

## Supporting Information

# Catalytic Hydrotrifluoromethylation of Styrenes and Unactivated Aliphatic Alkenes via an Organic Photoredox System

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## I. General Information

**General Methods.** Infrared (IR) spectra were obtained using a Jasco 260 Plus Fourier transform infrared spectrometer. Proton, carbon, and fluorine magnetic resonance spectra ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and  $^{19}\text{F}$  NMR) were recorded on a Bruker model DRX 400 or 600 ( $^1\text{H}$  NMR at 400 MHz or 600 MHz,  $^{13}\text{C}$  NMR at 100 MHz or 150 MHz, and  $^{19}\text{F}$  NMR at 376 MHz or 564 MHz) spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in solvent ( $^1\text{H}$  NMR:  $\text{CHCl}_3$  at 7.27 ppm). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the residual solvent peak ( $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  at 77.0 ppm). Chemical shifts for fluorine are reported in parts per million from  $\text{CFCl}_3$  ( $\delta$  0 ppm) as the external standard. NMR data are represented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, sept = septuplet, oct = octuplet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained using a Micromass Quattro II (triple quad) instrument with nanoelectrospray ionization. Analytical thin layer chromatography (TLC) was performed on SiliaPlate 250  $\mu\text{m}$  thick silica gel plates provided by Silicycle. Visualization was accomplished using fluorescence quenching,  $\text{KMnO}_4$  stain, or ceric ammonium molybdate (CAM) stain followed by heating. Organic solutions were concentrated under reduced pressure using a Büchi rotary evaporator with an ice water bath for volatile compounds. Purification of the reaction products was carried out by chromatography using Siliaflash-P60 (40-63  $\mu\text{m}$ ) or Siliaflash-T60 (5-20  $\mu\text{m}$ ) silica gel purchased from Silicycle.<sup>1</sup> All reactions were carried out under an inert atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise noted. Irradiation of photochemical reactions was carried out using a 15W PAR38 blue LED flood lamp purchased from EagleLight (Carlsbad, CA), with standard borosilicate glass vials purchased from Fisher Scientific. Gas chromatography (GC) was performed on an Agilent 6850 series instrument equipped with a split-mode capillary injection system and Agilent 5973 network mass spec detector (MSD). Yield refers to isolated yield of analytically pure material unless otherwise noted. GC yields were determined with 1,3-dimethoxybenzene as an internal standard. NMR yields were determined using hexamethyldisiloxane as an internal standard,

**Materials.** Commercially available reagents were purchased from Sigma Aldrich, Acros, Alfa Aesar, or TCI, and used as received unless otherwise noted. Diethyl ether ( $\text{Et}_2\text{O}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), tetrahydrofuran (THF), toluene, and dimethylformamide (DMF) were dried by passing through activated alumina columns under nitrogen prior to use. Chloroform ( $\text{CHCl}_3$ ) and 2,2,2-trifluoroethanol (TFE) were both distilled from anhydrous sodium sulfate and a small quantity of sodium bicarbonate prior to use. Other common solvents and chemical reagents were purified by standard published methods if noted.<sup>2</sup> 5-Hexen-1-ol (**1a**), *trans*-chalcone (**1m**), 1-phenyl-1-cyclohexene (**1n**), cinnamyl alcohol (**1o**), *trans*-anethole (**1q**), *trans*-*para*-methoxycinnamaldehyde, 2-methyl-2-propen-1-ol, 3-methyl-2-buten-1-ol, 3-chloro-2-methyl-1-

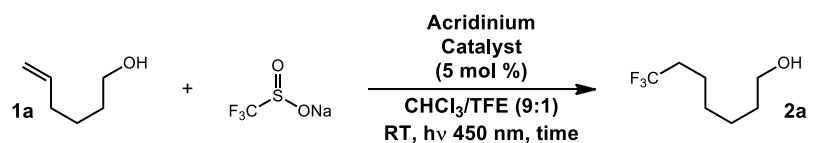
propene, 3,3-dimethylallyl bromide, allylamine, benzoyl chloride, *tert*-butylchlorodiphenylsilane, di-*tert*-butyl dicarbonate, *para*-toluenesulfonyl chloride, bis(((trifluoromethyl)sulfinyl)oxy)zinc, and phthalamide potassium salt were all purchased from Sigma Aldrich. Sodium trifluoromethanesulfinate (CF<sub>3</sub>SO<sub>2</sub>Na, Langlois reagent) was purchased from TCI.

## II. Optimization Studies

Both 5-Hexen-1-ol (**1a**), and *tert*-butyl((2-methylallyl)oxy)diphenylsilane (**1b**) were used for the optimization studies to account for substrate-dependent phenomena.

**General Method.** A flame-dried 2-dram vial was equipped with a magnetic stir-bar, *N*-Me-9-mesityl acridinium tetrafluoroborate (1.0-5.0 mol %), sodium trifluoromethanesulfinate (1.0 equiv), and solid substrate. The solvent, CHCl<sub>3</sub>/TFE (9:1), was added under an atmosphere of nitrogen to a concentration of approximately 0.20 M. Liquid substrates and reagents were added via microsyringe after the solvent. The vial was sealed with a Teflon-coated septum cap, and the reaction mixture was irradiated for the indicated period of time. Upon completion, deionized water was added, and the two phases were allowed to separate. The organic phase was collected, and the aqueous phase was extracted with two portions of dichloromethane equal to the reaction volume. The combined organic portions were passed through a short plug of SiO<sub>2</sub>. The internal standard was added and the samples were analyzed by either GC-MS, or <sup>1</sup>H NMR. The yields reported in Table S1 and S2 are by GC-MS and are the average for three trials unless otherwise noted. Table entry S13 (Baran's conditions) refers to the procedure given for the trifluoromethylation of heterocycles using CF<sub>3</sub>SO<sub>2</sub>Na (3.0 equiv) in dichloromethane/water with *tert*-butylhydroperoxide (5.0 equiv) being added very slowly at 0 °C.<sup>3</sup> The yields reported in Table S3 are by <sup>1</sup>H NMR and are the average of two separate trials.

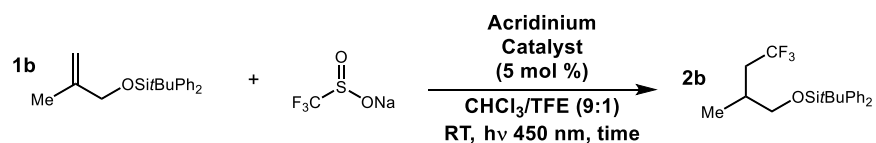
**Table S1.** Reaction Optimization Table for 5-Hexen-1-ol (**1a**).



Entry	Conditions	Time	Yield
<b>S1</b>	<i>Standard</i>	8 hr	27% <sup>a</sup>
<b>S2</b>	<i>Standard</i>	24 hr	44 %
<b>S3</b>	<i>Standard</i>	48 hr	59% <sup>a</sup>
<b>S4</b>	<i>Air</i>	24 hr	43%
<b>S5</b>	<i>2.5 mol % Catalyst</i>	24 hr	49%
<b>S6</b>	<i>1.0 mol % Catalyst</i>	24 hr	45%
<b>S7</b>	<i>No Methyl Thiosalicylate</i>	48 hr	29%
<b>S8</b>	<i>No TFE</i>	48 hr	4%

<sup>a</sup>GC yield for single trial

**Table S2.** Reaction Optimization Table for **1b**.



Entry	Conditions	Time	Yield
<b>S9</b>	<i>Standard</i>	48 hr	78%
<b>S10</b>	<i>No Methyl Thiosalicylate</i>	48 hr	47%
<b>S11</b>	<i>No TFE</i>	48 hr	10%
<b>S12</b>	<i>Zn(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub></i>	48 hr	15% <sup>a</sup>
<b>S13</b>	<i>Baran's Conditions</i>	48 hr	<5% <sup>a</sup>

<sup>a</sup>GC yield for single trial

**Table S3.** Reaction Optimization Table for Aryl-Substituted Substrate Anethole (**1q**).

Entry	Conditions	Conversion	Yield
<b>S14</b>	0.2 equiv. Methyl Thiosalicylate	100%	39%
<b>S15</b>	1.0 equiv. Methyl Thiosalicylate	100%	68%
<b>S16</b>	1.0 equiv. Thiophenol	96%	77%
<b>S17</b>	0.2 equiv. Thiophenol	98%	49%
<b>S18</b>	1.0 equiv. 2-phenylmalononitrile	78%	28%
<b>S19</b>	1.0 equiv. 9-cyanofluorene	96%	24%

### III. Preparation of Alkene Substrates

**tert-Butyl((2-methylallyl)oxy)diphenylsilane (1b).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>4</sup>

**2-Methylallyl benzoate (1c).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>5</sup>

**2-(2-Methylallyl)isoindoline-1,3-dione (1d).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>6</sup>

**Hex-5-en-1-yl 4-methylbenzenesulfonate (1e).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>7</sup>

**Hex-5-en-1-yl benzoate (1f).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>8</sup>

**tert-Butyl allylcarbamate (1g).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>9</sup>

**N-Allyl-4-methylbenzenesulfonamide (1h).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>10</sup>

**tert-Butyl-((3-methylbut-2-en-1-yl)oxy)diphenylsilane (1i).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>4</sup>

**3-Methylbut-2-en-1-yl benzoate (1j).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>5</sup>

**2-(3-Methylbut-2-en-1-yl)isoindoline-1,3-dione (1k).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>6</sup>

**(E)-(But-2-en-1-yloxy)-(tert-butyl)diphenylsilane (1l).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>11</sup>

**1-Chloro-4-(prop-1-en-1-yl)benzene (1p).** Prepared as a mixture of diastereomers (3.5:1 (*Z*):(*E*) ratio) according to a published procedure using ethyltriphenylphosphonium bromide; spectral data were in agreement with literature values.<sup>12</sup>

**(E)-3-(4-Methoxyphenyl)-prop-2-en-1-ol (1r).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>13</sup>

**(E)-2-(3-(4-Methoxyphenyl)allyl)isoindoline-1,3-dione (1s).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>14</sup>

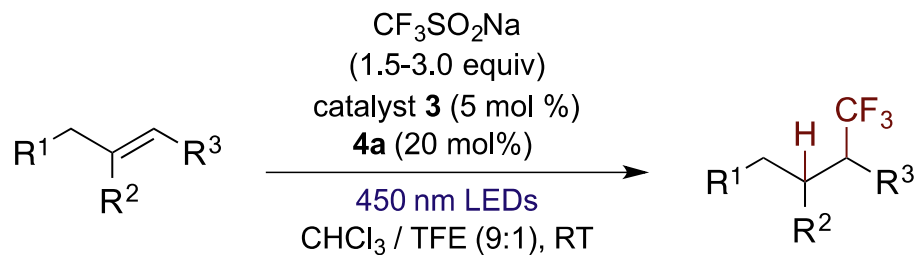
**2-Vinylnaphthalene (1t).** Prepared according to a published procedure; spectral data were in agreement with literature values.<sup>15</sup>

#### IV. Preparation of *N*-Me-9-Mesityl Acridinium Photocatalyst

The photocatalyst used in this study, *N*-Me-9-mesityl acridinium tetrafluoroborate, was synthesized by the method of Fukuzumi et al.<sup>16</sup> Tetrafluoroboric acid (diethyl ether complex) was substituted for perchloric acid during the hydrolysis. The spectral data matched the values reported in the literature for the perchlorate and hexafluorophosphate salts.<sup>16,17</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.60 (d, *J* = 9.0 Hz, 2H), 8.37 (t, *J* = 9.0 Hz, 2H), 7.84 (s, 4H), 7.23 (s, 2H), 4.81 (s, 3H), 2.46 (s, 3H), 1.68 (s, 6H).

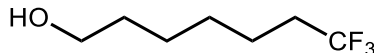
## V. General Procedures for Hydrotrifluoromethylation

### General Procedure A for the Hydrotrifluoromethylation of Alkyl-Substituted Alkenes.



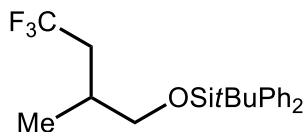
A flame-dried 2-dram vial was equipped with a magnetic stir-bar, *N*-Me-9-mesityl acridinium tetrafluoroborate (5.0 mol %), sodium trifluoromethanesulfinate (1.5-3.0 equiv), and substrate (1 mmol). The solvent, CHCl<sub>3</sub>/TFE (9:1), was added under a nitrogen atmosphere to a concentration of approximately 0.20 M. Liquid substrates were added via microsyringe after the solvent. Methyl thiosalicylate (20 mol%) was added via microsyringe. The vial was sealed with a Teflon-coated septum cap, and the reaction mixture was irradiated (450 nm) for 24 hours (unless some other time is indicated). Upon completion, saturated aqueous sodium bicarbonate was added, and the two phases were allowed to separate. The organic phase was collected, and the aqueous phase was extracted with two portions of dichloromethane equal to the reaction volume. The combined organic portions were passed through a short plug of SiO<sub>2</sub>. The solvent was removed under reduced pressure. The final products were isolated by silica gel chromatography using the conditions listed.

#### 7,7,7-Trifluoroheptan-1-ol (**2a**)



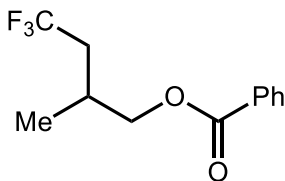
The average yield for the title compound was 50% (two trials) at the 1.25 mmol scale, using 2.0 equivalents Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (20% EtOAc/Hexanes) to yield a colorless oil. Analytical data for **2a** were in agreement with literature values:<sup>18,19</sup> <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 3.64 (t, *J* = 6.6 Hz, 2H), 2.13-2.00 (m, 2H), 1.66 (bs, 1H), 1.59-1.41 (m, 4H), 1.40-1.38 (m, 4H); <sup>19</sup>F NMR (376 MHz): δ -66.5 (t, *J* = 10.9 Hz).

**tert-Butyldiphenyl(4,4,4-trifluoro-2-methylbutoxy)silane (2b)**



The average yield for the title compound was 54% (two trials) at the 0.64 mmol scale, using 1.5 equivalents Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (5% dichloromethane/hexanes) to yield a colorless oil. Analytical data for **2b**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.67 (d,  $J = 8.0$  Hz, 4H), 7.46-7.39 (m, 6H), 3.59 (dd,  $J = 10$  Hz,  $J = 5.2$  Hz, 1H), 3.47 (dd,  $J = 10$  Hz,  $J = 6.4$  Hz, 1H), 2.47 (m, 1H), 2.07 (m, 1H), 1.92 (m, 1H), 1.09 (s, 9H), 1.06 (d,  $J = 6.4$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 150 MHz):  $\delta$  135.6, 133.5, 133.4, 129.8, 127.7, 127.5 (q,  $J = 127$  Hz), 67.7, 36.7 (q,  $J = 27.4$  Hz), 30.6 (q,  $J \sim 2$  Hz), 26.8, 19.3, 16.7;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -63.4 (t,  $J = 11.5$  Hz); **IR** (thin film): 3071, 2960, 2932, 2859, 1716, 1698, 1684, 1653, 1590 1558, 1541, 1507, 1488, 1472, 1428, 1389  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{21}\text{H}_{28}\text{F}_3\text{OSi}$  ( $[\text{M}+\text{H}]^+$ ) 381.1862, found 381.28.

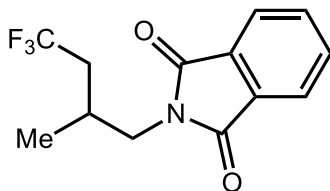
**4,4,4-Trifluoro-2-methylbutyl benzoate (2c)**



The average yield for the title compound was 69% (2 trials) at the 1.2 mmol scale, using 1.5 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (10% dichloromethane/hexanes) to yield a colorless oil. Analytical data for **2c**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06-8.04 (m, 2H), 7.61-7.56 (m, 1H), 7.49-7.44 (m, 2H), 4.29-4.19 (m, 2H), 2.45-2.31 (m, 2H), 2.15-2.01 (m, 1H) 1.18 (d,  $J = 6$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  166.3, 133.1, 129.9, 129.5, 128.4, 126.9 (q,  $J = 275$  Hz), 68.3, 37.2 (q,  $J = 28$  Hz), 27.9 (q,  $J = 2.3$  Hz), 17.0;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.6 (t,  $J = 11.1$  Hz); **IR** (thin film) 3066, 3035, 2975, 2948, 2890, 2341, 1967, 1918, 1869, 1844, 1828, 1792, 1771, 1724, 1684, 1633  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{12}\text{H}_{14}\text{F}_3\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ) 247.0946, found 247.08.

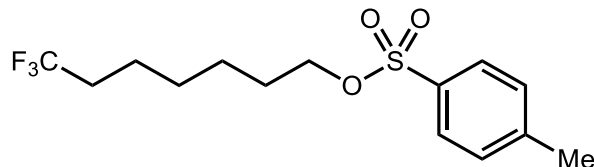


### 2-(4,4,4-Trifluoro-2-methylbutyl)isoindoline-1,3-dione (2d)



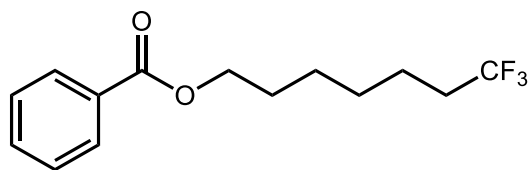
The average yield for the title compound was 69% (2 trials) at the 1.0 mmol scale, using 1.5 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (10% EtOAc/hexanes) to yield an off-white solid. Analytical data for **2d**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88-7.86 (m, 2H), 7.76-7.74 (m, 2H), 3.65 (dd,  $J = 13.8$  Hz,  $J = 7.2$  Hz, 1H), 3.59 (dd,  $J = 13.8$  Hz,  $J = 6.6$  Hz, 1H), 2.43-2.38 (m, 1H), 2.27-2.18 (m, 1H), 2.05-1.95 (m, 1H) 1.09 (d,  $J = 7.2$  Hz, 3H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  168.5, 134.2, 131.8, 123.5, 126.8 (q,  $J = 275.7$  Hz), 43.5, 38.1 (q,  $J = 27.9$  Hz), 27.9 (q,  $J \sim 2.4$  Hz), 17.7;  $^{19}\text{F NMR}$  (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.4 (t,  $J = 11.0$  Hz); **IR** (thin film) 3918, 3901, 3882, 1870, 3853, 3838, 3820, 3801, 3779, 3750, 3734, 3710, 3689, 3674, 3649, 3628, 3618, 3587, 3567, 3545, 2976, 2940, 2883, 1773, 1750, 1716, 1402, 1362  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{13}\text{H}_{13}\text{F}_3\text{NO}_2$  ( $[\text{M}+\text{H}]^+$ ) 272.0898, found 272.10.

### 7,7,7-Trifluoroheptyl 4-methylbenzenesulfonate (2e)



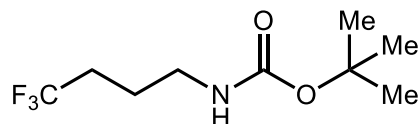
The average yield for the title compound was 64% (2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (10% EtOAc/hexanes) to yield a colorless oil. Analytical data for **2e** were in agreement with the literature values:<sup>18</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78 (d,  $J = 8.4$  Hz, 2H), 7.34 (d,  $J = 8.4$  Hz, 2H), 4.02 (t,  $J = 6.2$  Hz, 2H), 2.43 (s, 3H), 2.04-1.97 (m, 2H), 1.65-1.60 (m, 2H), 1.52-1.45 (m, 2H), 1.40-1.20 (m, 4H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.4 (t,  $J = 10.9$  Hz). **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{14}\text{H}_{20}\text{F}_3\text{O}_3\text{S}$  ( $[\text{M}+\text{H}]^+$ ) 325.1085, found 325.19.

### 7,7,7-Trifluoroheptyl benzoate (**2f**)



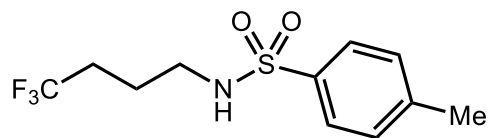
The average yield for the title compound was 42% (2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (5% Et<sub>2</sub>O/hexanes) to yield a colorless oil. Analytical data for **2f** were in agreement with the literature values.<sup>18,19</sup> **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.06-8.04 (m, 2H), 7.59-7.55 (m, 1H), 7.47-7.43 (m, 2H), 4.34 (t, *J* = 6.6 Hz, 2H), 2.12-2.06 (m, 2H), 1.82-1.78 (m, 2H), 1.62-1.58 (m, 2H), 1.50-1.45 (m, 4H); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -66.4 (t, *J* = 10.9 Hz). **LRMS (ESI):** *m/z* calculated for C<sub>14</sub>H<sub>18</sub>F<sub>3</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) 275.1259, found 275.16.

### *tert*-Butyl (4,4,4-trifluorobutyl)carbamate (**2g**)



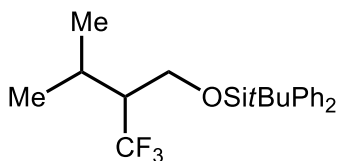
The average yield for the title compound was 25% (2 trials) at the 1.0-1.3 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (10% EtOAc/hexanes) to yield a white solid. Analytical data for **2g**: **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 4.60 (bs, 1H), 3.23-3.17 (m, 2H), 2.17-2.07 (m, 2H), 1.80-1.72 (m, 2H), 1.45 (s, 9H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 155.9, 127.0 (q, *J* = 274.6 Hz), 79.5, 39.4, 31.1 (q, *J* = 29.1 Hz), 28.3, 22.9; **<sup>19</sup>F NMR** (564 MHz, CDCl<sub>3</sub>) δ -66.2 (t, *J* = 11.0 Hz); **IR** (thin film) 3350, 2980, 1691, 1525, 1457, 1392, 1367, 1339, 1254 cm<sup>-1</sup>; **LRMS (ESI):** *m/z* calculated for C<sub>9</sub>H<sub>17</sub>F<sub>3</sub>NO<sub>2</sub> ([M+H]<sup>+</sup>) 228.1211, found 228.20.

#### 4-Methyl-N-(4,4,4-trifluorobutyl)-benzenesulfonamide (2h)



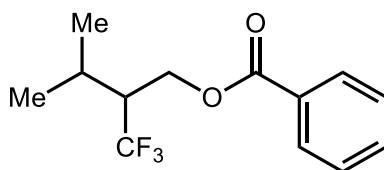
The average yield for the title compound was 32% (2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (5-20% EtOAc/hexanes) to yield an off-white solid. Analytical data for **2h**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.76-7.74 (d,  $J = 8.2$  Hz, 2H), 7.34-7.31 (d,  $J = 8.2$  Hz, 2H), 5.03 (t,  $J = 6.2$  Hz, 1H), 3.02-2.97 (m, 2H), 2.44 (s, 3H), 2.14-2.09 (m, 2H), 1.77-1.70 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  143.7, 136.6, 129.8, 127.0, 126.8 (q,  $J = 274.7$  Hz), 41.9, 30.8 (q,  $J = 29.1$  Hz), 22.4 (q,  $J = 2.9$  Hz), 21.5;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.2 (t,  $J = 10.7$  Hz); **IR** (thin film) 3261, 2952, 1598, 1494, 1442, 1393, 1320, 1306  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{11}\text{H}_{15}\text{F}_3\text{NO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ) 282.0776, found 282.09.

#### *tert*-Butyl-(3-methyl-2-(trifluoromethyl)butoxy)diphenylsilane (2i)



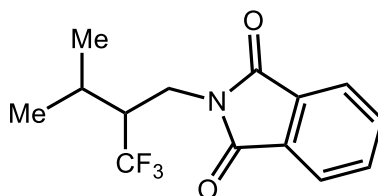
The average yield for the title compound was 51% (2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (5% dichloromethane/hexanes) to yield a colorless oil. Analytical data for **2i**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.69 (d,  $J = 7.2$  Hz, 4H), 7.45-7.37 (m, 6H), 3.87-3.83 (m, 2H), 2.26-2.23 (m, 1H), 2.19-2.16 (m, 1H), 1.09 (s, 9H), 1.03 (d,  $J = 7.2$  Hz, 3H), 1.00 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.62, 135.59, 133.1, 129.8, 127.8 (q,  $J = 280.6$  Hz), 127.7, 59.3 (q,  $J = 3.7$  Hz), 50.9 (q,  $J = 22.7$  Hz), 26.7, 25.1, 20.39, 19.7, 19.2;  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -64.8 (d,  $J = 10.2$  Hz); **IR** (thin film) 3072, 2962, 2933, 2894, 2859, 1658, 1590, 1550, 1529, 1472, 1428, 1391  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{22}\text{H}_{30}\text{F}_3\text{OSi}$  ( $[\text{M}+\text{H}]^+$ ) 395.2018, found 395.22.

### 3-Methyl-2-(trifluoromethyl)butyl benzoate (2j)



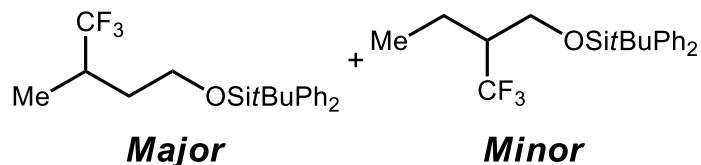
The average yield for the title compound was 54% (2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (10% dichloromethane/hexanes) to yield a colorless oil. Analytical data for **2j**:  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06-8.04 (m, 2H), 7.60-7.57 (m, 2H), 7.46 (t,  $J = 7.8$  Hz), 4.57-4.50 (m, 2H), 2.52-2.44 (m, 1H), 2.30-2.24 (m, 1H), 1.16 (d,  $J = 7.2$  Hz), 1.09 (d,  $J = 7.2$  Hz);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  166.2, 133.2, 129.6, 128.4, 127.3 (q,  $J = 280.1$  Hz), 59.9 (q,  $J = 3.0$  Hz), 47.9 (q,  $J = 24.1$ ), 25.6, 20.9, 19.0;  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.0 (d,  $J = 9.6$  Hz); **IR** (thin film) 1726, 1604, 1585, 1470, 1452, 1384  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{13}\text{H}_{16}\text{F}_3\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ) 261.1102, found 261.07.

### 2-(3-Methyl-2-(trifluoromethyl)butyl)isoindoline-1,3-dione (2k)



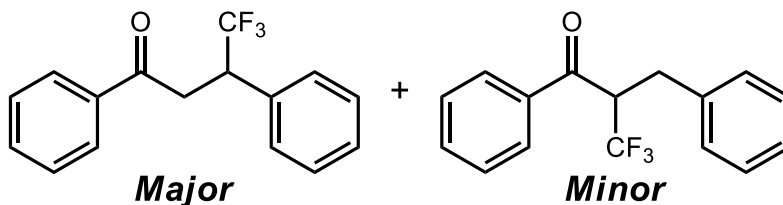
The average yield for the title compound was 69% (2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (30% dichloromethane/hexanes) to yield a colorless oil. Analytical data for **2k**:  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86-7.84 (m, 2H), 7.74-7.72 (m, 2H), 4.04 (dd,  $J = 14.4$  Hz,  $J = 8.8$ , 1H), 3.72 (dd,  $J = 14.4$  Hz,  $J = 5.2$ , 1H), 2.78-2.67 (m, 1H), 2.17-2.10 (m, 1H), 1.16 (d,  $J = 7.2$  Hz, 3H), 1.08 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.9, 134.1, 131.8, 127.4 (q,  $J = 280.5$  Hz), 123.4, 46.0 (q,  $J = 23.5$  Hz), 33.8 (q,  $J = 2.9$  Hz), 26.1, 19.7, 18.7;  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.4 (d,  $J = 9.6$  Hz); **IR** (thin film) 3545, 3478, 3222, 3087, 3063, 3033, 2970, 2886, 2783, 2701, 2639, 2476, 1952, 1908, 1775, 1718, 1615, 1520, 1467, 1371  $\text{cm}^{-1}$ ; **LRMS** (ESI):  $m/z$  calculated for  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{NO}_2$  ( $[\text{M}+\text{H}]^+$ ) 286.1055, found 286.22.

