

# Supporting Information

for

## A Si-Based Benzylic 1,4-Rearrangement/Cyclization Reaction

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## EXPERIMENTAL PART

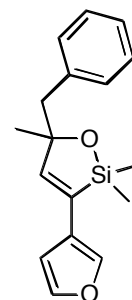
*General remarks:* Unless otherwise noted, all reactions were carried out in flame-dried glassware under a positive pressure of Ar. Acetone was distilled over calcium sulfate, all other anhydrous solvents were obtained from elution through alumina columns. All reagents were purchased commercially and used without further purification unless stated otherwise. Flash chromatography was performed with silica gel 60, 230-400 mesh. NMR spectra were measured on the following spectrometers: Unity Inova 300 (300 MHz for  $^1\text{H}$ -NMR, 75 MHz for  $^{13}\text{C}$ -NMR), Varia 400 (400 MHz for  $^1\text{H}$ -NMR, 100 MHz for  $^{13}\text{C}$ -NMR, 376 MHz for  $^{19}\text{F}$ -NMR), Mercury 400 (400 MHz for  $^1\text{H}$ -NMR, 100 MHz for  $^{13}\text{C}$ -NMR, 376 MHz for  $^{19}\text{F}$ -NMR, 61.4 MHz).  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR resonances were referenced to the residual solvent signal,  $^{19}\text{F}$ -NMR resonances were referenced to trichlorofluoromethane. IR spectra ( $\text{cm}^{-1}$ ) were obtained with a Perkin-Elmer FT-IR Paragon 500 spectrometer and with a Nicolet IR100 spectrometer. Melting points (uncorrected) were measured on a Thomas Hoover capillary melting point apparatus. 3-(2,2-Dibromovinyl)furan was synthesized according to a literature procedure,; see: Hayford, A. *et al. Org. Lett.* **2005**, 7, 2671-2673.

### A) BENZYLIC 1,4-REARRANGEMENT/CYCLIZATION REACTIONS

*General procedure A: synthesis of 2,5-dihydro-1,2-oxasiloles from  $\beta$ -silylated enones:* In a flame dried flask, a solution of the enone in THF was treated with [amount base] of a freshly prepared solution of [base] in THF/hexanes at  $-78^\circ\text{C}$ . After [reaction time 1], the reaction mixture was warmed to [temperature] and stirred for [reaction time 2]. The reaction was quenched by addition of phosphate buffer (pH=7) or ammonium chloride aq. sat., extracted with diethyl ether, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated *in vacuo*. The crude product was purified by column chromatography ( $\text{SiO}_2$ ).

5-Benzyl-5-methyl-3-(furan-3-yl)-2,2-dimethyl-2,5-dihydro-1,2-oxasilole

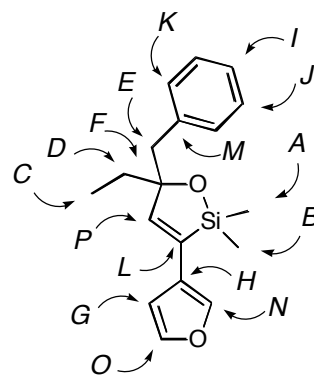
Following general procedure A. *Starting material:* benzyldimethylsilyl-1-(3-furanyl)but-1-en-3-one (312 mg, 1.10 mmol, 1.00 eq.); *volume THF:* 2.0 ml; *base:* Lithium trityltertbutylamide (250 mM solution in THF/hexanes; 4.82 ml, 1.21 mmol, 1.10 eq.);



reaction time 1: 3h; temperature: 0° C; reaction time 2: 1h; quenched with: ammonium chloride aq. sat.; column chromatography: hexane : diethyl ether = 50: 1 → 30:1. Yield: 268 mg (943 μmol, 86 %) of a slightly yellowish oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = -0.08 (s, 3 H, SiCH<sub>3</sub>), 0.29 (s, 3 H, SiCH<sub>3</sub>), 1.40 (s, CCH<sub>3</sub>), 2.89 (d, *J* = 13.2 Hz, 1 H, CH<sub>2</sub>Ph), 2.94 (d, *J* = 13.2 Hz, 1 H, CH<sub>2</sub>Ph), 6.50 (dd, *J*<sub>(1)</sub> = 2.0 Hz, *J*<sub>(2)</sub> = 0.8 Hz, 1 H, CH furyl), 6.74 (s, 1 H, C=C-H), 7.14-7.26 (m, 6 H, 1 CH furyl, 5 CH phenyl), 7.40 (t, *J* = 1.6 Hz, 1 H, CH furyl). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ = 0.3 (SiCH<sub>3</sub>), 1.4 (SiCH<sub>3</sub>), 29.1 (CCH<sub>3</sub>), 49.0 (CH<sub>2</sub>), 86.1 (C=C-C-O), 108.5 (C(4)H furyl), 122.9, 126.3, 127.8, 130.1, 130.9, 137.7 (phenyl ipso), 139.7, 143.8, 147.7. IR (neat): ν (cm<sup>-1</sup>) 3062, 3029, 2968, 2922, 1495, 1450, 1252, 1159, 1096, 1032, 967, 952, 903, 871, 849, 828, 791, 748, 700, 671, 594. HRMS (EI): M<sup>+</sup> calcd. for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>Si: 284.1233, found. 284.1238. C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>Si (284.43): calc. C 71.79, H 7.09; meas. C 71.87, H 6.96.

#### 5-Benzyl-5-ethyl-3-(furan-3-yl)-2,2-dimethyl-2,5-dihydro-1,2-oxasilole

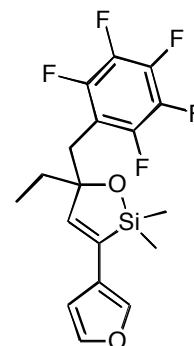
Following general procedure A. *Starting material*: benzyldimethylsilanyl-1-(3-furanyl)pent-1-en-3-one (200 mg, 670 μmol, 1.00 eq.); *volume THF*: 1.5 ml; *base*: Li-trityltertbutylamide (251 mM solution in THF/hexanes; 2.94 ml, 738 μmol, 1.10 eq.); *reaction time 1*: 2h 30min;



*temperature*: rt; *reaction time 2*: warming to rt during 5 min; *quenched with*: phosphate buffer; column chromatography: petrol ether : diethyl ether = 30: 1. Yield: 141 mg (472 μmol, 71 %) of a colorless solid. By performing COSY, HMQC and HMBC-NMR experiments, all hydrogen and carbon resonances could be assigned to the respective nuclei, thus allowing for disclosing the connectivity pattern of the nuclei with respect to each other and thus deducing the constitution and configuration of the silacycle. The <sup>13</sup>C nuclei are labeled as shown in the picture above. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ = -0.19 (s, 3 H, SiCH<sub>3</sub>), 0.29 (s, 3 H, SiCH<sub>3</sub>), 0.87 (t, *J* = 7.6 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.71 (dt, *J*<sub>d</sub> = 7.6 Hz, *J*<sub>t</sub> = 7.6 Hz, 1H, CH<sub>2</sub>CH<sub>3</sub>), 1.72 (dt, *J*<sub>d</sub> = 7.6 Hz, *J*<sub>t</sub> = 7.6 Hz, 1H, CH<sub>2</sub>CH<sub>3</sub>), 2.87 (d, *J* = 13 Hz, 1 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 2.87 (d, *J* = 13 Hz, 1 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 2.93 (d, *J* = 13 Hz, 1 H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 6.48 (m, 1 H, C<sub>(4)</sub>H of the furyl rest), 6.61 (s, 1 H, C=C-H olefin), 7.10-7.20 (m, 5 H, 5 CH phenyl), 7.22 (s, 1 H, C<sub>(2)</sub>H of the furyl rest), 7.37 (t, *J* = 1.6, 1 H, C<sub>(5)</sub>H of the furyl rest). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 50 MHz): δ = 0.3 (A or B), 0.8 (A or B), 8.7 (C), 33.6 (D), 48.2 (E), 89.2 (F), 108.6 (G), 122.9 (H), 126.3 (I), 127.7 (J), 131.2 (K), 131.6 (L), 137.5 (M), 139.6 (N), 143.6 (O), 146.0 (P). IR (neat): ν (cm<sup>-1</sup>) 3030, 2967, 2937, 2361,

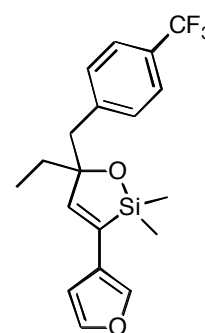
1604, 1496, 1454, 1375, 1252, 1159, 1076, 1031, 1001, 970, 926, 905, 871, 852, 790, 670, 670. mp: 41.5° C. HRMS (EI):  $M^+$  calcd. for  $C_{18}H_{22}O_2Si$ : 298.3872, found. 298.2944.

5-Ethyl-3-(furan-3-yl)-2,2-dimethyl-5-(2,3,4,5,6-pentafluorobenzyl)-2,5-dihydro-1,2-oxasilole



Following general procedure A. *Starting material*: (Z)-1-(dimethyl(2,3,4,5,6-pentafluorobenzyl)silyl)-1-(furan-3-yl)pent-1-en-3-one (100 mg, 256  $\mu$ mol, 1.00 eq.); *volume THF*: 0.8 ml; *base*: Li-triphenylmethylate (256 mM solution in THF/hexanes; 1.26 ml, 320  $\mu$ mol, 1.25 eq.); *reaction time 1*: 2h 15min; *temperature*:  $-78^\circ$  C; *reaction time 2*: 0min; *quenched with*: phosphate buffer (pH = 7); column chromatography: petrol ether : diethyl ether = 50: 1. Yield: 95 mg (245  $\mu$ mol, 95%) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = -0.07 (s, 3 H,  $SiCH_3$ ), 0.33 (s, 3 H,  $SiCH_3$ ), 0.90 (t,  $J$  = 7.6 Hz, 3 H,  $CH_2CH_3$ ), 1.79 (q,  $J$  = 7.6 Hz, 2 H,  $CH_2CH_3$ ), 2.95 (td,  $J_d$  = 13.6 Hz,  $J_d$  = 8.0 Hz, 1 H,  $SiCH_2$ ), 3.10 (td,  $J_d$  = 13.6 Hz,  $J_d$  = 8.0 Hz, 1 H,  $SiCH_2$ ), 6.48-6.49 (m, 1 H, CH furyl), 6.61 (t,  $J$  = 2.0 Hz, 1 H, CH furyl), 7.26 (s, 1 H, C=CH), 7.40 (t,  $J$  = 2.0 Hz, 1 H, CH furyl).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 0.4 ( $SiCH_3$ ), 0.9 ( $SiCH_3$ ), 8.7, 33.8, 34.5, 89.0, 108.6, 122.6, 126.5, 128.5, 129.7, 132.6, 138.8, 139.9, 143.9, 144.4.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 376.3 MHz):  $\delta$  = -140.5 (dd,  $J_1$  = 14.7 Hz,  $J_2$  = 7.5 Hz), -157.4 (t,  $J$  = 20.7 Hz), -163.7 to -163.9 (m). IR (neat):  $\nu$  ( $cm^{-1}$ ) 2971, 2940, 2881, 2641, 1656 (weak), 1520, 1505, 1464, 1454, 1426, 1377, 1297, 1253, 1160, 1125, 1094, 1078, 1034, 1014, 985, 917, 872, 855, 831, 790, 729, 701, 669. HRMS (ESI): ( $M - H$ ) $^+$  calcd. for  $C_{18}H_{16}F_5O_2Si$ : 387.08398, found. 387.08323.

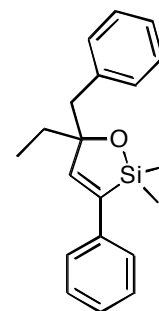
5-Ethyl-3-(furan-3-yl)-2,2-dimethyl-5-(4-(trifluoromethyl)benzyl)-2,5-dihydro-1,2-oxasilole



Following general procedure A. *Starting material*: (Z)-1-(dimethyl(4-(trifluoromethyl)benzyl)silyl)-1-(furan-3-yl)pent-1-en-3-one (100 mg, 272  $\mu$ mol, 1.00 eq.); *volume THF*: 0.8 ml; *base*: Li-trityltertbutylamide (256 mM solution in THF/hexanes; 1.33 ml, 340  $\mu$ mol, 1.25 eq.); *reaction time 1*: 2h 15min; *temperature*:  $-78^\circ$  C; *reaction time 2*: 0 min; *quenched with*: phosphate buffer; column chromatography: petrol ether : diethyl ether =

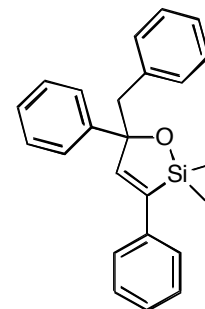
50 : 1. Yield: 87 mg (237  $\mu\text{mol}$ , 87%) of a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = -0.20 (s, 3 H,  $\text{SiCH}_3$ ), 0.31 (s, 3 H,  $\text{SiCH}_3$ ), 0.89 (t,  $J$  = 7.6 Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.73 (q,  $J$  = 7.6 Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 2.94-3.05 (m, 2 H,  $\text{SiCH}_2$ ), 6.50-6.52 (m, 1 H,  $\text{CH}$  furyl), 6.64 (s, 1 H,  $\text{C}=\text{CH}$ ), 7.25 (d,  $J$  = 8.0 Hz, 2 H,  $\text{CH}$  aryl), 7.41 (t,  $J$  = 1.6 Hz, 1 H,  $\text{CH}$  furyl), 7.48 (d,  $J$  = 8.0 Hz, 2 H,  $\text{CH}$  aryl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 0.3 ( $\text{SiCH}_3$ ), 0.8 ( $\text{SiCH}_3$ ), 8.7, 33.9, 47.8, 89.0, 108.5, 122.8, 124.7, 127.6, 129.5, 131.5, 132.4, 139.8, 141.8, 143.8, 145.3.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta$  = -62.7 (s). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3058, 2970, 2939, 2922, 2879, 1616 (weak), 1584, 1552, 1508, 1444, 1418, 1376, 1326, 1253, 1162, 1124, 1068, 1020, 1003, 971, 953, 922, 905, 872, 845, 825, 791, 728, 703, 671, 641, 621, 594. HRMS (ESI):  $(\text{MH})^+$  calcd. for  $\text{C}_{19}\text{H}_{22}\text{F}_3\text{O}_2\text{Si}$ : 367.1341, found. 367.1325.

#### 5-Benzyl-5-ethyl-2,2-dimethyl-3-phenyl-2,5-dihydro-1,2-oxasilole



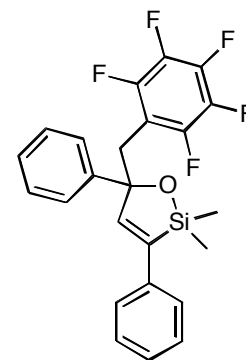
Following general procedure A. *Starting material*: (*Z*)-1-(benzyltrimethylsilyl)-1-phenylpent-1-en-3-one (2.00 g, 6.48 mmol, 1.00 eq.); *volume THF*: 7.0 ml; *base*: Li-diisopropylamide (800 mM solution in THF/hexanes; 8.10 ml, 6.48 mmol, 1.00 eq.); *reaction time 1*: 4h; *temperature*: rt; *reaction time 2*: warming to rt during 25 min; *quenched with*: ammonium chloride aq. sat.; column chromatography: petrol ether : diethyl ether = 30 : 1. 1.52 g (4.92 mmol, 76 %) of a colorless oil; yield based on recovered starting material: 86%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = -0.10 (s, 3 H,  $\text{SiCH}_3$ ), 0.41 (s, 3 H,  $\text{SiCH}_3$ ), 0.95 (t,  $J$  = 7.2 Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.81 (q,  $J$  = 7.2 Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 2.96 (d,  $J$  = 13.5 Hz,  $\text{CH}_2\text{Ph}$ ), 3.04 (d,  $J$  = 13.5 Hz,  $\text{CH}_2\text{Ph}$ ), 6.88 (s, 1 H,  $\text{C}=\text{CH}$ ), 7.17-7.39 (m, 10 H, 10  $\text{CH}_{\text{phenyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 0.9 ( $\text{SiCH}_3$ ), 1.5 ( $\text{SiCH}_3$ ), 8.9 ( $\text{CH}_2\text{CH}_3$ ), 34.0 ( $\text{CH}_2\text{CH}_3$ ), 48.4 ( $\text{CH}_2\text{Ph}$ ), 89.2 ( $\text{C}_{\text{quat.}}$ ), 126.4, 126.9, 127.3, 127.9, 129.0, 131.3, 137.7, 137.9, 142.2, 147.5. IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3028, 2966, 2936, 1601, 1492, 1454, 1251, 1125, 1087, 1072, 1030, 1008, 952, 924, 885, 856, 817, 796, 753, 698, 636. HRMS (EI):  $\text{M}^+$  calcd. for  $\text{C}_{20}\text{H}_{24}\text{OSi}$ : 308.1596, found. 308.1603.  $\text{C}_{20}\text{H}_{24}\text{OSi}$  (308.49): calc. C 77.87, H 7.84; meas. C 78.05, H 7.81.

### 5-Benzyl-2,2-dimethyl-3,5-diphenyl-2,5-dihydro-1,2-oxasilole



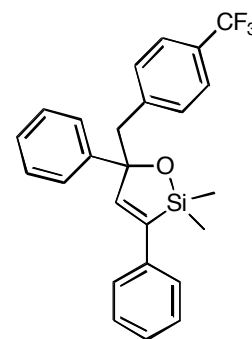
Following general procedure A. *Starting material*: (Z)-3-(benzyl(dimethylsilyl)-1,3-diphenylprop-2-en-1-one (30 mg, 84  $\mu\text{mol}$ , 1.00 eq.); *volume THF*: 0.2 ml; *base*: Li-diisopropylamide (256 mM solution in THF/hexanes; 657  $\mu\text{l}$ , 168  $\mu\text{mol}$ , 2.00 eq.); *reaction time 1*: 0min; *temperature*: 4° C; *reaction time 2*: 20h; *quenched with*: ammonium chloride aq. sat.; *column chromatography*: petrol ether : diethyl ether = 50 : 1. Yield: 26 mg (73  $\mu\text{mol}$ , 86 %) of a yellowish oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = -0.11 (s, 3 H,  $\text{SiCH}_3$ ), 0.34 (s, 3 H,  $\text{SiCH}_3$ ), 3.17 (d,  $J$  = 13.6 Hz,  $\text{CH}_2\text{Ph}$ ), 3.33 (d,  $J$  = 13.6 Hz,  $\text{CH}_2\text{Ph}$ ), 7.10-7.37 (m, 14 H,  $\text{C}=\text{CH}$  and 13  $\text{CH}_{\text{phenyl}}$ ), 7.50-7.54 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 0.6 ( $\text{SiCH}_3$ ), 1.5 ( $\text{SiCH}_3$ ), 49.9 ( $\text{CH}_2$ ), 89.3 ( $\text{C}_{\text{quat}}$ ), 125.1, 126.5, 126.9, 127.0, 127.4, 127.7, 128.5, 128.9, 131.5, 137.1, 137.6, 140.4, 146.5, 147.6 ( $\text{C}=\text{O}$ ). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3060, 3028, 2951, 2920, 1599, 1492, 1446, 1252, 1095, 1064, 1030, 1000, 954, 926, 899, 880, 854, 820, 788, 756, 697. HRMS (EI):  $\text{M}^+$  calcd. for  $\text{C}_{24}\text{H}_{24}\text{OSi}$ : 356.1596, found. 356.1582.

### 2,2-Dimethyl-5-(perfluorobenzyl)-3,5-diphenyl-2,5-dihydro-1,2-oxasilole



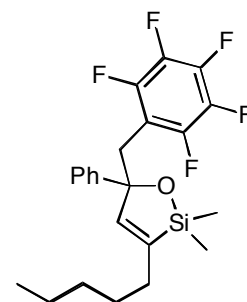
Following general procedure A. *Starting material*: (Z)-3-(dimethyl(perfluorobenzyl)silyl)-1,3-diphenylprop-2-en-1-one (85 mg, 190  $\mu\text{mol}$ , 1.00 eq.); *volume THF*: 0.4 ml; *base*: Li-diisopropylamide (798 mM solution in THF/hexanes; 300  $\mu\text{l}$ , 238  $\mu\text{mol}$ , 1.25 eq.); *reaction time 1*: 1h 40min; *temperature*: -78° C; *reaction time 2*: 0min; *quenched with*: phosphate buffer (pH = 7); *column chromatography*: petrol ether : diethyl ether = 30 : 1. Yield: 74 mg (167  $\mu\text{mol}$ , 88%) of a colorless solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = -0.04 (s, 3 H,  $\text{SiCH}_3$ ), 0.39 (s, 3 H,  $\text{SiCH}_3$ ), 3.31-3.40 (m, 2 H,  $\text{CH}_2$ ), 7.21-7.32 (m, 7 H, 7  $\text{CH}$ ), 7.36-7.41 (m, 2 H, 2  $\text{CH}$ ), 7.55-7.59 (m, 2 H, 2  $\text{CH}$ ).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 0.49 ( $\text{SiCH}_3$ ), 1.59 ( $\text{SiCH}_3$ ), 36.7 ( $\text{CH}_2$ ), 88.8 ( $\text{C}_{\text{quat}}$ ), 111.2, 124.9, 127.0, 127.5, 127.8, 128.7, 129.0, 137.0, 137.5, 140.0, 141.3, 145.4, 145.9, 146.0.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta$  = -140.3 (dd,  $J_1$  = 22.6 Hz,  $J_2$  = 7.9 Hz), -156.9 (t,  $J$  = 20.1 Hz), -163.8 to -163.6 (m). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3060, 3027, 1521 (C-F), 1503 (C-F), 1254, 1123, 1103, 1067, 987, 956, 910, 790, 698. mp = 84.5° C. HRMS (EI): ( $\text{MH}$ ) $^+$  calcd. for  $\text{C}_{24}\text{H}_{20}\text{OF}_5\text{Si}$ : 447.1204, found. 447.1192.  $\text{C}_{24}\text{H}_{19}\text{F}_5\text{OSi}$  (446.48): calc. C 64.56, H 4.29; meas. C 64.37, H 4.36.

2,2-Dimethyl-3,5-diphenyl-5-(4-(trifluoromethyl)benzyl)-2,5-dihydro-1,2-oxasilole



Following general procedure A. *Starting material*: (Z)-3-(dimethyl(4-(trifluoromethyl)benzyl)silyl)-1,3-diphenylprop-2-en-1-one (160 mg, 377  $\mu\text{mol}$ , 1.00 eq.); *volume THF*: 0.8 ml; *base*: Li-diisopropylamide (798 mM solution in THF/hexanes; 590  $\mu\text{l}$ , 471  $\mu\text{mol}$ , 1.25 eq.); *reaction time 1*: 1h 40min; *temperature*:  $-78^\circ\text{C}$ ; *reaction time 2*: 0min; *quenched with*: phosphate buffer (pH = 7); column chromatography: petrol ether : diethyl ether = 30 : 1. Yield: 144 mg (338  $\mu\text{mol}$ , 90%) of a colorless solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 0.00 (s, 3 H,  $\text{SiCH}_3$ ), 0.40 (s, 3 H,  $\text{SiCH}_3$ ), 3.29 (d,  $J$  = 13.2 Hz, 1 H,  $\text{CH}_2$ ), 3.38 (d,  $J$  = 13.2 Hz, 1 H,  $\text{CH}_2$ ), 7.23-7.36 (m, 9 H, 9 CH), 7.38-7.42 (m, 2 H, 2 CH), 7.49 (d,  $J$  = 7.6 Hz, 2 H, 2 CH), 7.53-7.56 (m, 2 H, 2 CH).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 0.65 ( $\text{SiCH}_3$ ), 1.48 ( $\text{SiCH}_3$ ), 49.7 ( $\text{CH}_2$ ), 89.1 ( $\text{C}_{\text{quat}}$ ), 124.6, 124.7, 125.1, 127.0, 127.1, 127.7, 128.7, 128.9, 129.0, 131.7, 137.3, 141.0, 141.4, 146.0, 147.1,  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta$  = -62.6. IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3058, 3026, 2954, 1618, 1491, 1446, 1418, 1326, 1254, 1164, 1122, 1067, 1020, 955, 922, 881, 849, 824, 789, 756, 697, 635, 609. mp =  $90.0^\circ\text{C}$ . HRMS (EI): ( $\text{MNa}$ ) $^+$  calcd. for  $\text{C}_{25}\text{H}_{23}\text{OF}_3\text{SiNa}$ : 447.1368, found. 447.1360.  $\text{C}_{25}\text{H}_{23}\text{F}_3\text{OSi}$  (424.53): calc. C 70.73, H 5.46; meas. C 70.52, H 5.62.

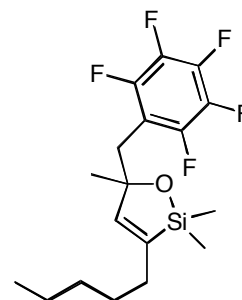
2,2,5-Dimethyl-3-pentyl-5-(2,3,4,5,6-pentafluorobenzyl)-5-phenyl-2,5-dihydro-1,2-oxasilole



Following general procedure A. *Starting material*: (Z)-3-(dimethyl(2,3,4,5,6-pentafluorobenzyl)silyl)-1-phenyloct-2-en-1-one (48 mg, 109  $\mu\text{mol}$ , 1.00 eq.); *volume THF*: 0.4 ml; *base*: Li-diisopropylamide (0.710 mM solution in THF/hexanes; 225  $\mu\text{l}$ , 160  $\mu\text{mol}$ , 1.47 eq.); *reaction time 1*: 50min; *temperature*:  $-78^\circ\text{C}$ ; *reaction time 2*: 0min; *quenched with*: phosphate buffer (pH = 7); column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: 29 mg (66  $\mu\text{mol}$ , 60%) of a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = -0.11 (s, 3 H,  $\text{SiCH}_3$ ), 0.17 (s, 3 H,  $\text{SiCH}_3$ ), 0.86 (t,  $J$  = 7.2 Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.08-1.36 (m, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 2.12 (t,  $J$  = 7.6 Hz, 2 H,  $\text{CH}_2\text{CH}_2$ ), 2.20-2.27 (m, 2 H, 2  $\text{SiCH}_2$ ), 6.65-6.67 (m,  $\text{C}=\text{CH}$ ), 7.23-7.29 (m, 1 H,  $\text{CH}$  aryl), 7.32-7.38 (m, 2 H, 2  $\text{CH}$  aryl), 7.48-7.52 (m, 2 H, 2  $\text{CH}$  aryl).  $^{13}\text{C}\{^1\text{H}\}$

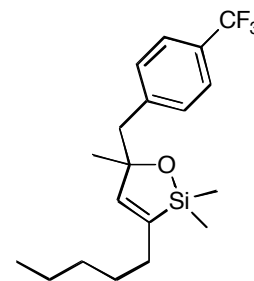
NMR /  $^{13}\text{C}\{^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 0.4$  ( $\text{SiCH}_3$ ), 0.8 ( $\text{SiCH}_3$ ), 14.1, 22.6, 29.5, 30.9, 31.7, 36.6, 88.4, 124.8, 127.2, 128.6, 137.4, 139.9, 143.3, 145.9, 146.0, 146.1.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta = -140.0$  (dd,  $J_1 = 23.3$  Hz,  $J_2 = 7.5$  Hz),  $-157.6$  (t,  $J = 20.7$  Hz),  $-164.1$  to  $-164.2$  (m). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 2960, 2929, 2858, 1656 (weak), 1600 (weak), 1520, 1505, 1447, 1300, 1252, 1123, 1105, 1056, 1025, 988, 967, 946, 909, 881, 856, 832, 787, 764, 700, 613. HRMS (EI): ( $\text{M}$ ) $^+$  calcd. for  $\text{C}_{23}\text{H}_{25}\text{F}_5\text{OSi}$ : 440.15949, found. 440.15811.

2,2,5-(Trimethyl-3-pentyl-5-(2,3,4,5,6-pentafluorobenzyl)-2,5-dihydro-1,2-oxasilole



Following general procedure A. *Starting material*: (*Z*)-4-(dimethyl(2,3,4,5,6-pentafluorobenzyl)silyl)non-3-en-2-one (48 mg, 128  $\mu\text{mol}$ , 1.00 eq.); *volume THF*: 0.4 ml; *base*: Li-diisopropylamide (0.710 mM solution in THF/hexanes; 225  $\mu\text{l}$ , 160  $\mu\text{mol}$ , 1.25 eq.); *reaction time 1*: 50min; *temperature*:  $-78^\circ\text{C}$ ; *reaction time 2*: 0min; *quenched with*: phosphate buffer (pH = 7); column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: 27 mg (71  $\mu\text{mol}$ , 56%) of a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = -0.13$  (s, 3 H,  $\text{SiCH}_3$ ), 0.17 (s, 3 H,  $\text{SiCH}_3$ ), 0.87 (t,  $J = 6.8$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.11-1.34 (m, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.39 (s, 3 H,  $\text{C}_{\text{quat}}\text{-CH}_3$ ), 2.13 (t,  $J = 7.2$  Hz, 2 H,  $\text{CH}_2\text{CH}_2$ ), 2.86 (d,  $J = 13.6$  Hz, 1 H,  $\text{SiCH}_2$ ), 3.01 (d,  $J = 13.6$  Hz, 1 H,  $\text{SiCH}_2$ ), 6.29 (t,  $J = 1.4$  Hz,  $\text{C}=\text{CH}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR /  $^{13}\text{C}\{^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 0.5$  ( $\text{SiCH}_3$ ), 1.4 ( $\text{SiCH}_3$ ), 14.1, 22.6, 29.3, 29.5, 30.9, 31.7, 35.2, 85.1, 128.5, 137.5, 139.8, 143.2, 145.8, 147.3.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta = -140.4$  (dd,  $J_1 = 23.3$  Hz,  $J_2 = 7.5$  Hz),  $-157.9$  (t,  $J = 20.7$  Hz),  $-164.1$  to  $-164.2$  (m). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 2961, 2928, 2858, 1656 (weak), 1521 (C-F), 1504 (C-F), 1452, 1371, 1301, 1251, 1159, 1123, 1092, 1001, 961, 934, 897, 864, 826, 785, 679. HRMS (ESI): ( $\text{MH}$ ) $^+$  calcd. for  $\text{C}_{18}\text{H}_{24}\text{F}_5\text{OSi}$ : 379.1517, found. 379.1512.

## 2,2,5-Trimethyl-3-pentyl-5-(4-(trifluoromethyl)benzyl)-2,5-dihydro-1,2-oxasilole

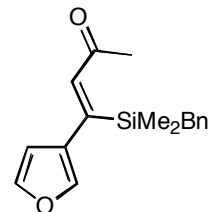


Following general procedure A. *Starting material*: (Z)-4-(dimethyl((4-trifluoromethyl)benzyl)silyl)non-3-en-2-one (92 mg, 256  $\mu\text{mol}$ , 1.00 eq.); *volume THF*: 0.8 ml; *base*: Li-triphenylmethylate (256 mM solution in THF/hexanes; 1.26 ml, 320  $\mu\text{mol}$ , 1.25 eq.); *reaction time 1*: 45min; *temperature*:  $-78^\circ\text{C}$ ; *reaction time 2*: 0min; *quenched with*: phosphate buffer (pH = 7); *column chromatography*: petrol ether : diethyl ether = 50 : 1. Yield: 40 mg (111  $\mu\text{mol}$ , 43%) of a colorless oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = -0.25 (s, 3 H,  $\text{SiCH}_3$ ), 0.16 (s, 3 H,  $\text{SiCH}_3$ ), 0.86 (t,  $J$  = 7.6 Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.11-1.31 (m, 6 H,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 1.33 (s, 3 H,  $\text{C}_{\text{quat}}\text{-CH}_3$ ), 2.11 (t,  $J$  = 7.2 Hz, 2 H,  $\text{CH}_2\text{CH}_2$ ), 2.83-2.90 (m, 2 H, 2  $\text{SiCH}_2$ ), 6.27 (t,  $J$  = 1.4 Hz,  $\text{C}=\text{CH}$ ), 7.22 (d,  $J$  = 8.0 Hz, 2 H,  $\text{CH}$  aryl), 7.47 (d,  $J$  = 8.0 Hz, 2 H,  $\text{CH}$  aryl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 0.5 ( $\text{SiCH}_3$ ), 1.6 ( $\text{SiCH}_3$ ), 14.2, 22.6, 29.4, 31.0, 31.7, 48.5, 85.1, 124.5, 126.0, 128.7, 131.4, 142.2, 142.8, 148.1.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta$  = -62.7 (s). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 2962, 2926, 2858, 1688 (weak), 1619 (weak), 1574, 1448, 1418, 1368, 1326, 1251, 1164, 1126, 1068, 1021, 964, 909, 850, 824, 784, 737, 681, 648. HRMS (EI): ( $\text{M} - \text{H}$ ) $^+$  calcd. for  $\text{C}_{19}\text{H}_{26}\text{F}_3\text{OSi}$ : 355.17050, found. 355.17125.

## B) SYNTHESIS OF $\beta$ -SILYLATED ENONES BY RU-CATALYZED *TRANS*-SELECTIVE HYDROSILYLATION OF YNONES

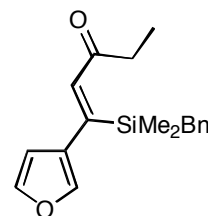
**General procedure B:** *trans-selective hydrosilylations of ynones*: In a flame dried Schlenk flask, a mixture of the ynone (1.00 eq.) and the respective substituted or unsubstituted benzyldimethylsilane (1.20 eq.) was dissolved in distilled acetone, cooled to  $0^\circ\text{C}$  and treated with catalytic amounts of  $[(\text{C}_5\text{Me}_5)\text{Ru}(\text{NCMe})_3]\text{PF}_6$ . The reaction mixture was stirred for [reaction time 1] at  $0^\circ\text{C}$  and for [reaction time 2] at rt, then all volatiles were evaporated and the crude product was purified by column chromatography ( $\text{SiO}_2$ ).

### Benzyltrimethylsilyl-1-(3-furanyl)but-1-en-3-one



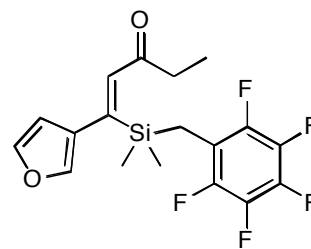
Synthesis according to general procedure B from 1-(3-furanyl)but-1-yn-3-one (1.23 g, 9.17 mmol, 1.00 eq.), benzyltrimethylsilane (1.74 ml, 1.65 g, 11.0 mmol, 1.20 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (46 mg, 92  $\mu$ mol, 0.01 eq.) in 13 ml distilled acetone. *Reaction time 1*: 15min. *Reaction time 2*: 3h. Column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: 2.02 g (7.10 mmol, 77 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 200 MHz):  $\delta$  = 0.10 (s, 6 H, 2  $SiCH_3$ ), 2.31 (s, 3 H,  $COCH_3$ ), 2.45 (s, 2 H,  $CH_2$ ), 5.94 (s, 1 H,  $C=C-H$ ), 6.84 (s, 1 H,  $CH$  furyl), 6.97-7.27 (m, 7 H, 2  $CH$  furyl & 5  $CH$  phenyl).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = -1.15 ( $SiCH_3$ ), 25.3, 31.1, 110.7, 124.3, 128.4, 128.7, 129.4, 139.3, 139.5, 140.5, 142.9, 153.5, 198.6 ( $C=O$ ). IR (neat):  $\nu$  ( $cm^{-1}$ ) 3060, 3024, 2953, 2899, 1685 ( $C=O$ ), 1600, 1548, 1493, 1452, 1416, 1358, 1320, 1256, 1248, 1205, 1187, 1160, 1077, 1056, 1031, 1003, 962, 929, 906, 872, 833, 789, 767, 726, 700, 644, 614, 597. HRMS (EI):  $M^+$  calcd. for  $C_{17}H_{20}O_2Si$  284.1233, found. 284.1228.

### Benzyltrimethylsilyl-1-(3-furanyl)pent-1-en-3-one



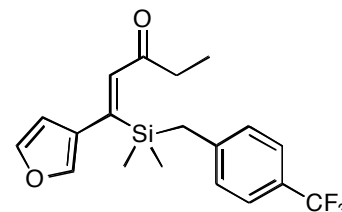
Synthesis according to general procedure B from 1-(3-furanyl)pent-1-yn-3-one (1.00 g, 6.75 mmol, 1.00 eq.), benzyltrimethylsilane (1.29 ml, 1.22 g, 8.10 mmol, 1.20 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (34 mg, 67.5  $\mu$ mol, 0.01 eq.) in 9.5 ml distilled acetone. *Reaction time 1*: 30min. *Reaction time 2*: 1h 15min. Column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: : 1.25 g (4.20 mmol, 62 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 200 MHz):  $\delta$  = 0.10 (s, 6 H,  $SiCH_3$ ), 1.16 (t,  $J$  = 7.4 Hz, 3 H,  $CH_2CH_3$ ), 2.47 (s, 2 H,  $SiCH_2$ ), 2.59 (q,  $J$  = 7.4 Hz, 2 H,  $CH_2CH_3$ ), 5.82 (t,  $J$  = 1.0 Hz, 1 H,  $C=CH$ ), 6.83 (s, 1 H,  $CH$  furan), 6.95-7.19 (m, 6 H,  $CH$  phenyl and 1  $CH$  furan), 7.26 (s, 1 H,  $CH$  furan).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = 0.00 ( $SiCH_3$ ), 9.46 ( $CH_2CH_3$ ), 26.5 ( $CH_2CH_3$ ), 38.1 ( $CH_2Ph$ ), 111.9, 125.4, 129.5, 129.9, 130.7, 140.3, 140.5, 141.7, 143.9, 153.8 ( $C=C-C=O$ ), 202.8 ( $C=O$ ). IR (neat):  $\nu$  ( $cm^{-1}$ ) 3024, 2976, 2897, 1687 ( $C=O$ ), 1599, 1549, 1492, 1452, 1410, 1358, 1248, 1205, 1160, 1126, 1027, 872, 832. HRMS (EI):  $M^+$  calcd. for  $C_{18}H_{22}O_2Si$  298.1389, found. 298.1387.

(Z)-1-(Dimethyl(2,3,4,5,6-pentafluorobenzyl)silyl)-1-(furan-3-yl)pent-1-en-3-one



Synthesis according to general procedure B from 1-(3-furanyl)pent-1-yn-3-one (150 mg, 1.01 mmol, 1.00 eq.) 2,3,4,5,6-pentafluorodimethylsilane (291 mg, 1.21 mmol, 1.20 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (26 mg, 5.1  $\mu$ mol, 0.05 eq.) in 2.0 ml dichloromethane. *Reaction time 1*: 1h. *Reaction time 2*: 0 min. Column chromatography: petrol ether : diethyl ether = 30 : 1. Yield: 326 mg (840  $\mu$ mol, 83 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 0.16 (s, 6 H,  $SiCH_3$ ), 1.12 (dt,  $J_t$  = 7.2 Hz,  $J_d$  = 0.8 Hz, 3 H,  $CH_2CH_3$ ), 2.44 (t,  $J$  = 2.4 Hz, 2 H,  $SiCH_2$ ), 2.58 (dq,  $J_q$  = 7.2 Hz,  $J_d$  = 0.8 Hz, 2 H,  $CH_2CH_3$ ), 6.20-6.21 (m, 1 H,  $CH$  furyl), 6.85 (d,  $J$  = 0.8 Hz, 1 H,  $C=CH$ ), 7.24-7.25 (m, 1 H,  $CH$  furyl), 7.34-7.35 (m, 1 H,  $CH$  furyl).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = -1.0 (2  $SiCH_3$ ), 8.1, 11.7, 36.8, 110.7, 115.0 (C-F), 128.9, 136.6 (C-F), 138.8 (C-F), 139.2, 139.5, 143.2, 145.7 (C-F), 151.0, 201.3.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 376.3 MHz):  $\delta$  = -142.8 (dd,  $J_1$  = 22.2 Hz,  $J_2$  = 7.5 Hz), -161.5 (t,  $J$  = 20.7 Hz), -164.2 to -164.2 (m). IR (neat):  $\nu$  ( $cm^{-1}$ ) 2979, 2912, 2904, 1690 (C=O), 1547, 1518 (C-F), 1501 (C-F), 1460, 1413, 1360, 1252, 1164, 1126, 1079, 1028, 966, 872, 837, 787. HRMS (ESI):  $(MH)^+$  calcd. for  $C_{18}H_{18}O_2SiF_5$ : 389.0996, found. 389.0990.  $C_{18}H_{17}F_5O_2Si$  (388.40): calc. C 55.66, H 4.44; meas. C 55.64, H 4.51.

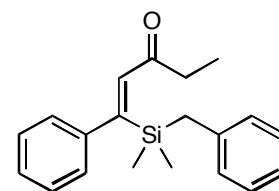
(Z)-1-(Dimethyl(4-(trifluoromethyl)benzyl)silyl)-1-(furan-3-yl)pent-1-en-3-one



Synthesis according to general procedure B from 1-(3-furanyl)pent-1-yn-3-one (150 mg, 1.01 mmol, 1.00 eq.) *p*-trifluoromethyldimethylsilane (264 mg, 1.21 mmol, 1.20 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (26 mg, 5.1  $\mu$ mol, 0.05 eq.) in 2.0 ml dichloromethane. *Reaction time 1*: 1h. *Reaction time 2*: 0 min. Column chromatography: petrol ether : diethyl ether = 30 : 1. Yield: 282 mg (859  $\mu$ mol, 85 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 0.12 (s, 6 H,  $SiCH_3$ ), 1.16 (t,  $J$  = 7.2 Hz, 3 H,  $CH_2CH_3$ ), 2.54 (s, 2 H,  $SiCH_2$ ), 2.60 (q,  $J$  = 7.6 Hz, 2 H,  $CH_2CH_3$ ), 5.96-5.97 (m, 1 H,  $CH$  furyl), 6.85 (s, 1 H,  $C=CH$ ), 7.03-7.04 (m, 1 H,  $CH$  furyl), 7.12 (d,  $J$  = 8.0 Hz,  $CH$  aryl), 7.29 (t,  $J$  = 1.0 Hz), 7.43 (d,  $J$  = 8.0 Hz,  $CH$  aryl).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = -1.2 (2  $SiCH_3$ ), 8.3, 25.9, 36.9, 110.6, 123.8, 125.2, 126.1, 128.8, 129.3, 139.2, 139.5, 143.0, 145.3, 151.9, 201.7.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 376.3 MHz):  $\delta$  = -62.4. IR (neat):  $\nu$  ( $cm^{-1}$ ) 2978, 2941, 2902, 1687 (C=O), 1614, 1560,

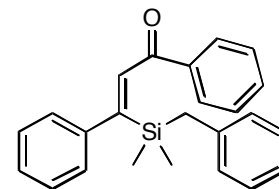
1546, 1460, 1417, 1360, 1325, 1250, 1209, 1162, 1124, 1067, 1027, 872, 849, 830, 798. HRMS (ESI): (MH)<sup>+</sup> calcd. for C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>SiF<sub>3</sub>: 367.1341, found. 367.1330.

(Z)-1-(Benzyldimethylsilyl)-1-phenylpent-1-en-3-one



Synthesis according to general procedure B from 1-phenylpent-1-yn-3-one (500 mg, 3.16 mmol, 1.00 eq.), benzyldimethylsilane (570 mg, 3.80 mmol, 1.20 eq.) and [(C<sub>5</sub>Me<sub>5</sub>)Ru(NCMe)<sub>3</sub>]PF<sub>6</sub> (32 mg, 64 μmol, 0.02 eq.) in 4.2 ml distilled acetone. *Reaction time 1*: 2 h 20 min. *Reaction time 2*: 1 h. Column chromatography: petrol ether : diethyl ether = 40 : 1. Yield: 798 mg (2.59 mmol, 82 %) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 0.03 (s, 6 H, 2 SiCH<sub>3</sub>), 1.17 (t, *J* = 7.6 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.43 (s, 2 H, SiCH<sub>2</sub>), 2.60 (q, *J* = 7.6 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 6.69-6.71 (m, 3 H, 3 CH), 6.99-7.01 (m, 2 H, 2 CH), 7.04-7.08 (m, 1 H, CH), 7.17-7.23 (m, 5 H, 5 CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz): δ = -1.5 (SiCH<sub>3</sub>), 8.3, 25.4, 37.1, 124.3, 126.5, 126.7, 128.1, 128.3, 128.8, 140.2, 140.5, 145.6, 163.6, 201.8. IR (neat): ν (cm<sup>-1</sup>) 3024, 2975, 2896, 1691, 1567, 1492, 1253, 1124, 1042, 835, 794, 764, 700. HRMS (EI): (MNa)<sup>+</sup> calcd. for C<sub>20</sub>H<sub>24</sub>ONaSi: 331.1494, found. 331.1488.

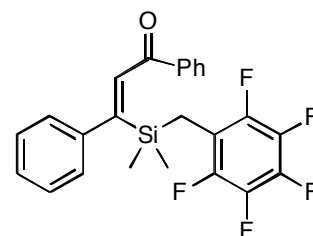
(Z)-3-(Benzyldimethylsilyl)-1,3-diphenylprop-2-en-1-one



Synthesis according to general procedure B from 1,3-diphenylprop-2-yn-1-one (410 mg, 1.99 mmol, 1.00 eq.), benzyldimethylsilane (378 μl, 359 mg, 2.39 mmol, 1.20 eq.) and [(C<sub>5</sub>Me<sub>5</sub>)Ru(NCMe)<sub>3</sub>]PF<sub>6</sub> (36 mg, 72 μmol, 0.036 eq.) in 2.5 ml distilled acetone. *Reaction time 1*: 15 min. *Reaction time 2*: 17 h. The catalyst was added in two equal portions (2x 18 mg) at the beginning of reaction time 1 and after 2.5 h at rt. Column chromatography: petrol ether : diethyl ether = 30 : 1. Yield: 317 mg (888 μmol, 45 %) of a colorless solid. Reisolated starting material: 159 mg (771 μmol, 39 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 0.14 (s, 6 H, 2 SiCH<sub>3</sub>), 2.55 (s, 2 H, CH<sub>2</sub>Ph), 6.83-6.88 (m, 2 H, CH<sub>phenyl</sub>), 7.05-7.13 (m, 2 H, CH<sub>phenyl</sub>), 7.19-7.32 (m, 6 H, CH<sub>phenyl</sub>), 7.49 (s, 1 H, C=CH), 7.51-7.67 (m, 3 H, CH<sub>phenyl</sub>), 8.07-8.12 (m, 2 H, CH<sub>phenyl</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75 MHz): δ = -1.4 (SiCH<sub>3</sub>), 25.7, 124.3, 126.7, 126.9, 128.2, 128.4, 128.8, 128.9, 129.0, 133.3, 138.1, 138.3, 140.5, 146.0, 165.7, 191.4 (C=O). IR (neat): ν (cm<sup>-1</sup>) 3058, 3024, 2953, 2896, 1656 (C=O), 1598,

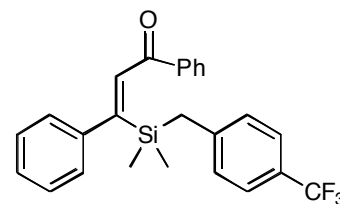
1561, 1492, 1449, 1407, 1346, 1254, 1208, 1179, 1155, 1057, 1036, 1020, 946, 885, 829, 792, 764, 699, 671, 610, 564. HRMS (EI):  $M^+$  calcd. for  $C_{24}H_{24}OSi$ : 356.1596, found. 356.1589.

(Z)-3-(Dimethyl(perfluorobenzyl)silyl)-1,3-diphenylprop-2-en-1-one



Synthesis according to general procedure B from 1,3-diphenylprop-2-yn-1-one (161 mg, 780  $\mu$ mol, 1.00 eq.), (2,3,4,5,6-pentafluorobenzyl)dimethylsilane (225 mg, 937  $\mu$ mol, 1.20 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (20 mg, 78  $\mu$ mol, 0.10 eq.) in 0.6 ml acetone. *Reaction time 1*: 3 min. *Reaction time 2*: 2 h 10 min. Column chromatography: petrol ether : diethyl ether = 20 : 1. Yield: 180 mg (403  $\mu$ mol, 52 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 0.16 (s, 6 H, 2  $SiCH_3$ ), 2.45 (dd,  $J_1$  = 2.2 Hz,  $J_2$  = 2.2 Hz, 2 H,  $SiCH_2$ ; coupling to fluorine), 7.07-7.09 (m, 2 H, 2  $CH$ ), 7.27-7.31 (m, 1 H,  $CH$ ), 7.34-7.38 (m, 2 H, 2  $CH$ ), 7.48-7.52 (m, 3 H, 3  $CH$ ), 7.57-7.61 (m, 1 H,  $CH$ ), 8.00-8.04 (m, 2 H, 2  $CH$ ).  $^{13}C\{^1H,^{19}F\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = -1.2 ( $SiCH_3$ ), 12.1 ( $SiCH_2$ ), 115.0, 126.6, 127.3, 128.5, 128.8, 129.0, 133.5, 137.6, 137.8, 138.2, 138.2, 144.5, 145.3, 164.3, 190.8.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 377 MHz):  $\delta$  = -142.6 (dd,  $J_1$  = 22.2 Hz,  $J_2$  = 7.5 Hz), -161.5 (t,  $J$  = 20.7 Hz), -164.1 to -164.2 (m). IR (neat):  $\nu$  ( $cm^{-1}$ ) 3059, 3026, 2956, 1657, 1598, 1564, 1518 (C-F), 1501 (C-F), 1448, 1346, 1252, 1209, 1163, 1120, 1036, 1020, 966, 835, 758, 699. HRMS (EI):  $(MH)^+$  calcd. for  $C_{24}H_{20}F_5OSi$ : 447.1204, found. 447.1192.

(Z)-3-(Dimethyl(4-(trifluoromethyl)benzyl)silyl)-1,3-diphenylprop-2-en-1-one

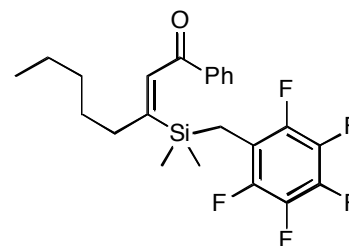


Synthesis according to general procedure B from 1,3-diphenylprop-2-yn-1-one (300 mg, 1.45 mmol, 1.00 eq.), (4-trifluoromethylbenzyl)dimethylsilane (521 mg, 2.39 mmol, 1.65 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (74 mg, 146  $\mu$ mol, 0.10 eq.) in 1.0 ml acetone. *Reaction time 1*: 5 min. *Reaction time 2*: 3 h 45 min. Column chromatography: petrol ether : diethyl ether = 30 : 1. Yield: 487 mg (1.15  $\mu$ mol, 79 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 0.11 (s, 6 H, 2  $SiCH_3$ ), 2.59 (s, 2 H,  $SiCH_2$ ), 6.79-6.81 (m, 2 H, 2  $CH$ ), 7.12 (d,  $J$  = 8.0 Hz, 2 H, 2  $CH$ ), 7.22-7.30 (m, 3 H, 3  $CH$ ), 7.43 (d,  $J$  = 8.0 Hz, 2 H, 2  $CH$ ), 7.47 (s, 1 H,  $CH$ ), 7.49-7.53 (m, 2 H, 2  $CH$ ), 7.58-7.63 (m, 1 H,  $CH$ ),

8.03-8.06 (m, 2 H, 2 CH).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = -1.4$  (SiCH<sub>3</sub>), 26.2 (SiCH<sub>2</sub>), 124.9, 125.2, 126.6, 126.6, 127.0, 128.3, 128.9, 129.0, 133.4, 138.0, 138.3, 145.2, 145.6, 164.9, 191.3.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 377 MHz):  $\delta = -62.4$ . IR (neat):  $\nu$  (cm<sup>-1</sup>) 3059, 2955, 2899, 1657, 1614, 1598, 1562, 1325, 1251, 1208, 1162, 1120, 1067, 1019, 849, 828, 759, 699. HRMS (EI): (MH)<sup>+</sup> calcd. for C<sub>25</sub>H<sub>24</sub>F<sub>3</sub>OSi: 425.1549, found. 425.1548. C<sub>25</sub>H<sub>23</sub>F<sub>3</sub>OSi (424.53): calc. C 70.73, H 5.46; meas. C 71.00, H 5.66.

(Z)-3-(Dimethyl(2,3,4,5,6-pentafluorobenzyl)silyl)-1-phenyloct-2-en-1-one

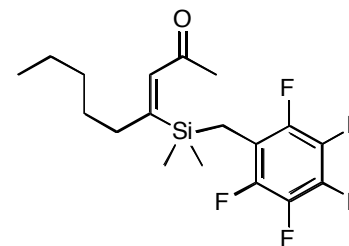
Synthesis according to general procedure B from 1-phenyloct-2-yn-1-one (202 mg, 1.01 mmol, 1.00 eq.), (2,3,4,5,6-pentafluorobenzyl)dimethylsilane (291 mg, 1.21 mmol, 1.20 eq.) and [(C<sub>5</sub>Me<sub>5</sub>)Ru(NCMe)<sub>3</sub>]PF<sub>6</sub> (26 mg, 5.1  $\mu\text{mol}$ , 0.05 eq.) in 2.0 ml acetone.



Reaction time 1: 3h 15min. Reaction time 2: 0 min. Column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: 291 mg (770  $\mu\text{mol}$ , 76%) of a colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 0.22$  (s, 6 H, 2 SiCH<sub>3</sub>), 0.91 (t,  $J = 6.8$  Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.31-1.41 (m, 6 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.35-2.39 (m, 2 H, CH<sub>2</sub>CH<sub>2</sub>), 2.48 (s, 2 H, SiCH<sub>2</sub>), 7.45-50 (m, 3 H, C=C-H & 2 CH aryl), 7.56 (t,  $J = 3.6$  Hz, 1 H, CH aryl), 7.96-7.99 (m, 2 H, 2 CH aryl).  $^{13}\text{C}\{^1\text{H}\}$  NMR /  $^{13}\text{C}\{^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = -1.8$  (SiCH<sub>3</sub>), 11.6, 14.2, 22.7, 29.7, 31.9, 39.4, 127.9 (C-F), 128.7, 128.8, 129.5 (C-F), 133.1, 135.4, 137.6 (C-F), 138.2, 144.6 (C-F), 165.4, 190.6 (C=O).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta = -142.6$  (dd,  $J_1 = 21.8$  Hz,  $J_2 = 7.1$  Hz), -161.9 (t,  $J = 21.8$  Hz), -164.4 to -164.5 (m). IR (neat):  $\nu$  (cm<sup>-1</sup>) 2958, 2932, 2861, 1657 (C=O), 1599, 1570, 1518 (C-F), 1500 (C-F), 1448, 1413, 1357, 1300, 1249, 1236, 1161, 1120, 1021, 966, 842, 781, 698. HRMS (ESI): (MH)<sup>+</sup> calcd. for C<sub>23</sub>H<sub>26</sub>F<sub>5</sub>OSi: 441.1673, found. 441.1669. C<sub>23</sub>H<sub>25</sub>F<sub>5</sub>OSi (440.52): calc. C 62.71, H 5.72; meas. C 62.83, H 5.88.

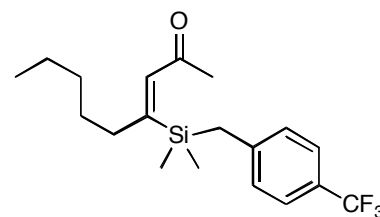
(Z)-4-(Dimethyl(2,3,4,5,6-pentafluorobenzyl)silyl)non-3-en-2-one

Synthesis according to general procedure B from non-3-yn-2-one (140 mg, 1.01 mmol, 1.00 eq.), (2,3,4,5,6-pentafluorobenzyl)dimethylsilane (291 mg, 1.21 mmol, 1.20 eq.) and



$[(C_5Me_5)Ru(NCMe)_3]PF_6$  (26 mg, 5.1  $\mu$ mol, 0.05 eq.) in 2.0 ml acetone. *Reaction time 1*: 1h 45min. *Reaction time 2*: 0 min. Column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: 291 mg (770  $\mu$ mol, 76 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 0.13 (s, 6 H, 2  $SiCH_3$ ), 0.87 (t,  $J$  = 6.8 Hz, 3 H,  $CH_2CH_3$ ), 1.22-1.25 (m, 6 H,  $CH_2CH_2CH_2$ ), 2.18-2.28 (m, 2 H,  $CH_2CH_2$ ), 2.23 (s, 3 H,  $C(O)CH_3$ ), 2.38 (s, 2 H,  $SiCH_2$ ), 6.70 (s, 1 H,  $C=C-H$ ).  $^{13}C\{^1H\}$  NMR /  $^{13}C\{^{19}F\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = -2.1 ( $SiCH_3$ ), 11.2, 14.1, 22.7, 29.6, 30.5, 31.8, 38.8, 115.2 ( $C-F$ ), 137.8 ( $C-F$ ), 138.4 ( $C=CH-C(CH_3)=O$ ), 143.3 ( $C-F$ ), 145.7 ( $C-F$ ), 163.5 ( $C=CH-C(CH_3)=O$ ), 198.3 ( $C=CH-C(CH_3)=O$ ).  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 376.3 MHz):  $\delta$  = -142.8 (dd,  $J_1$  = 23.0 Hz,  $J_2$  = 7.5 Hz), -161.9 (t,  $J$  = 20.7 Hz), -164.4 (dd,  $J_1$  = 21.8 Hz,  $J_2$  = 7.2 Hz). IR (neat):  $\nu$  ( $cm^{-1}$ ) 2959, 2933, 2862, 1691 ( $C=O$ ), 1574 ( $C-F$ ), 1518 ( $C-F$ ), 1501 ( $C-F$ ), 1469, 1417, 1359, 1301, 1259, 1198, 1163, 1121, 1019, 966, 837, 771, 709, 690, 640. HRMS (ESI):  $(MH)^+$  calcd. for  $C_{18}H_{24}F_5OSi$ : 379.1517, found. 379.1517.

(Z)-4-(Dimethyl((4-trifluoromethyl)benzyl)silyl)non-3-en-2-one

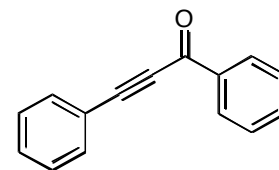


Synthesis according to general procedure B from non-3-yn-2-one (140 mg, 1.01 mmol, 1.00 eq.), (4-trifluoromethyl)benzyl)dimethylsilane (264 mg, 1.21 mmol, 1.20 eq.) and  $[(C_5Me_5)Ru(NCMe)_3]PF_6$  (26 mg, 5.1  $\mu$ mol, 0.05 eq.) in 2.0 ml acetone. *Reaction time 1*: 1h 45min. *Reaction time 2*: 0 min. Column chromatography: petrol ether : diethyl ether = 50 : 1. Yield: 293 mg (822  $\mu$ mol, 81 %) of a colorless oil.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 0.10 (s, 6 H, 2  $SiCH_3$ ), 0.85 (t,  $J$  = 7.2 Hz, 3 H,  $CH_2CH_3$ ), 1.08-1.24 (m, 6 H,  $CH_2CH_2CH_2$ ), 2.14-2.17 (m, 2 H,  $CH_2CH_2$ ), 2.25 (s, 3 H,  $C(O)CH_3$ ), 2.45 (s, 2 H,  $SiCH_2$ ), 6.70 (s, 1 H,  $C=C-H$ ), 7.10 (d,  $J$  = 8.0 Hz, 2 H,  $CH$  aryl), 7.41 (d,  $J$  = 8.0 Hz, 2 H,  $CH$  aryl).  $^{13}C\{^1H\}$  NMR /  $^{13}C\{^{19}F\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  = -2.4 ( $SiCH_3$ ), 14.1, 22.6, 25.5, 29.4, 30.8, 31.8, 39.1, 124.8, 125.1, 126.4, 128.7, 138.2, 145.5, 164.7, 198.5 ( $C=O$ ).  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 376.3 MHz):  $\delta$  = -62.5 (s). IR (neat):  $\nu$  ( $cm^{-1}$ ) 2959, 2933, 2862, 1688 ( $C=O$ ), 1614, 1574, 1468, 1418, 1359, 1325, 1246, 1197, 1162, 1123, 1068, 1018, 954, 849, 758, 680. HRMS (ESI):  $(MH)^+$  calcd. for  $C_{19}H_{28}F_3OSi$ : 357.1862, found. 357.1869.

## C) SYNTHESSES OF YNONES

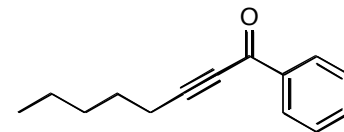
**General procedure C:** *synthesis of enones from terminal alkynes and amides:* In a flame dried round bottom flask, the alkyne (1.00 eq.) was dissolved in diethyl ether, cooled to  $-78^{\circ}\text{C}$  and slowly treated with *n*butyllithium (1.00 eq.). After the dropwise addition of the *N,N*-dimethyl amide (1.25 eq.), the reaction mixture was warmed to  $4^{\circ}\text{C}$  and stirred during several hours (*vide infra*). The reaction was transferred into vigorously stirred water, acidified with ammonium chloride aq. sat., extracted with diethyl ether, washed with brine, dried over  $\text{MgSO}_4$ , filtered, concentrated *in vacuo*, purified by column chromatography ( $\text{SiO}_2$ ) and stored under Ar in a refrigerator.

