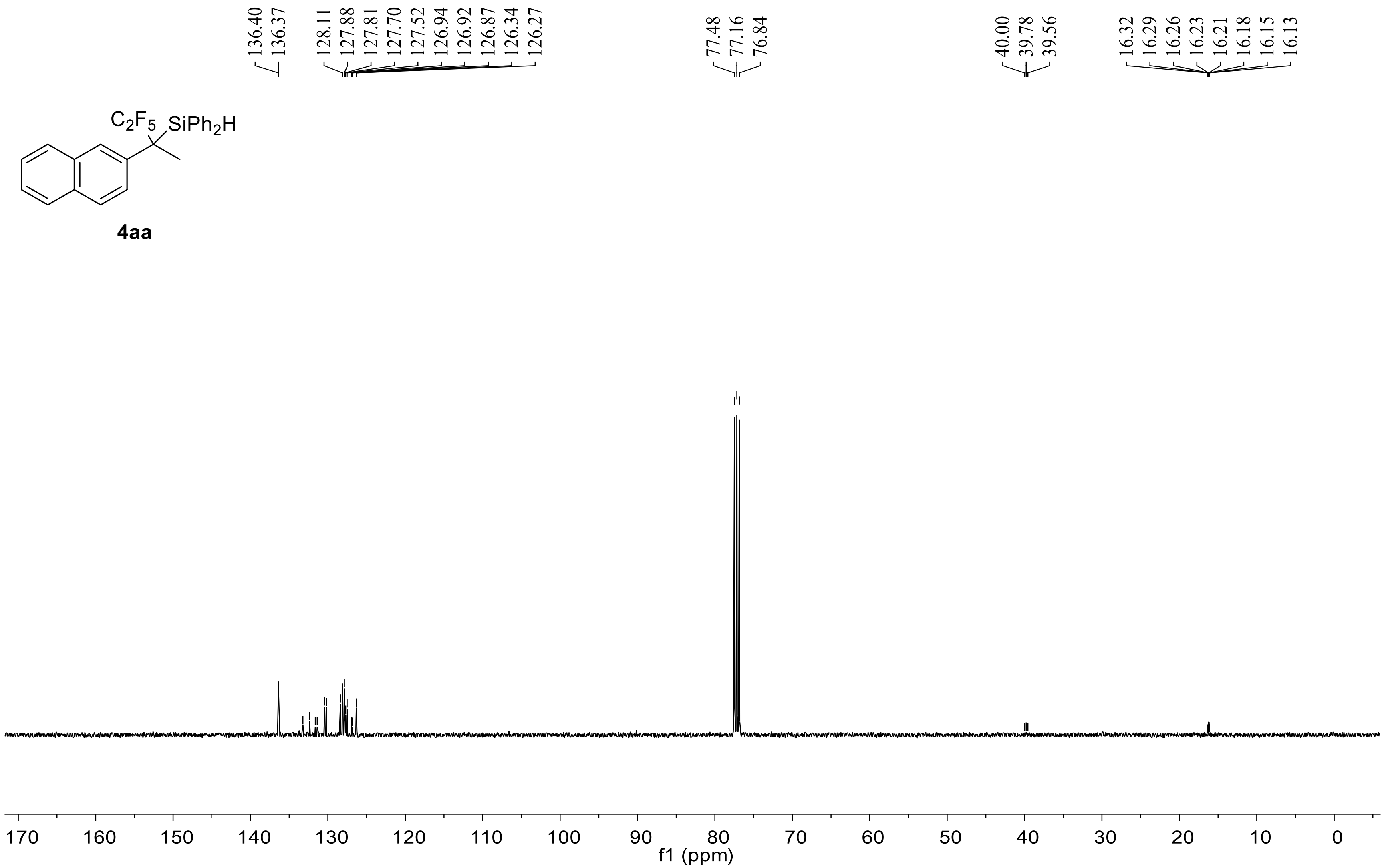
Supplementary Fig. 196. ^{13}C NMR (151 MHz, $CDCl_3$) of **4z**