***tert*-Butyldiphenyl(4,4,4-trifluoro-3-methylbutoxy)silane (2l, Major Regioisomer) and *tert*-Butyldiphenyl(2-(trifluoromethyl)butoxy)silane (2l, Minor Regioisomer).**



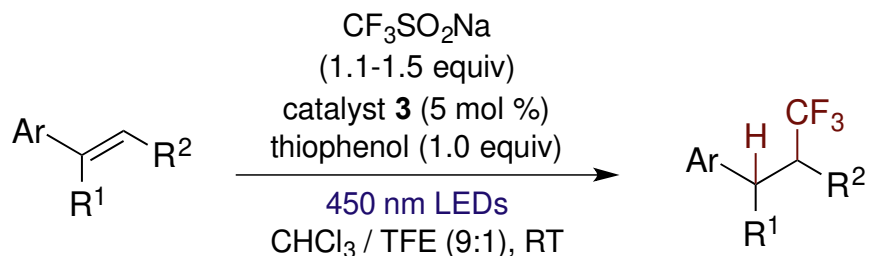
The average combined yield for the title compound was 45% (*major:minor* = 1.3:1, 2 trials) at the 1.0 mmol scale, using 2.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. Both title regioisomers were purified by column chromatography on silica gel (3% dichloromethane/hexanes) to yield colorless oils. Analytical data for **2l**: **<sup>1</sup>H NMR** for the major regioisomer (400 MHz, CDCl<sub>3</sub>): 7.67-7.65 (m, 4H), 7.45-7.38 (m, 6H), 3.79-3.69 (m, 2H), 2.49-2.45 (m, 1H), 2.03-1.97 (m, 1H), 1.48-1.41 (m, 1H), 1.08-1.06 (m, 12H); **<sup>13</sup>C NMR** for the major regioisomer (CDCl<sub>3</sub>, 100 MHz) δ 135.5, 133.6, 133.5, 129.7, 128.6 (q, *J* = 276.7 Hz), 127.7, 60.5, 34.5 (q, *J* = 26.3 Hz), 32.1 (q, *J* = 2 Hz), 26.8, 19.2, 12.3 (q, *J* = 3 Hz); **<sup>19</sup>F NMR** for the major regioisomer (376 MHz, CDCl<sub>3</sub>) δ -73.4 (d, *J* = 9.0 Hz); **IR** for the major regioisomer (thin film) 3072, 2958, 2932, 2858, 1590, 1472, 1428, 1390, 1377, 1346, 1326 cm<sup>-1</sup>; **LRMS** for the major regioisomer (ESI): *m/z* calculated for C<sub>21</sub>H<sub>28</sub>F<sub>3</sub>OSi ([M+H]<sup>+</sup>) 381.1862, found 381.17; **<sup>1</sup>H NMR** for the minor regioisomer (400 MHz, CDCl<sub>3</sub>): δ 7.68-7.66 (m, 4H), 7.46-7.39 (m, 6H), 3.80 (d, *J* = 4.8 Hz, 2H), 2.16-2.11 (m, 1H), 1.76-1.69 (m, 1H), 1.07 (s, 9H), 0.96 (t, *J* = 7.4 Hz, 3H); **<sup>13</sup>C NMR** for the minor regioisomer (CDCl<sub>3</sub>, 100 MHz) δ 135.59, 135.57, 133.2, 133.1, 129.8, 127.73, 127.72, 127.7 (q, *J* = 279.0 Hz), 60.1 (q, *J* = 3 Hz), 46.9 (q, *J* = 24 Hz), 26.7, 19.2, 18.0 (q, *J* ~ 2 Hz), 11.3; **<sup>19</sup>F NMR** for the minor regioisomer (376 MHz, CDCl<sub>3</sub>) δ -68.6 (d, *J* = 9.4 Hz); **IR** for the minor regioisomer (thin film) 3072, 3051, 2960, 2932, 2894, 2859, 1590, 1472, 1428, 1390, 1362, 1338, 1314 cm<sup>-1</sup>; **LRMS** for the minor regioisomer (ESI): *m/z* calculated for C<sub>21</sub>H<sub>28</sub>F<sub>3</sub>OSi ([M+H]<sup>+</sup>) 381.1862, found 381.23;

**4,4,4-Trifluoro-1,3-diphenylbutan-1-one (2m, Major Regioisomer) and 2-Benzyl-3,3,3-trifluoro-1-phenylpropan-1-one (2m, Minor Regioisomer)**



The average combined yield for the title compound was 31% (*major:minor* = 1.1:1, 2 trials) at the 1.0 mmol scale, using 3.0 equivalents of Langlois reagent, and an irradiation time of 24 hours. Both title regioisomers were purified by column chromatography on silica gel (5% Et<sub>2</sub>O/hexanes). Analytical data for both regioisomers (**2m**) were in agreement with the literature values: <sup>1</sup>H NMR for the major regioisomer<sup>20</sup> (400 MHz, CDCl<sub>3</sub>): 7.93-7.90 (m, 2H), 7.61-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.42-7.31 (m, 5H), 4.32-4.21 (m, 1H), 3.71 (dd, *J* = 17.8 Hz, *J* = 9.0 Hz), 3.61 (dd, *J* = 17.8 Hz, *J* = 4.2 Hz); <sup>19</sup>F NMR for the major regioisomer<sup>20</sup> (376 MHz, CDCl<sub>3</sub>) δ -69.6 (d, *J* = 9.8 Hz); <sup>1</sup>H NMR for the minor regioisomer<sup>21</sup> (400 MHz, CDCl<sub>3</sub>): δ 7.76-7.74 (m, 2H), 7.56-7.52 (m, 1H), 7.42-7.38 (m, 2H), 7.23-7.13 (m, 5H), 4.53-4.44 (m, 1H), 3.44 (dd, *J* = 13.8 Hz, *J* = 10.6 Hz), 3.21 (dd, *J* = 13.8 Hz, *J* = 3.8 Hz); <sup>19</sup>F NMR for the minor regioisomer<sup>21</sup> (376 MHz, CDCl<sub>3</sub>) δ -66.4 (d, *J* = 7.9 Hz).

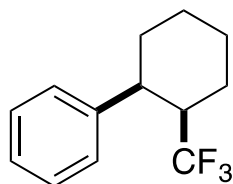
**General Procedure B for the Hydrotrifluoromethylation of Aryl-Substituted Alkenes.**



A flame-dried 2-dram vial was equipped with a magnetic stir-bar, *N*-Me-9-mesityl acridinium tetrafluoroborate (5.0 mol %), sodium trifluoromethanesulfonate (1.1-1.5 equiv), and substrate (1 mmol). The solvent, CHCl<sub>3</sub>/TFE (9:1), was added under a nitrogen atmosphere to a concentration of approximately 0.20 M. Liquid substrates were added via microsyringe after the solvent. The vial was sealed with a Teflon-coated septum cap. Thiophenol (1.0 equiv) was added via microsyringe through the septum cap and the reaction mixture was irradiated (450 nm) for 24 hours (unless some other time is indicated). Upon completion, saturated aqueous sodium bicarbonate

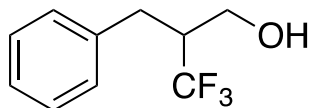
was added, and the two phases were allowed to separate. The organic phase was collected, and the aqueous phase was extracted with two portions of dichloromethane equal to the reaction volume. The combined organic portions were passed through a short plug of SiO<sub>2</sub>. The solvent was removed under reduced pressure. The final products were isolated by silica gel chromatography using the conditions listed.

**(2-(Trifluoromethyl)cyclohexyl)benzene (2n)**



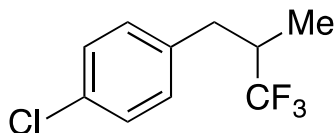
The average yield for the title compound was 51% as a mixture of diastereomers (*cis/trans* = 12:1) at the 1.0 mmol scale, using 1.1 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (100% pentane). Analytical data for **2n**: <sup>1</sup>H NMR for *cis* diastereomer (400 MHz, CDCl<sub>3</sub>): δ 7.32-7.31 (m, 4H), 7.26-7.22 (m, 1H), 3.14-3.10 (m, 1H), 2.69-2.60 (m, 1H), 2.18-2.08 (m, 2H), 1.98-1.92 (m, 1H), 1.87-1.80 (m, 1H), 1.76-1.70 (m, 2H), 1.65-1.51 (m, 2H); <sup>13</sup>C NMR for *cis* diastereomer (150 MHz, CDCl<sub>3</sub>) δ 143.1, 128.2, 128.1, 128.0 (q, *J* = 280.8 Hz), 126.4, 44.6 (q, *J* = 23.4 Hz), 42.0, 28.9, 24.8, 24.3, 22.2; <sup>19</sup>F NMR for *cis* diastereomer (376 MHz, CDCl<sub>3</sub>) δ -62.5 (s, br); <sup>19</sup>F NMR for *trans* diastereomer (376 MHz, CDCl<sub>3</sub>) -68.6 (d, *J* = 7.90 Hz); IR (thin film) 3089, 3063, 3030, 2940, 2873, 1604, 1496, 1452, 1400, 1383, 1313 cm<sup>-1</sup>; LRMS (GC-MS): *m/z* calculated for C<sub>13</sub>H<sub>15</sub>F<sub>3</sub> 228.11, found 228.1. Identification of the major and minor diastereomers were accomplished using <sup>1</sup>H NMR experiments (1D in CDCl<sub>3</sub>, 1D in C<sub>6</sub>D<sub>6</sub>, <sup>19</sup>F decoupled <sup>1</sup>H NMR in C<sub>6</sub>D<sub>6</sub>, COSY) and <sup>19</sup>F NMR. The *cis* diastereomer (major) has two methine protons which are both coupled to vicinal protons with *J* values that range from 4.6 to 5.2 Hz. The *trans* diastereomer (minor) has two methine protons which are both coupled to vicinal protons with *J* values of 3.6 and 11.6 Hz. The latter is consistent with the expectation for a pair of diaxial protons in the *trans* diastereomer. The Diastereomeric ratio was calculated using <sup>19</sup>F NMR peak areas.

### 2-Benzyl-3,3,3-trifluoropropan-1-ol (2o)



The average yield for the title compound was 51% (2 trials) at the 1.0 mmol scale, using 1.5 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (25% Et<sub>2</sub>O/pentane) to yield a yellow oil. Analytical data for **2o**: <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.35-7.33 (m, 2H), 7.28-7.25 (m, 3H), 3.84-3.80 (m, 1H), 3.71-3.67 (m, 1H), 3.08 (dd, *J* = 13.8 Hz, *J* = 4.2 Hz, 1H), 2.85 (dd, *J* = 13.8 Hz, *J* = 10.8 Hz), 2.52 (m, 1H), 1.56 (t, *J* = 6 Hz, 1H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 137.5, 129.1, 128.7, 127.6 (q, *J* = 279.3), 126.8, 58.7 (q, *J* = 2.7 Hz), 47.2 (q, *J* = 23.7 Hz), 30.5 (q, *J* = 2.55 Hz); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -69.1 (d, *J* = 9.0 Hz); IR (thin film) 3388, 3089, 3066, 3032, 2942, 2898, 1890, 1668, 1604, 1586, 1497, 1456, 1392 cm<sup>-1</sup>; LRMS (GC-MS): *m/z* calculated for C<sub>10</sub>H<sub>11</sub>F<sub>3</sub>O 204.08, found 204.1.

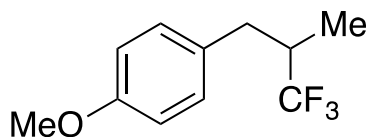
### 1-Chloro-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2p)



The average yield for the title compound was 56% (2 trials) at the 1.0 mmol scale, using 1.1 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (pentane) to yield a colorless oil. Analytical data for **2p**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.08 (m, 1H), 2.47 (t, *J* = 10.8 Hz, 1H), 2.43 (m, 1H), 1.04 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.5, 132.5, 130.4, 128.7, 128.0 (q, *J* = 278.1 Hz), 39.9 (q, *J* = 26 Hz), 35.0 (q, *J* = 2.7 Hz), 12.0 (q, *J* = 2.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -73.4 (d, *J* = 8.3 Hz); IR (thin film) 3031, 2987, 2949, 2892, 1901, 1600, 1494, 1467, 1411, 1378, 1335 cm<sup>-1</sup>; LRMS (GC-MS): *m/z* calculated for C<sub>10</sub>H<sub>10</sub>ClF<sub>3</sub> 222.04, found 222.0.

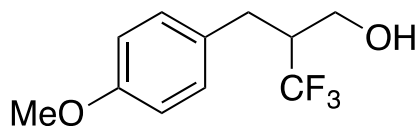


### 1-Methoxy-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2q)



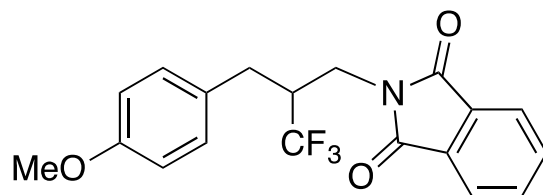
The average yield for the title compound was 64% (2 trials) at the 1.0 mmol scale, using 1.1 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (3% Et<sub>2</sub>O/pentane) to yield a yellow oil. Analytical data for **2q**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 3.06 (m, 1H), 2.42 (t, *J* = 10.4 Hz, 1H), 2.40 (m, 1H), 1.02 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 158.3, 130.1, 130.0, 126.3 (q, *J* = 278 Hz), 113.9, 55.2, 40.2 (q, *J* = 25.6 Hz), 34.7 (q, *J* = 2.7 Hz), 12.0 (q, 2.7 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -73.4 (d, 8.3 Hz); IR (thin film) 3033, 2994, 2949, 2838, 2550, 1887, 1613, 1585, 1515, 1466, 1422, 1387 cm<sup>-1</sup>; LRMS (GC-MS): *m/z* calculated for C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>O 218.09, found 218.1.

### 3,3,3-Trifluoro-2-(4-methoxybenzyl)propan-1-ol (2r)



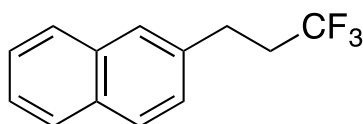
The average yield for the title compound was 67% (2 trials) at the 1.0 mmol scale, using 1.5 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (20% EtOAc/hexane) to yield a yellow oil. Analytical data for **2r**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 3.81 (s, 3H), 3.80 (m, 1H), 3.68 (dd, *J* = 12 Hz, *J* = 5.2 Hz), 2.97 (dd, *J* = 14.2 Hz, *J* = 4.8 Hz, 1H), 2.79 (dd, *J* = 14.2 Hz, *J* = 10 Hz, 1H), 2.47 (m, 1H), 1.62 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.4, 130.1, 129.4, 127.6 (q, *J* = 279.5 Hz), 114.1, 58.7 (q, 2.6 Hz), 55.2, 47.4 (q, *J* = 23.5 Hz), 29.6 (q, *J* ~ 2.5 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -69.1 (d, *J* = 9.0 Hz); IR (thin film): 3690, 3675, 3649, 3002, 2940, 2835, 2549, 1889, 1885, 1771, 1732, 1613, 1515, 1457, 1390, 1302; LRMS (GC-MS): *m/z* calculated for C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub> 234.09, found 234.1.

### 2-(3,3,3-Trifluoro-2-(4-methoxybenzyl)propyl)isoindoline-1,3-dione (2s)



The average yield for the title compound was 41% (2 trials) at the 1.0 mmol scale, using 1.5 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (25% EtOAc/hexane) to yield a yellow solid. Analytical data for **2s**: **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ: 7.74 (m, 2H), 7.67 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.94 (dd, *J* = 14.2 Hz, *J* = 7.2 Hz, 1H), 3.81 (dd, *J* = 14.2 Hz, *J* = 7.6 Hz, 1H), 3.64 (s, 3H), 3.27 (m, 1H), 3.13 (dd, *J* = 14.6 Hz, *J* = 4 Hz, 1H), 2.63 (dd, *J* = 14.6 Hz, *J* = 10 Hz, 1H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 167.8, 158.2, 133.9, 131.7, 129.4, 128.6, 127.0 (q, *J* = 278.9 Hz), 123.1, 113.9, 55.1, 42.0 (q, *J* = 24.6 Hz), 36.4 (q, *J* = ~3 Hz), 32.0 (q, *J* = 2.6 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ: -70.7 (d, *J* = 8.6 Hz); **IR** (thin film): 2978, 2933, 1966, 1716, 1698, 1683, 1653, 1635, 1615, 1541, 1457, 1417, 1383; **LRMS** (GC-MS): *m/z* calculated for C<sub>19</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>3</sub> 363.11, found 363.1.

### 2-(3,3,3-Trifluoropropyl)naphthalene (2t)



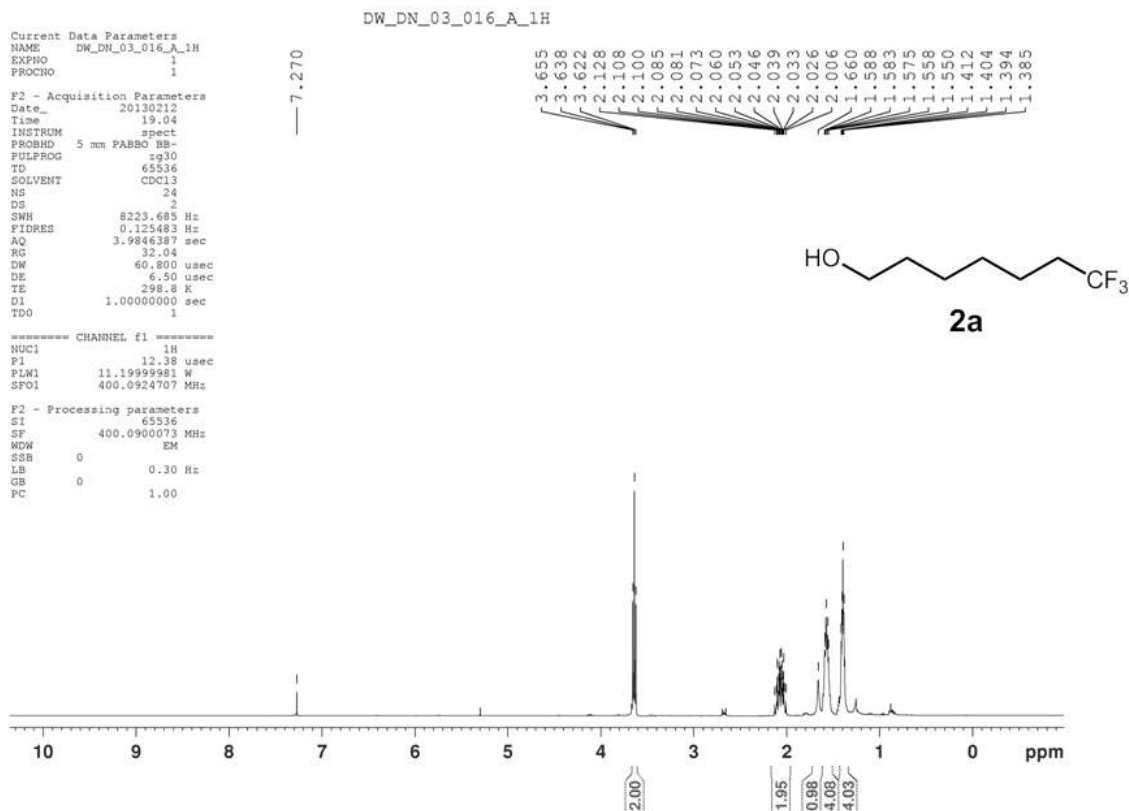
The average yield for the title compound was 29% (2 trials) at the 1.0 mmol scale, using 1.5 equivalents of Langlois reagent, and an irradiation time of 24 hours. The title compound was purified by column chromatography on silica gel (pentane) to yield a white solid. Analytical data for **2t**: **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.82 (m, 3H), 7.66 (m, 1H), 7.48 (m, 2H), 7.34 (m, 1H), 3.06 (m, 2H), 2.50 (m, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 136.4, 133.6, 132.3, 128.4, 127.7, 127.5, 126.7 (q, *J* = 275.1 Hz), 126.6, 126.5, 126.3, 125.7, 35.6 (q, *J* = 27.9 Hz), 28.4 (q, *J* = 3.2 Hz); **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -66.5 (t, *J* = 10.5 Hz); **IR** (thin film): 2978, 2867, 1793, 1716, 1698, 1684, 1653, 1616, 1558, 1507, 1456, 1438, 1382, 1306; **LRMS** (GC-MS): *m/z* calculated for C<sub>13</sub>H<sub>11</sub>F<sub>3</sub> 224.08, found 224.1.

## V. References

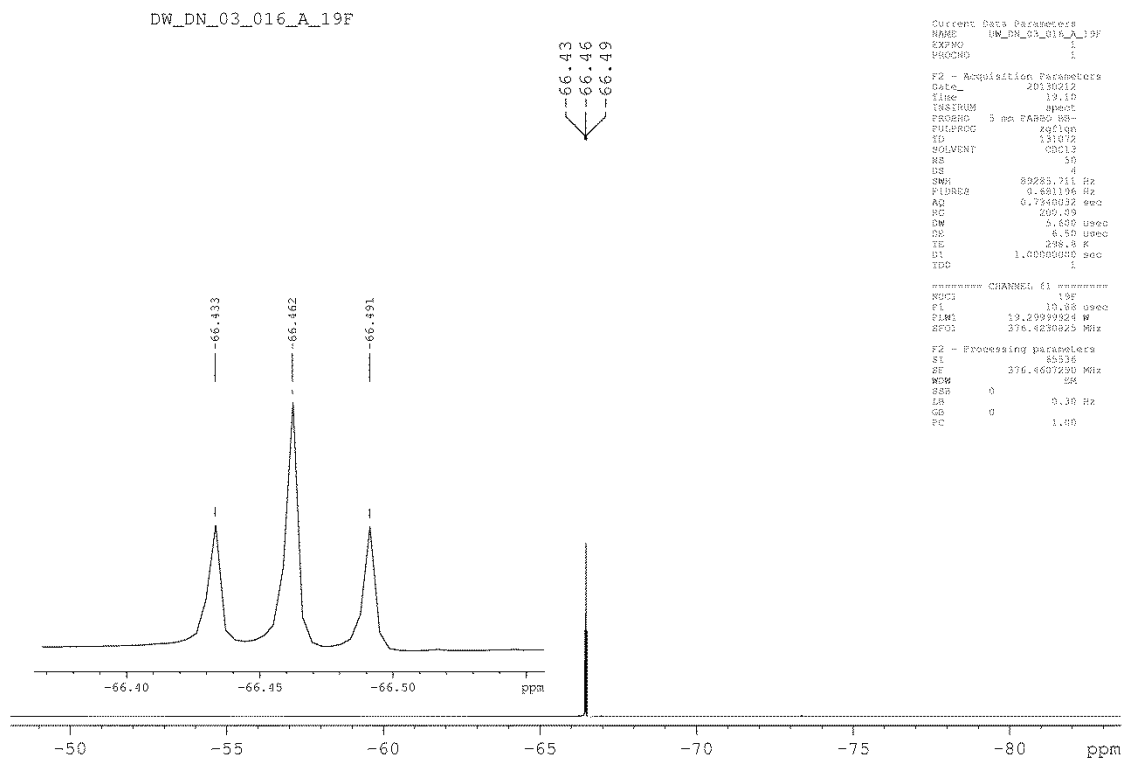
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## VI. $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR Spectra

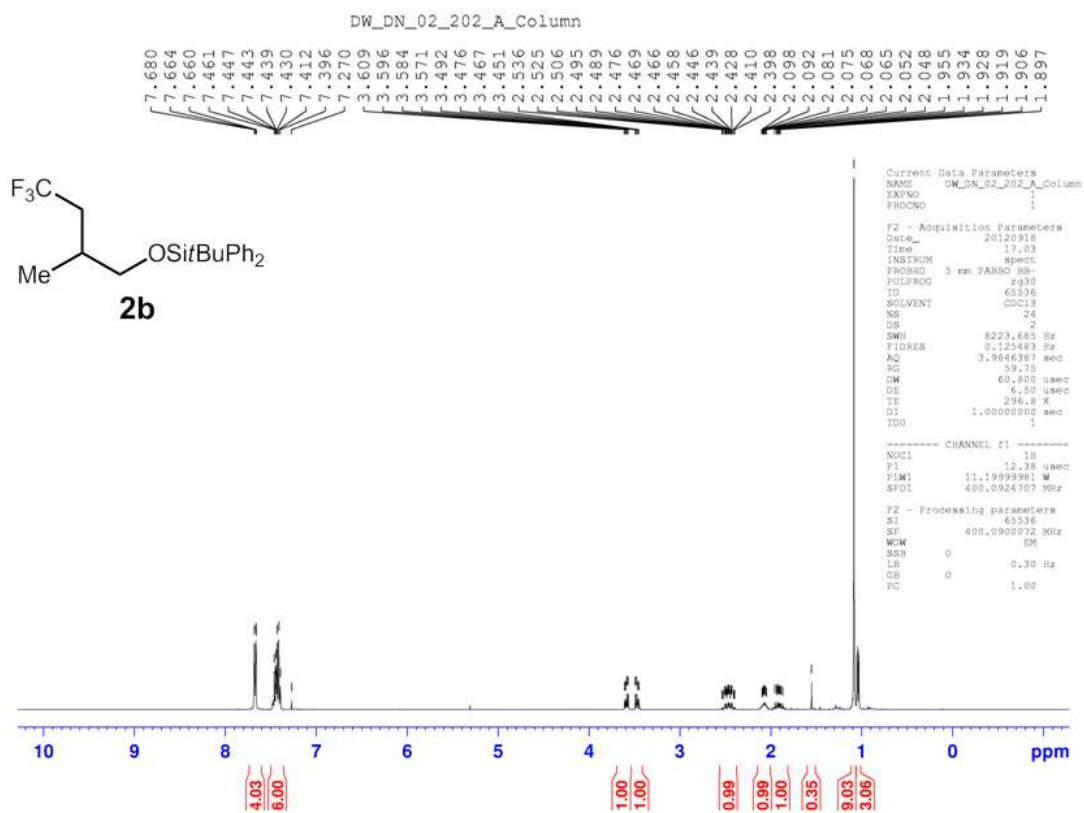
### 7,7,7-Trifluoroheptan-1-ol (2a) 7,7,7-Trifluoroheptan-1-ol (2a)



