

## Supporting Information

### Ru-based Nanoparticles Catalyzed Direct H/D Exchange of Silanes

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## 1. General information

All glassware was oven-dried at 110 °C for hours and cooled down under vacuum. Unless otherwise noted, all substrates were obtained from commercial suppliers and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. All new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS. The known compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR. <sup>1</sup>H and <sup>13</sup>C NMR data were recorded with Bruker (400 MHz) NMR spectrometer with tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument and accurate masses were reported for the molecular ion + Hydrogen (M+H). All chemical shifts ( $\delta$ ) were reported in ppm and coupling constants ( $J$ ) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for <sup>1</sup>H), CDCl<sub>3</sub> (77.16 ppm for <sup>13</sup>C), respectively.

The transmission electron microscopy (TEM) measurements were performed by JEM-2010 (HT) electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) was collected on a VG Multi Lab 2000 system with a monochromatic Al K $\alpha$  X-ray source (Thermo VG Scientific). Scanning transmission electron microscopy (STEM) imaging and energy-dispersive X-ray spectroscopy (EDX) mapping were acquired on a JEOL JEM-ARM200CF microscope operated at 200 kV with a Schottky cold-field emission gun in Wuhan University. The EDX elemental mapping was carried using the JEOL SDD-detector with two 100 mm<sup>2</sup> X-ray sensor.

The metal loading content was determined by Inductively coupled plasma mass spectrometry (ICP-MS), carried out in a PlasmaQuant MS (Analytik Jena, Germany). 10 mg of the Ru catalyst was solved in 10 mL aqua regia and allowed to stand for 24 hours to fully dissolved

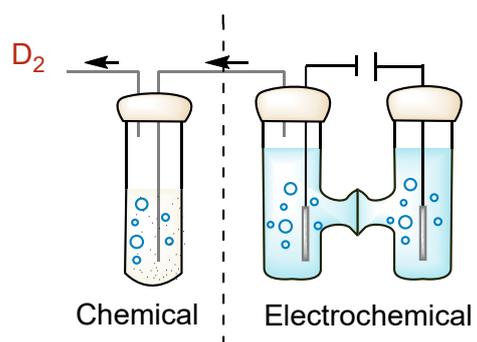
The location and percentage of deuterium incorporation were determined by <sup>1</sup>H NMR. Use the following formula to determine the degree of deuterium incorporation. Calibrate peaks based on signals corresponding to unmarked locations. The label location was determined by <sup>1</sup>H NMR based on chemical shift and peak multiplicity. In addition, deuterium incorporation was confirmed using high-resolution MS or GC-MS by comparing all labeled and unlabeled compounds (note that high-resolution MS is used here to confirm the results of quantitative NMR analysis).

$$\%deuteration = 100 - \left[ \left( \frac{\text{residual integral}}{\text{number of labelling sites}} \times 100 \right) \right]$$

## 2. Experimental Section

### (1) Graphical guide for the set-up

The experimental setup consisted of an electrolysis water device, which included a pair of divided electrochemical cells, two platinum plate electrodes (15 mm × 15 mm) serving as the cathode and anode, rubber plugs, a curved needle functioning as a guide tube, a single-port glass tube with a magnetic stirring bar as the reaction vessel, and an oil seal.



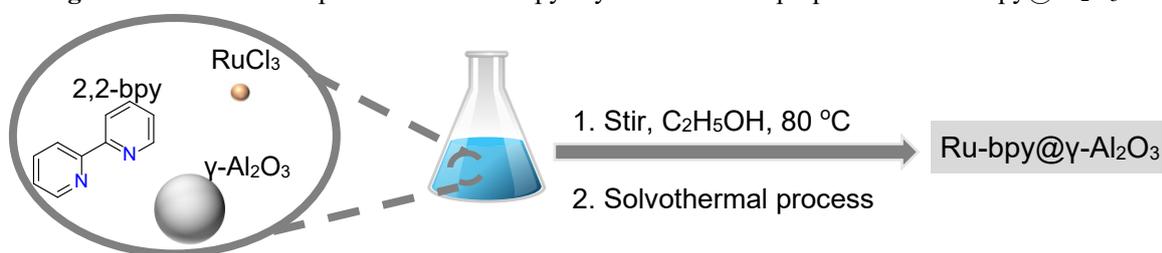
**Figure S1.** Graphical setup guide.

## (2) Experimental procedures

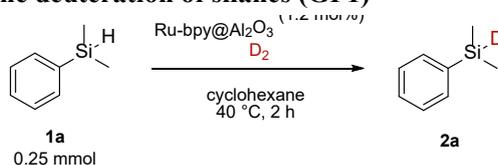
### General procedure for the preparation of Ru catalyst

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (103 mg, 0.5 mmol) and 2,2'-bipyridine (234 mg, 1.5 mmol) were stirred in ethanol (150 mL) for 2 h at 80 °C (rt to 80 °C). The support  $\gamma\text{-Al}_2\text{O}_3$  (2.0 g) was then added and the mixture was stirred at 80 °C for 15 h. At the end of the reaction, the mixture was cooled down at room temperature. Then the ethanol was removed in vacuum, leaving behind orange solid. The sample was transferred to a ceramic crucible and placed in the oven. The furnace was heated to 600 °C at a rate of 20 °C/min and held at 600 °C for 2 h under argon atmosphere. After the heating was turned off, the oven cooled naturally to room temperature. During the whole process, argon was constantly passed through the oven. Element analysis: Ru 0.8 wt%.

**Figure S2.** Schematic representation of the pyrolysis method for preparation of  $\text{Ru-bpy}@\text{Al}_2\text{O}_3$ .



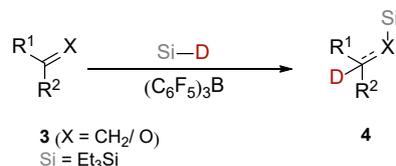
### General procedure for the deuteration of silanes (GP1)



In a 10 mL sealed tube fitted with a magnetic stirring bar, Ru catalyst (40 mg, 1.2 mol%) and solvent (toluene or cyclohexane, 4.0 mL) were added independently. Then the substrate (0.25 mmol) was added. In a divided electrochemical cell, saturated  $\text{Na}_2\text{SO}_4$  deuterium aqueous solution (25 mL) was added in each side of the anionic film, and platinum sheet electrodes were inserted in each side.  $\text{D}_2\text{O}$  underwent electrolysis at a constant current of 200 mA. After 5 minutes, the  $\text{D}_2$  generated at the cathode was introduced into the reaction system via a long needle. The top of the reaction pipe also connects with an oil seal to balance the pressure. The reaction was carried out at 40 °C for 4 h, and the resulting mixture was sonicated for 10 min and centrifuged or filtered to remove the catalyst, and then distilled to remove the solvent under reduced pressure.

### General procedure for gram-scale experiment

In a 10 mL sealed tube fitted with magnetic stirring bar, Ru catalyst (40 mg) and the substrate (3 g) was added independently. Then D<sub>2</sub> was passed into the reaction system as **GP1** at room

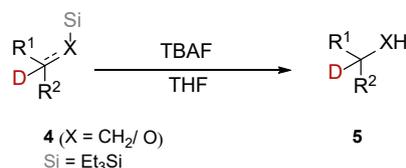


temperature for 24 h. The mixture was filtered and the solid was removed to obtain the desired product.

### General Procedure for hydrosilation of alkenes, ketones and aldehydes (GP2)

Desired products were prepared according to literature methods <sup>[1,2]</sup>, using laboratory triethylsilane-*d* **2g**. The substrate (0.5 mmol) and tris(pentafluorophenyl)borane (0.04 equiv.) were placed into a 4 mL vial containing a magnetic stir bar. Then the sealed tube was flushed with nitrogen 3 times and dry toluene (1.0 mL) was added to the vial. After 5min of stirring, triethylsilane-*d* (1.2 equiv.) was added to the mixture, and the reaction was performed for 12 h at room temperature. All substrates were filtered over silica gel (SiO<sub>2</sub>) with petroleum ether. After removal of all volatiles the desired products were obtained.

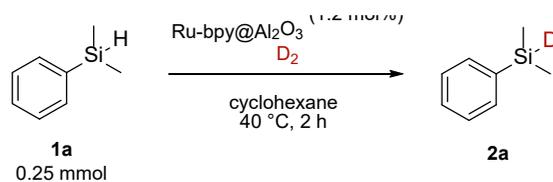
### General Procedure for deprotection of silyl ether (GP3)



Desired products were prepared according to literature method <sup>[3]</sup>. In a 10 mL sealed tube fitted with a magnetic stirring bar, the requisite silyl ether (0.50 mmol) and TBAF (0.5 mL, 1.0 M in THF) were added and stirred at 40 °C for 4 h. The solvent was removed under reduced pressure and the residue was purified by flash silica column chromatography.

### (3) Impact of reaction parameters

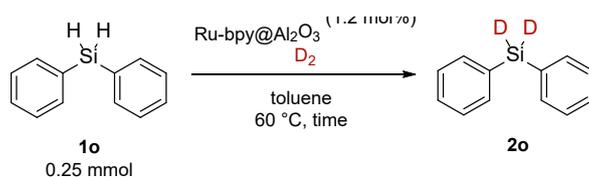
**Table S1.** Impact of reaction parameters



Entry	Variation from the standard conditions	D% of <b>2a</b> <sup>a</sup>
1 <sup>a</sup>	None	92%
2	Pd-bpy/ $\text{Al}_2\text{O}_3$	n.d.
3	Ni-bpy/ $\text{Al}_2\text{O}_3$	n.d.
4	Co-bpy/ $\text{Al}_2\text{O}_3$	n.d.
5	Toluene	91%
6	EA	66%
7	$\text{CH}_3\text{CN}$	25%
8	DMSO	n.d.
9	Dioxane	trace
10	$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ 1.2 mol%	n.d.

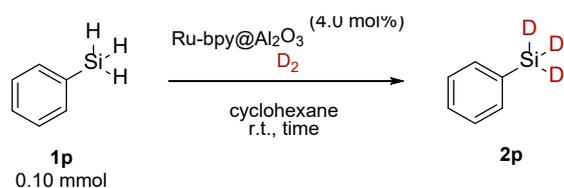
Reaction conditions: silane (0.25 mmol), catalyst (40.0 mg, 1.2 mol % Ru), cyclohexane (4.0 mL), 40 °C, 4 h.  $\text{D}_2\text{O}$  underwent electrolysis at a constant current of 200 mA, and  $\text{D}_2$  produced at the cathode was introduced into the reaction system. <sup>a</sup> Incorporation of the hydrogen isotope (D%) was determined by  $^1\text{H}$  NMR analysis.

**Table S2.** The influence of time for H/D exchange of diphenylsilane



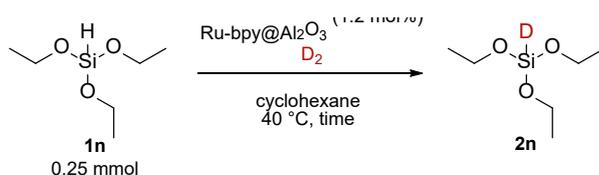
Entry	Time	D-incorp. <sup>a</sup>	Yield <sup>b</sup>
1	8 h	84%	75%
2	12 h	84%	61%
3	16 h	85%	42%

Reaction conditions: silane (0.25 mmol), catalyst (40.0 mg, 1.2 mol % Ru), toluene (4.0 mL),  $\text{Ph}_3\text{PO}$  (1.0 equiv.), 60 °C,  $\text{D}_2\text{O}$  underwent electrolysis at a constant current of 200 mA, and  $\text{D}_2$  produced at the cathode was introduced into the reaction system. <sup>a</sup> D-incorporation was determined by analysis of  $^1\text{H}$  NMR spectra. <sup>b</sup> Isolated yields of the Si–D/H mixtures was given.

**Table S3.** The influence of time for H/D exchange of phenylsilane

Entry	Time	D-incorp. <sup>a</sup>	Yield <sup>b</sup>
1	12 h	56%	40%
2	16 h	56%	23%
3	20 h	/	trace

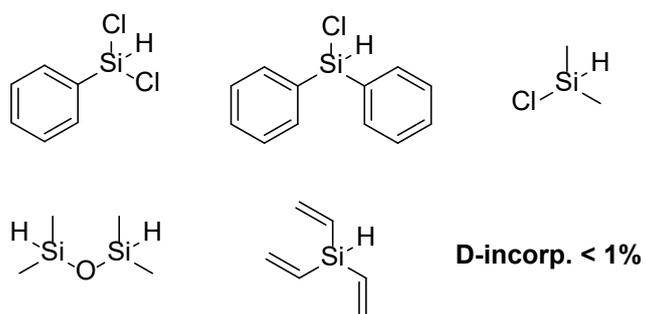
Reaction conditions: silane (0.10 mmol), catalyst (40.0 mg, 4.0 mol % Ru), cyclohexane (4.0 mL), Ph<sub>3</sub>PO (1.0 equiv.), r.t., D<sub>2</sub>O underwent electrolysis at a constant current of 200 mA, and D<sub>2</sub> produced at the cathode was introduced into the reaction system. <sup>a</sup>D-incorporation was determined by analysis of <sup>1</sup>H NMR spectra. <sup>b</sup> Isolated yields of the Si–D/H mixtures was given.

**Table S4.** The influence of time for H/D exchange of triethoxysilane

Entry	Time	D-incorp. <sup>a</sup>	Yield <sup>b</sup>
1	4 h	67%	62%
2	8 h	68%	40%
3	12 h	69%	17%

Reaction conditions: silane (0.25 mmol), catalyst (40.0 mg, 1.2 mol % Ru), cyclohexane (4.0 mL), 40 °C, D<sub>2</sub>O underwent electrolysis at a constant current of 200 mA, and D<sub>2</sub> produced at the cathode was introduced into the reaction system. <sup>a</sup>D-incorporation was determined by analysis of <sup>1</sup>H NMR spectra. <sup>b</sup> Isolated yields of the Si–D/H mixtures was given.

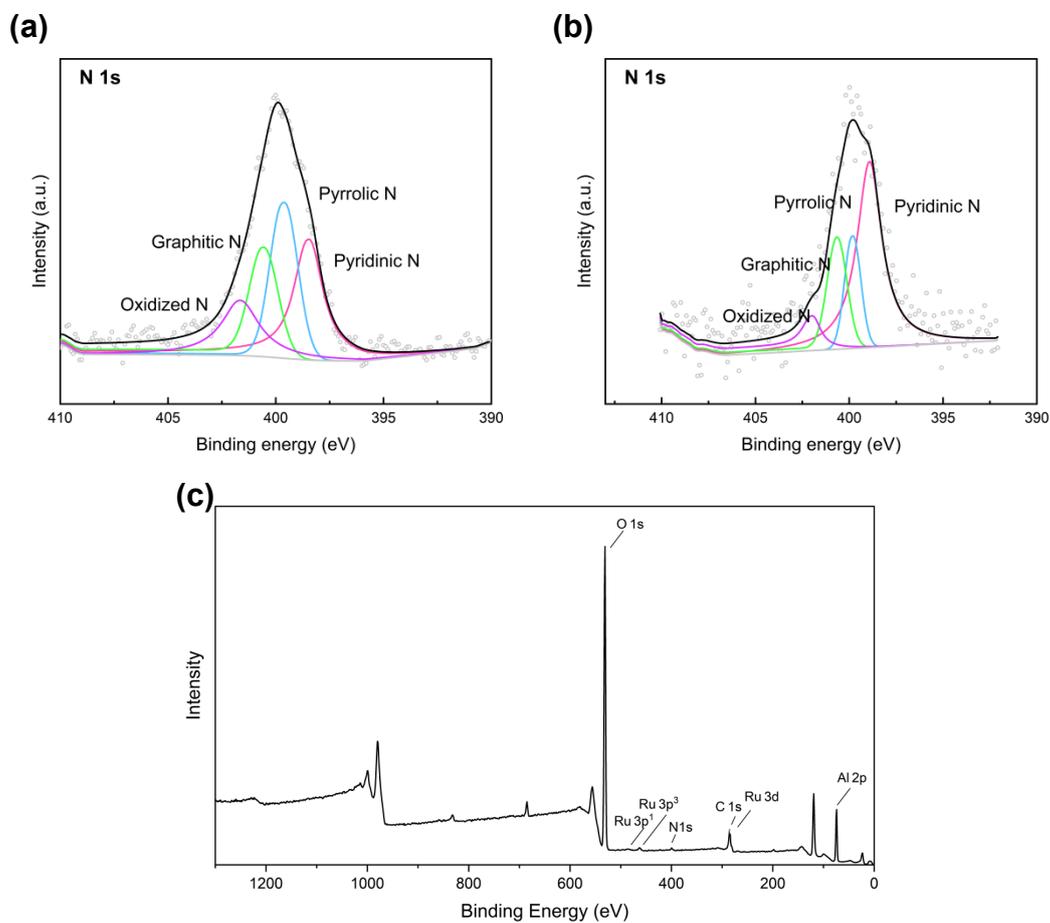
**(4) Incompatible substrates**



**Figure S3.** Incompatible substrates

### 3. Characterization of the catalyst

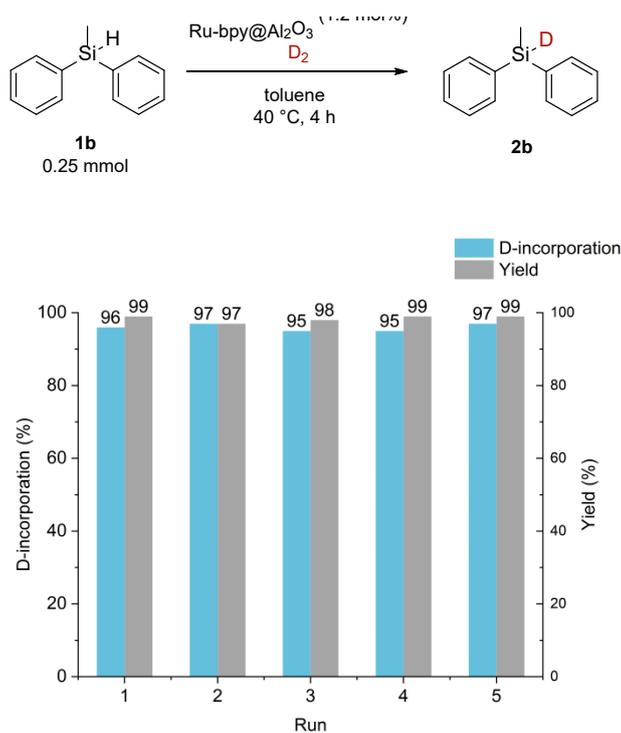
#### (1) The XPS spectra analysis



**Figure S4.** X-ray photoelectron spectroscopy (XPS) spectrum of Ru-bpy/Al<sub>2</sub>O<sub>3</sub>. (a) XPS of N 1s of fresh catalyst. (b) XPS of N 1s catalyst after 5 cycles. (c) XPS of survey.

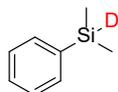
## (2) Catalyst recycling experiment

The substrate **1b** was deuterated according to **GP1**. The resulting mixture was centrifuged, and the organic layer was removed from the vial (3 times). The solid catalyst was washed with methanol (4 times) and acetone (2 times) and then it was reused immediately. The organic layer was collected for detection. After the removal of all volatiles under vacuum, the product was weighed. Then CDCl<sub>3</sub>(0.5 mL) was added for <sup>1</sup>H NMR analysis. These above operations were repeated for 5 times.



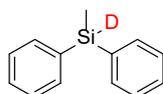
**Figure S5.** Catalyst recycling for the H-D exchange of silane.