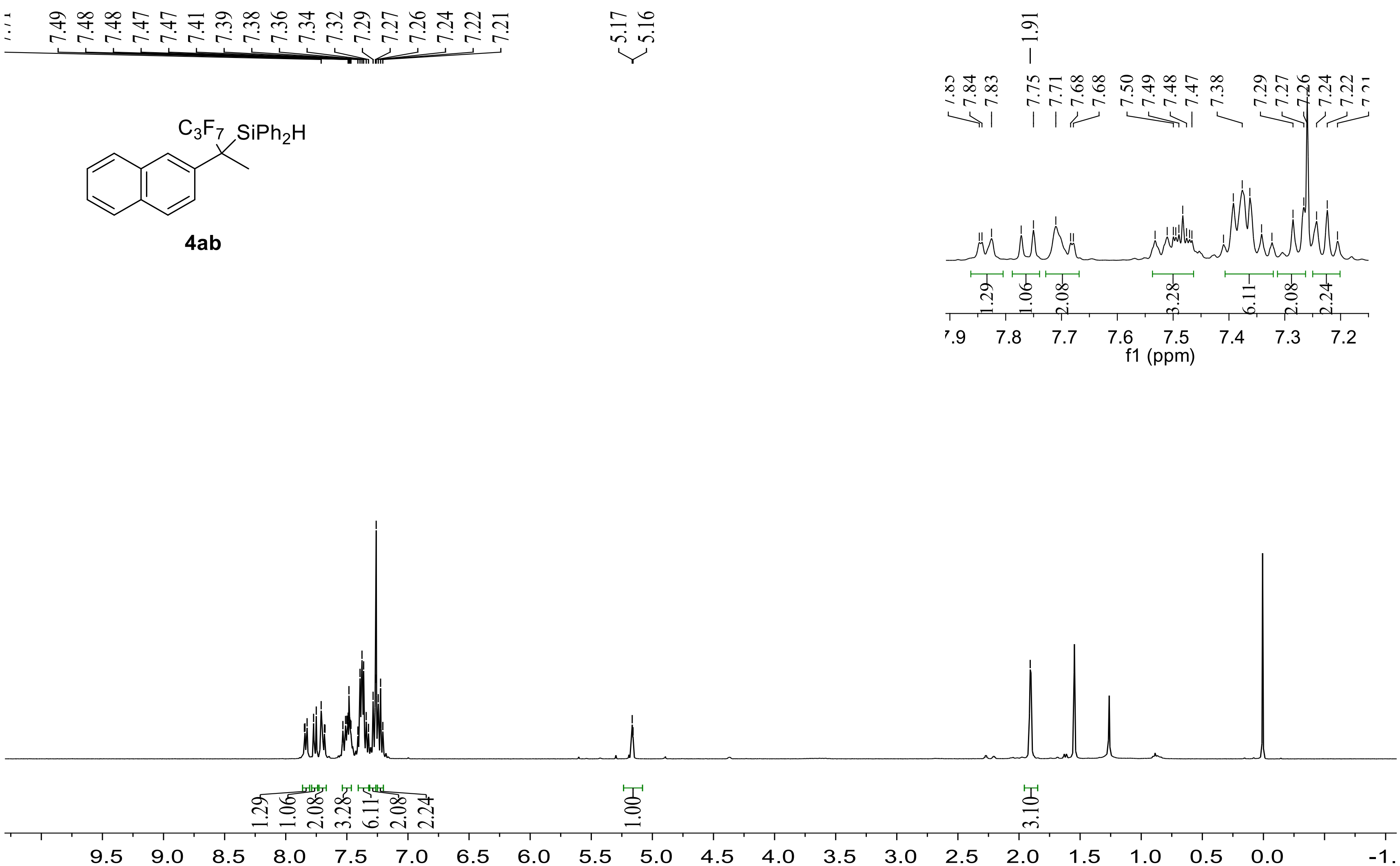
Supplementary Fig. 197. ^{1}H NMR (400 MHz, $CDCl_3$) of **4aa**



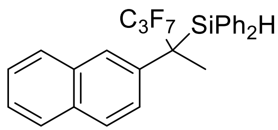
Supplementary Fig. 198. ^{19}F NMR (376 MHz, $CDCl_3$) of **4aa**



