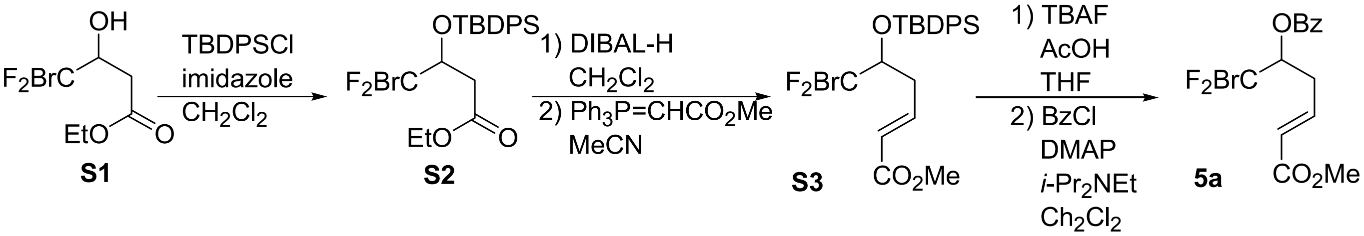
Supplementary Information

Contents

1. General

NMR (^{1}H, ^{13}C, and ^{19}F) spectra were recorded with a Jeol JNMAL-400 or Jeol JNM ECA-500 instruments (^{1}H, 500 or 400 MHz, ^{13}C. 125 MHz, ^{19}F. 470 MHz). Chemical sifts are reported relative to Me_4Si, except for fluorine-containing compounds where $CFCl_3$ was used as an internal standard. Mass spectra (MS) were taken in FAB mode with *m*-nitrobenzyl alcohol as a matrix. Column chromatography was carried out on silica gel (Micro Bead Silica Gel PSQ 100B, Fuji Silysia Chemical Ltd.) or neutral silica gel (Silica Gel 60N, Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed on precoated silica gel plate F_{254}. THF was distilled from benzophenone ketyl.

2. Preparation of 5a



4-Bromo-3-(*tert*-butyldiphenylsilanyloxy)-4,4-difluoro-butyric acid ethyl ester (S2)

To a CH_2Cl_2 (27 mL) solution of **S1**[1] (4.56 g, 18.4 mmol) was added imidazole (2.13 g, 31.3 mmol) at 0 ℃. After 20 min stirring of the resulting mixture, TBDPSCl (4.79 mL, 18.4 mmol) was dropwise added, then allowed to rt for 24 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/Et_2O = 10/1) of the organic layer gave **S2** (7.77 g, 87%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.12 (t, J = 7.2 Hz, 3H), 2.67-2.76 (m, 2H), 3.83-3.90 (m, 2H), 4.35-4.41 (m, 1H), 7.25-7.48 (m, 6H), 7.61-7.63 (m, 2H), 6.69-7.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 19.4, 26.9, 38.9, 61.0, 74.2 (dd, $J_{C,F}$ = 28.6 and 22.4 Hz), 124.5 (dd, $J_{C,F}$ = 312.3 and 308.7 Hz), 127.5, 127.6, 129.8, 130.1, 131.5, 132.8, 135.8, 136.3, 169.1. HRFAB-MS (*m/z*) 485.0959 (M^++H) calcd for $C_{22}H_{28}BrF_2O_3Si$ (M^++H) 485.0959.

6-Bromo-5-(*tert*-butyldiphenylsilanyloxy)-6,6-difluoro-hex-2-enoic acid methyl ester (S3)

To a stirred solution CH_2Cl_2 (80 mL) of **S2** (3.8 g, 7.83 mmol) was dropwise added DIBAL-H (1.0 mol.L in toluene, 15.7 mL, 15.7 mmol) over 3 min at −80 ℃. The resulting mixture was stirred further 30 min at same temperature. To the mixture was added aq. saturated Rochelle salt (*ca.* 100 mL) then allowed to warm to rt. The mixture was filtrated through a celite pad, the filtrate was partitioned between brine and CH_2Cl_2. The resulting organic layer was dried by Na_2SO_4 then evaporated all of volatiles. The residue was treated with MeCN (150 mL) and $Ph_3P=CHCO_2Me$ (7.85 g, 23.5 mmol). The mixture was stirred further 14 h at rt. The mixture was partitioned between brine and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 10/1) of the organic layer gave **S3** (2.77 g, 71%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 9H), 2.48-2.58 (m, 2H), 3.06 (s, 3H), 3.83-3.89 (m 1H), 5.67 (dt, J = 15.6 and 1.6 Hz, 1H), 6.67 (dt, J = 15.6 and 7.2 Hz, 1H), 7.38-7.48 (m, 6H), 7.66-7.68 (m, 4H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5, 26.8, 36.1, 51.4, 76.4 (dd, $J_{C,F}$ = 26.4 and 21.5 Hz), 124.2, 124.7 (dd, $J_{C,F}$ = 312.3, and 308.8 Hz), 127.7, 127.8, 130.1, 130.2, 131.7, 132.4, 136.0, 136.1, 142.3, 166.1. HRFAB-MS (*m/z*) 497.0983 (M^++H) calcd for $C_{23}H_{28}BrF_2O_3Si$ (M^++H) 497.0959.

Benzoic acid 1-(bromodifluoromethyl)-4-methoxycarbonyl-but-3-enyl ester (5a)

To a THF (30 mL) solution of **S3** (1.39 g, 2.79 mmol) was added AcOH (176 µL, 3.07 mmol) and TBAF (1.0 mol/L solution in THF, 3.07 mL, 3.07 mmol). The resulting mixture was stirred for 20 h at rt. The mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. After evaporation of all of volatiles, the residue was roughly purified by column chromatography on silica gel (hexane/AcOEt = 4.1) gave aclude alcohol. The residue was dissolved in CH_2Cl_2 (30 mL), then treated with *i*-Pr_2NEt

(486 µL, 2.77 mmol), DMAP (342 mg, 2.79 mmol) and BzCl (392 µL, 3.35 mmol). The mixture was stirred for 20 h at rt. The resulting mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/Et_2O = 3/1) of the organic layer gave **5a** (784 mg, 77%) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 2.77-2.86 (m, 1H), 2.88-2.95 (m, !H), 3.69 (s, 3H), 5.67 (ddd, *J* =16.8, 8.4 and 4.0 Hz, 1H), 5.97 (dt, *J* = 15.6 and 1.6 Hz, 1H), 6.89 (dt, *J* = 15.6 and 7.6 Hz, 1H), 7.47-7.51 (m, 2H), 7.60-7.65 (m, 1H), 8.07-8.09 (m, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 32.4, 51.6, 74.0 (t, $J_{C,F}$ = 31.1 Hz), 121.0 (t, $J_{C,F}$ = 310.0 Hz), 125.1, 128.4, 128.6, 130.1, 133.9, 140.4, 164.6, 165.9. HRFAB-MS (*m/z*) 363.0073 (M^++H) calcd for $C_{14}H_{14}BrF_2O_4$ (M^++H) 363.0044.

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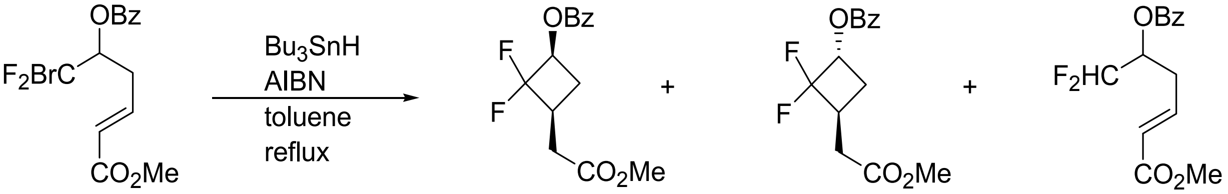
1) Jagodzinska, M.; Huguenot, F.; Zanda, M. *Tetrahedron* **2007**, *63*, 2042.

3. Radical reaction of 5a: General procedure for the redical cyclization reaction

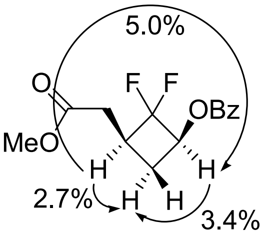


5a *cis-* **6a** *trans*-**6a** **7a**

To a refluxing solution of **5** (337 mg, 0.93 mmol) in toluene (9 mL) was dropwise added a toluene (9 mL) solution of Bu_3SnH (500 µL, 1.86 nnol) and AIBN (31 mg, 0.19 mmol) over 4 h. The resulting mixture was stirred further 1 h at same temperature. After evaporation of all of volatiles, the residue was roughly purified by column chromatography on silica gel (hexane/Et_2O = 3/1). The crude mixture was further purified by preparative TLC (hexane/AcOEt = 8/1). This gave a mixture of **7a** and *trans*-**6a** (102 mg, 39%,, the ratio of **7a**/*trans*-**6a** = 100:22, based on the integration of ^1H NMR) and *cis*-**6a** (57 mg, 22%, as an oil).

Physical data for *cis*-6a: ^1H NMR (400 MHz, $CDCl_3$) δ 1.67-1.75 (m, 1H), 2.55-2.79 (m, 3H), 2.87-2.99 (m, 1H), 3.71 (s, 1H), 5.35-5.44 (m, 1H), 7.44-7.48 (m, 2H), 7.57-7.61 (m, 1H), 8.04-8.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.5 (d, $J_{C,F}$ = 19.1 Hz), 31.8 (d, $J_{C,F}$ = 7.3 Hz). 36.5 (t, $J_{C,F}$ = 21.5 Hz), 51.9, 70.3 (dd, $J_{C,F}$ = 27.6 and 18.0 Hz), 119.5 (dd, $J_{C,F}$ = 298.0 and 278.9 Hz), 128.5, 128.9, 129.9, 133.5, 165.1, 171.3. HRFAB-MS (*m/z*) 285.0925 (M^++H) calcd for $C_{14}H_{15}F_2O_4$ (M^++H) 285.0938.

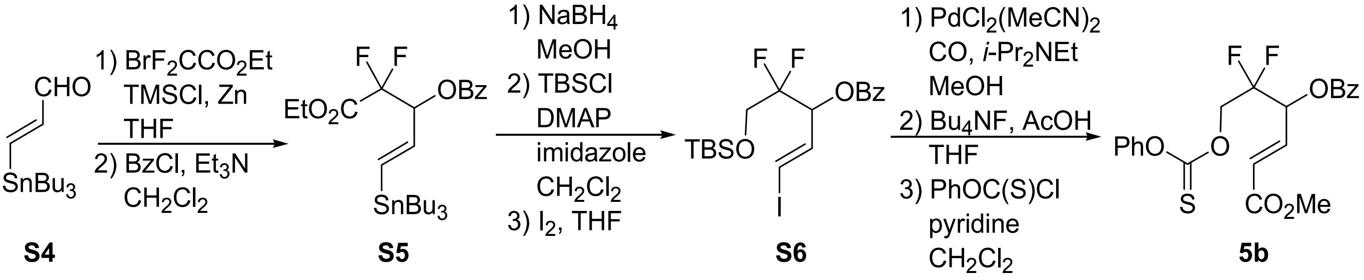
NOE experiments of *cis*-6a



Physical data for *trans*-6a: The physical data for *trans*-**6a** is illustrated at later stage.

Partial data for 7a: ^1H NMR (400 MHz, $CDCl_3$) δ 2.72-2.84 (m, 2H), 3.78 (s, 3H), 5.33-5.43 (m, 1H), 5.95 (ddd, $J_{C,F}$ = 57.6 and 54.4 Hz, *J* = 3.2 Hz, 1H), 5.99 (dt, *J* = 15.6 and 1.6 Hz, 1H), 6.94 (dt, *J* = 15.6 and 7.2 Hz, 1H), 7.45-7.49 (m, 2H), 7.58-7.63 (m, 1H), 8.04-8.09 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.2, 51.6, 70.4 (t, $J_{C,F}$ = 25.1 Hz), 113.4 (t, $J_{C,F}$ = 246.6 Hz), 124.8, 128.6, 128.8, 129.9, 133.7, 141.4, 165.3, 166.1. FAB-MS (*m/z*) 285 (M^++H).

4. Preparation of 5b

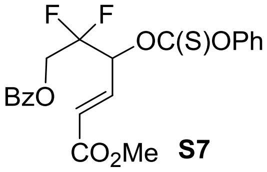


Benzoic acid 1-(ethoxycarbonyl-difluoromethyl)-3-tributylstannyl-allyl ester (S5)

To a THF (7 mL) suspension of activated Zn (1.38 g) was added TMSCl (190 μL, 1.38 mmol). The resulting mixture was stirred at 60 ℃ for 15 min, then cooled to rt. To the mixture was added THF (30 mL) and BrF_2CCO_2Et (2.72 mL, 21.2 mmol) then heated at 60 ℃ for 3 min. A vigorous reflux was observed during this period. The resulting Zn enolate solution was quickly transferred to a THF (30 mL) solution of **S4**$^{2)}$ (3.66 g, 10.6 mmol) at 0 ℃, then the mixture was stirred at rt for 2 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and AcOEt. Flush column chromatography on silica gel (hexane/Et_2O = 3/1) of the organic layer gave a crude alcohol (*ca*. 4.86 g). To a CH_2Cl_2 (50 mL) solution of above alcohol was added Et_3N (2.22 mL, 15.9 mmol) and BzCl (1.49 mL, 12.7 mmol) at 0℃. After 25h stirring of the resulting mixture at rt, this was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/Et_2O = 11/1) of the organic layer gave **S5** (5.28 g, 86% for two steps) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.98 (m, 15H), 1.22-1.33 (m, 9H), 1.54-1.57 (m, 6H), 4.25-4.33 (m, 2H), 5.89-6.12 (m, 2H), 6.54-6.74 (m, 1H), 7.44-7.48 (m, 2H), 7.58-7.62 (m, 1H), 8.01-8.08 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 9.6, 13.6, 13.9, 27.2, 29.0, 63.1, 75.0 (dd, $J_{C,F}$ = 29.8 and 25.0 Hz), 112.9 (dd, $J_{C,F}$ = 256.3 and 252.8 Hz), 128.6, 129.1, 130.0, 133.5, 135.3, 140.3, 162.5 (t, $J_{C,F}$ = 31.0 Hz), 164.5. HRFAB-MS (*m/z*) 575.2012 (M^++H) calcd for $C_{26}H_{41}$ F_2O_4Sn (M^++H) 575.1995.

Benzoic acid 1-[2-(*tert*-butyldimethylsiloxy)-1,1-difluoroethyl]-3-iodoallyl ester (S6)

To a MeOH (50 mL) solution of **S5** (5.11 g, 8.9 mmol) and AcOH (1.53 mL, 26.7 mmol) was portionwise added $NaBH_4$ (4.04 g, 106.8 mmol) at –40 ℃. The resulting mixture was stirred at 0 ℃ for 1 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and $CHCl_3$. After evaporation of all of volatiles of the organic layer, crude alcohol was obtained. To a CH_2Cl_2 (50 mL) solution of above alcohol was added DMAP (437 mg, 3.56 mmol), imidazole (727 mg, 10.68 mmol) and TBSCl (1.61 g, 10.68 mmol) at –40 ℃. The resulting mixture was stirred at 0 ℃ for 13 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and $CHCl_3$. After evaporation of all of volatiles of the organic layer, crude silyl ether was obtained. This was treated with THF (100 mL) and I_2 (4.52 g, 17.8 mmol). After 1 h stirring at rt of tne resulting mixture, this was partitioned between aq. saturated $Na_2S_2O_3$, aq. saturated $NaHCO_3$ and AcOEt. Column chromatography on silica gel (hexane/Et_2O = 15/1) of the organic layer gave **S6** (2.83 g, 66% for three steps) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.00 (s, 3H), 0.03 (s, 3H), 0.86 (s, 9H), 3.80-3.93 (m, 2H), 5.83 (ddd, J = 14.8, 8.8 and 7.2 Hz, 1H), 6.69 (dd, J = 14.8 and 7.2 Hz, 1H), 6.78 (d, J = 14.8 Hz, 1H), 7.44-7.48 (m, 2H), 7.57-7.61 (m, 1H), 8.04-8.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.7, 18.1, 25.6, 62.4 (dd, $J_{C,F}$ = 34.6 and 31.0 Hz), 72.6 (dd, $J_{C,F}$ = 32.4 and 25.1 Hz), 84.9, 119.2 (dd, $J_{C,F}$ = 251.3 and 247.8 Hz), 128.6, 129.1, 129.8, 133.6, 136.2, 164.4. HRFAB-MS (*m/z*) 483.0680 (M^++H) calcd for $C_{18}H_{26}$ F_2IO_3Si (M^++H) 483.0664.

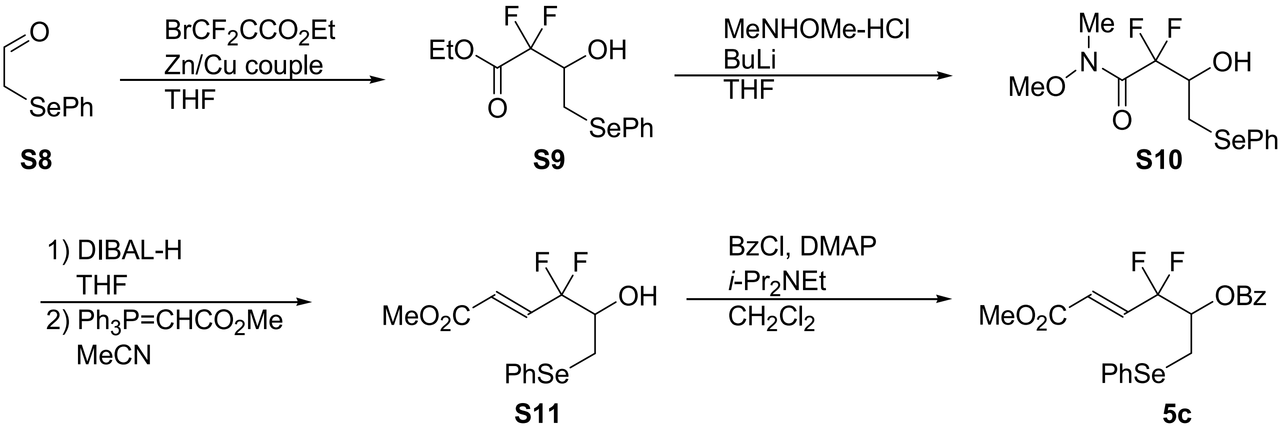


S7

Benzoic acid 1-(1,1-difluoro-2-phenoxythiocarbonyloxyethyl)-3-methoxycarbonylallyl ester (5b)

A mixture of **S6** (2.65 g, 5.52 mmol), $PdCl_2(MeCN)_2$ (285 mg, 1.1 mmol) and *i*-Pr_2NEt (1.01 mL, 5.8 mmol) in MeOH (40 mL) was heated at 50 ℃ under positive pressure of CO (1 atm). After 1.5h heating of the resulting mixture, this was filtrated through a celite pad, then the filtrate was partitioned between aq. saturated $NaHCO_3$ and AcOEt. Evaporation of the organic layer gave a crude methyl acrylate (*ca*. 2.21 g). To a mixture of above acrylate and AcOH (379 µL, mmol) in THF (40 mL) was added Bu_4NF (1.0 mol/L in THF, 6.62 mL, 6.62 mmol). The resulting mixture was stirred at rt for 3.5h. This was partitioned bwtween aq. saturated $NaHCO_3$ and AcOEt. Evaporation of the organic layer gave a crude alcohol. At this time, benzoyl migration was partially occurred to give an inseparable mixture (*ca*. 1:1). Therefore, this was used for next reaction without further purification. The mixture was dissolved in CH_2Cl_2 (40 mL), then treated with pyridine (893 µL, 11.04 mmol) and PhOC(S)Cl (764 µL, 5.52 mmol) at 0 ℃. After 1.5 h stirring of the resulting mixture, this was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/AcOEt = 3/1) gave a mixture of thiocarbonate **5b** and **S7** (*ca*. 1:1 mixture, 760 mg, 32% for three steps). Preparative TLC (hexane/AcOEt = 17/1, 8 times evolution) gave a pure **5b** as an oil: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.74 (s, 1H), 4.82-4.98 (m, 2H), 6.06-6.14 (m, 1H), 6.25 (dd, J = 15.6 and 1,6 Hz, 1H), 7.02 (dd, J = 15.6 and 5.6 Hz, 1H), 7.07-7.09 (m, 2H), 7.30-7.34 (m, 1H), 7.41-7.45 (m, 2H), 7.49-7.53 (m, 2H), 7.63-7.67 (m, 1H), 8.10-8.12 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 52.3, 69.9 (dd, $J_{C,F}$ = 34.6 and 29.8 Hz), 70.9 (dd, $J_{C,F}$ = 32.2 and 26.2 Hz), 118.5 (t, $J_{C,F}$ = 248.0 Hz), 122.0, 126.7, 127.3, 128.8, 129.2, 130.1, 130.4, 134.5, 136.7, 153.9, 164.6, 165.6, 194.5. HRFAB-MS (*m/z*) 437.0861 (M^++H) calcd for $C_{21}H_{19}F_2O_6S$ (M^++H) 437.0870.

