Supporting Information

Reductive Desymmetric Silylation of Biaryl Bis(triflates) Enabled by a Chiral Nickel/Picolinamide Complex

Zhe Chen, Junjie Zhang, and Chuan Wang*

Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

E-mail: chuanw@ustc.edu.cn

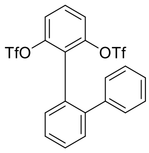
Table of Contents

General information

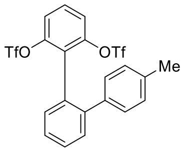
^{1}H, ^{13}C, ^{19}F and ^{31}P spectra were recorded in a $CDCl_3$ or Acetone-d_6 solution on Bruker Aescend 400 MHz or 500 MHz instruments. ^{19}F NMR were reported as ^{19}F exp. comp. pulse decoupling (^{19}F CPD) pulse decoupling (^{19}F CPD). The chemical shifts are given in ppm relative to the resonance of the solvent [^{1}H: δ ($CDCl_3$) = 7.26, ^{13}C: δ ($CDCl_3$) = 77.16 ppm], [^{1}H: δ (Acetone-d_6) = 2.05, ^{13}C: δ (Acetone-d_6) = 206.26 ppm] or relative to tetramethylsilane [^{1}H: δ ($SiMe_4$) = 0.00 ppm] as an internal standard. Multiplicities are given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); ddd (doublet of doublet of doublets); m (multiplets), etc. Coupling constants are reported as J values in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. HPLC analysis was performed on Thermo UltiMate 3000. Enantiomer excesses were determined by HPLC analysis employing Daicel chiral column (chiralpak AD-H, chiralpak IA, chiralpak IB, chiralcel OD-H) or Guangzhou FLM Scientific Instrument chiral column (chiral MD) with *n*-hexane/*i*-PrOH as the eluents. Flash chromatography was performed using 300-400 mesh silica gel with the indicated solvent system. All air- or moisture-sensitive reactions were protected with nitrogen atmosphere. All reactions were monitored through thin layer chromatography [Merck 60 F254 precoated silica gel plate (0.2 mm thickness)]. Subsequent to elution, spots were visualized using UV radiation (254 nm) on Spectroline Model ZF-7 254 nm. Other visualization methods include staining with a basic solution of potassium permanganate or acidic solution of ceric ammonium molybdate, followed by heating.

Unless otherwise noted, all reagents and starting materials were purchased from commercial vendors and used as received without further purification.

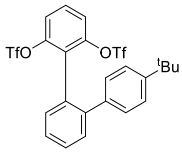
Synthesis of Starting Materials



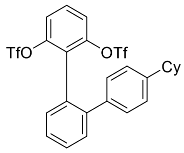
1a



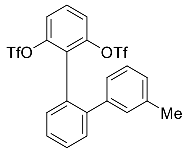
1b



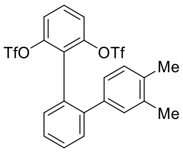
1c



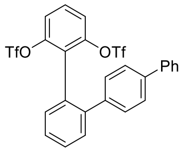
1d



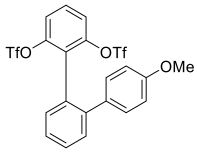
1e



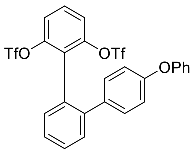
1f



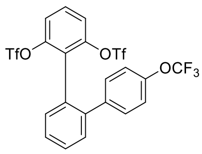
1g



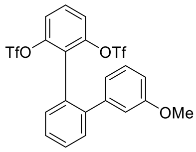
1h



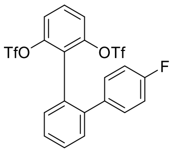
1i



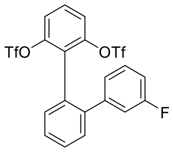
1j



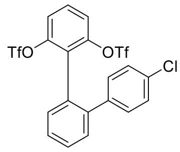
1k



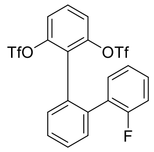
1l



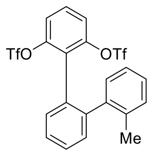
1m



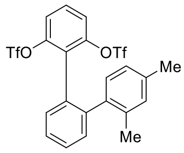
1n



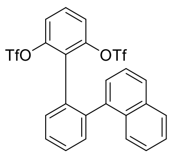
1o



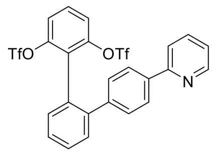
1p



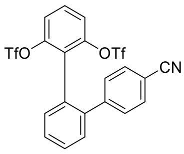
1q



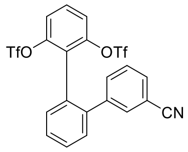
1r



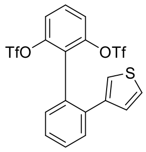
1s



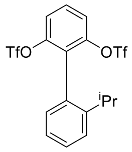
1t



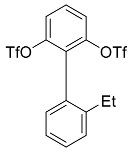
1u



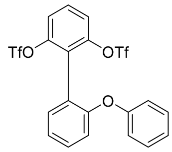
1v



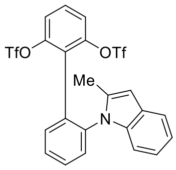
1w



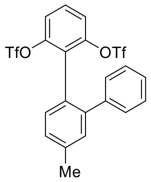
1x



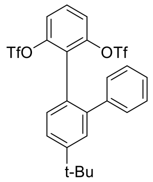
1y



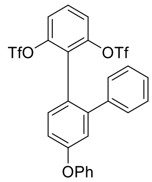
1z



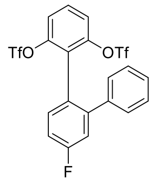
1aa



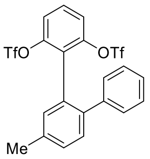
1ab



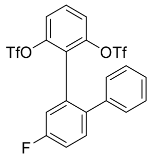
1ac



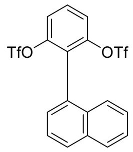
1ad



1ae



1af

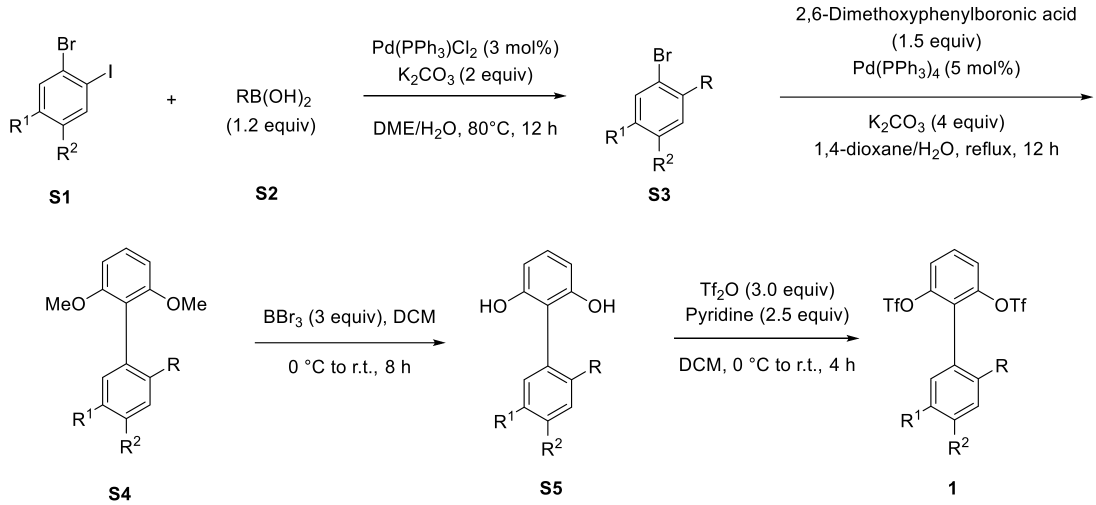


1ag

The biaryl bis(triflates) **1a** and **1ag** are known compounds in the literature[1], and their NMR data are consistent to the reported ones. The biaryl bis(triflates) **1b–1af** were prepared according to the following procedures. In the cases of the biaryl bis(triflates)

1v−1y, the corresponding aryl bromides **S3** are commercially available, and therefore, Step 1 was omitted.

General Procedure A for Preparation of Biaryl Bis(triflates) 1b–1y and 1aa–1af



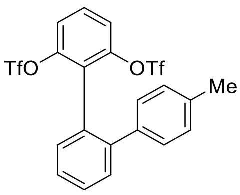
Step 1[2]**:** A mixture of K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv), the aryl iodides **S1** (5 mmol, 1.0 equiv), the aryl boronic acids **S2** (6 mmol, 1.2 equiv), and $PdCl_2(PPh_3)_2$ (52.6 mg, 0.15 mmol, 3 mol%) in water (8 mL) and DME (33 mL) was stirred at 80 °C for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with water (15 mL). The organic phase was separated, and the aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered through a pad of Celite, and concentrated under reduced pressure. The crude **S3** was used directly for the next step without further purification.

Step 2: A mixture of the crude **S3**, 2,6-dimethoxyphenylboronic acid (1.37 g, 7.5 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol, 5 mol%), and K_2CO_3 (3.76 g, 20 mmol, 4.0 equiv) in 1,4-dioxane (35 mL) and water (7 mL) was refluxed for 12 h under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was diluted with water (15 mL). The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered through a pad of Celite, and concentrated under reduced pressure. The crude **S4** was used directly for the next step without further purification.

Step 3: To a solution of the crude **S4** in dichloromethane (50 mL) was added dropwise BBr_3 (2.0 M in DCM, 7.5 mL, 15 mmol, 3.0 equiv) at 0 °C. The mixture was allowed to slowly warm up to room temperature and stir for 8 h. Next, the mixture was slowly poured into ice water (20 mL) and was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. The crude **S5** was used directly for the next step without further purification.

Step 4: To a solution of the crude **S5** and pyridine (0.99 g, 12.5 mmol, 2.5 equiv) in dichloromethane (50 mL) was added trifluoromethanesulfonic anhydride (4.23 g, 15 mmol, 3.0 equiv) at 0 °C. After stirring at room temperature for 4 h, the reaction was quenched with 3.0 M aqueous HCl solution. The aqueous phase was extracted three times with dichloromethane. and the combined organic layers were dried over Na_2SO_4. The combined organic layers were dried over Na_2SO_4, filtered through a pad of Celite, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether) to afford the corresponding biaryl bis(triflates) **1b–1y** and **1aa–1af**.

4''-Methyl-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1b)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (2.21 g, 41 % yield over 4 steps).

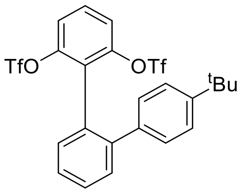
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.55 (t, *J* = 8.0 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.43 – 7.39 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.99 (m, 4H), 2.30 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.7 (2C), 142.7, 137.5, 137.0, 131.8, 130.6, 130.5, 130.2, 129.7, 128.9 (2C), 128.8 (2C), 127.1, 126.6, 121.7 (2C), 118.3 (q, *J* = 320.0 Hz, 2C), 21.2 ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ = −74.20 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{15}F_6O_6S_2^+$ $[M+H]^+$: 541.0209, found: 541.0226.

4''-(*tert*-Butyl)-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1c)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (2.56 g, 44 % yield over 4 steps).

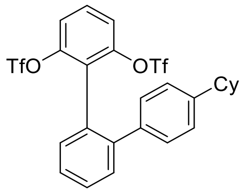
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.54 (t, *J* = 7.1 Hz, 1H), 7.49 (d, *J* = 7.1 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 1.26 (s, 9H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 150.2, 147.7 (2C), 142.6, 137.3, 131.8, 130.6, 130.5, 130.2, 129.7, 128.5 (2C), 127.0, 126.6, 125.0 (2C), 121.6 (2C), 118.3 (q, *J* = 320.0 Hz, 2C), 34.6, 31.4 (3C) ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ = −74.20 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{20}F_6NaO_6S_2^+$ $[M+Na]^+$: 605.0498, found: 605.0491.

4''-Cyclohexyl-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1d)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (3.08 g, 50 % yield over 4 steps).

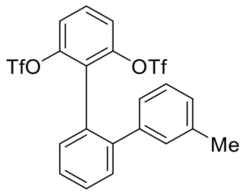
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.57 – 7.50 (m, 2H), 7.46 (td, *J* = 7.5, 1.6 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.09 – 7.05 (m, 4H), 2.47 (t, *J* = 11.3 Hz, 1H), 1.89 – 1.81 (m, 4H), 1.78 – 1.72 (m, 1H), 1.43 – 1.35 (m, 4H), 1.32 – 1.21 (m, 1H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.7 (2C), 147.2, 142.8, 137.8, 131.8, 130.6, 130.5, 130.1, 129.7, 128.8 (2C), 127.0, 126.7, 126.5 (2C), 121.6 (2C), 118.3 (d, *J* = 320.0 Hz, 2C), 44.2, 34.5 (2C), 27.0 (2C), 26.3 ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ = −74.24 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{22}F_6NaO_6S_2^+$ $[M+Na]^+$: 631.0654, found: 631.0642.

3''-Methyl-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1e)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (2.01 g, 37 % yield over 4 steps).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.58 – 7.53 (m, 1H), 7.51 – 7.43 (m, 3H), 7.40

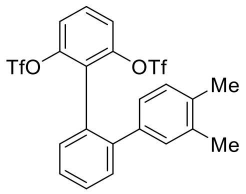
(d, J = 8.3 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.10 – 7.00 (m, 2H), 6.95 (s, 1H), 6.90 (d, J = 7.5 Hz, 1H), 2.23 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.6 (2C), 142.8, 140.3, 137.7, 131.8, 130.5, 130.4, 130.2, 129.9, 129.7, 128.0, 127.9, 127.2, 126.7, 125.9, 121.6 (2C), 118.3 (q, J = 320.5 Hz, 2C), 21.3 ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ = −74.23 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{15}F_6O_6S_2^+$ [M+Na]$^+$: 541.0209, found: 541.0216.

3'',4''-Dimethyl-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1f)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (2.33 g, 42 % yield over 4 steps).

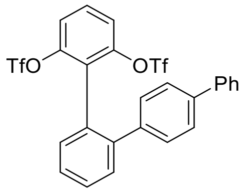
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.54 (td, J = 7.8, 1.5 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.40 (d, J = 1.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 6.98 – 6.90 (m, 2H), 6.85 (d, J = 1.7 Hz, 1H), 2.20 (s, 3H), 2.14 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.7 (2C), 142.8, 137.9, 136.3, 135.6, 131.8, 130.6, 130.5, 130.3, 130.1, 129.6, 129.3, 126.9, 126.6, 126.2, 121.6 (2C), 118.3 (q, J = 320.3 Hz, 2C), 19.6, 19.5 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.26 (s, 6F) ppm

HRMS (ESI) m/z calculated for $C_{22}H_{17}F_6O_6S_2^+$ [M+H]$^+$: 555.0365, found: 555.0377.

[1,1':2',1'':4'',1'''-Quaterphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1g)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (2.05 g, 34 % yield over 4 steps).

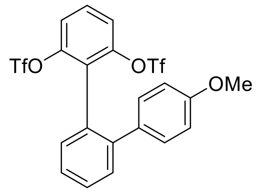
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.58 – 7.52 (m, 4H), 7.51 – 7.44 (m, 3H), 7.44 – 7.38 (m, 4H), 7.32 (d, J = 7.4 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.22 – 7.18 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.7 (2C), 142.3, 140.5, 139.9, 139.4, 132.0, 130.6, 130.4, 130.3, 129.9, 129.4 (2C), 128.9 (2C), 127.5, 127.4, 127.1 (2C), 126.70 (2C), 126.72, 121.8 (2C), 118.3 (q, J = 320.2 Hz, 2C) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.14 (s, 6F) ppm

HRMS (ESI) m/z calculated for $C_{26}H_{16}F_6NaO_6S_2^+$ [M+Na]$^+$: 625.0185, found: 625.0199.

4''-Methoxy-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1h)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a yellow solid (0.78 g, 14 % yield over 4 steps).

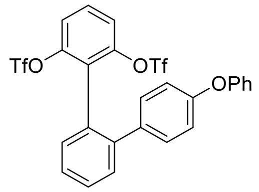
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.54 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 158.9, 147.7 (2C), 142.3, 132.9, 131.9, 130.5 (2C), 130.2, 130.1 (2C), 129.7, 126.9, 126.6, 121.8 (2C), 117.0 (t, *J* = 320.3 Hz, 2C), 113.6 (2C), 55.3 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.19 (s, 6F) ppm

HRMS (ESI) m/z calculated for $C_{21}H_{14}F_6NaO_7S_2^+$ [M+Na]$^+$: 578.9977, found: 578.9985.

4''-Phenoxy-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1i)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a yellow solid (2.60 g, 42 % yield over 4 steps).

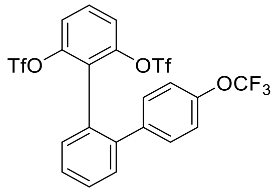
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.47 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.15 – 7.12 (m, 2H), 7.12 – 7.02 (m, 5H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.0, 156.7, 147.7 (2C), 142.0, 135.4, 132.0, 130.5, 130.4 (2C), 130.3, 129.9 (2C), 127.3 (2C), 126.7, 123.6 (2C), 121.8 (2C), 119.2 (2C), 118.3 (2C), 118.3 (q, *J* = 320.3 Hz, 2C) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.17 (s, 6F) ppm

HRMS (ESI) m/z calculated for $C_{26}H_{16}F_6NaO_7S_2^+$ [M+Na]$^+$: 641.0134, found: 641.0129.

4''-(Trifluoromethoxy)-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1j)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (3.11 g, 51 % yield over 4 steps).

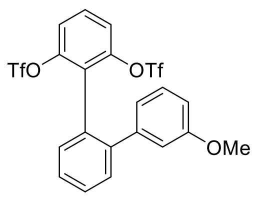
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.58 (td, *J* = 7.5, 1.4 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.43 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.15 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.6 (2C), 147.6, 141.3, 139.1, 132.1, 130.5, 130.4 (2C), 130.2, 130.0, 127.8, 126.7, 124.4, 121.9 (2C), 120.5 (2C), 120.1 (q, *J* = 256.8), 118.3 (q, *J* = 320.1 Hz, 2C) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −57.90 (s, 3F), −74.19 (s, 6F) ppm

HRMS (ESI) m/z calculated for $C_{21}H_{11}F_9NaO_7S_2^+$ [M+Na]$^+$: 632.9695, found: 632.9707.

3''-Methoxy-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1k)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a brown solid (1.28 g, 23 % yield over 4 steps).

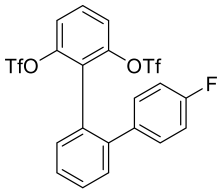
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 – 7.54 (m, 2H), 7.53 – 7.48 (m, 1H), 7.48 – 7.41 (m, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.17 (t, *J* = 7.9 Hz, 1H), 6.83 – 6.79 (m, 2H), 6.72 – 6.69 (m, 1H), 3.64 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.2, 147.6 (2C), 142.6, 141.8, 132.0, 130.5, 130.4, 130.2, 129.8, 129.2, 127.4, 126.6, 121.8 (2C), 121.6, 118.1 (q, *J* = 320.0 Hz, 2C), 114.0, 113.6, 55.1 ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −74.30 (s, 6F) ppm

HRMS (ESI) m/z calculated for $C_{21}H_{14}F_6NaO_7S_2^+$ [M+Na]$^+$: 578.9977, found: 578.9974.

4''-Fluoro-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1l)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (1.68 g, 31 % yield over 4 steps).

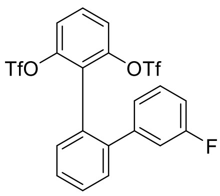
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.55 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.43 – 7.39 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.94 – 6.87 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.3 (d, *J* = 246.6 Hz), 147.6 (2C), 141.7, 136.4, 132.0, 130.7, 130.6, 130.6, 130.3, 130.0, 127.5 (2C), 126.7, 121.8 (2C), 118.3 (q, *J* = 320.2 Hz, 2C), 115.1 (d, *J* = 21.4 Hz, 2C).

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.16 (s, 6F), -115.16 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{11}F_{7}NaO_{6}S_{2}^{+}$ $[M+Na]^{+}$: 566.9777, found: 566.9754.

3''-Fluoro-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1m)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (2.40 g, 44 % yield over 4 steps).

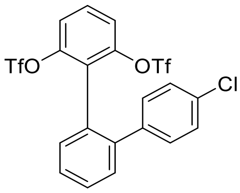
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.58 (td, *J* = 7.5, 1.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.48 – 7.43 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.18 (td, *J* = 8.0, 6.1 Hz, 1H), 6.97 – 6.86 (m, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 162.5 (d, *J* = 245.8 Hz), 147.6 (2C), 142.7, 142.6, 141.4 (d, *J* = 2.2 Hz), 132.1, 130.4 (d, *J* = 11.7 Hz), 130.2, 130.0, 129.6 (d, *J* = 8.2 Hz), 127.8, 126.7, 124.8 (d, *J* = 2.8 Hz), 121.8 (2C), 118.3 (q, *J* = 320.4 Hz, 2C), 116.0 (d, *J* = 22.2 Hz), 114.3 (d, *J* = 21.1 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.19 (s, 6F), −113.40 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{11}F_{7}NaO_{6}S_{2}^{+}$ $[M+Na]^{+}$: 566.9777, found: 566.9796.

4''-Chloro-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1n)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (2.02 g, 36 % yield over 4 steps).

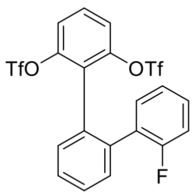
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.59 – 7.54 (m, 1H), 7.52 – 7.45 (m, 3H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.5 (2C), 141.4, 138.9, 133.5, 132.1, 130.5, 130.4, 130.3 (2C), 130.1, 128.6, 128.4 (2C), 127.7, 126.6, 121.9 (2C), 118.3 (d, *J* = 320.0 Hz, 2C) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.12 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{12}{}^{35}ClF_6O_6S_2^+$ [M+H]$^+$: 560.9663, found: 566.9662.

2''-Fluoro-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1o)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (2.45 g, 4.5 mmol, 45 % yield over 4 steps).

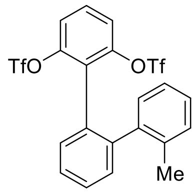
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.58 (t, *J* = 7.5 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.45 – 7.39 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24 –7.17 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.97 – 6.88 (m, 1H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 159.5 (d, *J* = 247.3 Hz), 147.7 (2C), 136.6, 131.7 (d, *J* = 2.8 Hz, 2C), 131.2, 129.9 (d, *J* = 4.9 Hz), 129.7 (d, *J* = 8.2 Hz), 129.5, 128.04, 127.97, 127.7, 127.6, 123.8 (d, *J* = 3.7 Hz), 121.2 (2C), 118.3 (q, *J* = 320.4 Hz, 2C), 115.6 (d, *J*=22.7 Hz) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.14 (s, 3F), −115.22 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{12}F_6NaO_6S_2^+$ [M+H]$^+$: 544.9958, found: 544.9970.

2''-Methyl-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1p)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (1.24 g, 23 % yield over 4 steps).

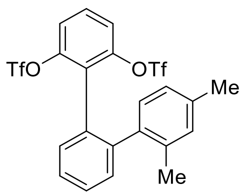
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.58 – 7.52 (m, 1H), 7.50 (td, *J* = 7.4, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.20 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.87 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.18 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 149.7, 147.9 (2C), 141.8, 139.1, 136.2, 131.6, 130.9, 130.4, 129.9, 129.5, 129.4, 127.5, 127.2, 125.0, 121.8, 121.0 (2C), 118.4 (q, *J* = 320.2 Hz, 2C), 19.6 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.17 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{14}F_6NaO_6S_2^+$ $[M+Na]^+$: 563.0028, found: 563.0027.

2'',4''-Dimethyl-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1q)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (2.00 g, 36 % yield over 4 steps).

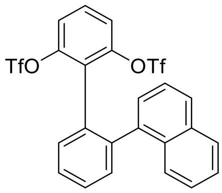
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.53 (td, *J* = 7.3, 1.9 Hz, 1H), 7.48 (td, *J* = 7.4, 1.5 Hz, 1H), 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.41 – 7.33 (m, 3H), 7.21 – 7.16 (m, 1H), 6.99 – 6.96 (m, 1H), 6.78 – 6.70 (m, 2H), 2.23 (s, 3H), 2.15 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.9, 147.7, 141.9, 137.1, 136.3, 135.9, 131.6, 131.2 (2C), 130.2, 129.8, 129.5, 129.4, 127.7, 127.0, 125.8, 121.1, 121.0, 118.4 (q, *J* = 320.3 Hz, 2C), 21.1, 19.6 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.15 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{22}H_{17}F_6O_6S_2^+$ $[M+H]^+$: 555.0365, found: 555.0372.

2'-(Naphthalen-1-yl)-[1,1'-biphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1r)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (0.81 g, 1.4 mmol, 14 % yield over 4 steps).

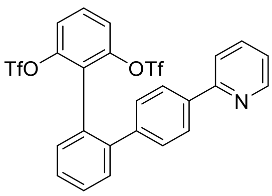
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.82 – 7.79 (m, 1H), 7.75 – 7.70 (m, 2H), 7.68 – 7.61 (m, 2H), 7.59 – 7.55 (m, 2H), 7.49 – 7.44 (m, 1H), 7.42 – 7.38 (m, 1H), 7.34 – 7.27 (m, 3H), 7.21 (dd, *J*=7.0, 1.2, 1H), 7.06 – 7.00 (m, 1H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.7, 147.6, 140.8, 137.6, 133.5, 131.8, 131.7, 131.7, 130.1, 129.8, 129.7, 128.5, 128.0, 128.0, 127.6, 127.0, 126.3, 126.0, 125.9, 124.7, 121.0, 120.9, 118.3 (q, *J*=320.1) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −73.96 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{15}F_6O_6S_2^+$ $[M+H]^+$: 577.0209, found: 577.0207.

4''-(Pyridin-2-yl)-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1s)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 15:1) as a pink solid (1.27 g, 21 % yield over 4 steps).

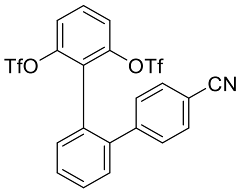
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.67 (d, *J* = 4.6 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.61 – 7.55 (m, 1H), 7.54 (d, *J* = 6.4 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.46 – 7.40 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.19 (m, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 157.0, 149.8, 147.6 (2C), 142.2, 141.1, 138.2, 136.9, 132.0, 130.6, 130.29, 130.26, 130.0, 129.4 (2C), 127.5, 126.7, 126.6 (2C), 122.3, 121.8 (2C), 120.6, 118.3 (q, *J* = 320.4 Hz, 2C) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.11 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{16}F_6O_6S_2^+$ $[M+H]^+$: 604.0318, found: 604.0322.

4''-Cyano-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1t)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) as a white solid (0.88 g, 14 % yield over 4 steps).

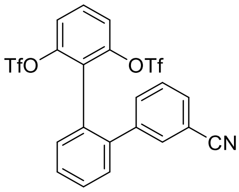
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 – 7.56 (m, 1H), 7.55 – 7.52 (m, 1H), 7.51 – 7.46 (m, 3H), 7.46 – 7.40 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.5 (2C), 145.2, 140.7, 132.4, 132.0 (2C), 130.6, 130.5, 130.4, 129.7 (2C), 129.6, 128.5, 126.6, 122.0 (2C), 118.8, 118.2 (q, *J* = 320.4 Hz, 2C), 111.3 ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −74.07 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{12}NF_6O_6S_2^+$ $[M+H]^+$: 552.0005, found: 552.0018.

3''-Cyano-[1,1':2',1''-terphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1u)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) as a colorless oil (1.71 g, 31 % yield over 4 steps).

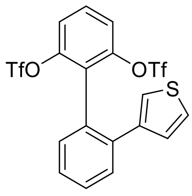
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.61 (td, *J* = 7.5, 1.5 Hz, 1H), 7.58 – 7.50 (m, 3H), 7.49 – 7.44 (m, 3H), 7.41 – 7.37 (m, 1H), 7.35 – 7.30 (m, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.4 (2C), 141.7, 140.3, 133.4, 132.5, 132.3, 131.1, 130.6, 130.54, 130.46, 129.6, 129.0, 128.4, 126.7, 122.0 (2C), 118.5, 118.2 (q, *J* = 320.3 Hz, 2C), 112.4 ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −74.06 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{11}NF_6NaO_6S_2^+$ $[M+Na]^+$: 573.9824, found: 573.9829.

2'-(Thiophen-3-yl)-[1,1'-biphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1v)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 9:1) as a white solid (1.92 g, 36 % yield over 3 steps).

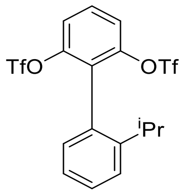
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.58 – 7.55 (m, 1H), 7.54 (dd, *J*=7.1, 1.4, 1H), 7.52 – 7.48 (m, 1H), 7.47 – 7.43 (m, 1H), 7.40 – 7.37 (m, 1H), 7.36 – 7.33 (m, 2H), 7.18 (dd, *J*=5.0, 3.0, 1H), 6.94 (dd, *J*=3.0, 1.3, 1H), 6.87 (dd, *J*=5.0, 1.4, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.7 (2C), 140.7, 137.4, 132.0, 130.5, 130.3, 130.2, 129.9, 128.3, 127.3, 126.6, 125.3, 123.3, 122.0 (2C), 118.3 (q, *J*=320.1, 2C) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −74.18 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{11}F_6O_6S_3^+$ $[M+H]^+$: 532.9616, found: 532.9634.

2'-Isopropyl-[1,1'-biphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1w)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (2.27 g, 46 % yield over 3 steps).

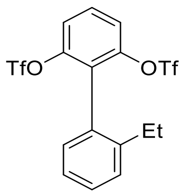
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.60 – 7.55 (m, 1H), 7.52 – 7.44 (m, 4H), 7.30 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 2.51 (p, *J* = 6.8 Hz, 1H), 1.20 (d, *J* = 6.8 Hz, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.0 (2C), 147.9, 131.1, 130.7, 130.4, 130.0, 126.3, 126.2, 125.7, 121.7, 118.3 (d, *J* = 320.0 Hz, 2C), 31.1 (2C), 24.0 (2C) ppm.

^{19}F NMR (376 MHz, Chloroform-d) δ = −74.28 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{17}H_{14}F_6NaO_6S_2^+$ $[M+Na]^+$: 515.0028, found: 515.0022.

2'-Ethyl-[1,1'-biphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1x)

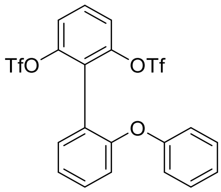


The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (1.96 g, 41 % yield over 3 steps).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.47 – 7.41 (m, 1H), 7.38 – 7.29 (m, 4H), 7.19 (td, *J* = 7.3, 1.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 2.30 (q, *J* = 7.6 Hz, 2H), 1.07 (t, *J* = 7.6 Hz, 3H) ppm.

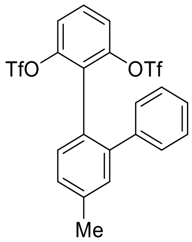
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.0 (2C), 143.1, 131.1, 130.7, 130.2, 130.0, 128.3, 127.2, 125.8, 121.9 (2C), 118.4 (q, J = 320.3 Hz, 2C), 25.7, 13.9 ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ = −74.30 (s, 6F) ppm.
HRMS (ESI) m/z calculated for $C_{16}H_{13}F_6O_6S_2^+$ [M+H]$^+$: 479.0052, found: 479.0057.

2'-Phenoxy-[1,1'-biphenyl]-2,6-diyl bis(trifluoromethanesulfonate) (1y)



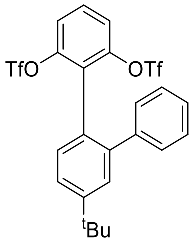
The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (1.36 g, 25 % yield over 3 steps).
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.59 – 7.51 (m, 1H), 7.48 – 7.43 (m, 2H), 7.41 – 7.38 (m, 1H), 7.37 – 7.32 (m, 3H), 7.21 – 7.13 (m, 2H), 7.10 – 6.99 (m, 2H), 6.84 (d, J = 8.4 Hz, 1H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.2, 155.4, 148.3 (3C), 132.5, 131.5, 130.0 (2C), 127.4, 124.6, 122.3, 121.7 (2C), 120.7 (2C), 118.5 (q, J = 320.4 Hz, 2C), 118.4, 116.0 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = −73.98 (s, 6F) ppm.
HRMS (ESI) m/z calculated for $C_{20}H_{13}F_6O_7S_2^+$ [M+H]$^+$: 543.0001, found: 543.0013.

4'-Methyl-[1,1':2',1''-terphenyl]-2,6-*d*iyl bis(trifluoromethanesulfonate) (1aa)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a yellow oil (2.38 g, 44 % yield over 4 steps).
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.44 – 7.39 (m, 1H), 7.34 – 7.30 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.23 – 7.18 (m, 3H), 7.16 – 7.13 (m, 2H), 2.48 (s, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.9 (2C), 142.5, 140.6, 140.2, 131.8, 131.3, 130.6, 129.6, 129.0 (2C), 128.1, 128.0 (2C), 127.2, 123.7, 121.6 (2C), 118.3 (q, J = 320.1 Hz, 2C), 21.5 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.18 (s, 6F) ppm.
HRMS (ESI) m/z calculated for $C_{21}H_{15}F_6O_6S_2^+$ [M+H]$^+$: 541.0209, found: 541.0208.

4'-(*tert*-Butyl)-[1,1':2',1''-terphenyl]-2,6-*d*iyl bis(trifluoromethanesulfonate) (1ab)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a white solid (2.68 g, 46 % yield over 4 steps).

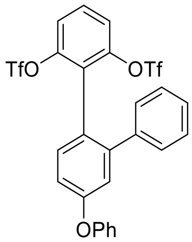
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.51 – 7.47 (m, 2H), 7.45 – 7.39 (m, 1H), 7.34 – 7.26 (m, 3H), 7.23 – 7.18 (m, 3H), 7.15 – 7.10 (m, 2H), 1.39 (s, 9H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 153.5, 147.8 (2C), 142.2, 141.1, 131.5, 130.4, 129.5, 129.0 (2C), 128.1 (2C), 127.5, 127.2, 124.3, 123.6, 121.6 (2C), 118.3 (q, *J* = 320.3 Hz, 2C), 35.0, 31.3 (3C) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.26 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{21}F_6O_6S_2^+$ $[M+H]^+$: 583.0678, found: 583.0670.

4'-Phenoxy-[1,1':2',1''-terphenyl]-2,6-*d*iyl bis(trifluoromethanesulfonate) (1ac)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 15:1) as a white solid (1.98 g, 32 % yield over 4 steps).

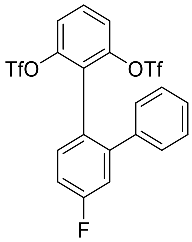
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.47 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.15 – 7.12 (m, 2H), 7.12 – 7.02 (m, 5H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 158.8, 156.8, 147.8 (2C), 144.6, 139.9, 133.6, 130.08 (2C), 130.05, 129.8, 128.8 (2C), 128.1 (2C), 127.6, 123.9, 121.7 (2C), 121.3, 120.6, 119.3 (2C), 118.3 (q, *J* = 320.3 Hz, 2C), 117.5 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.13 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{16}F_6O_7S_2^+$ $[M+H]^+$: 619.0314, found: 619.0325.

4'-Fluoro-[1,1':2',1''-terphenyl]-2,6-*d*iyl bis(trifluoromethanesulfonate) (1ad)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a yellow oil (1.20 g, 22 % yield over 4 steps).

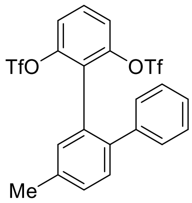
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.34 – 7.27 (m, 2H), 7.19 – 7.15 (m, 2H), 7.14 – 7.06 (m, 5H), 7.04 – 6.99 (m, 2H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 163.6 (d, *J*=250.1), 147.7, 145.3 (d, *J*=8.3), 139.3, 133.9 (d, *J*=9.0), 130.2, 129.5, 128.8, 128.3, 127.9, 122.8 (d, *J*=2.9), 121.8, 119.6 (q, *J*=320.1), 117.6 (d, *J*=22.2), 114.5 (d, *J*=21.3) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.23 (s, 6F), −110.93 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{12}F_{7}O_{6}S_{2}^{+}$ [M+H]$^{+}$: 544.9958, found: 544.9969.

5'-Methyl-[1,1':2',1''-terphenyl]-2,6-*d*iyl bis(trifluoromethanesulfonate) (1ae)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a brown oil (1.78 g, 33 % yield over 4 steps).

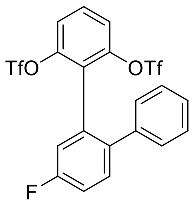
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.46 – 7.37 (m, 3H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.24 (s, 1H), 7.23 – 7.18 (m, 3H), 7.15 – 7.09 (m, 2H), 2.46 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.7 (2C), 140.4, 139.7, 137.2, 132.3, 130.9, 130.5, 130.4, 129.7, 129.0 (2C), 128.0 (2C), 127.1, 126.4, 121.6 (2C), 118.3 (q, *J* = 320.3 Hz, 2C), 21.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.27 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{16}F_{6}O_{6}S_{2}^{+}$ [M+H]$^{+}$: 541.0209, found: 541.0216.

5'-Fluoro-[1,1':2',1''-terphenyl]-2,6-*d*iyl bis(trifluoromethanesulfonate) (1af)



The title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a brown oil (2.23 g, 44 % yield over 4 steps).

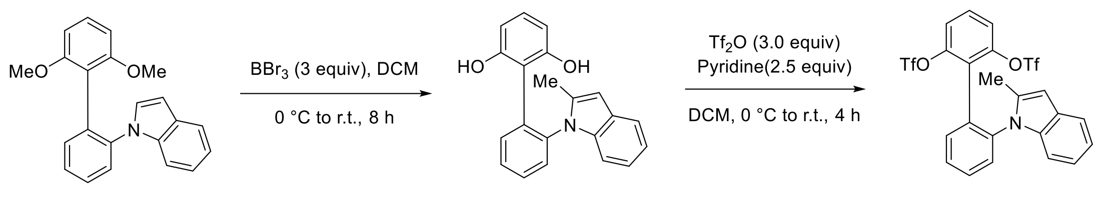
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.51 – 7.45 (m, 2H), 7.33 – 7.26 (m, 3H), 7.25 – 7.19 (m, 3H), 7.17 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.13 – 7.07 (m, 2H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 161.6 (d, *J* = 248.3 Hz), 147.7 (2C), 147.4, 139.4, 139.0 (d, *J* = 3.5 Hz), 132.3 (d, *J* = 8.1 Hz), 130.4, 129.0 (2C), 128.8, 128.3, 128.2 (2C), 127.5, 121.8 (2C), 118.7 (d, *J* = 23.1 Hz), 118.3 (q, *J* = 320.4 Hz, 2C), 117.3 (d, *J* = 21.0 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.08 (s, 6F), −114.90 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{11}F_7NaO_6S_2^+$ $[M+Na]^+$: 566.9777, found: 566.9781.

Procedure for Preparation of Biaryl Bis(triflate) 1z



S4z **S5z** **1z**

The crude **S4z** was prepared according to Step 2 of the general procedure A employing the commercially available precursors and used directly without further purification.

Step 1：To a solution of the crude **S4z** in dichloromethane (50 mL) was added dropwise BBr_3 (2.0 M in DCM, 7.5 mL, 15 mmol, 3.0 equiv) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 8 h. Next, the mixture was slowly poured into ice water (20 mL) and was extracted three times with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered through a pad of celite, and concentrated under reduced pressure. The crude **S5z** was used directly for the next step without further purification.

Step 2：To a solution of the crude **S5z** and pyridine (0.99 g, 12.5 mmol, 2.5 equiv) in dichloromethane (50 mL) was added trifluoromethanesulfonic anhydride (4.23 g, 15 mmol, 3.0equiv) at 0 °C slowly. After stirring at room temperature for 4 h, the reaction was quenched with 3.0 M aqueous HCl solution at 0 °C. The aqueous phase was extracted three times with dichloromethane. and the combined organic layers were dried over Na_2SO_4. The combined organic layers were dried over Na_2SO_4, filtered through a pad of Celite, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to afford *2'-(2-methyl-1H-indol-1-yl)-[1,1'-biphenyl]-2,6-diyl bis(trifluoromethane-*

sulfonate) (**1z**) as a white solid (0.69 g, 24 % yield over 3 steps).

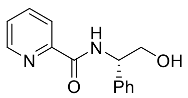
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.66 – 7.61 (m, 1H), 7.59 – 7.56 (m, 1H), 7.55 – 7.52 (m, 2H), 7.50 – 7.46 (m, 1H), 7.40 (t, *J*=8.4, 1H), 7.29 – 7.24 (m, 3H), 7.14 (t, *J*=6.4 Hz, 1H), 7.10 (t, *J*=7.4 Hz, 1H), 6.57 (s, 1H), 2.15 (d, *J*=1.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.9, 139.2, 137.1, 133.0, 131.3 (2C), 130.3, 129.1, 128.1, 127.8, 127.3, 125.8, 125.4, 122.4, 121.7 (2C), 119.9, 118.8, 118.3 (q, *J* =319.8 Hz, 2C), 112.8, 110.6, 9.6 ppm.

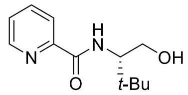
^{19}F NMR (376 MHz, Chloroform-*d*) δ = −73.96 (s, 6F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{16}F_{6}NO_{6}S_{2}^{+}$ $[M+H]^{+}$: 580.0318, found: 580.0334.

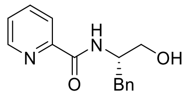
Synthesis of Chiral Picolinamide Ligands



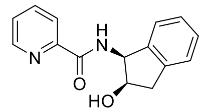
L1



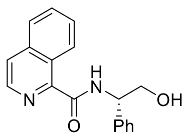
L2



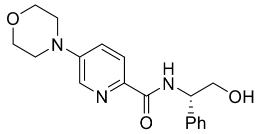
L3



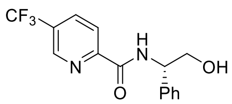
L4



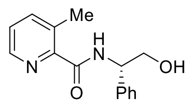
L5



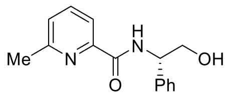
L6



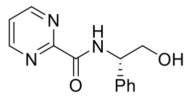
L7



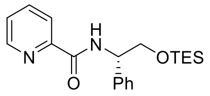
L8



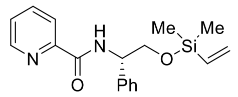
L9



L10



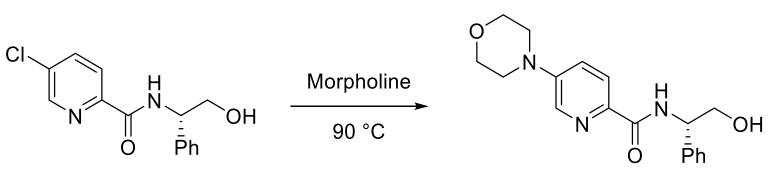
L11



L12

The ligands **L1**[3], **L2**[4], **L3**[5], **L4**[6], **L5**[7], **L7**[8], **L8**[9] and **L9**[10] are known compounds in the literature, and their NMR data are consistent to the reported ones. The preparation of other ligands (**L6**, **L10**, **L11**, and **L12**) and their characterization data are provided below.

Procedure for Synthesis of Ligand L6



L6' **L6**

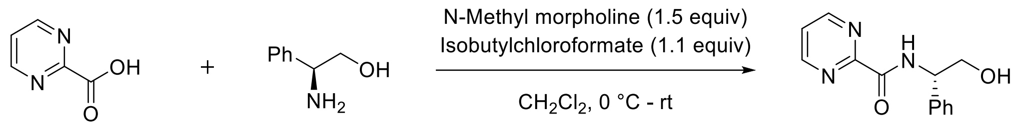
To a 100 mL screw-cap vial equipped with a magnetic stir bar was added **L6'**[11] (1.16 g, 4.2 mmol, 1.0 equiv) and morpholine (5 mL), successively. The reaction mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the reaction was diluted with EtOAc and washed with H_2O. The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1) to afford *(S)-N-(2-hydroxy-1-phenylethyl)-5-morpholinopicolinamide* (**L6**) as a colorless oil (1.32 g, 96 % yield).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.72 (d, J = 7.8 Hz, 1H), 8.15 (d, J = 5.8 Hz, 1H), 7.56 (d, J = 2.7 Hz, 1H), 7.42 – 7.22 (m, 5H), 6.67 (dd, J = 5.9, 2.7 Hz, 1H), 5.32 – 5.17 (m, 1H), 3.95 (d, J = 5.5 Hz, 2H), 3.83 – 3.75 (m, 4H), 3.69 – 3.50 (m, 1H), 3.38 – 3.25 (m, 4H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 165.3, 156.1, 150.3, 148.8, 139.2, 128.7 (2C), 127.7, 126.9 (2C), 109.6, 106.8, 66.3 (2C), 56.1, 46.0 (2C), 40.6 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{22}N_3O_3^+$ [M+H]$^+$: 328.1656, found: 328.1662.

Procedure for Synthesis of Ligand L10



L10

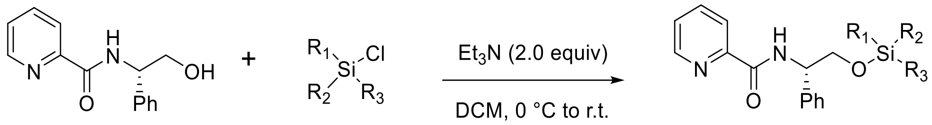
N-Methyl morpholine (842 µL, 7.66 mmol, 1.5 equiv) was added dropwise to a solution of pyrimidine-2-carboxylic acid (0.62 g, 5.0 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (50 mL) under an atmosphere of nitrogen at 0 °C. After stirring for 15 min, isobutylchloroformate (768 µL, 5.8 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred for an additional 30 min before a solution of (*S*)-(+)-2-phenylglycinol (0.82 g, 6.0 mmol, 1.2 equiv) and *N*-methyl morpholine (645 µL, 5.9 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added dropwise. After stirring for 1 h, the reaction was allowed to warm up to room temperature and stirred for 15 h. Next, the reaction mixture was diluted with CH_2Cl_2, washed with saturated aqueous NH_4Cl solution (30 mL ×2) and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel (EtOAc/ petroleum ether = 1:1) to give *(S)-N-(2-hydroxy-1-phenylethyl)pyrimidine-2-carboxamide* (**L10**) as a yellow solid (0.86 g, 71% yield).

^{1}H NMR (400 MHz, Chloroform-d) δ = 8.88 – 8.79 (m, 2H), 8.73 (d, J = 7.4 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 5.42 – 5.29 (m, 1H), 4.02 (d, J = 5.1 Hz, 2H), 3.60 – 3.18 (br, 1H) ppm.

^{13}C NMR (101 MHz, Chloroform-d) δ = 162.5, 157.5 (2C), 138.8, 128.9 (2C), 128.0 (2C), 127.0 (2C), 122.7, 66.3, 56.2 ppm.

HRMS (ESI) m/z calculated for $C_{13}H_{13}N_3NaO_2^+$ [M+Na]$^+$: 266.0900, found: 266.0904.

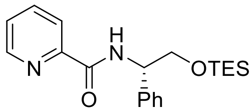
General Procedure B for Synthesis of Ligands L11 and L12



L1 (2.0 equiv) **L11** or **L12**

To a solution of ligand **L1** (242 mg, 1.0 mmol, 1.0 equiv) in DCM (5 mL) was added Et_3N (202 mg, 2.0 mmol, 2.0 equiv) at 0 °C. Next, the corresponding chlorosilanes (2.0 mmol, 2.0 equiv) were added dropwise at 0 °C. The reaction was stirred at room temperature for 12 h. The mixture was filtered through a pad of Celite, and concentrated under reduced pressure. The residue was purified through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to afford the corresponding ligands.

(*S*)-*N*-(1-Phenyl-2-((triethylsilyl)oxy)ethyl)picolinamide (L11)



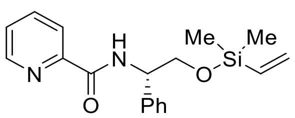
Colorless oil (324 mg, 91% yield).

^{1}H NMR (500 MHz, Acetone-*d*$_6$) δ = 8.93 – 8.86 (m, 1H), 8.64 (d, *J* = 4.7 Hz, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.98 (td, *J* = 7.8, 1.7 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.50 – 7.44 (m, 2H), 7.37 – 7.31 (m, 2H), 7.29 – 7.22 (m, 1H), 5.25 (dt, *J* = 8.5, 4.9 Hz, 1H), 4.11 – 4.00 (m, 2H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.57 (d, *J* = 7.8 Hz, 6H) ppm.

^{13}C NMR (126 MHz, Acetone-*d*$_6$) δ = 163.9, 150.9, 149.1, 141.6, 138.3, 128.9 (2C), 127.8, 127.7 (2C), 127.2, 122.6, 66.8, 55.5, 6.8 (3C), 4.7 (3C) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{29}N_2O_2Si^+$ $[M+H]^+$: 357.1993, found: 357.2006.

(*S*)-*N*-(2-((Dimethyl(vinyl)silyl)oxy)-1-phenylethyl)picolinamide (L12)



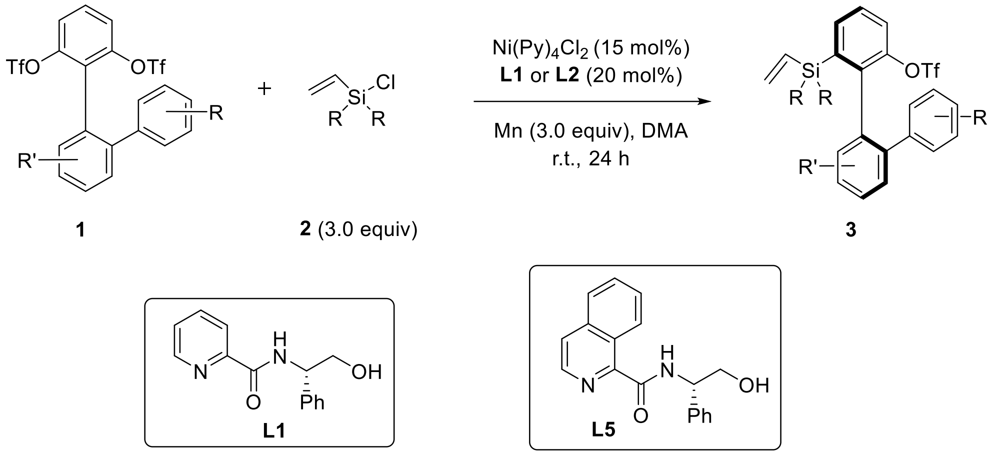
Colorless oil (280 mg, 86% yield).

^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ = 8.80 (d, *J* = 7.6 Hz, 1H), 8.63 – 8.60 (m, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.97 – 7.90 (m, 1H), 7.61 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.10 – 5.88 (m, 2H), 5.72 (dd, *J* = 19.9, 4.5 Hz, 1H), 5.22 (dt, *J* = 9.8, 5.1 Hz, 1H), 4.00 (d, *J* = 5.1 Hz, 2H), 0.07 (s, 3H), 0.06 (s, 3H) ppm.

^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ = 163.8, 150.7, 149.0, 141.3, 138.2, 137.7, 133.6, 128.8 (2C), 127.7, 127.6 (2C), 127.0, 122.4, 66.5, 55.3, –2.3, –2.4 ppm.

HRMS (ESI) m/z calculated for $C_{18}H_{22}N_2O_2NaSi^+$ $[M+H]^+$: 349.1343, found: 349.1343.

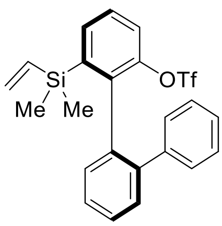
General Procedure C for Nickel-Catalyzed Reductive Desymmetric Silylation



In a nitrogen-filled glove box, $Ni(Py)_4Cl_2$ (13.8 mg, 0.03 mmol. 15 mol%), ligand **L1**[a] (9.7 mg, 0.04 mmol, 20 mol%), and Mn (33.0 mg, 0.6 mmol, 3.0 equiv) were added to a reaction tube equipped with a magnetic stir bar. Subsequently, a solution of the bis(triflates) **1** (0.2 mmol, 1.0 equiv) and the chlorosilane **2** (0.6 mmol, 3.0 equiv) in dry DMA (1.0 mL, 0.2 M) was added to the reaction mixture. The reaction tube was sealed and removed from the glove box. The reaction was stirred at room temperature for 24 h before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3 × 20 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether) to give the products **3**.

[a] In the case of **3ay**, ligand **L5** was used instead of **L1**.

(R)-6-(Dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3aa)



According to the general procedure, the title compound **3aa** was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (74.1 mg, 80% yield, 91% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.1 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.19 – 7.15 (m, 3H), 7.11 – 7.05 (m, 3H), 6.05 – 5.88 (m, 2H), 5.63 (dd, *J* = 19.8, 3.9 Hz, 1H), 0.13 (s, 6H) ppm.

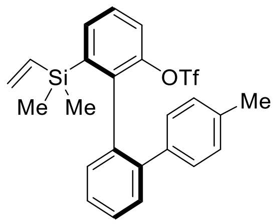
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 146.8, 142.8, 141.6, 140.8, 140.7, 138.0, 135.3, 134.8, 132.6, 132.2, 130.1, 129.3, 129.3 (2C), 128.6, 127.8 (2C), 126.8, 126.8, 121.8, 118.3 (q, *J* = 320.1 Hz), −1.2, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.73 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{22}F_3O_3SSi^+$ $[M+H]^+$: 463.1006, found: 463.1004

HPLC-data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 8.3 (major), 9.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4''-methyl-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ba)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (77.1 mg, 81% yield, 92% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.63 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.08 (d, *J* = 8.2 Hz, 1H), 7.00 – 6.94 (m, 4H), 6.12 – 5.86 (m, 2H), 5.62 (dd, *J* = 19.8, 3.9 Hz, 1H), 2.28 (s, 3H), 0.11 (s, 6H). ppm.

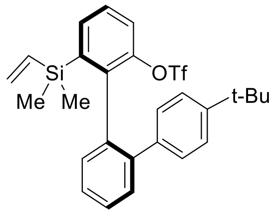
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 146.8, 142.8, 141.5, 140.9, 138.1, 137.8, 136.4, 135.2, 132.5, 132.2, 130.1, 134.7, 129.3, 129.1 (2C), 128.6 (2C), 128.5, 126.5, 121.8, 118.3 (q, *J* = 320.0 Hz), 21.2, –1.2, –1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.72 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_3SSi^+$ $[M+H]^+$: 477.1157, found: 477.1162.

HPLC-data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.3 mL/min): t_R = 10.3 (major), 11.5 (minor).

***(R)*-4''-(*tert*-Butyl)-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ca)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (77.7 mg, 75% yield, 92% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.40 – 7.30 (m, 3H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.04 – 5.88 (m, 2H), 5.61 (dd, *J* = 19.8, 3.9 Hz, 1H), 1.28 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H) ppm.

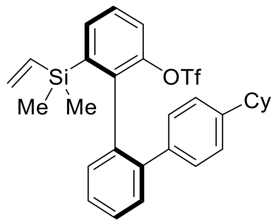
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 149.6, 146.9, 142.7, 141.4, 140.9, 138.1, 137.6, 135.2, 134.6, 132.5, 132.2, 130.1, 129.3, 128.9 (2C), 128.5, 126.5, 124.7 (2C), 121.7, 118.3 (q, *J* = 320.1 Hz), 34.5, 31.4 (3C), −1.3, −2.0 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.73 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{27}H_{29}F_3NaO_3SSi^+$ $[M+Na]^+$: 541.1451, found: 541.1453.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane, flow rate = 0.3 mL/min): t_R = 12.9 (major), 13.6 (minor).

***(R)*-4''-Cyclohexyl-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3da)**

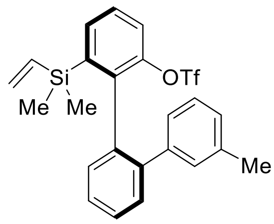


According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (81.6 mg, 75% yield, 92% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.62 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.39 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.02 – 6.95 (m, 4H), 6.04 – 5.85 (m, 2H), 5.60 (dd, *J* = 19.8, 4.0 Hz, 1H), 2.47 – 2.38 (m, 1H), 1.88 – 1.70 (m, 5H), 1.42 – 1.24 (m, 5H), 0.09 (s, 3H), 0.08 (s, 3H). ppm.

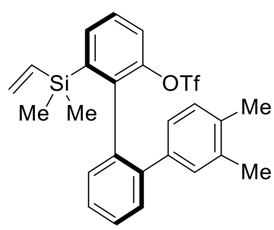
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 146.9, 146.6, 142.7, 141.5, 140.9, 138.1, 138.0, 135.2, 134.7, 132.5, 132.2, 130.1, 129.2, 129.2, 128.5, 126.5, 126.3, 121.7, 118.3 (q, J = 320.6 Hz), 44.2, 34.5, 27.0, 26.3, −1.3, −1.9 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.73 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{29}H_{32}F_3O_3SSi^+$ $[M+H]^+$: 545.1788, found: 545.1797.
HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 15.3 (major), 16.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-3''-methyl-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ea)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (78.1 mg, 82% yield, 90% *ee*).
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.63 (dd, J = 7.5, 1.2 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.27 (s, 1H), 7.23 – 7.21 (m, 2H), 7.18 – 7.15 (m, 3H), 7.10 – 7.07 (m, 2H), 7.05 (dd, J = 8.2, 1.1 Hz, 1H), 6.11 – 5.87 (m, 2H), 5.64 (dd, J = 19.9, 3.9 Hz, 1H), 2.48 (s, 3H), 0.14 (s, 3H), 0.13 (s, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.0, 142.9, 141.3, 141.0, 140.9, 139.1, 138.2, 135.3, 132.5, 132.1, 131.8, 130.8, 129.3 (2C), 128.5, 127.7 (2C), 127.4, 126.7, 121.7, 118.3 (q, J = 320.0 Hz), 21.5, −1.2, −1.9 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.70 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_3SSi^+$ $[M+H]^+$: 477.1162, found: 477.1172.
HPLC-data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 10.0 (major), 11.8 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-3'',4''-*d*imethyl-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3fa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (51.0 mg, 52% yield, 91% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.62 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.30 (d, *J* = 1.4 Hz, 1H), 7.08 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.92 – 6.86 (m, 2H), 6.76 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.08 – 5.85 (m, 2H), 5.61 (dd, *J* = 19.6, 4.2 Hz, 1H), 2.18 (s, 3H), 2.11 (s, 3H) 0.11 (s, 3H), 0.10 (s, 3H) ppm.

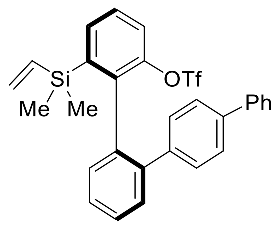
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 146.7, 142.8, 141.5, 141.0, 138.2, 138.1, 135.9, 135.2, 135.1, 134.7, 132.5, 132.1, 130.8, 130.0, 129.2, 129.0, 128.5, 126.5, 126.4, 121.8, 118.3 (q, *J* = 320.0 Hz), 19.8, 19.5, −1.3, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.79 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{26}F_3O_3SSi^+$ $[M+H]^+$: 491.1319, found: 491.1324.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 9.1 (major), 9.9 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-[1,1':2',1'':4'',1'''-quaterphenyl]-2-yl trifluoromethanesulfonate (3ga)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (74.3 mg, 69% yield, 87% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.67 (d, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.56 – 7.49 (m, 2H), 7.47 – 7.39 (m, 5H), 7.38 – 7.32 (m, 3H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.12 – 7.09 (m, 1H), 6.07 – 5.85 (m, 2H), 5.65 (dd, *J* = 19.8, 3.9 Hz, 1H), 0.16 (s, 3H), 0.15 (s, 3H) ppm.

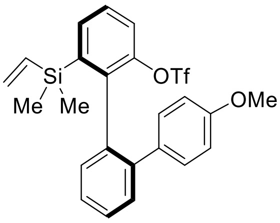
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 146.9, 142.8, 141.2, 140.8, 140.7, 139.8, 139.4, 138.0, 135.3, 134.8, 132.6, 132.3, 130.0, 129.7 (2C), 129.4, 128.9 (2C), 128.7, 127.4, 127.1 (2C), 126.9, 126.5 (2C), 121.9, 118.3 (q, *J* = 320.8 Hz), −1.2, −1.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.66 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{29}H_{26}F_3O_3SSi^+$ $[M+H]^+$: 539.1319, found: 539.1313.

HPLC-data: (Chiral OD-H column, λ = 254 nm, hexane/isopropanol = 99.4/0.6, flow rate = 0.5 mL/min): t_R = 12.7 (major), 13.5 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4''-methoxy-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ha)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:2) as a colorless oil (67.9 mg, 62% yield, 91% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.63 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.41 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.10 – 7.05 (m, 1H), 7.00 – 6.95 (m, 2H), 6.72 – 6.68 (m, 2H), 6.04 – 5.86 (m, 2H), 5.61 (dd, *J* = 19.4, 4.4 Hz, 1H), 3.75 (s, 3H), 0.11 (s, 6H) ppm.

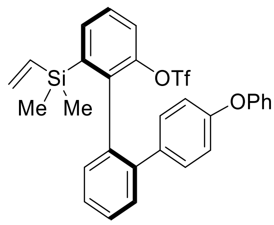
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 158.5, 146.8, 142.7, 141.2, 140.9, 138.0, 135.3, 134.6, 133.2 (2C), 132.6, 132.2, 130.4 (2C), 129.9, 129.3, 128.6, 126.4, 121.9, 118.3 (d, *J* = 320.9 Hz), 113.3, 55.3, −1.2, −1.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.74 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_4SSi^+$ $[M+H]^+$: 493.1111, found: 493.1111.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 26.5 (major), 29.8 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4''-phenoxy-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ia)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:2) as a colorless oil (89.8 mg, 81% yield, 89% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.63 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.02 – 5.85 (m, 2H), 5.61 (dd, J = 19.4, 4.3 Hz, 1H), 0.11 (s, 6H) ppm.

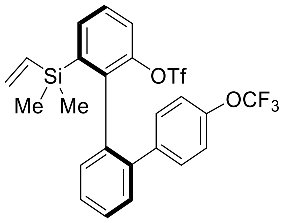
^{13}C NMR (101 MHz, Chloroform-d) δ = 157.1, 156.2, 146.8, 142.7, 140.9, 140.7, 137.9, 135.7, 135.3, 134.7, 132.6, 132.3, 130.6 (2C), 129.9, 129.8 (2C), 129.4, 128.7, 126.7, 123.4, 121.8, 119.1 (2C), 118.3 (q, J = 320.2 Hz), 118.1 (2C), −1.2, −2.0 ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ = −74.71 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{29}H_{26}F_3O_4SSi^+$ $[M+H]^+$: 555.1268, found: 555.1274.

HPLC-data: (Chiralpak IB column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 23.5 (major), 32.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4''-(trifluoromethoxy)-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3ja)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 50:1) as a colorless oil (86.3 mg, 79% yield, 81% *ee*).

^{1}H NMR (500 MHz, Chloroform-d) δ = 7.64 (dd, J = 7.5, 1.2 Hz, 1H), 7.52 (t, J = 7.3, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.32 (m, 2H), 7.10 – 7.05 (m, 3H), 7.01 (d, J = 8.1 Hz, 2H), 5.98 – 5.86 (m, 2H), 5.60 (dd, J = 18.2, 5.6 Hz, 1H), 0.12 (s, 3H), 0.11 (s, 3H) ppm.

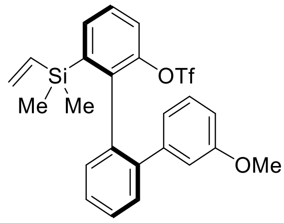
^{13}C NMR (126 MHz, Chloroform-d) δ = 148.2, 146.8, 142.7, 140.3, 140.2, 139.4, 137.7, 135.4, 134.8, 132.8, 132.4, 130.6 (2C), 130.0, 129.5, 128.9, 127.3, 121.9, 120.5 (q, J = 258.2 Hz), 120.2 (2C), 118.3 (q, J = 320.3 Hz), −1.1, −2.0 ppm.

^{19}F NMR (471 MHz, Chloroform-d) δ = -57.84 (s, 3F), −74.72 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{20}F_6NaO_4SSi^+$ $[M+Na]^+$: 569.0648, found: 569.0656.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 9.2 (major), 10.1 (minor).

(R)-6-(Dimethyl(vinyl)silyl)-3''-methoxy-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ka)



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 50:1) as a colorless oil (54.1 mg, 55% yield, 82% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.63 (d, *J* = 7.5 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.40 (t, *J* = 6.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.16 – 7.02 (m, 2H), 6.06 – 5.81 (m, 2H), 6.57 (s, 1H), 6.06 – 5.81 (m, 2H), 5.61 (dd, *J* = 19.2, 4.6 Hz, 1H), 3.56 (s, 3H), 0.12 (s, 1H), 0.11 (s, 1H) ppm.

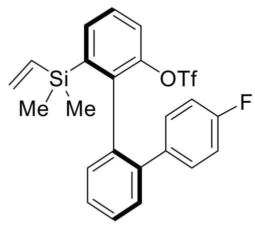
^{13}C NMR (126 MHz, Chloroform-*d*) δ =158.9, 146.9, 142.8, 142.1, 141.4, 140.8, 137.9, 135.2, 134.7, 132.6, 132.2, 130.0, 129.3, 128.9, 128.6, 126.9, 121.9 (2C), 118.3 (q, *J* = 320.1 Hz), 114.1, 113.6, 55.1, −1.2, −1.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.73 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_4SSi^+$ $[M+H]^+$: 493.1111, found: 493.1120.

HPLC-data: (Chiral OD-H column, λ = 254 nm, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min): t_R = 8.9 (major), 9.7 (minor).

(R)-6-(Dimethyl(vinyl)silyl)-4''-fluoro-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3la)

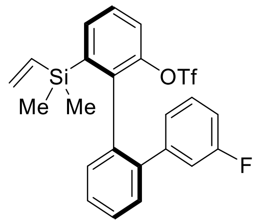


According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (64.3 mg, 67% yield, 90% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.89 – 6.80 (m, 2H), 6.02 – 5.86 (m, 2H), 5.61 (dd, *J* = 19.0, 4.8 Hz, 1H), 0.12 (s, 6H) ppm.

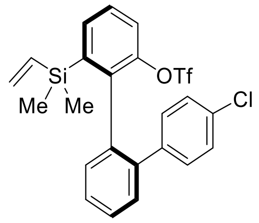
^{13}C NMR (126 MHz, Chloroform-*d*) δ =161.9 (d, *J* = 245.8 Hz), 146.8, 142.7, 140.6, 140.5, 137.9, 136.8 (d, *J* = 3.6 Hz), 135.4, 134.8, 132.7, 132.3, 130.8 (d, *J* = 8.2 Hz, 2C), 130.0, 129.4, 128.8, 126.9, 121.9, 118.3 (q, *J* = 320.0 Hz), 114.8 (d, *J* = 21.2 Hz, 2C), −1.1, −1.9 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.72 (s, 3F), −115.88 (s, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{23}H_{20}F_4NaO_3SSi^+$ $[M+Na]^+$: 503.0731, found: 503.0738.
HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 9.2 (major), 10.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-3''-fluoro-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ma)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (59.5 mg, 62% yield, 82% *ee*).
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 6.6 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.30 (m, 2H), 7.17 – 7.08 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.82 (m, 2H), 6.77 (d, *J* = 10.3 Hz, 1H), 6.01 – 5.86 (m, 2H), 5.61 (dd, *J* = 18.9, 4.9 Hz, 1H), 0.12 (s, 6H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 162.3 (d, *J* = 245.0 Hz), 146.8, 143.02, 142.96, 142.7, 140.3 (d, *J* = 3.2 Hz), 137.8, 135.4, 134.8, 132.8, 132.4, 129.9, 129.4, 129.2 (d, *J* = 8.3 Hz), 128.9, 127.3, 125.0 (d, *J* = 2.8 Hz), 121.9, 118.3 (q, *J* = 320.0 Hz), 116.2 (q, *J* = 22.1 Hz), 113.8 (d, *J* = 21.1 Hz), −1.1, −2.0 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.71 (s, 3F), −113.93 (s, 1F) ppm.
HRMS (ESI) m/z calculated for $C_{23}H_{21}F_4O_3SSi^+$ $[M+H]^+$: 481.0911, found: 481.0929.
HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/.4, flow rate = 0.5 mL/min): t_R = 10.8 (major), 12.9 (minor).

(R)-4''-Chloro-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3na)



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (66.5 mg, 67% yield, 85% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.31 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.00 – 5.84 (m, 2H), 5.60 (dd, *J* = 18.7, 5.0 Hz, 1H), 0.12 (s, 3H), 0.11 (s, 3H) ppm.

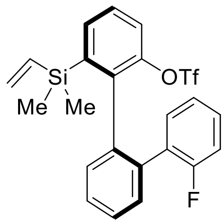
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 146.7, 142.7, 140.41, 140.35, 139.3, 137.8, 135.4, 134.7, 133.0, 132.8, 132.4, 130.5 (2C), 129.9, 129.5, 128.9, 128.1 (2C), 127.2, 122.0, 118.3 (q, *J* = 320.2 Hz), −1.1, −1.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.68 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{21}{}^{35}ClF_3O_3SSi^+$ $[M+H]^+$: 497.0616, found: 497.0608.

HPLC-data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 10.0 (major), 11.2 (minor).

(R)-6-(Dimethyl(vinyl)silyl)-2''-fluoro-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3oa)



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (71.0 mg, 74% yield, 82% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.57 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.42 – 7.37 (m, 2H), 7.36 – 7.29 (m, 1H), 7.29 –7.21 (m, 1H), 7.18 – 7.07 (m, 1H), 7.02 – 6.93 (m, 2H), 6.94 – 6.82 (m, 2H), 6.08 – 5.82 (m, 2H), 5.59 (dd, *J* = 19.9, 3.8

Hz, 1H), 0.07 (s, 3H), 0.05 (s, 3H) ppm.

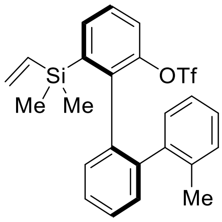
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 159.5 (d, *J* = 247.8 Hz), 146.7, 143.1, 140.0, 138.5, 136.1, 135.9, 135.3, 132.3, 132.1, 132.0 (d, *J* = 3.5 Hz), 130.9 (d, *J* = 1.4 Hz), 129.2 (d, *J* = 8.1 Hz), 128.8, 128.6, 128.1 (d, *J* = 14.9 Hz), 127.5, 123.4 (d, *J* = 3.6 Hz), 121.4, 118.3 (q, *J* = 320.0 Hz), 115.5 (d, *J* = 22.9 Hz), −1.3, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.63 (s, 3F), −113.35 ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{20}F_4NaO_3SSi^+$ $[M+Na]^+$: 503.0731, found: 503.0734.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 14.1 (major), 15.7 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-2''-methyl-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3pa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 50:1) as a colorless oil (41.9 mg, 44% yield, 70% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.52 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.36 – 7.30 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.95 – 5.82 (m, 2H), 5.57 (dd, *J* = 18.8, 5.0 Hz, 1H), 2.23 (s, 3H), 0.07 (s, 6H) ppm.

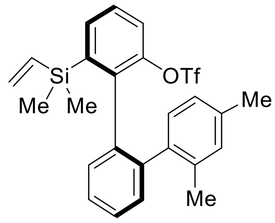
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.3, 142.8, 140.6, 140.4, 139.1, 138.1, 136.9, 135.7, 134.9, 132.7, 132.0, 131.0, 130.8, 129.9, 128.45, 128.38, 126.8, 126.7, 124.2, 121.5, 118.4 (q, *J* = 320.1 Hz), 20.0, −1.0, −1.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.14 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_3SSi^+$ $[M+H]^+$: 477.1162, found: 477.1175.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 14.3 (major), 15.6 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-2'',4''-*d*imethyl-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3qa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (51.0 mg, 52% yield, 70% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.49 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.30 – 7.26 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.18 – 7.11 (m, 1H), 6.97 – 6.83 (m, 2H), 6.57 – 6.25 (m, 2H), 6.07 – 5.75 (m, 2H), 5.56 (d, *J* = 4.6 Hz, 1H), 2.13 (m, 6H), 0.04 (s, 3H), 0.03 (s, 3H) ppm.

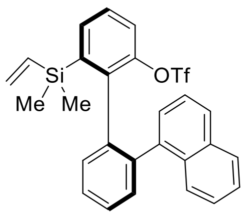
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 147.3, 142.8, 140.7, 140.6, 138.2, 136.6, 136.3, 135.7, 134.9, 132.6, 132.0 (2C), 131.5, 131.2, 129.9, 128.4 (2C), 126.5, 125.1, 121.6, 118.4 (q, *J* = 320.6 Hz), 21.1, 19.9, −1.0, −1.8 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.15 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{25}H_{26}F_3O_3SSi^+$ $[M+H]^+$: 491.1319, found: 491.1327.

HPLC-data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 11.1 (major), 14.5 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-2'-(naphthalen-1-yl)-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (3ra)**

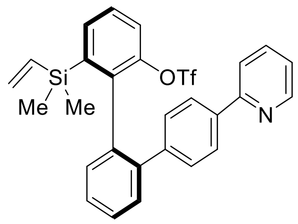


According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (mg, 33% yield, 3% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.96 (d, *J*=7.7, 1H), 7.83 – 7.78 (m, 1H), 7.65 (d, *J*=8.3, 1H), 7.60 (d, *J*=7.5, 1H), 7.56 – 7.52 (m, 1H), 7.52 – 7.50 (m, 2H), 7.49 – 7.42 (m, 3H), 7.20 (t, *J*=7.8, 1H), 7.13 – 7.04 (m, 1H), 6.90 – 6.73 (m, 2H), 6.11 – 5.98 (m, 2H), 5.70 (dd, *J*=19.0, 4.8, 1H), 0.22 (s, 3H), 0.21 (s, 3H) ppm.

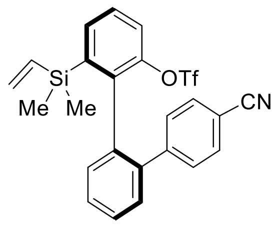
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.2, 142.7, 140.7, 139.7, 138.1, 137.6, 136.4, 135.0, 133.9, 132.8, 132.3, 132.3, 132.1, 128.4, 128.4, 127.9, 127.4 (2C), 127.05, 126.98, 125.9, 125.8, 124.1, 121.6, 118.2 (q, *J*=320.5), −0.9, −1.7 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.54 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{27}H_{24}F_3O_3SSi^+$ [M+H]$^+$: 513.1162, found: 513.1157.
HPLC-data: (ChiralpakAD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 11.5 (major), 13.8 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4''-(pyridin-2-yl)-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3sa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (87.3 mg, 81% yield, 85% *ee*).
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.65 (d, *J* = 4.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.22 – 7.17 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.04 – 5.87 (m, 2H), 5.62 (dd, *J* = 19.7, 4.0 Hz, 1H), 0.14 (s, 3H), 0.13 (s, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.1, 149.8, 146.8, 142.7, 141.5, 141.0, 140.7, 137.9, 137.7, 136.9, 135.3, 134.8, 132.7, 132.4, 130.0, 129.7 (2C), 129.4, 128.8, 127.0, 126.3 (2C), 122.2, 122.0, 120.6, 118.3 (q, *J* = 320.4 Hz), −1.2, −1.9 ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.67 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{28}H_{25}F_3O_3SSi^+$ [M+H]$^+$: 540.1271, found: 540.1282.
HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R = 10.4 (major), 11.1 (minor).

***(R)*-4''-Cyano-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ta)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 90:10) as a colorless oil (68.2 mg, 70% yield, 16% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.55 (t, *J* = 7.5, 1H), 7.50 – 7.44 (m, 3H), 7.42 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.06 (dd, *J* = 8.2, 0.9 Hz, 1H), 5.97 – 5.86 (m, 2H), 5.60 (dd, *J* = 13.9, 9.8 Hz, 1H), 0.13 (s, 6H) ppm.

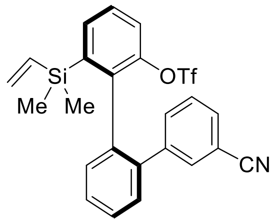
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 146.7, 145.6, 142.8, 139.9, 139.7, 137.5, 135.5, 134.8, 133.0, 132.6, 131.7 (2C), 129.9 (2C), 129.8, 129.7, 129.2, 128.0, 122.0, 118.1, 119.0, 110.7, −1.0, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.63 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{20}F_3NNaO_3SSi^+$ $[M+Na]^+$: 510.0777, found: 510.0759.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 96/4, flow rate = 0.5 mL/min): t_R = 8.4 (minor), 8.8 (major).

***(R)*-3''-Cyano-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3ua)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 90:10) as a colorless oil (49.7 mg, 51% yield, 45% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.66 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.55 (t, *J* = 7.6, 1H), 7.52 – 7.42 (m, 2H), 7.44 – 7.37 (m, 1H), 7.40 – 7.30 (m, 3H), 7.34 – 7.24 (m, 2H), 7.06 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.95 – 5.85 (m, 2H), 5.67 – 5.54 (m, 1H), 0.15 (s, 3H), 0.13 (s, 3H) ppm.

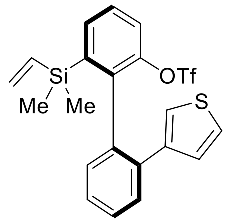
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 146.6, 142.8, 142.0, 139.8, 139.2, 137.5, 135.6, 134.9, 133.6, 133.1, 132.7, 132.5, 130.5, 129.8, 129.7, 129.3, 128.8, 127.9, 121.9, 118.7, 118.3 (q, *J* = 320.0 Hz), 112.0, −1.0, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.64 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{21}F_3NO_3SSi^+$ $[M+H]^+$: 488.0958, found: 488.0968.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 97.5/2.5, flow rate = 0.5 mL/min): t_R = 8.4 (major), 9.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-2'-(thiophen-3-yl)-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (3va)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:2) as a colorless oil (67.4 mg, 72% yield, 30% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.64 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47 (t, *J* = 7.5, 1H), 7.42 – 7.38 (m, 1H), 7.38 – 7.34 (m, 1H), 7.28 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.18 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.0 Hz, 1H), 6.81 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.76 (dd, *J* = 3.0, 1.4 Hz, 1H), 6.02 – 5.82 (m, 2H), 5.57 (dd, *J* = 19.2, 4.6 Hz, 1H), 0.05 (s, 6H) ppm.

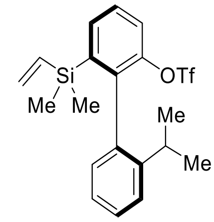
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.2, 142.8, 141.1, 140.9, 137.8, 136.4, 135.4, 134.4, 132.6, 132.3, 129.32, 129.28, 128.8, 128.4, 126.7, 124.7, 123.1, 121.9, 118.28 (q, *J* = 320.0 Hz), −1.5, −2.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.71 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{20}F_3O_3S_2Si^+$ $[M+H]^+$: 469.0570, found: 469.0568.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min): t_R = 7.5 (major), 8.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-2'-isopropyl-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (3wa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether) as a colorless oil (61.6 mg, 72% yield, 87% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.68 – 7.63 (m, 1H), 7.47 – 7.38 (m, 2H), 7.37

– 7.33 (m, 2H), 7.20 (t, *J* = 7.4, 1H), 7.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.00 – 5.84 (m, 2H), 5.57 (dd, *J* = 18.0, 5.8 Hz, 1H), 2.55 – 2.44 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.00 (s, 3H), −0.03 (s, 3H). ppm.

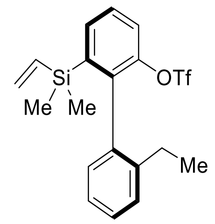
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.6, 147.3, 142.8, 140.5, 138.2, 135.4, 134.4, 132.5, 131.4, 129.3, 128.6, 125.6, 125.1, 121.7, 118.4 (q, *J* = 320.1 Hz), 30.4, 24.0 (2C), −1.4, −1.8 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.61 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{20}H_{24}F_3O_3SSi^+$ [M+H]$^+$: 429.1162, found: 429.1163.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.9/0.1, flow rate = 0.5 mL/min): t_R = 12.2 (major), 12.8 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-2'-ethyl-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (3xa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:0) as a colorless oil (55.5 mg, 67% yield, 81% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.33 (m, 2H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.23 (td, *J* = 7.5, 1.1 Hz, 1H), 7.13 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.98 – 5.84 (m, 2H), 5.54 (dd, *J* = 17.2, 6.6 Hz, 1H), 2.29 (q, *J* = 7.7 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.00 (s, 3H), −0.03 (s, 3H) ppm.

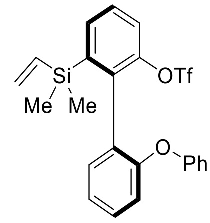
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 149.5, 144.7, 144.5, 142.8, 139.9, 137.3, 137.1, 134.4, 133.4, 131.2, 130.7, 129.5, 127.2, 123.8, 120.4 (q, *J* = 320.0 Hz), 28.0, 15.9, 0.3, 0.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.63 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{19}H_{22}F_3O_3SSi^+$ [M+H]$^+$: 415.1006, found: 415.1005.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 12.1 (minor), 12.5 (major).

_(R)_-6-(Dimethyl(vinyl)silyl)-2'-phenoxy-[1,1'-biphenyl]-2-yl trifluoromethane-sulfonate (3ya)



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 50:1) as a colorless oil (38.2 mg, 40% yield, 84% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.57 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.27 – 7.20 (m, 4H), 7.18 – 7.14 (m, 1H), 7.07 – 6.98 (m, 2H), 6.97 – 6.93 (m, 2H), 6.70 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.07 – 5.80 (m, 2H), 5.53 (dd, *J* = 20.1, 3.8 Hz, 1H), 0.06 (s, 3H), 0.03 (s, 3H) ppm.

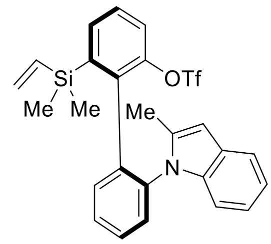
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 156.3, 155.8, 148.2, 142.9, 138.1, 137.7, 135.2, 133.2, 132.4, 130.3, 129.9 (2C), 128.8, 126.4, 124.2, 121.7, 121.6, 120.7 (2C), 118.5 (q, *J* = 320.1 Hz), 115.8, −1.7, −2.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.56 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{22}F_3O_4SSi^+$ $[M+H]^+$: 479.0955, found: 479.0953.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 9.2 (minor), 9.8 (major).

(*R*)-6-(dimethyl(vinyl)silyl)-2'-(2-methyl-1H-indol-1-yl)-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (3za)



According to the general procedure I, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) as a colorless oil (mg, 55% yield, 89% *ee*).

^{1}H NMR (500 MHz, Acetone-*d$_6$*) δ = 7.82 – 7.78 (m, 1H), 7.69 (ddd, *J* = 8.1 Hz, 5.6, 3.5, 1H), 7.59 (d, *J*=7.9 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.51 – 7.47 (m, 1H), 7.46 (d, *J*=7.8 Hz, 1H), 7.41 (d, *J*=8.2 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.09 – 7.05 (m, 1H), 6.53 – 6.46 (m, 1H), 6.12 – 5.89 (m, 2H), 5.70 (dd, *J*=20.1 Hz, 3.7, 1H), 2.06 (d, *J*=1.1 Hz, 3H), 0.23 (s, 3H), 0.22 (s, 3H) ppm.

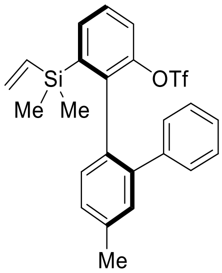
^{13}C NMR (126 MHz, Acetone-*d$_6$*) δ = 148.3, 143.4, 139.3, 138.9, 138.5, 137.8, 136.6, 134.4, 133.30, 133.29, 131.0, 130.2, 129.6, 127.7, 127.3, 126.2, 122.7, 122.6, 120.4, 119.4, 118.9 (d, J=319.5), 112.4, 111.5, 9.4, –1.0, –1.9 ppm.

^{19}F NMR (471 MHz, Acetone-*d$_6$*) δ = −70.49 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{25}F_3NO_3SSi^+$ $[M+H]^+$: 516.1271, found: 516.1287.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99/1, flow rate = 0.5 mL/min): t_R = 9.5 (major), 10.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4'-methyl-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3aaa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (59.0 mg, 62% yield, 90% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5, 1H), 7.47 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.41 (t, *J* = 7.4, 1H), 7.37 – 7.31 (m, 2H), 7.11 – 7.04 (m, 2H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.96 (s, 1H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.06 – 5.90 (m, 2H), 5.65 (dd, *J* = 19.8, 3.9 Hz, 1H), 2.23 (s, 3H), 0.15 (s, 3H), 0.14 (s, 3H) ppm.

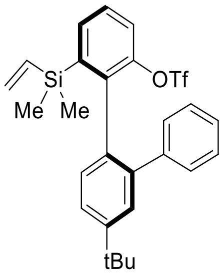
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.0, 142.9, 141.3, 141.0, 139.1, 138.2, 135.3, 132.5, 132.1, 131.8, 130.8, 129.3 (2C), 128.5, 127.7 (2C), 127.4, 126.7, 123.4, 121.7, 118.3 (d, *J* = 320.0 Hz), 21.5, −1.1, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.79 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_3SSi^+$ $[M+H]^+$: 477.1162, found: 477.1164.

HPLC-data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 10.8 (major), 12.0 (minor).

(R)-4'-(tert-Butyl)-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3aba)



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a white solid (66.3 mg, 64% yield, 91% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.61 (d, *J* = 7.4 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.15 (m, 2H), 7.10 – 7.01 (m, 3H), 6.02 – 5.81 (m, 2H), 5.60 (dd, *J* = 19.9, 3.9 Hz, 1H), 1.39 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H) ppm.

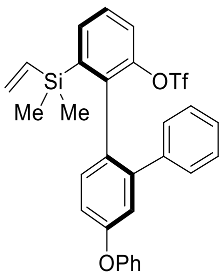
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 152.6, 146.9, 143.0, 141.5, 141.0, 140.8, 138.1, 135.2, 132.3, 131.8 (2C), 129.4 (2C), 128.4, 127.8 (2C), 127.1, 126.7, 123.6, 121.8, 118.3 (q, *J* = 320.3 Hz), 34.9, 31.5 (3C), −1.2, −1.9 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.79 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{27}H_{29}F_3NaO_3SSi^+$ $[M+Na]^+$: 541.1451, found: 541.1439.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.9/0.1, flow rate = 0.5 mL/min): t_R = 7.2 (major), 8.2 (minor).

(R)-6-(Dimethyl(vinyl)silyl)-4'-phenoxy-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3aca)



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:2) as a colorless oil (45.4 mg, 41% yield, 92% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.56 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.34 – 7.27 (m, 2H), 7.24 – 7.18 (m, 2H), 7.10 – 7.05 (m, 5H), 7.04 – 7.00 (m, 3H), 6.99 – 6.96 (m, 3H), 6.03 – 5.84 (m, 2H), 5.57 (dd, J = 19.7, 4.0 Hz, 1H), 0.11 (s, 3H), 0.10 (s, 3H) ppm.

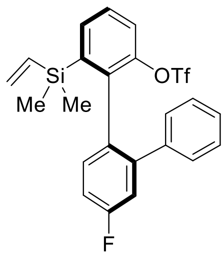
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 157.9, 157.4, 147.1, 143.4, 142.9, 140.3, 140.2, 138.0, 135.3, 133.8, 132.7, 130.0, 129.9 (2C), 129.2 (2C), 128.7, 127.9 (2C), 127.1, 123.5, 121.8, 120.6, 118.8 (2C), 118.4 (q, J = 320.5 Hz), 117.3, −1.1, −1.8 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.69 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{29}H_{26}F_3O_4SSi^+$ $[M+H]^+$: 555.1268, found: 555.1282.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 11.1 (major), 12.8 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-4'-fluoro-[1,1':2',1''-terphenyl]-2-yl trifluoro-methanesulfonate (3ada)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (71.1 mg, 74% yield, 80% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.63 (d, J = 7.4 Hz, 1H), 7.34 (t, J = 7.8 Hz, 1H), 7.32 – 7.27 (m, 1H), 7.21 – 7.16 (m, 4H), 7.14 – 7.03 (m, 4H), 6.04 – 5.88 (m, 2H), 5.62 (dd, J = 19.6, 4.1 Hz, 1H), 0.16 (s, 3H), 0.13 (s, 3H) ppm.

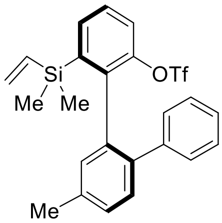
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 163.3 (d, J = 248.8 Hz), 146.9, 143.9, 143.8, 143.0, 139.7 (d, J = 18.9 Hz), 137.8, 135.3, 133.9 (d, J = 8.3 Hz), 132.8, 130.8 (d, J = 3.0 Hz), 129.1 (2C), 128.9, 128.0 (2C), 127.4, 121.9, 118.3 (q, J = 320.1 Hz), 116.9 (d, J = 22.0 Hz), 113.6 (d, J = 21.1 Hz), −1.1, −1.9 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.68 (s, 3F), −112.87 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{20}F_4NaO_3SSi^+$ $[M+Na]^+$: 503.0731, found: 503.0745.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 14.7 (major), 17.0 (minor).

***(R)*-6-(Dimethyl(vinyl)silyl)-5'-methyl-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3aea)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (58.1 mg, 61% yield, 85% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.64 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.19 – 7.14 (m, 3H), 7.13 (s, 1H), 7.08 – 7.01 (m, 3H), 6.17 – 5.87 (m, 2H), 5.61 (dd, *J* = 19.7, 4.0 Hz, 1H), 2.42 (s, 3H), 0.14 (s, 3H), 0.11 (s, 3H) ppm.

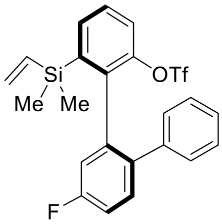
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 146.8, 142.7, 141.0, 140.8, 138.6, 138.2, 136.4, 135.2, 134.4, 133.0, 132.3, 130.0, 129.9, 129.2 (2C), 128.5, 127.8 (2C), 126.6, 121.8, 118.3 (q, *J* = 320.2 Hz), 21.0, −1.1, −2.1 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.75 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{24}H_{24}F_3O_3SSi^+$ $[M+H]^+$: 477.1162, found: 477.1168.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 14.7 (minor), 15.6 (major).

***(R)*-6-(Dimethyl(vinyl)silyl)-5'-fluoro-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3afa)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (69.1 mg, 72% yield, 80% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.18 – 7.15 (m, 3H), 7.11 – 7.08 (m, 1H), 7.07 – 7.03 (m, 3H), 6.08 – 5.89 (m, 2H), 5.63 (dd, *J* = 19.3, 4.4 Hz, 1H), 0.18 (s, 3H), 0.15 (s, 3H) ppm.

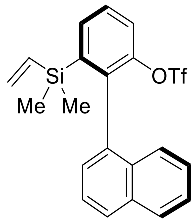
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 161.5 (d, *J* = 247.9 Hz), 146.6, 142.7, 139.8, 139.5 (d, J = 1.1 Hz), 137.9 (d, J = 3.5 Hz), 137.7, 136.6 (d, J = 7.8 Hz), 135.3, 132.8, 131.8 (d, J = 8.1 Hz), 129.3 (2C), 129.1, 127.9 (2C), 127.0, 121.9, 119.2 (d, J = 22.0 Hz), 118.4 (q, J = 320.2 Hz), 116.0 (d, J = 21.0 Hz), −1.2, −2.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.63 (s, 3F), −115.88 (s, 1F) ppm.

HRMS (ESI) m/z calculated for $C_{23}H_{21}F_4O_3SSi^+$ $[M+H]^+$: 481.0911, found: 481.0916.

HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 11.5 (major), 12.5 (minor).

***(R)*-3-(Dimethyl(vinyl)silyl)-2-(naphthalen-1-yl)phenyl trifluoromethanesulfonate (3aga)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (54.1 mg, 62% yield, 78% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.98 – 7.85 (m, 2H), 7.72 (dd, J = 7.4, 1.1 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.44 – 7.35 (m, 3H), 7.25 (d, J = 8.6 Hz, 1H), 5.84 – 5.65 (m, 2H), 5.40 (dd, J = 19.1, 4.7 Hz, 1H), −0.20 (s, 3H), −0.22 (s, 3H) ppm.

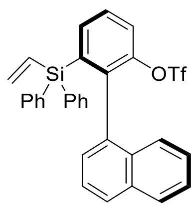
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.1, 143.6, 139.6, 137.7, 135.3, 133.6, 133.3, 132.9, 132.1, 129.3, 129.1 (2C), 128.3, 126.4, 126.1, 125.8, 124.7, 121.9, 118.2 (q, J = 320.2 Hz), −1.9, −2.0 ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.64 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{21}H_{20}F_3O_3SSi^+$ $[M+H]^+$: 437.0849, found: 437.0853.

HPLC-data: (Chiral MD column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 11.1 (major), 12.9 (minor).

***(R)*-3-(Dimethyl(vinyl)silyl)-2-(naphthalen-1-yl)phenyl trifluoromethanesulfonate (3agb)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil

(69.5 mg, 62% yield, 88% *ee*).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.66 (dd, *J* = 6.9, 1.8 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.47 – 7.42 (m, 1H), 7.40 – 7.35 (m, 1H), 7.26 – 7.25 (m, 1H), 7.24 – 7.21 (m, 6H), 7.21 – 7.17 (m, 4H), 7.17 – 7.14 (m, 1H), 7.03 (dd, *J* = 7.0, 1.1 Hz, 1H), 5.62 – 5.53 (m, 1H), 5.22 (d, *J* = 9.6 Hz, 2H) ppm.

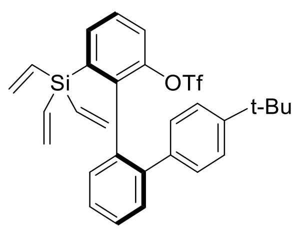
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.4, 140.6, 140.5, 137.5, 136.2, 135.9 (2C), 135.5 (2C), 134.9, 133.9, 133.7, 133.3, 133.1, 132.6, 132.5, 129.5, 129.4, 129.2, 129.0, 128.1, 127.8 (2C), 127.7 (2C), 126.2, 125.8, 125.7, 124.6, 122.5, 118.2 (q, *J* = 320.1 Hz) ppm.

^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.63 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{31}H_{24}F_3O_3SSi^+$ $[M+H]^+$: 561.1162, found: 561.1249.

HPLC-data: (Chiral OD-H column, λ = 254 nm, hexane/isopropanol = 99.5/0.5, flow rate = 0.5 mL/min): t_R = 15.5 (minor), 15.6 (major).

***(R)*-4''-(tert-Butyl)-6-(trivinylsilyl)-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate (3cc)**



According to the general procedure, the title compound was isolated through column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) as a colorless oil (56.4 mg, 52% yield, 83% *ee*).

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.65 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.26 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.03 (dd, *J* = 14.5, 3.7 Hz, 3H), 5.88 (dd, *J* = 20.2, 14.5 Hz, 3H), 5.67 (dd, *J* = 20.2, 3.7 Hz, 3H), 1.26 (s, 9H) ppm.

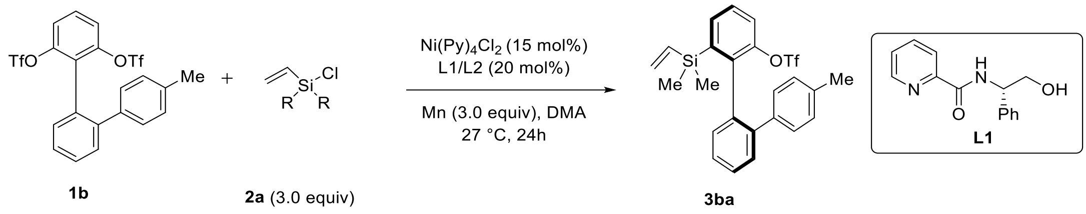
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 149.6, 147.0, 141.6, 141.3, 140.0, 137.7, 136.2, 135.9 (2C), 134.8, 133.6 (2C), 132.3, 130.0, 129.3, 129.0 (2C), 128.4, 126.5, 124.7 (2C), 122.1, 118.3 (q, *J* = 320.8, Hz), 34.5, 31.4 (3C) ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.70 (s, 3F) ppm.

HRMS (ESI) m/z calculated for $C_{29}H_{29}F_3NaO_3SSi^+$ $[M+Na]^+$: 565.1451, found: 565.1462.

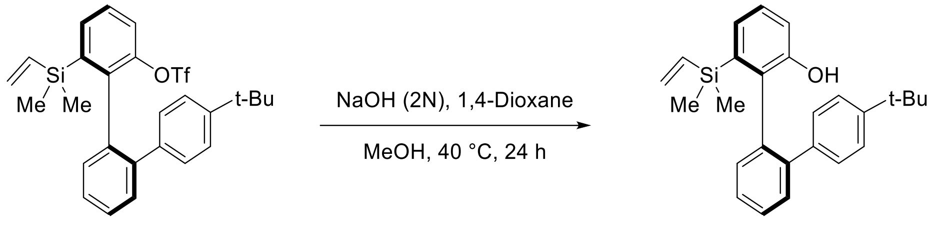
HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.8/0.2, flow rate = 0.5 mL/min): t_R = 6.9 (major), 7.5 (minor).

Procedure for Synthesis of Compound 3ba on a 1.0 mmol Scale



In a nitrogen-filled glove box, $Ni(Py)_4Cl_2$ (69 mg, 0.15 mmol 15 mol%), ligand L1 (48mg, 0.2 mmol, 20 mol%), and Mn (165.0 mg, 3.0 mmol, 3.0 equiv) were added to a reaction tube equipped with a magnetic stir bar. Subsequently, a solution of the bis(triflates) **1b** (526.0 mg, 1.0 mmol, 1.0 equiv) and the chlorosilane **2a** (0.42 mL, 3.0 mmol, 3.0 equiv) in dry DMA (5.0 mL, 0.2 M) was added to the reaction mixture. The reaction tube was sealed and removed from the glove box. The reaction was stirred at room temperature for 30 h before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3 × 20 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether) to afford the desired product **3ba** (357.1 mg, 75% yield, 91% *ee*).

Derivatizations of the Silylation Products



3ca **4**

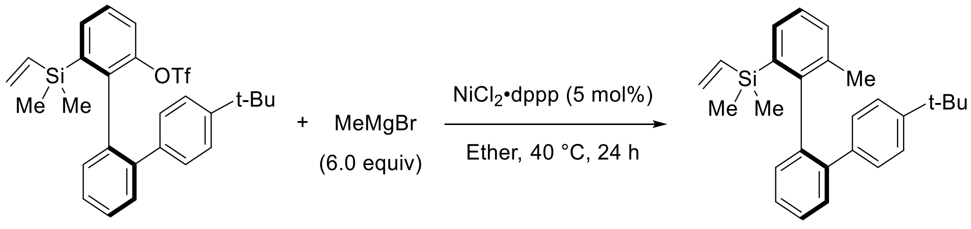
To a solution of **3ca** (51.8 mg, 0.1 mmol, 92% *ee*) in MeOH (0.3 mL) and 1,4-dioxane (0.6 mL) was added NaOH aqueous solution (2 N) at 0 ℃, slowly. The resulting mixture was stirred at 40℃ for 24 h. The mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate = 20/1) to afford *(R)-4''-(tert-butyl)-6-(dimethyl(vinyl)silyl)-[1,1':2',1''-terphenyl]-2-ol* (**4**) (35.5 mg, 92% yield, 84% *ee*) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.56 – 7.47 (m, 2H), 7.40 (td, *J* = 7.4, 1.6 Hz, 1H), 7.30 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.15 – 7.09 (m, 3H), 6.83 (dd, *J* = 8.0, 1.1 Hz, 1H), 5.93 – 5.75 (m, 2H), 5.47 (dd, *J* = 20.0, 4.0 Hz, 1H), 4.65 (s, 1H), 1.26 (s, 9H), −0.06 (s, 6H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 152.3, 150.1, 141.7, 139.1, 138.8, 136.9, 135.1, 133.4, 132.8, 131.5, 130.8, 129.4, 128.9 (2C), 128.5, 127.7, 127.6, 125.0 (2C), 116.1, 34.5, 31.4 (3C), −1.5, −2.0 ppm.

HRMS (ESI) m/z calculated for $C_{26}H_{31}O_3Si^+$ $[M+H]^+$: 387.2133, found: 387.2131.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 95/5, flow rate = 0.5 mL/min): t_R = 8.9 (minor), 10.2 (major).



3ca **5**

To a solution of **3ca** (51.8 mg, 0.1 mmol, 92% *ee*) and $NiCl_2$·dppp (2.7 mg, 0.005 mol, 5 mol%) in ether was added MeMgBr (0.6 mmol, 0.2 mL, 3 M in THF, 6.0 equiv) dropwise under nitrogen flow at 0 ℃. The resulting mixture was stirred at 40 ℃ under nitrogen for 24 h. The mixture was filtered and concentrated under reduced pressure.

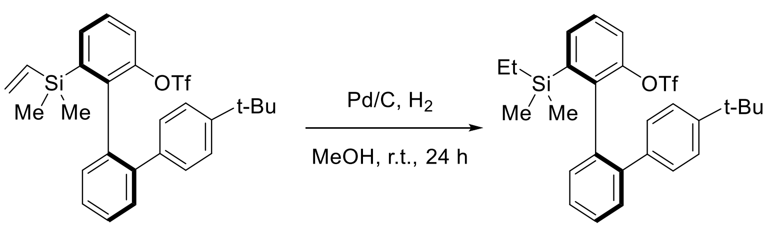
The crude product was purified by flash column chromatography (silica gel, petroleum ether) to afford *(R)-(4''-(tert-butyl)-6-methyl-[1,1':2',1''-terphenyl]-2-yl)dimethyl-(vinyl)silane* (**5**) (31.1 mg, 81% yield, 85% *ee*) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.49 – 7.44 (m, 2H), 7.44 – 7.41 (m, 1H), 7.35 – 7.31 (m, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.14 (m, 3H), 7.08 – 7.03 (m, 3H), 6.02 – 5.76 (m, 2H), 5.51 (dd, *J* = 20.1, 3.8 Hz, 1H), 1.73 (s, 3H), 1.26 (s, 9H), −0.02 (s, 3H), −0.03 (s, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*) δ = 149.4, 147.3, 141.1, 140.3, 139.4, 138.1, 135.8, 132.9, 131.3, 131.2, 130.7, 130.0, 129.1 (2C), 128.0 (2C), 126.7, 126.5, 124.7 (2C), 34.5, 31.4 (3C), 20.6, −1.3, −1.8 ppm.

HRMS (ESI) m/z calculated for $C_{27}H_{32}NaSi^+$ $[M+H]^+$: 407.2165, found: 407.2173.

HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.6/0.4, flow rate = 0.5 mL/min): t_R = 8.4 (major), 8.9 (minor).



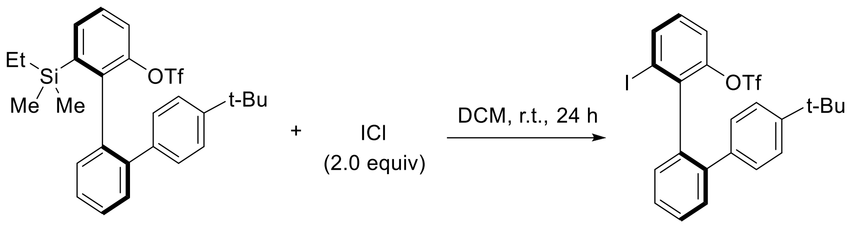
To a solution of **3ca** (51.8 mg, 0.1 mmol, 92% *ee*) in MeOH (2.0 mL) was added Pd/C (12.4 mg, 0.01 mmol) at 25 °C. The resulting mixture was stirred at room temeperature in an atmosphere of hydrogen gas for 24 h. The mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether) to afford *(R)-4''-(tert-butyl)-6-(ethyldimethylsilyl)-[1,1':2',1''-terphenyl]-2-yl trifluoromethane-sulfonate* (**6**) (51.5 mg, 99% yield, 90% *ee*) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.60 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 1.27 (s, 9H), 0.86 (t, *J* = 7.9 Hz, 3H), 0.62 – 0.55 (m, 2H), −0.04 (s, 3H), −0.07 (s, 3H) ppm.

^{13}C NMR (126 MHz, Chloroform-*d*) δ = 149.7, 147.0, 143.4, 141.3, 140.9, 137.6, 134.9, 134.7, 132.0, 130.1, 129.2, 128.9 (2C), 128.5, 126.5, 124.8 (2C), 121.5, 118.3 (q, *J* = 320.1 Hz), 34.5, 31.4 (3C), 8.5, 7.6, −2.0, −2.4 ppm.

^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.75 (s, 3F) ppm.

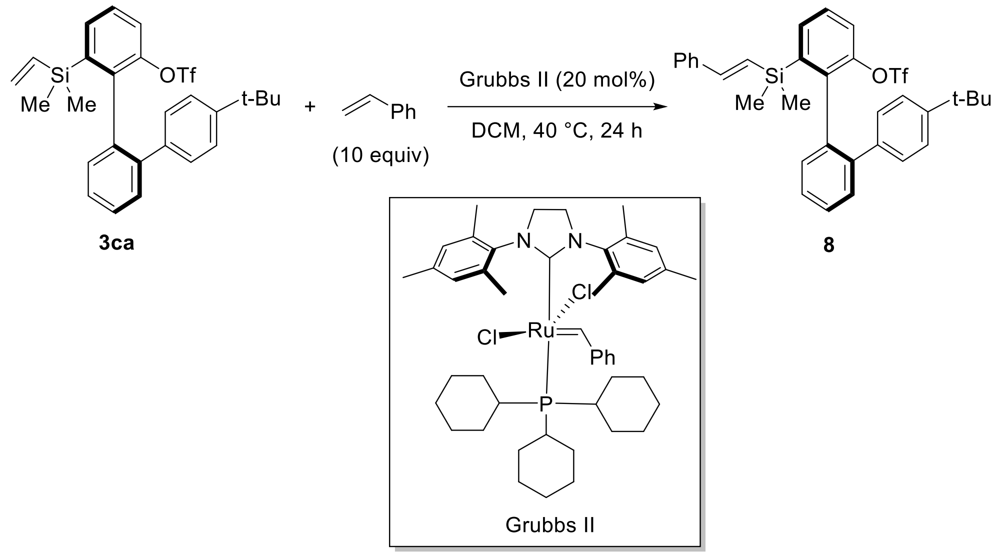
HRMS (ESI) m/z calculated for $C_{27}H_{32}F_3O_3SSi^+$ $[M+H]^+$: 521.1788, found: 521.1804.
HPLC-data: (Chiralpak IA column, λ = 254 nm, hexane/isopropanol = 99.8/0.2, flow rate = 0.5 mL/min): t_R = 8.0 (major), 8.6 (minor).



6 **7**

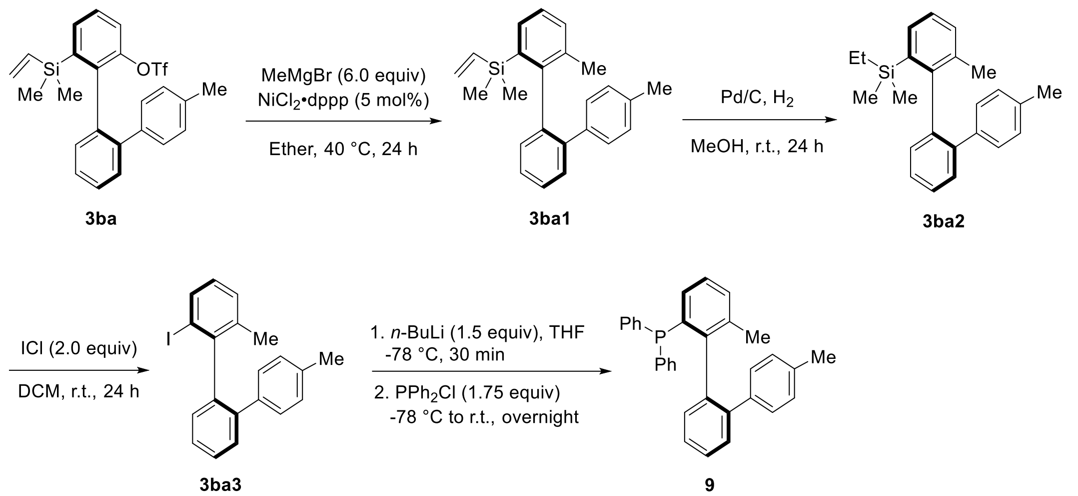
To a solution of **6** (51.5 mg, 0.1 mmol, 90% *ee*) in DCM (1.0 mL) was added ICl (0.2 mmol, 1.0 M in DCM, 0.2 mL, 2.0 equiv) at 0 °C, slowly. The resulting mixture was stirred at room temperature for 24 h. The mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether) to afford *(R)-4''-(tert-butyl)-6-iodo-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate* (**7**) (37.5 mg, 67% yield, 87% *ee*) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.91 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.47 – 7.40 (m, 2H), 7.29 – 7.25 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.12 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.09 – 7.04 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 1H), 1.26 (s, 9H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 150.0, 146.0, 141.5, 140.4, 139.0, 137.5, 136.4, 131.6, 130.30, 130.27, 129.5, 128.7 (2C), 127.0, 124.8 (2C), 121.2, 118.3 (q, *J* = 320.0 Hz), 103.1, 34.6, 31.4 (3C) ppm.
^{19}F NMR (376 MHz, Chloroform-*d*) δ = −74.75 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{23}H_{20}F_3INaO_3S^+$ $[M+Na]^+$: 583.0022, found: 583.0021.
HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.8/0.2, flow rate = 0.5 mL/min): t_R = 15.4 (major), 17.3 (minor).



To a solution of **3ca** (51.8 mg, 0.1 mmol, 92% ee) and styrene (104 mg, 1.0 mmol, 10 equiv) in DCM was added Grubbs II (16 mg, 20 mol%). The resulting mixture was stirred at 40 °C under nitrogen for 24 h. The mixture was filtered and concentrated under reduced pressure. The crude products were purified by flash column chromatography (silica gel, petroleum ether) to afford *(R,E)-4''-(tert-butyl)-6-(dimethyl(styryl)silyl)-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate* (**8**) (26.1 mg, 44% yield, 87% *ee*) as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.66 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.34 – 7.28 (m, 5H), 7.24 (d, *J* = 6.9 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 19.1 Hz, 1H), 6.22 (d, *J* = 19.1 Hz, 1H), 1.25 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H) ppm.
^{13}C NMR (126 MHz, Chloroform-*d*) δ = 149.6, 147.0, 144.9, 142.9, 141.5, 140.9, 138.2, 137.6, 135.2, 134.6, 132.2, 130.2, 129.3 (2C), 128.9 (2C), 128.61, 128.59, 128.3, 127.3, 126.7 (2C), 126.5, 124.7 (2C), 121.7, 118.3 (q, *J* = 320.0 Hz), 34.5, 31.4 (3C), −0.8, −1.6 ppm.
^{19}F NMR (471 MHz, Chloroform-*d*) δ = −74.71 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{33}H_{33}F_3NaO_3SSi^+$ $[M+Na]^+$: 617.1764, found: 617.1762.
HPLC-data: (Chiralpak AD-H column, λ = 254 nm, hexane/isopropanol = 99.7/0.3, flow rate = 0.5 mL/min): t_R = 16.9 (minor), 19.0 (major).



Step 1: To a solution of **3ba** (103.6 mg, 0.2 mmol, 91% *ee*) and $NiCl_2$·dppp (5.4 mg, 0.01 mol, 5 mol%) in ether was added MeMgBr (1.2 mmol, 0.4 mL, 3M in THF, 6.0 equiv) dropwise under nitrogen flow at 0 °C. The resulting mixture was stirred at 40 °C under nitrogen for 24 h. The mixture was filtered and concentrated under reduced pressure to afford the crude product 3ba1 which can be directly used for the next step.

Step 2: To a solution of the crude product of the previous step in MeOH (4.0 mL) was added Pd/C (24.8 mg, 0.02 mmol) at room temperature. The resulting mixture was stirred at room temperature under an atmosphere of hydrogen gas for 24 h. The mixture was filtered and concentrated under reduced pressure to afford the crude product 3ba2 which can be directly used for the next step.

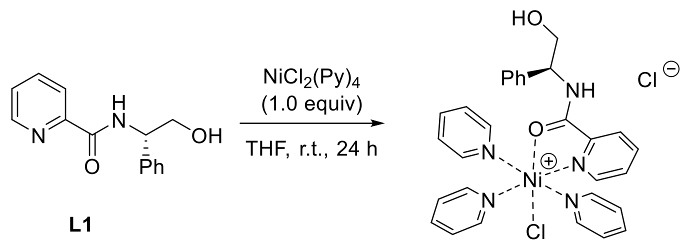
Step 3: To a solution of the crude product of the previous step in DCM (2.0 mL) was added ICl (0.4 mmol, 1.0 M in DCM, 0.4 mL, 2.0 equiv) at 0 °C, slowly. The resulting mixture was stirred at room temperature for 24 h. After the mixture was passed through a short pad of silica gel, the filtrated was concentrated under reduced pressure, to afford the crude product **3ba3**, which was directly used for the next step.

Step 4: The crude **3ba3** was dissolved in dry THF (1 mL) at room temperature under nitrogen atmosphere. Subsequently, *n*-Buli (0.12 mL, 2.5 M in hexane, 0.3 mmol, 1.5 equiv) was added dropwise to the reaction mixture by syringe at –78 °C. After stirring for 30 min at –78 °C, chlorodiphenylphosphine (77.2 mg, 0.35 mmol) in THF (0.5 mL) was added dropwise to the reaction mixture. The reaction was allowed to warm up to room temperature and stirred overnight. The mixture was filtered through a pad of celite and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate = 20/1) to afford *(R)-(4'',6-dimethyl-[1,1':2',1''-terphenyl]-2-yl)diphenylphosphane* (**9**) (11.5 mg, 26 % yield over 4 steps, 86% *ee*) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.45 (d, *J* = 6.7 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.30 – 7.26 (m, 3H), 7.23 – 7.14 (m, 5H), 7.15 – 7.08 (m, 5H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.89-6.83 (m, 3H), 6.74 (d, *J* = 6.8 Hz, 1H), 2.29 (s, 3H), 1.98 (s, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 147.4 (d, *J* = 32.7 Hz), 145.6, 140.6 (d, *J* = 1.8 Hz), 138.9, 138.8, 138.7, 136.8 (d, *J* = 6.4 Hz), 136.1, 134.1 (d, *J* = 20.1 Hz, 2C), 133.2 (d, *J* = 18.8 Hz, 2C), 132.1 (d, *J* = 1.5 Hz), 131.2 (d, *J* = 2.9 Hz), 130.7, 130.1, 129.4 (d, *J* = 1.9 Hz, 2C), 128.5, 128.4 (3C), 128.3 (d, *J* = 7.2 Hz, 2C), 128.2 (d, *J* = 5.8 Hz, 2C), 127.9, 127.8, 127.4, 126.5, 29.9, 21.2 ppm.
^{31}P NMR (162 MHz**,** Chloroform-*d***)** δ = –13.8 ppm.
HRMS (ESI) m/z calculated for $C_{32}H_{28}P$ $[M+H]^+$: 443.1923, found: 443.1928.
HPLC-data: (Chiralcel OD-H column, λ = 254 nm, hexane/isopropanol = 99.3/0.7, flow rate = 0.8 mL/min): t_R = 7.8 (major), 9.6 (minor).

Preliminary Mechanistic Studies

Synthesis of [Ni(II)Cl(Py)$_3$•L1]Cl

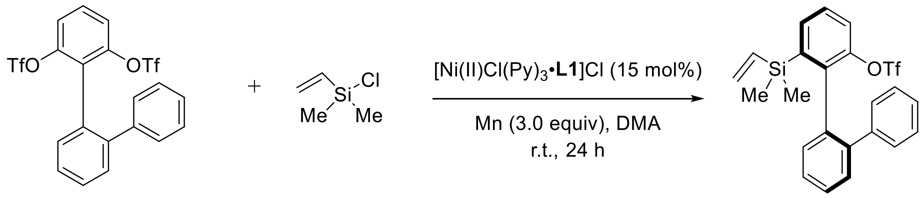


L1

[Ni(II)Cl(Py)$_3$•**L1**]Cl, 70%

To a solution of (*R*)-*N*-(2-hydroxy-1-phenylethyl) picolinamide (**L1**) (484.2 mg, 2.0 mmol, 1.0 equiv) in tetrahydrofuran (10 mL) was added Ni(Py)$_4$Cl$_2$ (0.920 g, 2.0 mmol, 1.0 equiv). After stirring at room temperature for 24 h, the reaction mixture was filtered and dried in vacuo to give [Ni(II)Cl(Py)$_3$•**L1**]Cl as a blue solid (0.853 g, 70%). The structure of [Ni(II)Cl(Py)$_3$•**L1**]Cl was determined by X-ray crystal structure analysis.

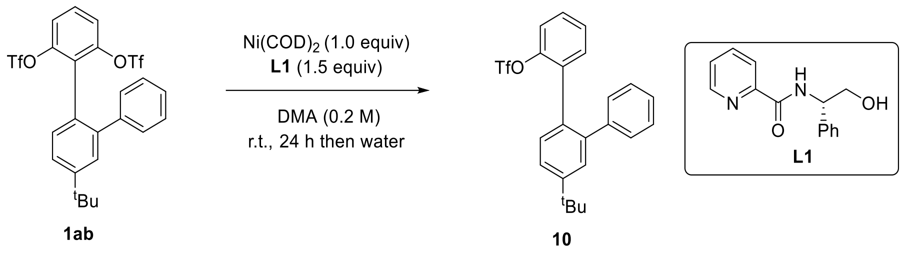
Catalytic reactivity of [Ni(II)Cl(Py)$_3$•L1]Cl



1a 2a 3aa

In a nitrogen-filled glove box, [Ni(II)Cl(Py)$_3$•**L1**]Cl (18.2 mg, 0.03 mmol. 15 mol%) and Mn (33.0 mg, 0.6 mmol, 3.0 equiv) were added to a reaction tube equipped with a magnetic stir bar. Subsequently, a solution of the bis(triflate) **1a** (105.0 mg, 0.2 mmol, 1.0 equiv) and chlorodimethyl(vinyl)silane (**2a**) (72.4 mg, 0.6 mmol, 3.0 equiv) in dry DMA (1.0 mL, 0.2 M) was added to the reaction mixture. The reaction tube was sealed and removed from the glove box. The reaction was stirred at room temperature for 24 h before it was quenched by addition of water. The aqueous phase was extracted with ethyl acetate (3 × 20 mL), and the combined organic phases were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether) to afford the product **3aa** (65.9 mg, 72% yield, 89% *ee*).

Stoichiometric reaction with $Ni(COD)_2$



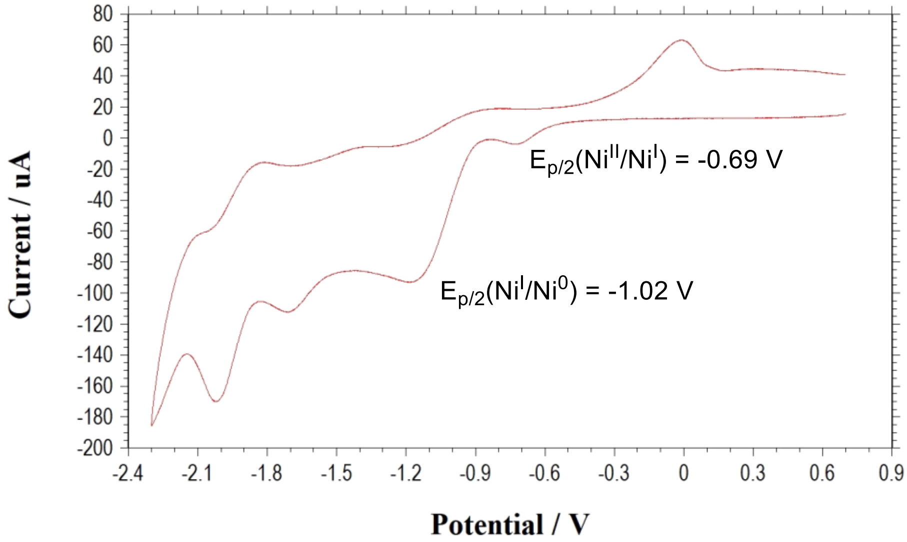
In a nitrogen-filled glove box, $Ni(COD)_2$ (28.0 mg, 0.1 mmol, 1.0 equiv) and ligand **L1** (36.4 mg, 0.15 mmol, 1.5 equiv) were added to a reaction tube equipped with a magnetic stir bar. Subsequently, a solution of **1ab** (52.6 mg, 0.1 mmol, 1.0 equiv) in dry DMA (1.0 mL, 0.2 M) was added to the reaction mixture. The reaction tube was sealed and removed from the glove box. The reaction was stirred at room temperature for 24 h and then quenched with water. The aqueous phase was extracted with ethyl acetate (3 × 20 mL), and the combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude materials were purified through column chromatography on silica gel (petroleum ether) to give *4'-(tert-butyl)-[1,1':2',1''-terphenyl]-2-yl trifluoromethanesulfonate* (**10**) (18.2 mg, 42% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.48 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 7.23 – 7.18 (m, 3H), 7.16 – 7.08 (m, 3H), 1.39 (s, 9H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*) δ = 152.1, 146.9, 141.6, 141.4, 135.5, 133.1, 131.03, 130.96, 129.6 (2C), 128.8, 128.1, 127.9 (2C), 127.5, 126.8, 124.4, 121.7, 118.4 (q, J = 320.5 Hz), 34.9, 31.5 (3C) ppm.
^{19}F NMR (376 MHz, Chloroform-d) δ = −74.53 (s, 3F) ppm.
HRMS (ESI) m/z calculated for $C_{23}H_{22}F_3O_3S^+$ $[M+H]^+$: 435.1236, found: 435.1242.

Cyclic Voltammetry Experiments

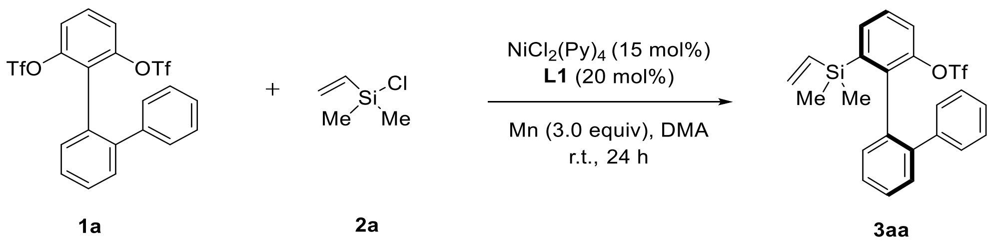
The following experiments were conducted on an electrochemical workstation CHI 760D. A glassy carbon working electrode (0.07 cm2) was employed alongside a platinum flag counter electrode and an Ag/AgCl (KCl sat.) reference electrode. The distance between the working and reference electrode was 1 cm. The first scan is shown in the following section and the main text unless otherwise specified.

1. CV of [Ni(II)Cl(Py)$_3$•L1]Cl



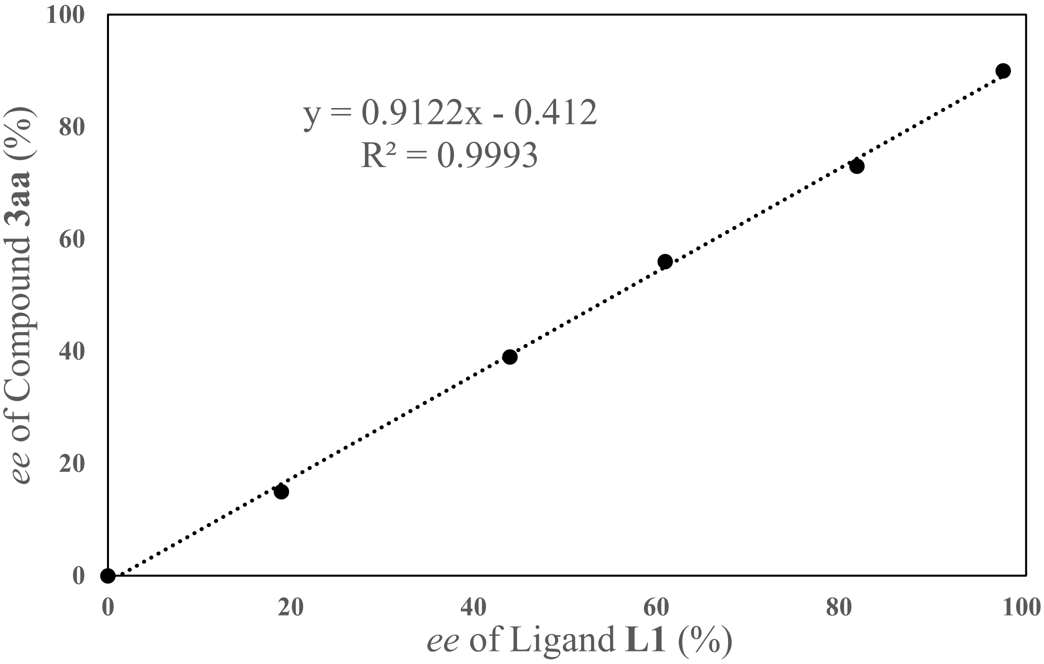
Voltammogram of 1 mM [Ni(II)Cl(Py)$_3$•**L1**]Cl in DMA with 0.1 M TBAPF$_6$ supporting electrolyte, ν = 100 mV/s.

Non-Linear Effect Study



In a nitrogen-filled glove box, $NiCl_2(Py)_4$ (13.8 mg, 0.03 mmol. 15 mol%), ligand **L1** (9.7 mg, 0.04 mmol, 20 mol%) with different enantiomeric excesses (17, 44, 61, 82, 100% *ee*) and Mn (33.0 mg, 0.6 mmol, 3.0 equiv) were added to a reaction tube equipped with a magnetic stir bar. Subsequently, a solution of the bis(triflate) **1a** (105.0 mg, 0.2 mmol, 1.0 equiv) and chlorodimethyl(vinyl)silane (**2a**) (72.4mg, 0.6 mmol, 3.0 equiv) in dry DMA (1.0 mL, 0.2 M) was added to the reaction mixture. The reaction tube was sealed and removed from the glove box. The reaction was stirred at room temperature for 24 h. After completion, the crude materials were purified through column chromatography on silica gel (petroleum ether) to give the product **3aa** and the *ee* values were determined by HPLC on a chiral stationary phase.

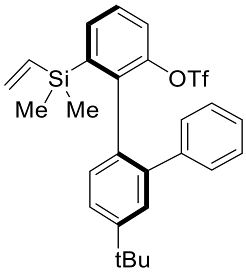
ee of **L1** (%)	0	17	44	61	82	100
ee of **3aa** (%)	0	15	39	56	73	90



Crystal Data and Structural Refinement

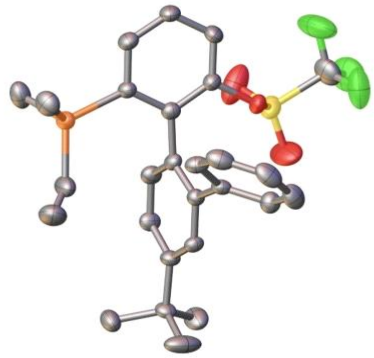
2.1 X-ray structure of the 3aba

CCDC 2452324 contains the supplementary crystallographic data for the compound **3aba**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.



3aba

≡



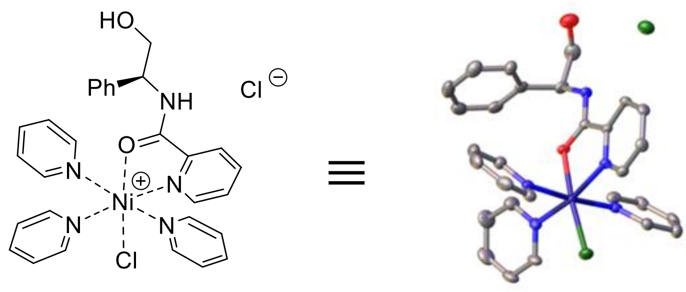
Identification code	250121cz	
Empirical formula	$C_{54} H_{58} F_6 O_6 S_2 Si_2$	
Formula weight	1037.30	
Temperature	170.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.7587(16) Å	a= 90°.
b = 14.161(3) Å	b= 102.373(9)°.	
c = 9.8462(15) Å	g = 90°.	
Volume	1329.0(4) $Å^3$	
Z	1	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	1.254 mm^{-1}	
F(000)	544	
Crystal size	0.17 x 0.17 x 0.05 mm^3	
Theta range for data collection	3.999 to 55.089°.	
Index ranges	$-11\leq h\leq 10$, $-15\leq k\leq 17$, $-11\leq l\leq 11$	
Reflections collected	12173	

Independent reflections	4670 [R(int) = 0.0774]
Completeness to theta = 53.594°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.1796
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4670 / 1 / 321
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1538
R indices (all data)	R1 = 0.0616, wR2 = 0.1598
Absolute structure parameter	0.031(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.606 and -0.465 e.Å^{-3}
Flack parameter	0.031(18)

2.1 Synthesis and X-ray structure of the complex

To a solution of (*R*)-*N*-(2-hydroxy-1-phenylethyl) picolinamide (L1) (484.2 mg, 2.0 mmol) in tetrahydrofuran (10 mL) was added $Ni(Py)_4Cl_2$ (0.920 g, 2.0 mmol). The mixture was stirred at 25 °C for 24 h. The reaction mixture was filtered and dried in vacuo to give the blue solid (0.853 g, 70%).

CCDC 2452325 contains the supplementary crystallographic data for [Ni(II)Cl(Py)$_3$•**L1**]Cl. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.



[Ni(II)Cl(Py)$_3$•**L1**]Cl

Identification code	240912cz
Empirical formula	$C_{29} H_{29} Cl_2 N_5 Ni O_2$
Formula weight	609.18

Temperature	170.00 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.06990(10) Å	a= 90°.
	b = 17.0862(3) Å	b= 90°.
	c = 19.4067(3) Å	g = 90°.
Volume	3007.46(8) $Å^3$	
Z	4	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	4.785 mm^{-1}	
F(000)	1264	
Crystal size	0.17 x 0.17 x 0.05 mm^3	
Theta range for data collection	2.998 to 54.913°.	
Index ranges	-11<=h<=8, -20<=k<=20, -23<=l<=18	
Reflections collected	26975	
Independent reflections	5561 [R(int) = 0.0592]	
Completeness to theta = 53.594°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5172	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5561 / 0 / 358	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.1053	
R indices (all data)	R1 = 0.0528, wR2 = 0.1111	
Absolute structure parameter	0.037(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.795 and -0.518 e.$Å^{-3}$	
Flack parameter	0.037(7)	

References

[1] Kamikawa, T.; Hayashi, T. Enantioposition-Selective Arylation of Biaryl Ditriflates by Palladium-Catalyzed Asymmetric Grignard Cross-Coupling. *Tetrahedron* **1999**, *55*, 3455−3466.

[2] Ma, W.; Liu, L.-C.; An, K.; He, T.; He, W. Rhodium-Catalyzed Synthesis of Chiral Monohydrosilanes by Intramolecular C−H Functionalization of Dihydrosilanes. *Angew. Chem., Int. Ed*. **2021**, *60*, 4245−4251.

[3] Bisht, N.; Singh, P.; Babu, S. A. Pd(II)-Catalyzed, Picolinamide-Aided γ-(sp2)-C–H Functionalization of Racemic and Enantiopure α-Methylbenzylamine and Phenylglycinol Scaffolds. *Synthesis* **2022**, *54,* 4059– 4094.

[4] Li, Z.; Shi, H.; Chen, X.; Peng, L.; Li, Y.; Yin, G. Nickel-Catalyzed Regio- and Enantioselective Borylative Coupling of Terminal Alkenes with Alkyl Halides Enabled by an Anionic Bisoxazoline Ligand. *J. Am. Chem. Soc*. **2023**, *145*, 13603–13614.

[5] Ganesh, M.; Seidel, D. Catalytic Enantioselective Additions of Indoles to Nitroalkenes. *J. Am. Chem. Soc*. **2008**, *130*, 16464–16465.

[6] Kim, R. S.; Kgoadi, L. O.; Hayes, J. C.; Rainboth, D. P.; Mudd, C. M.; Yap, G. P. A.; Watson, D. A. Nickel-Catalyzed Atroposelective Cross-Electrophile Coupling of Aryl Halides: A General and Practical Route to Diverse MOP-Type Ligands. *J. Am. Chem. Soc.* **2024**, *146*, 17606–17612.

[7] Liu, Z.-J.; Lu, X.; Wang, G.; Li, L.; Jiang, W.-T.; Wang, Y.-D.; Xiao, B.; Fu, Y. Directing Group in Decarboxylative Cross-Coupling: Copper-Catalyzed Site-Selective C–N Bond Formation from Nonactivated Aliphatic Carboxylic Acids. *J. Am. Chem. Soc.* **2016**, *138*, 9714–9719.

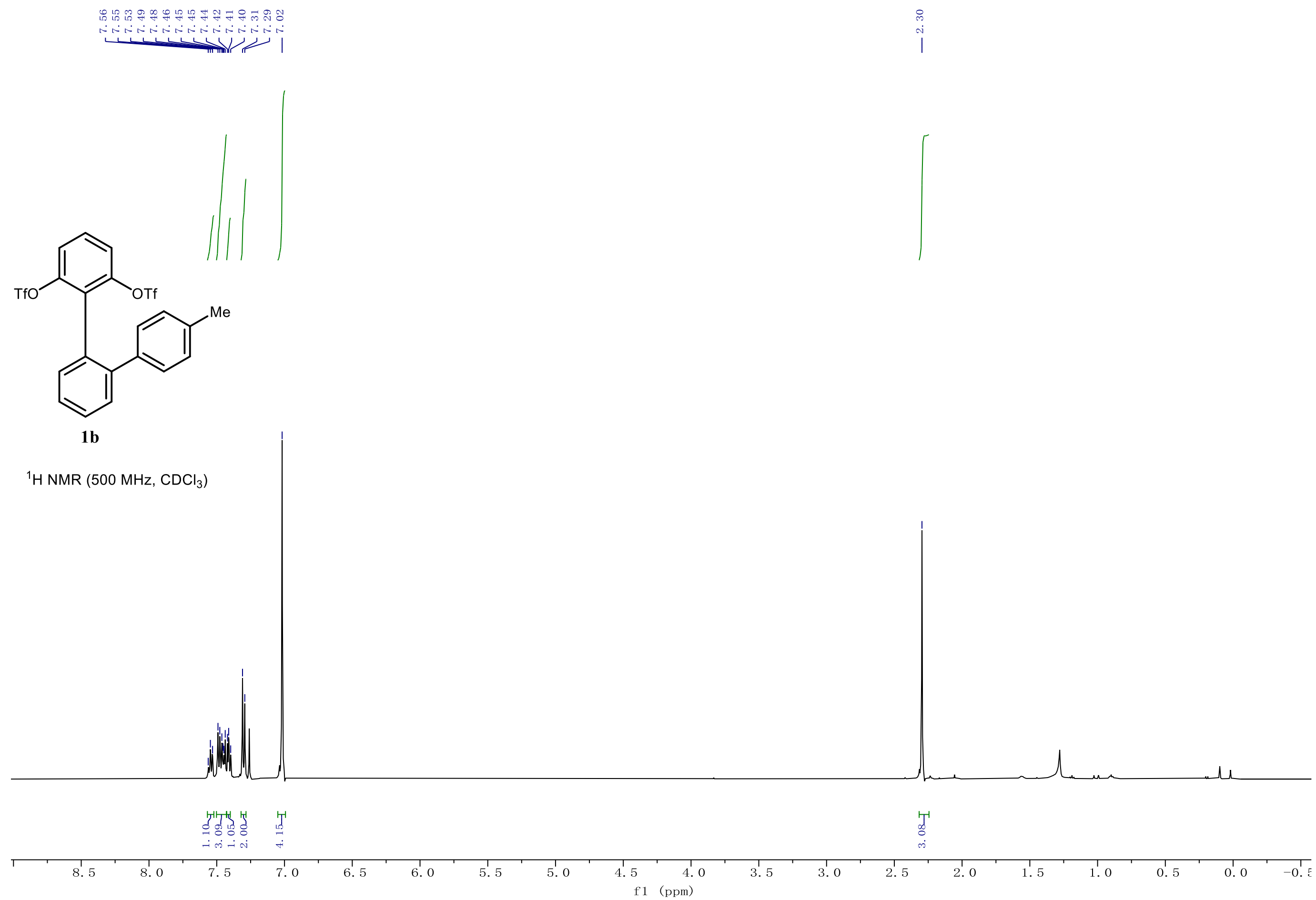
[8] Weinstein, A. B.; Stahl, S. S. Reconciling the Stereochemical Course of Nucleopalladation with the Development of Enantioselective Wackertype Cyclizations. *Angew. Chem., Int. Ed.* **2012**, *51*, 11505–11509.

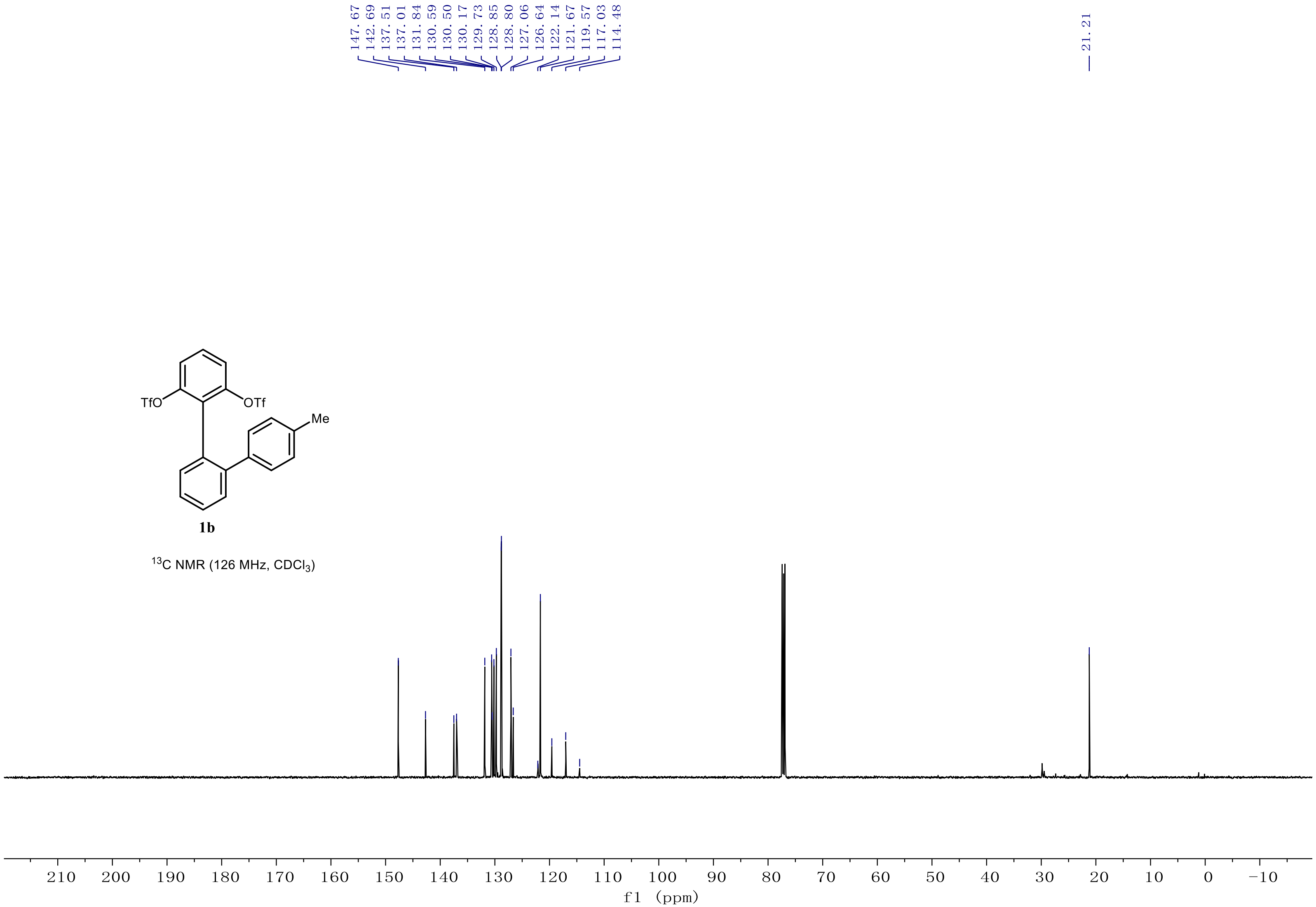
[9] Du, W.; Gu, Q.; Li, Y.; Lin, Z.; Yang, D. Enantioselective Palladium-Catalyzed Oxidative Cascade Cyclization of Aliphatic Alkenyl Amides. *Org. Lett*. **2017**, *19*, 316–319.

[10] Lux, M. C.; Boby, M. L.; Brooks, J. L.; Tan, D. S. Synthesis of Bicyclic Ethers by a Palladium-Catalyzed Oxidative Cyclization-Redox Relay-π-Allyl-Pd Cyclization Cascade Reaction. *Chem. Commun*. **2019**, *55*, 7013–7016.