### 1,3-Diphenylprop-2-yn-1-one



Synthesis according to general procedure C from phenylacetylene (1.87 ml, 1.74 g, 17.0 mmol, 1.00 eq.) and *N,N*-dimethylbenzamide (3.17 g, 21.3 mmol, 1.25 eq.) in 50 ml diethyl ether. *Reaction time:* 3.0 h. Column chromatography: petrol ether : diethyl ether = 10 : 1. Yield: 1.94 g (9.41 mmol, 55 %) of a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 7.42-7.55 (m, 5 H, 5  $\text{CH}_{\text{phenyl}}$ ), 7.61-7.70 (m, 3 H, 3  $\text{CH}_{\text{phenyl}}$ ), 8.21-8.25 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  = 87.2 (C $\equiv$ C), 93.4 (C $\equiv$ C), 120.4, 128.9, 129.0, 129.9, 131.1, 133.4, 134.4, 137.1, 178.3 (C=O). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3063, 3034, 2200 (C $\equiv$ C), 1641, 1598, 1581, 1490, 1450, 1316, 1287, 1210, 1172, 1071, 1032, 1013, 996, 921, 815, 794, 758, 698, 627, 620. Known substance: CAS 7338-94-5. See: Wang, B. *et al. J. Org. Chem.* 2005, 70, 6126-6128.

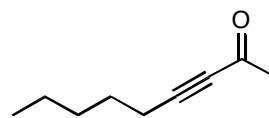
### 1-Phenyloct-2-yn-1-one



Synthesis according to general procedure C from 1-heptyne (3.35 ml, 2.45 g, 25.5 mmol, 1.00 eq.) and *N,N*-dimethylbenzamide (4.75 g, 31.9 mmol, 1.25 eq.) in 75 ml diethyl ether. *Reaction time:* 6.5 h. Column chromatography: petrol ether : diethyl ether = 20 : 1. Yield: 4.11 g (20.5 mmol, 81 %) of a white solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  = 0.93 (t,  $J$  = 7.2 Hz, 3 H,  $\text{CH}_3$ ), 1.32-1.49 (m, 4 H, 2  $\text{CH}_2$ ), 1.63-1.74 (m, 2 H,  $\text{CH}_2$ ), 2.50 (t,  $J$  = 7.2 Hz, 2 H,  $\text{CH}_2$ ), 7.44-7.51 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ), 7.60 (tt,  $J_{(a)}$  = 7.2 Hz,  $J_{(b)}$  = 3.9 Hz, 1 H, 2  $\text{CH}_{\text{phenyl}}$ ), 8.12-8.16 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ).

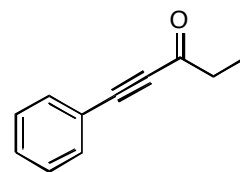
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 14.2, 19.4, 22.4, 27.8, 31.4, 79.9$  ( $\text{C}\equiv\text{C}$ ),  $97.2$  ( $\text{C}\equiv\text{C}$ ),  $128.8, 128.8, 134.1, 137.2, 178.5$  ( $\text{C}=\text{O}$ ). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ )  $3064, 2957, 2933, 2871, 2236$  ( $\text{C}\equiv\text{C}$ ),  $2202$  ( $\text{C}\equiv\text{C}$ ),  $1645$  ( $\text{C}=\text{O}$ ),  $1599, 1581, 1450, 1423, 1379, 1313, 1265, 1175, 1116, 1070, 1024, 1002, 978, 942, 917, 870, 796, 702$ . Known substance: CAS 27259-10-5. See: Wang, B. *et al. J. Org. Chem.* 2005, 70, 6126-6128.

#### Non-3-yn-2-one



Synthesis according to general procedure C from 1-heptyne (4.46 ml, 3.27 g, 34.0 mmol, 1.00 eq.) and *N,N*-dimethylacetamide (3.95 ml, 3.70 g, 42.5 mmol, 1.25 eq.) in 100 ml diethyl ether. *Reaction time*: 18.5 h. Column chromatography: petrol ether : diethyl ether = 10 : 1. Yield: 3.74 g (27.1 mmol, 80 %) of a yellowish oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 0.91$  (t,  $J = 7.2$  Hz, 3 H,  $\text{CH}_3$ ),  $1.30\text{-}1.44$  (m, 4 H, 2  $\text{CH}_2$ ),  $1.53\text{-}1.64$  (m, 2 H,  $\text{CH}_2$ ),  $2.32\text{-}2.38$  (m, 5 H,  $\text{CH}_2$  and  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta = 14.1, 19.1, 22.3, 27.6, 31.2, 33.0, 81.6$  ( $\text{C}\equiv\text{C}$ ),  $94.4$  ( $\text{C}\equiv\text{C}$ ),  $185.1$  ( $\text{C}=\text{O}$ ). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ )  $2958, 2934, 2872, 2209$  ( $\text{C}\equiv\text{C}$ ),  $1676$  ( $\text{C}=\text{O}$ ),  $1467, 1423, 1359, 1328, 1228, 1107, 1073, 1019, 962, 910, 732$ . Known substance: CAS 27259-09-2. See: Georgy, M. *et al. J. Org. Chem.* 2007, 72, 3543-3549.

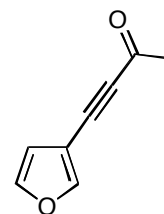
#### 1-Phenylpent-1-yn-3-one



In a flame dried 250 ml round bottom flask, a solution of phenylacetylene (1.87 ml, 1.74 g, 17.0 mmol, 1.00 eq.) in 50 ml diethyl ether was treated with *n*BuLi (2.4 M in hexanes; 7.1 ml, 17.0 mmol, 1.00 eq.) at  $-78^\circ\text{C}$ . After 45 min, *N*-methoxy-*N*-methylpropionamide (2.49 g, 21.3 mmol, 1.25 eq.) was added dropwise the reaction mixture was stirred for 20 min at constant temperature, warmed to  $4^\circ\text{C}$  and stirred for further 17 h. The reaction was transferred into a mixture of ammonium chloride aq. sat. (90 ml) and HCl aq. 2N (22 ml) and extracted with diethyl ether. The organic phases were dried over  $\text{Na}_2\text{SO}_4$ , filtered and condensed to dryness. Purification by column chromatography (petrol ether : diethyl ether = 30 : 1) gave the product as a colorless liquid. Yield: 2.60 g (16.5 mmol, 97 %).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 1.23$  (t,  $J = 9.6$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ),  $2.71$  (q,  $J = 9.6$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ),  $7.37\text{-}7.49$  (m, 3 H, 3  $\text{CH}_{\text{phenyl}}$ ),  $7.57\text{-}7.60$  (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR

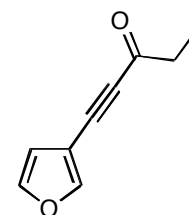
(CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 8.4 (CH<sub>3</sub>), 39.1 (CH<sub>2</sub>), 87.9 (C $\equiv$ C), 90.0 (C $\equiv$ C), 120.3, 128.9, 130.9, 133.3, 188.9 (C=O). IR (neat):  $\nu$  (cm<sup>-1</sup>) 3061, 2980, 2939, 2905, 2880, 2201 (C $\equiv$ C), 1674 (C=O), 1489, 1459, 1444, 1409, 1378, 1352, 1309, 1283, 1258, 1160, 1113, 1046, 987, 959, 759, 690. Known substance: CAS 19307-74-5. See: Dehmlow, E.V. *et al. Chem. Ber.* 1968, 101, 410-426.

#### 1-(3-Furanyl)but-1-yn-3-one



In a dry 250 ml round bottom flask, a solution of 3-(2,2-dibromovinyl)furan (3.10 g, 12.3 mmol, 1.00 eq.) in 25 ml THF was treated with n-butyllithium (2.5 M in hexanes, 10.8 ml, 27.1 mmol, 2.20 eq.) at -78° C. After stirring for 45 min at constant temperature, a solution of *N*-methoxy-*N*-methylacetamide (1.57 ml, 1.52 g, 14.8 mmol, 1.20 eq.) was added dropwise. The reaction solution was warmed to 4° C and stirred for 22 h. After being warmed to rt, the reaction mixture was then transferred into a mixture of a sat. aq. solution of ammonium chloride (117 ml) and 2 N HCl (29 ml). Then the reaction was extracted with diethyl ether (3 x), washed with sodium bicarbonate aq. sat., dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo* (in order to prevent loss of the volatile product, the solvents were evaporated with a RV at rt). The crude product was purified by column chromatography (petrol ether : diethyl ether = 20 : 1) to give the title substance as a colorless oil. Yield: 1.23 g (9.17 mmol, 75 %; the two step process from 3-furaldehyde gave a yield of 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  = 2.37 (s, 3 H, CH<sub>3</sub>), 6.50 (dd,  $J_{(d(1))}$  = 2.0 Hz,  $J_{(d(1))}$  = 0.6 Hz, 1 H, CH furan), 7.39 (t,  $J$  = 1.6 Hz, 1 H, CH furan), 7.76 (m, 1 H, CH furan). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 32.7 (CH<sub>3</sub>), 82.8 (C $\equiv$ C), 91.3 (C $\equiv$ C), 105.3, 112.8, 143.8, 149.4, 184.4 (C=O). IR (neat):  $\nu$  (cm<sup>-1</sup>) 3146, 2206 (C $\equiv$ C), 1673 (C=O), 1509, 1418, 1359, 1302, 1189, 1158, 1085, 1018, 990, 872, 802, 740, 610, 597. HRMS (EI): M<sup>+</sup> calcd. for C<sub>8</sub>H<sub>6</sub>O<sub>2</sub> 134.0368, found. 134.0363.

#### 1-(3-Furanyl)pent-1-yn-3-one



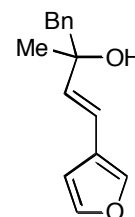
In a dry 250 ml round bottom flask, a solution of 3-(2,2-dibromovinyl)furan (5.04 g, 20.0 mmol, 1.00 eq.) in 40 ml THF was treated with n-butyllithium (2.5 M in hexanes, 17.6 ml, 44.0 mmol, 2.20 eq.) at -78° C. After stirring for 90 min at constant temperature, a solution of *N*-methoxy-*N*-methylpropionamide (2.81 g, 24.0 mmol, 1.20 eq.) in 16 ml THF was added

during 5 min. The reaction solution was first warmed to 0° C, then stirred at rt for 15 h. The reaction mixture was then transferred into a mixture of a sat. aq. solution of ammonium chloride (190 ml) and 2 N HCl (47 ml). Finally, the reaction was extracted with diethyl ether (3 x), dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo* (in order to prevent loss of the volatile product, the solvents were evaporated with a RV at rt). The crude product was purified by column chromatography (ether : diethyl ether = 20 : 1) to give the title substance as a colorless oil. Yield: 2.05 g (13.7 mmol, 70 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ = 1.20 (t, *J* = 7.4 Hz, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 2.66 (q, *J* = 7.4 Hz, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 6.54 (dd, *J*<sub>1</sub> = 1.8 Hz, *J*<sub>2</sub> = 0.6 Hz, 1 H, CH), 7.43 (d, *J* = 1.8 Hz, 1 H, CH), 7.81 (d, *J* = 0.6 Hz, 1 H, CH). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100 MHz): δ = 8.3 (CH<sub>3</sub>), 38.8 (CH<sub>2</sub>), 83.0 (C≡C), 90.7 (C≡C), 105.4, 112.8, 143.8, 149.2, 188.5 (C=O). IR (neat): ν (cm<sup>-1</sup>) 3146, 2981, 2941, 2203 (C≡C), 1673 (C=O), 1509, 1460, 1410, 1355, 1291, 1159, 1128, 1084, 1051, 1017, 872, 798, 739. HRMS (EI): M<sup>+</sup> calcd. for C<sub>9</sub>H<sub>8</sub>O<sub>2</sub> 148.0524, found. 148.0518.

## D) DEGRADATION REACTIONS

**General procedure D:** *synthesis of allylic alcohols from 2,5-dihydro-1,2-oxasiloles (protodesilylation reaction):* In a flame dried Schlenk flask, a solution of the 2,5-dihydro-1,2-oxasilole in THF was treated at in this order with CuI and TBAF at room temperature, stirred for [reaction time], filtered over a short pad of silica gel and extracted with diethyl ether / water. The organic phases were dried over MgSO<sub>4</sub>, filtered, condensed to dryness and purified by column chromatography (SiO<sub>2</sub>).

(*E*)-4-(Furan-3-yl)-2-methyl-1-phenylbut-3-en-2-ol

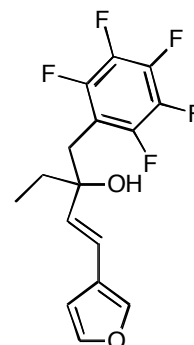


Synthesis according to general procedure D from 5-benzyl-5-methyl-3-(furan-3-yl)-2,2-dimethyl-2,5-dihydro-1,2-oxasilole (46 mg, 164 μmol, 1.00 eq.) in 1.0 ml THF. CuI: (47 mg, 246 μmol, 1.50 eq.). TBAF: (1 M in THF, 410 μl, 210 μmol, 2.5 eq.). Reaction time: 2d. Chromatography: petrol ether : diethyl ether = 3 : 1. Yield: 30.3 mg (133 μmol, 81 %) of a colorless solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 1.35 (s, 3 H, CH<sub>3</sub>), 1.62 (s, 1 H, OH), 2.85 (d, *J* = 13.2 Hz, 1 H, CH<sub>2</sub>Ph), 2.92 (d, *J* = 13.2 Hz, 1 H, CH<sub>2</sub>Ph), 6.05 (dd, *J*<sub>(1)</sub> = 17.2 Hz, *J*<sub>(2)</sub> = 1.2 Hz, 1 H, CH=CH), 6.37 (d, *J* = 17.2 Hz, 1 H, CH=CH), 6.49-6.40 (m, 1 H, CH furyl), 7.19-7.37 (m, 7 H, 2 CH furyl and 5 CH

phenyl).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 28.01$  ( $\text{CH}_3$ ), 49.4 ( $\text{CH}_2$ ), 73.1 ( $\text{C}_{\text{quat}}$ ), 107.8, 117.5, 124.0, 126.9, 128.4, 130.9, 136.2, 137.0, 140.6, 143.7. IR (neat): 3558, 3421, 3028, 2974, 2925, 2868, 1663 (weak), 1602 (weak), 1495, 1454, 1372, 1289, 1161, 1091, 1072, 1024, 968, 935, 871, 779, 756, 720, 701. mp = 56.0° C. HRMS (EI):  $\text{M}^+$  calcd. for  $\text{C}_{15}\text{H}_{16}\text{O}_2$ : 228.1150, found. 228.1140.  $\text{C}_{15}\text{H}_{16}\text{O}_2$  (228.29): calc. C 78.92, H 7.06; meas. C 78.88, H 7.00.

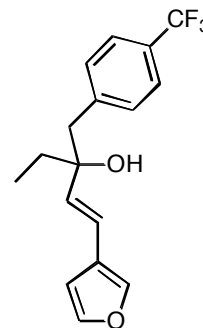
(*E*)-1-(Furan-3-yl)-3-(perfluorobenzyl)pent-1-en-3-ol

Synthesis according to general procedure D from 5-ethyl-3-(furan-3-yl)-2,2-dimethyl-5-(2,3,4,5,6-pentafluorobenzyl)-2,5-dihydro-1,2-oxasilole (80 mg, 206  $\mu\text{mol}$ , 1.00 eq.) in 0.5 ml THF. CuI: (80 mg, 421  $\mu\text{mol}$ , 2.04 eq.). TBAF: (1.0 M in THF; 732  $\mu\text{l}$ , 732  $\mu\text{mol}$ , 3.55 eq.). Reaction time: 2h. Chromatography: petrol ether : diethyl ether = 5 : 1. Yield: 59 mg (179  $\mu\text{mol}$ , 87 %) of a clear, colorless oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 0.98$  (t,  $J = 7.2$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.60 (s, 1 H, OH), 1.75 (q,  $J = 7.2$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 2.97 (d,  $J = 13.8$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 3.05 (d,  $J = 13.8$  Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 5.94 (d,  $J = 15.9$  Hz, 1 H,  $\text{HC}=\text{CH}$ ), 6.34 (d,  $J = 15.9$  Hz, 1 H,  $\text{HC}=\text{CH}$ ), 6.51-6.52 (m, 1 H, 1  $\text{CH}_{\text{furyl}}$ ), 7.38-7.39 (m, 2 H, 2  $\text{CH}_{\text{furyl}}$ ).  $^{13}\text{C}\{^1\text{H}, ^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 8.08$  ( $\text{CH}_2\text{CH}_3$ ), 34.0 ( $\text{CH}_2\text{CH}_3$ ), 34.9 ( $\text{CH}_2\text{Ph}$ ), 76.2 ( $\text{C}_{\text{quat}}$ ), 107.7, 111.1, 119.3, 123.6, 132.5, 137.5, 140.0, 140.7, 143.8, 145.7.  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 376.3 MHz):  $\delta = -140.9$  (dd,  $J_1 = 22.6$  Hz,  $J_2 = 7.5$  Hz), -156.9 (t,  $J = 21.1$  Hz), -163.5 to -163.4 (m). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3480, 2974, 2940, 1657 (weak), 1522 (C-F), 1503 (C-F), 1301, 1162, 1124, 1075, 1025, 972, 872, 779. HRMS (EI): ( $\text{MH}$ ) $^+$  calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{F}_5$ : 333.09140, found. 333.09175.



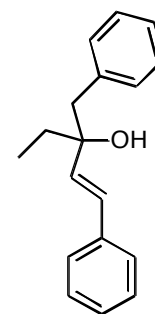
(*E*)-1-(Furan-3-yl)-3-(4-(trifluoromethyl)benzyl)pent-1-en-3-ol

Synthesis according to general procedure D from 5-ethyl-3-(furan-3-yl)-2,2-dimethyl-5-(4-(trifluoromethyl)benzyl)-2,5-dihydro-1,2-oxasilole (64 mg, 175  $\mu\text{mol}$ , 1.00 eq.) in 0.5 ml THF. CuI: (64 mg, 337  $\mu\text{mol}$ , 1.93 eq.). TBAF: (1.0 M in THF; 616  $\mu\text{l}$ , 616  $\mu\text{mol}$ , 3.52 eq.). Reaction time: 2h. Chromatography: petrol ether : diethyl ether = 5 : 1. Yield: 48 mg (153  $\mu\text{mol}$ , 88 %) of a colorless solid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 0.97$  (t,  $J = 7.5$  Hz, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.54 (s, 1 H, OH), 1.68 (q,  $J = 7.5$  Hz, 2 H,  $\text{CH}_2\text{CH}_3$ ), 2.93-3.02



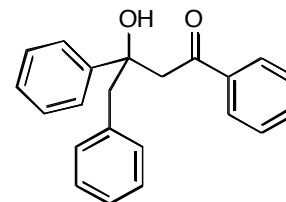
(m, 2 H,  $CH_2Ph$ ), 5.96 (d,  $J = 16.2$  Hz, 1 H,  $HC=CH$ ), 6.36 (d,  $J = 16.2$  Hz, 1 H,  $HC=CH$ ), 6.52-6.53 (m, 1 H,  $CH_{furyl}$ ), 7.34 (d,  $J = 8.1$  Hz, 2 H, 2  $CH_{phenyl}$ ), 7.39-7.40 6.52-6.53 (m, 2 H, 2  $CH_{furyl}$ ), 7.56 (d,  $J = 8.1$  Hz, 2 H, 2  $CH_{phenyl}$ ).  $^{13}C\{^1H, ^{19}F\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta = 8.15$  ( $CH_2CH_3$ ), 33.7 ( $CH_2CH_3$ ), 47.7 ( $CH_2Ph$ ), 75.6 ( $C_{quat}$ ), 107.7, 119.0, 123.8, 124.5, 125.1, 129.0, 131.2, 134.1, 140.6, 141.2, 143.8.  $^{19}F\{^1H\}$  NMR ( $CDCl_3$ , 376.3 MHz):  $\delta = -62.8$  IR (neat):  $\nu$  ( $cm^{-1}$ ) 3467, 2971, 2936, 1619, 1418, 1326, 1163, 1123, 1068, 1021, 969, 872, 778. mp = 58.0° C. HRMS (EI): (MH)<sup>+</sup> calcd. for  $C_{17}H_{18}O_2F_3$ : 311.12589, found. 311.12592.

(*E*)-3-Benzyl-1-phenylpent-1-en-3-ol



In a 10 ml Schlenk flask, a solution of 5-benzyl-5-ethyl-2,2-dimethyl-3-phenyl-2,5-dihydro-1,2-oxasilole (200 mg, 648  $\mu$ mol, 1.00 eq.) in 1.0 ml THF was treated in this order with CuI (184 mg, 972  $\mu$ mol, 1.50 eq.) and TBAF (1.0 M in THF; 1.62 ml, 1.62 mmol, 2.50 eq.) at 0° C, then warmed to rt and stirred for 1 h 50 min. Then the reaction mixture was stirred at 45° C for 17 h, cooled to rt, filtered over a short pad of silica gel and extracted with diethyl ether / water. The organic phases were dried over  $MgSO_4$ , filtered and condensed to dryness. Purification by column chromatography (petrol ether : diethyl ether = 5 : 1) gave the product as a colorless oil. Yield: 147 mg (583  $\mu$ mol, 90 %).  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta = 0.99$  (t,  $J = 7.2$  Hz, 3 H,  $CH_2CH_3$ ), 1.63 (s, 1 H, OH), 1.71 (q,  $J = 7.2$  Hz, 2 H,  $CH_2CH_3$ ), 2.93 (d,  $J = 13.2$  Hz, 1 H,  $CH_2Ph$ ), 2.99 (d,  $J = 13.2$  Hz, 1 H,  $CH_2Ph$ ), 6.27 (d,  $J = 16.0$  Hz, 1 H,  $HC=CH$ ), 6.51 (d,  $J = 16.0$  Hz, 1 H,  $HC=CH$ ), 7.23-7.40 (m, 10 H, 10  $CH_{phenyl}$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ , 100 MHz):  $\delta = 8.33$  ( $CH_2CH_3$ ), 33.7 ( $CH_2CH_3$ ), 48.1 ( $CH_2Ph$ ), 75.8 ( $C_{quat}$ ), 126.6, 126.9, 127.6, 128.4, 128.7, 128.8, 131.0, 135.3, 136.9, 137.4. IR (neat):  $\nu$  ( $cm^{-1}$ ) 3566, 3467, 3060, 3027, 2967, 2935, 2878, 1600, 1494, 1452, 1346, 1261, 1120, 1073, 1030, 971, 744, 695. HRMS (ESI): (MNa)<sup>+</sup> calcd. for  $C_{18}H_{20}ONa$ : 275.1412, found. 275.1409.  $C_{18}H_{20}O$  (252.35): calc. C 85.67, H 7.99; meas. C 85.73, H 8.06.

### 3-Hydroxy-1,3,4-triphenylbutan-1-one

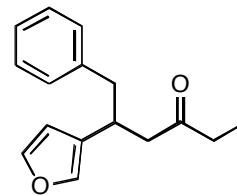


Preparation from 5-benzyl-2,2-dimethyl-3,5-diphenyl-2,5-dihydro-1,2-oxasilole (*Tamao-Fleming oxidation*): In a flame dried 10 ml Schlenk flask, a solution of 5-benzyl-2,2-dimethyl-3,5-diphenyl-2,5-dihydro-1,2-oxasilole (60 mg, 168  $\mu$ mol, 1.0 eq.) in 0.8 ml DMF was treated at room temperature and in this order with powdered activated molecular sieves 4Å (90 mg),  $\text{KHCO}_3$  (126 mg, 1.26 mmol, 7.5 eq.), dry *m*CPBA (340 mg, 1.68 mmol, 10 eq.) and  $\text{KHF}_2$  (152 mg, 1.68 mmol, 10 eq.). The reaction mixture was stirred at rt for 36 h and at 60° C for 10 h, then cooled to rt, diluted with a mixture of hexane:AcOEt=1:1, filtered through a filter paper, and extracted with water (in order to remove DMF). The organic phases were dried over  $\text{MgSO}_4$ , filtered and condensed to dryness. Column chromatography (petrol ether : diethyl ether = 5 : 1) gave the product as a colorless solid. Yield: 34 mg (108  $\mu$ mol, 64%).

Independent preparation from 1,3-diphenyl-1,3-propanedione (*Grignard addition*): In a flame dried 1000 ml round bottom flask, a suspension of Mg(s, powder) (4.88 g, 199 mmol, 10 eq.) in 200 ml diethyl ether was treated with a crystal of iodine at 35° C. Subsequently, a solution of benzyl bromide (2.36 ml, 3.40 g, 19.9 mmol, 1.00 eq.) was added during 2 h, then the reaction mixture was stirred at constant temperature for 2 h 30 min. After cooling to rt, the mixture was filtered under exclusion of air (in order to remove excess Mg(s)), cooled to 0° C. Then, a solution of 1,3-diphenyl-1,3-propanedione (1.47 g, 6.57 mmol, 0.33 eq.) in 10 ml diethyl ether was added during 1 h, the reaction mixture was warmed to rt and stirred during 20 h. The reaction was quenched by addition of phosphate buffer (pH = 7), the organic phase was dried over  $\text{MgSO}_4$ , filtered and condensed to dryness. The crude material was washed with a mixture of petrol ether : diethyl ether = 20 : 1 thus giving the pure product as a white solid. Yield (compared to 1,3-diphenyl-1,3-propanedione): 849 mg (2.68 mmol, 41%); this yield could be improved by crystallization of the remaining crude material.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 3.11 (d,  $J$  = 13.6 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 3.18 (d,  $J$  = 13.6 Hz, 1 H,  $\text{CH}_2\text{Ph}$ ), 3.25 (d,  $J$  = 17.2 Hz, 1 H,  $\text{PhC(O)CH}_2$ ), 3.94 (d,  $J$  = 17.2 Hz, 1 H,  $\text{PhC(O)CH}_2$ ), 4.93 (s, 1 H, OH), 7.04-7.06 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ), 7.20-7.29 (m, 6 H, 6  $\text{CH}_{\text{phenyl}}$ ), 7.35-7.38 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ), 7.42-7.46 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ), 7.55-7.59 (m, 1 H, 1  $\text{CH}_{\text{phenyl}}$ ), 7.85-7.87 (m, 2 H, 2  $\text{CH}_{\text{phenyl}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 46.2 ( $\text{CH}_2$ ), 50.5 ( $\text{CH}_2$ ), 76.4 ( $\text{C}_{\text{quat}}$ ), 125.4, 126.8, 127.0, 128.1, 128.3, 128.3, 128.9, 131.1, 133.9, 136.9, 137.3, 146.3, 201.7 (C=O). IR (neat):  $\nu$  ( $\text{cm}^{-1}$ ) 3476, 3060, 3027, 2919, 1670, 1596, 1578, 1560, 1542, 1495, 1448, 1404, 1375, 1348, 1214, 1181, 1159, 1096, 1076, 1060, 1021, 1002, 915, 772, 750, 700, 689, 669. mp = 118.0° C.  $\text{C}_{22}\text{H}_{20}\text{O}_2$  (316.39): calc. C 83.51, H 6.37; meas. C 83.35, H 6.20. This substance is

literature known (CAS 13272-52-1), but has so far not been characterized by modern standards: see Cannone, P.; Bilodeau *Can. J. Chem.* 1966, 44, 2849-2854.

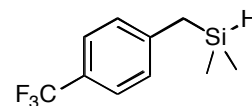
#### 5-(Furan-3-yl)-6-phenylhexan-3-one



In a flame dried 20 ml Schlenk flask, a solution of benzyldimethylsilyl-1-(3-furanyl)pent-1-en-3-one (17.6 mg, 59.0  $\mu\text{mol}$ , 1.00 eq.) in 0.5 ml DMF was treated with TBAF (1.0 M in THF, 131  $\mu\text{l}$ , 131  $\mu\text{mol}$ , 2.20 eq.) at 0° C. After 10 min, H<sub>2</sub>O<sub>2</sub> (30% in H<sub>2</sub>O ; 110  $\mu\text{l}$ ) was added upon which the clear yellow solution turned colorless immediately. The solution was stirred at 80° C for 14h, then cooled to rt, mixed with water and extracted with diethyl ether. The organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated *in vacuo* (RV), and chromatographed (petrol ether : diethyl ether = 10 : 1). Yield : 12 mg (46  $\mu\text{mol}$ , 78%) of a colorless oil. Note : protodesilylation rather than *Tamao-Fleming* oxidation was observed. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 0.99 (t,  $J$  = 7.5 Hz, 3 H, CH<sub>3</sub>), 2.27-2.38 (m, CH<sub>2</sub>CH<sub>3</sub>), 2.60-2.68 (m, 2 H, CH<sub>2</sub>Ph or CH<sub>2</sub>C(O)CH<sub>2</sub>CH<sub>3</sub>), 2.81-2.89 (m, 2 H, CH<sub>2</sub>Ph or CH<sub>2</sub>C(O)CH<sub>2</sub>CH<sub>3</sub>), 6.27 (s, 1 H, R<sub>3</sub>CH), 7.12 (d,  $J$  = 7.5 Hz, 2 H, 2 CH phenyl), 7.12-7.12 (m, 1 H, CH furyl), 7.20 (t,  $J$  = 7.5 Hz, 1 H, CH phenyl), 7.27 (t,  $J$  = 8.0 Hz, 2 H, 2 CH phenyl), 7.34-7.35 (m, 1 H, CH furyl). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  = 7.8 (CH<sub>3</sub>), 33.4, 36.9, 42.3, 47.8, 109.7, 126.5, 127.7, 128.5, 129.5, 139.2, 139.9, 143.1, 210.6 (C=O). IR (neat):  $\nu$  (cm<sup>-1</sup>) 3134, 3063, 3028, 2977, 2938, 1714 (C=O), 1604, 1498, 1455, 1412, 1362, 1159, 1112, 1061, 1026, 931, 874, 785, 750, 701. HRMS (EI): M<sup>+</sup> calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>: 242.13068, found. 242.13117.

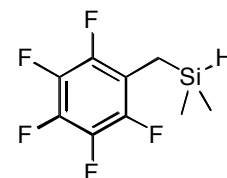
## E) SYNTHESSES OF BENZYL SILANES

### (4-Trifluoromethylbenzyl)dimethylsilane

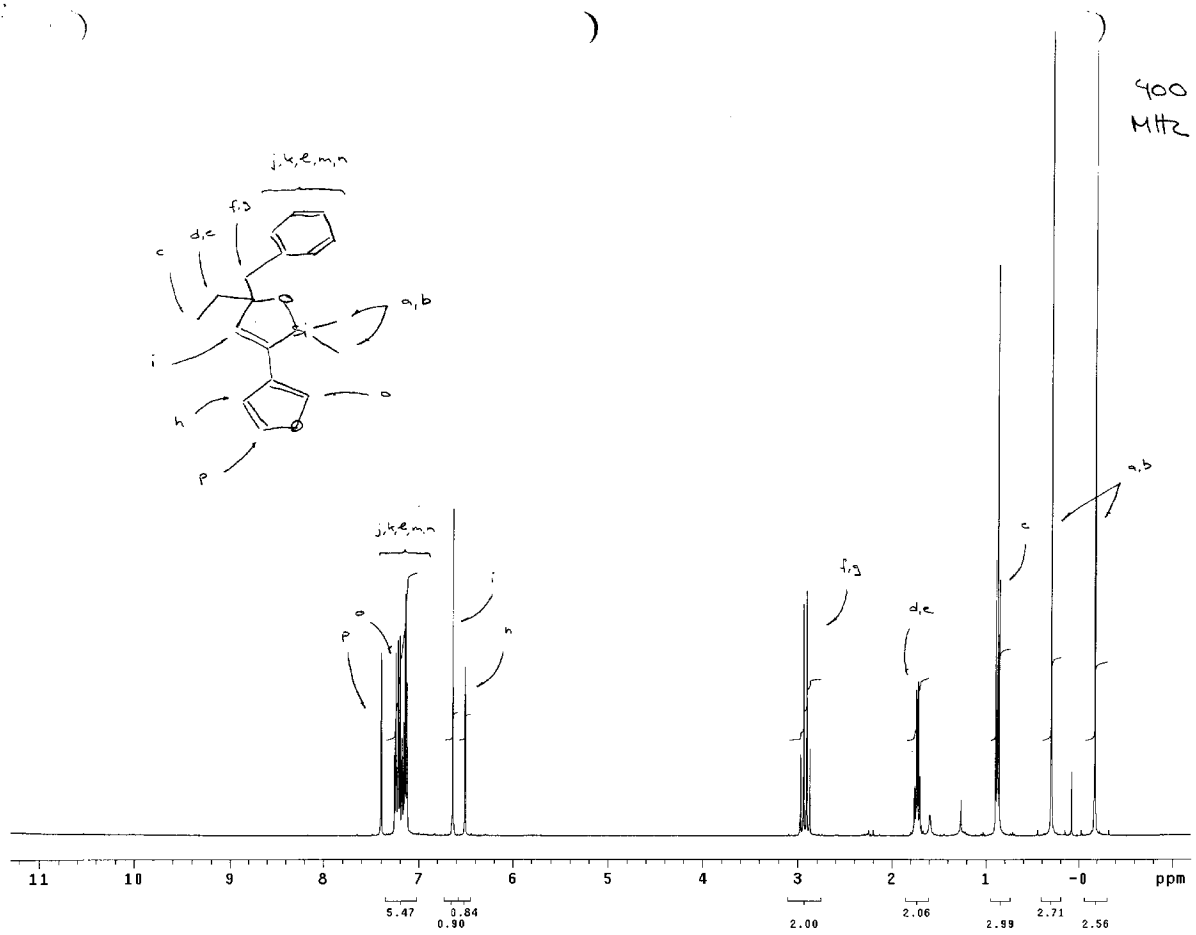


In a flame dried 1 l round bottom flask, Mg powder (2.44 g, 99.6 mmol, 10.0 eq.) was suspended in 100 ml diethyl ether. After the addition of dimethylchlorosilane (2.36 g, 24.9 mmol, 2.50 eq.) and iodine (approx. 10 mg), the reaction mixture was warmed to 35° C. A solution of 4-trifluoromethylbenzylbromide (2.38 g, 9.96 mmol, 1.00 eq.) in 2.0 ml diethyl ether was added during 2h 30min with the help of a syringe pump and the reaction mixture was stirred for 12h. The reaction mixture was filtered over celite, condensed to dryness (RV) and chromatographed (SiO<sub>2</sub>, petrol ether : diethyl ether = 50 : 1). Yield: 922 mg (4.22 mmol, 42%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 0.07-0.08 (m, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.22 (d, *J* = 3.6 Hz, 2 H, CH<sub>2</sub>), 3.81 (heptet, *J* = 3.6 Hz, 1 H, SiH), 7.12 (d, *J* = 8.4 Hz, 2 H, 2 CH phenyl), 7.47 7.12 (d, *J* = 8.4 Hz, 2 H, 2 CH phenyl). <sup>13</sup>C {<sup>1</sup>H, <sup>19</sup>F} NMR (CDCl<sub>3</sub>, 100 MHz): δ = -4.6 (SiCH<sub>3</sub>), 24.8 (SiCH<sub>2</sub>), 124.8, 125.5, 126.8, 128.4, 144.9. <sup>19</sup>F {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376.3 MHz): δ = -62.5. IR (neat): ν (cm<sup>-1</sup>) 2962, 2902, 2124 (Si-H), 1615, 1418, 1327, 1254, 1211, 1187, 1163, 1124, 1082, 1068, 1018, 886, 846, 629, 603.

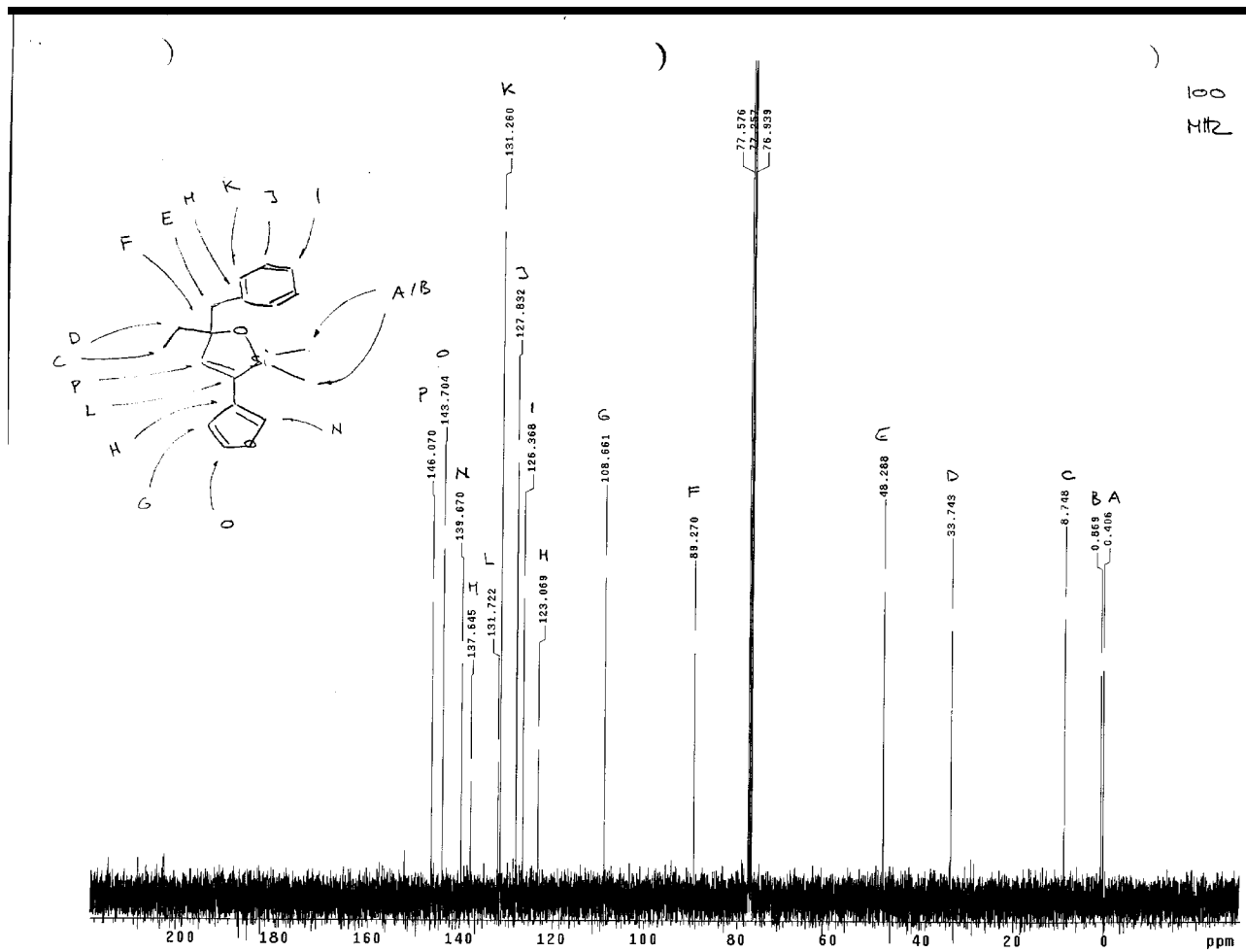
### (2,3,4,5,6-Pentafluorobenzyl)dimethylsilane



In a flame dried 1 l round bottom flask, Mg powder (2.44 g, 99.6 mmol, 10.0 eq.) was suspended in 100 ml diethyl ether. After the addition of dimethylchlorosilane (2.36 g, 24.9 mmol, 2.50 eq.) and iodine (approx. 10 mg), the reaction mixture was warmed to 35° C. A solution of 2,3,4,5,6-pentafluorobenzylbromide (2.60 g, 9.96 mmol, 1.00 eq.) in 5.0 ml diethyl ether was added during 2h with the help of a syringe pump and the reaction mixture was stirred for further 15 min. The reaction mixture was filtered over celite, condensed to dryness (RV) and chromatographed (SiO<sub>2</sub>, petrol ether : diethyl ether = 50 : 1). Yield: 1.33 g (5.53 mmol, 56%) of a colorless oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 0.12-0.14 (m, 6 H, Si(CH<sub>3</sub>)<sub>2</sub>), 2.15-2.17 (m, 2 H, CH<sub>2</sub>), 3.81 (nonaplet, *J* = 2.0 Hz, 1 H, SiH). <sup>19</sup>F {<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 376.3 MHz): δ = -144.0 (dd, *J*<sub>1</sub> = 22.2 Hz, *J*<sub>2</sub> = 7.5 Hz), -161.2 (t, *J* = 20.7 Hz), -164.8 to -164.9 (m). Known substance: CAS 58751-80-7. See: Winecoff, W.F. *et al. J. Org. Chem.* 1973, 38, 2544-2545.

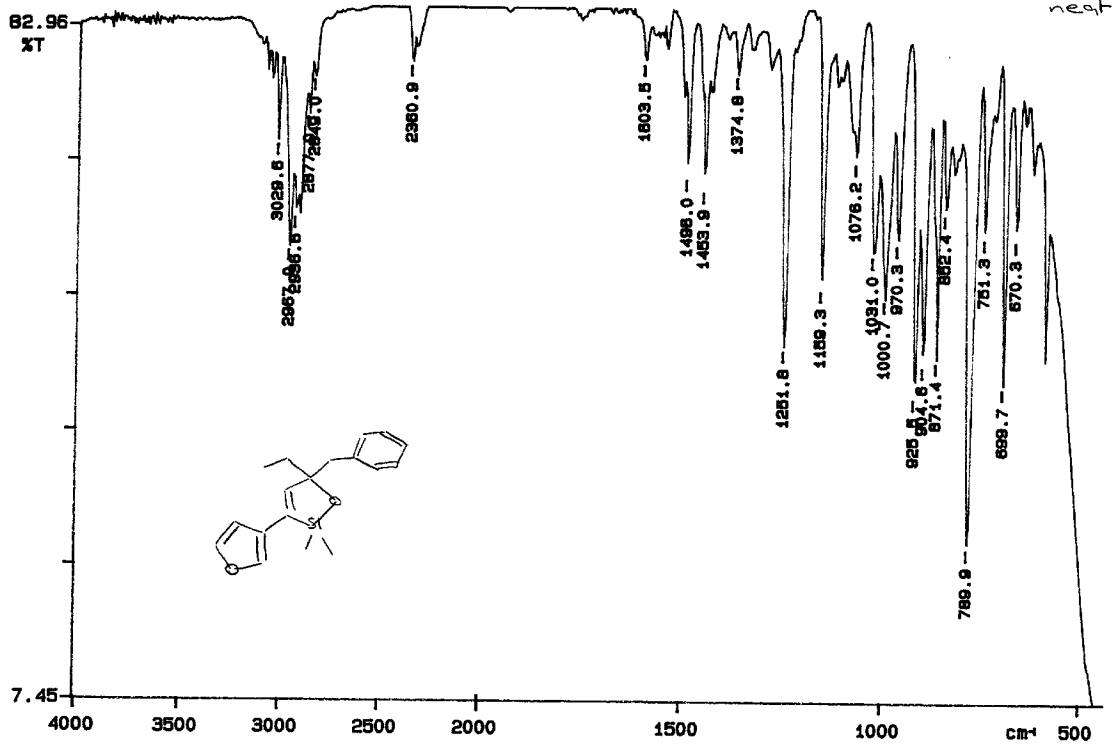


ab07



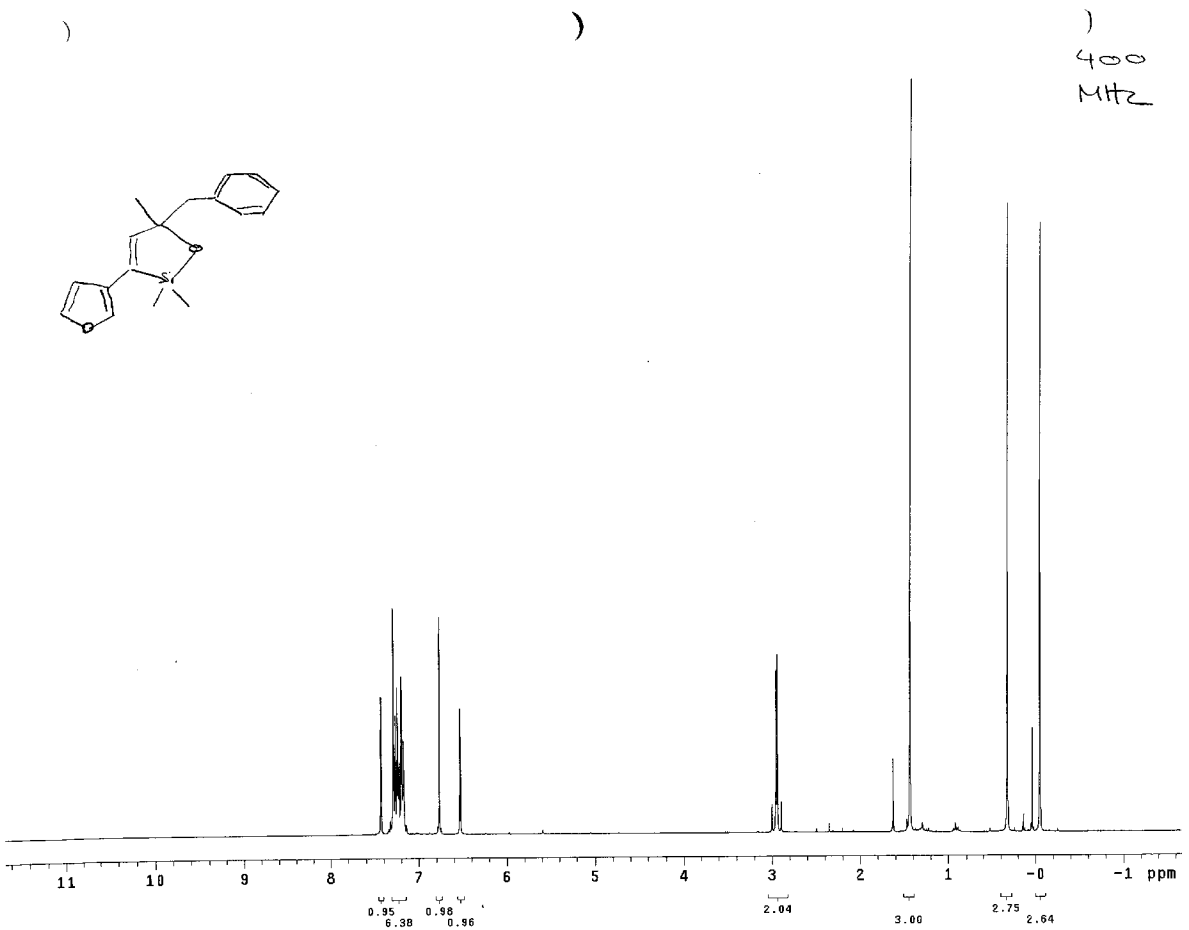
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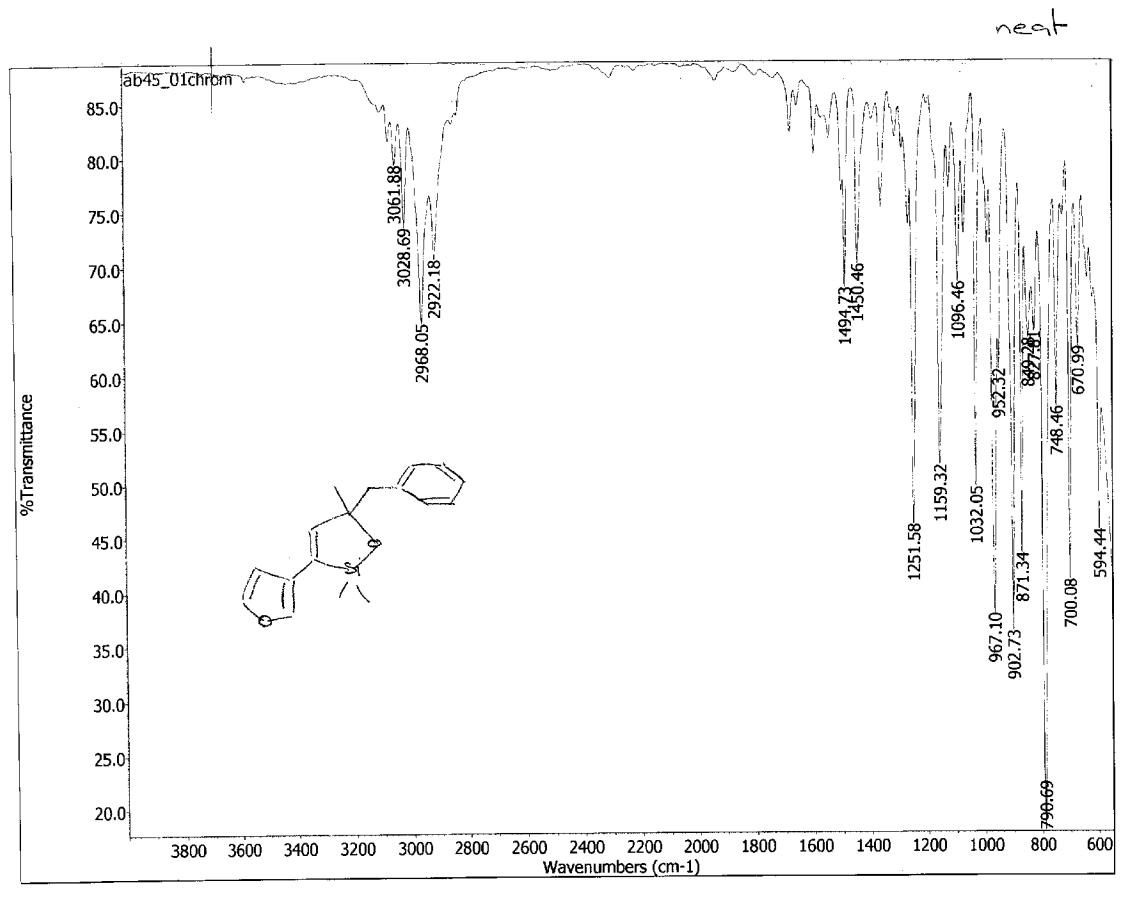
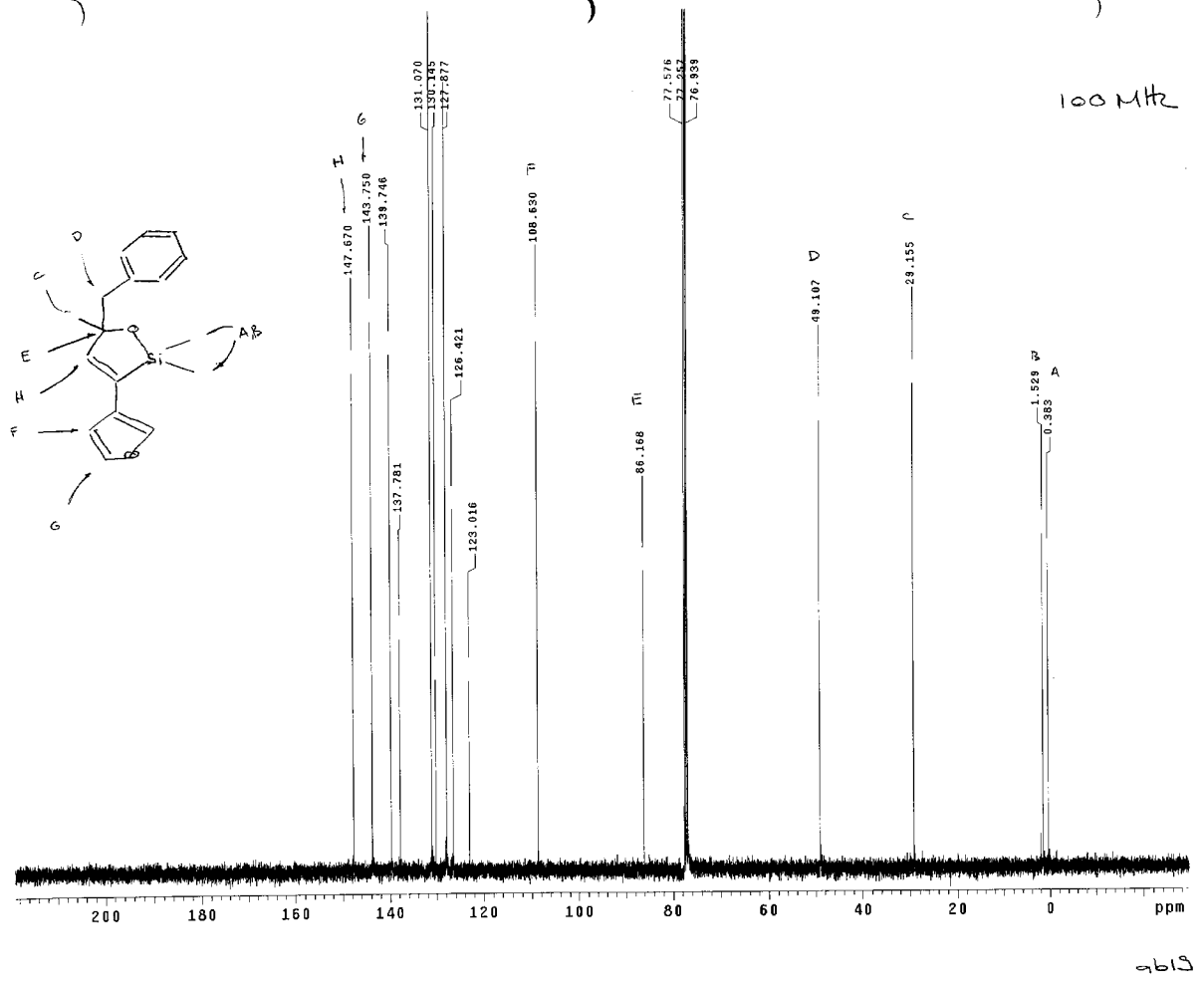


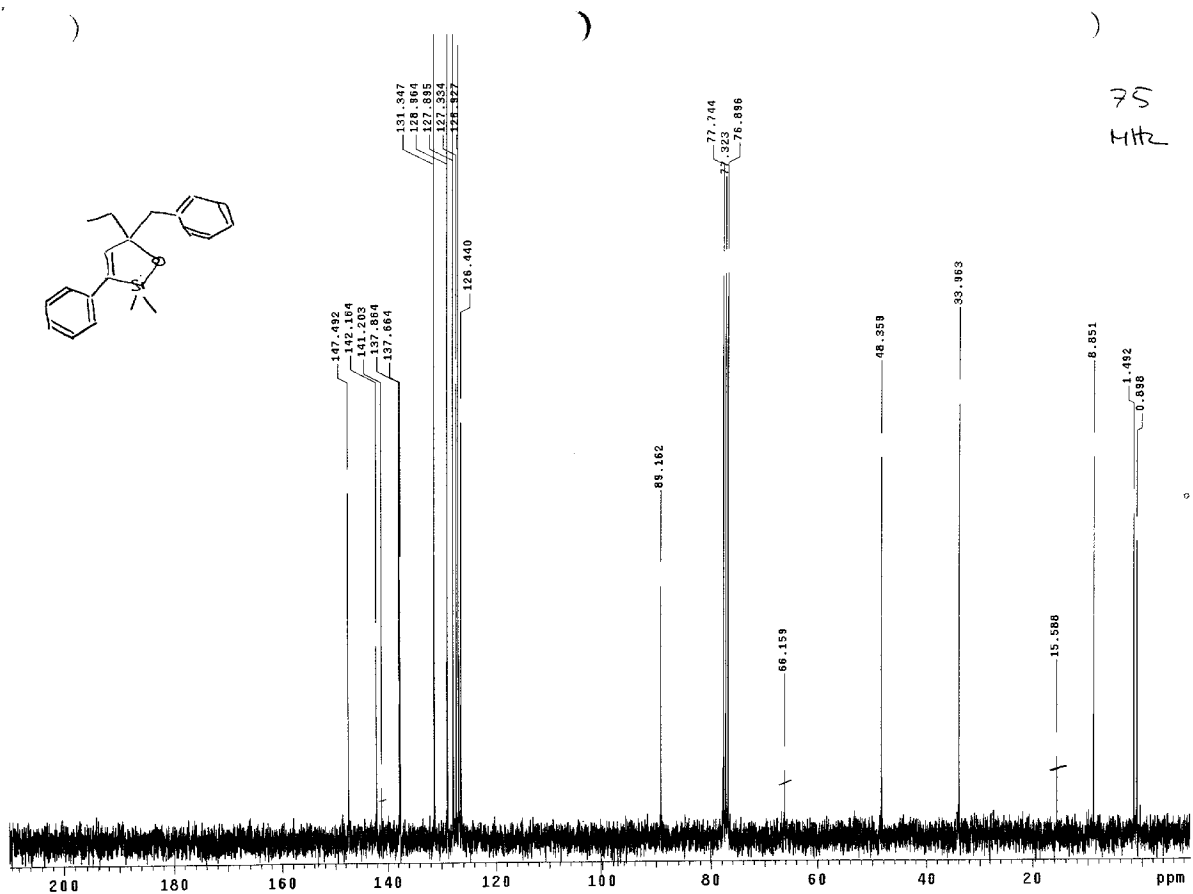
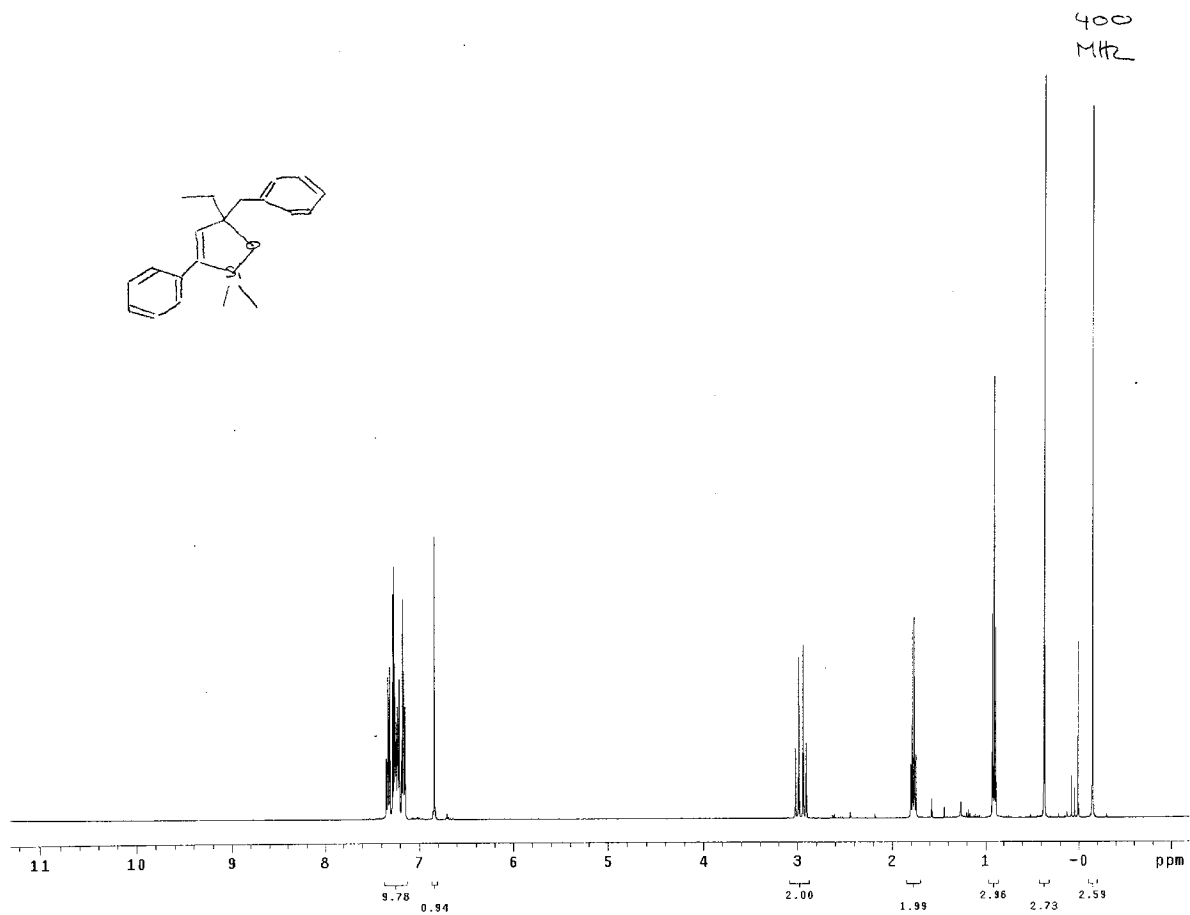
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ab07