5. Preparation of 5c



2,2-Difluoro-3-hydroxy-4-phenylselenenyl-butyric acid ethyl ester (S9)

To a stirring mixture of $Cu(OAc)_2$ (106 mg, o.59 mmol) in AcOH (20 mL) was added activated Zn powder (1.9 g) at 110 ℃. The resulting suspension was vigorously stirred further 3 min at same temperature. After decantation of most of AcOH, the crude Zn/Cu couple was sequentially washed by AcOH (20 mL) and Et_2O (20 mL). To a THF (70 mL) suspension of above wet Zn/Cu couple was carefully added ethyl bromodifluoroacetate (3.0 mL, 23.4 mmol) at 80 ℃, then refluxed further 5 min. The resulting zinc enolate was cooled at 0 ℃. To this, a THF (20 mL) solution of **S8**3) (2.9 g, 14.6 mmol) was dropwise added. The resulting mixture was stirred at rt further 1 h. After filtration of the mixture through a celite pad, the filtrate was partitioned between aq. saturated $NaHCO_3$ and AcOEt. Column chromatography on silica gel (hexane/Et_2O = 3/1) of the organic layer gave **S9** (2.98 g, 63%)

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2) Senapati, B. K.; Gao, L.; Lee, S. II; Hwang, G-S.; Ryu, D. H. *Org. Lett.* **2010**, *12*, 5088.

as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, J = 7.4 Hz, 3H), 2.79 (br-s, 1H), 3.08 (dd, J = 12.6 and 10.4 Hz, 1H), 3.26 (dd, J = 12.6 and 3.0 Hz, 1H), 4.10-2.18 (m, 1H), 4.35 (q, J = 7.4 Hz, 2H), 7.29-7.31 (m, 3H), 7.53-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 28.2, 63.3, 70.3 (dd, $J_{C,F}$ = 30.0 and 25.2 Hz), 113.8 (dd, $J_{C,F}$ = 259.1 and 254.3 Hz), 127.8, 128.2, 129.4, 133.2, 163.0 (t, $J_{C,F}$ = 32.2 Hz). FAB-MS (*m/z*) 324 (M^++H). Anal. Calcd for $C_{12}H_{14}F_2O_3Se\cdot 1/2\ H_2O$: C, 43.39; H, 4.55. Found: C, 43.79; H, 4.24.

2,2-Difluoro-3-hydroxy-*N*-methoxy-*N*-methyl-4-phenylselenenyl butyramide (S10)

To a THF (150 mL) suspension of *N*,*O*-dimethylhydroxylamine hydrochloride (8.52 g, 81.4 mmol, previously dried by P_2O_5 under vacuum condition for 2 days) was dropwise added BuLi (2.69 mol/L in hexane, 65.0 mL, 174.7 mmol) at −80 ℃. The resulting solution was allowed to rt for 5 min. To the mixture was added **S9** (7.06 g, 21.8 mmol) in THF (50 mL) at −80 ℃ then rinsed by using further THF (20 mL). After 1 h stirring of the mixture, this was partitioned between aq. saturated NH_4Cl and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 1/1) of the organic layer gave **S10** (5.24 g, 71%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06-3.17 (m, 2H), 3.23-3.26 (m, 4H), 3.73 (s, 3H), 4.30-4.38 (m, 1H), 7.21-7.31 (m, 3H), 7.51-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.7, 33.1, 62.2, 71.2 (dd, $J_{C,F}$ = 28.6 and 25.1 Hz), 115.3 (dd, $J_{C,F}$ = 263.3 and 259.6 Hz), 127.5, 129.4, 131.1, 133.1, 163.0. HRFAB-MS (*m/z*) 340.0293 (M^++H) calcd for $C_{12}H_{16}F_2NO_3Se$ (M^++H) 340.0263.

4,4-Difluoro-5-hydroxy-6-phenylselenohex-2-enoic acid methyl ester (S11)

To a THF (90 mL) solution of **S10** (3.75 g, 11.09 mmol) was dropwise added DIBAL-H (1.0 mol/L in toluene, 44.4 mL, 44.4 mmol) at −80 ℃. After 15 min stirring of the resulting mixture, this was allowed to rt for 5 min. The mixture was partitioned between 0.5 N HCl and AcOEt. The organic layer was filtrated through a celite pad then the filtrate was evaporated. This gave a crude aldehyde, which was used to the next step without further purification. An MeCN (90 mL) solution of the aldehyde was treated with $Ph_3P=CHCO_2Me$ (11.1 g, 33.3 mmol). The resulting suspension was stirred at rt for 15 h. This was partitioned between brine and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 4/1) of the organic layer gave **S11** (2.07 g, 56%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (d, J = 4.0 Hz, 1H), 2.87 (dd, J = 13.2 and 10.4 Hz, 1H), 3.16 (dd, J = 13.2 and 2.4 Hz, 1H), 3.72 (s, 3H), 3.79-3.82 (m, 1H), 6.25-6.28 (m, 1H), 6.80-6.90 (m, 1H), 7.20-7.24 (m, 3H), 7.46-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.3, 52.2, 71.7 (t, $J_{C,F}$ = 30.6 Hz), 118.8 (t, $J_{C,F}$ = 245.5 Hz), 126.4 (t, $J_{C,F}$ = 8.4 Hz), 127.9, 128.1, 129.4, 133.3, 136.6 (t, $J_{C,F}$ = 26.4 Hz), 165.2. HRFAB-MS (*m/z*) 336.0089 (M^++H) calcd for $C_{13}H_{14}F_2O_3Se$ (M^++H) 336.0076.

Benzoic acid 2,2-difluoro-4-methoxycarbonyl-1-phenylselenomethyl-but-3-enyl ester (5c)

To a CH_2Cl_2 (20 mL) solution of **S11** (623 mg, 1.86 mmol) was added DMAP (228 mg, 1.86 mmol), *i*-Pr_2NEt (648 µL, 3.72 mmol) and BzCl (326 µL, 2.79 mmol) at 0 ℃. The resulting mixture was stirred at 0 ℃ for 4 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/AcOEt = 6/1) of the organic layer gave **5c** (639 mg, 78%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.20 (dd, J = 13.6 and 10.0 Hz, 1H), 3.33 (dd, J = 13.6 and 3.2 Hz, 1H), 3.78 (s, 3H), 5.63-5.68 (m, 1H), 6.36 (d, J = 15.6 Hz, 1H), 6.81-6.91 (m, 1H), 7.23-7.24 (m, 3H), 7.44-7.47 (m, 2H), 7.52-7.54 (m, 2H), 7.59-7.63 (m, 1H), 7.97-7.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.6, 52.2, 72.5 (t, $J_{C,F}$ = 29.8 Hz), 117.9 (dd, $J_{C,F}$ = 245.6 and 243.2 Hz), 126.9 (t, $J_{C,F}$ = 8.3 Hz), 127.8, 128.6, 128.7, 129.2, 129.9, 133.5, 133.7, 136.0 (t, $J_{C,F}$ = 25.0 Hz), 164.9, 164.9. HRFAB-MS (*m/z*) 440.0353 (M^++H) calcd for $C_{20}H_{18}F_2O_4Se$ (M^++H) 440.0338.

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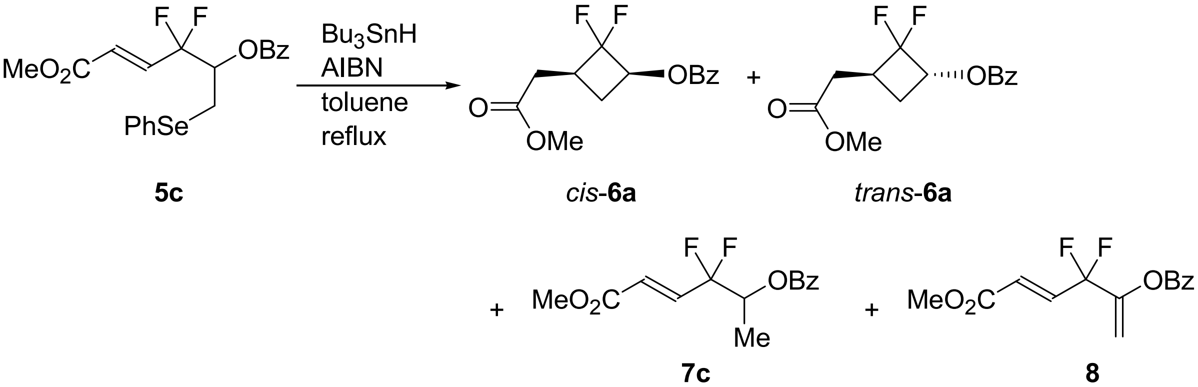
3) Abbas, M.; Bethke, J.; Wessjohann, L. A. *Chem. Commun.* **2006**, 541.

6. Radical reaction of 5c

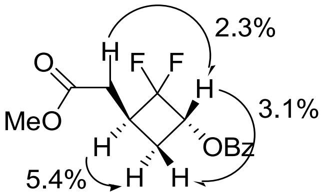


5c *cis*-**6a** *trans*-**6a** **7c** **8**

Compound **5c** (220 mg, 0.5 mmol) was treated by the procedure described for the reaction of **5a**. Column chromatography on silica gel (hexane/Et_2O = 9/1) gave an inseparable mixture of **7c** and **8** (27 mg, 12% and 7% respectively, calcurated by integration of ^{1}H NMR) and a mixture of **6a** (hexane/Et_2O = 5/1). This was purified by preparative TLC (hexane/AcOEt = 20/1, 7 times evolution). This gave *cis*-**6a** (60 mg, 48%, oil) and *trans*-**6a** (31 mg, 24%, oil) respectively.

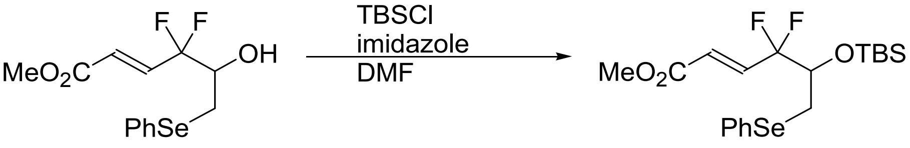
Physical data for *trans*-6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05-2.14 (m, 1H), 2.19-2.29 (m, 1H), 2.46 (dd, J = 16.8 and 8.8 Hz, 1H), 2.65-2.72 (m, 1H), 3.65 (s, 3H), 5.40-5.48 (m, 1H), 7.34-7.41 (m, 2H), 7.51-7.55 (m, 1H), 8.00-8.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.0 (dd, $J_{C,F}$ = 10.9 and 4.9 Hz), 33.0 (d, $J_{C,F}$ = 22.8 Hz), 52.2, 72.2 (dd, $J_{C,F}$ = 30.0 and 19.1 Hz), 119.2 (t, $J_{C,F}$ = 289.6 Hz), 128.5, 129.0, 129.9, 133.4, 165.2, 171.3. HRFAB-MS (*m/z*) 285.0961 (M^++H) calcd for $C_{14}H_{15}F_2O_4$ (M^++H) 285.0938.

NOE experiments of *trans*-6a



Physical data for 7c and 8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (d, J = 6.4 Hz, 3H), 3.77 (s, 4.8H), 5.33-5.40 (m, 1H), 5.46 (dd, J = 3.2 and 1.2 Hz, 0.6H), 5.59 (d, J = 3.2 Hz, 0.6H), 6.28-6.38 (m, 1.6H), 6.79-6.91 (m, 1.6H), 7.37-7.49 (m, 3.2H), 7.56-7.63 (m, 1.6H), 8.00-8.07 (m, 3.2H); ^{13}C NMR for **7c** (125 MHz, $CDCl_3$) δ 13.7, 52.2, 70.4 (t, $J_{C,F}$ = 31.0 Hz), 118.3 (t, $J_{C,F}$ = 242.0 Hz), 126.7 (t, $J_{C,F}$ = 8.4 Hz), 128.5, 129.8, 130.2, 133.6, 136.4 (t, $J_{C,F}$ = 25.1 Hz), 165.1; ^{13}C NMR for **8** (125 MHz, $CDCl_3$) δ 52.2, 107.2 (t, $J_{C,F}$ = 3.6 Hz), 114.2 (t, 232.3 Hz), 126.3 (t, $J_{C,F}$ = 8.3 Hz), 128.8, 129.2, 129.9, 134.0, 137.1 (t, $J_{C,F}$ =28.6 Hz), 146.3 (t, $J_{C,F}$ = 29.8 Hz), 165.0. FAB-MS (*m/z*) 285 (M^++H) for **7c**, 263 (M^+–F) for **8**.

7. Preparation of 5d



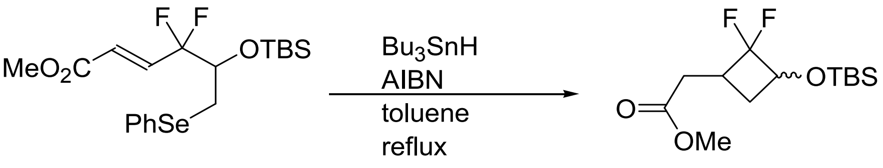
S11 **5d**

5-(*tert*-Butyldimethylsiloxy)-4,4-difluoro-6-phenylseleno-hex-2-enoic acid methyl ester (5d)

To a DMF (6 mL) solution of **S11** (373 mg, 1,11 mmol) was added imidazole (302 mg, 4.44 mmol) and TBSCl (335 mg, 2.22 mmol). The resulting solution was stirred at rt for 4 days. The mixture was partitioned between aq. saturated $NaHCO_3$ and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 11/1) of the organic layer gave **5d** (260 mg, 52%) as an oil: ^{1}H NMR (400 MHz,

$CDCl_3$) δ –0.06 (s, 3H), 0.00 (s, 3H), 0.76 (s, 9H), 2.71 (dd, J = 12.4 and 4.8 Hz, 1H), 2.98 (dt, J = 12.4 and 2.8 Hz, 1H), 3.66 (s, 3H), 3.94-4.01 (m, 1H), 6.17 (dq, J = 16.0 and 1.2 Hz, 1H), 6.75 (ddd, J = 16.0, 14.8 and 9.6 Hz, 1H), 7.09-7.15 (m, 3H), 7.31-7.34 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.7, –4.4, .18.2, 25.8 29.5 (d, $J_{C,F}$ = 6.0 Hz), 52.2, 74.5 (dd, $J_{C,F}$ = 32.2 and 27.4 Hz), 119.4 (t, $J_{C,F}$ = 244.4 Hz), 126.3 (t, $J_{C,F}$ = 7.2 Hz), 127.1, 129.2, 130.1, 132.4, 136.4 (t, $J_{C,F}$ = 25.0 Hz), 165.3. HRFAB-MS (m/z) 451.0967 (M^++H) calcd for $C_{19}H_{29}F_2O_3SiSe$ (M^++H) 451.1019.

8. Radical reaction of 5d

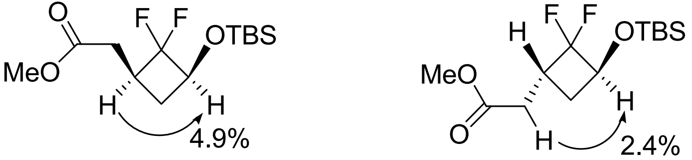


5d **6d**

Compound **5d** (2.17 g, 4.82 mmol) was treated by the procedure described for the reaction of **5a**. Column chromatography on silica gel (hexane/Et_2O = 15/1) gave **6d** (1.29 g, 91%, *ca.* 2:1 of inseparable mixture) as an oil:

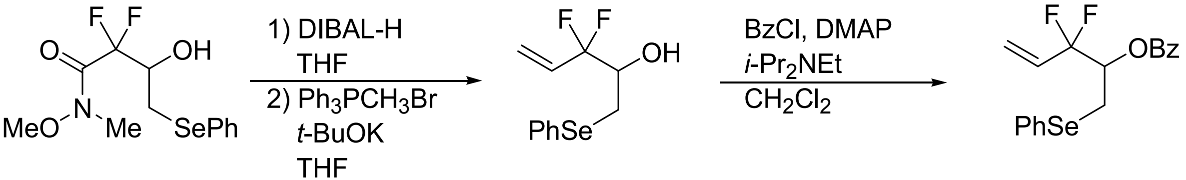
Physical data for 6d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 1.5H), 0.09 (s, 3H), 0.10 (s, 1.5H), 0.10 (s, 3H), 0.90 (s, 13.5H), 1.35-1.42 (m, 1H), 1.87-1.90 (m, 1H), 2.35-2.41 (m, 1.5H), 2.48-2.53 (m, 1H), 2.57-2.70 (m, 2.5H), 3.05-3.10 (m, 0.5H), 3.69 (s, 3H), 3.69 (s, 1.5H), 4.26-4.33 (m, 1H), 4.42-4.48 (m, 0.5H); ^{13}C NMR (125 MHz, $CDCl_3$) of *cis*-**6d**: δ –5.2, –5.0, 18.1, 25.6, 29.6 (d, $J_{C,F}$ = 22.8 Hz), 31.8 (d, $J_{C,F}$ = 7.2 Hz), 35.0 (t, $J_{C,F}$ = 22.7 Hz), 51.8, 70.4 (dd, $J_{C,F}$ = 25.0 and 17.9 Hz), 121.2 (dd, $J_{C,F}$ = 296.9 and 277.8 Hz), 171.8. ^{13}C NMR (125 MHz, $CDCl_3$) of *trans*-**6d**: δ –5.2, –5.0, 18.1, 25.6, 29.0 (dd, , $J_{C,F}$ =14.4 and 3.6 Hz), 33.5 (d, $J_{C,F}$ = 3.6 Hz), 37.5 (t, $J_{C,F}$ = 21.5 Hz), 51.8, 71.8 (dd, $J_{C,F}$ = 27.4 and 19.1 Hz), 120.5 (dd, $J_{C,F}$ = 290.9 and 286.2 Hz), 171.6. HRFAB-MS (m/z) 295.1537 (M^++H) calcd for $C_{13}H_{25}F_2O_3Si$ (M^++H) 295.1541.