#### 4. Procedure and analytical data of compounds



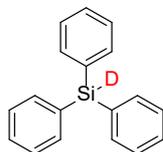
**Dimethyl(phenyl)silane-*d* (2a):** According to **GP1**, cyclohexane (4.0 mL), the product **2a** (0.25 mmol, 98%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature [6].

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.55 (dd,  $J = 6.4, 2.9$  Hz, 2H), 7.36 (dd,  $J = 5.0, 1.9$  Hz, 3H), 4.43 (p,  $J = 3.8$  Hz, 0.07H), 0.34 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 134.2, 129.3, 128.0, -3.7.



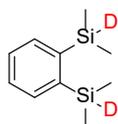
**Methylphenylsilane-*d* (2b):** According to **GP1**, toluene (4.0 mL), the product **2b** (0.25 mmol, 99%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature [7].

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.57 – 7.53 (m, 4H), 7.40 – 7.30 (m, 6H), 4.94 (q,  $J = 3.8$  Hz, 0.03H), 0.61 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.4, 135.0, 129.7, 128.1, -5.0.



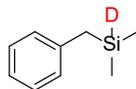
**Triphenylsilane-*d* (2c):** According to **GP1**, toluene (4.0 mL), the product **2c** (0.25 mmol, 99%) was isolated as white solid. The analytical data agree to those previously reported in the literature [8].

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.63 – 7.55 (m, 6H), 7.45 – 7.33 (m, 9H), 5.48 (s, 0.07H).  $^{13}\text{C}$  NMR (101 MHz, None)  $\delta$  135.9, 133.4, 130.0, 128.2.



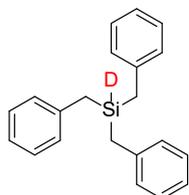
**1,2-bis(dimethylsilyl)benzene-*d*<sub>2</sub> (2d):** According to **GP1**, toluene (4.0 mL), the product **2d** (0.23 mmol, 90%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature [9].

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.57 (dd,  $J = 5.5, 3.3$  Hz, 2H), 7.35 (dd,  $J = 5.5, 3.3$  Hz, 2H), 4.68 (p,  $J = 3.7$  Hz, 0.06H), 0.35 (s, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 134.4, 128.5, -2.6.



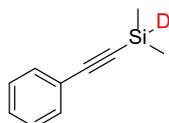
**[(Dimethylsilyl-*d*)methyl]benzene (2e):** According to **GP1**, cyclohexane (4.0 mL), the product **2e** (0.22 mmol, 88%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature [9].

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.31 (t,  $J = 6.6$  Hz, 2H), 7.15 (dd,  $J = 18.6, 7.5$  Hz, 3H), 4.05 (dp,  $J = 7.0, 3.5$  Hz, 0.06H), 2.24 (s, 2H), 0.15 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.1, 128.4, 128.3, 124.3, 24.3, -4.7.



**Tribenzylsilane-*d* (2f):** According to **GP1**, toluene (4.0 mL), the product **2f** (0.25 mmol, 99%) was isolated as white solid. The analytical data agree to those previously reported in the literature [10].

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.20 (t,  $J = 7.6$  Hz, 6H), 7.08 (t,  $J = 7.4$  Hz, 3H), 6.97 (d,  $J = 7.5$  Hz, 6H), 4.04 (p,  $J = 3.4$  Hz, 0.03H), 2.11 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 128.6, 128.6, 124.7, 20.5.



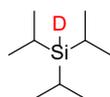
**dimethyl(phenylethynyl)silane-*d* (2g):** According to **GP1**, cyclohexane (4.0 mL), the product **2g** (0.18 mmol, 73%) was isolated as colorless liquid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.47 (dd,  $J = 5.6, 2.2$  Hz, 2H), 7.35 – 7.21 (m, 3H), 4.27 (p,  $J = 4.0$  Hz, 0.10H), 0.31 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  132.1, 128.9, 128.4, 123.0, 106.5, 91.2, -2.8, -2.9. HRMS (EI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{11}\text{DSi}$  ( $\text{M}+\text{H}$ ) $^+$ : 161.0771, found : 161.0763 .



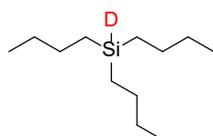
**Triethylsilane-*d* (2h):** According to general procedure for gram-scale experiment, no solvent, the product **2h** (1.89g, 63%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[11]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  3.61 (dt,  $J = 6.3, 3.3$  Hz, 0.03H), 0.98 (t,  $J = 7.9$  Hz, 9H), 0.60 (td,  $J = 7.9, 5.0$  Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  6.7, 6.0.



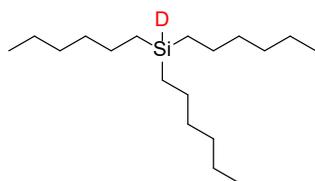
**Triisopropylsilane-*d* (2i):** According to **GP1**, cyclohexane (4.0 mL), the product **2i** (0.23 mmol, 90%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[11]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  3.31 (s, 0.09H), 1.43 (s, 3H), 1.06 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  19.5, 10.4.



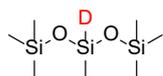
**Tributylsilane-*d* (2j):** According to **GP1**, toluene (4.0 mL), the product **2j** (0.24 mmol, 94%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[11]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  3.67 (p,  $J = 3.2$  Hz, 0.09H), 1.33 (q,  $J = 3.7$  Hz, 12H), 0.89 (t,  $J = 6.6$  Hz, 9H), 0.63 – 0.54 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  27.1, 26.5, 14.0, 11.2.



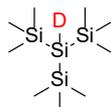
**Trihexylsilane-*d* (2k):** According to **GP1**, toluene (4.0 mL), the product **2k** (0.25 mmol, 98%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[11]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  3.67 (p,  $J = 3.3$  Hz, 0.08H), 1.37 – 1.24 (m, 24H), 0.88 (t,  $J = 6.7$  Hz, 9H), 0.61 – 0.53 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  33.2, 31.8, 24.8, 22.8, 14.3, 11.4.



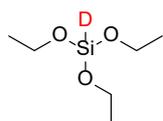
**Bis(trimethylsilyloxy)methylsilane-*d* (2l):** According to **GP1**, cyclohexane (4.0 mL), the product **2l** (0.23 mmol, 92%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[12]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  4.63 (t,  $J = 1.6$  Hz, 0.07H), 0.18 – 0.05 (m, 21H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  1.8, 1.8.



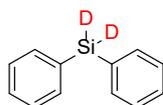
**Tris(trimethylsilyl)silane-*d* (2m):** According to **GP1**, cyclohexane (4.0 mL), the product **2m** (0.23 mmol, 93%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[13]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  2.15 (s, 0.12H), 0.19 (s, 27H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  2.0.



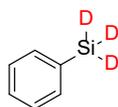
**Triethoxysilane-*d* (2n):** According to **GP1**, cyclohexane (4.0 mL), the product **2n** (0.16 mmol, 62%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[14]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  4.29 (s, 0.33H), 3.90 – 3.83 (m, 6H), 1.25 (t,  $J = 7.0$  Hz, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  58.5, 18.3.



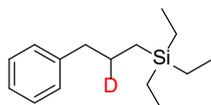
**Diphenylsilane-*d*<sub>2</sub> (2o):** According to **GP1**, toluene (4.0 mL), Ph<sub>3</sub>PO (1.0 equiv.), 60 °C, 8 h, the product **2o** (0.19 mmol, 75%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[15]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.60 (d,  $J = 7.7$  Hz, 4H), 7.39 (dd,  $J = 12.4, 7.3$  Hz, 6H), 4.92 (d,  $J = 3.6$  Hz, 0.32H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.8, 131.6, 130.0, 128.3.



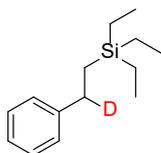
**Phenylsilane-*d*<sub>3</sub> (2p):** According to **GP1**, cyclohexane (4.0 mL), Ph<sub>3</sub>PO (1.0 equiv.), 60 °C, 8 h, the product **2p** (0.10 mmol, 40%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[16]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 7.9 Hz, 2H), 7.34 (dt, *J* = 12.4, 6.8 Hz, 3H), 4.20 (s, 1.3 H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.0, 123.0, 128.3.



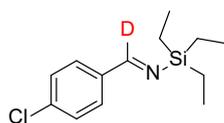
**Triethyl(3-phenylpropyl-2-*d*)silane (4a):** According to **GP2**, CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (5 mol%), the product **4a** (65%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[17]</sup>.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.27 (m, 2H), 7.26 – 7.19 (m, 3H), 2.66 (d, *J* = 7.7 Hz, 2H), 1.71 – 1.58 (m, 1.06H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.61 (d, *J* = 8.8 Hz, 2H), 0.55 (q, *J* = 7.9 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.9, 128.6, 128.4, 125.7, 40.3, 26.2 – 25.6 (m), 11.4, 7.6, 3.5.



**Triethyl(2-phenylethyl-2-*d*)silane (4b):** According to **GP2**, CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (5 mol%), the product **4b** (89%) was isolated as colorless liquid. The analytical data agree to those previously reported in the literature <sup>[18]</sup>.

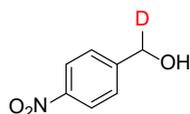
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.10 (m, 3H), 2.65 – 2.54 (m, 1.03H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.88 (d, *J* = 9.9 Hz, 2H), 0.55 (q, *J* = 8.0 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.7, 128.4, 127.8, 125.6, 30.20 – 29.65 (m), 13.7, 7.6, 3.4.



**(4-chlorophenyl)-N-(triethylsilyl)methanimine-*d* (4c):** Desired products were prepared according to literature methods<sup>[4]</sup>, using laboratory triethylsilane-*d* (**2g**). Triethylsilane (1.0 equiv) was added to a solution of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (3.0 mol%) in CDCl<sub>3</sub> (0.5 mL) in a NMR tube, and the solution was shaken briefly followed by the addition of the corresponding nitrile (0.5 mmol) and dibromomethane (0.5 equiv. As internal standard) under argon atmosphere. After 1 h, the

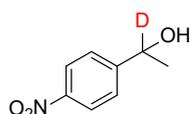
reaction mixture was subjected to  $^1\text{H}$  NMR spectroscopy and crude NMR yields (73%) were measured on the basis of an internal standard.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.98 (s, 0.03H), 7.73 (d,  $J = 8.5$  Hz, 2H), 7.38 (d,  $J = 8.4$  Hz, 2H), 0.99 (t,  $J = 7.9$  Hz, 9H), 0.75 (q,  $J = 7.7$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 166.9, 166.6, 137.5, 137.2, 129.6, 128.8, 7.0, 3.7. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{19}\text{DCINSi}$  ( $\text{M}+\text{H}$ ) $^+$ : 255.1189, found : 255.1190.



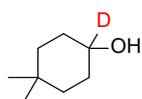
**(4-nitrophenyl)methan-*d*-ol (5d):** According to **GP2** and **GP3**, the product **5d** (68%) was isolated as yellow solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.20 (d,  $J = 8.6$  Hz, 2H), 7.53 (d,  $J = 8.3$  Hz, 2H), 4.82 (d,  $J = 8.6$  Hz, 1.03H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 147.4, 127.2, 123.8, 64.1 – 63.5 (m). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{10}\text{H}_{18}\text{D}_2\text{NO}_4$  ( $\text{M}+\text{H}$ ) $^+$ : 220.1512, found : 220.1515.



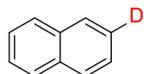
**1-(4-nitrophenyl)ethan-1-*d*-1-ol (5e):** According to **GP2** and **GP3**, the product **5e** (92%) was isolated as yellow solid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.21 – 8.12 (m, 2H), 7.53 (dd,  $J = 8.8, 2.3$  Hz, 2H), 5.01 (q,  $J = 6.8, 6.2$  Hz, 0.03H), 2.44 (d,  $J = 30.2$  Hz, 1H), 1.50 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 147.2, 126.2, 123.8, 69.5 – 68.9 (m), 25.4. HRMS (ESI)  $m/z$  calcd for  $\text{C}_8\text{H}_8\text{DNO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 169.0718, found : 169.0719.



**4,4-dimethylcyclohexan-1-*d*-1-ol (5f):** According to **GP2** and **GP3**, the product **5f** (72%) was isolated as colorless liquid.

$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  3.61 (tt,  $J = 9.0, 4.2$  Hz, 0.06H), 1.74 (dt,  $J = 13.4, 4.5$  Hz, 2H), 1.51 – 1.37 (m, 5H), 1.28 – 1.15 (m, 2H), 0.92 (d,  $J = 9.0$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  36.8, 31.2, 30.8, 29.7, 26.0. HRMS (ESI)  $m/z$  calcd for  $\text{C}_7\text{H}_6\text{DNO}_3$  ( $\text{M}+\text{H}$ ) $^+$ : 155.0562, found : 155.0562.



**Naphthalene-2-*d* (6g):** Desired products were prepared according to literature methods<sup>[5]</sup>, using laboratory triethylsilane-*d* **2g**. An oven-dried screw-cap test tube containing a stirring bar was charged with the aryl ether (0.50 mmol), Ni(COD)<sub>2</sub> (7.0 mg, 5 mol%) and PCy<sub>3</sub> (14.0 mg, 10 mol%) inside the drybox. Then, the flask was removed from the drybox and Et<sub>3</sub>SiD (96 μL, 0.60 mmol) and toluene (1 mL) were added by syringe under a N<sub>2</sub> atmosphere. The mixture was stirred in a pre-heated oil bath (110 °C) for 14 h. The mixture was then allowed to warm to room temperature, diluted with ethyl acetate (5 mL). The filtrate was concentrated and purified by column chromatography on silica gel (eluting with hexanes/ethyl acetate mixtures). The product **6g** (80%) was isolated as white solid.

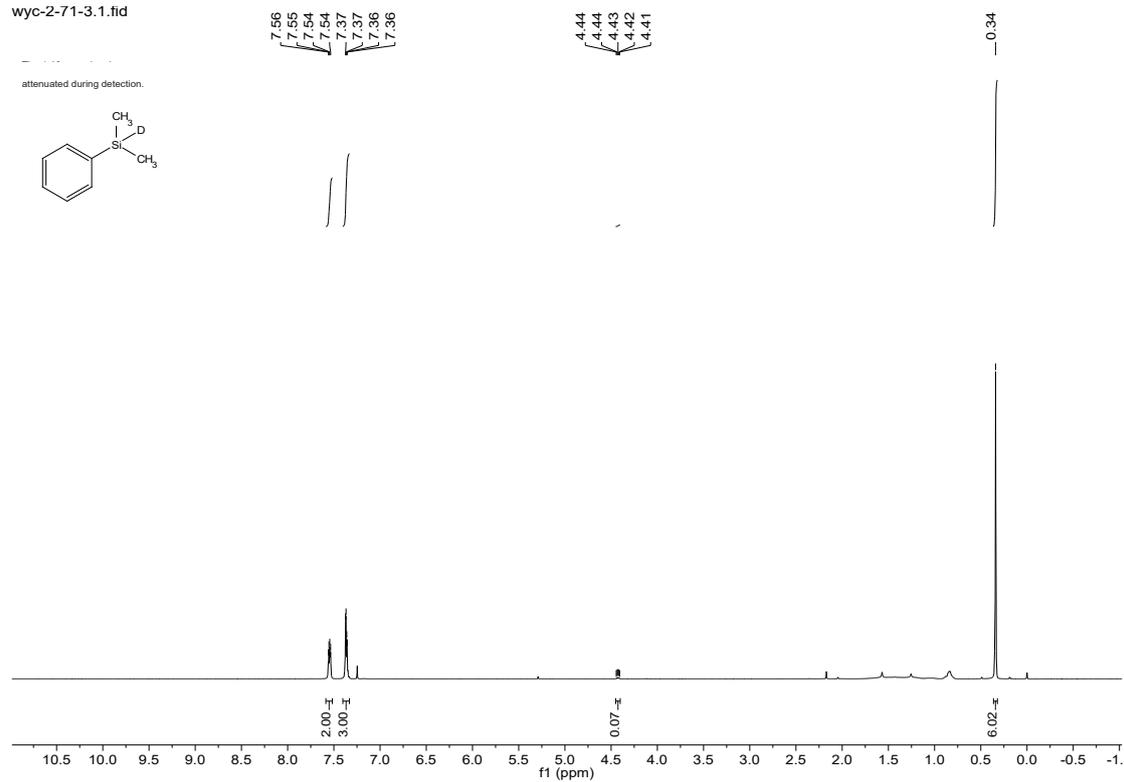
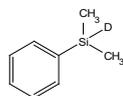
<sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dd, *J* = 6.0, 3.2 Hz, 4H), 7.47 (dd, *J* = 6.2, 3.1 Hz, 3.09H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 133.6, 128.0, 126.0. HRMS (ESI) *m/z* calcd for C<sub>10</sub>H<sub>7</sub>D (M+H)<sup>+</sup>: 130.0762, found : 130.0763.

