Supplementary Information for

Copper-catalyzed silylation of aryl and alkenyl triflates with silylboronic esters avoiding base-mediated borylation

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General remarks.

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon atmosphere. Nuclear magnetic resonance spectra were taken on a Varian System 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) spectrometer using residual chloroform (^{1}H, δ = 7.26), $CDCl_3$ (^{13}C, δ = 77.16) as an internal standard. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer. Column chromatography was carried out using Merck Kieselgel 60. Unless otherwise noted, commercially available reagents were used without purification. Solvents were dried over activated molecular sieves 3Å.

Preparation of trialkylsilylboronic esters.[1]

A Schlenk tube equipped with a magnetic stirring bar was charged with tris(*N,N*-tetramethylene)phosphoric acid triamide (TPPA) (10 mL), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (10 mL), a hexaalkyl disilane (12.5 mmol), and the solution was cooled to –60 °C under nitrogen atmosphere (caution: all liquid materials must be distilled before reaction setup). MeLi in diethy ether (12.5 mmol) was added via syringe at once and the mixture was immediately warmed to 20 °C. The reaction mixture was stirred at 20 °C for 5 minutes and was cooled to –60 °C. To the solution was added *i*-PrO–B(pin) (2.32 g, 12.5 mmol), and the mixture was stirred at 20 °C for 1 h. The reaction mixture was directly subjected to silica gel-column chromatography (the outside diameter of chromatographic-tube was 84 mm; 300 g of silica gel and an eluent consisting of hexane/ethyl acetate = 30:1 were used) to isolate a trialkylsilylboronic ester as colorless oil. A trialkylsilylboronic ester was detected with TLC analysis using Seebach's stain and stored under nitrogen atmosphere in refrigerator.

Preparation of aryl triflates.

A solution of trifluoromethanesulfonic anhydride (3.4 g, 12 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of the corresponding phenol (10 mmol) and pyridine (1.8 mL, 20 mmol) in anhydrous CH_2Cl_2 (10 mL) at rt. After completion of the addition, the mixture was stirred for 1 h. The mixture was then diluted with Et_2O (15 mL), quenched with 10 % aq. HCl and washed successively with sat. $NaHCO_3$ and brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by silica gel-column chromatography to give the triflates (hexane:ethyl acetate = 10:1 as an eluent).

Preparation of alkenyl triflates.

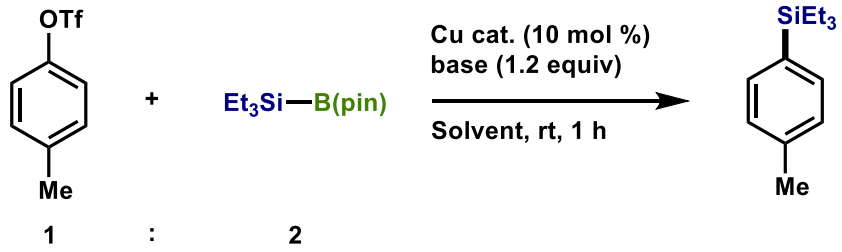
A solution of trifluoromethanesulfonic anhydride (3.4 g, 12 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a solution of the corresponding ketone (10 mmol) and sodium carbonate (2.1 g, 20 mmol) in anhydrous CH_2Cl_2 (10 mL) at rt. After completion of the addition, the mixture was stirred for 1 h. The mixture was then diluted with Et_2O (15 mL), quenched with 10% aq. HCl and washed successively with sat. $NaHCO_3$ and brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure and the residue was purified by silica gel-column chromatography to give the triflates (hexane:ethyl acetate = 10:1 as an eluent).

Preparation of TfO–C_6H_4–B(dan) and TfO–C_6H_4–B(pin).[2]

A flask equipped with a magnetic stirring bar was charged with (pin)B–B(dan) (3.5 g, 12 mmol) or (pin)B–B(pin) (3.0 g, 12 mmol), CuI (0.11 g, 0.60 mmol), THF (20 mL), tricyclohexylphosphine (20 wt% toluene solution, 1.7 g, 1.2 mmol), potassium *tert*-butoxide (1.0 M THF solution, 7.2 mL, 7.2 mmol) and 4-bromophenyl triflate (1.8 g, 6.0 mmol). After the mixture was stirred at rt for 2 h, the mixture was diluted with ethyl acetate and the organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The product was isolated by silica gel-column chromatography (hexane:ethyl acetate = 10:1 as an eluent).

Optimization of reaction conditions.

A Schlenk tube equipped with a magnetic stirring bar was charged with Et_3Si–B(pin) (0.15 g, 0.60 mmol), a copper salt (0.030 mmol), a ligand (0.060 mmol), THF (1.0 mL), a base (0.36 mmol) and *p*-tolyl triflate (72 mg, 0.30 mmol), and the mixture was stirred at rt for 1 h. The yields of the product were determined by GC.



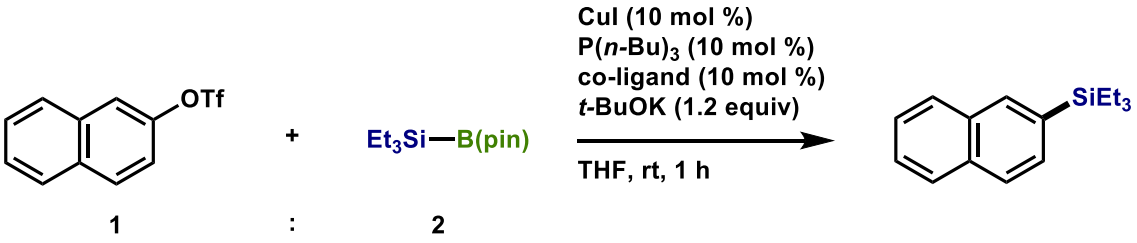
1 : 2

Cu cat.	base	Solvent	GC Yield
none	*t*-BuOK	THF	0%
CuI	*t*-BuOK	THF	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	34%[a]
CuTc/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	9%
CuSCN/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	10%
[Cu(MeCN)$_4$PF$_6$/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	7%
[Cu(MeCN)$_4$BF$_4$/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	26%
CuBr•SMe$_2$/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	27%
CuCl/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	THF	29%
CuI/PPh$_3$ (1:2)	*t*-BuOK	THF	21%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	hexane	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	toluene	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	DCM	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	DMF	24%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	MeCN	23%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	ether	5%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	1,4-dioxane	23%
CuI/P(*n*-Bu)$_3$ (1:2)	MeONa	THF	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOK	2-Me-THF	30%
CuI/P(*n*-Bu)$_3$ (1:2)	MeOK	THF	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuOLi	THF	0%
CuI/P(*n*-Bu)$_3$ (1:2)	*t*-BuONa	THF	trace
CuI/P(*n*-Bu)$_3$/4,4'-Phbpy (1:1:1)	*t*-BuOK	THF	67%[a]

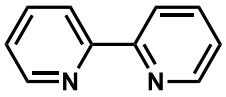
[a] Isolated yield.

Optimization of reaction conditions: effect of co-ligands.

A Schlenk tube equipped with a magnetic stirring bar was charged with Et_3Si–B(pin) (0.15 g, 0.60 mmol), copper iodide (5.4 mg, 0.030 mmol), tri-*n*-butyl phosphine (6.1 mg, 0.030 mmol), a co-ligand (0.030 mmol), THF (1.0 mL), potassium *tert*-butoxide (1.0 M THF solution, 0.36 mmol) and 2-naphthyl triflate (83 mg, 0.30 mmol), and the mixture was stirred at rt for 1 h. The yields of the product were determined by GC.



co-ligands



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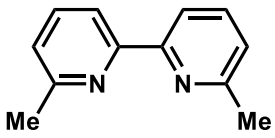

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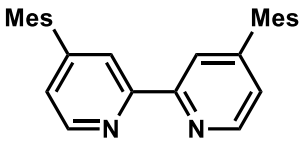

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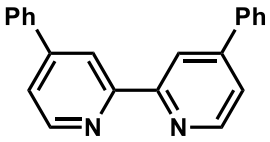

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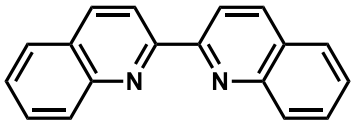

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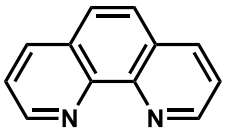

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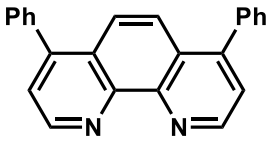

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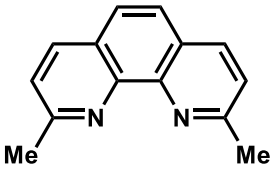

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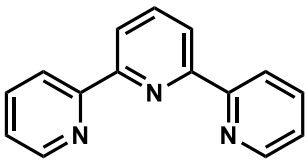

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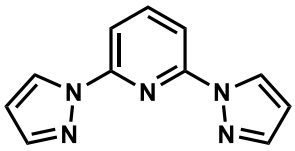
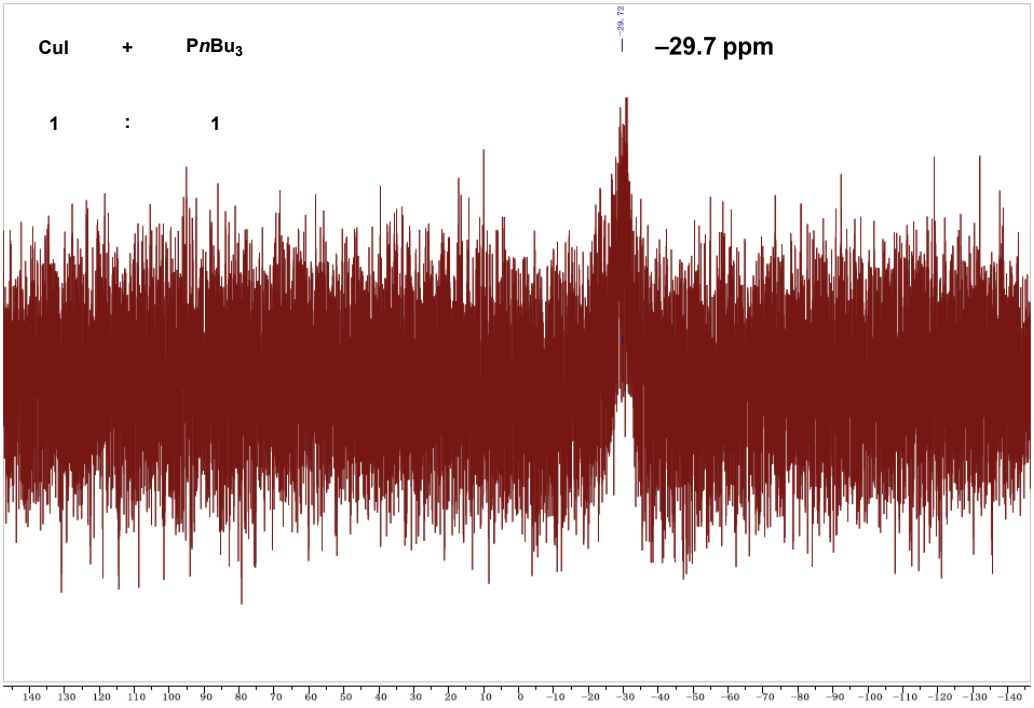
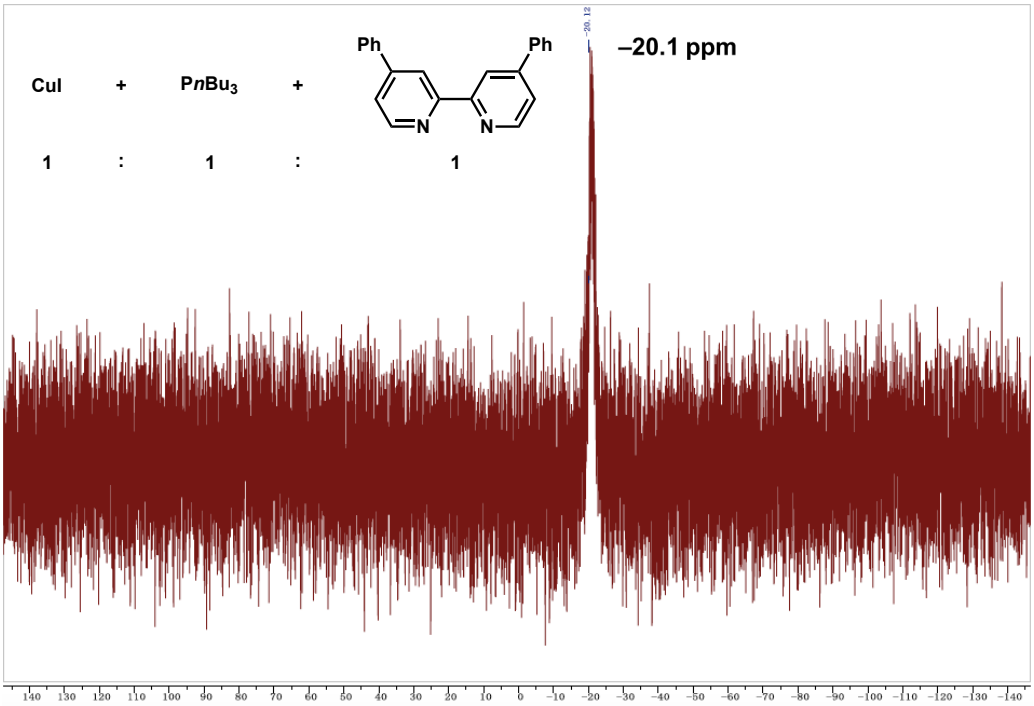


70%

^{31}P NMR analysis of catalysts.

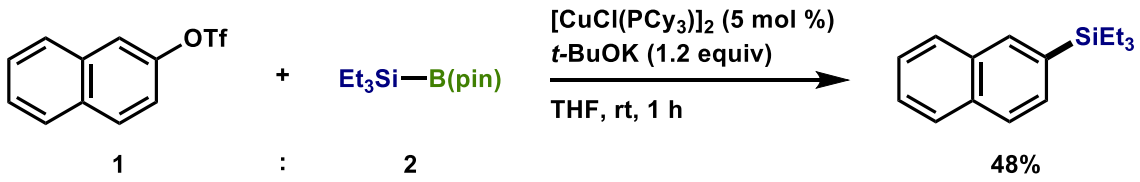
A Schlenk tube equipped with a magnetic stirring bar was charged with copper iodide (5.4 mg, 0.030 mmol), tri-*n*-butyl phosphine (6.1 mg, 0.030 mmol), 4,4'-Phbpy (9.3 mg, 0.030 mmol; for the bottom spectrum), and THF (1.0 mL), and the mixture was stirred at rt for 5 min. The mixture was transferred to an NMR tube equipped with a septum under an argon atmosphere and was analyzed by ^{31}P NMR.





Copper-catalyzed silylation of 2-naphthyl triflate using $[CuCl(PCy_3)]_2$

A Schlenk tube equipped with a magnetic stirring bar was charged with $Et_3Si–B(pin)$ (0.15 g, 0.60 mmol), $[CuCl(PCy_3)]_2$ (11.4 mg, 0.015 mmol), THF (1.0 mL), potassium *tert*-butoxide (1.0 M THF solution, 0.36 mmol) and 2-naphthyl triflate (83 mg, 0.30 mmol), and the mixture was stirred at rt for 1 h. The yield was determined by GC.



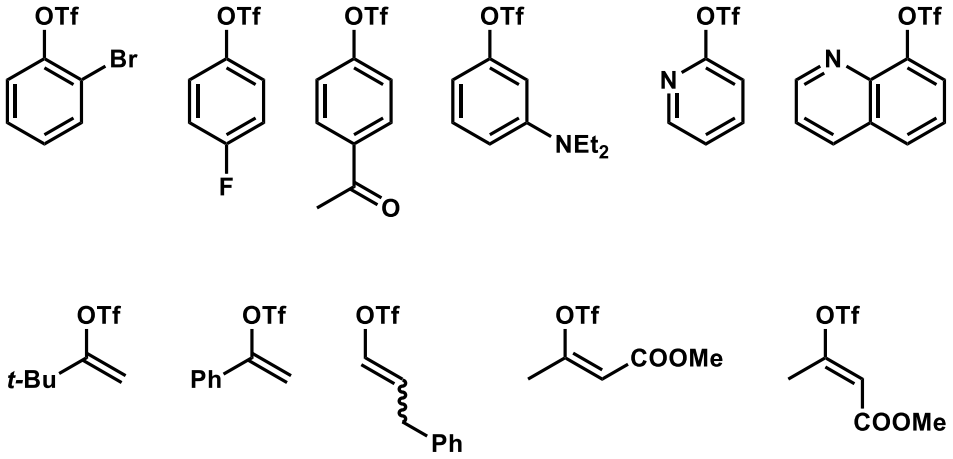
Copper-catalyzed silylation of aryl/alkenyl triflates: a general procedure.