NOE experiments of 6d: The NOE experiments were carried out as a mixture of two diastereomers.



cis-**6d** (major) *trans*-**6d** (minor)

9. Preparation of 5e



S9 **S12** **5e**

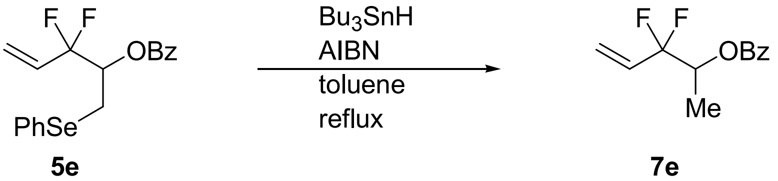
3,3-Difluoro-1-phenylselenopent-4-en-2-ol (S12)

To a THF (30 mL) solution of **S9** (1.25 g, 3.7 mmol) was dropwise added DIBAL-H (1.0 mol/L in toluene, 14.8 mL, 14.8 mmol) at –80 ℃. The resulting mixture was allowed to rt for 5 min. This was partitioned between 0.5 N HCl and AcOEt. The organic layer was dried by Na_2SO_4, then through a celite pad. Evaporation of the filtrate gave a crude aldehyde(*ca,* 1.12 g). This was used for the next step without further purification. To a THF (20 mL) suspension of Ph_3PCH_3Br (4.64 g, 13.0 mmol) was dropwise added *t*-BuOK (1.0 mol/L in THF, 11.1 mL, 11.1 mmol) at 0 ℃. The resulting yellowish suspension was stirred at rt for 1 h. To the mixture was added above aldehyde in THF (20 mL) at −80 ℃. The mixture was stirred further 1 h at rt. The mixture was partitioned between aq. saturated NH_4Cl and AcOEt. Column chromatography on silica gel (hexane/Et_2O = 4/1) gave **S12** (757 mg, 74%) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 2.67 (d, J = 4.0 Hz, 1H), 2.95 (dd, J = 13.2 and 10.4 Hz, 1H), 3.23 (dd, J = 13.2 and 2.8 Hz, 1H), 3.83-3.92 (m, 1H), 5.56 (d, J = 10.8 Hz, 1H), 5.70-5.75 (m, 1H), 5.94-6.07 (m, 1H), 7.27-7.31 (m, 3H), 7.52-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.4, 71.9 (t, $J_{C,F}$ = 29.9 Hz), 119.3 (t, $J_{C,F}$ = 245.4 Hz), 121.5 (t, $J_{C,F}$ = 9.5 Hz), 127.7, 128.5, 129.4, 129.6 (t, $J_{C,F}$ = 26.4 Hz), 133.2. HRFAB-MS (*m/z*) 278.0015 (M^++H) calcd for $C_{11}H_{12}F_2OSe$ (M^++H) 278.0021.

Benzoic acid 2,2-difluoro-1-phenylselenomethyl-but-3-enyl ester (5e)

To a CH_2Cl_2 (25 mL) solution of **S12** (680 mg, 2.45 mmol) was treated with BzCl (374 μL, 3.2 mmol), DMAP (601 mg, 4.9 mmol) and *i*-Pr_2NEt (854 μL, 4.0 mmol). The resulting solution was stirred at 0 ℃ for 3 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/AcOEt = 9/1) gave **5e** (874 mg, 94%) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 3.20 (dd, J = 13.6 and 10.4 Hz, 1H), 3.32 (dd, J = 13.6 and 2.8 Hz, 1H), 5.51 (dd, J = 11.2 and 0.4 Hz, 1H), 5.56-5.64 (m, 1H), 5.69-5.74 (m, 1H), 5.85-5.98 (m, 1H), 7.20-7.22 (m, 3H), 7.40-7.44 (m, 2H), 7.49-7.59 (m, 3H), 7.95-7.97 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.7 (t, $J_{C,F}$ = 35.9 Hz), 72.8 (dd, $J_{C,F}$ = 33.5 and 30.0 Hz), 118.3 (dd, $J_{C,F}$ = 247.8 and 244.1 Hz), 122.1 (t, $J_{C,F}$ = 9.6 Hz), 127.6, 128.4, 129.0, 129.1, 129.2, 129.5 (t, $J_{C,F}$ = 25.1 Hz), 129.9, 133.4, 133.6, 165.1. HRFAB-MS (*m/z*) 382.0287 (M^++H) calcd for $C_{18}H_{16}F_2O_2Se$ (M^++H) 382.0284.

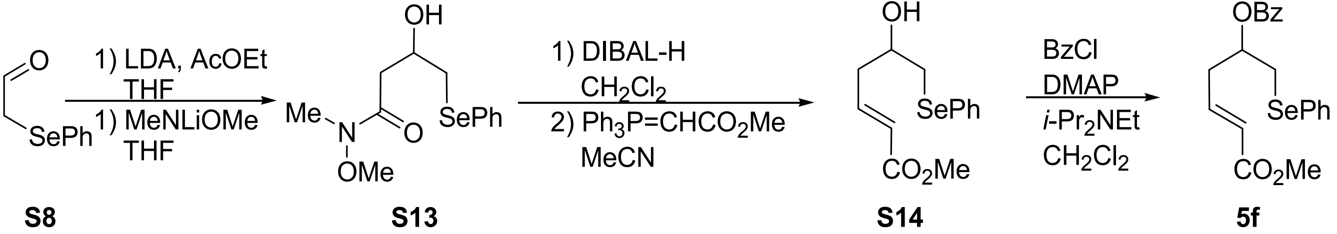
10. Radical reaction of 5e



Compound **5e** (529 mg, 1.39 mmol) was treated by the procedure described for the reaction of **5a**. Column chromatography on silica gel (hexane/Et_2O = 20/1) gave **7e** (227 mg, 72%) as an oil.

Physical data for 7e ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, J = 6.4 Hz, 3H), 5.36-5.44 (m, 1H), 5.56 (d, J = 11.2 Hz, 1H), 5.77 (dt, J = 17.2 and 2.4 Hz, 1H), 5.93-6.06 (m, 1H), 7.44-7.48 (m, 2H), 7.57-7.61 (m, 1H), 8.03-8.06 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 70.6 (t, $J_{C,F}$ = 31.1 Hz), 118.7 (dd, $J_{C,F}$ = 245.3 and 242.9 Hz), 121.6 (t, $J_{C,F}$ = 9.6 Hz), 128.4, 129.8 (t, $J_{C,F}$ = 21.6 Hz), 129.8, 130.0, 165.2. HRFAB-MS (*m/z*) 226.0820 (M^++H) calcd for $C_{12}H_{12}F_2O_2$ (M^++H) 226.0805.

11. Preparation of 5f



3-Hydroxy-N-methoxy-N-methyl-4-(phenylseleno)butyramide (S13)

To a THF (25 mL) solution of diisopropylamine (2.11 mL, 15.1 mmol) was dropwise added BuLi (2.66 mol/L in hexane, 5.7 mL, 15.1 mmol) at −80 ℃. The resulting mixture was further stirred for 10 min at same temperature then 10 min at rt. To the mixture was dropwise added AcOEt (1.48 mL, 15.1 mmol) at −80 ℃ then stirred further 1 h at same temperature. To the resulting lithium enolate solution was dropwise added **S8** (1.5 g, 7.53 mmol) in THF (20 mL) over 3 min. The mixture was stirred at −80 ℃ for 30 min. The mixture was partitioned between aq. saturated NH_4Cl and AcOEt. Evaporation of the organic layer gave a crude ester (*ca.* 2.12 g) which was used for next step without further purification. To a stirred suspension of *N*,*O*-dimethylhydroxylamine hydrochloride (2.13 g, 21.8 mmol) in THF (40 mL) was dropwise added BuLi (2.66 mol/L in hexane, 16.4 mL, 43.7 mmol) at −40 ℃. The mixture was stirred at rt for 10 min. To the resulting lithium amide solution was added above ester in THF (15 mL) at −40 ℃ then stirred for 1 h at same temperature. The mixture was partitioned between aq. saturated NH_4Cl and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 1/4) gave **S13** (1.29 g, 57% for two steps) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61-2.67 (m, 1H), 2.81-2.84 (m, 1H), 3.08 (dd, *J* = 12.8 and 6.4 Hz, 1H), 3.13 (dd, *J* = 12.8 and 6.4 Hz, 1H), 3.17 (s, 3H), 3.65 (s, 3H), 3.97 (br-d, 1H), 4.19-4.21 (m, 1H), 7.24-7.29 (m, 3H), 7.52-7.55 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.7, 34.1, 37.1, 61.1, 67.4, 126.9, 129.0, 129.7, 132.5, 172.9. HRFAB-MS (*m/z*) 304.0438 (M^++H) calcd for $C_{12}H_{18}NO_3Se$ (M^++H) 304.0452.

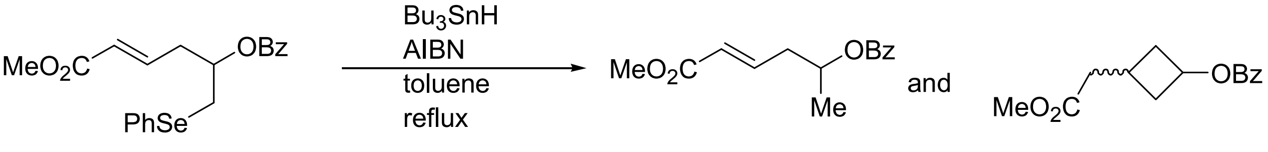
5-Hydroxy-6-(phenylseleno)-hex-2-enoic acid methyl ester (S14)

To a CH_2Cl_2 (30 mL) solution of **S13** (1.27 g, 4.2 mmol) was dropwise added DIBAL-H (0.99 mol/L in toluene, 9.3 mL, 9.2 mmol) at −80 ℃. After 30 min stirring at same temperature, further DIBAL-H (4.23 mL, 4.2 mmol) then stirred for 1 h. The mixture was partitioned between aq. saturated NH_4Cl and CH_2Cl_2. Evaporation of the organic layer gave a crude aldehyde. This was dissolved in MeCN (40 mL) then treated with Ph_3P=$CHCO_2Me$ (3.09 g, 9.24 mmol). The resulting suspension was stirred at rt for 24h. After evaporation of all of volatiles, the residue was purified by column chromatography on silica gel (hexane/AcOEt = 2/1). This gave **S14** (507 mg, 40% for two steps) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40-2.53 (m, 3H), 2.91 (dd, *J* = 13.2 and 8.8 Hz, 1H), 3.12 (dd, *J* = 13.2 and 4.0 Hz, 1H), 3.72 (s, 3H), 3.78-3.84 (m, 1H), 5.88 (dt, *J* = 15.6 and 1.2 Hz, 1H), 6.94 (dt, *J* = 15.6 and 7.5 Hz, 1H), 7.27-7.30 (m, 3H), 7.51-7.56 (m,2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 36.5, 39.0, 51.5, 68.6, 123.7, 127.6, 128.7, 129.3, 133.3, 144.5, 166.6. HRFAB-MS (*m/z*) 300.0288 (M^++H) calcd for $C_{13}H_{16}O_3Se$ (M^++H) 300.0265.

Benzoic acid 4-methoxycarbonyl-1-(phenylselenomethyl)-but-3-enyl ester (5f)

To a mixture of **S14** (500 mg, 1.67 mmol), DMAP (410 mg, 3.34 mmol) and *i*-Pr_2NEt (580 μL, 3.34 mmol) in CH_2Cl_2 (17 mL) was added BzCl (254 μL, 2.17 mmol) at 0 ℃. After 30 min stirring of the resulting mixture at rt, this was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/Et_2O = 3/1) gave **5f** (575 mg, 85%) as a solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.73-2.83 (m, 1H), 3.15 (dd, *J* = 12.8 and 6.4 Hz, 1H), 3.27 (dd, *J* = 12.8 and 6.0 Hz, 1H), 3.71 (s, 3H), 5.31-5.38 (m, 1H), 5.89 (dd, *J* = 15.6 and 0.8 Hz, 1H), 6.92 (dt, *J* = 15.6 and 7.2 Hz, 1H), 7.20-7.26 (m, 3H), 7.39-7.45 (m, 2H), 7.53-7.57 (m, 3H), 7.92-7.94 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.6, 36.1, 51.5, 72.4, 124.4, 127.4, 128.3, 129.2, 129.7, 129.8, 133.0, 133.1, 145.0, 165.7, 166.4. HRFAB-MS (*m/z*) 404.0514 (M^++H) calcd for $C_{20}H_{20}O_4Se$ (M^++H) 404.0527.

12. Radical reaction of 5f

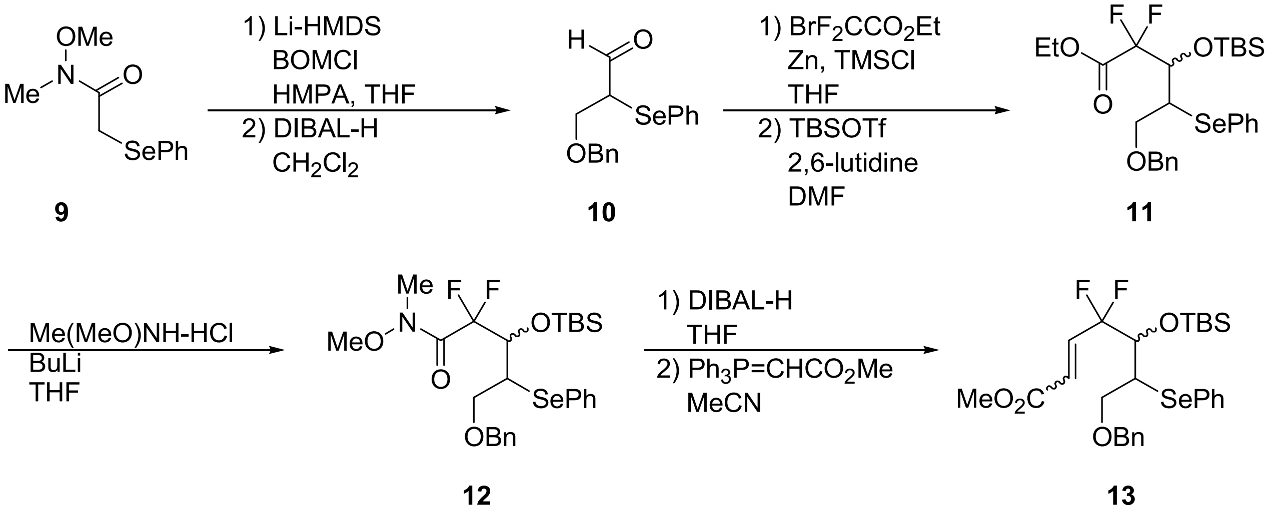


5f **7f** **6f**

Compound **5f** (403 mg, 1.0 mmol) was treated by the procedure described for the reaction of **5a**. Column chromatography on silica gel (hexane/Et_2O = 3/1) gave **7f** and **6f** [206 mg, 83%, *ca.* 1:0.20:0.16 (**7f**, 61%, **6f**, 22% respectively), calculated by integration of ^{1}H NMR] as an inseparable mixture.

Physical data for a mixture of 7f and 6f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (d, J = 6.4 Hz, 3H), 1.88-1.92 (m, 0.47H), 2.26-2.82 (m, 3.6H), 3.67 (s, 0.6H), 3.68 (s, 0.3H), 3.72 (s, 3H), 5.08-5.15 (m, 0.2H), 5.24-5.35 (m, 1.16H), 5.94 (d, J = 15.6 Hz, 1H), 6.98 (dt, J = 15.6 and 7.2 Hz, 1H), 7.42-7.46 (m, 2.86H), 7.54-7.58 (m, 1.6H), 8.02-8.06 (m, 2.84H); ^{13}C NMR for **7f** (125 MHz, $CDCl_3$) δ 19.7, 38.5, 51.5, 69.7, 123.9, 128.3, 129.5, 130.3, 132.9, 143.7, 165.6, 166.5. Partial ^{13}C NMR for **6f** (125 MHz, $CDCl_3$) δ 23.8, 25.6, 34.7, 36.3, 39.9, 40.8, 66.0, 68.8, 172.6, 172.8. FAB-MS (*m/z*) 249 (M^++H).

13. Preparatio of radical precursor 13



3-Benzyloxy-2-phenylselenenylpropionaldehyde (10)

To a THF (160 mL) solution of **9**[4,5)] (13.66 g, 52.9 mmol) was dropwise added Li-HMDS (1.0 mol/L in THF, 58.2 mL, 58.2 mmol) at −80 ℃ over 10 min. The resulting mixture was stirred further 30 min at same temperature. To this was sequentially added freshly distilled BOMCl (8.35 mL, 60.84 mmol) and HMPA (18.4 mL, 105.8 mmol). The mixture was slowly warmed to −55 ℃ then stirred further 20 h at same temperature. The mixture was partitioned between aq. saturated $NaHCO_3$ and AcOEt then dried by Na_2SO_4. After evaporation of all of volatiles of the organic layer, the residue was roughly purified by column chromatography on neutral silica gel (hexane/Et_2O = 6/4). This gave crude benzyl ether (14.08 g) as an oil. This benzyl ether was used for the next step without further purification. To a THF (90 mL) solution of above residue was dropwise added DIBAL-H (1.0 mol/L in toluene, 63.5 mL, 63.5 mmol) at −80 ℃ over 10 min. The resulting mixture was stirred further 45 min at same temperature. Then, the mixture was treated with aq. saturated Rochelle salt (*ca*. 100 mL) and stirred at rt for 1 h. The resulting mixture was partitioned between brine and Et_2O. Column chromatography on neutral silica gel (hexane/Et_2O = 3/1) of the organic layer gave an unstable aldehyde **10** (7.9 g, 47% for two steps) as a yellowish oil: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.81-3.89 (m, 3H), 4.53 (s, 2H), 7.28-7.55 (m, 10H), 9.49 (d, J = 3.2 Hz, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 51.4, 67.5, 73.7, 126.0, 128.1, 128.7, 129.3, 129.7 (2C), 136.3, 138.2, 192.9. HRFAB-MS (*m/z*) 321.0384 (M^++H) calcd for $C_{16}H_{17}O_2Se$ (M^++H) 321.0394.

5-Benzyloxy-3-(*tert*-butyldimethylsilanyloxy)-2,2-difluoro-4-phenylselenenyl-pentanoic acid ethyl ester (11) To a THF (10 mL) suspension of activated zinc (2.52 g) was added TMSCl (342 µL, 2.7 mmol). The resulting mixture was heated at 60 ℃. After 15 min stirring of the resulting mixture, THF (50 mL) and BrF_2CCO_2Et (4.93 mL, 38.5 mmol) were sequentially added, then heated at 60℃ for 5 min. The resulting THF solution which include zinc enolate was quickly transferred *via* cannula to a THF (50 mL) solution of **10** (6.14 g, 19.23 mmol) which was cooled at 0 ℃. The resulting mixture was stirred at rt for 2 h. The mixture was partitioned between 0.5 N HCl and AcOEt. Column chromatography (hexane/AcOEt = 3:1) of the organic layer gave a clude alcohol (7.29 g) as an oil. This was used for the next step without further purification. The crude alcohol was dissolved in DMF (70 mL). This was treated with 2,6-lutidine (7.25 mL, 65.6 mmol) and TBSOTf (7.53 mL, 32.8 mmol). The resulting mixture was stirred at rt for 4 days. This was partitioned between aq. saturated $NaHCO_3$ and AcOEt, then 0.5 N HCl and AcOEt. Column chromatography on neutral silica gel (hexane/Et_2O = 11/1) of the organic layer gave **11** (8.23 g, 77% for two steps) as a diastereomixture (*ca.* 5:1). Analytical samples were prepared by preparative TLC (hexane/AcOEt = 40/1, 4 times evolution). This gave *major*-**11** (slow moving) and *minor*-**11** (fast moving) each as an oil.

Physical data for *major*-11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 1.25 (dt, J = 7.6 and 0.4 Hz, 3H), 3.63-3.70 (m, 2H), 3.95 (dd, J = 9.6 and 6.8 Hz, 1H), 4.19 (q, 7.6 Hz, 2H), 4.47-4.60 (m, 3H), 7.23-7.35 (m, 8H), 7.54-7.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.3, −4.7, 13.8, 18.4, 25.7, 45.6, 63.0, 70.3, 71.6 (t, $J_{C,F}$ = 29.9 Hz), 72.3, 77.2, 114.2 (t, $J_{C,F}$ = 256.1 Hz), 127.6, 127.7, 127.8, 128.4, 129.1, 134.1, 137.7, 163.3 (t, $J_{C,F}$ = 32.3 Hz) ; ^{19}F NMR (470 MHz, $CDCl_3$) δ −111.5 (m). HRFAB-MS (*m/z*) 558.1531 (M^++H) calcd for $C_{26}H_{36}F_2O_4SiSe$ (M^++H) 558.1516.

