Supporting Information

Nickel-Catalyzed Ligand Controlled Silylation and Reduction of Aryl Ammonium Salts

*Alexander W. Rand and John Montgomery**

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055

jmontg@umich.edu

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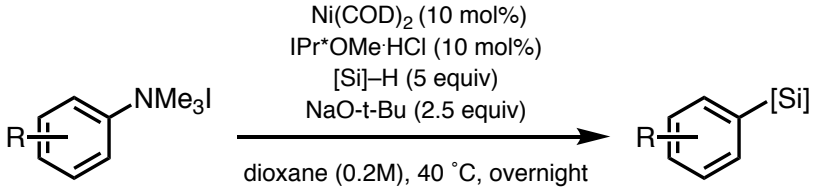
I) General Experimental Details

All reagents were used as received unless otherwise noted. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, Inc. Model # SPS400-3 and PS-400-3). Et_3SiH (Sigma-Aldrich), $BnMe_2SiH$ (Sigma-Aldrich), $PhMe_2SiH$ (Sigma-Aldrich), and (TMSO)MeSiH (TCI Chemicals) were passed through basic alumina and distilled before use and stored under nitrogen. IPr*OMe (made from known procedure[1]), IMes·HCl (made from known procedure[2]), other N-heterocyclic carbenes (Sigma-Aldrich), and NaO-t-Bu (Strem Chemicals) were stored and weighed in an inert atmosphere glovebox

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 (250 μm silica gel) glass plates and compounds were visualized with UV light and p-anisaldehyde, potassium permanganate or ceric ammonium molybdate stains. Flash column chromatography was performed using Kieselgel 60 (230-400 mesh) silica gel. Eluent mixtures are reported as v:v percentages of the minor constituent in the major constituent. All compounds purified by column chromatography were sufficiently pure for use in further experiments unless otherwise indicated. ^1H NMR spectra were collected at 400 MHz on a Varian MR400, at 500 MHz on a Varian Inova 500 or Varian vnmrs 500, or at 700 MHz on a Varian vnmrs 700 instrument. The proton signal of the residual, nondeuterated solvent (δ 7.26 for $CHCl_3$) was used as the internal reference for ^1H NMR spectra. ^{13}C NMR spectra were completely heterodecoupled and measured at 125 MHz or 175 MHz. Chloroform-d (δ 77.00) was used as an internal reference. High resolution mass spectra were recorded on a VG 70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory. GCMS analysis was carried out on a HP 6980 Series GC system with HP-5MS column (30 m x 0.250 mm x 0.25 μm). GCFID analysis was carried out on a HP 6980N Series GC system with a HP-5 column (30 m x 0.32 mm x 0.25 μm).

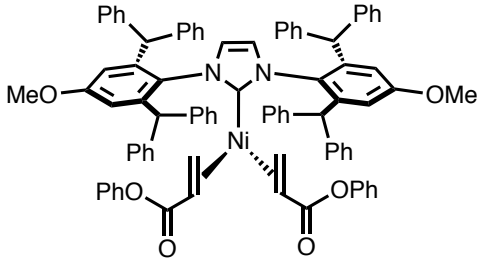
II) General Procedures

General procedure for nickel-catalyzed silylation of aryl ammonium salts:



To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.1 equiv), *N,N'*-Bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazolium chloride (IPr*OMe·HCl) (9.8 mg, 0.01 mmol, 0.1 equiv), NaO-*t*-Bu (24 mg, 0.25 mmol, 2.5 equiv), and ammonium salt (0.1 mmol, 1 equiv) were combined under inert atmosphere and suspended in 0.5 mL of dioxane at rt. Silane (0.5 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 ºC overnight. Upon completion, the reaction mixture was quenched with 1 mL EtOAc and run through a silica gel plug with 5 mL EtOAc. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography.

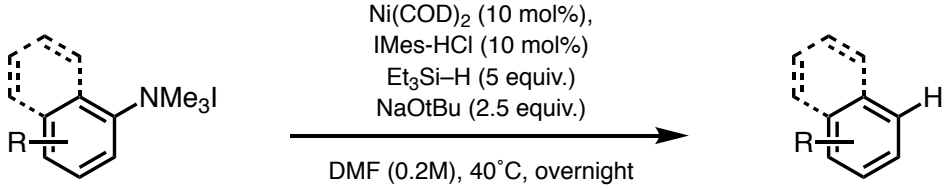
Modified general procedure using air-tolerant nickel(0) catalyst:



Ni(IPr*OMe)(phenyl acrylate)$_2$

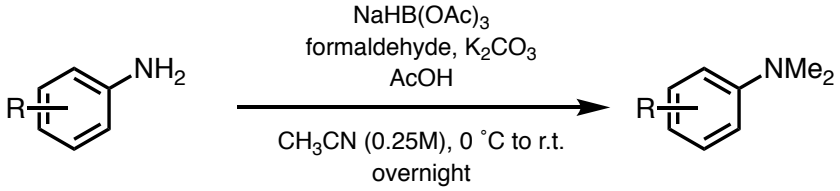
To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added (1,3-Bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazol-2-ylidene)bis(phenyl acrylate)nickel(0) (**Ni(IPr*OMe)(phenyl acrylate)$_2$**) (26 mg, 0.01 mmol, 0.1 equiv), NaO-*t*-Bu (48 mg, 0.50 mmol, 2.5 equiv), and ammonium salt **2a** (68mg, 0.2 mmol, 1 equiv) were combined under inert atmosphere and suspended in 1.0 mL of dioxane at rt. Triethylsilane (156μL, 1.0 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 ºC overnight. Upon completion, the reaction mixture was quenched with 1 mL EtOAc and run through a silica gel plug with 5 mL EtOAc. Analysis of the crude reaction mixture by GCFID using tridecane as an internal standard showed 76% yield of aryl silane **2a** and 13% yield of **3a**. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by flash chromatography (100% hexanes) to give **2a** as a colorless oil in 67% yield (35.9 mg, 0.134 mmol).

General procedure for nickel-catalyzed reduction of aryl ammonium salts:



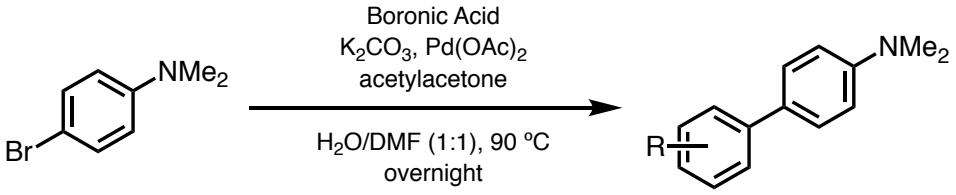
To an oven-dried 8 mL vial equipped with a Teflon-coated magnetic stir bar was added $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.1 equiv), 1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride (IMes·HCl) (3.4 mg, 0.01 mmol, 0.1 equiv), NaO-*t*-Bu (24 mg, 0.25 mmol, 2.5 equiv), and ammonium salt (0.1 mmol, 1 equiv) were combined under inert atmosphere and dissolved in 0.5 mL of DMF at rt. Triethylsilane (80 µL, 0.5 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 ºC overnight. Upon completion, the reaction mixture was quenched with 1 mL EtOAc and run through a silica gel plug with 5 mL EtOAc. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by silica gel chromatography.

General procedures for reductive amination:



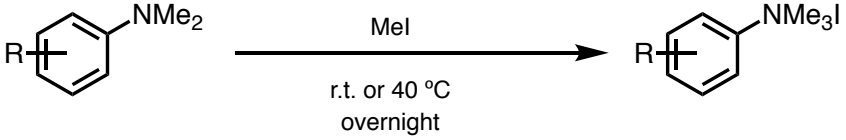
To an appropriately sized round-bottom flask equipped with a Teflon-coated magnetic stir bar under a nitrogen atmosphere were added aniline (1 equiv) and CH_3CN (0.25M). The flask was cooled to 0 ºC before adding formaldehyde solution (37%) (6 equiv) and K_2CO_3 (2 equiv). After 1 hour of stirring $NaHB(OAc)_3$ (3 equiv) was added followed by the slow addition of AcOH (11 equiv). The solution was warmed to room temperature after 30 min and stirred overnight. The reaction was quenched with H_2O and EtOAc. The solution was basified with sat. $NaHCO_3$ and extracted with 3xEtOAc. The organics were dried over brine, then Na_2SO_4 and concentrated before purifying by silica gel column chromatography.

General procedures for Suzuki-Miura coupling:



To an appropriately sized round-bottom flask equipped with a Teflon-coated magnetic stir bar and a reflux condenser was added 4-bromo-dimethylaniline (1.00 equiv), arylboronic acid (1.50 equiv), K_2CO_3 (2.00 equiv), $Pd(OAc)_2$ (0.01 equiv), and acetylacetone (0.02 equiv). The flask was backfilled with N_2 three times before adding H_2O (0.66M) and DMF (0.66M). The reaction was heated to 90 ºC overnight. The reaction was cooled and quenched with Et_2O and the organics were washed 1x H_2O, 2x brine. The organics were then dried over $MgSO_4$ and concentrated before purifying by silica gel column chromatography.[3]

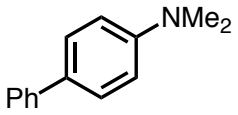
General procedures for ammonium salt formation:



To an appropriately sized vial equipped with a Teflon-coated magnetic stir bar and a reflux

condenser was added *N,N*-dimethylaniline (1.00 equiv) and MeI (10.00 equiv). The vial was sealed and stirred until a white precipitate formed. Electron deficient aniline typically required heating to 40 ºC overnight while electron rich anilines reached full conversion in a few hours. The solid was then filtered washed copiously with Et_2O and rigorously dried on high vac for several hours. The trimethylammonium salts were used as is in subsequent chemistry. [4]

III) Starting Material Synthesis

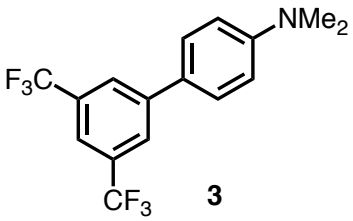


2

N,*N*-dimethyl-[1,1'-biphenyl]-4-amine (**2**)

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (1.00 g, 5.00 mmol, 1.00 equiv), phenylboronic acid (914 mg, 7.5 mmol, 1.50 equiv), K_2CO_3 (1.38 g, 10.00 mmol, 2.00 equiv), $Pd(OAc)_2$ (11 mg, 0.05 mmol, 0.01 equiv), acetylacetone (10 mg, 0.10 mmol, 0.02 equiv), H_2O (7.5 mL), and DMF (7.5 mL). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 87% yield (690 mg, 3.49 mmol). The spectral data matches that previously reported in the literature. [3]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.61 – 7.53 (m, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.26 (m, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.00 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.11, 141.36, 129.38, 128.77, 127.83, 126.42, 126.11, 112.90, 40.71.

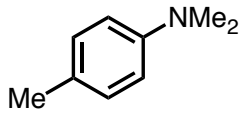


3

N,*N*-dimethyl-3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-amine

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar were brought into a N_2 glovebox and $Pd(PPh_3)_4$ (34.7 mg, 0.03 mmol, 3 mol%) was added. The round bottom was sealed with a septa and removed from the glovebox. 4-bromo-*N,N*-dimethylaniline (200 mg, 1.00 mmol, 1.00 equiv) and 3,5-bis(trifluoromethyl)phenylboronic acid (257 mg, 1.00 mmol, 1.00 equiv) were added, followed by toluene (10 mL, 0.1M), EtOH (3 mL, 0.33M), and Sat. Na_2CO_3 (5 mL). A reflux consensor was added and the reaction was heated to 80 ºC overnight. The reaction was cooled to room temperature and quenched with H_2O (20 mL) and Et_2O (20 mL). The mixture was then extracted 2x20 mL Et_2O. The organic layers were washed with 50 mL brine, then dried over $MgSO_4$. The organics were concentrate and purificated by flash chromatography (100% to 95:5 hexanes/EtOAc) gave the title compound as a white solid in quantitative yield (333 mg, 1.00 mmol).[5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 7.74 (s, 1H), 7.63 – 7.47 (m, 2H), 6.90 – 6.74 (m, 2H), 3.04 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.98, 143.38, 132.01 (q, *J* = 32.9 Hz), 127.96, 126.04, 123.74 (q, *J* = 273.6 Hz), 119.56 – 118.93 (m), 112.76, 40.45.
^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.91.

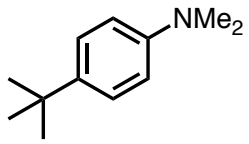


6

N,*N*,4-trimethylaniline (**6**)

The general procedure for reductive amination was followed using *p*-toluidine (107 mg, 1.00 mmol, 1.00 equiv), $NaHB(OAc)_3$ (636 mg, 3.00 mmol, 3.00 equiv), formaldehyde solution (37%) (0.45 mL, 6.00 mmol, 6.00 equiv), K_2CO_3 (276 mg, 2.00 mmol, 2.00 equiv), AcOH (0.7 mL, 11.00 mmol, 11.00 equiv), CH_3CN (4 mL, 0.25M). Purification by flash chromatography (100% to 95:5 hexanes/EtOAc) gave the title compound as a colorless oil in 23% yield (31 mg, 0.23 mmol). The spectral data matches that previously reported in the literature. [6]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 2.92 (s, 6H), 2.28 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.97, 129.71, 126.22, 113.34, 41.21, 20.39.

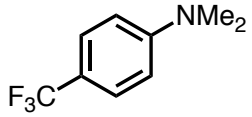


7

4-(*tert*-butyl)-*N*,*N*-dimethylaniline (**7**)

The general procedure for reductive amination was followed using 4-(*tert*-butyl)aniline (597 mg, 4.00 mmol, 1.00 equiv), $NaHB(OAc)_3$ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K_2CO_3 (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH_3CN (8 mL, 0.2M). Purification by flash chromatography (100% to 95:5 hexanes/EtOAc) gave the title compound as a colorless oil in quantitative yield (710 mg, 4.00 mmol). The spectral data matches that previously reported in the literature.[7]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 6.81 – 6.71 (m, 2H), 2.93 (s, 6H), 1.31 (s, 9H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.71, 139.51, 125.98, 112.76, 40.99, 33.89, 31.67.

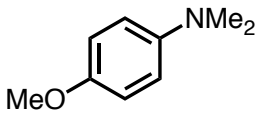


8

N,*N*-dimethyl-4-(trifluoromethyl)aniline (**8**)

The general procedure for reductive amination was followed using 4-aminobenzotrifluoride (1.40 mL, 11.18 mmol, 1.00 equiv), $NaHB(OAc)_3$ (7.00 g, 34.54 mmol, 3.0 equiv), formaldehyde solution (37%) (4.99 mL, 67.08 mmol, 6.00 equiv), K_2CO_3 (3 g, 22.36 mmol, 2.00 equiv), AcOH (5 mL, 79.99 mmol, 7.09 equiv), CH_3CN (56 mL, 0.2M). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 36% yield (751 mg, 4.02 mmol). The spectral data matches that previously reported in the literature.[8]

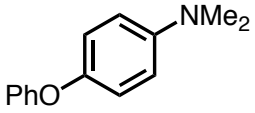
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 3.01 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.45, 126.44 (q, *J* = 3.8 Hz), 117.59 (q, *J* = 32.6 Hz), 111.28, 40.19.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -60.86.



9
4-methoxy-*N*,*N*-dimethylaniline (**9**)

The general procedure for reductive amination was followed using *p*-anisidine (493mg, 4.00 mmol, 1.00 equiv), $NaHB(OAc)_3$ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K_2CO_3 (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH_3CN (8 mL, 0.2M). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a light yellow solid in 99% yield (600 mg, 3.97 mmol). The spectral data matches that previously reported in the literature.[9]

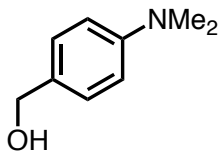
^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.86 (d, *J* = 9.2 Hz, 2H), 6.80 – 6.74 (m, 2H), 3.78 (s, 3H), 2.88 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.08, 145.90, 115.01, 114.74, 55.87, 41.95.



10
N,*N*-dimethyl-4-phenoxyaniline (**10**)

The general procedure for reductive amination was followed using 4-phenoxyaniline (741mg, 4.00 mmol, 1.00 equiv), $NaHB(OAc)_3$ (2.54 g, 12.00 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K_2CO_3 (1.11 g, 8.00 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH_3CN (8 mL, 0.2M). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a clear oil in 94% yield (600 mg, 3.75 mmol). The spectral data matches that previously reported in the literature.[10]

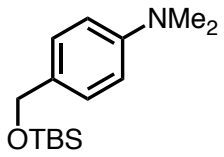
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 7.5 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.95 – 6.91 (m, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 2.94 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.23, 147.80, 147.43, 129.62, 122.05, 121.06, 117.28, 114.08, 41.36.



11'
(4-(dimethylamino)phenyl)methanol (**11'**)

To an oven-dried 10-mL round-bottom flask containing a Teflon-coated magnetic stir bar under a nitrogen atmosphere was added 4-dimethylaminobenzaldehyde (149 mg, 1.00 mmol, 1.00 equiv) and THF (2.5 mL, 0.25M). The flask was cooled to 0 ºC and $LiAlH_4$ (38 mg, 1.00 mmol, 1.00 equiv) was added. The reaction was stirred for 4 hours at 0 ºC before quenching with MeOH (2 mL) and H_2O (2 mL). The reaction was diluted with 10 mL H_2O and extracted 3x10 mL Et_2O. The organic layers were dried with 20 mL brine and then $MgSO_4$ before concentrating. Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a clear oil in 95% yield (144 mg, 0.952 mmol). The spectral data matches that previously reported in the literature. [11]

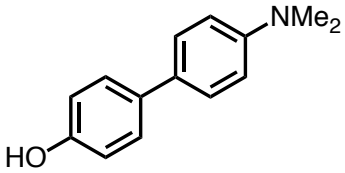
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.3 Hz, 2H), 6.84 – 6.62 (m, 2H), 4.57 (s, 2H), 2.96 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.51, 129.02, 128.77, 112.76, 65.51, 40.79.



11

4-(((*tert*-butyldimethylsilyl)oxy)methyl)-*N*,*N*-dimethylaniline (**11**)
To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar under a nitrogen atmosphere were added **11'**(1.00 g, 6.61 mmol, 1.00 equiv) and DCM (6.60 mL, 1M). The solution was cooled to 0 ºC before adding TBSCl (1.00 g, 6.61 mmol, 1.00 equiv) and imidazole (900 mg, 13.22 mmol, 2.00 equiv). The reaction was then warmed to room temperature and stirred for 15 min. The reaction was quenched with sat. $NaHCO_3$ and extracted 3x30 mL hexanes. The organics were dried 1x30 mL brine and Na_2SO_4 before concentrating. The title compound was obtained in yield as a clear oil in 94% yield (1.65 g, 6.23 mmol) pure by NMR.

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.64 (s, 2H), 2.93 (s, 6H), 0.93 (s, 9H), 0.08 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.07, 129.66, 127.66, 112.76, 65.15, 40.95, 26.17, 25.80, -4.97.
HRMS (ESI) (m/z): [M+H] calculated for $C_{15}H_{27}NOSi$, 266.1940, found, 266.1945.



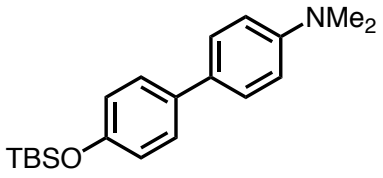
12'

4'-(dimethylamino)-[1,1'-biphenyl]-4-ol (**12'**)

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (200 mg, 1.00 mmol, 1.00 equiv), 4-hydroxyphenylboronic acid (207mg, 1.5 mmol, 1.50 equiv), K_2CO_3 (275 mg, 2.00 mmol, 2.00 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.01 equiv), acetylacetone (2 mg, 0.02 mmol, 0.02 equiv), H_2O (2 mL), and DMF (2 mL). Purification by flash chromatography (70:30 hexanes/EtOAc) gave the title compound as a white solid in 95% yield (203 mg, 0.952 mmol). The spectral data matches that previously reported in the

literature.[12]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.74 (br), 7.52 – 7.34 (m, 4H), 6.95 – 6.72 (m, 4H), 2.97 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.30, 149.76, 134.27, 129.54, 127.69, 127.44, 115.68, 113.33, 40.95.
HRMS (EI) (m/z): [M] calculated for $C_{20}H_{29}NOSi$, 328.2091, found, 328.2096.

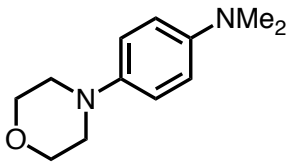


12

4'-((*tert*-butyldimethylsilyl)oxy)-*N*,*N*-dimethyl-[1,1'-biphenyl]-4-amine (**12**)

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar under a nitrogen atmosphere were added **12'**(670 mg, 3.14 mmol, 1.00 equiv) and DCM (6.28 mL, 0.5M). The solution was cooled to 0 ºC before adding TBSCl (473 mg, 3.14 mmol, 1.00 equiv) and imidazole (428 mg, 6.28 mmol, 2.00 equiv). The reaction was then warmed to room temperature and stirred for 15 min. The reaction was quenched with sat. $NaHCO_3$ and extracted 3x30 mL hexanes. The organics were dried 1x30 mL brine and Na_2SO_4 before concentrating. The title compound was obtained in yield as an off-white crystalline solid in 76% yield (780 mg, 2.39 mmol) pure by NMR.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.3 Hz, 2H), 2.98 (s, 6H), 1.01 (s, 9H), 0.23 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.40, 149.73, 134.57, 129.41, 127.45, 127.34, 120.34, 113.04, 40.83, 25.88, 18.39, -4.22.



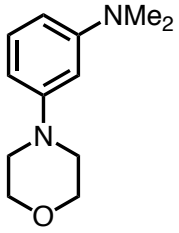
13

N,*N*-dimethyl-4-morpholinoaniline (**13**)

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar were brought into a N_2 glovebox and $Pd_2(dba)_3$ (11.4 mg, 0.0125 mmol, 0.5 mol%), P(*tert*-Bu)$_3$ (5.1 mg, 0.05 mmol, 1 mol%), and NaO-*t*-Bu (250 mg, 2.50 mmol, 1.00 equiv) were added. The round bottom was sealed with a septa and removed from the glovebox. Toluene (5 mL, 0.5M) and morpholine (0.27 mL, 3.12 mmol, 1.25 equiv) were added, followed by 3-bromo-*N*,*N*-dimethylaniline (500 mg, 2.50 mmol, 1.00 equiv). The reaction was stirred at room temperature overnight. The reaction was quenched with 20 mL H_2O and extracted 3x30 mL Et_2O. The organics were washed with 60 mL brine and dried over $MgSO_4$ before concentrating. Purification by flash chromatography (90:10 to 1:1 hexanes/EtOAc) gave the title compound as a yellowish

powder in 62% yield (320 mg, 1.55 mmol). The spectral data matches that previously reported in the literature.[13]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.90 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 9.0 Hz, 2H), 3.89 – 3.84 (m, 4H), 3.08 – 3.01 (m, 4H), 2.88 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.98, 138.24, 120.93, 115.53, 66.59, 58.13, 47.97.

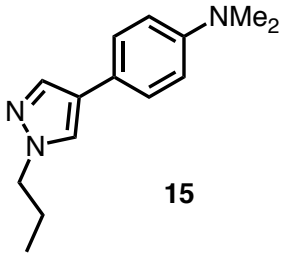


14

N,*N*-dimethyl-3-morpholinoaniline (**14**)

To an oven-dried 25-mL round-bottom flask containing a Teflon-coated magnetic stir bar were brought into a N_2 glovebox and $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.5 mol%), P(*tert*-Bu)$_3$ (10.1 mg, 0.05 mmol, 1 mol%), and NaO-*t*-Bu (481 mg, 5.00 mmol, 1.00 equiv) were added. The round bottom was sealed with a septa and removed from the glovebox. Toluene (10 mL, 0.5M) and morpholine (0.54 mL, 6.25 mmol, 1.25 equiv) were added, followed by 3-bromo-*N,N*-dimethylaniline (1.00 g, 5.00 mmol, 1.00 equiv). The reaction was stirred at room temperature overnight. The reaction was quenched with 20 mL H_2O and extracted 3x30 mL Et_2O. The organics were washed with 60 mL brine and dried over $MgSO_4$ before concentrating. Purification by flash chromatography (70:30 hexanes/EtOAc) gave the title compound as a yellowish oil in 35% yield (360 mg, 1.80 mmol). The spectral data matches that previously reported in the literature.[13]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (t, *J* = 8.1 Hz, 1H), 6.34 (dd, *J* = 8.2, 2.1 Hz, 2H), 6.28 (s, 1H), 3.86 (t, *J* = 4.7 Hz, 4H), 3.16 (t, *J* = 4.7 Hz, 4H), 2.94 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.66, 151.83, 129.76, 105.63, 105.11, 100.89, 67.21, 50.00, 40.90.



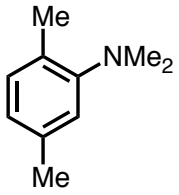
15

N,*N*-dimethyl-4-(1-propyl-1*H*-pyrazol-4-yl)aniline (**15**)

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (400 mg, 2.00 mmol, 1.00 equiv), 1-propylpyrazole-4-boronic acid (462mg, 3.00 mmol, 1.50 equiv), K_2CO_3 (553 mg, 4.00 mmol, 2.00 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.01 equiv),

acetylacetone (4 mg, 0.04 mmol, 0.02 equiv), H_2O (7 mL), and DMF (7 mL). Purification by flash chromatography (80:20 hexanes/EtOAc) gave the title compound as a white solid in 76% yield (350 mg, 1.52 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 0.8 Hz, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.09 (t, *J* = 7.1 Hz, 2H), 2.96 (s, 6H), 1.92 (q, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.45, 136.17, 126.49, 125.09, 123.07, 121.47, 113.18, 54.08, 40.86, 23.93, 11.34.
HRMS (ESI) (m/z): [M+H] calculated for $C_{14}H19N_3$, 230.1657, found, 230.1649.

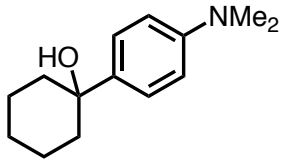


16

N,*N*,2,5-tetramethylaniline (**16**)

The general procedure for reductive amination was followed using 2,5-dimethylaniline (0.5 mL, 4.06 mmol, 1.00 equiv), $NaHB(OAc)_3$ (2.59 g, 12.20 mmol, 3.00 equiv), formaldehyde solution (37%) (1.05 mL, 14.00 mmol, 3.52 equiv), K_2CO_3 (1.12 g, 8.12 mmol, 2.00 equiv), AcOH (2 mL, 34.70 mmol, 8.70 equiv), CH_3CN (8 mL, 0.2M). Aqueous workup gave the title compound as a clear oil, pure by NMR, in 76% yield (450 mg, 3.09 mmol). The spectral data matches that previously reported in the literature.[14]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.04 (d, *J* = 7.5 Hz, 1H), 6.84 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 2.69 (s, 6H), 2.31 (s, 3H), 2.28 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.46, 136.07, 131.12, 128.97, 123.33, 119.26, 44.39, 21.36, 18.10.



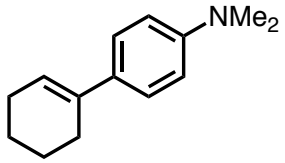
17'

1-(4-(dimethylamino)phenyl)cyclohexan-1-ol (**17'**)

To an oven-dried 10--mL round-bottom flask containing a Teflon-coated magnetic stir bar were added freshly ground magnesium metal (64 mg, 2.62 mmol, 1.05 equiv) and 4-bromodimethylaniline (500 mg, 2.50 mmol, 1.00 equiv). THF (4 mL) was added along with a small crystal of I_2 (to activate the magnesium) and the mixture was stirred until nearly all of the magnesium was consumed. The mixture was cooled in a salt/ice bath for 10 minutes before adding cyclohexanone (0.23 mL, 2.25 mmol, 0.90 equiv) dropwise. The reaction was then stirred

for 1 hour before warming to room temperature overnight. The solution was poured into a sat. NH_4Cl solution and extracted 3x20 mL DCM. The organics were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (90:10 to 80:20 hexanes/EtOAc) gave the title compound as a white solid in 45% yield (224 mg, 1.02 mmol). The spectral data matches that previously reported in the literature.[15]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 8.9, 2.2 Hz, 2H), 6.78 (dd, *J* = 8.9, 2.2 Hz, 2H), 2.98 (s, 6H), 1.93 – 1.72 (m, 8H), 1.64 (dd, *J* = 11.1, 4.7 Hz, 2H), 1.40 – 1.26 (m, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.36, 137.50, 125.46, 112.41, 72.48, 40.66, 38.80, 25.66, 22.38.

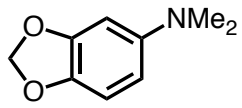


17

N,*N*-dimethyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-amine (**17**)

To an oven-dried 8-mL vial containing a Teflon-coated magnetic stir bar were added **17'** (224 mg, 1.02 mmol, 1.00 equiv) and trifluoroacetic acid (1.30 mL, 0.8M). The vial was sealed with a Teflon cap and stirred at room temperature for 15 min. The reaction was then poured into a flask containing 20 mL of a sat. $NaHCO_3$. The contents were then transferred to a separatory funnel and extracted 3x10 mL Et_2O. The organic layers were dried over Mg_2SO_4 and concentrated to give the title compound as a white solid in quantitative yield (210 mg, 1.02 mmol), which was pure by NMR. The spectral data matches that previously reported in the literature.[15]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 2H), 6.01 (s, 1H), 2.94 (s, 6H), 2.39 (q, *J* = 5.2 Hz, 2H), 2.19 (dq, *J* = 6.4, 3.2 Hz, 2H), 1.77 (q, *J* = 5.9 Hz, 2H), 1.66 (q, *J* = 5.9 Hz, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.64, 136.12, 131.33, 125.67, 121.70, 112.63, 40.87, 27.48, 26.01, 23.36, 22.50.

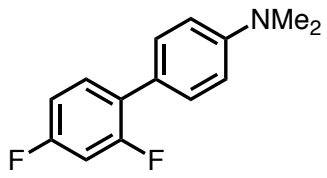


18

N,*N*-dimethylbenzo[*d*][1,3]dioxol-5-amine (**18**)

A modified general procedure for reductive amination was followed using 3,4-(dimethyleneoxy)aniline (2 g, 14.06 mmol, 1.00 equiv), NaH_3BCN (917 mg, 14.06 mmol, 1.00 equiv), formaldehyde solution (37%) (3.60 mL, 45.2 mmol, 3.10 equiv), $ZnCl_2$ (1 g, 7.30 mmol, 0.50 equiv), MeOH (70 mL, 0.2M). Aqueous workup gave the title compound as a clear oil, pure by NMR, in 14% yield (340 mg, 1.97 mmol). The spectral data matches that previously reported in the literature.[16]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 8.5 Hz, 1H), 6.42 (d, *J* = 2.5 Hz, 1H), 6.17 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.87 (s, 2H), 2.86 (s, 6H).



19

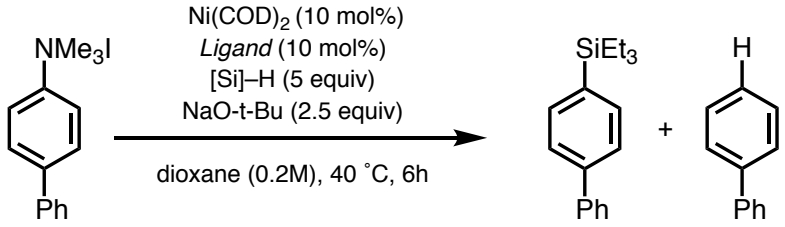
2',4'-difluoro-*N*,*N*-dimethyl-[1,1'-biphenyl]-4-amine (**19**)

The general procedure for Suzuki-Miura coupling was followed using 4-bromo-dimethylaniline (400 mg, 2.00 mmol, 1.00 equiv), 2,4-difluoroophenylboronic acid (472mg, 3.00 mmol, 1.50 equiv), K_2CO_3 (553 mg, 4.00 mmol, 2.00 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.01 equiv), acetylacetone (4 mg, 0.04 mmol, 0.02 equiv), H_2O (7 mL), and DMF (7 mL). Purification by flash chromatography (95:5 to 90:10 hexanes/EtOAc) gave the title compound as an off-white solid in quantitative yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 2H), 7.36 (dd, *J* = 8.9, 6.6 Hz, 1H), 6.89 (dddd, *J* = 13.3, 11.3, 8.5, 2.7 Hz, 2H), 6.82 – 6.76 (m, 2H), 3.00 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.63, 162.54, 150.14, 130.90 (q, *J* = 5.3 Hz) 129.70 (d, *J* = 3.2 Hz), 122.88, 112.45, 111.43 (dd, *J* = 3.6 Hz), 104.43 (d, *J* = 25.4 Hz), 104.22 (d, *J* = 25.3 Hz), 40.62.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -113.56 (p, *J* = 7.6 Hz), -114.04 (q, *J* = 9.0 Hz).
HRMS (ESI) (m/z): [M+H] calculated for $C_{14}H_{13}F_2N$, 234.1094, found, 234.1090.

IV) Supplemental Tables

Table S1: Ligand screening for the optimization of the silylation of **1a**

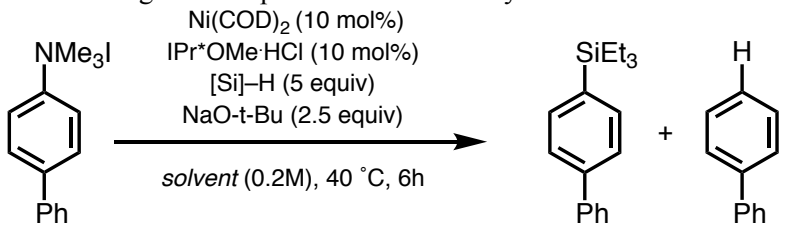


1a **2a** **3a**

Entry	Ligand	Yield **2a** (%)[a]	Yield **3a** (%)[a]
1	PPh_3	<1	5
2	PCy_3	<1	<1
3	ICy·HCl	<1	1
4	IMes·HCl	<1	1
5	IPr·HCl	14	7
6	IPr^{Me}·HCl	21	5
7	IPr^{Cl}·HCl	12	8
8	IPr*OMe·HCl	89	11
9	none	<1	<1
10[b]	none	10	90

Following the general procedure for silylation of ammonium salts, reaction were run for 6 hours, and quenched. [a] Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. [b] Used DMF instead of dioxane

Table S2: Solvent screening for the optimization of the silylation of **1a**



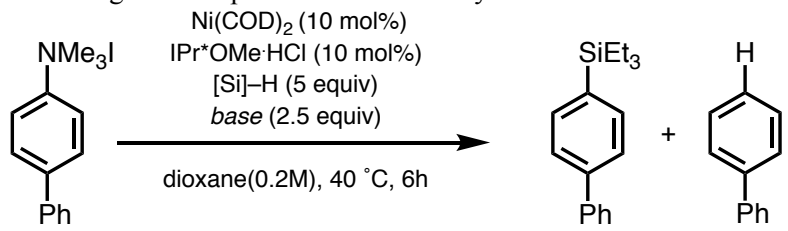
1a **2a** **3a**

Entry	Solvent	Yield **2a** (%)[a]	Yield **3a** (%)[a]
1	MeOH	<1	1
2	CH_3CN	<1	5
3	DME	<1	3
4	toluene	6	4
5	Et_2O	5	6
6	THF	65	37
7	dioxane	89	11

Following the general procedure for silylation of ammonium salts, reaction were run for 6 hours, and quenched. [a] Yield determined by GCFID of the crude reaction mixture using tridecane as an

internal standard.

Table S3: Base screening for the optimization of the silylation of **1a**

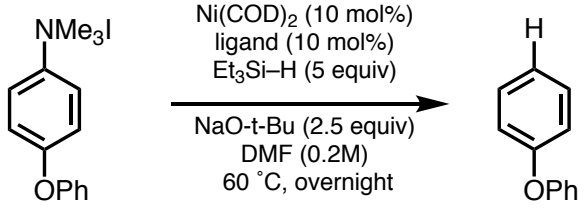


1a **2a** **3a**

Entry	Base	Yield **2a** (%)[a]	Yield **3a** (%)[a]
1	none	<1	<1
2	NaOMe	24	<1
3	LiO-*t*-Bu	41	5
4	KO-*t*-Bu	48	7
5	NaO-*t*-Bu	89	11
6[b]	NaO-*t*-Bu	72	13
7	Cs_2CO_3	<1	<1
8	Et_3N	48	7
9	pyridine	55	12

Following the general procedure for silylation of ammonium salts, reaction were run for 6 hours, and quenched. [a] Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. [b] 1 equiv base used.

Table S4: Ligand screening for the optimization of the reduction of **8**

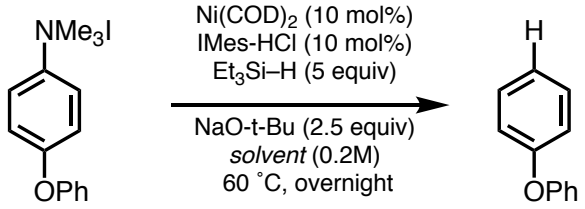


8 **4a**

Entry	Ligand	Yield **4a** (%)[a]
1	none	15
2[b]	PPh_3	45
3[b]	PCy_3	31
4	IMes·HCl	56
5	SIMes·HCl	47
6	IAd ·HCl	46
8	IPr*OMe·HCl	49

Following the general procedure for silylation of ammonium salts, reaction were run for 12 hours, and quenched. [a] Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. [b] Reaction run for 6 hours.

Table S5: Solvent screening for the optimization of the reduction of **8**

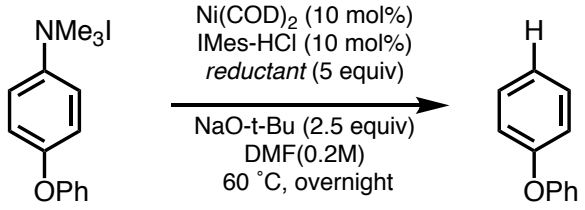


8 **4a**

Entry	Solvent	Yield **4a** (%)[a]
1	dioxane	29
2	THF	27
3	DMF	56
4[b]	DMF	58
5[c]	DMF	51
6[d]	DMF	60

Following the general procedure for silylation of ammonium salts, reaction were run for 12 hours, and quenched. [a] Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard. [b] Reaction run at 80 ºC. [c] Reaction run at 40 ºC. [d] Reaction run at room temperature (21˚C).

Table S6: Reductant screening for the optimization of the reduction of **8**



8 **4a**

Entry	Reductant	Yield **4a** (%)[a]
1	Et_2SiH_2	54
2	Et_3SiH	56
3	Ph_3SiH	48
4	*i*-Pr_3SiH	24
5	$Me(OTMS)_2SiH$	18
6	Ti(*i*-OPr)$_4$	42

Following the general procedure for silylation of ammonium salts, reaction were run for 12 hours, and quenched. [a] Yield determined by GCFID of the crude reaction mixture using tridecane as an internal standard.

V) Calibration Curves

Solutions containing a constant concentration of an internal standard (tridecane (0.164 M) and varying concentrations of the desired product (0.05, 0.10, 0.15 and 0.20 M) were prepared in ethyl acetate. Each was analyzed by GC-FID and the response factor (F) calculated by solving equation S1 for the area of product to give equation S2, where the response factor (F) is the slope. Yields of crude reactions mixtures, containing a known amount of internal standard, were then determined by solving Equation S1 for the concentration of the product to give Equation S3 and filling in the known data from a crude reaction.

$$(\boldsymbol{Area\ of\ Product})/(\boldsymbol{Concentration\ of\ Product})=\boldsymbol{F}*(\boldsymbol{Area\ of\ Standard})/(\boldsymbol{Concentration\ of\ Standard})$$

(Equation S1)

$$(\boldsymbol{Area\ of\ Product}) =\boldsymbol{F}*((\boldsymbol{Area\ of\ Standard})(\boldsymbol{Concentration\ of\ Product})/(\boldsymbol{Concentration\ of\ Standard}))$$

(Equation S2)

$$(\boldsymbol{Concentration\ of\ Product}) =(\boldsymbol{Concentration\ of\ Standard})(\boldsymbol{Area\ of\ Product})/(\boldsymbol{F}*(\boldsymbol{Area\ of\ Standard}))$$

(Equation S3)

Calibration curve for [1,1'-biphenyl]-4-yltriethylsilane (Compound 2a):

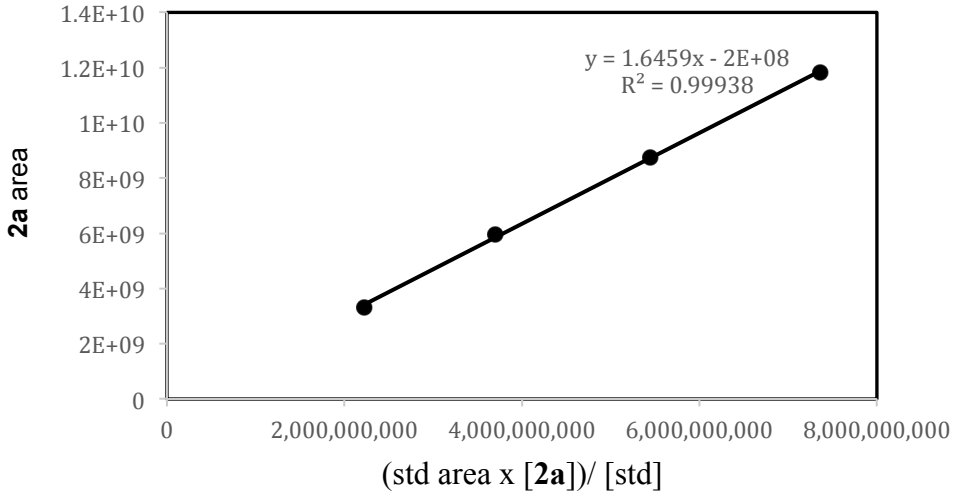


Figure 1: Plot of **2a** area versus (std area x [**2a**]) / [std] fitted to y = *m*x + *b* where *m* = 1.6459 and *b* = -2 x 10^8 with a R^2 of 0.9994.

mmol 2a	mmol tridecane	Area IS	Area Pdt.
0.048420739	0.16403	7535226346	3329460100
0.08715733	0.16403	6961574030	5961048038
0.143027414	0.16403	6242681983	8751150218
0.192938021	0.16403	6254367926	11816631504

Calibration curve for [1,1'-biphenyl]-4-yl(benzyl)dimethylsilane (2b):

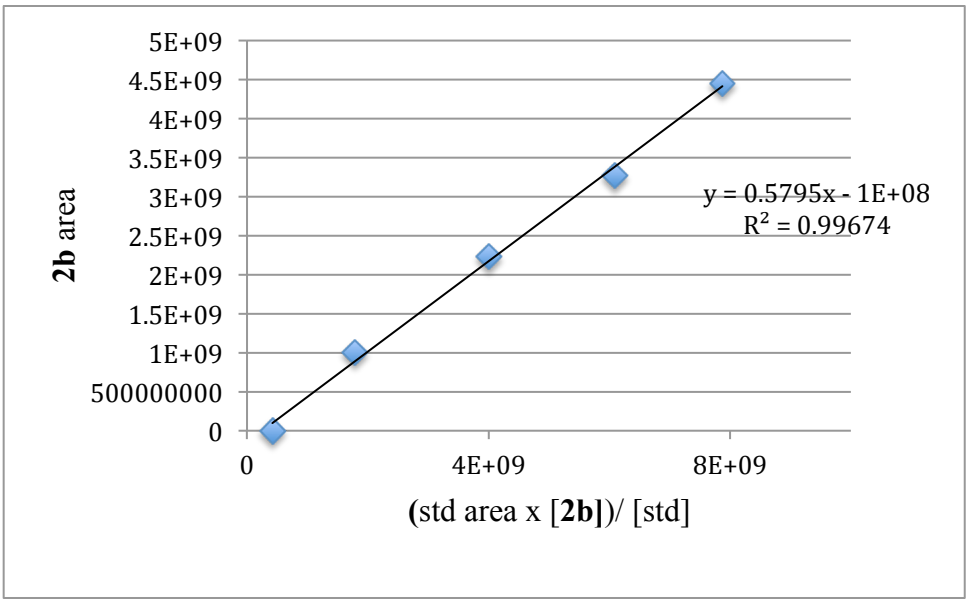


Figure S2: Plot of **2b** area versus (std area x [**2b**]) / [std] fitted to y = *m*x + *b* where *m* = 0.5795 and *b* = -1 x 10^8 with a R^2 of 0.99674.

mmol 2b	mmol tridecane	Area IS	Area Pdt.
9.91768E-06	0.164026904	3947284982	419876796
0.049919006	0.164026904	3315120257	1789461089
0.102152137	0.164026904	3575670979	3999385208
0.150418196	0.164026904	3564399649	6087760854
0.199345433	0.164026904	3665141539	7872337807

Calibration curve for biphenyl (3a):

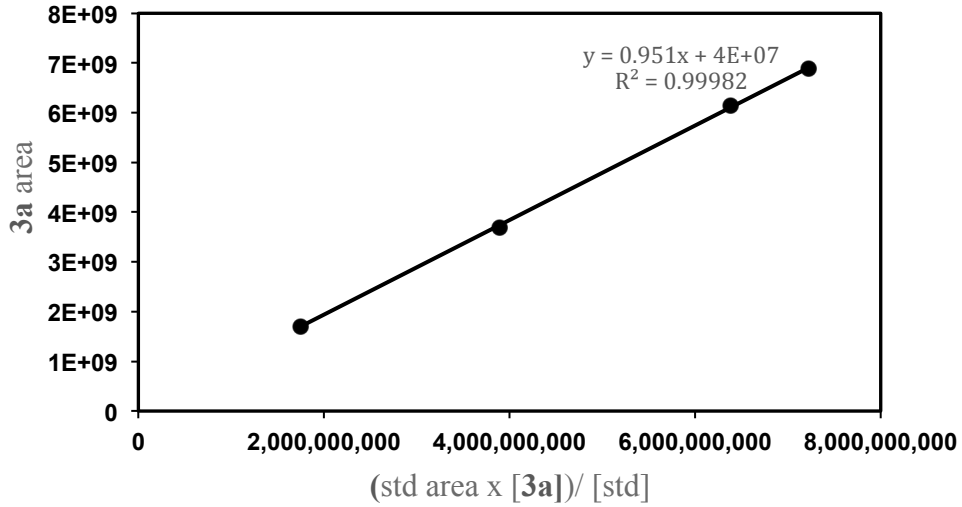


Figure S3: Plot of analyte area versus (std area x [**3a**]) / [std] fitted to y = *m*x + *b* where *m* = 0.951 and *b* = 4 x 10^7 with a R^2 of 0.9998.

mmol 3a	mmol tridecane	Area IS	Area Pdt.
0.0509	0.16403	5647778523	1707314294
0.0966	0.16403	6596748815	3699921557
0.1582	0.16403	6622184645	6149186696
0.192	0.16403	6176751384	6891778392
0.0509	0.16403	5647778523	1707314294

Calibration curve for diphenyl ether (4a):

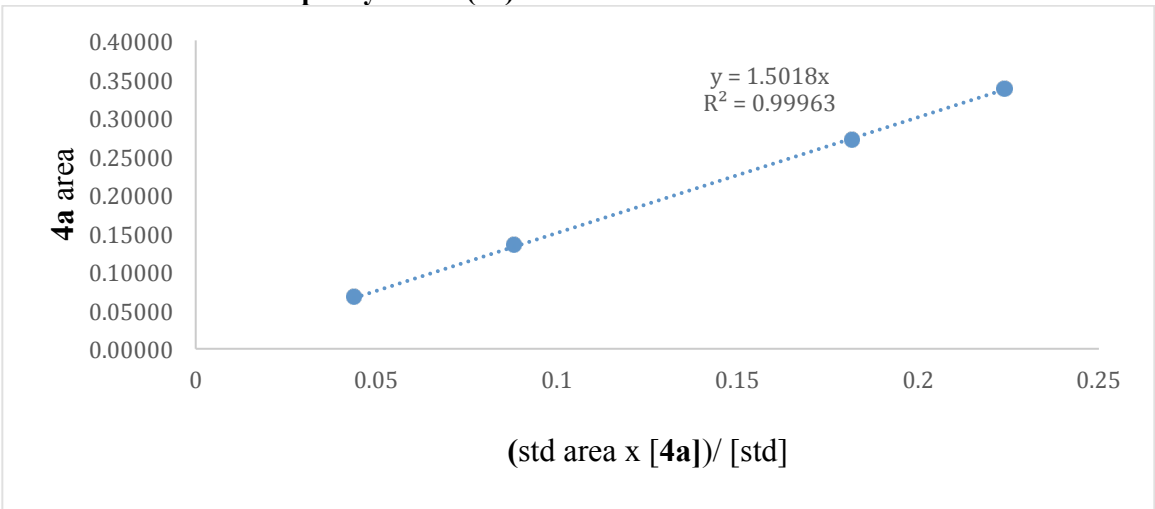


Figure S4: Plot of **4a** area versus (std area x [**4a**]) / [std] fitted to y = *m*x + *b* where *m* = 1.5018 and *b* = 0 with a R^2 of 0.99963.

mmol 4a	mmol tridecane	Area IS	Area Pdt.
0.067830908	0.164026904	3611778993	964667595
0.134567768	0.164026904	3522436673	1891415126
0.202398676	0.164026904	3360770109	3112052070
0.270229584	0.164026904	3320105098	3676856664
0.336966444	0.164026904	3504987328	4783168130

Calibration curve for trifluorotolunene (19b):

