Supporting Information

Efficient Synthesis of α-Tertiary α-Silylamines from Aryl Sulfonylimidates via One-Pot, Sequential C–Si/C–C Bond Formations

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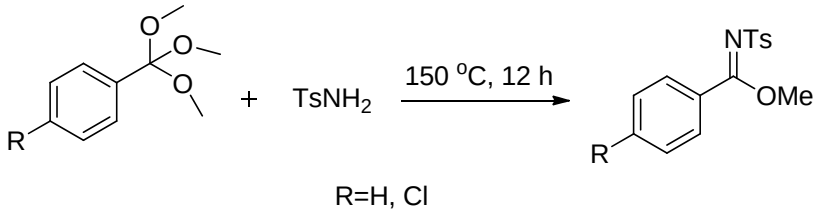
1. General experimental information

All reactions were carried out under an argon atmosphere in flame-dried glassware with magnetic stirring. THF and Et_2O were freshly distilled from sodium/benzophenone. CH_2Cl_2 was distilled from CaH_2. Other solvents and commercial reagents were used without additional purification. Purification of the reaction products was carried out by flash column chromatography using 200–300 mesh silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid or anisaldehyde stain followed by heating. Unless otherwise noted, yields refer to chromatographically and spectroscopically pure compounds. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI). Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a 400 MHz (^{1}HNMR at 400 MHz and ^{13}CNMR at 100 MHz) spectrometer with solvent resonance as the internal standard (^{1}HNMR: $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm; ^{13}C NMR: $CDCl_3$ at 77.23 ppm, C_6D_6 at 128.06 ppm). NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. Melting points were reported uncorrected.

2. General procedure for the preparation of aryl tosylimidates

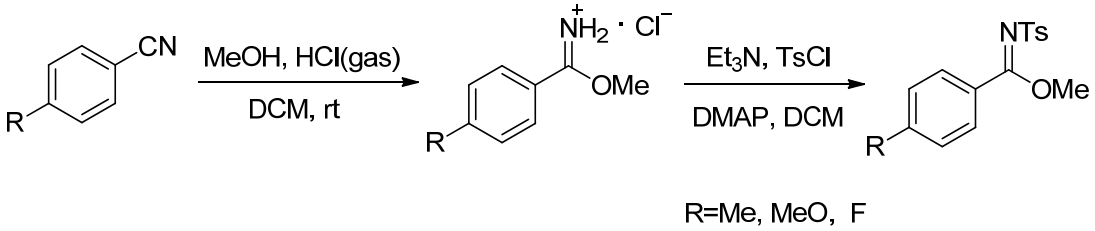
2.1 Method A:[1]



Scheme S1. General procedure for the preparation of aryl tosylimidates: Method A

A round-bottomed flask was charged with *p*-Toluenesulfonamide (1.0 equiv) and orthoester (1.2 equiv). The reaction mixture was stirred at 150 °C for 12 h. The crude oil was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 20:1:0.3 to 10:1:0.3, gradient elution) to give the aryl tosylimidate.

2.2 Method B:[2, 3]



Scheme S2. General procedure for the preparation of aryl tosylimidates: Method B

A three-neck flask was equipped with a gas inlet tube and a gas outlet tube, and it was charged with nitrile (1.0 equiv), MeOH (1.2 equiv), and DCM (10 mL). HCl gas (excess, prepared with concentrated sulfuric acid and NaCl, dried with concentrated sulfuric acid) was bubbled into the solution for 3 h with stir while a temperature of 15–25 °C was maintained. Then the reaction mixture was stirred at room temperature for another 6 h before 40 mL of Et_2O was added. After the mixture was stirred for 3 h at room temperature, the solid (methyl zimidate hydrochloride) was filtered, washed with Et_2O, and vacuum-dried. The solid (1.0 equiv, 10 mmol, without further

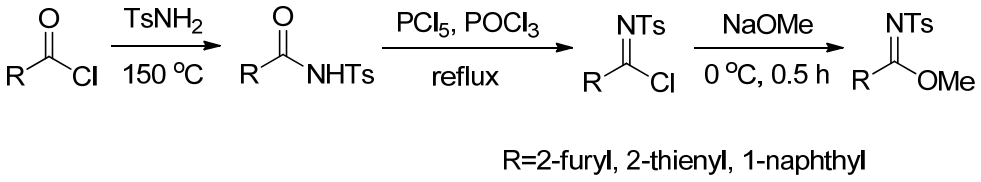
1. Kochi, T.; Ellman, J. A. *J. Am. Chem. Soc.* **2004**, *126*, 15652.

2. Reider, P. J.; Conn, R. S. E.; Davis, P.; Grenda, V. J.; Zambito, A. J.; Grabowski, E. J. *J. Org. Chem.* **1987**, *52*, 3326.

3. Alves, M.J.; Durães, M.M.; Fortes, A.G. *Tetrahedron* **2004**, *60*, 6541.

purification) was stirred in CH_2Cl_2 (30 mL) at room temperature and Et_3N (2.5 equiv) was added dropwise to the reaction mixture. After it was stirred at room temperature for 0.5 h, TsCl (2.0 equiv) and DMAP (4-dimethylaminopyridine, 1.0 equiv) were added in sequence. The reaction mixture was stirred for 3 d. The reaction mixture was diluted with CH_2Cl_2, and washed with a 1.0 M solution of HCl, aqueous sodium bicarbonate, and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 20:1:0.3 to 7:1:0.3, gradient elution) to give the aryl tosylimidate.

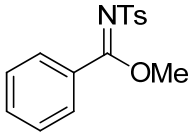
2.3 Method C:[4, 5]



Scheme S3. General procedure for the preparation of aryl tosylimidates: Method C

A mixture of *p*-Toluenesulfonamide (1.0 equiv) and acyl chloride (1.1–1.5 equiv) was stirred at 150 °C for 1–2 h. The crude product was recrystallized from ethanol to give a white solid *N*-tosylamide. *N*-tosylamide (1.0 equiv) and PCl_5 (1.05 equiv) was dissolved in $POCl_3$ (20 equiv), and the reaction mixture was refluxed for 0.5–1 h. The solvent was removed in vacuo, and the crude product was recrystallized from diethyl ether to give a white solid *N*-tosylzimidoyl chloride. A solution of sodium methoxide (5.0 equiv) in MeOH was slowly added dropwise to *N*-tosylzimidoyl chloride (1.0 equiv) in THF at 0 °C. The solution was stirred at 0 °C for 0.5 h. The crude product was purified by column chromatography (*n*-hexane/EtOAc/CH_2Cl_2, gradient elution) to give the aryl tosylimidate.

3. Characterization data of aryl tosylimidates (1a–1h)

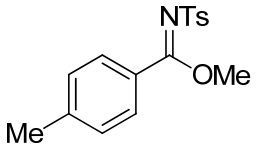


(1a): Method A was followed with $TsNH_2$ (1.71 g, 10 mmol) and Trimethyl

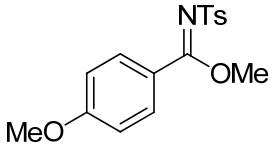
4. Fan, L. Y.; Gao, F. F.; Jiang, W. H.; Deng, M. Z.; Qian, C. T. *Org. Biomol. Chem.* **2008**, *6*, 2133.

5. Barcock, R. A.; Chadwick, D. J.; Storr, R. C.; Fuller, L. S.; Young, J. H. *Tetrahedron* **1994**, *50*, 4149.

orthobenzoate (2.65 g, 15 mmol). Purification by column chromatography afforded 2.73 g (94%) of **1a** as a white solid. The pure **1a** was recrystallized from EtOAc/*n*-hexane to afford a colorless needles: mp 125−126 ^{o}C (lit.[6] mp 123−124 ^{o}C); R_f = 0.29 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.1 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H).



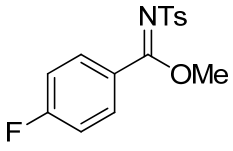
(1b): According to the Method B, *p*-Tolunitrile (3.6 g, 30 mmol) was used and afforded methyl 4-methylbenzimidate hydrochloride (crude product, 4.8 g, 86%) as a white solid. Methyl 4-methylbenzimidate hydrochloride (1.86 g, appro. 10 mmol) in 30 mL CH_2Cl_2, Et_3N (3.5 mL, 25 mmol), TsCl (3.82 g, 20 mmol), and DMAP (1.22 g, 10 mmol) were used and the reaction mixture was refluxed for 3 d. It was purified by column chromatography to afford **1b (**1.74 g, 58%) as a white solid. The pure **1b** was recrystallized from EtOAc/*n*-hexane to afford a colorless needles: mp 98−99 ^{o}C; R_f = 0.33 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.81 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 4H), 3.87 (s, 3H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 170.2, 143.6, 143.1, 139.9, 129.8, 129.4, 129.0, 128.4, 126.8, 56.2, 21.9, 21.7; HRMS: (ESI) calculated for $C_{16}H_{18}NO_3S$ ($[M+H]^+$): 304.1007, found: 304.0994.



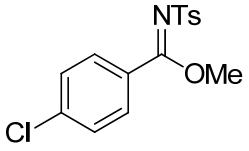
(1c): According to the Method B, 4-Methoxybenzonitrile (4.0 g, 30 mmol) was used and afforded methyl 4-methoxybenzimidate hydrochloride (crude product, 4.8 g, 79%) as a white solid. Methyl 4-methoxybenzimidate hydrochloride (1.86 g, appro. 10 mmol) in 30 mL CH_2Cl_2, Et_3N (3.5 mL, 25 mmol), TsCl (3.82 g, 20 mmol), and DMAP (1.22 g, 10 mmol) were used and the reaction mixture was stirred at room temperature for 3 d. It was purified by column chromatography to afford **1c** (0.99 g, 31%) as a white solid. The pure **1c** was recrystallized from EtOAc/*n*-hexane to afford a colorless needles: mp 119−120 ^{o}C; R_f = 0.21 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 2.42 (s, 3H);

6. Bundgaard, H.; Larsen, J. D. *J. Med. Chem.* **1988**, *31*, 2066.

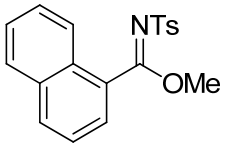
^{13}C NMR (100 MHz, CDCl3) δ 169.4, 163.5, 143.0, 140.1, 132.4, 129.4, 126.7, 123.1, 113.7, 56.1, 55.7, 21.7; HRMS: (ESI) calculated for $C_{16}H_{18}NO_4S$ ($[M+H]^+$): 320.0957, found: 320.0895.



(1d): According to the Method B, 4-fluorobenzonitrile (4.84 g, 40 mmol) was used and afforded methyl 4-fluorobenzimidate hydrochloride (crude product, 6.9 g, 91%) as a white solid. Methyl 4-fluorobenzimidate hydrochloride (1.90 g, appro. 10 mmol) in 30 mL CH_2Cl_2, Et_3N (3.5 mL, 25 mmol), TsCl (3.82 g, 20 mmol), and DMAP (1.22 g, 10 mmol) were used and the reaction mixture was refluxed for 3 d. It was purified by column chromatography to afford **1d** (0.69 g, 22%) as a white solid. The pure **1d** was recrystallized from EtOAc/*n*-hexane to afford a colorless needles: mp 105−106 ^{o}C; R_f = 0.30 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 165.5 (d, J_{CF} = 254.4 Hz), 143.3, 139.6, 132.4 (d, J_{CF} = 9.2 Hz), 129.5, 127.4 (d, J_{CF} = 3.3 Hz), 126.8, 115.6 (d, J_{CF} = 22.1 Hz), 56.4, 21.8; HRMS: (ESI) calculated for $C_{15}H_{15}FNO_3S$ ($[M+H]^+$): 308.0757, found: 308.0751.

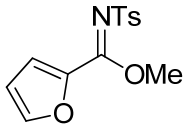


(1e): Method A was followed with $TsNH_2$ (0.52 g, 3.0 mmol) and trimethyl 4-chloroorthobenzoate (0.81 g, 3.75 mmol). Purification by column chromatography afforded 0.75 g (77%) of **1e** as a white solid. The pure **1e** was recrystallized from EtOAc/*n*-hexane to afford a colorless needles: mp 117−118 ^{o}C; R_f = 0.32 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 169.0, 143.4, 139.5, 139.2, 131.1, 129.7, 129.5, 128.7, 126.8, 56.4, 21.8; HRMS: (ESI) calculated for $C_{15}H_{15}ClNO_3S$ ($[M+H]^+$): 324.0461, found: 324.0455.



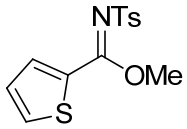
(1f): Method C was followed with $TsNH_2$ (1.20 g, 7 mmol) and 1-naphthoyl chloride (1.56 g, 8 mmol). The reaction mixture was stirred for 2 h at 150 ^{o}C. Then PCl_5 (1.62 g, 7.8 mmol) and $POCl_3$ (5 mL) was added to the reaction mixture of the previous step (without

further purification). The reaction was refluxed for 1 h and the solvent was removed in vacuo. The crude product was recrystallized from diethyl ether to give a white solid *N*-tosyl-1-naphthimidoyl chloride (1.42 g, total yield 59%). A solution of sodium methoxide (0.54 g, 10 mmol) in MeOH was slowly added dropwise to *N*-tosyl-1-naphthimidoyl chloride (1.42 g, 4.1 mmol) in THF at 0 ^{o}C. The solution was stirred at 0 ^{o}C for 0.5 h. The crude product was purified by column chromatography (n-hexane:EtOAc:CH_2Cl_2 = 10:1:0.3 to 5:1:0.3, gradient elution) to give the aryl tosylimidate **1f** (1.39g, 99%). The pure **1f** was recrystallized from EtOAc/*n*-hexane to afford a colorless crystals: mp 122−123 ^{o}C; R_f = 0.20 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 7.1, 0.9 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.46 (dd, *J* = 7.6, 3.5 Hz, 1H), 7.44 – 7.42(m, 1H), 7.42 – 7.38 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 2H), 4.09 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 171.9, 143.1, 137.6, 133.1, 131.1, 129.5, 129.4, 129.0, 128.5, 127.3, 127.2, 126.9, 126.5, 124.70, 124.65, 56.4, 21.5; HRMS: (ESI) calculated for $C_{19}H_{18}NO_3S$ ($[M+H]^+$): 340.1007, found: 340.1008.



(1g): Method C was followed with $TsNH_2$ (3.42 g, 20 mmol) and 2-Furoyl chloride (3.92 g, 30 mmol). The reaction mixture was stirred for 2 h at 150 ^{o}C. Then PCl_5 (4.58 g, 22 mmol) and $POCl_3$ (15 mL) was added to the reaction mixture of the previous step (without further purification). The reaction was refluxed for 1 h and the solvent was removed in vacuo. The crude product was purified by column chromatography (n-hexane:EtOAc:CH_2Cl_2 = 10:1:0.3 to 5:1:0.3, gradient elution) to give a white solid *N*-tosylfuran-2-carbimidoyl chloride (1.47 g, total yield 26%). A solution of sodium methoxide (0.54 g, 10 mmol) in MeOH was slowly added dropwise to *N*-tosylfuran-2-carbimidoyl chloride (1.42 g, 5 mmol) in THF at 0 ^{o}C. The solution was stirred at 0 ^{o}C for 0.5 h. The crude product was purified by column chromatography (n-hexane:EtOAc:CH_2Cl_2 = 10:1:0.3 to 5:1:0.3, gradient elution) to give the aryl tosylimidate **1g** (1.32g, 95%). The pure **1g** was recrystallized from EtOAc/*n*-hexane to afford a pale yellow crystals.: mp 117−118 ^{o}C; R_f = 0.23 (*n*-hexane:EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.84 (m, 3H), 7.69 (d, *J* = 0.7 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 1.7 Hz, 1H), 3.85 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 147.6, 143.1, 142.8, 140.3, 129.3, 126.7, 123.4, 112.9, 55.5, 21.7; HRMS: (ESI) calculated for $C_{13}H_{14}NO_4S$ ($[M+H]^+$): 280.0644, found:

280.0646.



(1h): Method C was followed with $TsNH_2$ (5.13 g, 30 mmol) and 2-thenoyl chloride (5.13 g, 35 mmol). The reaction mixture was stirred for 1 h at 130 ^oC. The crude product was recrystallized from ethanol to give a white solid *N*-tosylthiophene-2-carboxamide (6.4 g, 76%). *N*-tosylthiophene-2-carboxamide (2.81 g, 10 mmol) and PCl_5 (2.29 g, 11 mmol) was dissolved in $POCl_3$ (15 mL), and the reaction mixture was refluxed for 1 h. The solvent was removed in vacuo. The crude product was recrystallized from diethyl ether to give a white solid *N*-tosylthiophene-2-carbimidoyl chloride (1.48 g, 51%). A solution of sodium methoxide (1.08 g, 20 mmol) in MeOH was slowly added dropwise to *N*-tosylfuran-2-carbimidoyl chloride (1.20 g, 4 mmol) in THF at 0 ^oC. The solution was stirred at 0 ^oC for 0.5 h. The crude product was purified by column chromatography (n-hexane:EtOAc:CH_2Cl_2 = 20:1:0.3 to 10:1:0.3, gradient elution) to give a white solid **1h** (1.13g, 96%). The pure **1h** was recrystallized from EtOAc/*n*-hexane to afford a colorless crystals: mp 71−72 ^oC; R_f = 0.28 (*n*-hexane:EtOAc = 5:1); ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 4.0, 1.1 Hz, 1H), 7.90 (d, J = 8.3 Hz, 2H), 7.66 (dd, J = 5.0, 1.1 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.21 (dd, J = 5.0, 4.1 Hz, 1H), 3.83 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 161.5, 143.2, 140.0, 138.0, 134.0, 130.8, 129.5, 128.7, 126.6, 55.9, 21.8; HRMS: (ESI) calculated for $C_{13}H_{14}NO_3S_2$ ($[M+H]^+$): 296.0415, found: 296.0418.

4. Preparation of silyl-lithium Reagent

4.1 Preparation of dimethylphenylsilyllithium ($LiSiMe_2Ph$)[7]

Lithium wire (0.50 g, 70 mmol) was stirred rapidly for 15 min in hexane (20 mL) under argon. The hexane was removed and the lithium suspended in THF (15 mL). The mixture was stirred rapidly with chlorodimethylphenylsilane (3.0 mL, 18 mmol) and some splinters of glass at 0 ^oC for 6 h to give a deep red solution (appro. 1.0 M). The solution was stored at –18 ^oC.

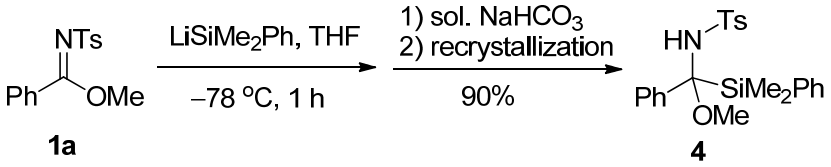
4.2 Preparation of diphenylmethylsilyllithium ($LiSiMePh_2$)[8]

7. Fleming, I.; Roberts, R. S.; Smith, S. C. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1209.

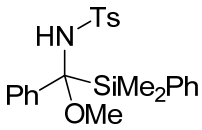
8. Nielsen, L.; Lindsay, K. B.; Faber J.; Nielsen, N. C.; Skrydstrup T. *J. Org. Chem.*, **2007**, *72*, 10035.

Hexane-washed lithium wire (0.050 g, 7 mmol) was suspended in dry THF (1.2 mL) under argon. The mixture was stirred rapidly with chlorodiphenylmethylsilane (0.21 mL, 1.0 mmol) and some splinters of glass at room temperature for 4 h to give a deep black-red solution (appro. 0.8 M). The solution was used within several hours.

5. Procedure for the preparation of compound 4

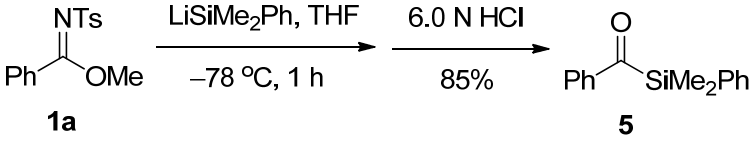


Scheme S4. Procedure for the preparation of compound **4**



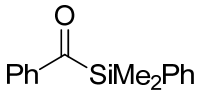
(4): 1a (115.7 mg, 0.4 mmol) was dissolved in 2.0 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Dimethylphenylsilyllithium (appro. 1.0 M solution in THF, 0.48 mL, 0.48 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1 h at –78 °C. Then it was quenched at –78 °C by the addition of 3.0 mL of saturated aqueous sodium bicarbonate. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for 15 minutes. The reaction mixture was diluted with 40 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with brine (2×15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford a white solid (crude product). The solid was recrystallized from *n*-hexane/CH_2Cl_2 to afford the product **4** (153.5 mg, 90%) as a white solid: mp 115−116 °C; R_f = 0.29 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4, 2H), 7.39 – 7.31 (m, 3H), 7.25 (t, *J* = 6.6, 2H), 7.21 – 7.13 (m, 5H), 7.08 – 7.02 (m, 2H), 5.31 (s, 1H), 2.71 (s, 3H), 2.41 (s, 3H), 0.50 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.4, 139.2, 136.7, 135.3, 129.4, 129.3, 127.9, 127.5, 127.4, 127.19, 127.16, 90.7, 49.1, 21.8, –3.7, –4.2; HRMS: (ESI) calculated for $C_{23}H_{27}NNaO_3SSi$ ($[M+Na]^+$): 448.1379, found: 448.1376.

6. Procedure for the preparation of compound 5



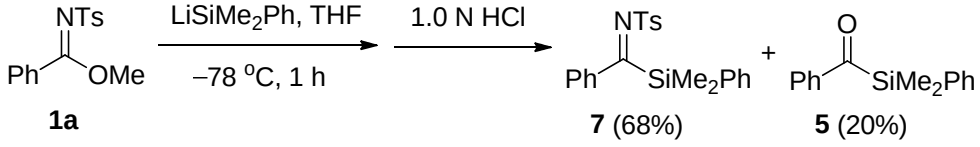
1a **5**

Scheme S5. Procedure for the preparation of compound **5**



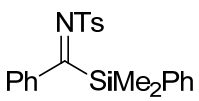
(5): 1a (86.8 mg, 0.3 mmol) was dissolved in 1.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to anhydrous –78 °C. Dimethylphenylsilyllithium (appro. 1.0 M solution in THF, 0.36 mL, 0.36 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 °C. Then it was quenched at –78 °C by the addition of 3.0 mL of 6.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature (a lot of white solid will be separated out, 1 mL THF and 1 mL CH_2Cl_2 should be added to dissolve it.) and then stirred rapidly for an additional 1.5 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:Et_2O = 100:1) yielding pure product **5** (61.3 mg, 85%) as a yellow solid: mp 55−56 °C; R_f = 0.61 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.63 – 7.57 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.42 – 7.34 (m, 5H), 0.63 (s, 6H). The ^{1}H NMR spectrum of this compound matched the reported spectral data.[9]

7. Procedure for the preparation of compound 7



1a **7** (68%) **5** (20%)

Scheme S6. Procedure for the preparation of compound **7**

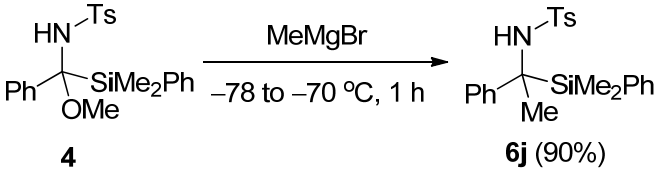


(7): 1a (144.7 mg, 0.5 mmol) was dissolved in 2.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was

9. Azuma, H.; Okano, K.; Tokuyama, H. *Chem. Lett.* **2011**, *40*, 959.

cooled to –78 °C. Dimethylphenylsilyllithium (appro. 1.0 M solution in THF, 0.6 mL, 0.6 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 °C. Then it was quenched at –78 °C by the addition of 4.0 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature (a lot of white solid will be separated out, 1 mL THF and 1 mL CH_2Cl_2 should be added to dissolve it.) and then stirred rapidly for an additional 2 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 100:1:0.3 to 20:1:0.3, gradient elution) yielding product **7** (134.6 mg, 68% yield) as a white solid and product **5** (24.5 mg, 20% yield). The product **7** could be recrystallized from Et_2O/*n*-pentane to afford a white solid. The analytic data of **7**: mp 92−93 °C; R_f = 0.36 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, C_6D_6) δ 7.95 (d, J = 7.2 Hz, 2H), 7.59 – 7.20 (m, 4H), 7.10 (d, J = 7.2 Hz, 3H), 6.94 (s, 3H), 6.72 (d, J = 7.1 Hz, 2H), 1.83 (s, 3H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 202.5, 143.1, 139.5, 134.6, 130.2, 129.50, 129.46, 128.39, 128.36, 128.1, 128.0, 127.9, 126.1, 21.2, –3.8; HRMS: (ESI) calculated for $C_{22}H_{24}NO_2SSi$ ($[M+H]^+$): 394.1297, found: 394.1292.