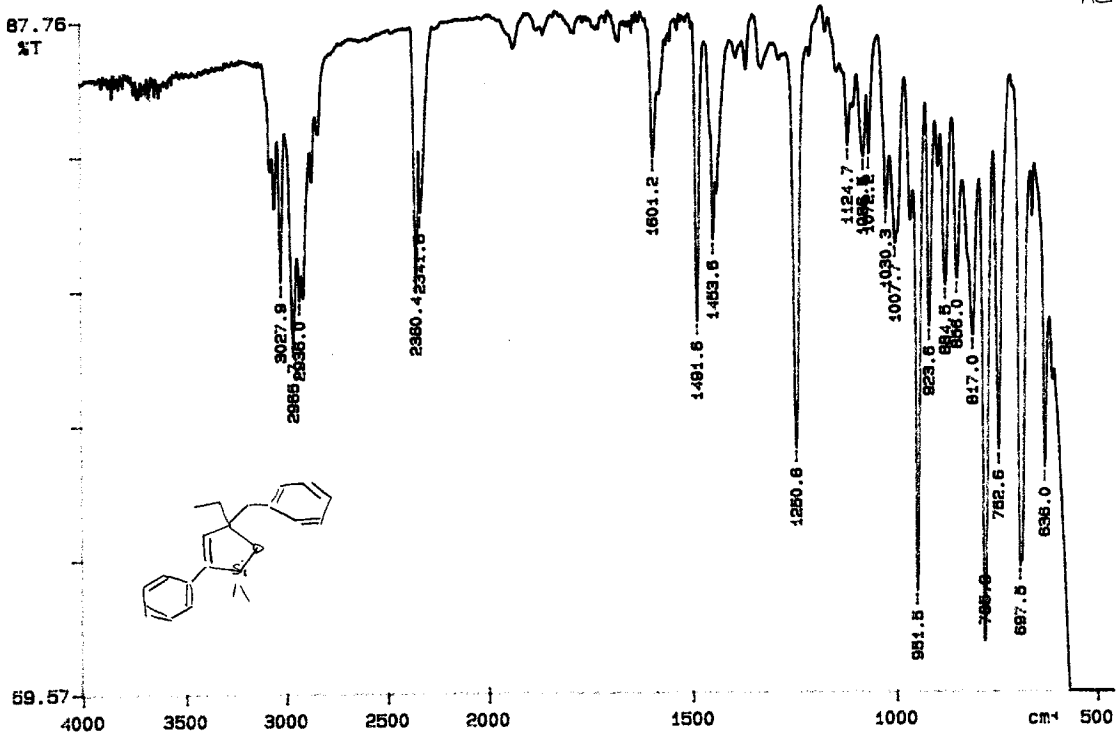
ab13





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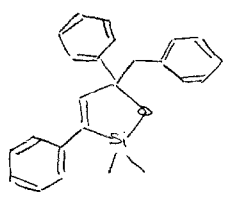
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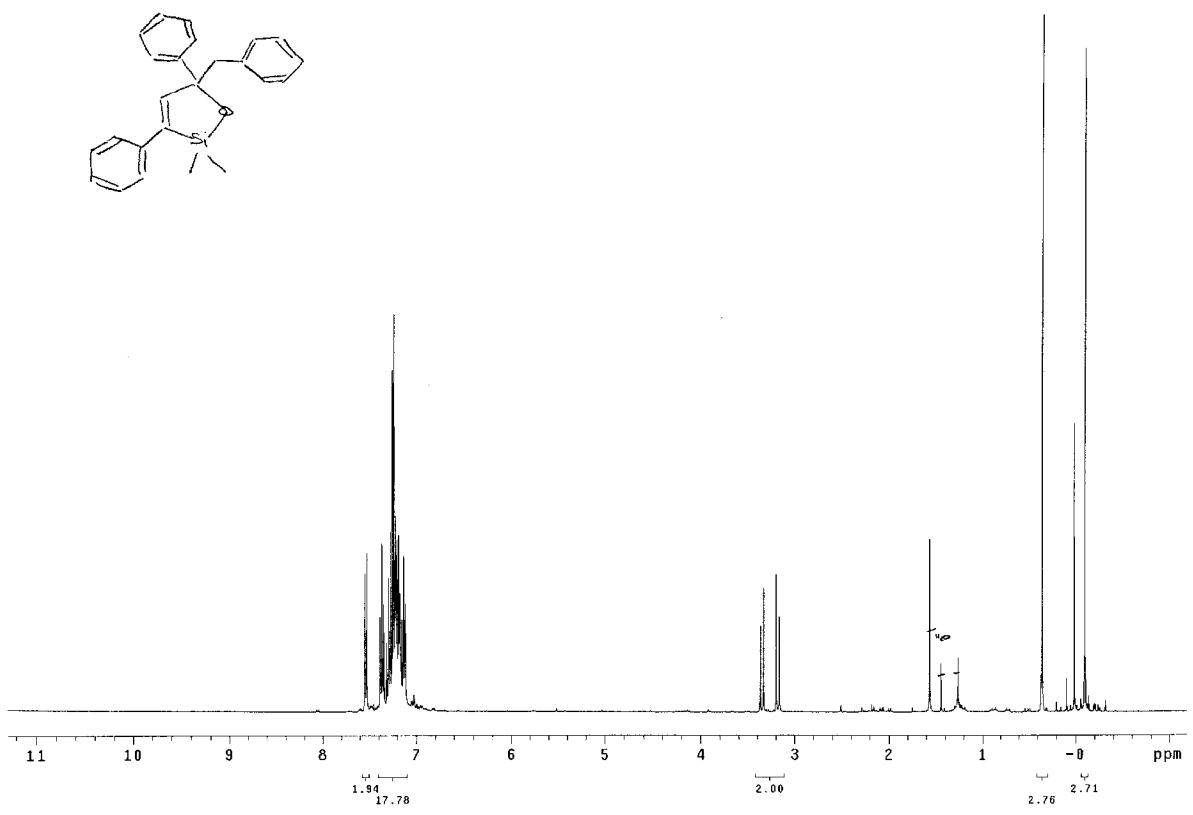
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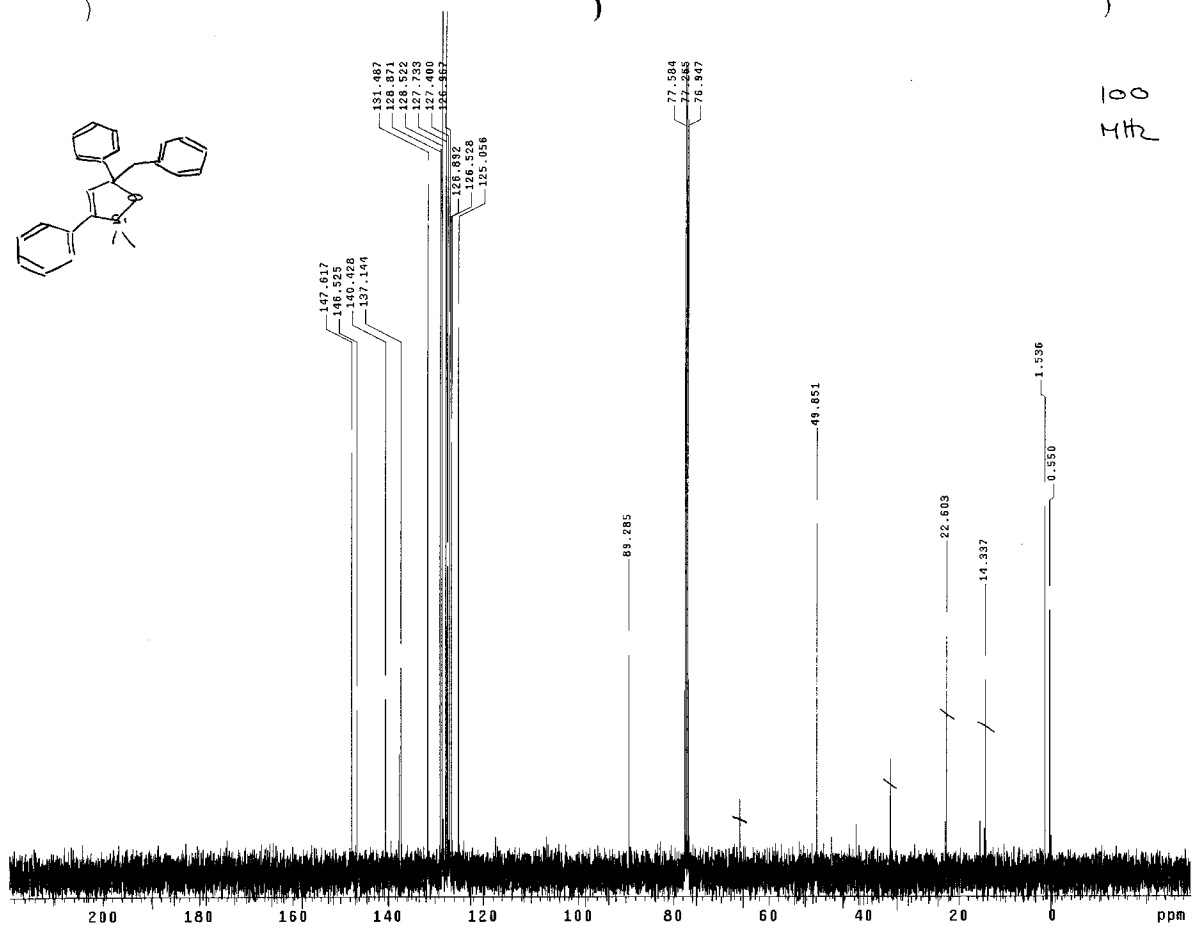
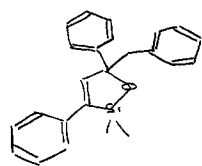
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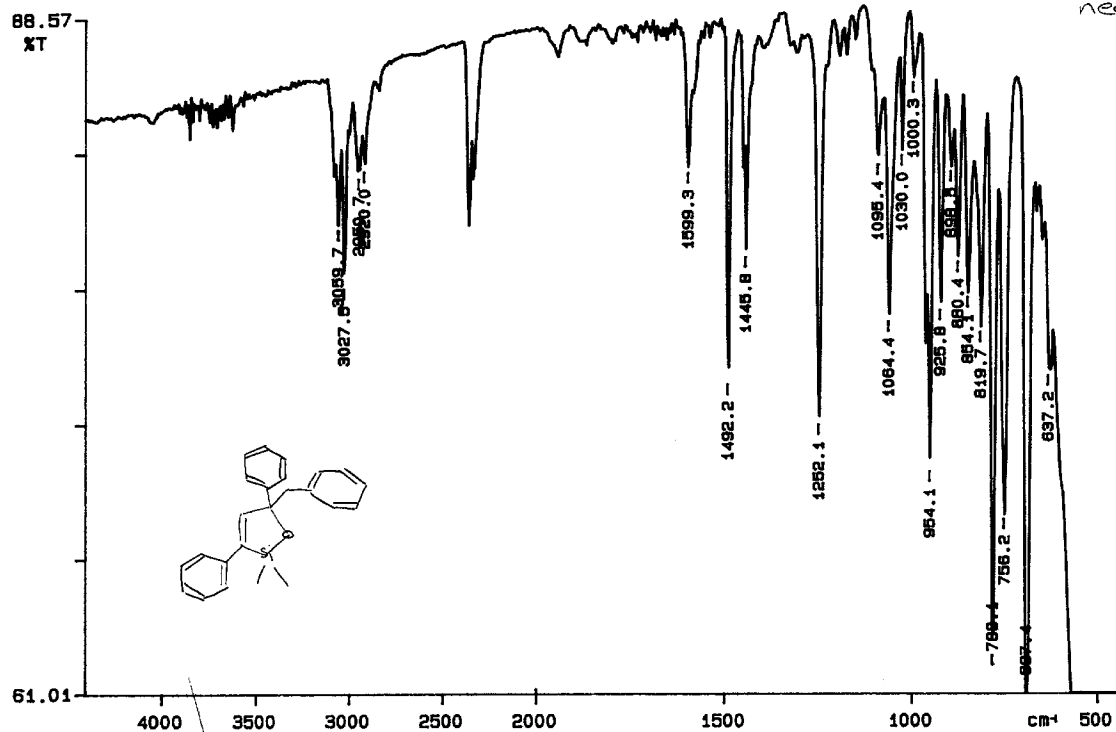
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MHz



9661

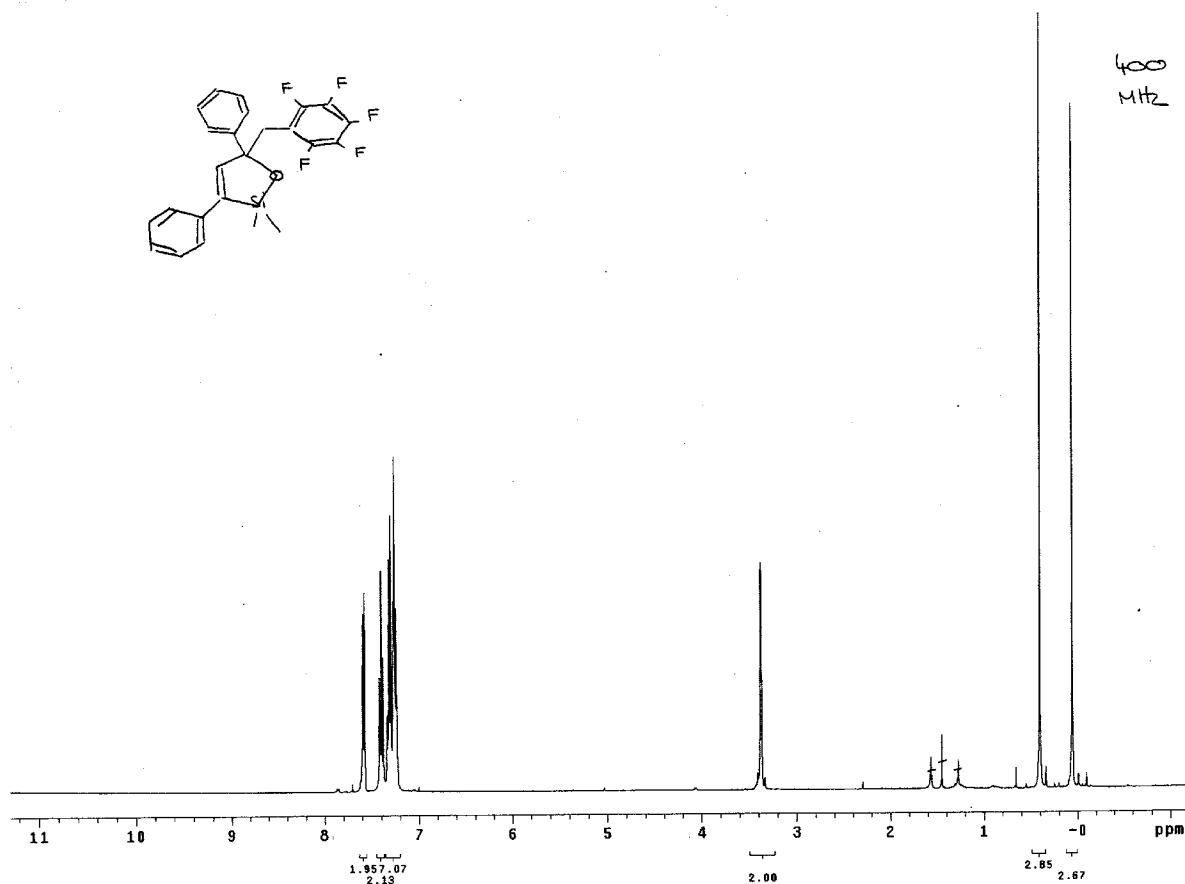
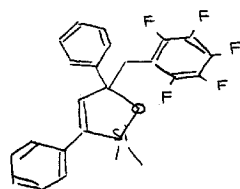


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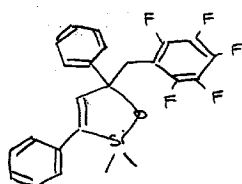


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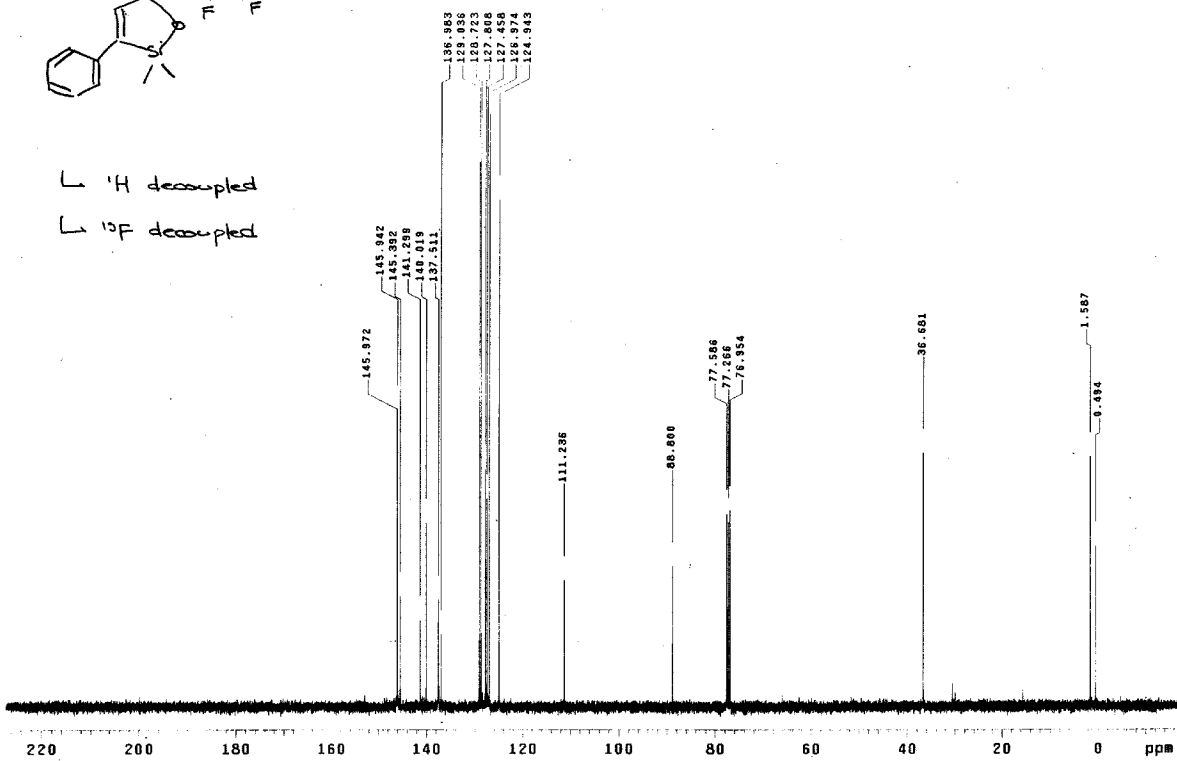
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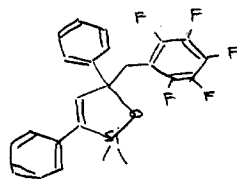
ab151



↳ <sup>1</sup>H decoupled  
↳ <sup>19</sup>F decoupled

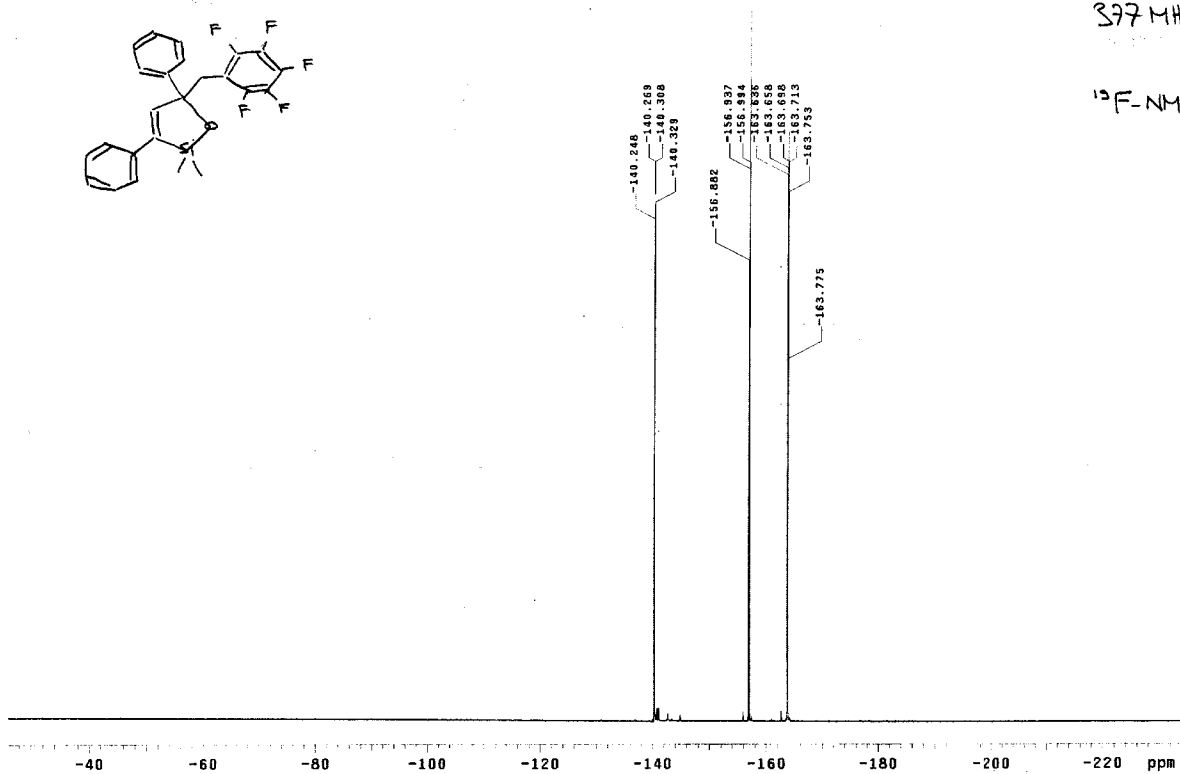


ab151

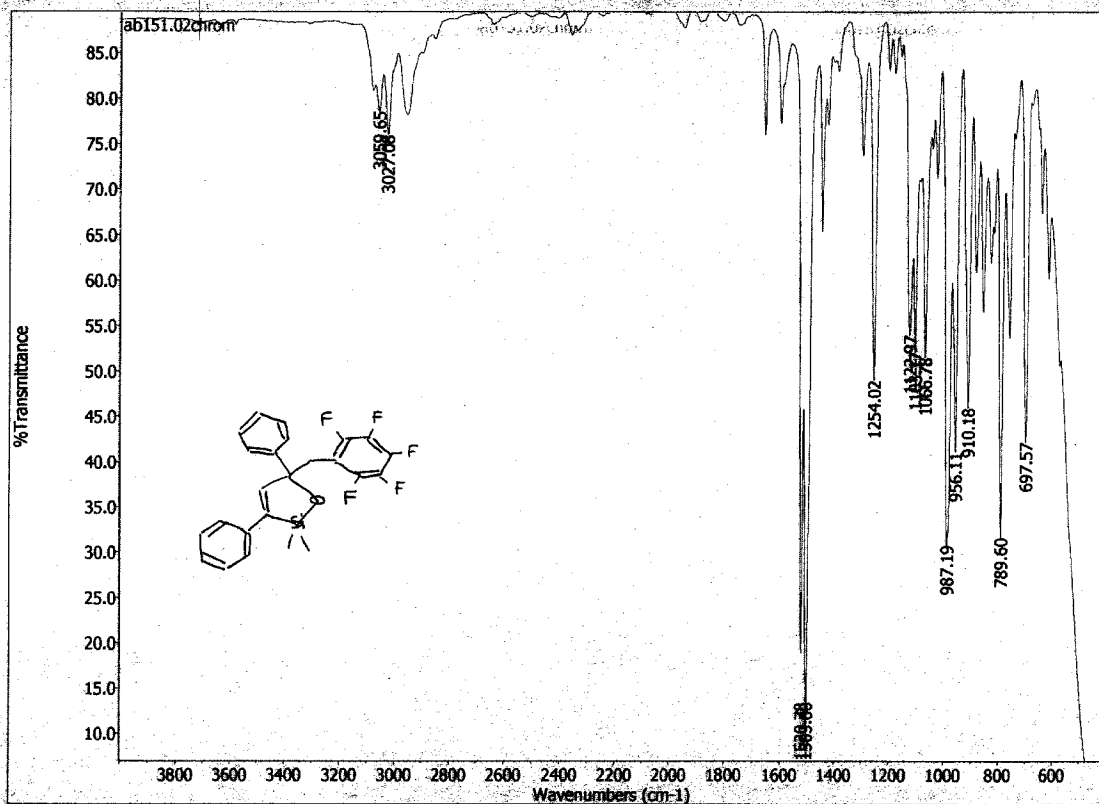


397 MHz

<sup>19</sup>F-NMR

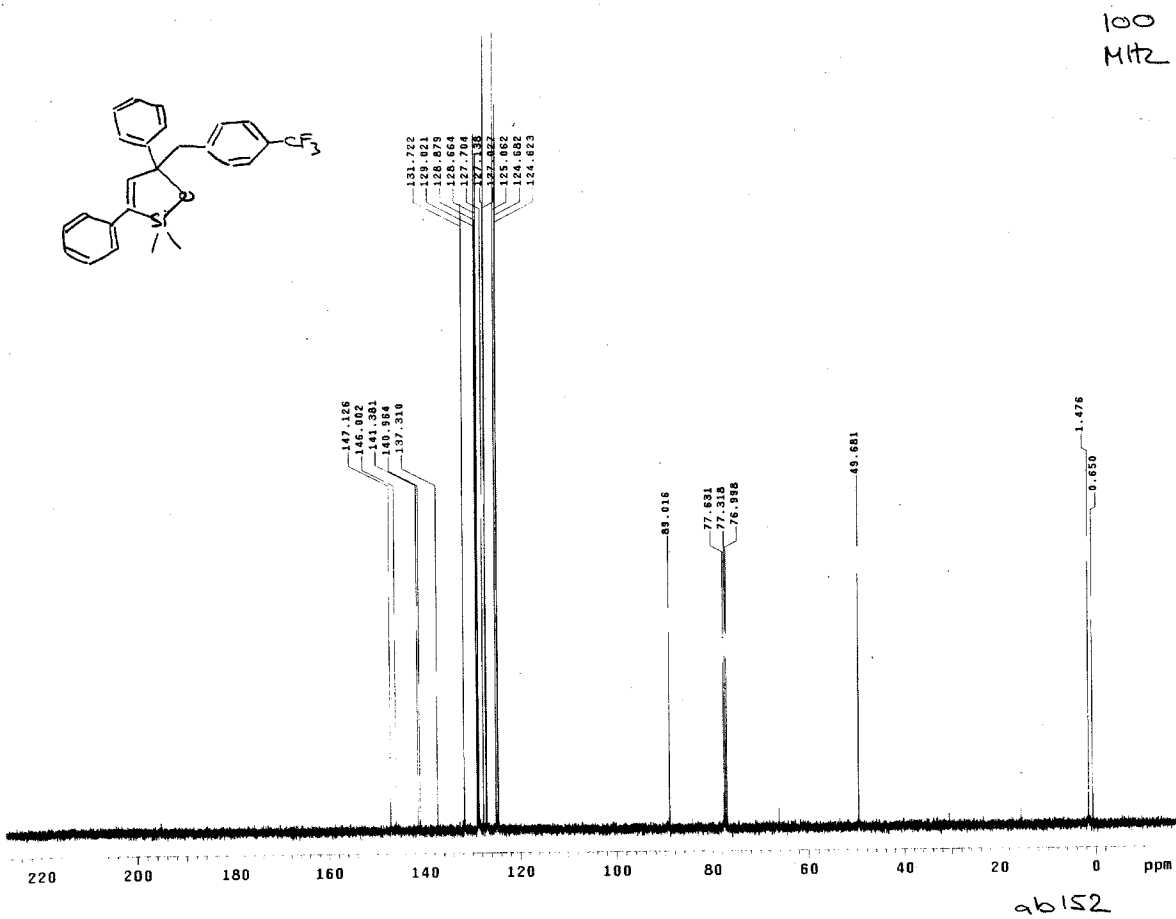
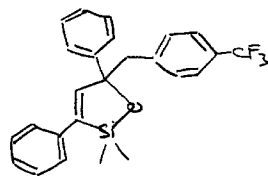
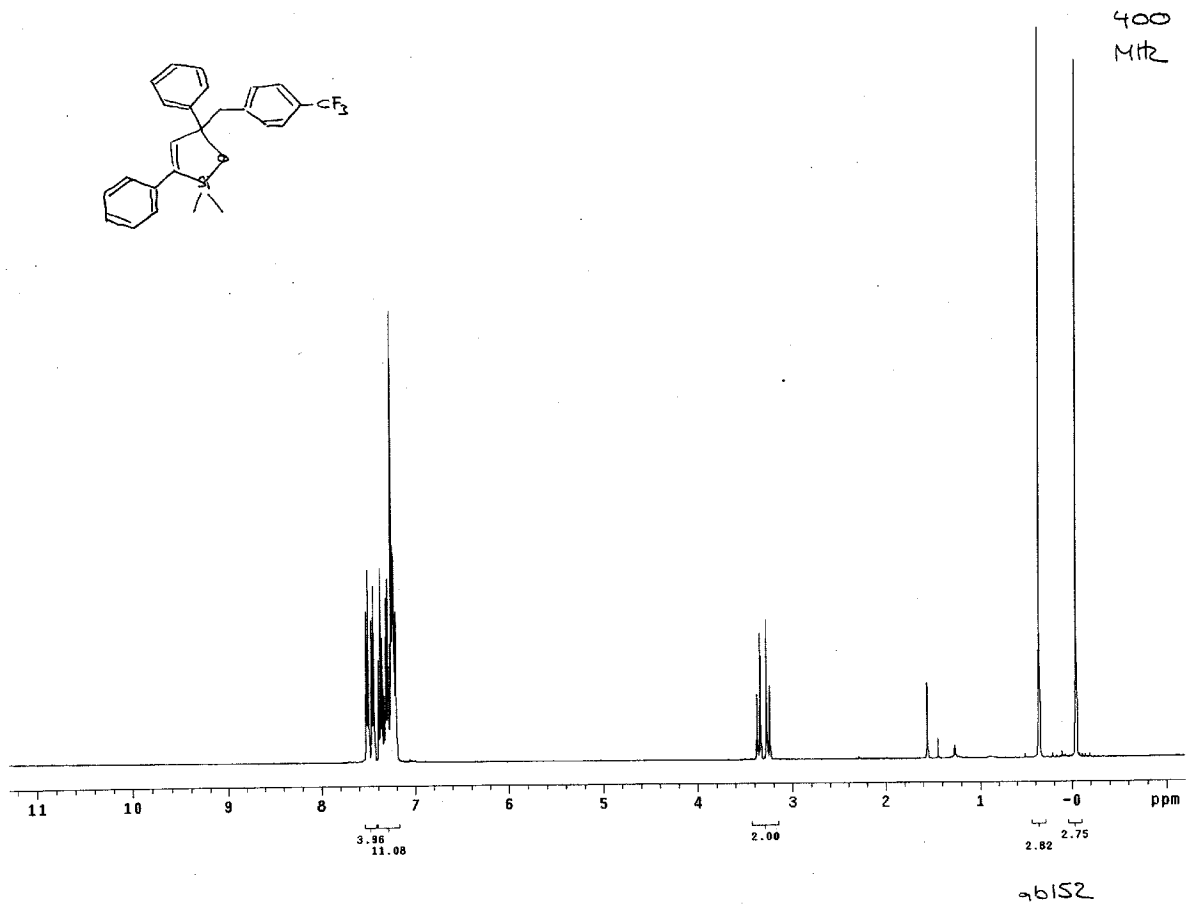
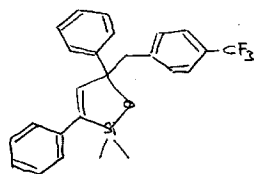


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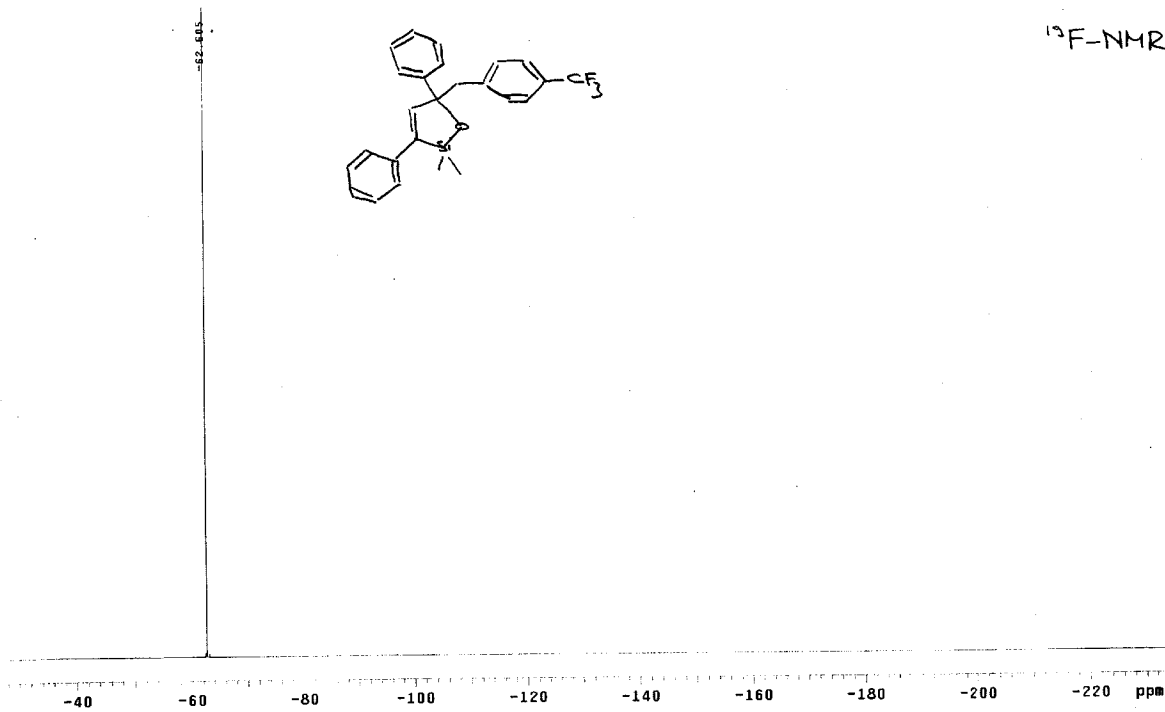
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ab151

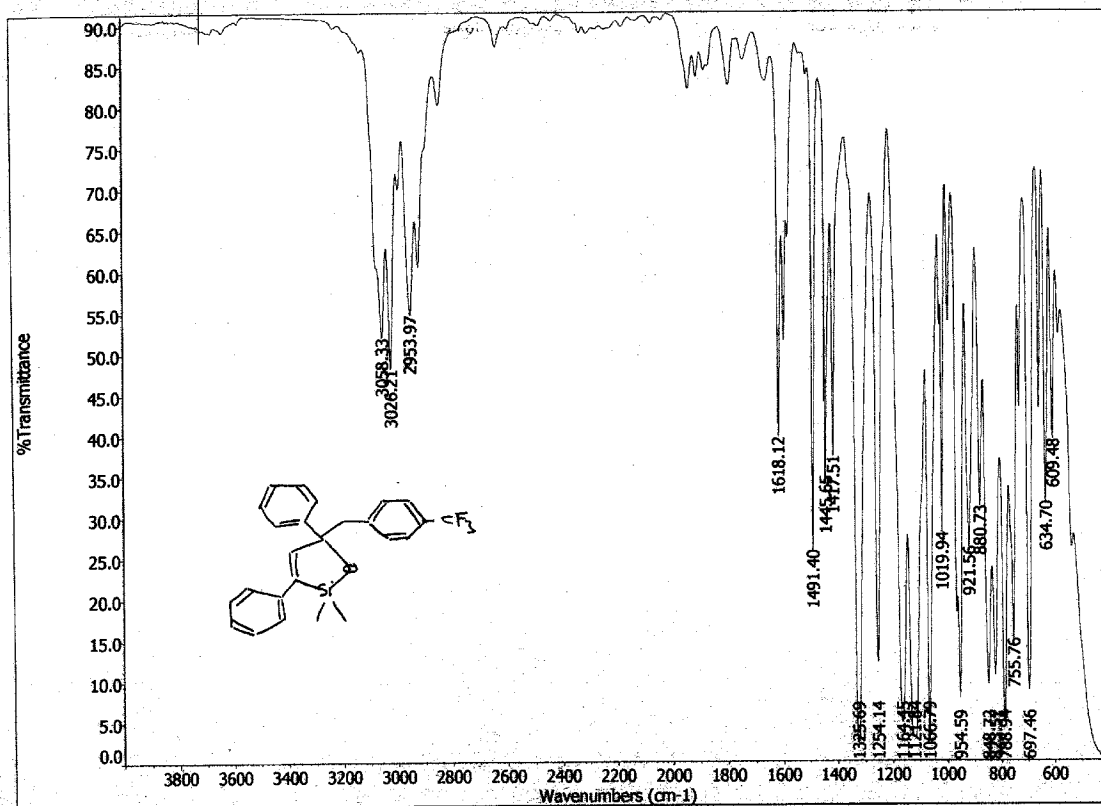


377  
MHz

<sup>13</sup>F-NMR

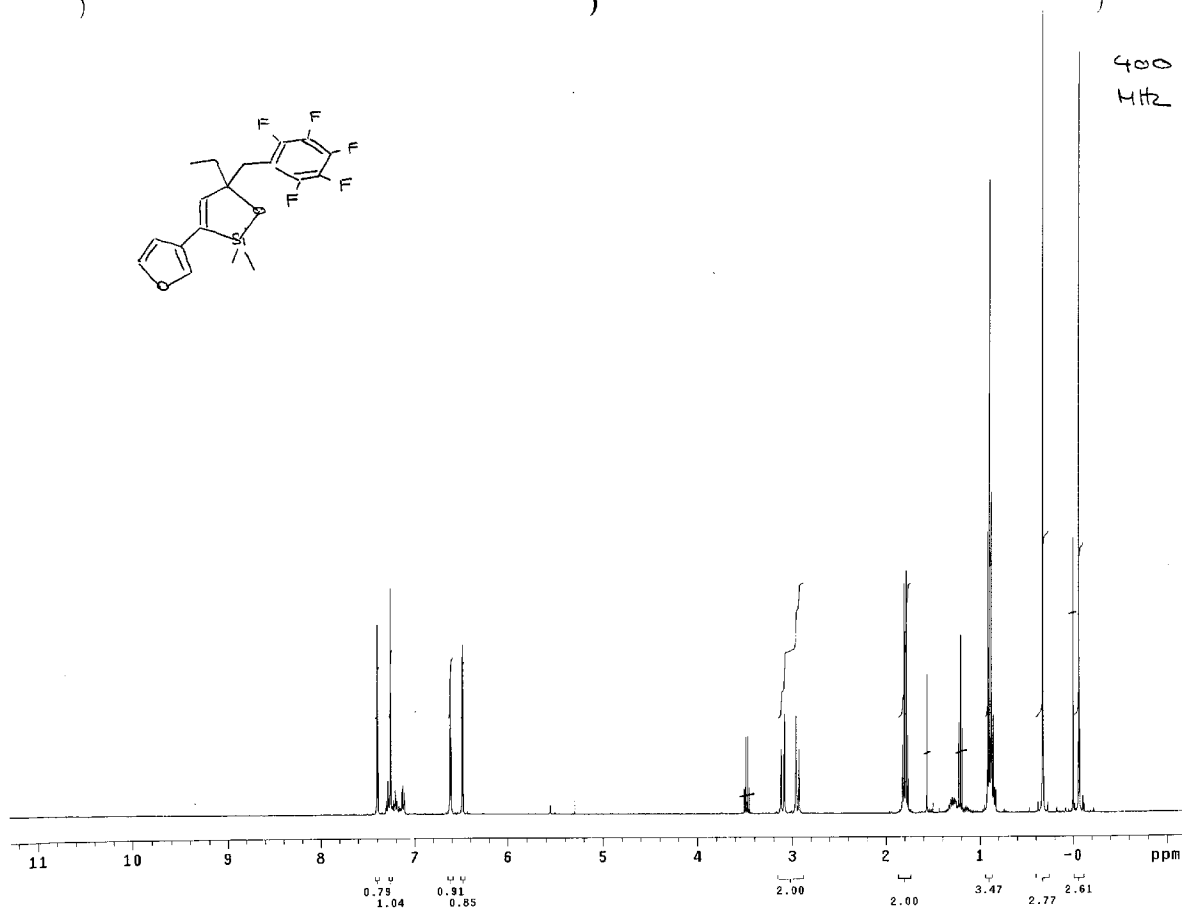
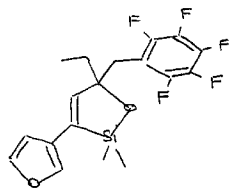


ab 152



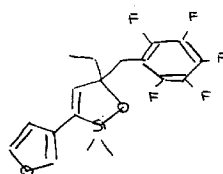
neat

ab 152

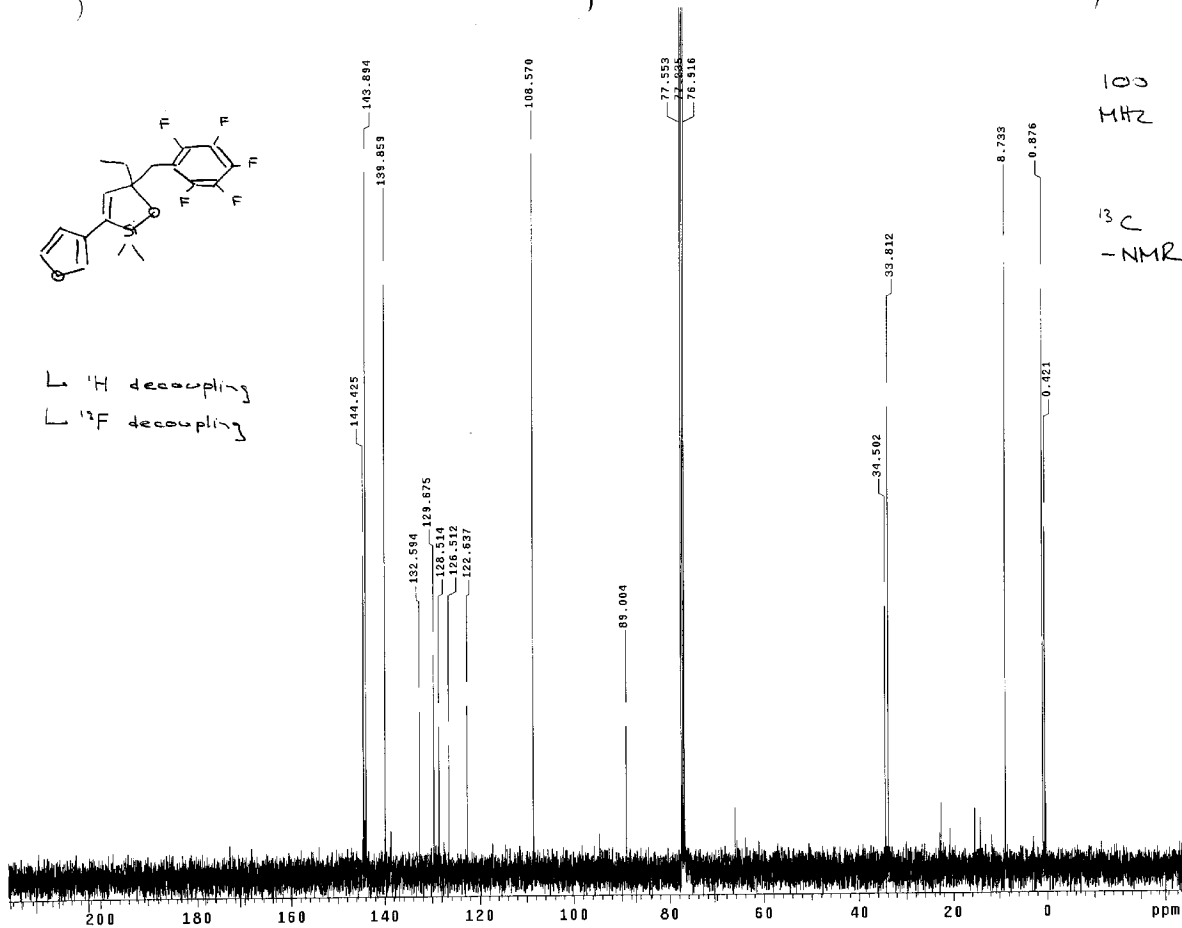


400  
MHz

ab121



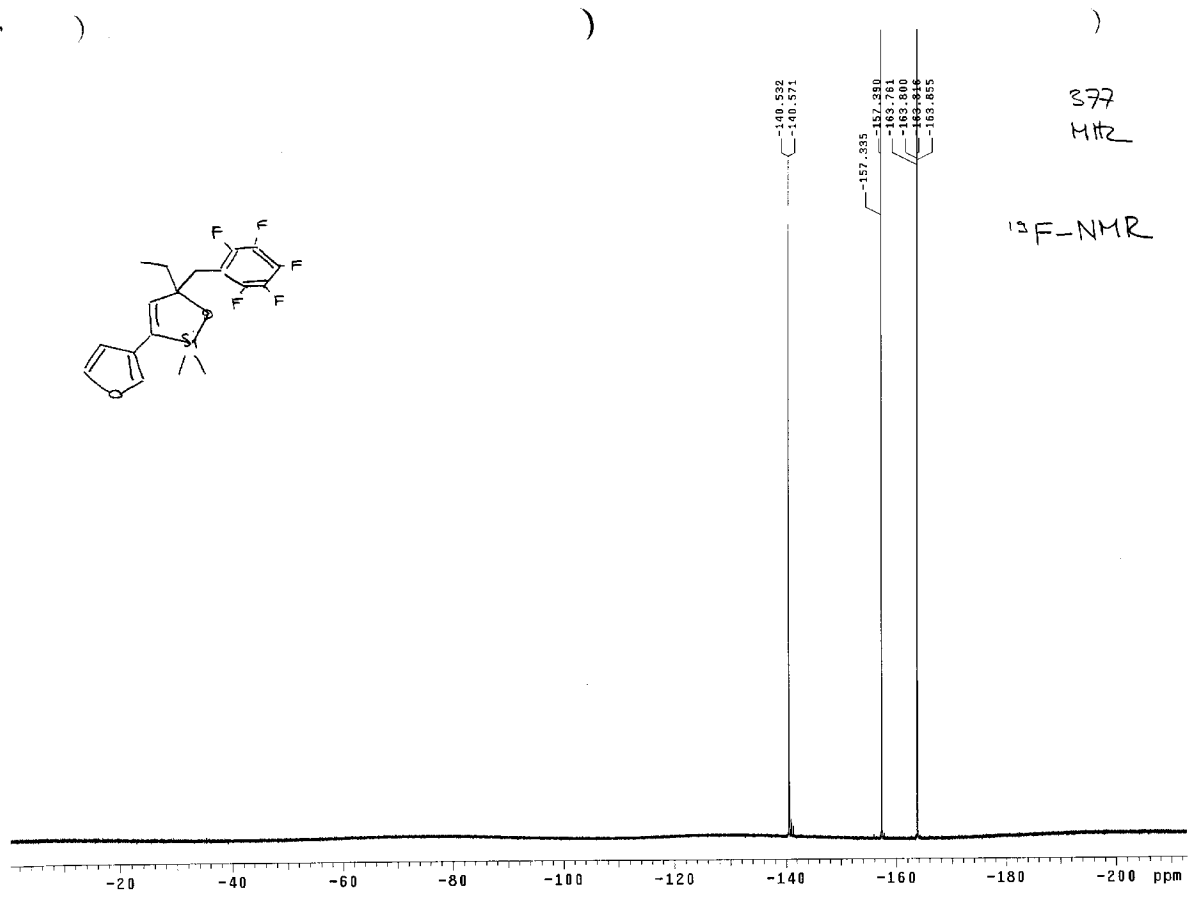
L <sup>1</sup>H decoupling  
L <sup>13</sup>F decoupling



100  
MHz

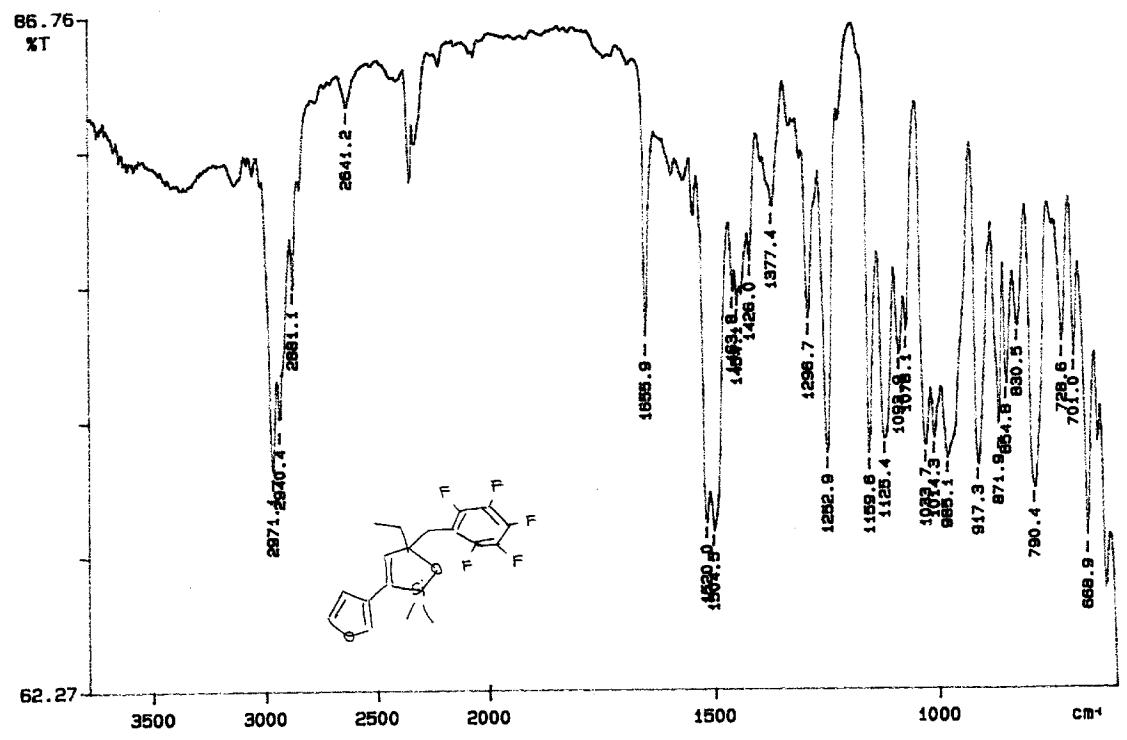
<sup>13</sup>C  
-NMR

ab121



ab121

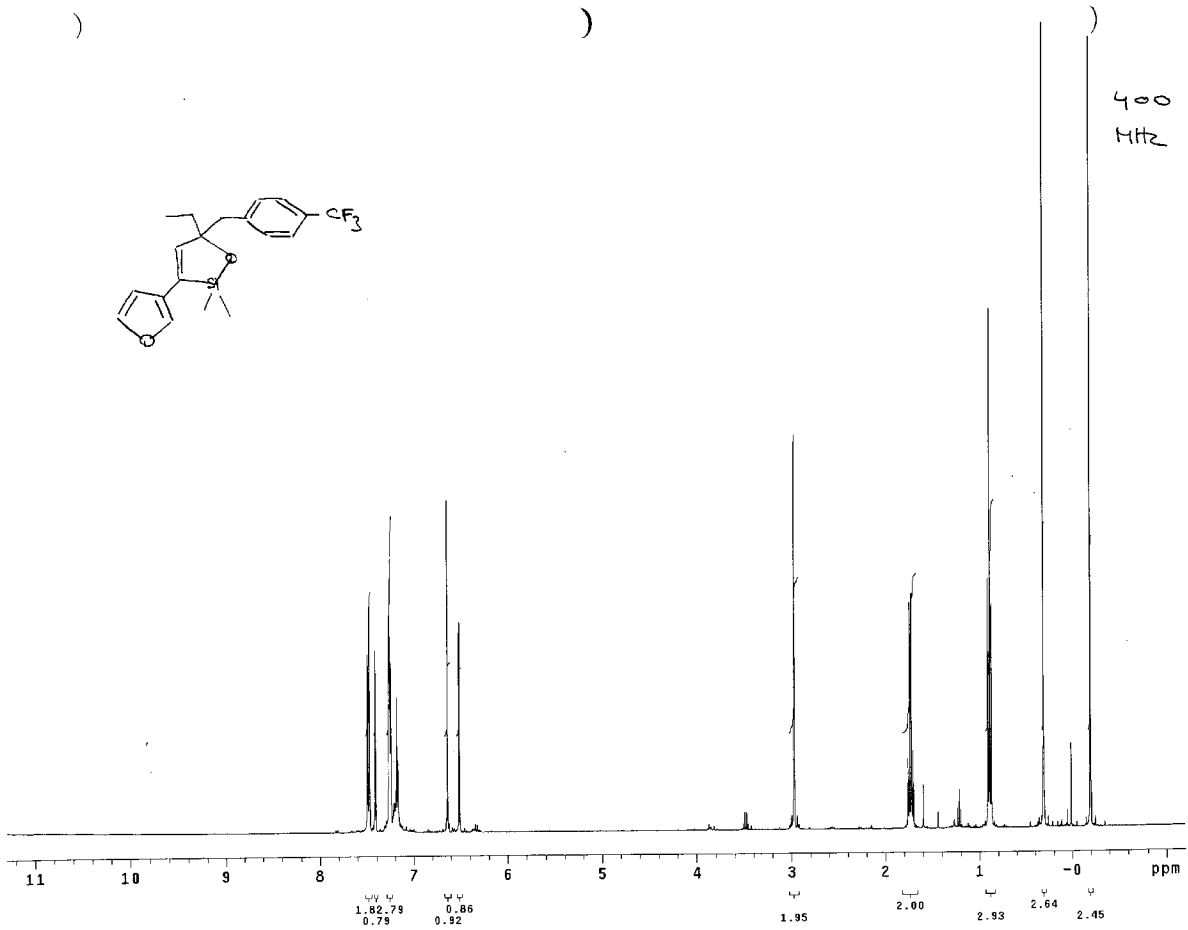
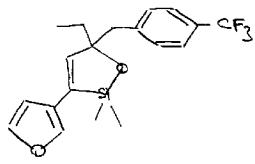
PERKIN ELMER



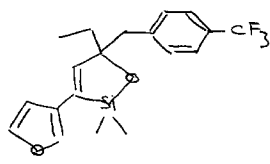
neat

07/06/09 15:49  
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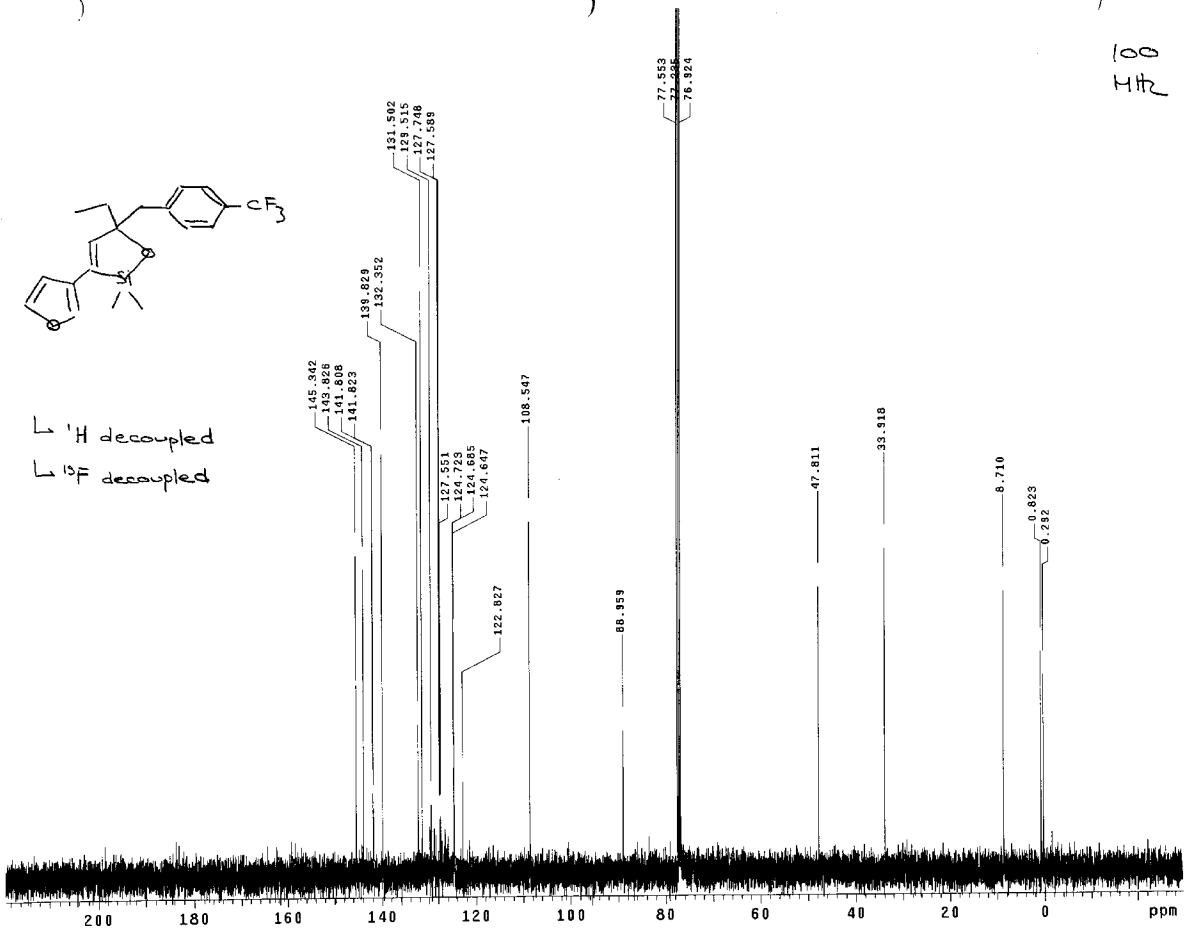
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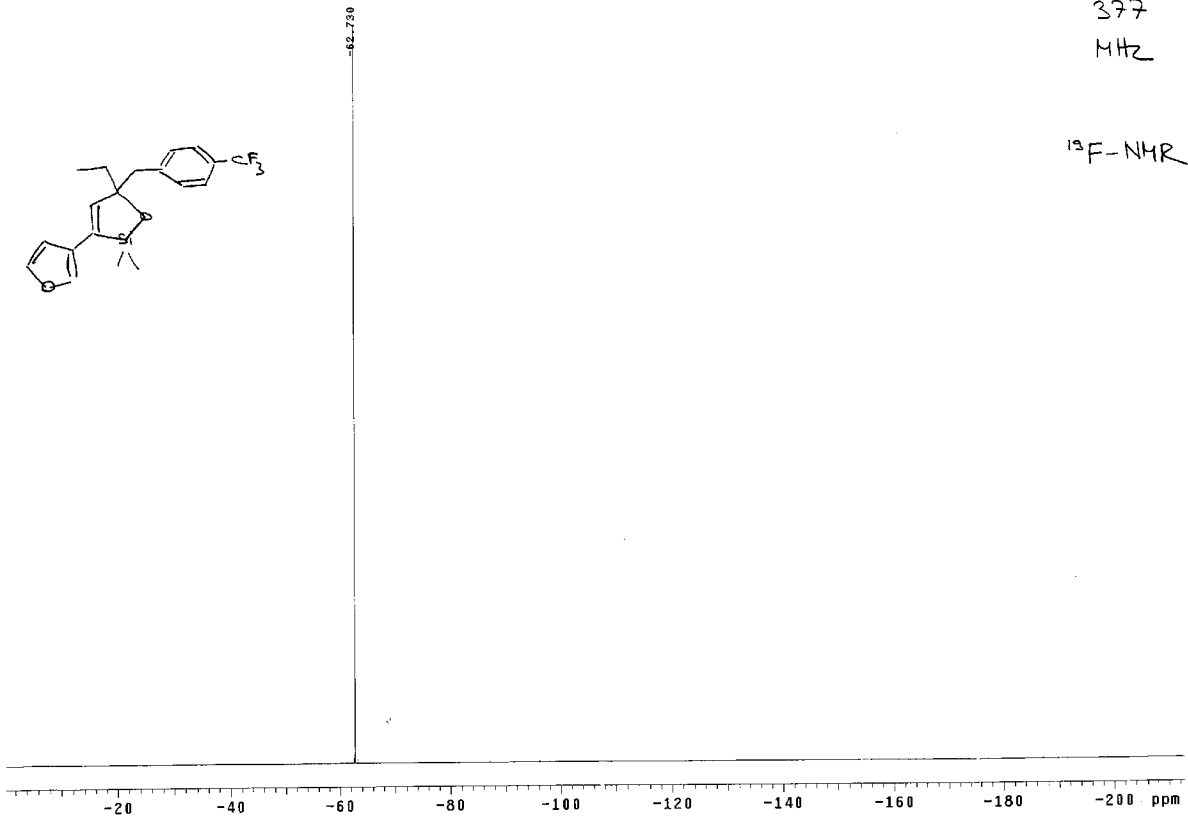
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L <sup>1</sup>H decoupled  
L <sup>19</sup>F decoupled