A Schlenk tube equipped with a magnetic stirring bar was charged with a silylbonic ester (0.60 mmol), copper iodide (5.4 mg, 0.030 mmol), tri-*n*-butyl phosphine (6.1 mg, 0.030 mmol), 4,4'-diphenyl-2,2'-bipyridine (9.3 mg, 0.030 mmol), THF (1.0 mL), potassium *tert*-butoxide (1.0 M THF solution, 0.36 mmol) and an aryl/alkenyl triflate (0.30 mmol). After the mixture was stirred at rt for 1 h, the mixture was diluted with ethyl acetate, and the organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The product was isolated by silica gel-column chromatography (hexane as an eluent).

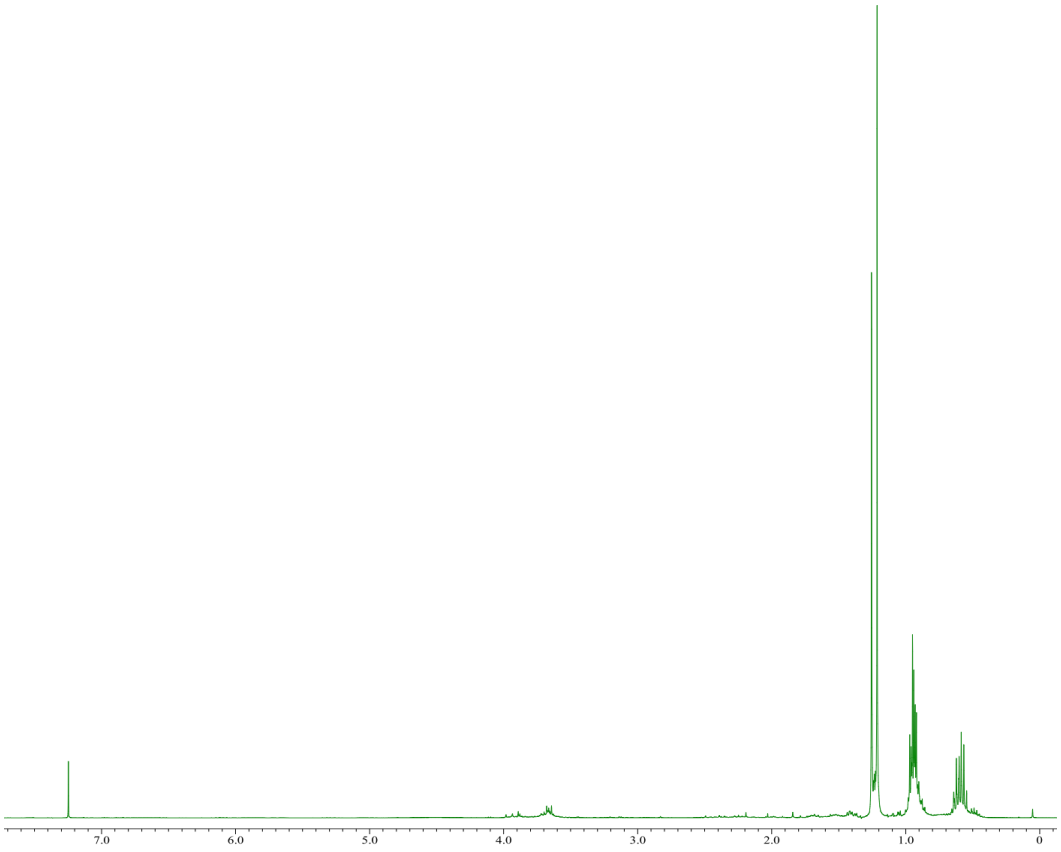
Radical trap experiments.

A Schlenk tube equipped with a magnetic stirring bar was charged with a $Et_3Si–B(pin)$ (0.15 g, 0.60 mmol), copper iodide (5.4 mg, 0.030 mmol), tri-*n*-butyl phosphine (6.1 mg, 0.030 mmol), 4,4'-diphenyl-2,2'-bipyridine (9.3 mg, 0.030 mmol), THF (1.0 mL), potassium *tert*-butoxide (1.0 M THF solution, 0.36 mmol), 2-naphthyl triflate (83 mg, 0.30 mmol), and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO). After the mixture was stirred at rt for 1 h, the mixture was diluted with ethyl acetate, and the organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The product was isolated by silica gel-column chromatography (hexane as an eluent).

Unsuccessful substrates.

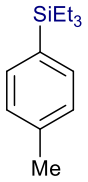


Any detectable by-products such as homocoupling products or deoxyprotonated arenes/alkenes were not observed in the reactions with the above substrates. For example, the ^{1}H NMR spectrum of the crude reaction mixture with the *Z*-alkenyl triflate prepared from methyl acetoacetate is shown below.



Characterization of products.

triethyl(p-tolyl)silane (1a)[3]

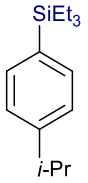


Isolated in 67% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.39 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.7 Hz, 2H), 2.35 (s, 3H), 0.96 (t, J = 8.0 Hz, 9H), 0.78 (q, J = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 138.41, 134.18, 133.64, 128.47, 21.39, 7.35, 3.35.

triethyl(4-isopropylphenyl)silane (1b)[3]

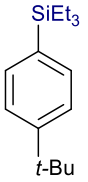


Isolated in 68% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 2.91 (sept, J = 6.8 Hz, 1H), 1.28 (d, J = 6.9 Hz, 6H), 0.97 (t, J = 7.9 Hz, 9H), 0.79 (q, J = 7.8 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 149.43, 134.41, 126.00, 34.17, 24.02, 7.60, 3.61.

(4-(tert-butyl)phenyl)triethylsilane (1c)[3]

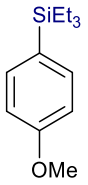


Isolated in 70% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 1.36 (s, 9H), 1.02 (t, J =7.8 Hz, 9H), 0.84 (q, J = 7.8 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 151.65, 134.21, 133.97, 124.75, 34.73, 31.42, 7.62, 3.61.

triethyl(4-methoxyphenyl)silane (1d)[3]

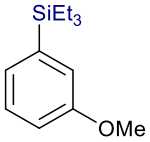


Isolated in 48% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 (d, J = 6.8 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 0.96 (t, J = 8.0 Hz, 9H), 0.77 (q, J = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 160.34, 135.71, 128.28, 113.61, 55.06, 7.55, 3.66.

triethyl(3-methoxyphenyl)silane (1e)[4]

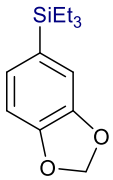


Isolated in 52% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 (dd, J = 8.2, 7.2 Hz, 1H), 7.08 (dt, J = 7.2, 1.0 Hz, 1H), 7.04 (dd, J = 2.8, 0.9 Hz, 1H), 6.89 (ddd, J = 8.2, 2.7, 1.0 Hz, 1H), 3.82 (s, 3H), 0.97 (t, J = 7.9 Hz, 9H), 0.79 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 159.02, 139.33, 128.95, 126.64, 120.06, 113.79, 55.17, 7.54, 3.49.

benzo[d][1,3]dioxol-5-yltriethylsilane (1f)[3]

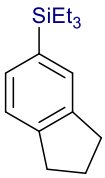


Isolated in 44% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 6.98 (dd, J = 7.6, 1.1 Hz, 1H), 6.96 (s, 1H), 6.86 (d, J = 7.4 Hz, 1H), 5.94 (s, 2H), 0.97 (t, J = 7.9 Hz, 9H), 0.77 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 148.29, 147.45, 130.43, 128.19, 113.57, 108.66, 100.55, 7.49, 3.66.

(2,3-dihydro-1H-inden-5-yl)triethylsilane (1g)[5]

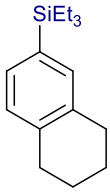


Isolated in 67% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 (s, 1H), 7.34 – 7.21 (m, 2H), 2.91 – 2.95 (m, 4H), 2.08 (pentet, J = 7.5 Hz, 2H), 0.98 (t, J = 7.6 Hz, 9H), 0.80 (q, J = 7.6 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 145.15, 143.68, 134.70, 132.20, 130.30, 124.06, 33.08, 32.94, 25.28, 7.62, 3.69.

triethyl(5,6,7,8-tetrahydronaphthalen-2-yl)silane (1h)[3]

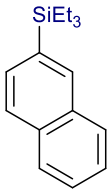


Isolated in 76% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 (d, J = 7.5 Hz, 1H), 7.21 (s, 1H), 7.08 (d, J = 7.5 Hz, 1H), 2.84 – 2.74 (m, 4H), 1.82 – 1.84 (m, 4H), 0.99 (t, J = 7.9 Hz, 9H), 0.79 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 138.01, 136.52, 135.35, 134.03, 131.41, 128.69, 29.58, 29.55, 23.47, 23.35, 7.62, 3.60.

triethyl(naphthalen-2-yl)silane (1i)[3]

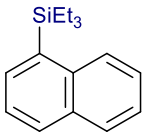


Isolated in 77% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.99 (d, J = 4.3 Hz, 1H), 7.94 – 7.81 (m, 3H), 7.61 (dd, J = 8.2, 1.3 Hz, 1H), 7.58 – 7.50 (m, 2H), 1.01 (t, J = 7.5 Hz, 9H), 0.89 (q, J = 7.6 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 135.15, 134.95, 133.77, 133.11, 130.75, 128.15, 127.83, 126.89, 126.27, 125.89, 7.59, 3.55.

triethyl(naphthalen-1-yl)silane (1j)[3]

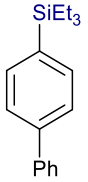


Isolated in 53% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 8.15 (d, J = 7.2 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.72 (dd, J = 6.8, 1.3 Hz, 1H), 7.58 – 7.46 (m, 3H), 1.13 – 0.96 (m, 15H)

^{13}C NMR (101 MHz, Chloroform-d) 137.70, 135.35, 134.61, 133.57, 129.74, 129.23, 128.05, 125.70, 125.37, 125.20, 7.81, 4.69.

[1,1'-biphenyl]-4-yltriethylsilane (1k)[4]

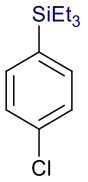


Isolated in 88% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 – 7.53 (m, 6H), 7.42 – 7.46 (m, 2H), 7.36 (t, J = 7.5 Hz, 1H), 1.00 (t, J = 7.9 Hz, 9H), 0.84 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 141.58, 141.34, 136.37, 134.84, 128.88, 127.42, 127.27, 126.54, 7.58, 3.57.

(4-chlorophenyl)triethylsilane (1l)[6]

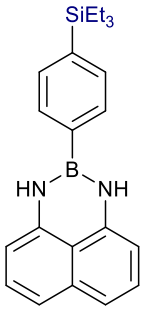


Isolated in 30% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 0.97 (t, J = 7.7 Hz, 9H), 0.78 (q, J = 7.7 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 135.86, 135.67, 135.17, 128.07, 7.44, 3.43.

2-(4-(triethylsilyl)phenyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine (1m)



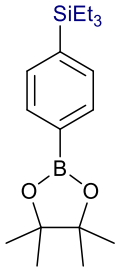
Isolated in 42% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 (d, J = 8.1 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.15 (dd, J = 8.3, 7.2 Hz, 2H), 7.07 (dd, J = 8.4, 0.9 Hz, 2H), 6.43 (dd, J = 7.3, 1.0 Hz, 2H), 6.05 (brs, 2H), 1.06 – 0.93 (m, 9H), 0.91 – 0.77 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 141.22, 140.26, 136.47, 134.16, 130.68, 127.74, 119.99, 117.91, 106.14, 7.54, 3.39.

HRMS Calcd for $C_{22}H_{28}BN_2Si$: $[M+H]^+$, 359.2109 Found: *m/z* 359.2110

triethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (1n)[7]

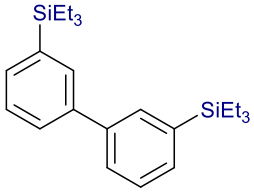


Isolated in 47% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 1.34 (s, 12H), 0.96 (t, J = 7.8 Hz, 9H), 0.80 (q, J = 7.7 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 141.44, 133.89, 133.67, 83.86, 24.97, 7.49, 3.38.

3,3'-bis(triethylsilyl)-1,1'-biphenyl (1o)[8]

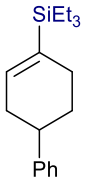


Isolated in 52% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.72 (dt, J = 1.9, 0.8 Hz, 2H), 7.60 (t, J = 1.8 Hz, 2H), 7.50 (dt, J = 7.2, 1.4 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 1.07 – 1.00 (m, 18H), 0.86 (q, J = 7.7 Hz, 12H).

^{13}C NMR (101 MHz, Chloroform-d) δ 140.99, 138.14, 133.33, 133.18, 128.15, 127.89, 7.61, 3.55.

triethyl(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)silane (1p)[3]

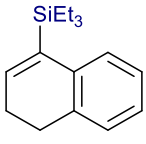


Isolated in 90% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 (dd, J = 7.8, 6.9 Hz, 2H), 7.28 – 7.19 (m, 3H), 6.09 (dt, J = 4.2, 2.1 Hz, 1H), 2.81 (tdd, J = 10.7, 5.5, 2.8 Hz, 1H), 2.45 – 2.34 (m, 1H), 2.27 – 2.18 (m, 3H), 1.97 (dtt, J = 11.0, 4.5, 2.3 Hz, 1H), 1.74 (tdd, J = 12.5, 9.2, 6.4 Hz, 1H), 0.98 (t, J = 7.9 Hz, 9H), 0.63 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 147.72, 136.66, 135.65, 128.50, 127.06, 126.06, 40.27, 35.30, 30.29, 28.39, 7.65, 2.72.

(3,4-dihydronaphthalen-1-yl)triethylsilane (1q)[3]

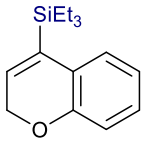


Isolated in 88% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.26 (d, J = 6.8 Hz, 1 H), 7.22 – 7.08 (m, 3H), 6.45 (t, J = 4.5 Hz, 1H), 2.73 (t, J = 7.9 Hz, 2H), 2.28 (ddd, J = 9.1, 7.2, 4.6 Hz, 2H), 0.95 (t, J = 7.9 Hz, 9H), 0.80 (q, J = 8.0 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 141.33, 137.20, 136.25, 134.89, 127.86, 126.32, 126.30, 126.17, 28.31, 24.45, 7.66, 4.05.

(2H-chromen-4-yl)triethylsilane (1r)



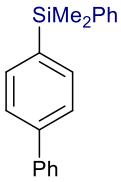
Isolated in 54% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.18 (dd, J = 7.6, 1.6 Hz, 1H), 7.10 (td, J = 7.7, 1.6 Hz, 1H), 6.88 (td, J = 7.5, 1.3 Hz, 1H), 6.83 (dd, J = 8.0, 1.3 Hz, 1H), 6.10 (t, J = 3.8 Hz, 1H), 4.67 (d, J = 3.8 Hz, 2H), 1.02 – 0.89 (m, 9H), 0.78 (q, J = 7.9 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-d) δ 153.73, 133.54, 132.65, 128.60, 126.93, 125.74, 121.31, 116.42, 65.19, 7.56, 3.70.

HRMS Calcd for $C_{15}H_{23}OSi$: $[M+H]^+$, 247.1513 Found: *m/z* 247.1513

[1,1'-biphenyl]-4-yldimethyl(phenyl)silane (1s)[9]

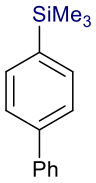


Isolated in 70% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.54 (m, 8H), 7.48 – 7.33 (m, 6H), 0.61 (6H, s).

