Supporting Information

Palladium-Catalyzed Cyclization Reaction of 1,6-Enynes and Disilanes to Synthesize of Silyl Benzofurans

Bo Zhao,[a,‡] Tianqiang Wang,[b,‡] Jinyao Xie,[a] Guojun Yu,[c] Guangwei Hu,[a] Jiaze Qin,[a] Chengcheng Zhang,[a] Rulong Yan[a,*]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000 Gansu, China.

[b] Chengdu Guibao Science and Technology Co., Ltd, Chengdu 610041 Sichuan, China.

[c] Jinchuan Nickel Capital Industrial Co., Ltd, Jinchang 737100 Gansu, China.

‡ These authors contributed equally.

* Corresponding author: E-mail: yanrl@lzu.edu.cn; Fax: +81-931-8912596.

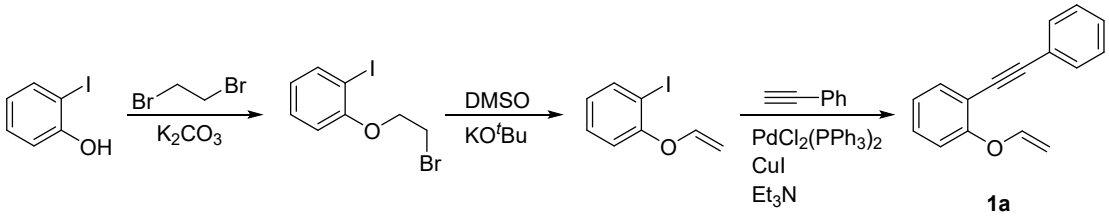
Table of Contents

I. General remark

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 M and Mercury 300 M in $CDCl_3$. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of ^{1}H NMR and ^{13}C NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. Unless otherwise noted, commercially available reagents and solvents were used without further purification.

II. Experimental Procedures

General procedure for the synthesis of substrate



Substrates 1-(phenylethynyl)-2-(vinyloxy) benzenes **1a**-**1t** were prepared by the literature procedures.[1]

Synthesis of 1-(2-Bromoethoxy)-2-iodobenzene from 2-Iodophenol

To a stirred solution of 2-iodophenol (4.55 mmol, 1.00 g) and 1,2-dibromoethane (22.75 mmol, 2 mL) in acetone (50 mL) was added K_2CO_3 (9.10 mmol, 1.26 g). The resulting mixture was stirrer at room temperature for overnight. The reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (20 mL x 3). The organic layer was washed with brine (10 mL), dried over Na_2SO_4 and concentrated by rotary evaporator under reduced pressure. The crude product was purified by column chromatography over silica gel using hexane on silica gel. A white solid of 1-(2-bromoethoxy)-2-iodobenzene was obtained in 76% yield (1.13 g).

Synthesis of 1-Iodo-2-(vinyloxy)benzene from 1-(2-Bromoethoxy)-2-iodobenzene

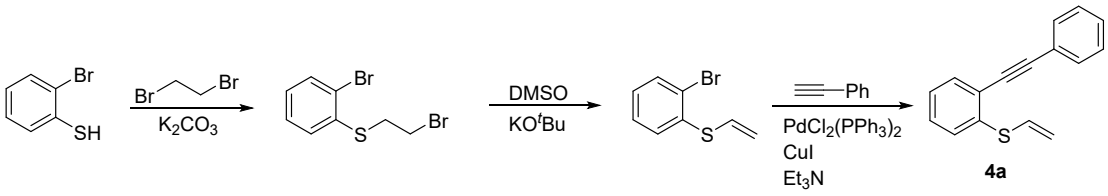
A solution of 1-(2-bromoethoxy)-2-iodobenzene (1.33 mmol, 436 mg) in DMSO (10 mL) was stirred at 0 ℃. To this stirrer solution was added KO^{t}Bu (2.0 mmol, 224 mg) in portions under nitrogen. The resulting mixture was stirred at room temperature for 2

h. The reaction was quenched with water (100 mL) and extracted with CH_2Cl_2 (50 mL x 4). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated by rotary evaporator under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane. 1-Iodo-2-(vinyloxy)benzene was obtained as a yellow oil in 68% yield (415 mg).

Synthesis of 1-(Phenylethynyl)-2-(vinyloxy) benzene (1a) from 1-Iodo-2-(vinyloxy)benzene

To a solution of 1-iodo-2-(vinyloxy)benzene (1.00 mmol, 246 mg) and phenyl acetylene (1.10 mmol, 112 mg) in trimethylamine (degassed, 8 mL) was added $PdCl_2(PPh_3)$ (0.02 mmol, 14 mg) and CuI (0.04 mmol, 8 mg) under nitrogen. The resulting mixture was stirrer at room temperature for 6 h. The reaction mixture was filtered and washed with diethyl ether. The combined filtrate was concentrate under reduced pressure and the residue was purified by column chromatography over silica gel using hexane. A yellow oil of **1a** was obtained in 85% yield (187 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.49-7.43 (m, 3 H), 7.30-7.19 (m, 4 H), 7.01-6.93 (m, 2 H), 6.62-6.57 (m, 1 H), 4.74-4.69 (m, 1 H), 4.42-4.38 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.6, 133.5, 131.6, 129.6, 128.3, 123.3, 117.2, 114.5, 95.1, 95.0, 94.0, 84.9.

Preparation of (2-(Phenylethynyl)phenyl)(vinyl)sulfane (4a)



(2-(Phenylethynyl)phenyl)(vinyl)sulfane substrates were prepared by the literature procedure[2].

Preparation of (2-Bromoethyl)(2-bromophenyl)sulfane from 2-Bromothiophenol

To a stirred solution of 2-bromothiophenol (5.29 mmol, 1.00 g) and 1, 2-dibromoethane (26.45 mmol, 2.3 mL) in acetone (50 mL) was added K_2CO_3 (10.58 mmol, 1.46 g). The resulting mixture was stirrer at room temperature for overnight. The reaction was quenched with water (10 mL) and extracted with CH_2Cl_2 (20 mL x 3). The

organic layer was washed with brine (50 mL), dried over Na_2SO_4 and concentrate by rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel using hexane. A white solid was obtained in 98% yield (1.24 g).

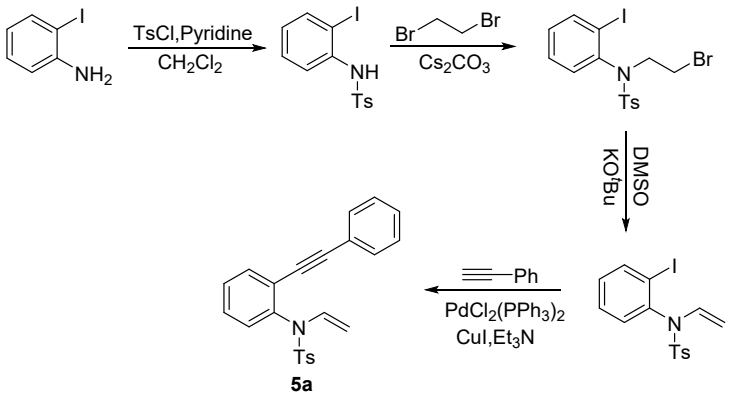
Preparation of (2-Bromophenyl)(vinyl)sulfane from (2-Bromoethyl)(2-bromophenyl)sulfane

A solution of (2-bromoethyl)(2-bromophenyl)sulfane (3.89 mmol, 1.15 g) in DMSO (10 mL) was stirred at 0 ºC. To this stirrer solution was added KO^{t}Bu (5.06 mmol, 0.568 g) in portions under nitrogen. The resulting mixture was stirrer at room temperature for 2h. The reaction was quenched with water (100 mL) and extracted with CH_2Cl_2 (50 mL x 4). The organic layer was washed with brine (100 mL) dried over Na_2SO_4 and concentrate by rotary evaporator under vacuum. The product was purified by column chromatography on silica gel using hexane. A yellow oil of 2-Bromophenyl)(vinyl)sulfane was obtained in 67% yield (560 mg).

Preparation of (2-(Phenylethynyl)phenyl)(vinyl)sulfane from (2-Bromophenyl)(vinyl)sulfane

To a solution of (2-bromophenyl)(vinyl)sulfane (1.5 mmol, 323 mg) and phenyl acetylene (2.25 mmol, 230 mg) in trimethylamine (degassed, 8 mL) was added $PdCl_2(PPh_3)$ (0.045 mmol, 32 mg,) and CuI (0.09 mmol, 18 mg) under nitrogen. The resulting mixture was stirrer at 80 ℃ for 5 h, progress of reaction was monitored by TLC. After completion, reaction allowed to cool to room temperature. The reaction mixture was filtered and washed with diethyl ether. The combined filtrate was concentrate and the residue was purified by column chromatography on silica gel using hexane. A yellow oil of **4a** was obtained in 70% yield (250 mg). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.58-7.51 (m, 3 H), 7.35-7.32 (m, 4 H), 7.29-7.25 (m,1 H), 7.21-7.16 (m, 1 H), 6.23-6.56 (m, 1 H), 5.56-5.52 (m, 1 H), 5.50-5.48 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 138.0, 132.6, 131.6, 130.3, 128.7, 128.5, 128.5, 126.2, 123.2, 123.0, 118.1, 95.6, 87.0.

Preparation of 4-Methyl-*N*-(2-(phenylethynyl)phenyl)-*N*-vinylbenzene-sulfonamide (5a)



4-Methyl-N-(2-(phenylethynyl)phenyl)-N-vinylbenzene-sulfonamide substrates were prepared by the literature procedure[3].

Preparation of *N*-(2-Iodophenyl)-4-methylbenzenesulfonamide from 2-Iodoaniline

To a stirrer solution of 2-iodoaniline (10 mmol, 2.19 g) and pyridine (20 mmol, 1.6 ml) in DCM (30 mL) was added TsCl (11 mmol, 2.01 g) at 0 ºC. The reaction mixture was stirrer at 0 ºC for 1h and then allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted by 100 mL of CH_2Cl_2, washed with 1 M aqueous HCl (50 mL), saturated $NaHCO_3$ (50 mL) and brine (20 mL). The organic layer was separated, dried over Na_2SO_4 and concentrated under vacuo. The resulting mixture was purified by column chromatography on silica gel using hexane/EtOAc (95/5) eluent which resulted a white solid *N*-(2-Iodophenyl)-4-methylbenzenesulfonamide in 83% yield (6.22 g).

Preparation of *N*-(2-Bromoethyl)-N-(2-iodophenyl)-4-methylbenzenesulfonamide from *N*- (2-Iodophenyl)-4-methylbenzenesulfonamide

To a stirrer solution of (16.08 mmol, 6.0 g) and 1, 2-dibromoethane (160.8 mmol, 14 mL) in 30 mL acetonitrile was added Cs_2CO_3 (40.2 mmol, 13.01 g). The mixture was heated to reflux and stirred until the starting material was finished (monitored by TLC) and then allowed to cool to room temperature. Next, the reaction was quenched with water (50 mL) and extracted with CH_2Cl_2 (50 mL x 4). The organic layer was washed with brine (50 mL), dried over Na_2SO_4 and concentrate by rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel using hexane/EtOAc (95/5) eluent. A white solid was obtained in 77% yield (5.93 g).

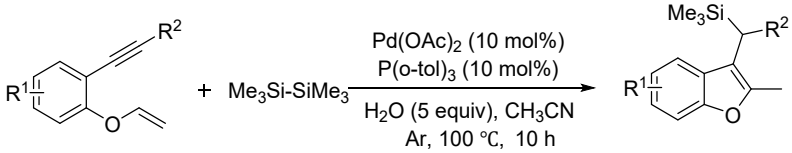
Preparation of *N*-(2-Iodophenyl)-4-methyl-N-vinylbenzenesulfonamide from *N*-(2- Bromoethyl)-N-(2-iodophenyl)-4-methylbenzenesulfonamide

A solution of *N*-(2-bromoethyl)-N-(2-iodophenyl)-4-methylbenzenesulfonamide (20.55 mmol, 9.87 g) in DMSO (25 mL) was stirred at 0 ºC. To this stirrer solution was added KO^{t}Bu (20.55 mmol, 3.5 g) in portions under nitrogen. The resulting mixture was stirrer at room temperature for 2 h. The reaction was quenched with water (100 mL) and extracted with CH_2Cl_2 (50 mL x 4). The organic layer was washed with brine (50 mL), dried over Na_2SO_4 and concentrate by rotary evaporator under vacuum. The crude product was purified by column chromatography on silica gel using hexane/ EtOAc (95/5). A yellow oil was obtained in 68% yield (5.58g).

Preparation of 4-Methyl-*N*-(2-(phenylethynyl)phenyl)-N-vinylbenzenesulfonamide from *N*- (2-Iodophenyl)-4-methyl-N-vinylbenzenesulfonamide

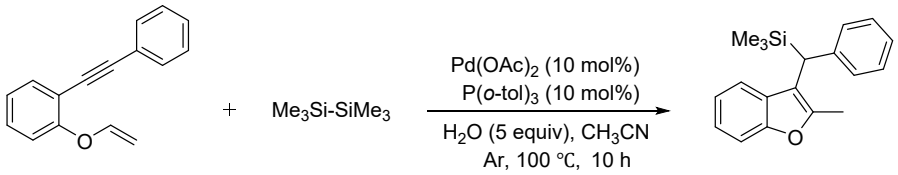
To a solution of *N*-(2-iodophenyl)-4-methyl-N-vinylbenzenesul-fonamide (1.0 mmol, 399 mg) and phenyl acetylene (1.5 mmol, 0.16 mL) in trimethylamine (degassed, 5 mL) was added $PdCl_2(PPh_3)$ (0.03 mmol, 21 mg) and CuI (0.06 mmol, 12 mg) under nitrogen. The resulting mixture was stirrer at room temperature for 6 h. The reaction mixture was filtered and washed with diethyl ether (10 mL x 3). The combined filtrate was concentrate and the residue was purified by column chromatography on silica gel using hexane/NEt_3(99/1). A yellow oil of **5a** was obtained in 93% yield (350 mg).^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.61 (d, *J* = 8.4 Hz, 2 H), 7.57-7.54 (m, 1 H), 7.38-7.35 (m,2 H), 7.32-7.29 (m, 5 H), 7.21-7.15 (m, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 4.32-4.30 (m, 1 H), 3.86-3.81 (m, 1 H), 2.22 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 143.7, 136.8, 136.5, 133.4, 133.1, 131.5, 131.5, 129.6, 129.2, 128.4, 128.0, 127.5, 124.8, 122.9, 94.1, 93.8, 85.7, 21.4.

General procedure for the synthesis of silyl benzofuran derivatives 3aa-3au



To a schlenk tube were added 1,6-enynes (0.3 mmol), hexamethyldisilane (3.0 equiv), H_2O (5.0 equiv), catalyst (0.03 mmol), ligand (0.03 mmol), and CH_3CN (3.0 ml). Then the mixture was stirred at 100 ℃ for 8 h under Ar (TLC monitored). The reaction mixture was extracted with ethyl acetate and saturated NaCl solution. Then the organic phase was combined and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography, eluting with petroleum ether/DCM (10:1) to afford the desired products.

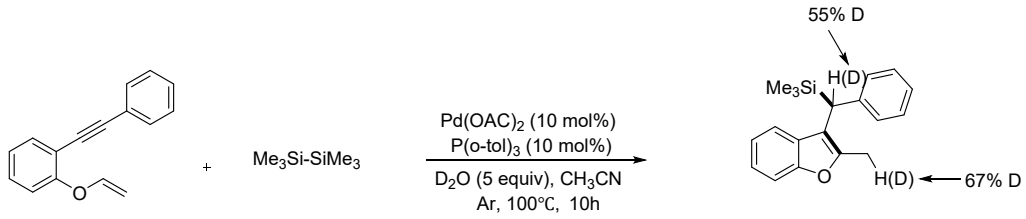
Large-scale preparation of 3aa



To a schlenk tube were added 1,6-enynes **1a** (3 mmol), hexamethyldisilane (3.0 equiv), H_2O (5.0 equiv), catalyst (0.3 mmol), ligand (0.3 mmol), and CH_3CN (4.0 ml). Then the mixture was stirred at 100 ℃ for 8 h under Ar (TLC monitored). The reaction mixture was extracted with ethyl acetate and saturated NaCl solution. Then the organic phase was combined and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography, eluting with petroleum ether/DCM (10:1) to separate **3aa**.

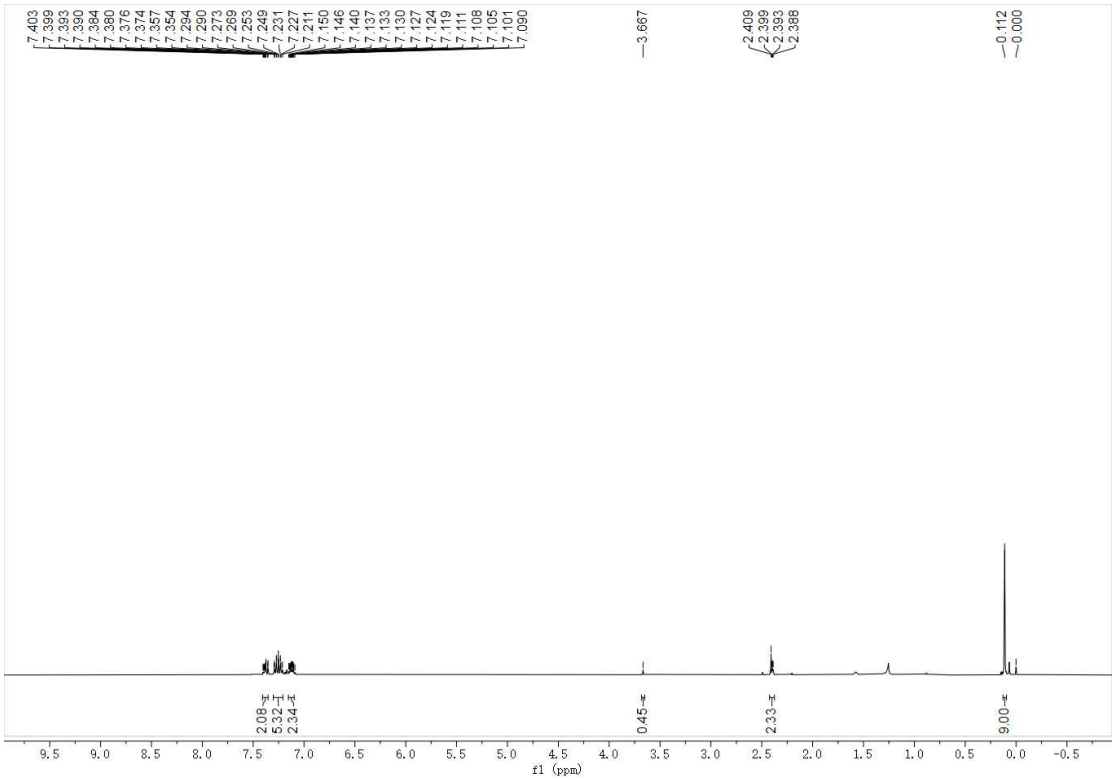
III. Mechanistic Studies

The Isotope Experiment:

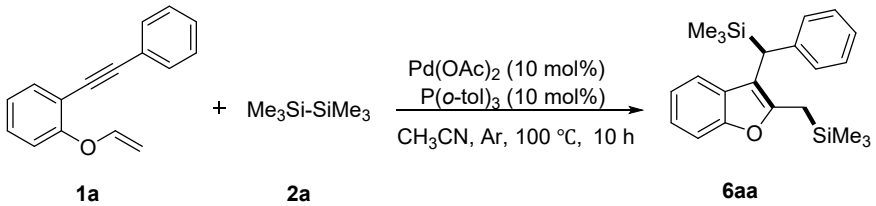


To a schlenk tube were added 1,6-enynes **1a** (0.3 mmol), **2a** (3.0 equiv), D_2O (5.0 equiv), catalyst (0.03 mmol), ligand (0.03 mmol), and CH_3CN (3.0 ml). Then the mixture was stirred at 100 ℃ for 8 h under Ar (TLC monitored). The reaction mixture was extracted with ethyl acetate and saturated NaCl solution. Then the organic phase

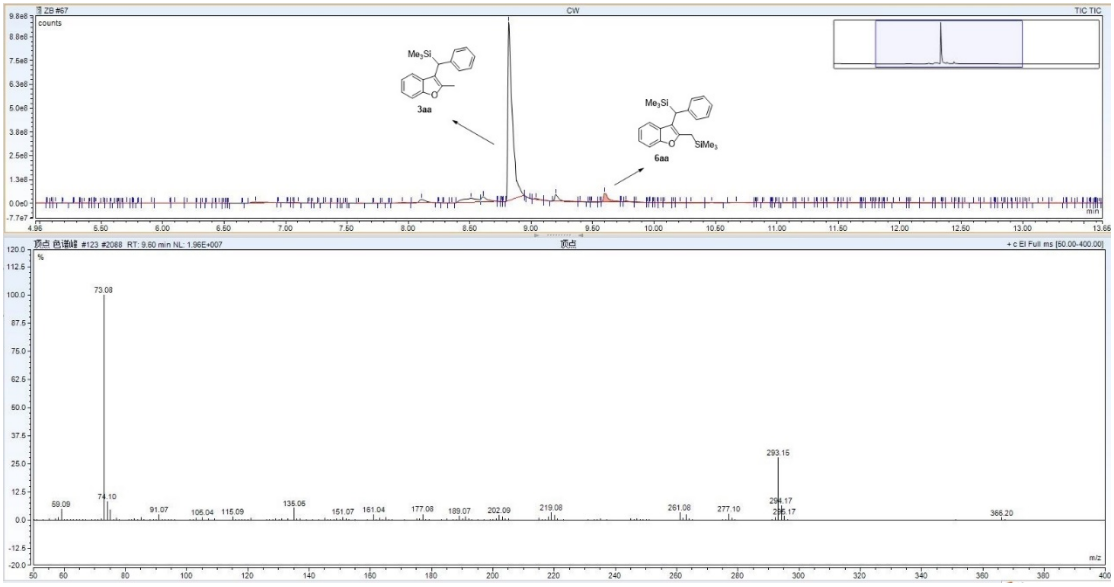
was combined and dried with anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the crude product was purified by column chromatography, eluting with petroleum ether/DCM (10:1) to afford **3aa-D** in 75% yield, and ^1H NMR spectra were recorded in $CDCl_3$. ^1H NMR ($CDCl_3$, 400 MHz) δ = 7.40-7.35 (m, 2 H), 7.29-7.21 (m, 5 H), 7.15-7.09 (m, 2 H), 3.67 (s, 0.45 H), 2.41-2.39 (m, 2.33 H), 0.11 (s, 9 H).



Water removal treatment of solvent was performed with sodium and the control experiment was conducted immediately after the water removal process. When H_2O was not added to the reaction and dry CH_3CN was used as solvent, the bis-silylated product **6aa** was monitored by GC-MS under the optimized conditions.

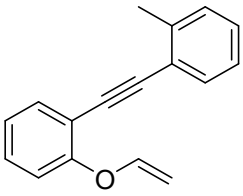


1a **2a** **6aa**



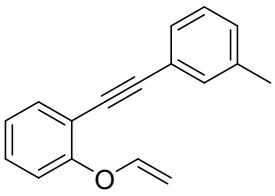
IV. The data of products

By using different substituted phenyl acetylene, various substrates (**1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s and 1t**) were synthesized. Yields and analytical data for these substrates listed below.



1-methyl-2-((2-(vinyloxy)phenyl)ethynyl)benzene (1b)

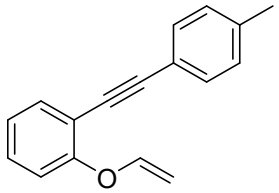
Yellow oil (1.0 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.50 (m, 2 H), 7.30-7.25 (m, 1 H), 7.21 (d, *J* = 4.4 Hz, 1 H), 7.17-7.13 (m, 1 H), 7.06 (t, *J* = 14.8 Hz, 1 H), 7.01 (d, *J* = 8.4 Hz, 1 H), 6.71-6.65 (m, 1 H), 4.78-4.74 (m, 1 H), 4.45-4.43 (m, 1 H), 2.54 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.9, 148.5, 140.4, 133.3, 131.7, 129.5, 129.4, 128.3, 125.5, 123.3, 123.1, 117.0, 114.9, 94.9, 94.8, 93.1, 88.9, 20.7.



1-(*m*-tolylethynyl)-2-(vinyloxy)benzene (1c)

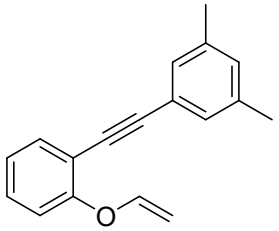
Yellow oil (1.0 g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.51 (m, 1

H), 7.37-7.34 (m, 2 H), 7.31-7.27 (m, 1 H), 7.24-7.21 (m, 1 H), 7.13 (d, *J* = 7.6 Hz, 1 H), 7.07 (t, *J* = 15.2 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 6.71-6.65 (m, 1 H), 4.81-4.78 (m, 1 H), 4.48-4.46 (m, 2 H), 2.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.7, 137.9, 133.5, 132.1, 129.5, 129.2, 128.7, 128.2, 123.1, 117.2, 114.7, 95.0, 94.3, 84.6, 21.2.



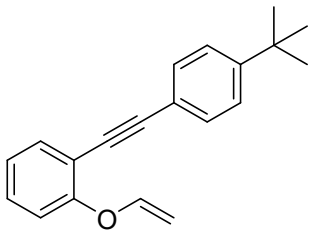
1-(*p*-tolylethynyl)-2-(vinyloxy)benzene (1d)

Yellow oil (1.1 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.50 (m, 1 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.31-7.24 (m, 1 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 7.07 (t, *J* = 14.8 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 6.71-6.66 (m, 1 H), 4.80-4.76 (m, 1 H), 4.47-4.45 (m, 1 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.9, 148.7, 138.4, 133.5, 131.5, 129.4, 129.0, 123.3, 120.3, 117.3, 114.9, 94.9, 94.3, 84.3, 21.5.