Physical data for *minor*-11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 3H), 0.15 (s, 3H), 0.93 (s, 9H), 1.31 (t, J = 7.6 Hz, 3H), 3.49-3.56 (m, 2H), 3.77 (t, J = 10.0 Hz, 1H), 4.22-4.40 (m, 3H), 4.49 (d, J = 12.0 Hz, 1H), 4.56 (t, J = 9.2 Hz, 1H), 7.22-7.36 (m, 8H), 7.53-7.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.3, −4.7, 13.8, 18.4, 25.7, 45.6, 63.0, 70.3, 71.6 (t, $J_{C,F}$ = 29.9 Hz), 72.3, 77.2, 114.2 (t, $J_{C,F}$ = 256.1 Hz), 127.6, 127.7, 127.8, 128.4, 129.1, 134.2, 137.7, 163.3 (t, $J_{C,F}$ = 32.4 Hz) ; ^{19}F NMR (470 MHz, $CDCl_3$) δ −111.1 (d, J = 263.4 Hz), −114.8 (d, J = 263.4 Hz). HRFAB-MS (*m/z*) 558.1531 (M^++H) calcd for $C_{26}H_{36}F_2O_4SiSe$ (M^++H) 558.1516.

5-Benzyloxy-3-(*tert*-butyldimethylsilyloxy)-2,2-difluoro-4-phenylselenenyl-pentanoic acid methoxymethyl amide (12) To a THF (80 mL) suspension of *N*, *O*-dimethylhydroxylamine hydrochloride (4.05 g, 41.57 mmol, previously dried by P_2O_5 under vacuum condition for 2 days) was dropwise added BuLi (2.64 mol/L in hexane, 31.5 mL, 83.2 mmol) at −80 ℃. After 5 min stirring, this was allowed to rt for 10 min. The resulting mixture was cooled at −80 ℃, then added a THF (50 mL) solution of **11** (7.73 g, 13.86 mmol, *ca.* 5:1 mixture of two stereoisomers) *via* cannula. The mixture was stirred at same temperature for 24 h. Then the mixture was partitioned between aq. saturated NH_4Cl and AcOEt. Column chromatography on neutral silica gel (hexane/AcOEt = 2/1) of the organic layer gave **12** (7.14 g, 90% as a 5:1 of diastereomeric mixture). Analytical samples were prepared by preparative TLC (hexane/AcOEt = 8/1, five times evolution). This gave *major*-**12** (slow moving) and *minor*-**12** (fast moving) each as an oil

Physical data for *major*-12: ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.08 (s, 3H), 0.00 (s, 3H), 0.76 (s, 9H), 2.98 (s, 3H), 3.39 (s, 3H), 3.52-3.59 (m, 2H), 3.88-3.89 (m, 1H), 4.36 (d, J = 15.2 Hz, 1H), 4.43 (d, J = 15.2 Hz, 1H), 4.56-4.63 (m, 1H), 7.10-7.29 (m, 8H), 7.44-7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.0, −4.3. 18.4, 25.8, 33.1, 45.5, 61.7, 68.9, 72.9, 74.1 (t, $J_{C,F}$ = 22.7 Hz), 116.3 (t, $J_{C,F}$ = 256.4 Hz), 127.4, 127.6, 127.7, 128.2, 129.1, 129.6, 134.8, 138.2, 162.9 (t, $J_{C,F}$ = 28.6 Hz) ; ^{19}F NMR (470 MHz, $CDCl_3$) δ −108.4 (d, J = 254.3 Hz), −114.1 (d, J = 254.3 Hz). HRFAB-MS (*m/z*) 574.1683 (M^++H) calcd for $C_{26}H_{38}F_2NO_4SiSe$ (M^++H) 574.1703.

Physical data for *minor*-12: ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.04 (s, 3H), 0.00 (s, 3H), 0.83 (s, 9H), 3.09 (br-s, 3H), 3.42-3.45 (m, 2H), 3.61 (s, 3H), 3.68-3.73 (m, 1H), 4.24 (d, J = 12.0 Hz, 1H), 3.70 (d, J = 12.0 Hz, 1H) 4,74 (dd, J = 15.2 and 9.6 Hz, 1H), 7.12-7.25 (m, 8H), 7.48-7.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.2, −4.6, 18.4, 28.8, 33.4, 45.5, 61.8, 70.5, 70.5 (t, $J_{C,F}$ = 28.6 Hz), 72.2, 116.3 (t, $J_{C,F}$ = 254.0 Hz), 127.4, 127.5, 127.6, 127.7, 128.2, 129.0, 134.5, 138.9, 162.9 (t, $J_{C,F}$ = 28.6 Hz) ; ^{19}F NMR (470 MHz, $CDCl_3$) δ −110.6 (d, J = 254.3 Hz), −114.4 (d, J = 254.3 Hz). HRFAB-MS (*m/z*) 574.1683 (M^++H) calcd for $C_{26}H_{38}F_2NO_4SiSe$ (M^++H) 574.1703.

7-Benzyloxy-5-(*tert*-butyldimethylsilyloxy)-4,4-difluoro-6-phenylselenenyl-hept-2-enoic acid methyl ester (13) To a stirred solution of **12** (7.0 g, 12.2 mmol, *ca.* 5:1 mixture of two stereoisomers) in THF (100 mL) was dropwise added DIBAL-H (1.0 mol/L in toluene, 36.7 mL, 36.7 mmol) at −80 ℃.

The resulting mixture was stirred for 15 min at rt. The mixture was partitioned between 0.5 N HCl and AcOEt. The organic layer was dried by Na_2SO_4, then filtrated through a celite pad. The filtrate was evaporated. The crude aldehyde was dissolved in MeCN (100 mL), then treated with $Ph_3P{=}CHCO_2Me$ (12.26 g, 36.7 mmol). The resulting mixture was stirred at rt for 14 h. This was partitioned between brine and AcOEt. Column chromatography on silica gel (hexane/Et_2O = 4/1) of the organic layer gave **13** (6.45 g, 93%for two steps as a diastereomixture, *major*-(*E*)-**13**:(*Z*)-**13**:*minor*-(*E*)-**13** = 1.0:0.14:0.22 calcurated by integration of ^{1}HNMR). Analytical samples were prepared by preparative TLC (hexane/AcOEt = 50/1, seven times evolution). This gave *major*-(*E*)-**13**, (*Z*)-**13** and *minor*-(*E*)-**13** respectively each as an oil.

Physical data for *major*-(*E*)-13: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 3H), 0.13 (s, 3H), 0.90 (s, 9H), 3.59-3.67 (m, 2H), 3.75(s, 3H), 3.89 (dd, *J* = 10.0 and 5.6 Hz, 1H), 4.34 (ddd, *J* = 12.8, 7.2 and 1.6 Hz, 1H), 4.46 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 6.23 (dt, *J* = 16.0 and 1.6 Hz, 1H), 6.89 (ddd, *J* = 16.0, 13.6 and 11.2 Hz, 1H), 7.24-7.34 (m, 8H), 7.52-7.54 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.8, –4.7, 18.3, 25.8, 45.4 (d, $J_{C,F}$ = 3.6 Hz), 52.1, 69.2, 73.0, 76.4 (t, $J_{C,F}$ = 29.8 Hz), 119.3 (t, $J_{C,F}$ = 245.6 Hz), 125.6 (t, $J_{C,F}$ = 8.4 Hz), 127.6, 127.6, 127.7, 128.3, 129.2, 129.7, 134.2, 137.3 (t, $J_{C,F}$ = 25.1 Hz), 137.9, 165.3; ^{19}F NMR (470 MHz, $CDCl_3$) δ –101.3 (d, *J* = 254.3 Hz), –107.4 (d, *J* = 254.3 Hz). HRFAB-MS (*m/z*) 570.1523 (M^++H) calcd for $C_{27}H_{36}F_2O_4SiSe$ (M^++H) 570.1516.

Physical data for (*Z*)-13: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 3.62-3.72 (m, 2H), 3.66 (s, 3H), 4.02 (dd, *J* = 10.0 and 6.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.66-4.72 (m, 1H), 5.97 (d, *J* = 12.4 Hz, 1H), 6.02 (dt, *J* = 24.8 and 12.4 Hz, 1H), 7.23-7.32 (m, 8H), 7.53-7.56 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –4.7, –4.6, 18.4, 25.9, 46.4, 52.0, 69.2, 73.0, 76.4 (t, $J_{C,F}$ = 26.3 Hz), 119.6 (t, $J_{C,F}$ = 247.8 Hz), 125.9 (t, $J_{C,F}$ = 6.0 Hz), 127.5, 127.6, 127.8, 128.3, 129.1, 130.0, 133.7 (t, $J_{C,F}$ = 27.5 Hz), 134.1, 138.1, 165.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ –100.5 (d, *J* = 245.2 Hz), –101.7 (dd, *J* = 245.2 and 18.2 Hz). HRFAB-MS (*m/z*) 570.1485 (M^++H) calcd for $C_{27}H_{36}F_2O_4SiSe$ (M^++H) 570.1516.

Physical data for *minor*-(*E*)-13: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.12 (s, 3H), 0,92 (s, 9H), 3.35-3.38 (m, 1H), 3.62 (ddd, *J* = 10.0, 4.8 and 1.6 Hz, 1H), 3.76-3.81 (m, 1H), 3.78 (s, 3H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.56 (dd, *J* = 12.4 and 4.4 Hz, 1H), 6.26 (dt, *J* = 16.0 and 1.6 Hz, 1H), 7.16-7.35 (m, 9H), 7.39-7.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.3, –4.5, 18.3, 25.8, 29.7, 45.9 (d, $J_{C,F}$ = 6.0 Hz), 52.0, 70.6, 72.5, 73.0 (dd, $J_{C,F}$ = 34.6 and 28.6 Hz), 119.6 (t, $J_{C,F}$ = 243.2 Hz), 124.1 (t, $J_{C,F}$ = 8.3 Hz), 127.4, 127.8, 127.8, 128.4, 129.1, 129.7, 133.4, 137.4 (t, $J_{C,F}$ = 23.9 Hz), 137.6, 165.6; ^{19}F NMR (470 MHz, $CDCl_3$) δ –99.4 (d, *J* = 254.3 Hz), –108.8 (d, *J* = 254.3 Hz). HRFAB-MS (*m/z*) 570.1568 (M^++H) calcd for $C_{27}H_{36}F_2O_4SiSe$ (M^++H) 570.1516.

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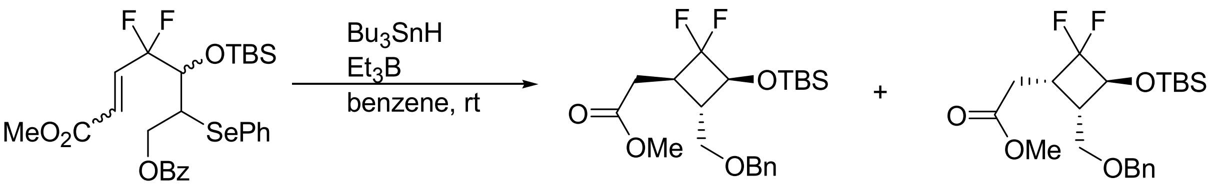
4) Shen, Z.; Khan, H. A.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 2916.

5) Barluenga, S.; Moulin, E.; Lopez, P.; Winssinger, N. *Chem. Eur. J.* **2005**, *11*, 4935.

14-1. Radical cyclization of 13: Transformation to [4-Benzyloxymethyl-3-(*tert*-butyldimethylsiloxy)-2,2-difluorocyclobutyl]-acetic acid methyl ester (14) (Table 2, entry 5)

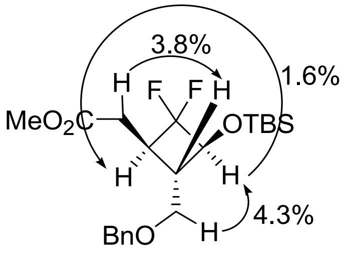


13 *trans, trans*-**14** *trans, cis*-**14**

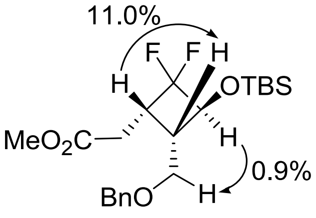
(2.6:1)

To a benzene (230 mL) solution of **13** (6.52 g, 11.45 mmol, 1.0:0.14:0.22 of diastereomeric mixture) and freshly opened Et_3B (1.0 mol/L in THF, 5.73 mL, 5.73 mmol) was dropwise added Bu_3SnH (6.16 mL, 22.9 mmol) over 24h using motor driven syringe at rt. When half volume of Bu_3SnH was transferred to the reaction mixture (*ca.* 12h), further Et_3B (5.73 mL, 5.73 mmol) was added then continued to stir further 12h at rt. After evaporation of all of volatiles, the residue was purified by column chromatography on silica gel (hexane/Et_2O = 4/1). This gave **14** (3.71 g, 78% , oil) as a diastereomeric mixture (*trans,trans*-**14**/*trans,cis*-**14** = *ca.* 2.6:1 based on the integration of ^{1}H NMR): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 1.16H), 0.07 (s, 3H), 0.08 (s, 1.16H), 0.09 (s, 3H), 0.88 (s, 3.47H), 0.89 (s, 9H), 1.86-1.90 (m, 1H), 2.39-2.49 (m, 0.39H), 2.48-2.70 (m, 3.77H), 3.13-3.21 (m, 0.39H), 3.53-3.62 (m, 2.77H), 3.63 (s, 1.16H), 3.64 (s, 3H), 4.22-4.28 (m, 1H), 4.31-4.36 (m, 0.39H), 4.43 (d, J = 12.1 Hz, 0.39H), 4.48 (d, J = 12.1 Hz, 0.39H), 4.51 (d, J = 12.0 Hz, 1H), 4.54 (d, J = 12.0 Hz, 1H), 7.27-7.36 (m, 6.95H); ^{13}C NMR (125 MHz, $CDCl_3$) for *trans, trans*-**14** δ –5.2. –5.1, 18.1, 25.6, 31.4 (d, $J_{C,F}$ = 6.0 Hz), 37.1, (dd, $J_{C,F}$ = 19.6 and 19.2 Hz), 42.7 (d, $J_{C,F}$ = 21.6 Hz), 51.8, 68.0 (d, $J_{C,F}$ = 2.4 Hz), 71.8 (dd, $J_{C,F}$ = 25.2 and 18.0 Hz), 73.3, 119.9 (dd, $J_{C,F}$ = 297.5 and 177.1 Hz), 127.5, 127.6, 128.4, 138.1, 171.8. ^{13}C NMR (125 MHz, $CDCl_3$) for *trans, cis*-**14** δ –5.5, 18.2, 25.6, 29.6, 39.0 (d, $J_{C,F}$ = 15.5 Hz), 39.2 (t, $J_{C,F}$ = 21.5 Hz), 51.6, 66.9 (d, $J_{C,F}$ = 2.4 Hz), 72.8 (dd, $J_{C,F}$ =26.4 and 20.4 Hz), 73.3, 120.0 (dd, $J_{C,F}$ = 293.9 and 282.0 Hz), 127.2, 127.8, 128.3, 137.8, 172.1; ^{19}F NMR (470 MHz, $CDCl_3$) for *trans*-**14** δ –91.8 (d, J = 190.7 Hz), –136.2 (d, J = 190.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) for *cis*-**14** δ –103.7 (d, J = 199.8 Hz), –117.4 (d, J = 199.8 Hz). HRFAB-MS (*m/z*) 415.2130 (M^++H) calcd for $C_{21}H_{33}F_2O_4Si$ (M^++H) 415.2116.

NOE experiments of 14: The NOE experiments were carried out as a mixture of two diastereomers.



trans, trans-**14**



trans, cis-**14** (minor)

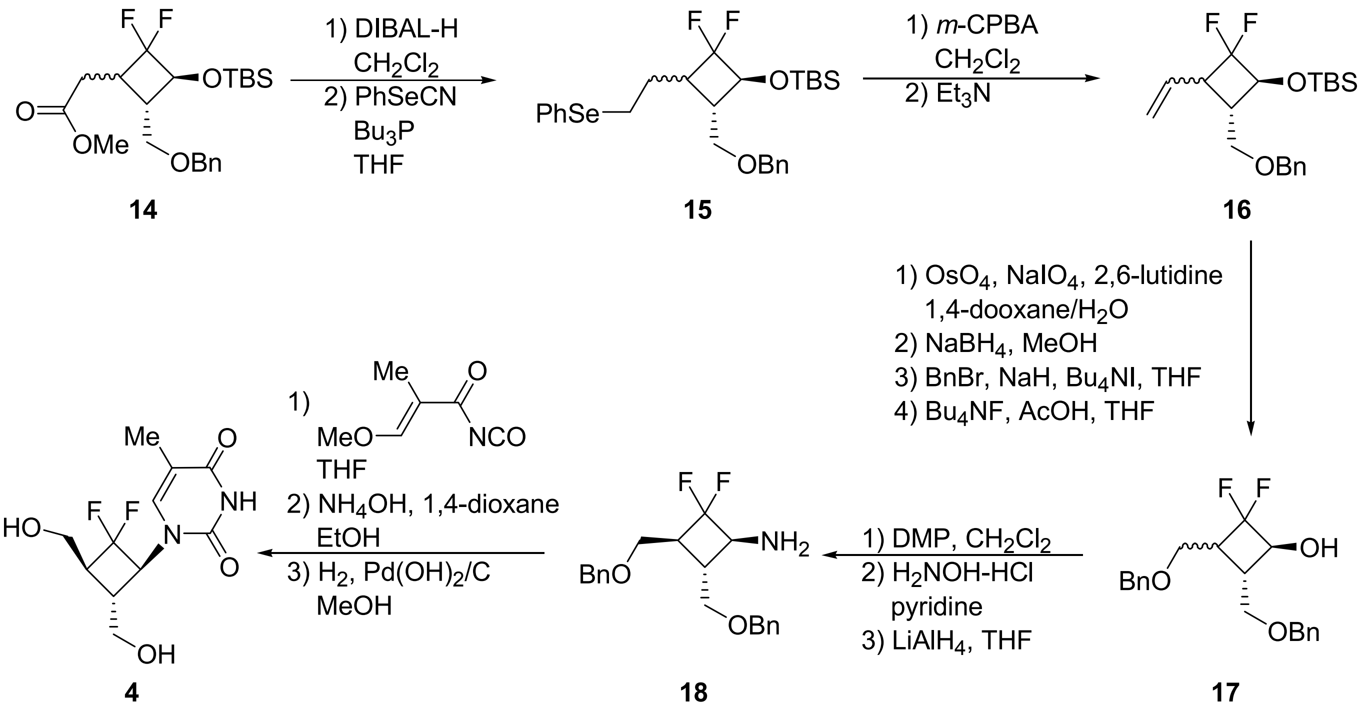
14-2. Radical reaction of *major*-(*E*)-13

Compound *major*-(*E*)-**13** (219 mg, 0.38 mmol) was treated with a same procedure described for **13**. This gave a mixture of **14** (112 mg, 71%, *trans*-**14**/*cis*-**14** = *ca.* 2.6:1 based on the integration of ^{1}H NMR).

14-3. Radical reaction of (*Z*)-13

Compound (*Z*)-**13** (106 mg, 0.19 mmol) was treated with a same procedure described for **13**. This gave a mixture of **14** (49 mg, 64%, *trans,trans*-**14**/*trans,cis*-**14** = *ca.* 1:1 based on the integration of ^{1}H NMR).