^{13}C NMR (101 MHz, Chloroform-d) δ 142.02, 141.22, 138.31, 137.14, 134.82, 134.34, 129.30, 128.91, 128.01, 127.53, 127.31, 126.71, –2.21.

[1,1'-biphenyl]-4-yltrimethylsilane (1t)[10]

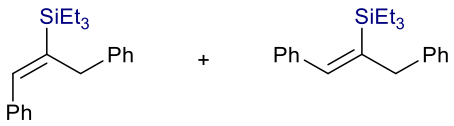


Isolated in 51% yield as Colorless solid.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.56 (m, 6H), 7.49 – 7.41 (m, 2H), 7.36 (t, J = 7.6 Hz, 1H), 0.40 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-d) δ 141.76, 141.34, 139.38, 133.97, 128.90, 127.47, 127.32, 126.65, –0.94.

Mixture of (*E*)-(1,3-Diphenylprop-1-en-2-yl)triethylsilane (1u) and (*Z*)-(1,3-Diphenylprop-1-en-2-yl)triethylsilane (1'u)[3]



Isolated in 79% yield as Colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.11 (m, **1u** + **1'u**), 7.02 (d, J = 6.9 Hz, 1H, **1u**), 3.77 (d, J = 3.5 Hz, 2H, **1u**), 3.58 (d, J = 1.7 Hz, 2H, **1'u**), 0.90 (t, J = 7.9 Hz, 9H, **1u**), 0.76 (t, J = 7.9 Hz, 9H, **1'u**), 0.53 (q, J = 7.3 Hz, 6H, **1u**), 0.38 (q, J = 7.3 Hz, 6H, **1'u**).

^{13}C NMR (101 MHz, Chloroform-d) δ 145.11, 140.99, 140.48, 139.30, 138.08, 129.52, 128.82, 128.59, 128.41, 128.34, 127.75, 127.02, 126.05, 44.86, 36.62, 7.59, 7.47, 4.27, 3.26.

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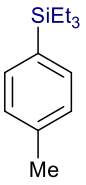
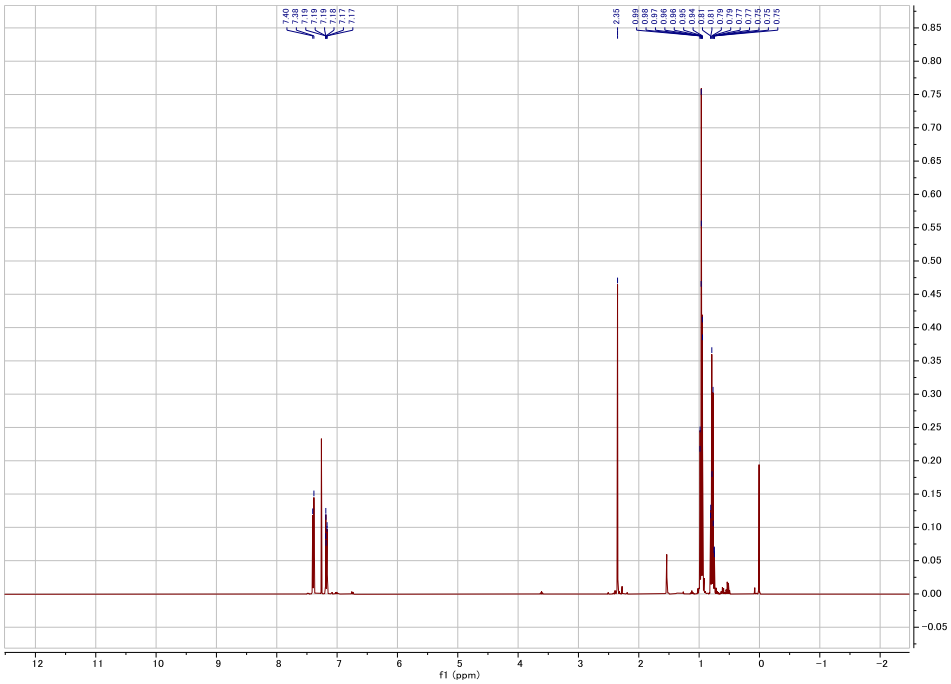
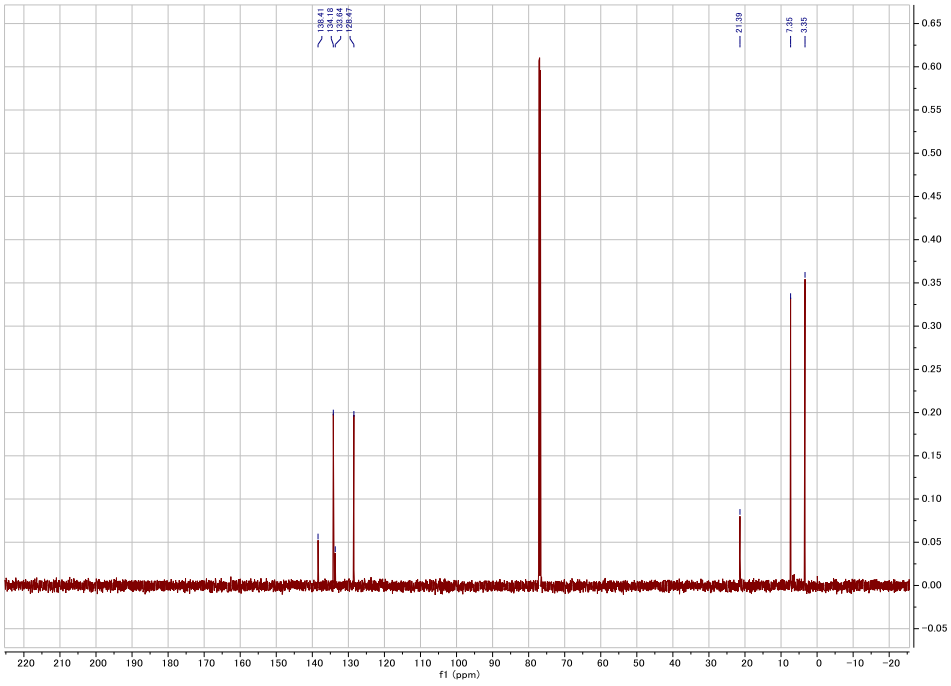
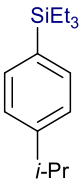
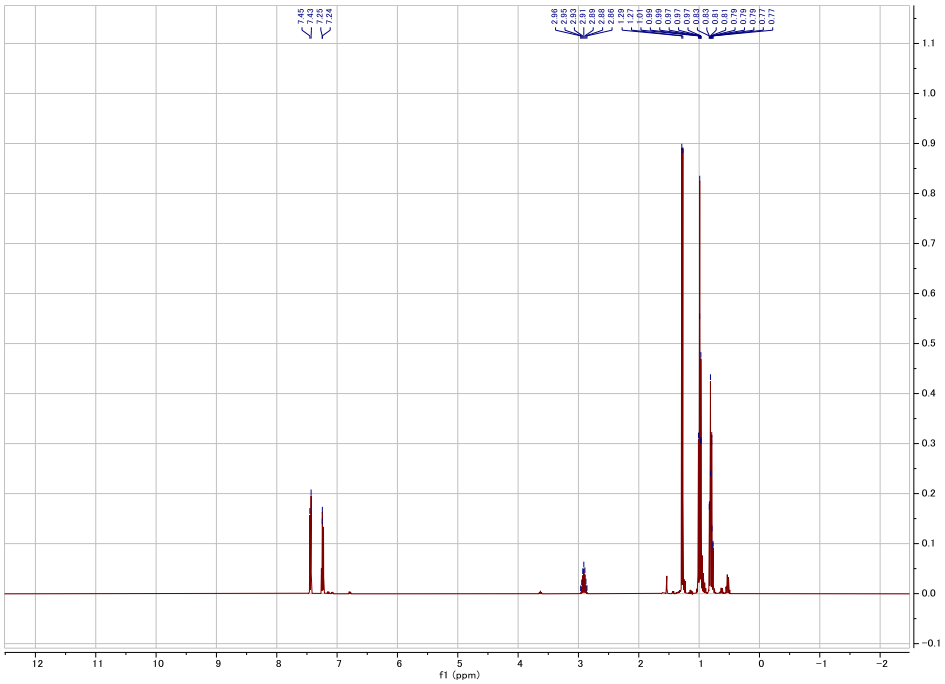
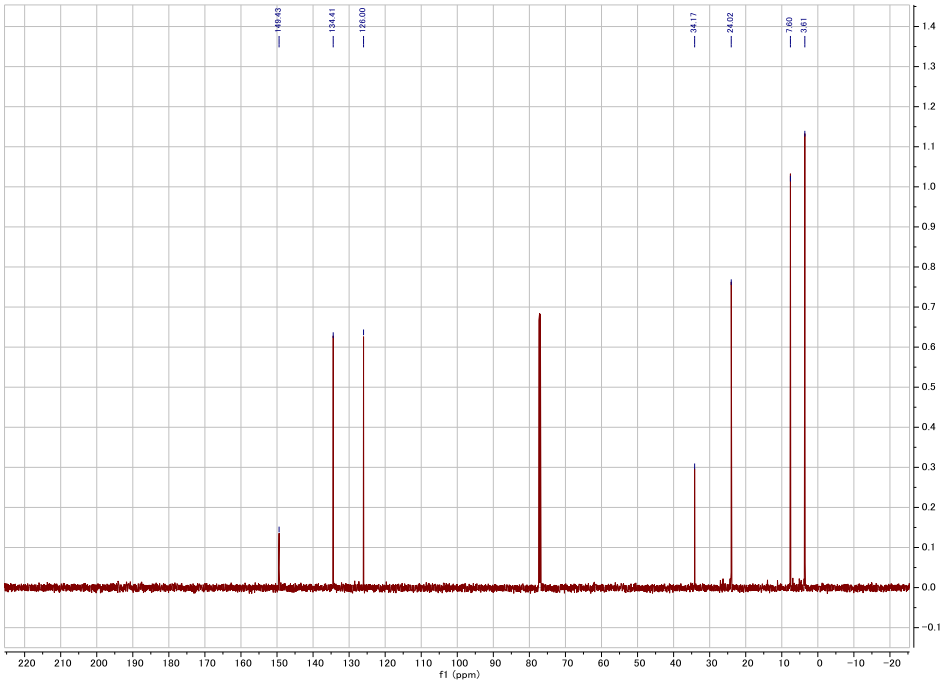

SiEt3
Me

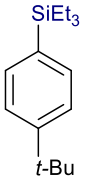

7.40
7.38
7.19
7.19
7.19
7.18
7.17
7.17
7.17
2.35
0.99
0.98
0.97
0.96
0.96
0.95
0.84
0.81
0.81
0.79
0.79
0.78
0.77
0.77
0.75
0.75
f1 (ppm)

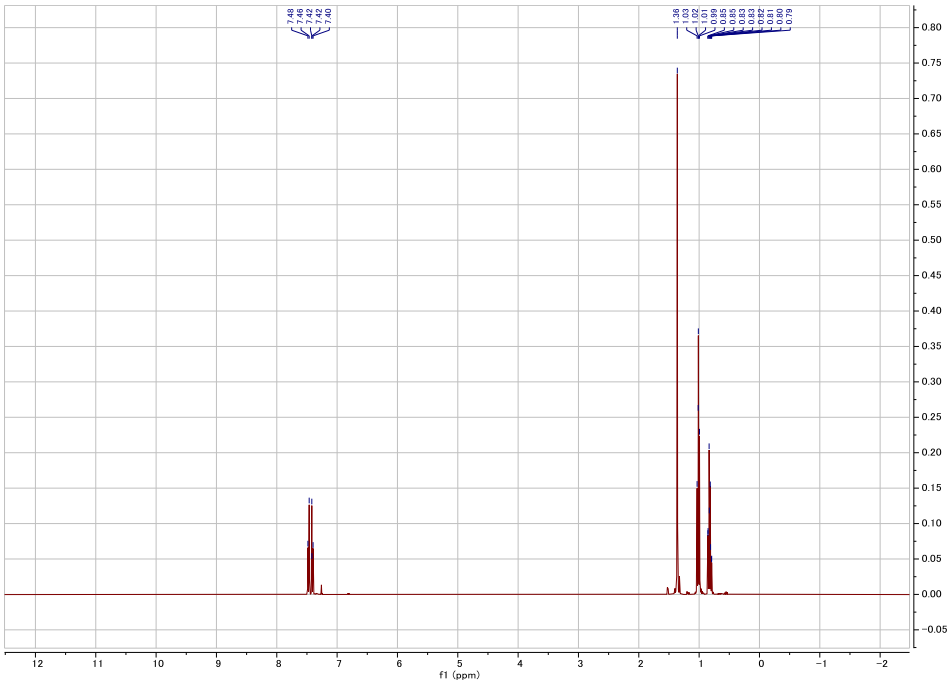

138.41
134.18
133.64
128.47
21.39
7.45
3.35
f1 (ppm)

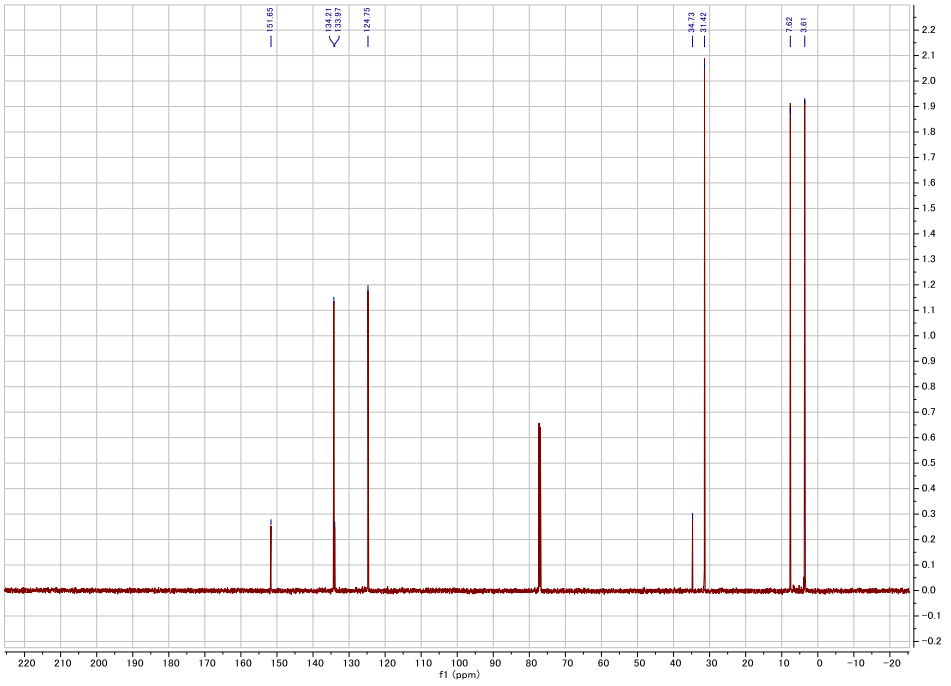

SiEt3
i-Pr


7.45
7.43
7.25
7.24
2.96
2.95
2.93
2.91
2.89
2.88
2.86
1.27
1.01
0.99
0.98
0.97
0.97
0.83
0.83
0.81
0.81
0.79
0.79
0.78
0.77
0.77
f1 (ppm)


149.43
134.41
126.00
34.17
24.02
7.60
3.81
f1 (ppm)


