

Electronic supplementary information

A nickel-catalyzed silylation reaction of alkyl aryl sulfoxides with silylzinc reagents

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1. General information

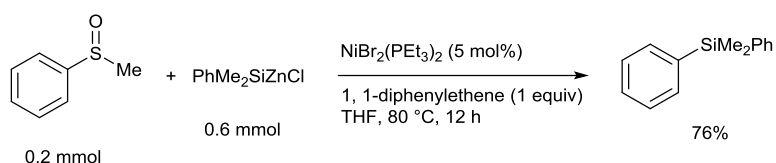
All reactions were performed under nitrogen atmosphere using standard Schlenk and vacuum line techniques. Tetrahydrofuran was purified by JC Meyer Phoenix Solvent Systems. 1,4-Dioxane were distilled over sodium and degassed prior to use. Dimethyl sulfoxide (DMSO) was dried over CaH₂, fractionally distilled under reduced pressure and degassed prior to use. Dichloromethane (DCM) was distilled over CaH₂ and degassed prior to use. CPME (extra dry) was purchased from Energy Chemical and degassed prior to use. ZnCl₂ were purchased from commercial vendors and dried under vacuum at 140 °C for 12 h prior to use. Other chemicals were obtained from commercial vendors and used as received. Silylzinc reagents were prepared according to reported procedure.¹ The concentration of the silylzinc solution was titrated using Knochel's method.² Aryl sulfoxides were synthesized according to the literature procedures.³⁻⁶ NMR spectra were recorded on a Bruker AV400 spectrometer at 25 °C. The chemical shifts of the ¹H NMR spectra were referenced to TMS and the chemical shifts of the ¹³C NMR spectra were referenced to internal solvent resonances. High-resolution mass spectra (HR-MS) were acquired on a Thermo Fisher LTQ Orbitrap XL mass spectrometer.

2. General procedure for the nickel-catalyzed silylations of aryl sulfoxides

NiBr₂(PEt₃)₂ (4.5 mg, 5 mol %), sulfoxides (0.2 mmol) and THF (1.5 cm³) were charged to a Schlenk tube under nitrogen. Then, a solution of silicon zinc reagent (1.5 cm³, 0.4 M solution in THF, 0.6 mmol) was added. The resultant mixture was stirred at 80 °C for 12 h and then cooled to room temperature. A 10% aqueous solution of NH₄Cl (10 cm³) was added. The resultant mixture was diluted with EtOAc (3 × 5 cm³). The combined organic phases were dried over anhydrous Na₂SO₄, concentrated by rotary evaporation, and purified by column chromatography (silica gel).

3. Mechanistic studies

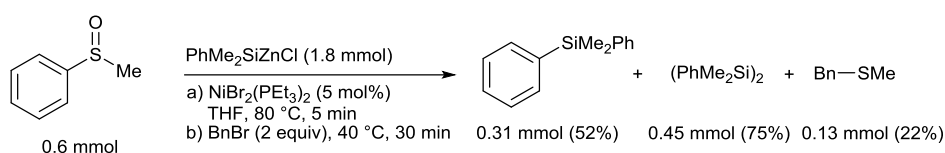
(1) Effect of 1,1-diphenylethene additive



NiBr₂(PEt₃)₂ (4.5 mg, 5 mol %), PhS(O)Me (28 mg, 0.2 mmol) and THF (1.5 cm³) were charged to a Schlenk tube under nitrogen. Then PhMe₂SiZnCl solution (1.5 cm³, 0.4 M solution in THF, 0.6 mmol) and 1,1-diphenylethene (36 mg, 0.2 mmol) were successively

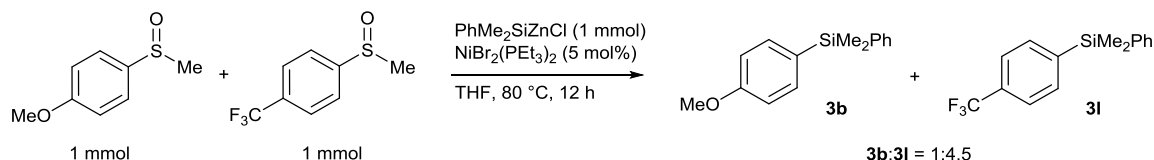
added to the Schlenk tube. The mixture was stirred at 80 °C for 12 h and then cooled to room temperature. A 10% aqueous solution of NH₄Cl (10 cm³) was added. The resultant mixture was extracted with EtOAc (5 cm³ × 3). The combined organic phases were dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The residue was dissolved in CDCl₃ and its ¹H NMR spectrum was determined. The yield was obtained on the basis of the ¹H NMR spectrum using C₂H₂Cl₄ as an internal standard.

(2) Methanesulfenate anion trap experiment



Ni(PEt₃)₂Br₂ (13.5 mg, 5 mol%), PhS(O)Me (84.1 mg, 0.6 mmol) and THF (1.5 cm³) were successively charged to a Schlenk tube under nitrogen. To the stirred mixture a solution of PhMe₂SiZnCl (4.5 cm³, 0.4 M solution in THF, 1.8 mmol) was added at room temperature. The mixture was stirred at 80 °C for 5 min. and then cooled to room temperature. Benzyl bromide (205 mg, 1.2 mmol) was added. The resulting mixture was stirred at 40 °C for 30 min. Saturated aqueous solution of NH₄Cl (10 cm³) was added and the mixture was extracted with EtOAc (10 cm³ × 3). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was dissolved in CDCl₃ and its ¹H NMR spectrum was determined. The yields were obtained on the basis of the ¹H NMR spectrum using C₂H₂Cl₄ as an internal standard.

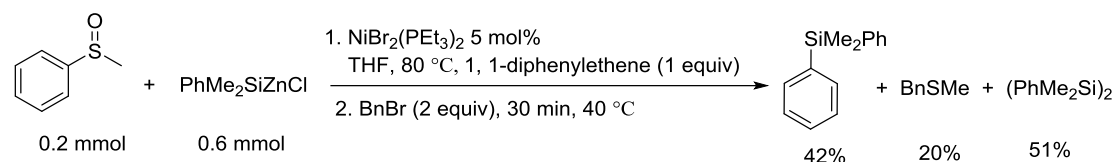
(3) Intermolecular competition experiment



NiBr₂(PEt₃)₂ (22.5 mg, 5 mol %), *p*-MeOC₆H₄S(O)Me (170.2 mg, 1 mmol), *p*-CF₃C₆H₄-S(O)Me (208.2 mg, 1 mmol), and THF (1.5 cm³) were charged to a Schlenk tube under nitrogen. A solution of PhMe₂SiZnCl (2.5 cm³, 0.4 M solution in THF, 1 mmol) was added. The mixture was stirred at 80 °C for 12 h and then cooled to room temperature. A 10% aqueous solution of NH₄Cl (10 cm³) was added. The resultant mixture was extracted with EtOAc (10 cm³ × 3). The combined organic phases were dried over anhydrous Na₂SO₄,

concentrated by rotary evaporation, and purified by column chromatography (silica gel) to give a mixture of **3b** and **3l**. The ratio of **3b** and **3l** was determined by ¹H NMR spectrum of the mixture.

(4) Methanesulfenate anion trap experiment in the presence of 1,1-diphenylethene

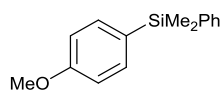


NiBr₂(PEt₃)₂ (4.5 mg, 5 mol %), PhS(O)Me (28 mg, 0.2 mmol) and THF (1.5 cm³) were charged to a Schlenk tube under nitrogen. A solution of PhMe₂SiZnCl (1.5 cm³, 0.4 M solution in THF, 0.6 mmol) and 1,1-diphenylethene (36 mg, 0.2 mmol) were successively added. The mixture was stirred at 80 °C for 5 min. and then cooled to room temperature. Benzyl bromide (68.4 mg, 0.4 mmol) was added, and the resulting mixture was stirred at 40 °C for 30 min. The reaction mixture was added saturated aqueous solution of NH₄Cl (10 cm³) and then extracted with EtOAc (10 cm³ × 3). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was dissolved in CDCl₃ and its ¹H NMR spectrum was determined. The yields were obtained on the basis of the ¹H NMR spectrum using C₂H₂Cl₄ as an internal standard.

4. Characterization data for the silylation products

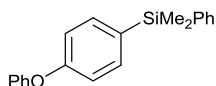
Pure **3a** cannot be obtained in this transformation. A mixture of **3a** and (PhMe₂Si)₂ was obtained.

1. (4-methoxyphenyl)dimethyl(phenyl)silane (**3b**).⁷



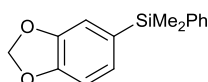
Colorless oil (33 mg, 68%). ¹H NMR (500 MHz, CDCl₃): δ 7.52–7.47 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.36–7.29 (m, 3H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 0.51 (s, 6H). ¹³C NMR (126 MHz, CDCl₃): δ 160.6, 138.8, 135.8, 134.3, 129.1, 127.9, 113.7, 55.2, –2.1.

2. dimethyl(4-phenoxyphenyl)(phenyl)silane (**3c**).⁷



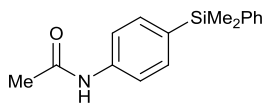
Colorless oil (43 mg, 70%). ^1H NMR (400 MHz, CDCl_3): δ 7.56–7.50 (m, 2H), 7.47 (d, $J = 8.5$ Hz, 2H), 7.39–7.29 (m, 5H), 7.11 (t, $J = 7.4$ Hz, 1H), 7.06–7.00 (m, 2H), 6.98 (d, $J = 8.5$ Hz, 2H), 0.54 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 158.6, 156.8, 138.5, 135.9, 134.3, 132.2, 129.9, 129.3, 128.0, 123.7, 119.5, 118.1, –2.1.

3. benzo[*d*][1,3]dioxol-5-yl(dimethyl(phenyl)silyl)silane (**3d**).⁷



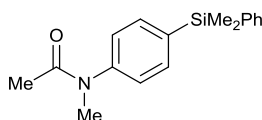
Colorless oil (24 mg, 47%). ^1H NMR (400 MHz, CDCl_3): δ 7.54–7.48 (m, 2H), 7.38–7.32 (m, 3H), 7.00 (dd, $J = 7.6, 1.0$ Hz, 1H), 6.95 (s, 1H), 6.84 (d, $J = 7.6$ Hz, 1H), 5.93 (s, 2H), 0.52 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 148.6, 147.5, 138.4, 134.2, 131.4, 129.3, 128.4, 128.0, 113.6, 108.7, 100.7, –2.1.

4. N-(4-(dimethyl(phenyl)silyl)phenyl)acetamide (**3e**).⁸



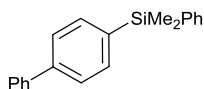
White solid (39 mg, 73%). ^1H NMR (500 MHz, CDCl_3): δ 7.55 (b, 1H), 7.52–7.43 (m, 4H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.38–7.30 (m, 3H), 2.15 (s, 3H), 0.52 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 168.7, 138.8, 138.3, 135.1, 134.2, 133.8, 129.2, 127.9, 119.3, 24.7, –2.2.

5. N-(4-(dimethyl(phenyl)silyl)phenyl)-*N*-methylacetamide (**3f**).⁸



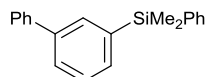
White solid (42 mg, 74%). ^1H NMR (500 MHz, CDCl_3): δ 7.58–7.51 (m, 4H), 7.42–7.35 (m, 3H), 7.16 (d, $J = 7.9$ Hz, 2H), 3.26 (s, 3H), 1.88 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 170.7, 145.3, 138.4, 137.7, 135.7, 134.2, 129.5, 128.1, 126.5, 37.2, 22.6, –2.3.

6. [1,1'-biphenyl]-4-yl(dimethyl(phenyl)silyl)silane (**3g**).⁷



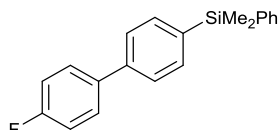
White solid (41 mg, 71%). ^1H NMR (400 MHz, CDCl_3): δ 7.64–7.52 (m, 8H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.40–7.31 (m, 4H), 0.58 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 142.0, 141.2, 138.3, 137.1, 134.8, 134.3, 129.3, 128.9, 128.0, 127.5, 127.3, 126.7, -2.2.

7. [1,1'-biphenyl]-3-yl dimethyl(phenyl)silane (**3h**).⁸



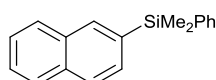
Colorless oil (43 mg, 75%). ^1H NMR (400 MHz, CDCl_3): δ 7.74 (s, 1H), 7.60–7.52 (m, 5H), 7.50 (dt, $J = 7.3, 1.2$ Hz, 1H), 7.45–7.38 (m, 3H), 7.37–7.31 (m, 4H), 0.59 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 141.6, 140.7, 138.9, 138.2, 134.3, 133.3, 133.1, 129.3, 128.9, 128.4, 128.2, 128.0, 127.4, 127.3, -2.2.

8. (4'-fluoro-[1,1'-biphenyl]-4-yl) dimethyl(phenyl)silane (**3i**).⁸



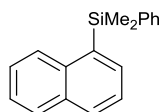
White solid (49 mg, 80%). ^1H NMR (500 MHz, CDCl_3): δ 7.64–7.47 (m, 8H), 7.42–7.32 (m, 3H), 7.12 (t, $J = 8.7$ Hz, 2H), 0.58 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 162.7 (d, $J = 247.4$ Hz), 141.0, 138.2, 137.3, 137.24, 137.19, 134.6 (d, $J = 56.5$ Hz), 129.3, 128.8 (d, $J = 8.1$ Hz), 128.0, 126.5, 115.8 (d, $J = 21.5$ Hz), -2.2. ^{19}F NMR (471 MHz, CDCl_3): δ -115.56.

9. dimethyl(naphthalen-2-yl)(phenyl)silane (**3j**).⁷



Colorless oil (34 mg, 64%). ^1H NMR (400 MHz, CDCl_3): δ 8.02 (s, 1H), 7.85–7.78 (m, 3H), 7.61–7.52 (m, 3H), 7.51–7.44 (m, 2H), 7.40–7.32 (m, 3H), 0.63 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 138.4, 135.8, 135.0, 134.4, 133.8, 133.0, 130.5, 129.3, 128.2, 128.0, 127.8, 127.2, 126.6, 126.1, -2.2.

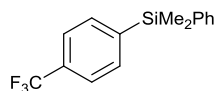
10. dimethyl(naphthalen-1-yl)(phenyl)silane (**3k**).⁷



Colorless oil (27 mg, 51%). ^1H NMR (500 MHz, CDCl_3): δ 7.92 (d, $J = 8.5$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.73 (dd, $J = 6.8, 1.1$ Hz, 1H), 7.56–7.52 (m, 2H),

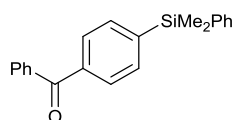
7.49–7.45 (m, 1H), 7.45–7.41 (m, 1H), 7.38–7.30 (m, 4H), 0.70 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 139.0, 137.1, 135.9, 134.8, 134.3, 133.6, 130.4, 129.2, 129.1, 128.8, 128.0, 125.8, 125.5, 125.2, –0.8.

11. dimethyl(phenyl)(4-(trifluoromethyl)phenyl)silane (**3l**).⁹



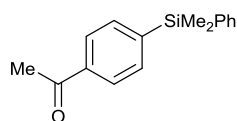
Colorless oil (50 mg, 89%). ^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, $J = 8.1$ Hz, 2H), 7.58 (d, $J = 8.1$ Hz, 2H), 7.54–7.47 (m, 2H), 7.42–7.33 (m, 3H), 0.58 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 143.5, 137.2, 134.6, 134.3, 131.2 (q, $J = 32.3$ Hz), 129.6, 128.1, 124.5 (q, $J = 3.8$ Hz), 124.4 (d, $J = 273.2$ Hz), –2.5. ^{19}F NMR (376 MHz, CDCl_3): δ –62.90.

12. (4-(dimethyl(phenyl)silyl)phenyl)(phenyl)methanone (**3m**).⁸



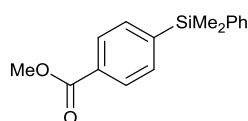
Colorless oil (52 mg, 82%). ^1H NMR (400 MHz, CDCl_3): δ 7.84–7.79 (m, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.1$ Hz, 2H), 7.61–7.51 (m, 3H), 7.47 (t, $J = 7.6$ Hz, 2H), 7.42–7.33 (m, 3H), 0.60 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 197.0, 144.2, 138.1, 137.6, 137.4, 134.3, 134.2, 132.6, 130.2, 129.5, 129.2, 128.4, 128.1, –2.4.

13. 1-(4-(dimethyl(phenyl)silyl)phenyl)ethan-1-one (**3n**).⁸



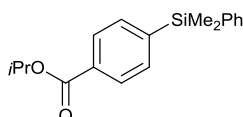
Colorless oil (37 mg, 73%). ^1H NMR (500 MHz, CDCl_3): δ 7.91 (d, $J = 8.1$ Hz, 2H), 7.62 (d, $J = 8.1$ Hz, 2H), 7.51 (dd, $J = 7.6, 1.7$ Hz, 2H), 7.42–7.33 (m, 3H), 2.60 (s, 3H), 0.58 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 198.6, 145.2, 137.5, 137.4, 134.5, 134.3, 129.5, 128.1, 127.4, 26.8, –2.5.

14. methyl 4-(dimethyl(phenyl)silyl)benzoate (**3o**).⁸



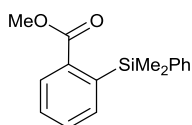
Colorless oil (45 mg, 84%). ^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.54–7.46 (d, $J = 6.0$ Hz, 2H), 7.42–7.31 (m, 3H), 3.91 (s, 3H), 0.57 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 167.4, 144.7, 137.5, 134.3, 130.7, 129.5, 128.7, 128.1, 52.3, –2.4.

15. isopropyl 4-(dimethyl(phenyl)silyl)benzoate (**3p**).⁸



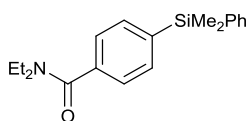
White solid (45 mg, 76%). ^1H NMR (500 MHz, CDCl_3): δ 7.99 (d, $J = 7.8$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 6.5$ Hz, 2H), 7.40–7.31 (m, 3H), 5.30–5.20 (m, 1H), 1.36 (d, $J = 6.2$ Hz, 6H), 0.57 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 166.4, 144.5, 137.5, 134.3, 134.2, 131.5, 129.5, 128.6, 128.1, 68.5, 22.1, –2.4.

16. methyl 2-(dimethyl(phenyl)silyl)benzoate (**3q**).



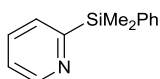
Colorless oil (43 mg, 80%). ^1H NMR (500 MHz, CDCl_3): δ 7.99 (dd, $J = 7.3, 1.5$ Hz, 1H), 7.62–7.57 (m, 1H), 7.52–7.42 (m, 4H), 7.35–7.29 (m, 3H), 3.62 (s, 3H), 0.59 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 168.7, 140.1, 139.9, 136.9, 136.4, 133.8, 131.5, 130.2, 129.3, 128.7, 127.8, 51.9, –0.8. HR-MS (EI): m/z 270.1071 [M]⁺, calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{Si}$ 270.1065.

17. 4-(dimethyl(phenyl)silyl)-*N,N*-diethylbenzamide (**3r**).⁸



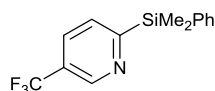
Colorless oil (40 mg, 65%). ^1H NMR (400 MHz, CDCl_3): δ 7.56–7.48 (m, 4H), 7.40–7.30 (m, 5H), 3.54 (b, 2H), 3.25 (b, 2H), 1.24 (b, 3H), 1.11 (b, 3H), 0.56 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3): δ 171.4, 139.7, 137.9, 137.8, 134.3, 134.3, 129.4, 128.0, 125.6, 43.3, 39.3, 14.4, 13.0, –2.4.

18. 2-(dimethyl(phenyl)silyl)pyridine (**3s**).⁸



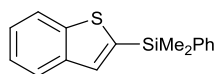
Colorless oil (37 mg, 88%). ^1H NMR (500 MHz, CDCl_3): δ 8.80 (d, $J = 4.6$ Hz, 1H), 7.63–7.57 (m, 2H), 7.54 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.40–7.33 (m, 3H), 7.22–7.15 (m, 1H), 0.62 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 166.7, 150.4, 137.4, 134.4, 134.1, 129.9, 129.4, 128.0, 123.0, –3.0.

19. 2-(dimethyl(phenyl)silyl)-4-(trifluoromethyl)pyridine (**3t**).



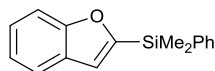
Colorless oil (52 mg, 93%). ^1H NMR (400 MHz, CDCl_3): δ 9.04 (s, 1H), 7.76 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.62–7.57 (m, 2H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.42–7.35 (m, 3H), 0.64 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 172.1, 146.7 (q, $J = 3.8$ Hz), 136.3, 134.3, 130.9 (q, $J = 3.6$ Hz), 129.8, 129.1, 128.2, 125.6 (q, $J = 32.9$ Hz), 123.8 (q, $J = 273.2$ Hz), –3.2. ^{19}F NMR (376 MHz, CDCl_3): δ –62.72. HR-MS (ESI): m/z 282.0920 $[\text{M}+\text{H}]^+$, calcd for $\text{C}_{14}\text{H}_{15}\text{NF}_3\text{Si}$ 282.0917.

20. benzo[b]thiophen-2-yl dimethyl(phenyl)silane (**3u**).⁷



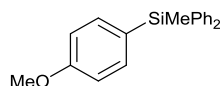
Colorless oil (40 mg, 75%). ^1H NMR (400 MHz, CDCl_3): δ 7.87–7.83 (m, 1H), 7.80–7.76 (m, 1H), 7.63–7.57 (m, 2H), 7.47 (s, 1H), 7.40–7.34 (m, 3H), 7.33–7.25 (m, 2H), 0.65 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 144.0, 141.1, 140.2, 137.3, 134.1, 132.4, 129.7, 128.1, 124.5, 124.2, 123.7, 122.3, –1.4.

21. benzofuran-2-yl dimethyl(phenyl)silane (**3v**).⁷



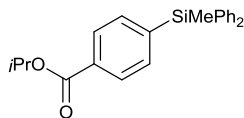
Colorless oil (34 mg, 68%). ^1H NMR (400 MHz, CDCl_3): δ 7.65–7.58 (m, 2H), 7.56 (d, $J = 7.5$ Hz, 1H), 7.50 (d, $J = 8.7$ Hz, 1H), 7.41–7.33 (m, 3H), 7.30–7.24 (m, 1H), 7.22–7.15 (m, 1H), 6.99 (d, $J = 0.7$ Hz, 1H), 0.63 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 161.7, 158.5, 136.3, 134.2, 133.1, 129.8, 128.1, 124.6, 122.5, 121.2, 117.8, 111.6, –2.9.

22. (4-methoxyphenyl)(methyl)diphenylsilane (**4a**).⁸



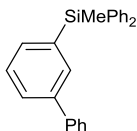
Colorless oil (35 mg, 57%). ^1H NMR (400 MHz, CDCl_3): δ 7.54–7.47 (m, 4H), 7.43 (d, $J = 8.6$ Hz, 2H), 7.40–7.31 (m, 6H), 6.91 (d, $J = 8.5$ Hz, 2H), 3.81 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 160.8, 136.9, 136.7, 135.4, 129.4, 128.0, 127.0, 113.8, 55.2, –3.1.

23. isopropyl 4-(methyl-diphenylsilyl)benzoate (**4b**).⁸



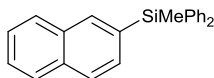
White solid (45 mg, 62%). ^1H NMR (500 MHz, CDCl_3): δ 8.00 (d, $J = 8.0$ Hz, 2H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.51–7.46 (m, 4H), 7.44–7.39 (m, 2H), 7.39–7.33 (m, 4H), 5.30–5.20 (m, 1H), 1.36 (d, $J = 6.2$ Hz, 6H), 0.85 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ 166.3, 142.4, 135.5, 135.4, 135.3, 131.8, 129.8, 128.7, 128.1, 68.5, 22.1, –3.4.

24. [1,1'-biphenyl]-3-yl(methyl)diphenylsilane (**4c**).



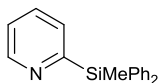
White solid (44 mg, 63%). ^1H NMR (400 MHz, CDCl_3): δ 7.48–7.18 (m, 15H), 7.13 (t, $J = 7.6$ Hz, 2H), 7.07–7.00 (m, 2H), 0.10 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ 150.2, 144.0, 138.0, 137.7, 135.3, 134.7, 129.9, 129.5, 129.4, 129.1, 127.9, 127.7, 127.1, 126.2, –3.2. HR-MS (ESI): m/z 351.1564 $[\text{M}+\text{H}]^+$, calcd for $\text{C}_{25}\text{H}_{23}\text{Si}$ 351.1557.

25. methyl(naphthalen-2-yl)diphenylsilane (**4d**).⁷



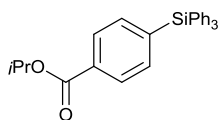
Colorless oil (33 mg, 51%). ^1H NMR (400 MHz, CDCl_3): δ 8.01 (s, 1H), 7.86–7.75 (m, 3H), 7.62–7.52 (m, 5H), 7.52–7.44 (m, 2H), 7.44–7.32 (m, 6H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 136.4, 136.2, 135.5, 134.0, 133.7, 133.0, 131.3, 129.6, 128.4, 128.1, 127.9, 127.2, 126.8, 126.1, –3.2.

26. 2-(methyl-diphenylsilyl)pyridine (**4e**).



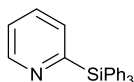
Colorless oil (44 mg, 80%). ^1H NMR (500 MHz, CDCl_3): δ 8.84 (d, $J = 4.8$ Hz, 1H), 7.58 (dd, $J = 7.7, 1.4$ Hz, 4H), 7.52 (dt, $J = 7.6, 1.6$ Hz, 1H), 7.43 (d, $J = 7.5$ Hz, 1H), 7.41–7.32 (m, 6H), 7.22–7.17 (m, 1H), 0.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3): δ 164.9, 150.6, 135.4, 134.2, 131.1, 129.6, 128.0, 123.1, –3.9. HR-MS (ESI): m/z 276.1203 $[\text{M}+\text{H}]^+$, calcd for $\text{C}_{18}\text{H}_{18}\text{NSi}$ 276.1201.

27. isopropyl 4-(triphenylsilyl)benzoate (**5a**).⁸



White solid (42.2 mg, 50%). ^1H NMR (500 MHz, CDCl_3): δ 8.02 (d, $J = 8.3$ Hz, 2H), 7.65 (d, $J = 8.3$ Hz, 2H), 7.58–7.52 (m, 6H), 7.48–7.41 (m, 3H), 7.41–7.35 (m, 6H), 5.32–5.20 (m, 1H), 1.36 (d, $J = 6.3$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 166.3, 140.5, 136.5, 136.4, 133.6, 132.0, 130.0, 128.7, 128.1, 68.6, 22.1.

28. 2-(triphenylsilyl)pyridine (**5b**).