## 7,7,7-Trifluoroheptan-1-ol (2a)

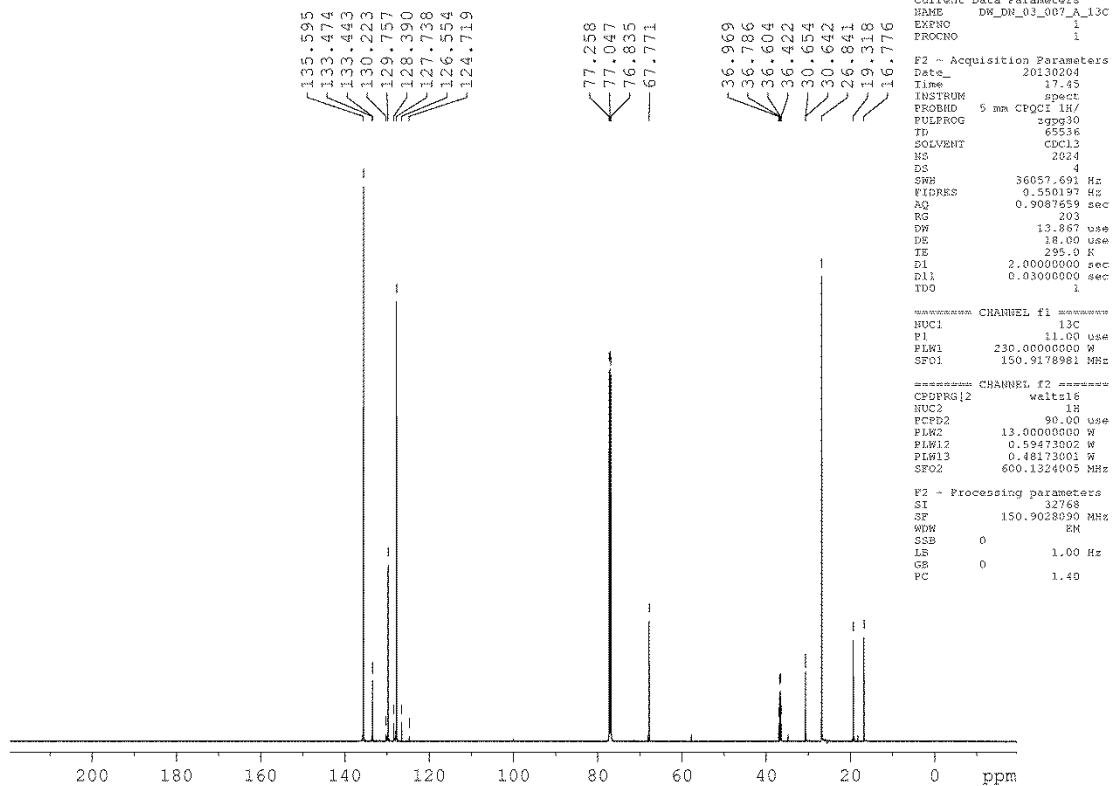


### *tert*-Butyldiphenyl(4,4,4-trifluoro-2-methylbutoxy)silane (**2b**)

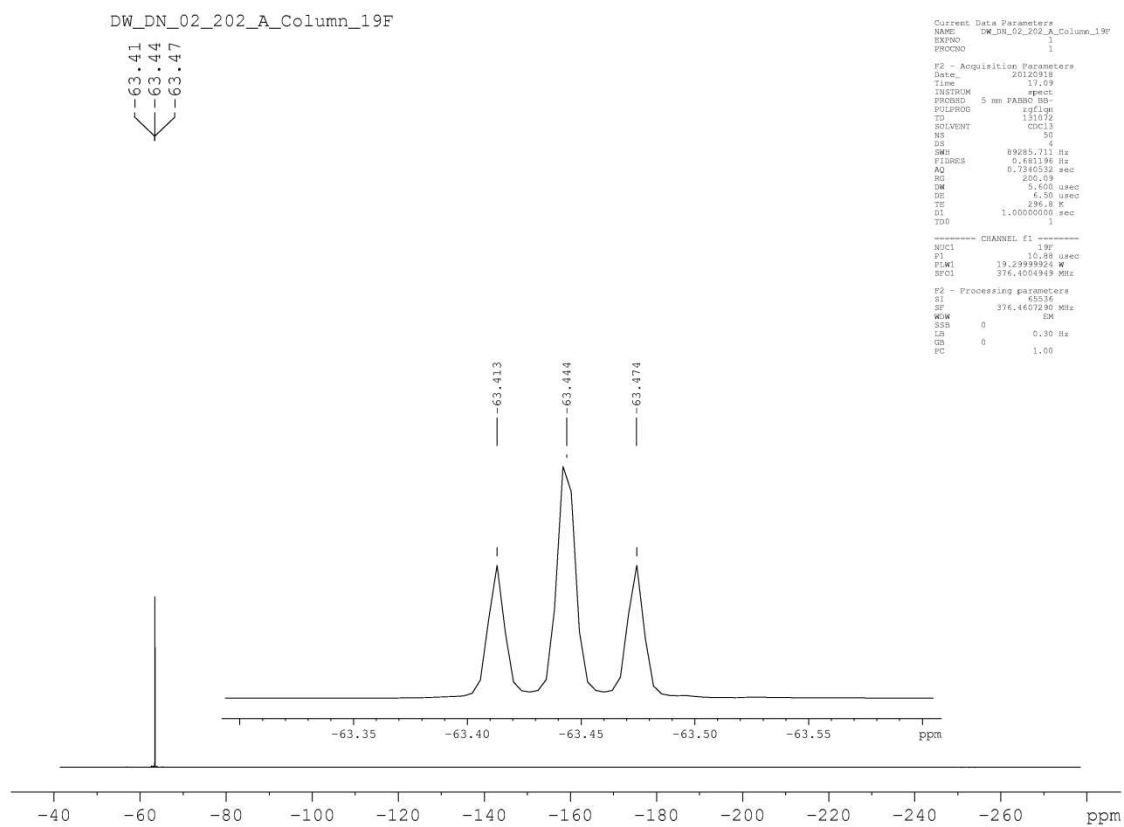


### *tert*-Butyldiphenyl(4,4,4-trifluoro-2-methylbutoxy)silane (2b)

DW\_DN\_03\_007\_A\_13C

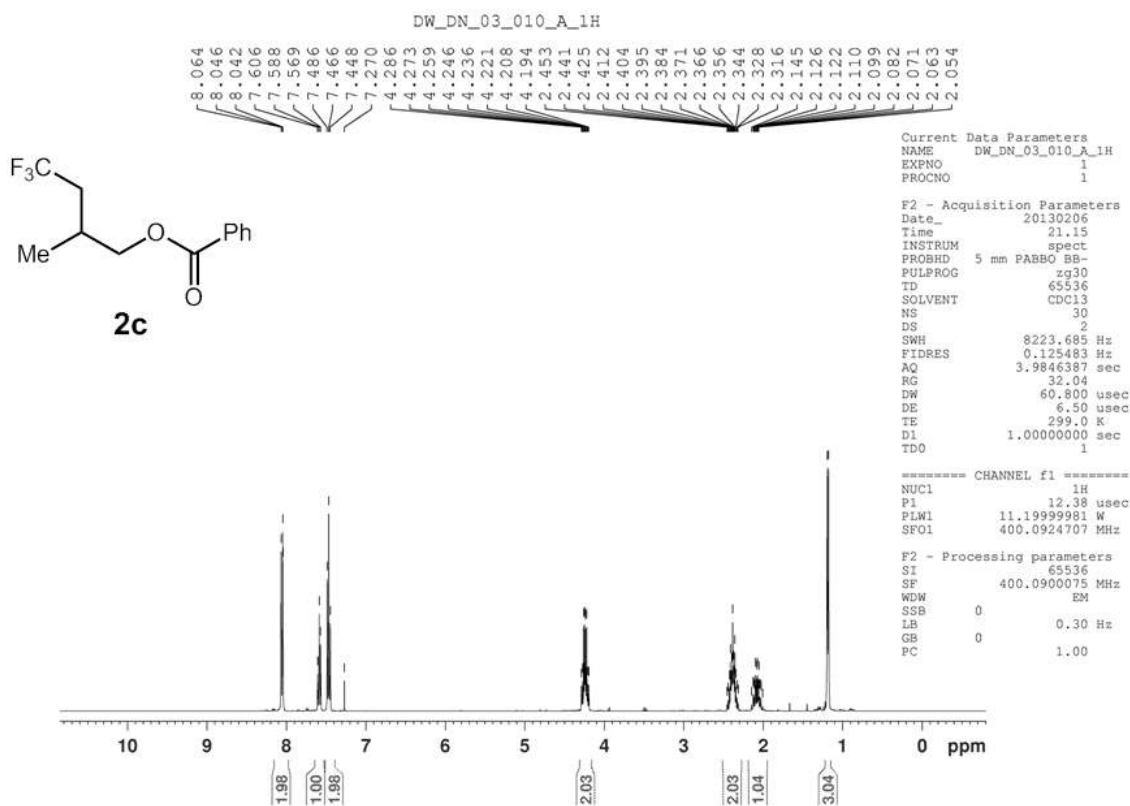


### *tert*-Butyldiphenyl(4,4,4-trifluoro-2-methylbutoxy)silane (2b)

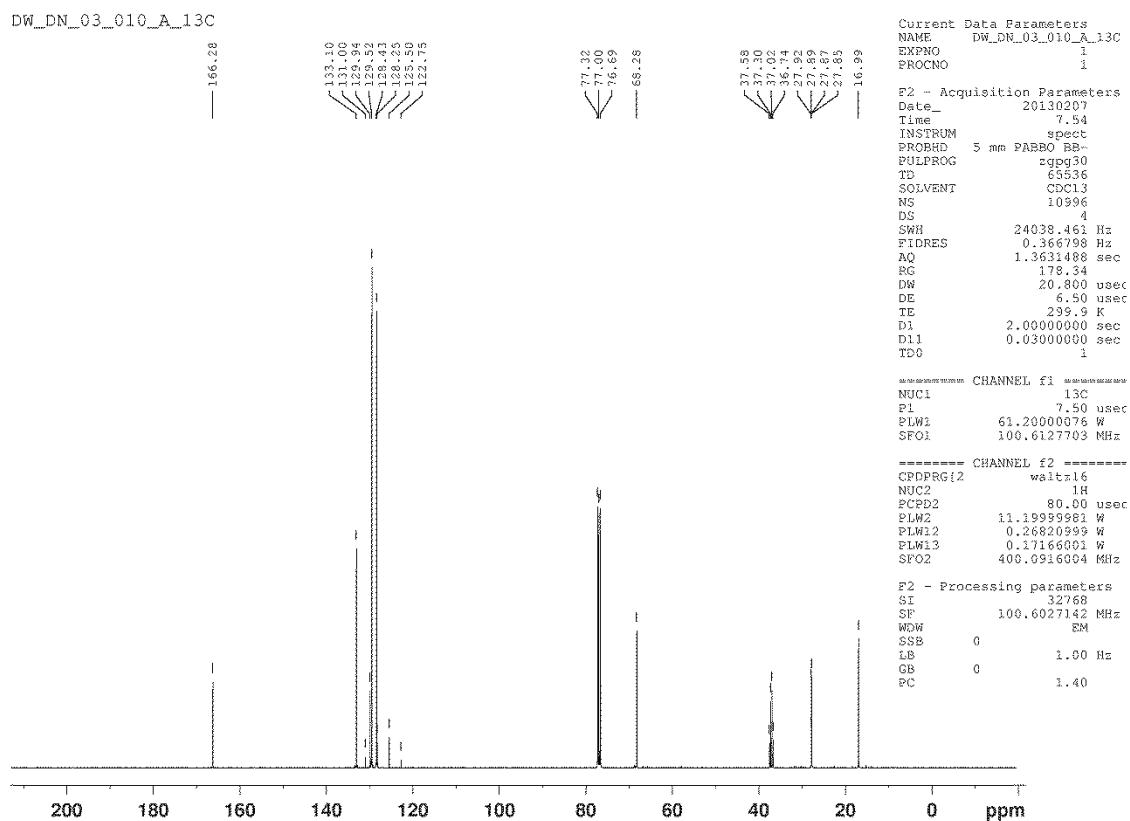




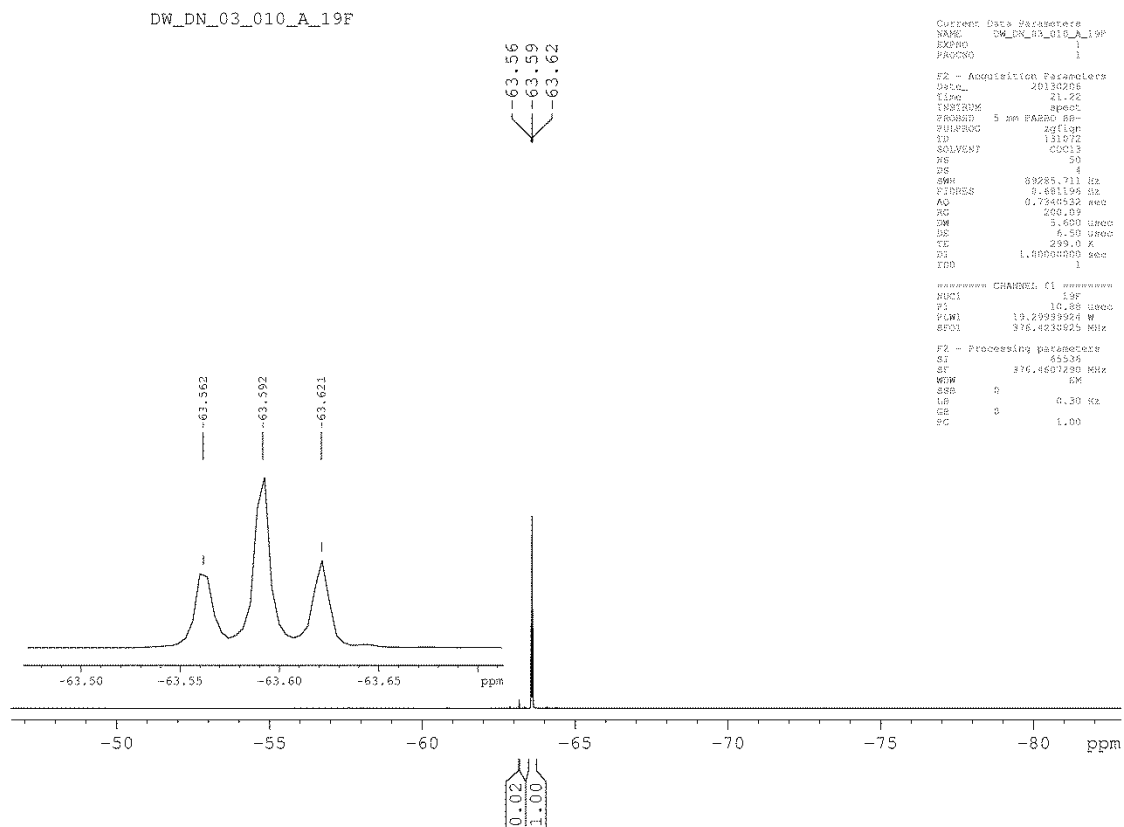
### 4,4,4-Trifluoro-2-methylbutyl benzoate (2c)



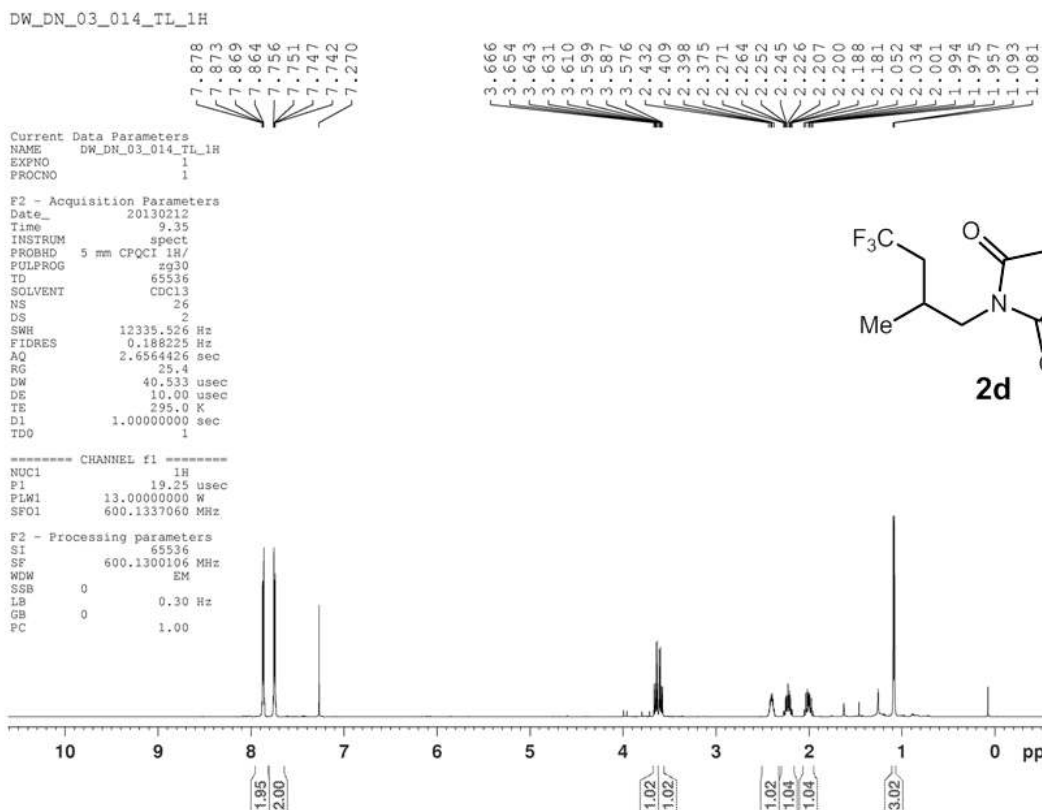
### 4,4,4-Trifluoro-2-methylbutyl benzoate (2c)



### 4,4,4-Trifluoro-2-methylbutyl benzoate (2c)

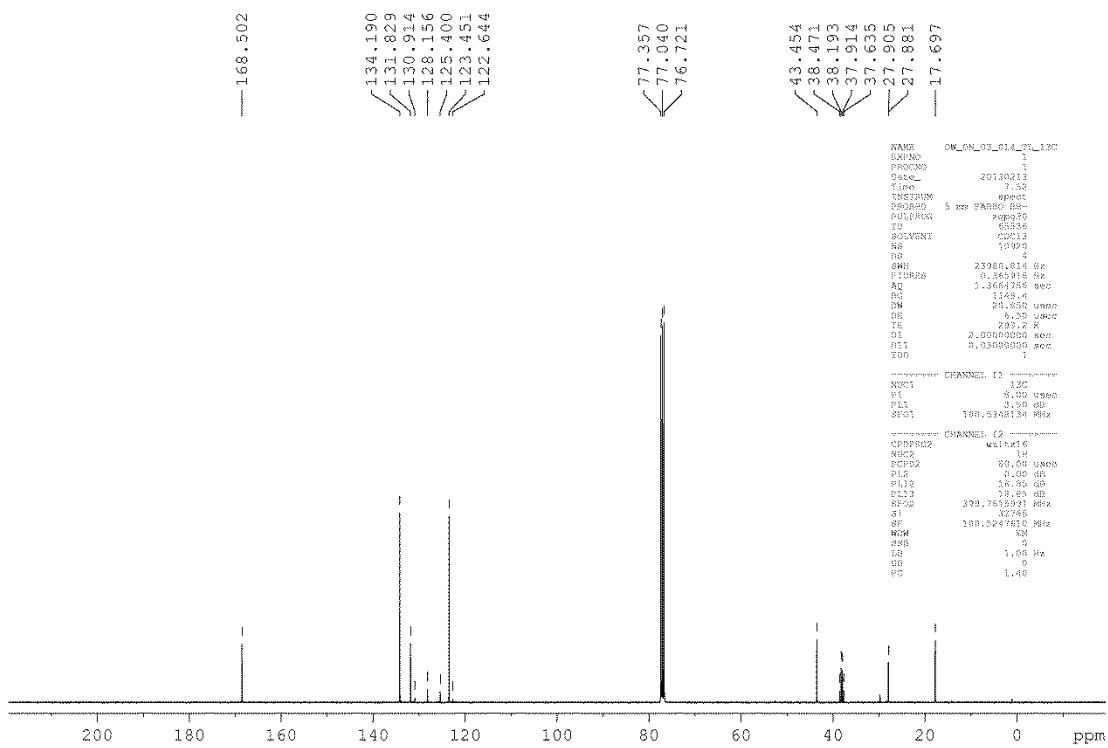


## 2-(4,4,4-Trifluoro-2-methylbutyl)isoindoline-1,3-dione (2d)



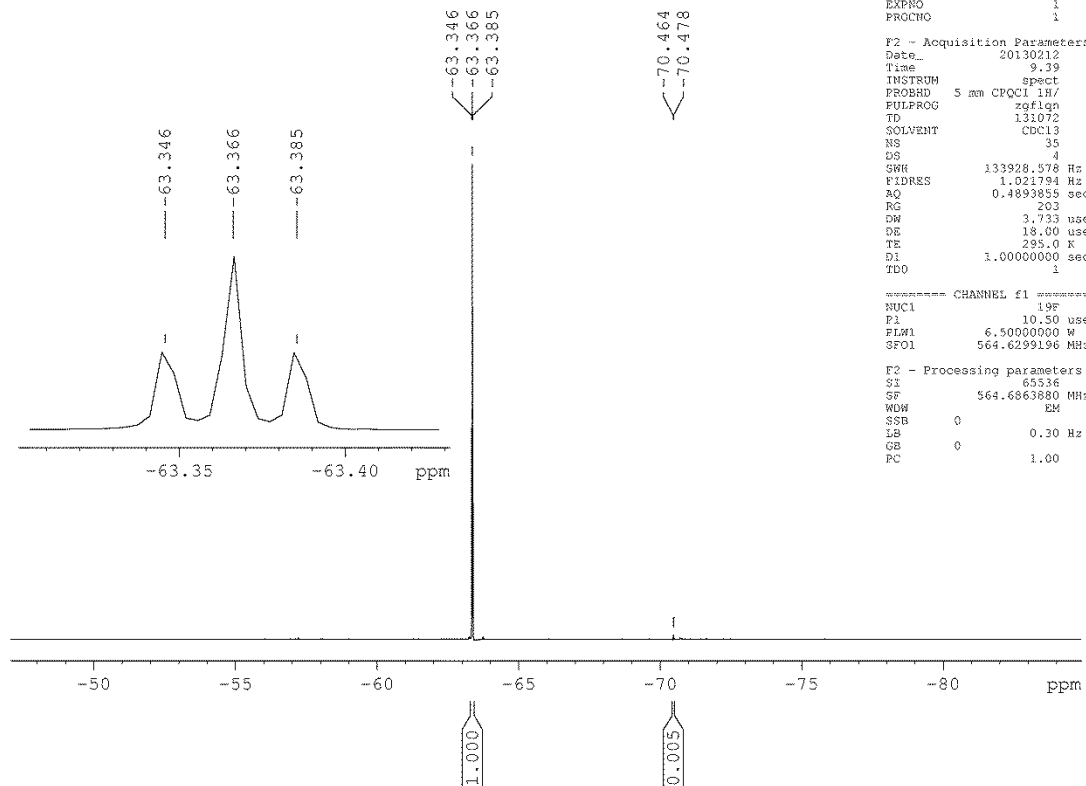
2-(4,4,4-Trifluoro-2-methylbutyl)isoindoline-1,3-dione (2d)

DW\_DN\_03\_014\_TL\_13C

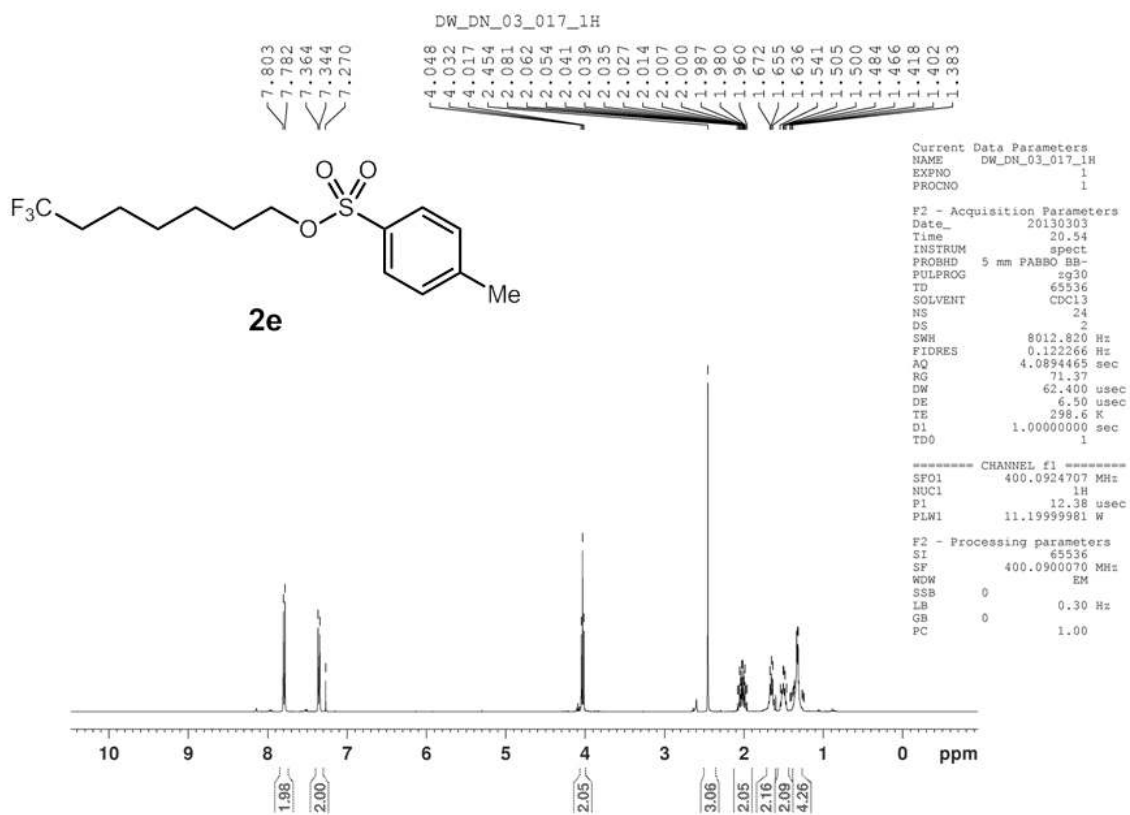


## 2-(4,4,4-Trifluoro-2-methylbutyl)isoindoline-1,3-dione (2d)

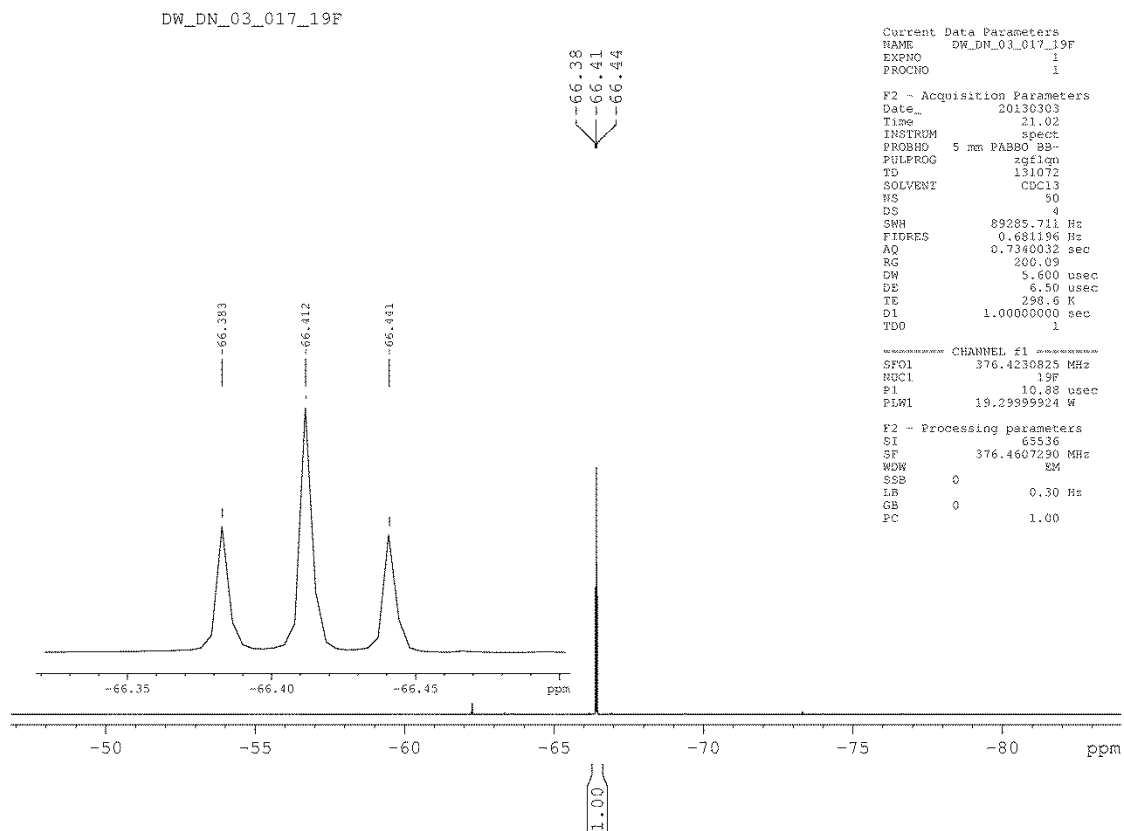
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### 7,7,7-Trifluoroheptyl 4-methylbenzenesulfonate (2e)