## 5. NMR spectrum

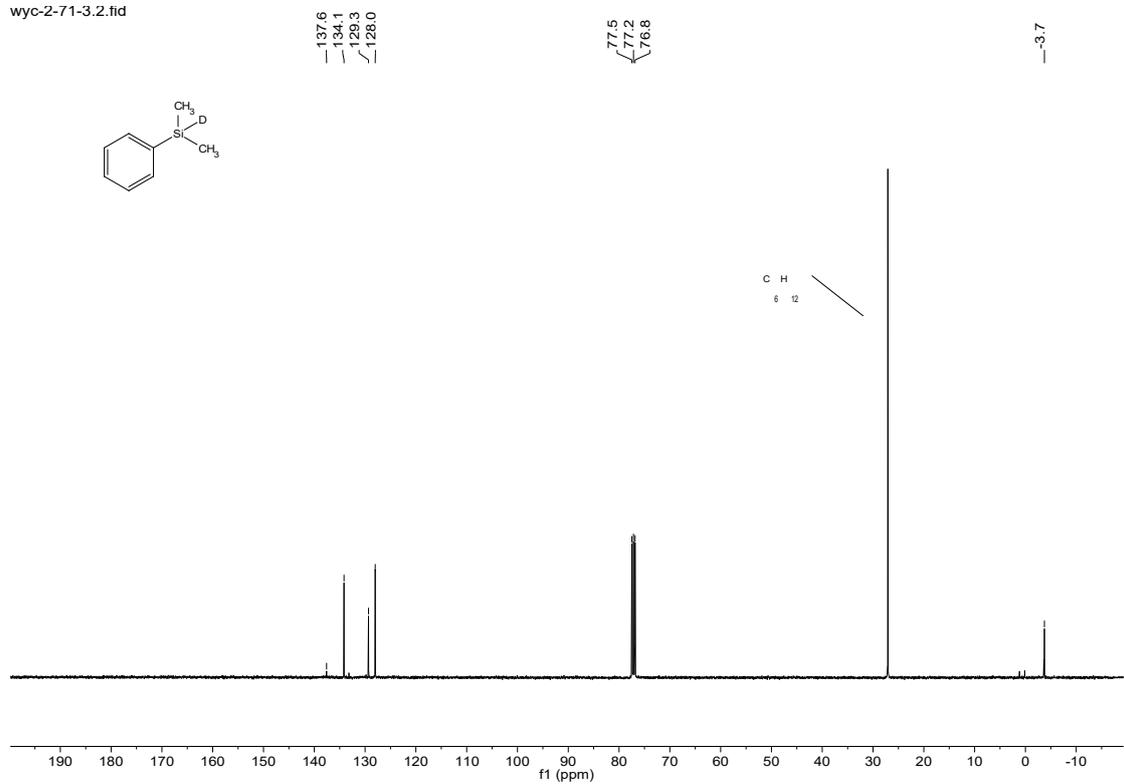
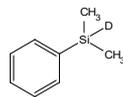
2a

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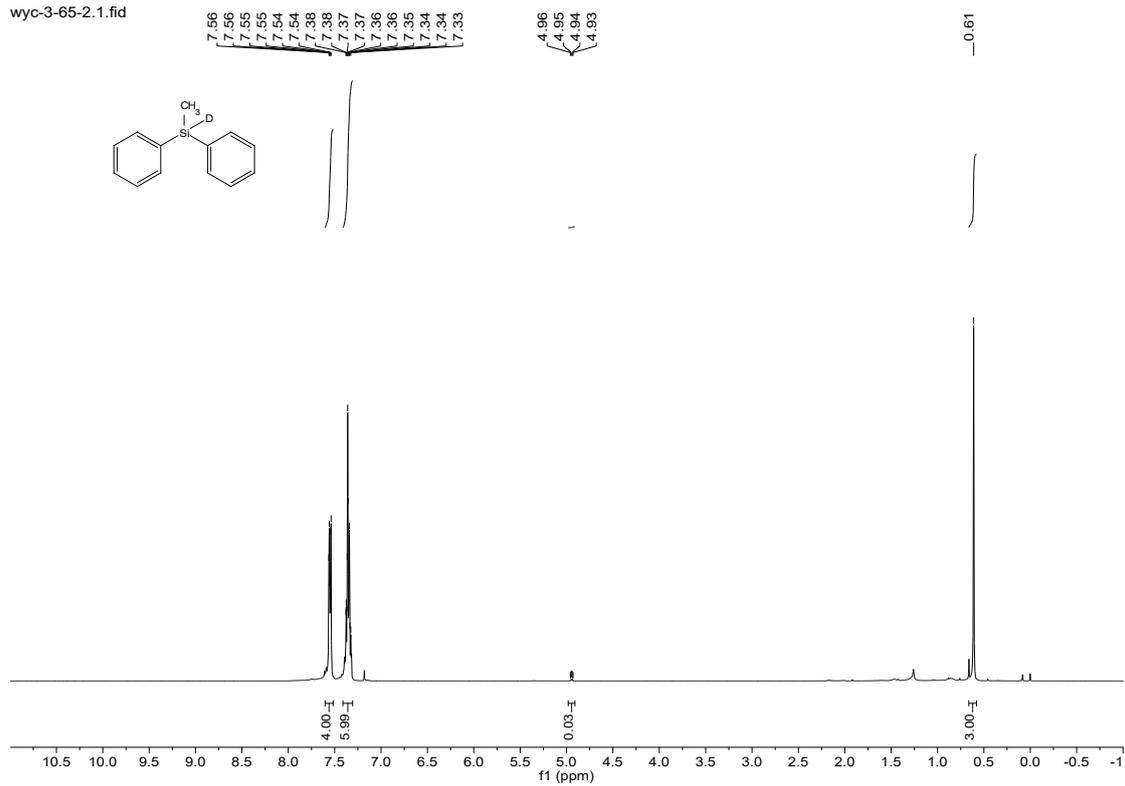


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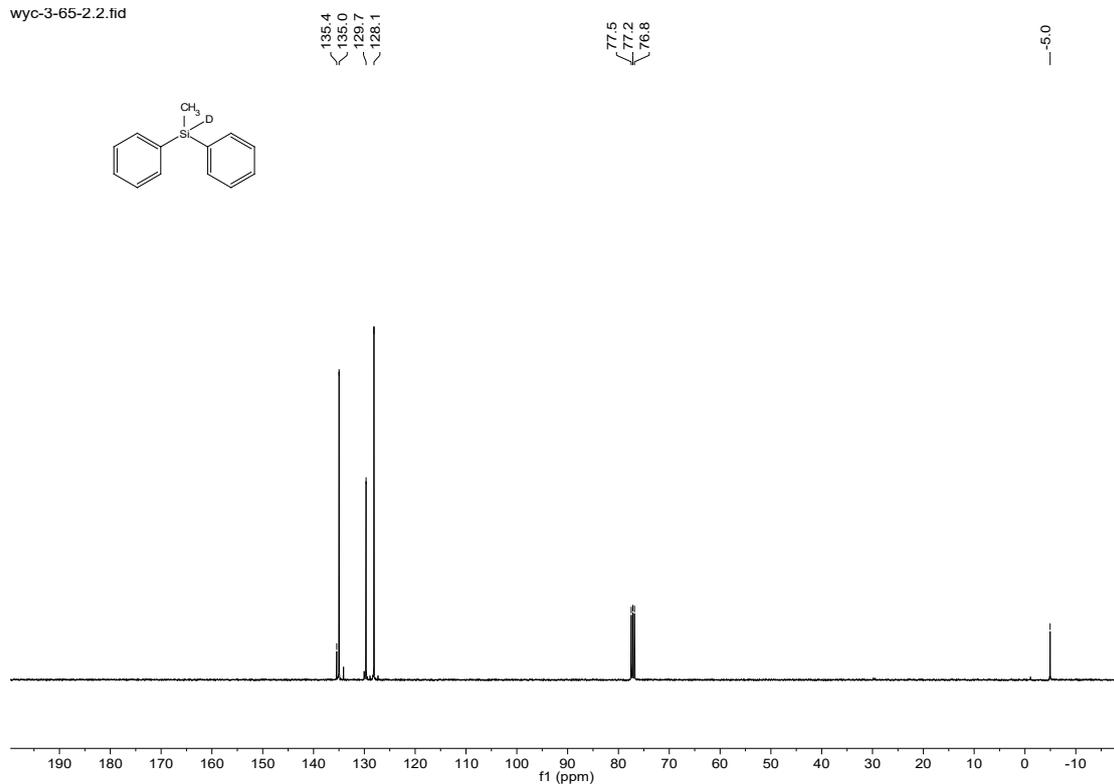


2b

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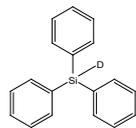


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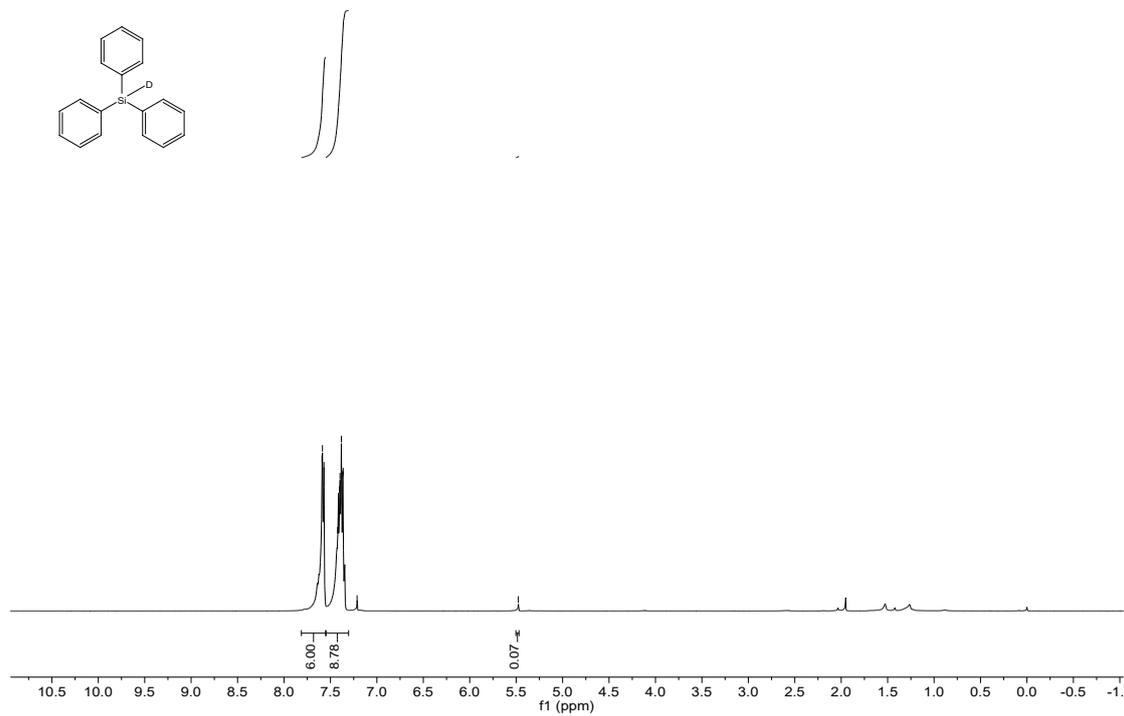


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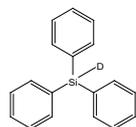
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7.59  
7.57  
7.57  
7.42  
7.41  
7.41  
7.40  
7.40  
7.39  
7.38  
7.37  
7.36  
7.21  
-5.48

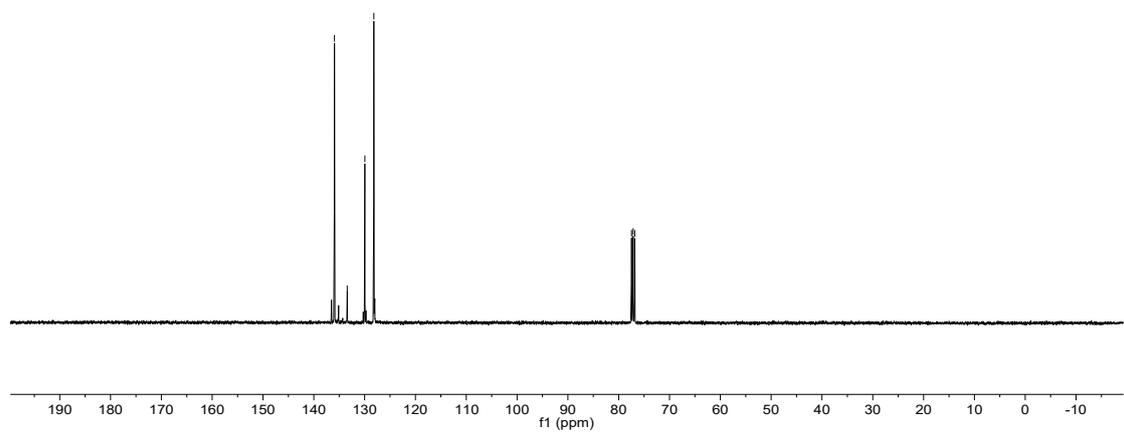


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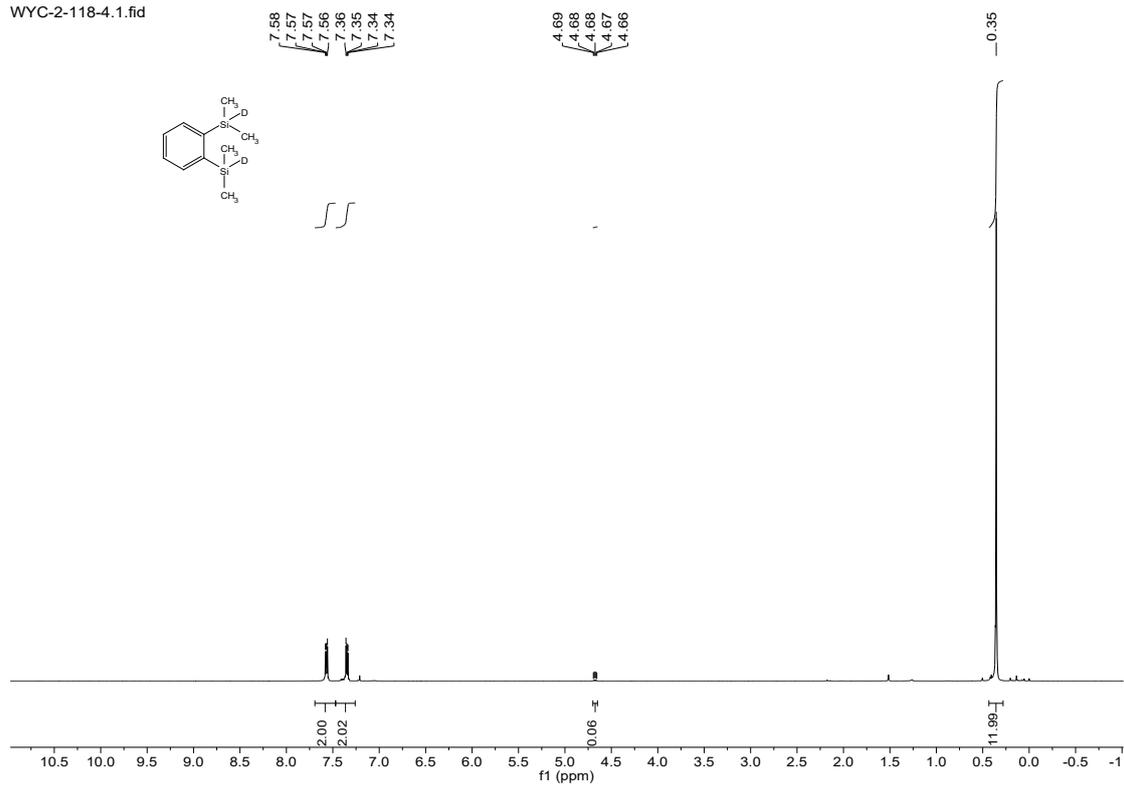
135.9  
133.4  
130.0  
128.2

77.5  
77.2  
76.8

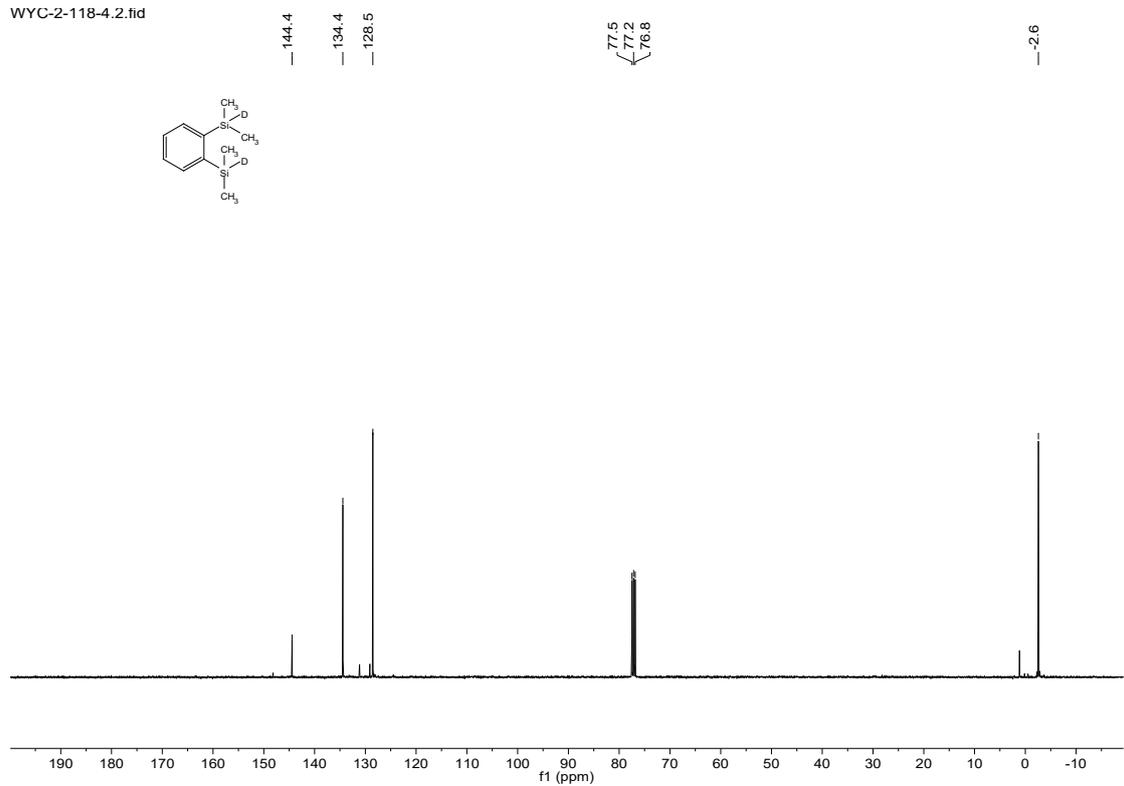


2d

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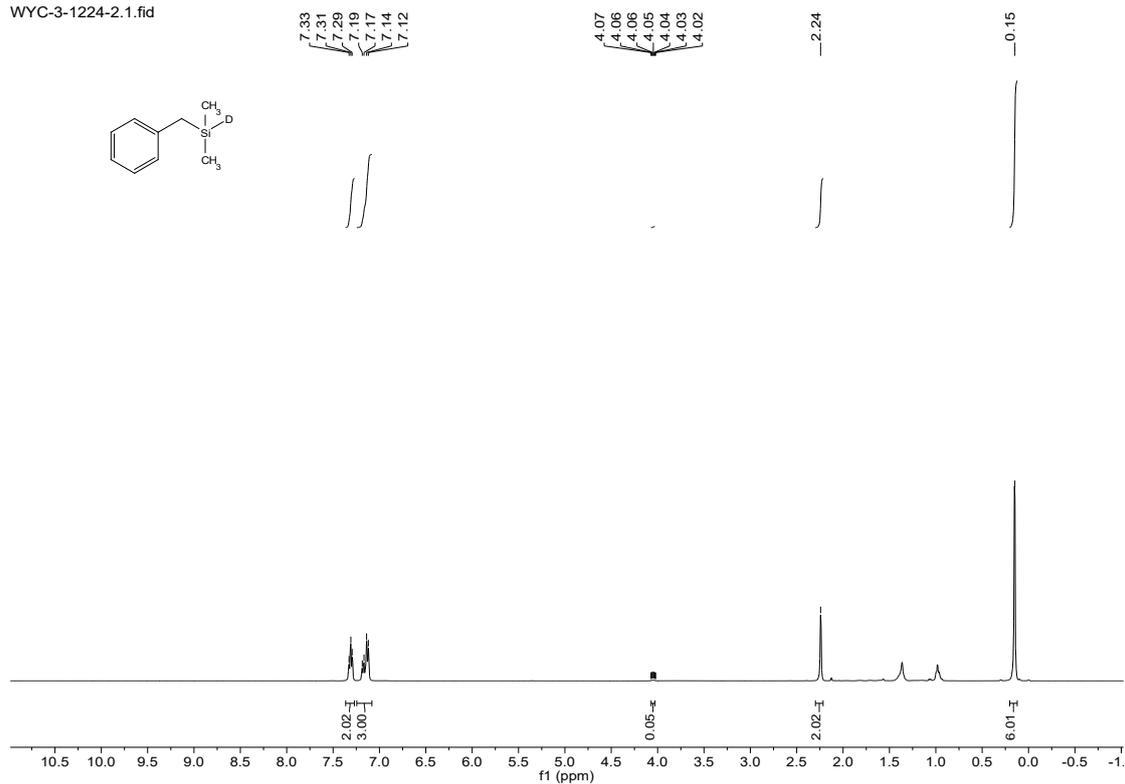
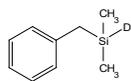