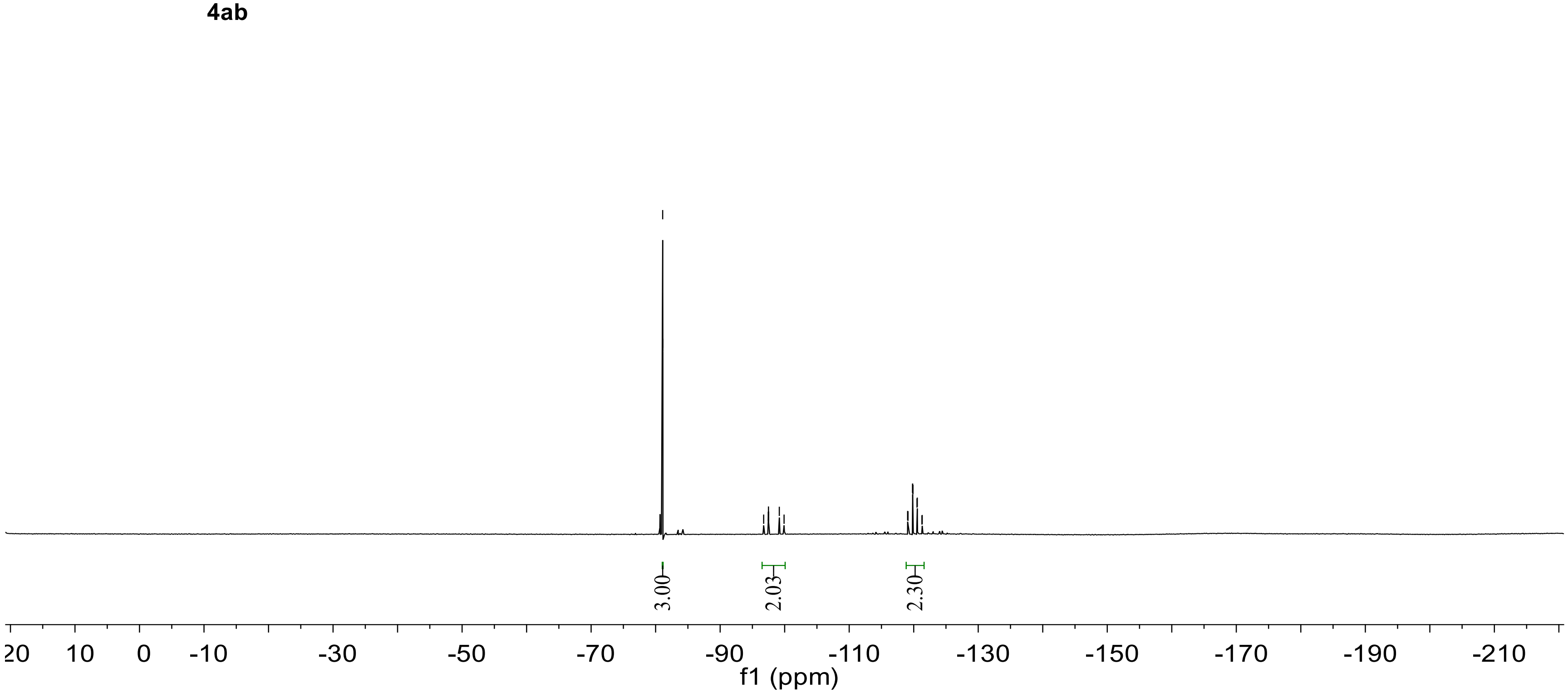
Supplementary Fig. 199. ^{13}C NMR (101 MHz, $CDCl_3$) of **4aa**