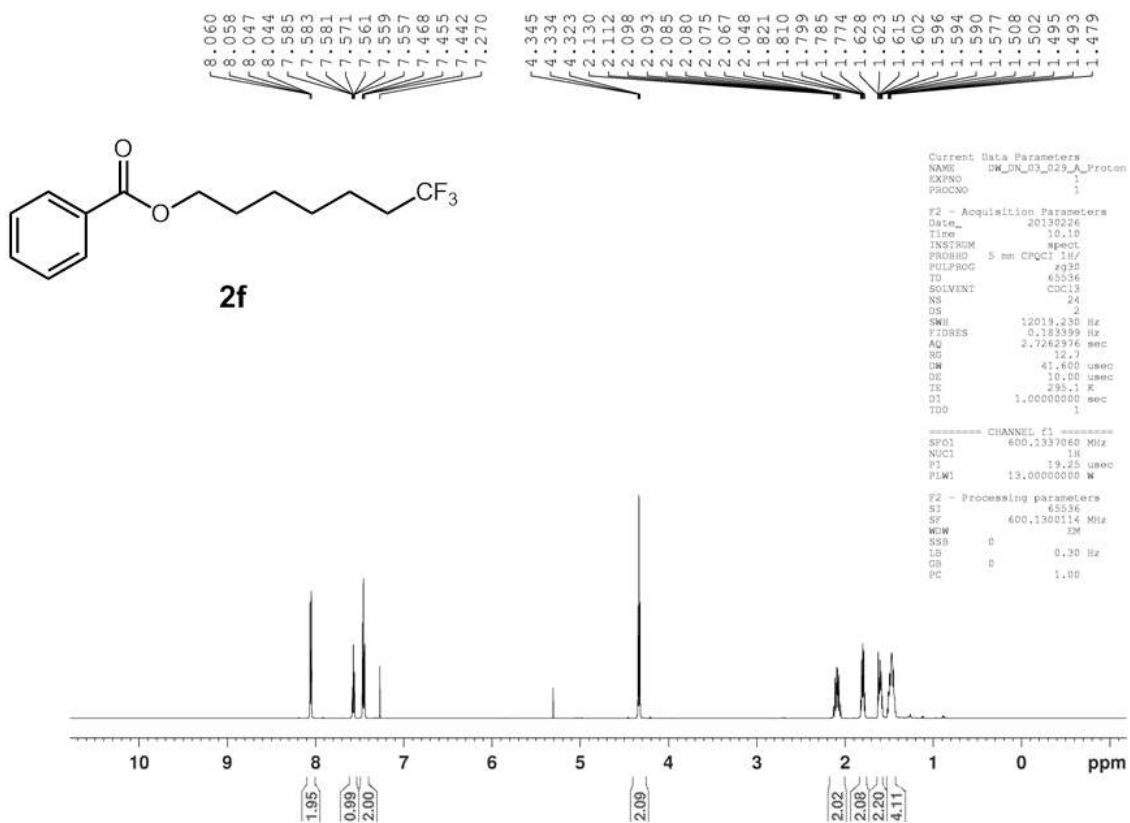


## 7,7,7-Trifluoroheptyl 4-methylbenzenesulfonate (2e)



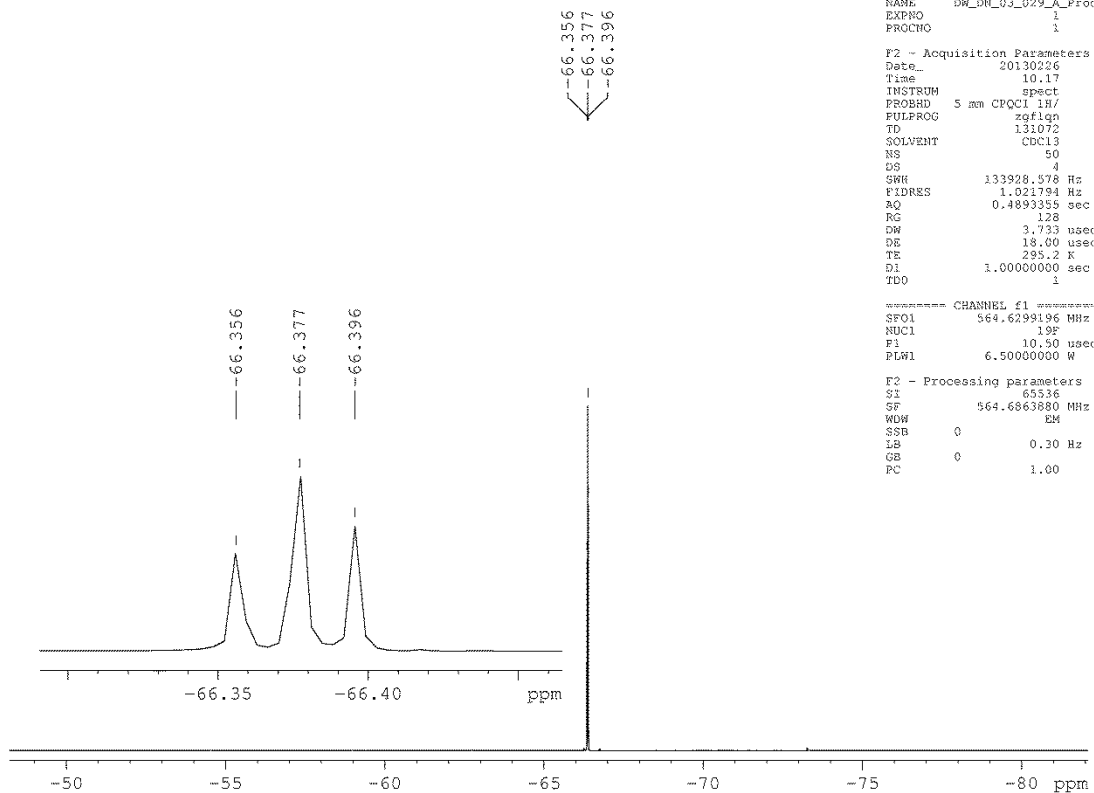


### 7,7,7-Trifluoroheptyl benzoate (2f)

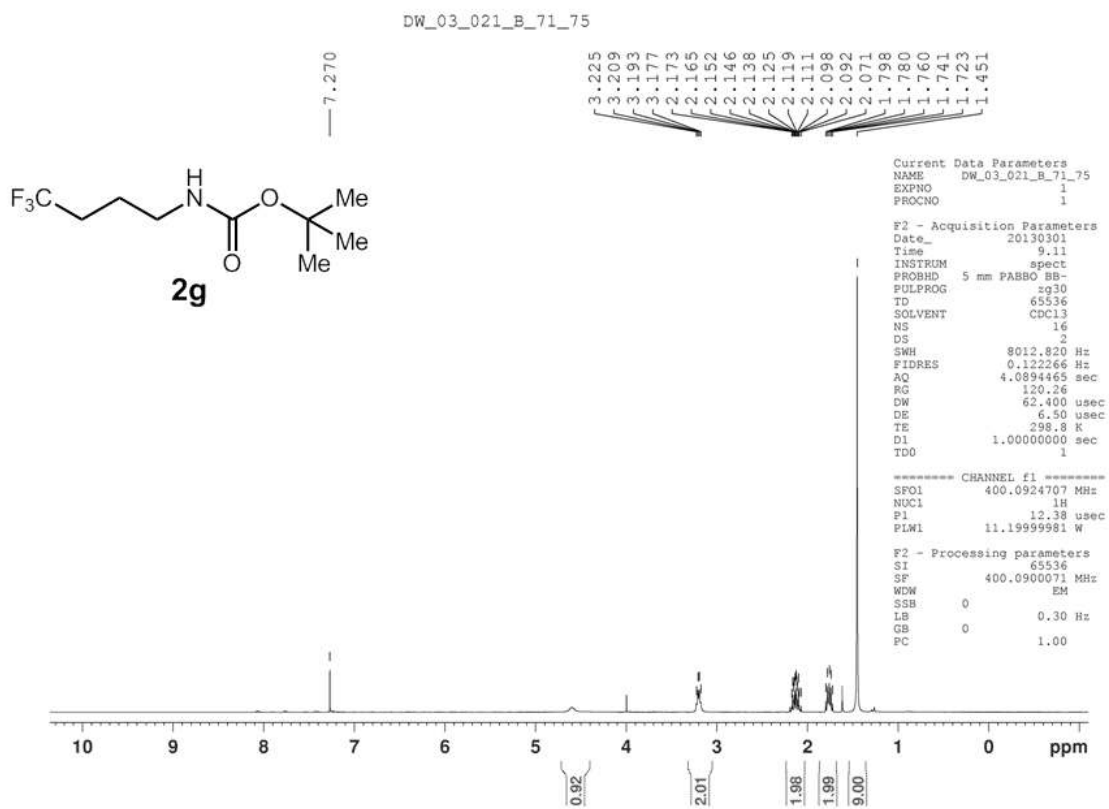


## 7,7,7-Trifluoroheptyl benzoate (2f)

DW\_DN\_03\_029\_A\_Product\_19F

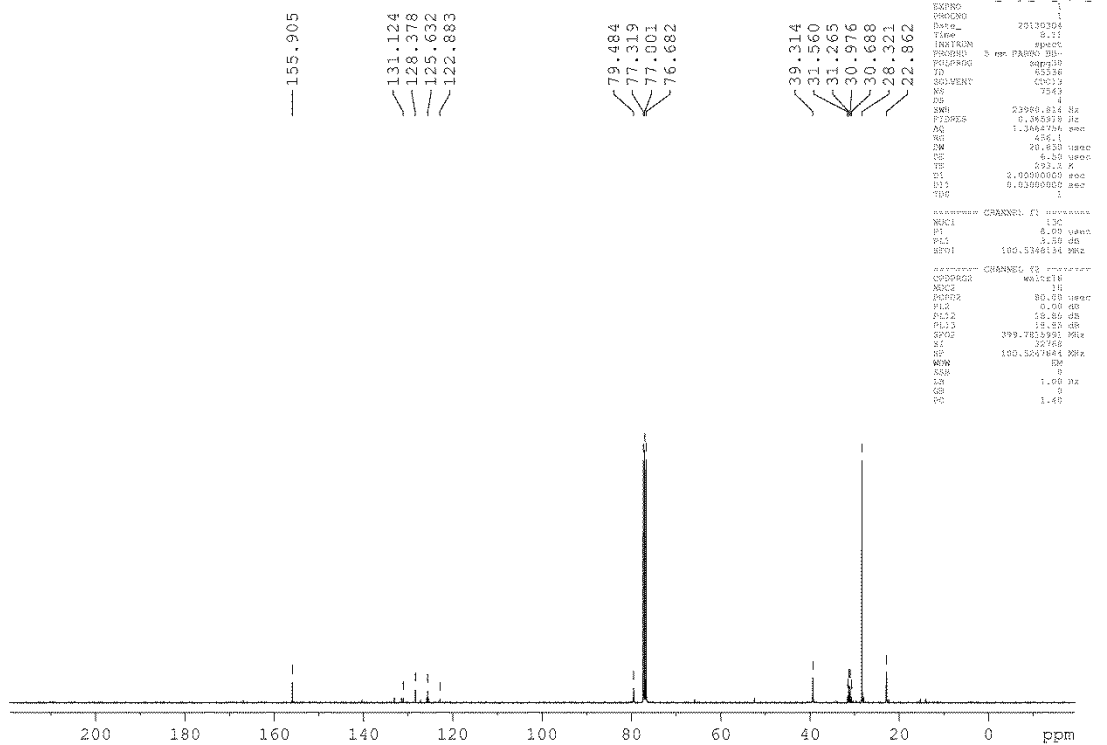


***tert*-Butyl (4,4,4-trifluorobutyl)carbamate (2g)**



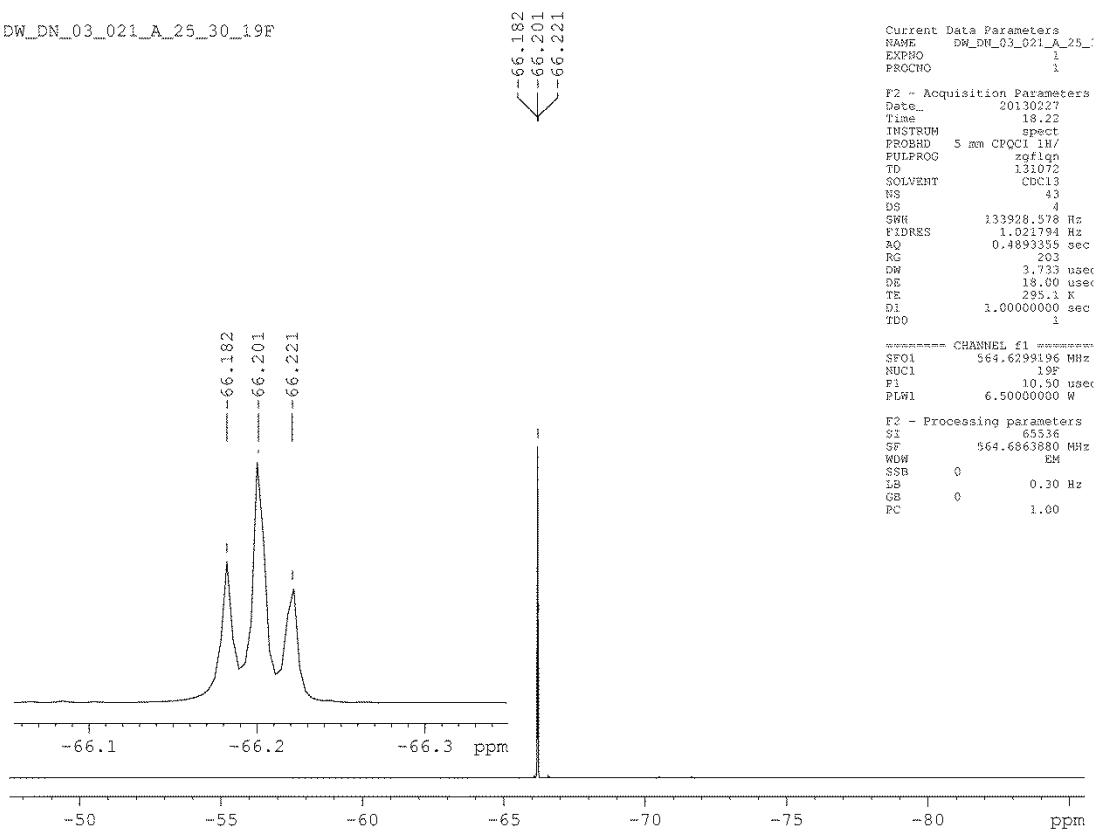
### *tert*-Butyl (4,4,4-trifluorobutyl)carbamate (2g)

DW\_Allyl\_Boc\_Amine\_13C



**tert-Butyl (4,4,4-trifluorobutyl)carbamate (2g)**

DW\_DN\_03\_021\_A\_25\_30\_19F



### 4-Methyl-N-(4,4,4-trifluorobutyl)-benzenesulfonamide (2h)

DW\_DN\_03\_020\_A\_1H

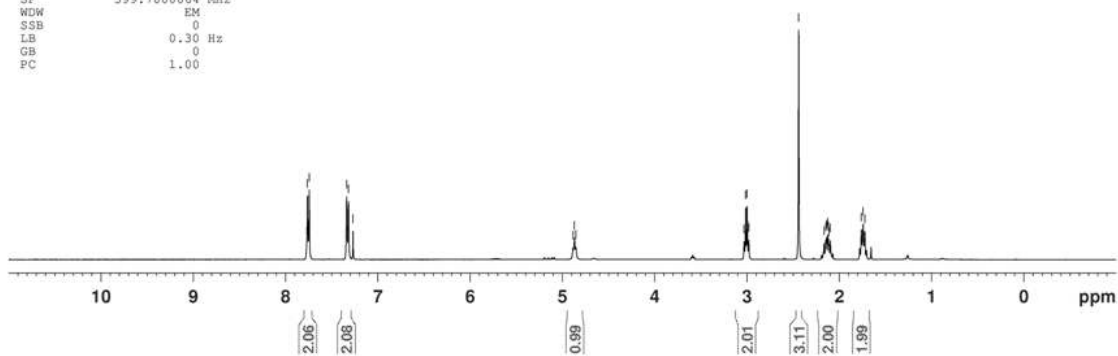
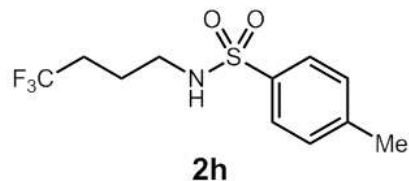
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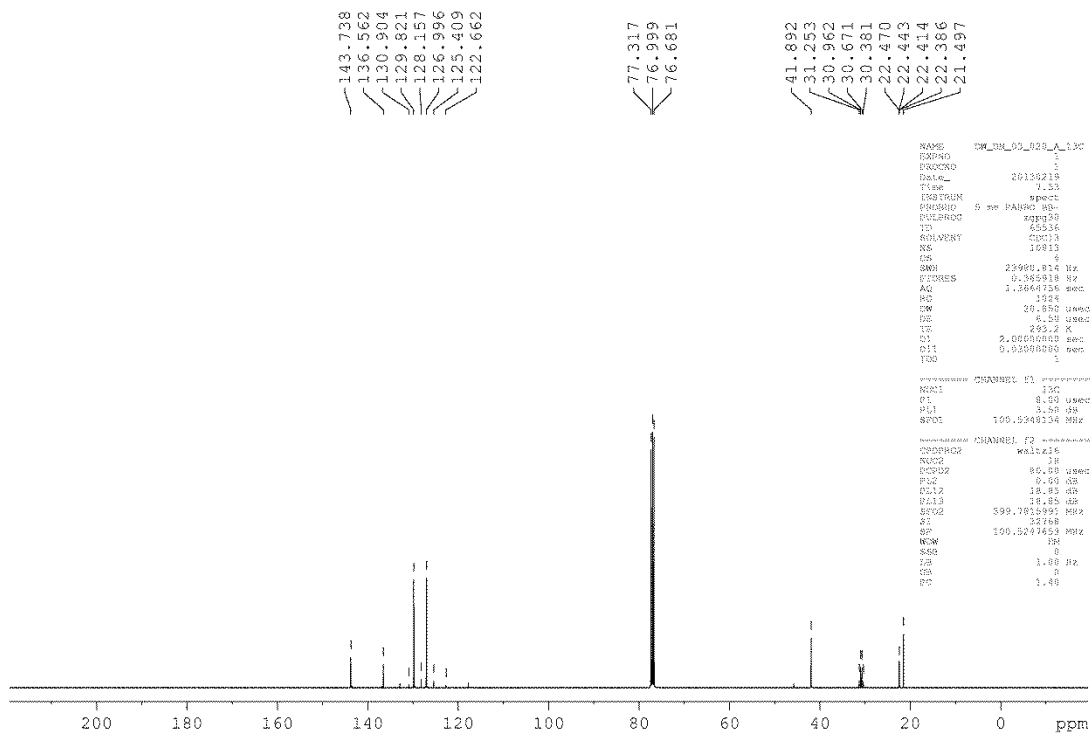
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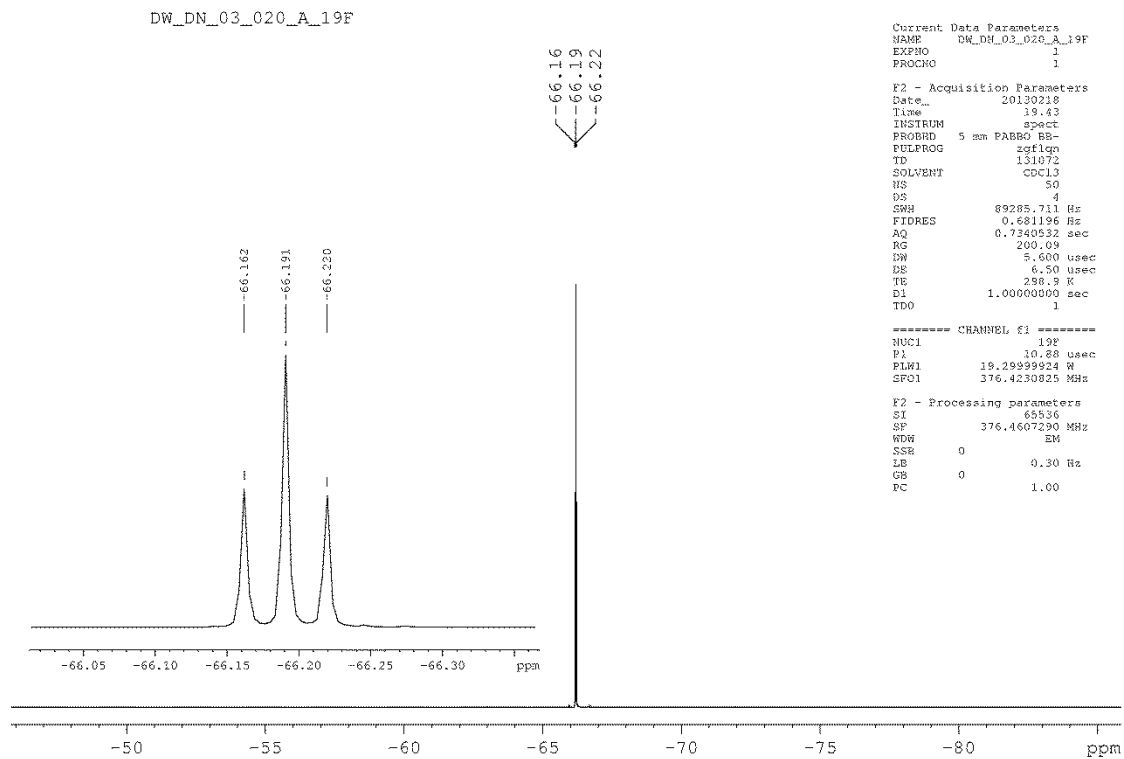