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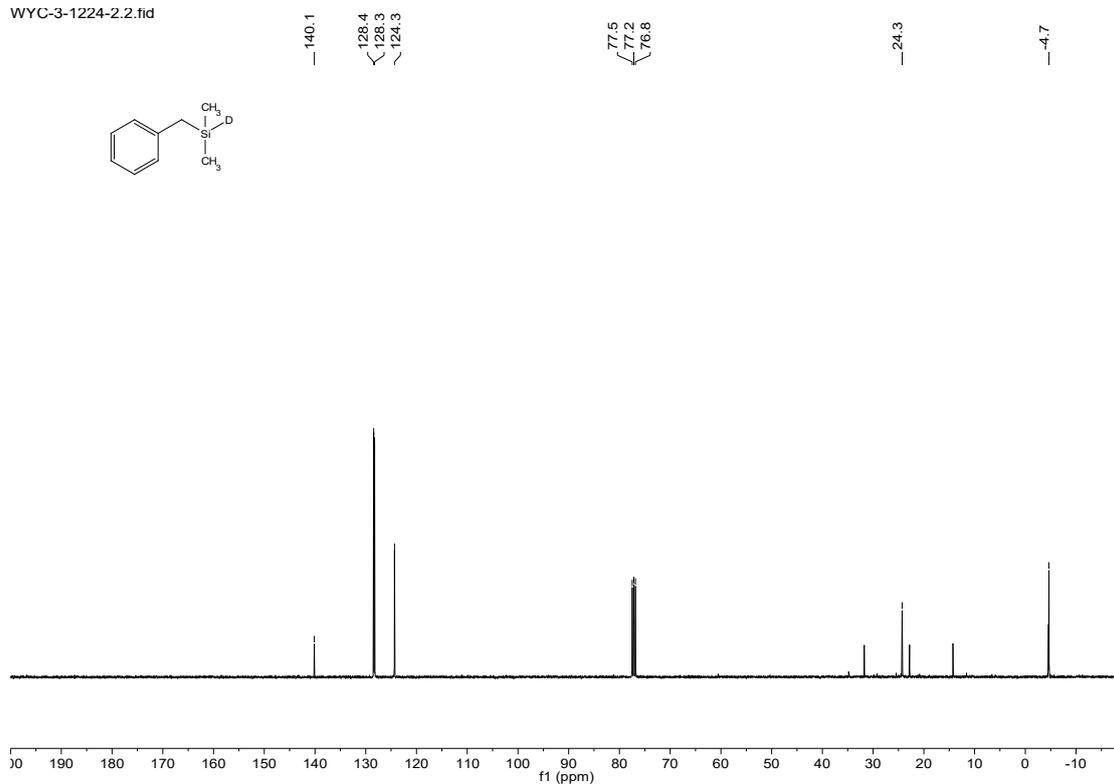
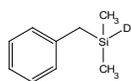


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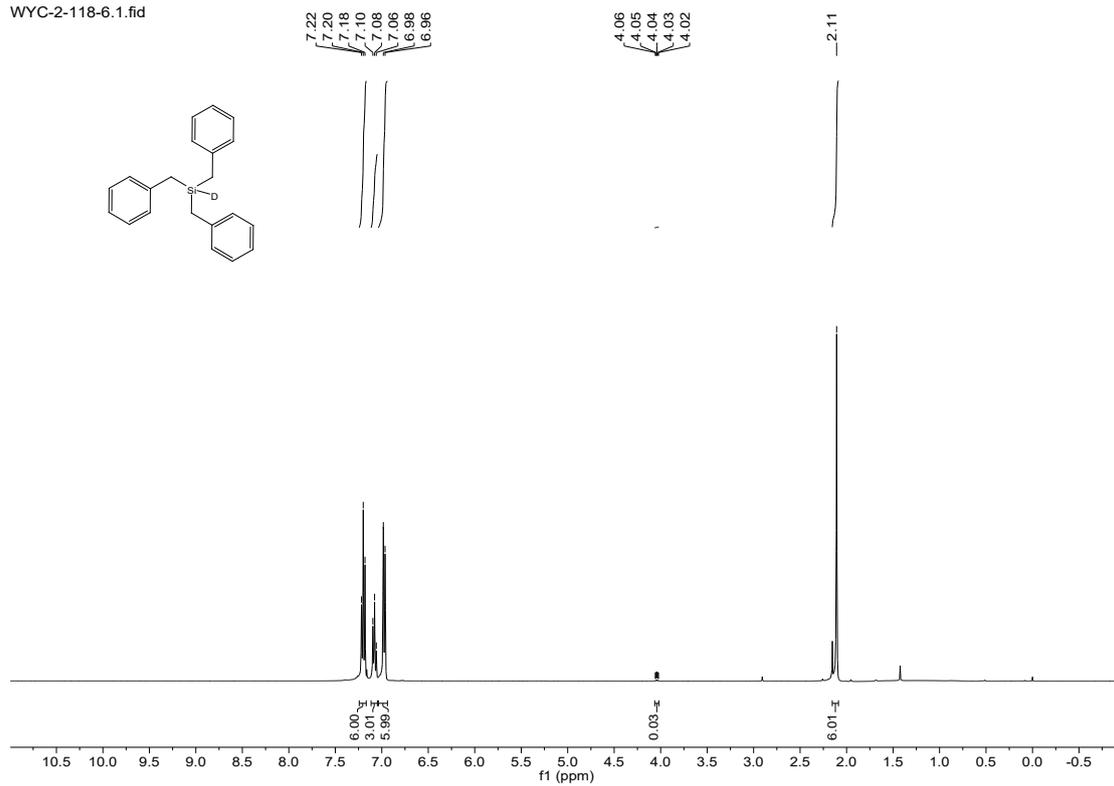


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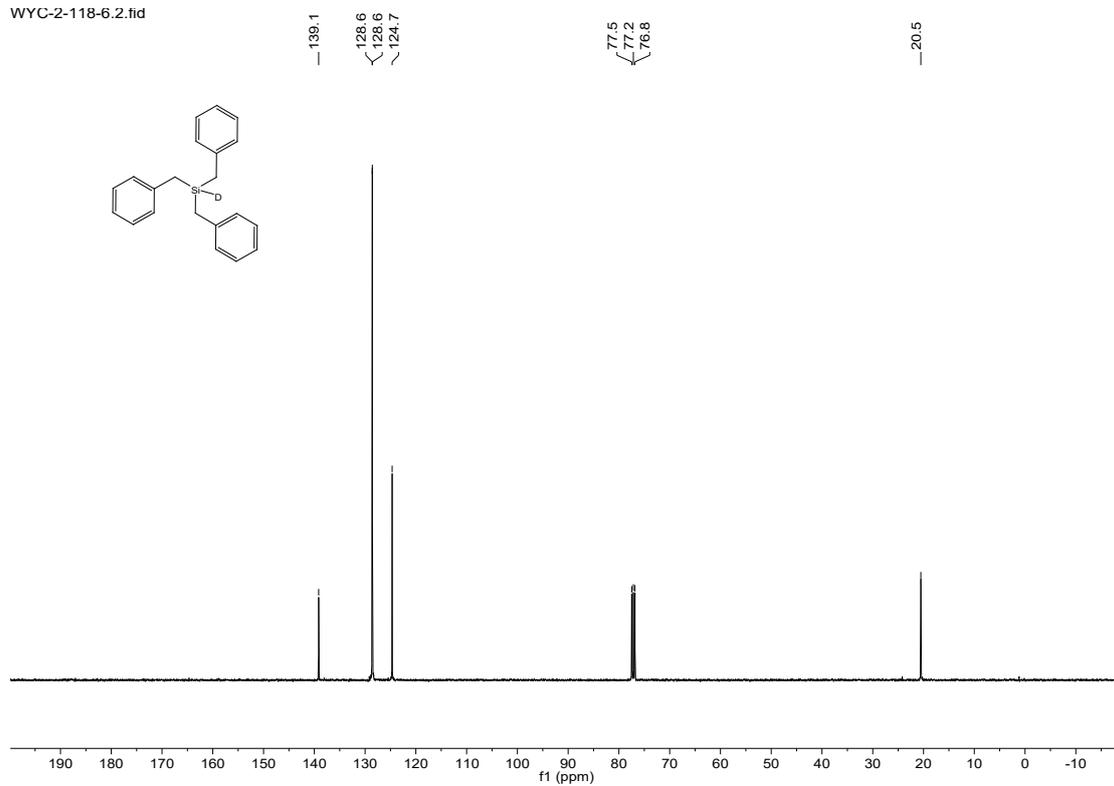


2f

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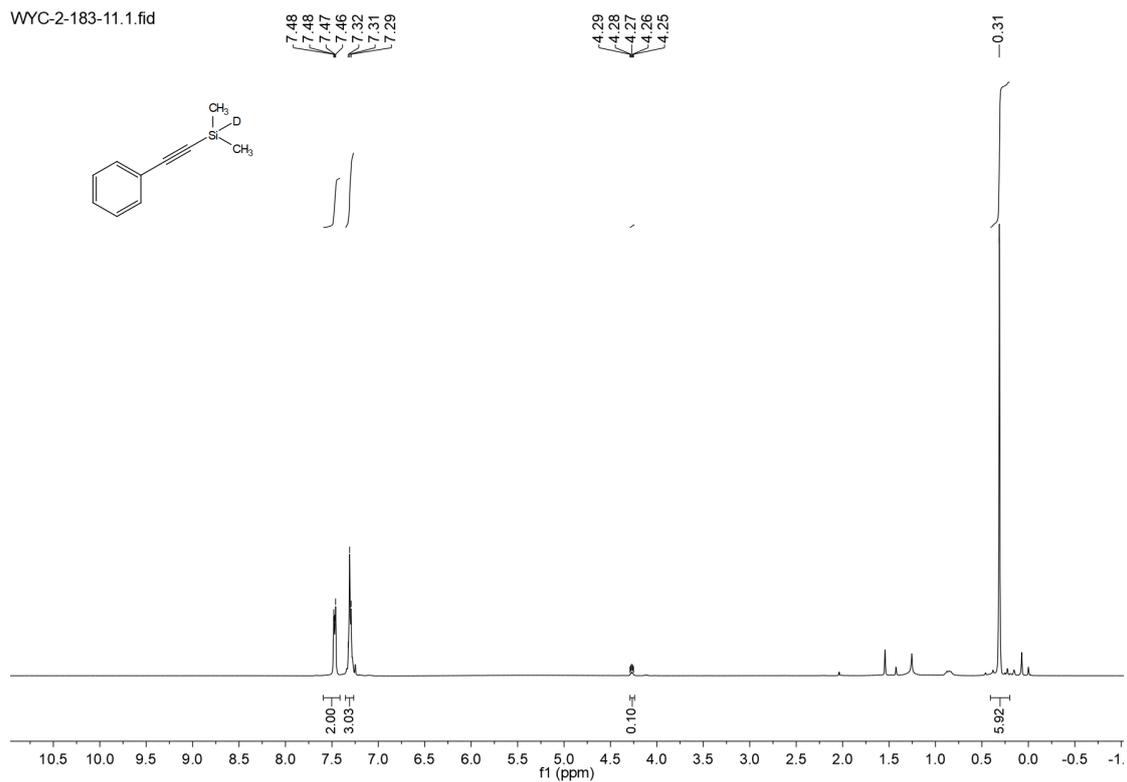


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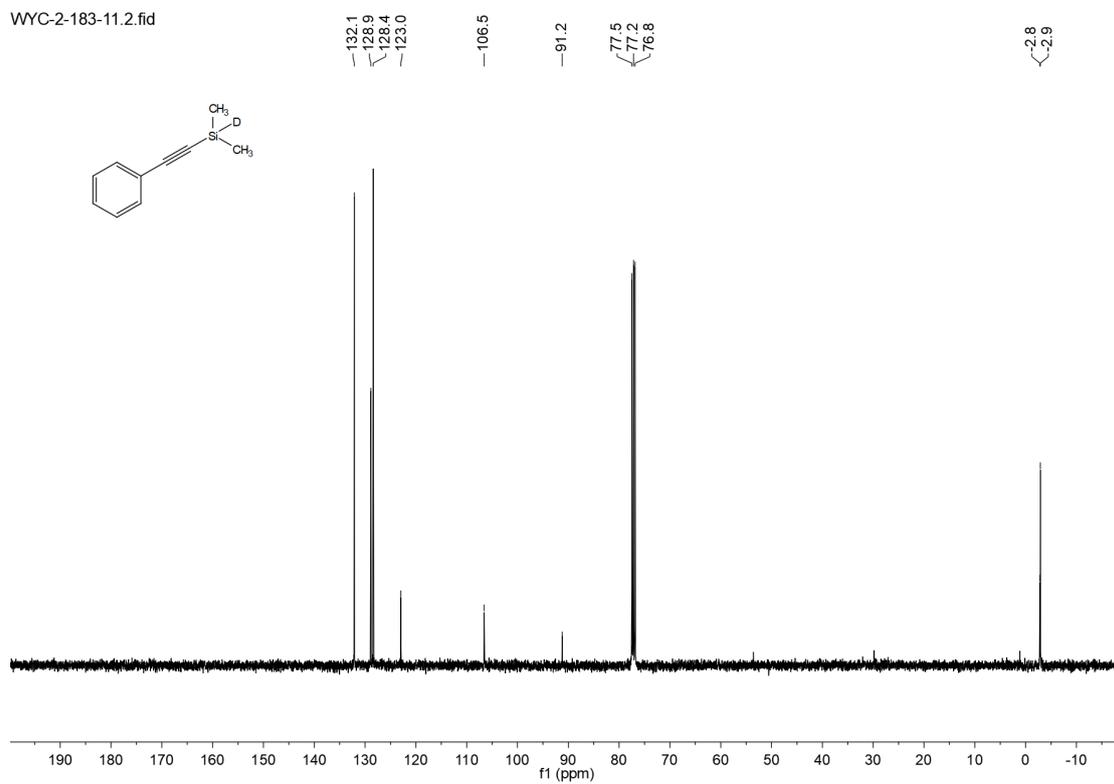


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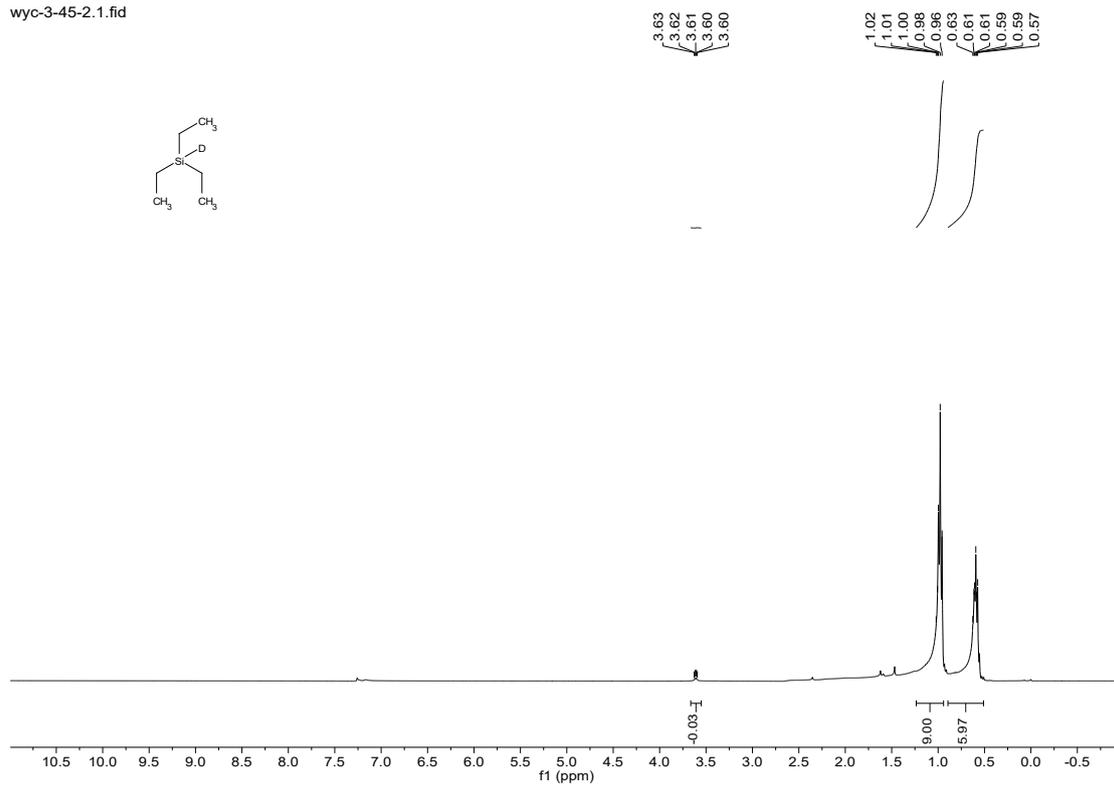
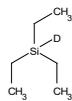


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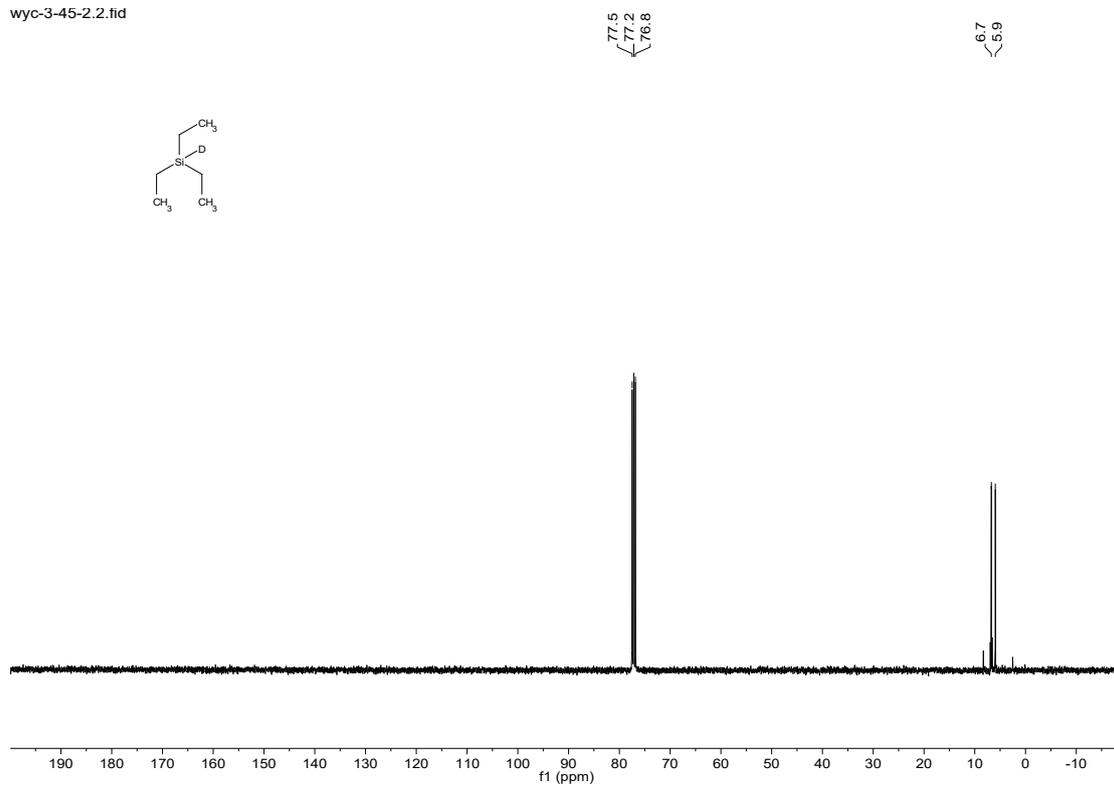
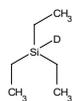