[11] Abu-Elfotoh, A.-M.; Nguyen, D. P. T.; Chanthamath, S.; Phomkeona, K.; Shibatomi, K.; Iwasa, S. Water-Soluble Chiral Ruthenium(II) Phenyloxazoline Complex: Reusable and Highly Enantioselective Catalyst for Intramolecular Cyclopropanation Reactions. *Adv. Synth. Catal.* **2012**, *354*, 3435– 3439.

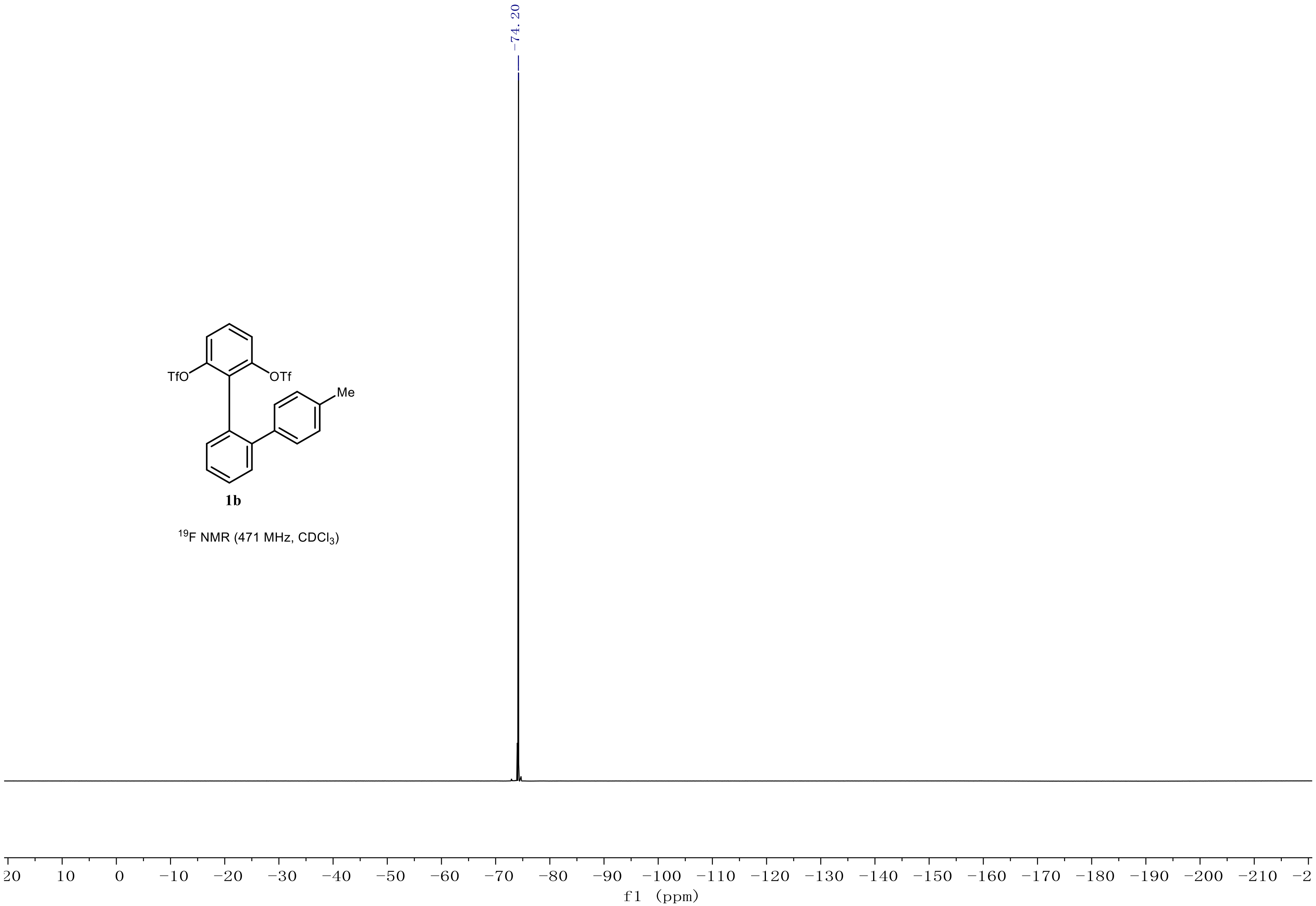
^{1}H-, ^{13}C-, ^{19}F and ^{31}P-NMR Spectra





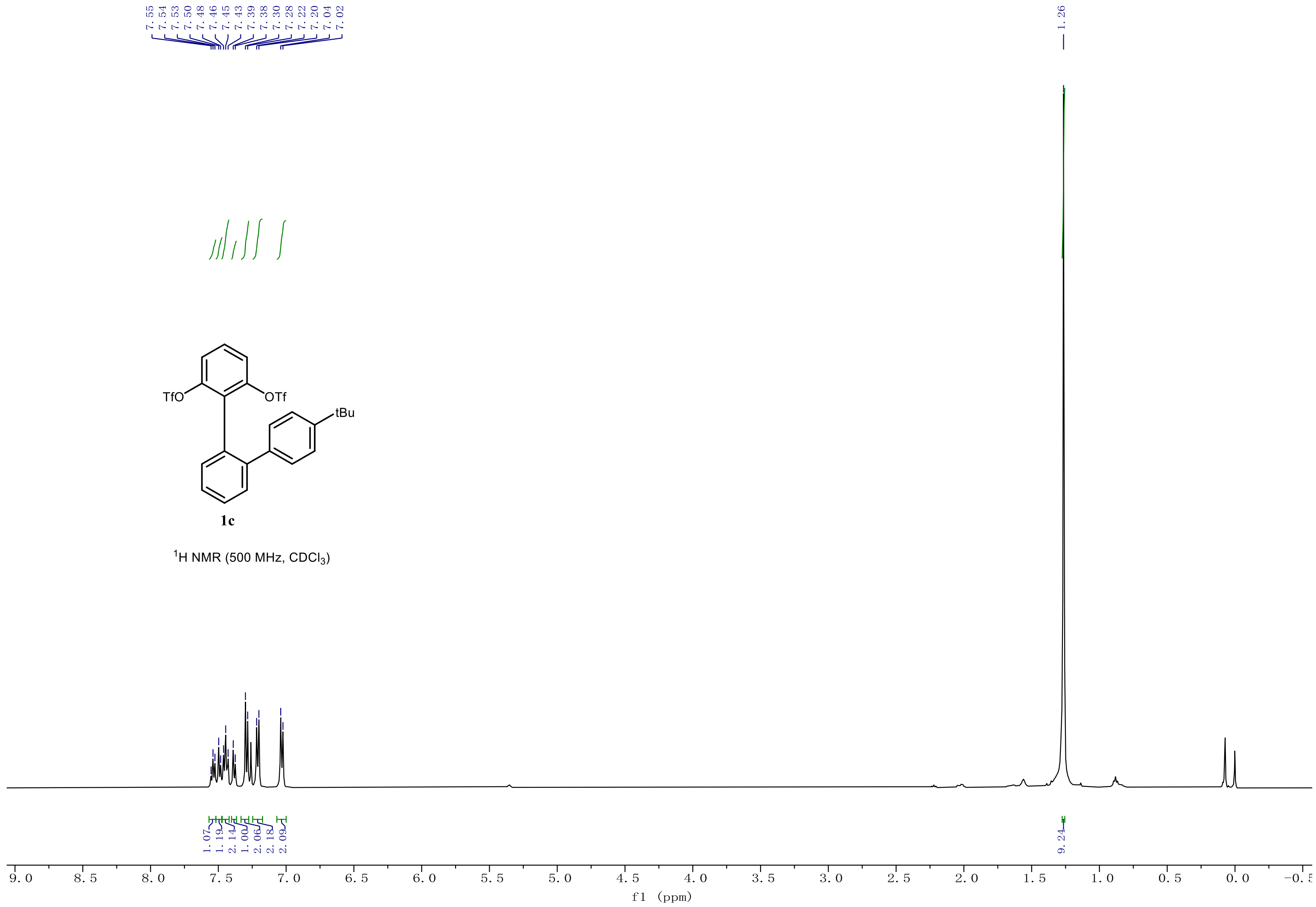
1b

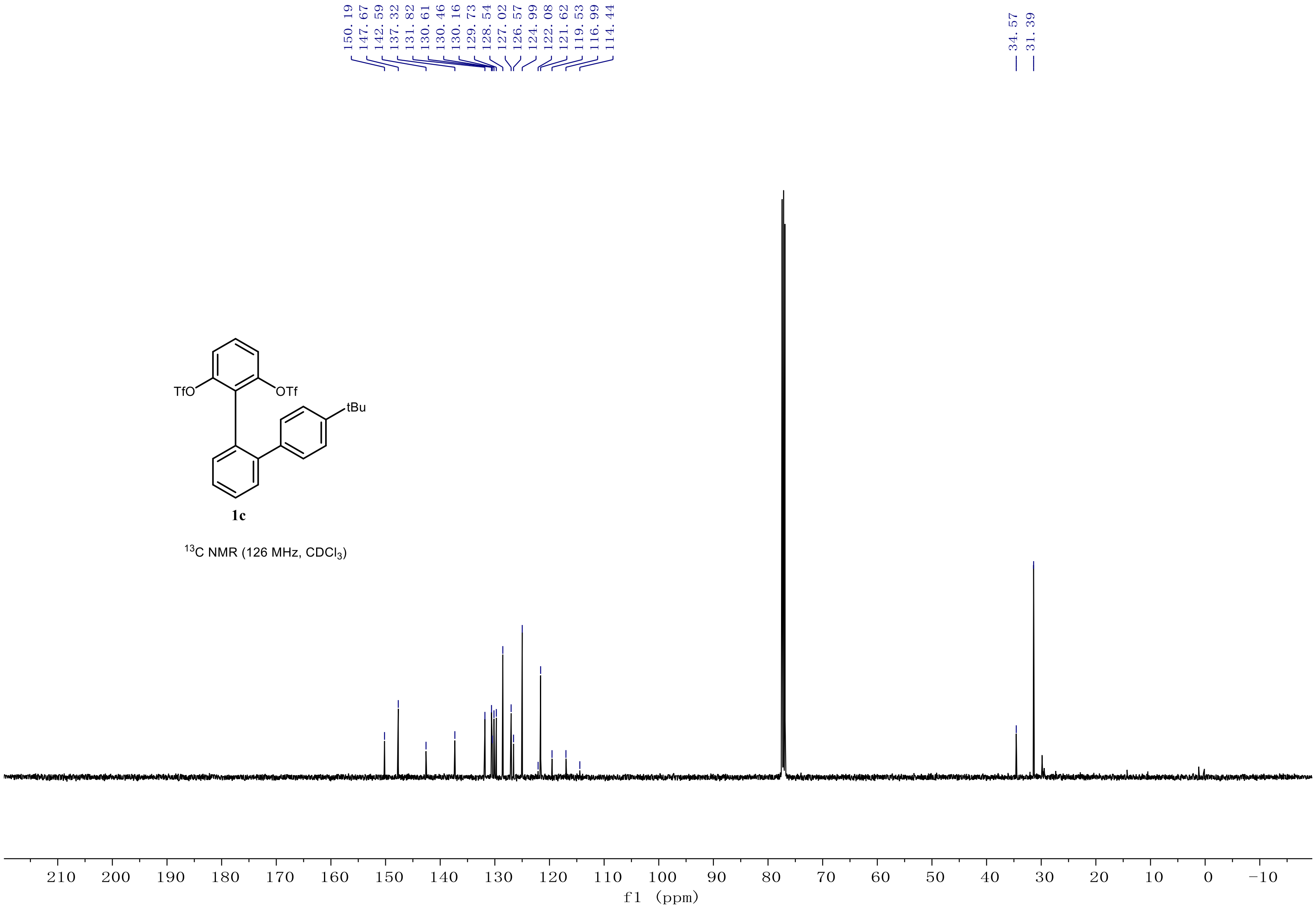
^{13}C NMR (126 MHz, $CDCl_3$)



1b

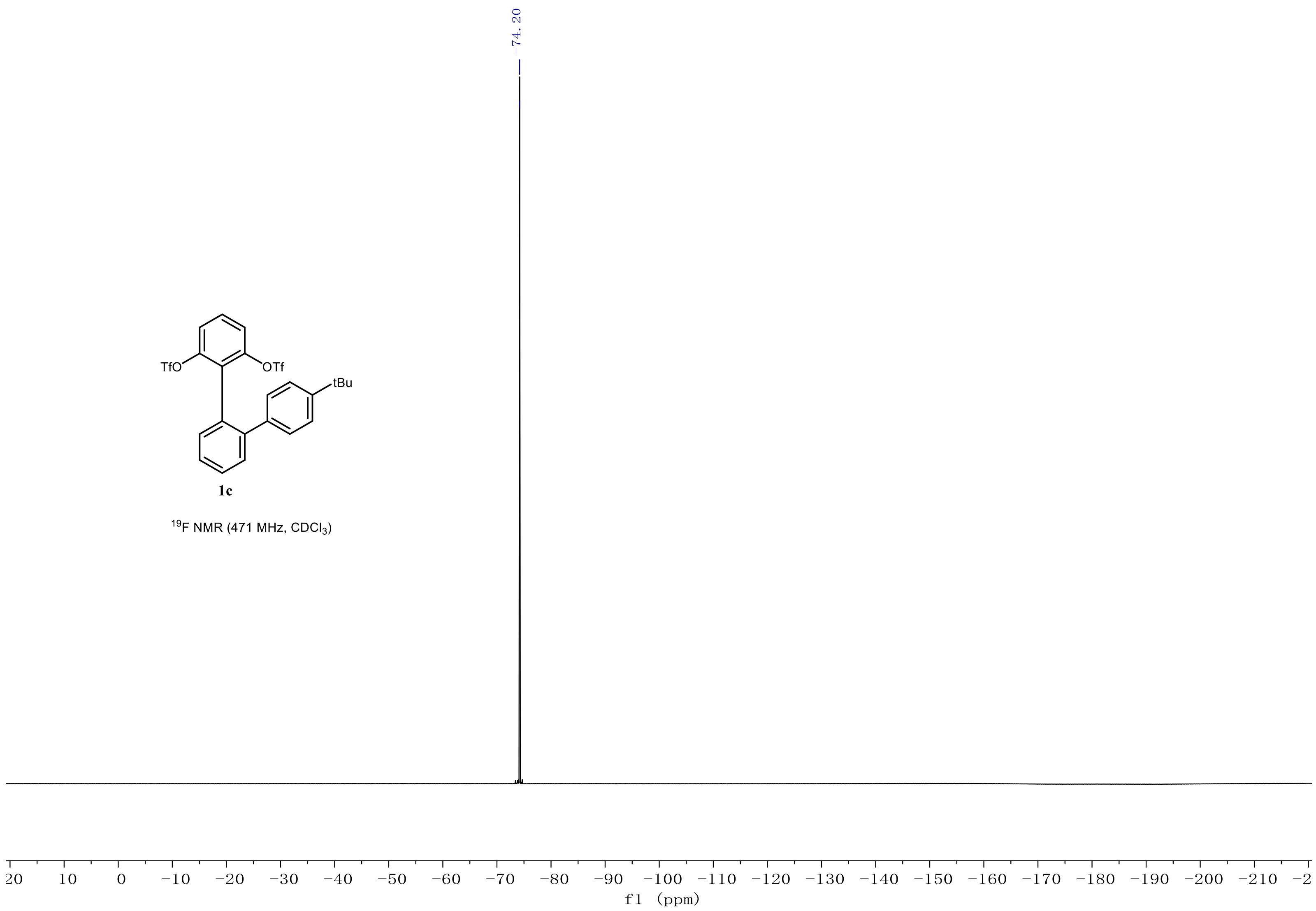
^{19}F NMR (471 MHz, $CDCl_3$)

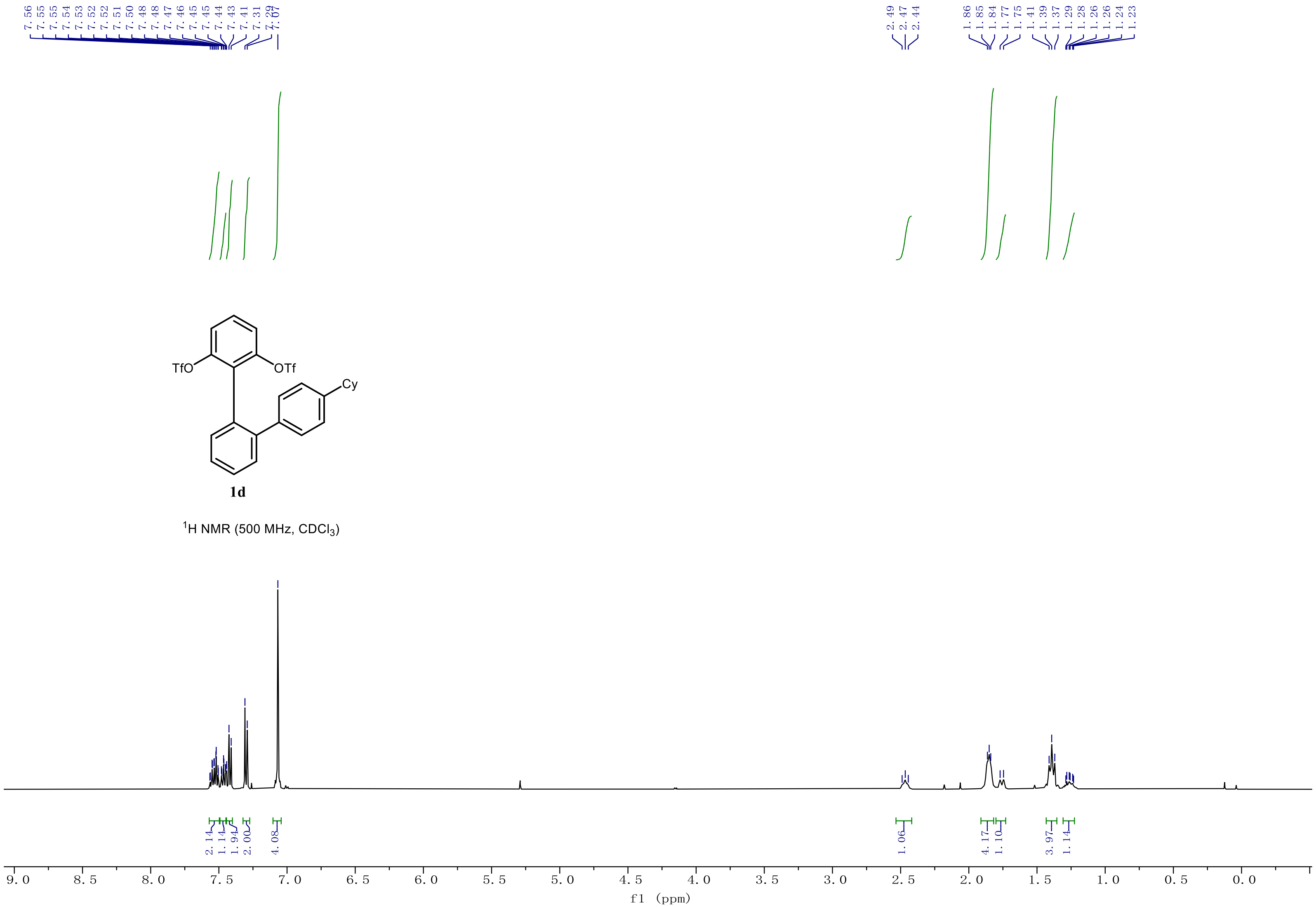

7.55 7.54 7.53 7.50 7.48 7.46 7.45 7.43 7.39 7.38 7.30 7.28 7.22 7.20 7.04 7.02
1.26
TfO
OTf
tBu
1c
^{1}H NMR (500 MHz, CDCl$_3$)
1.07 1.19 2.14 1.00 2.06 2.18 2.09
9.24
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)



1c

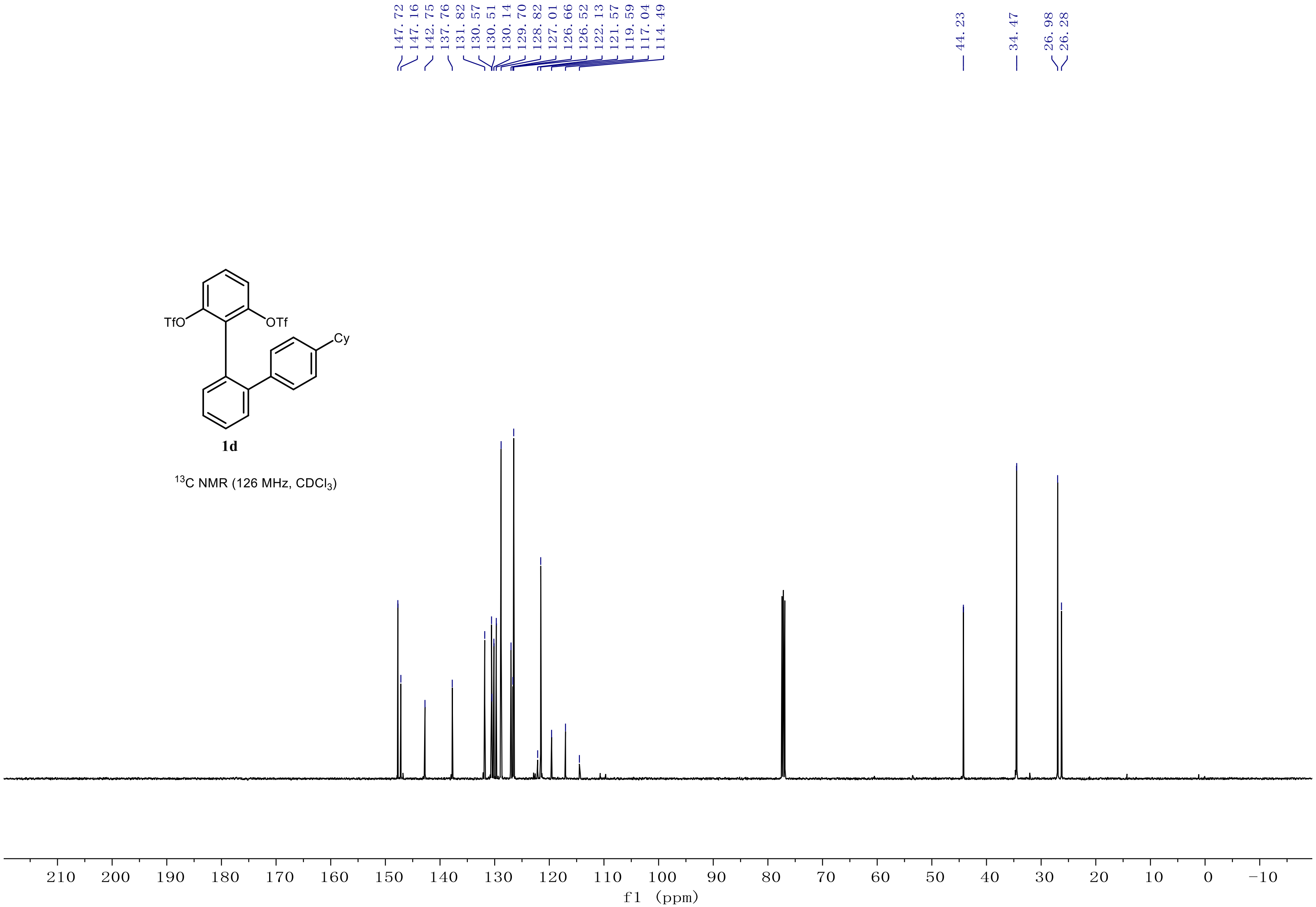
^{13}C NMR (126 MHz, $CDCl_3$)


−74.20
TfO
OTf
tBu
1c
19F NMR (471 MHz, CDCl3)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



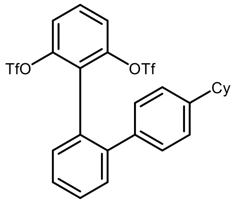
1d

^{1}H NMR (500 MHz, $CDCl_3$)



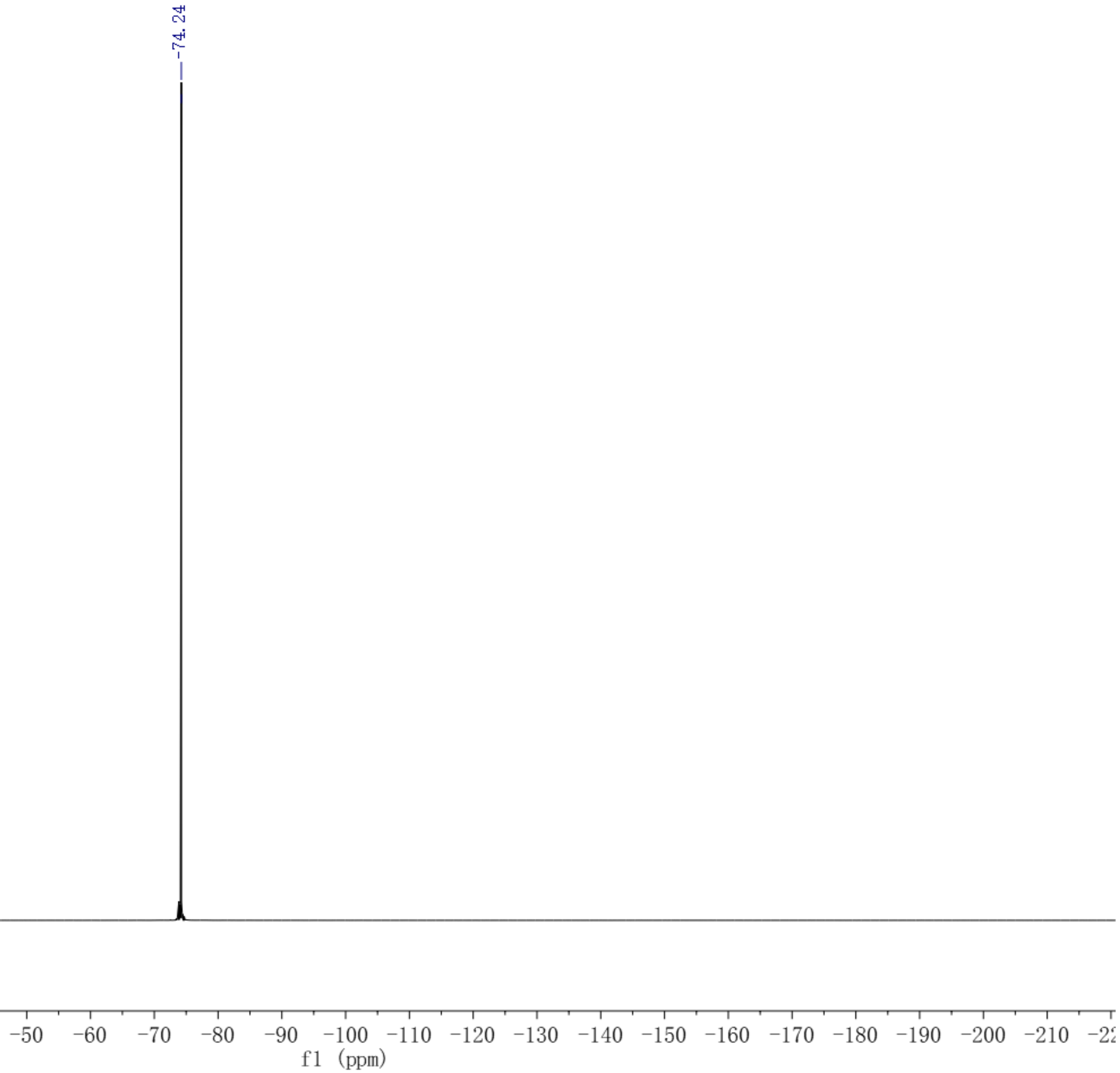
1d

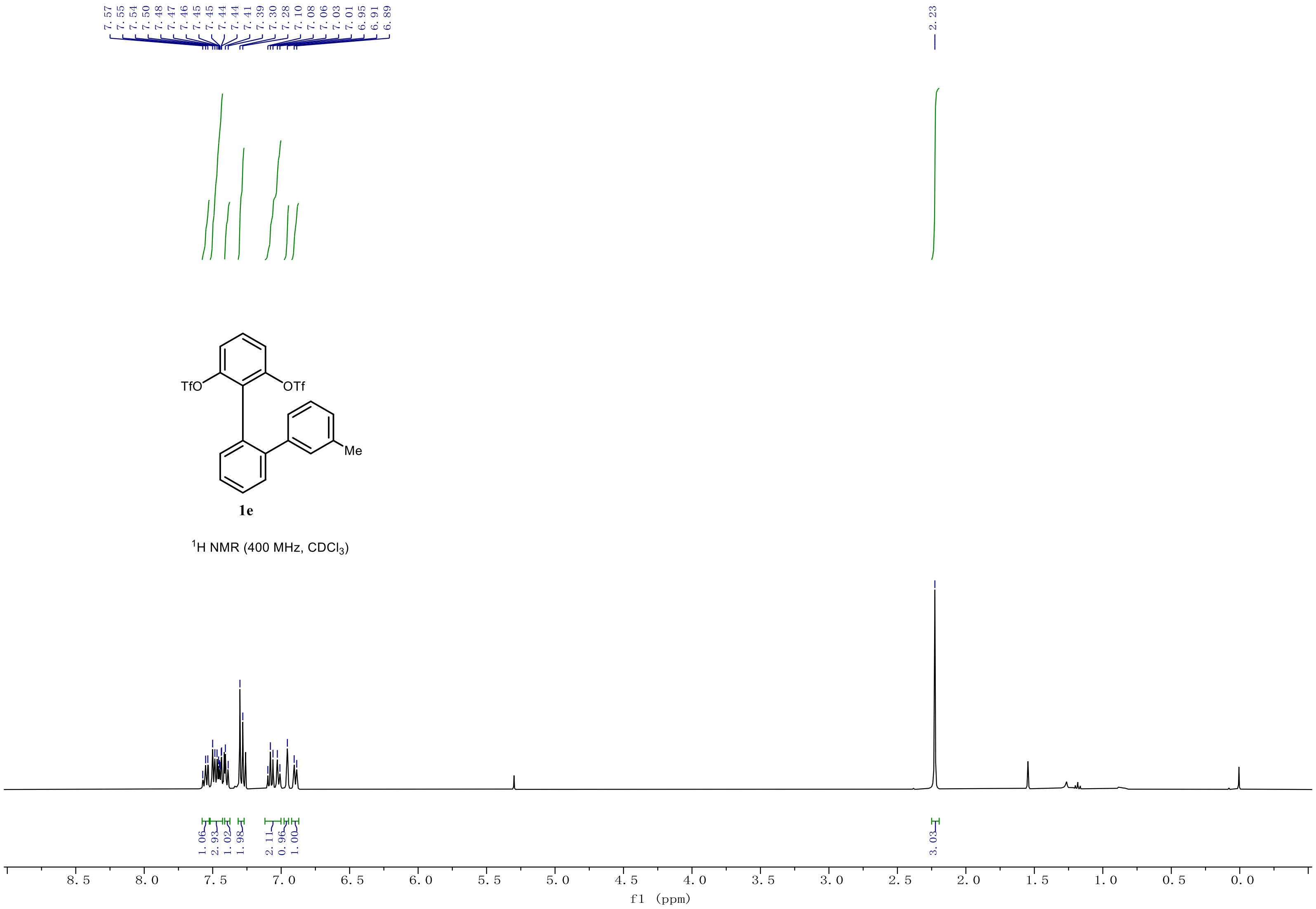
^{13}C NMR (126 MHz, $CDCl_3$)



1d

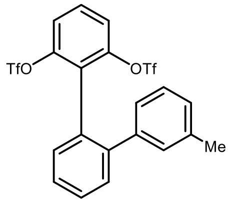
^{19}F NMR (471 MHz, $CDCl_3$)





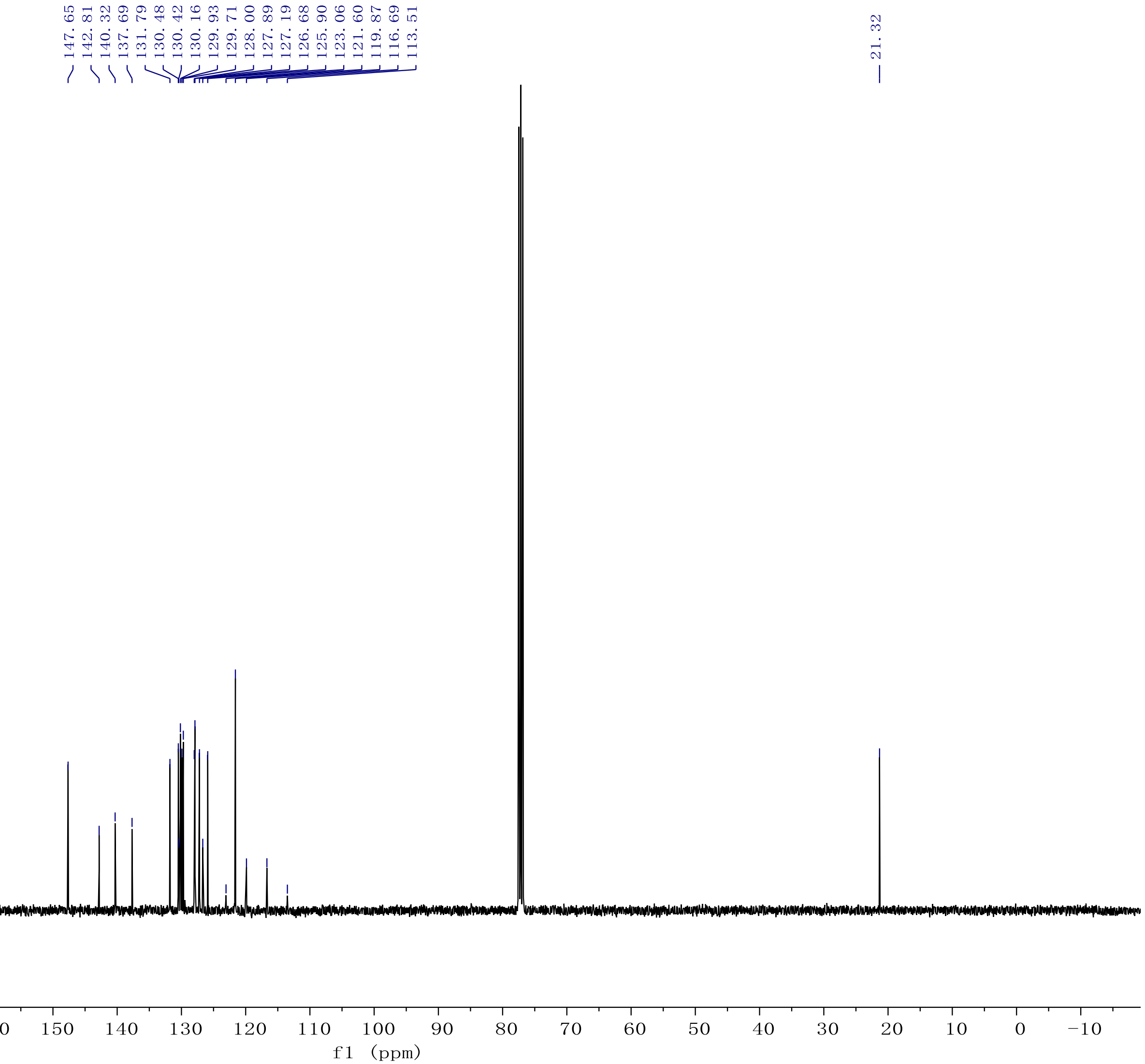
1e

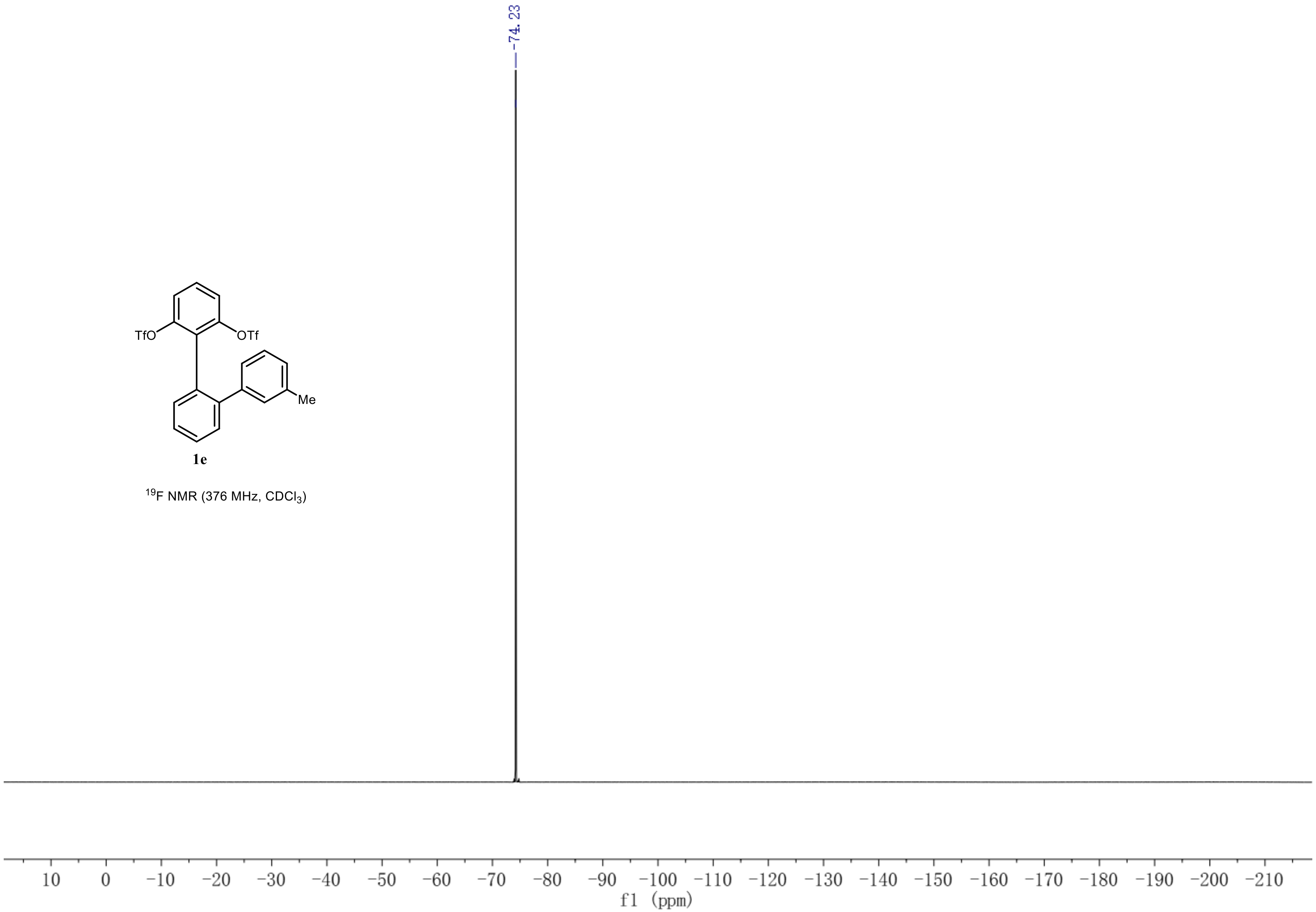
^{1}H NMR (400 MHz, $CDCl_3$)



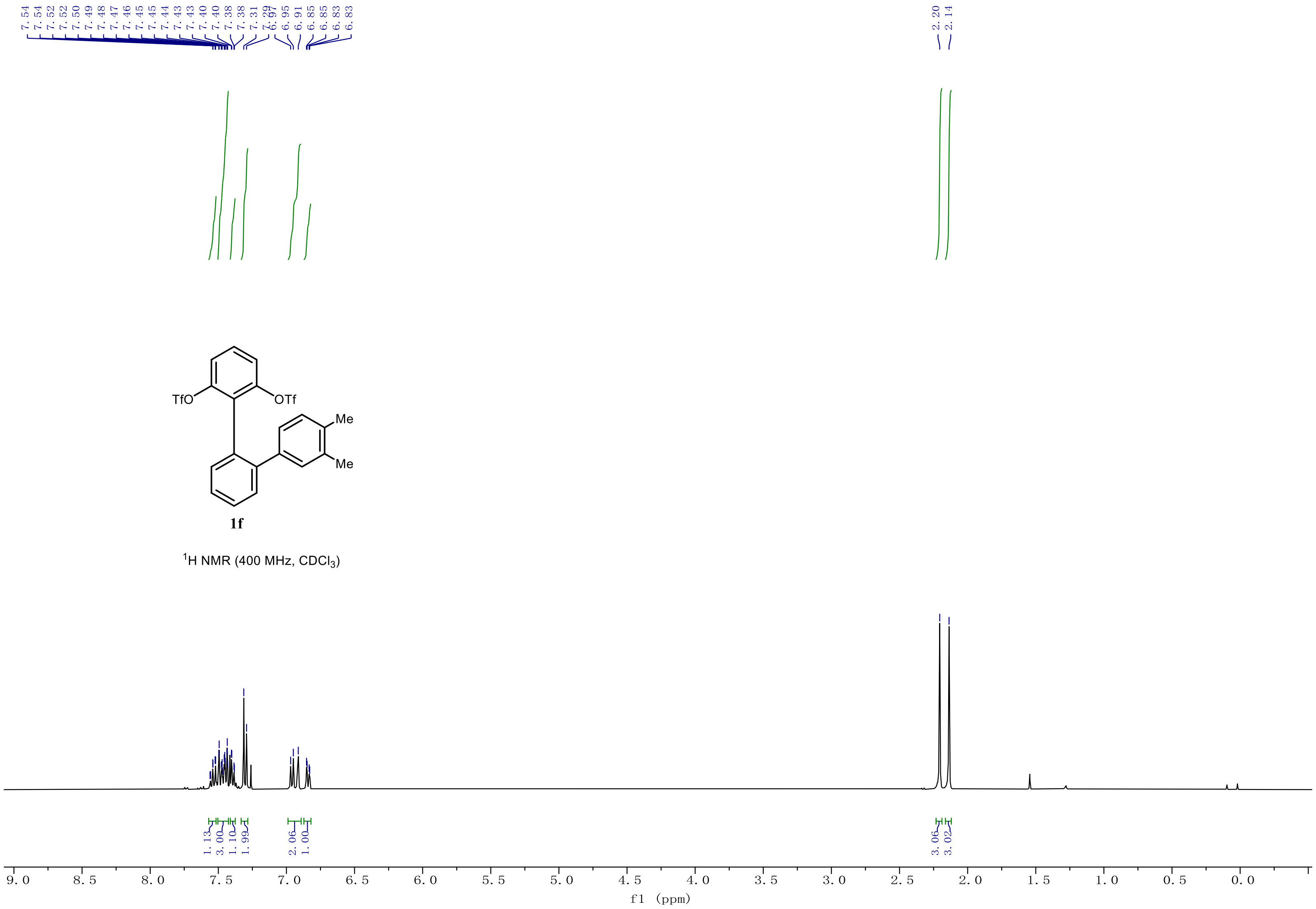
1e

^{13}C NMR (101 MHz, $CDCl_3$)



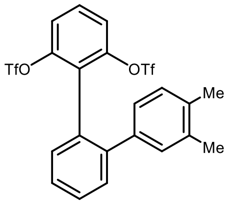


-74.23
TfO
OTf
Me
1e
^{19}F NMR (376 MHz, $CDCl_3$)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)



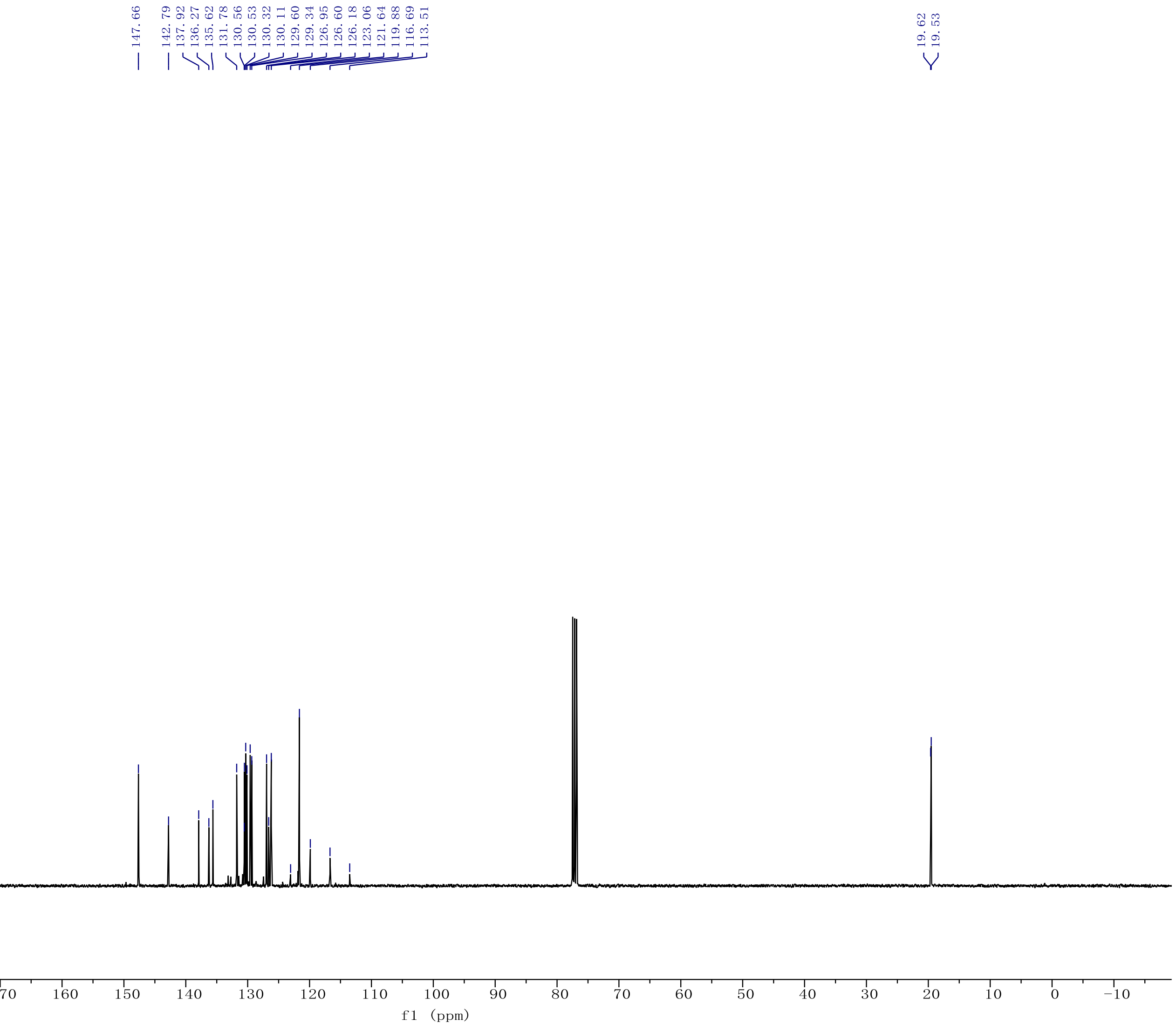
1f

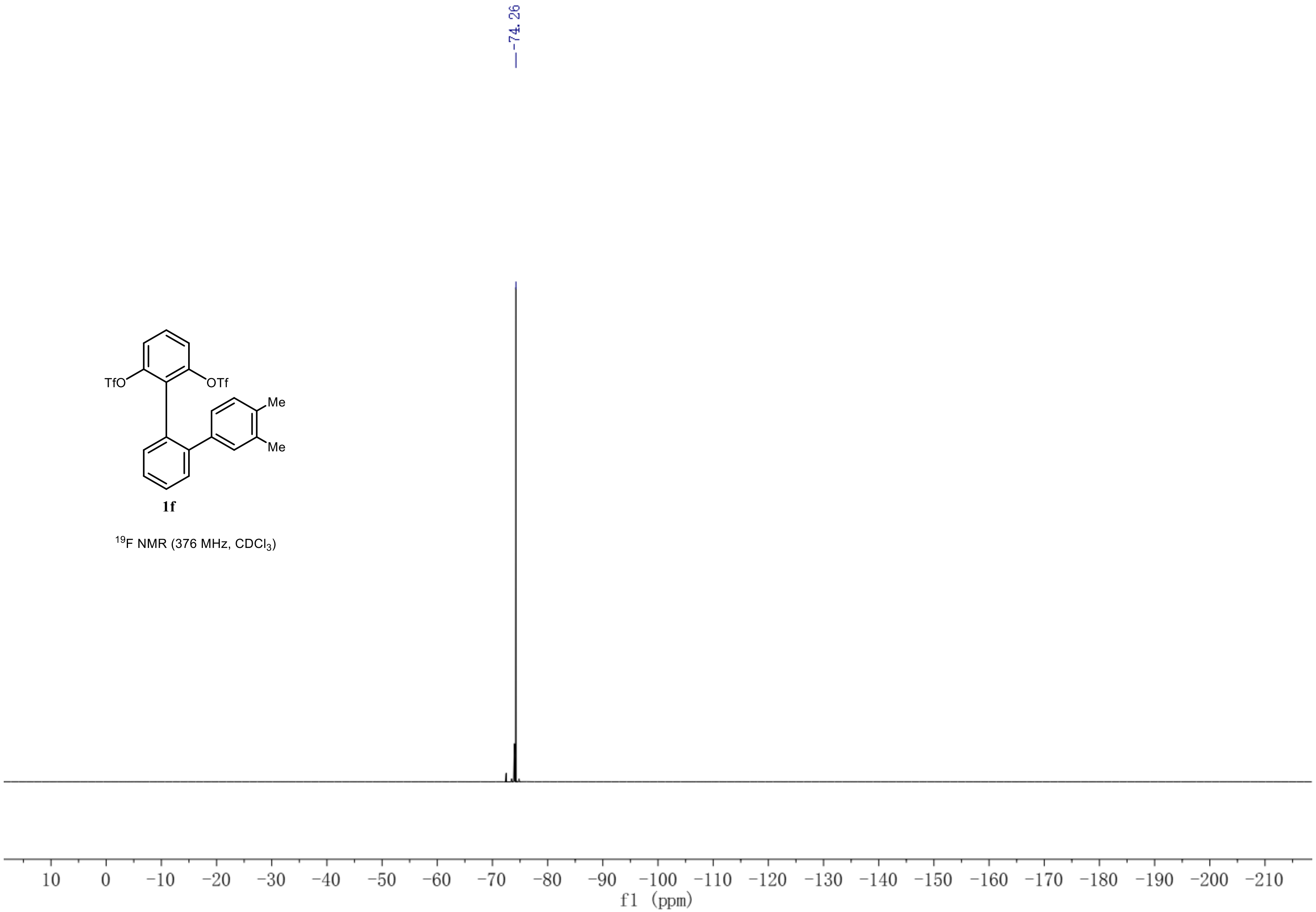
^1H NMR (400 MHz, $CDCl_3$)



1f

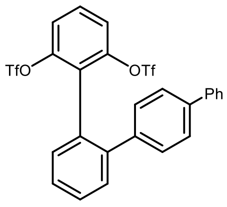
^{13}C NMR (101 MHz, $CDCl_3$)





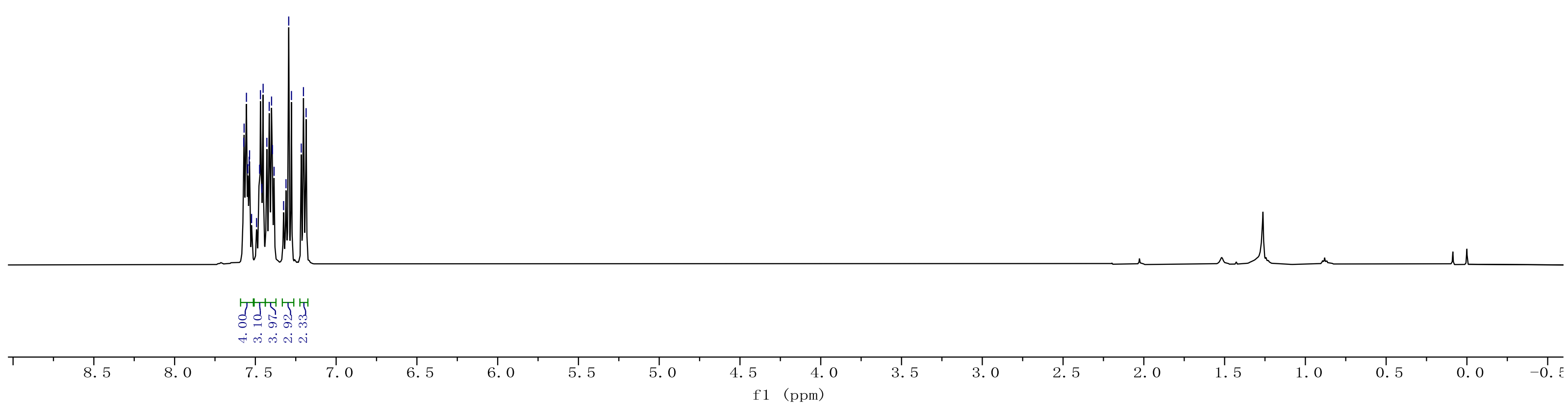
1f

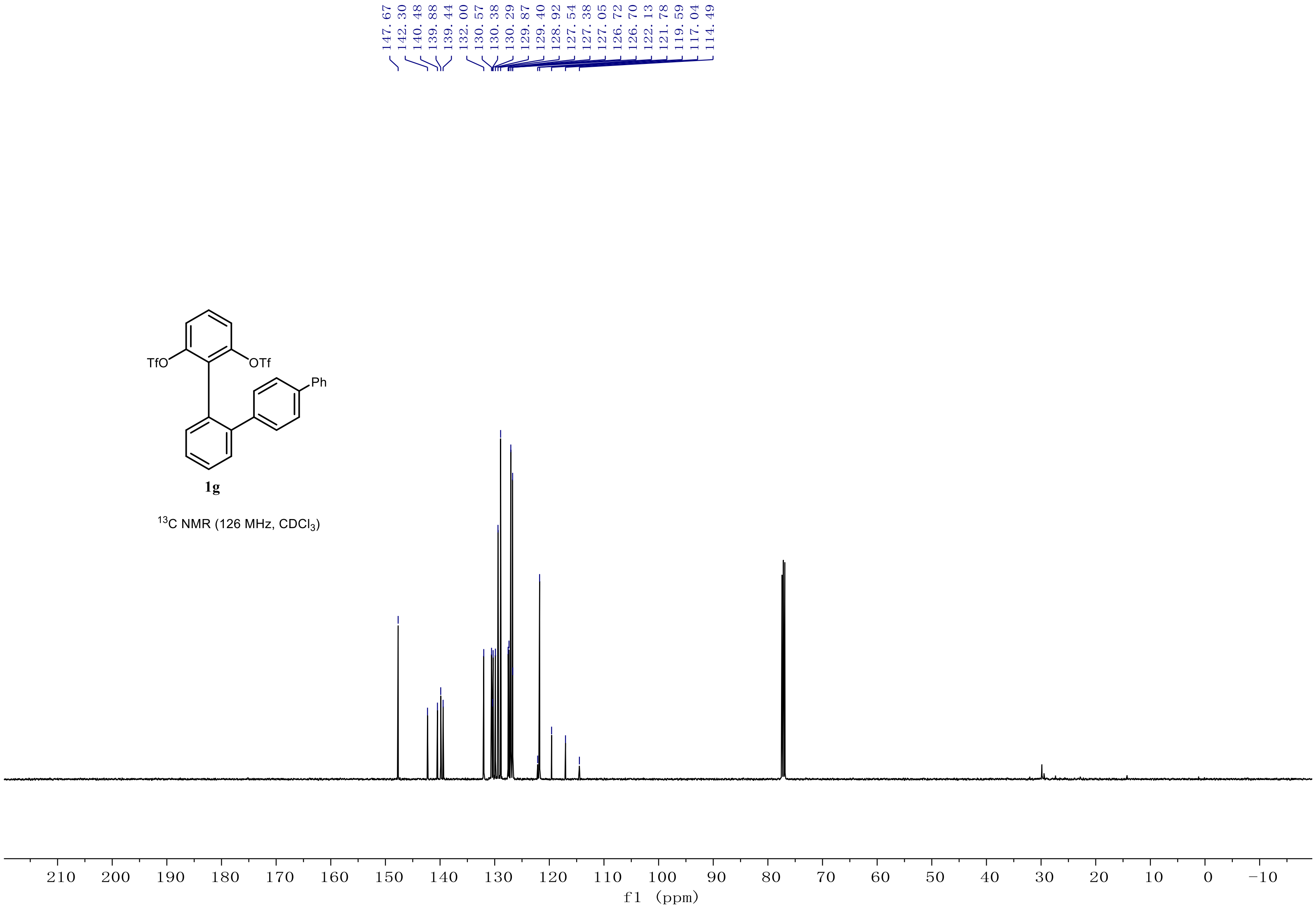
^{19}F NMR (376 MHz, $CDCl_3$)

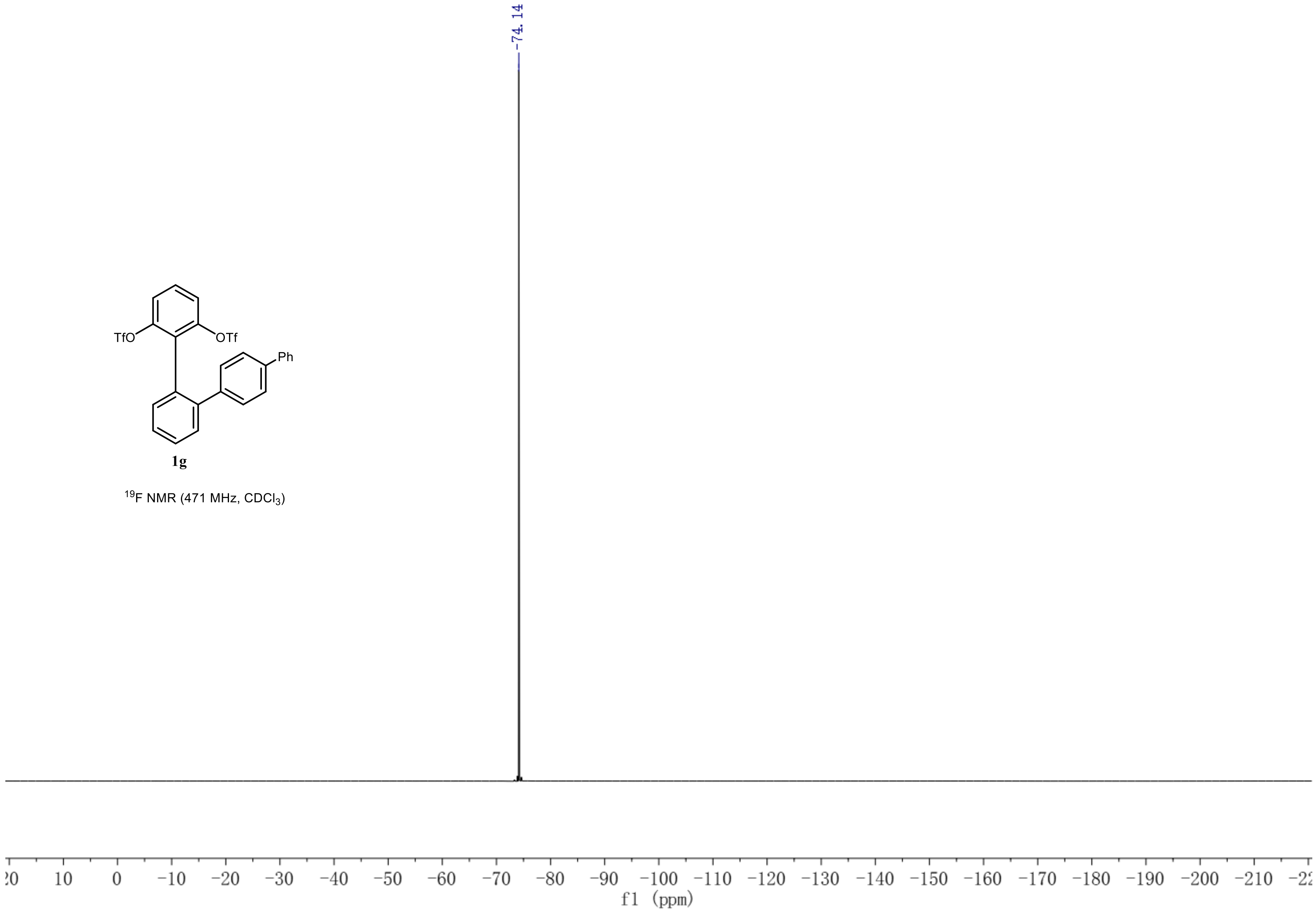


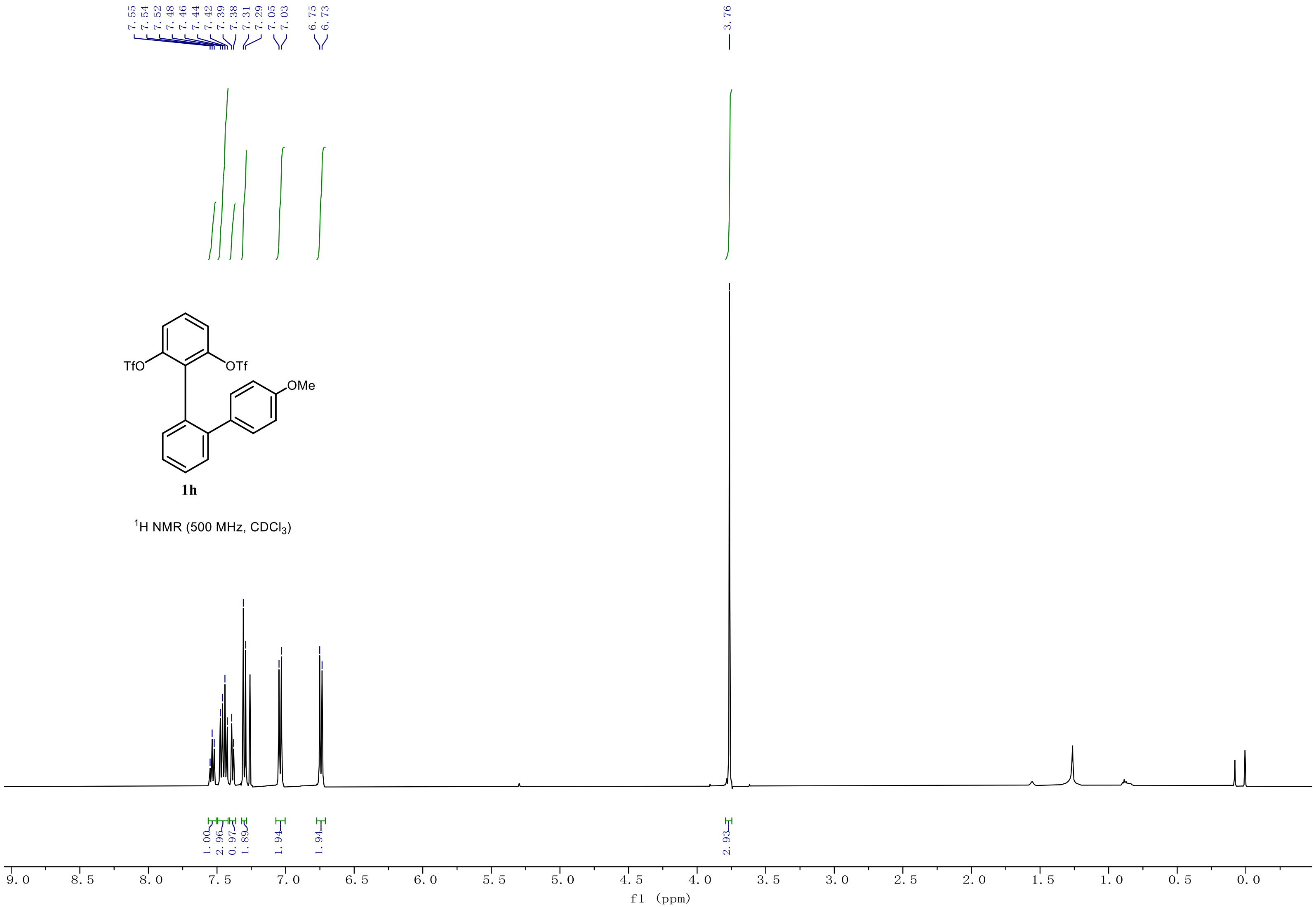
1g

^{1}H NMR (500 MHz, $CDCl_3$)

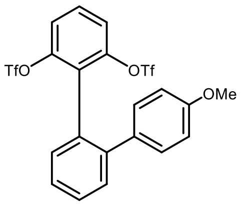



147.67
142.30
140.48
139.88
139.44
132.00
130.57
130.38
130.29
129.87
129.40
128.92
127.54
127.38
127.05
126.72
126.70
122.13
121.78
119.59
117.04
114.49
TfO
OTf
Ph
1g
^{13}C NMR (126 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-74.14
TfO
OTf
Ph
1g
^{19}F NMR (471 MHz, $CDCl_3$)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

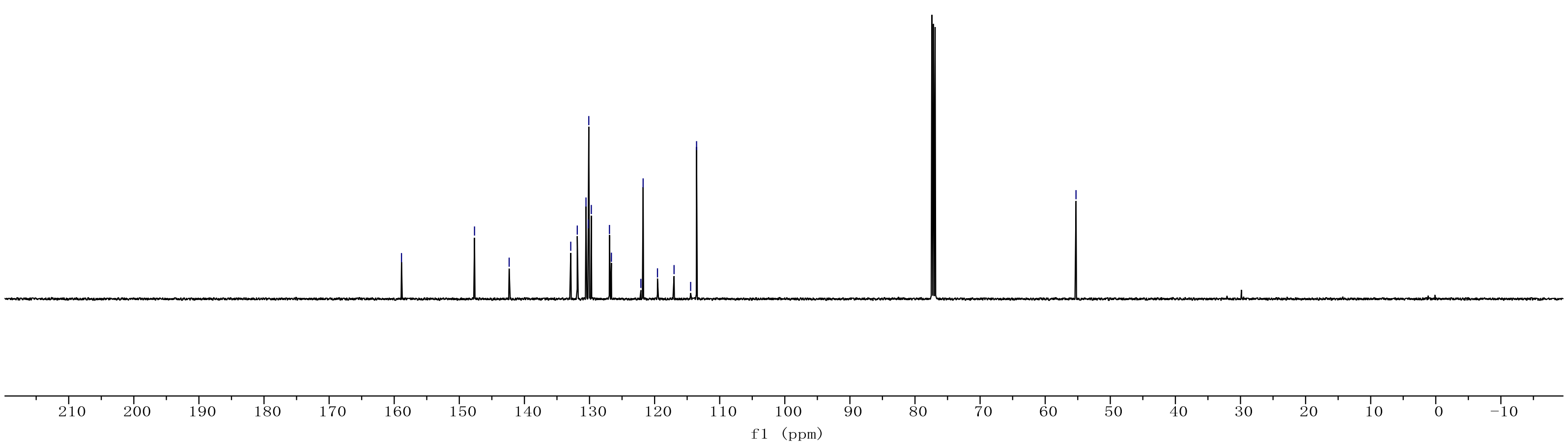


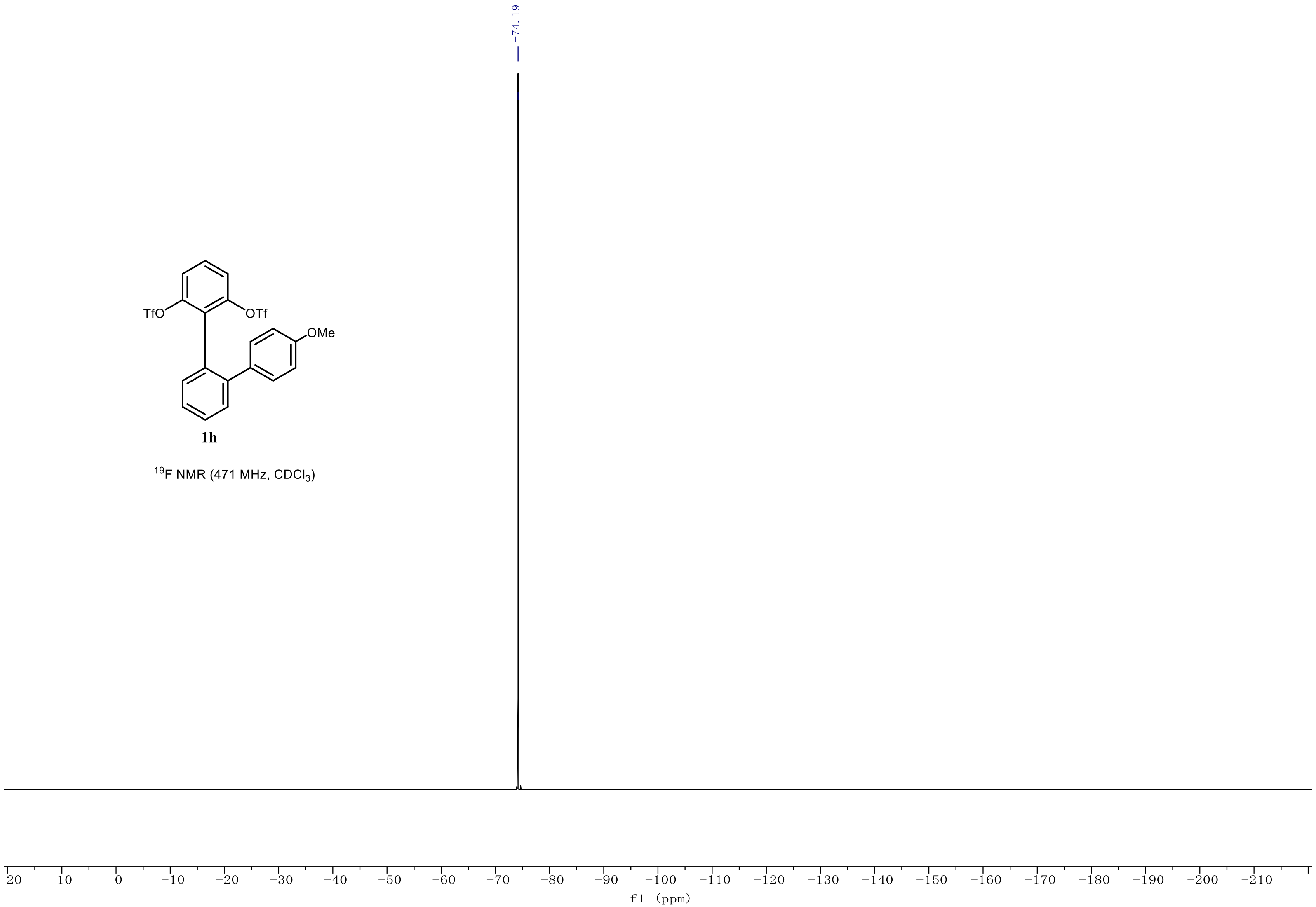
7.55
7.54
7.52
7.48
7.46
7.44
7.42
7.39
7.38
7.31
7.29
7.05
7.03
6.75
6.73
3.76
TfO
OTf
OMe
1h
^{1}H NMR (500 MHz, $CDCl_3$)
1.00
2.96
0.97
1.89
1.94
1.94
2.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



1h

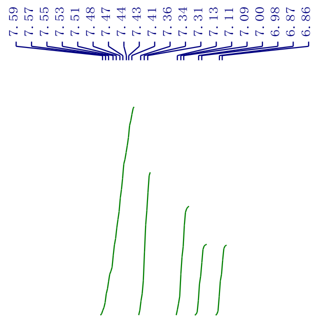
^{13}C NMR (126 MHz, CDCl$_3$)

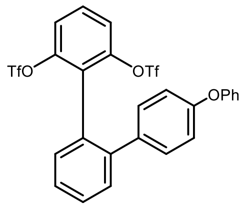




1h

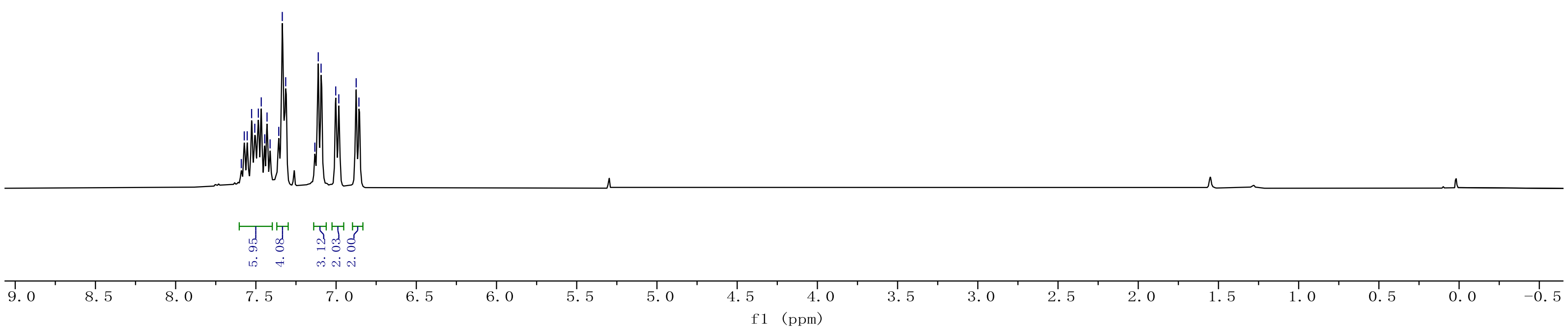
^{19}F NMR (471 MHz, $CDCl_3$)

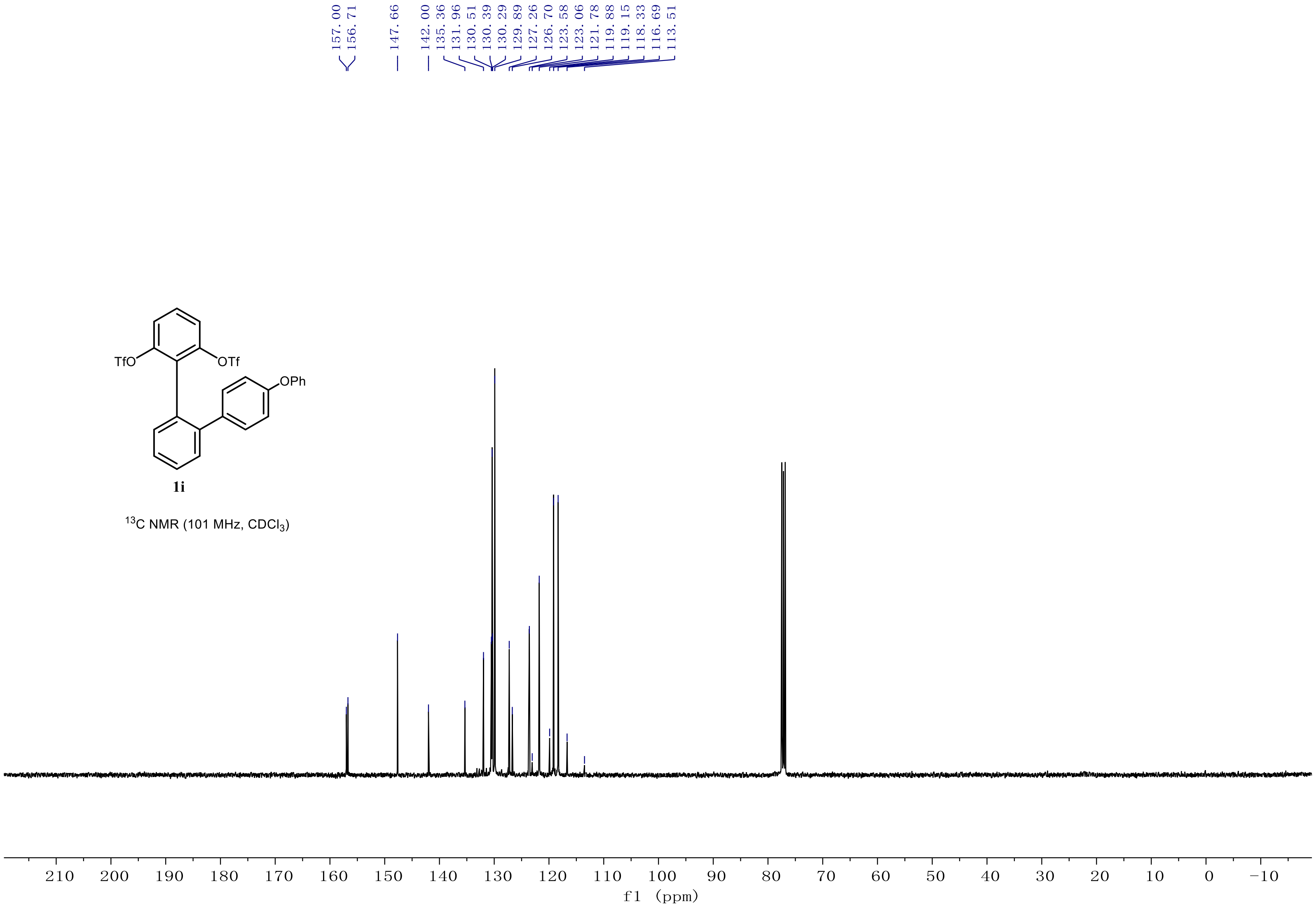




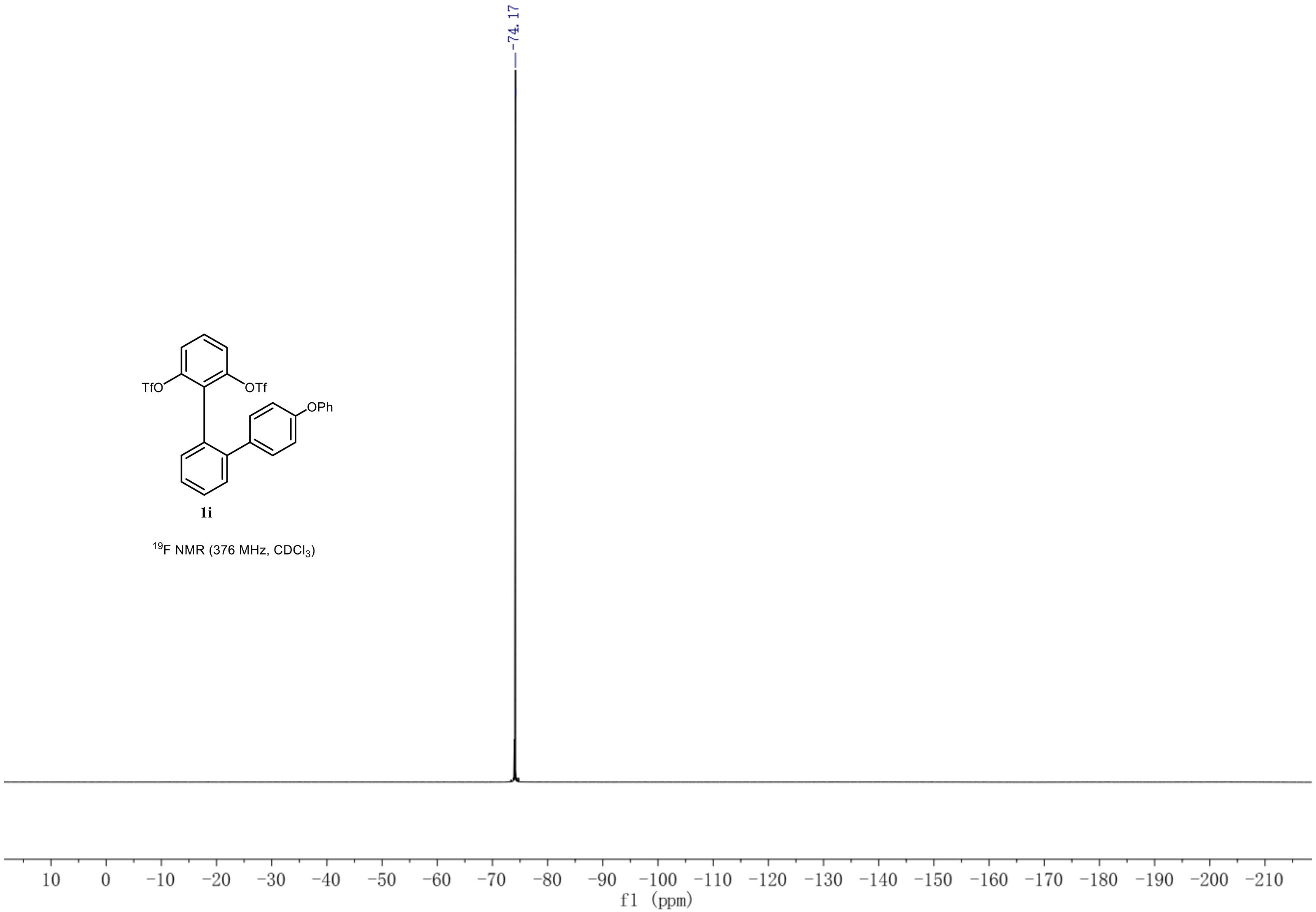
1i

^{1}H NMR (400 MHz, $CDCl_3$)



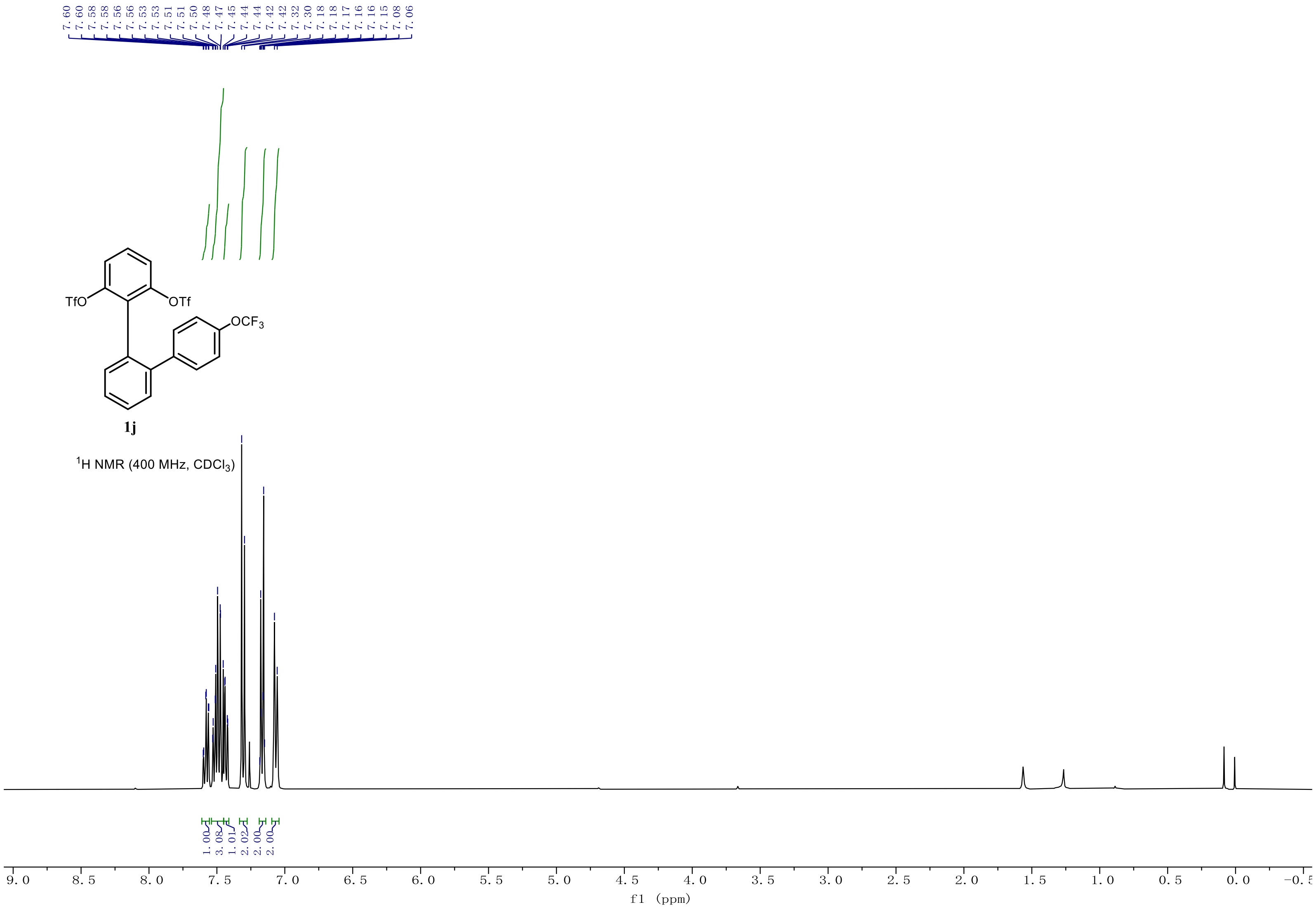


157.00
156.71
147.66
142.00
135.36
131.96
130.51
130.39
130.29
129.89
127.26
126.70
123.58
123.06
121.78
119.88
119.15
118.33
116.69
113.51
TfO
OTf
OPh
1i
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

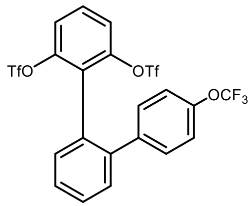


1i

^{19}F NMR (376 MHz, $CDCl_3$)

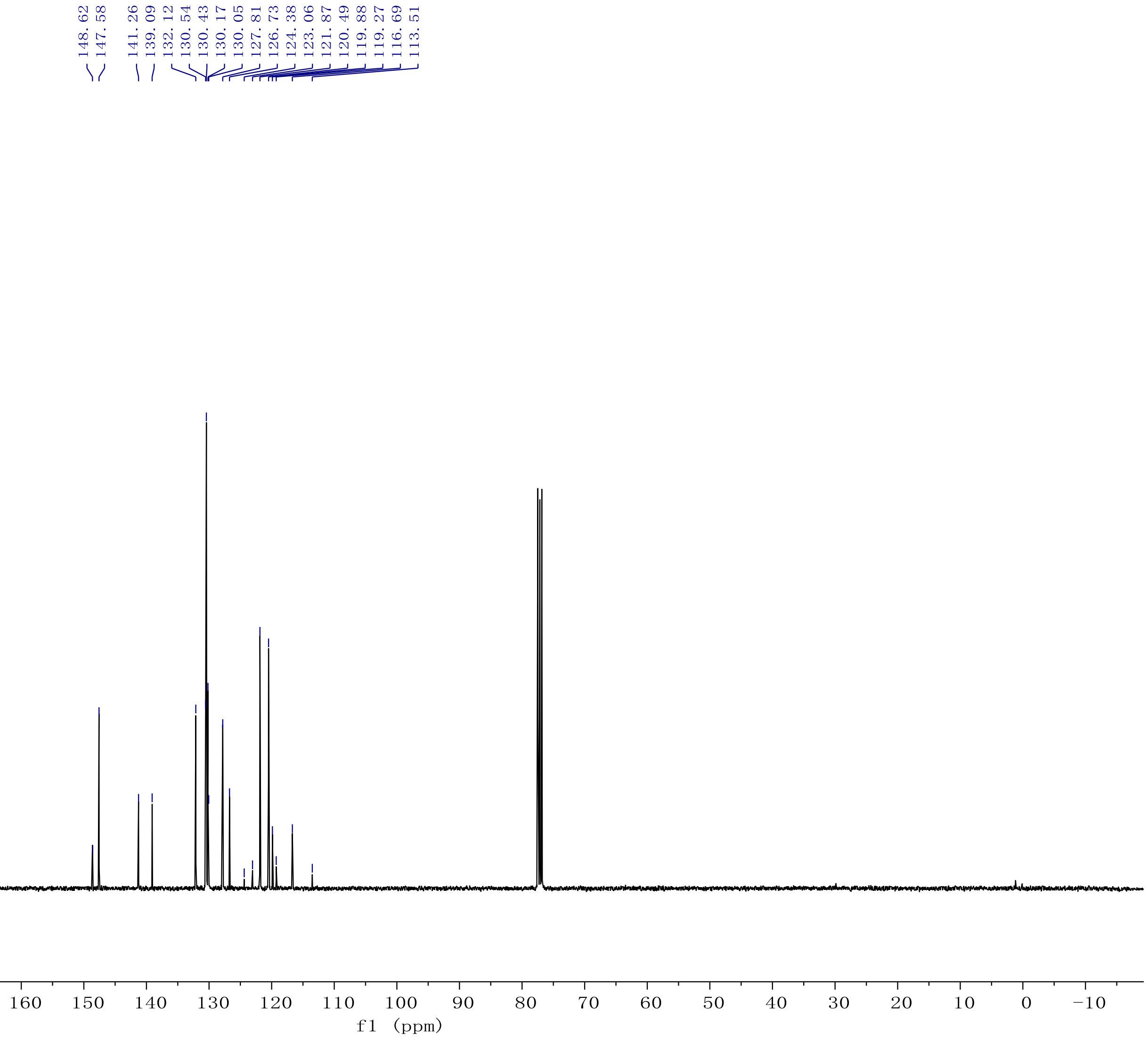


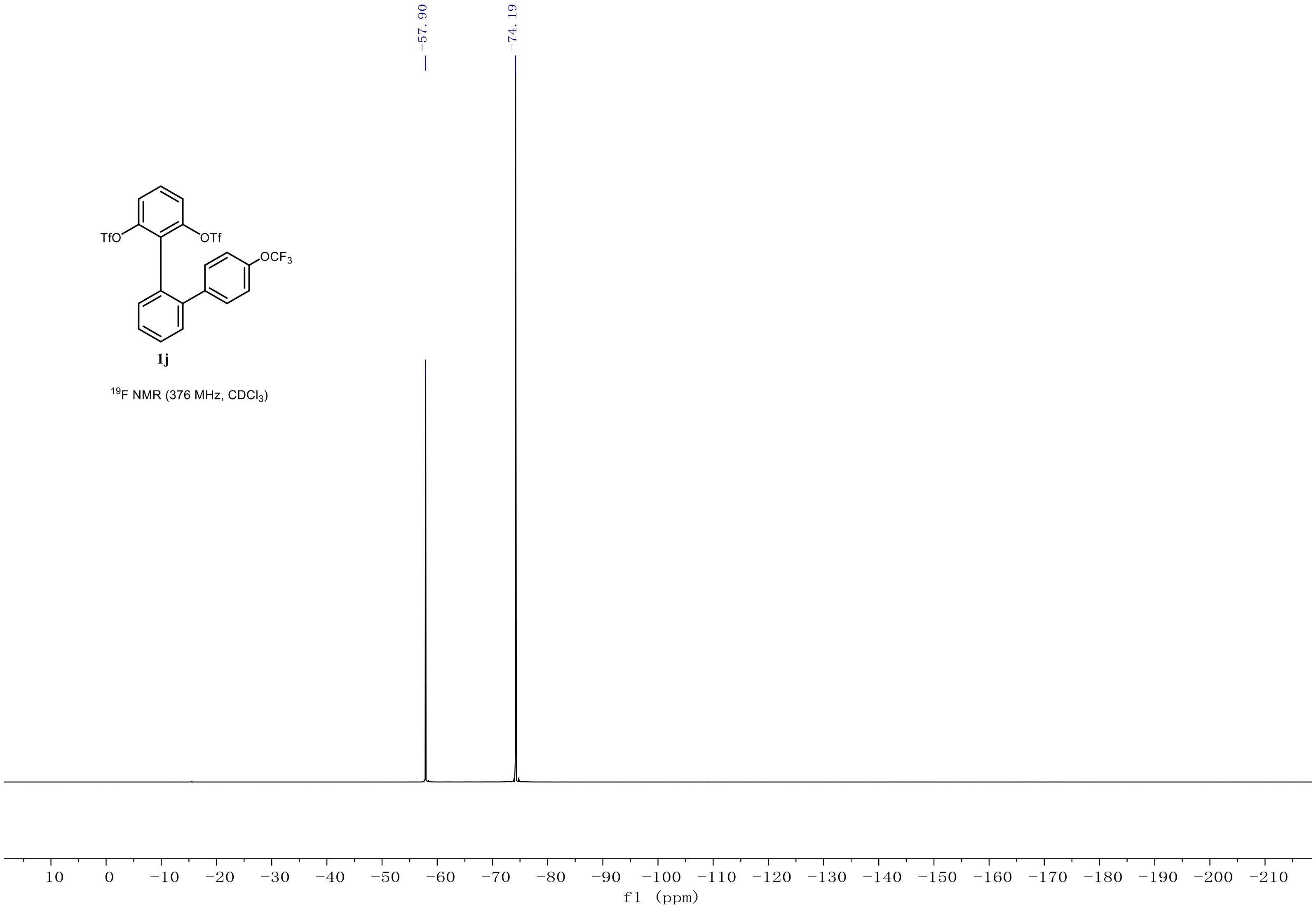
7.60 7.60 7.58 7.58 7.56 7.56 7.53 7.53 7.51 7.51 7.50 7.48 7.47 7.45 7.44 7.44 7.42 7.42 7.32 7.30 7.18 7.18 7.17 7.16 7.16 7.15 7.08 7.06
TfO
OTf
OCF_3
1j
^{1}H NMR (400 MHz, $CDCl_3$)
1.00 3.08 1.01 2.02 2.00 2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

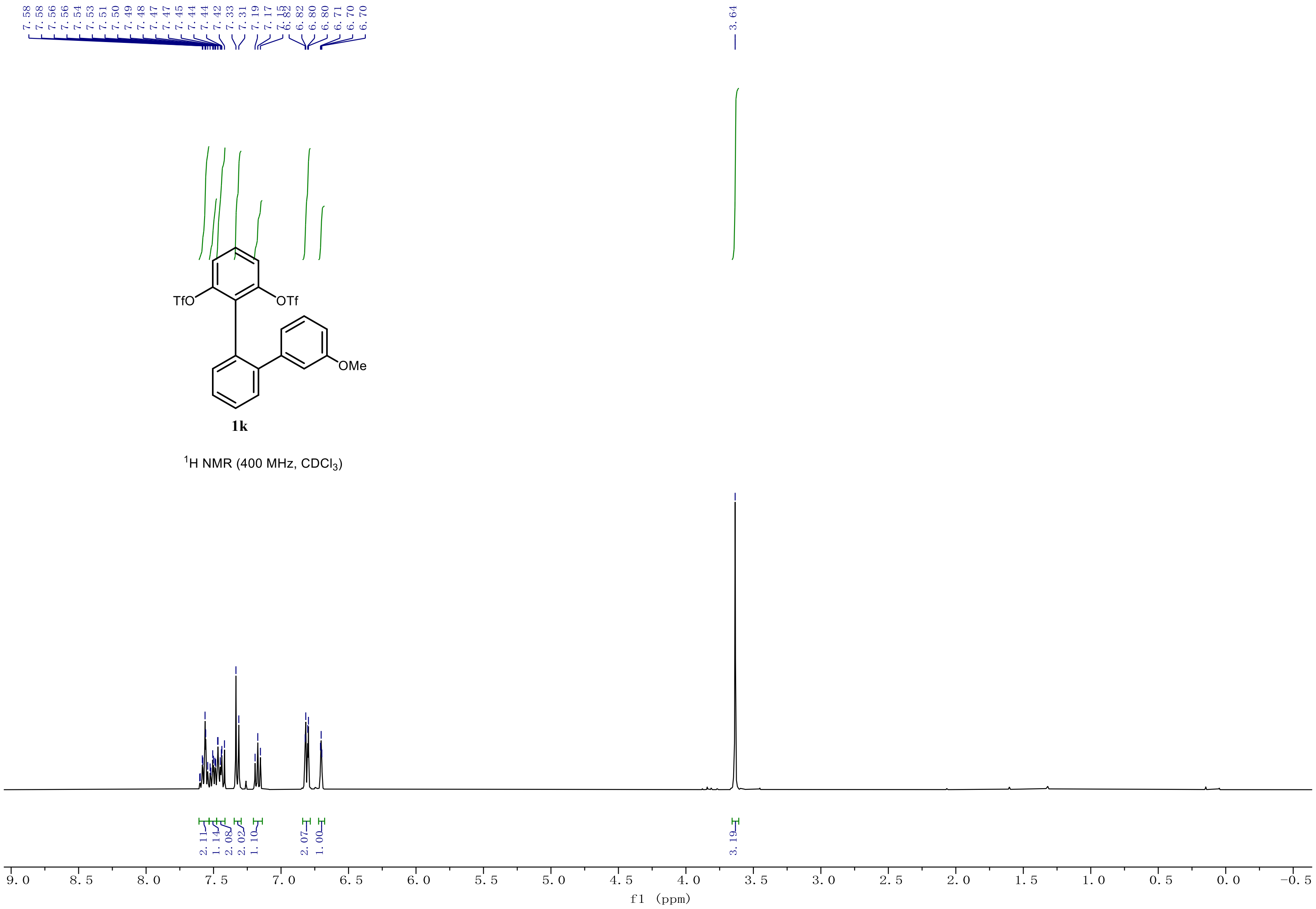


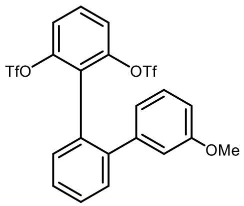
1j

^{13}C NMR (101 MHz, $CDCl_3$)



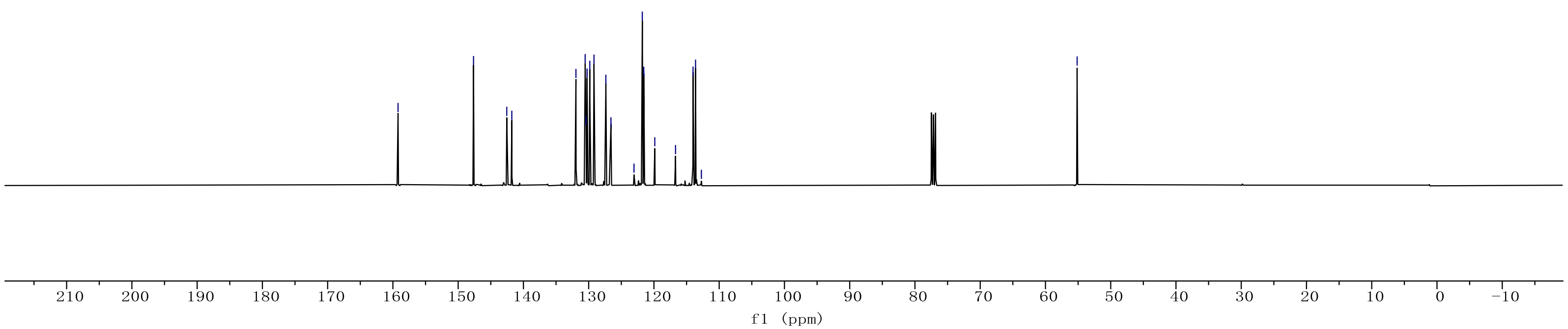

-57.90
-74.19
TfO
OTf
OCF3
1j
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

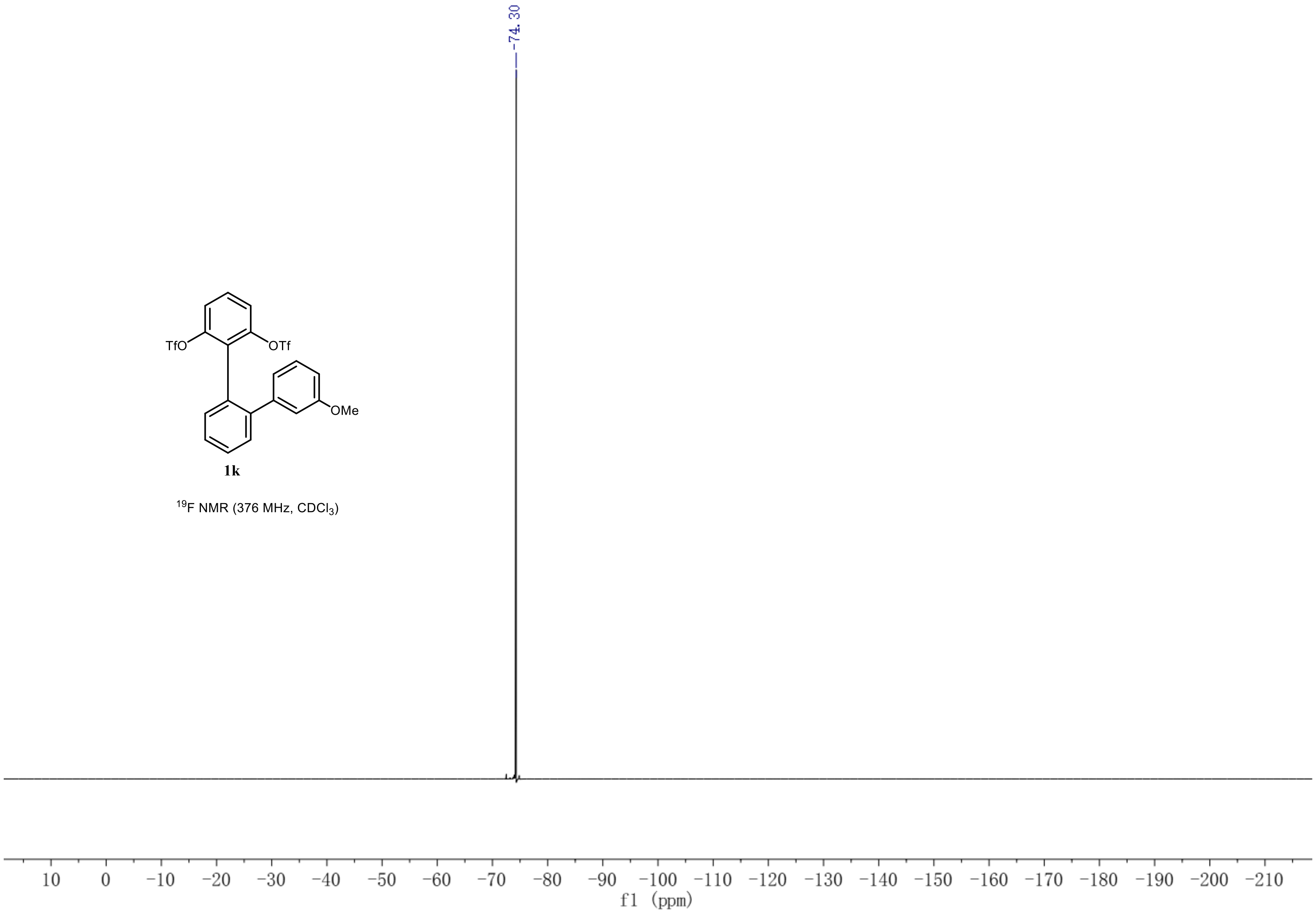

7.58 7.58 7.56 7.56 7.54 7.53 7.51 7.50 7.49 7.48 7.47 7.47 7.45 7.44 7.44 7.42 7.33 7.31 7.19 7.17 7.15 6.83 6.82 6.80 6.80 6.71 6.70 6.70
3.64
TfO
OTf
OMe
1k
^{1}H NMR (400 MHz, $CDCl_3$)
2.11 1.14 2.08 2.02 1.10 2.07 1.00 3.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



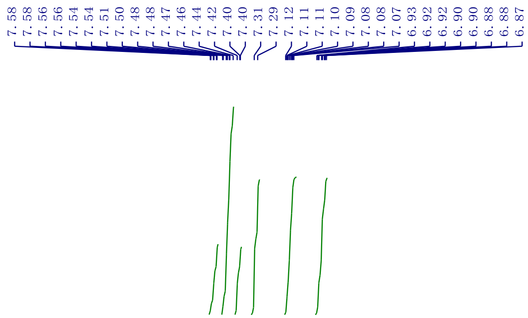
1k

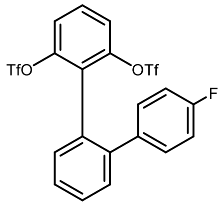
^{13}C NMR (101 MHz, $CDCl_3$)





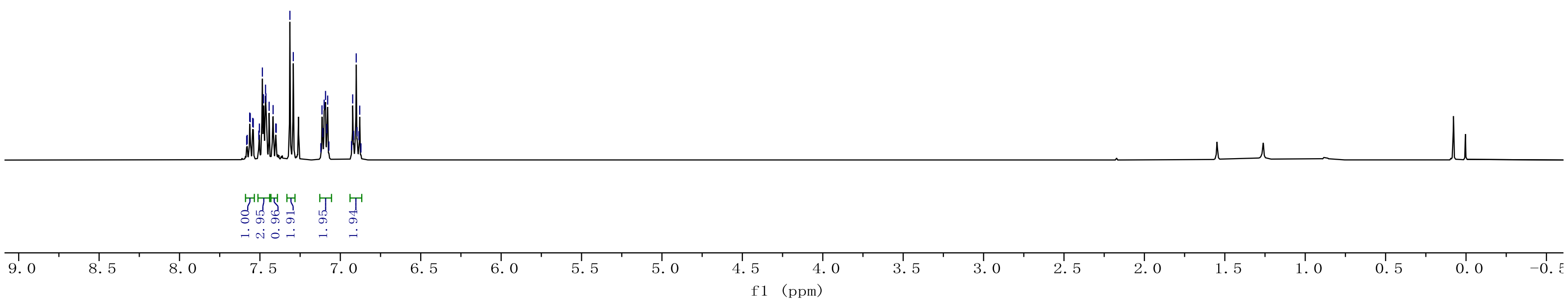
-74.30
TfO
OTf
OMe
1k
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

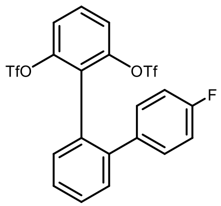




1l

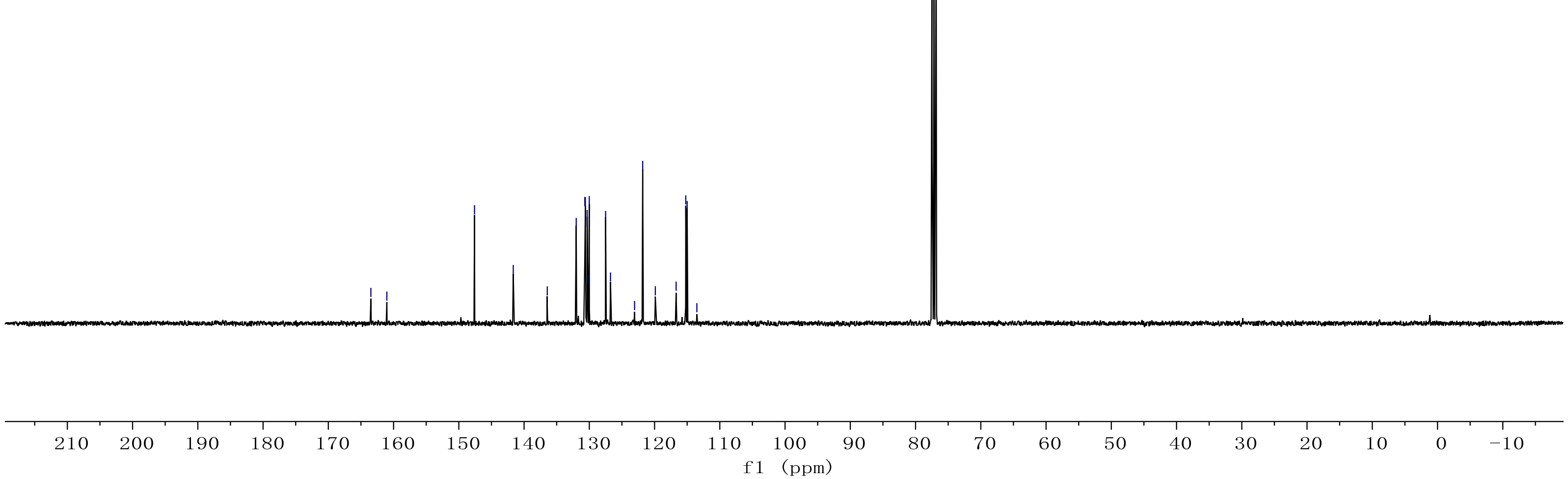
^{1}H NMR (400 MHz, $CDCl_3$)

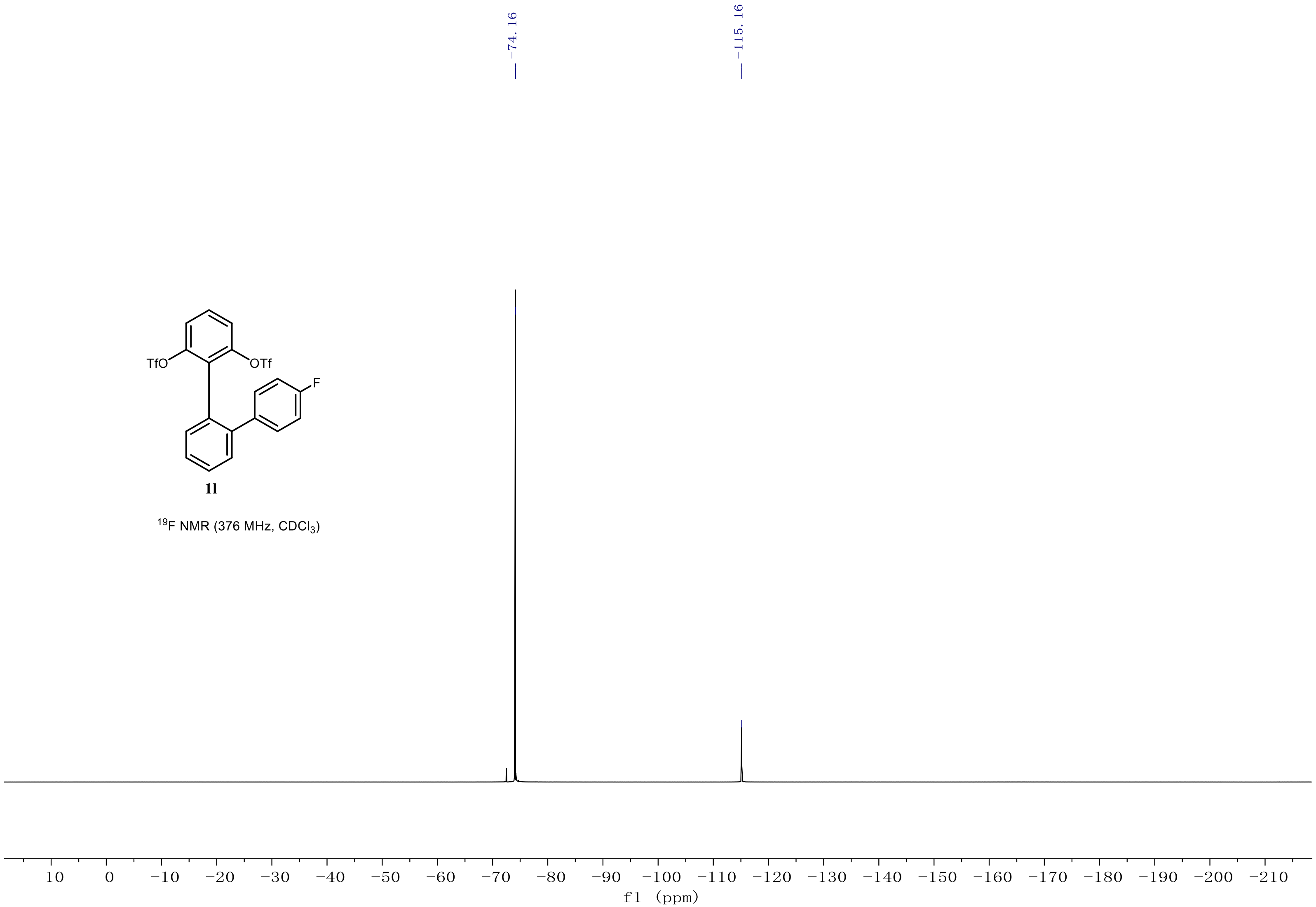




1l

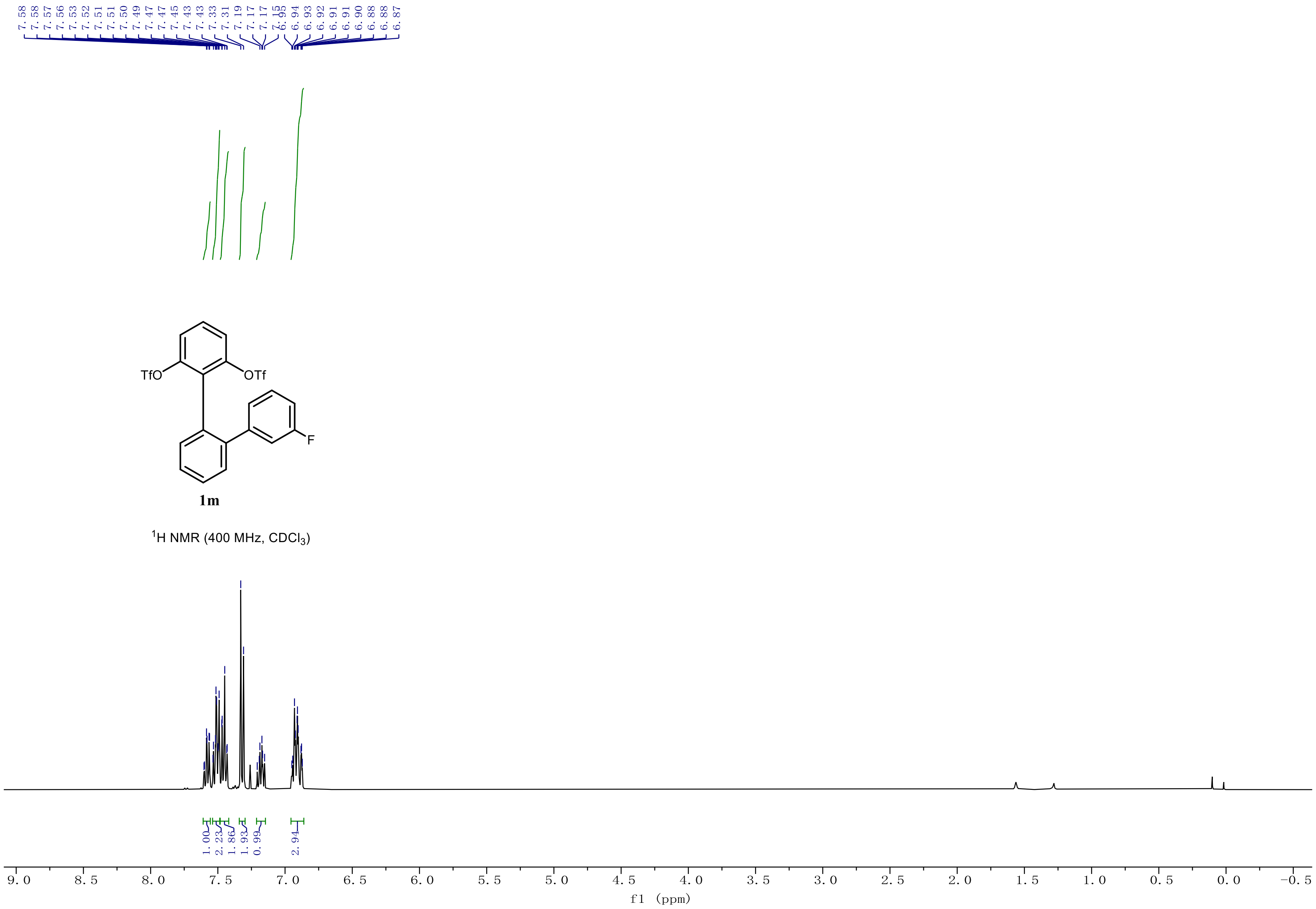
^{13}C NMR (101 MHz, $CDCl_3$)





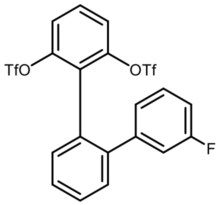
1l

[19]F NMR (376 MHz, $CDCl_3$)



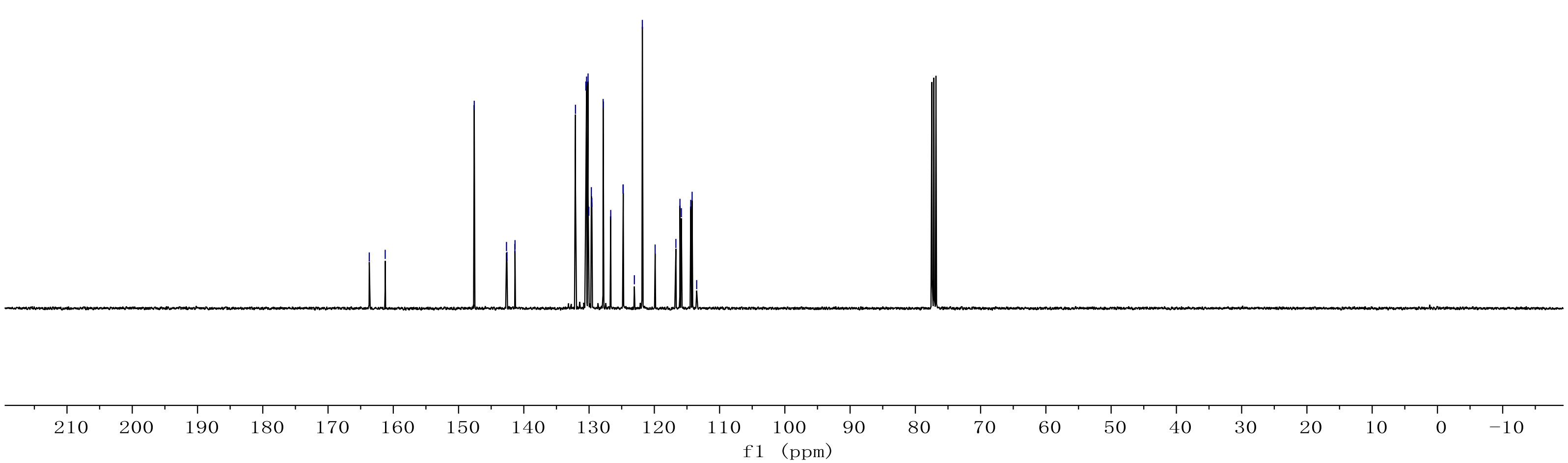
1m

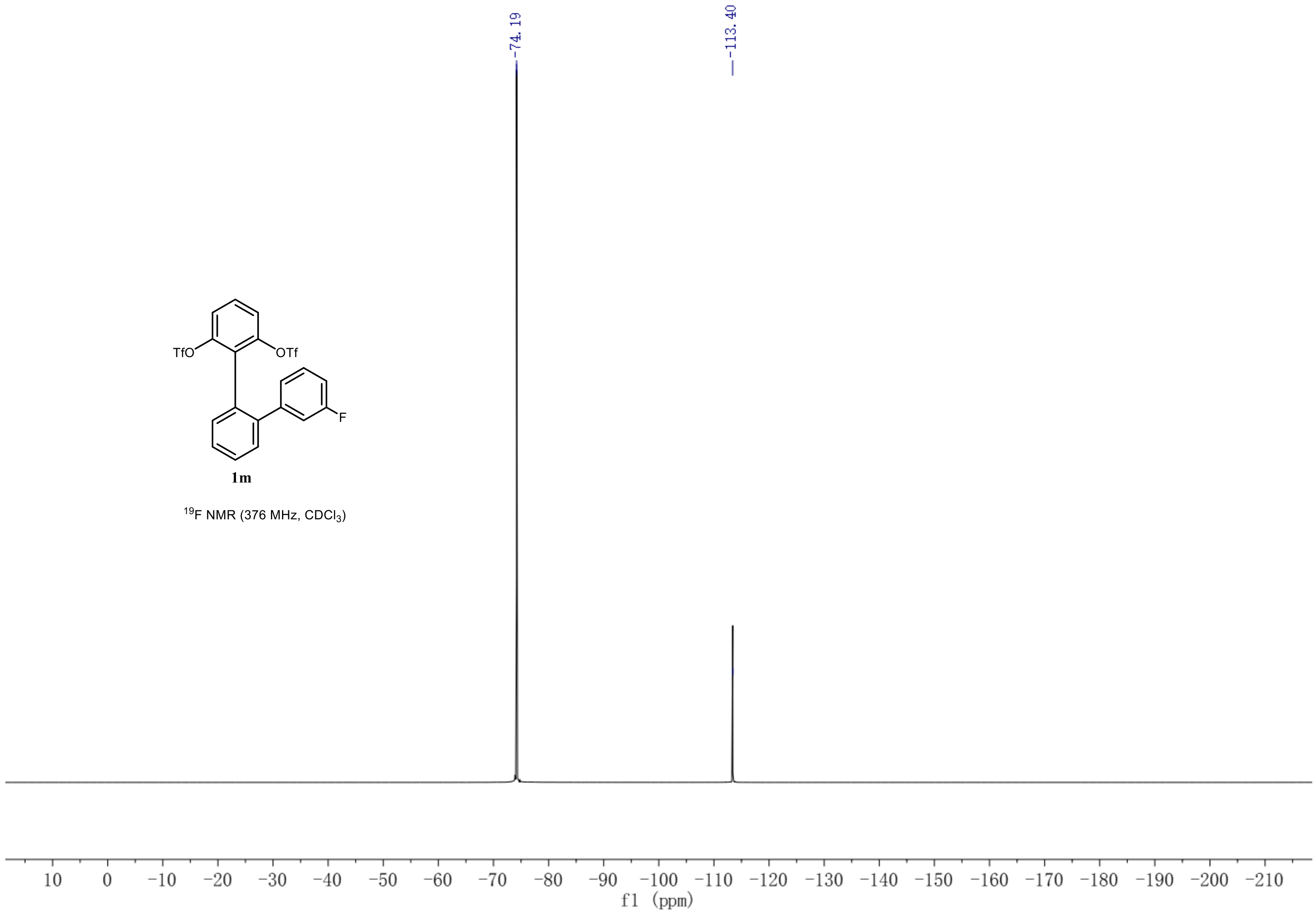
^{1}H NMR (400 MHz, $CDCl_3$)



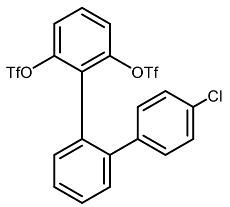
1m

^{13}C NMR (101 MHz, $CDCl_3$)



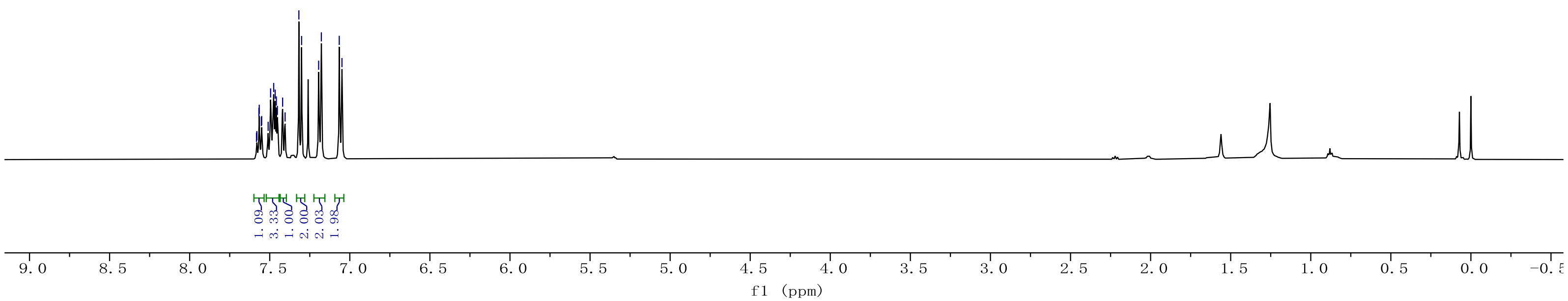


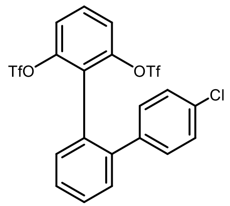
-74.19
-113.40
1m
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



1n

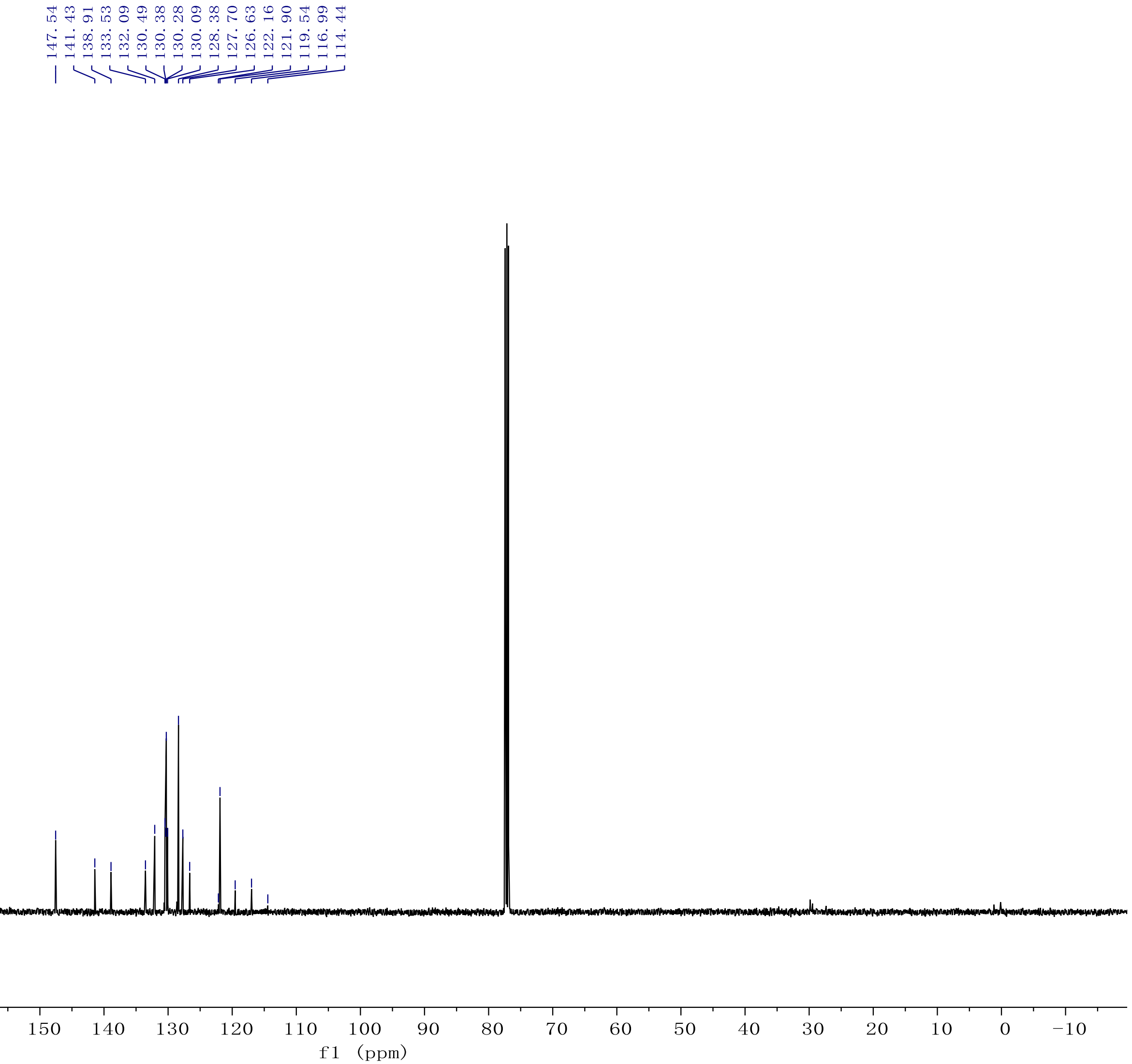
^{1}H NMR (500 MHz, $CDCl_3$)

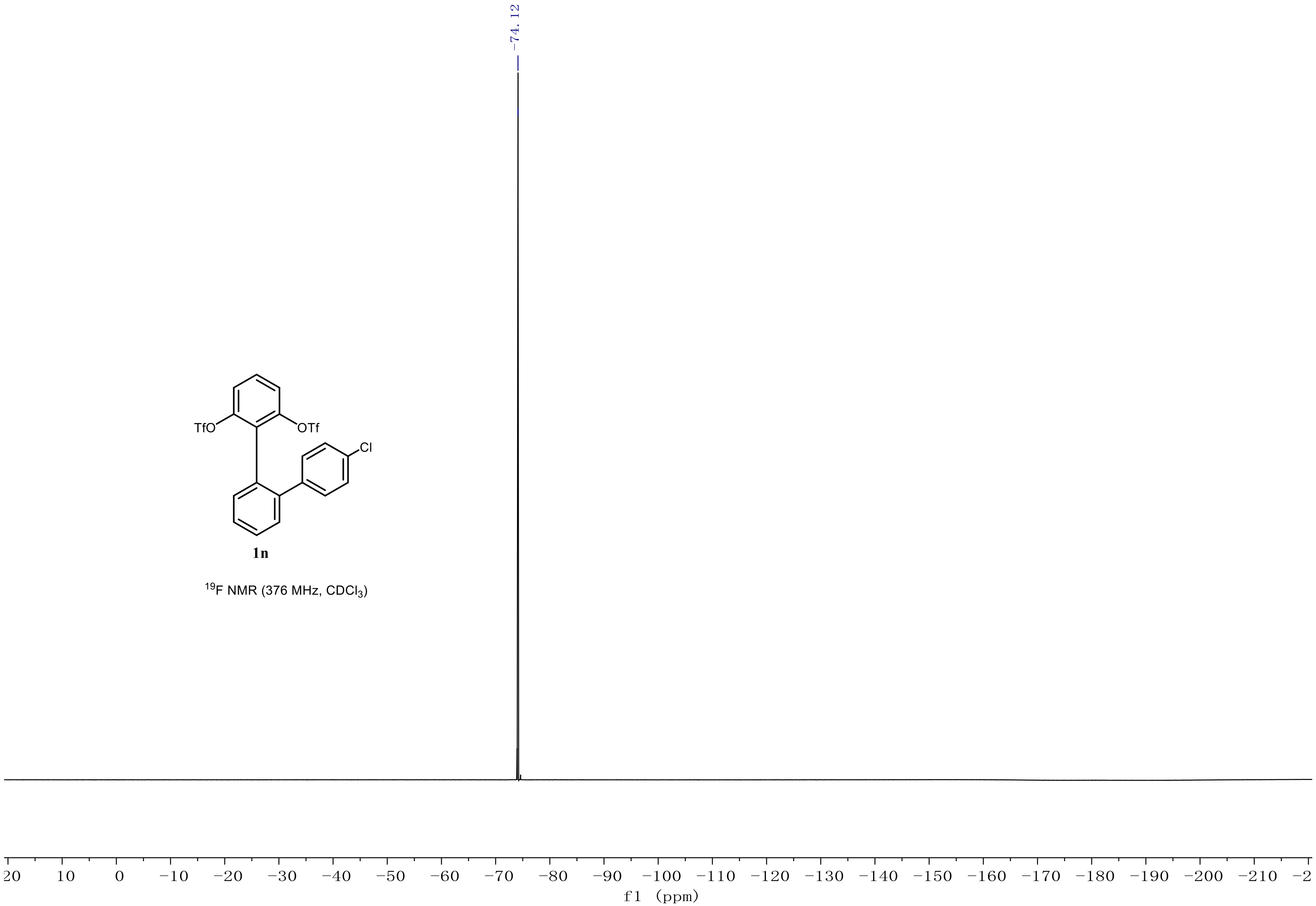




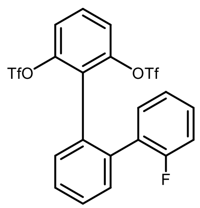
1n

^{13}C NMR (101 MHz, $CDCl_3$)



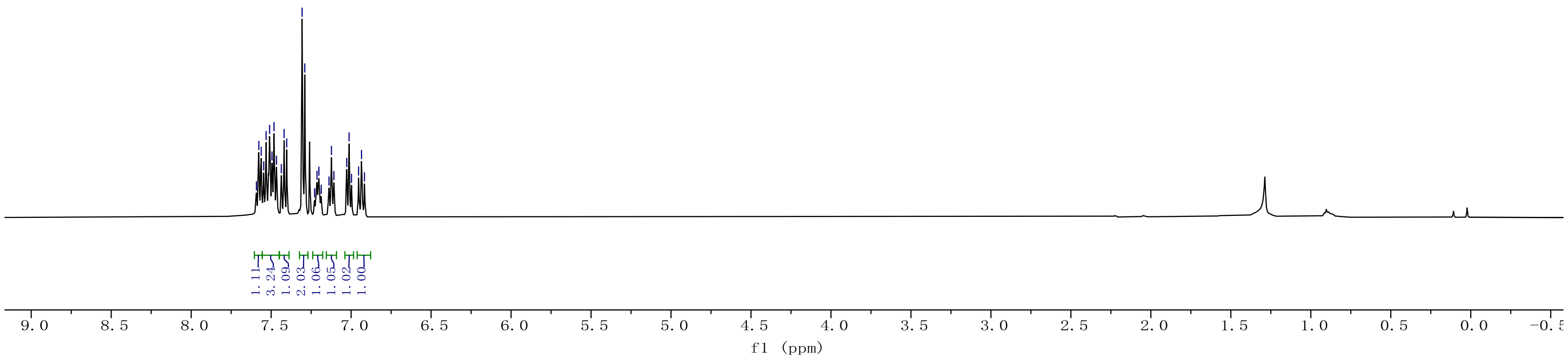


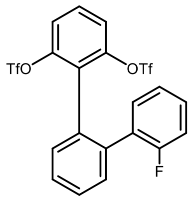
−74.12
TfO
OTf
Cl
1n
^{19}F NMR (376 MHz, CDCl$_3$)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



1o

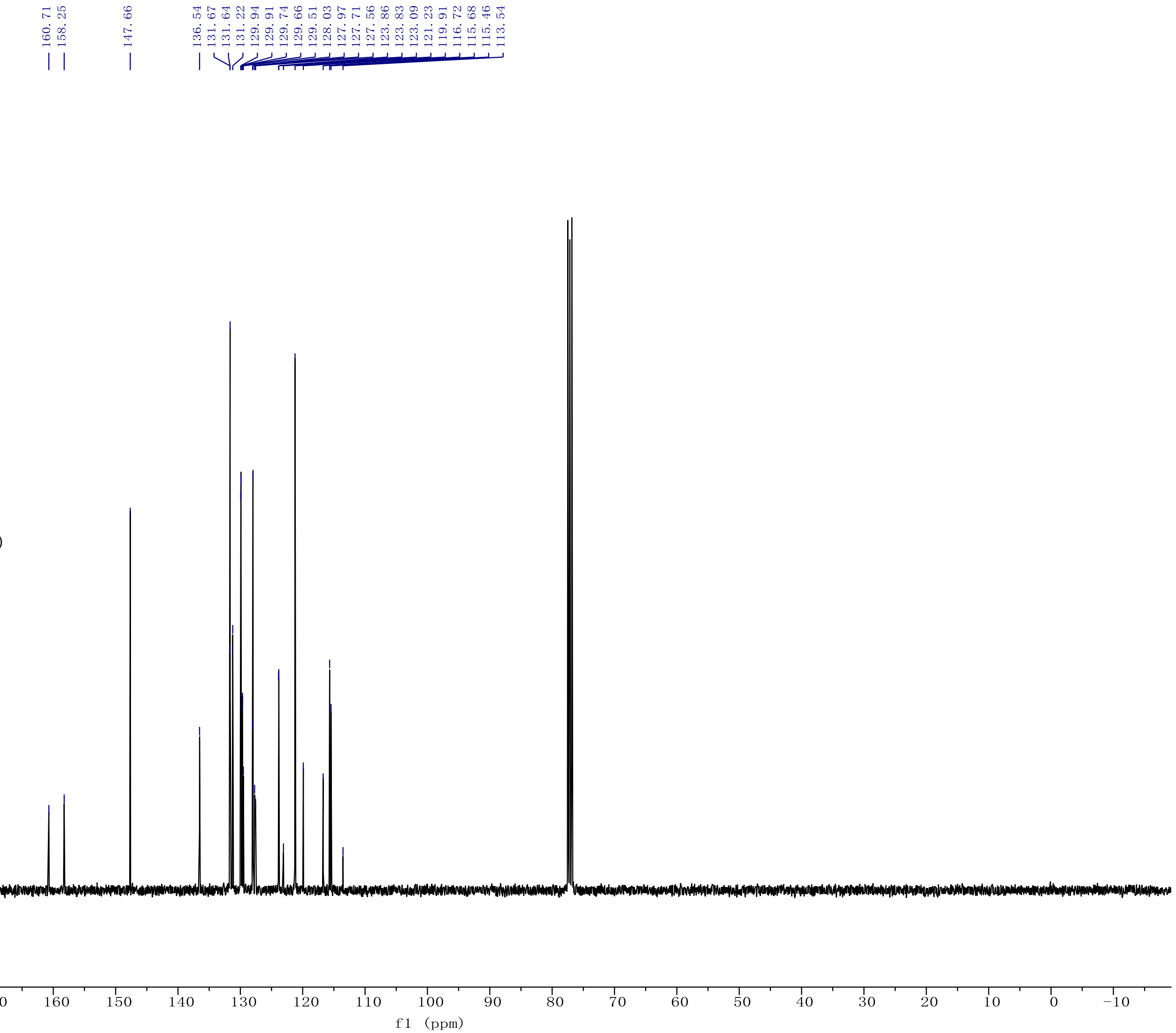
[1]H NMR (500 MHz, $CDCl_3$)