### 4-Methyl-N-(4,4,4-trifluorobutyl)-benzenesulfonamide (2h)

DW\_DN\_03\_020\_A\_13C

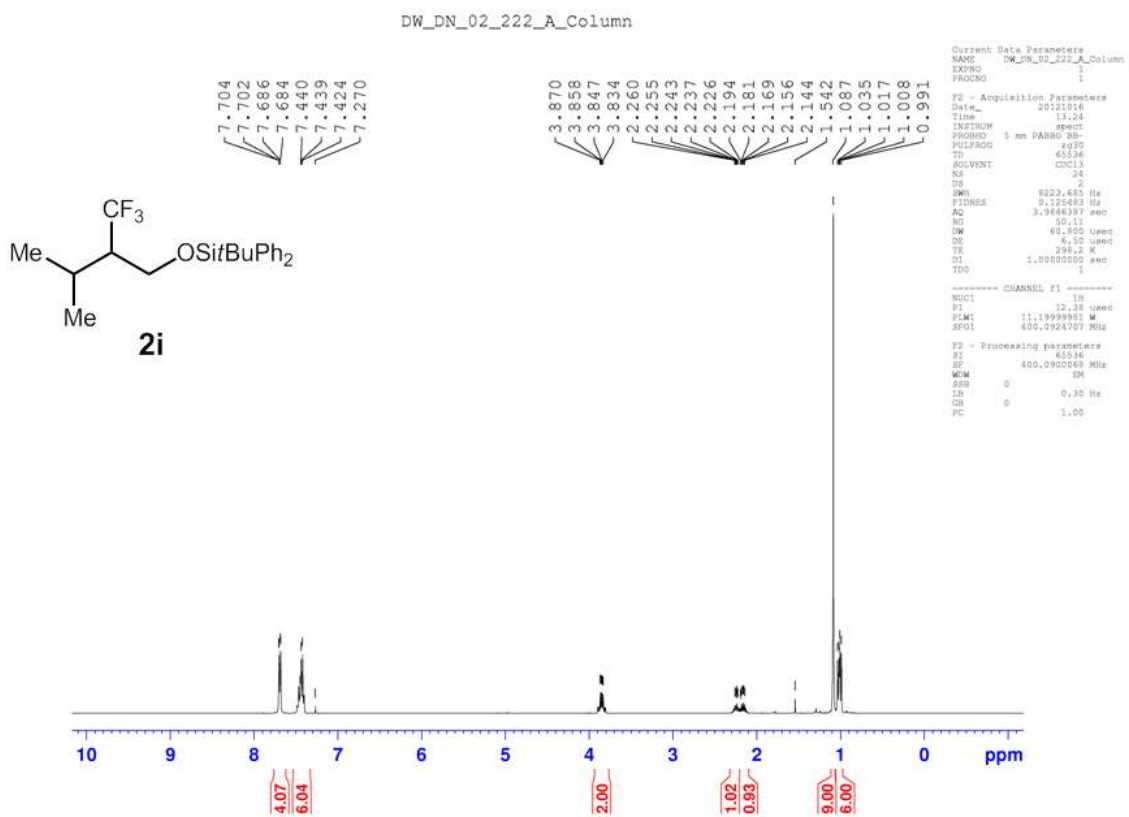


### 4-Methyl-N-(4,4,4-trifluorobutyl)-benzenesulfonamide (2h)



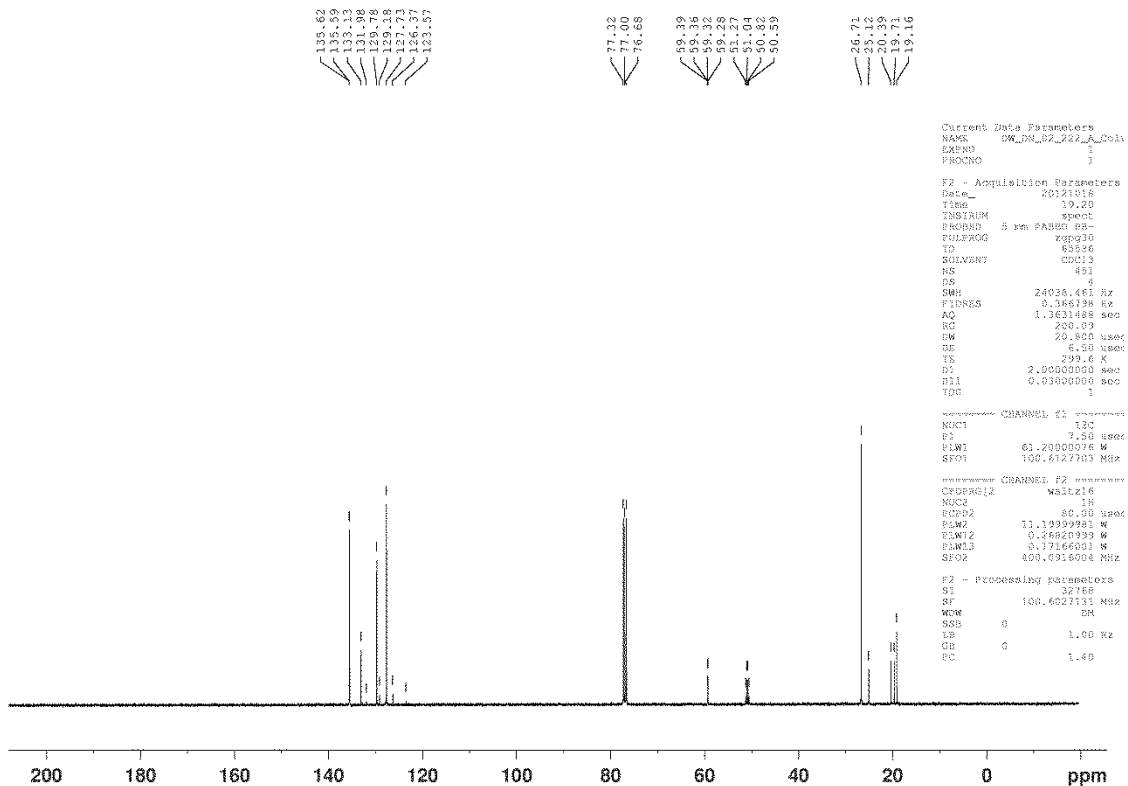


### *tert*-Butyl-(3-methyl-2-(trifluoromethyl)butoxy)diphenylsilane (**2i**)

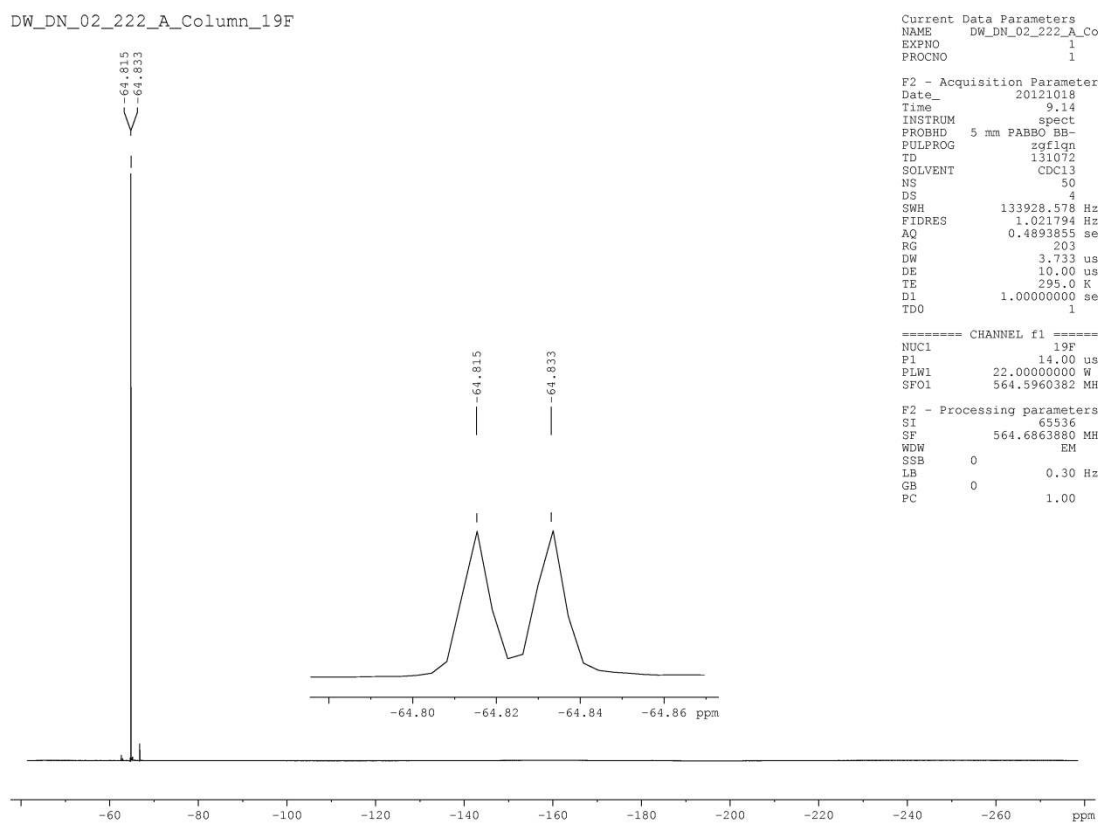


### *tert*-Butyl-(3-methyl-2-(trifluoromethyl)butoxy)diphenylsilane (2i)

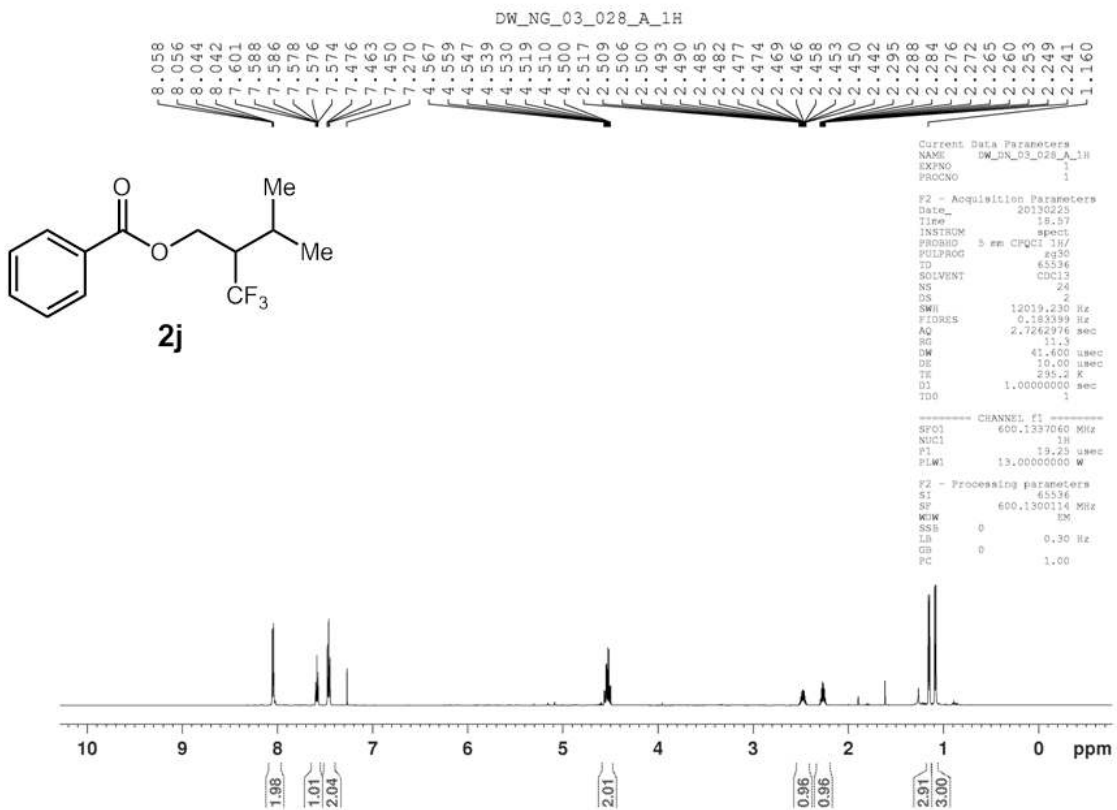
DW\_DN\_02\_222\_A\_Column\_13C



***tert*-Butyl-(3-methyl-2-(trifluoromethyl)butoxy)diphenylsilane (2i)**

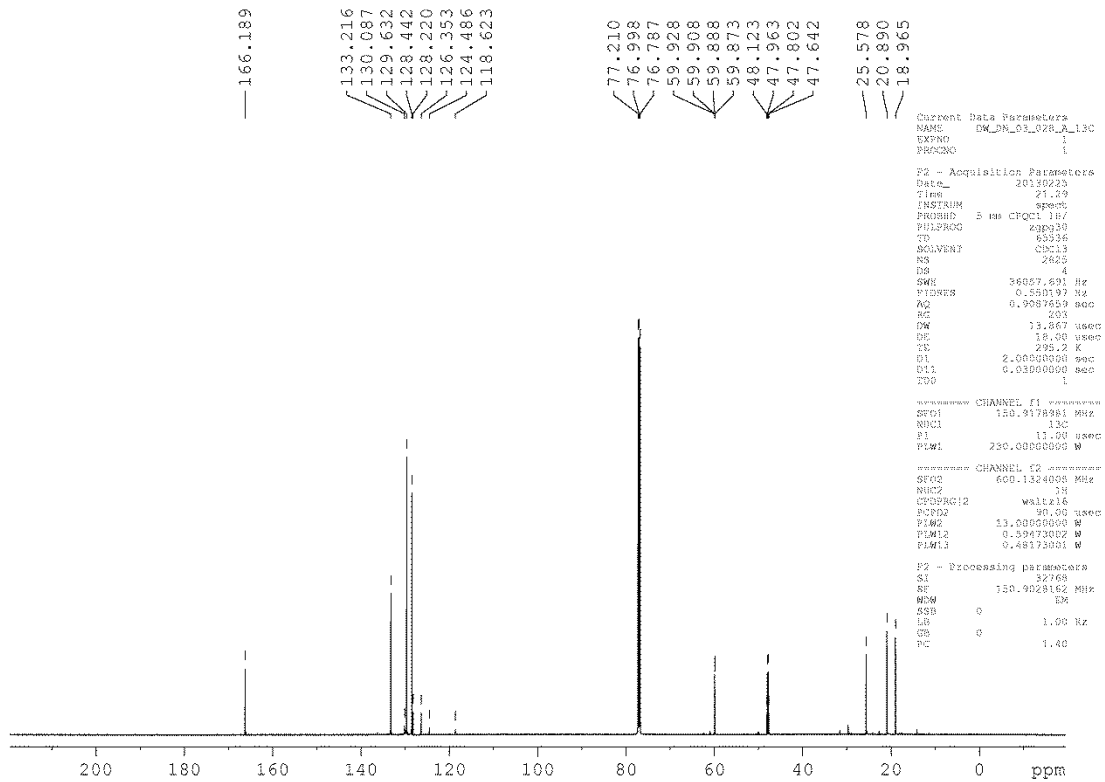


### 3-Methyl-2-(trifluoromethyl)butyl benzoate (2j)



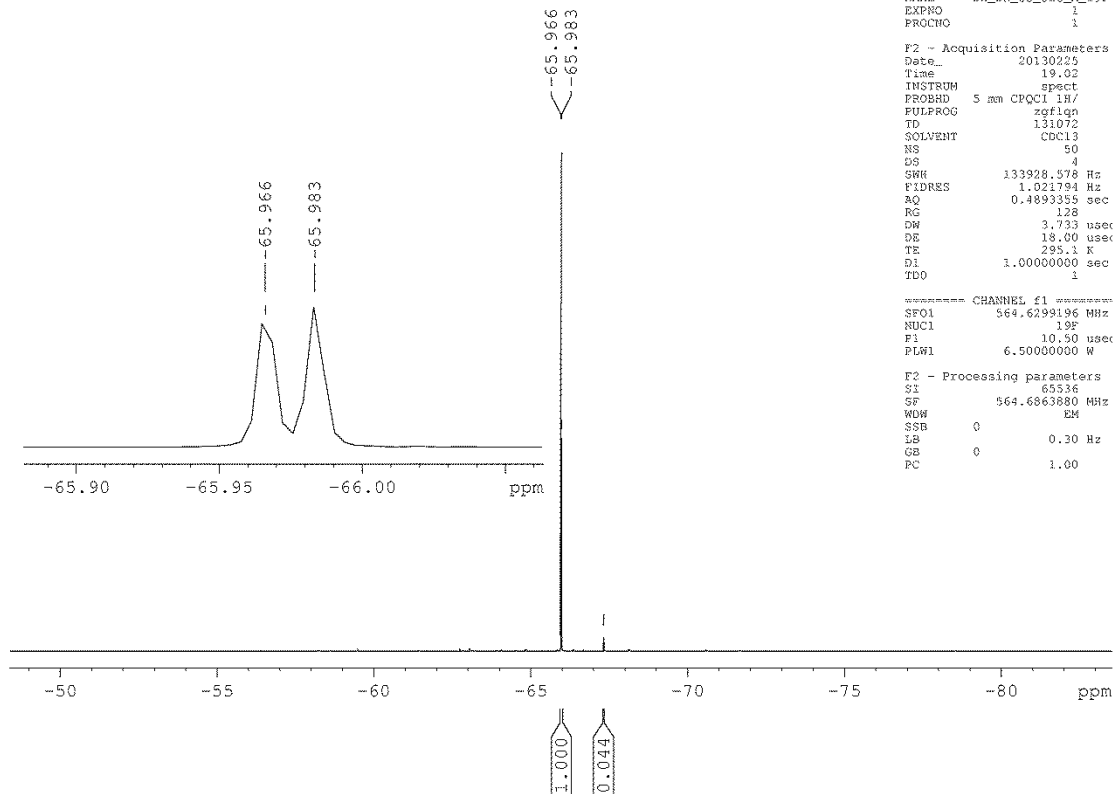
### 3-Methyl-2-(trifluoromethyl)butyl benzoate (2j)

DW\_DN\_03\_028\_A\_13C

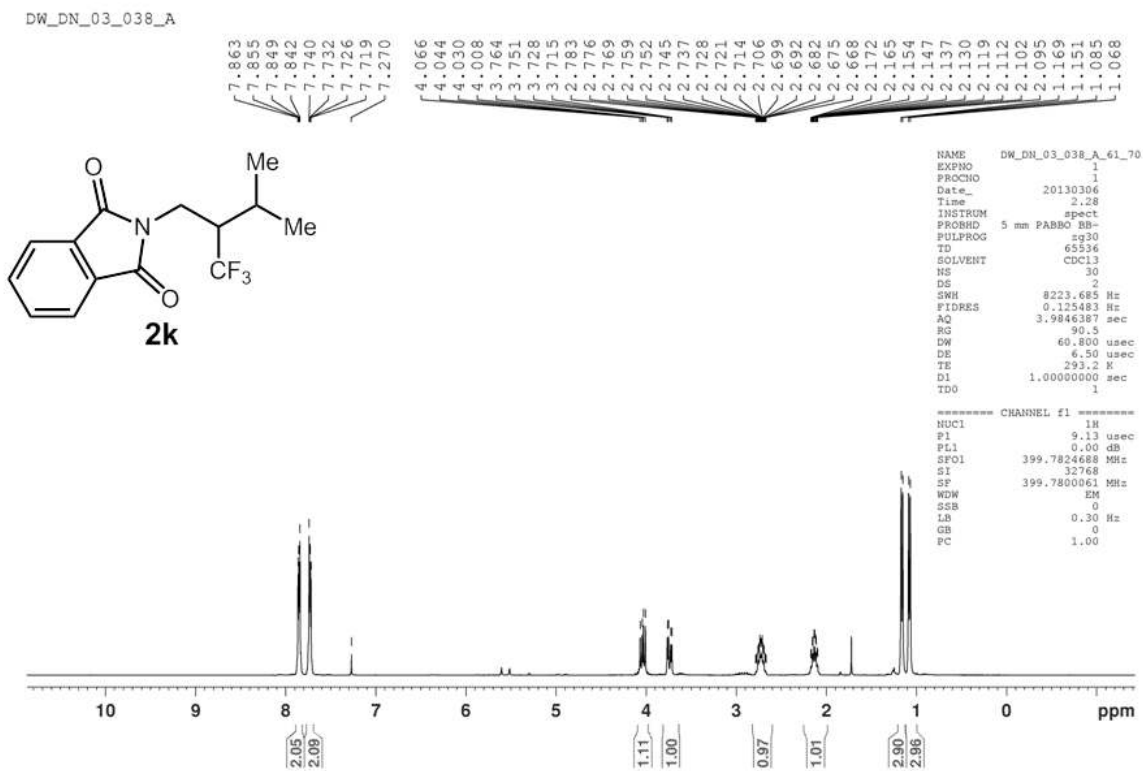


### 3-Methyl-2-(trifluoromethyl)butyl benzoate (2j)

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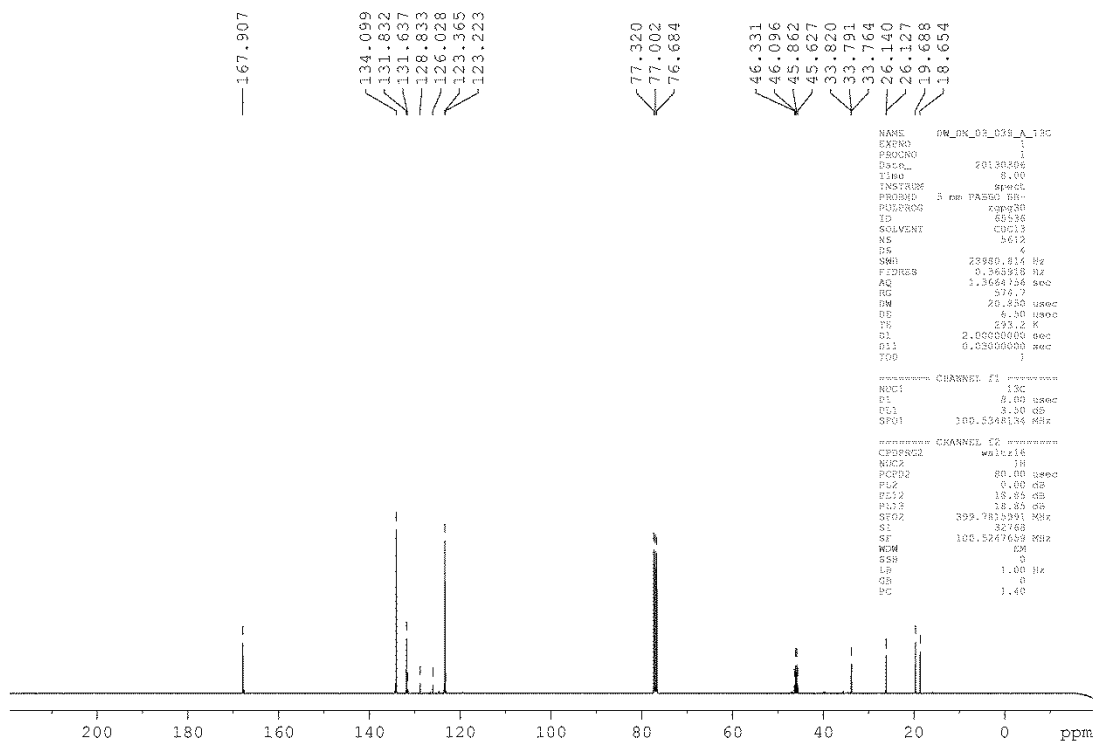


## 2-(3-Methyl-2-(trifluoromethyl)butyl)isoindoline-1,3-dione (2k)



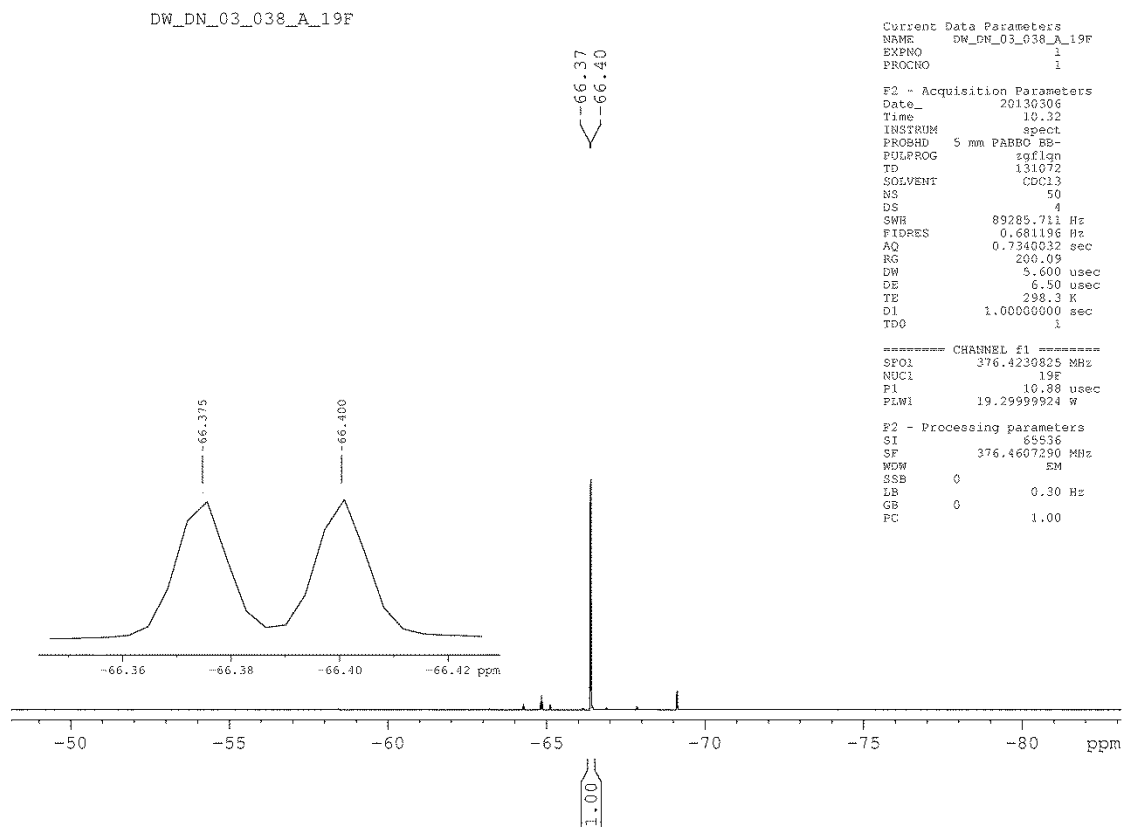
## 2-(3-Methyl-2-(trifluoromethyl)butyl)isoindoline-1,3-dione (2k)

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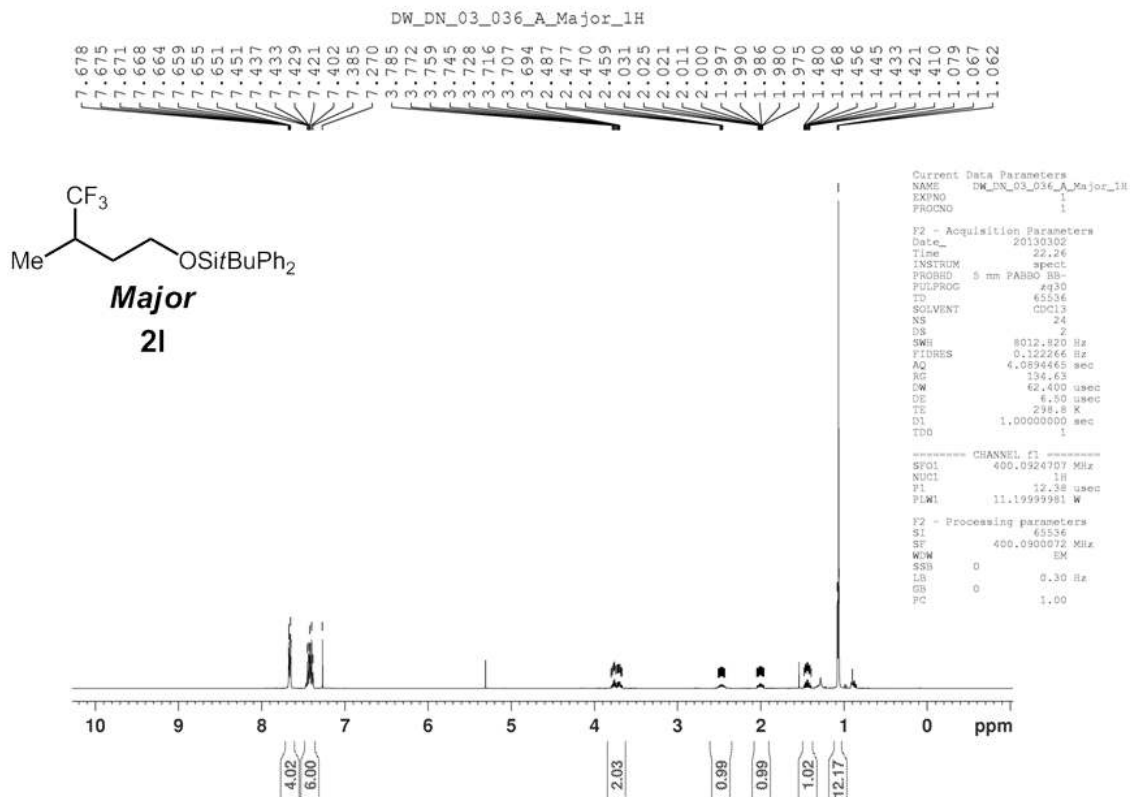