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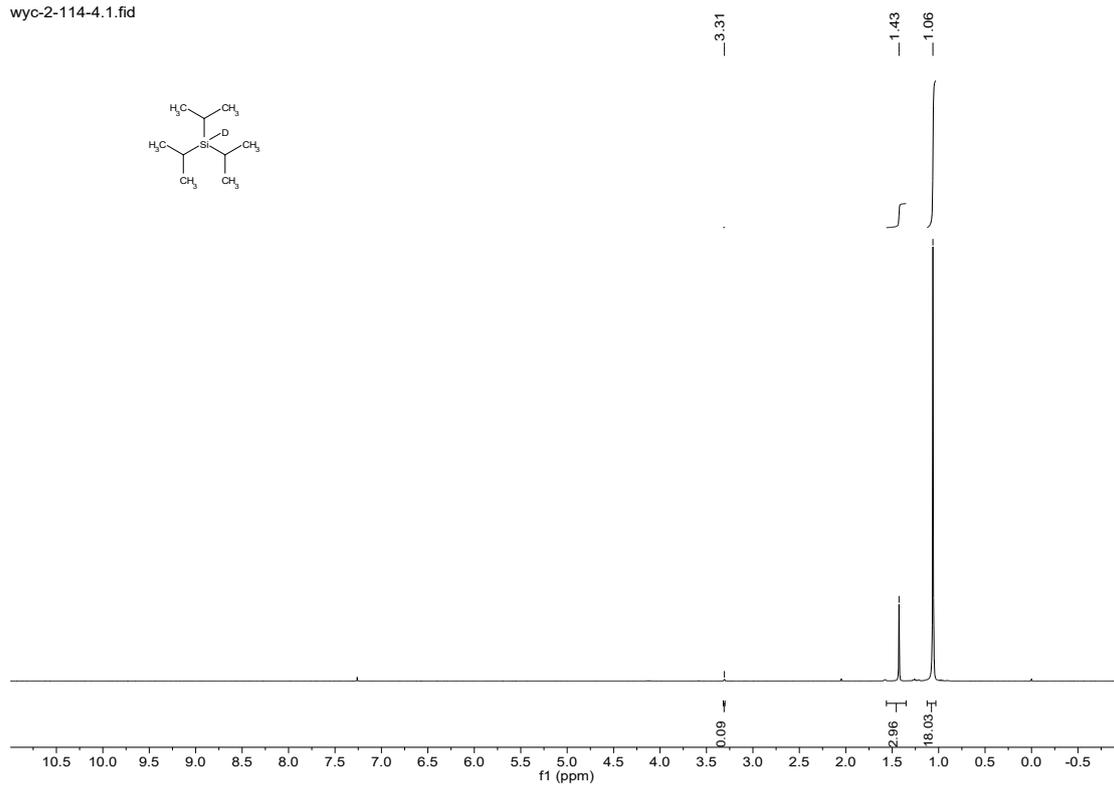


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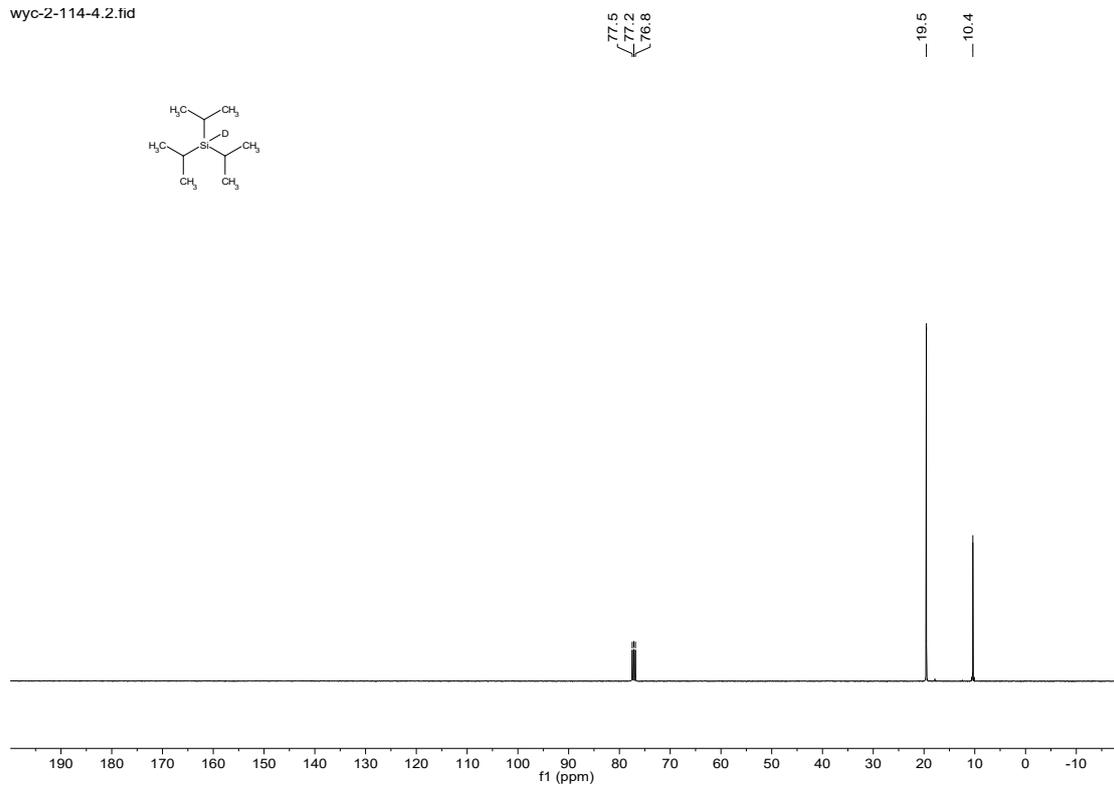


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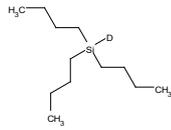


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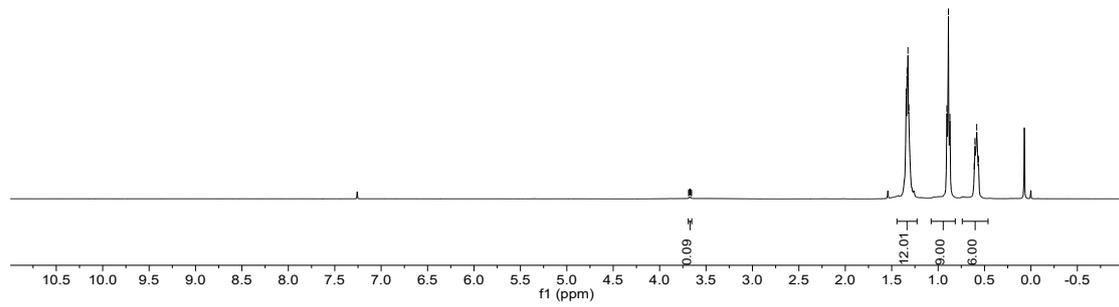
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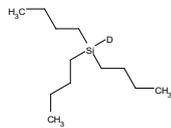


3.69  
3.68  
3.67  
3.66

1.34  
1.33  
1.33  
1.32  
0.91  
0.89  
0.87  
0.81  
0.60  
0.58  
0.56

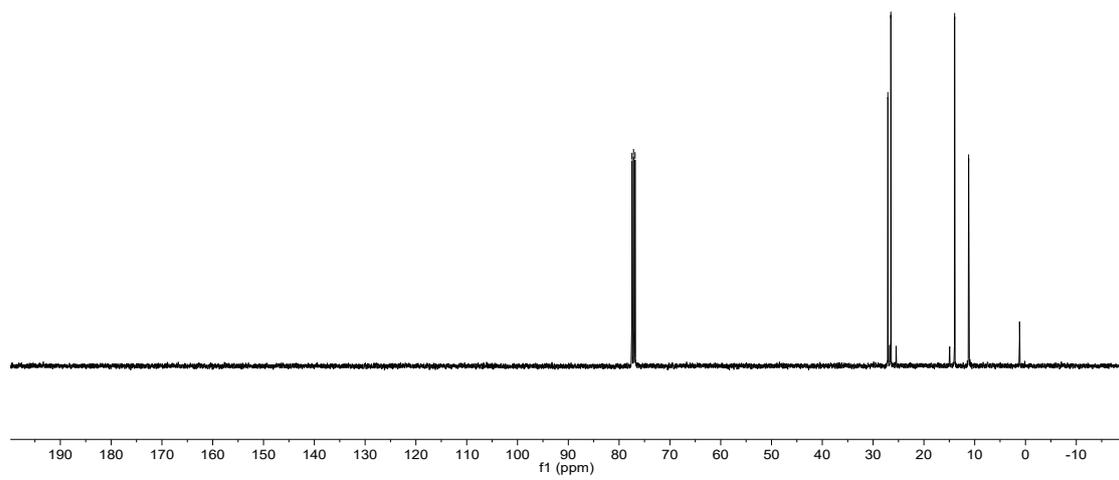


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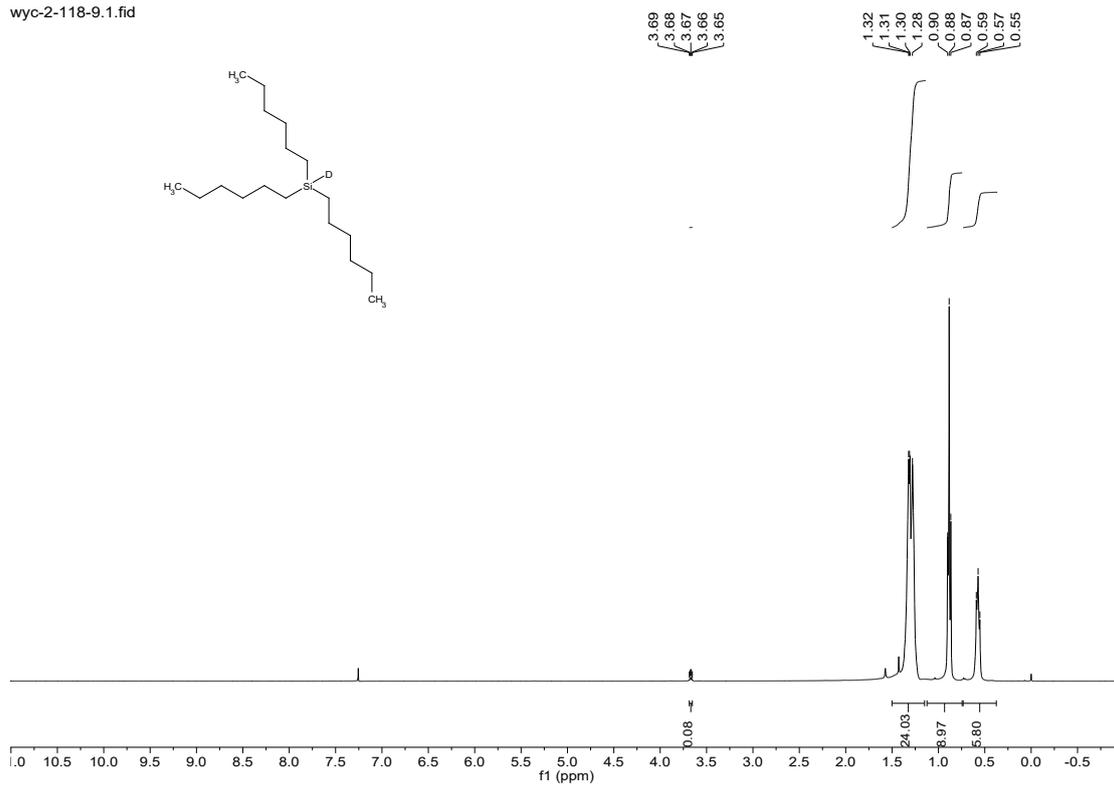
77.5  
77.2  
76.8

27.1  
26.5  
14.0  
11.2

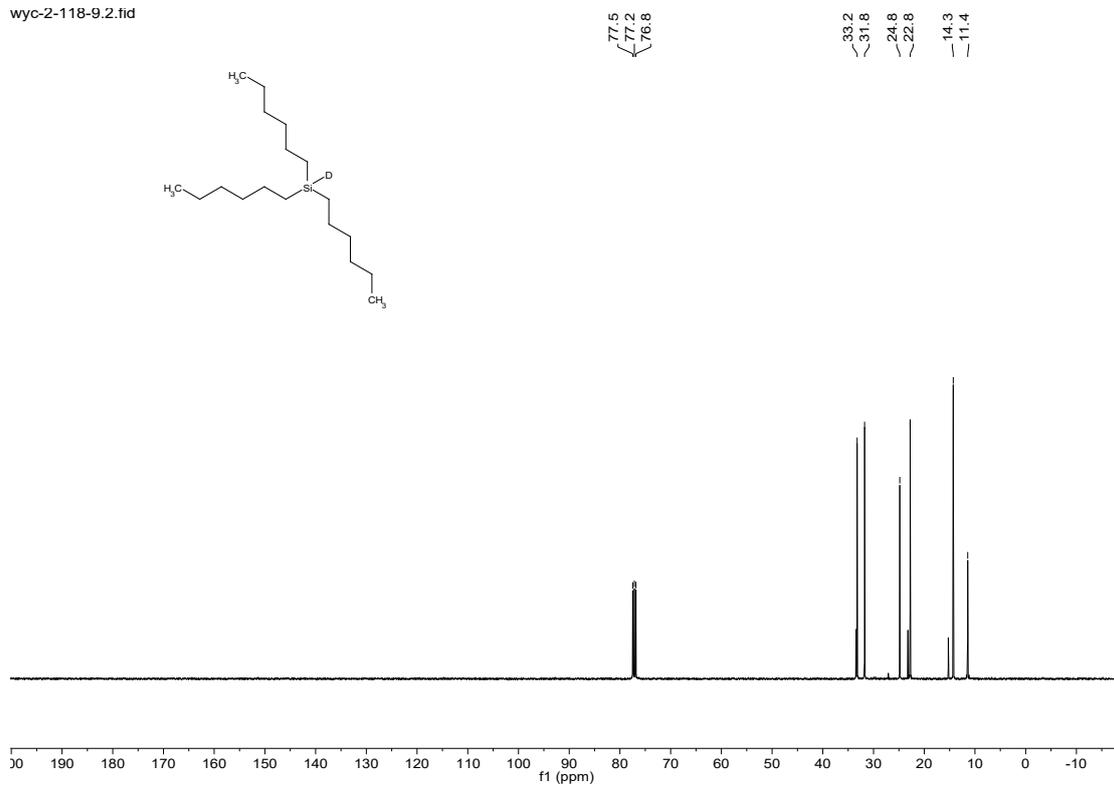


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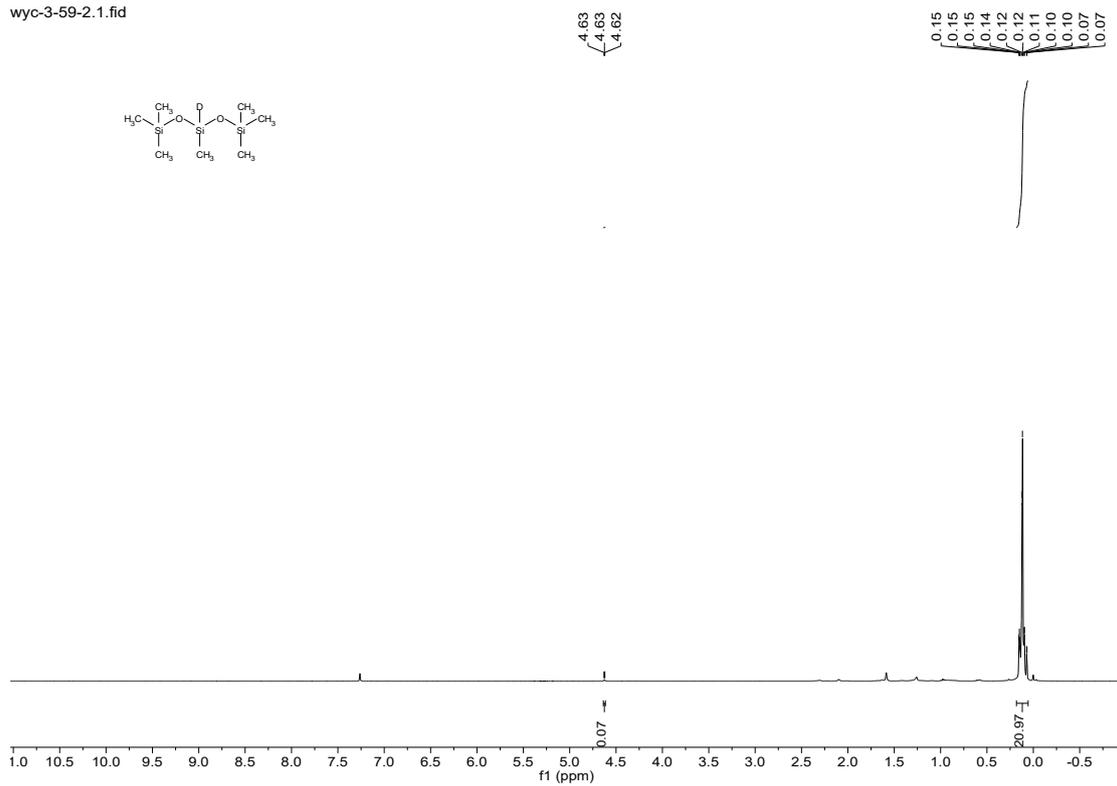


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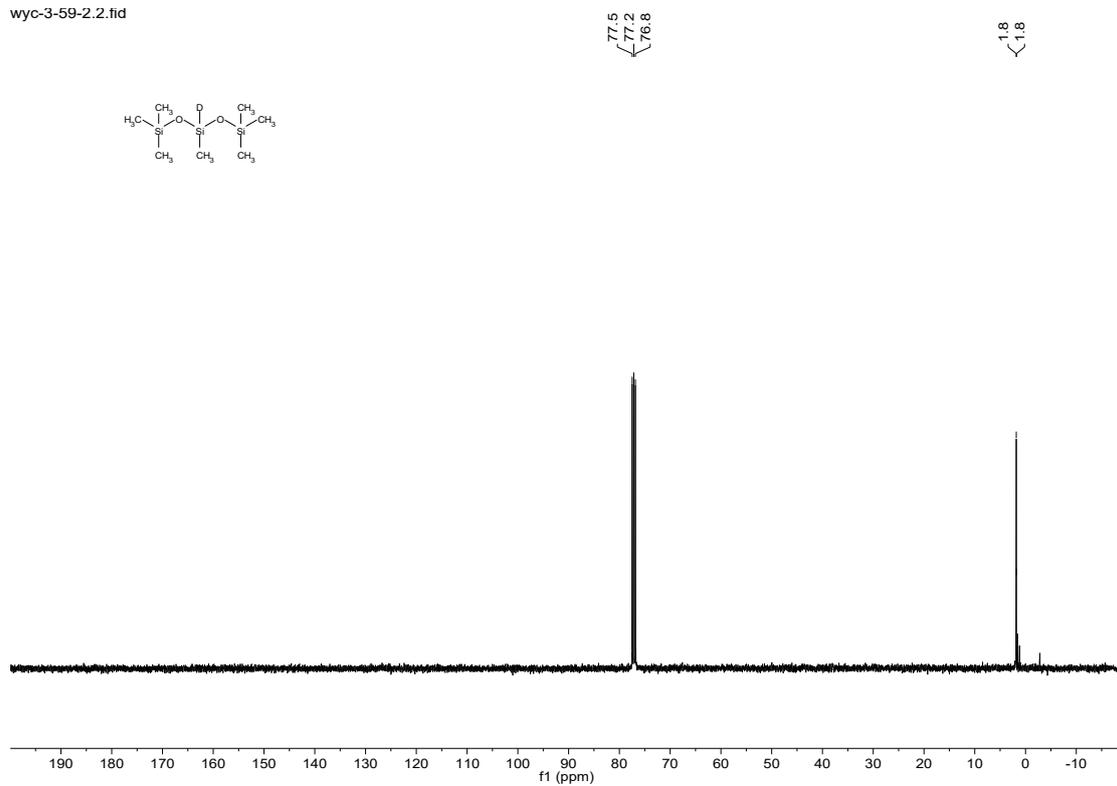