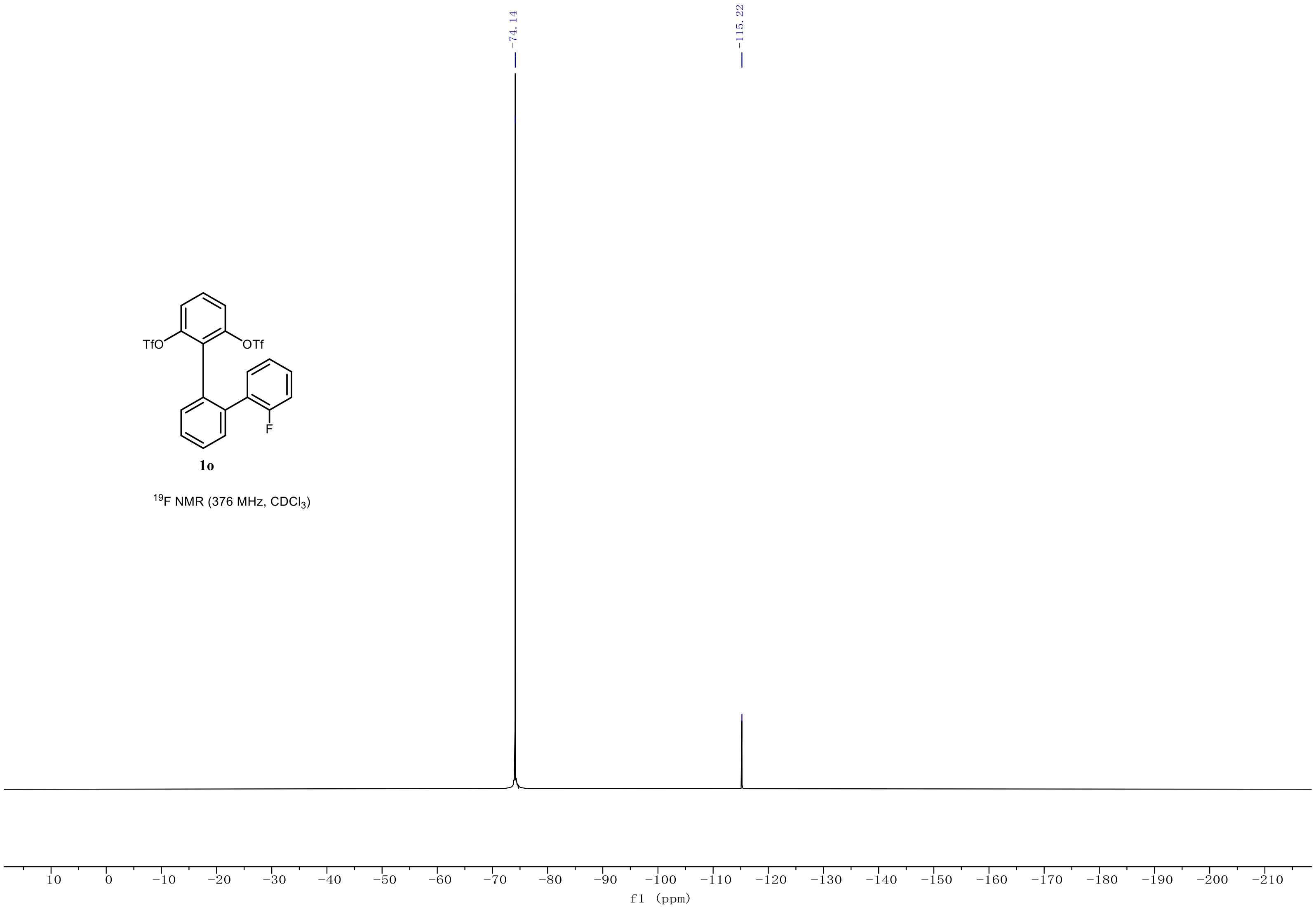


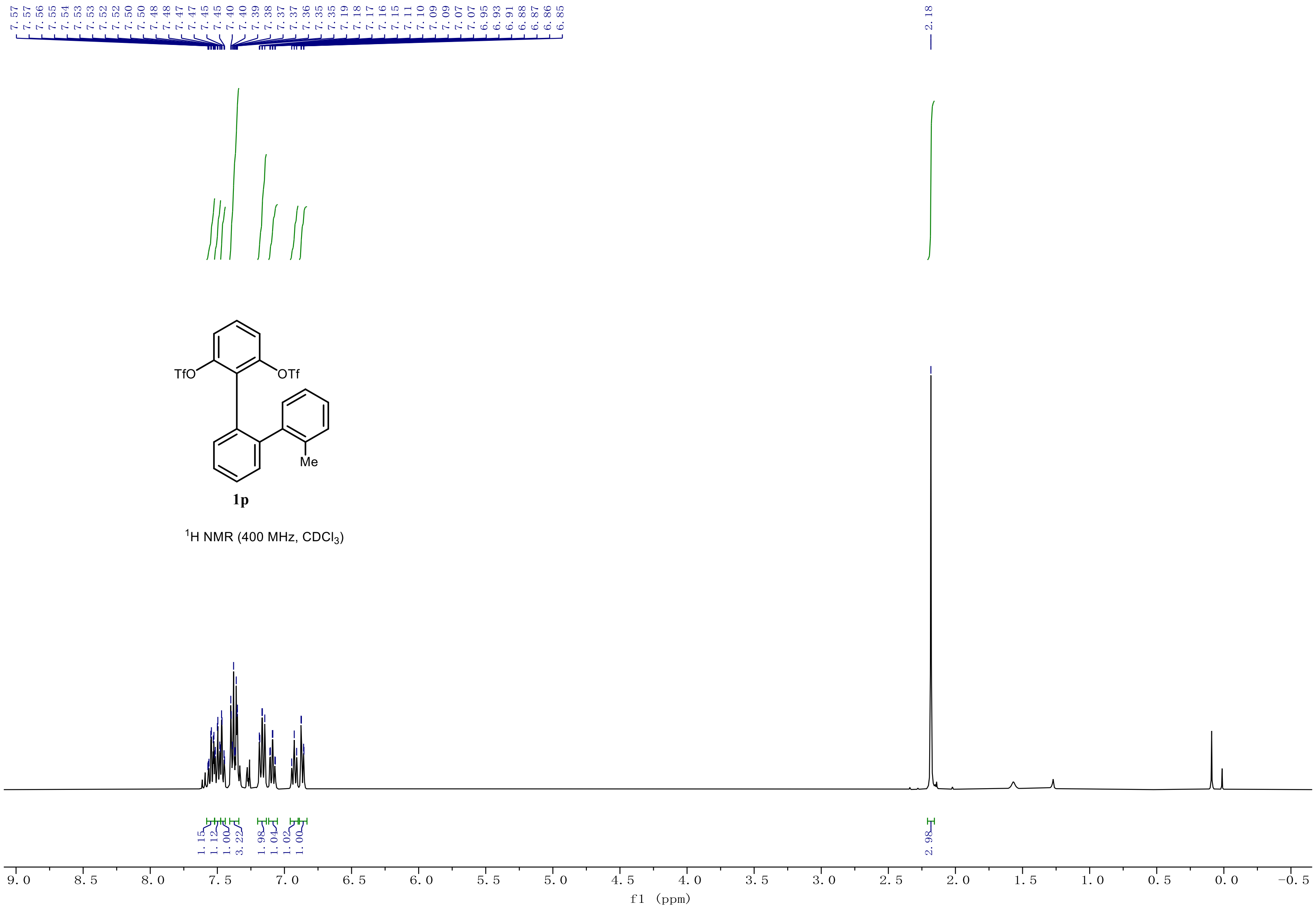


1o

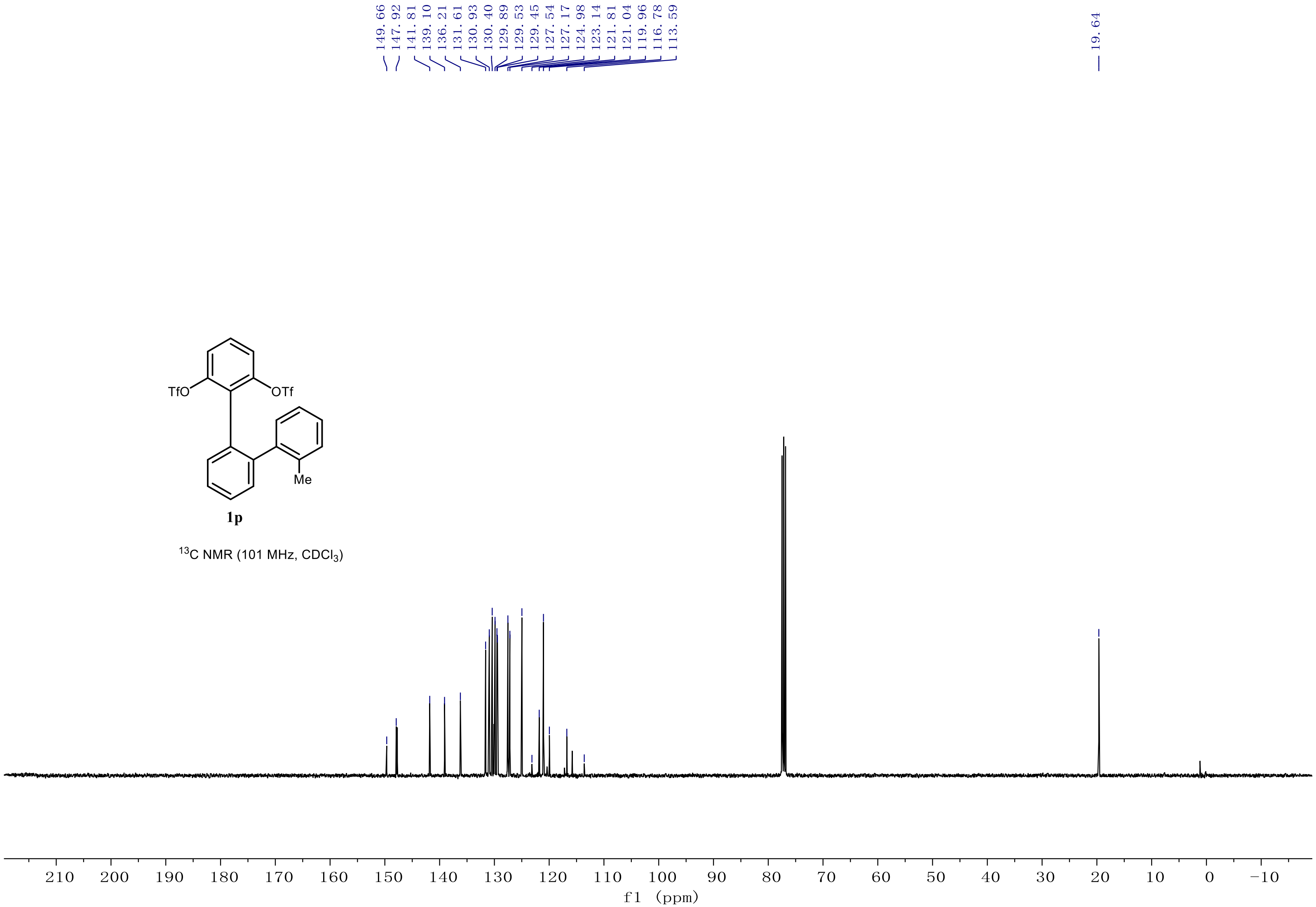
^{13}C NMR (101 MHz, $CDCl_3$)




-74.14
-115.22
TfO
OTf
F
1o
^{19}F NMR (376 MHz, $CDCl_3$)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



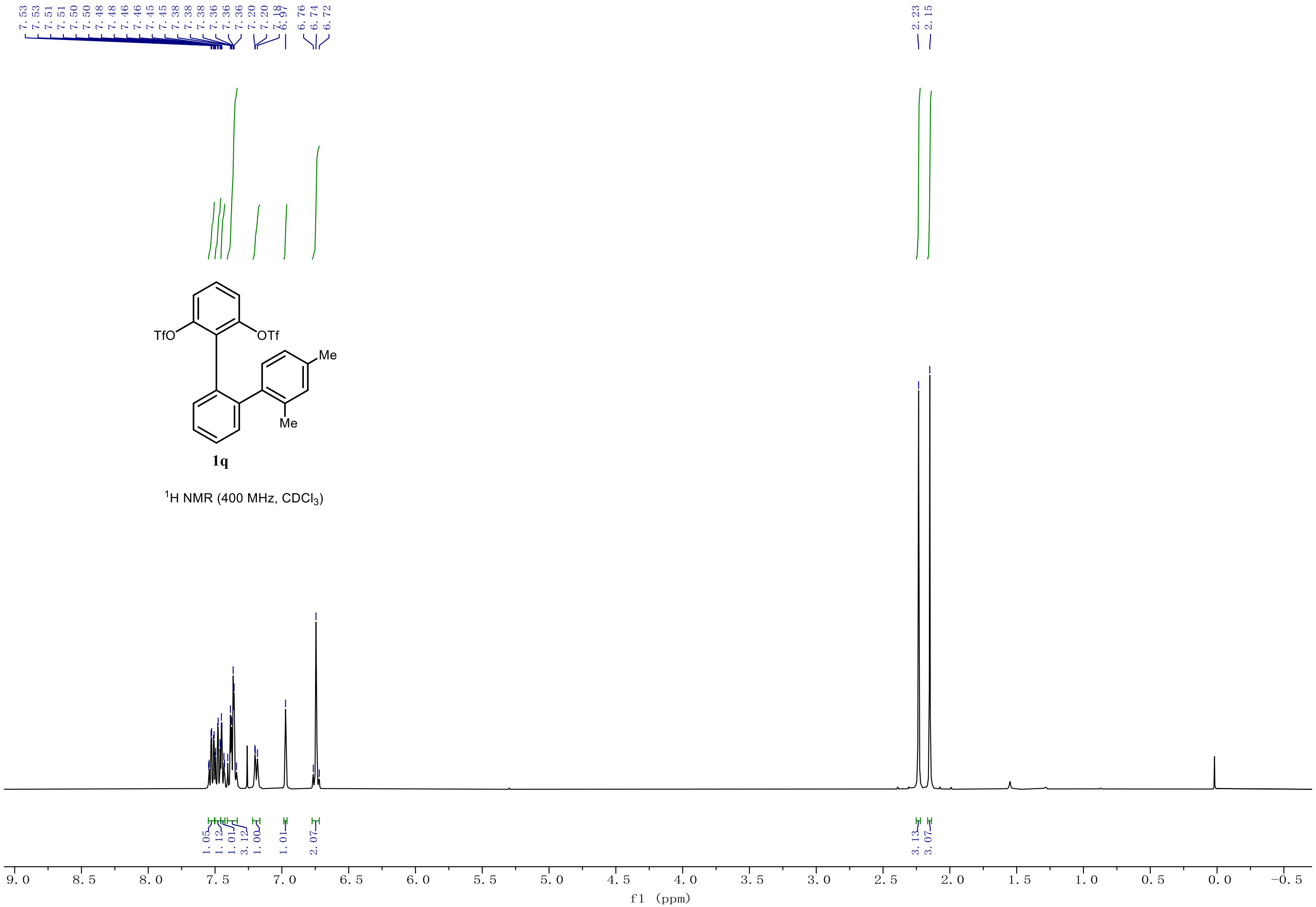
TfO
OTf
Me
1p
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

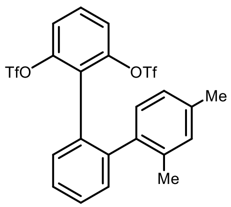


1p

^{13}C NMR (101 MHz, $CDCl_3$)

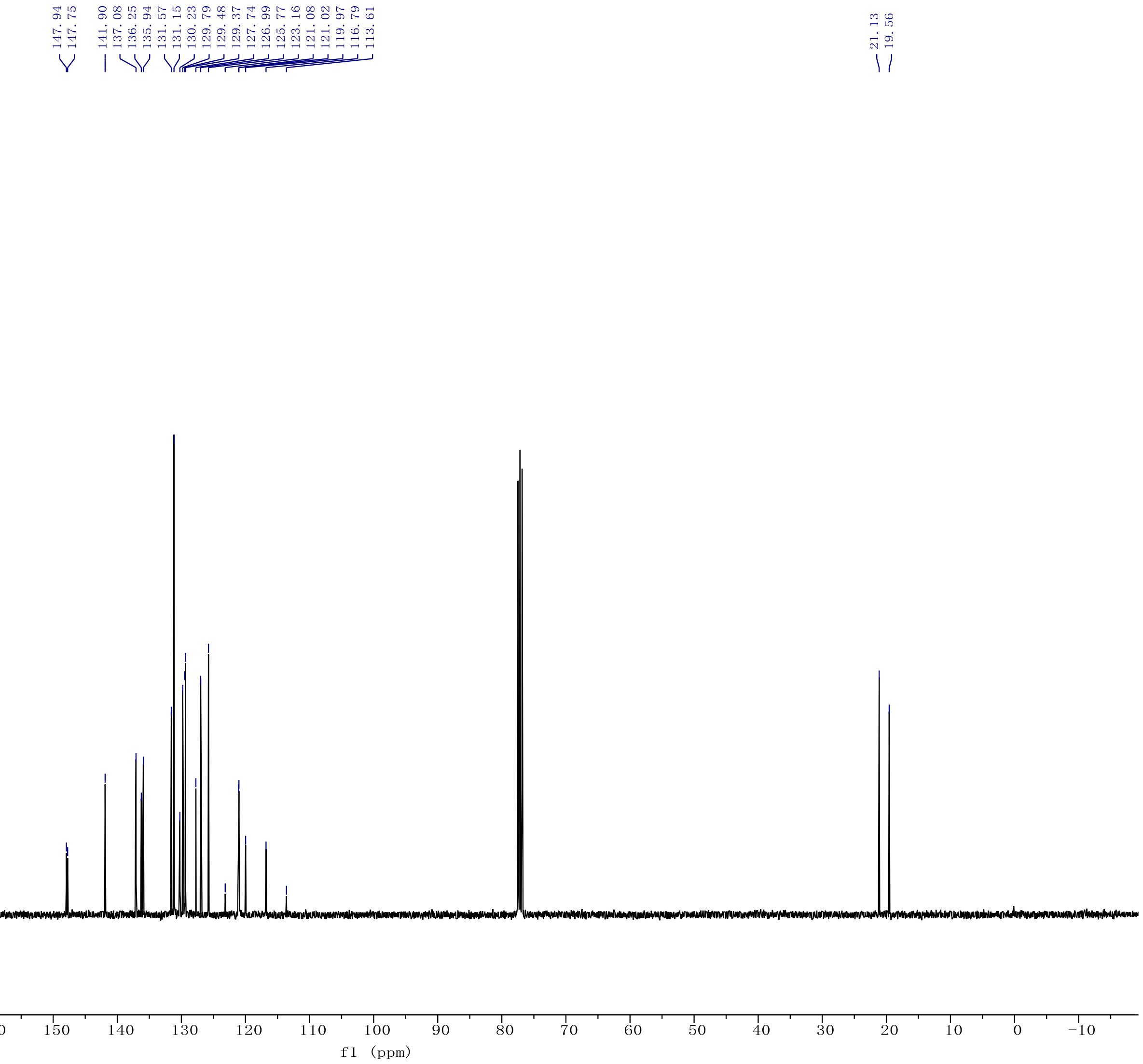
-74.17
TfO
OTf
Me
1p
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

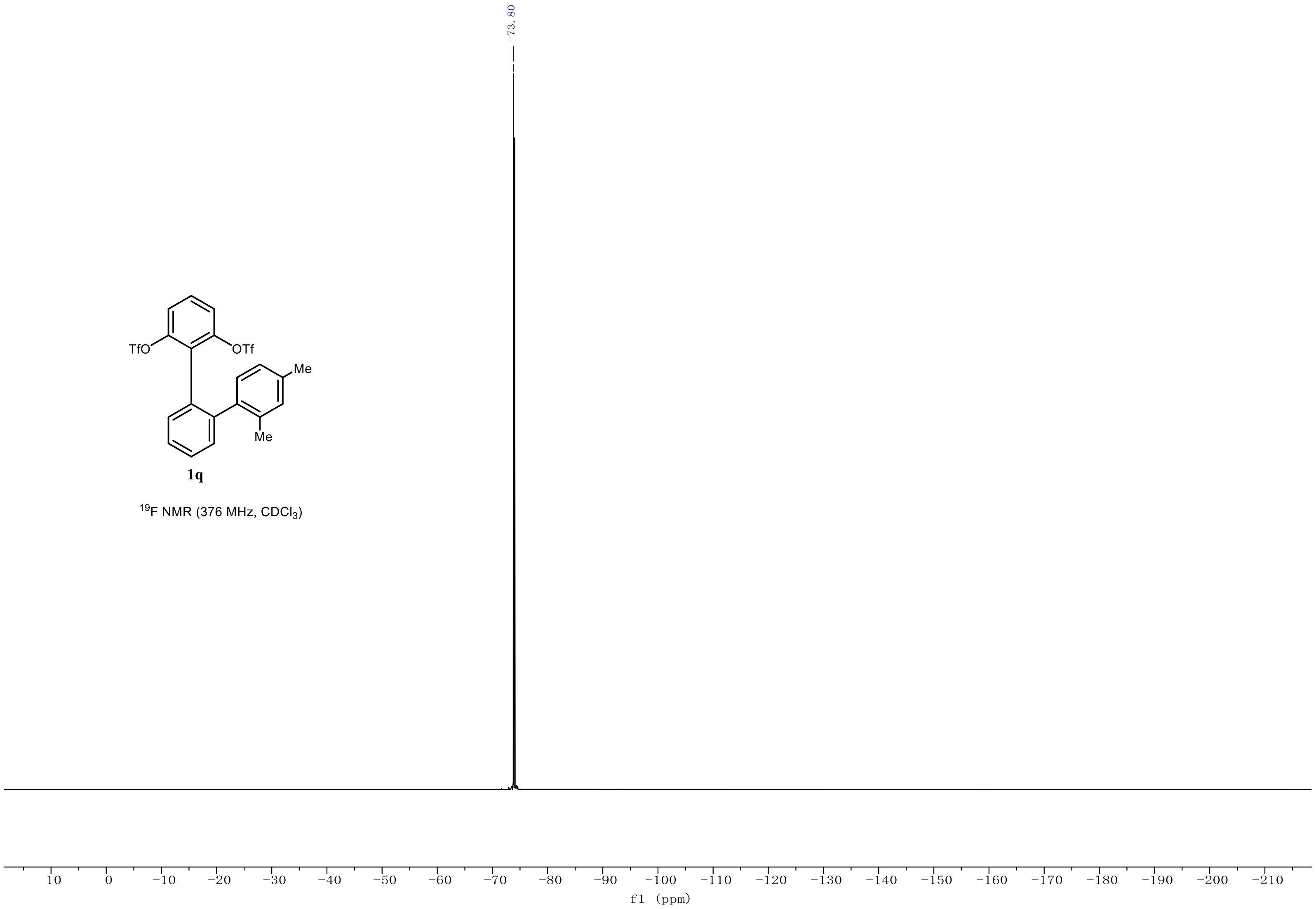

7.53
7.53
7.51
7.51
7.50
7.50
7.48
7.48
7.46
7.46
7.45
7.45
7.38
7.38
7.38
7.36
7.36
7.36
7.20
7.20
7.18
6.97
6.76
6.74
6.72
2.23
2.15
TfO
OTf
Me
Me
1q
^{1}H NMR (400 MHz, CDCl$_3$)
1.05
1.12
1.01
3.12
1.00
1.01
2.07
3.13
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

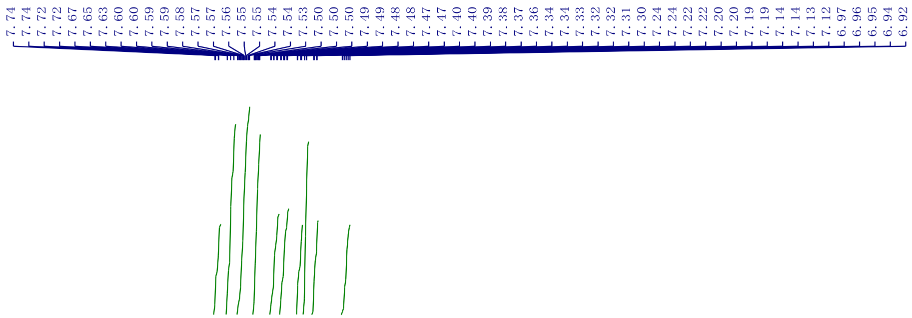


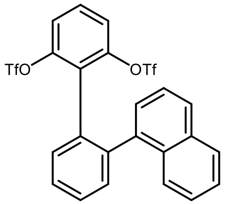
1q

^{13}C NMR (101 MHz, $CDCl_3$)



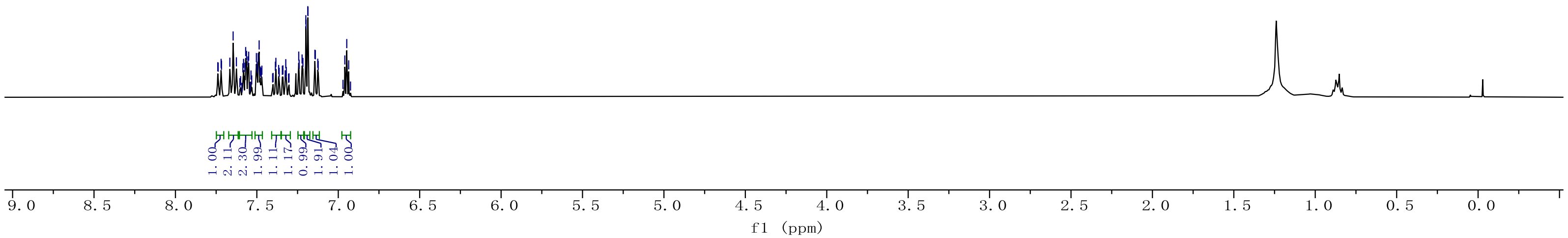

−73.80
TfO
OTf
Me
Me
1q
19F NMR (376 MHz, CDCl3)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

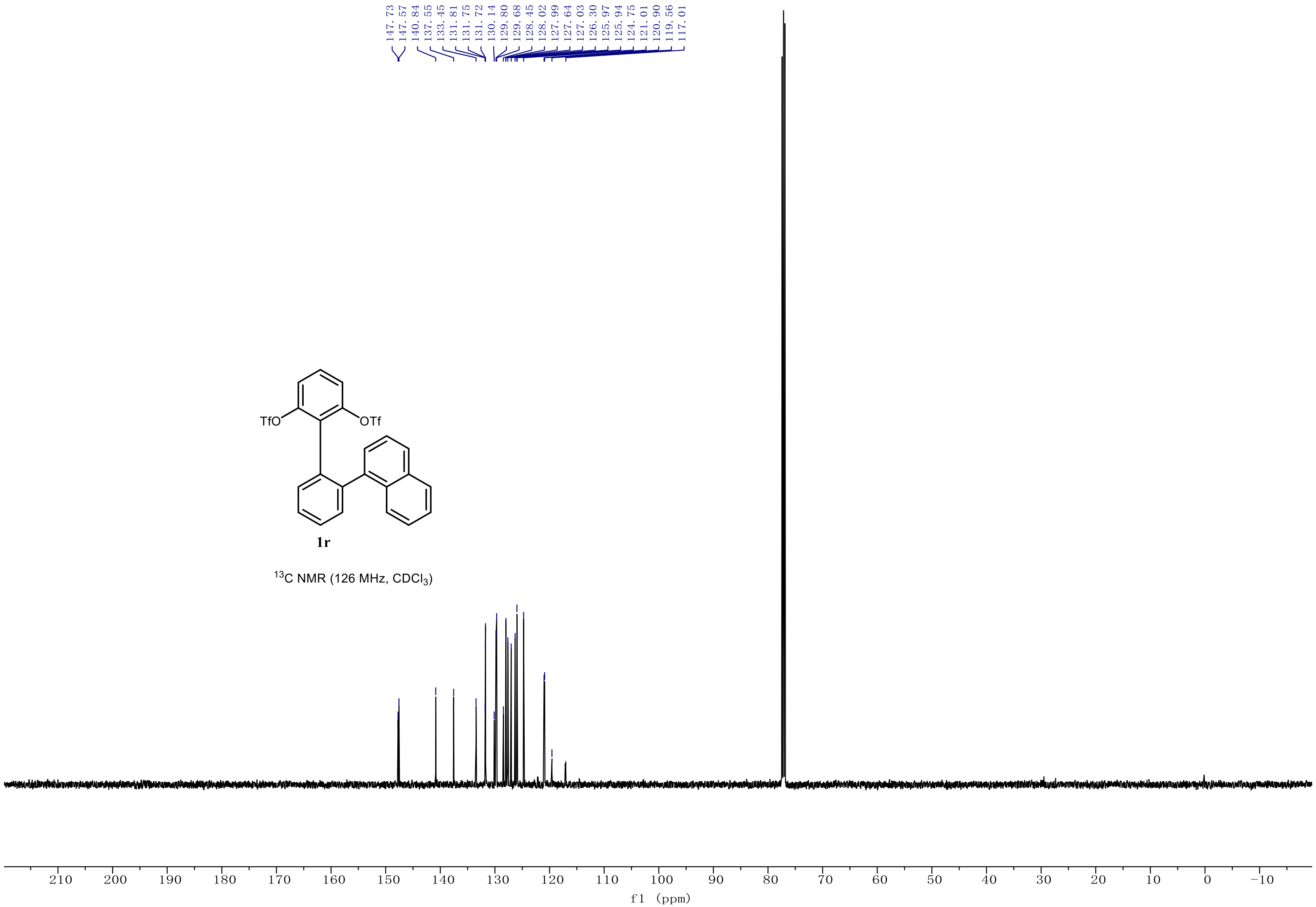




1r

^{1}H NMR (400 MHz, $CDCl_3$)

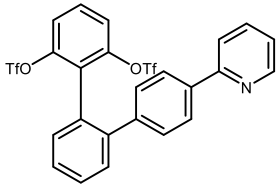




1r

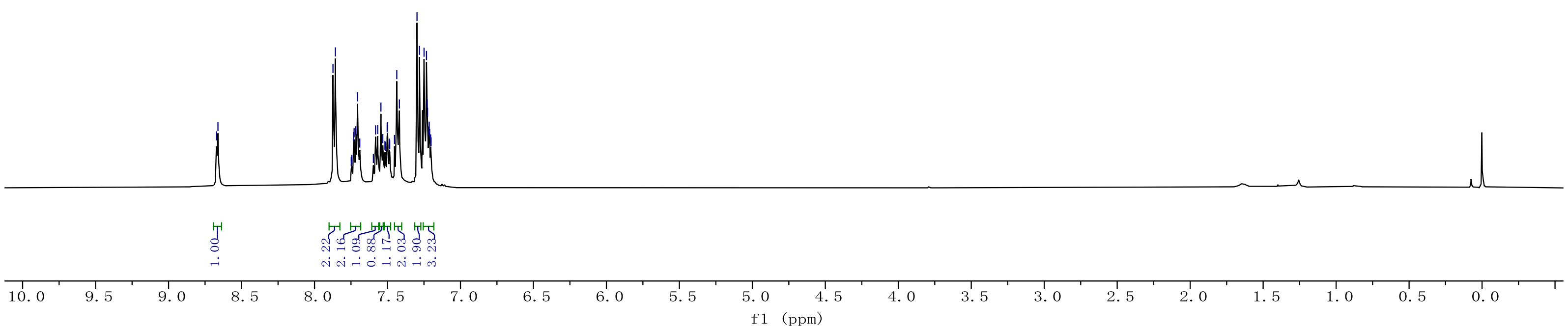
^{13}C NMR (126 MHz, $CDCl_3$)

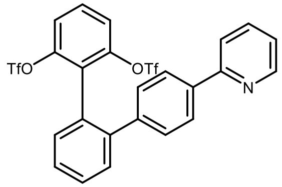

-73.96
TfO
OTf
1r
19F NMR (471 MHz, CDCl3)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



1s

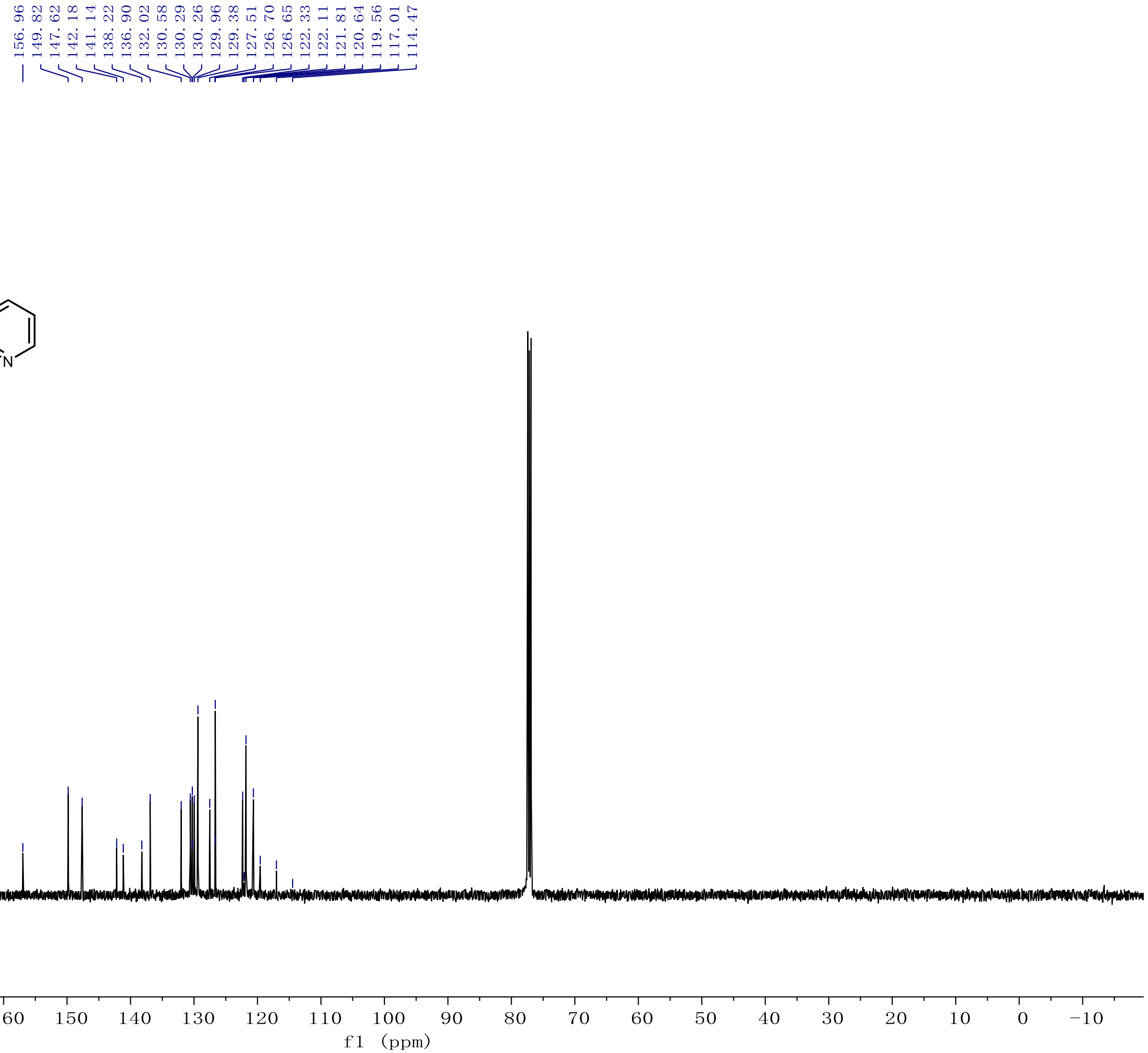
^1H NMR (500 MHz, $CDCl_3$)

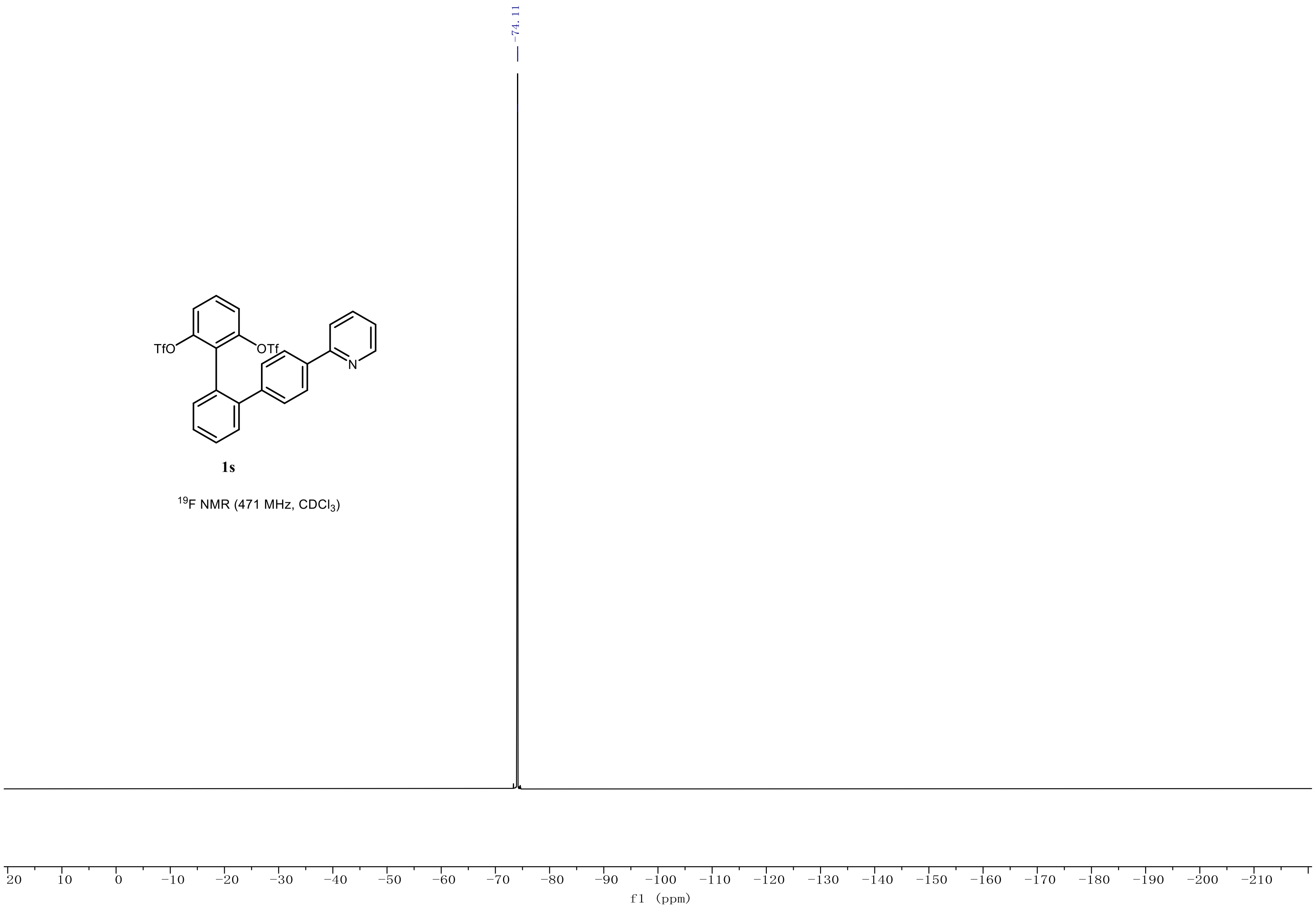




1s

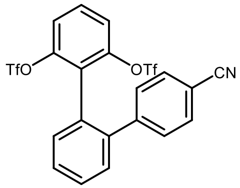
^{13}C NMR (126 MHz, $CDCl_3$)





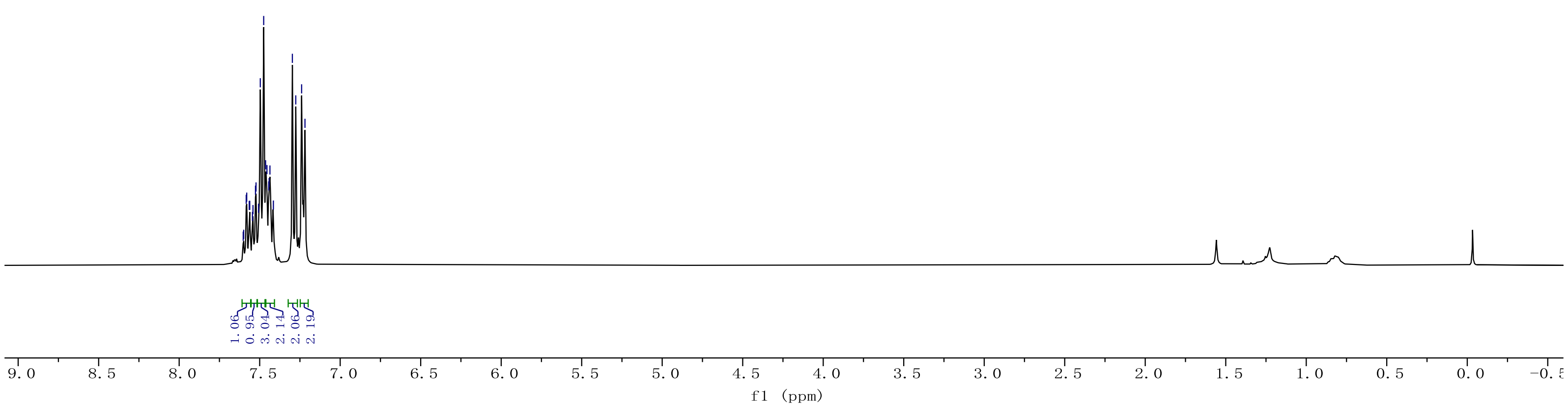
1s

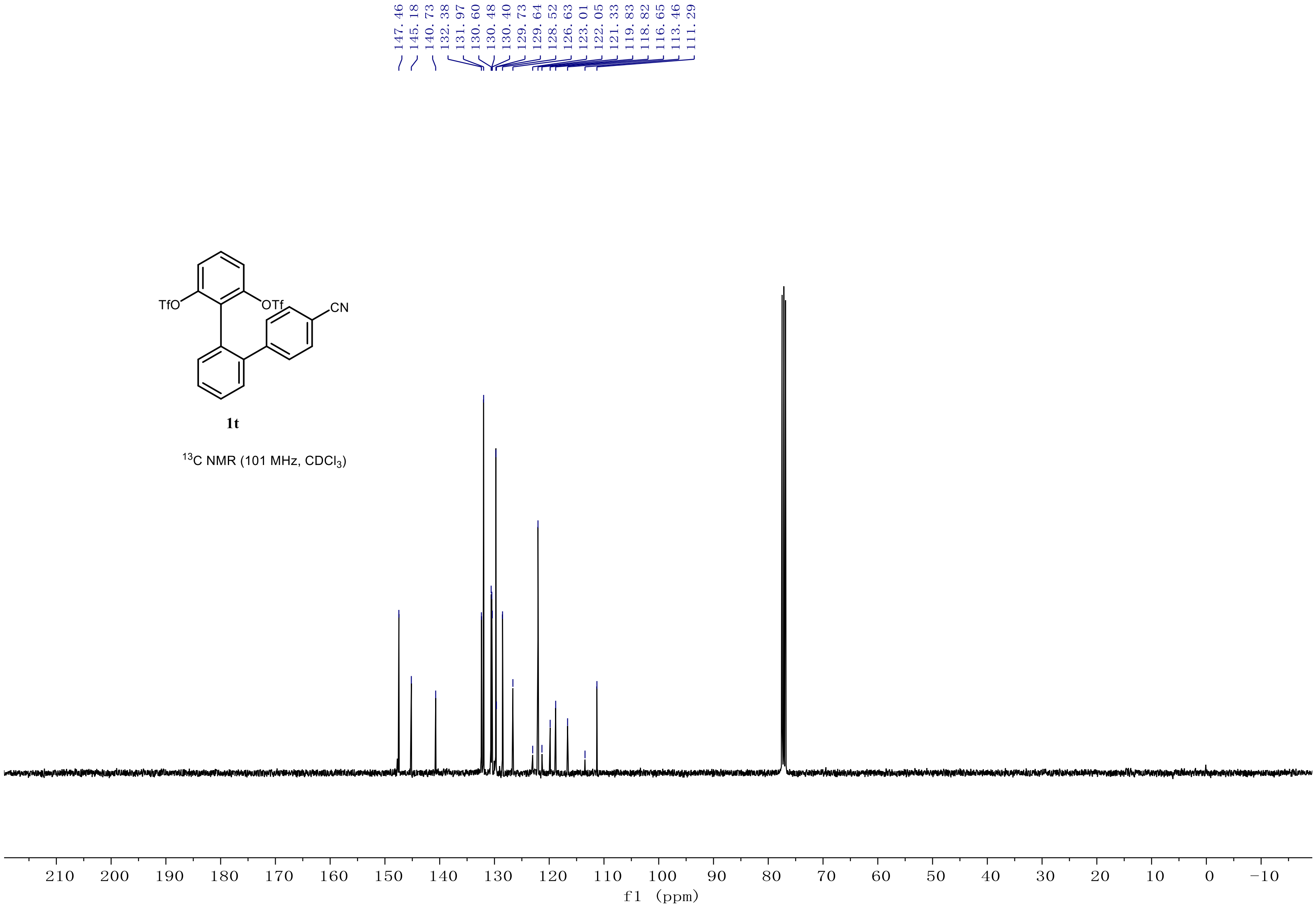
^{19}F NMR (471 MHz, $CDCl_3$)



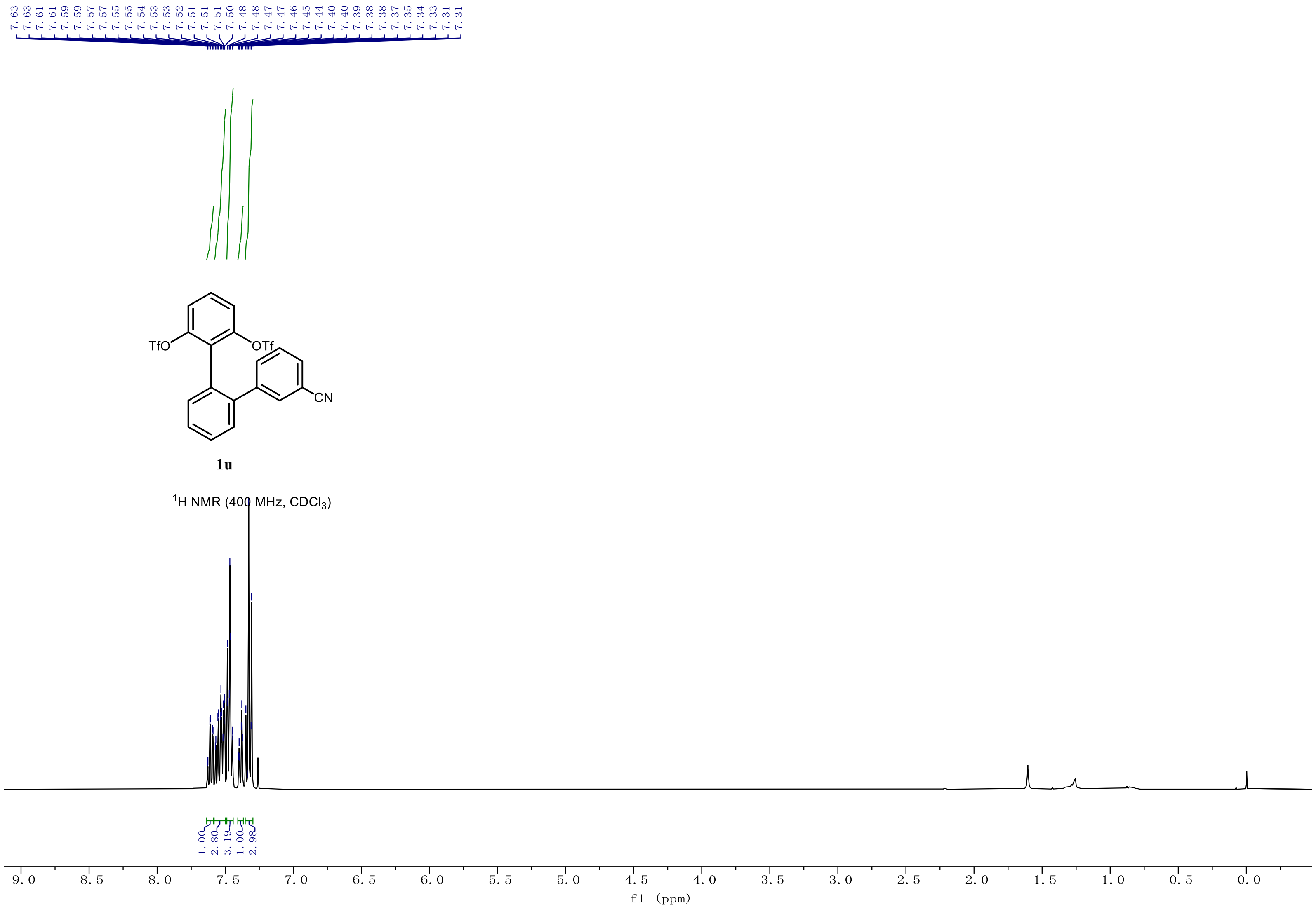
1t

^{1}H NMR (400 MHz, $CDCl_3$)

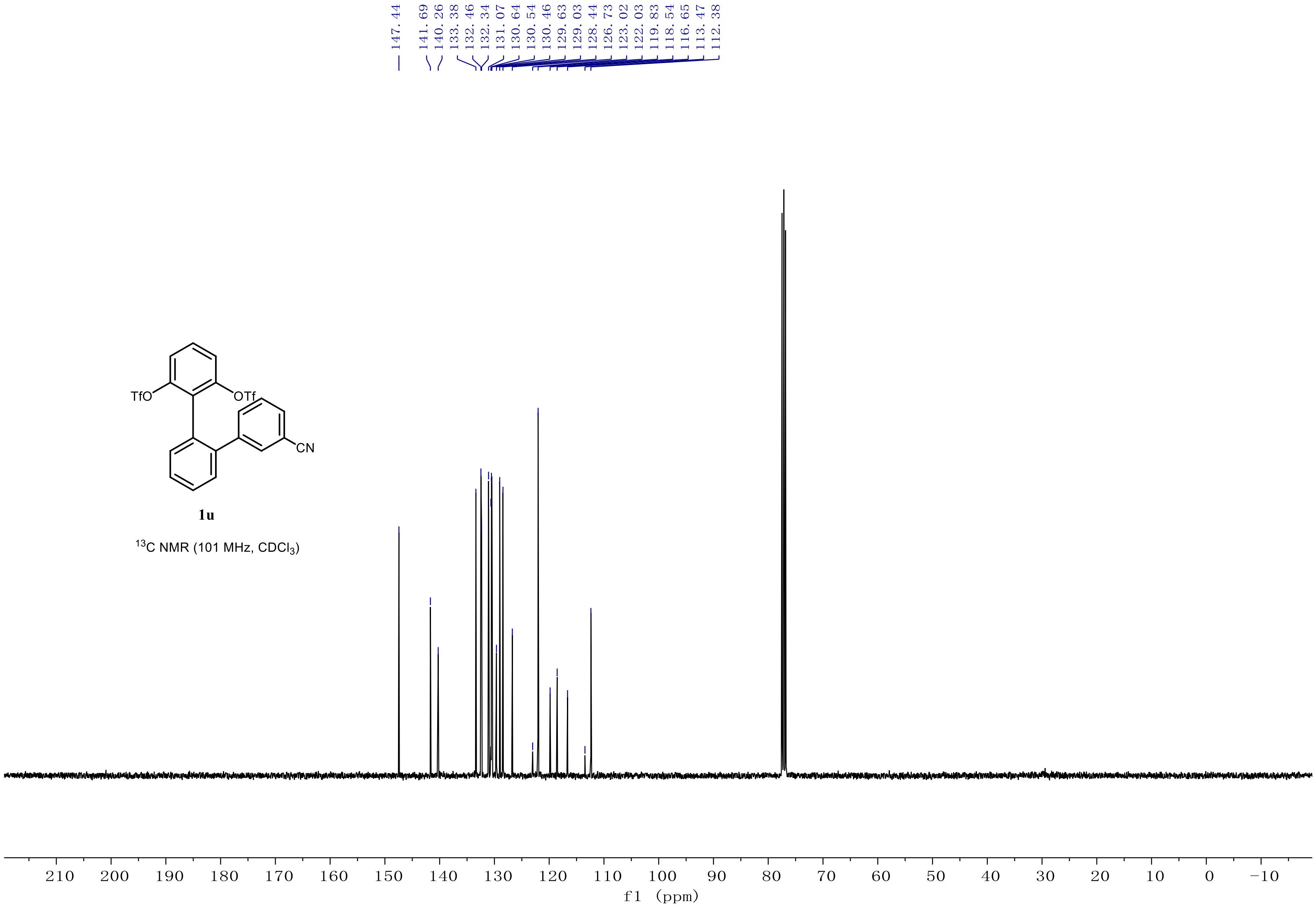



147.46
145.18
140.73
132.38
131.97
130.60
130.48
130.40
129.73
129.64
128.52
126.63
123.01
122.05
121.33
119.83
118.82
116.65
113.46
111.29
TfO
OTf
CN
1t
13C NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


-74.07
TfO
OTf
CN
1t
^{19}F NMR (376 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



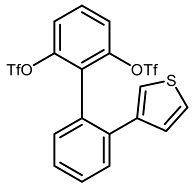
TfO
OTf
CN
1u
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)



1u

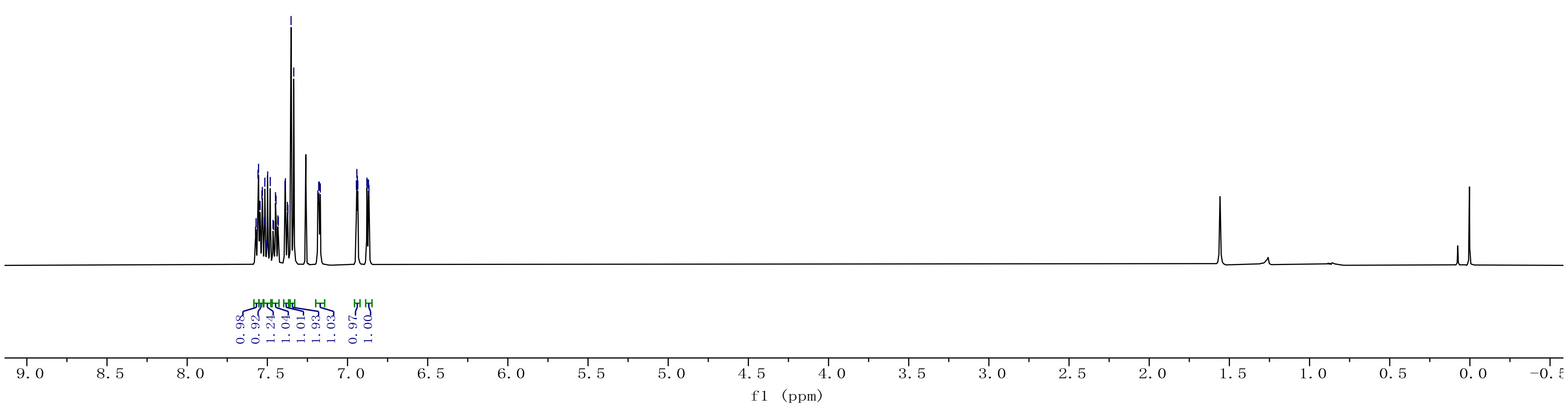
^{13}C NMR (101 MHz, $CDCl_3$)

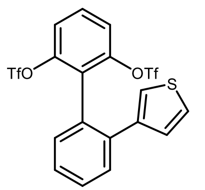

-74.06
TfO
OTf
CN
1u
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



1v

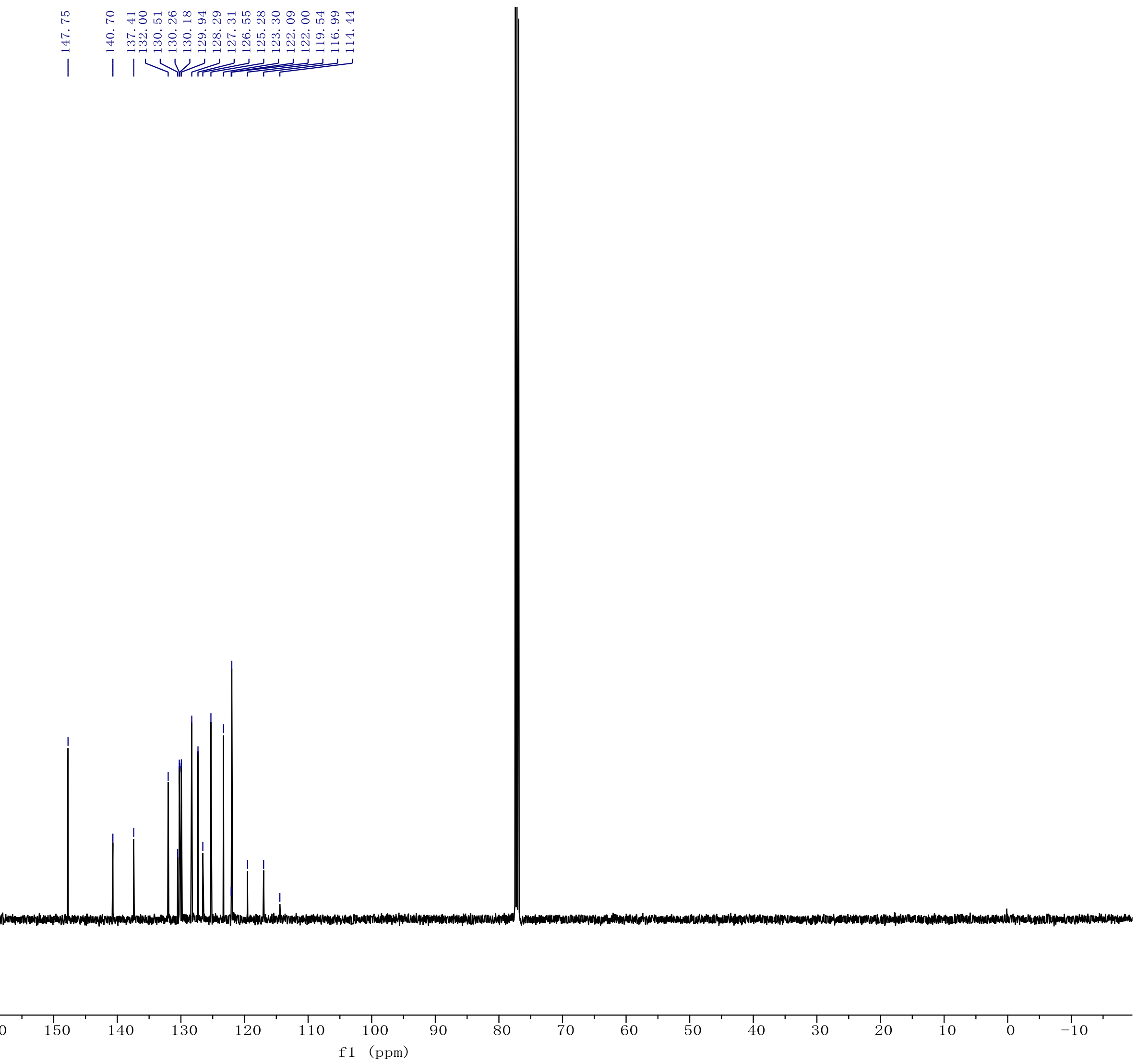
^{1}H NMR (500 MHz, CDCl$_3$)

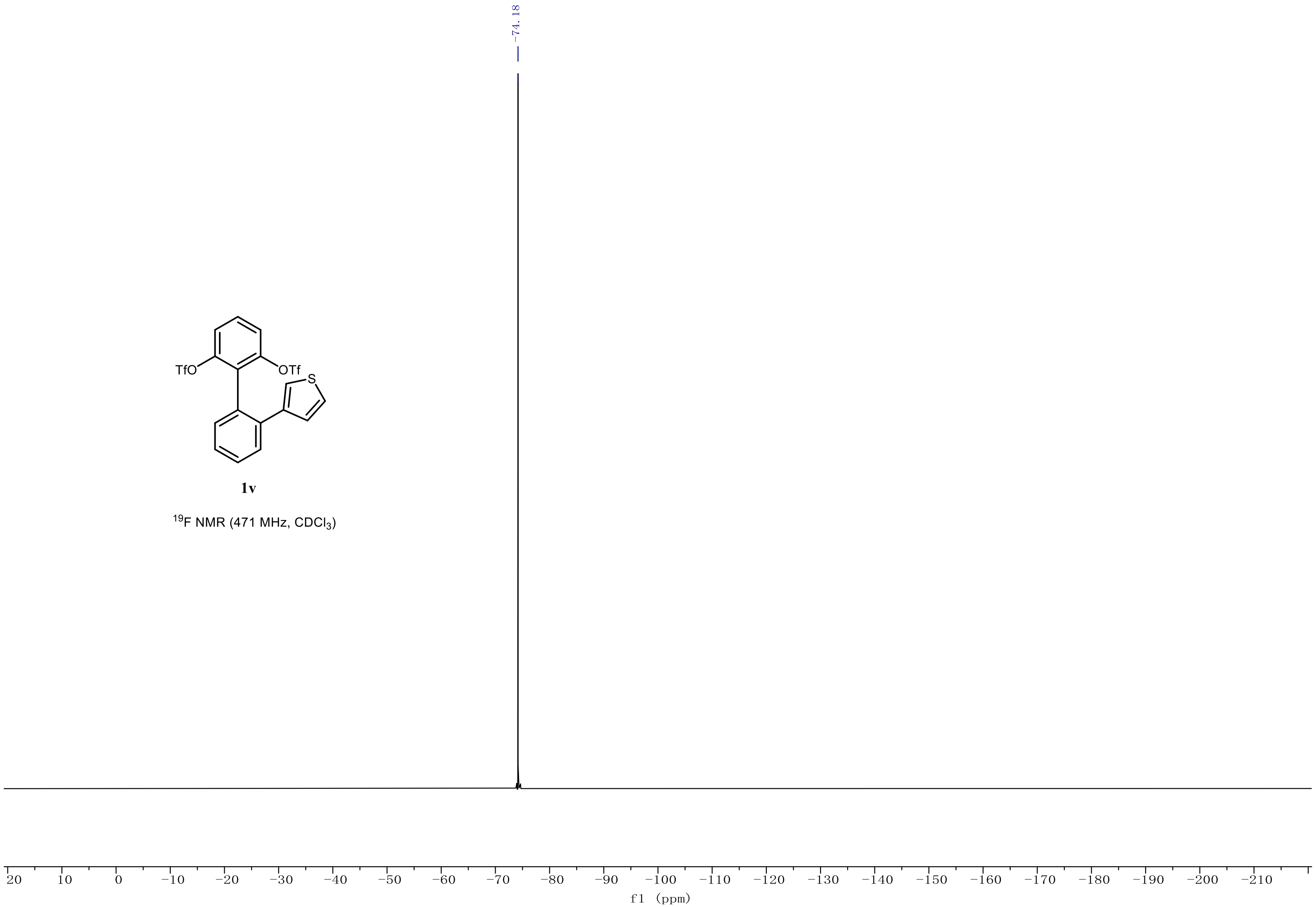


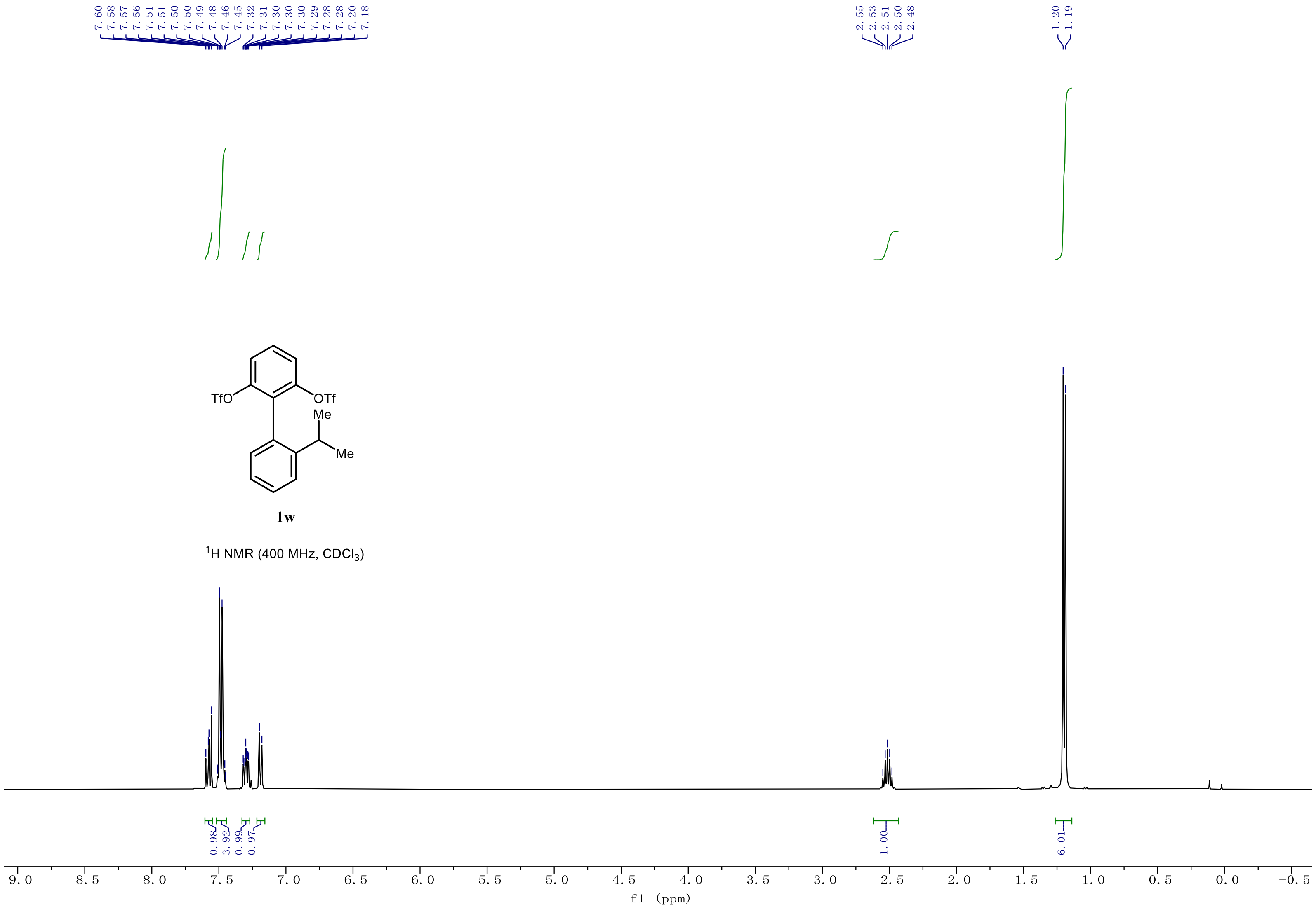


1v

^{13}C NMR (126 MHz, $CDCl_3$)

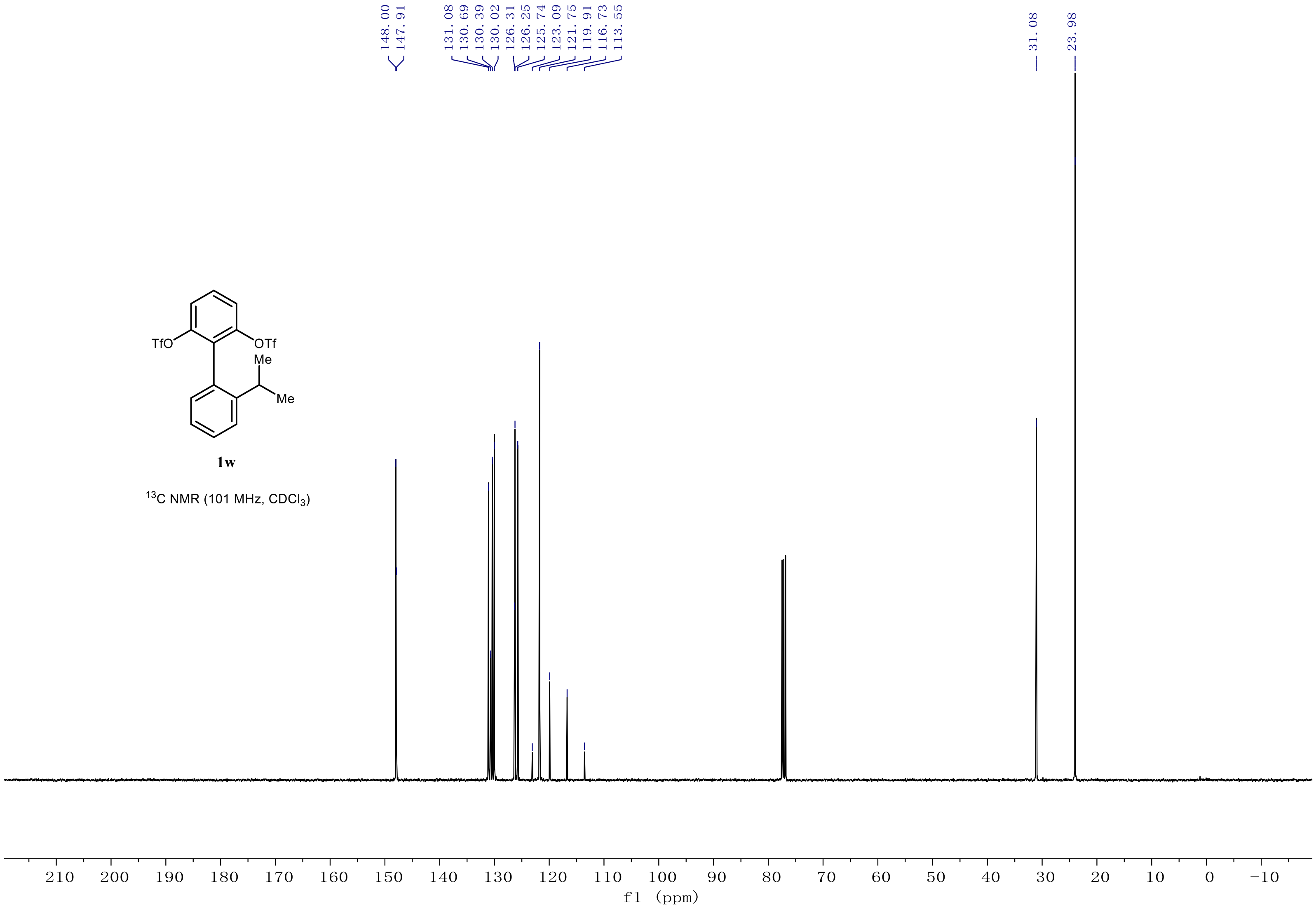



-74.18
TfO
OTf
S
1v
19F NMR (471 MHz, CDCl3)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



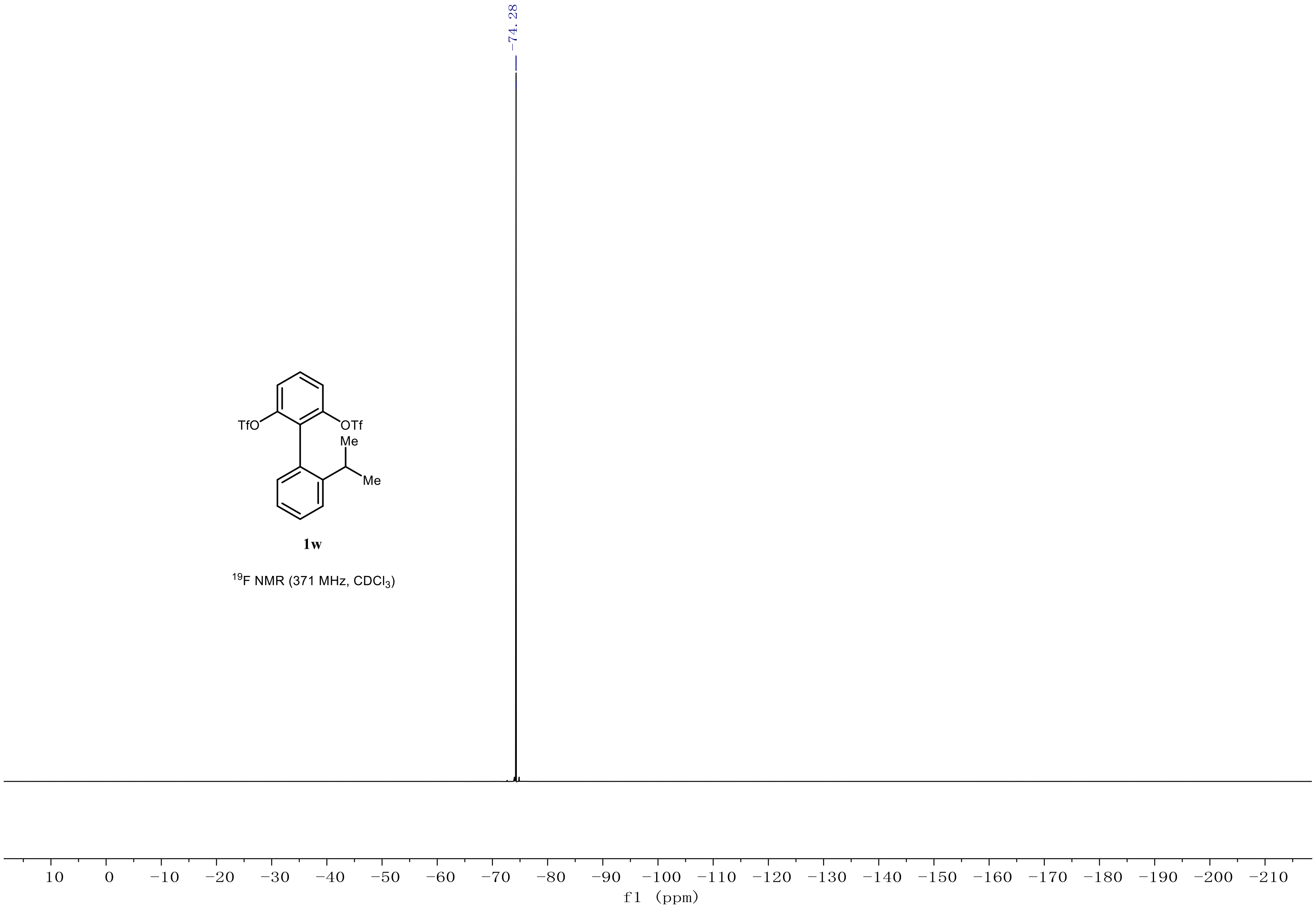
1w

^{1}H NMR (400 MHz, $CDCl_3$)



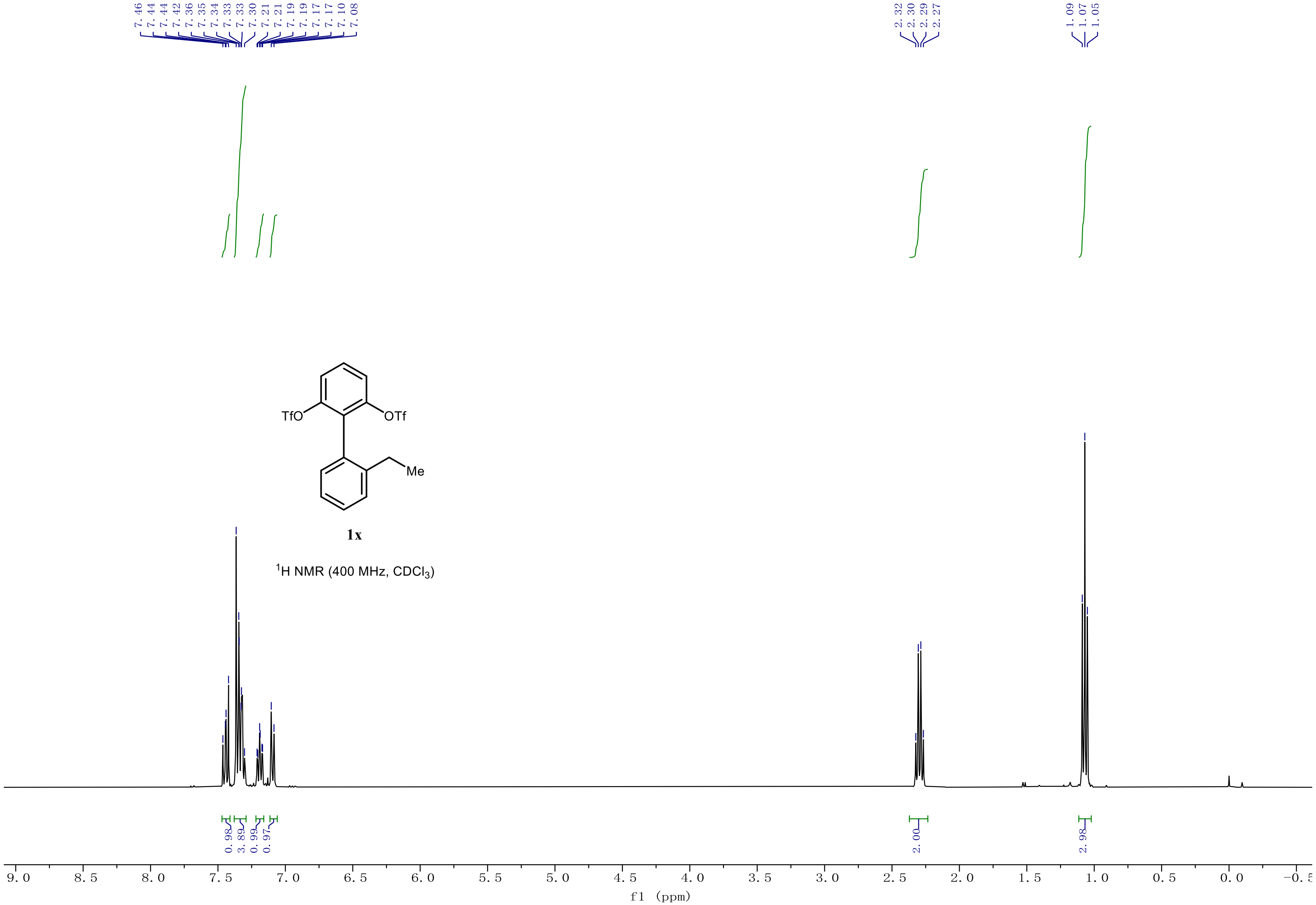
1w

^{13}C NMR (101 MHz, $CDCl_3$)



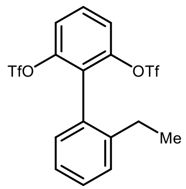
1w

^{19}F NMR (371 MHz, $CDCl_3$)



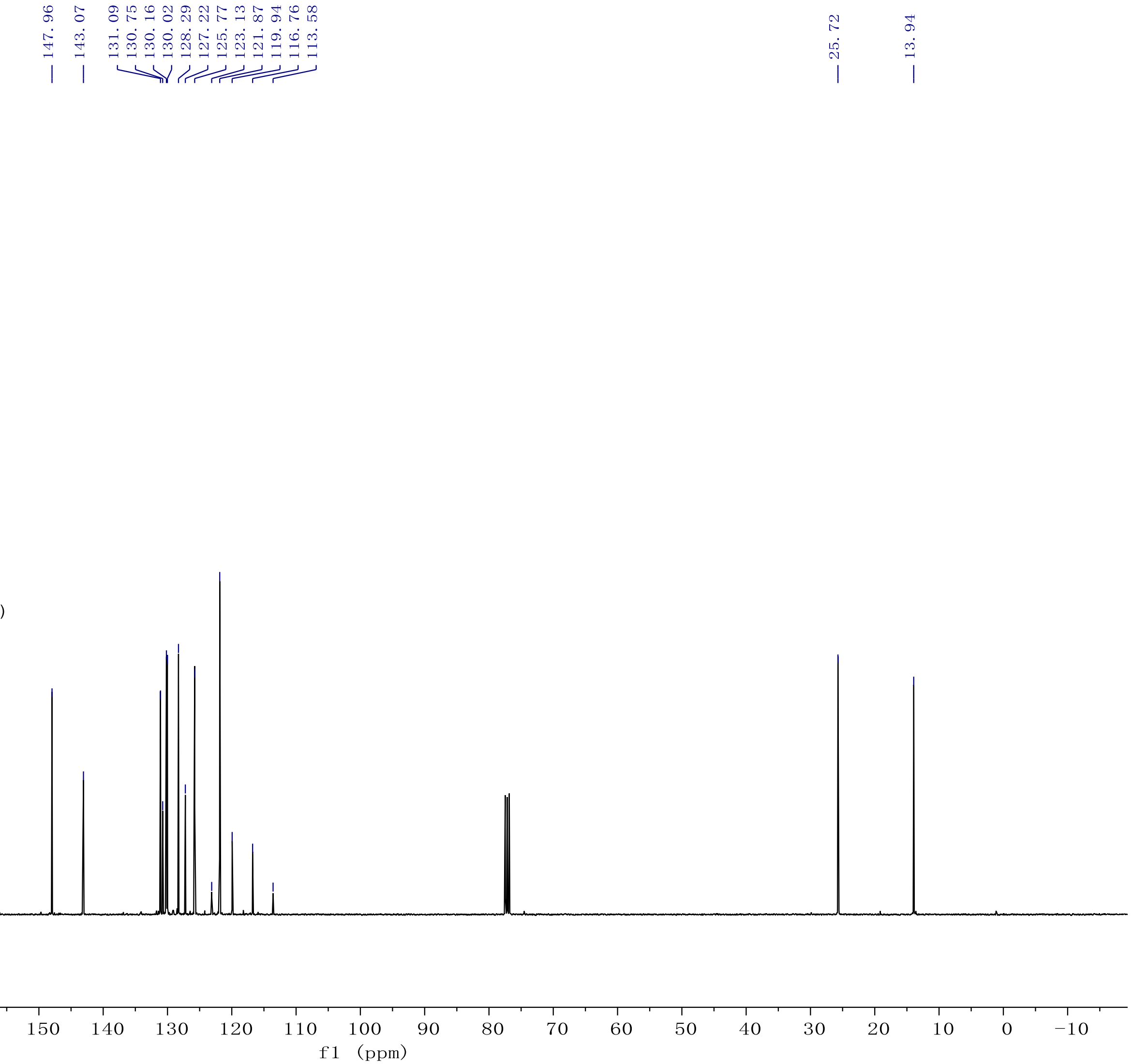
1x

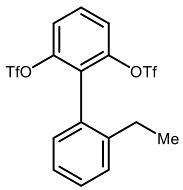
^{1}H NMR (400 MHz, $CDCl_3$)



1x

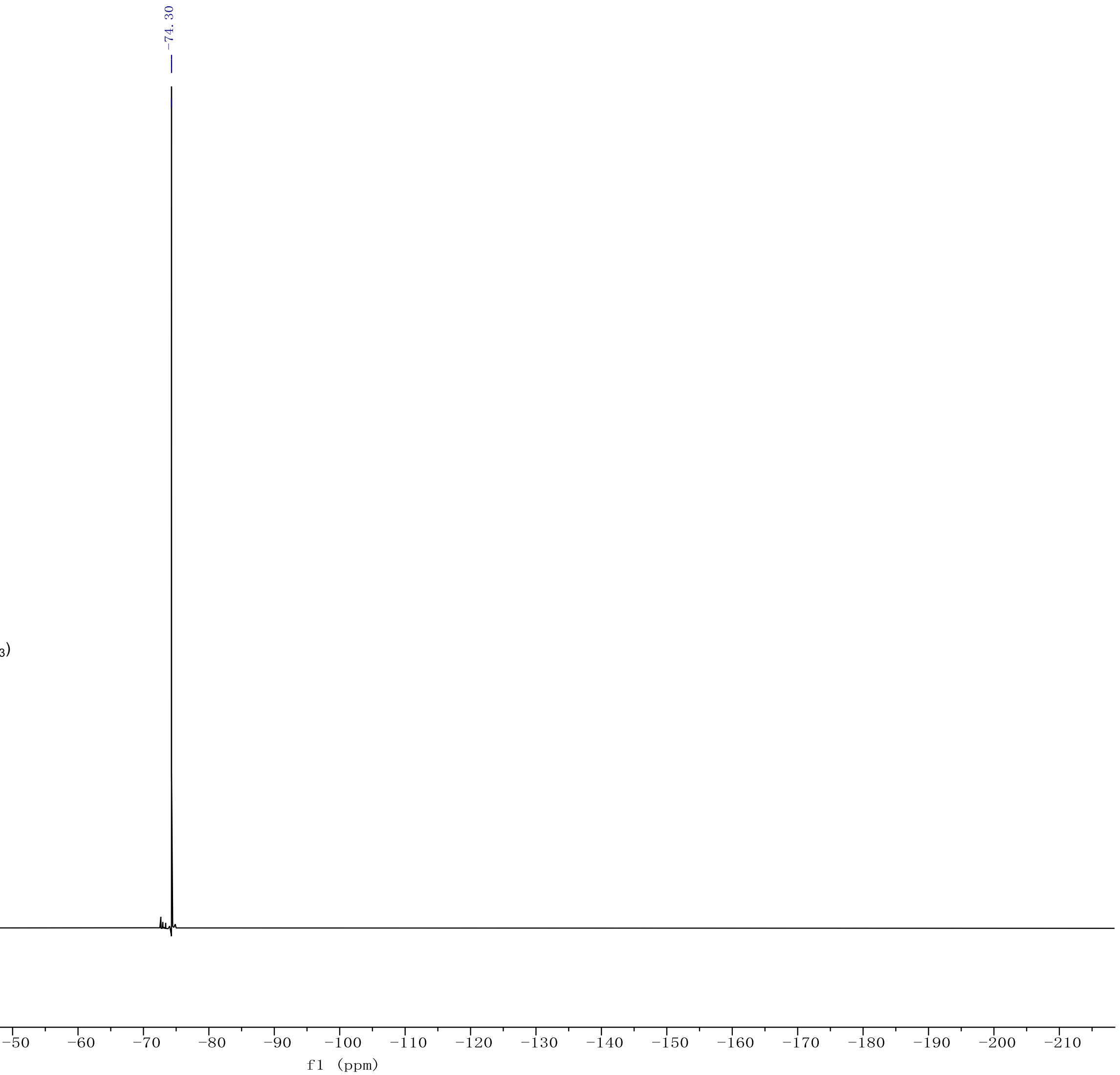
^{13}C NMR (101 MHz, $CDCl_3$)

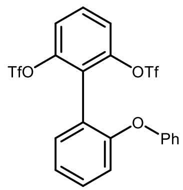




1x

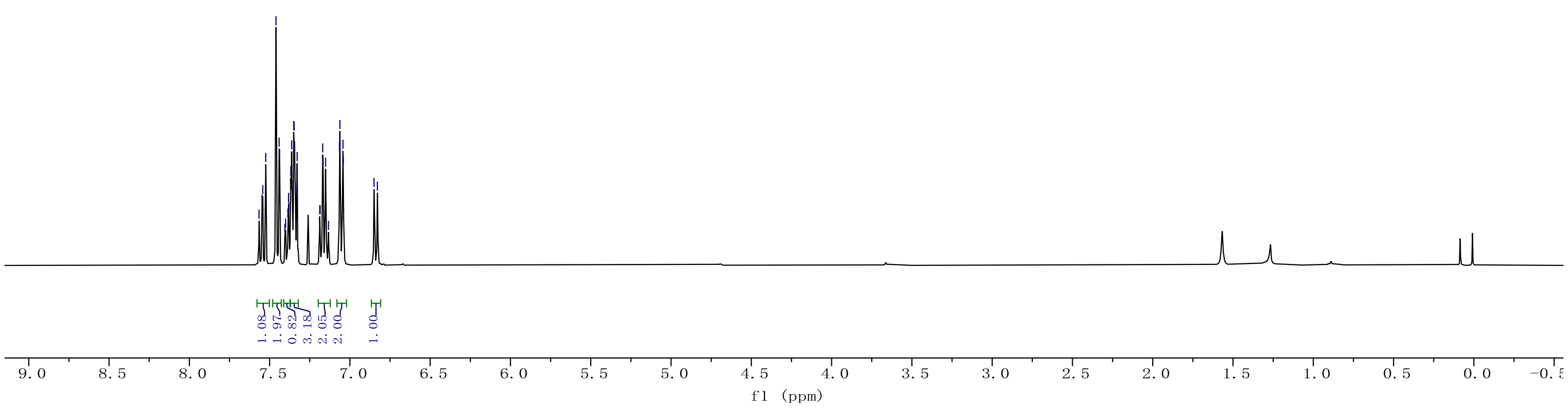
^{19}F NMR (376 MHz, $CDCl_3$)





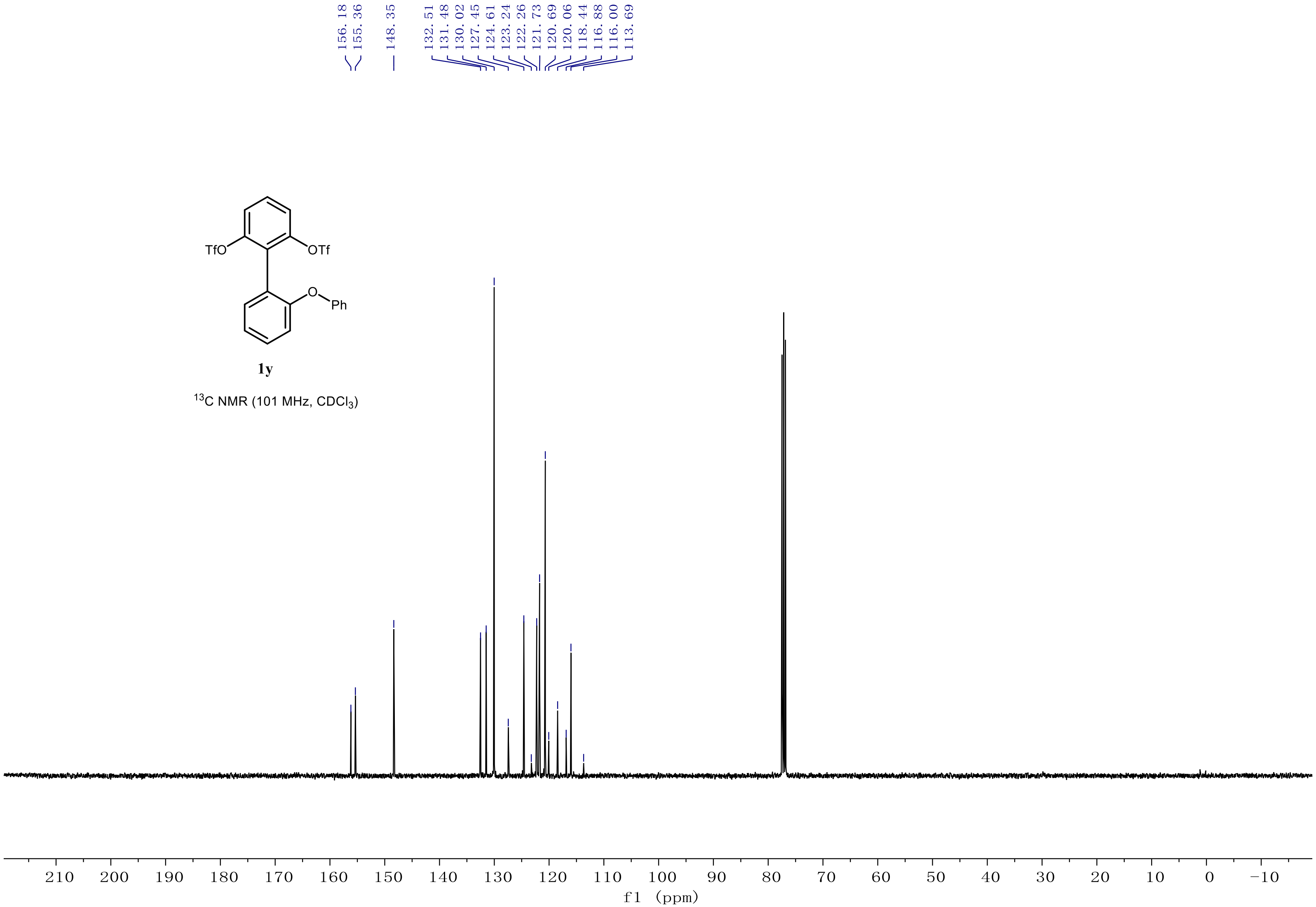
1y

^1H NMR (400 MHz, $CDCl_3$)

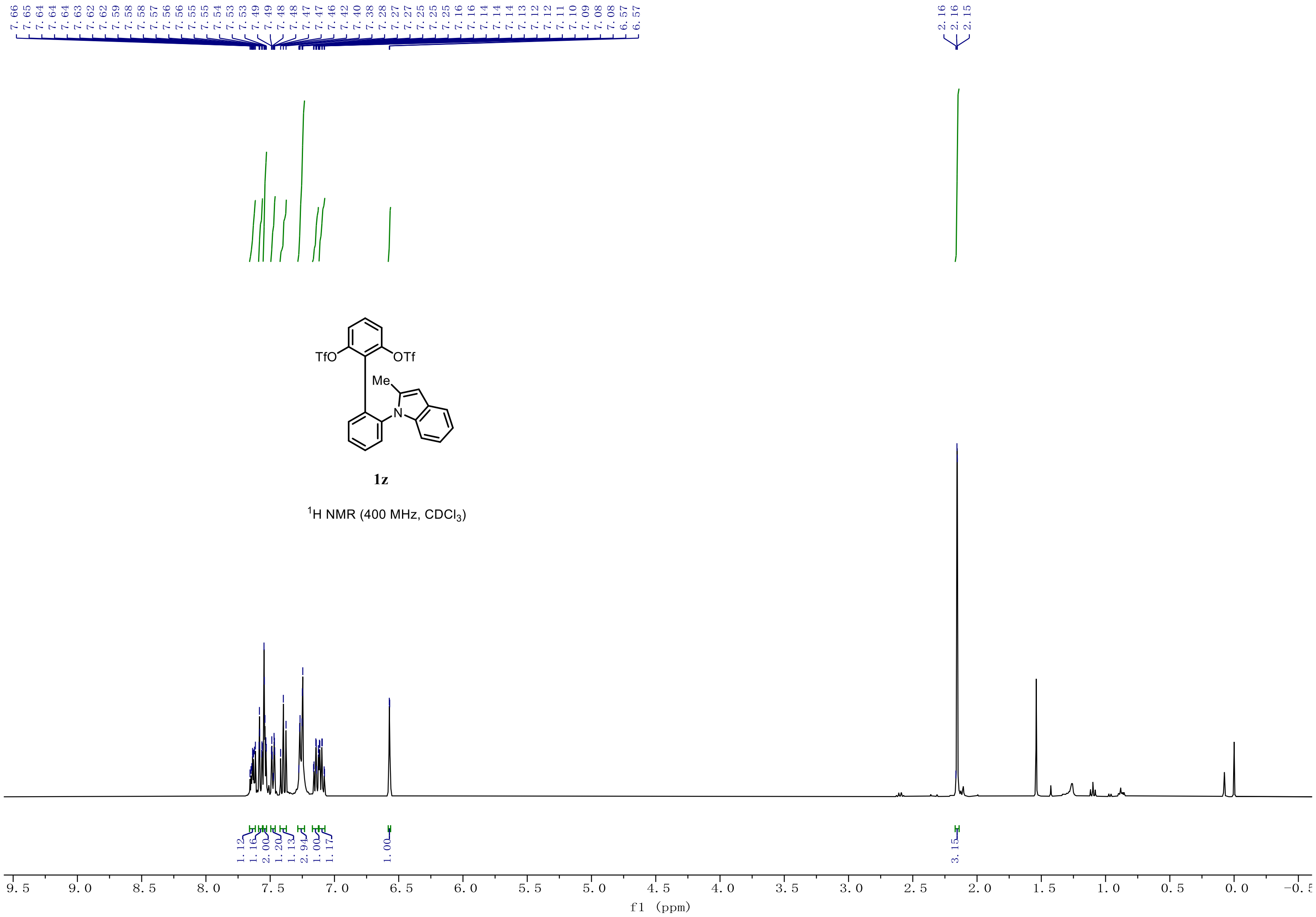


1y

^{13}C NMR (101 MHz, $CDCl_3$)

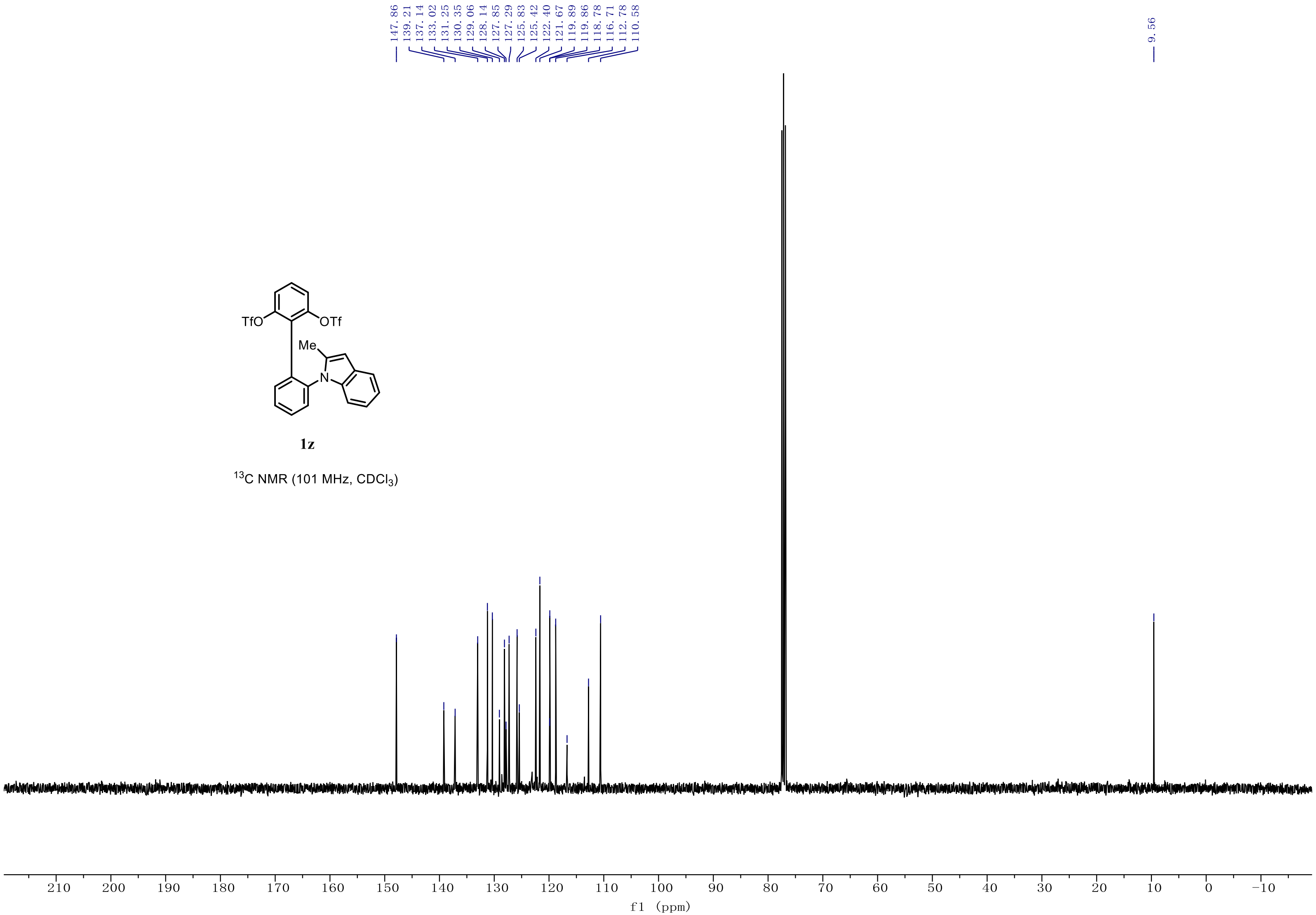


^{19}F NMR (376 MHz, $CDCl_3$)



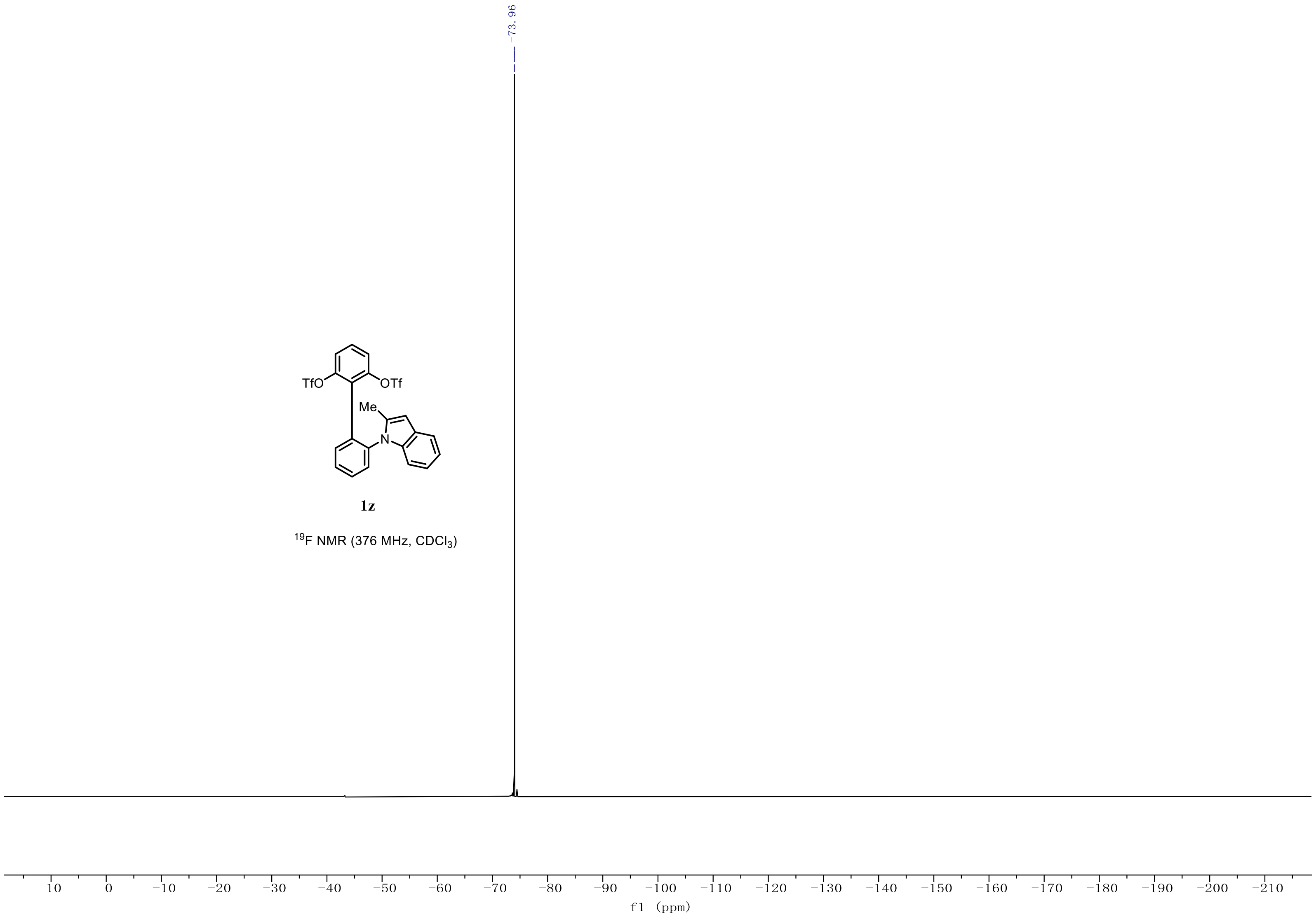
1z

^{1}H NMR (400 MHz, $CDCl_3$)



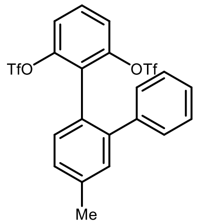
1z

^{13}C NMR (101 MHz, $CDCl_3$)



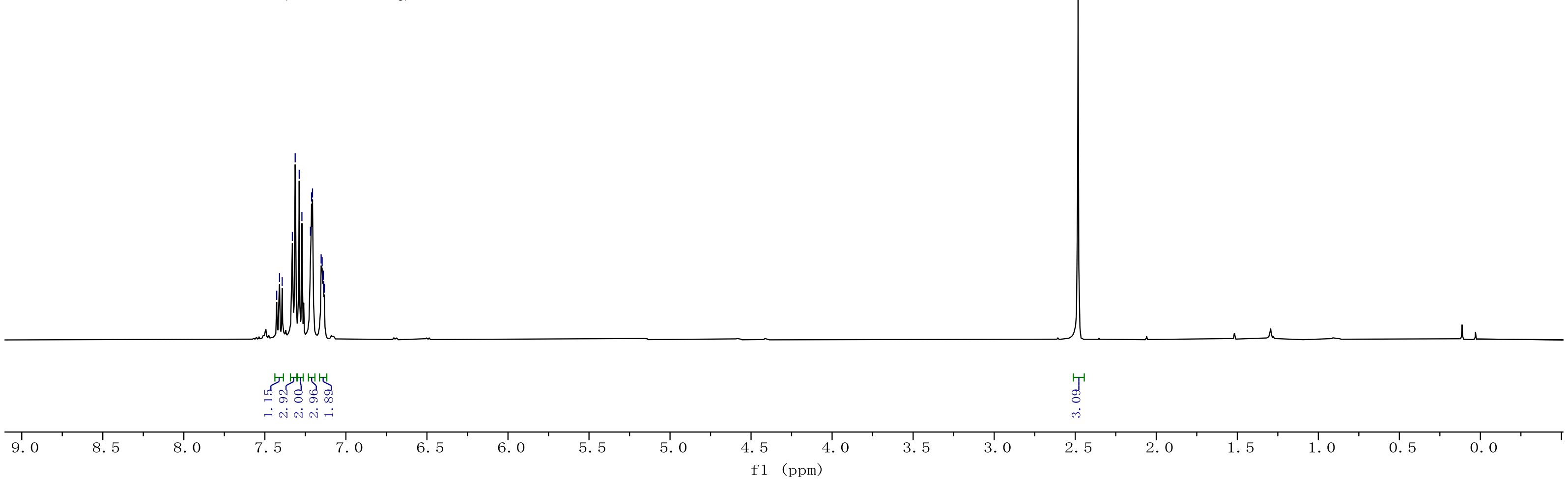
1z

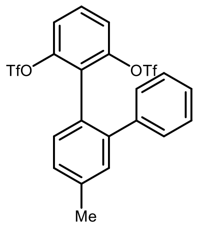
^{19}F NMR (376 MHz, $CDCl_3$)



1aa

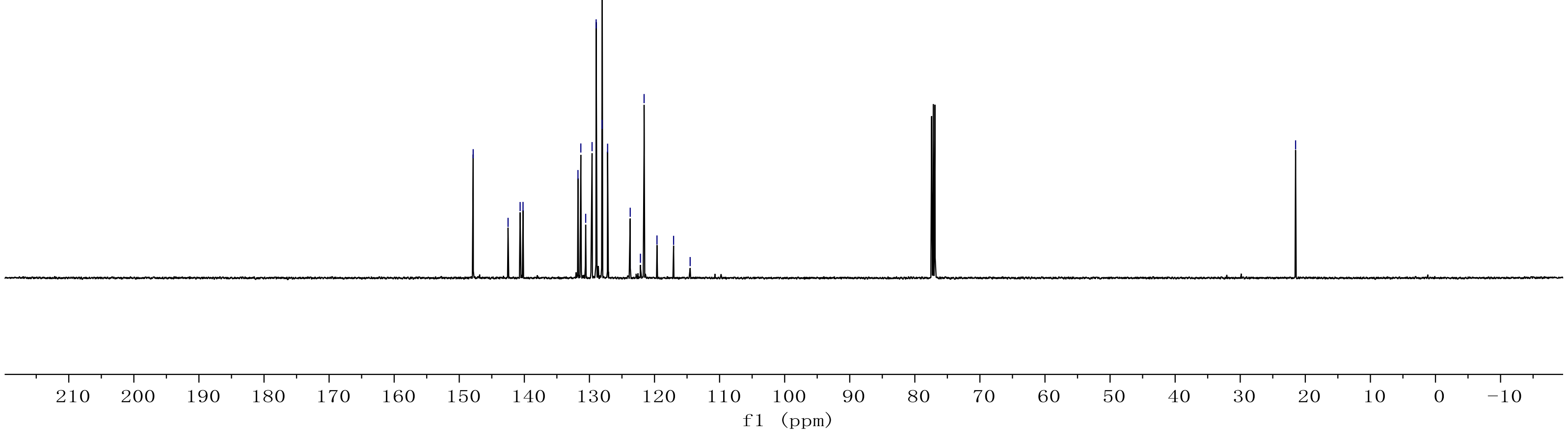
^{1}H NMR (500 MHz, $CDCl_3$)

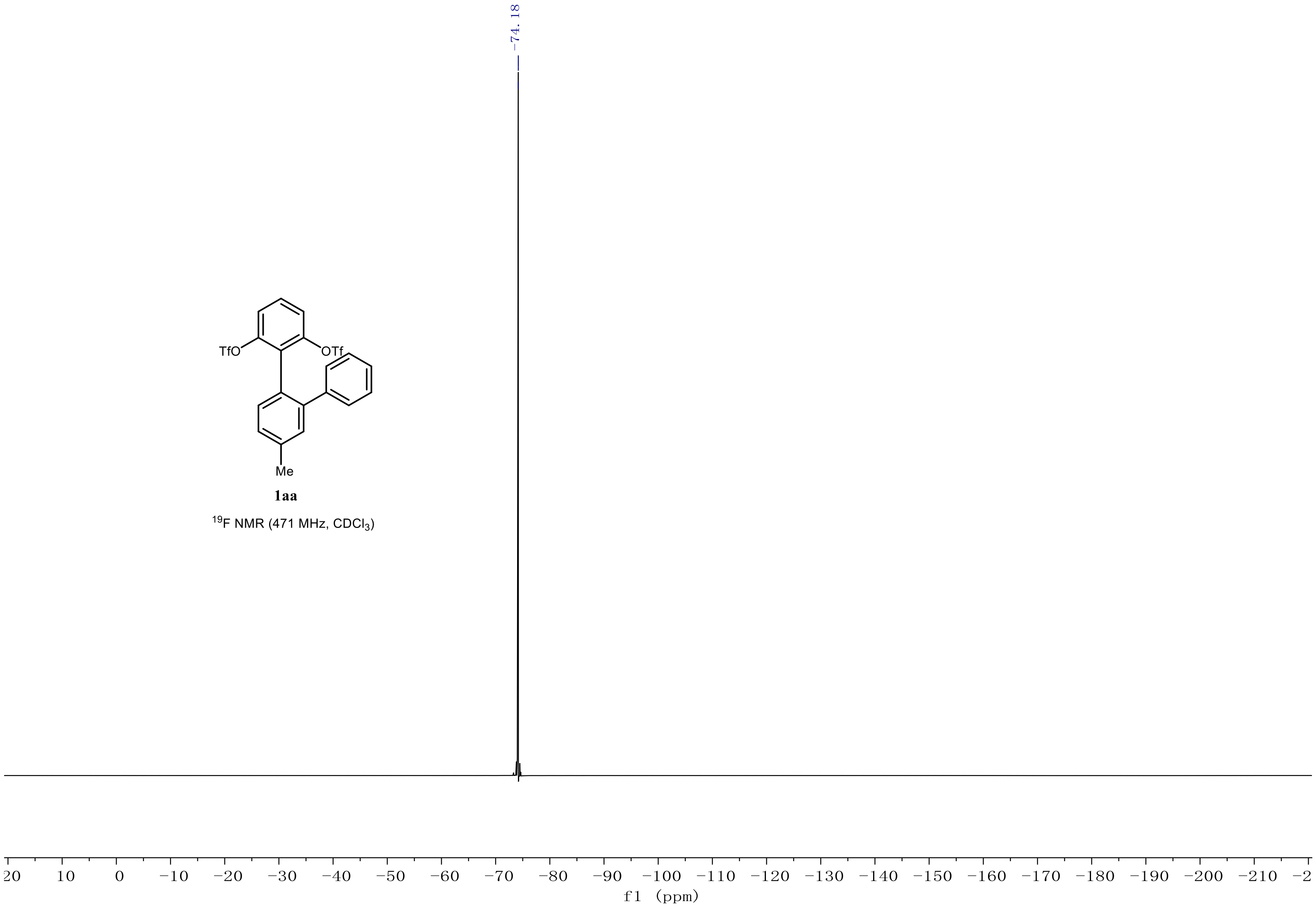




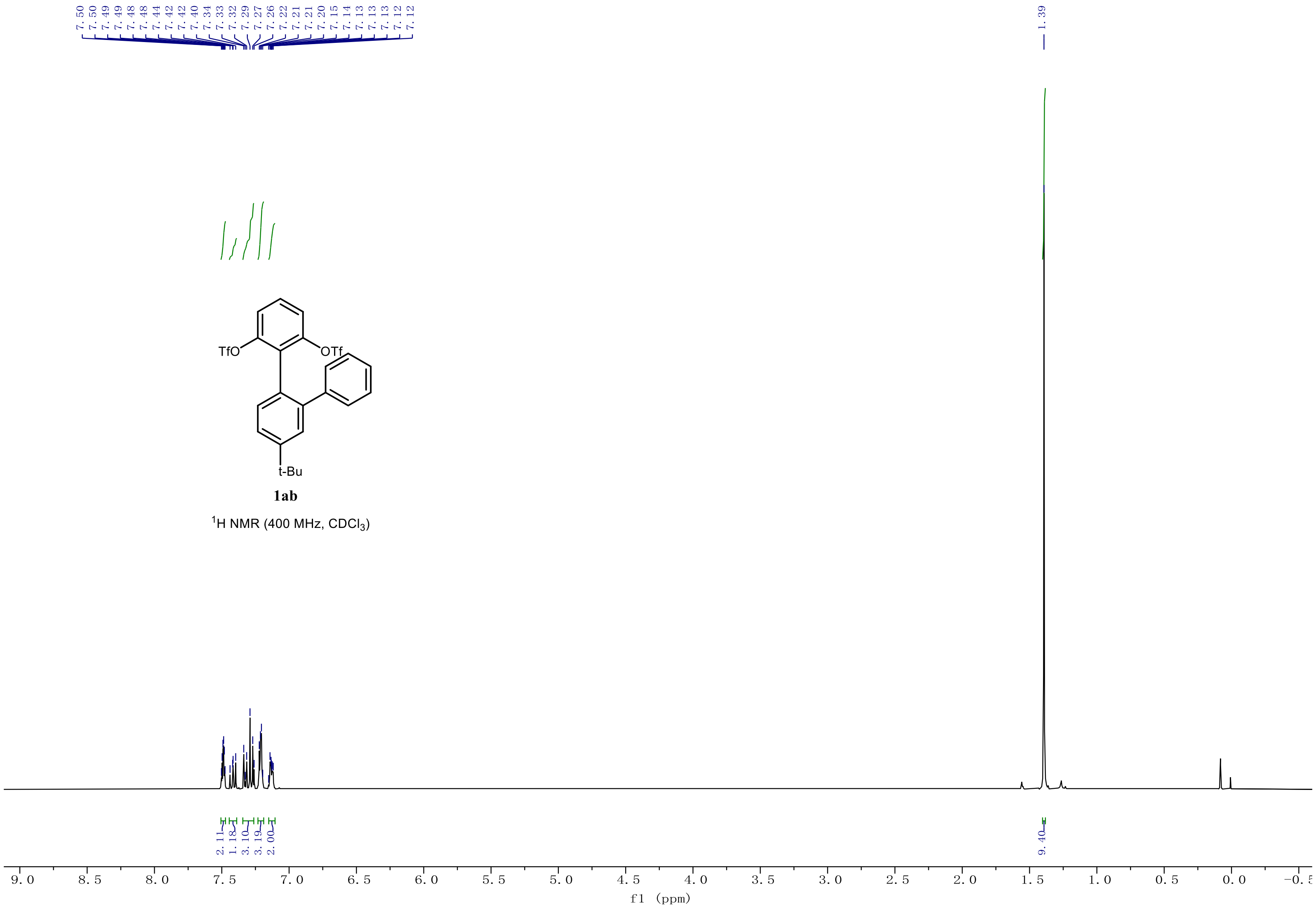
1aa

^{13}C NMR (126 MHz, $CDCl_3$)



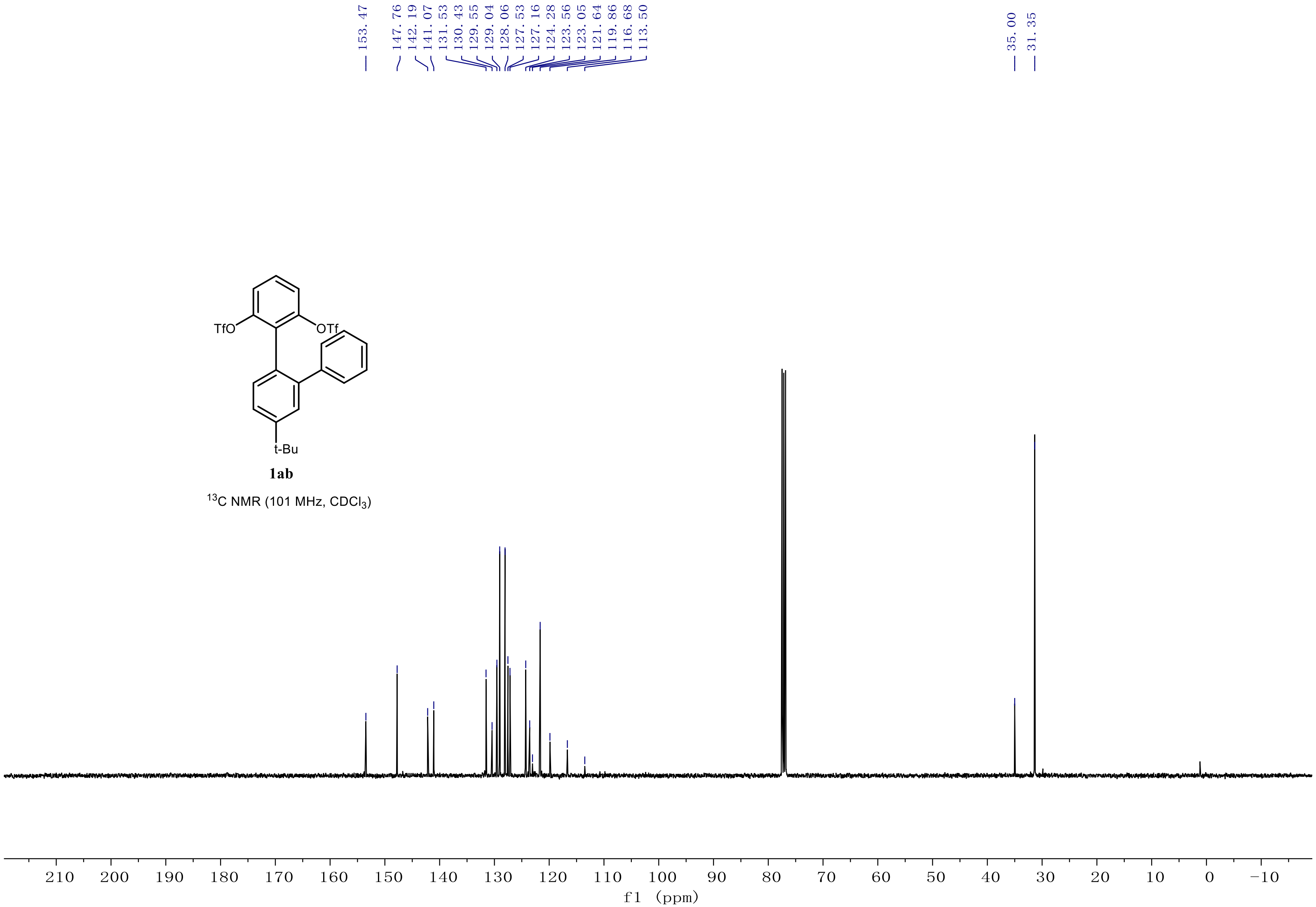


−74.18
TfO
OTf
Me
1aa
19F NMR (471 MHz, CDCl3)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



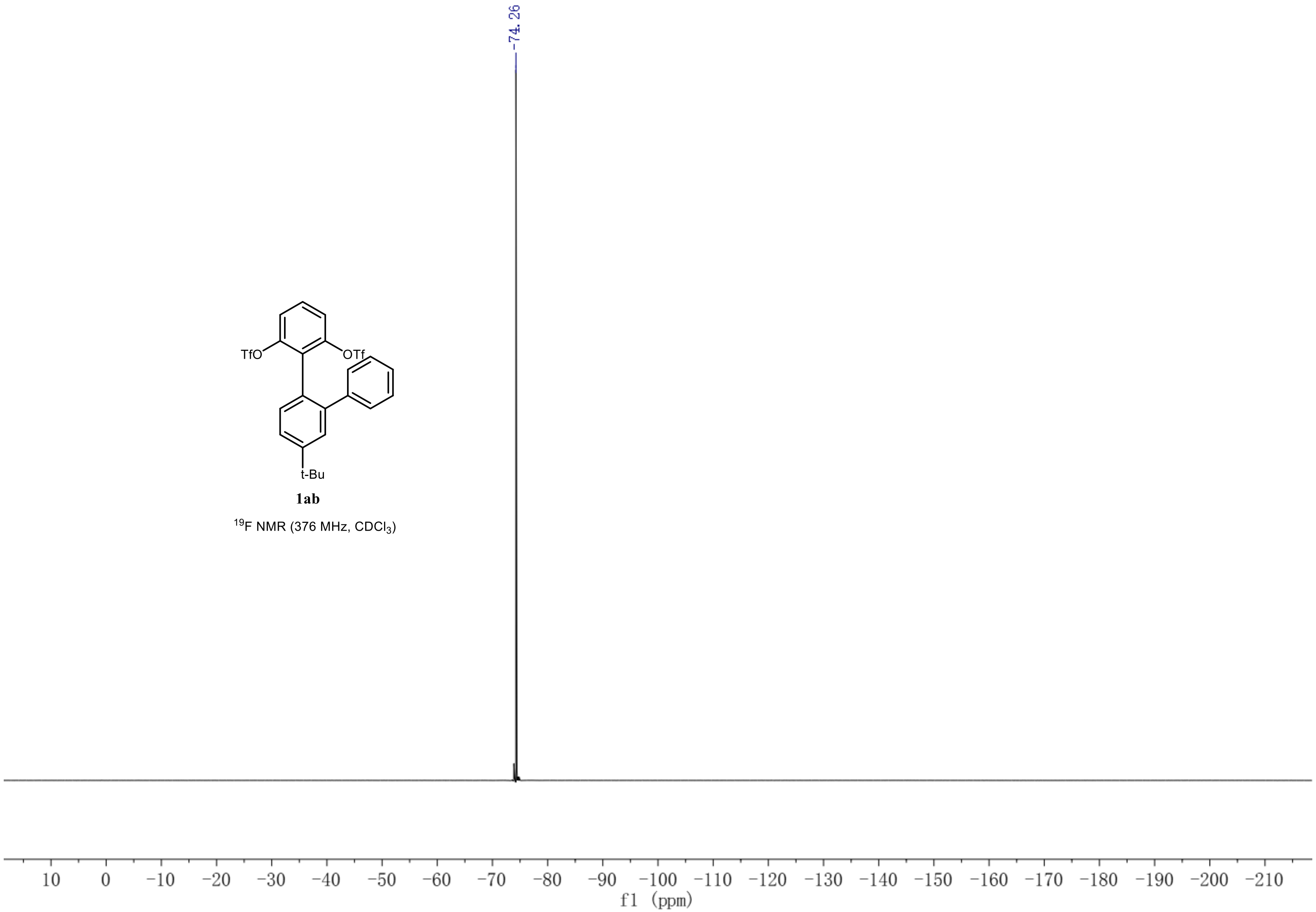
1ab

^{1}H NMR (400 MHz, $CDCl_3$)



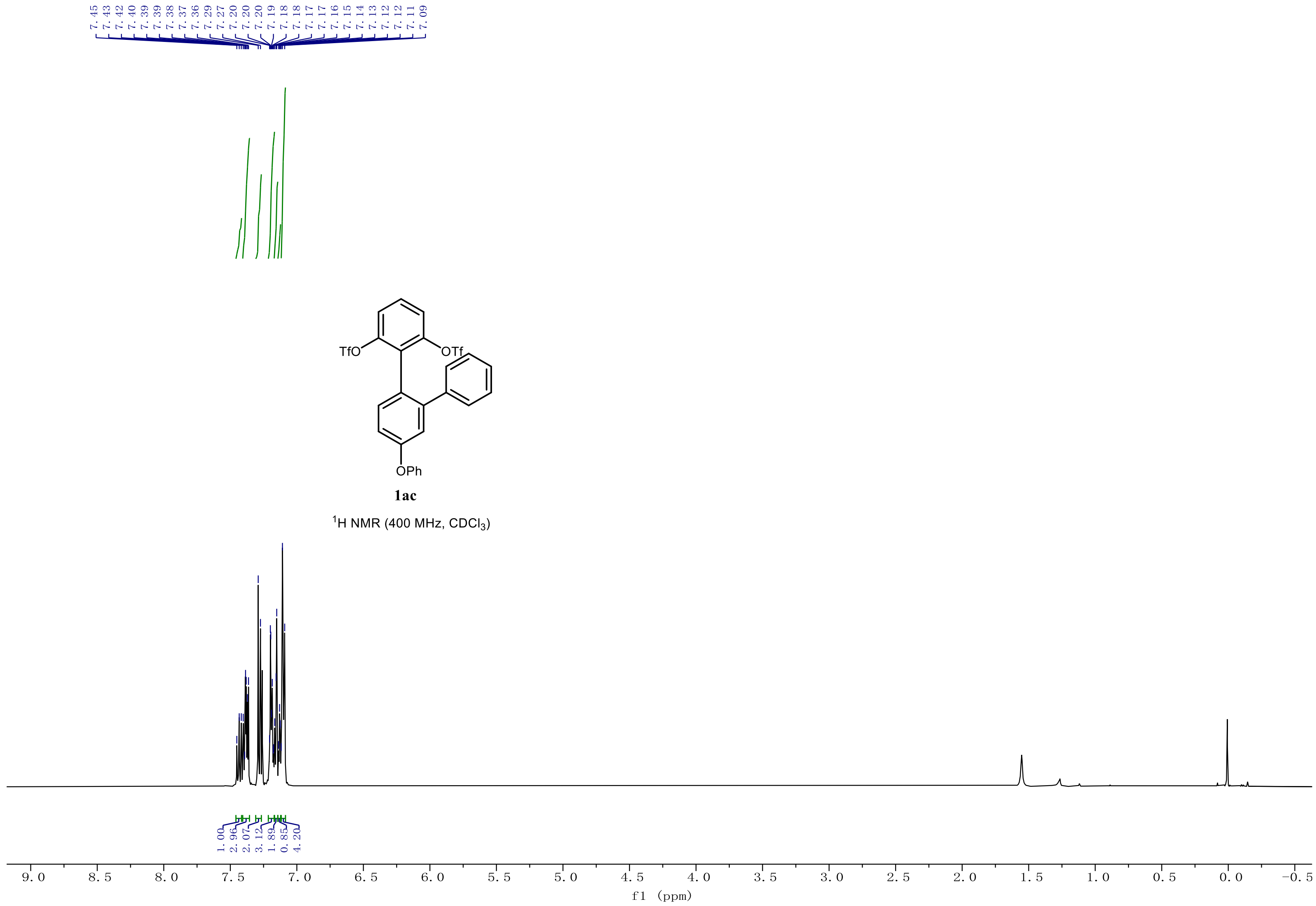
1ab

^{13}C NMR (101 MHz, $CDCl_3$)



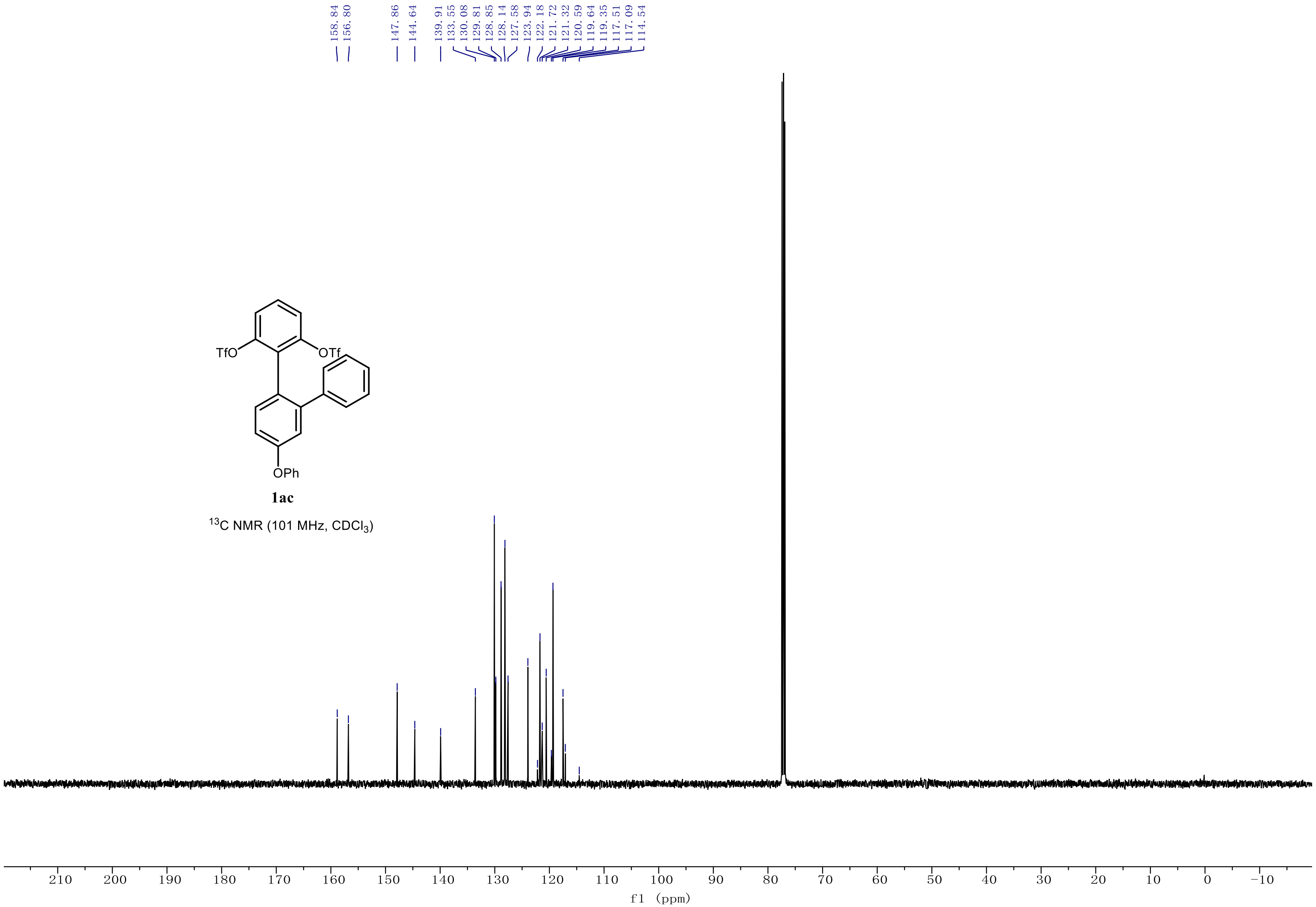
1ab

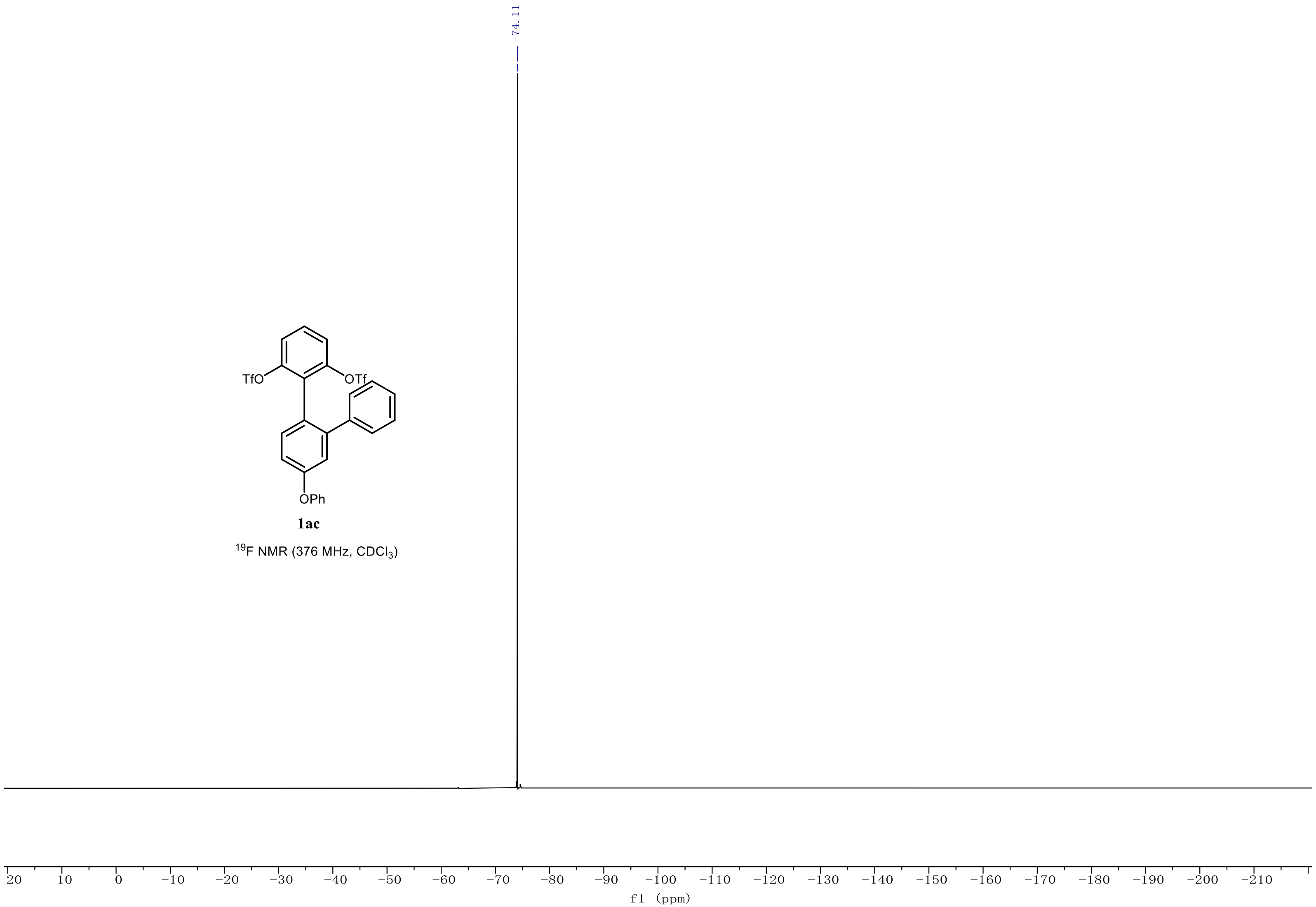
^{19}F NMR (376 MHz, CDCl$_3$)



1ac

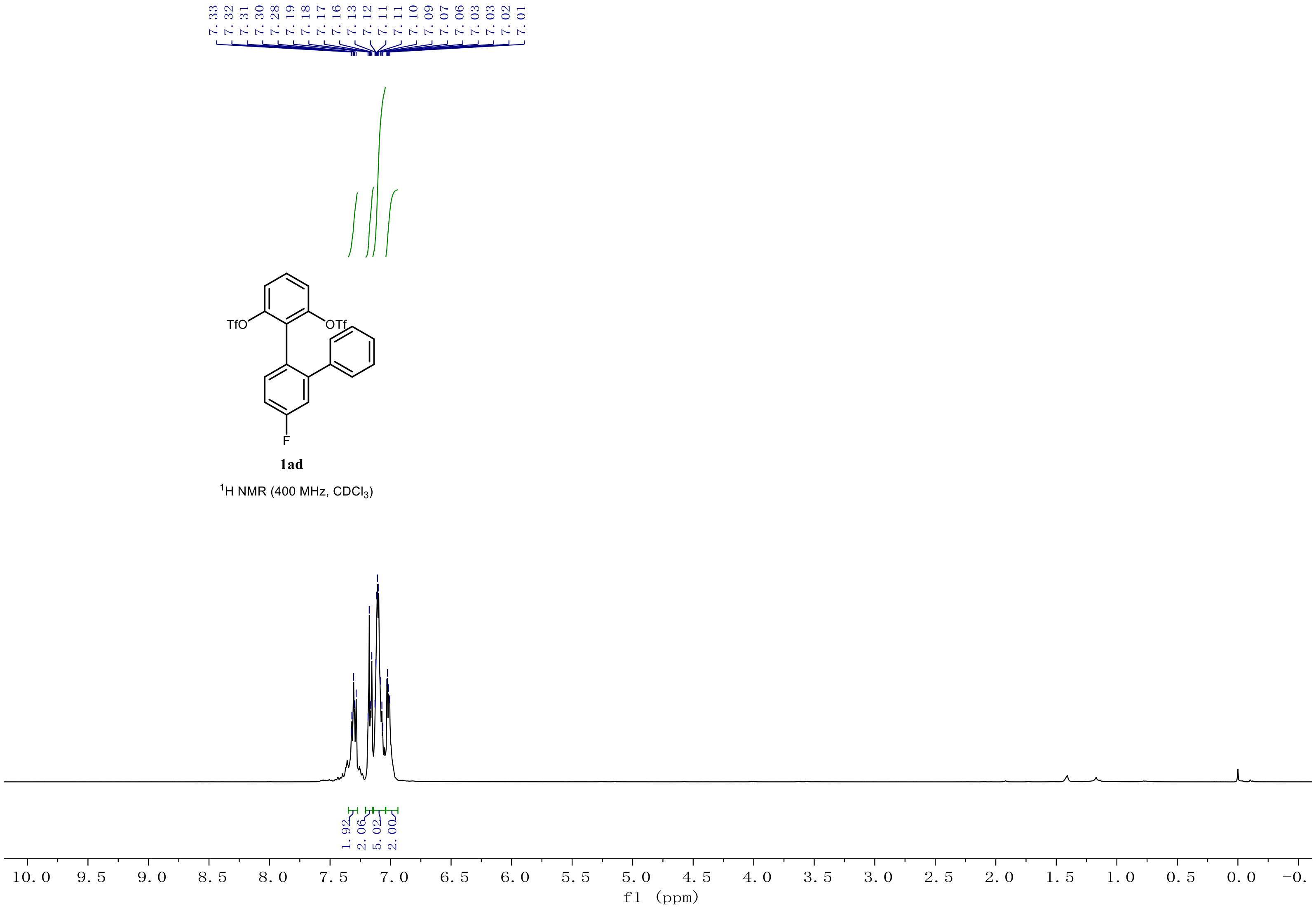
^{1}H NMR (400 MHz, $CDCl_3$)


158.84
156.80
147.86
144.64
139.91
133.55
130.08
129.81
128.85
128.14
127.58
123.94
122.18
121.72
121.32
120.59
119.64
119.35
117.51
117.09
114.54
TfO
OTf
OPh
1ac
^{13}C NMR (101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



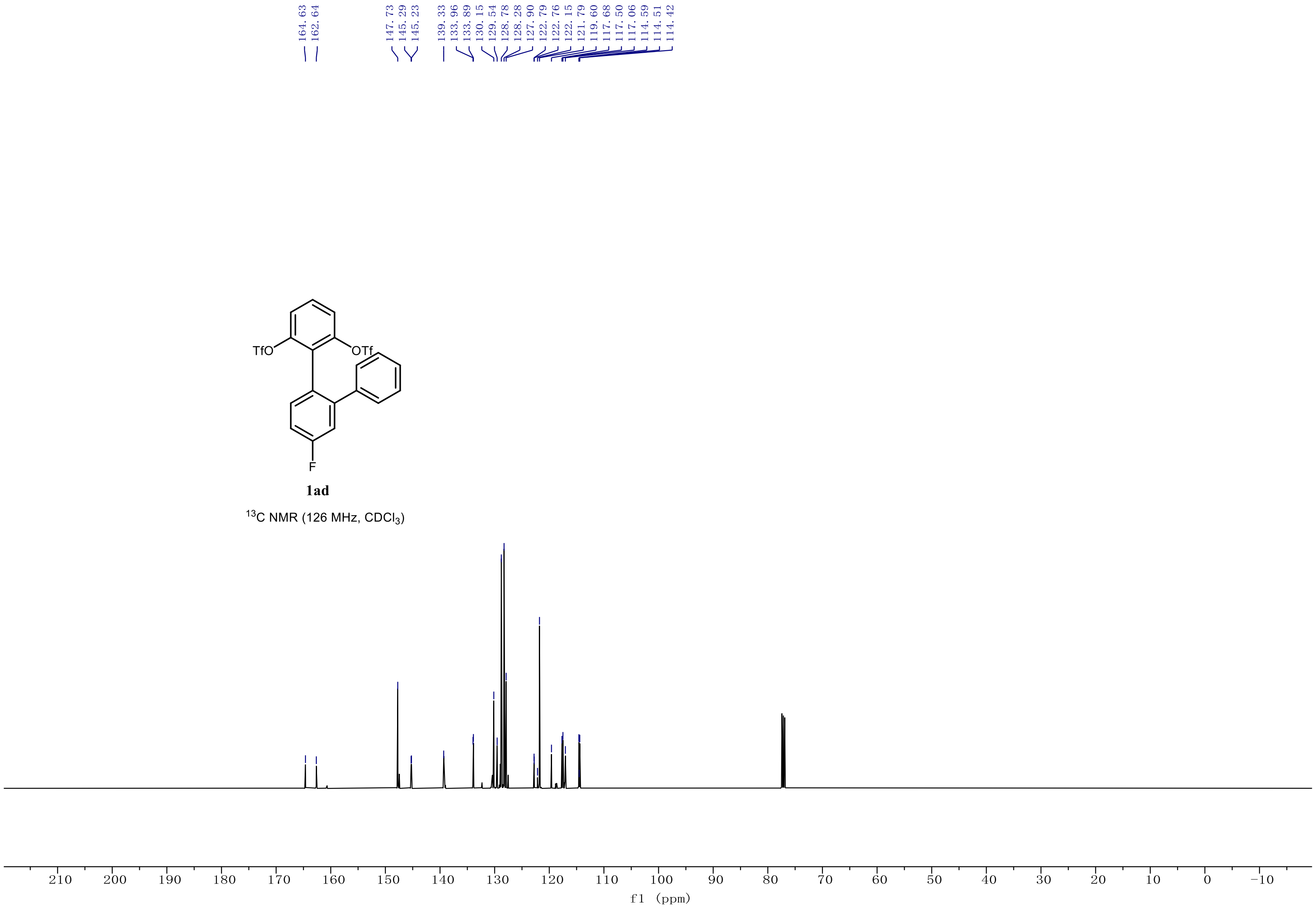
1ac

^{19}F NMR (376 MHz, $CDCl_3$)



1ad

^{1}H NMR (400 MHz, $CDCl_3$)