## 2-(3-Methyl-2-(trifluoromethyl)butyl)isoindoline-1,3-dione (2k)

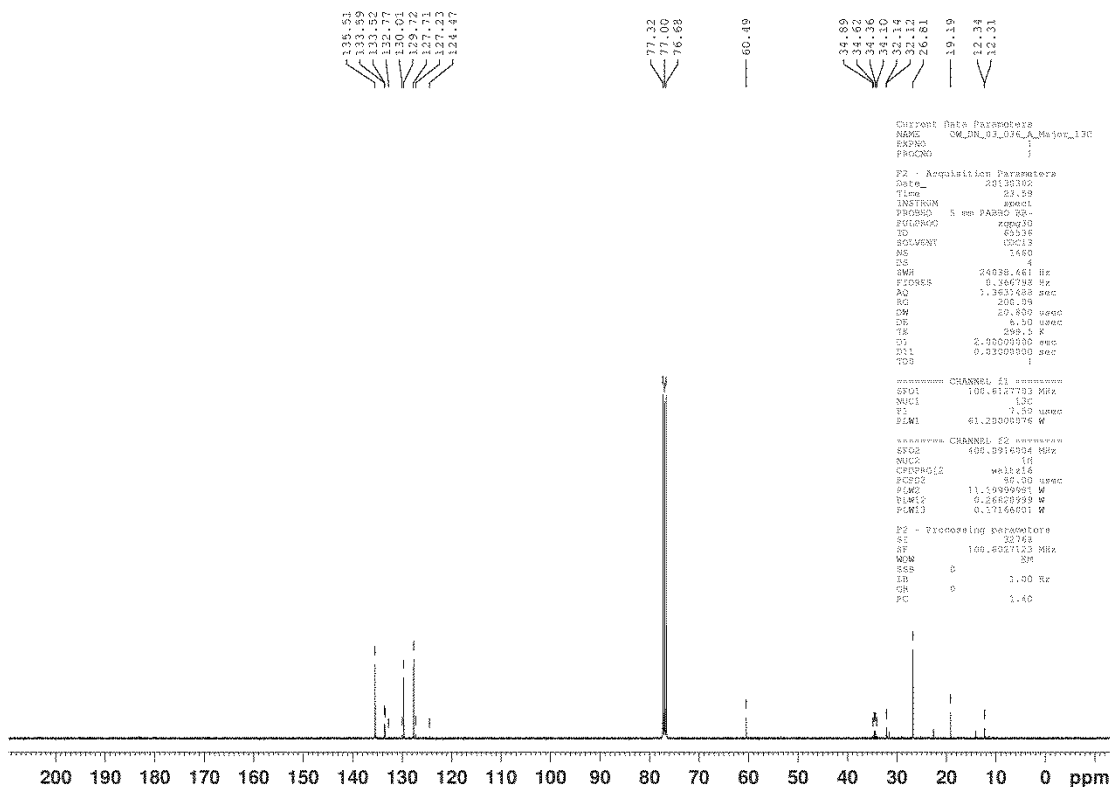


***tert*-Butyldiphenyl(4,4,4-trifluoro-3-methylbutoxy)silane (2l, Major Regioisomer)**

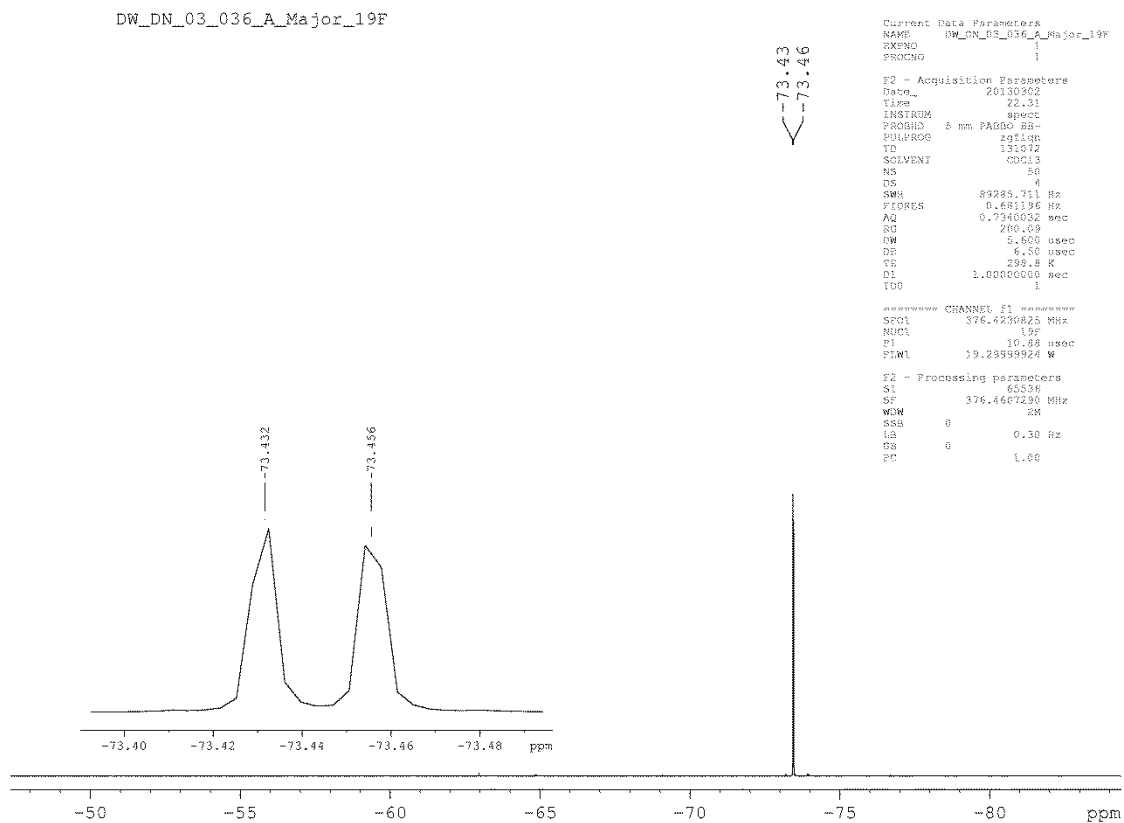


### *tert*-Butyldiphenyl(4,4,4-trifluoro-3-methylbutoxy)silane (2l, Major Regioisomer)

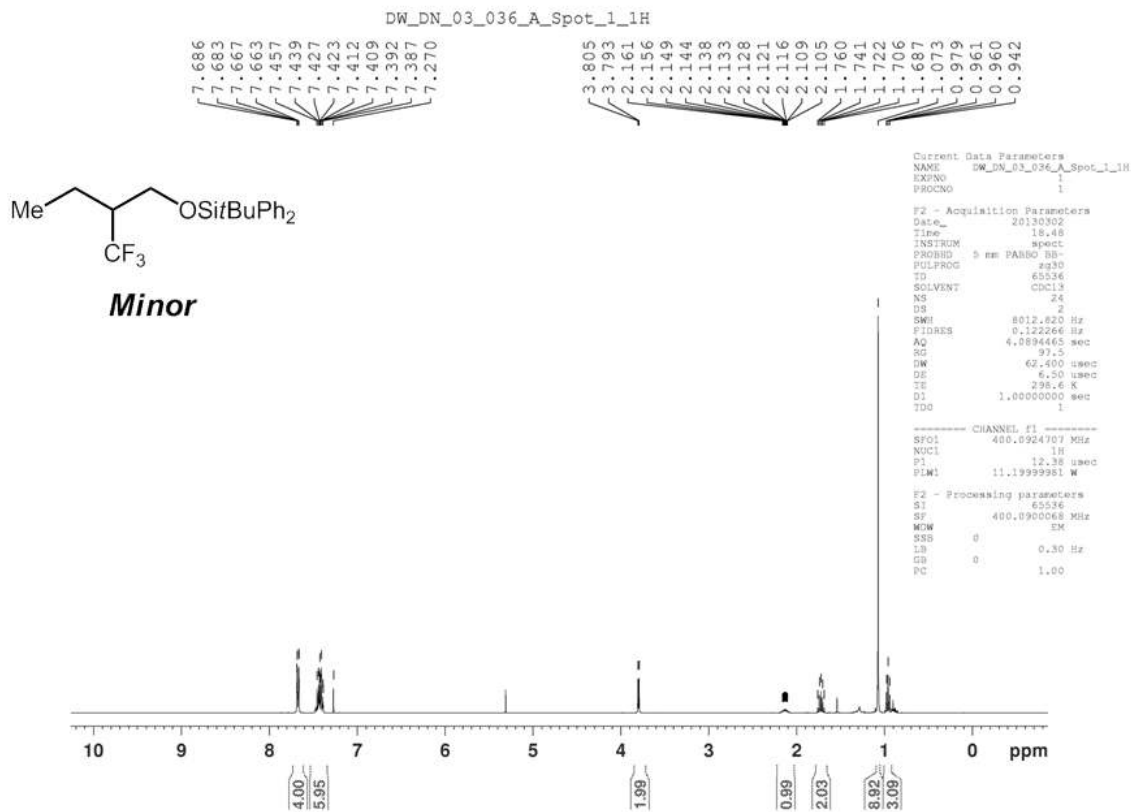
DW\_DN\_03\_036\_A\_Major\_13C



### *tert*-Butyldiphenyl(4,4,4-trifluoro-3-methylbutoxy)silane (2l, Major Regioisomer)

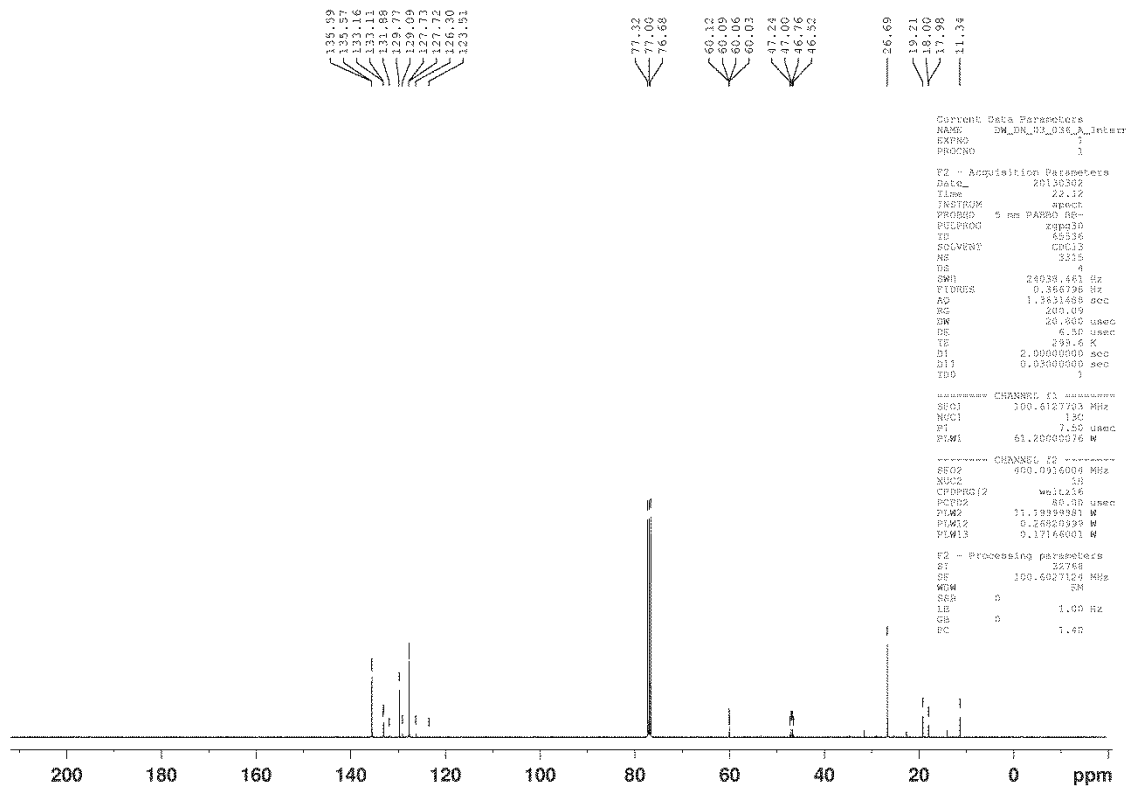


***tert*-Butyldiphenyl(2-(trifluoromethyl)butoxy)silane (2l, Minor Regioisomer)**

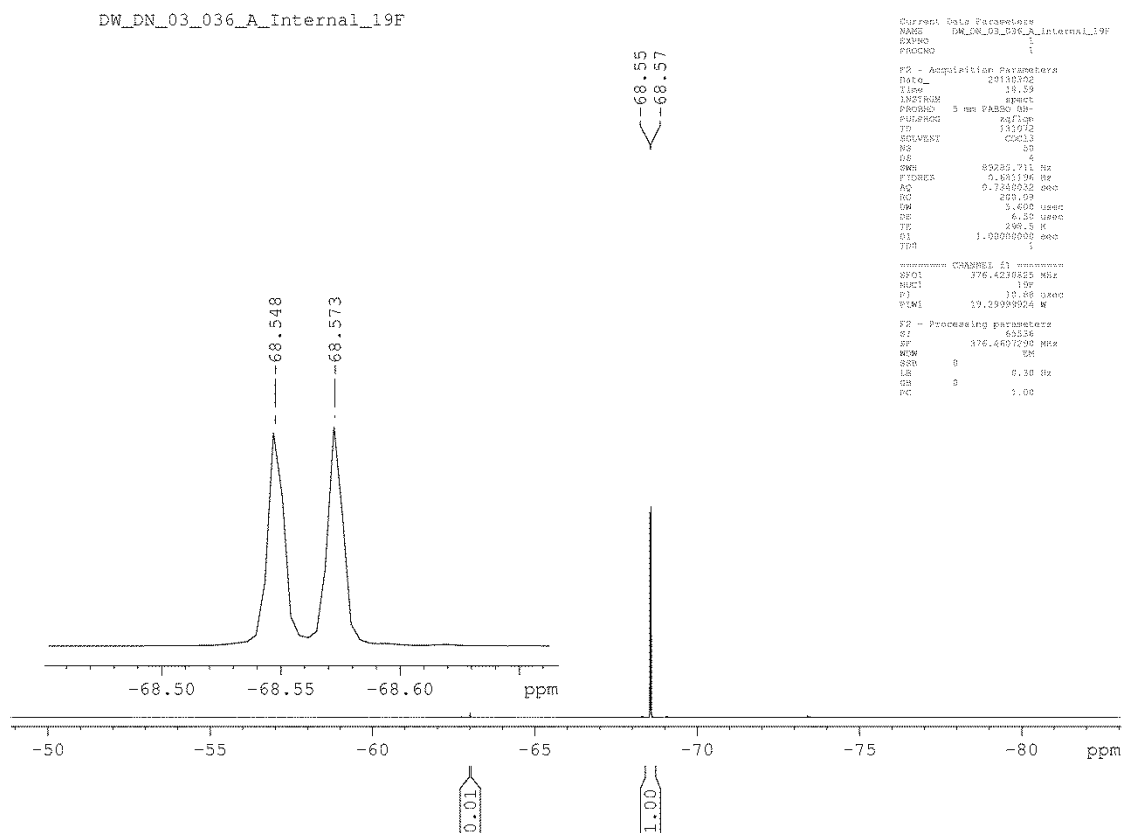


### *tert*-Butyldiphenyl(2-(trifluoromethyl)butoxy)silane (2l, Minor Regioisomer)

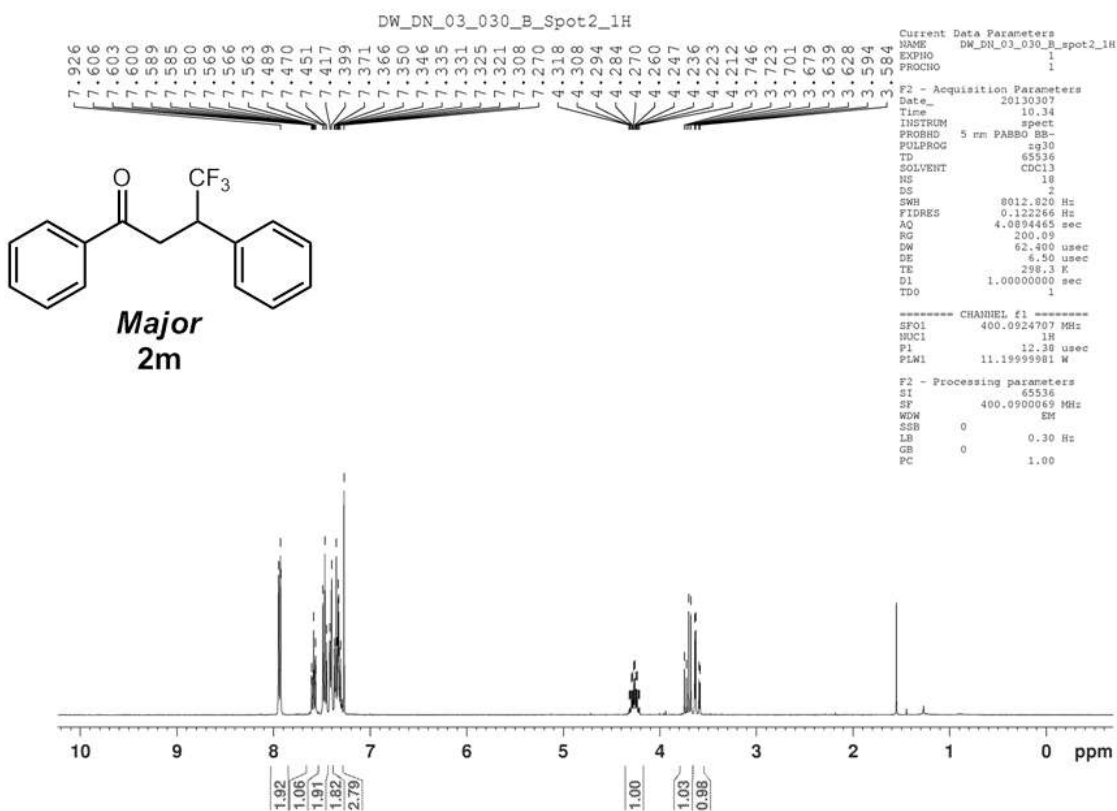
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### *tert*-Butyldiphenyl(2-(trifluoromethyl)butoxy)silane (2l, Minor Regioisomer)

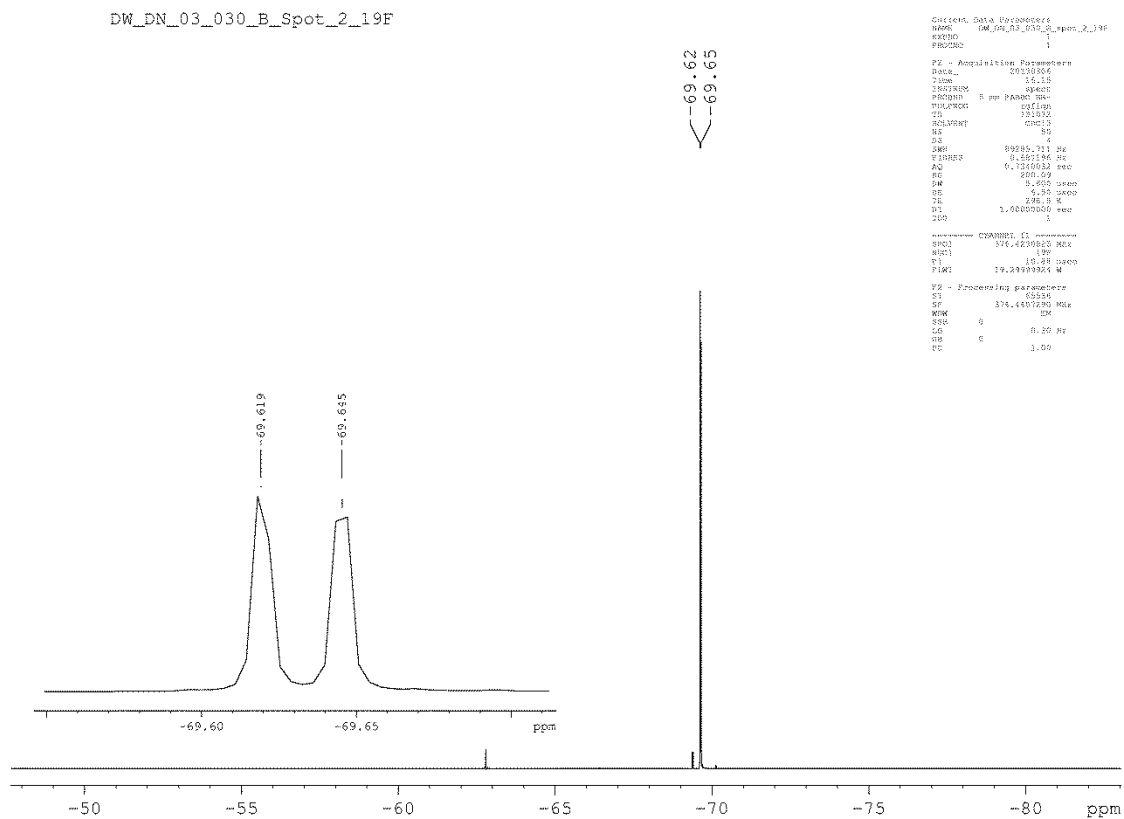


### 4,4-Trifluoro-1,3-diphenylbutan-1-one (2m, Major Regioisomer)

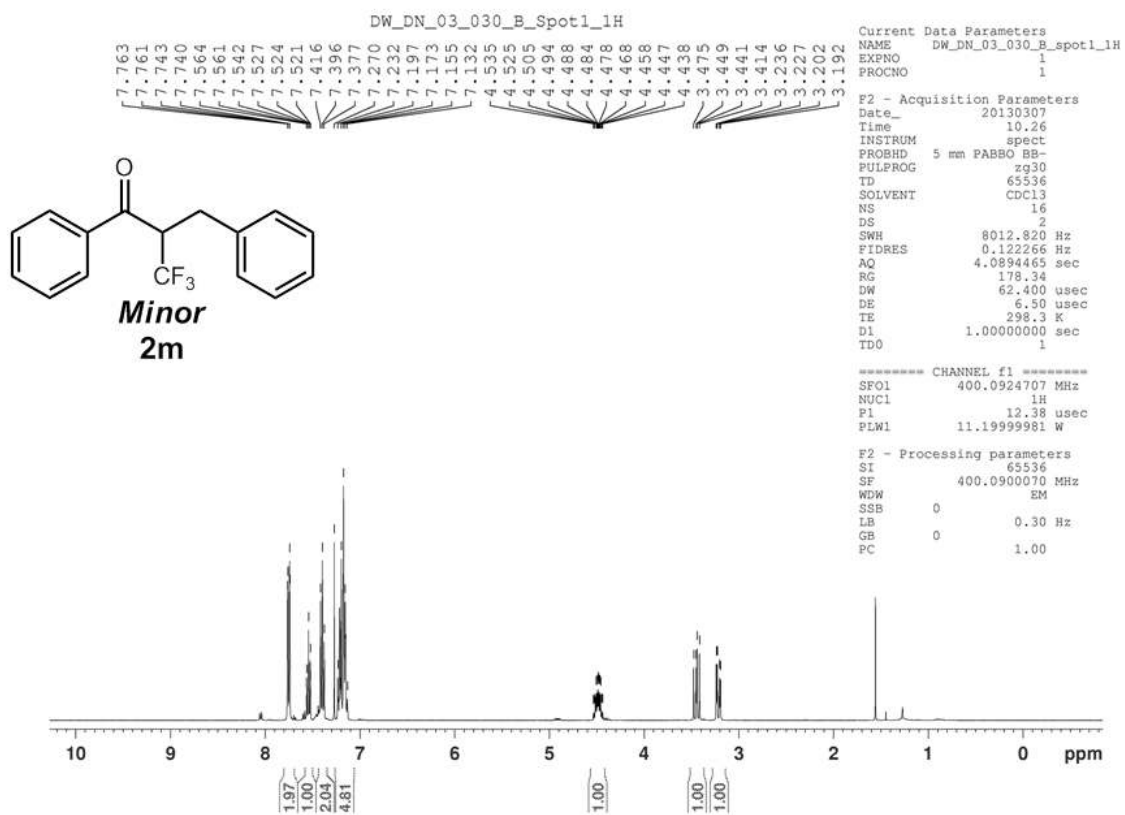




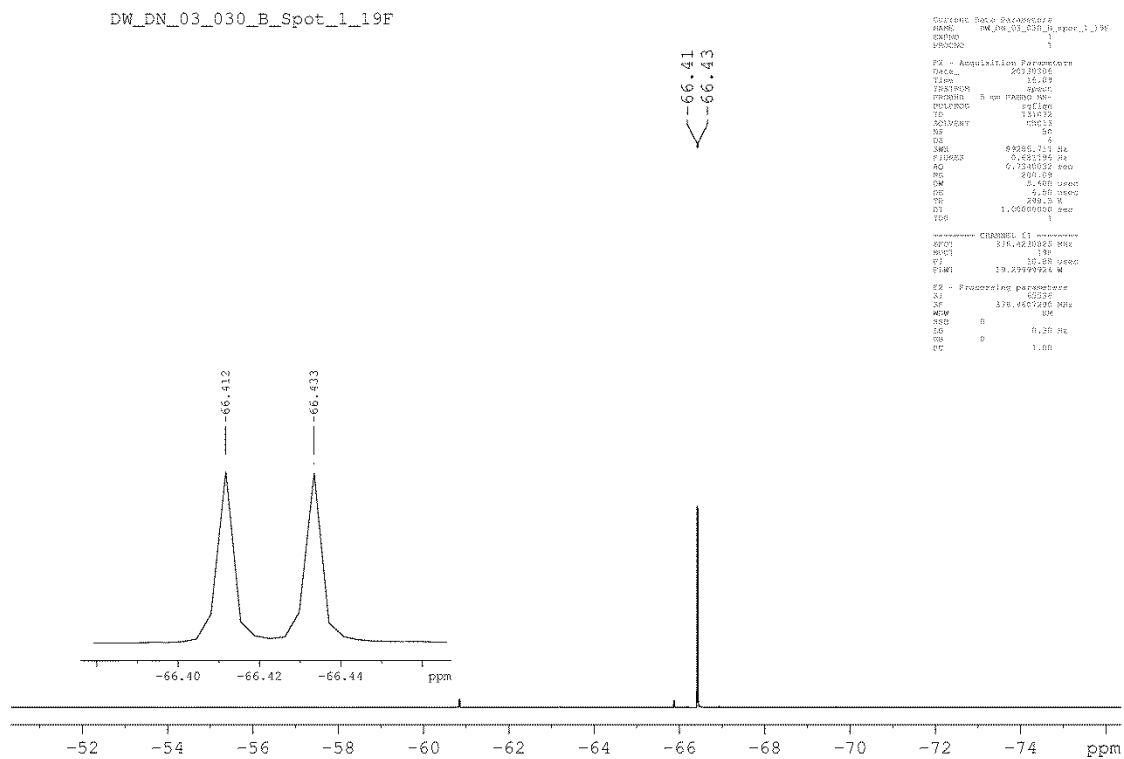
### 4,4,4-Trifluoro-1,3-diphenylbutan-1-one (2m, Major Regioisomer)



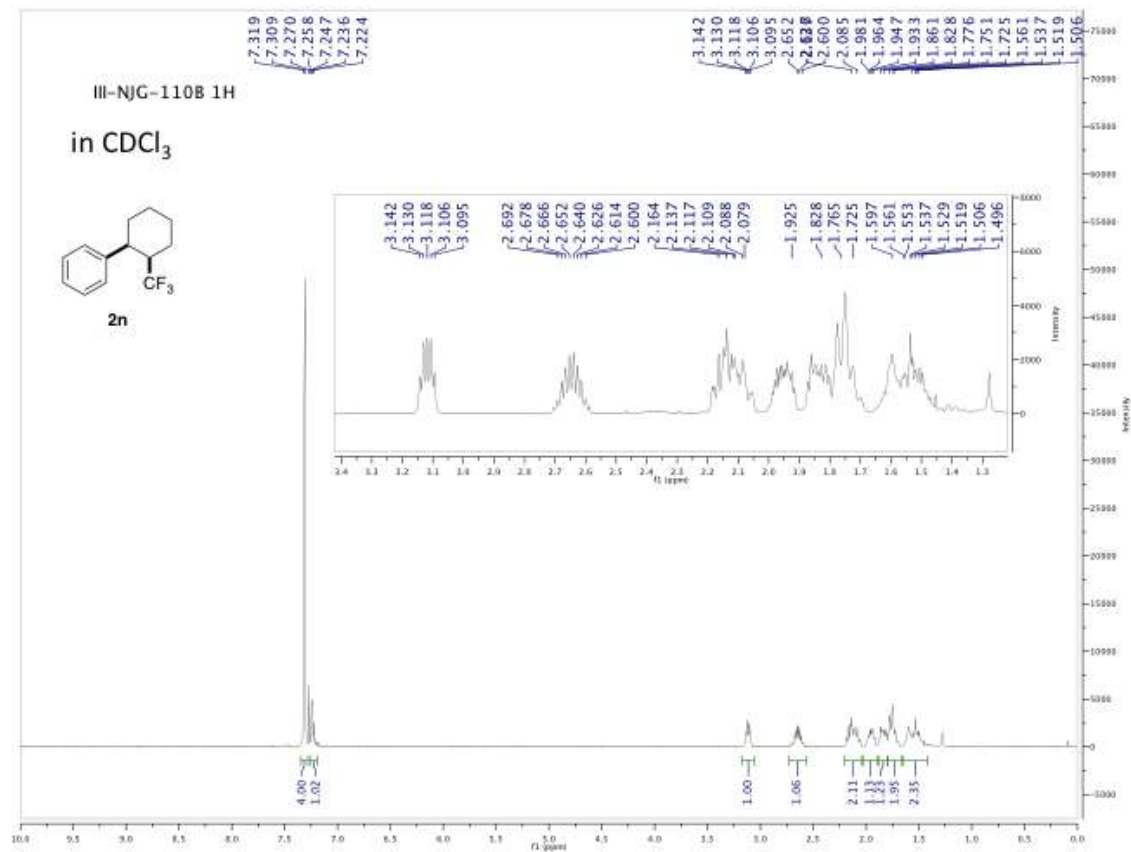
## 2-Benzyl-3,3,3-trifluoro-1-phenylpropan-1-one (2m, Minor Regioisomer)



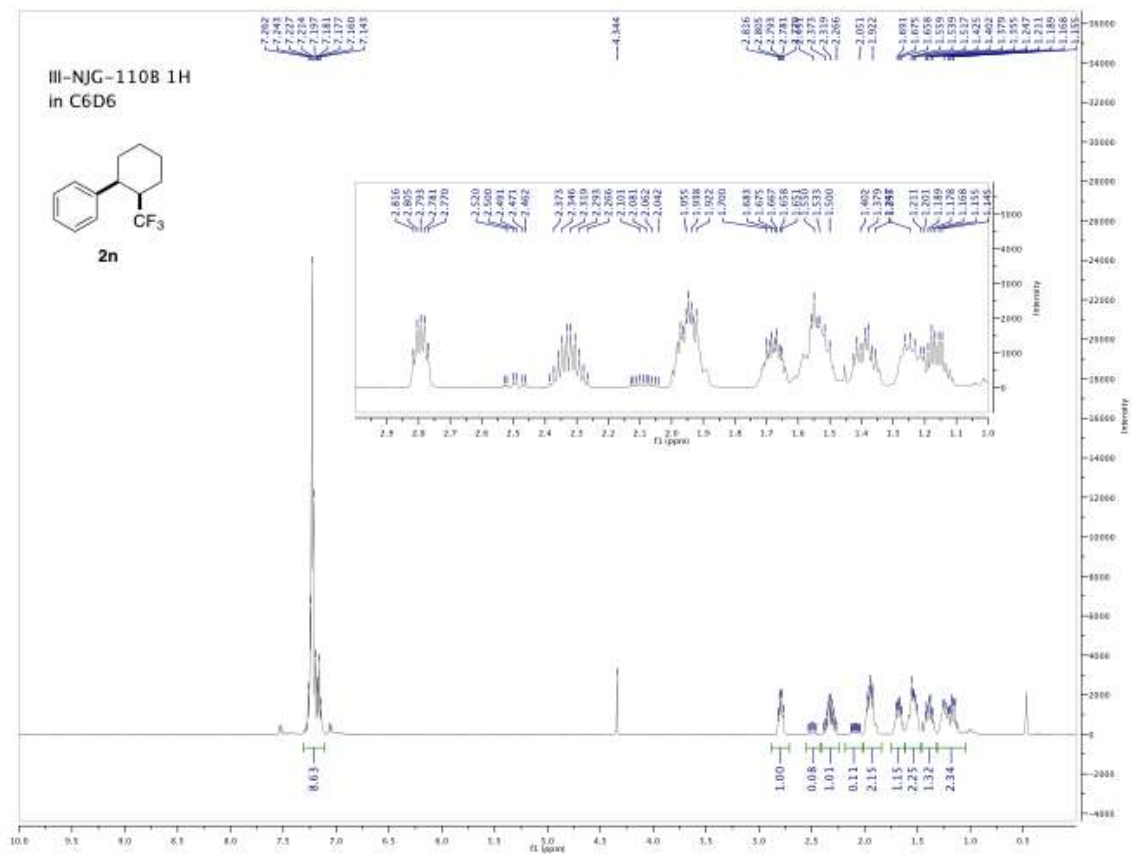
## 2-Benzyl-3,3,3-trifluoro-1-phenylpropan-1-one (2m, Minor Regioisomer)