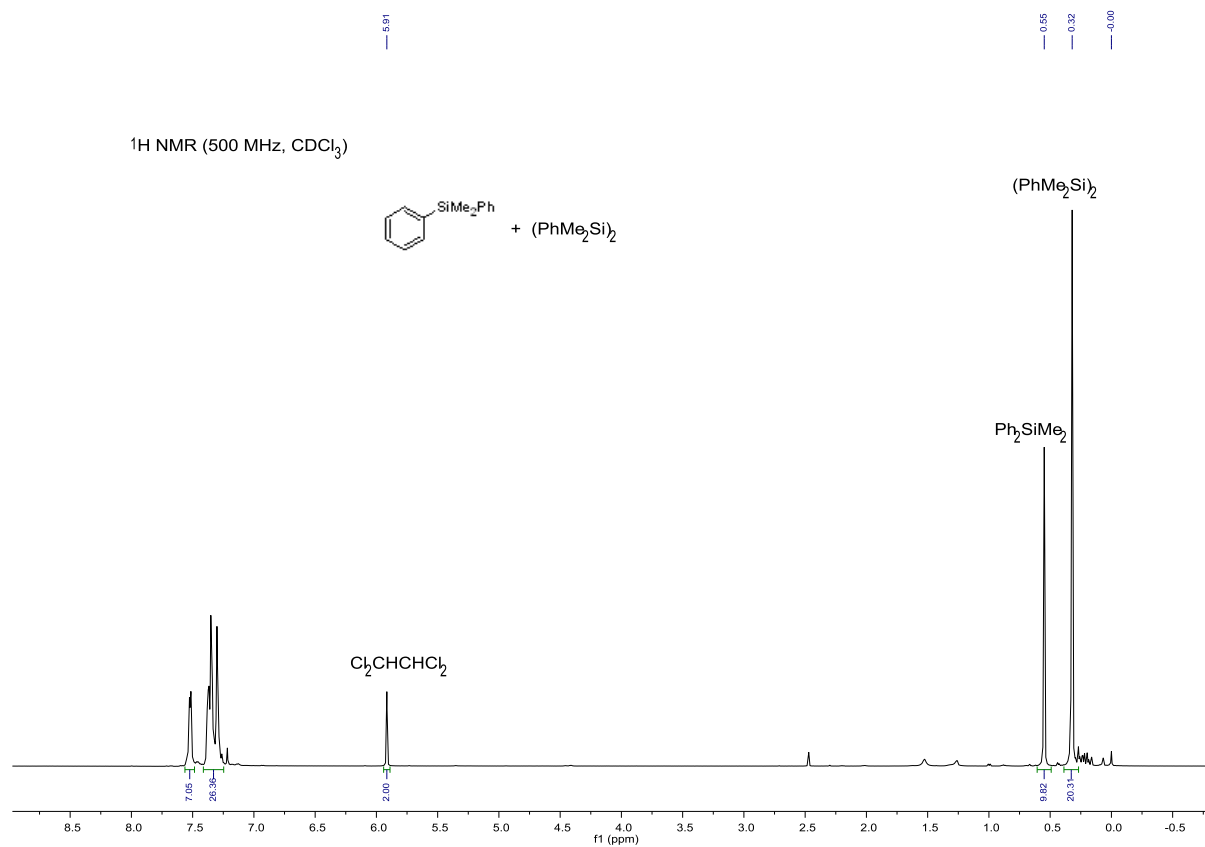
Drak brown solid (38 mg, 57%). ^1H NMR (500 MHz, CDCl_3): δ 8.90 (d, $J = 4.8$ Hz, 1H), 7.63 (dd, $J = 7.9, 1.3$ Hz, 6H), 7.53 (dt, $J = 7.6, 1.7$ Hz, 1H), 7.46 (d, $J = 7.5$ Hz, 1H), 7.44–7.38 (m, 3H), 7.38–7.32 (m, 6H), 7.24–7.19 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3): δ 163.6, 150.6, 136.6, 134.2, 133.7, 132.2, 129.8, 128.0, 123.2. HR-MS (ESI): m/z 338.1360 $[\text{M}+\text{H}]^+$, calcd for $\text{C}_{23}\text{H}_{20}\text{NSi}$ 338.1359.

References

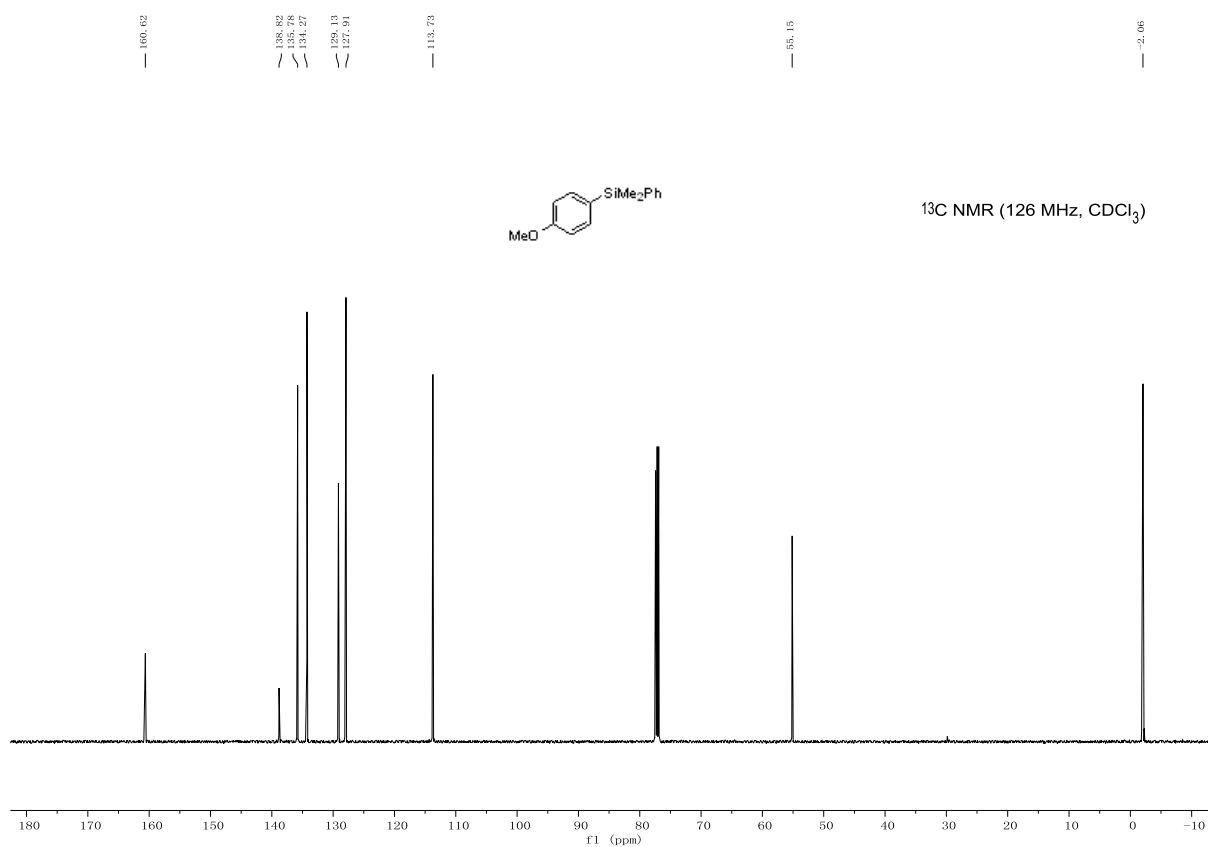
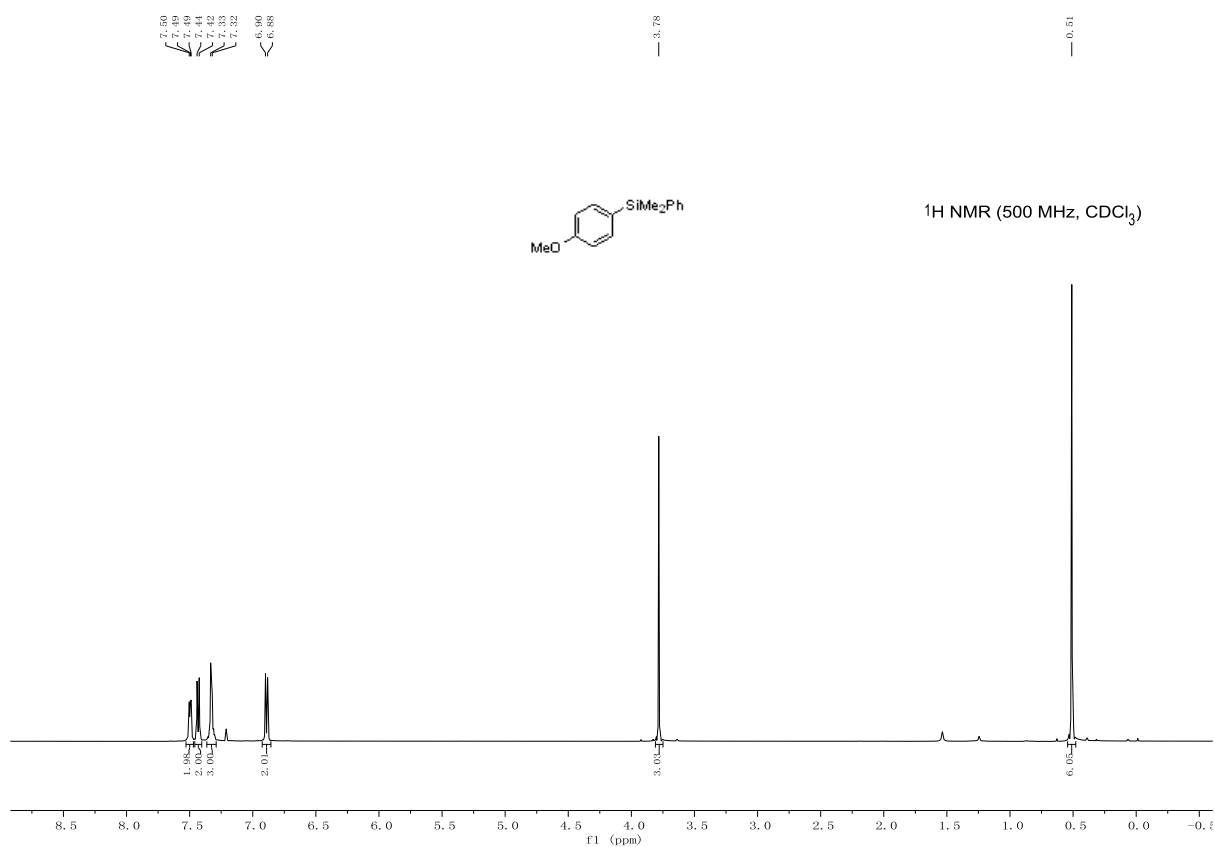
- 1 C. K. Chu, Y.-F. Liang and G. C. Fu, *J. Am. Chem. Soc.*, 2016, **138**, 6404.
- 2 A. Krasovskiy and P. Knochel, *Synthesis*, 2006, 890.
- 3 J. Drabowicz, P. Łyżwa, M. Popielarczyk and M. Mikołajczyk, *Synthesis*, 1990, 937.
- 4 K. Yamamoto, S. Otsuka, K. Nogi and H. Yorimitsu, *ACS Catal.*, 2017, **7**, 7623.
- 5 Y.-H. Li, G. Bao and X.-F. Wu, *Chem. Sci.*, 2020, **11**, 2187.
- 6 T. Itoh and T. Mase, *J. Org. Chem.*, 2006, **71**, 2203.
- 7 W. Srimontree, W. Lakornwong and M. Rueping, *Org. Lett.*, 2019, **21**, 9330.
- 8 Y.-Y. Kong and Z.-X. Wang, *Adv. Synth. Catal.*, 2019, **361**, 5440.
- 9 H. Guo, X. Chen, C. Zhao and W. He, *Chem. Commun.*, 2015, **51**, 17410.

5. Copies of NMR spectra of the silylation products

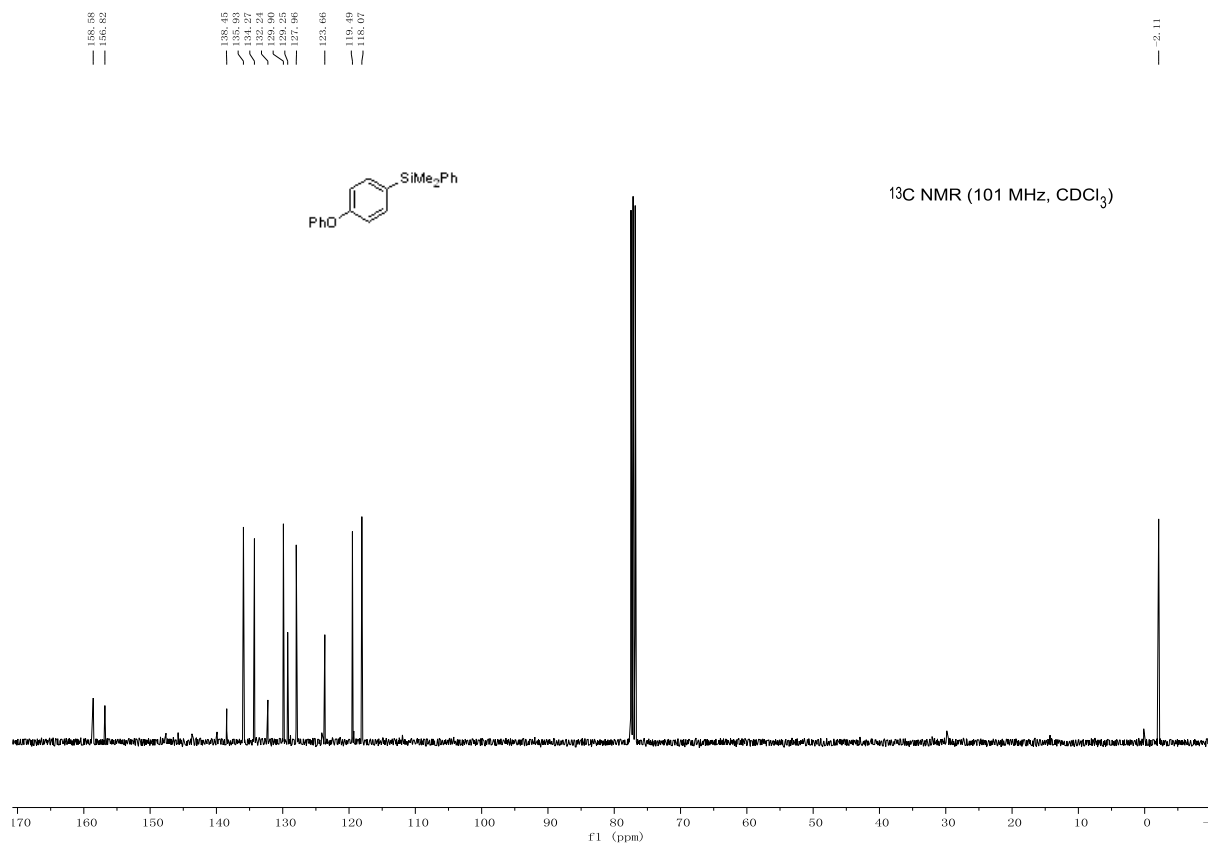
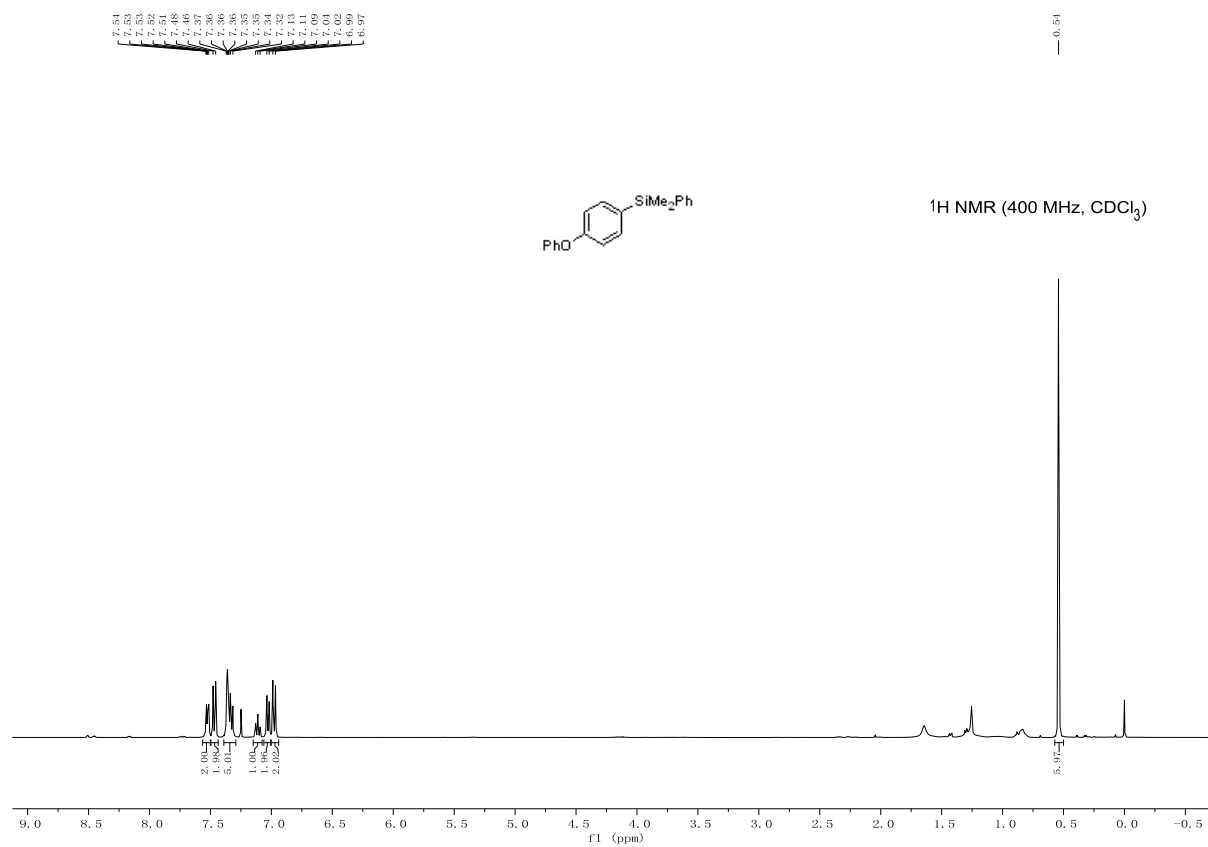
^1H NMR spectrum of mixture of dimethyldiphenylsilane (**3a**) and $(\text{PhMe}_2\text{Si})_2$



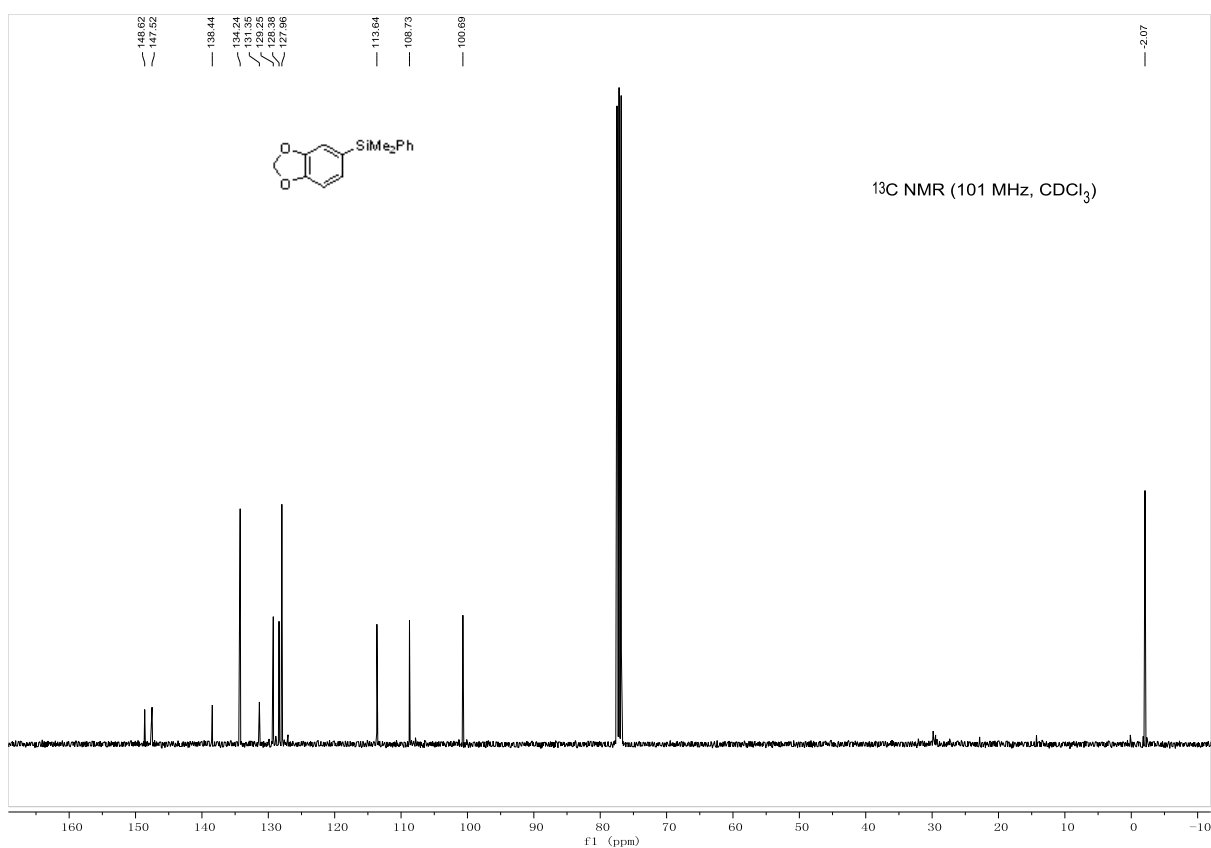
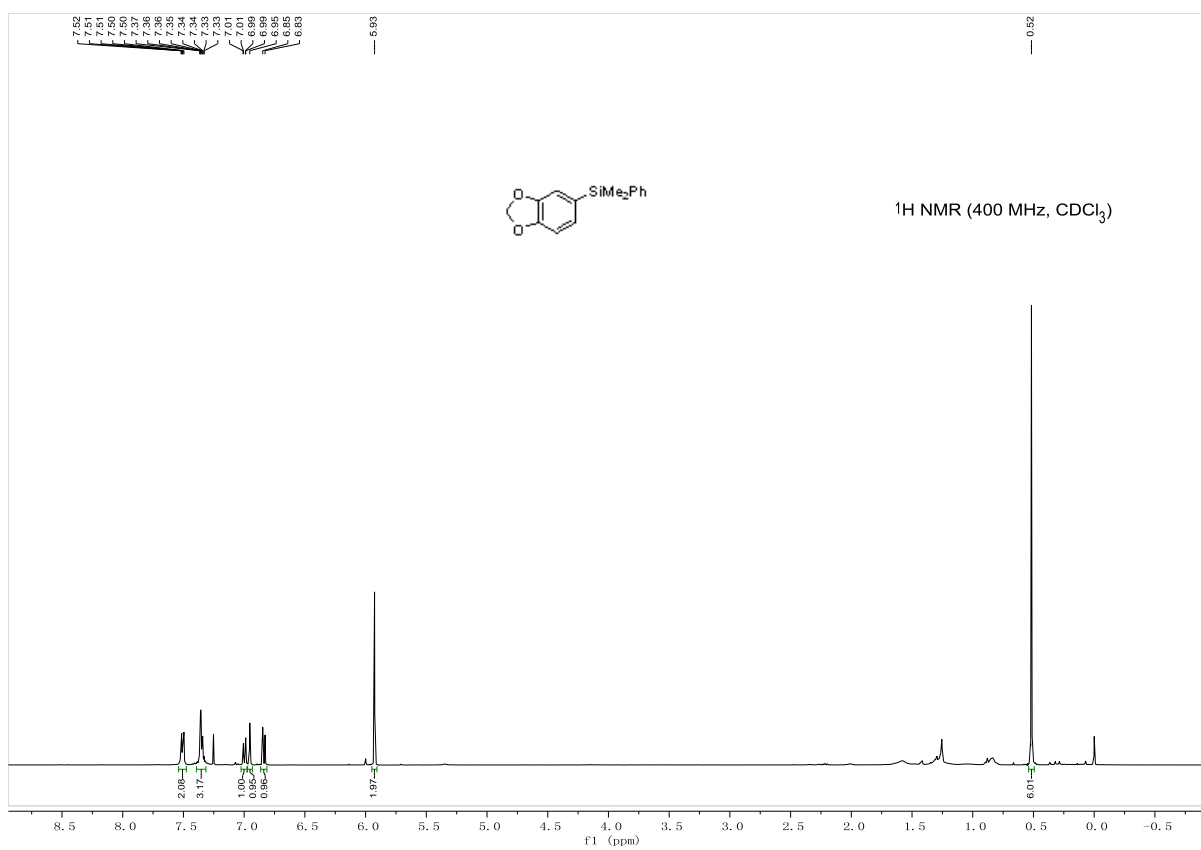
(4-Methoxyphenyl)dimethyl(phenyl)silane (**3b**)