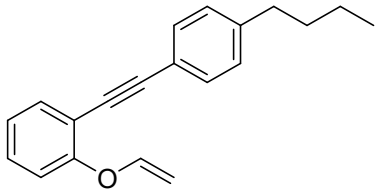
1,3-dimethyl-5-((2-(vinyloxy)phenyl)ethynyl)benzene (1e)

Yellow oil (1.1 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.51 (m, 1 H), 7.31-7.25 (m, 1 H), 7.20 (s, 2 H), 7.08 (t, *J* = 15.2 Hz, 1 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 6.97 (s, 1 H), 6.72-6.67 (m, 1 H), 4.81-4.77 (m, 1 H), 4.48-4.46 (m, 1 H),2.31 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.7, 137.8, 133.6, 130.2, 129.4, 129.3, 123.3, 123.0, 117.3, 114.9, 94.9, 94.5, 84.3, 21.1.



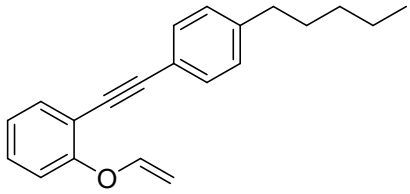
1-((4-(tert-butyl)phenyl)ethynyl)-2-(vinyloxy)benzene (1f)

Yellow oil (1.3 g, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.47 (m, 3 H), 7.38-7.34 (m, 2 H), 7.30-7.25 (m, 1 H), 7.09-7.04 (m, 1 H), 7.03-7.00 (m, 1 H), 7.07-7.00 (m, 1 H), 6.71-6.65 (m, 1 H), 4.80-4.75 (m, 1 H), 4.64-4.43 (m, 1 H), 1.32 (d, *J* = 3.6 Hz, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.9, 151.6, 148.7, 133.4, 131.3, 129.5, 125.2, 123.2, 120.3, 117.2, 114.9, 94.9, 94.7, 94.3, 84.3, 34.8, 31.3, 31.2, 31.1.



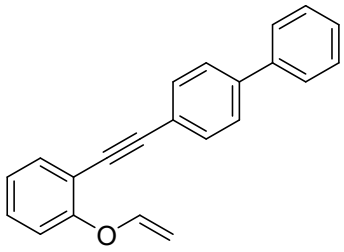
1-((4-butylphenyl)ethynyl)-2-(vinyloxy)benzene (1g)

Yellow oil (1.2 g, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.50 (m, 1 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.30-7.26 (m, 1 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.07 (t, *J* = 15.2 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 6.71-6.66 (m, 1 H), 4.79-4.75 (m, 1 H), 4.46-4.44 (m, 1 H), 2.61 (t, *J* = 15.6 Hz, 2 H), 1.63-1.56 (m, 2 H), 1.38-1.32 (m, 2 H), 0.92 (t, *J* = 14.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.9, 148.7, 143.4, 133.5, 131.5, 129.4, 128.4, 123.3, 120.5, 117.3, 114.9, 94.8, 94.4, 84.3, 35.6, 33.4, 22.3, 13.9.



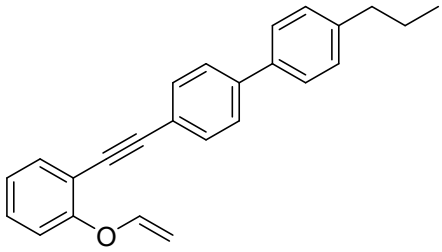
1-((4-pentylphenyl)ethynyl)-2-(vinyloxy)benzene (1h)

Yellow oil (1.2 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.51 (d, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 8.0 Hz, 2 H), 7.29-7.25 (m, 1 H), 7.14 (d, *J* = 7.6 Hz, 2 H), 7.06 (t, *J* = 14.8 Hz, 1 H), 7.01 (d, *J* = 8.0 Hz, 1 H), 6.70-6.65 (m, 1 H), 4.79-4.75 (m, 1 H), 4.46-4.44 (m, 1 H), 2.60 (t, *J* = 15.2 Hz, 2 H), 1.64-1.57 (m, 2 H), 1.36-1.28 (m, 4 H), 0.89 (t, *J* = 13.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.9, 148.7, 143.5, 133.5, 131.5, 129.4, 123.3, 120.5, 117.3, 114.9, 94.8, 94.4, 84.3, 35.9, 31.4, 30.9, 22.5, 14.0.



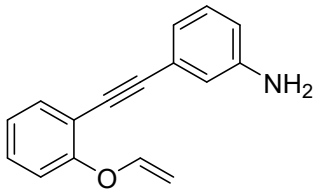
4-((2-(vinyloxy)phenyl)ethynyl)-1,1'-biphenyl (1i)

Yellow oil (1.3 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.62-7.52 (m, 7 H), 7.42 (t, *J* = 14.8 Hz, 2 H), 7.35-7.31 (m, 1 H), 7.30-7.26 (m, 1 H), 7.07 (t, *J* = 15.2 Hz, 1 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 6.71-6.66 (m, 1 H), 4.82-4.79 (m, 1 H), 4.48-4.46 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.6, 141.0, 140.3, 133.5, 132.0, 129.6, 128.8, 127.6, 127.0, 126.9, 123.3, 122.2, 117.2, 114.6, 95.1, 94.0, 85.7.



4-propyl-4'-((2-(vinyloxy)phenyl)ethynyl)-1,1'-biphenyl (1j)

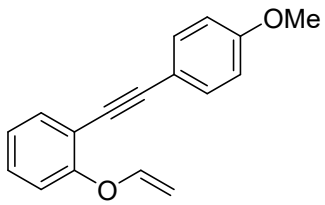
Yellow oil (1.4 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.61-7.50 (m, 7 H), 7.31-7.22 (m, 3 H), 7.07 (t, *J* = 14.8 Hz, 1 H), 7.02 (d, *J* = 9.2 Hz, 1 H), 4.82-4.78 (m, 1 H), 4.48-4.46 (m, 1 H), 2.64-2.60 (m, 2 H), 1.72-1.62 (m, 1 H), 0.98-0.94 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.7, 142.3, 141.0, 137.7, 133.5, 132.0, 129.6, 129.0, 126.8, 126.7, 123.3, 121.9, 117.2, 114.7, 95.1, 94.1, 85.5, 37.7, 24.5, 13.9.



3-((2-(vinyloxy)phenyl)ethynyl)aniline (1k)

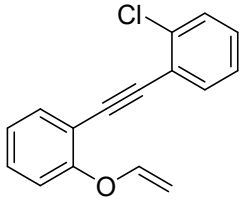
Yellow oil (0.9 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.52-7.49 (m, 1 H), 7.30-7.25 (m, 1 H), 7.13-6.94 (m, 4 H), 6.85-6.84 (m, 1 H), 6.70-6.61 (m, 2 H), 4.81-4.76 (m, 1 H), 4.47-4.45 (m, 1 H), 3.68 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$,

ppm): δ = 156.9, 148.6, 146.2, 146.2, 133.5, 129.5, 129.2, 123.9, 123.3, 122.0, 117.7, 117.1, 115.4, 114.6, 95.0, 94.3, 84.3.



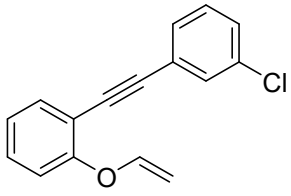
1-((4-methoxyphenyl)ethynyl)-2-(vinyloxy)benzene (1l)

Yellow oil (1.0 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.43-7.39 (m, 3 H), 7.21-7.15 (m, 1 H), 7.00-6.92 (m, 2 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.62-6.57 (m, 1 H), 4.72-4.68 (m, 1 H), 4.39-4.37 (m, 1 H), 3.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 159.6, 156.8, 148.7, 133.3, 133.0, 129.2, 123.3, 117.2, 115.4, 114.9, 113.9, 94.9, 94.1, 83.6, 55.2.



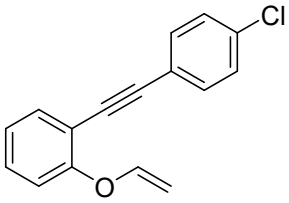
1-chloro-2-((2-(vinyloxy)phenyl)ethynyl)benzene (1m)

Yellow oil (1.1 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57-7.54 (m, 2 H), 7.41-7.39 (m, 1 H), 7.32-7.28 (m, 1 H), 7.23-7.20 (m, 2 H), 7.07 (t, *J* = 14.8 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.72-6.67 (m, 1 H), 4.81-4.77 (m, 1 H), 4.47-4.45 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.4, 135.9, 133.6, 133.2, 130.0, 129.2, 126.4, 123.3, 116.9, 114.1, 95.1, 90.7, 90.2.



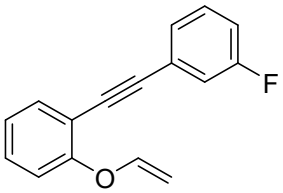
1-((3-chlorophenyl)ethynyl)-2-(vinyloxy)benzene (1n)

Yellow oil (1.1 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.51 (m, 2 H), 7.44-7.41 (m, 1 H), 7.35-7.27 (m, 3 H), 7.09 (t, *J* = 14.8 Hz, 1 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 4.83-4.79 (m, 1 H), 4.51-4.49 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.1, 148.4, 134.1, 133.6, 131.4, 130.0, 129.7, 129.5, 128.5, 125.0, 123.3, 117.1, 114.0, 95.4, 92.5, 86.2.



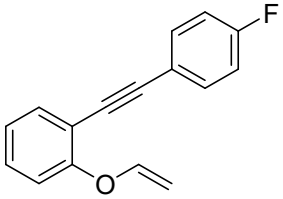
1-((4-chlorophenyl)ethynyl)-2-(vinyloxy)benzene (1o)

Yellow oil (1.1 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.52-7.45 (m, 3 H), 7.32-7.28 (m, 3 H), 7.09-7.01 (m, 2 H), 6.70-6.64 (m, 1 H), 4.82-4.78 (m, 1 H), 4.49-4.47 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.5, 134.3, 133.5, 132.8, 129.8, 128.6, 123.3, 121.8, 117.1, 114.2, 95.2, 92.9, 86.0.



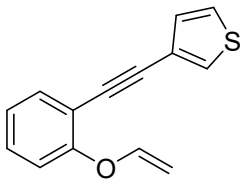
1-((3-fluorophenyl)ethynyl)-2-(vinyloxy)benzene (1p)

Yellow oil (1.0 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.51 (m, 1 H), 7.34-7.27 (m, 3 H), 7.25-7.22 (m, 1 H), 7.10-7.07 (m, 1 H), 7.05-7.01 (m, 2 H), 6.70-6.65 (m, 1 H), 4.82-4.78 (m, 1 H), 4.50-4.47 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.6, 161.1, 157.1, 148.5, 133.6, 130.0, 129.9, 129.8, 127.5, 125.1, 123.3, 118.4, 118.2, 117.2, 115.7, 115.5, 114.1, 95.3, 92.7, 85.9.



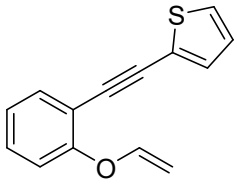
1-((4-fluorophenyl)ethynyl)-2-(vinyloxy)benzene (1q)

Yellow oil (1.0 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.50 (m, 3 H), 7.32-7.28 (m, 1 H), 7.10-7.00 (m, 4 H), 6.70-6.65 (m, 4 H), 4.81-4.77 (m, 1 H), 4.48-4.46 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 163.8, 161.3, 157.0, 148.6, 133.6, 133.5, 129.8, 129.6, 123.4, 123.3, 119.5, 117.3, 117.1, 115.8, 115.6, 115.5, 115.4, 114.4, 95.2, 95.0, 93.0, 84.7.



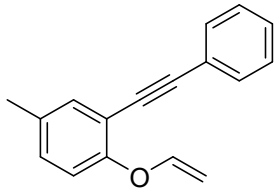
3-((2-(vinyloxy)phenyl)ethynyl)thiophene (1r)

Yellow oil (0.9 g, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.53-7.50 (m, 2 H), 7.31-7.26 (m, 2 H), 7.21-7.20 (m, 1 H), 7.08-7.04 (m, 1 H), 7.02-7.00 (m, 1 H), 4.81-4.77 (m, 1 H), 4.48-4.46 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.5, 133.5, 129.9, 129.5, 128.7, 125.2, 123.3, 122.4, 117.1, 114.5, 95.2, 89.2, 84.51.



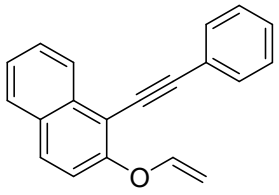
2-((2-(vinyloxy)phenyl)ethynyl)thiophene (1s)

Yellow oil (1.0 g, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.51-7.48 (m, 1 H), 7.31-7.27 (m, 3 H), 7.08-6.98 (m, 3 H), 6.68-6.63 (m, 1 H), 4.82-4.77 (m, 1 H), 4.49-4.47 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 156.8, 148.4, 133.3, 131.9, 129.8, 127.3, 127.0, 123.3, 123.3, 117.0, 114.2, 95.4, 88.7, 87.2.



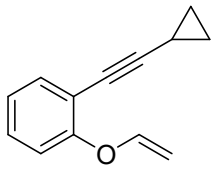
4-methyl-2-(phenylethynyl)-1-(vinyloxy)benzene (1t)

Yellow oil (0.9 g, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.55-7.52 (m, 2 H), 7.35-7.31 (m, 4 H), 7.10-7.07 (m, 1 H), 6.92 (d, *J* = 8.4 Hz, 1 H), 6.68-6.63 (m, 1 H), 4.75-4.71 (m, 1 H), 4.42-4.40 (m, 1 H), 2.30 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 154.8, 149.2, 133.8, 133.0, 131.6, 130.3, 128.3, 128.2, 123.4, 117.5, 114.4, 94.1, 93.7, 85.2, 20.5.



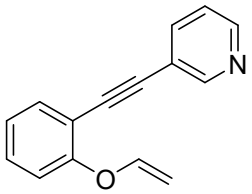
1-(phenylethynyl)-2-(vinyloxy)naphthalene (1u)

Yellow oil (1.0 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.41-8.38 (m, 1 H), 7.81-7.77 (m, 2 H), 7.67-7.64 (m, 2 H), 7.60-7.56 (m, 1 H), 7.47-7.43 (m, 1 H), 7.40-7.34 (m, 3 H), 7.26 (d, *J* = 8.0 Hz, 1 H), 6.82-6.77 (m, 1 H), 4.80-4.76 (m, 1 H), 4.48-4.46 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 155.6, 149.4, 134.2, 131.6, 130.1, 130.0, 128.4, 128.3, 128.2, 127.4, 125.8, 125.4, 123.5, 118.3, 109.9, 99.5, 94.4, 83.1.



1-(cyclopropylethynyl)-2-(vinyloxy)benzene (1v)

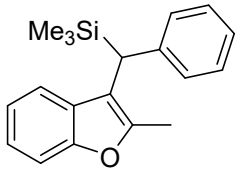
White oil (0.7 g, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.38-7.36 (m, 1 H), 7.23-7.18 (m, 1 H), 7.01-6.93 (m, 2 H), 6.62-6.57 (m, 1 H), 4.74-4.70 (m, 1 H), 4.42-4.40 (m, 1 H), 1.51-1.44 (m, 1 H), 0.87-0.81 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.0, 148.6, 133.6, 128.6, 123.1, 117.1, 115.2, 98.4, 94.6, 71.0, 8.7, 0.4.



1w

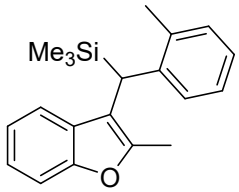
3-((2-(vinyloxy)phenyl)ethynyl)pyridine (1w)

Yellow oil (0.8 g, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.79-8.78 (m, 1 H), 8.55-8.53 (m, 1 H), 7.83-7.80 (m, 1 H), 7.55-7.53 (m, 1 H), 7.36-7.25 (m, 2 H), 7.12-7.03 (m, 2 H), 6.71-6.65 (m, 1 H), 4.83-4.79 (m, 1 H), 4.51-4.49 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 157.1, 152.2, 148.5, 148.3, 138.3, 133.5, 130.2, 123.3, 122.9, 120.5, 117.0, 113.8, 95.4, 90.5, 88.3.



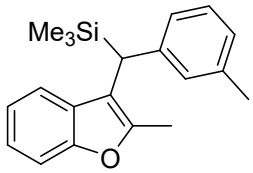
trimethyl((2-methylbenzofuran-3-yl)(phenyl)methyl)silane (3aa)

Yellow oil (67.9 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.65-7.60 (m, 2 H), 7.55-7.52 (m, 2 H), 7.50-7.46 (m, 2 H), 7.43-7.40 (m, 1 H), 7.39-7.34 (m, 2 H), 3.92 (s, 1 H), 2.66 (s, 3 H), 0.37 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =153.9, 150.5, 142.0, 129.8, 128.6, 128.3, 125.1, 122.8, 121.7, 120.6, 115.6, 110.5, 33.4, 12.7, -0.5; HRMS calcd for $C_{19}H_{22}OSi$ $[M+H]^+$ 295.1513; found: 295.1518. IR (neat, cm^{-1}): 2926, 1493, 1452, 1250, 838.



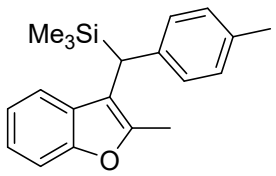
trimethyl((2-methylbenzofuran-3-yl)(o-tolyl)methyl)silane (3ab)

Yellow oil (42.5 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.64 (d, *J* = 7.6 Hz, 1 H), 7.37-7.30 (m, 2 H), 7.23-7.18 (m, 1 H), 7.12-7.08 (m, 3 H), 7.06-7.02 (m, 1 H), 3.63 (s, 1 H), 2.34 (s, 3 H), 2.14 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.8, 149.8, 139.5, 138.3, 130.9, 130.3, 129.7, 126.0, 125.3, 122.6, 121.6, 120.3, 114.3, 110.3, 30.3, 20.0, 13.0, -0.6; HRMS calcd for $C_{20}H_{24}OSi$ $[M+H]^+$ 309.1669; found: 309.1670. IR (neat, cm^{-1}): 2926, 1496, 1454, 1249, 837.



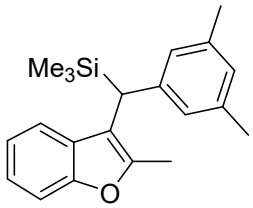
trimethyl((2-methylbenzofuran-3-yl)(m-tolyl)methyl)silane (3ac)

Yellow oil (56.4 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.45-7.39 (m, 2 H), 7.22-7.18 (m, 1 H), 7.17-7.13 (m, 3 H), 7.12-7.11 (m, 1 H), 6.99-6.97 (m, 1 H), 3.67 (s, 1 H), 2.45 (s, 3 H), 2.31 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.4, 141.9, 137.8 129.8, 129.5, 128.1, 125.9, 125.6, 122.8, 121.7, 120.6, 115.7, 110.5, 33.3, 21.6, 12.8, -0.5. HRMS calcd for $C_{20}H_{24}OSi$ $[M+H]^+$ 309.1669; found: 309.1665. IR (neat, cm^{-1}): 2925, 1496, 1454, 1249, 838.



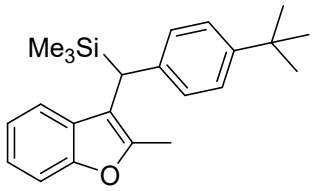
trimethyl((2-methylbenzofuran-3-yl)(p-tolyl)methyl)silane (3ad)

Yellow oil (60.1 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.51 (m, 2 H), 7.35-7.32 (m, 3 H), 7.28-7.25 (m, 1 H), 7.21-7.19 (m, 2 H), 3.78 (s, 1 H), 2.56 (s, 3 H), 2.45 (s, 3 H), 0.27 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.3, 138.8, 134.5, 129.8, 129.0, 128.6, 122.7, 121.7, 120.6, 115.8, 110.5, 32.8, 20.9, 12.7, -0.5. HRMS calcd for $C_{20}H_{24}OSi$ $[M+H]^+$ 309.1669; found: 309.1674. IR (neat, cm^{-1}): 2922, 1495, 1454, 1250, 838.



((3,5-dimethylphenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3ae)

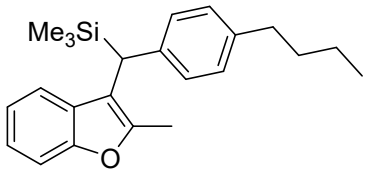
Yellow oil (63.8 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.57-7.49 (m, 2 H), 7.38-7.25 (m, 3 H), 7.04 (d, *J* = 3.2 Hz, 2 H), 6.91 (s, 1 H), 3.74 (s, 1 H), 2.55 (d, *J* = 3.2 Hz, 3 H), 2.38 (d, *J* = 2.8 Hz, 6 H), 0.25 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.4, 141.8, 137.5, 129.9, 126.8, 126.5, 122.7, 121.7, 120.6, 115.8, 110.5, 33.2, 21.4, 12.8, -0.5; HRMS calcd for $C_{21}H_{26}OSi$ $[M+H]^+$ 323.1826; found: 323.1825. IR (neat, cm^{-1}): 2918, 1454, 1248, 1187, 830.



((4-(tert-butyl)phenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3af)

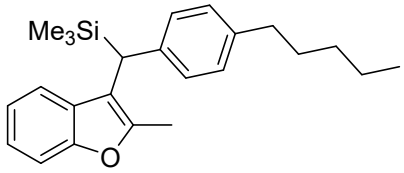
Yellow oil (76.7 mg, 73% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.44-7.39 (m, 2 H), 7.30-7.28 (m, 1 H), 7.27-7.25 (m, 3 H), 7.20-7.18 (m, 1 H), 7.16-7.14 (m, 1 H), 3.68 (s, 1 H), 2.44 (s, 3 H), 1.32 (s, 9 H), 0.15 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 154.0, 150.4, 147.8, 138.7, 129.8, 128.2, 125.1, 122.7, 121.6, 120.7, 115.8, 110.5, 34.2, 32.7, 31.4, 12.7, -0.5; HRMS calcd for $C_{23}H_{30}OSi$ $[M+H]^+$ 351.2139;

found: 351.2137. IR (neat, cm^{-1}): 2960, 1515, 1454, 1250, 838.



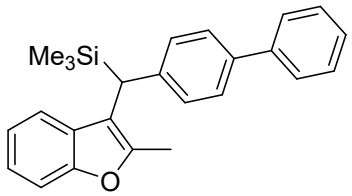
((4-butylphenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3ag)

Yellow oil (71.8 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.43-7.39 (m, 2 H), 7.24-7.22 (m, 2 H), 7.20-7.18 (m, 1 H), 7.16-7.12 (m, 1 H), 7.09-7.07 (m, 2 H), 3.67 (s, 1 H), 2.59 (t, *J* = 15.6 Hz, 2 H), 2.44 (s, 3 H), 1.64-1.56 (m, 2 H), 1.40-1.34 (m, 2 H), 0.97-0.93 (m, 3 H), 0.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.4, 139.6, 139.0, 129.8, 128.5, 128.3, 122.7, 121.7, 120.6, 115.8, 110.5, 35.1, 33.6, 32.8, 22.4, 14.0, 12.8, -0.5; HRMS calcd for $C_{23}H_{30}OSi$ $[M+H]^+$ 351.2139; found: 351.2139. IR (neat, cm^{-1}): 2922, 1508, 1454, 1250, 1005, 837.



trimethyl((2-methylbenzofuran-3-yl)(4-pentylphenyl)methyl)silane (3ah)

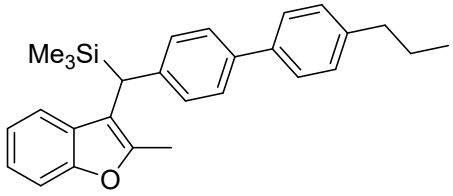
Yellow oil (66.7 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42-7.39 (m, 2 H), 7.24-7.22 (m, 2 H), 7.20-7.18 (m, 1 H), 7.16-7.12 (m, 1 H), 7.09-7.07 (m, 2 H), 3.67 (s, 1 H), 2.57 (t, *J* = 15.6 Hz, 2 H), 2.44 (s, 3 H), 1.67-1.58 (m, 2 H), 1.36-1.33 (m, 4 H), 0.92 (t, *J* = 13.6 Hz, 3 H), 0.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.4, 139.6, 138.9, 129.8, 128.5, 122.7, 121.6, 120.6, 115.8, 110.5, 35.4, 32.8, 31.6, 31.1, 22.5, 14.0, 12.8, -0.5; HRMS calcd for $C_{24}H_{32}OSi$ $[M+H]^+$ 365.2295; found: 365.2292. IR (neat, cm^{-1}): 2926, 2119, 1508, 1454, 1249, 837.



([1,1'-biphenyl]-4-yl(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3ai)

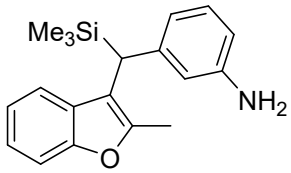
Yellow oil (81.0 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.71-7.68 (m, 2 H), 7.62-7.60 (m, 2 H), 7.53-7.51 (m, 4 H), 7.49-7.47 (m, 2 H), 7.46-7.43 (m, 1 H),

7.34-7.24 (m, 2 H), 3.85 (s, 1 H), 2.57 (s, 3 H), 0.28 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 154.0, 150.6, 141.2, 140.9, 137.9, 129.7, 128.9, 128.7, 126.9, 126.8, 122.9, 121.8, 120.6, 115.5, 110.6, 33.2, 12.8, -0.5; HRMS calcd for $C_{25}H_{26}OSi$ $[M+H]^+$ 371.1826; found: 371.1821. IR (neat, cm^{-1}): 2920, 1492, 1454, 1249, 835.



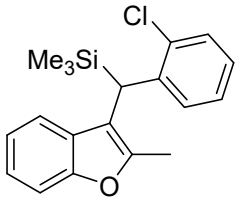
trimethyl((2-methylbenzofuran-3-yl)(4'-propyl-[1,1'-biphenyl]-4-yl)methyl)silane (3aj)

Yellow oil (82.8 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.48-7.45 (m, 4 H), 7.42 (d, *J* = 8 Hz, 1 H), 7.38 (d, *J* = 8 Hz, 1 H), 7.33 (d, *J* = 8 Hz, 2 H), 7.23-7.19 (m, 2 H), 7.18-7.10 (m, 2 H), 3.70 (s, 1 H), 2.66-2.58 (m, 3 H), 2.43 (s, 3 H), 1.70-1.63 (m, 3 H), 0.98-0.94 (m, 3 H), 0.14 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 154.0, 150.5, 141.5, 140.8, 138.2, 137.8, 129.7, 128.9, 128.8, 126.7, 126.6, 122.8, 121.8, 120.6, 115.6, 110.6, 37.7, 33.1, 24.5, 13.9, 12.8, -0.5; HRMS calcd for $C_{28}H_{32}OSi$ $[M+H]^+$ 413.2295; found: 413.2296. IR (neat, cm^{-1}): 2928, 1496, 1454, 1250, 836.