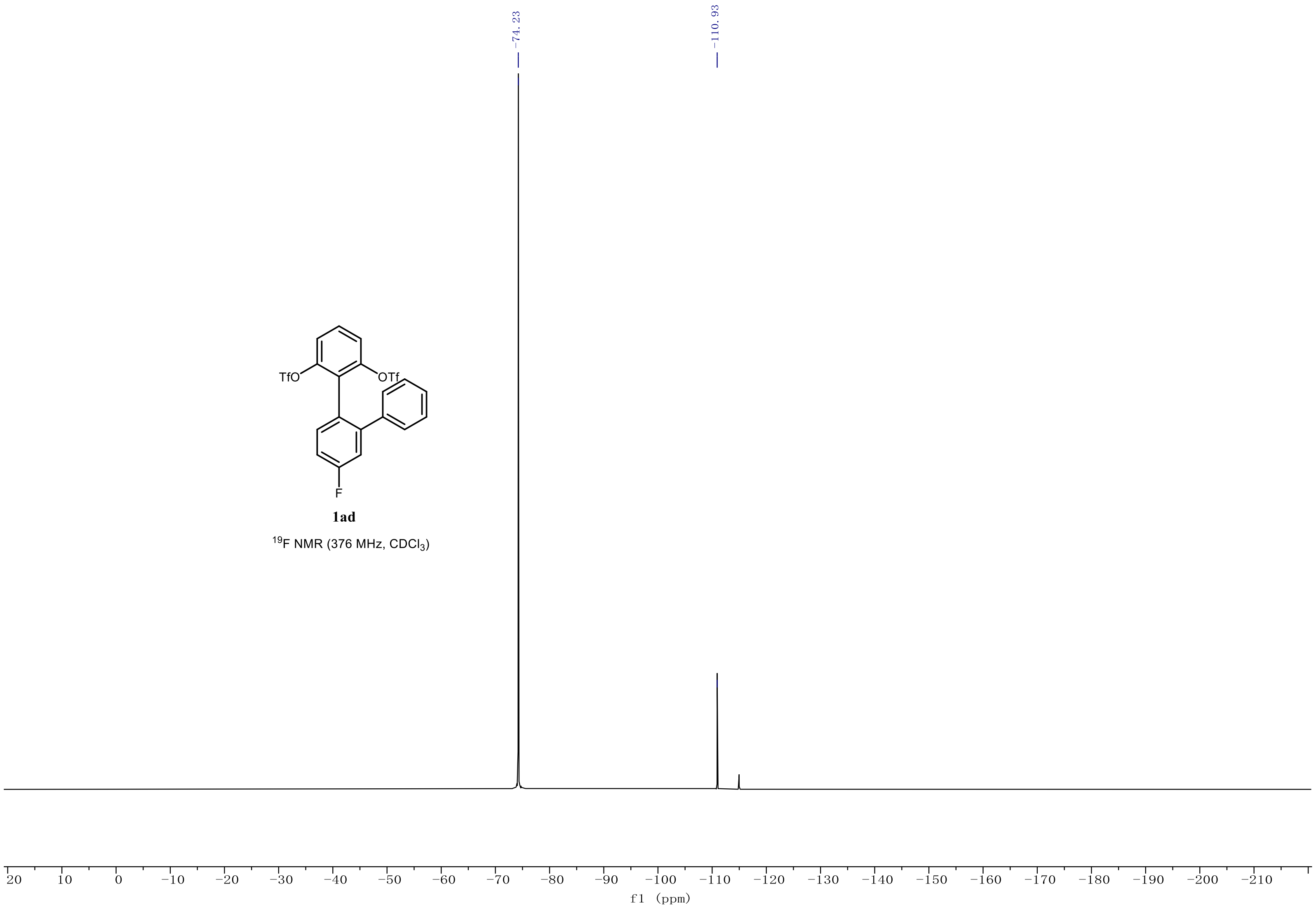


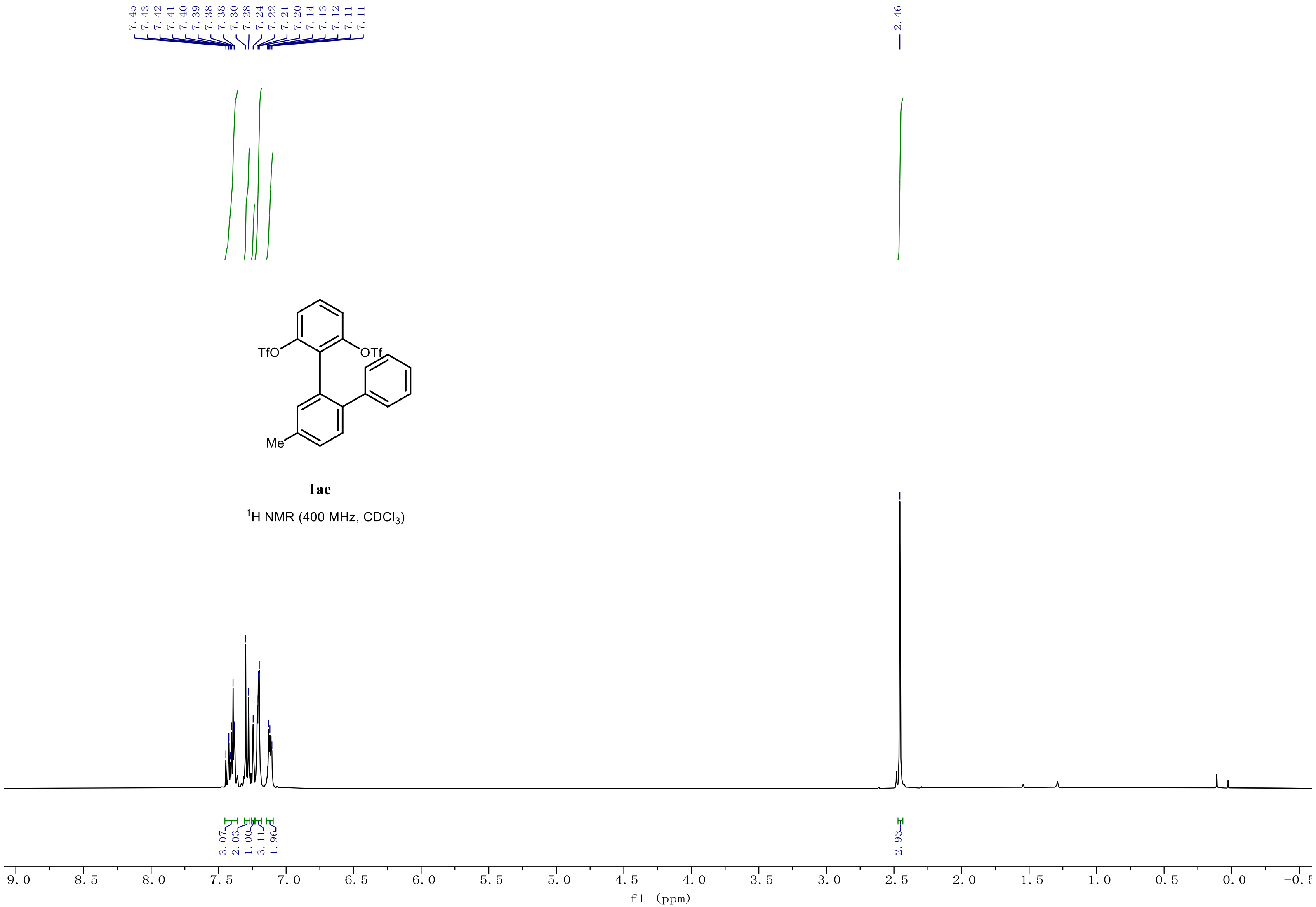
1ad

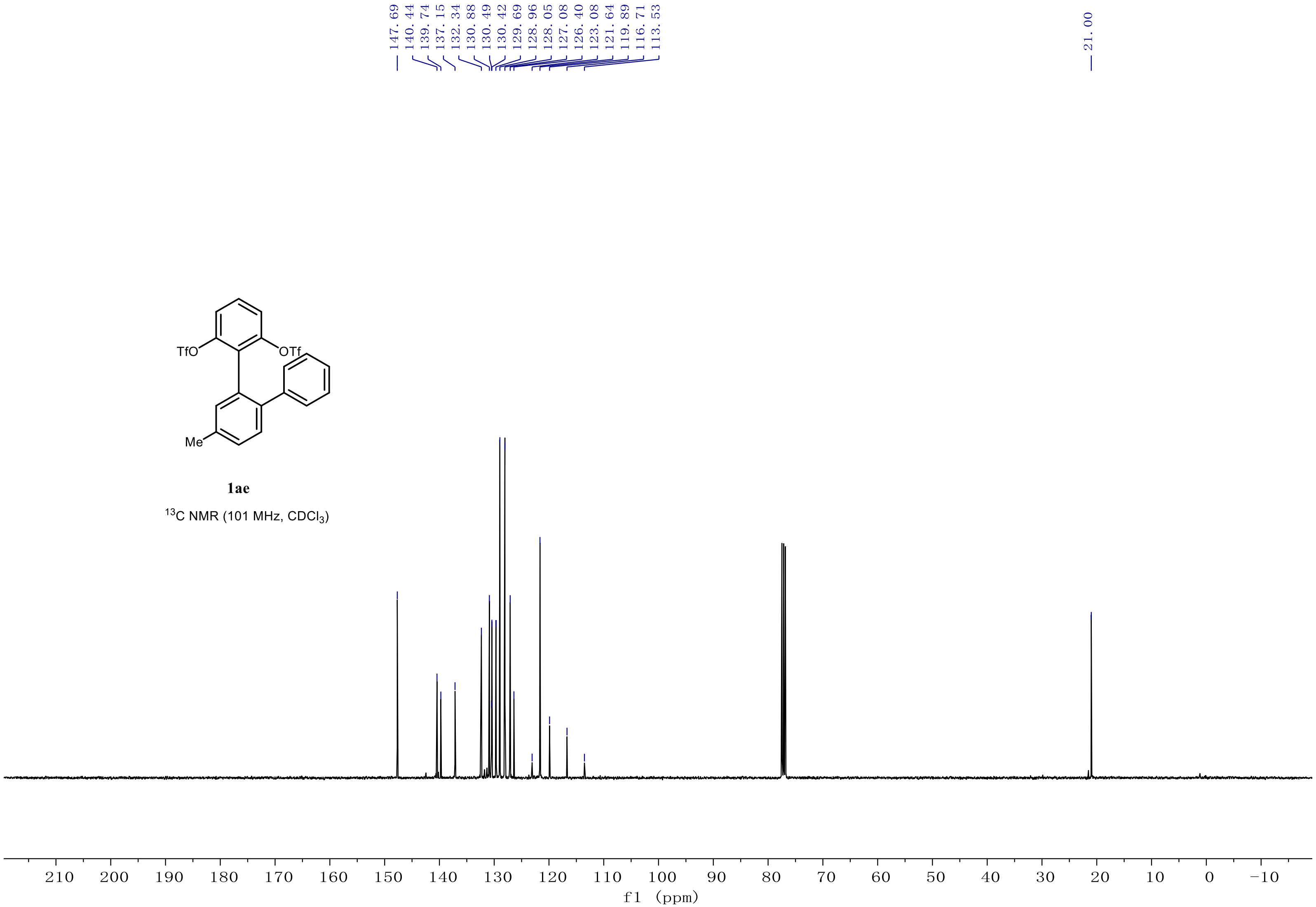
^{13}C NMR (126 MHz, $CDCl_3$)

1ad

^{19}F NMR (376 MHz, $CDCl_3$)




7.45
7.43
7.42
7.41
7.40
7.39
7.38
7.38
7.30
7.28
7.24
7.22
7.21
7.20
7.14
7.13
7.12
7.11
7.11
2.46
TfO
OTf
Me
1ae
^{1}H NMR (400 MHz, CDCl$_3$)
3.07
2.03
1.00
3.11
1.96
2.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

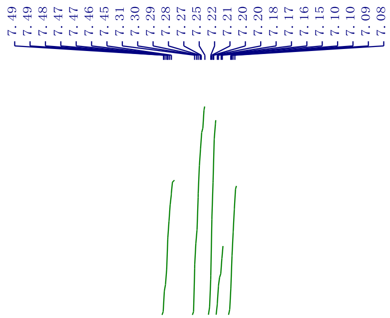


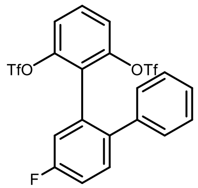
1ae

^{13}C NMR (101 MHz, $CDCl_3$)

1ae

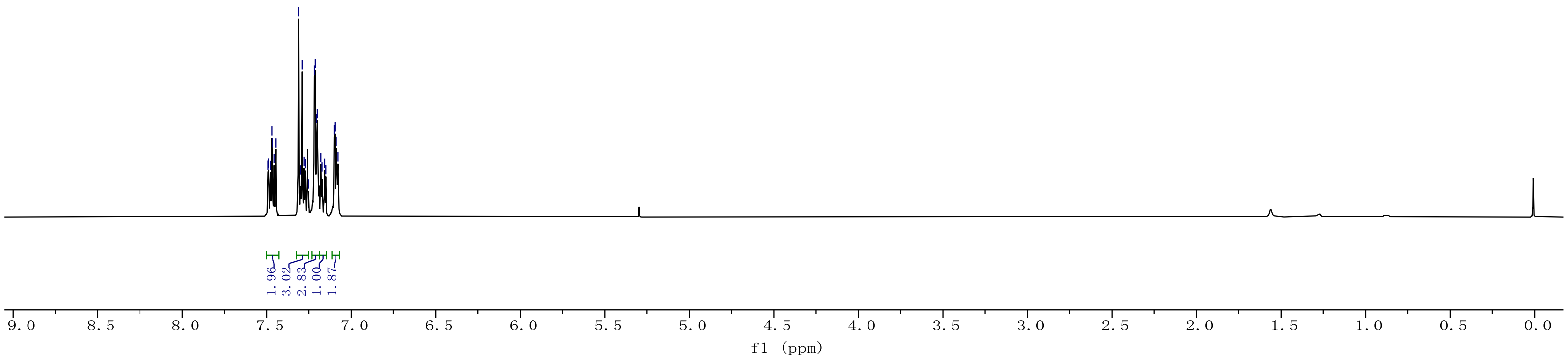
^{19}F NMR (376 MHz, $CDCl_3$)

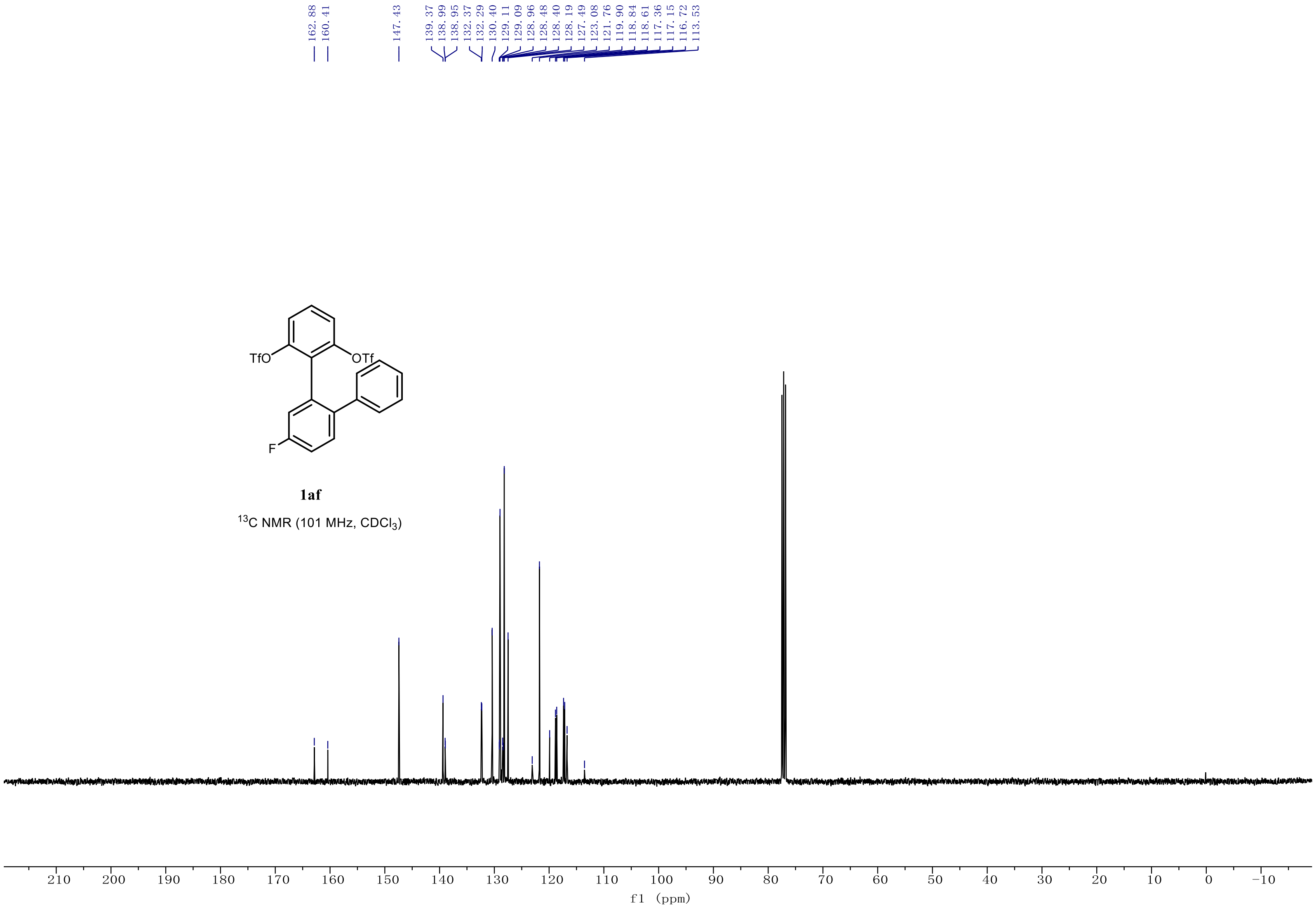




1af

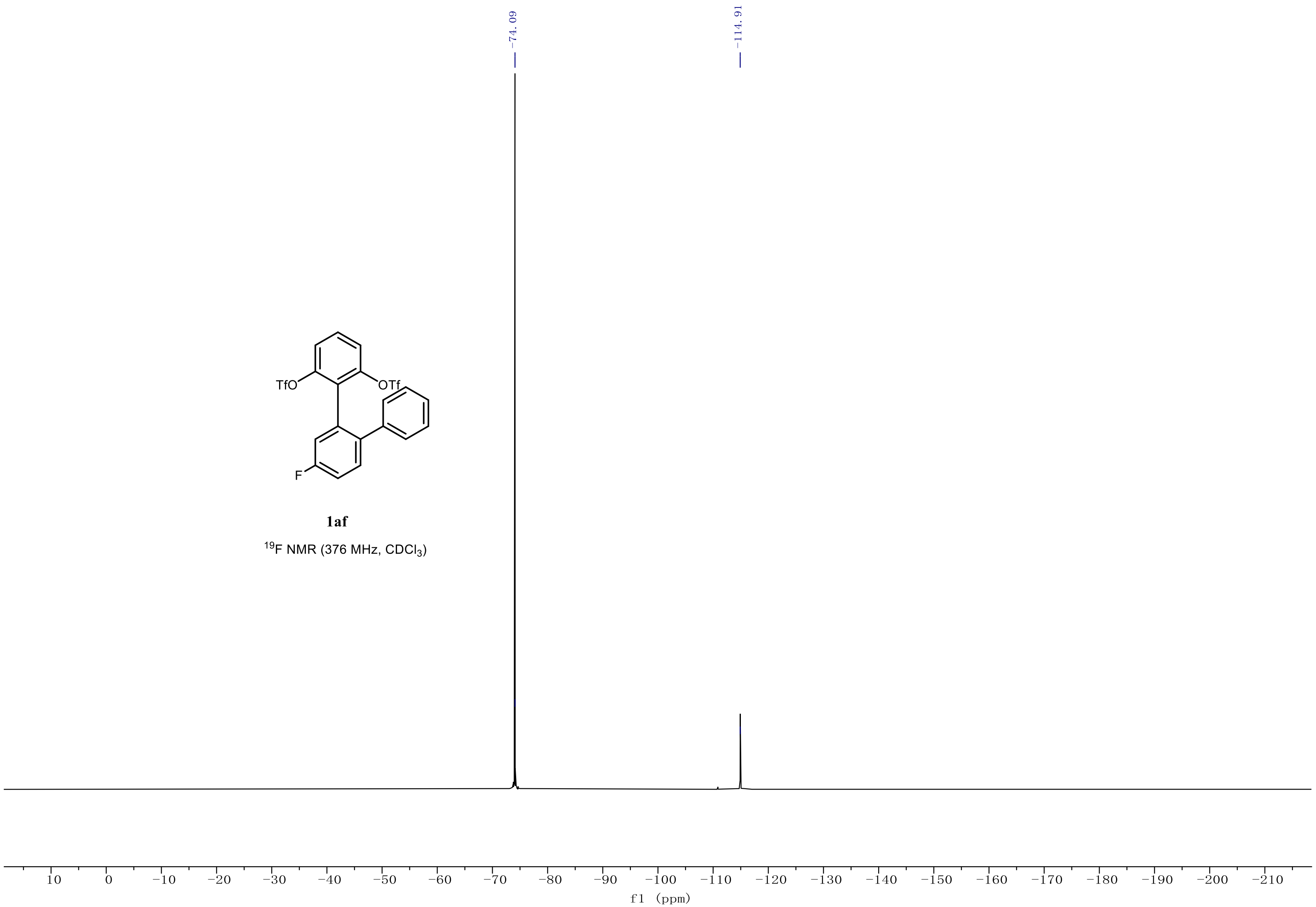
^{1}H NMR (400 MHz, $CDCl_3$)



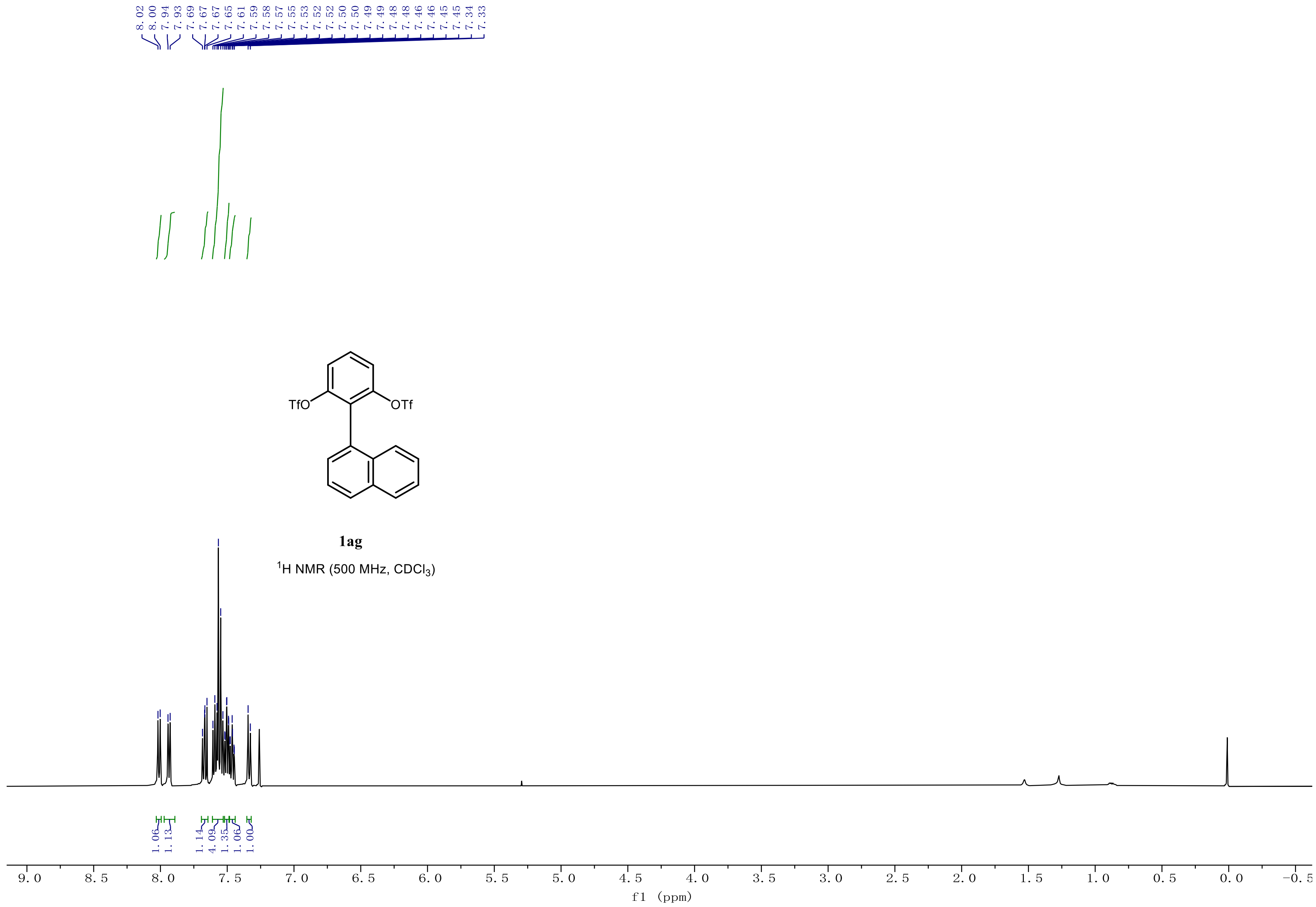


1af

^{13}C NMR (101 MHz, $CDCl_3$)

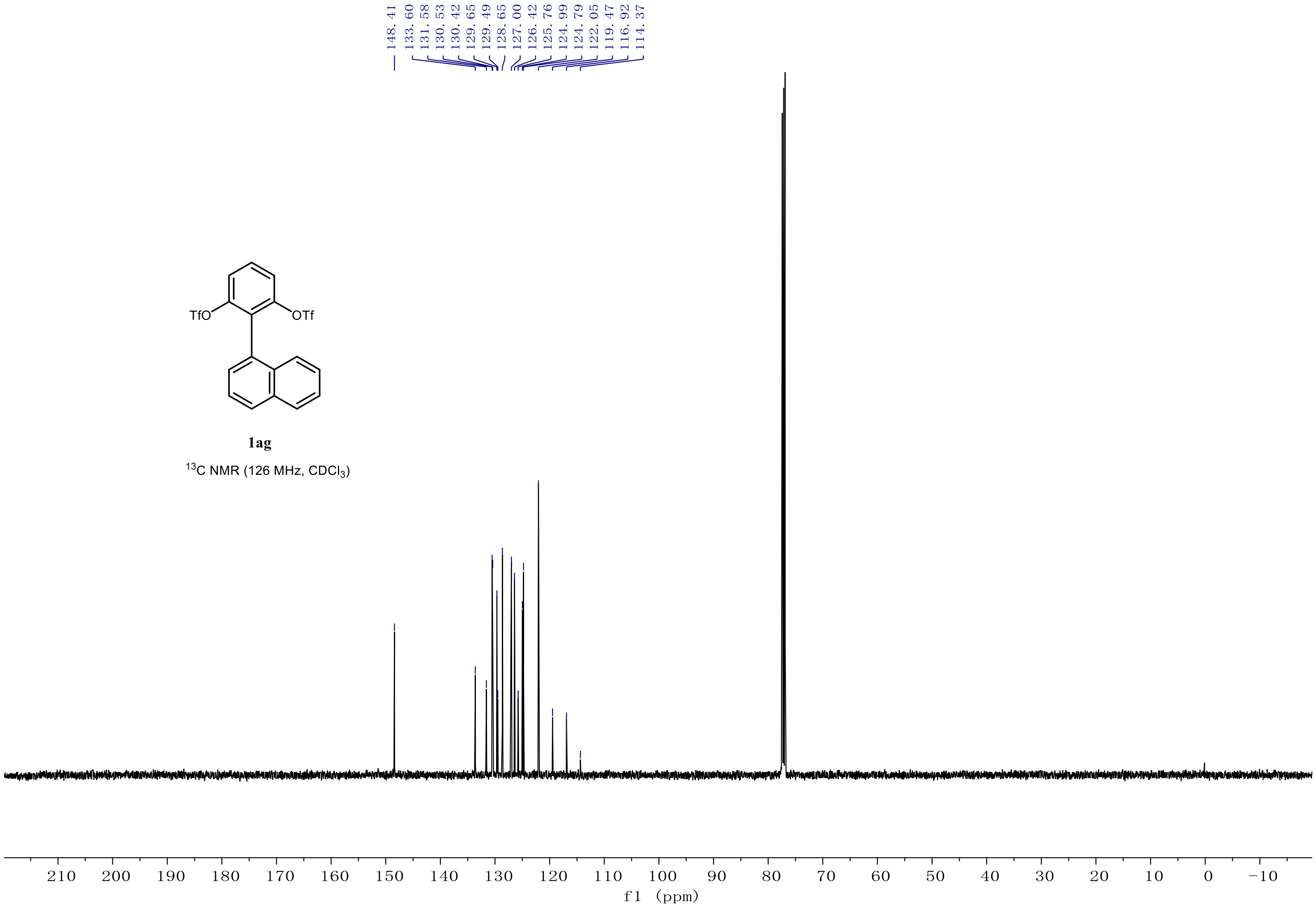


-74.09
-114.91
TfO
OTf
F
1af
^{19}F NMR (376 MHz, CDCl$_3$)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



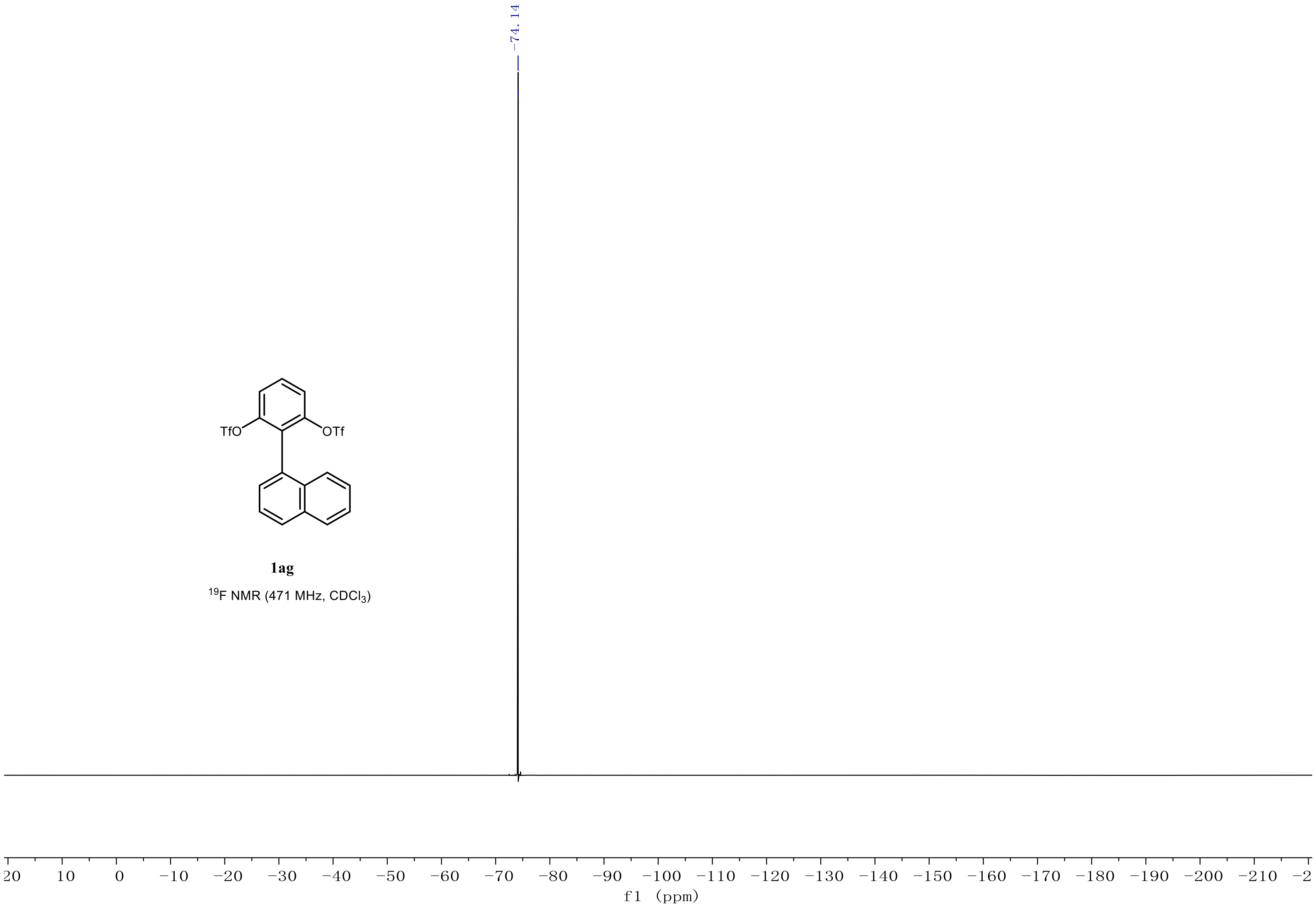
1ag

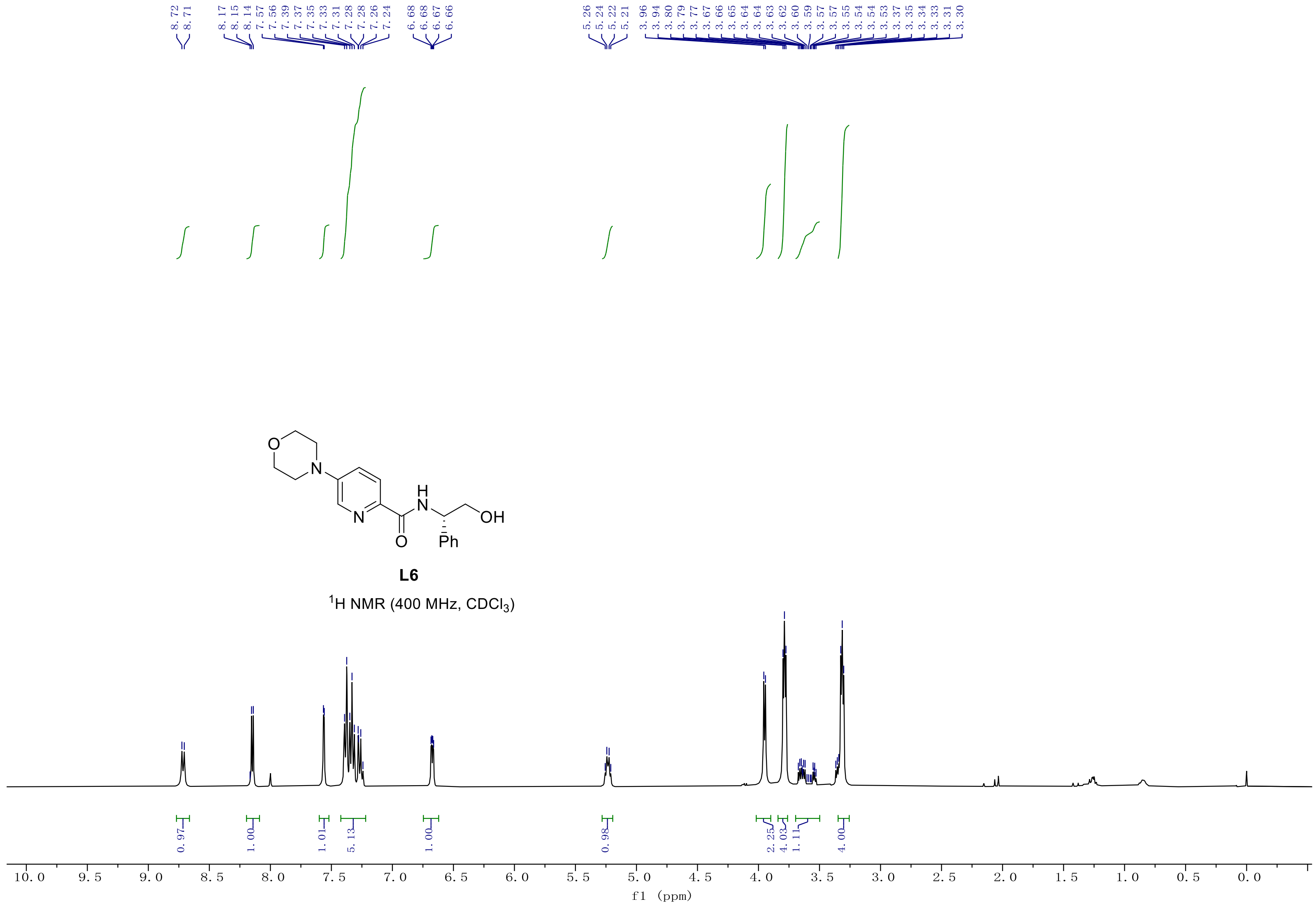
^{1}H NMR (500 MHz, $CDCl_3$)



1ag

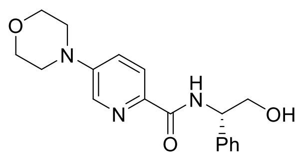
^{13}C NMR (126 MHz, $CDCl_3$)


−74.14
TfO
OTf
1ag
19F NMR (471 MHz, CDCl3)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−2
f1 (ppm)



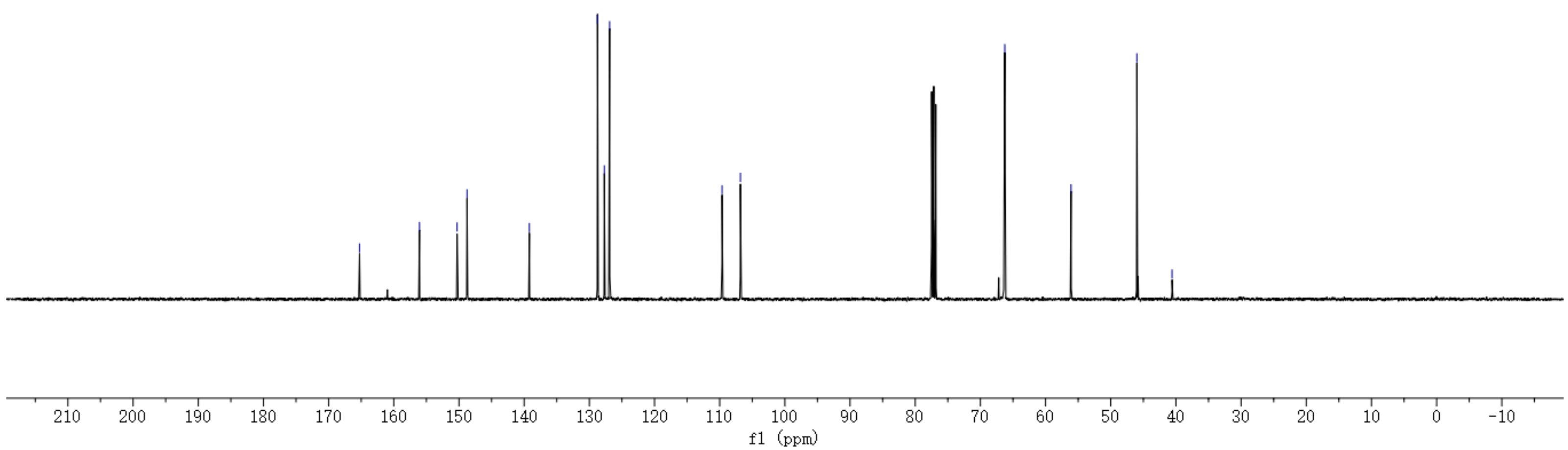
L6

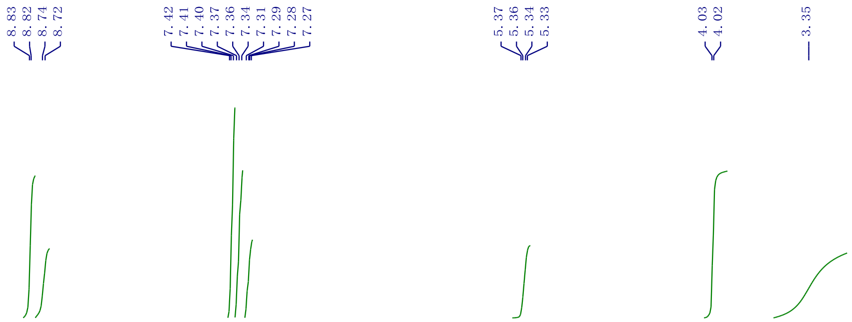
^{1}H NMR (400 MHz, $CDCl_3$)

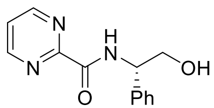


L6

^{13}C NMR (101 MHz, $CDCl_3$)

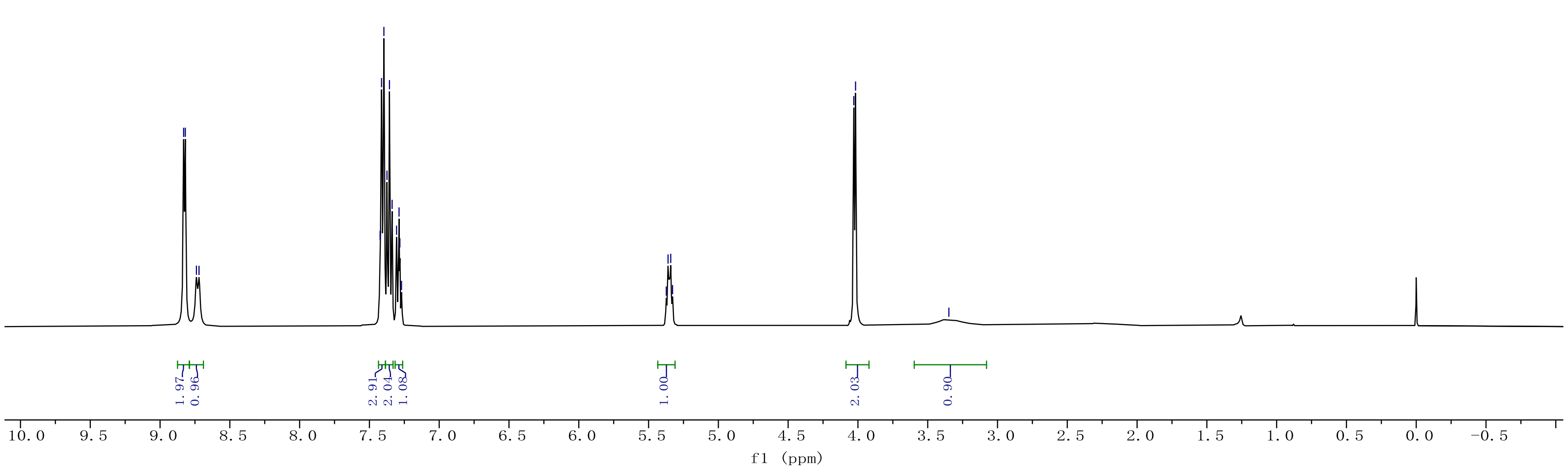


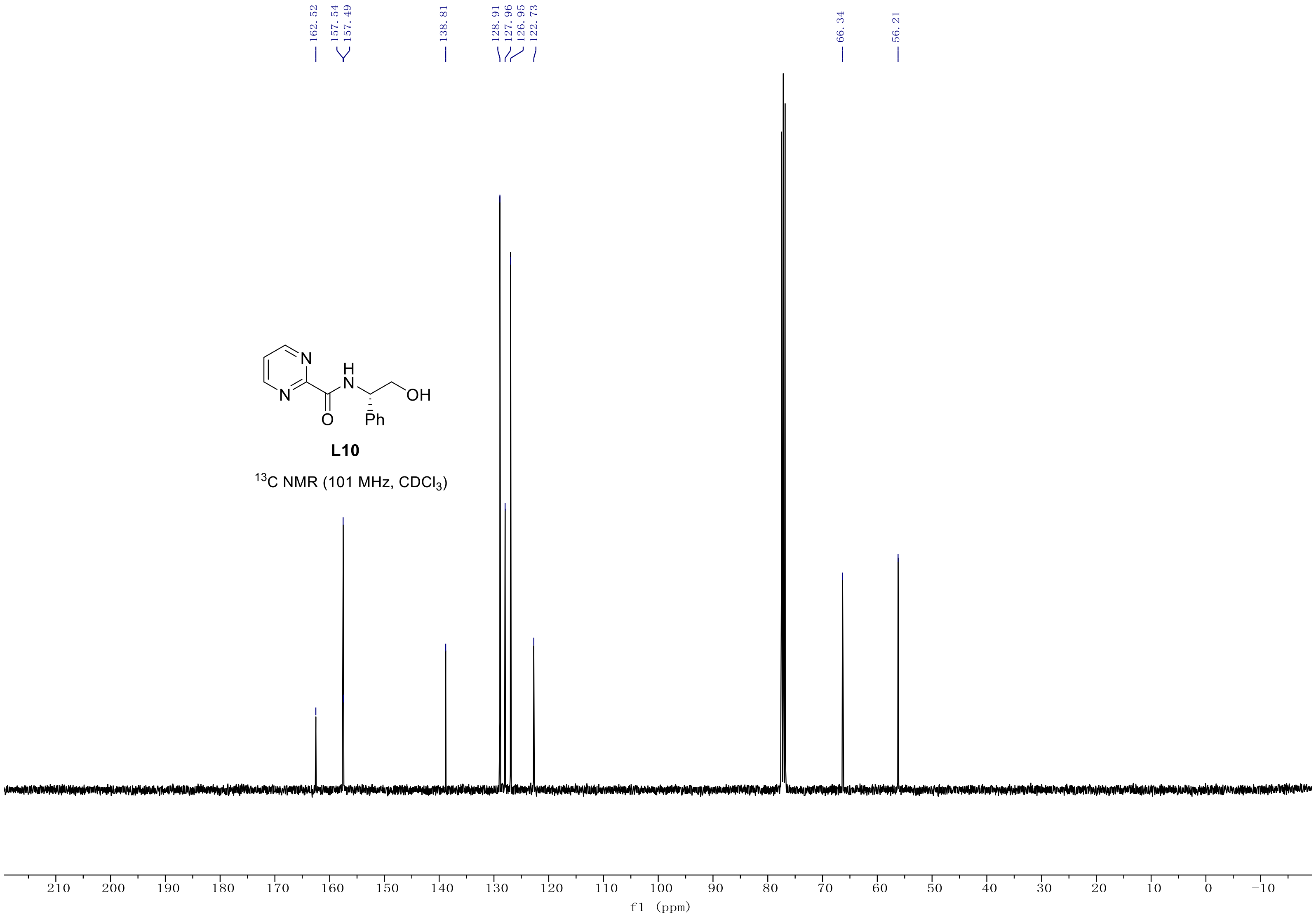




L10

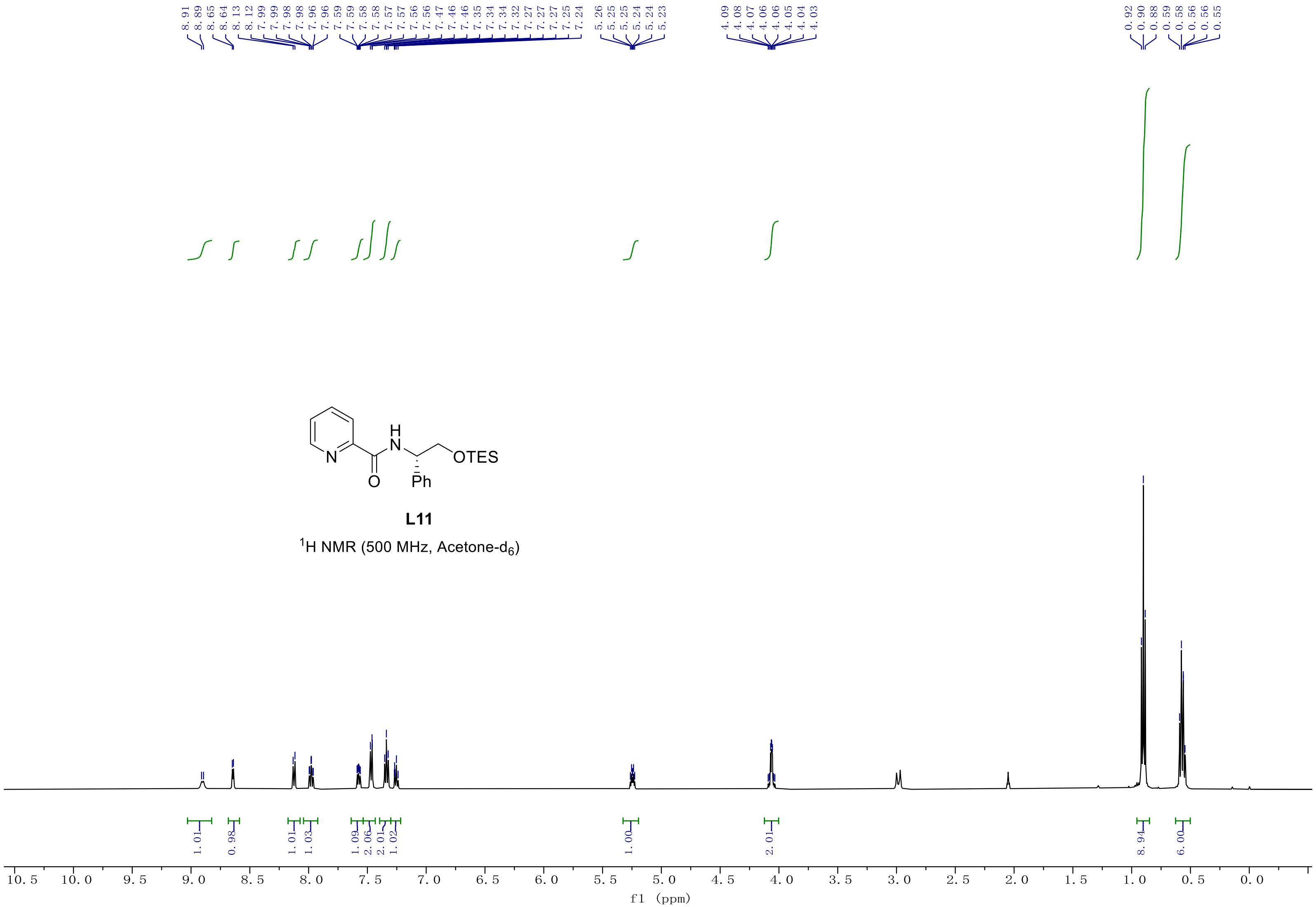
^{1}H NMR (400 MHz, $CDCl_3$)

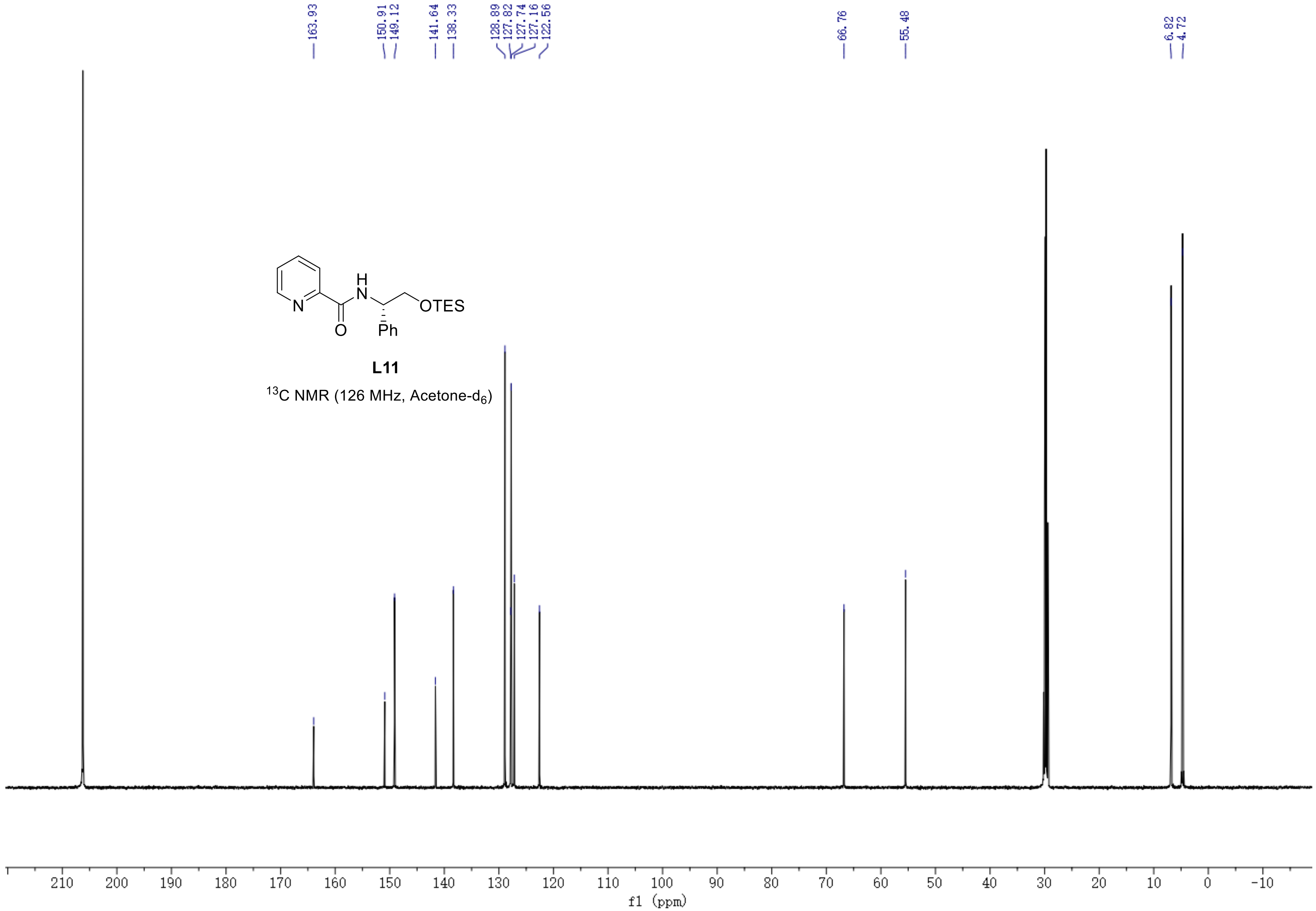


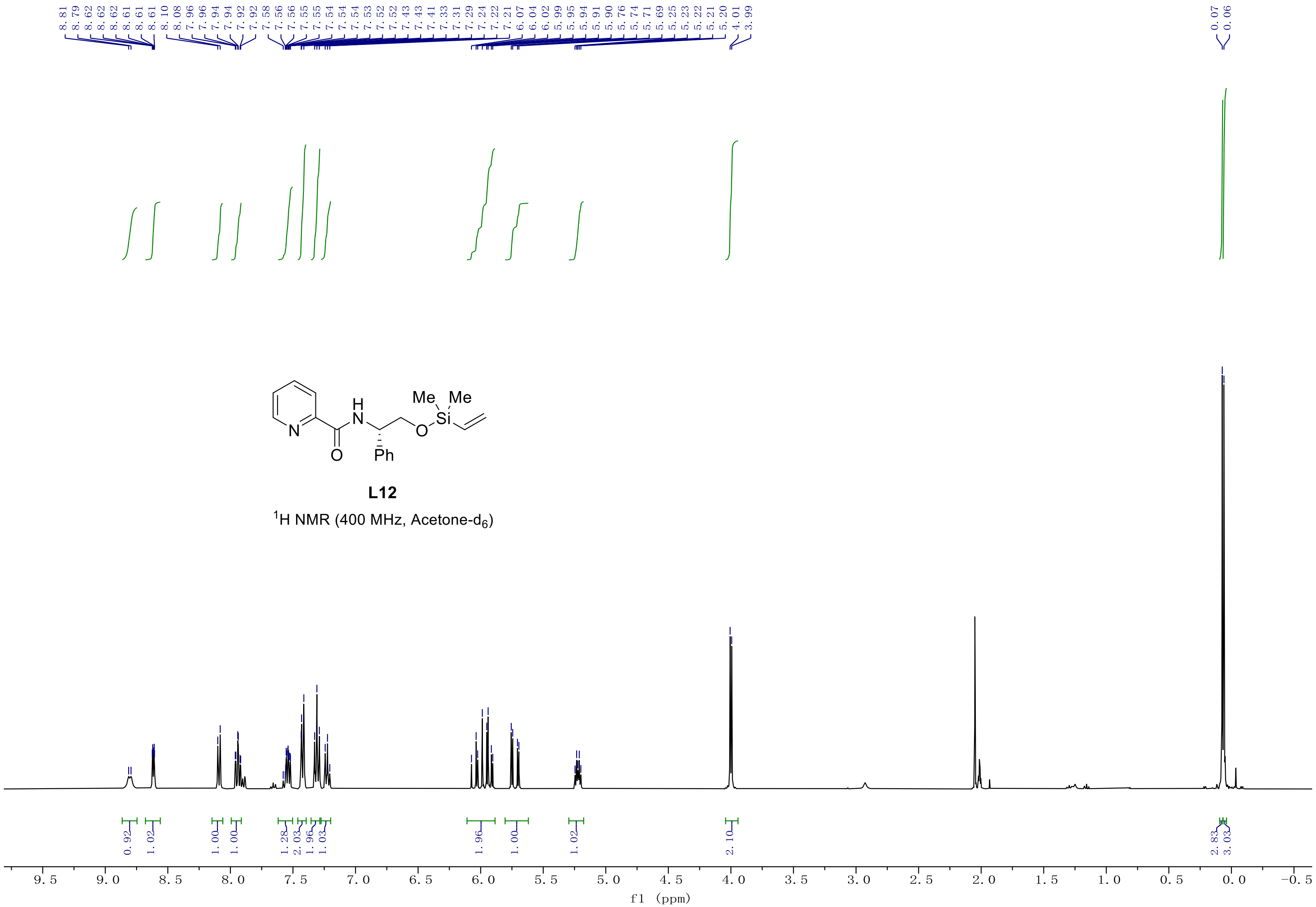


L10

^{13}C NMR (101 MHz, $CDCl_3$)

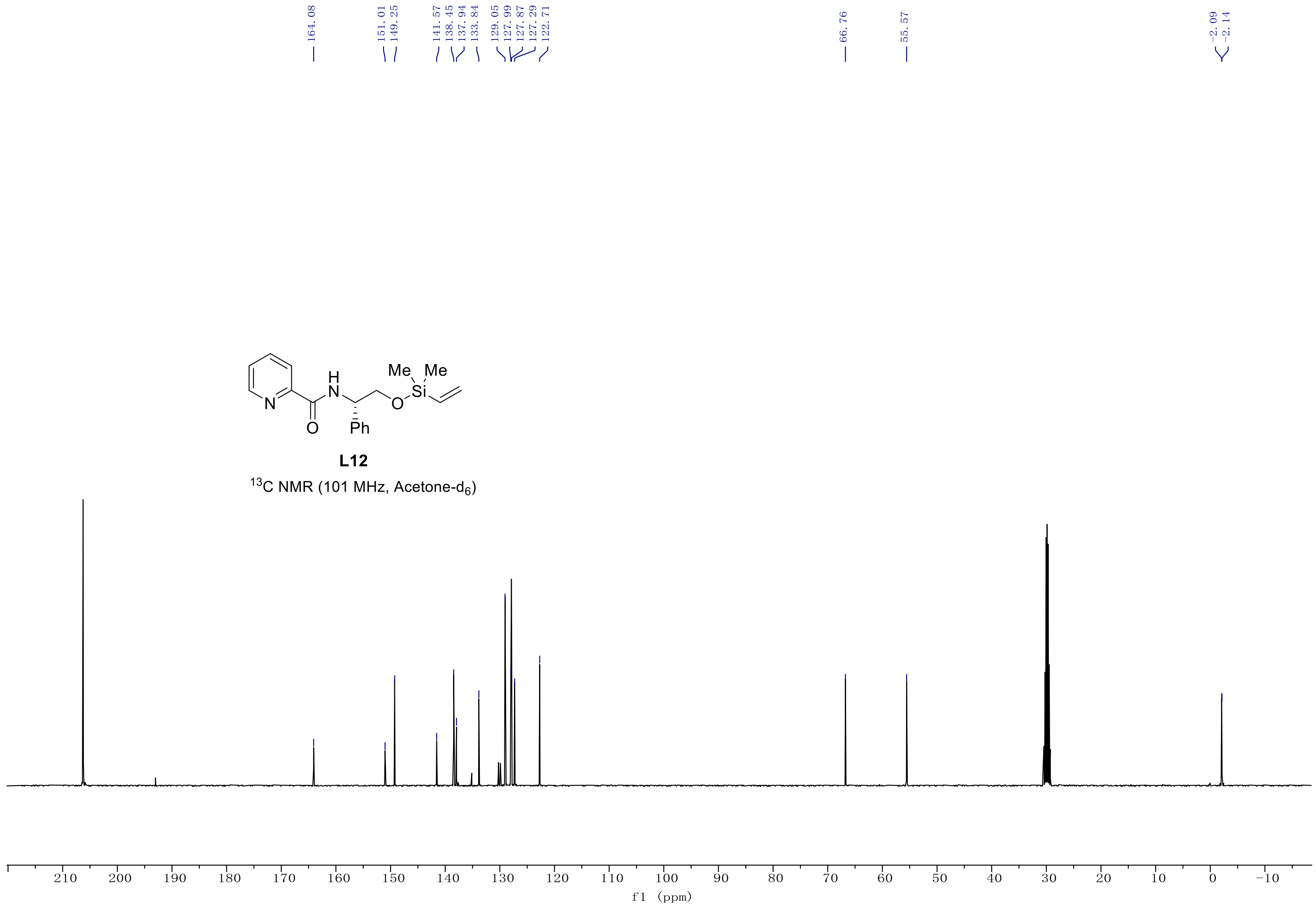

8.91 8.89 8.65 8.64 8.13 8.12 7.99 7.99 7.98 7.96 7.96 7.59 7.59 7.58 7.58 7.57 7.57 7.56 7.56 7.47 7.46 7.46 7.35 7.34 7.34 7.32 7.27 7.27 7.27 7.25 7.24
5.26 5.25 5.25 5.24 5.24 5.23
4.09 4.08 4.07 4.06 4.06 4.05 4.04 4.03
0.92 0.90 0.88 0.59 0.58 0.56 0.56 0.55
H
N
N
O
OTES
Ph
L11
^{1}H NMR (500 MHz, Acetone-d$_6$)
1.01 0.98 1.01 1.03 1.09 2.06 2.01 1.02 1.00 2.01 8.94 6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

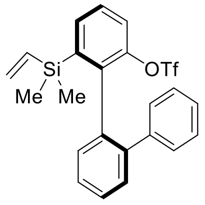

163.93
150.91
149.12
141.64
138.33
128.89
127.82
127.74
127.16
122.56
66.76
55.48
6.82
4.72
N
H
N
O
OTES
Ph
L11
13C NMR (126 MHz, Acetone-d6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



L12

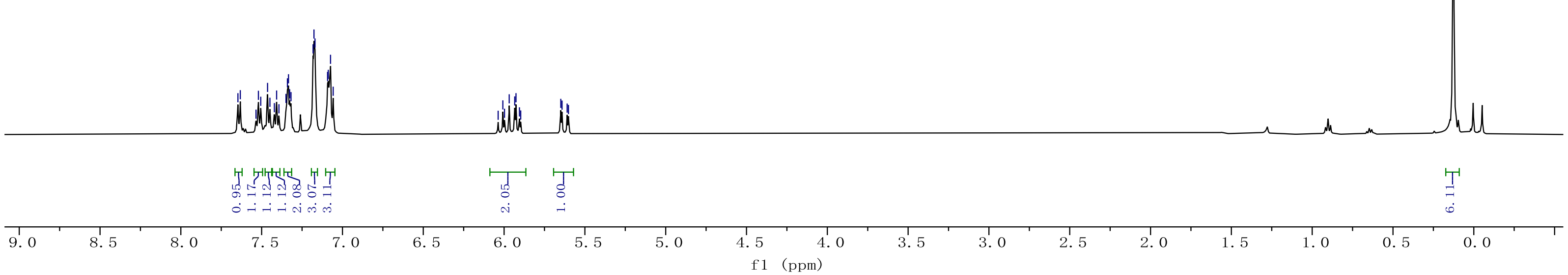
^{1}H NMR (400 MHz, Acetone-d_6)

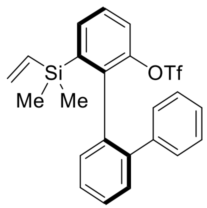

164.08
151.01
149.25
141.57
138.45
137.94
133.84
129.05
127.99
127.87
127.29
122.71
66.76
55.57
-2.09
-2.14
H
N
N
O
Ph
O
Si
Me
Me
L12
^{13}C NMR (101 MHz, Acetone-d$_6$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



3aa

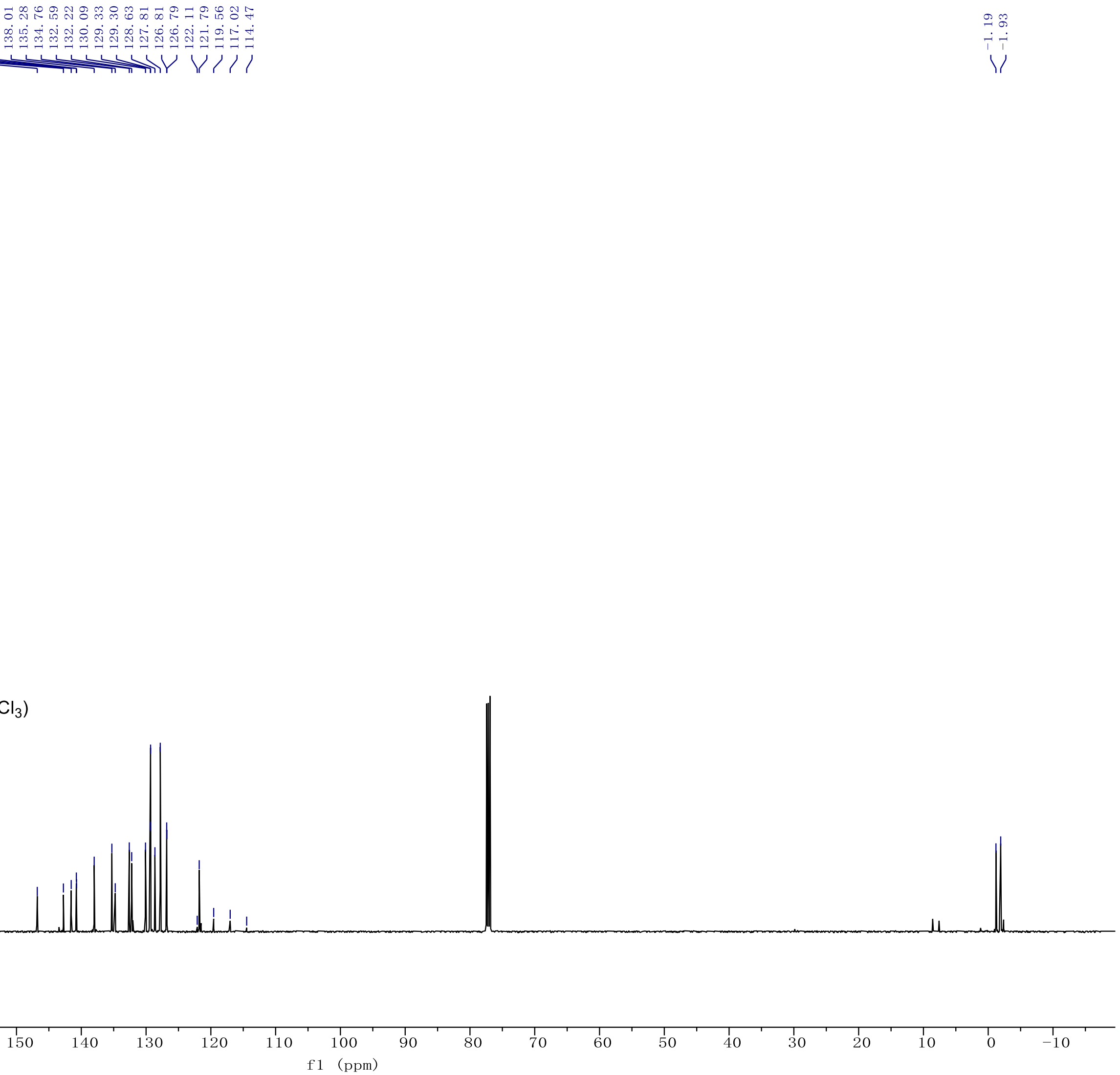
^{1}H NMR (500 MHz, $CDCl_3$)

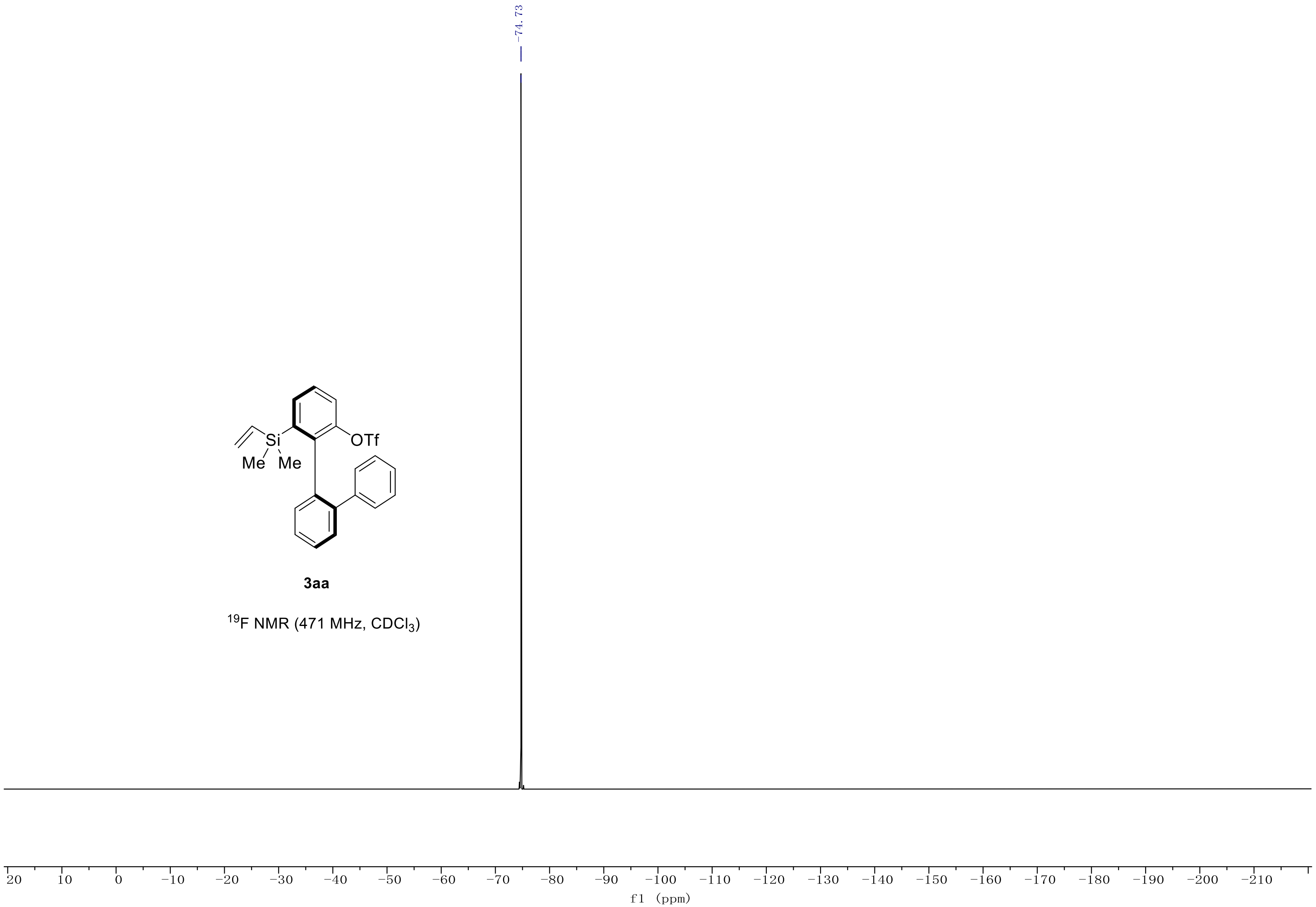




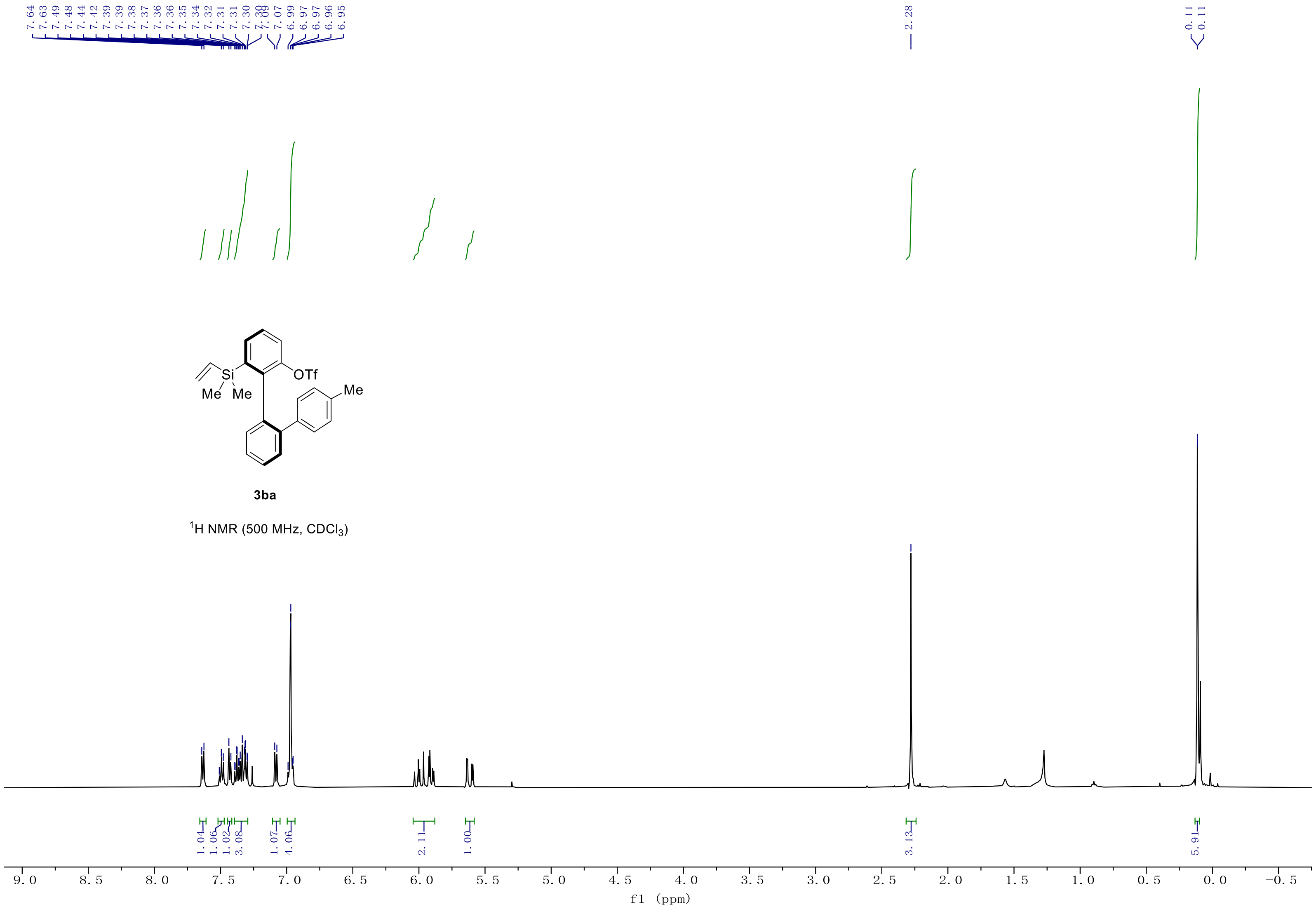
3aa

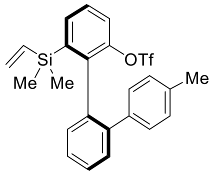
^{13}C NMR (126 MHz, $CDCl_3$)





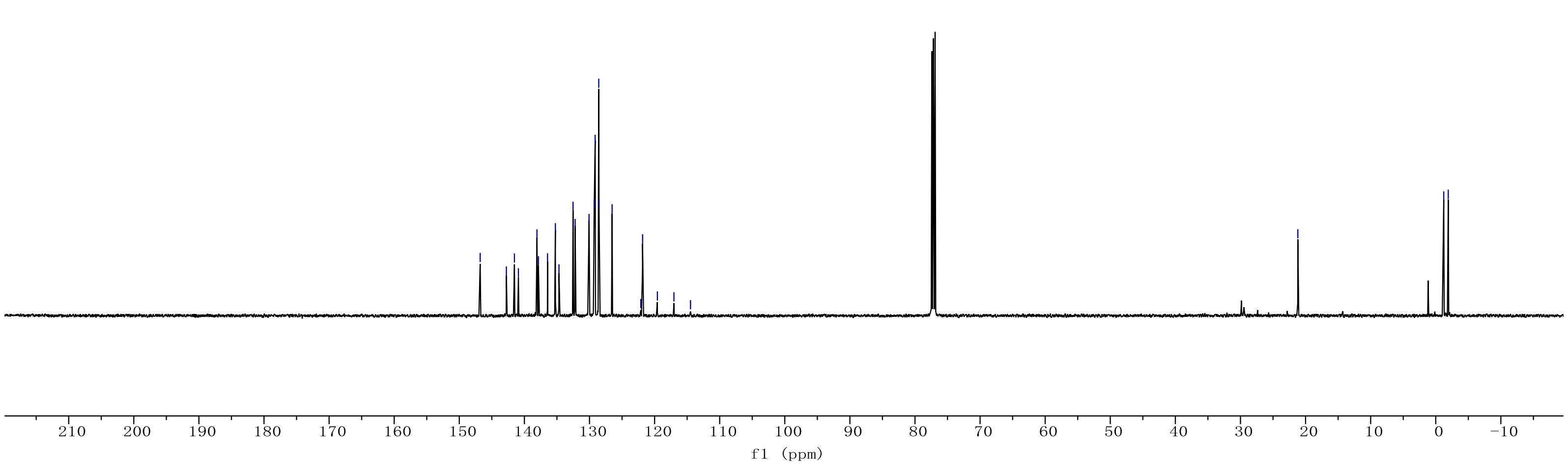
-74.73
OTf
Si
Me Me
3aa
^{19}F NMR (471 MHz, $CDCl_3$)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

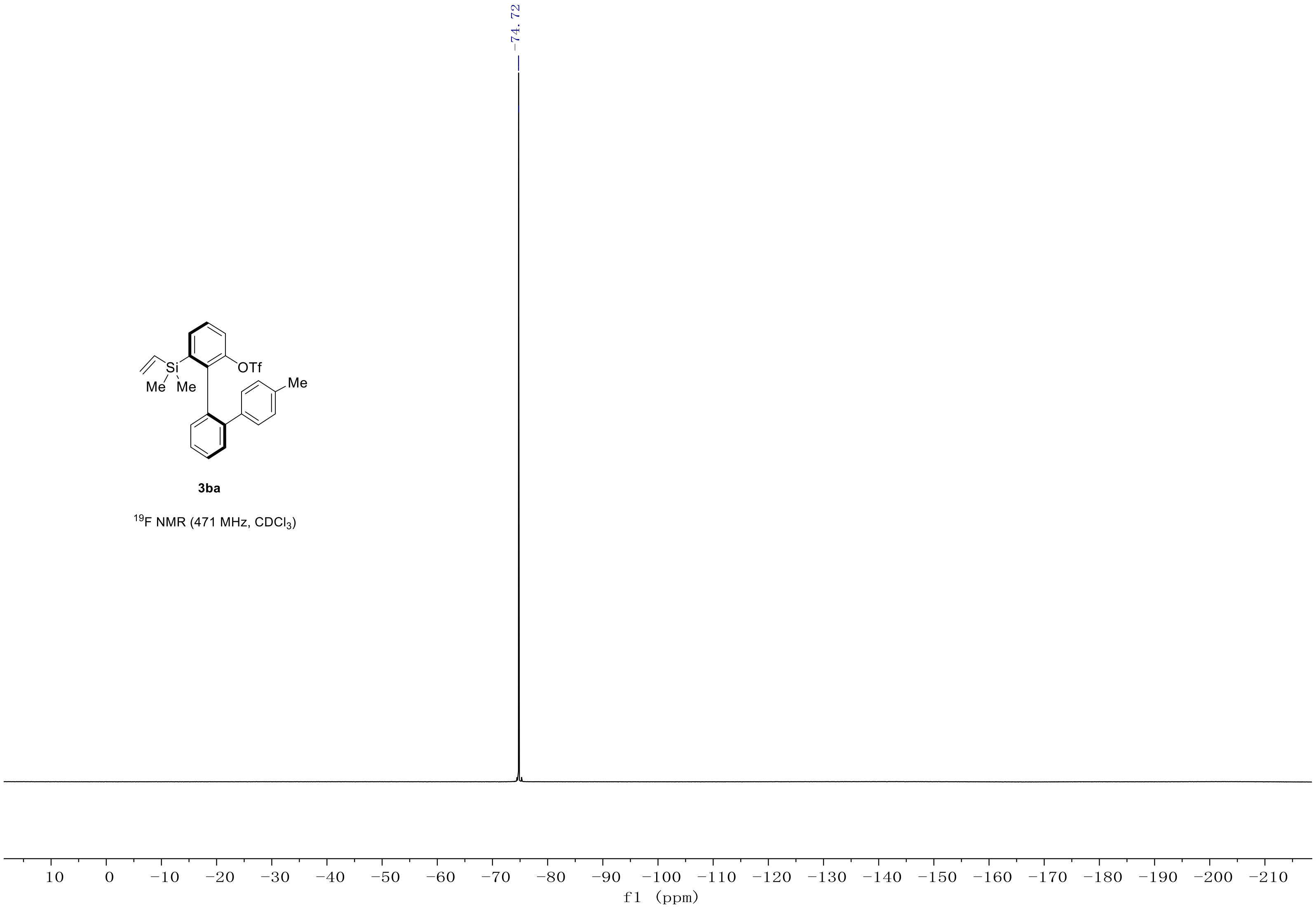

7.64
7.63
7.49
7.48
7.44
7.42
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.32
7.31
7.31
7.30
7.30
7.09
7.07
6.99
6.97
6.97
6.96
6.95
2.28
0.11
0.11
Si
OTf
Me
Me
Me
3ba
1H NMR (500 MHz, CDCl3)
1.04
1.06
1.02
3.08
1.07
4.06
2.11
1.00
3.13
5.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3ba

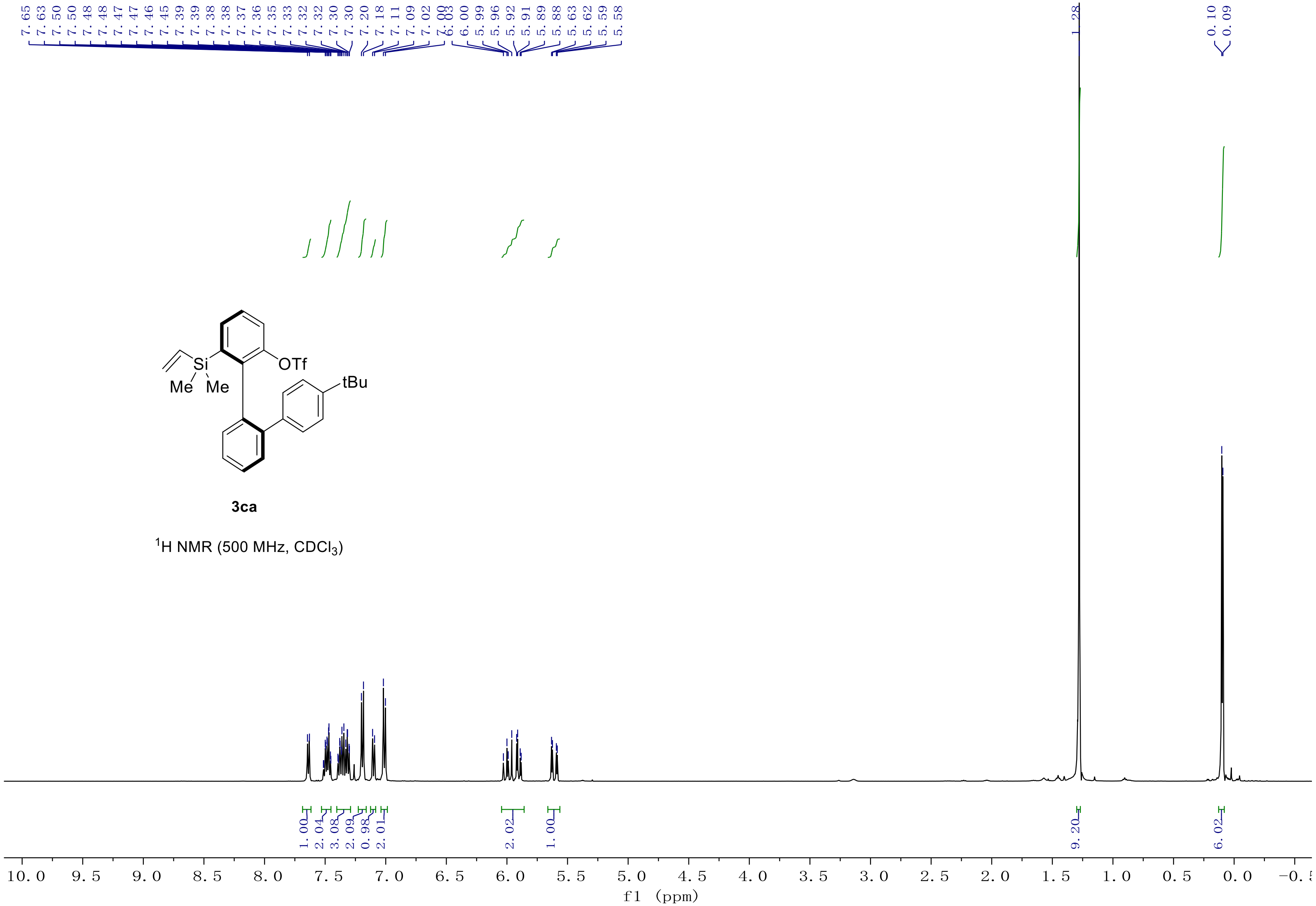
^{13}C NMR (126 MHz, $CDCl_3$)





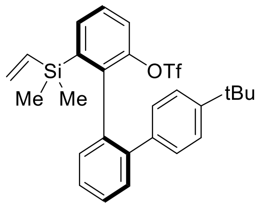
3ba

^{19}F NMR (471 MHz, $CDCl_3$)



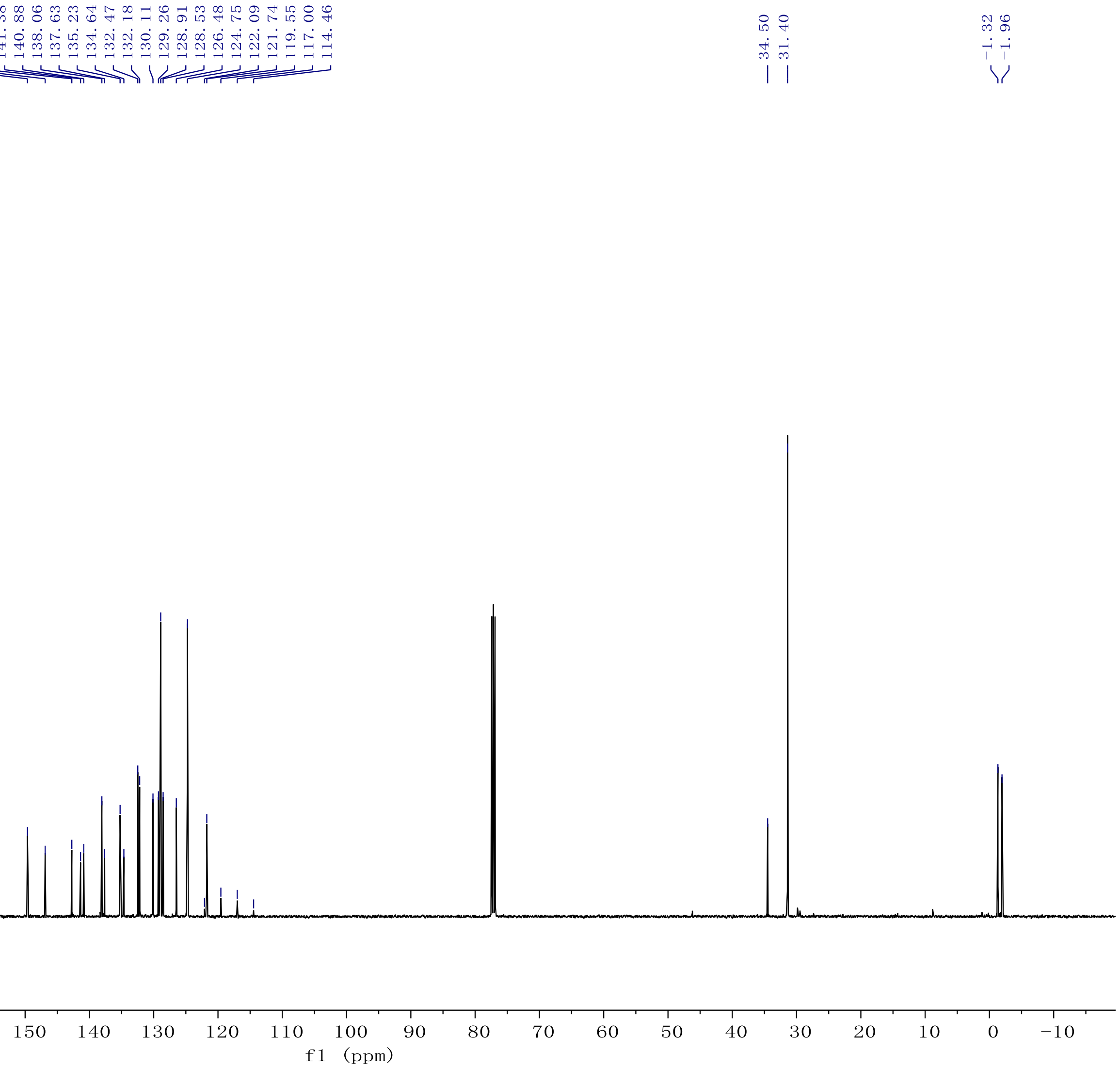
3ca

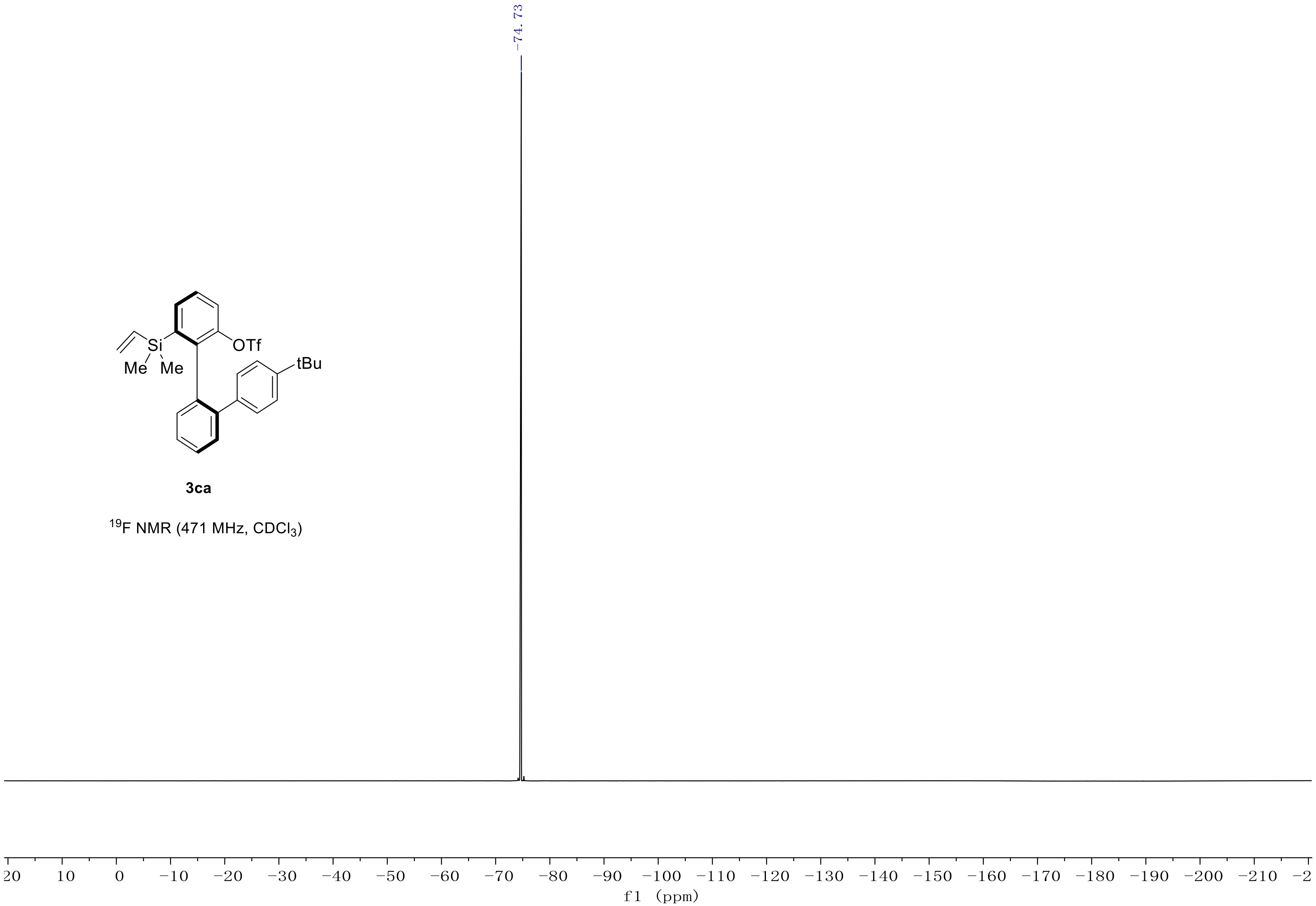
^{1}H NMR (500 MHz, $CDCl_3$)



3ca

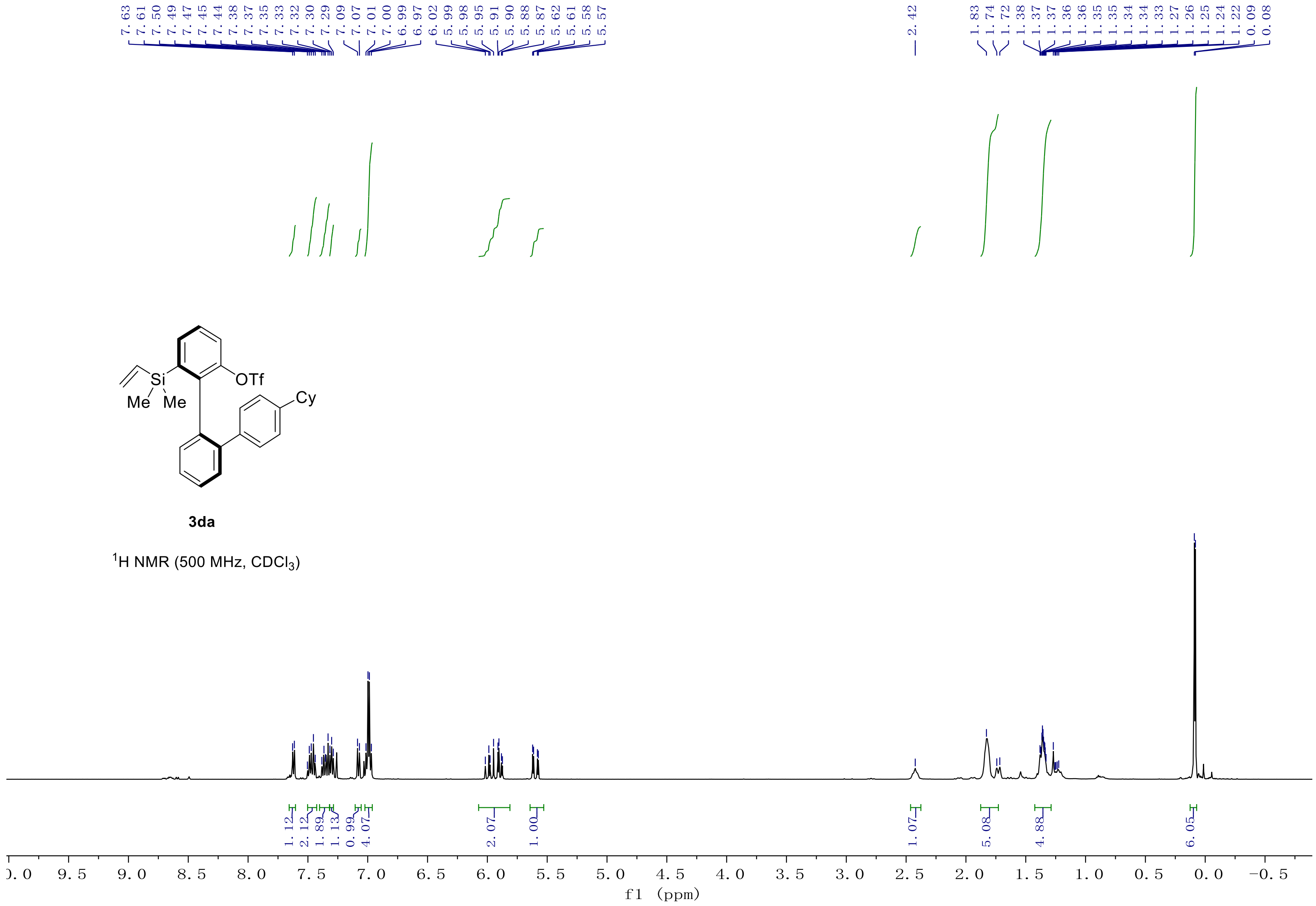
^{13}C NMR (120 MHz, CDCl$_3$)

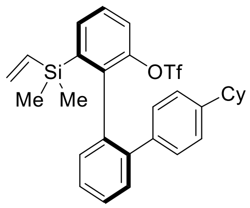




3ca

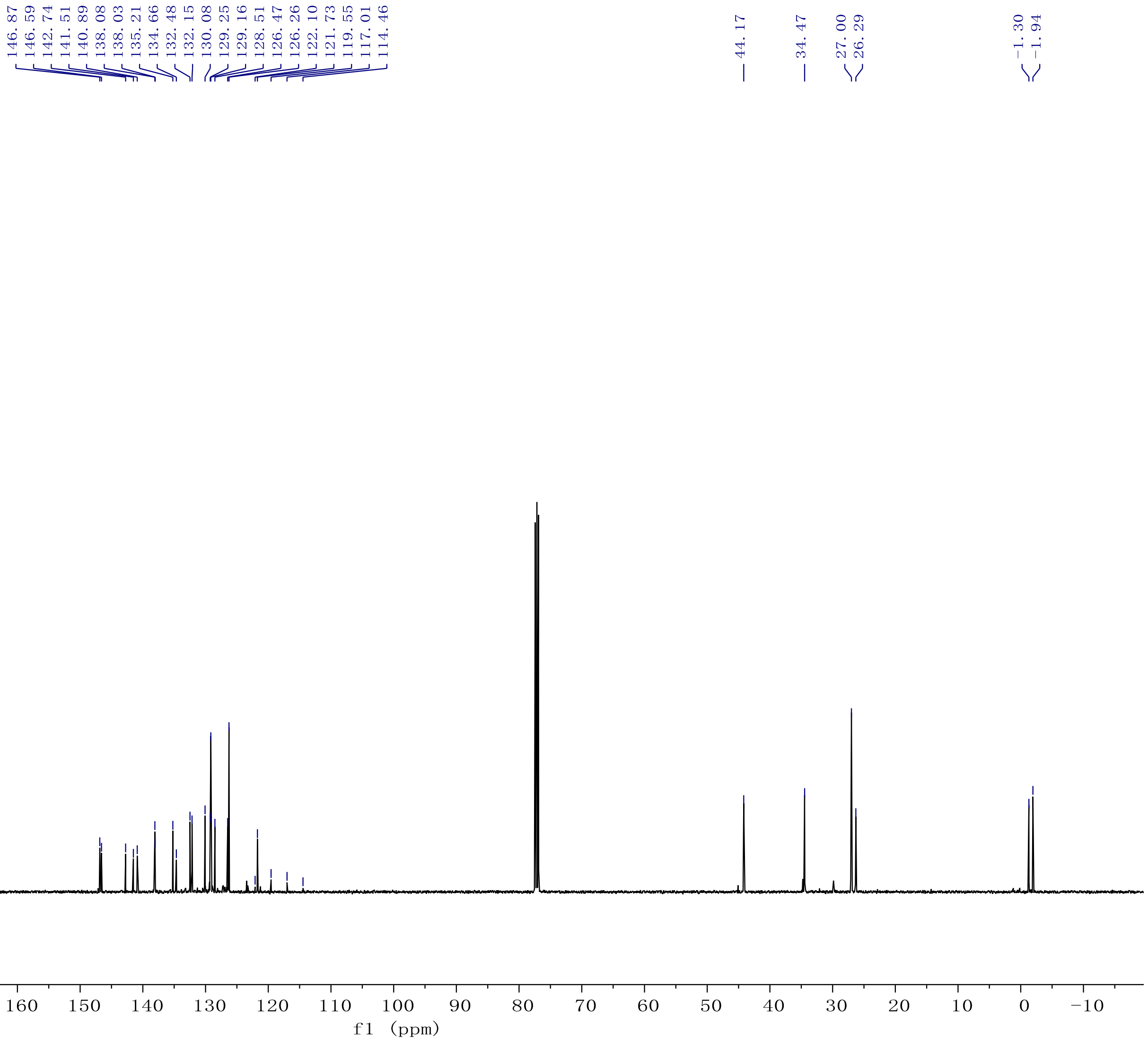
^{19}F NMR (471 MHz, $CDCl_3$)

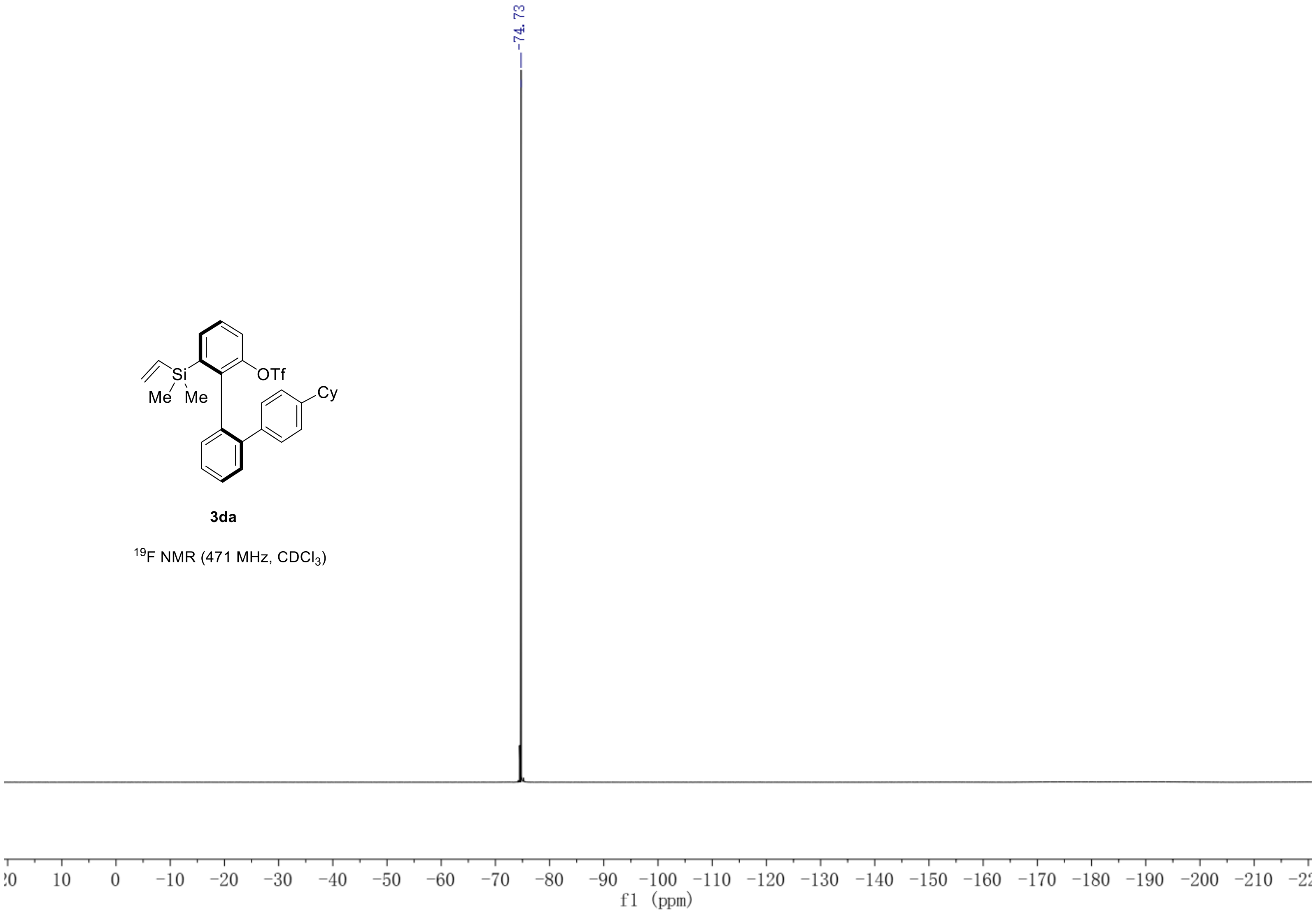

OTf
Si
Me
Me
Cy
3da
1H NMR (500 MHz, CDCl3)
f1 (ppm)



3da

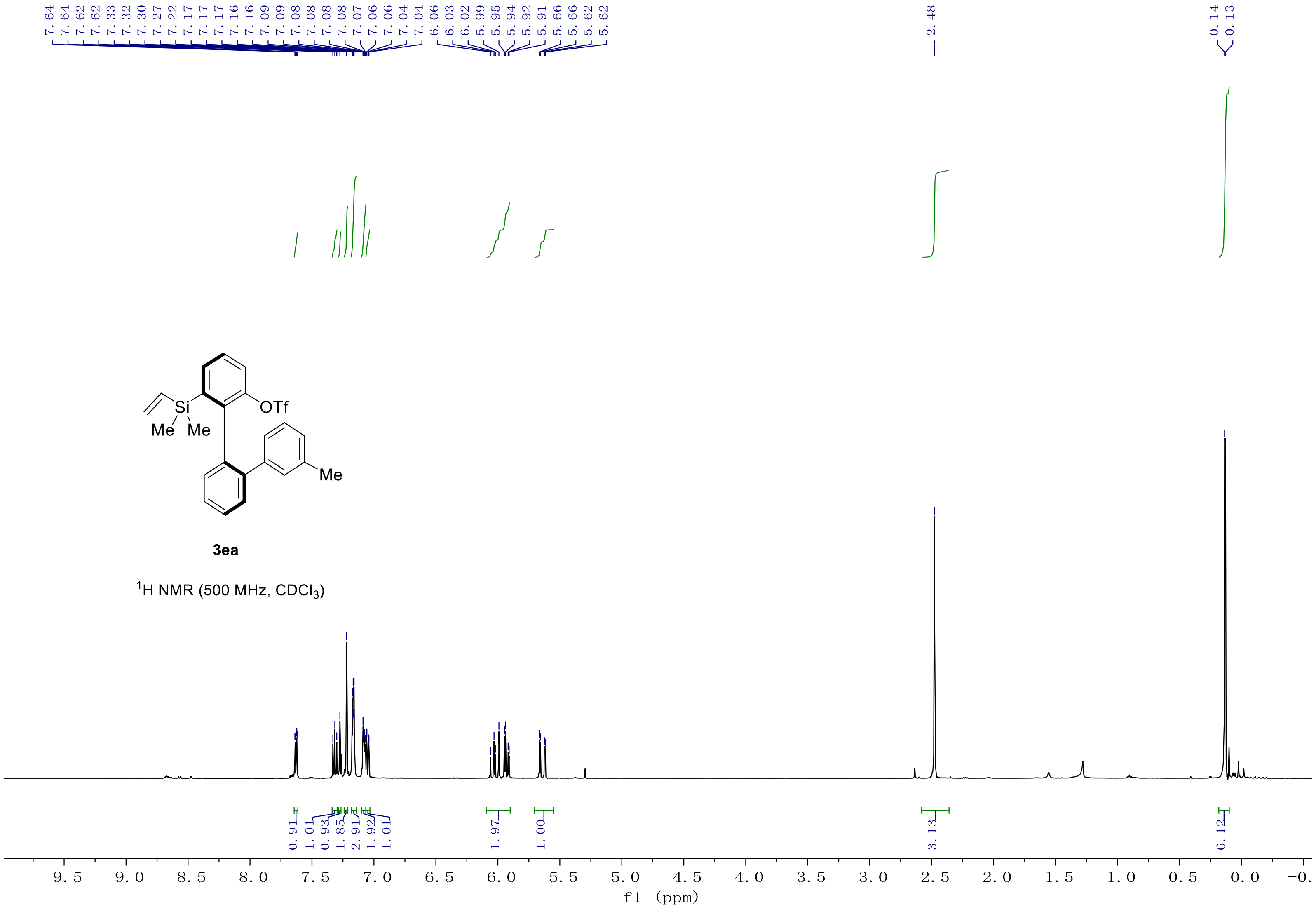
^{13}C NMR (126 MHz, $CDCl_3$)

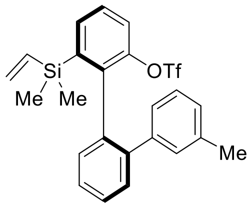




3da

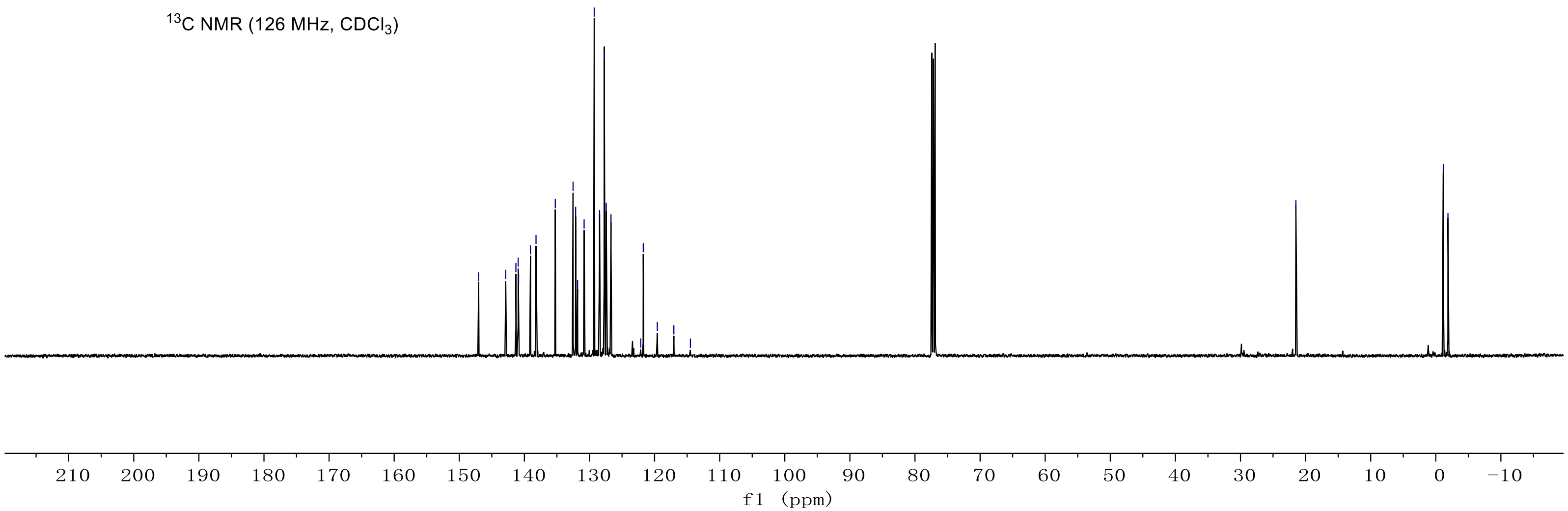
^{19}F NMR (471 MHz, $CDCl_3$)

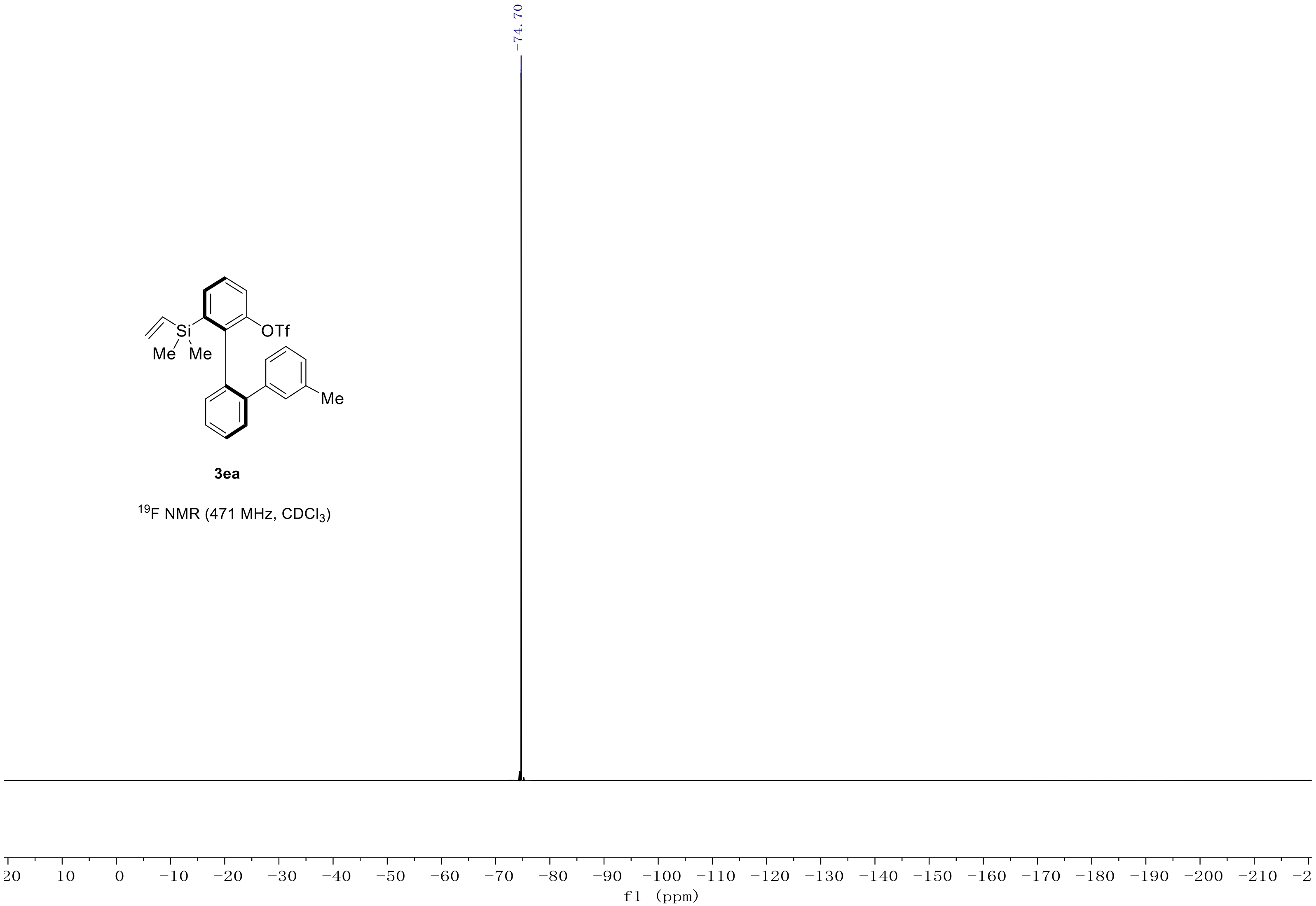

7.64 7.64 7.62 7.62 7.33 7.32 7.30 7.27 7.22 7.17 7.17 7.17 7.16 7.16 7.09 7.09 7.08 7.08 7.08 7.08 7.07 7.06 7.06 7.04 7.04 6.06 6.03 6.02 5.99 5.95 5.94 5.92 5.91 5.66 5.66 5.62 5.62
2.48
0.14 0.13
OTf
Si
Me Me
Me
3ea
1H NMR (500 MHz, CDCl3)
0.91 1.01 0.93 1.85 2.91 1.92 1.01
1.97
1.00
3.13
6.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



3ea

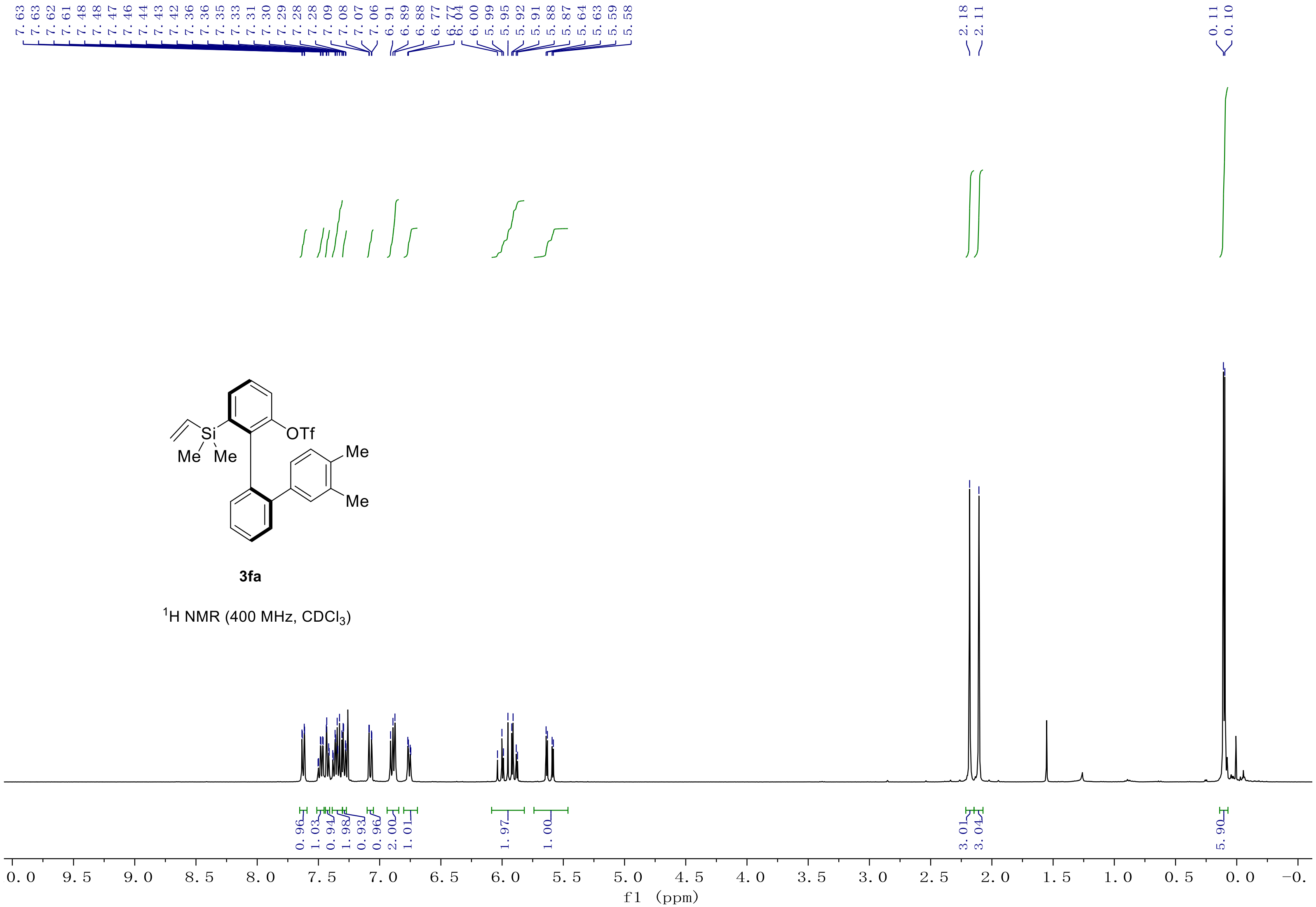
^{13}C NMR (126 MHz, $CDCl_3$)



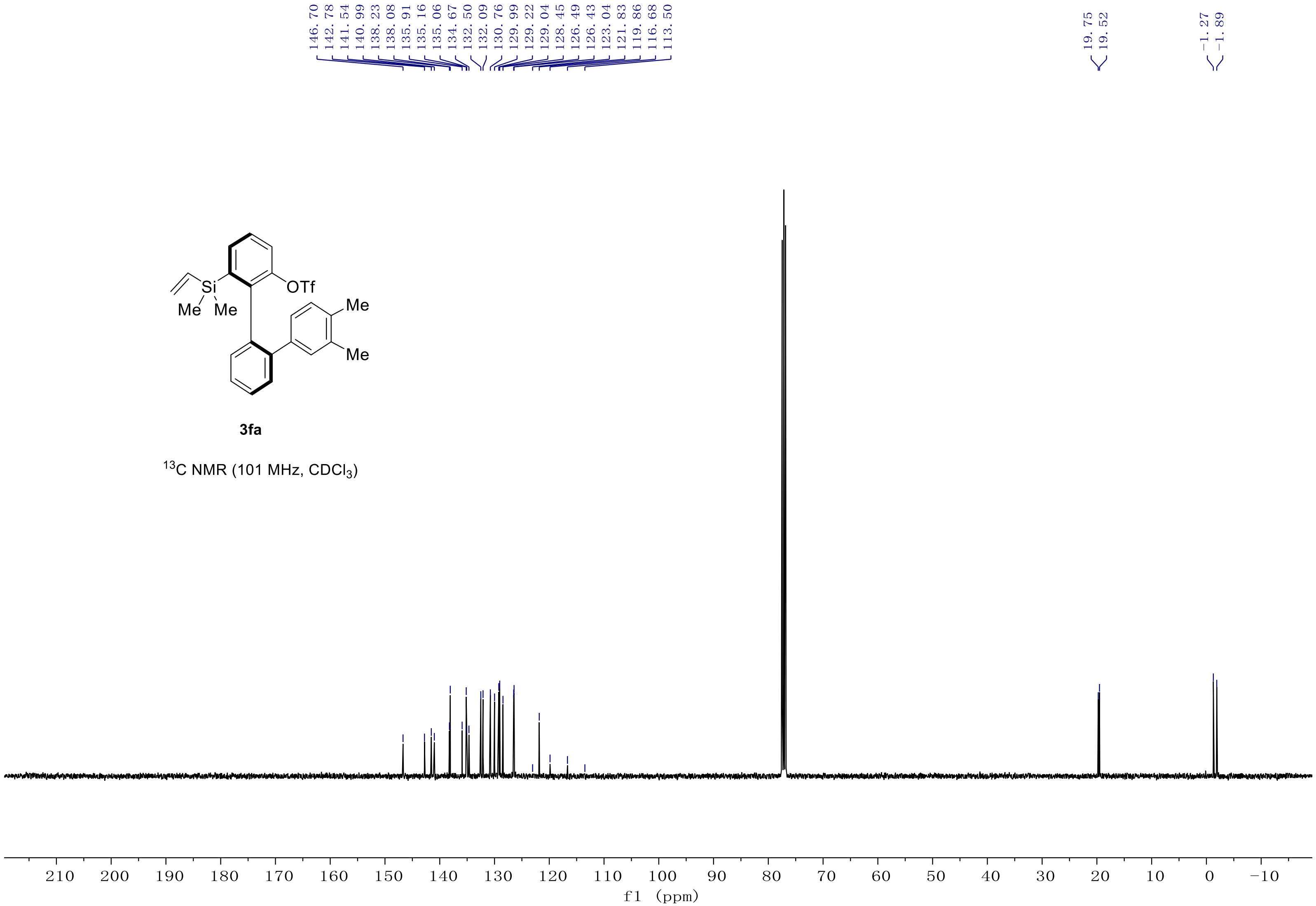


3ea

^{19}F NMR (471 MHz, $CDCl_3$)

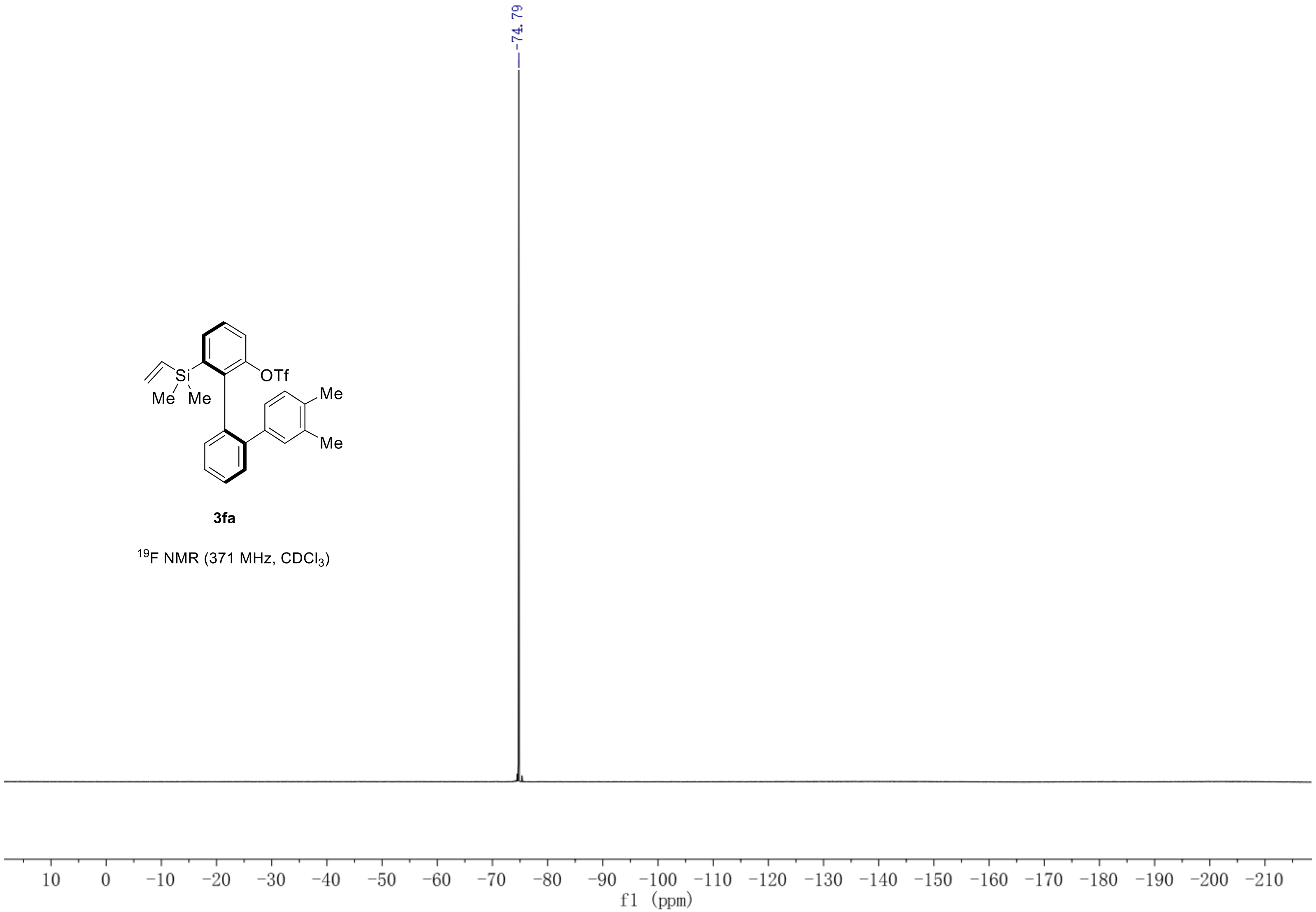


OTf
Si
Me
Me
Me
Me
3fa
1H NMR (400 MHz, CDCl3)
f1 (ppm)



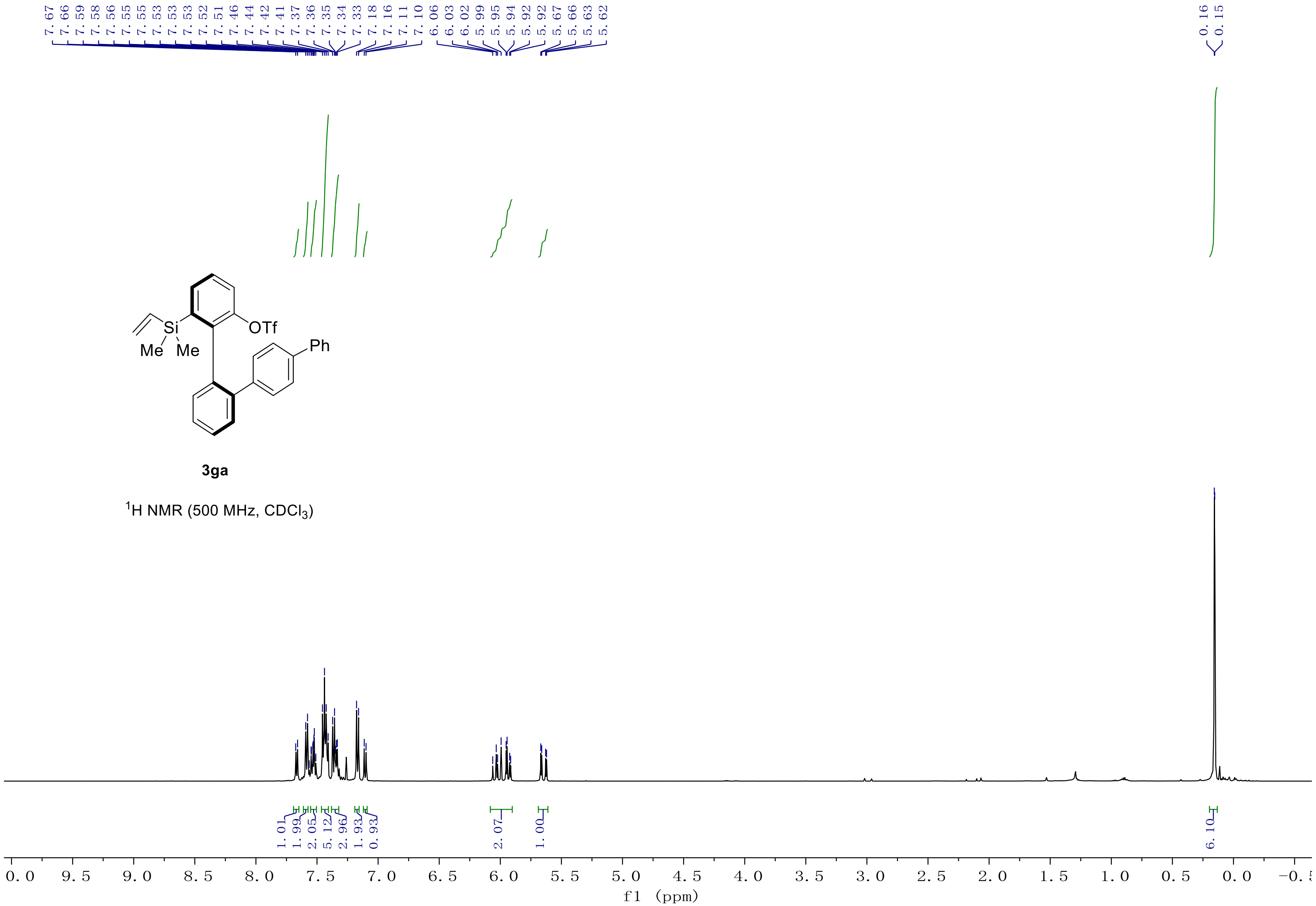
3fa

^{13}C NMR (101 MHz, $CDCl_3$)



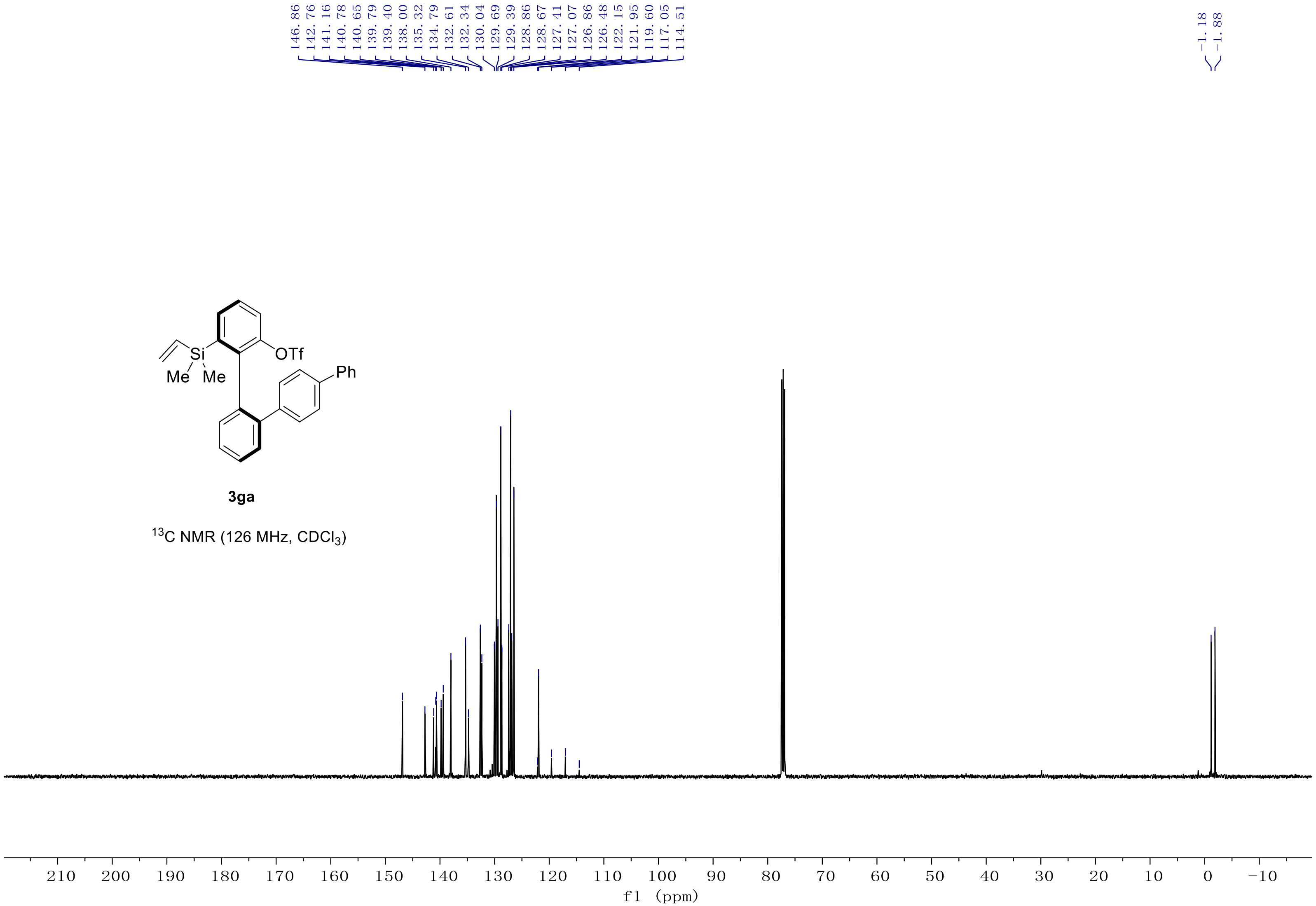
3fa

^{19}F NMR (371 MHz, $CDCl_3$)



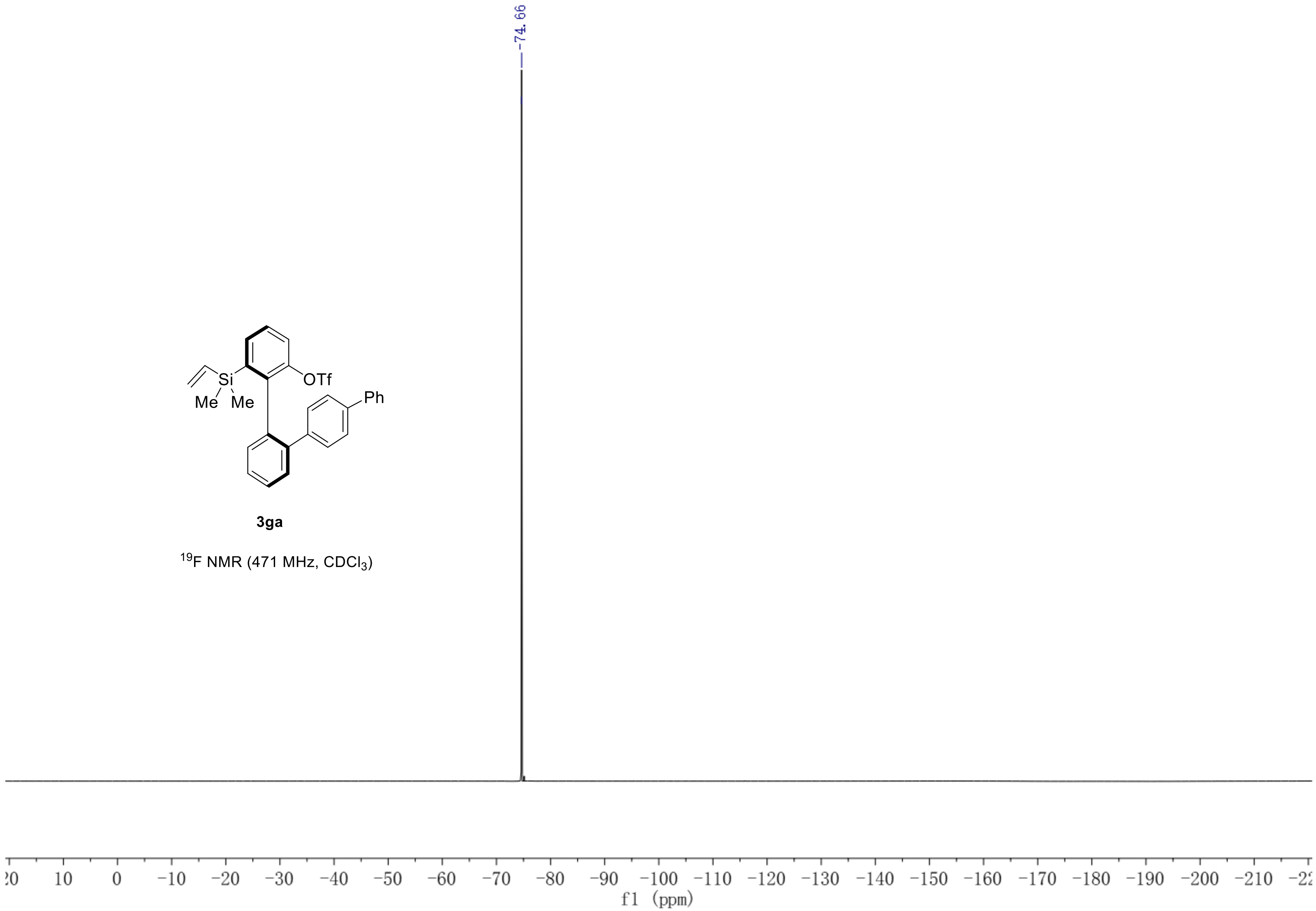
3ga

^{1}H NMR (500 MHz, $CDCl_3$)



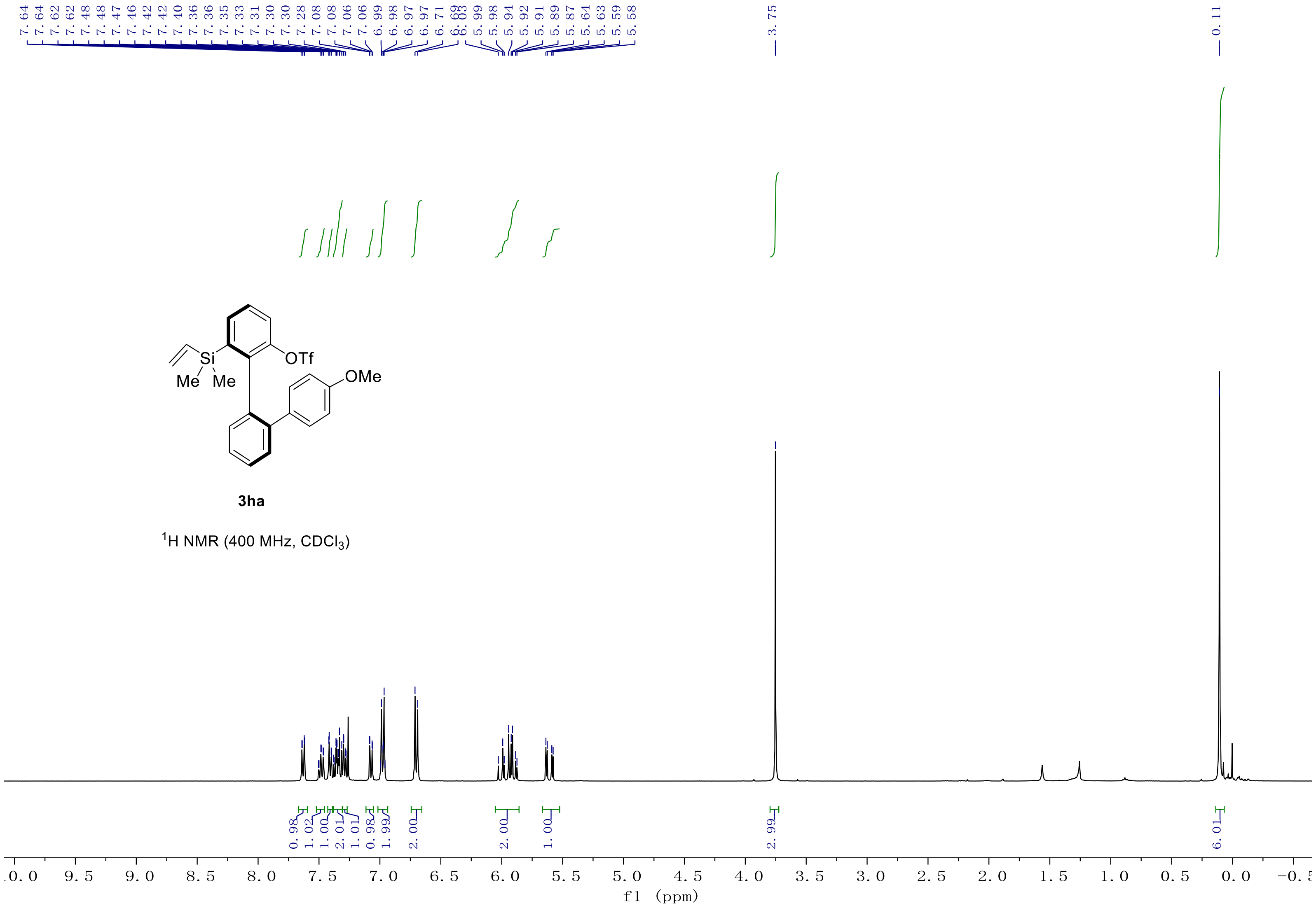
3ga

^{13}C NMR (126 MHz, $CDCl_3$)