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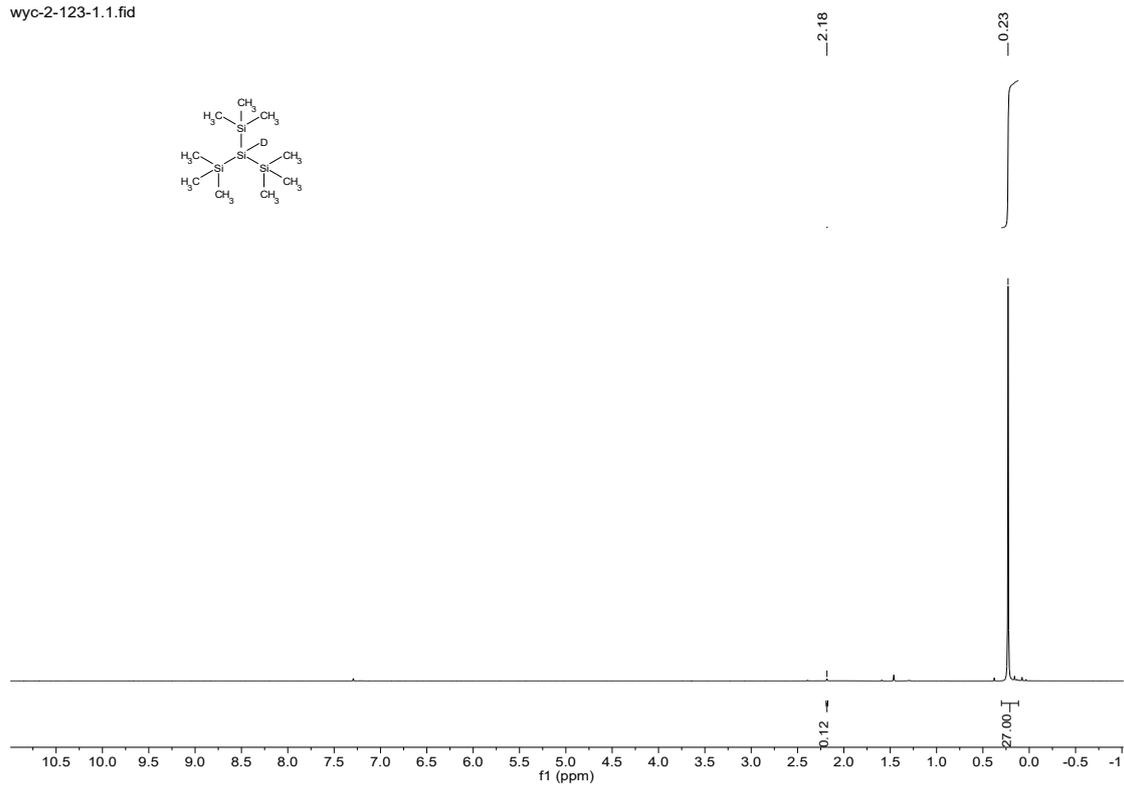


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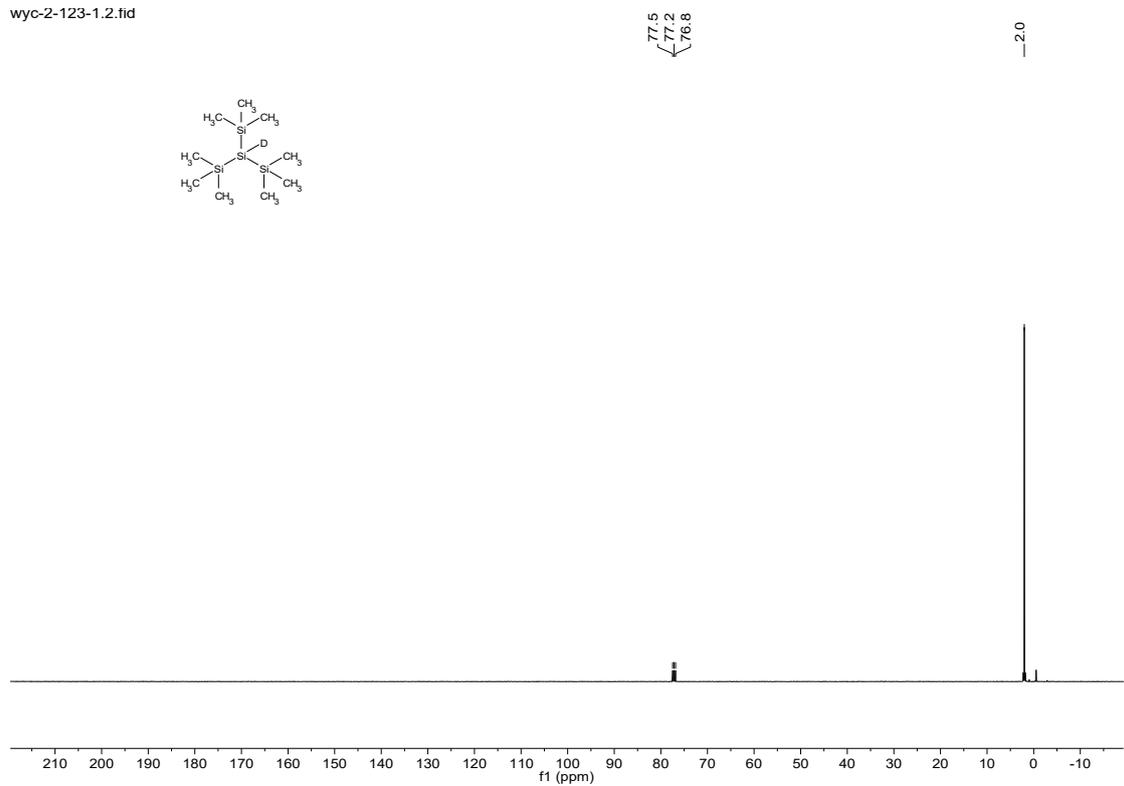


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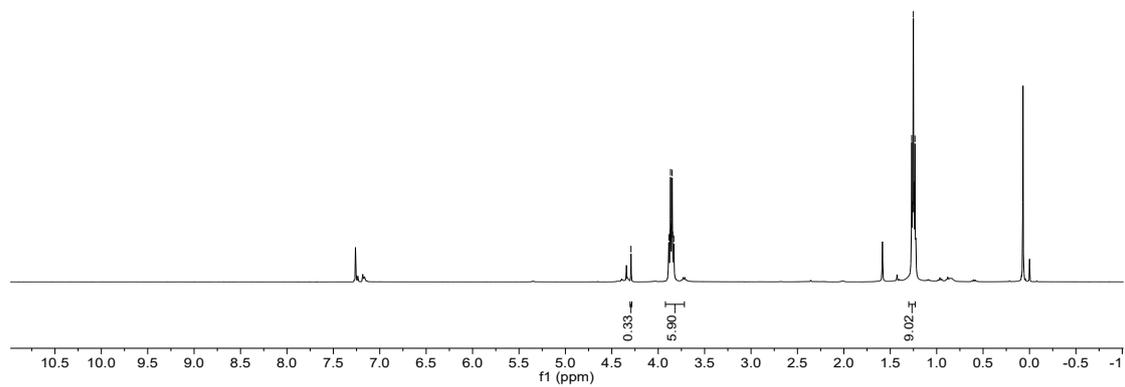
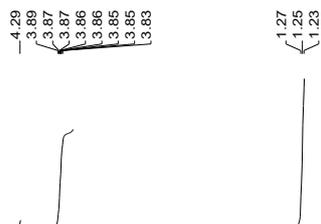
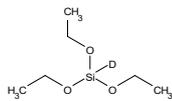


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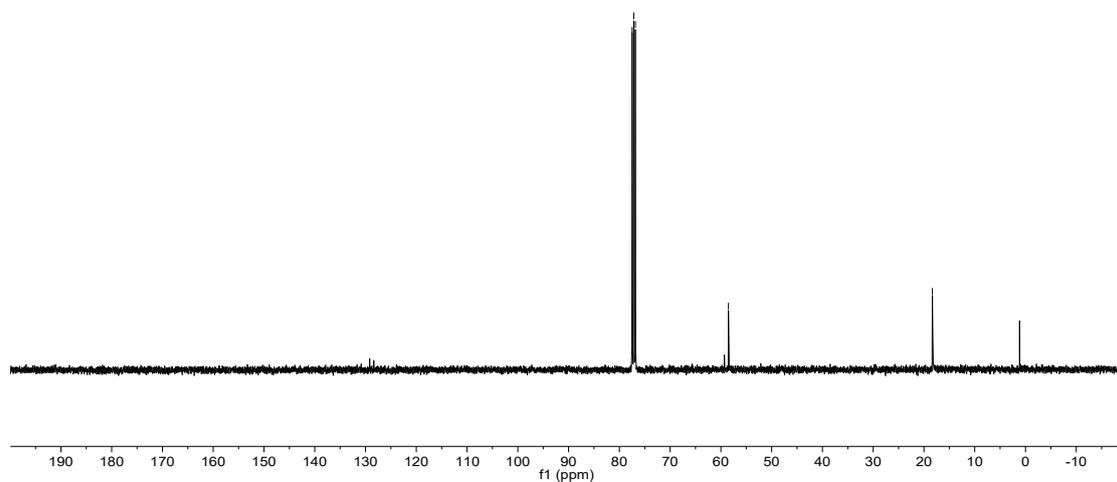
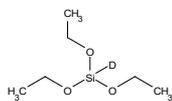


# 2n

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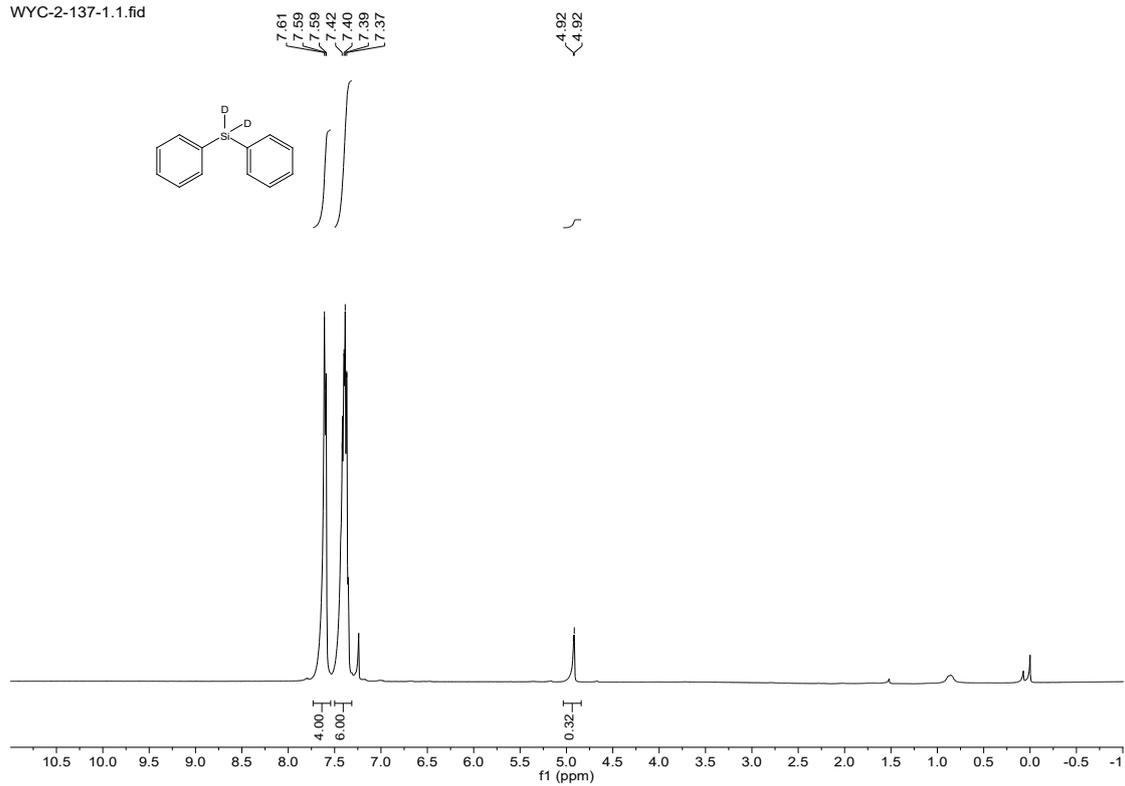


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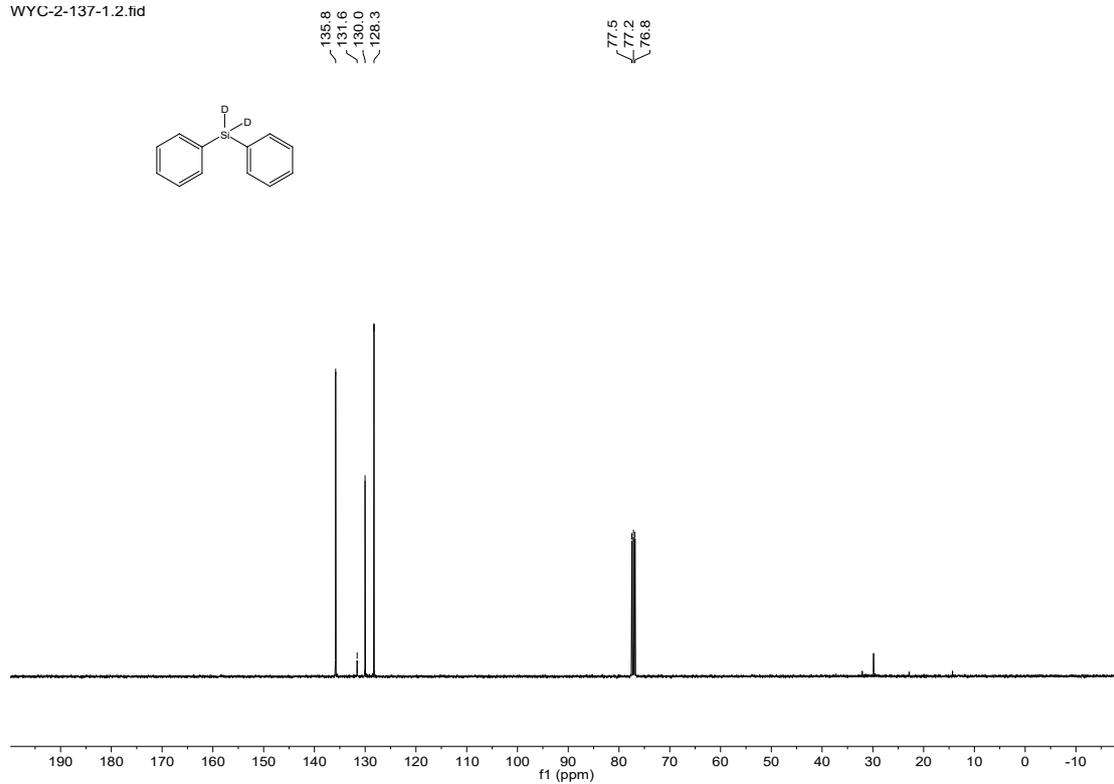


2o

WYC-2-137-1.1.fid

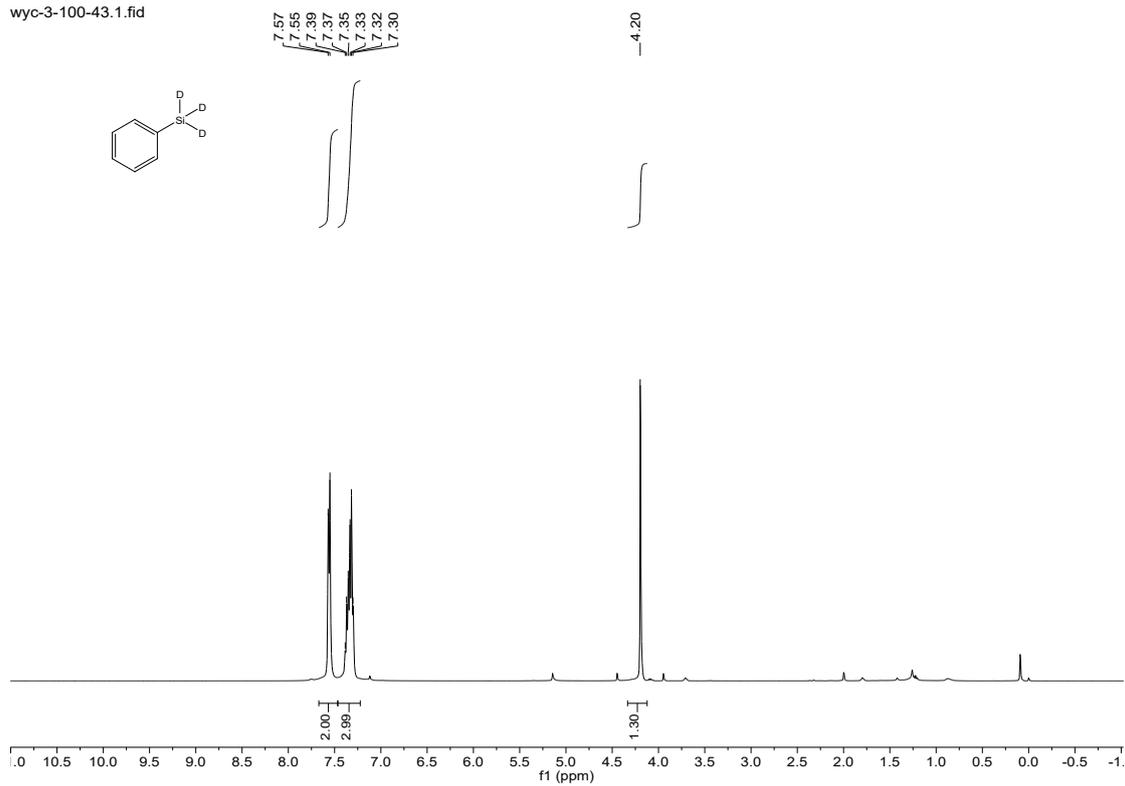


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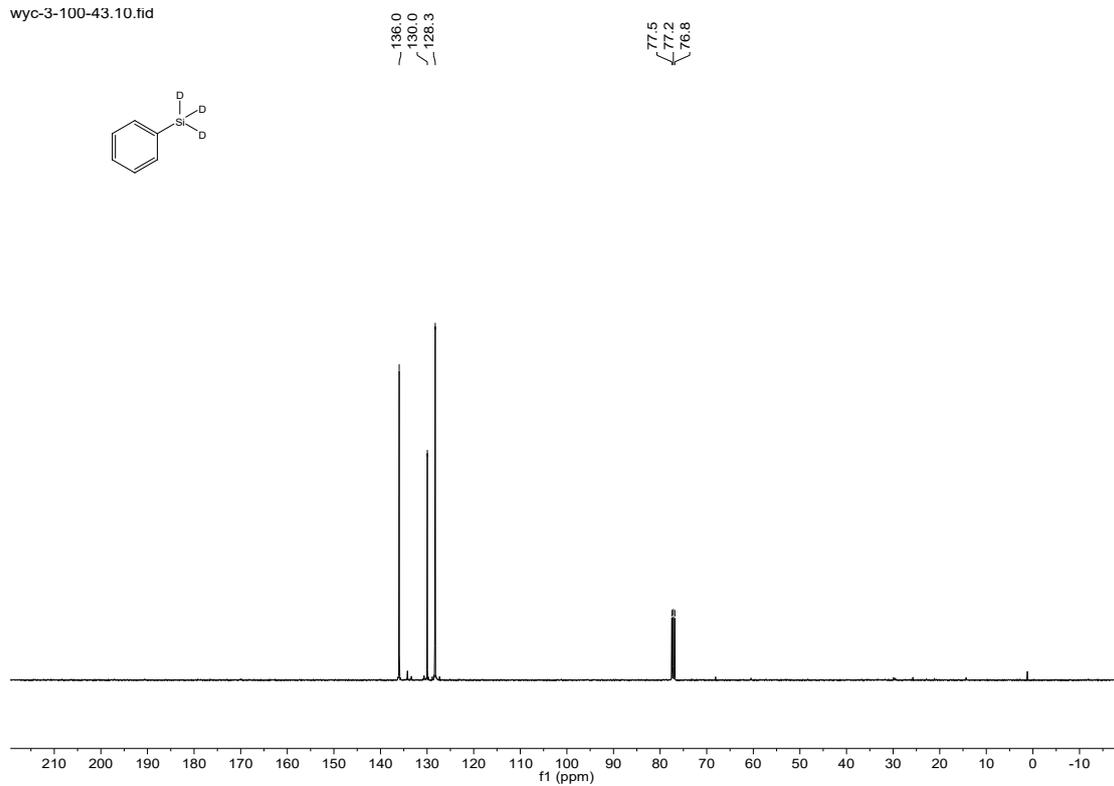