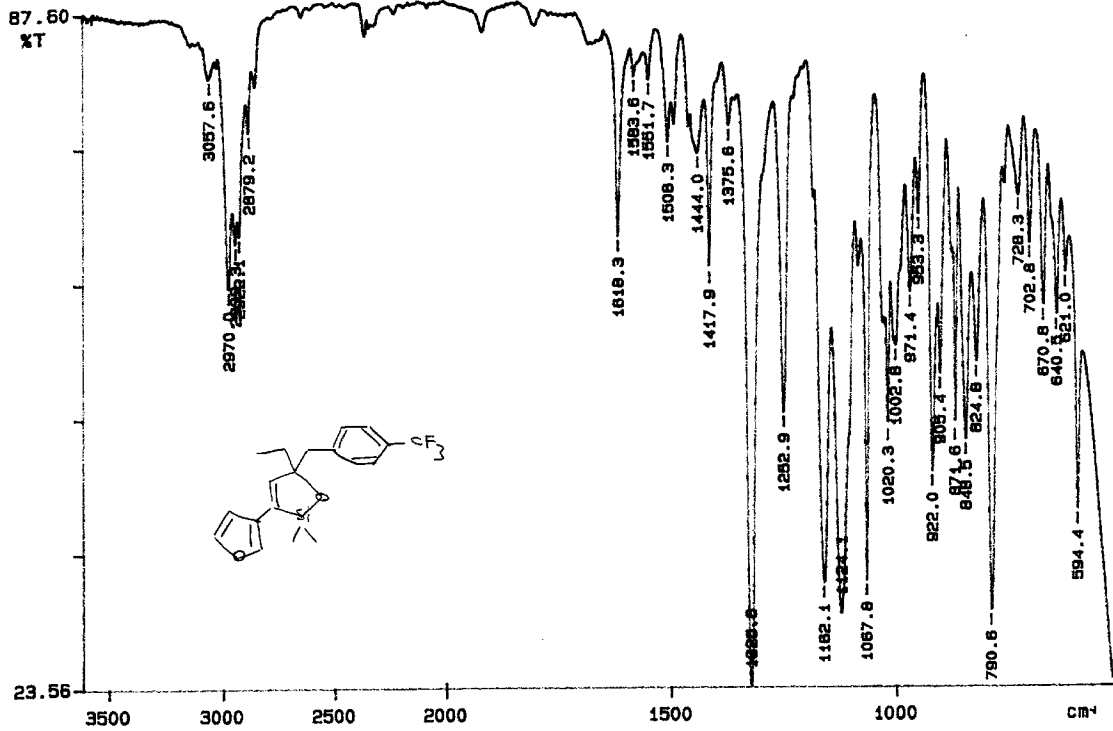


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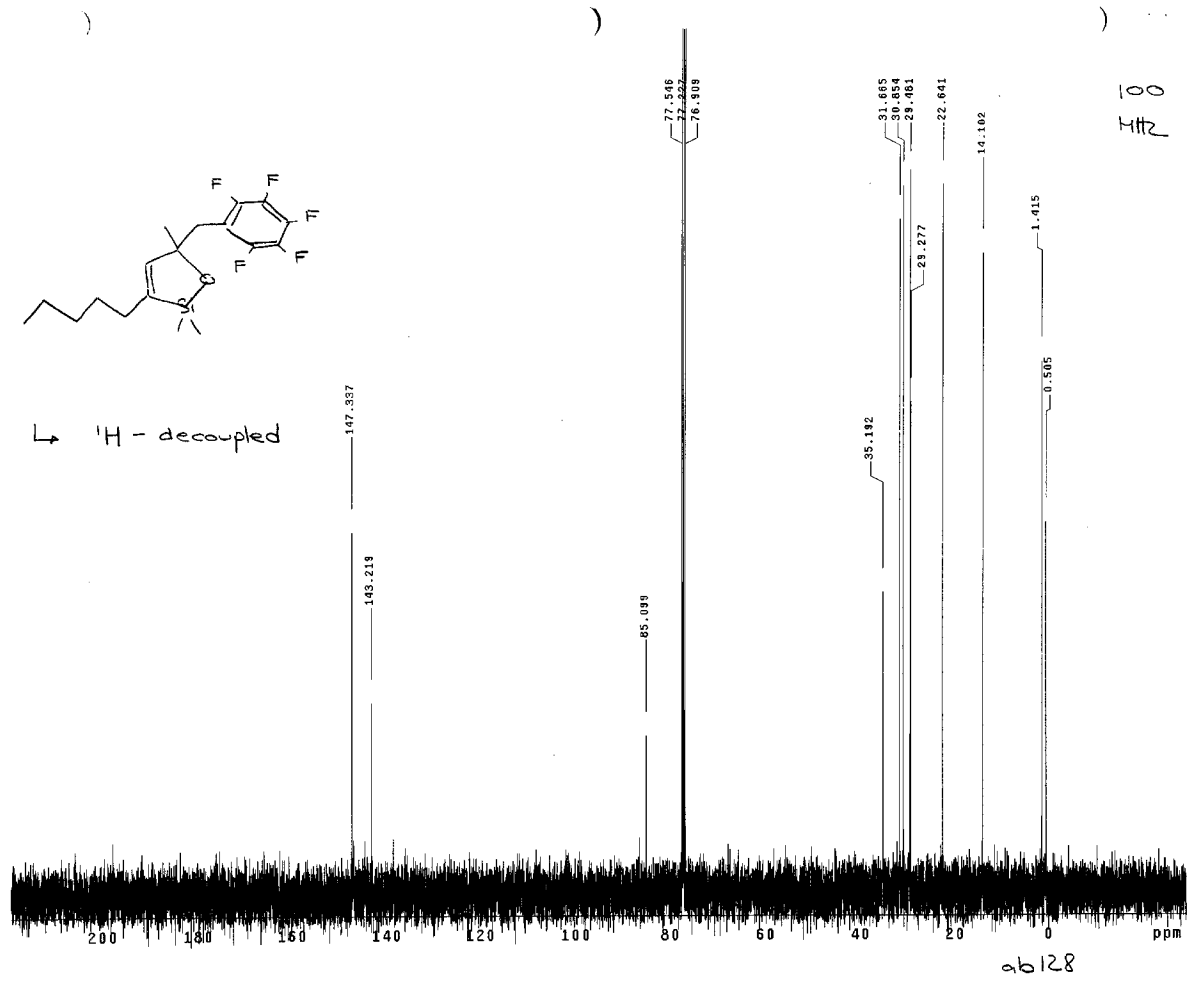
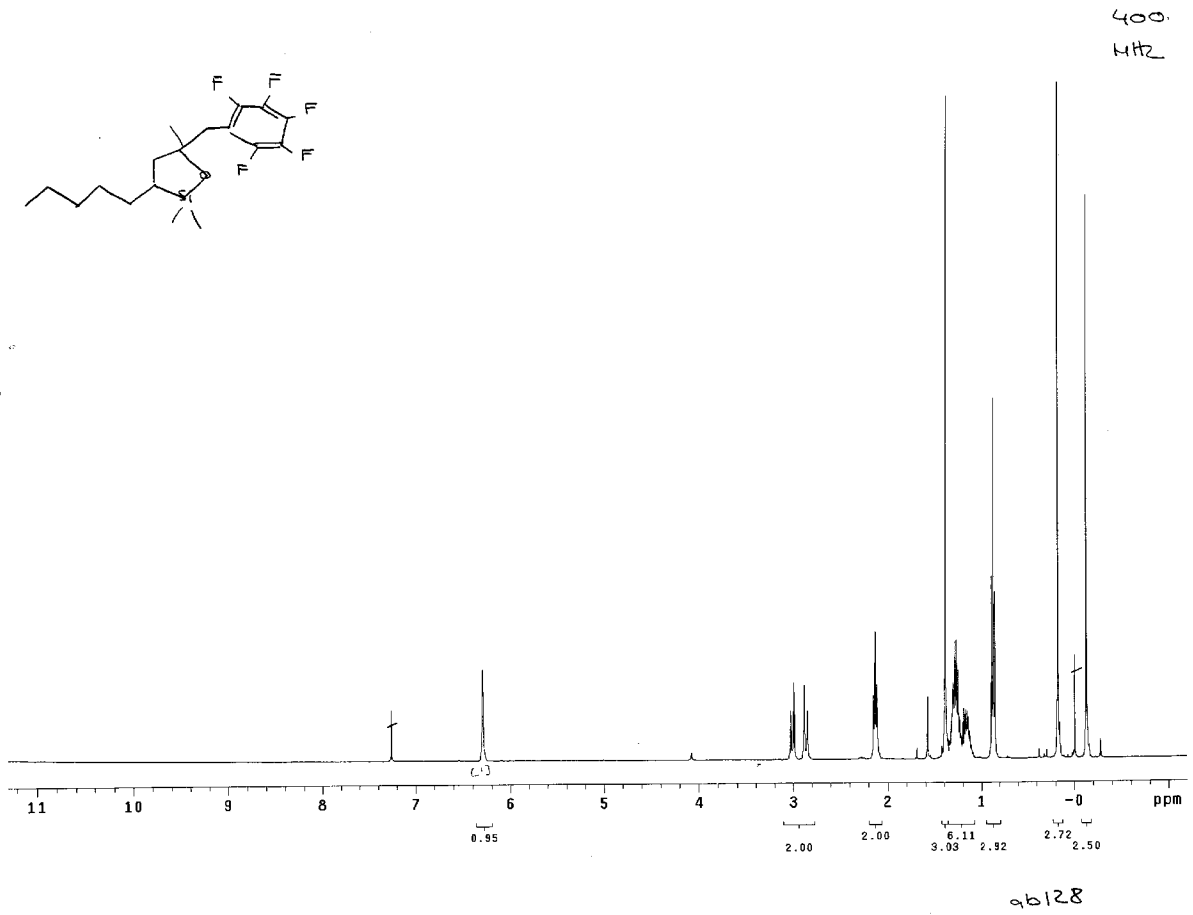
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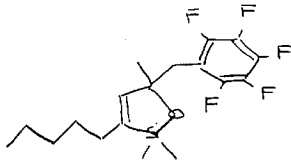
PERKIN ELMER



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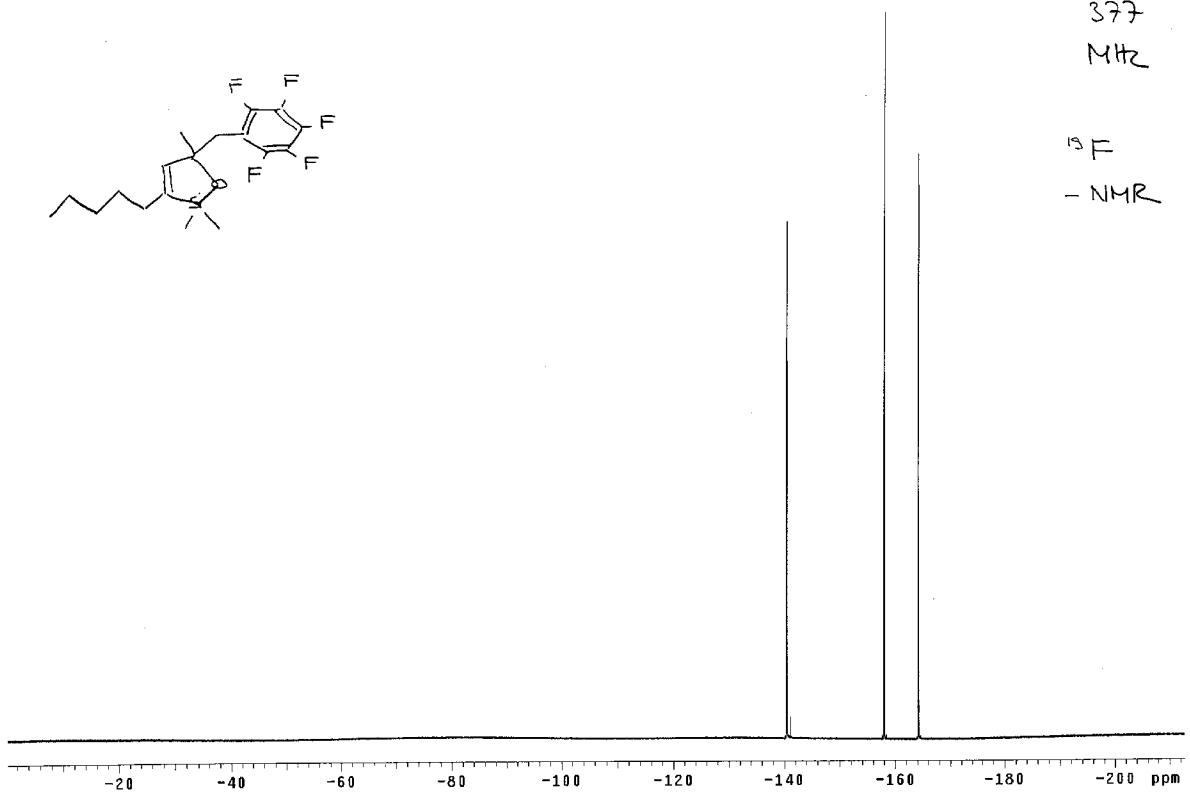
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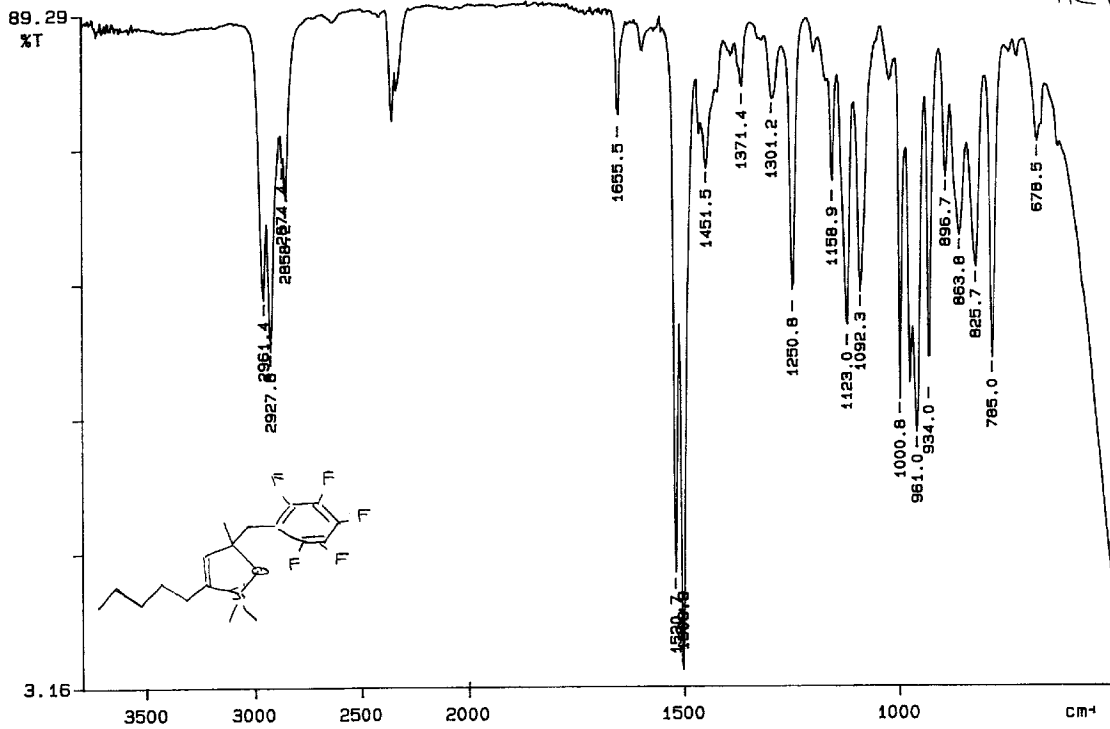
377  
MHz

<sup>19</sup>F  
- NMR



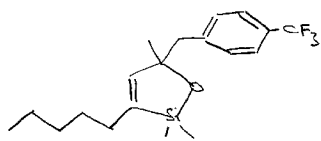
ab128

PERKIN ELMER

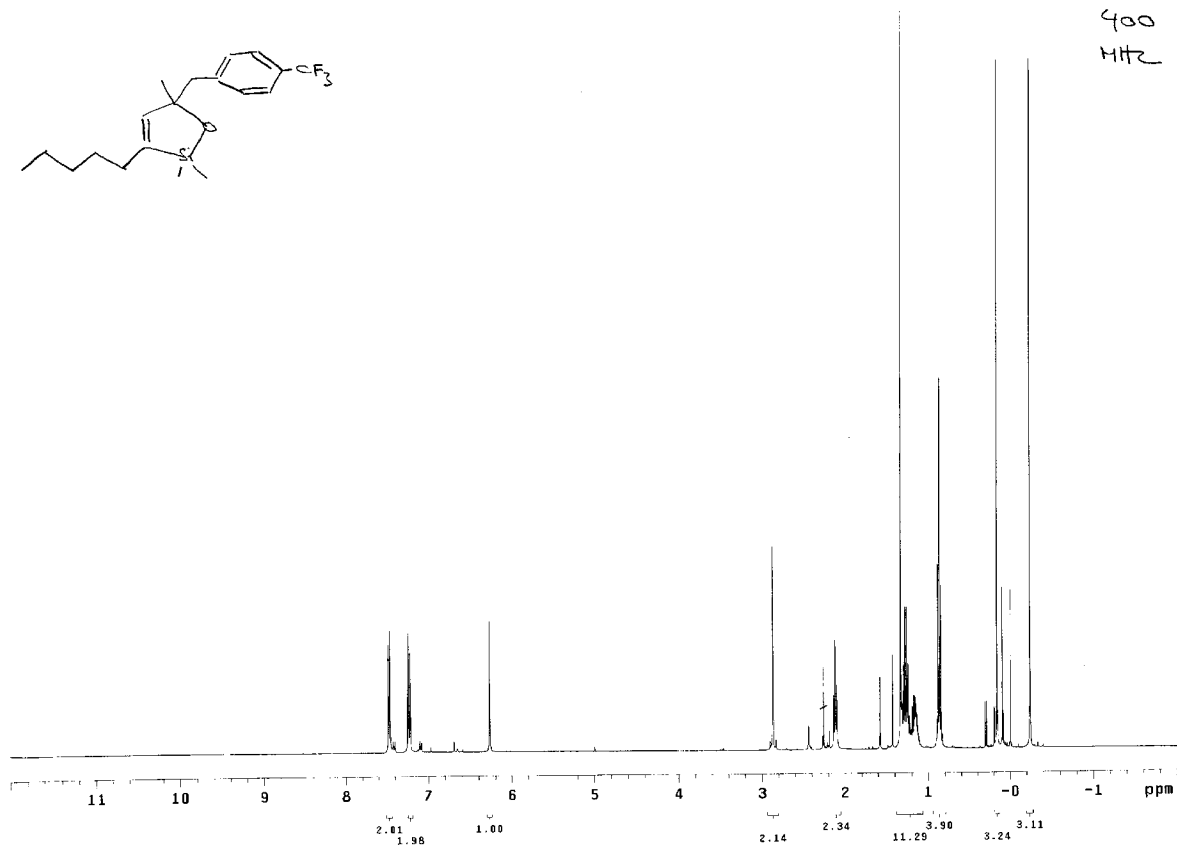


07/06/19 09:55  
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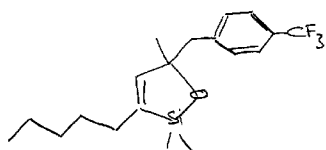
ab128



400  
MHz

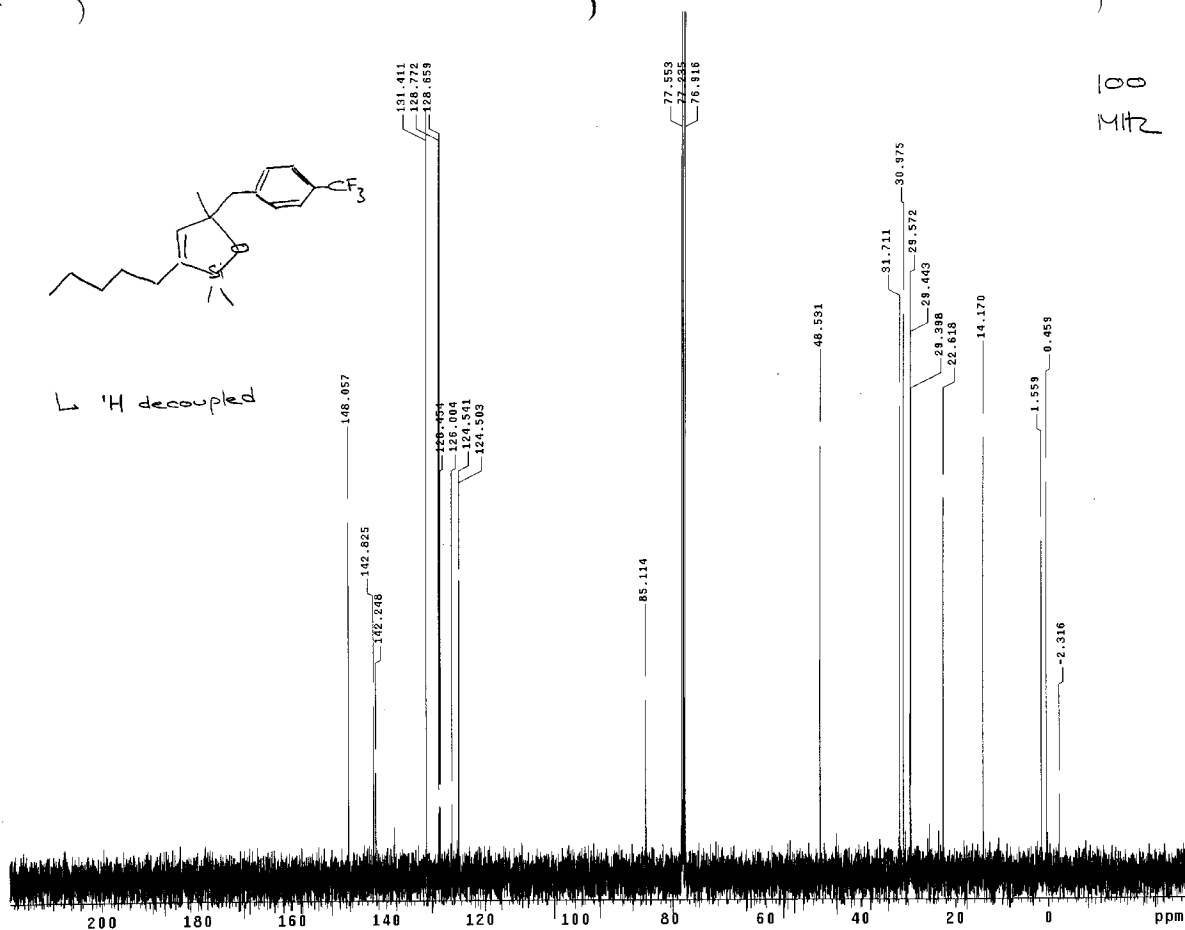


ab129

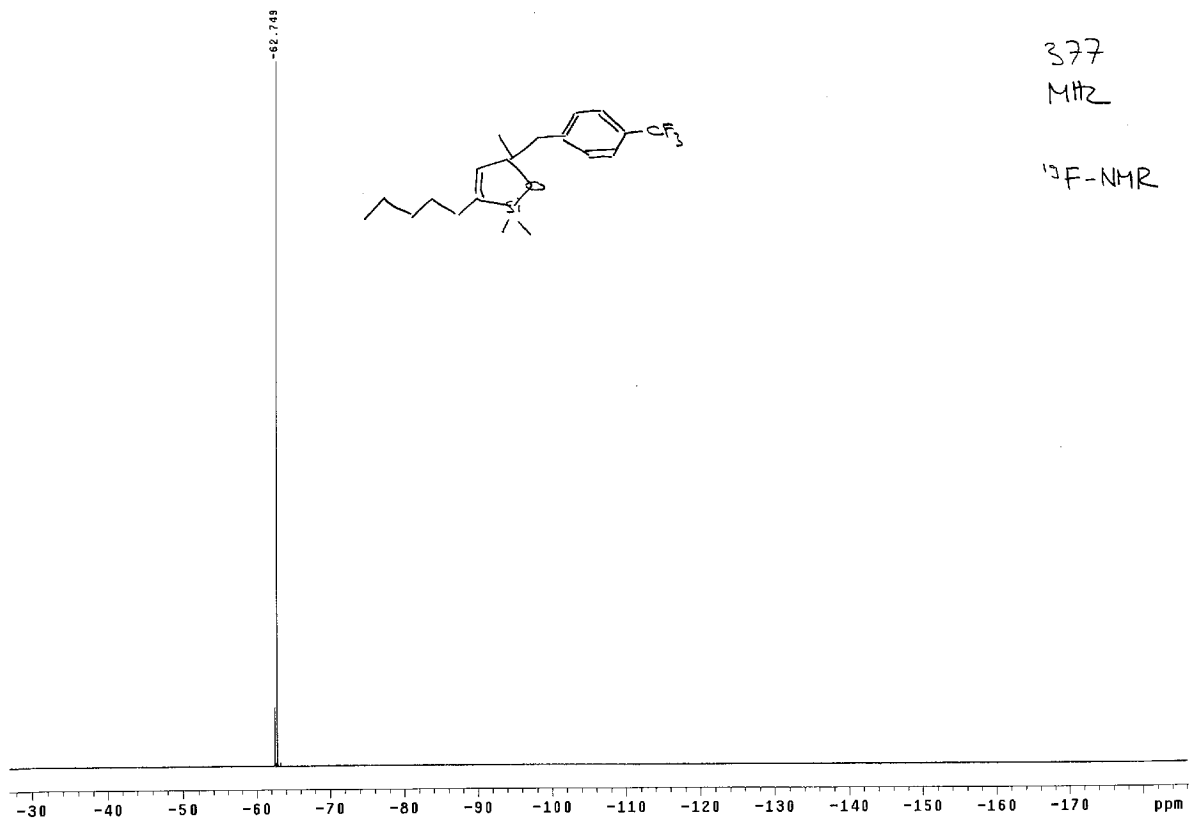


L<sup>1</sup>H decoupled

100  
MHz

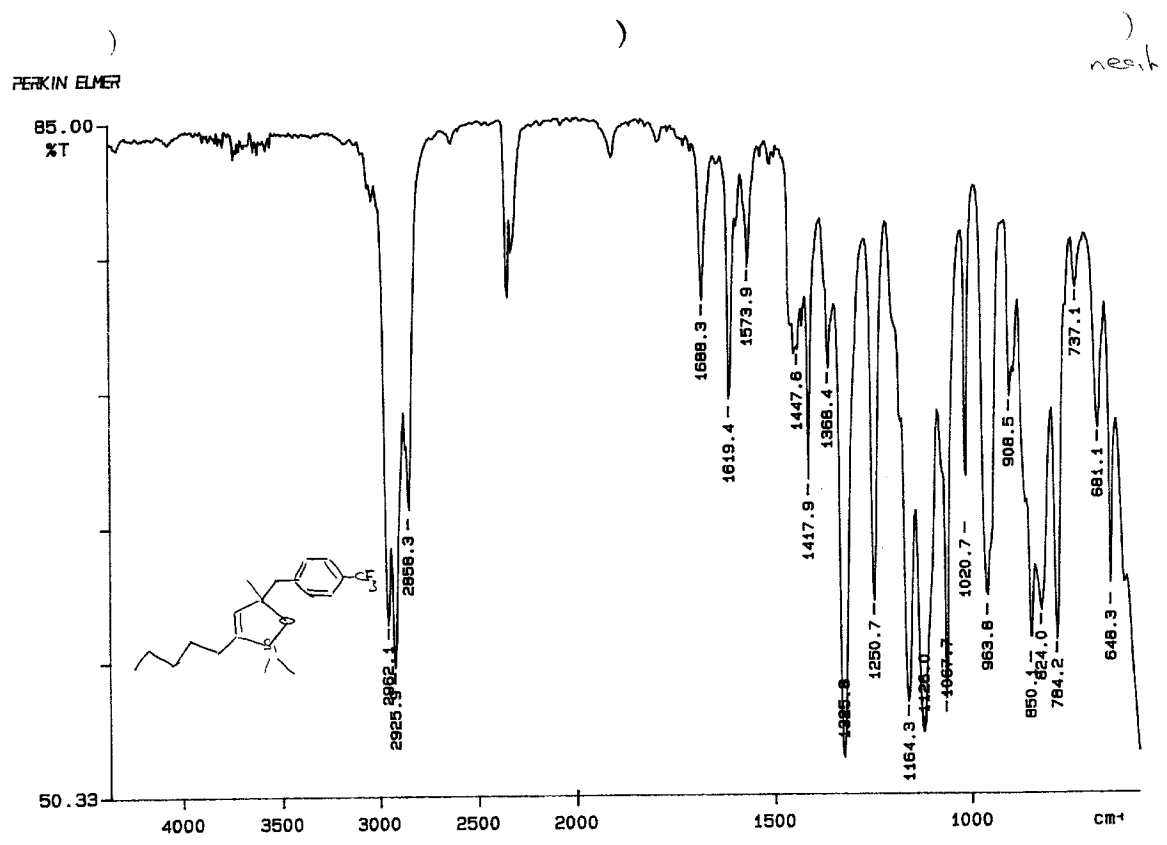


ab129



377  
MHz  
<sup>13</sup>F-NMR

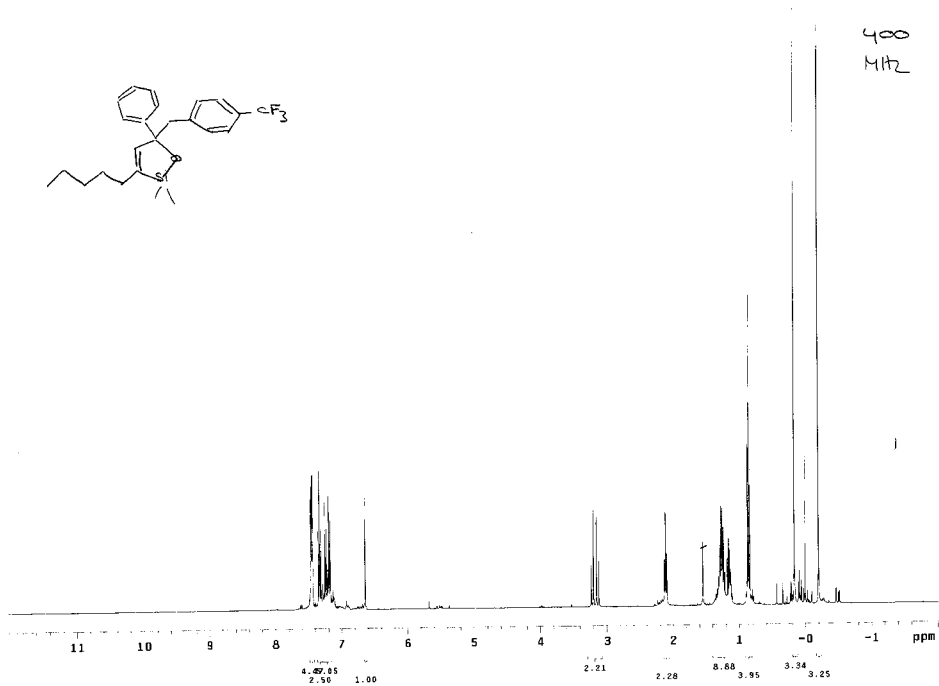
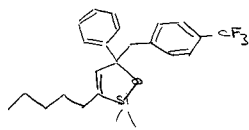
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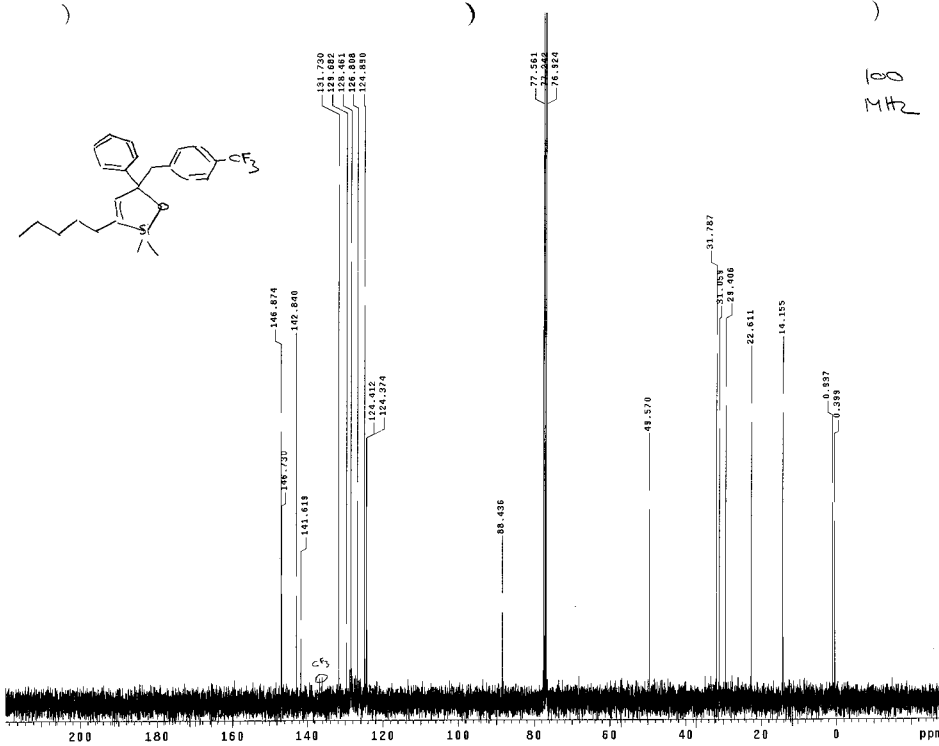
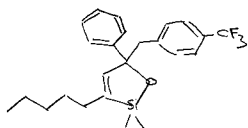
rest

07/06/21 10:27  
X: 4 scans, 4.0cm-1, flat

ab129



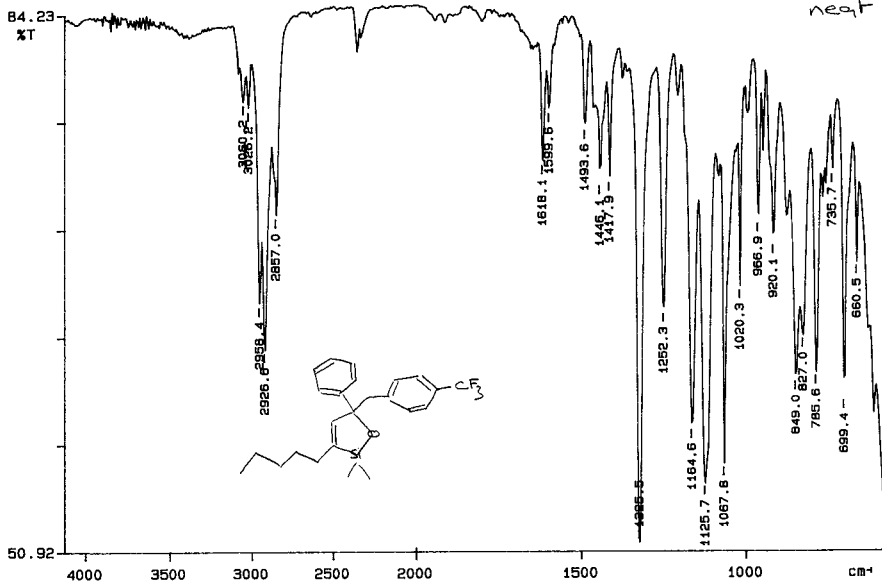
ab131



ab131

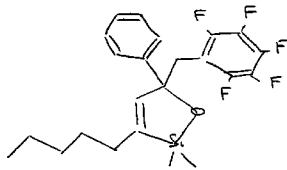
PERKIN ELMER

84.23  
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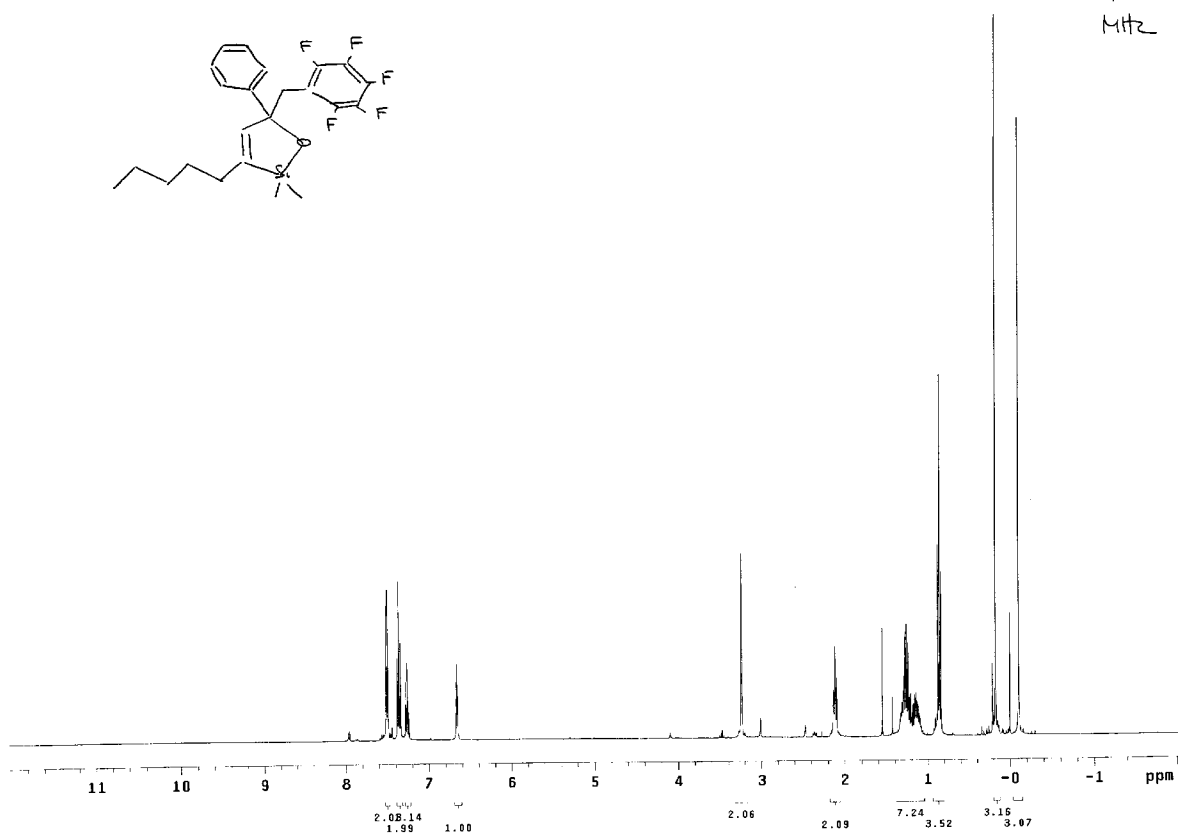


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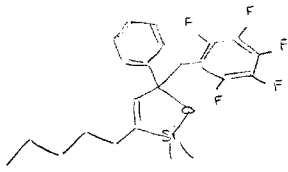
ab 131



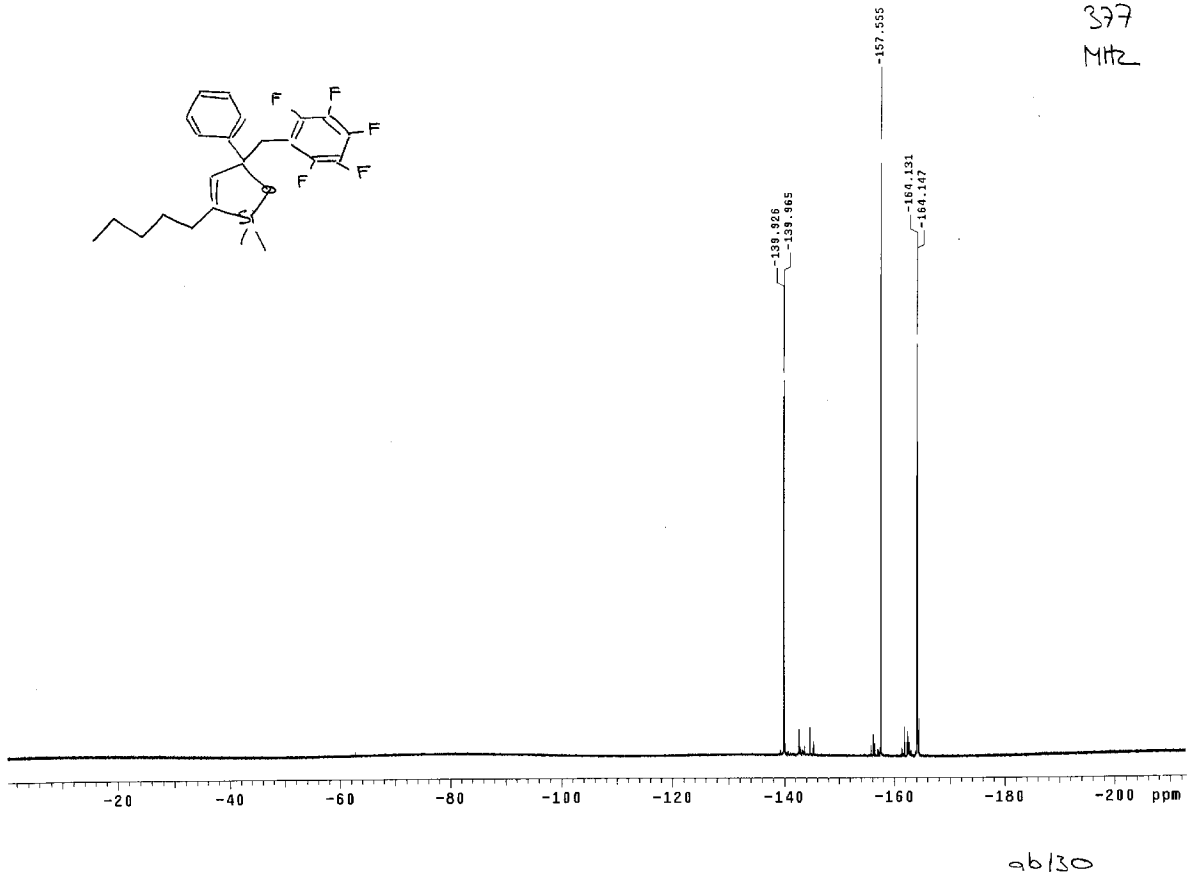
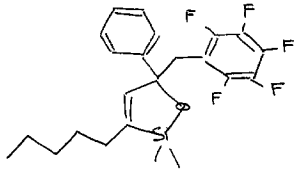
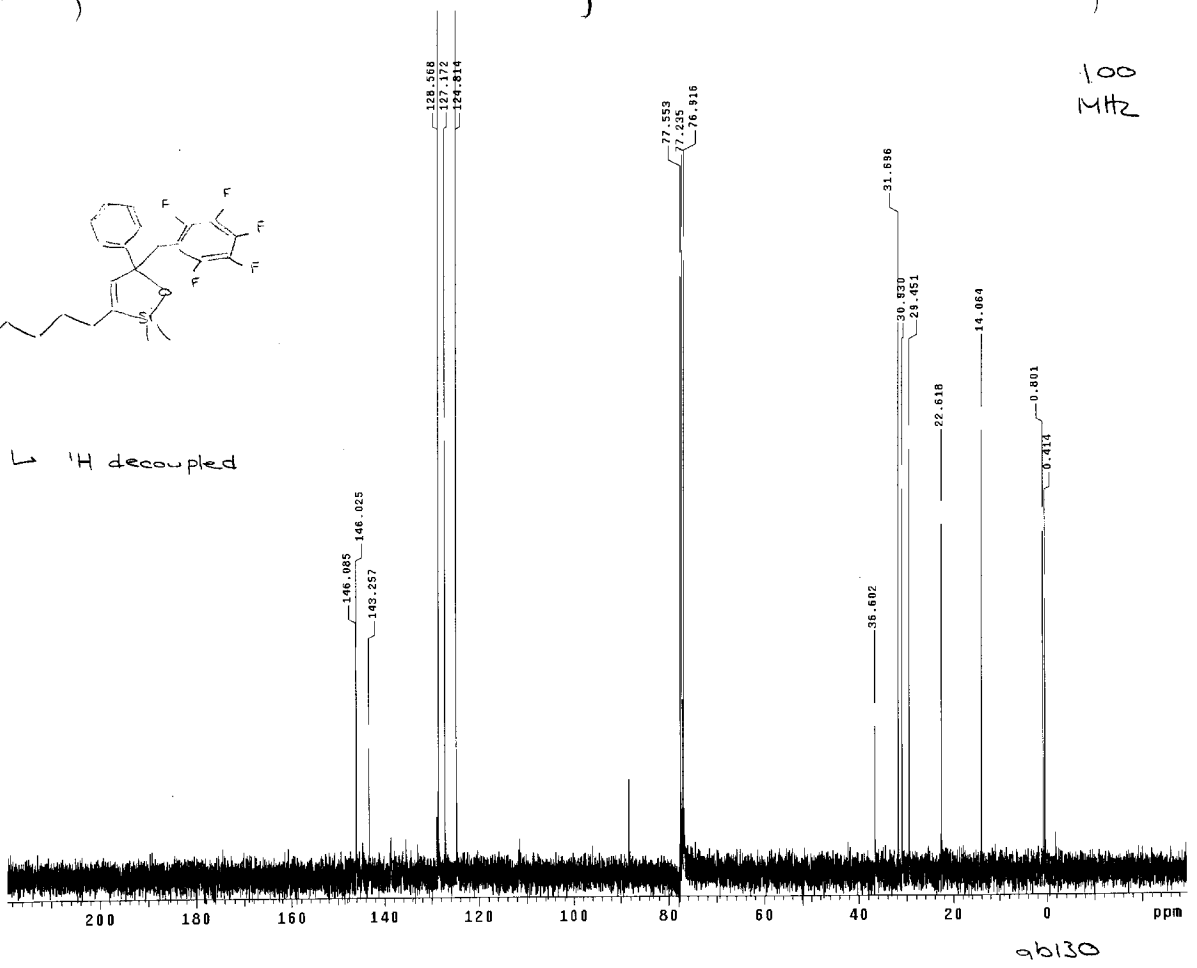
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MHz



ab 130

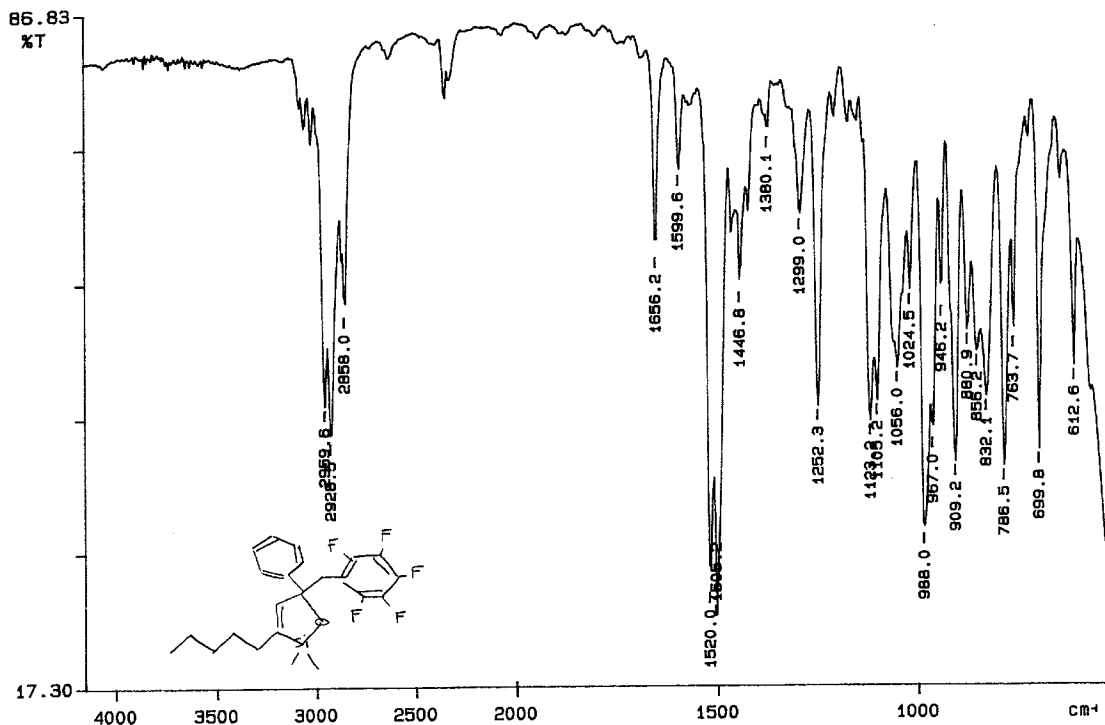


L <sup>1</sup>H decoupled



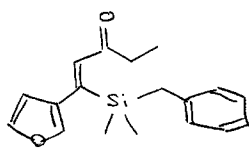
PERKIN ELMER

neat

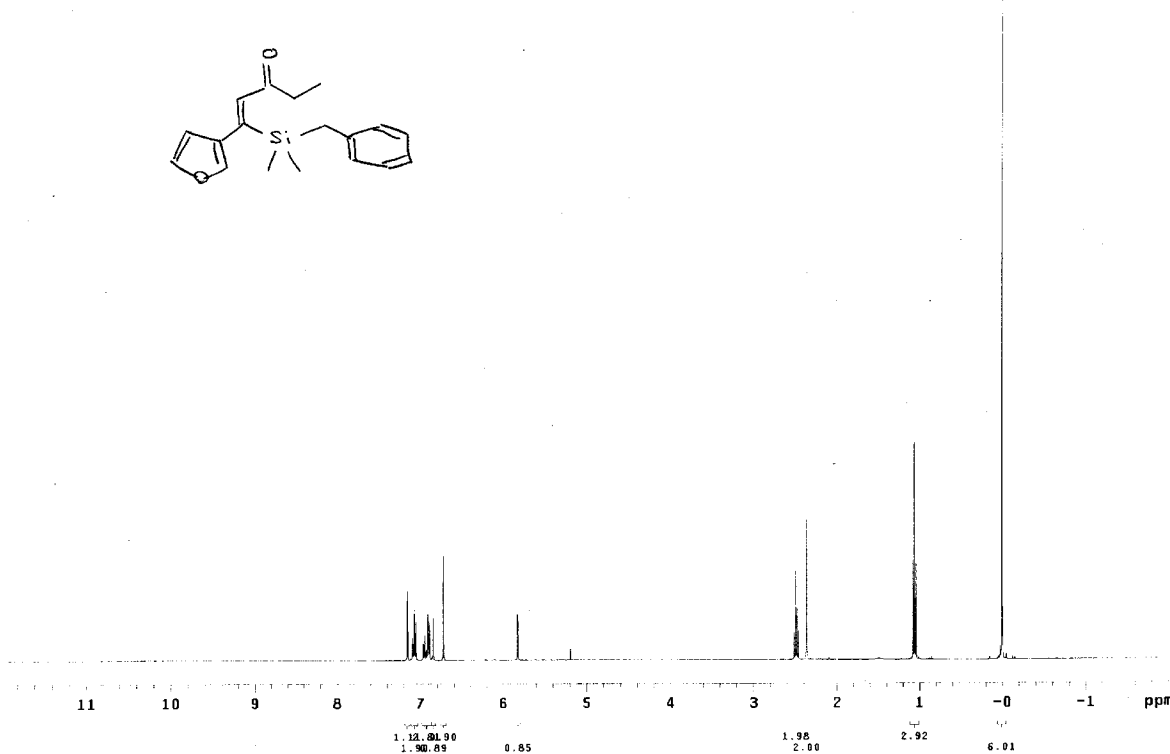


07/06/20 15:11  
X: 4 scans, 4.0cm-1

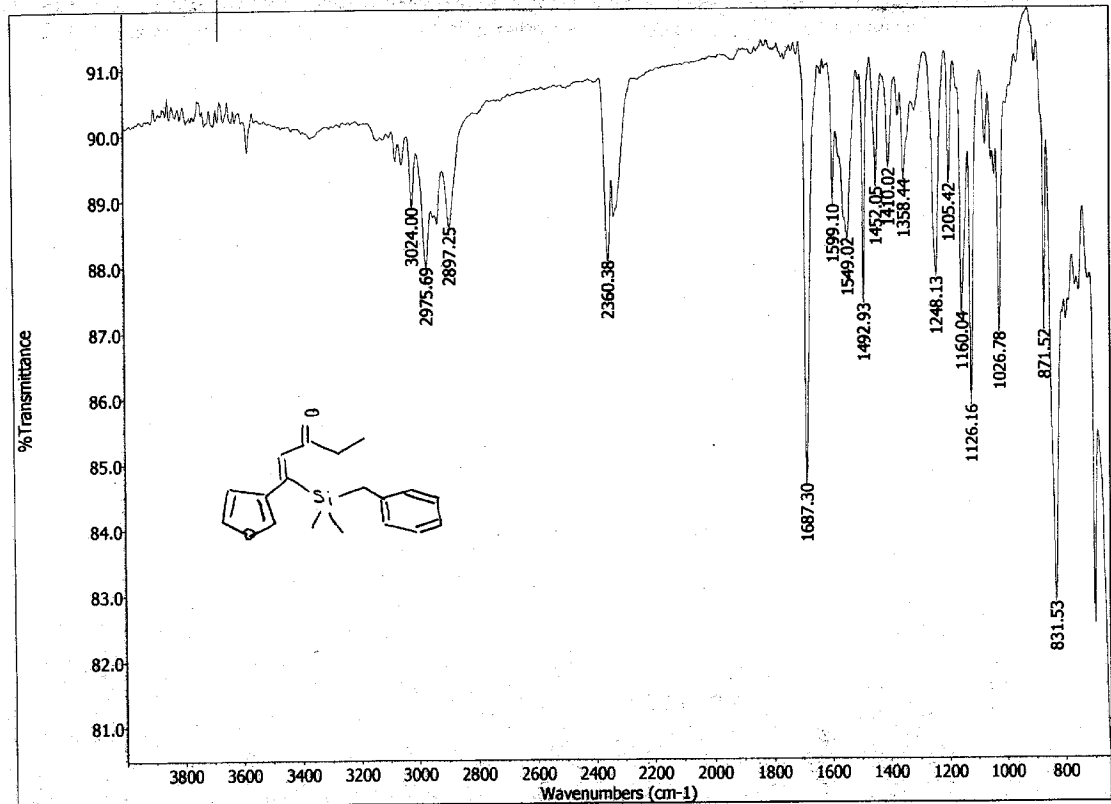
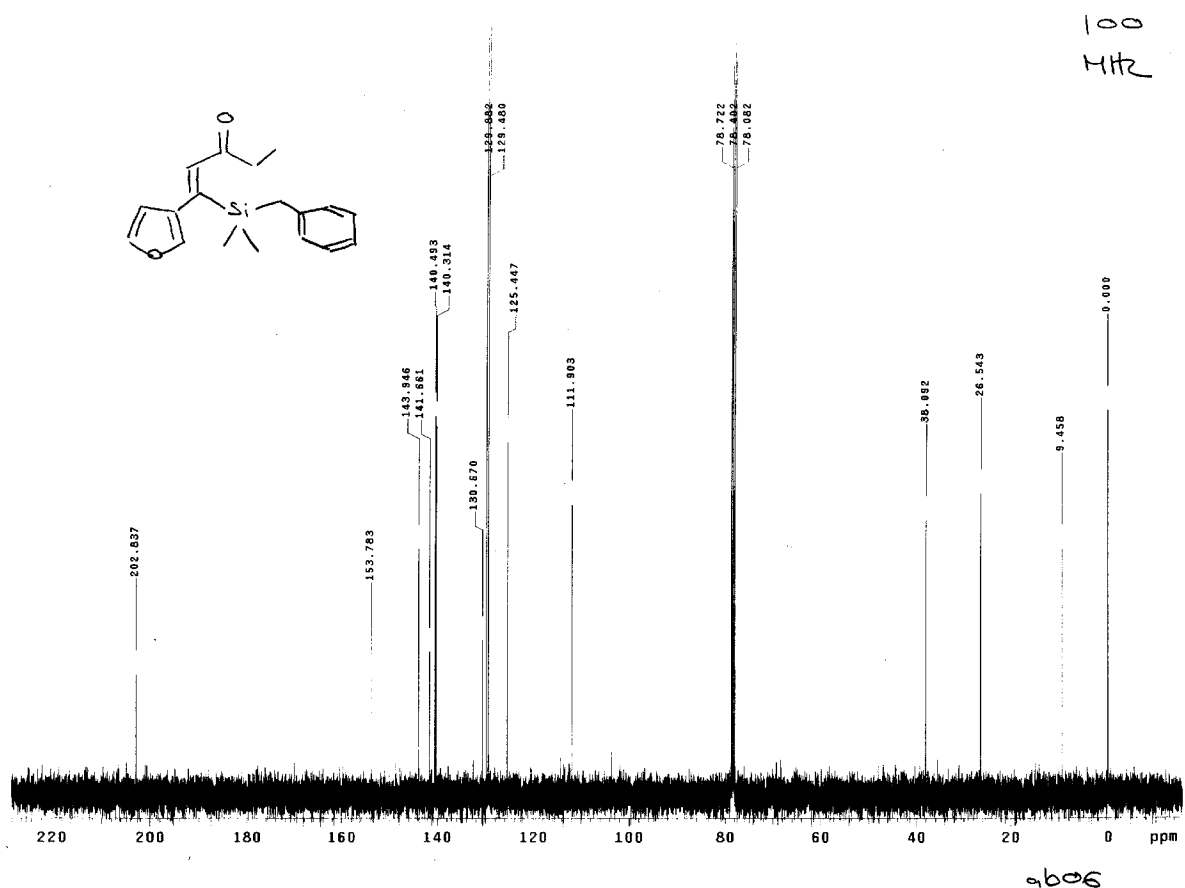
96130



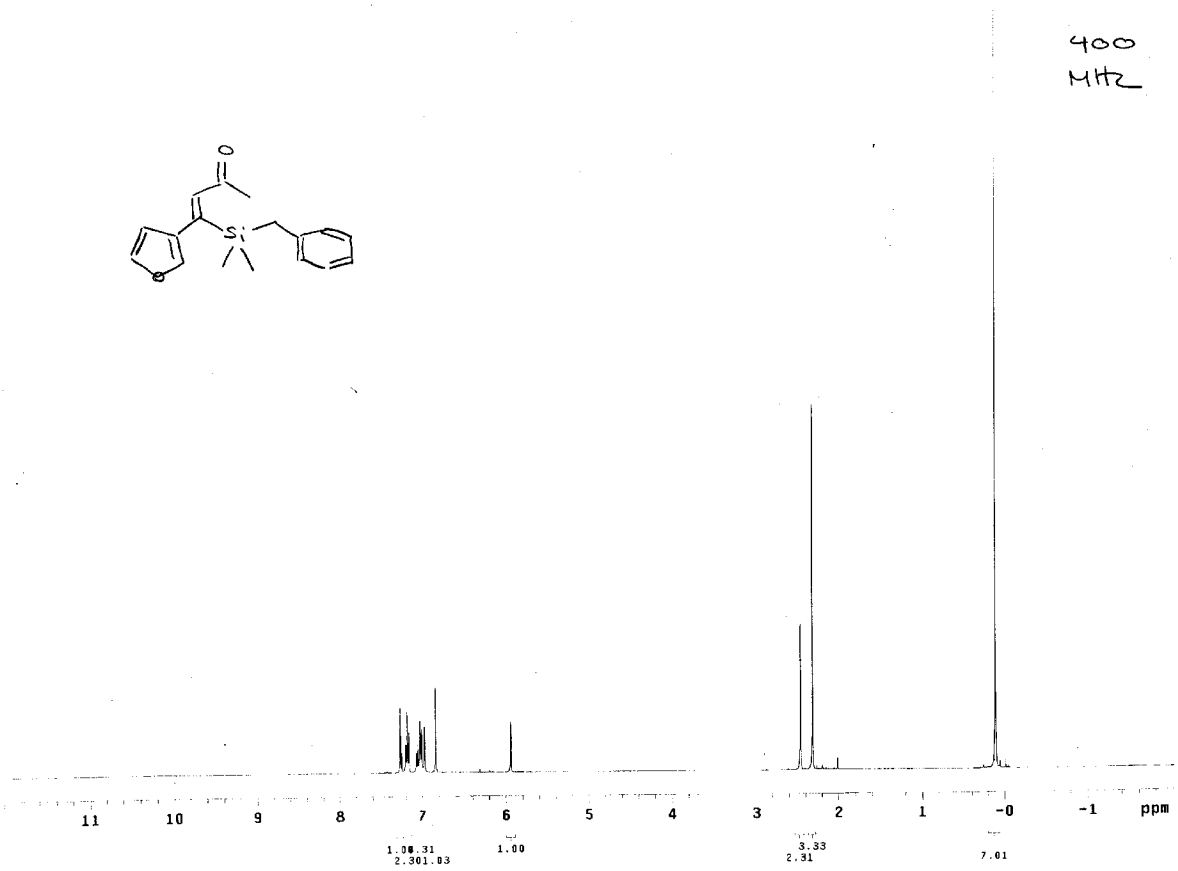
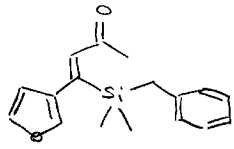
400  
MHz