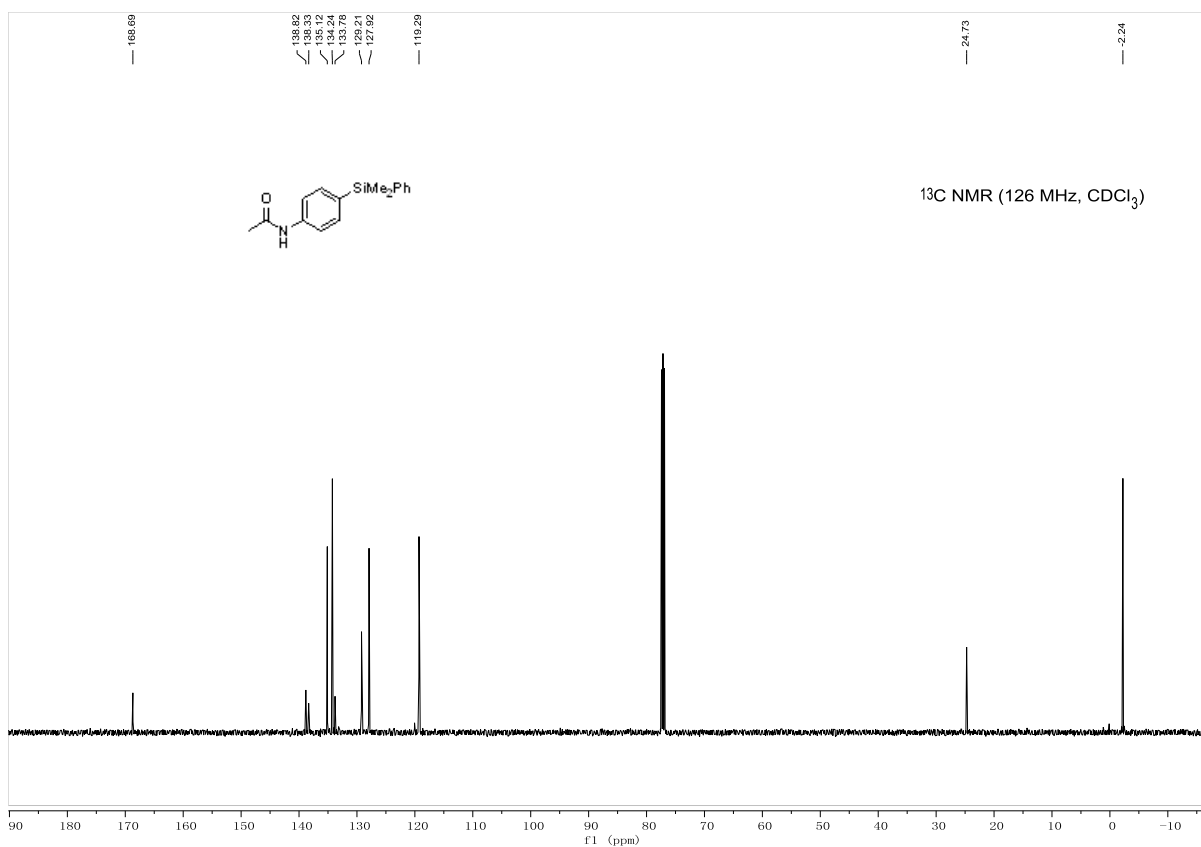
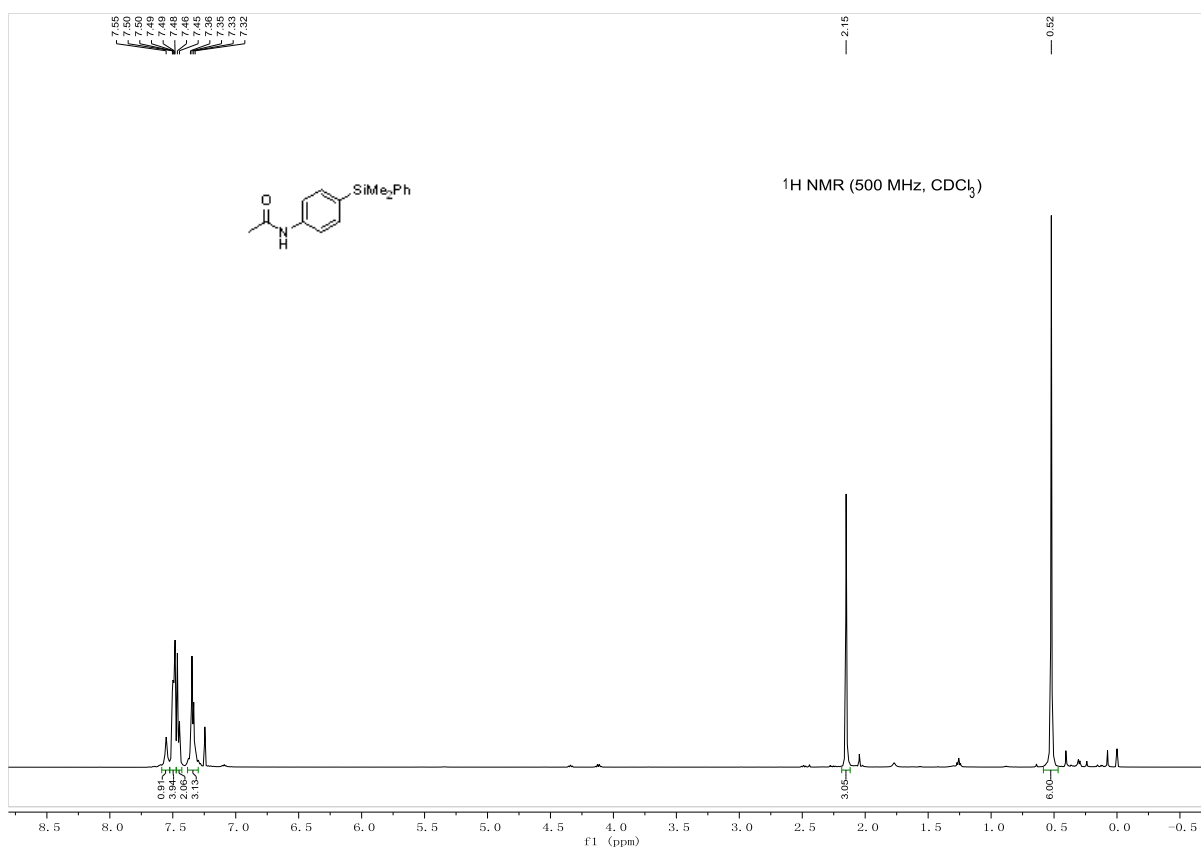
Dimethyl(4-phenoxyphenyl)(phenyl)silane (**3c**)



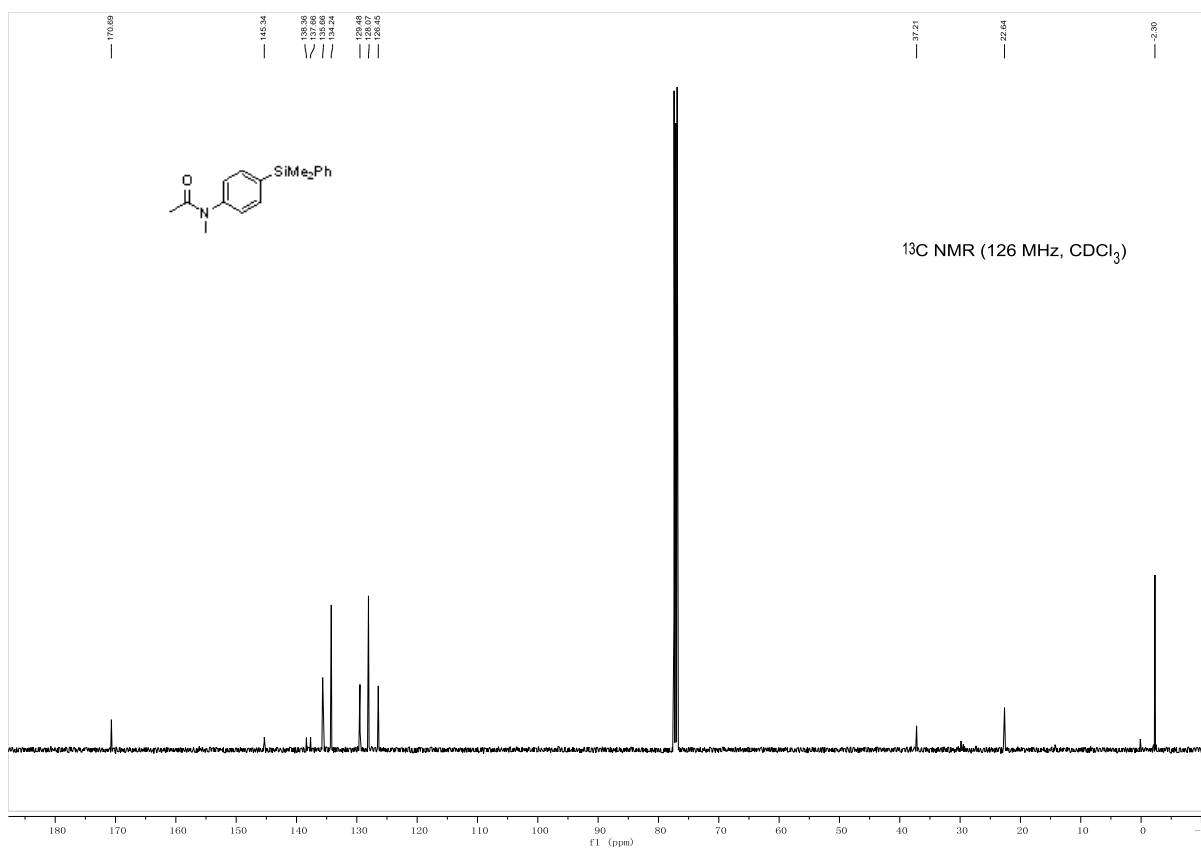
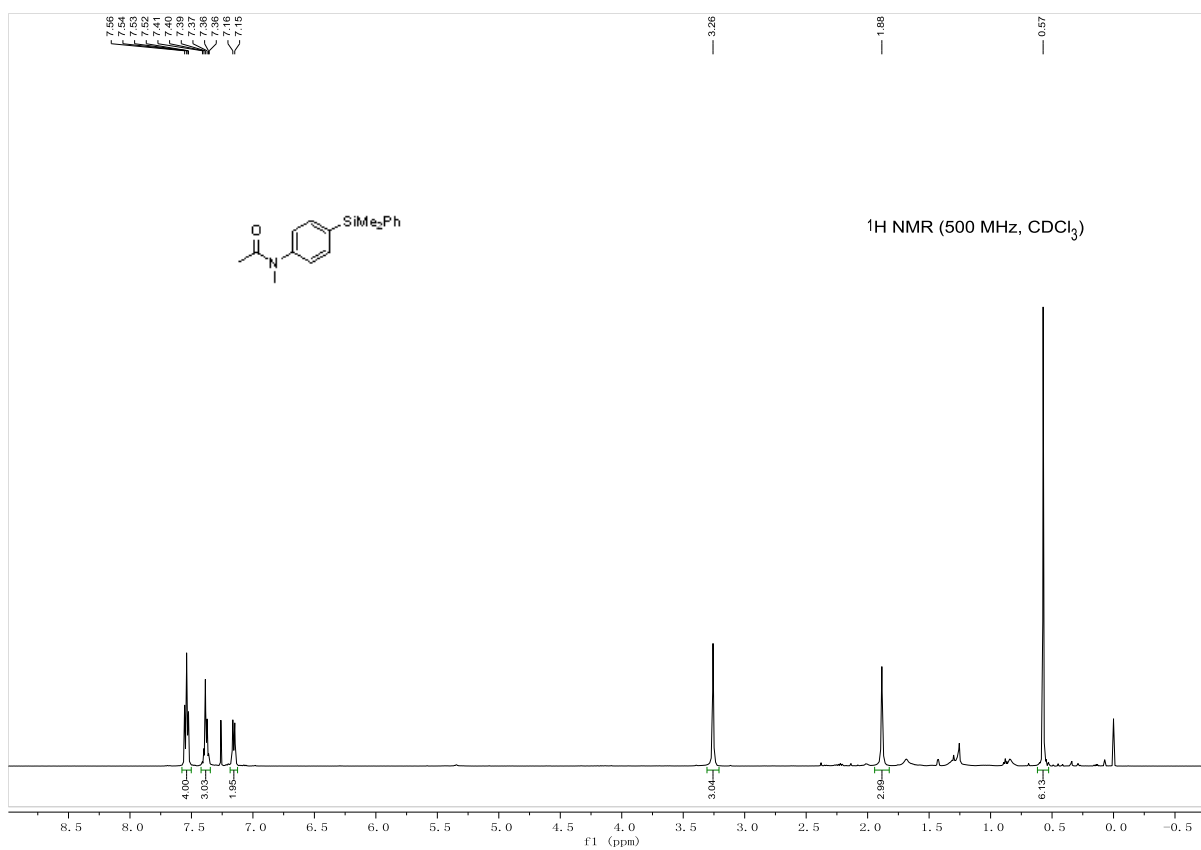
Benzo[d][1,3]dioxol-5-yl dimethyl(phenyl)silane (**3d**)



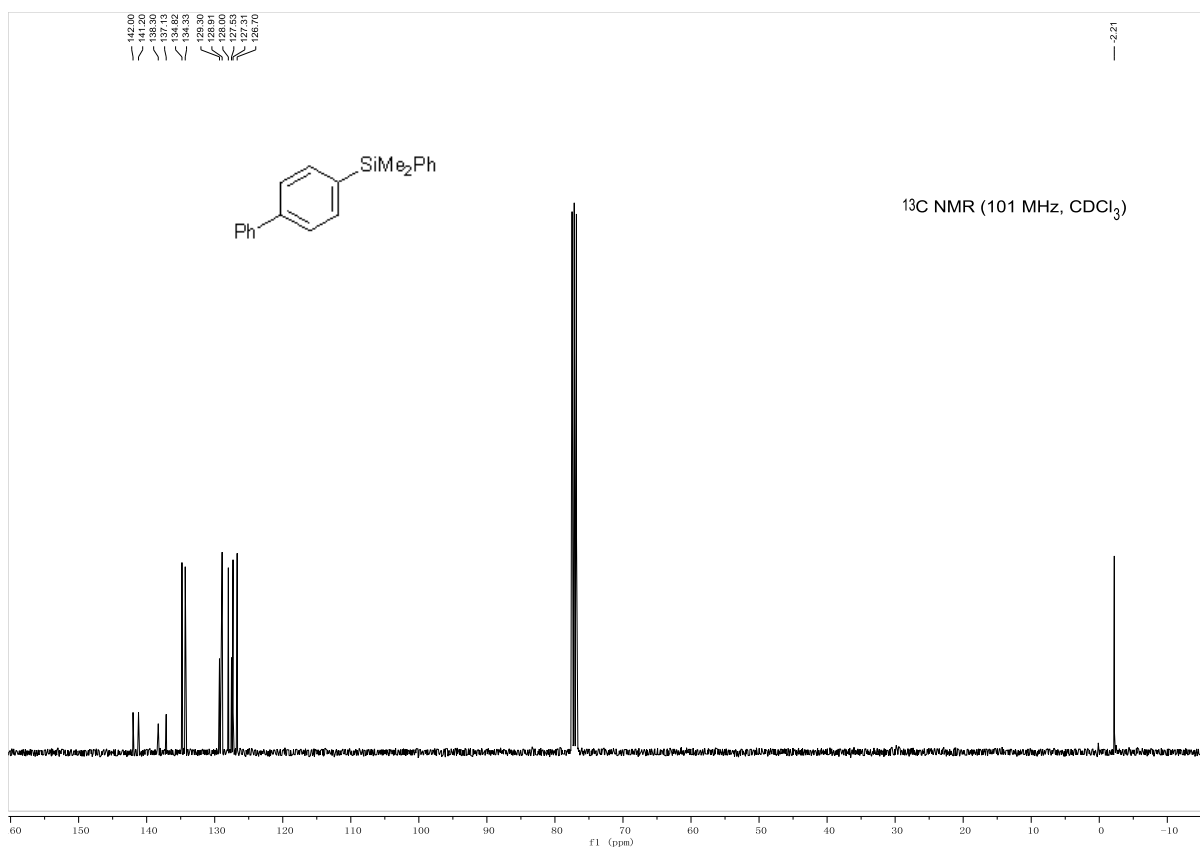
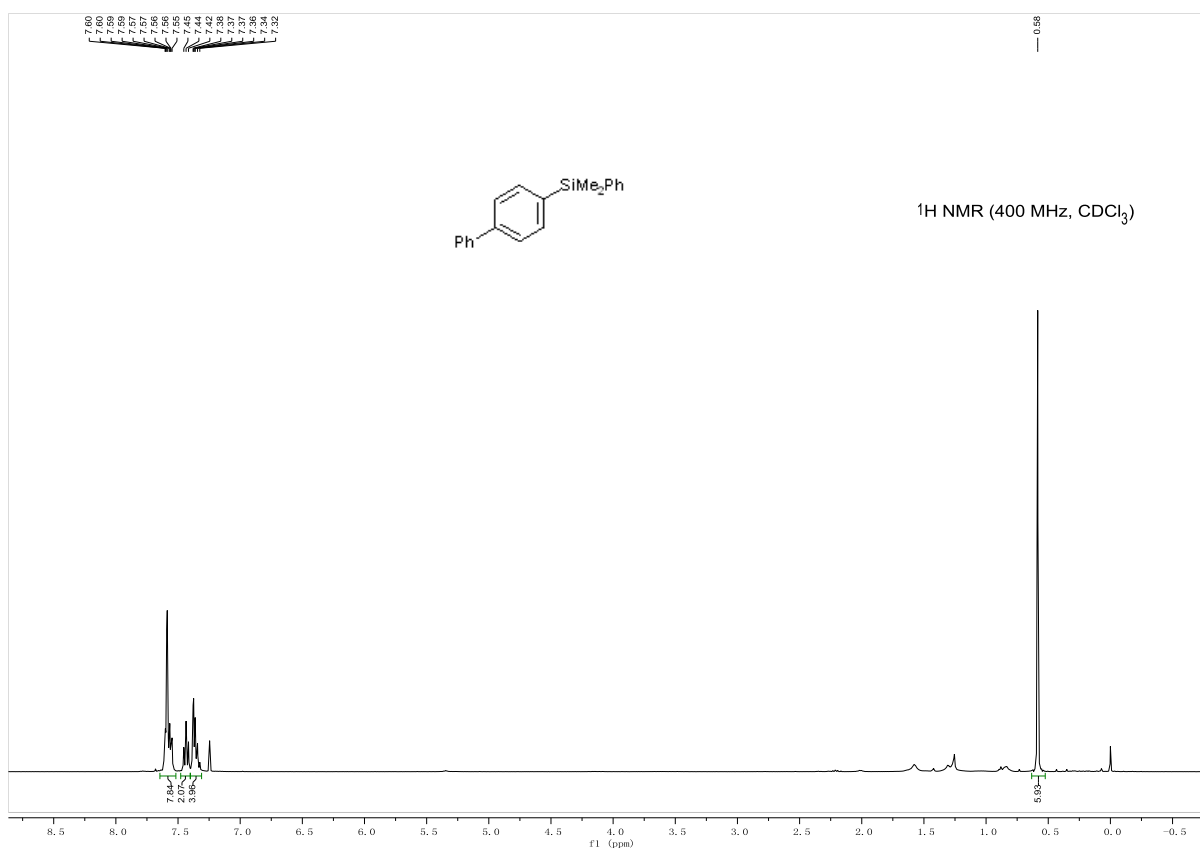
N-(4-(Dimethyl(phenyl)silyl)phenyl)acetamide (**3e**)



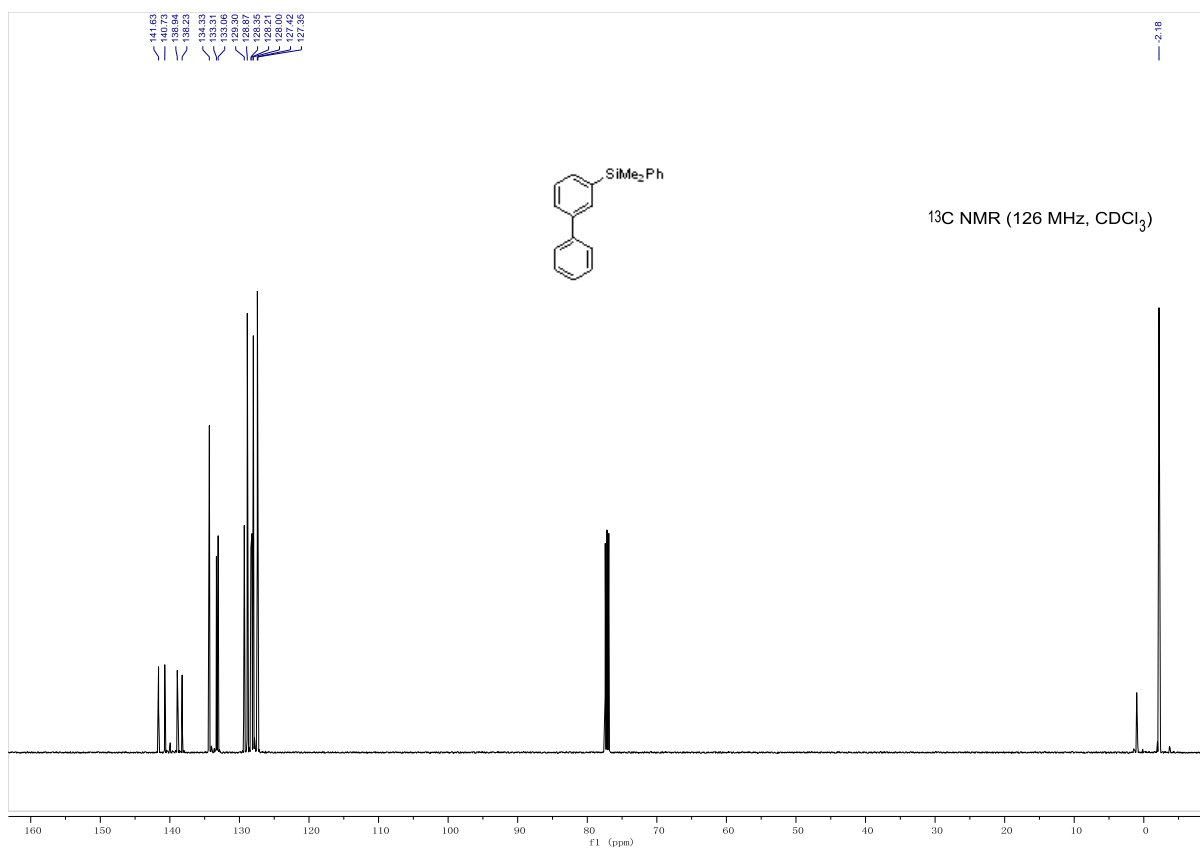
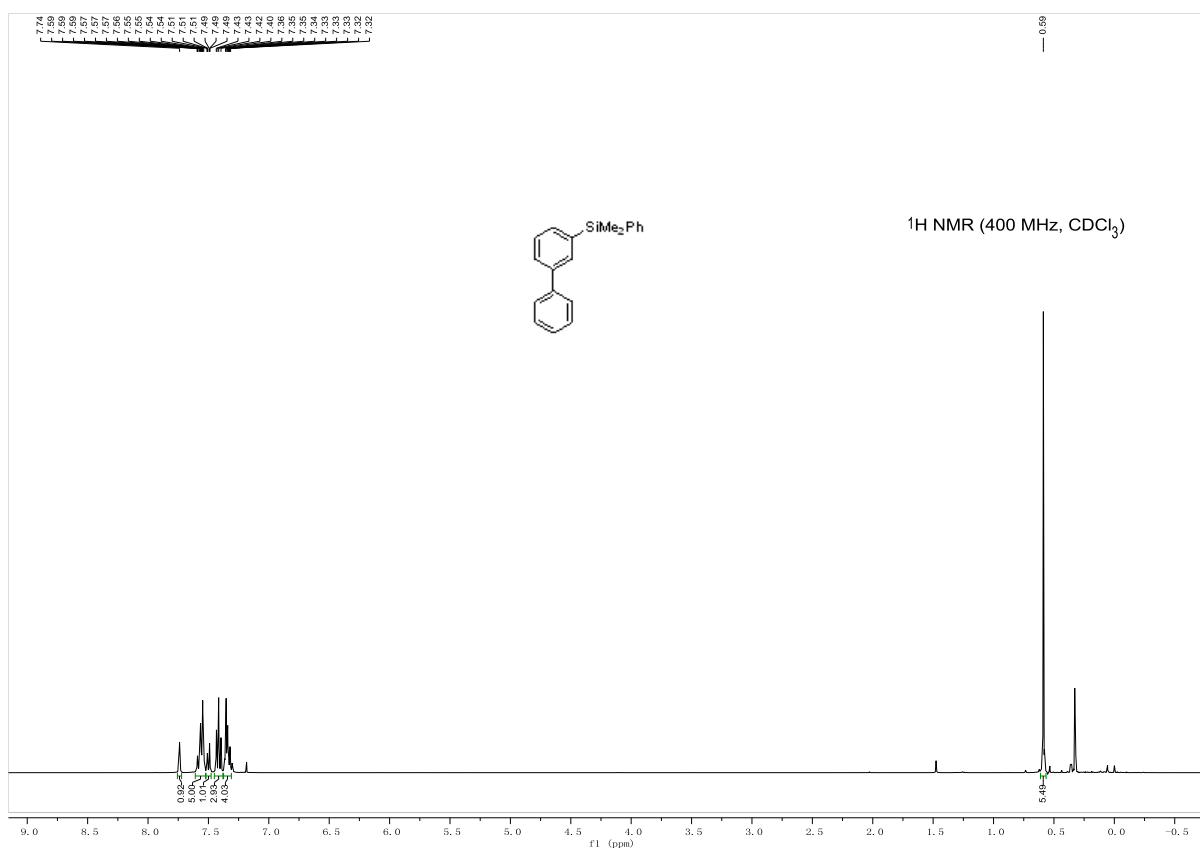
N-(4-(Dimethyl(phenyl)silyl)phenyl)-N-methylacetamide (**3f**)



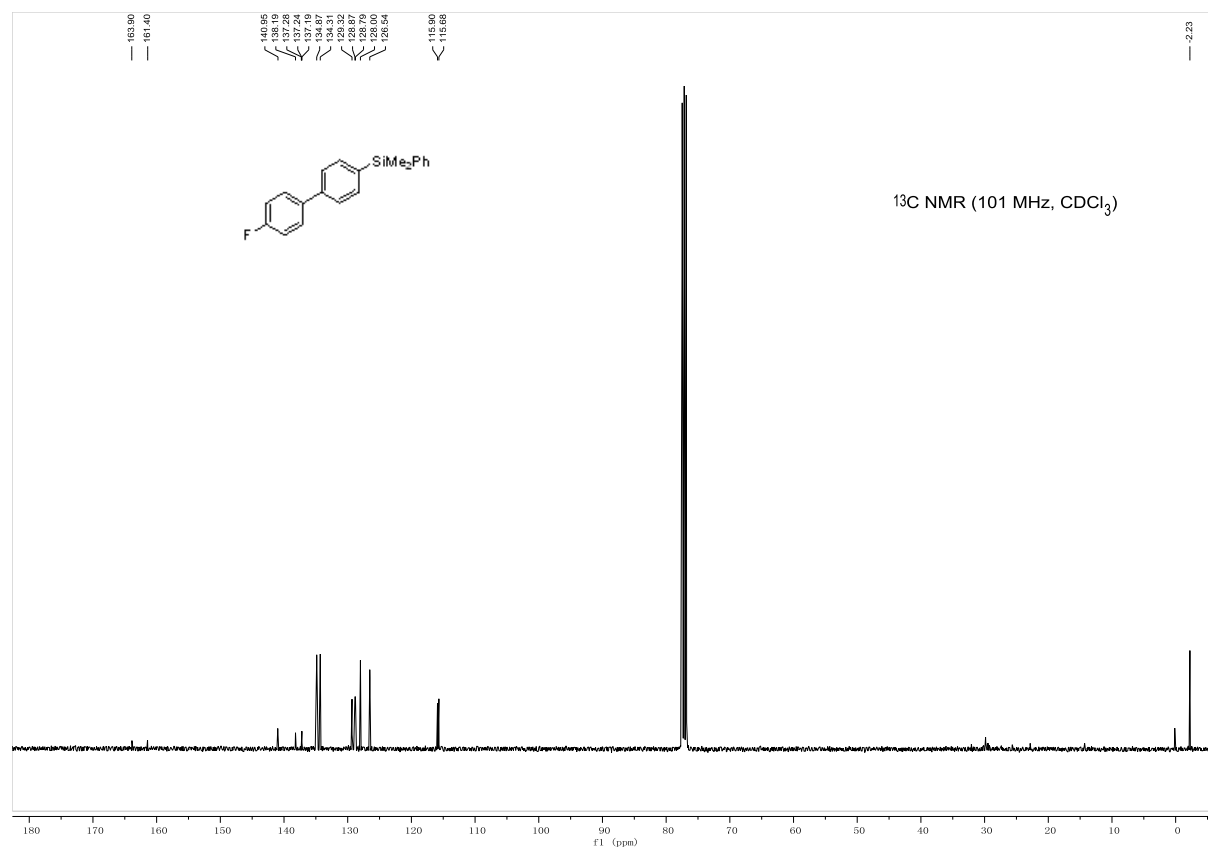
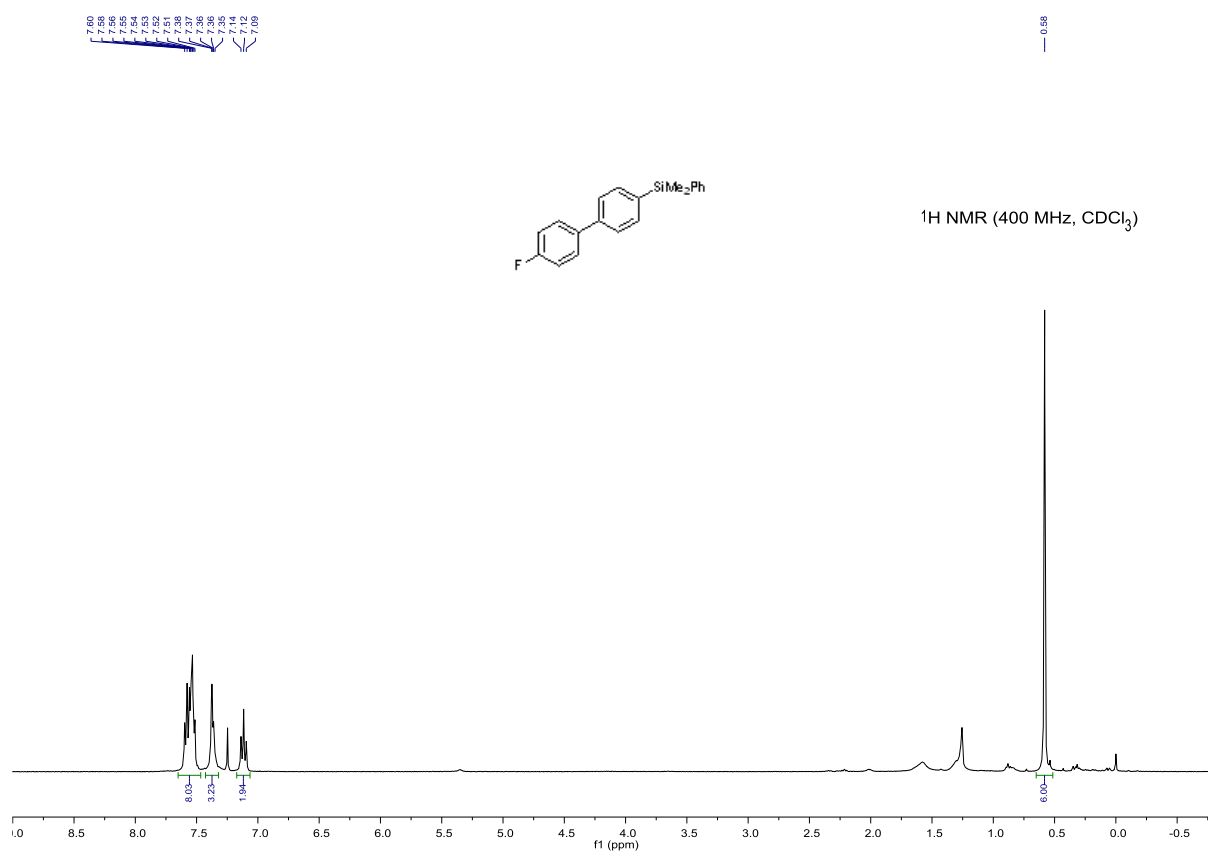
[1,1'-Biphenyl]-4-yl dimethyl(phenyl)silane (**3g**)