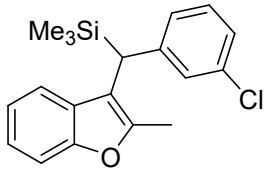
3-((2-methylbenzofuran-3-yl)(trimethylsilyl)methyl)aniline (3ak)

Yellow oil (55.6 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ= 7.46 (d, *J* = 7.2 Hz, 1 H), 7.41 (d, *J* = 8 Hz, 1 H), 7.23-7.14 (m, 2 H), 7.07 (t, *J* = 15.6 Hz, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.60 (s, 1 H), 6.51-6.48 (m, 1 H), 3.62 (s, 3 H), 2.45 (s, 3 H), 0.15 (s, 9 H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.5, 146.3, 143.3, 129.9, 129.0, 122.7, 121.7, 120.7, 119.0, 115.6, 115.4, 112.1, 110.5, 33.3, 12.7, -0.4. HRMS calcd for $C_{19}H_{23}NOSi$ $[M+H]^+$310.1622; found: 310.1620. IR (neat, cm^{-1}): 2918, 1600, 1490, 1454, 1248, 834.



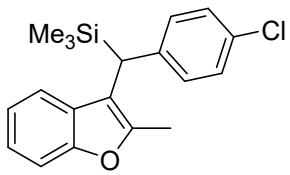
((2-chlorophenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3am)

Yellow oil (51.2 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.78-7.75 (m, 1 H), 7.61-7.58 (m, 1 H), 7.45-7.42 (m, 2 H), 7.35-7.30 (m, 1 H), 7.25-7.18 (m, 3 H), 4.18 (s, 1 H), 2.57 (s, 3 H), 0.27 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 151.0, 139.6, 135.0, 131.1, 130.0, 129.6, 127.0, 126.4, 122.6, 121.7, 120.3, 114.2, 110.5, 30.3, 20.0, 13.0, -0.6; HRMS calcd for $C_{19}H_{21}ClOSi$ $[M+H]^+$ 329.1123; found: 329.1120. IR (neat, cm^{-1}): 2919, 1452, 1250, 1175, 838, 731.



((3-chlorophenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3an)

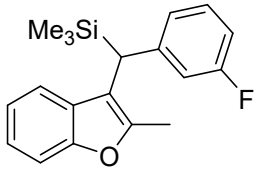
Yellow oil (62.0 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ= 7.54-7.50 (m, 2 H), 7.39-7.38 (m, 1 H), 7.36-7.33 (m, 1 H), 7.32-7.31 (m, 2 H), 7.30-7.25 (m, 2 H), 3.79 (s, 1 H), 2.56 (s, 3 H), 0.27 (s, 9 H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.7, 144.3, 134.0, 129.5, 128.5, 126.5, 125.3, 123.0, 121.9, 120.3, 115.0, 110.7, 33.3, 12.8, -0.6. HRMS calcd for $C_{19}H_{21}ClOSi$ $[M+H]^+$ 329.1123; found: 329.1126. IR (neat, cm^{-1}): 2922, 1455, 1250, 1181, 837, 746.



((4-chlorophenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3ao)

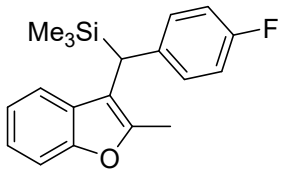
Yellow oil (70.8 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.54-7.48 (m, 2 H), 7.36 (s, 4 H), 7.34-7.32 (m, 1 H), 7.30-7.26 (m, 1 H), 3.78 (s, 1 H), 2.56 (s, 3 H), 0.27 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.6, 140.6, 130.8, 129.8, 129.5, 128.4, 123.0, 121.9, 120.4, 115.2, 110.7, 32.9, 12.7, -0.6; HRMS calcd for $C_{19}H_{21}ClOSi$ $[M+H]^+$ 329.1123; found: 329.1126. IR (neat, cm^{-1}): 2922, 1458, 1452,

1250, 838, 743.



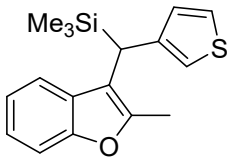
((3-fluorophenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3ap)

Yellow oil (54.3 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42-7.40 (m, 2 H), 7.25-7.20 (m, 2 H), 7.20-7.14 (m, 1 H), 7.10-7.08 (m, 1 H), 7.02-6.98 (m, 1 H), 6.87-6.83 (m, 1 H), 3.70 (s, 1 H), 2.45 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 164.1, 161.7, 154, 150.7, 144.9 (d, *J* = 7 Hz), 129.6 (d, *J* = 8 Hz), 124.0 (d, *J* = 2 Hz), 123.0, 121.9, 120.4, 115.2 (d, *J* = 21 Hz), 112.0 (d, *J* = 21 Hz), 33.42 (d, *J* = 2 Hz), 12.74, -0.6 ; ^{19}F NMR (377 MHz, $CDCl_3$, ppm): δ = -113.16; HRMS calcd for $C_{19}H_{21}FOSi$ $[M+H]^+$ 313.1419; found: 313.1424. IR (neat, cm^{-1}): 2923, 1452, 1432, 1250, 1184, 834.



((4-fluorophenyl)(2-methylbenzofuran-3-yl)methyl)trimethylsilane (3aq)

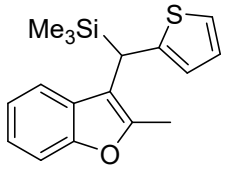
Yellow oil (65.5 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.42-7.35 (m, 2 H), 7.29-7.25 (m, 2 H), 7.21-7.19 (m, 1 H), 7.16-7.14 (m, 1 H), 6.98-6.94 (m, 2 H), 3.66 (s, 1 H), 2.44 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 160.8 (d, *J* = 161.0 Hz), 154.0, 150.5, 137.6 (d, *J* = 2 Hz), 129.9 (d, *J* = 5 Hz), 129.5, 122.9, 121.8, 120.4, 115.6, 115.1, 114.9, 110.6, 32.5, 12.7, -0.6; ^{19}F NMR (377 MHz, $CDCl_3$, ppm): δ = -119.18; HRMS calcd for $C_{19}H_{21}FOSi$ $[M+H]^+$ 313.1419; found: 313.1419. IR (neat, cm^{-1}): 2923, 1458, 1439, 1250, 1195, 834.



trimethyl((2-methylbenzofuran-3-yl)(thiophen-3-yl)methyl)silane (3ar)

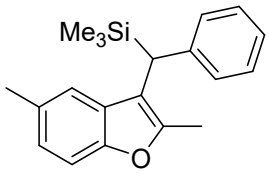
Yellow oil (61.2 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.38-7.35 (m,

1 H), 7.29-7.27 (m, 1 H), 7.23-7.21 (m, 1 H), 7.19-7.15 (m, 1 H), 7.11-7.07 (m, 1 H), 6.98-6.94 (m, 2 H), 3.66 (d, *J* = 1.2 Hz, 1 H), 2.37 (s, 3 H), 0.11 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 154.0, 150.0, 141.4, 129.3, 129.1, 124.9, 122.8, 121.6, 120.7, 120.0, 115.4, 110.5, 28.5, 12.6, -0.7; HRMS calcd for $C_{17}H_{20}OSSi$ $[M+H]^+$ 301.1077; found: 301.1073. IR (neat, cm^{-1}): 2923, 1456, 1250, 834, 738.



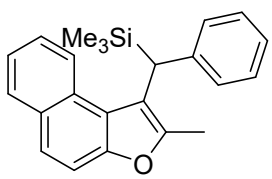
trimethyl((2-methylbenzofuran-3-yl)(thiophen-2-yl)methyl)silane (3as)

Yellow oil (55.8 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.36 (d, *J* =8.4 Hz, 1 H), 7.32-7.29 (m, 1 H), 7.18-7.14 (m, 1 H), 7.10-7.06 (m, 2 H), 6.91-6.89 (m, 2 H), 3.82 (s, 1 H), 2.39 (s, 3 H), 0.15 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 154.0, 150.0, 145.3, 128.9, 126.3, 124.7, 123.1, 122.9, 121.6, 120.6, 115.5, 110.5, 28.2, 12.7, -0.9; HRMS calcd for $C_{17}H_{20}OSSi$ $[M+H]^+$ 301.1077; found: 301.1074. IR (neat, cm^{-1}): 2924, 1452, 1250, 834, 740.



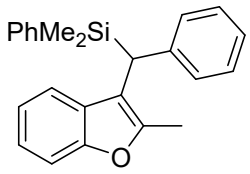
((2,5-dimethylbenzofuran-3-yl)(phenyl)methyl)trimethylsilane (3at)

Yellow oil (64.7 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.45-7.38 (m, 5 H), 7.34-7.33 (m, 1 H), 7.30-7.27 (m, 1 H), 7.15-7.13 (m, 1 H), 3.81 (s, 1 H), 2.55 (s, 6 H), 0.28 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 152.3, 150.7, 142.2, 131.0, 130.0, 128.5, 128.3, 125.0, 124.0, 120.4, 115.4, 110.0, 33.4, 21.5, 12.9, -0.5; HRMS calcd for $C_{20}H_{24}OSi$ $[M+H]^+$ 309.1669; found: 309.1667. IR (neat, cm^{-1}): 2926, 1496, 1463, 1250, 838.



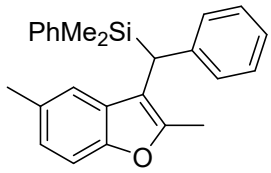
trimethyl((2-methylnaphtho[2,1-b]furan-1-yl)(phenyl)methyl)silane (3au)

Yellow oil (67.1 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.00-7.92 (m, 2 H), 7.70-7.62 (m, 2 H), 7.57-7.50 (m, 1 H), 7.42-7.35 (m, 3 H), 7.30-7.26 (m, 2 H), 7.18-7.15 (m, 1 H), 4.38 (s, 1 H), 2.51 (s, 3 H), 0.20 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 151.6, 142.0, 128.9, 128.4, 126.3, 125.2, 125.1, 124.7, 124.5, 123.6, 123.5, 123.1, 112.3, 112.2, 100.4, 33.47, 29.7, -0.0; HRMS calcd for $C_{23}H_{24}OSi$ $[M+H]^+$ 345.1669; found: 345.1666. IR (neat, cm^{-1}): 2922, 1472, 1395, 1246, 1011, 838.



dimethyl((2-methylbenzofuran-3-yl)(phenyl)methyl)(phenyl)silane (3ba)

Yellow oil (79.0 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.56-7.53 (m, 1 H), 7.37-7.34 (m, 4 H), 7.33-7.26 (m, 2 H), 7.23-7.16 (m, 4 H), 7.15-7.10 (m, 2 H), 7.07-7.00 (m, 1 H), 3.92 (s, 1 H), 2.19 (s, 3 H), 0.42 (s, 3 H), 0.30 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 153.9, 150.8, 141.4, 138.4, 134.1, 129.6, 129.2, 128.8, 128.2, 127.7, 125.2, 122.8, 121.6, 120.8, 115.0, 110.5, 33.2, 12.5, -1.7, -2.8; HRMS calcd for $C_{24}H_{24}OSi$ $[M+H]^+$ 357.1669; found: 357.1667. IR (neat, cm^{-1}): 2914, 1456, 1246, 1118, 830.



((2,5-dimethylbenzofuran-3-yl)(phenyl)methyl)dimethyl(phenyl)silane (3bt)

Yellow oil (67.7 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.37-7.32 (m, 4 H), 7.30-7.28 (m, 2 H), 7.24-7.17 (m, 4 H), 7.13-7.09 (m, 1 H), 7.15-7.10 (m, 2 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 6.87 (s, 1 H), 3.89 (s, 1 H), 2.28 (s, 3 H), 2.20 (s, 3 H), 0.39 (s, 3 H), 0.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 152.3, 151.0, 141.6, 138.4, 134.2, 130.8, 129.7, 128.7, 128.2, 127.7, 125.1, 124.0, 120.9, 114.7, 109.9, 33.5, 21.4, 12.6, -1.6, -2.9; HRMS calcd for $C_{25}H_{26}OSi$ $[M+H]^+$ 371.1826; found: 371.1828. IR (neat, cm^{-1}): 2923, 1468, 1258, 1011, 829.

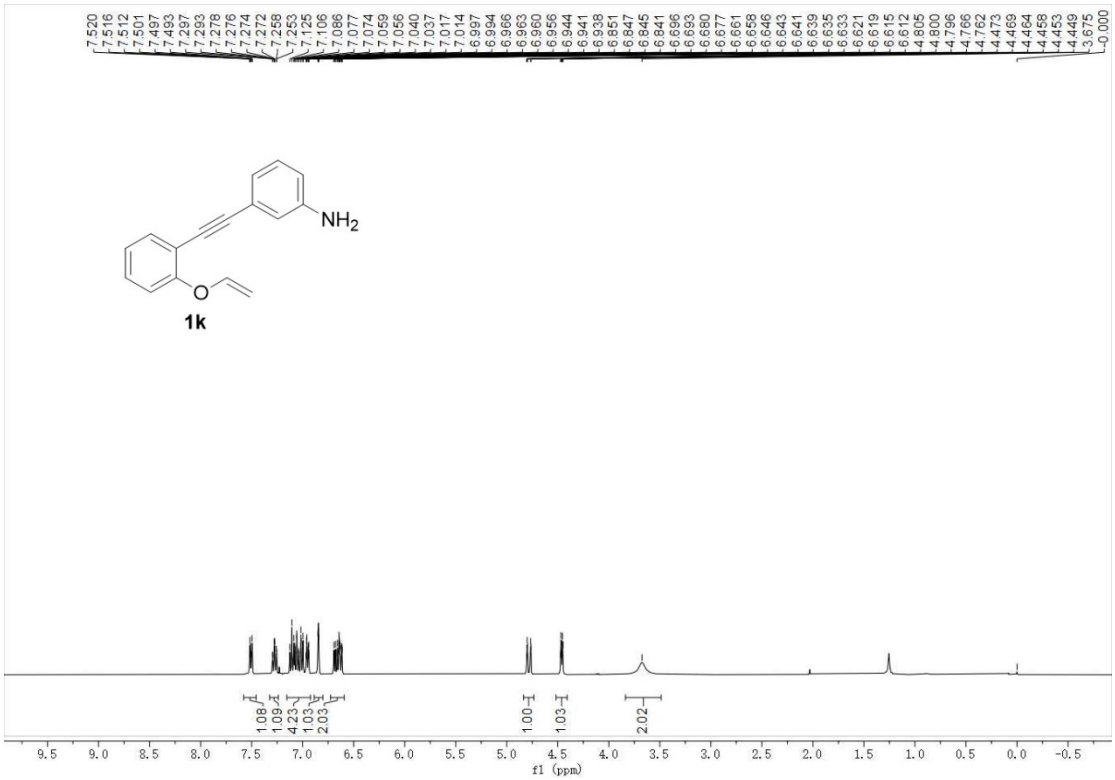
V. References

[1] N. Sakiyama, K. Noguchi and K. Tanaka, *Angew. Chem. Int. Ed*. **2012**, 51, 5976.

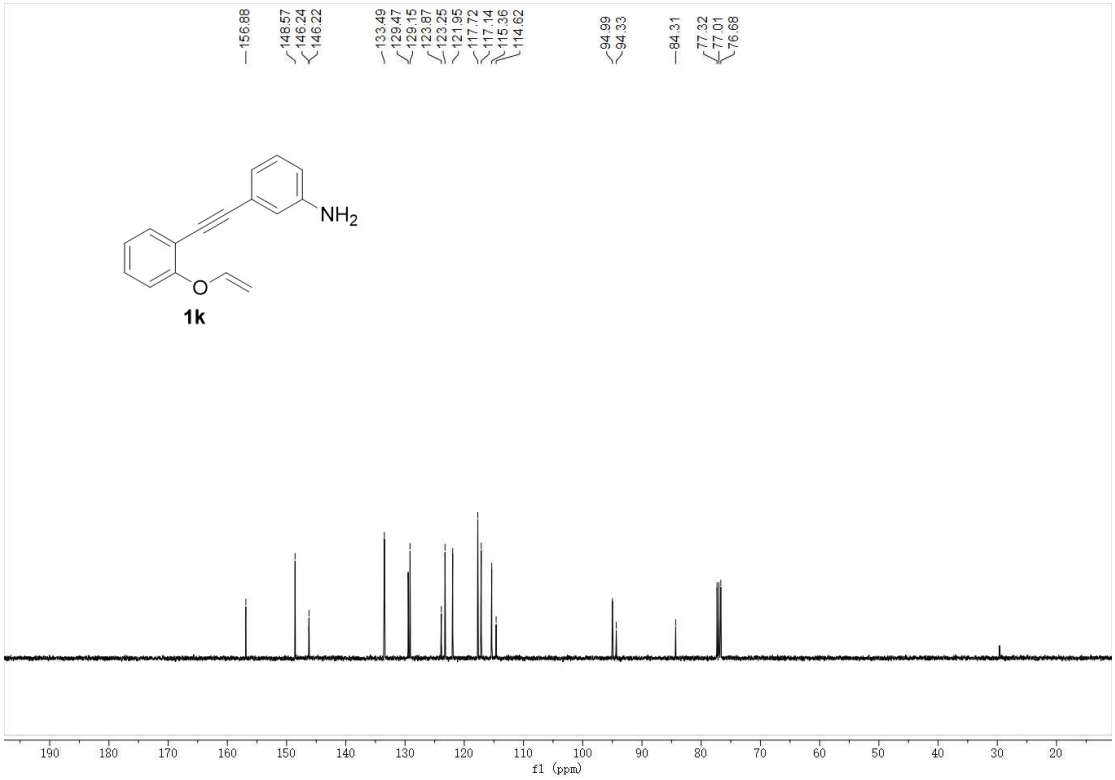
[2] Q.-H. Chen, P. N. Praveen Rao and E. E. Knaus, *Bioorg. Med. Chem*. **2005**, 13, 6425.

[3] Z. Pan, S. M. Pound, N. R. Rondla and C. J. Douglas, *Angew. Chem. Int. Ed.* **2014**, 53, 5170.

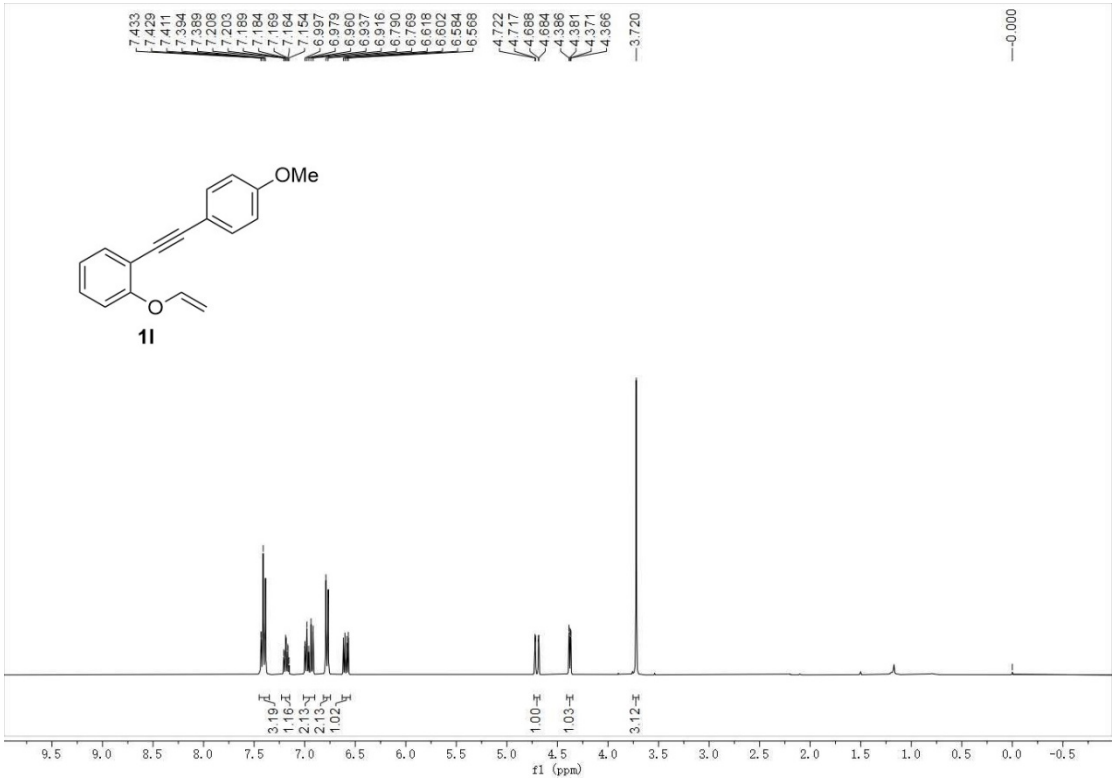
VI. NMR spectra



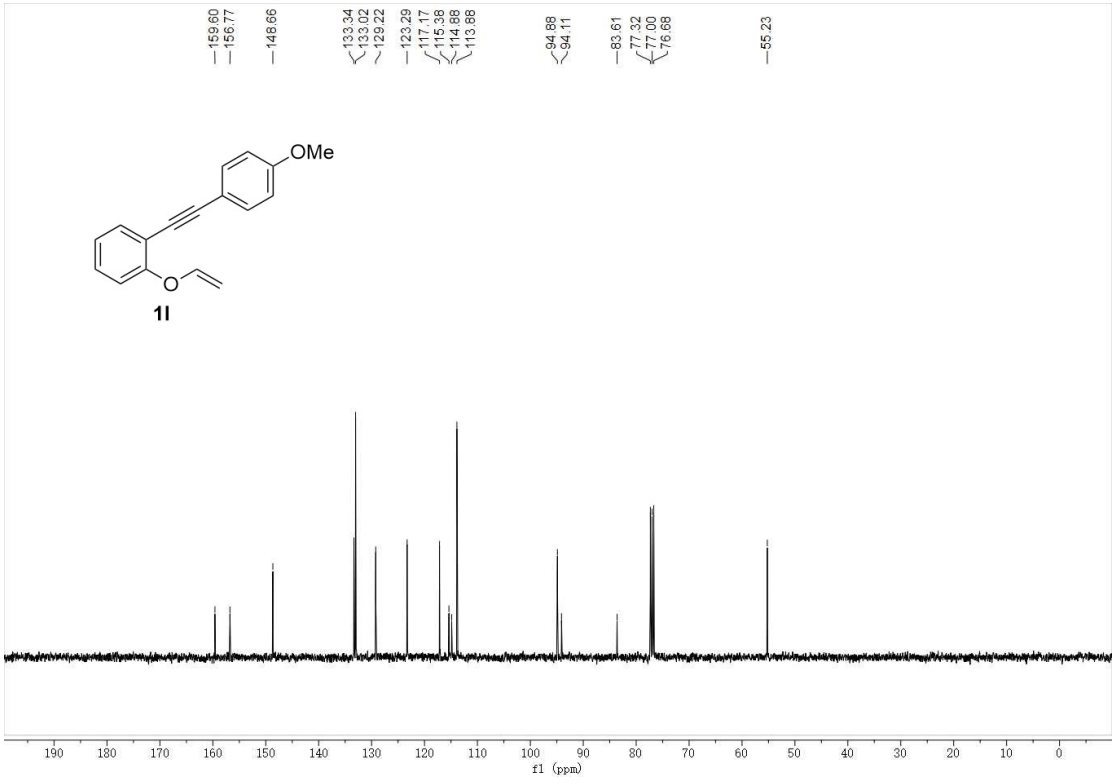
^{1}H NMR spectrum of **1k** (400 MHz, $CDCl_3$)



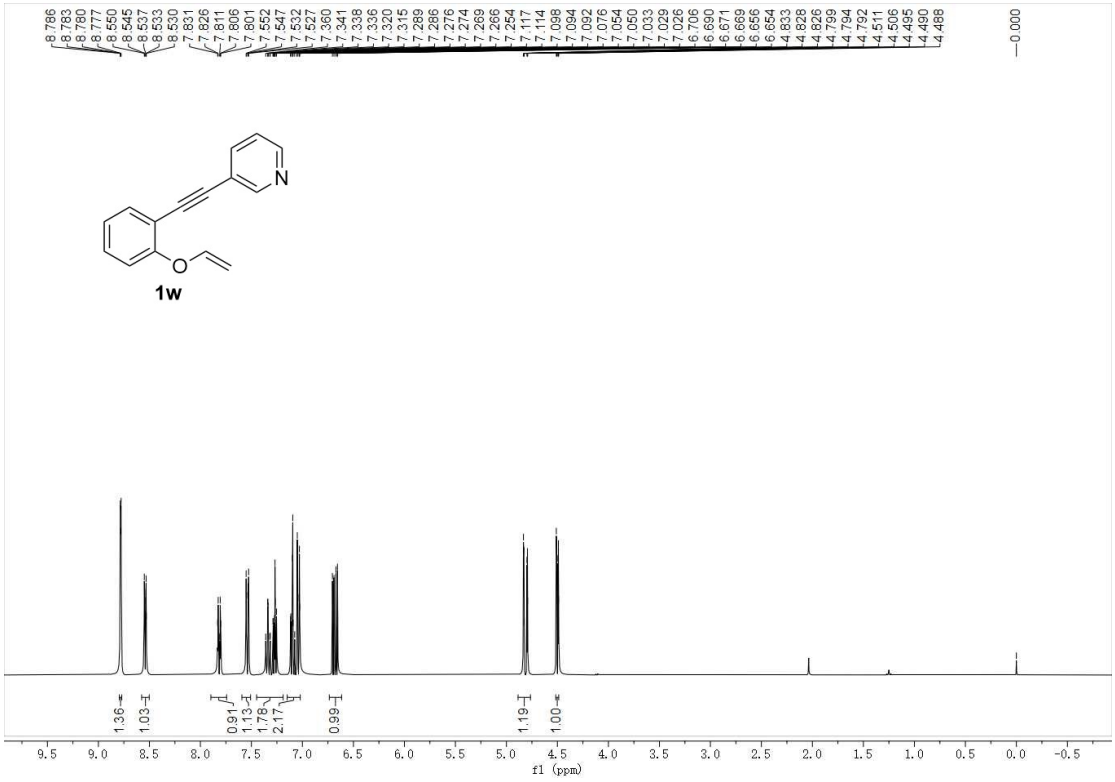
^{13}C NMR spectrum of **1k** (100 MHz, $CDCl_3$)