SiEt3
t-Bu


7.48
7.48
7.42
7.42
7.40
1.36
1.03
1.02
1.01
0.99
0.85
0.85
0.83
0.83
0.82
0.81
0.80
0.79
f1 (ppm)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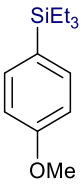
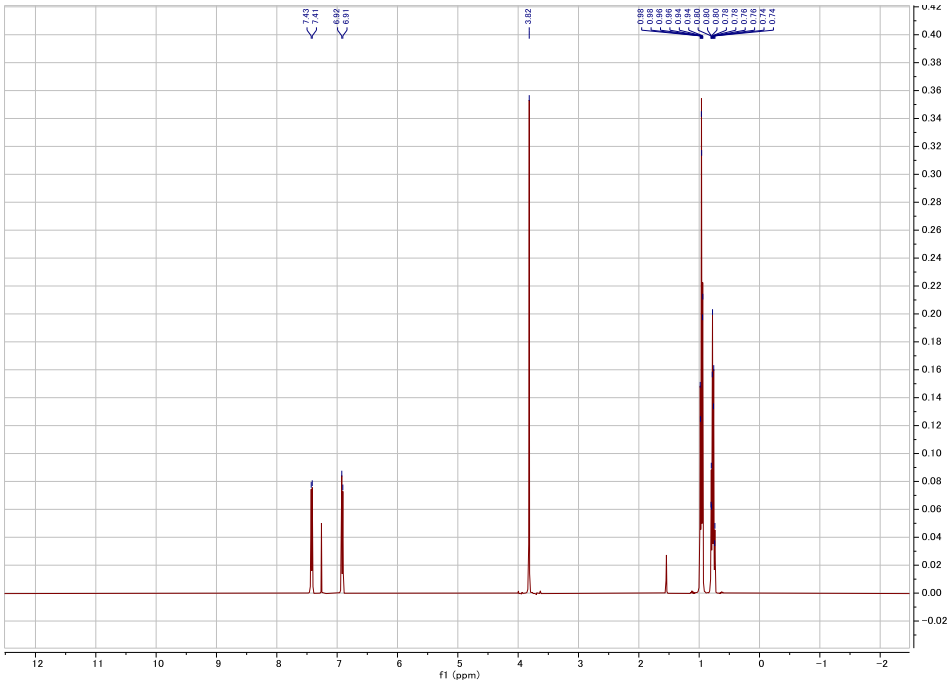
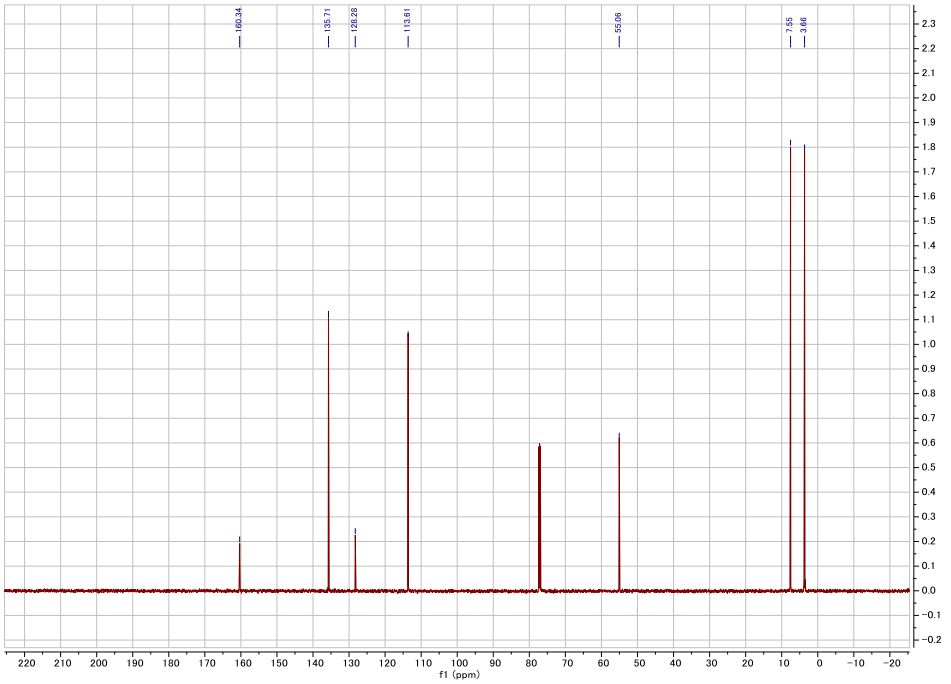
133.97
124.75
34.73
31.42
7.62
3.61
f1 (ppm)


SiEt3
OMe


7.43
7.41
6.92
6.81
3.82
0.98
0.96
0.94
0.80
0.78
0.76
0.74
f1 (ppm)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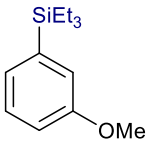
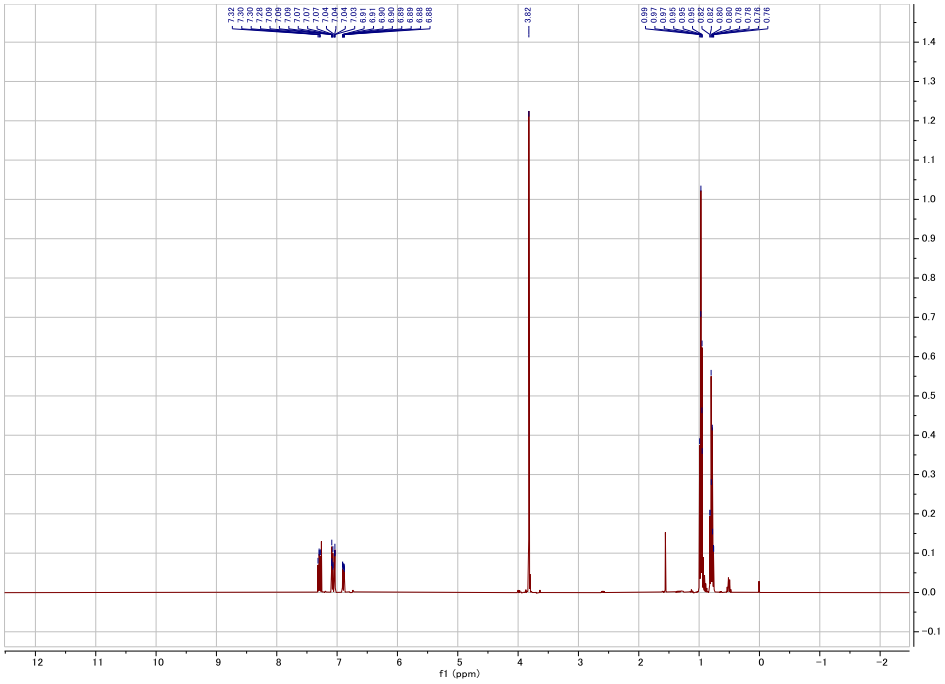
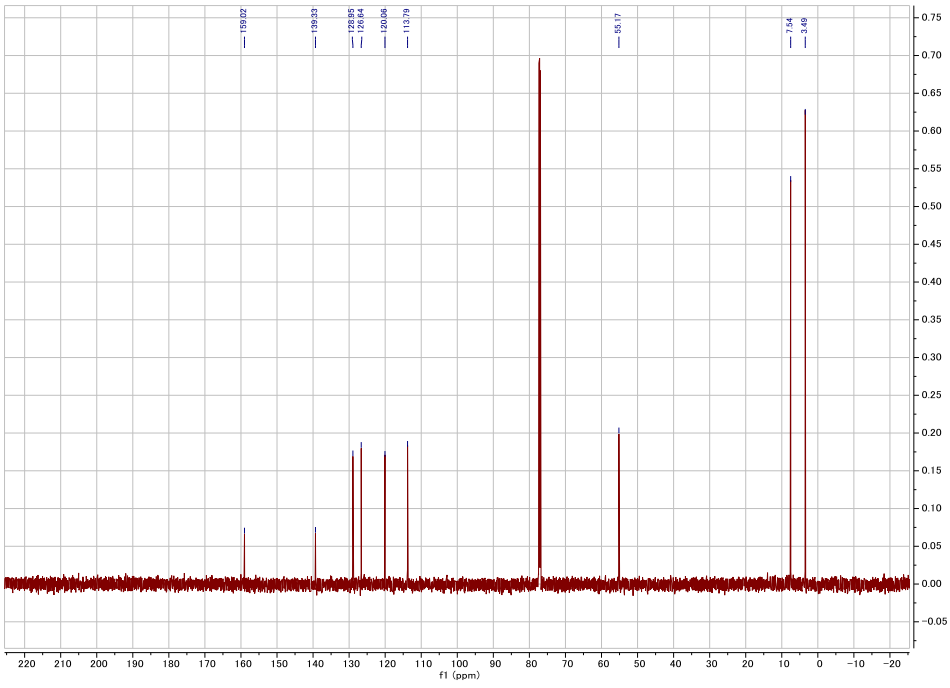
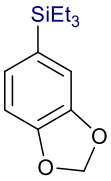
135.71
128.28
113.61
55.06
7.55
3.66
f1 (ppm)


SiEt3
OMe


7.32
7.30
7.30
7.28
7.09
7.09
7.09
7.09
7.07
7.07
7.07
7.07
7.04
7.04
7.04
7.04
6.91
6.91
6.90
6.90
6.89
6.89
6.89
6.89
6.88
6.88
3.82
0.99
0.97
0.97
0.97
0.95
0.95
0.95
0.82
0.80
0.80
0.80
0.78
0.78
0.78
0.76
f1 (ppm)


159.02
139.33
128.85
126.64
120.06
113.79
55.17
7.54
3.49
f1 (ppm)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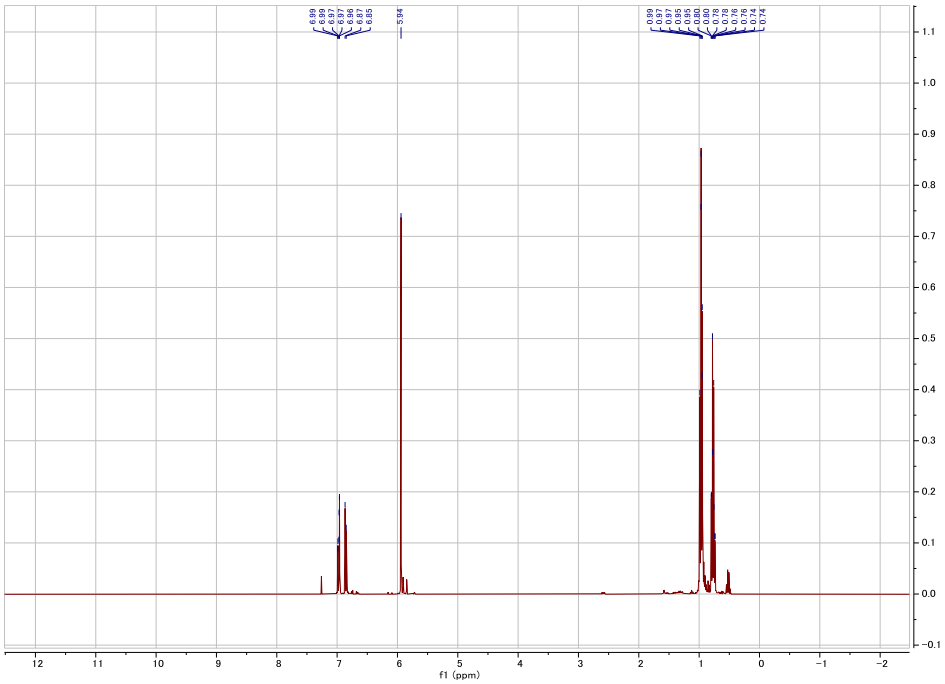
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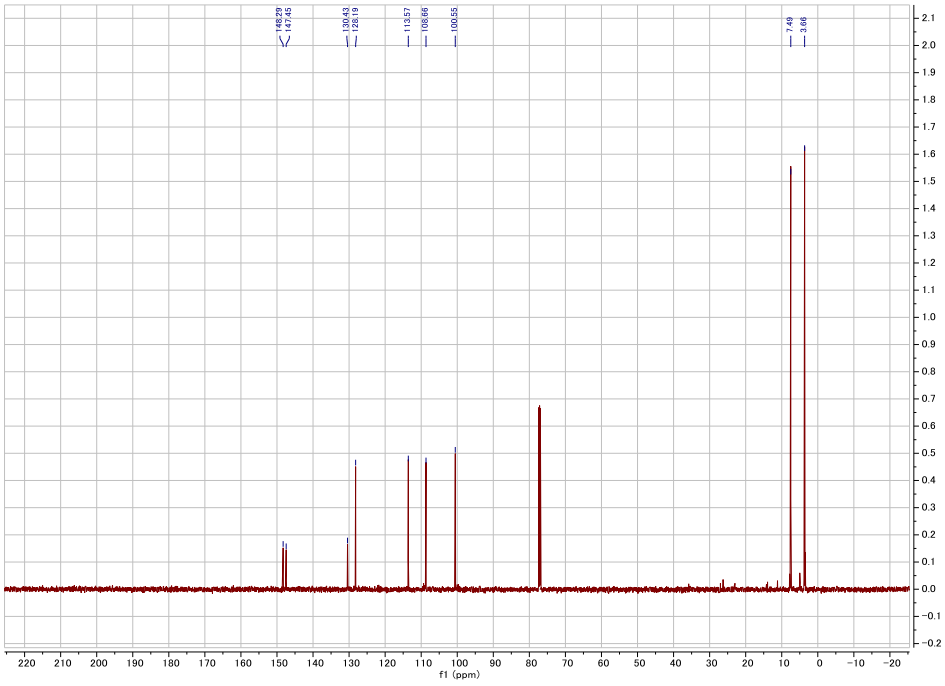
6.89
6.87
6.87
6.86
6.86
6.85
5.94
0.99
0.97
0.97
0.95
0.95
0.80
0.80
0.78
0.78
0.76
0.76
0.74
0.74
f1 (ppm)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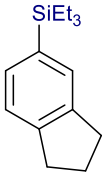
128.19
113.57
108.66
100.55
7.49
3.66
f1 (ppm)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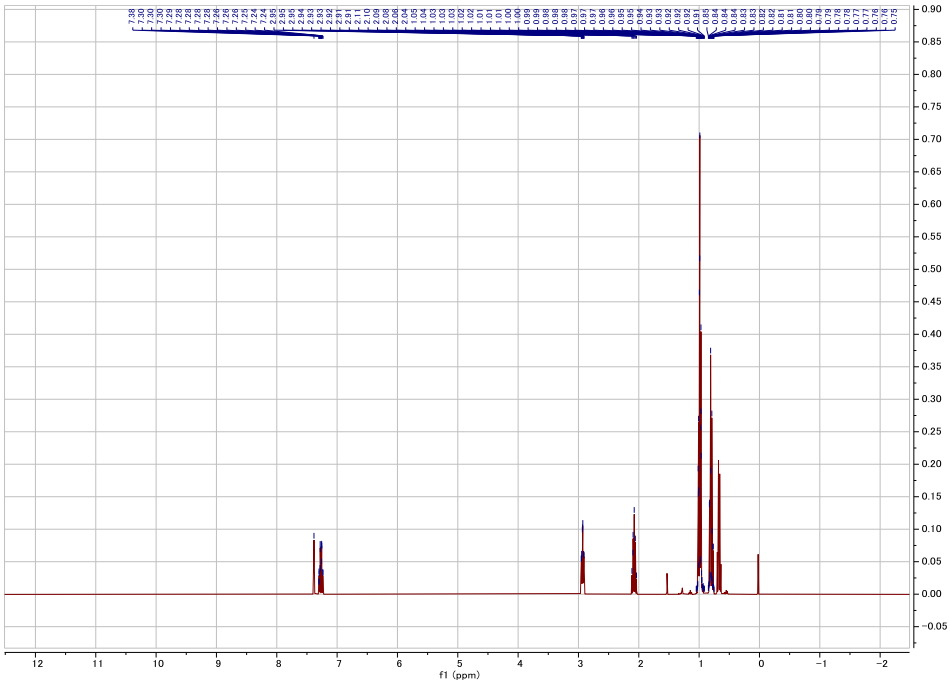
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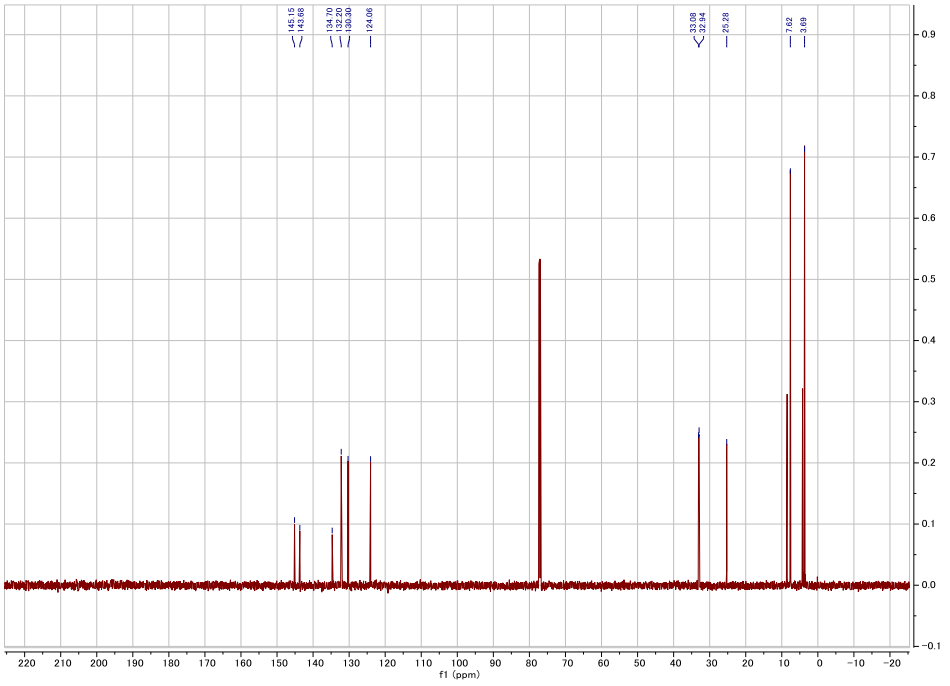
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124.06
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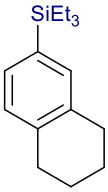
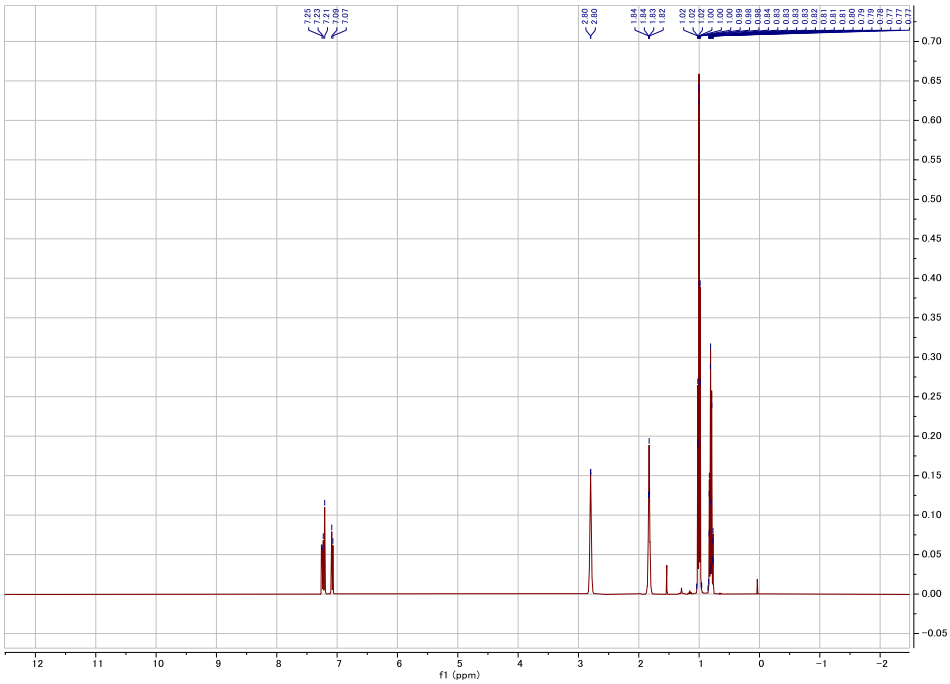
32.64
25.28
7.62
3.69
f1 (ppm)