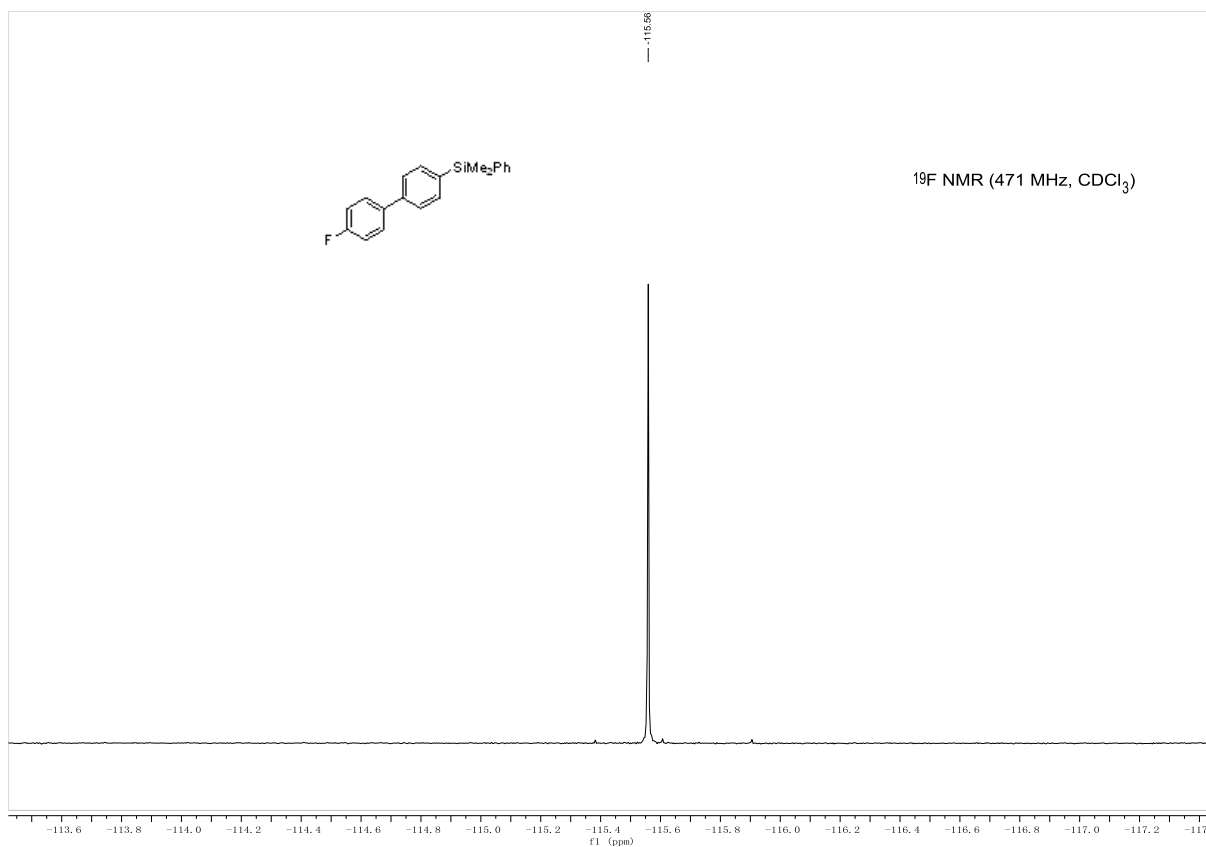


[1,1'-Biphenyl]-3-yl dimethyl(phenyl)silane (**3h**)

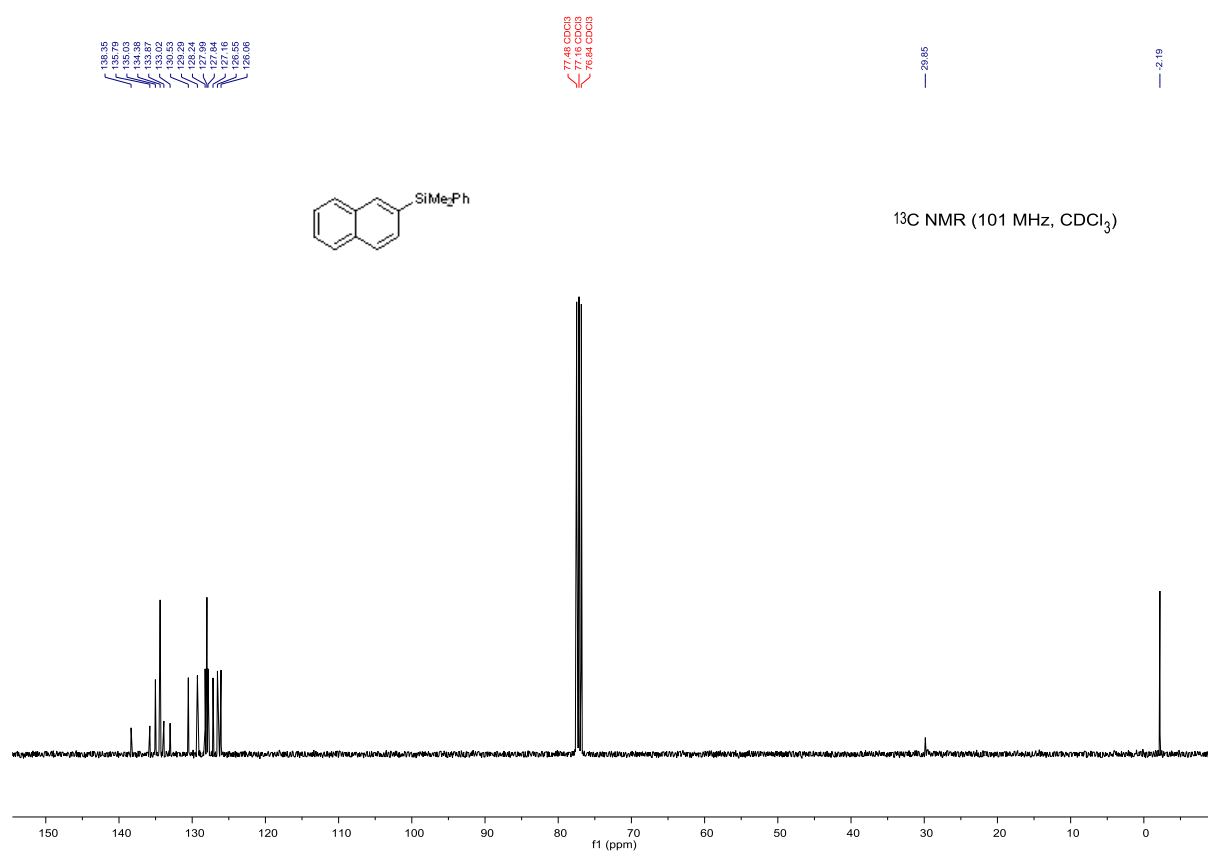
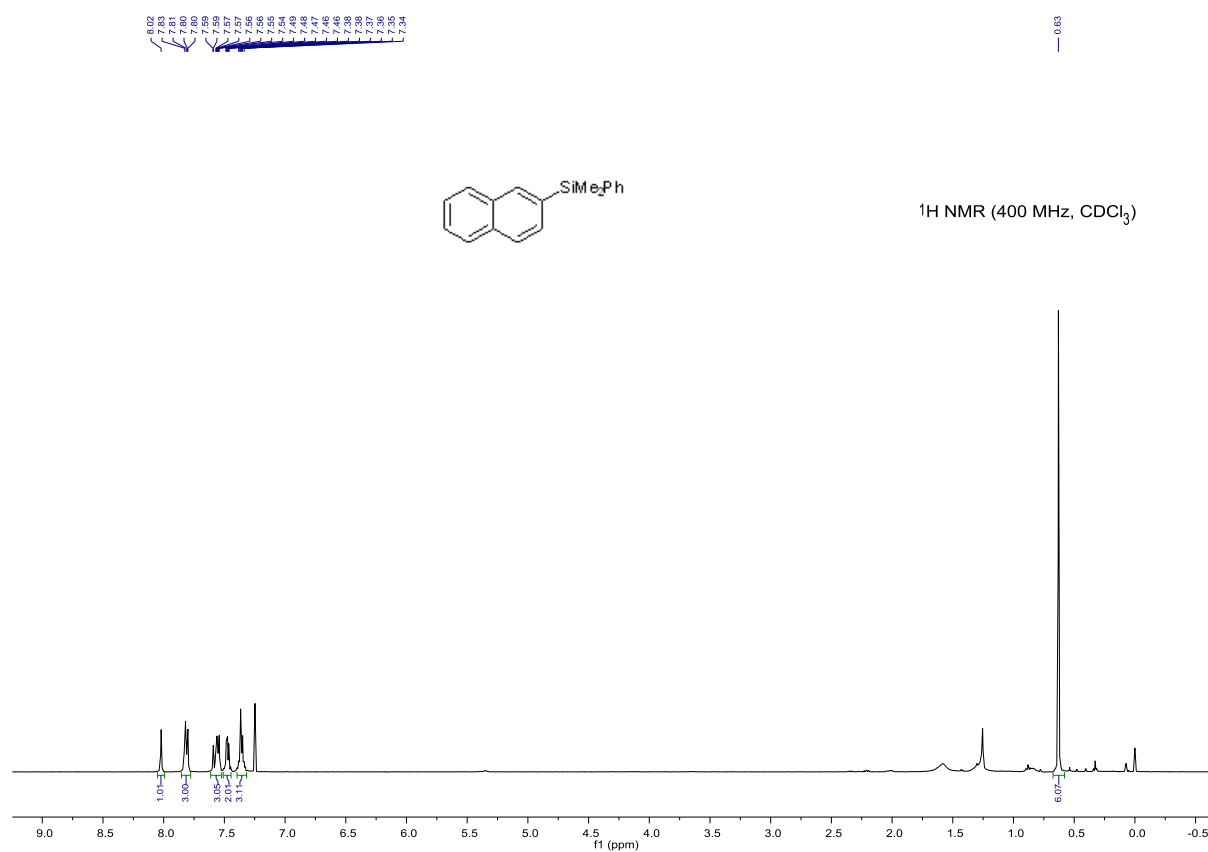


(4'-Fluoro-[1,1'-biphenyl]-4-yl)dimethyl(phenyl)silane (**3i**)

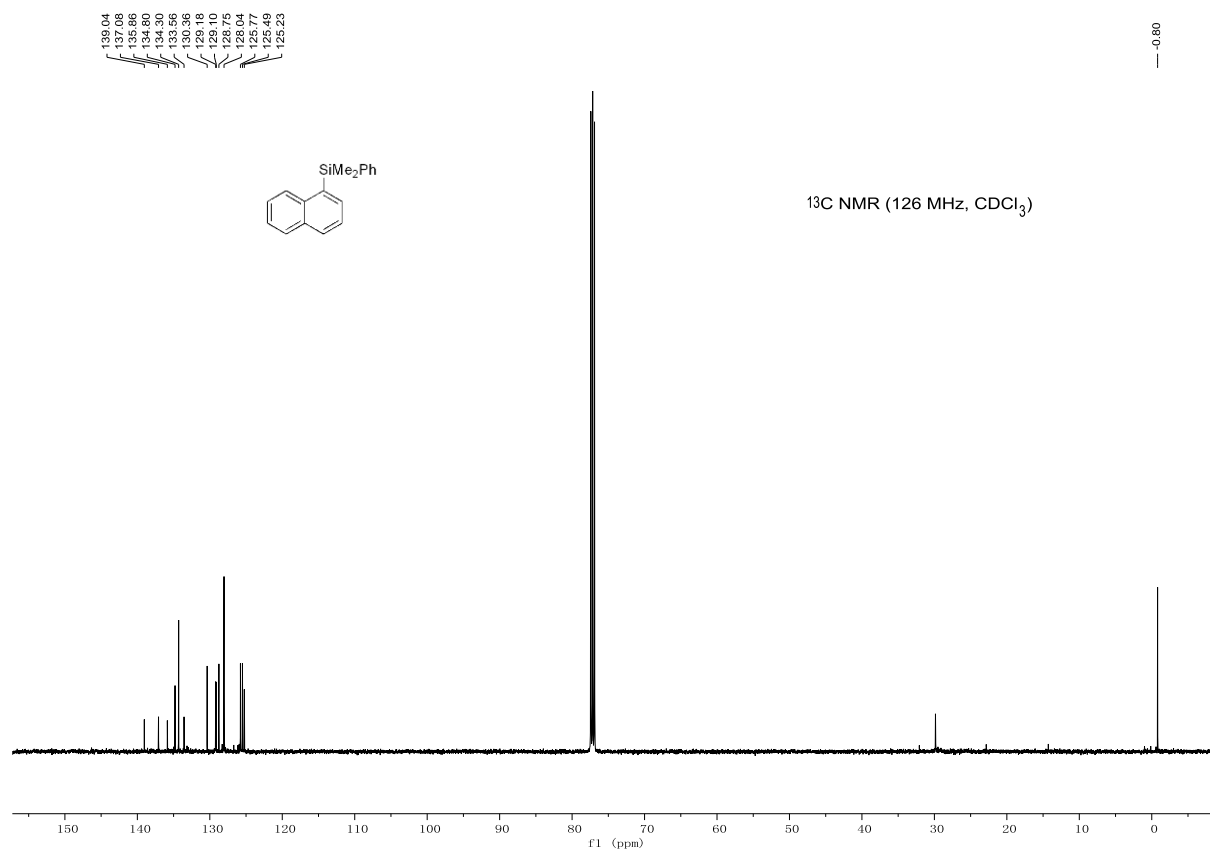
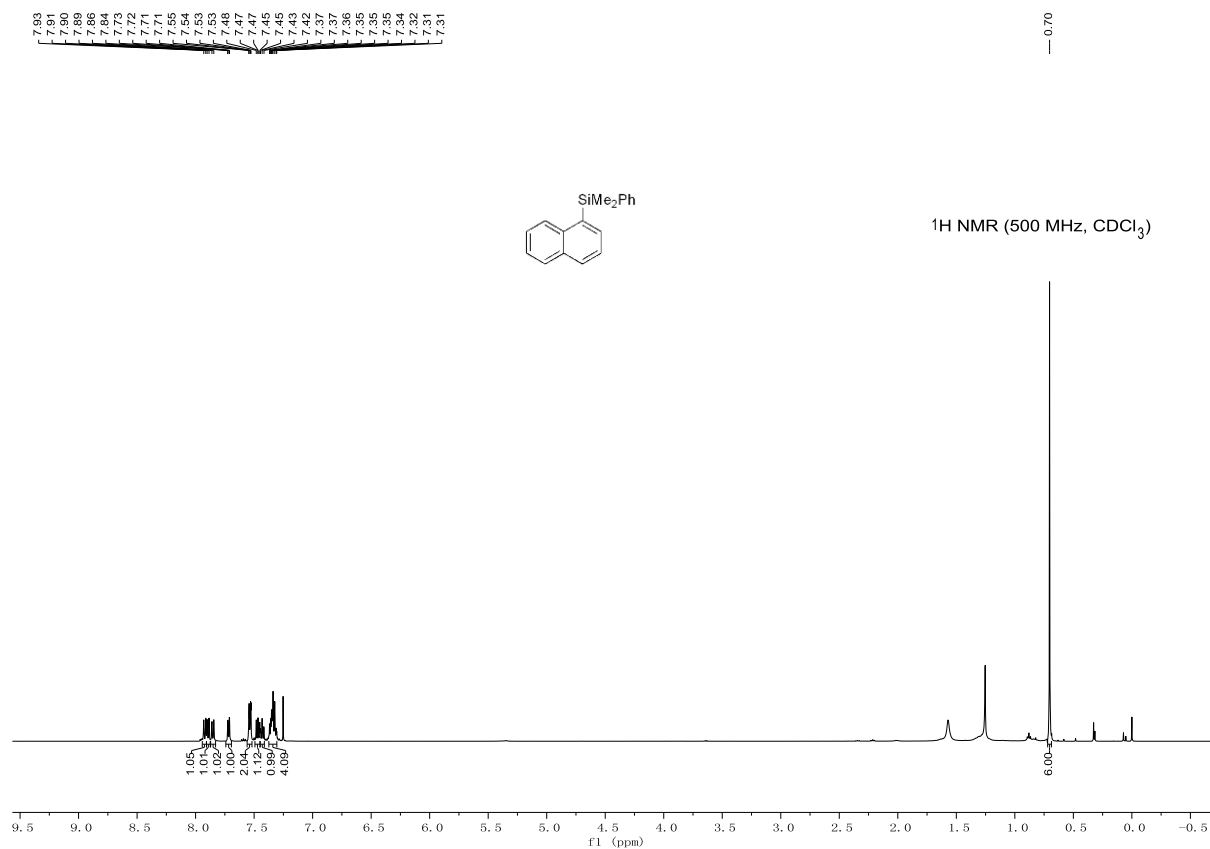




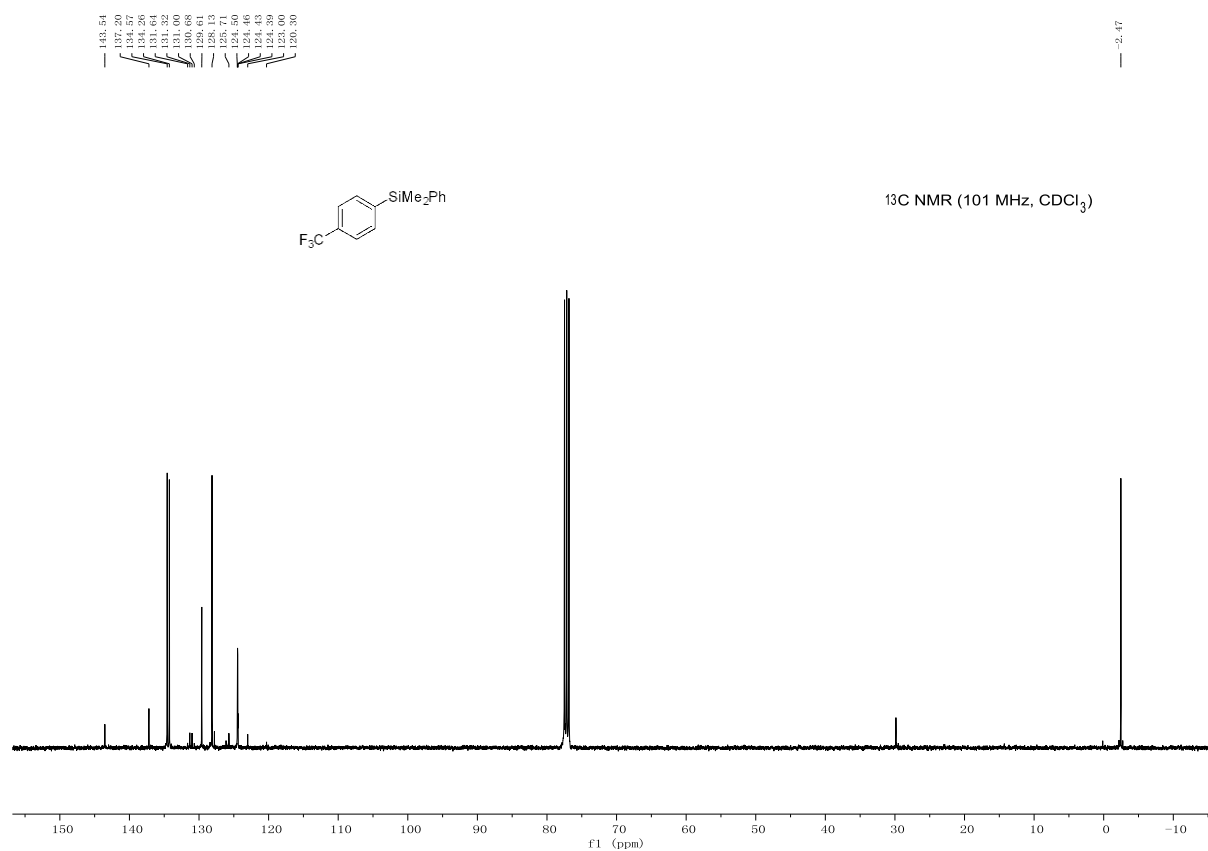
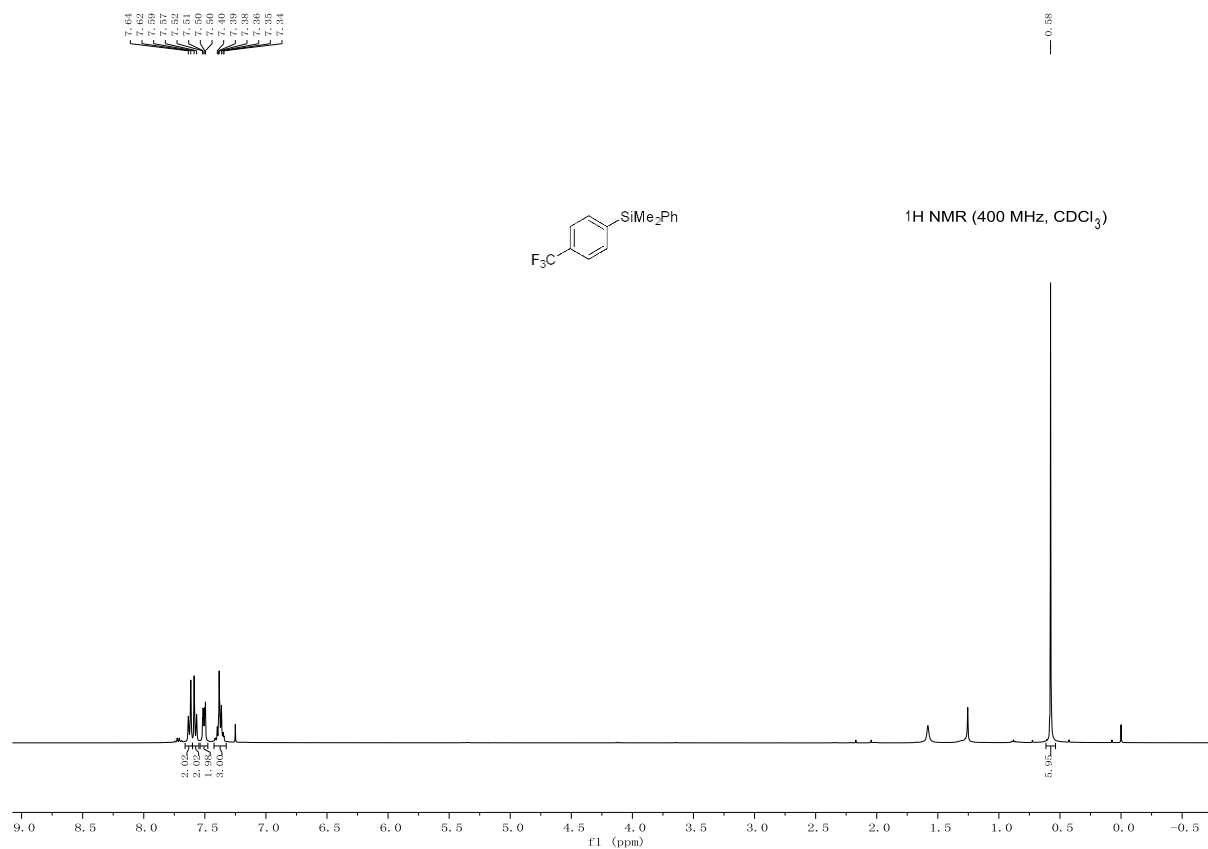
Dimethyl(naphthalen-2-yl)(phenyl)silane (**3j**)

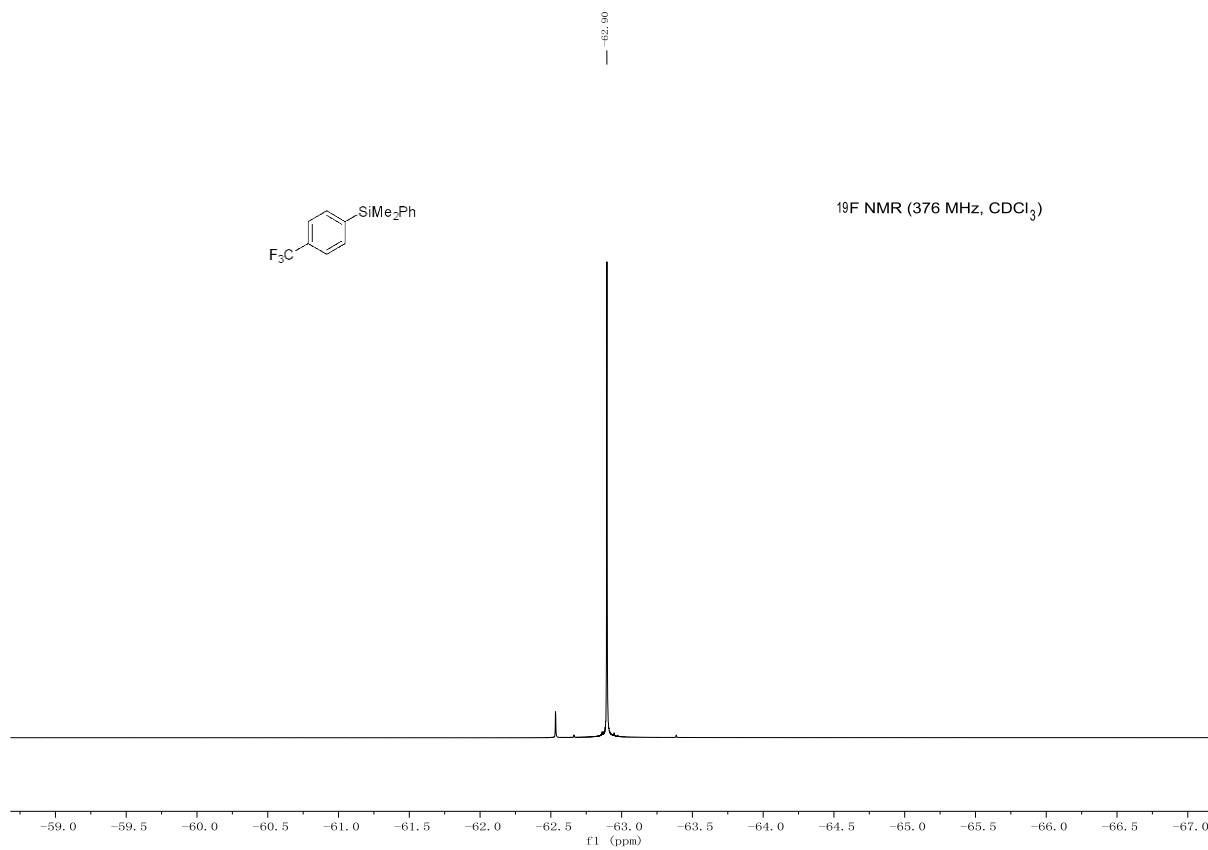


Dimethyl(naphthalen-1-yl)(phenyl)silane (**3k**)