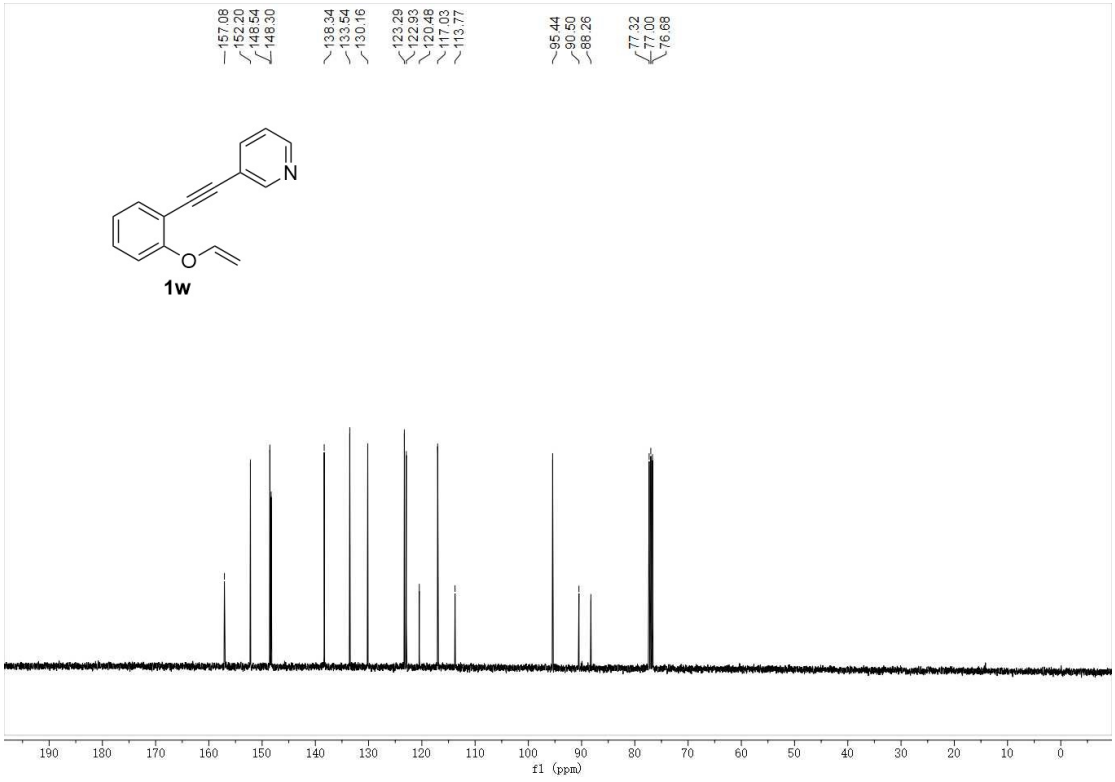
^{1}H NMR spectrum of **1l** (400 MHz, $CDCl_3$)



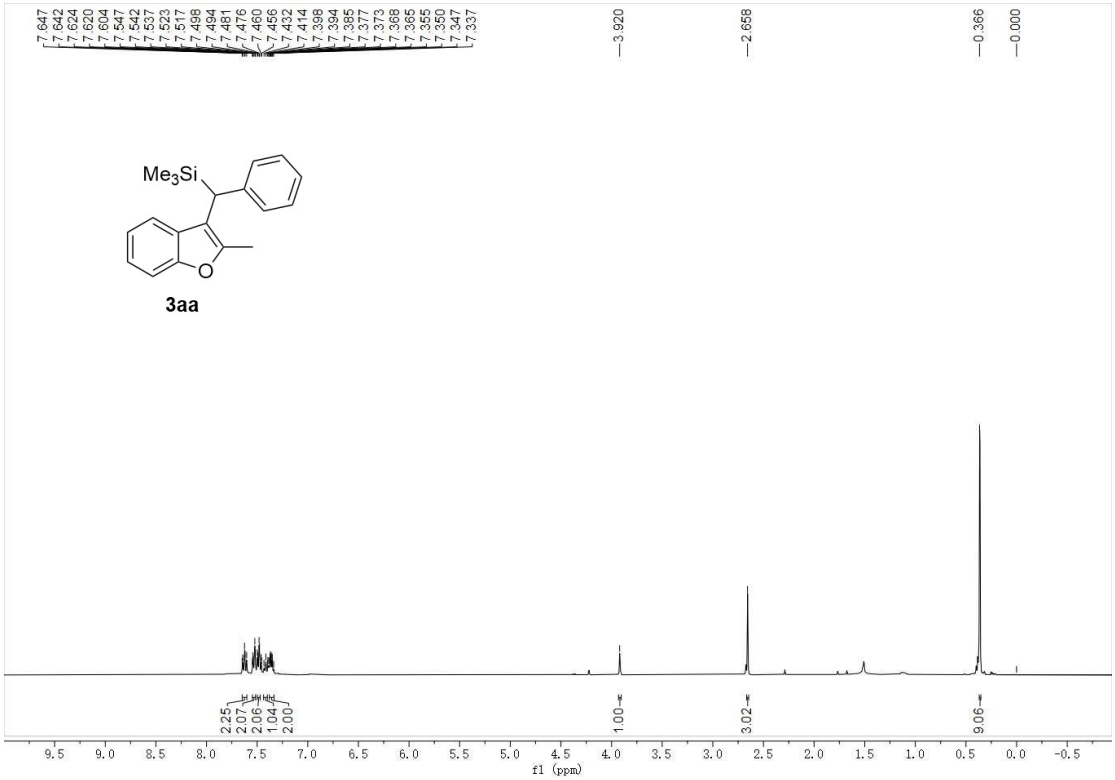
^{13}C NMR spectrum of **1l** (100 MHz, $CDCl_3$)



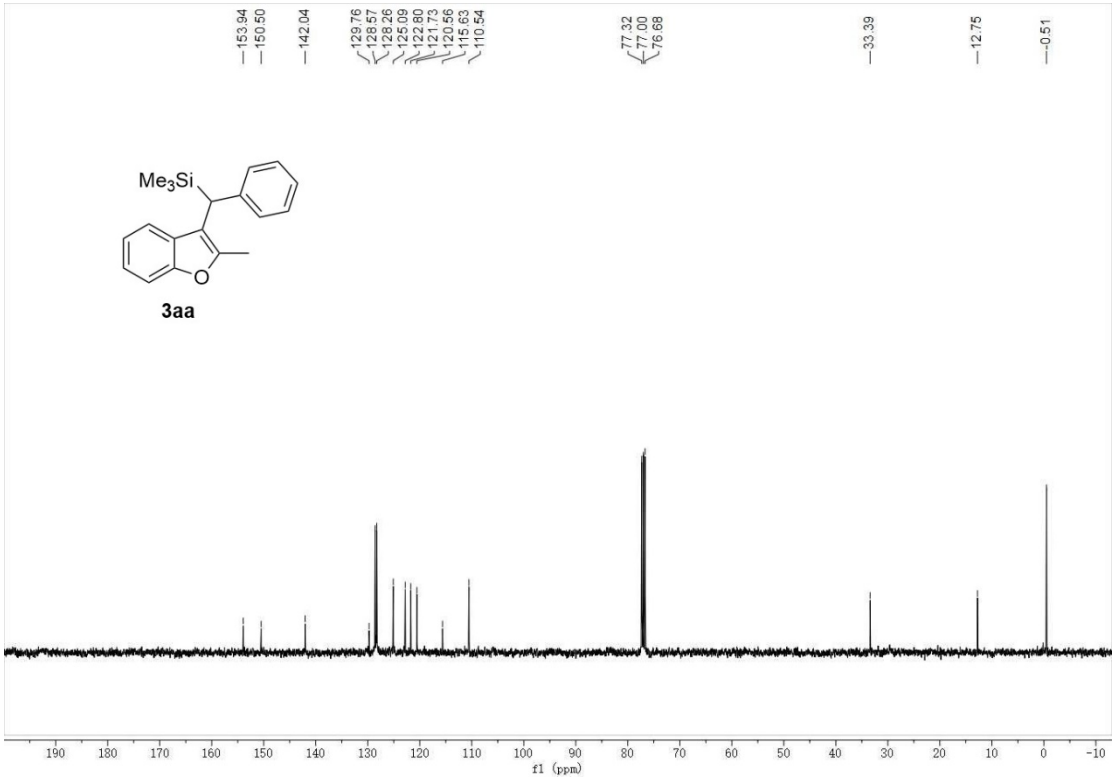
^{1}H NMR spectrum of **1w** (400 MHz, $CDCl_3$)



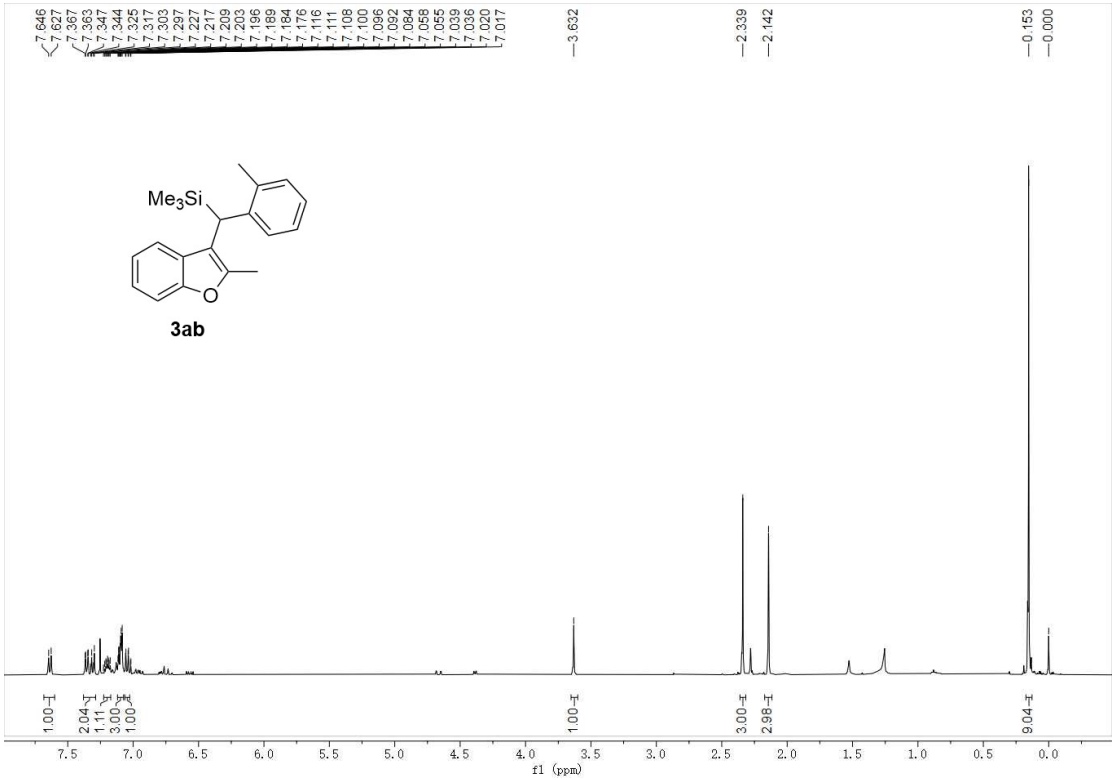
^{13}C NMR spectrum of **1w** (100 MHz, $CDCl_3$)



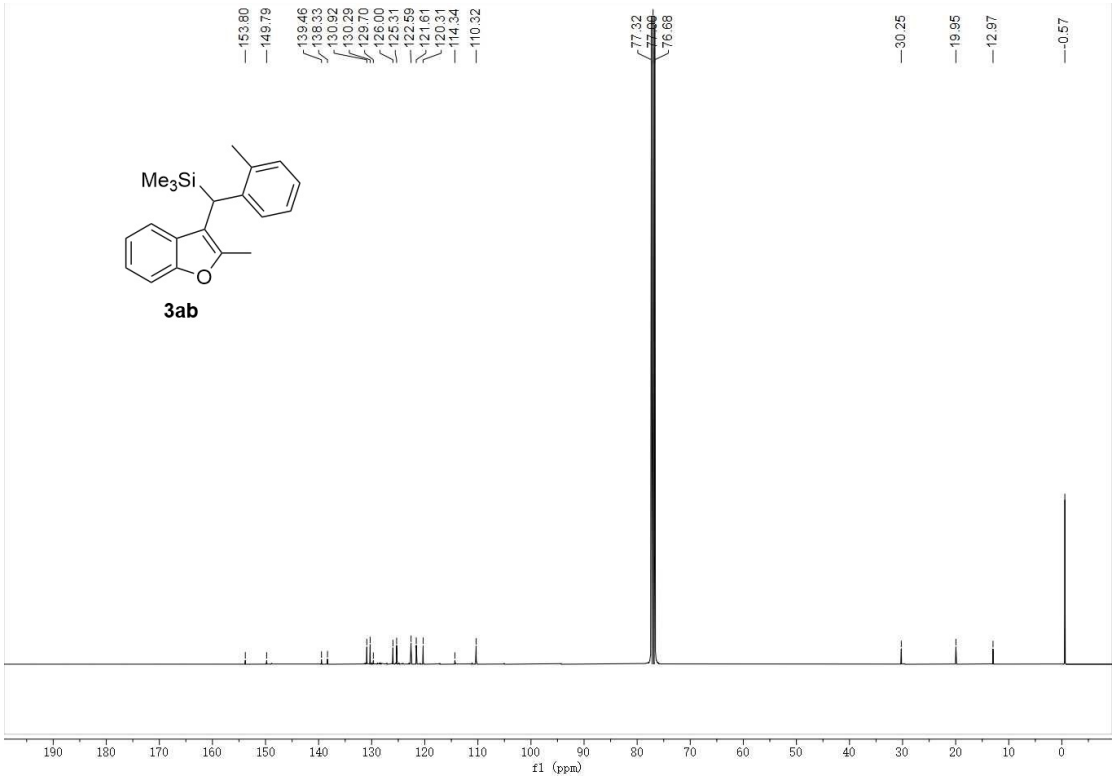
^{1}H NMR spectrum of **3aa** (400 MHz, $CDCl_3$)



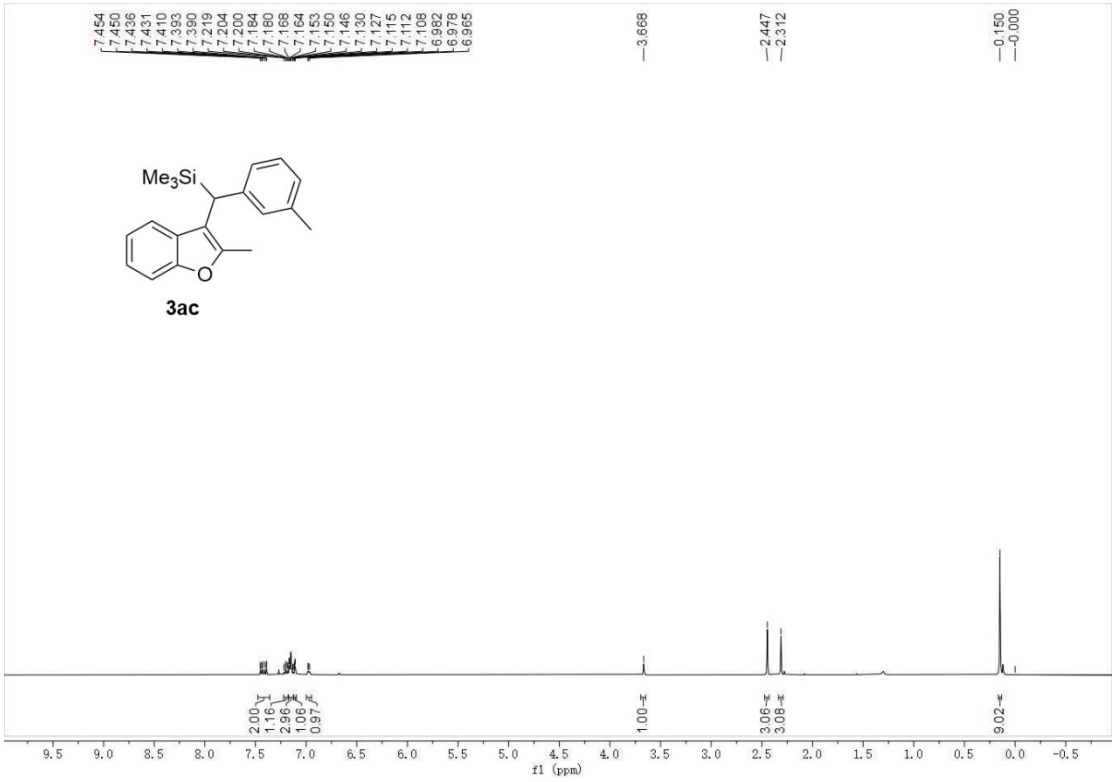
^{13}C NMR spectrum of **3aa** (100 MHz, $CDCl_3$)



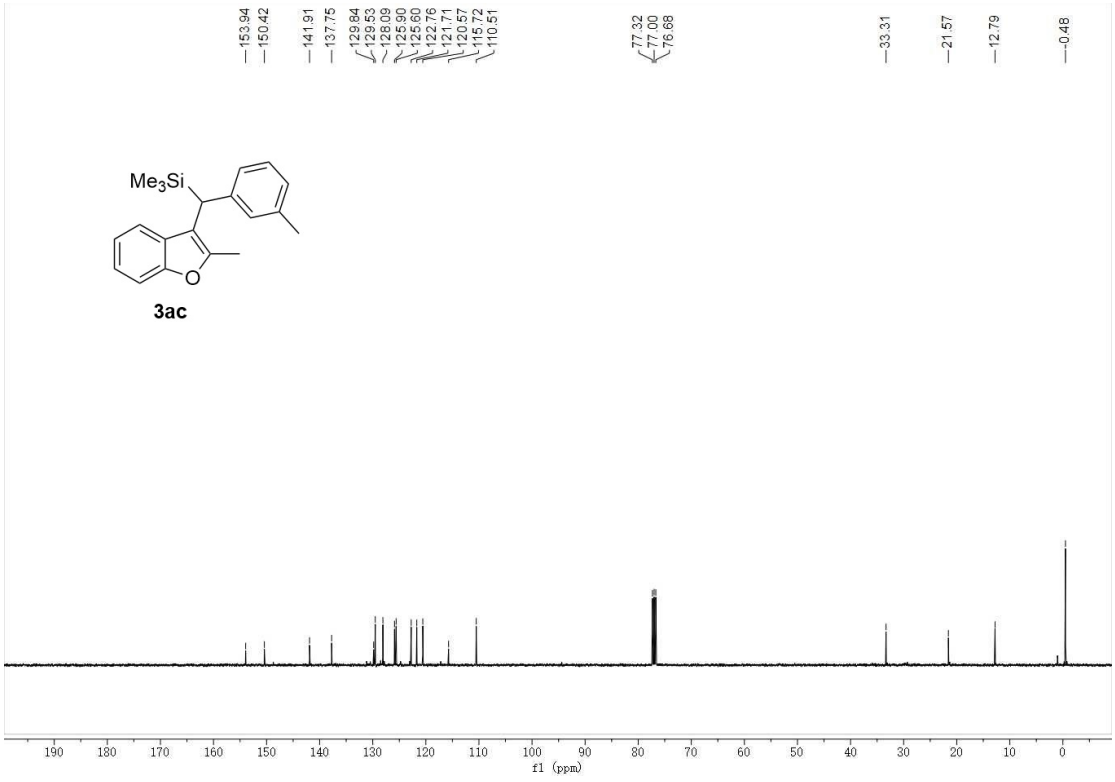
^{1}H NMR spectrum of **3ab** (400 MHz, $CDCl_3$)



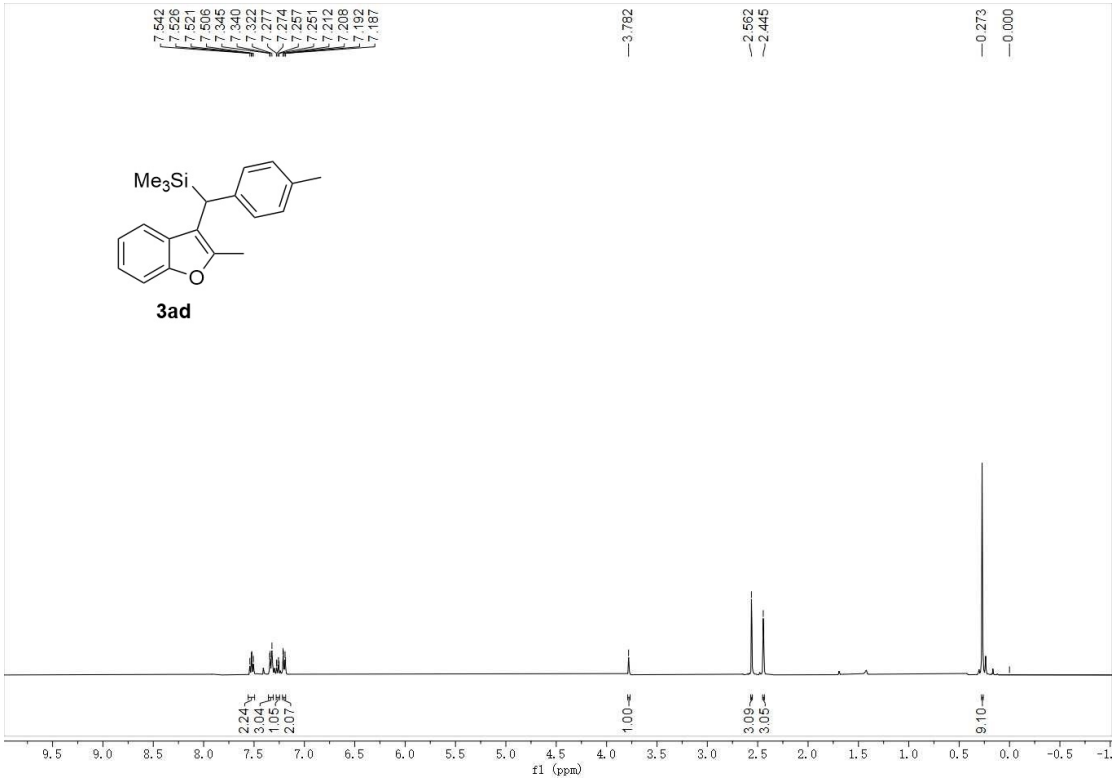
^{13}C NMR spectrum of **3ab** (100 MHz, $CDCl_3$)



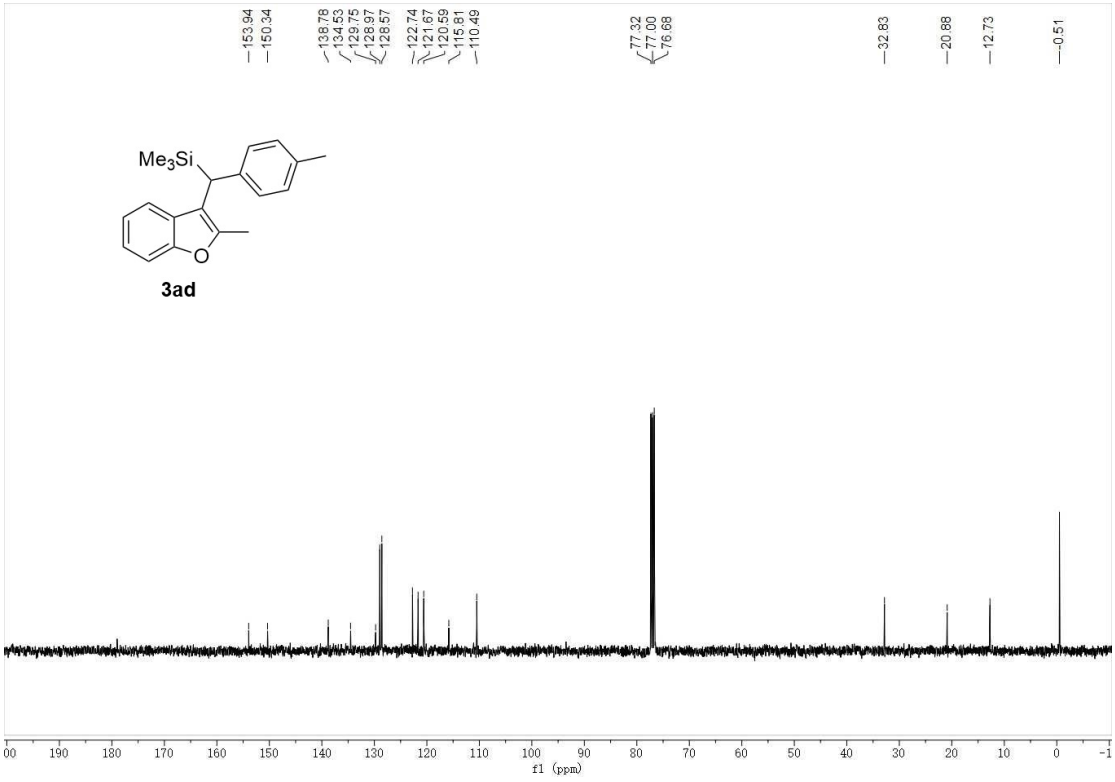
^{1}H NMR spectrum of **3ac** (400 MHz, $CDCl_3$)