SiEt3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7.23
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7.07
2.80
2.80
1.84
1.84
1.83
1.82
1.02
1.02
1.00
1.00
1.00
0.99
0.98
0.98
0.84
0.83
0.83
0.83
0.82
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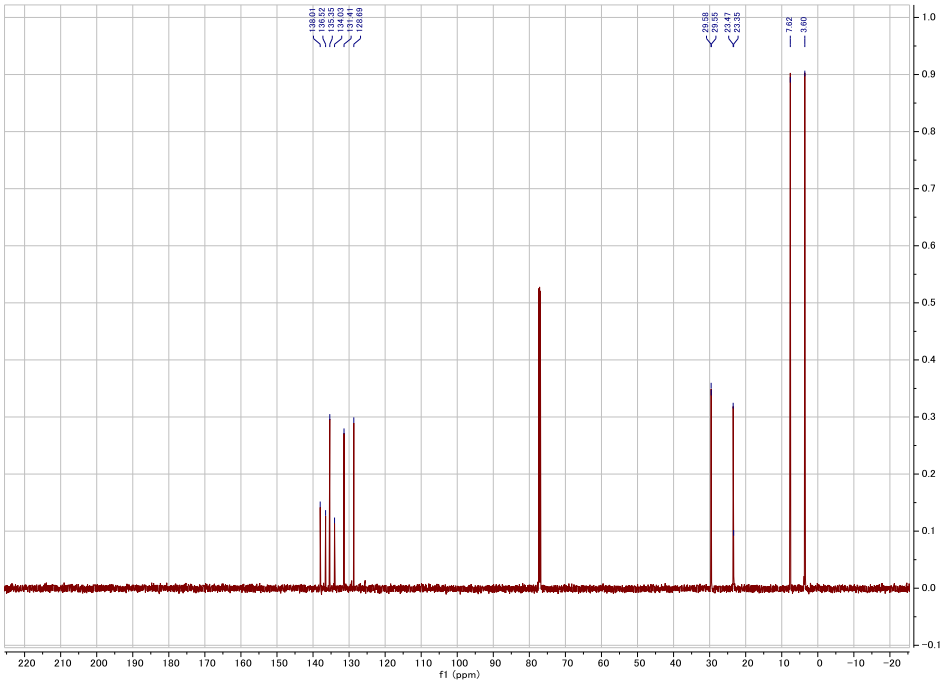
0.81
0.80
0.79
0.79
0.78
0.77
0.77
0.77
f1 (ppm)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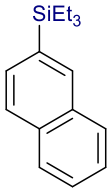
29.58
29.35
23.47
23.35
7.62
3.60
f1 (ppm)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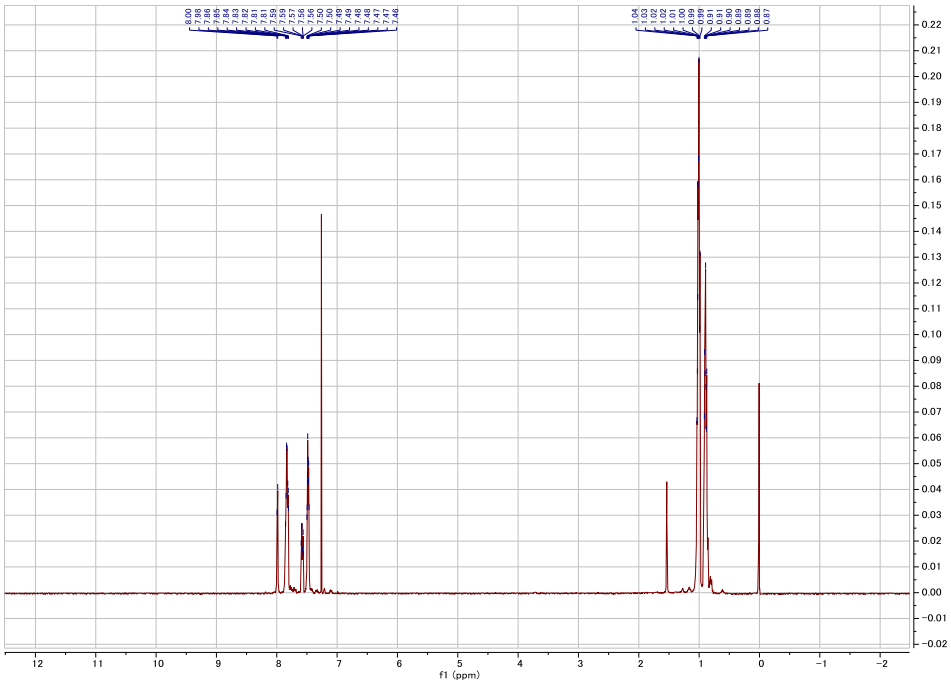
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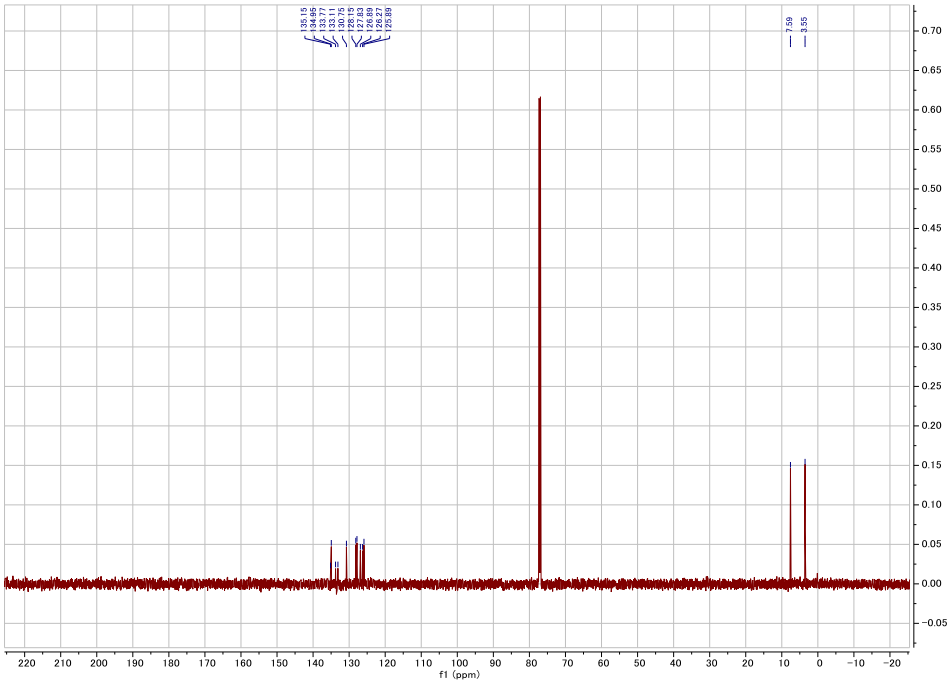
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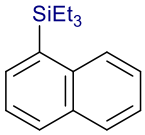
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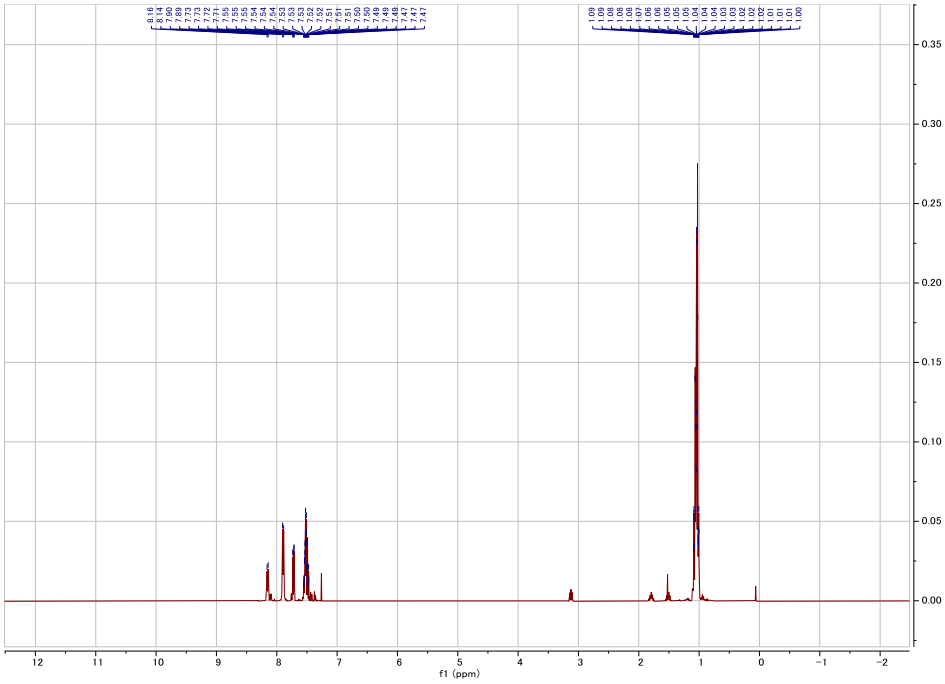
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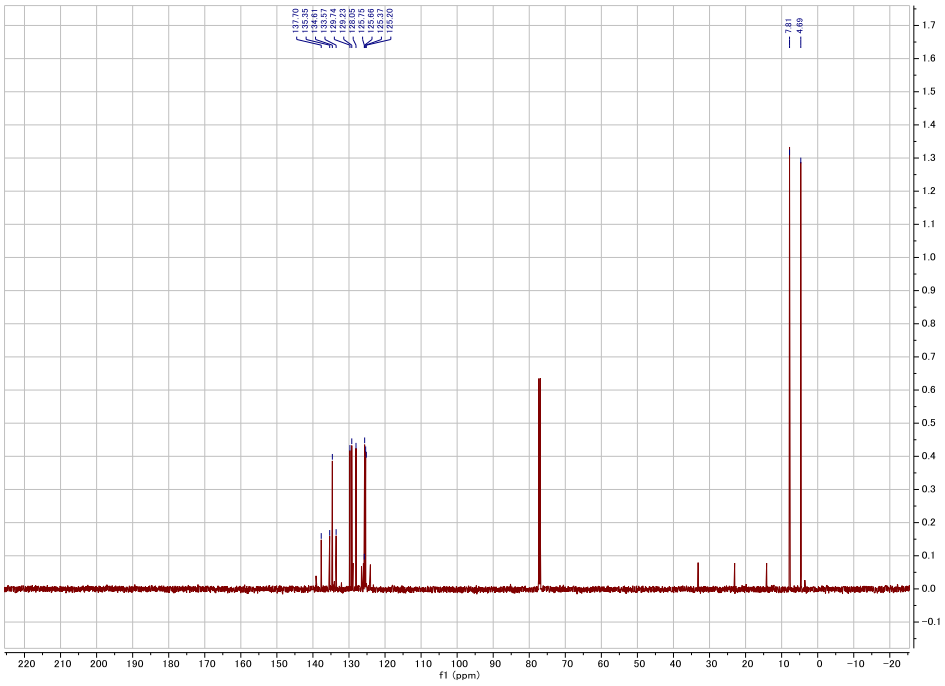
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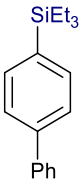
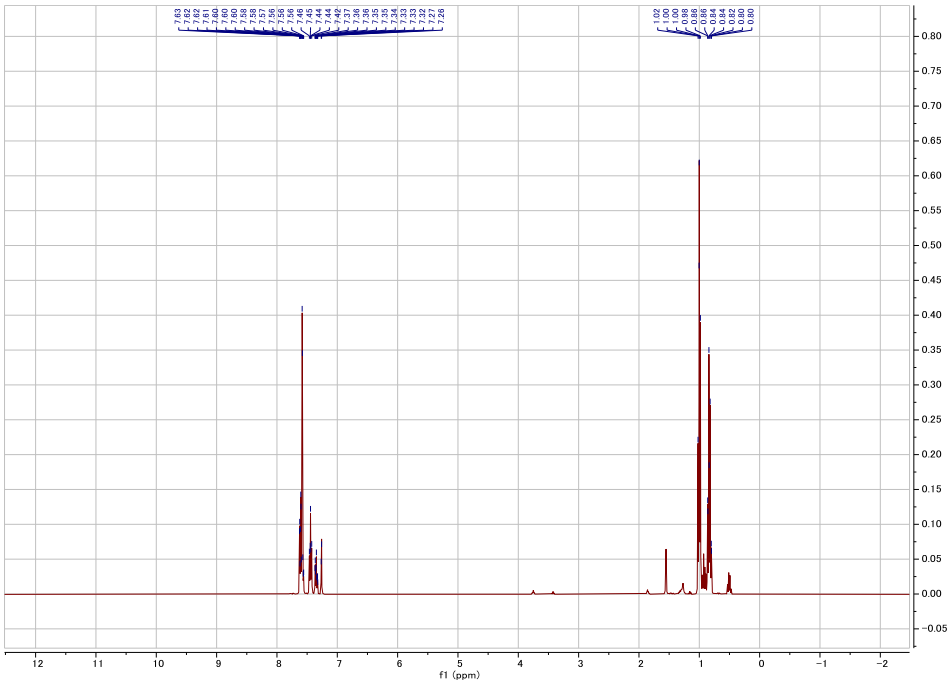