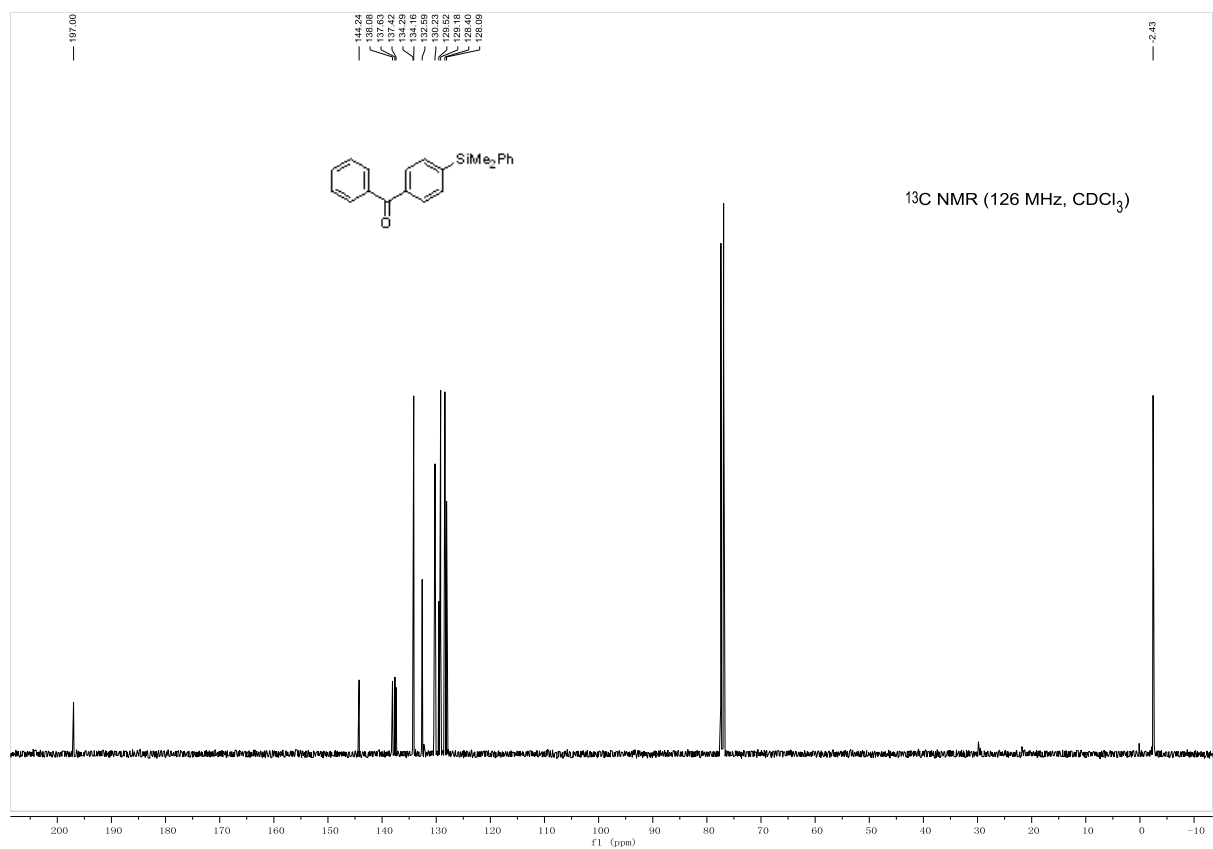
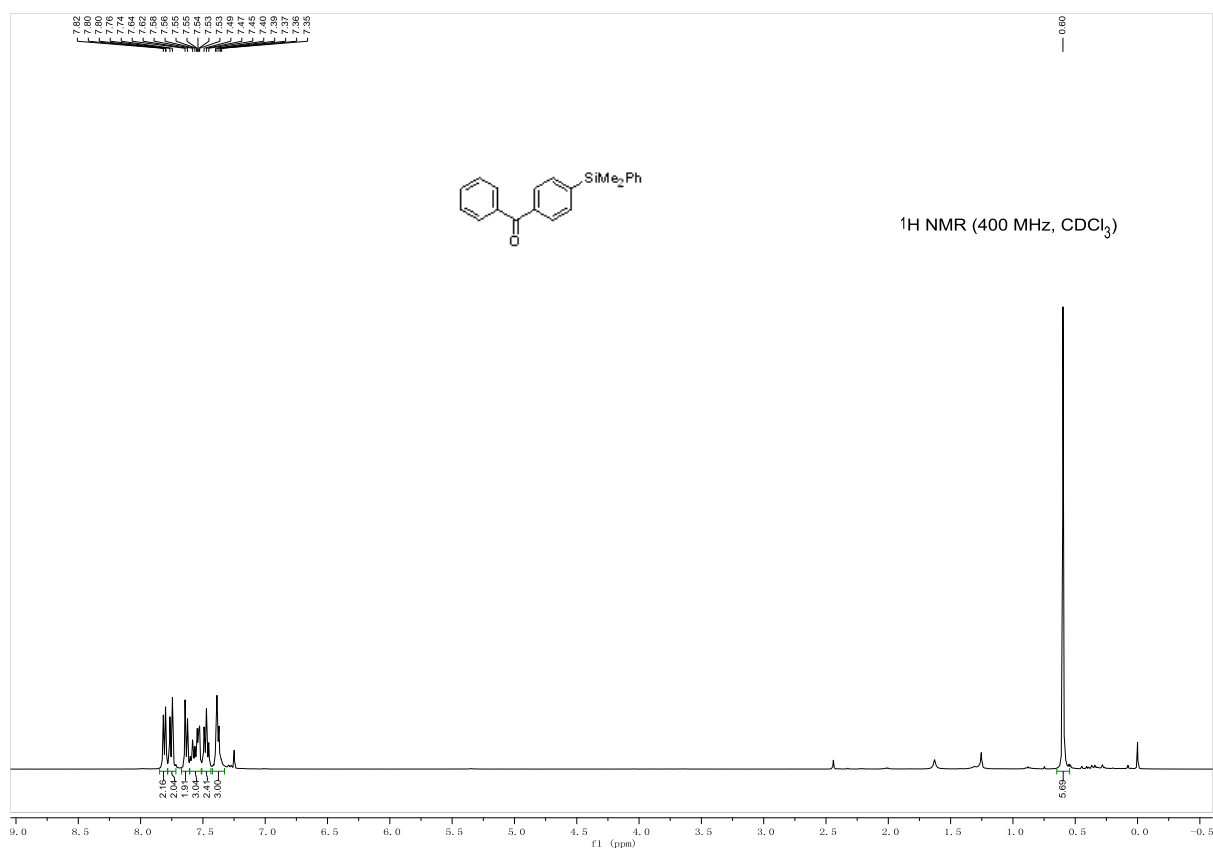


Dimethyl(phenyl)(4-(trifluoromethyl)phenyl)silane (**3l**)

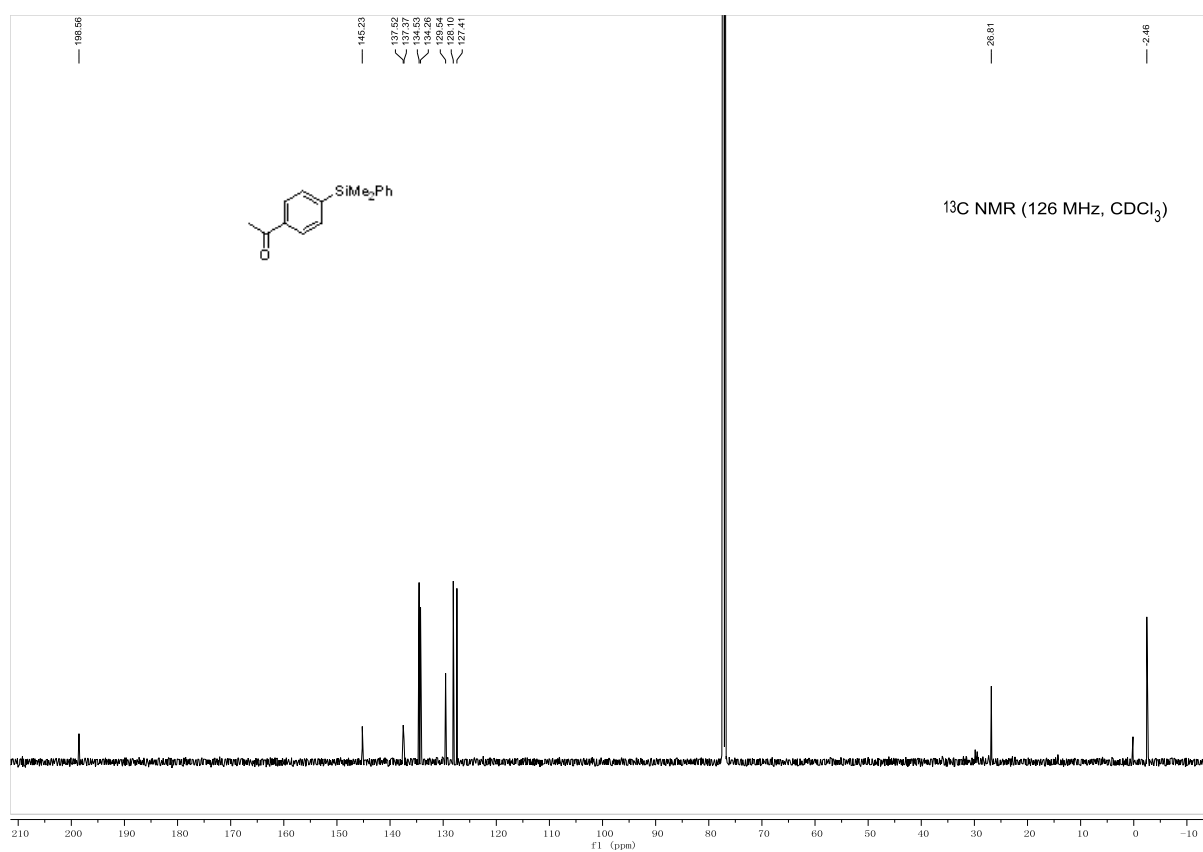
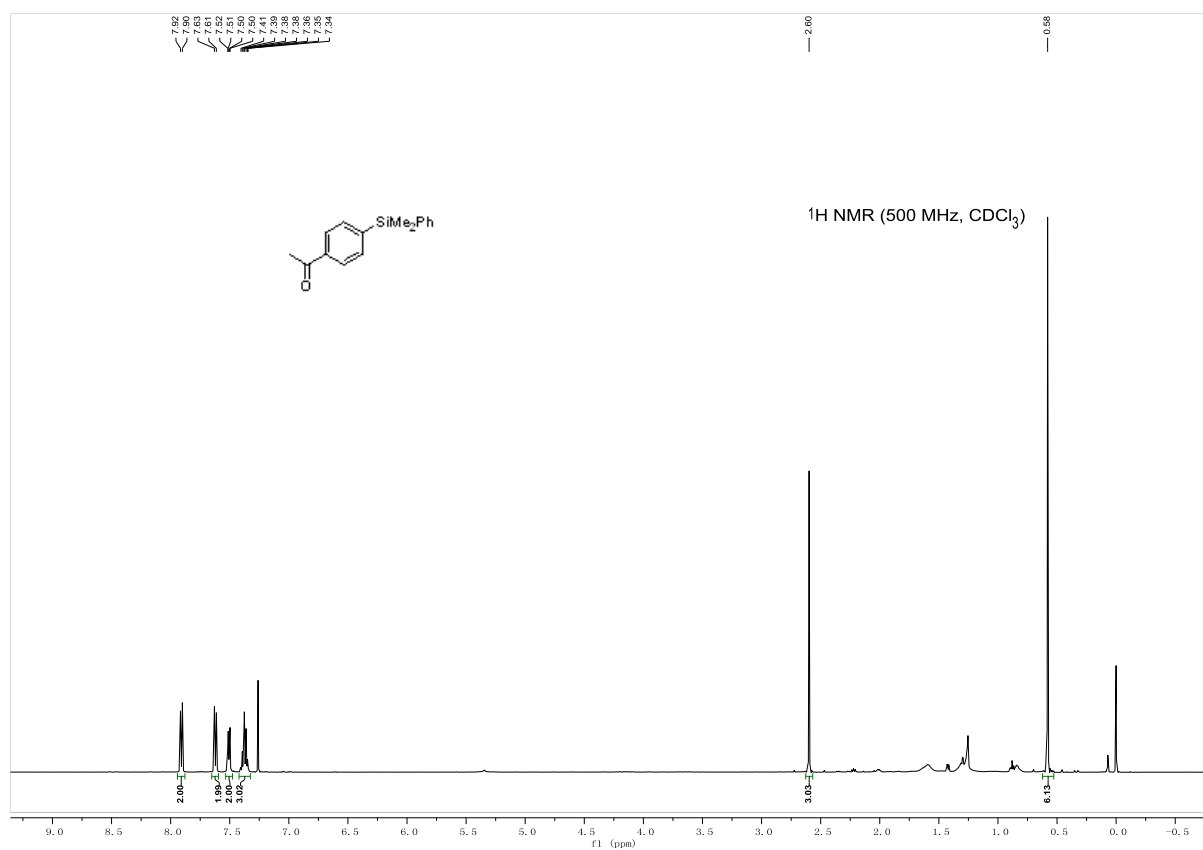




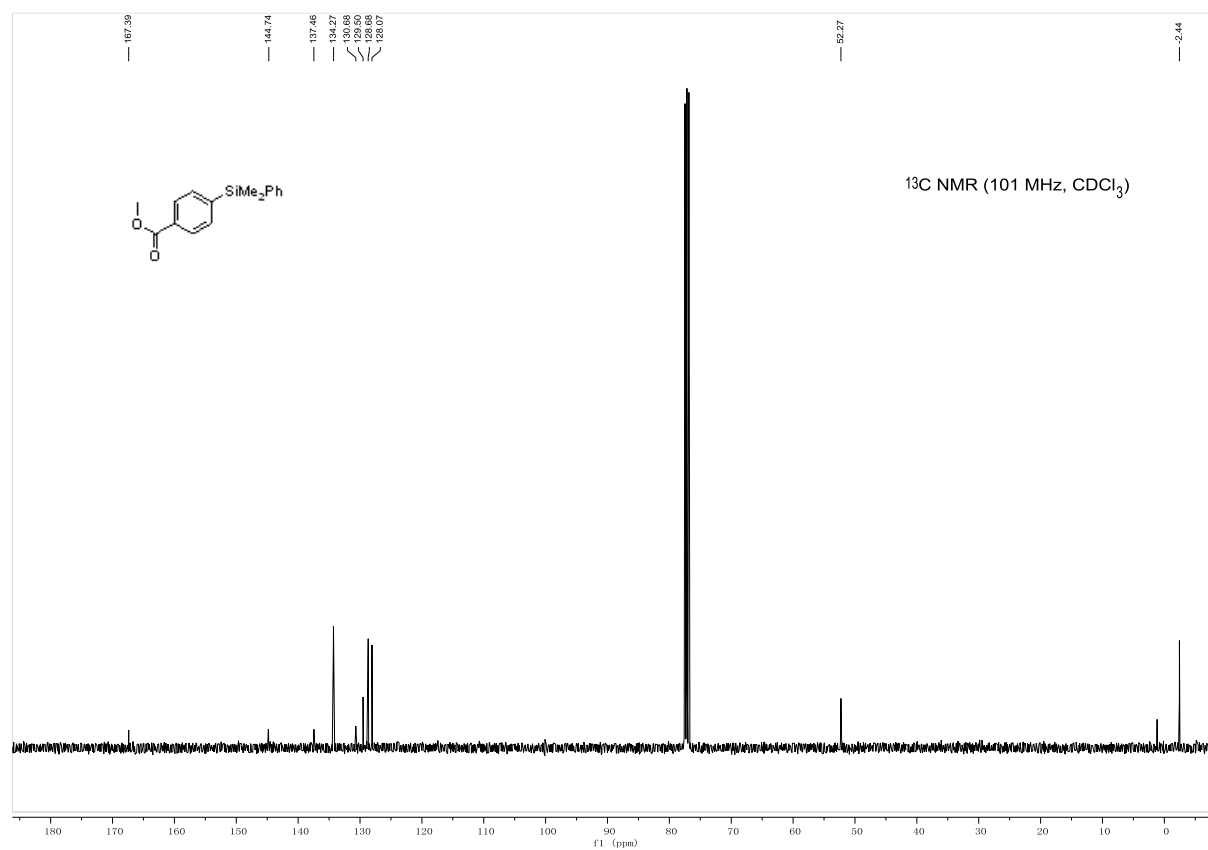
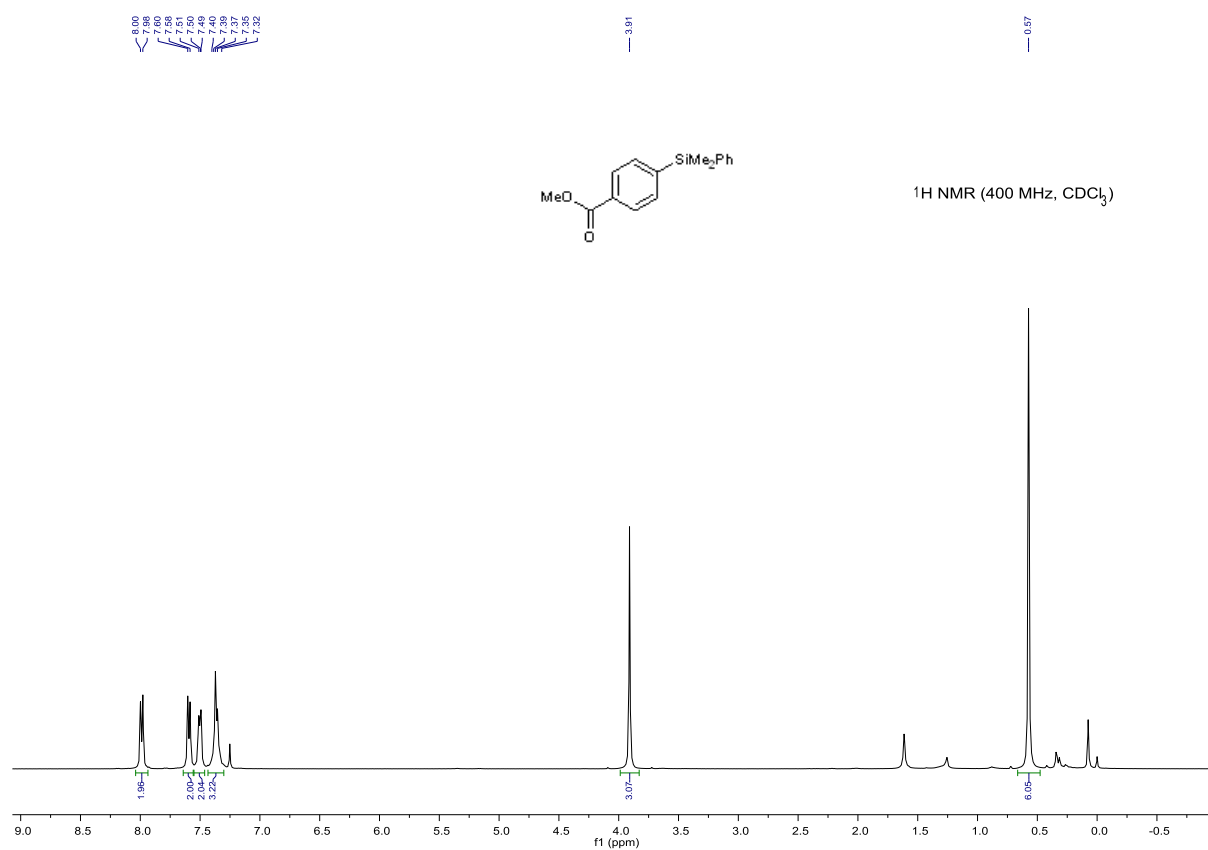
(4-(Dimethyl(phenyl)silyl)phenyl)(phenyl)methanone (**3m**)



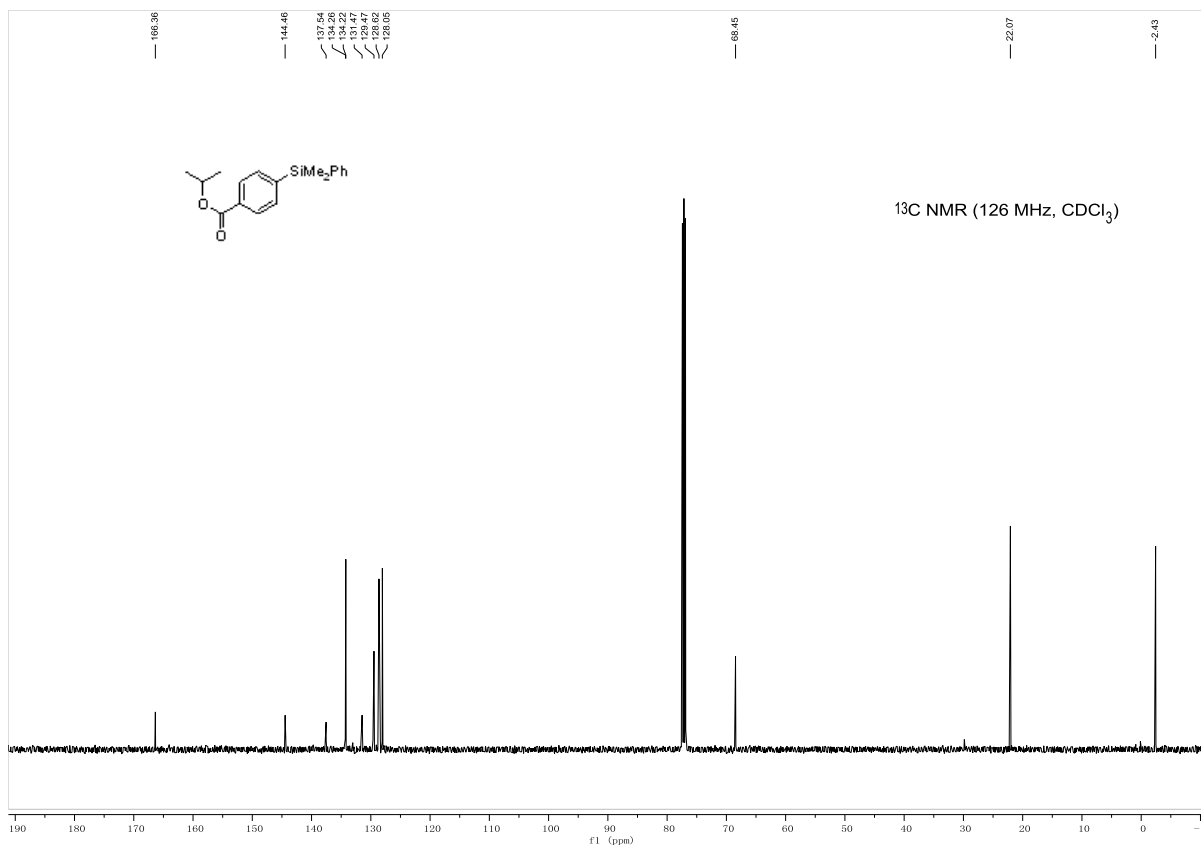
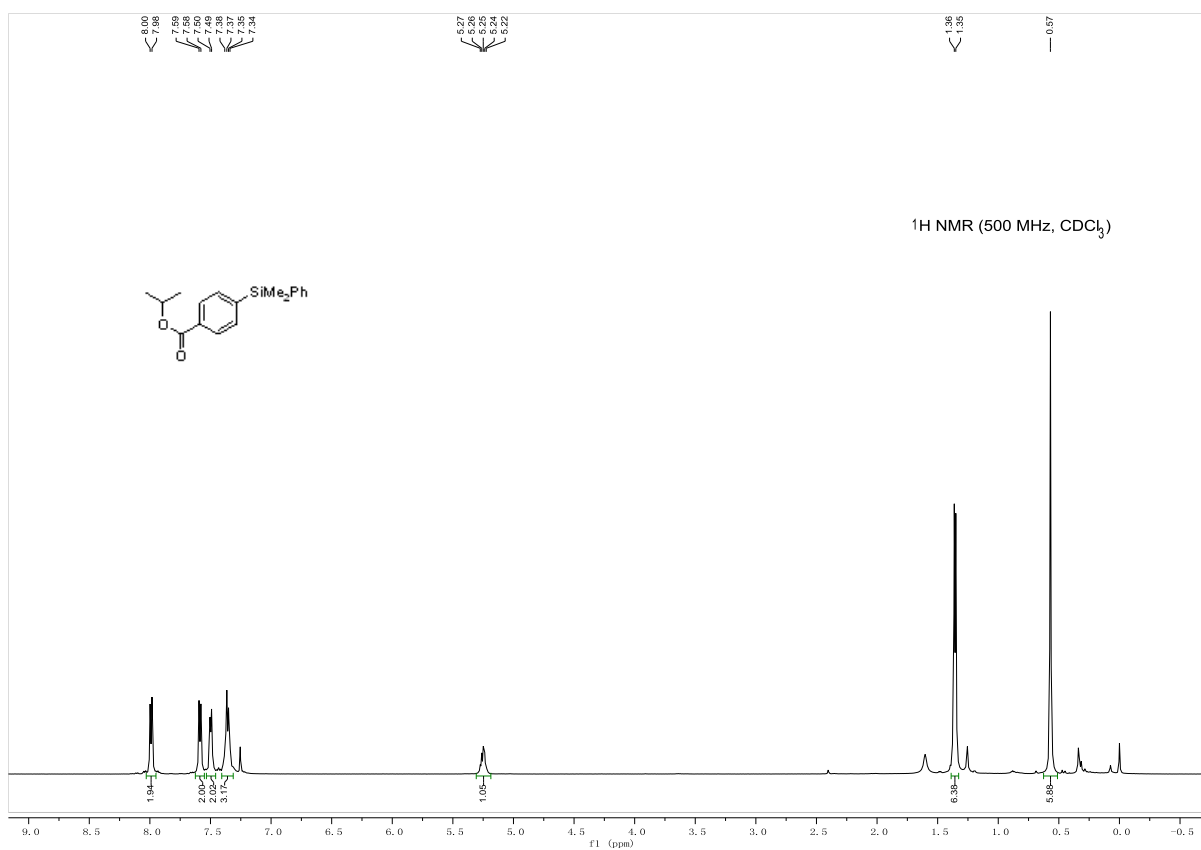
1-(4-(Dimethyl(phenyl)silyl)phenyl)ethan-1-one (**3n**)