8. The reaction of compound 4 and Grignard reagent (MeMgBr)



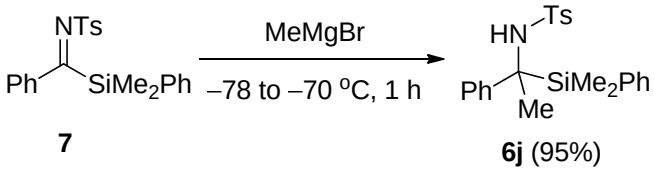
4 **6j** (90%)

Scheme S7. The reaction of compound **4** and Grignard reagent (MeMgBr)

Compound **4** (85.2 mg, 0.2 mmol) was dissolved in 2.0 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Methylmagnesium bromide (3.0 M solution in Et_2O, 0.2 mL, 0.6 mmol) was added dropwise, and the reaction mixture was allowed to warm slowly to –70 °C over 1 h. Then it was quenched at –70 °C by the addition of 3.0 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 0.5 h. The reaction

mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product **6j** (73.7 mg, 90%).

9. The reaction of compound 7 and Grignard reagent (MeMgBr)

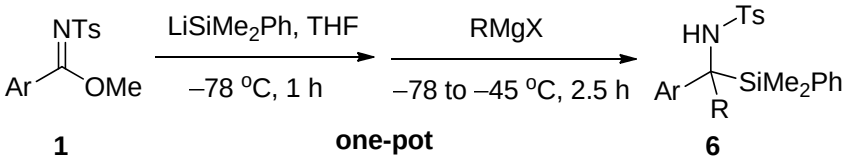


7 **6j** (95%)

Scheme S8. The reaction of compound **7** and Grignard reagent (MeMgBr)

Compound **7** (78.7 mg, 0.2 mmol) was dissolved in 2.0 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Methylmagnesium bromide (3.0 M solution in Et_2O, 0.2 mL, 0.6 mmol) was added dropwise, and the reaction mixture was allowed to warm slowly to –70 °C over 1 h. Then it was quenched at –70 °C by the addition of 3 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 0.5 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product **6j** (77.7 mg, 95%).

10. General procedure for the synthesis of α,α-dibranched α-silylamines



1 **one-pot** **6**

Scheme S9. General procedure for the synthesis of α,α-dibranched α-Silylamines

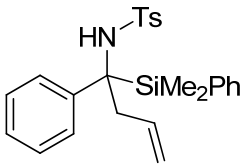
Aryl tosylimidate (dissolved in THF, 1.0 equiv) was added to a flame-dried schlenk flask

equipped with a magnetic stirring bar under argon. The solution was cooled to –78 ^{o}C. Silyl lithium (1.2 equiv) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 ^{o}C. Grignard reagent (1.5 equiv) was added dropwise, and and the reaction mixture was allowed to warm slowly to –45 ^{o}C over 2.5 h. Then it was quenched at –45 ^{o}C by the addition of 3 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product.

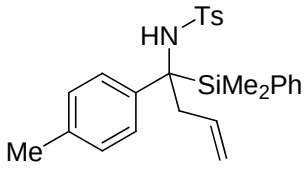
11. The procedure for gram-scale preparation of 6a

1a (1.157g, 4 mmol) was dissolved in 20 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 ^{o}C. Dimethylphenylsilyllithium (appro. 1.0 M in THF, 4.2 mL, 4.2 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1 h at –78 ^{o}C. Allylmagnesium bromide (1.0 M solution in THF, 6.0 mL, 6.0 mmol) was added dropwise, and the reaction mixture was allowed to warm slowly to –45 ^{o}C over 2.5 h. Then it was quenched at –45 ^{o}C by the addition of 10 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 100 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×15 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product **6a** (1.649 g, 95%).

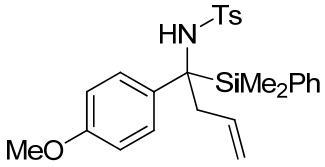
12. Characterization data of *α*-silylamines (6a–6r, 8, 9)



(6a): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6a** (116.6 mg, 89%) as a white solid: mp 150−151 ^{o}C; R_f = 0.36 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.20 – 7.12 (m, 4H), 7.10 – 7.02 (m, 3H), 6.98 – 6.91 (m, 2H), 5.80 – 5.64 (m, 1H), 5.07 – 4.92 (m, 2H), 4.77 (s, 1H), 3.16 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.89 (dd, *J* = 15.3, 8.0 Hz, 1H), 2.39 (s, 3H), 0.35 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.3, 140.4, 135.4, 135.2, 134.1, 129.8, 129.4, 127.8, 127.6, 127.3, 127.2, 125.9, 119.1, 58.2, 38.9, 21.7, –3.7, –3.8; HRMS: (ESI) calculated for $C_{25}H_{29}NNaO_2SSi$ ($[M+Na]^+$): 458.1586, found: 458.1589.

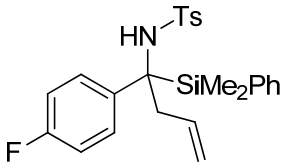


(6b): According to the general procedure for α-silylamines, **1b** (91.0 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6b** (122.5 mg, 91%) as a white solid: mp 116−117 ^{o}C; R_f = 0.40 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.21 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.14 (dd, *J* = 8.5, 0.5 Hz, 2H), 6.86 (q, *J* = 8.5 Hz, 4H), 5.78 – 5.61 (m, 1H), 5.04 – 4.89 (m, 2H), 4.75 (s, 1H), 3.13 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.87 (dd, *J* = 15.3, 7.9 Hz, 1H), 2.39 (s, 3H), 2.27 (s, 3H), 0.34 (s, 3H), 0.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 140.4, 138.2, 135.6, 135.4, 135.3, 134.2, 129.7, 129.4, 128.3, 127.7, 127.3, 127.2, 118.9, 57.9, 38.8, 21.7, 21.1, –3.70, –3.72; HRMS: (ESI) calculated for $C_{26}H_{31}NNaO_2SSi$ ($[M+Na]^+$): 472.1742, found: 472.1746.

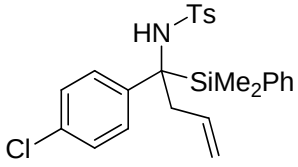


(6c): According to the general procedure for α-silylamines, **1c**

(95.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6c** (122.8 mg, 88%) as a white solid: mp 117−118 ^{o}C; R_f = 0.25 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.19 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 5.80 – 5.66 (m, 1H), 5.04 – 4.93 (m, 2H), 4.74 (s, 1H), 3.76 (s, 3H), 3.12 (dd, *J* = 15.2, 5.5 Hz, 1H), 2.86 (dd, *J* = 15.2, 7.9 Hz, 1H), 2.39 (s, 3H), 0.35 (s, 3H), 0.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.9, 140.4, 135.6, 135.2, 134.1, 133.2, 129.8, 129.4, 128.5, 127.8, 127.2, 119.0, 112.9, 57.5, 55.4, 39.0, 21.7, –3.65, –3.71; HRMS: (ESI) calculated for $C_{26}H_{31}NNaO_3SSi$ ($[M+Na]^+$): 488.1692, found: 488.1689.

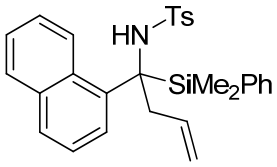


(6d): According to the general procedure for α-silylamines, **1d** (92.2 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6d** (126.1 mg, 93%) as a white solid: mp 129−130 ^{o}C; R_f = 0.35 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 7.4 Hz, 4H), 6.92 – 6.82 (m, 2H), 6.73 (t, *J* = 8.5 Hz, 2H), 5.86 – 5.67 (m, 1H), 5.04 (d, *J* = 13.2 Hz, 2H), 4.80 (s, 1H), 3.17 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.89 (dd, *J* = 15.1, 7.9 Hz, 1H), 2.40 (s, 3H), 0.34 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_{CF} = 245.2 Hz), 143.2, 140.4, 137.1 (d, J_{CF} = 3.1 Hz), 135.1, 135.0, 134.1, 130.0, 129.5, 128.9 (d, J_{CF} = 7.8 Hz), 127.9, 127.2, 119.2, 114.3 (d, J_{CF} = 21.2 Hz), 57.7, 39.3, 21.7, –3.9; HRMS: (ESI) calculated for $C_{25}H_{28}FNNaO_2SSi$ ($[M+Na]^+$): 476.1492, found: 476.1496.

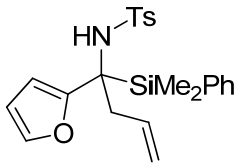


(6e): According to the general procedure for α-silylamines, **1e** (97.1 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol)

were used and afforded the product **6e** (126.2 mg, 90%) as a white solid: mp 117−118 °C; R_f = 0.35 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.16 –7.09 (m, 4H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.80 – 5.64 (m, 1H), 4.99 (d, *J* = 13.6 Hz, 2H), 4.80 (s, 1H), 3.12 (dd, *J* = 15.3, 5.4 Hz, 1H), 2.83 (dd, *J* = 15.3, 8.0 Hz, 1H), 2.36 (s, 3H), 0.29 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 140.3, 140.11, 135.1, 134.7, 134.1, 131.8, 130.1, 129.5, 128.7, 128.0, 127.6, 127.1, 119.2, 57.8, 39.2, 21.7, –3.9; HRMS: (ESI) calculated for $C_{25}H_{28}ClNNaO_2SSi$ ($[M+Na]^+$): 492.1196, found: 492.1201.

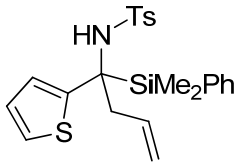


(6f): According to the general procedure for α-silylamines, **1f** (101.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used. But after allylmagnesium bromide was added dropwise, the reaction mixture was allowed to warm slowly to –60 °C over 1 h. The reaction was quenched at –60 °C by the addition of 3 mL of 1.0 M solution of HCl. Standard operation followed, purification by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 25:1:0.3, gradient elution) and afforded the product **6f** (87.9 mg, 60%) as a white solid: mp 179−180 °C; R_f = 0.40 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.9 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.26 – 7.17 (m, 4H), 7.15 – 7.06 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.03 – 5.88 (m, 1H), 5.21 – 5.08 (m, 2H), 4.94 (s, 1H), 3.55 (dd, *J* = 15.0, 5.2 Hz, 1H), 3.13 (dd, *J* = 15.1, 7.6 Hz, 1H), 2.32 (s, 3H), 0.44 (s, 3H), 0.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 138.9, 136.74, 136.67, 135.2, 134.7, 133.7, 131.8, 129.5, 129.0, 128.8, 128.5, 128.2, 127.7, 127.1, 126.4, 125.0, 124.7, 124.3, 120.1, 58.4, 41.5, 21.6, –0.2, –1.3; HRMS: (ESI) calculated for $C_{29}H_{31}NNaO_2SSi$ ($[M+Na]^+$): 508.1742, found: 508.1741.

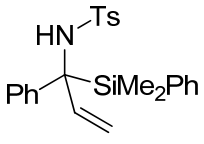


(6g): According to the general procedure for α-silylamines, **1g** (83.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL,

0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6g** (69.0 mg, 54%) as a white solid: mp 141−142 °C; R_f = 0.34 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.28 (m, 7H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.87 (s, 1H), 6.08 (s, 1H), 5.88 (s, 1H), 5.84 – 5.70 (m, 1H), 5.14 – 4.99 (m, 2H), 4.81 (s, 1H), 2.97 (ddd, *J* = 36.7, 14.9, 6.8 Hz, 2H), 2.36 (s, 3H), 0.38 (s, 3H), 0.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 142.5, 141.0, 139.3, 135.1, 135.0, 134.3, 130.1, 129.2, 128.0, 127.2, 118.8, 110.4, 107.5, 52.8, 38.8, 21.7, –3.4, –3.6; HRMS: (ESI) calculated for $C_{23}H_{27}NNaO_3SSi$ ($[M+Na]^+$): 448.1379, found: 448.1380.

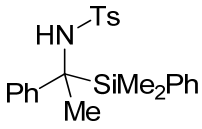


(6h): According to the general procedure for α-silylamines, **1h** (88.6 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6h** (46.5 mg, 35%) as a white solid: mp 151−152 °C; R_f = 0.35 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 3.6 Hz, 1H), 7.34 – 7.21 (m, 4H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 4.4 Hz, 1H), 6.66 (s, 1H), 6.25 (s, 1H), 5.86 – 5.70 (m, 1H), 5.15 – 5.00 (m, 2H), 4.83 (s, 1H), 3.20 (dd, *J* = 15.1, 5.5 Hz, 1H), 2.96 (dd, *J* = 14.9, 7.8 Hz, 1H), 2.38 (s, 3H), 0.41 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.6, 143.0, 140.2, 135.2, 133.9, 130.0, 129.4, 127.9, 127.2, 126.4, 125.2, 123.2, 119.4, 56.4, 41.0, 21.7, –3.5, –3.6; HRMS: (ESI) calculated for $C_{23}H_{27}NNaO_2S_2Si$ ($[M+Na]^+$): 464.1150, found: 464.1150.

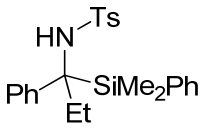


(6i): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and vinylmagnesium bromide (freshly prepared, appro. 1.0 M solution in THF, 0.9 mL, 0.9 mmol) were used. But after vinylmagnesium bromide was added dropwise, the reaction mixture was allowed to warm slowly to –50 °C over 2 h. The reaction was quenched at –50 °C by the addition of 3 mL of 1.0 M solution of HCl. Standard operation followed, column chromatography afforded the title compound **6i** (76.3 mg, 60%) as a white solid: mp 154−155 °C;

R_f = 0.31 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.17 – 7.02 (m, 7H), 6.15 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.27 (d, *J* = 13.5 Hz, 1H), 5.24 (d, *J* = 7.2 Hz, 1H), 4.84 (s, 1H), 2.38 (s, 3H), 0.32 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 140.9, 139.3, 135.7, 135.1, 133.8, 130.3, 129.1, 128.1, 127.8, 127.4, 127.1, 126.1, 116.4, 61.5, 21.7, –5.0; HRMS: (ESI) calculated for $C_{24}H_{27}NNaO_2SSi$ ($[M+Na]^+$): 444.1429, found: 444.1409.

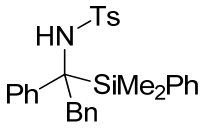


(6j): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and methylmagnesium bromide (3.0 M solution in Et_2O, 0.15 mL, 0.45 mmol) were used and afforded the product **6j** (106.2 mg, 86%) as a white solid: mp 159−160 ^{o}C (lit.[10] mp 163 ^{o}C); R_f = 0.31 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.6 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 1.4 Hz, 1H), 7.15 – 7.03 (m, 5H), 6.95 – 6.89 (m, 2H), 4.91 (s, 1H), 2.34 (s, 3H), 1.69 (s, 3H), 0.29 (s, 3H), 0.15 (s, 3H). The ^{1}H NMR spectrum of this compound matched the reported spectral data.[10]

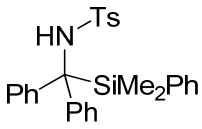


(6k): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and ethylmagnesium bromide (3.0 M solution in Et_2O, 0.15 mL, 0.45 mmol) were used and afforded the product **6k** (112.1 mg, 88%) as a white solid: mp 171−172 ^{o}C; R_f = 0.38 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.2 Hz, 2H), 7.22 – 7.15 (m, 4H), 7.13 – 7.04 (m, 3H), 7.00 – 6.92 (m, 2H), 4.72 (s, 1H), 2.40 (s, 3H), 2.30 (dq, *J* = 14.4, 1H), 2.14 (dq, *J* = 14.4, 7.1 Hz, 1H), 0.74 (t, *J* = 7.2 Hz, 3H), 0.36 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.6, 140.5, 136.1, 135.0, 129.6, 129.4, 127.8, 127.7, 127.2, 127.1, 125.8, 59.6, 26.7, 21.7, 8.7, –3.7, –4.1; HRMS: (ESI) calculated for $C_{24}H_{29}NNaO_2SSi$ ($[M+Na]^+$): 446.1586, found: 446.1585.

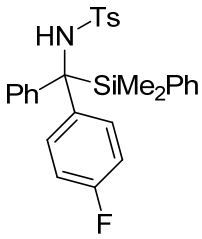
10. Vyas, D. J.; Frohlich, R.; Oestreich, M. *Org. Lett.* **2011**, *13*, 2094.



(6l): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and benzylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6l** (103.4 mg, 71%) as a white solid: mp 120−121 ^{o}C; R_f = 0.40 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.16 – 6.94 (m, 12H), 6.97 (d, *J* = 6.8 Hz, 2H), 4.76 (s, 1H), 3.78 (d, *J* = 15.3 Hz, 1H), 3.43 (d, *J* = 15.3 Hz, 1H), 2.38 (s, 3H), 0.43 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.1, 140.1, 136.69, 136.67, 135.4, 130.9, 129.4, 129.3, 128.3, 127.68, 127.64, 127.5, 127.0, 126.7, 126.2, 59.8, 39.8, 21.7, –3.27, –3.29; HRMS: (ESI) calculated for $C_{29}H_{31}NNaO_2SSi$ ($[M+Na]^+$): 508.1742, found: 508.1732.

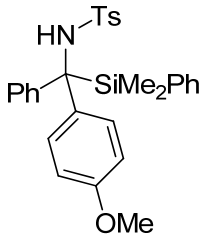


(6m): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36mL, 0.36mmol), and phenylmagnesium bromide (3.0 M solution in Et_2O, 0.15 mL, 0.45mmol) were used and afforded the product **6m** (92.8 mg, 66%) as a white solid: mp 184−185 ^{o}C; R_f = 0.33 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dq, *J* = 8.0, 4.1 Hz, 1H), 7.36 (d, *J* = 4.4 Hz, 4H), 7.27 (t, *J* = 3.8, 3.0 Hz, 4H), 7.15 – 7.03 (m, 6H), 6.81 (q, *J* = 8.4 Hz, 4H), 5.21 (s, 1H), 2.29 (s, 3H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.2, 140.0, 135.6, 135.0, 130.1, 129.6, 128.8, 128.4, 127.5, 126.5, 126.2, 62.6, 21.6, –3.2; HRMS: (ESI) calculated for $C_{28}H_{30}NO_2SSi$ ($[M+H]^+$): 472.1767, found: 472.1762.



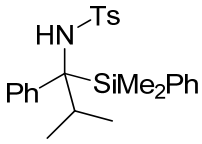
(6n): 1a (86.8 mg, 0.3 mmol) was dissolved in 1.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 ^{o}C. Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 ^{o}C and

then was allowed to warm slowly to –55 °C. 4-fluorophenylmagnesium bromide (1.0 M solution in THF, 3.0 mL, 3.0 mmol) was added dropwise at –55 °C, and the reaction mixture was allowed to warm slowly to –22 °C over 3 h. Then it was quenched at –22 °C by the addition of 3 mL of 1.0M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL). The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 20:1:0.3, gradient elution) yielding pure product **6n** (79.5 mg, 54%) as a white solid: mp 192−193 °C; R_f = 0.30 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 1H), 7.39 – 7.33 (m, 4H), 7.30 – 7.24 (m, 2H), 7.23 – 7.17 (m, 2H), 7.16 – 7.08 (m, 3H), 6.84 (q, *J* = 8.4 Hz, 4H), 6.71 (t, *J* = 8.6 Hz, 2H), 5.28 (s, 1H), 2.30 (s, 3H), 0.29 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, J_{CF} = 246.2 Hz), 142.1, 140.4, 140.0, 135.9 (d, J_{CF} = 3.3 Hz), 135.3, 134.9, 131.6 (d, J_{CF} = 7.9 Hz), 130.3, 129.1, 128.9, 128.5, 127.7, 126.6, 126.2, 114.2 (d, J_{CF} = 21.2 Hz), 62.1, 21.5, –3.1, –3.4; HRMS: (ESI) calculated for $C_{28}H_{28}FNNaO_2SSi$ ($[M+Na]^+$): 512.1492, found: 512.1497.

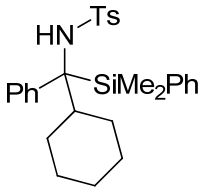


(6o): 1a (86.8 mg, 0.3 mmol) was dissolved in 1.5 mL THF and added to a flame-dried schlenk flask equipped with a magnetic stirring bar under argon. The solution was cooled to –78 °C. Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol) was added dropwise to the solution via syringe. The reaction mixture was stirred for 1h at –78 °C and then was allowed to warm slowly to –58 °C. 4-methoxyphenylmagnesium bromide (1.0 M solution in THF, 3.0 mL, 3.0 mmol) was added dropwise at –58 °C, and the reaction mixture allowed to warm slowly to –25 °C over 4 h. Then it was quenched at –25 °C by the addition of 3 mL of 1.0 M solution of HCl. The resulting heterogeneous mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The reaction mixture was diluted with 30 mL EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc (2×5 mL).

The organic extracts were washed with saturated aqueous sodium bicarbonate (15 mL) and brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography (*n*-hexane:EtOAc:CH_2Cl_2 = 50:1:0.3 to 15:1:0.3, gradient elution) yielding pure product **6o** (87.3 mg, 58%) as a white solid: mp 183−184 ^oC; R_f = 0.22 (*n*-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 1H), 7.39 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 7.17 – 7.09 (m, 5H), 6.87 – 6.76 (m, 4H), 6.52 (d, *J* = 9.2, 2H), 5.21 (s, 1H), 3.75 (s, 3H), 2.29 (s, 3H), 0.31 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 141.7, 140.9, 140.0, 135.7, 135.0, 131.9, 131.4, 130.1, 128.9, 128.7, 128.4, 127.5, 126.31, 126.27, 112.7, 62.0, 55.3, 21.6, –3.1, –3.4; HRMS: (ESI) calculated for $C_{29}H_{31}NNaO_3SSi$ ($[M+Na]^+$): 524.1692, found: 524.1690.



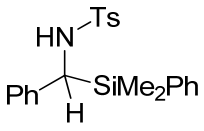
(6p): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THD (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and iospropylmagnesium bromide (2.0 M solution in THF, 0.23 mL, 0.46 mmol) were used and afforded the product **6p** (70.6 mg, 54%) as a white solid and **6r** (44.8 mg, 38%) as a white solid. The analytic data of **6p**: mp 165−166 ^oC; R_f = 0.41 (*n*-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.33 (m, 1H), 7.32 – 7.26 (m, 6H), 7.22 – 7.06 (m, 5H), 4.47 (s, 1H), 2.73 – 2.62 (m, 1H), 2.45 (s, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.29 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.0, 140.8, 136.9, 135.4, 129.7, 129.6, 127.9, 127.8, 127.6, 126.6, 125.8, 66.2, 33.3, 21.8, 20.0, 18.8, –0.3, –2.5; HRMS: (ESI) calculated for $C_{25}H_{31}NNaO_2SSi$ ($[M+Na]^+$): 460.1742, found: 460.1742.



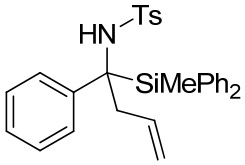
(6q): (1) According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and cyclohexylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **6q** (37.4 mg, 26%) as a white solid and **6r** (67.9 mg, 57%) as a white solid.

(2) According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in

THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and cyclohexylmagnesium bromide (treated with 10 mmol% $ZnCl_2$ in advance: 1.0 mL 1.0 M cyclohexylmagnesium bromide in THF and 0.1 mL 1.0 M $ZnCl_2$ in Et_2O were stirred at room temperature for 1 h under argon before that was used, 0.5 mL, 0.45 mmol, 1.5 equiv) were used and afforded the product **6q** (79.1 mg, 55%) and trace of **6r**. The analytic data of **6q**: mp 165−167 ^oC; R_f = 0.44 (*n*-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.34 (m, 1H), 7.33 – 7.26 (m, 5H), 7.21 – 7.05 (m, 5H), 4.47 (s, 1H), 2.45 (s, 3H), 2.23 (t, *J* = 8.8 Hz, 1H), 1.89 (d, *J* = 8.6 Hz, 1H), 1.78 – 1.66 (m, 3H), 1.61 (d, *J* = 12.5 Hz, 1H), 1.32 – 1.20 (m, 2H), 1.19 – 1.12 (m, 2H), 1.09 – 0.98 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.5, 141.0, 137.0, 135.3, 129.7, 129.6, 127.9, 127.7, 127.6, 126.7, 125.7, 66.1, 44.6, 30.5, 28.3, 27.4, 27.1, 26.6, 21.7, –0.2, –2.6; HRMS: (ESI) calculated for $C_{28}H_{35}NNaO_2SSi$ ($[M+Na]^+$): 500.2055, found: 500.2051.