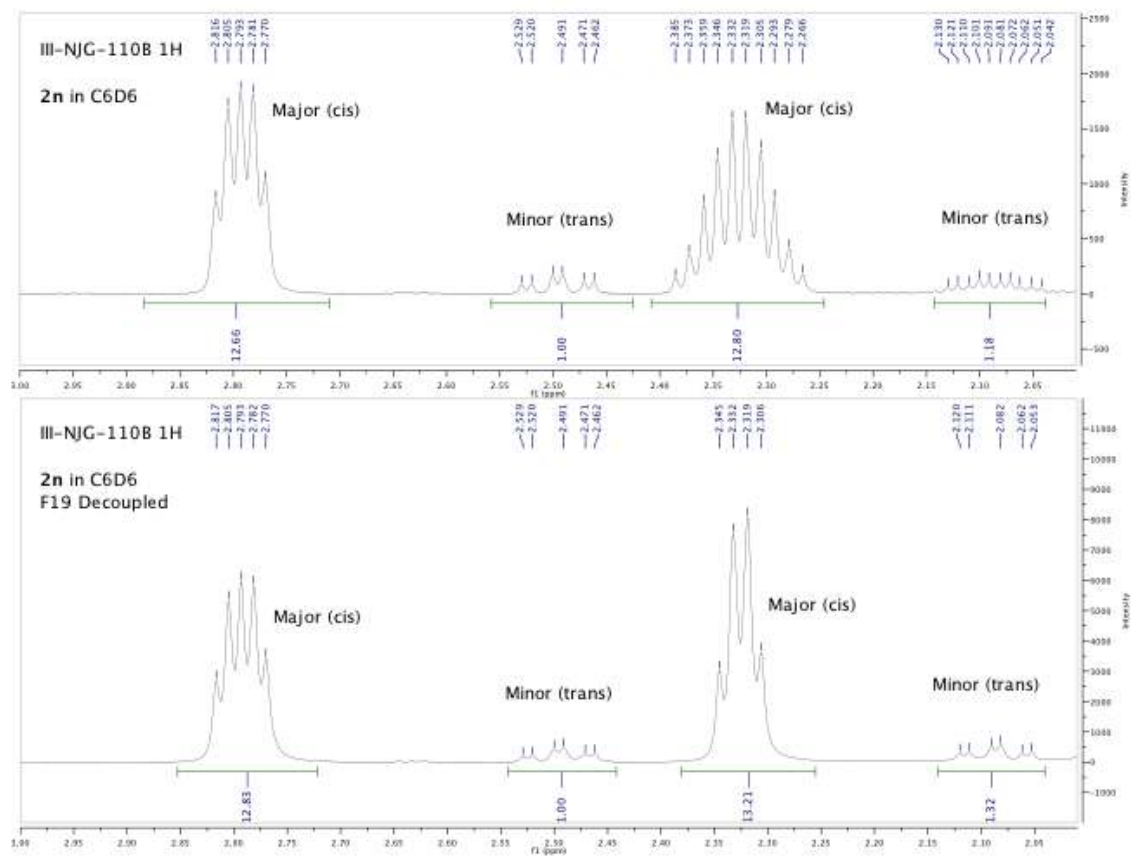
(2-(Trifluoromethyl)cyclohexyl)benzene (2n) (CDCl<sub>3</sub>)



(2-(Trifluoromethyl)cyclohexyl)benzene (2n) (C<sub>6</sub>D<sub>6</sub>)

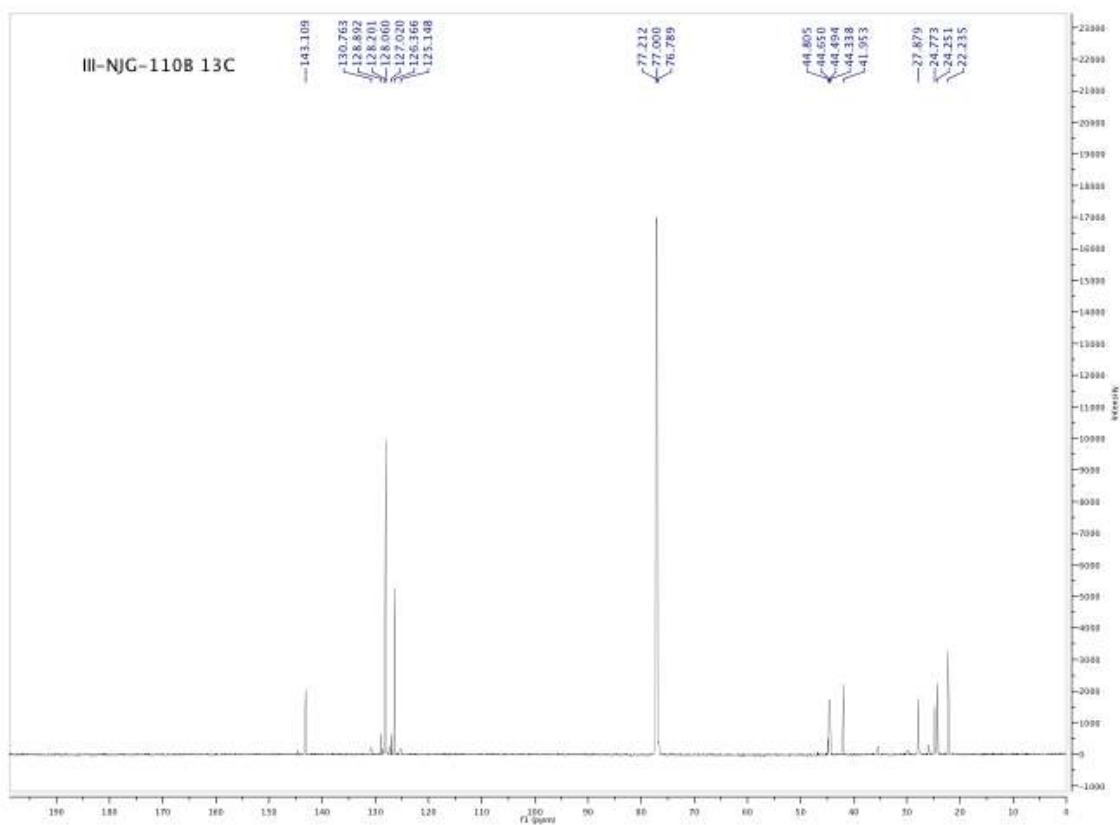


(2-(Trifluoromethyl)cyclohexyl)benzene (2n) in (C<sub>6</sub>D<sub>6</sub>, <sup>19</sup>F-Decoupling)





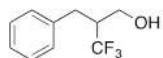
(2-(Trifluoromethyl)cyclohexyl)benzene (2n) (CDCl<sub>3</sub>)



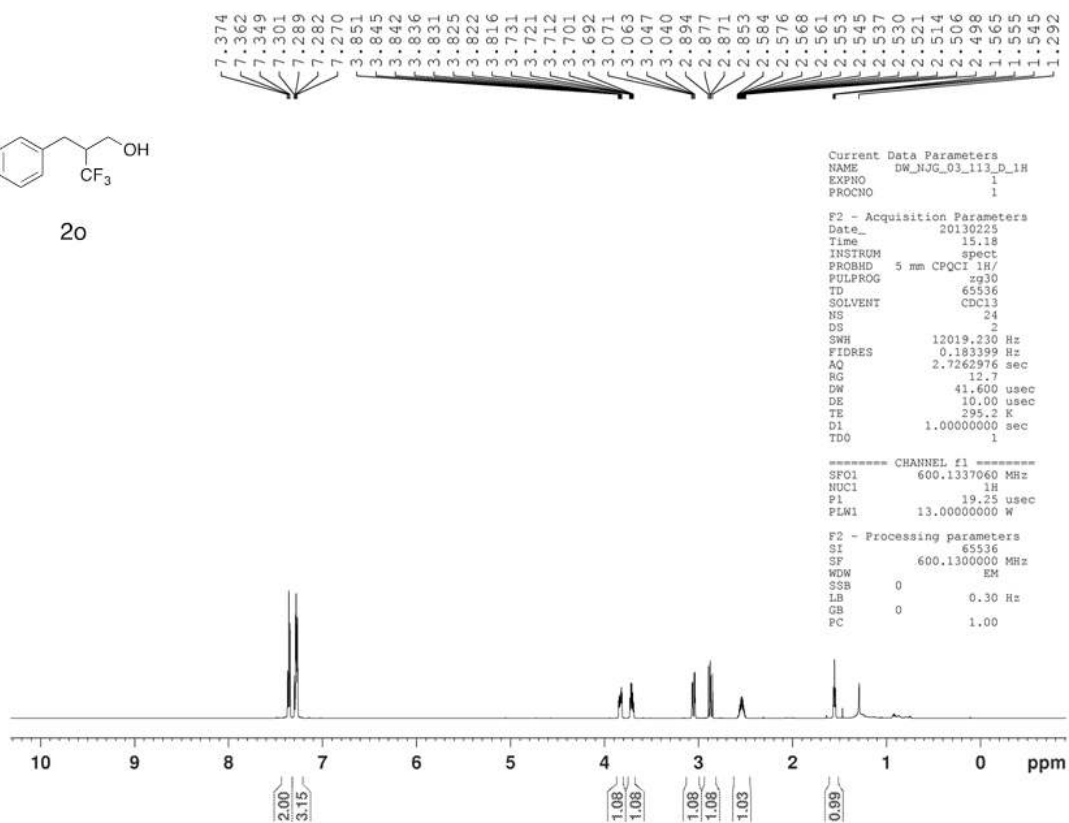




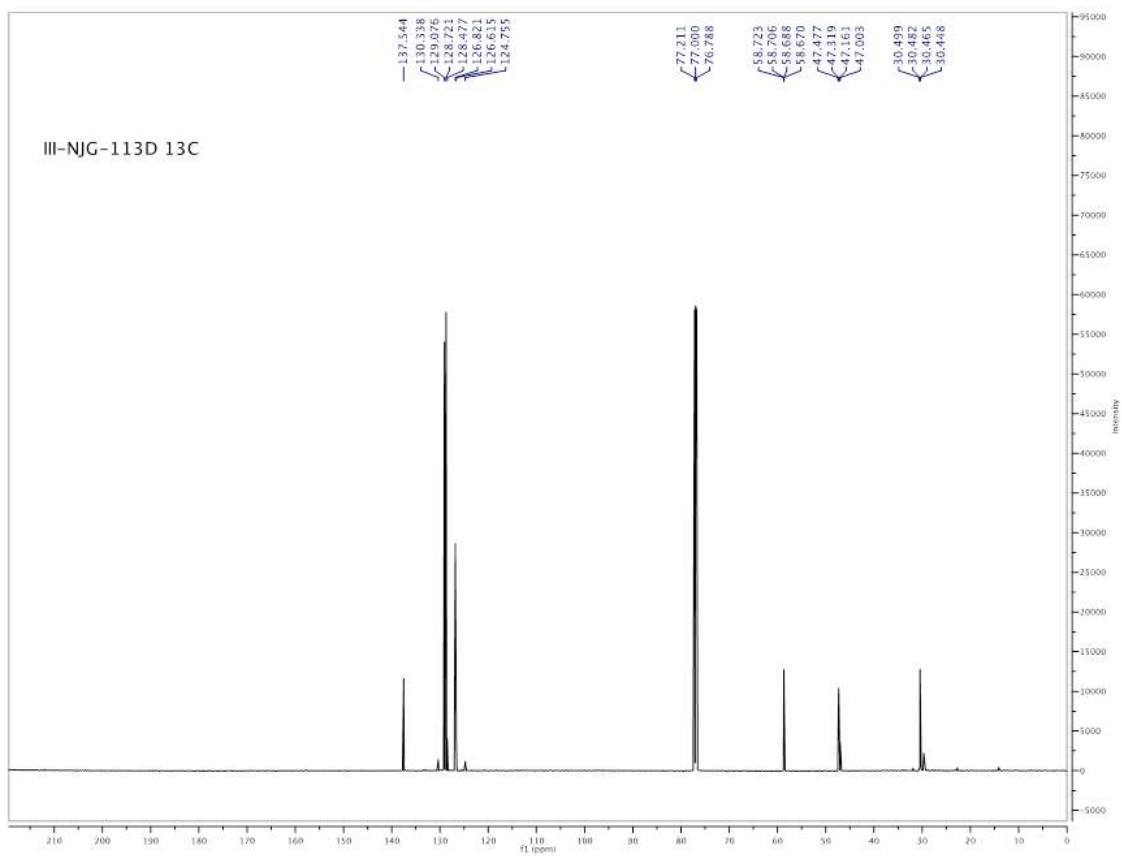
## 2-Benzyl-3,3,3-trifluoropropan-1-ol (2o)



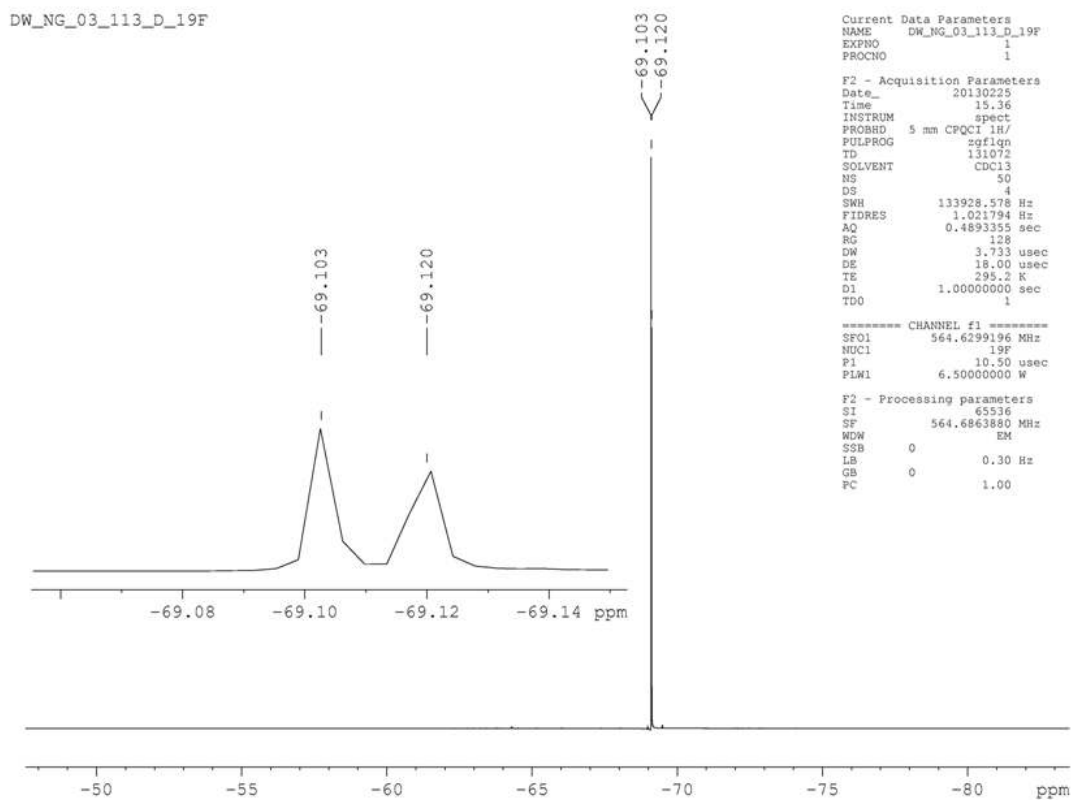
2o



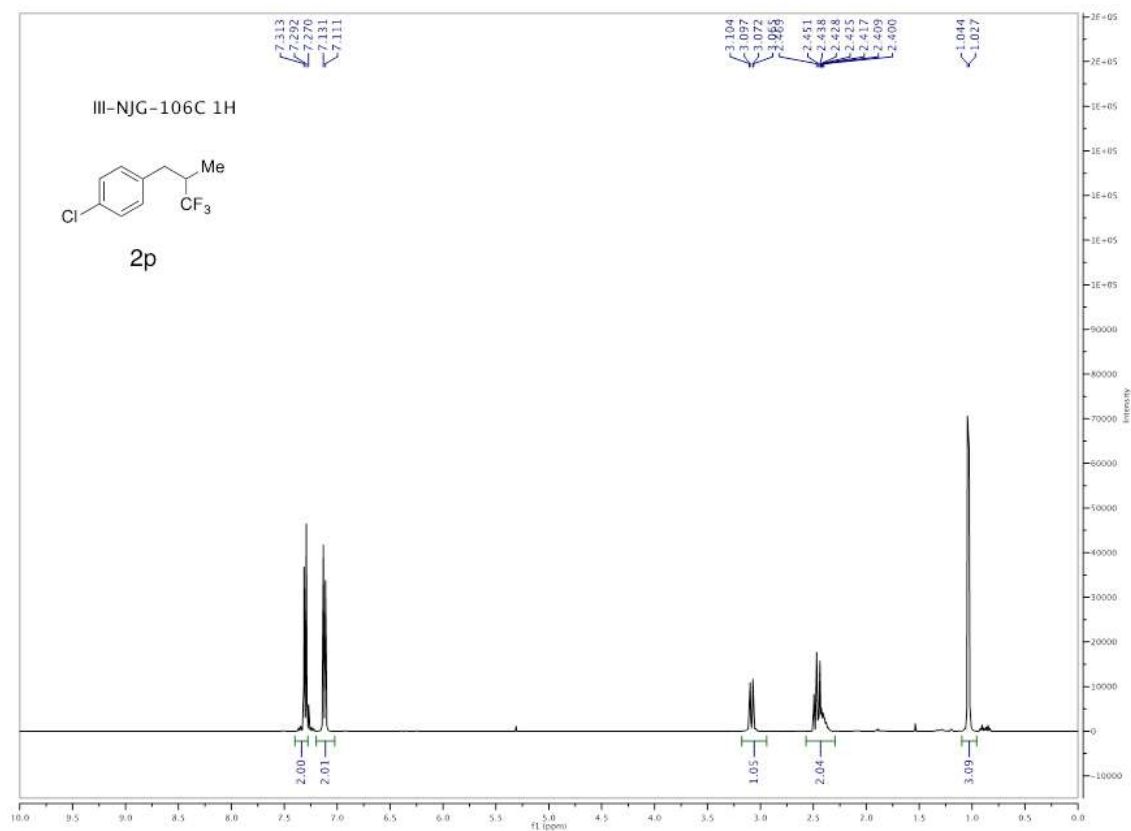
## 2-Benzyl-3,3,3-trifluoropropan-1-ol (2o)



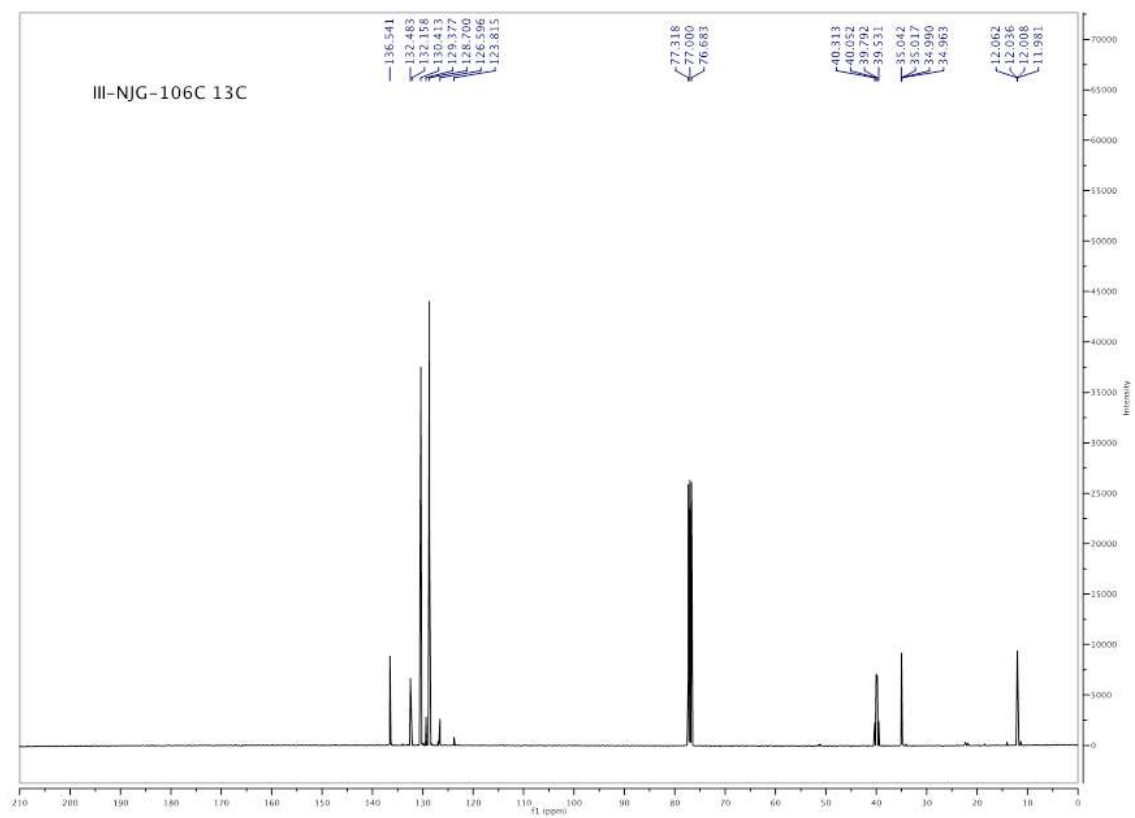
## 2-Benzyl-3,3,3-trifluoropropan-1-ol (2o)



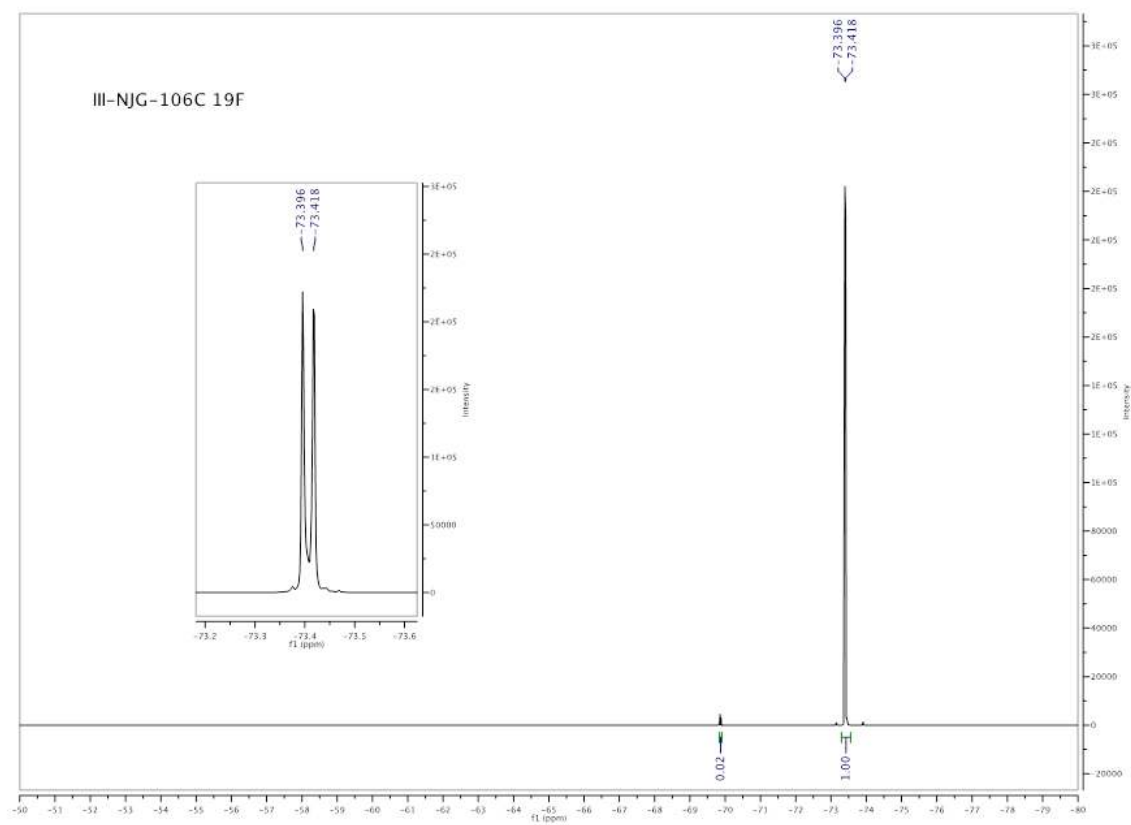
### 1-Chloro-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2p)



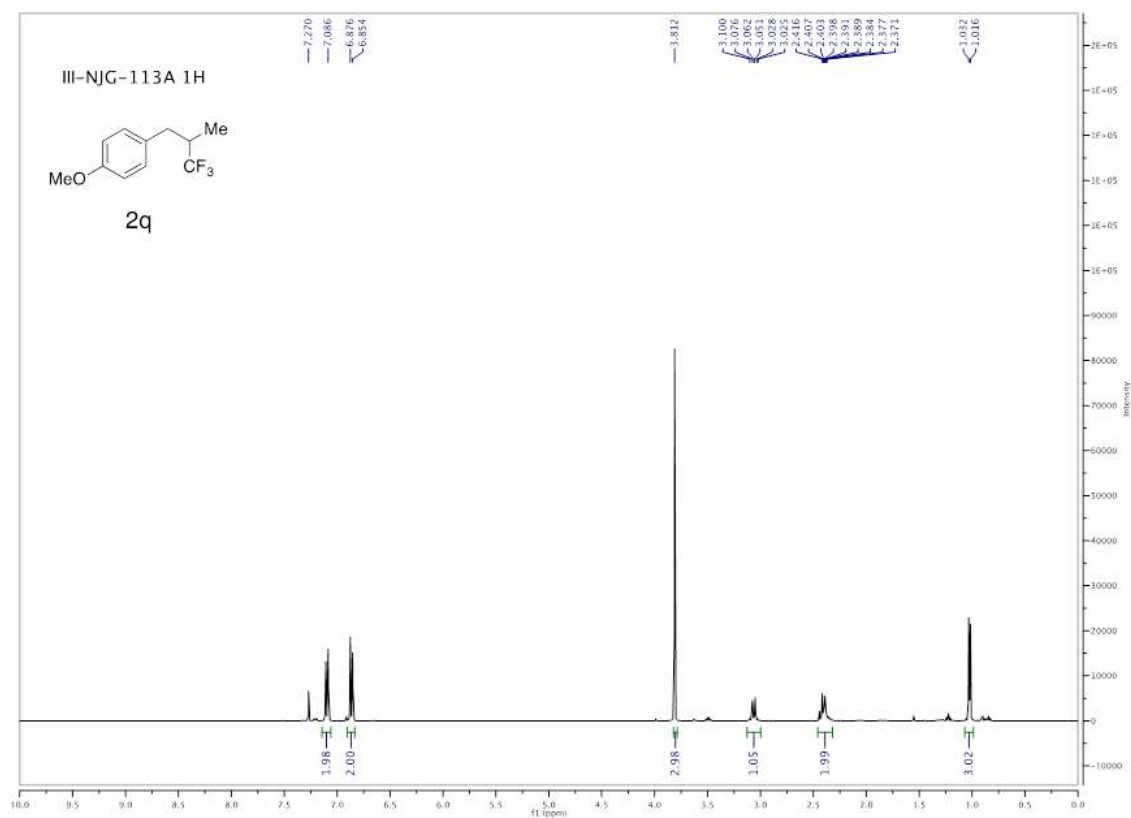
### 1-Chloro-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2p)