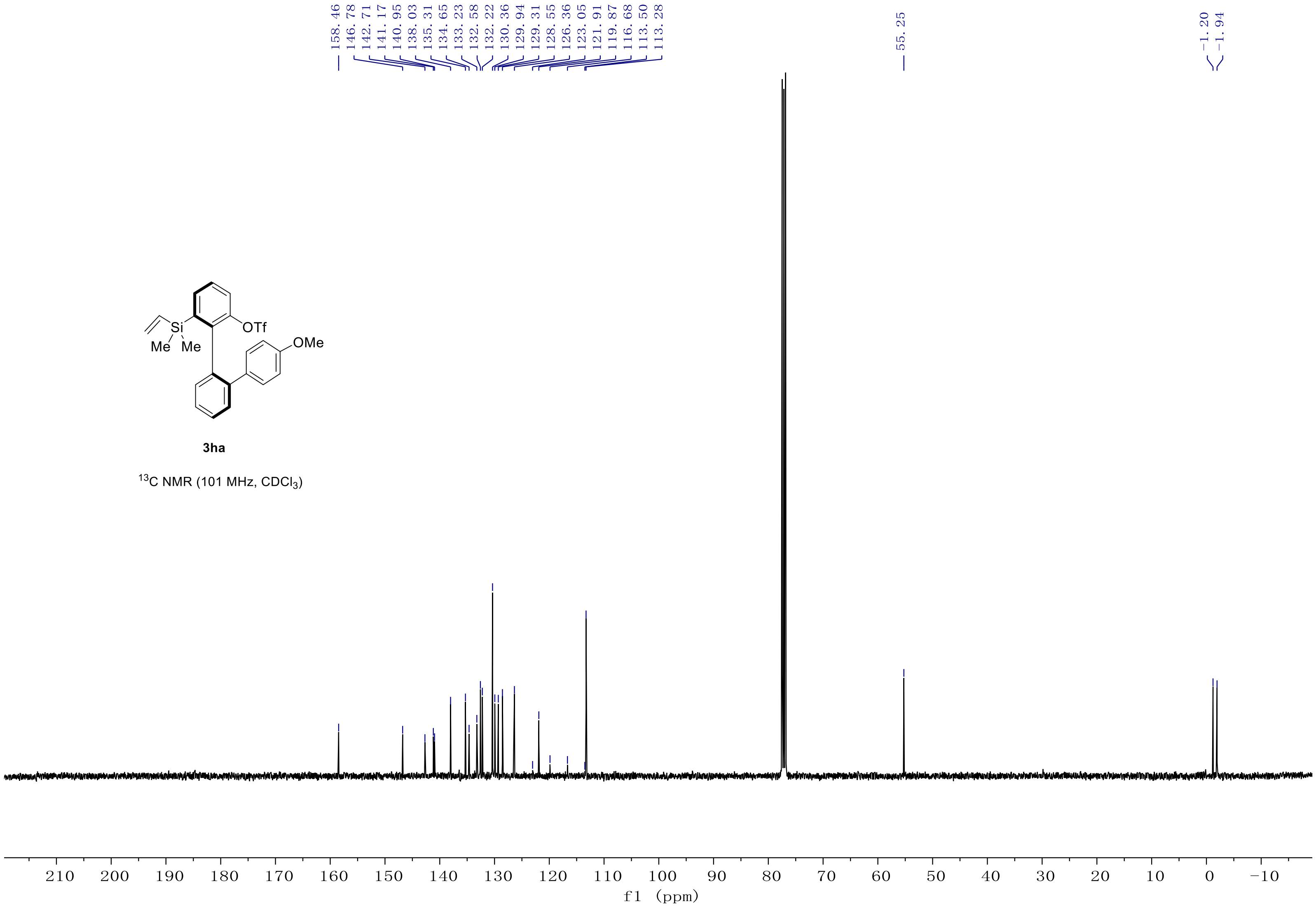
3ga

^{19}F NMR (471 MHz, $CDCl_3$)



3ha

[1]H NMR (400 MHz, $CDCl_3$)

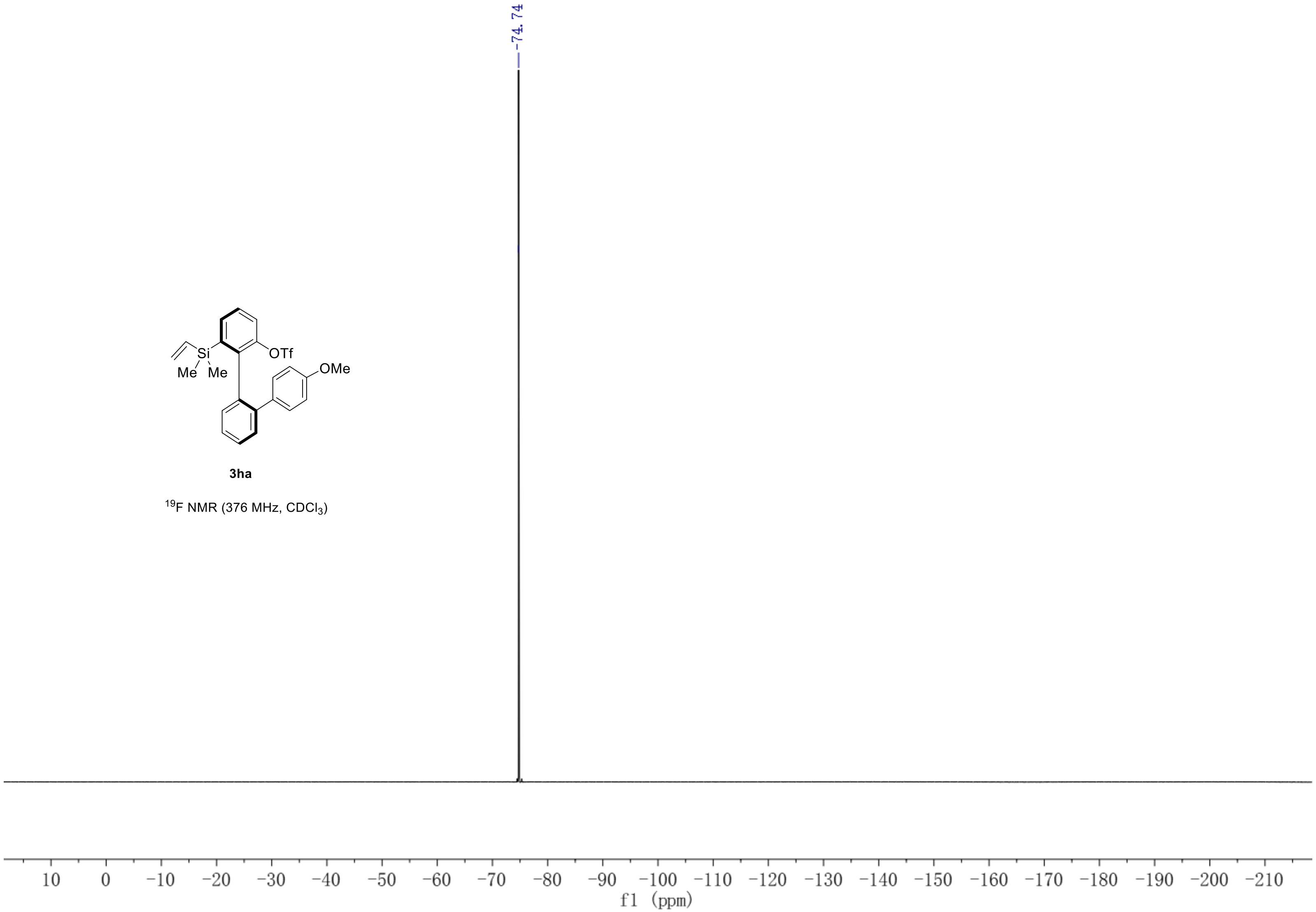


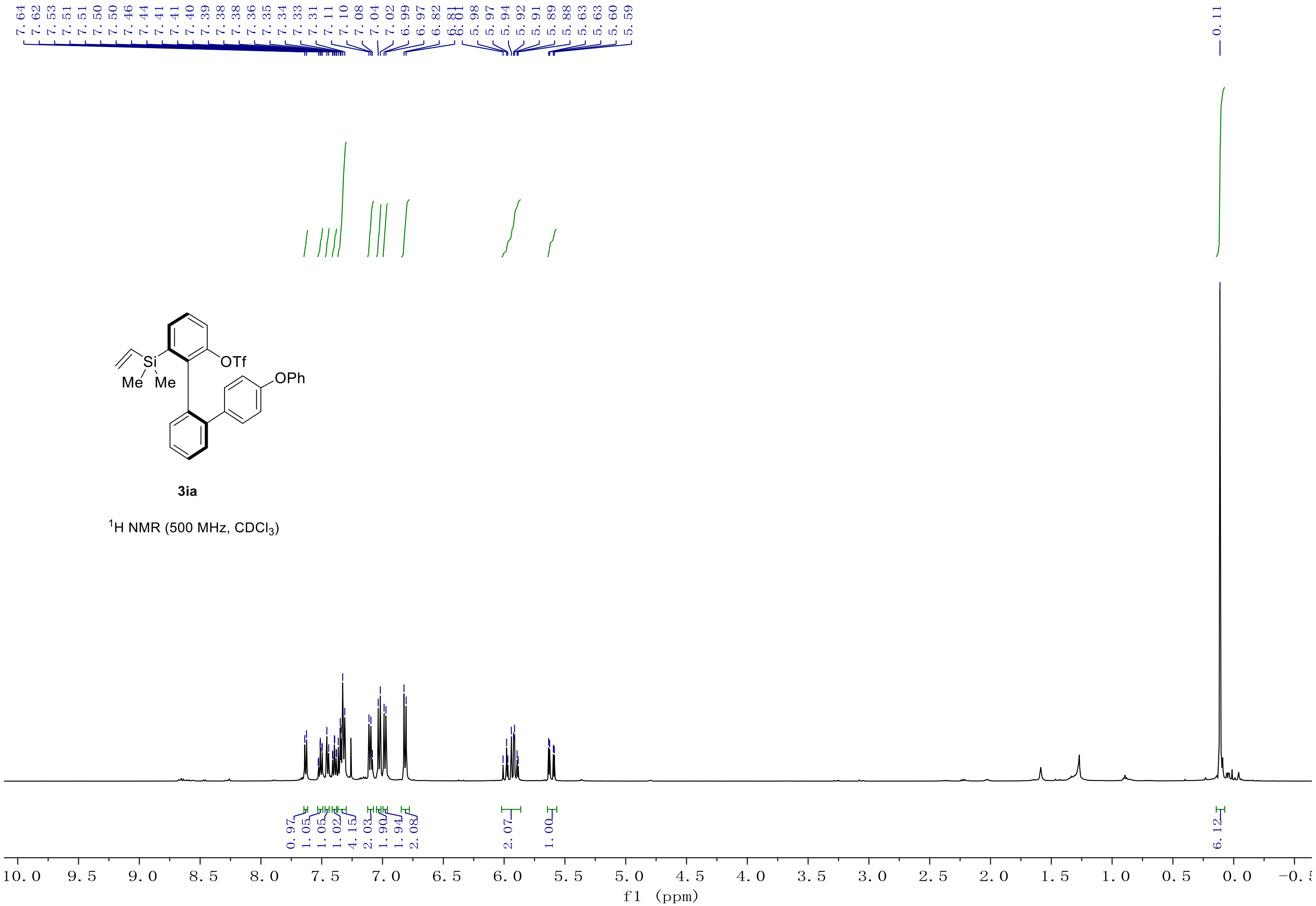
3ha

^{13}C NMR (101 MHz, $CDCl_3$)

3ha

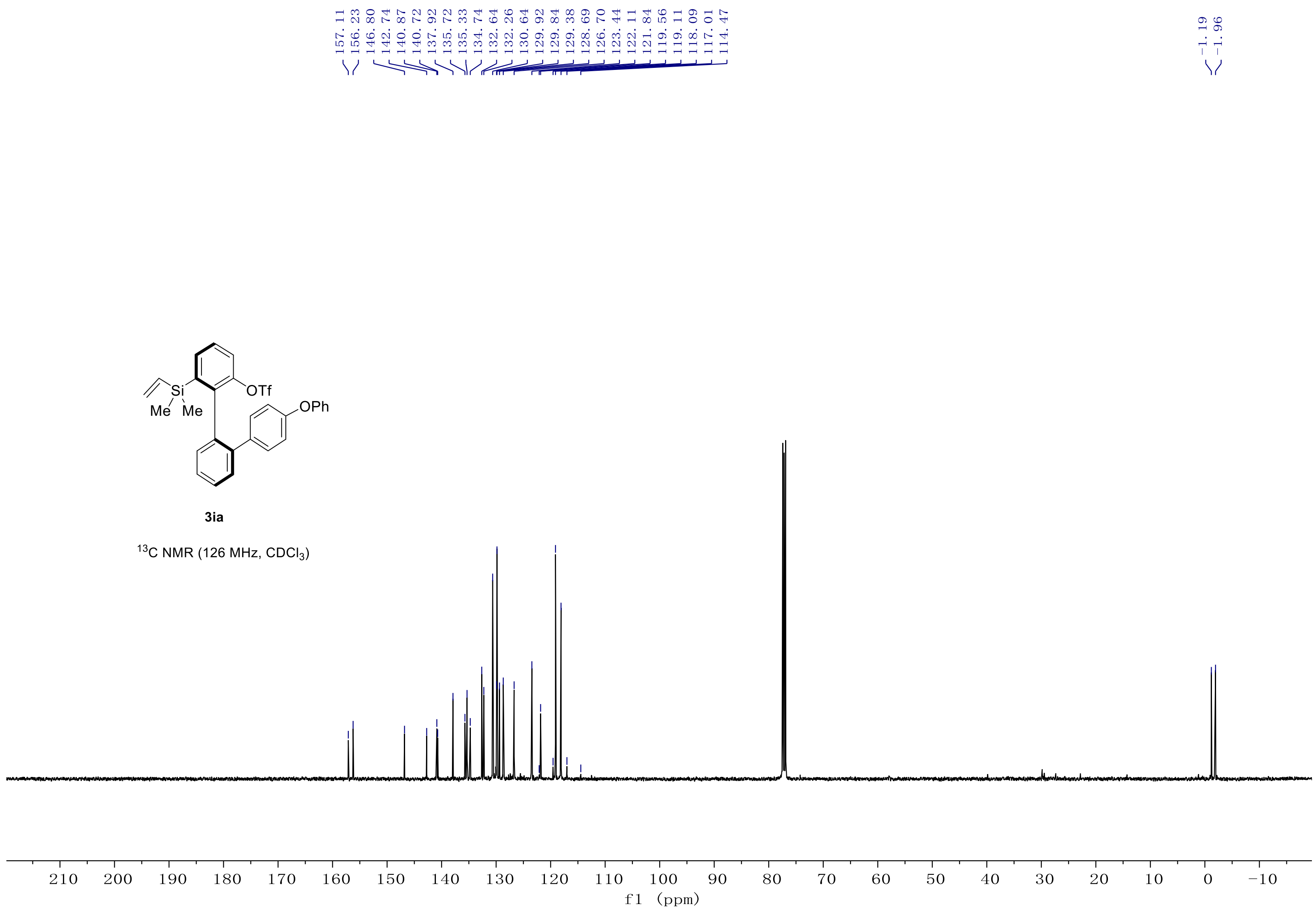
^{19}F NMR (376 MHz, $CDCl_3$)

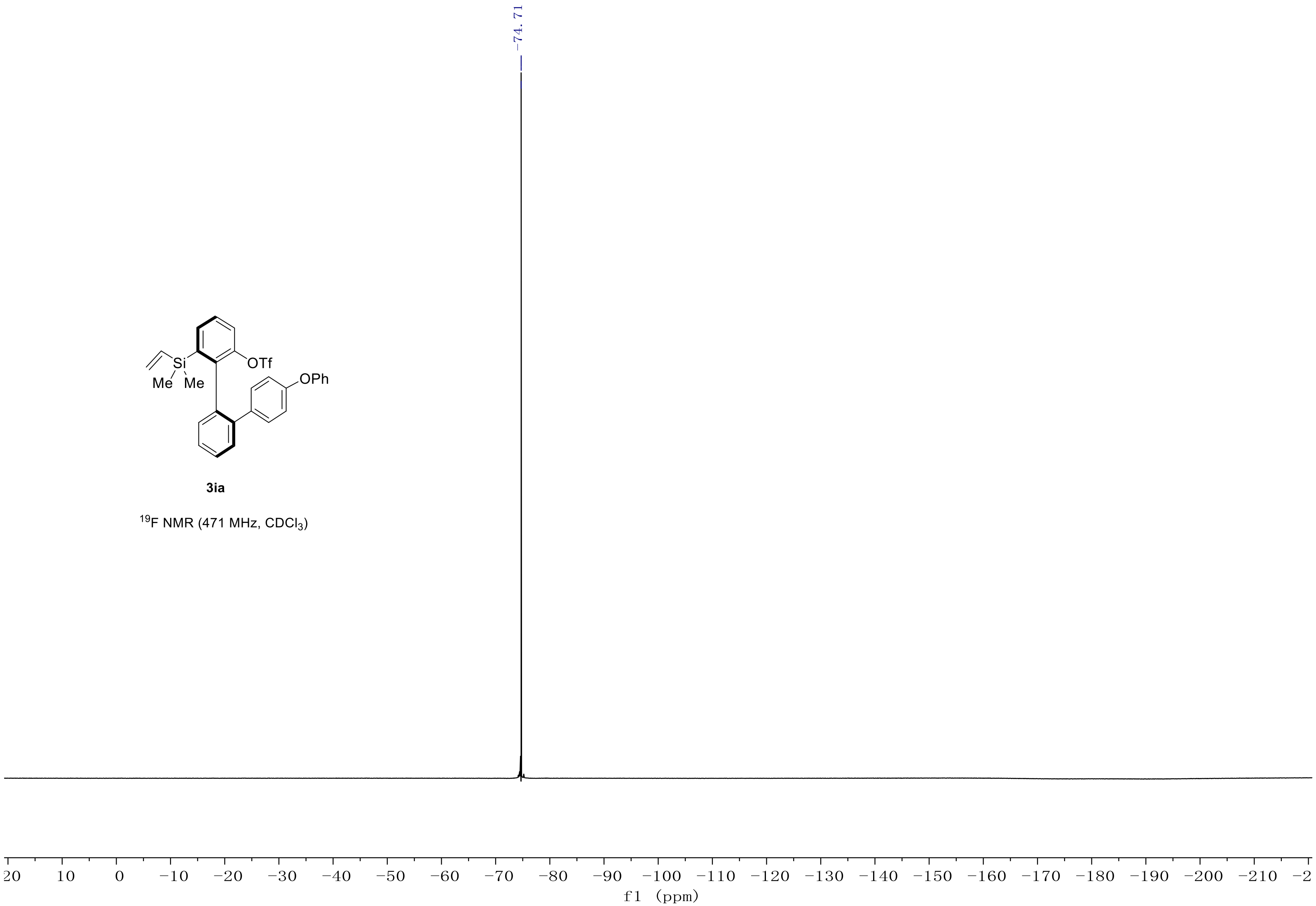




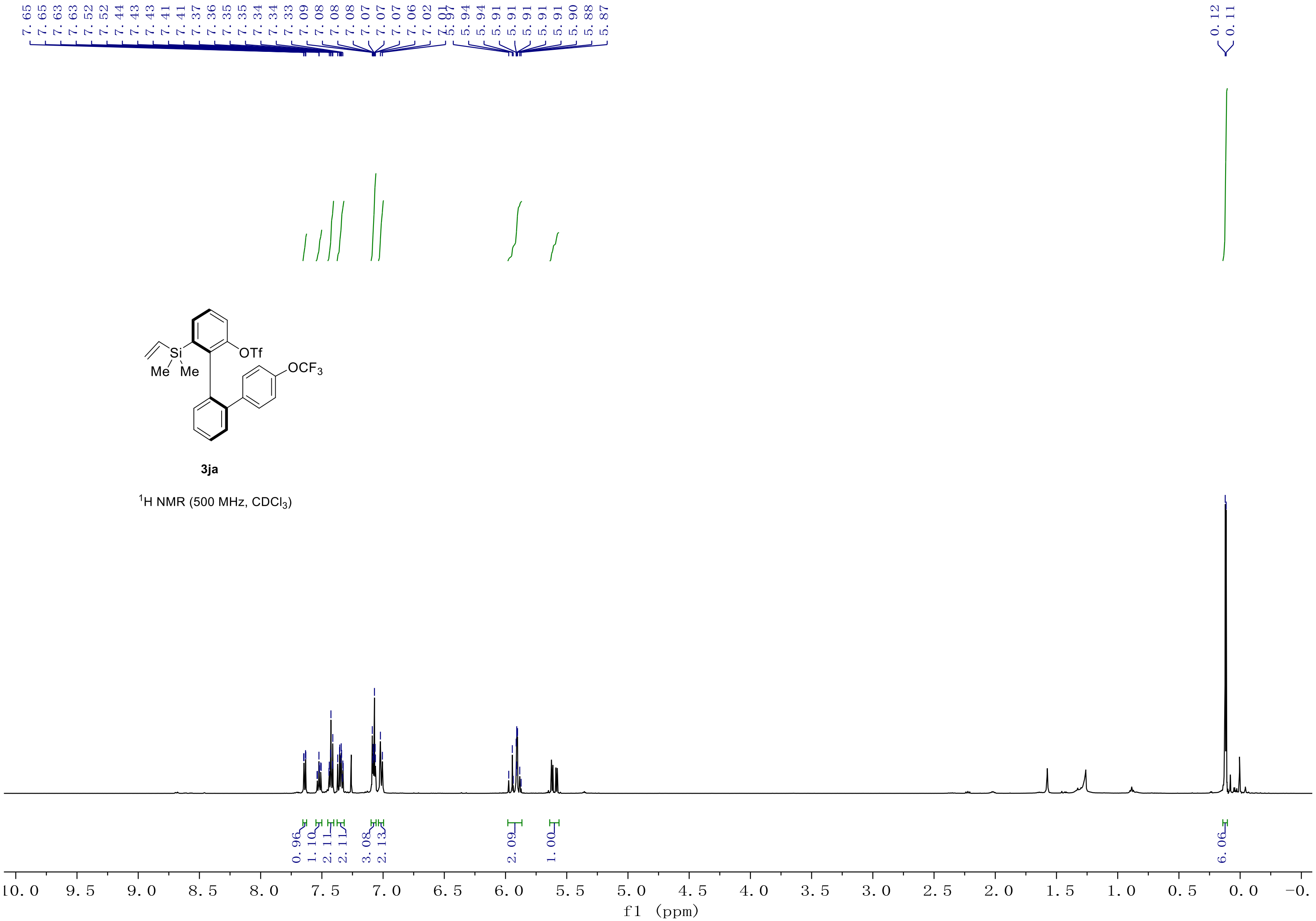
3ia

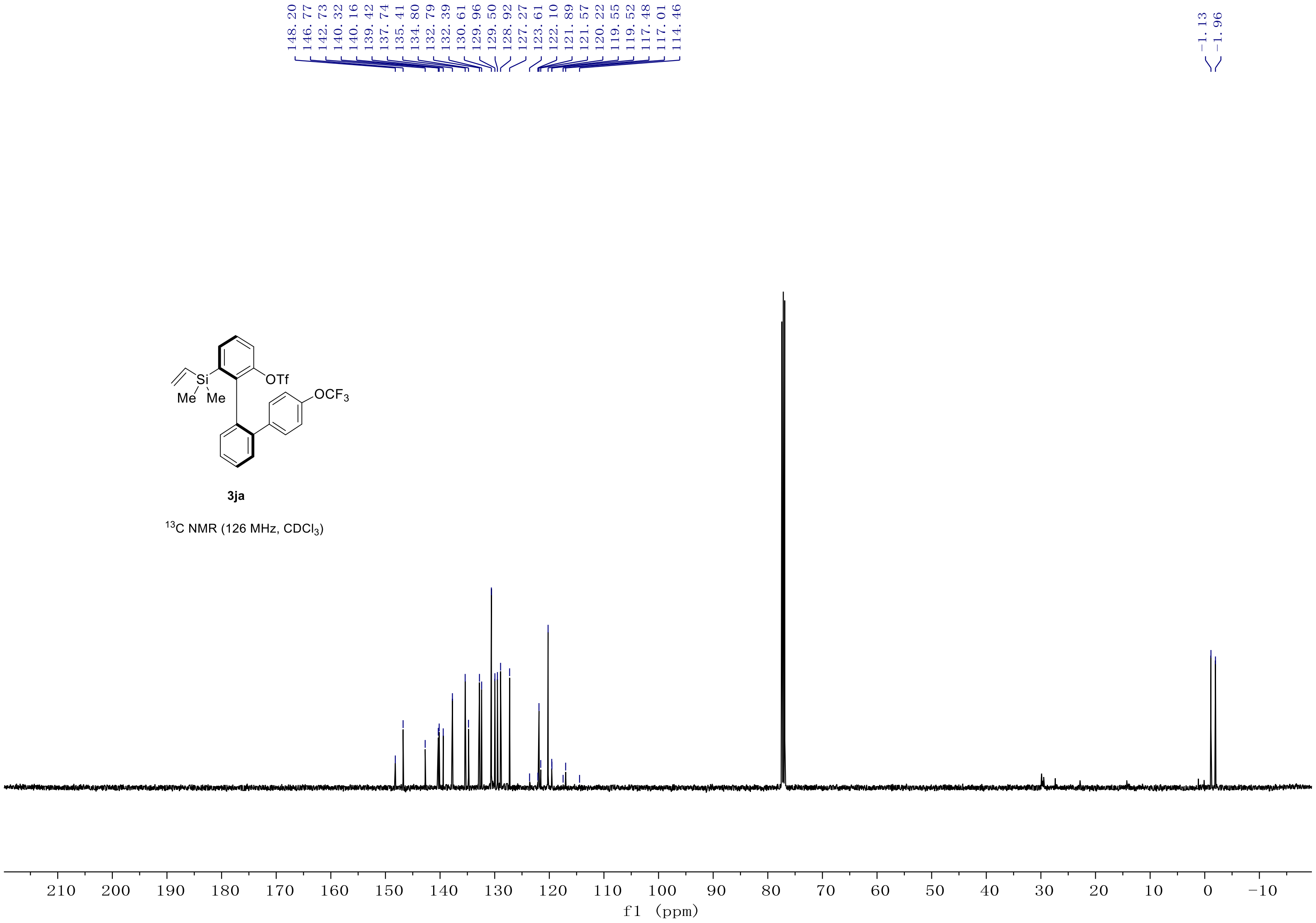
^{1}H NMR (500 MHz, $CDCl_3$)


157.11
156.23
146.80
142.74
140.87
140.72
137.92
135.72
135.33
134.74
132.64
132.26
130.64
129.92
129.84
129.38
128.69
126.70
123.44
122.11
121.84
119.56
119.11
118.09
117.01
114.47
-1.19
-1.96
Si
Me
Me
OTf
OPh
3ia
^{13}C NMR (126 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



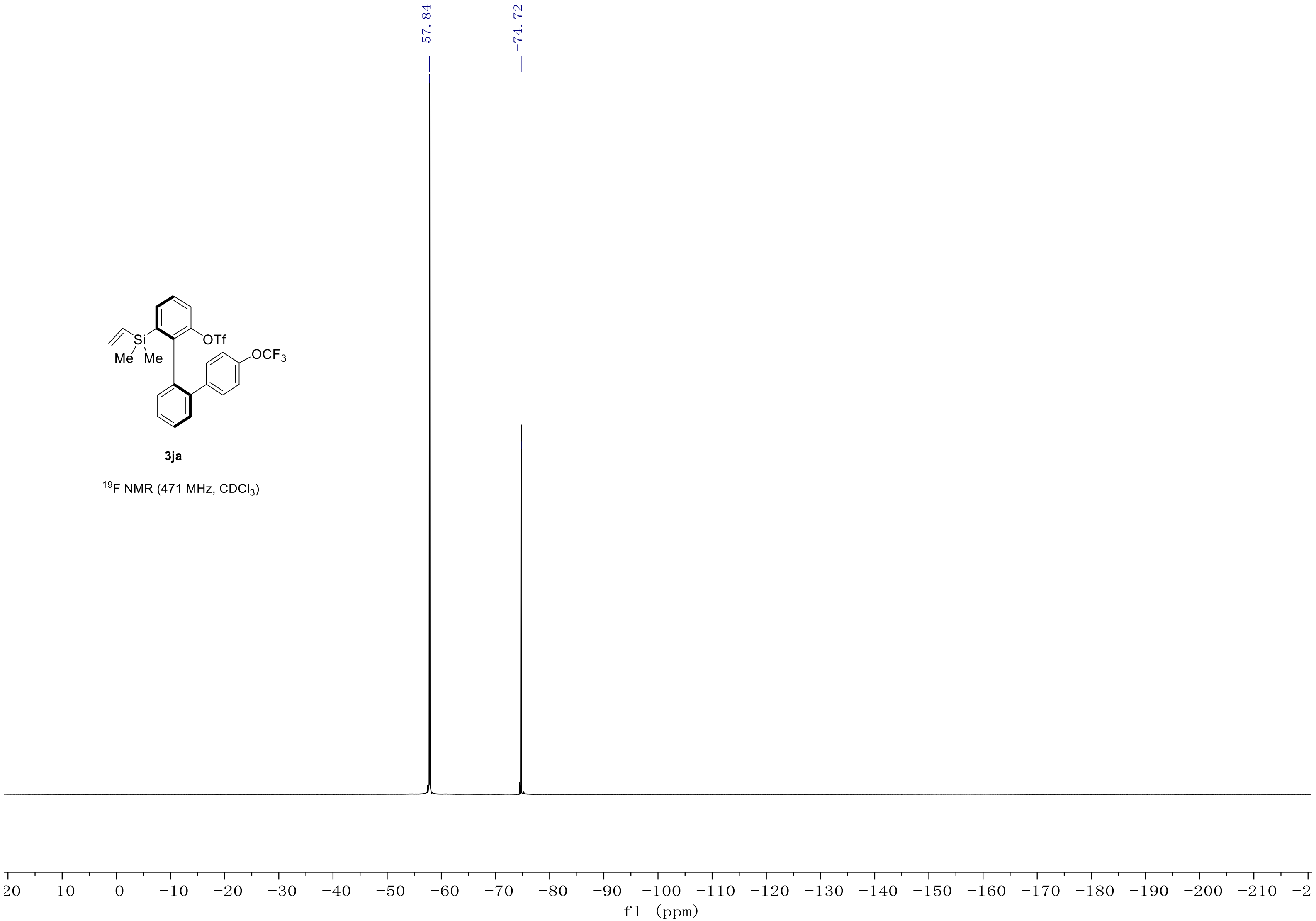
^{19}F NMR (471 MHz, $CDCl_3$)


7.65 7.65 7.63 7.63 7.52 7.52 7.44 7.43 7.43 7.41 7.41 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.09 7.08 7.08 7.08 7.07 7.07 7.07 7.06 7.02 7.01 5.97 5.94 5.94 5.91 5.91 5.91 5.91 5.91 5.90 5.88 5.87
0.12 0.11
OTf
Si
Me
Me
OCF3
3ja
1H NMR (500 MHz, CDCl3)
0.96 1.10 2.11 2.11 3.08 2.13 2.09 1.00 6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)



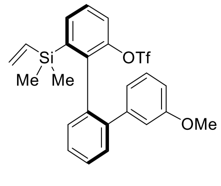
3ja

^{13}C NMR (126 MHz, $CDCl_3$)



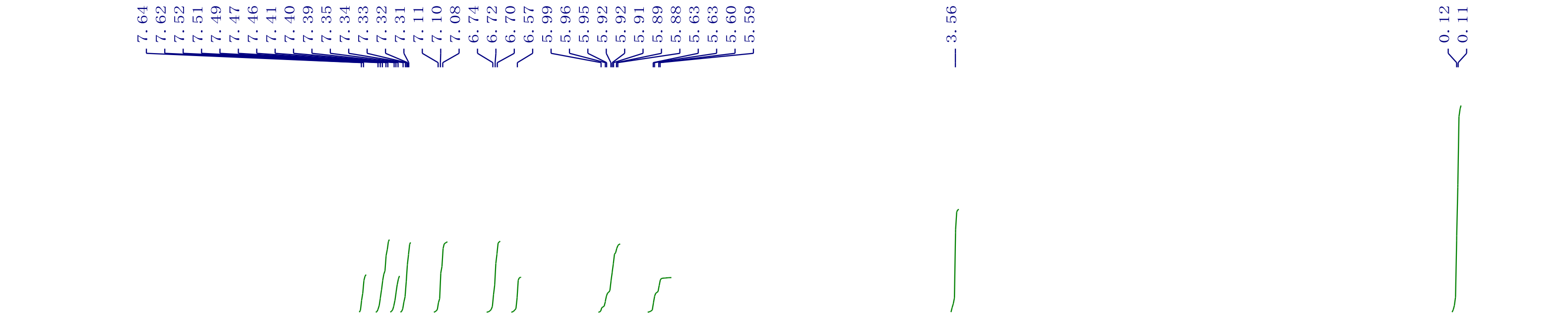
3ja

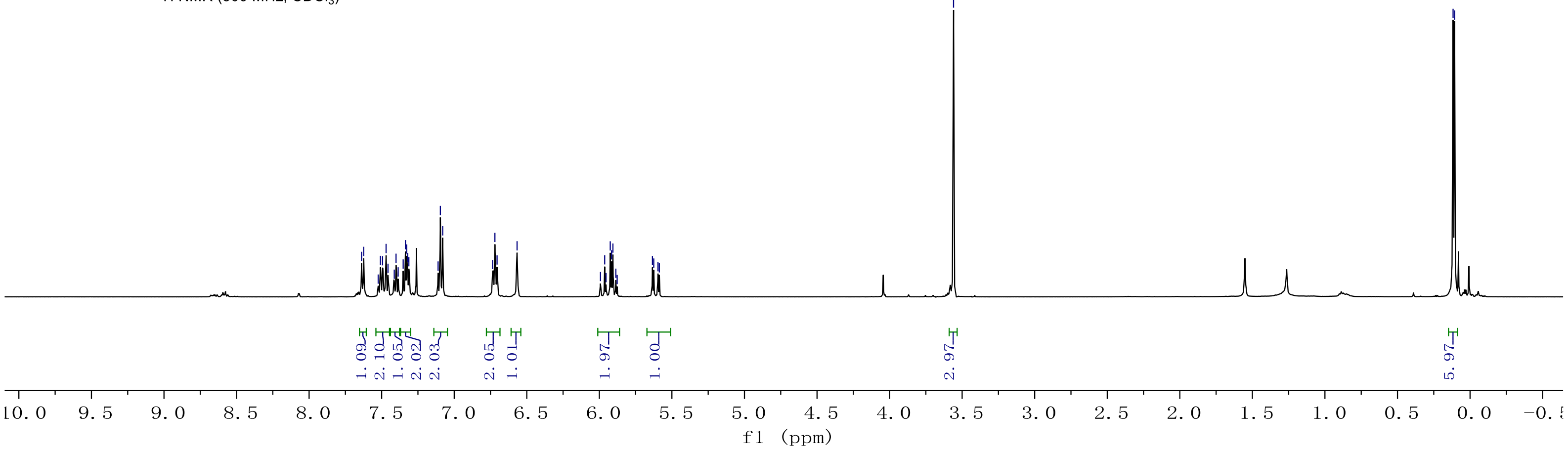
^{19}F NMR (471 MHz, $CDCl_3$)

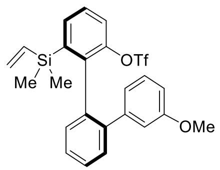


3ka

[1]H NMR (500 MHz, $CDCl_3$)

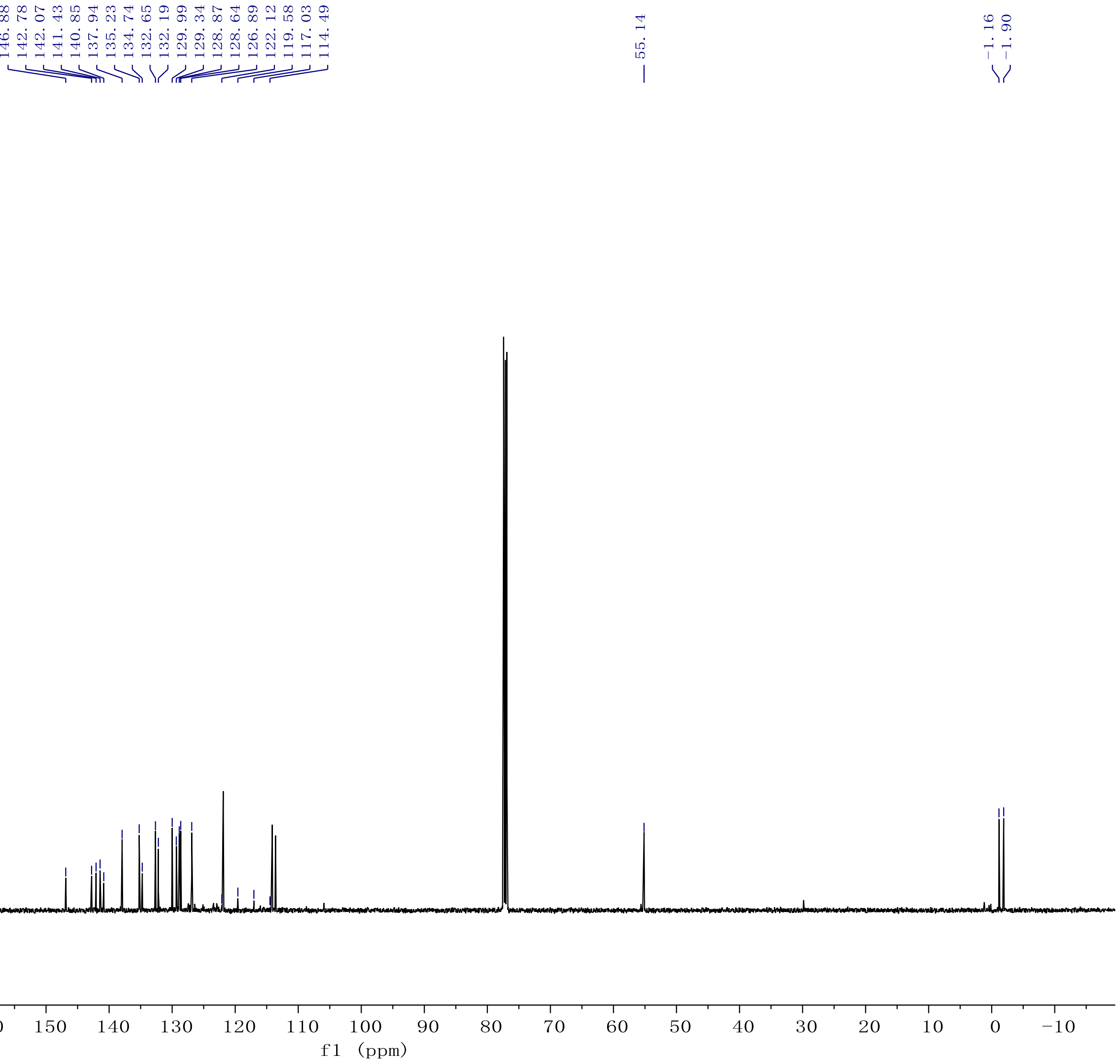


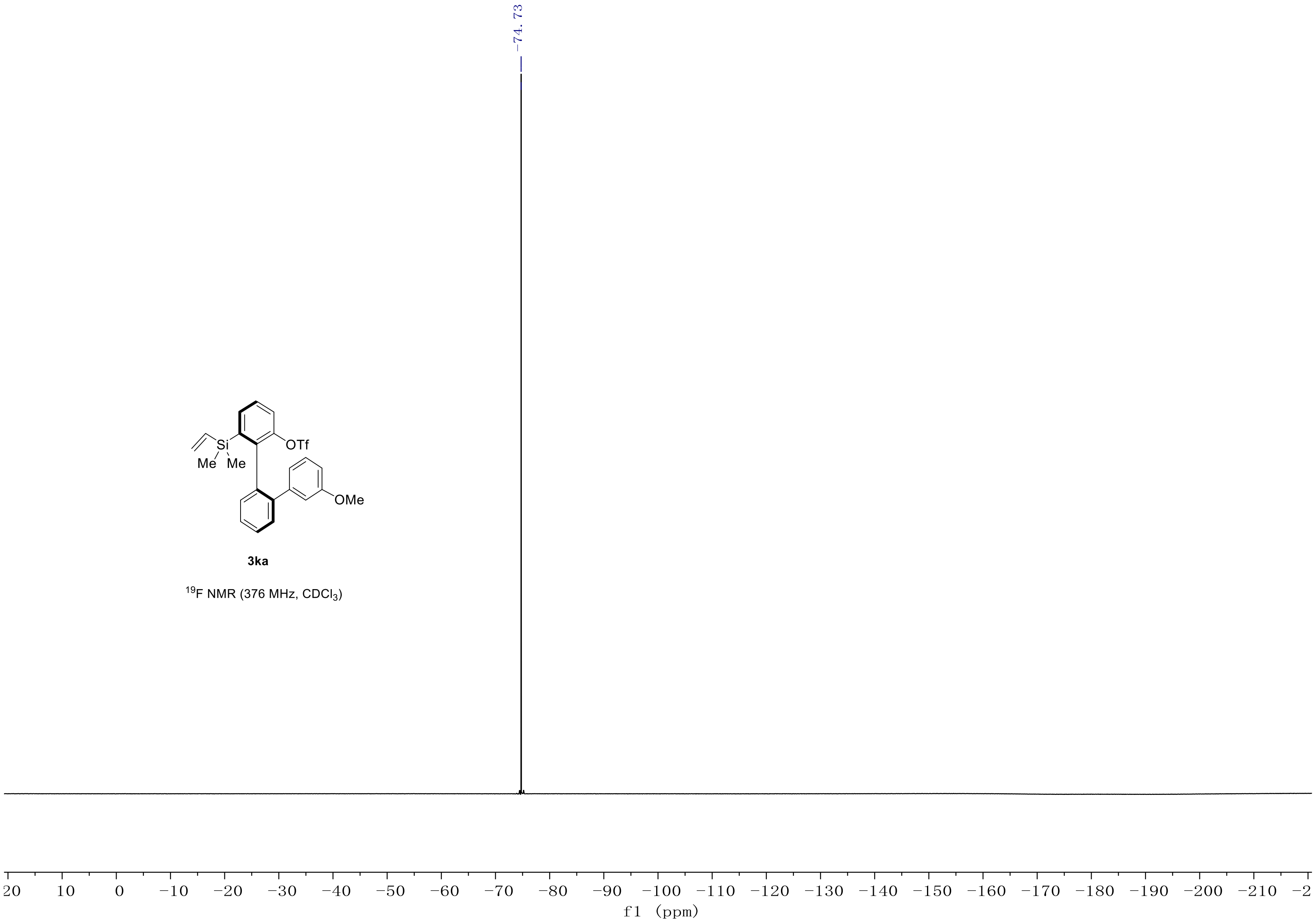




3ka

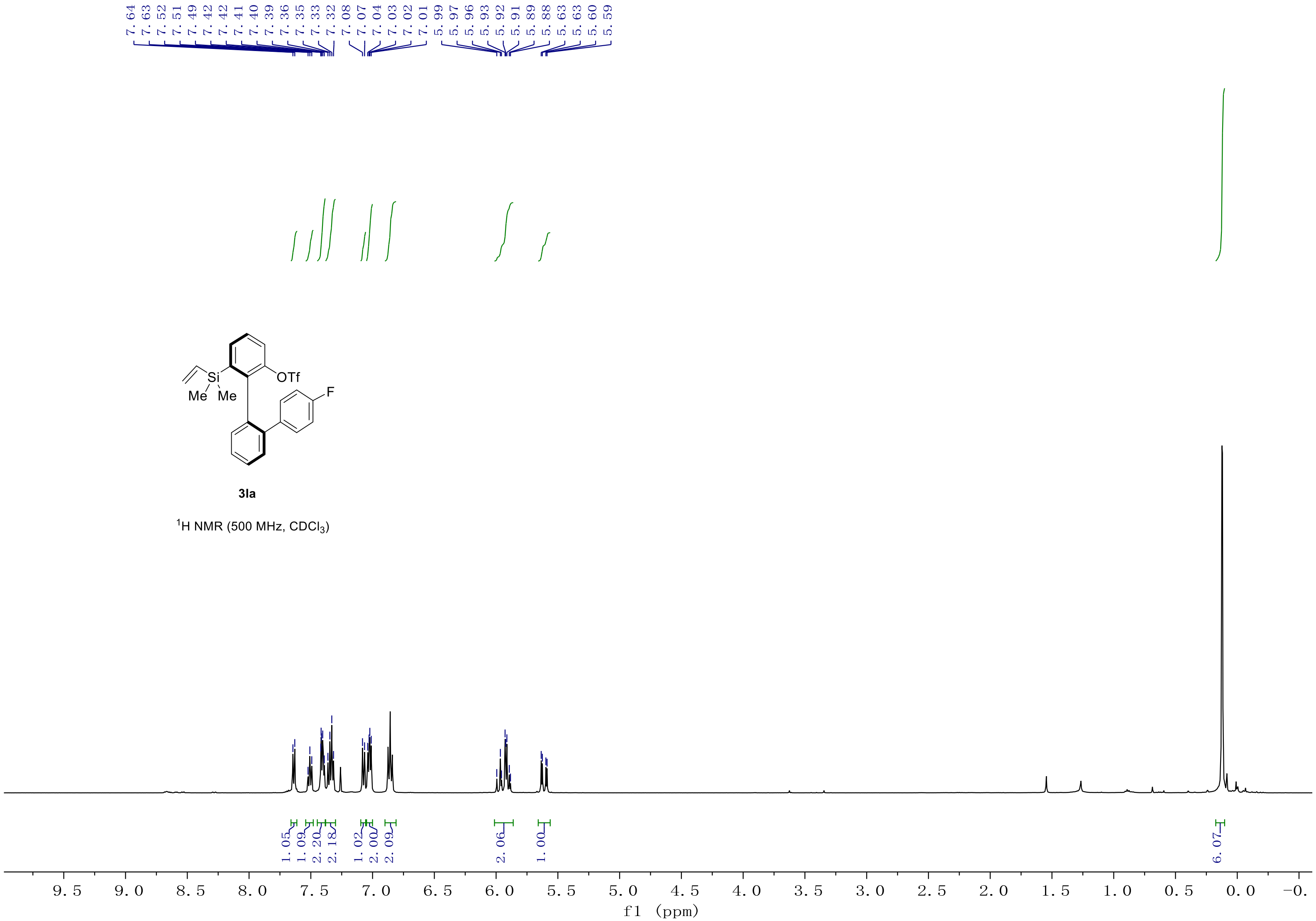
^{13}C NMR (126 MHz, $CDCl_3$)





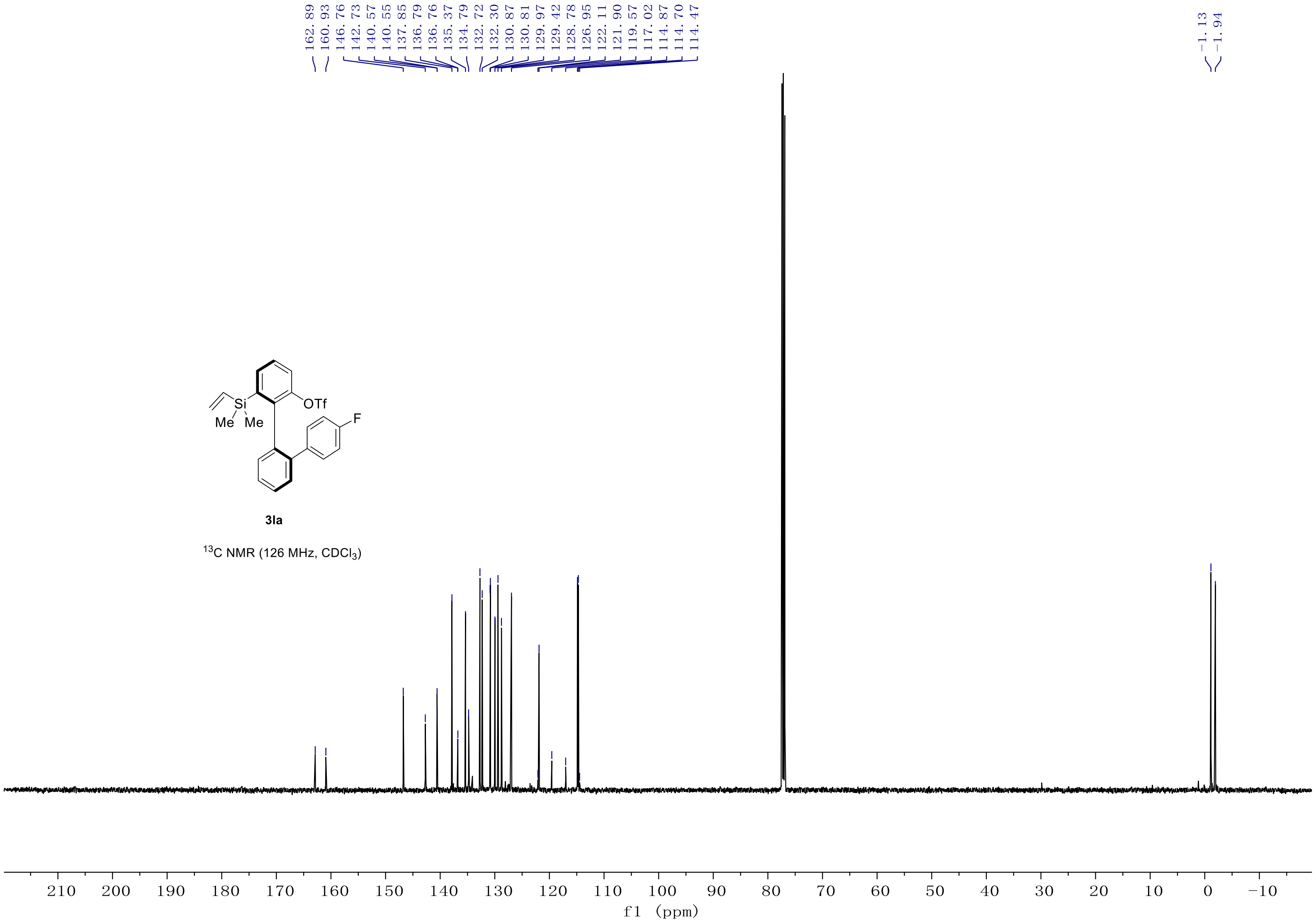
3ka

^{19}F NMR (376 MHz, $CDCl_3$)



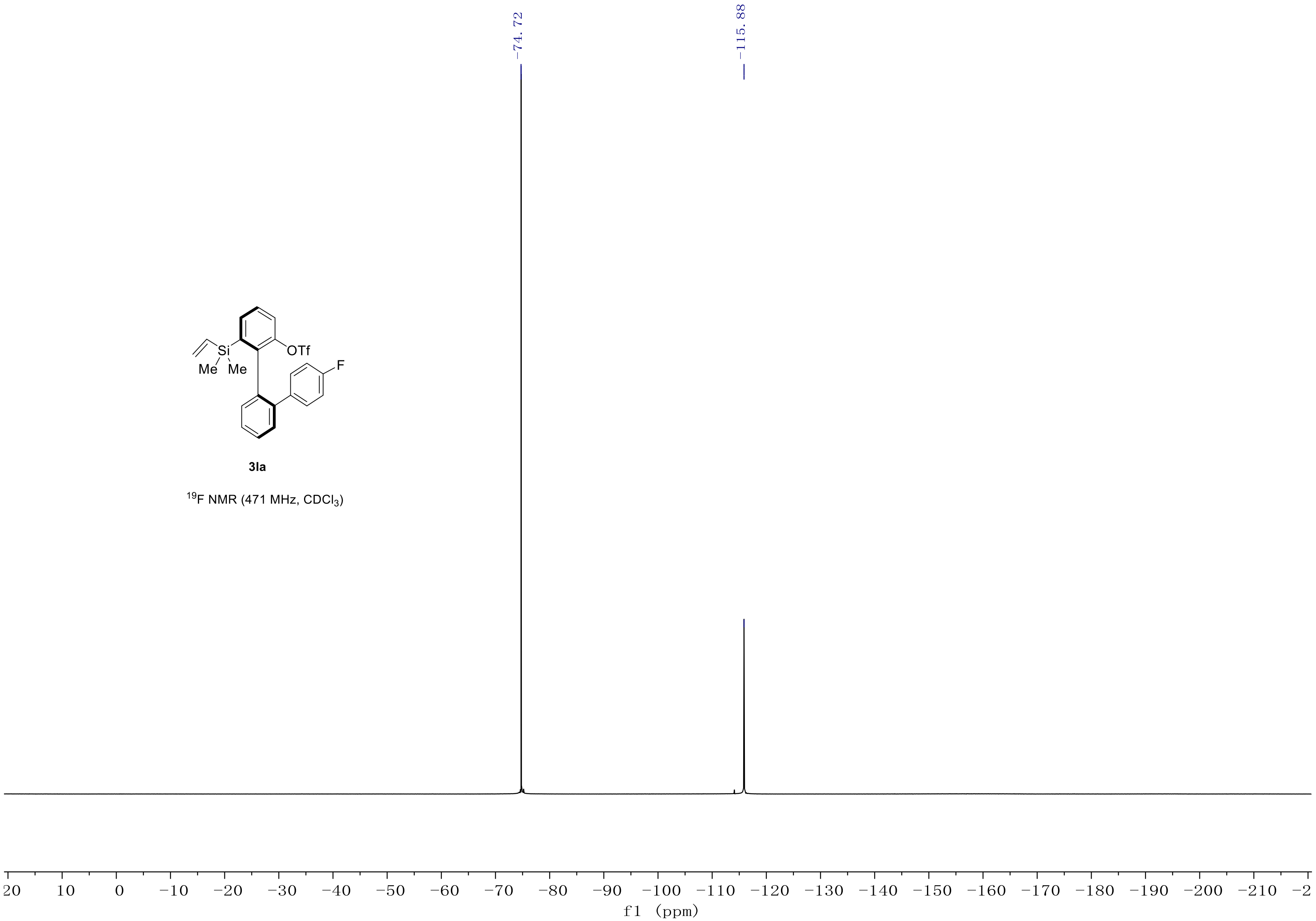
3la

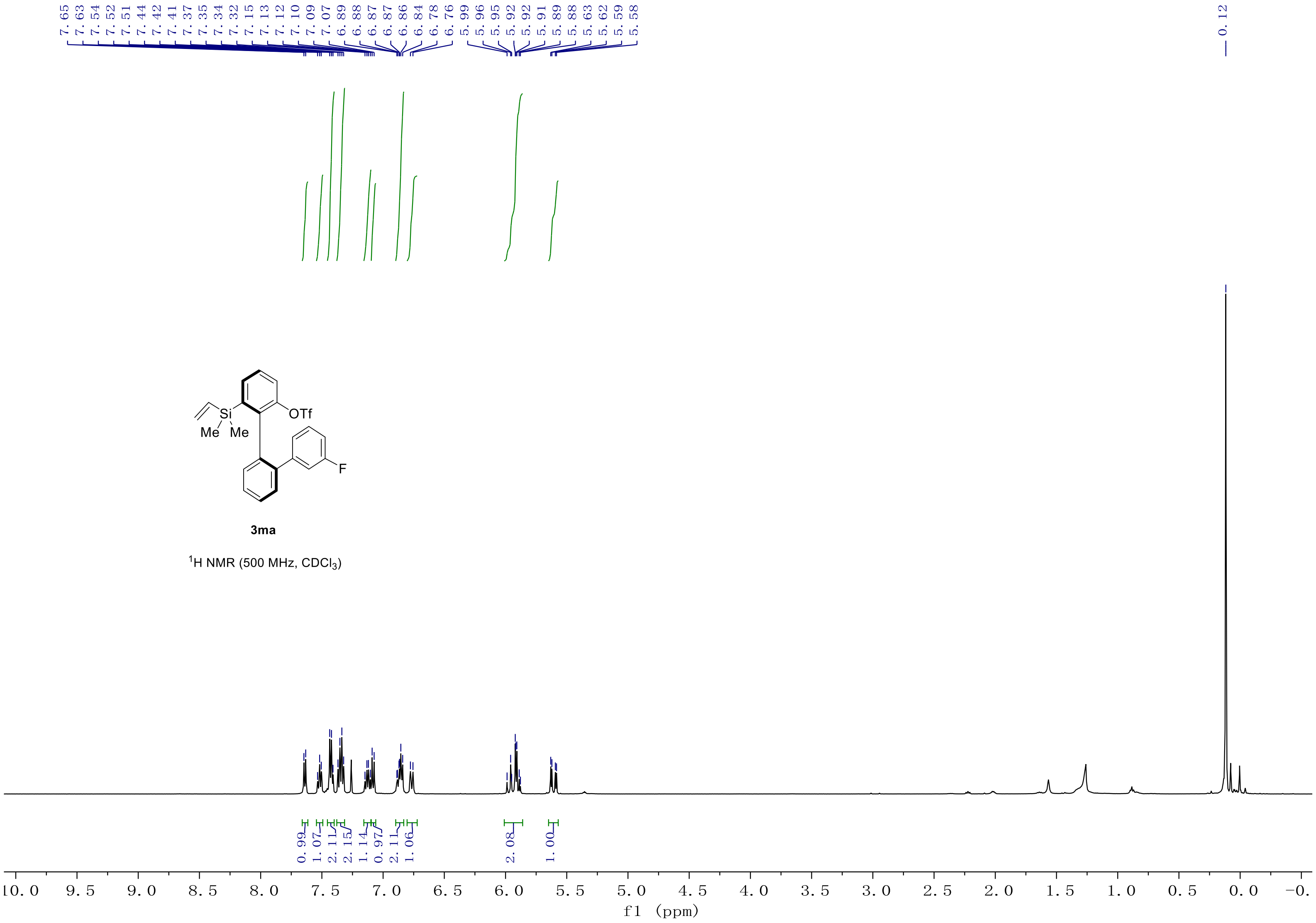
^{1}H NMR (500 MHz, $CDCl_3$)



3la

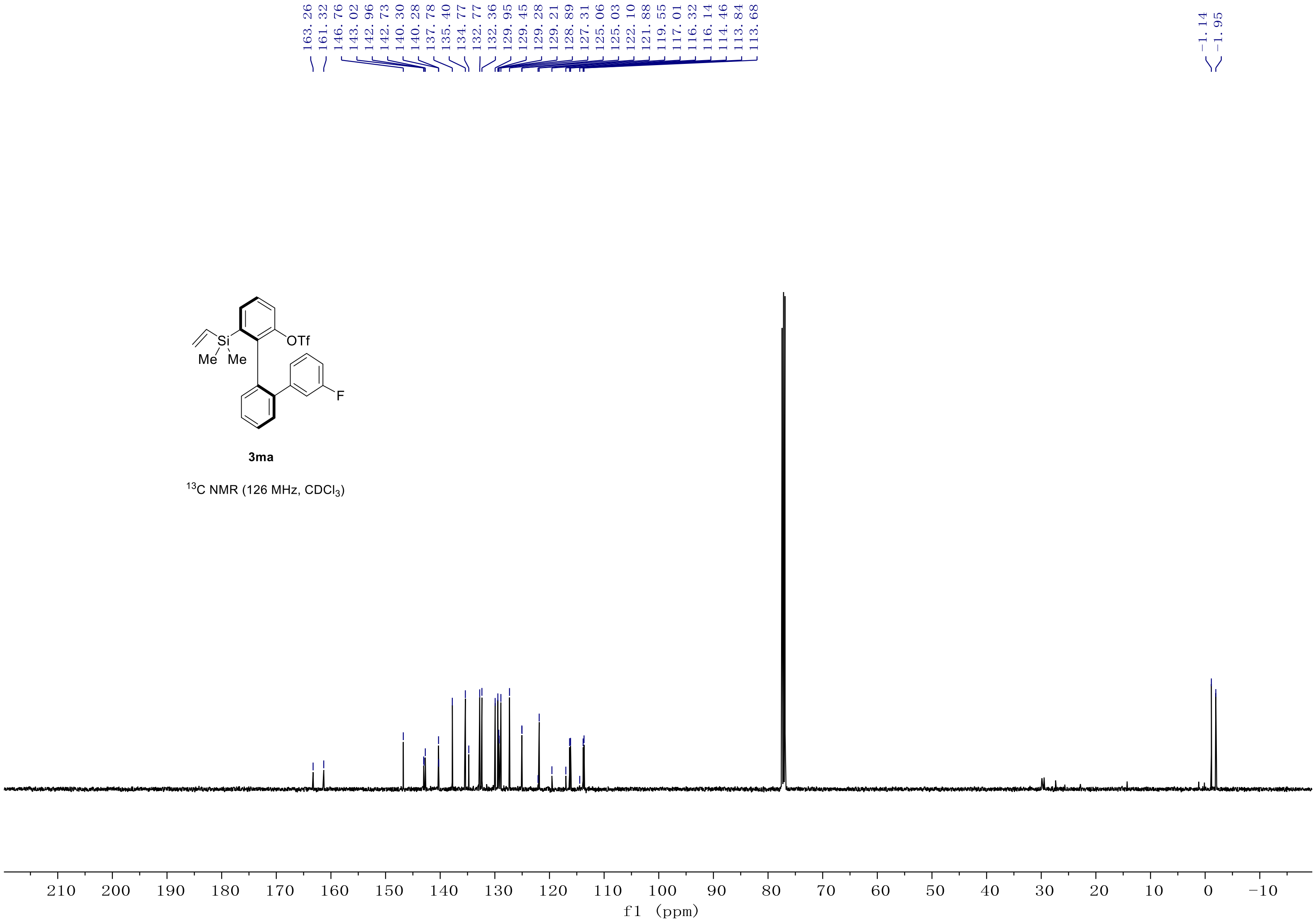
^{13}C NMR (126 MHz, $CDCl_3$)

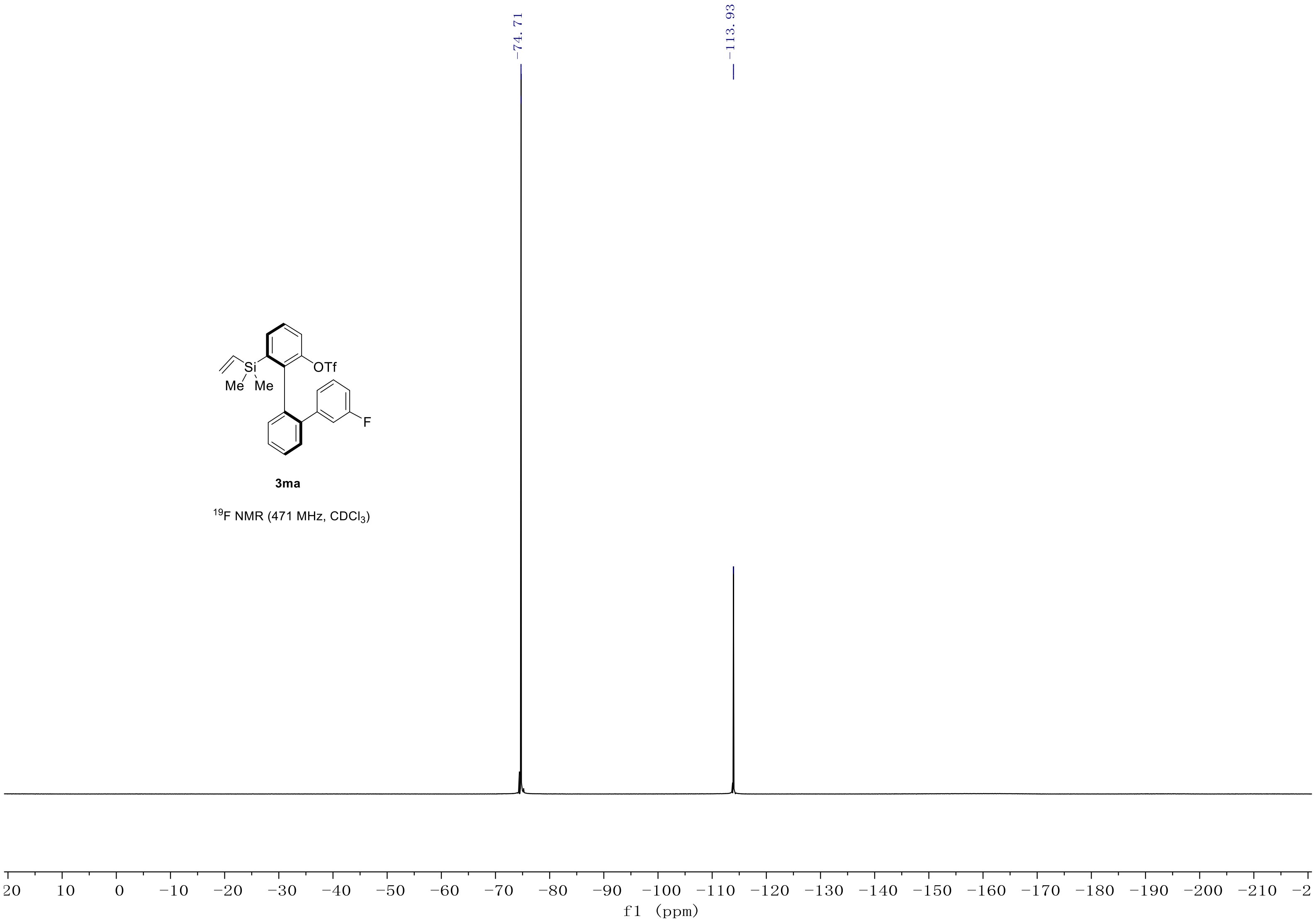

Si
Me
Me
OTf
F
3la
^{19}F NMR (471 MHz, $CDCl_3$)
−74.72
−115.88
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

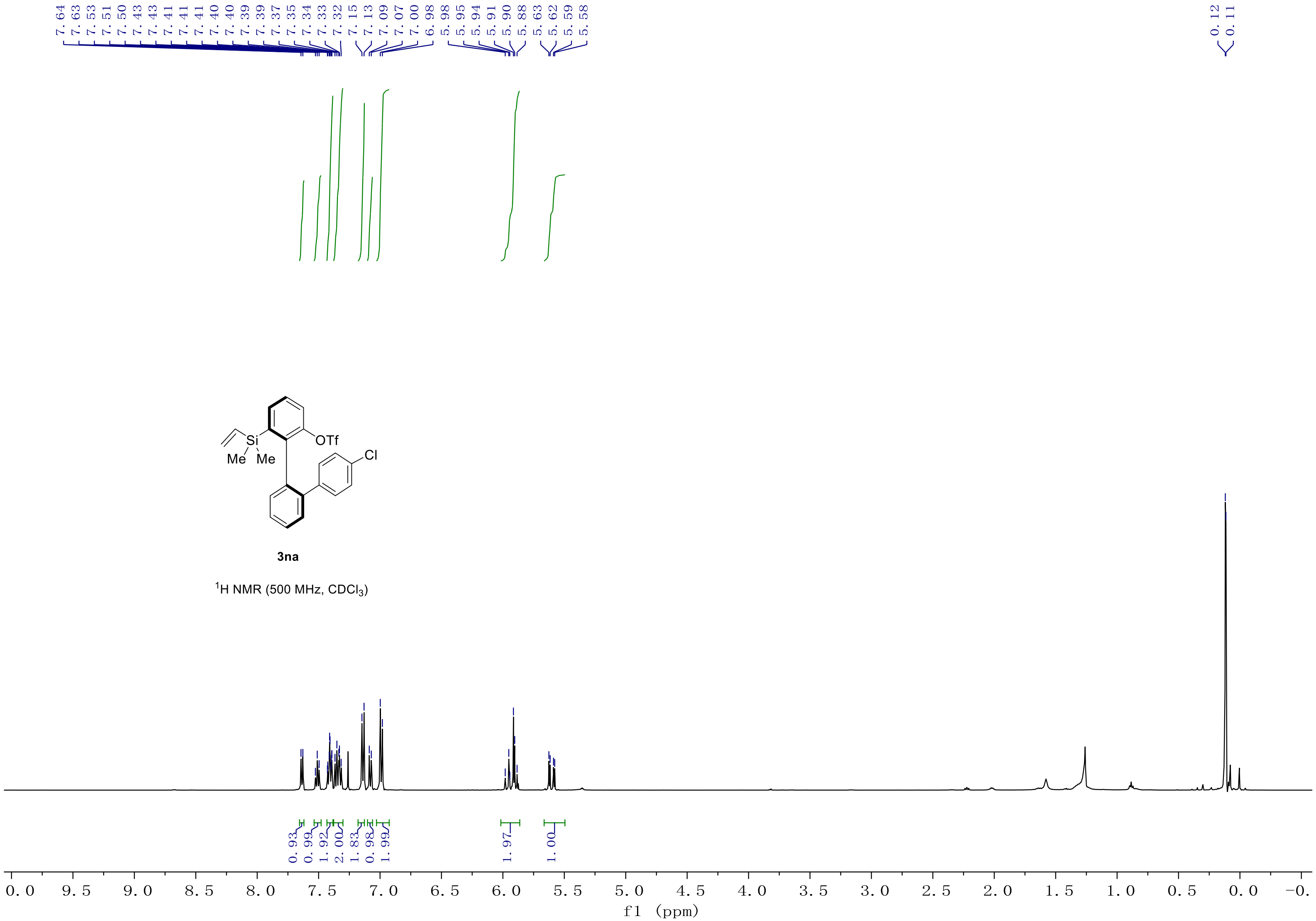


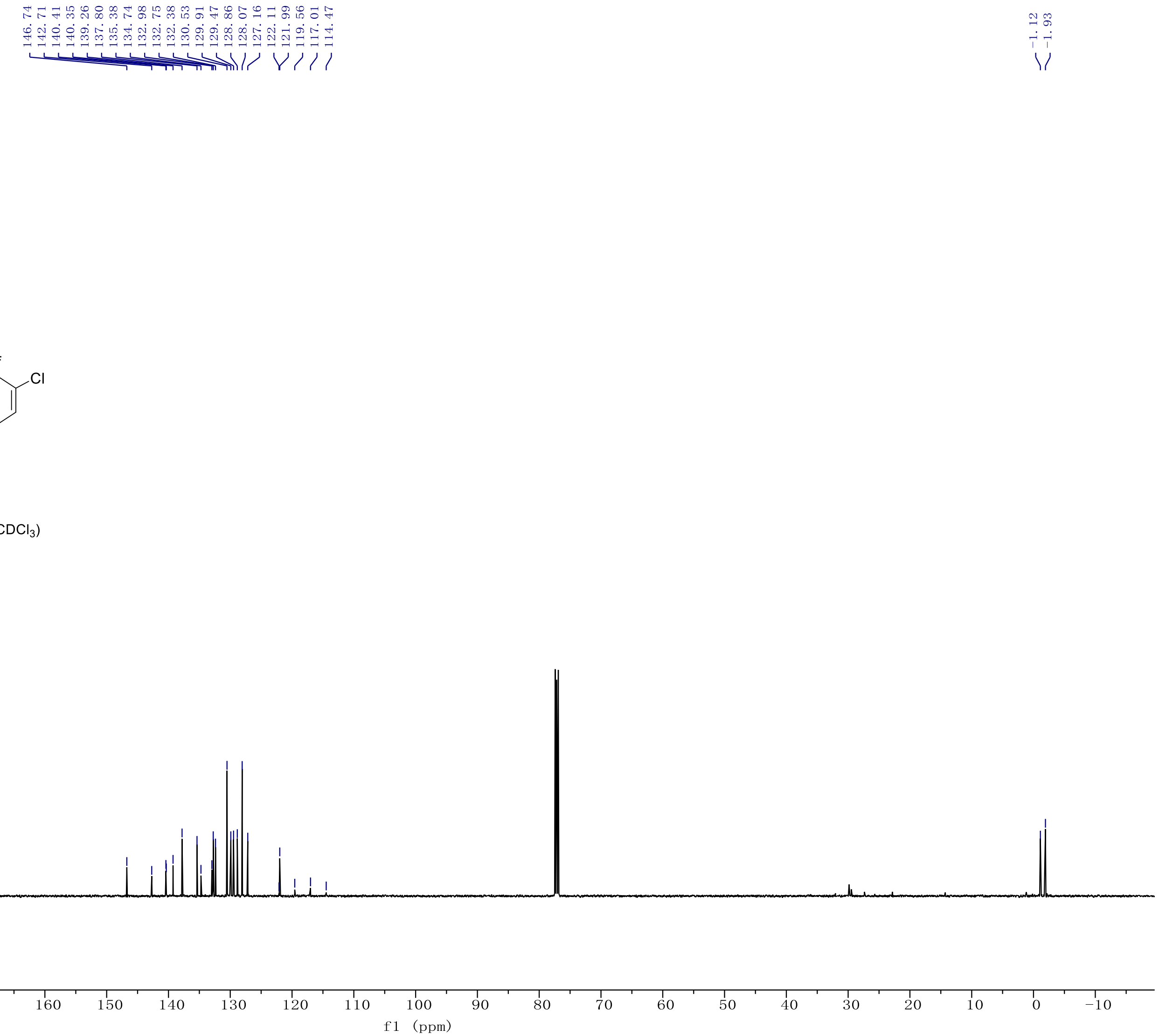
3ma

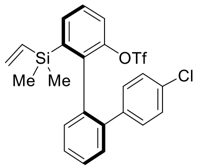
^{1}H NMR (500 MHz, $CDCl_3$)


163.26
161.32
146.76
143.02
142.96
142.73
140.30
140.28
137.78
135.40
134.77
132.77
132.36
129.95
129.45
129.28
129.21
128.89
127.31
125.06
125.03
122.10
121.88
119.55
117.01
116.32
116.14
114.46
113.84
113.68
-1.14
-1.95
Si
Me
Me
OTf
F
3ma
^{13}C NMR (126 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-74.71
-113.93
OTf
Si
Me
Me
F
3ma
19F NMR (471 MHz, CDCl3)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

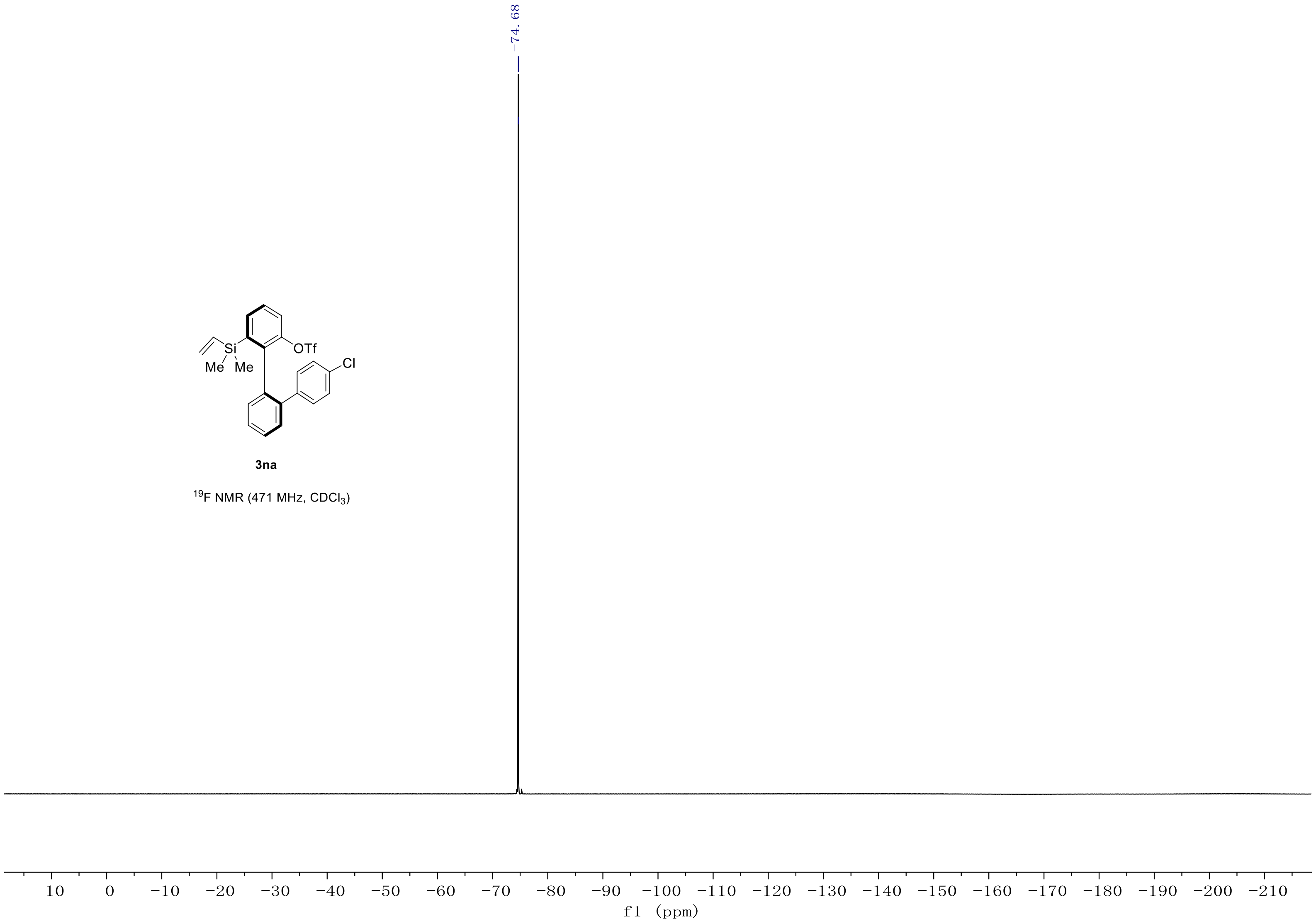

7.64 7.63 7.53 7.51 7.50 7.43 7.43 7.41 7.41 7.41 7.40 7.40 7.39 7.39 7.37 7.35 7.34 7.33 7.32 7.15 7.13 7.09 7.07 7.00 6.98 5.98 5.95 5.94 5.91 5.90 5.88 5.63 5.62 5.59 5.58
0.12 0.11
Si
Me Me
OTf
Cl
3na
^{1}H NMR (500 MHz, CDCl$_3$)
0.93 0.99 1.92 2.00 1.83 0.98 1.99
1.97
1.00
f1 (ppm)





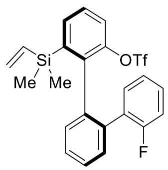
3na

^{13}C NMR (126 MHz, $CDCl_3$)



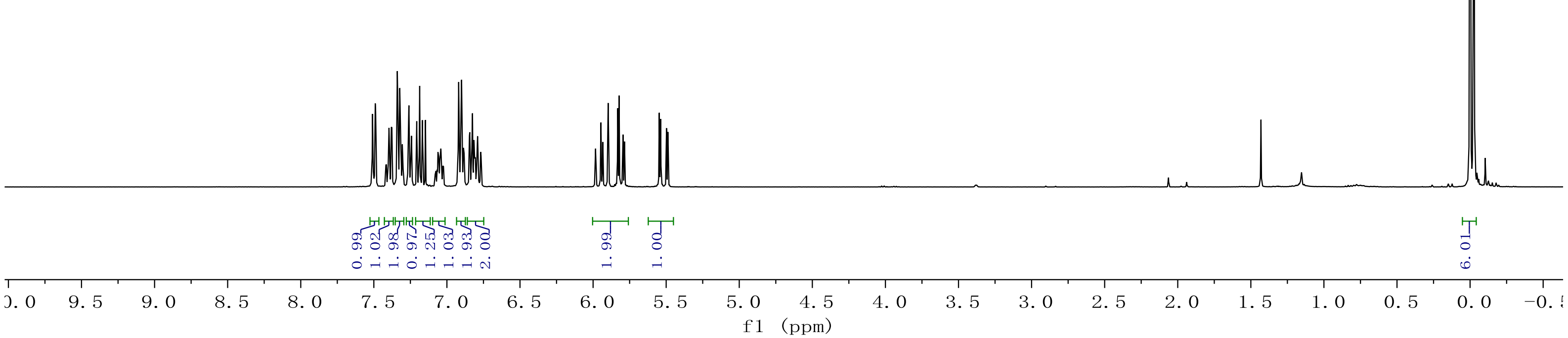
3na

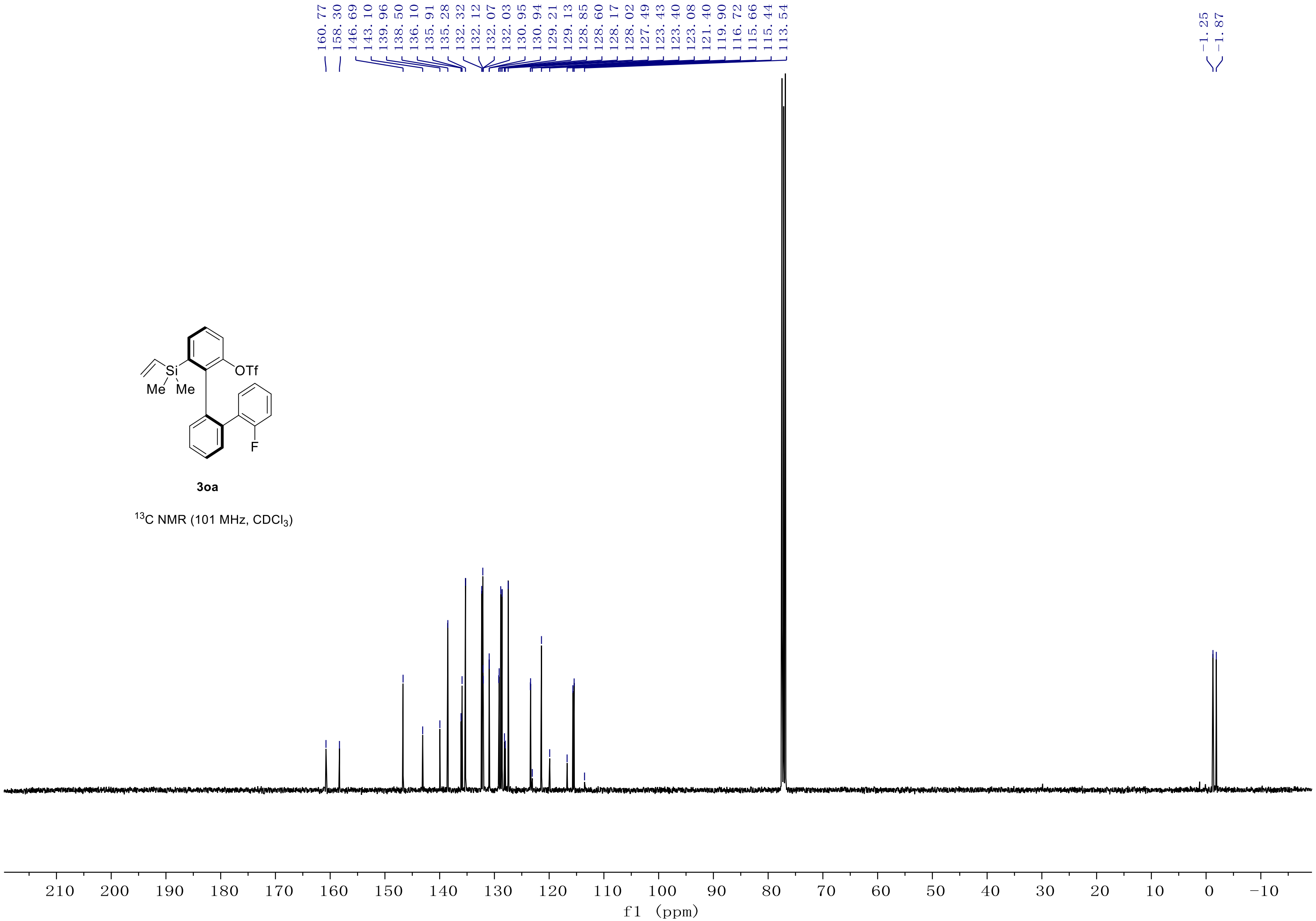
^{19}F NMR (471 MHz, $CDCl_3$)



3oa

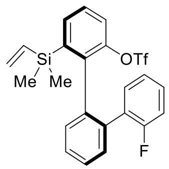
^{1}H NMR (400 MHz, $CDCl_3$)





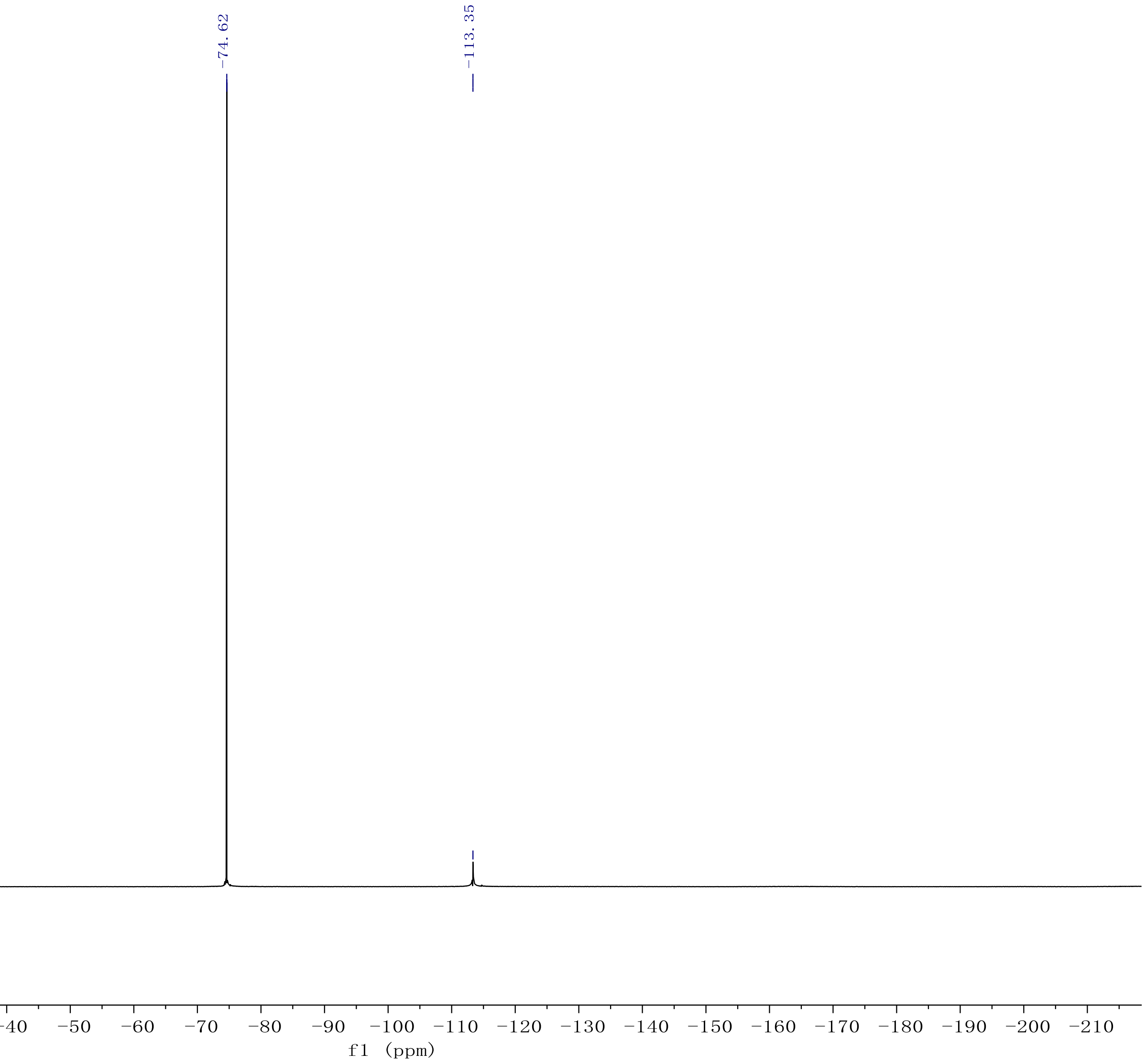
3oa

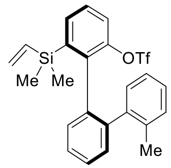
^{13}C NMR (101 MHz, $CDCl_3$)



3oa

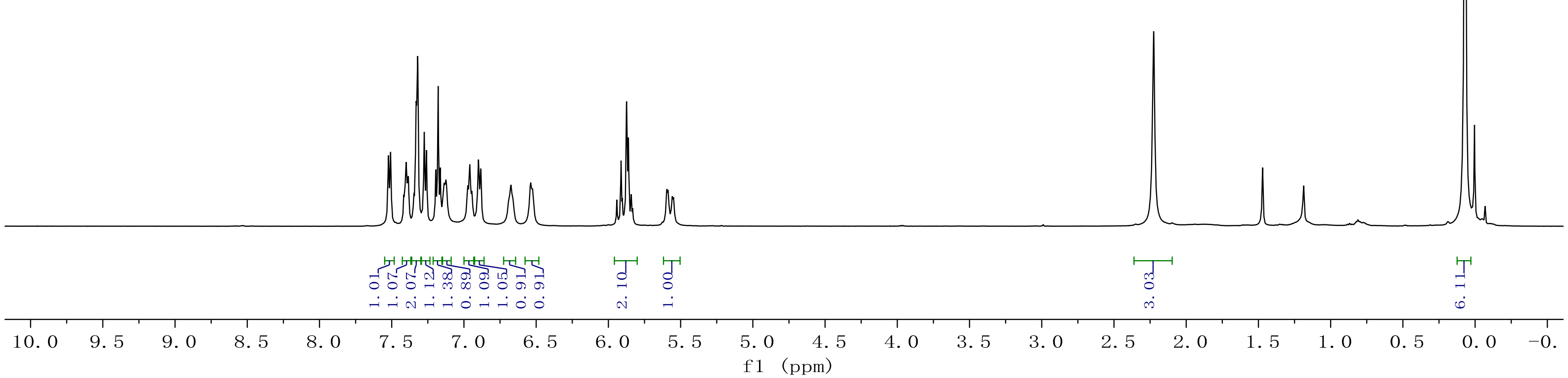
^{19}F NMR (376 MHz, $CDCl_3$)

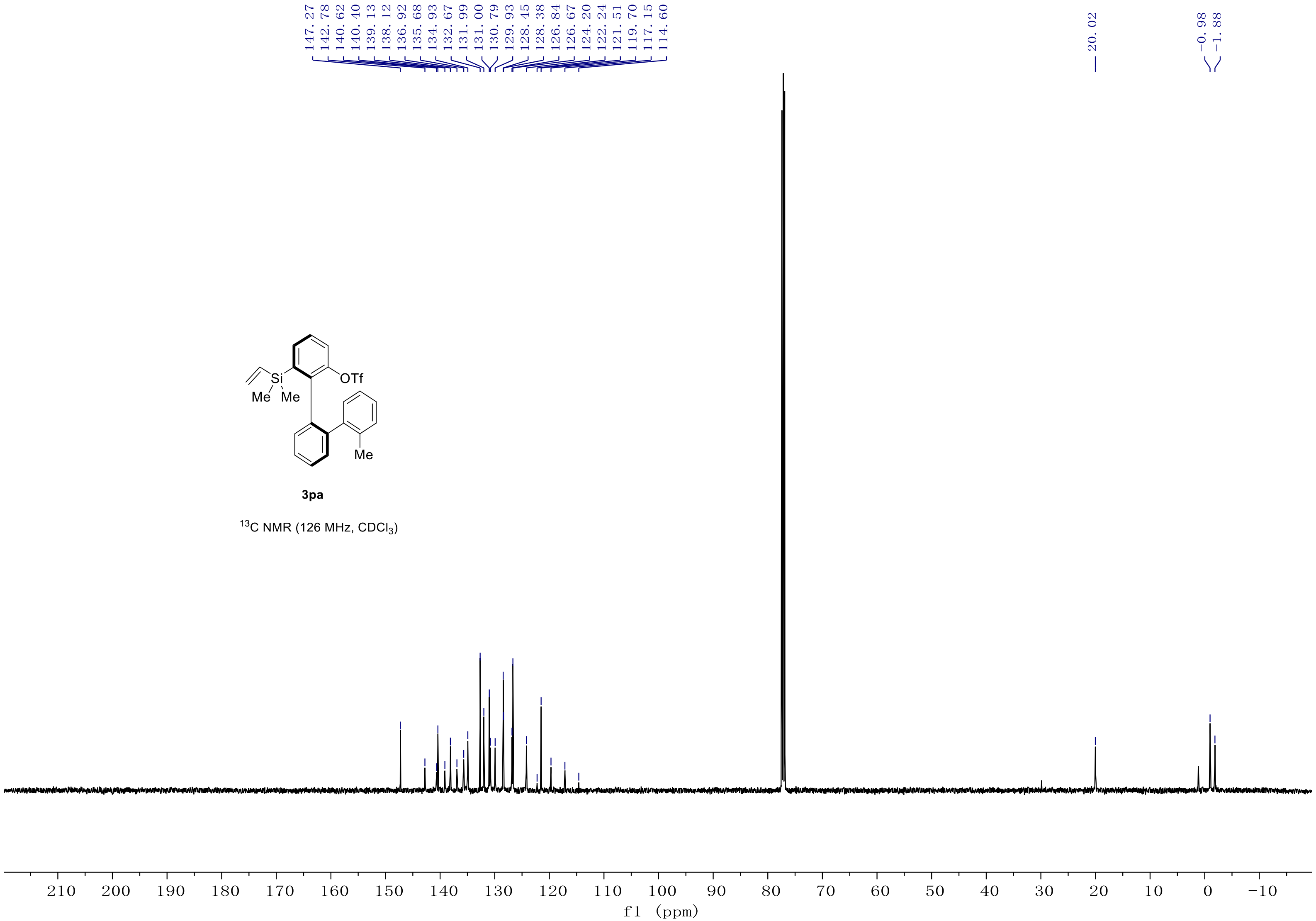




3pa

^{1}H NMR (500 MHz, $CDCl_3$)

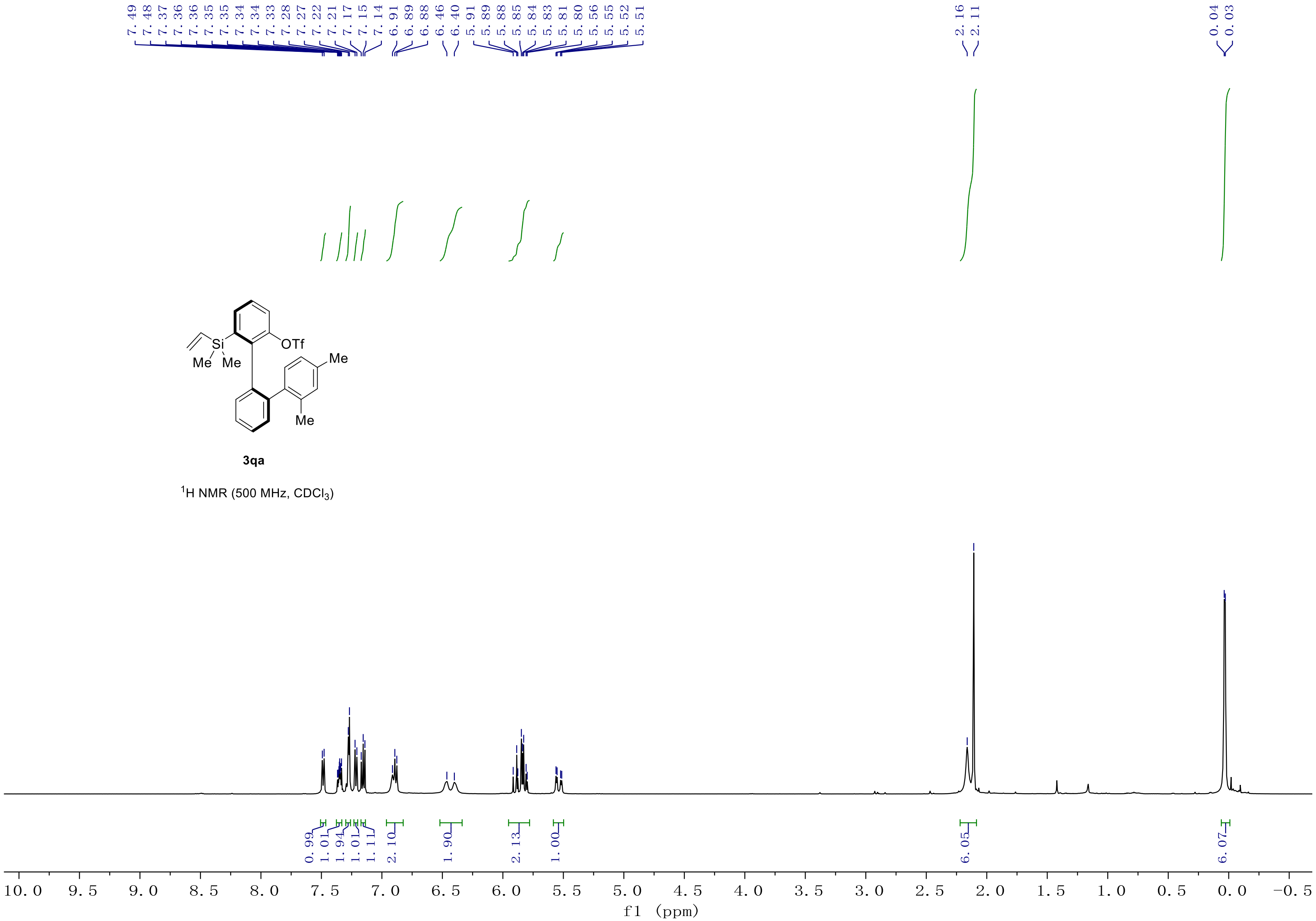




3pa

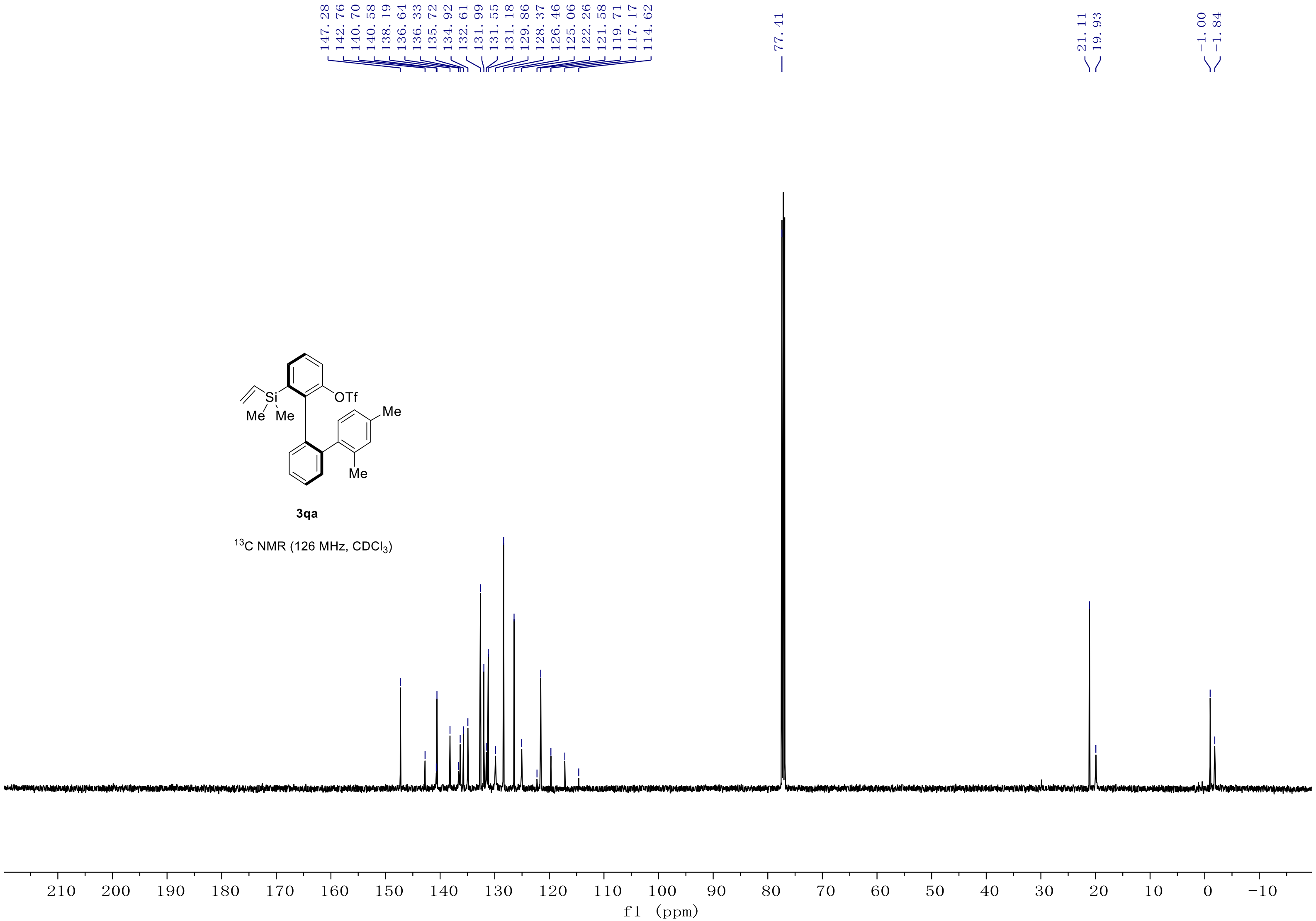
^{13}C NMR (126 MHz, $CDCl_3$)

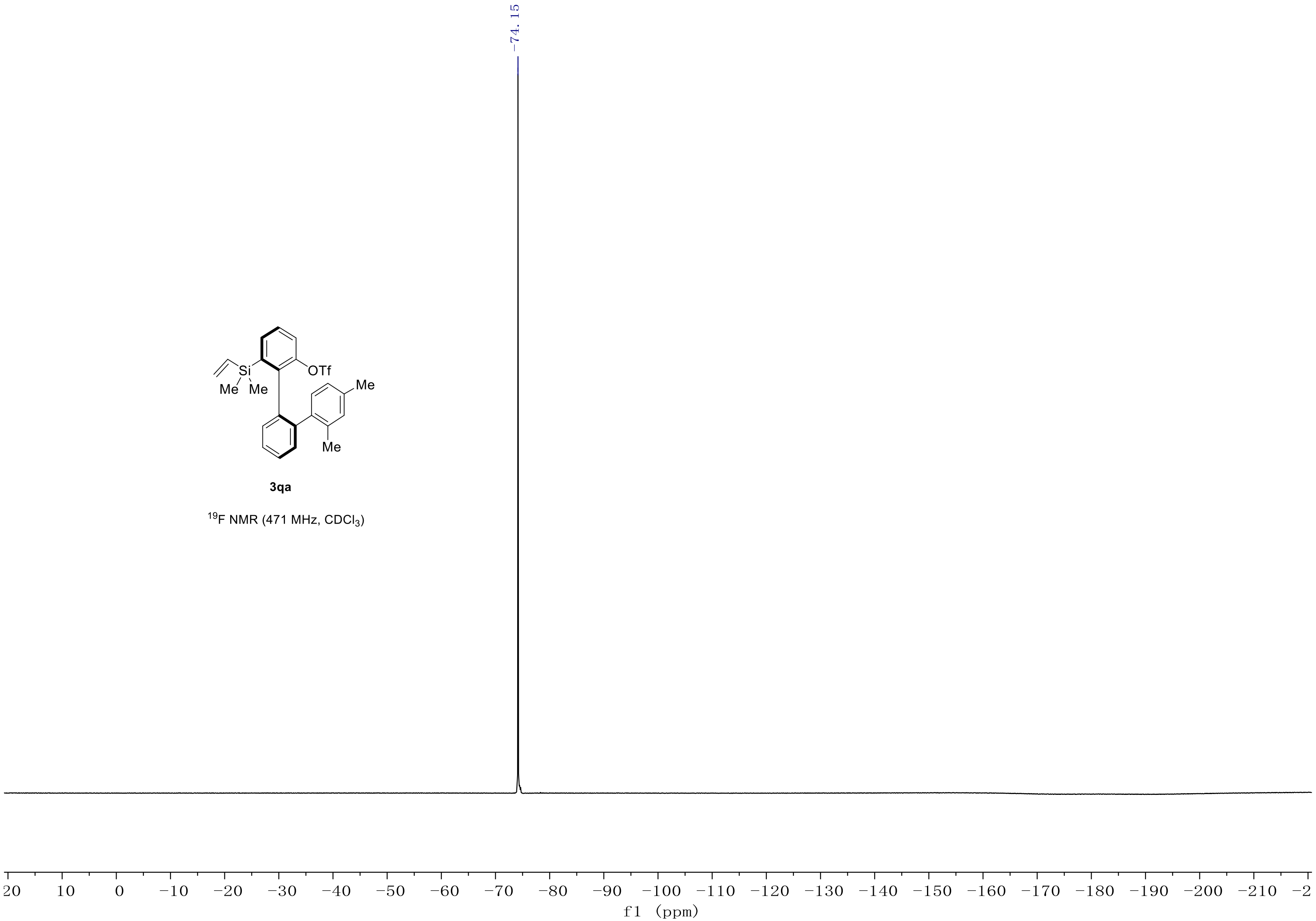
-74.14
OTf
Si
Me
Me
Me
3pa
^{19}F NMR (471 MHz, CDCl$_3$)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

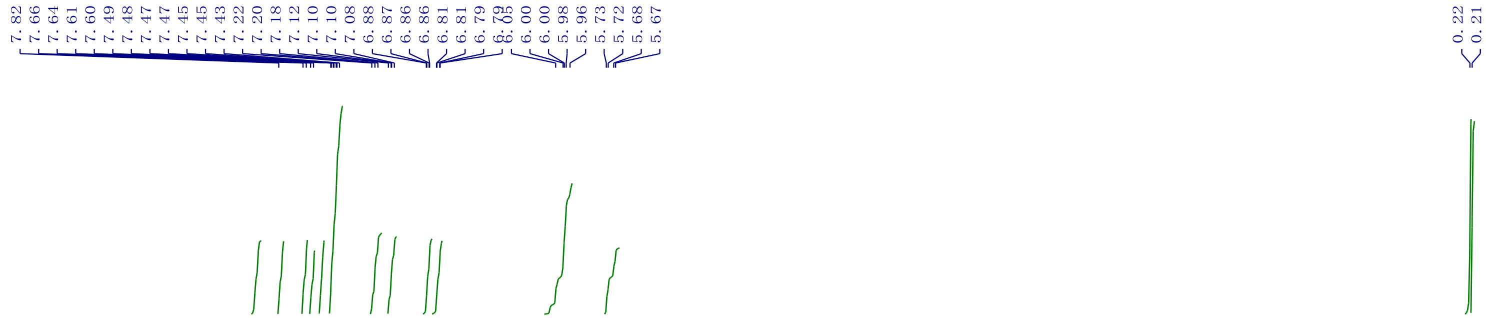


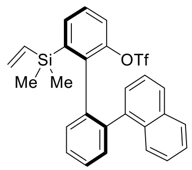
3qa

^{1}H NMR (500 MHz, $CDCl_3$)


147.28
142.76
140.70
140.58
138.19
136.64
136.33
135.72
134.92
132.61
131.99
131.55
131.18
129.86
128.37
126.46
125.06
122.26
121.58
119.71
117.17
114.62
77.41
21.11
19.93
-1.00
-1.84
OTf
Si
Me
Me
Me
Me
3qa
^{13}C NMR (126 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

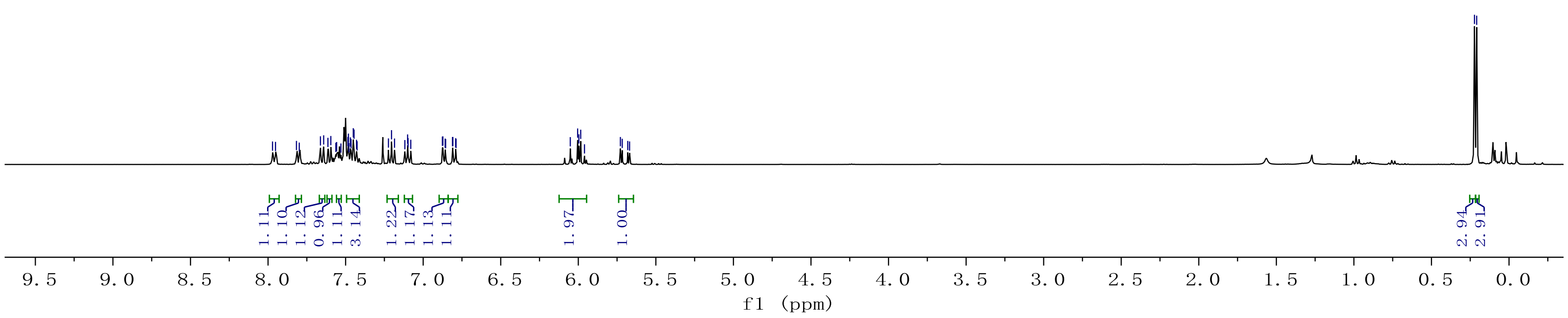

−74.15
OTf
Si
Me Me
Me
Me
3qa
^{19}F NMR (471 MHz, $CDCl_3$)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

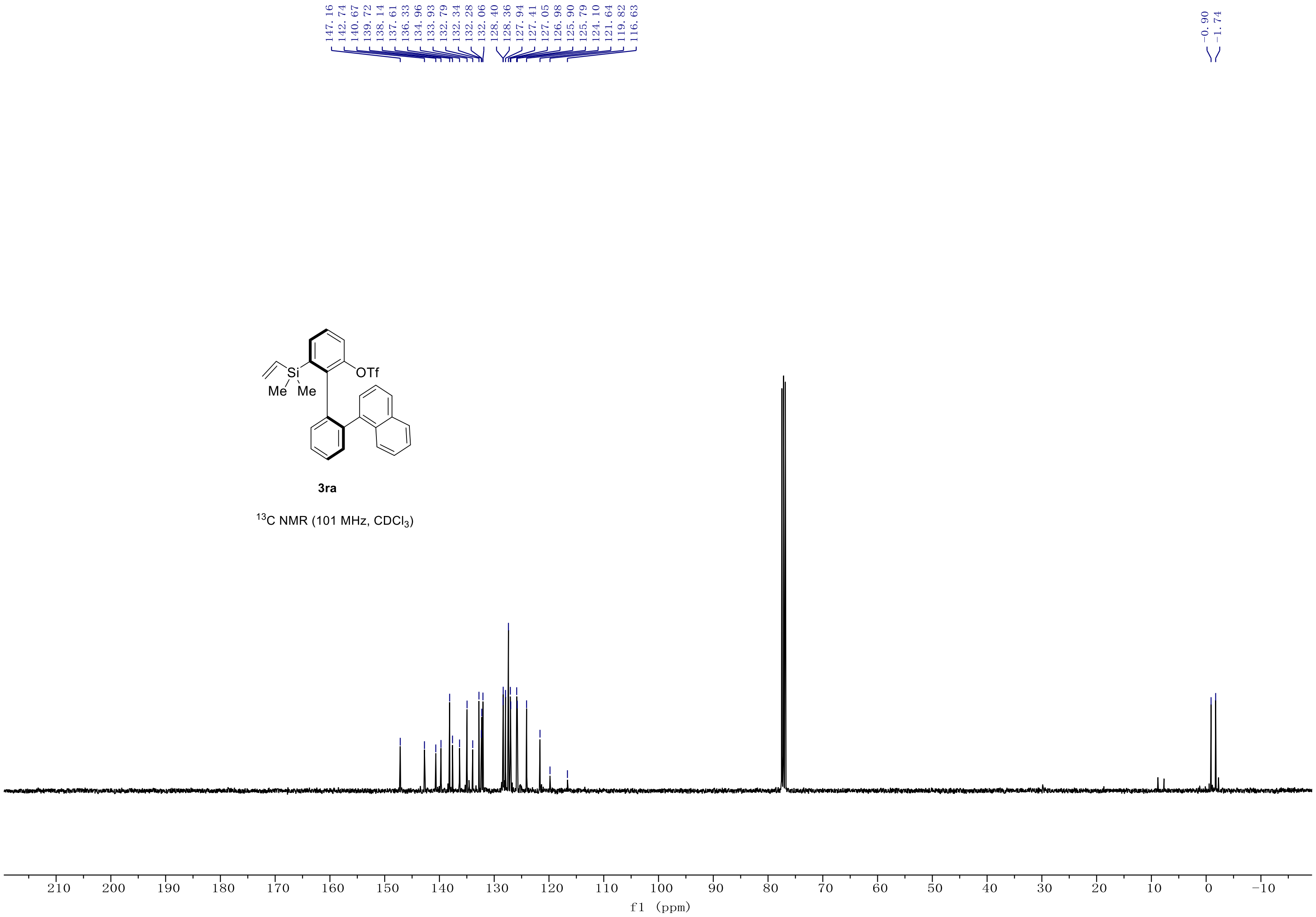




3ra

^{1}H NMR (400 MHz, $CDCl_3$)



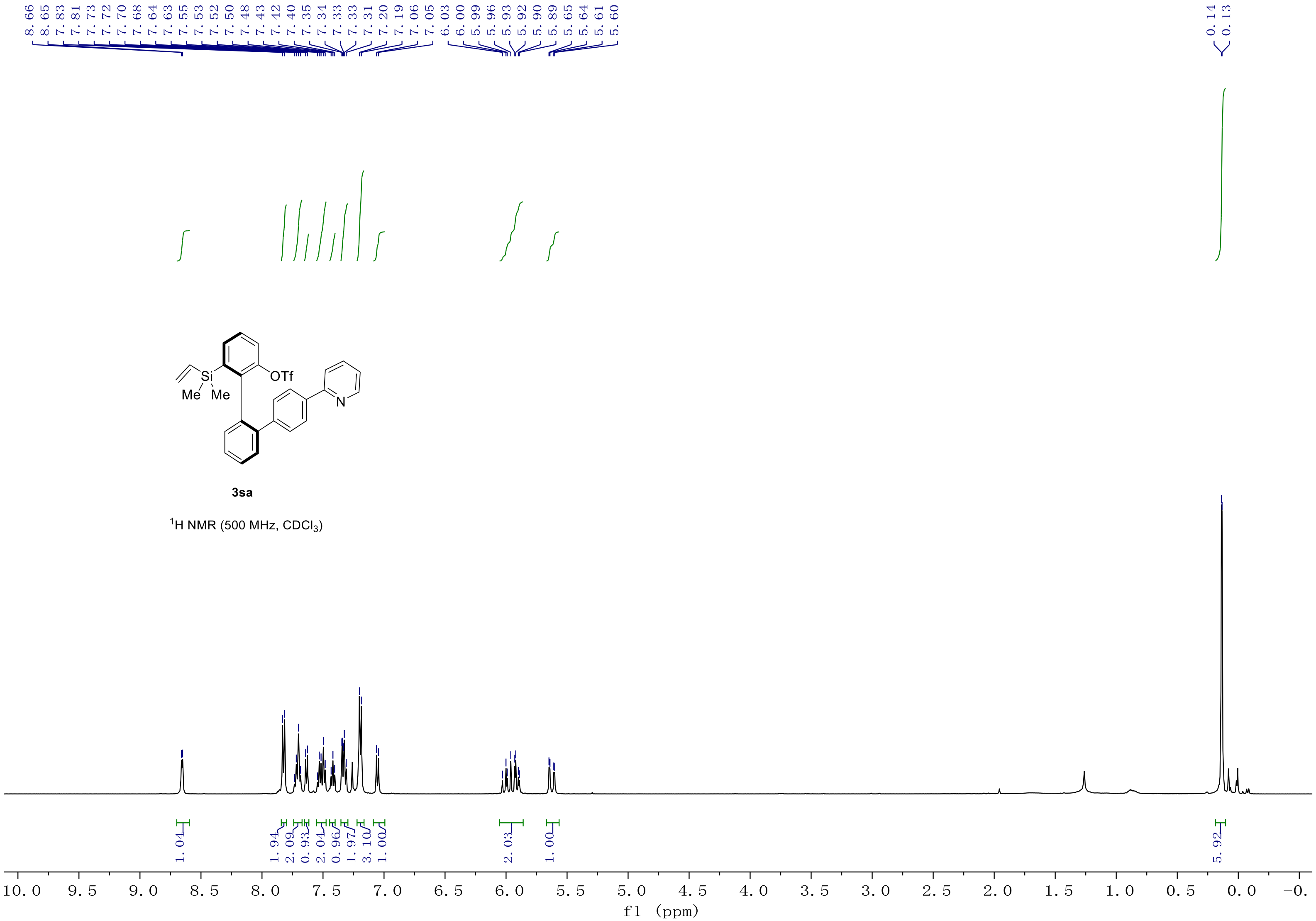


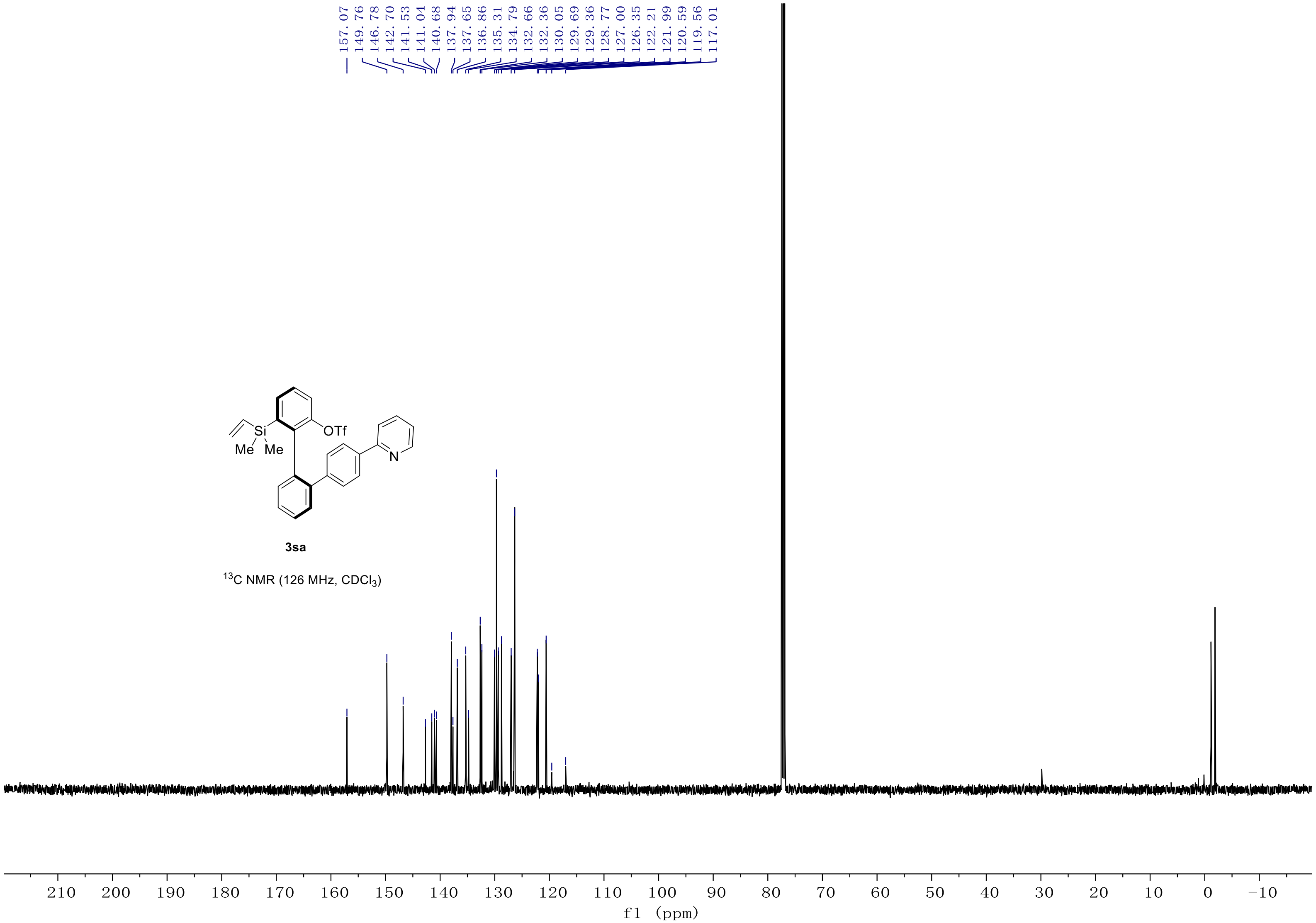
3ra

^{13}C NMR (101 MHz, $CDCl_3$)

3ra

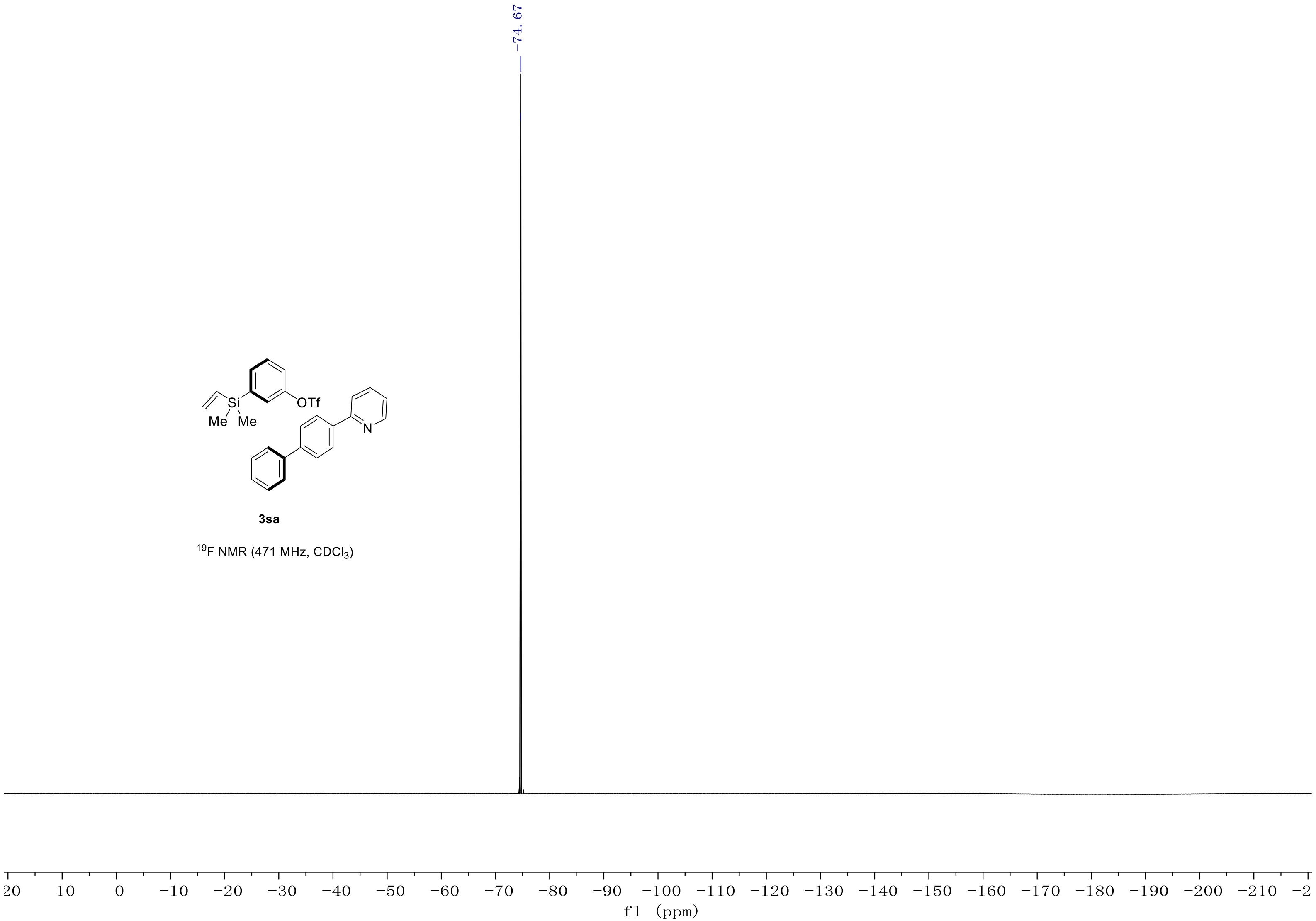
^{19}F NMR (376 MHz, $CDCl_3$)


8.66
8.65
7.83
7.81
7.73
7.72
7.70
7.68
7.64
7.63
7.55
7.53
7.52
7.50
7.48
7.43
7.42
7.40
7.35
7.34
7.33
7.33
7.31
7.20
7.19
7.06
7.05
6.03
6.00
5.99
5.96
5.93
5.92
5.90
5.89
5.65
5.64
5.61
5.60
0.14
0.13
OTf
Si
Me
Me
N
3sa
1H NMR (500 MHz, CDCl3)
1.04
1.94
2.09
0.93
2.04
0.96
1.97
3.10
1.00
2.03
1.00
5.92
f1 (ppm)



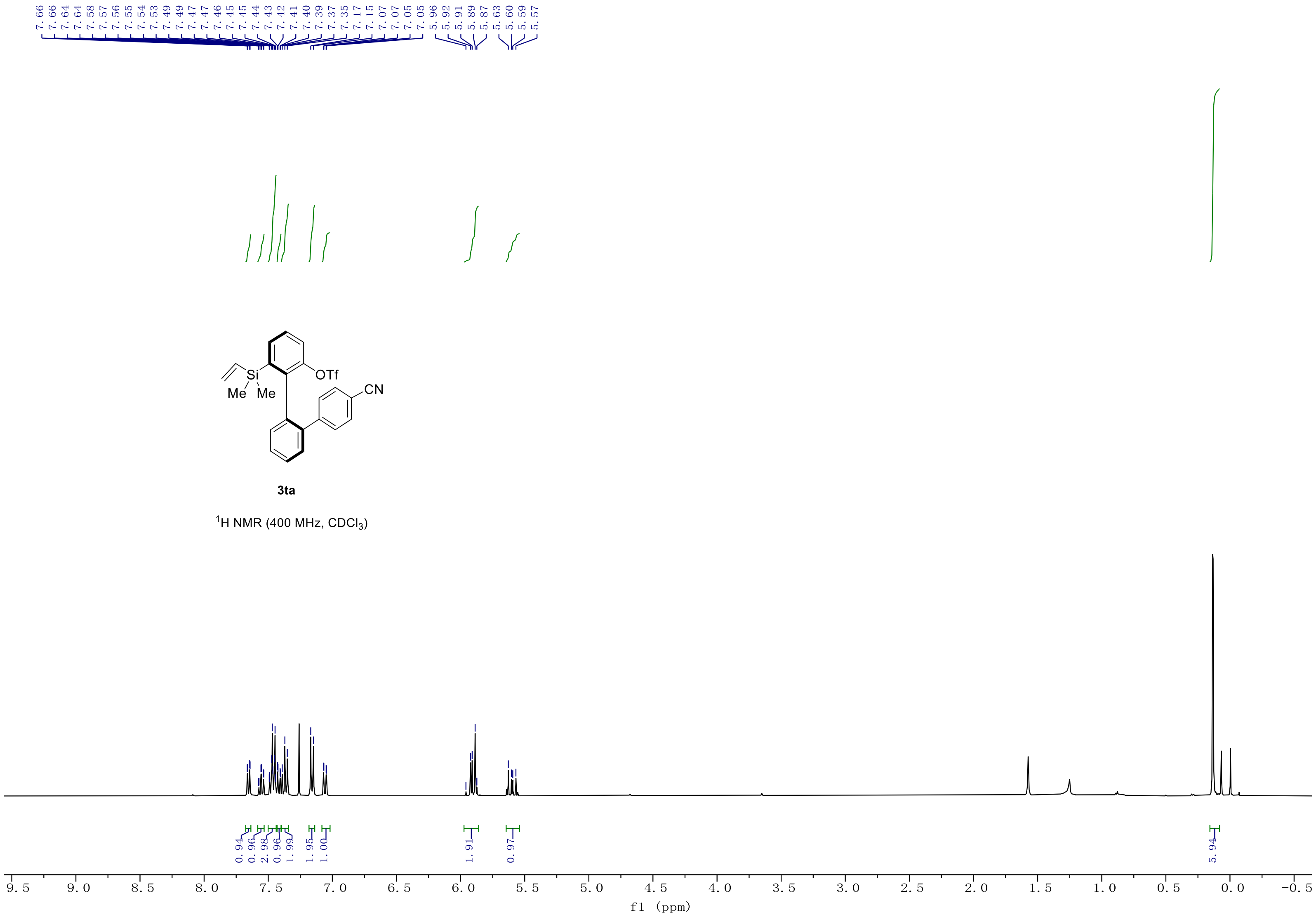
3sa

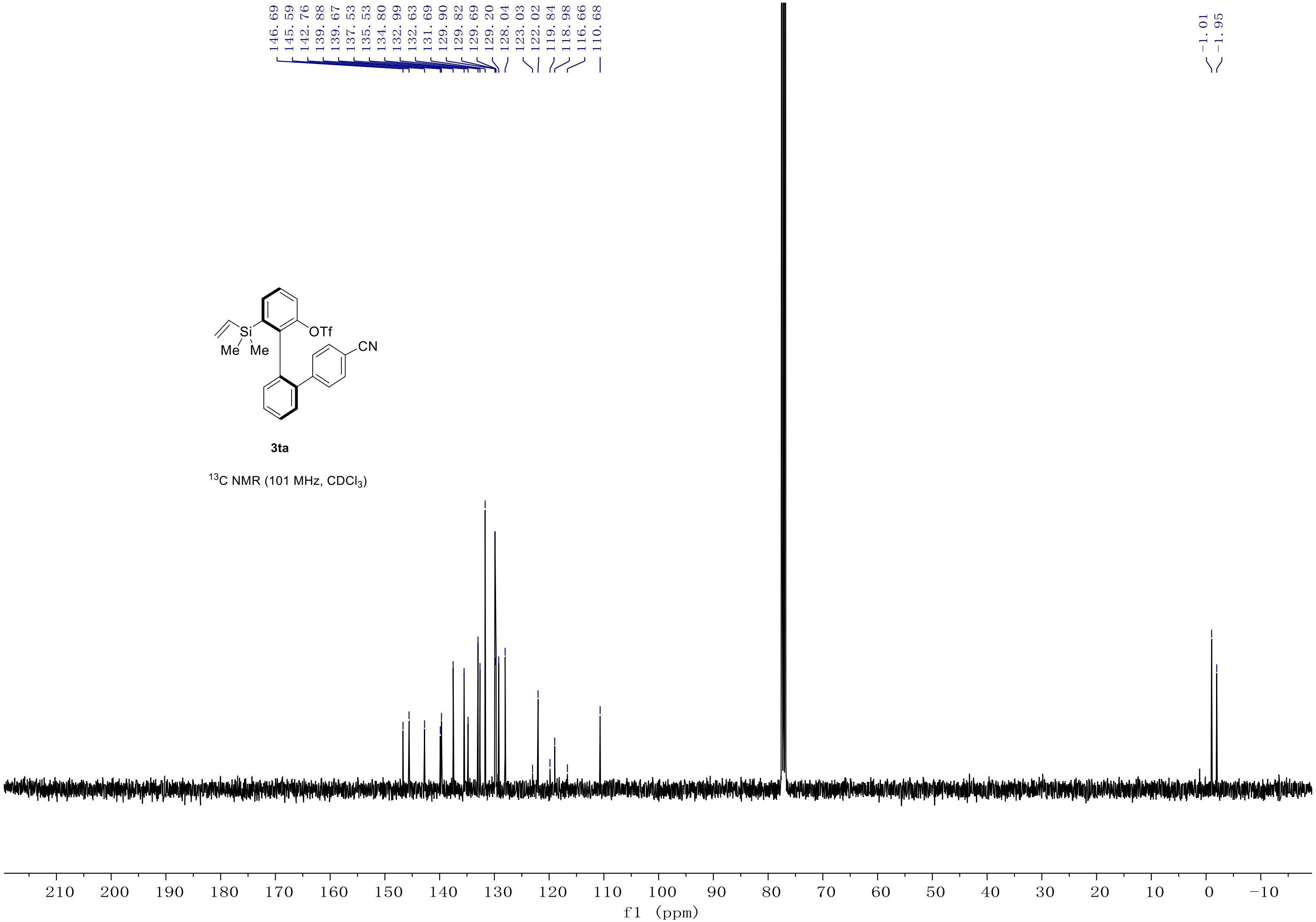
^{13}C NMR (126 MHz, $CDCl_3$)



3sa

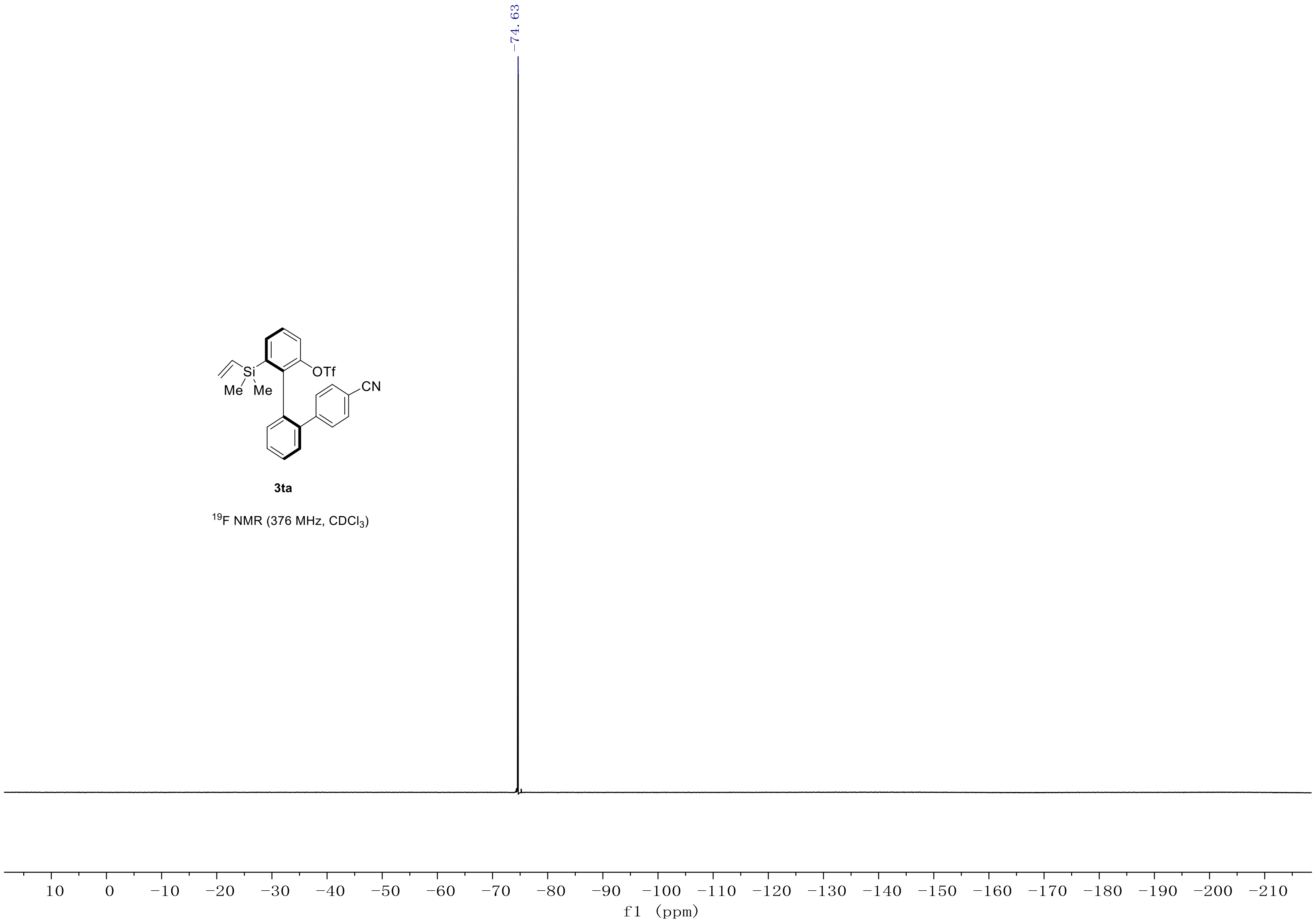
^{19}F NMR (471 MHz, $CDCl_3$)

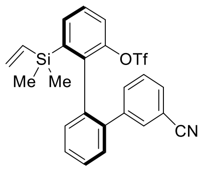

3ta
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)



3ta

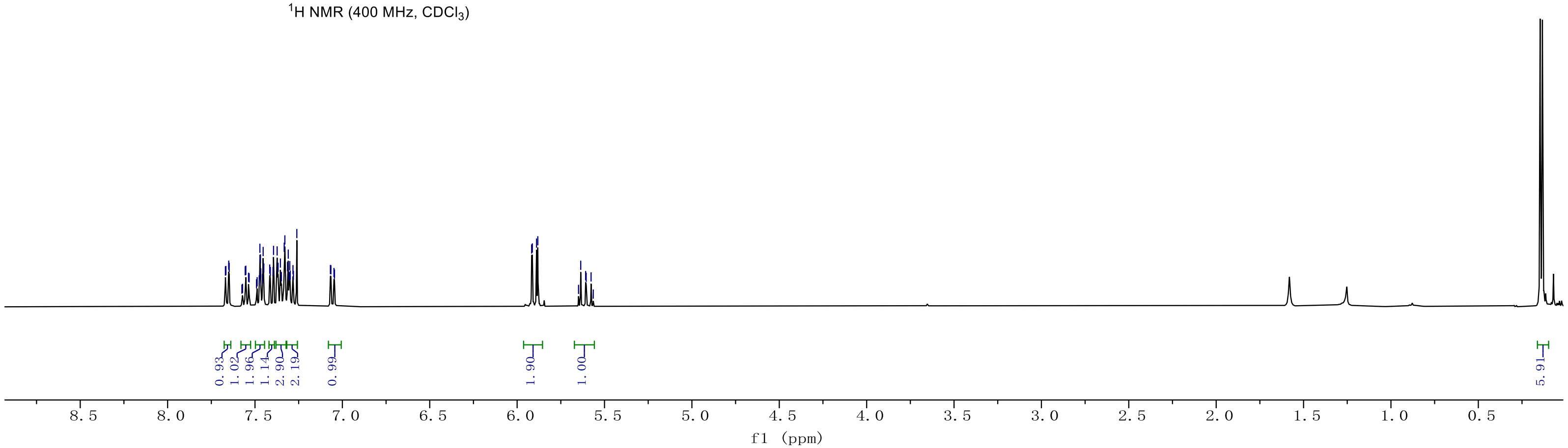
^{13}C NMR (101 MHz, $CDCl_3$)

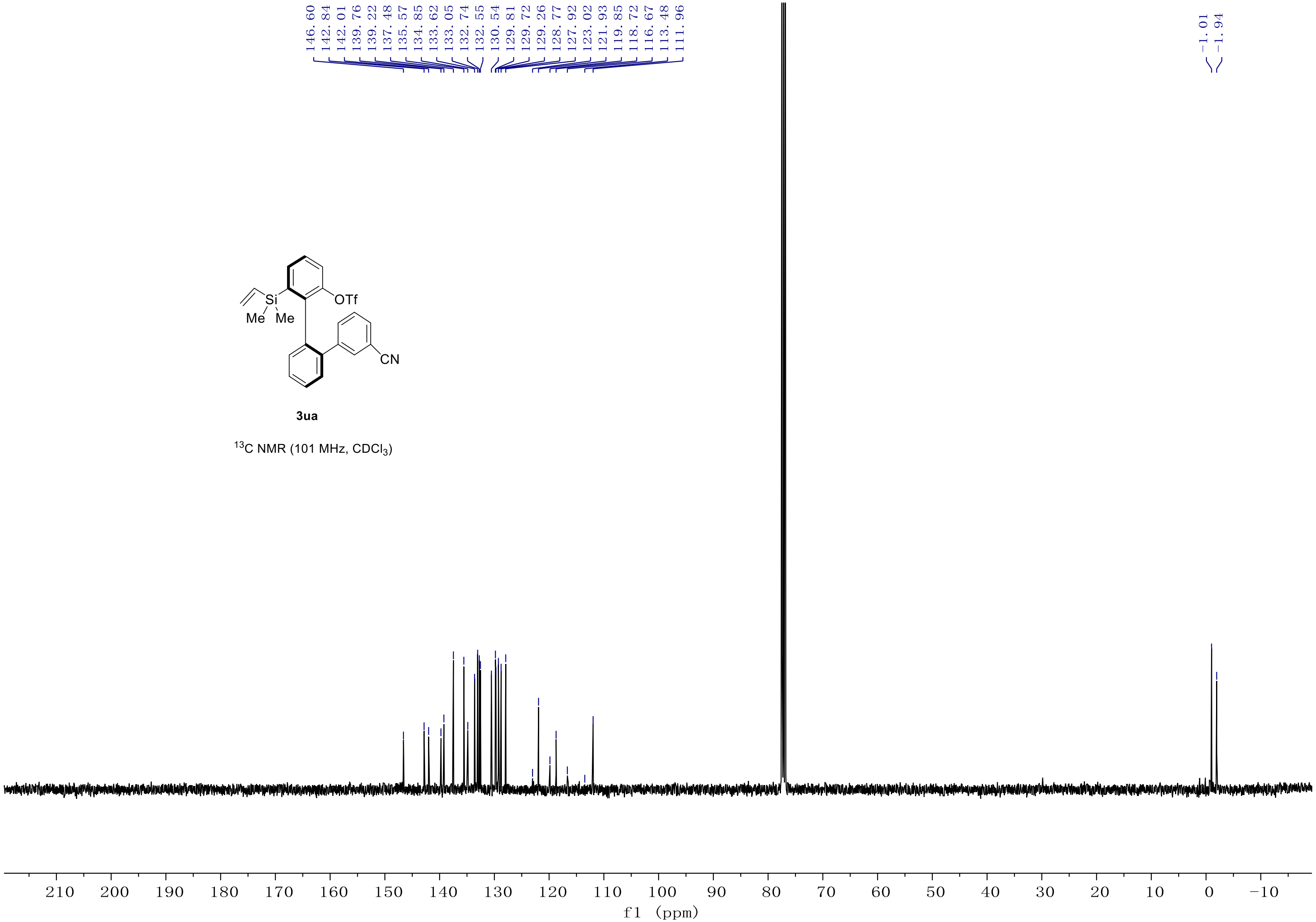

-74.63
OTf
CN
Si
Me
Me
3ta
19F NMR (376 MHz, CDCl3)
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)