SiEt3
Ph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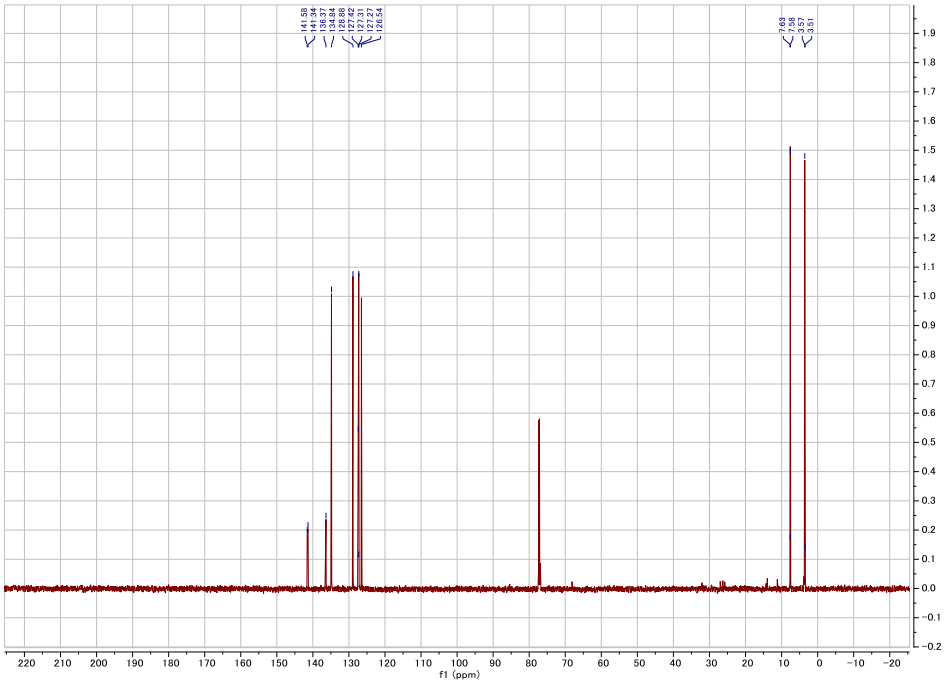
7.62
7.62
7.61
7.60
7.60
7.60
7.58
7.58
7.57
7.56
7.56
7.45
7.45
7.44
7.44
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.32
7.27
7.26
1.02
1.00
1.00
0.98
0.96
0.95
0.84
0.83
0.80
0.80
f1 (ppm)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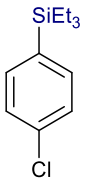
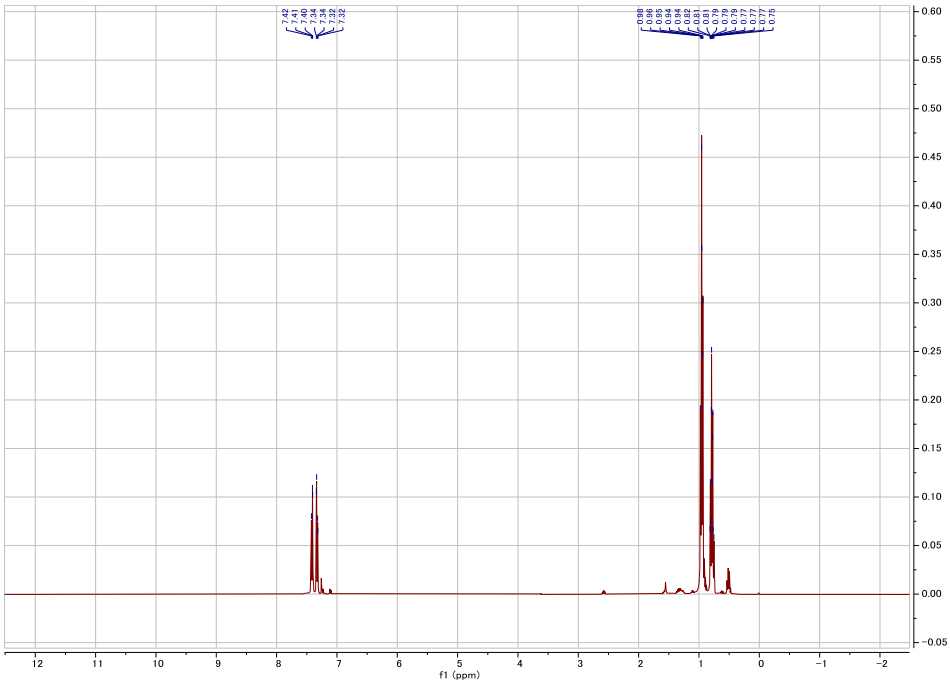
141.34
136.94
136.37
134.84
129.88
127.42
127.31
127.27
126.54
7.63
7.56
53.57
53.51
f1 (ppm)


SiEt3
Cl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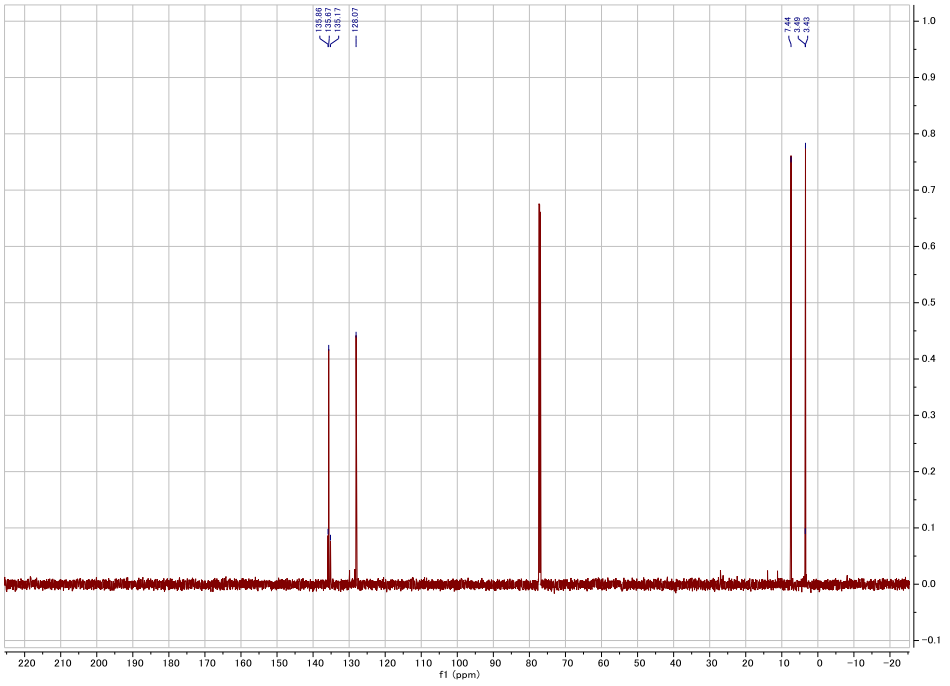
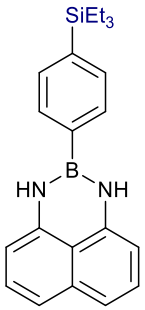
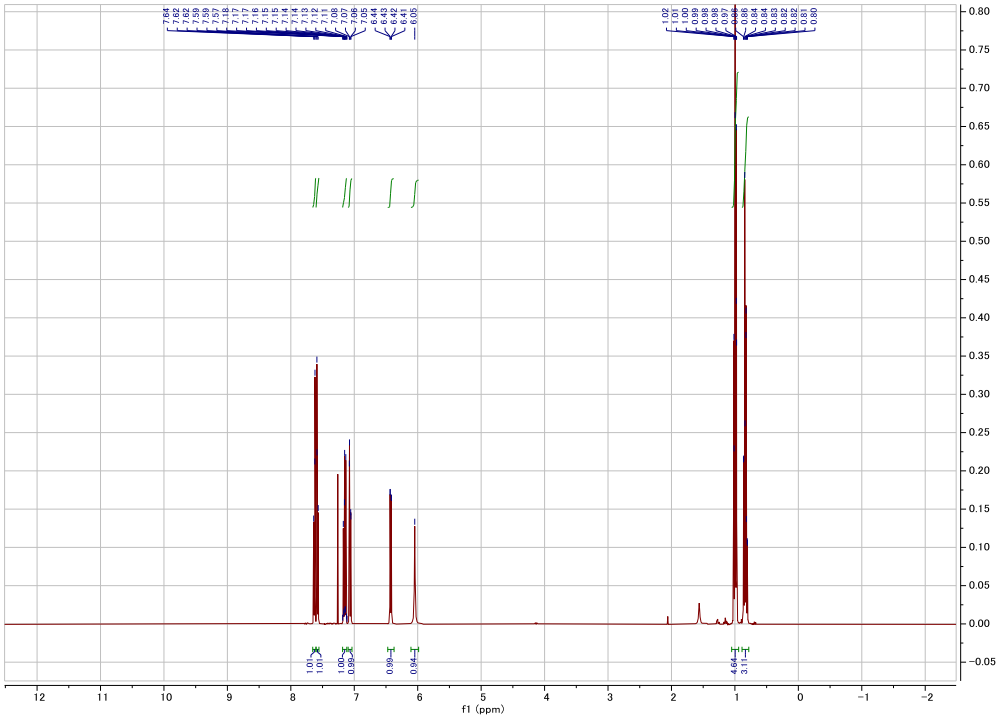
7.34
7.32
7.32
0.98
0.96
0.95
0.94
0.84
0.82
0.81
0.81
0.79
0.79
0.77
0.77
0.77
0.75
f1 (ppm)


135.86
135.67
135.17
128.07
7.44
3.49
3.43
f1 (ppm)


SiEt3
HN
B
NH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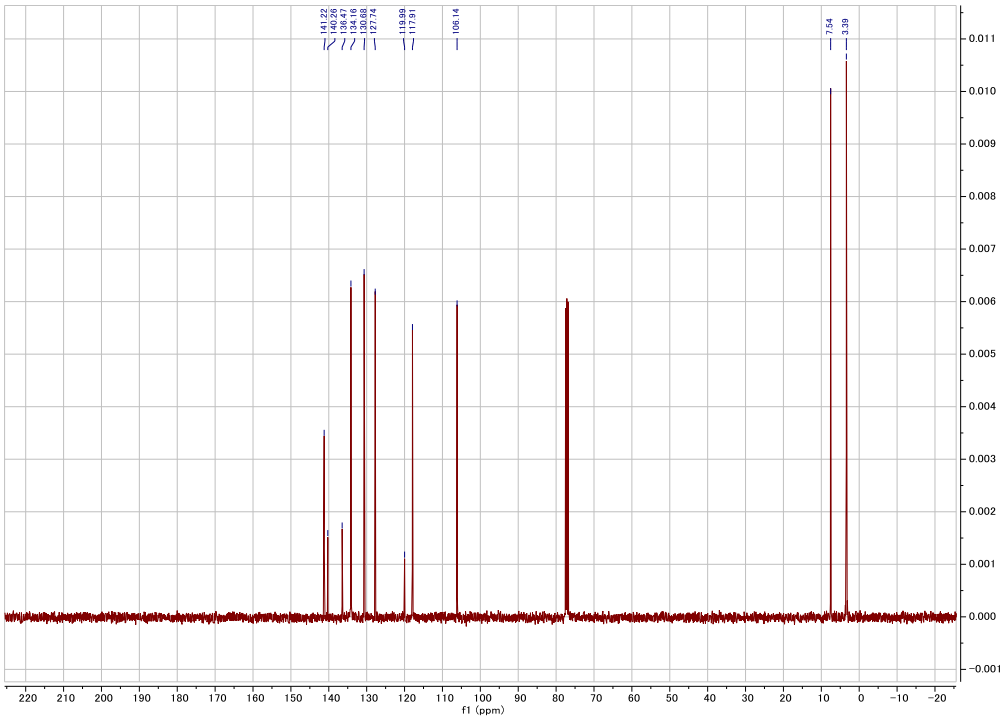
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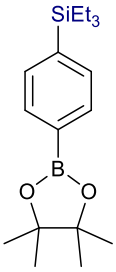
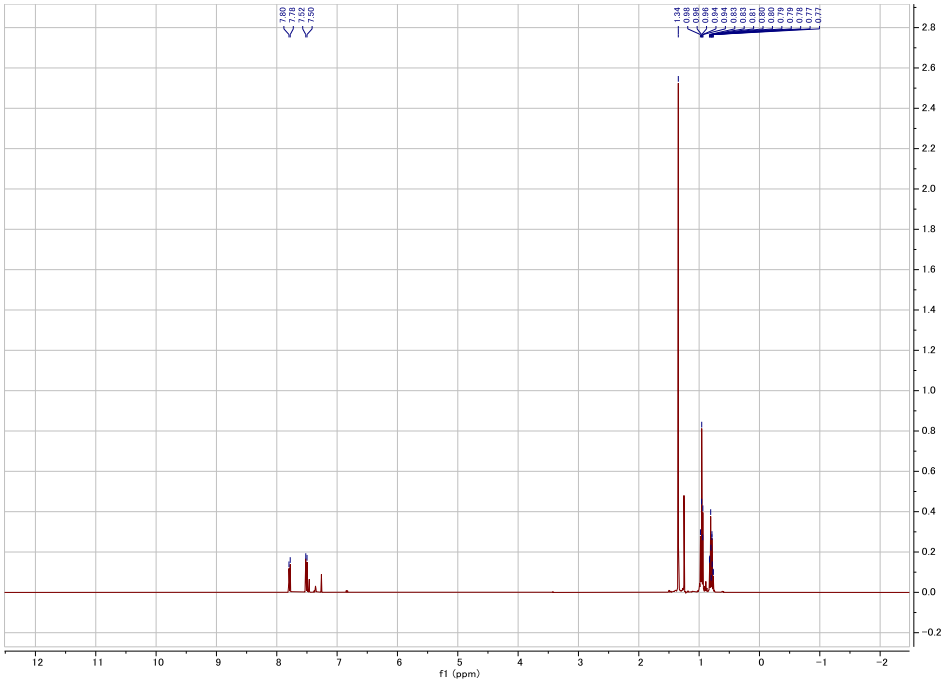