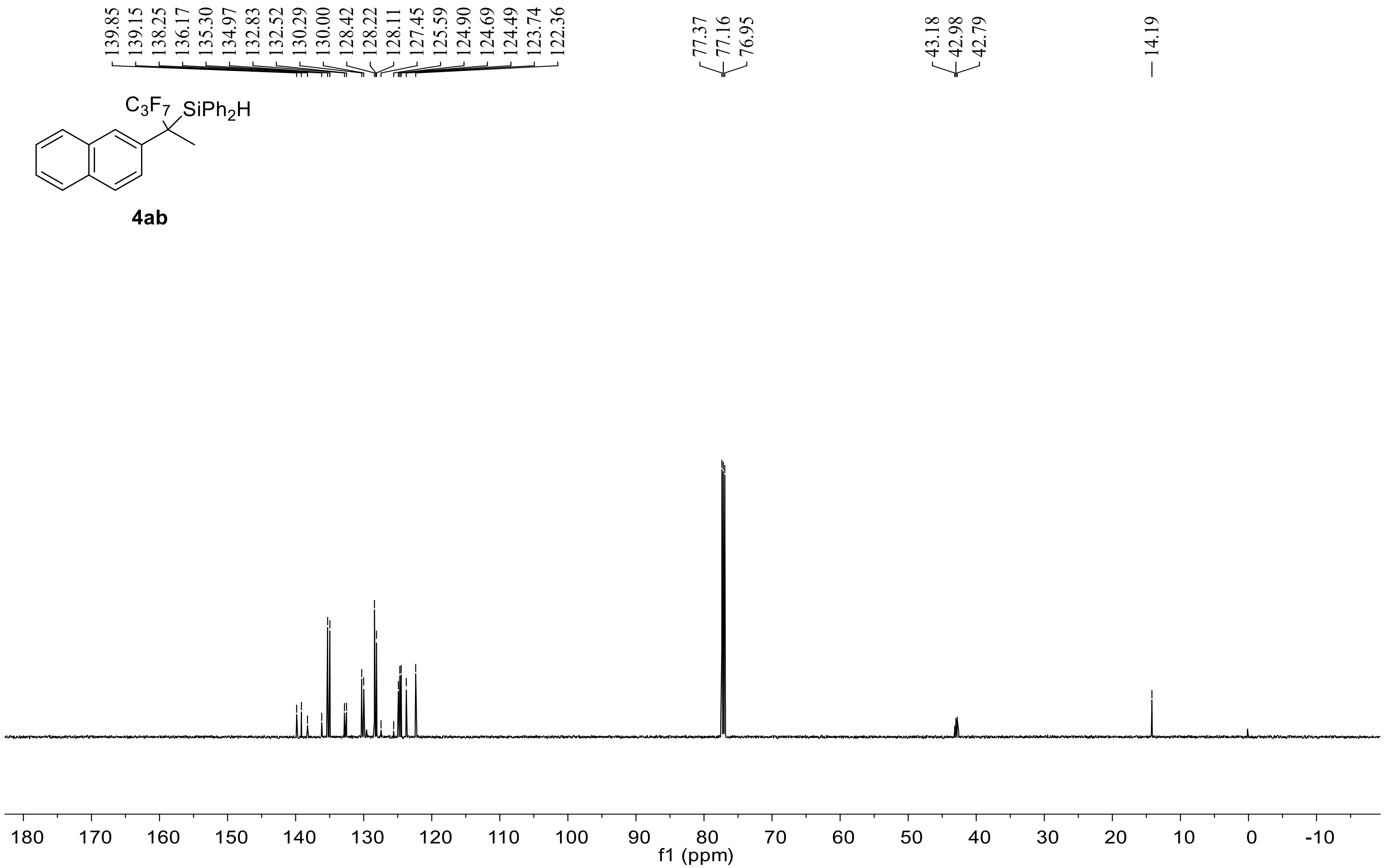
Supplementary Fig. 200. ^{1}H NMR (400 MHz, $CDCl_3$) of **4ab**