3ua

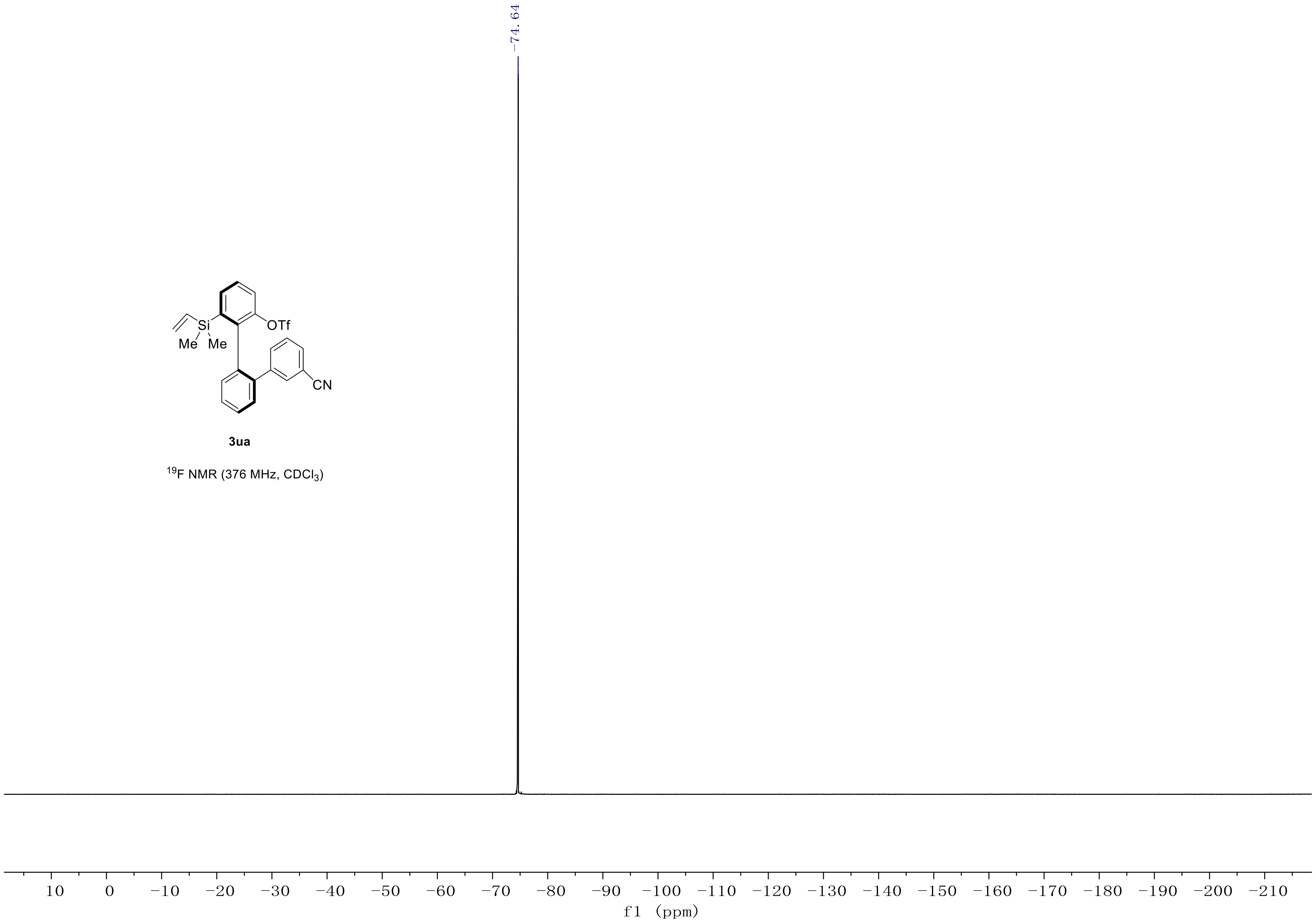
^{1}H NMR (400 MHz, $CDCl_3$)





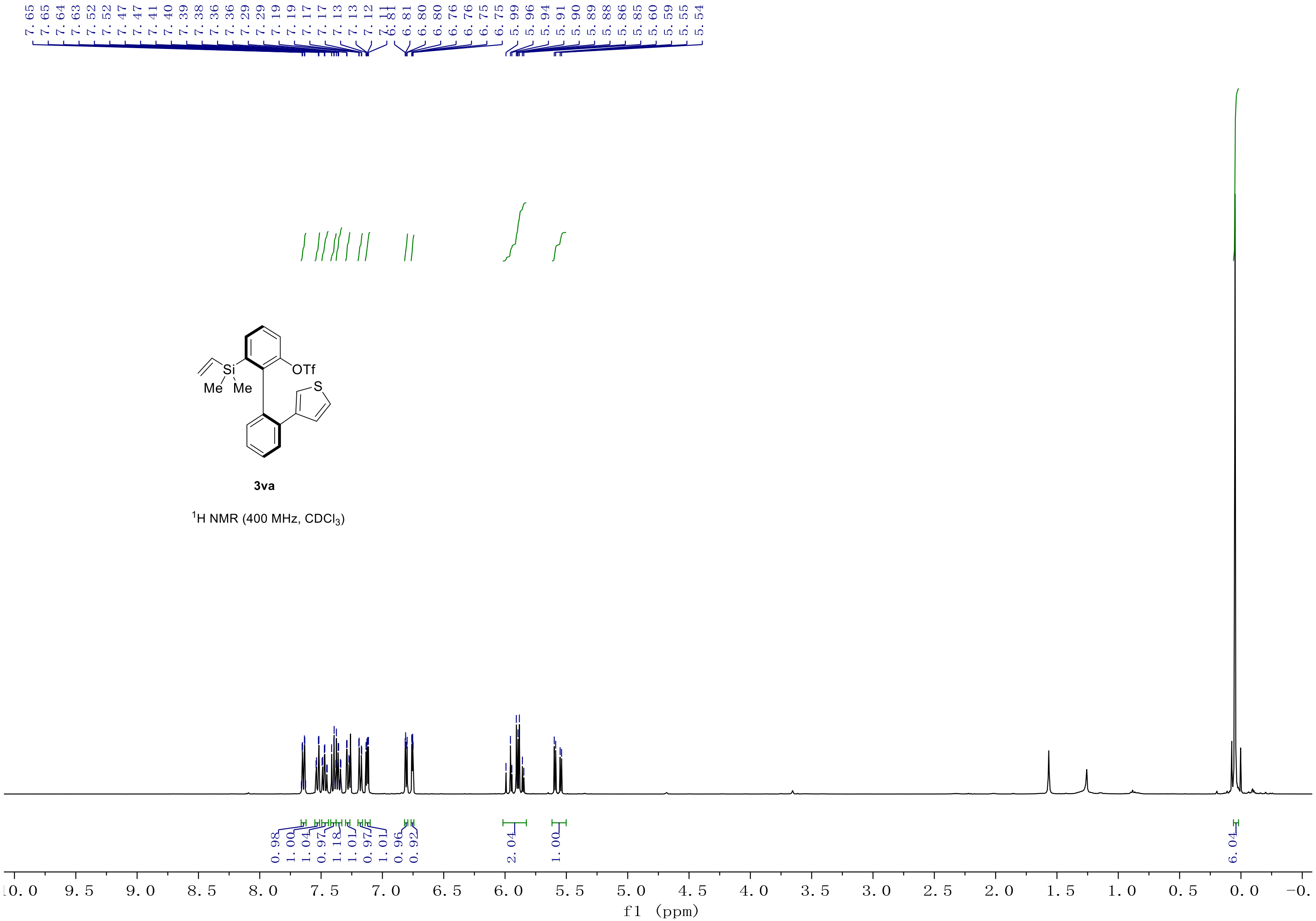
3ua

^{13}C NMR (101 MHz, $CDCl_3$)



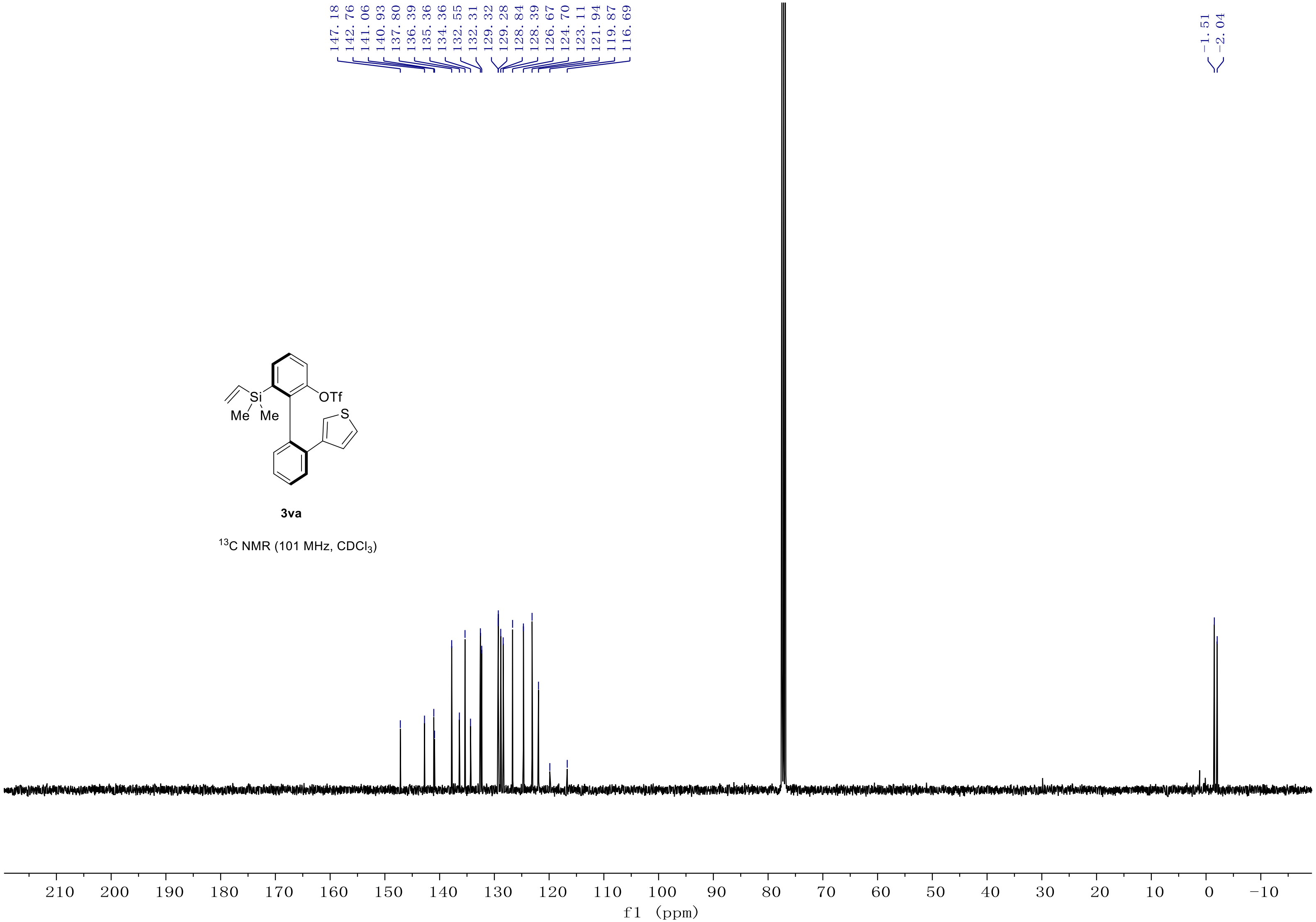
3ua

^{19}F NMR (376 MHz, $CDCl_3$)



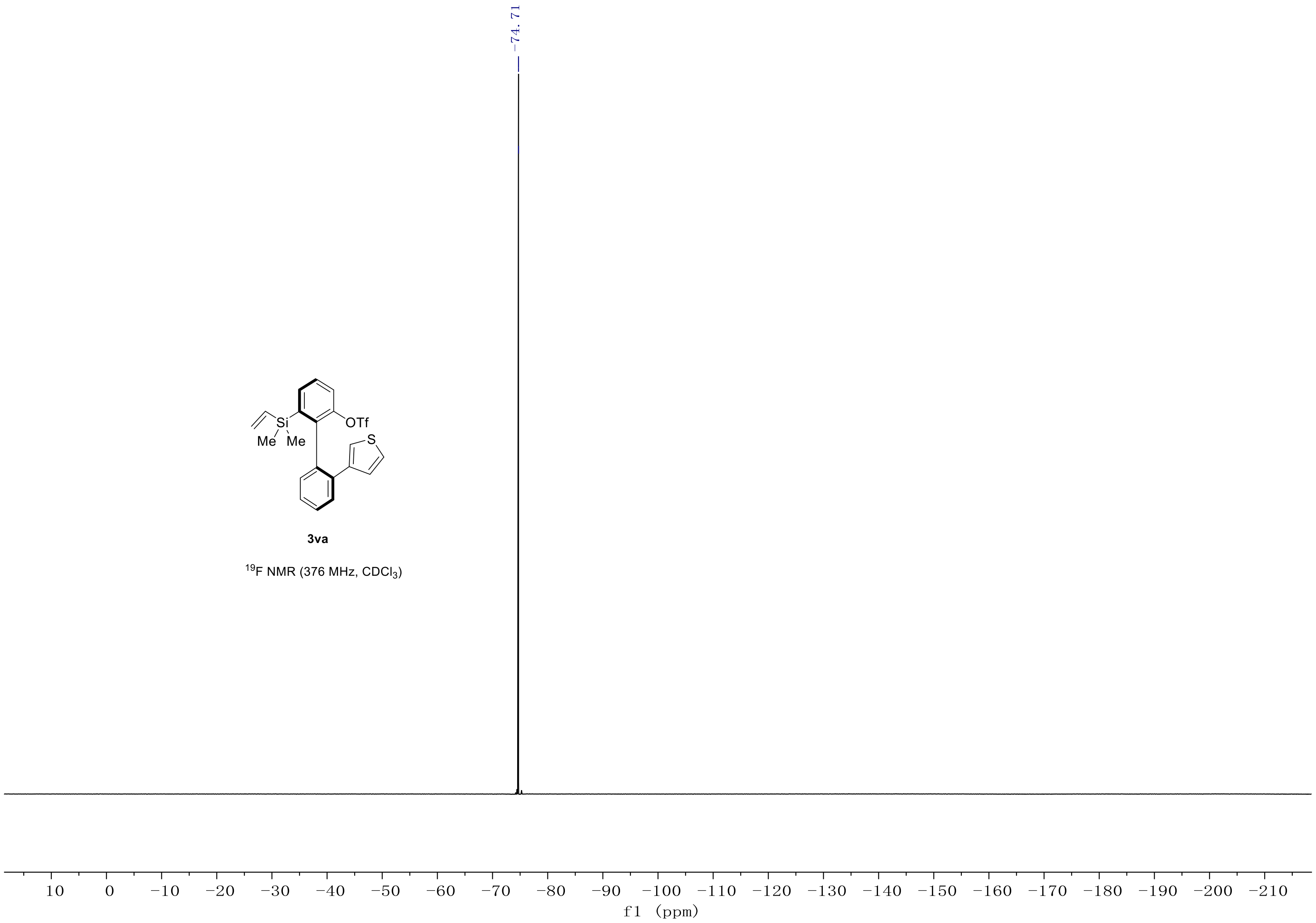
3va

^{1}H NMR (400 MHz, $CDCl_3$)

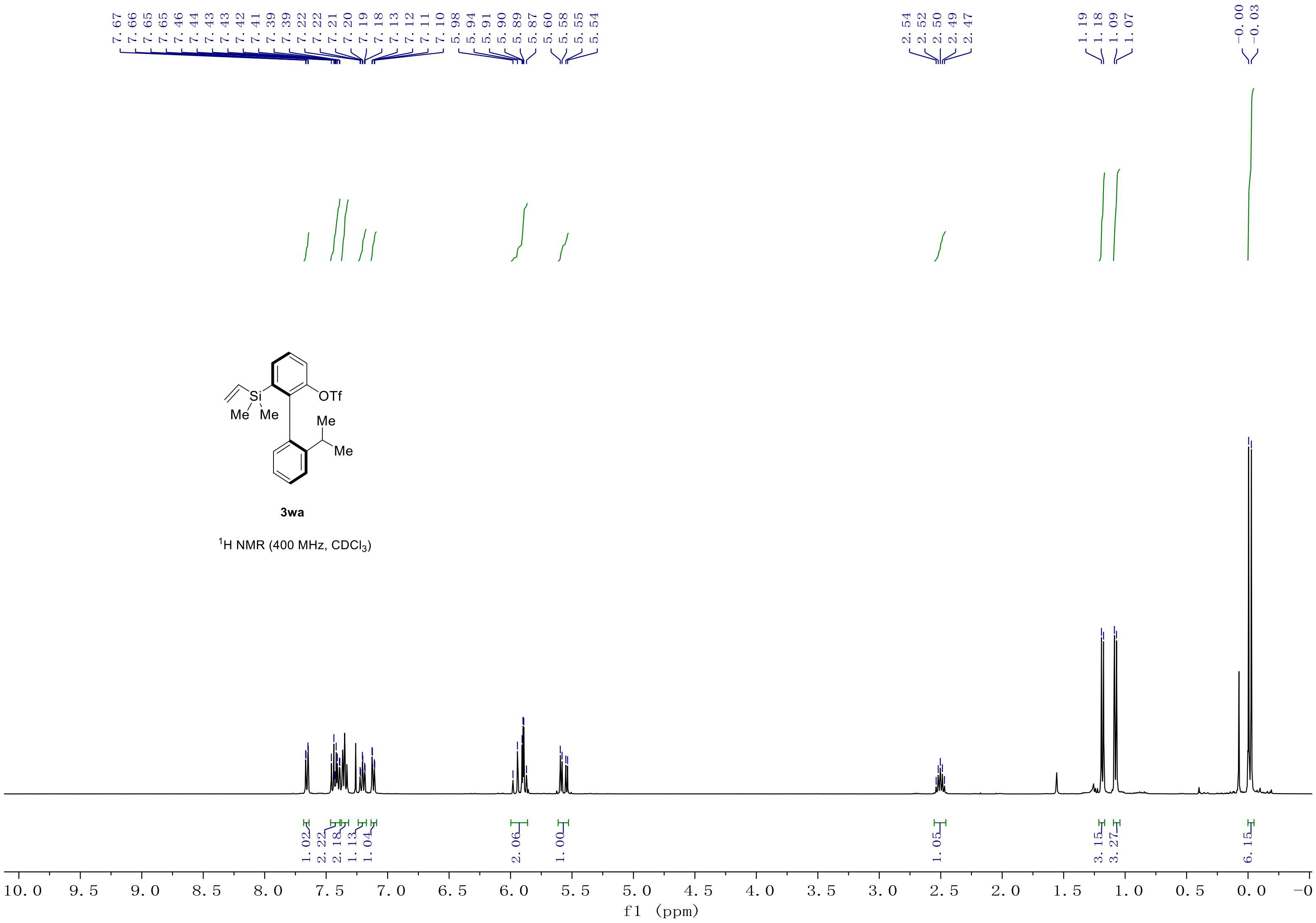


3va

^{13}C NMR (101 MHz, $CDCl_3$)

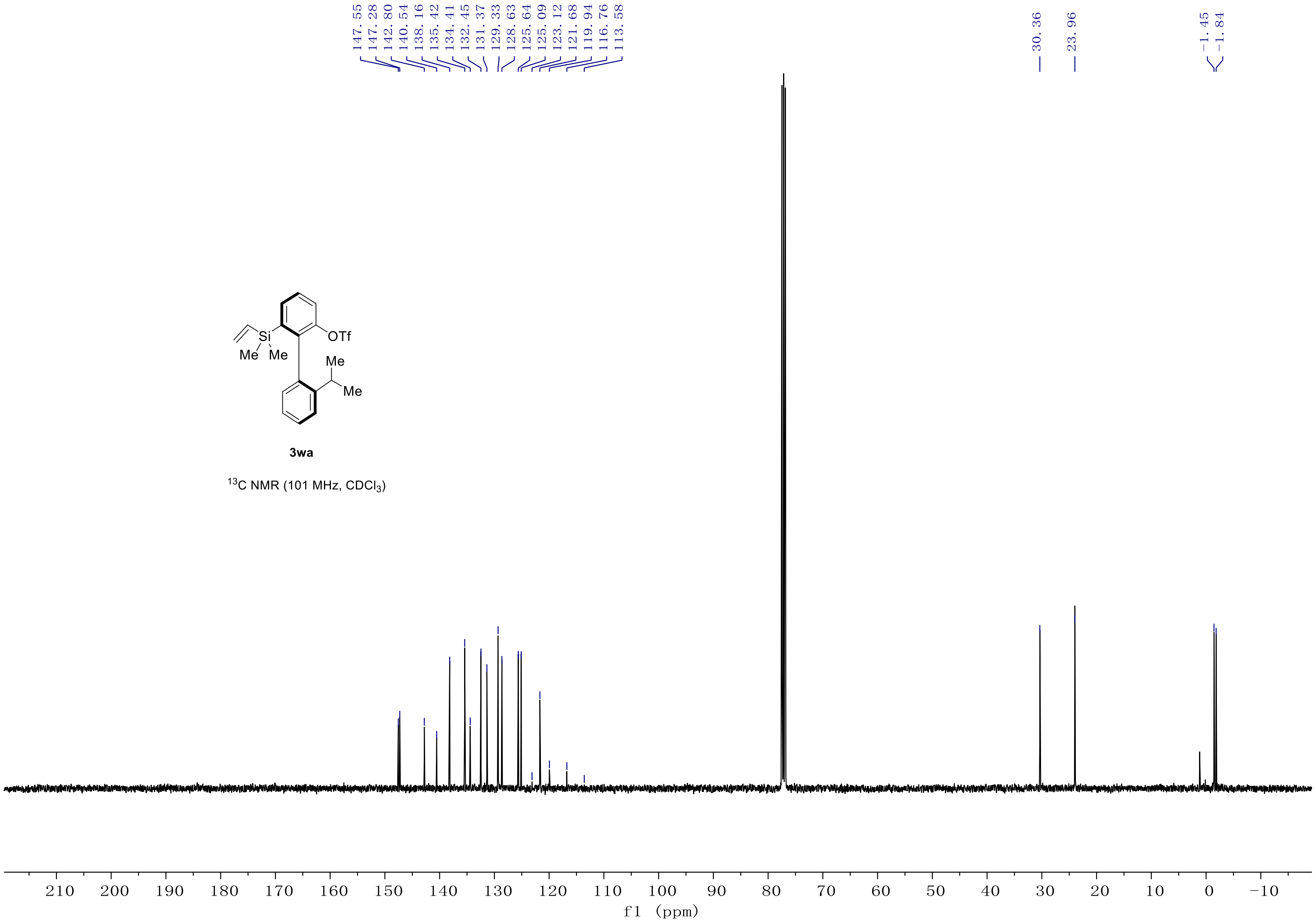


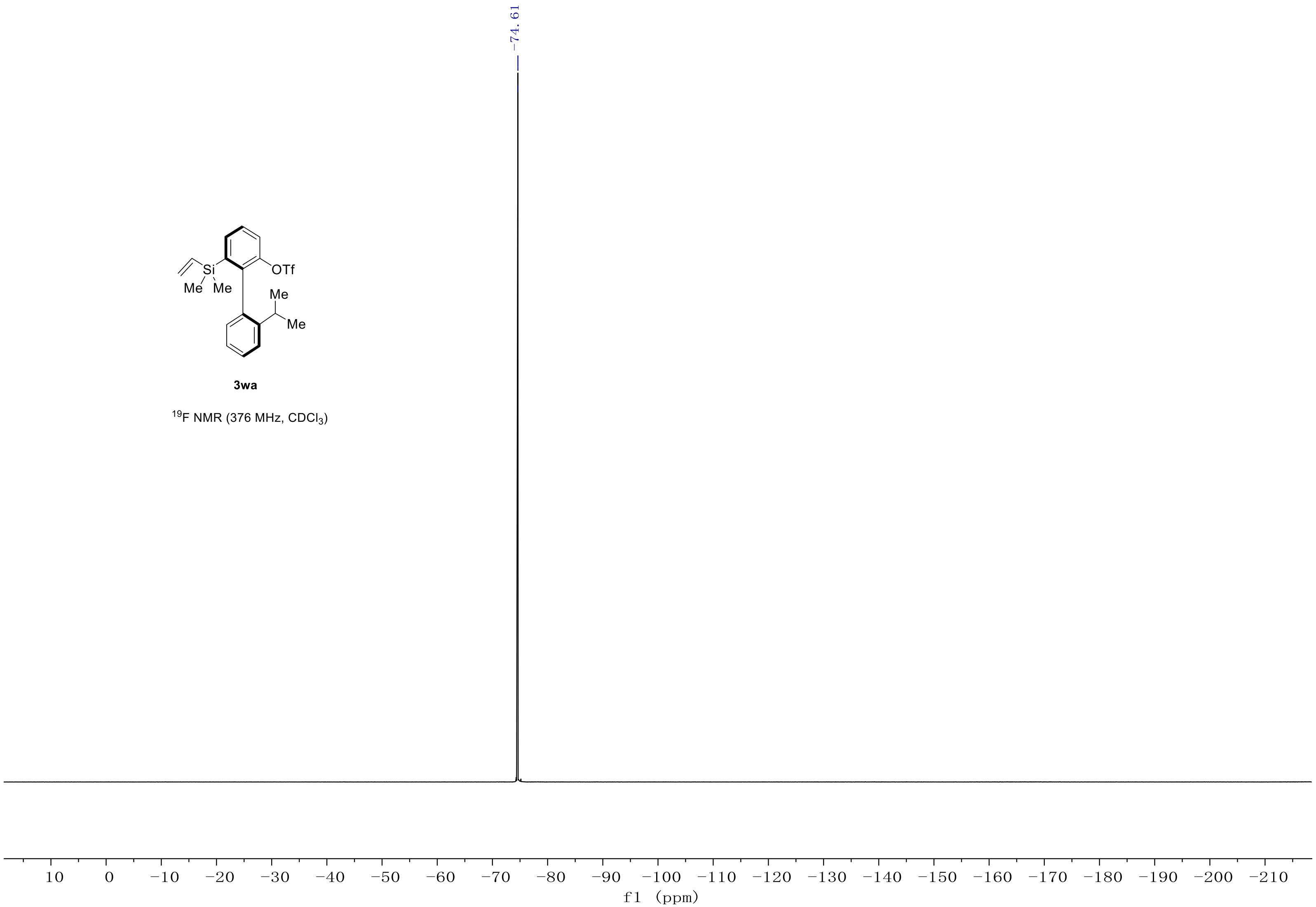
−74.71
OTf
Si
Me
Me
S
3va
^{19}F NMR (376 MHz, $CDCl_3$)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



3wa

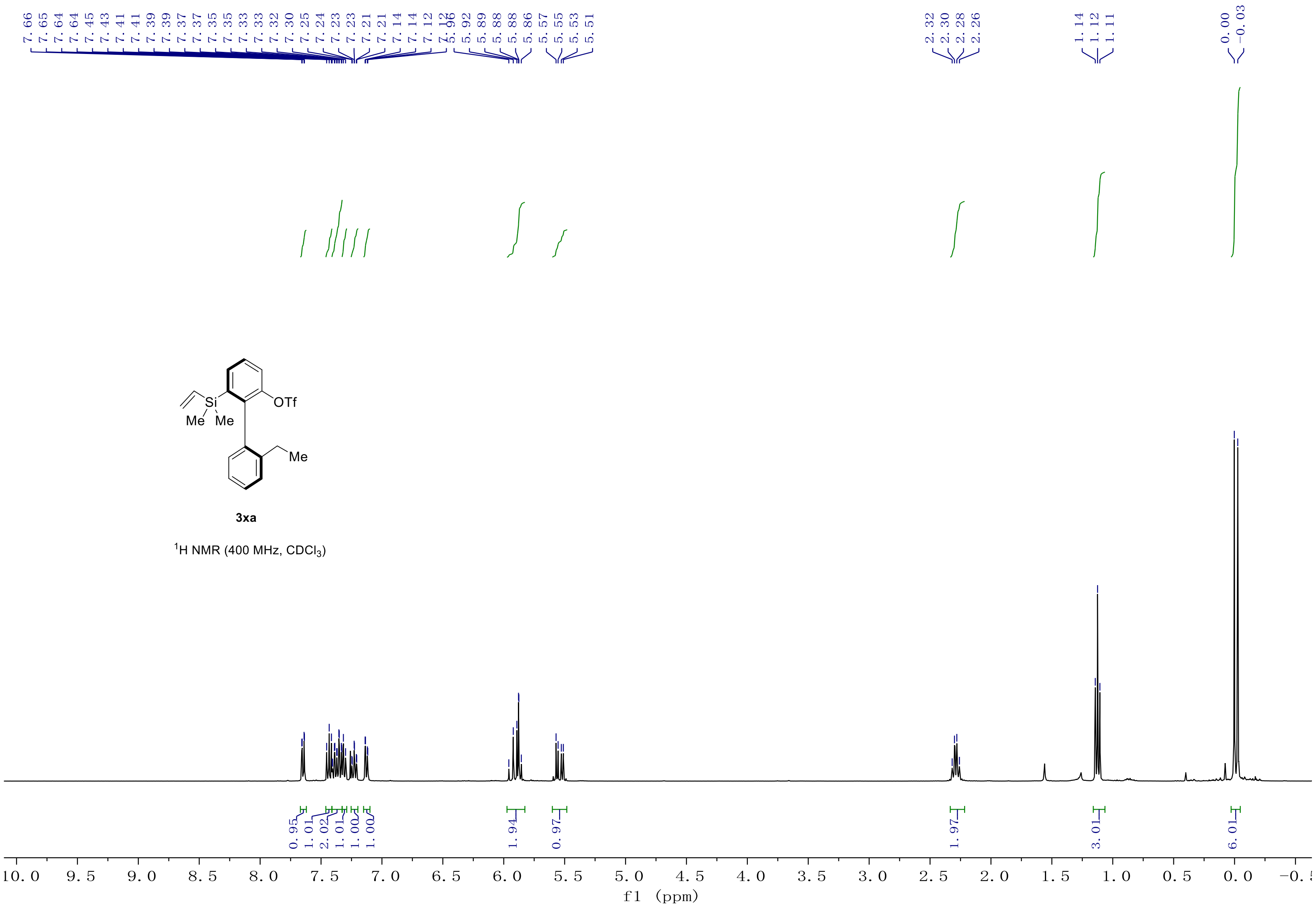
^{1}H NMR (400 MHz, $CDCl_3$)


147.55
147.28
142.80
140.54
138.16
135.42
134.41
132.45
131.37
129.33
128.63
125.64
125.09
123.12
121.68
119.94
116.76
113.58
30.36
23.96
-1.45
-1.84
Si
Me
Me
OTf
Me
Me
3wa
^{13}C NMR (101 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



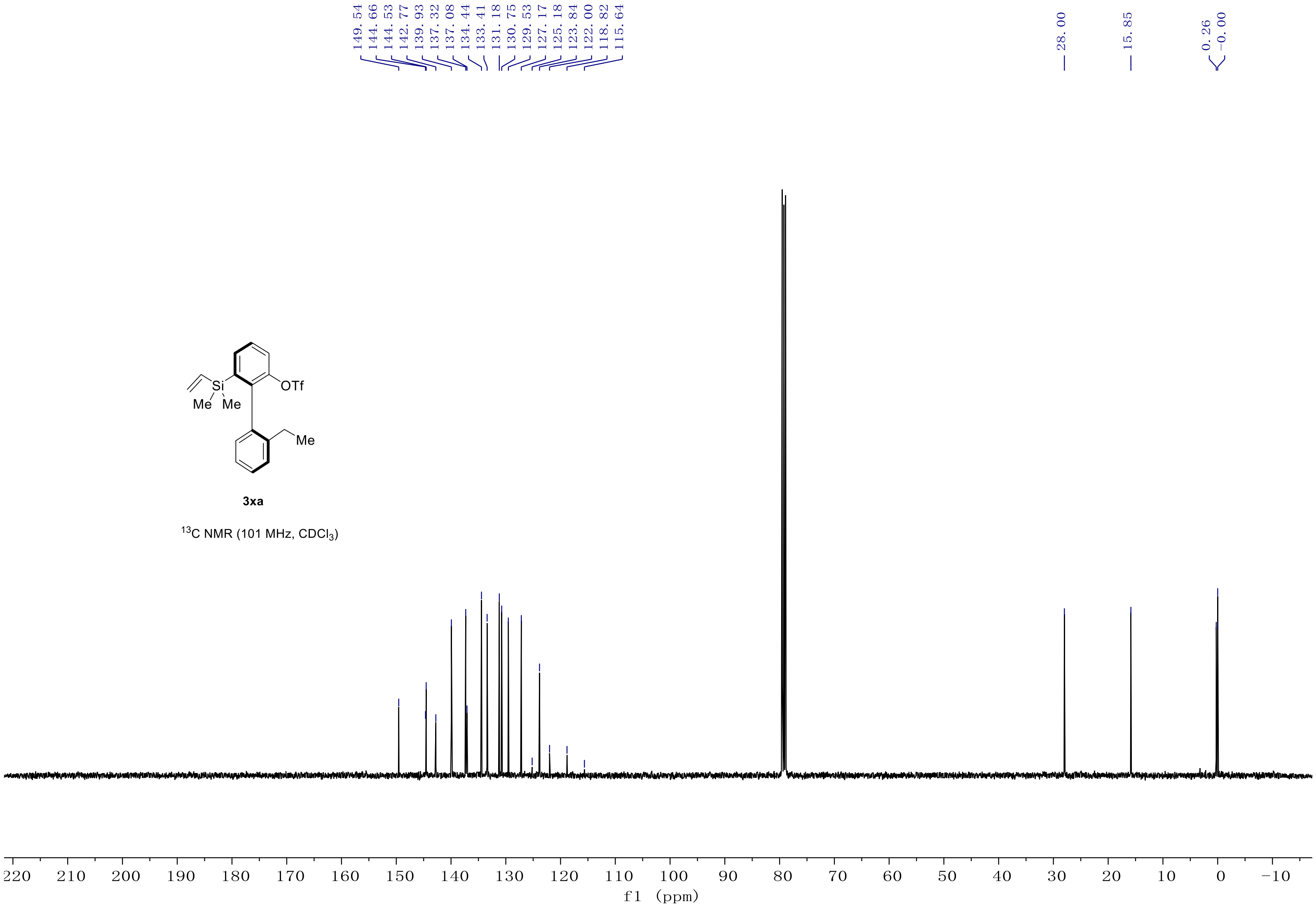
3wa

^{19}F NMR (376 MHz, $CDCl_3$)



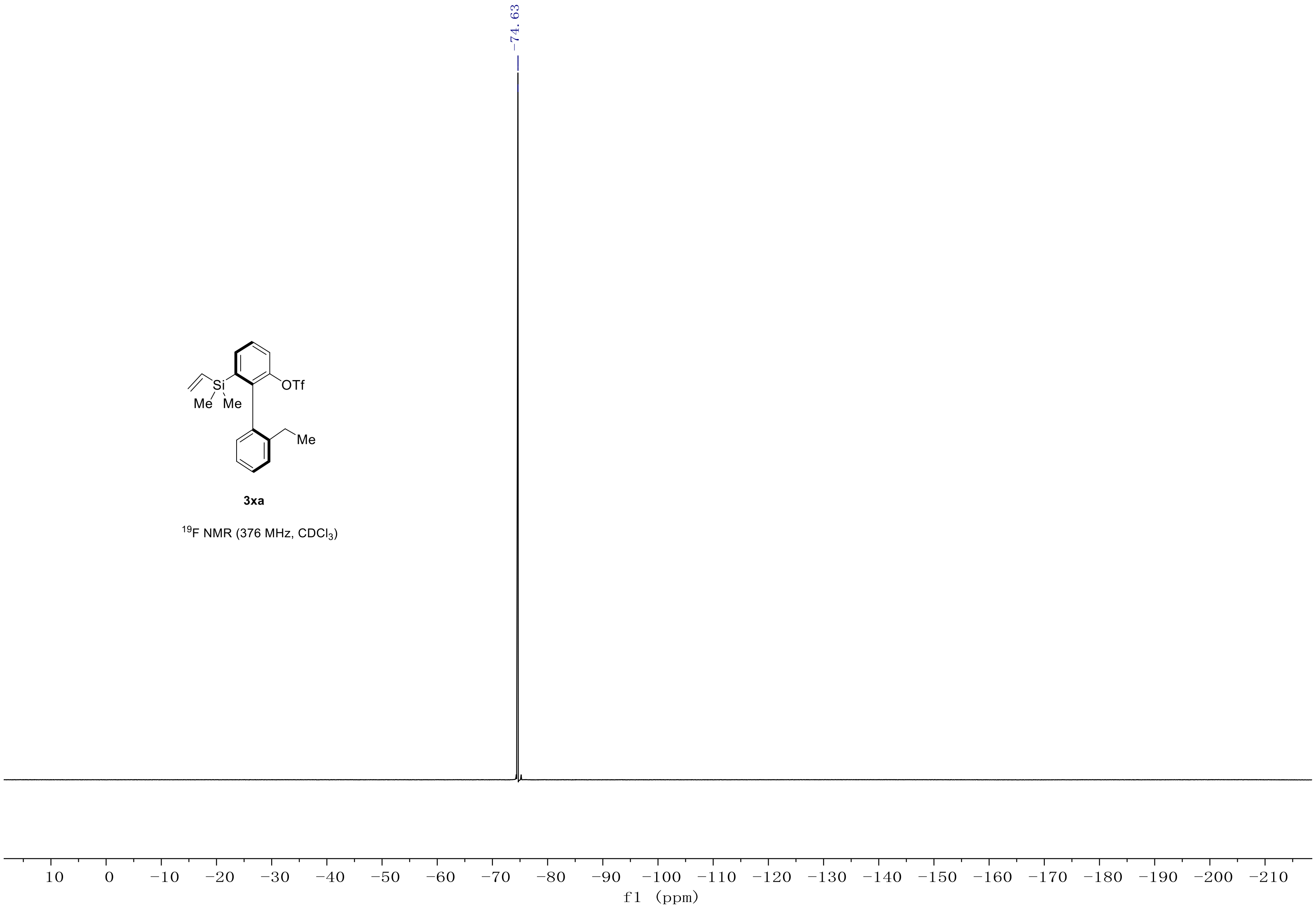
3xa

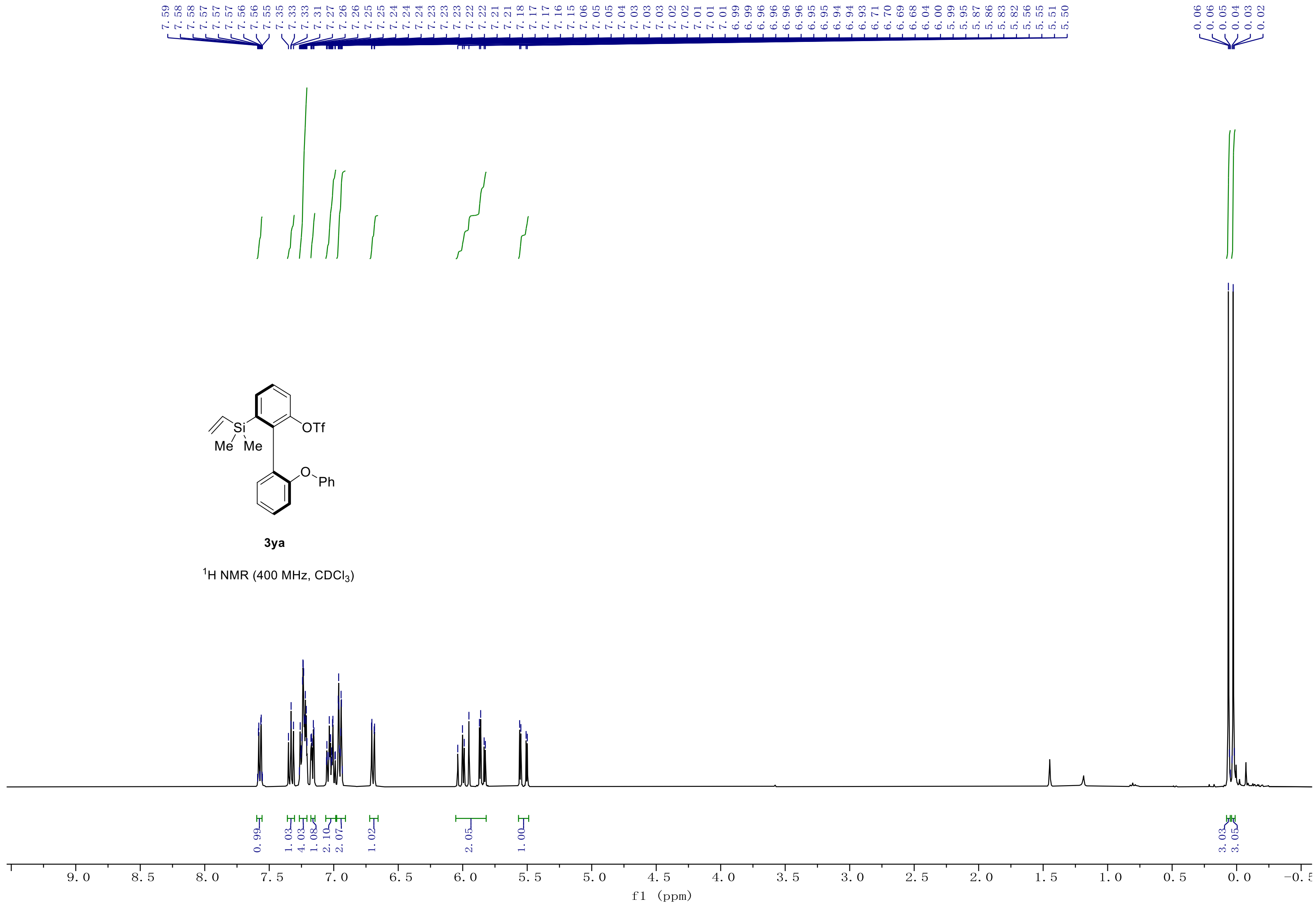
^1H NMR (400 MHz, $CDCl_3$)



3xa

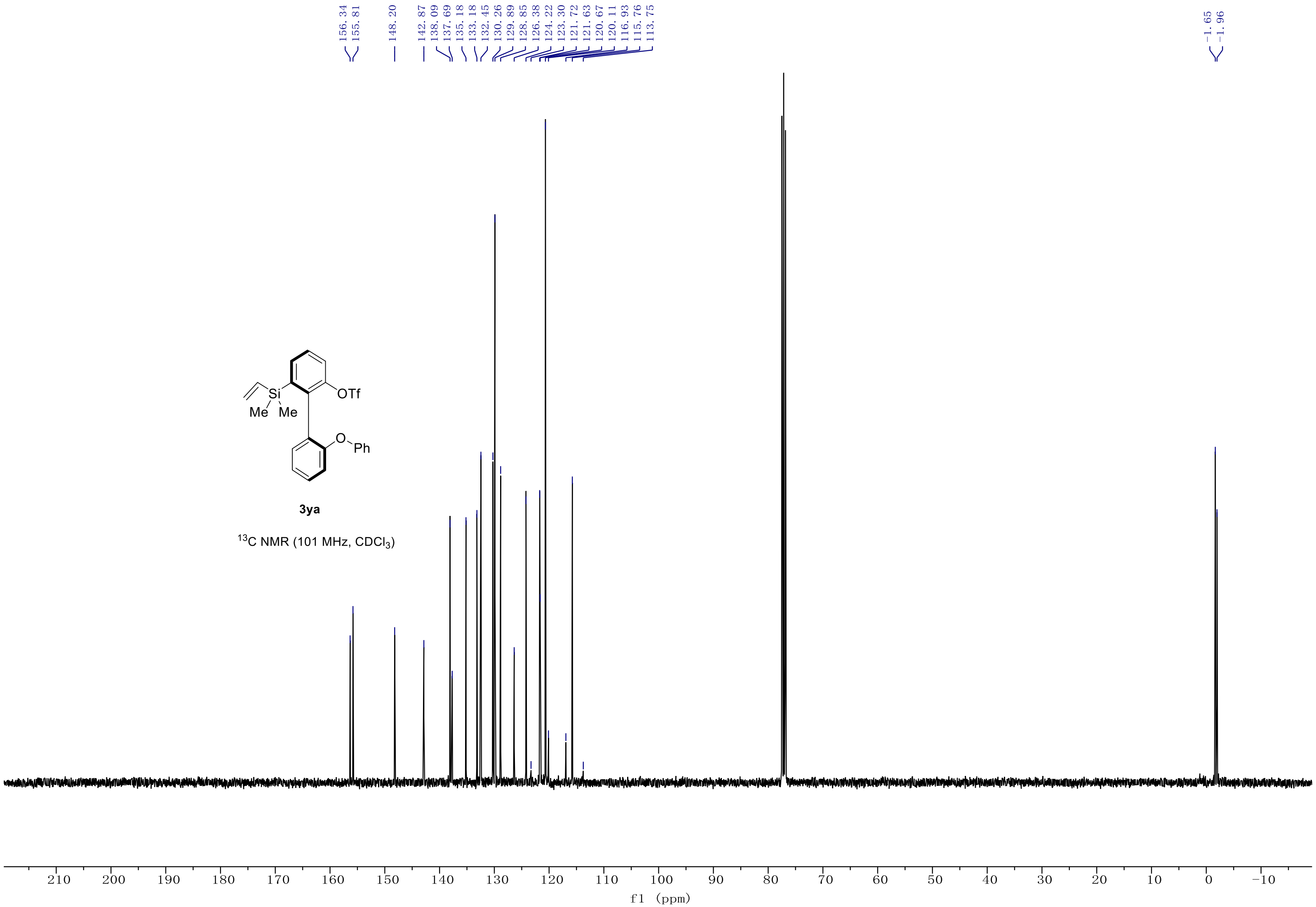
^{13}C NMR (101 MHz, $CDCl_3$)


OTf
Si
Me
Me
Me
3xa
^{19}F NMR (376 MHz, $CDCl_3$)
−74.63
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



3ya

^{1}H NMR (400 MHz, $CDCl_3$)

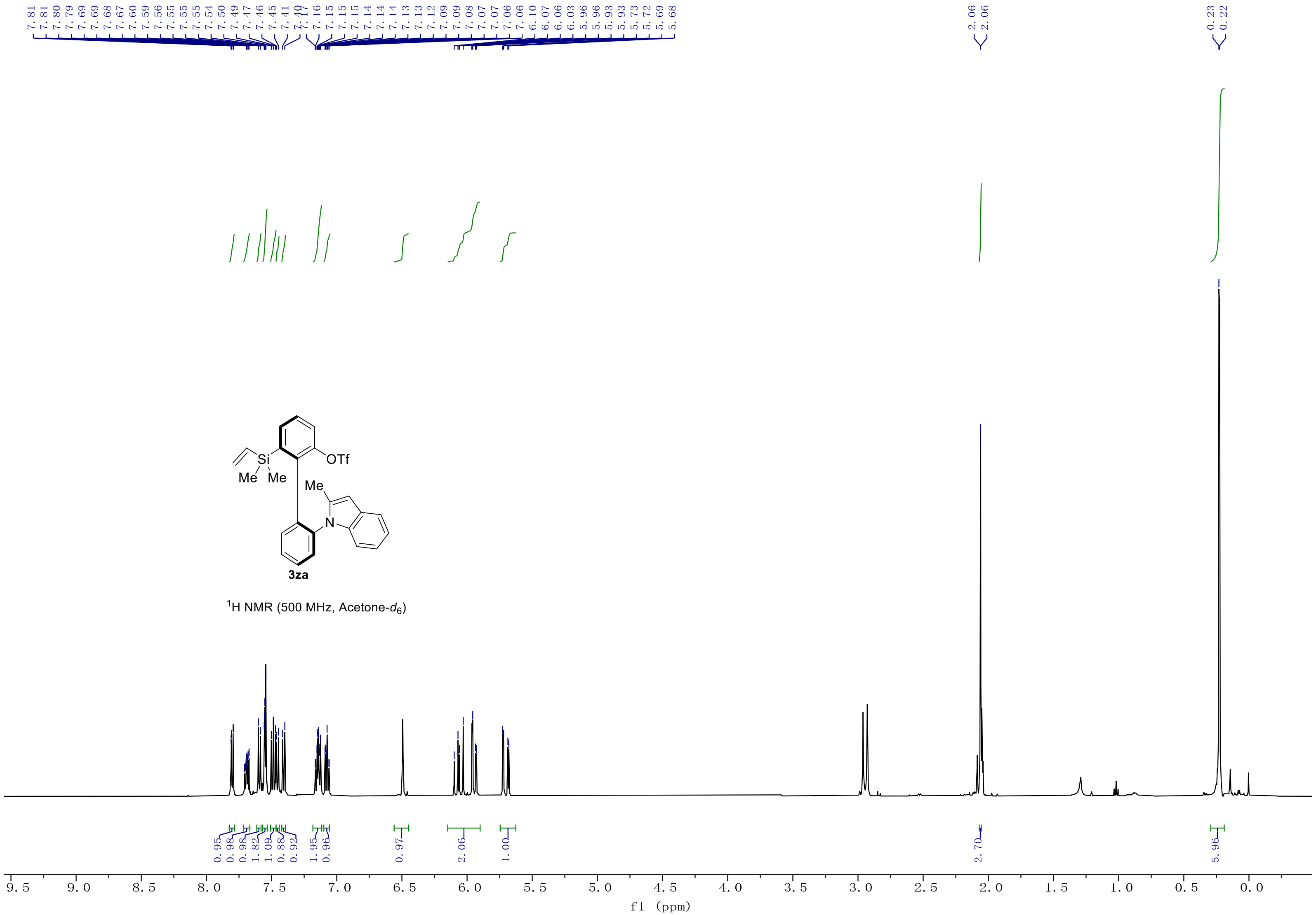


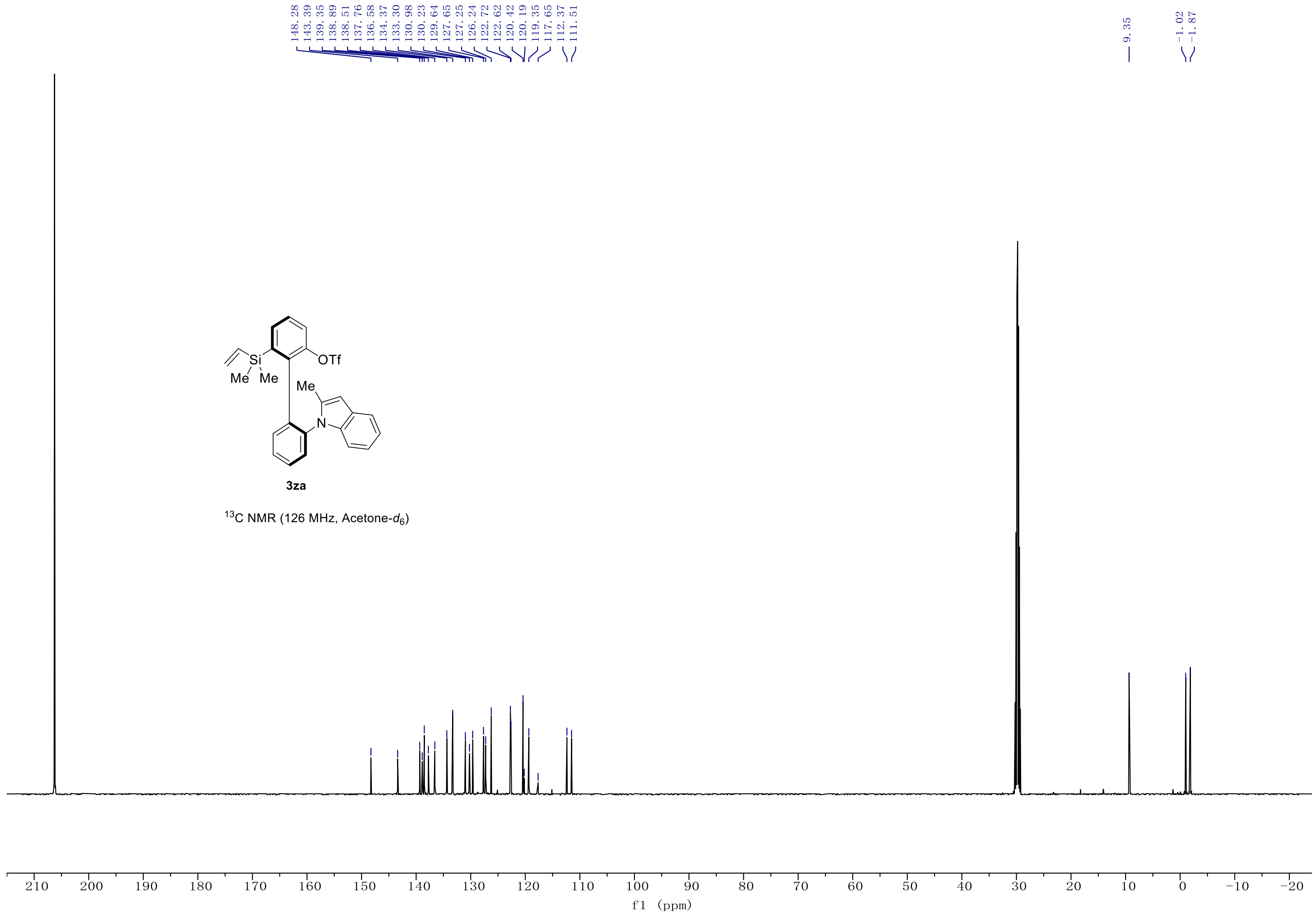
3ya

^{13}C NMR (101 MHz, $CDCl_3$)

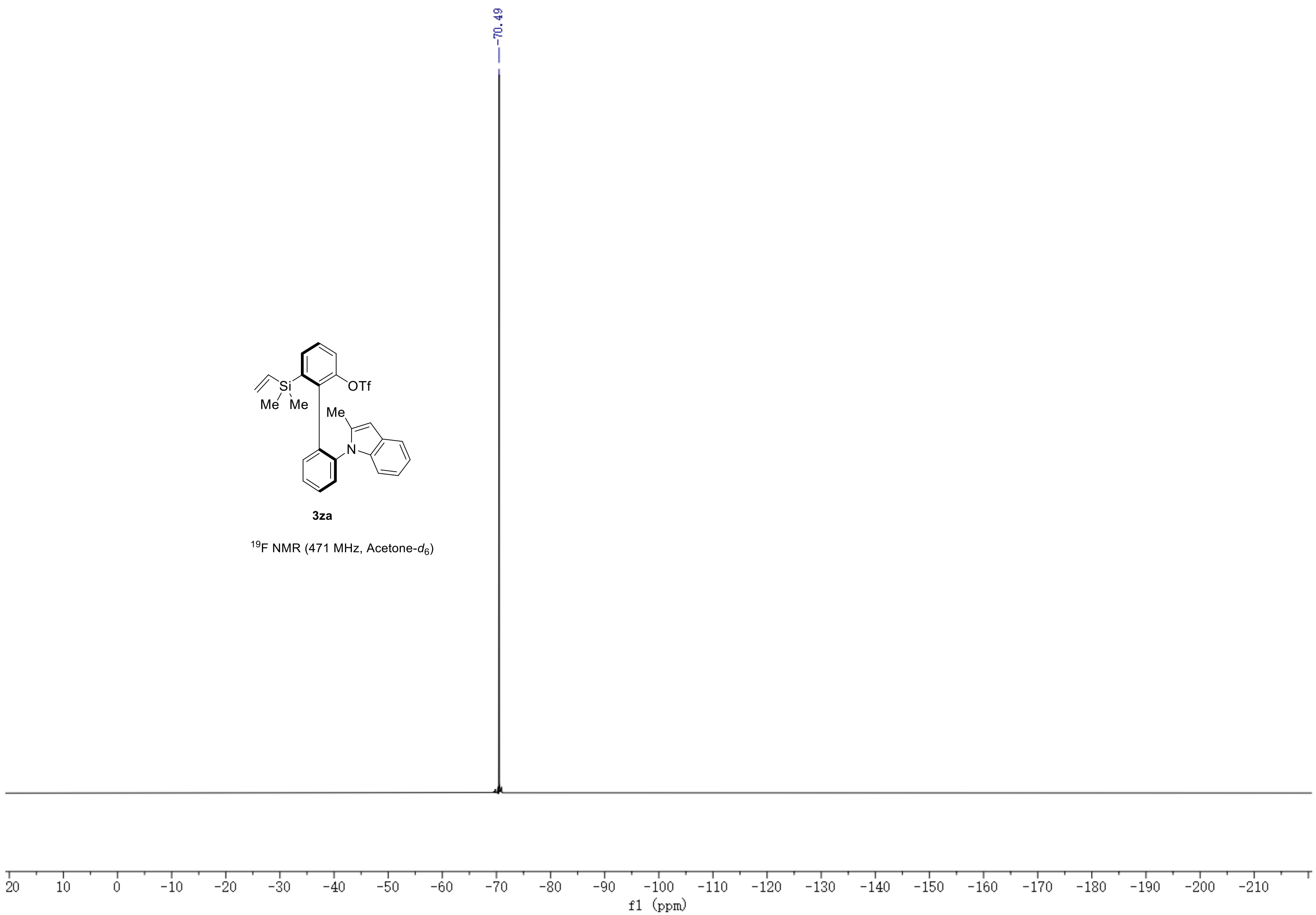
3ya

^{19}F NMR (376 MHz, $CDCl_3$)

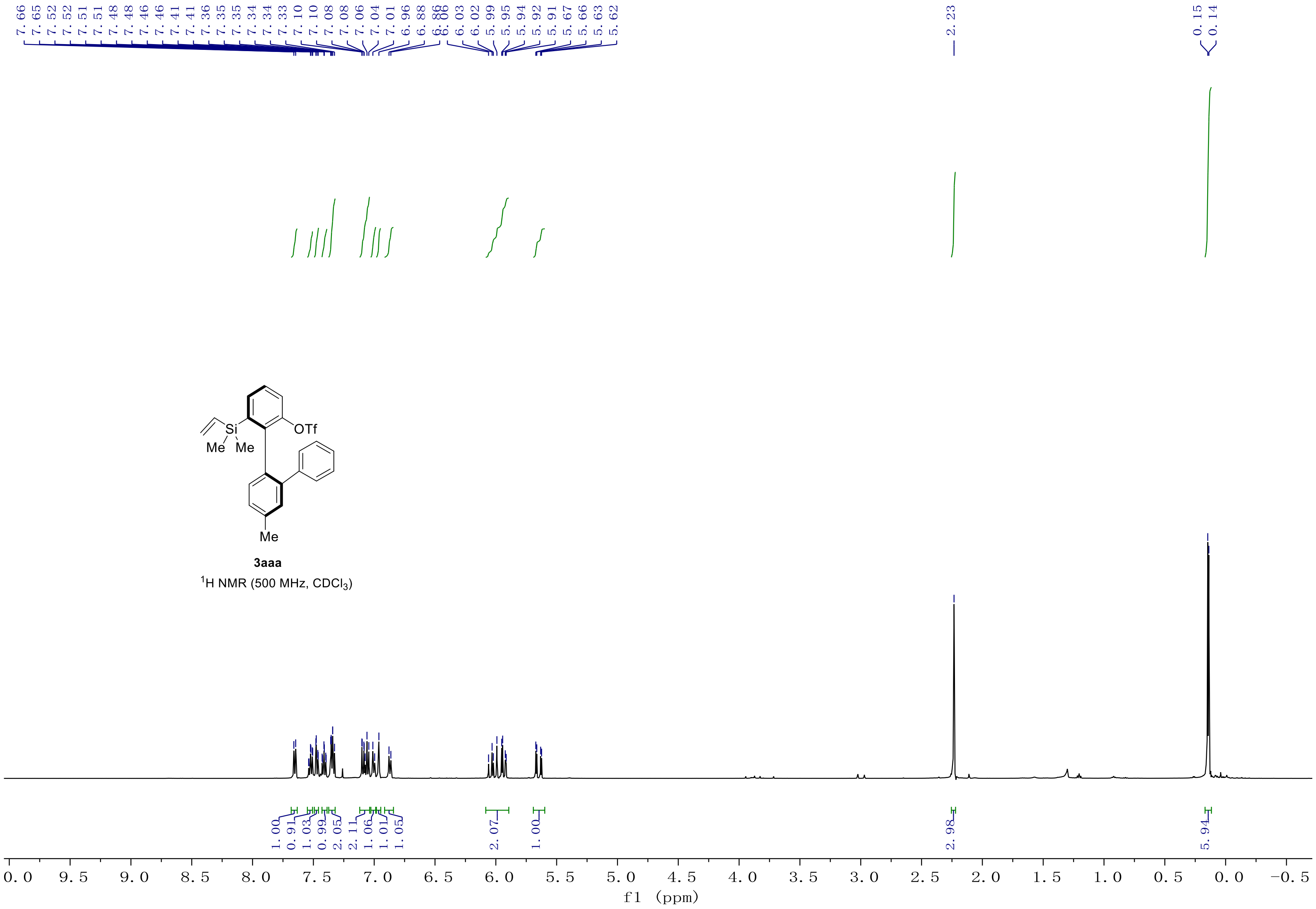

7.81 7.81 7.80 7.79 7.69 7.69 7.68 7.67 7.60 7.59 7.56 7.55 7.55 7.55 7.54 7.50 7.49 7.47 7.46 7.45 7.41 7.40 7.17 7.16 7.15 7.15 7.15 7.14 7.14 7.14 7.13 7.13 7.12 7.09 7.09 7.08 7.07 7.07 7.06 7.06 6.10 6.07 6.06 6.03 5.96 5.96 5.93 5.73 5.72 5.69 5.68
2.06 2.06
0.23 0.22
Si
Me
Me
OTf
Me
N
3za
1H NMR (500 MHz, Acetone-d6)
0.95 0.98 0.98 1.82 1.09 0.88 0.92
1.95 0.96
0.97
2.06
1.00
2.70
5.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

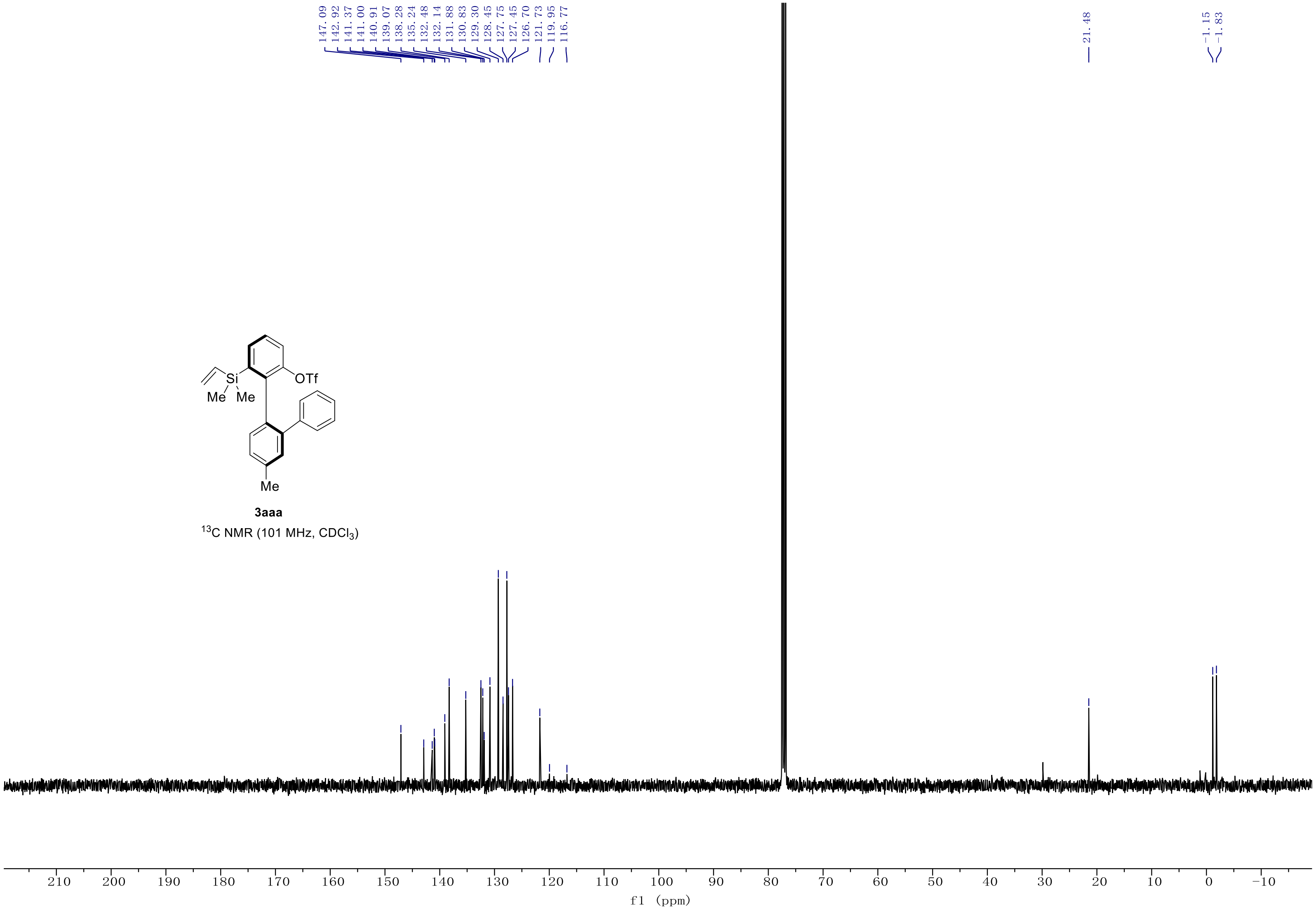


148.28
143.39
139.35
138.89
138.51
137.76
136.58
134.37
133.30
130.98
130.23
129.64
127.65
127.25
126.24
122.72
122.62
120.42
120.19
119.35
117.65
112.37
111.51
9.35
-1.02
-1.87
Si
Me
Me
OTf
Me
N
3za
^{13}C NMR (126 MHz, Acetone-d_6)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



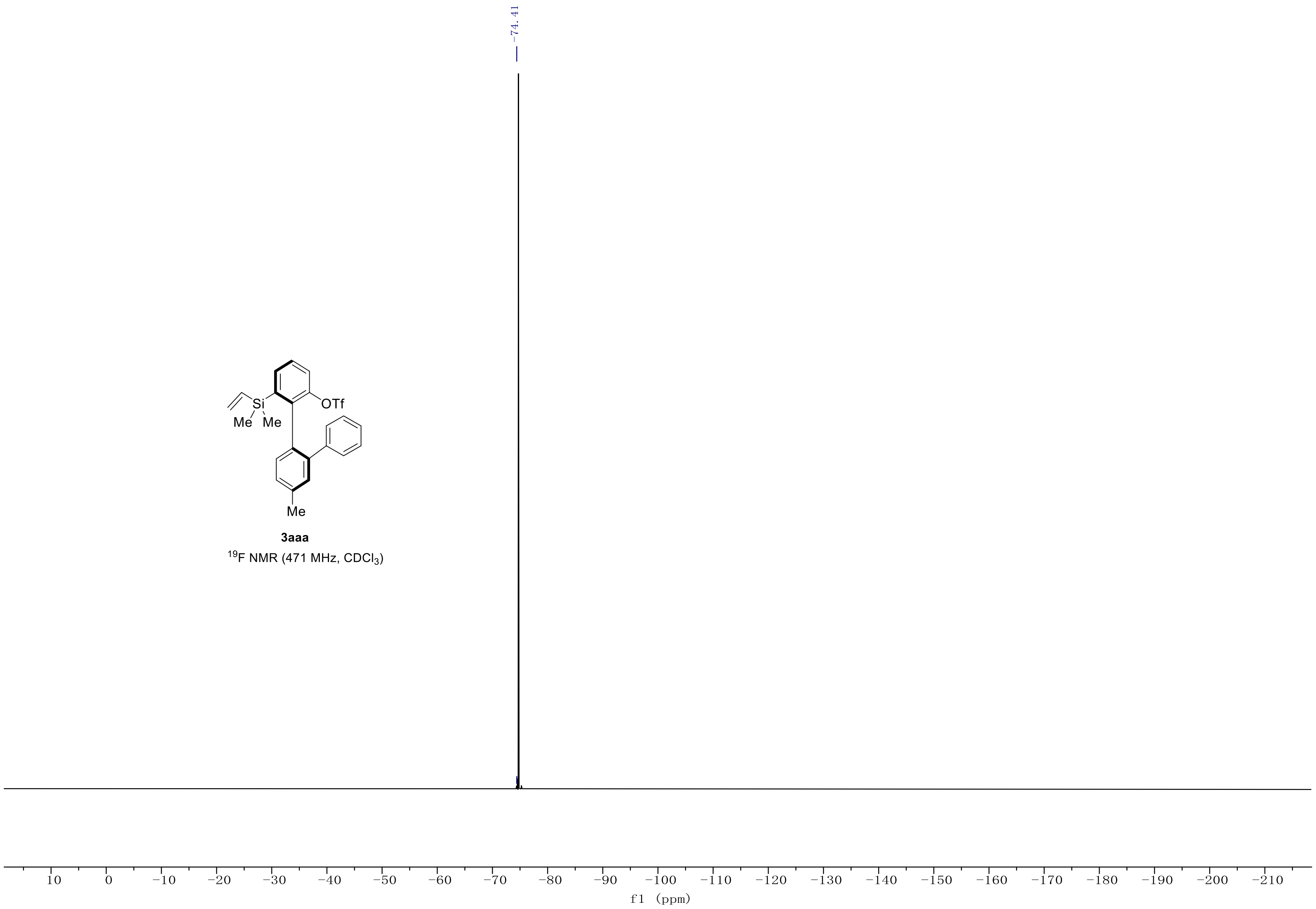
-70.49
OTf
Si
Me
Me
Me
N
3za
[19]F NMR (471 MHz, Acetone-d_6)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


3aaa
^{1}H NMR (500 MHz, CDCl$_3$)
f1 (ppm)

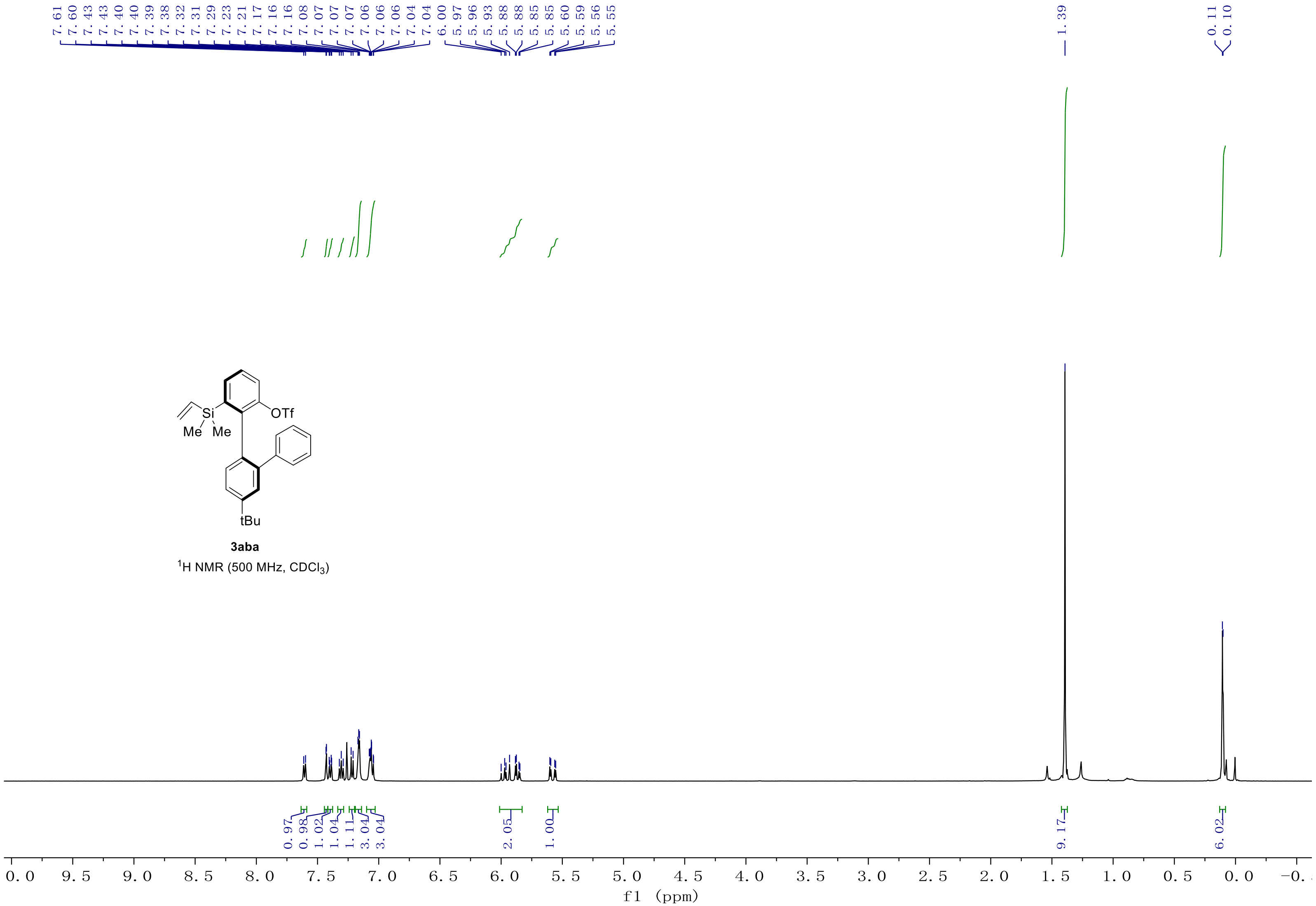


3aaa

^{13}C NMR (101 MHz, $CDCl_3$)

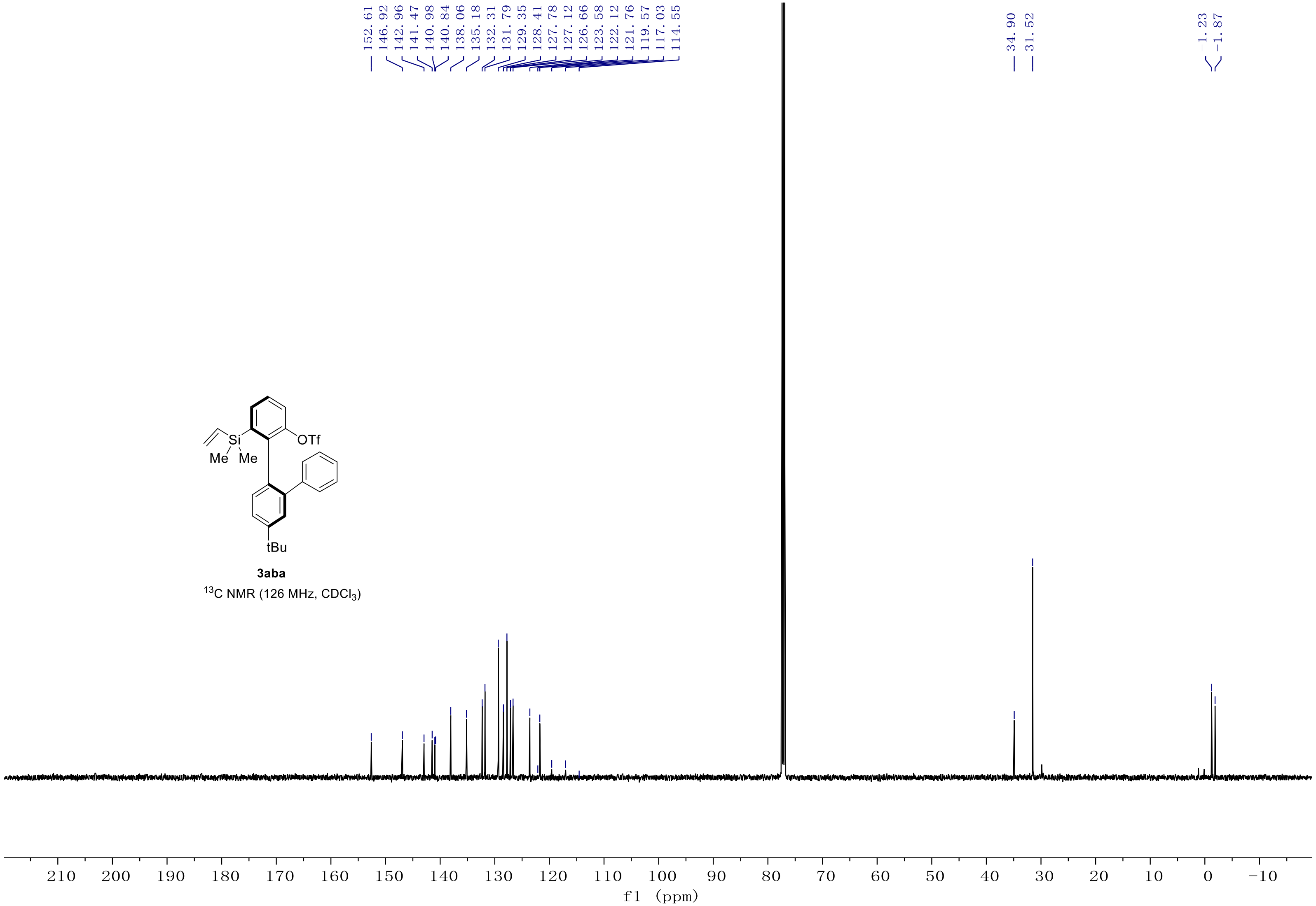


−74.41
OTf
Si
Me
Me
Me
3aaa
^{19}F NMR (471 MHz, $CDCl_3$)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



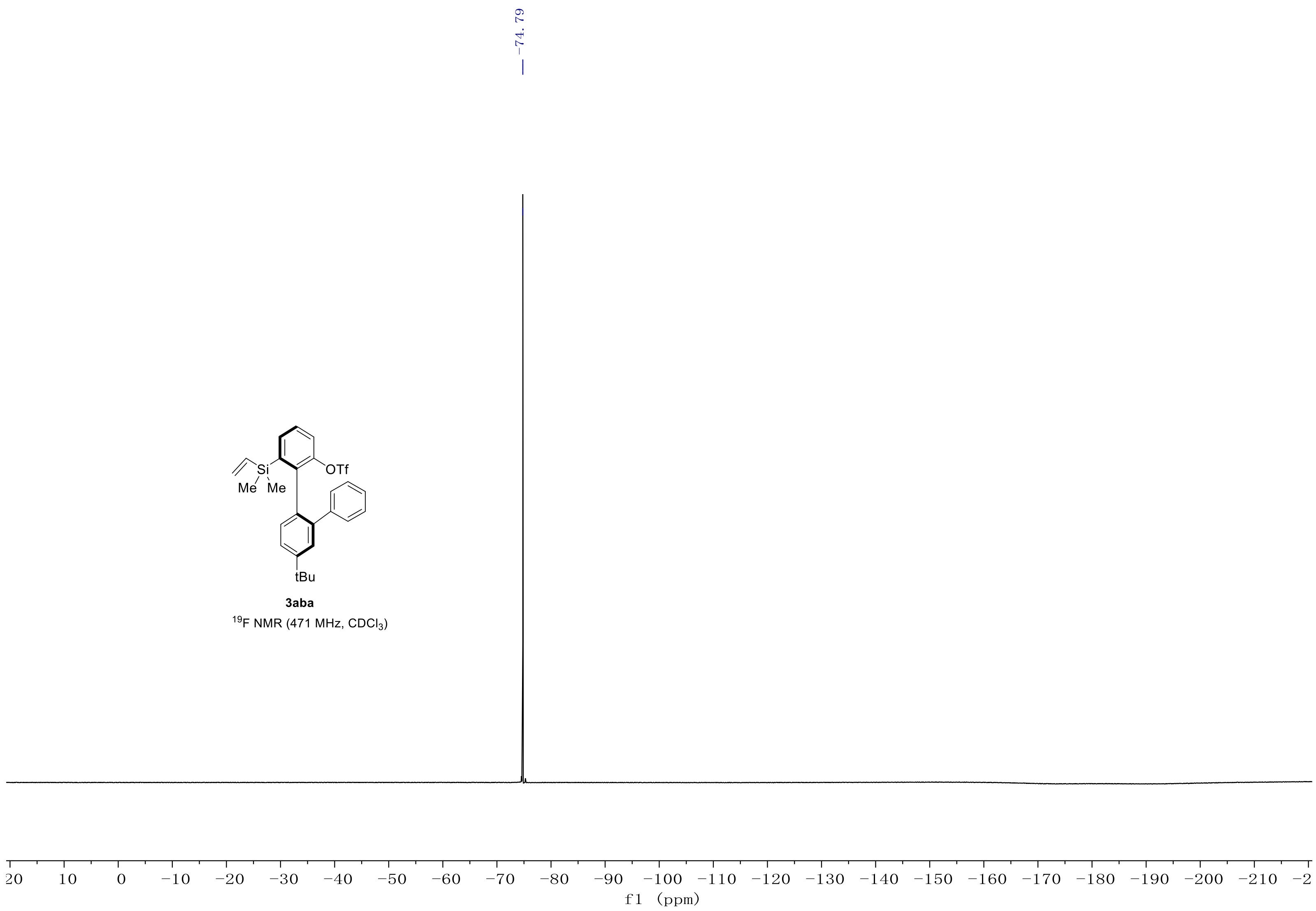
3aba

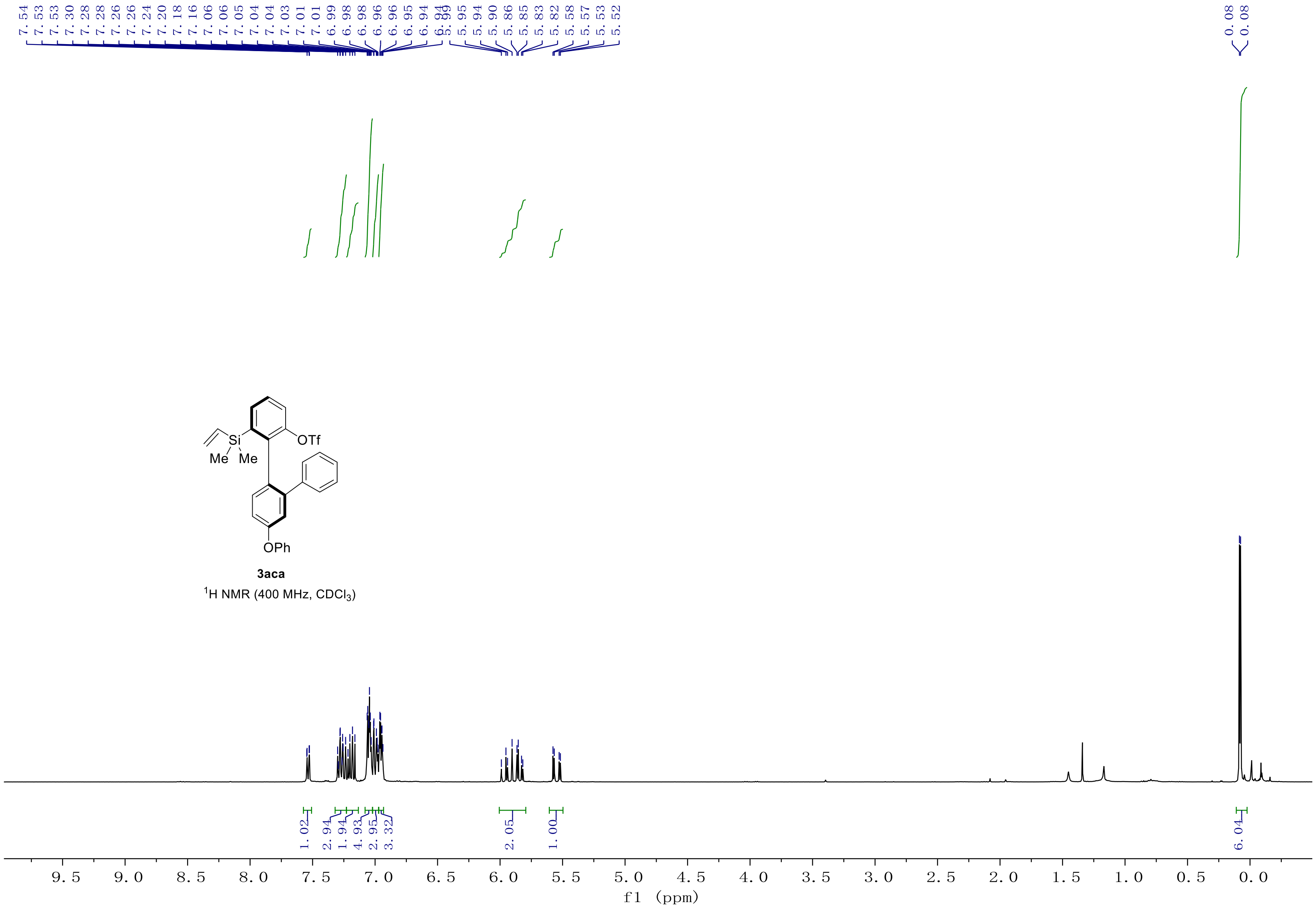
^{1}H NMR (500 MHz, $CDCl_3$)



3aba

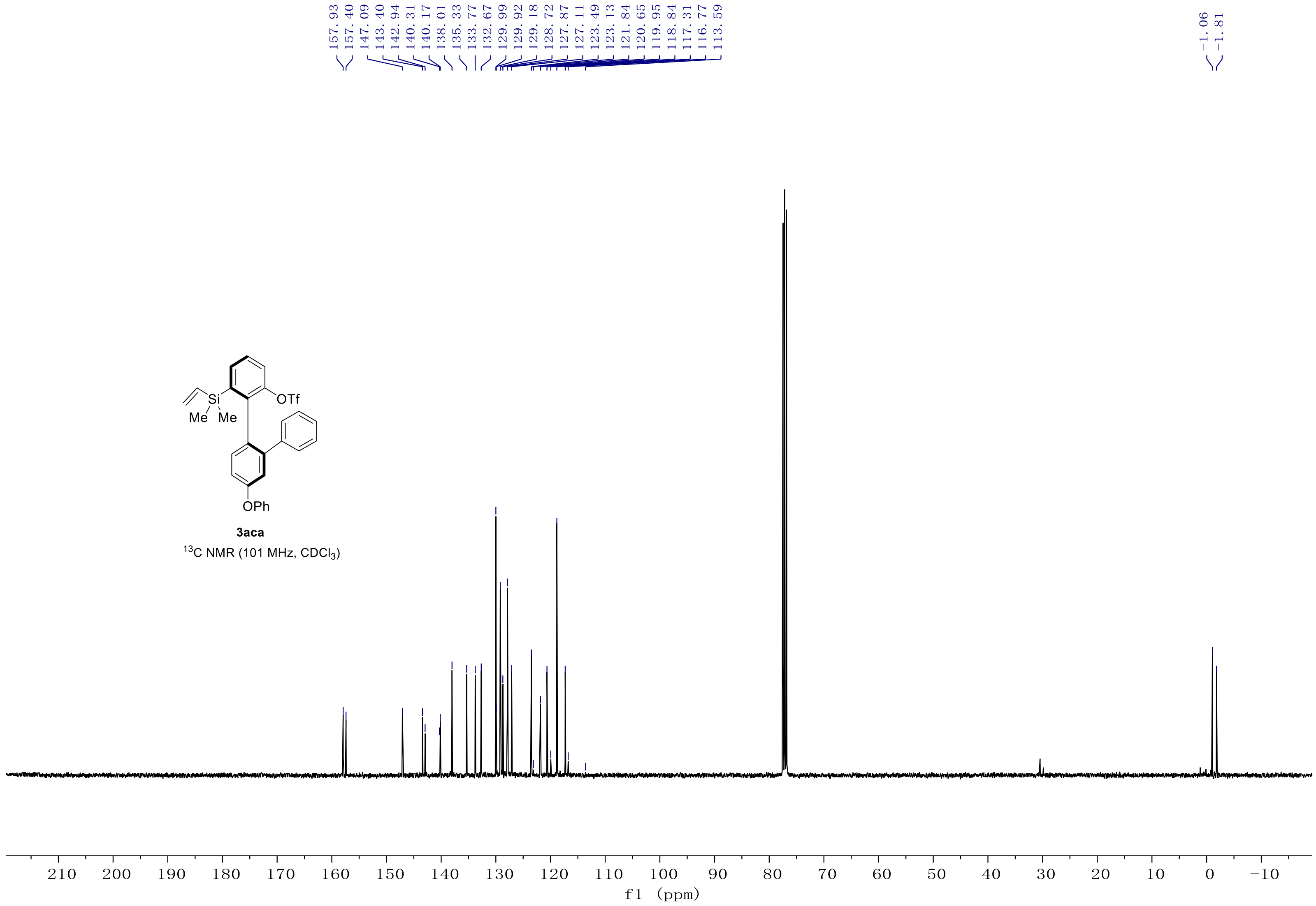
^{13}C NMR (126 MHz, $CDCl_3$)


−74.79
OTf
Si
Me Me
tBu
3aba
^{19}F NMR (471 MHz, $CDCl_3$)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)



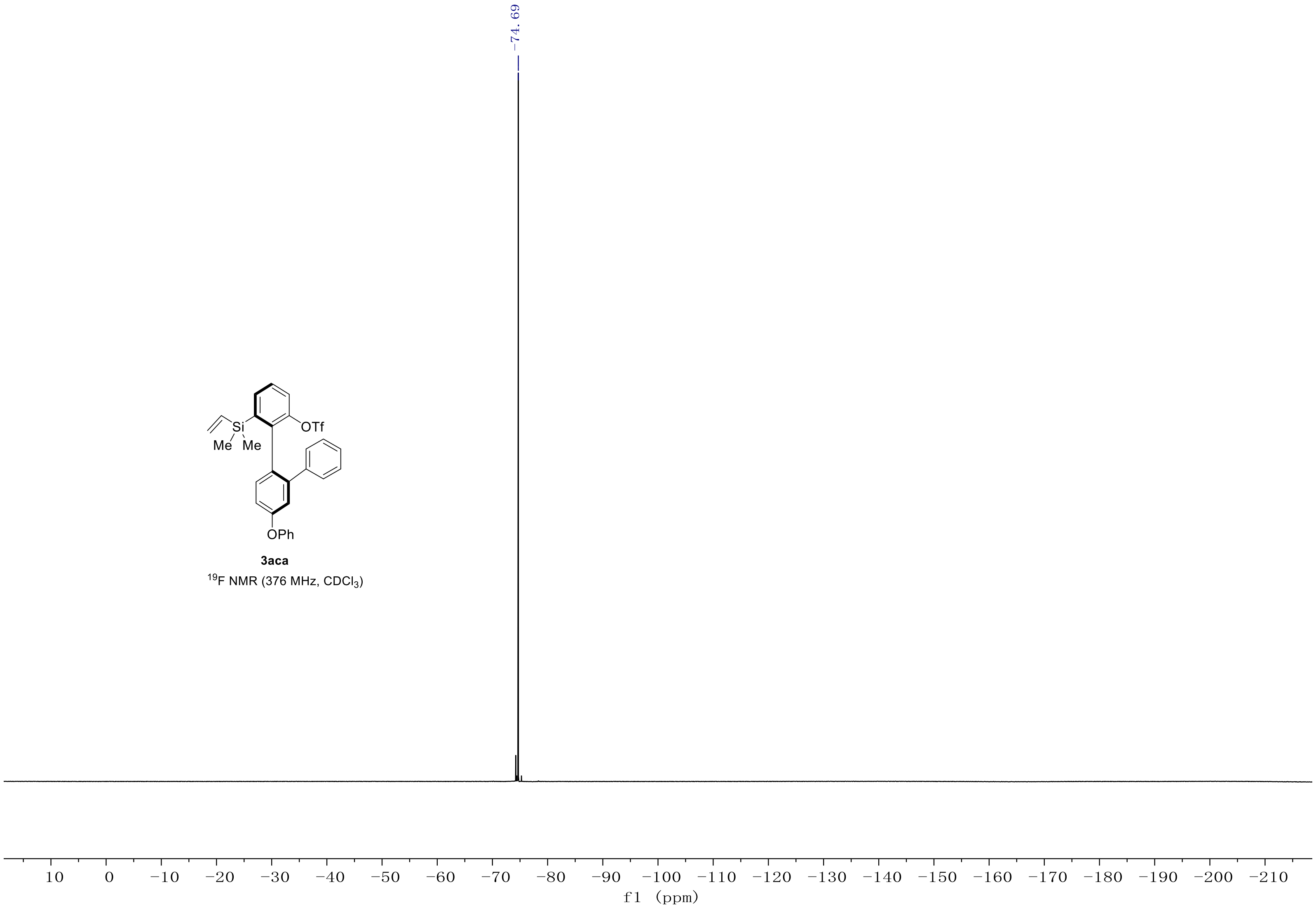
3aca

^{1}H NMR (400 MHz, $CDCl_3$)



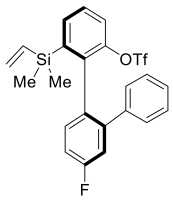
3aca

^{13}C NMR (101 MHz, $CDCl_3$)



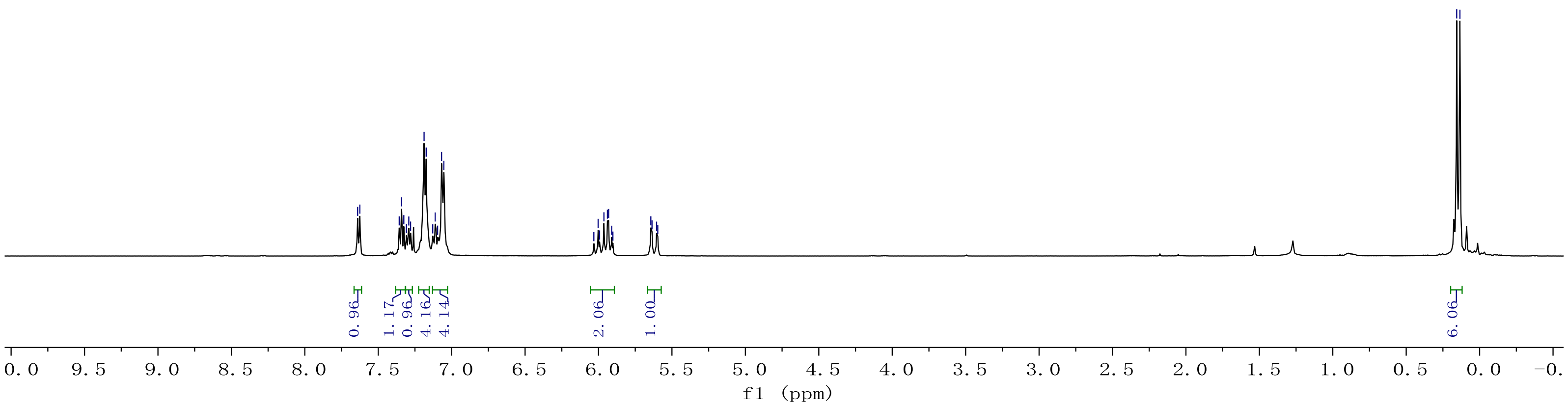
3aca

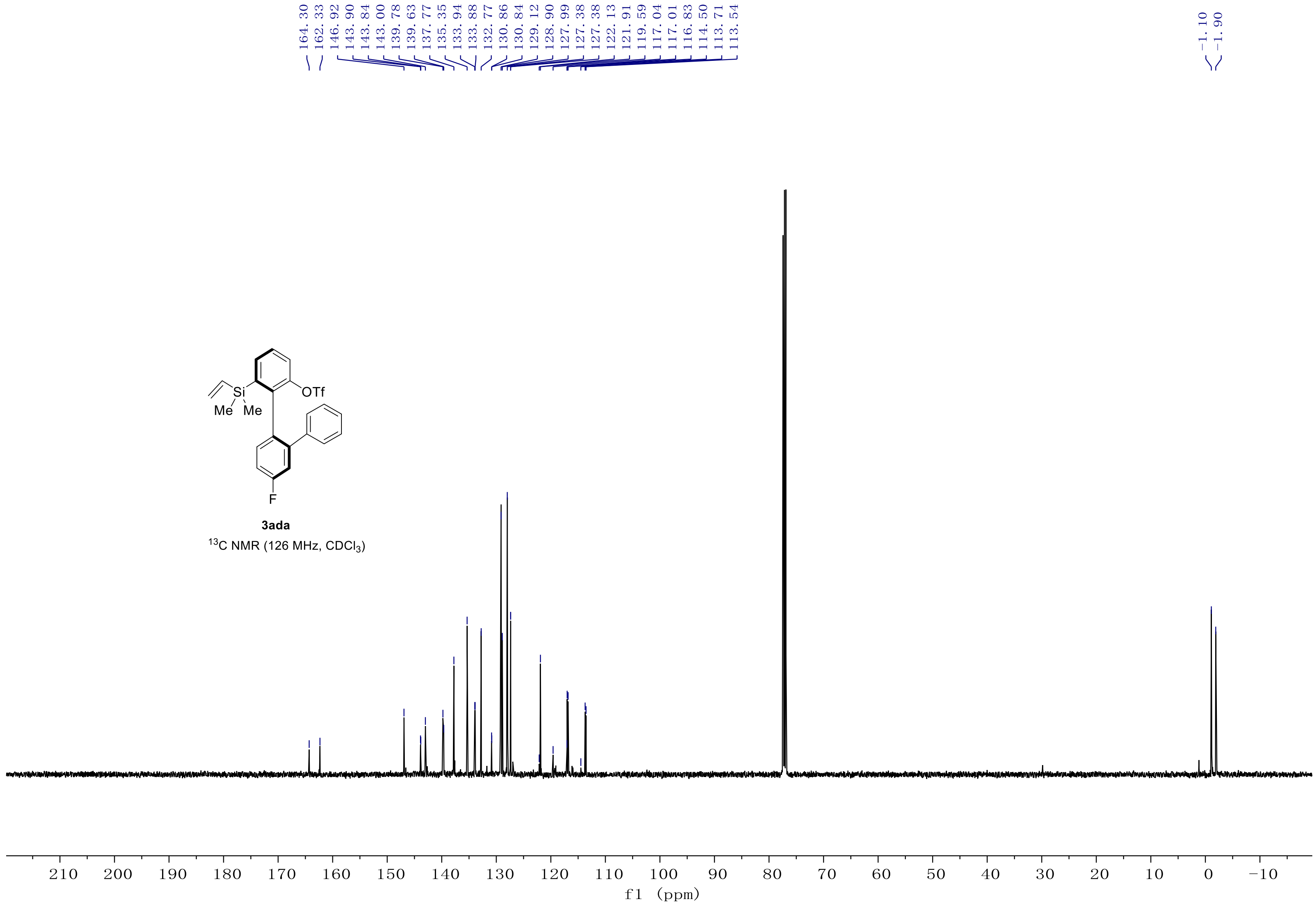
^{19}F NMR (376 MHz, $CDCl_3$)

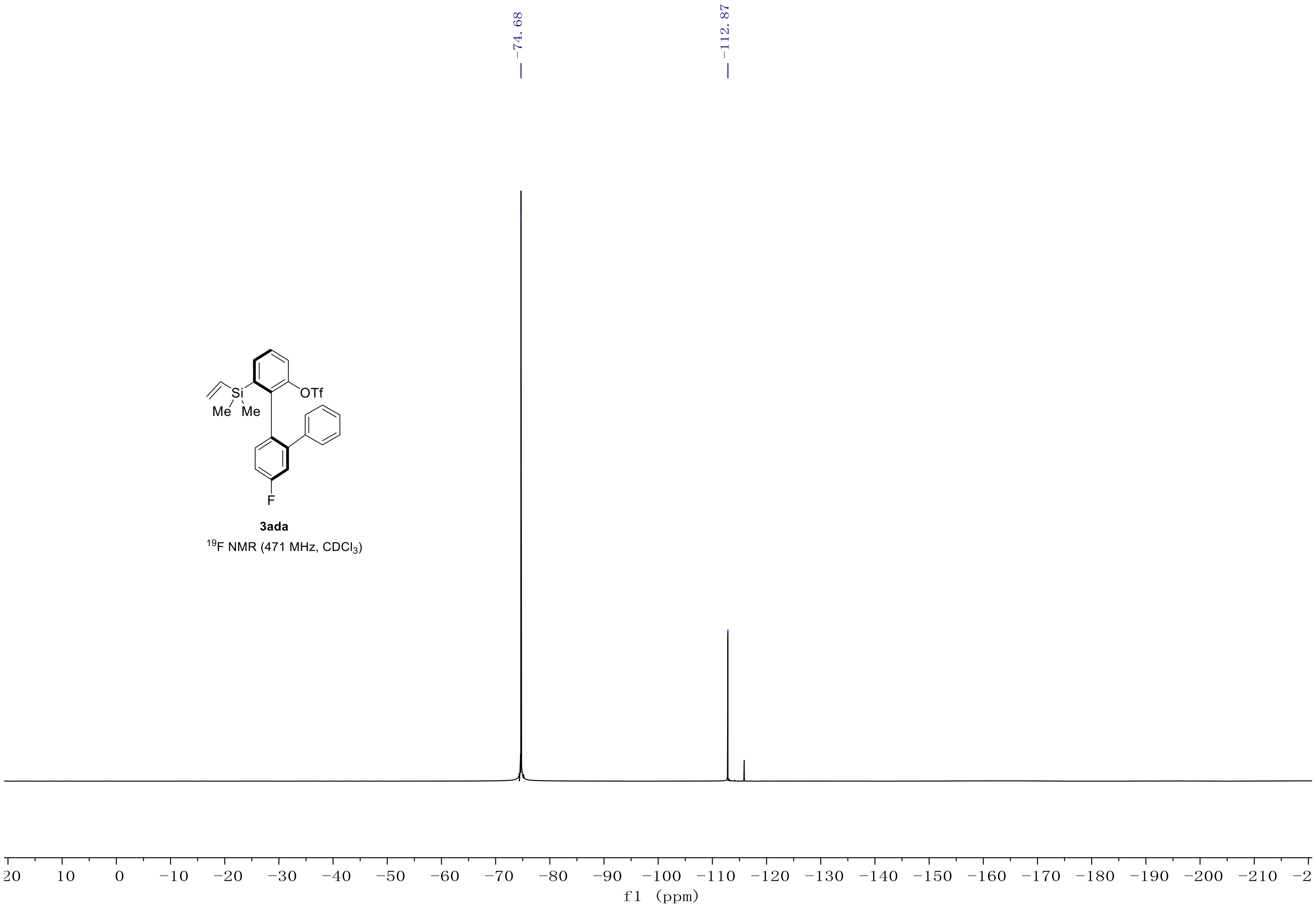


3ada

^1H NMR (500 MHz, $CDCl_3$)

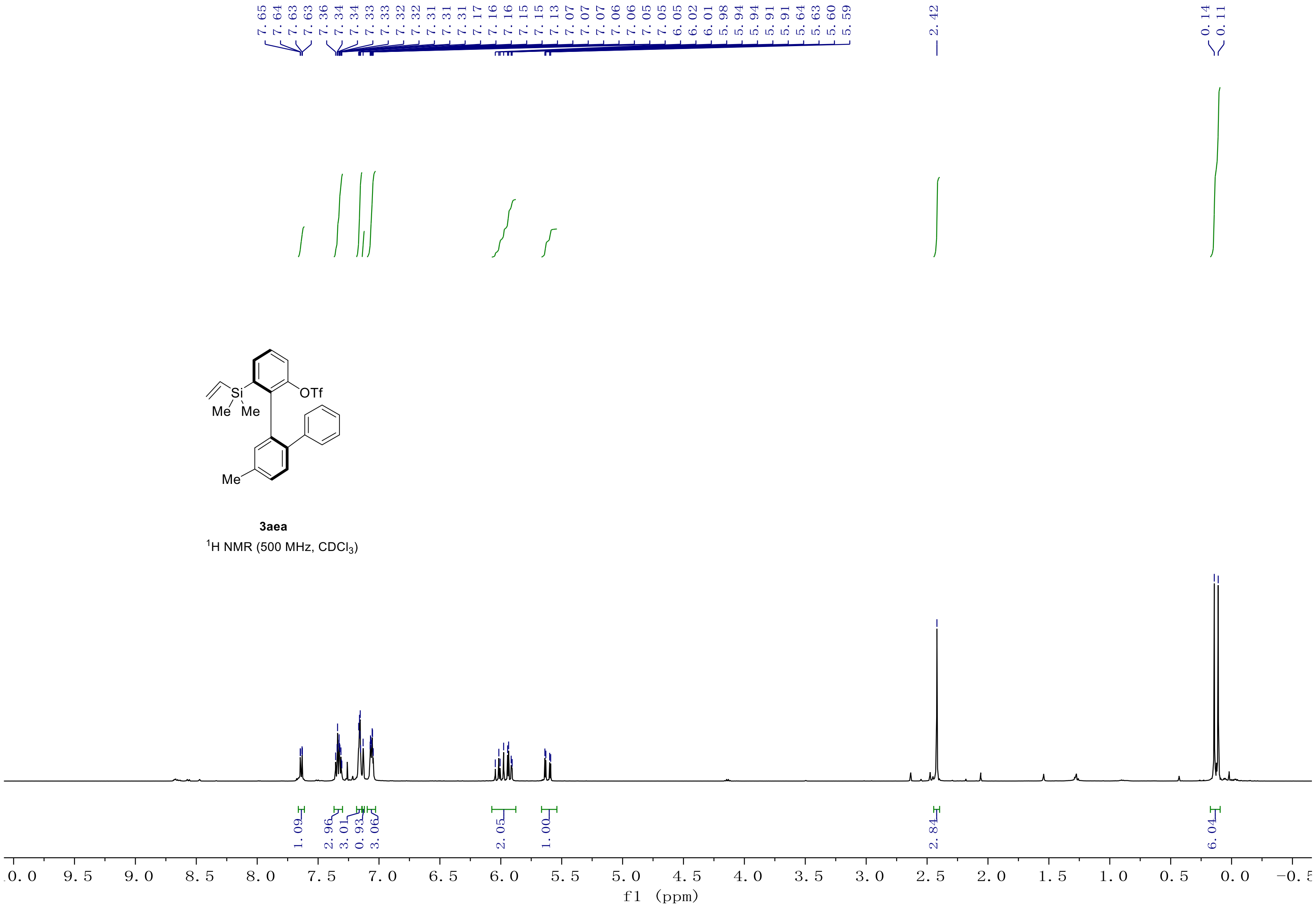




164.30
162.33
146.92
143.90
143.84
143.00
139.78
139.63
137.77
135.35
133.94
133.88
132.77
130.86
130.84
129.12
128.90
127.99
127.38
127.38
122.13
121.91
119.59
117.04
117.01
116.83
114.50
113.71
113.54
-1.10
-1.90
Si
Me
Me
OTf
F
3ada
^{13}C NMR (126 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



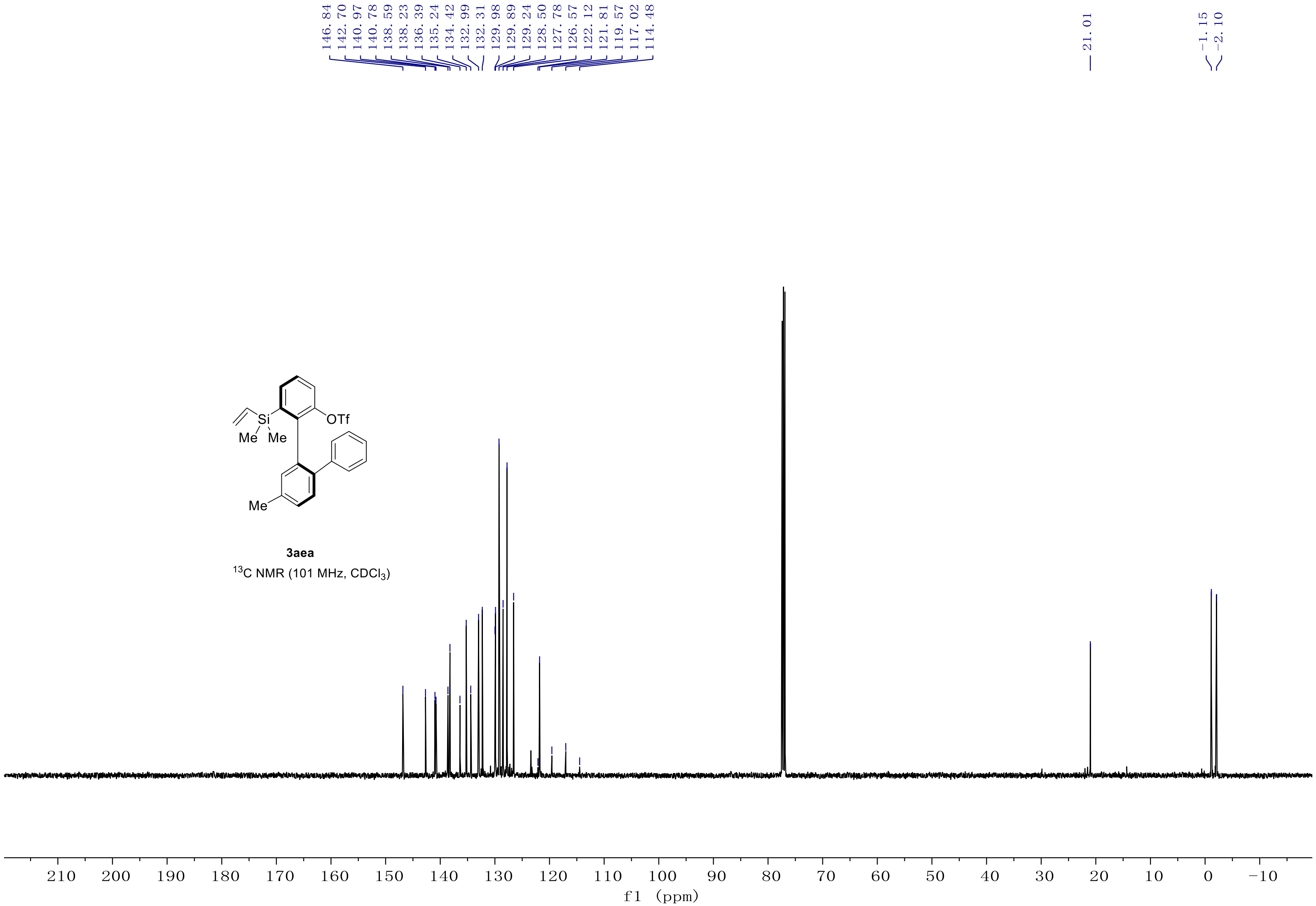
3ada

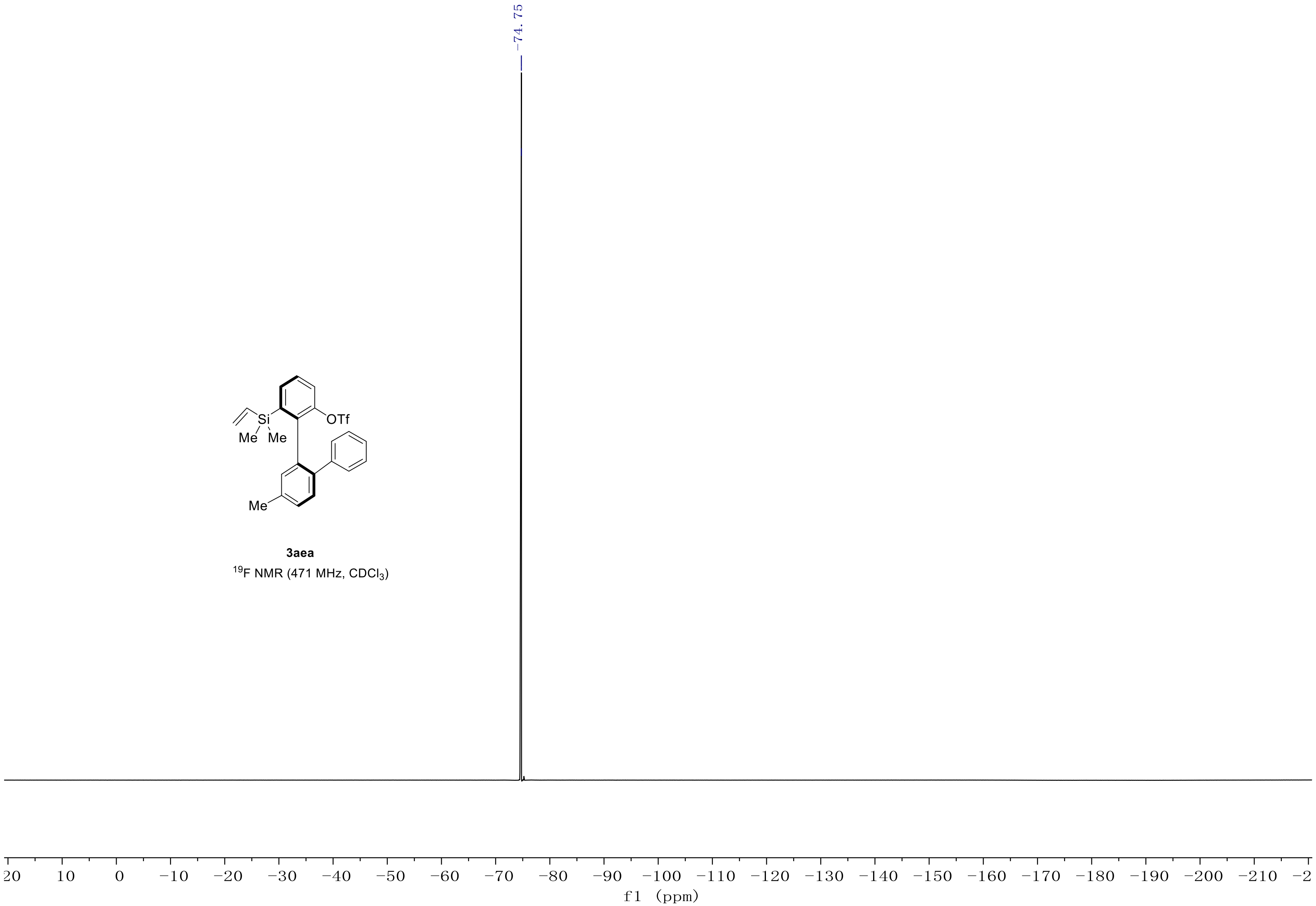
^{19}F NMR (471 MHz, $CDCl_3$)

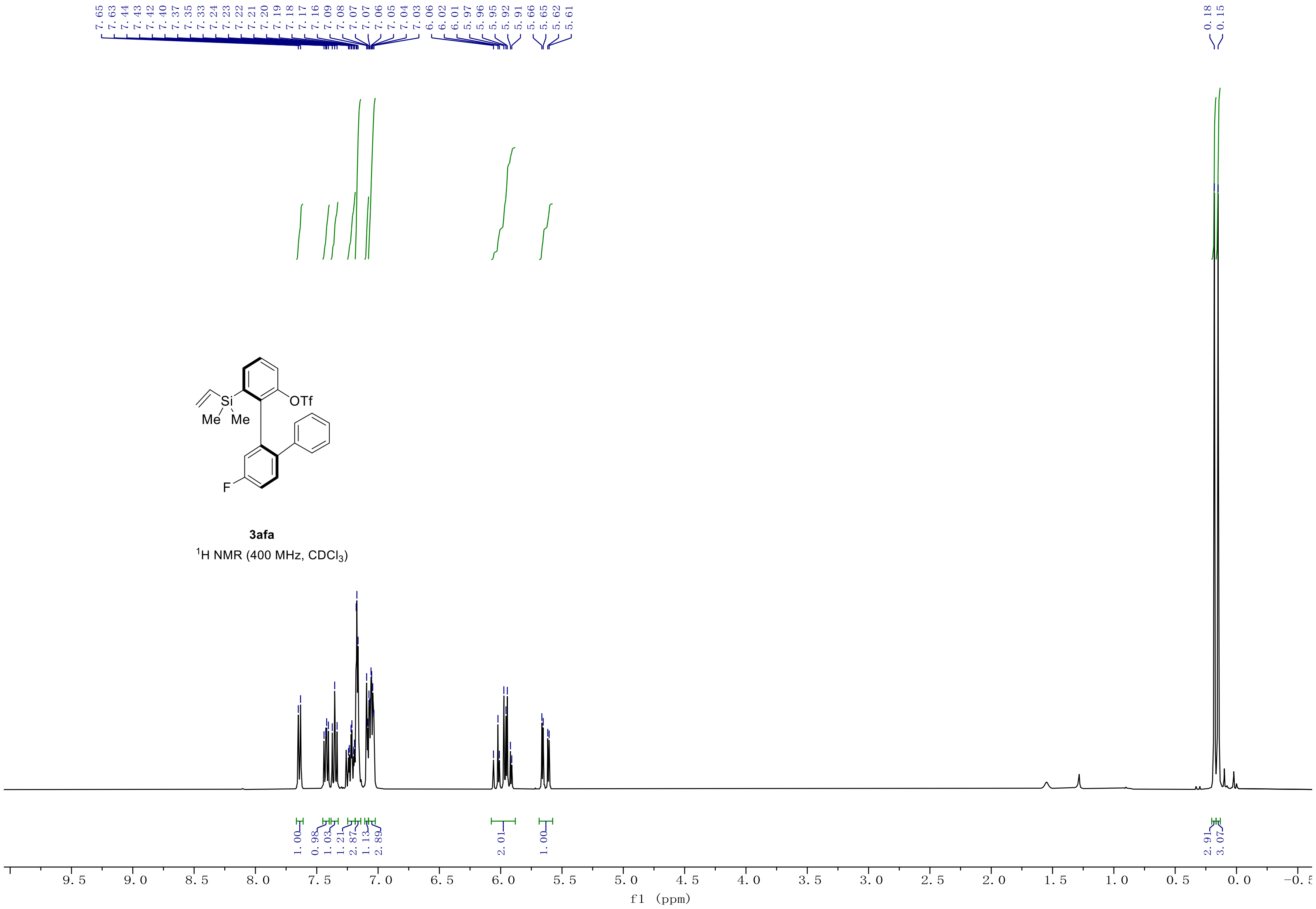


3aea

^{1}H NMR (500 MHz, $CDCl_3$)

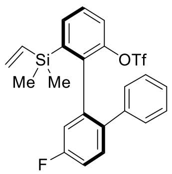

146.84
142.70
140.97
140.78
138.59
138.23
136.39
135.24
134.42
132.99
132.31
129.98
129.89
129.24
128.50
127.78
126.57
122.12
121.81
119.57
117.02
114.48
21.01
-1.15
-2.10
OTf
Si
Me
Me
Me
3aea
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-74.75
3aea
^{19}F NMR (471 MHz, $CDCl_3$)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2
f1 (ppm)



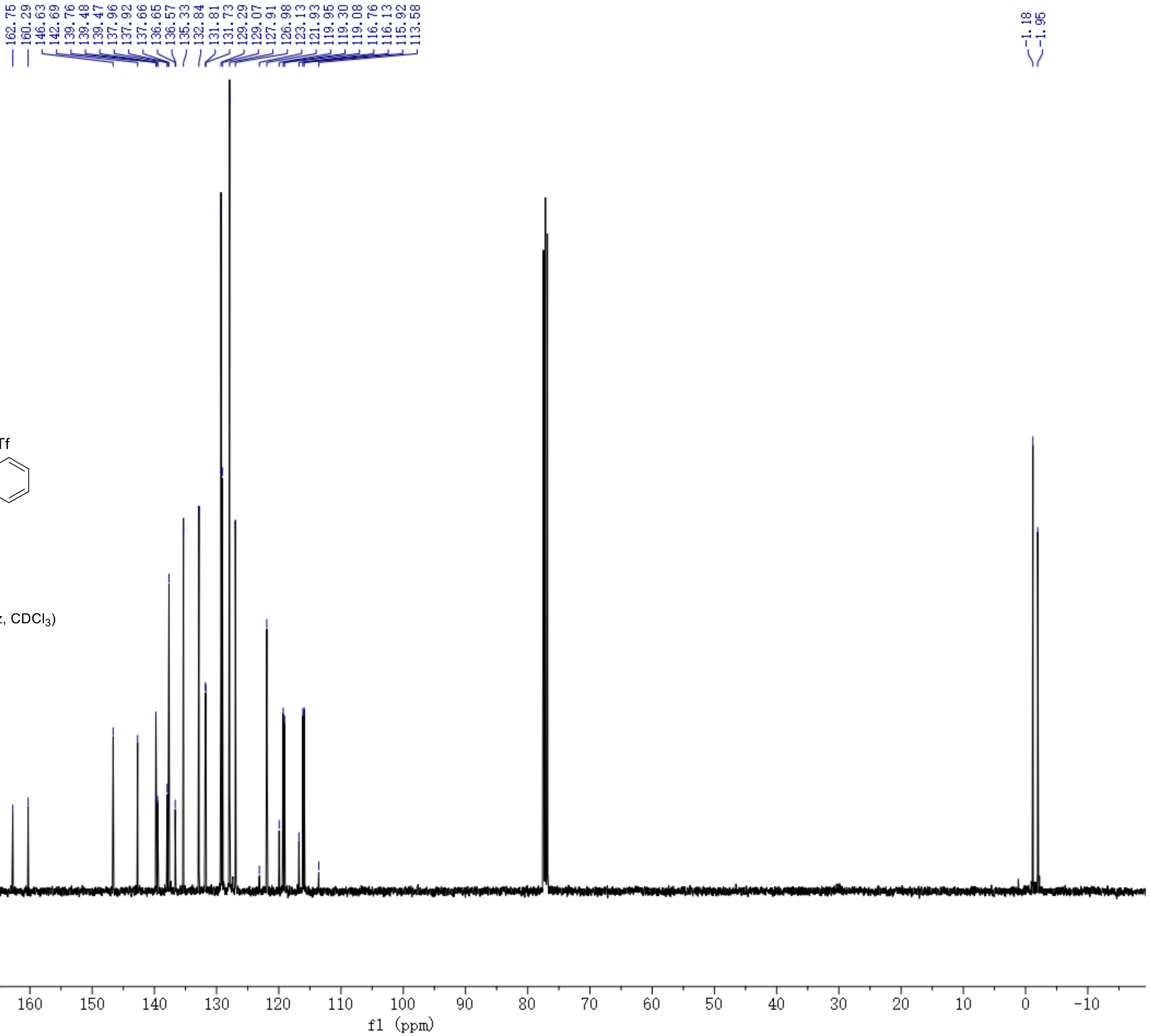
3afa

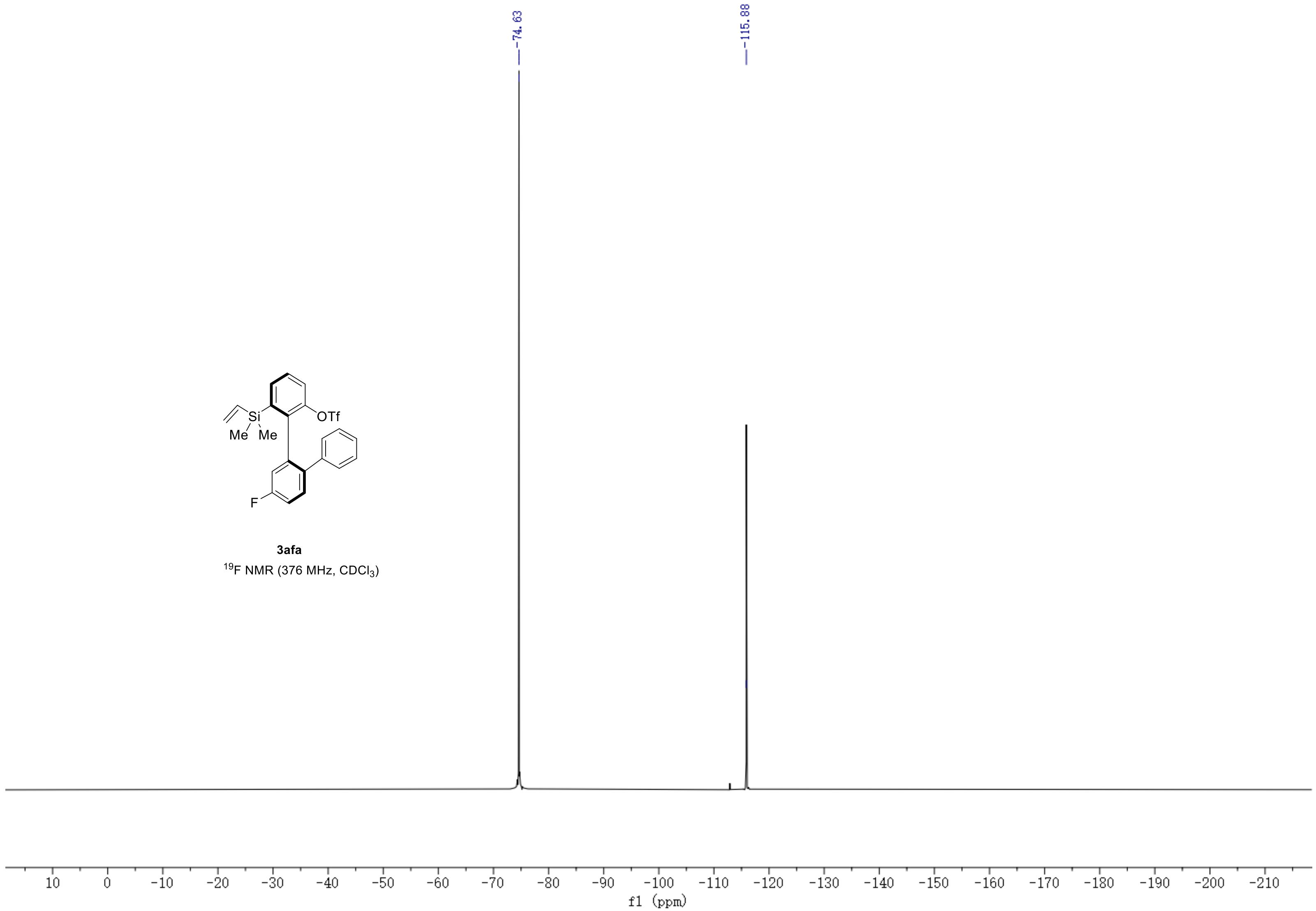
^{1}H NMR (400 MHz, $CDCl_3$)



3afa

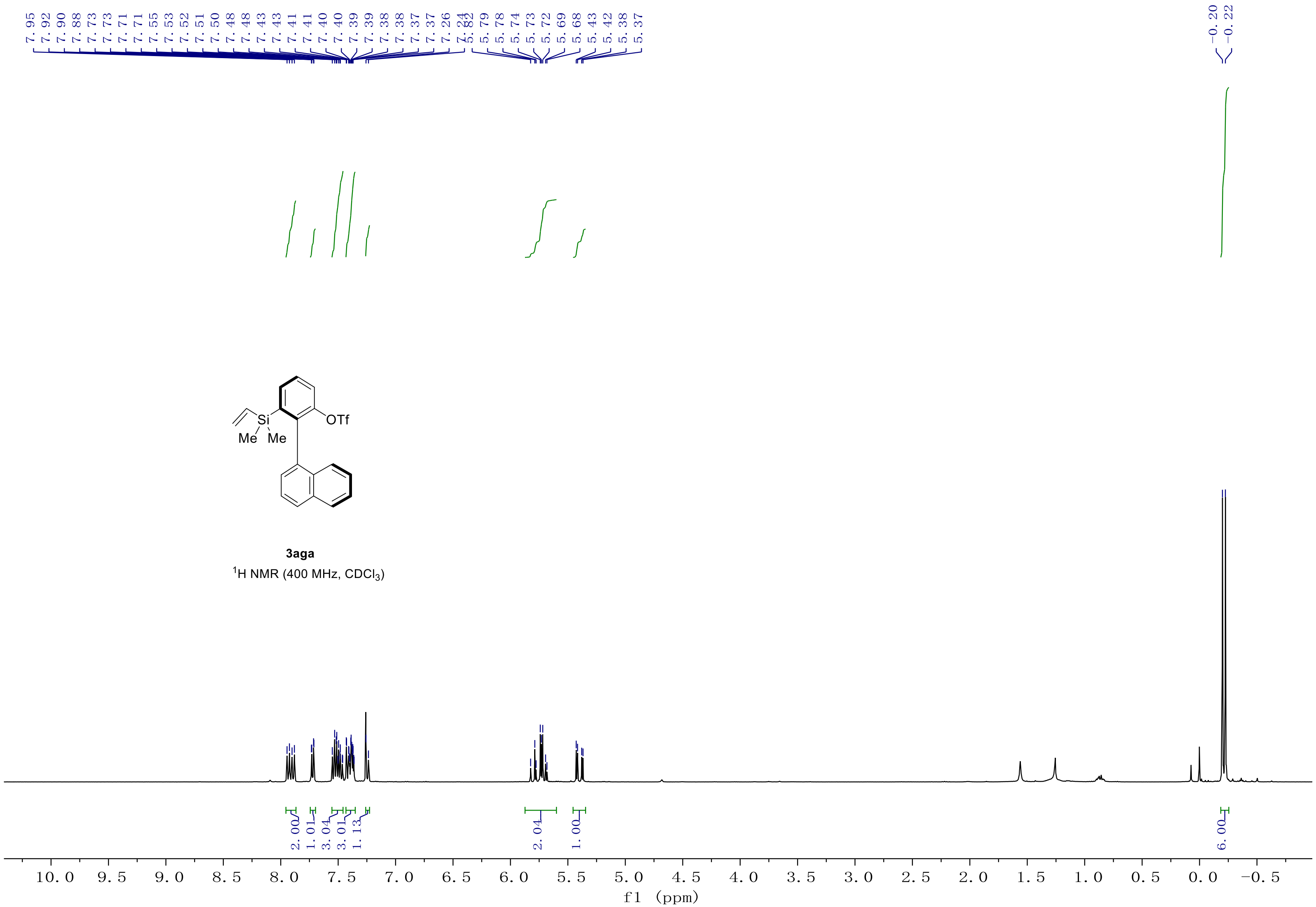
^{13}C NMR (101 MHz, $CDCl_3$)





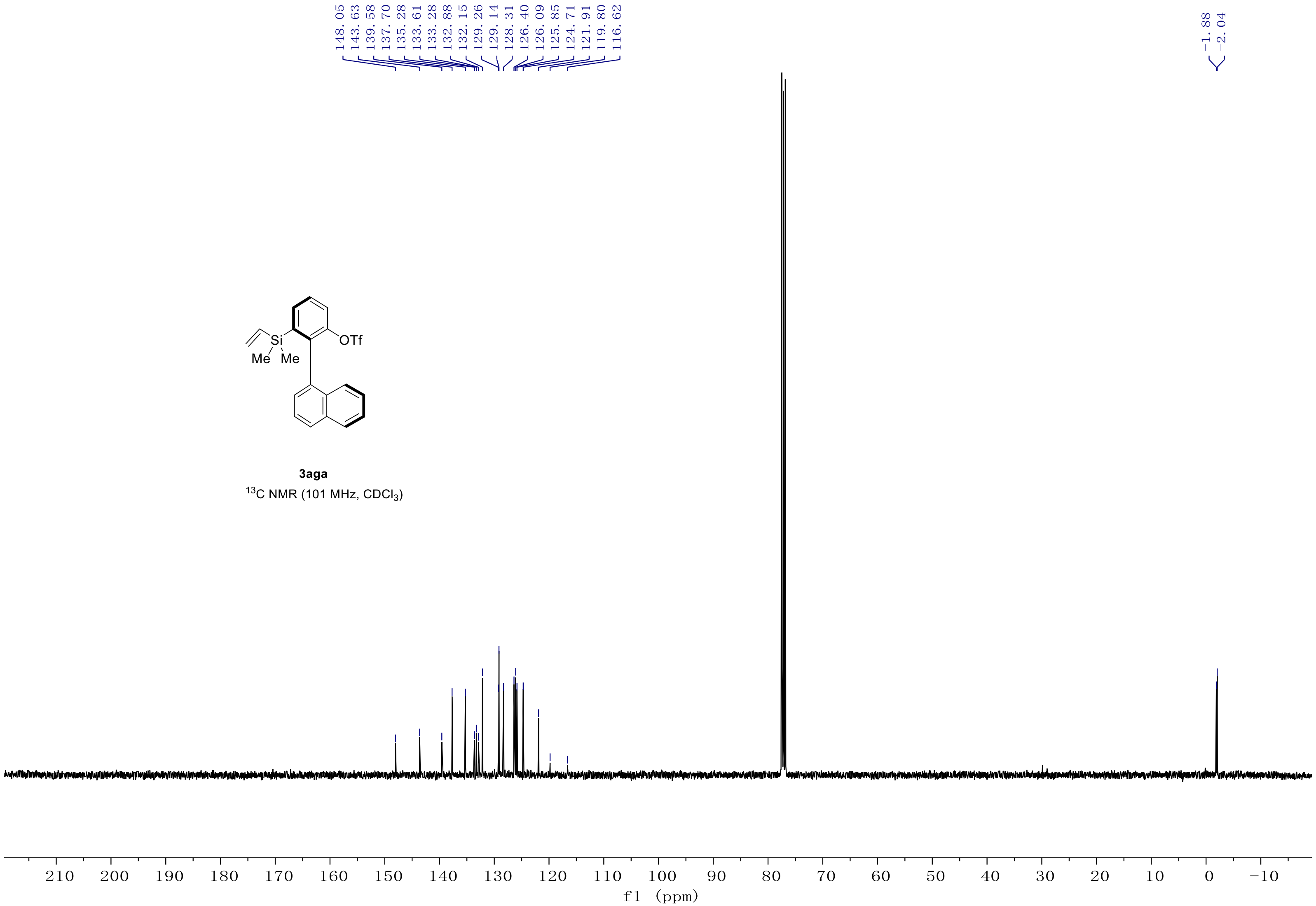
3afa

^{19}F NMR (376 MHz, $CDCl_3$)



3aga

^{1}H NMR (400 MHz, $CDCl_3$)

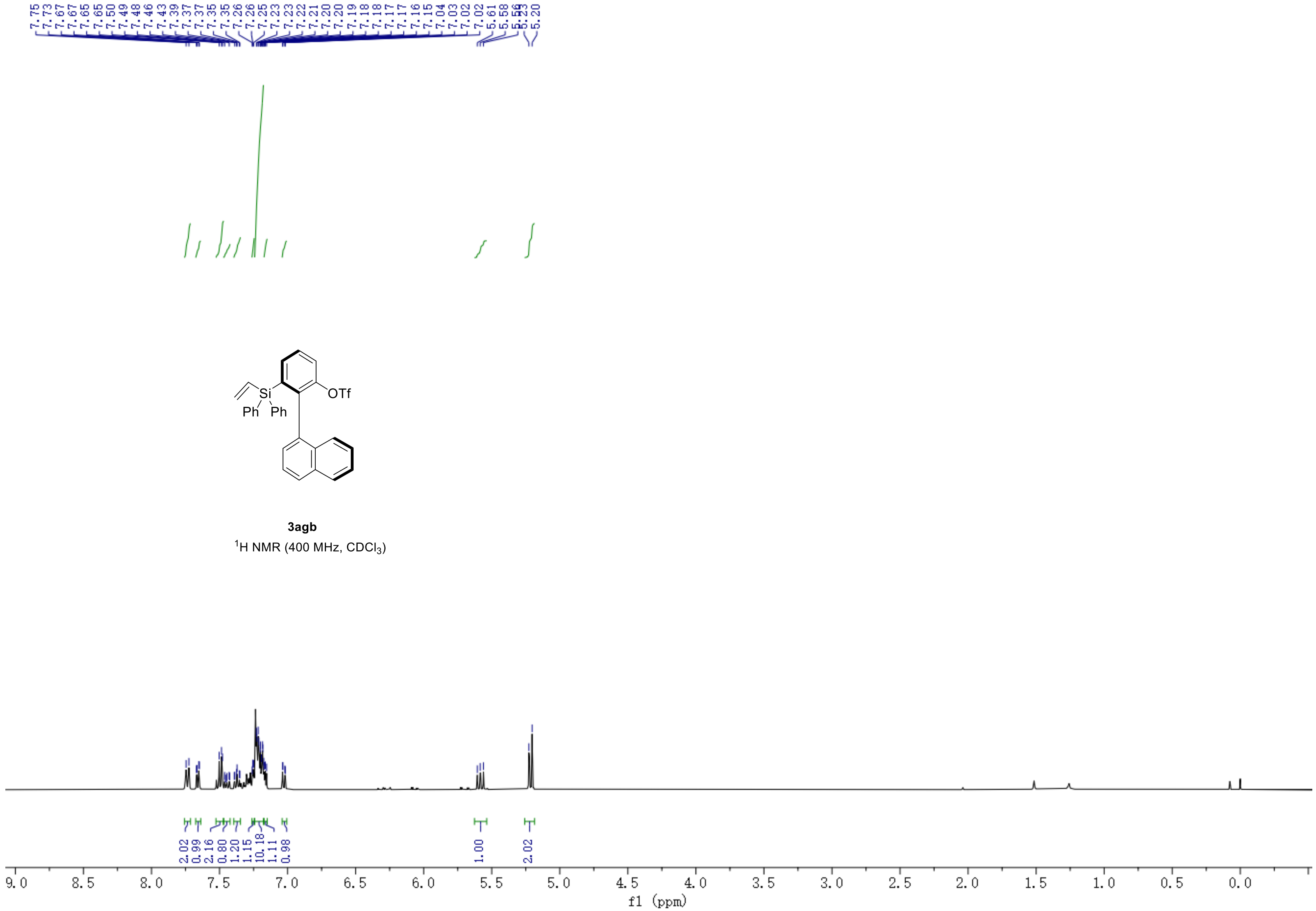


3aga

^{13}C NMR (101 MHz, $CDCl_3$)

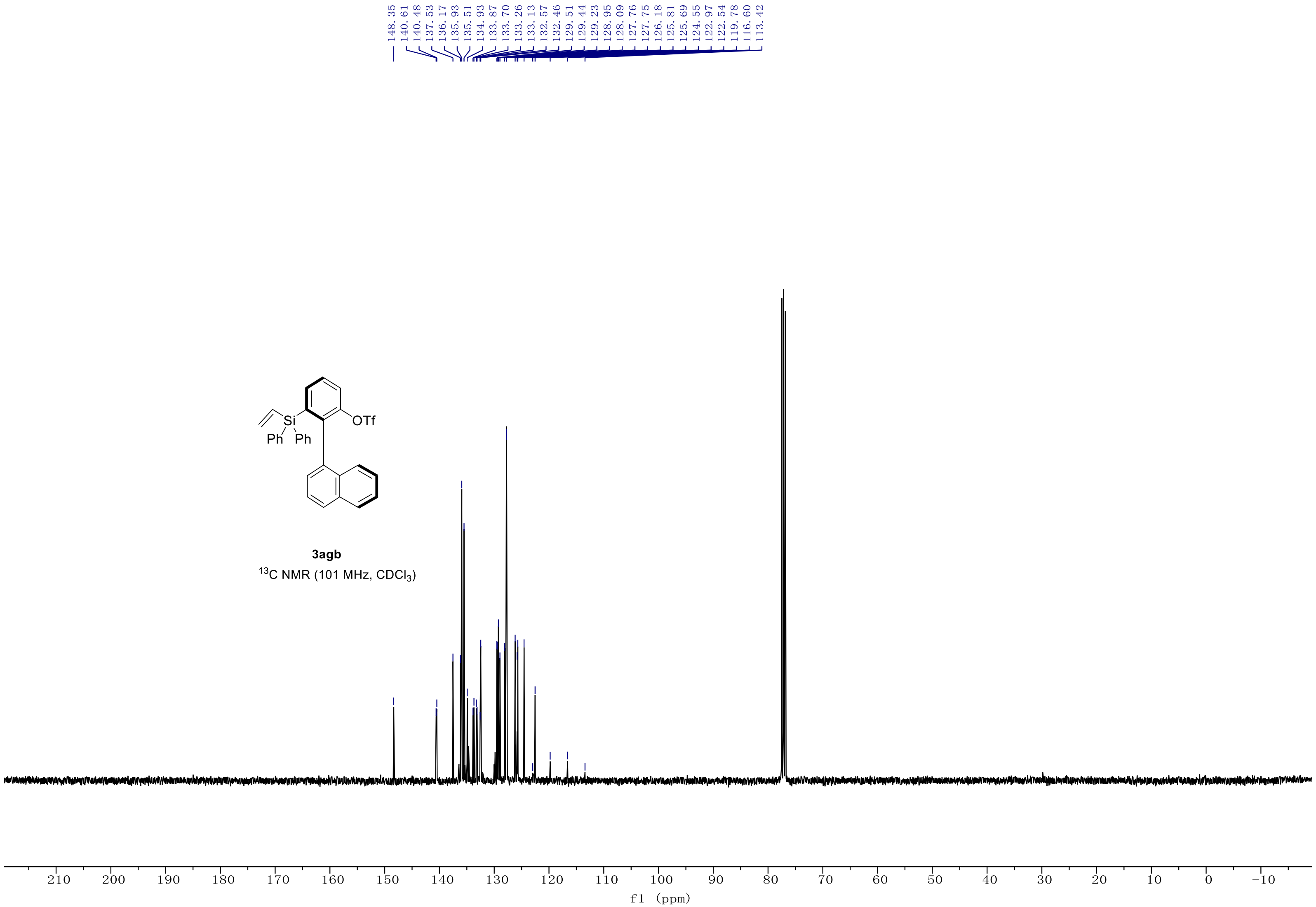
3aga

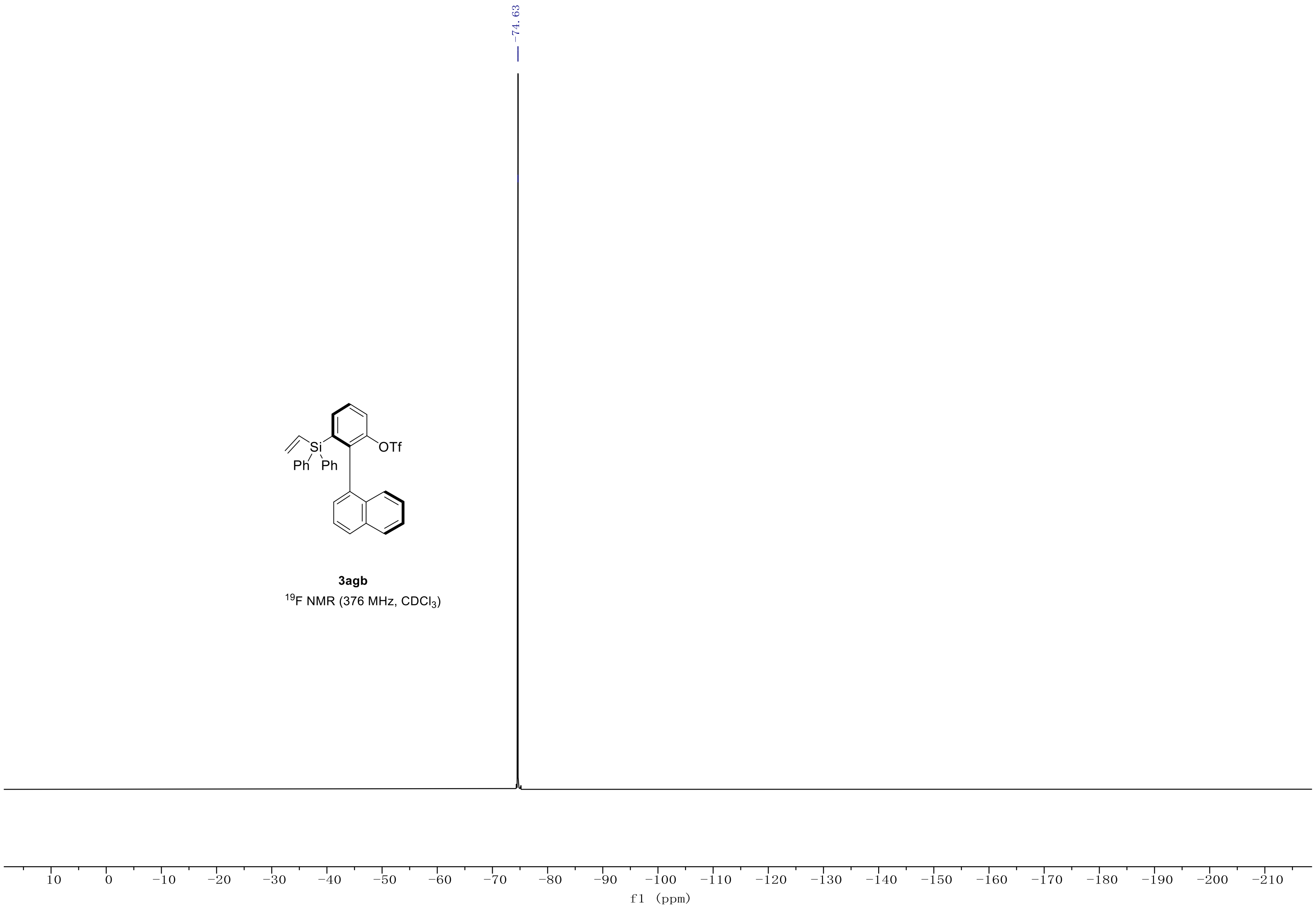
^{19}F NMR (376 MHz, $CDCl_3$)