### 1-Chloro-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2p)

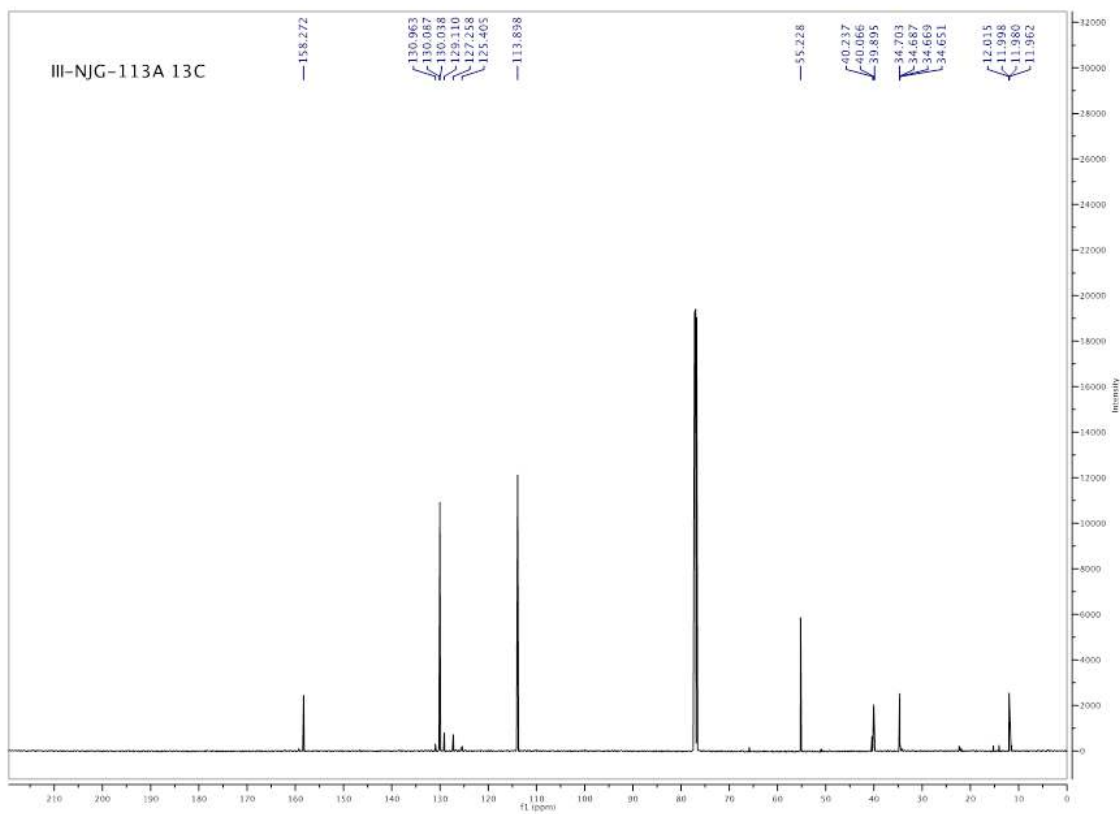


### 1-Methoxy-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2q)

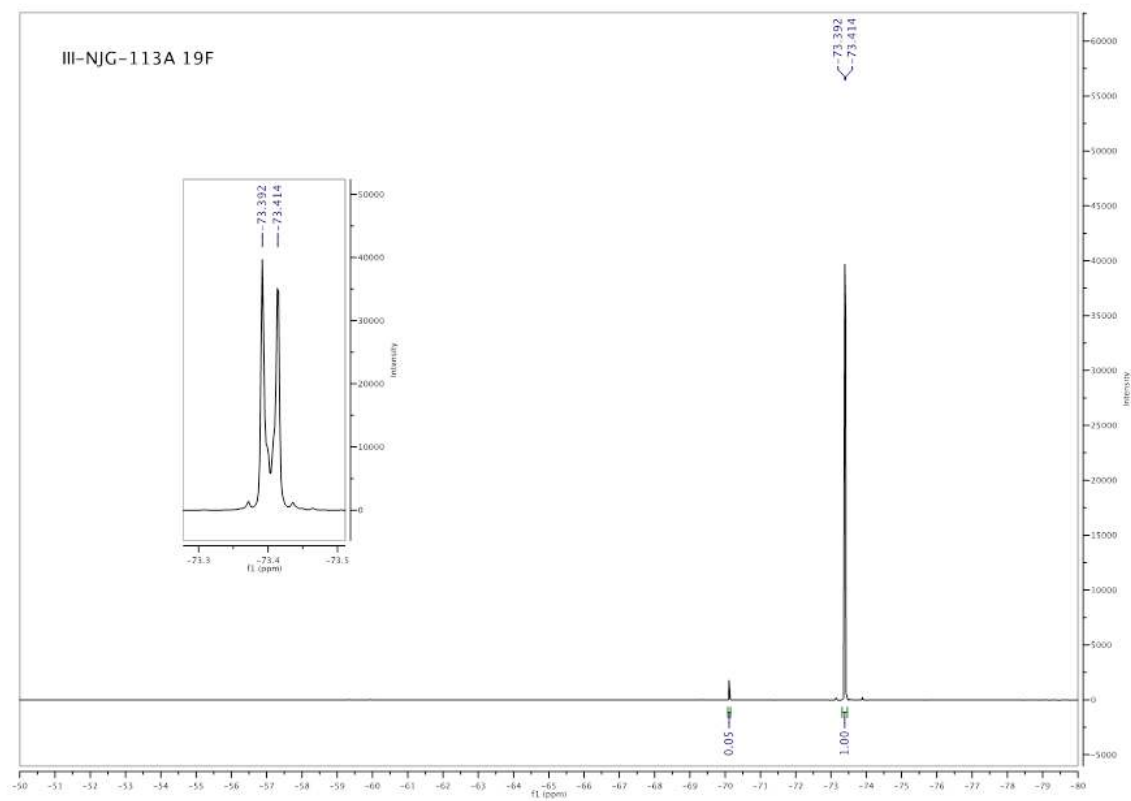




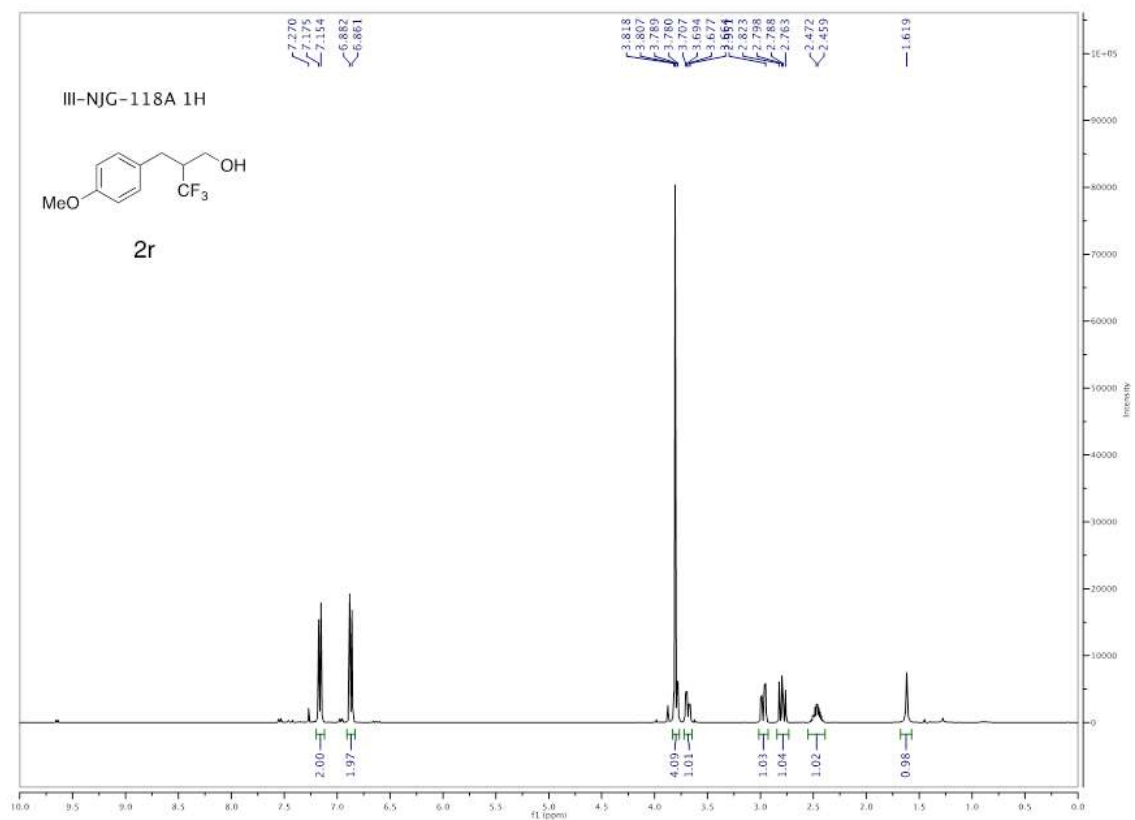
### 1-Methoxy-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2q)



### 1-Methoxy-4-(3,3,3-trifluoro-2-methylpropyl)benzene (2q)

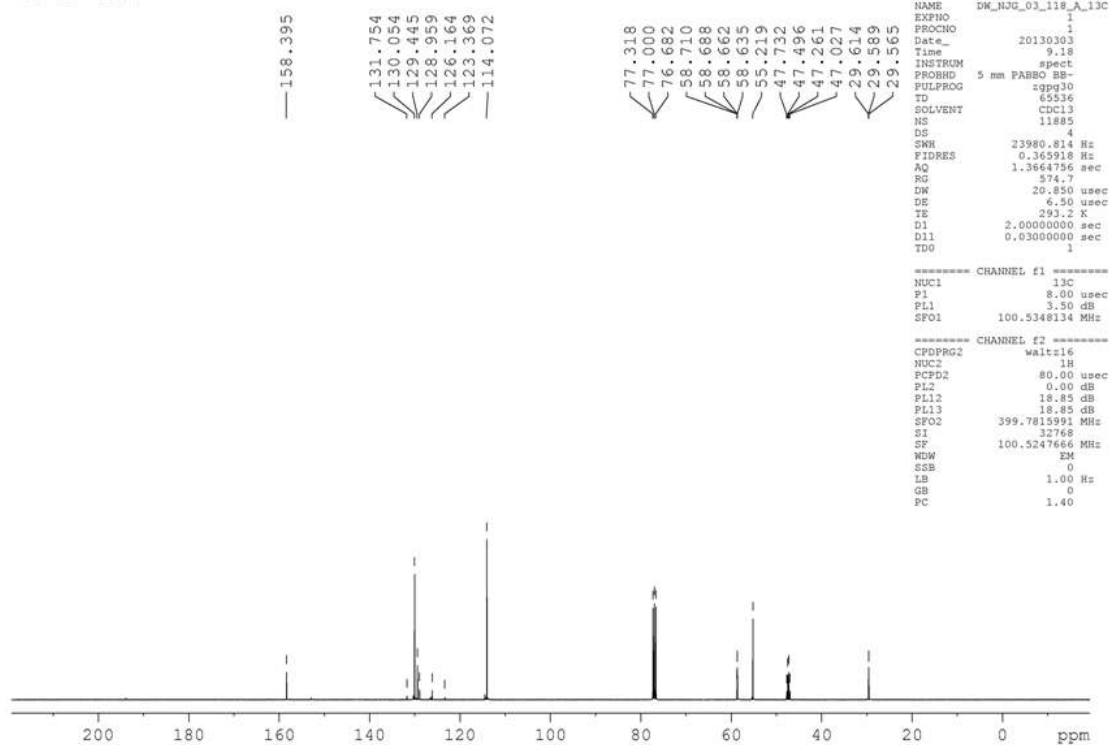


### 3,3,3-Trifluoro-2-(4-methoxybenzyl)propan-1-ol (2r)

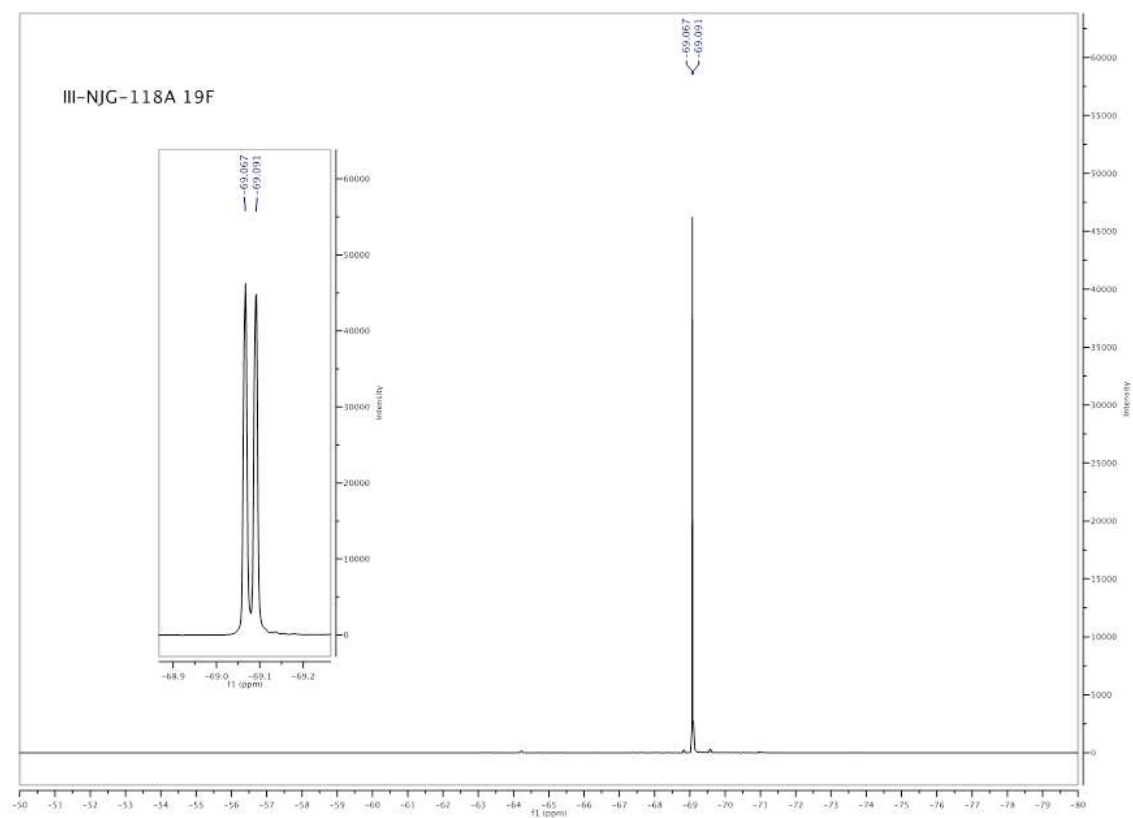


### 3,3,3-Trifluoro-2-(4-methoxybenzyl)propan-1-ol (2r)

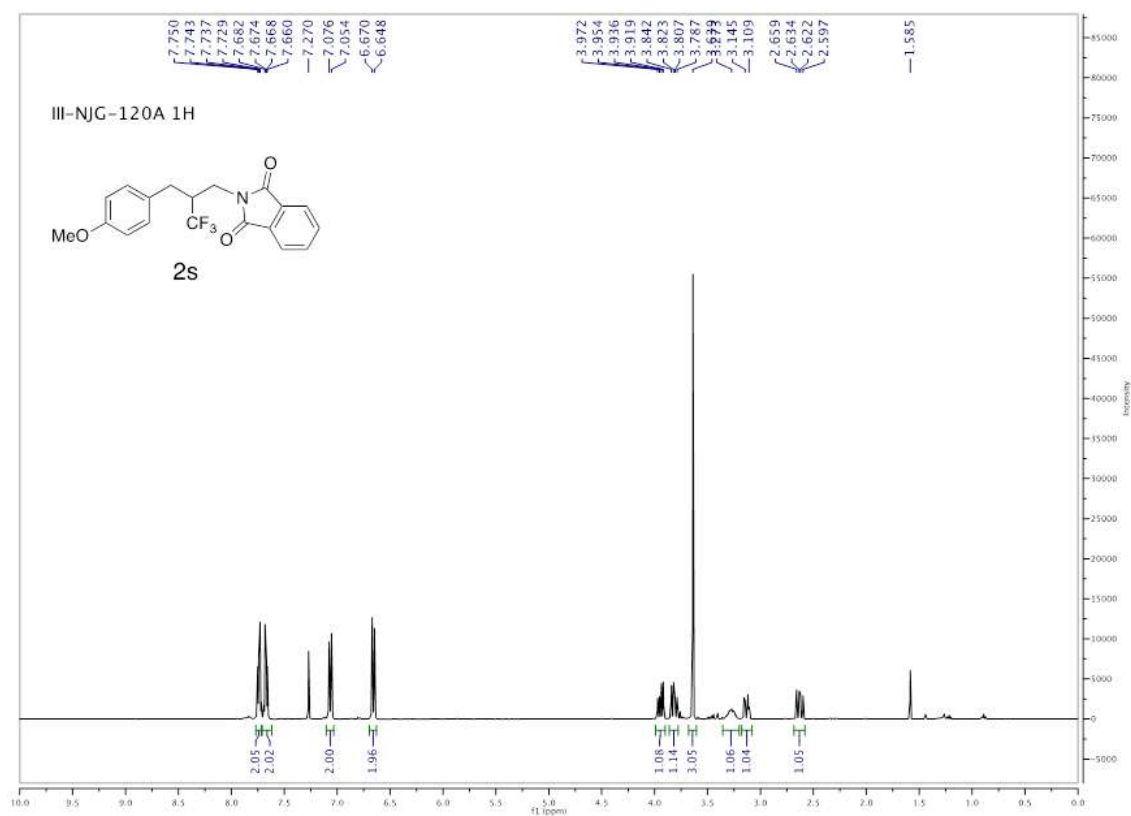
NJG\_03\_118\_A\_13C



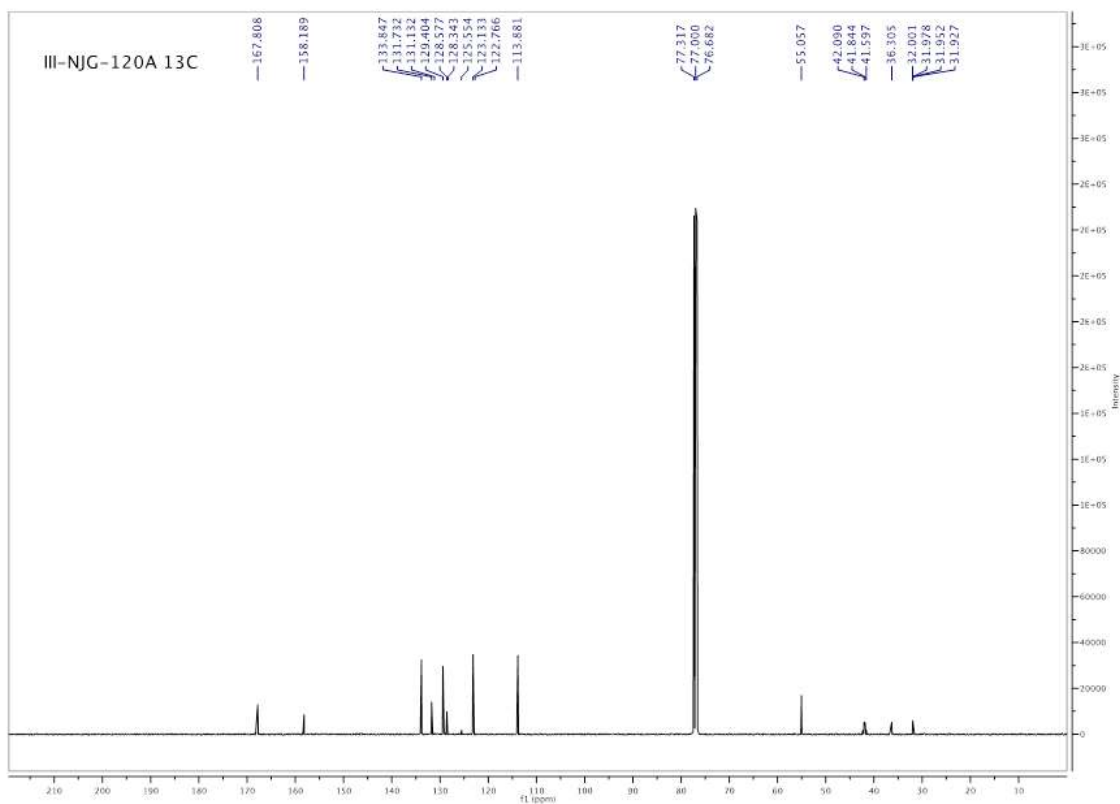
**3,3,3-Trifluoro-2-(4-methoxybenzyl)propan-1-ol (2r)**



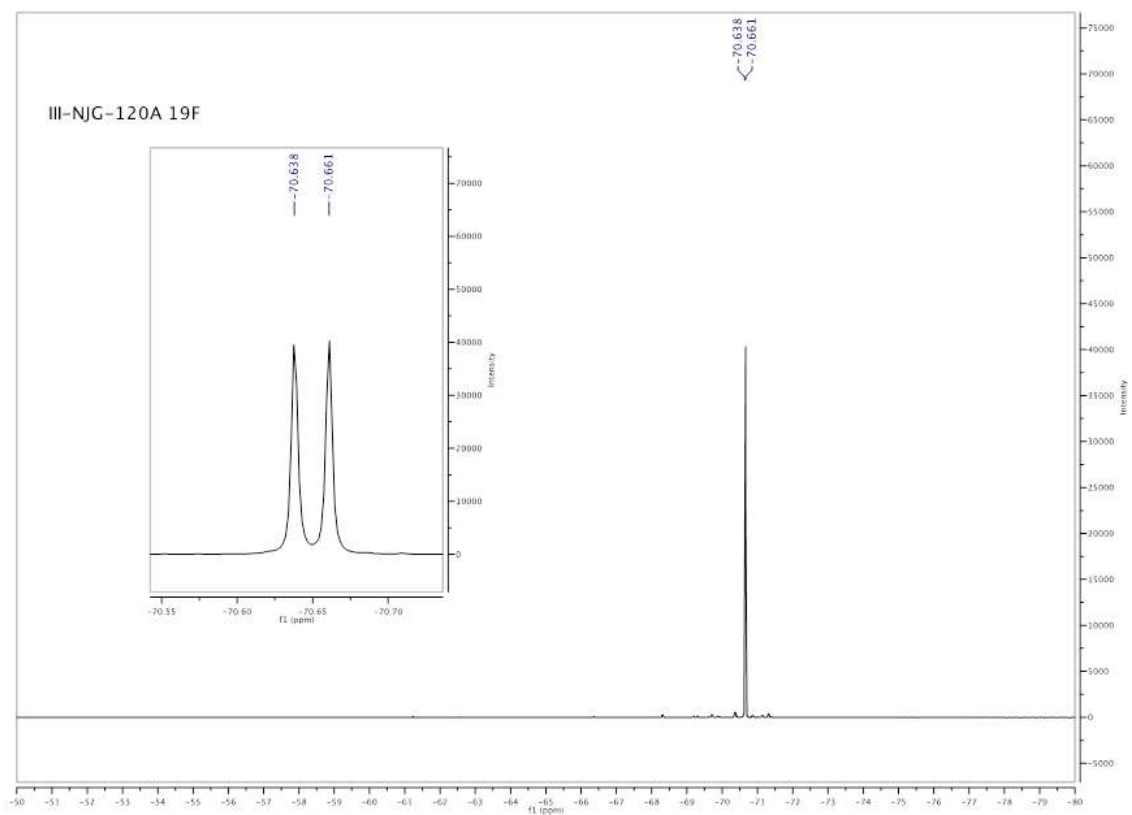
## 2-(3,3,3-Trifluoro-2-(4-methoxybenzyl)propyl)isoindoline-1,3-dione (2s)



**2-(3,3,3-Trifluoro-2-(4-methoxybenzyl)propyl)isoindoline-1,3-dione (2s)**

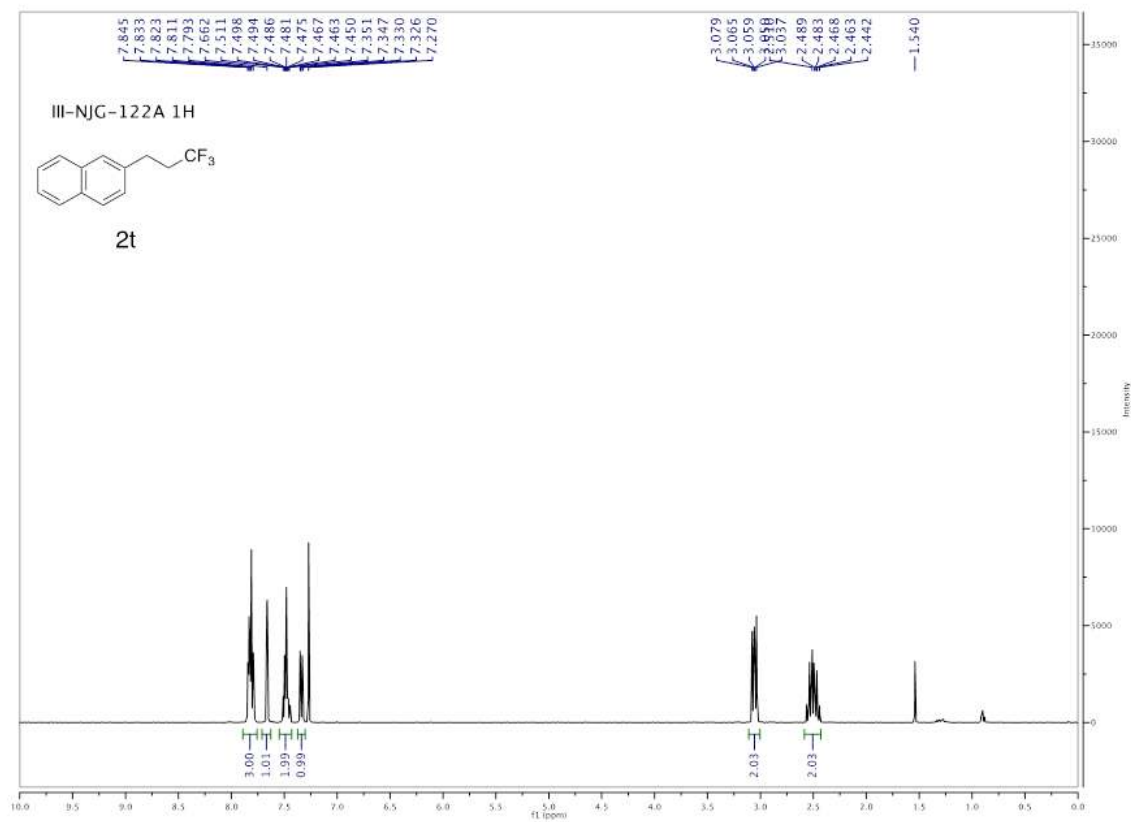


**2-(3,3,3-Trifluoro-2-(4-methoxybenzyl)propyl)isoindoline-1,3-dione (2s)**

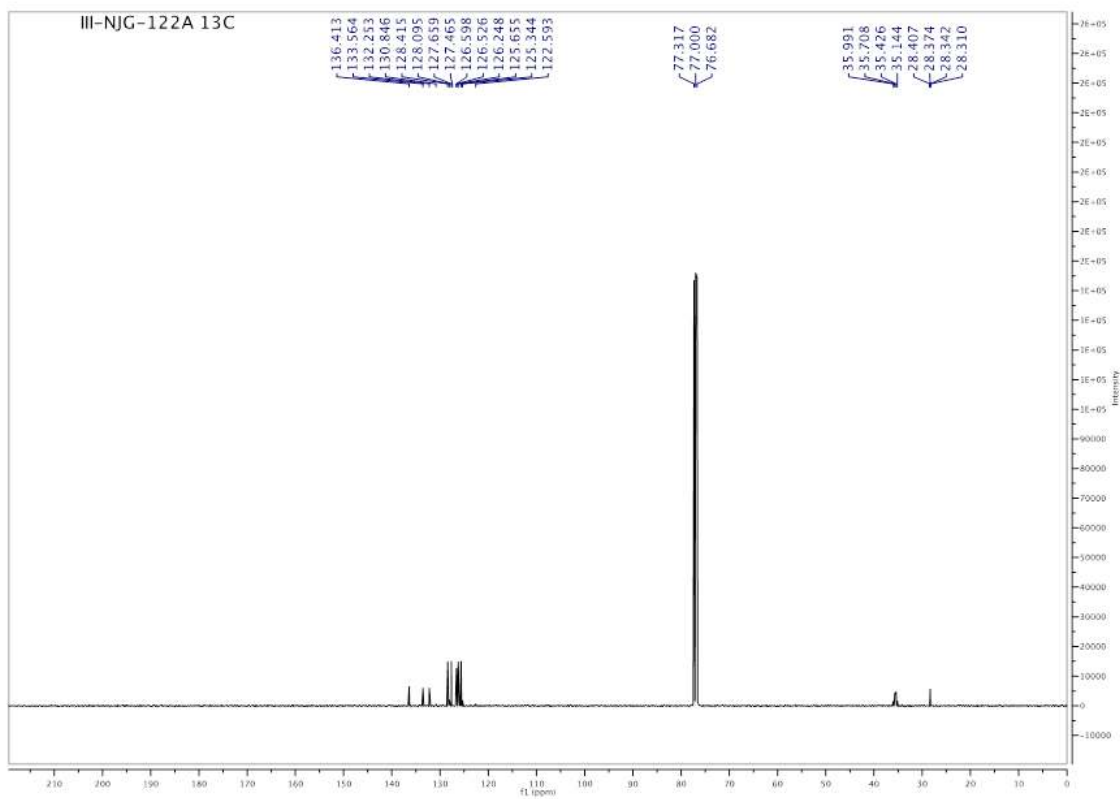




## 2-(3,3,3-Trifluoropropyl)naphthalene (2t)



## 2-(3,3,3-Trifluoropropyl)naphthalene (2t)



## 2-(3,3,3-Trifluoropropyl)naphthalene (2t)