9606

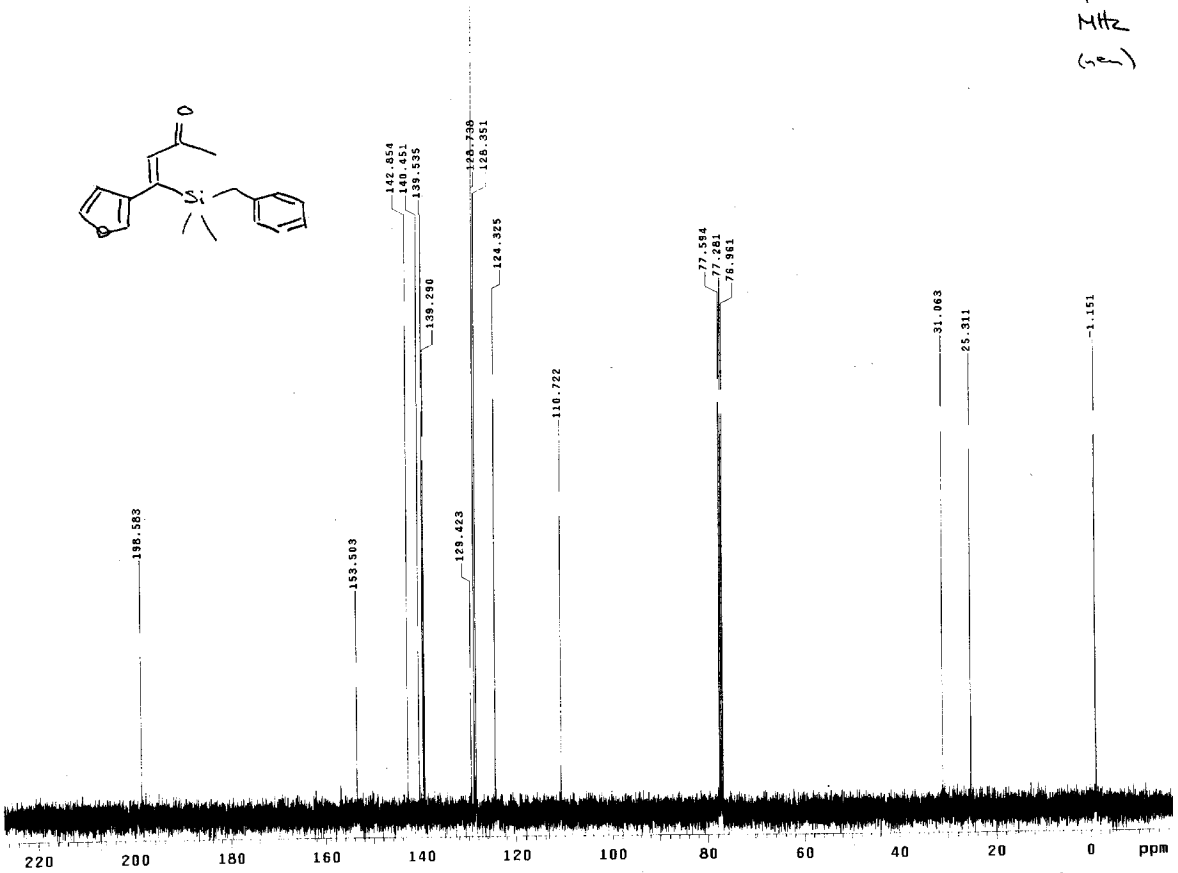
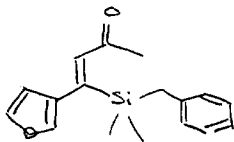


400  
MHz



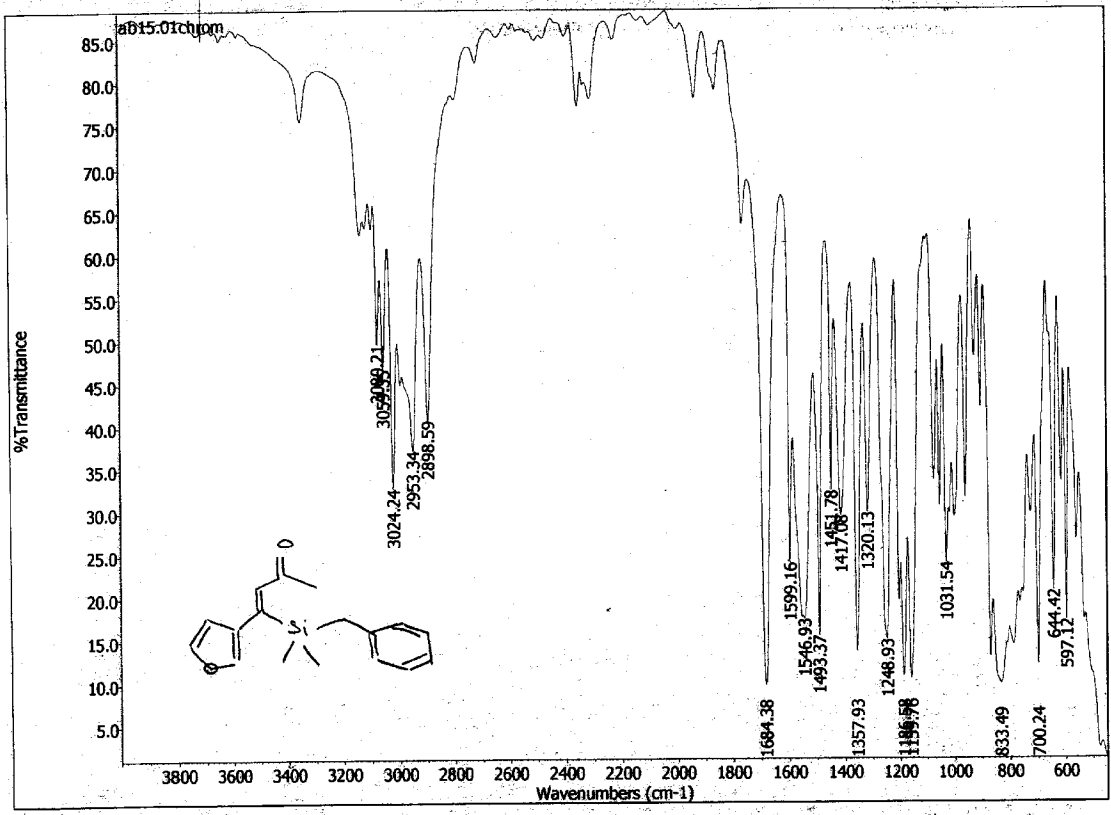
ab15

400  
MHz  
(CDCl<sub>3</sub>)

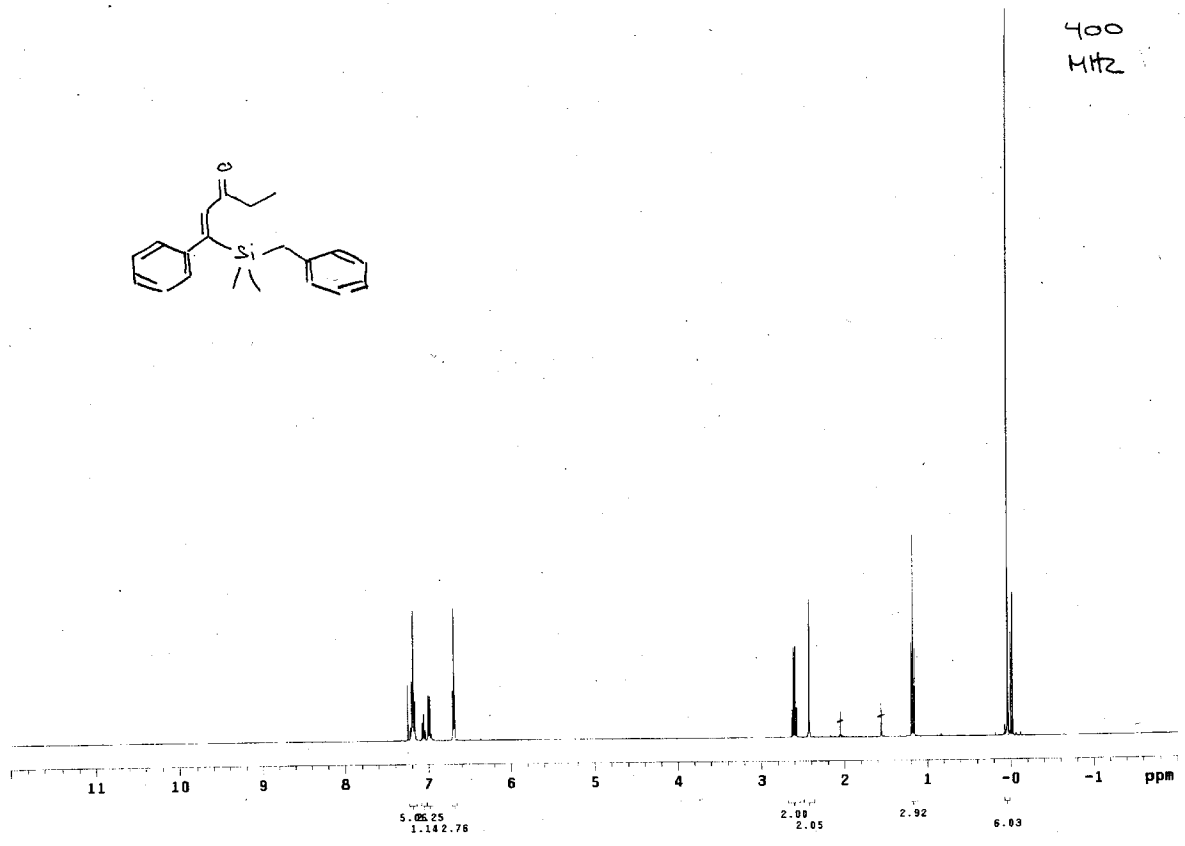
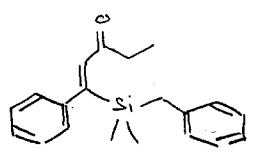


ab15

nest



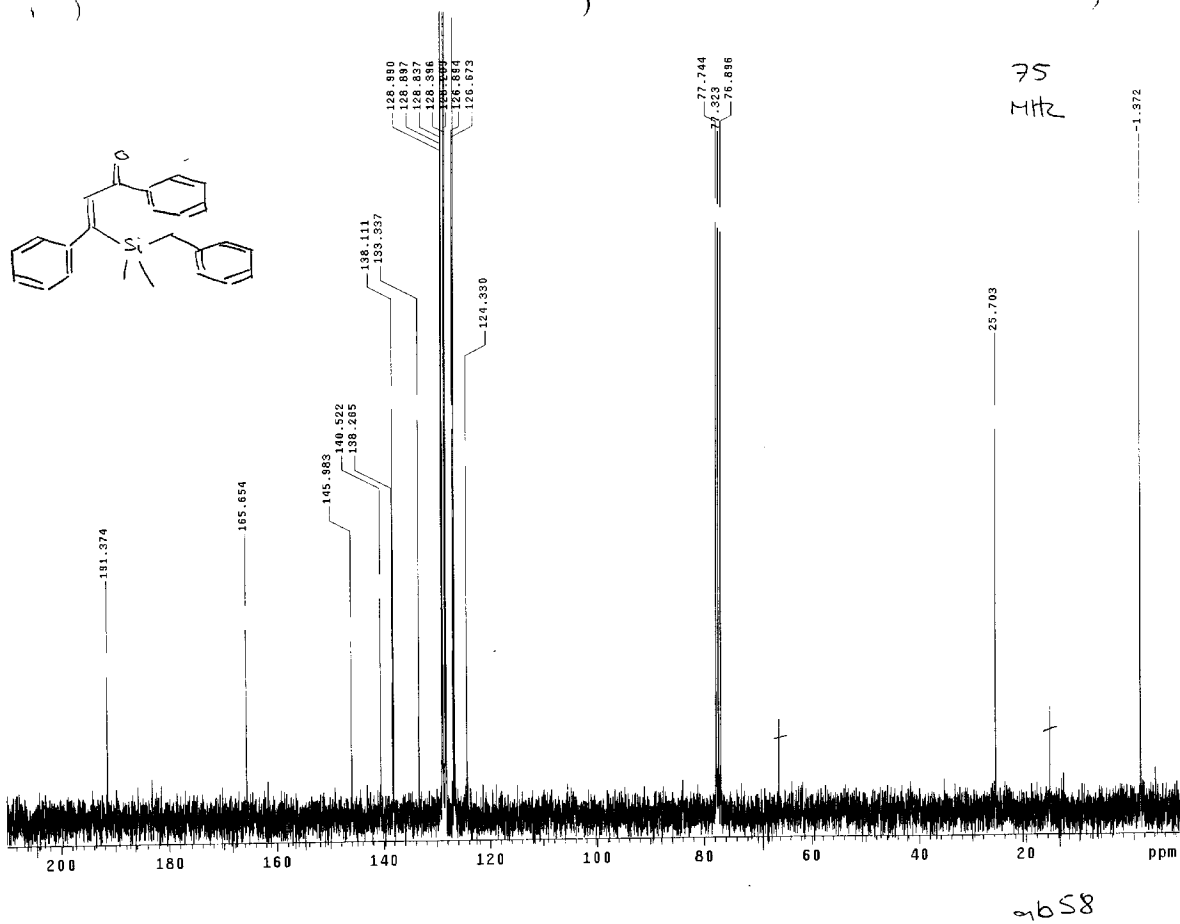
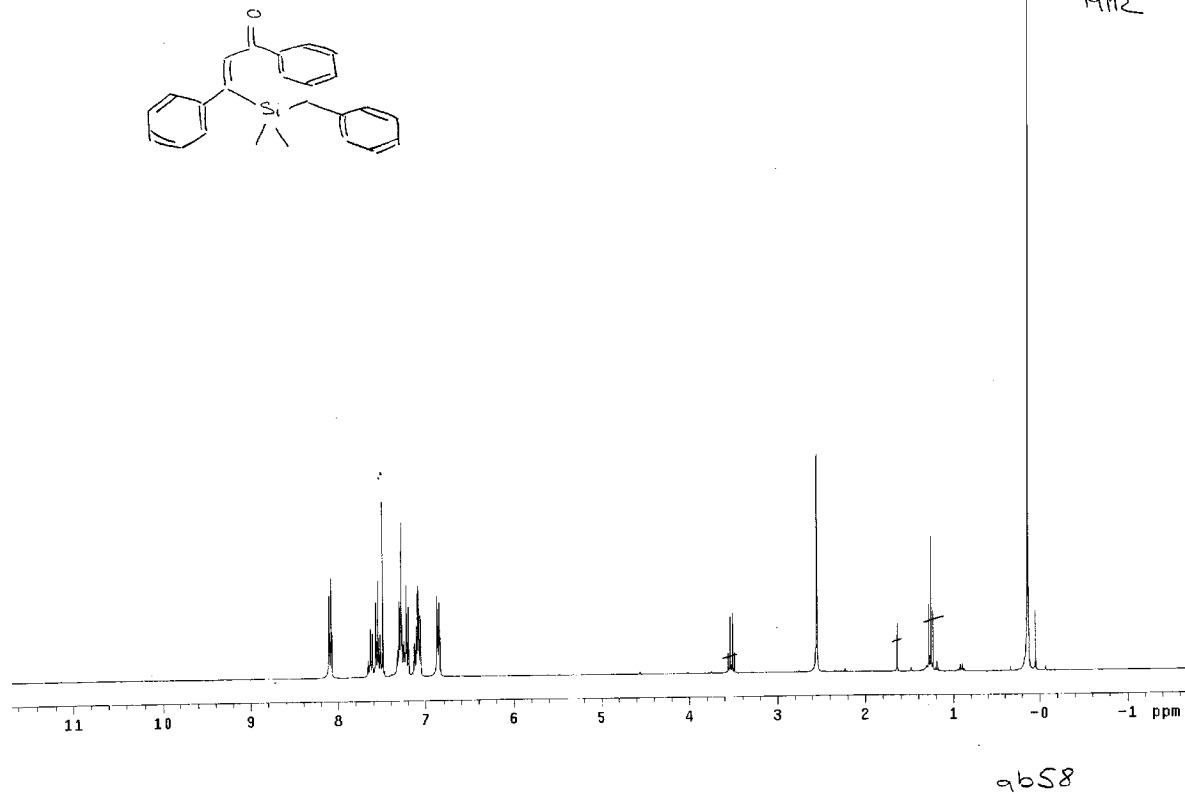
ab15



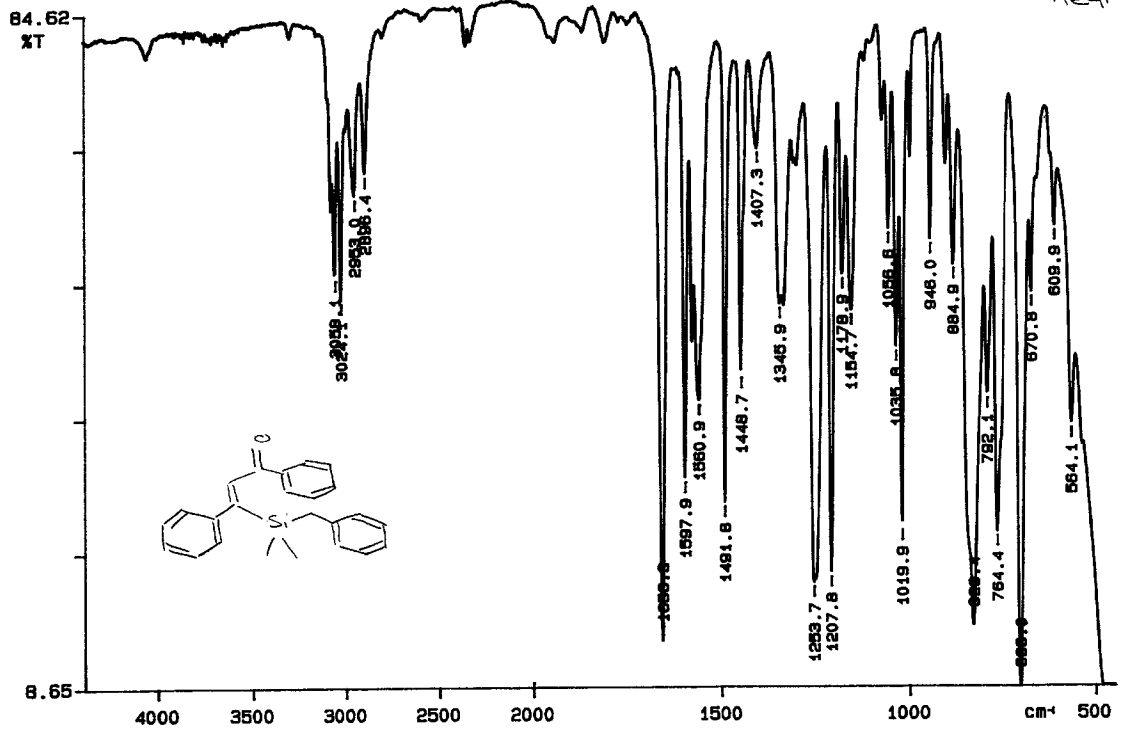
400 MHz

ab148



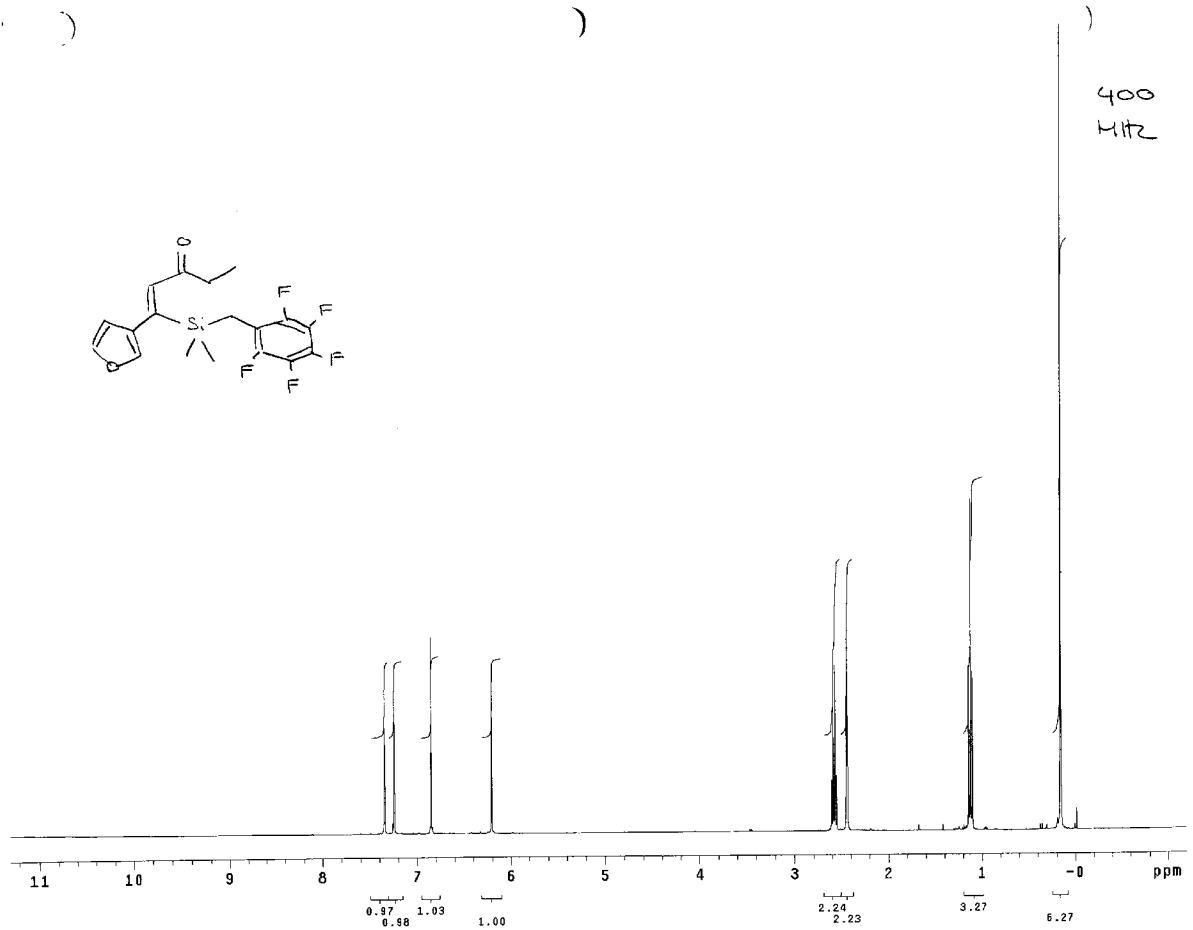


PERKIN ELMER

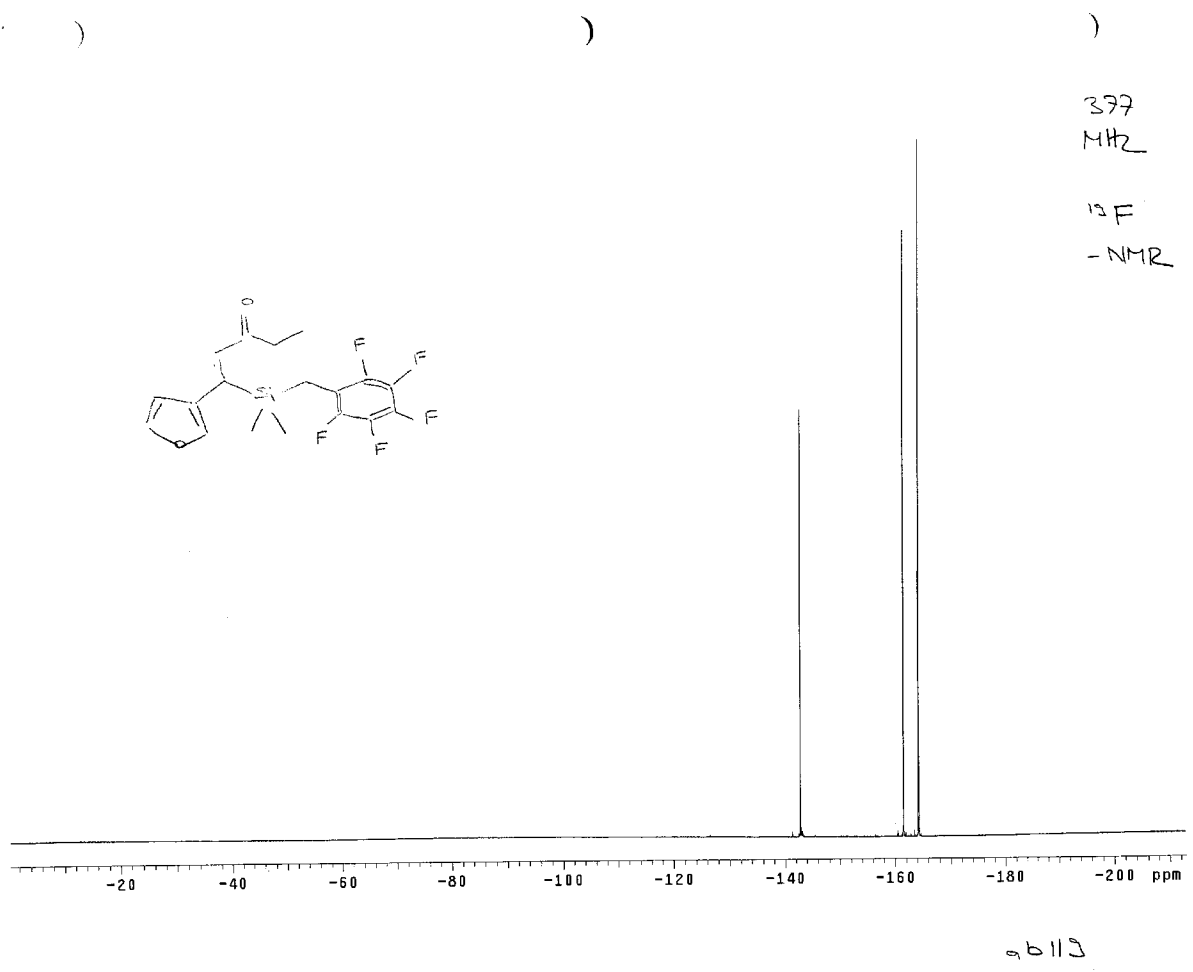
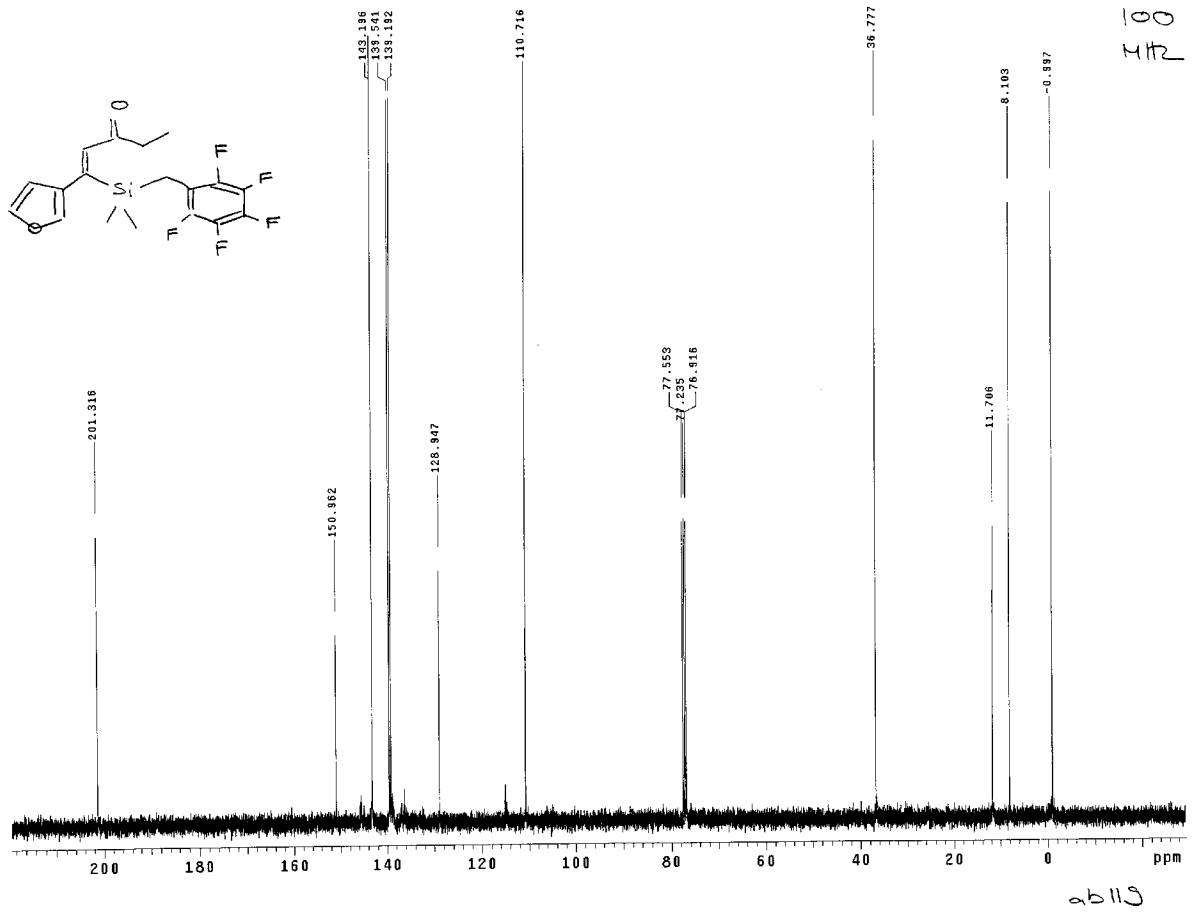


06/11/24 17:23  
X: 4 scans, 4.0cm-1

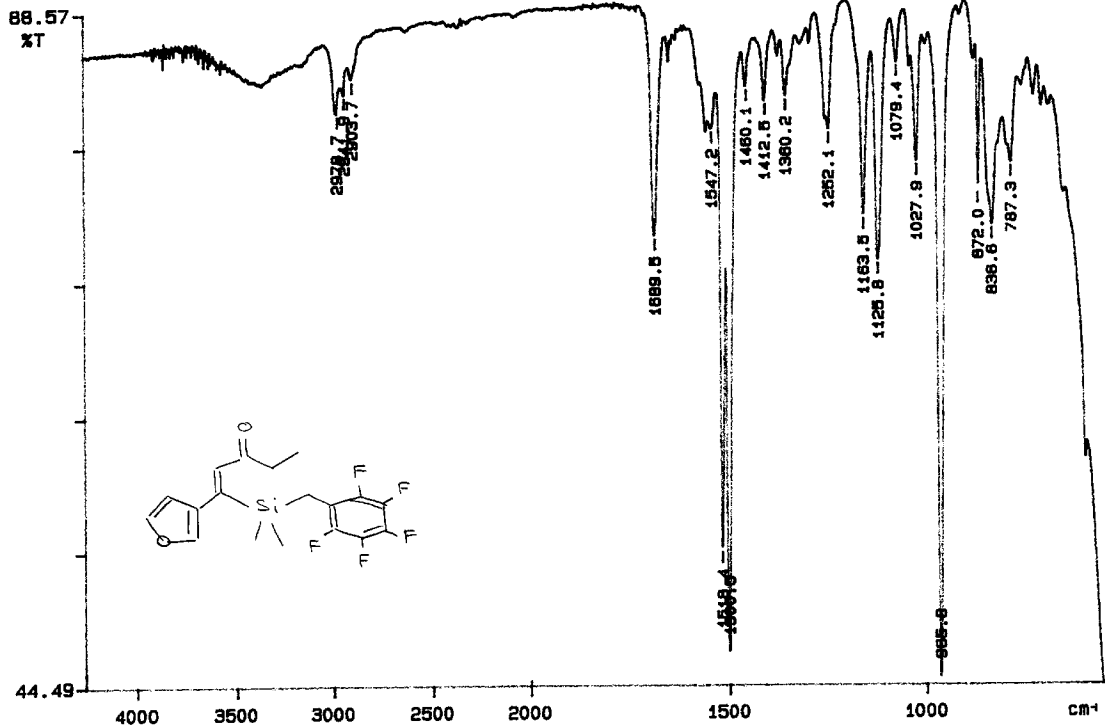
ab 58



ab 113

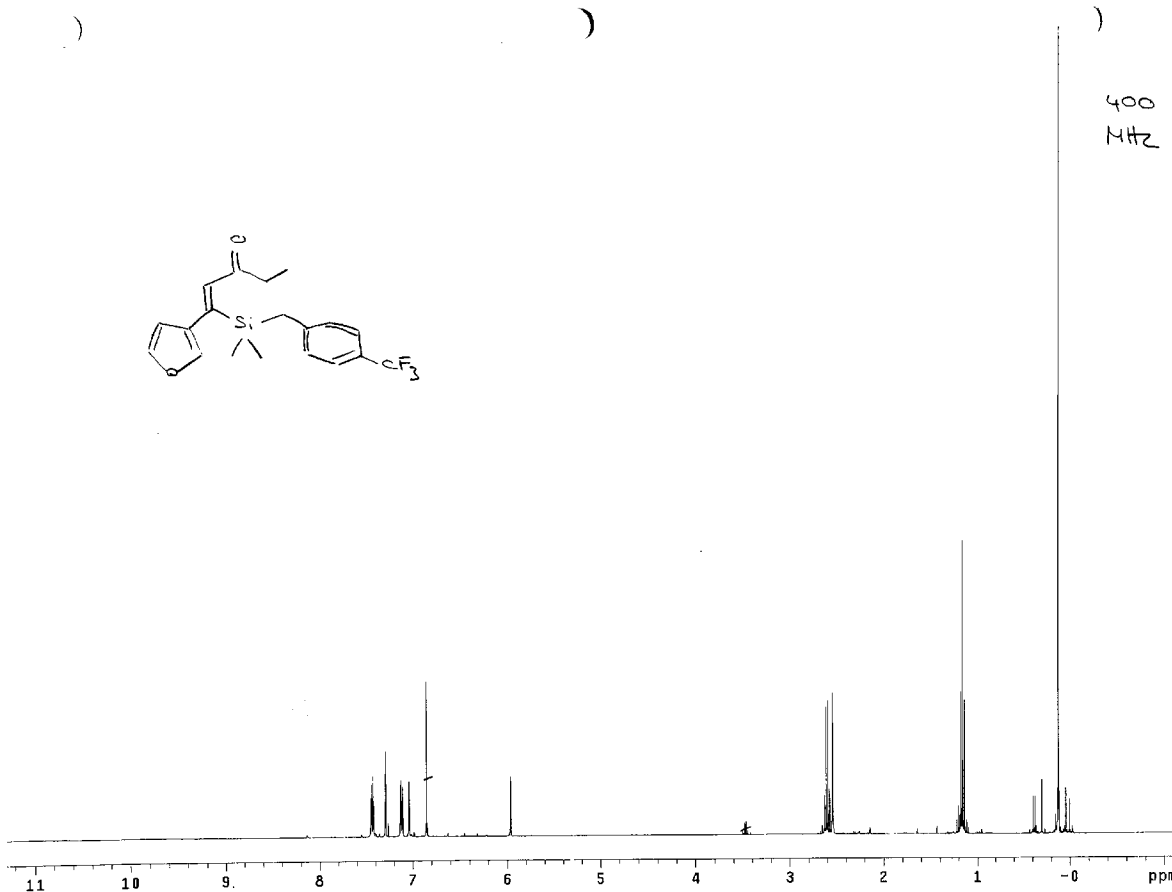


PERKIN ELMER

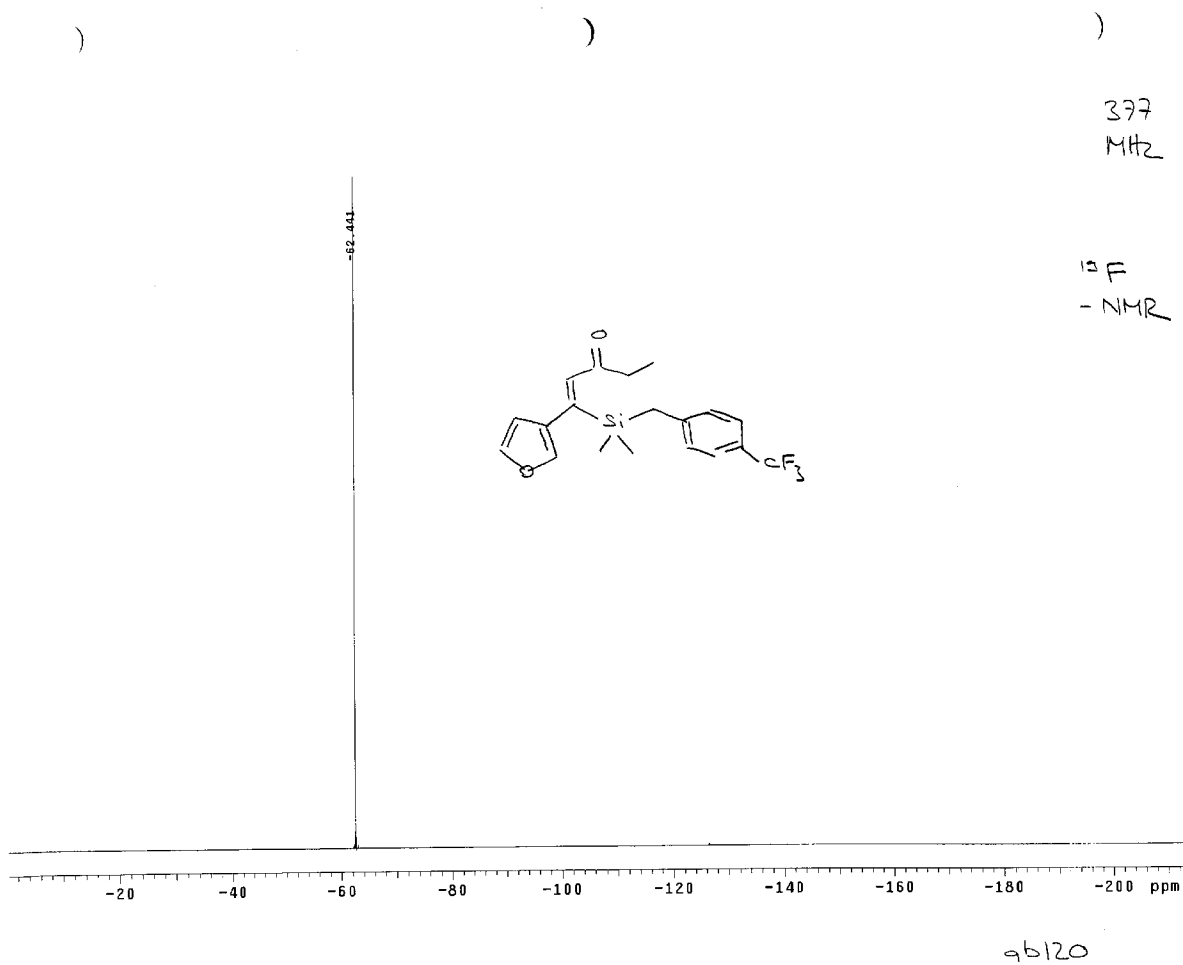
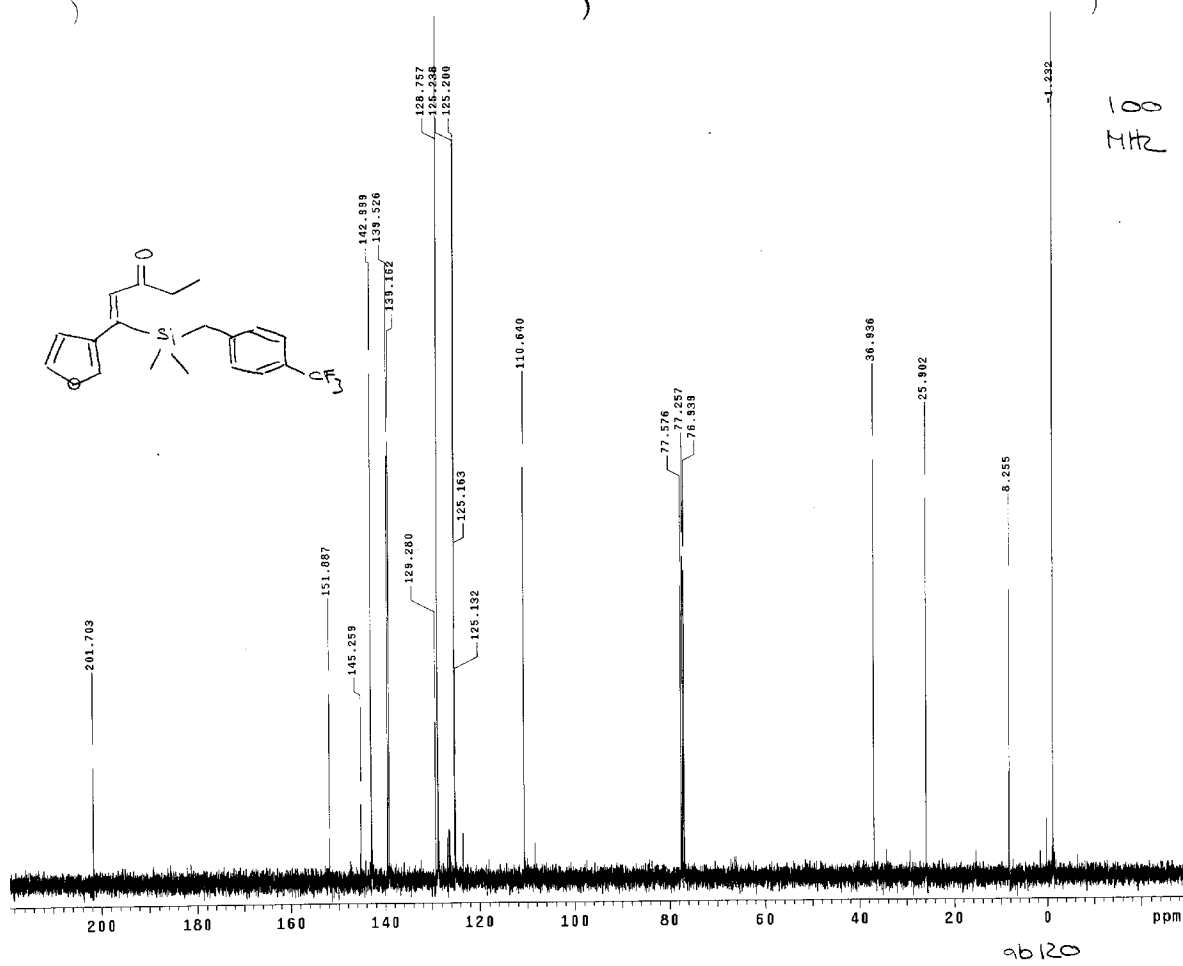


07/06/07 10:33  
X: 4 scans, 4.0cm-1

96119

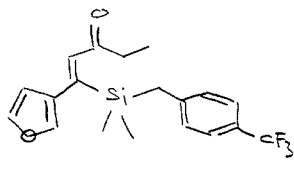
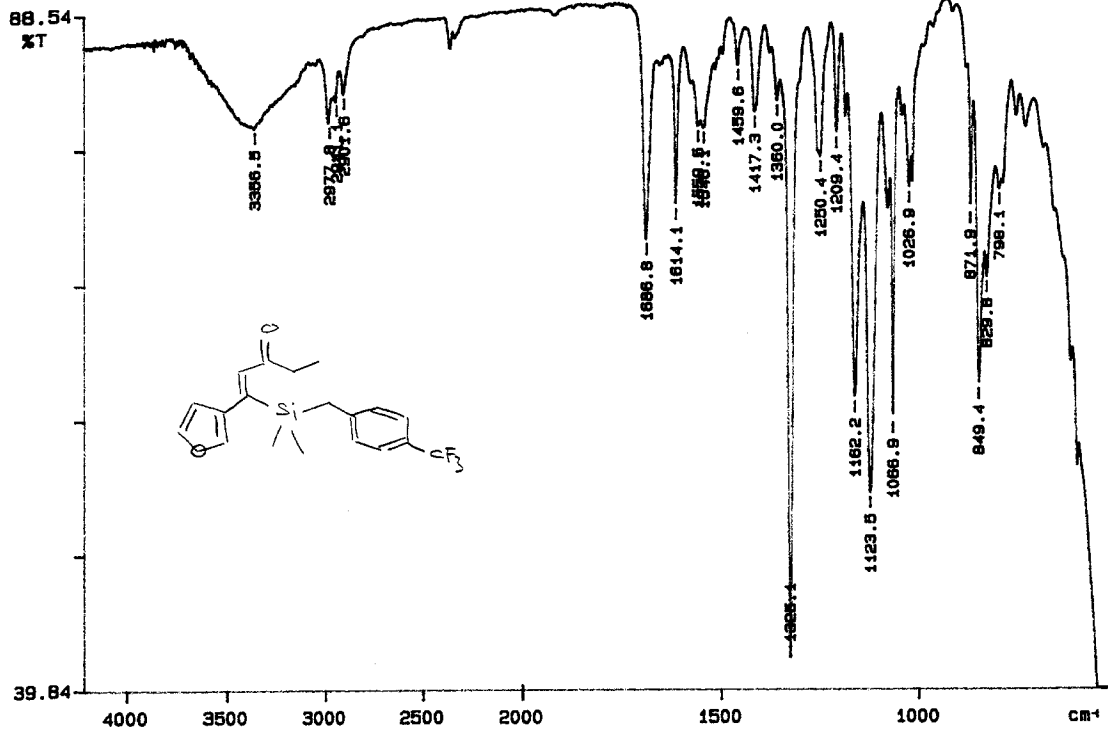


96120



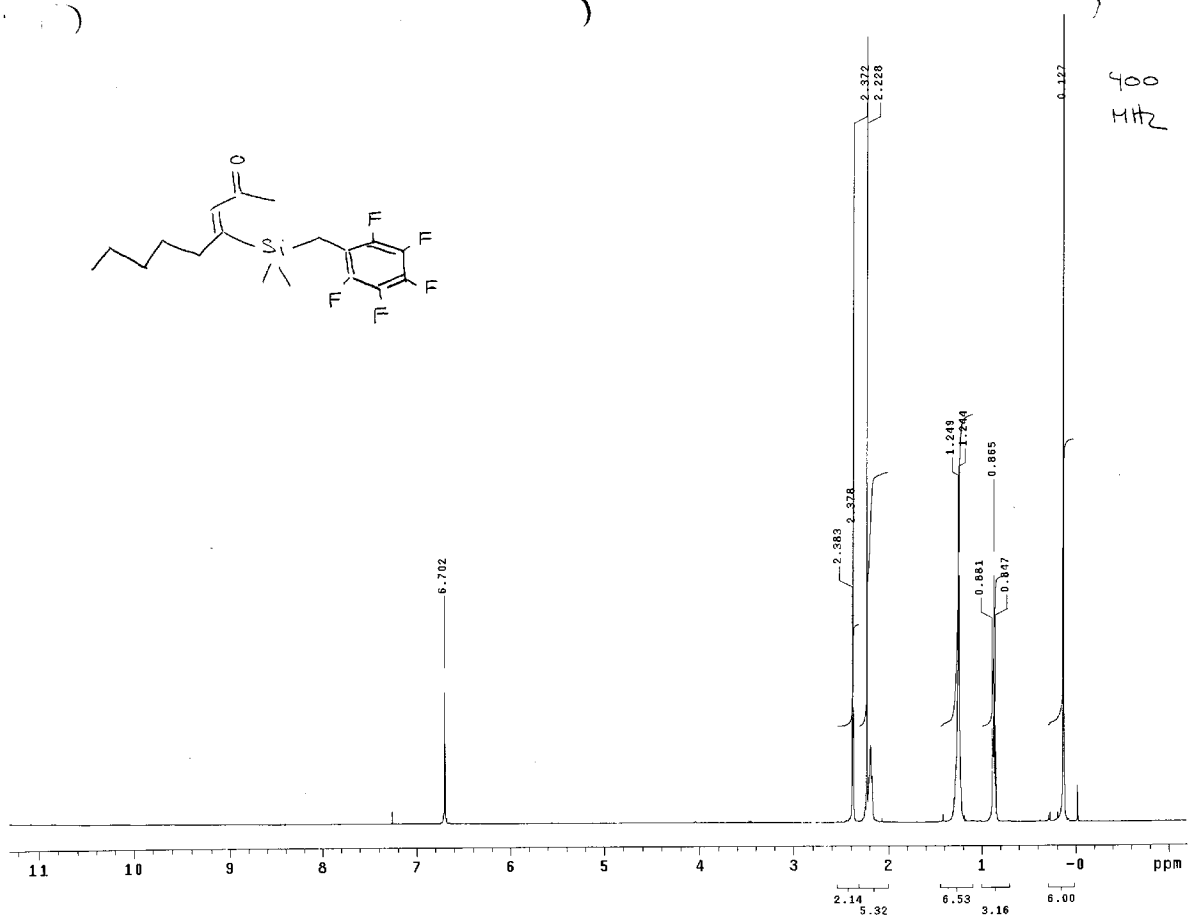
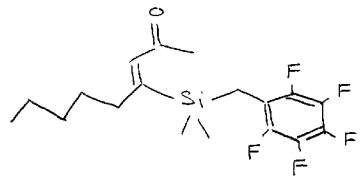
PERKIN ELMER

neat



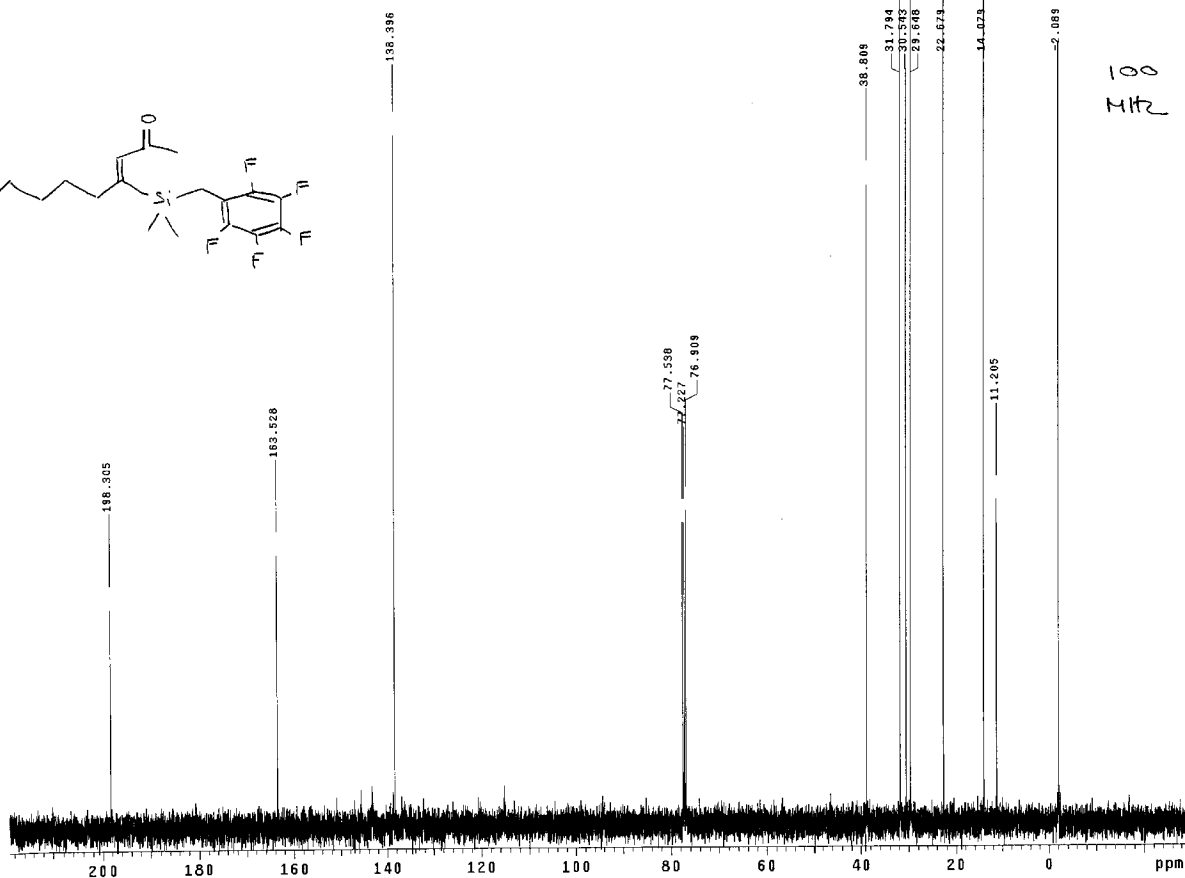
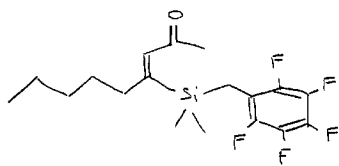
07/06/07 10:55  
X: 4 scans, 4.0cm⁻¹

ab120



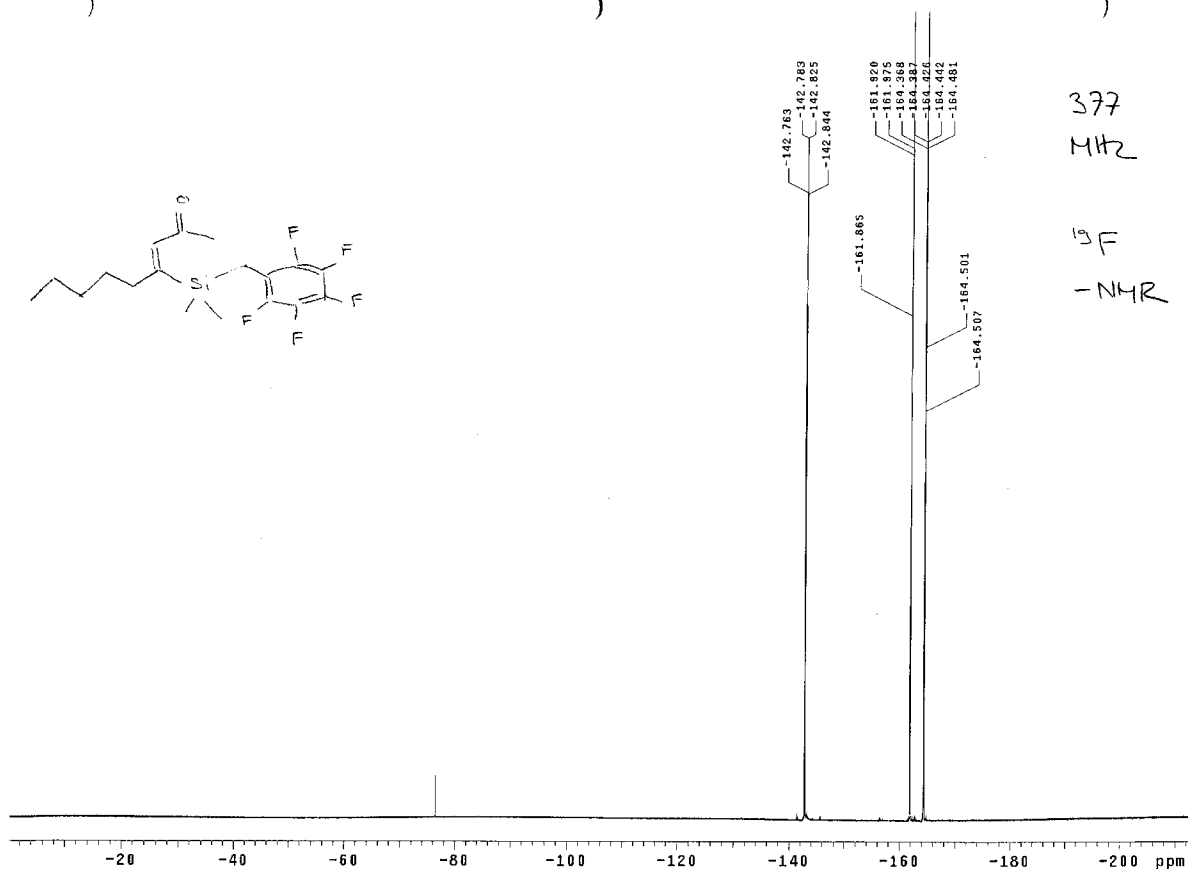
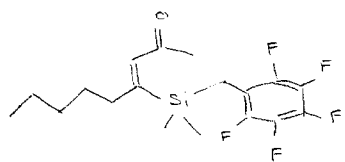
400 MHz

ab124



100  
MHz

ab124

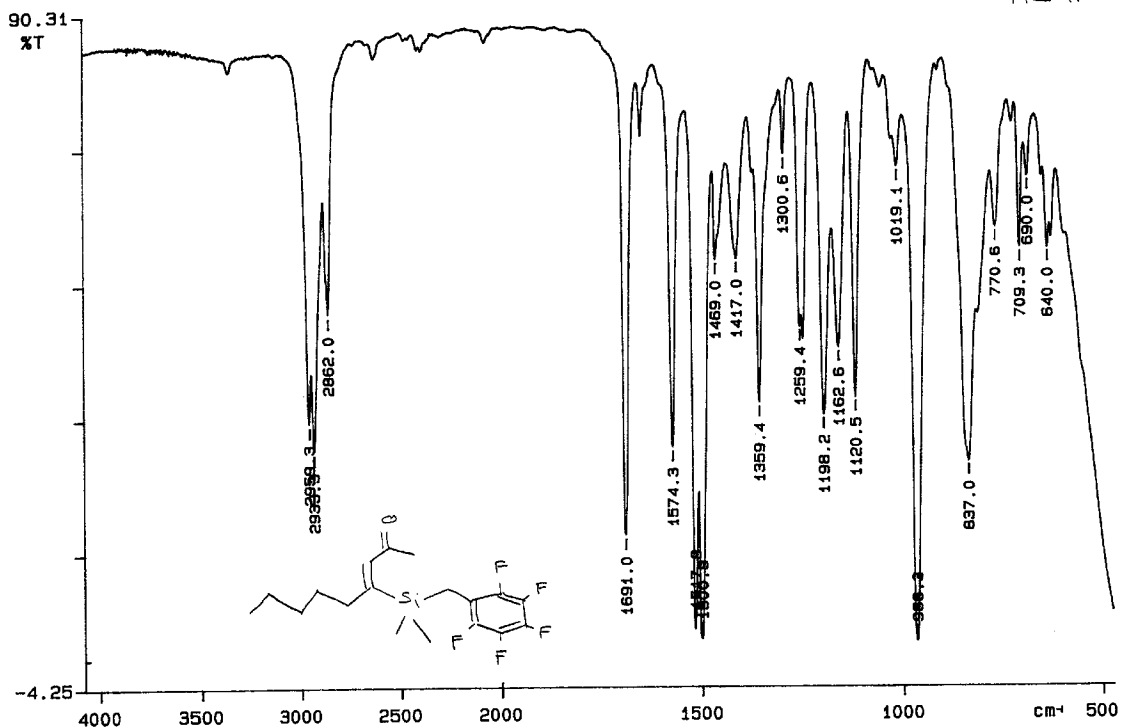


377  
MHz

19F  
-NMR

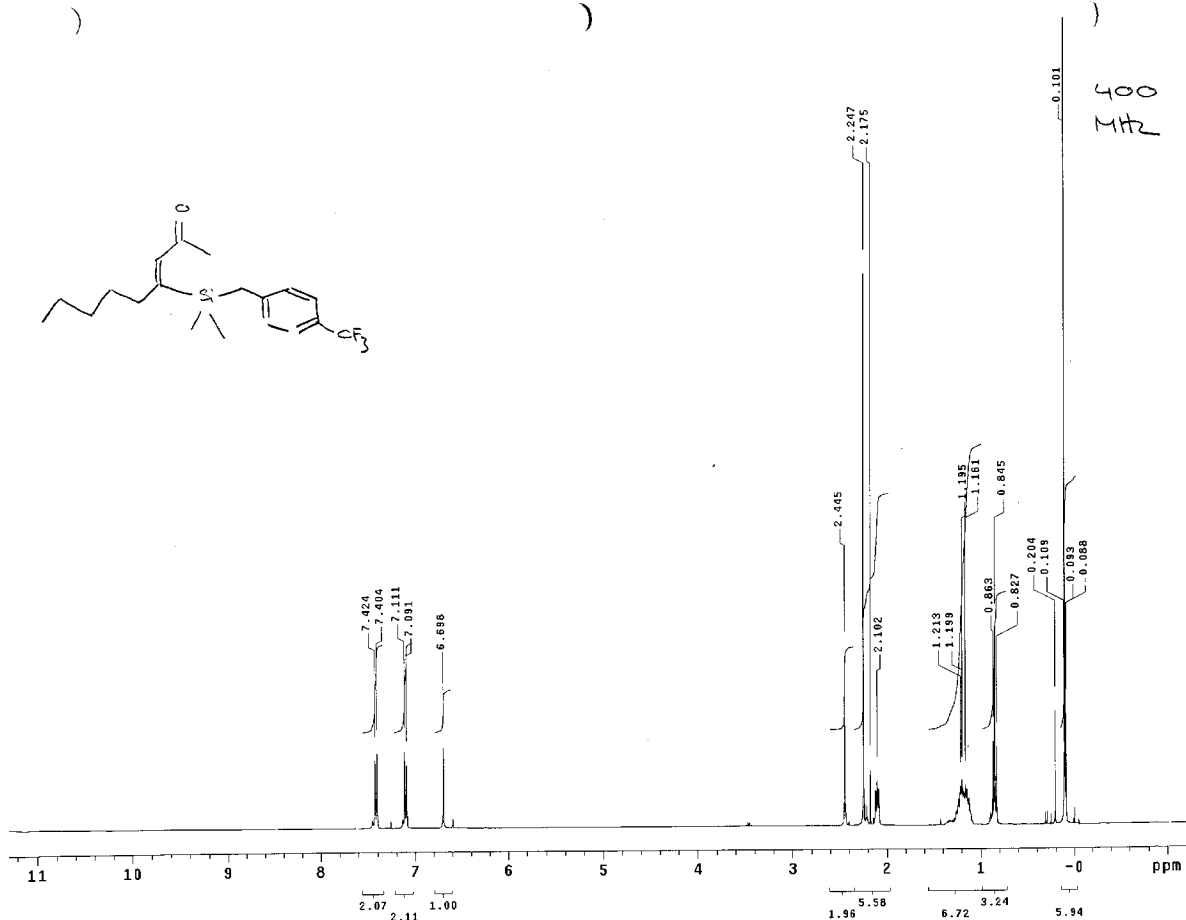
ab124

PERKIN ELMER

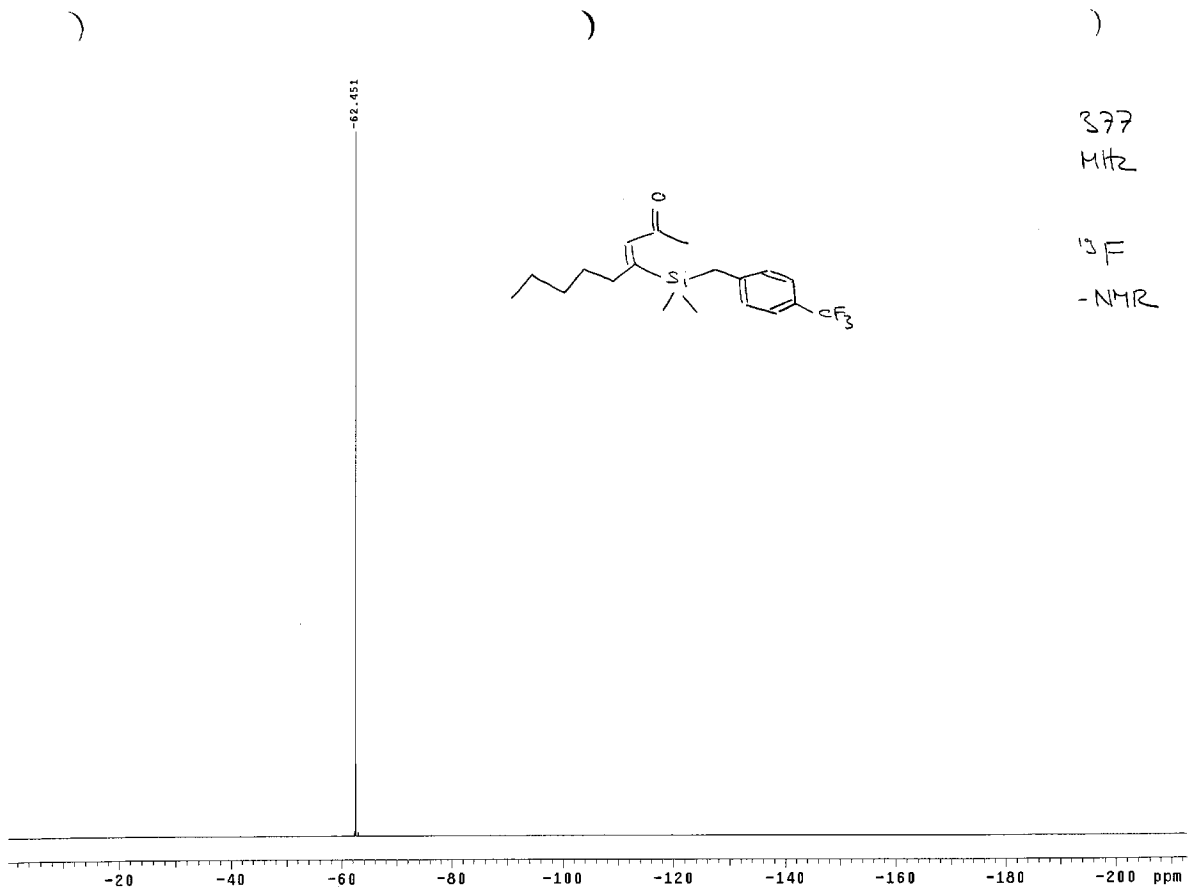
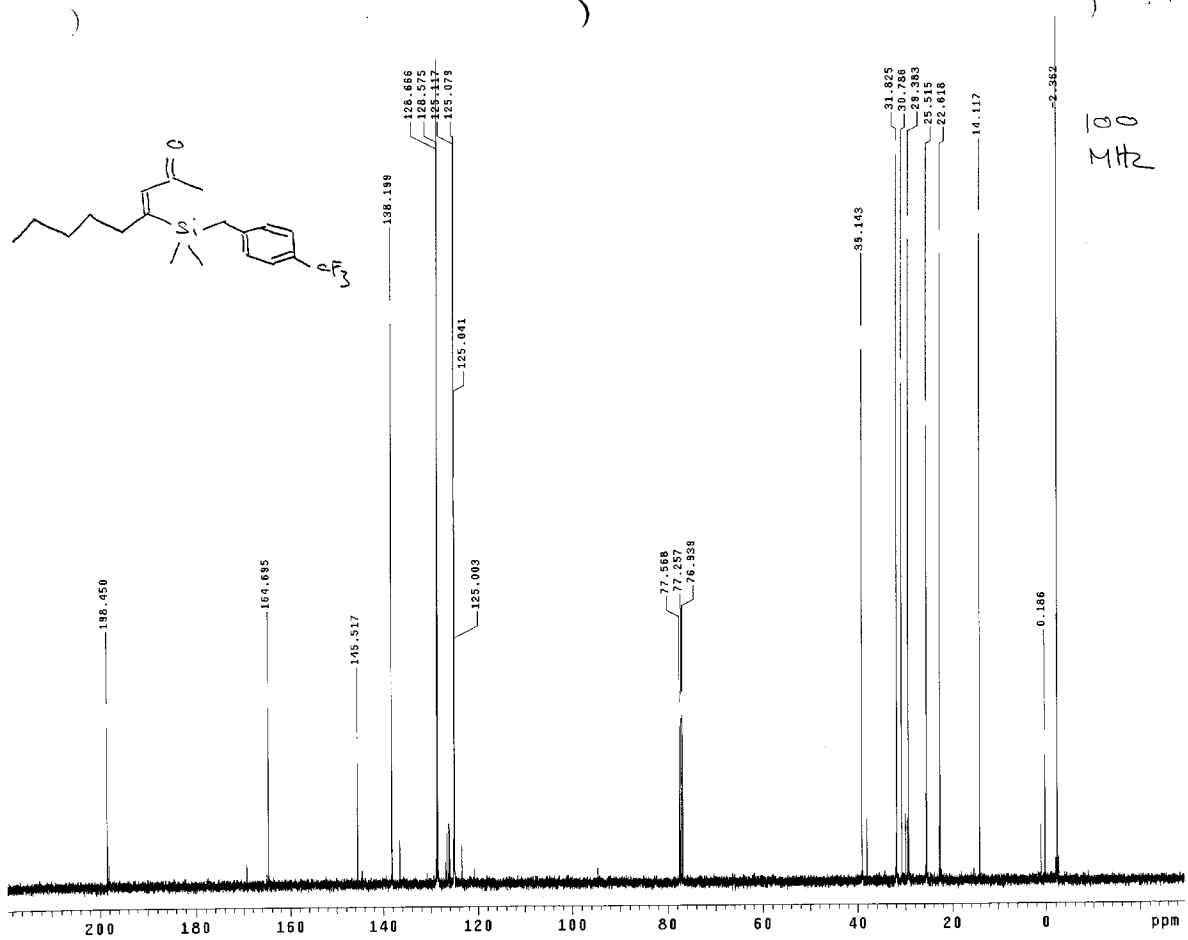