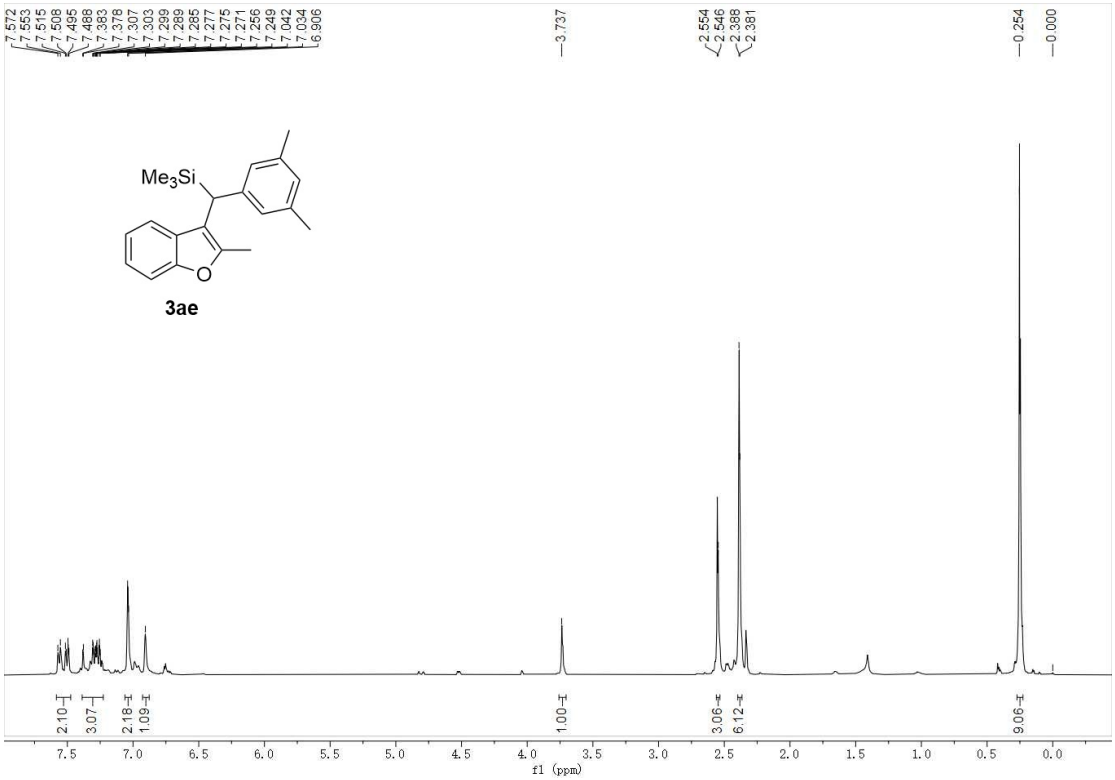
^{13}C NMR spectrum of **3ac** (100 MHz, $CDCl_3$)



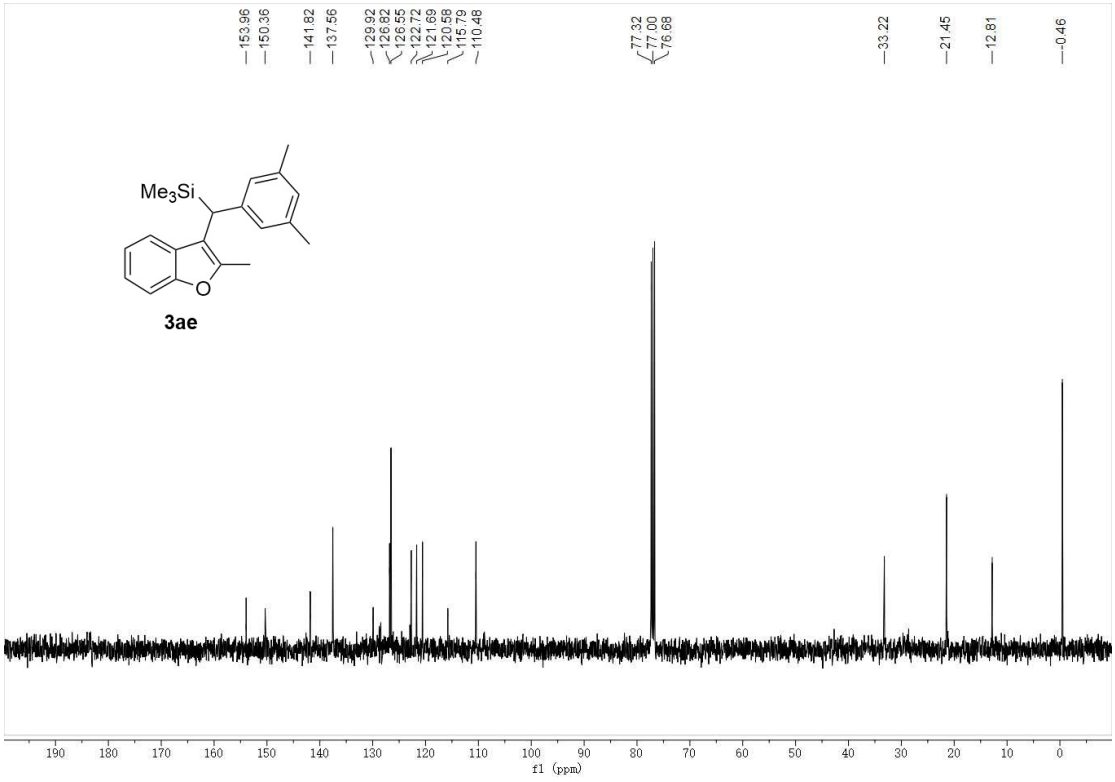
^{1}H NMR spectrum of **3ad** (400 MHz, $CDCl_3$)



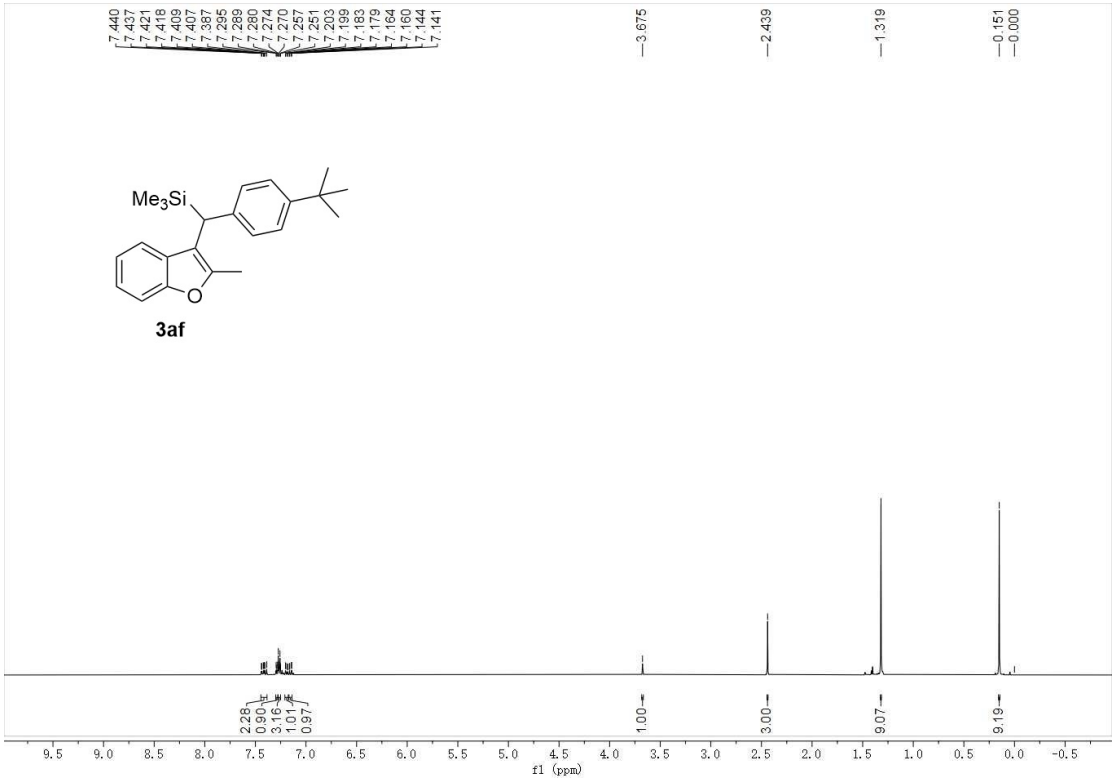
^{13}C NMR spectrum of **3ad** (100 MHz, $CDCl_3$)



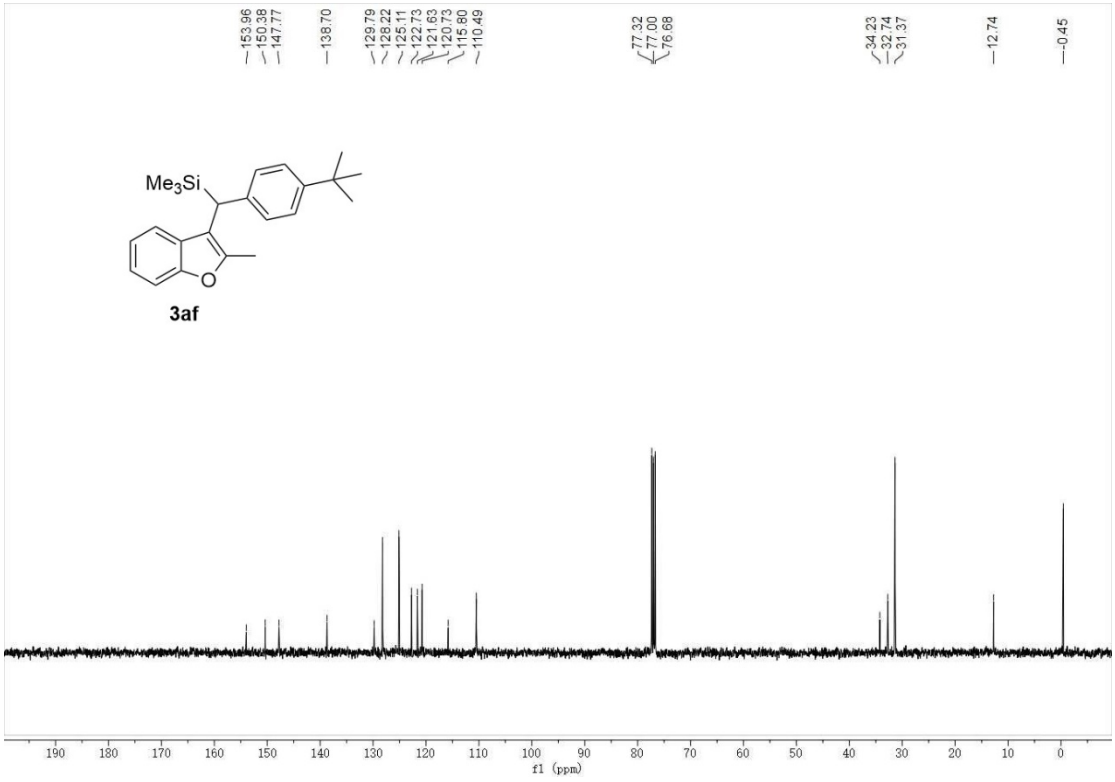
^{1}H NMR spectrum of **3ae** (400 MHz, $CDCl_3$)



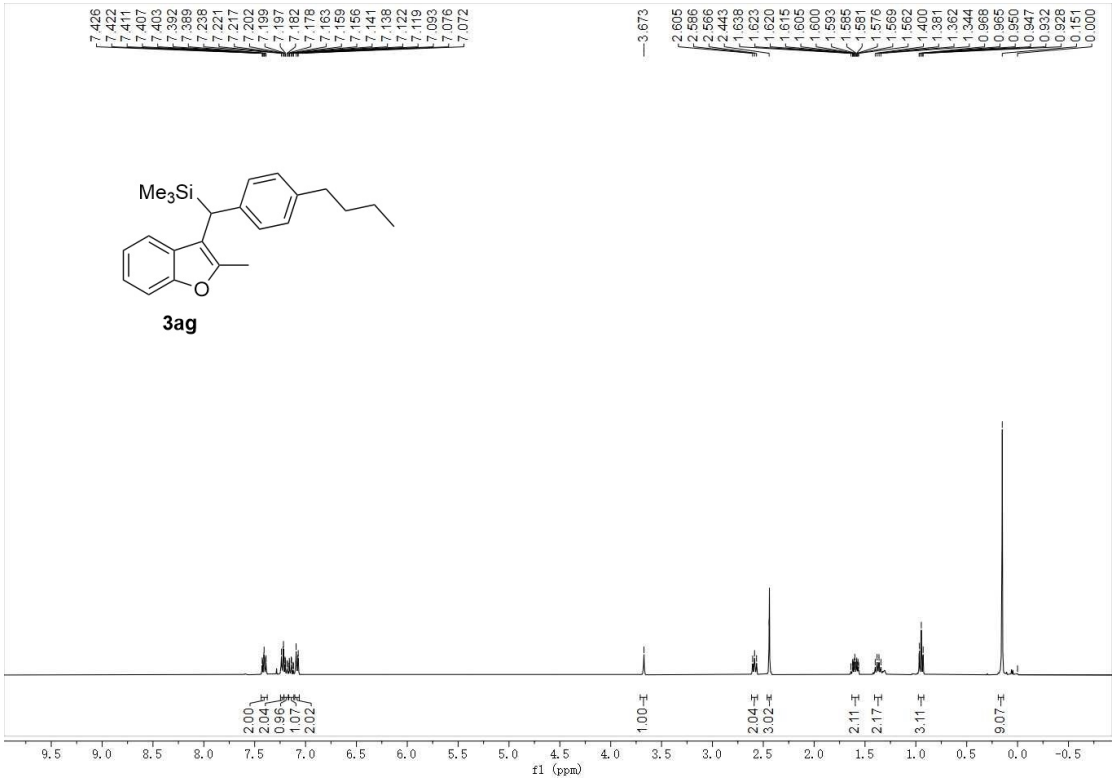
^{13}C NMR spectrum of **3ae** (100 MHz, $CDCl_3$)



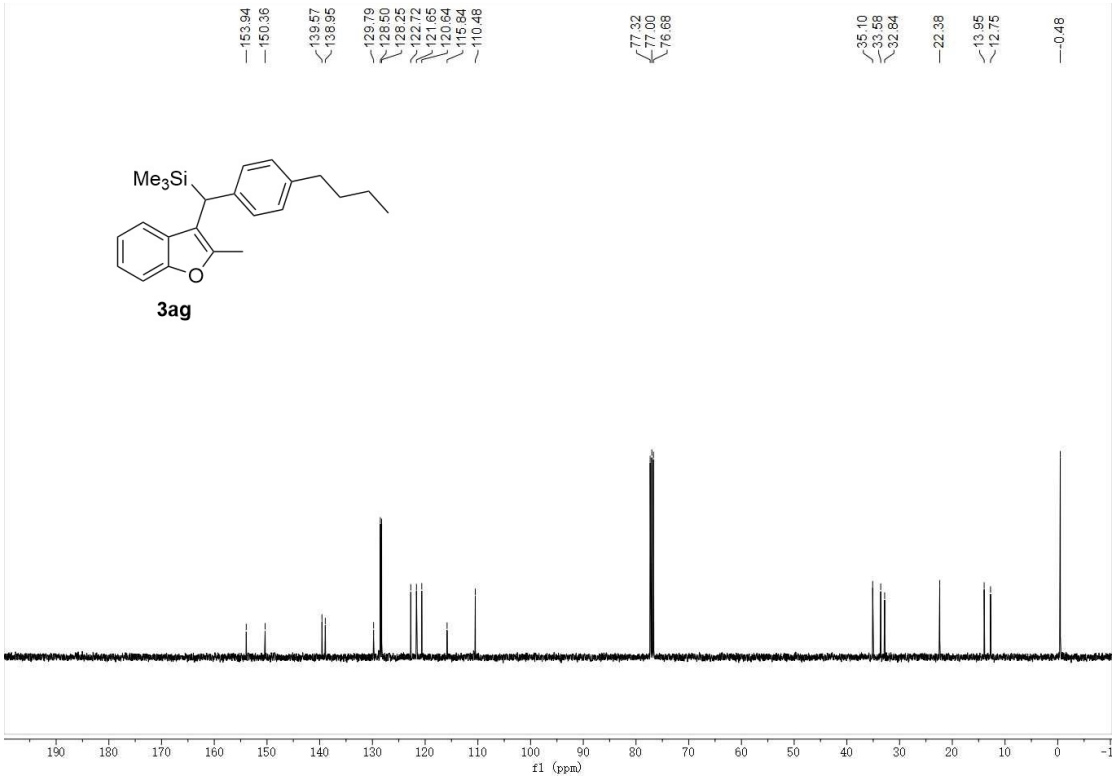
^{1}H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



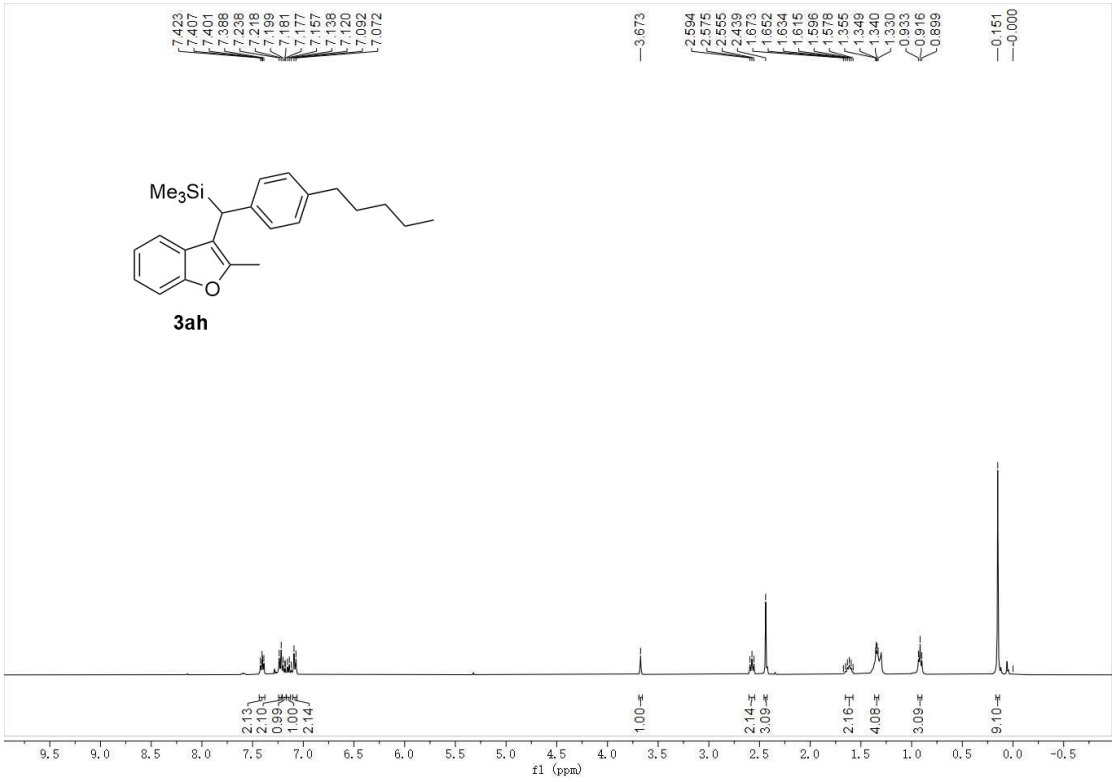
^{13}C NMR spectrum of **3af** (100 MHz, $CDCl_3$)



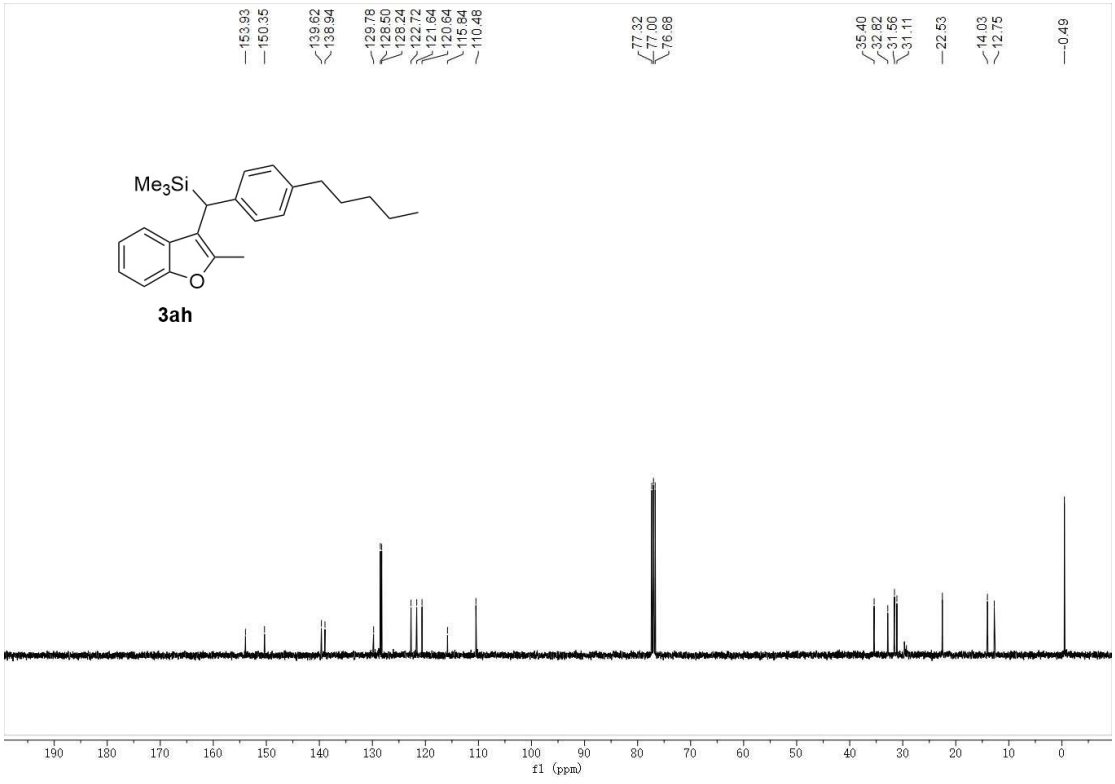
^{1}H NMR spectrum of **3ag** (400 MHz, $CDCl_3$)



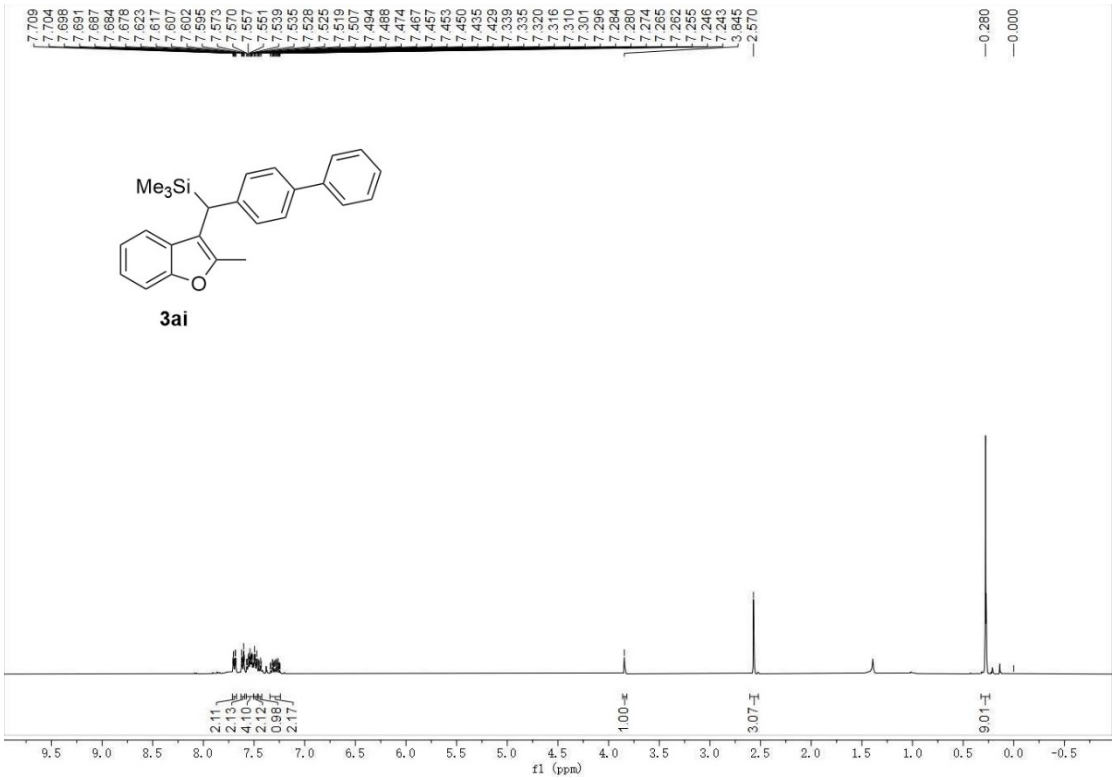
^{13}C NMR spectrum of **3ag** (100 MHz, $CDCl_3$)



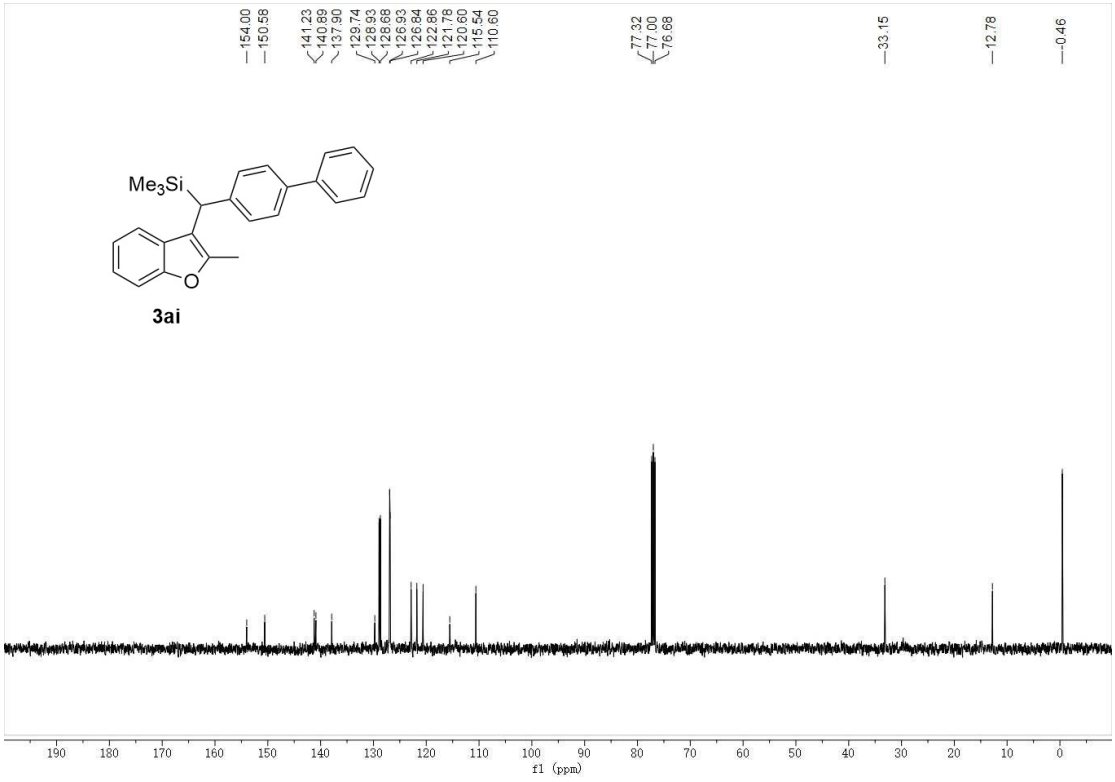
^{1}H NMR spectrum of **3ah** (400 MHz, $CDCl_3$)