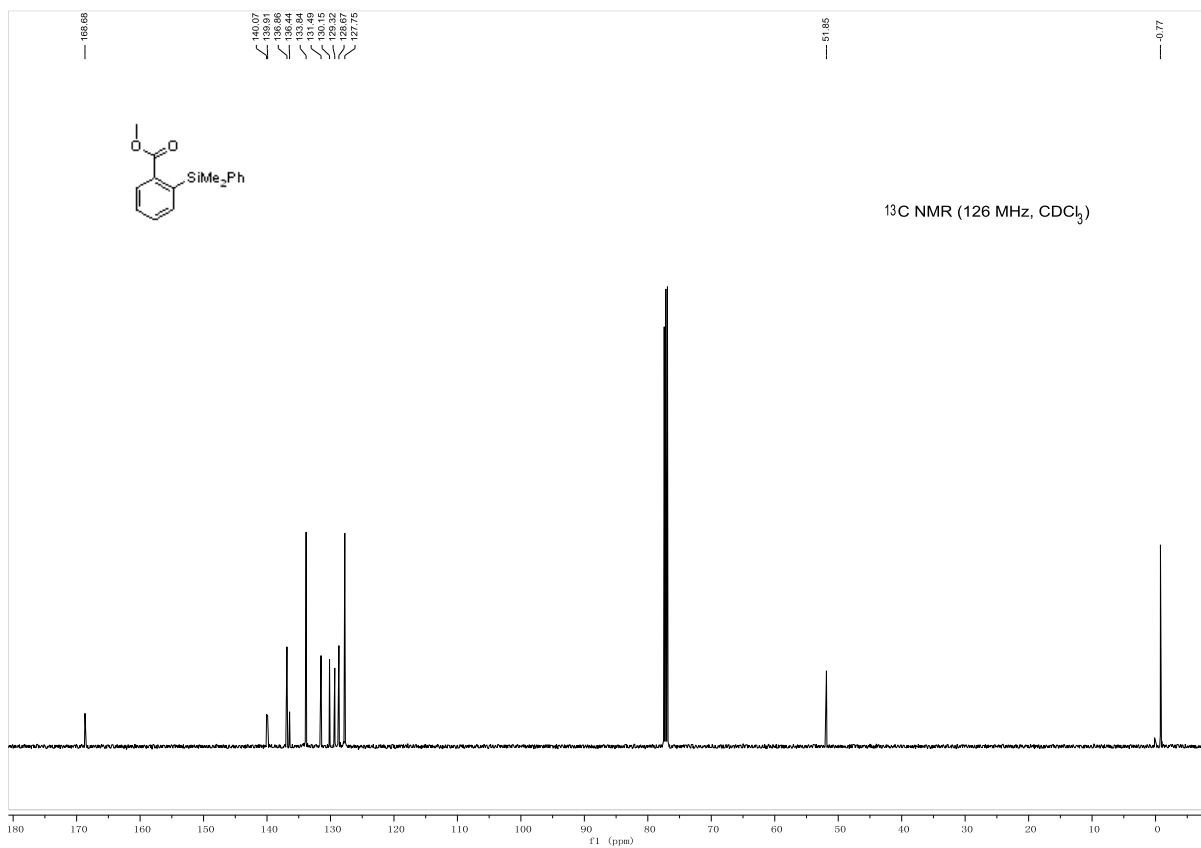
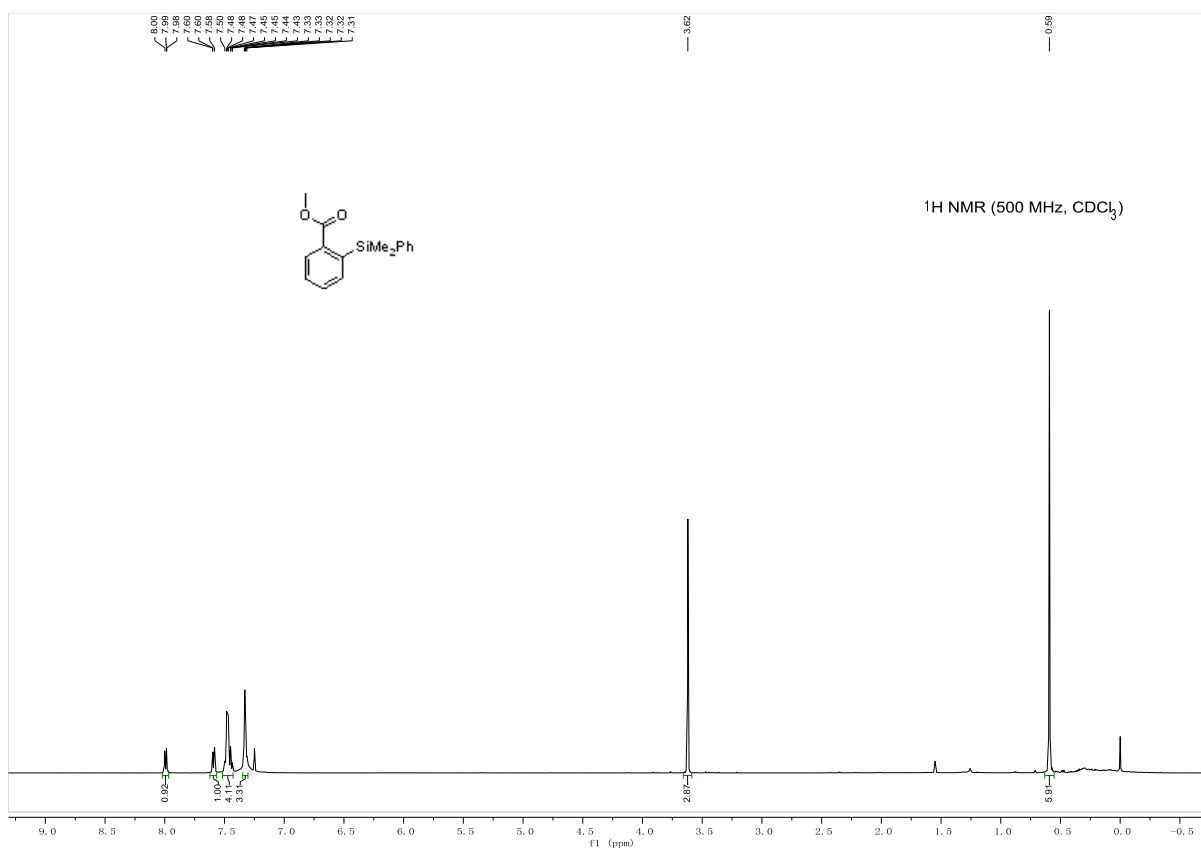
Methyl 4-(dimethyl(phenyl)silyl)benzoate (**30**)



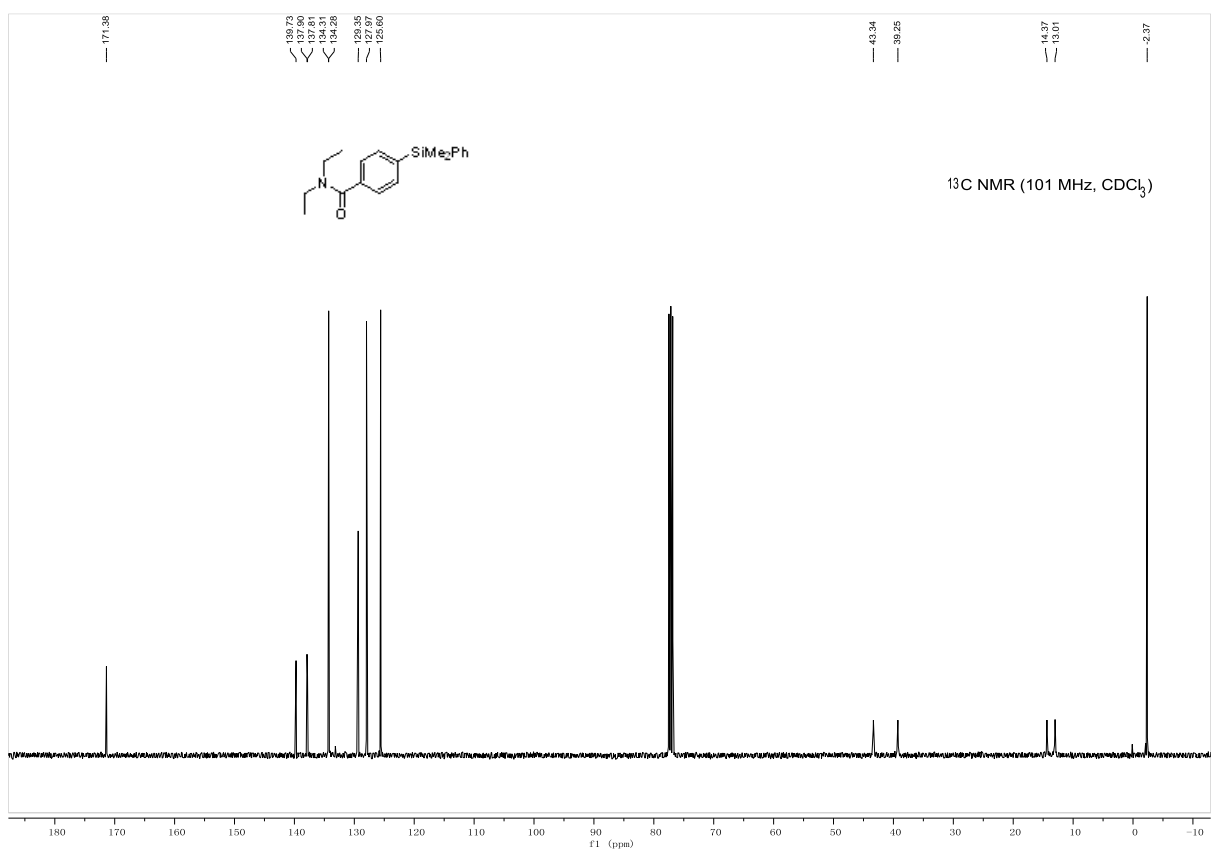
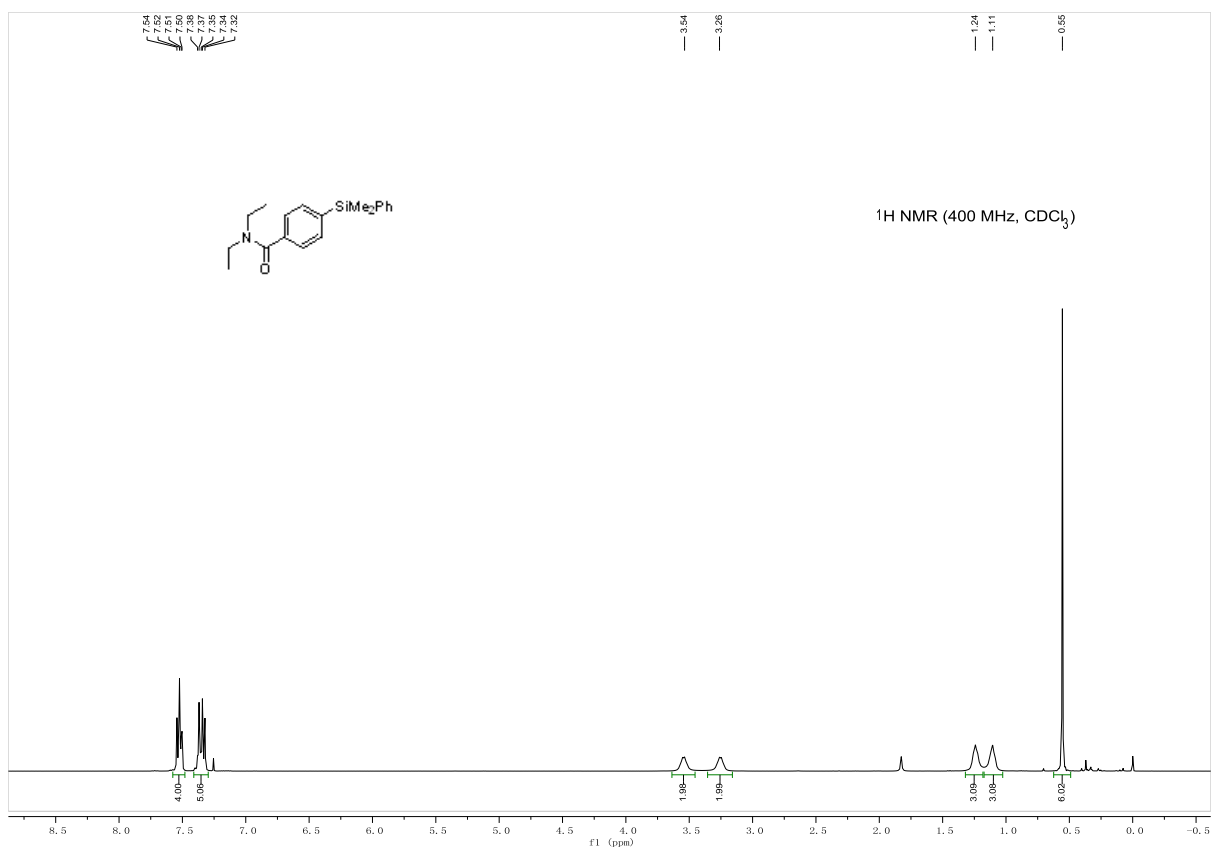
Isopropyl 4-(dimethyl(phenyl)silyl)benzoate (**3p**)



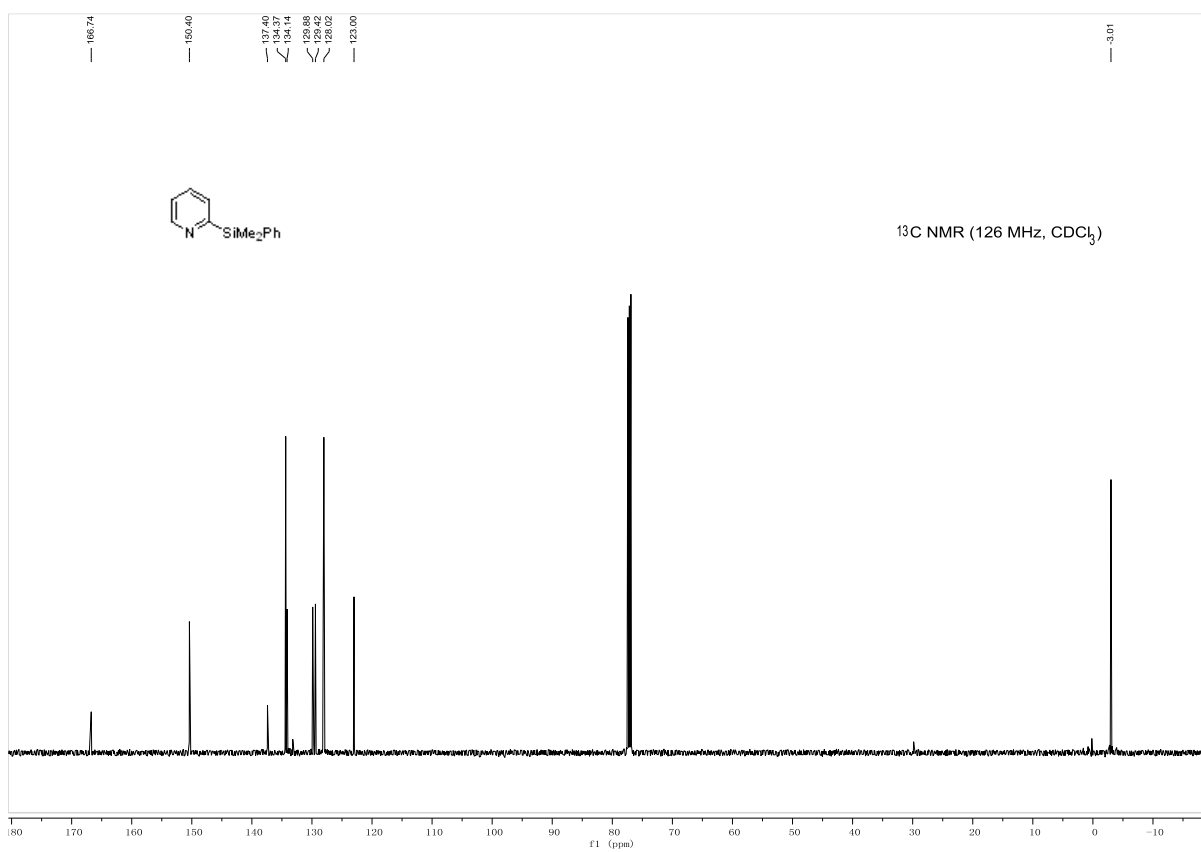
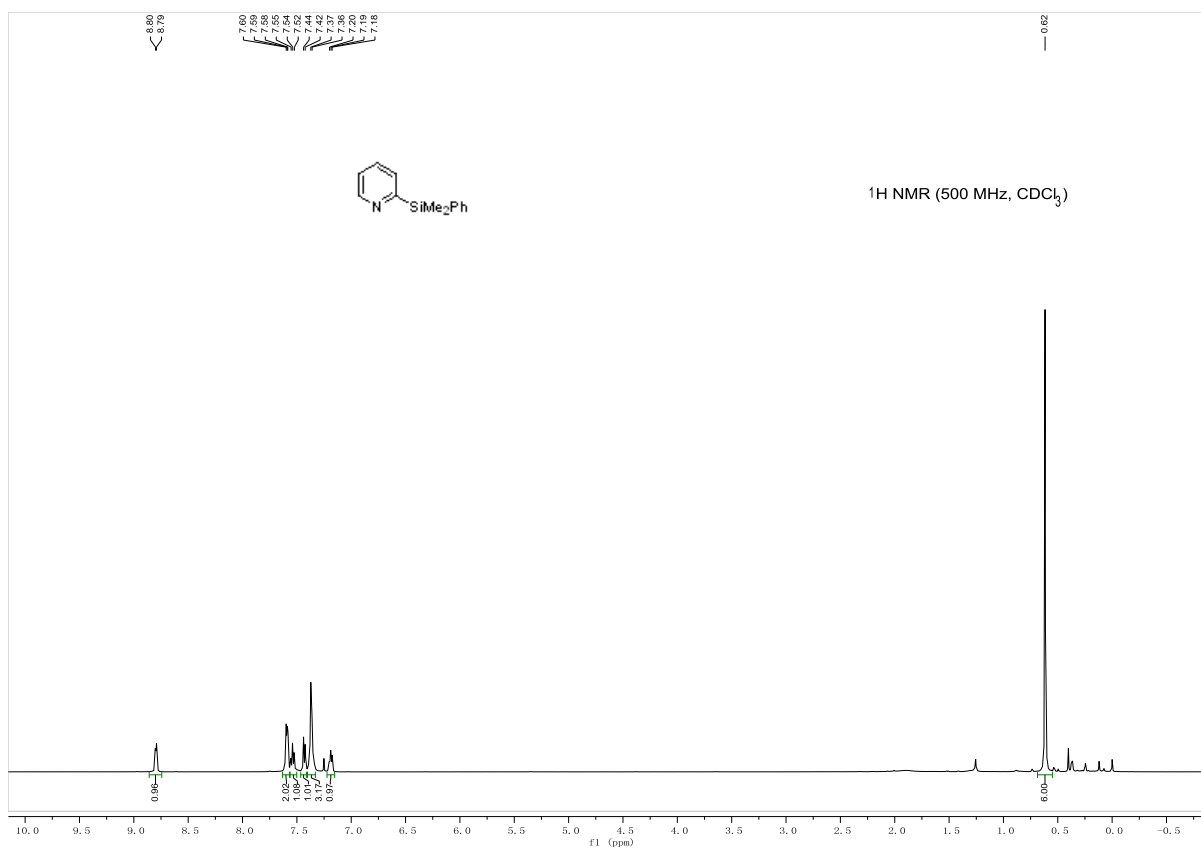
Methyl 2-(dimethyl(phenyl)silyl)benzoate (**3q**).



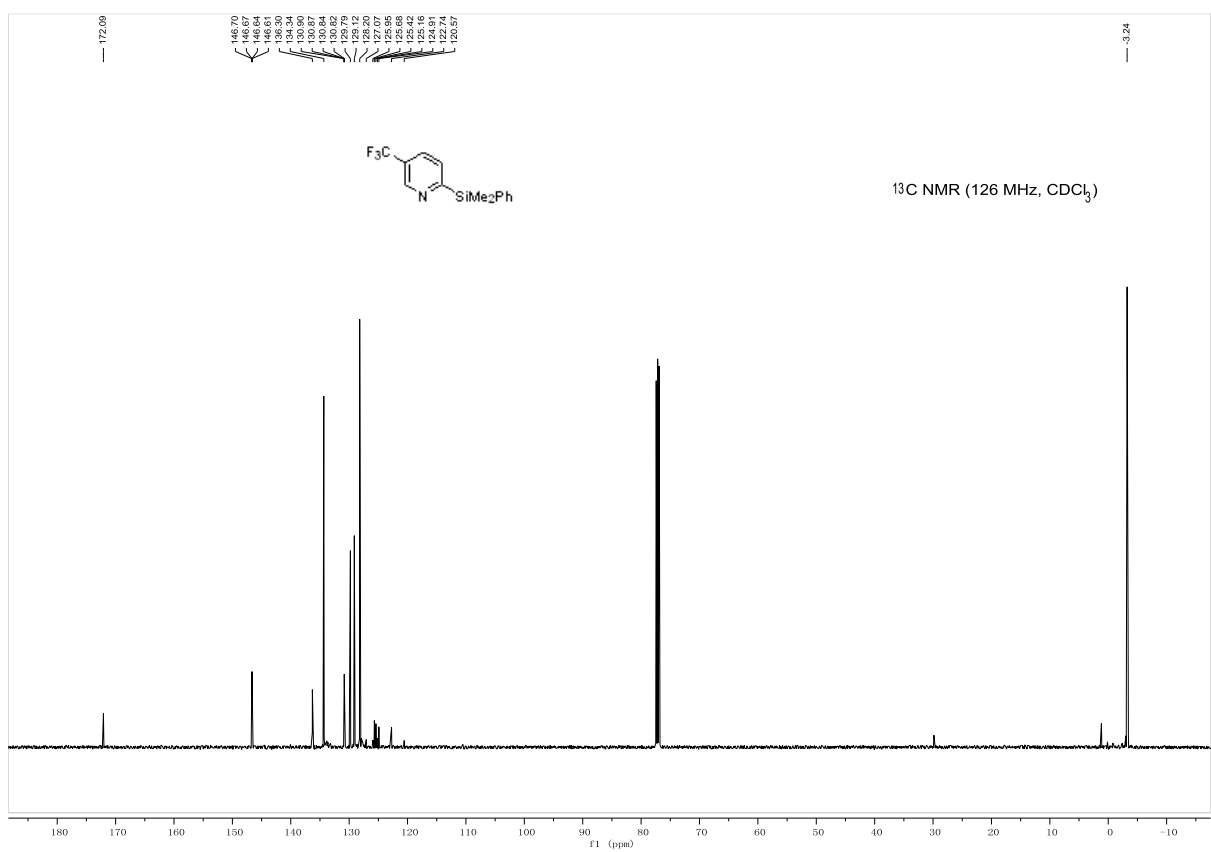
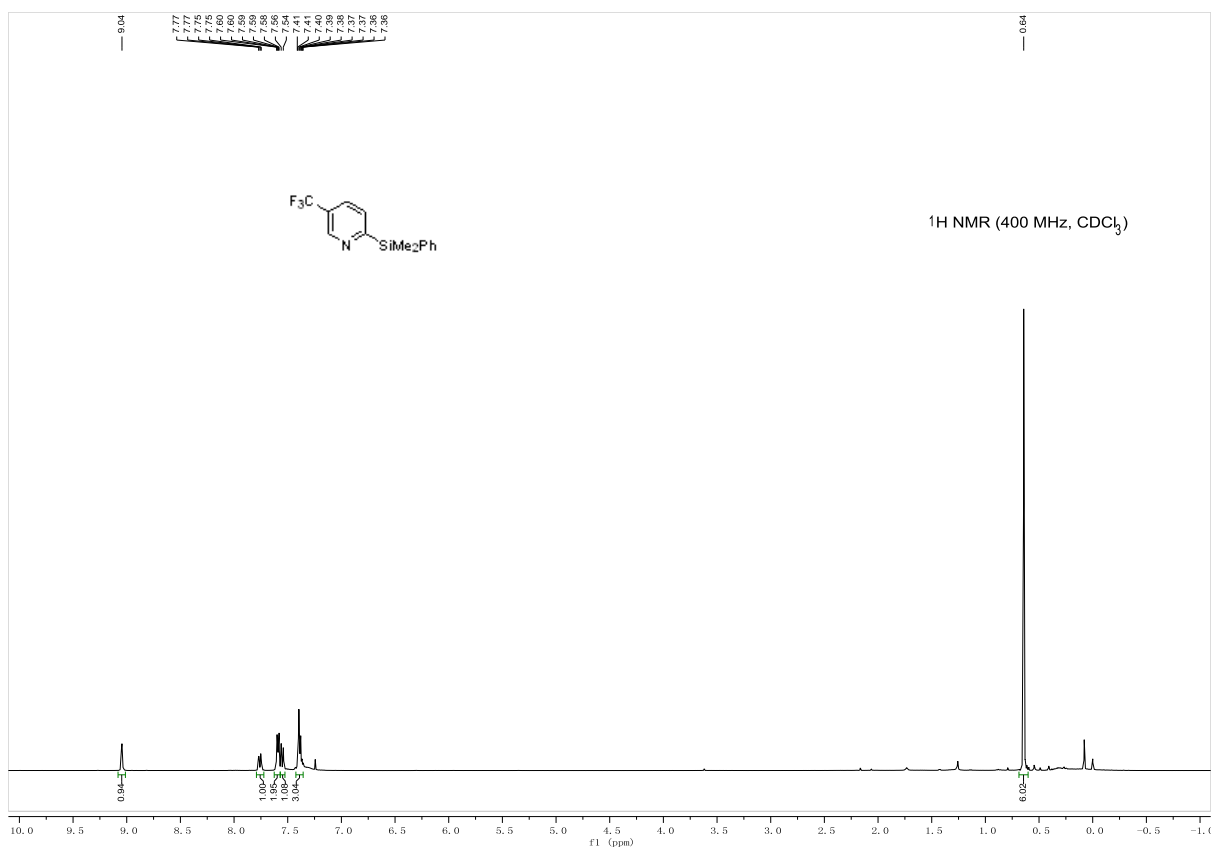
4-(Dimethyl(phenyl)silyl)-N,N-diethylbenzamide (**3r**)