SiEt3
B
O
O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0.98
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0.84
0.84
0.84
0.83
0.83
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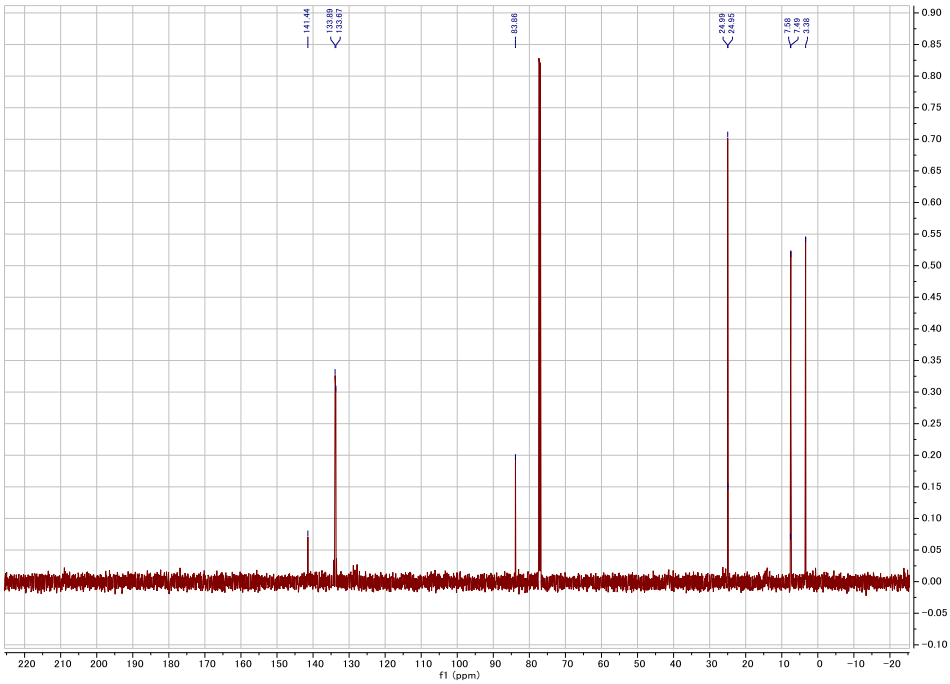
0.80
0.80
0.79
0.79
0.79
0.78
0.77
0.77
f1 (ppm)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83.86
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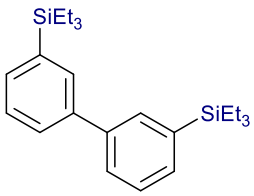
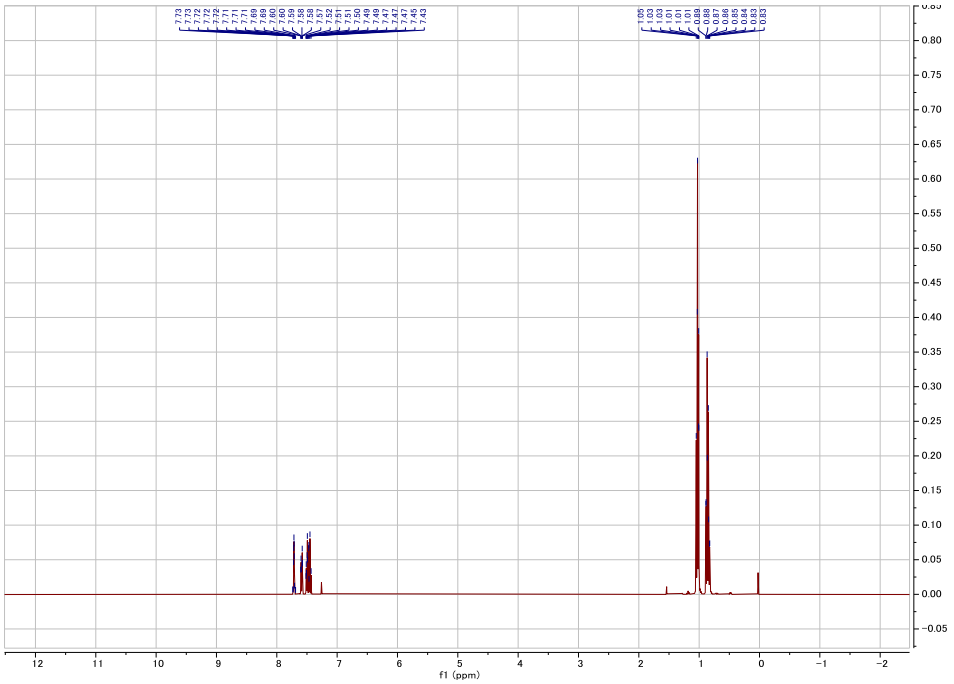
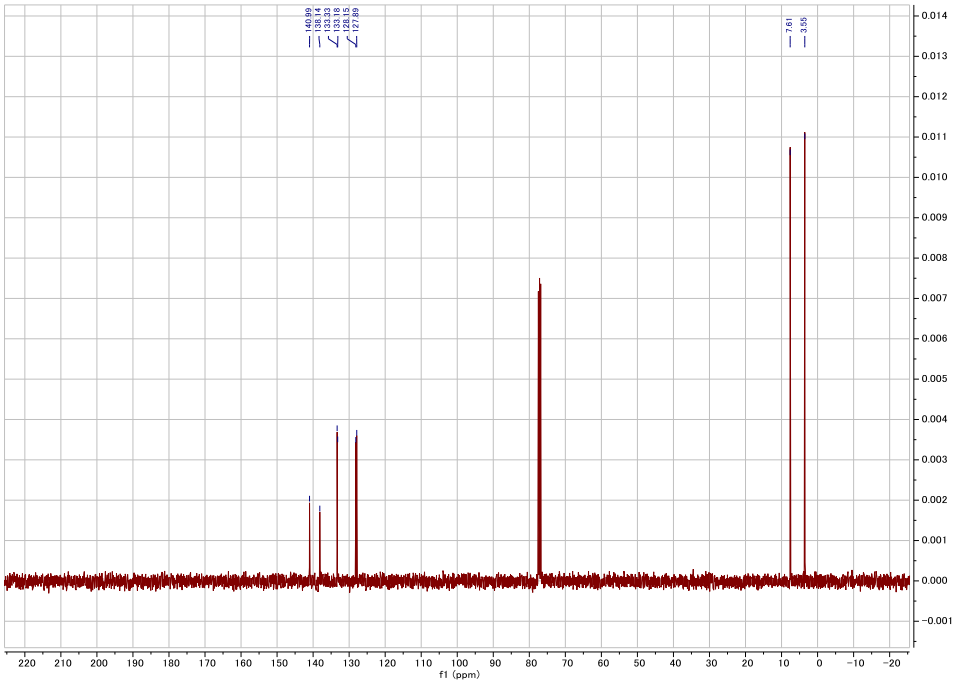
24.95
7.58
7.49
3.38
f1 (ppm)


SiEt3
SiEt3


f1 (ppm)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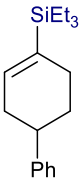
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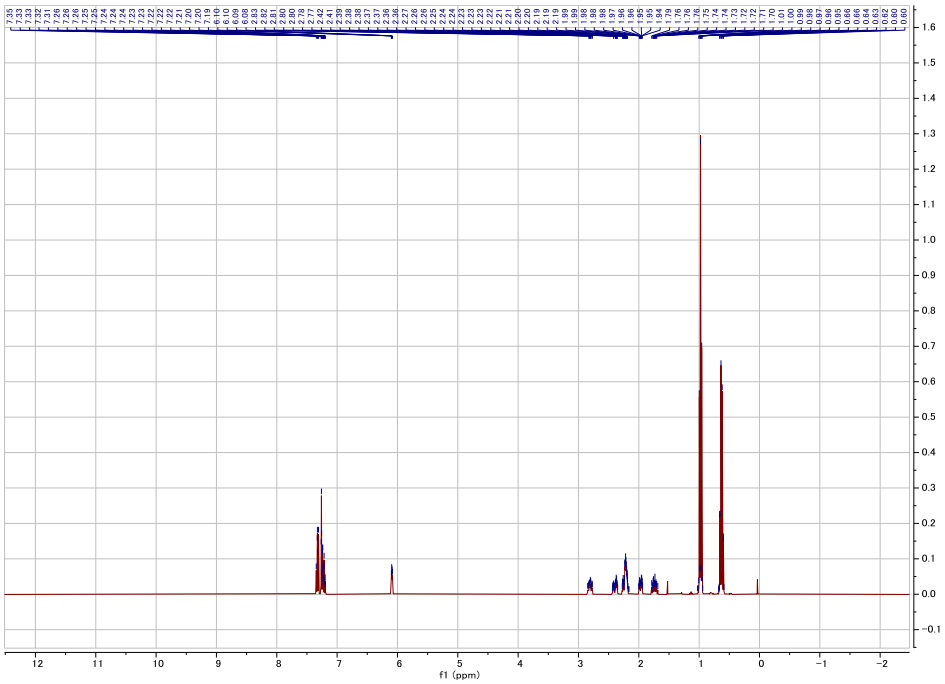
Ph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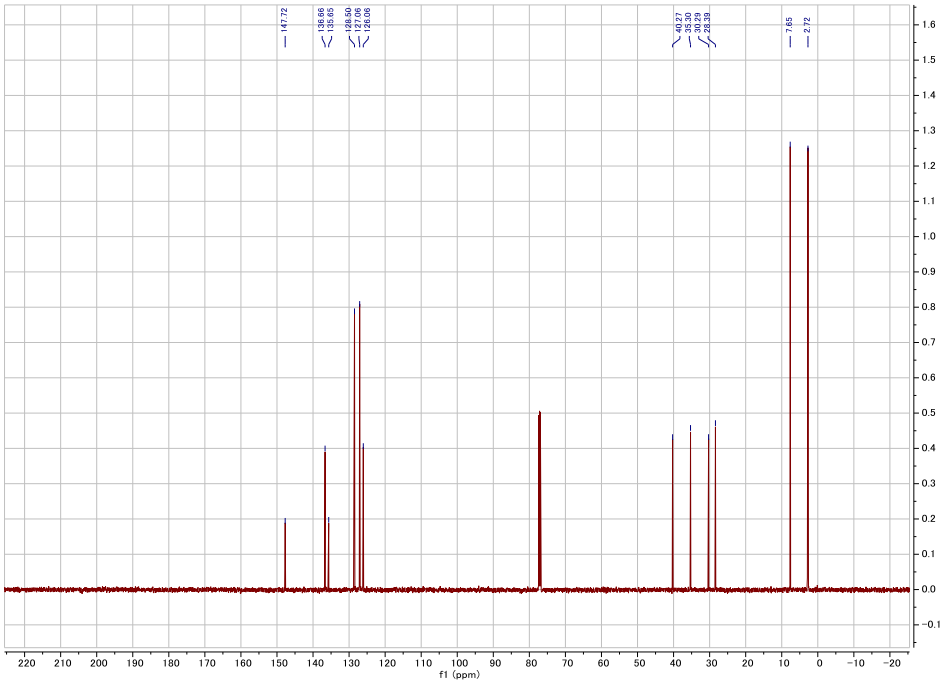
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126.06
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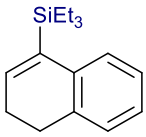
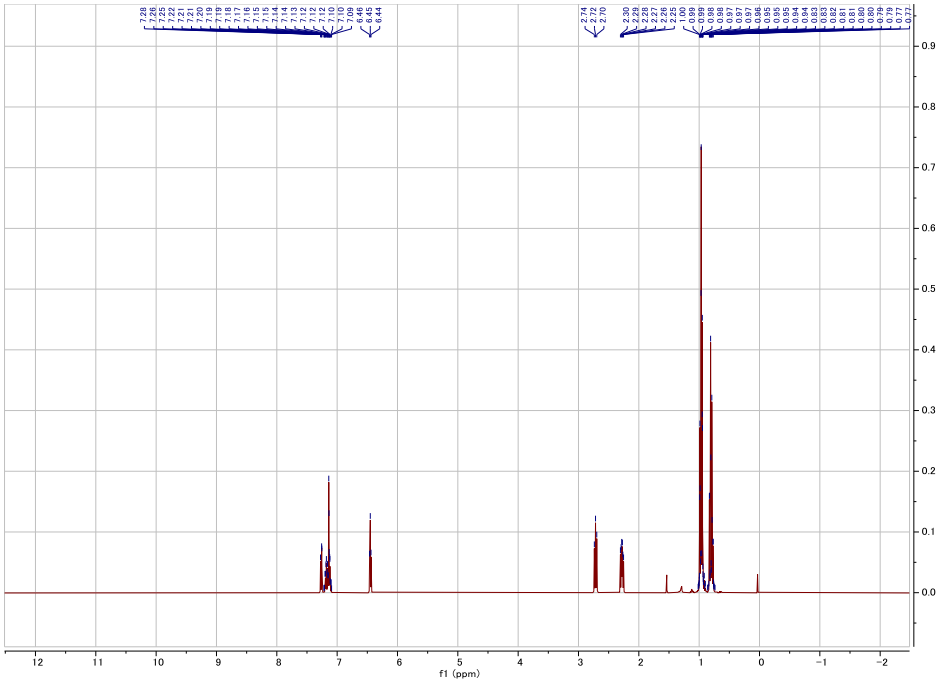
35.30
30.29
28.39
7.65
2.72
f1 (ppm)


SiEt3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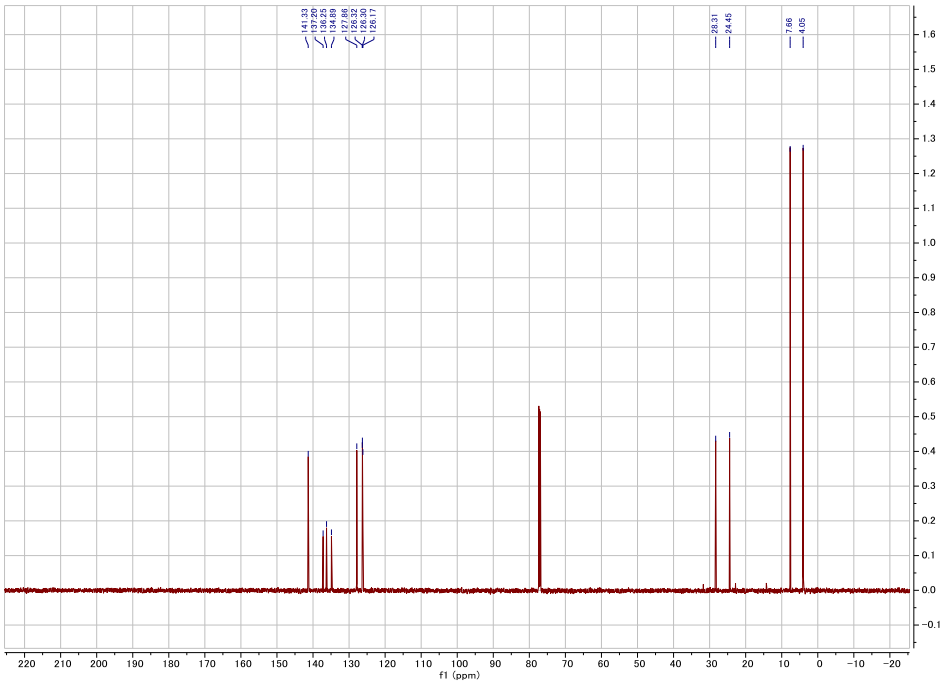
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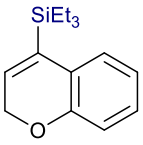
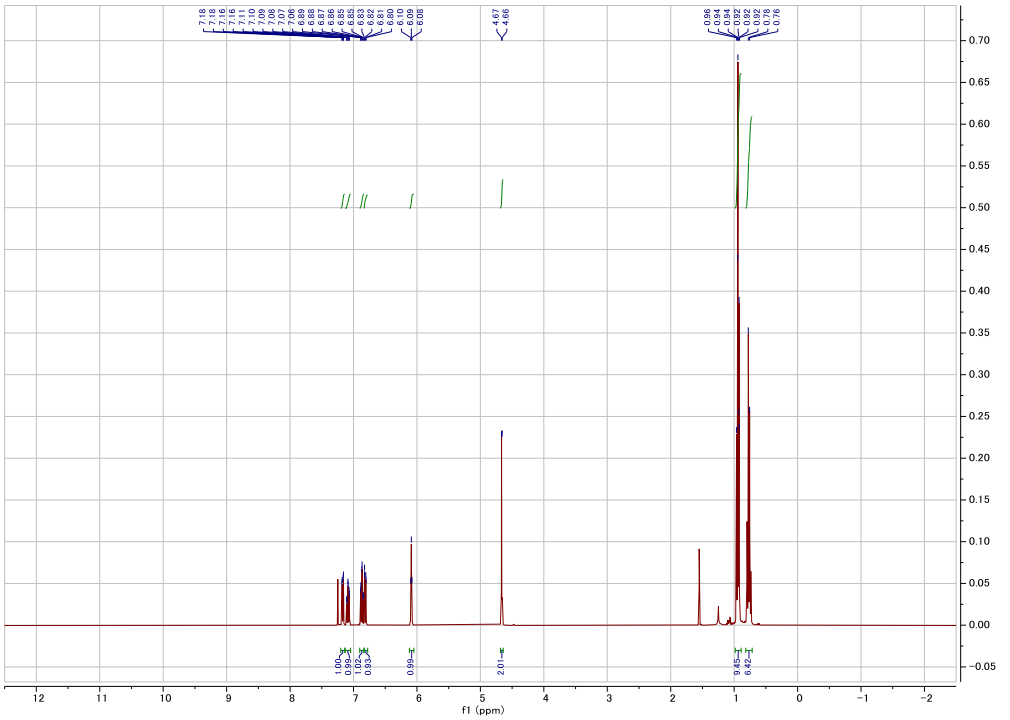