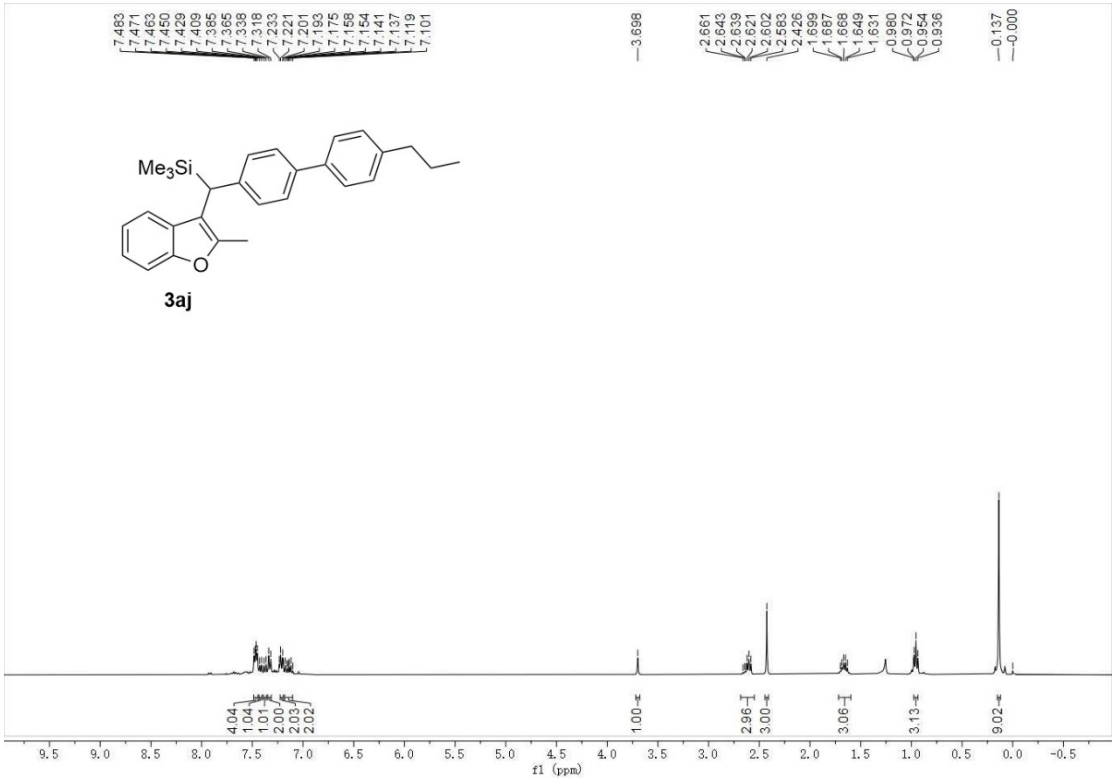
^{13}C NMR spectrum of **3ah** (100 MHz, $CDCl_3$)



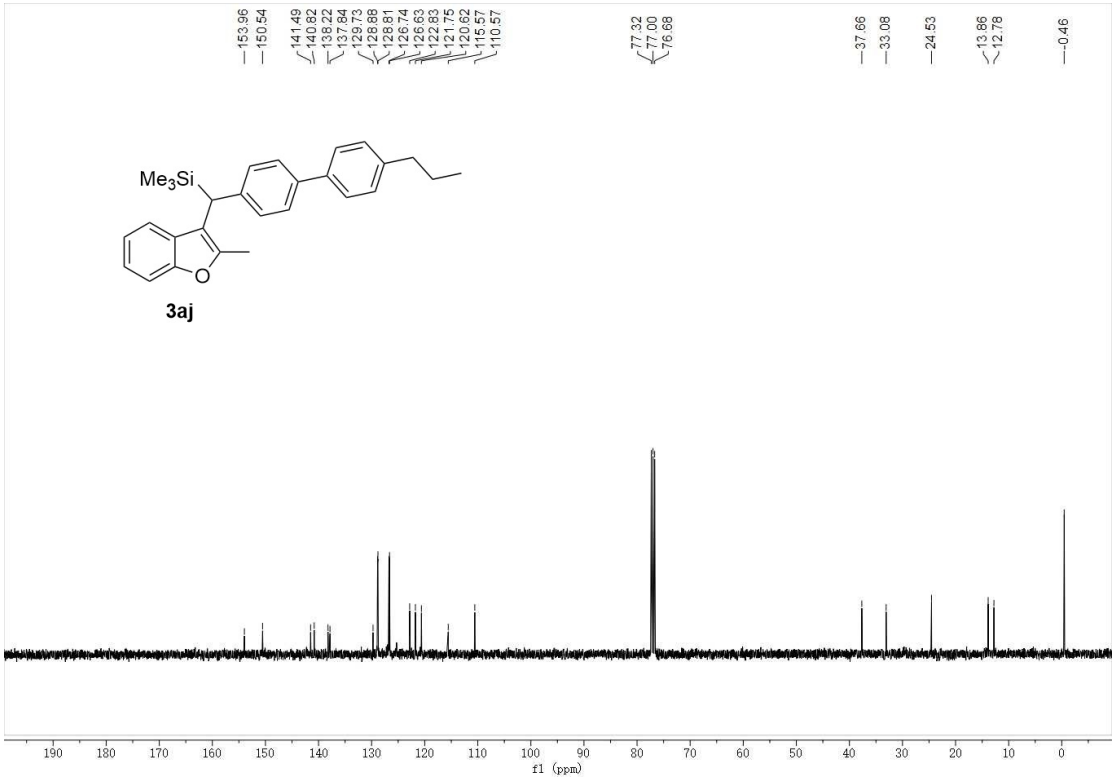
^{1}H NMR spectrum of **3ai** (400 MHz, $CDCl_3$)



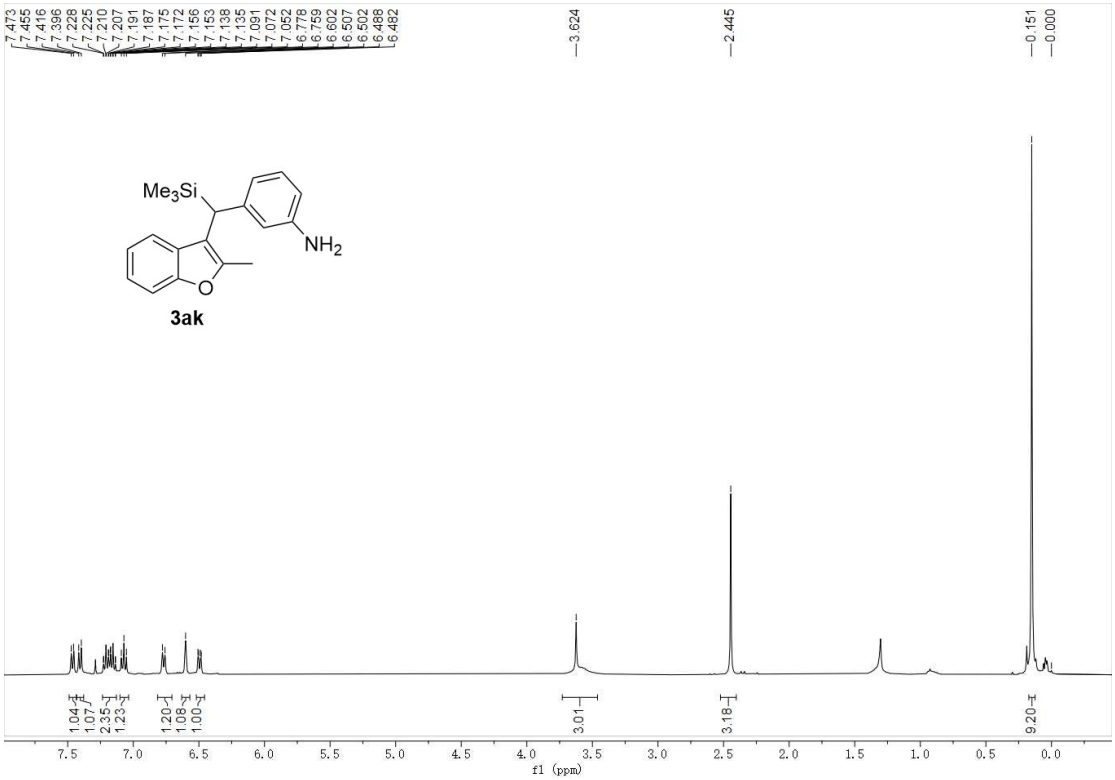
^{13}C NMR spectrum of **3ai** (100 MHz, $CDCl_3$)



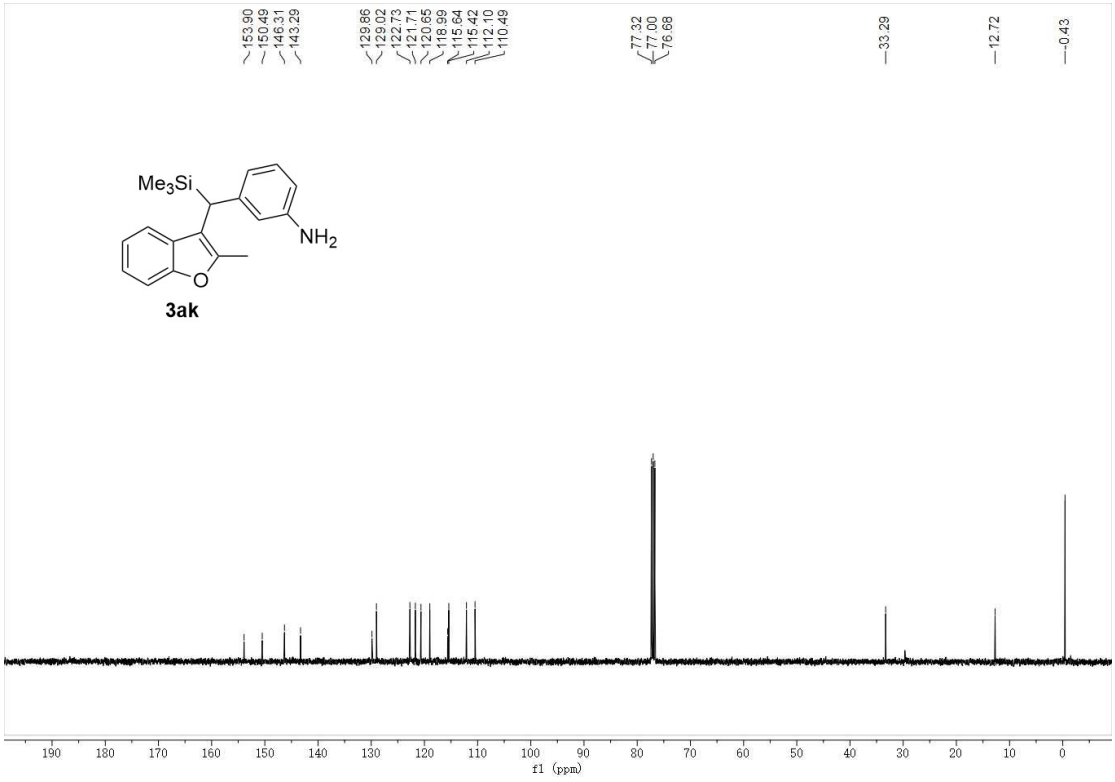
^{1}H NMR spectrum of **3aj** (400 MHz, $CDCl_3$)



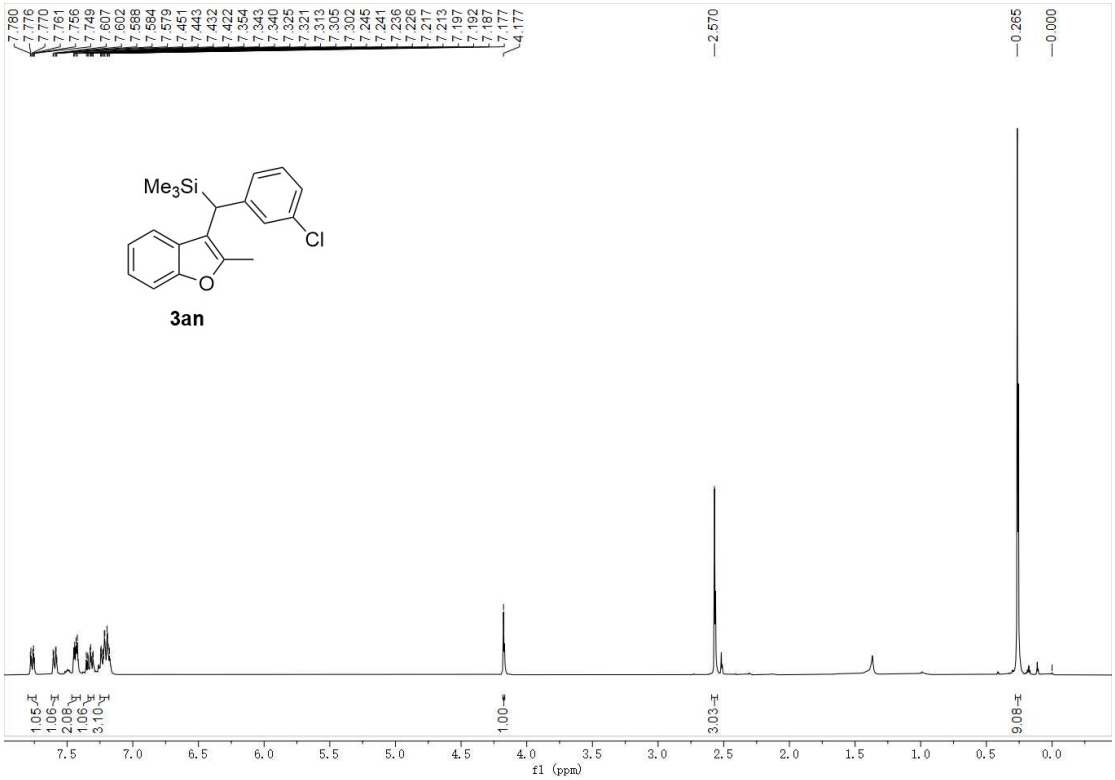
^{13}C NMR spectrum of **3aj** (100 MHz, $CDCl_3$)



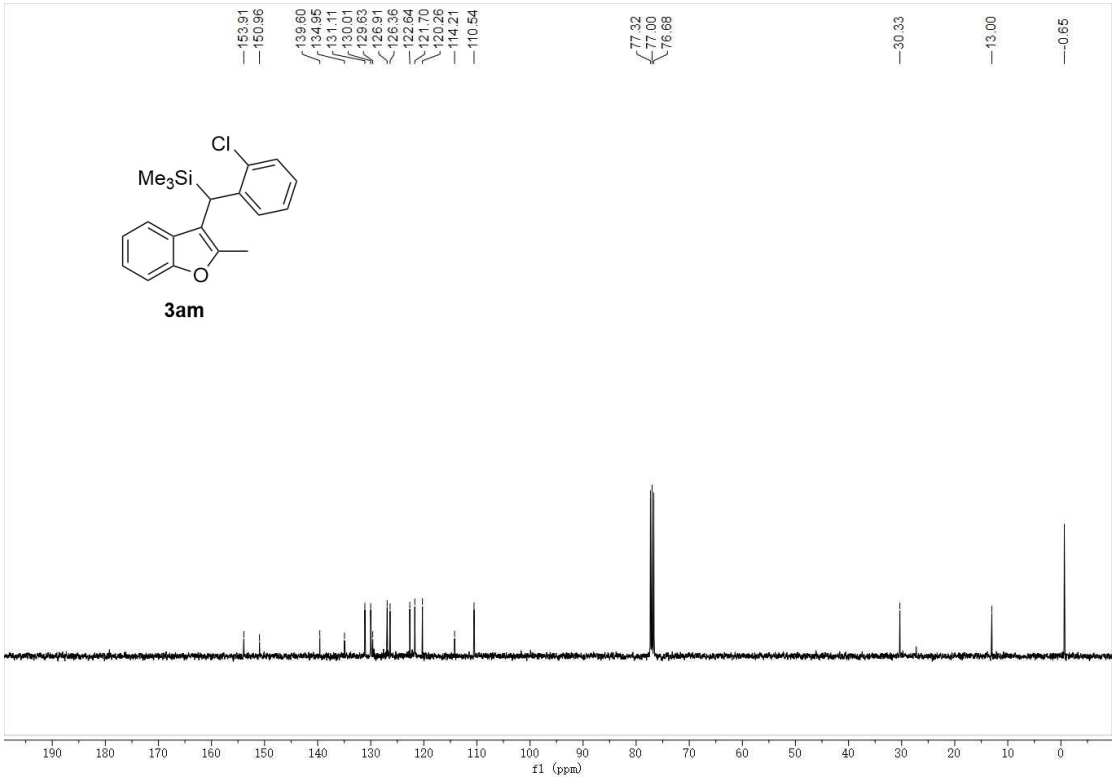
^{1}H NMR spectrum of **3ak** (400 MHz, $CDCl_3$)



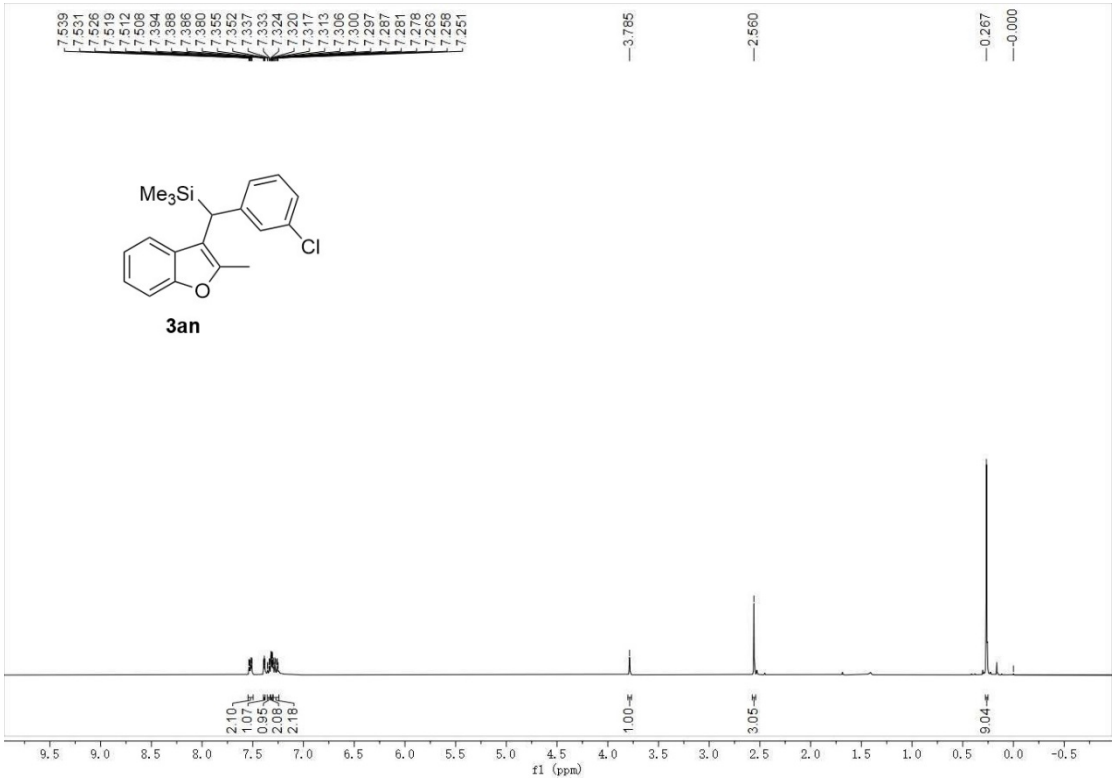
^{13}C NMR spectrum of **3ak** (100 MHz, $CDCl_3$)



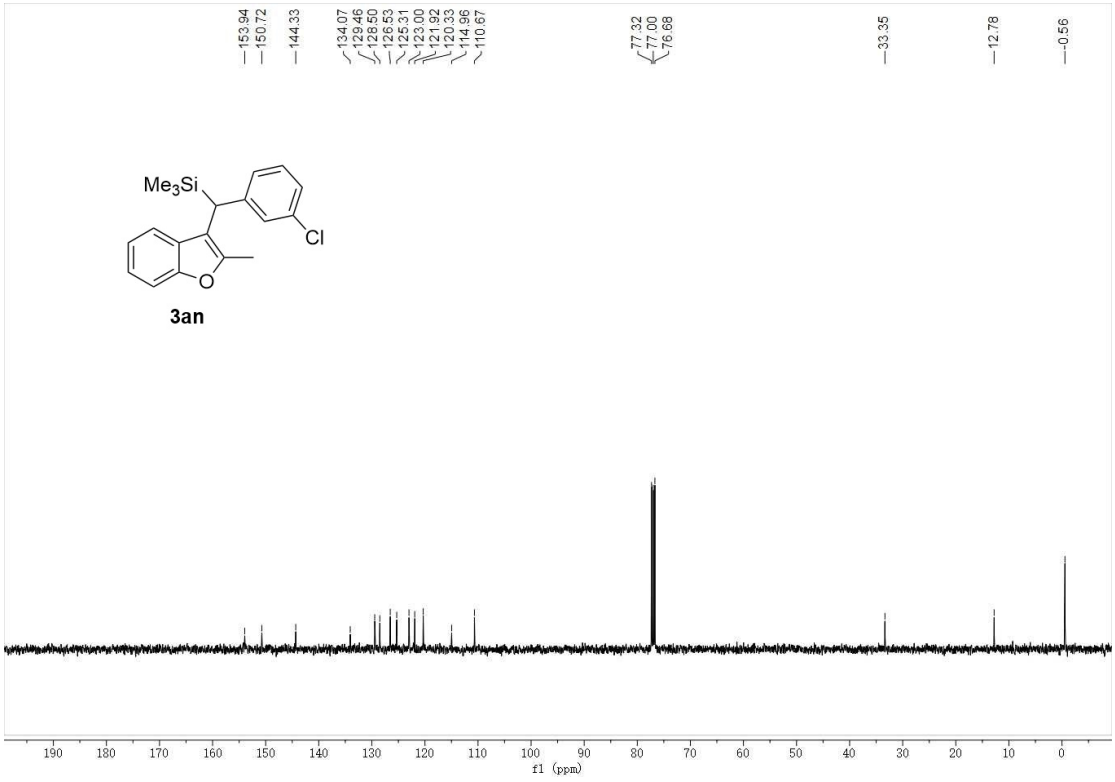
^{1}H NMR spectrum of **3am** (400 MHz, $CDCl_3$)



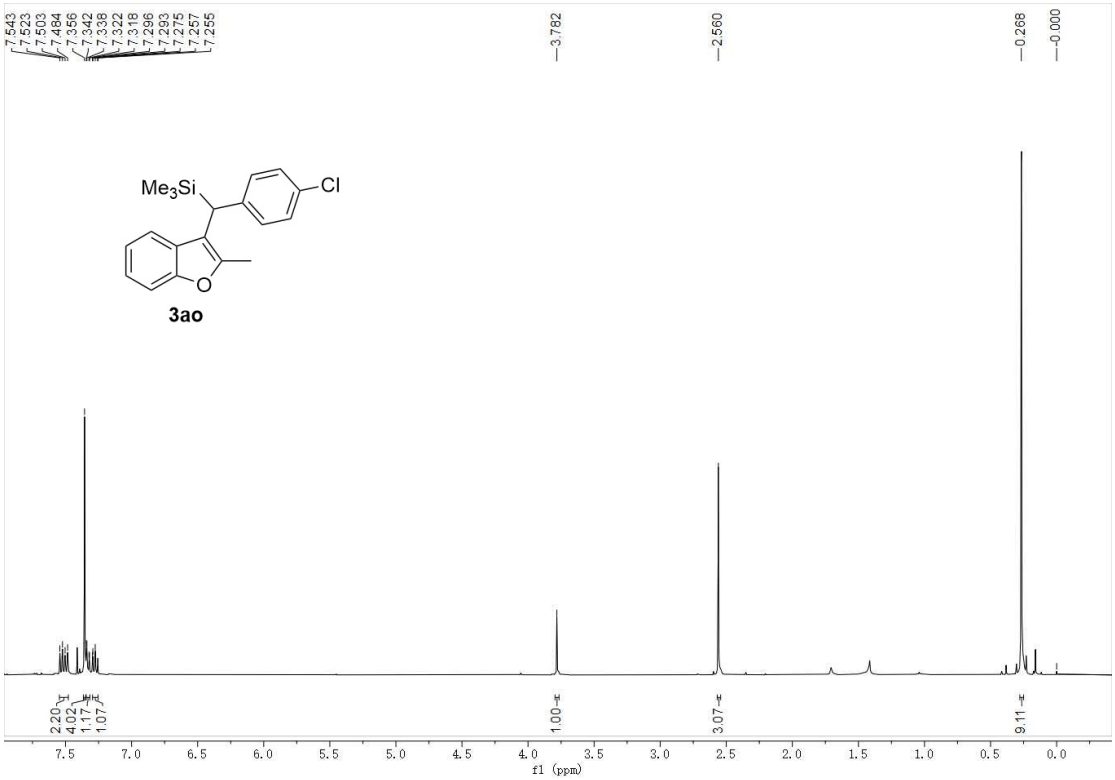
^{13}C NMR spectrum of **3am** (100 MHz, $CDCl_3$)