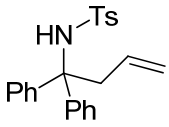


(6r): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Dimethylphenylsilyllithium (appro. 1.0 M in THF, 0.36 mL, 0.36 mmol), and *tert*-butylmagnesium chloride (1.0 M solution in THF, 3.0 mL, 3.0 mmol) were used and afforded the product **6r** (99.2 mg, 84%) as a white solid: R_f = 0.27 (*n*-hexane:EtOAc = 6:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 1H), 7.38 – 7.26 (m, 6H), 7.05 – 6.98 (m, 3H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.73 – 6.66 (m, 2H), 4.75 (d, *J* = 8.0 Hz, 1H), 4.11 (d, *J* = 8.0 Hz, 1H), 2.29 (s, 3H), 0.28 (s, 3H), 0.20 (s, 3H). The ^1H NMR spectrum of this compound matched the reported spectral data.[10]



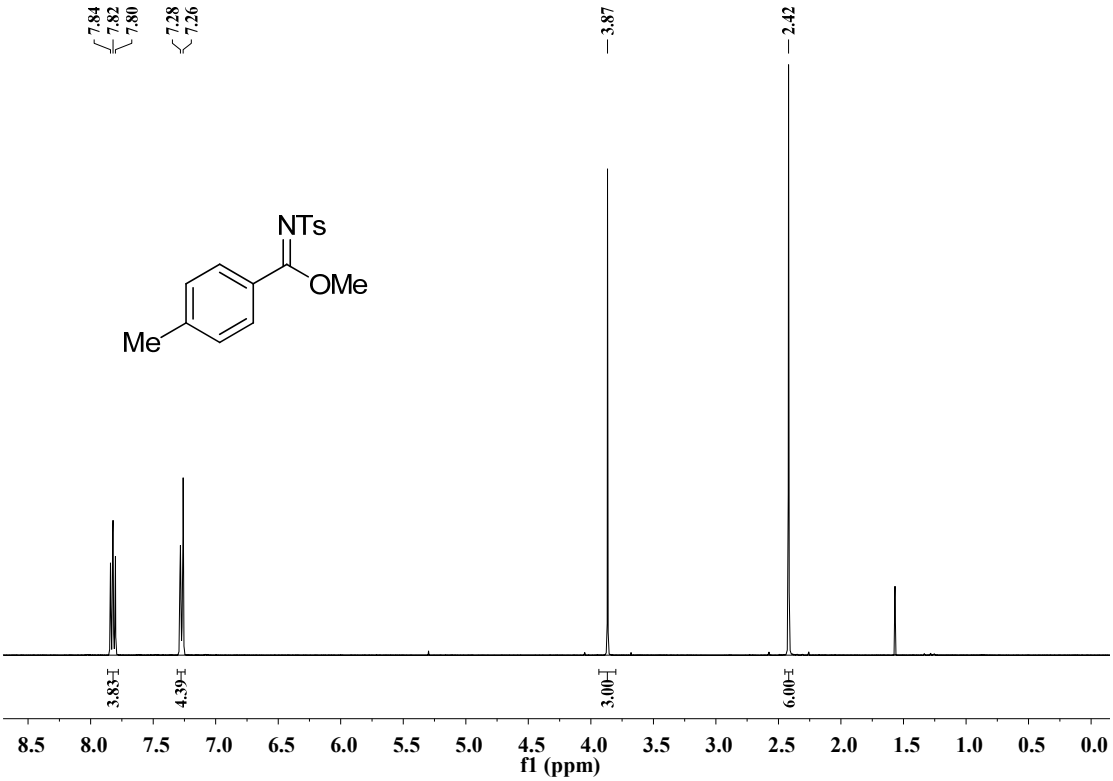
(8): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), Diphenylmethylsilyllithium (appro. 0.8 M in THF, 0.45 mL, 0.36 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used. But after allylmagnesium bromide was added dropwise, the reaction mixture was allowed to warm slowly to –35 ^oC over 2 h. The reaction was quenched at –35 ^oC by the addition of 3 mL of 1.0 M solution of HCl. Standard operation followed column chromatography afforded the title

compound **8** (131.3 mg, 88%) as a white solid: mp 123−124 °C; R_f = 0.34 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.44 – 7.35 (m, 4H), 7.33 – 7.27 (m, 6H), 7.08 (t, *J* = 8.0 Hz, 3H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 7.7 Hz, 2H), 5.84 – 5.70 (m, 1H), 5.03 (s, 1H), 4.94 (s, 1H), 4.90 (d, *J* = 4.3 Hz, 1H), 3.19 (ddd, *J* = 22.7, 15.4, 6.8 Hz, 2H), 2.37 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.4, 140.3, 136.1, 135.8, 134.9, 133.8, 133.1, 130.1, 130.0, 129.3, 128.0, 127.8, 127.5, 127.2, 126.1, 118.7, 58.1, 39.8, 21.7, –4.4; HRMS: (ESI) calculated for $C_{30}H_{31}NNaO_2SSi$ ($[M+Na]^+$): 520.1742, found: 520.1735.

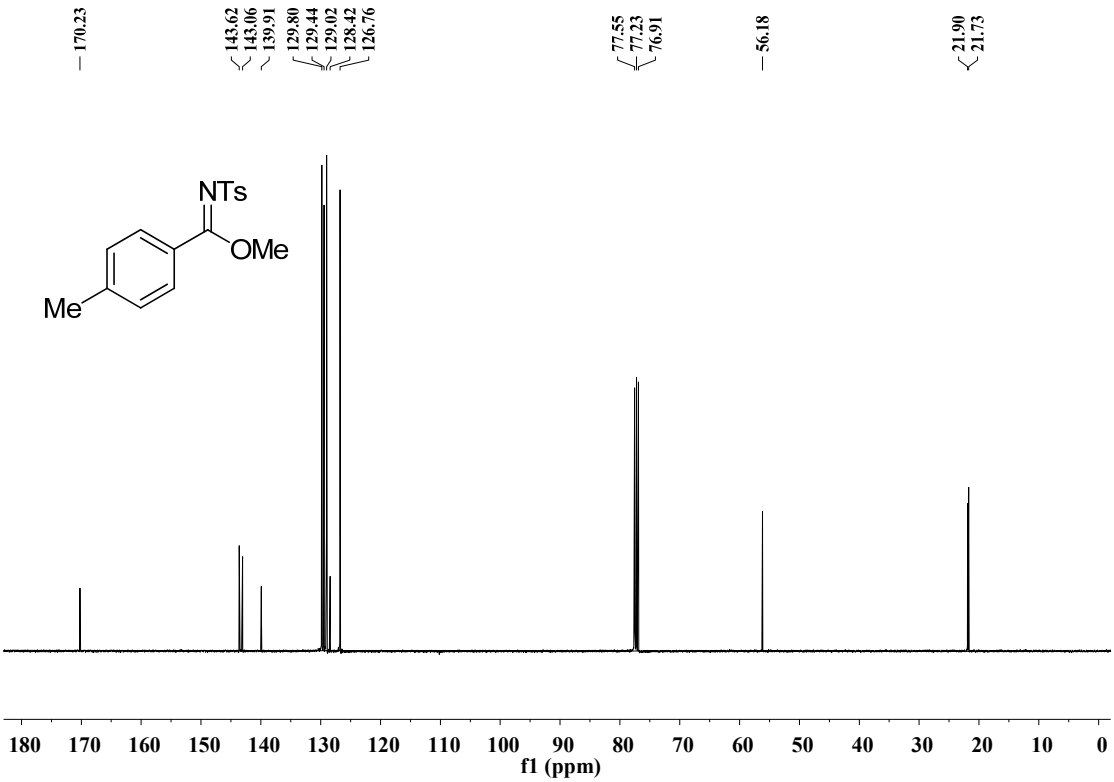


(9): According to the general procedure for α-silylamines, **1a** (86.8 mg, 0.3 mmol) dissolved in THF (1.5 mL), phenyl lithium (1.9 M in *n*-butyl ether, 0.24 mL, 0.45 mmol), and allylmagnesium bromide (1.0 M solution in THF, 0.45 mL, 0.45 mmol) were used and afforded the product **9** (109.5 mg, 97%) as a white solid: mp 113−114 °C; R_f = 0.29 (*n*-hexane:EtOAc = 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.06 (m, 12H), 6.96 (d, *J* = 8.3 Hz, 2H), 5.46 – 5.35 (m, 1H), 5.34 (s, 1H), 5.26 (dd, *J* = 17.1, 2.0 Hz, 1H), 5.15 (dd, *J* = 9.9, 2.0 Hz, 1H), 3.31 (d, *J* = 6.9 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.4, 139.2, 133.0, 129.0, 128.2, 127.9, 127.3, 127.1, 121.2, 66.5, 45.2, 21.6; HRMS: (ESI) calculated for $C_{23}H_{23}NNaO_2S$ ($[M+Na]^+$): 400.1347, found: 400.1344.

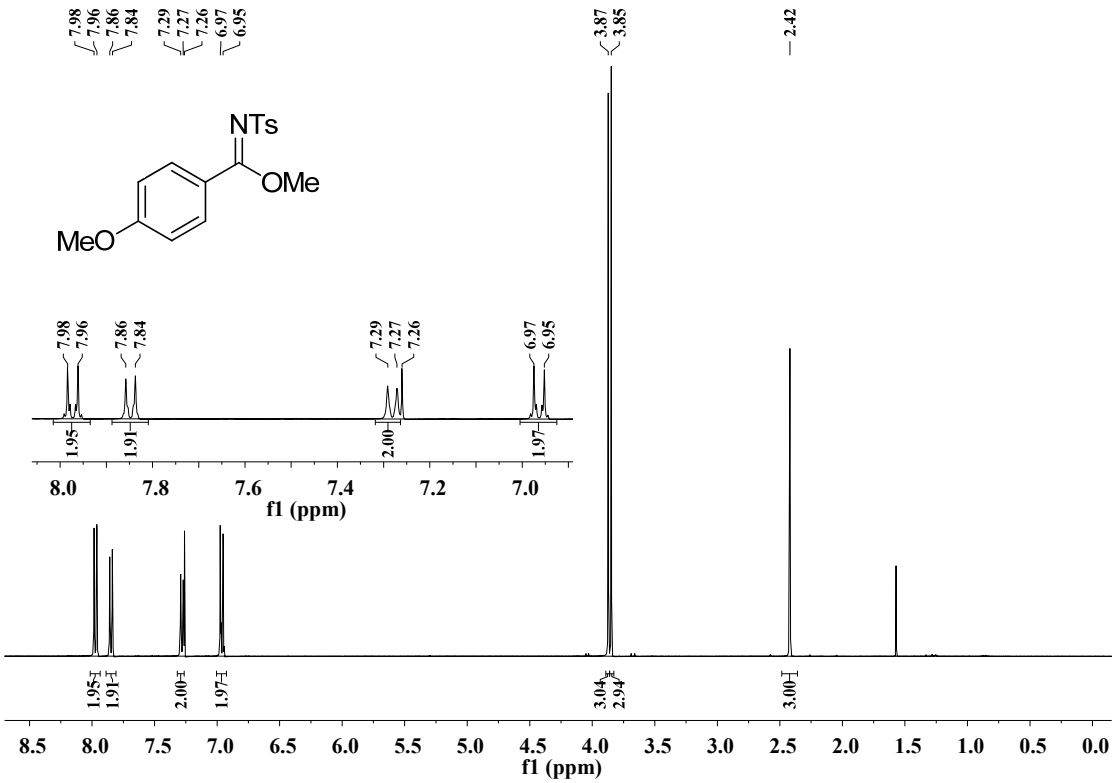
13. NMR Spectra of all new compounds



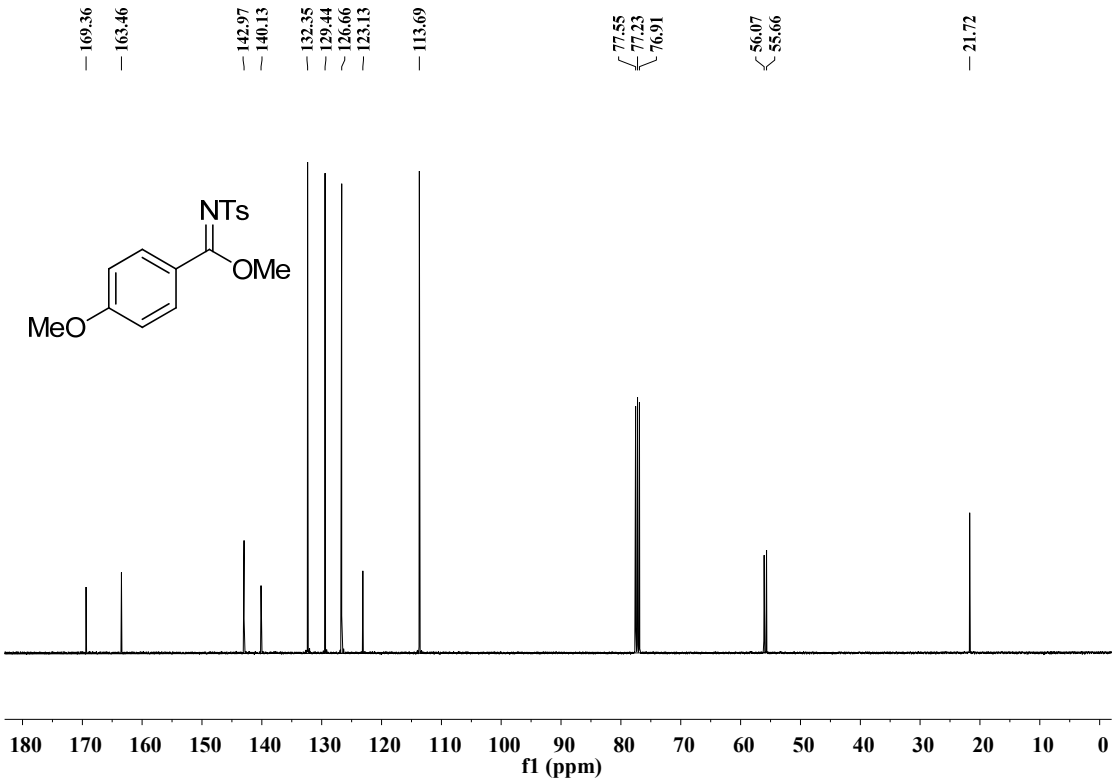
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1b**



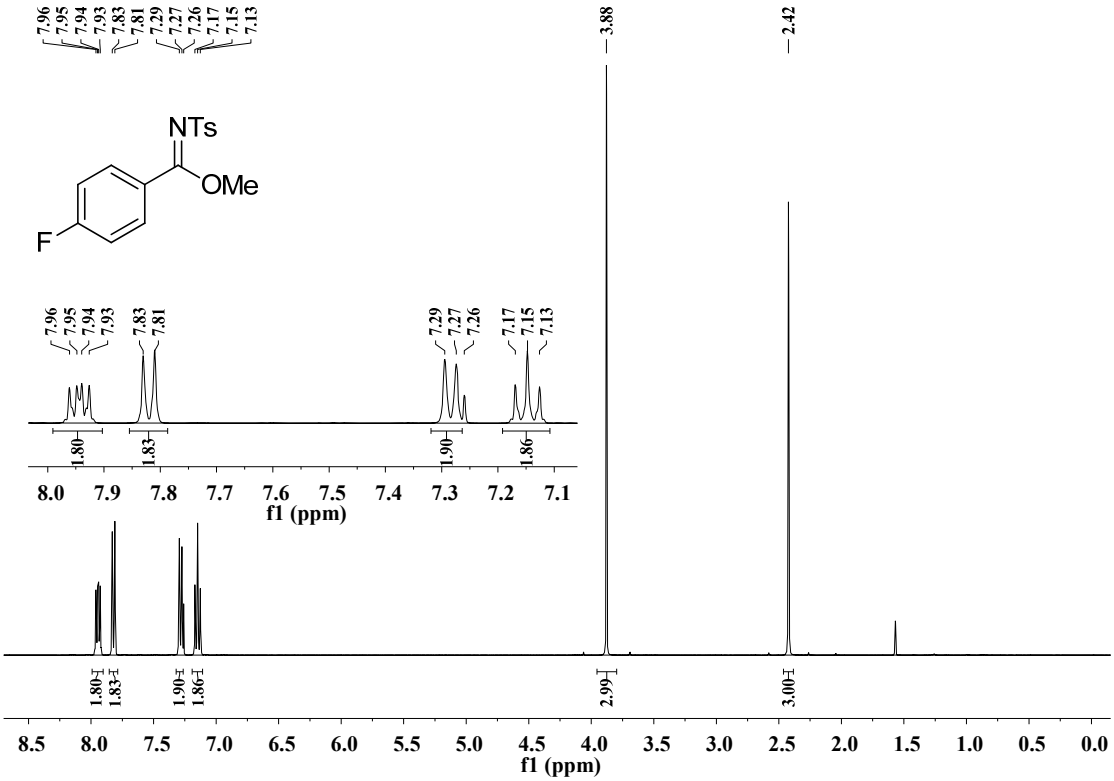
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1b**



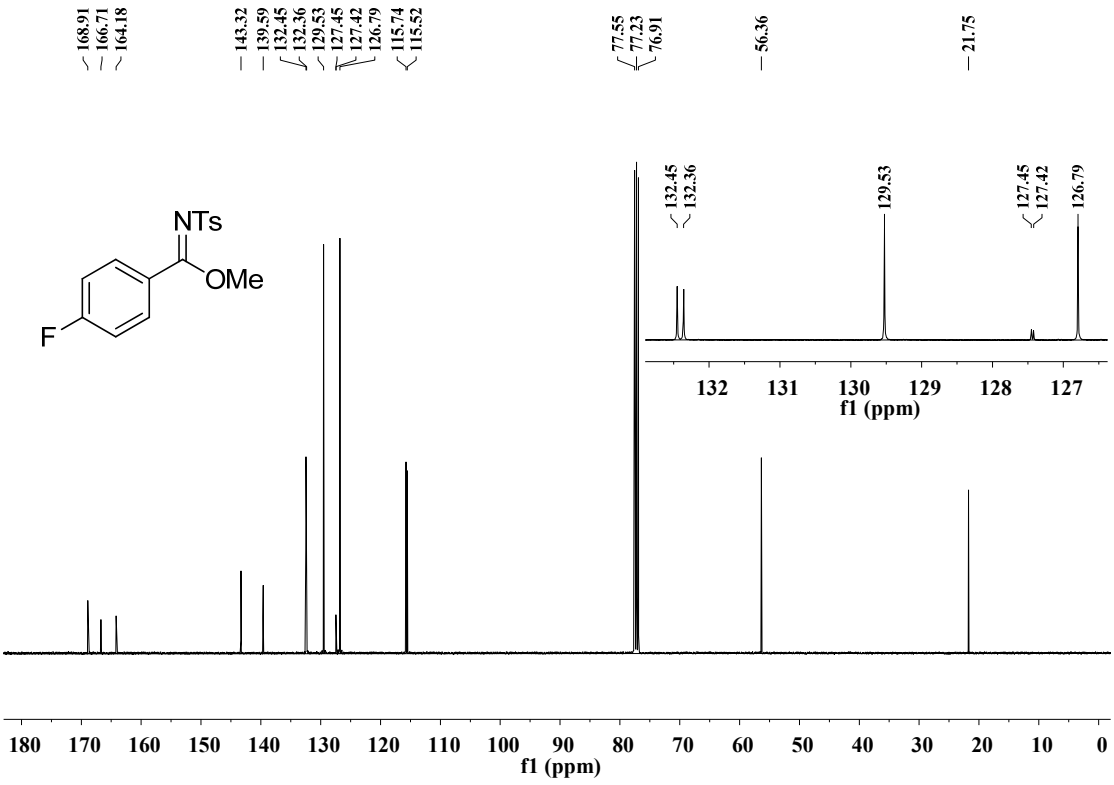
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1c**



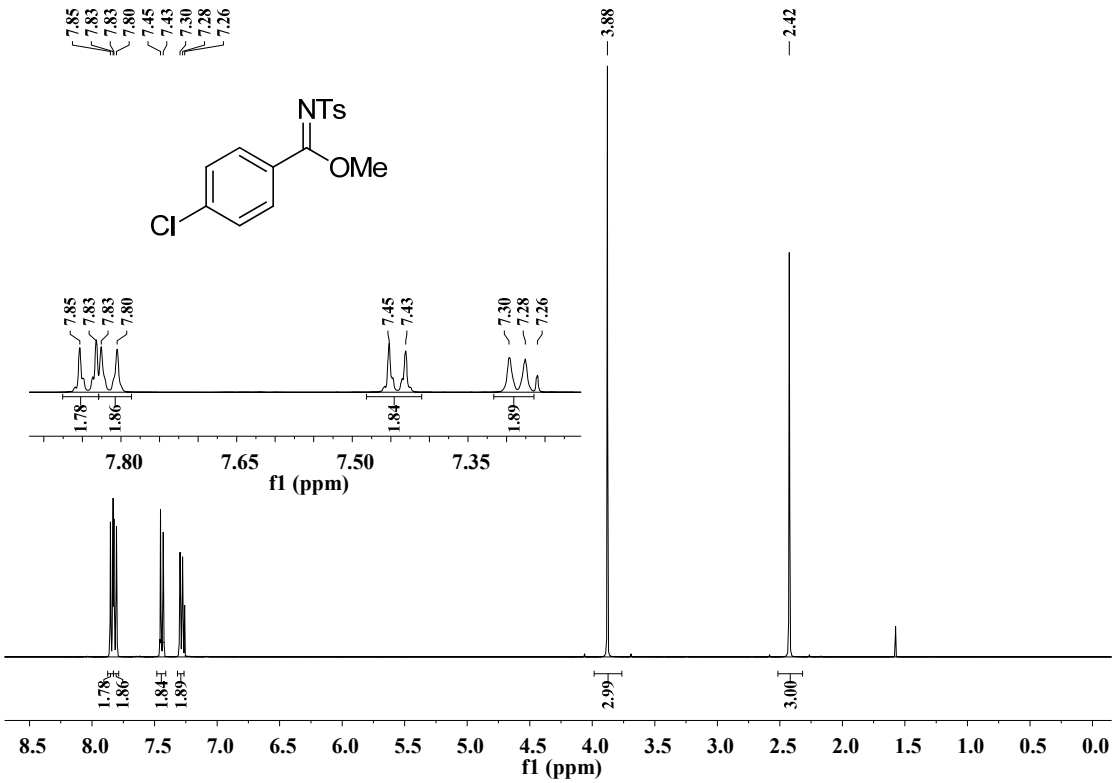
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1c**



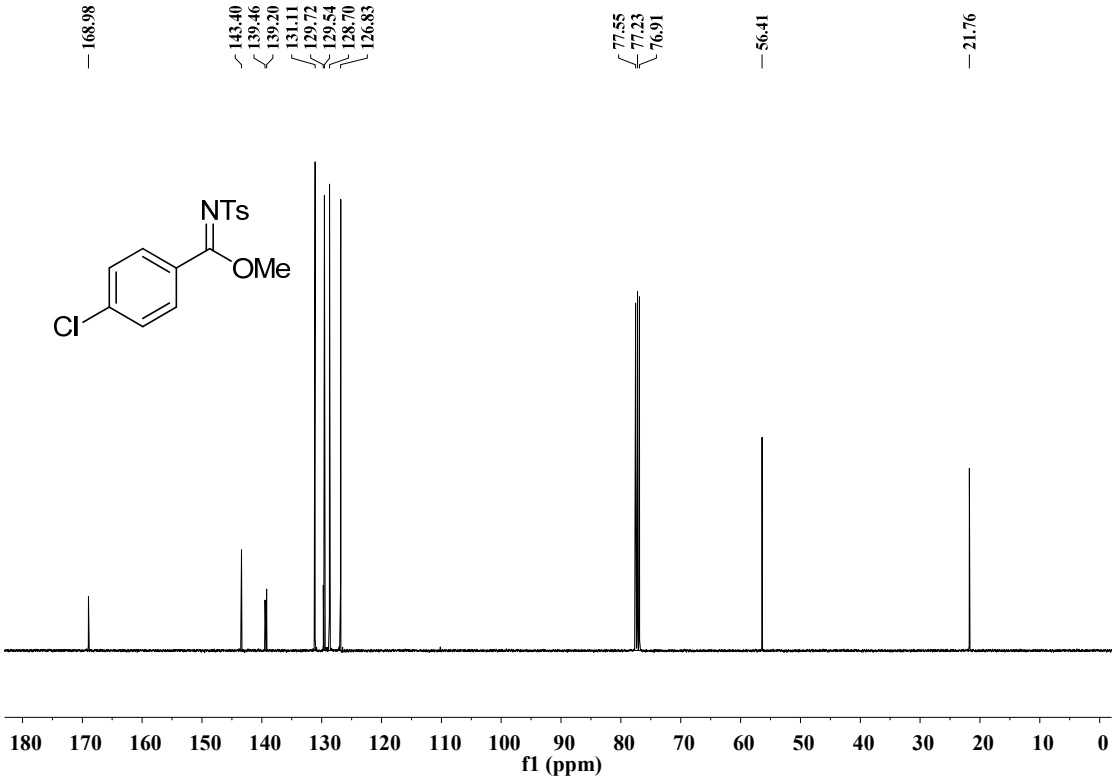
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1d**