3agb

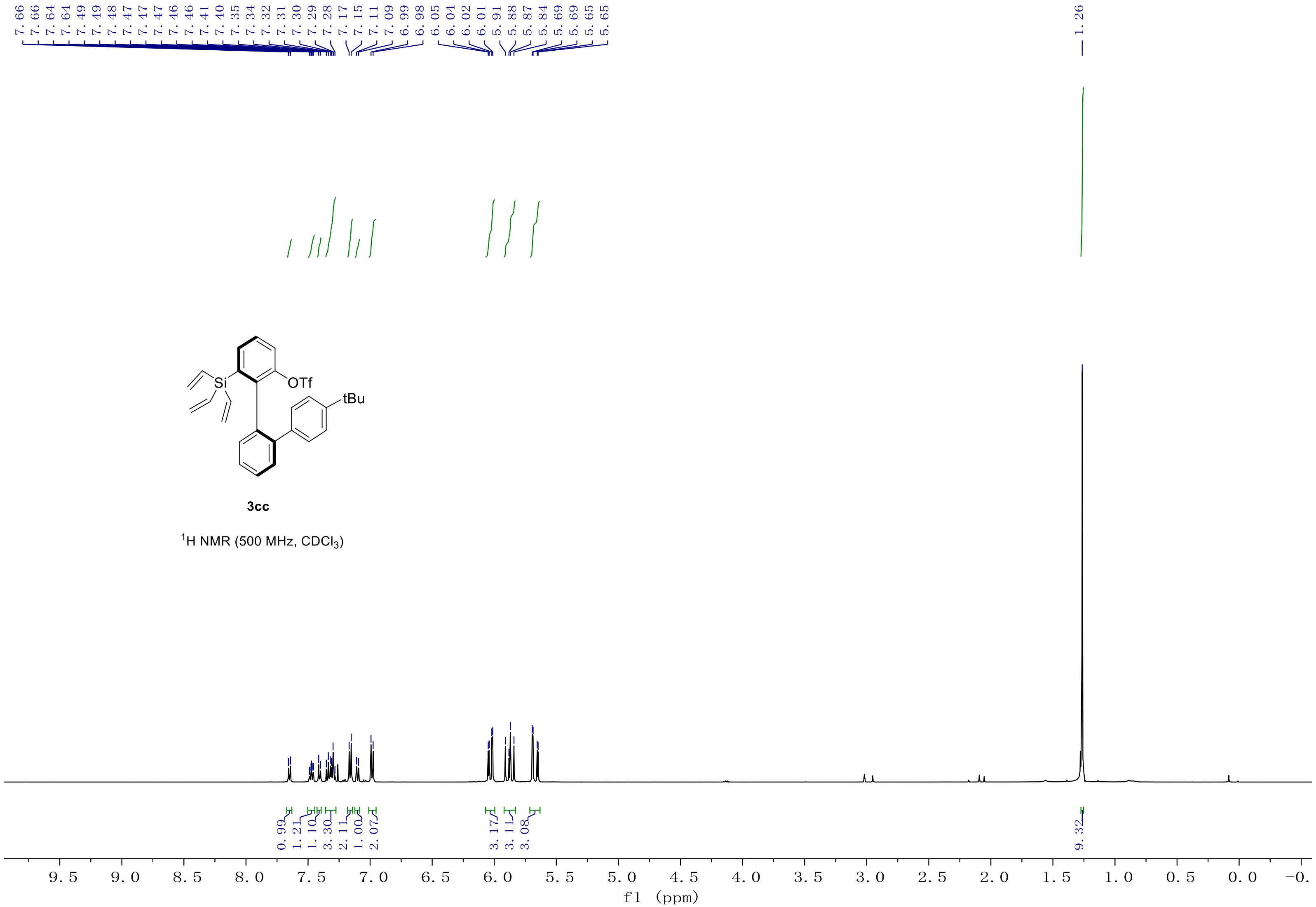
^{1}H NMR (400 MHz, $CDCl_3$)

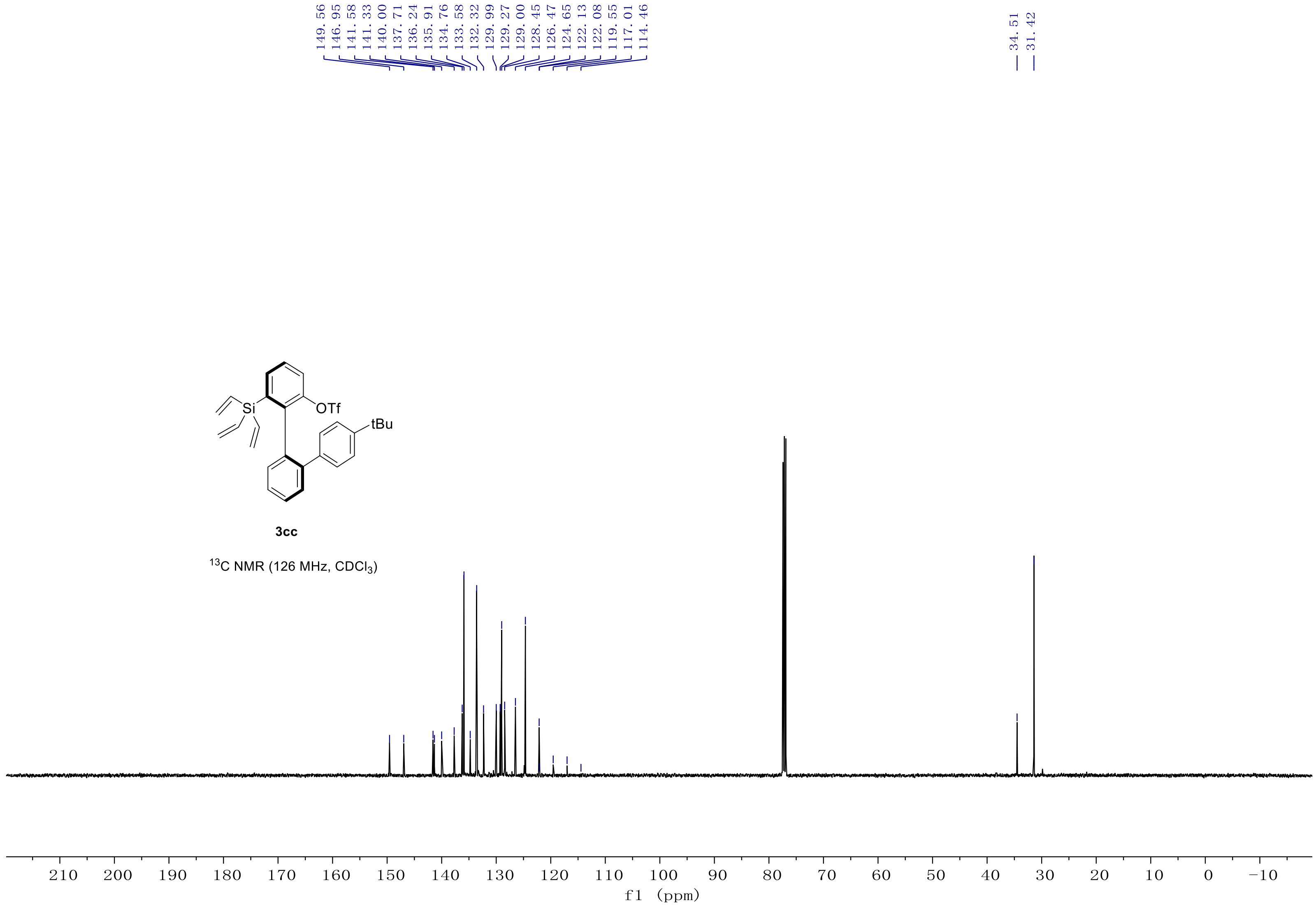

148.35
140.61
140.48
137.53
136.17
135.93
135.51
134.93
133.87
133.70
133.26
133.13
132.57
132.46
129.51
129.44
129.23
128.95
128.09
127.76
127.75
126.18
125.81
125.69
124.55
122.97
122.54
119.78
116.60
113.42
Si
Ph
Ph
OTf
3agb
^{13}C NMR (101 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



3agb

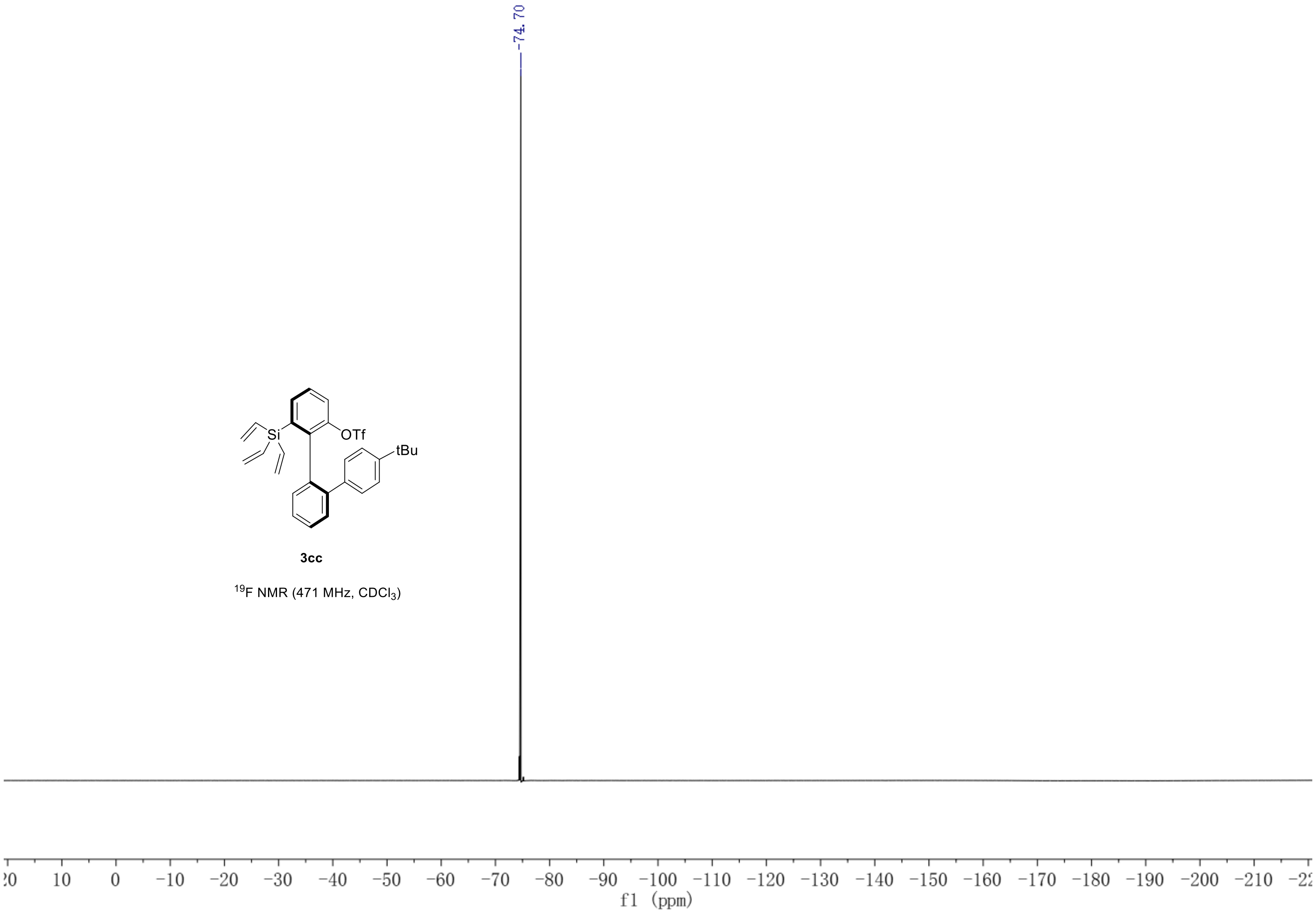
^{19}F NMR (376 MHz, $CDCl_3$)


OTf
Si
tBu
3cc
1H NMR (500 MHz, CDCl3)
f1 (ppm)



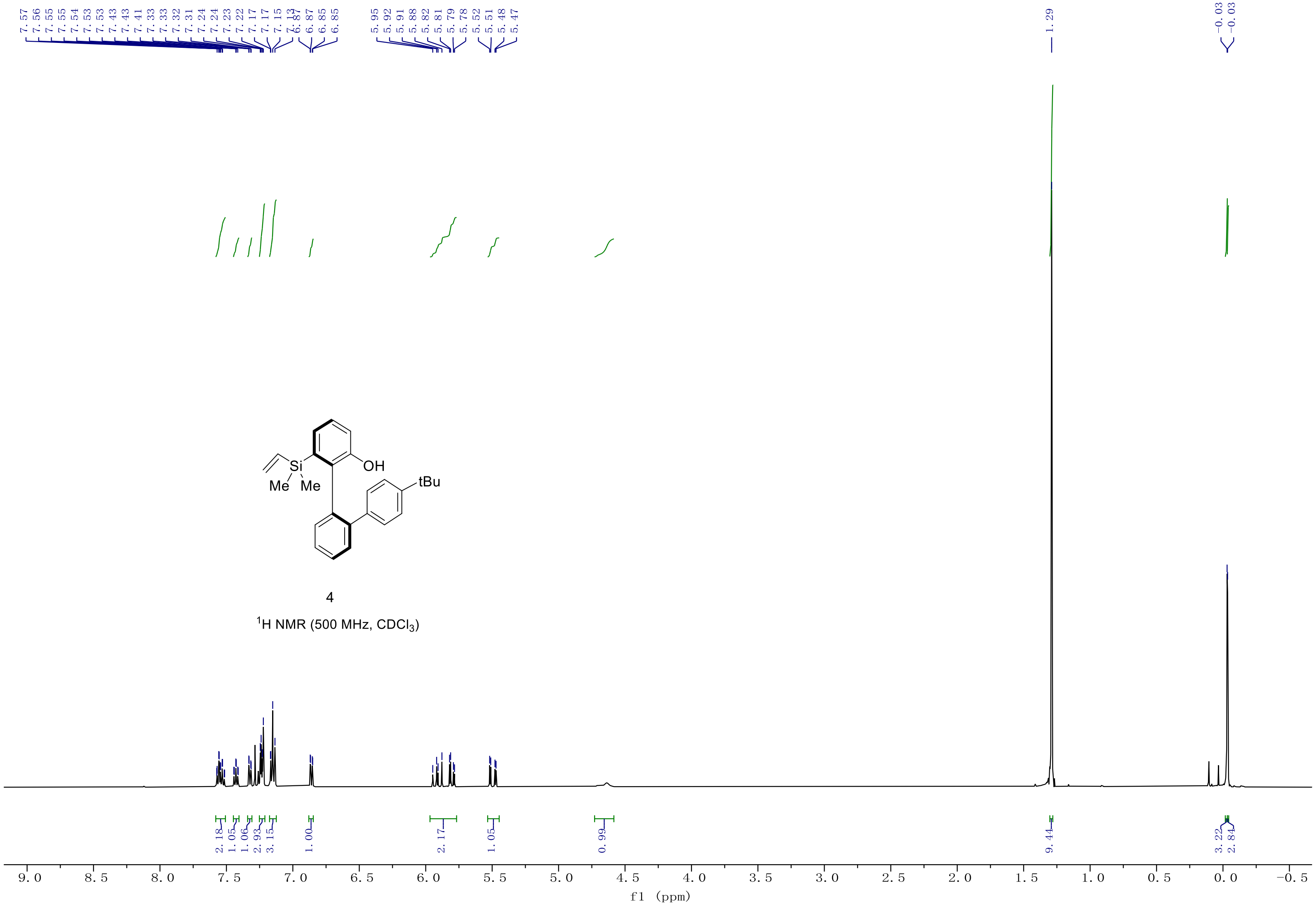
3cc

^{13}C NMR (126 MHz, $CDCl_3$)

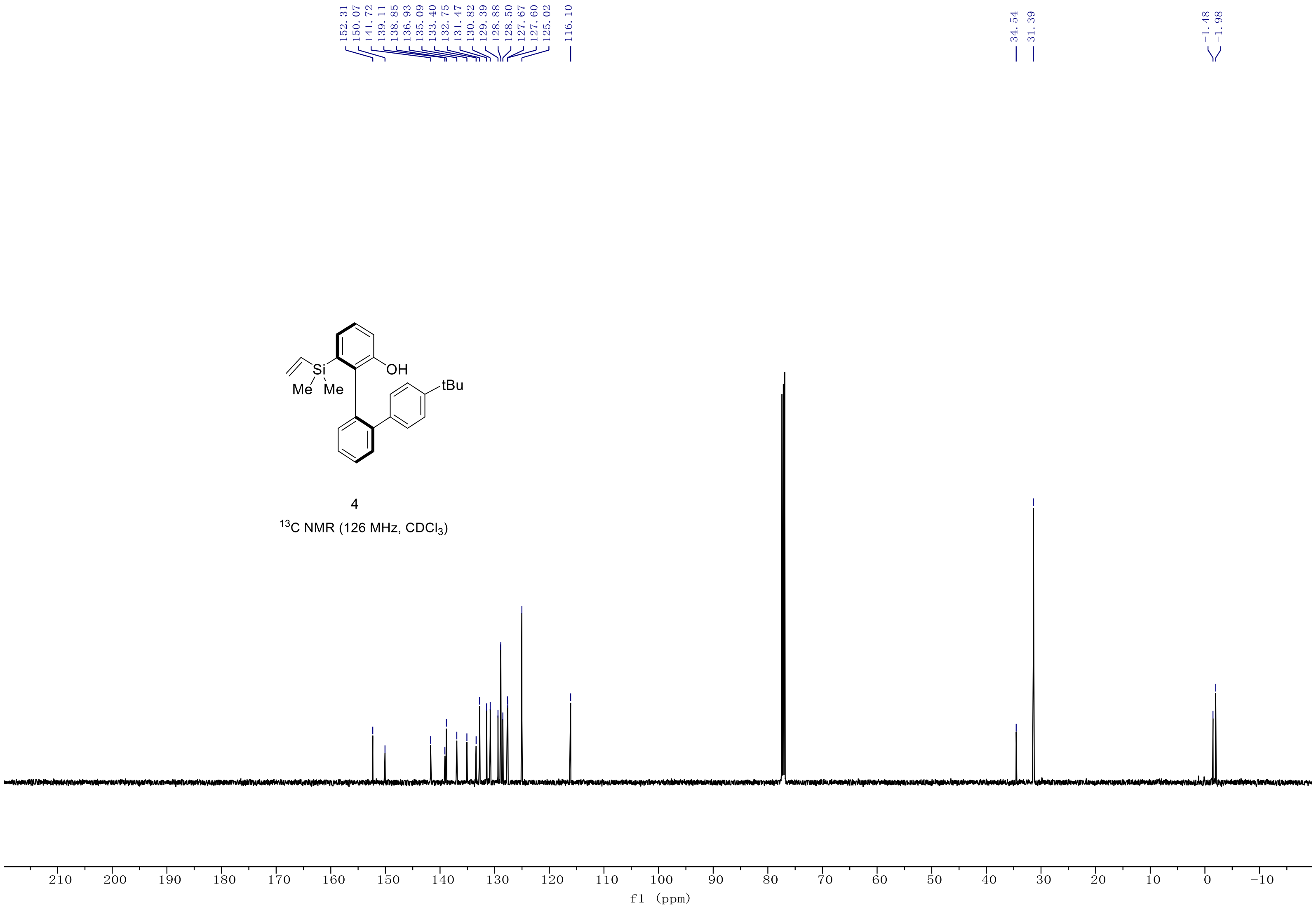


3cc

^{19}F NMR (471 MHz, $CDCl_3$)

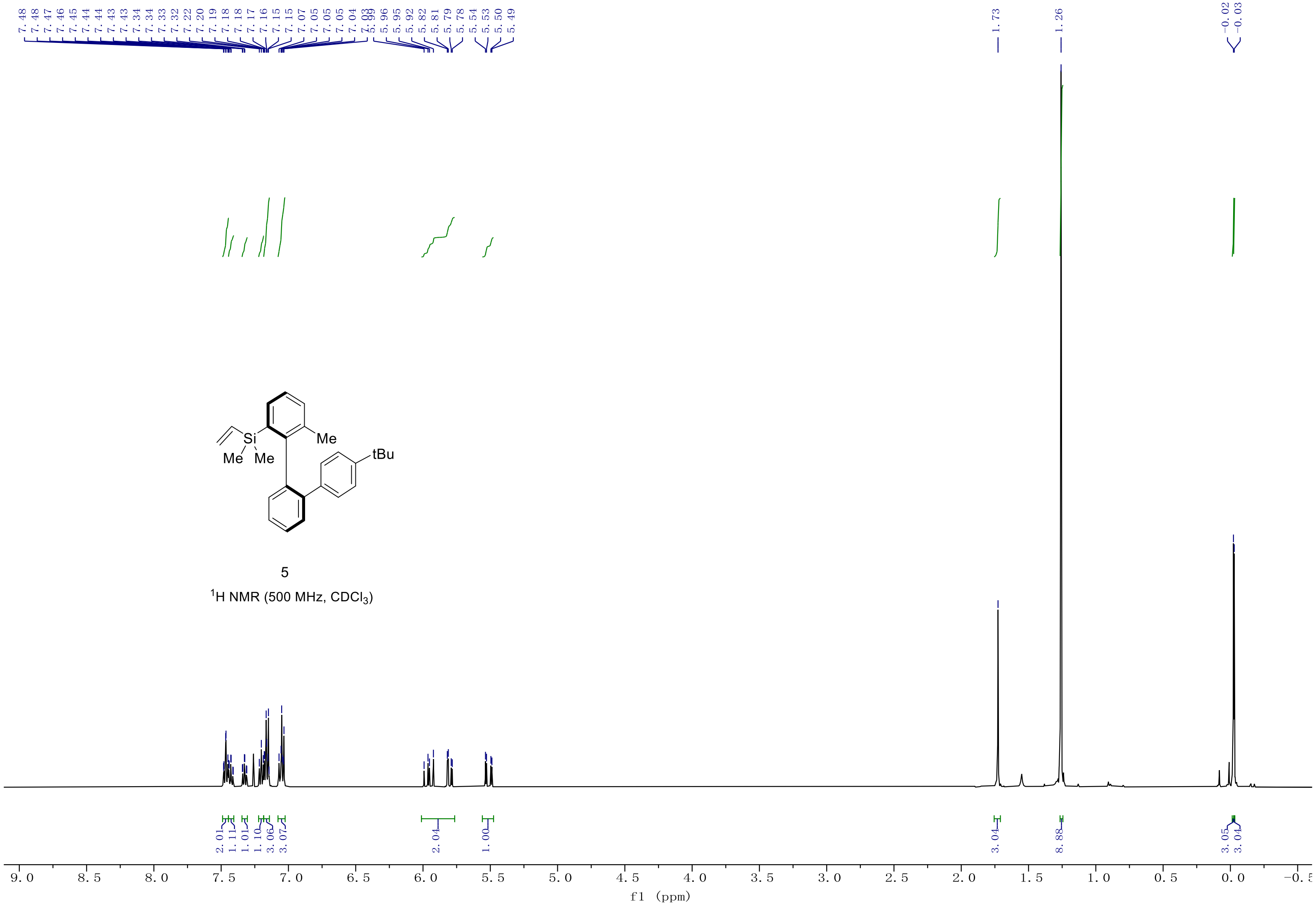


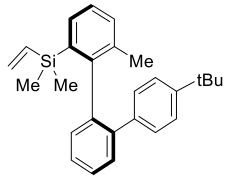
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.43
7.43
7.41
7.33
7.33
7.32
7.31
7.24
7.24
7.23
7.22
7.17
7.17
7.15
7.13
6.87
6.87
6.85
6.85
5.95
5.92
5.91
5.88
5.82
5.81
5.79
5.78
5.52
5.51
5.48
5.47
1.29
-0.03
-0.03
Si
Me
Me
OH
tBu
4
^{1}H NMR (500 MHz, $CDCl_3$)
2.18
1.05
1.06
2.93
3.15
1.00
2.17
1.05
0.99
9.44
3.22
2.84
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



4

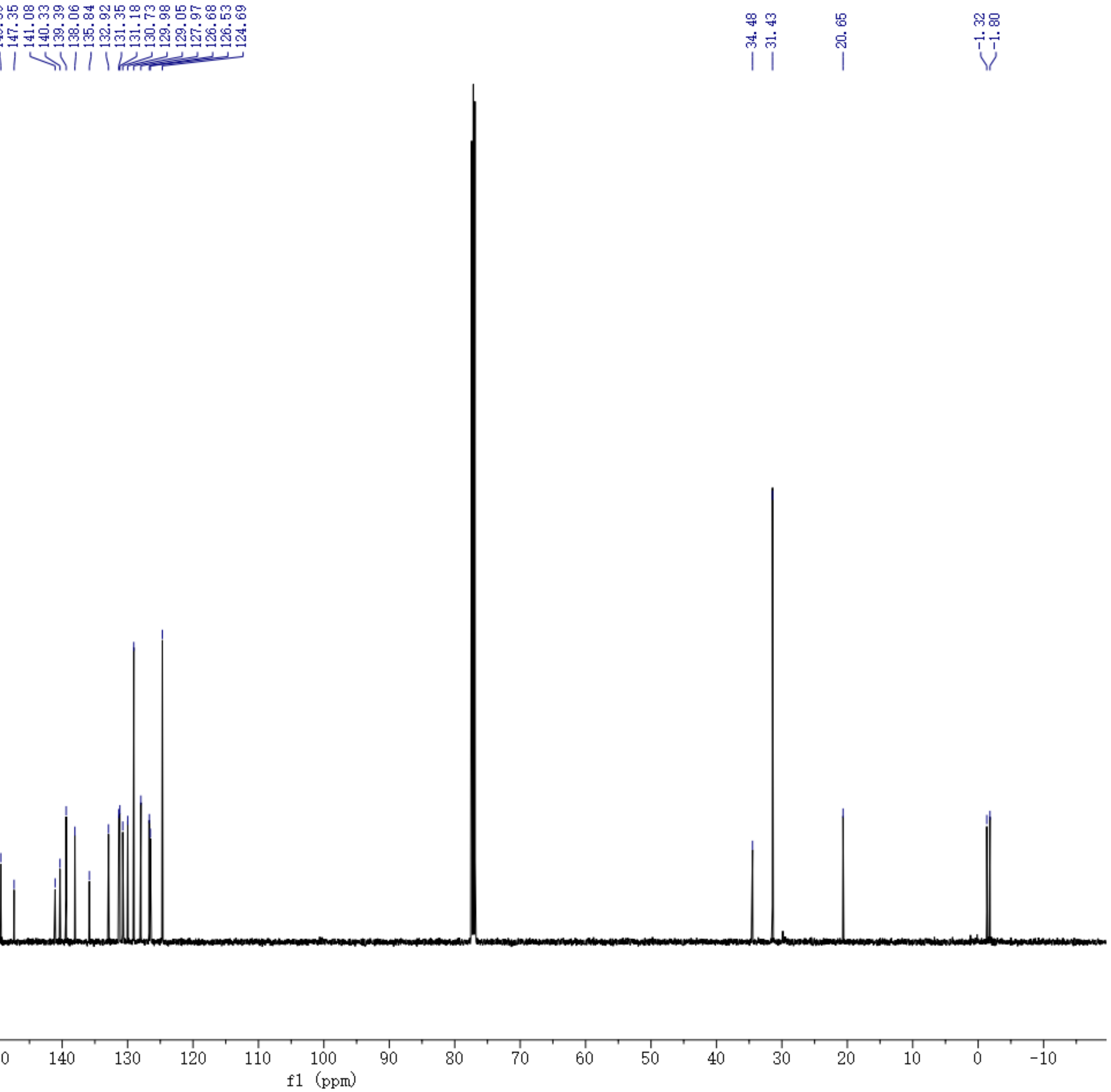
^{13}C NMR (126 MHz, $CDCl_3$)

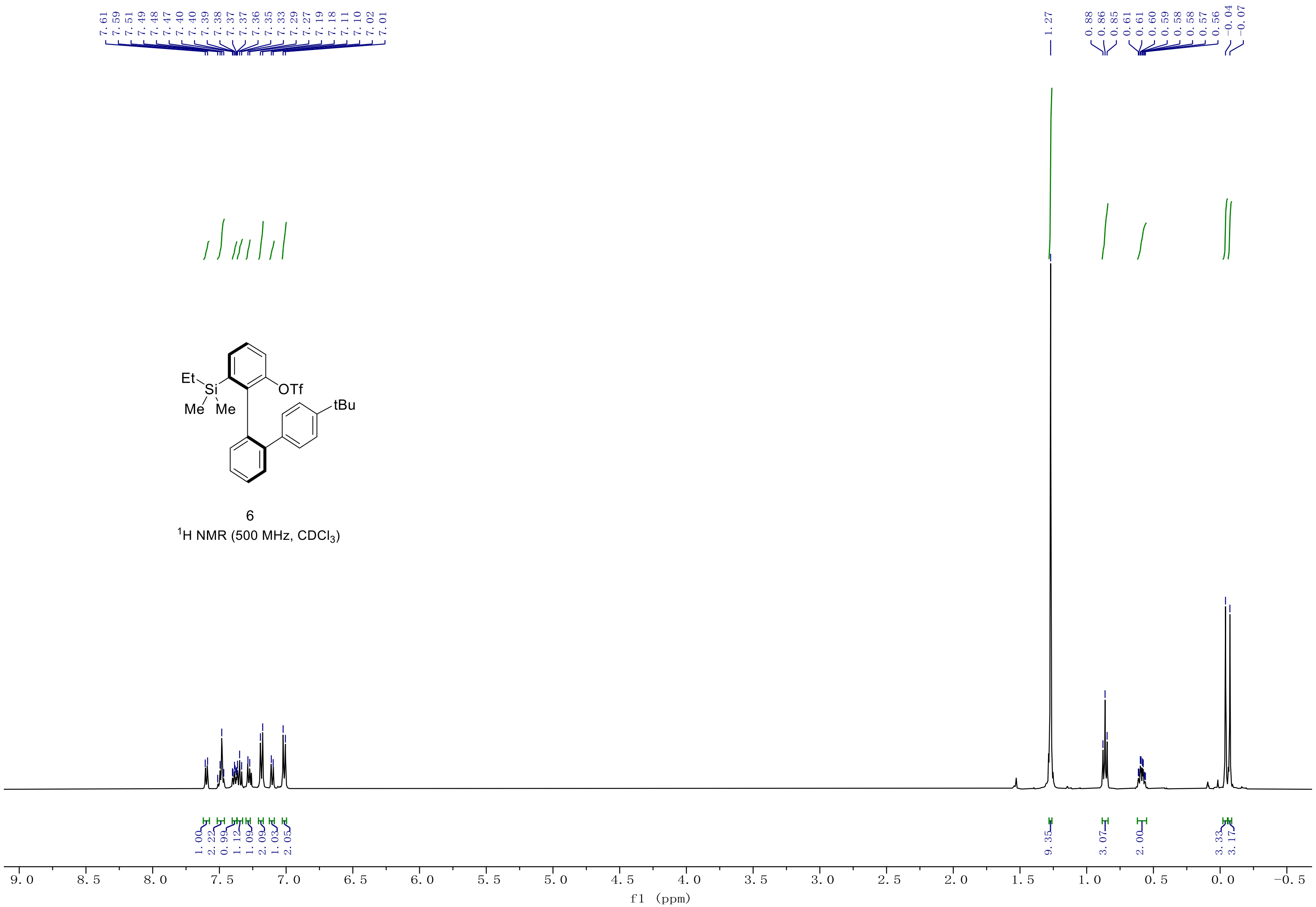

7.48 7.48 7.47 7.46 7.45 7.44 7.44 7.43 7.43 7.34 7.34 7.33 7.32 7.22 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.07 7.05 7.05 7.05 7.04 7.03 5.99 5.96 5.95 5.92 5.82 5.81 5.79 5.78 5.54 5.53 5.50 5.49
1.73
1.26
-0.02 -0.03
Si
Me
Me
Me
tBu
5
^{1}H NMR (500 MHz, $CDCl_3$)
2.01 1.11 1.01 1.10 3.06 3.07
2.04
1.00
3.04
8.88
3.05 3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



5

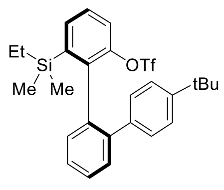
^{13}C NMR (126 MHz, $CDCl_3$)





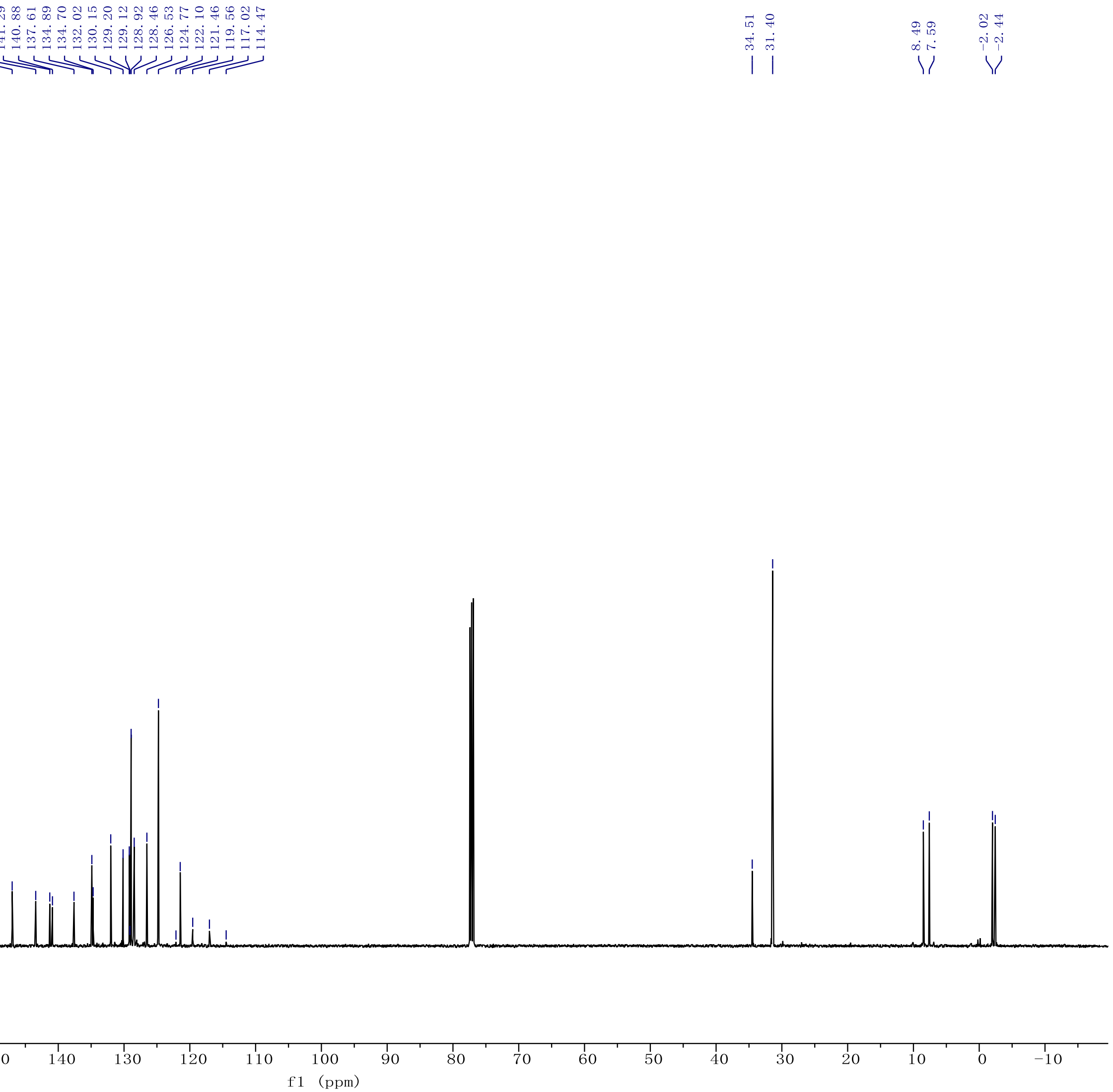
6

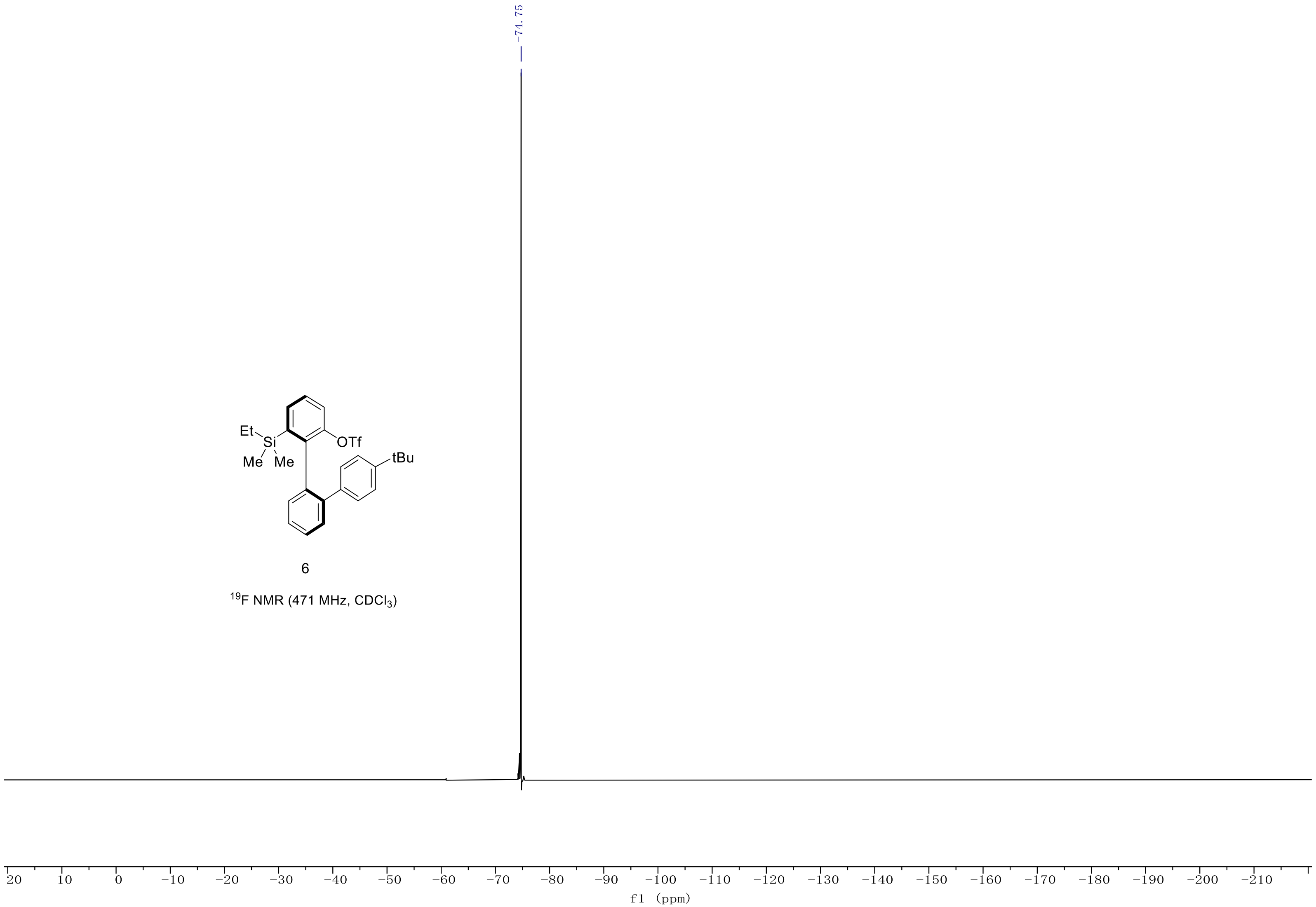
^{1}H NMR (500 MHz, $CDCl_3$)



6

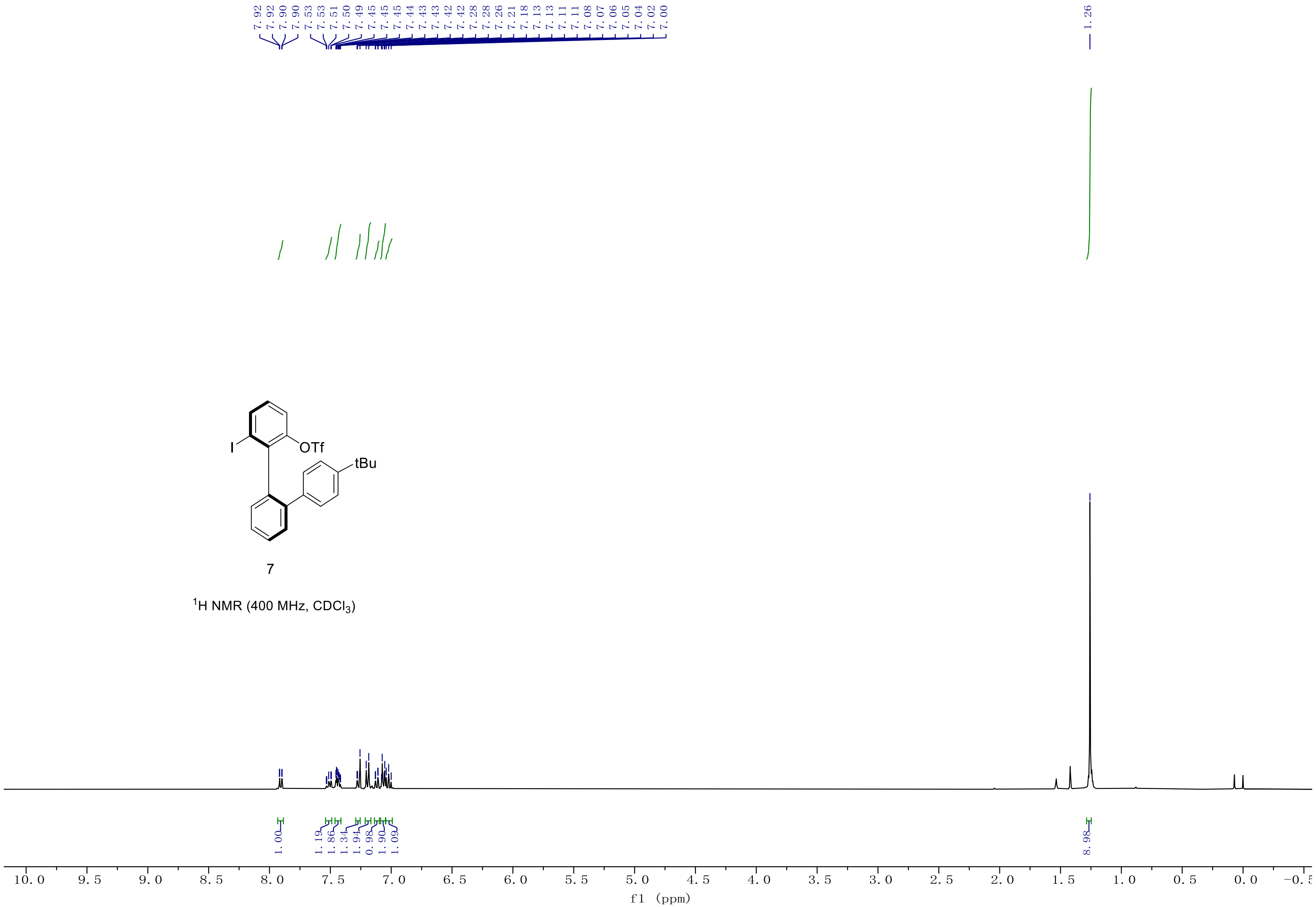
^{13}C NMR (126 MHz, $CDCl_3$)





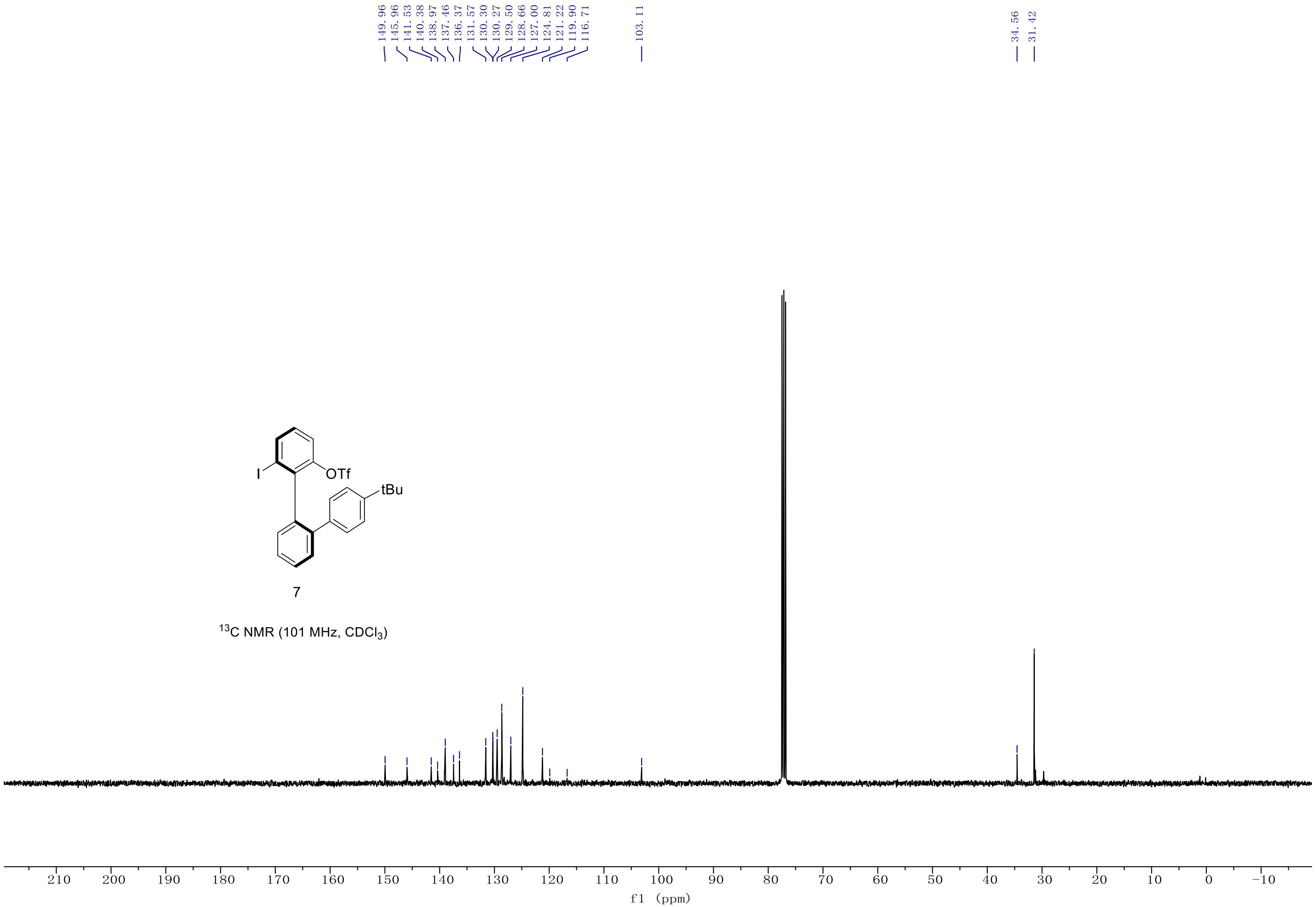
6

^{19}F NMR (471 MHz, CDCl$_3$)



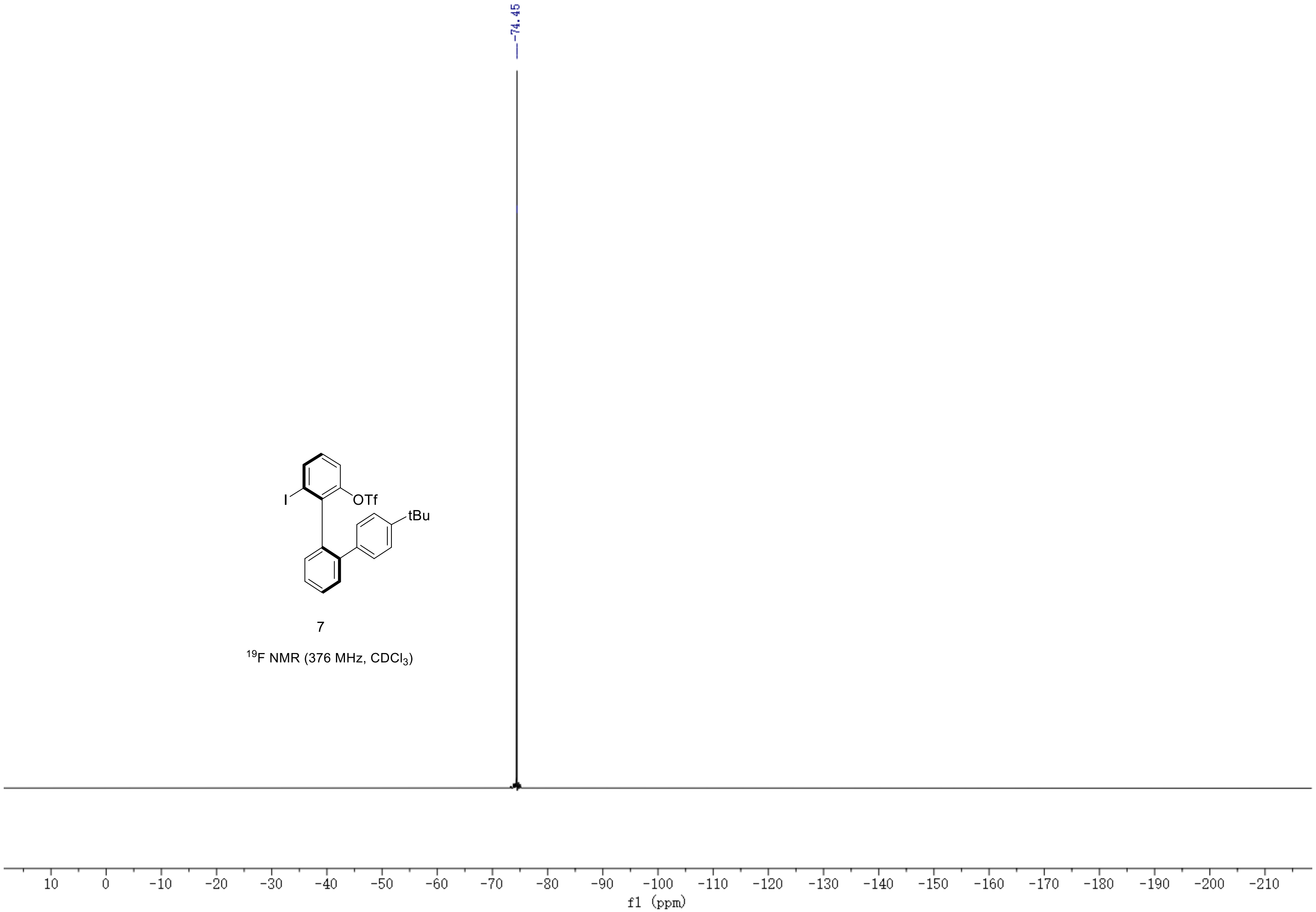
7

^{1}H NMR (400 MHz, $CDCl_3$)

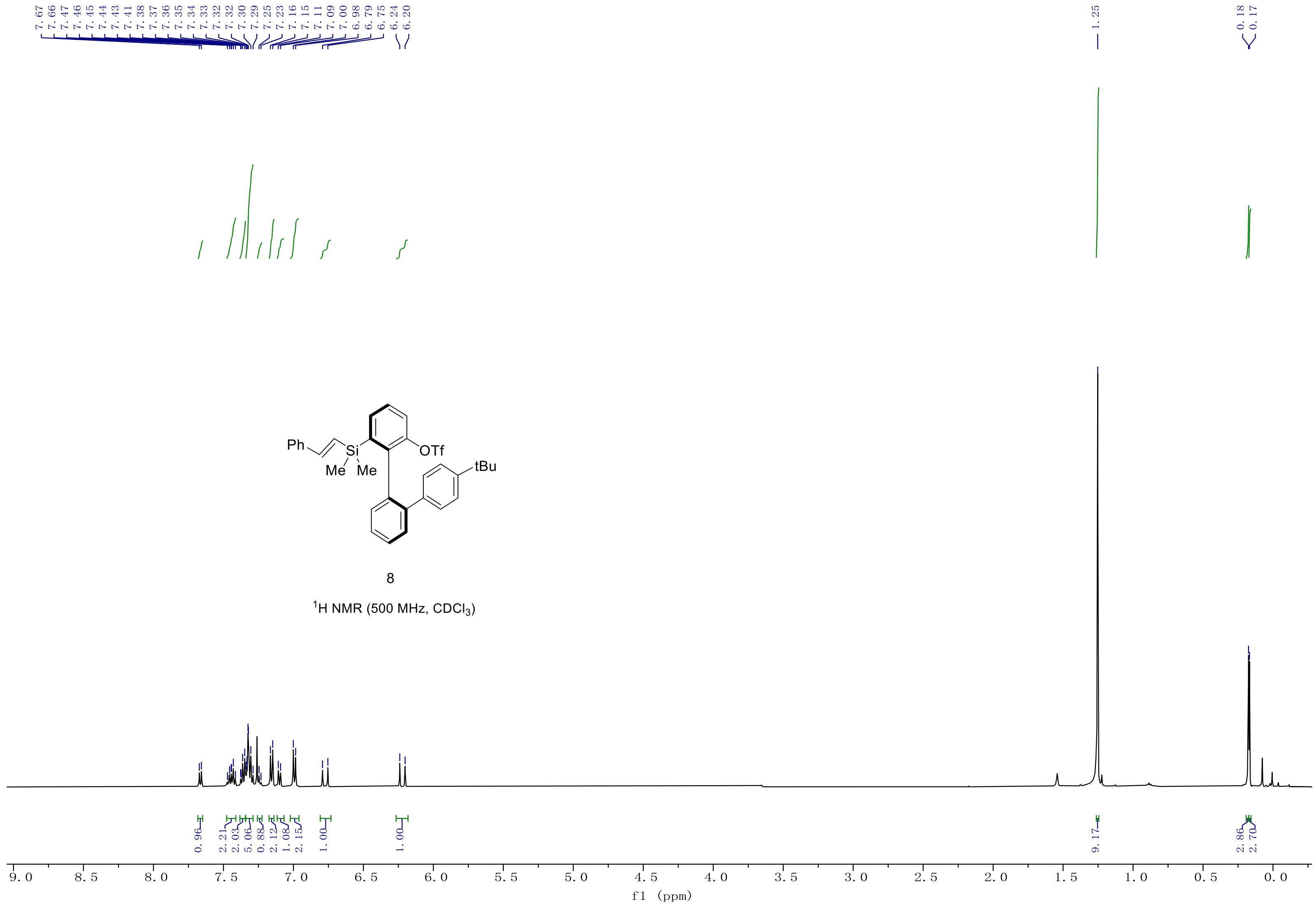


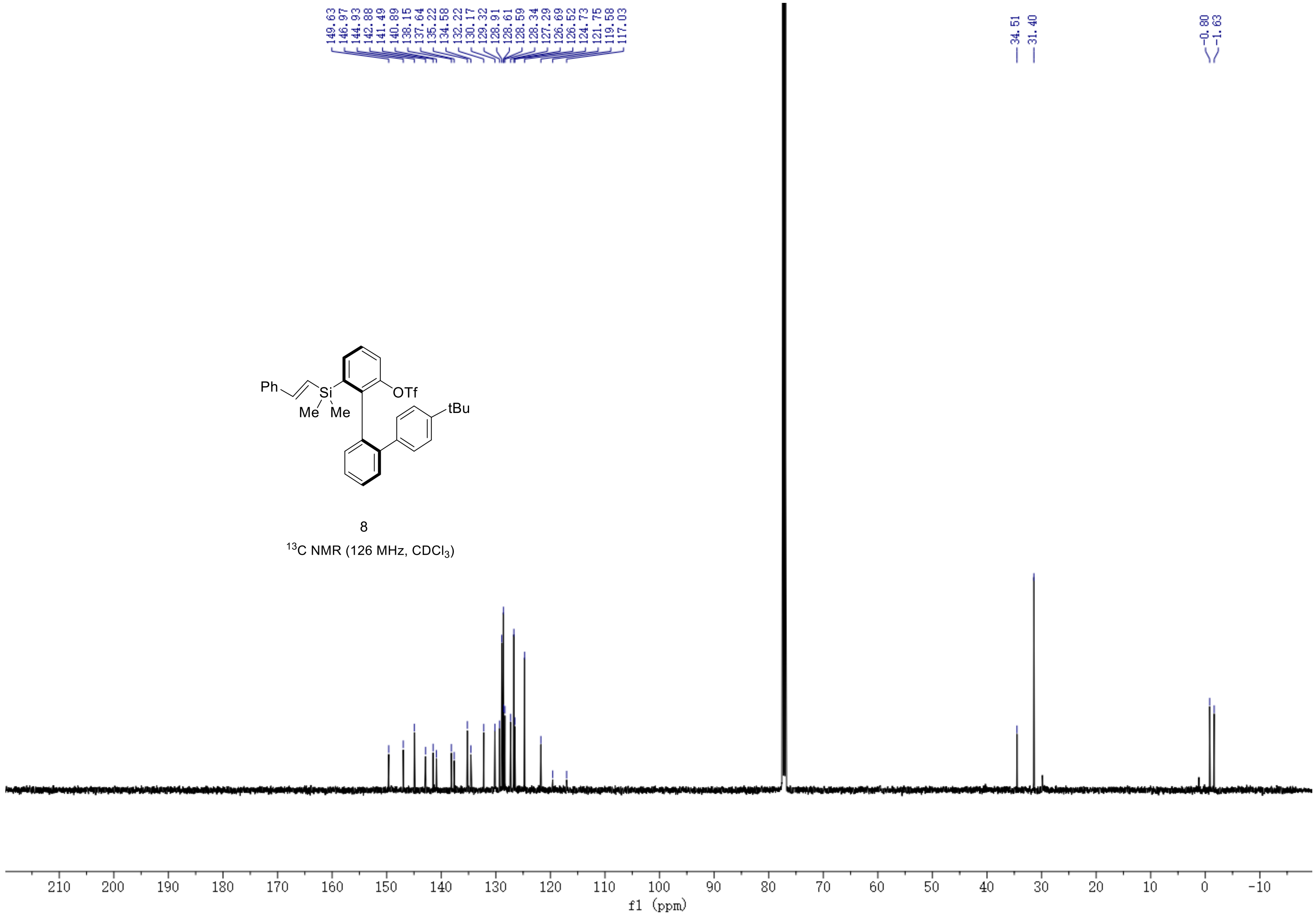
7

^{13}C NMR (101 MHz, $CDCl_3$)



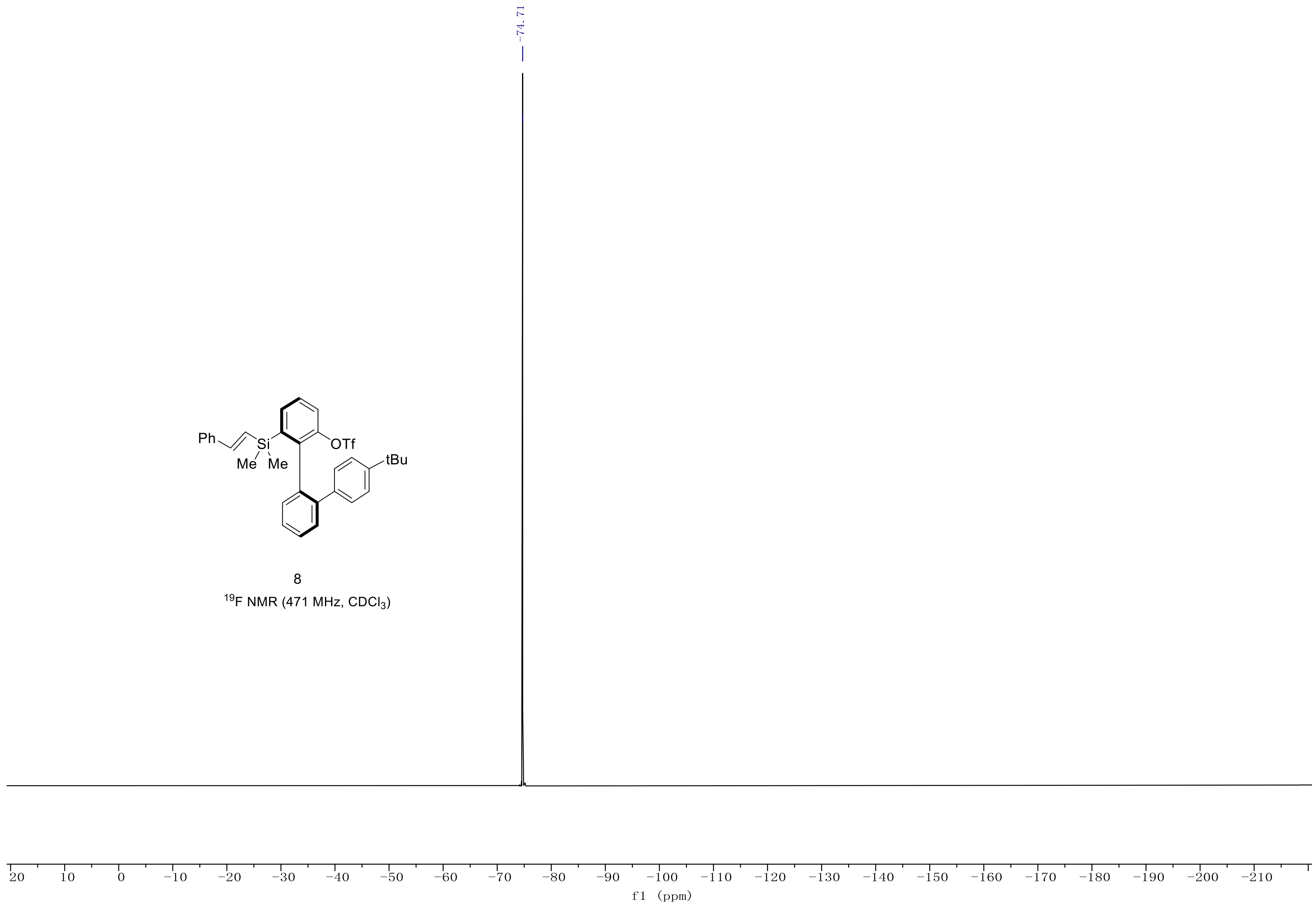
-74.45
7
19F NMR (376 MHz, CDCl3)
OTf
I
tBu
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.67 7.66 7.47 7.46 7.45 7.44 7.43 7.41 7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.32 7.30 7.29 7.25 7.23 7.16 7.15 7.11 7.09 7.00 6.98 6.79 6.75 6.24 6.20
1.25
0.18 0.17
Ph
Si
Me Me
OTf
tBu
8
^{1}H NMR (500 MHz, CDCl$_3$)
0.96 2.21 2.03 5.06 0.88 2.12 1.08 2.15 1.00 1.00 9.17 2.86 2.70
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

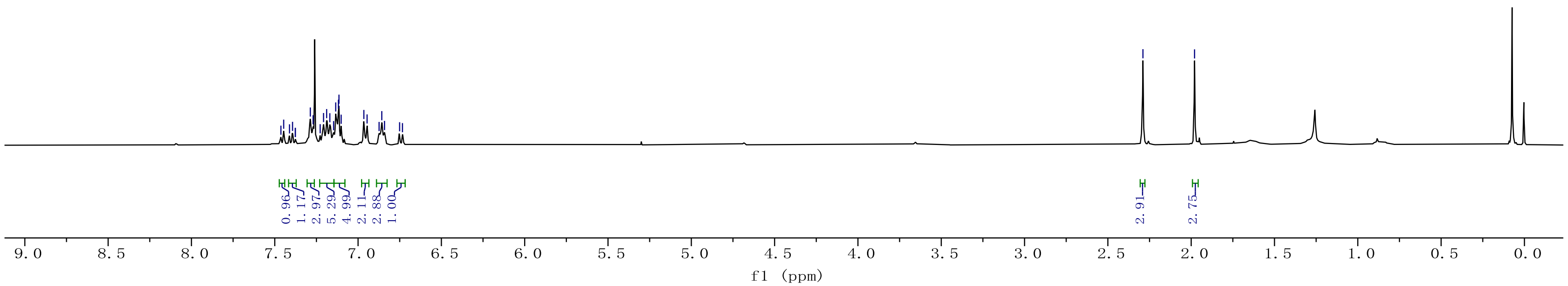


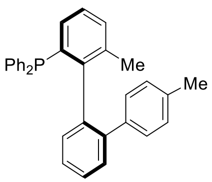
8

^{13}C NMR (126 MHz, $CDCl_3$)



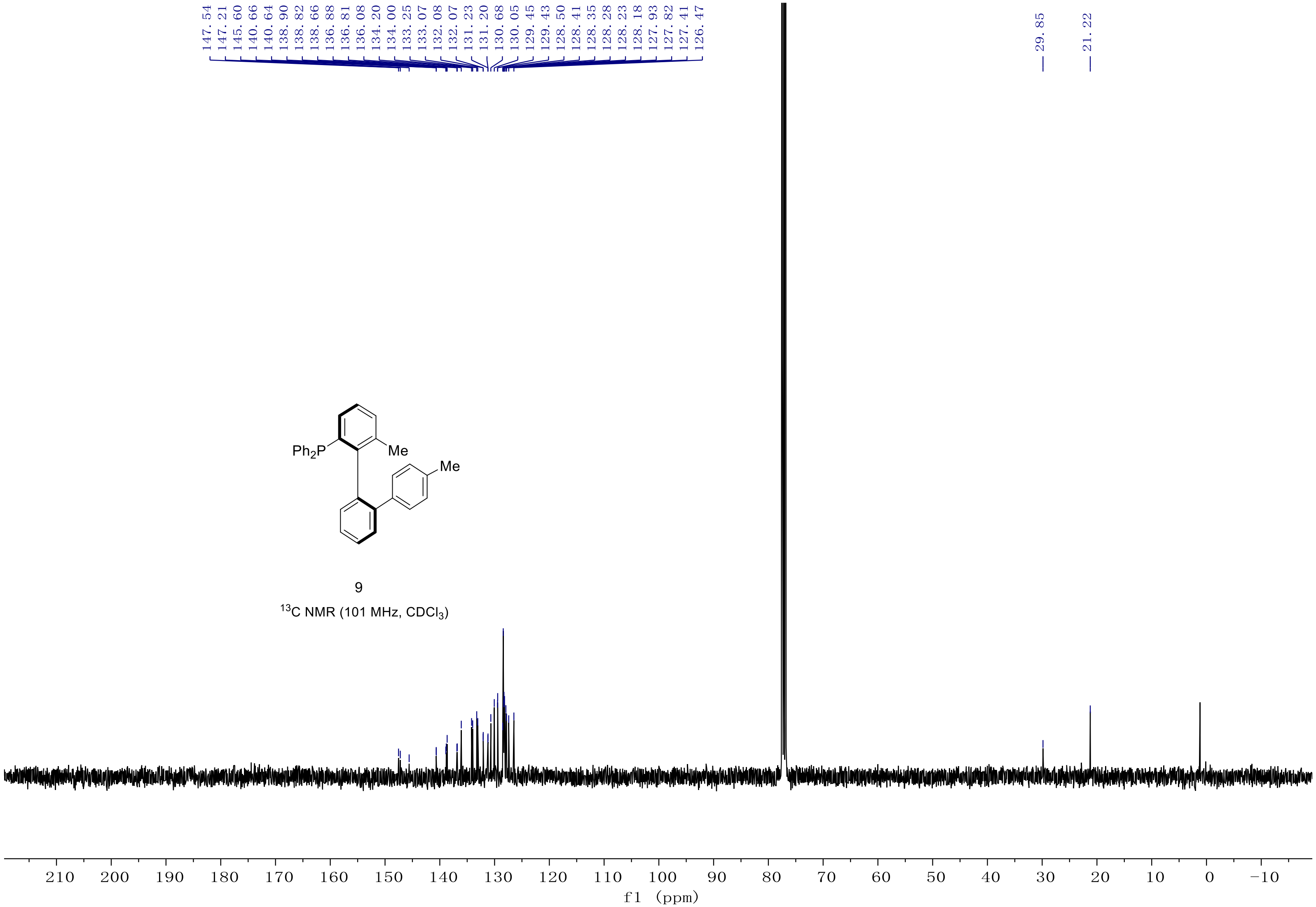
−74.71
Ph
Si
Me
Me
OTf
tBu
8
^{19}F NMR (471 MHz, $CDCl_3$)
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



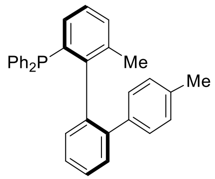
9

^1H NMR (400 MHz, $CDCl_3$)



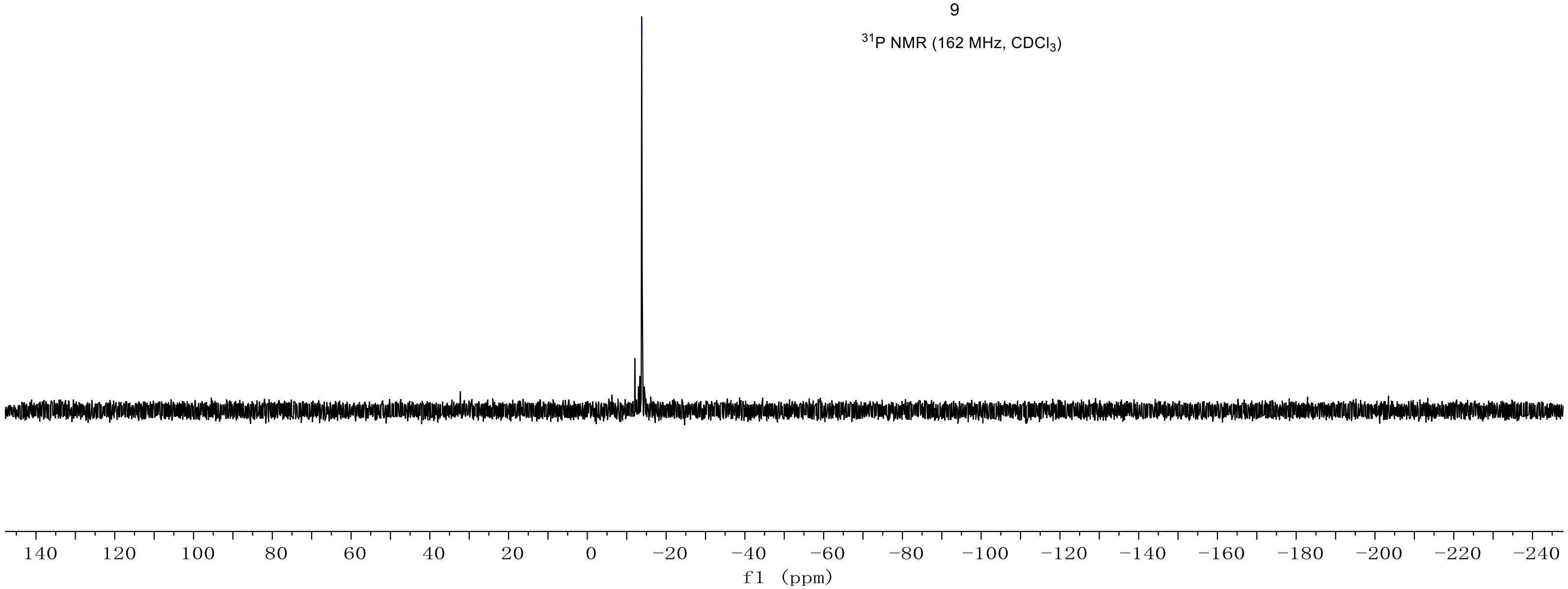
9

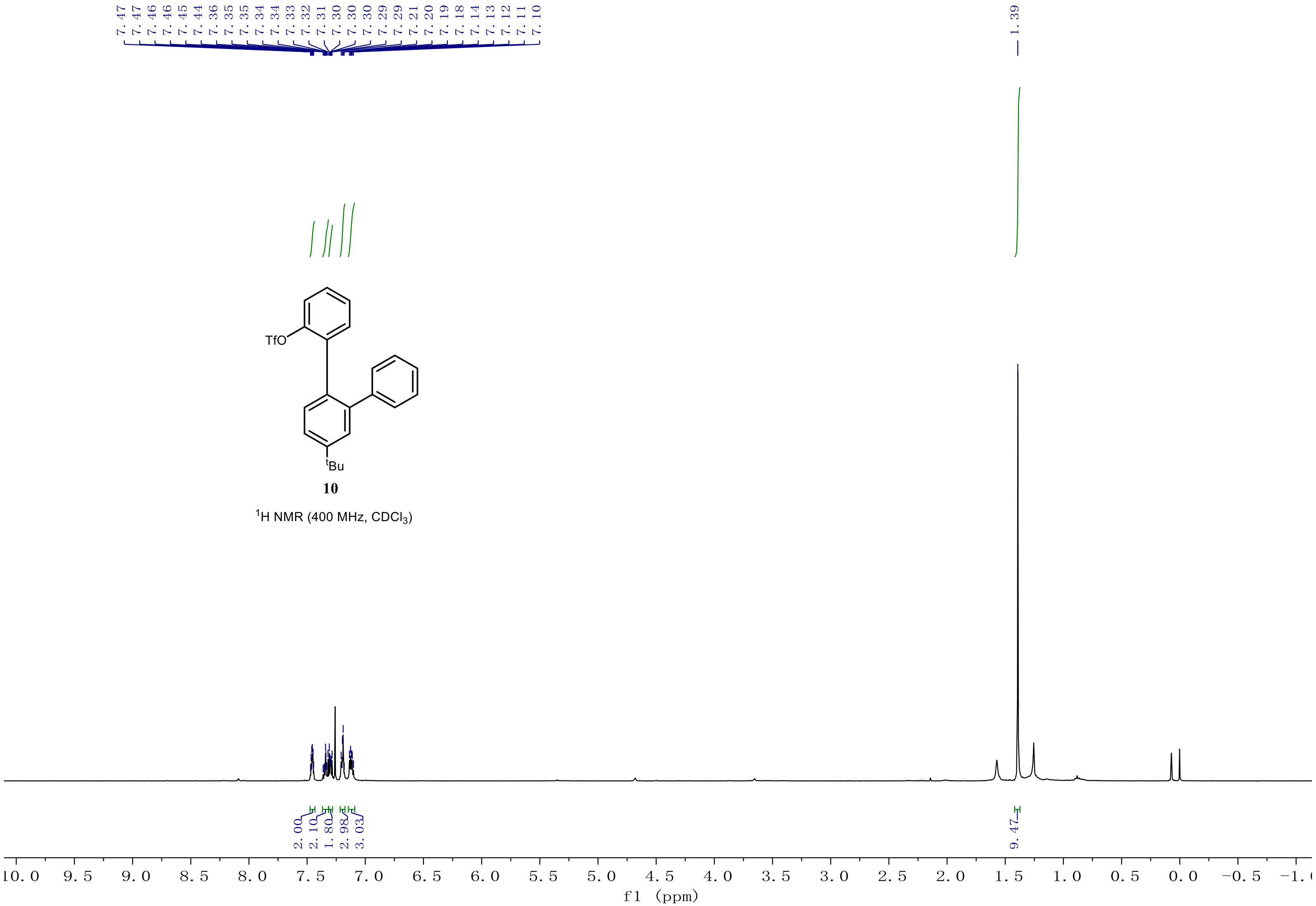
^{13}C NMR (101 MHz, $CDCl_3$)

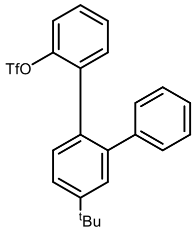


9

^{31}P NMR (162 MHz, $CDCl_3$)

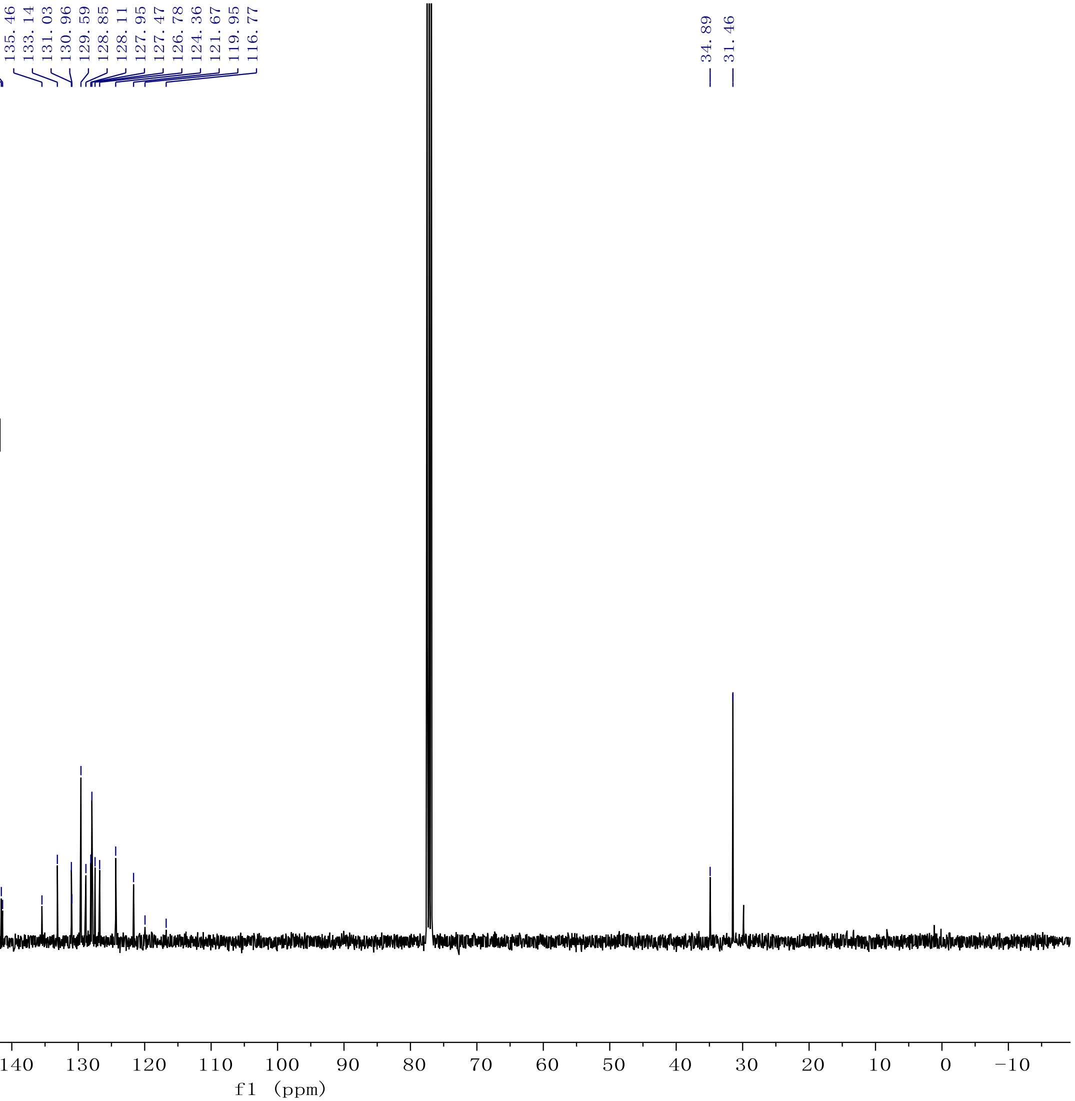


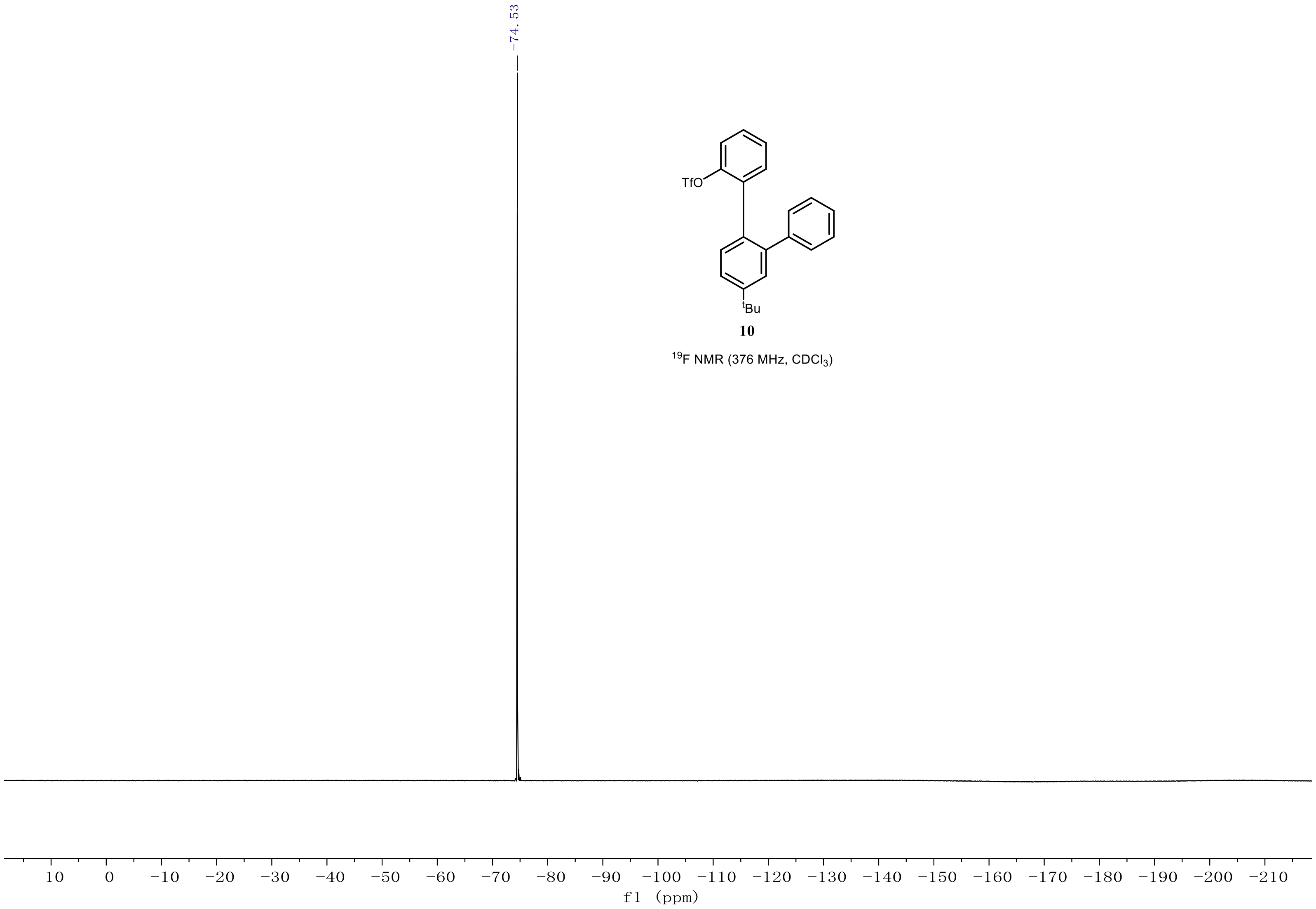

7.47 7.47 7.46 7.46 7.45 7.44 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.31 7.30 7.30 7.30 7.29 7.29 7.21 7.20 7.19 7.18 7.14 7.13 7.12 7.11 7.10
1.39
TfO
tBu
10
1H NMR (400 MHz, CDCl3)
2.00 2.10 1.80 2.98 3.03
9.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



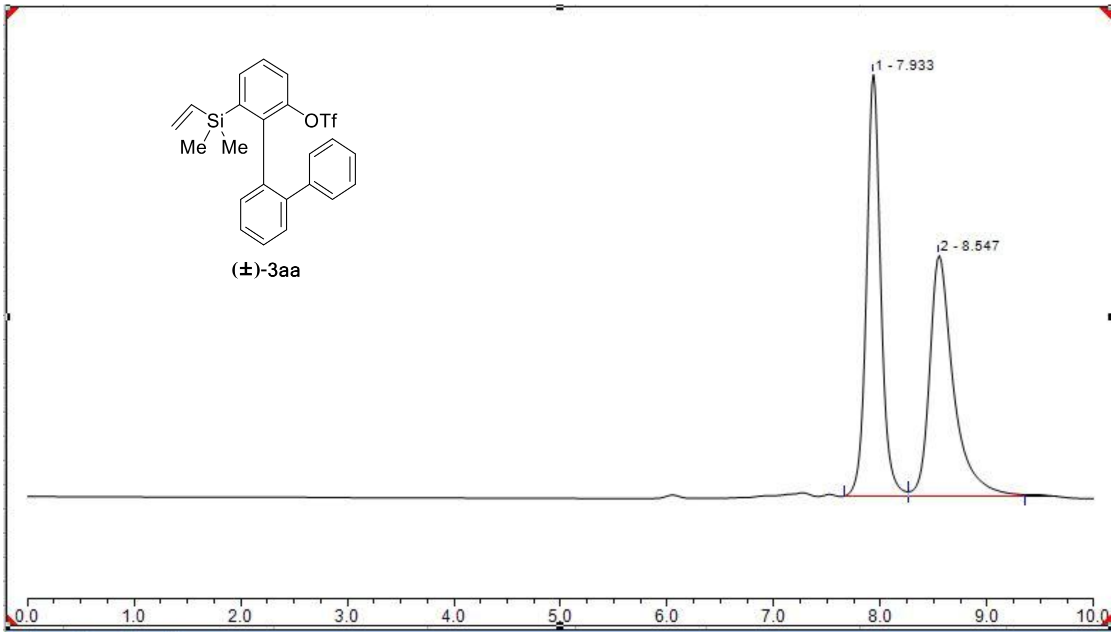
10

^{13}C NMR (101 MHz, $CDCl_3$)



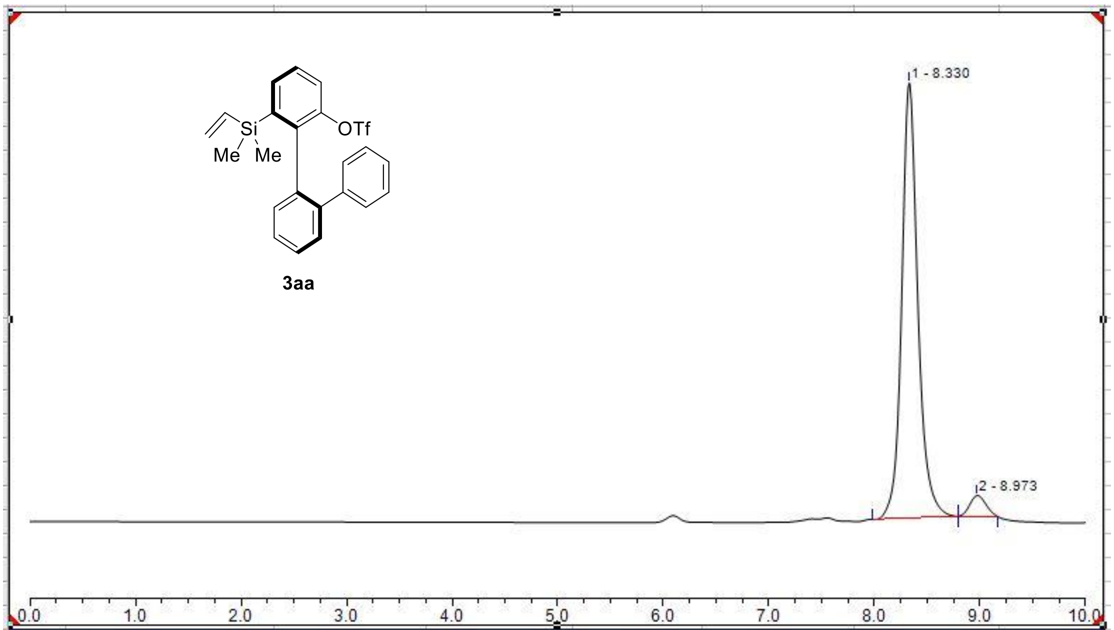

−74.53
TfO
tBu
10
19F NMR (376 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

HPLC Chromatograms



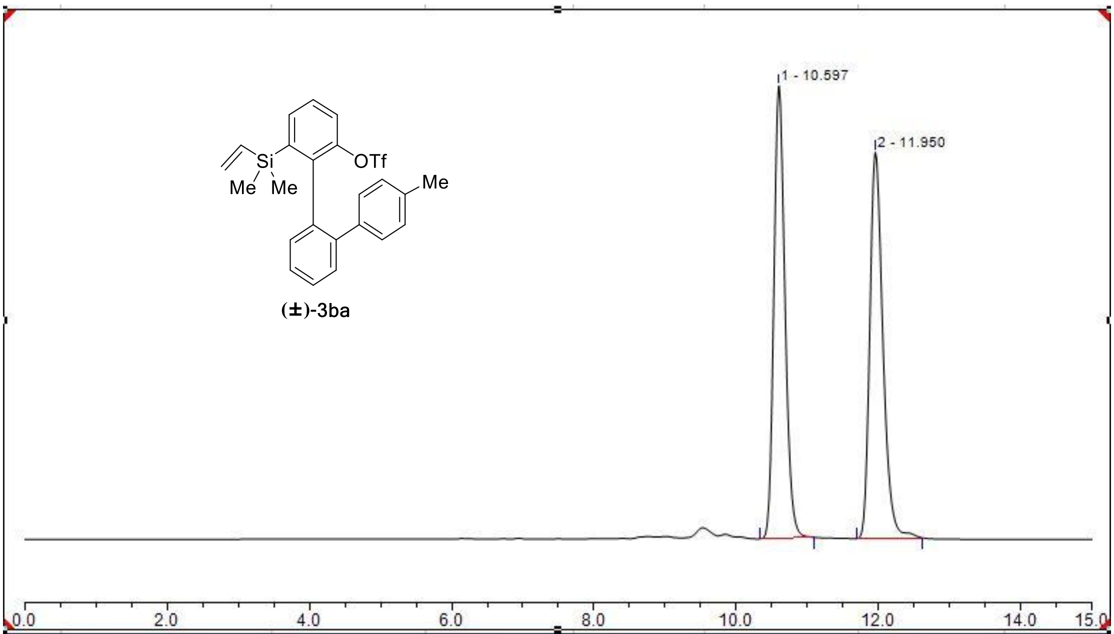
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.933	33.568	216.376	51.04	63.64	n.a.
2		8.547	32.196	123.634	48.96	36.36	n.a.
Total:			**65.764**	**340.009**	**100.00**	**100.00**	



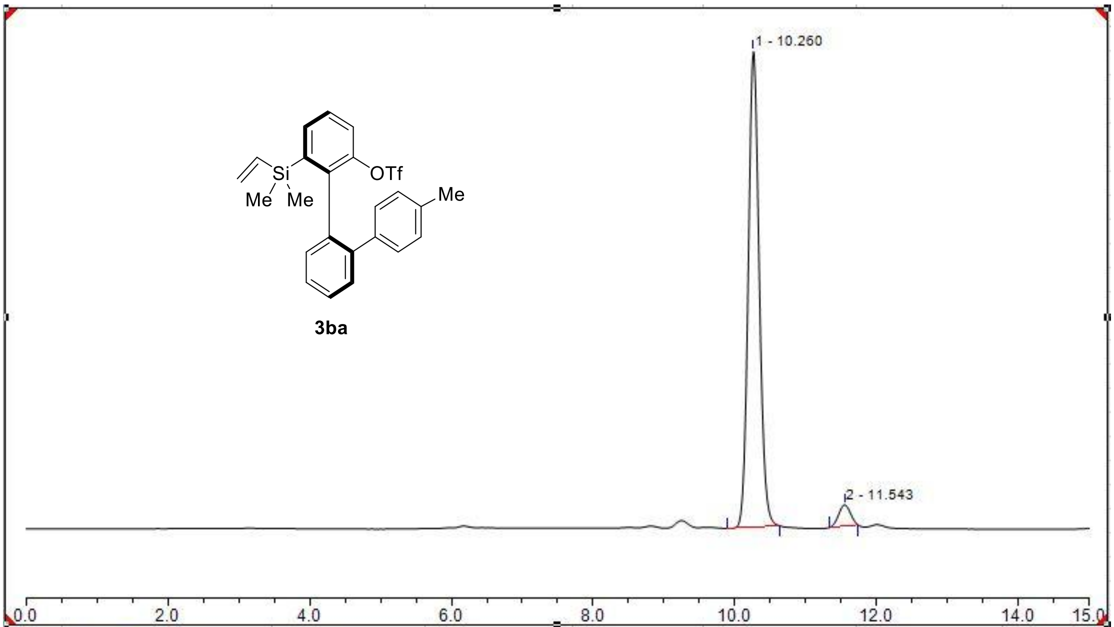
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.330	53.205	300.732	95.45	95.42	n.a.
2		8.973	2.535	14.422	4.55	4.58	n.a.
Total:			**55.740**	**315.154**	**100.00**	**100.00**	



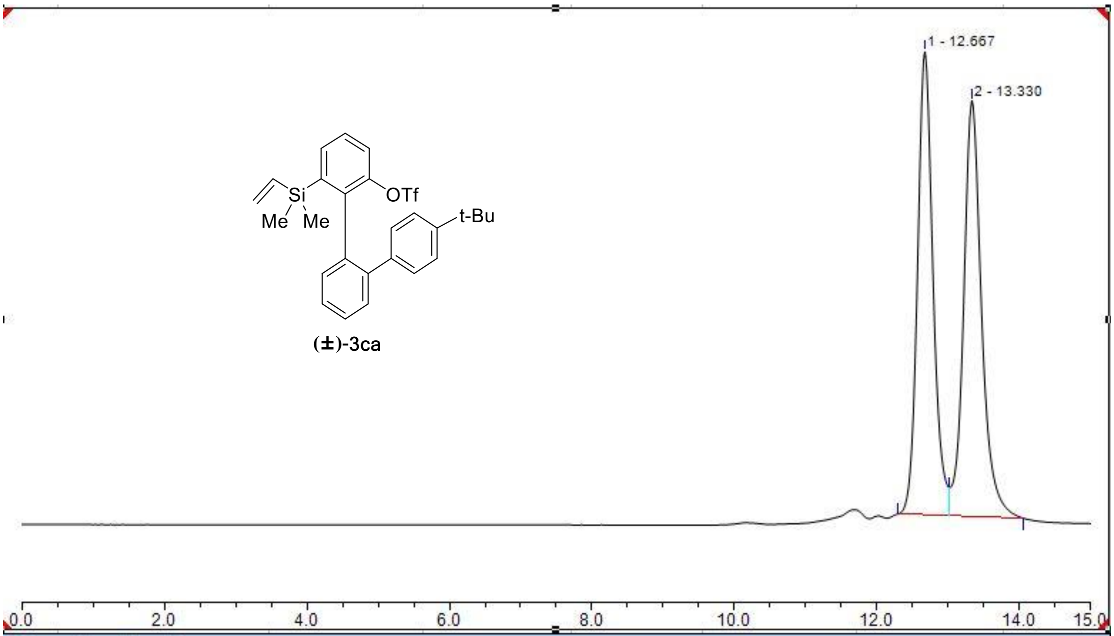
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.597	27.881	154.562	49.80	53.95	n.a.
2		11.950	28.101	131.935	50.20	46.05	n.a.
Total:			**55.982**	**286.497**	**100.00**	**100.00**	



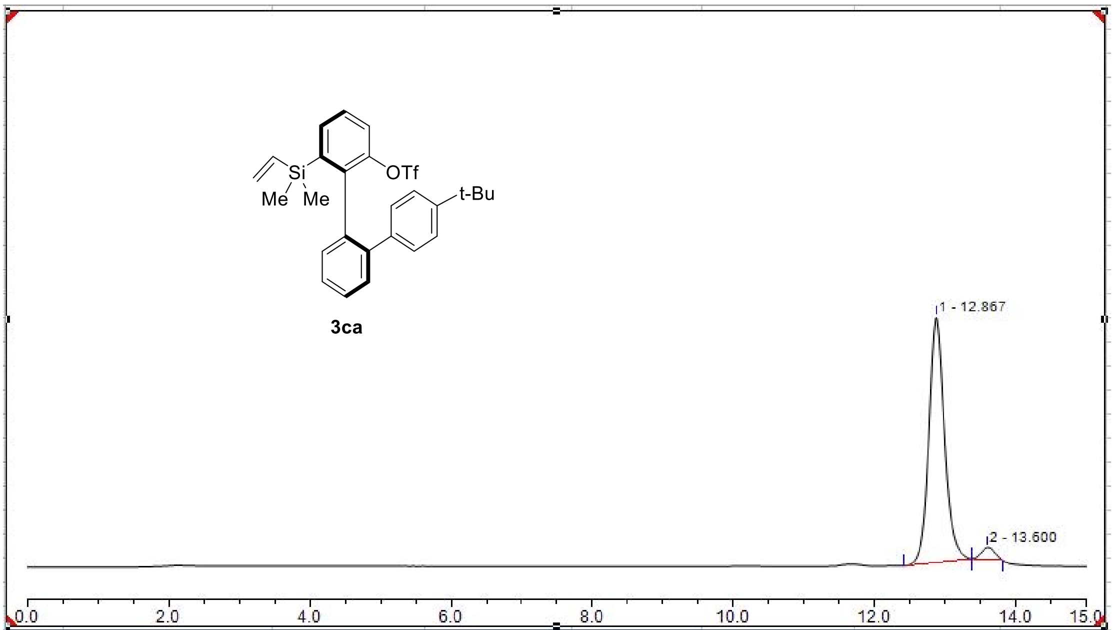
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.260	13.089	73.504	95.39	95.69	n.a.
2		11.543	0.632	3.307	4.61	4.31	n.a.
Total:			**13.721**	**76.811**	**100.00**	**100.00**	



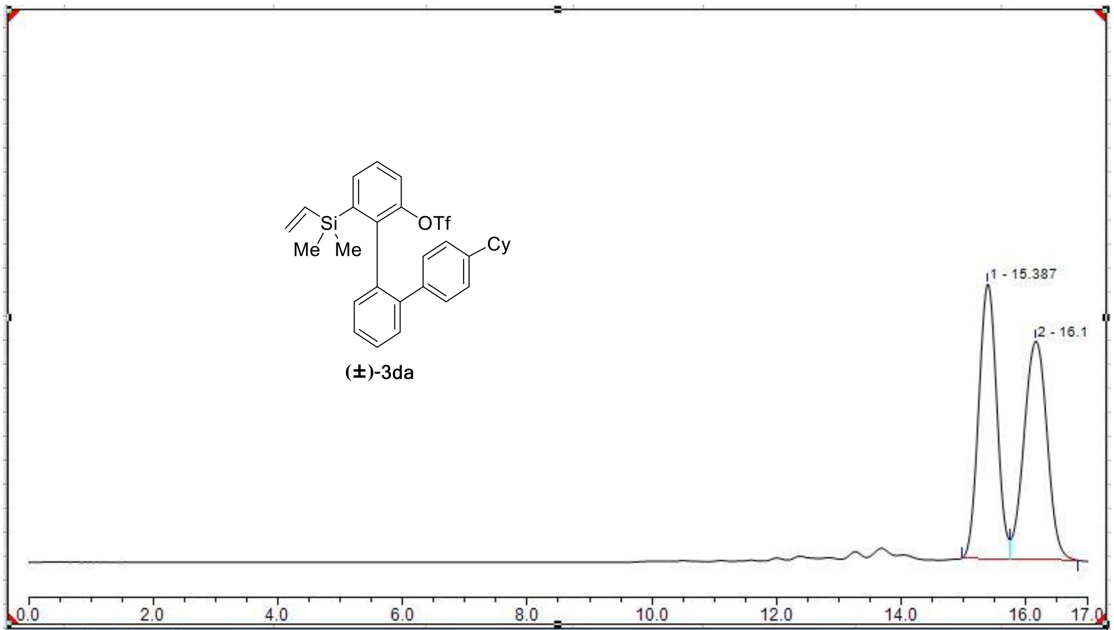
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.667	15.921	63.144	49.02	52.68	n.a.
2		13.330	16.555	56.716	50.98	47.32	n.a.
Total:			**32.476**	**119.860**	**100.00**	**100.00**	



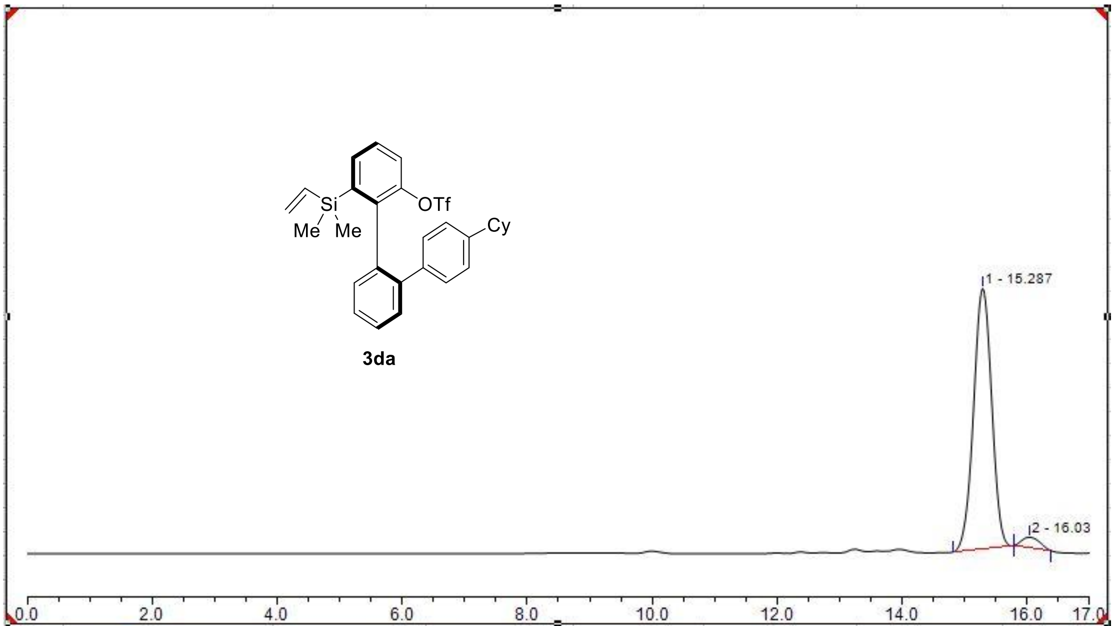
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.867	22.802	88.695	95.97	95.23	n.a.
2		13.600	0.958	4.439	4.03	4.77	n.a.
Total:			**23.760**	**93.135**	**100.00**	**100.00**	



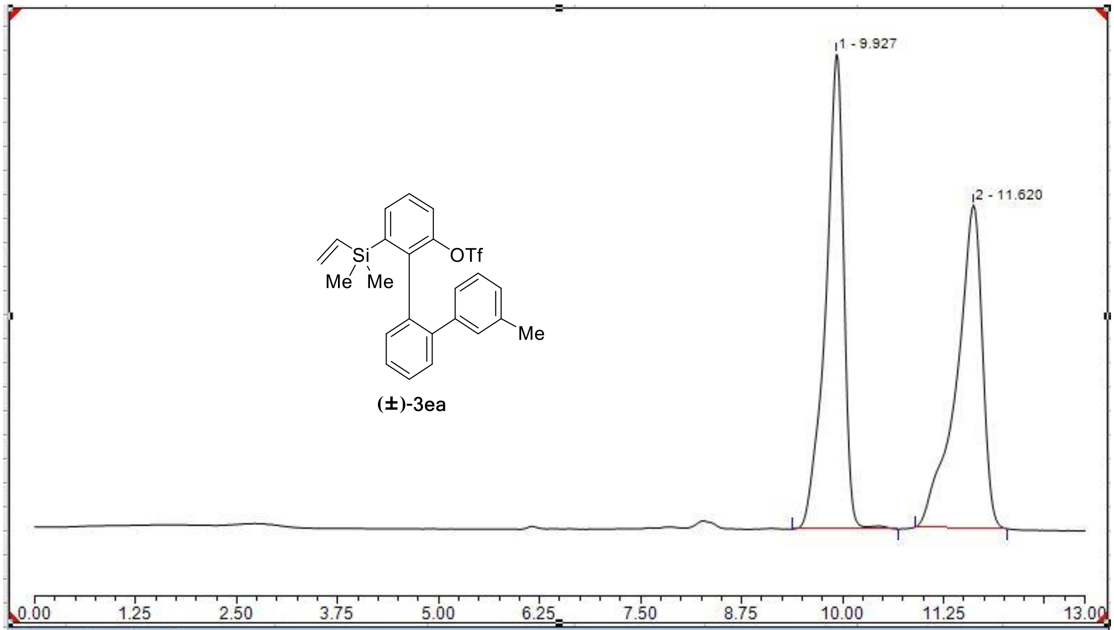
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.387	30.176	90.062	49.56	55.74	n.a.
2		16.157	30.715	71.523	50.44	44.26	n.a.
Total:			**60.891**	**161.585**	**100.00**	**100.00**	



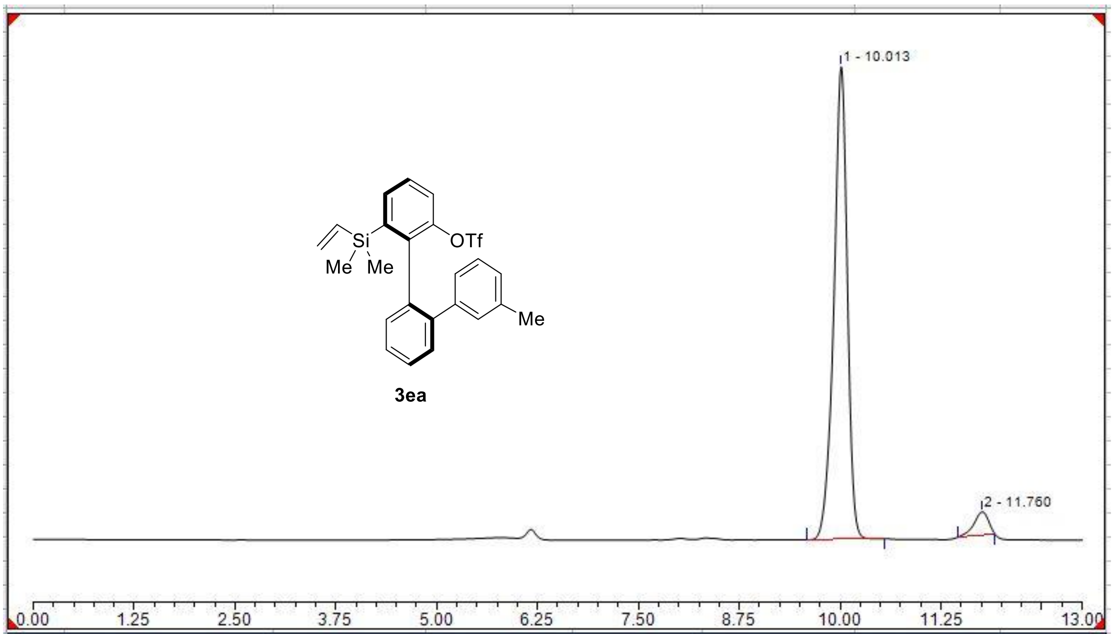
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.287	112.665	336.246	96.11	96.15	n.a.
2		16.033	4.558	13.478	3.89	3.85	n.a.
Total:			**117.223**	**349.724**	**100.00**	**100.00**	



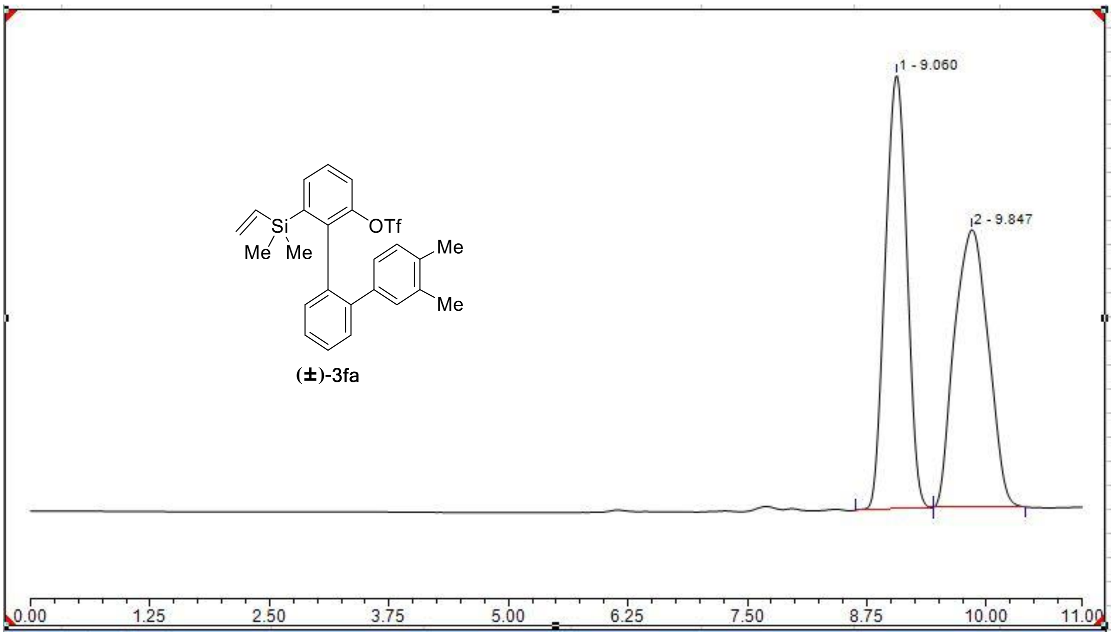
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.927	9.558	36.812	50.56	59.48	n.a.
2		11.620	9.346	25.073	49.44	40.52	n.a.
Total:			**18.904**	**61.885**	**100.00**	**100.00**	



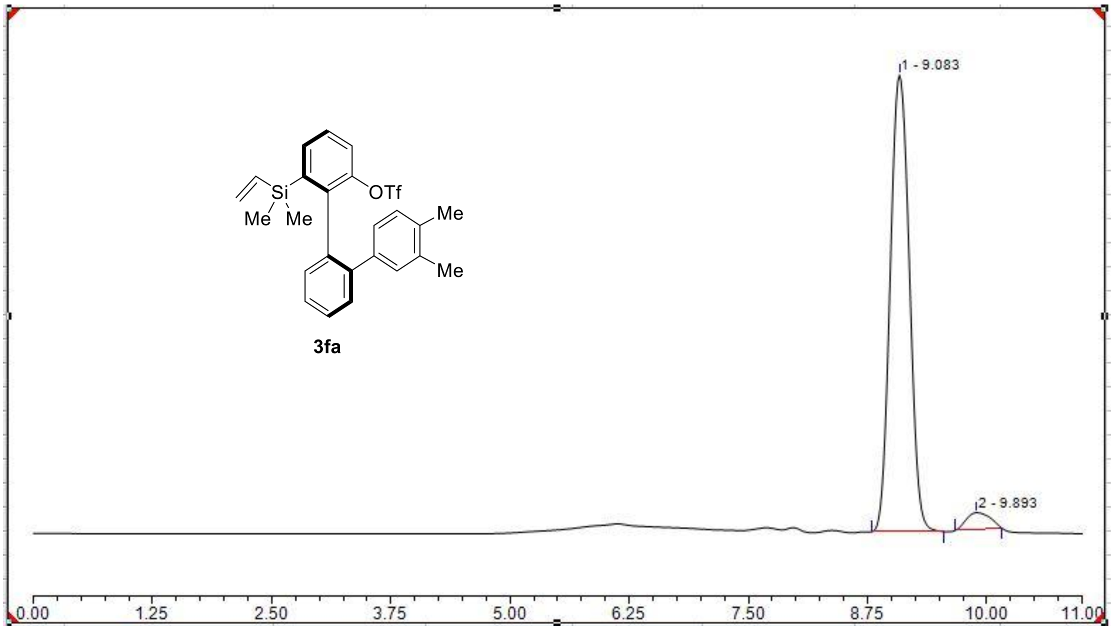
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.013	31.392	162.723	94.90	95.25	n.a.
2		11.760	1.688	8.108	5.10	4.75	n.a.
Total:			**33.080**	**170.831**	**100.00**	**100.00**	



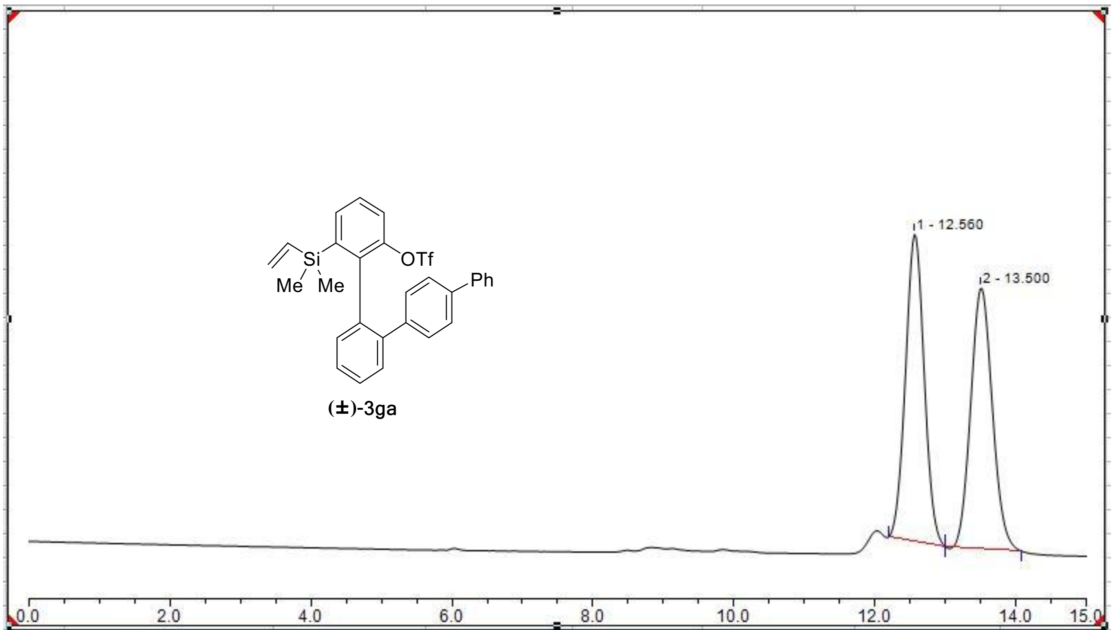
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.060	13.668	52.195	49.90	60.98	n.a.
2		9.847	13.723	33.399	50.10	39.02	n.a.
Total:			**27.391**	**85.594**	**100.00**	**100.00**	



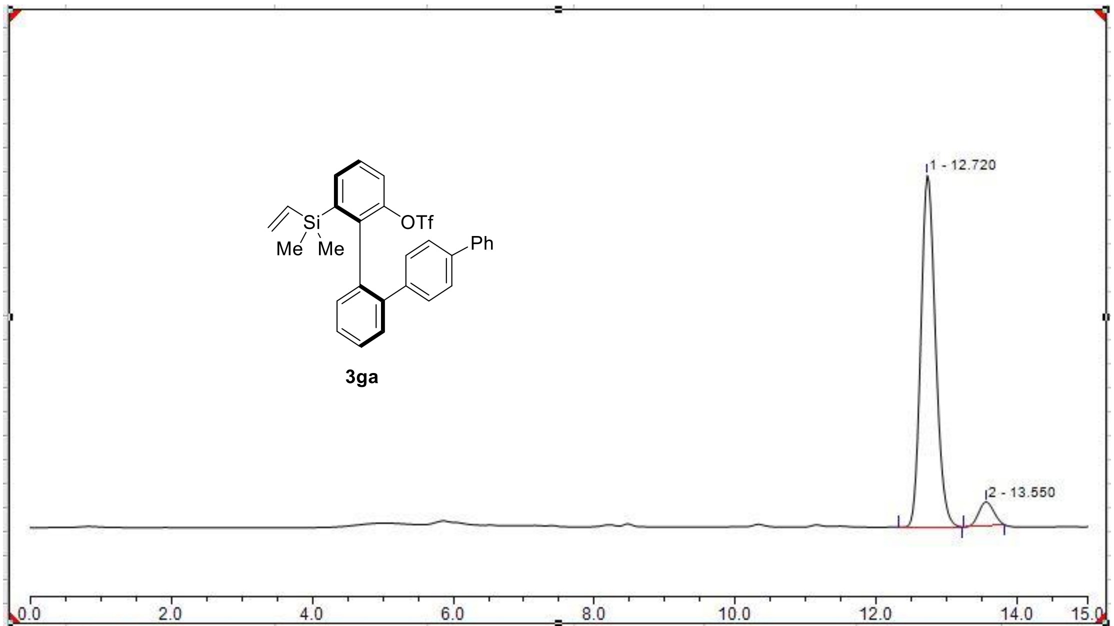
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.083	18.201	78.674	95.59	96.45	n.a.
2		9.893	0.840	2.891	4.41	3.55	n.a.
Total:			**19.041**	**81.565**	**100.00**	**100.00**	



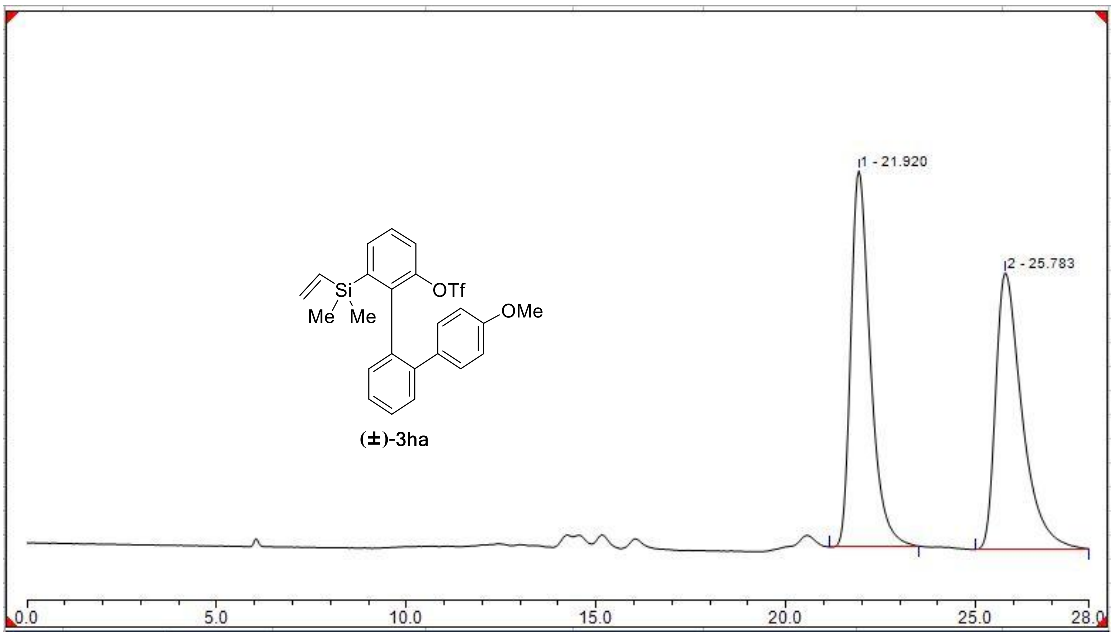
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.560	8.885	29.114	50.45	54.08	n.a.
2		13.500	8.726	24.722	49.55	45.92	n.a.
Total:			**17.611**	**53.836**	**100.00**	**100.00**	



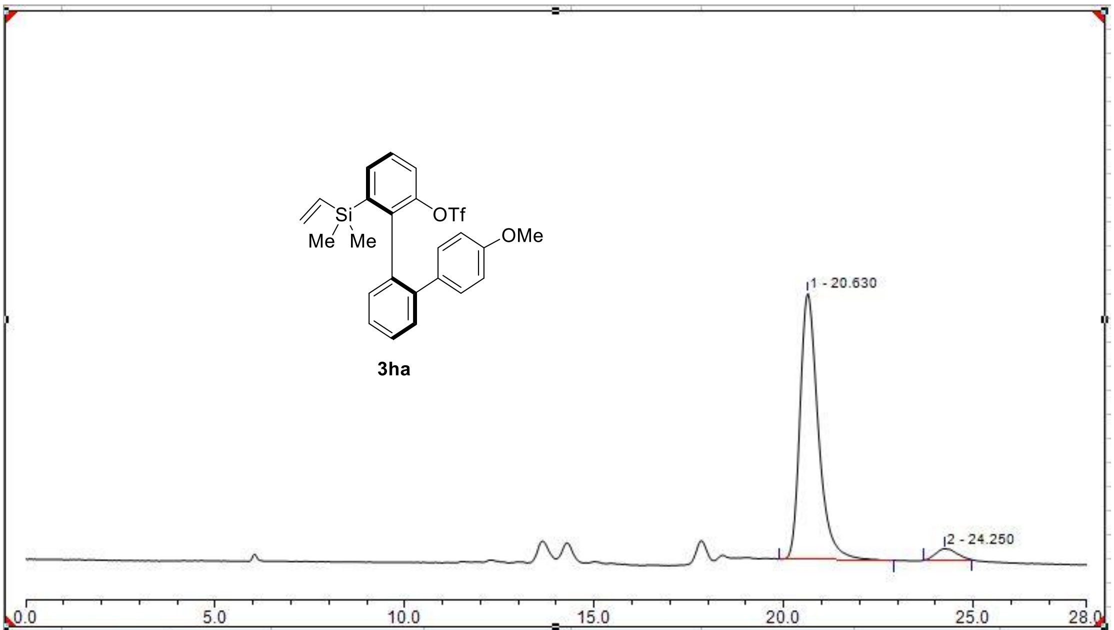
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.720	130.981	546.741	93.47	93.65	n.a.
2		13.550	9.151	37.047	6.53	6.35	n.a.
Total:			**140.132**	**583.787**	**100.00**	**100.00**	



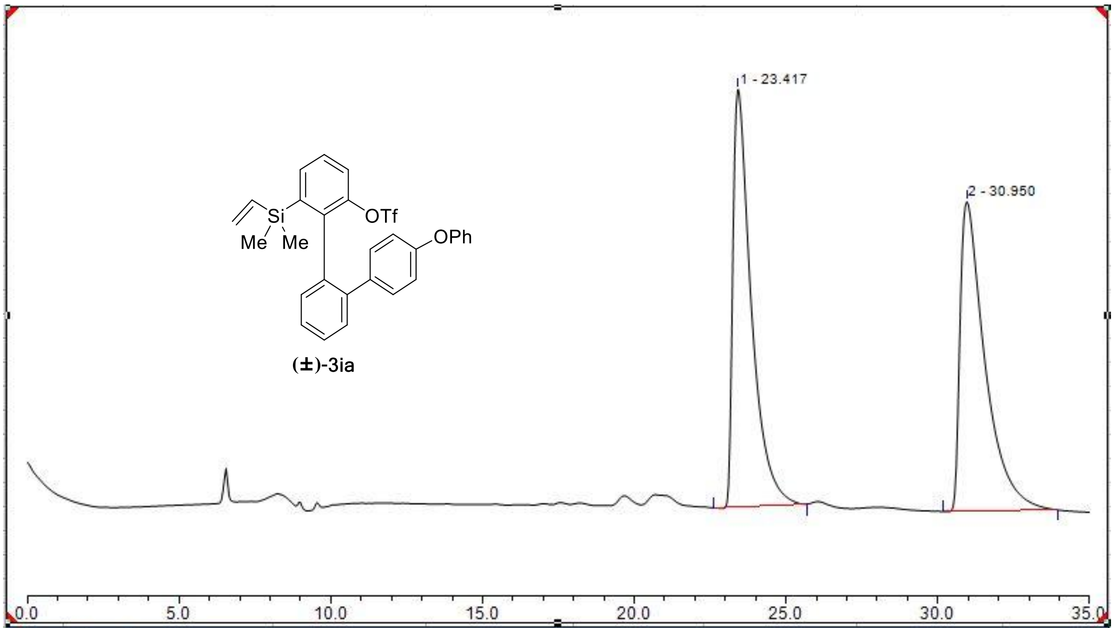
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		21.920	8.494	14.227	50.21	57.64	n.a.
2		25.783	8.422	10.457	49.79	42.36	n.a.
Total:			16.915	24.684	100.00	100.00	



Integration Results

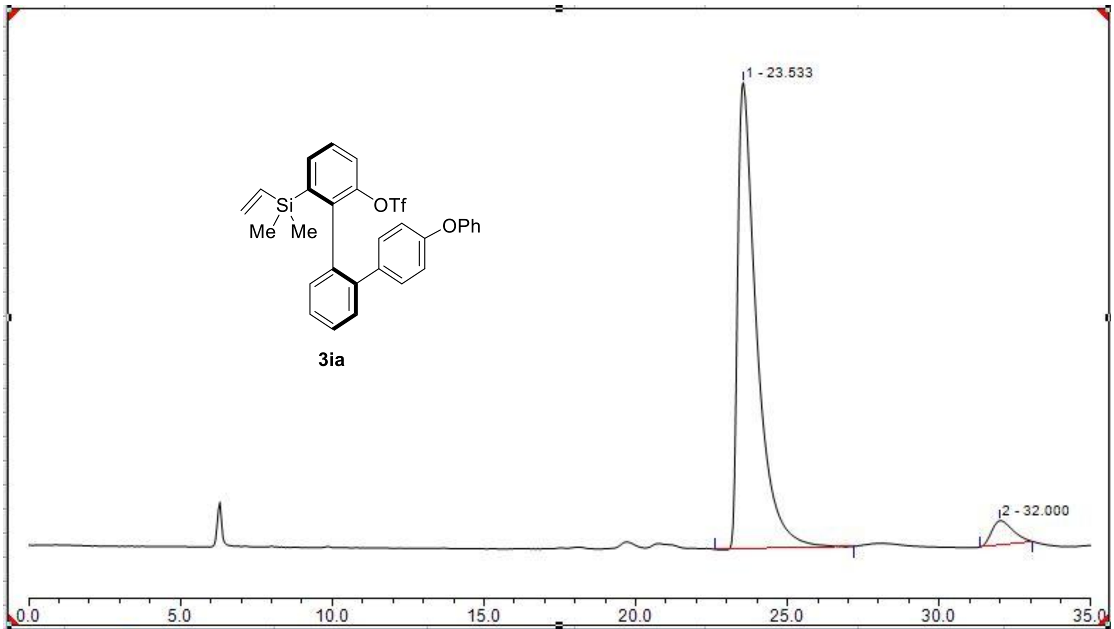
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		20.630	4.071	7.321	95.30	95.88	n.a.
2		24.250	0.201	0.314	4.70	4.12	n.a.
Total:			4.271	7.635	100.00	100.00	



Integration Results

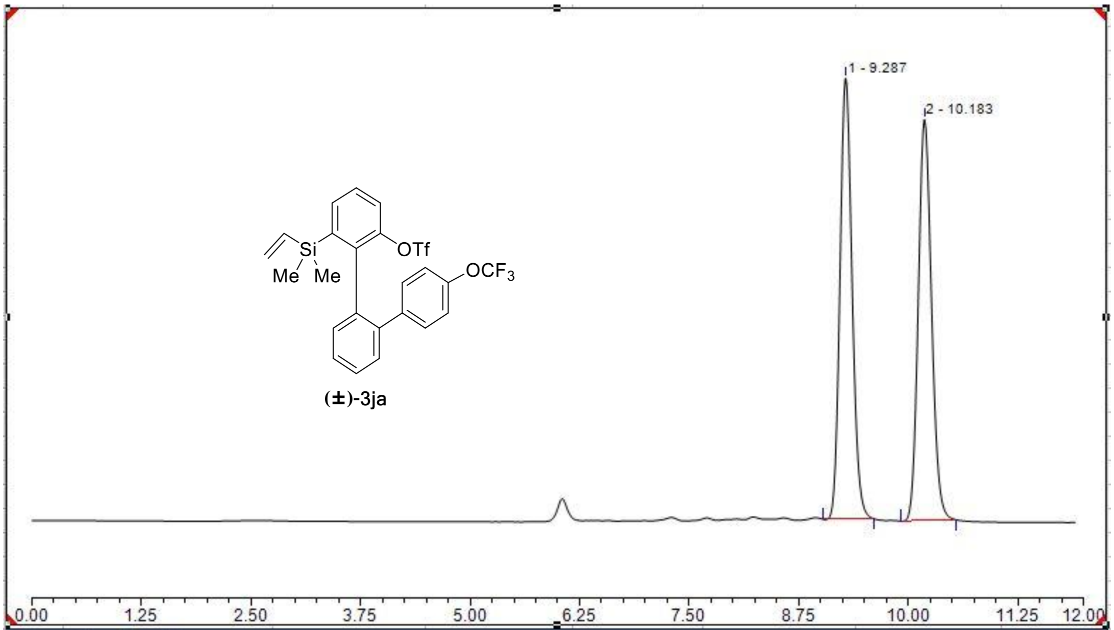
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.417	45.446	64.636	49.91	57.43	n.a.
2		30.950	45.601	47.903	50.09	42.57	n.a.
Total:			**91.046**	**112.539**	**100.00**	**100.00**	

0.