15. Synthesis of 4



3-Benzyloxymethyl-2-*tert*-butyldimethylsiloxy-1,1-difluoro-4-(phenylseleno)ethylcyclobutane (15)
To a stirred solution of **14** [3.5 g, 8.44 mmol, diastereomeric mixture (*ca*. 2.6:1)] in CH_2Cl_2 (85 mL) was dropwise added DIBAL-H (1.0 mol/L in toluene, 33.8 mL, 33.8 mmol) at −80 ℃. The resulting mixture was stirred further 20 min at rt. The mixture was partitioned between 0.5 N HCl and CH_2Cl_2. Evaporation of all of volatiles of the organic layer gave a crude alcohol (*ca*. 3.3 g). This was used for next step without further purification. To a THF (85 mL) solution of above alcohol was added PhSeCN (2.07 mL, 16.9 mmol) and Bu_3P (4.22 mL, 16.9 mmol) at 0 ℃. The resulting mixture was further stirred for 16 h at same temperature. This was partitioned between aq. saturated $NaHCO_3$ and AcOEtt. Column chromatography on neutral silica gel (hexane/Et_2O = 7/1) of the organic layer gave a mixture of **15** (4.32 g, 97% for two steps, *ca*. 3:1 of diastereomeric mixture). Analytical samples were prepared by preparative TLC (hexane/AcOEt = 50/1, four times evolution). This gave *major*-**15** (fast moving) and *minor*-**15** (slow moving) respectively each as an oil.

Physical data for *major*-15: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 3H), 0.08 (s, 3H), 0.89 (s, 9H), 1.79-1.89 (m, 2H), 1.97-2.06 (m, 1H), 2.31-2.39 (m, 1H), 2.84 (ddd, J = 12.0, 8.8 and 6.4 Hz, 1H), 2.94 (ddd, J = 12.0, 9.2 and 6.0 Hz, 1H), 3.52 (d, J = 4.4 Hz, 2H), 4.12-4.18 (m, 1H), 4.49-4.51 (m, 2H), 7.23-7.36 (m, 8H), 7.45-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.2, −5.0, 18.1, 25.0. 25.6, 27.3 (d, $J_{C,F}$ = 4.8 Hz), 41.2, (t, $J_{C,F}$ = 20.3 Hz), 42.6 (d, $J_{C,F}$ = 23.4 Hz), 68.5, 71.6 (dd, $J_{C,F}$ = 23.8 and 17.9 Hz), 73.1, 120.7 (dd, $J_{C,F}$ = 293.3 and 274.2 Hz), 126.9, 127.6, 127.7, 128.4m 129.1, 129.8, 132.6, 138.0; ^{19}F NMR (470 MHz, $CDCl_3$) δ −90.0 (d, J = 199.8 Hz), −137.2 (d, J = 199.8 Hz). HRFAB-MS (*m/z*) 527.1700 (M^++H) calcd for $C_{26}H_{37}F_2O_2SiSe$ (M^++H) 527.1696.

Physical data for *minor*-15: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.07 (s, 3H), 0.88 (s, 9H), 1.79-1.96 (m, 2H), 2.34-2.43 (m, 1H), 2.75-2.80 (m, 1H), 2.85 (ddd, J = 12.0, 10.0 and 6.4 Hz, 1H), 2.99 (ddd, J = 12.0, 10.4 and 5.2 Hz, 1H), 3.48 (t, J = 10.0 Hz, 1H), 3.53 (dd, J = 10.0 and 4.8 Hz, 1H), 4.13-4.20 (m, 1H), 4.43 (t, J = 12.4 Hz, 2H), 7.23-7.34 (m, 8H), 7.46-7.48 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −5.2, −5.0, 18.1, 25.6, 25.8, 29.7, 39.3 (d, $J_{C,F}$ = 17.9 Hz), 43.0 (t, $J_{C,F}$ = 20.3 Hz), 67.3 (d, $J_{C,F}$ = 3.6 Hz), 73.2, 73.6 (dd, $J_{C,F}$ = 27.4 and 20.3 Hz), 120.6 (dd, $J_{C,F}$ = 293.3 and 281.4 Hz), 126.8, 127.7, 127.8, 128.4, 129.0, 129.9, 132.5, 137.8; ^{19}F NMR (470 MHz, $CDCl_3$) δ −104.6 (d, J = 199.8 Hz), −115.2 (d, J = 199.8 Hz). HRFAB-MS (*m/z*) 527.1700 (M^++H) calcd for $C_{26}H_{37}F_2O_2SiSe$ (M^++H) 527.1696.

3-Benzyloxymethyl-2-*tert*-butyldimethylsiloxy-1,1-difluoro-4-vinylcyclobutane (16)

To a CH_2Cl_2 (80 mL) solution of **15** (4.2 g, 7.99 mmol, *ca*. 2.6:1 of diastereomeric mixture) was treated with *m*-CPBA (70%, 1.99 g, 8.07mmol) at 0 ℃. The resulting mixture was stirred for 10 min at same temperature, then added Et_3N (5.58 mL, 40 mmol). The mixture was refluxed for 20 h. The mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Column chromatography on silica gel (hexane/Et_2O = 60/1) of the organic layer gave an inseparable mixture of **16** (2.52 g, 86% for two steps, 2.6:1) as an oil. Analytical sample was prepared by preparative TLC (hexane/AcOEt = 40/1, *ca*. 2:1 mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.09 (s, 4.5H), 0.10 (s, 4.5H), 0.90 (s, 13.5H), 2.02-2.09 (m, 1H), 2.45-2.49 (m, 0.5H), 2.79-2.88 (m, 1H), 3.30-3.34 (m, 0.5H), 3.49-3.62 (m, 3H), 4.23-4.30 (m, 1H), 4.33-4.44 (m, 0.5H), 4.47-4.55 (m, 3H), 5.15-5.21 (m, 3H), 5.75 (dt, J = 16.4 and 9.6 Hz, 0.5H), 5.84 (ddd, J = 17.2, 10.4 and 7.6 Hz, 1H), 7.27-7.37 (m, 7.5H); ^{13}C NMR for ***major*-16** (125 MHz, $CDCl_3$) δ −5.2, −5.0, 18.1, 25.6, 42.4 (d, $J_{C,F}$ = 23.9 Hz), 44.4 (dd, $J_{C,F}$ = 22.7 and 19.1 Hz), 67.0 (d, $J_{C,F}$ = 2.4 Hz), 71.4 (dd, $J_{C,F}$ = 23.9 and 17.9 Hz), 73.0, 118.9, 120.1 (dd, $J_{C,F}$ = 296.3 and 274.8 Hz), 127.5, 127.6, 128.4, 130.7 (d, $J_{C,F}$ = 6.0 Hz), 138.1; ^{19}F NMR for ***major*-16** (470 MHz, $CDCl_3$) δ −91.4 (d, J = 190.7 Hz), −136.0 (d, J = 190.7 Hz); ^{13}C NMR for ***minor*-16** (125 MHz, $CDCl_3$) δ −5.2, −5.0, 18.1, 25.6, 40.7 (d, $J_{C,F}$ = 17.9 Hz), 48.0 (t, $J_{C,F}$ = 21.5Hz), 67.4 (d, $J_{C,F}$ = 3.6 Hz), 73.1, 73.6 (dd, $J_{C,F}$ = 26.2 and 19.1 Hz), 119.7 (dd, $J_{C,F}$ = 294.5 and 281.4 Hz), 120.2, 127.6, 127.8, 128.3, 130.0 (t, $J_{C,F}$ = 3.6 Hz), 138.1; ^{19}F NMR for ***minor*-16** (470 MHz, $CDCl_3$) δ −100.2 (d, J = 199.8 Hz), −118.0 (d, J = 199.8 Hz). HRFAB-MS (*m/z*) 369.2086 (M^++H) calcd for $C_{20}H_{31}F_2O_2Si$ (M^++H) 369.2061.

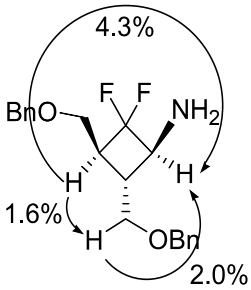
3,4-Bis-benzyloxymethyl-2,2-difluorocyclobutanol (17)

To a mixture of **16** (2.7 g, 7.35 mmol, *ca*. 2.6:1 of diastereomeric mixture), $NaIO_4$ (12.56 g, 58.8 mmol) and 2,6-lutidine (1.63 mL, 14.7 mmol) in 1,4-dioxane/H_2O (3/1, 200 mL) was added OsO_4 (0.16 mol/L in H_2O, 938 μL, 0.15 mmol). The resulting suspension was stirred at rt for 7 h. After filtration of the mixture through a celite pad, the filtrate was evaporated below 30 ℃ until half volume of the volatiles were removed. To the residue was added MeOH (100 mL) and $NaBH_4$ (2.78 g, 73.5 mmol) at 0 ℃. The mixture was stirred further 30 min at same temperature, then added acetone (3 mL). The mixture was filtrated through a celite pad, then the filtrate was evaporated. The residue was partitioned between 1 N HCl and CH_2Cl_2. Flush column chromatography on silica gel (hexane/AcOEt = 1/1) of the organic layer gave crude alcohol (*ca*. 2.25 g). This was used for next step without further purification. To an anhydrous THF (30 mL) solution of above alcohol was added NaH (60%, 294 mg, 7.35 mmol) at 0 ℃. After 20 min stirring of the resulting mixture, this was treated with BnBr (1.05 mL, 8.82 mmol) and Bu_4NI (2.71 g, 7.35 mmol). The mixture was stirred further 6 h at rt. Then, this was partitioned between aq. saturated NH_4Cl and AcOEt. After evaporation of all of volatiles of the organic layer, this was dissolved in THF (50 mL), then added AcOH (1.26 mL, 22.05 mmol) and Bu_4NF (1.0 mol/L in THF, 16.2 mL, 16.2 mmol). After 14 h stirring of the resulting mixture at rt, the mixture was partitioned between aq. saturated $NaHCO_3$ and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 1/1) of the organic layer gave an inseparable mixture of **17** (1.66 g, 65% for four steps, *ca*. 3.0:1) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86-1.93 (m, 1H), 2,05 (br-s, 1.3H), 2.39-2.42 (m, 0.3H), 2.56-2.68 (m, 1H), 2.90-2.92 (m, 0.3H), 3.55 (dd, J = 9.6 and 4.8 Hz, 1H), 3.59-3.64 (m, 2.6H), 3.67-3.77 (m, 1,6H), 4.20-4.27 (m, 1H), 4.34-4.41 (m, 0.3H), 4.43-4.57 (m, 5.2H), 7.28-7.37 (m, 13H); ^{13}C NMR for ***major*-17** (125 MHz, $CDCl_3$) δ 40.7 (d, $J_{C,F}$ = 20.3 Hz), 41.9 (t, $J_{C,F}$ = 20.3 Hz), 66.0 (d, $J_{C,F}$ = 6.0 Hz), 68.6 (d, $J_{C,F}$ = 2.4 Hz), 72.3 (dd, $J_{C,F}$ = 25.0 and 19.1 Hz), 73.0, 73.1, 119.9 (dd, $J_{C,F}$ = 295.7 and 271.9 Hz), 127.5, 127.6, 127.7, 127.7, 128.4, 128.4, 137.9, 138.0; ^{19}F NMR for ***major*-17** (470 MHz, $CDCl_3$) δ −92.7 (d, J = 199.8 Hz), −137.6 (d, J = 199.8 Hz); ^{13}C NMR for ***minor*-17** (125 MHz, $CDCl_3$) δ 39.9 (d, $J_{C,F}$ = 17.9 Hz), 43.1 (t, $J_{C,F}$ = 20.3 Hz), 64.8, 67.6 (d, $J_{C,F}$ = 3.6 Hz), 73.2, 73.3, 74.3 (dd, $J_{C,F}$ = 25.1 and 19.1 Hz), 120.1 (dd, $J_{C,F}$ = 287.4 and 270.7 Hz), 127.6, 127.6, 127.7, 127.8, 128.4, 128.5, 137.8, 137.9; ^{19}F NMR for ***minor*-17** (470 MHz, $CDCl_3$) δ −104.6 (d, J = 199.8 Hz), −120.1 (d, J = 199.8 Hz). HRFAB-MS (*m/z*) 349.1613 (M^++H) calcd for $C_{20}H_{23}F_2O_3$ (M^++H) 349.1615.

(±)-*t*-3,*c* -4-3,4-Bis(benzyloxymethyl)-1,1-difluorocyclobut-*r*-2-ylamine (18)

To a CH_2Cl_2 (20mL) solution of **17** (700 mg, 2.01 mmol, *ca*. 3:1) was added Dess-Martin periodinane (1.45 g, 3.42 mmol). The resulting mixture was stirred for 1 h at rt. To the mixture was added brine (50 mL) then stirred further 20 min. The mixture was partitioned between aq. saturated $NaHCO_3$ and CH_2Cl_2. Evaporation of all of volatiles of the organic layer gave a crude aldehyde (*ca*. 950 mg).The aldehyde was dissolved in pyridine (30 mL). The pyridine solution was treated with $HONH_2 \cdot HCl$ (1.4 g, 20.1 mmol). The resulting mixture was stirred for 3 days at rt. The resulting mixture was partitioned between $NaHCO_3$ and CH_2Cl_2. Flush column chromatography on silica gel (hexane/AcOEt = 1/1) gave a crude oxime (589 mg). This was well dried under vacuum condition by using P_2O_5 for 20 h. This was used for next reaction without further purification. To a THF (20 mL) solution of above oxime was dropwise added $LiAlH_4$ (1.0 mol/L in THF, 4.02 mL, 4.02 mmol) at –40 ℃. After 30 min stirring of the resulting mixture –40 ℃, this was stirred further 2 h at rt. The mixture was carefully treated with H_2O (6 mL), aq. 15%NaOH (6 mL) and H_2O (6 mL) sequentially. After filtration of the mixture through a celite pad, the filtrate was partitioned between brine and AcOEt. Column chromatography on silica gel (hexane/AcOEt = 1/3) of the organic layer gave **18** (220 mg, 32% for three steps) as an oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (br-s, 2H), 1.62-1.69 (m, 1H), 2.62-2.75 (m, 1H), 3.49 (dt, *J* = 11.6 and 8.4 Hz, 1H), 3.56 (dd, *J* = 9.8 and 4.8 Hz, 1H), 3.60 (dd, *J* = 9.8 and 4.8 Hz, 1H), 3.63-3.67 (m, 2H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.53 (s, 2H), 4.54 (d, *J* = 12.0 Hz, 1H), 7.26-7.35 (m, 10J); ^{13}C NMR (125 MHz, $CDCl_3$) δ 40.1 (d, $J_{C,F}$ = 20.4 Hz), 43.4 (t, $J_{C,F}$ = 20.4 Hz), 56.5 (t, $J_{C,F}$ = 22.8 Hz), 66.3 (d, $J_{C,F}$ = 7.3 Hz), 69.0 (d, $J_{C,F}$ = 2.4 Hz), 73.0, 73.1, 120.8 (dd, $J_{C,F}$ = 300.4 and 271.6 Hz), 127.5, 127.5, 127.6, 127.6, 128.3, 128.4, 138.1, 138.2; ^{19}F NMR (470 MHz, $CDCl_3$) δ –91.8 (d, *J* = 190.7 Hz), –136.7 (dd, *J* = 190.7 and 18.2 Hz). HRFAB-MS (*m/z*) 348.1786 (M^++H) calcd for $C_{20}H_{24}F_2NO_2$ (M^++H) 348.1775.

NOE experiments of 18



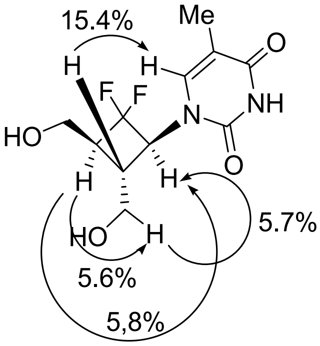
18

(±)-1-[*t*-3,*c*-4-3,4-Bis(hydroxymethyl)-1,1-difluorocyclobut-*r*-2-yl]-thymine (4)

To a CH_2Cl_2 (2.7 mL) solution of β-methoxy-α-metacrylic acid[6] (208 mg, 1.79 mmol) was added oxalyl chloride (172 μL, 1.97 mmol) and DMF (one drop) at rt. The resulting mixture was stirred for 40 min at same temperature. After evaporation of all of volatiles, the residue was dissolved in dry benzene (3.5 mL) then added a benzene (3.5 mL) suspension of silver cyanate (295 mg, 1.97 mmol). The mixture was refluxed for 30 min, then cooled to rt. The resulting supernatant solution include isocyanate (**19**) was slowly transferred over 1.5 min *via* cannula to a THF (9.3 mL) solution of **18** (207 mg, 0.596 mmol) at –40 ℃. The resulting mixture was stirred for 40 min at same temperature. After worming to rt of the mixture, this was stirred further 2 h at rt. The residue was roughly purified by flush column chromatography on silica gel (hexane/AcOEt = 1/1). This gave a crude adduct, which was used for next reaction without further purification. The above residue was dissolved in EtOH (10 mL), 1,4-dioxane (10 mL) and 29% NH_4OH[7] (20 mL). The resulting solution was heated at 110 ℃ in a shield tube for 15 h. After evaporation of all of volatiles, the residue was dissolved in MeOH (20 mL). This was treated with 20 wt % of $Pd(OH)_2$ (200 mg) under positive pressure of H_2 (1 atm) at rt for 4 h. After filtration through a celite pad, the filtrate was purified by preparative TLC ($CHCl_3$/acetone = 1/1). This gave **4** (93 mg, 56% for three steps). This was recrystalyzed from MeOH/1,2-dichloroethane. Mp = 235-237 ℃; ^1H NMR (500 MHz, CD_3OD) δ 1.90 (s, 3H), 2.60-2.63 (m, 1H), 2.65-2.75 (m, 1H), 3.67

(dd, *J* = 11.5 and 4.6 Hz, 1H), 3.71 (dd, *J* = 11.5 and 4.6 Hz, 1H), 3.76 (dd, *J* = 11.5 and 5.7 Hz, 1H), 3.85 (dd, *J* = 11.5 and 8.0 Hz, 1H), 5.10-5.16 (m, 1H), 7.52 (s, 1H); ^{13}C NMR (125 MHz, CD_3OD) δ 12.8, 37.6 (d, $J_{C,F}$ = 16.7 Hz), 46.4 (t, $J_{C,F}$ = 19.1 Hz), 58.0 (dd, $J_{C,F}$ = 25.0 and 17.9 Hz), 59,0 (d, $J_{C,F}$ = 7.2 Hz), 61.9, 111.8, 121.9 (dd, $J_{C,F}$ = 295.7 and 271.8 Hz), 140.1 (d, $J_{C,F}$ = 2.4 Hz), 153.4, 166.7; ^{19}F NMR (470 MHz, CD_3OD) δ −86.4 (d, *J* = 196.2 Hz), −132.7 (d, *J* = 196.2 Hz). FAB-MS (*m/z*) 277 (M^++H) Anal. Calcd for $C_{11}H_{14}F_2$ N_2O_4: C, 47.83; H, 5.11; N, 10.14. Found: C, 47.48; H, 5.06; N, 10.02.

NOE experiments of 4



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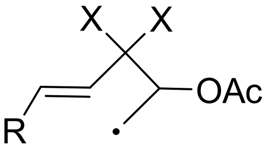
6) Csuk, R.; Scholz, Y. *Tetrahedron* **1995**, *51*, 7193.
7) Wang, P.; Agrofoglio, L. A.; Newton, M. G.; Chu, C. K. *J. Org. Chem.* **1999**, *64*, 4173.