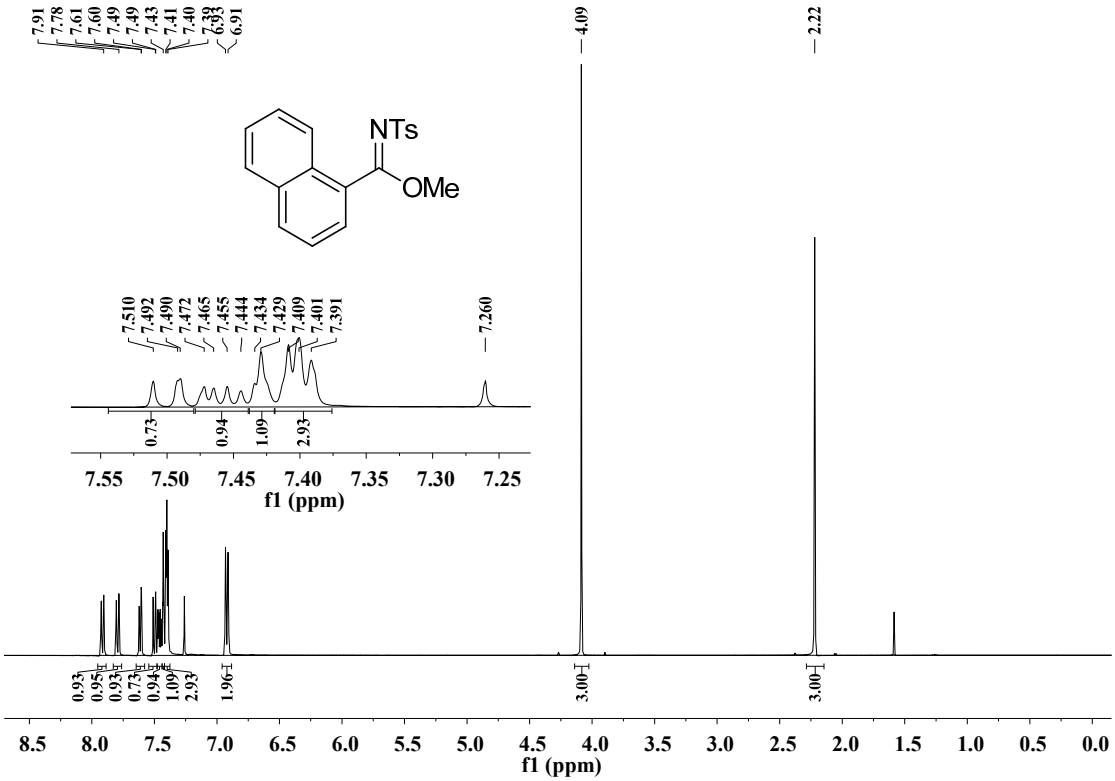
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1d**



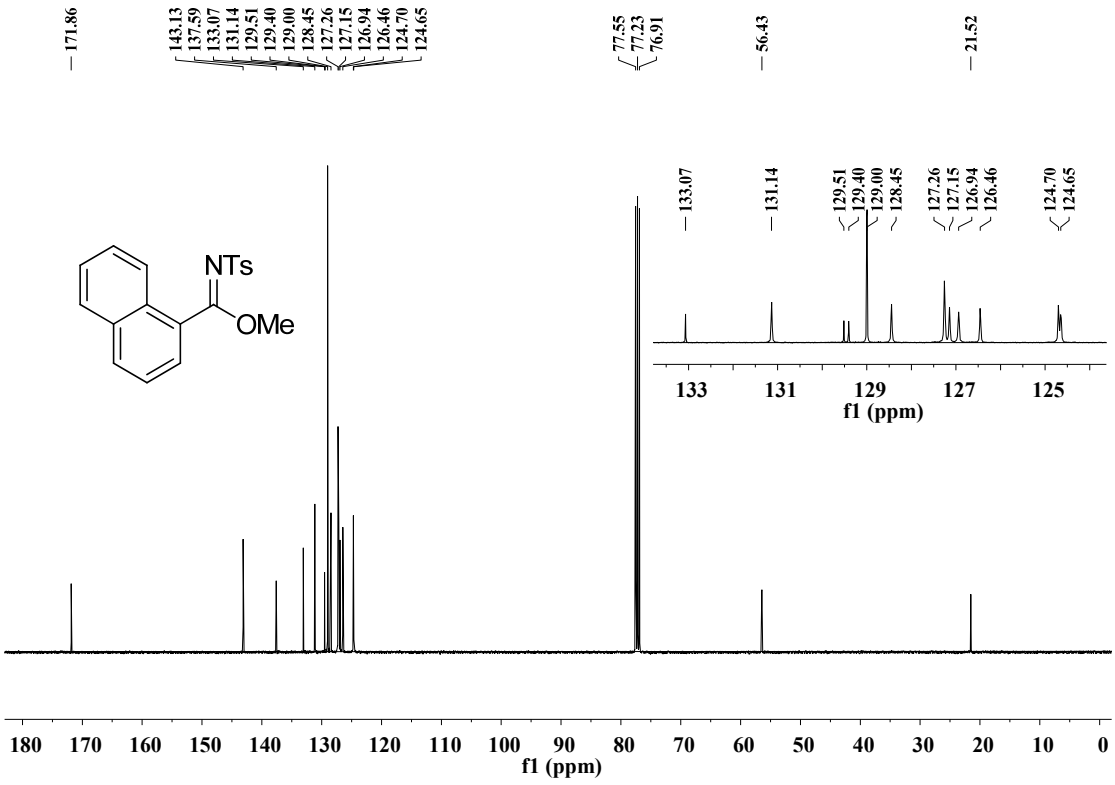
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1e**



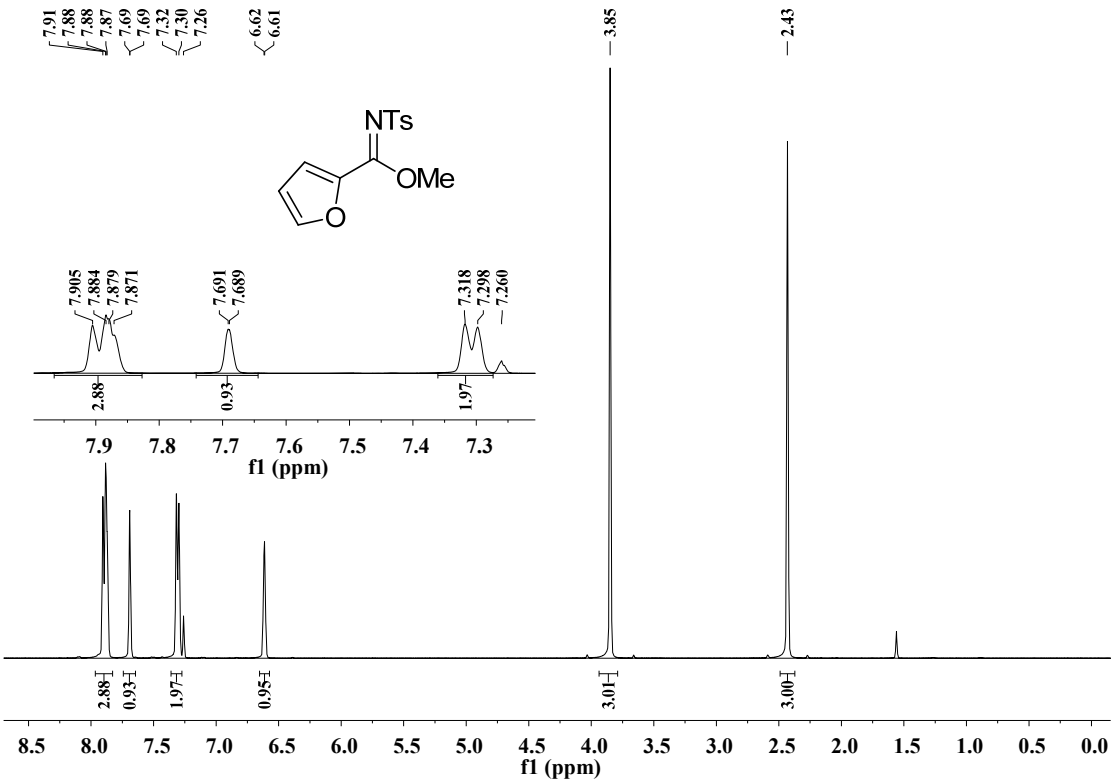
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1e**



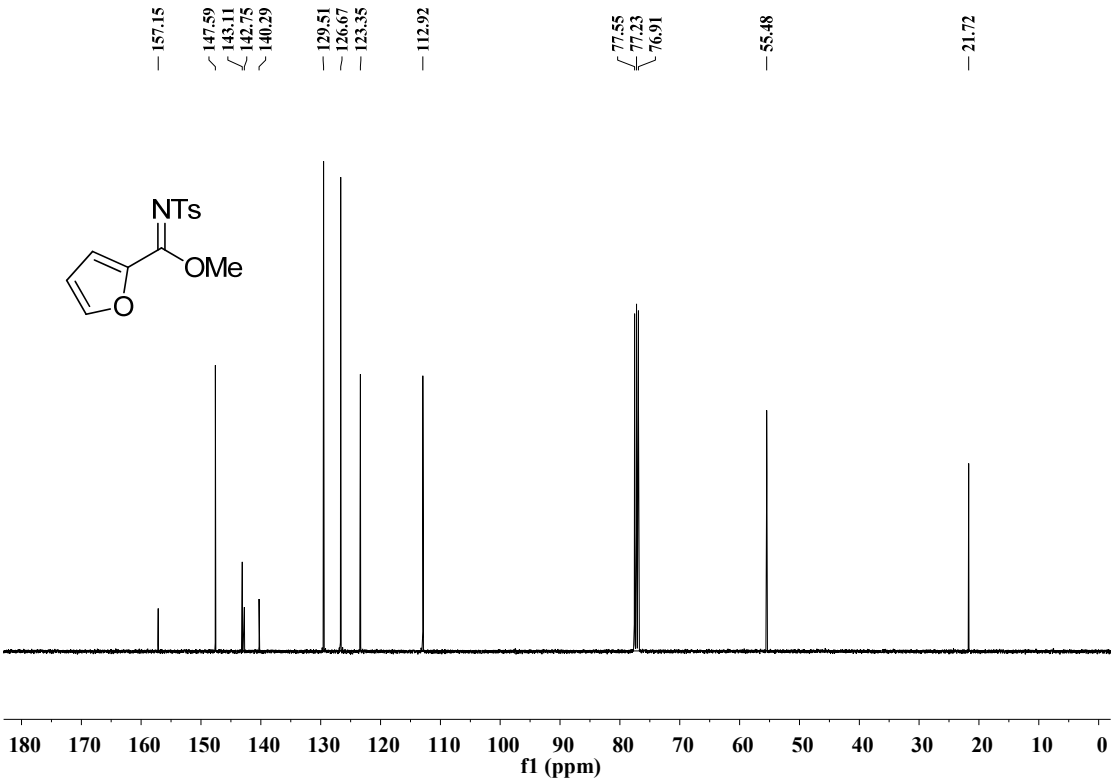
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1f**



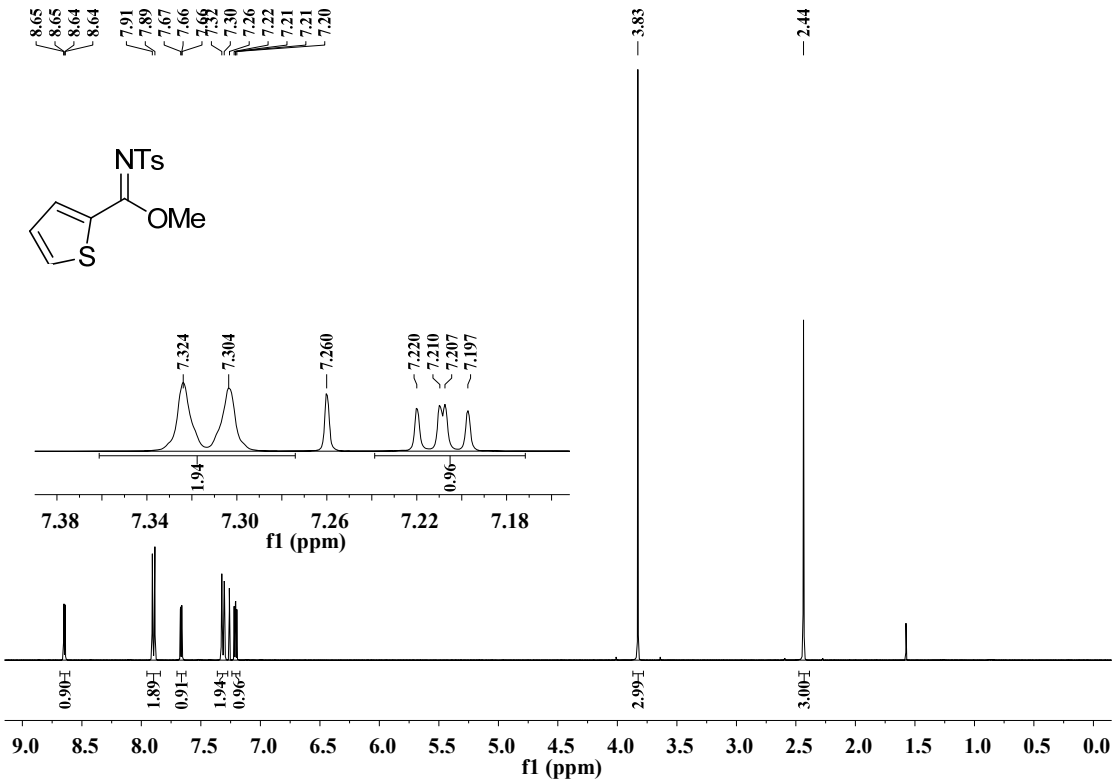
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1f**



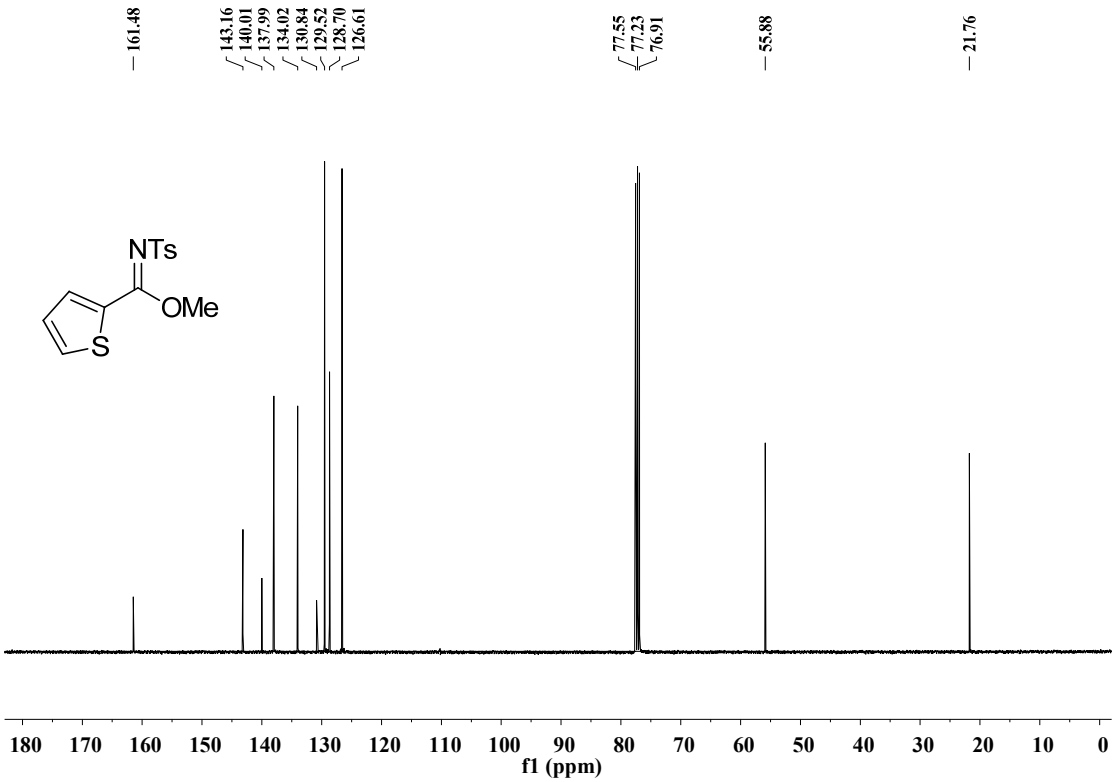
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1g**



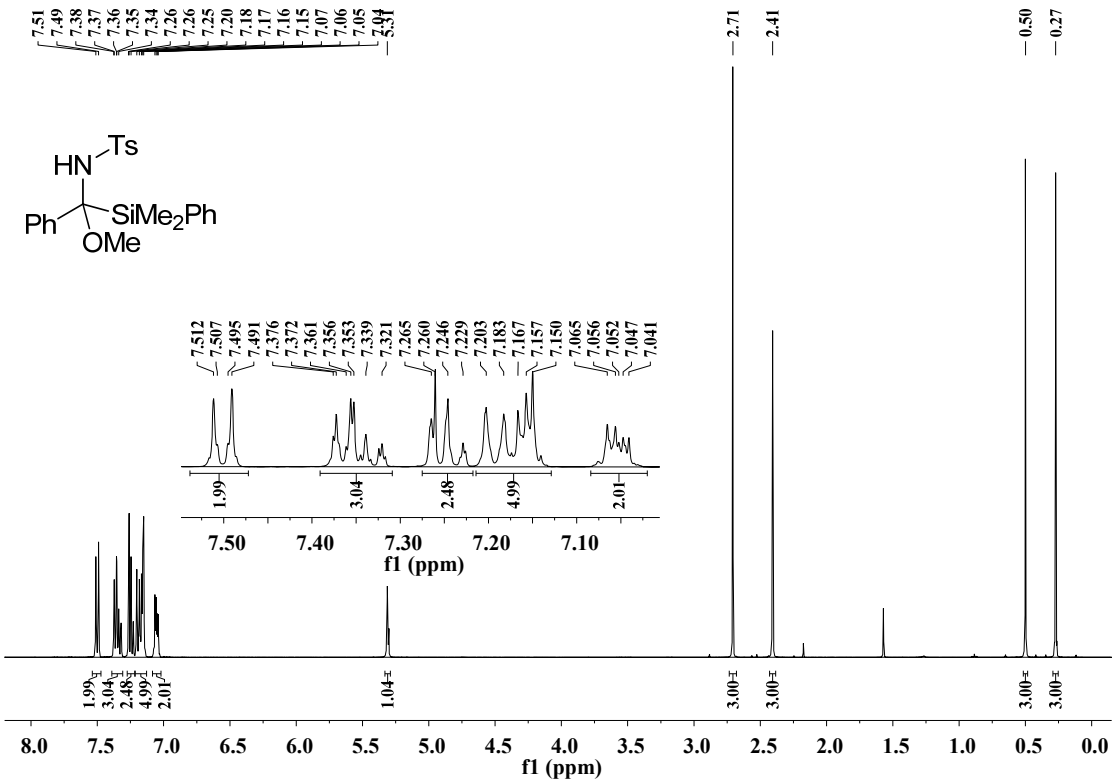
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1g**



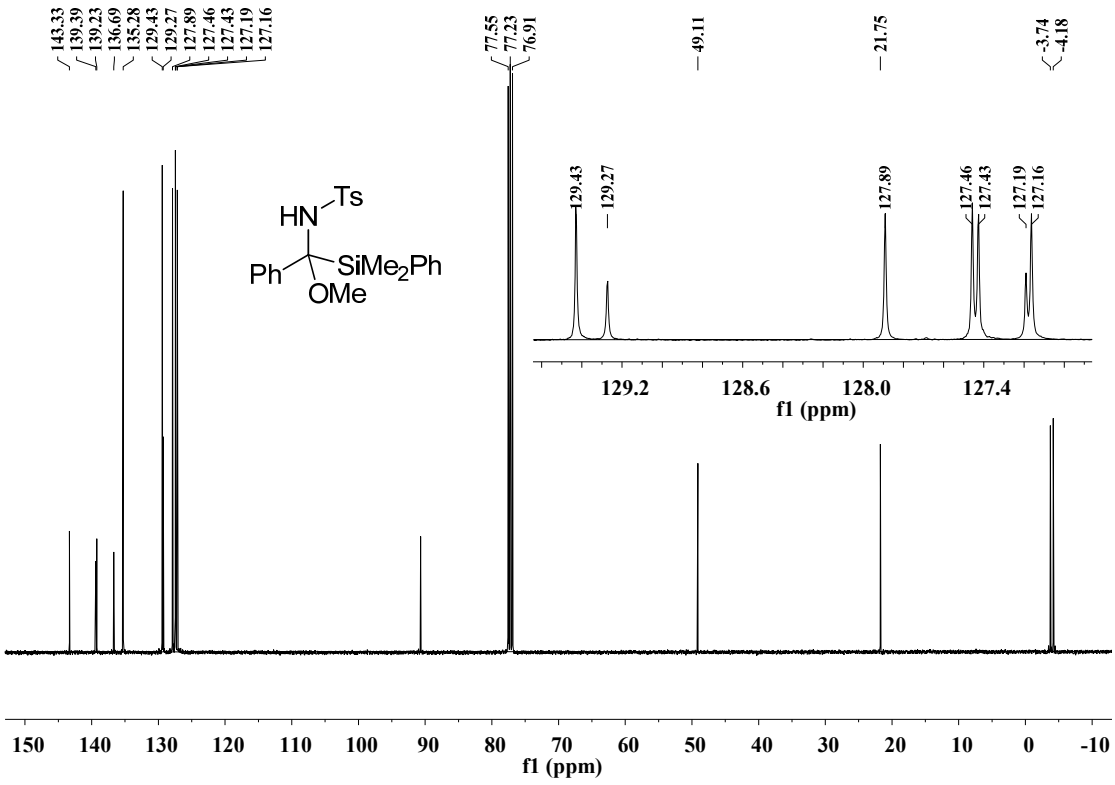
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1h**



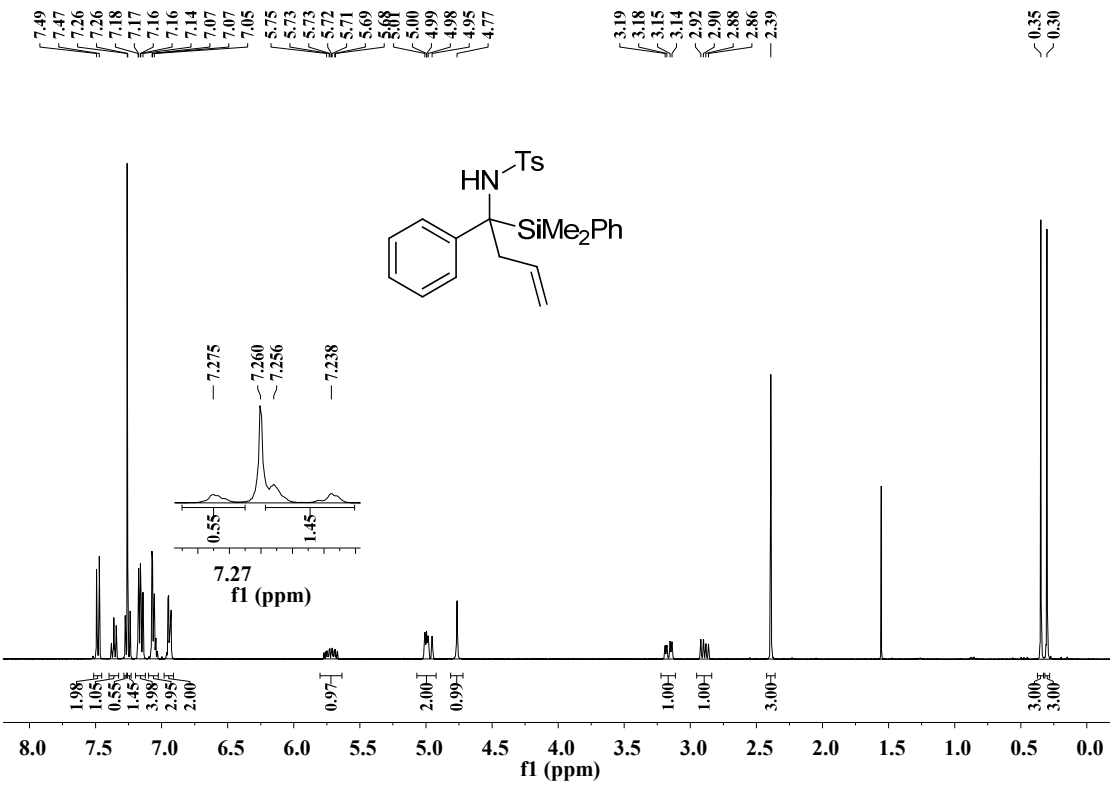
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **1h**



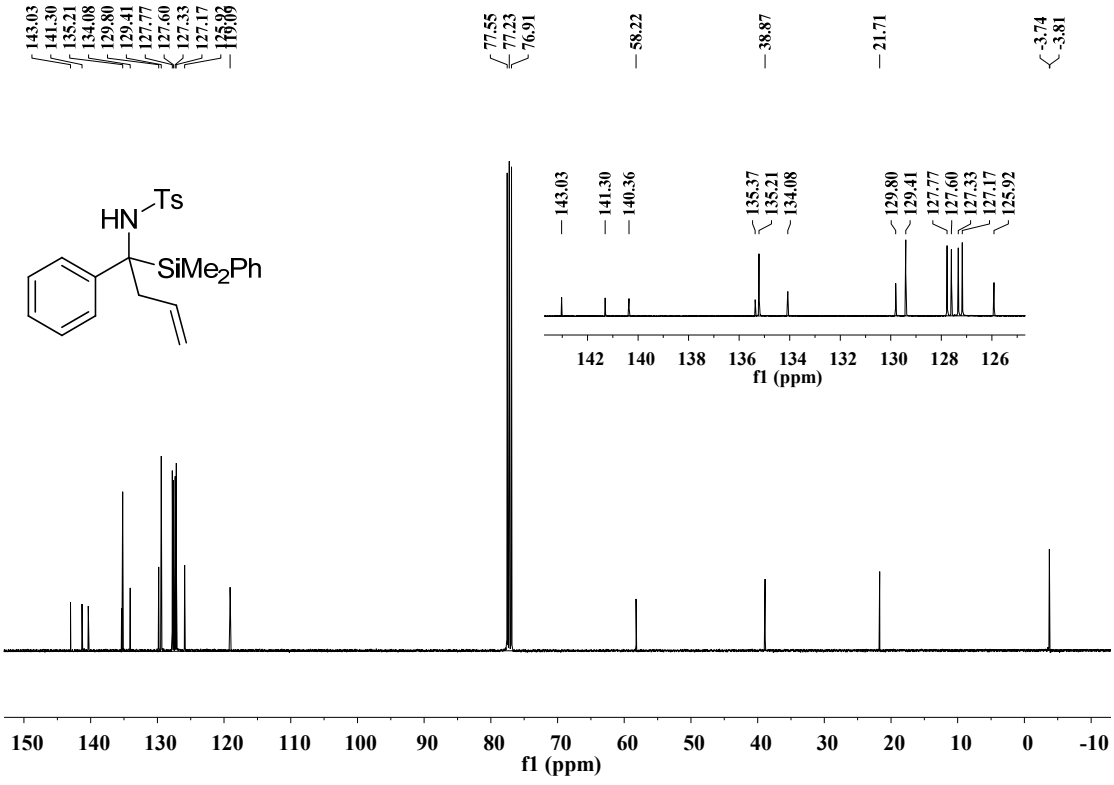
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4**