2p

wyc-3-100-43.1.fid

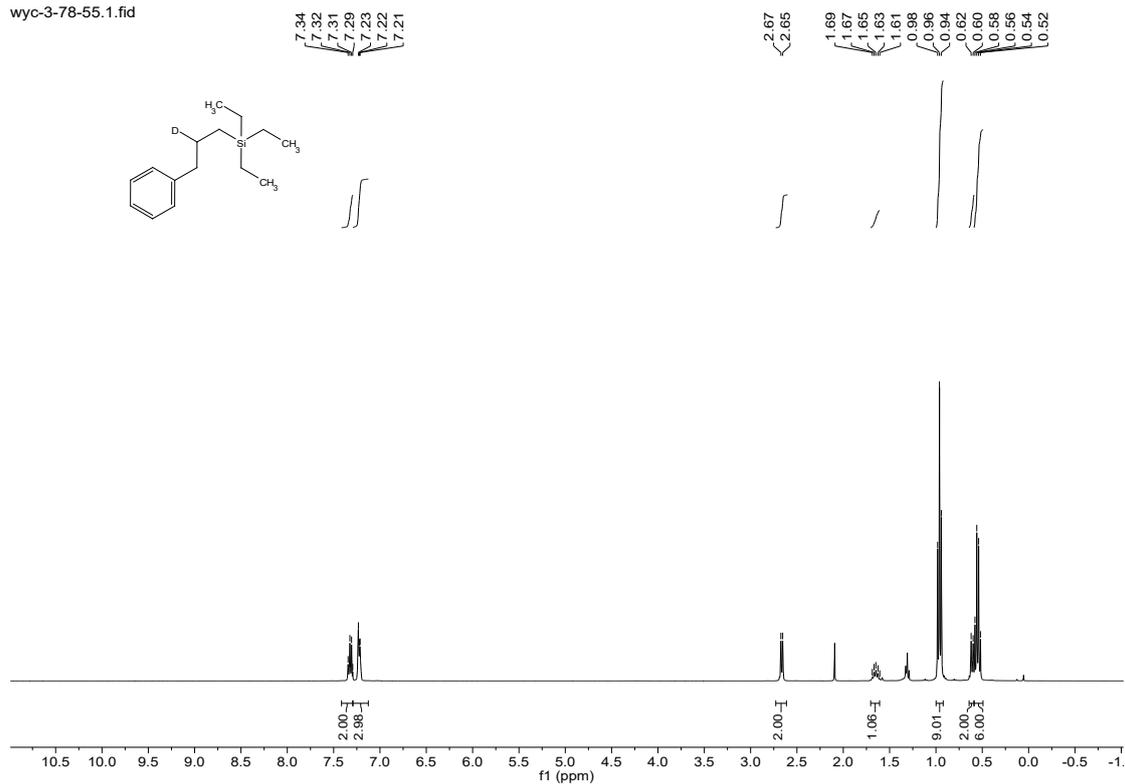


wyc-3-100-43.10.fid

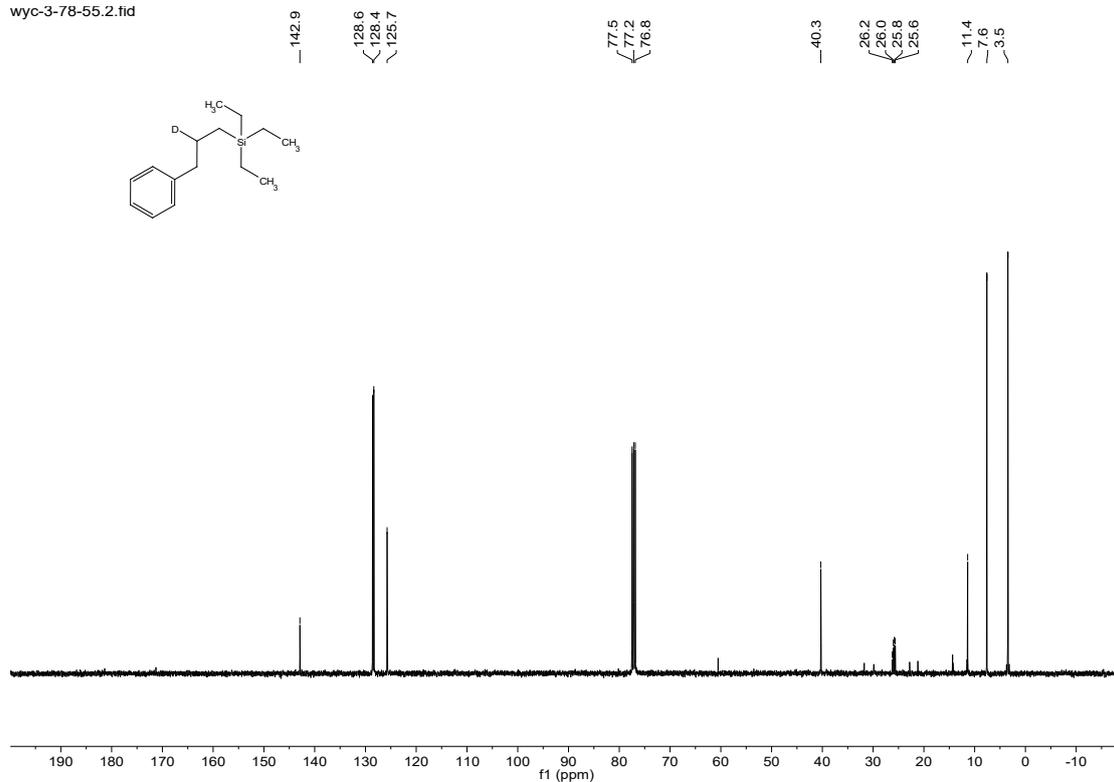


4a

wyc-3-78-55.1.fid

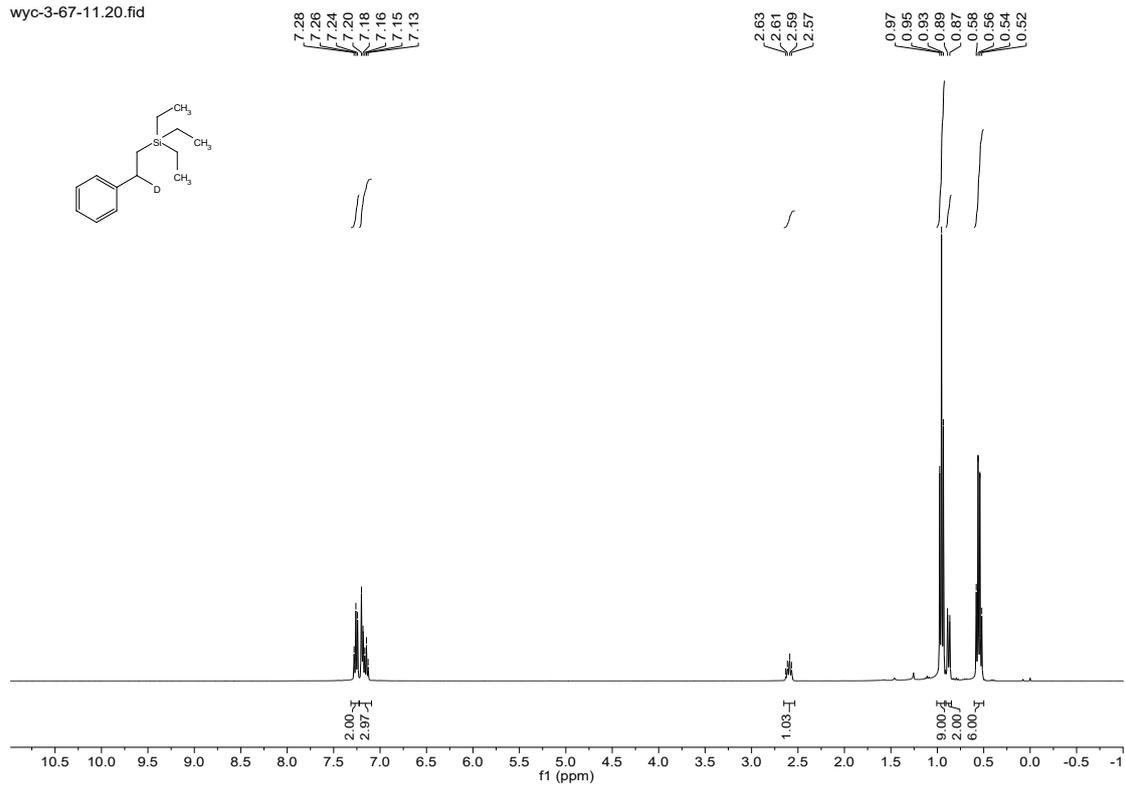


wyc-3-78-55.2.fid

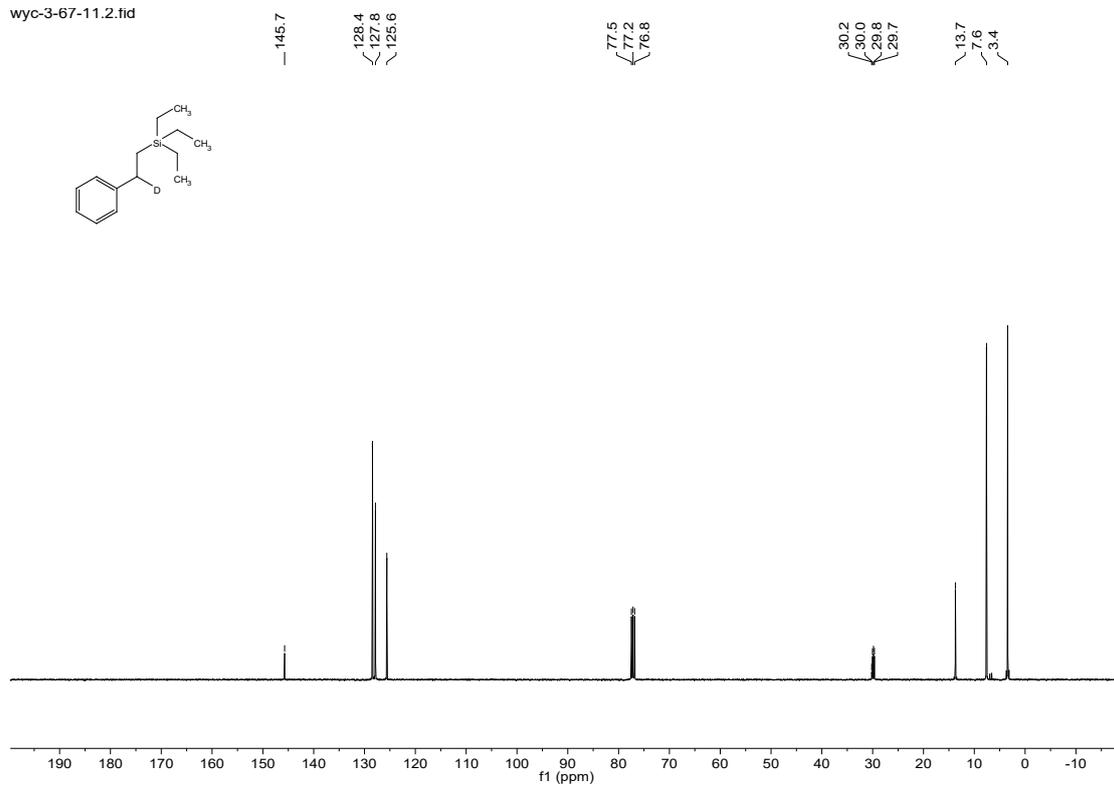


4b

wyc-3-67-11.20.fid

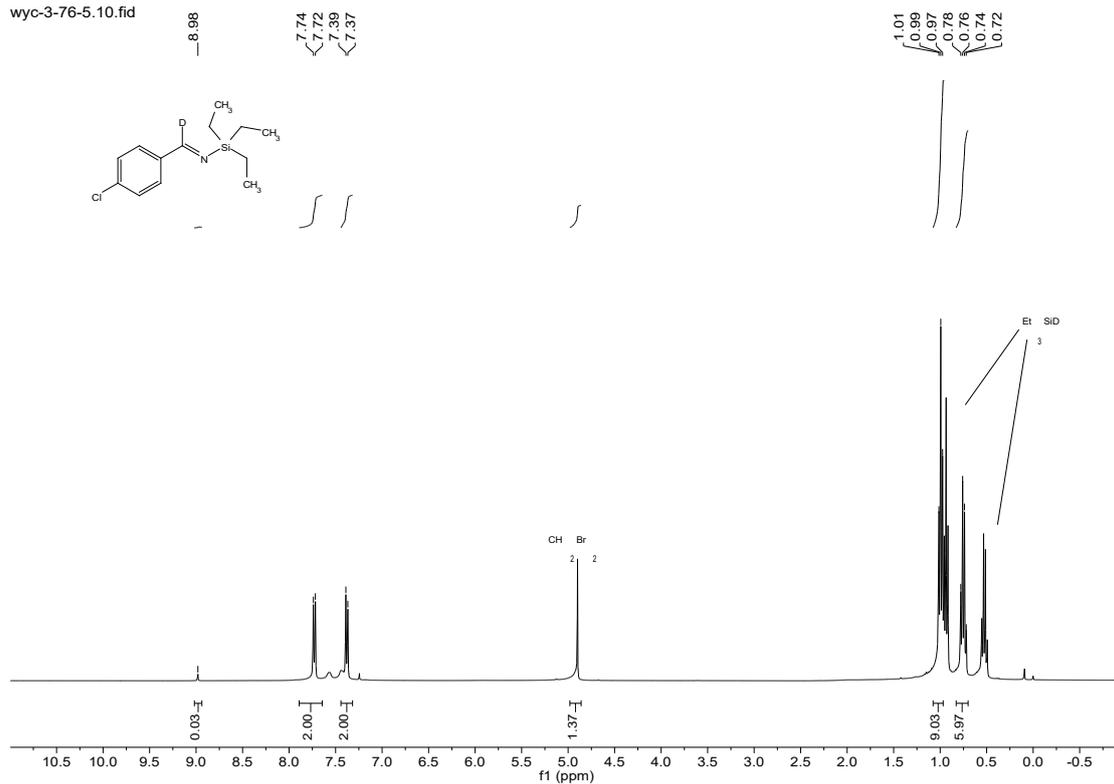


wyc-3-67-11.2.fid

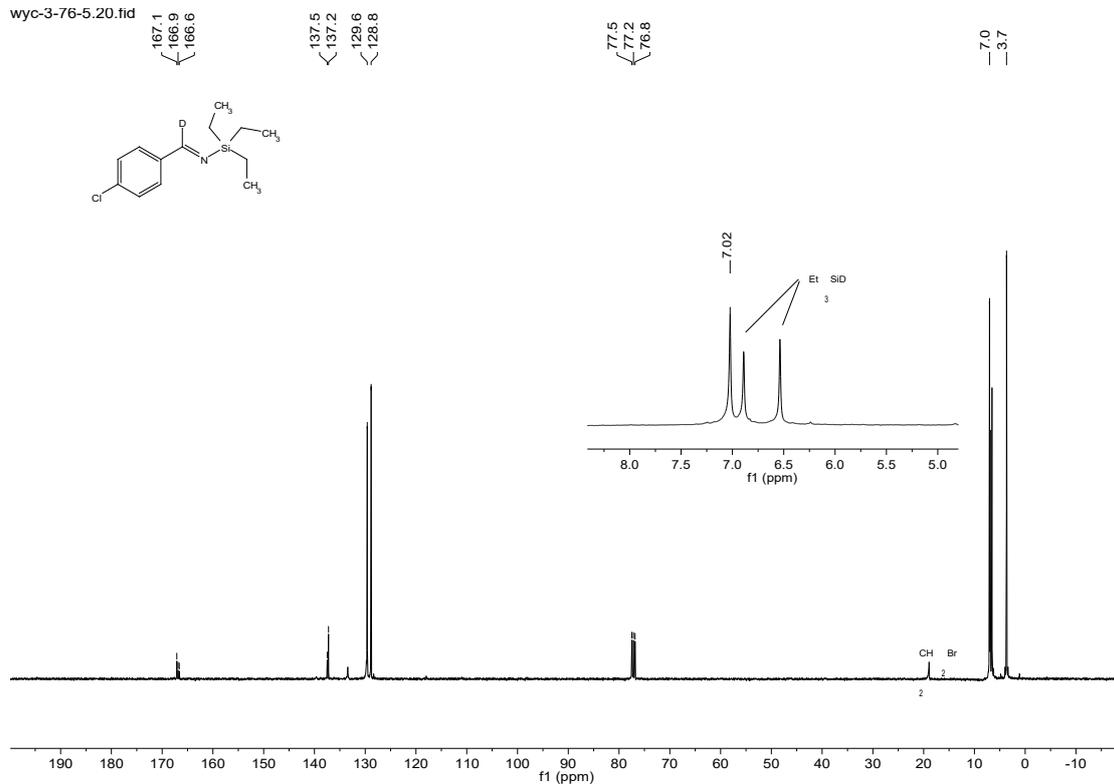


# 4c

wyc-3-76-5.10.fid

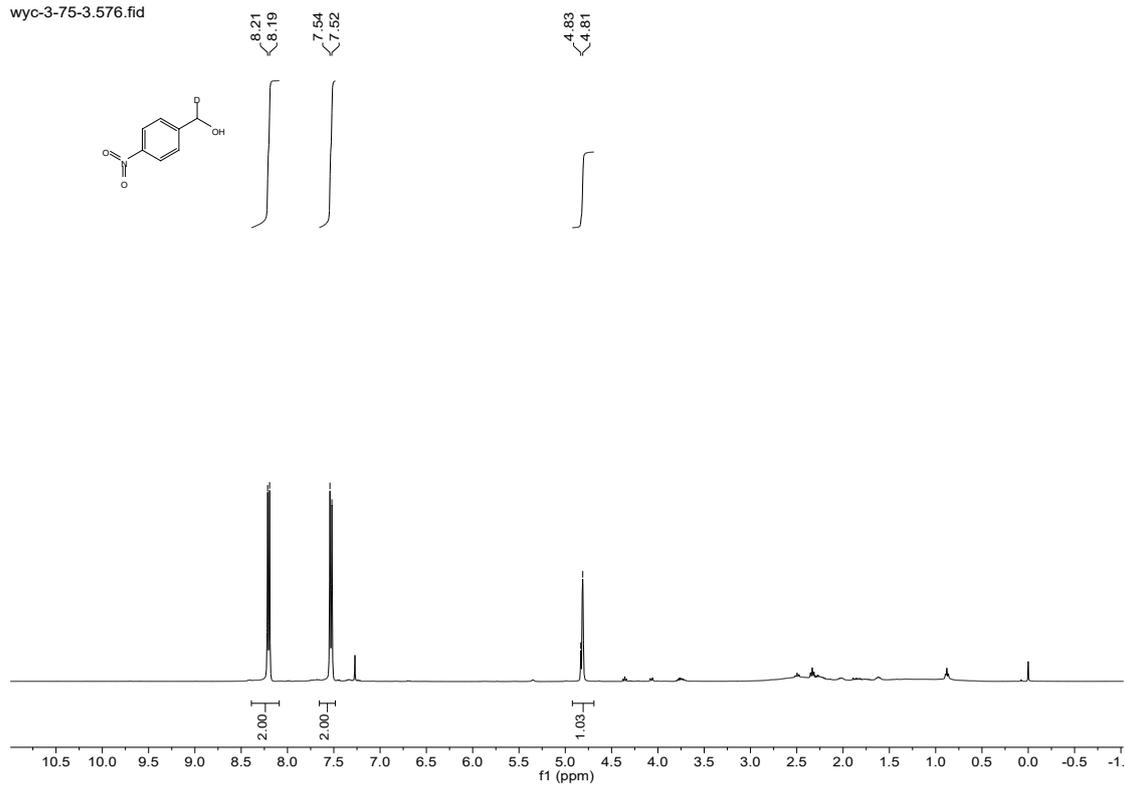


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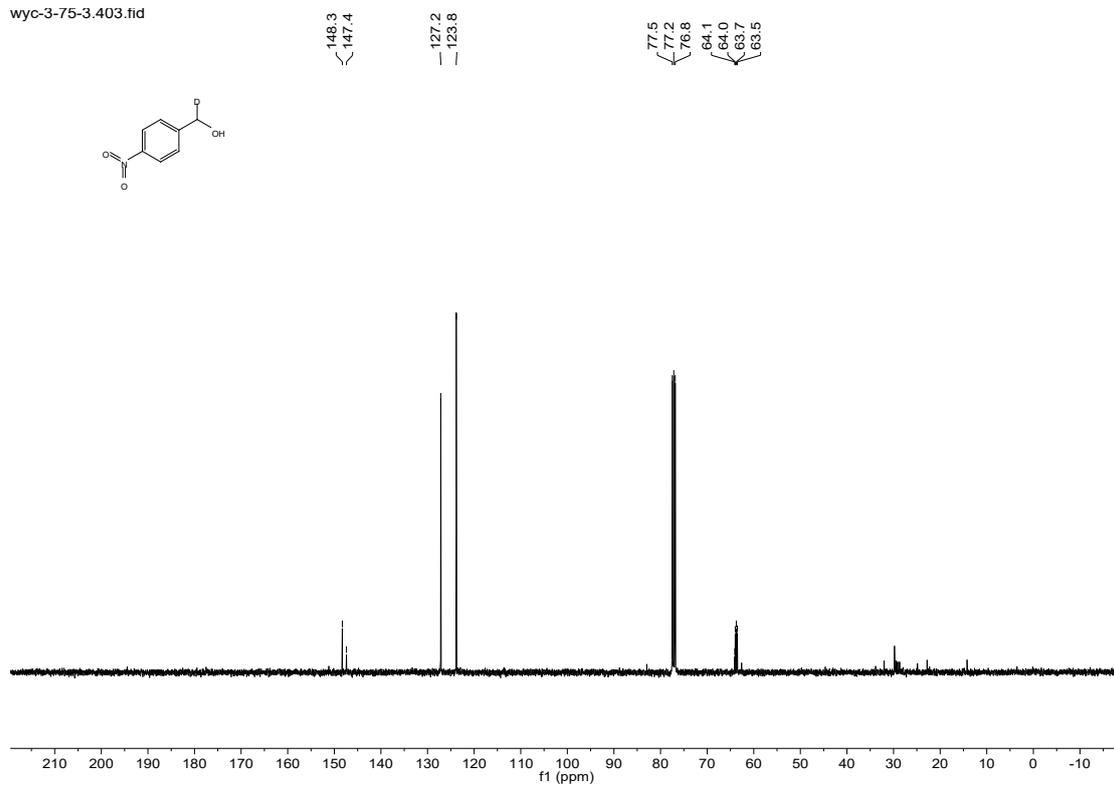


# 5d

wyc-3-75-3.576.fid

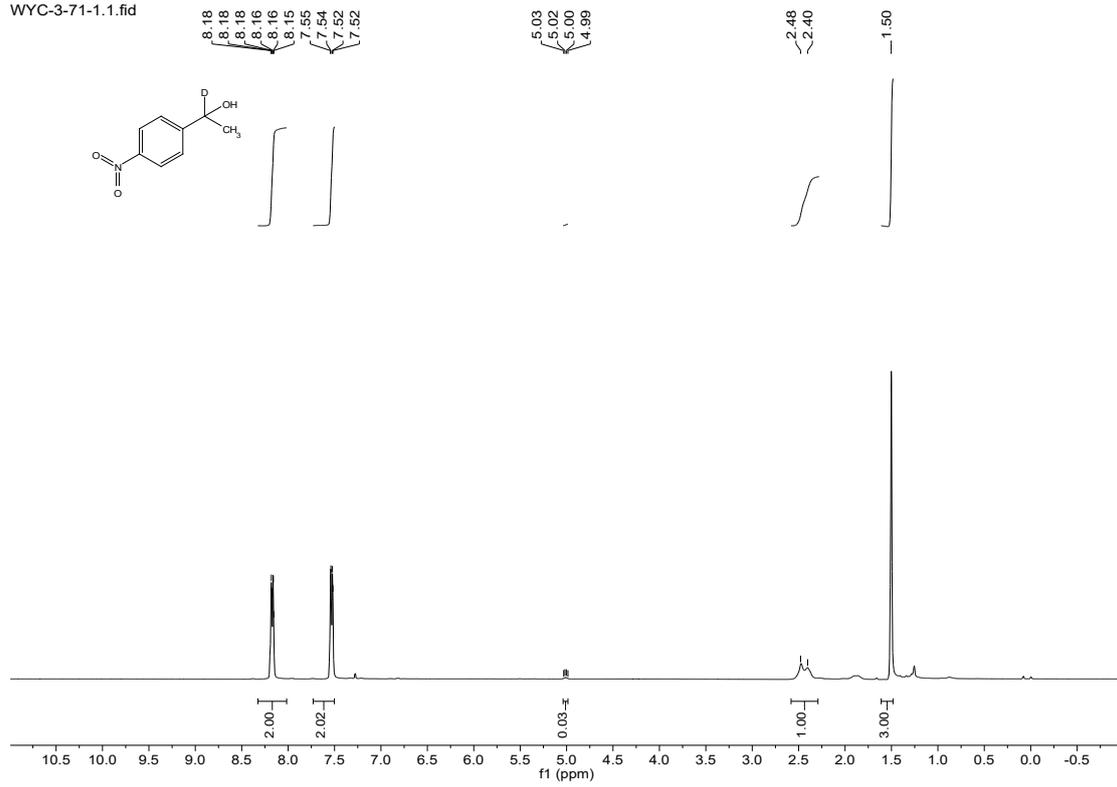