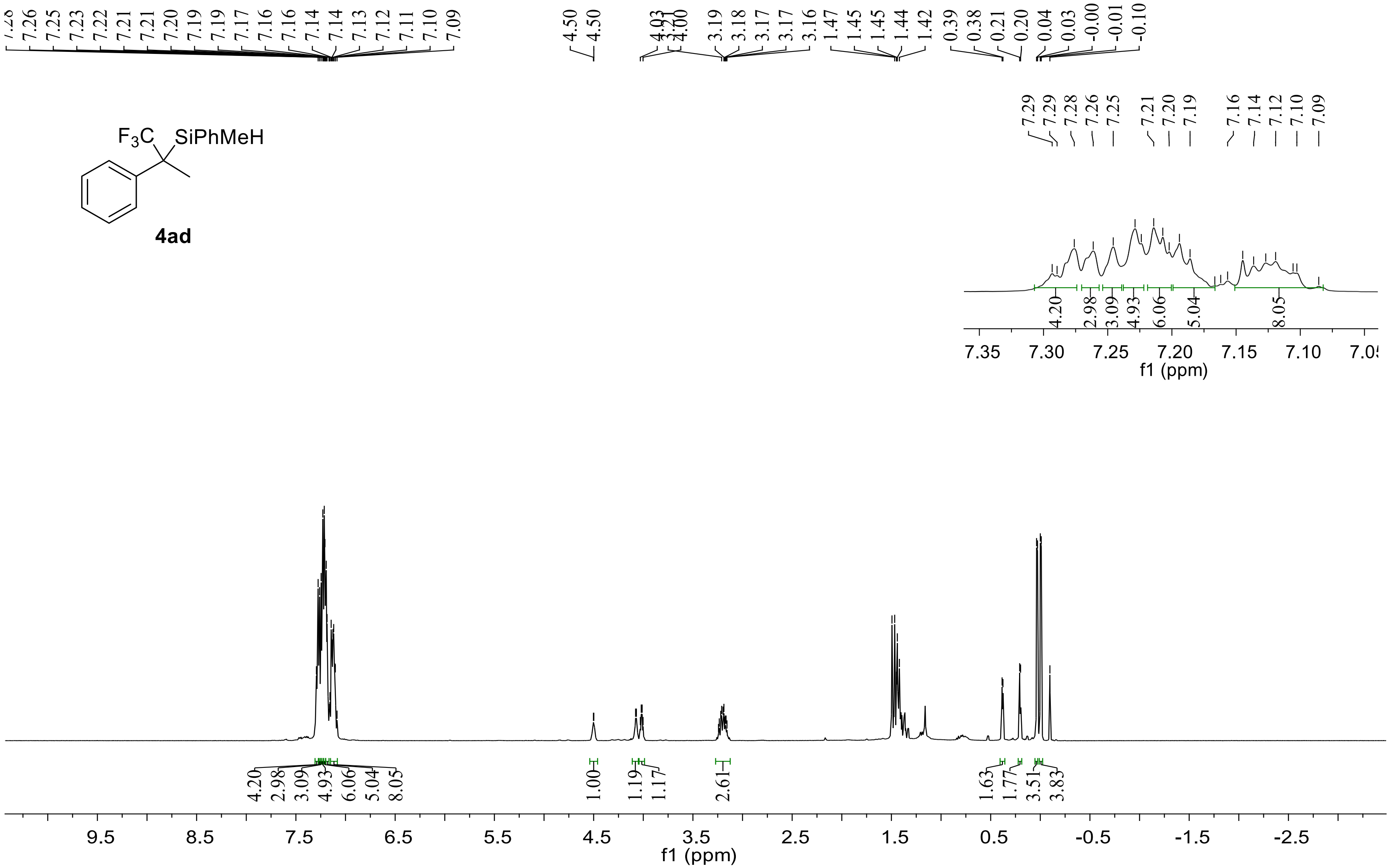
4ab



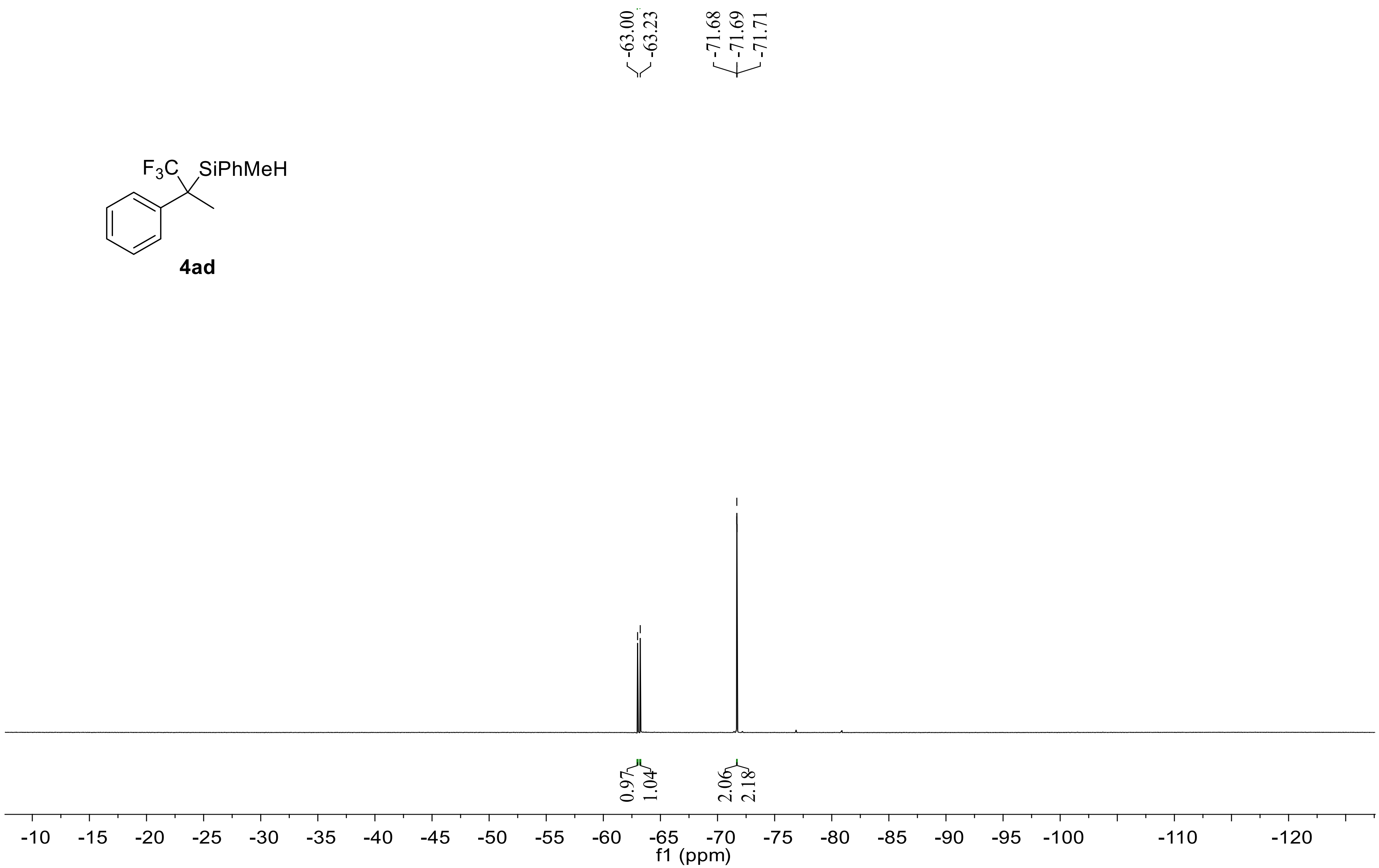
Supplementary Fig. 201. ^{19}F NMR (376 MHz, $CDCl_3$) of **4ab**