07/06/20 13:54  
X: 4 scans, 4.0cm-1

26124

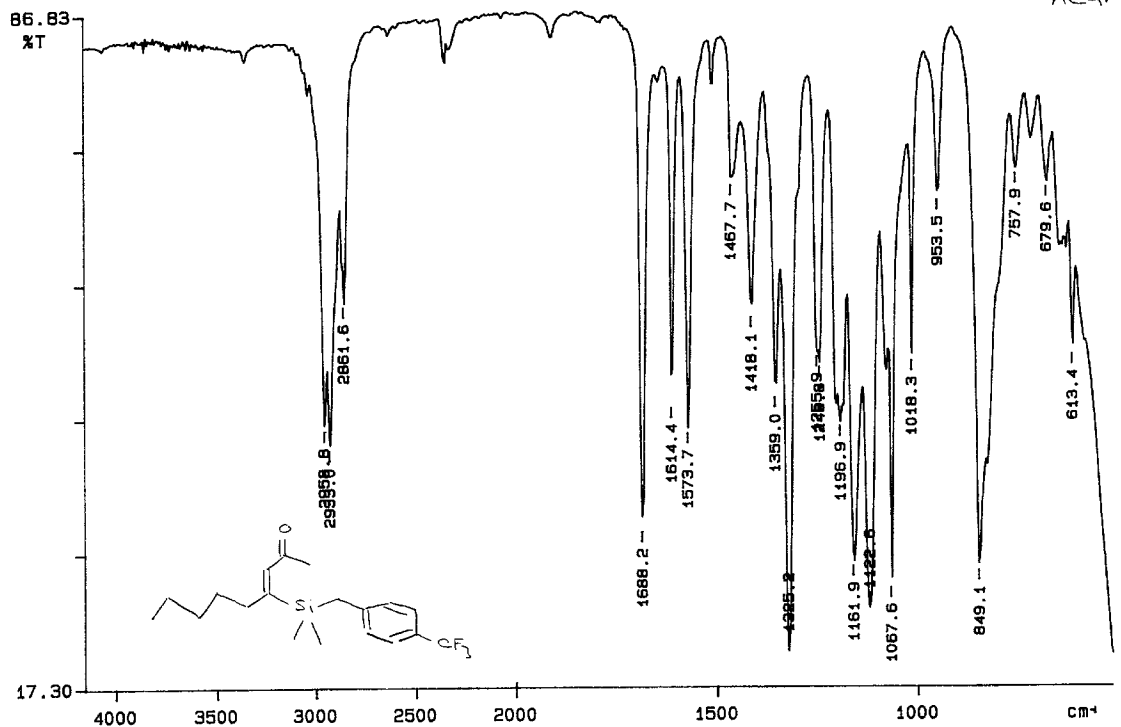


26125



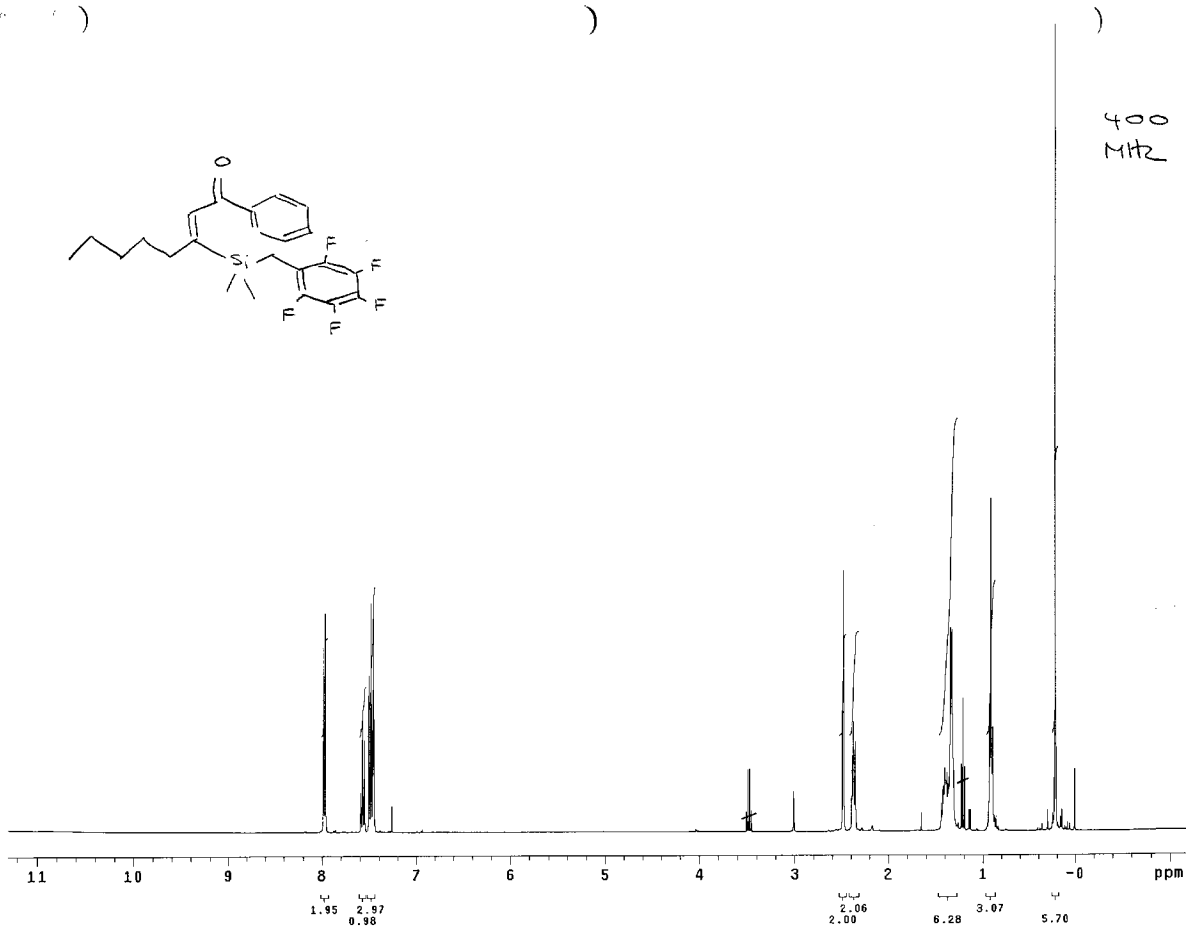
ab125

PERKIN ELMER

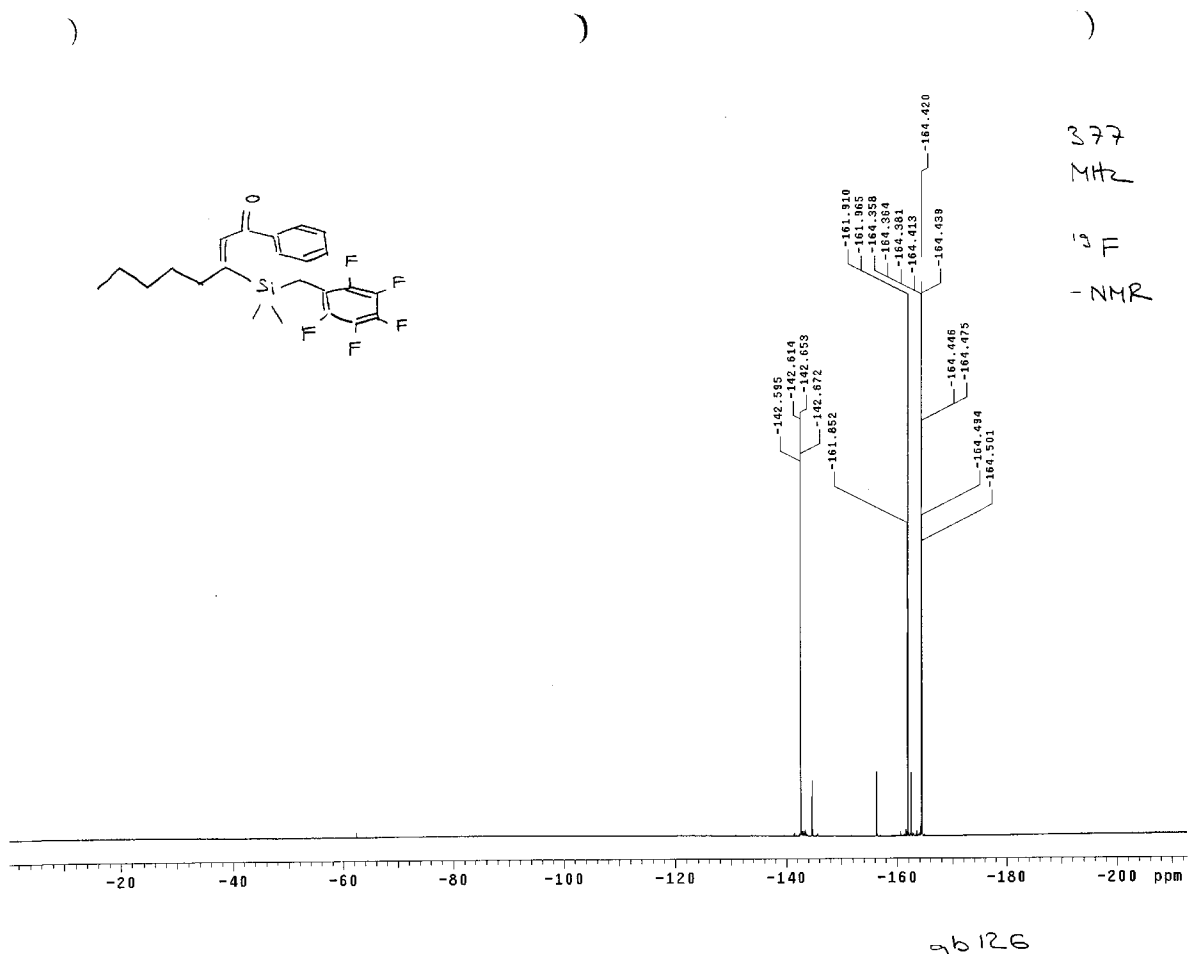
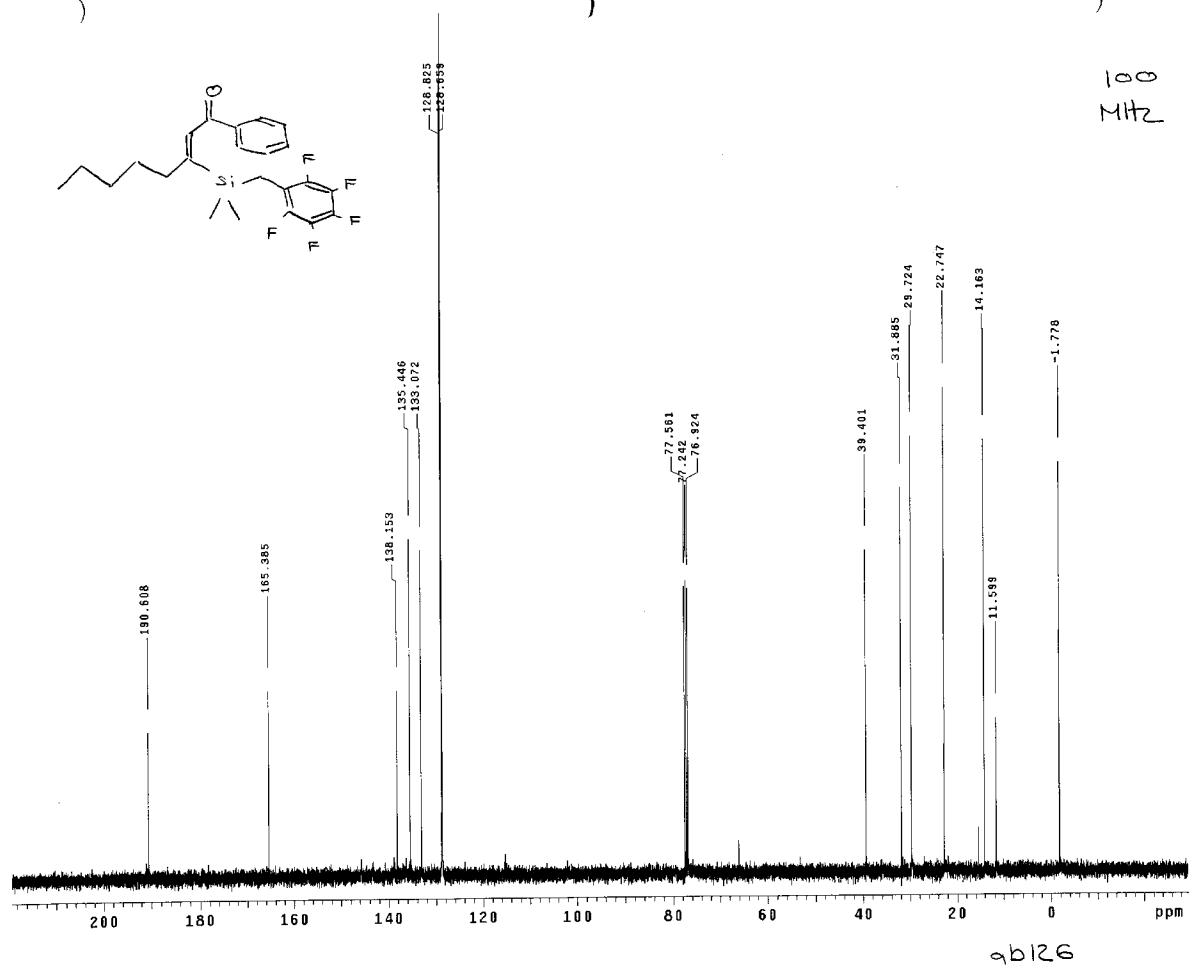


07/06/20 14:08  
X: 4 scans, 4.0cm<sup>-1</sup>

ab125

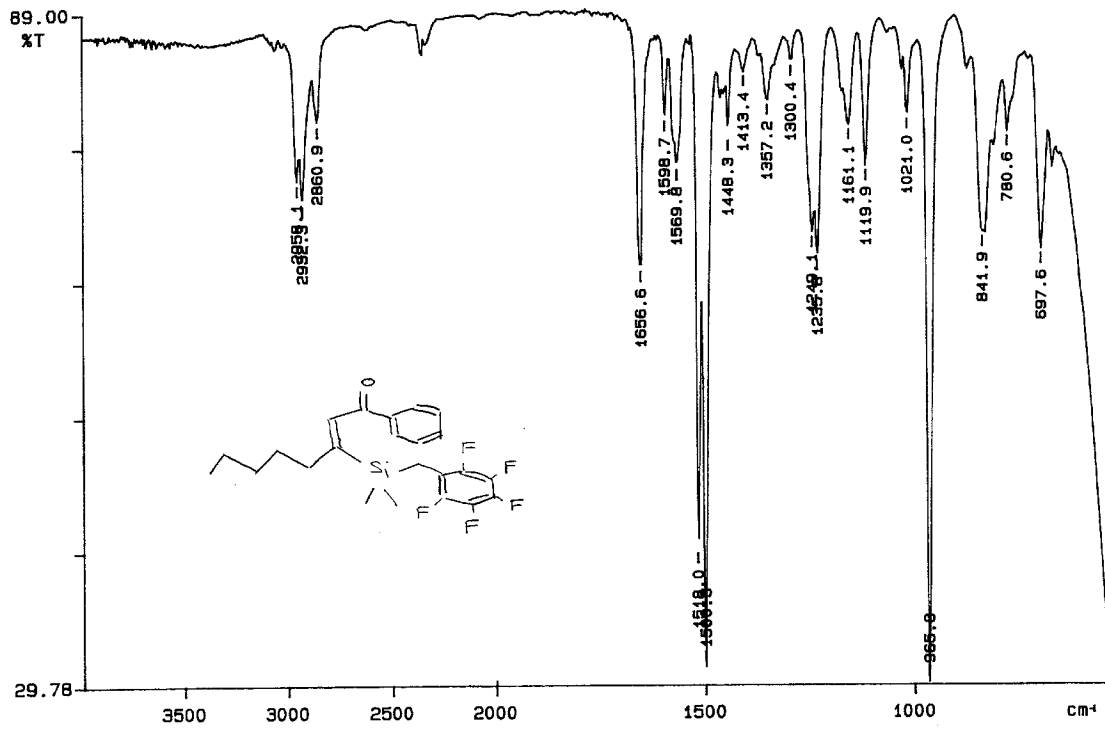


ab126



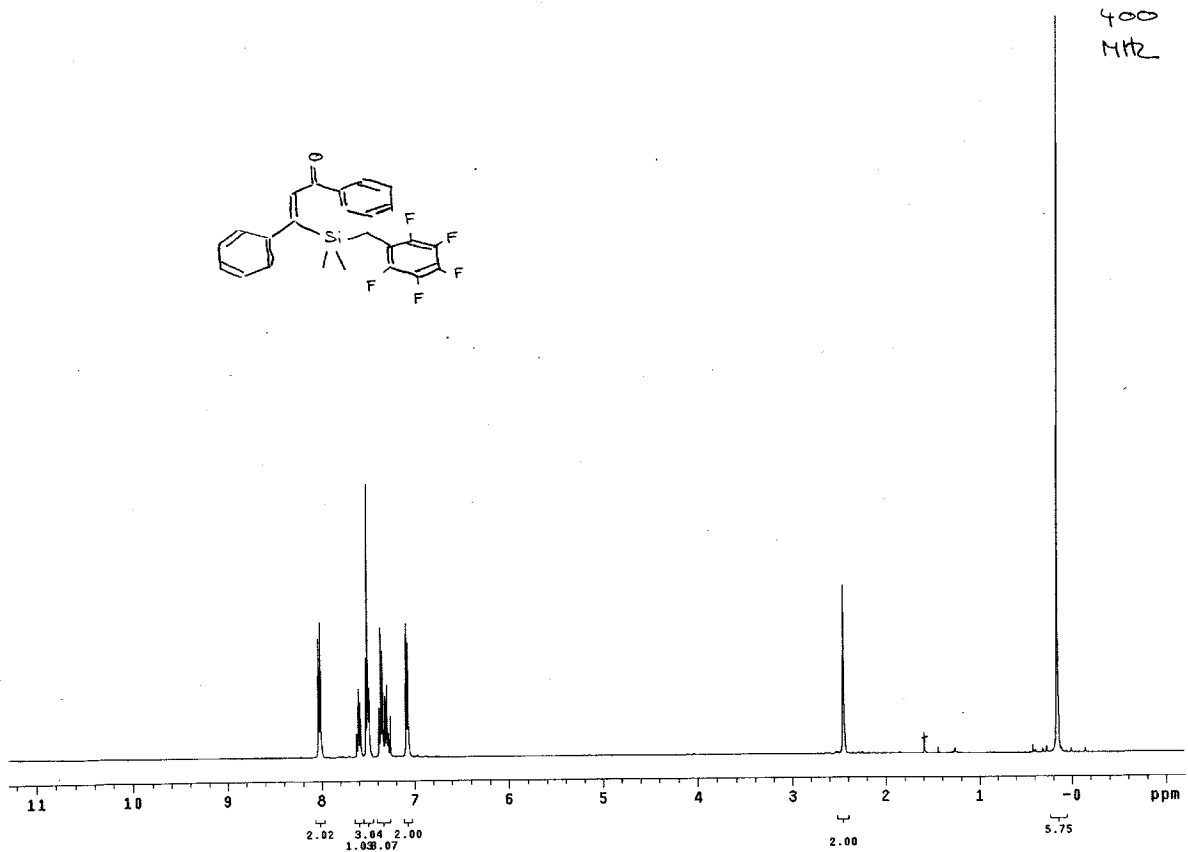
PERKIN ELMER

neat



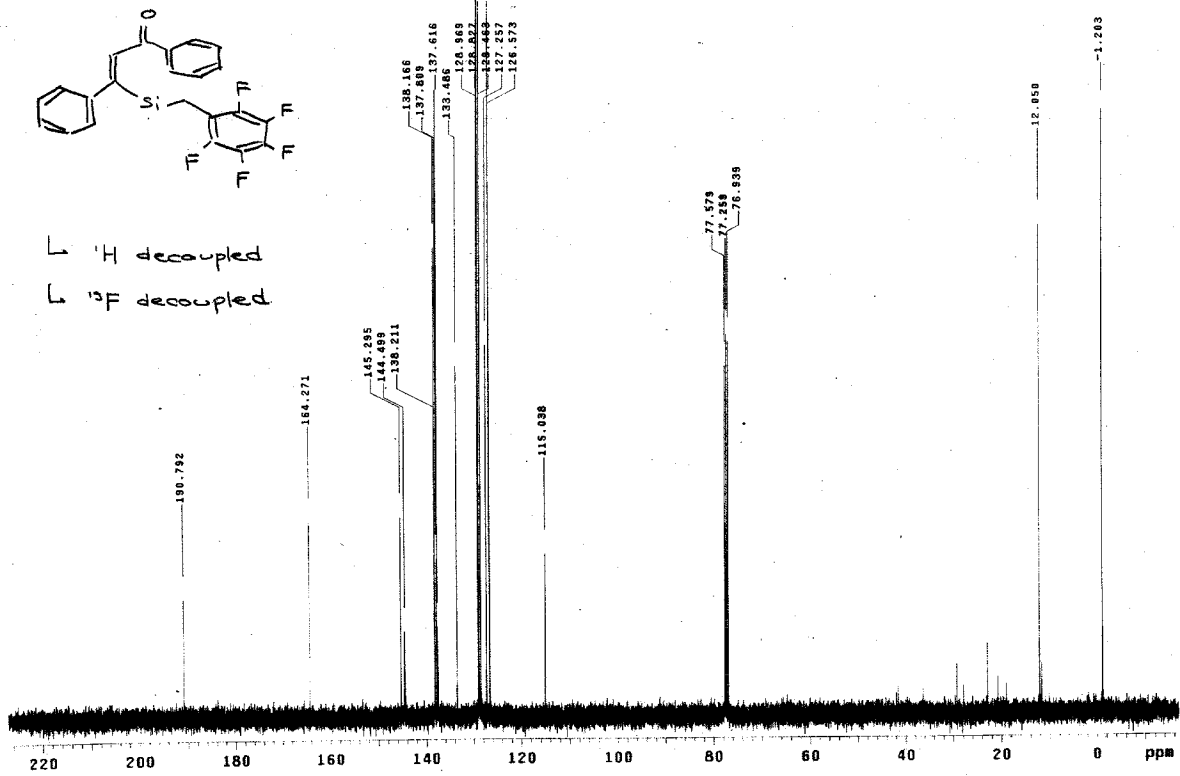
07/06/20 10:07  
X: 4 scans, 4.0cm-1

ab126

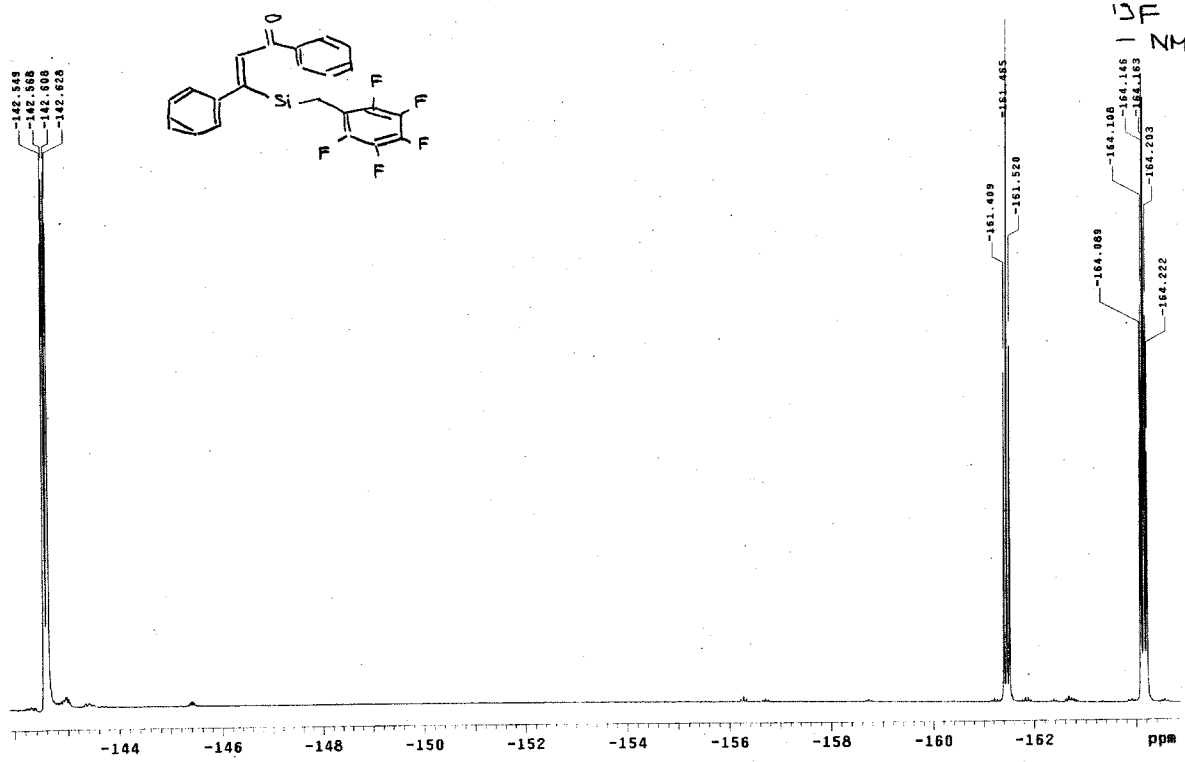


400  
MHz

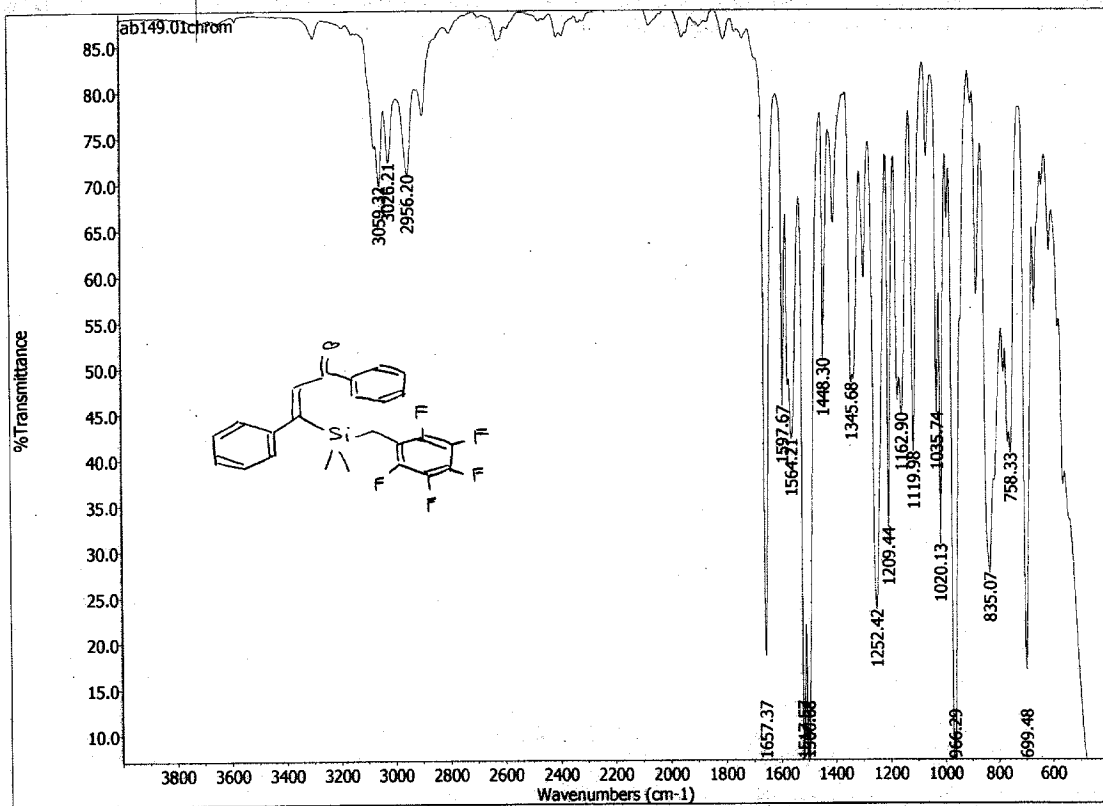
ab149



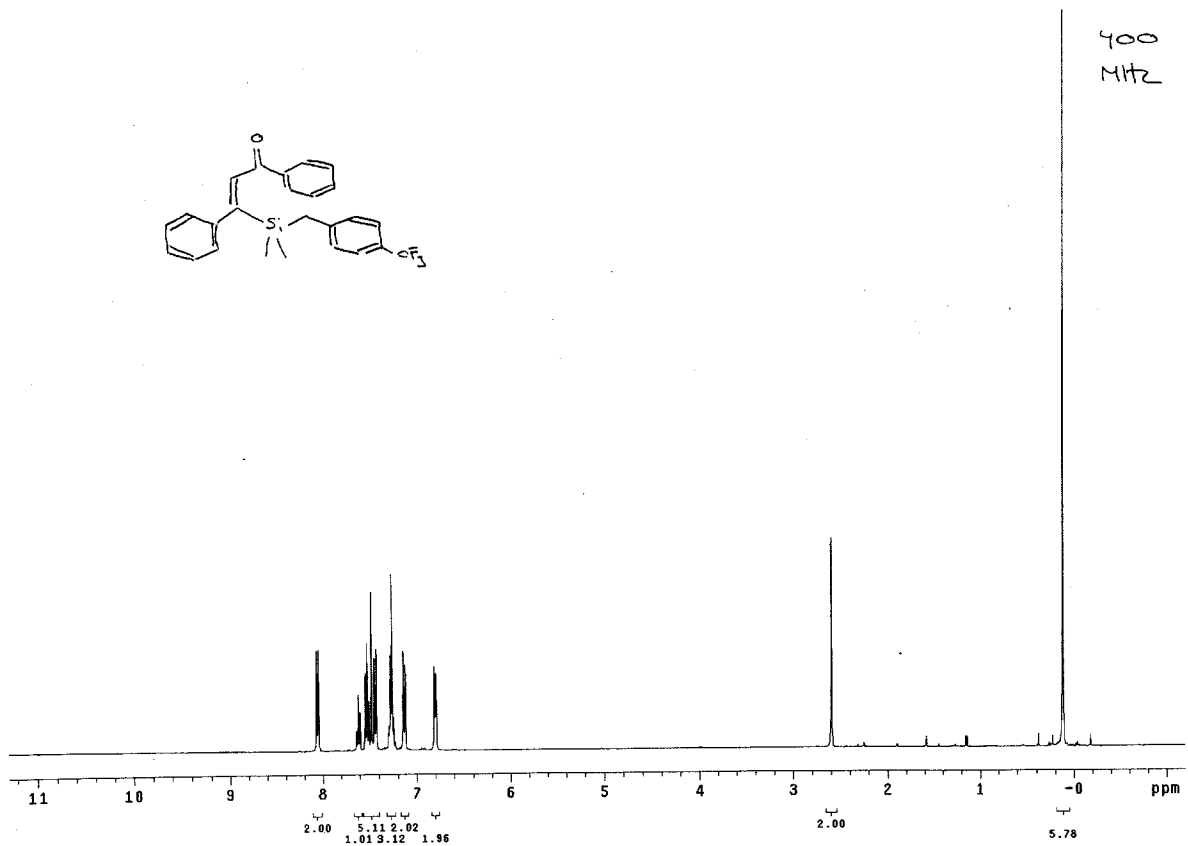
9b149



9b149

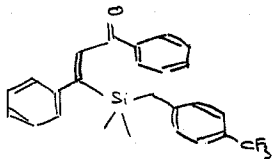


ab149



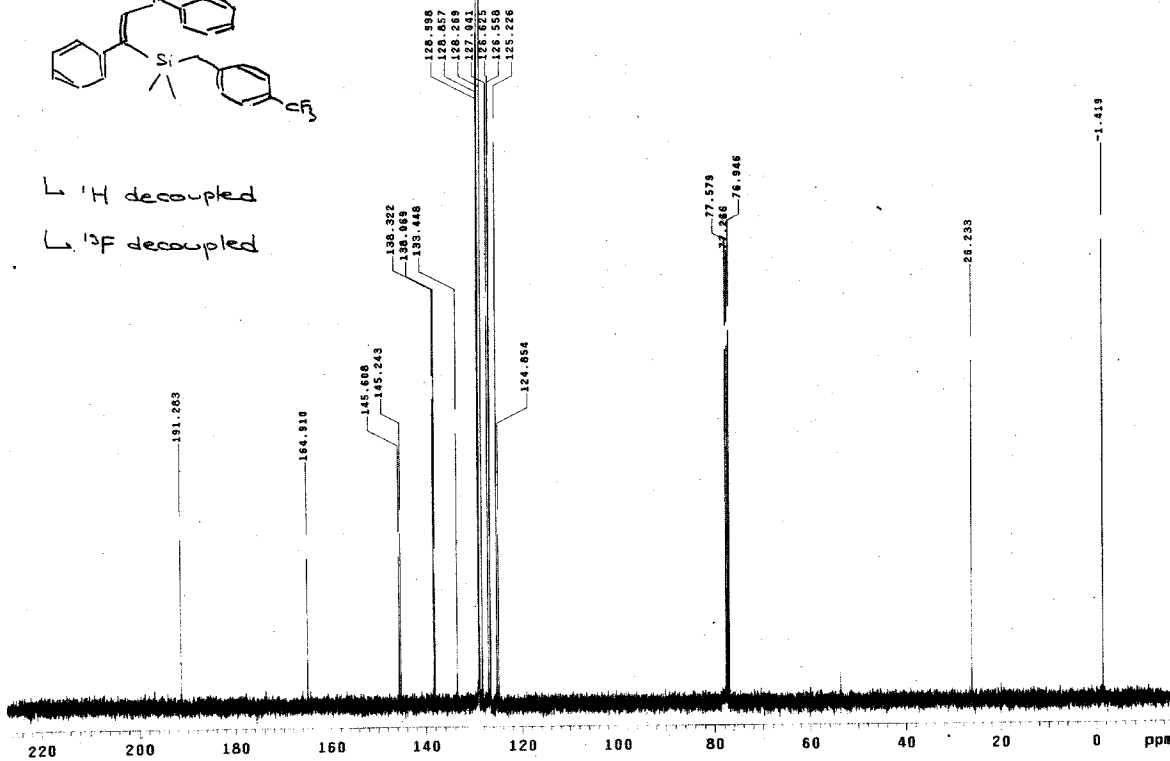
ab150

100  
MHz



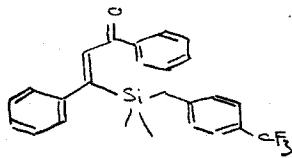
L <sup>1</sup>H decoupled

L <sup>13</sup>F decoupled

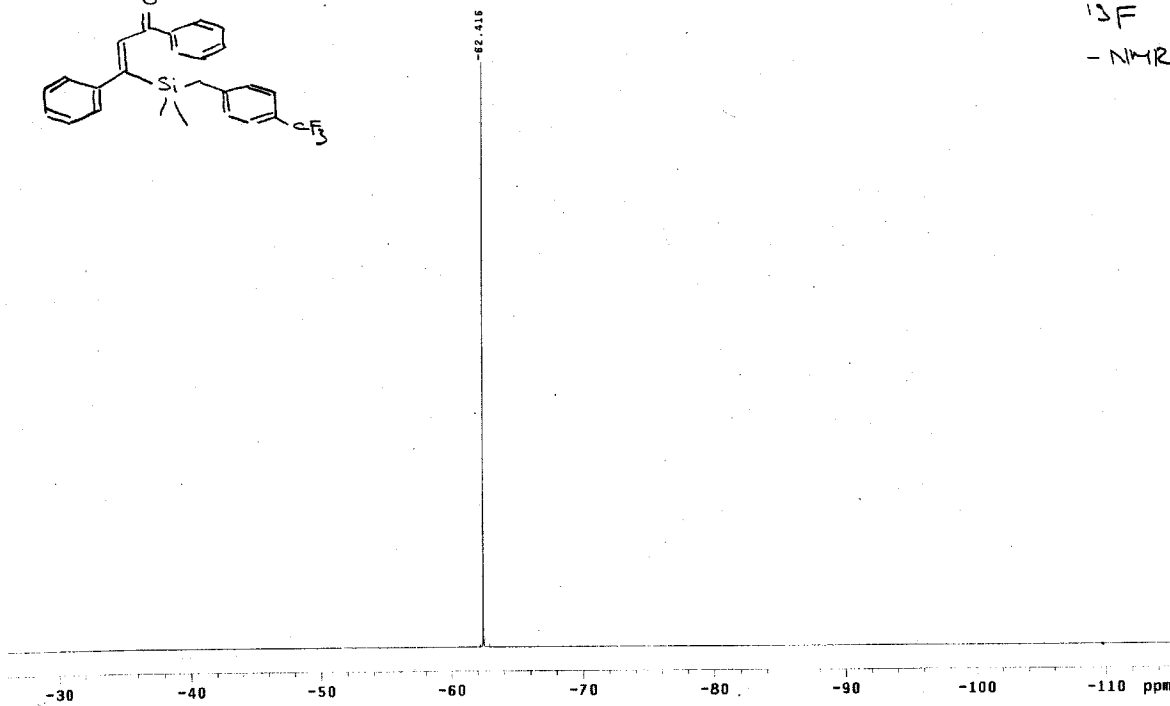


ab150

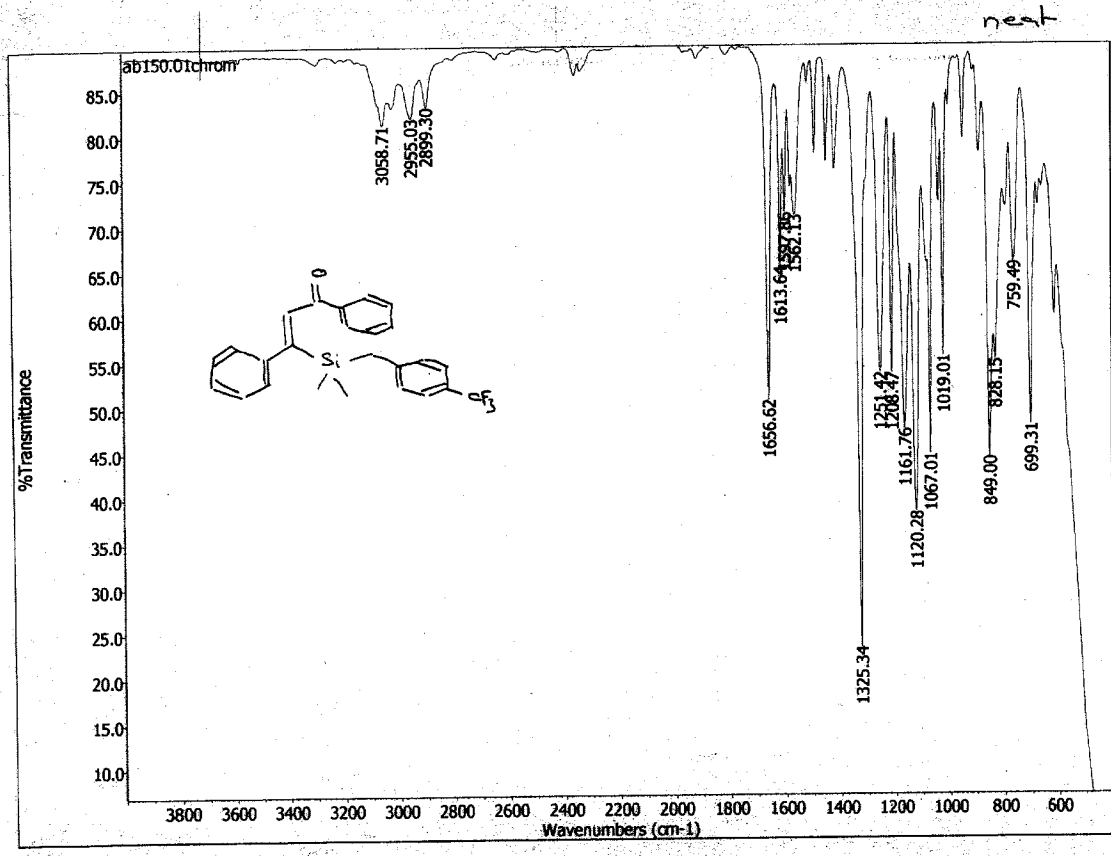
377  
MHz



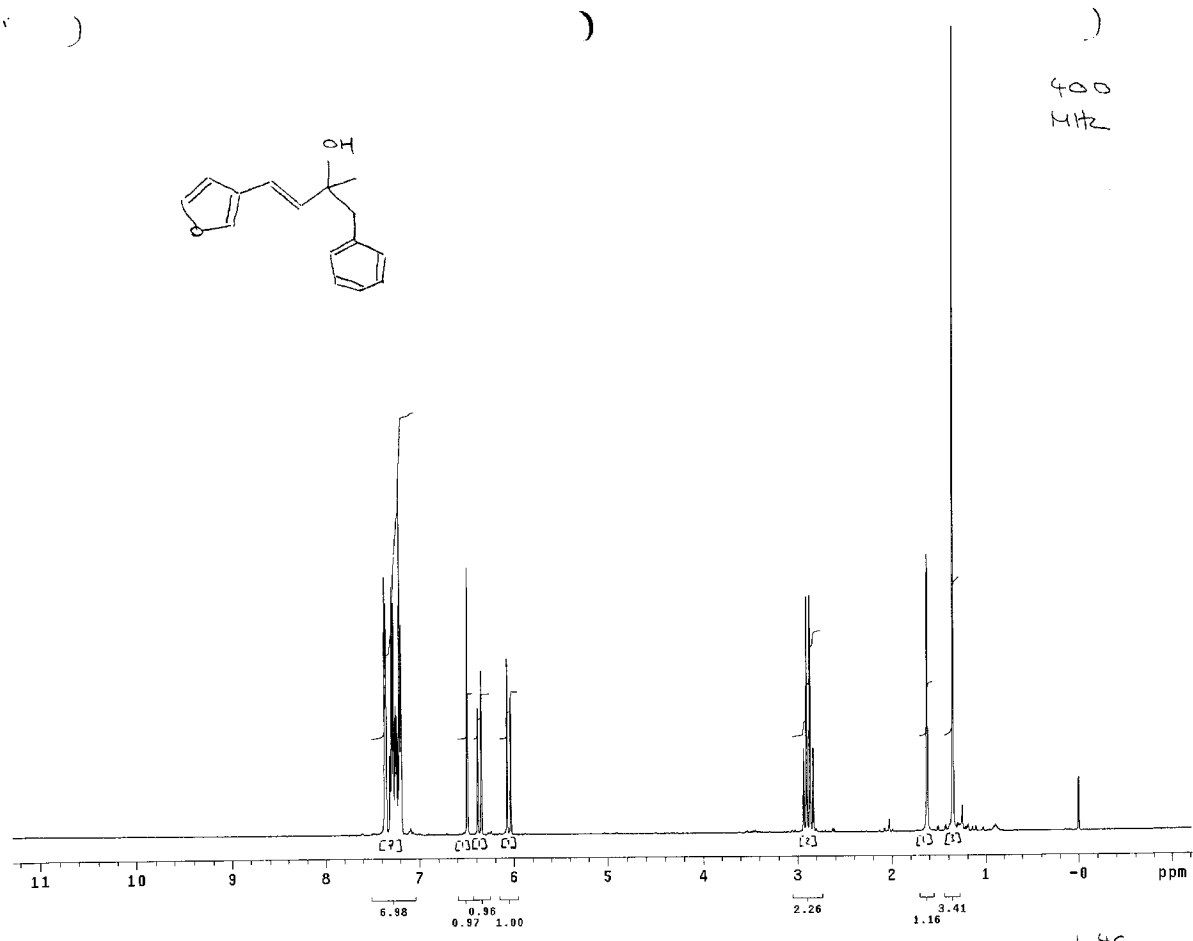
<sup>13</sup>F  
- NMR



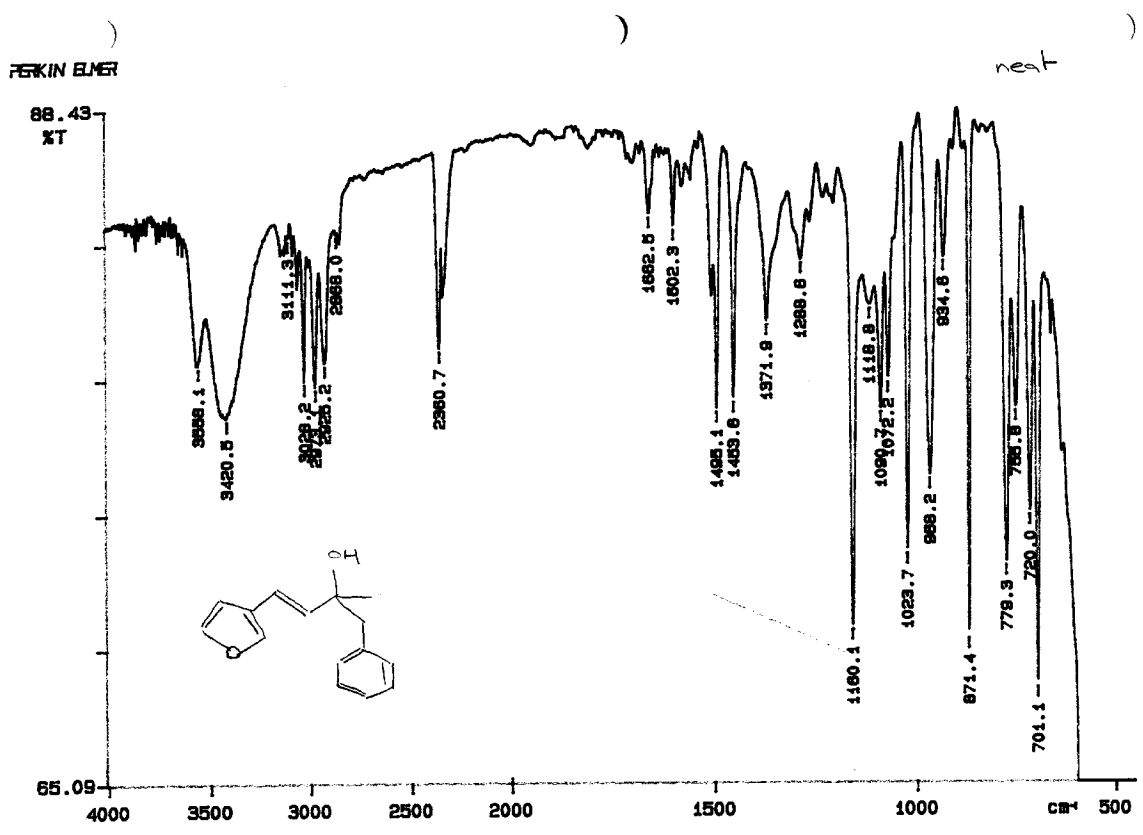
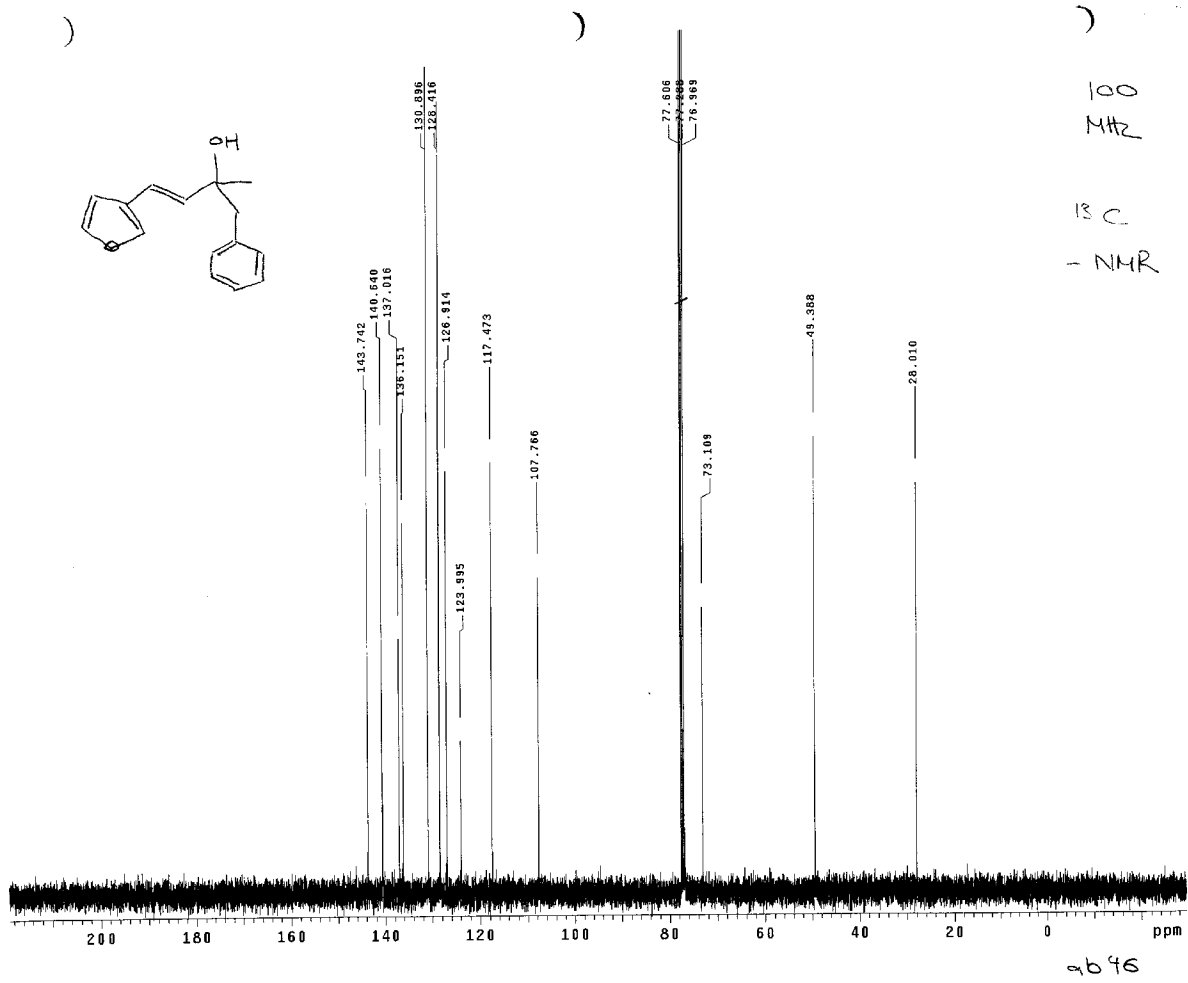
ab150



ab150



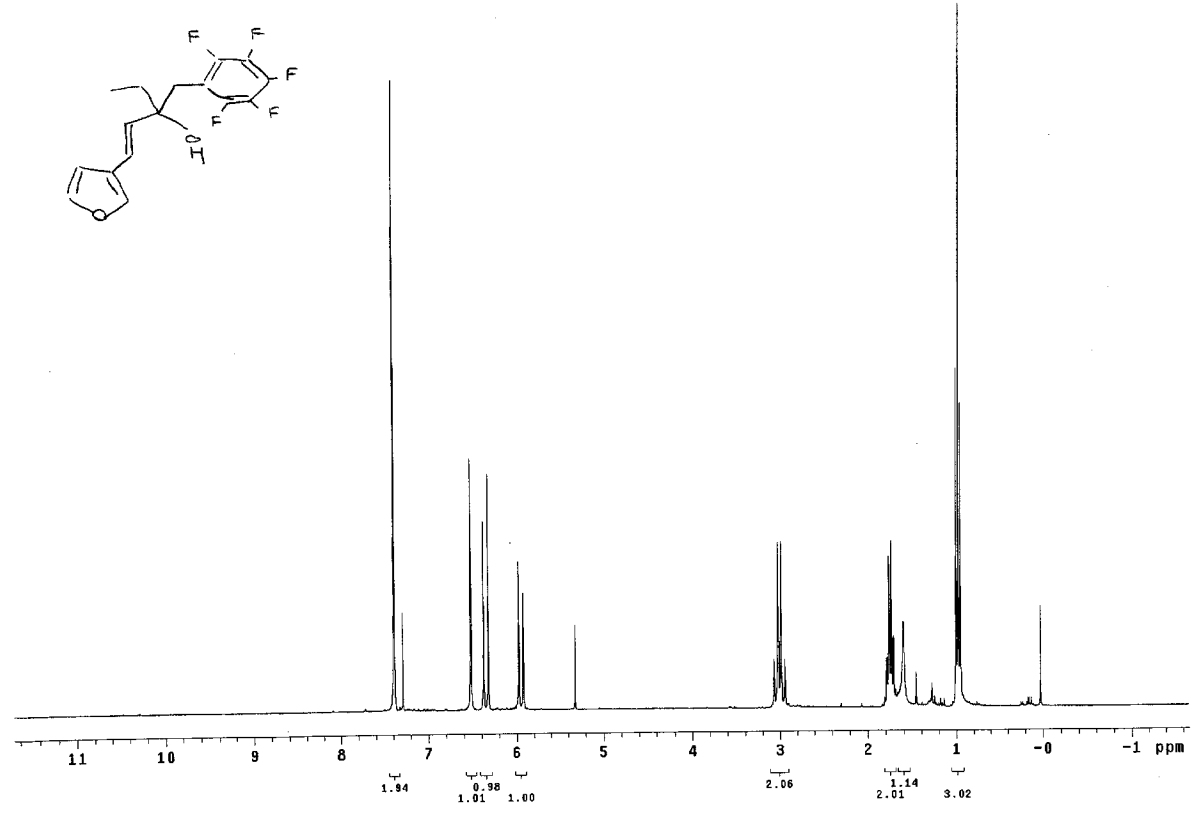
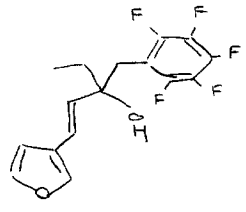
ab46