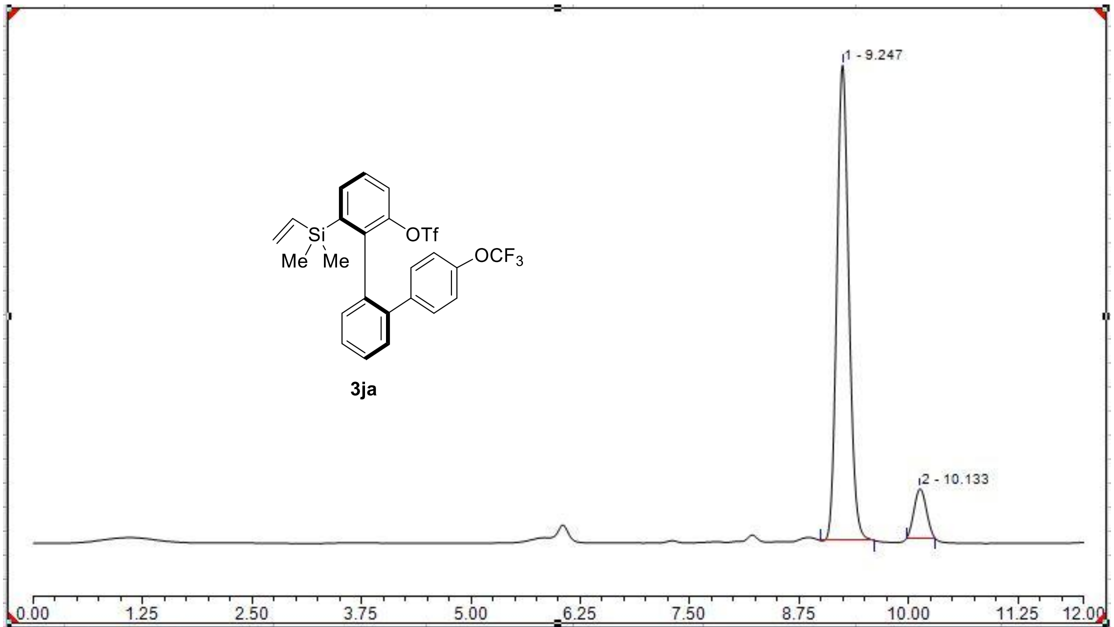
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.533	34.822	48.032	94.49	95.06	n.a.
2		32.000	2.032	2.495	5.51	4.94	n.a.
Total:			**36.854**	**50.527**	**100.00**	**100.00**	



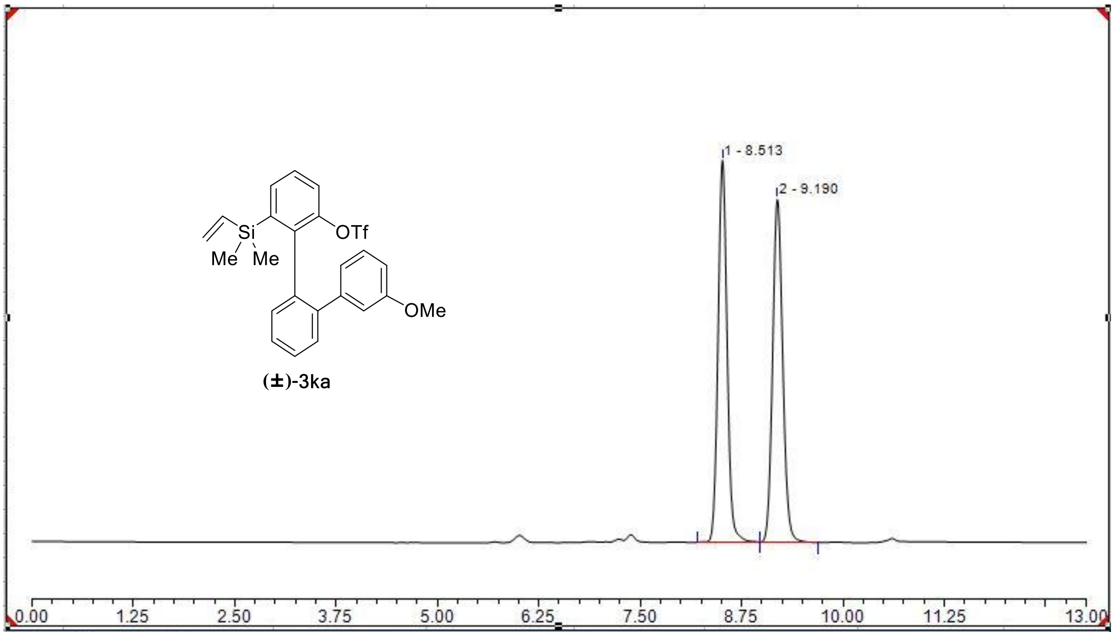
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.287	19.316	121.120	50.02	52.36	n.a.
2		10.183	19.298	110.194	49.98	47.64	n.a.
Total:			**38.615**	**231.315**	**100.00**	**100.00**	



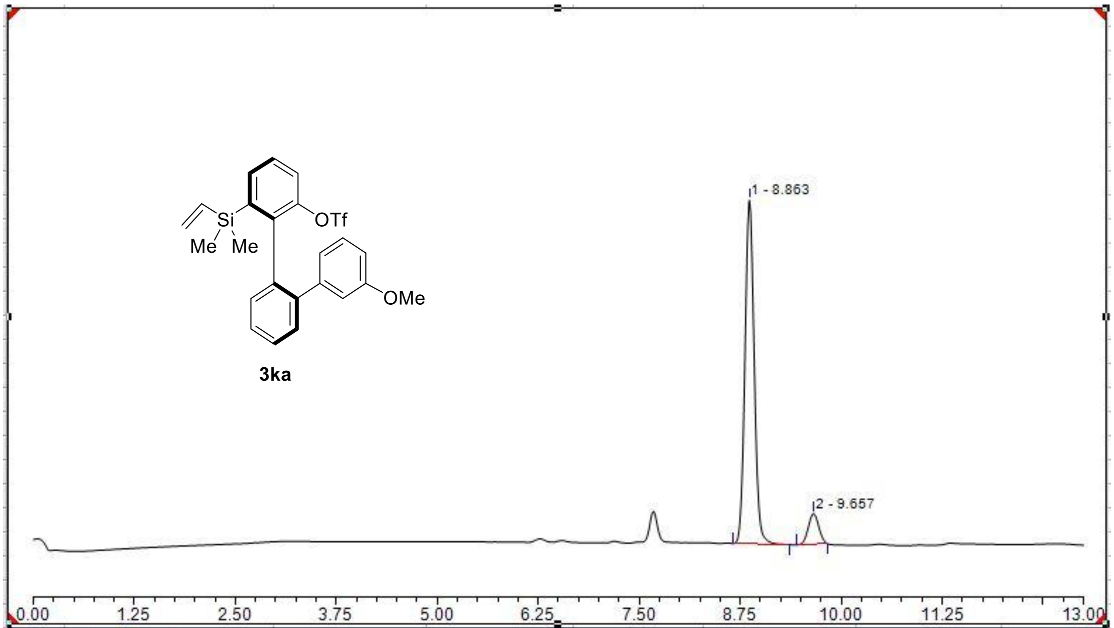
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.247	31.180	196.474	90.37	90.54	n.a.
2		10.133	3.324	20.533	9.63	9.46	n.a.
Total:			**34.504**	**217.007**	**100.00**	**100.00**	



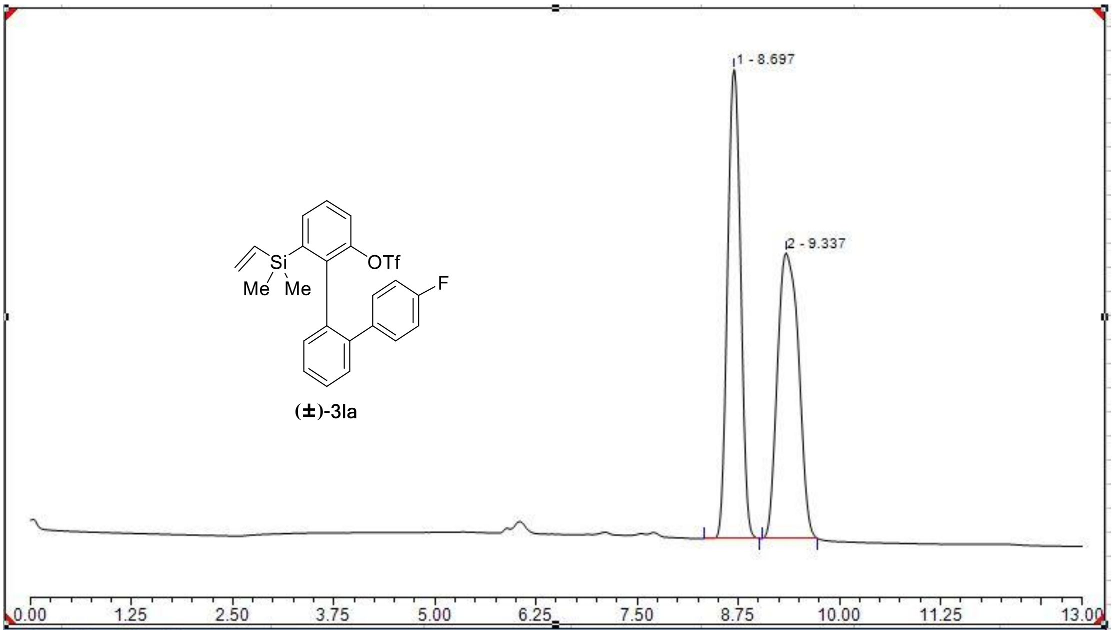
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.513	18.652	144.046	50.03	52.69	n.a.
2		9.190	18.628	129.319	49.97	47.31	n.a.
Total:			**37.280**	**273.365**	**100.00**	**100.00**	



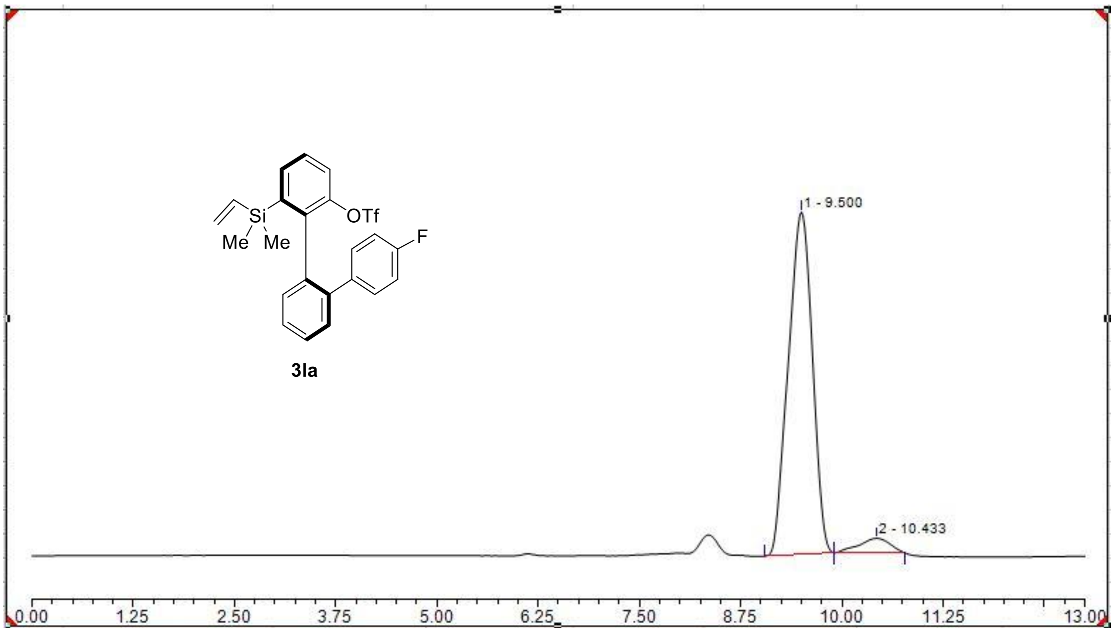
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.863	4.292	32.516	90.80	91.80	n.a.
2		9.657	0.435	2.904	9.20	8.20	n.a.
Total:			**4.727**	**35.419**	**100.00**	**100.00**	



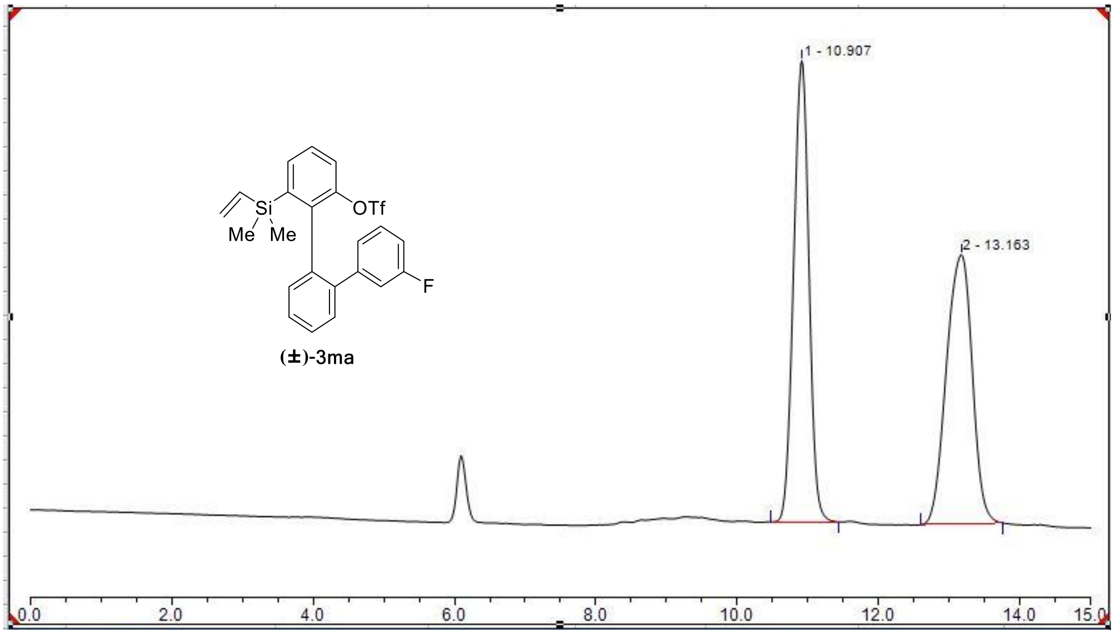
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.697	24.107	128.955	50.27	62.13	n.a.
2		9.337	23.843	78.588	49.73	37.87	n.a.
Total:			**47.950**	**207.544**	**100.00**	**100.00**	



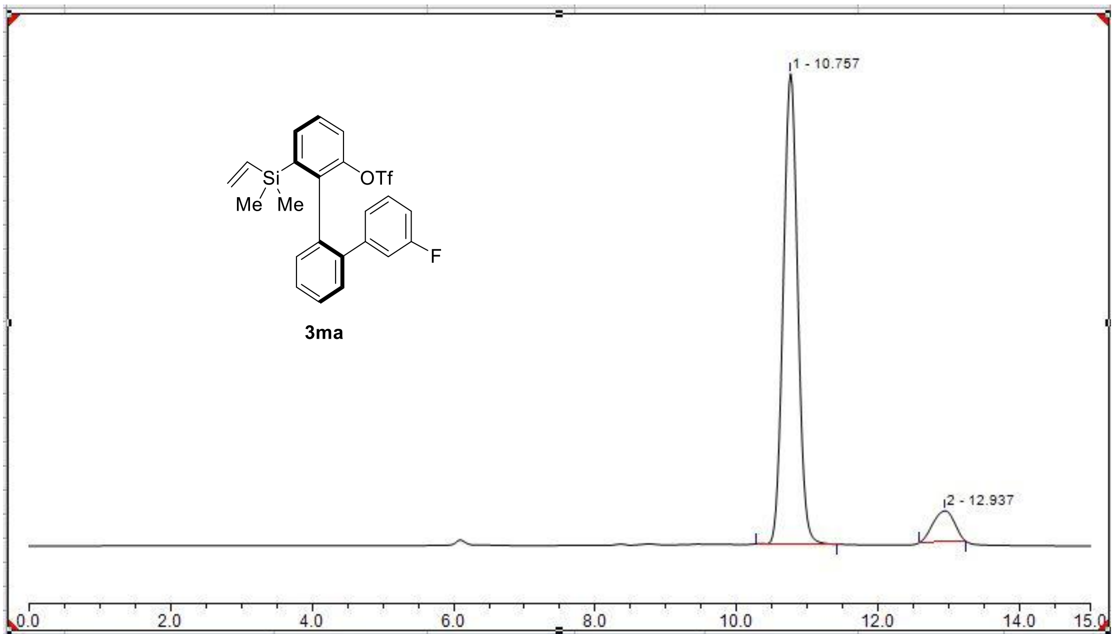
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.500	15.162	44.109	94.82	95.97	n.a.
2		10.433	0.828	1.852	5.18	4.03	n.a.
Total:			**15.990**	**45.961**	**100.00**	**100.00**	



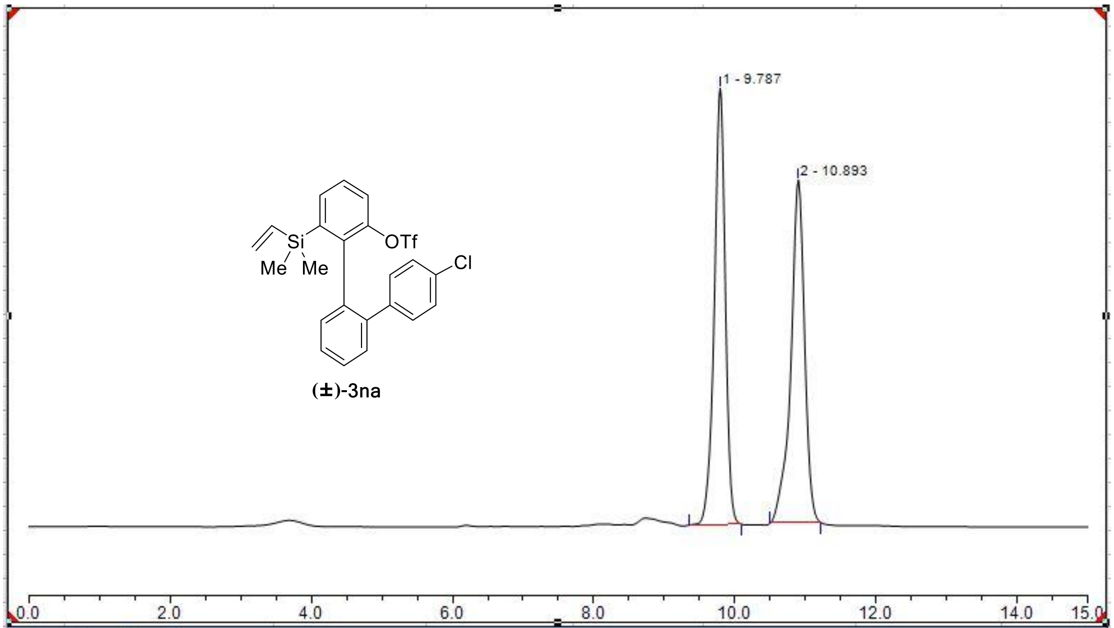
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.907	6.963	27.748	50.40	63.12	n.a.
2		13.163	6.851	16.213	49.60	36.88	n.a.
Total:			**13.814**	**43.961**	**100.00**	**100.00**	



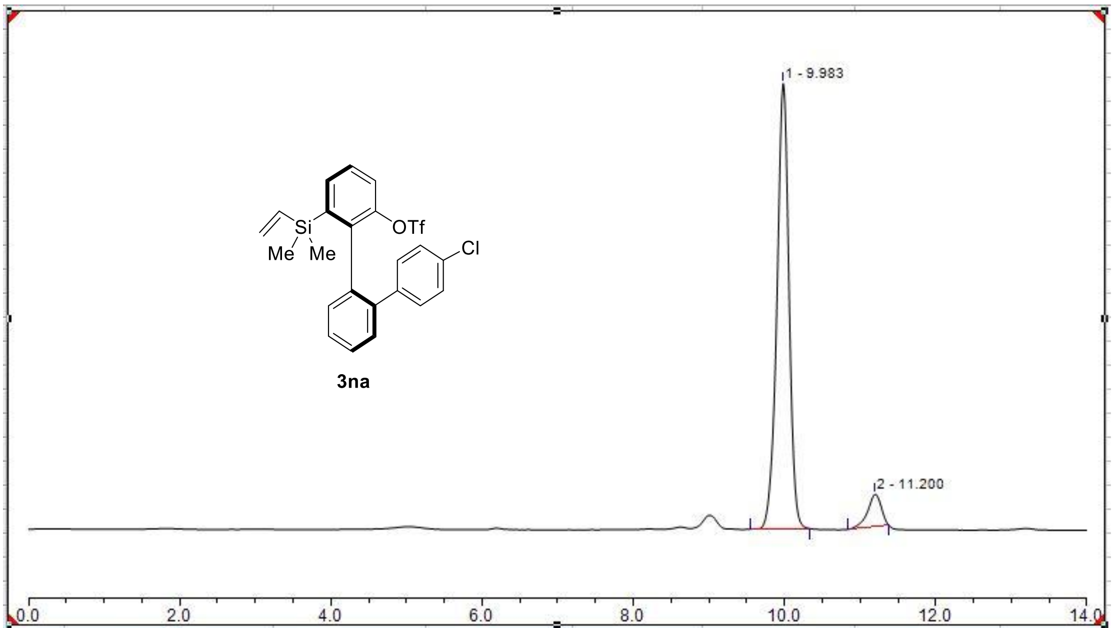
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.757	104.588	444.354	91.11	93.84	n.a.
2		12.937	10.200	29.187	8.89	6.16	n.a.
Total:			**114.788**	**473.541**	**100.00**	**100.00**	



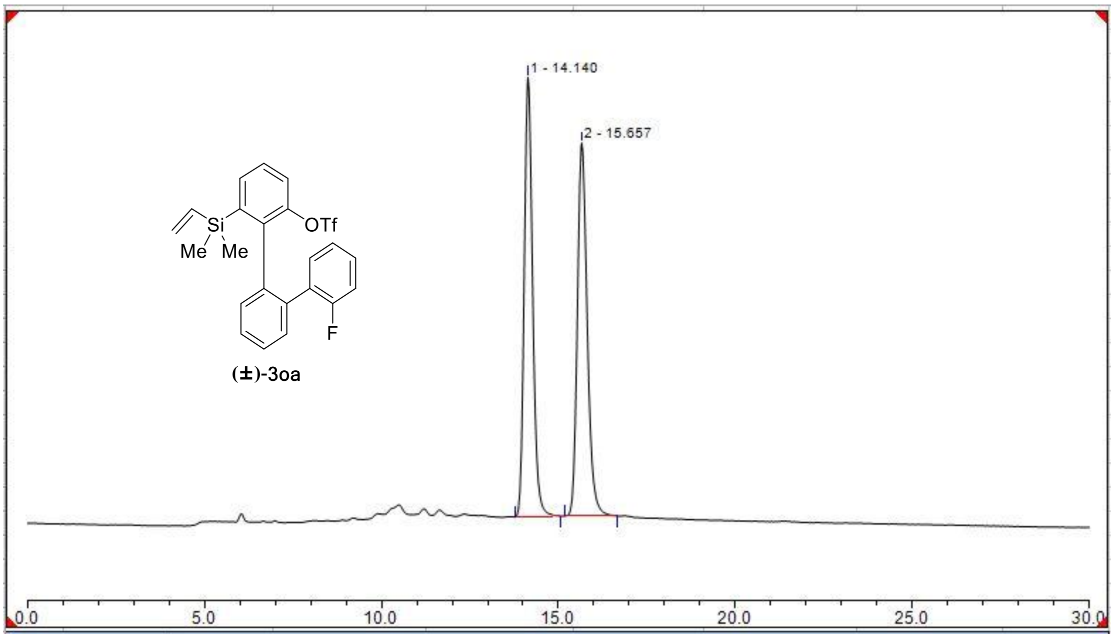
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.787	12.216	67.676	50.48	55.97	n.a.
2		10.893	11.982	53.232	49.52	44.03	n.a.
Total:			**24.198**	**120.908**	**100.00**	**100.00**	



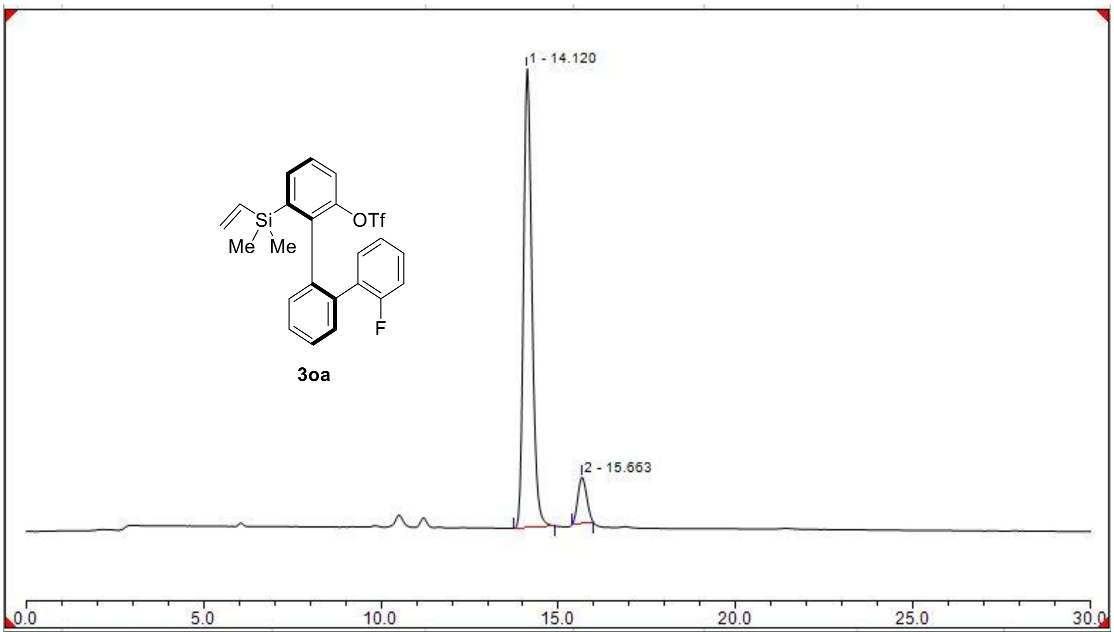
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.983	12.760	69.142	92.47	93.24	n.a.
2		11.200	1.039	5.011	7.53	6.76	n.a.
Total:			**13.800**	**74.153**	**100.00**	**100.00**	



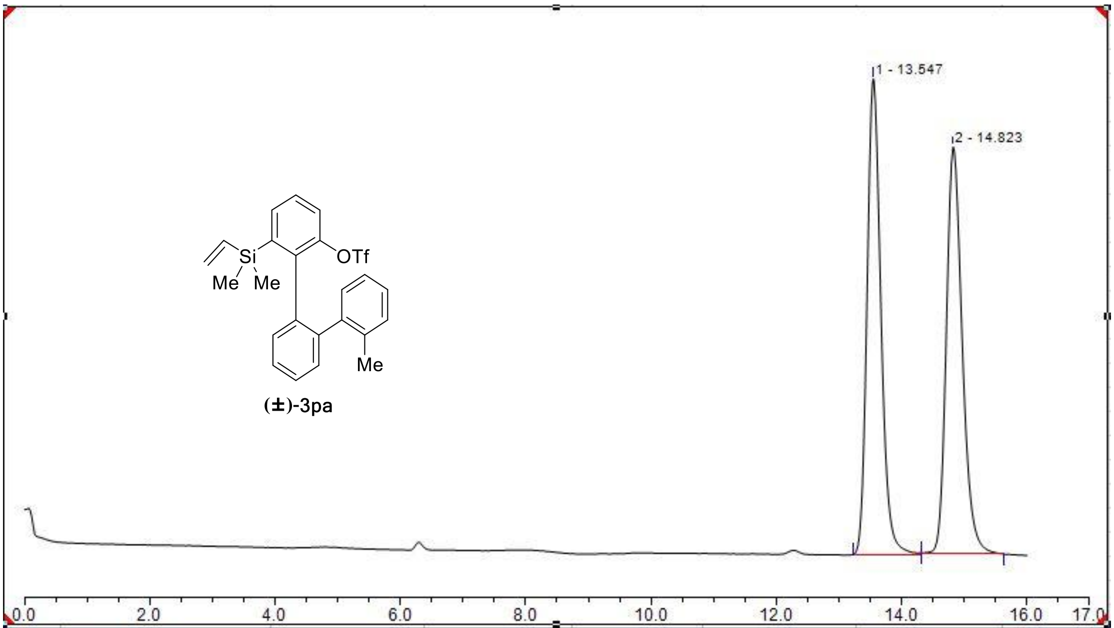
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.140	3.322	12.079	50.08	54.07	n.a.
2		15.657	3.311	10.262	49.92	45.93	n.a.
Total:			**6.633**	**22.341**	**100.00**	**100.00**	



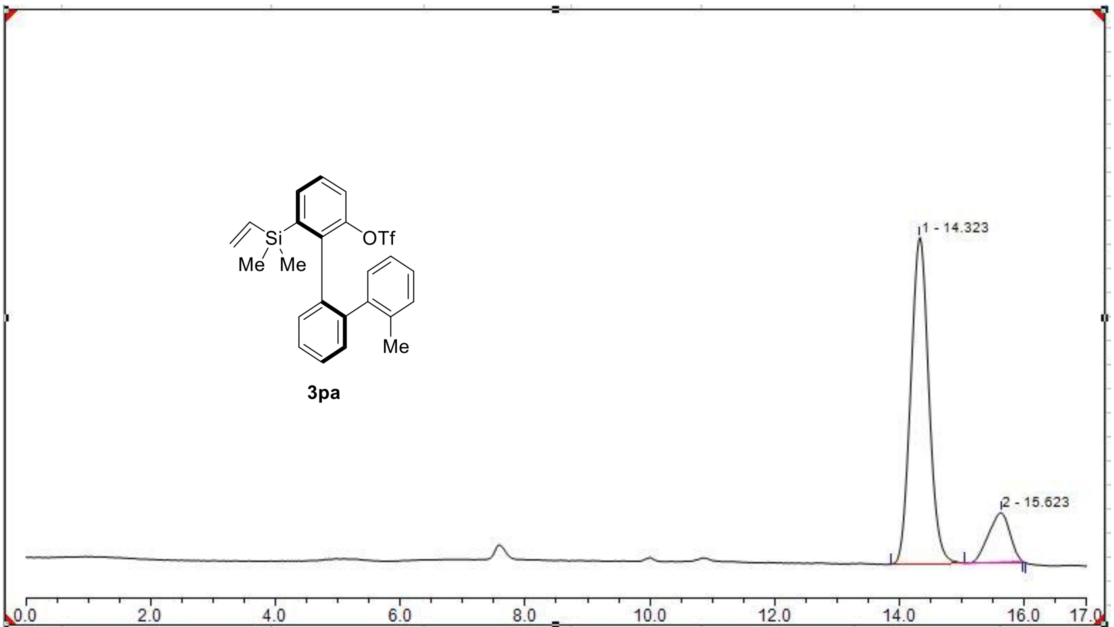
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.120	9.666	35.372	90.49	90.82	n.a.
2		15.663	1.015	3.575	9.51	9.18	n.a.
Total:			**10.681**	**38.946**	**100.00**	**100.00**	



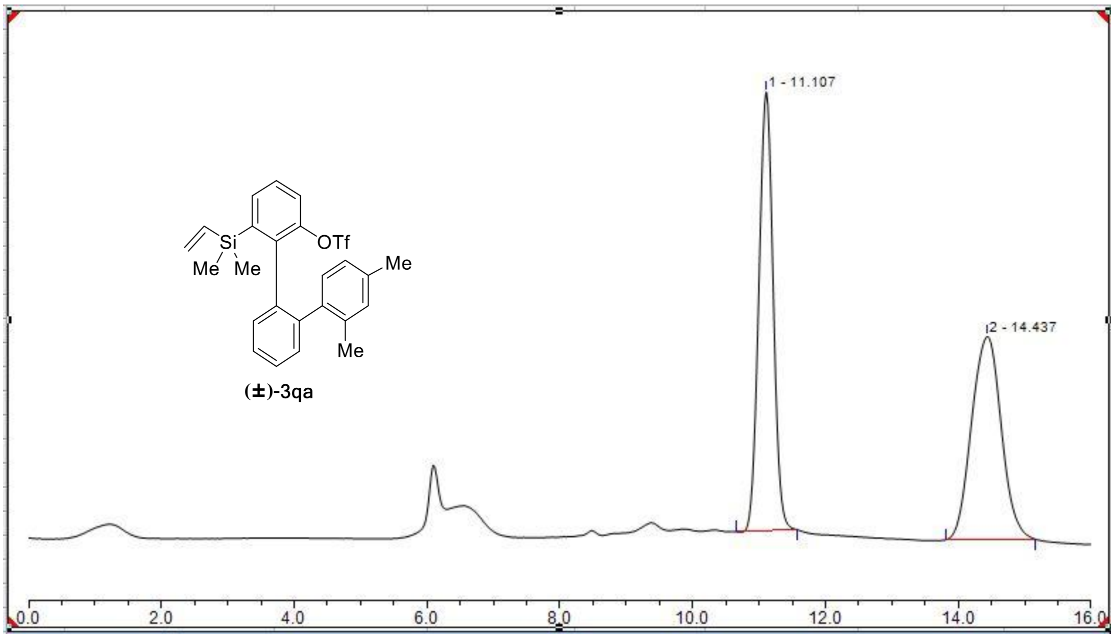
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.547	7.273	28.540	50.17	53.87	n.a.
2		14.823	7.225	24.440	49.83	46.13	n.a.
Total:			**14.498**	**52.980**	**100.00**	**100.00**	



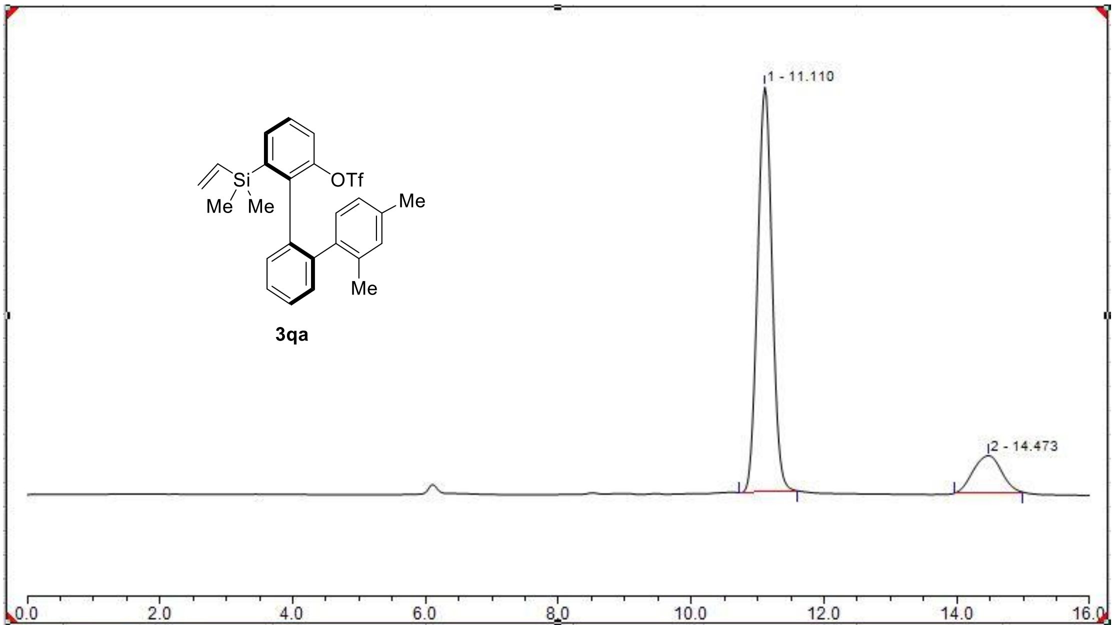
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.323	3.026	8.996	84.91	86.84	n.a.
2		15.623	0.538	1.363	15.09	13.16	n.a.
Total:			**3.564**	**10.359**	**100.00**	**100.00**	



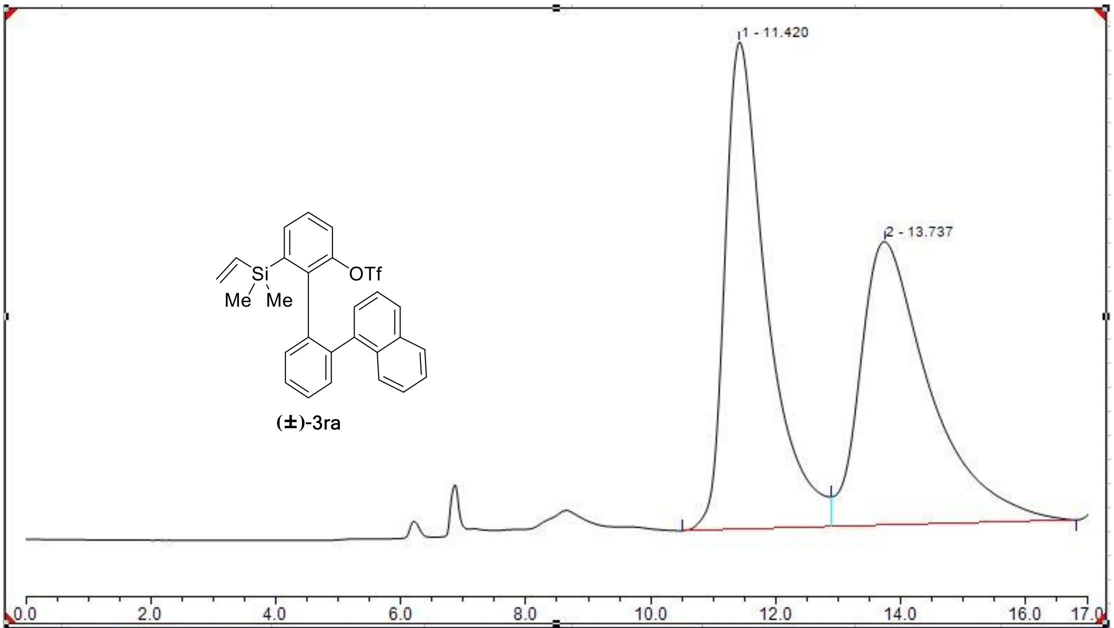
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.107	9.405	37.685	51.04	68.36	n.a.
2		14.437	9.023	17.440	48.96	31.64	n.a.
Total:			**18.428**	**55.125**	**100.00**	**100.00**	



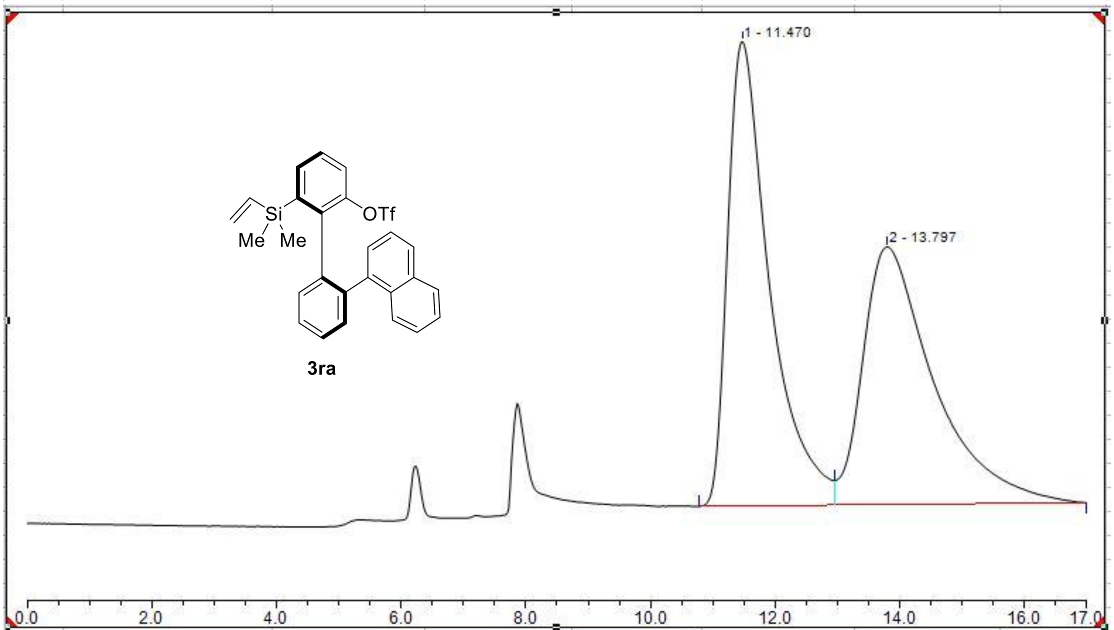
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.110	52.514	208.768	84.84	91.63	n.a.
2		14.473	9.387	19.081	15.16	8.37	n.a.
Total:			**61.901**	**227.849**	**100.00**	**100.00**	



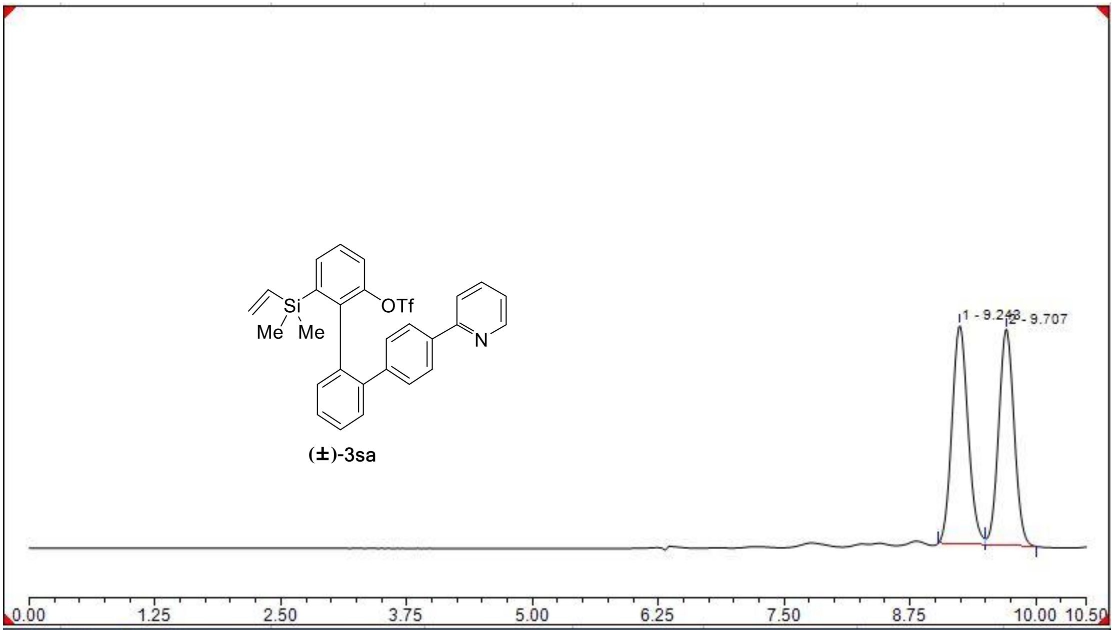
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.420	71.679	92.224	50.77	63.21	n.a.
2		13.737	69.497	53.676	49.23	36.79	n.a.
Total:			**141.175**	**145.900**	**100.00**	**100.00**	



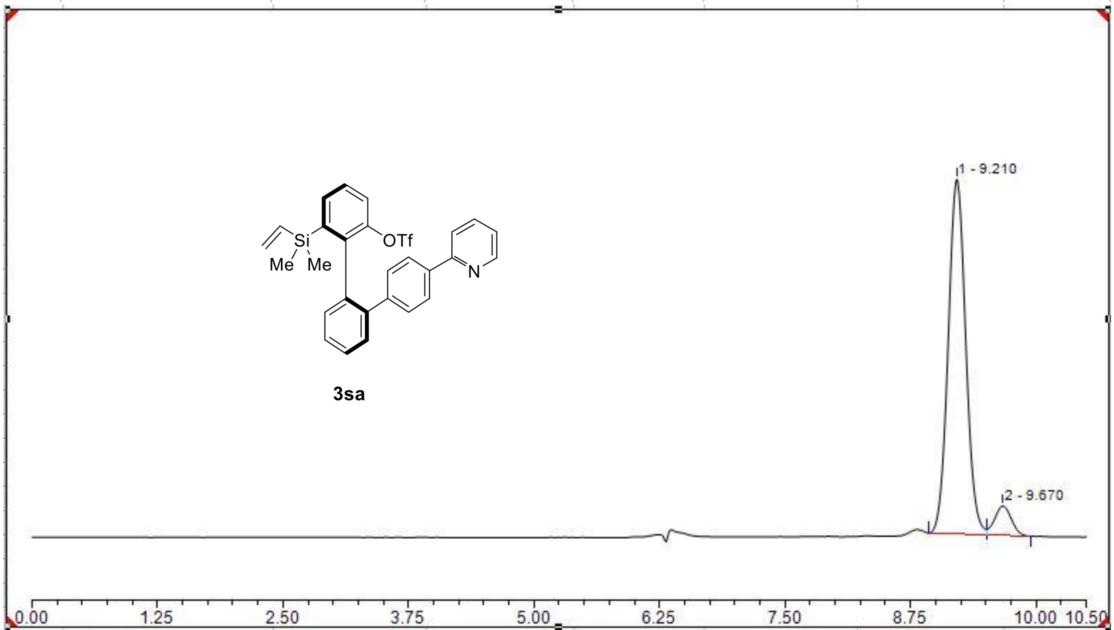
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.470	25.037	31.996	51.63	64.32	n.a.
2		13.797	23.458	17.750	48.37	35.68	n.a.
Total:			**48.495**	**49.746**	**100.00**	**100.00**	



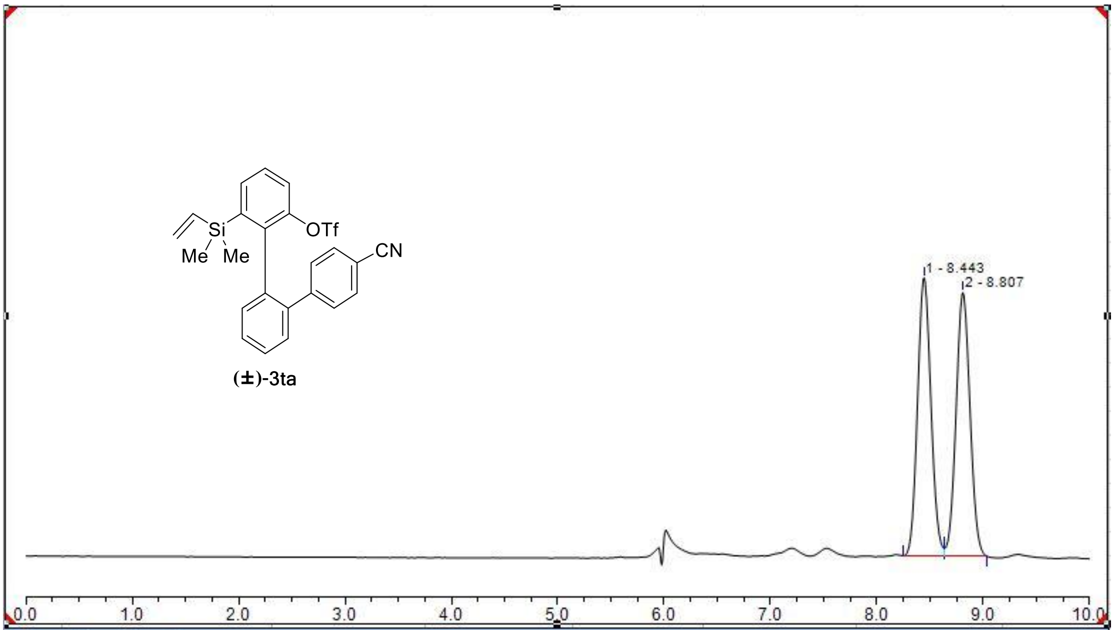
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.243	8.989	48.672	51.18	50.27	n.a.
2		9.707	8.575	48.141	48.82	49.73	n.a.
Total:			**17.564**	**96.812**	**100.00**	**100.00**	



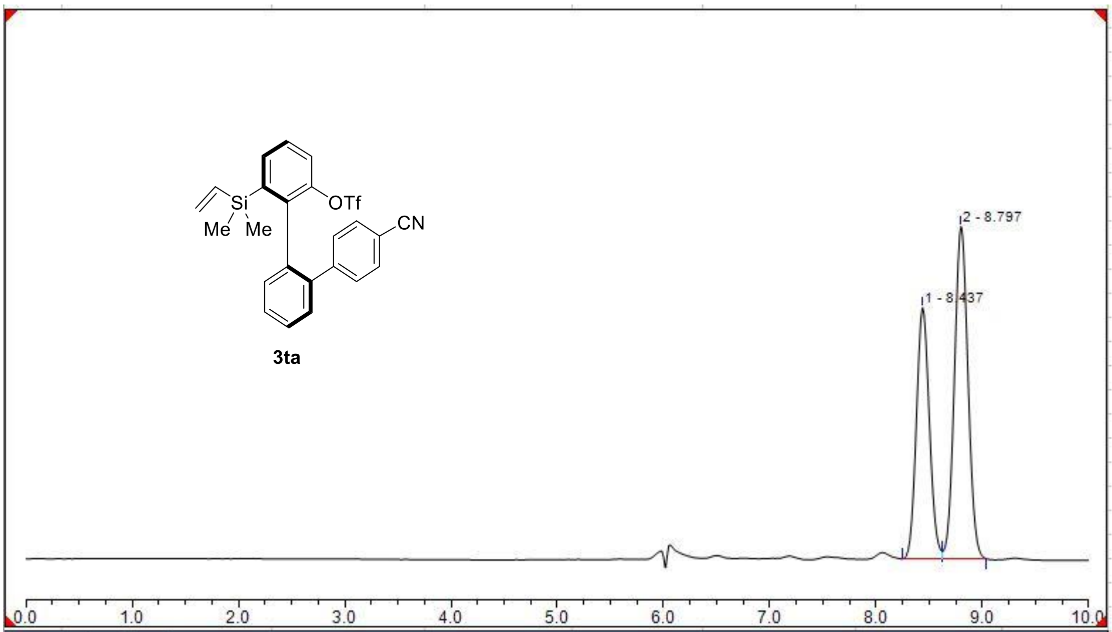
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.210	6.151	30.420	92.65	92.32	n.a.
2		9.670	0.488	2.529	7.35	7.68	n.a.
Total:			**6.639**	**32.950**	**100.00**	**100.00**	



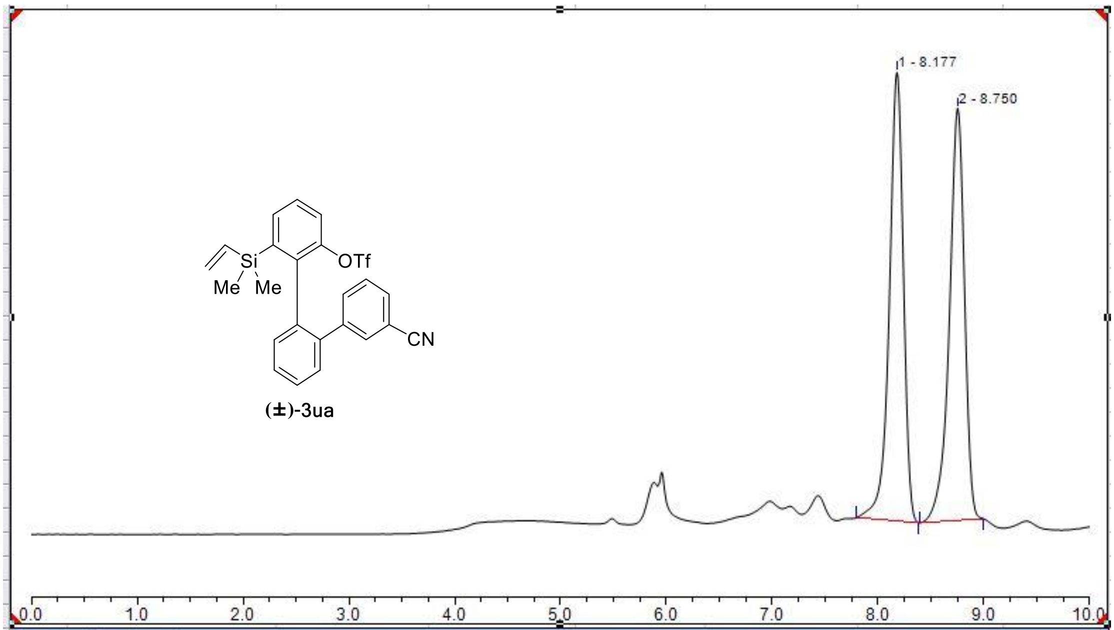
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.443	2.225	15.278	50.34	51.36	n.a.
2		8.807	2.195	14.467	49.66	48.64	n.a.
Total:			**4.419**	**29.744**	**100.00**	**100.00**	



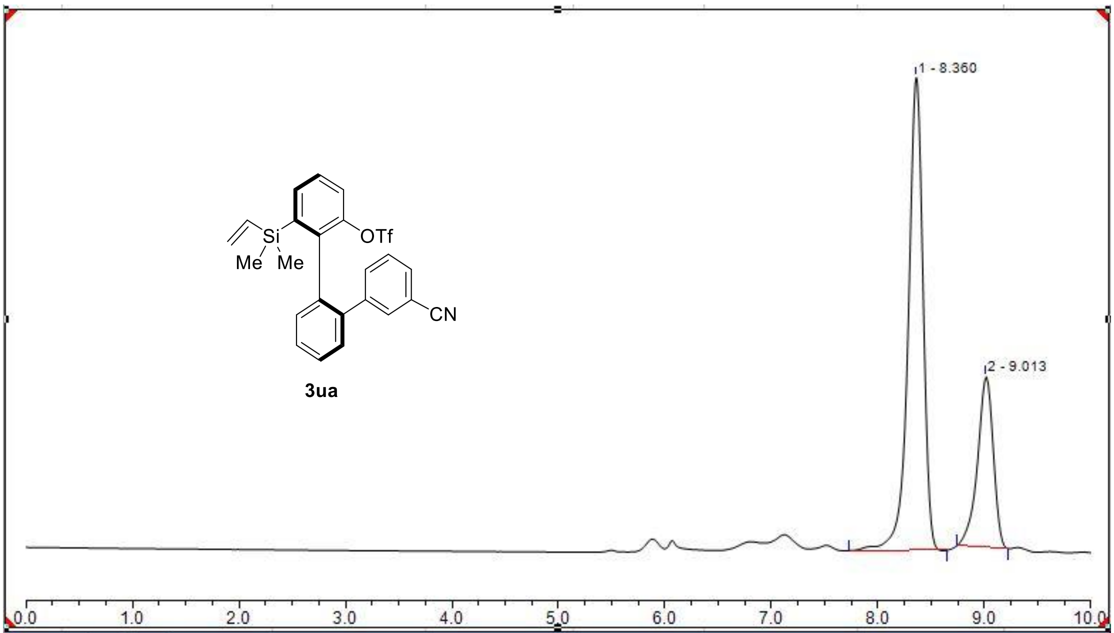
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.437	1.948	13.793	42.02	43.07	n.a.
2		8.797	2.688	18.230	57.98	56.93	n.a.
Total:			**4.635**	**32.023**	**100.00**	**100.00**	



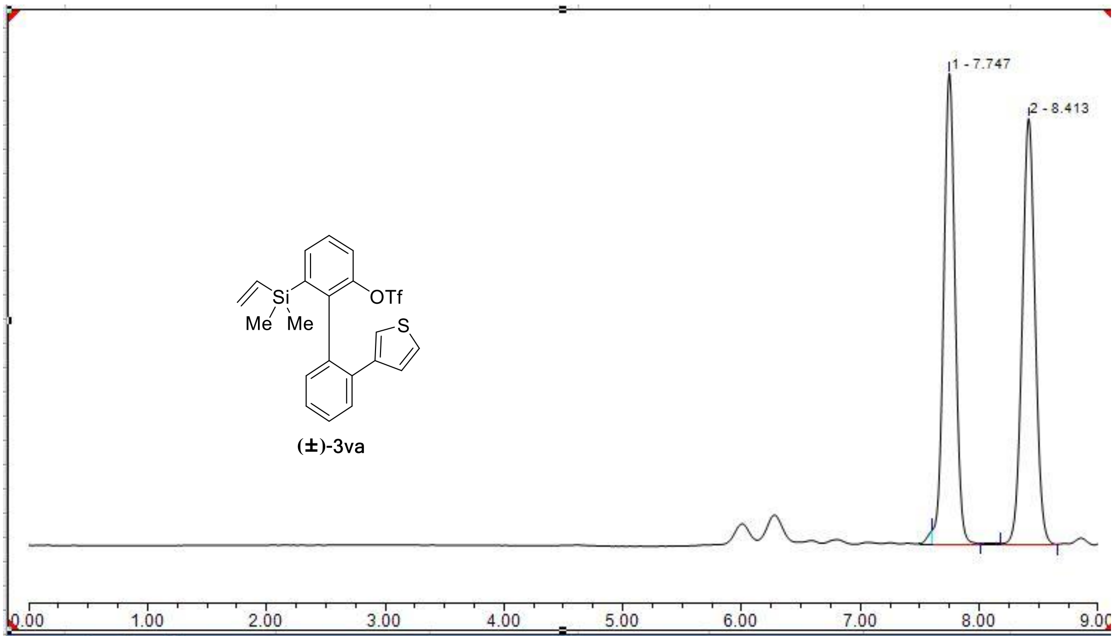
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.177	5.952	38.672	50.22	52.11	n.a.
2		8.750	5.900	35.537	49.78	47.89	n.a.
Total:			**11.851**	**74.209**	**100.00**	**100.00**	



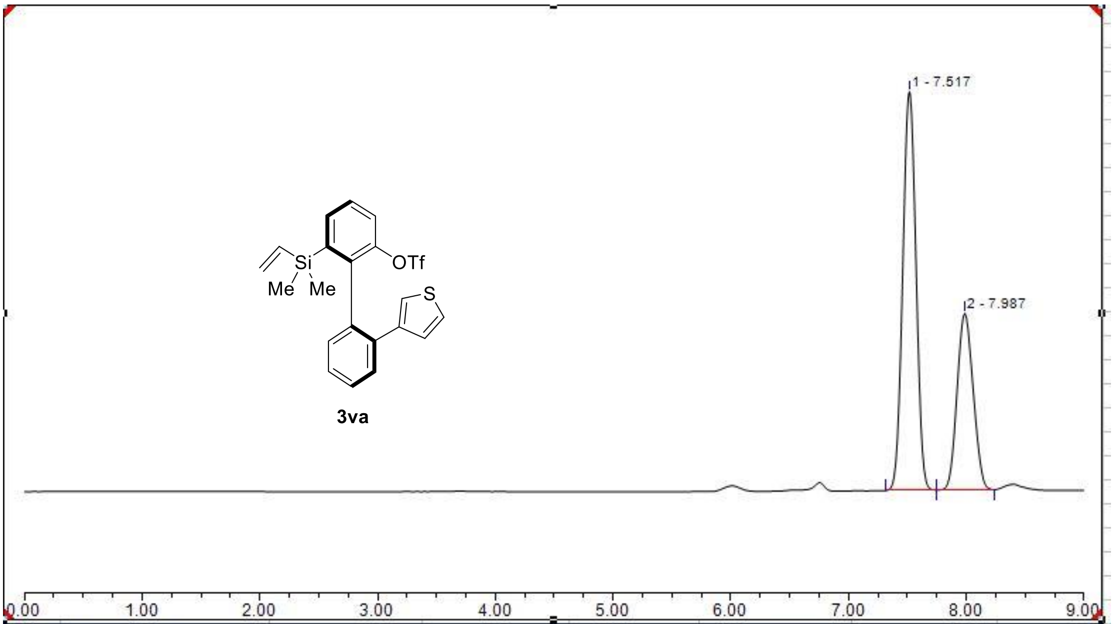
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.360	15.633	97.221	72.23	73.49	n.a.
2		9.013	6.011	35.077	27.77	26.51	n.a.
Total:			**21.644**	**132.297**	**100.00**	**100.00**	



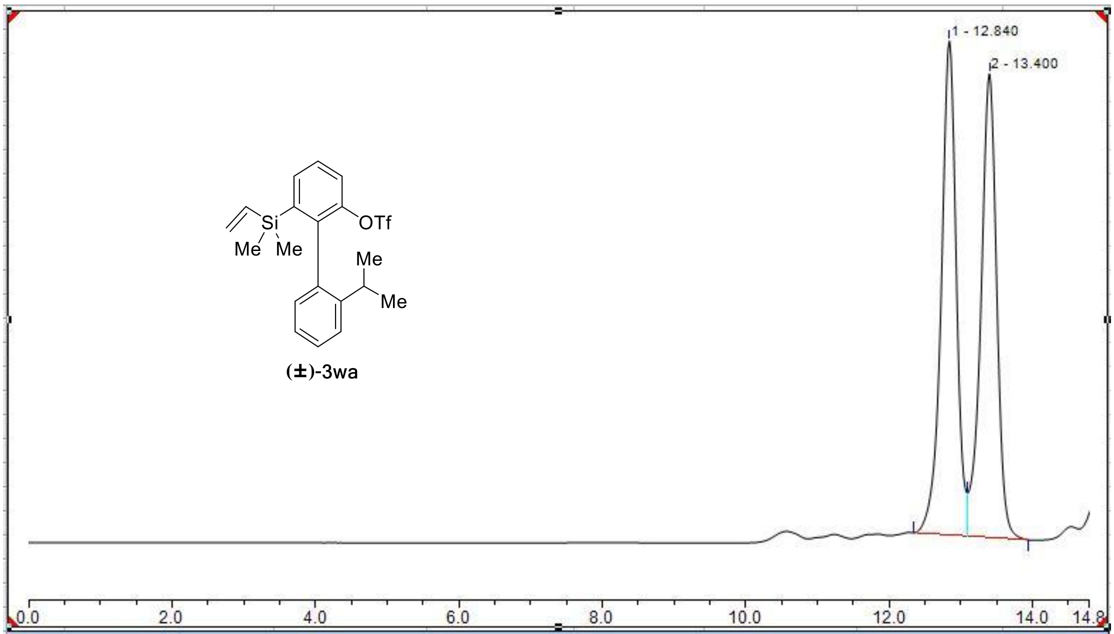
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.747	4.925	44.187	49.54	52.51	n.a.
2		8.413	5.016	39.967	50.46	47.49	n.a.
Total:			**9.941**	**84.154**	**100.00**	**100.00**	



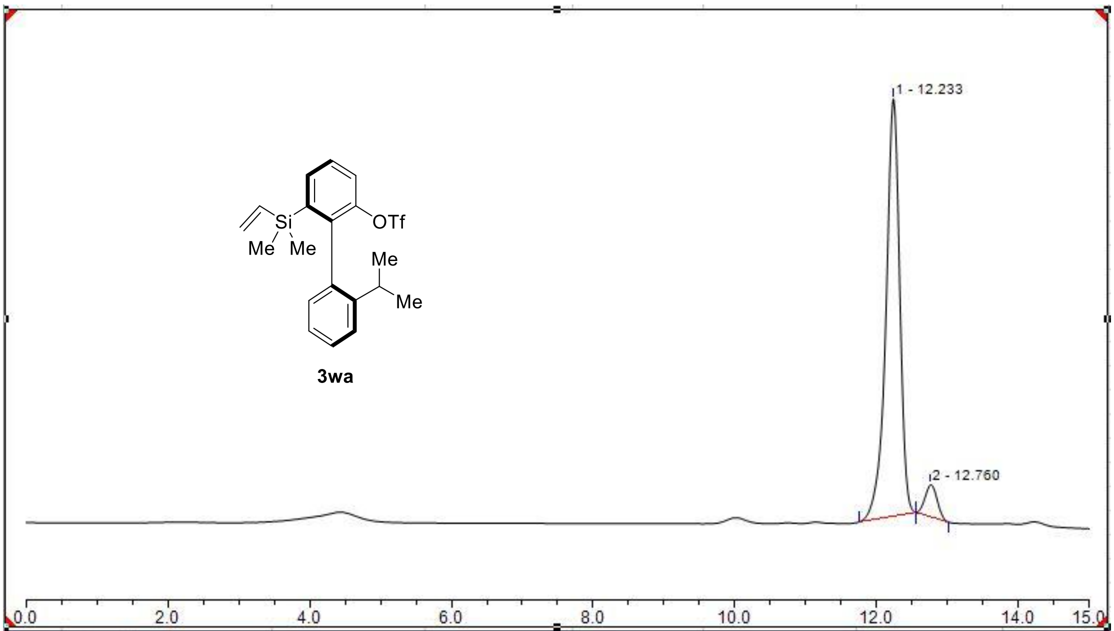
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.517	26.774	206.227	64.96	69.30	n.a.
2		7.987	14.444	91.378	35.04	30.70	n.a.
Total:			**41.217**	**297.604**	**100.00**	**100.00**	



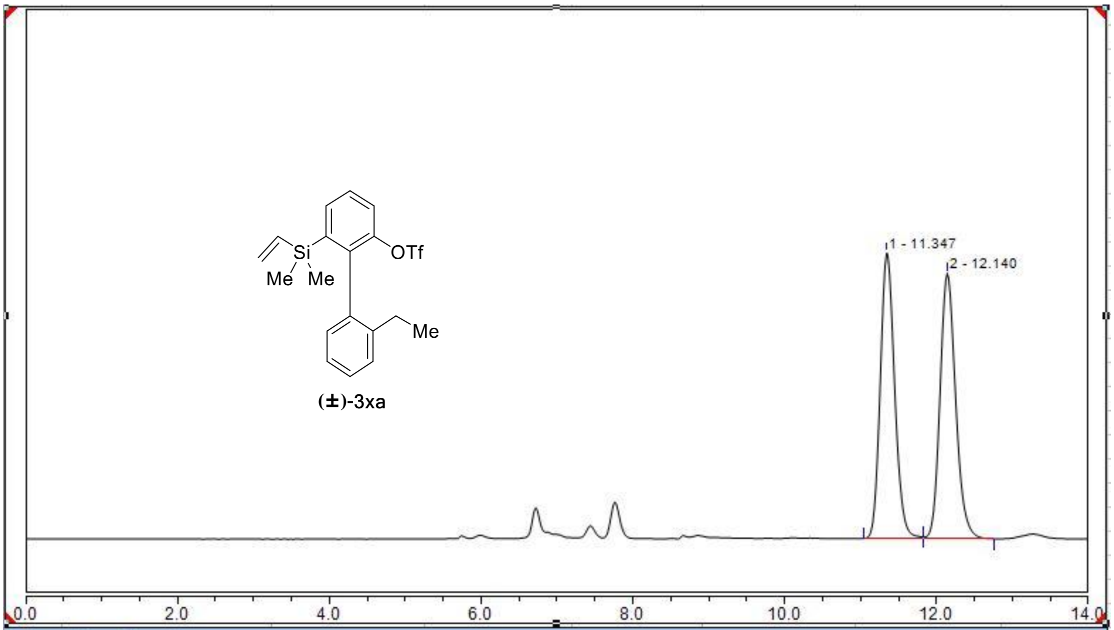
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.840	45.636	186.863	50.48	51.58	n.a.
2		13.400	44.764	175.382	49.52	48.42	n.a.
Total:			**90.401**	**362.244**	**100.00**	**100.00**	



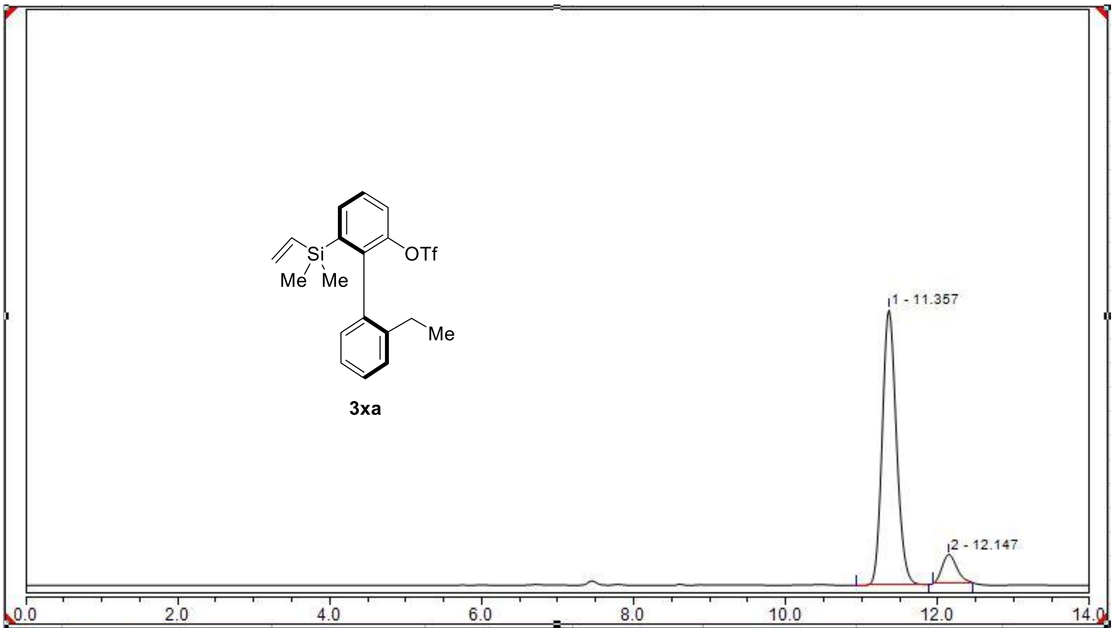
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.233	25.683	114.533	93.64	92.82	n.a.
2		12.760	1.743	8.864	6.36	7.18	n.a.
Total:			**27.426**	**123.397**	**100.00**	**100.00**	



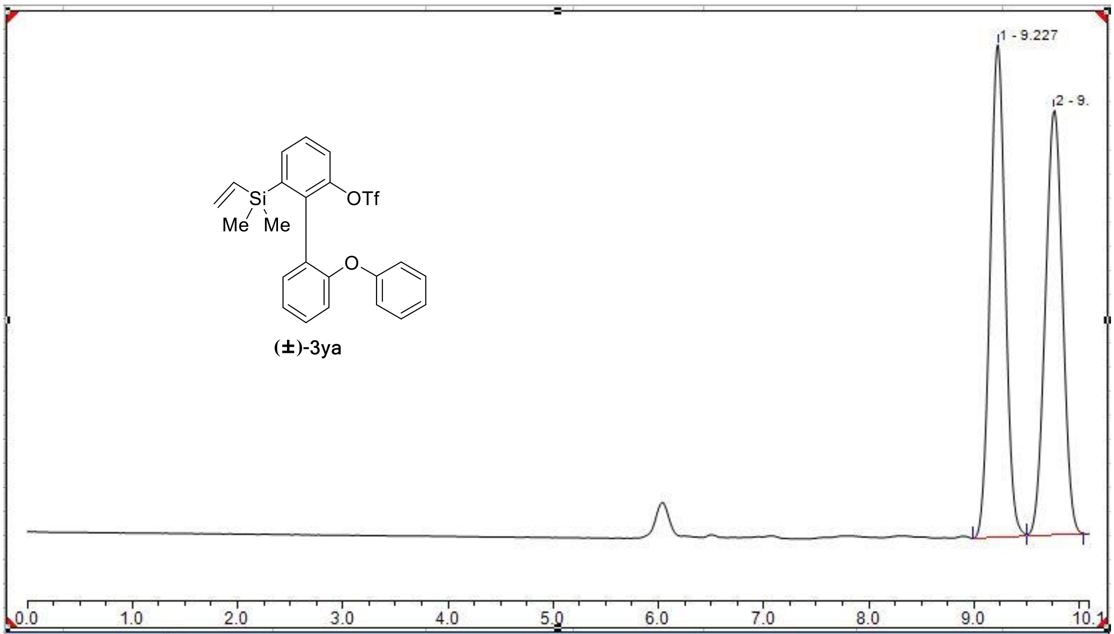
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.347	5.912	26.971	49.73	51.82	n.a.
2		12.140	5.977	25.078	50.27	48.18	n.a.
Total:			**11.889**	**52.049**	**100.00**	**100.00**	



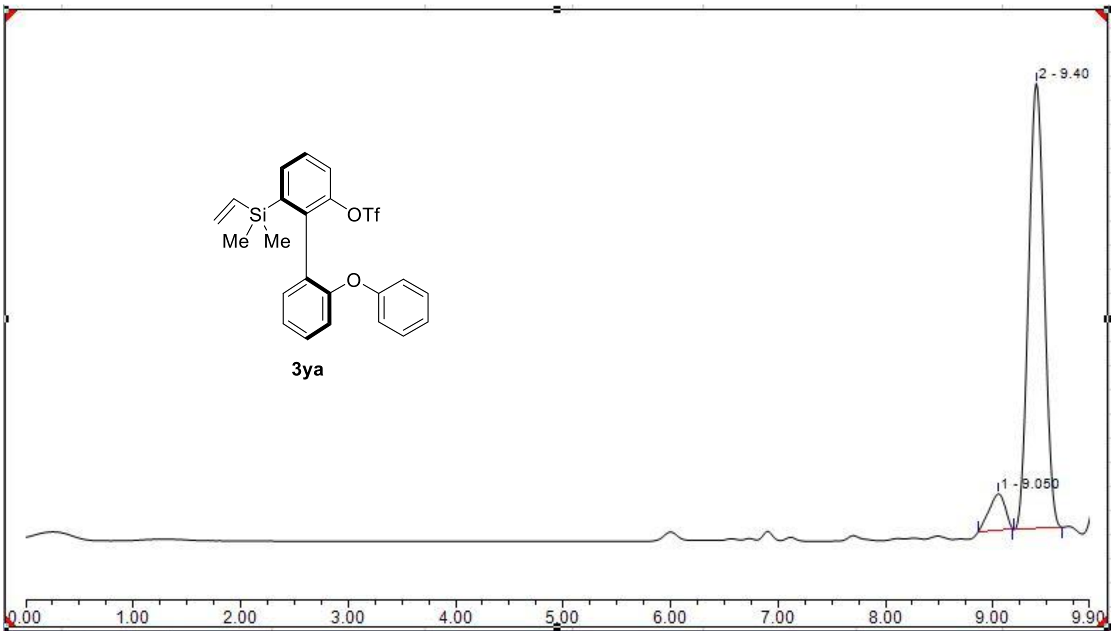
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.357	41.306	191.263	90.40	90.64	n.a.
2		12.147	4.386	19.763	9.60	9.36	n.a.
Total:			**45.692**	**211.026**	**100.00**	**100.00**	



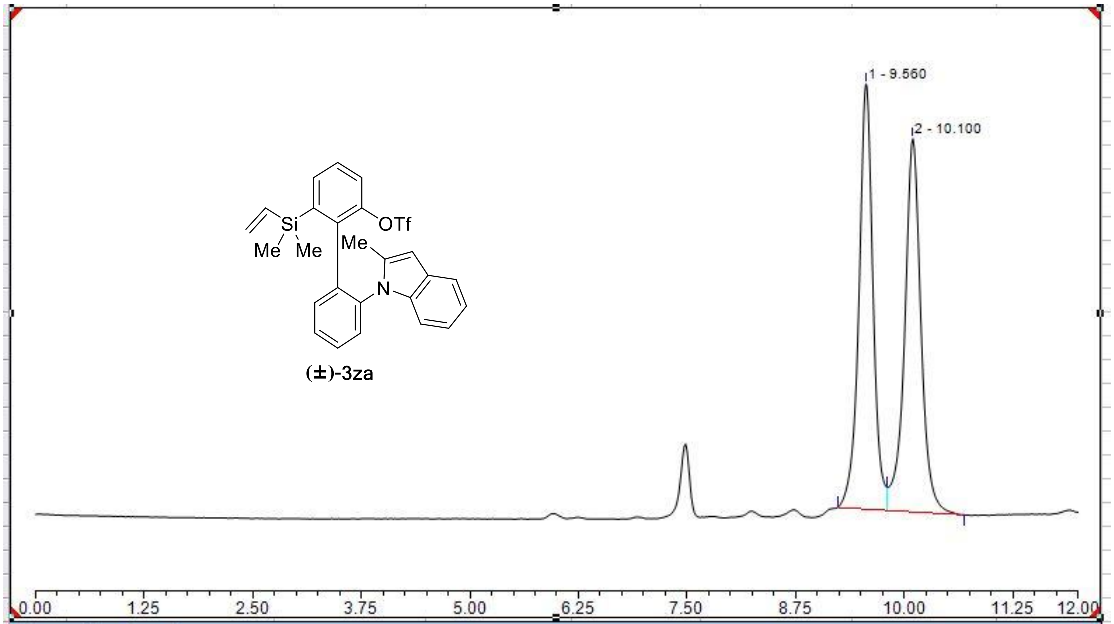
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.227	6.322	38.063	50.40	53.68	n.a.
2		9.763	6.223	32.842	49.60	46.32	n.a.
Total:			**12.544**	**70.905**	**100.00**	**100.00**	



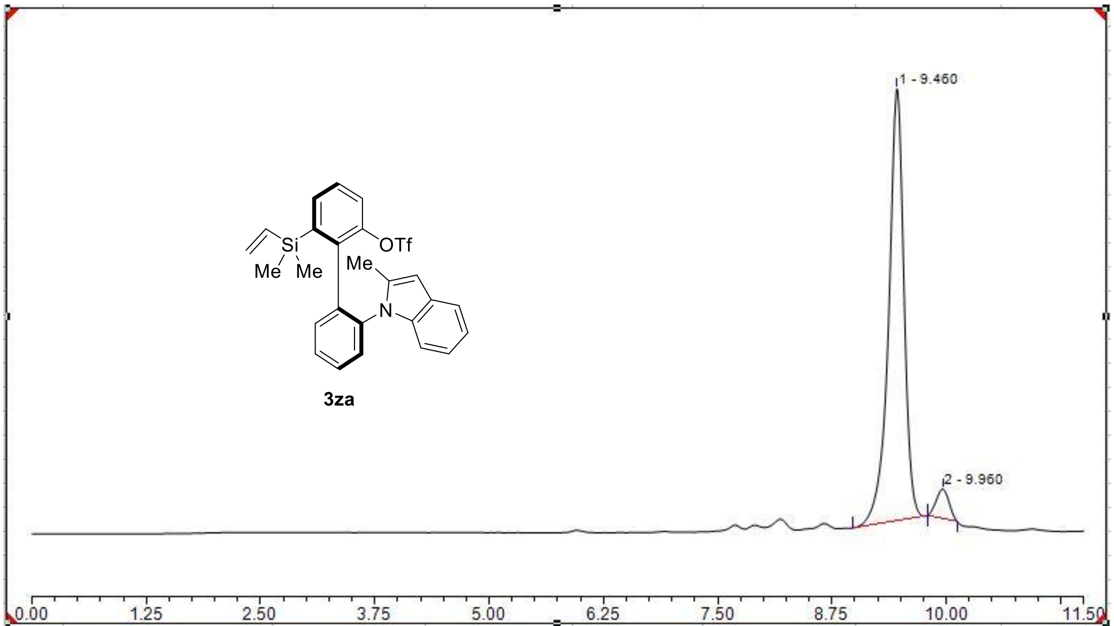
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.050	2.173	12.539	7.79	7.59	n.a.
2		9.403	25.731	152.737	92.21	92.41	n.a.
Total:			**27.904**	**165.277**	**100.00**	**100.00**	



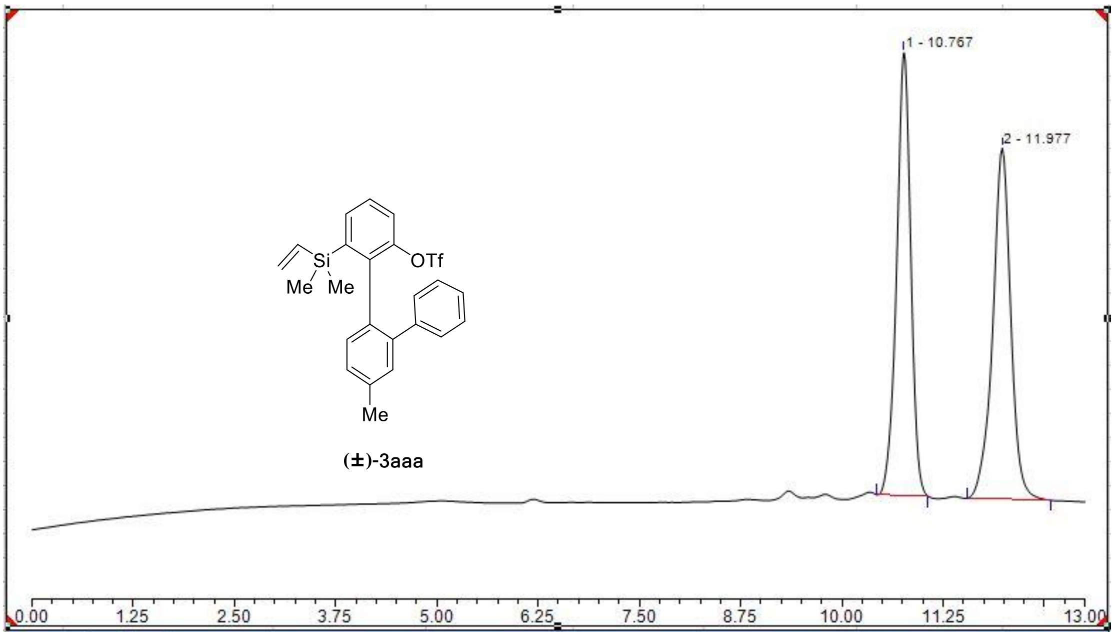
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.560	2.232	11.823	49.60	53.25	n.a.
2		10.100	2.268	10.379	50.40	46.75	n.a.
Total:			**4.500**	**22.203**	**100.00**	**100.00**	



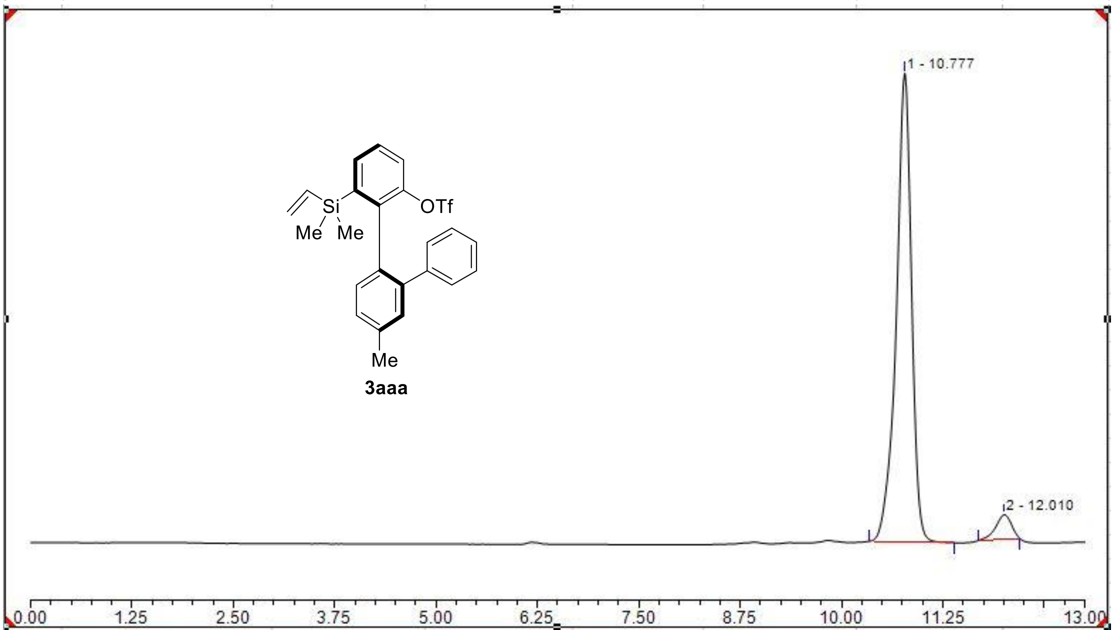
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.460	7.207	37.162	94.59	93.59	n.a.
2		9.960	0.412	2.544	5.41	6.41	n.a.
Total:			**7.619**	**39.707**	**100.00**	**100.00**	



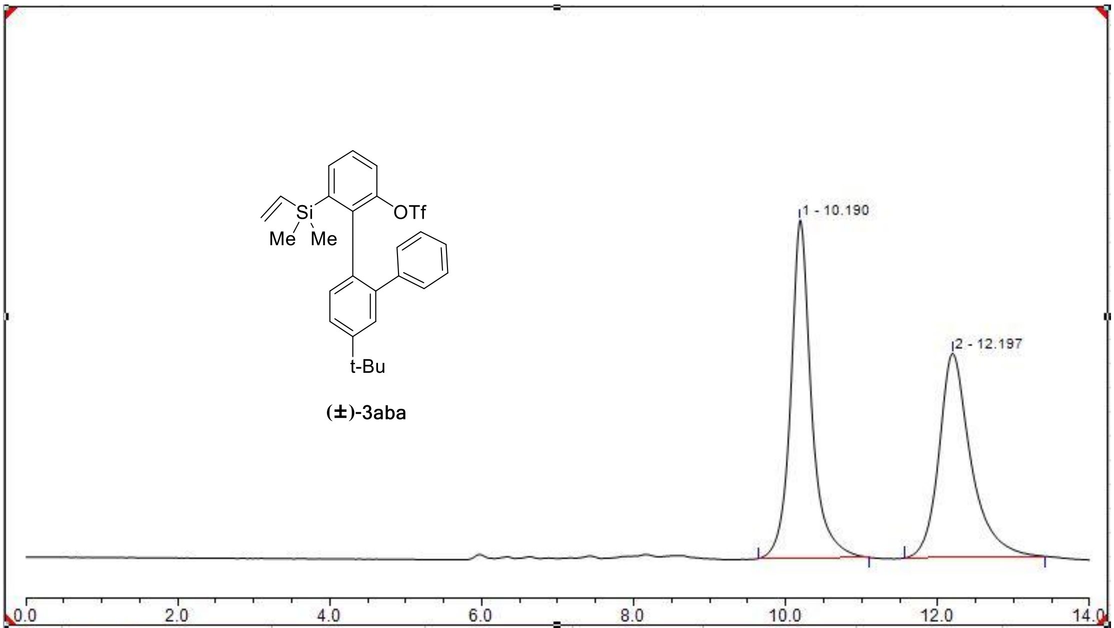
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.767	6.918	34.243	49.73	55.78	n.a.
2		11.977	6.993	27.142	50.27	44.22	n.a.
Total:			**13.911**	**61.385**	**100.00**	**100.00**	



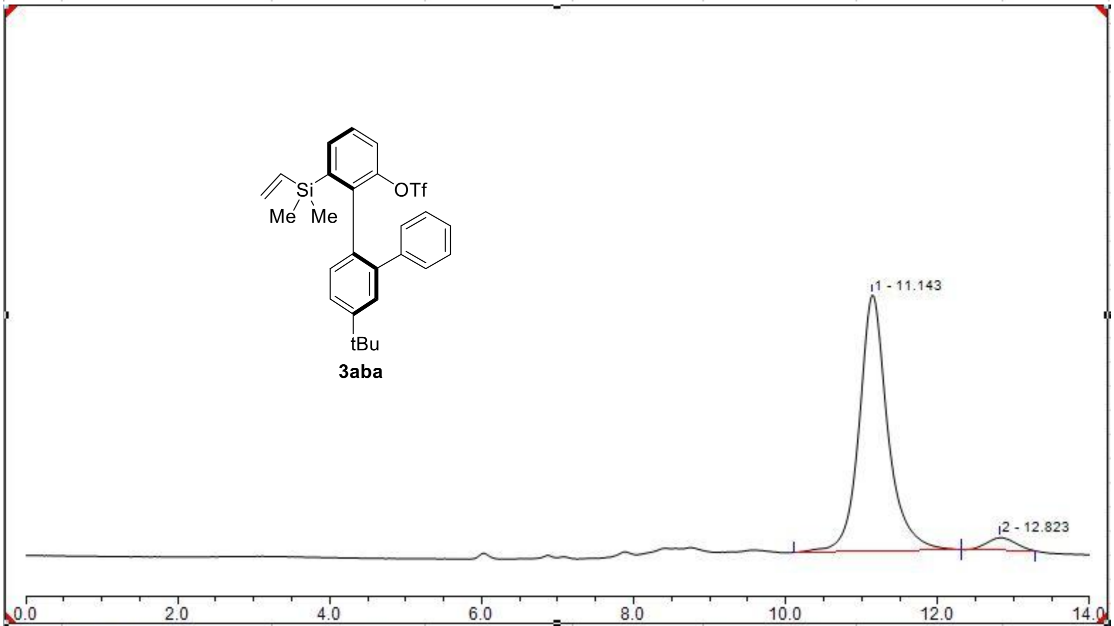
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.777	9.632	44.195	94.80	94.99	n.a.
2		12.010	0.529	2.329	5.20	5.01	n.a.
Total:			**10.160**	**46.524**	**100.00**	**100.00**	



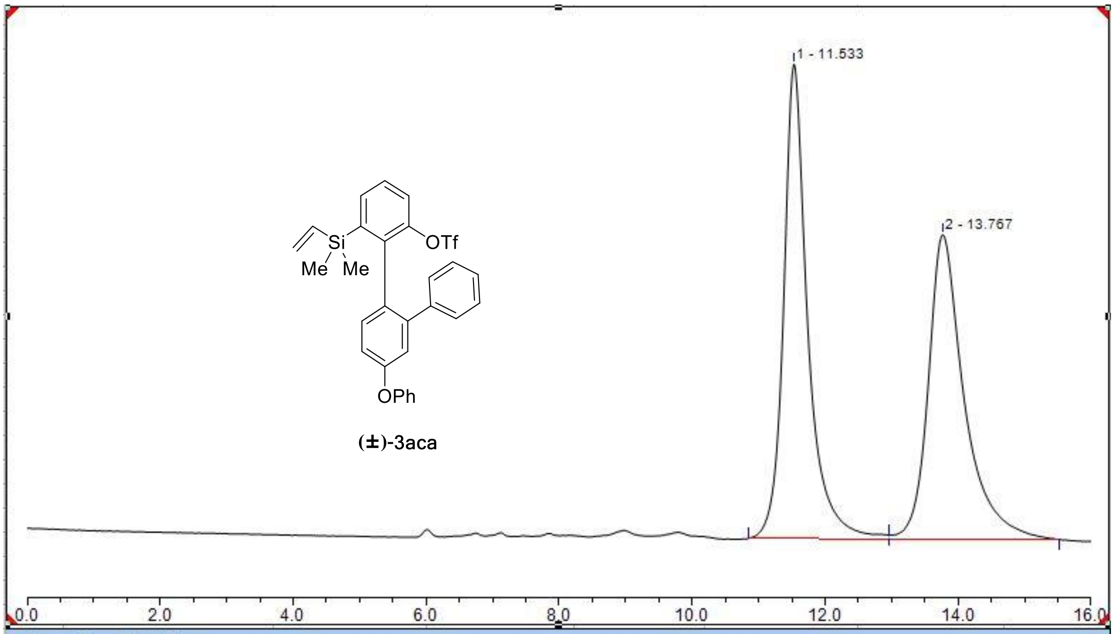
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.190	5.872	18.536	51.83	62.34	n.a.
2		12.197	5.458	11.196	48.17	37.66	n.a.
Total:			**11.330**	**29.732**	**100.00**	**100.00**	



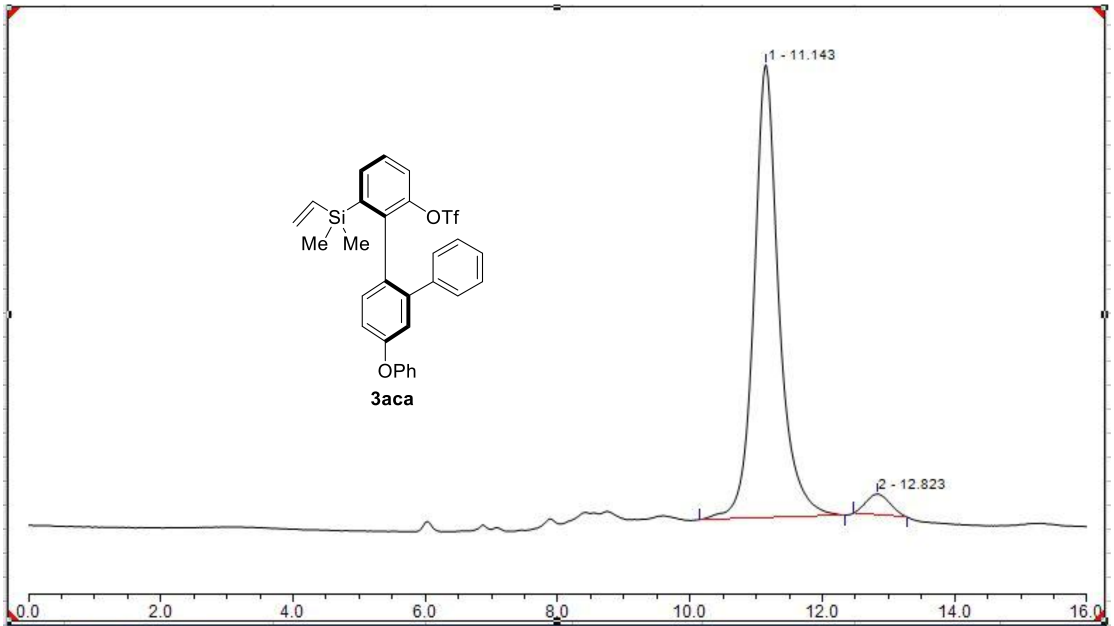
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.143	6.149	14.058	95.30	95.31	n.a.
2		12.823	0.303	0.692	4.70	4.69	n.a.
Total:			**6.453**	**14.751**	**100.00**	**100.00**	



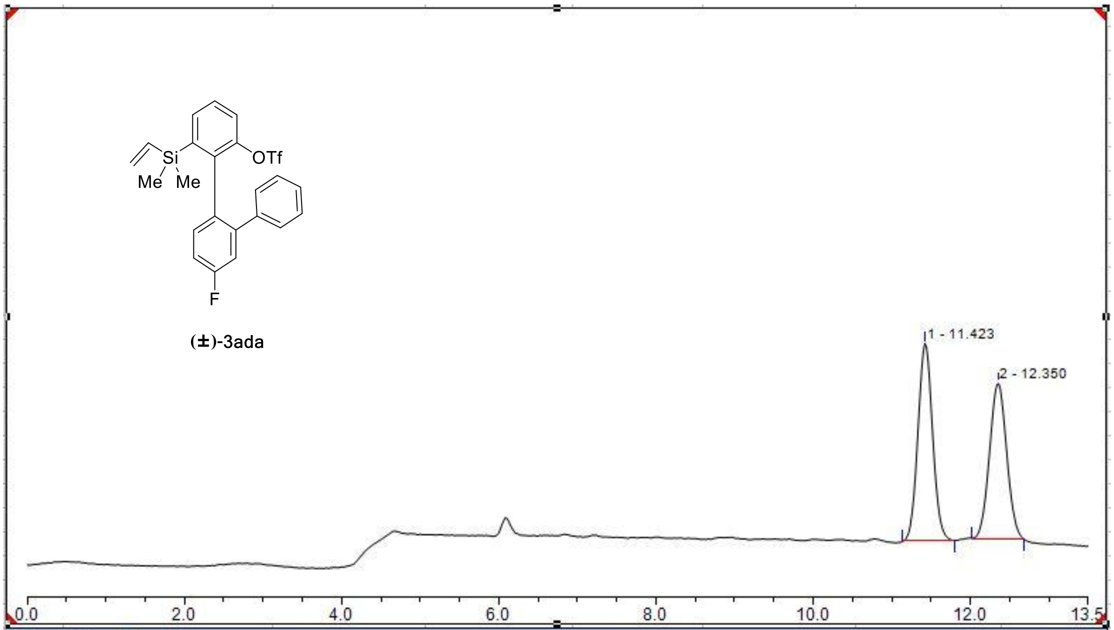
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.533	6.166	14.641	51.23	60.91	n.a.
2		13.767	5.871	9.398	48.77	39.09	n.a.
Total:			**12.038**	**24.039**	**100.00**	**100.00**	



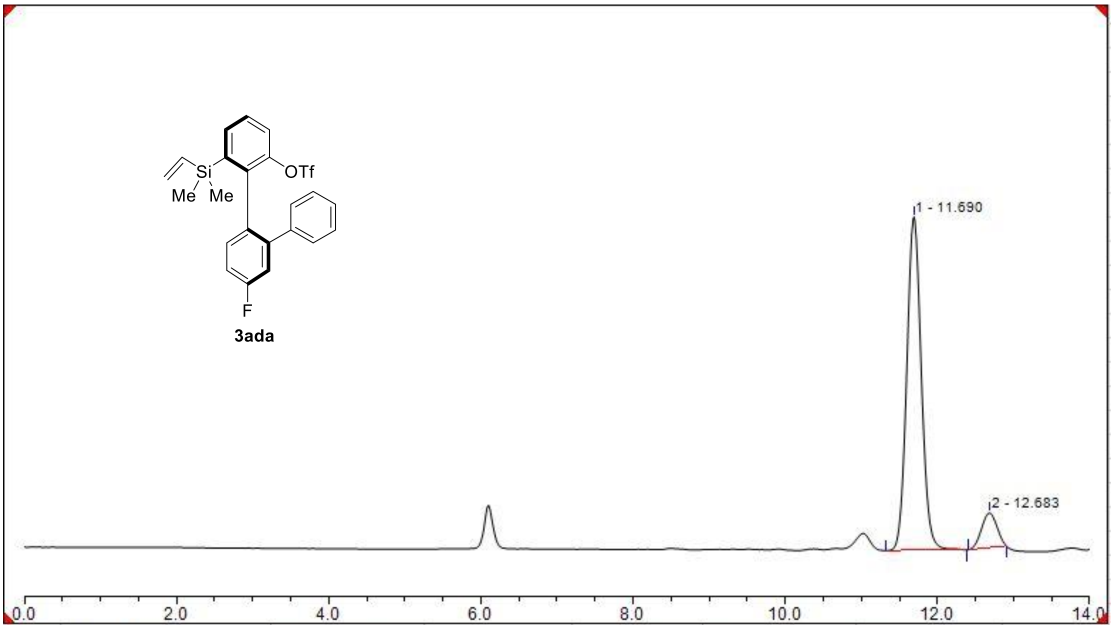
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.143	6.142	14.055	95.80	95.58	n.a.
2		12.823	0.270	0.650	4.20	4.42	n.a.
Total:			**6.412**	**14.705**	**100.00**	**100.00**	



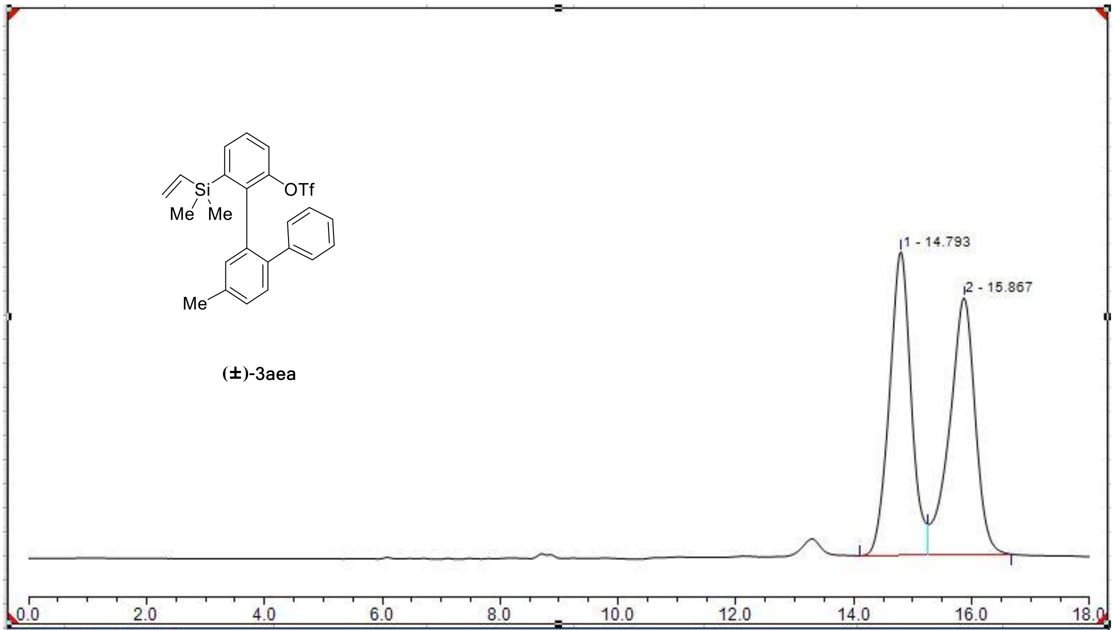
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.423	0.772	3.571	52.04	55.92	n.a.
2		12.350	0.712	2.815	47.96	44.08	n.a.
Total:			**1.484**	**6.386**	**100.00**	**100.00**	

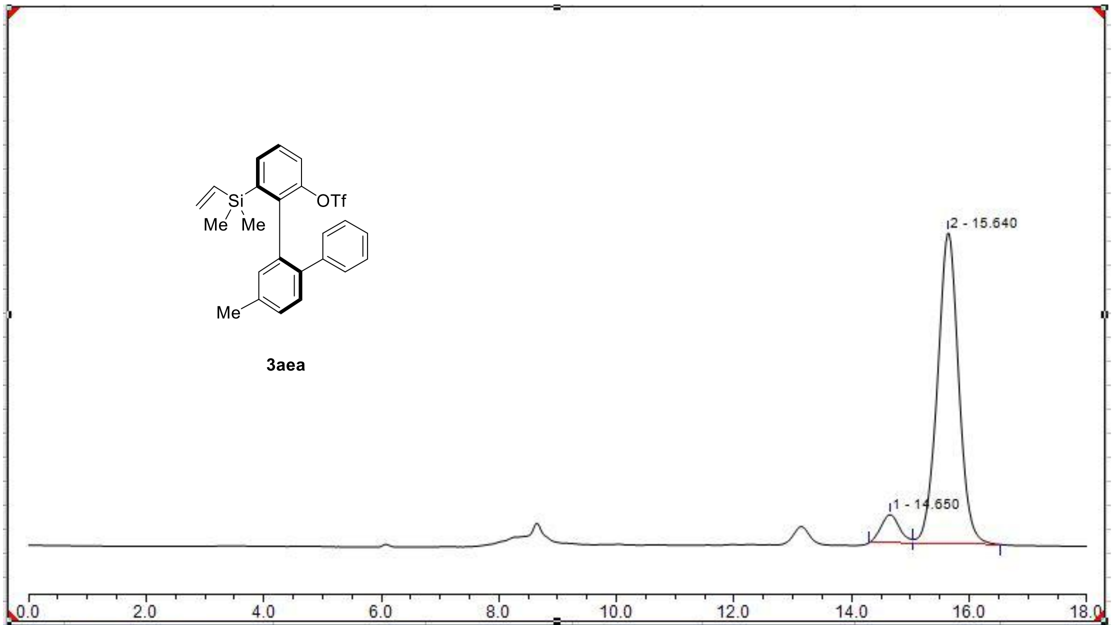


Integration Results

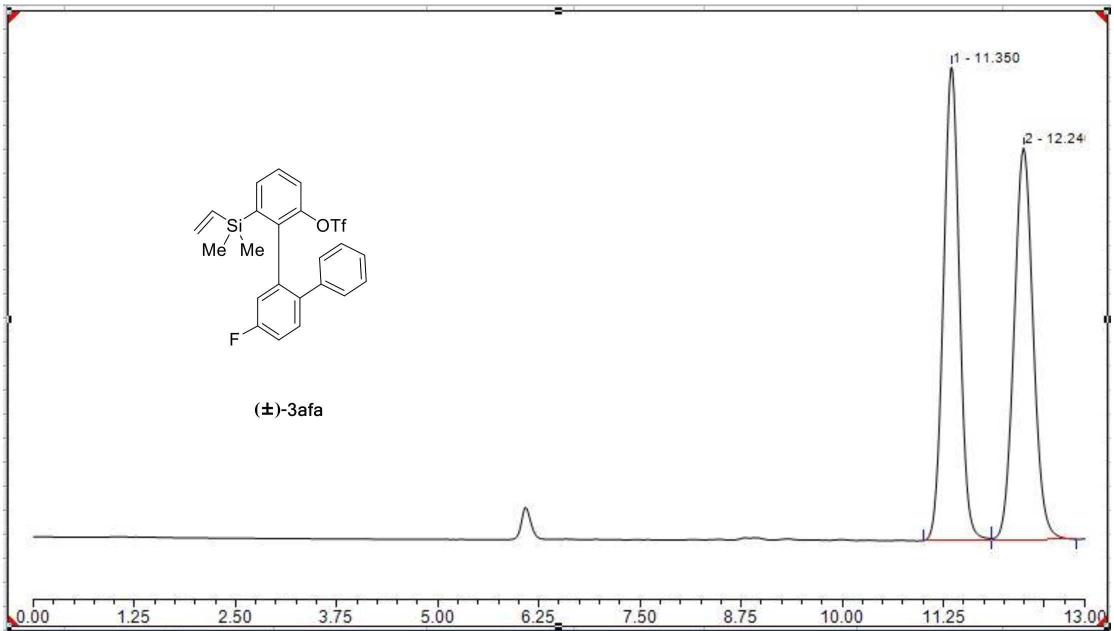
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.690	8.219	37.148	90.11	90.55	n.a.
2		12.683	0.902	3.878	9.89	9.45	n.a.
Total:			**9.121**	**41.025**	**100.00**	**100.00**	



Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.793	18.974	44.461	50.03	54.19	n.a.
2		15.867	18.949	37.579	49.97	45.81	n.a.
Total:			**37.924**	**82.040**	**100.00**	**100.00**	

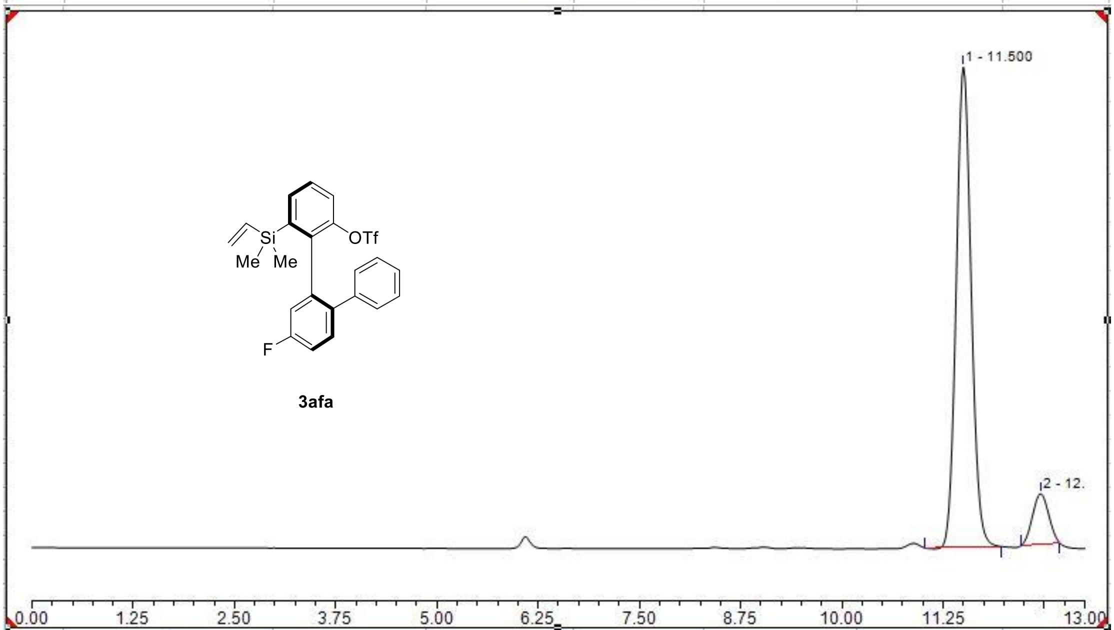


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.650	1.168	3.174	7.42	8.34	n.a.
2		15.640	14.564	34.899	92.58	91.66	n.a.
Total:			**15.731**	**38.073**	**100.00**	**100.00**	



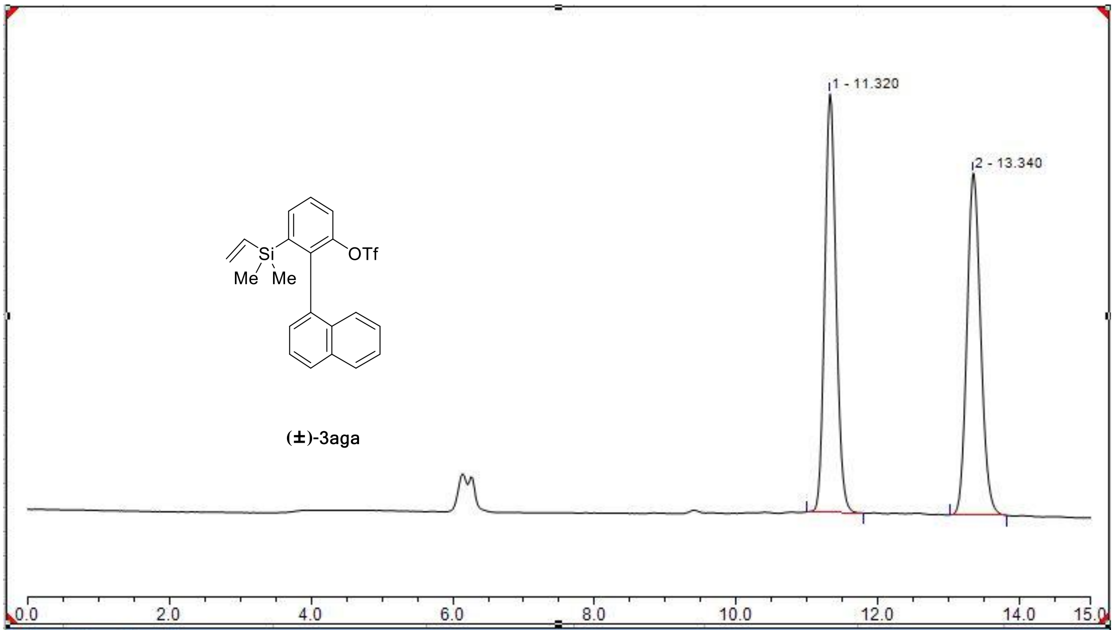
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.350	18.566	81.448	50.19	54.70	n.a.
2		12.240	18.428	67.450	49.81	45.30	n.a.
Total:			**36.994**	**148.898**	**100.00**	**100.00**	



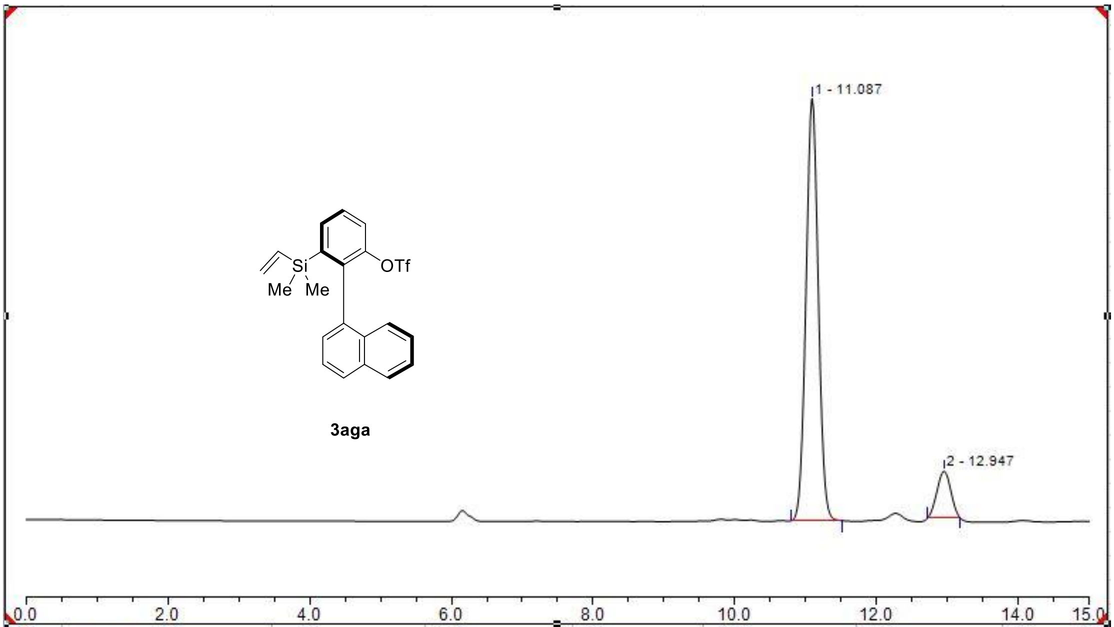
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.500	42.235	197.867	89.78	90.44	n.a.
2		12.453	4.806	20.906	10.22	9.56	n.a.
Total:			**47.040**	**218.773**	**100.00**	**100.00**	



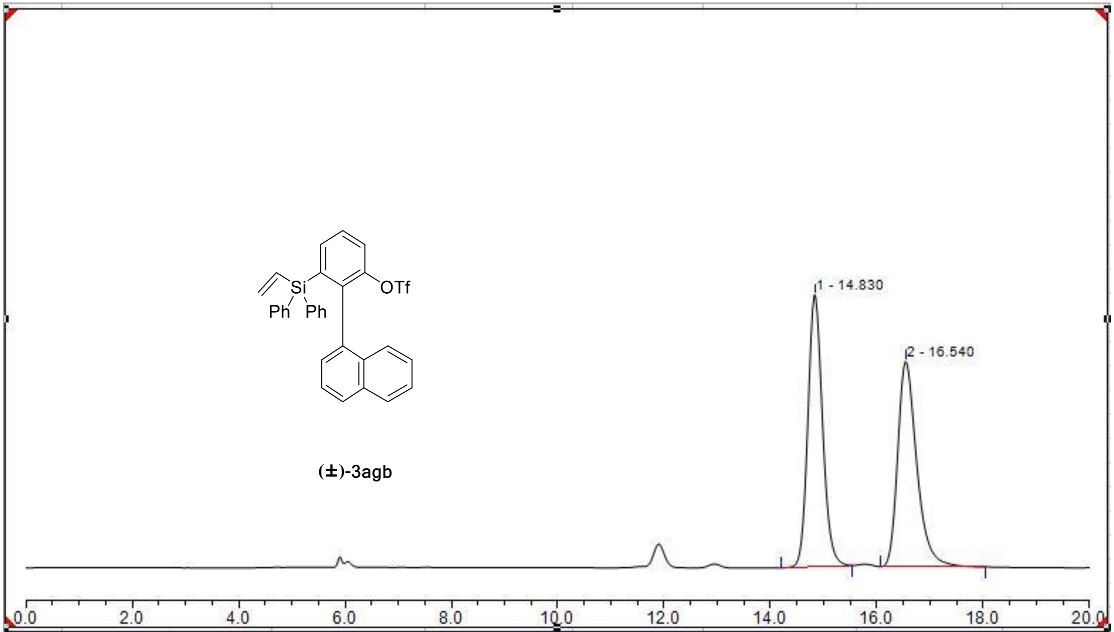
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.320	4.640	25.149	50.15	55.02	n.a.
2		13.340	4.612	20.559	49.85	44.98	n.a.
Total:			**9.252**	**45.708**	**100.00**	**100.00**	



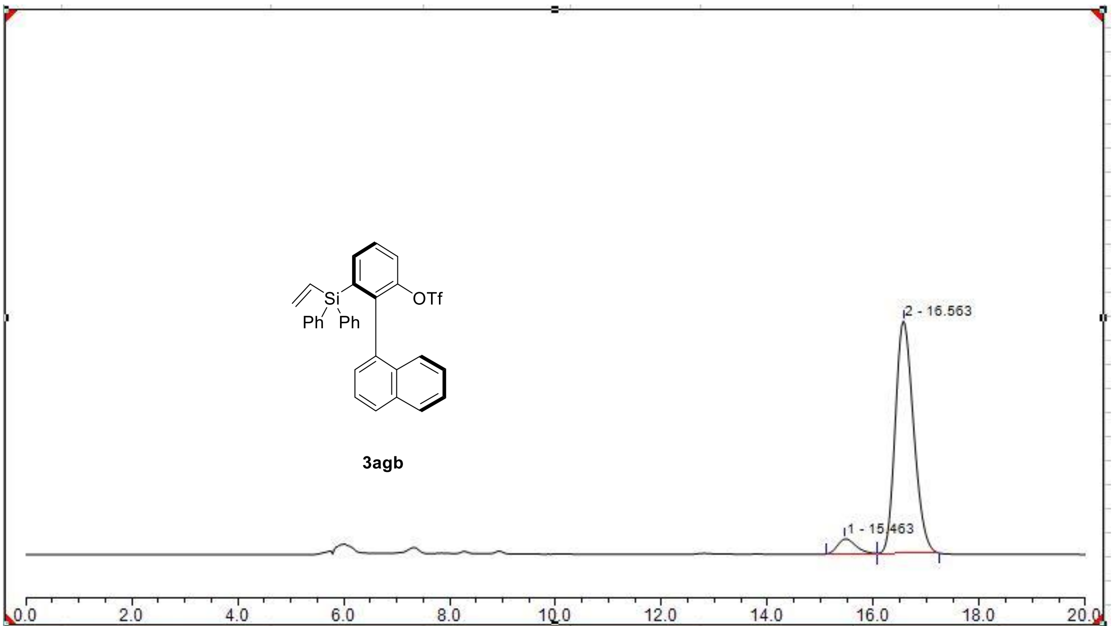
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.087	23.200	115.939	89.10	90.09	n.a.
2		12.947	2.839	12.760	10.90	9.91	n.a.
Total:			**26.039**	**128.699**	**100.00**	**100.00**	



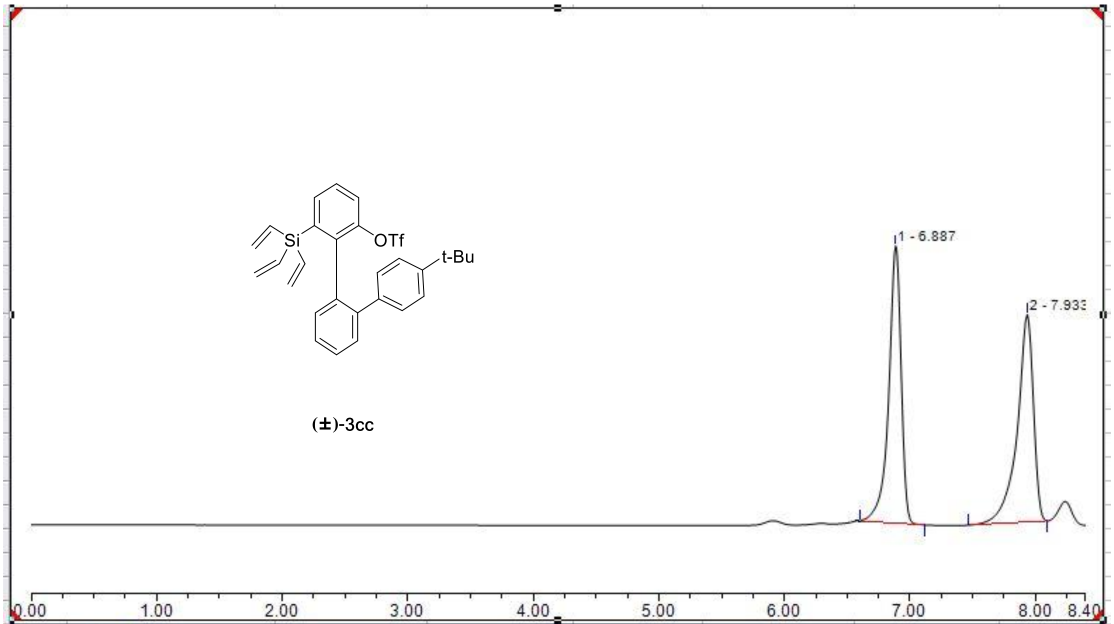
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.830	31.225	97.910	50.43	56.98	n.a.
2		16.540	30.698	73.929	49.57	43.02	n.a.
Total:			**61.924**	**171.839**	**100.00**	**100.00**	



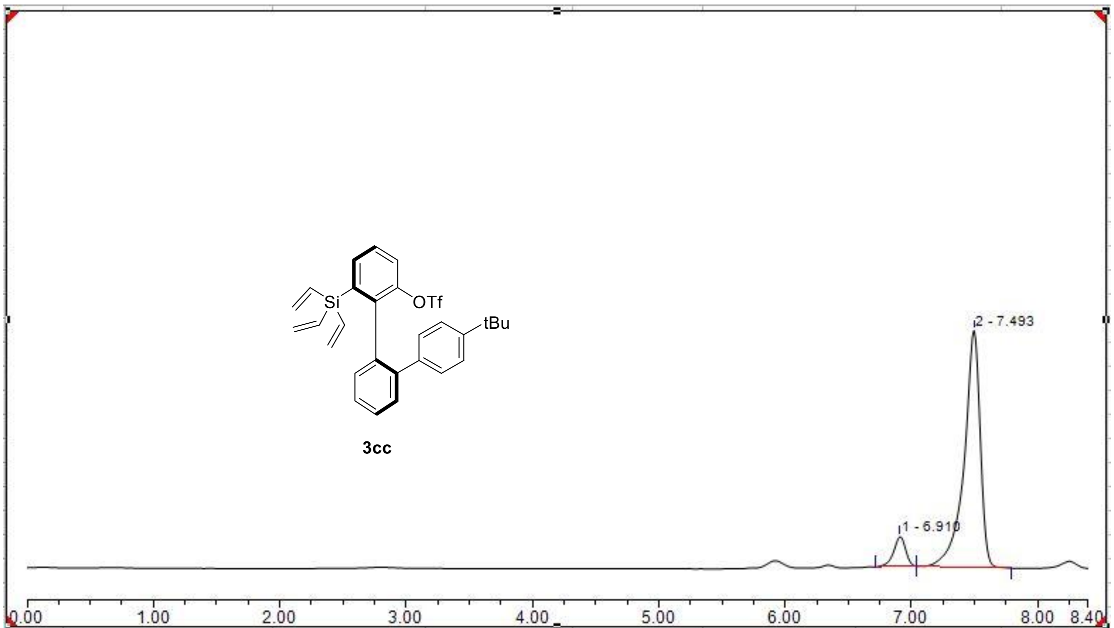
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.463	0.781	1.948	6.10	6.10	n.a.
2		16.563	12.020	30.001	93.90	93.90	n.a.
Total:			**12.800**	**31.949**	**100.00**	**100.00**	



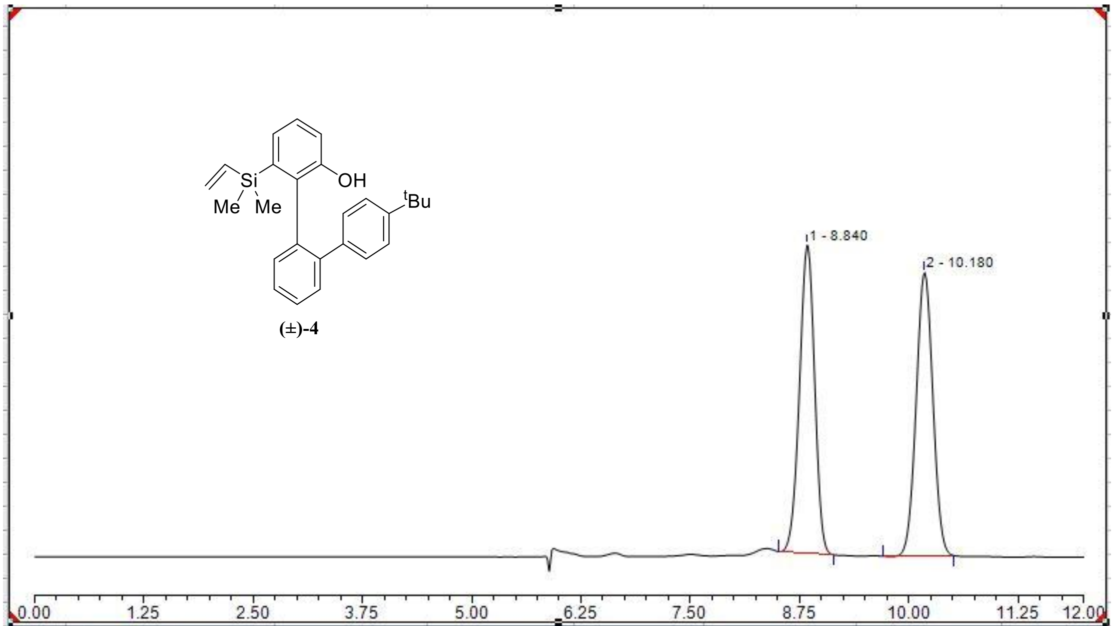
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.887	24.704	216.038	50.56	57.21	n.a.
2		7.933	24.157	161.574	49.44	42.79	n.a.
Total:			**48.861**	**377.611**	**100.00**	**100.00**	



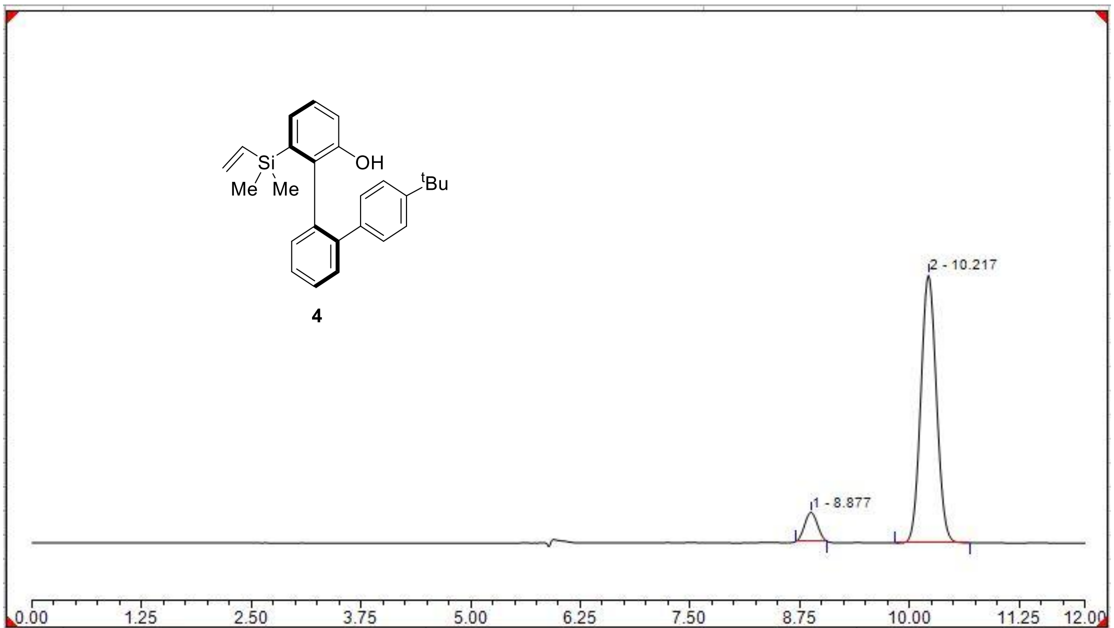
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.910	1.195	10.824	8.63	11.23	n.a.
2		7.493	12.662	85.556	91.37	88.77	n.a.
Total:			**13.857**	**96.380**	**100.00**	**100.00**	



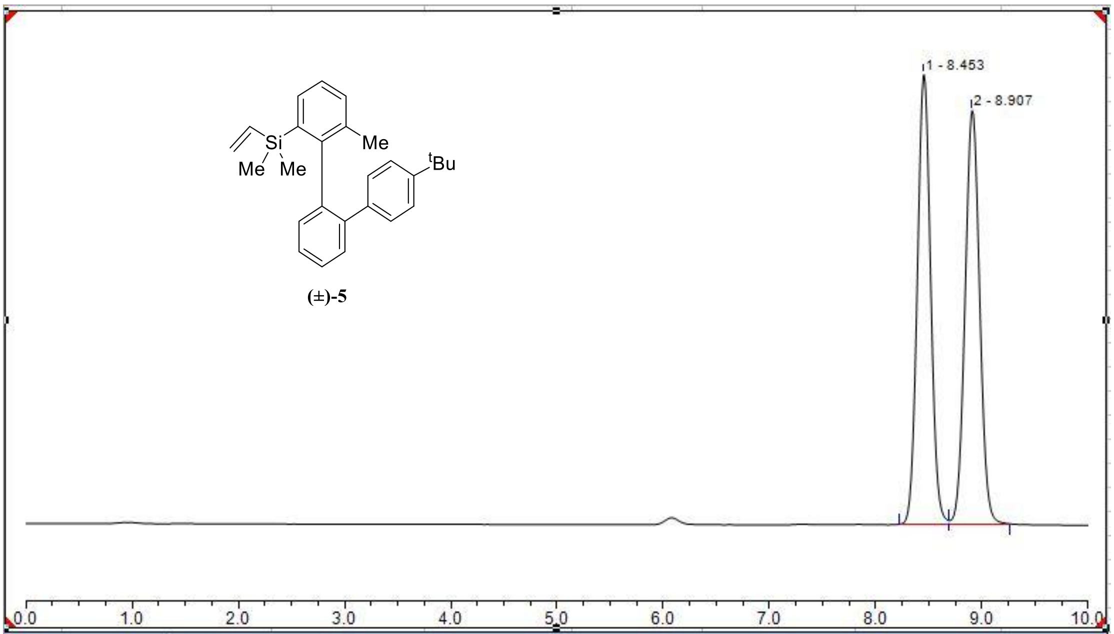
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.840	9.089	45.183	49.66	52.06	n.a.
2		10.180	9.213	41.599	50.34	47.94	n.a.
Total:			**18.302**	**86.781**	**100.00**	**100.00**	



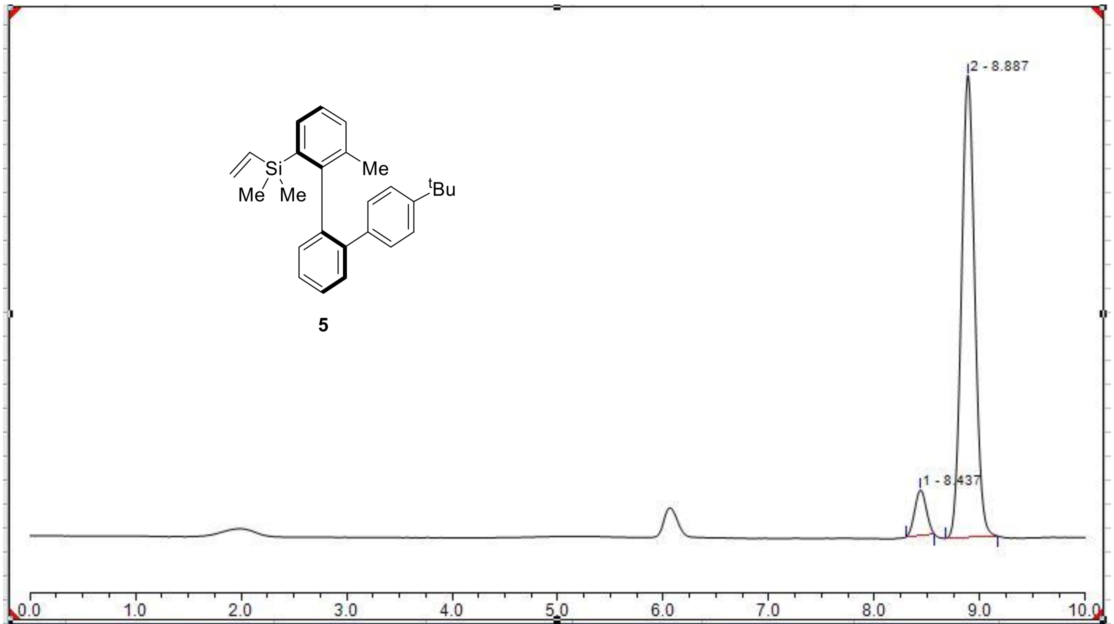
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.877	1.853	10.998	8.14	9.79	n.a.
2		10.217	20.905	101.304	91.86	90.21	n.a.
Total:			**22.758**	**112.302**	**100.00**	**100.00**	



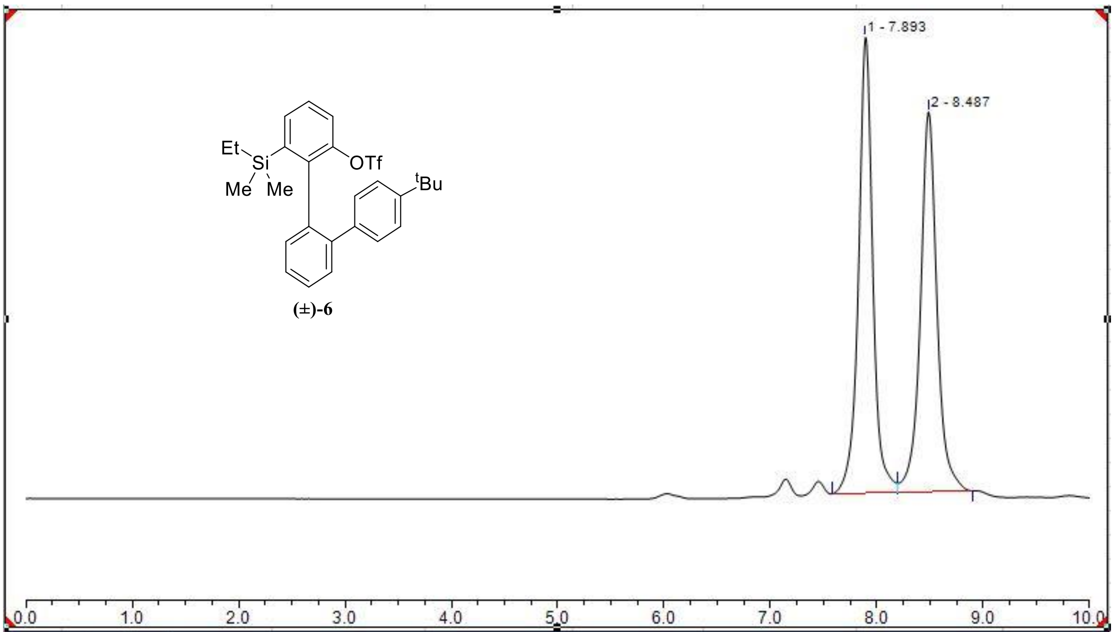
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.453	17.899	123.512	49.80	52.08	n.a.
2		8.907	18.040	113.634	50.20	47.92	n.a.
Total:			**35.939**	**237.147**	**100.00**	**100.00**	



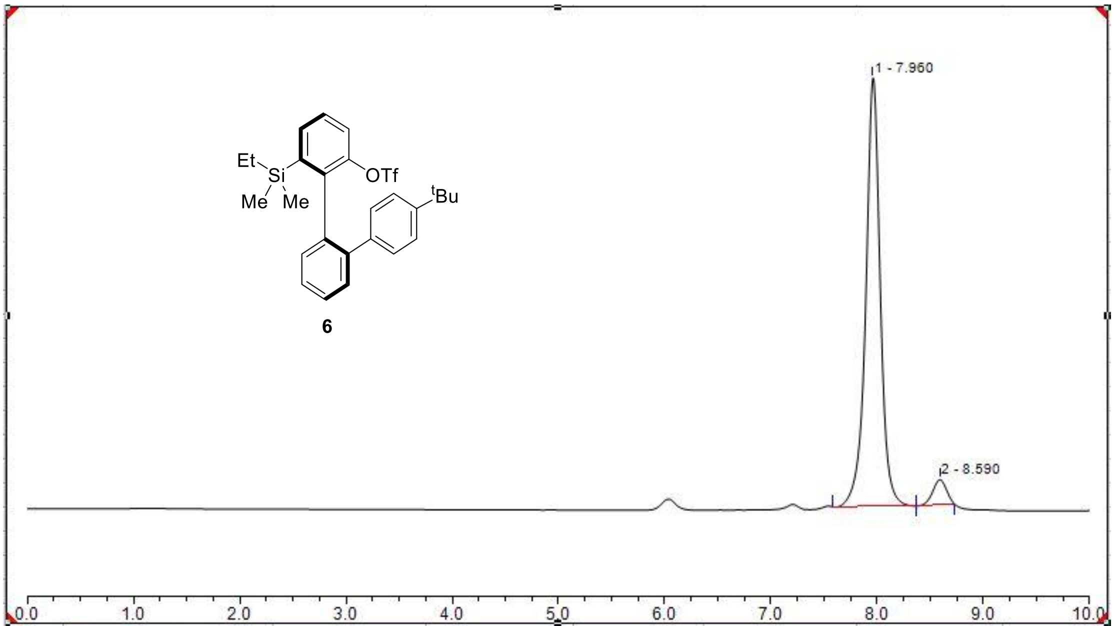
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.437	0.545	4.344	7.87	9.00	n.a.
2		8.887	6.378	43.913	92.13	91.00	n.a.
Total:			**6.923**	**48.257**	**100.00**	**100.00**	



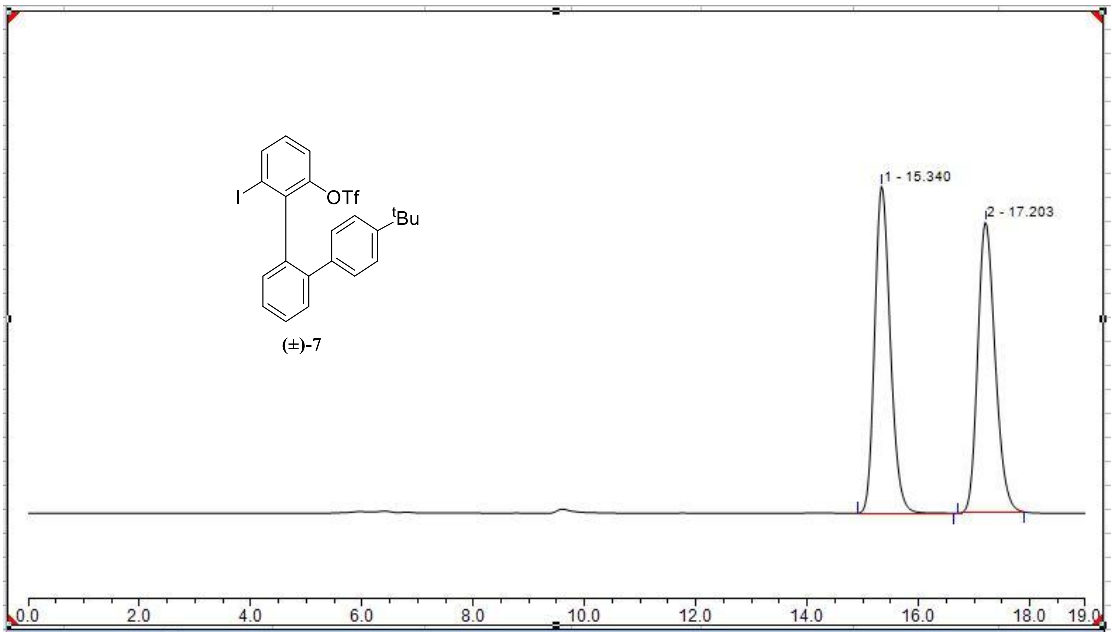
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.893	36.641	234.574	50.85	54.55	n.a.
2		8.487	35.412	195.449	49.15	45.45	n.a.
Total:			**72.053**	**430.023**	**100.00**	**100.00**	



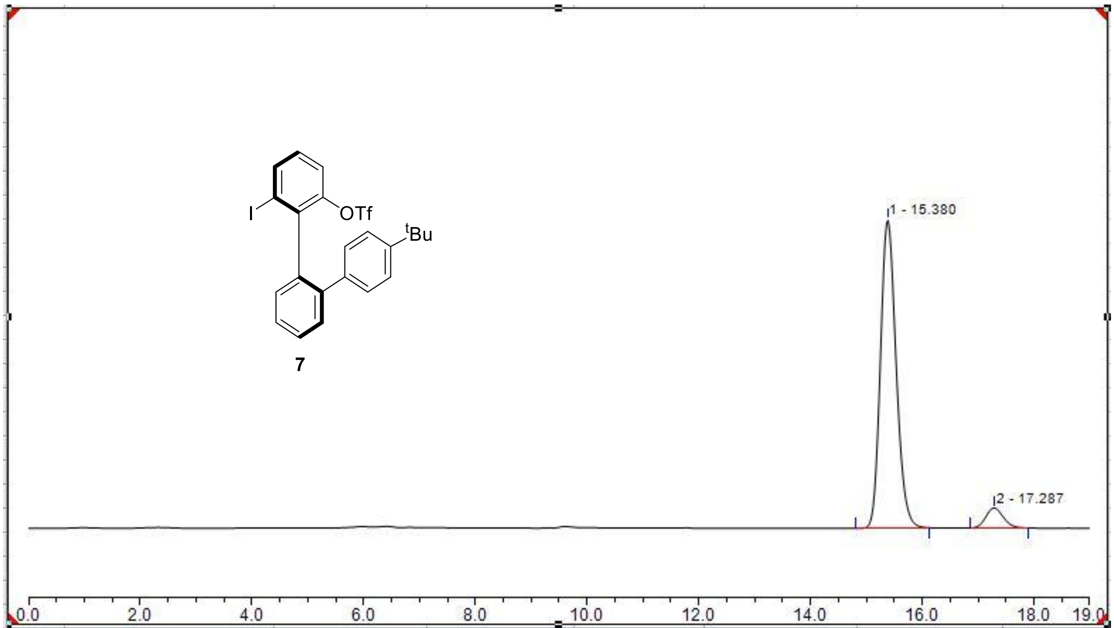
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.960	16.251	103.072	94.83	94.50	n.a.
2		8.590	0.885	5.997	5.17	5.50	n.a.
Total:			**17.136**	**109.069**	**100.00**	**100.00**	



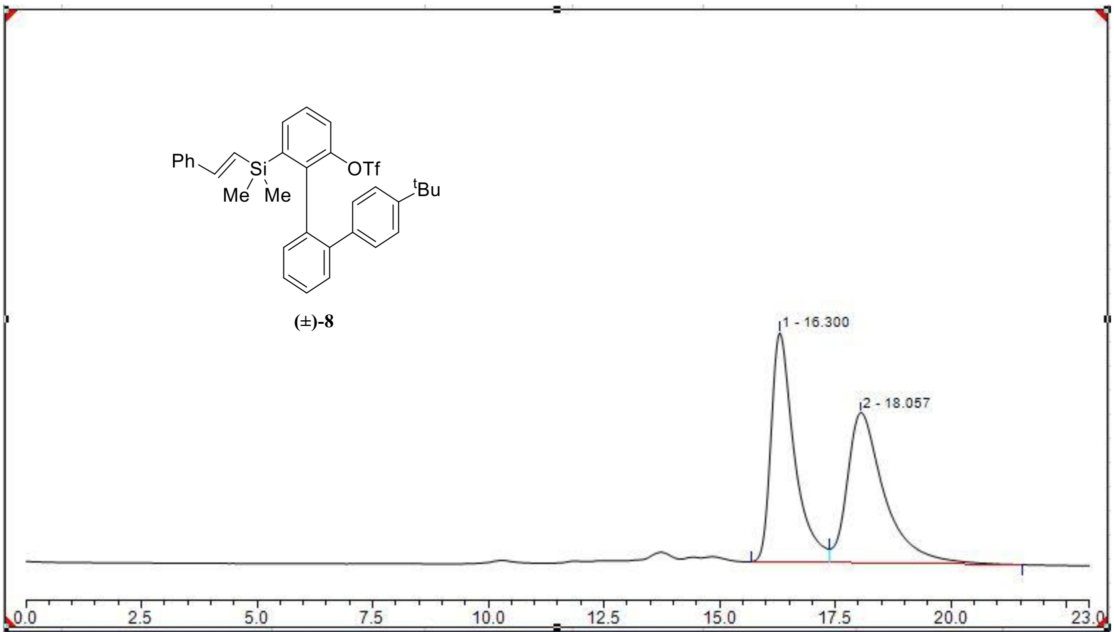
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.340	66.096	203.272	50.21	52.96	n.a.
2		17.203	65.541	180.579	49.79	47.04	n.a.
Total:			**131.637**	**383.851**	**100.00**	**100.00**	



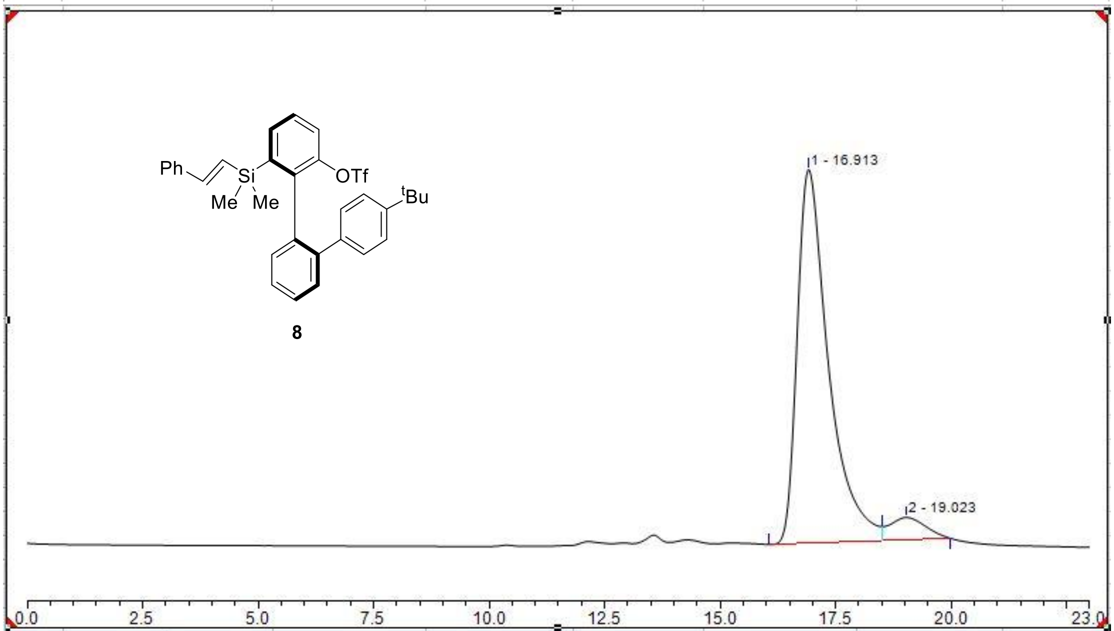
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		15.380	77.262	238.260	93.25	93.88	n.a.
2		17.287	5.596	15.521	6.75	6.12	n.a.
Total:			**82.858**	**253.780**	**100.00**	**100.00**	



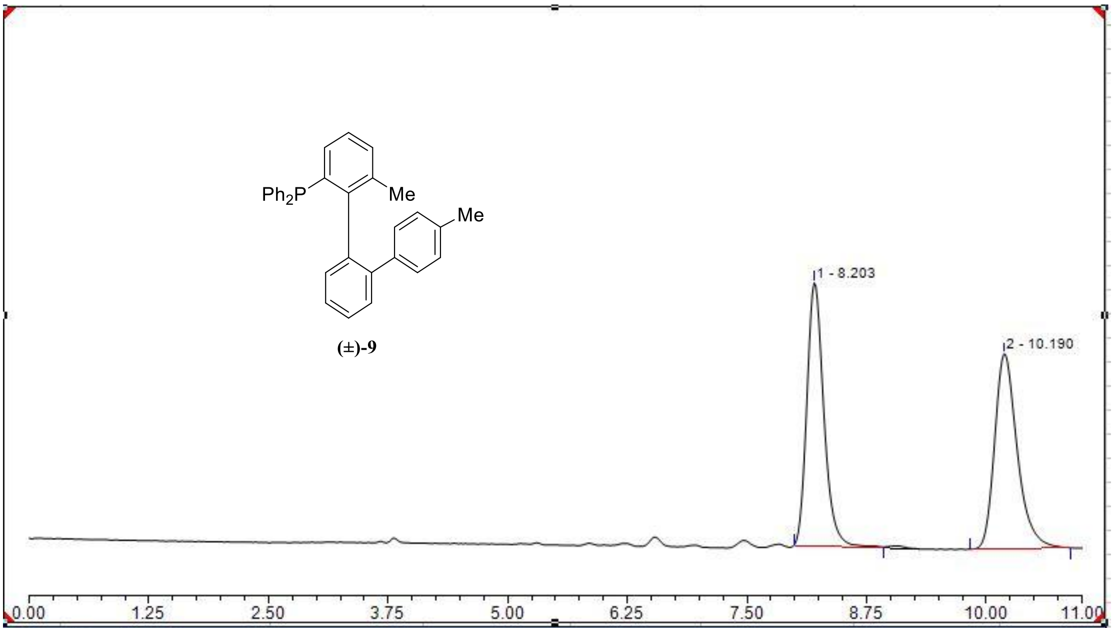
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.300	19.538	33.389	48.84	60.38	n.a.
2		18.057	20.467	21.910	51.16	39.62	n.a.
Total:			**40.005**	**55.299**	**100.00**	**100.00**	



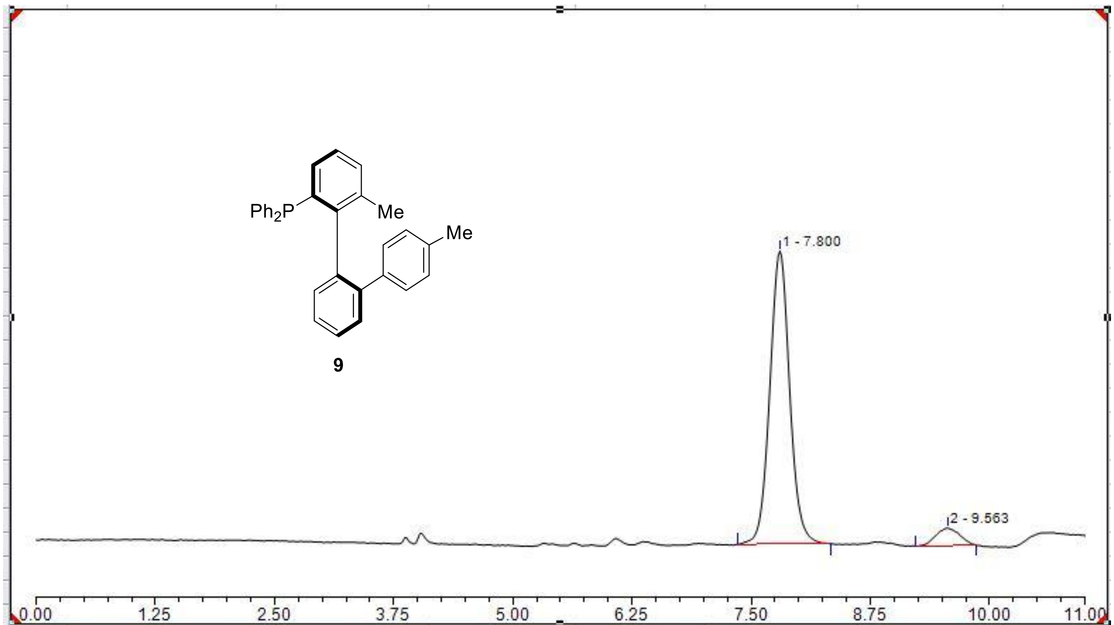
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.913	55.478	70.623	93.53	94.33	n.a.
2		19.023	3.835	4.243	6.47	5.67	n.a.
Total:			**59.313**	**74.865**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.203	2.055	9.978	50.41	57.46	n.a.
2		10.190	2.021	7.386	49.59	42.54	n.a.
Total:			**4.076**	**17.364**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.800	1.340	5.557	93.16	94.33	n.a.
2		9.563	0.098	0.334	6.84	5.67	n.a.
Total:			**1.438**	**5.891**	**100.00**	**100.00**	