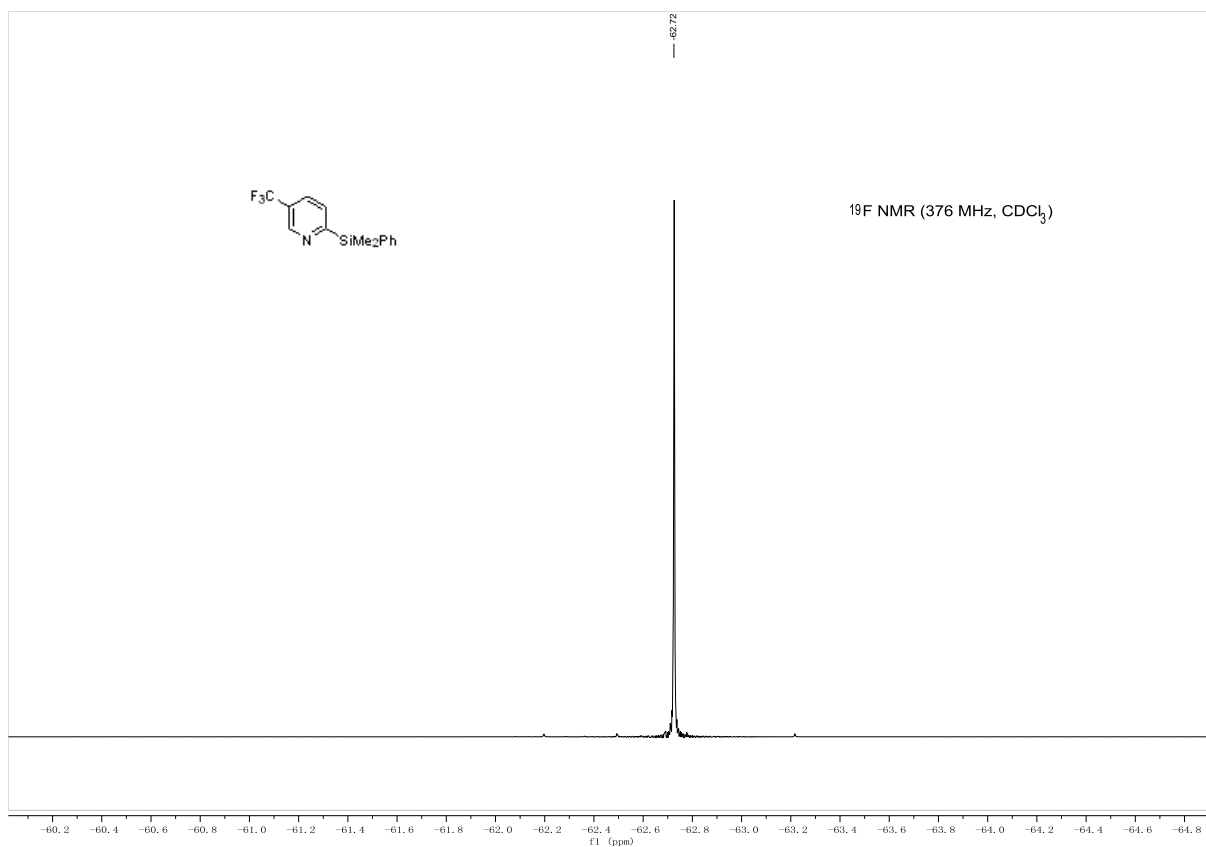


2-(Dimethyl(phenyl)silyl)pyridine (3s)

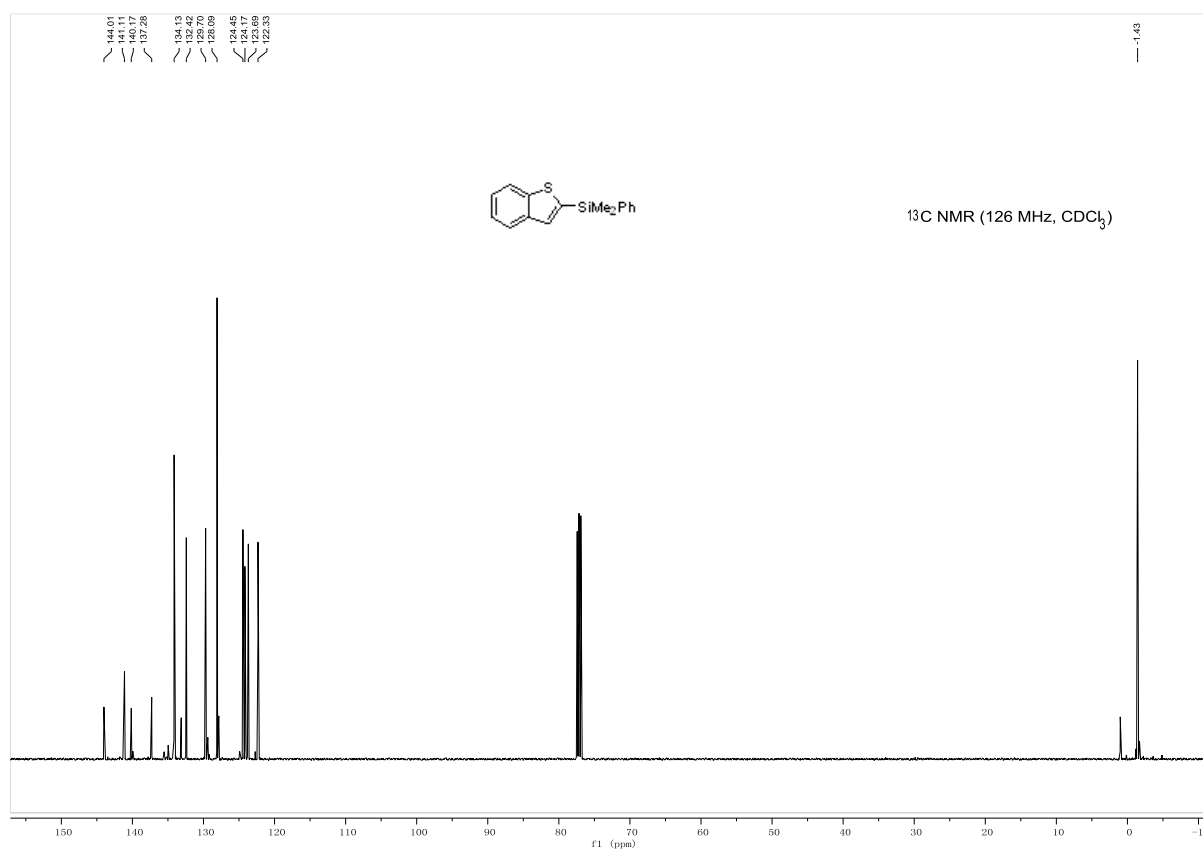
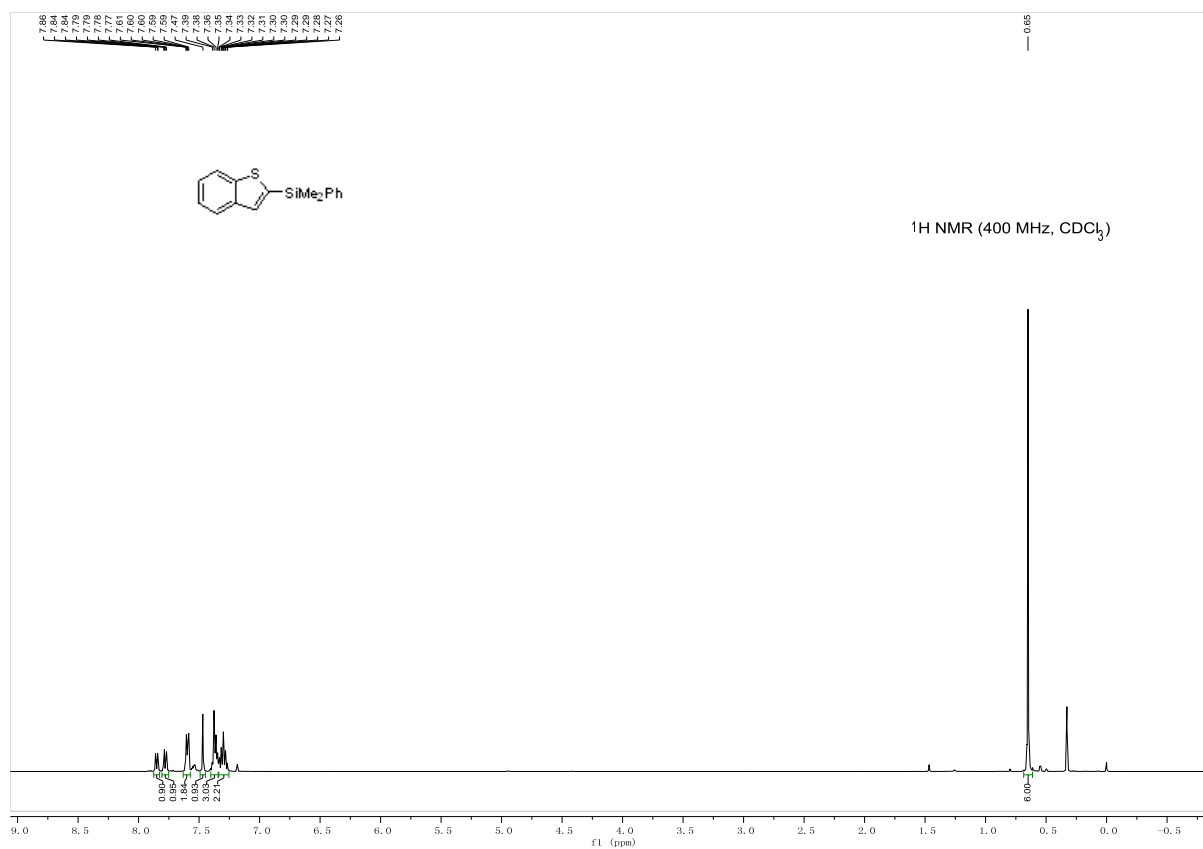


2-(Dimethyl(phenyl)silyl)-4-(trifluoromethyl)pyridine (3t)

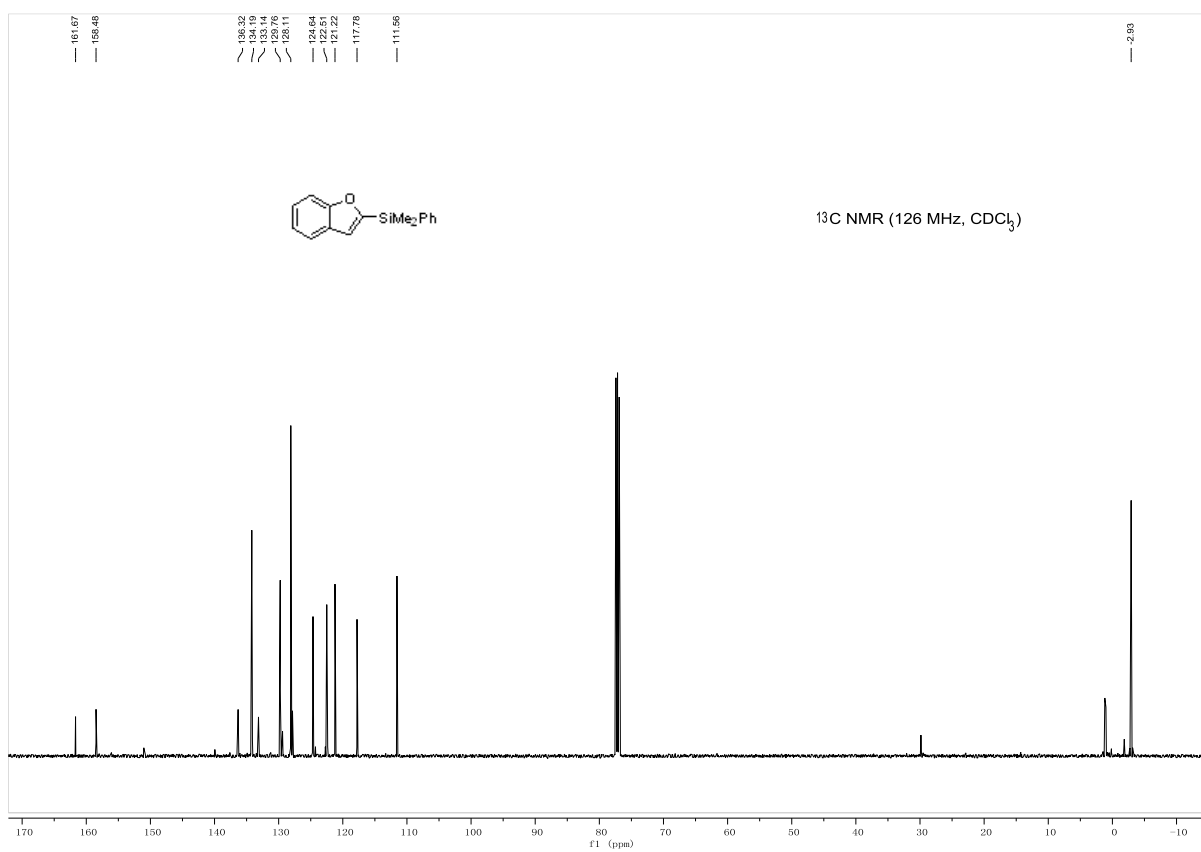
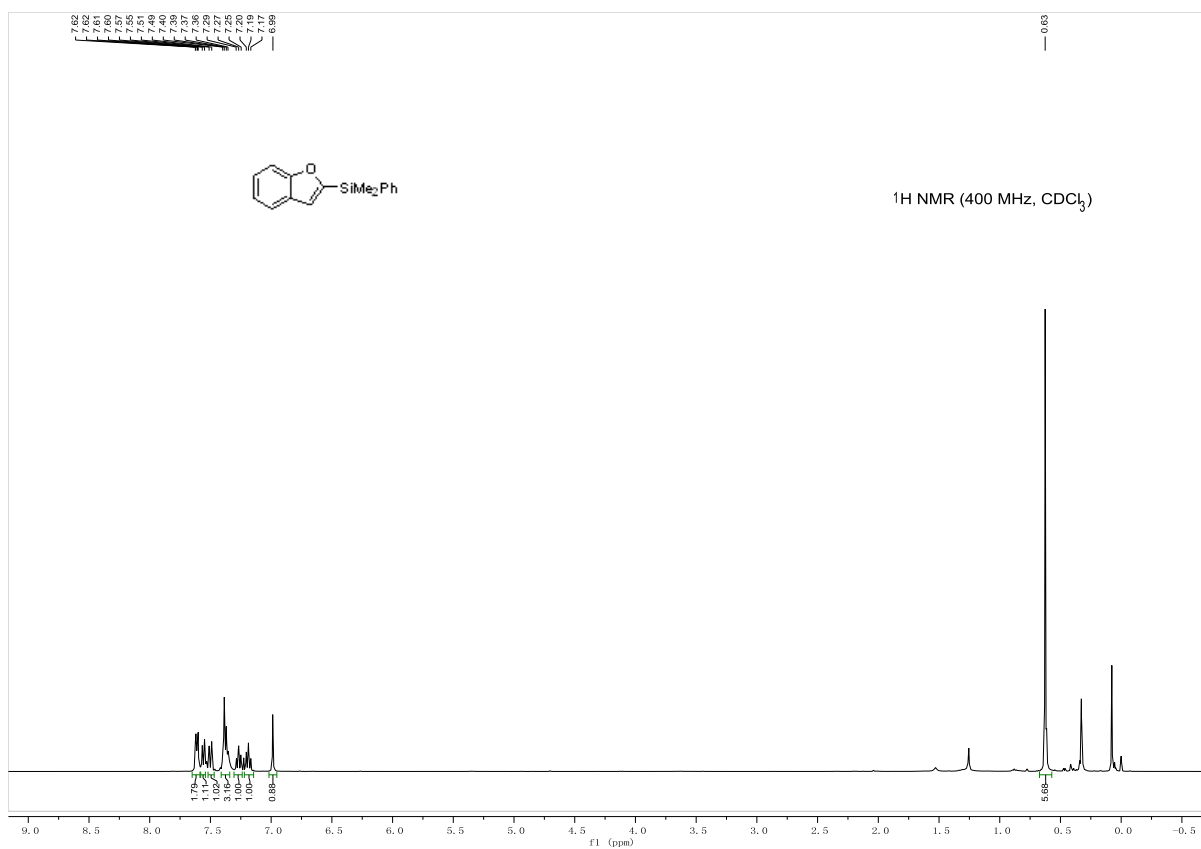




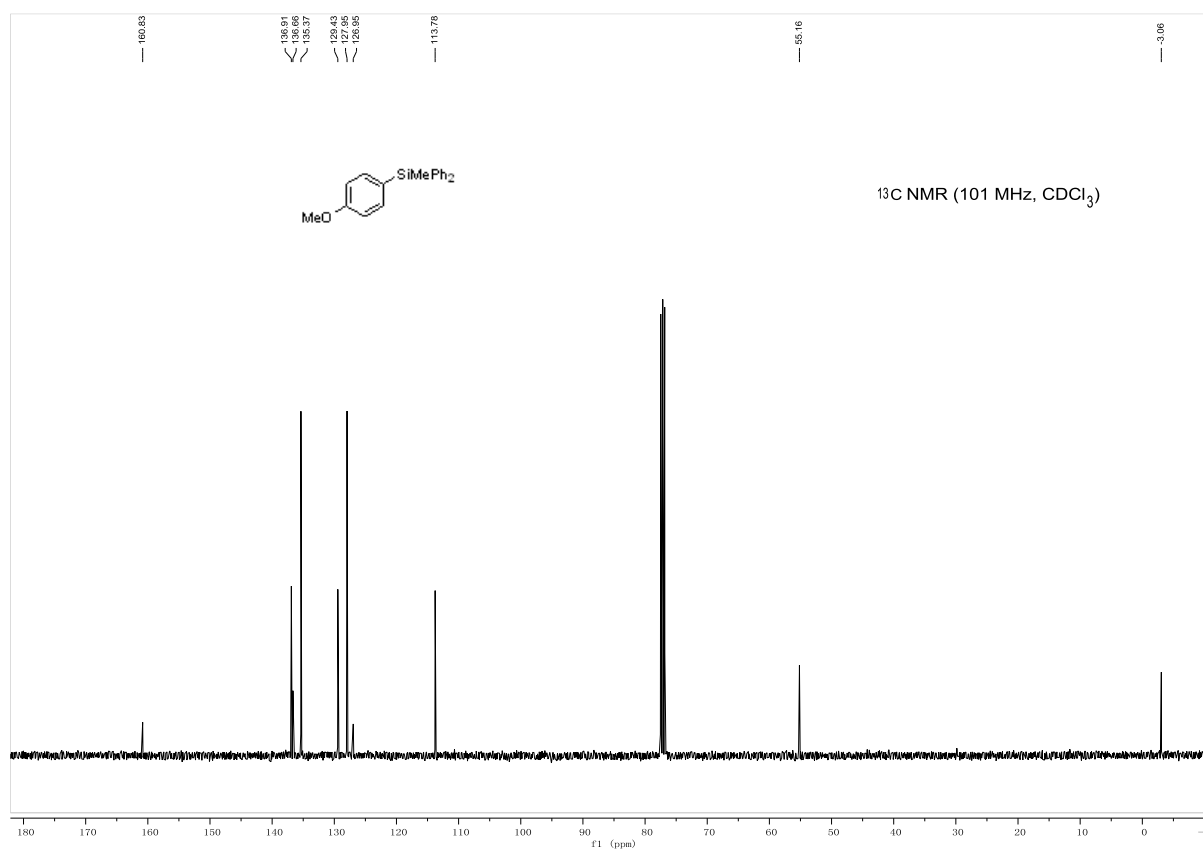
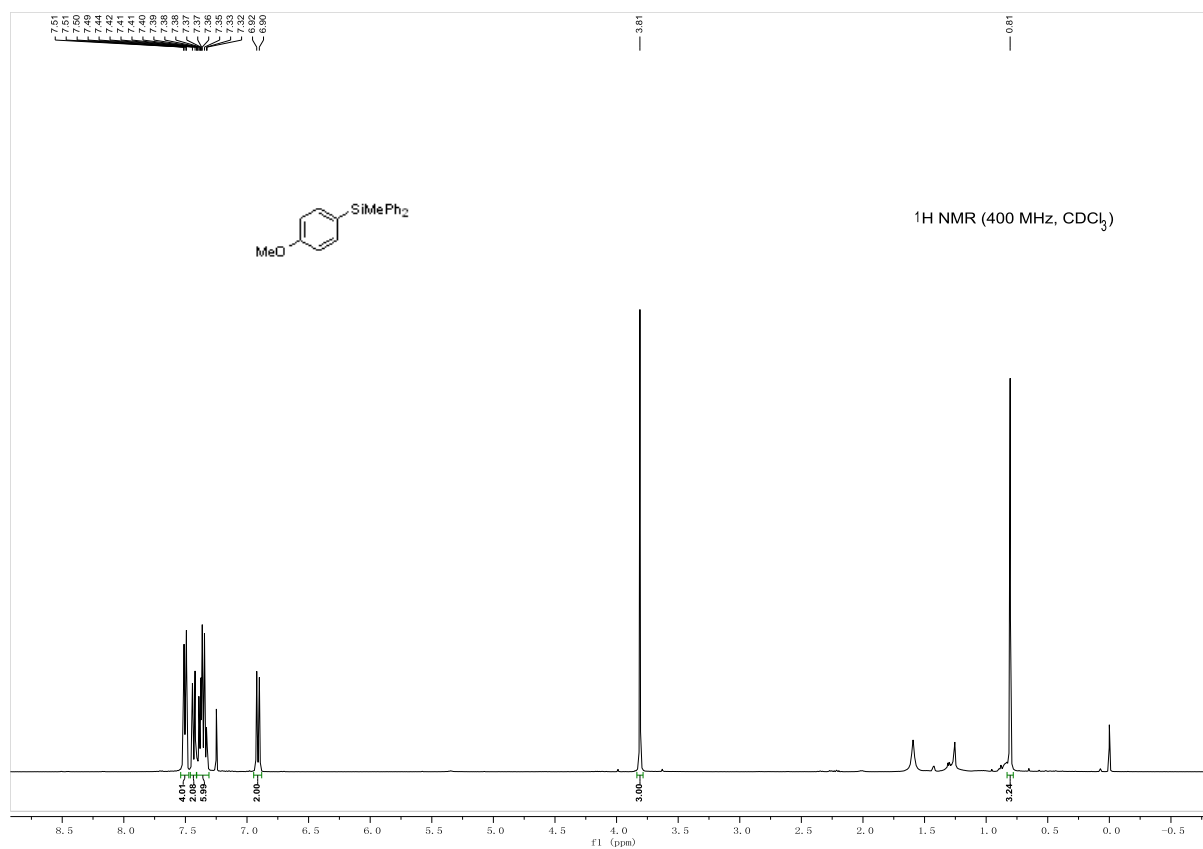
Benzo[b]thiophen-2-yl dimethyl(phenyl)silane (**3u**)



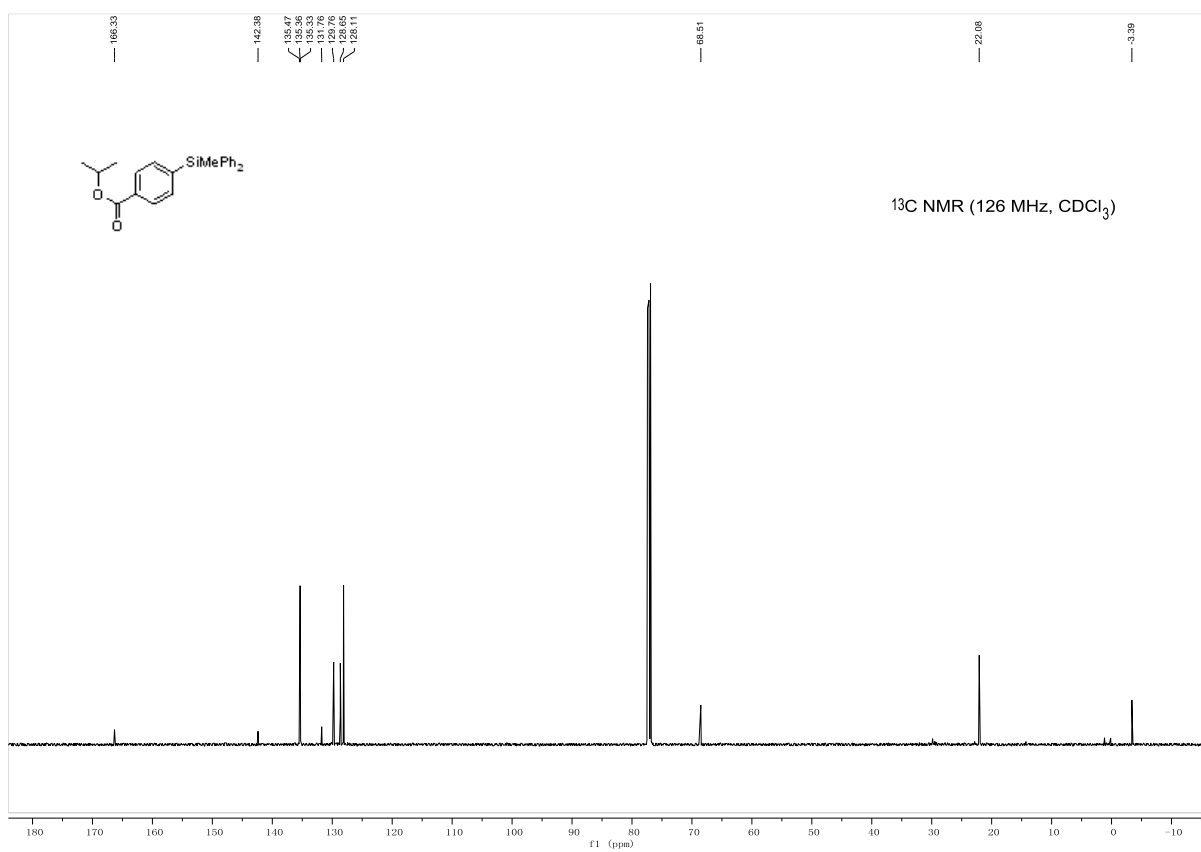
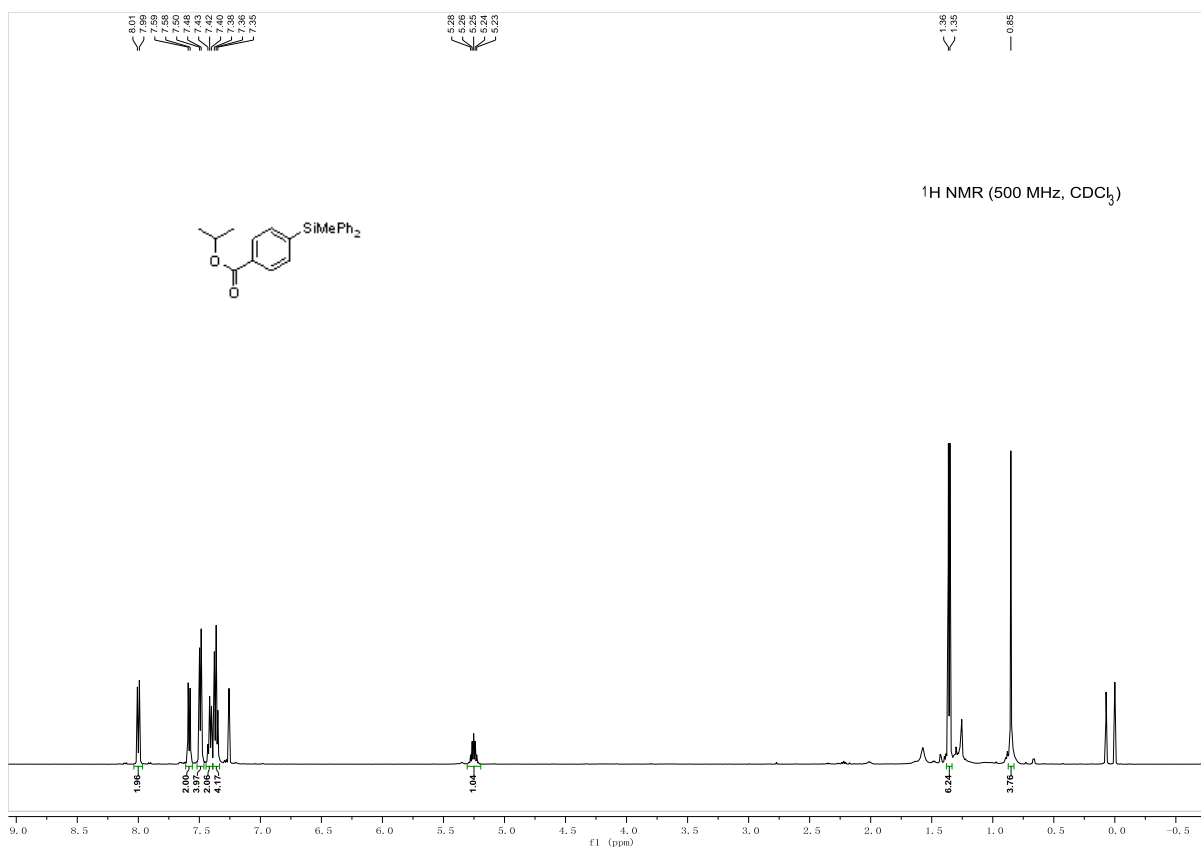
Benzofuran-2-yl dimethyl(phenyl)silane (**3v**)