06/10/30 16:55  
X: 4 scans, 4.0cm-1

9696

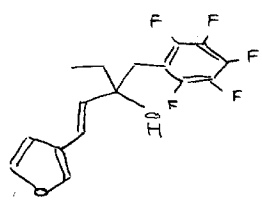
300  
MHz



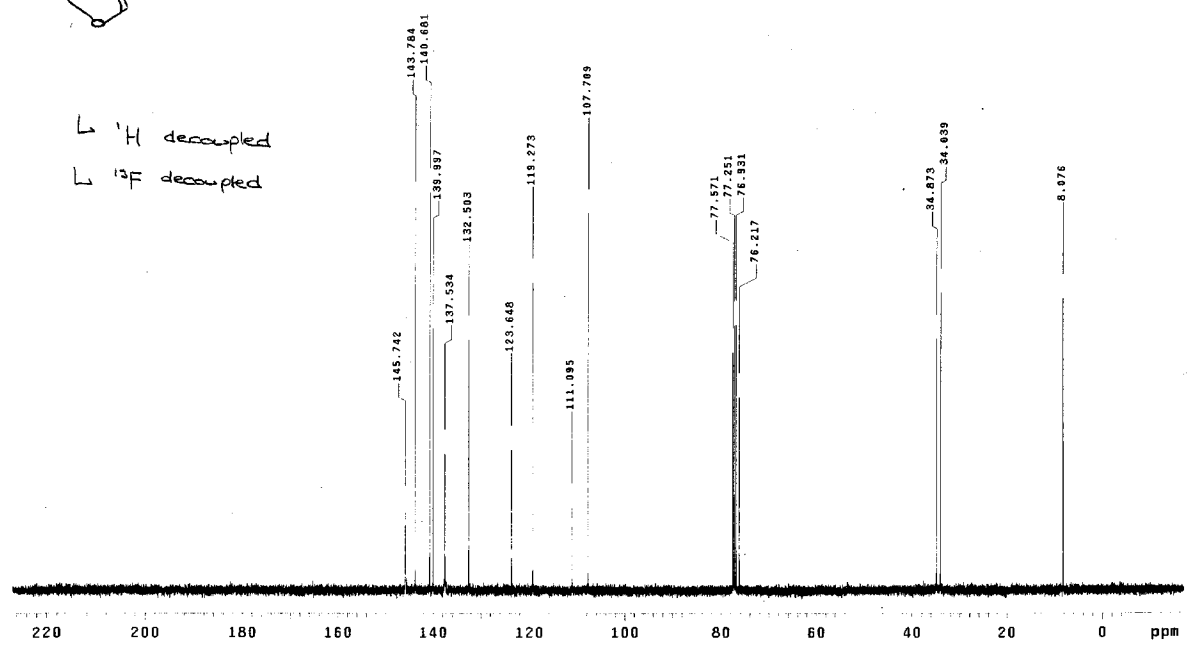
ab146

100  
MHz

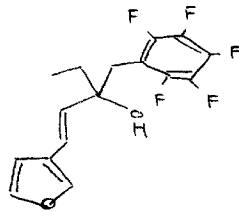
<sup>13</sup>C  
- NMR



↳ <sup>1</sup>H decoupled  
↳ <sup>13</sup>C decoupled

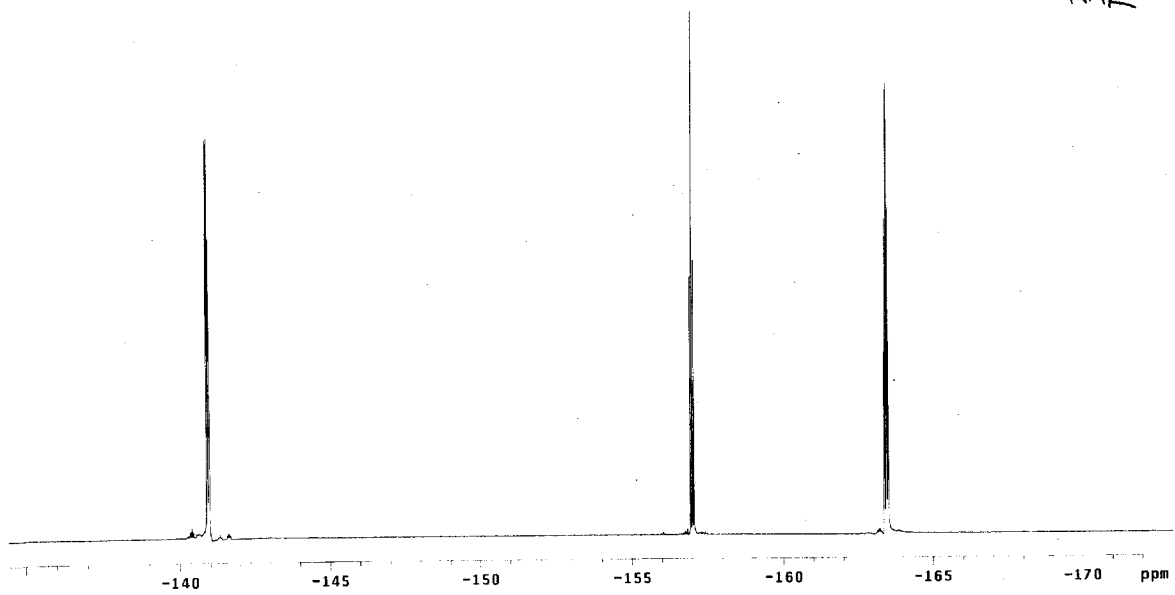


ab146

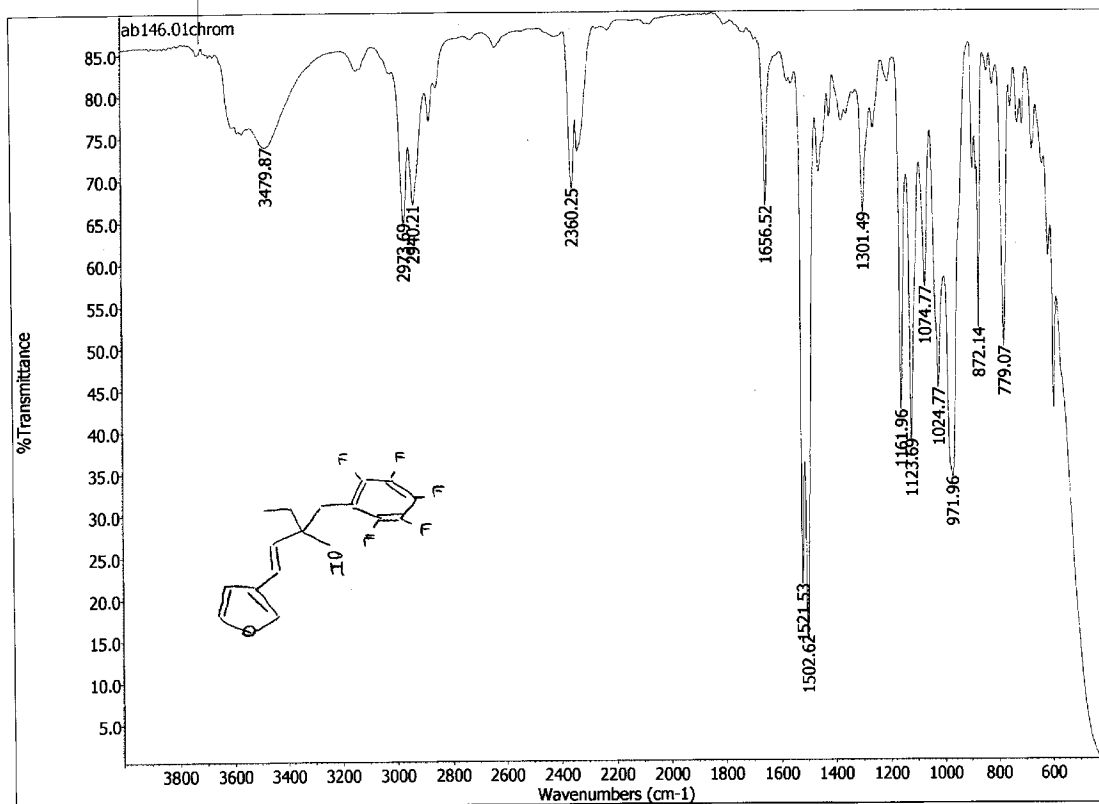


376  
MHz

<sup>19</sup>F  
-NMR



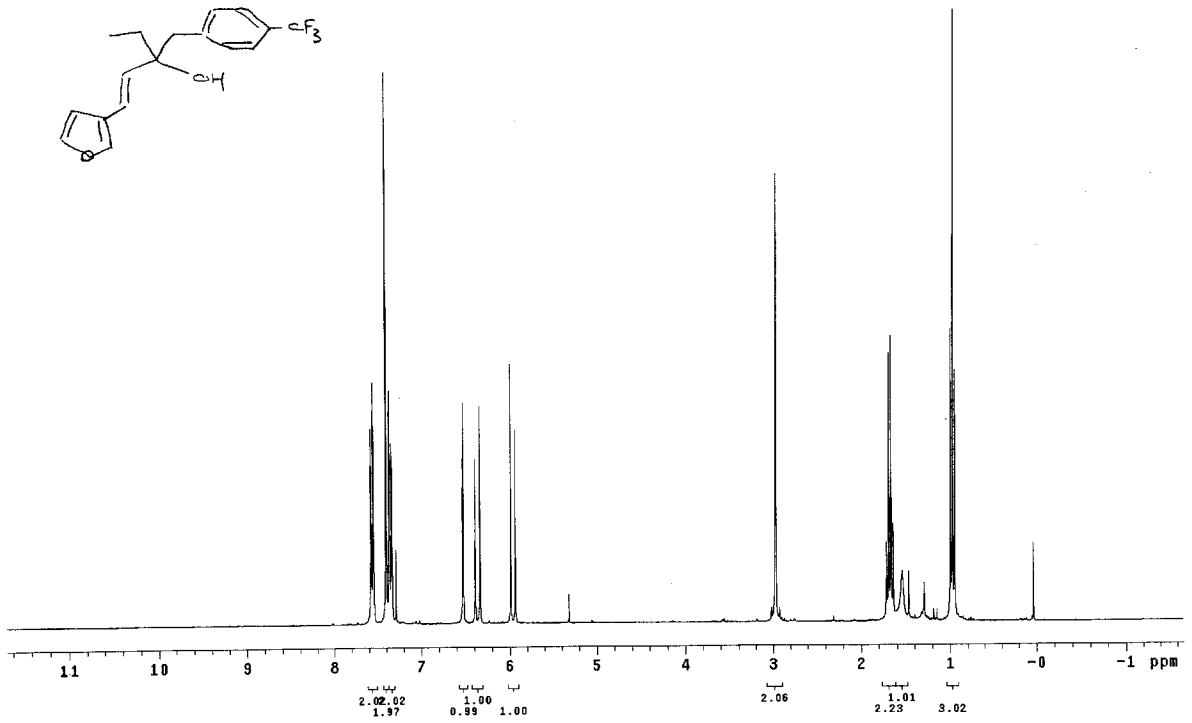
ab146



neat

ab146

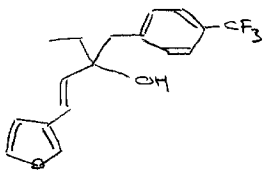
300  
MHz



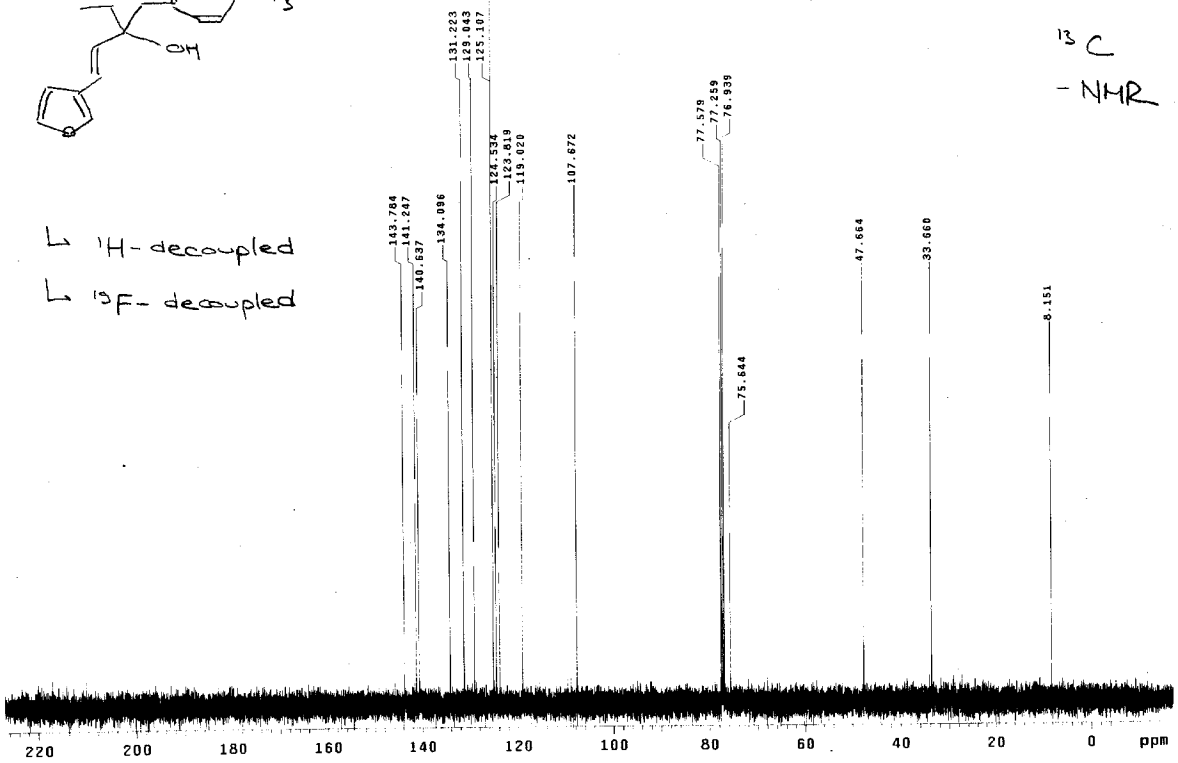
ab147

100  
MHz

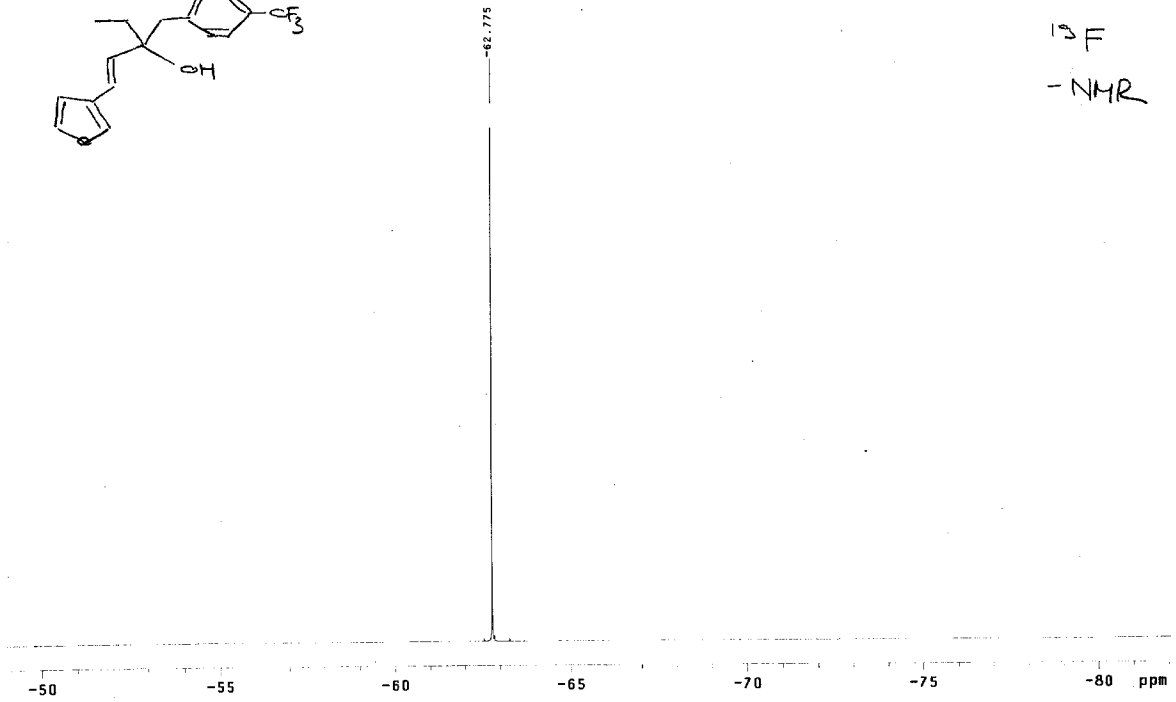
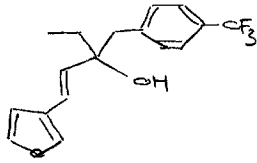
<sup>13</sup>C  
- NMR



↳ <sup>1</sup>H-decoupled  
↳ <sup>13</sup>F-decoupled



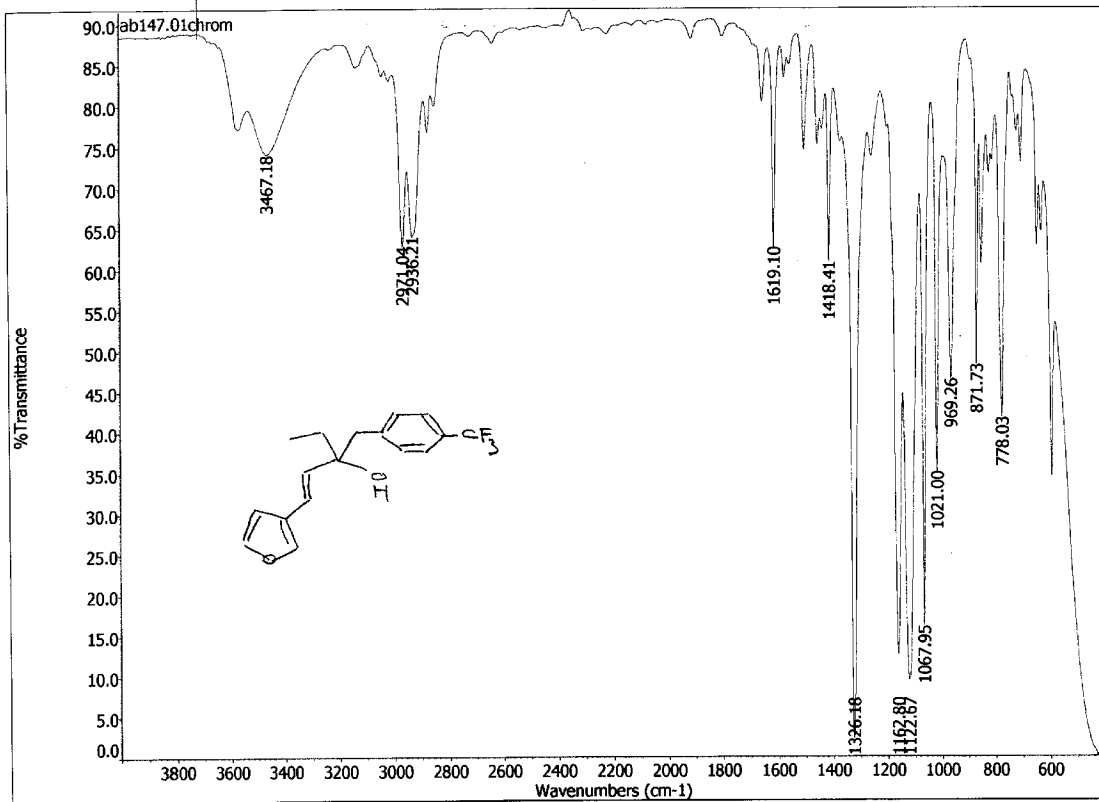
ab147



376  
MHz

13C  
-NMR

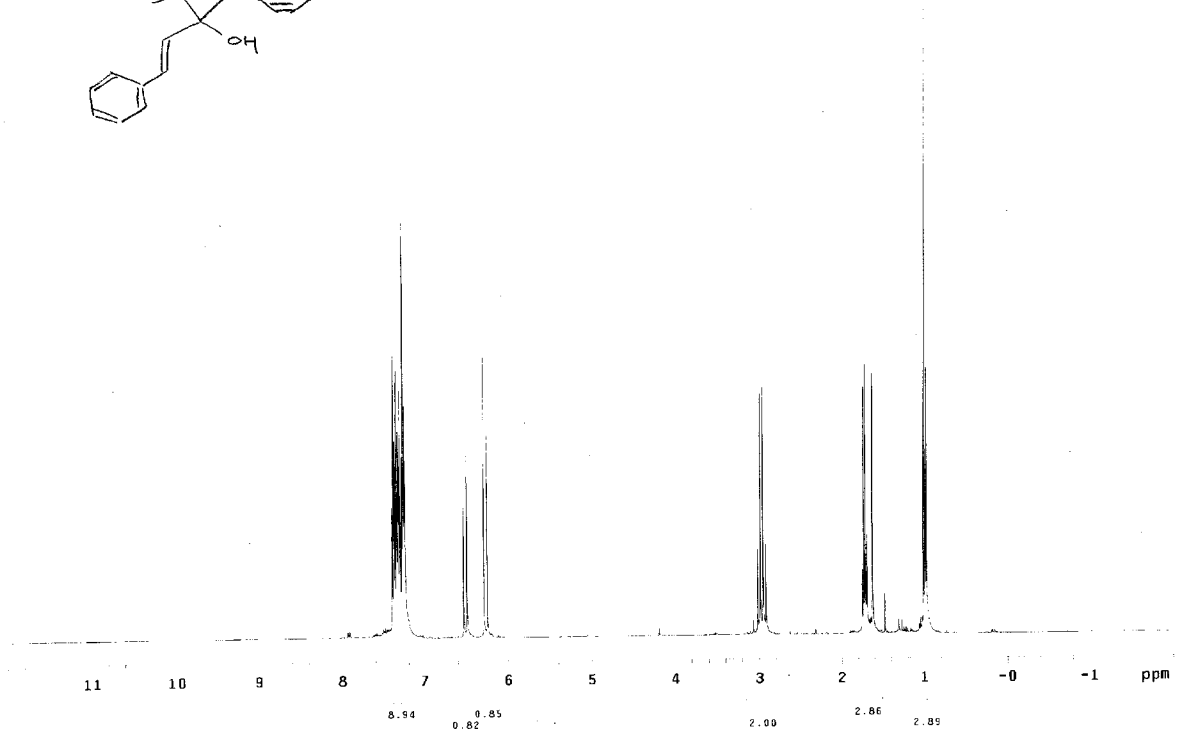
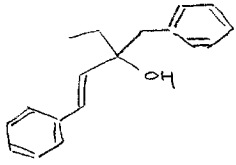
96147



neat

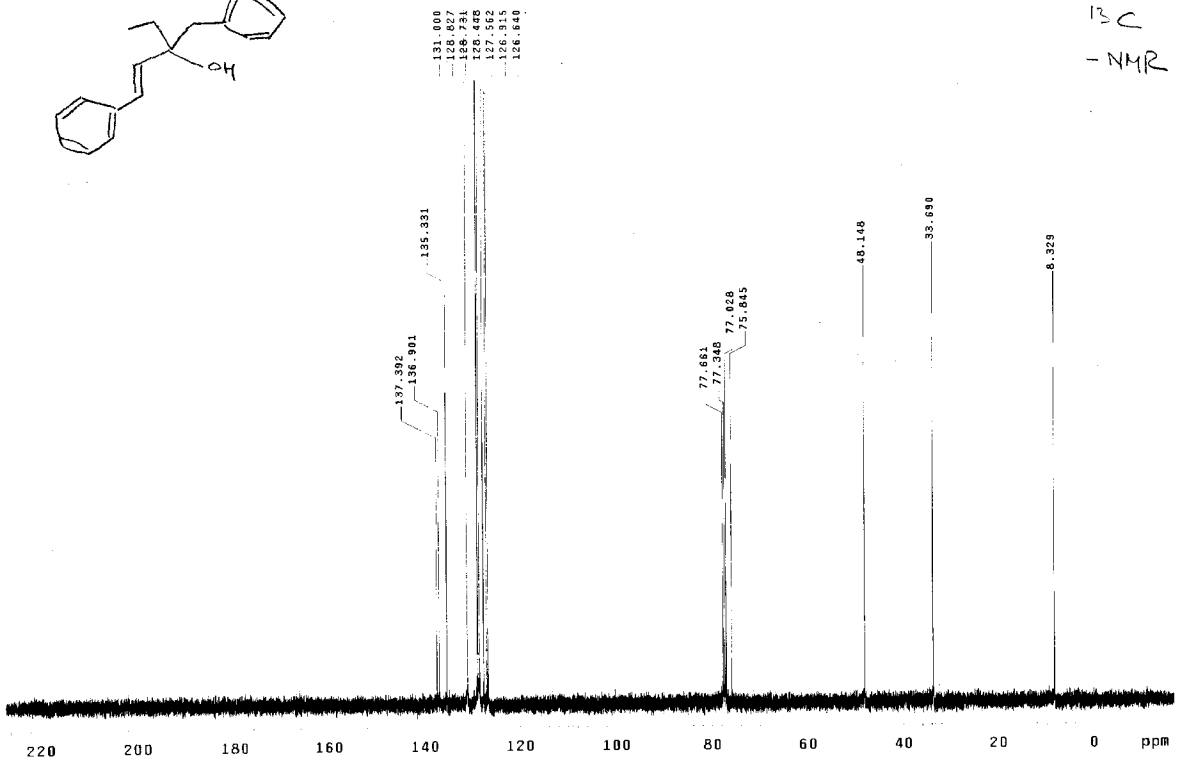
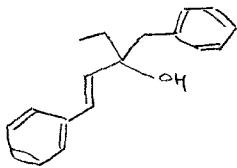
96147

400  
MHz



ab194

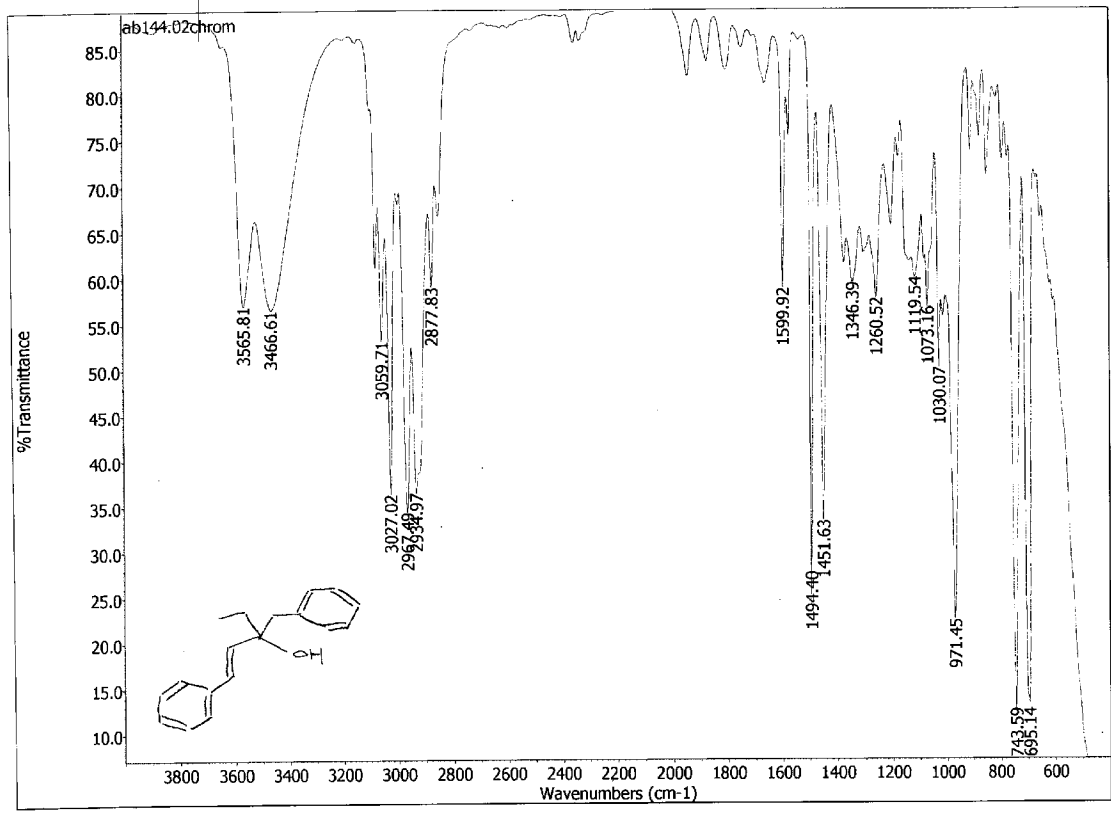
100  
MHz



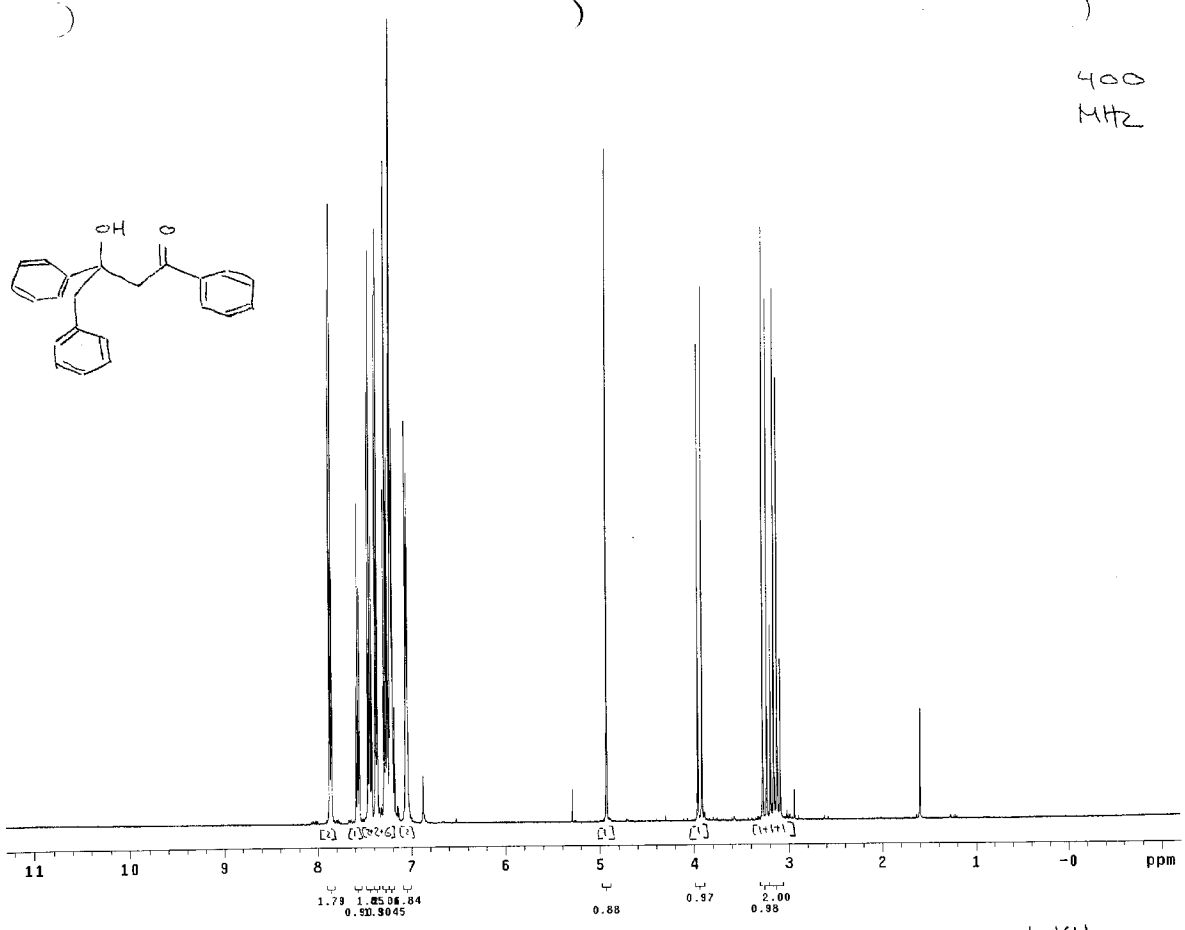
<sup>13</sup>C  
-NMR

ab194

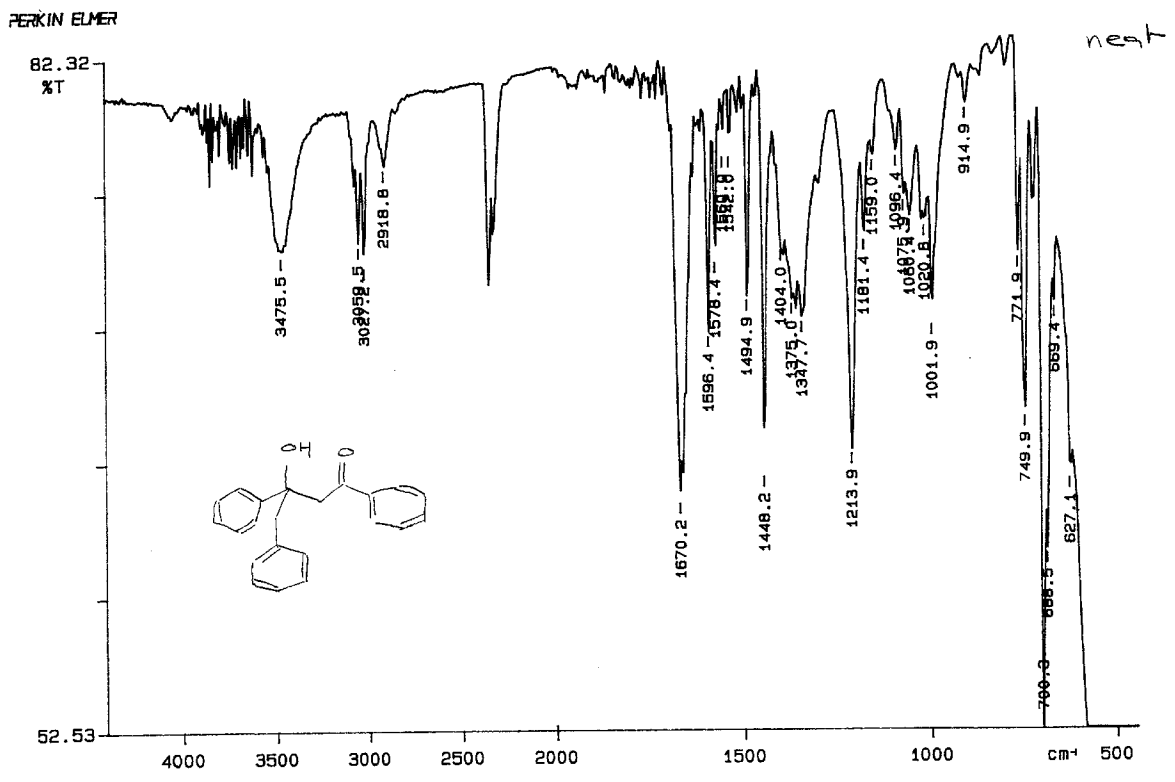
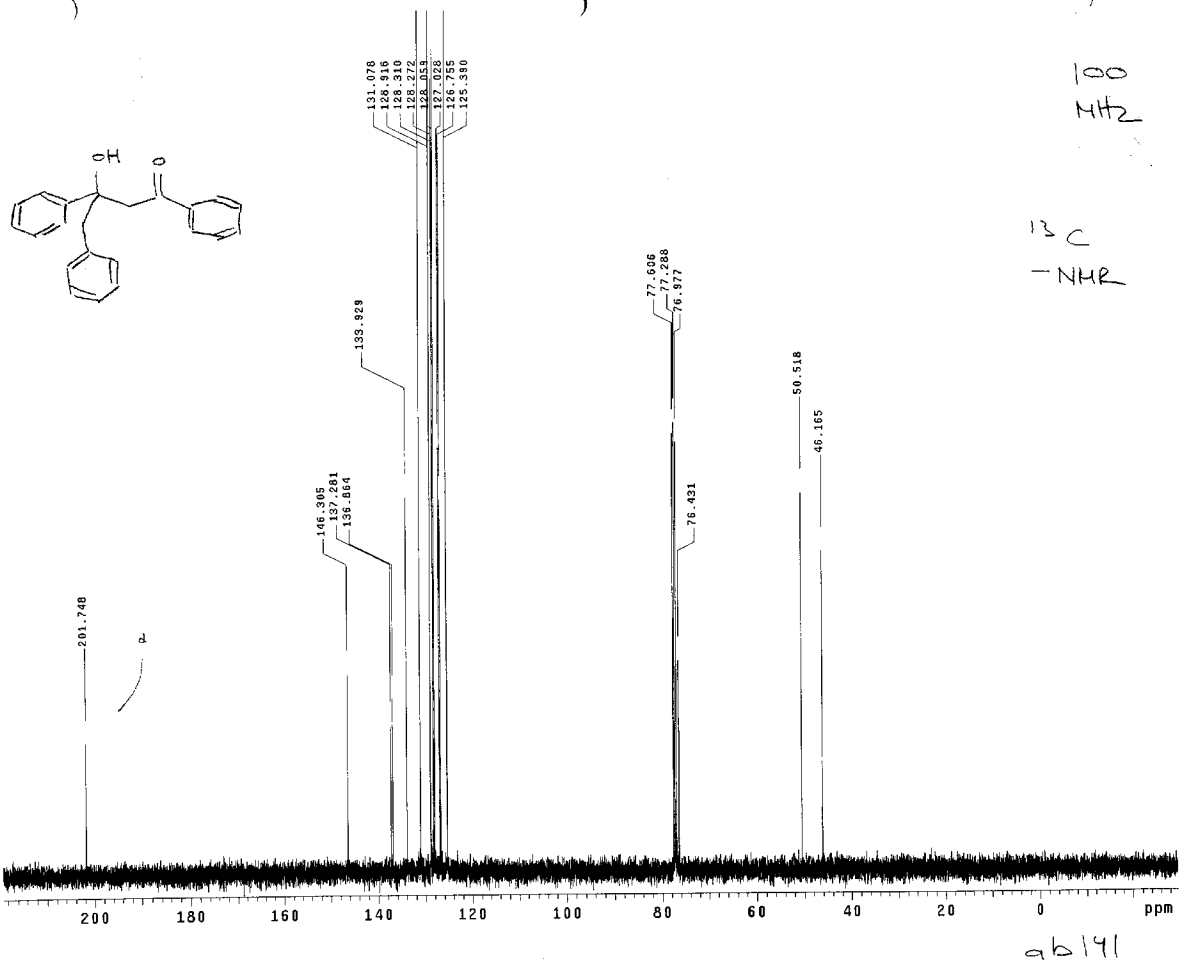
neat



ab144

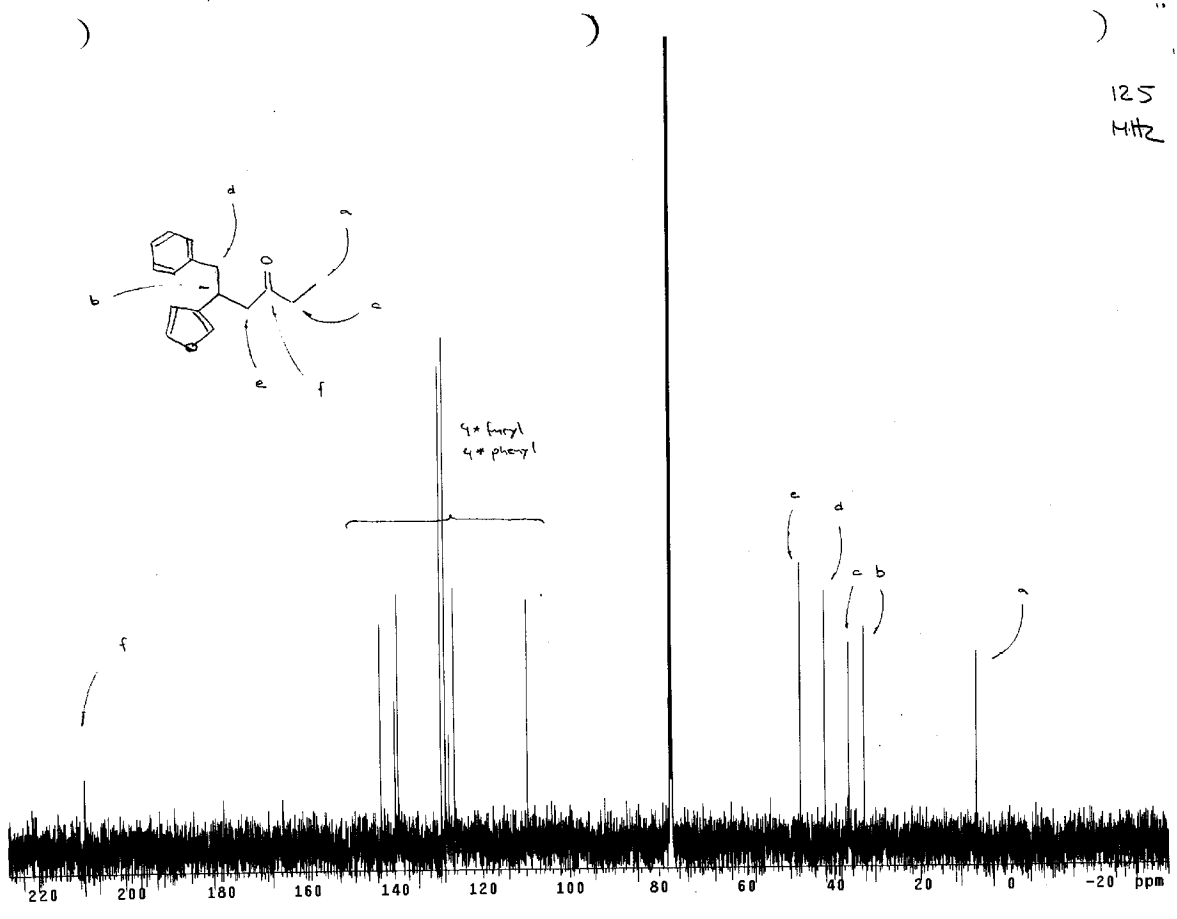
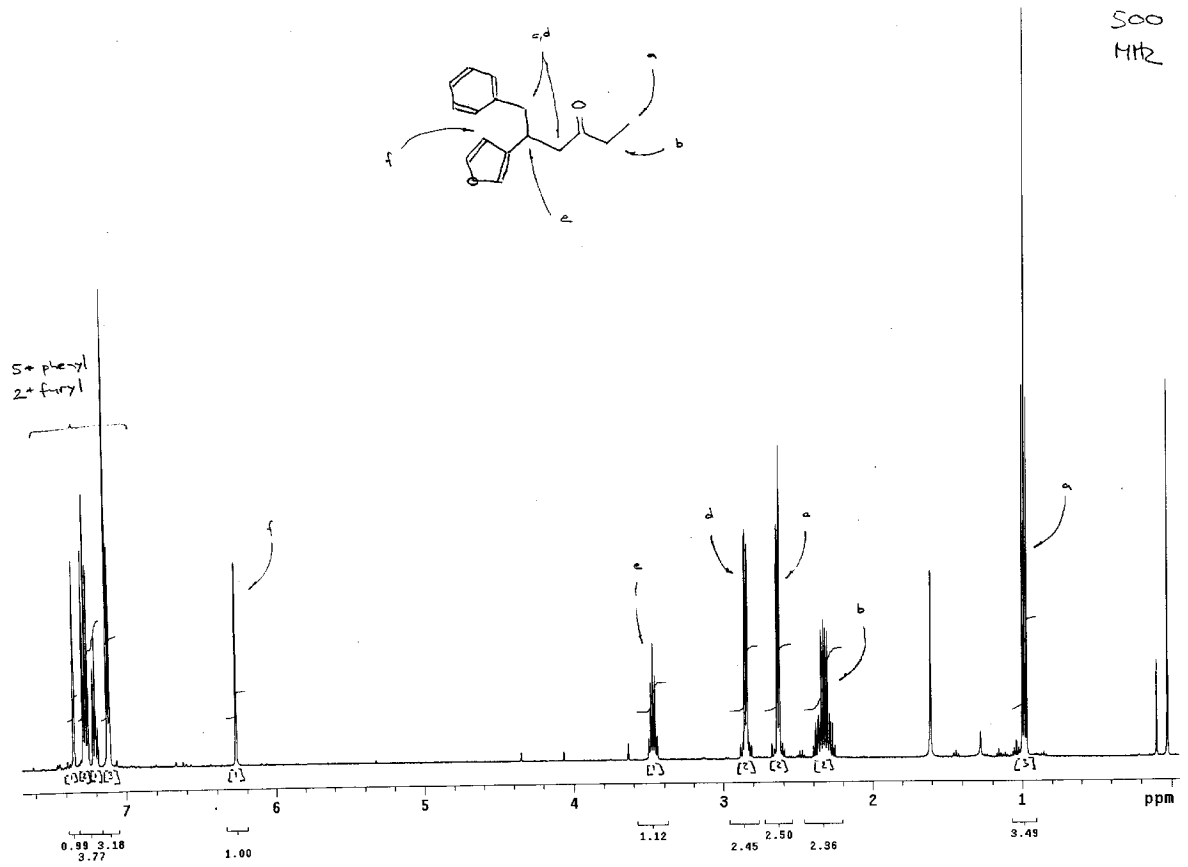


ab141

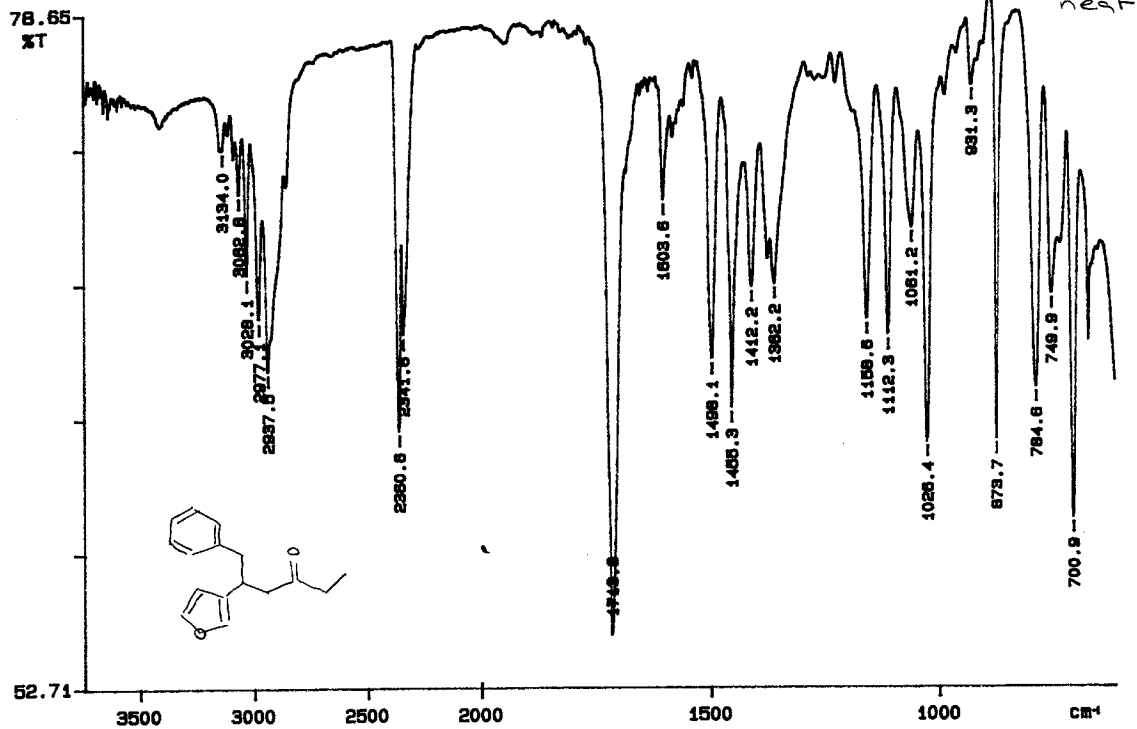


07/08/30 12:49  
X: 4 scans, 4.0cm-1

ab141

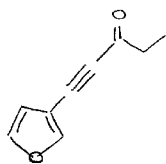


PERKIN ELMER

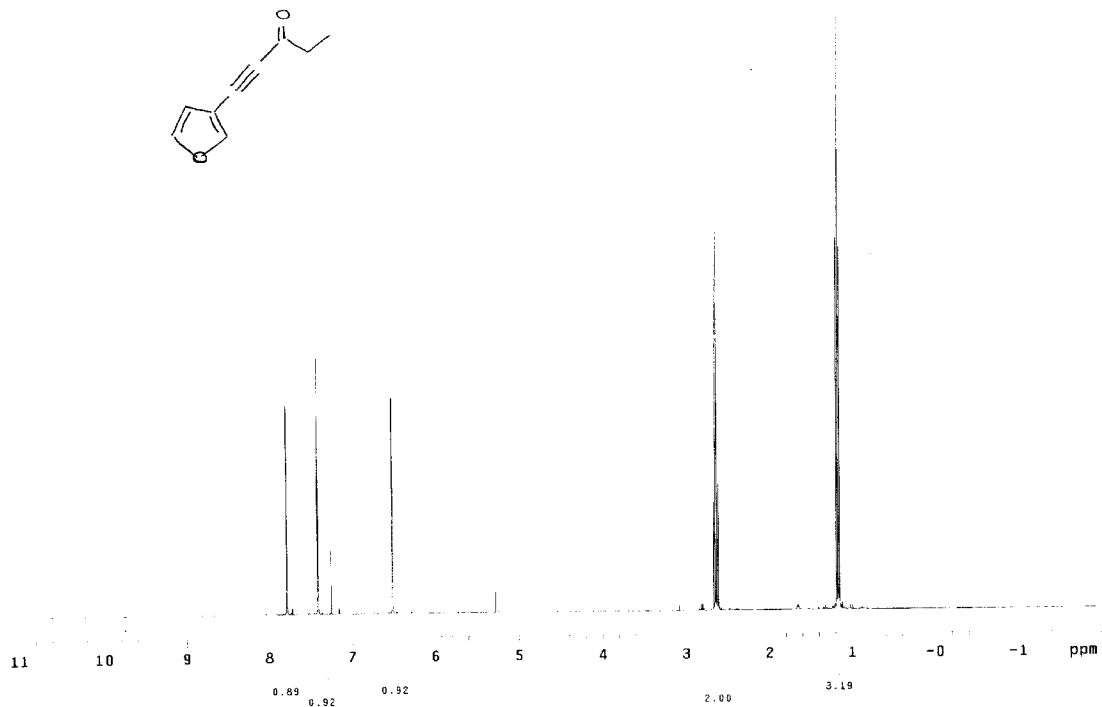


07/02/07 18:42  
X: 4 scans, 4.0cm-1, flat

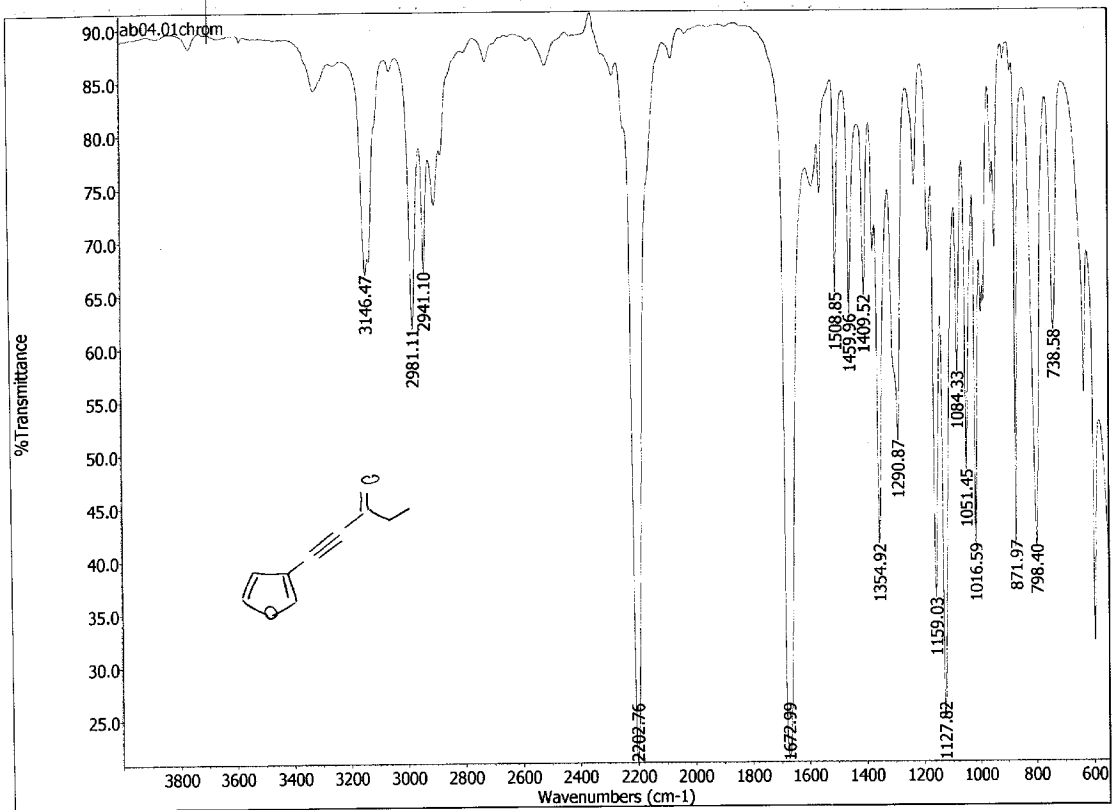
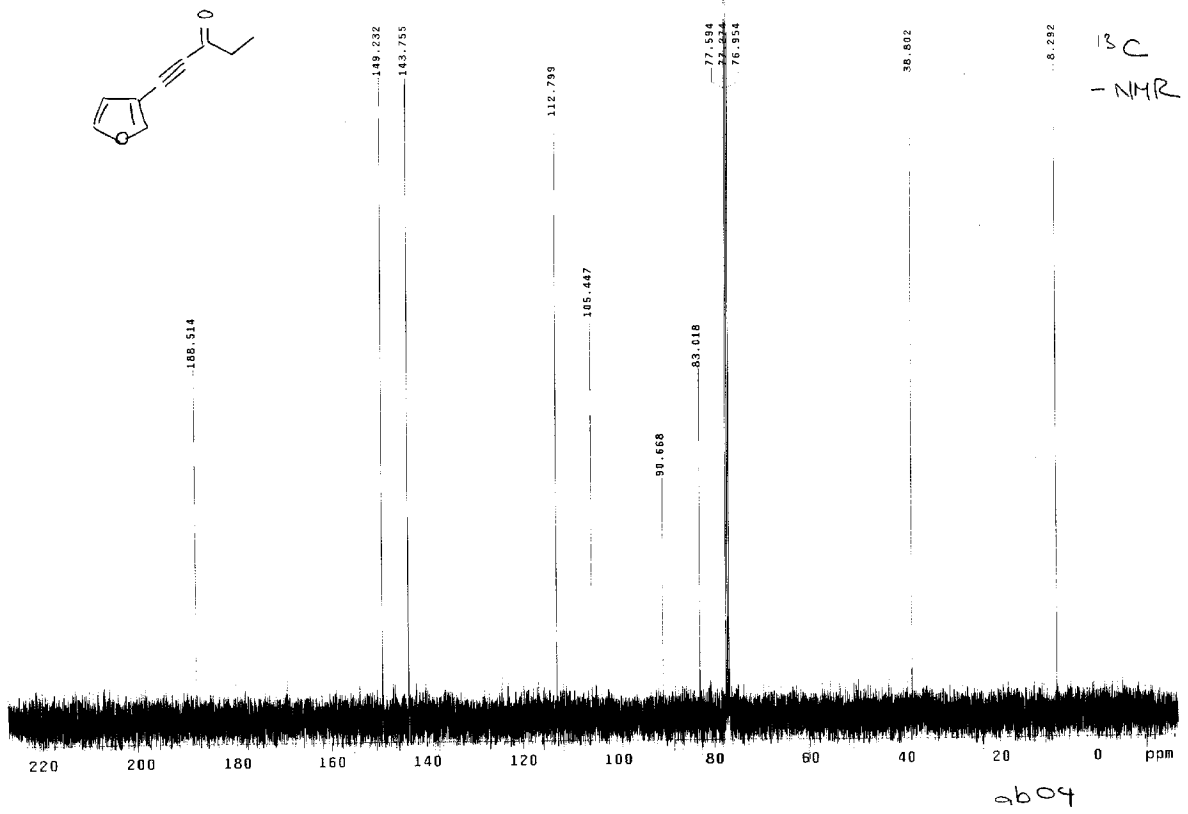
2686



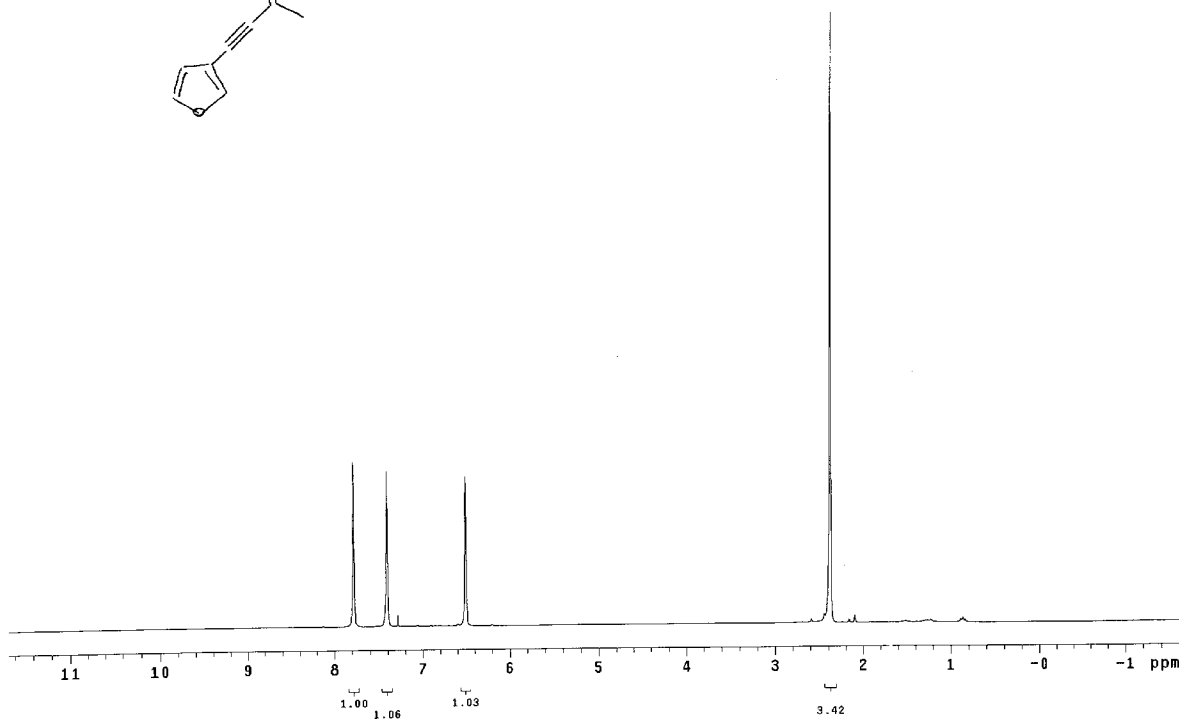
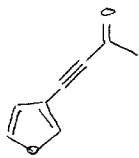
400  
MHz



2604

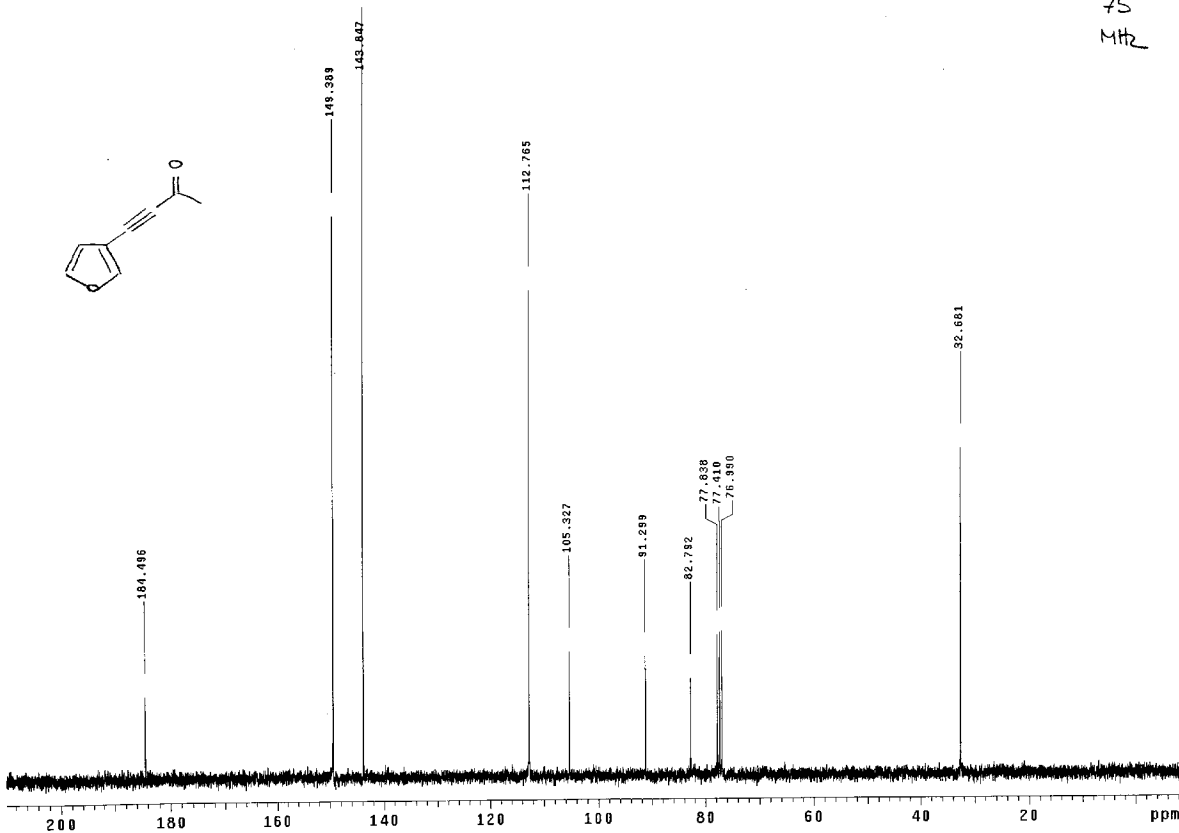
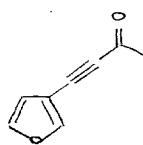