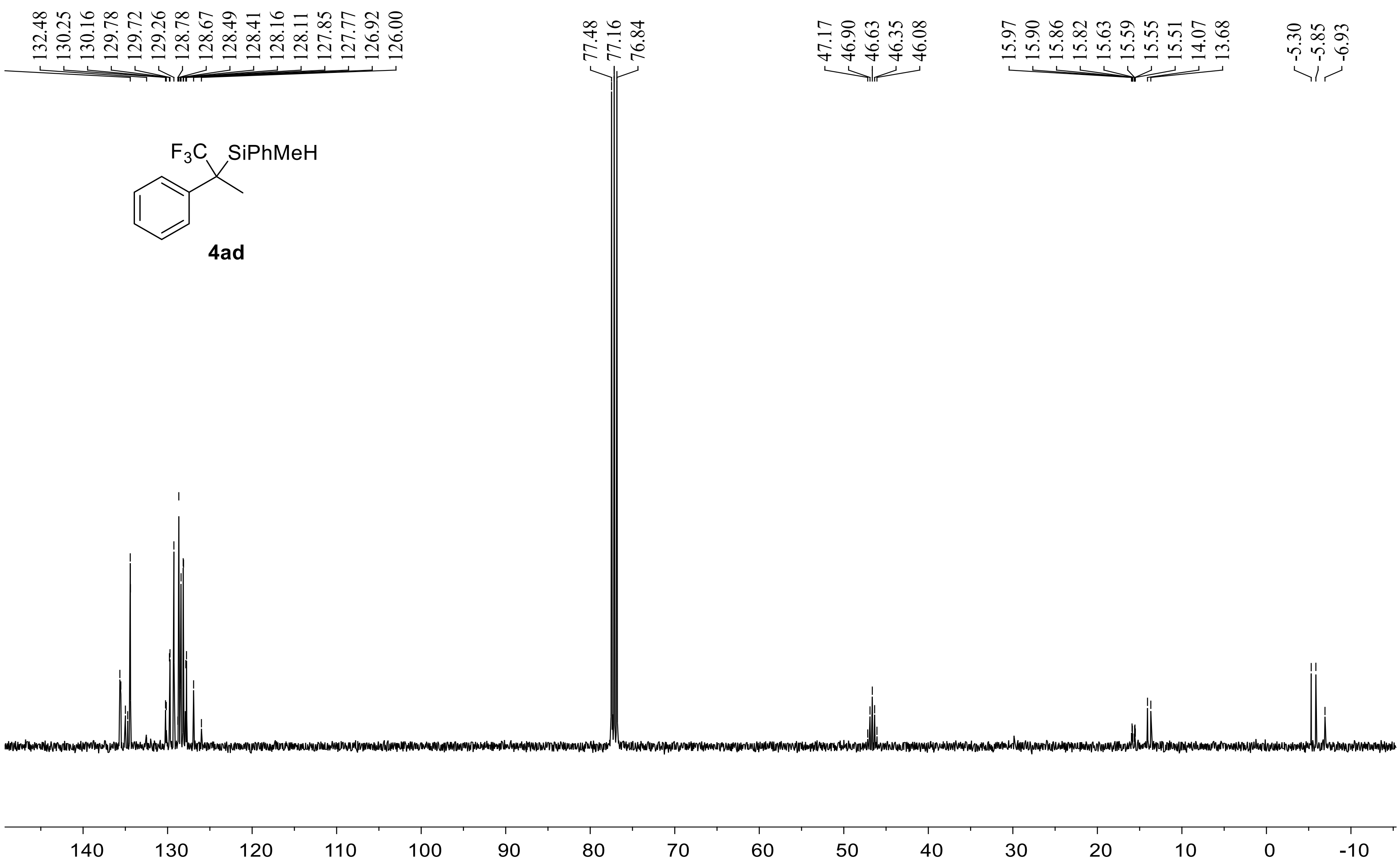
Supplementary Fig. 202. ^{13}C NMR (101 MHz, $CDCl_3$) of **4ab**