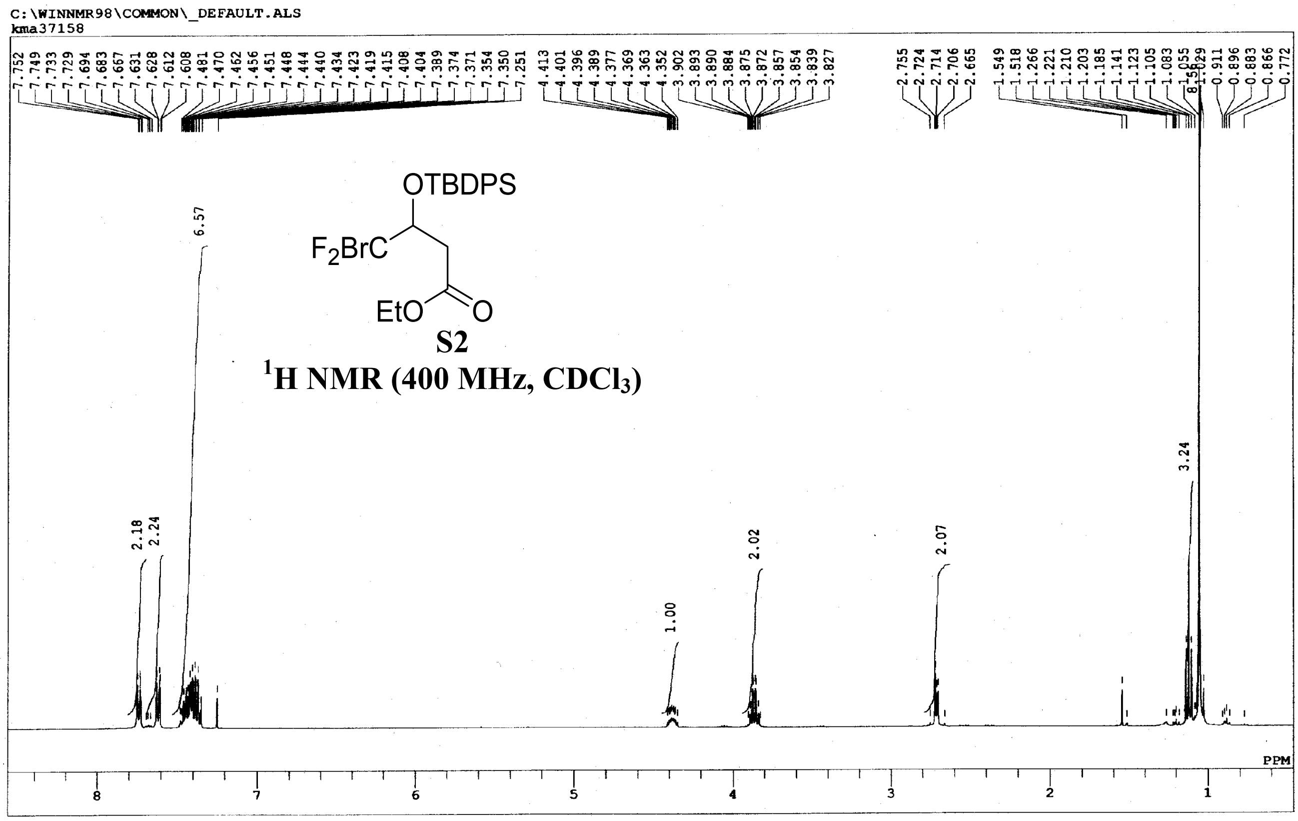
16. Table SI-1. SOMO and LUMO values of model radical intermediates 5c'-5f'

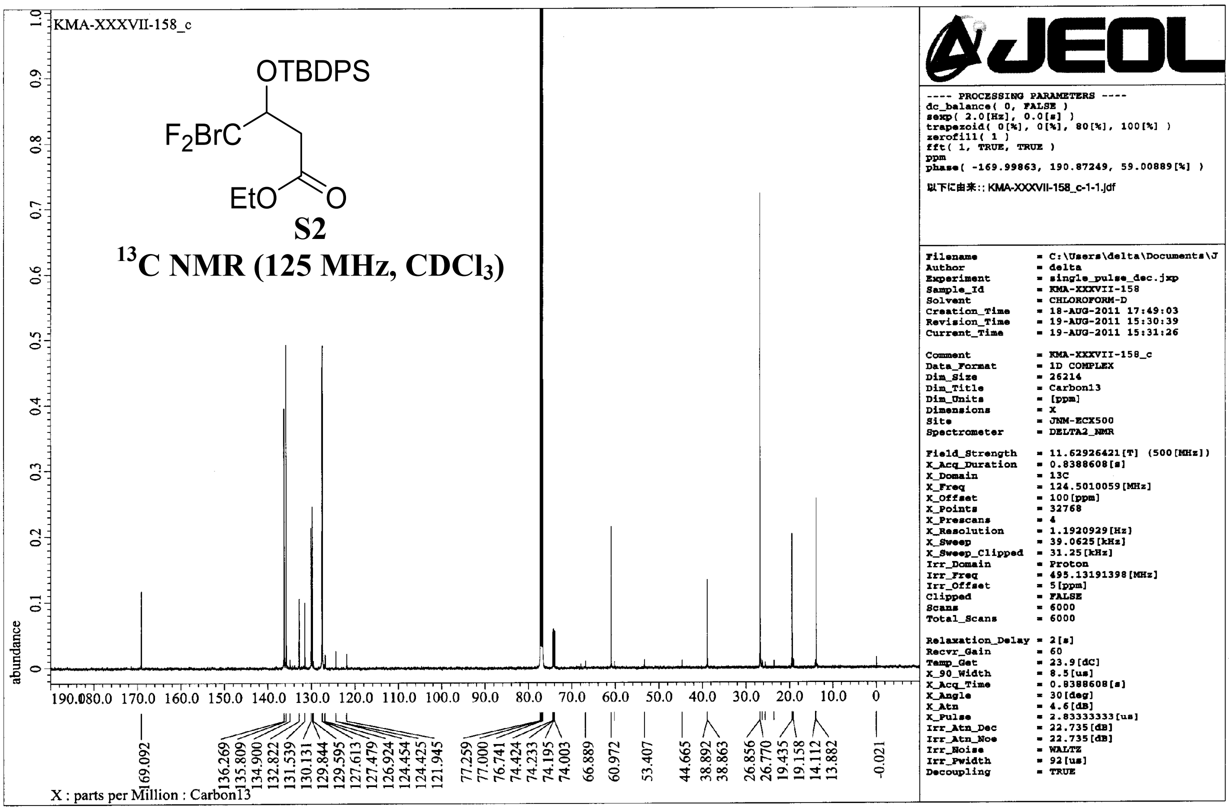


5c′ R = CO_2Me, X = F
5e′ R = H, X = F
5f′ R = CO_2Me, X = H

radical	SOMO (eV)[a]	LUMO (eV)[b]
5c′	−0.22456	0.03084
5e′	−0.21952	0.04128
5f′	−0.22244	0.04433

[a]Calculations were carried out by usingUB3LYP/6-31G.
[b]Calculations were carried out by usingUB3LYP/6-31G ※.





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Revision_Time       = 19-AUG-2011 15:30:39
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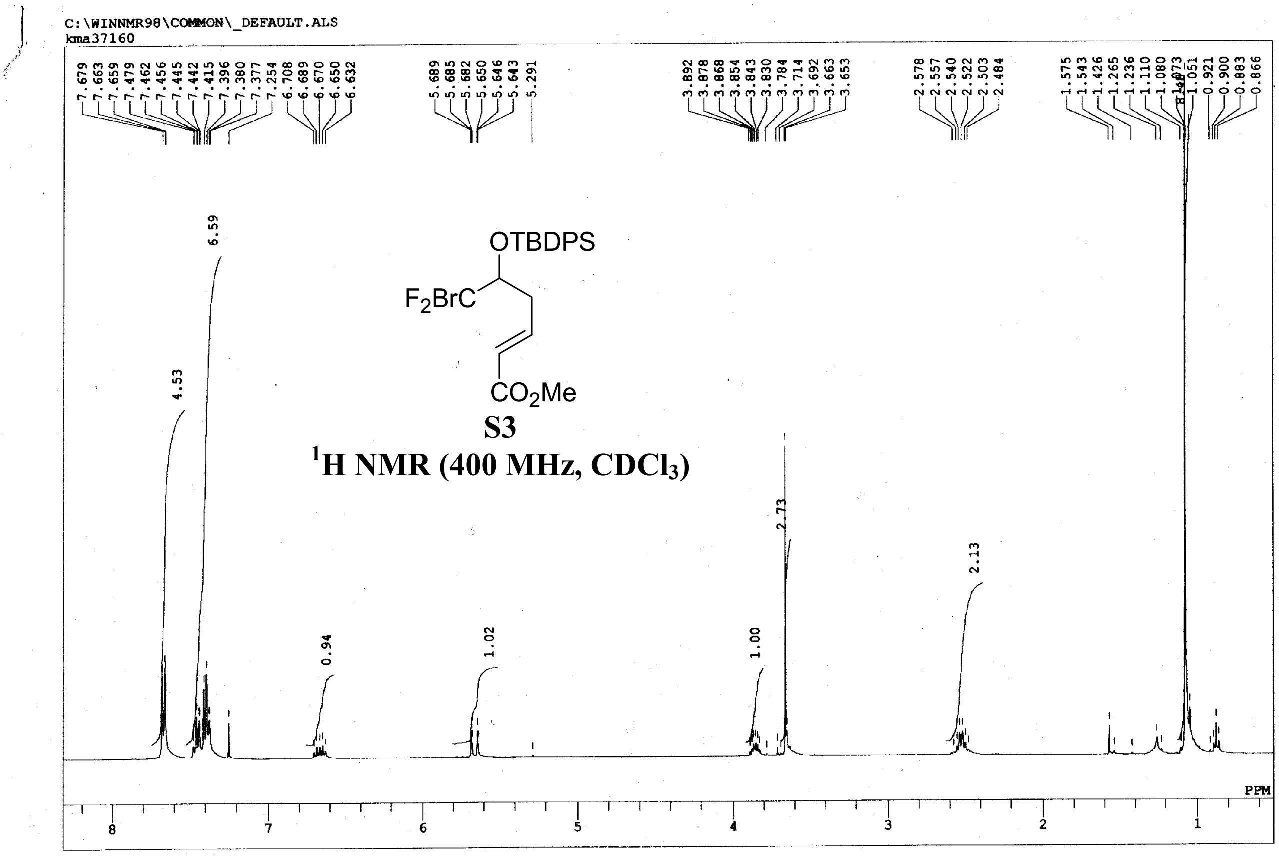

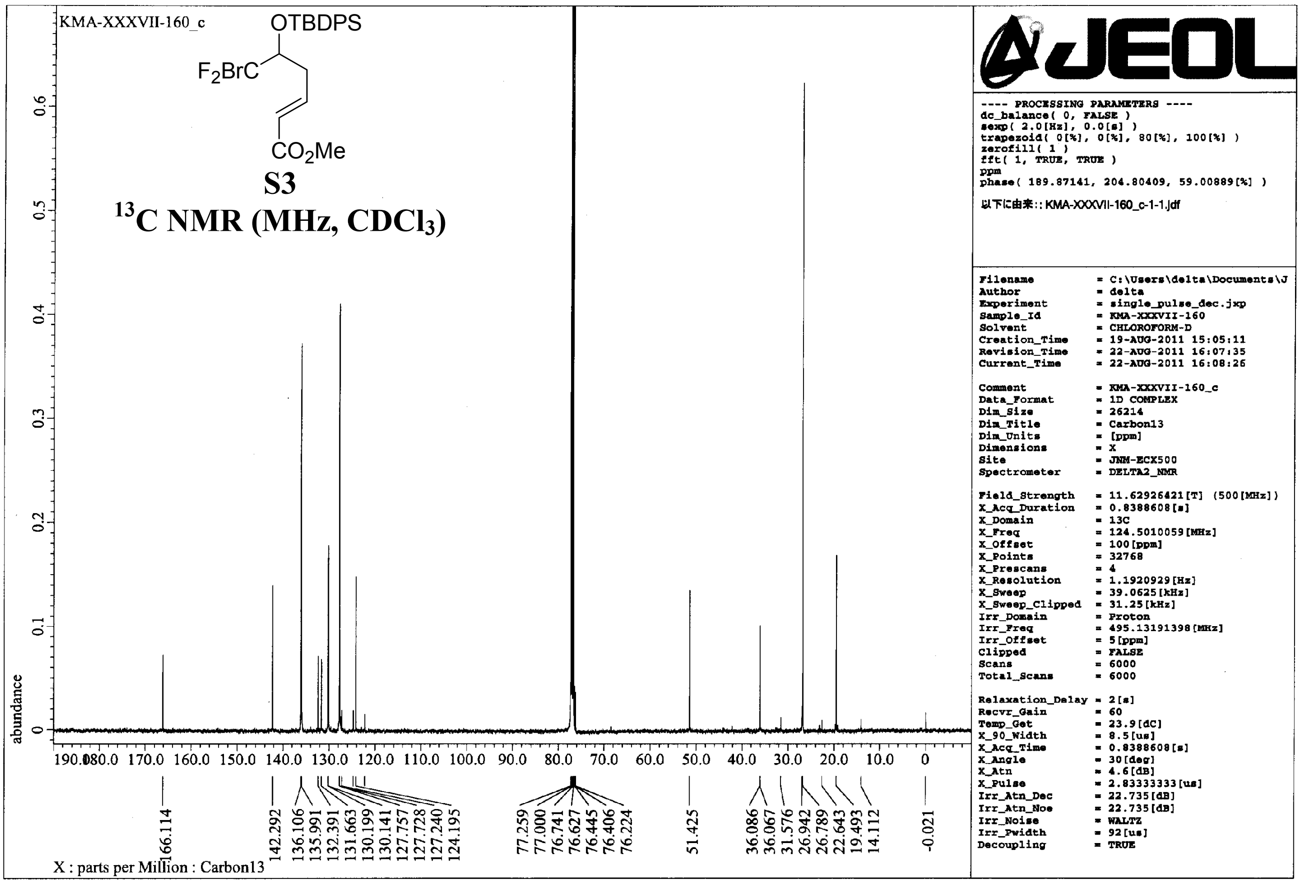

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Revision_Time     = 22-AUG-2011 16:07:35
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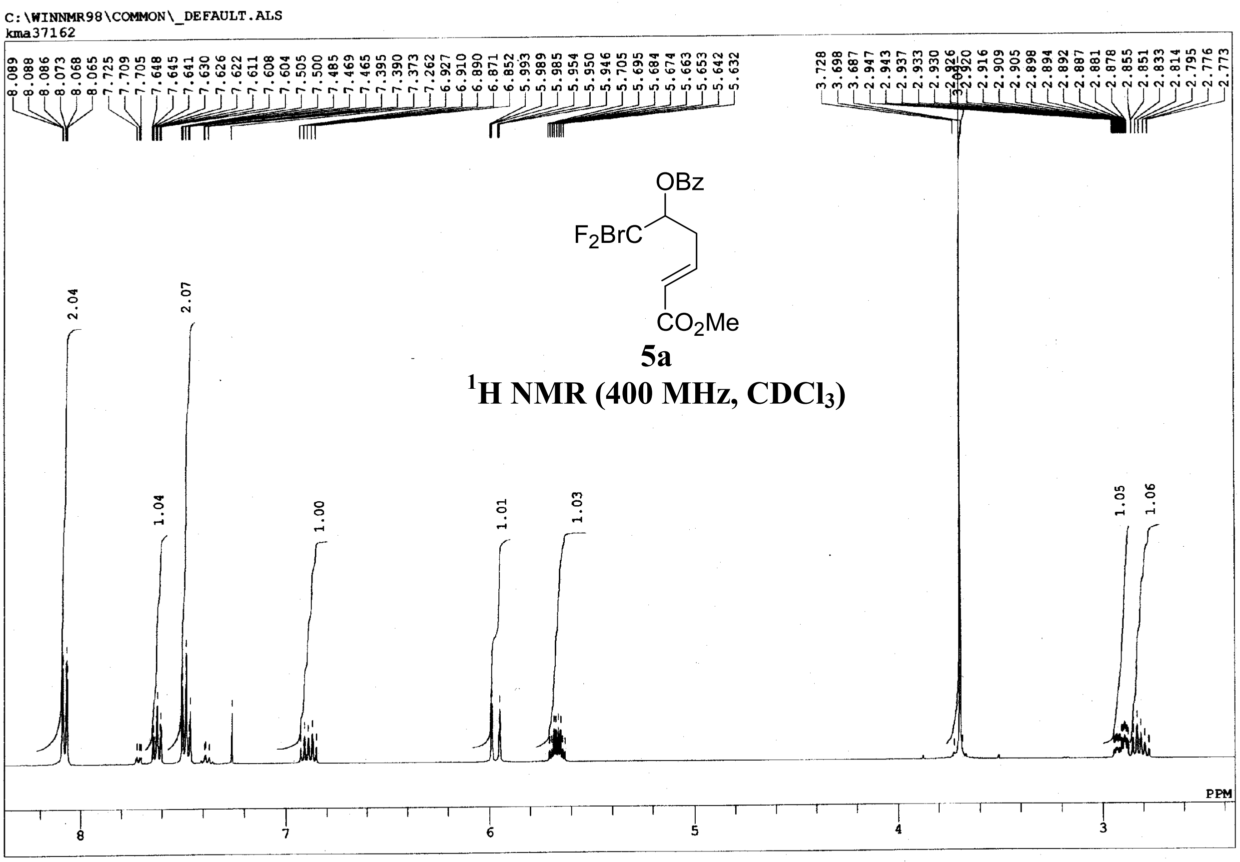
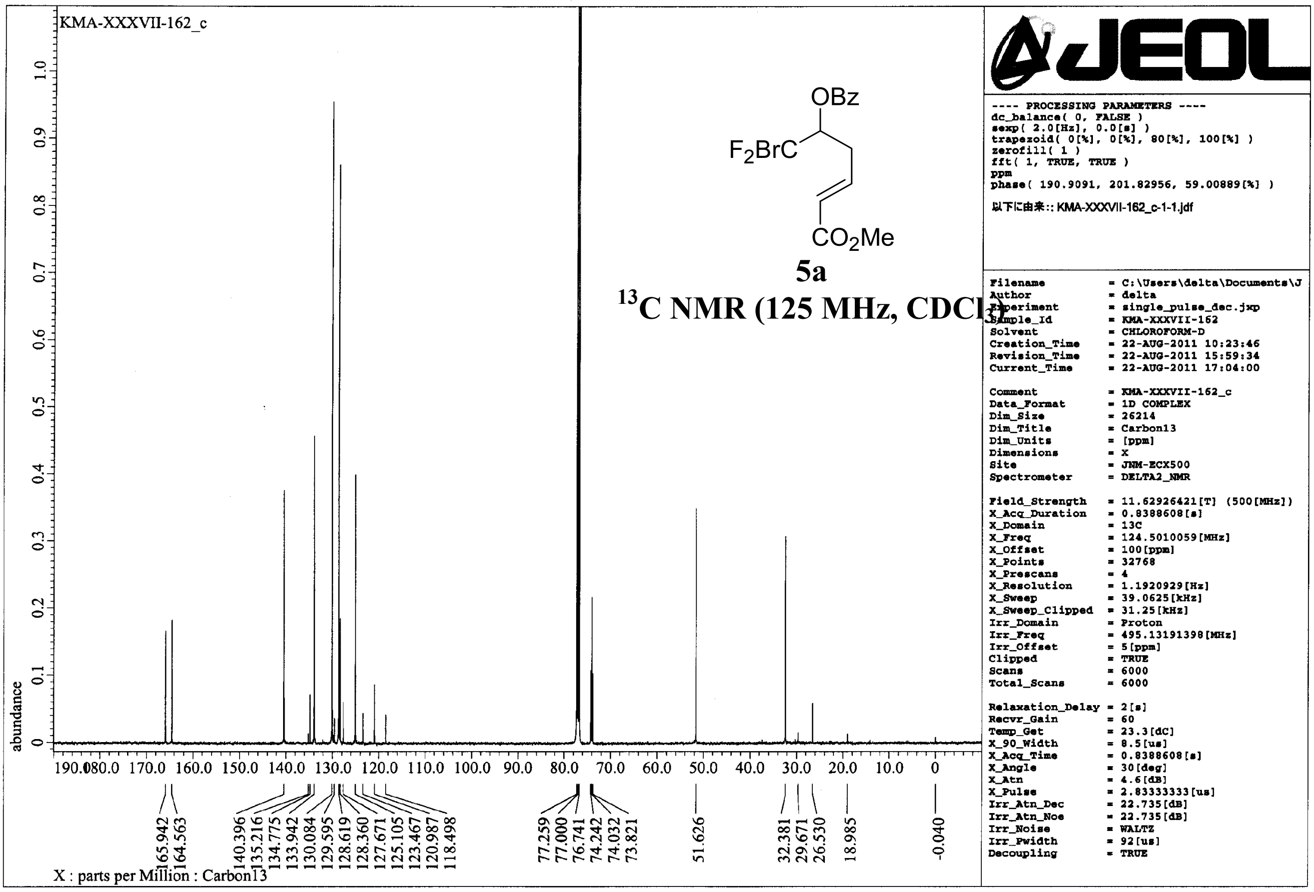
```