300  
MHz

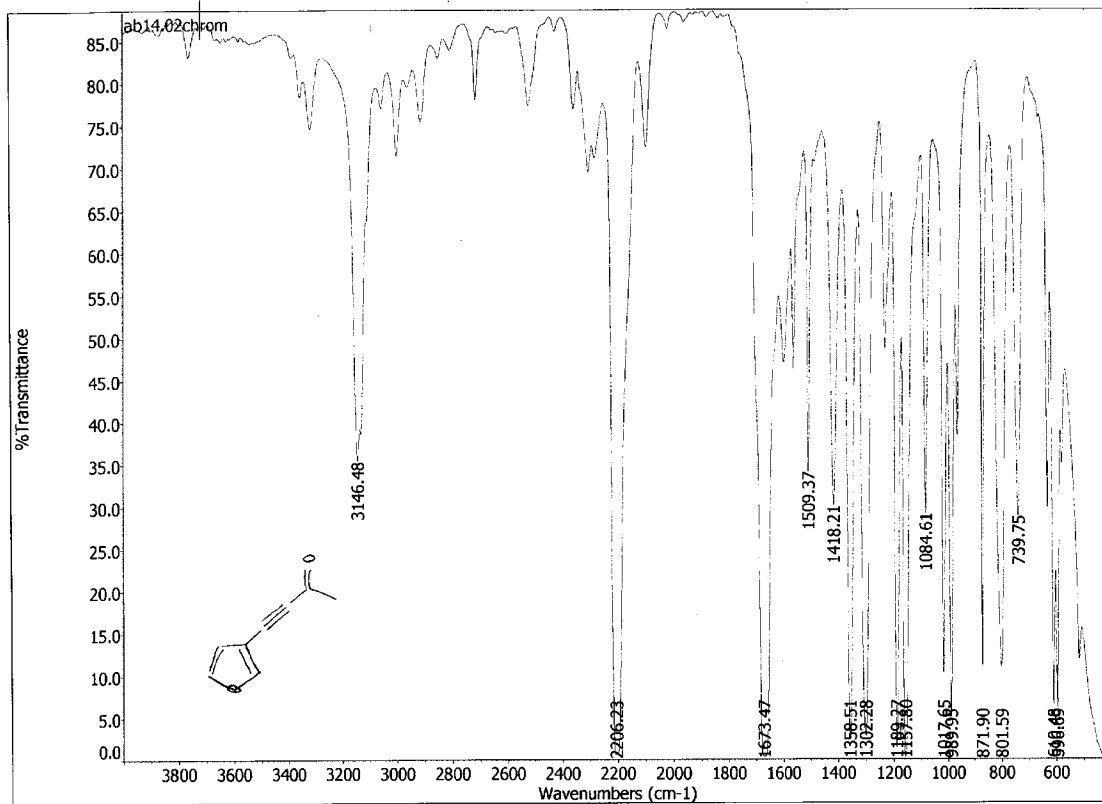


a614

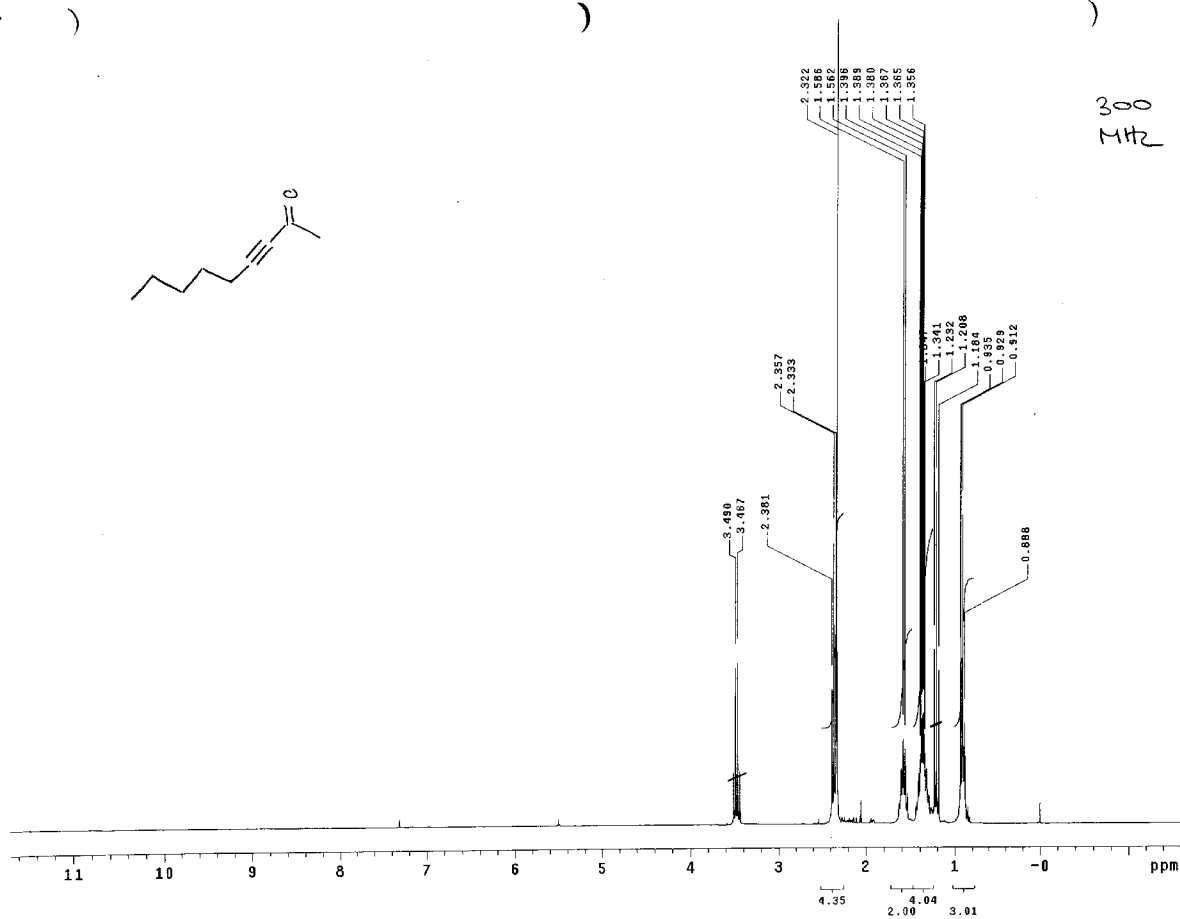
75  
MHz



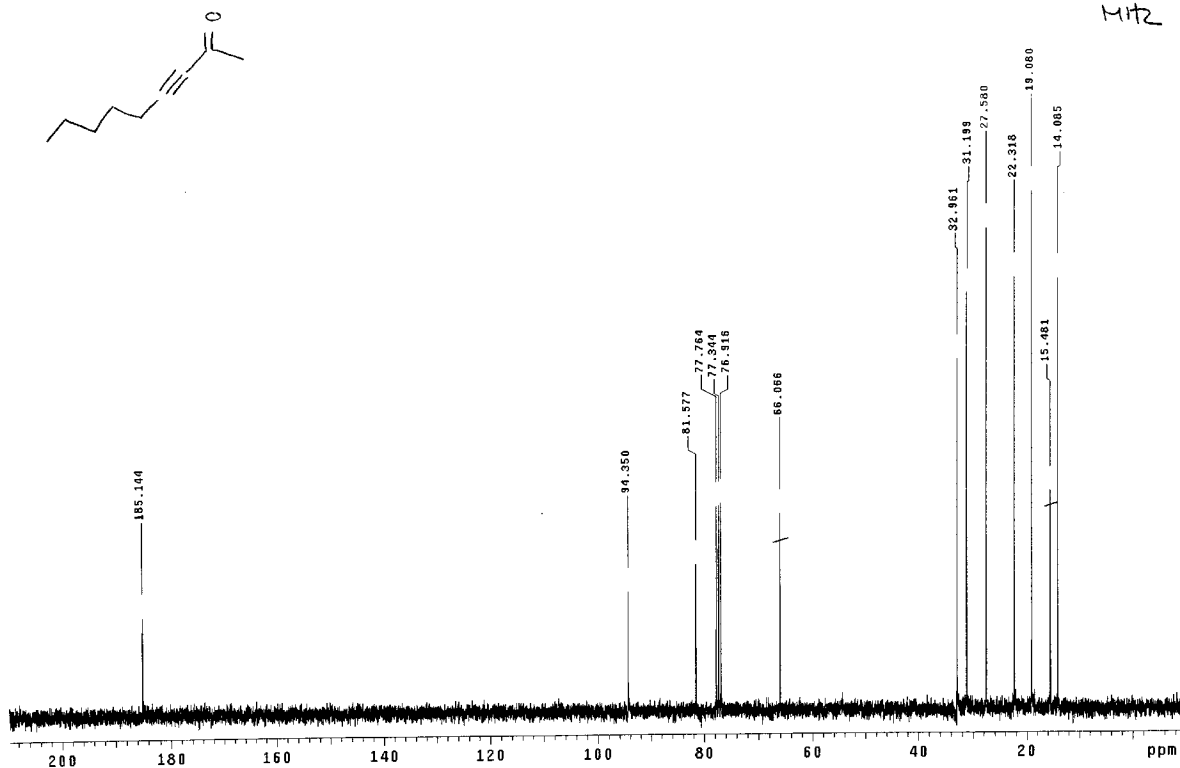
a614



ab 14

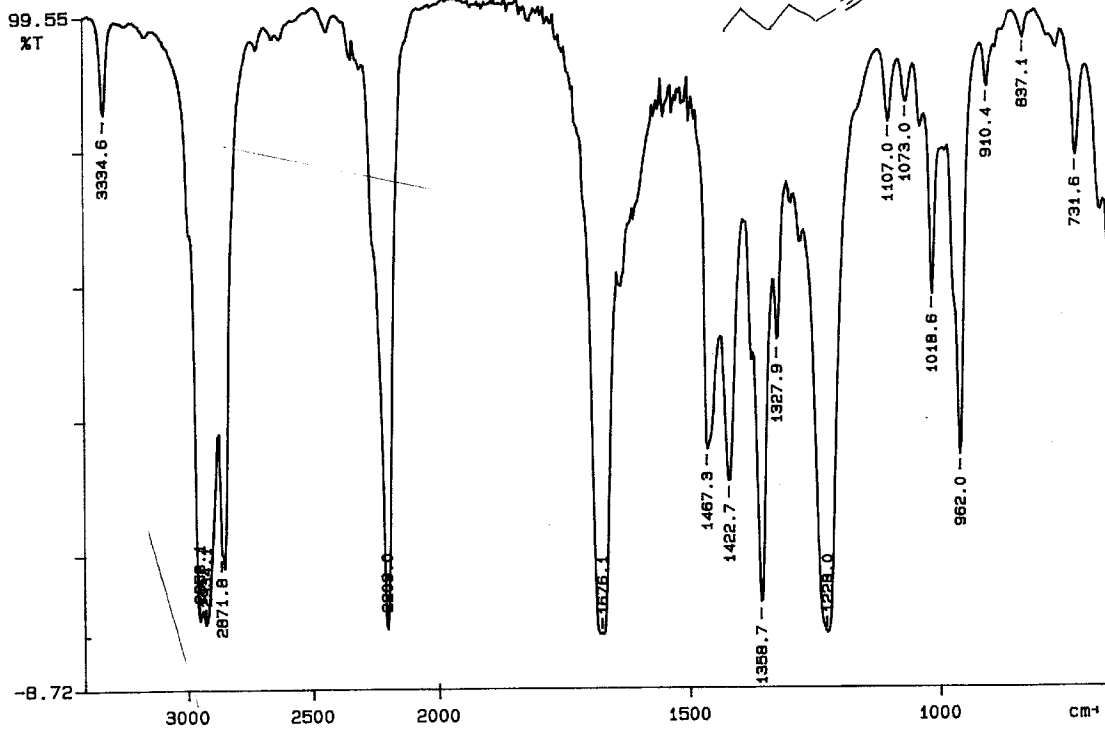


ab 53



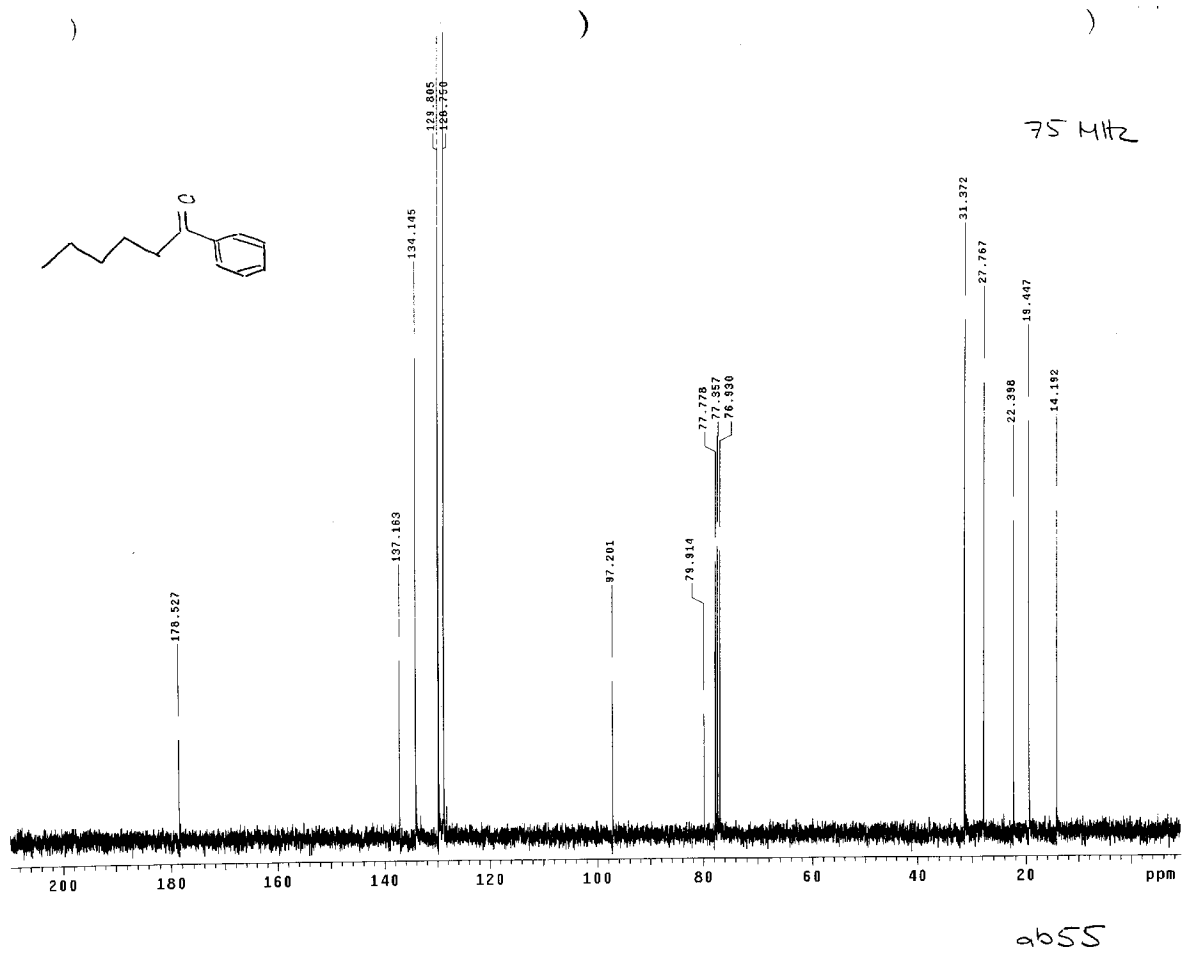
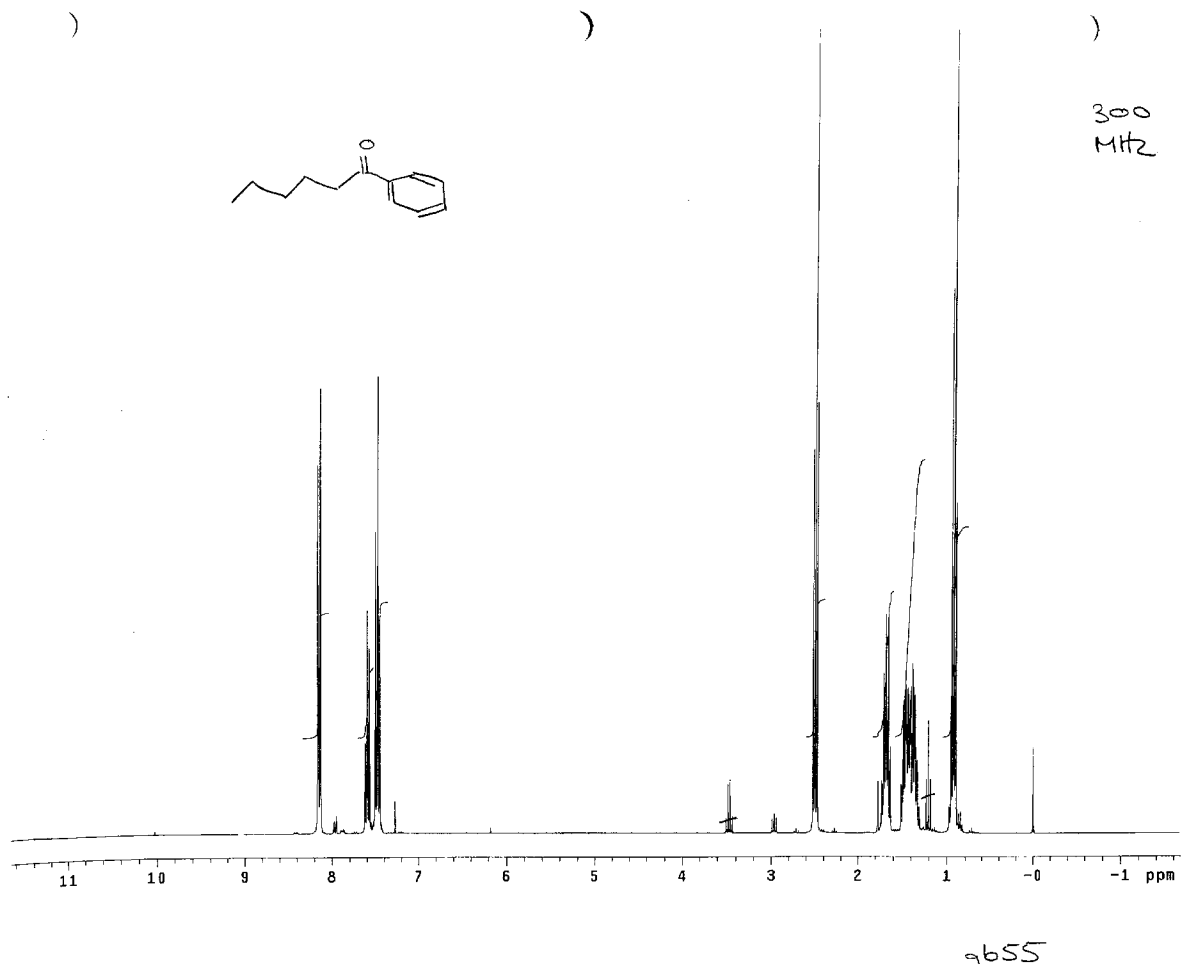
ab53

PERKIN ELMER

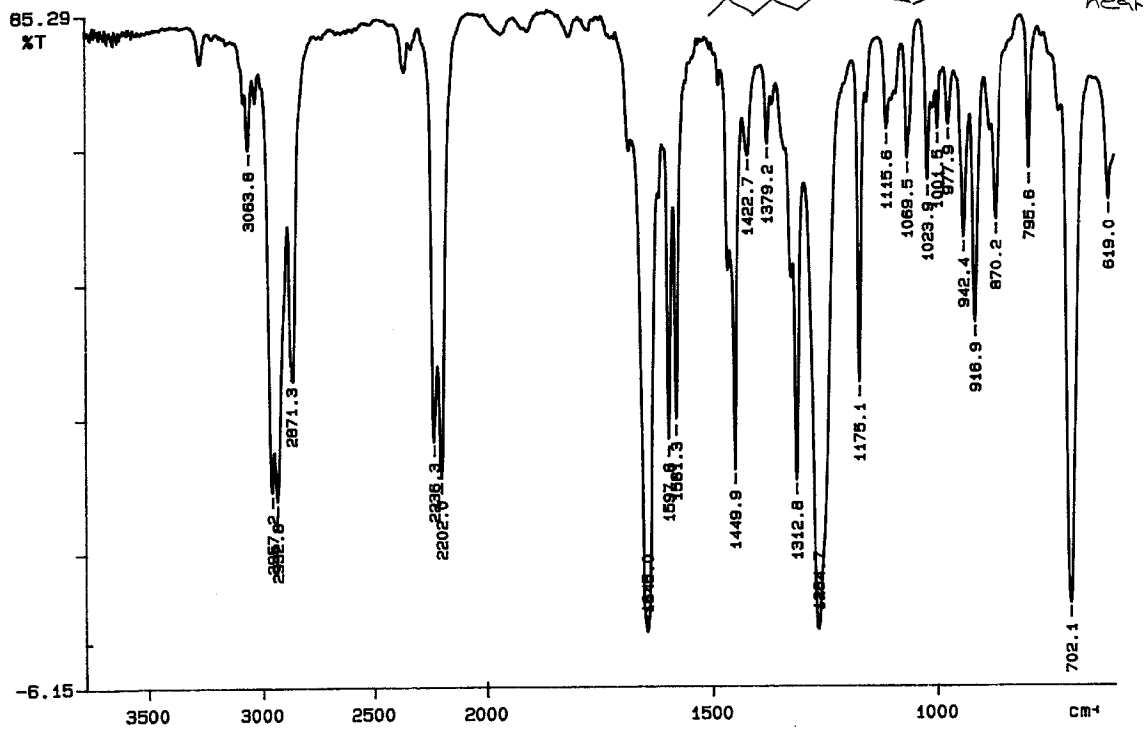


06/11/18 16:12  
X: 4 scans, 4.0cm-1

ab53



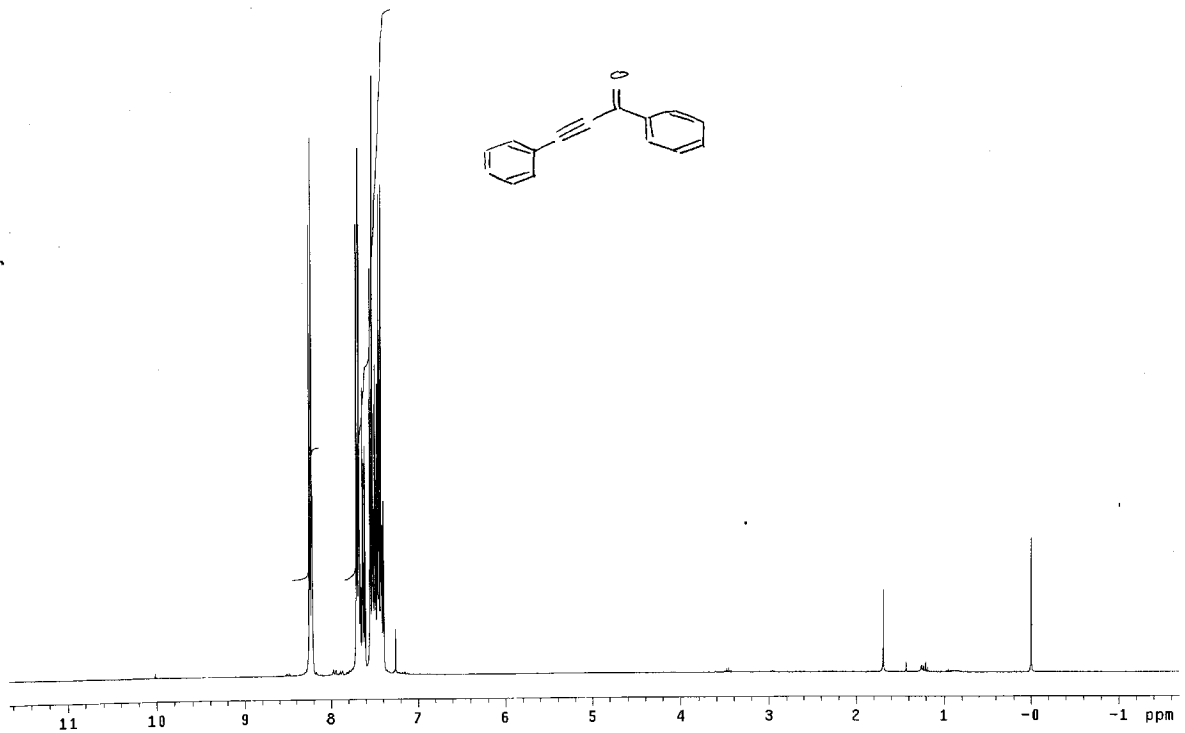
PERKIN ELMER



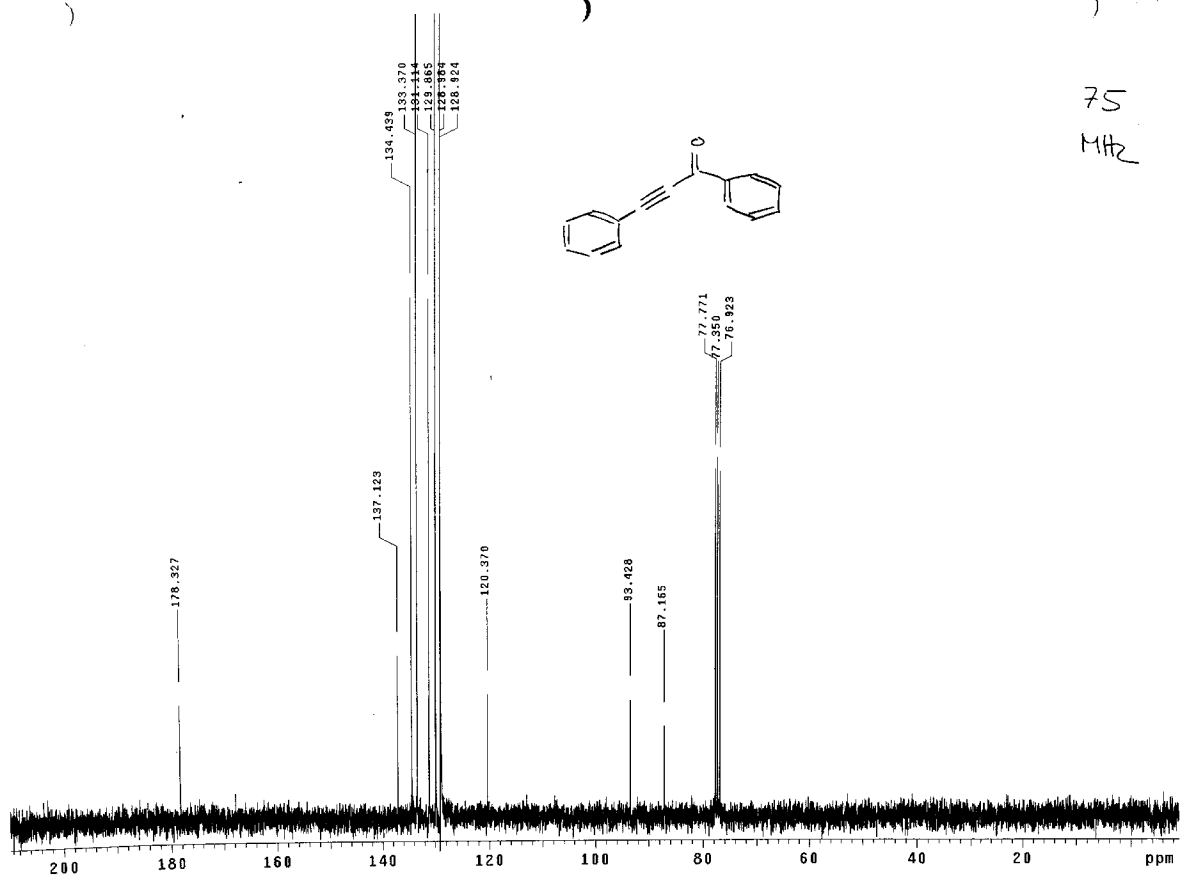
06/11/22 11:11  
X: 4 scans, 4.0cm-1

ab55

300  
MHz

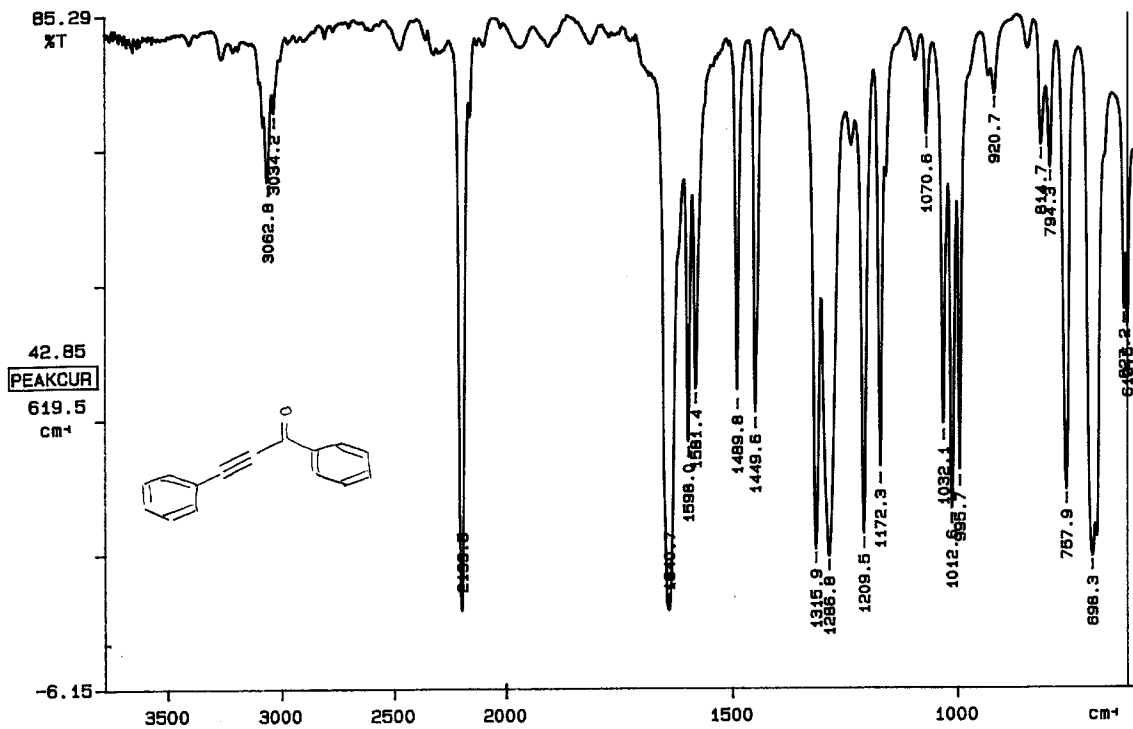


ab56



ab56

PERKIN ELMER

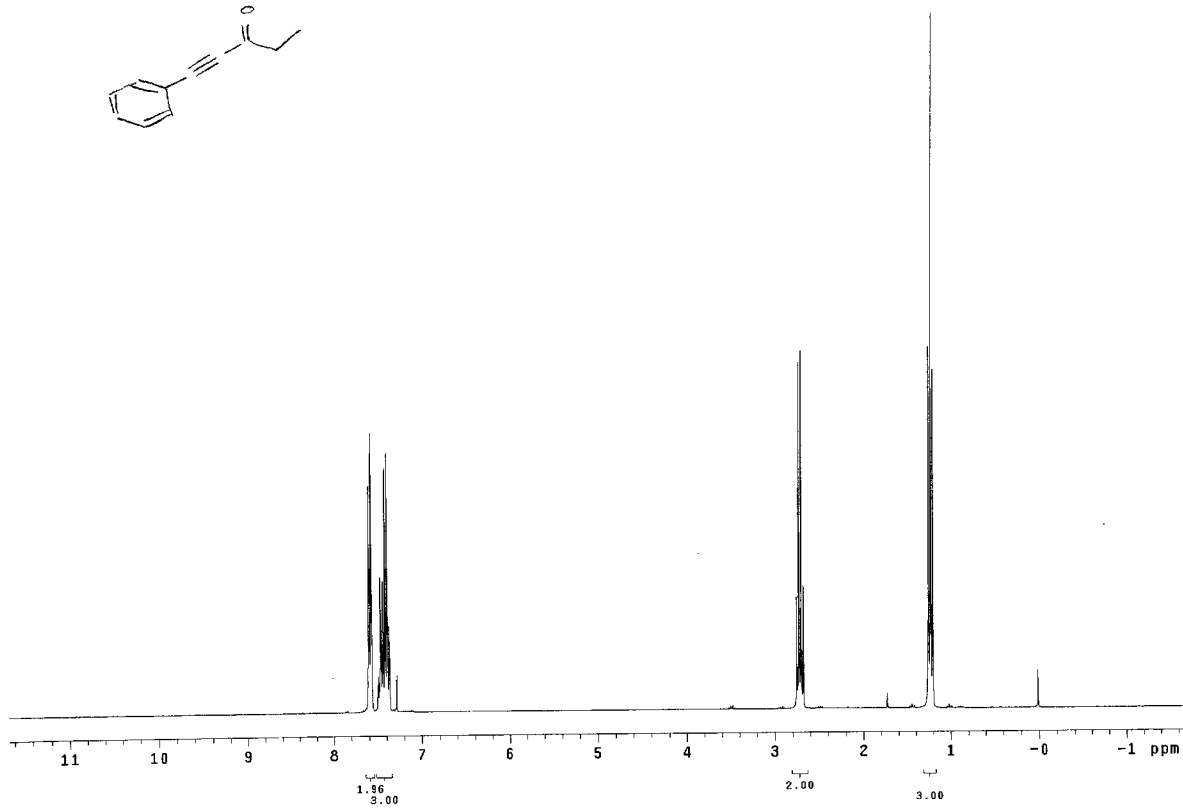
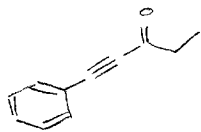


42.85  
PEAKCUR  
619.5  
cm⁻¹

06/11/22 10:56  
X: 4 scans, 4.0cm⁻¹

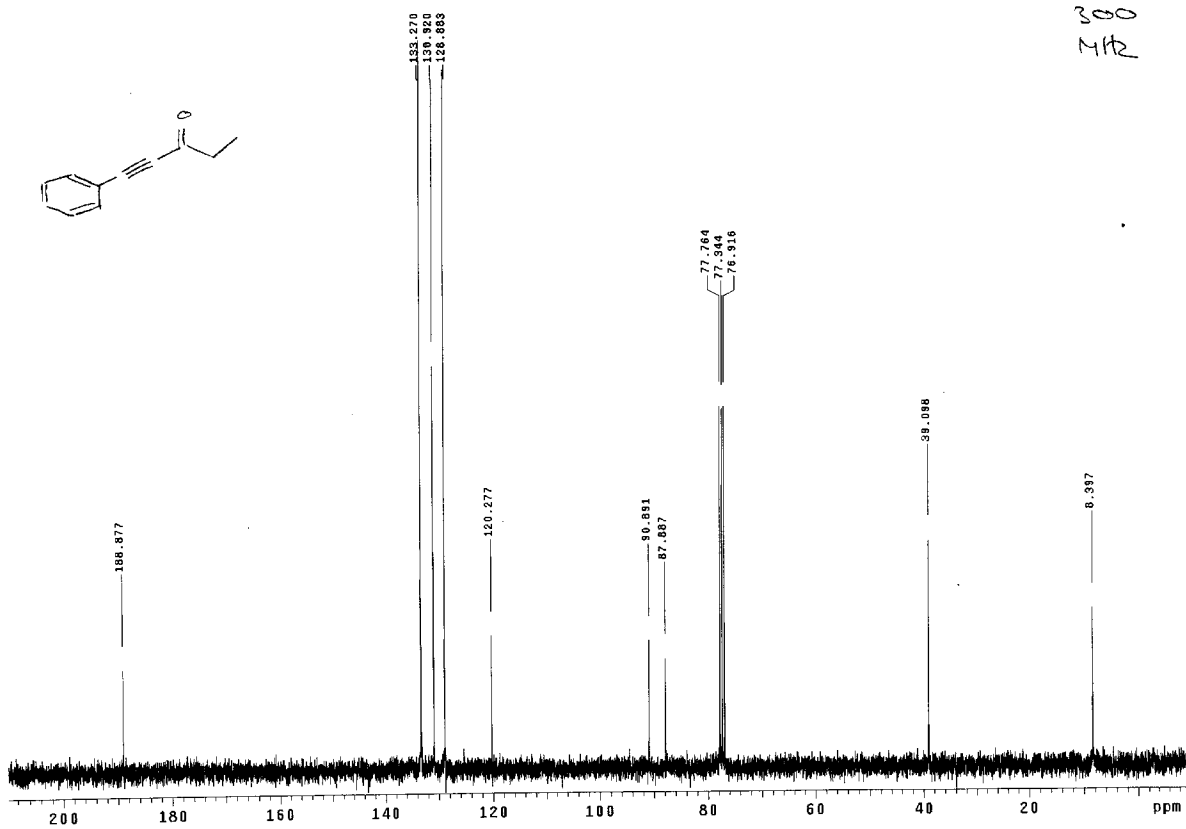
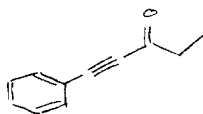
ab56

300  
MHz



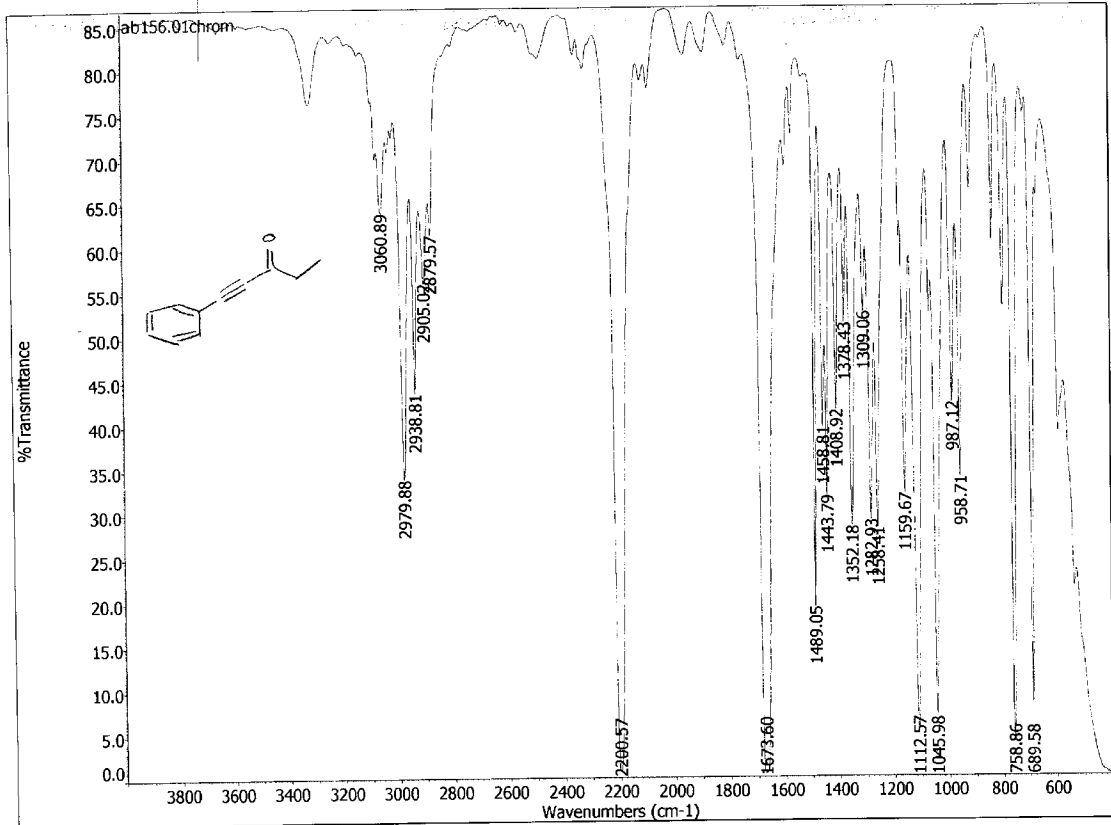
96156

300  
MHz

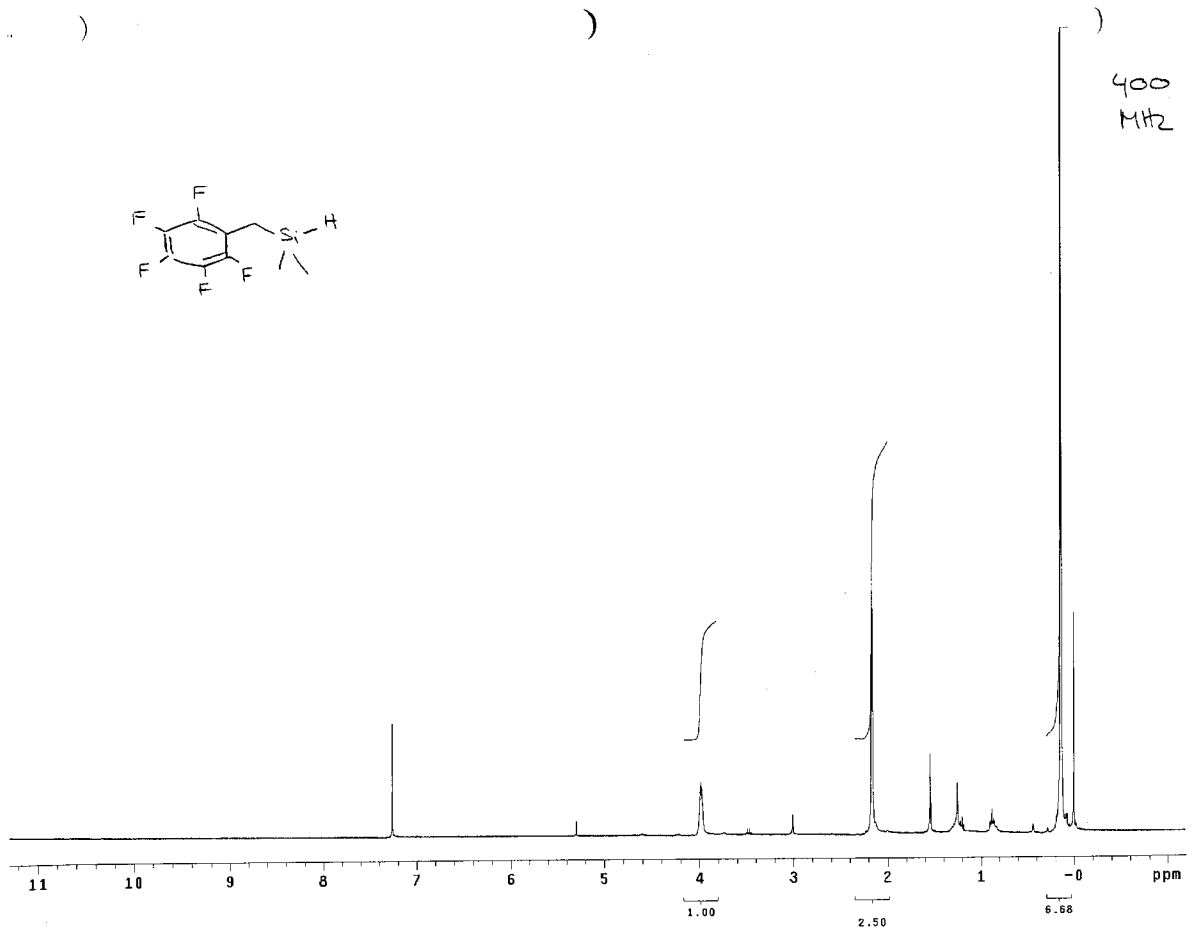
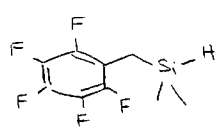


96156

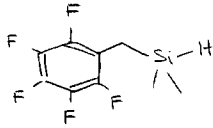
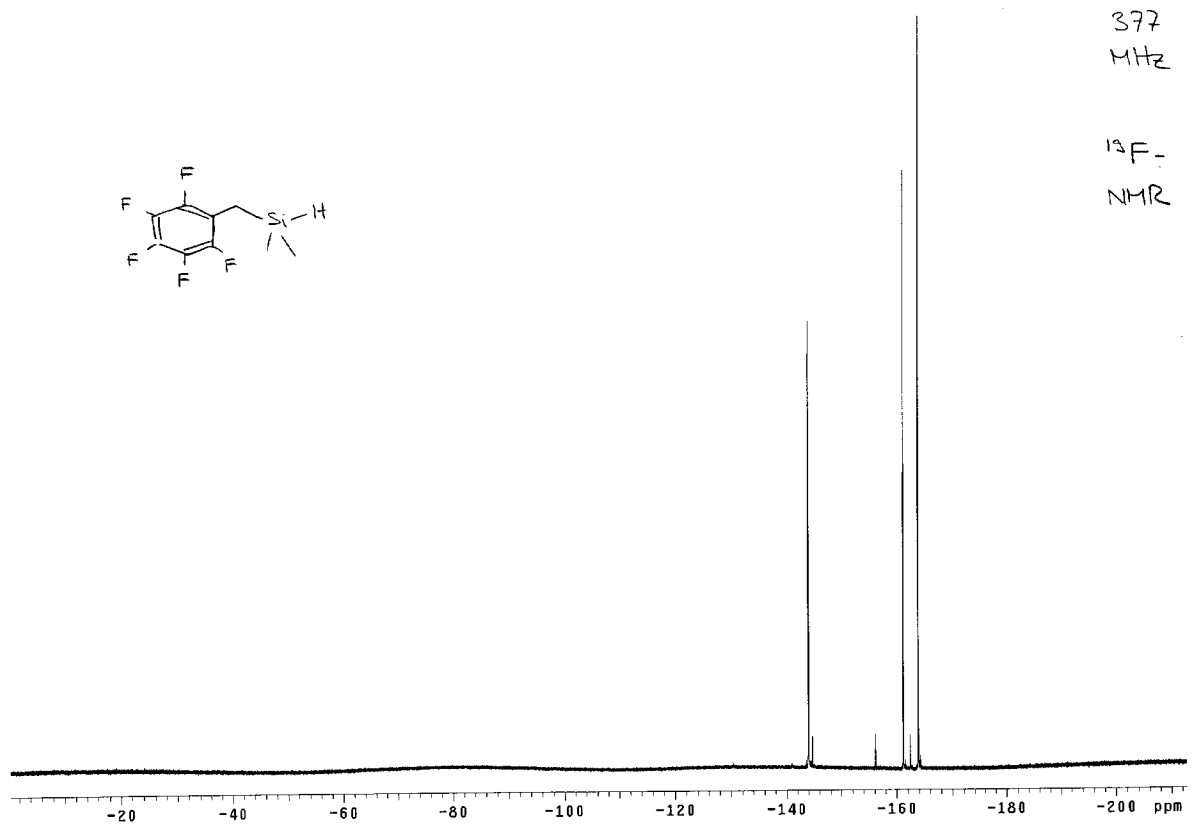
neat



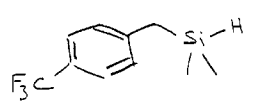
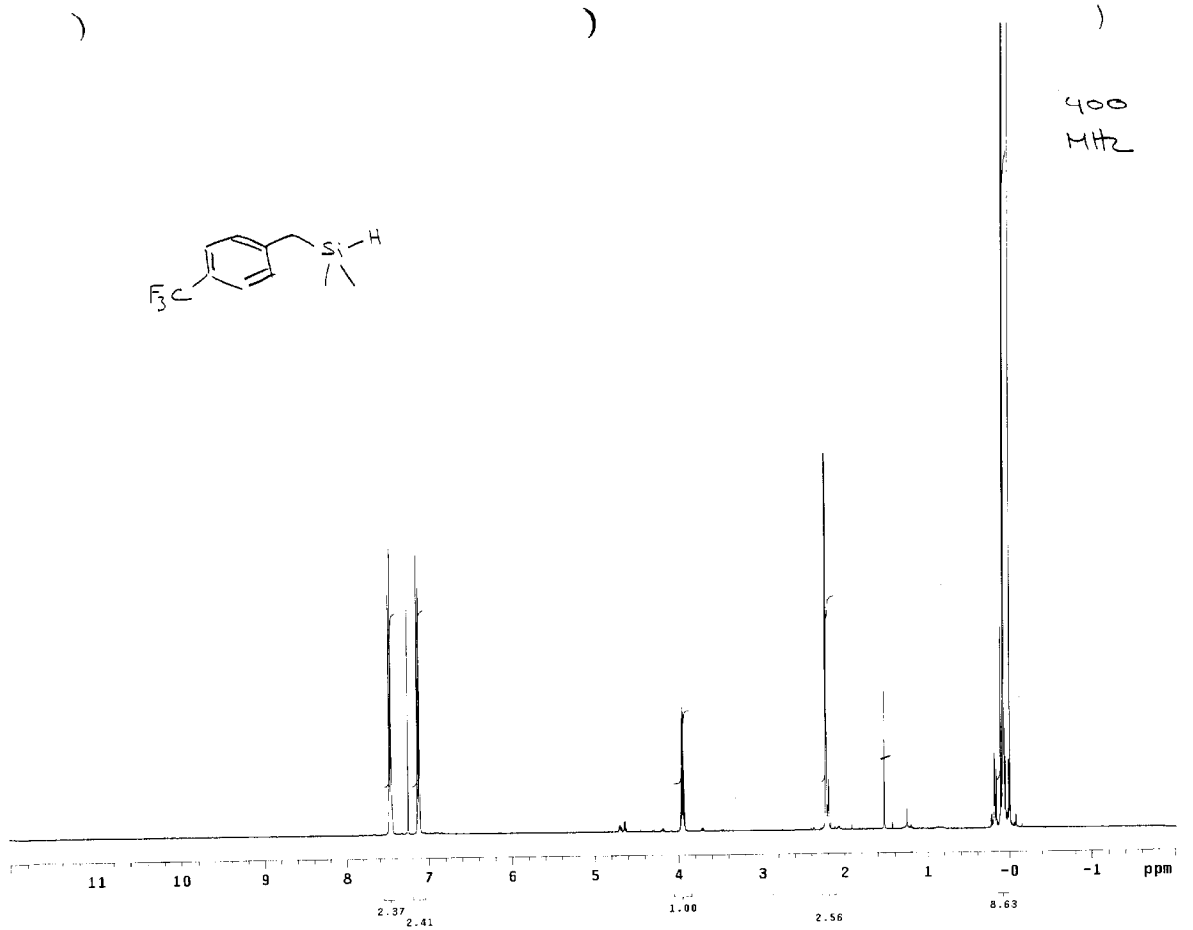
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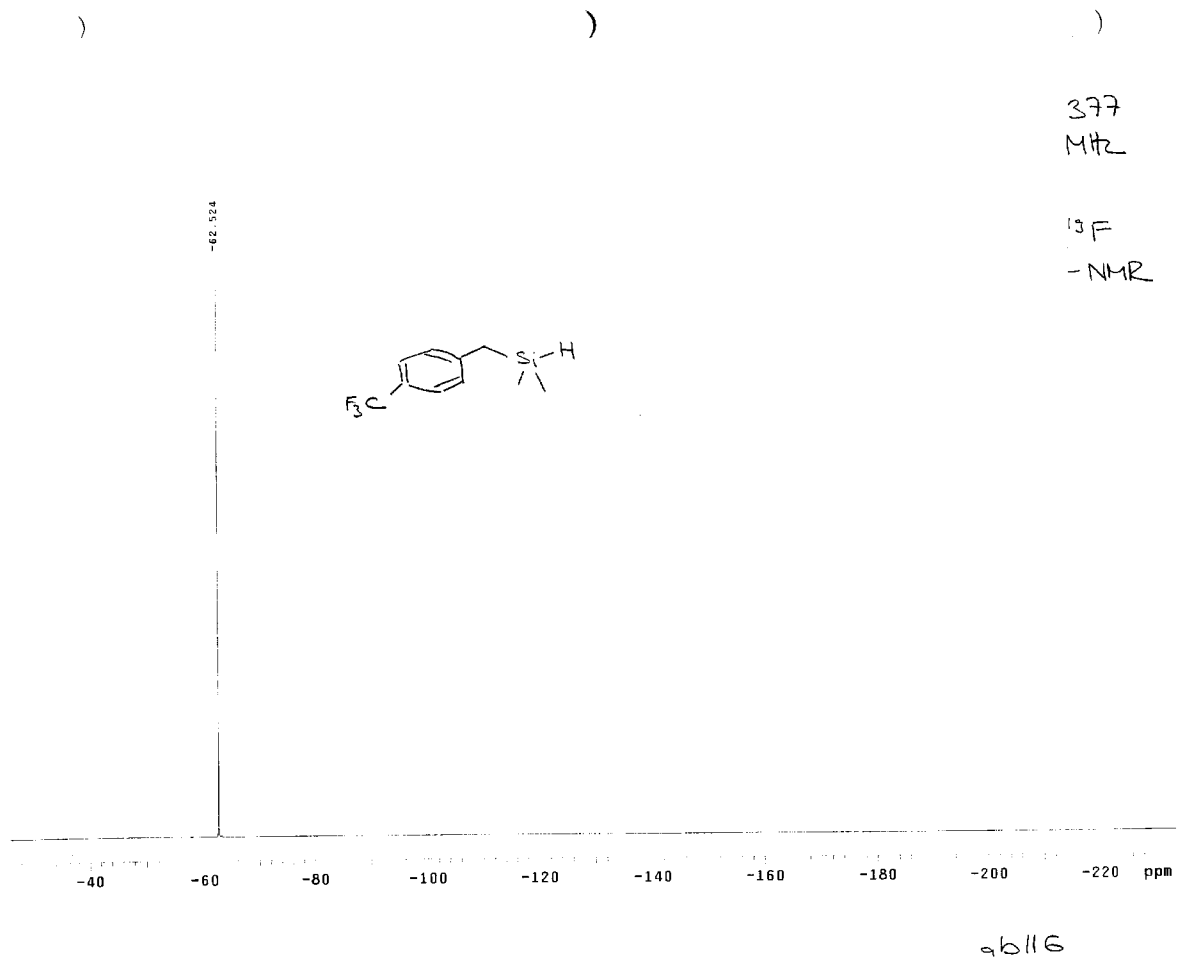
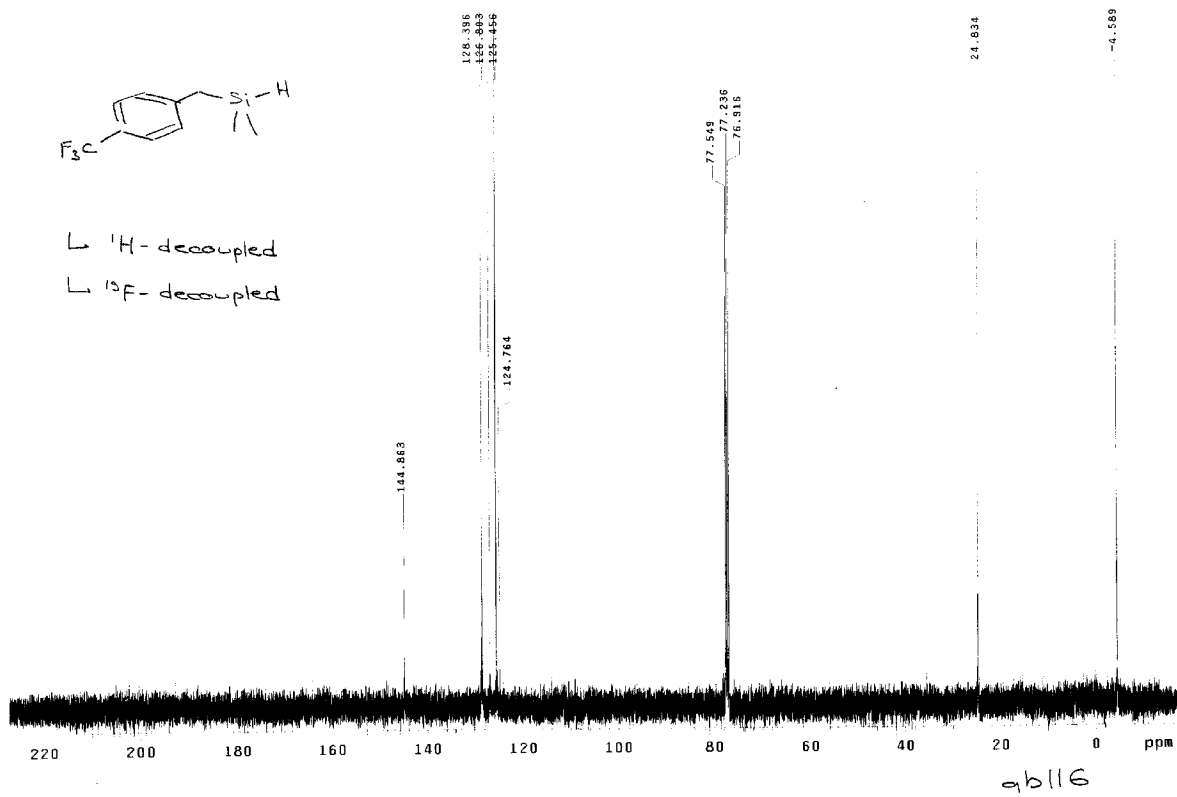
9b114



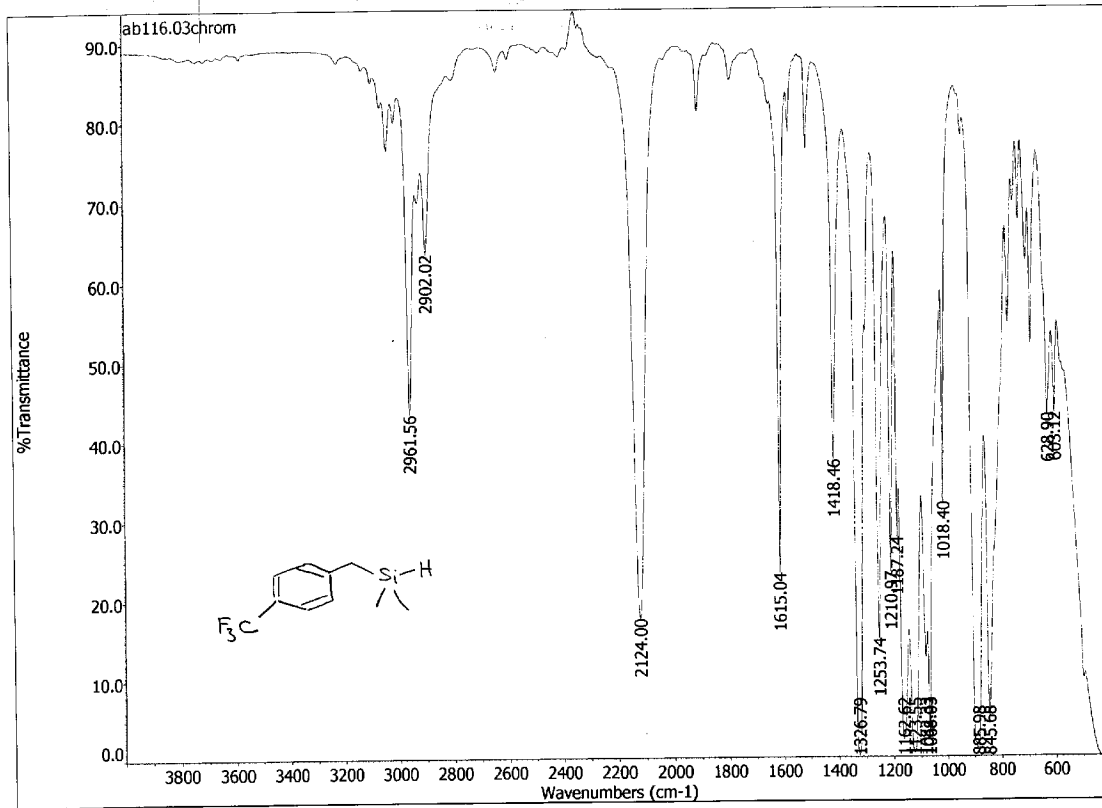
qb114



qb116



neat



96116