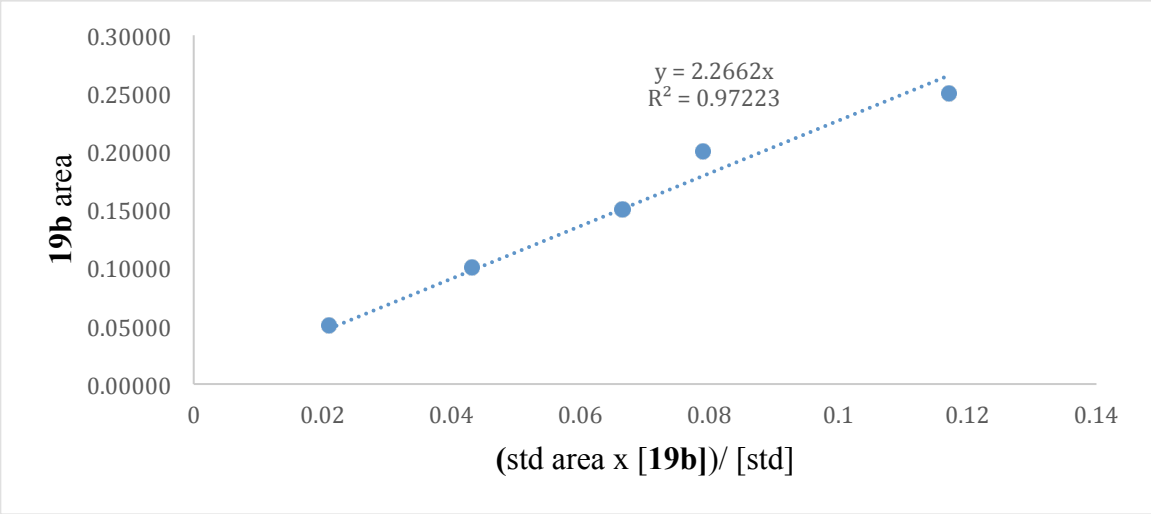


Figure S5: Plot of **19b** area versus (std area x [**19b**]) / [std] fitted to y = *m*x + *b* where *m* = 2.2662 and *b* = 0 with a R^2 of 0.97223.

mmol 19b	mmol tridecane	Area IS	Area Pdt.
0.050030799	0.16403	4492524320	574994724
0.100061597	0.16403	3927418367	1032274349
0.150092396	0.16403	4914023783	1990948584
0.200123195	0.16403	3902305473	1878381691
0.250153994	0.16403	4893566950	3494602386

Calibration curve for anisole (19c):

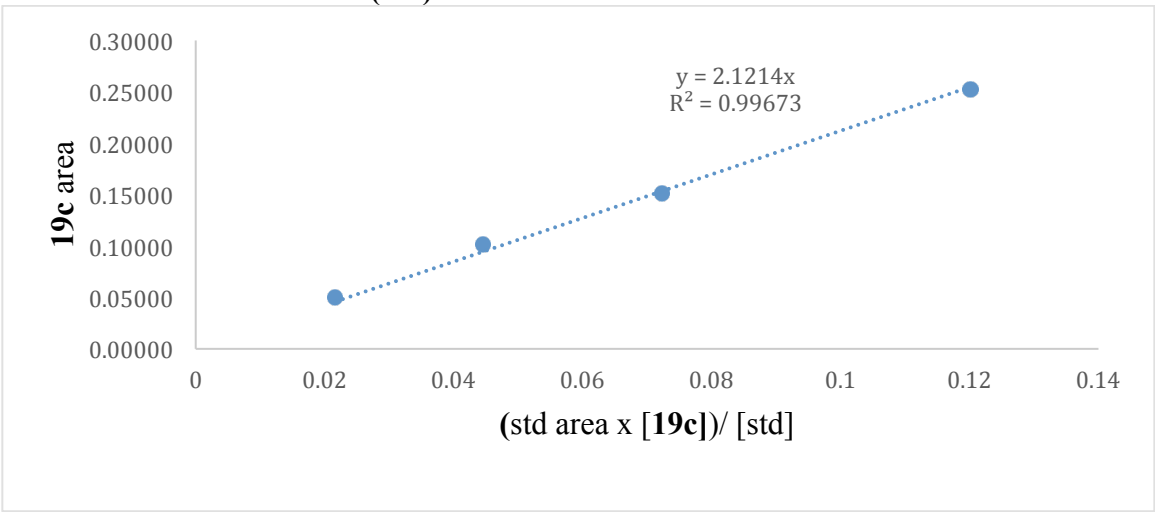


Figure S6: Plot of **19c** area versus (std area x [**19c**]) / [std] fitted to y = *m*x + *b* where *m* = 2.1214 and *b* = 0 with a R^2 of 0.99673.

mmol 19c	mmol tridecane	Area IS	Area Pdt.
0.0501862	0.164026904	4000104738	527950383
0.101301774	0.164026904	3537739243	960449091
0.151487974	0.164026904	3236629289	1427195136
0.201674174	0.164026904	3602495138	1828214896
0.252789749	0.164026904	3975653755	2912617178

Calibration curve for naphthalene (19e):

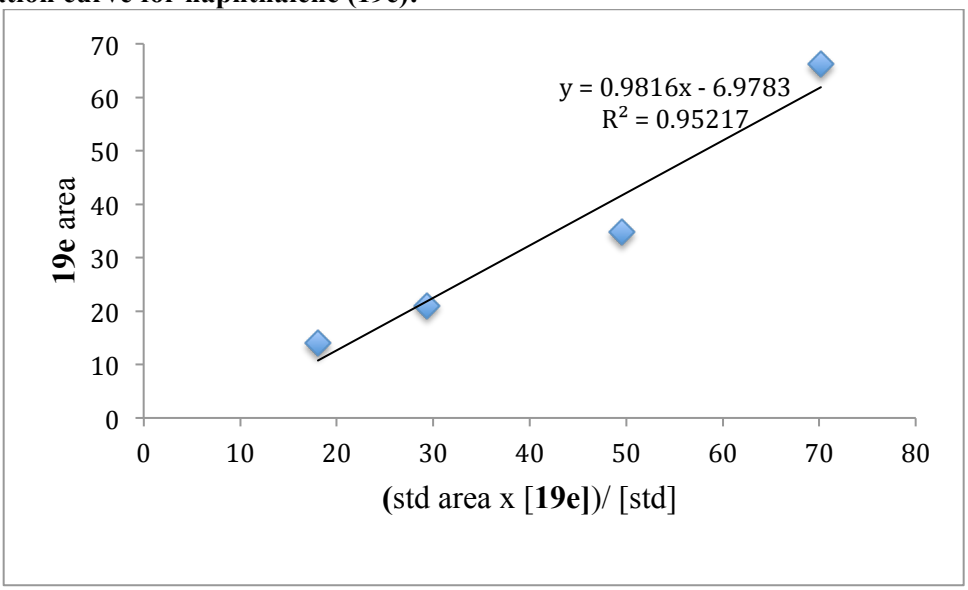


Figure S7: Plot of **19e** area versus (std area x [**19e**]) / [std] fitted to y = *m*x + *b* where *m* = 0.9816 and *b* = -6.9783 with a R^2 of 0.95217.

mmol 19e	mmol tridecane	Area IS	Area Pdt.
0.049153468	0.16403	5560584759	1352944750
0.103768433	0.16403	7185032978	3353404616
0.154482328	0.16403	6904005775	4614671198
0.201295155	0.16403	6790282011	6296395603

Calibration curve for *t*-butylbenzene (19f):

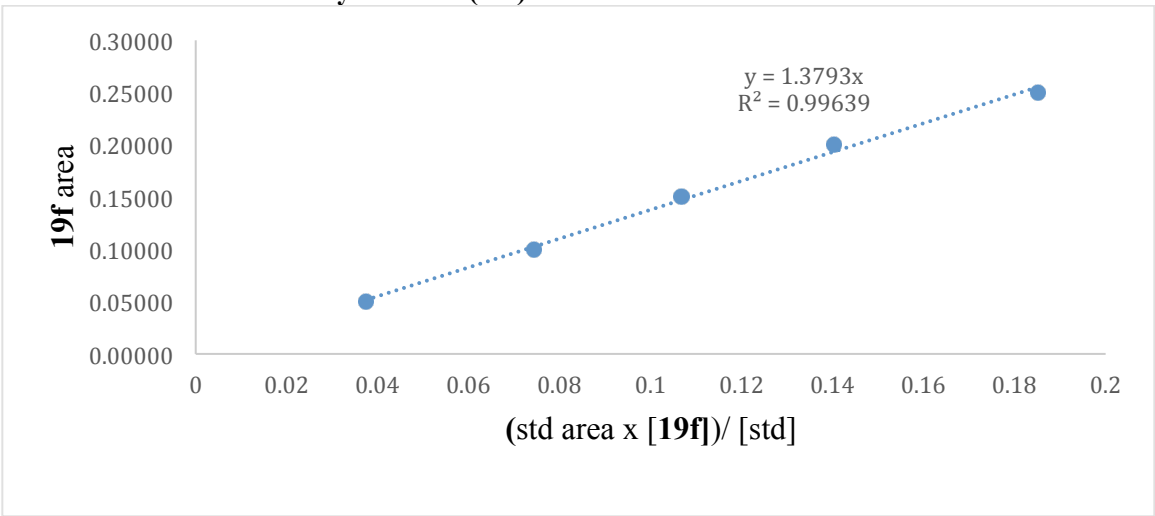


Figure S8: Plot of **19f** area versus (std area x [**19f**]) / [std] fitted to y = *m*x + *b* where *m* = 1.3793 and *b* = 0 with a R^2 of 0.99639.

mmol 19f	mmol tridecane	Area IS	Area Pdt.
0.049738489	0.16403	2518295474	574090525
0.100122932	0.16403	3255077022	1477595029
0.149861422	0.16403	3930989531	2559730260
0.200245865	0.16403	3546712147	3032026099
0.249984354	0.16403	3479578042	3925217274

Calibration curve for *p*-xylene (19g)

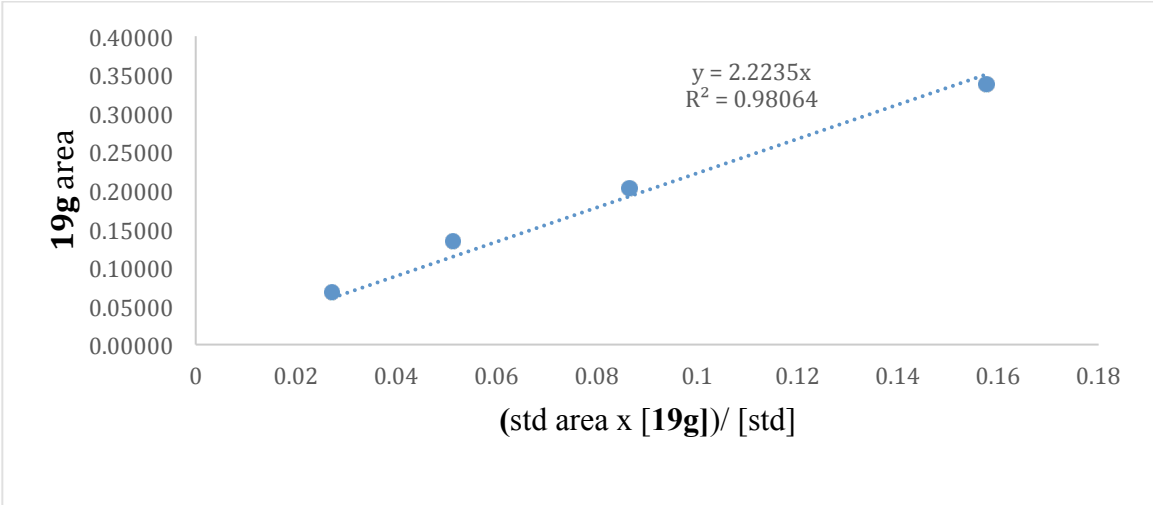


Figure S9: Plot of **19g** area versus (std area x [**19g**]) / [std] fitted to y = *m*x + *b* where *m* = 2.2235 and *b* = 0 with a R^2 of 0.98064.

mmol 19g	mmol tridecane	Area IS	Area Pdt.
0.067830908	0.164026904	3288937475	545232412
0.134567768	0.164026904	3669199995	1145416244
0.202398676	0.164026904	3546770818	1870406001
0.270229584	0.164026904	3601846681	2352337673
0.336966444	0.164026904	2666629964	2562696982

Calibration curve for pyridine (19i):

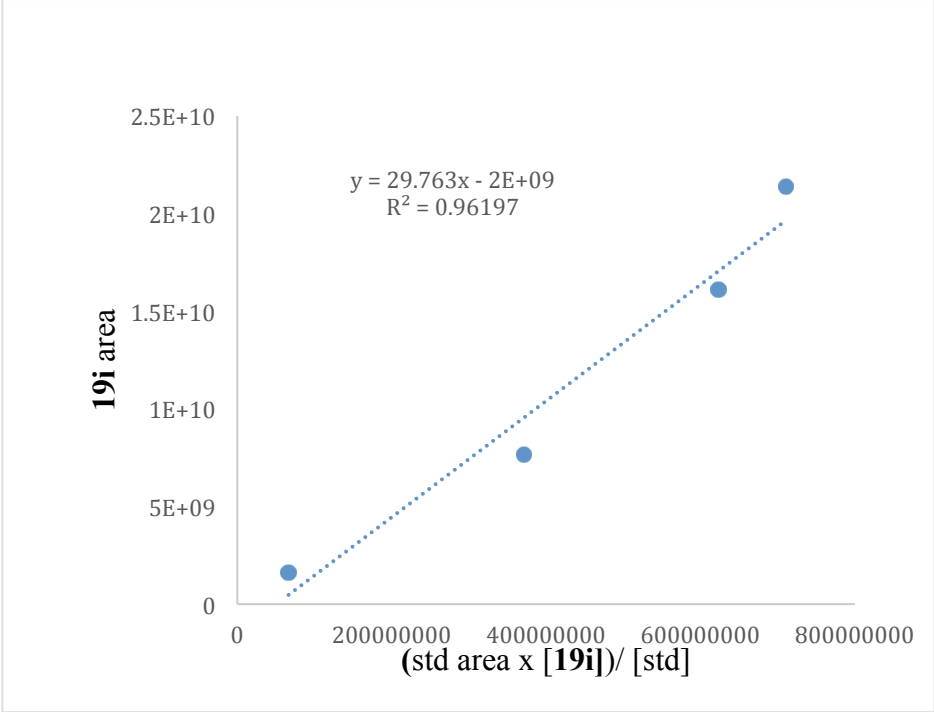
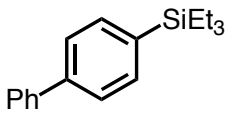


Figure S10: Plot of **19i** area versus (std area x [**19i**]) / [std] fitted to y = *m*x + *b* where *m* = 29.763 and *b* = -2 x 10^9 with a R^2 of 0.96197.

mmol 19i	mmol tridecane	Area IS	Area Pdt.
0.062134632	0.164026904	4233992225	66403740
0.31067316	0.164026904	4031783804	371135414
0.62134632	0.164026904	4249091608	623374155
0.93201948	0.164026904	3760306370	710497433

VI) Silylation Substrates

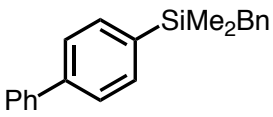


2a

[1,1'-biphenyl]-4-yltriethylsilane (**2a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **2** (73 mg, 0.215 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 86% yield (50 mg, 0.186 mmol). The spectral data matches that previously reported in the literature.[17]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.62 (m, 6H), 7.59 (d, *J* = 1.5 Hz, 2H), 7.45 (dd, *J* = 8.3, 6.9 Hz, 1H), 7.40 – 7.30 (m, 1H), 1.01 (t, *J* = 7.8 Hz, 9H), 0.84 (q, *J* = 7.3 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.56, 141.33, 136.38, 134.83, 128.88, 127.41, 127.27, 126.52, 7.60, 3.57.

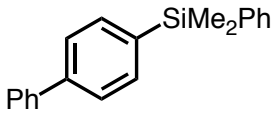


2b

[1,1'-biphenyl]-4-yl(benzyl)dimethylsilane (**2b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **2** (66 mg, 0.194 mmol) and dimethybenzylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes to 98:2 hex/EtOAc) gave the title compound as a white solid in 85% yield (50 mg, 0.165 mmol). The spectral data matches that previously reported in the literature.[17]

^{1}H NMR (400MHz, Chloroform-*d*) δ 7.68-7.57 (m, 4H), 7.54 (d, *J*= 8.0 Hz, 2H), 7.46 (dd, *J*= 8.3, 6.8 Hz, 2H), 7.4-7.33 (m, 1H), 7.20 (t, *J*= 7.5 Hz, 2H), 7.13-7.02 (m, 2H), 6.98 (d, *J*= 7.3 Hz, 2H), 2.35 (s, 2H), 0.29 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.92, 141.18, 139.76, 137.37, 134.36, 128.92, 128.28, 128.13, 127.54, 127.29, 126.58, 124.25, 26.35, -3.24.



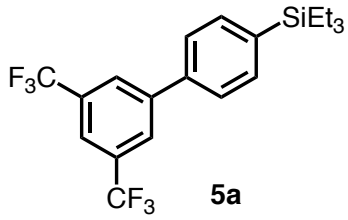
2c

[1,1'-biphenyl]-4-yldimethyl(phenyl)silane (**2c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **2** (73 mg, 0.215 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (9.4 mg, 0.1 equiv, 0.01 mmol), and dimethyphenylsilane (156 µL, 1 mmol). Purification by flash

chromatography (100% hexanes) gave the title compound in an inseparable mixture with phenyldimethyldisilane as a colorless oil. 65% yield (41 mg, 0.14 mmol) by NMR analysis. The spectral data matches that previously reported in the literature.[18]

^{1}H NMR (500MHz, Chloroform-*d*) δ 7.65-7.53 (m, 8H), 7.45 (t, *J*= 7.7 Hz, 2H), 7.41-7.32 (m, 4H), 0.60 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.01, 141.20, 138.30, 137.13, 134.81, 134.33, 129.29, 128.90, 127.99, 127.53, 127.31, 126.70, 32.22, -2.19.

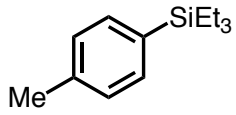


5a

(3',5'-bis(trifluoromethyl)-[1,1'-biphenyl]-4-yl)triethylsilane (**5a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **5** (45.7 mg, 0.100 mmol) and triethylsilane (80 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (98%). The spectral data matches that previously reported in the literature.[19]

^{1}H NMR (500MHz, Chloroform-*d*) δ 8.02 (d, *J*=1.6Hz, 2H), 7.85 (s, 1H), 7.63 (d, *J*=8.1Hz, 2H), 7.59 (d, *J*=8.1Hz, 2H), 0.99 (t, *J*= 7.8 Hz, 9H), 0.84 (q, *J*=7.8 Hz, 6H).
^{13}C NMR (176 MHz, Chloroform-*d*) δ 143.51, 138.79, 138.52, 132.23 (q, *J*= 33.3Hz), 127.35, 126.55, 123.55 (q, *J*= 272.8Hz), 121.04 (m), 7.52, 3.46.

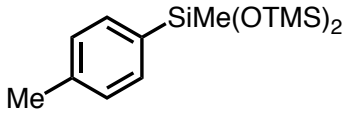


6a

triethyl(*p*-tolyl)silane (**6a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **6** (54 mg, 0.195 mmol) and triethylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (90%). The spectral data matches that previously reported in the literature.[19]

^{1}H NMR (400MHz, Chloroform-*d*) δ 7.39 (d, *J*= 7.9 Hz), 2H), 7.17 (d, *J*= 7.5 Hz, 2H), 2.35 (s, 3H), 0.96 (t, *J*= 7.7 Hz, 9H), 0.77 (q, *J*=7.6 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.62, 134.38, 133.38, 128.67, 7.58, 3.56.

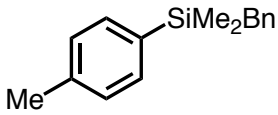


6b

1,1,1,3,5,5,5-heptamethyl-3-(*p*-tolyl)trisiloxane (**6b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **6** (57 mg, 0.206 mmol) and 1,1,1, 3, 5, 5, 5-heptamethyltrisiloxane (272 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (81%).

^{1}H NMR (400MHz, Chloroform-*d*) δ 7.44 (d, *J*= 7.8 Hz), 2H), 7.17 (d, *J*= 7.5 Hz, 2H), 2.35 (s, 3H), 0.25 (s, 3H), 0.10 (s, 18H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.36, 135.17, 133.43, 128.54, 21.70, 2.03, 0.28.
HRMS (EI) (m/z): [M] calculated for $C_{14}H_{28}O_2Si_3$, 312.1397, found, 312.1409.

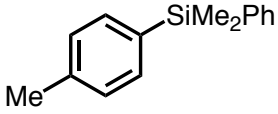


6c

benzyldimethyl(*p*-tolyl)silane (**6c)**

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **6** (28 mg, 0.101 mmol) and dimethybenzylsilane (80 µL, 0.5 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (79%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 4H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.03 – 6.91 (m, 2H), 2.38 (s, 3H), 2.31 (s, 2H), 0.24 (s, 5H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.94, 139.03, 134.96, 133.89, 128.71, 128.45, 128.22, 124.16, 26.42, 21.62, -3.22.
HRMS (EI) (m/z): [M] calculated for $C_{16}H_{20}Si$, 240.1334, found, 240.1343.

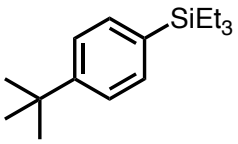


6d

dimethyl(phenyl)(*p*-tolyl)silane (**6d**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **6** (56 mg, 0.202 mmol) and dimethyphenlsilane (156 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (74%). The spectral data matches that previously reported in the literature.[18]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dt, *J* = 4.7, 2.3 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.31 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 0.56 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.38, 134.32, 134.30, 129.23, 129.15, 128.80, 127.94, 127.91, 21.62, -2.16.

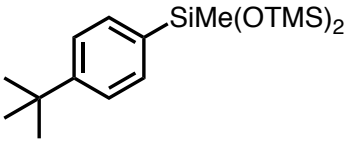


7a

(4-(*tert*-butyl)phenyl)triethylsilane (**7a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **7** (62 mg, 0.194 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 76% yield (37 mg, 0.149 mmol). The spectral data matches that previously reported in the literature.[17]

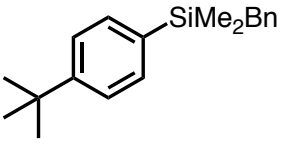
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 6.5 Hz, 2H), 1.32 (s, 9H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.78 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.64, 134.19, 133.97, 124.74, 34.74, 31.42, 7.63, 3.61.



7b

3-(4-(*tert*-butyl)phenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**7b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **7** (68 mg, 0.213 mmol) and 1,1,1, 3, 5, 5, 5-heptamethyltrisiloxane (272 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 46% yield (34 mg, 0.096 mmol).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 1.33 (s, 9H), 0.26 (s, 3H), 0.12 (s, 18H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.43, 135.16, 133.83, 133.27, 124.65, 34.82, 31.41, 2.04, 0.41.

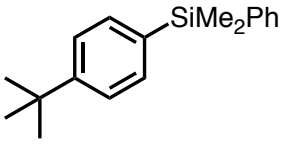


7c

benzyl(4-(*tert*-butyl)phenyl)dimethylsilane (**7c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **7** (64 mg, 0.200 mmol) and dimethybenzylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 41% yield (23 mg, 0.081 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 2H), 2.30 (s, 2H), 1.33 (s, 9H), 0.22 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.16, 140.01, 135.15, 133.73, 128.47, 128.24, 124.85, 124.16, 34.80, 31.40, 26.36, -3.23.
HRMS (EI) (m/z): [M] calculated for $C_{19}H_{26}Si$, 282.1804, found, 282.1814.

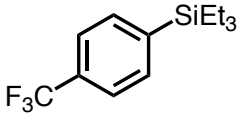


7d

(4-(*tert*-butyl)phenyl)dimethyl(phenyl)silane (**7d**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **7** (67 mg, 0.210 mmol) and dimethyphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 93% yield (53 mg, 0.198 mmol). The spectral data matches that previously reported in the literature.[18]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.53 (ddd, *J* = 7.5, 4.9, 2.3 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.36 (dd, *J* = 4.7, 2.7 Hz, 3H), 1.32 (s, 9H), 0.54 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.15, 138.65, 134.76, 134.31, 134.20, 129.14, 127.90, 124.92, 34.79, 31.39, -2.18.

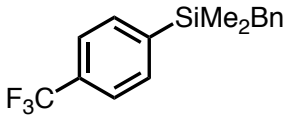


8a

triethyl(4-(trifluoromethyl)phenyl)silane (**8a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **8** (68 mg, 0.205 mmol) and triethylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (50%). The spectral data matches that previously reported in the literature.[20]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 0.96 (t, *J* = 7.7 Hz, 9H), 0.81 (q, *J* = 7.7 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.84, 142.74, 134.56, 130.82 (q, *J* = 31.8 Hz), 124.28 (q, *J* = 3.7 Hz), 7.43, 3.32.
^{19}F NMR (377 MHz, Chloroform-*d*) δ -62.91.

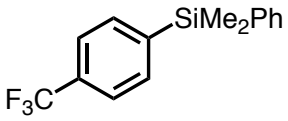


8b

benzyldimethyl(4-(trifluoromethyl)phenyl)silane (**8b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **8** (66 mg, 0.199 mmol) and dimethybenzylsilane (63 µL, 0.4 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (52%). Purification by preparative TLC (100% hexanes) gave the title compound as a clear oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 2H), 0.29 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.57, 139.11, 134.14, 131.02, 128.41, 128.37, 124.48, 124.34 (q, *J* = 3.8 Hz), 26.00, -3.42.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.92.
HRMS (EI) (m/z): [M] calculated for $C_{16}H_{17}F_3Si$, 294.1052, found, 294.1062.

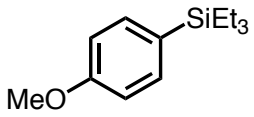


8c

dimethyl(phenyl)(4-(trifluoromethyl)phenyl)silane (**8c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **8** (65 mg, 0.196 mmol) and dimethyphenlsilane (62 µL, 0.4 mmol). Yield determined by NMR of the crude reaction mixture using fluorobenzene as an internal standard (47%). Purification by preparative TLC (100% hexanes) gave the title compound as a clear oil. The spectral data matches that previously reported in the literature.[18]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.45 – 7.33 (m, 1H), 0.59 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.54, 137.21, 134.57, 134.26, 131.19 (d, *J* = 32.4 Hz), 129.61, 128.14, 124.45 (q, *J* = 3.7 Hz), -2.45.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.95.



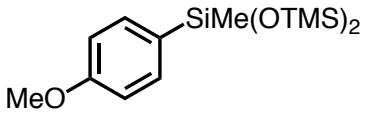
9a

triethyl(4-methoxyphenyl)silane (**9a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **9** (58 mg, 0.198 mmol) and triethylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude

reaction mixture using CH_2Br_2 as an internal standard (98%). The spectral data matches that previously reported in the literature.[21]

^{1}H NMR (500MHz, Chloroform-*d*) δ 7.42 (d, *J*= 8.6 Hz), 2H), 6.91(d, *J*= 8.6 Hz, 2H), 3.81 (s, 3H), 0.96 (t, *J*= 7.9 Hz, 9H), 0.76 (q, *J*= 7.9 Hz, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.30, 135.70, 128.28, 113.59, 55.11, 7.34, 3.65.

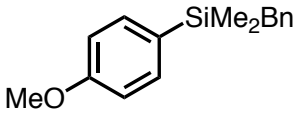


9b

3-(4-methoxyphenyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (**9b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **9** (29 mg, 0.096 mmol) and 1,1,1, 3, 5, 5, 5-heptamethyltrisiloxane (136 µL, 0.5 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (59%). The spectral data matches that previously reported in the literature.[22]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H), 0.25 (s, 3H), 0.10 (s, 18H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.79, 134.91, 129.96, 113.42, 55.13, 2.02, 0.33.

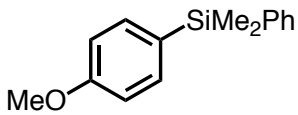


9c

benzyl(4-methoxyphenyl)dimethylsilane (**9c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **9** (58 mg, 0.198 mmol) and dimethybenzylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (98%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.33 (m, 2H), 7.23 – 7.14 (m, 2H), 7.12 – 7.04 (m, 1H), 7.00 – 6.88 (m, 3H), 3.83 (s, 3H), 2.29 (s, 2H), 0.24 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.57, 139.96, 135.29, 129.39, 128.44, 128.20, 124.14, 113.63, 55.16, 26.61, -3.12.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{16}H_{20}OSi$, 279.1176, found, 279.1179.

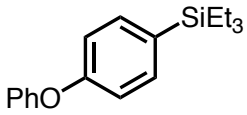


9d

(4-methoxyphenyl)dimethyl(phenyl)silane (**9d**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **9** (58 mg, 0.198 mmol) and dimethyphenlsilane (156 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (92%). The spectral data matches that previously reported in the literature.[18]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.37 (m, *J* = 5.8 Hz, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 0.56 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 160.63, 138.82, 135.78, 134.27, 129.13, 127.91, 113.74, 55.16, -2.04.

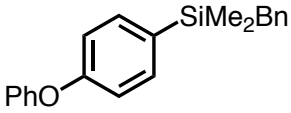


10a

triethyl(4-phenoxyphenyl)silane (**10a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **10** (70 mg, 0.197 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 89% yield (50 mg, 0.176 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.78 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.24, 156.98, 135.85, 129.86, 123.53, 119.43, 119.02, 118.01, 7.56, 3.63.
HRMS (EI) (m/z): [M] calculated for $C_{18}H_{24}OSi$, 284.1596, found, 284.1609.

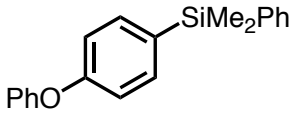


10b

benzyldimethyl(4-phenoxyphenyl)silane (**10b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **10** (73 mg, 0.206 mmol) and dimethybenzylsilane (64 µL, 0.4 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 72% yield (47 mg, 0.148 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 8.1 Hz, 2H), 7.20 (t, *J* = 6.6 Hz, 29H), 7.15 (t, *J* = 7.9, 1H), 7.09 (d, *J* = 6.9 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 6.6 Hz, 2H), 6.96 (d, *J* = 7.1 Hz, 2H), 2.31 (s, 0H), 0.27 (s, 1H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.46, 156.95, 139.77, 135.46, 132.53, 129.90, 128.44, 128.24, 124.22, 123.59, 119.37, 118.10, 26.50, -3.16.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{21}H_{22}OSi$, 341.1332, found, 341.1338.

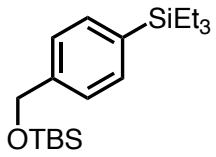


10c

dimethyl(4-phenoxyphenyl)(phenyl)silane (**10c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **10** (70 mg, 0.197 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (9.4 mg, 0.1 equiv, 0.01 mmol), and dimethyphenylsilane (156 μL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound in an inseparable mixture with phenyldimethyldisilane as a colorless oil. 68% yield (41 mg, 0.1348 mmol) by NMR analysis.

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.53 (ddd, *J* = 7.4, 5.1, 2.1 Hz, 3H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.30 (m, 5H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 0.54 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.60, 156.84, 138.44, 135.93, 134.27, 132.24, 129.89, 129.25, 127.97, 123.65, 119.49, 118.08, -2.09.
HRMS (EI) (m/z): [M] calculated for $C_{20}H_{20}OSi$, 304.1283, found, 304.1294.

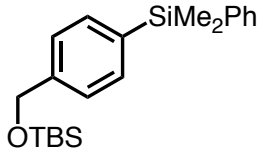


11a

tert-butyldimethyl((4-(triethylsilyl)benzyl)oxy)silane (**11a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **11** (80 mg, 0.196 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (18.8 mg, 0.1 equiv, 0.01 mmol), triethylsilane (160 μL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a yellow solid in 46% yield (31 mg, 0.091 mmol).

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 4.74 (s, 2H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.95 (s, 9H), 0.78 (q, *J* = 7.8 Hz, 6H), 0.10 (s, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.05, 135.80, 134.29, 125.46, 65.08, 26.13, 18.60, 7.56, 3.54, -5.11.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{19}H_{36}OSi_2$, 359.2197, found, 359.2197.

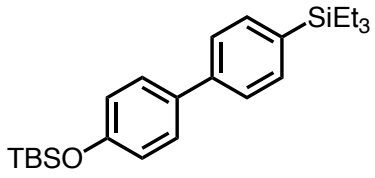


11b

tert-butyl((4-(dimethyl(phenyl)silyl)benzyl)oxy)dimethylsilane (**11b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **11** (81 mg, 0.199 mmol), 30 mg of 4Å molecular sieves powder, IPr*OMe free carbene (9.4 mg, 0.1 equiv, 0.01 mmol), and dimethyphenylsilane (156 μL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as an off white solid in 57% yield (40 mg, 0.113 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 3.0, 1.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.34 (m, 3H), 7.31 (d, *J* = 7.7 Hz, 2H), 4.74 (s, 2H), 0.94 (s, 9H), 0.54 (s, 6H), 0.10 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.57, 138.54, 136.60, 134.31, 134.29, 129.18, 127.92, 125.57, 65.01, 26.12, 18.59, -2.18, -5.11.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{21}H_{32}OSi_2$, 379.1884, found, 379.1895.

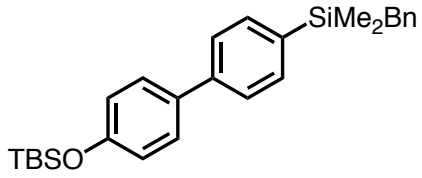


12a

tert-butyldimethyl((4'-(triethylsilyl)-[1,1'-biphenyl]-4-yl)oxy)silane (**12a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **12** (97 mg, 0.207 mmol) and triethylsilane (160 μL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 56% yield (46 mg, 0.115 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (m, 4H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 1.00 (s, 9), 0.82 (q, *J* = 7.4 Hz, 6H), 0.23 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.46, 141.23, 135.52, 134.78, 134.37, 128.19, 126.10, 120.47, 25.86, 18.40, 7.60, 3.59, -4.21.
HRMS (EI) (m/z): [M] calculated for $C_{24}H_{38}OSi_2$, 398.2461, found, 398.2473.



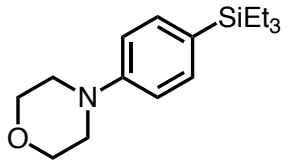
12b

benzyl(4'-((*tert*-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-4-yl)dimethylsilane (**12b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **12** (251 mg, 0.535 mmol) and dimethybenzylsilane (421 μL, 2.66 mmol). Purification by flash chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a colorless oil in 76% yield (175 mg, 0.404 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.52 – 7.44 (m, 4H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 2.33 (s, 2H), 1.01 (s, 9H), 0.27 (s, 6H), 0.23 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.57, 141.61, 139.83, 136.55, 134.32, 134.21, 128.48, 128.27, 128.23, 126.16, 124.22, 120.50, 26.40, 25.86, -3.22, -4.21.

HRMS (ESI) (m/z): [M+Na] calculated for $C_{27}H_{36}OSi_2$, 455.2197, found, 455.2200.

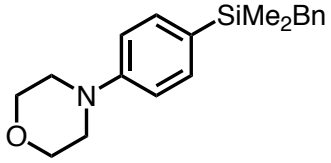


13a

4-(4-(triethylsilyl)phenyl)morpholine (**13a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **13** (73 mg, 0.210 mmol) and triethylsilane (160 μL, 1 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 86% yield (51 mg, 0.184 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 3.86 (dd, *J* = 5.8, 3.9 Hz, 4H), 3.20 (dd, *J* = 5.9, 3.8 Hz, 4H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.77 (q, *J* = 7.6 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.55, 135.44, 127.01, 114.78, 67.08, 48.83, 7.59, 3.66.
HRMS (ESI) (m/z): [M+H] calculated for $C_{16}H_{27}NOSi$, 278.1940, found, 278.1936.

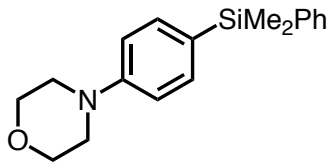


13b

4-(4-(benzyldimethylsilyl)phenyl)morpholine (**13b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **13** (70 mg, 0.201 mmol) and dimethybenzylsilane (160 μL, 1 mmol). Purification by flash chromatography (95:5 to 90:10 hexanes/EtOAc) gave the title compound as a white solid in 76% yield (47 mg, 0.151 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 3.89 – 3.84 (m, 4H), 3.20 (t, *J* = 4.9 Hz, 4H), 2.28 (s, 2H), 0.21 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.86, 140.08, 135.01, 128.46, 128.19, 128.08, 124.10, 114.80, 67.04, 48.85, 26.61, -3.15.
HRMS (ESI) (m/z): [M+H] calculated for $C_{19}H_{25}NOSi$, 312.1784, found, 312.1786.

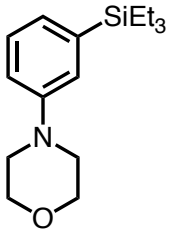


13c

4-(4-(dimethyl(phenyl)silyl)phenyl)morpholine (**13c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **13** (67 mg, 0.198 mmol) and dimethyphenylsilane (156 μL, 1 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 78% yield (46 mg, 0.155 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 6.2 Hz, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 4.6 Hz, 4H), 3.19 (t, *J* = 4.7 Hz, 4H), 0.52 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.89, 138.99, 135.49, 134.28, 129.06, 127.86, 127.66, 114.84, 67.02, 48.77, -2.07.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{18}H_{23}NOSi$, 298.1622, found, 298.1628.

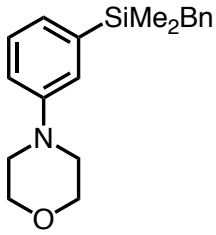


14a

4-(3-(triethylsilyl)phenyl)morpholine (**14a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **14** (70 mg, 0.201 mmol) and triethylsilane (160 μL, 1 mmol). Purification by flash chromatography (100% hexanes to 95:5 hexanes/EtOAc) gave the title compound as a white solid in 81% yield (45 mg, 0.162 mmol). The spectral data matches that previously reported in the literature.[17]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 2.6 Hz, 1H), 7.03 (dd, *J* = 7.2, 1.1 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.92 – 3.84 (m, 4H), 3.17 (dd, *J* = 5.8, 3.8 Hz, 4H), 0.97 (t, *J* = 7.7 Hz, 9H), 0.79 (q, *J* = 7.8 Hz, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.71, 138.52, 128.61, 126.25, 121.76, 116.37, 67.17, 49.73, 7.61, 3.55.
HRMS (ESI) (m/z): [M+H] calculated for $C_{18}H_{23}NOSiO$, 298.1627, found, 298.1628.



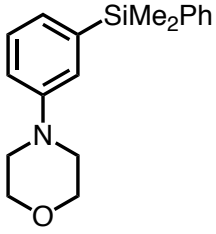
14b

4-(3-(benzyldimethylsilyl)phenyl)morpholine (**14b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **14** (69 mg, 0.198 mmol) and dimethybenzylsilane (160 μL, 1 mmol). Purification by flash

chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 85% yield (53 mg, 0.167 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 7.00 (d, *J* = 7.1 Hz, 1H), 6.98 – 6.88 (m, 4H), 3.90 – 3.82 (m, 4H), 3.16 – 3.10 (m, 4H), 2.29 (s, 2H), 0.24 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.66, 139.88, 139.48, 128.73, 128.49, 128.24, 125.62, 121.32, 116.73, 67.13, 49.66, 26.38, -3.20.
HRMS (ESI) (m/z): [M+H] calculated for $C_{19}H_{25}NOSi$, 312.1784, found, 312.1791.

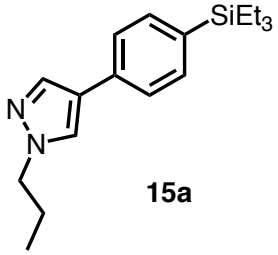


14c

4-(3-(dimethyl(phenyl)silyl)phenyl)morpholine (**14c)**

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **14** (70 mg, 0.201 mmol) and dimethyphenylsilane (156 µL, 1 mmol). Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a white solid in 70% yield (42 mg, 0.141 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.49 (m, 2H), 7.40 – 7.32 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.97 – 6.88 (m, 1H), 3.89 – 3.81 (m, 4H), 3.17 – 3.10 (m, 4H), 0.54 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.78, 139.21, 138.42, 134.32, 129.21, 128.83, 127.92, 126.19, 121.65, 116.69, 67.12, 49.59, -2.17.



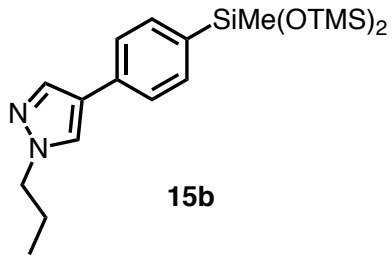
15a

1-propyl-4-(4-(triethylsilyl)phenyl)-1*H*-pyrazole (**15a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **15** (73 mg, 0.197 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 81% yield (48 mg, 0.160 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.64 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 4.11 (t, *J* = 7.0 Hz, 2H), 1.93 (h, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.94

(t, *J* = 7.4 Hz, 3H), 0.80 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.76, 135.23, 134.90, 133.19, 126.14, 124.87, 122.89, 54.20, 23.89, 11.30, 7.56, 3.53.
HRMS (ESI) (m/z): [M+H] calculated for $C_{18}H_{28}N_2OSi$, 301.2100, found, 301.2092.

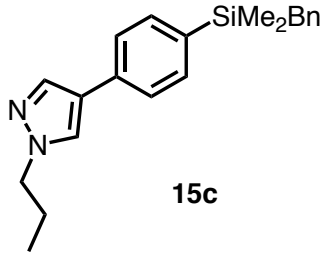


15b

4-(4-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)phenyl)-1-propyl-1*H*-pyrazole (**15b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **15** (35 mg, 0.094 mmol) and 1,1,1, 3, 5, 5, 5-heptamethyltrisiloxane (136 µL, 0.5 mmol). Purification by flash chromatography (90:10 to 80:20 hexanes/EtOAc) gave the title compound as a white solid in 27% yield (10 mg, 0.018 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.65 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 7.8 Hz, 2H), 4.11 (t, *J* = 7.1 Hz, 2H), 1.93 (h, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.27 (s, 3H), 0.11 (s, 18H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.80, 136.35, 133.96, 133.83, 126.19, 124.75, 122.86, 54.22, 23.90, 11.32, 2.03, 0.22.
HRMS (ESI) (m/z): [M+H] calculated for $C_{19}H_{34}N_2O_2Si_3$, 407.2006, found, 407.2003.

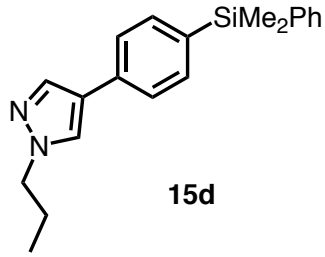


15c

4-(4-(benzyldimethylsilyl)phenyl)-1-propyl-1*H*-pyrazole (**15c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **15** (36 mg, 0.097 mmol) and dimethybenzylsilane (80 µL, 0.5 mmol). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 93% yield (30 mg, 0.090 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.65 (s, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.10 – 7.04 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 4.12 (t, *J* = 7.1 Hz, 2H), 2.31 (s, 2H), 1.94 (q, *J* = 7.2 Hz, 2H), 0.96 (dd, *J* = 7.9, 6.8 Hz, 3H), 0.26 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.78, 136.76, 136.18, 134.43, 133.53, 128.45 (d, *J* = 2.5 Hz), 128.23, 126.18, 124.86, 124.19, 54.21, 26.38, 23.88, 11.31, -3.26.
HRMS (ESI) (m/z): [M+H] calculated for $C_{21}H_{26}N_2Si$, 335.1944, found, 335.1938.

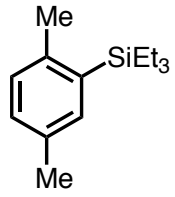


15d

4-(4-(dimethyl(phenyl)silyl)phenyl)-1-propyl-1*H*-pyrazole (**15d**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **15** (36 mg, 0.097 mmol) and dimethyphenylsilane (78 μL, 0.5 mmol). Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a white solid in 72% yield (22 mg, 0.069 mmol).

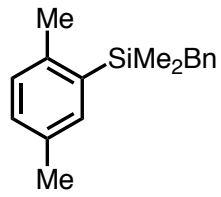
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.64 (s, 1H), 7.57 – 7.49 (m, 4H), 7.49 – 7.45 (m, 2H), 7.40 – 7.33 (m, 3H), 4.11 (t, *J* = 7.1 Hz, 2H), 1.93 (q, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H), 0.57 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 138.44, 136.78, 135.93, 134.90, 134.29, 133.62, 129.21, 128.96, 127.94, 126.20, 124.98, 54.20, 23.87, 11.29, -2.21.
HRMS (ESI) (m/z): [M+H] calculated for $C_{20}H_{24}N_2Si$, 321.1787, found, 321.1781.



16a

(2,5-dimethylphenyl)triethylsilane (**16a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **16** (58 mg, 0.198 mmol) and triethylsilane (160 μL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (35%). The spectral data matches that previously reported in the literature.[23]
^{1}H NMR (500MHz, Chloroform-*d*) δ 7.22 (s, 1H), 7.05 (q, *J*= 7.8 Hz, 2H), 2.39 (s, 3H), 2.31 (s, 3H), 0.95 (t, *J*= 8 Hz, 9H), 0.85 (q, *J*= 7.9 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.81, 136.30, 135.31, 133.83, 129.84, 129.78, 22.61, 21.30, 7.78, 4.16.

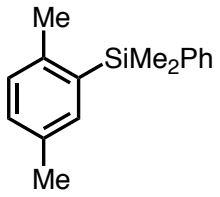


16b

benzyl(2,5-dimethylphenyl)dimethylsilane (**16b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **16** (58 mg, 0.198 mmol) and dimethybenzylsilane (160 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (65%).

^{1}H NMR (500MHz, Chloroform-*d*) δ 7.22 (d, *J*= 1.8 Hz, 1H), 7.19 (t, *J*= 7.5 Hz, 2H), 7.08 (qd, *J*= 8.1, 7.5, 4.9 Hz, 3H), 7.00- 6.92 (m, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 0.28 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.58, 140.11, 136.60, 135.57, 134.17, 130.20, 130.01, 128.48, 128.25, 124.21, 26.36, 22.84, 21.20, -1.95.
HRMS (EI) (m/z): [M] calculated for $C_{17}H_{22}Si$, 254.1491, found, 254.1489.

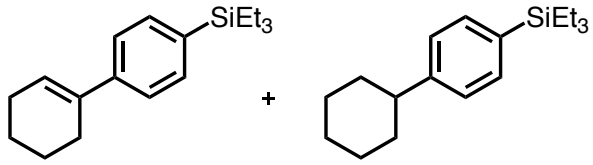


16c

(2,5-dimethylphenyl)dimethyl(phenyl)silane (**16c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **16** (58 mg, 0.198 mmol) and dimethyphenlsilane (156 µL, 1 mmol). Yield determined by NMR of the crude reaction mixture using CH_2Br_2 as an internal standard (47%).

^{1}H NMR (500MHz, Chloroform-*d*) δ 7.56- 7.44 (m, 2H), 7.41- 7.28 (m, 4H), 7.13 (dd, *J*= 7.7, 2.1 Hz, 1H), 7.05 (dd, *J*= 7.7, 2.0 Hz, 1H), 2.33 (s, 3H), 2.22 (s, 3H), 0.58 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.07, 139.24, 136.15, 134.32, 134.15, 134.11, 130.43, 129.99, 128.99, 127.93, 22.77, 21.24, -1.18.
HRMS (EI) (m/z): [M] calculated for $C_{16}H_{20}Si$, 240.1334, found, 240.1344.



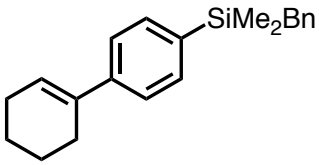
17a **17a'**

triethyl(2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)silane (**17a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **17** (137 mg, 0.399 mmol) and triethylsilane (192 µL, 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash chromatography (100% hexanes) gave the title compound as a white solid in 45% yield (49 mg, 0.180 mmol) and the hydrogenated product in 10% yield (11mg, 0.040 mmol).

17a:
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 6.16 (tt, *J* = 3.9, 1.7 Hz, 1H), 2.42 (tq, *J* = 6.5, 2.3 Hz, 2H), 2.21 (dh, *J* = 6.1, 2.8 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.70 – 1.62 (m, 2H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.78 (q, *J* = 7.8 Hz, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.94, 136.61, 135.42, 134.33, 125.04, 124.25, 27.36, 26.08, 23.23, 22.35, 7.58, 3.56.

17a':
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 6.6 Hz, 2H), 7.19 (d, *J* = 6.9 Hz, 2H), 2.58 – 2.42 (m, 1H), 1.96 – 1.80 (m, 3H), 1.74 (d, *J* = 13.1 Hz, 1H), 1.41 (h, *J* = 12.4 Hz, 3H), 1.31 – 1.18 (m, 1H), 0.96 (t, *J* = 7.7 Hz, 9H), 0.77 (q, *J* = 8.0 Hz, 7H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.64, 134.37, 134.34, 126.37, 44.66, 34.48, 27.10, 26.36, 7.62, 3.62.
HRMS (EI) (m/z): [M] calculated for $C_{18}H_{30}Si$, 274.2117, found, 274.2125.

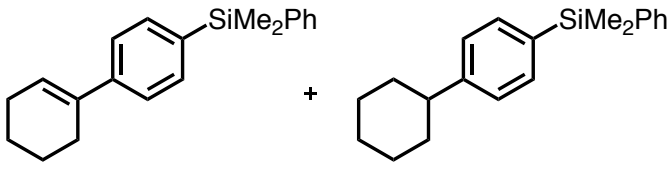


17b

benzyldimethyl(2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)silane (**17b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **17** (136 mg, 0.396 mmol) and dimethybenzylsilane (190 μL, 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a white solid in 59% yield (72 mg, 0.234 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 2H), 6.16 (tt, *J* = 4.1, 1.7 Hz, 1H), 2.42 (dq, *J* = 6.1, 3.8, 3.1 Hz, 2H), 2.30 (s, 2H), 2.22 (dq, *J* = 6.3, 3.5 Hz, 2H), 1.79 (ddt, *J* = 12.0, 8.6, 4.5 Hz, 1H), 1.71 – 1.62 (m, 2H), 0.23 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.40, 139.91, 136.60, 133.84, 128.46, 128.23, 125.30, 124.37, 124.17, 27.39, 26.39, 26.08, 23.20, 22.32, -3.24.
HRMS (EI) (m/z): [M] calculated for $C_{21}H_{26}Si$, 306.1804, found, 306.1811.