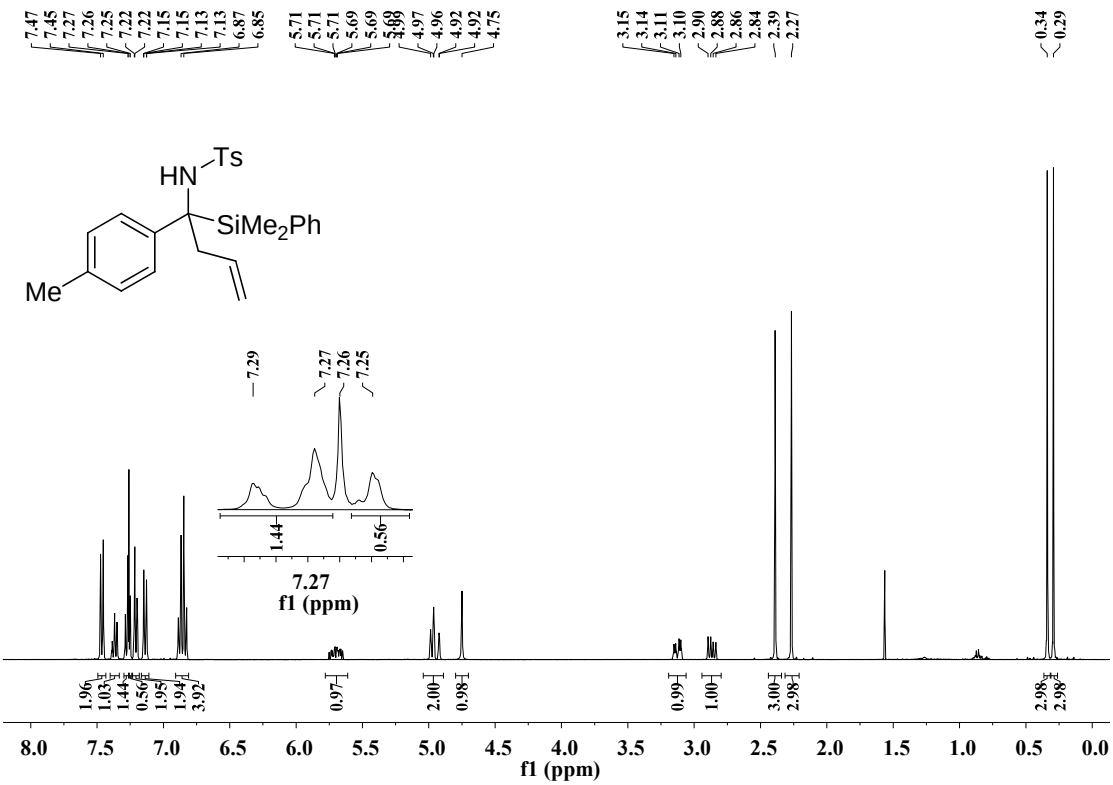
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **4**



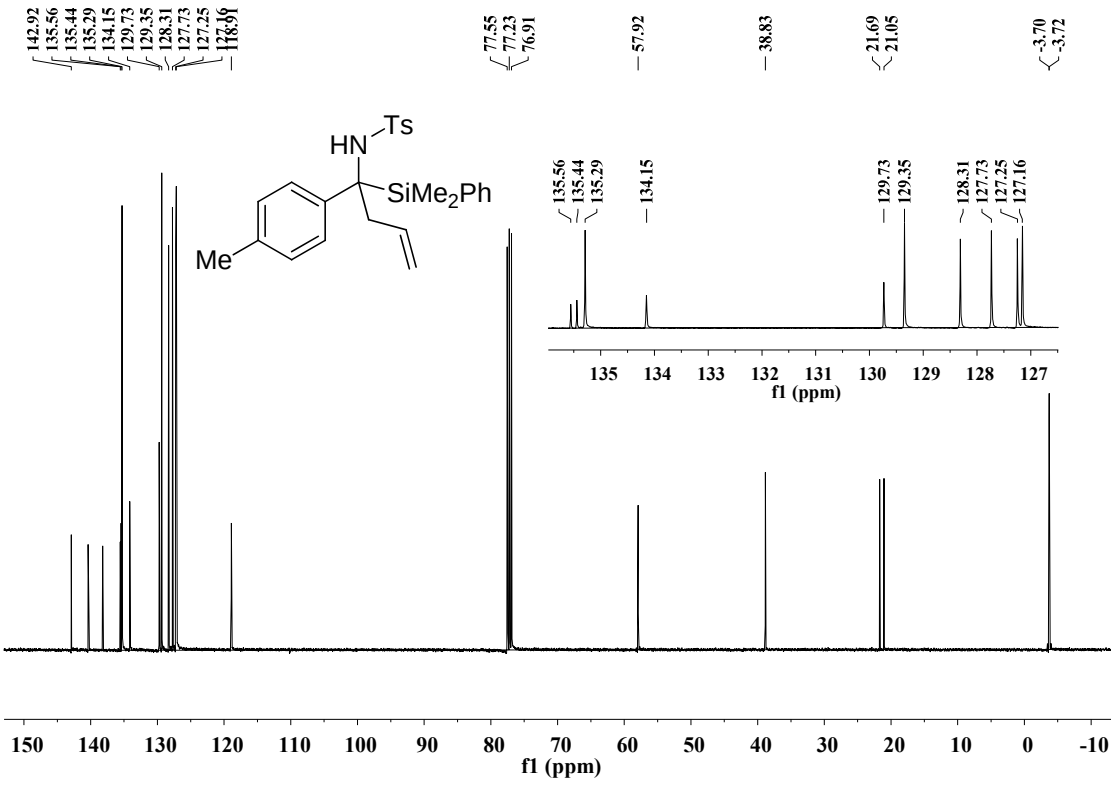
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6a**



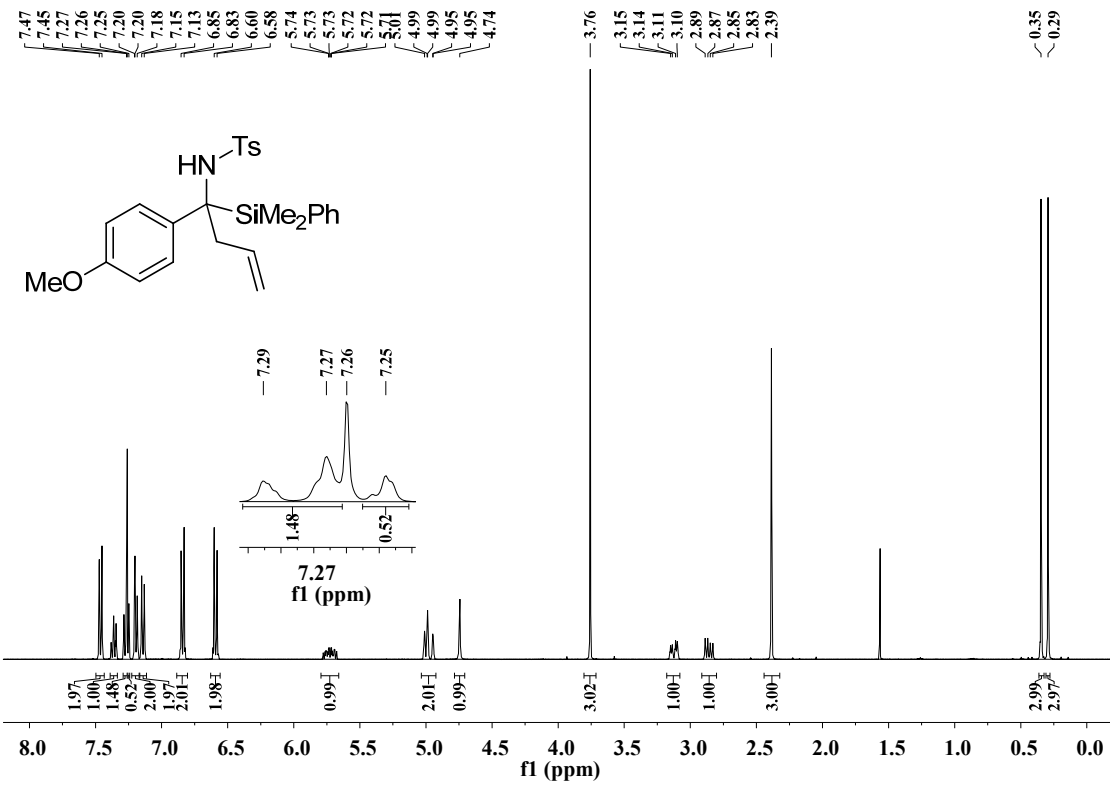
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6a**



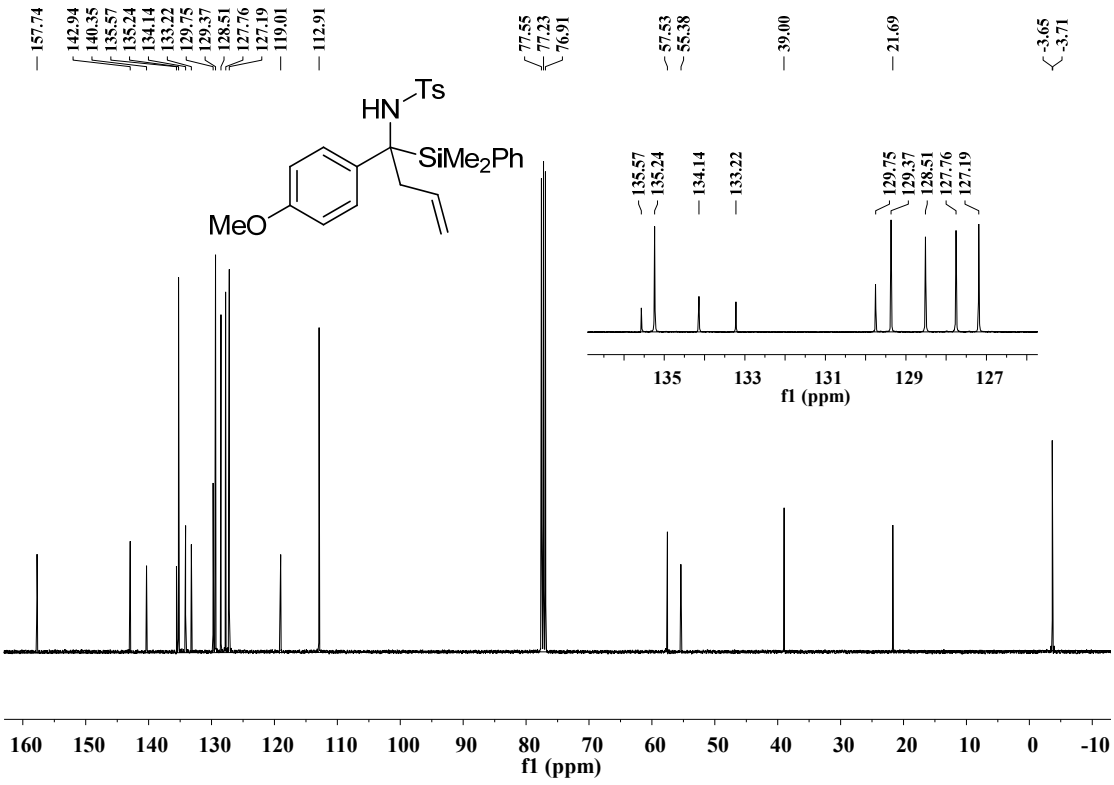
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6b**



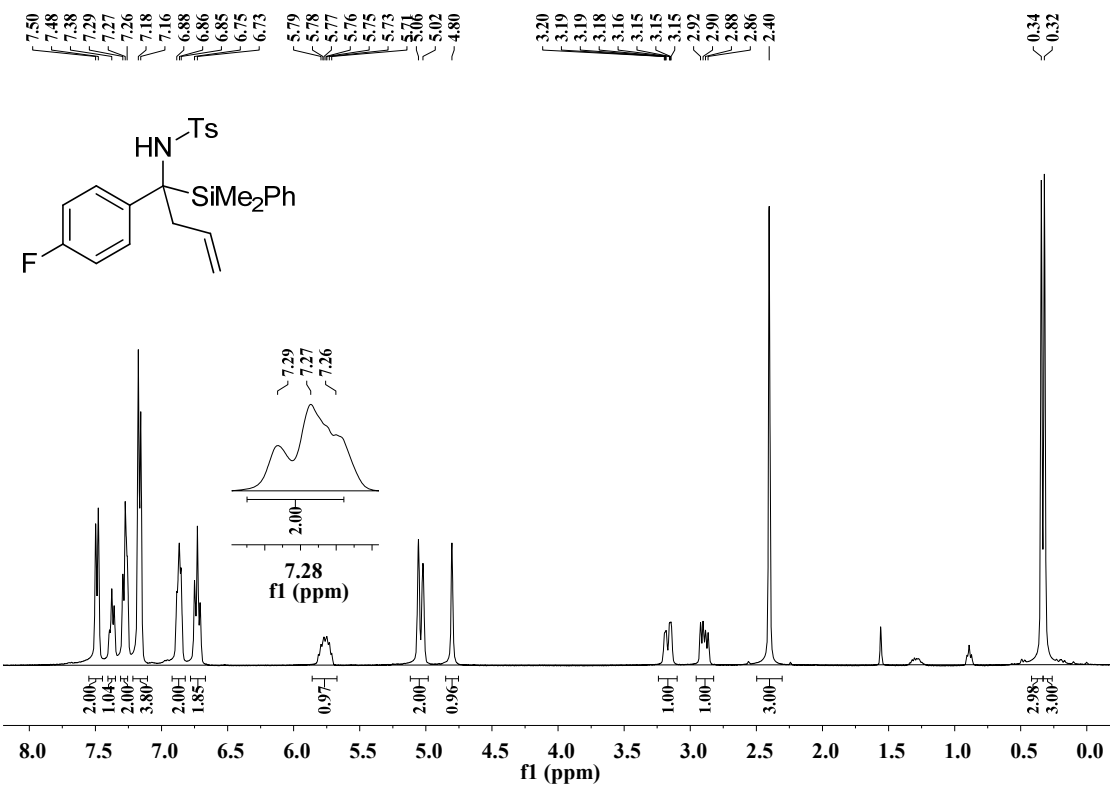
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6b**



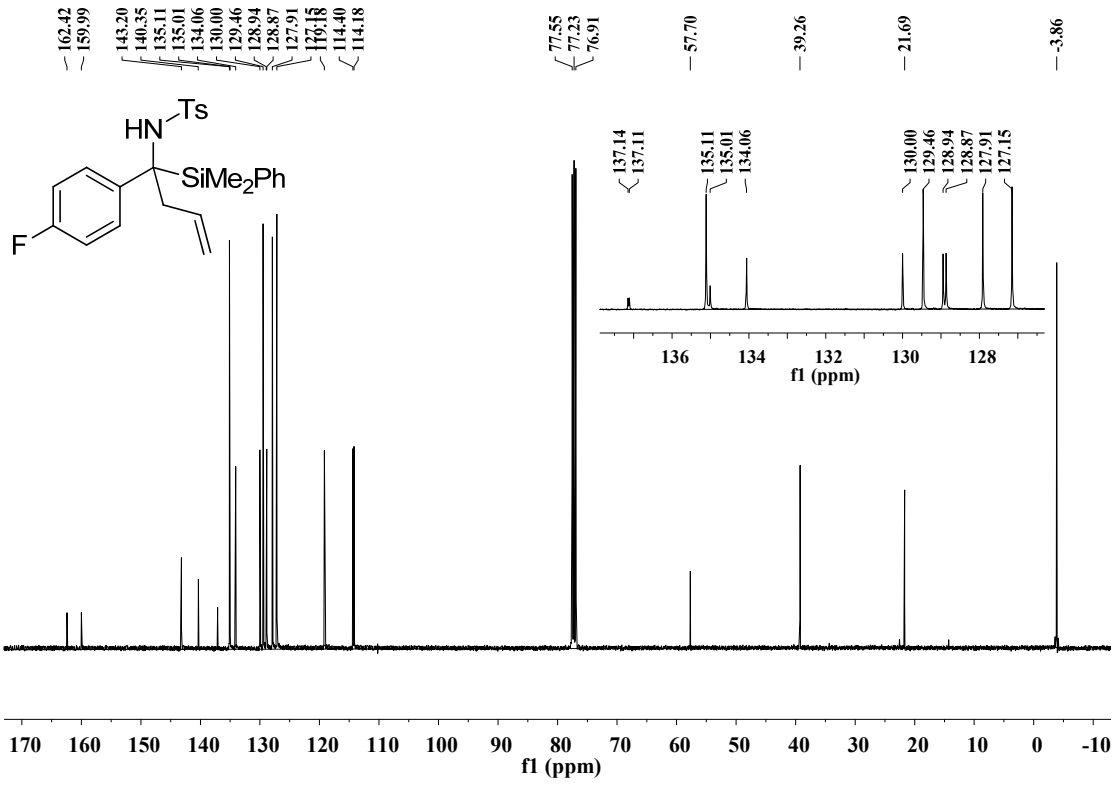
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6c**



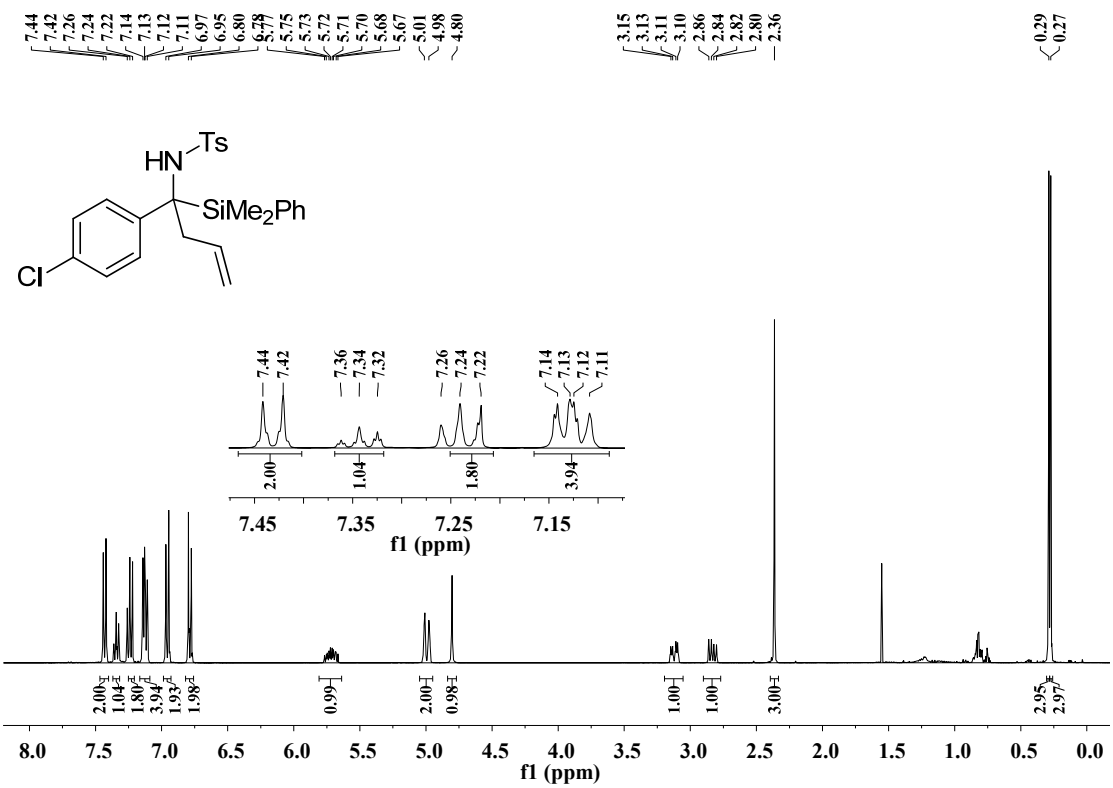
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6c**



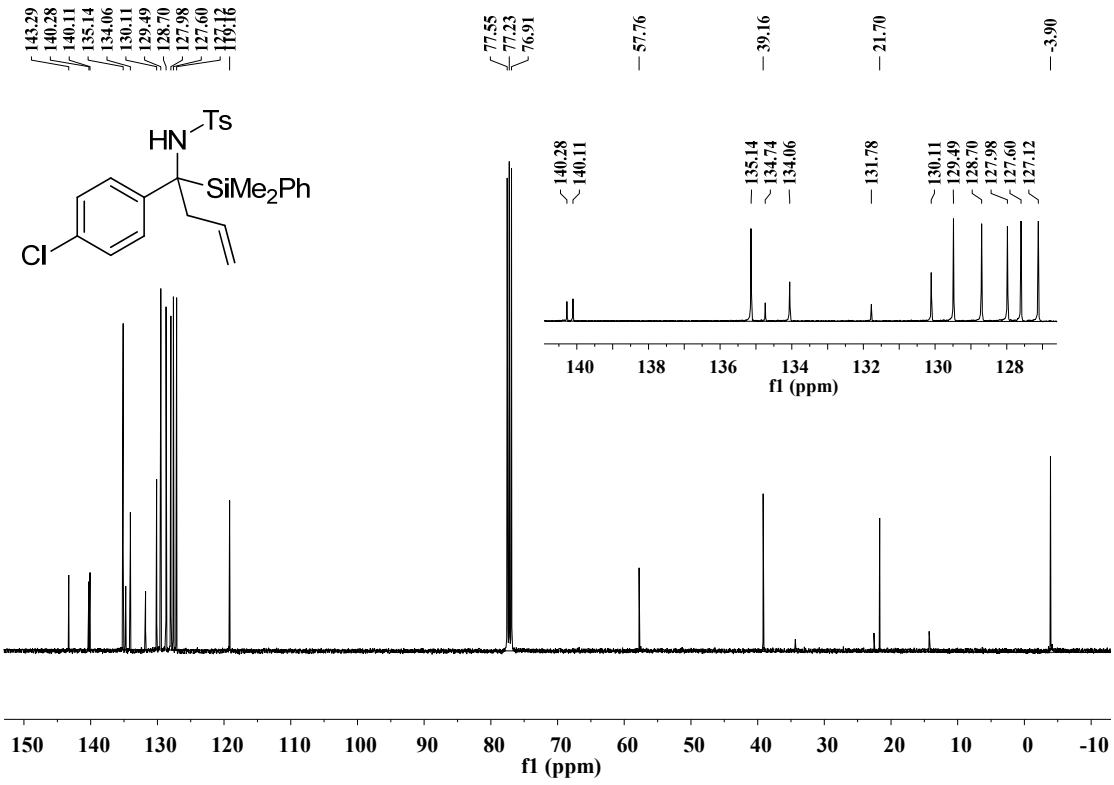
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6d**



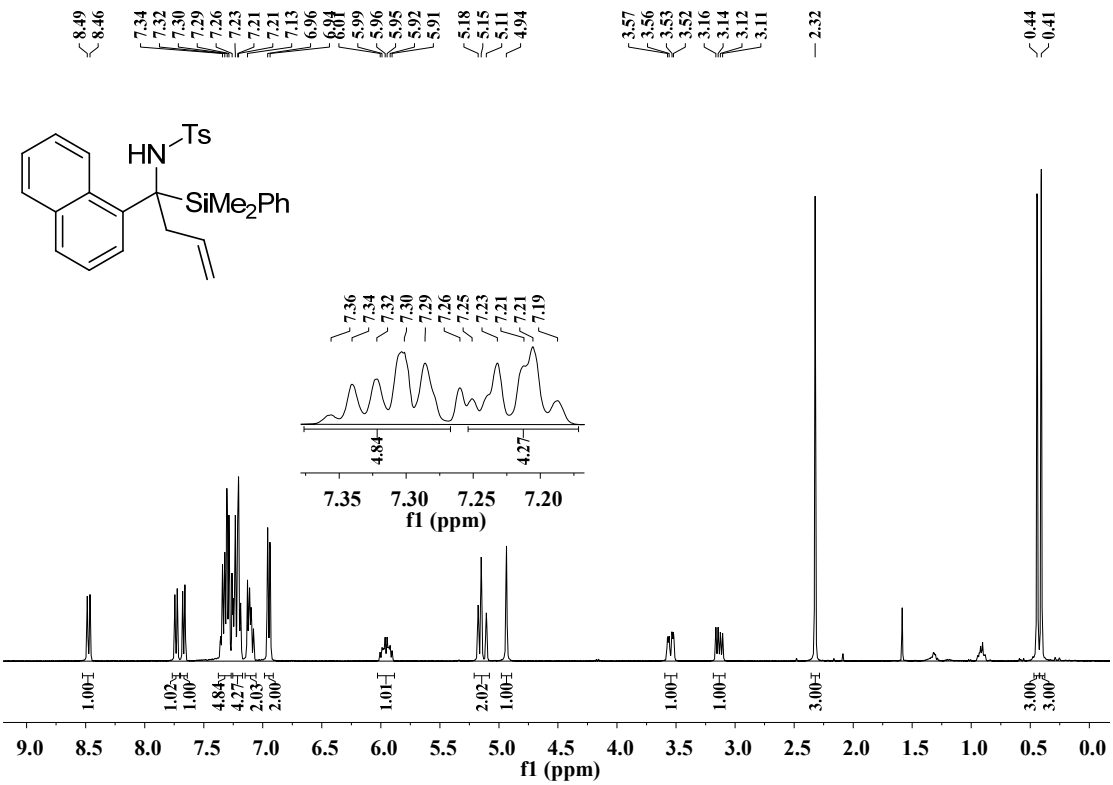
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6d**