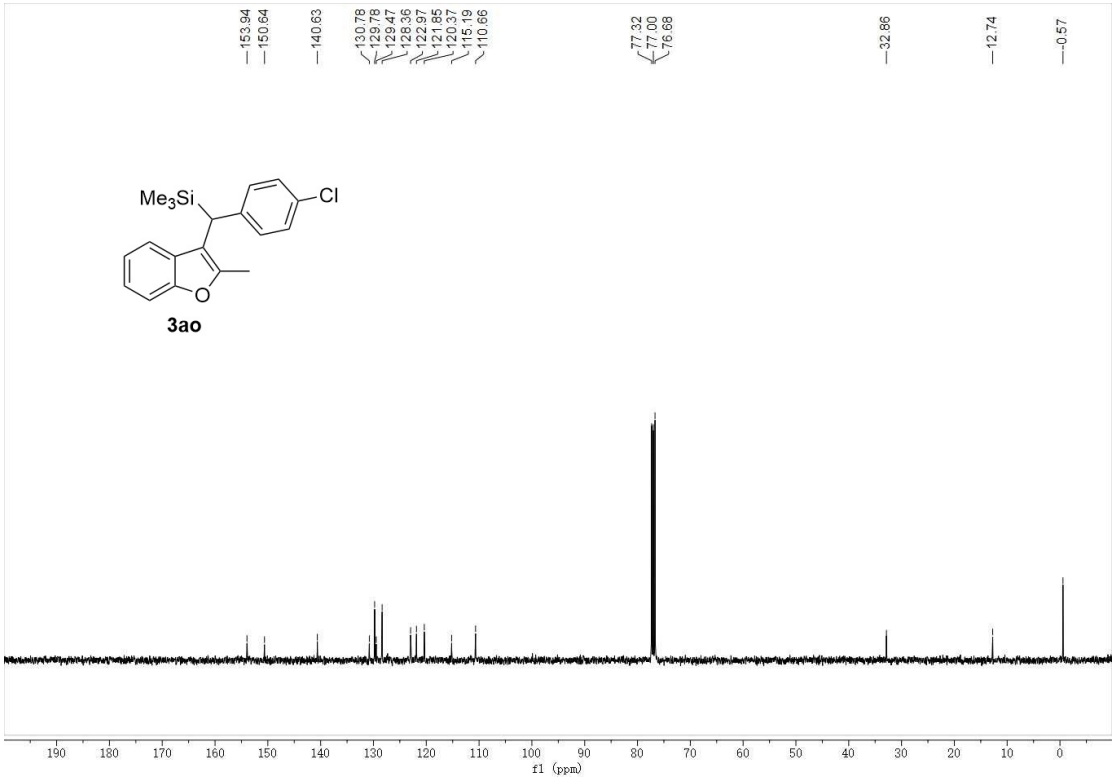
^{1}H NMR spectrum of **3an** (400 MHz, $CDCl_3$)



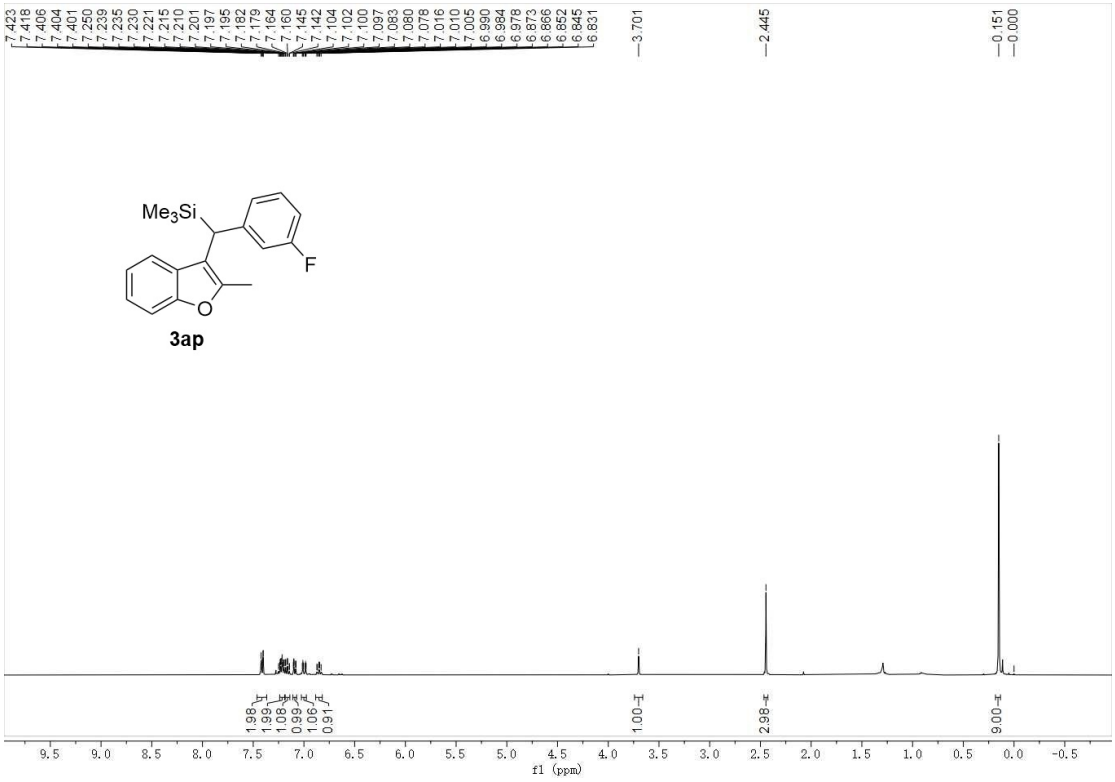
^{13}C NMR spectrum of **3an** (100 MHz, $CDCl_3$)



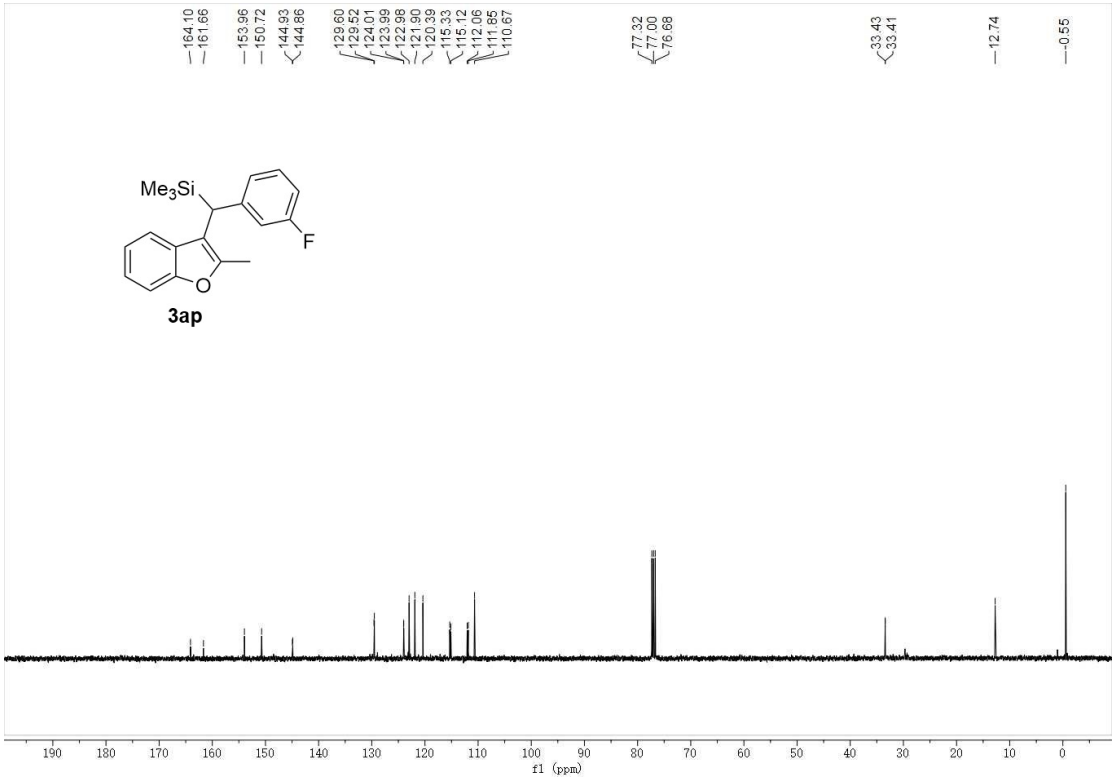
^{1}H NMR spectrum of **3ao** (400 MHz, $CDCl_3$)



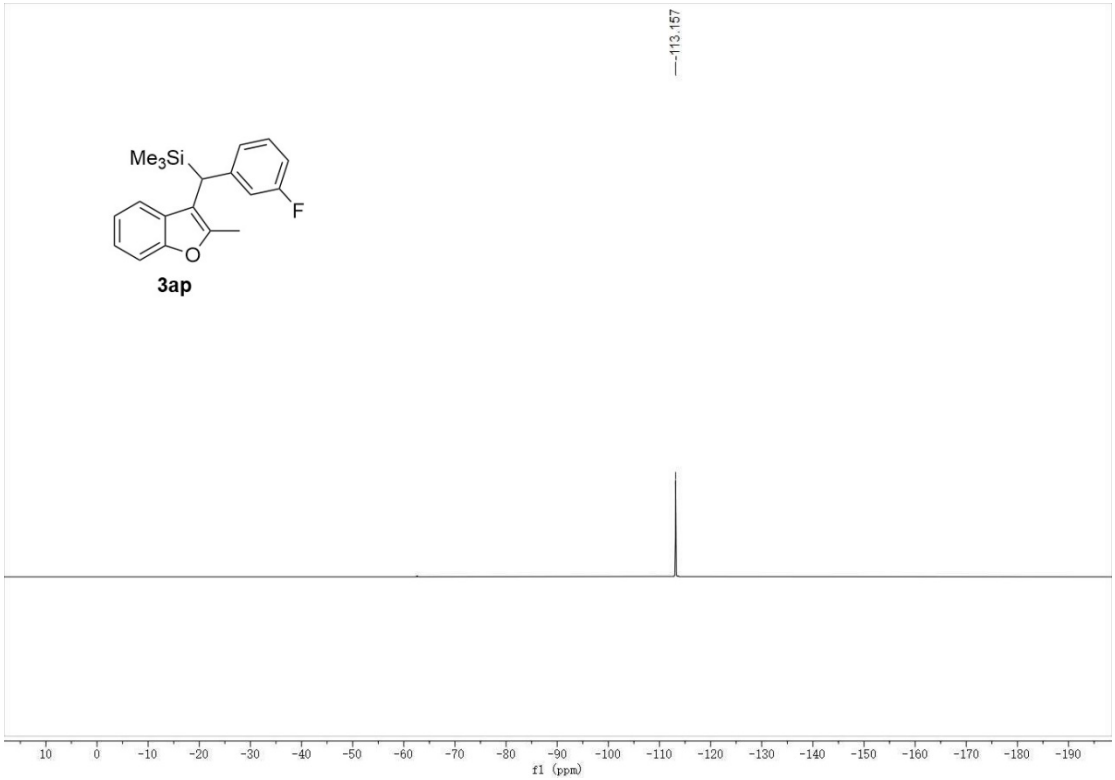
^{13}C NMR spectrum of **3ao** (100 MHz, $CDCl_3$)



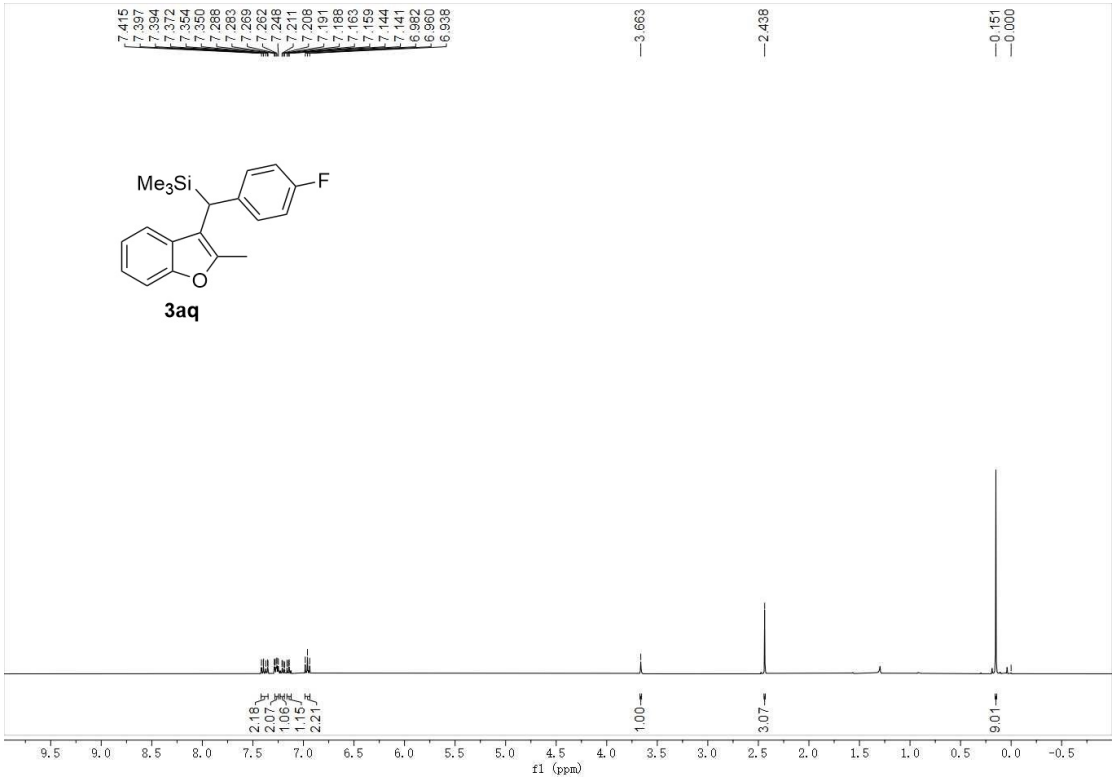
^{1}H NMR spectrum of **3ap** (400 MHz, $CDCl_3$)



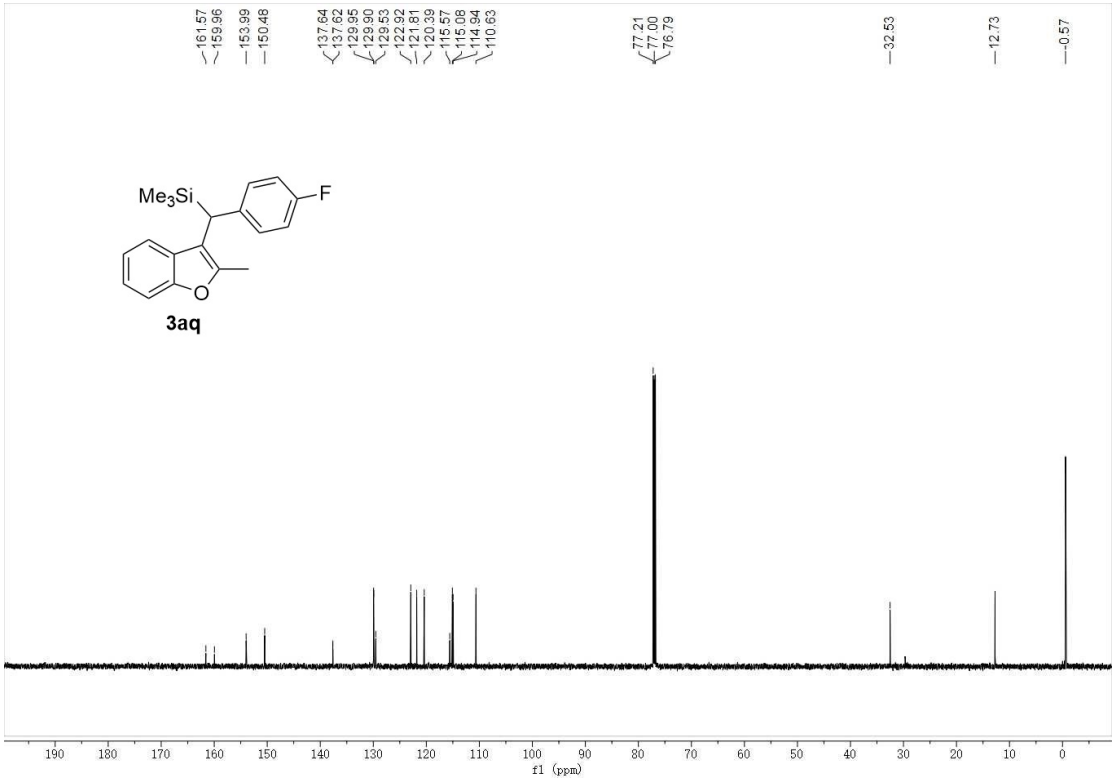
^{13}C NMR spectrum of **3ap** (100 MHz, $CDCl_3$)



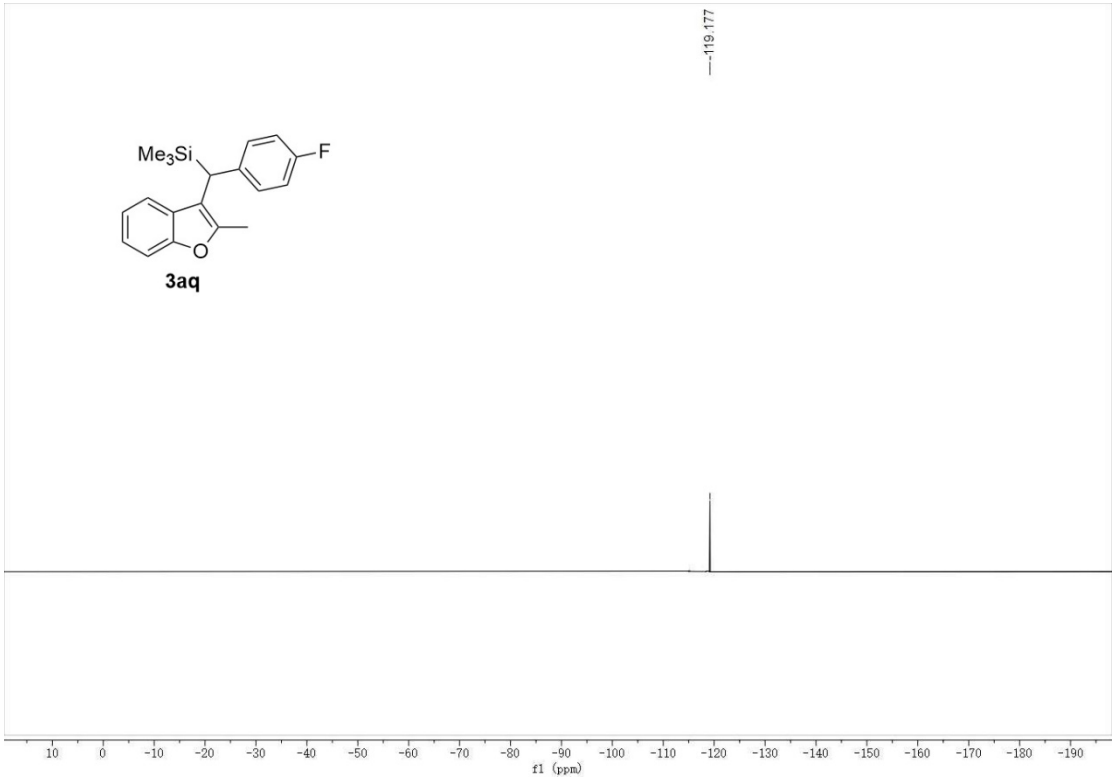
^{19}F NMR spectrum of **3ap** (377 MHz, $CDCl_3$)



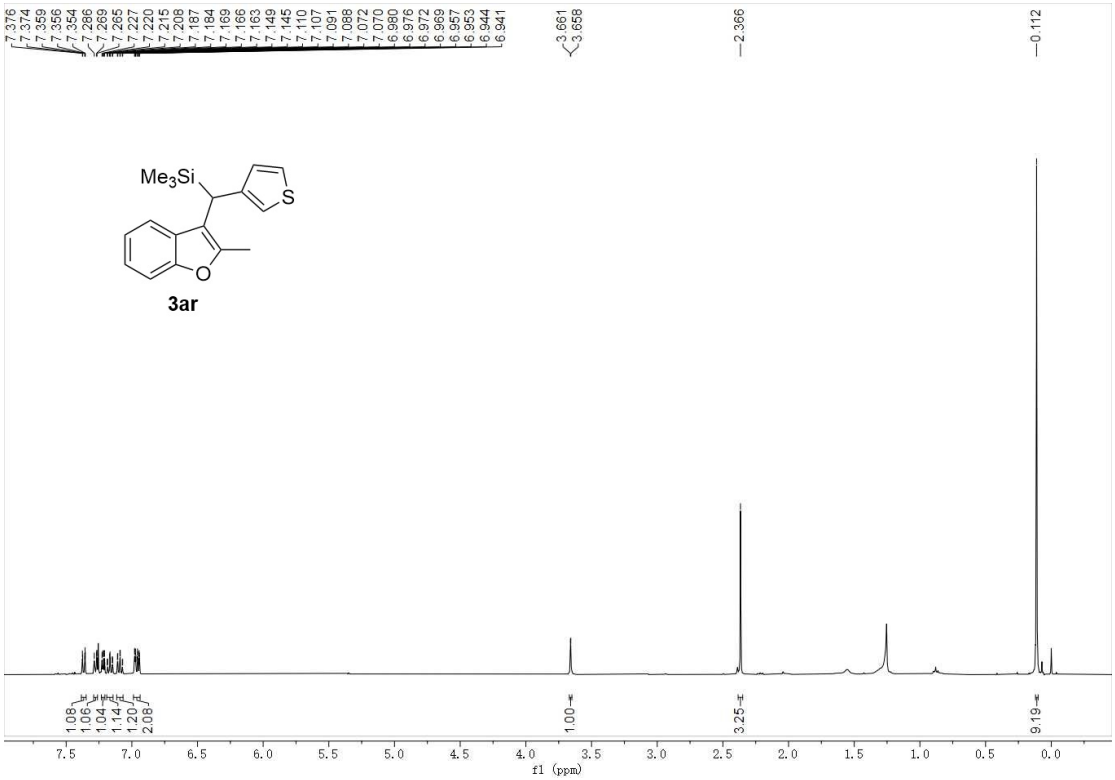
^{1}H NMR spectrum of **3aq** (400 MHz, $CDCl_3$)



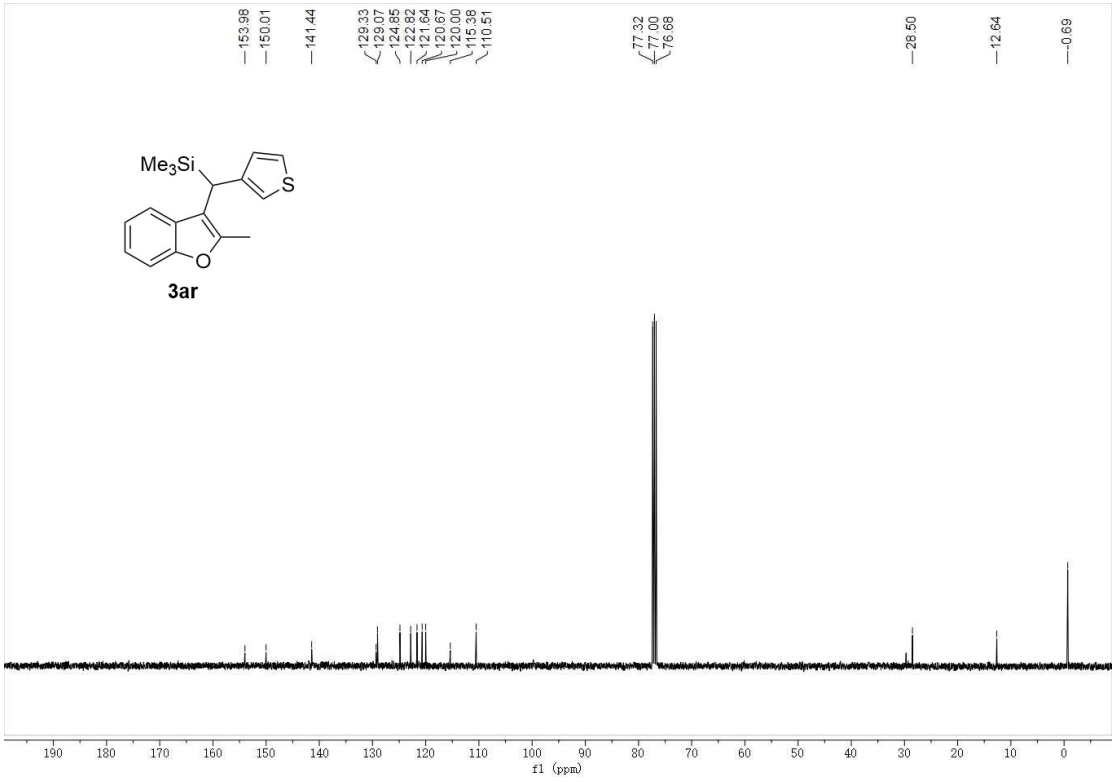
^{13}C NMR spectrum of **3aq** (100 MHz, $CDCl_3$)



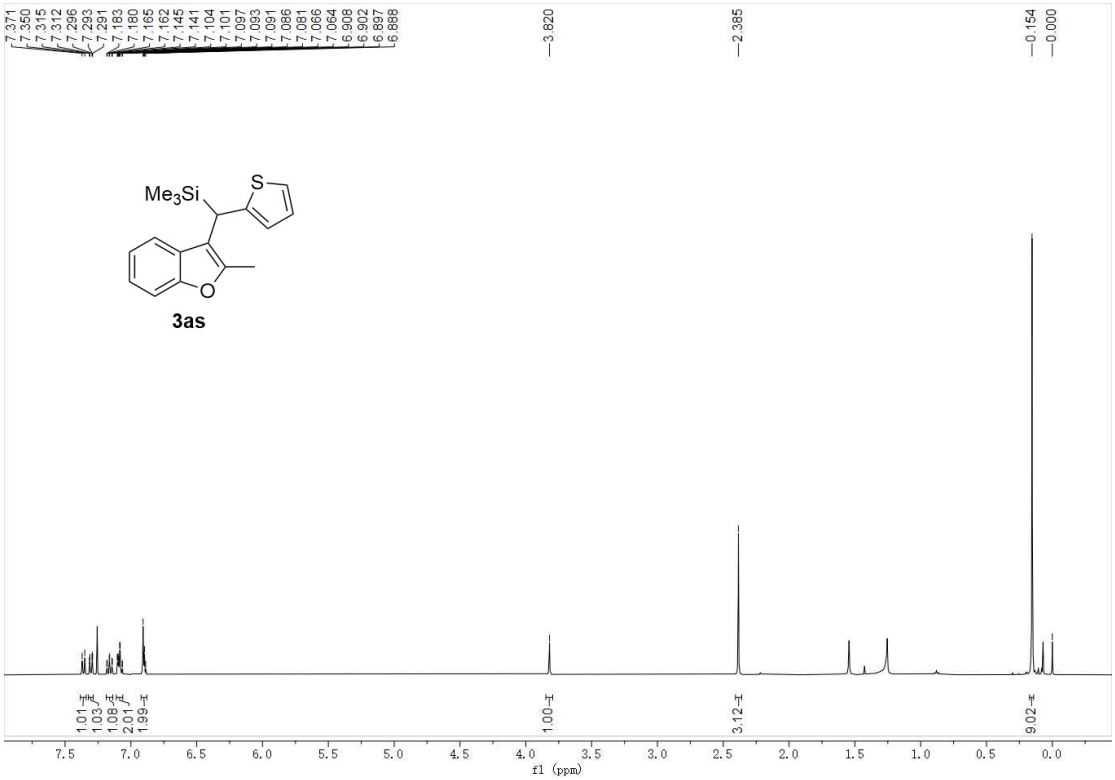
^{19}F NMR spectrum of **3aq** (377 MHz, $CDCl_3$)