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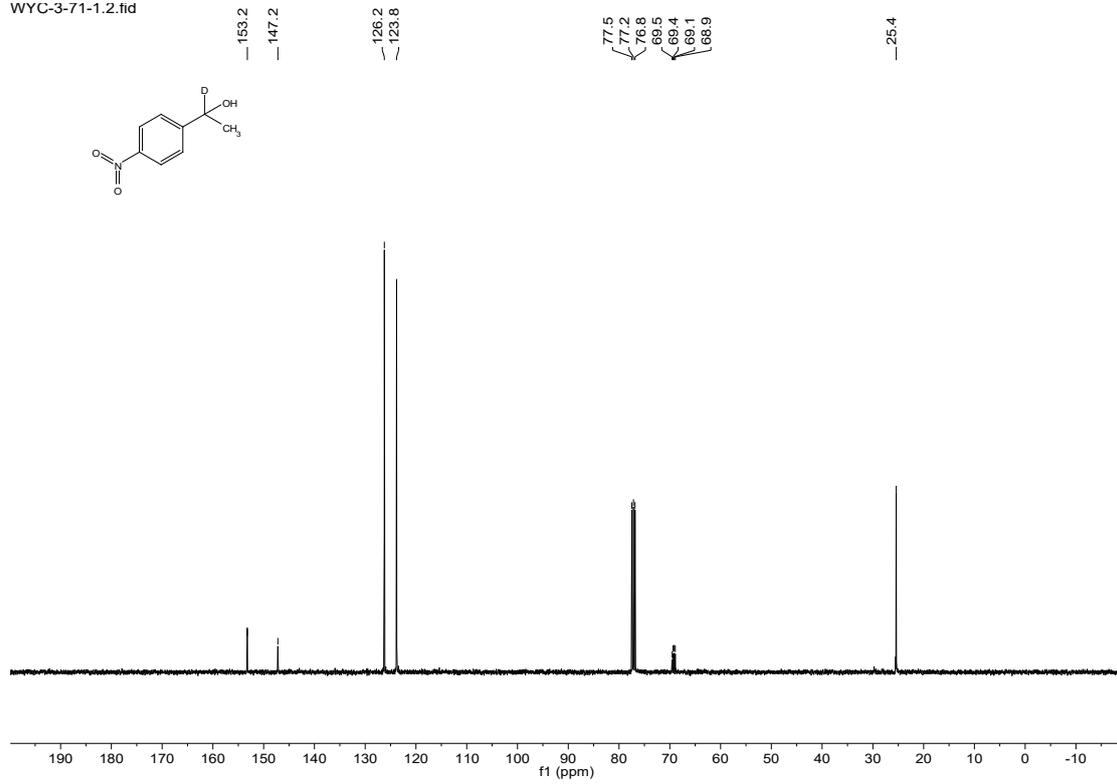


5e

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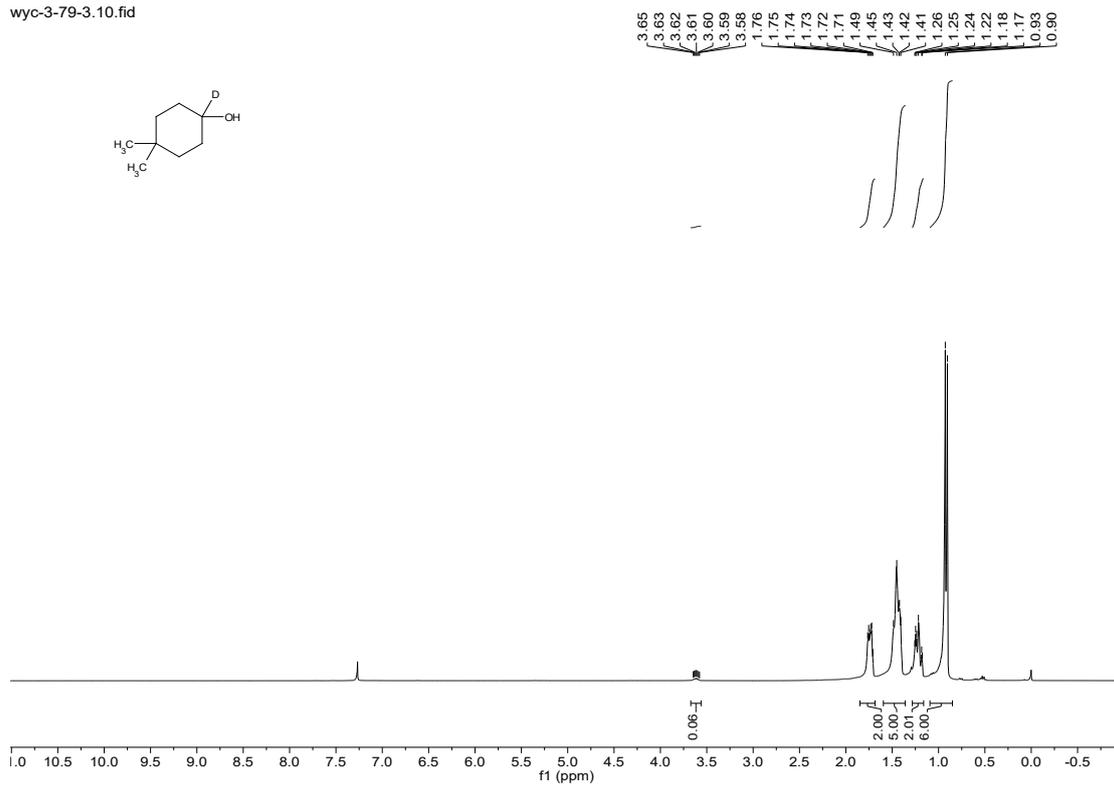
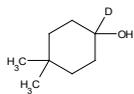


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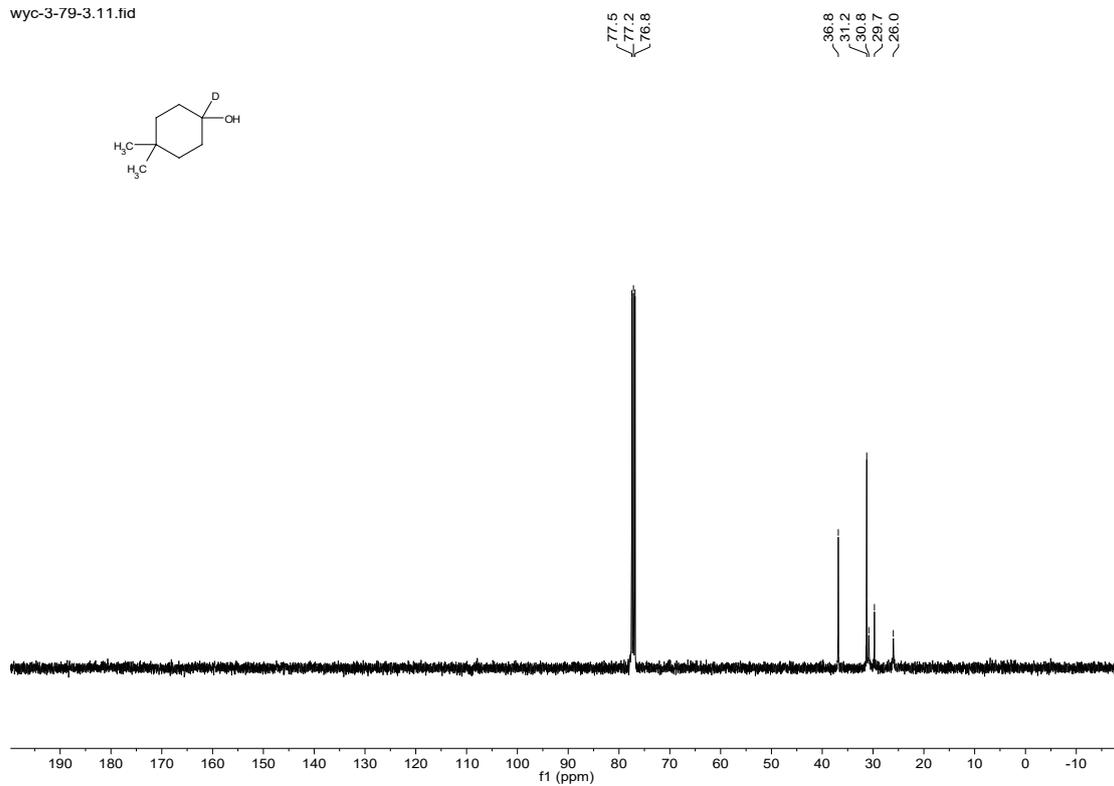
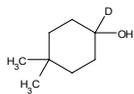


5f

wyc-3-79-3.10.fid

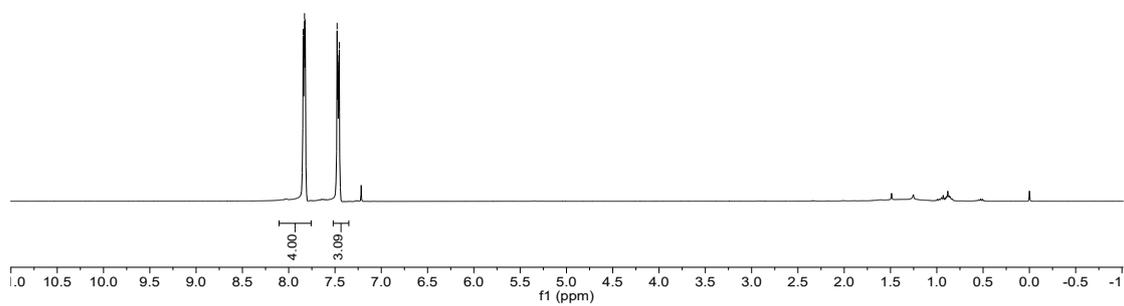
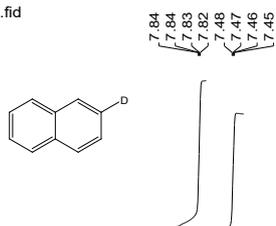


wyc-3-79-3.11.fid

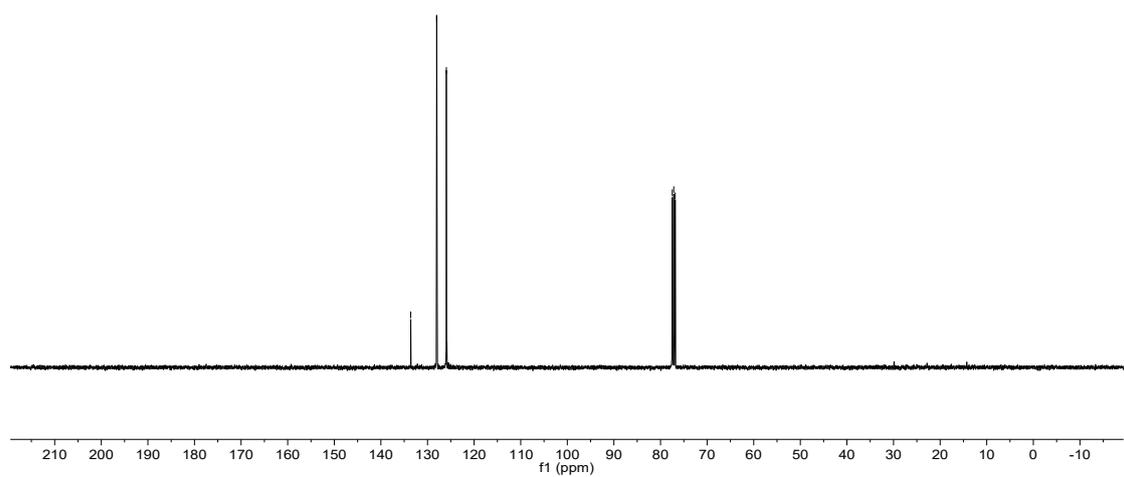
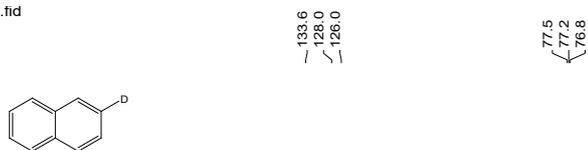


6g

wyc-3-69-1.1.fid



wyc-3-69-1.2.fid



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