```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 190.9091, 201.82956, 59.00889[%] )

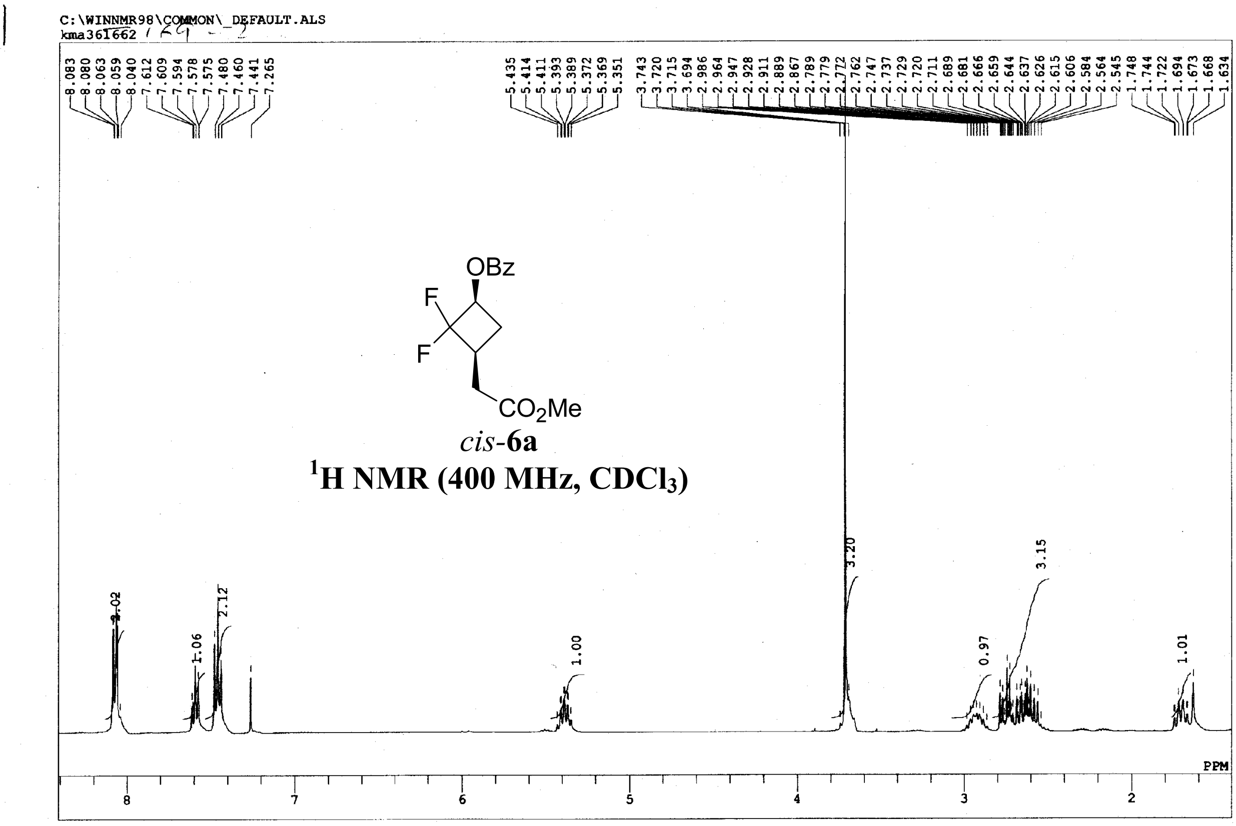
以下に由来:: KMA-XXXVII-162_c-1-1.jdf

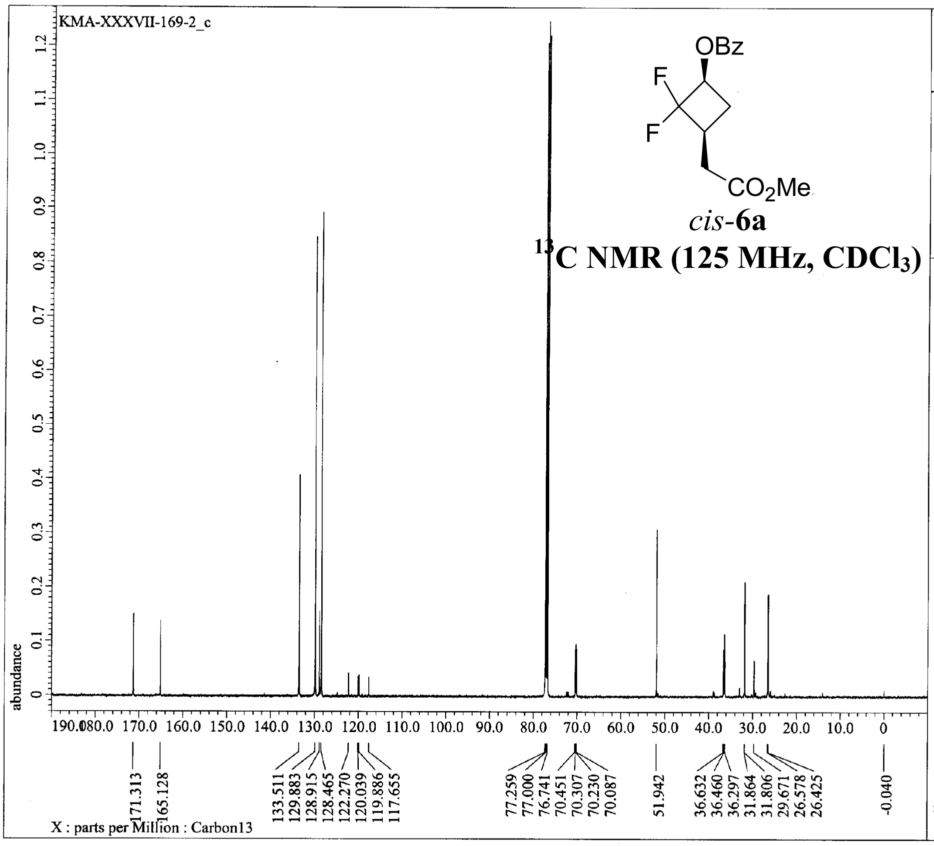
Filename             = C:\Users\delta\Documents\J
Author               = delta
Experiment           = single_pulse_dec.jxp
Sample_Id            = KMA-XXXVII-162
Solvent              = CHLOROFORM-D
Creation_Time        = 22-AUG-2011 10:23:46
Revision_Time        = 22-AUG-2011 15:59:34
Current_Time         = 22-AUG-2011 17:04:00

Comment              = KMA-XXXVII-162_c
Data_Format          = 1D COMPLEX
Dim_Size             = 26214
Dim_Title            = Carbon13
Dim_Units            = [ppm]
Dimensions           = X
Site                 = JNM-ECX500
Spectrometer         = DELTA2_NMR

Field_Strength       = 11.62926421[T] (500[MHz])
X_Acq_Duration       = 0.8388608[s]
X_Domain             = 13C
X_Freq               = 124.5010059[MHz]
X_Offset             = 100[ppm]
X_Points             = 32768
X_Prescans           = 4
X_Resolution         = 1.1920929[Hz]
X_Sweep              = 39.0625[kHz]
X_Sweep_Clipped      = 31.25[kHz]
Irr_Domain           = Proton
Irr_Freq             = 495.13191398[MHz]
Irr_Offset           = 5[ppm]
Clipped              = TRUE
Scans                = 6000
Total_Scans          = 6000

Relaxation_Delay     = 2[s]
Recvr_Gain           = 60
Temp_Get             = 23.3[dC]
X_90_Width           = 8.5[us]
X_Acq_Time           = 0.8388608[s]
X_Angle              = 30[deg]
X_Atn                = 4.6[dB]
X_Pulse              = 2.83333333[us]
Irr_Atn_Dec          = 22.735[dB]
Irr_Atn_Noe          = 22.735[dB]
Irr_Noise            = WALTZ
Irr_Pwidth           = 92[us]
Decoupling           = TRUE
```





```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 199.07248, 191.04239, 59.04322[%] )

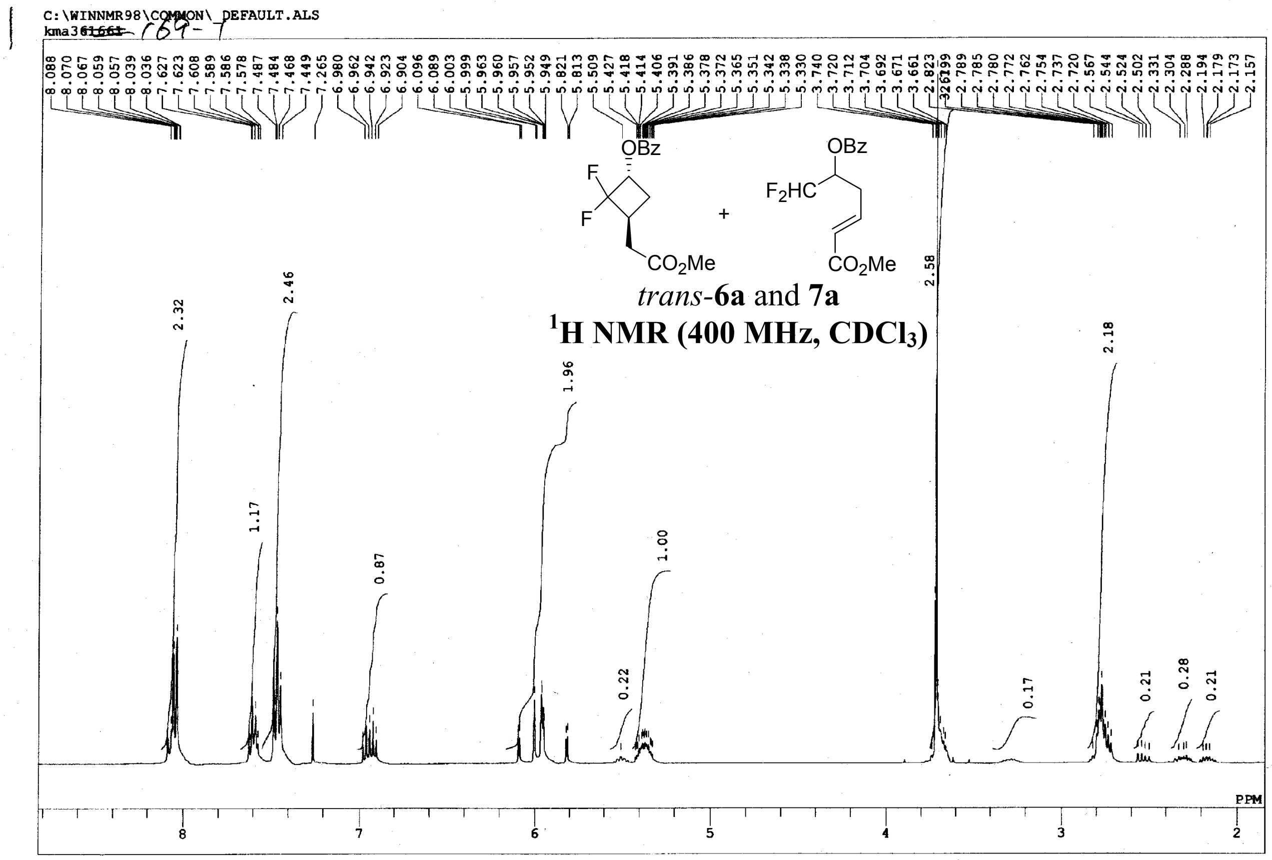
以下に由来:: KMA-XXXVII-169-2_c-2-1.jdf
```

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = single_pulse_dec.jxp
Sample_Id         = KMA-XXXVII-169-1
Solvent           = CHLOROFORM-D
Creation_Time     = 26-AUG-2011 17:08:45
Revision_Time     = 27-AUG-2011 14:11:32
Current_Time      = 27-AUG-2011 14:12:44

Comment           = KMA-XXXVII-169-2_c
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

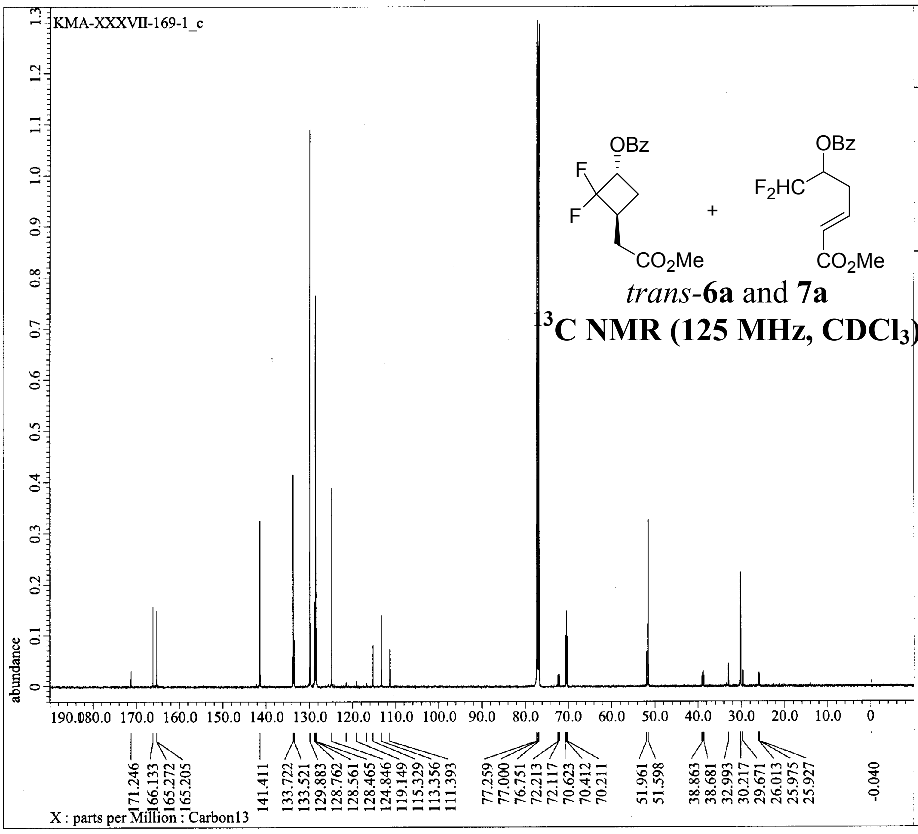
Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
X_Sweep_Clipped   = 31.25[kHz]
Irr_Domain        = Proton
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = TRUE
Scans             = 6000
Total_Scans       = 6000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 23.3[dC]
X_90_Width        = 8.5[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 4.6[dB]
X_Pulse           = 2.83333333[us]
Irr_Atn_Dec       = 22.735[dB]
Irr_Atn_Noe       = 22.735[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
```



trans-**6a** and **7a**

^{1}H NMR (400 MHz, $CDCl_3$)



trans-**6a** and **7a**

^{13}C NMR (125 MHz, $CDCl_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 190.53961, 202.21778, 59.192[%] )

以下に由来:: KMA-XXXVII-169-1_c-1-1.jdf
```

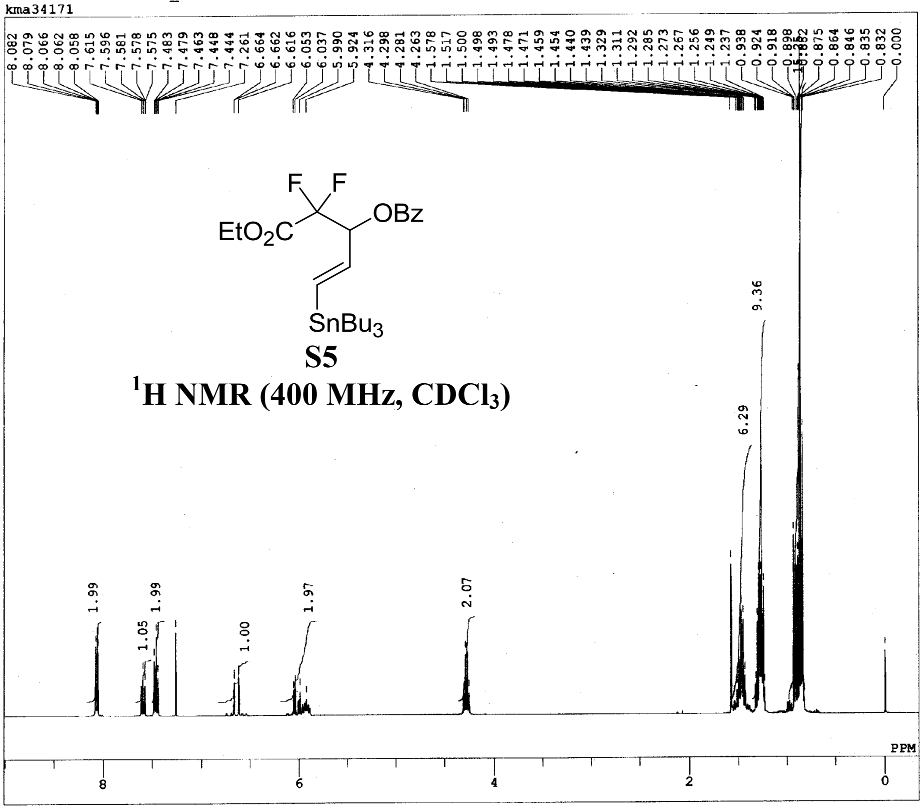
```
Filename           = C:\Users\delta\Documents\J
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = KMA-XXXVII-169-1
Solvent            = CHLOROFORM-D
Creation_Time      = 25-AUG-2011 15:13:11
Revision_Time      = 27-AUG-2011 13:22:09
Current_Time       = 27-AUG-2011 13:24:43

Comment            = KMA-XXXVII-169-1_c
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.62926421[T] (500[MHz])
X_Acq_Duration     = 0.8388608[s]
X_Domain           = 13C
X_Freq             = 124.5010059[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.1920929[Hz]
X_Sweep            = 39.0625[kHz]
X_Sweep_Clipped    = 31.25[kHz]
Irr_Domain         = Proton
Irr_Freq           = 495.13191398[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 6000
Total_Scans        = 6000

Relaxation_Delay   = 2[s]
Recvr_Gain         = 60
Temp_Get           = 23.8[dC]
X_90_Width         = 8.5[us]
X_Acq_Time         = 0.8388608[s]
X_Angle            = 30[deg]
X_Atn              = 4.6[dB]
X_Pulse            = 2.83333333[us]
Irr_Atn_Dec        = 22.735[dB]
Irr_Atn_Noe        = 22.735[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```