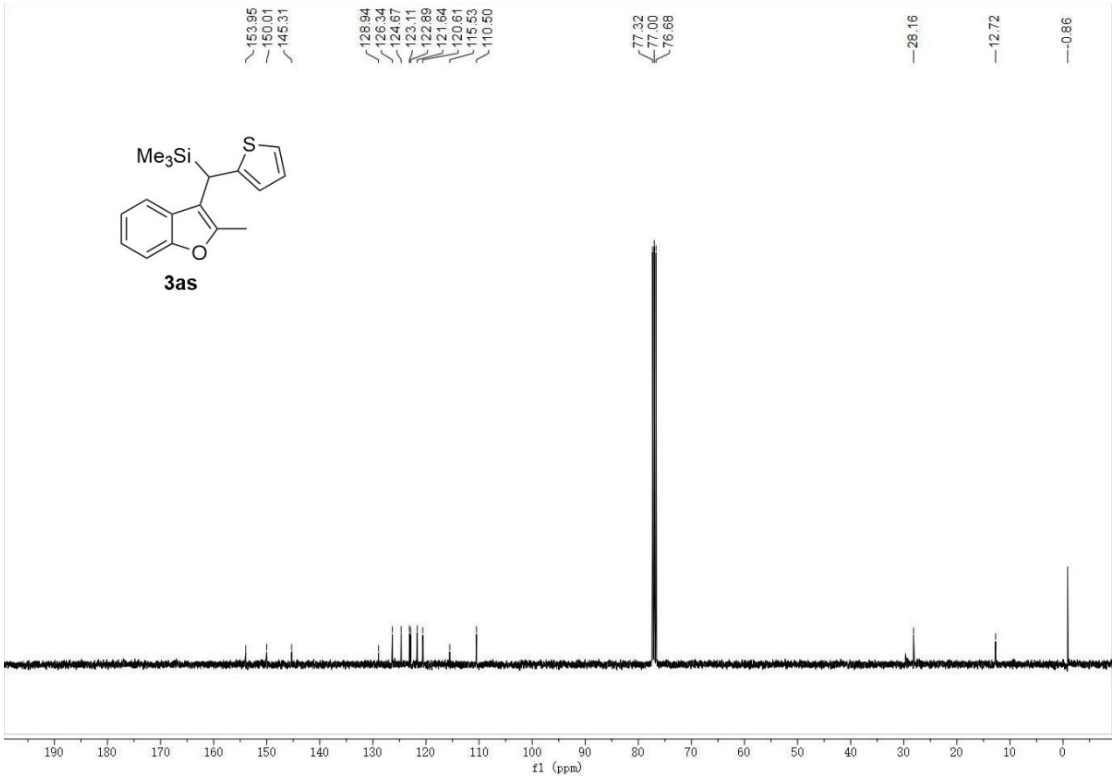
^{1}H NMR spectrum of **3ar** (400 MHz, $CDCl_3$)



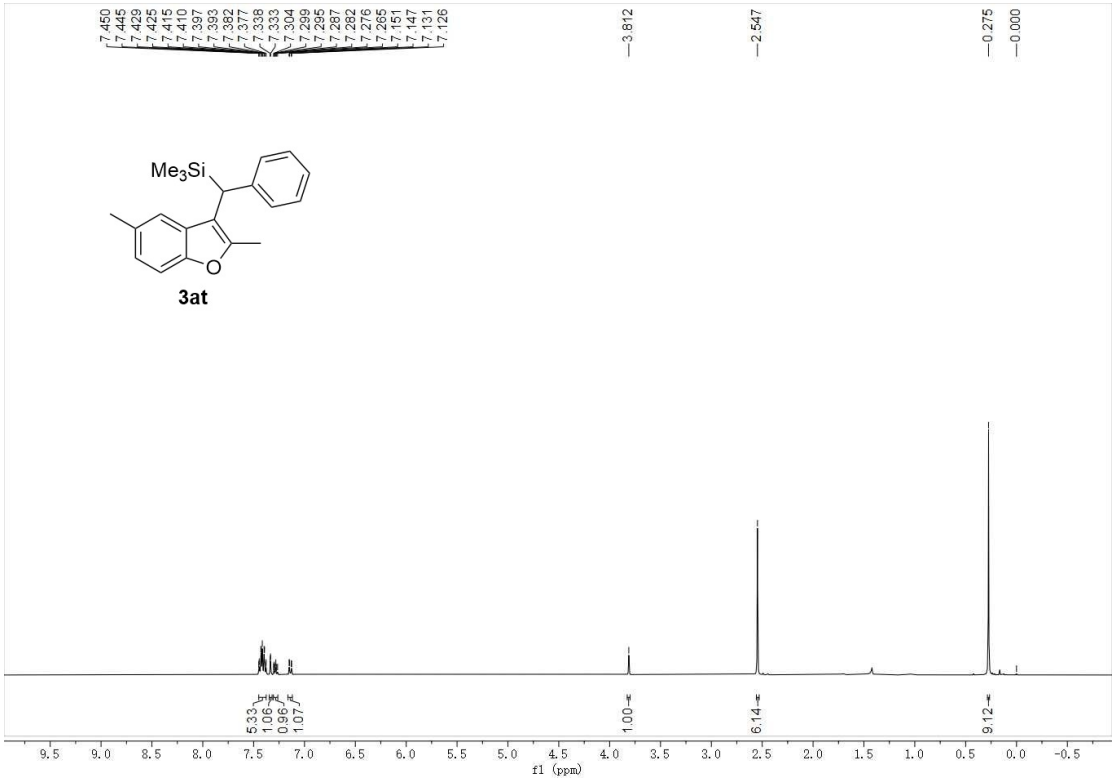
^{13}C NMR spectrum of **3ar** (100 MHz, $CDCl_3$)



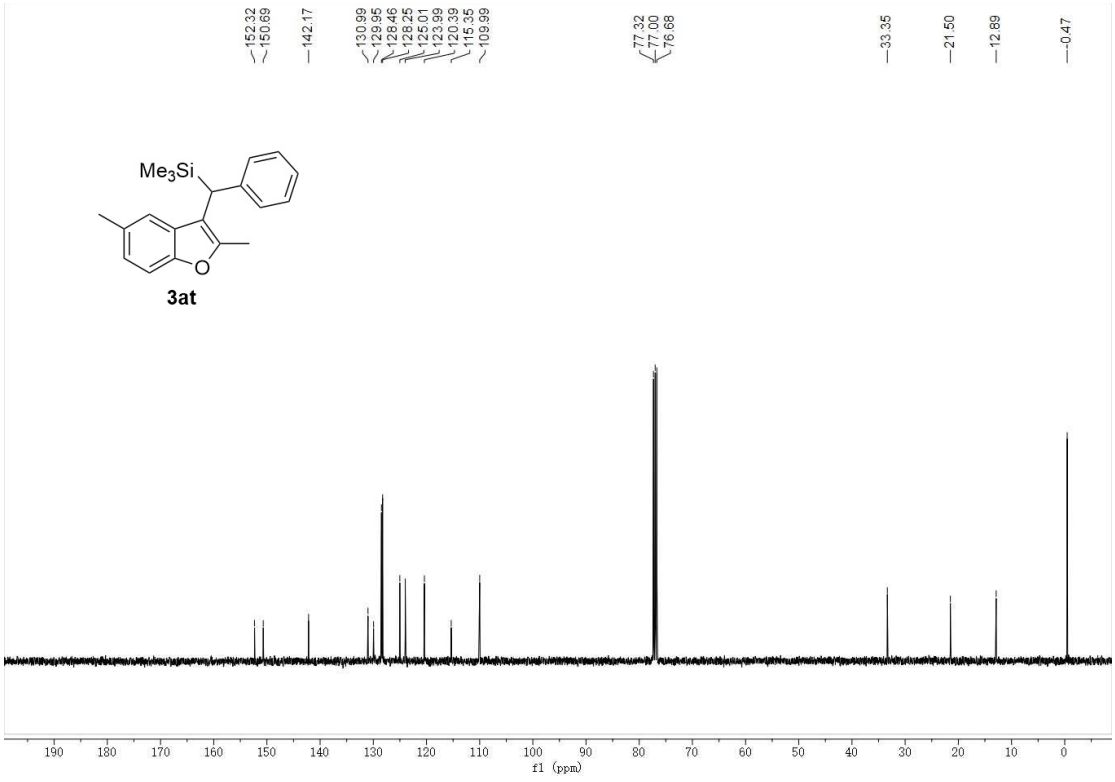
^{1}H NMR spectrum of **3as** (400 MHz, $CDCl_3$)



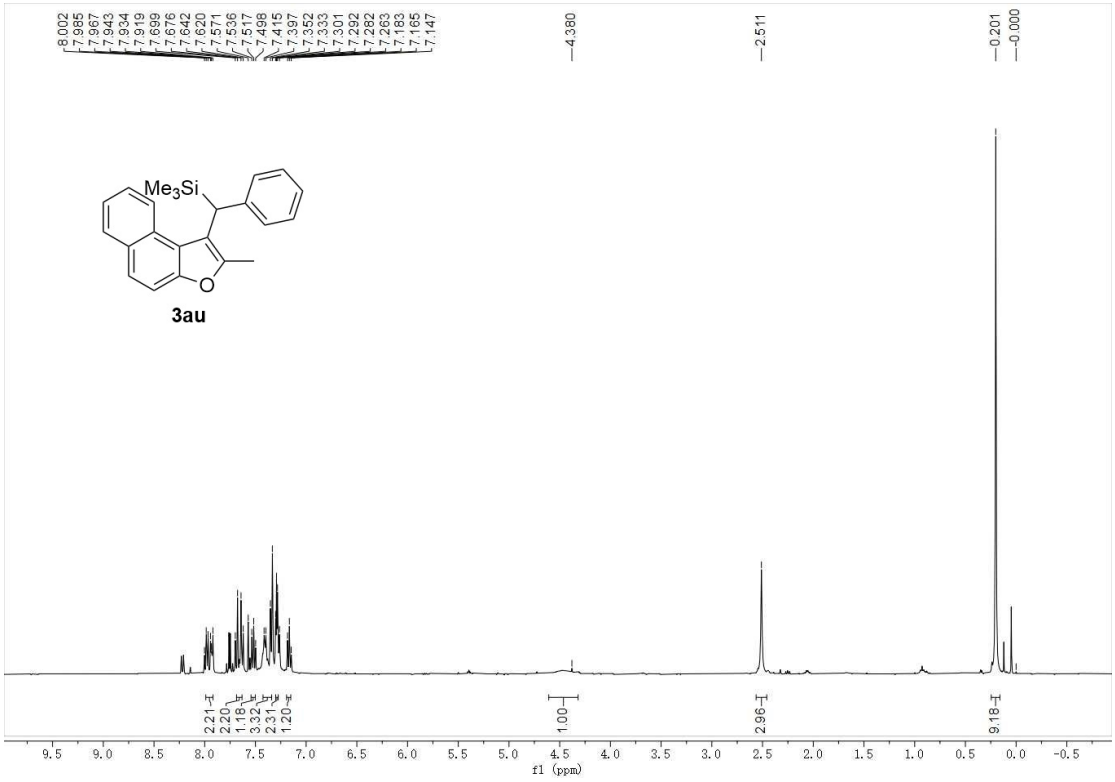
^{13}C NMR spectrum of **3as** (100 MHz, $CDCl_3$)



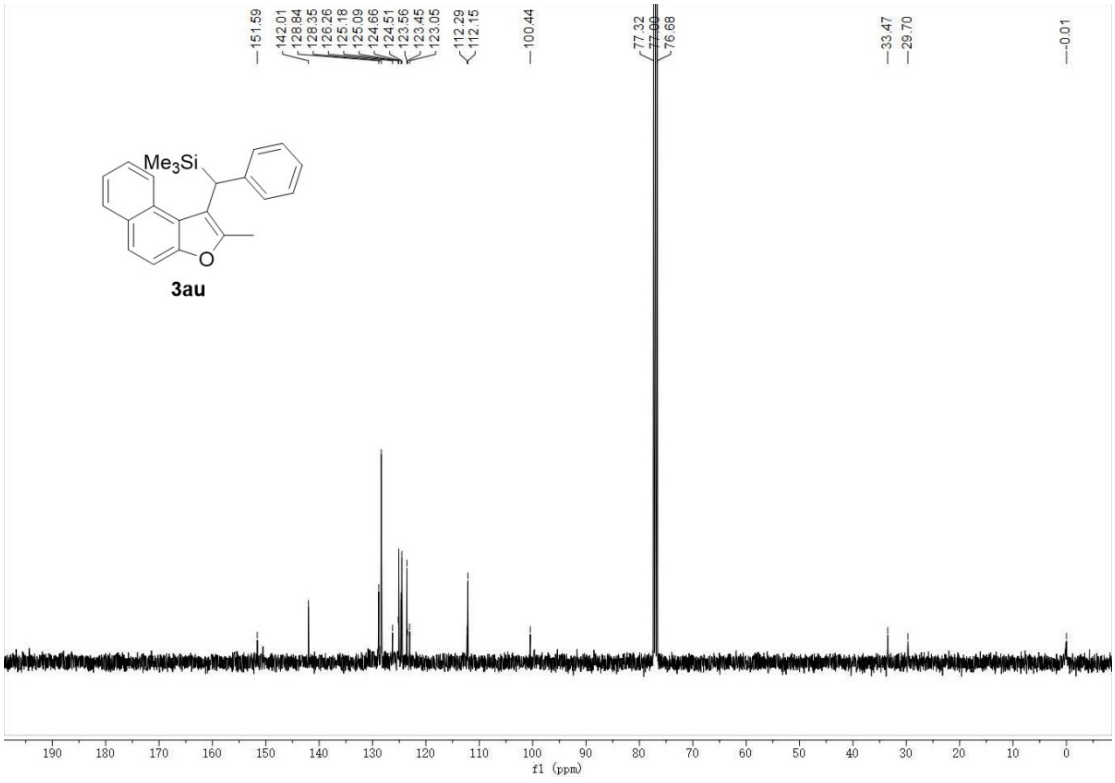
^{1}H NMR spectrum of **3at** (400 MHz, $CDCl_3$)



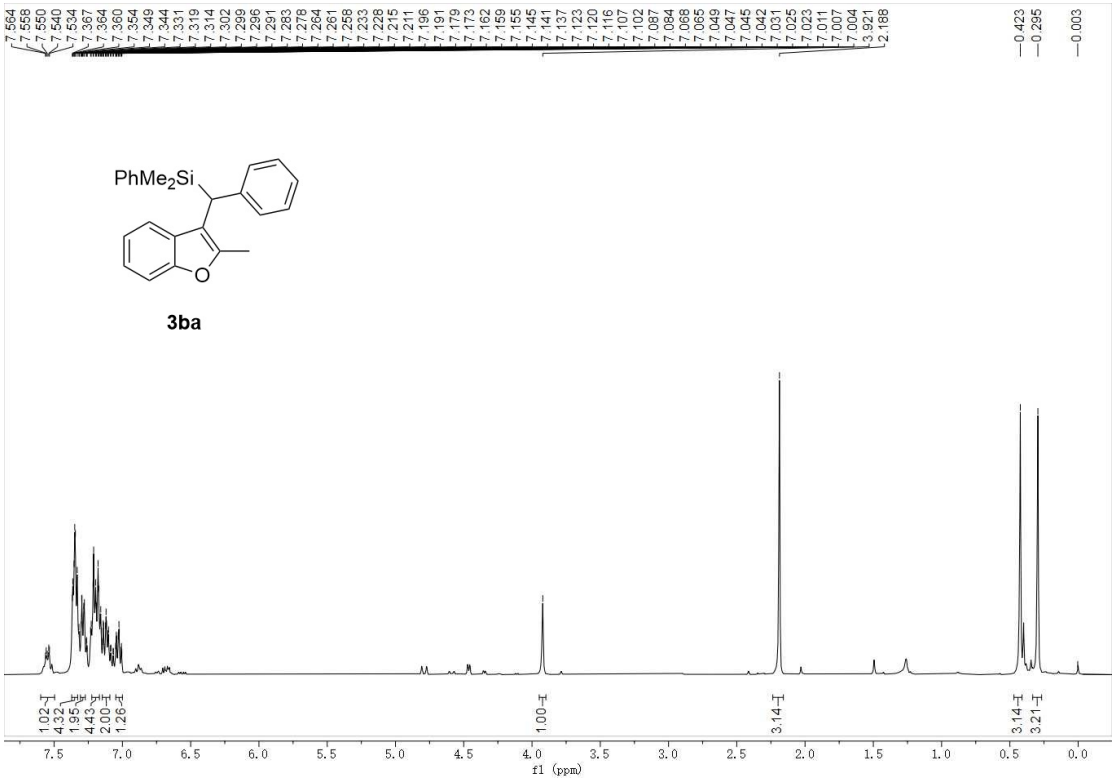
^{13}C NMR spectrum of **3at** (100 MHz, $CDCl_3$)



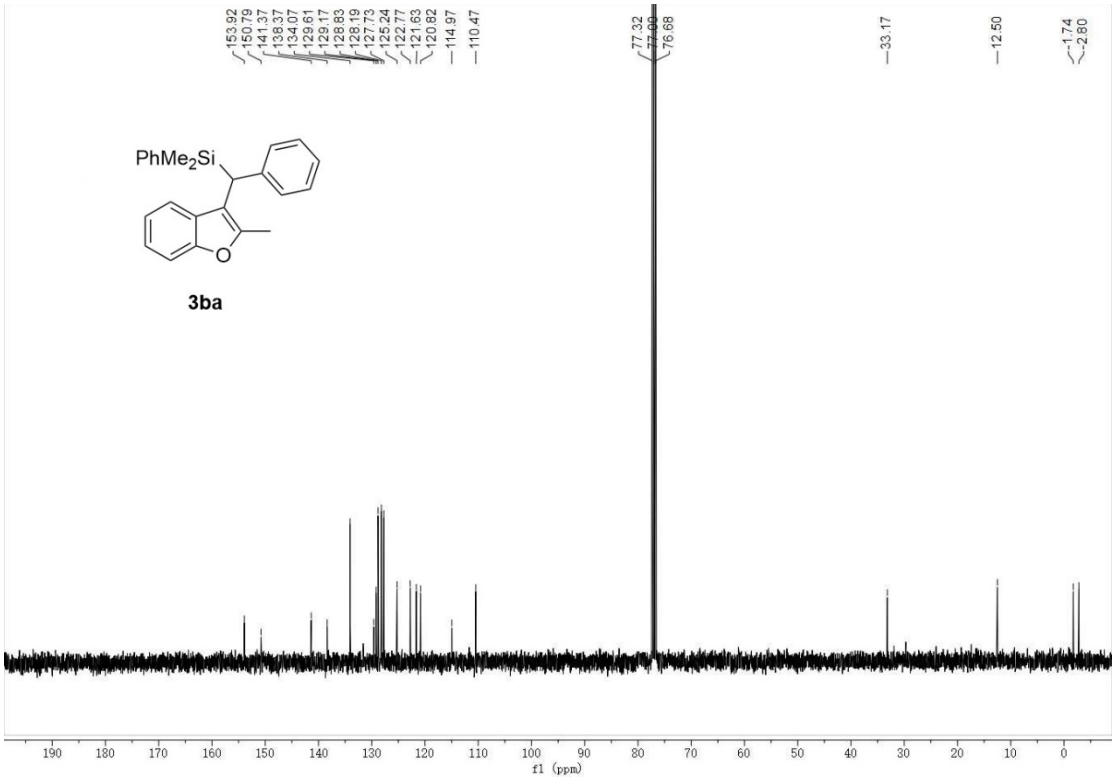
^{1}H NMR spectrum of **3au** (400 MHz, $CDCl_3$)



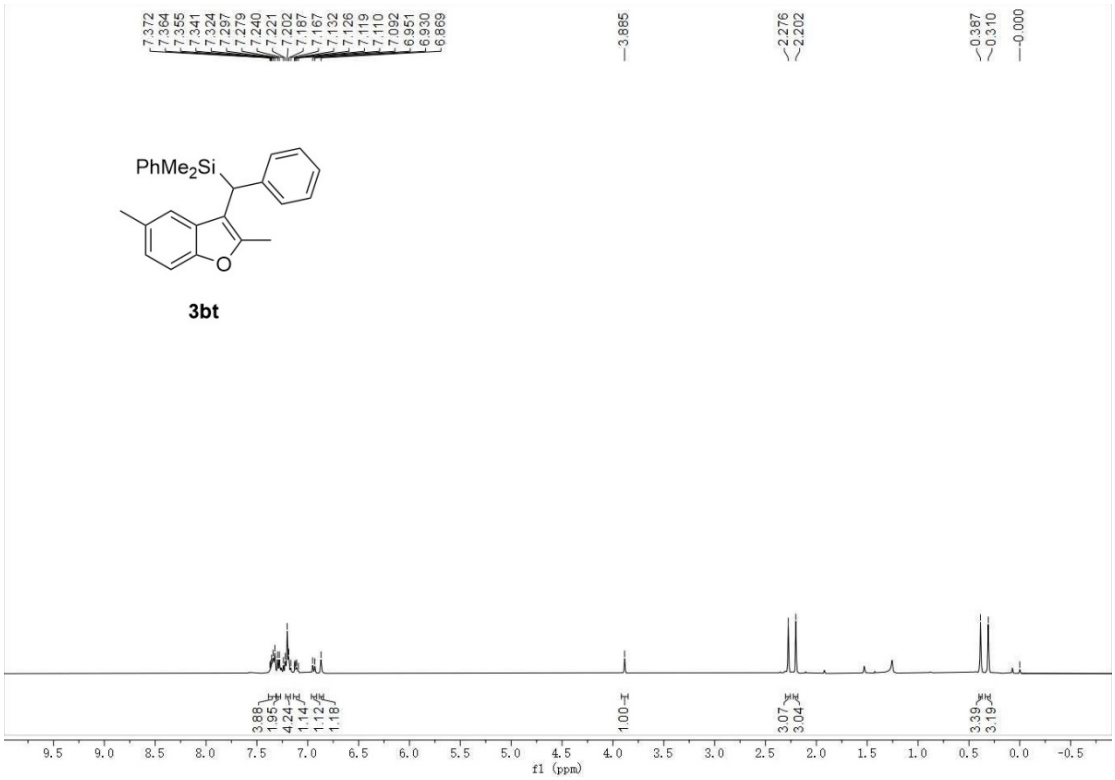
^{13}C NMR spectrum of **3au** (100 MHz, $CDCl_3$)



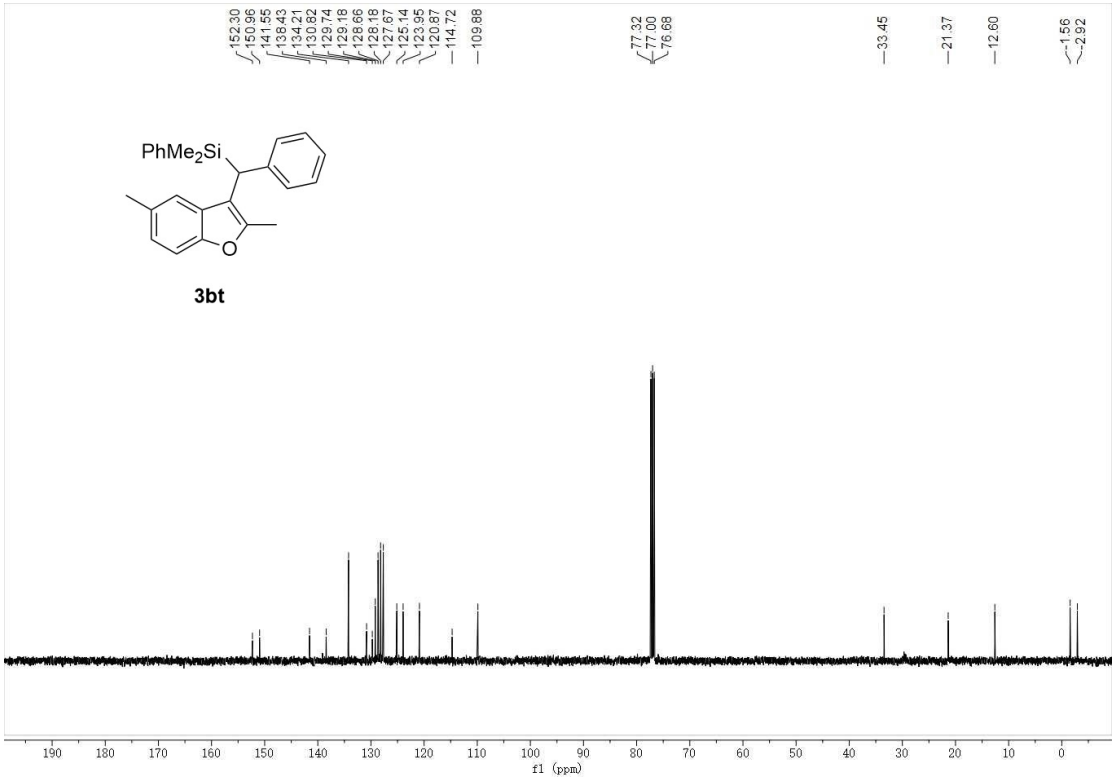
^{1}H NMR spectrum of **3ba** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3ba** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **3bt** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **3bt** (100 MHz, $CDCl_3$)