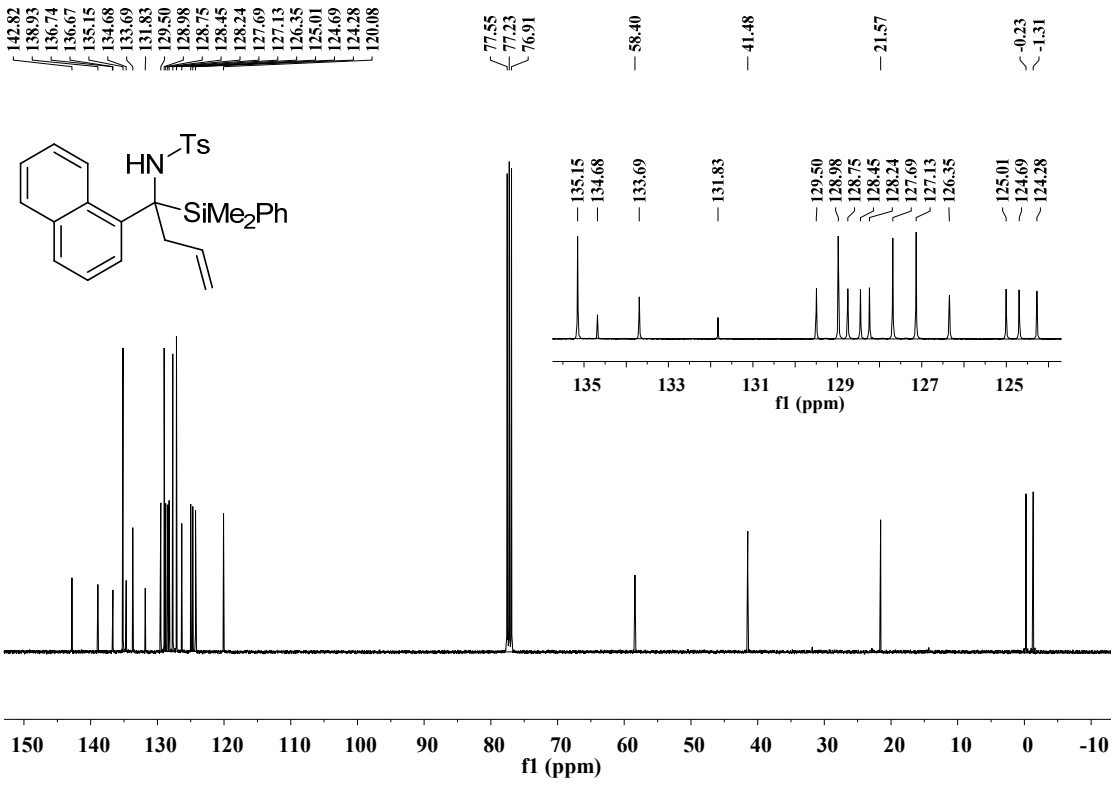
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6e**



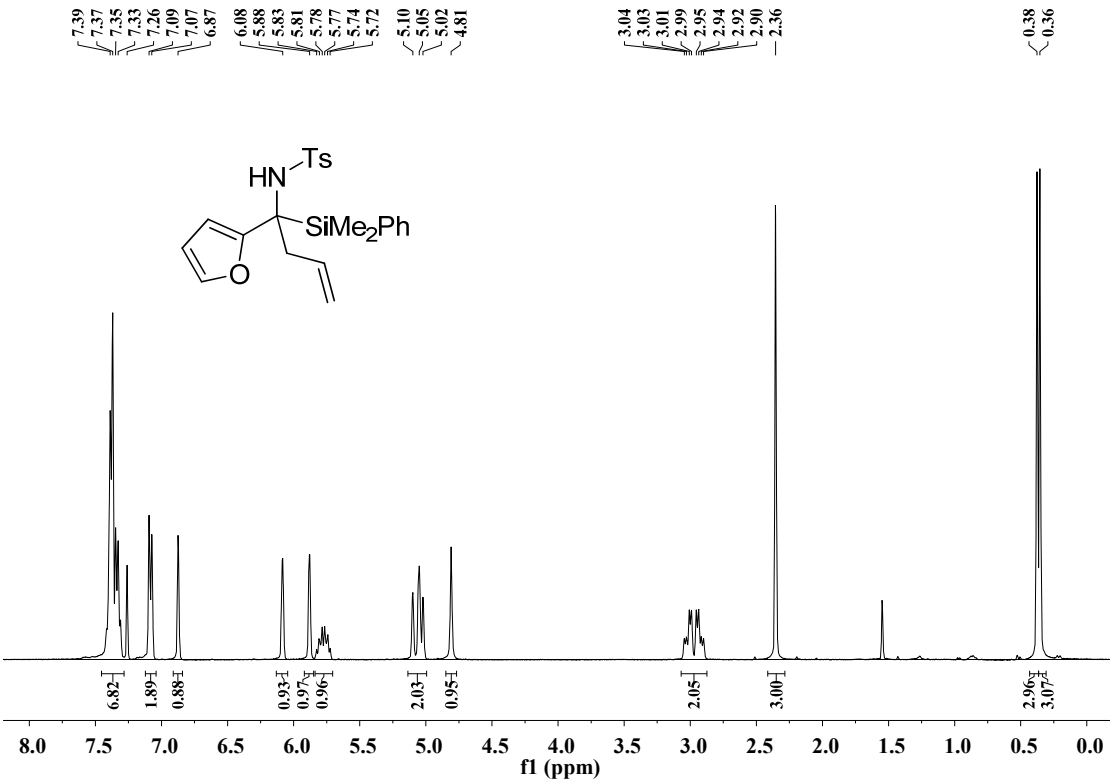
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6e**



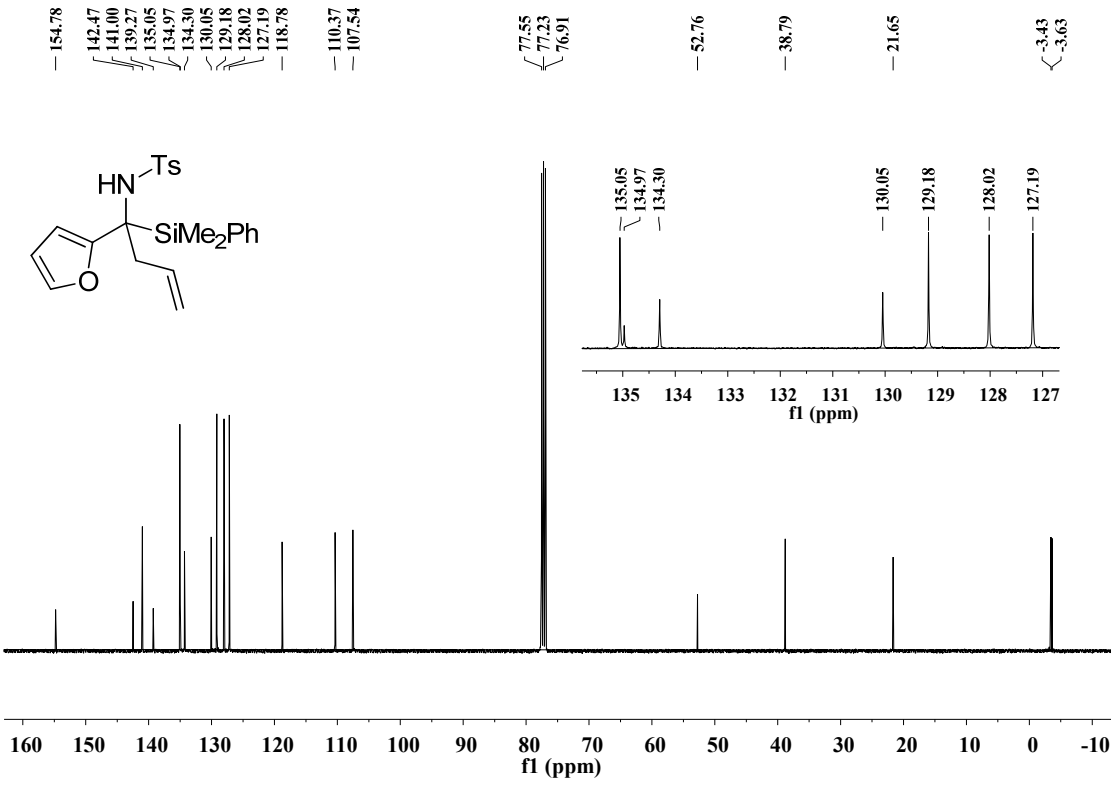
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6f**



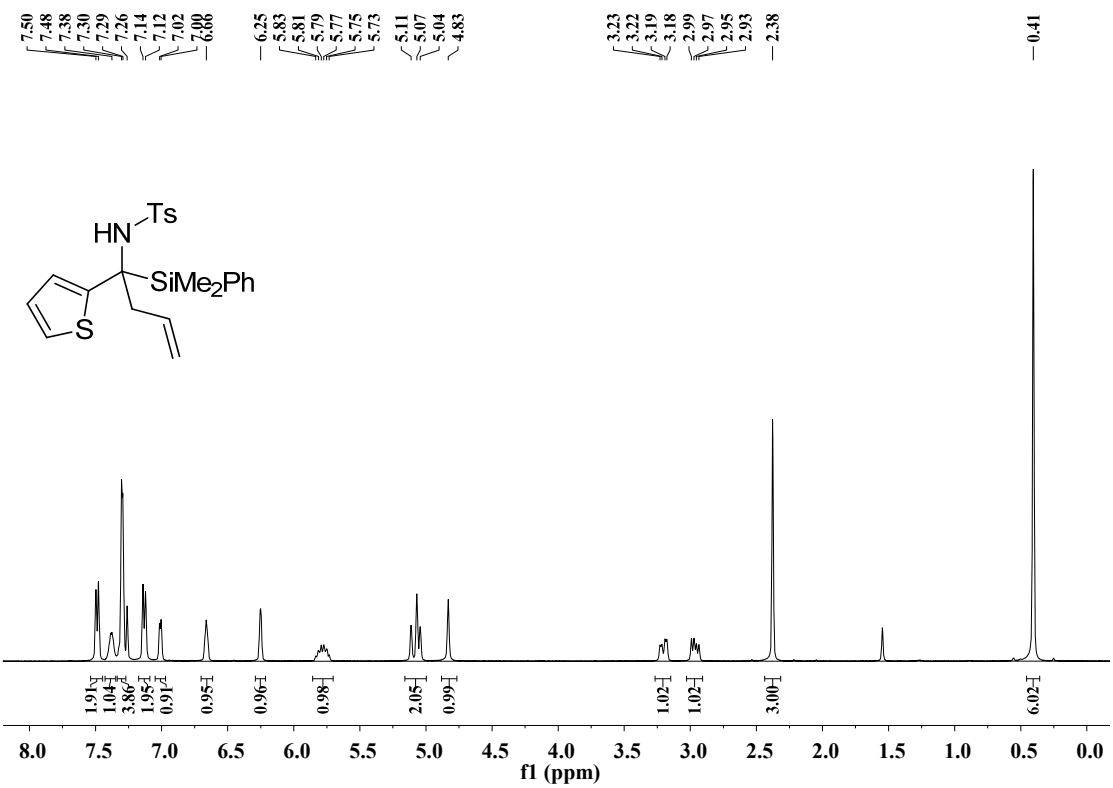
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6f**



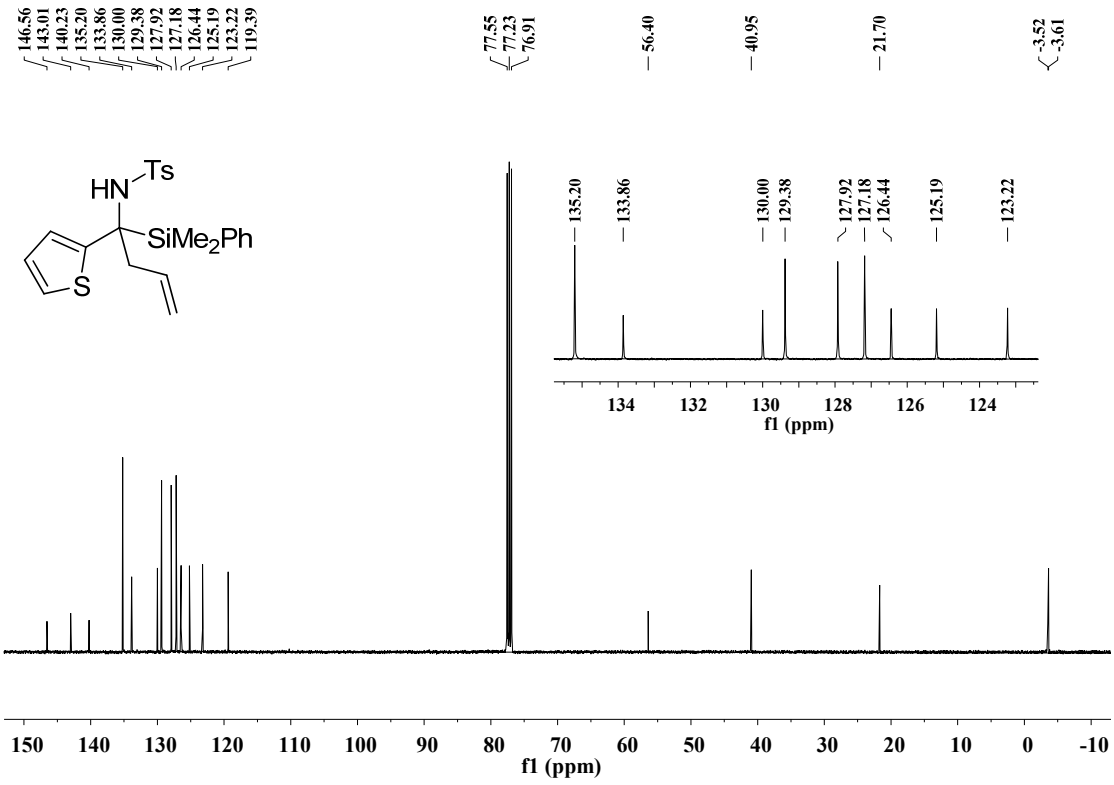
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6g**



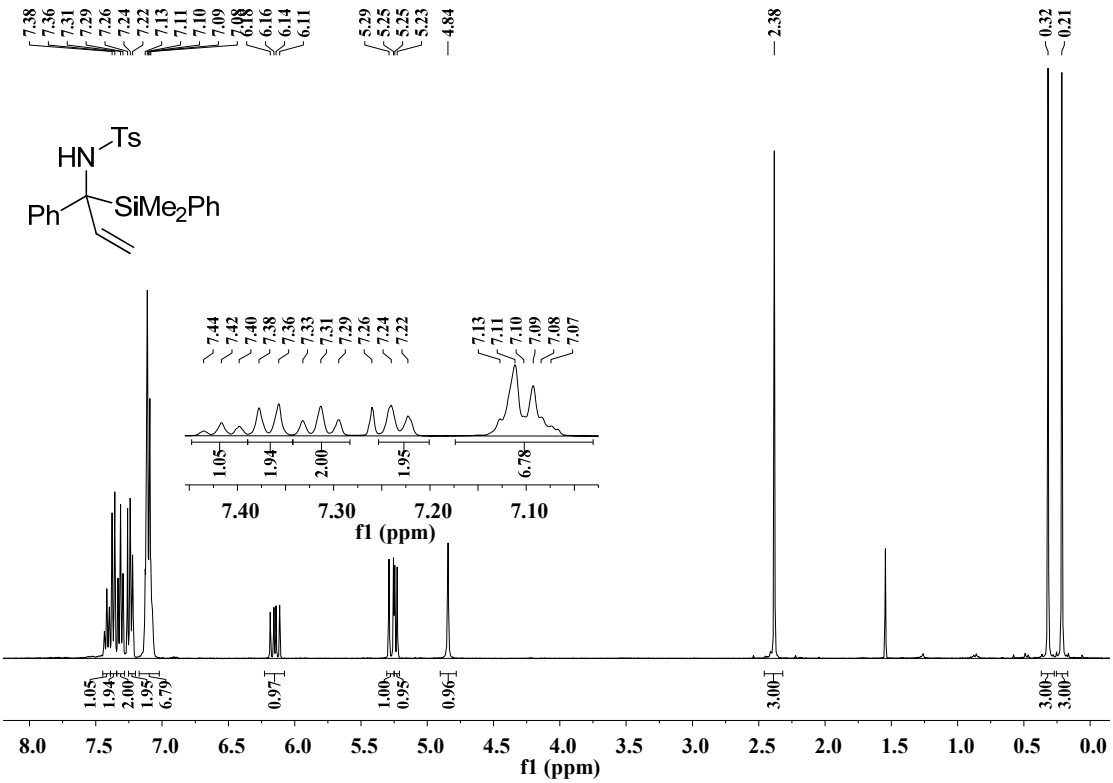
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6g**



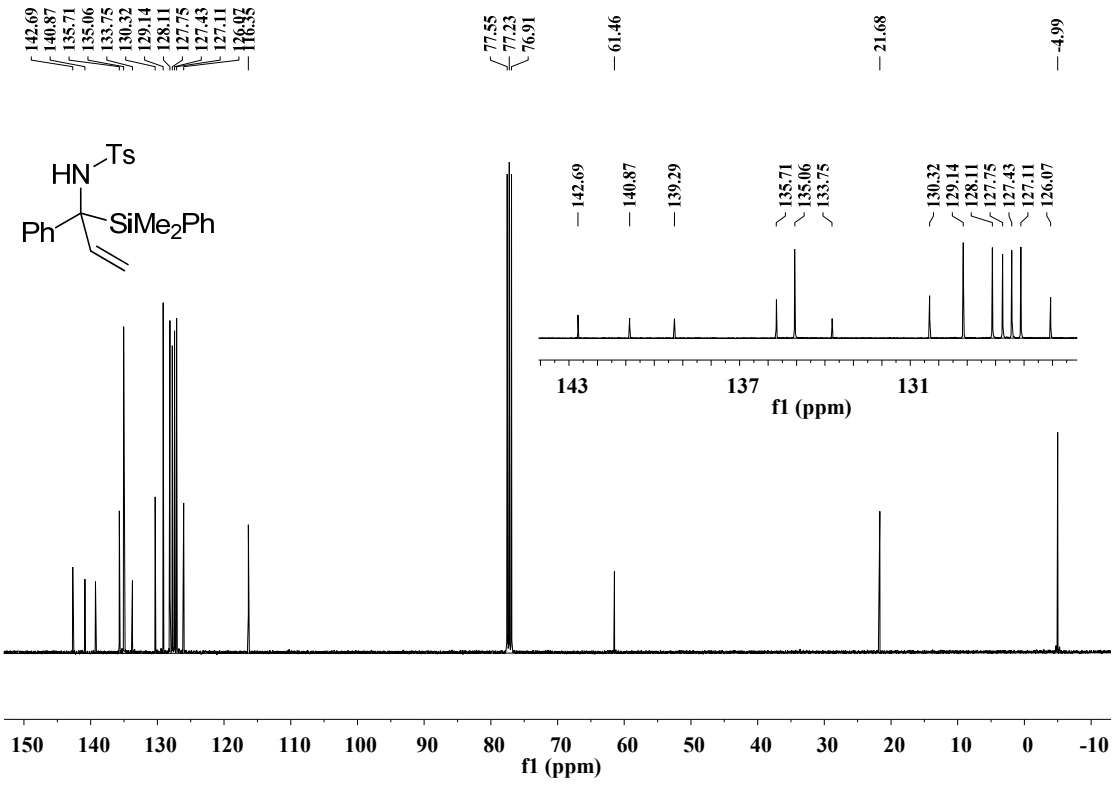
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6h**



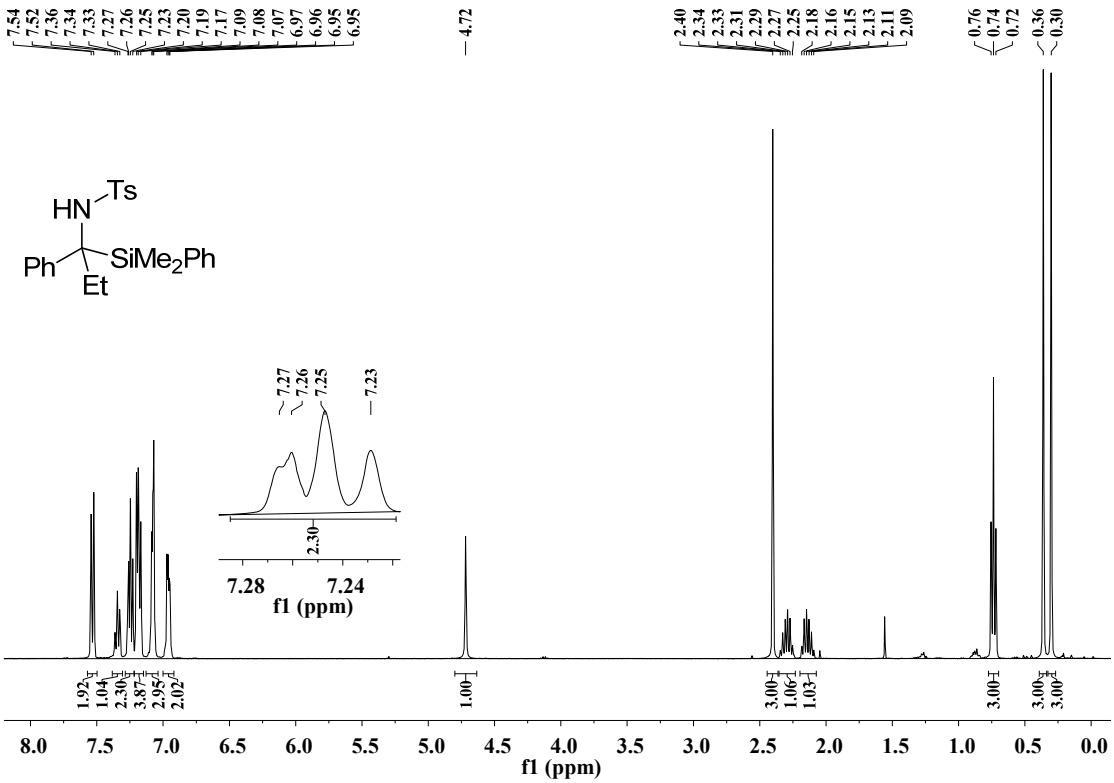
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6h**



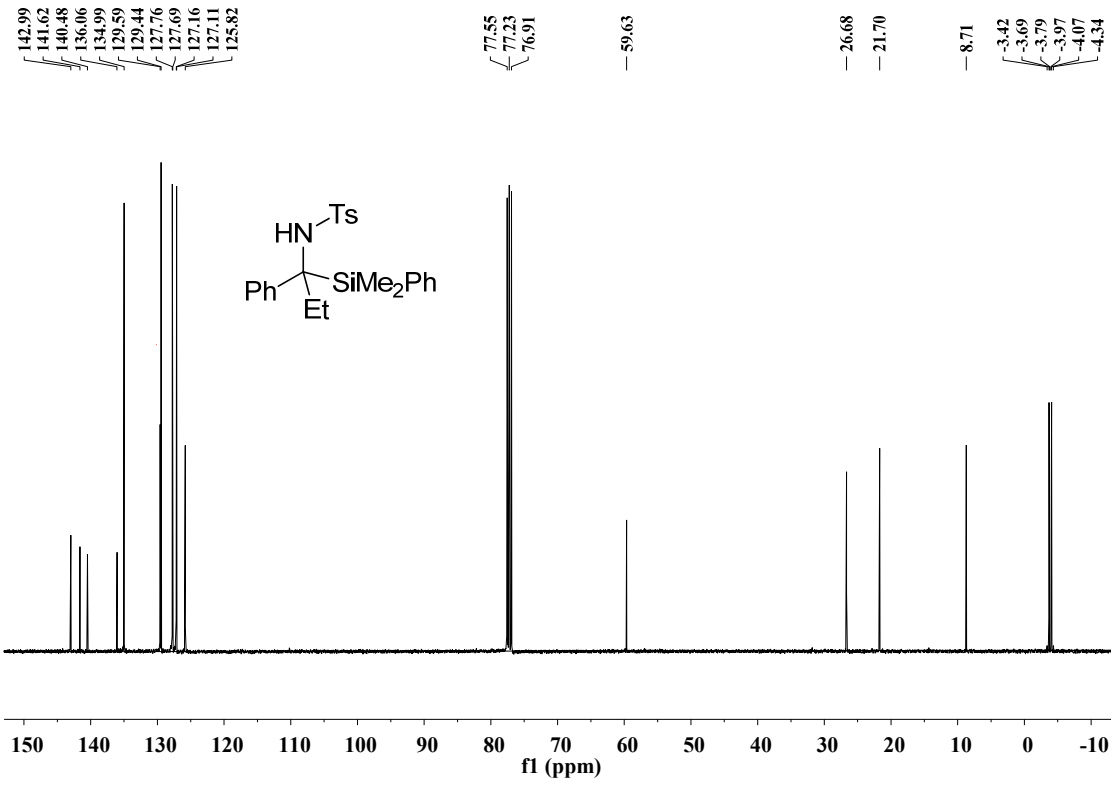
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6i**