Supplementary Fig. 203. ^{1}H NMR (400 MHz, $CDCl_3$) of **4ad**



Supplementary Fig. 204. ^{19}F NMR (377 MHz, $CDCl_3$) of **4ad**



Supplementary Fig. 205. ^{13}C NMR (101 MHz, $CDCl_3$) of **4ad**

4. Supplementary References

[1] Schäfe, M., Stünkel, T., Daniliuc, C., Gilmour, R. Regio-and Enantiose lectiveIntermolecular Aminofluorination of Alkenesvia Iodine(I)/Iodine(III) Catalysis. *Angew. Chem. Int. Ed.* **61**, e202205508 (2022).

[2] Qiu, J., Wang, C. C., Zhou, L., Lou, Yi. X., Yang, K., Song, Q. L. Ni-Catalyzed Radical-Promoted Defluoroalkylborylation of Trifluoromethyl Alkenes To Access gem-Difluorohomoallylic Boronates. *Org. Lett.* **24**, 2446−2451 (2022).

[3] Ichitsuka, T., Fujita, T., Arita, T., Ichikawa, J. Double C-F Bond Activation throughb-Fluorine Elimination: Nickel-Mediated [3+2] Cycloaddition of 2-Trifluoromethyl-1-alkenes withAlkynes. *Angew. Chem. Int. Ed.* **53**, 7564 –7568 (2014).

[4] Zhang, J, J., Yang, J, D., Cheng, J, -P. Chemoselective catalytic hydrodefluorination of trifluoromethylalkenes towards mono-/gem-difluoroalkenes under metal-free condit. *Nature Communications.* **12**, 2835 (2021).

[5] Chen, J. H., Cheng, B., Cao, M, Y., Lu, Z. Iron-Catalyzed Asymmetric Hydrosilylation of 1,1-DisubstitutedAlkenes. *Angew. Chem. Int. Ed.* **54**, 4661 –4664 (2015).

[6] Long, P, W., He, T., Oestreich, M. $B(C_6F_5)_3$-Catalyzed Hydrosilylation of Vinylcyclopropanes. *Org. Lett.* **22**, 7383−7386 (2020).

[7] Becke, A. D. *J. Chem. Phys.*, **1993**, 98, 5648.

[8] Lee, C., Yang, W. & Parr, R. G. *Phys. Rev. B.,* **1988***,* 37, 785.

[9] Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.,* **2011**, 32, 1456.

[10] Becke, A. D.; Johnson, E. R. *J. Chem. Phys*., **2005**, 123, 154101.

[11] Zhao, Y. & Truhlar, D. G. *Theor. Chem. Acc*., **2008**, 119, 525.

[12] Cancès, E., Mennucci, B. & Tomasi, J. *J. Chem. Phys.*, **1997**, 107, 3032.

[13] Legault, C. Y. CYLview, 1.0b; Universitéde Sherbrooke: **2009** (http://www.cylview.org).