SiEt3
O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7.18
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7.09
7.08
7.07
7.07
7.06
6.89
6.88
6.87
6.86
6.85
6.85
6.83
6.82
6.81
6.80
6.10
6.09
6.08
4.67
4.66
0.96
0.94
0.94
0.92
0.92
0.92
0.78
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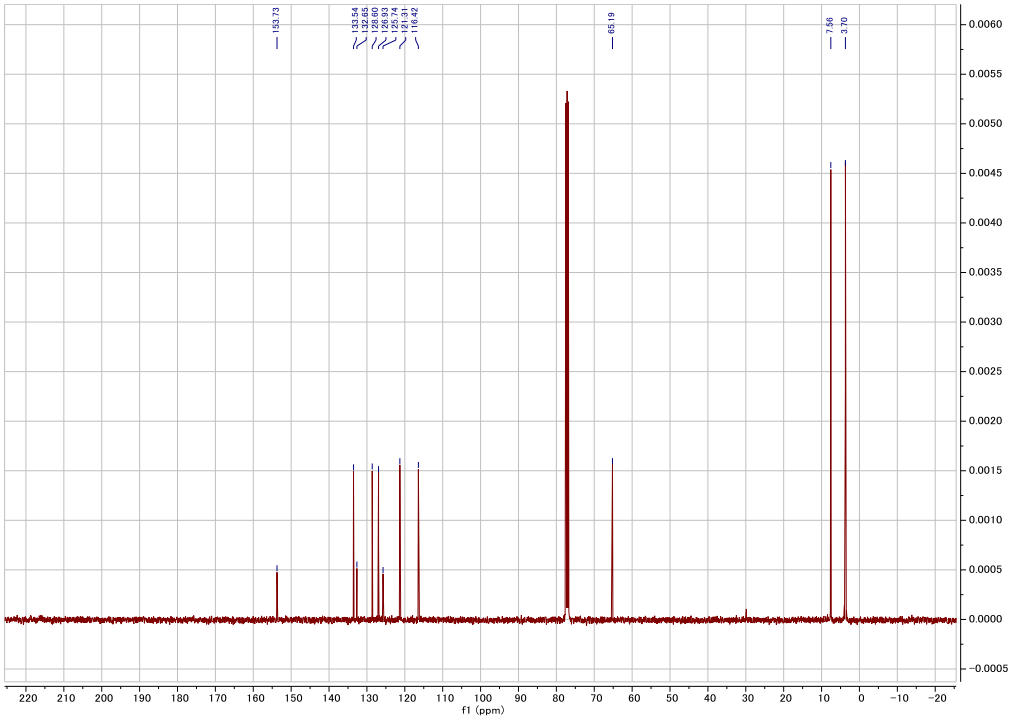
0.99
1.02
0.93
0.99
2.01
9.45
6.42
f1 (ppm)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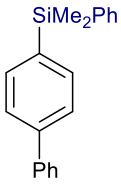
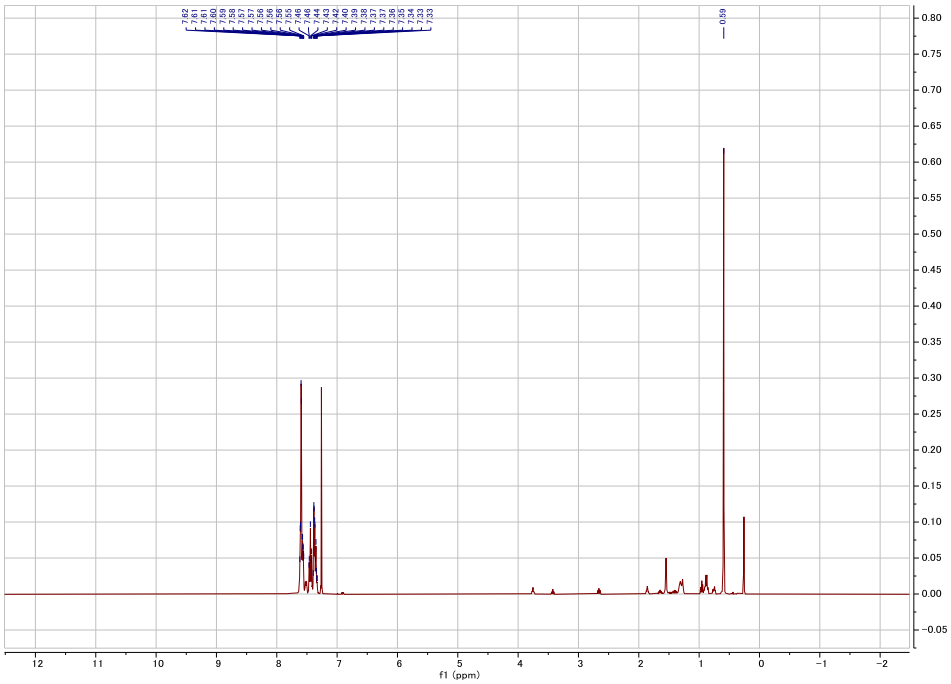
3.70
f1 (ppm)


SiMe2Ph
Ph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7.57
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7.46
7.46
7.44
7.43
7.42
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7.36
7.35
7.34
7.33
7.33
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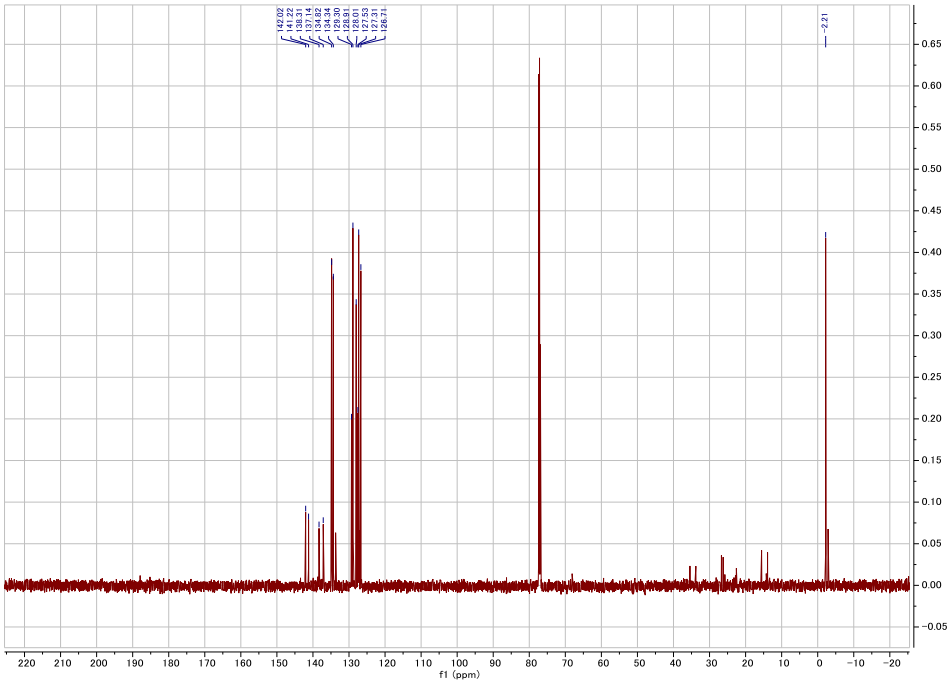
f1 (ppm)


142.02
141.22
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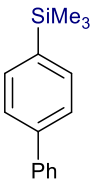
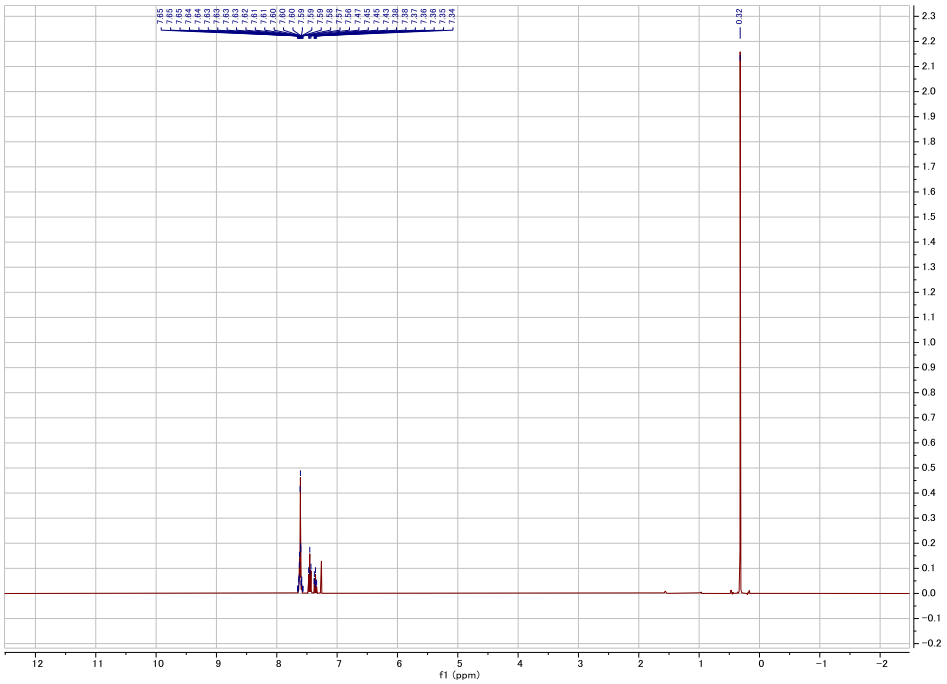
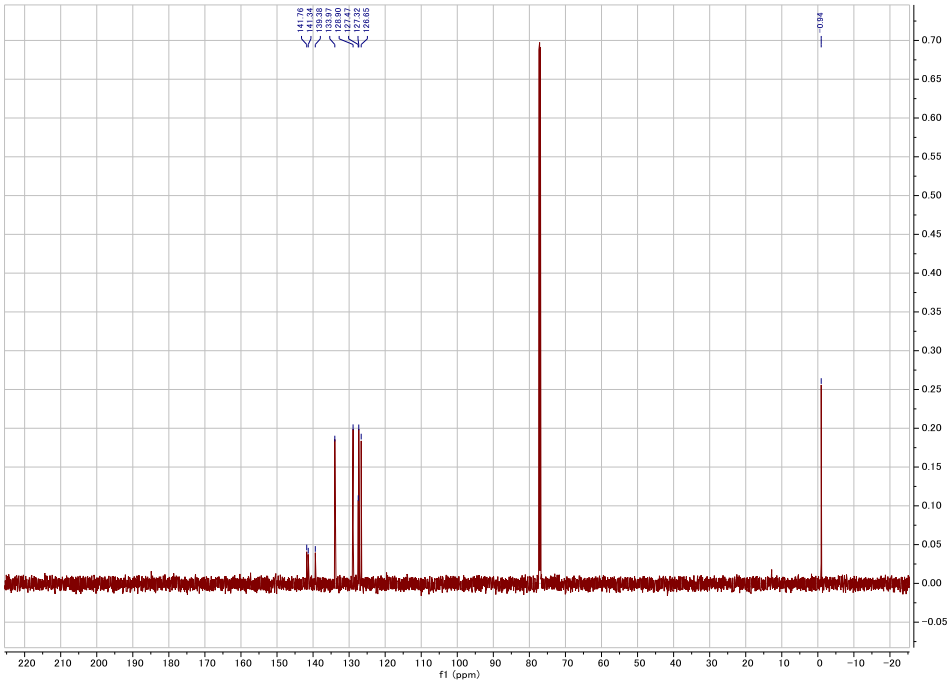
137.14
134.82
134.34
134.30
128.91
128.61
128.53
127.31
126.71
-2.21
f1 (ppm)


SiMe3
Ph


f1 (ppm)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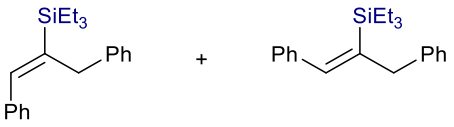
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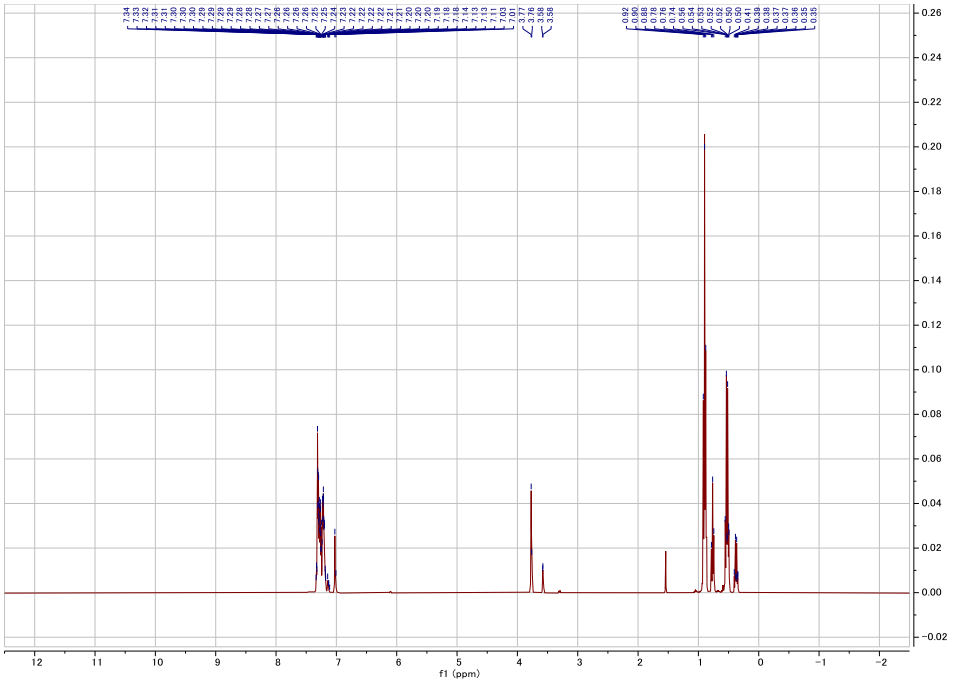
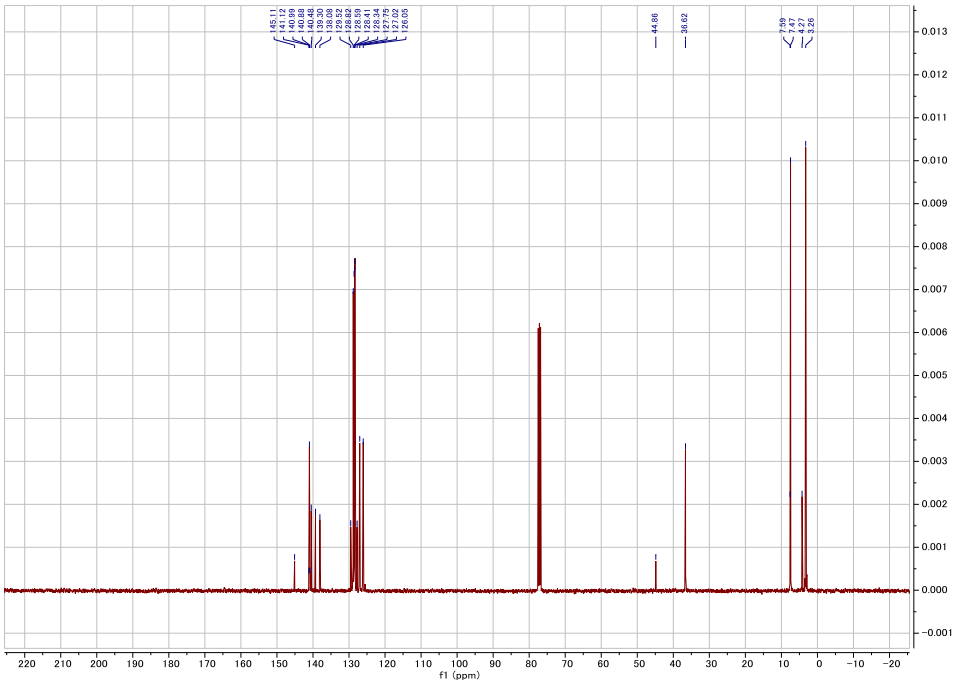
Ph
Ph
+
SiEt3
Ph
Ph


f1 (ppm)


f1 (ppm)