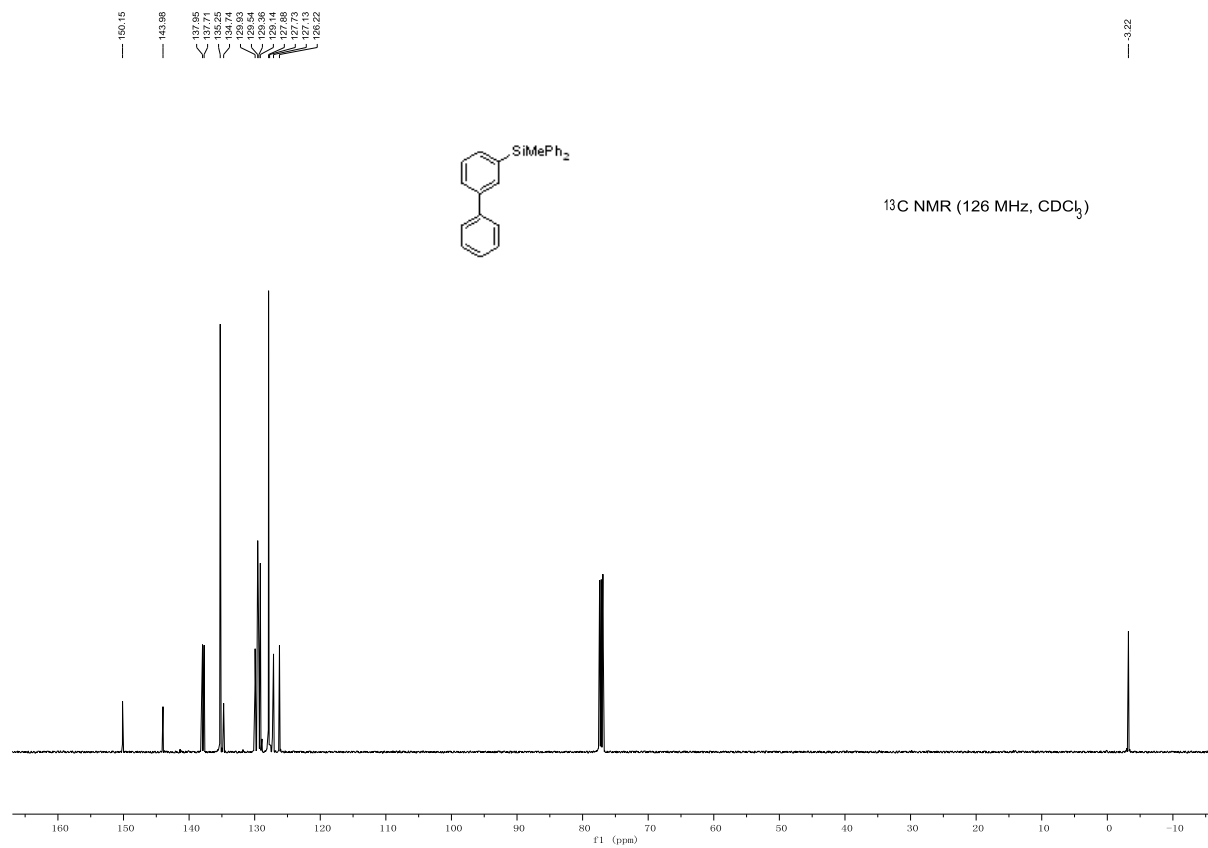
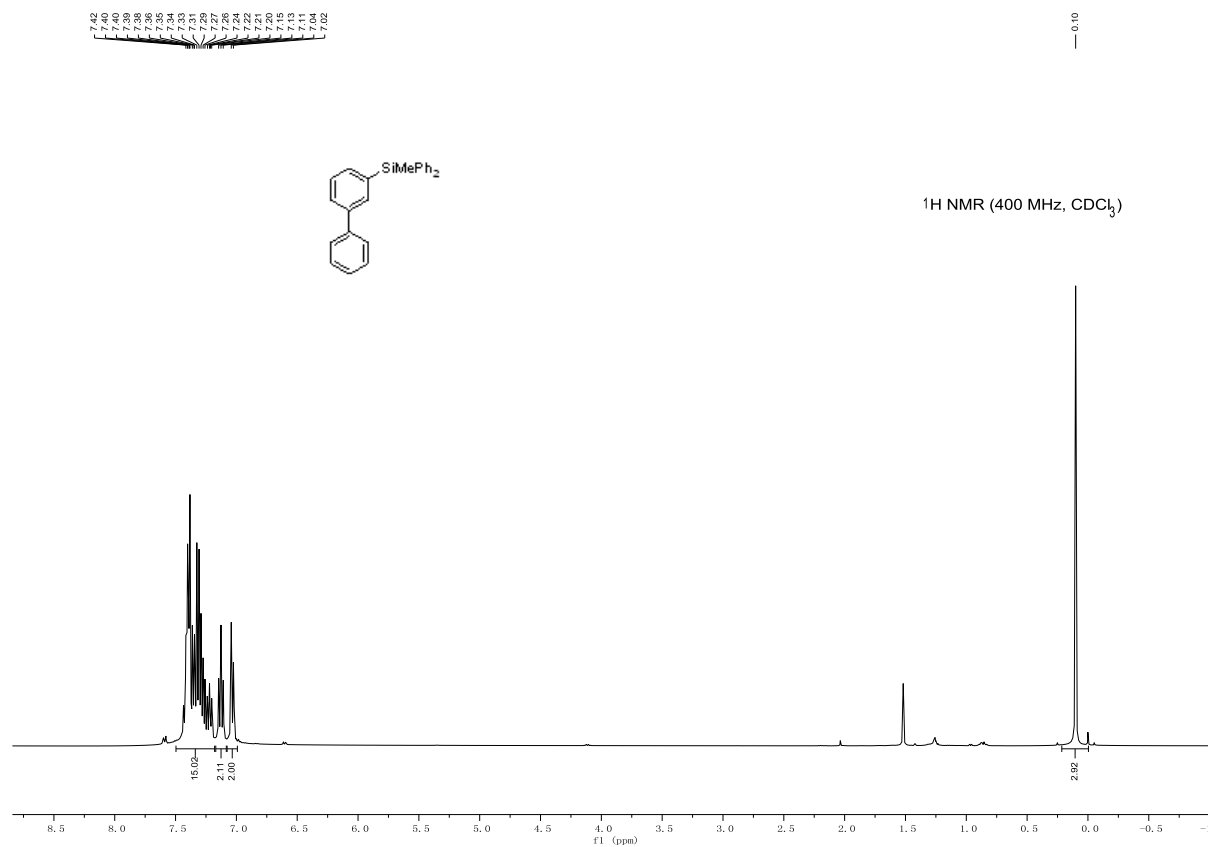
(4-Methoxyphenyl)(methyl)diphenylsilane (**4a**)



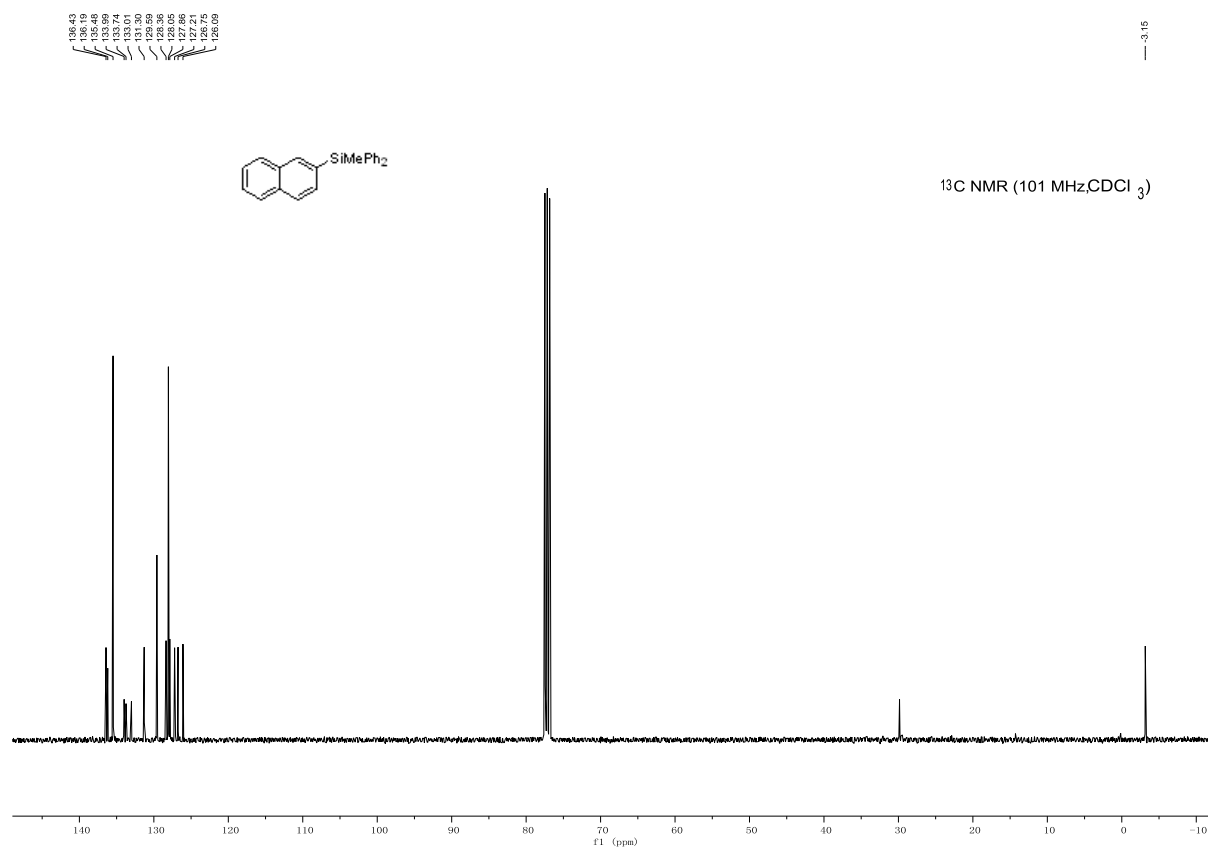
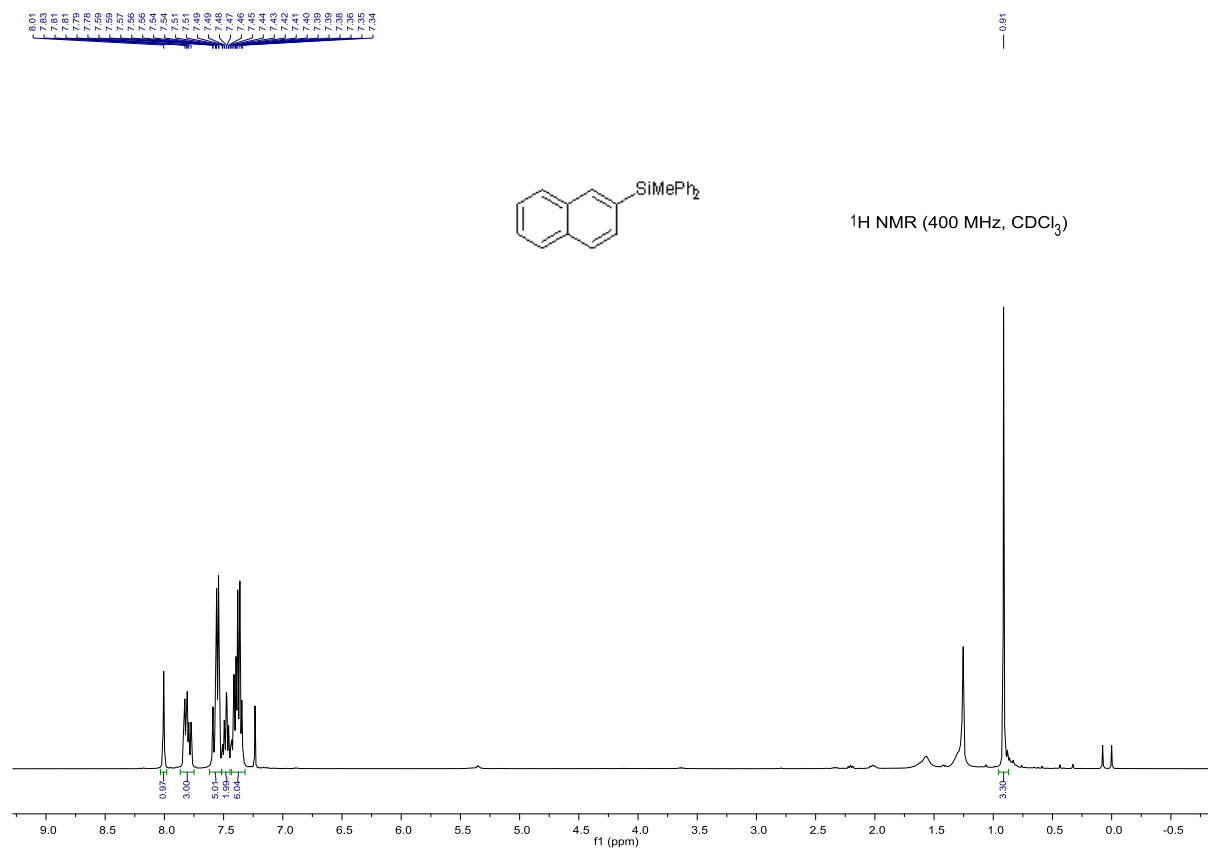
Isopropyl 4-(methyldiphenylsilyl)benzoate (**4b**)



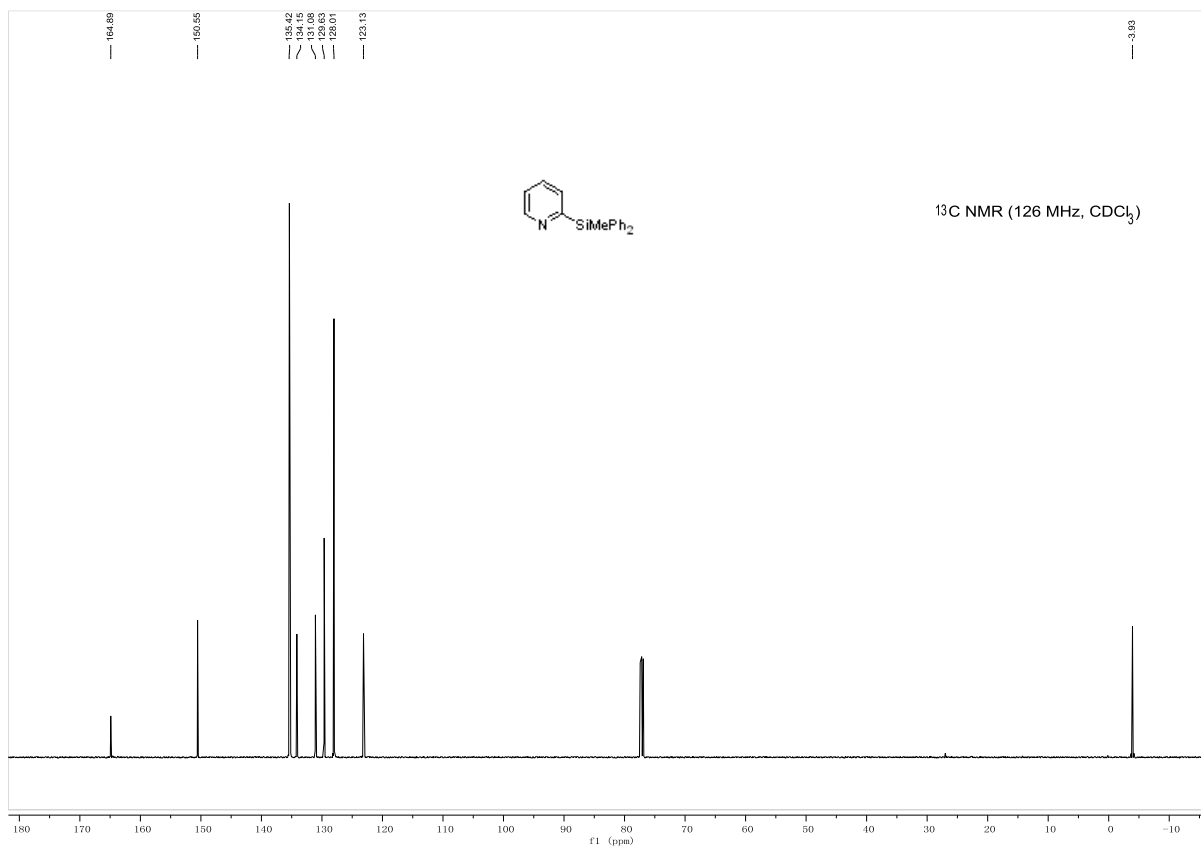
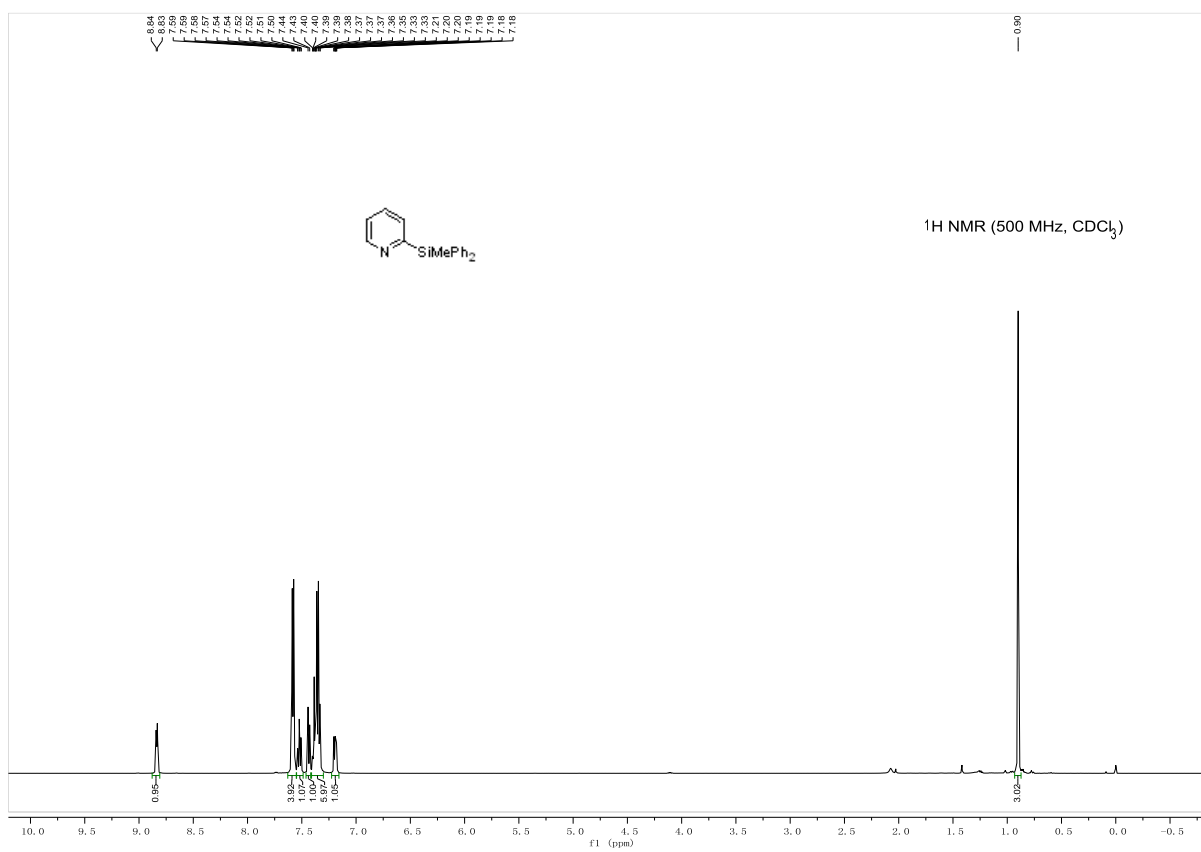
[1,1'-Biphenyl]-3-yl(methyl)diphenylsilane (**4c**)



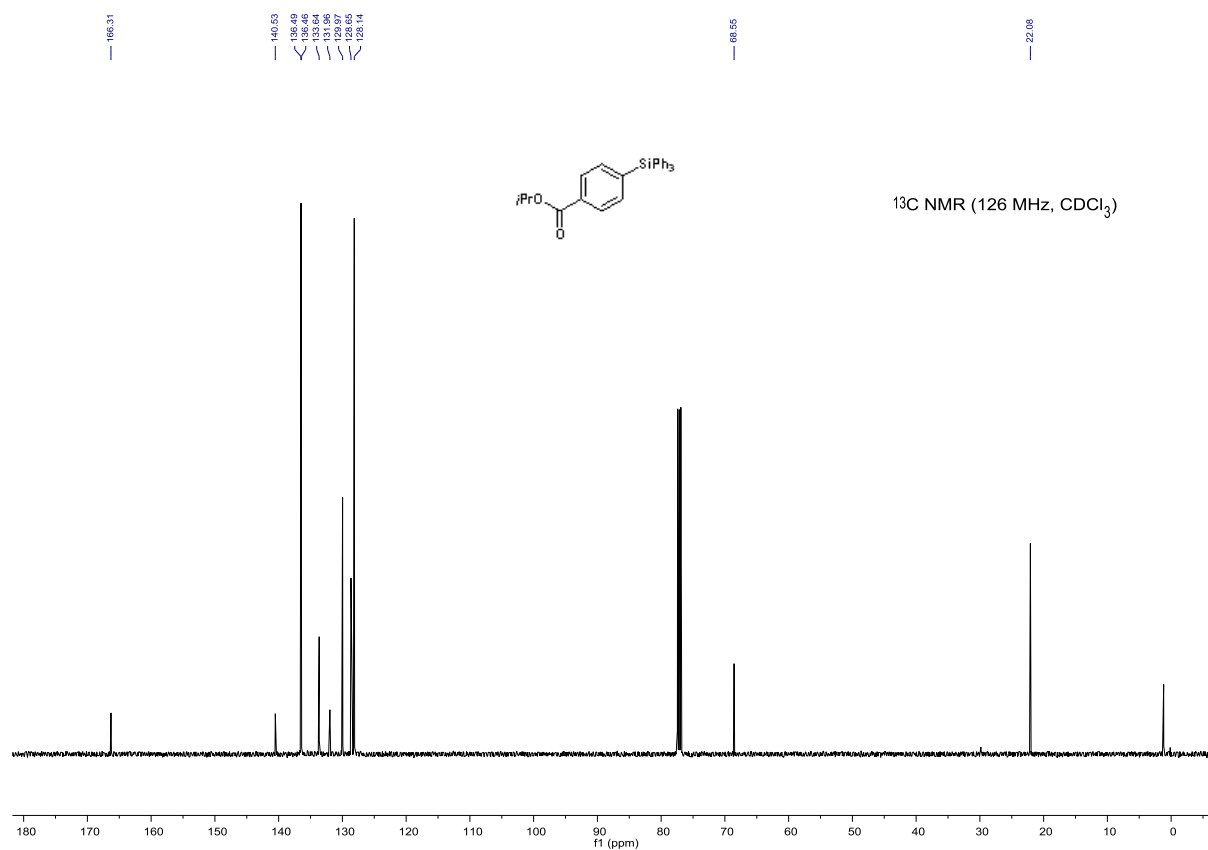
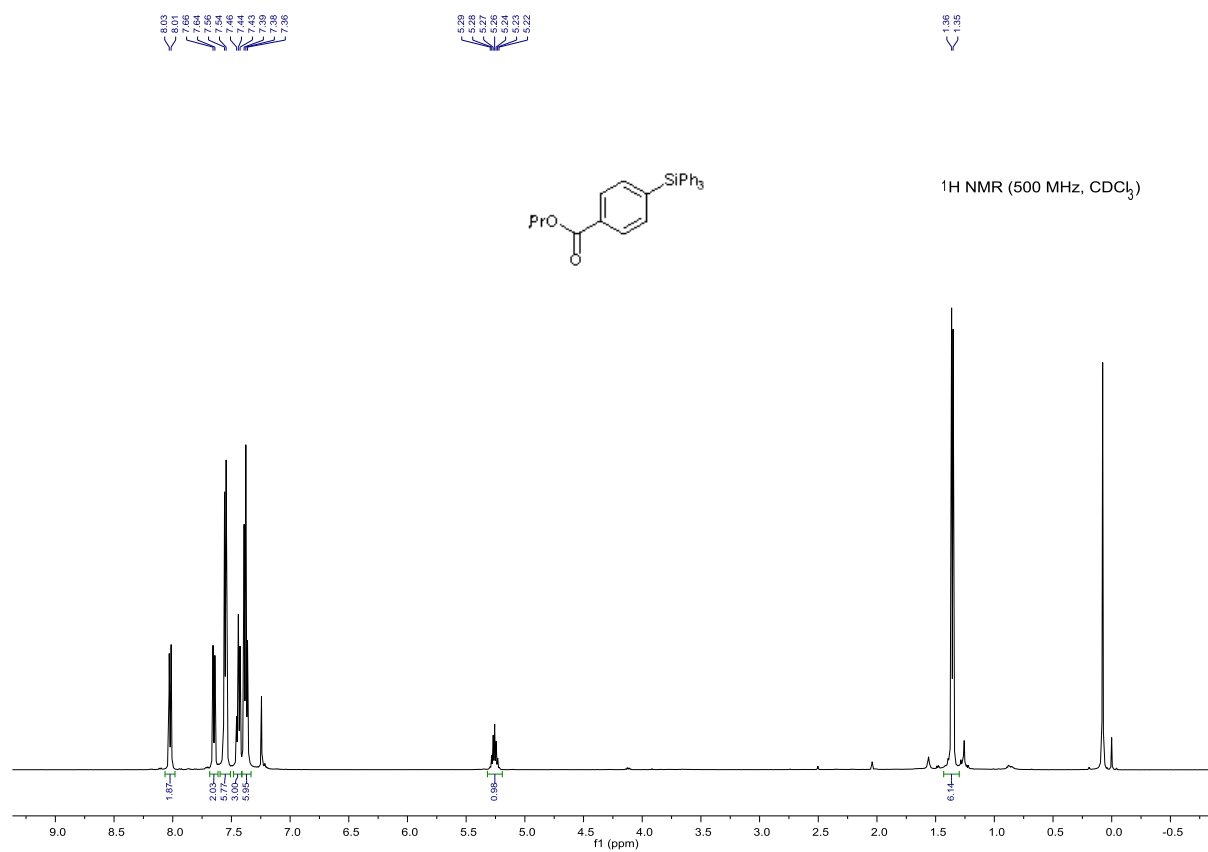
Methyl(naphthalen-2-yl)diphenylsilane (**4d**)



2-(Methyldiphenylsilyl)pyridine (**4e**)



Isopropyl 4-(triphenylsilyl)benzoate (**5a**)



2-(Triphenylsilyl)pyridine (**5b**)