17c **17c'**

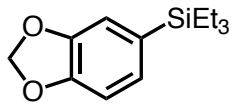
dimethyl(phenyl)(2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-yl)silane (**17c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **17** (138 mg, 0.402 mmol) and dimethyphenylsilane (187 μL, 1.2 mmol). Reaction was run under a stream of nitrogen in order to prevent hydrogenation of the product. Purification by flash

chromatography (100% hexanes to 98:2 hexanes/EtOAc) gave the title compound as a white solid in 56% yield (65 mg, 0.222 mmol) and the hydrogenated product in 27% yield (32mg, 0.109 mmol).

17c:
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.58 – 7.49 (m, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.36 (dt, *J* = 10.5, 3.6 Hz, 5H), 6.15 (tt, *J* = 5.7, 2.6 Hz, 1H), 2.41 (tq, *J* = 6.4, 2.1 Hz, 2H), 2.21 (dddd, *J* = 8.9, 6.6, 4.4, 2.5 Hz, 2H), 1.78 (ddt, *J* = 8.4, 6.1, 3.8 Hz, 2H), 1.70 – 1.61 (m, 2H), 0.54 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.48, 136.10, 134.31, 133.14, 129.39, 129.16, 127.91, 127.84, 125.34, 124.47, 27.38, 26.06, 23.19, 22.30, -2.19.
HRMS (EI) (m/z): [M] calculated for $C_{20}H_{24}Si$, 292.1647, found, 292.1646.

17c':
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 (dd, *J* = 4.8, 2.5 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.40 – 7.32 (m, 5H), 7.20 (d, *J* = 7.5 Hz, 2H), 2.49 (dt, *J* = 11.6, 5.7 Hz, 1H), 1.93 – 1.79 (m, 4H), 1.74 (d, *J* = 13.1 Hz, 1H), 1.49 – 1.32 (m, 4H), 1.32 – 1.19 (m, 1H), 0.54 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.16, 134.38, 134.32, 129.23, 129.13, 127.94, 127.89, 126.55, 44.70, 34.45, 27.05, 26.32, -2.15.
HRMS (EI) (m/z): [M] calculated for $C_{20}H_{26}Si$, 294.1804, found, 294.1812.

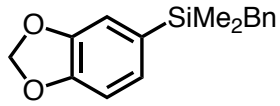


18a

benzo[*d*][1,3]dioxol-5-yltriethylsilane (**18a**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **18** (60 mg, 0.195 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 68% yield (32 mg, 0.135 mmol). The spectral data matches that previously reported in the literature.[19]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 7.6 Hz, 1H), 6.94 (s, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 2H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.75 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.26, 147.42, 130.44, 128.18, 113.57, 108.66, 100.55, 7.52, 3.66.

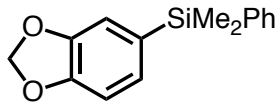


18b

benzo[*d*][1,3]dioxol-5-yl(benzyl)dimethylsilane (**18b**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **18** (60 mg, 0.195 mmol) and dimethybenzylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 79% yield (42 mg, 0.155 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (t, *J* = 7.6 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.97 – 6.90 (m, 4H), 6.90 (s, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.95 (s, 2H), 2.27 (s, 2H), 0.22 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.54, 147.45, 139.75, 128.42, 128.24, 127.86, 124.23, 113.19, 108.65, 100.67, 26.54, -3.08.
HRMS (EI) (m/z): [M] calculated for $C_{16}H_{18}O_2Si$, 270.1076, found, 270.1084.



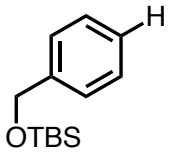
18c

benzo[*d*][1,3]dioxol-5-yldimethyl(phenyl)silane (**18c**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **18** (61 mg, 0.199 mmol) and dimethyphenylsilane (156 μL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a colorless oil in 60% yield (31 mg, 0.119 mmol).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.47 (m, 2H), 7.40 – 7.31 (m, 3H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 5.93 (s, 2H), 0.53 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.63, 147.53, 138.45, 134.24, 131.36, 129.25, 128.39, 127.96, 113.65, 108.74, 100.69, -2.05.
HRMS (EI) (m/z): [M] calculated for $C_{15}H_{16}O_2Si$, 256.0920, found, 256.0921.

VII) Reduction Substrates

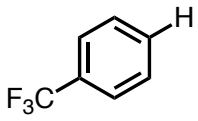


19a

(benzyloxy)(*tert*-butyl)dimethylsilane (**19a**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **11** (41 mg, 0.101 mmol) and triethylsilane (80 μL, 0.5 mmol) in dioxane at 60 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc and the solution was evaporated under reduced pressure. The yield was determined using CH_2Br_2 (7 μL) as an internal standard (68%) by ^{1}H NMR. The spectral data matches that previously reported in the literature. [24]

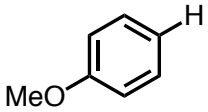
^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 4.4 Hz, 5H), 4.75 (s, 2H), 1.24 (s, 9H), 0.10 (s, 6H).



19b

trifluorotoluene (**19b**)

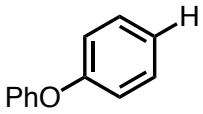
The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **8** (33 mg, 0.100 mmol) and triethylsilane (80 μL, 0.5 mmol) in dioxane at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (67%).



19c

anisole (**19c**)

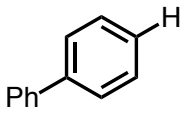
The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **9** (29 mg, 0.989 mmol) and triethylsilane (80 μL, 0.5 mmol) in DMF at room temperature for 2 hours. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (20%).



4a

diphenylether (**4a**)

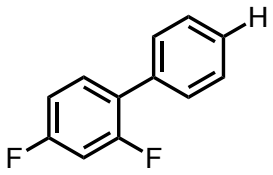
The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **10** (36 mg, 0.101 mmol) and triethylsilane (80 µL, 0.5 mmol) in DMF at room temperature for 2 hours. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (60%).



3a

biphenyl (**3a**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **2** (36 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in DMF at room temperature for overnight. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (98%).

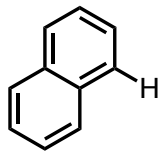


19d

2,4-difluoro-1,1'-biphenyl (**19d**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **13** (75 mg, 0.200 mmol) and triethylsilane (160 µL, 1 mmol) at room temperature. Purification by flash chromatography (100% hexanes/) gave the title compound as a white solid in 67% yield (25 mg, 0.134 mmol) with approximately 10% of an impurity that could not be separated by silica chromatography. The spectral data matches that previously reported in the literature.[25]

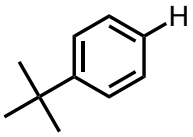
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.41 – 7.34 (m, 1H), 7.01 – 6.83 (m, 2H).
^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.62 (p, *J* = 8.0 Hz), -113.66 (q, *J* = 9.2 Hz).



19e

naphthalene (**19e**)

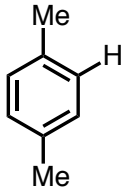
The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide (63 mg, 0.201 mmol) and triethylsilane (160 µL, 1 mmol) in DMF at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (81%).



19f

tert-butylbenzene (**19f**)

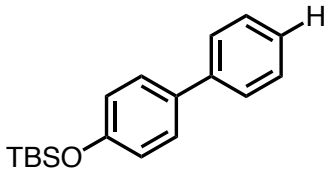
The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **7** (32 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (75%).



19g

p-xylene (**19g**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **16** (29 mg, 0.100 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 60 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (15%).

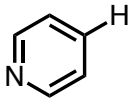


19h

([1,1'-biphenyl]-4-yloxy)(*tert*-butyl)dimethylsilane (**19h**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **12** (48 mg, 0.102 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 40 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc and the solution was evaporated under reduced pressure. The yield was determined using CH_2Br_2 (7 µL) as an internal standard (80%) by ^{1}H NMR. The spectral data matches that previously reported in the literature.[17]

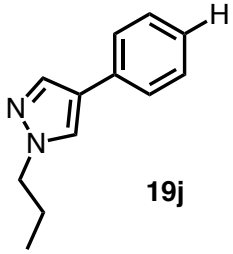
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 2H), 7.50 – 7.45 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 1.01 (s, 9H), 0.24 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.42, 141.04, 134.43, 128.81, 128.22, 126.88, 126.78, 120.46, 25.86, 18.39, -4.22.



19i

pyridine (**19i**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide (26 mg, 0.098 mmol) and triethylsilane (80 µL, 0.5 mmol) in dioxane at 90 ºC. The crude reaction mixture was passed through a short silica gel plug with EtOAc. The yield was determined by GC-FID analysis using tridecane as an internal standard due to volatility of the product (37%).



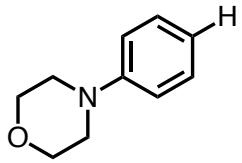
19j

4-phenyl-1-propyl-1*H*-pyrazole (**19j**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **15** (77 mg, 0.207 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (90:10% hexanes/EtOAc) gave the title compound as a white solid in 90% yield (35 mg, 0.189 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.63 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.30 (m, 2H), 7.25 – 7.16 (m, 1H), 4.11 (t, *J* = 7.1 Hz, 2H), 2.35 – 1.83 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 136.71, 132.93, 128.97, 126.40, 126.07, 125.61, 122.89, 54.22, 23.91, 11.33.
HRMS (ESI) (m/z): [M+H] calculated for $C_{12}H_{14}N_2$, 187.1235, found, 187.1226.



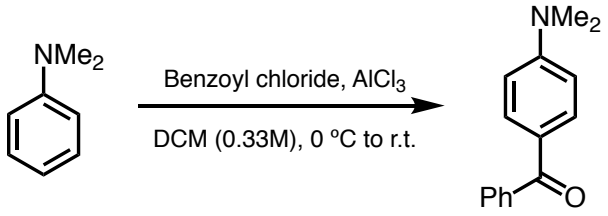
19k

4-phenylmorpholine (**19k**)

The general procedure for reduction was followed using *N,N,N*-trimethylanilimium iodide **13** (67 mg, 0.192 mmol) and triethylsilane (160 µL, 1 mmol) at 60 ºC. Purification by flash chromatography (95:5% hexanes/EtOAc) gave the title compound as a white solid in 90% yield (20 mg, 0.150 mmol). The spectral data matches that previously reported in the literature.[26]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (t, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.89 (t, *J* = 7.3 Hz, 1H), 3.87 (t, *J* = 4.8 Hz, 4H), 3.17 (t, *J* = 4.8 Hz, 4H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 151.42, 129.32, 120.18, 115.85, 67.09, 49.51.

VIII) Synthetic Demonstrations

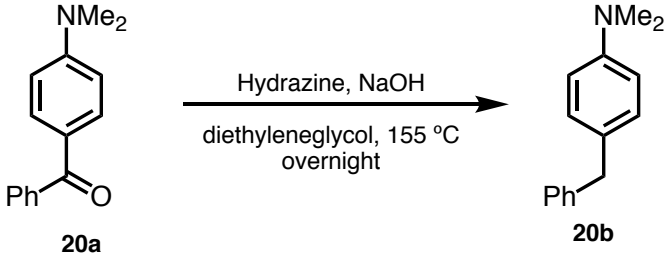


20 **20a**

(4-(dimethylamino)phenyl)(phenyl)methanone (**20a**)

To a suspension of $AlCl_3$ (520 mg, 3.92 mmol, 1.00 equiv) in DCM (12.5 mL) at 0 ºC was slowly added benzoylchloride (0.46 mL, 3.92 mmol, 1.00 equiv). Dimethylaniline (0.52 mL, 4.12 mmol, 1.05 equiv was then added dropwise and the reaction was stirred at 0 ºC for 4 hours before stirring at room temperature for 3 hours. Dilute reaction mixture with DCM and add ~15 mL H_2O. Wash organic layer 2x20 mL H_2O, 2x20 mL sat. $NaHCO_3$, 1x20 mL brine. Dry organic layer over Na_2SO_4 and concentrate. Purification by flash chromatography (90:10 hexanes/EtOAc) gave the title compound as a yellow solid in 43% yield (401 mg, 1.69 mmol) (*p*-/*o*- benzoylation observed in ~2:1 ratio).[27]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 9.0 Hz, 2H), 7.75 – 7.68 (m, 2H), 7.57 – 7.50 (m, 1H), 7.48 – 7.42 (m, 2H), 6.68 (d, *J* = 9.0 Hz, 2H), 3.08 (s, 6H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.26, 153.42, 139.44, 132.86, 131.22, 129.57, 128.12, 124.91, 110.67, 40.19.

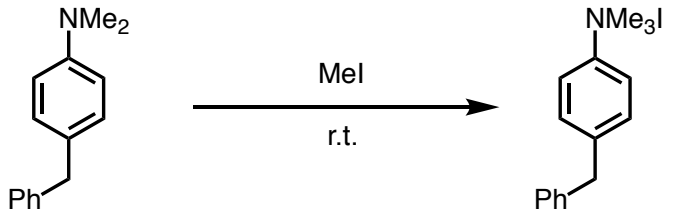


20a **20b**

4-benzyl-*N*,*N*-dimethylaniline (**20b**)

NaOH (1.02g, 25.5 mmol, 5 equiv) and hydrazine hydrate (1.25g, 25.5 mmol, 5 equiv) were added to a round bottom containing **20a** (1.17g, 5.1 mmol, 1 equiv) in ethyleneglycol (30 mL). A reflux condenser was attached and the mixture was heated to 155 ºC overnight. The reaction mixture was cooled to room temperature and diluted with 50 mL EtOAc and 50 mL H_2O. The mixture was then extracted 2x50 mL EtOAc. The organic layers were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (95:5 hexanes/EtOAc) gave the title compound as a clear oil in 80% yield (860 mg, 4.08 mmol).[27]

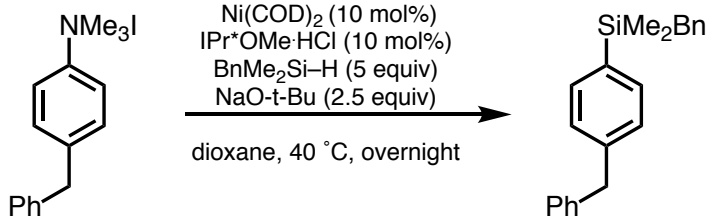
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.15 (m, 3H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 2H), 2.91 (s, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 149.28, 142.20, 129.67, 129.38, 128.94, 128.47, 113.09, 41.06, 40.98.
HRMS (EI) (m/z): [M] calculated for $C_{17}H_{34}O_2Si$, 377.1759, found, 377.1764.



20b **21**

4-benzyl-*N*,*N*,*N*-trimethylammoniumaniline iodide (**21**)

To a dry vial with a stirbar was added **20b** (860 mg, 4.07 mmol, 1 equiv) and MeI (2.55 mL, 41.00 mmol, 10 equiv). The vial was sealed with a teflon cap and stirred until the reaction solidified (~5 hours). The contents were suspended in Et_2O and filtered, washing with 3x15 mL Et_2O to remove any unreacted starting material. The ammonium salt was dried on high vac for ~2 hours and used as is for subsequent reactions. The product was obtained as a white crystalline powder in 83% yield (1.2g, 2.80 mmol) and used without further purification.

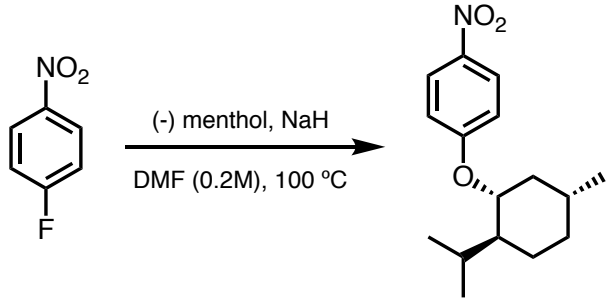


21 **22**

benzyl(4-benzylphenyl)dimethylsilane (**22**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **21** (76 mg, 0.215 mmol) and benzyldimethylsilane (158 μL, 1 mmol). Purification by flash chromatography (100% hexanes) gave an inseparable mixture of the title compound in 66% yield (45 mg, 0.142 mmol) and 1,2-dibenzyl-1,1,2,2-tetramethyldisilane (12 mg, 0.040 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.1, 2.6 Hz, 2H), 7.31 (td, *J* = 7.7, 7.2, 2.3 Hz, 2H), 7.20 (dq, *J* = 14.3, 6.1 Hz, 7H), 7.11 – 7.03 (m, 2H), 6.95 (dd, *J* = 8.0, 2.7 Hz, 2H), 4.00 (s, 2H), 2.30 (d, *J* = 2.7 Hz, 2H), 0.23 (d, *J* = 2.8 Hz, 6H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.15, 141.07, 139.88, 135.93, 134.06, 129.11, 128.61, 128.50, 128.45, 128.23, 128.14, 126.24, 124.18, 124.04, 42.09, 32.20, 28.99, 26.37, 0.74, -3.25.
HRMS (EI) (m/z): [M] calculated for $C_{22}H_{24}Si$, 316.1647, found, 316.1641.

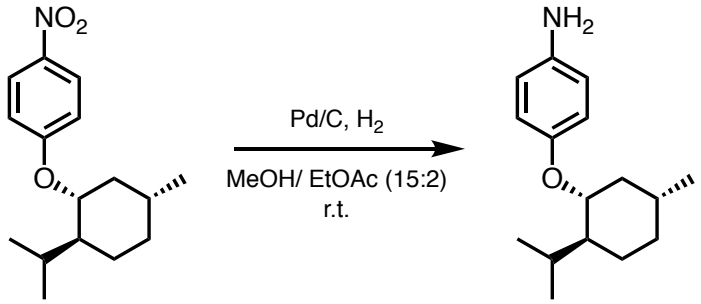


23 **23a**

1-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-4-nitrobenzene (**23a**)

A solution of (–)-menthol (3.4g, 21.7 mmol, 2.0 equiv) in DMF (4 mL) was added dropwise to a flame dried 20 mL scintillation vial equipped with a stir bar containing a solution of NaH (60% dispersion in mineral oil) (120mg, 30 mmol, 3.0 equiv) in DMF (1 mL) at 0 ºC. After 30min the vial was allowed to warm to room temperature. 4-fluoro-nitrobenzene (1.06 mL, 10 mmol, 1.0 equiv) was added slowly and the vial was sealed with a Teflon cap and headed to 90 ºC for 48 hours. The solution was then cooled to room temperature, transferred to a separatory funnel, and diluted with 30 mL diethyl ether. The organics were then washed 2x50 mL 5M NaOH solution and 1x50 mL brine. The organic layer was dried with sodium sulfate before concentrating. The product can be obtained via Kugelrohr distillation at 0.5 bar at 80 ºC through the removal of unreacted 4-fluoro-nitrobenzene and excess menthol. The product was obtained as a yellow crystalline solid. The discoloration was removed through Purification by flash chromatography (90:10 hexanes/EtOAc) to give the title compound as a white crystalline solid in 30% yield (1.72 g, 6.2 mmol).

^{1}H NMR (401 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.16 (td, *J* = 10.6, 4.2 Hz, 1H), 2.20 – 2.04 (m, 2H), 1.85 – 1.69 (m, 2H), 1.63 – 1.46 (m, 2H), 1.18 – 1.01 (m, 3H), 0.93 (t, *J* = 7.5 Hz, 6H), 0.75 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (176 MHz, Chloroform-*d*) δ 163.85, 141.13, 126.22, 115.13, 78.53, 47.96, 40.00, 34.43, 31.54, 26.38, 23.90, 22.19, 20.74, 16.77.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{16}H_{23}NO_3$, 300.1570, found, 300.1580.

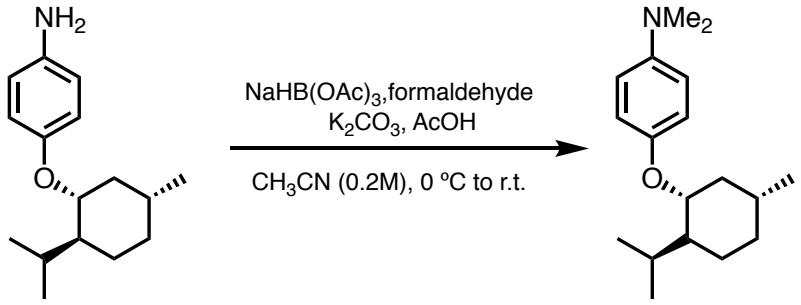


23a **23b**

4-(((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)aniline (**23b**)

To a round bottom equipped with a stir bar was added **23a** (400 mg, 1.44 mmol) and palladium on carbon (10%) (40 mg, 2.5 mol%). The flask was backfilled three times with nitrogen before adding methanol (15 mL) and EtOAc (2 mL). The flask was then backfilled three times with H_2 before attaching a H_2 balloon. The reaction was left to stir at room temperature overnight. The contents of the flask were then filtered through Celite with EtOAc. The filtrate was concentrated to give the title compound as a reddish solid in 97% yield (344 mg, 1.39 mmol).

^{1}H NMR (700 MHz, Chloroform-*d*) δ 6.75 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 1H), 3.82 (td, *J* = 10.5, 4.2 Hz, 1H), 3.42 (s, 2H), 2.28 (pd, *J* = 7.0, 2.7 Hz, 1H), 2.11 (dtd, *J* = 12.6, 3.8, 1.9 Hz, 1H), 1.69 (dt, *J* = 14.3, 3.7 Hz, 2H), 1.45 (ddt, *J* = 13.3, 10.4, 3.2 Hz, 1H), 1.39 (tdq, *J* = 12.6, 6.6, 3.3 Hz, 1H), 1.10 – 1.02 (m, 1H), 1.01 – 0.94 (m, 1H), 0.92 (dd, *J* = 24.6, 6.8 Hz, 7H), 0.80 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (176 MHz, Chloroform-*d*) δ 151.50, 140.24, 118.09, 116.51, 79.17, 48.34, 40.73, 34.70, 31.60, 26.03, 23.70, 22.32, 21.02, 16.58.
HRMS (ESI) (m/z): [M+H] calculated for $C_{16}H_{25}NO$, 248.2009, found, 248.2016.

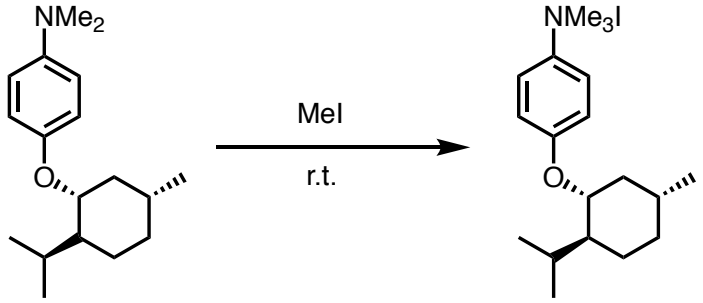


23b **23c**

4-(((1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-*N*,*N*-dimethylaniline (**23c**)

To a round bottom equipped with a stir bar was dissolved **23b** (344 mg, 1.39 mmol, 1.0 equiv) in acetonitrile (5 mL). K_2CO_3 (384 mg, 2.78 mmol, 2.0 equiv) and an aqueous formaldehyde solution (37%) (0.62 mL, 8.34 mmol, 6.0 equiv) were added and the reaction was stirred for 30 min. The reaction was then cooled in an ice bath for 5 min before adding sodium triacetoxyborohydride (883 mg, 4.17 mmol, 3.0 equiv) in 200 mg portions over 5 min. Acetic acid (1 mL) was slowly added and the reaction was warmed and allowed to stir at room temperature overnight. Quench the reaction with 15mL H_2O and 15 mL EtOAc. Basify with sat. $NaHCO_3$ and extract 3x25 mL EtOAc. Wash organic layers with 1x25 mL brine and dry over sodium sulfate before concentrating. The product was obtained as a light brown crystalline solid in 88% yield (336 mg, 1.21 mmol) with no need for further purification.[28]

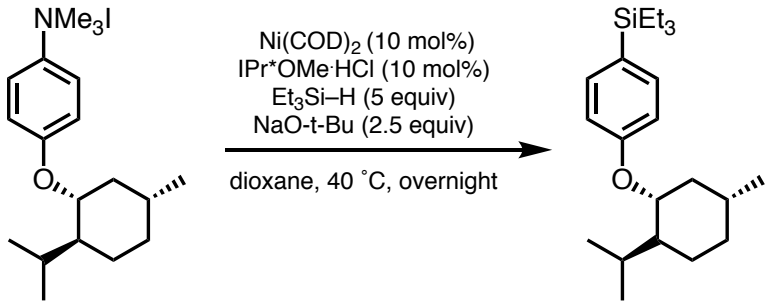
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 3.85 (td, *J* = 10.5, 4.2 Hz, 1H), 2.87 (s, 6H), 2.29 (pd, *J* = 7.1, 2.7 Hz, 1H), 2.12 (d, *J* = 12.4 Hz, 1H), 1.70 (dt, *J* = 14.6, 3.8 Hz, 2H), 1.55 – 1.33 (m, 3H), 1.07 (td, *J* = 13.2, 9.6 Hz, 2H), 0.98 (m, 1H), 0.92 (dd, *J* = 15.7, 6.7 Hz, 6H), 0.80 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.57, 145.97, 117.81, 114.88, 79.02, 48.34, 41.91, 40.76, 34.73, 31.61, 26.06, 23.74, 22.34, 21.04, 16.62.
HRMS (ESI) (m/z): [M+H] calculated for $C_{18}H_{29}NO$, 276.2327, found, 276.2323.



23c **24**

4-(((1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)-*N*,*N*,*N*-trimethylammoniumaniline iodide (**21**)

To a dry vial with a stirbar was added **23c** (336 mg, 1.21 mmol, 1 equiv) and MeI (0.75 mL, 12.10 mmol, 10 equiv). The vial was sealed with a teflon cap and stirred until the reaction solidified (~5 hours). The contents were suspended in Et_2O and filtered, washing with 3x10 mL Et_2O to remove any unreacted starting material. The ammonium salt was dried on high vac for ~2 hours and used as is for subsequent reactions. The product was obtained as a white powder in 83% yield (419 mg, 1.00 mmol) and used without further purification.

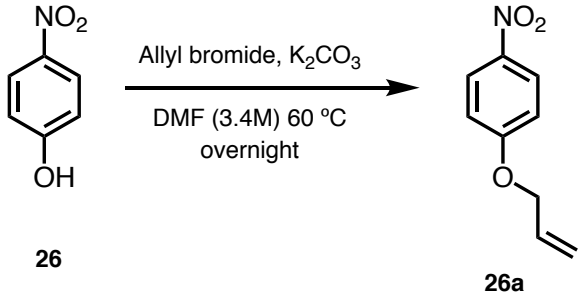


24 **25**

triethyl(4-(((1*R*,2*R*,5*R*)-2-isopropyl-5-methylcyclohexyl)oxy)phenyl)silane (**25**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **24** (87 mg, 0.208 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a clear oil in 58% yield (40 mg, 0.121 mmol).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.06 (td, *J* = 10.5, 4.3 Hz, 1H), 2.20 (ddt, *J* = 16.5, 12.8, 3.7 Hz, 1H), 1.72 (dd, *J* = 11.8, 3.1 Hz, 1H), 1.60 – 1.38 (m, 1H), 1.10 (qd, *J* = 12.6, 2.9 Hz, 1H), 1.05 – 0.87 (m, 12H), 0.84 – 0.71 (m, 7H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.10, 135.73, 127.87, 115.28, 77.04, 48.18, 40.46, 34.70, 31.58, 26.17, 23.87, 22.30, 20.96, 16.76, 7.61, 3.71.
HRMS (EI) (m/z): [M] calculated for $C_{22}H_{38}OSi$, 346.2692, found, 346.2682.

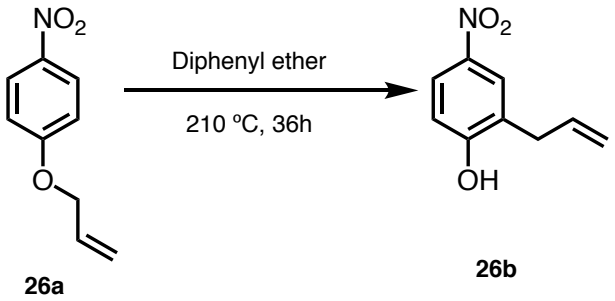


26 **26a**

1-(allyloxy)-4-nitrobenzene (**26a**)

To a solution of **26** (1g, 7.19 mmol, 1.00 equiv) in DMF (3 mL, 2.4M) was added K_2CO_3 (1g, 7.19 mmol, 1.00 equiv). Allylbromide (0.68 mL, 7.90 mmol, 1.10 equiv) was added and a reflux condenser was added before heating to 60 ºC overnight. Upon cooling to room temperature, 20 mL H_2O and 20 mL Et_2O were added and the reaction mixture was extracted 2x20 mL Et_2O. The combined organics were then washed 2x20 mL 1M NaOH, 1x20 mL brine, and dried over $MgSO_4$ before concentrating. The product was obtained via Kugelrohr distillation to give a yellow oil that was carried on to the next step without further purification.[29]

^{1}H NMR (401 MHz, Chloroform-*d*) δ 8.20 (d, *J* = 9.3 Hz, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.04 (ddt, *J* = 17.4, 10.6, 5.3 Hz, 1H), 5.44 (dt, *J* = 17.3, 1.5 Hz, 1H), 5.35 (dt, *J* = 10.6, 1.4 Hz, 1H), 4.64 (dt, *J* = 5.4, 1.6 Hz, 2H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.71, 141.73, 132.01, 126.03, 118.82, 114.84, 69.54.

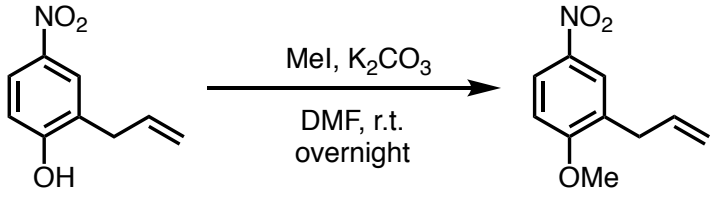


26a **26b**

2-allyl-4-nitrophenol (**26b**)

Crude **26a** (~1.3g) and an equal weight of diphenylether were added to a round bottom equipped with a reflux condenser. The mixture was heated to 210 ºC for 36 hours. The reaction was cooled to room temperature and diluted with 30 mL Et_2O. The organics were extracted 3x30 mL 6M NaOH. The combined aqueous layers were acidified with conc. HCl. The acidic aqueous solution was then extracted 3X30 mL Et_2O. The ether layers were combined and dried over $MgSO_4$. The product can be recrystallized. Product was obtained as a yellow crystalline solid in 46% over two steps (593 mg, 3.31 mmol).[29]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.01 (ddt, *J* = 16.8, 10.4, 6.6 Hz, 1H), 5.88 (br, 1H), 5.30 – 5.16 (m, 2H), 3.47 (d, *J* = 6.4 Hz, 2H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 159.90, 141.77, 134.72, 126.60, 126.54, 124.44, 118.19, 116.01, 34.79.

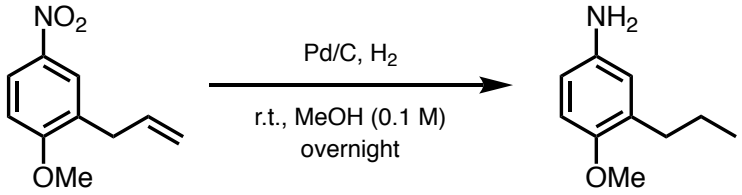


26b **27**

2-allyl-1-methoxy-4-nitrobenzene (**27**)

In a dry round bottom, **26b** (1.00 g, 5.58 mmol, 1 equiv) was dissolved in DMF (10 mL). K_2CO_3 (1.77g, 12.84 mmol, 2.3 equiv) was added followed by MeI (0.80 mL, 12.84 mmol, 2.3 equiv). The mixture was stirred at room temperature overnight. The reaction was quenched with 50 ml Et_2O and 50 ml H_2O. The organics were washed 2x40 mL 1M NaOH, then 1x40 mL brine followed by drying of the organics over $MgSO_4$. The product was obtained as pure a yellow oil in 97% yield (1.05 g, 5.41 mmol) with no need for further purification.[30]

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 9.0, 2.8 Hz, 1H), 8.05 (d, *J* = 2.8 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 5.96 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.21 – 5.03 (m, 2H), 3.94 (s, 3H), 3.41 (d, *J* = 6.6 Hz, 2H).
^{13}C NMR (176 MHz, Chloroform-*d*) δ 162.41, 141.44, 135.16, 130.04, 125.44, 124.16, 117.14, 109.80, 56.23, 34.07.
HRMS (ESI) (m/z): [M+H] calculated for $C_{10}H_{15}NO$, 194.0812, found, 194.0811.

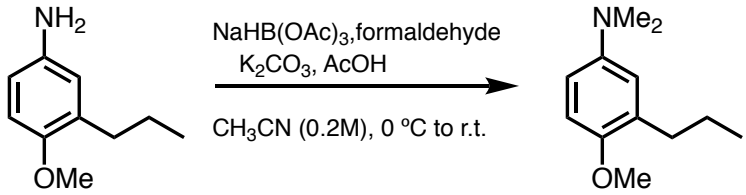


27 **27a**

4-methoxy-3-propylaniline (**27a**)

To a round bottom equipped with a stir bar was added **27** (1.05 g, 5.43 mmol) and palladium on carbon (10%) (144 mg, 2.5 mol%). The flask was backfilled three times with nitrogen before adding methanol (50 mL). The flask was then backfilled three times with H_2 before attaching a H_2 balloon. The reaction was left to stir at room temperature overnight. The contents of the flask were then filtered through Celite with DCM. The filtrate was concentrated to give the title compound in quantitative yield as an off-white crystalline solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.68 (d, *J* = 8.3 Hz, 1H), 6.57 – 6.47 (m, 2H), 3.75 (s, 3H), 3.37 (s, 2H), 2.55 – 2.47 (m, 3H), 1.58 (h, *J* = 7.3 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.02, 139.68, 132.35, 117.86, 113.26, 111.96, 56.21, 32.40, 23.24, 14.26.
HRMS (ESI) (m/z): [M+H] calculated for $C_{10}H_{15}NO$, 166.1226, found, 166.1225.



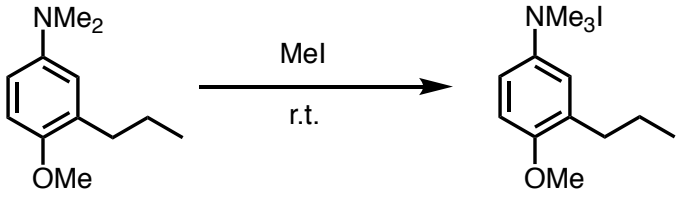
27a **27b**

4-methoxy-*N*,*N*-dimethyl-3-propylaniline (**27b**)

To a round bottom equipped with a stir bar was dissolved **27a** (897 mg, 5.43 mmol, 1.0 equiv) in acetonitrile (25 mL). K_2CO_3 (1.5 g, 10.86 mmol, 2.0 equiv) and an aqueous formaldehyde solution (37%) (2.42 mL, 32.58 mmol, 6.0 equiv) were added and the reaction was stirred for 30 min. The reaction was then cooled in an ice bath for 5 min before adding sodium triacetoxyborohydride (3.45 mg, 16.29 mmol, 3.0 equiv) in 500 mg portions over 5 min. Acetic

acid (2.5 mL) was slowly added and the reaction was warmed and allowed to stir at room temperature overnight. Quench the reaction with 50mL H_2O and 50 mL EtOAc. Basify with sat. $NaHCO_3$ and extract 3x50 mL EtOAc. Wash organic layers with 1x25 mL brine and dry over sodium sulfate before concentrating. The product was obtained as a crystalline solid in 83% yield (876 mg, 4.51 mmol) with no need for further purification.

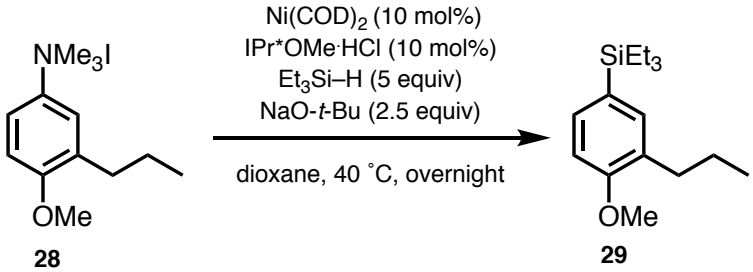
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.78 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 3.2 Hz, 1H), 6.60 (dd, *J* = 8.8, 3.1 Hz, 1H), 3.77 (s, 3H), 2.86 (s, 6H), 2.57 (dd, *J* = 8.8, 6.7 Hz, 2H), 1.62 (h, *J* = 7.4 Hz, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.36, 145.66, 132.02, 116.69, 111.85, 111.83, 56.24, 42.06, 32.93, 23.49, 14.33.
HRMS (ESI) (m/z): [M+H] calculated for $C_{12}H_{19}NO$, 194.1545, found, 194.1536.



27b **28**

4-methoxy- 3-propyl-*N,N,N*-trimethylammoniumaniline iodide (**28**)

To a dry vial with a stirbar was added **27b** (860 mg, 4.53 mmol, 1 equiv) and MeI (2.82 mL, 45.30 mmol, 10 equiv). The vial was sealed with a teflon cap and stirred until the reaction solidified (~5 hours). The contents were suspended in Et_2O and filtered, washing with 3x15 mL Et_2O to remove any unreacted starting material. The ammonium salt was dried on high vac for ~2 hours and used as is for subsequent reactions. The product was obtained as a white crystalline powder in 88% yield (1.33g, 3.99 mmol) and used without further purification.



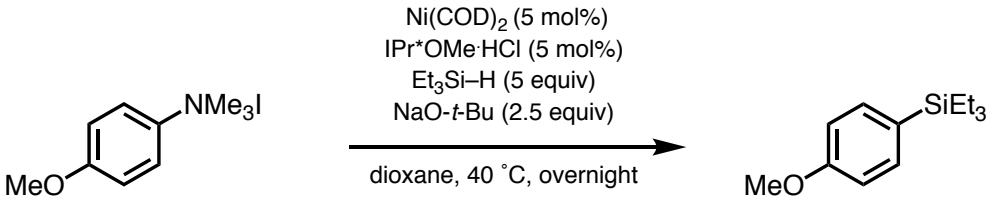
28 **29**

triethyl(4-methoxy-3-propylphenyl)silane (**29**)

The general procedure for silylation was followed using *N,N,N*-trimethylanilimium iodide **28** (67 mg, 0.200 mmol) and triethylsilane (160 µL, 1 mmol). Purification by flash chromatography (100% hexanes) gave the title compound as a clear oil in 77% yield (41 mg, 0.154 mmol).

^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.22 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 2.75 – 2.36 (m, 2H), 1.61 (q, *J* = 7.5 Hz, 2H), 1.11 – 0.87 (m, 9H), 0.76 (q, *J* = 7.9 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.31, 136.02, 133.28, 130.39, 127.70, 109.84, 55.18, 32.60, 23.20, 14.27, 7.63, 3.72.
HRMS (ESI) (m/z): [M+Na] calculated for $C_{16}H_{28}OSi$, 287.1802, found, 287.1802.

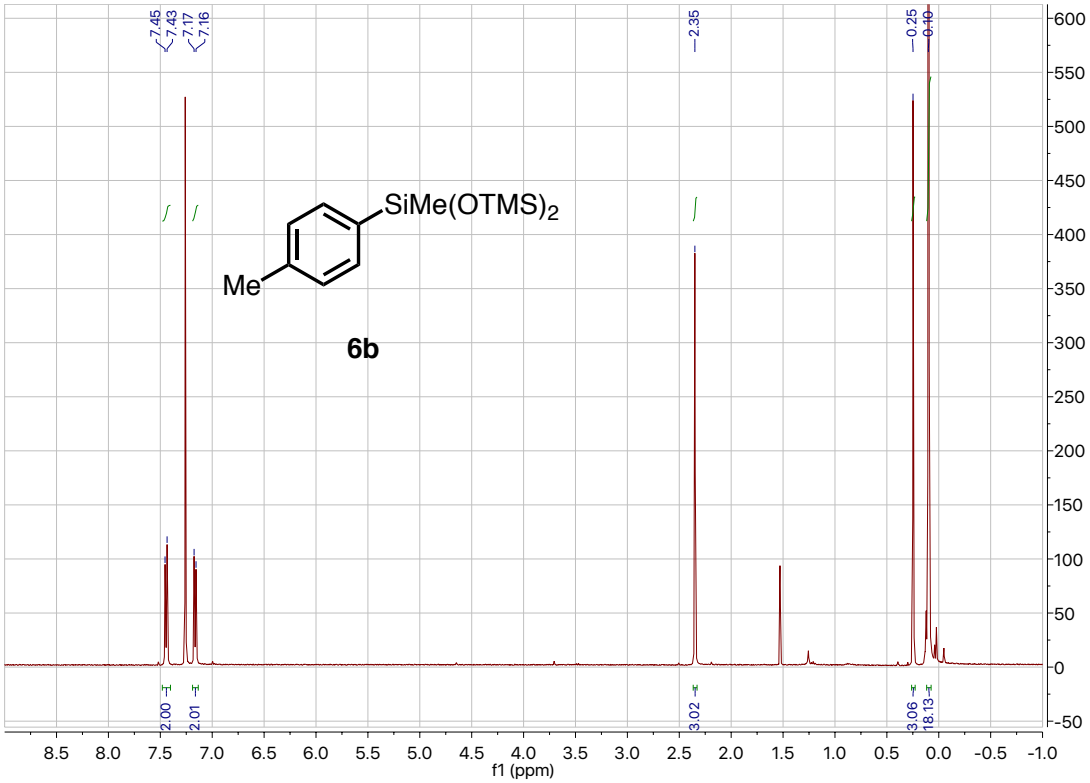
IX) Large Scale Silylation

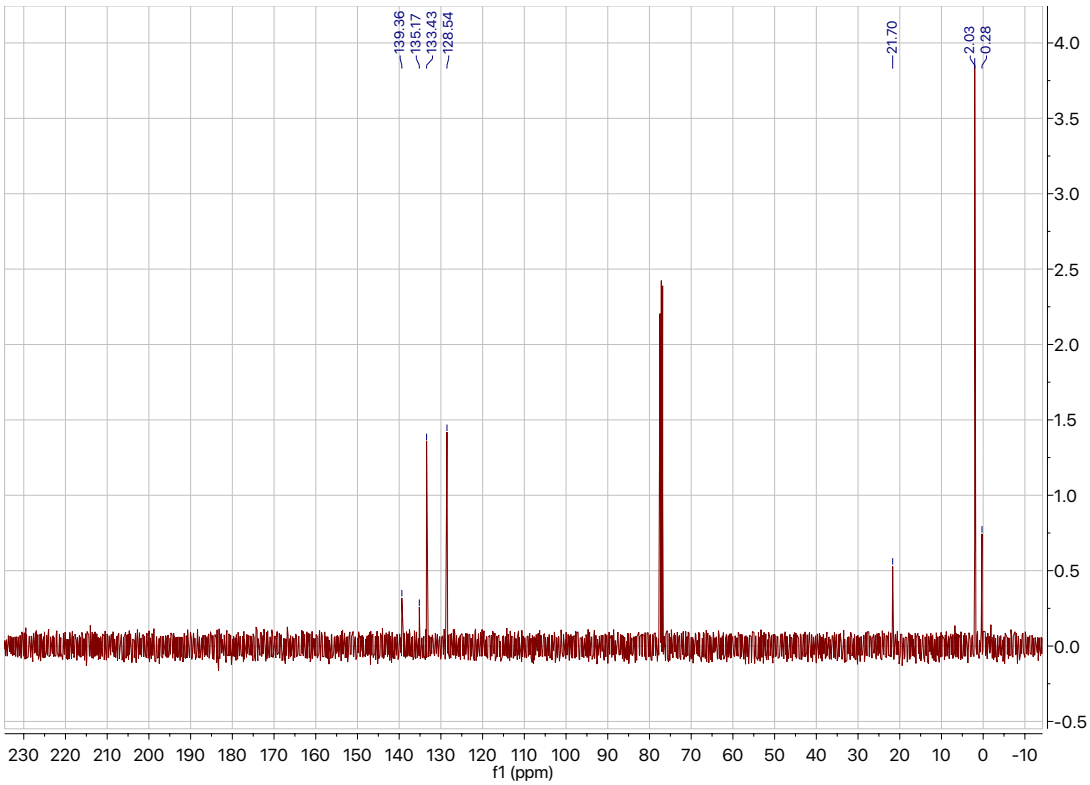


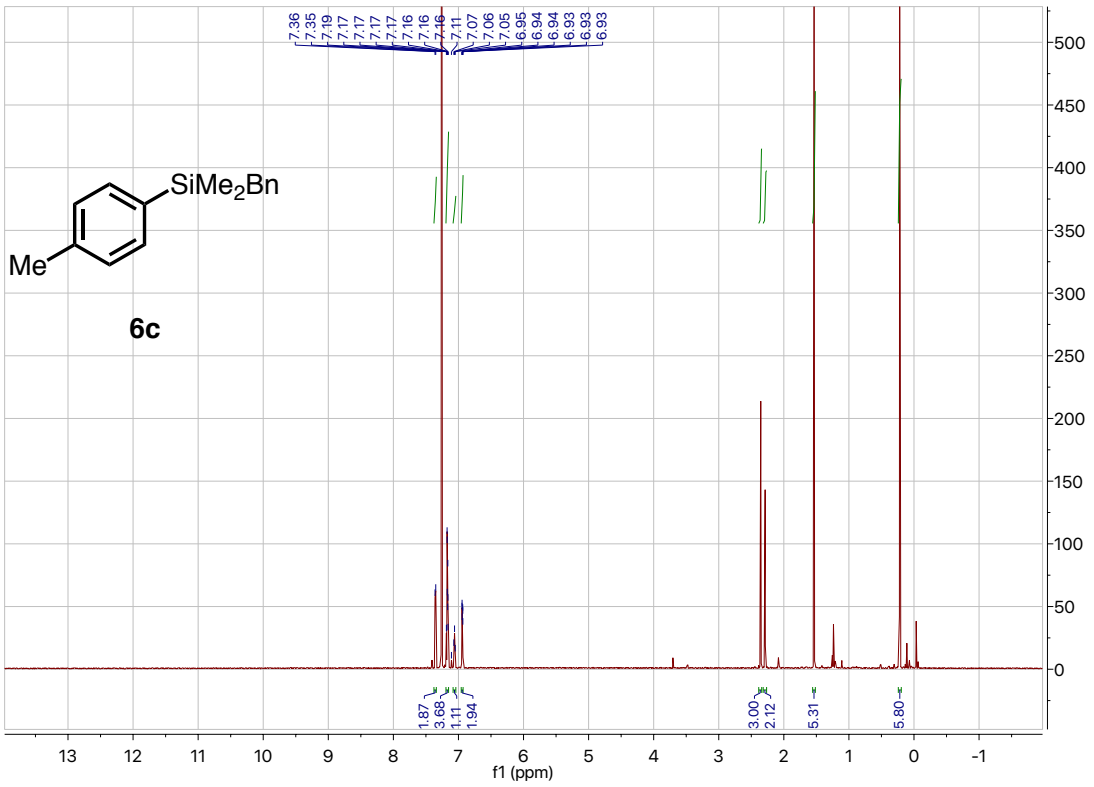
9 **9a**

To a 50 mL round bottom was added $Ni(COD)_2$ (45 mg, 0.16 mmol, 0.05 equiv), *N,N'*-Bis(2,6-bis(diphenylmethyl)-4-methoxyphenyl)imidazolium chloride (IPr*OMe·HCl) (160 mg, 0.16 mmol, 0.05 equiv), NaO-*t*-Bu (787 mg, 8.17 mmol, 2.5 equiv), and **9** (3.27 mmol, 1 equiv) were combined under inert atmosphere and suspended in 15 mL of dioxane at rt. Silane (2.61 mL, 16.35 mmol, 5 equiv) was added and the vial was sealed with a Teflon cap before removing from the glovebox to heat to 40 ºC overnight. Upon completion, the reaction mixture was filtered through Celite with DCM, the solvent was removed by rotary evaporation, and the crude reaction mixture was purified by silica gel chromatography (100% hexanes to 95:5 hexanes/ EtOAc) to give the title compound as a clear oil in 78% yield (569 mg, 2.55 mmol).