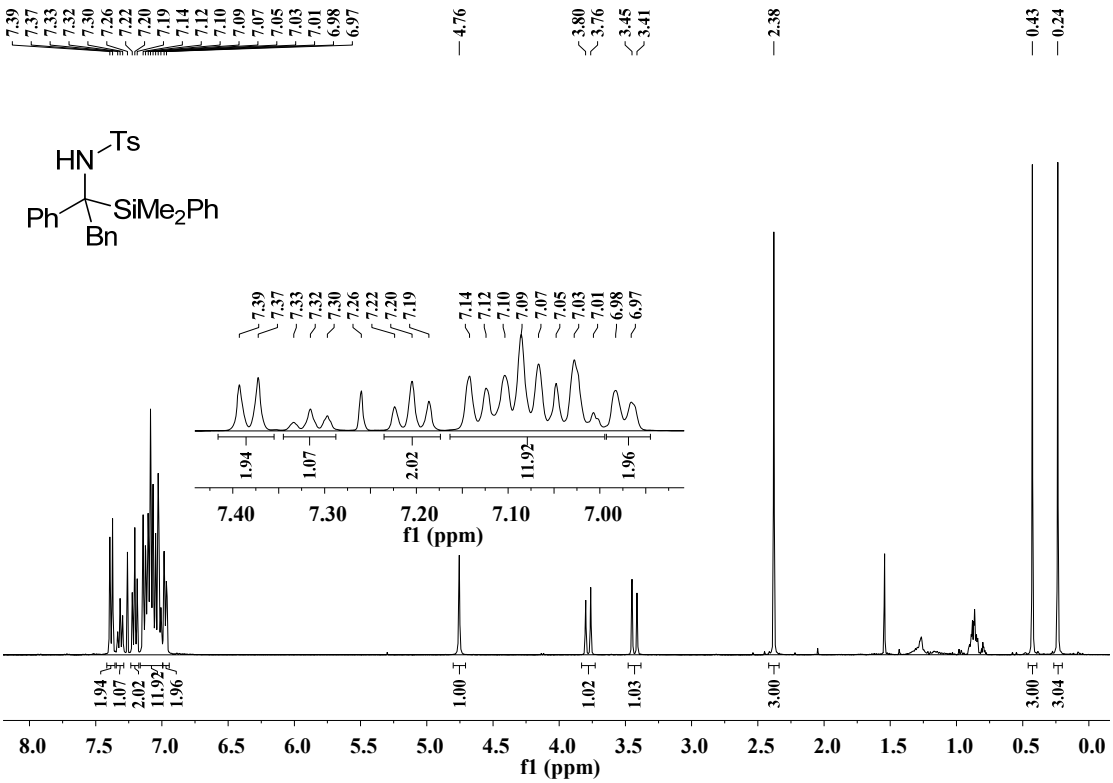
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6i**



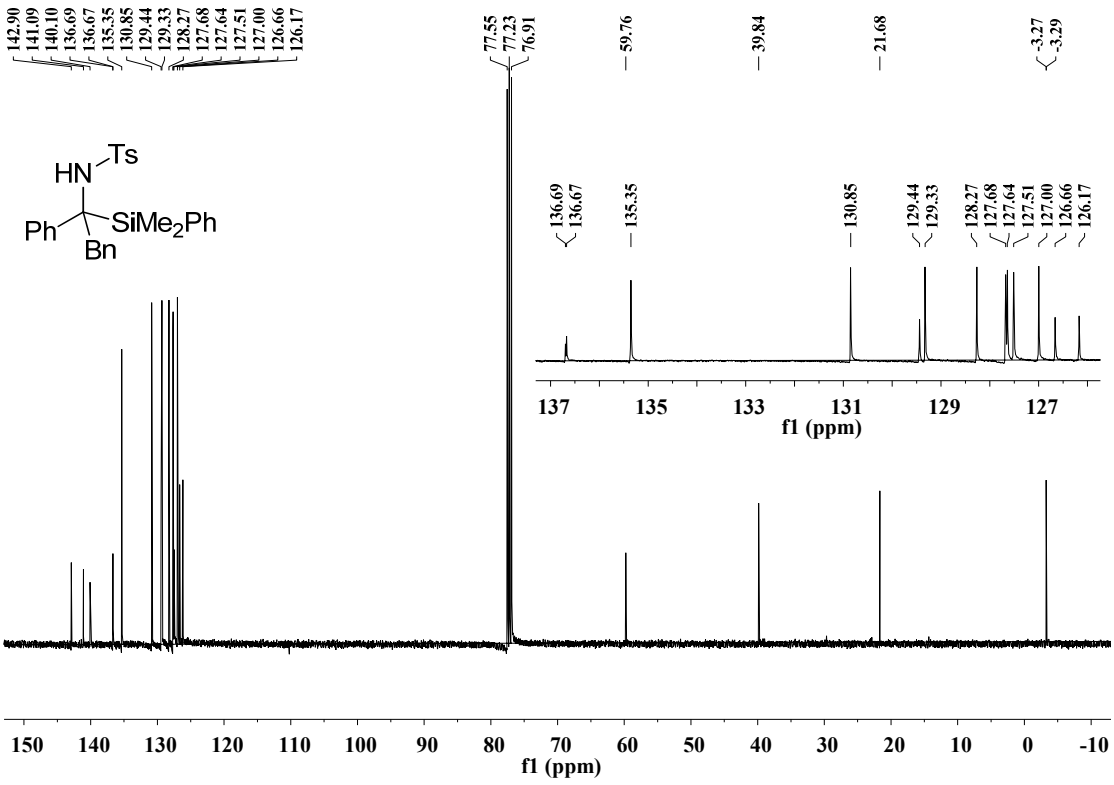
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6k**



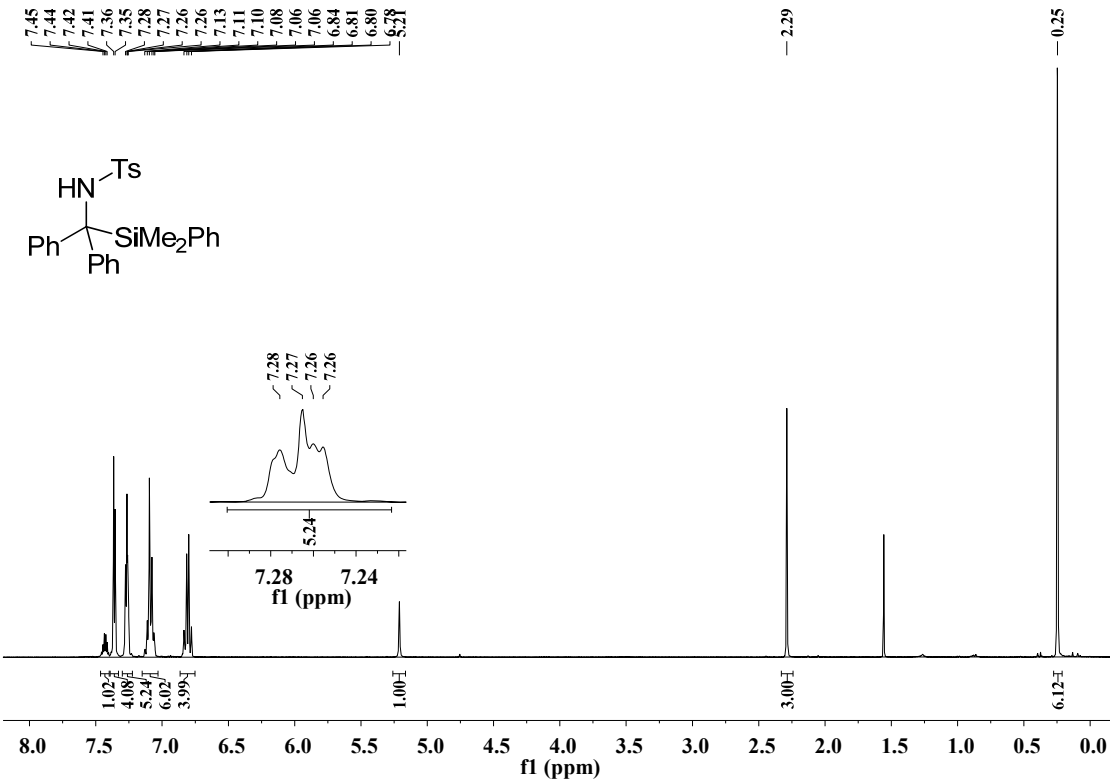
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6k**



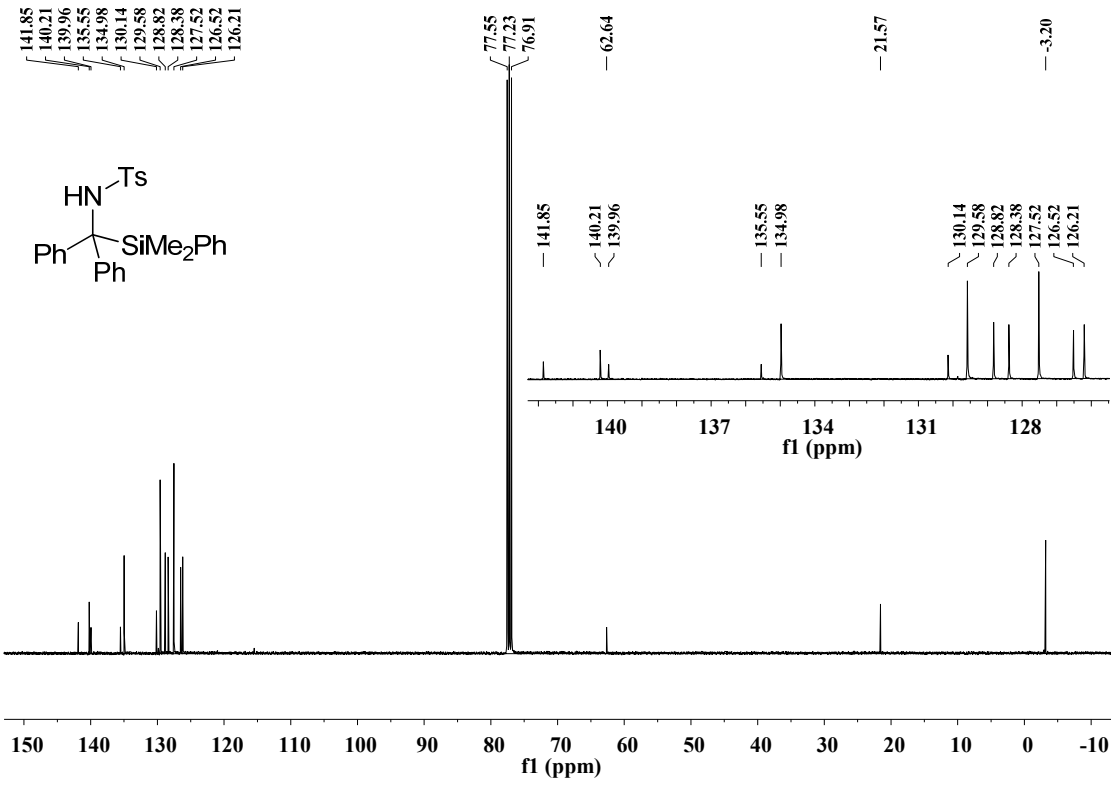
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6l**



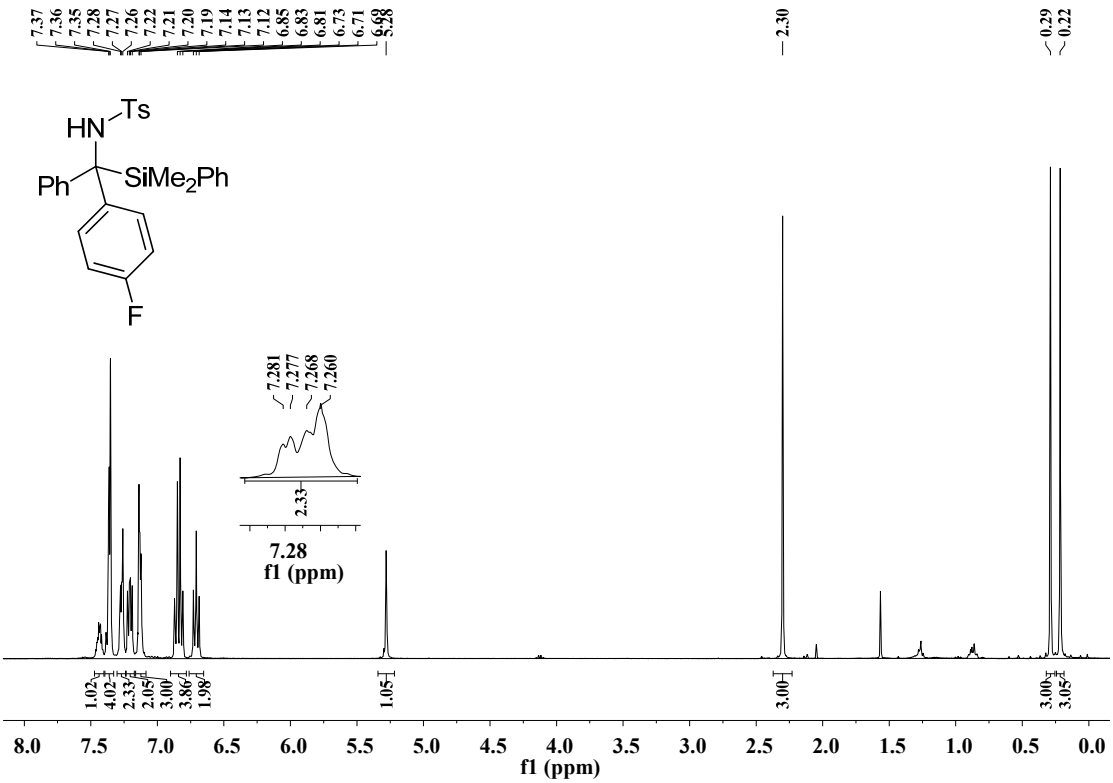
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6l**



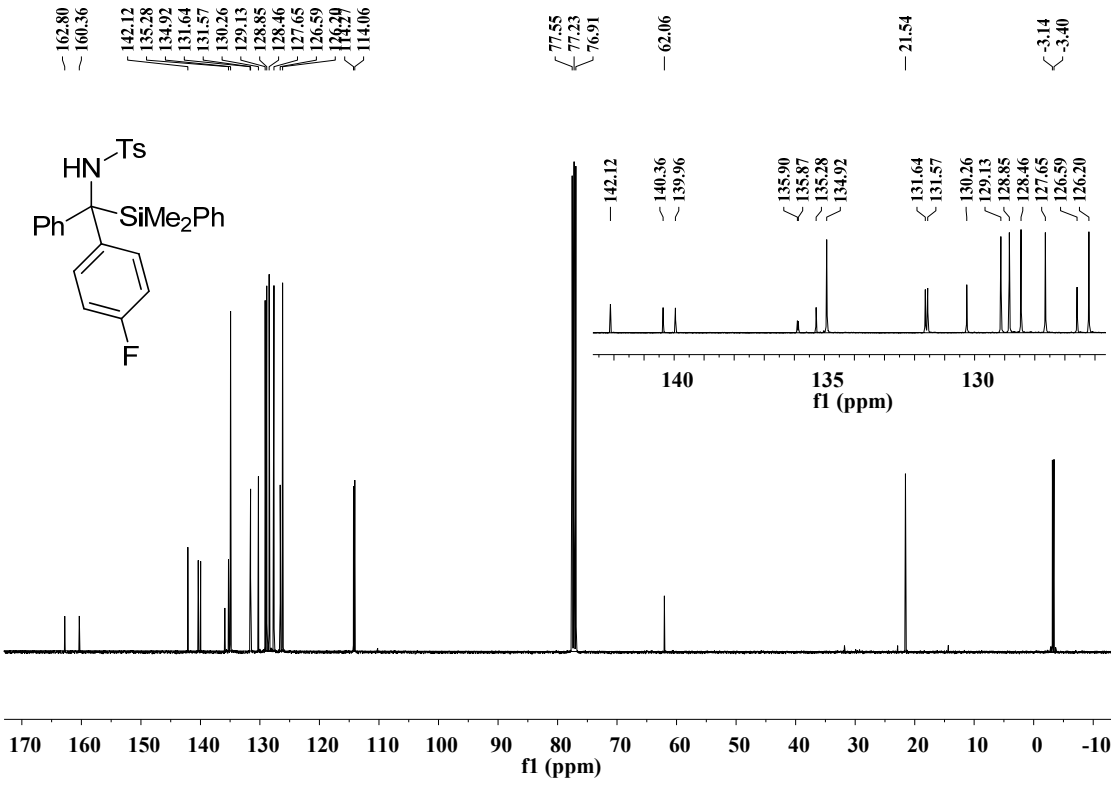
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6m**



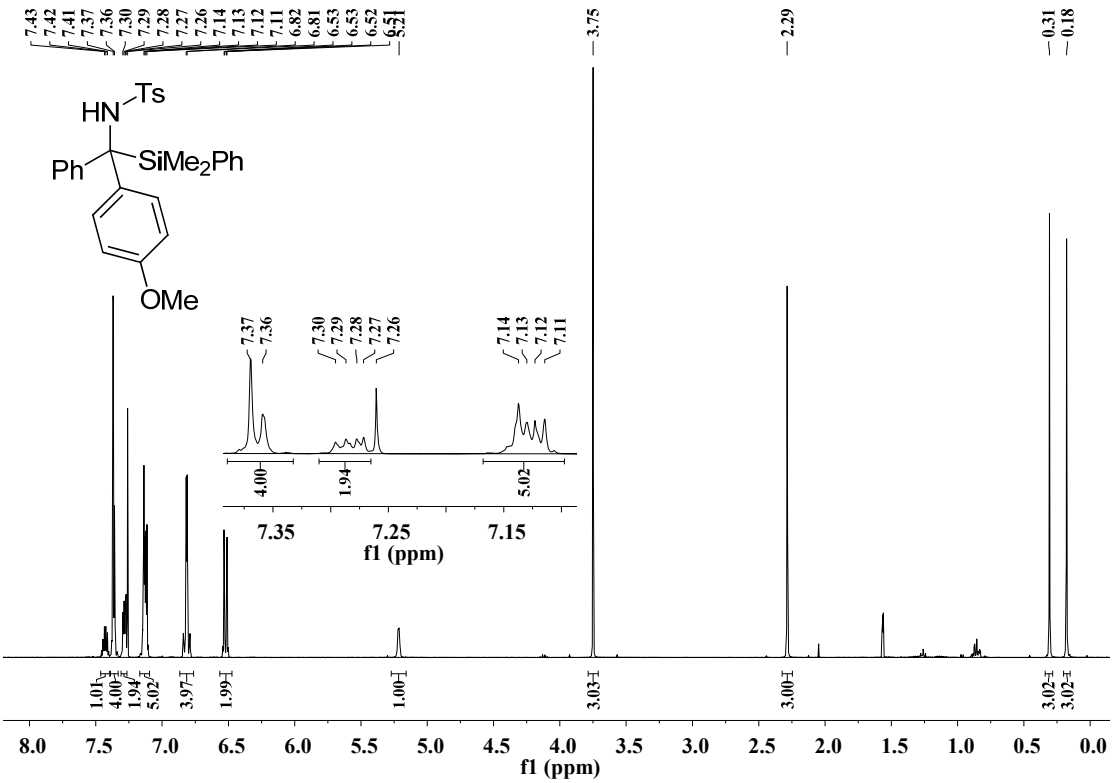
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6m**



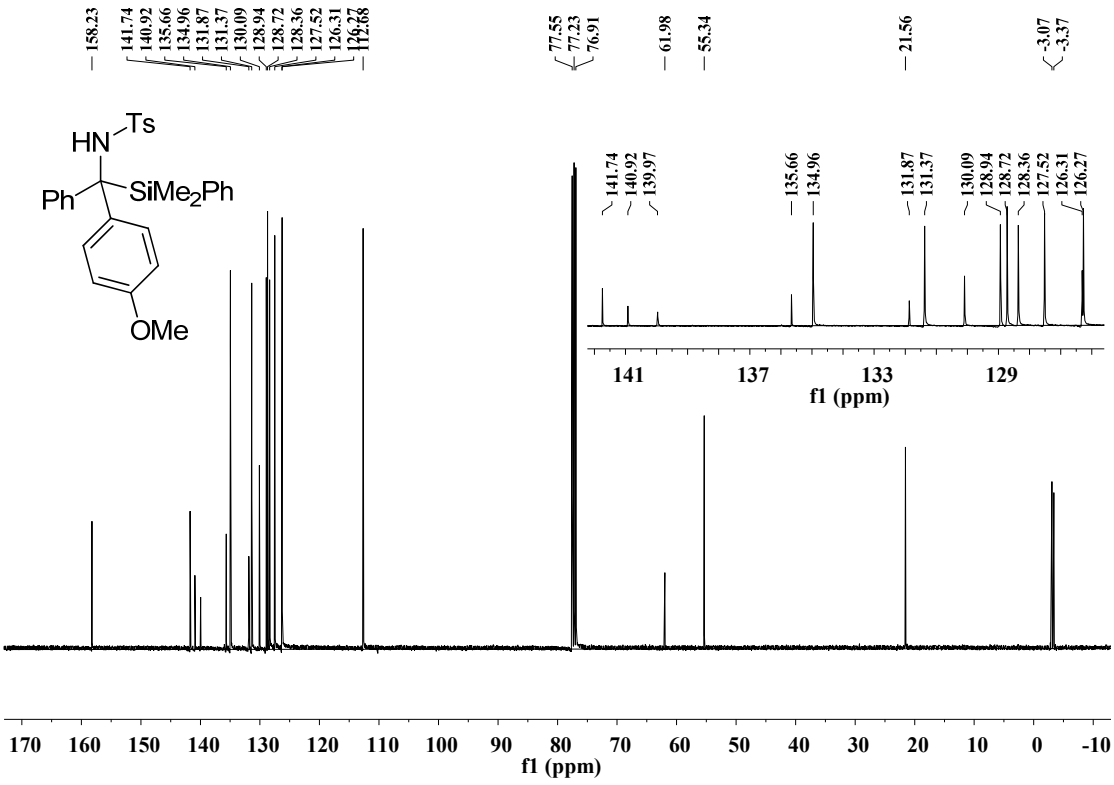
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6n**



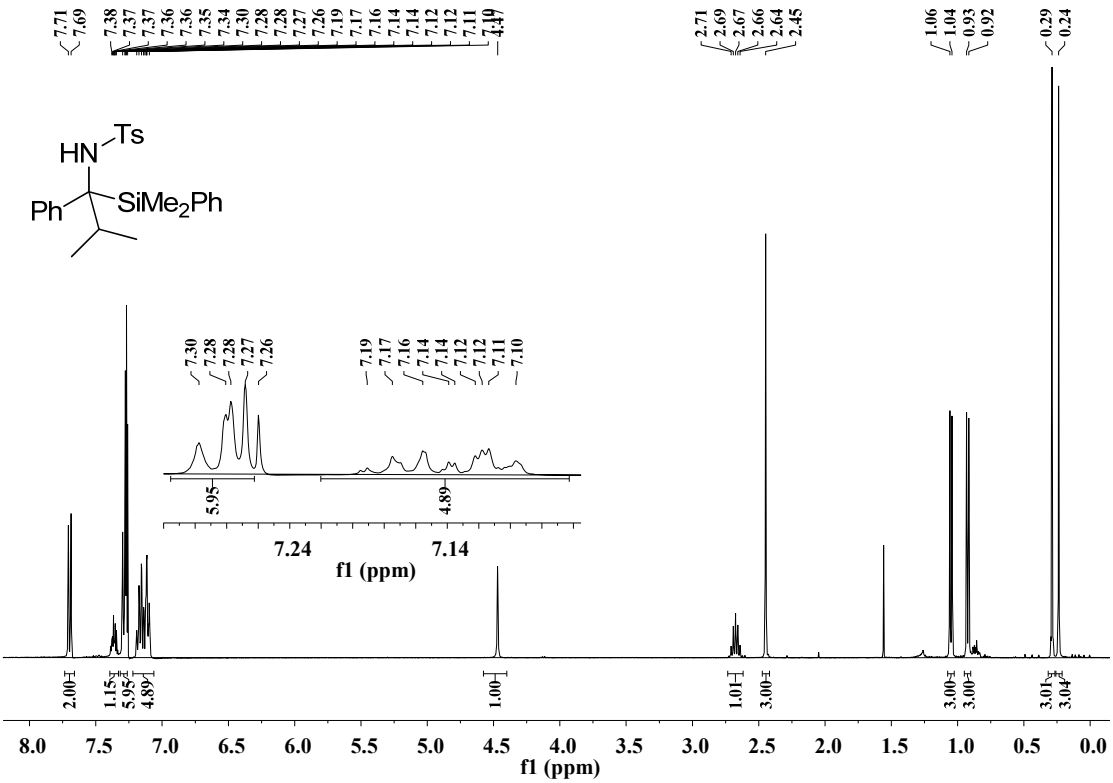
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6n**