X) NMR Spectra



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7.16
7.11
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7.06
7.05
6.95
6.94
6.94
6.93
6.93
6.93
SiMe2Bn
Me
6c
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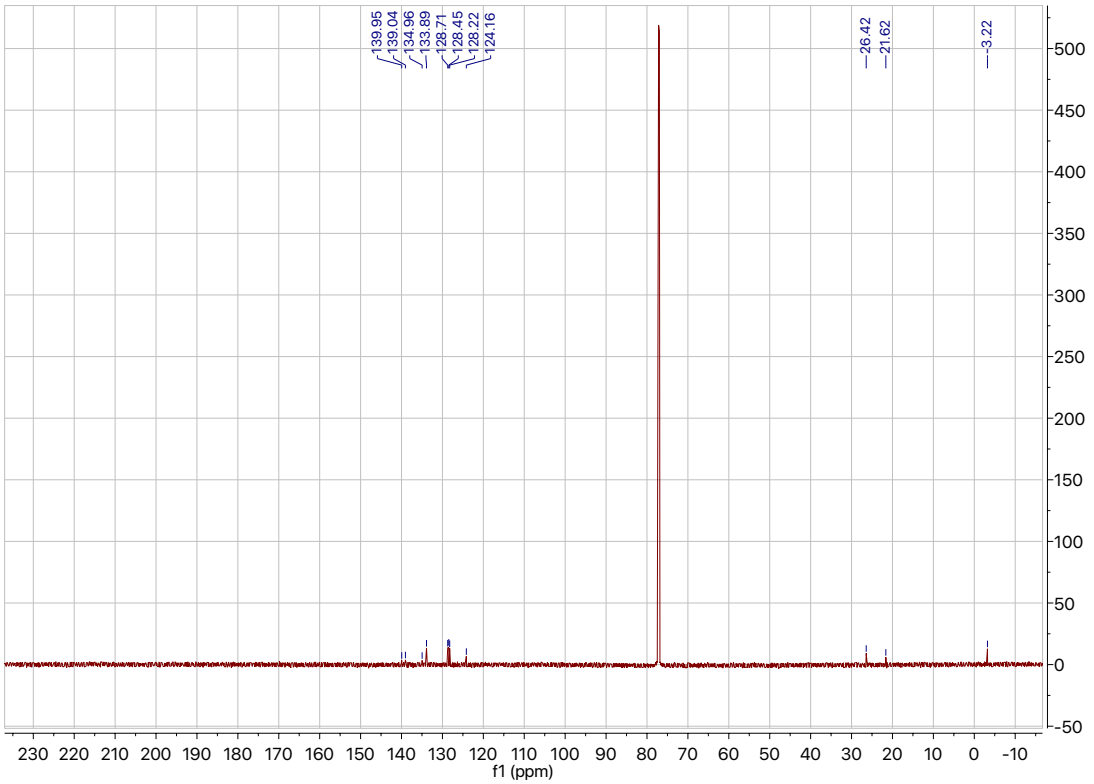
1.11
1.94
3.00
2.12
5.31
5.80
f1 (ppm)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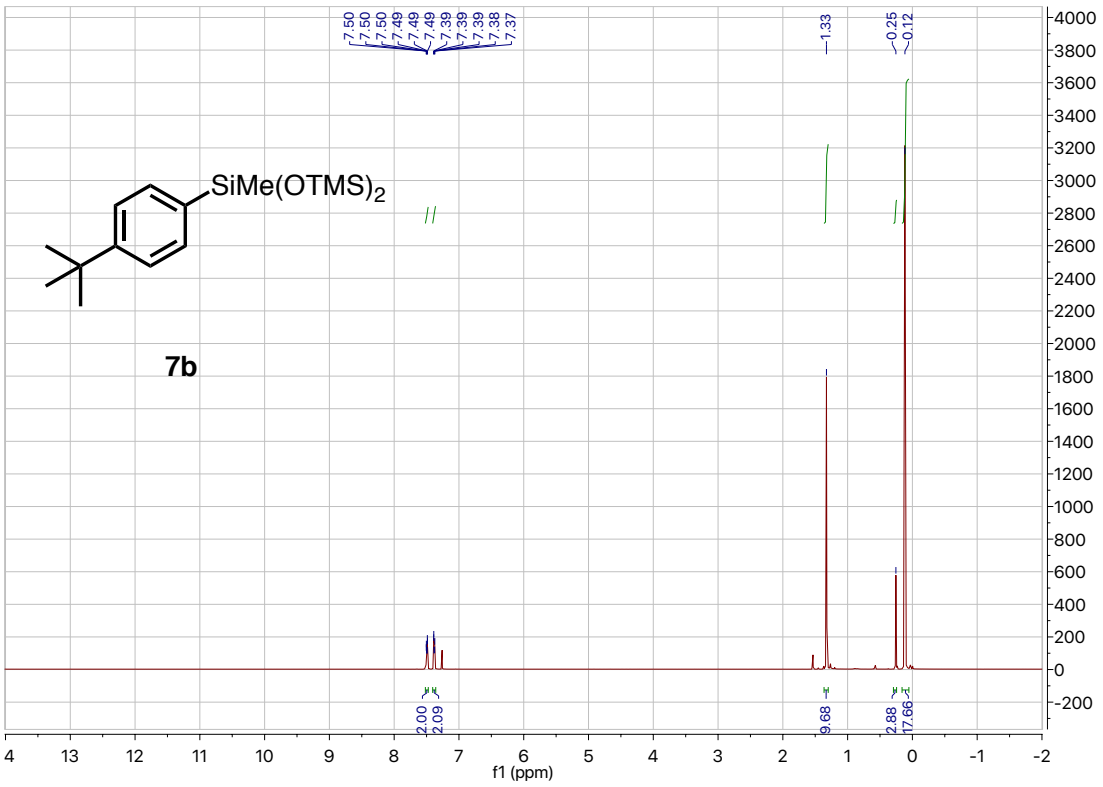
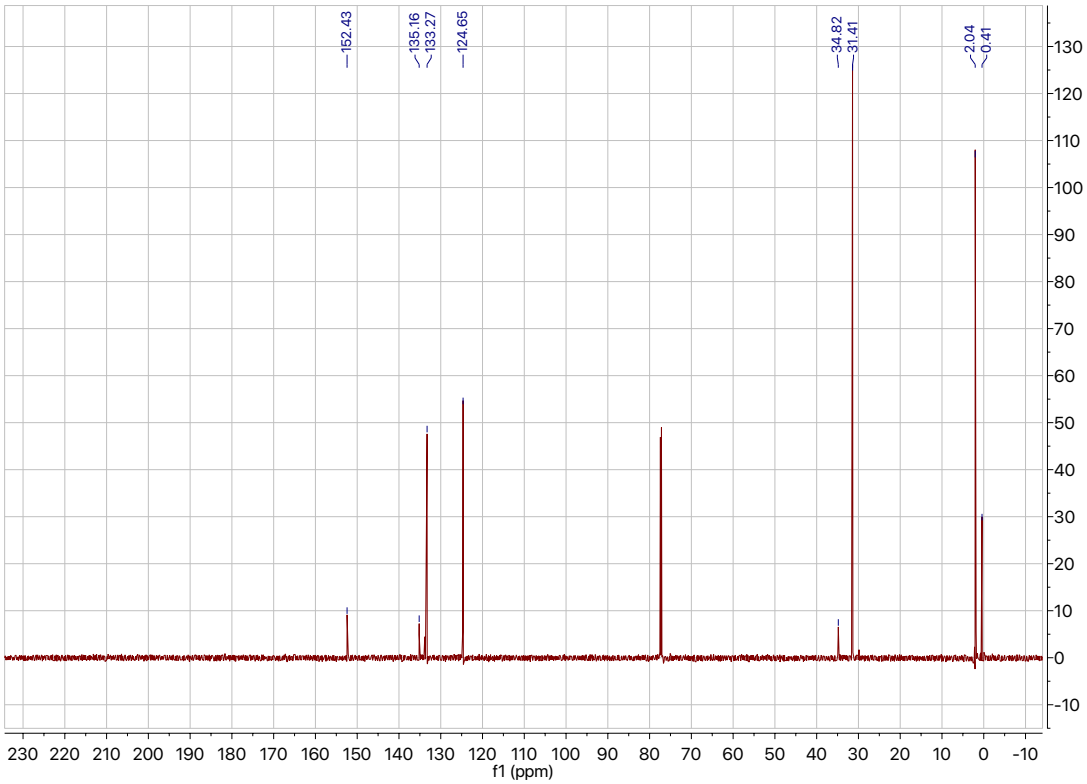
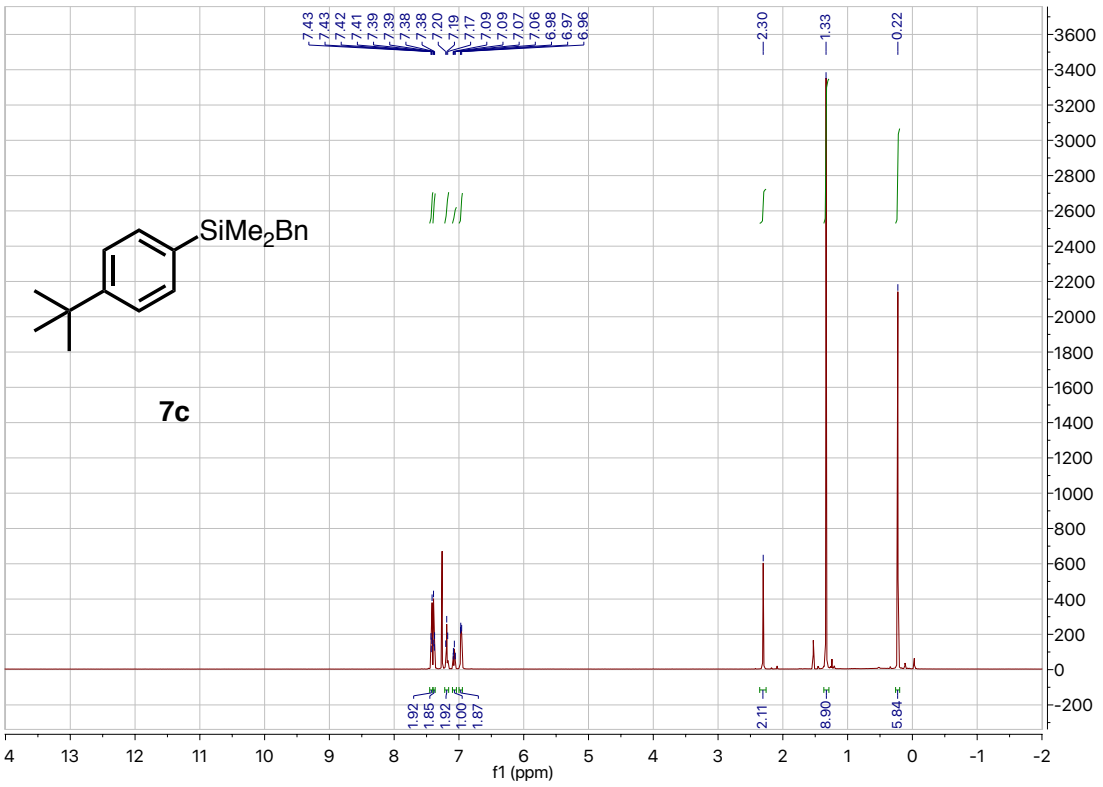
133.89
128.71
128.45
128.22
124.16
26.42
21.62
-3.22
f1 (ppm)


SiMe(OTMS)2
7b
f1 (ppm)


f1 (ppm)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6.96
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1.33
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1.00
1.87
2.11
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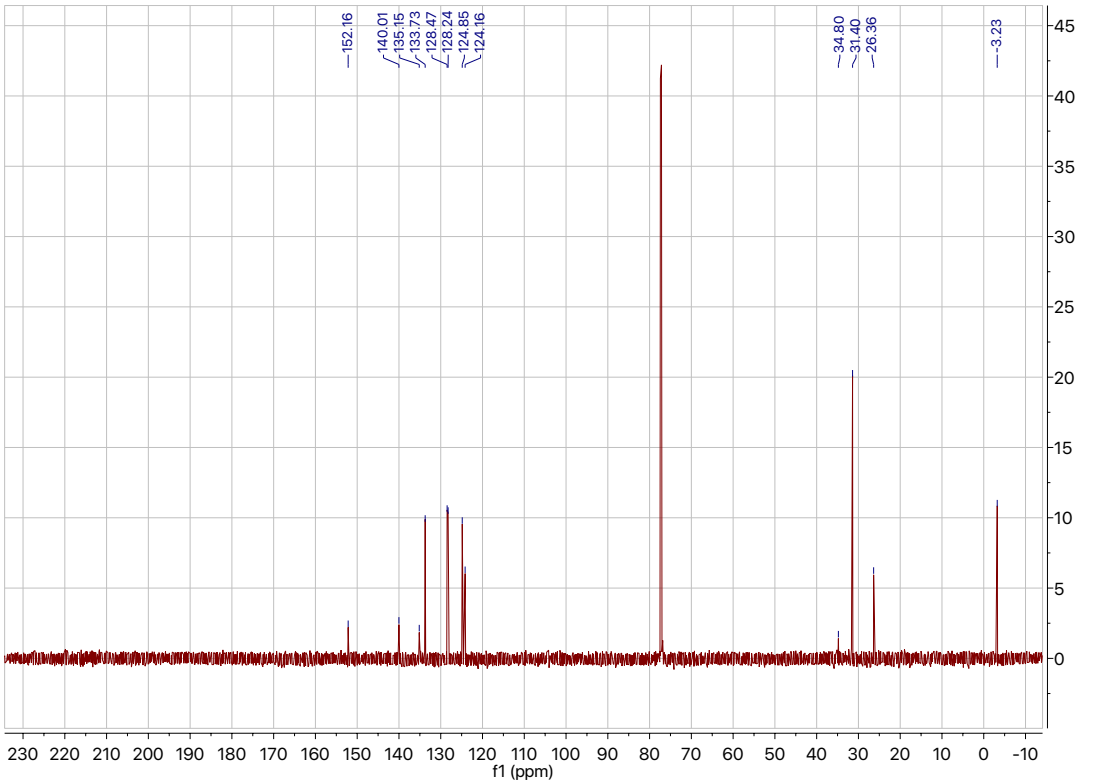
5.84
f1 (ppm)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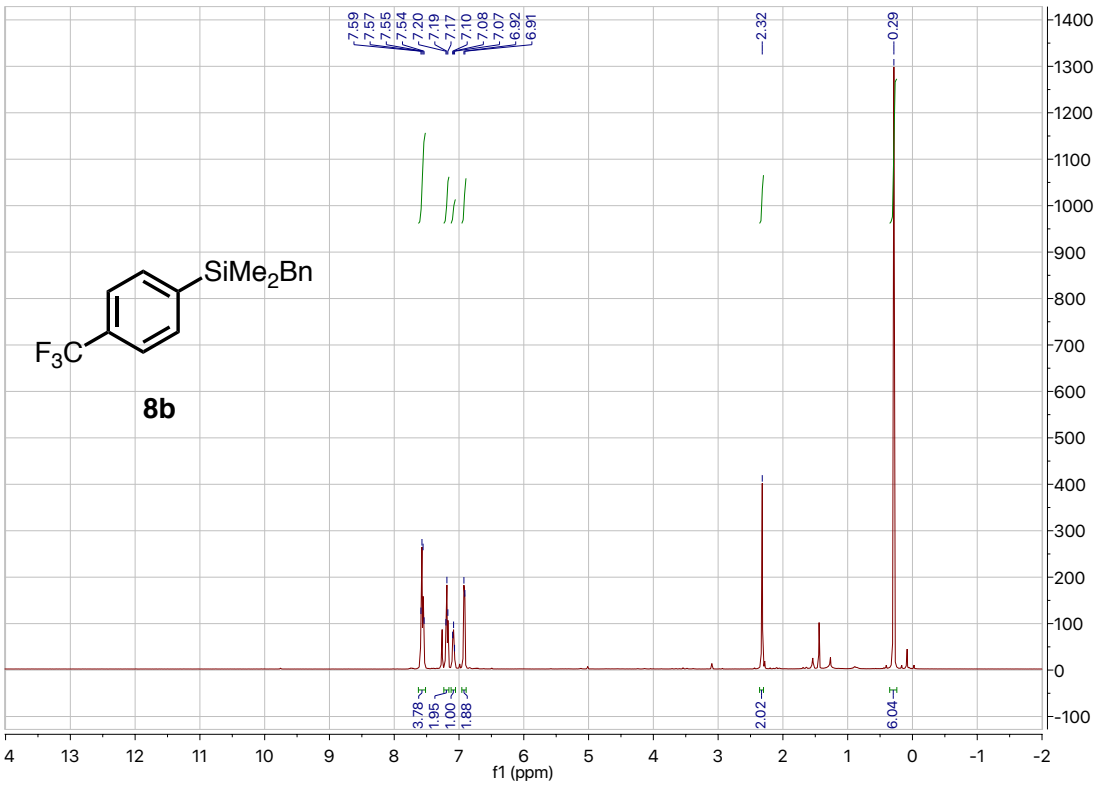
f1 (ppm)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7.08
7.07
6.92
6.91
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0.29
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F3C
8b
3.78
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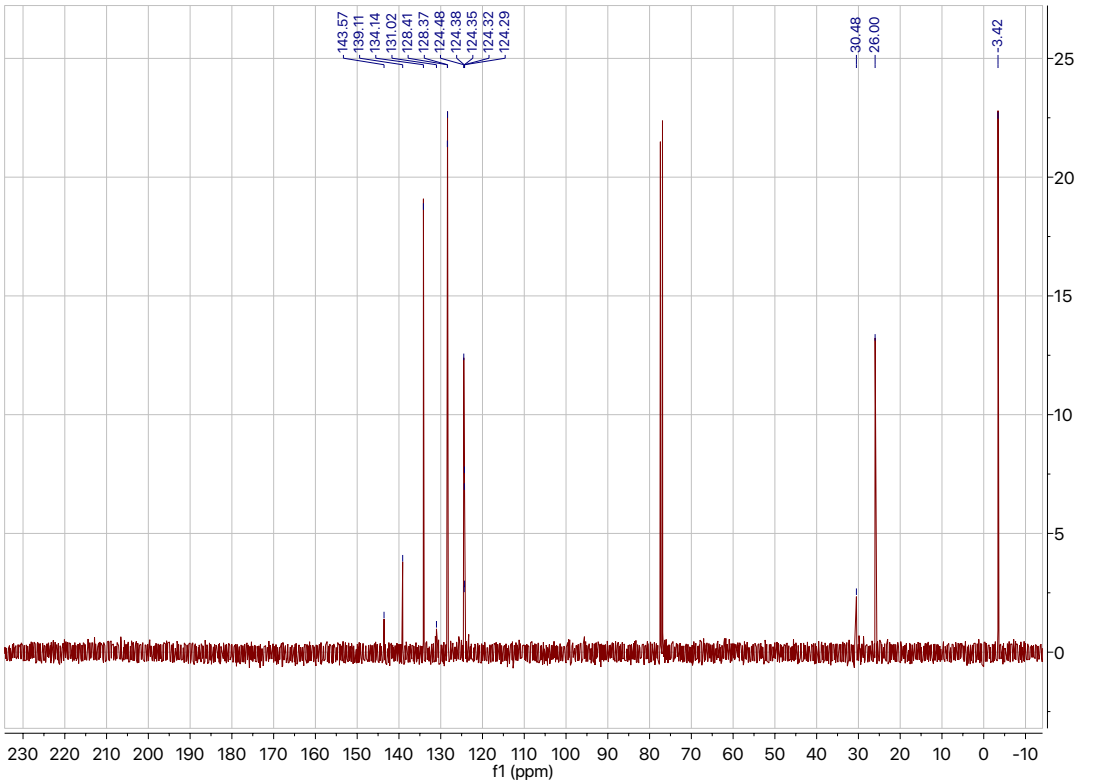
6.04
f1 (ppm)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124.38
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124.32
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30.48
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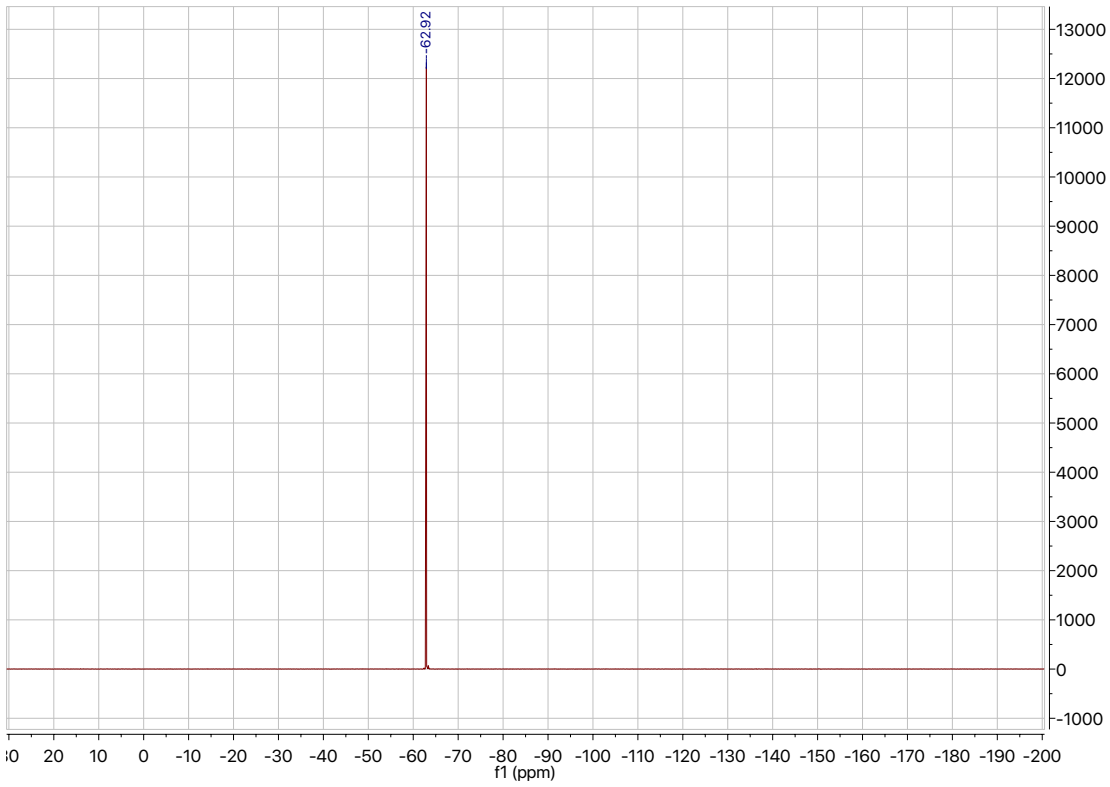
-3.42
f1 (ppm)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10000
9000
8000
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6000
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4000
3000
2000
1000
0
-1000
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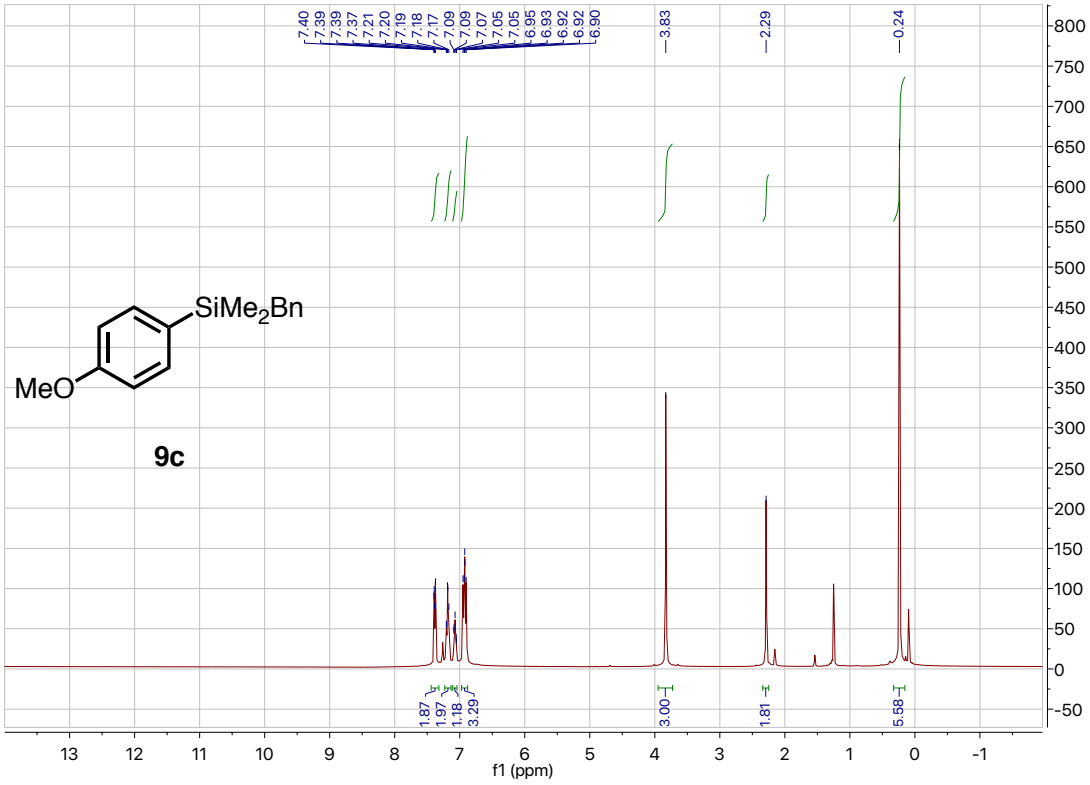
f1 (ppm)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7.18
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7.09
7.09
7.07
7.05
7.05
6.95
6.93
6.92
6.92
6.90
3.83
2.29
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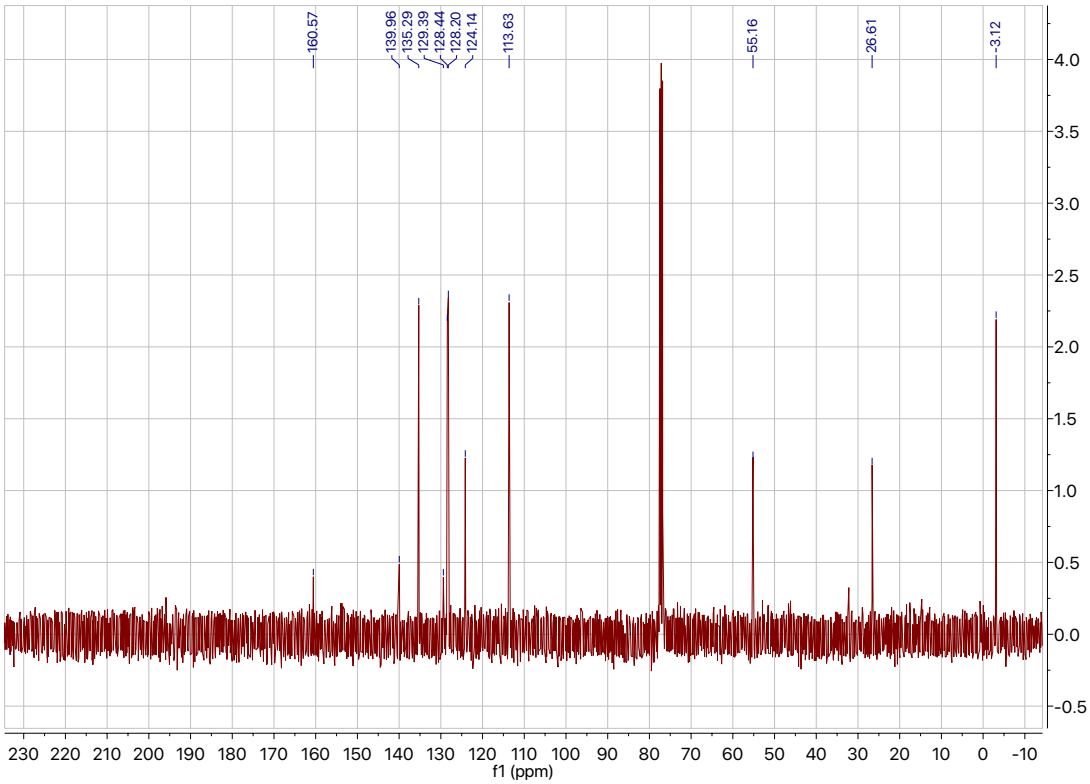
MeO
9c
1.87
1.97
1.18
3.29
3.00
1.81
5.58
f1 (ppm)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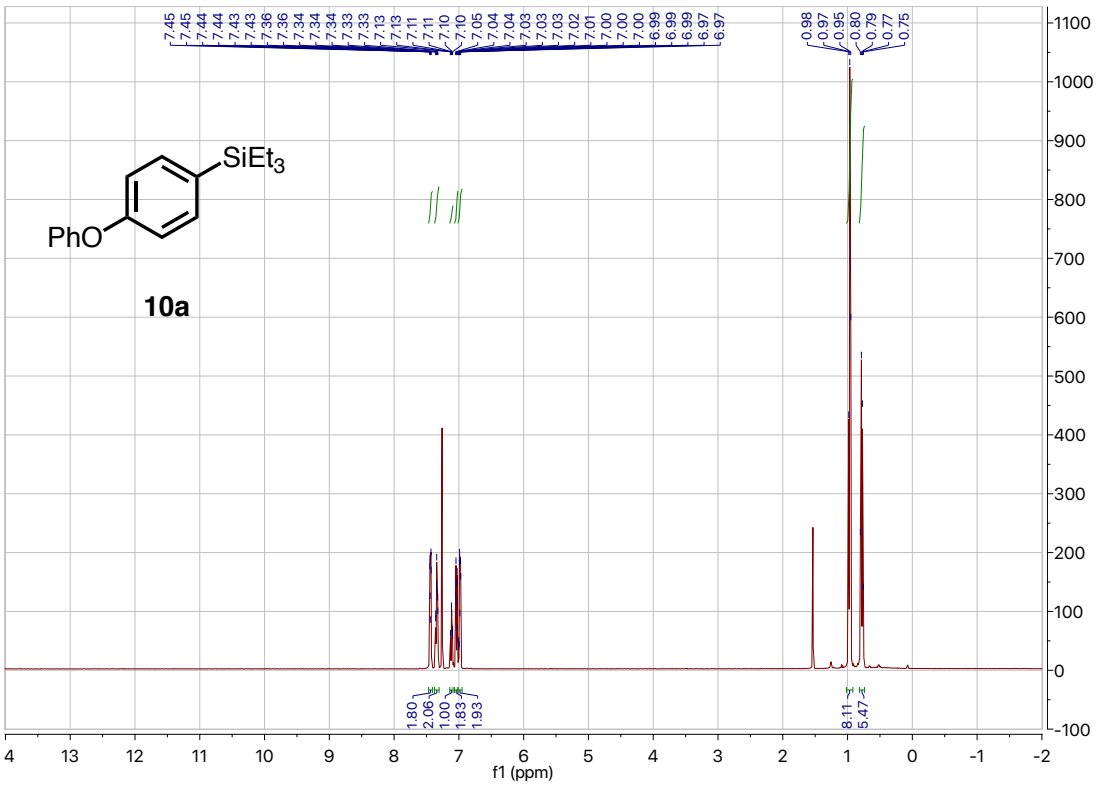
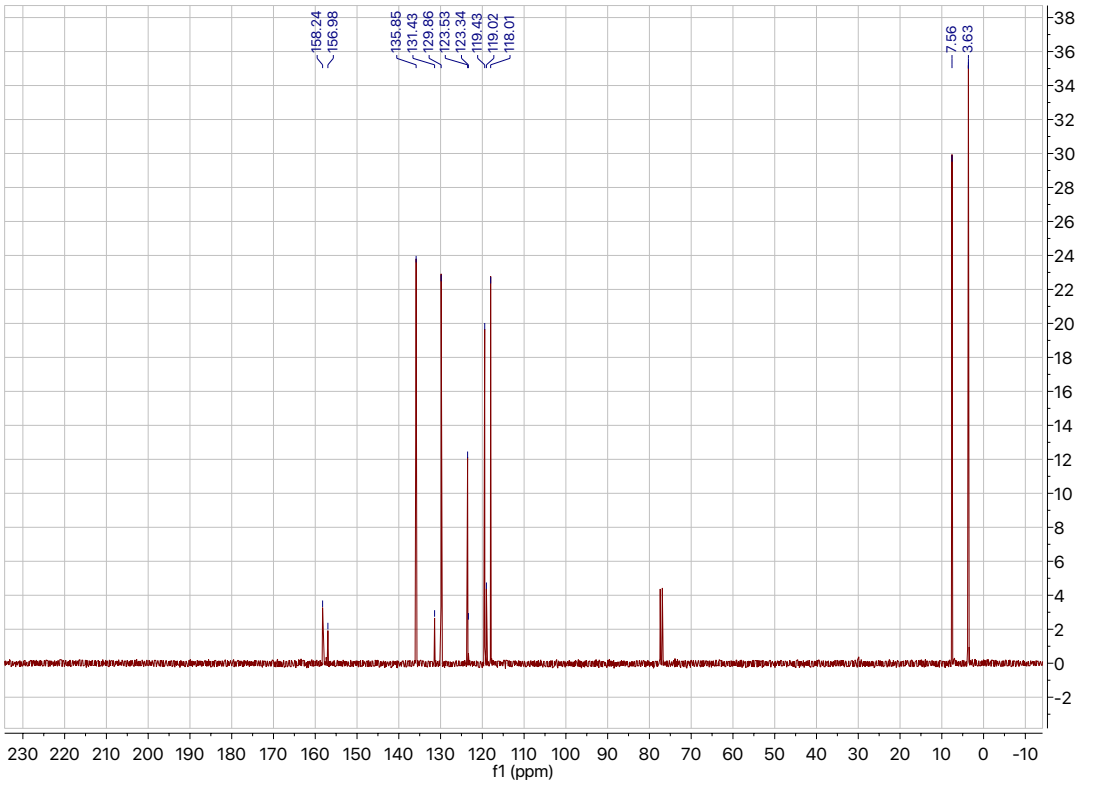
124.14
113.63
55.16
26.61
-3.12
f1 (ppm)


SiEt3
PhO
10a
f1 (ppm)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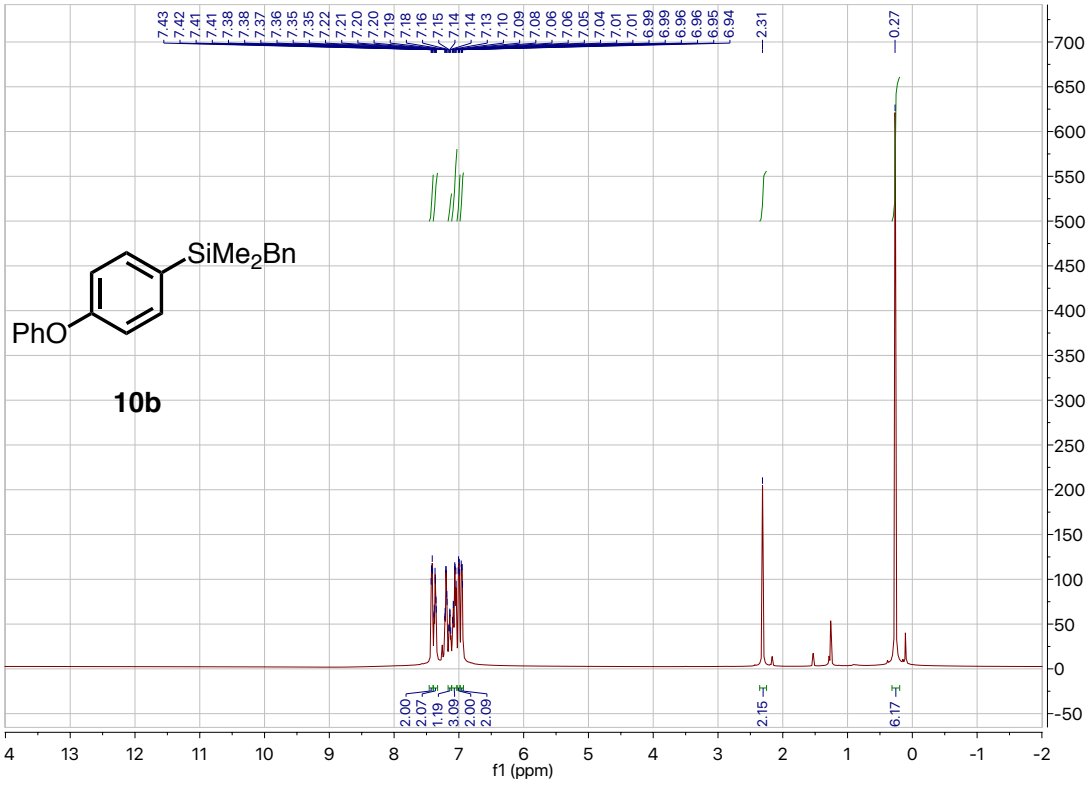
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7.19
7.18
7.16
7.15
7.14
7.14
7.13
7.10
7.09
7.08
7.06
7.06
7.05
7.04
7.01
7.01
6.99
6.99
6.96
6.96
6.95
6.94
2.31
0.27
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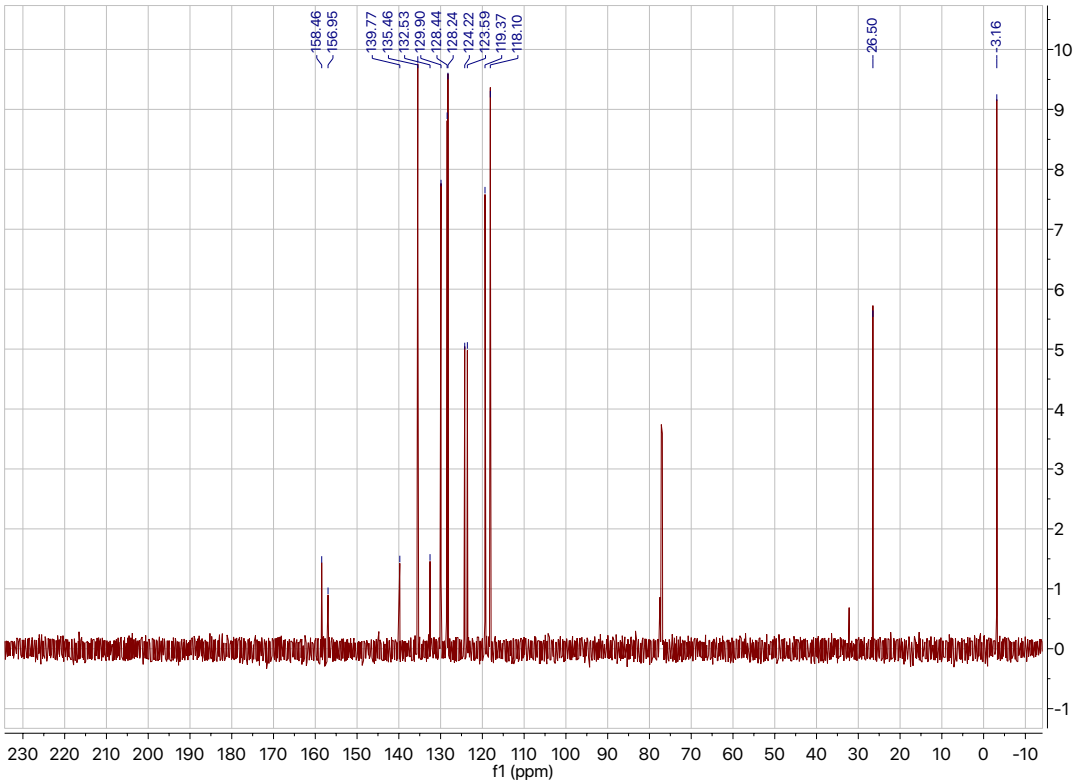
PhO
10b
2.00
2.07
1.19
3.09
2.00
2.09
2.15
6.17
f1 (ppm)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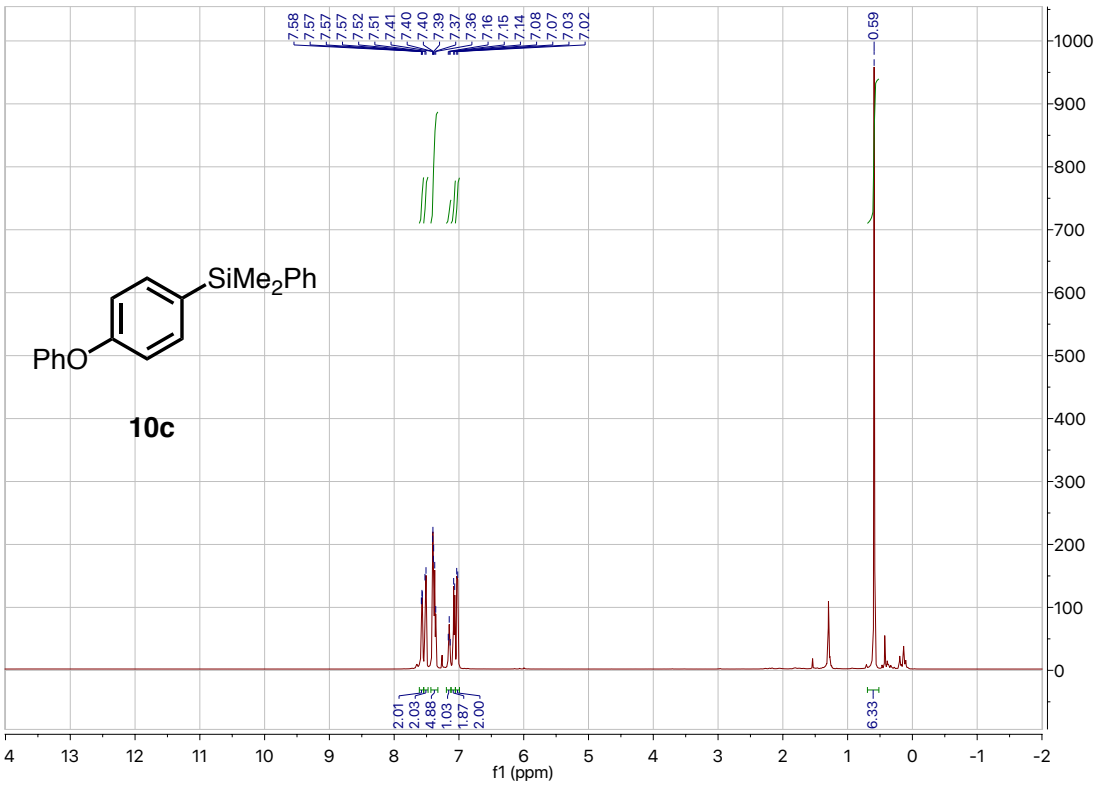
-3.16
f1 (ppm)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7.16
7.15
7.14
7.08
7.07
7.03
7.02
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SiMe2Ph
PhO
10c
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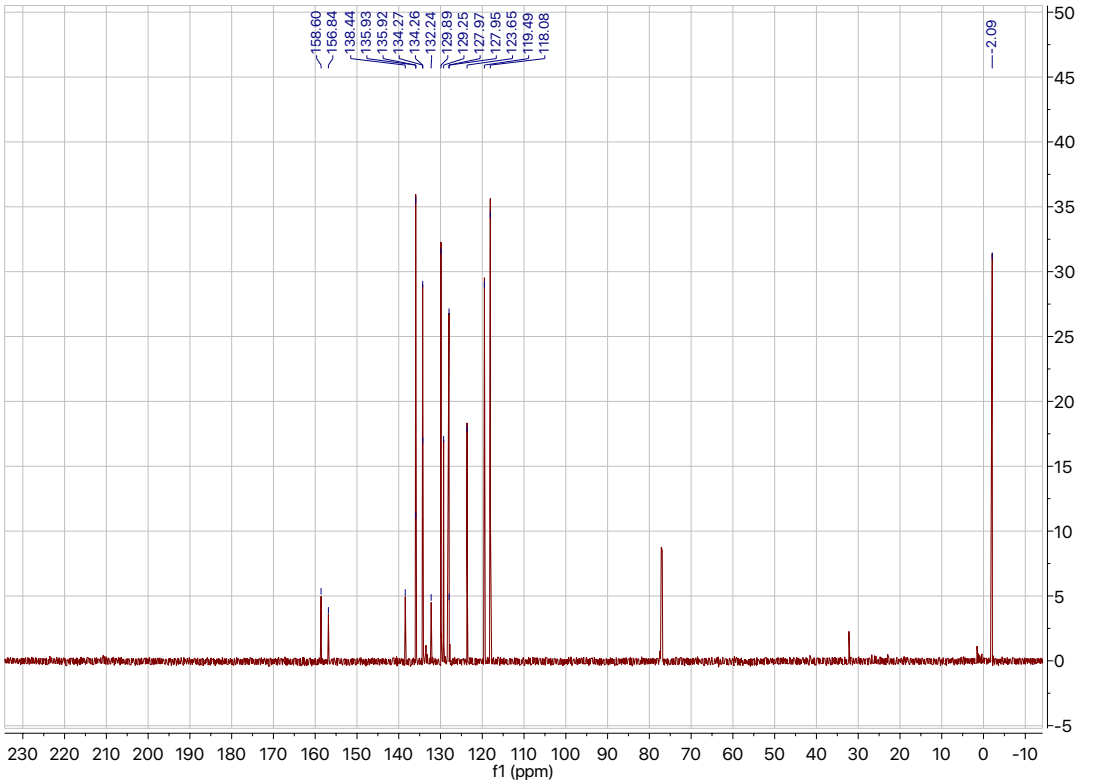
2.03
4.88
1.03
1.87
2.00
6.33
f1 (ppm)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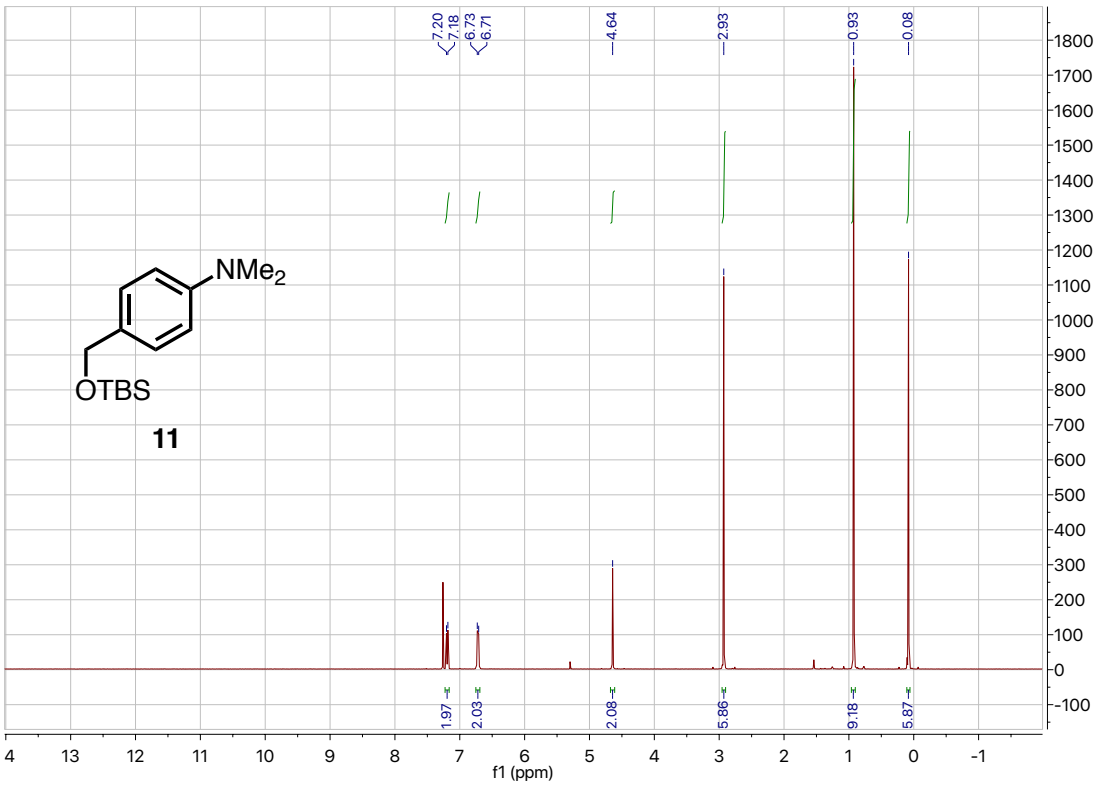
129.25
127.97
127.95
123.65
119.49
118.08
2.09
f1 (ppm)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7.18
6.73
6.71
4.64
2.93
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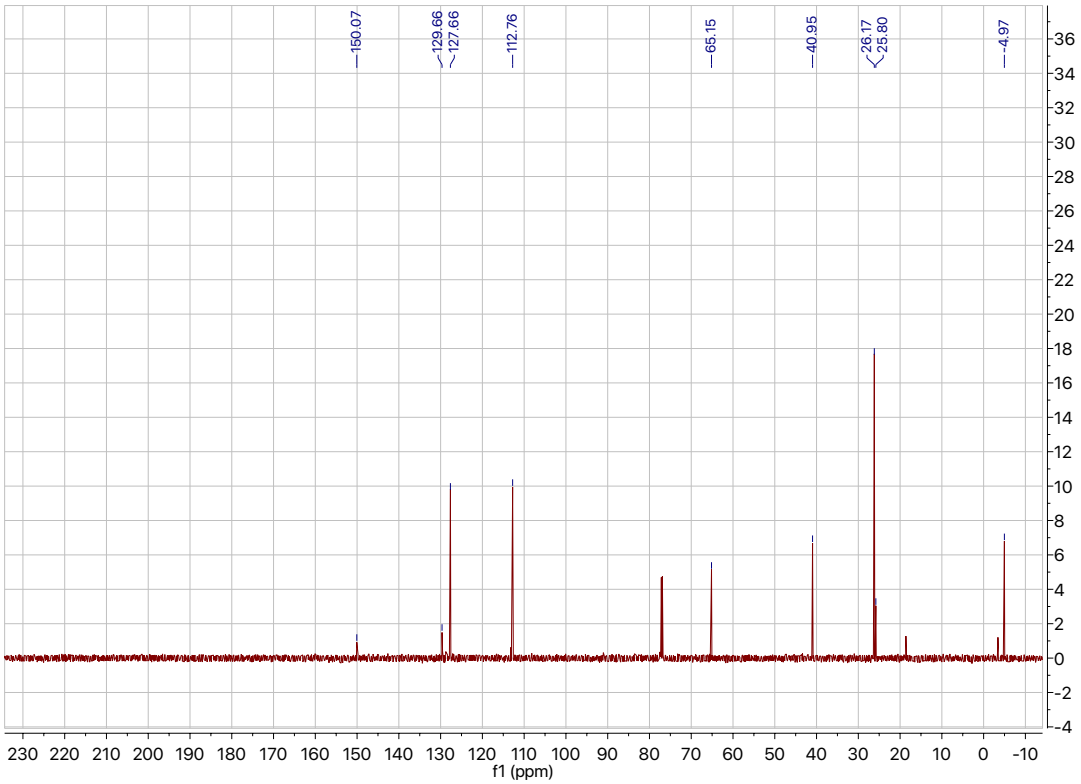
OTBS
11
1.97
2.03
2.08
5.86
9.18
5.87
f1 (ppm)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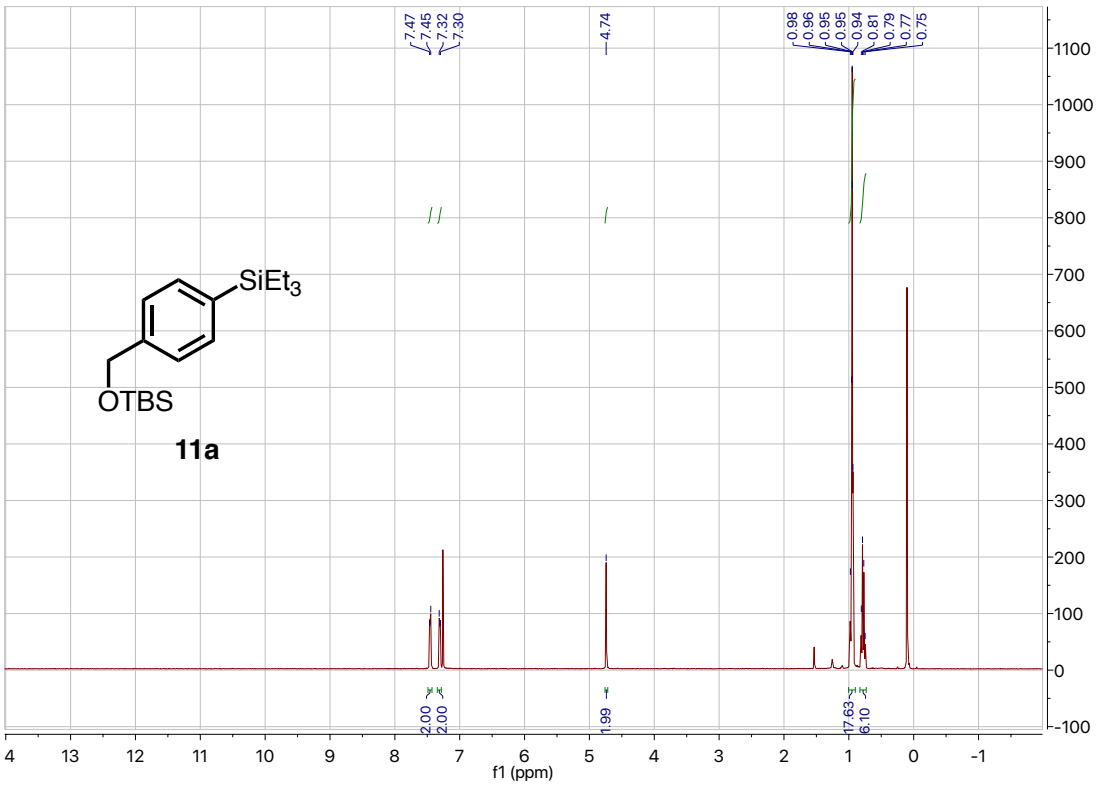
40.95
26.17
25.80
-4.97
f1 (ppm)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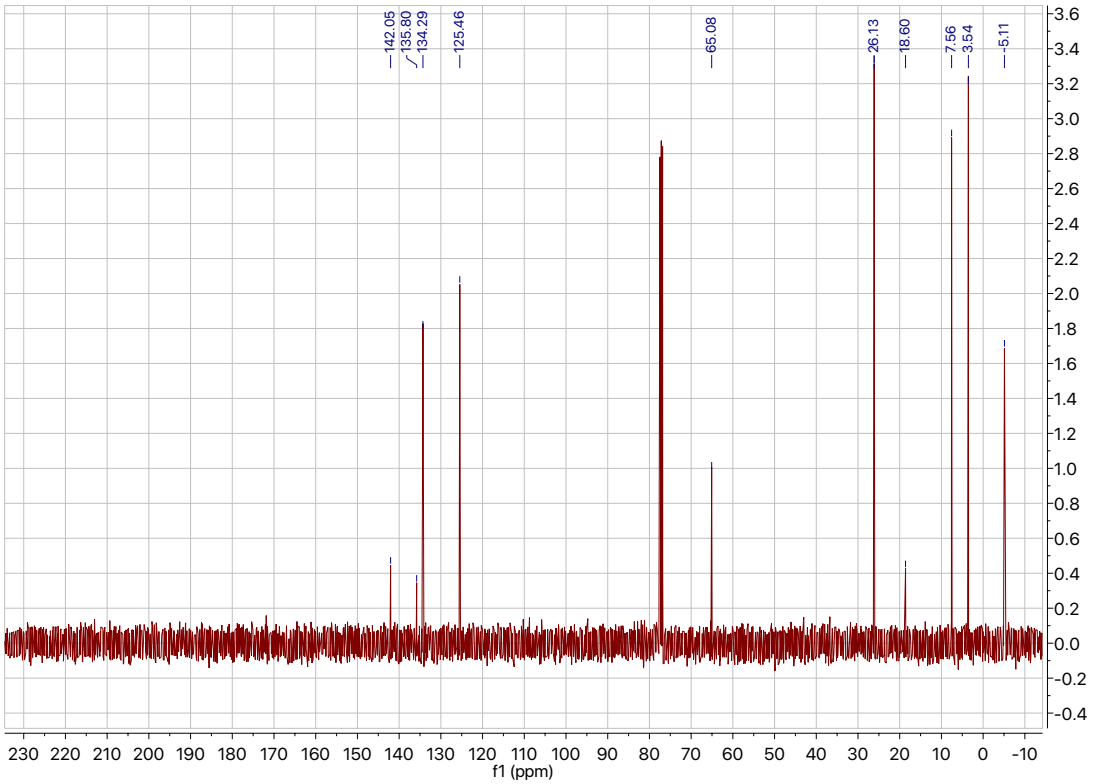
7.45
7.32
7.30
4.74
0.98
0.96
0.95
0.95
0.94
0.81
0.79
0.77
0.75
SiEt3
OTBS
11a
2.00
2.00
1.99
17.63
6.10
f1 (ppm)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134.29
125.46
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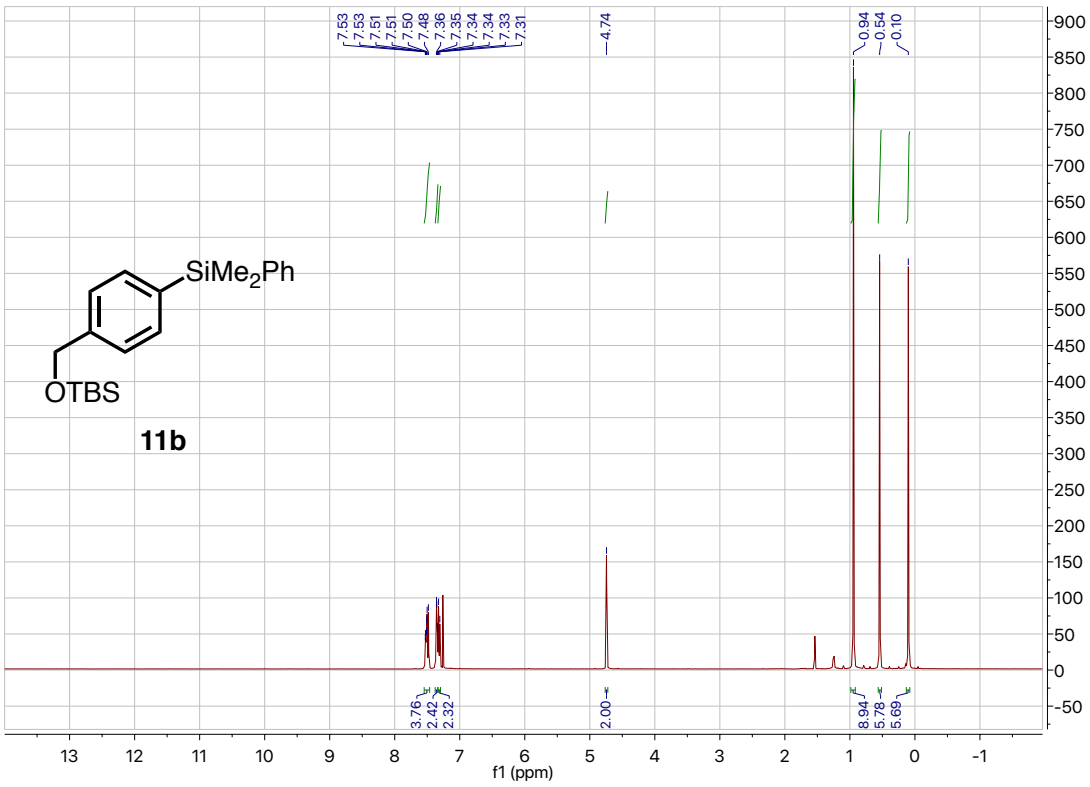
26.13
18.60
7.56
3.54
-5.11
f1 (ppm)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7.36
7.35
7.34
7.34
7.33
7.31
4.74
0.94
0.54
0.10
SiMe2Ph
OTBS
11b
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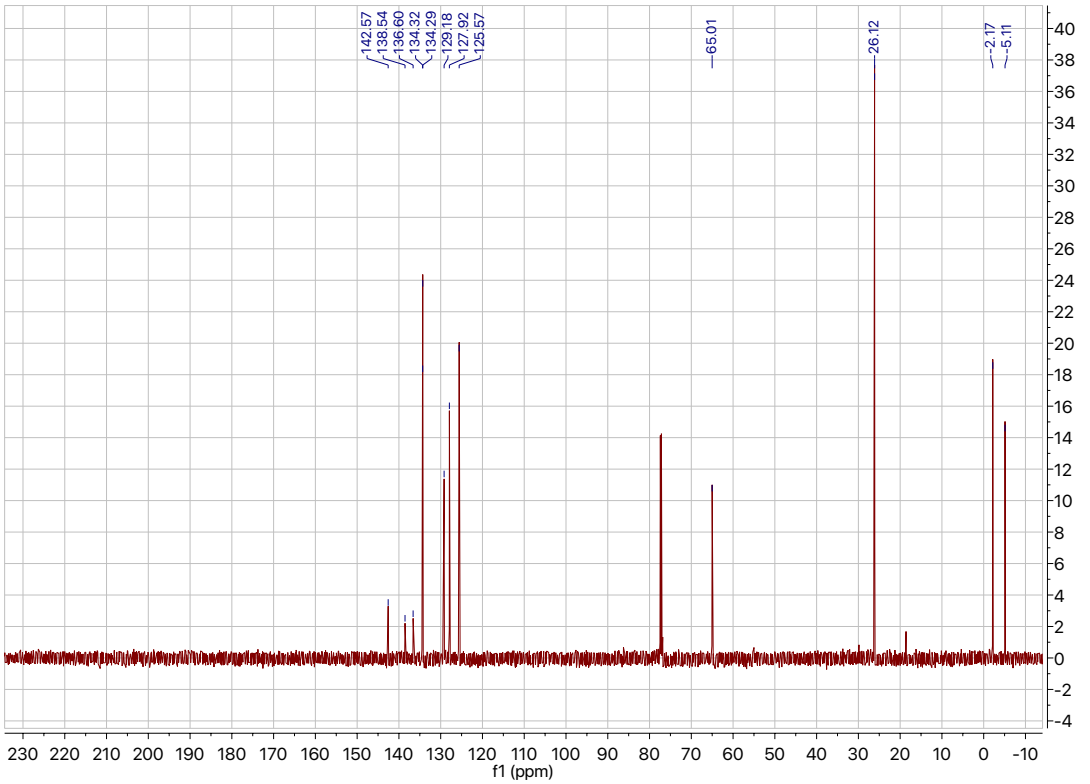
2.42
2.32
2.00
8.94
5.78
5.69
f1 (ppm)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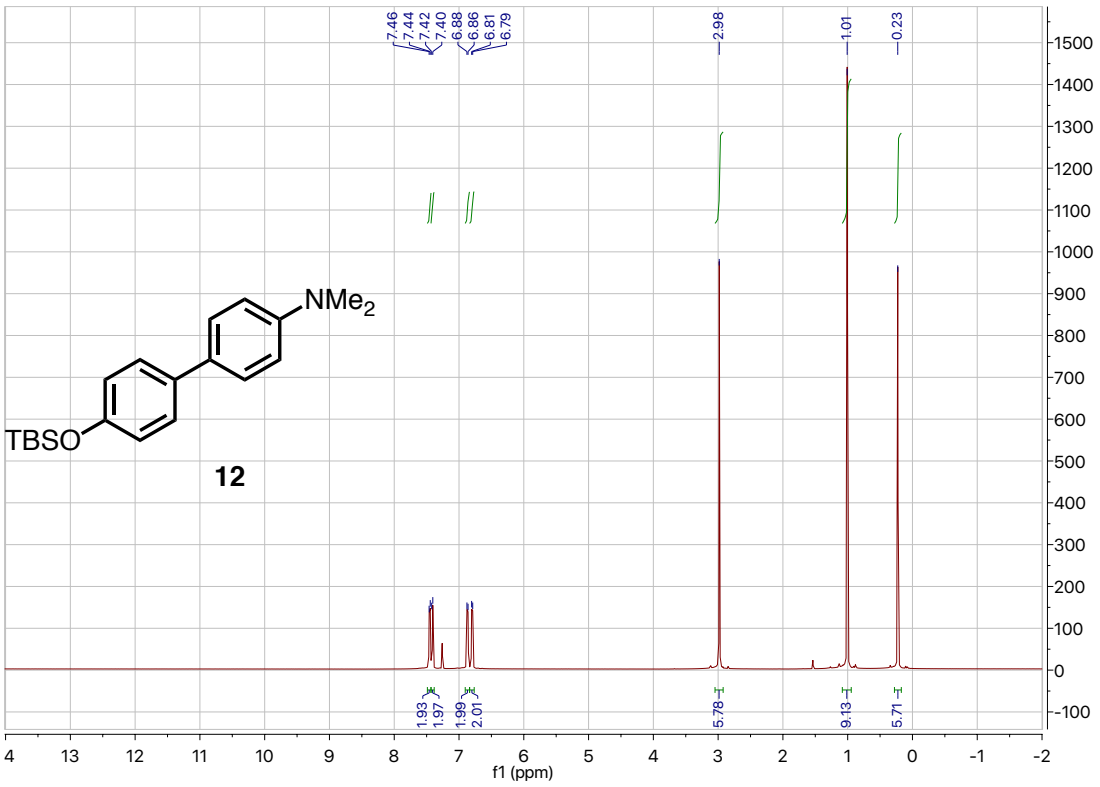
127.92
125.57
65.01
26.12
-2.17
-5.11
f1 (ppm)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7.44
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7.40
6.88
6.86
6.81
6.79
2.98
1.01
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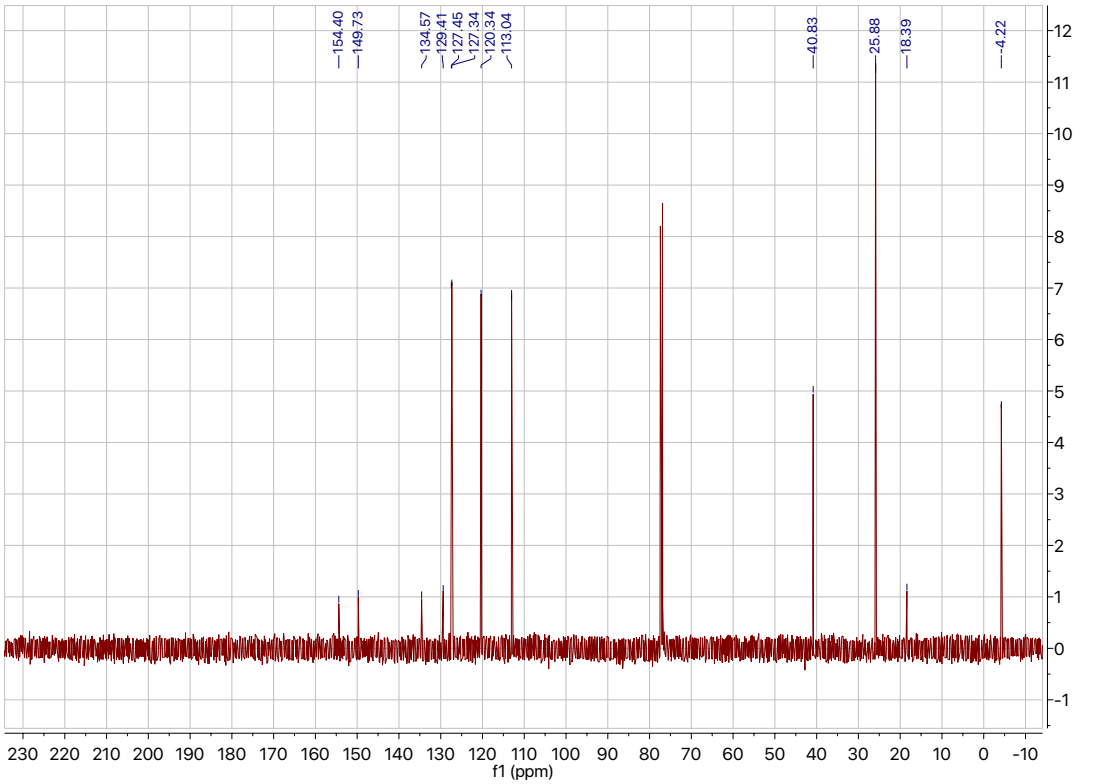
NMe2
TBSO
12
1.93
1.97
1.99
2.01
5.78
9.13
5.71
f1 (ppm)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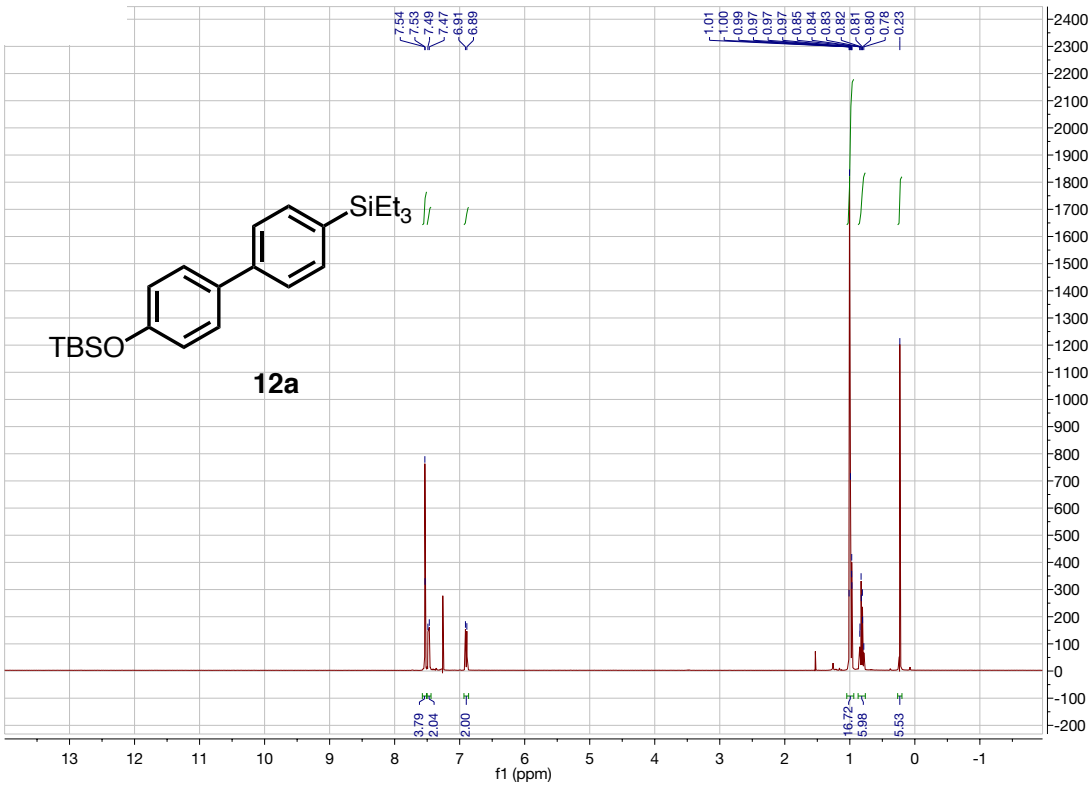
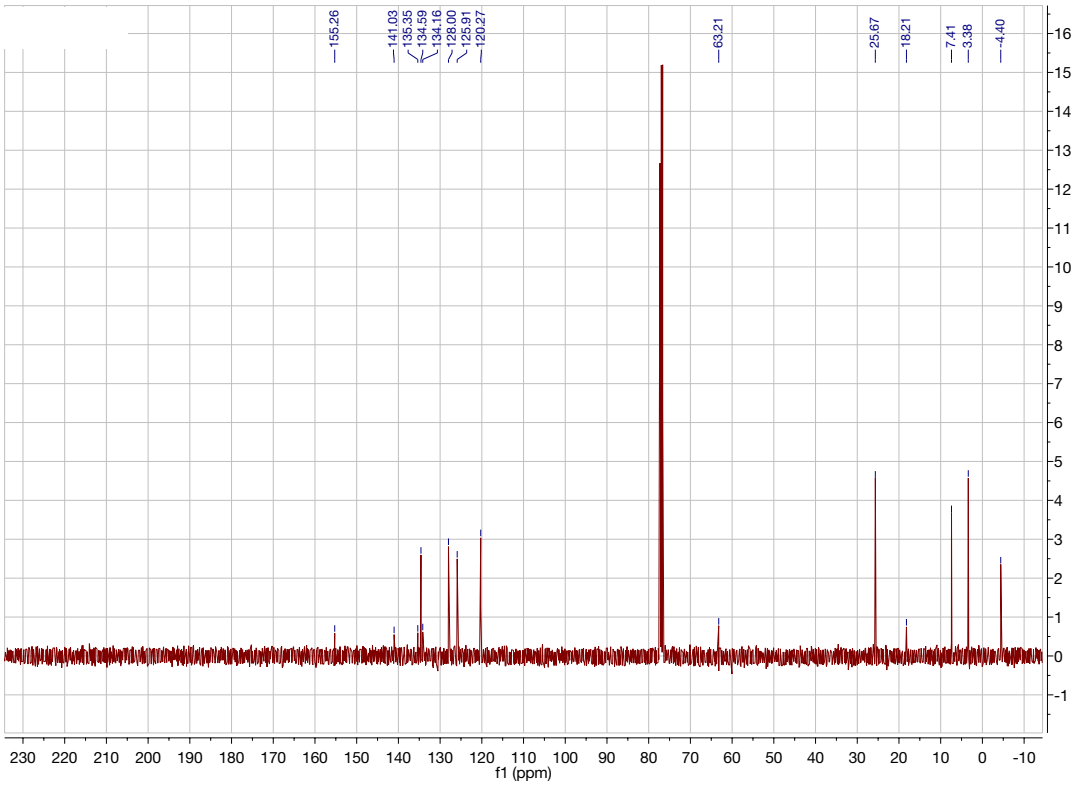
f1 (ppm)


SiEt3
TBSO
12a
f1 (ppm)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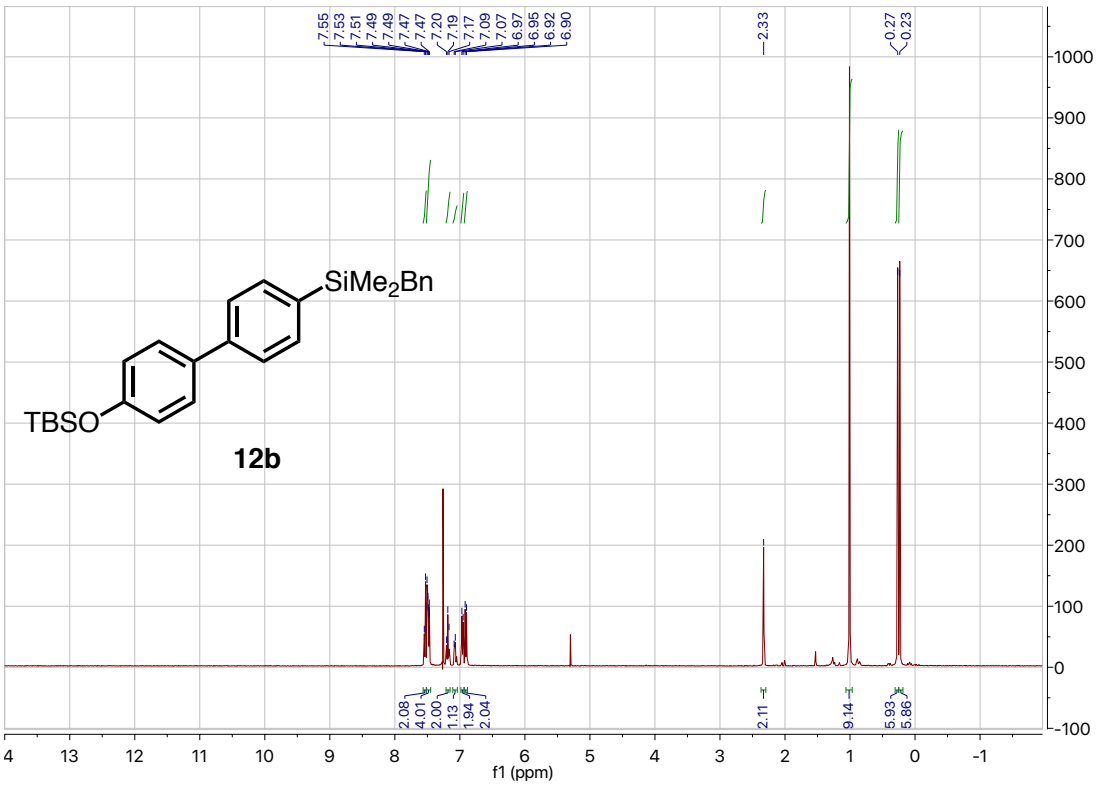
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7.47
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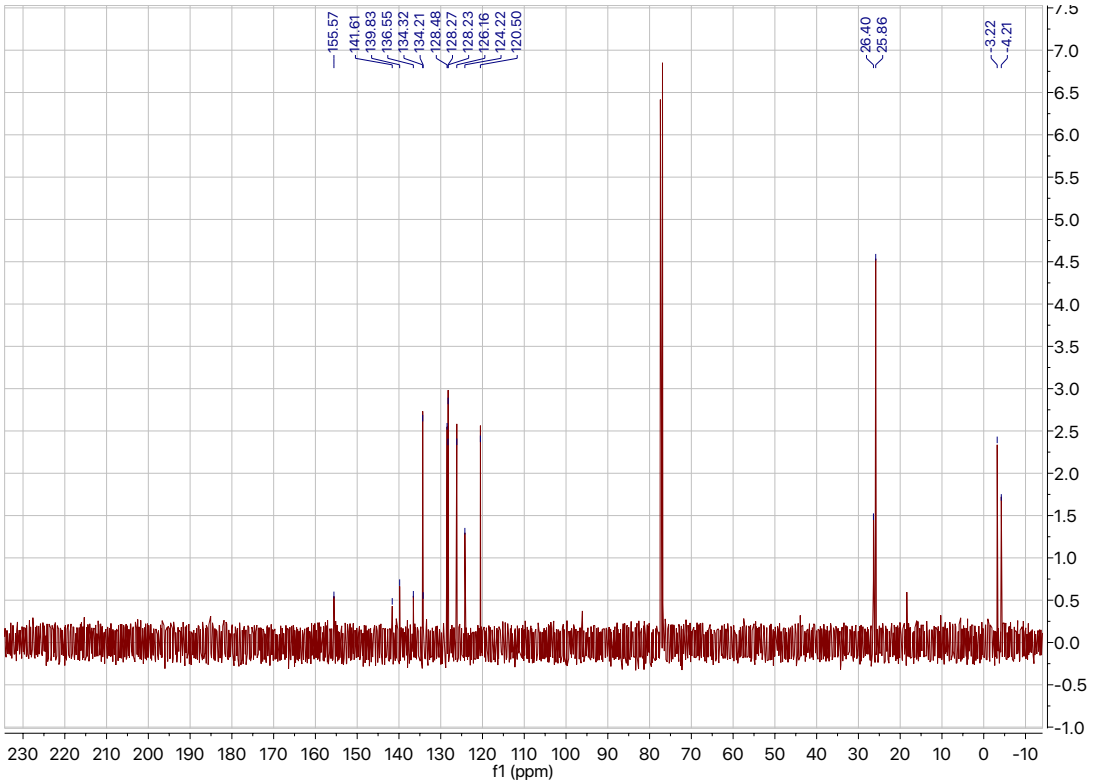
7.17
7.09
7.07
6.97
6.95
6.92
6.90
2.33
0.27
0.23
SiMe2Bn
TBSO
12b
2.08
4.01
2.00
1.13
1.94
2.04
2.11
9.14
5.93
5.86
f1 (ppm)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120.50
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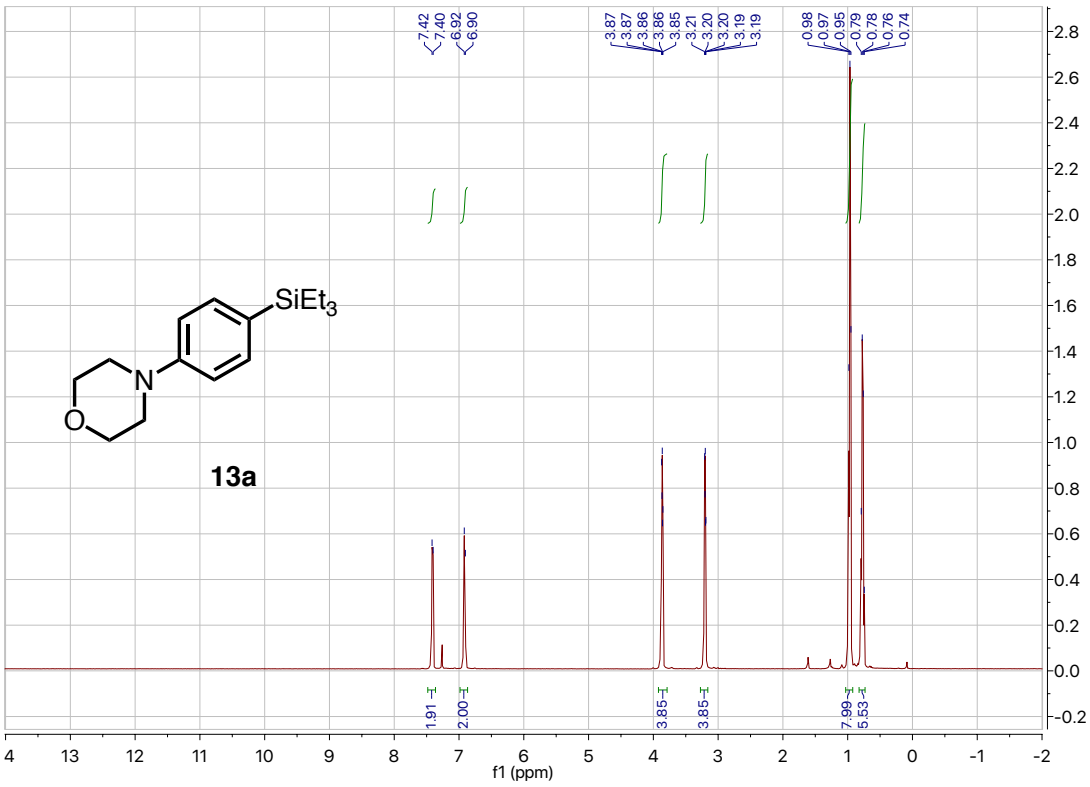
25.86
-3.22
-4.21
f1 (ppm)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3.86
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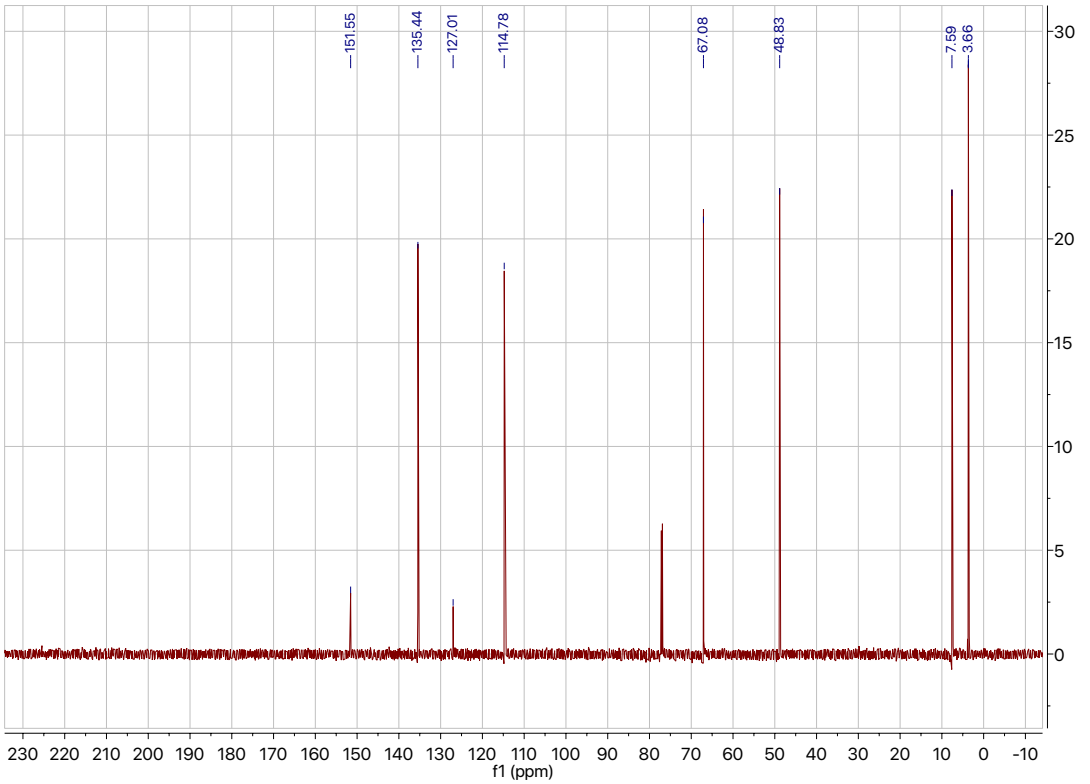
3.20
3.20
3.19
3.19
0.98
0.97
0.95
0.79
0.78
0.76
0.74
SiEt3
N
O
13a
1.91
2.00
3.85
3.85
7.99
5.53
f1 (ppm)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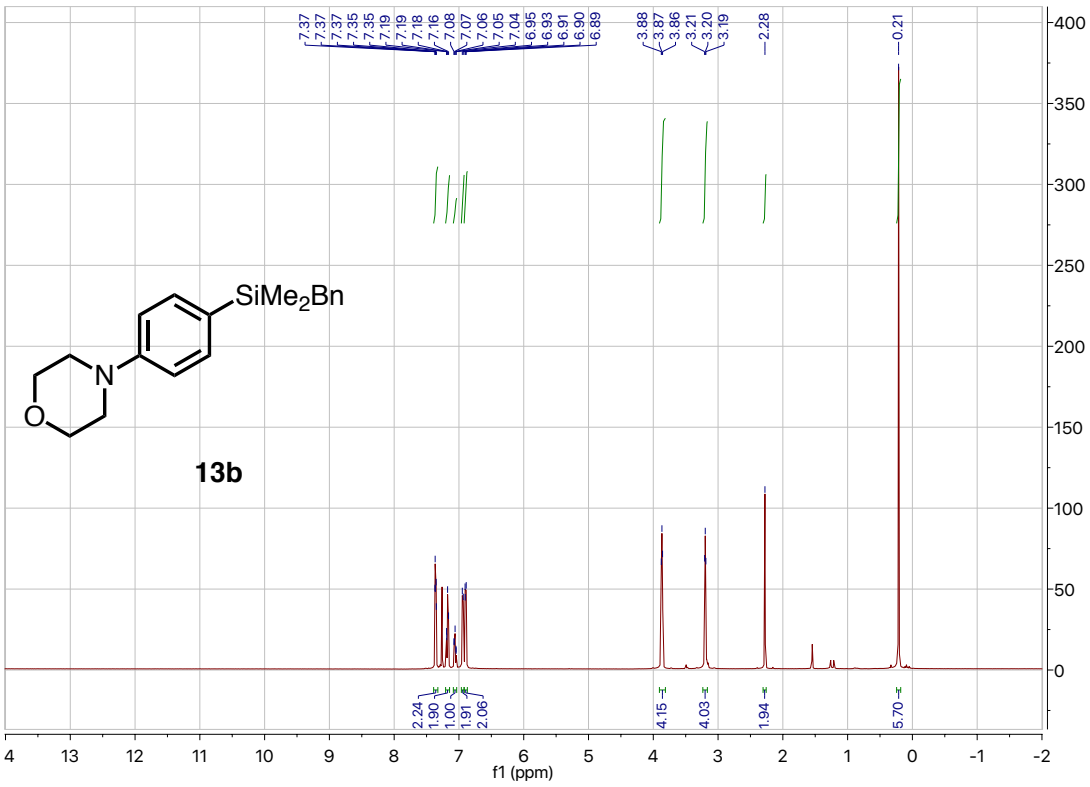
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7.04
6.95
6.93
6.91
6.90
6.89
3.88
3.87
3.86
3.21
3.20
3.19
2.28
0.21
SiMe2Bn
N
O
13b
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1.00
1.91
2.06
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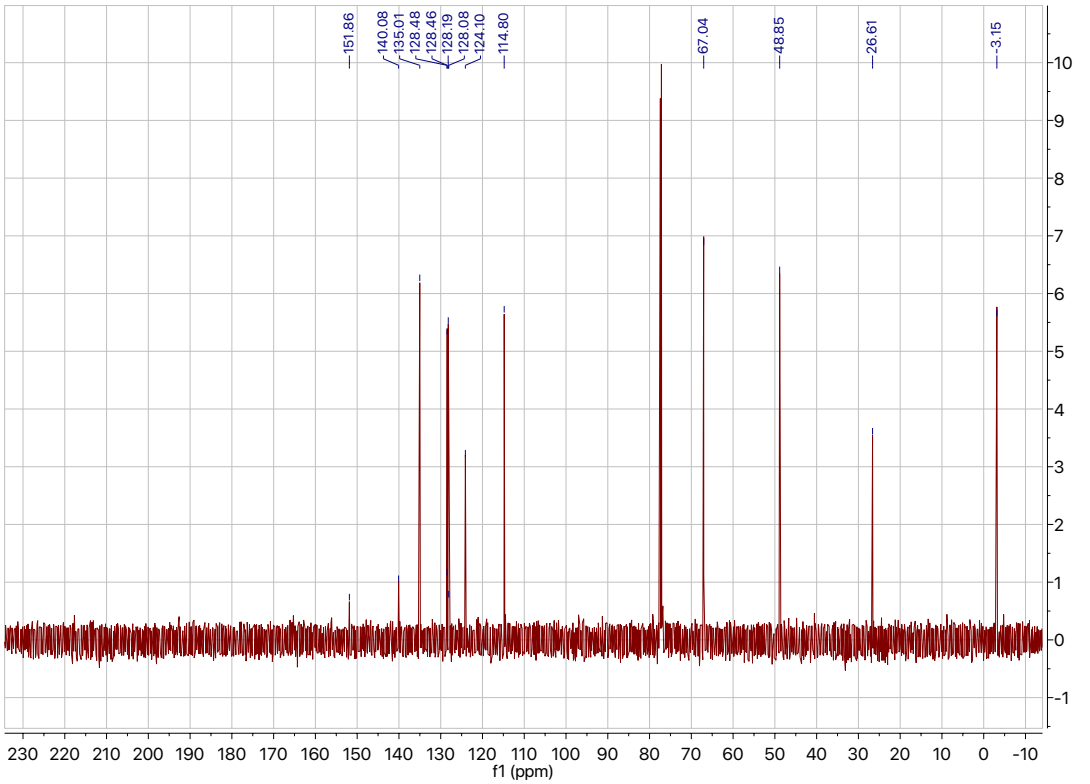
4.03
1.94
5.70
f1 (ppm)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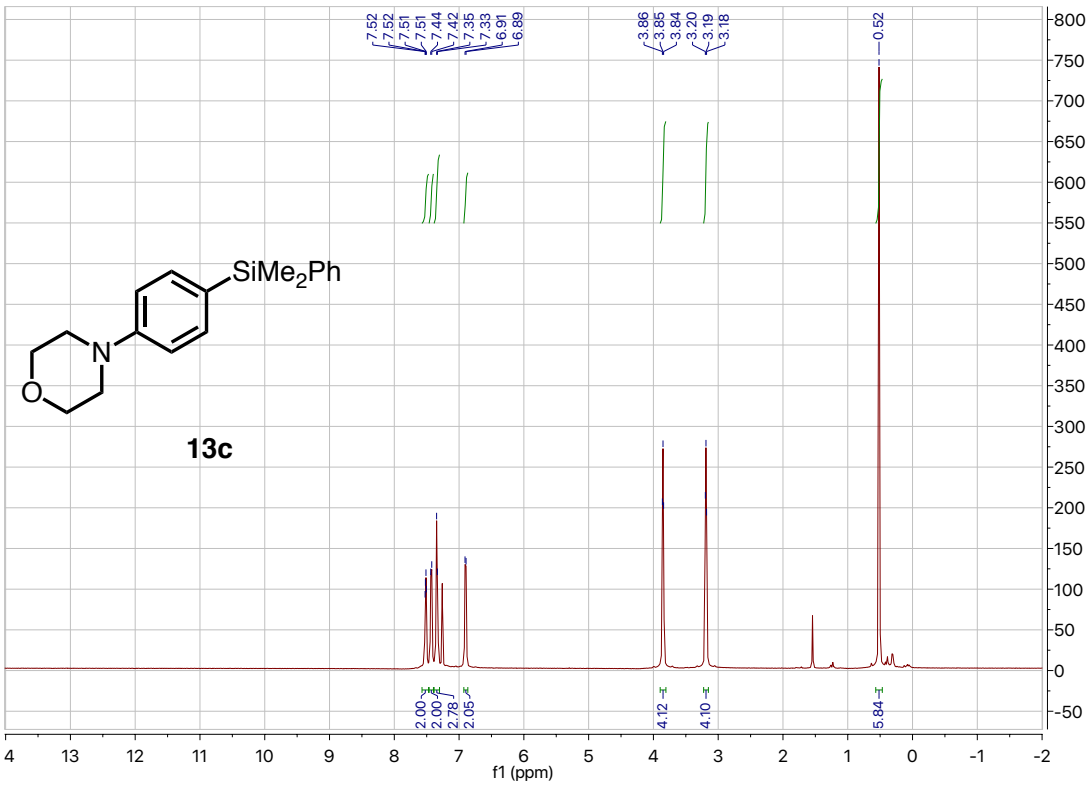
f1 (ppm)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7.33
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6.89
3.86
3.85
3.84
3.20
3.19
3.18
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SiMe2Ph
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O
13c
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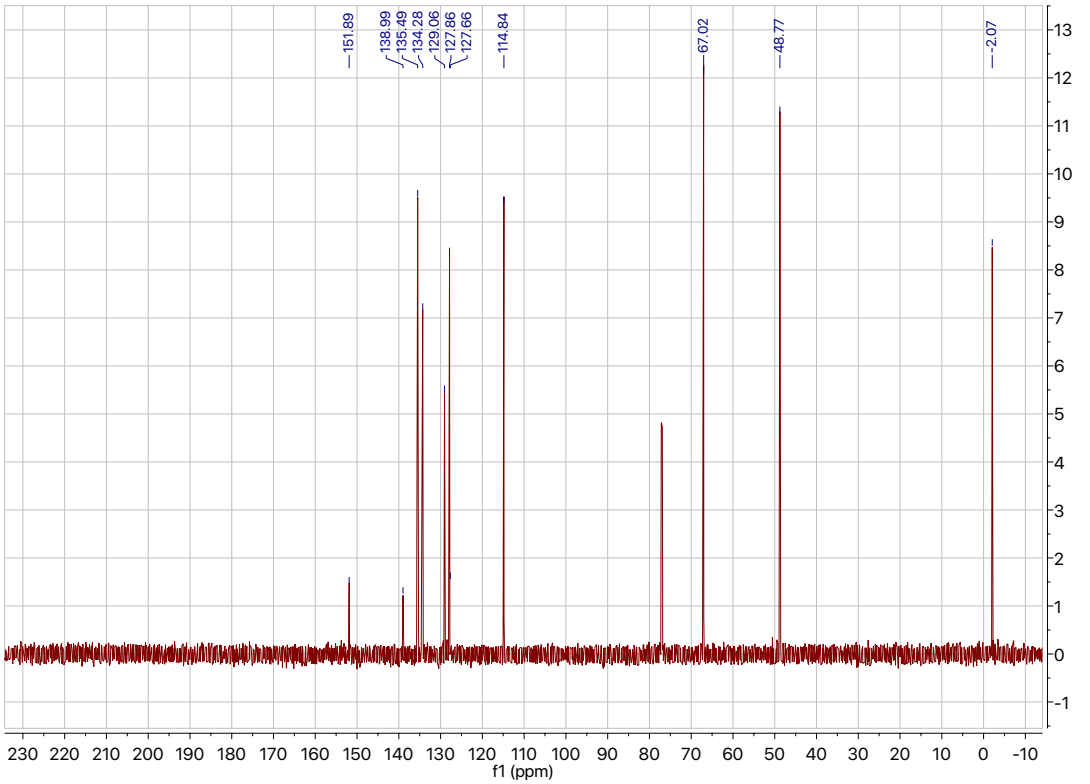
2.00
2.78
2.05
4.12
4.10
5.84
f1 (ppm)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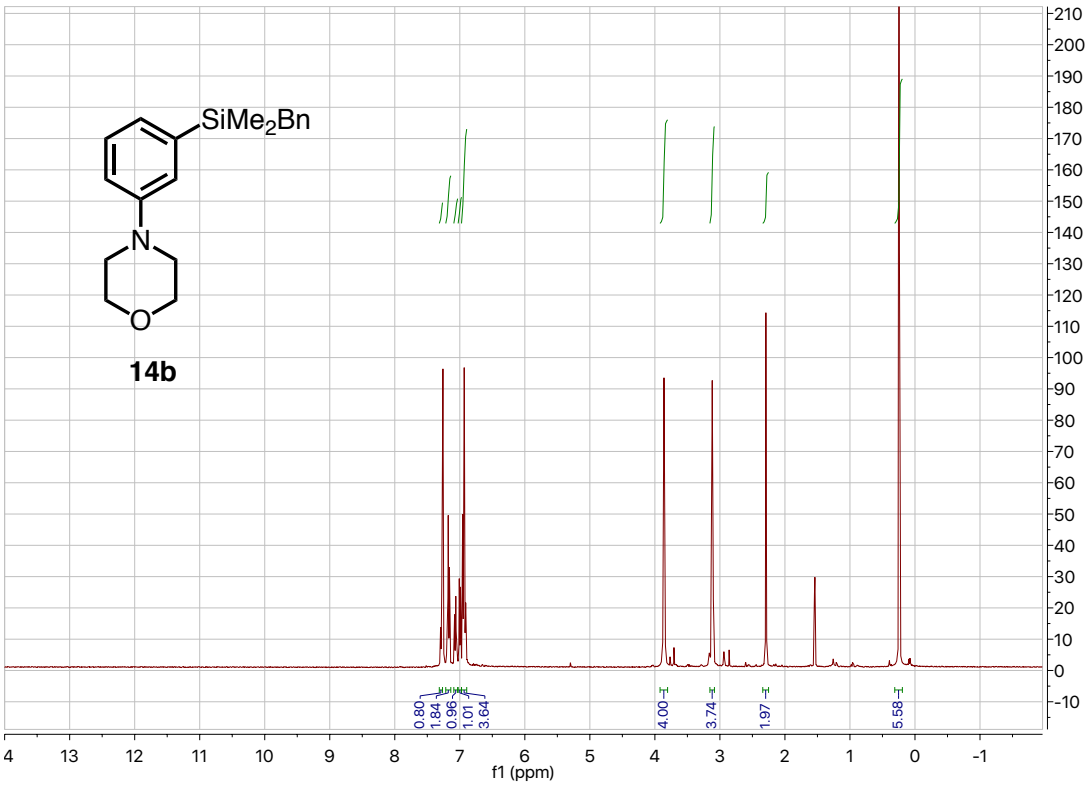
2.07
f1 (ppm)