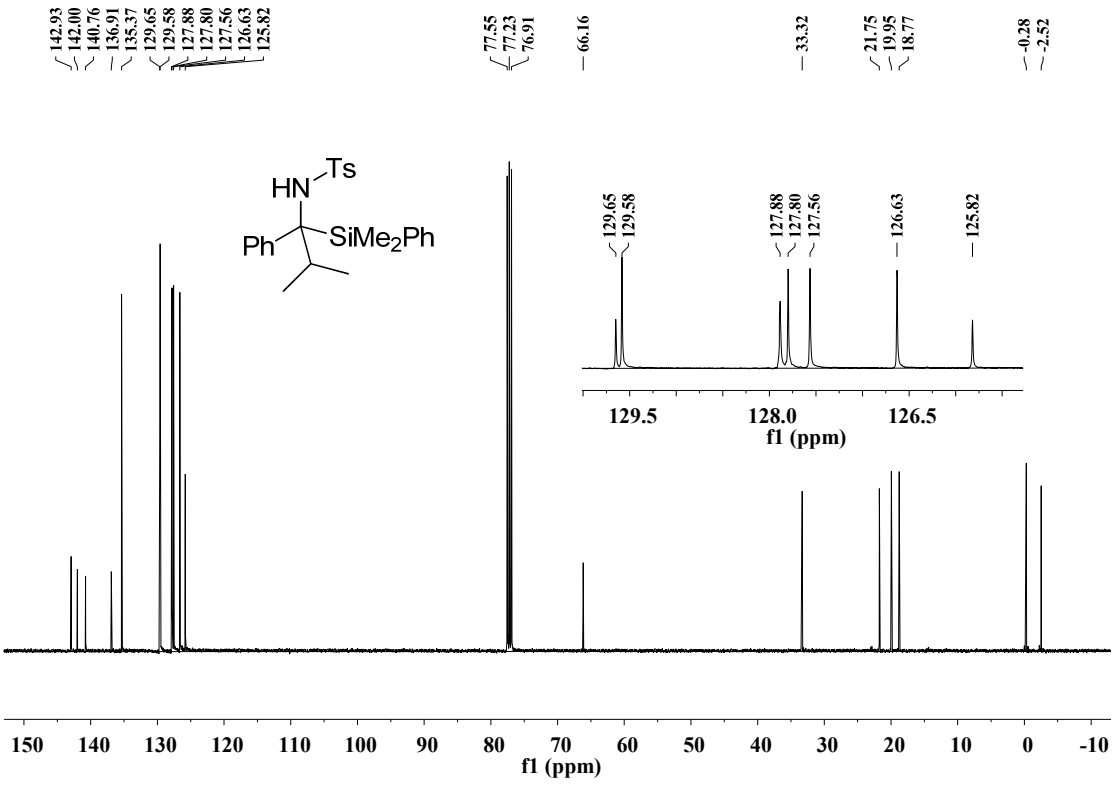
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6o**



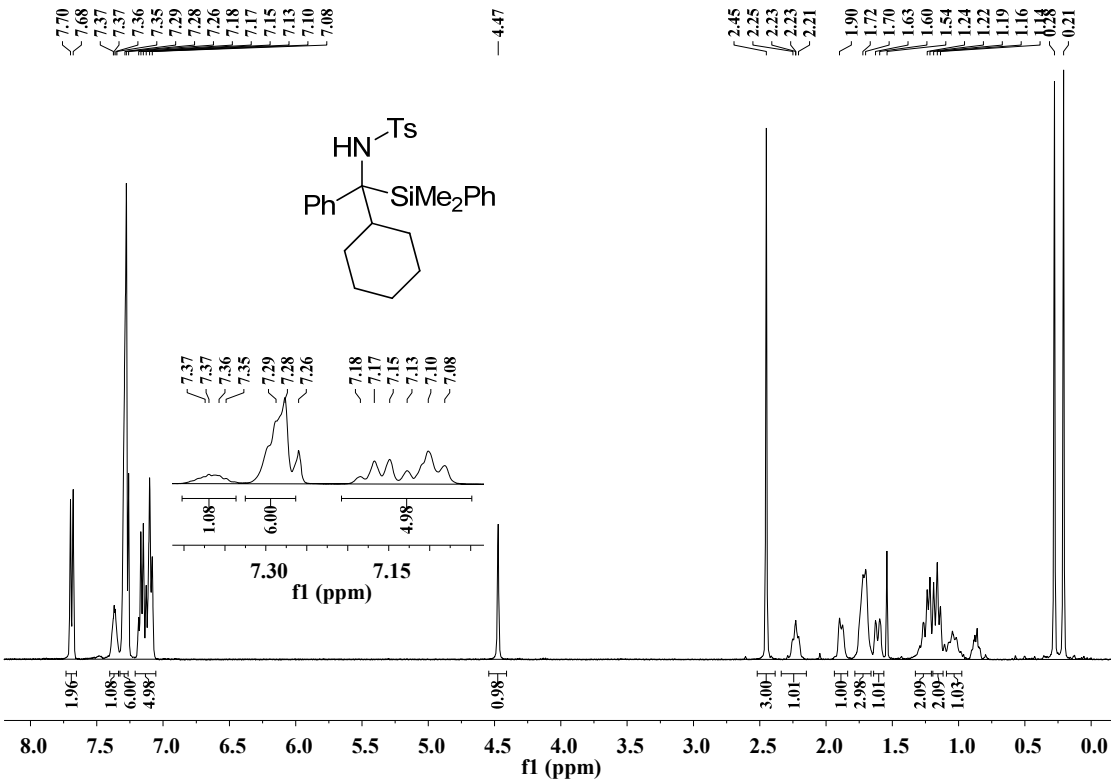
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6o**



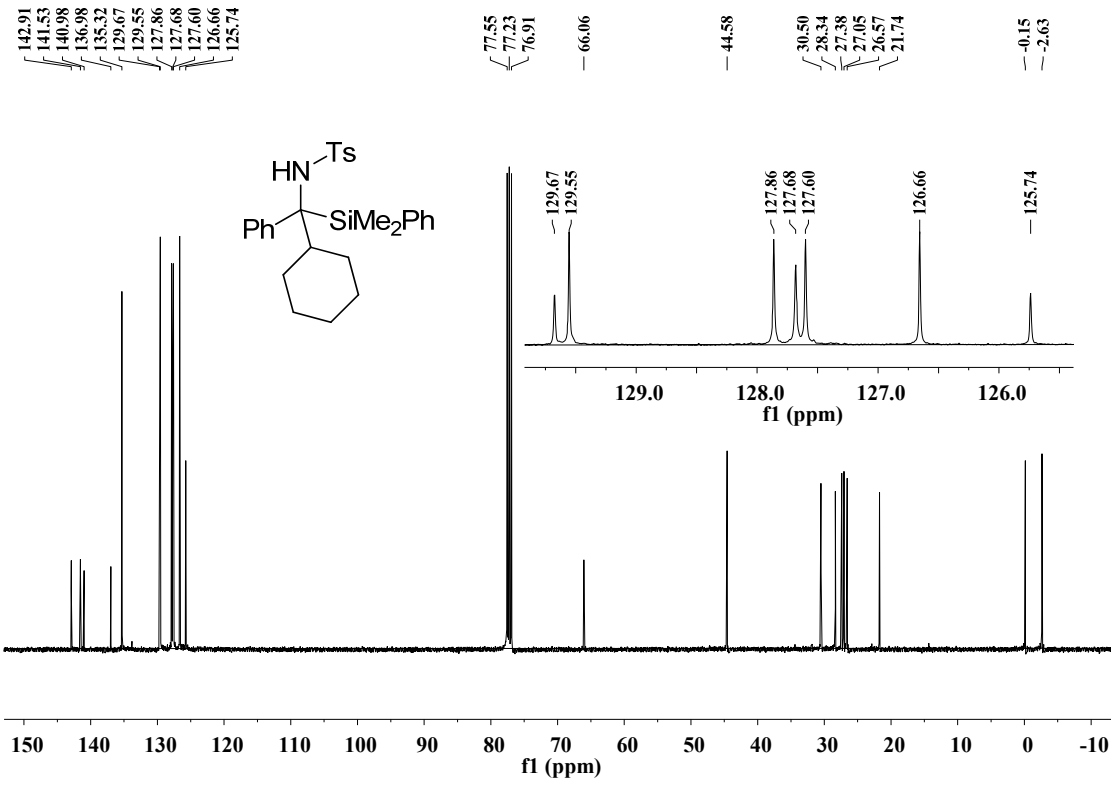
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6p**



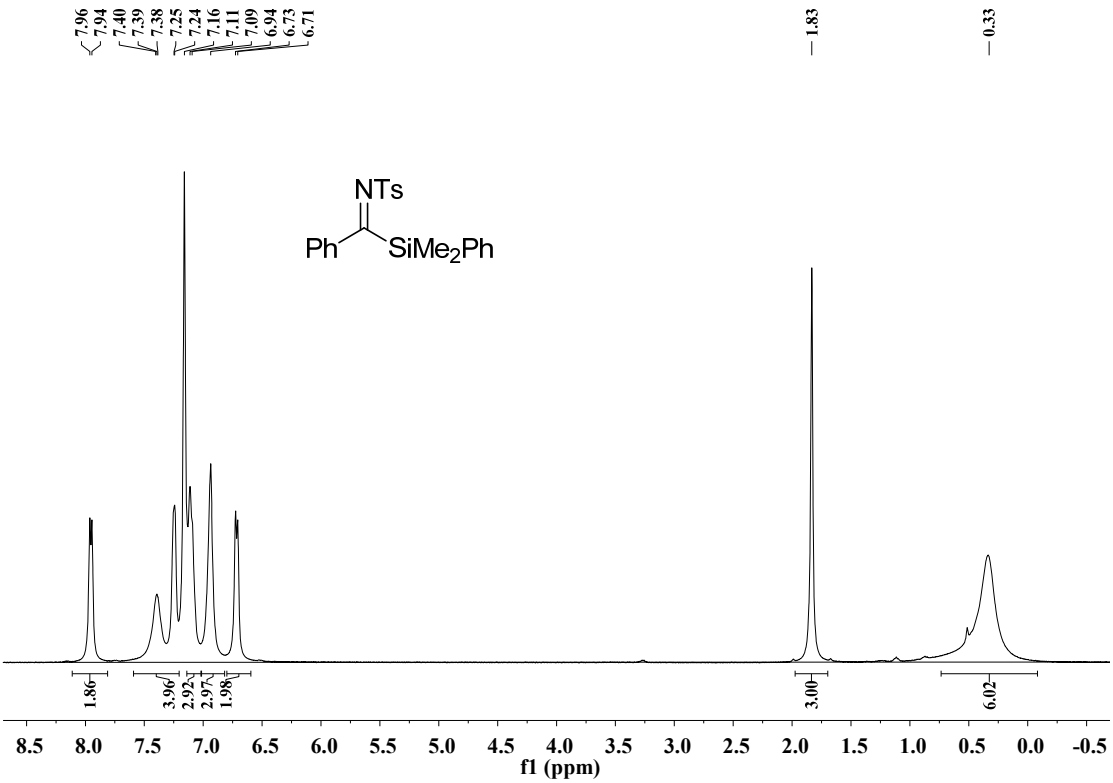
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6p**



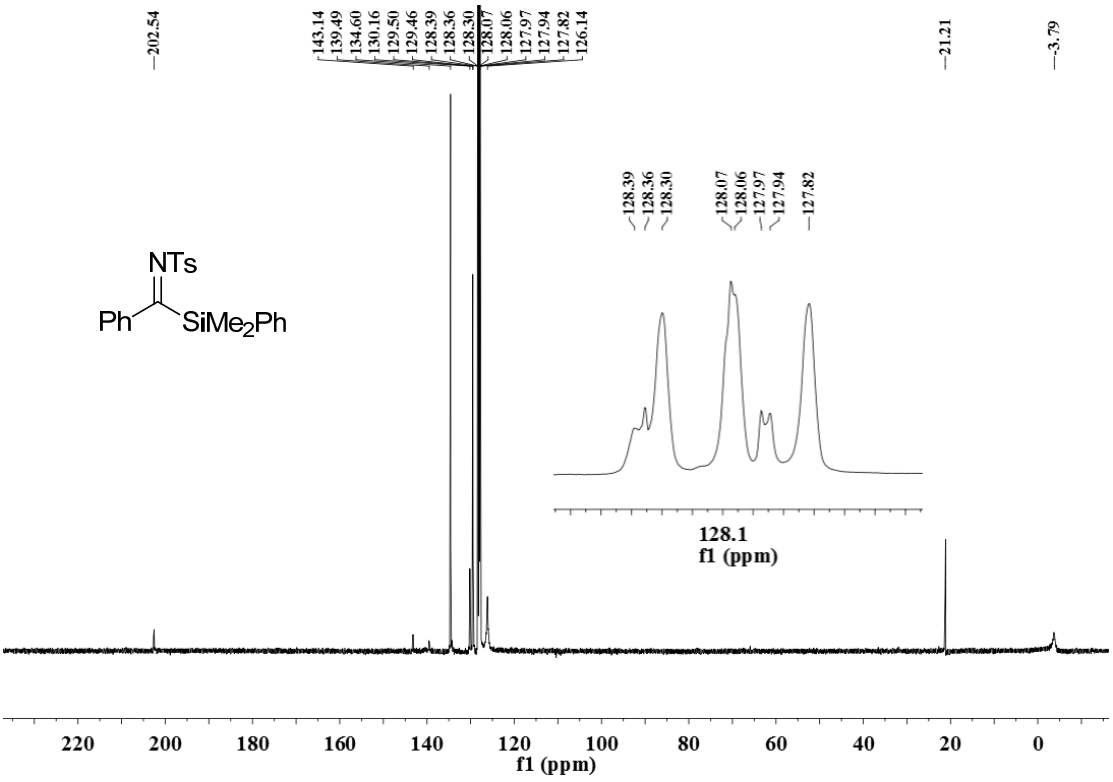
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **6q**



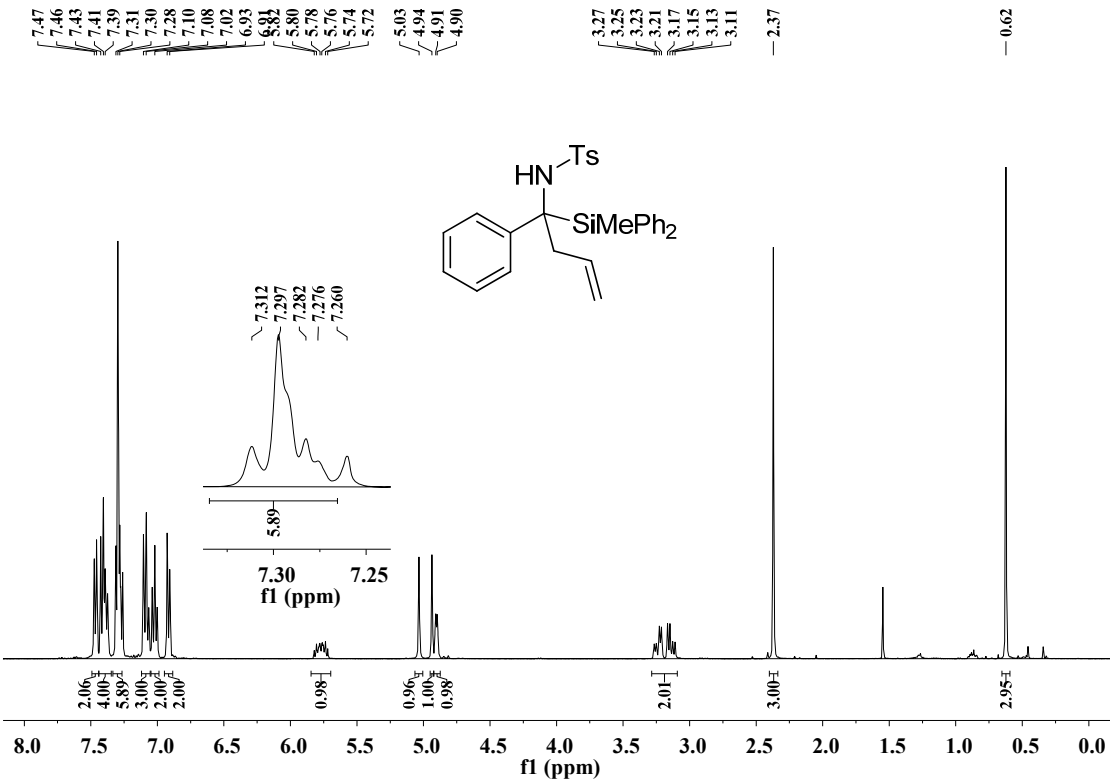
^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **6q**



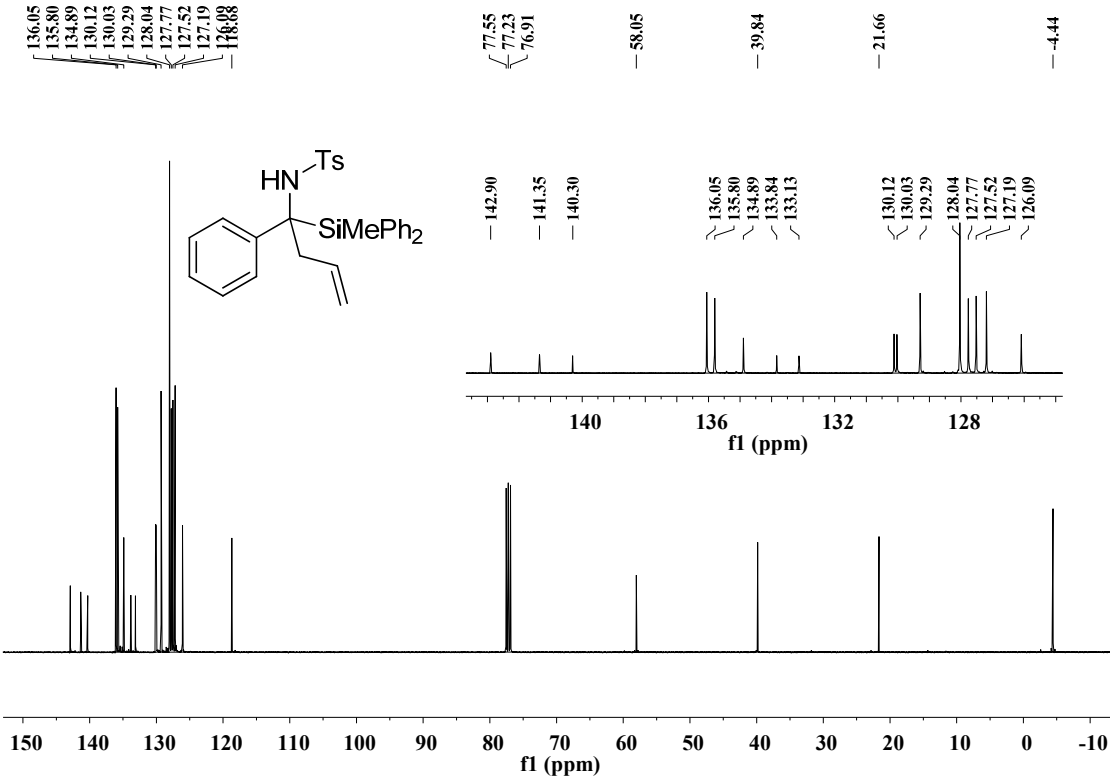
^{1}H NMR spectrum (C_6D_6, 400 MHz) of **7**



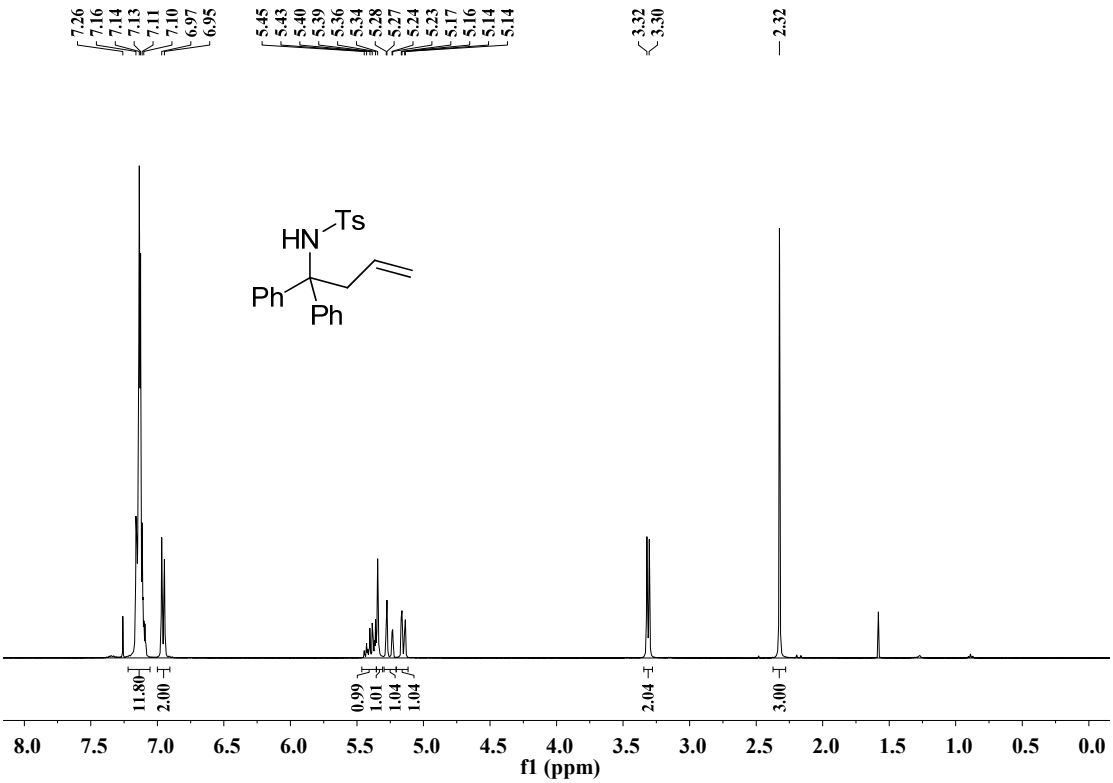
^{13}C NMR spectrum (C_6D_6, 100 MHz) of **7**



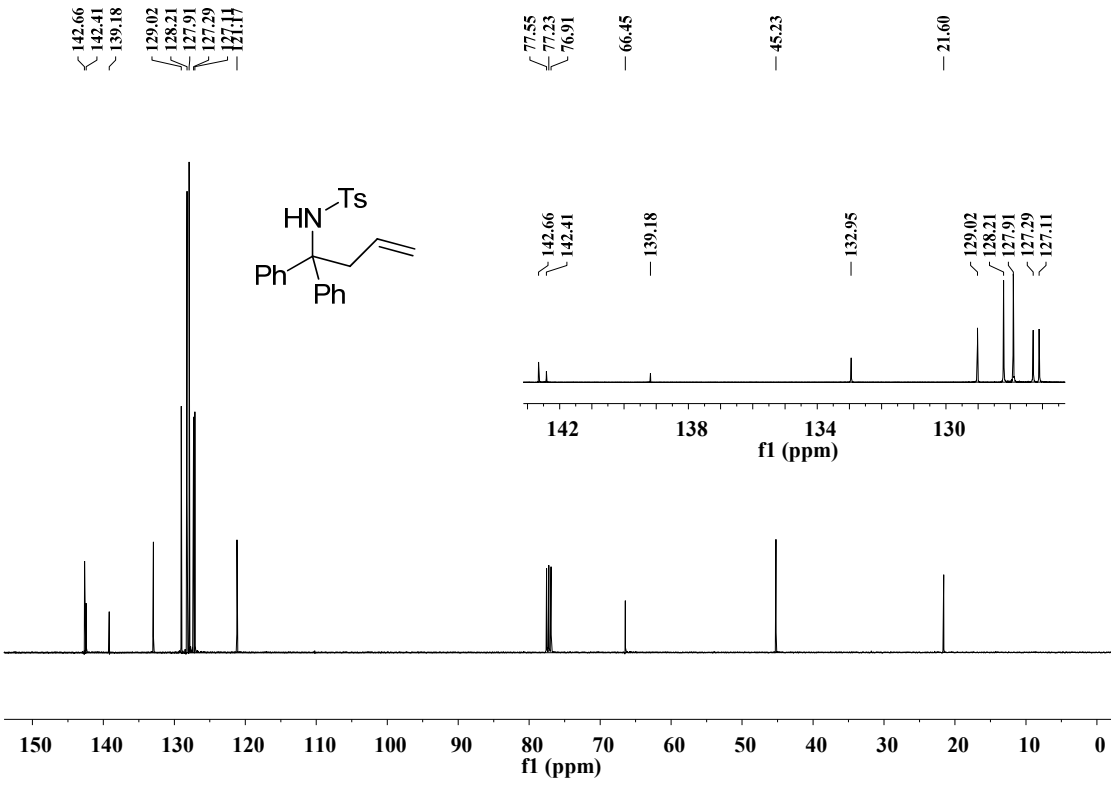
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **8**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **8**



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **9**



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of **9**