SiMe2Bn
N
O
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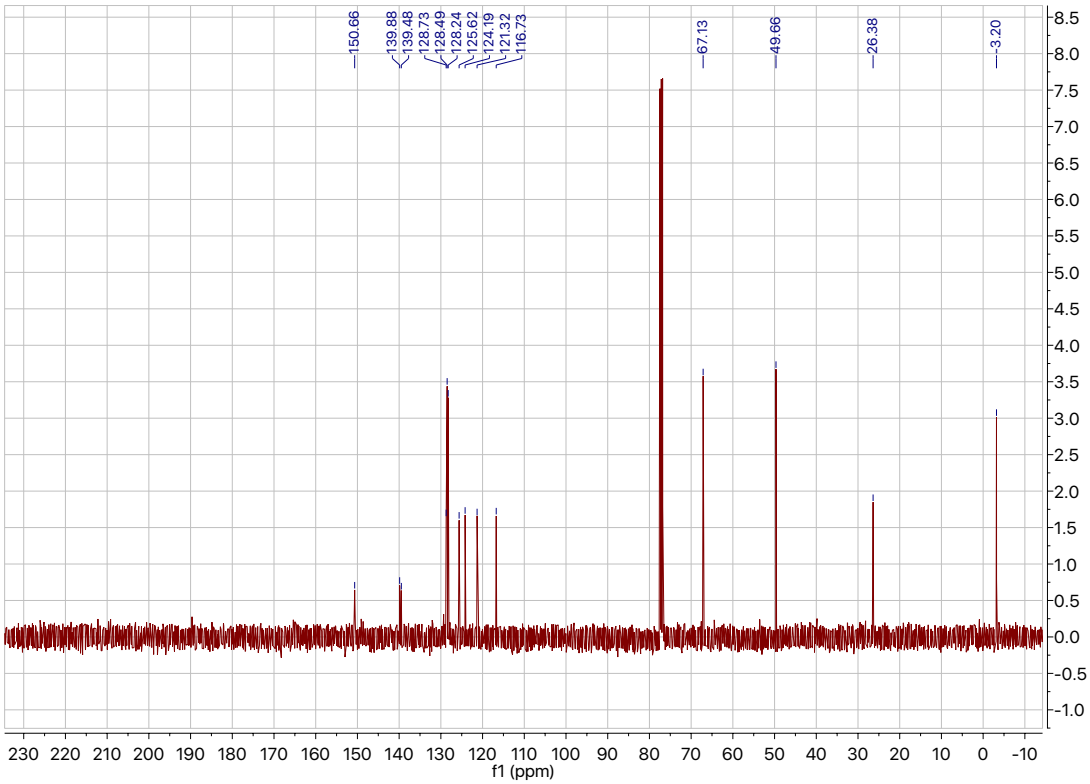
3.64
4.00
3.74
1.97
5.58
f1 (ppm)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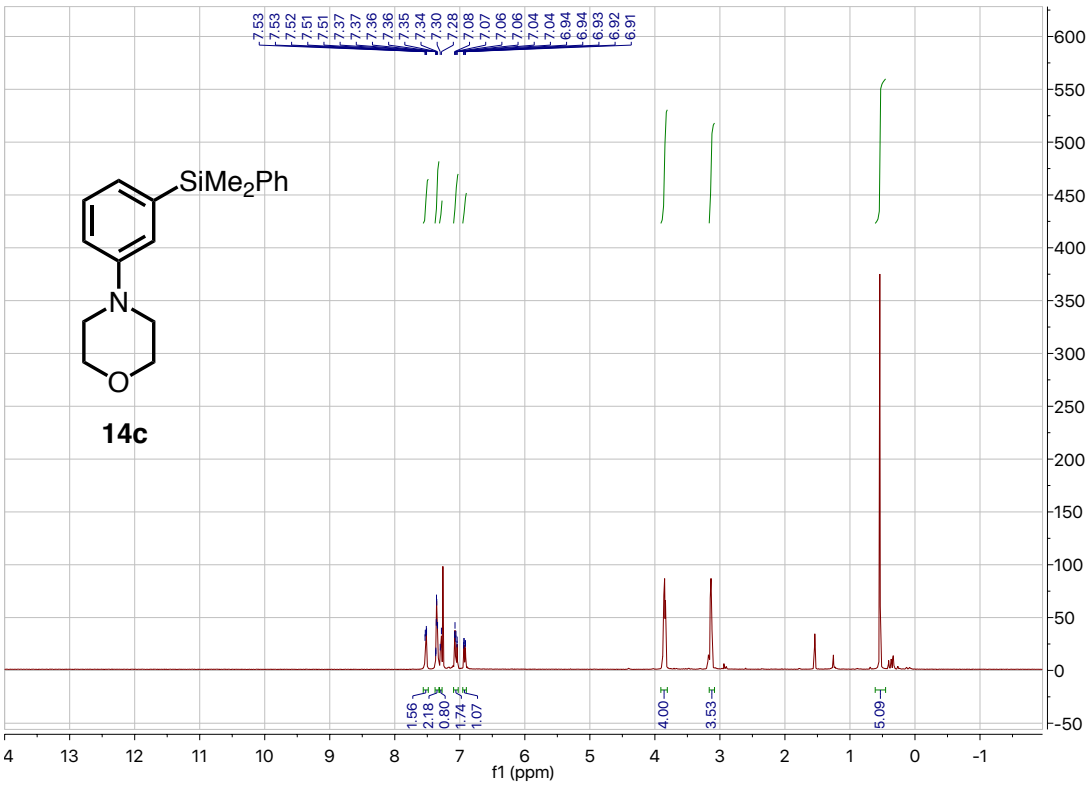
3.20
f1 (ppm)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7.06
7.06
7.04
7.04
6.94
6.94
6.93
6.92
6.91
SiMe2Ph
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O
14c
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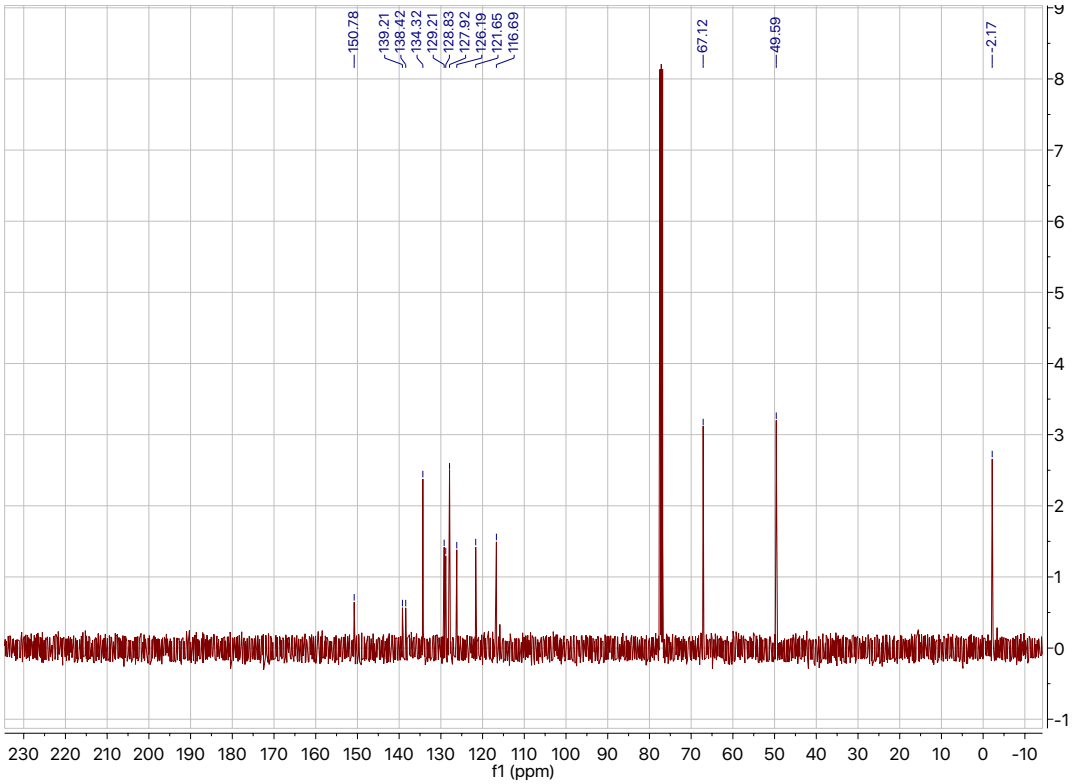
0.80
1.74
1.07
4.00
3.53
5.09
f1 (ppm)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126.19
121.65
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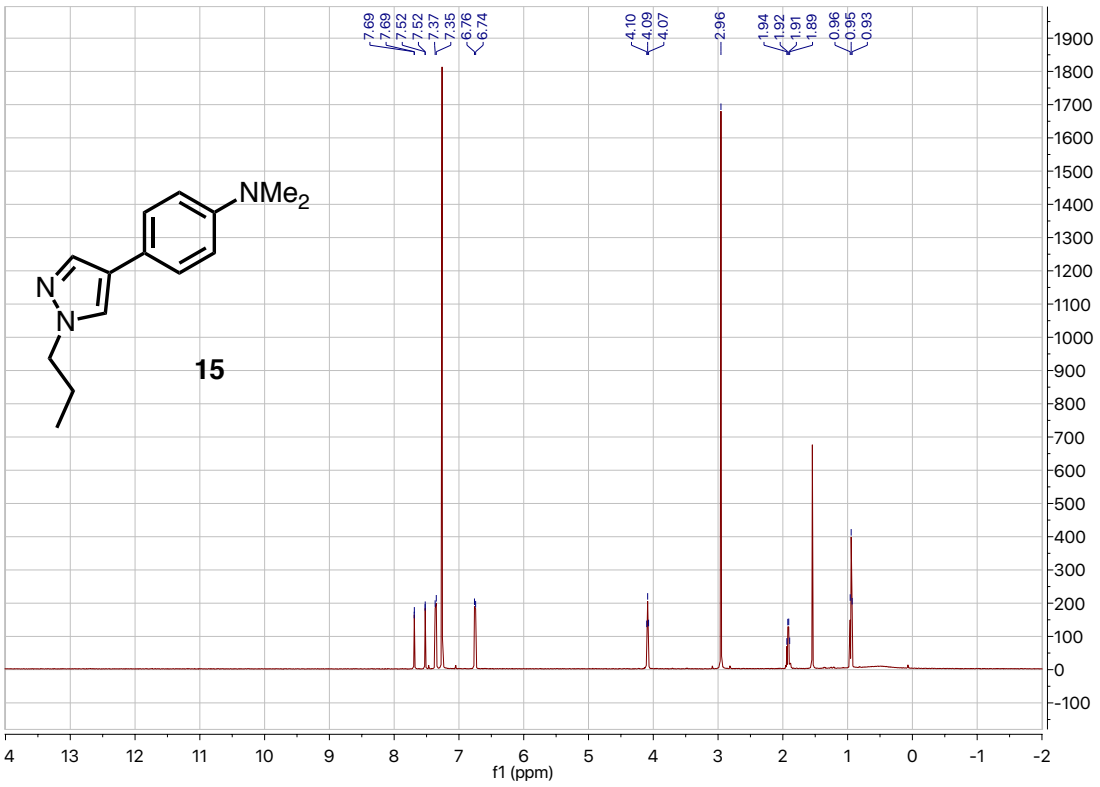
67.12
49.59
2.17
f1 (ppm)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4.09
4.07
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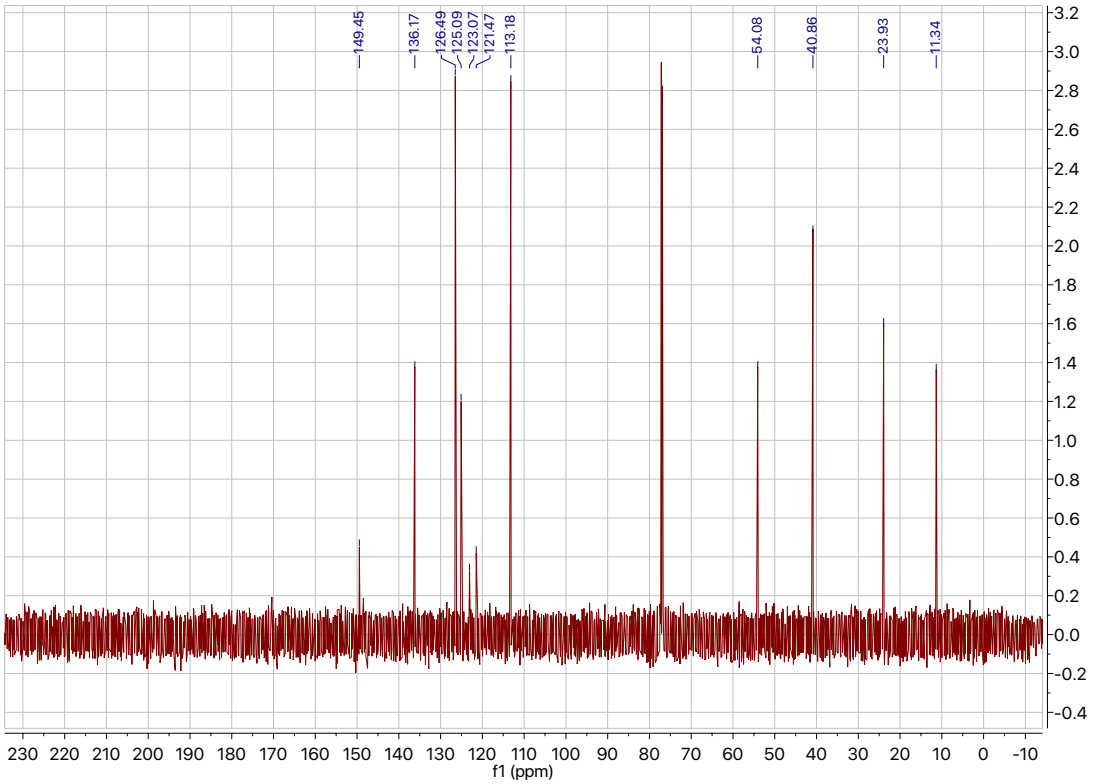
1.91
1.89
0.96
0.95
0.93
NMe2
N
N
15
f1 (ppm)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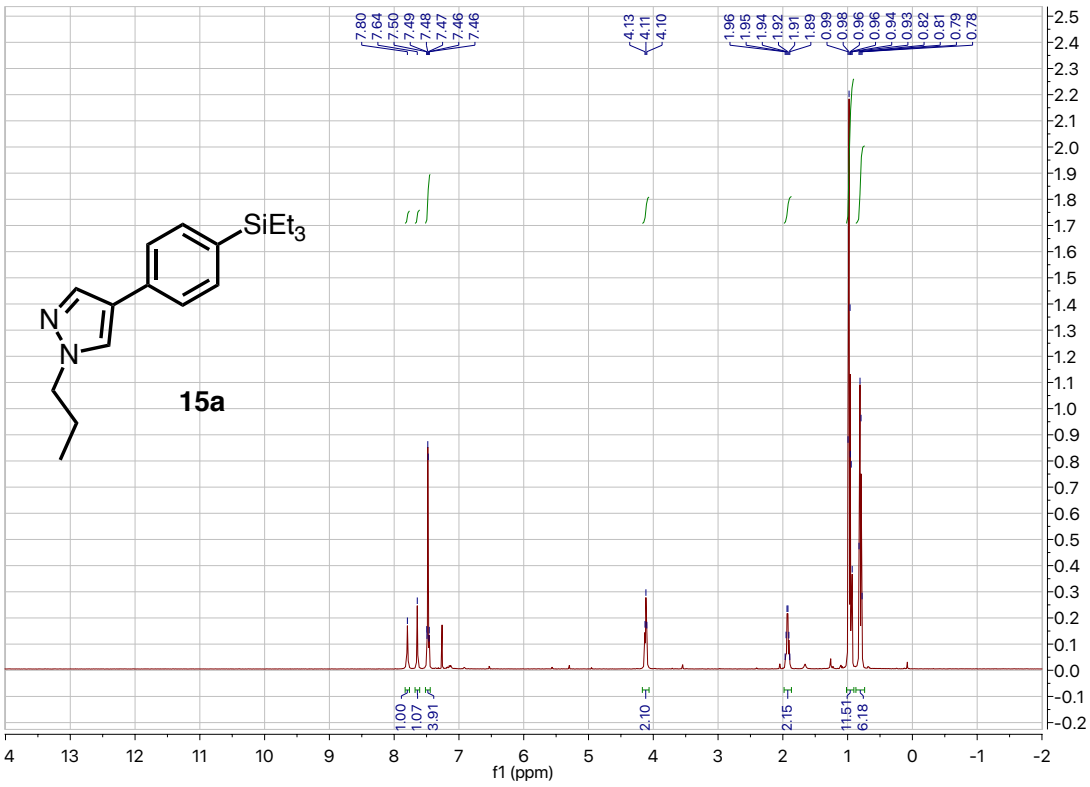
54.08
40.86
23.93
11.34
f1 (ppm)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7.46
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4.11
4.10
1.96
1.95
1.94
1.92
1.91
1.89
0.99
0.98
0.96
0.96
0.94
0.93
0.82
0.81
0.79
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SiEt3
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N
15a
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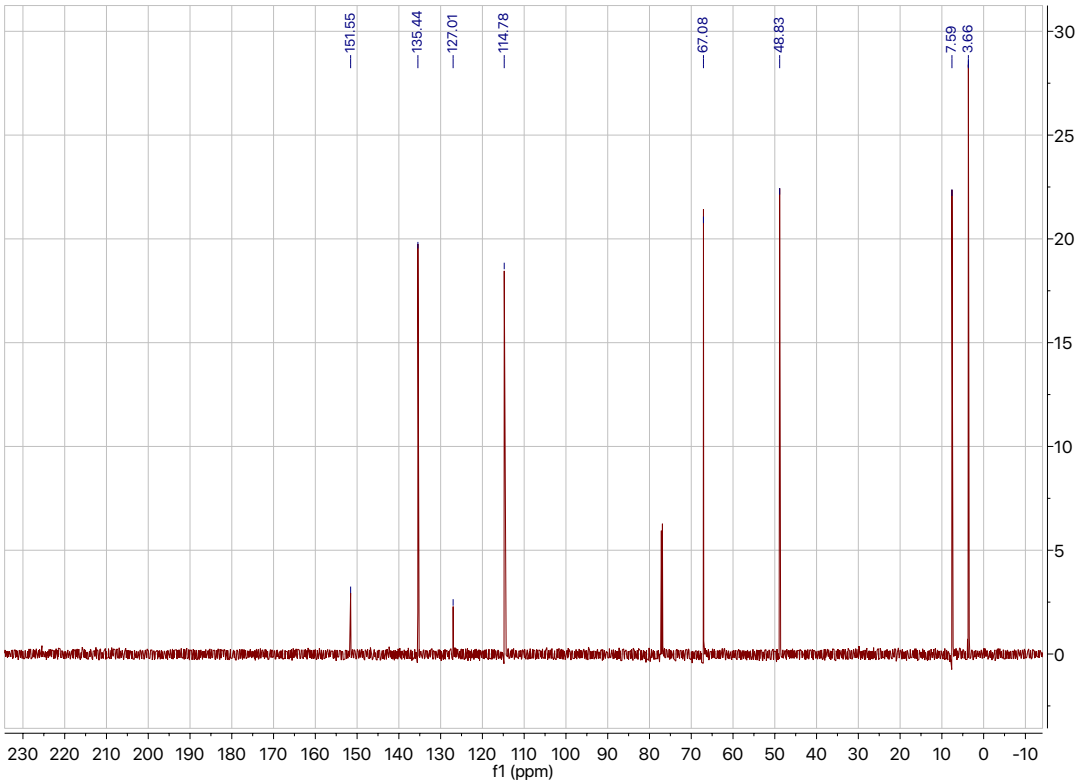
1.07
3.91
2.10
2.15
11.51
6.18
f1 (ppm)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67.08
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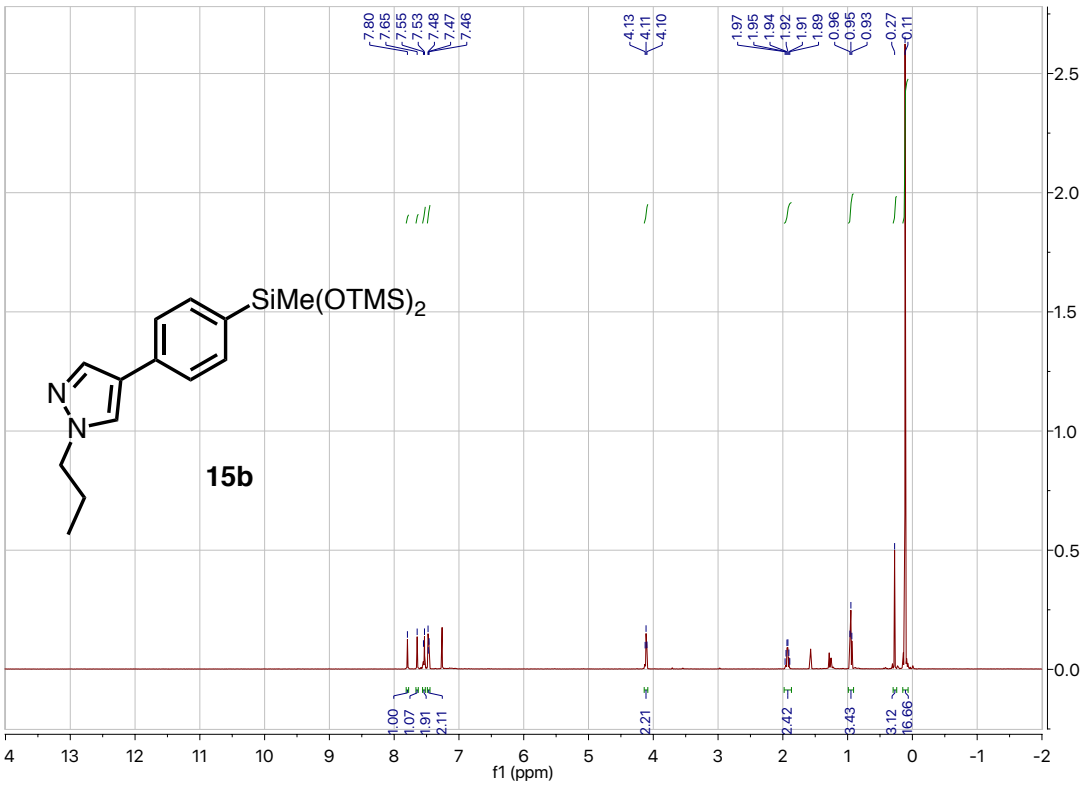
7.59
3.66
f1 (ppm)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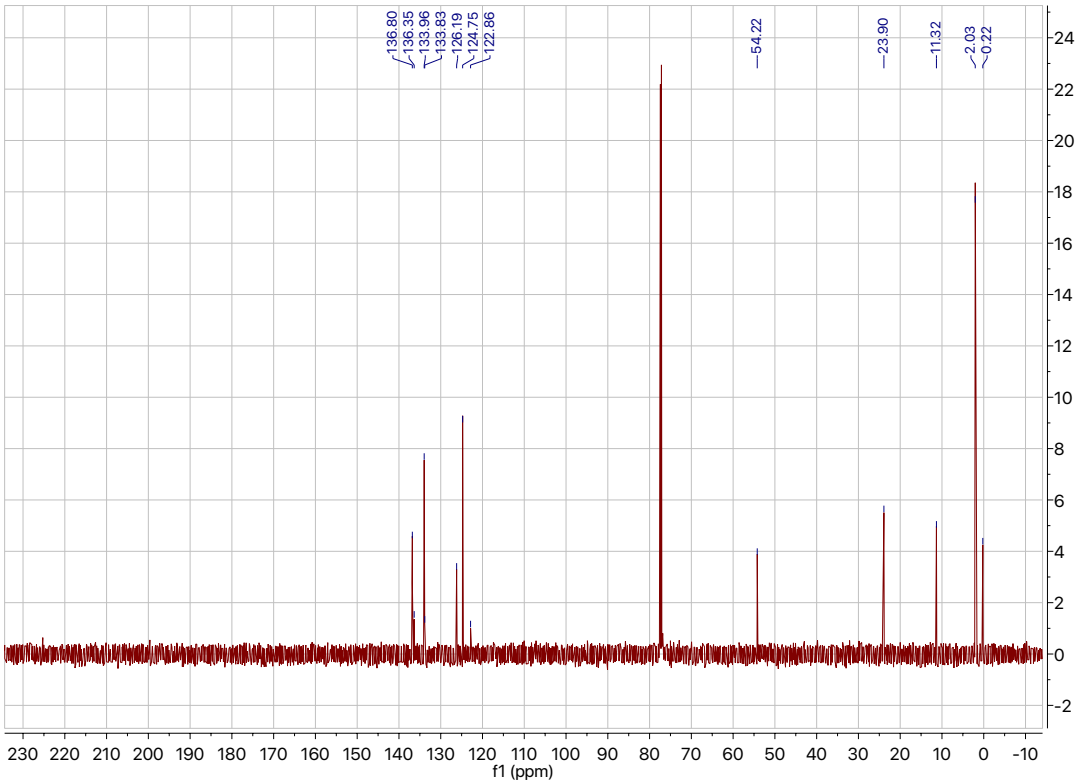
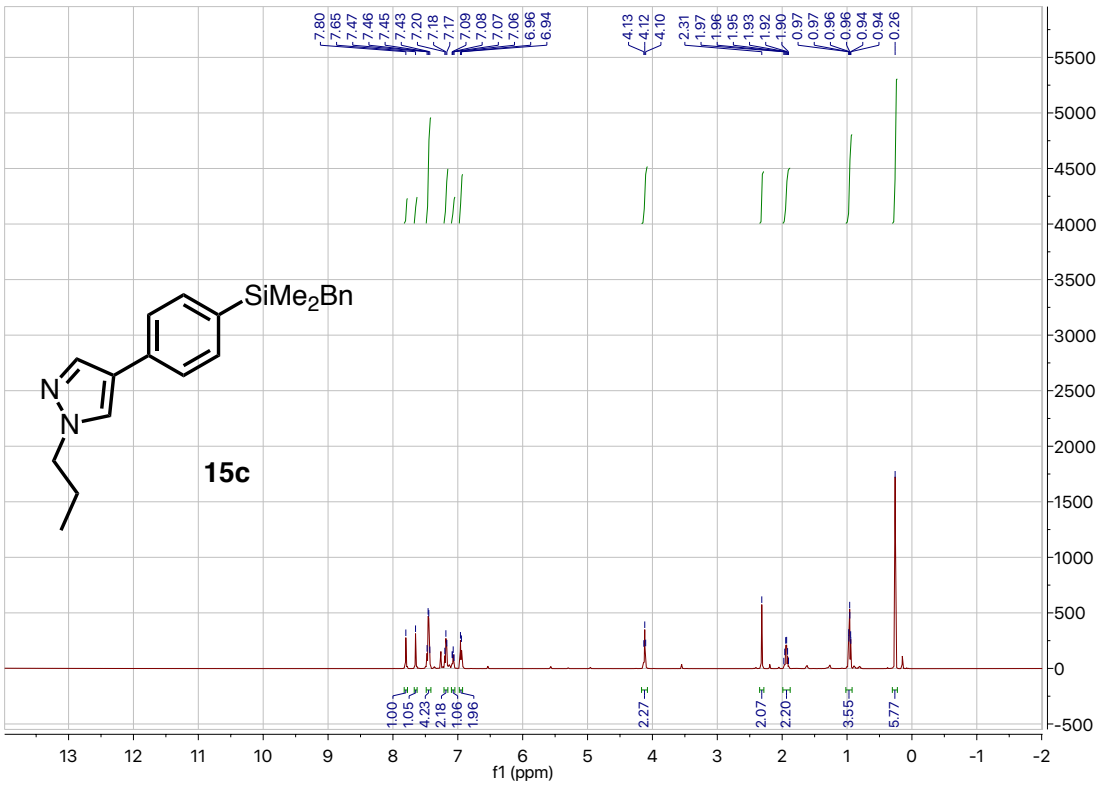
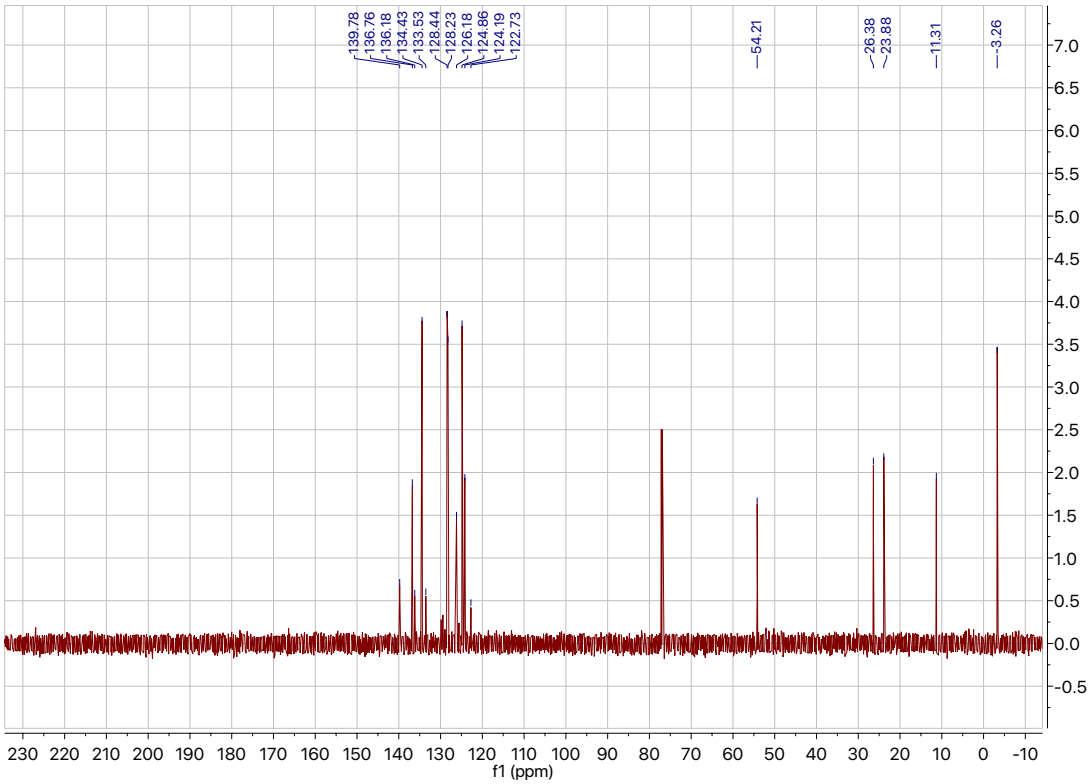
7.48
7.47
7.46
4.13
4.11
4.10
1.97
1.95
1.94
1.92
1.91
1.89
0.96
0.95
0.93
0.27
0.11
SiMe(OTMS)2
N
N
15b
1.00
1.07
1.91
2.11
2.21
2.42
3.43
3.12
16.86
f1 (ppm)


136.80
136.35
133.96
133.83
126.19
124.75
122.86
54.22
23.90
11.32
2.03
0.22
f1 (ppm)


7.80
7.65
7.47
7.46
7.45
7.43
7.20
7.18
7.17
7.09
7.08
7.07
7.06
6.96
6.94
4.13
4.12
4.10
2.31
1.97
1.96
1.95
1.93
1.92
1.90
0.97
0.97
0.96
0.96
0.94
0.94
0.26
SiMe2Bn
N
N
15c
1.00
1.05
4.23
2.18
1.06
1.96
2.27
2.07
2.20
3.55
5.77
f1 (ppm)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136.18
134.43
133.53
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128.23
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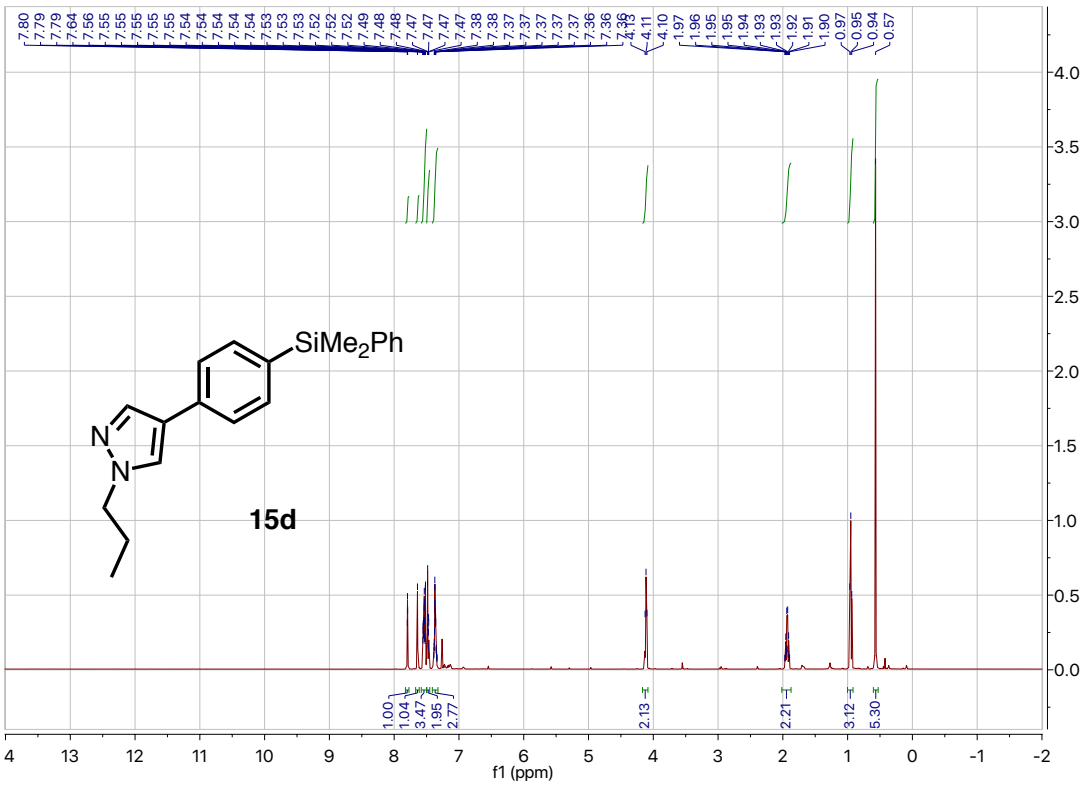
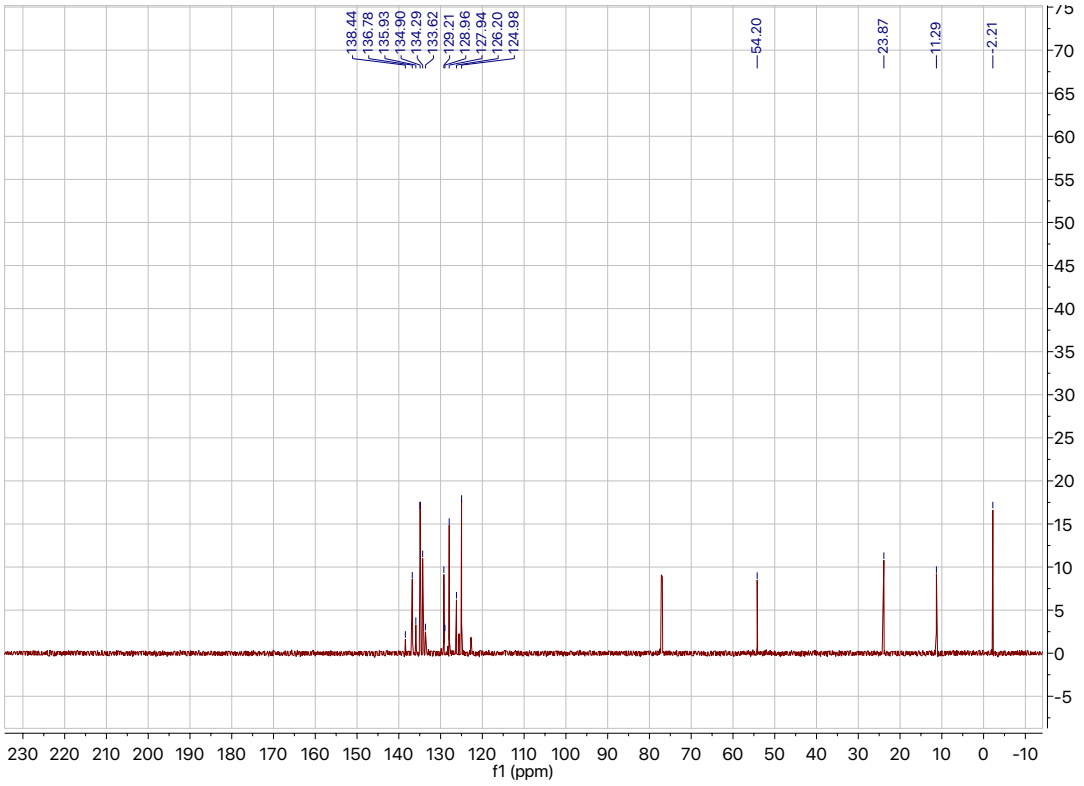
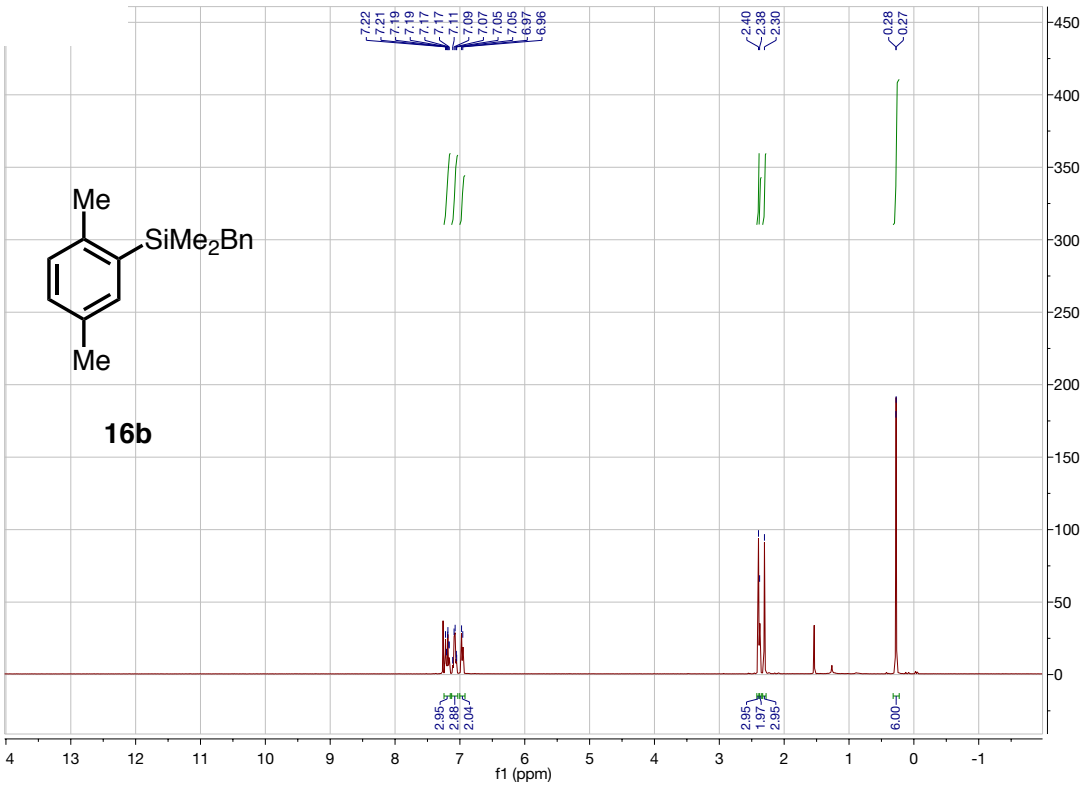
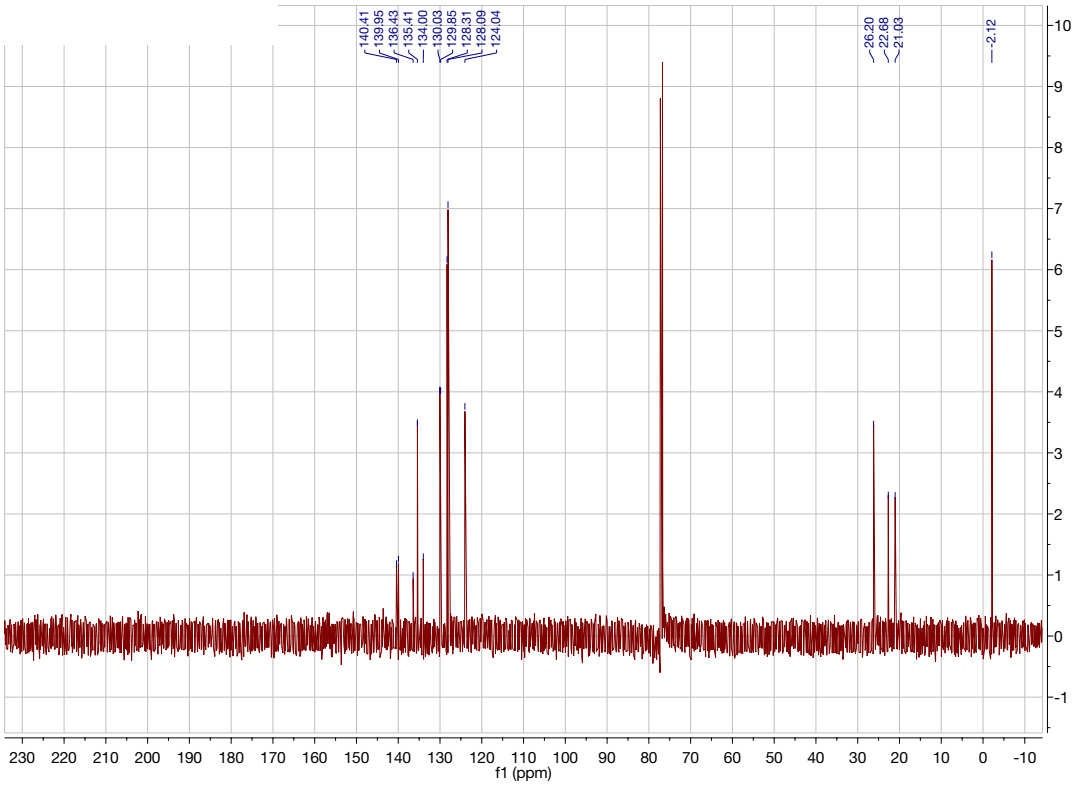
124.19
122.73
54.21
26.38
23.88
11.31
3.26
f1 (ppm)


SiMe2Ph
15d
f1 (ppm)


f1 (ppm)


Me
SiMe2Bn
Me
16b
f1 (ppm)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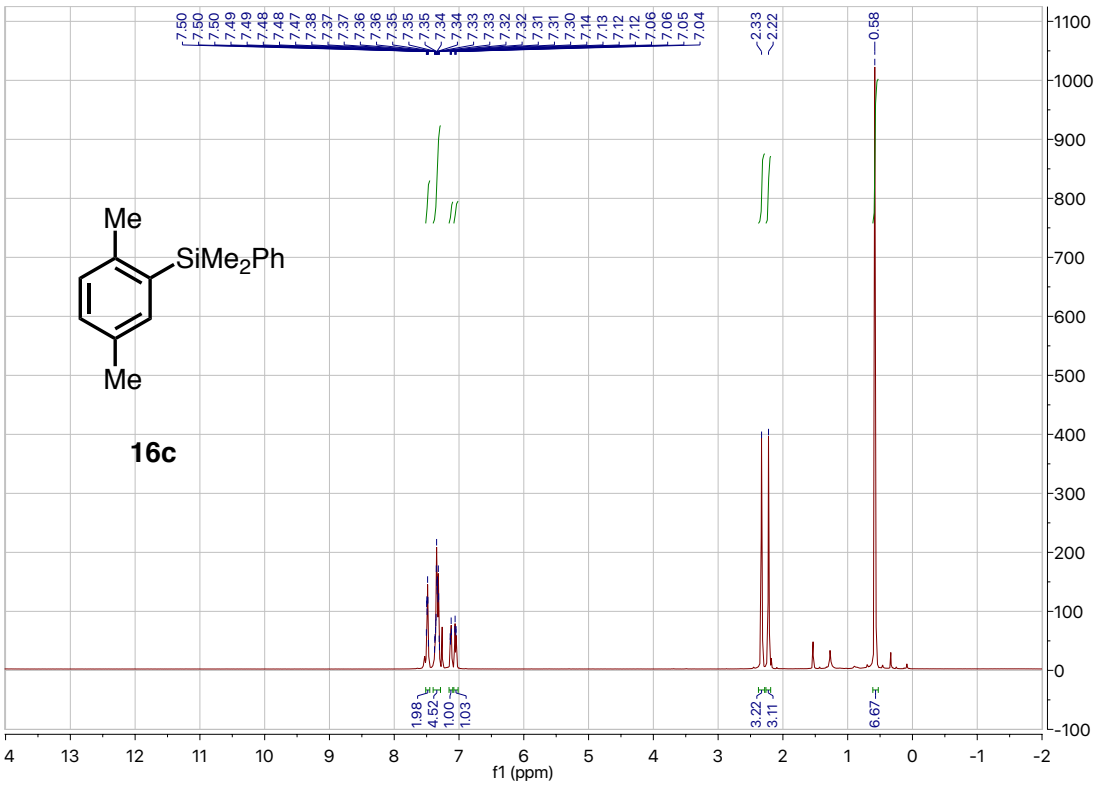
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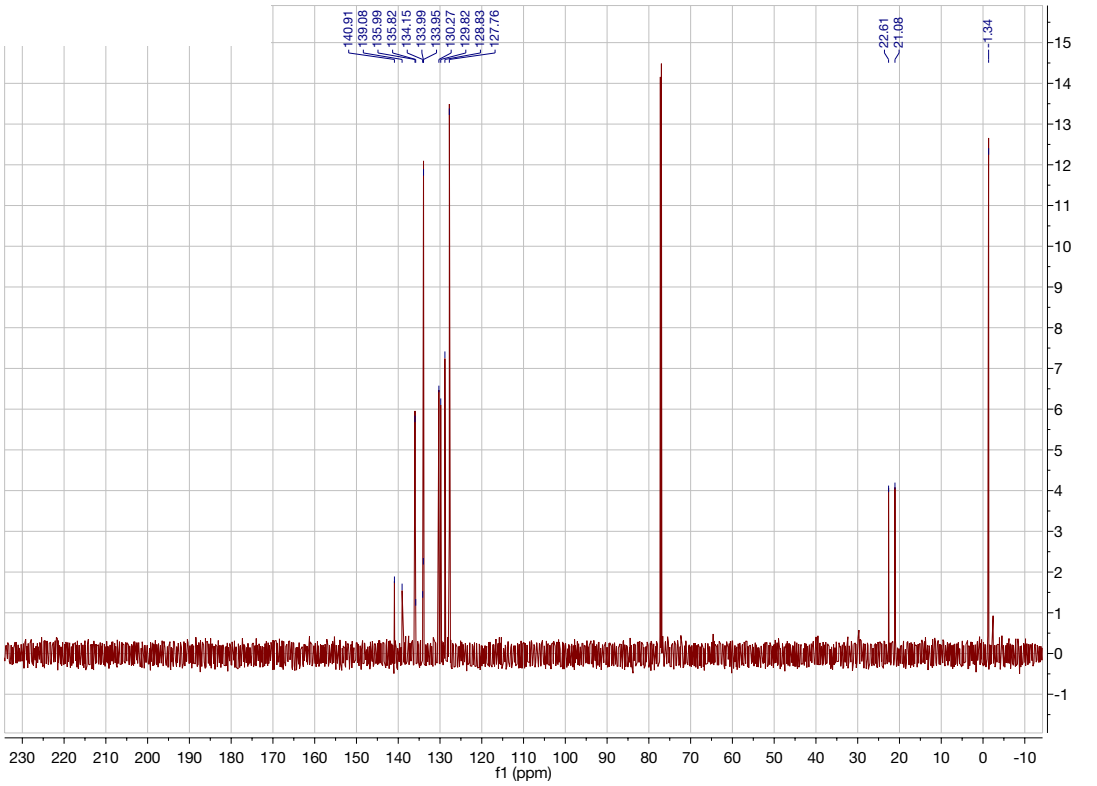
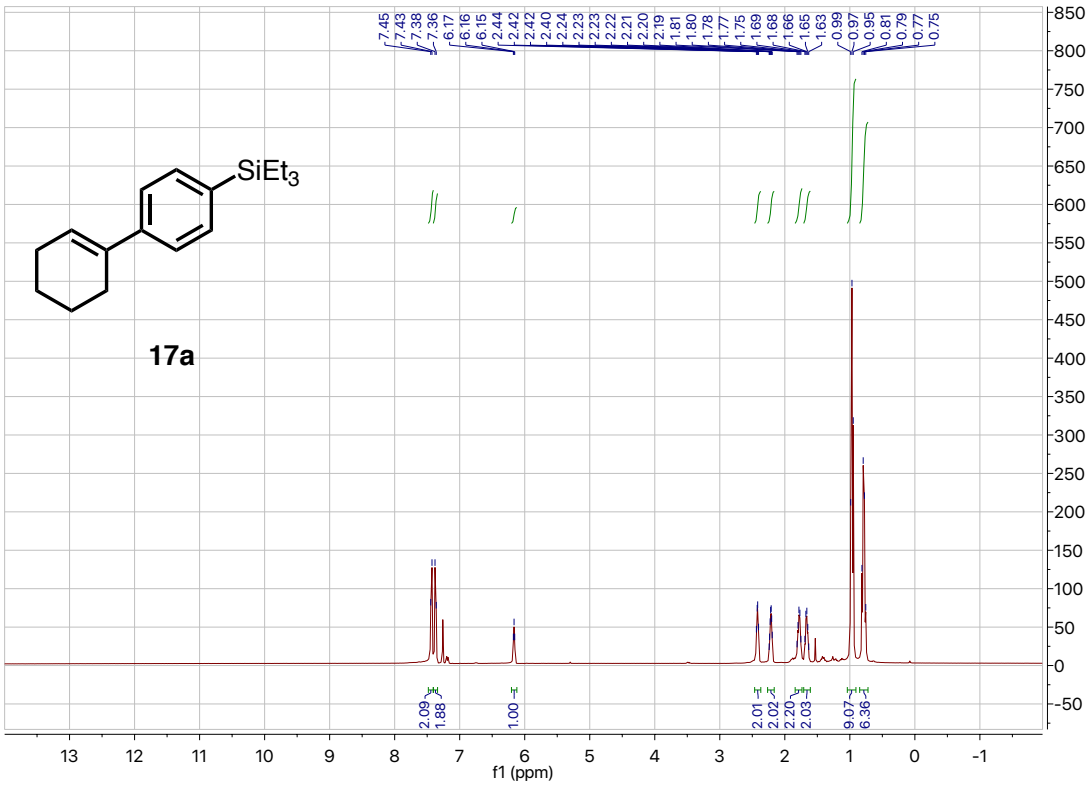
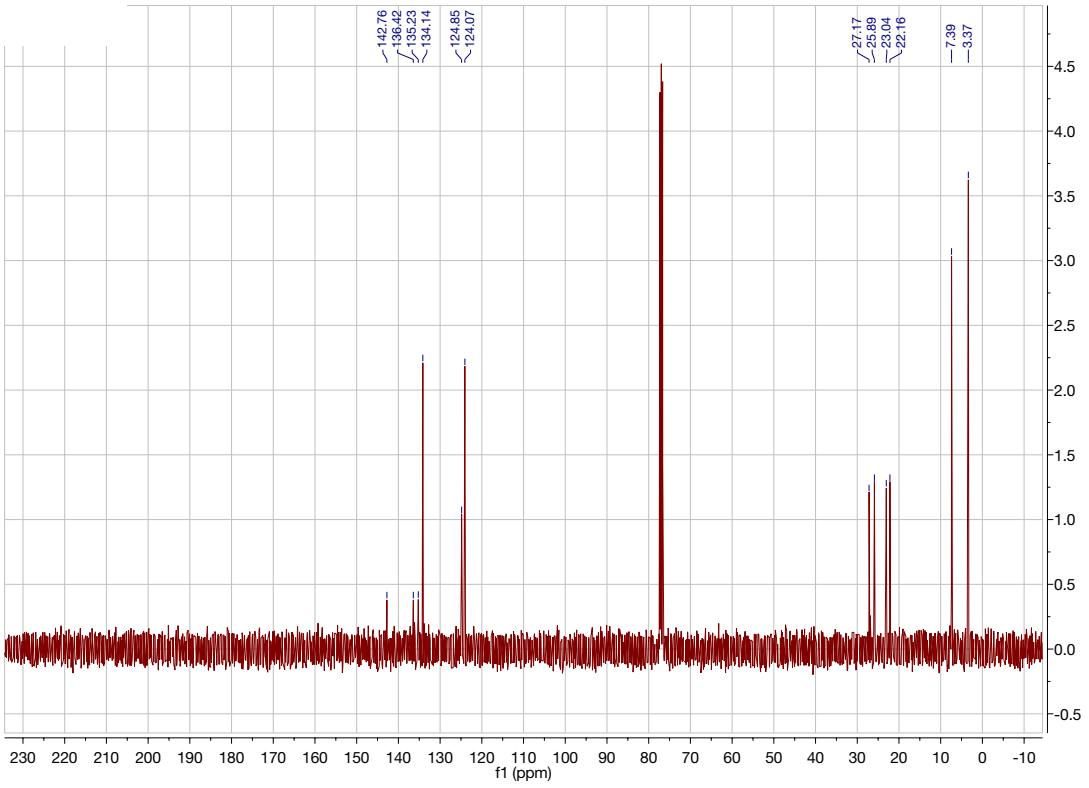
Me
16c
f1 (ppm)


f1 (ppm)


SiEt3
17a
f1 (ppm)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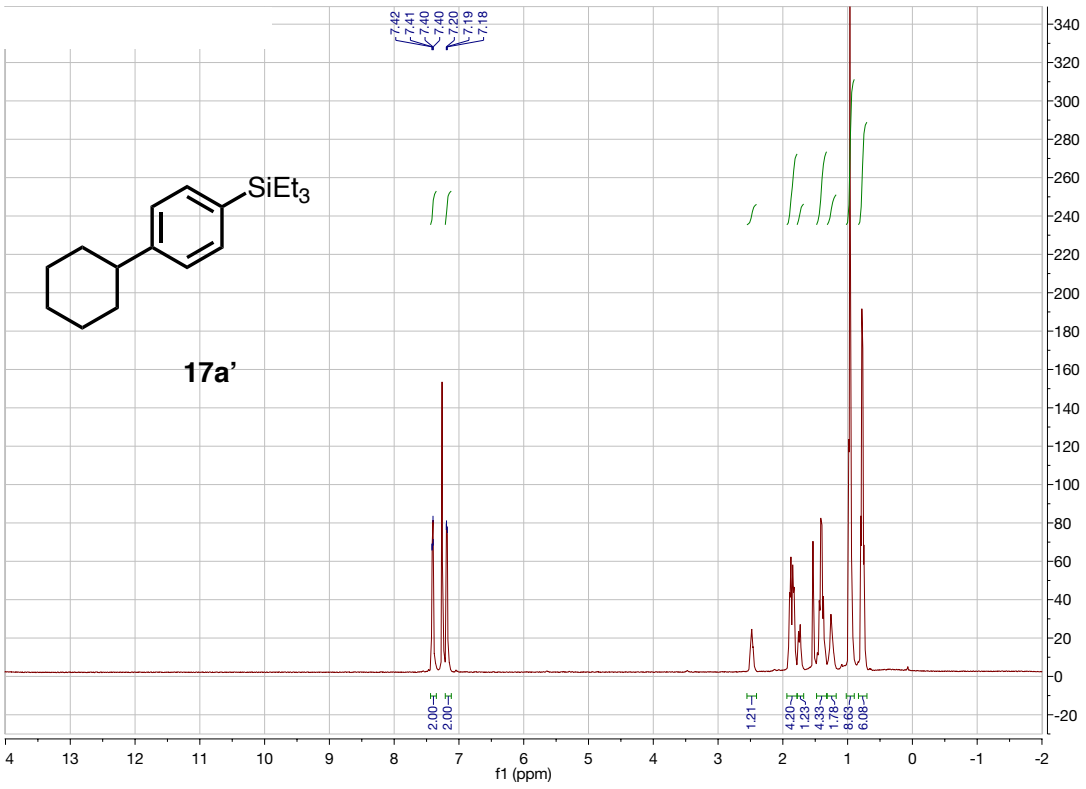
7.42
7.41
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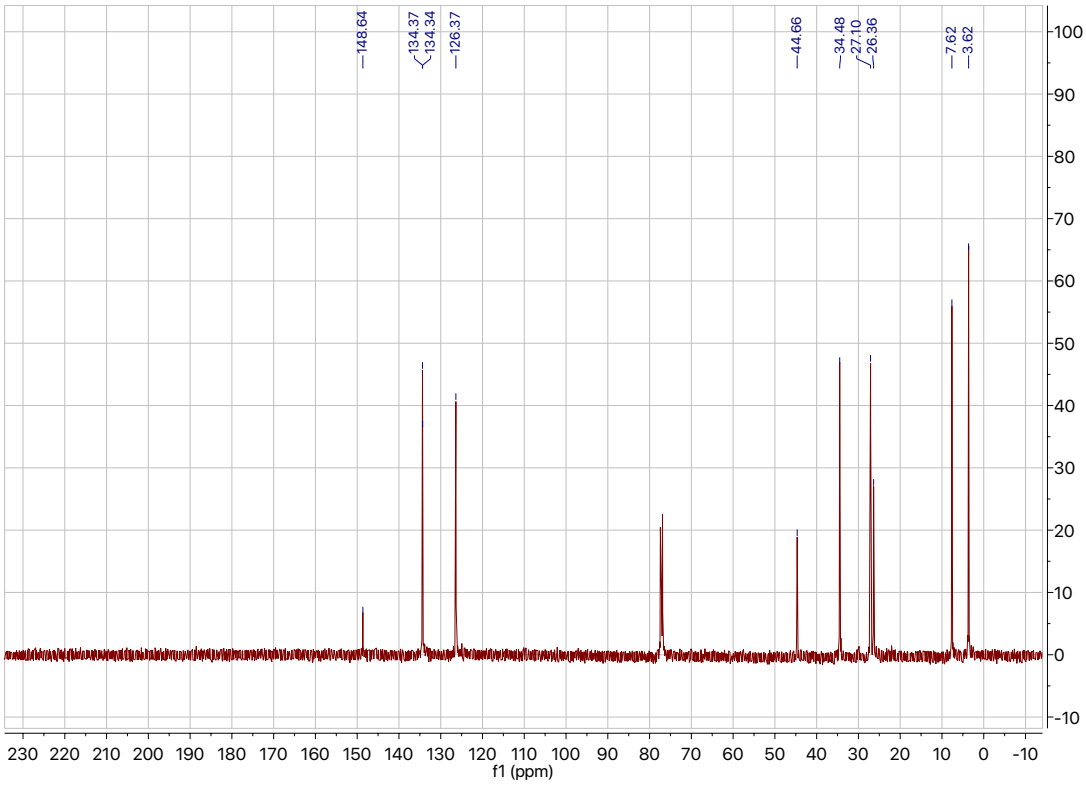
7.20
7.19
7.18
SiEt3
17a'
2.00
2.00
1.21
4.20
1.23
4.33
1.78
8.63
6.08
f1 (ppm)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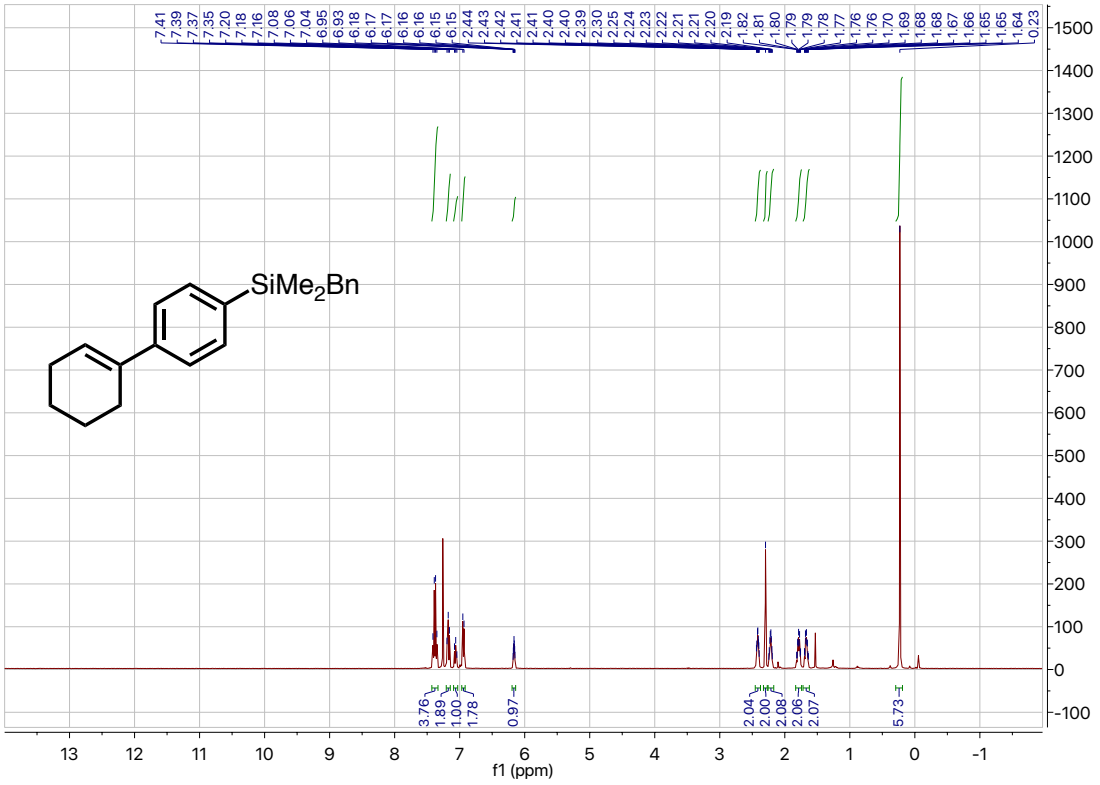
134.34
126.37
44.66
34.48
27.10
26.36
7.62
3.62
f1 (ppm)


SiMe2Bn
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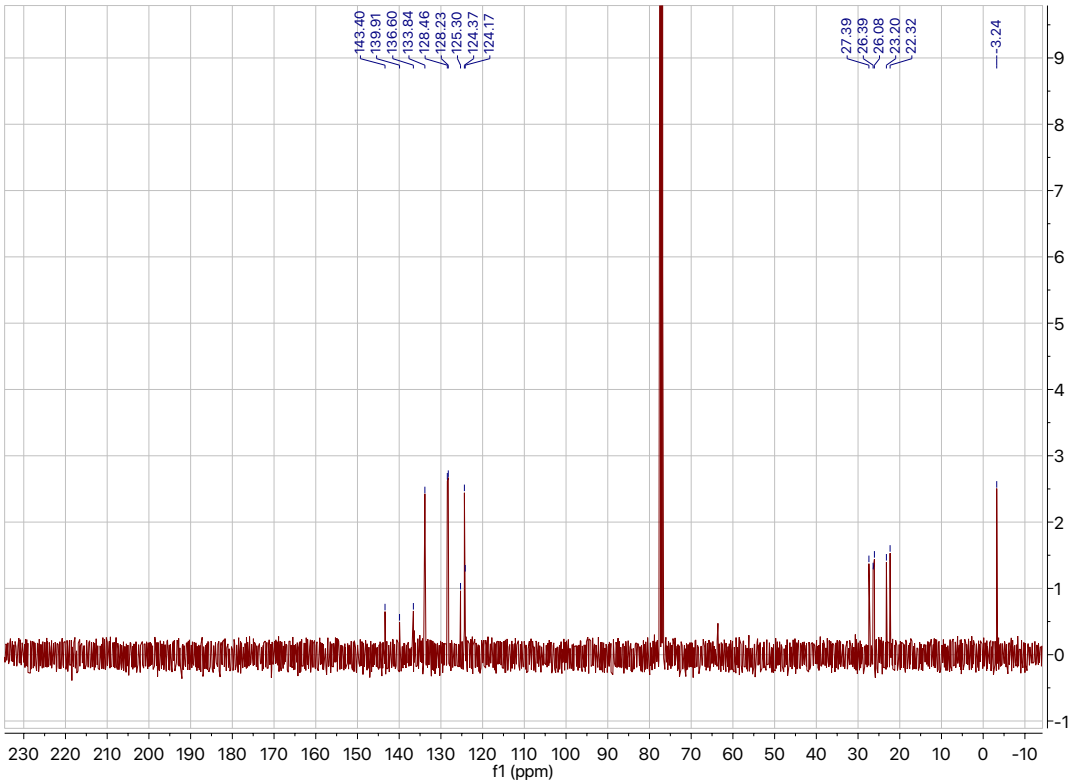
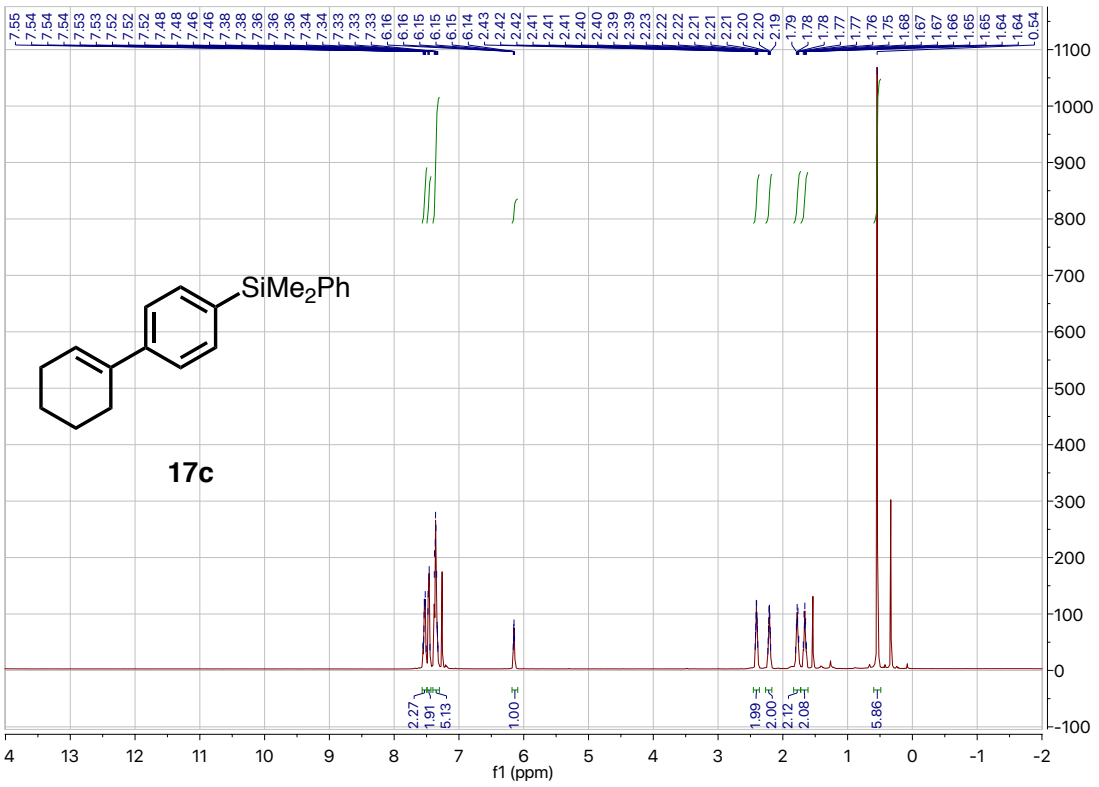
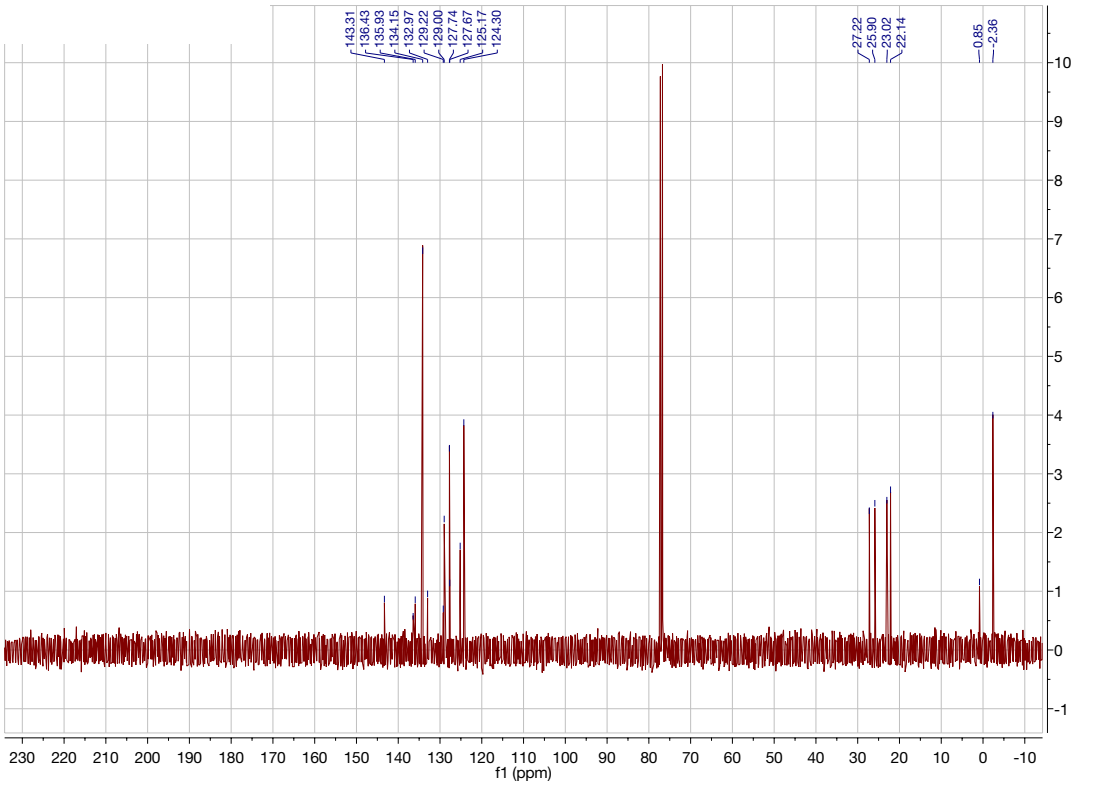
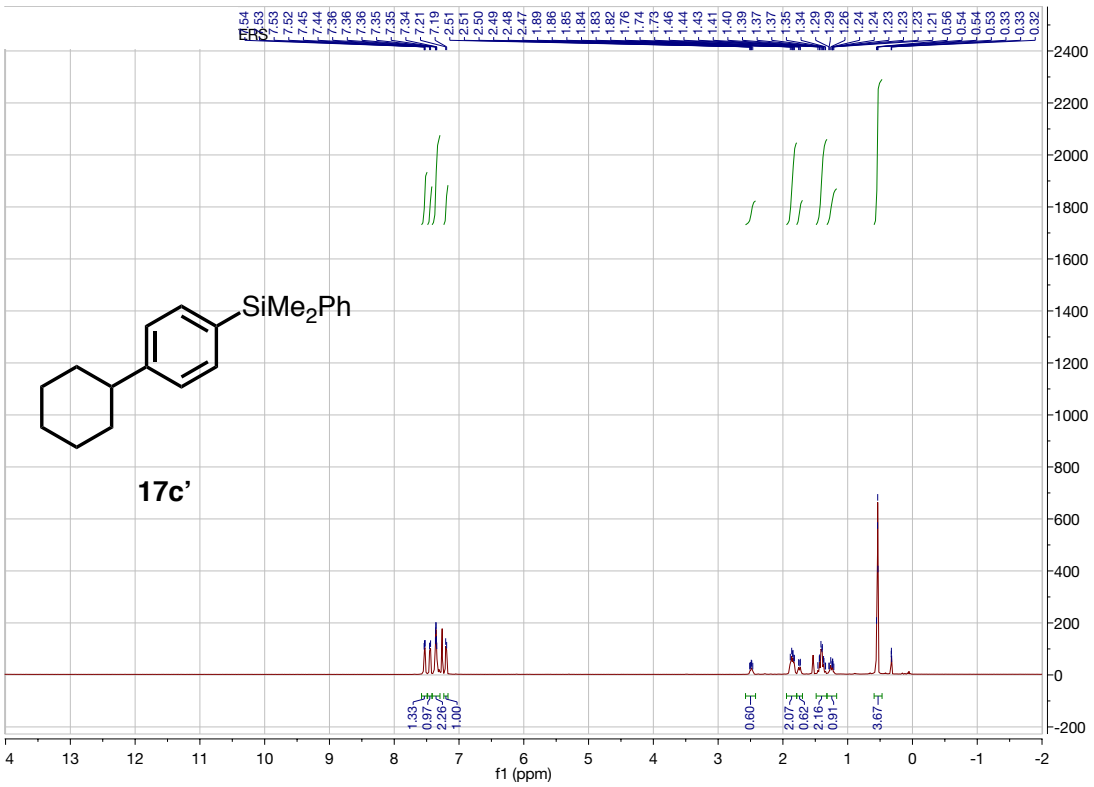
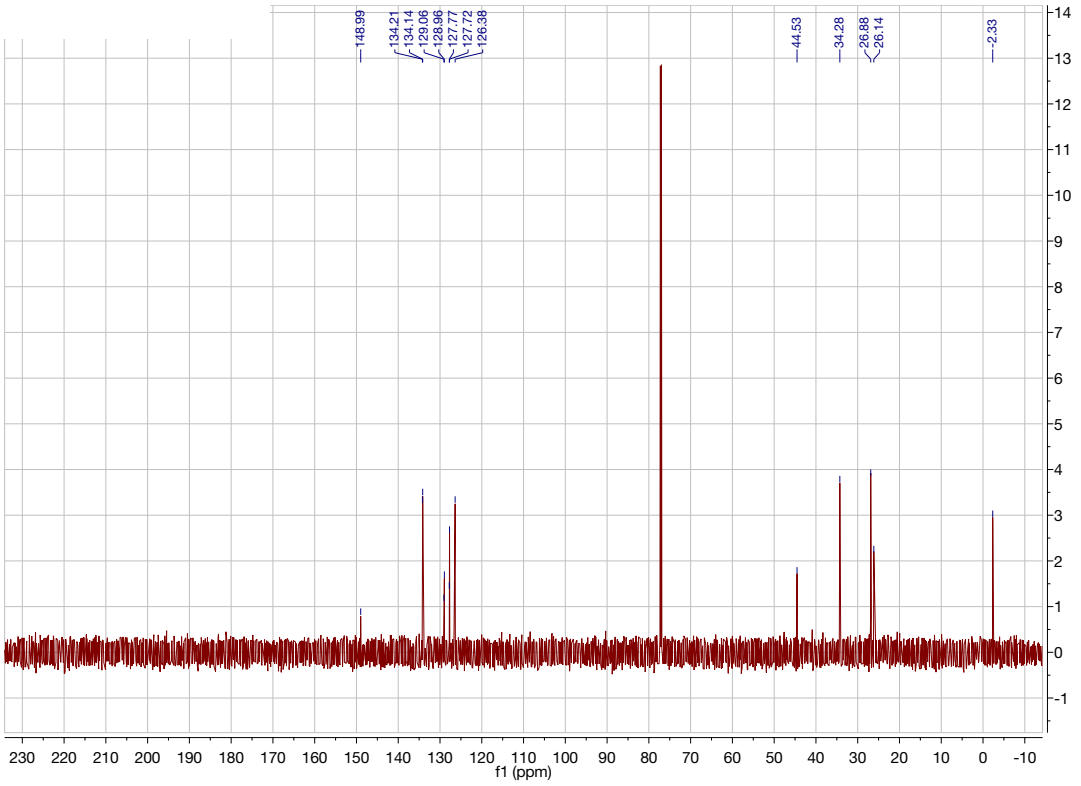

f1 (ppm)


SiMe2Ph
17c
f1 (ppm)


f1 (ppm)


SiMe2Ph
17c'
f1 (ppm)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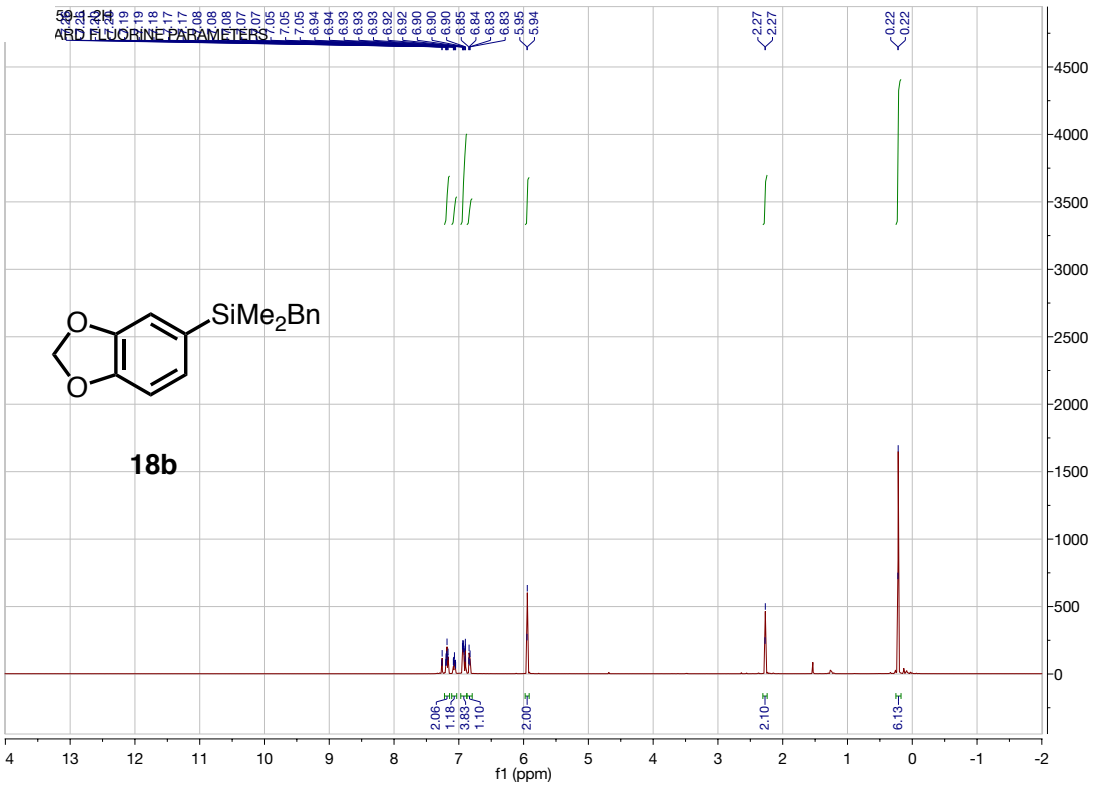
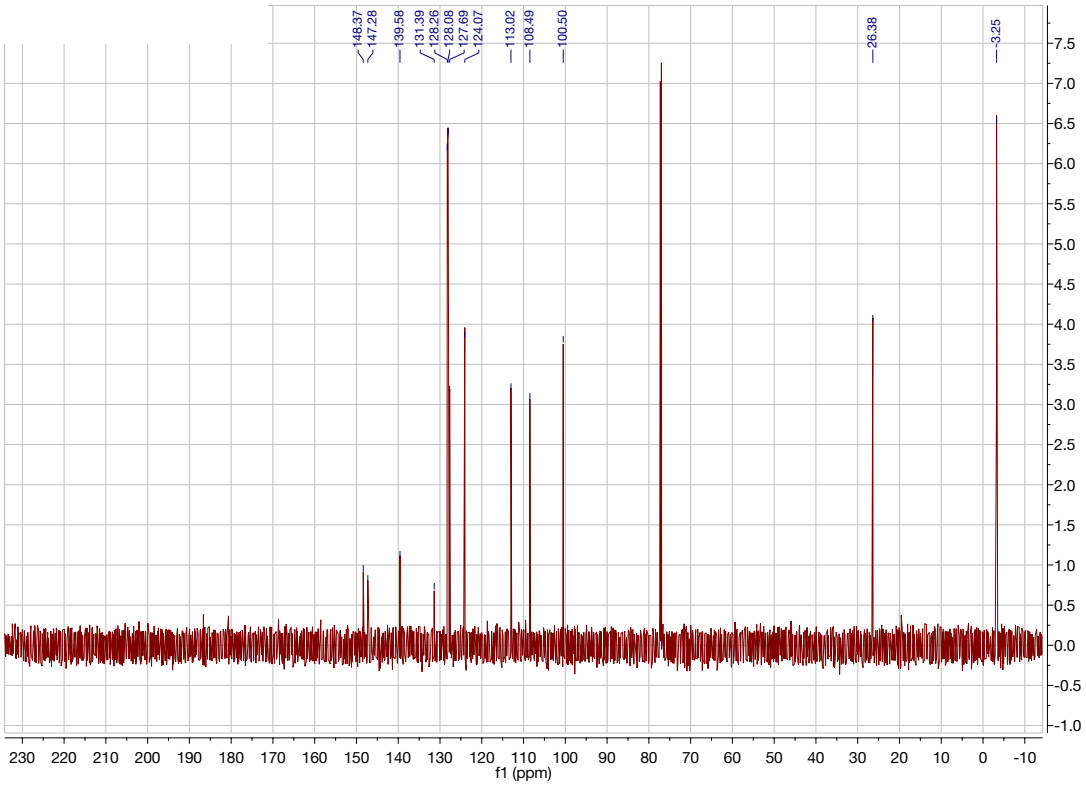

ARD FLUORINE PARAMETERS
SiMe2Bn
18b
f1 (ppm)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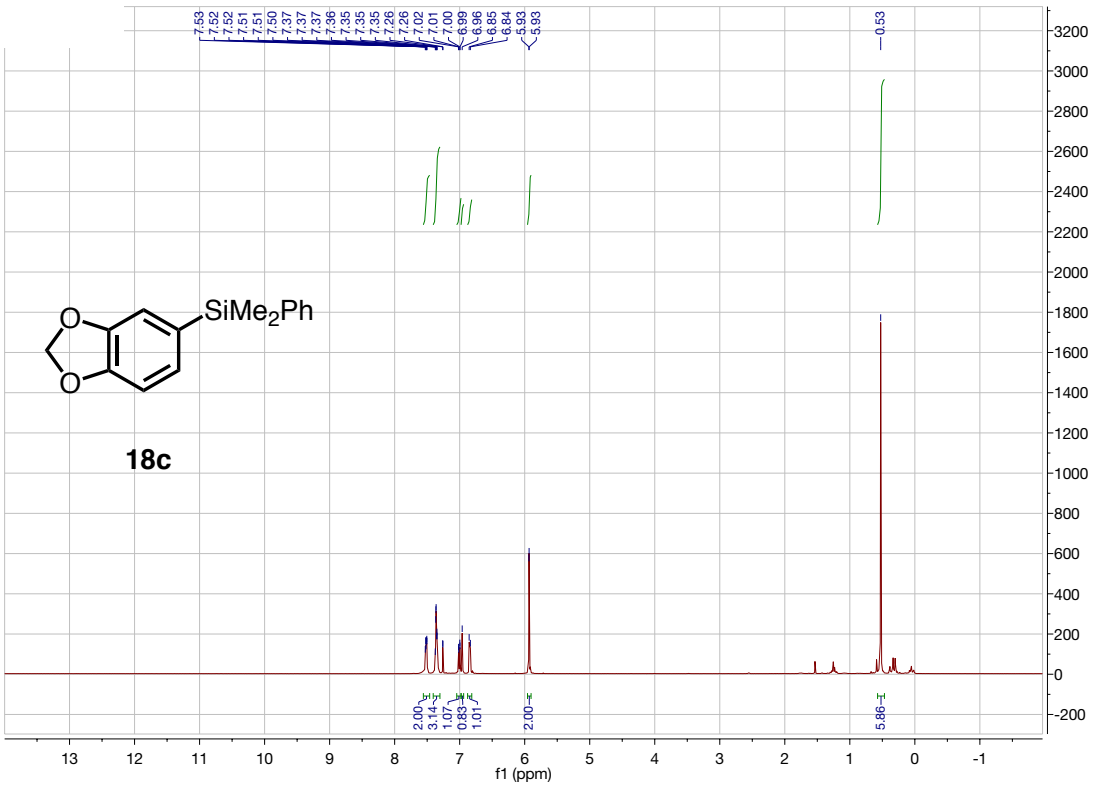
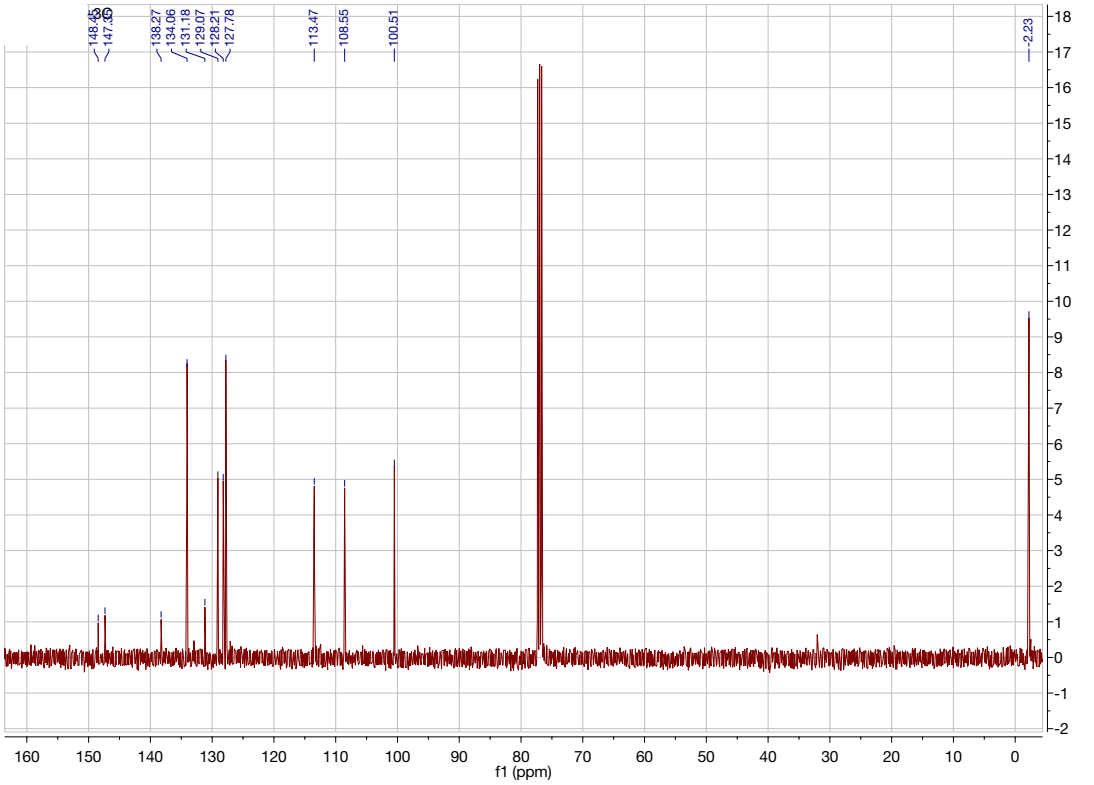

SiMe2Ph
18c
f1 (ppm)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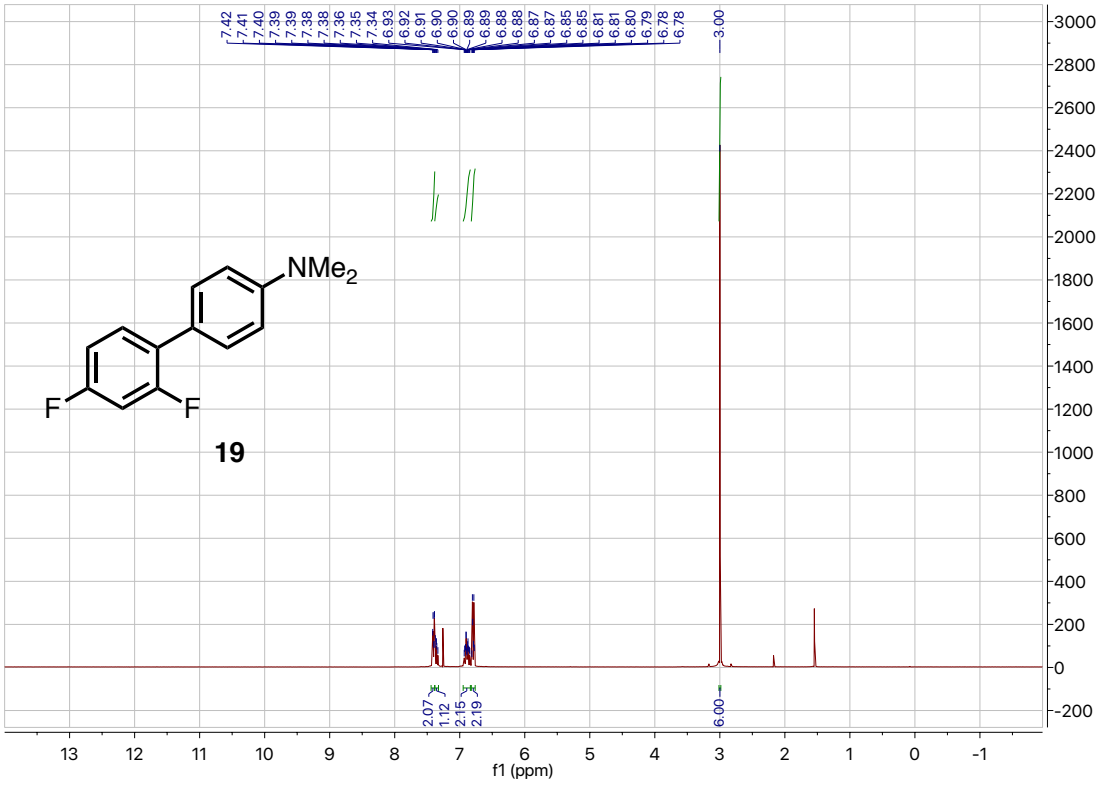
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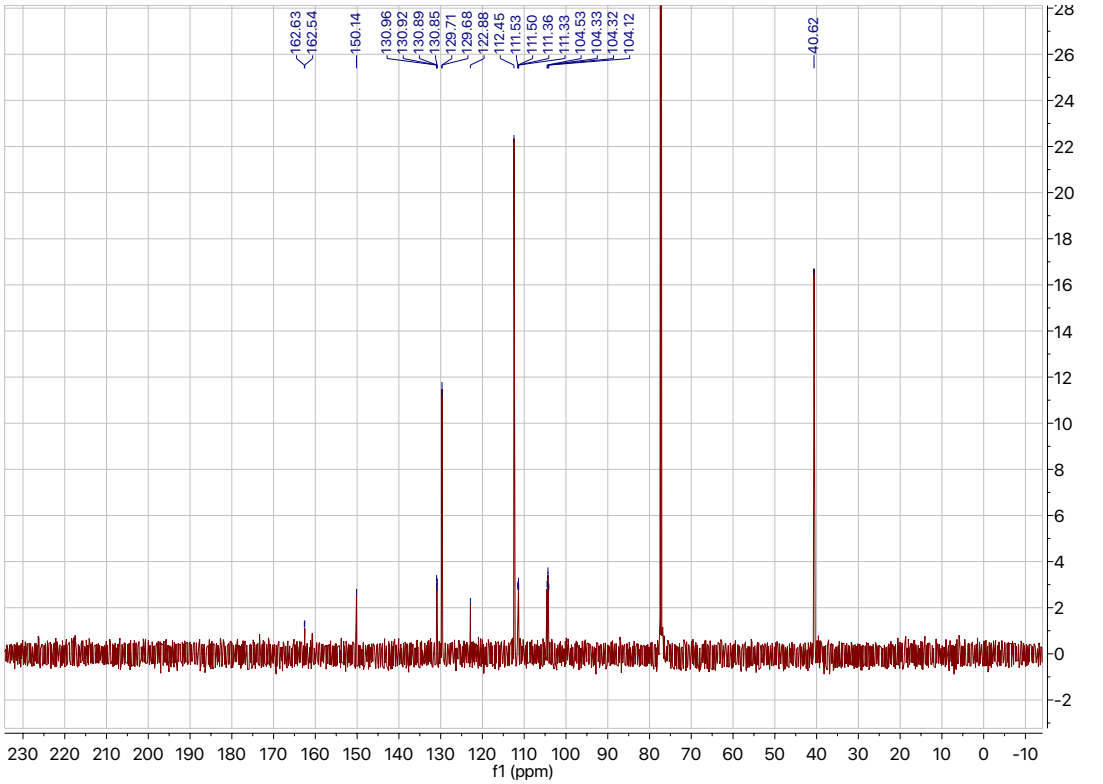
7.38
7.36
7.35
7.34
6.93
6.92
6.91
6.90
6.90
6.89
6.89
6.88
6.88
6.87
6.87
6.85
6.85
6.81
6.81
6.80
6.79
6.78
6.78
3.00
NMe2
F
F
19
2.07
1.12
2.15
2.19
6.00
f1 (ppm)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130.92
130.89
130.85
129.71
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112.45
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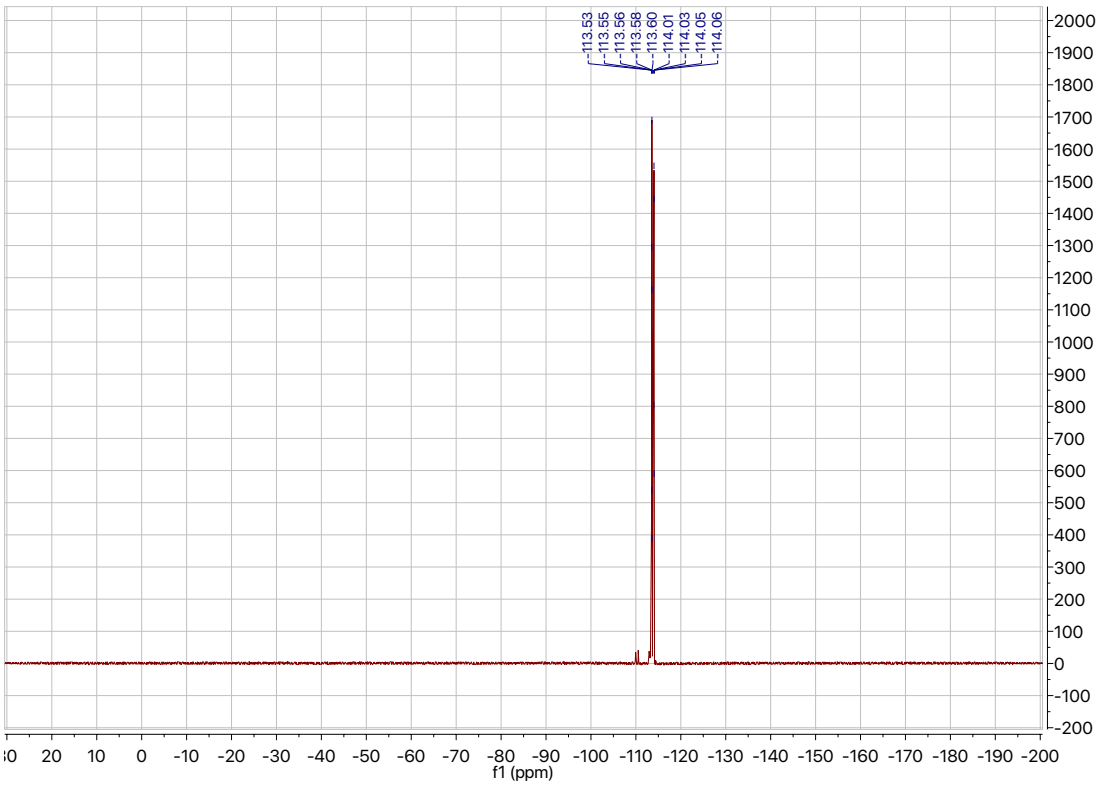
111.50
111.36
111.33
104.53
104.33
104.32
104.12
40.62
f1 (ppm)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-113.56
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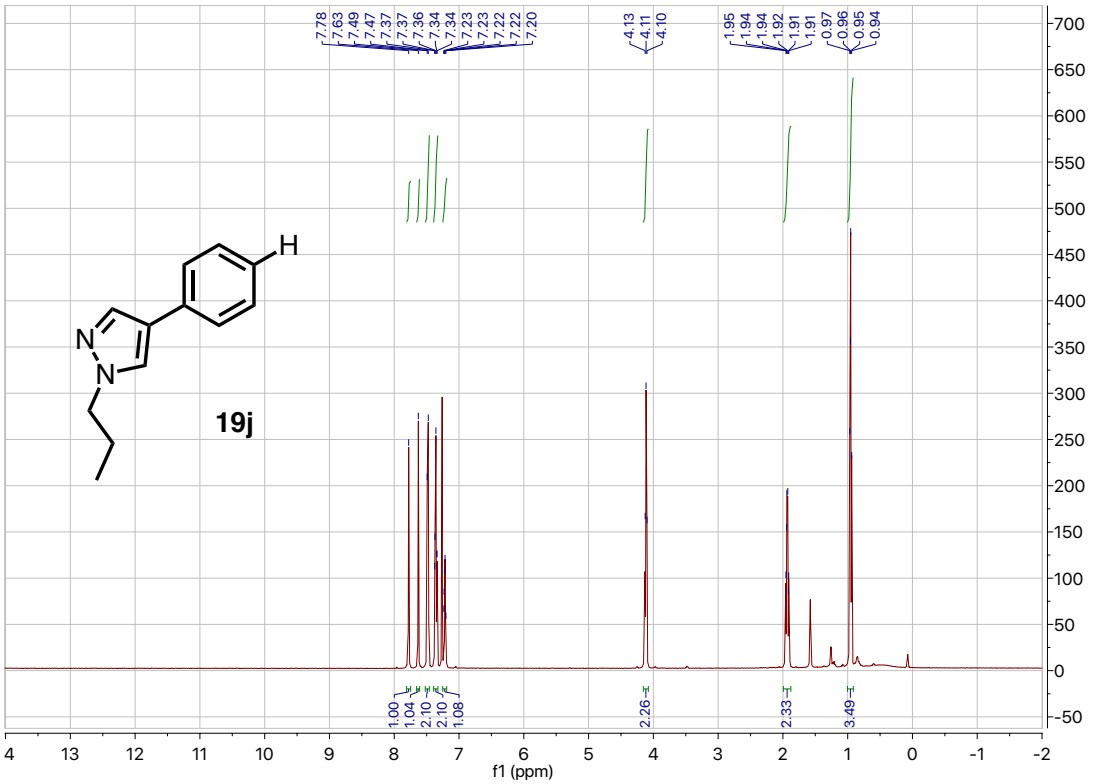
-114.01
-114.03
-114.05
-114.06
f1 (ppm)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7.23
7.23
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7.22
7.20
4.13
4.11
4.10
1.95
1.94
1.94
1.92
1.91
1.91
0.97
0.96
0.95
0.94
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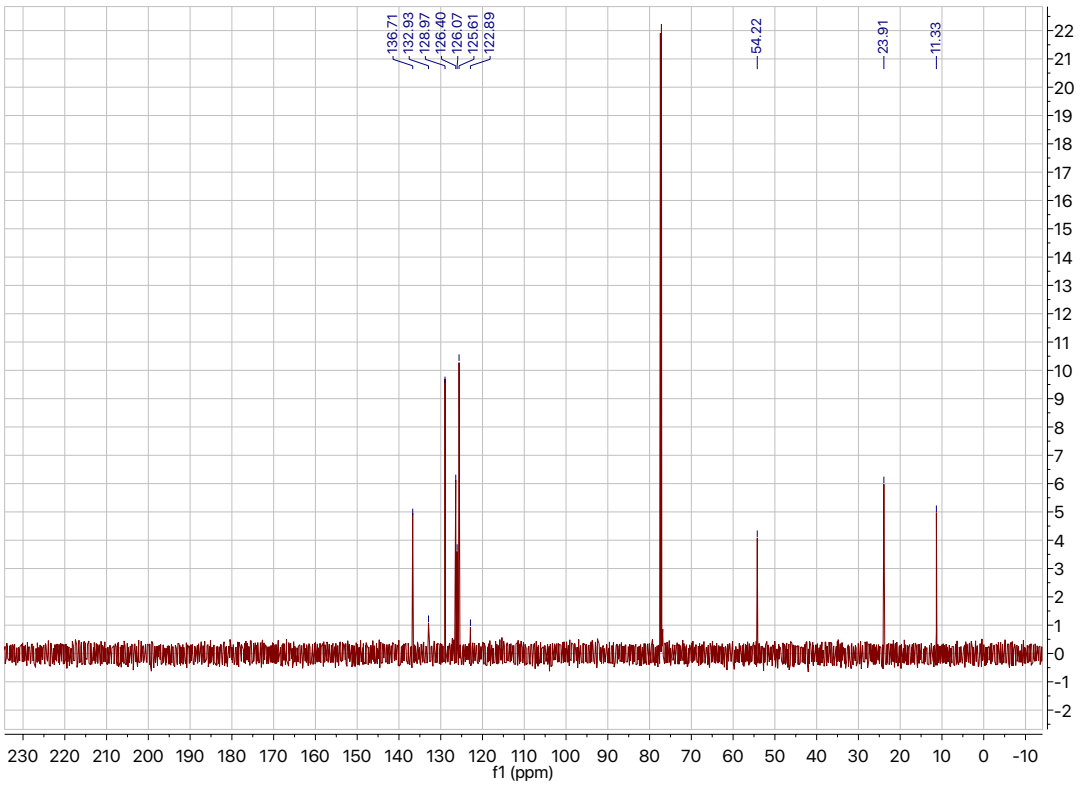
1.04
2.10
2.10
1.08
2.26
2.33
3.49
N
N
H
19j
f1 (ppm)


136.71
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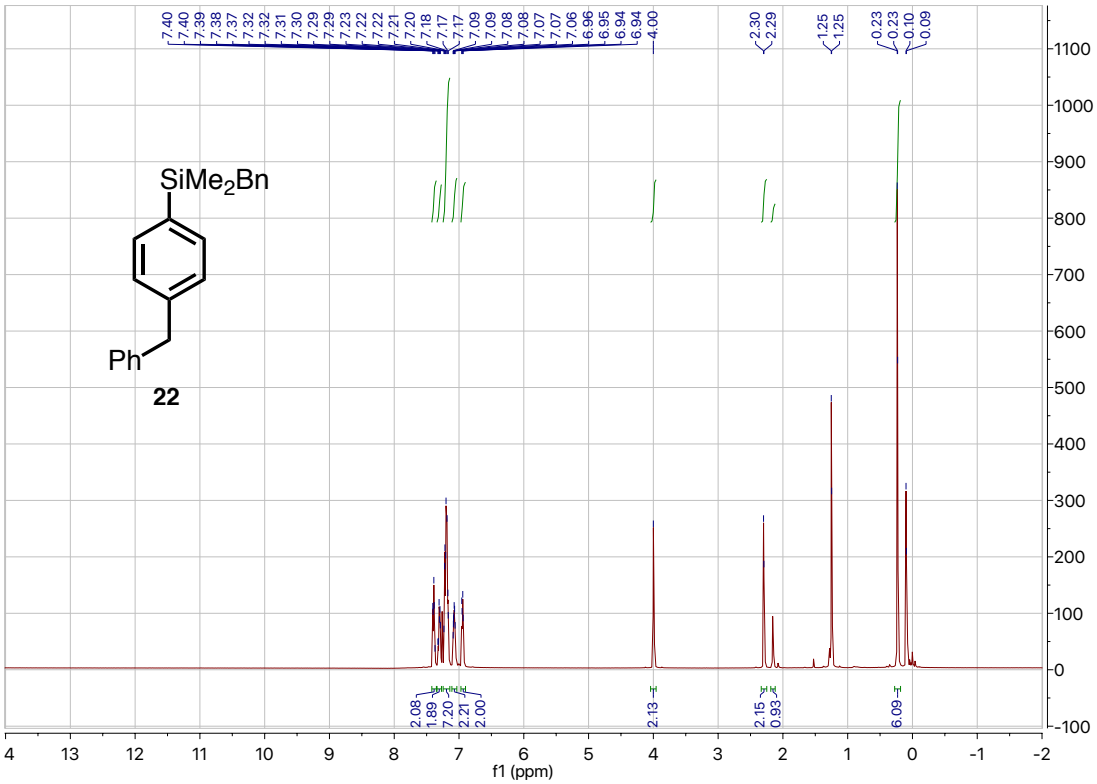
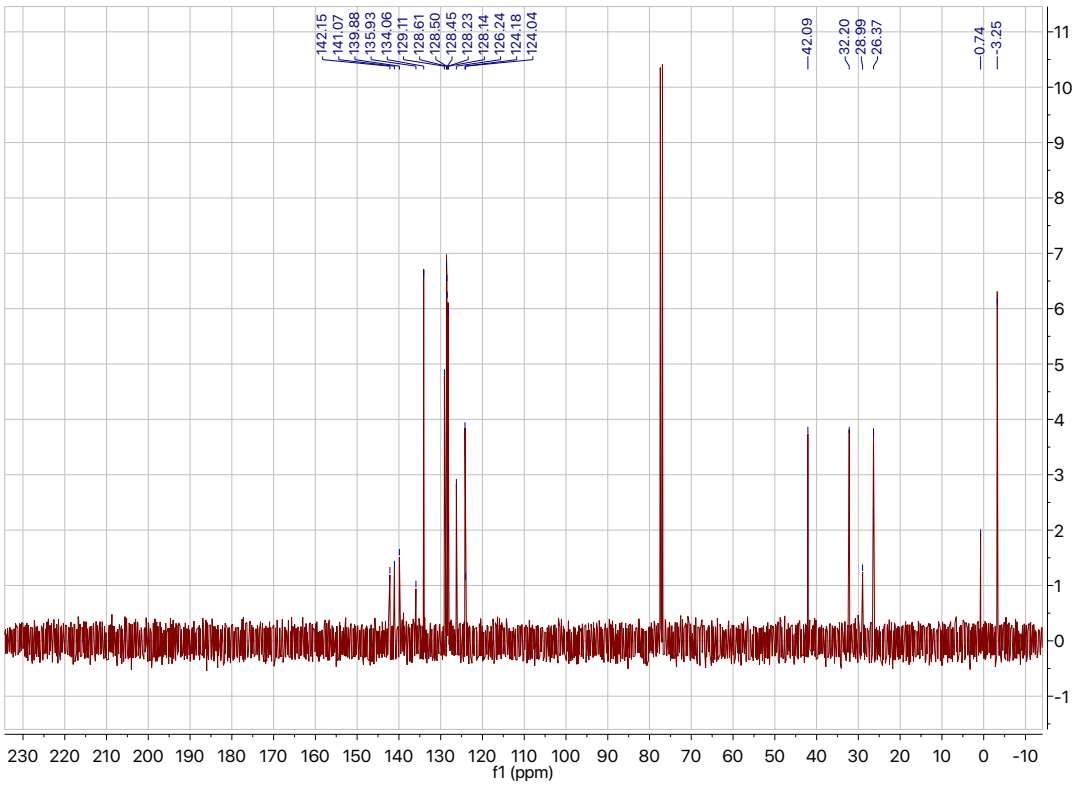
128.97
126.40
126.07
125.61
122.89
54.22
23.91
11.33
f1 (ppm)


SiMe2Bn
Ph
22
f1 (ppm)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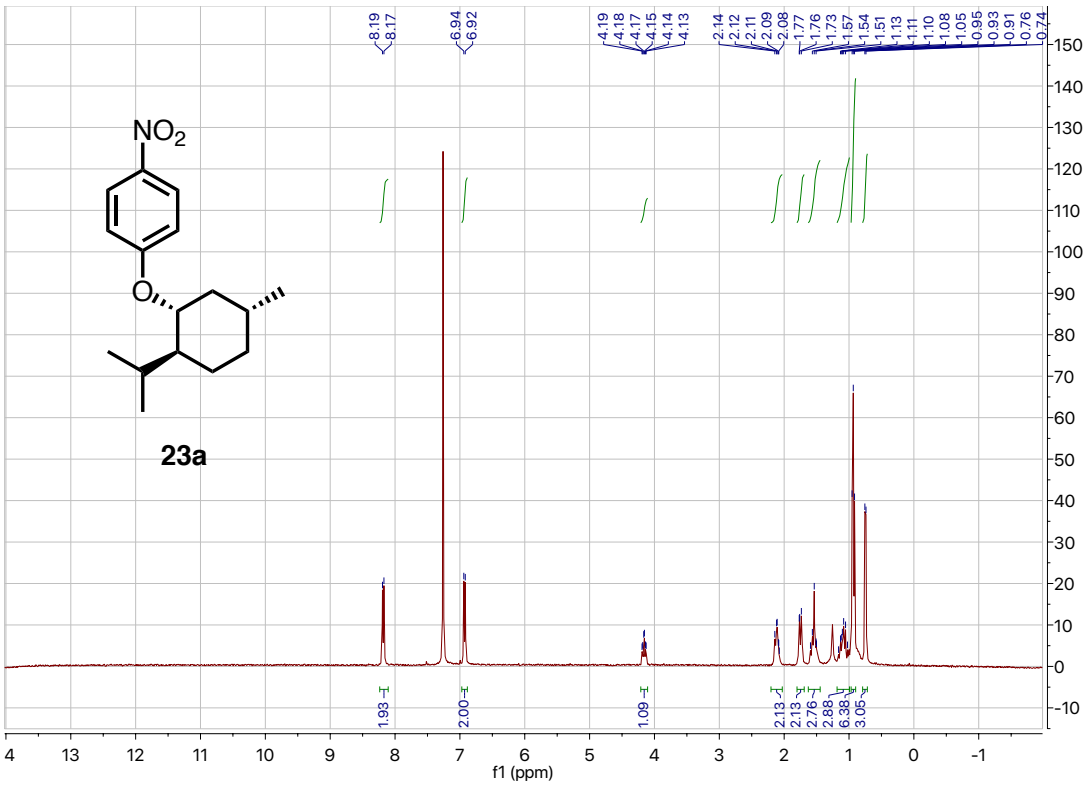
141.07
139.88
135.93
134.06
129.11
128.61
128.50
128.45
128.23
128.14
126.24
124.18
124.04
42.09
32.20
28.99
26.37
0.74
-3.25
f1 (ppm)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4.19
4.18
4.17
4.15
4.14
4.13
2.14
2.12
2.11
2.09
2.08
1.77
1.76
1.73
1.57
1.54
1.51
1.13
1.11
1.10
1.08
1.05
0.95
0.93
0.91
0.76
0.74
NO2
O
23a
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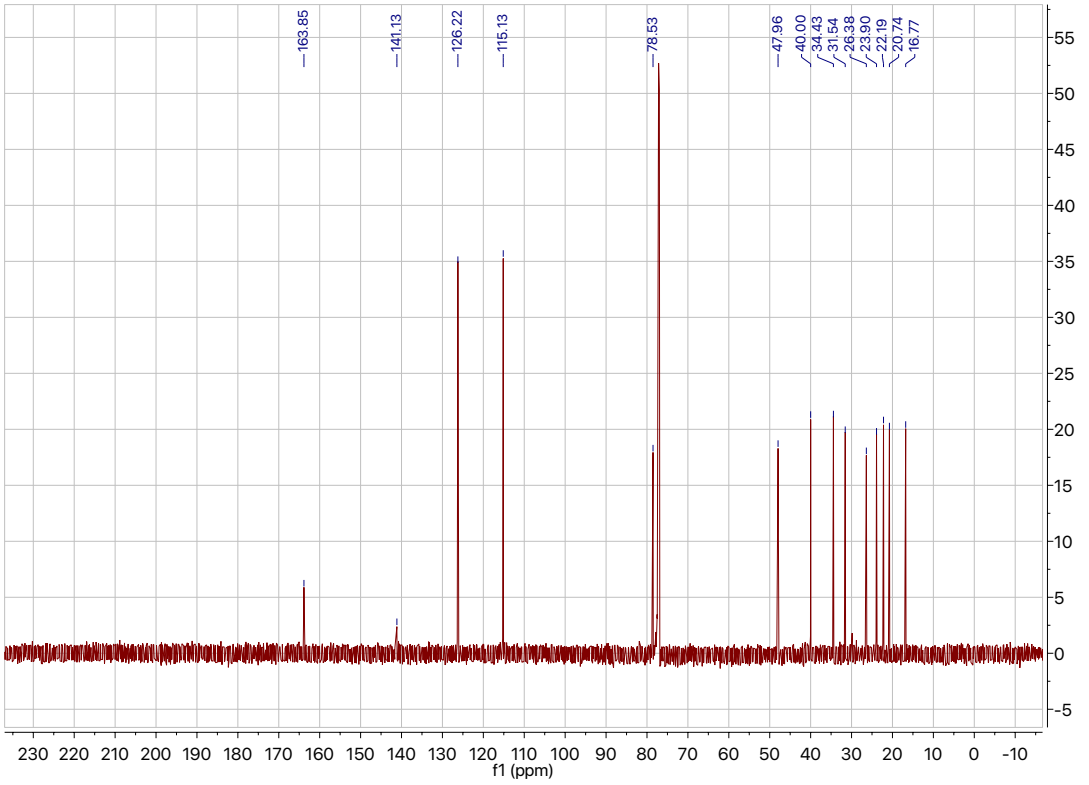
2.00
1.09
2.13
2.13
2.76
2.88
6.38
3.05
f1 (ppm)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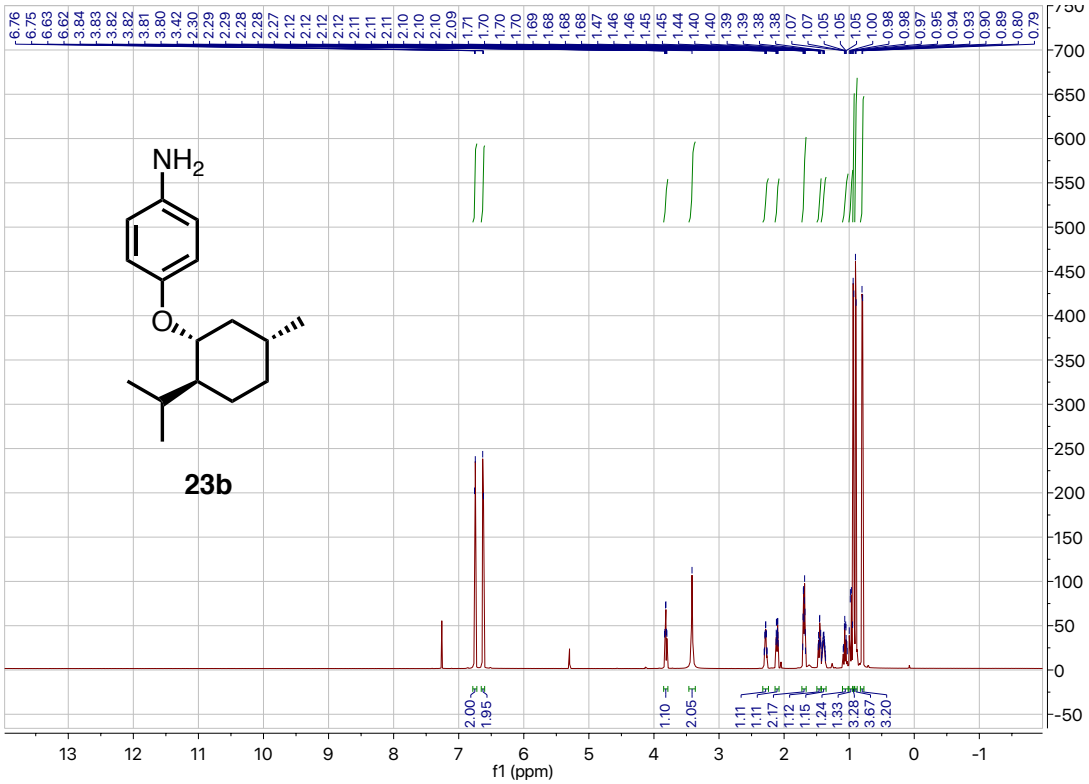
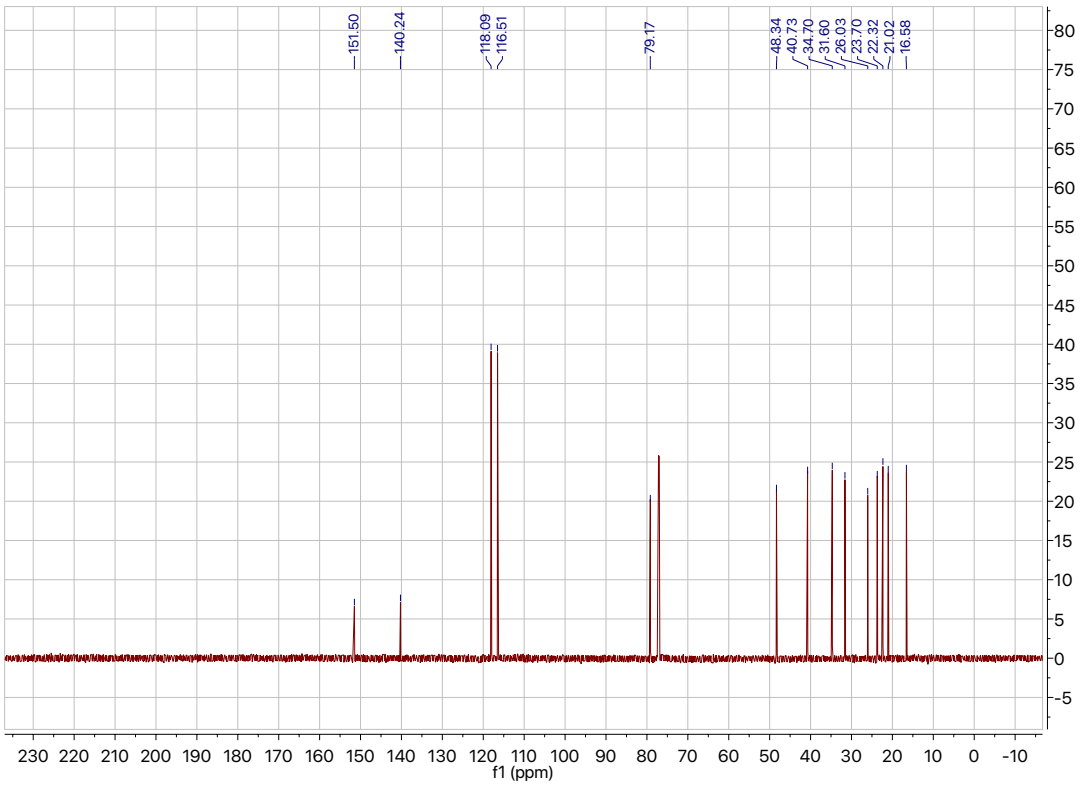
34.43
31.54
26.38
23.90
22.19
20.74
16.77
f1 (ppm)


NH2
O
23b
f1 (ppm)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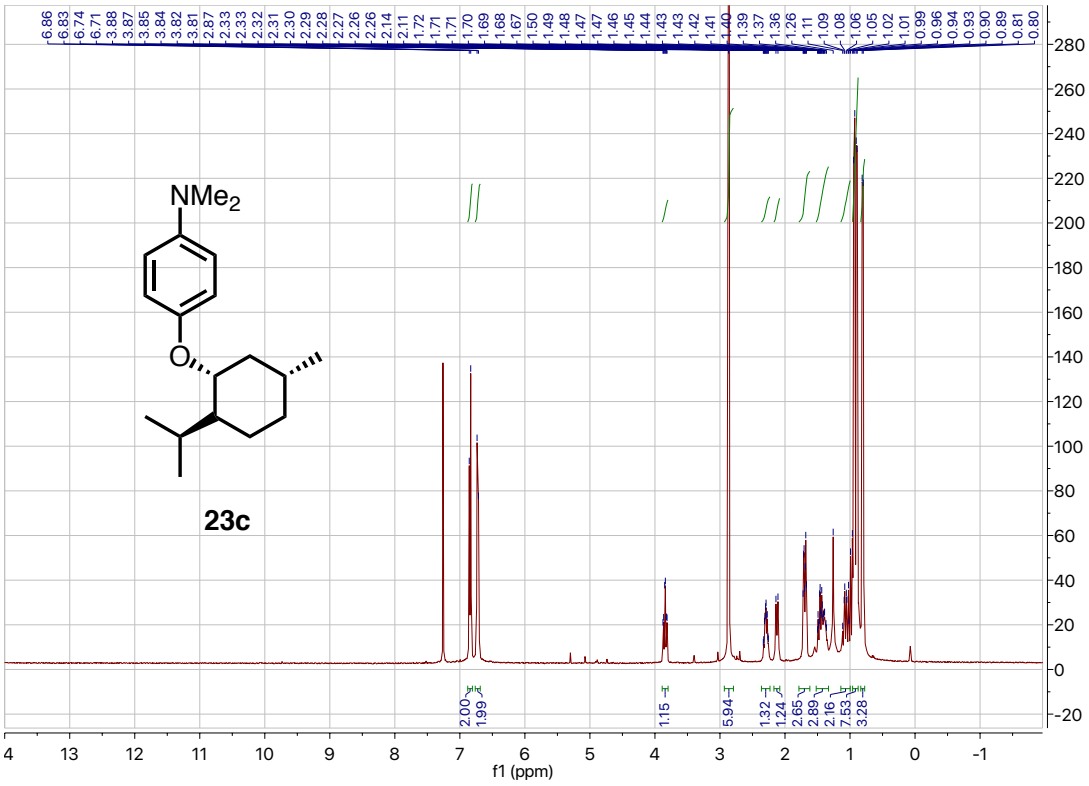
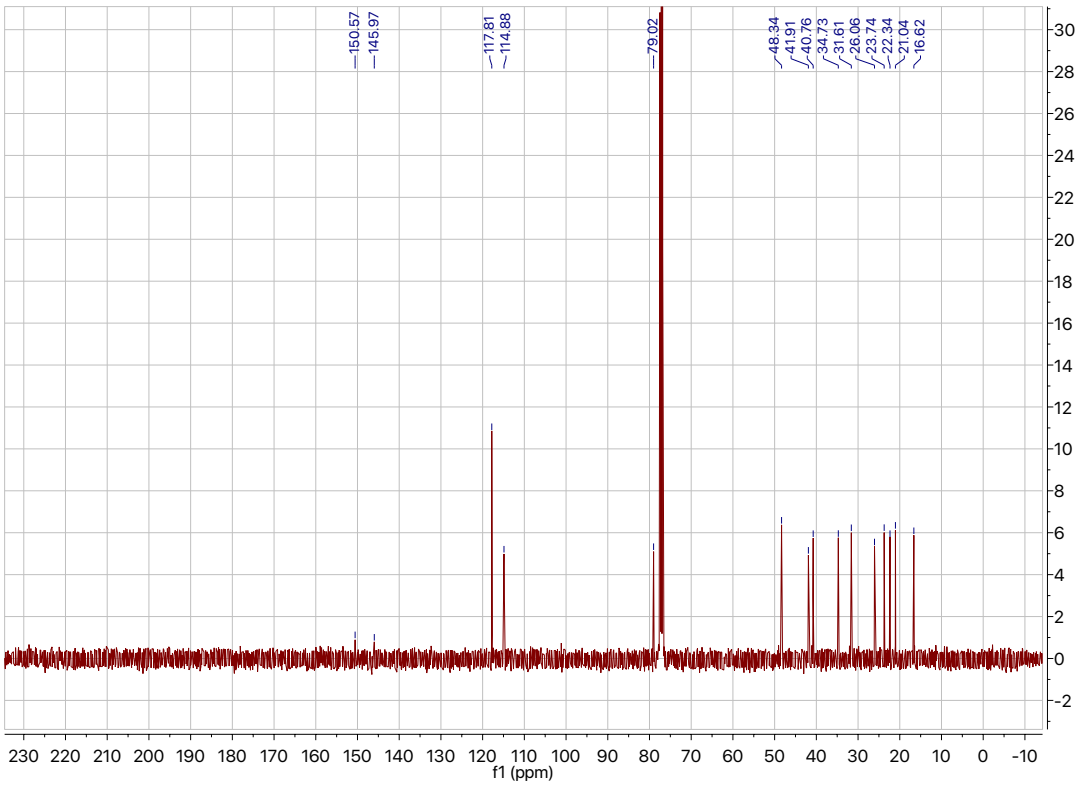
31.60
26.03
23.70
22.32
21.02
16.58
f1 (ppm)


NMe2
O
23c
f1 (ppm)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114.88
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48.34
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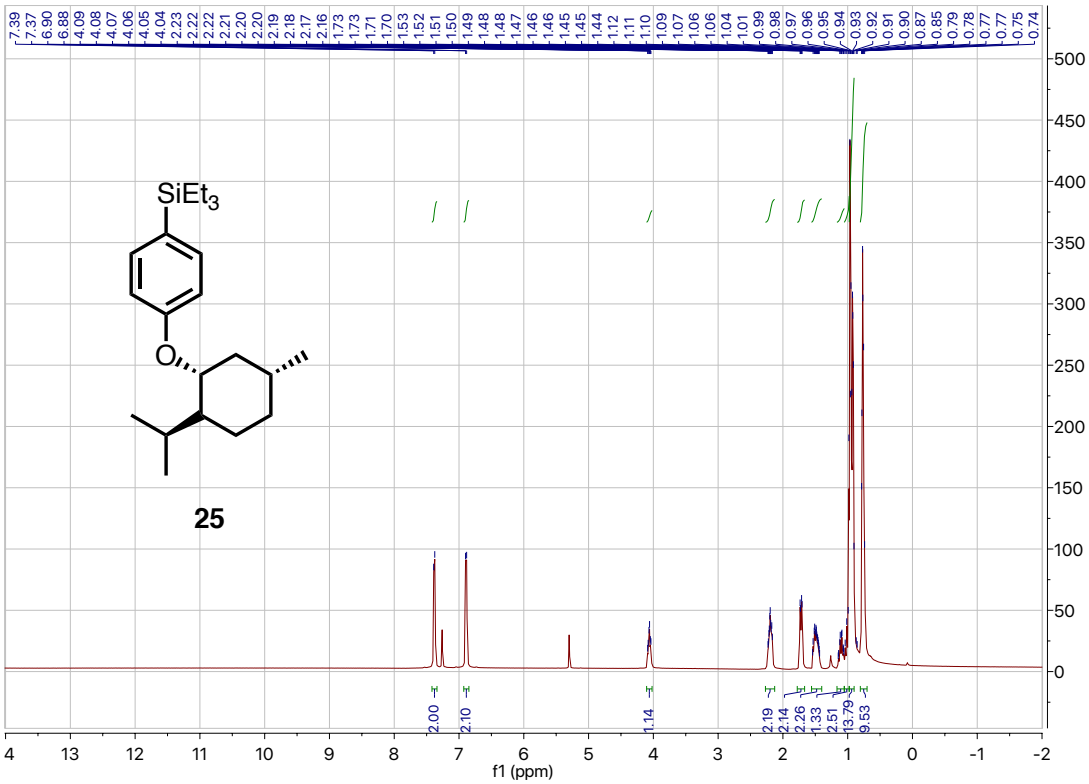
31.61
26.06
23.74
22.34
21.04
16.62
f1 (ppm)


SiEt3
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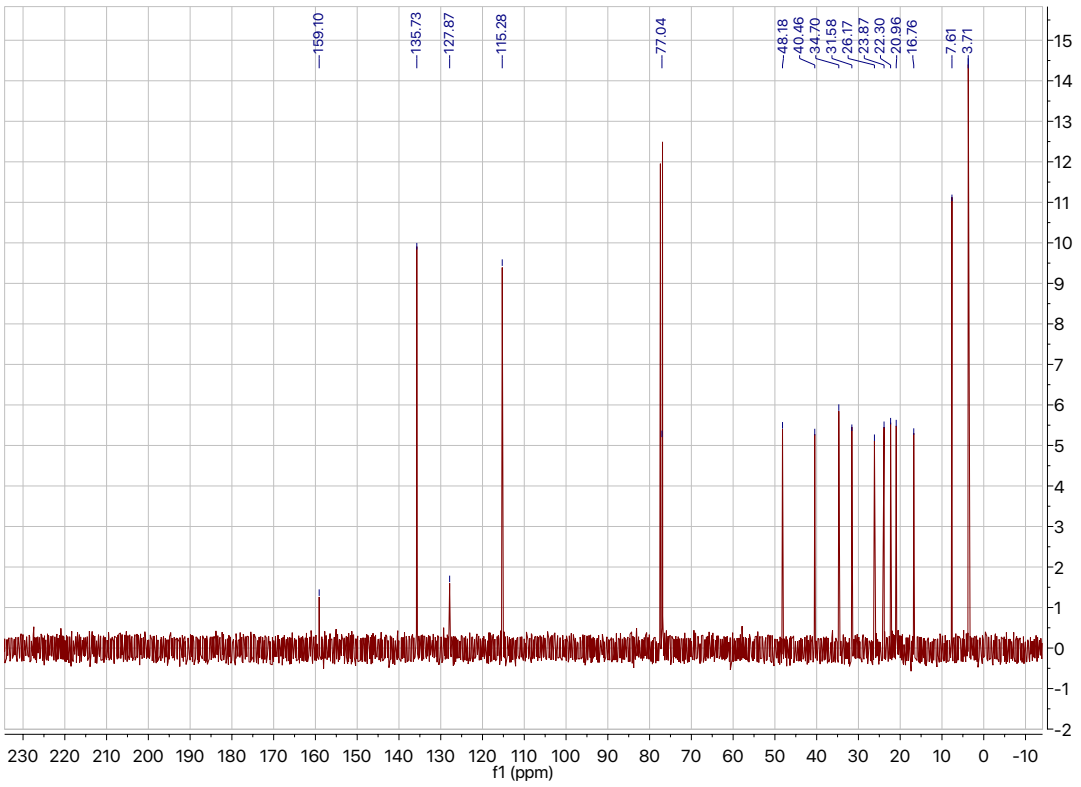
2.14
2.26
1.33
2.51
13.79
9.53
f1 (ppm)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77.04
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31.58
26.17
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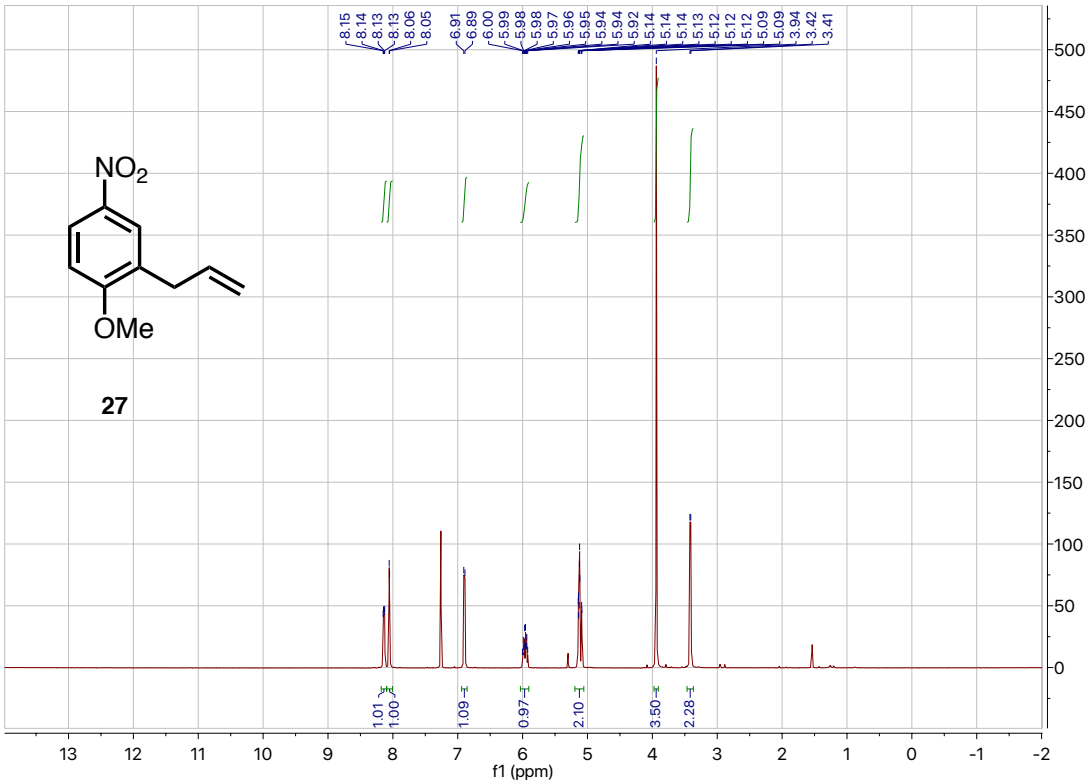
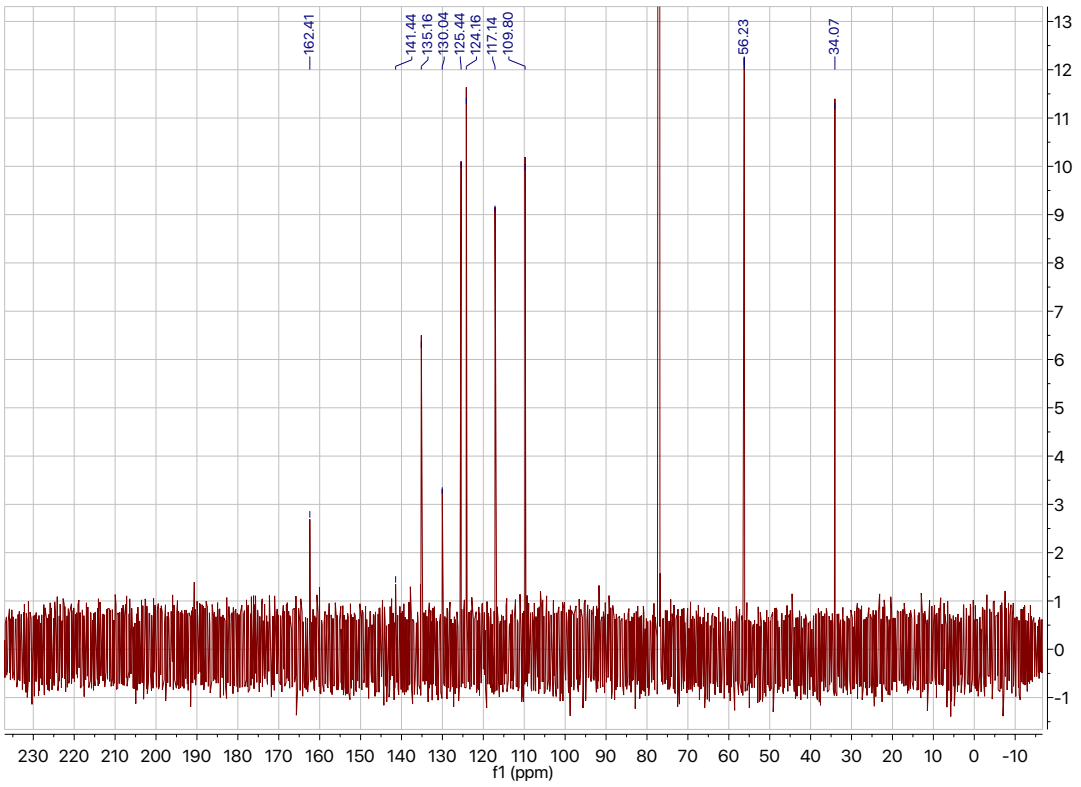
22.30
20.96
16.76
7.61
3.71
f1 (ppm)


NO2
OMe
27
f1 (ppm)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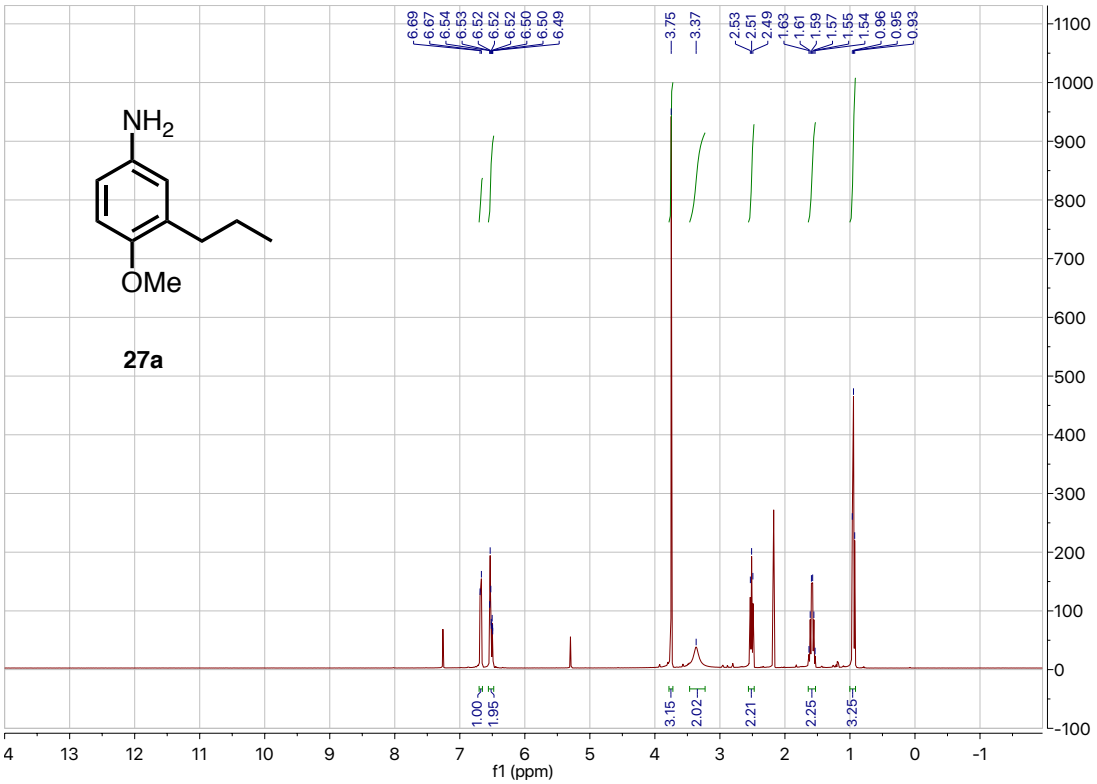
56.23
34.07
f1 (ppm)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6.50
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6.49
3.75
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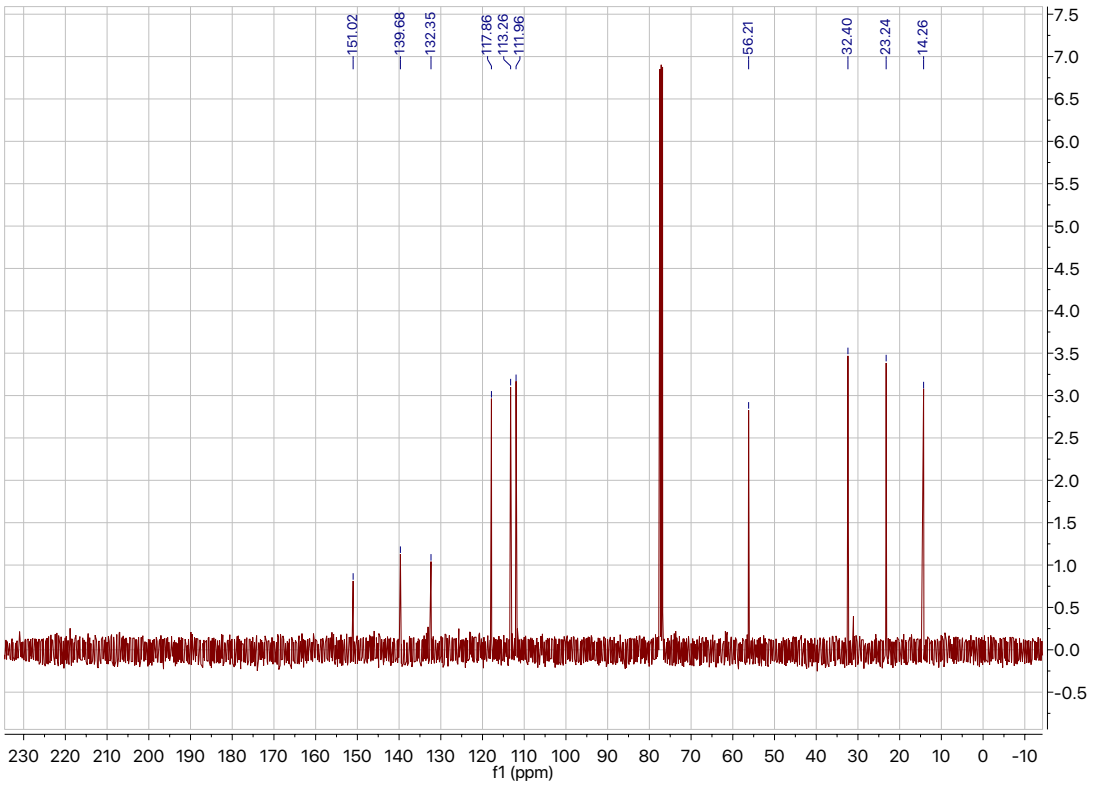
2.53
2.51
2.49
1.63
1.61
1.59
1.57
1.55
1.54
0.96
0.95
0.93
1.00
1.95
3.15
2.02
2.21
2.25
3.25
f1 (ppm)

NH2
OMe

27a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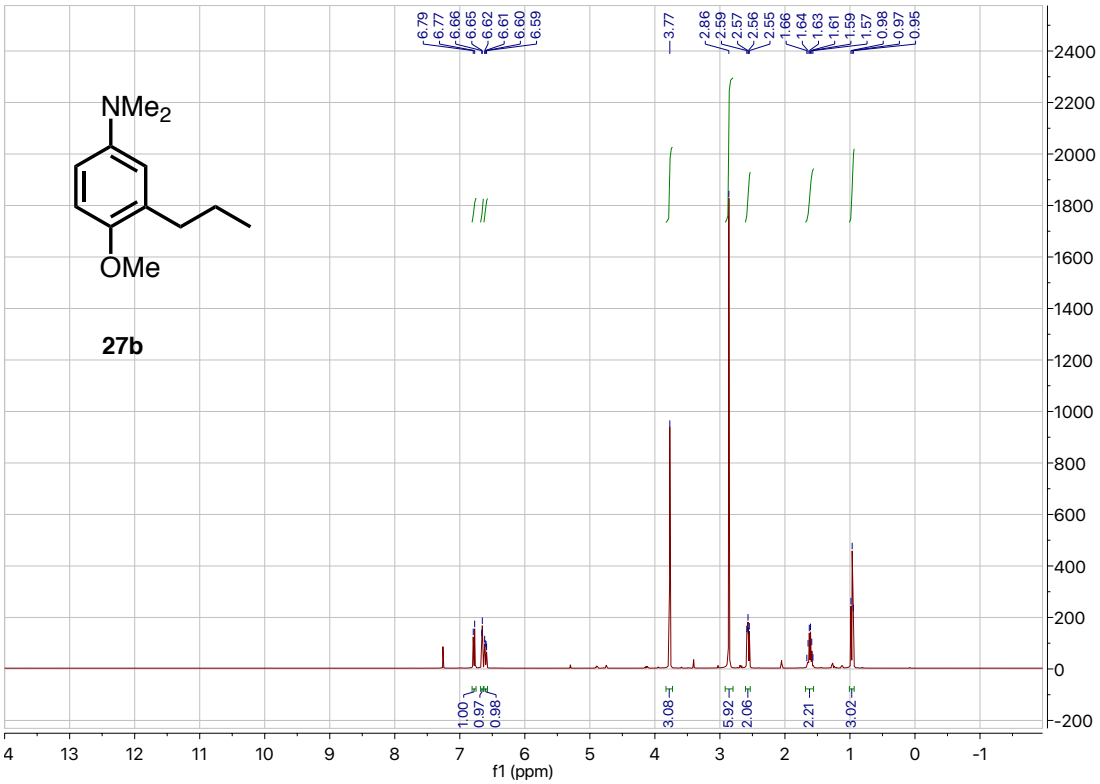
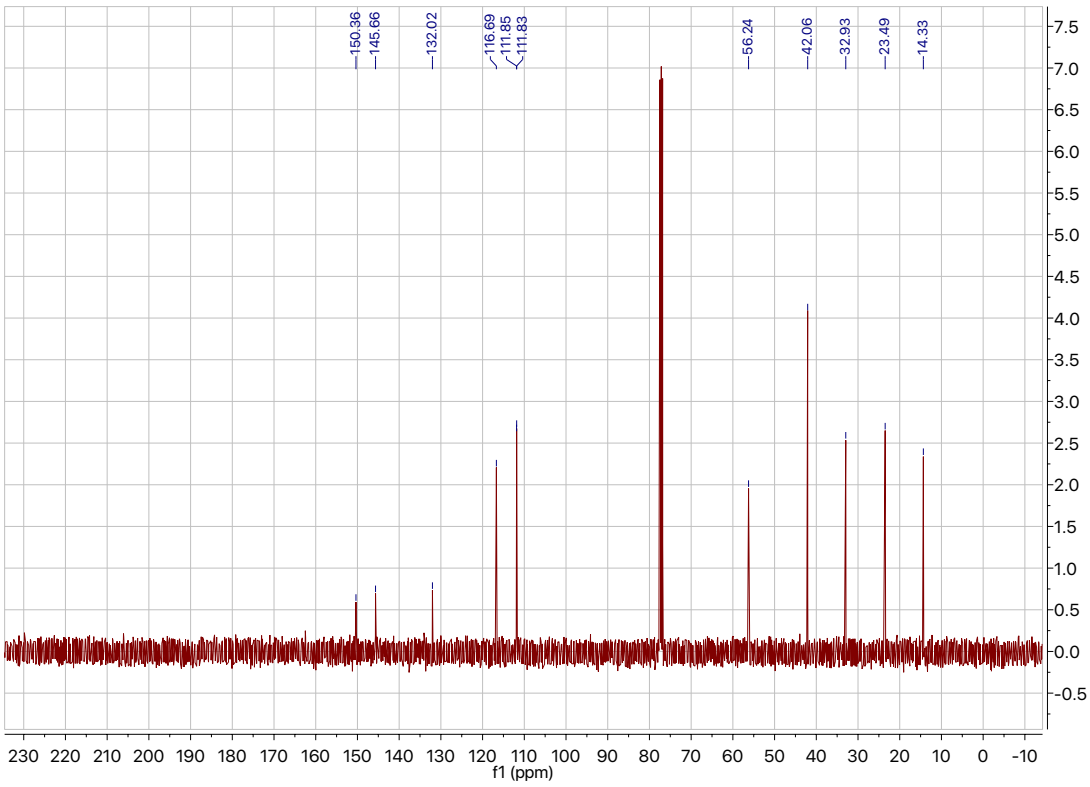
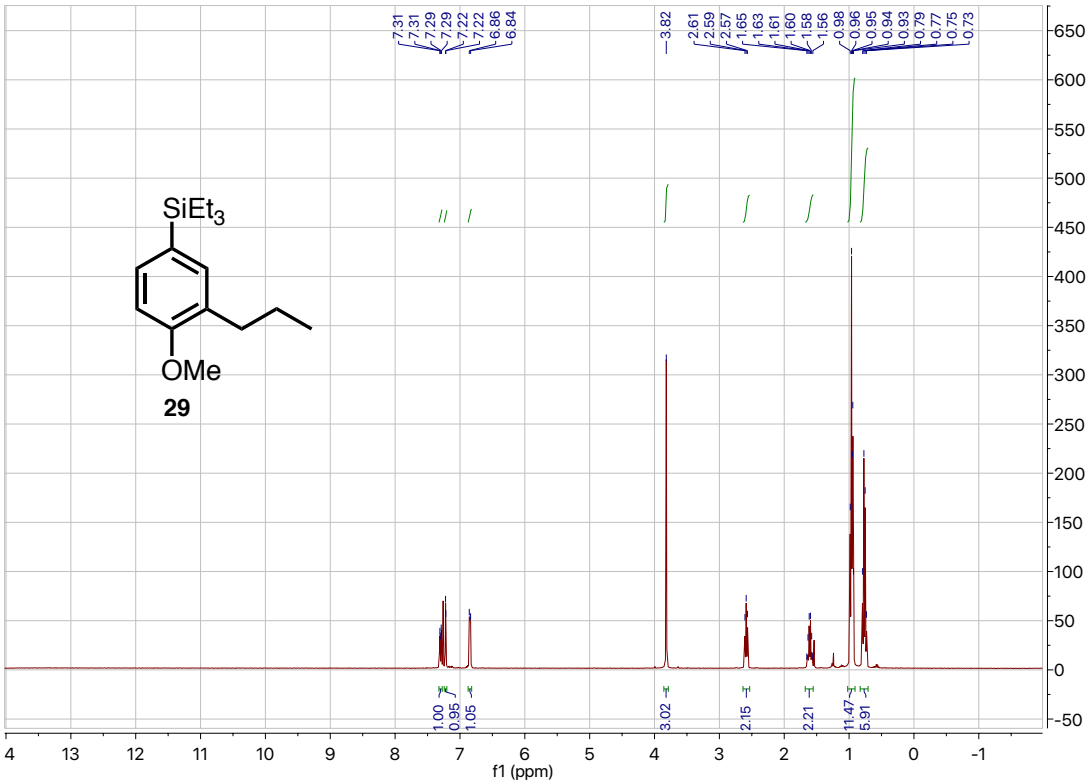
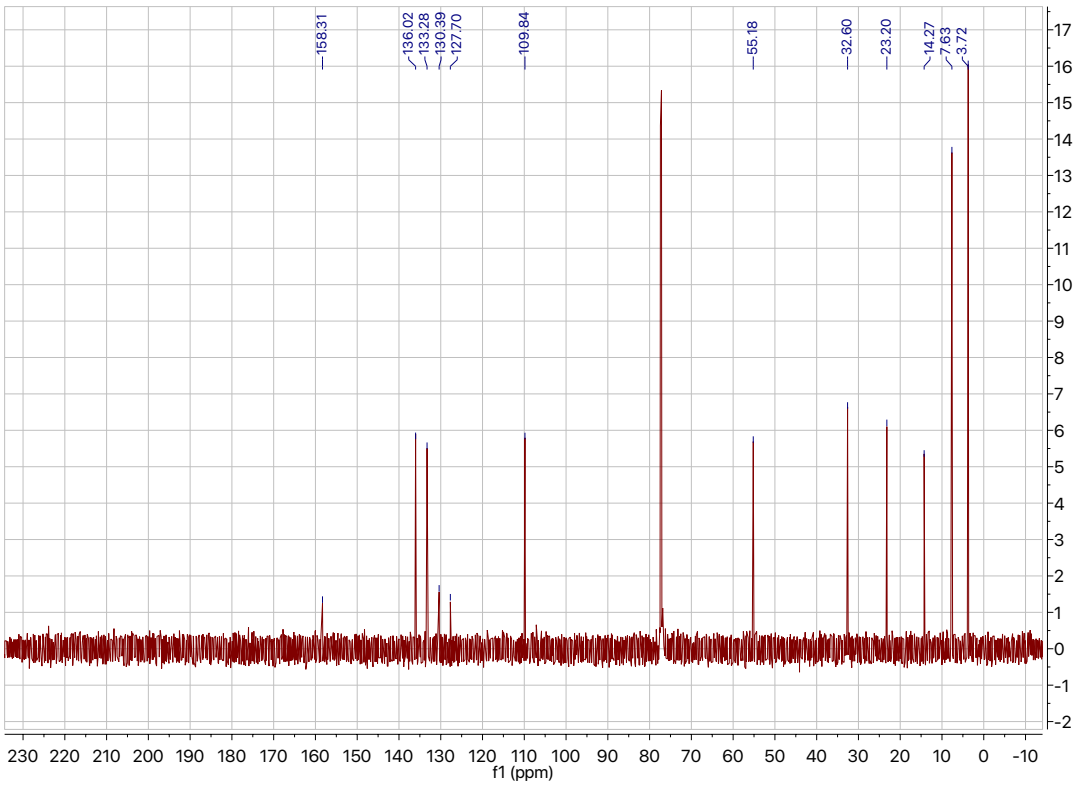

NMe2
OMe
27b
6.79
6.77
6.66
6.65
6.62
6.61
6.60
6.59
3.77
2.86
2.59
2.57
2.56
2.55
1.66
1.64
1.63
1.61
1.59
1.57
0.98
0.97
0.95
1.00
0.97
0.98
3.08
5.92
2.06
2.21
3.02
f1 (ppm)


150.36
145.66
132.02
116.69
111.85
111.83
56.24
42.06
32.93
23.49
14.33
f1 (ppm)


SiEt3
OMe
29
7.31
7.29
7.22
6.86
6.84
3.82
2.61
2.59
2.57
1.65
1.63
1.61
1.60
1.58
1.56
0.98
0.96
0.95
0.94
0.93
0.79
0.77
0.75
0.73
1.00
0.95
1.05
3.02
2.15
2.21
11.47
5.91
f1 (ppm)


158.31
136.02
133.28
130.39
127.70
109.84
55.18
32.60
23.20
14.27
7.63
3.72
f1 (ppm)

XI) References

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