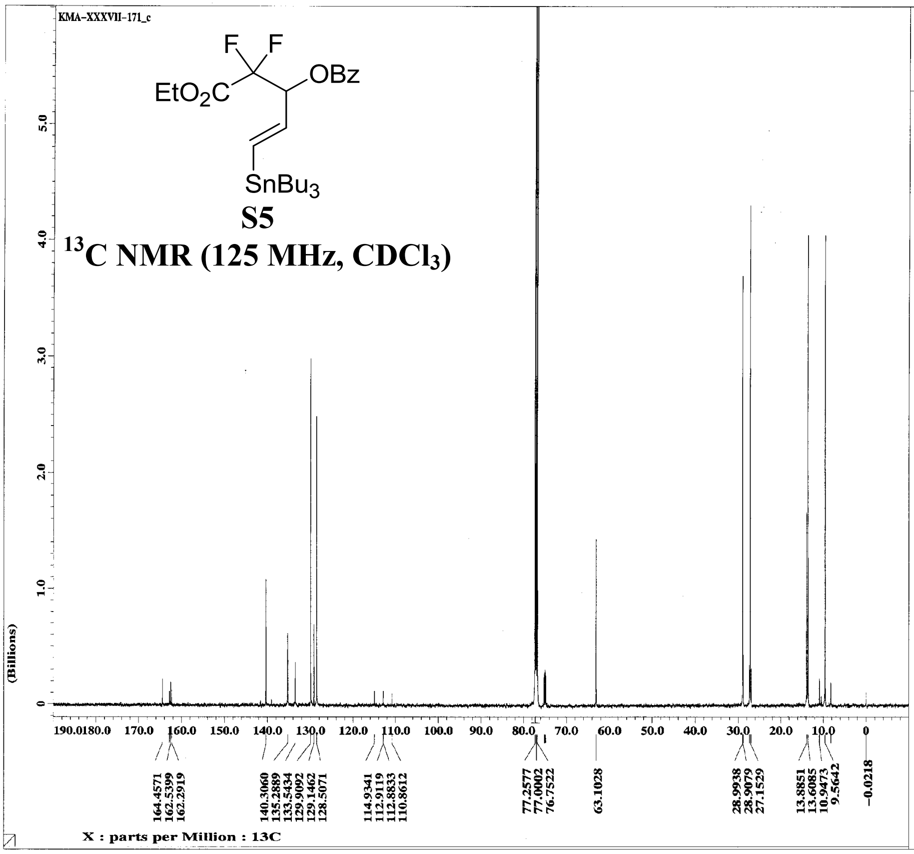
```
C:\WINNMR98\COMMON\_DEFAULT.ALS
kma34171
```



S5

^{1}H NMR (400 MHz, CDCl$_3$)

```
DFILE   C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT   kma34171
DATIM   Tue Aug 23 14:26:59 2011
OBNUC   1H
EXMOD   NON
OBFRQ          399.65 MHz
OBSET          124.00 KHz
OBFIN        10500.00 Hz
POINT           32768
FREQU         7992.01 Hz
SCANS              40
ACQTM          4.1001 sec
PD             2.9000 sec
PW1              5.80 usec
IRNUC   1H
CTEMP            23.4 c
SLVNT   CDCL3
EXREF            0.00 ppm
BF               0.12 Hz
RGAIN              12
```



S5

^{13}C NMR (125 MHz, CDCl$_3$)

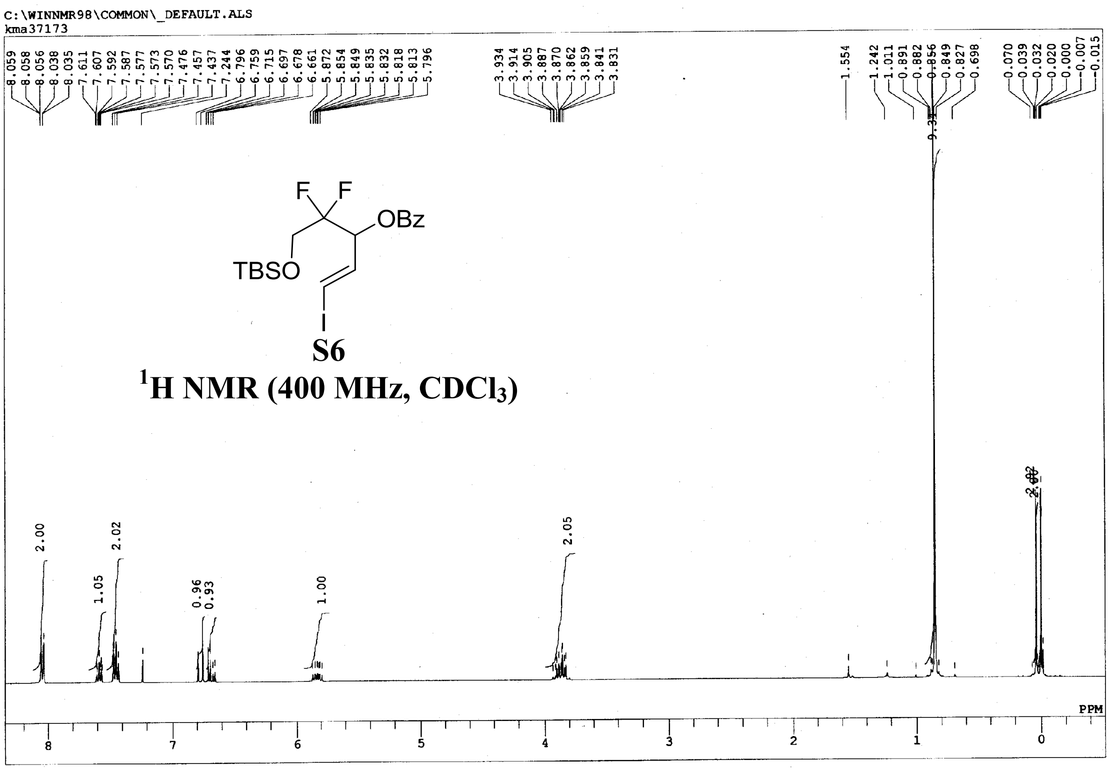
JEOL

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-171_c.1
File Name            = KMA-XXXVII-171_c.5
Author               = delta
Sample ID            = KMA-XXXVII-171
Content              = KMA-XXXVII-171_c
Creation Date        =  7-SEP-2011 01:03:18

Revision Date        =  7-SEP-2011 17:43:06
Spec Site            = ECA 500

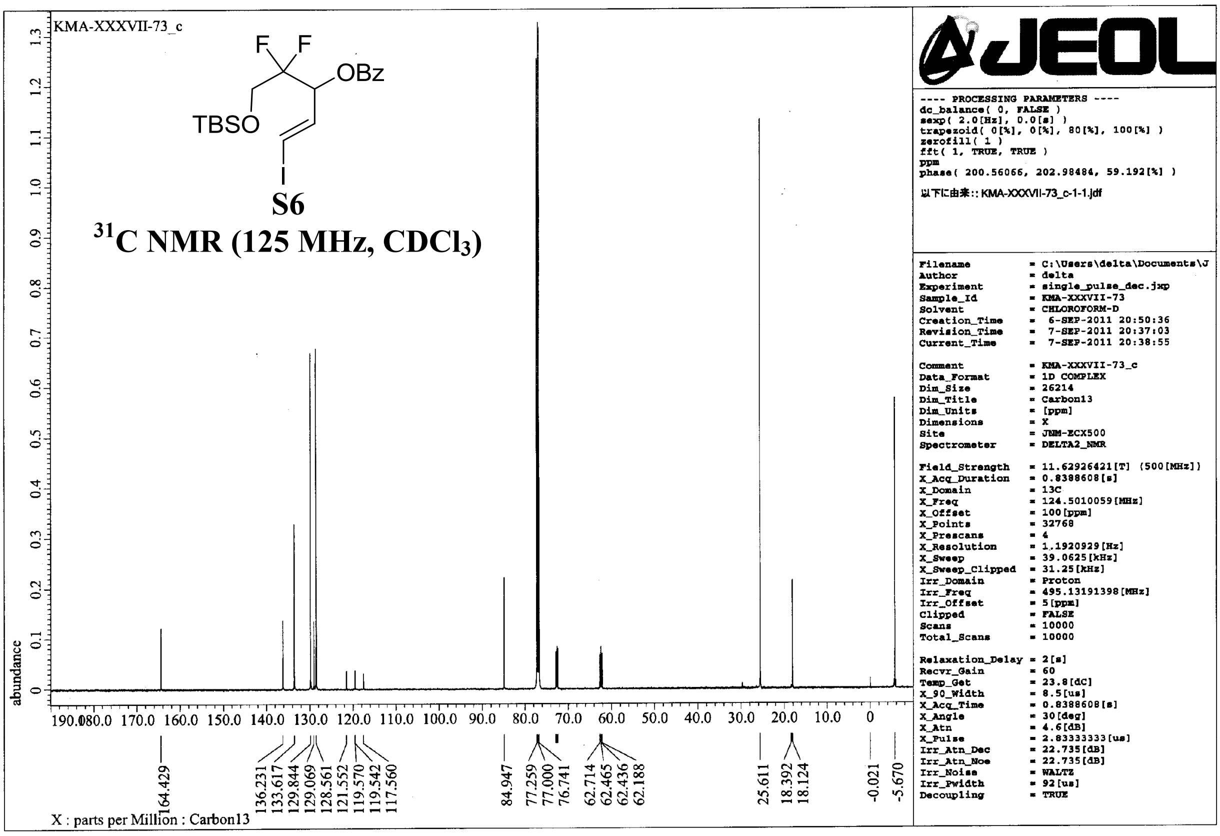
Spec Type            = DELTA2_NMR
Data Format          = 1D COMPLEX
Dimensions           = X
Dim Title            = 13C
Dim Size             = 26214
Dim Units            = [ppm]
Field_strength       = 11.7473579[T] (500[MH
X_acq_duration       = 0.83361792[s]
X_domain             = 13C
X_freq               = 125.76529768[MHz]
X_offset             = 100[ppm]
X_points             = 32768
X_prescans           = 4
X_resolution         = 1.19959034[Hz]
X_sweep              = 39.3081761[kHz]
Irr_domain           = 1H
Irr_freq             = 500.15991521[MHz]
Irr_offset           = 5.0[ppm]
Mod_return           = 1
Scans                = 10000
Total_scans          = 10000

X_90_width           = 10.5[us]
X_acq_time           = 0.83361792[s]
X_angle              = 30[deg]
X_atn                = 6.8[dB]
X_pulse              = 3.5[us]
Irr_atn_dec          = 19.6[dB]
Irr_atn_noe          = 21.6[dB]
Irr_noise            = WALTZ
Decoupling           = TRUE
Initial_wait         = 1[s]
Noe                  = TRUE
Noe_time             = 2[s]
Relaxation_delay     = 2[s]
Repetition_time      = 2.83361792[s]
Experiment           = single_pulse_dec
Recvr_gain           = 60
Solvent              = CHLOROFORM-D
```



S6

^{1}H NMR (400 MHz, $CDCl_3$)



S6

^{31}C NMR (125 MHz, $CDCl_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 200.56066, 202.98484, 59.192[%] )

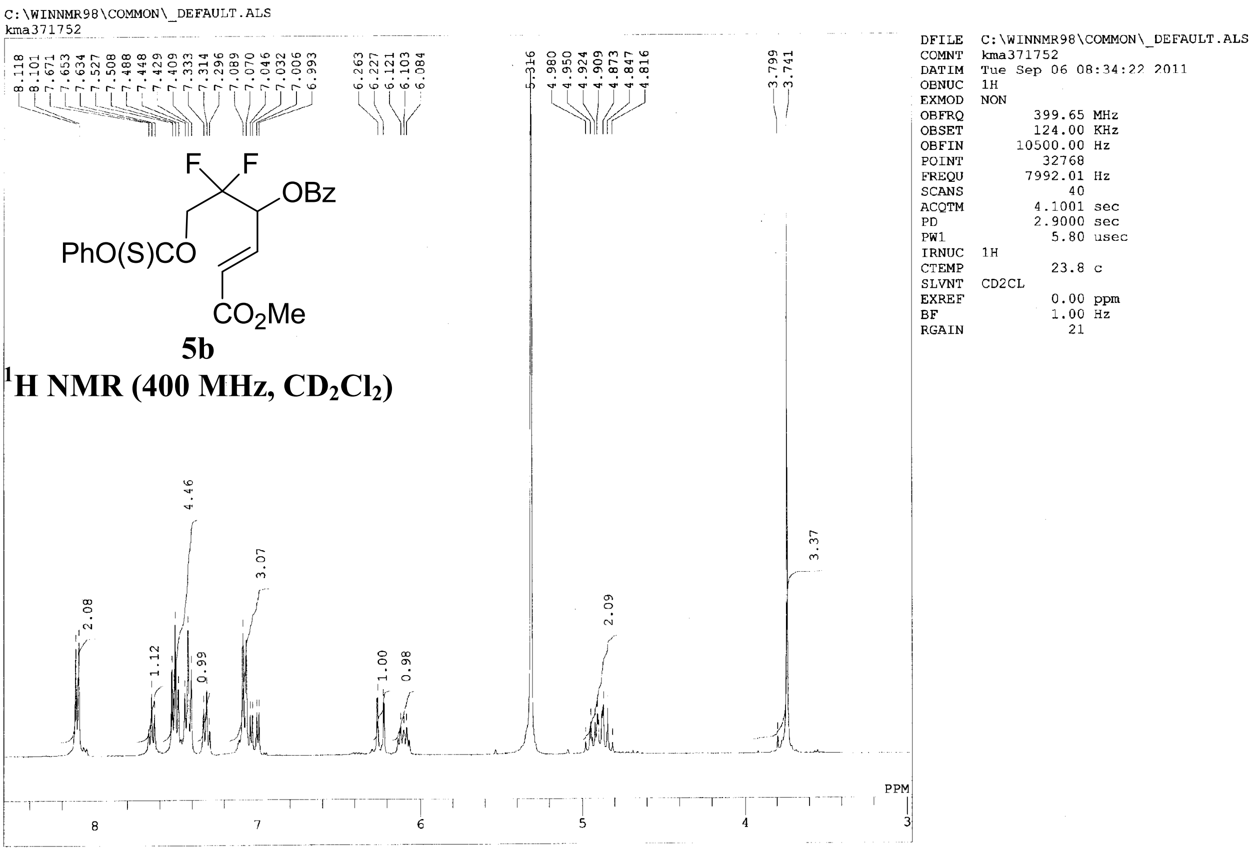
以下に由来:: KMA-XXXVII-73_c-1-1.jdf

Filename            = C:\Users\delta\Documents\J
Author              = delta
Experiment          = single_pulse_dec.jxp
Sample_Id           = KMA-XXXVII-73
Solvent             = CHLOROFORM-D
Creation_Time       =  6-SEP-2011 20:50:36
Revision_Time       =  7-SEP-2011 20:37:03
Current_Time        =  7-SEP-2011 20:38:55

Comment             = KMA-XXXVII-73_c
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.62926421[T] (500[MHz])
X_Acq_Duration      = 0.8388608[s]
X_Domain            = 13C
X_Freq              = 124.5010059[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.1920929[Hz]
X_Sweep             = 39.0625[kHz]
X_Sweep_Clipped     = 31.25[kHz]
Irr_Domain          = Proton
Irr_Freq            = 495.13191398[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 10000
Total_Scans         = 10000

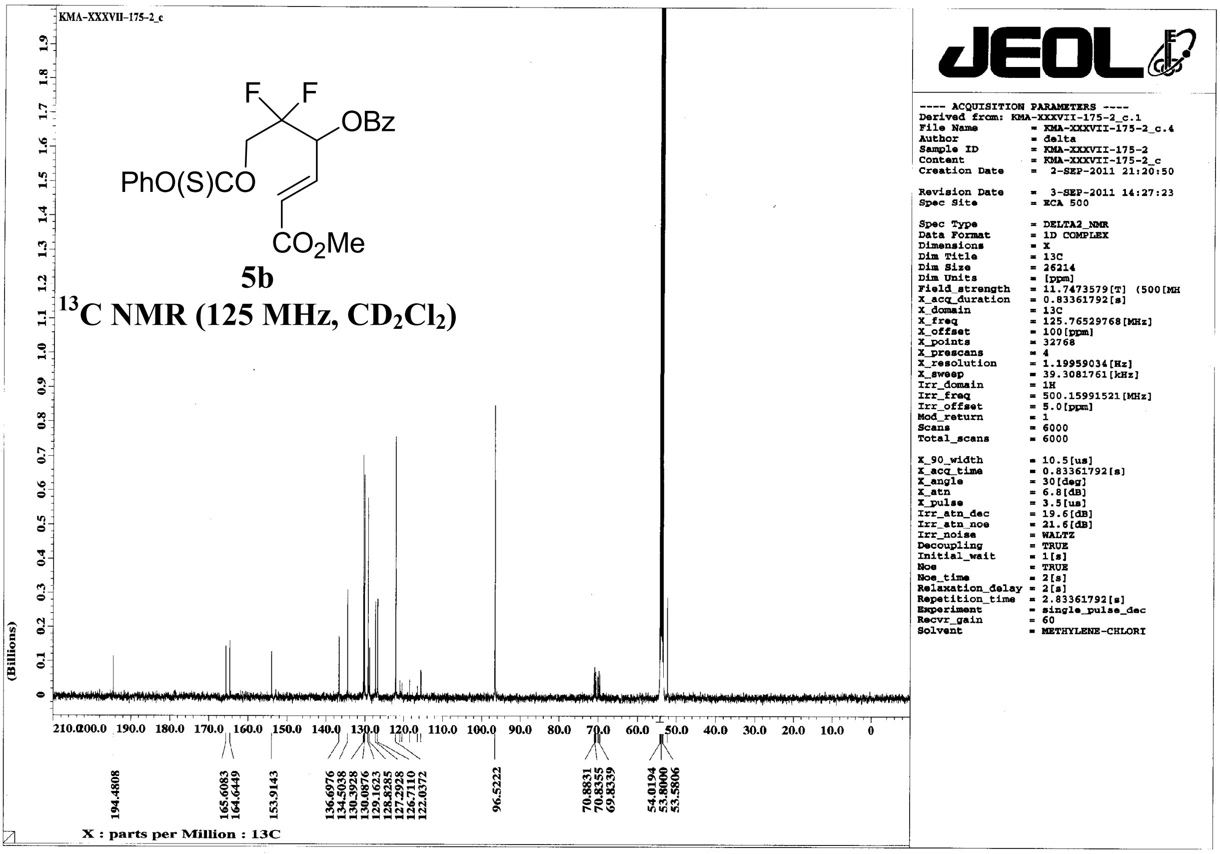
Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 23.8[dC]
X_90_Width          = 8.5[us]
X_Acq_Time          = 0.8388608[s]
X_Angle             = 30[deg]
X_Atn               = 4.6[dB]
X_Pulse             = 2.83333333[us]
Irr_Atn_Dec         = 22.735[dB]
Irr_Atn_Noe         = 22.735[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```



```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT  kma371752
DATIM  Tue Sep 06 08:34:22 2011
OBNUC  1H
EXMOD  NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT          32768
FREQU        7992.01 Hz
SCANS             40
ACQTM         4.1001 sec
PD            2.9000 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           23.8 c
SLVNT  CD2CL
EXREF           0.00 ppm
BF              1.00 Hz
RGAIN             21
```

5b

^{1}H NMR (400 MHz, CD_2Cl_2)



```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-175-2_c.1
File Name          = KMA-XXXVII-175-2_c.4
Author             = delta
Sample ID          = KMA-XXXVII-175-2
Content            = KMA-XXXVII-175-2_c
Creation Date      =  2-SEP-2011 21:20:50

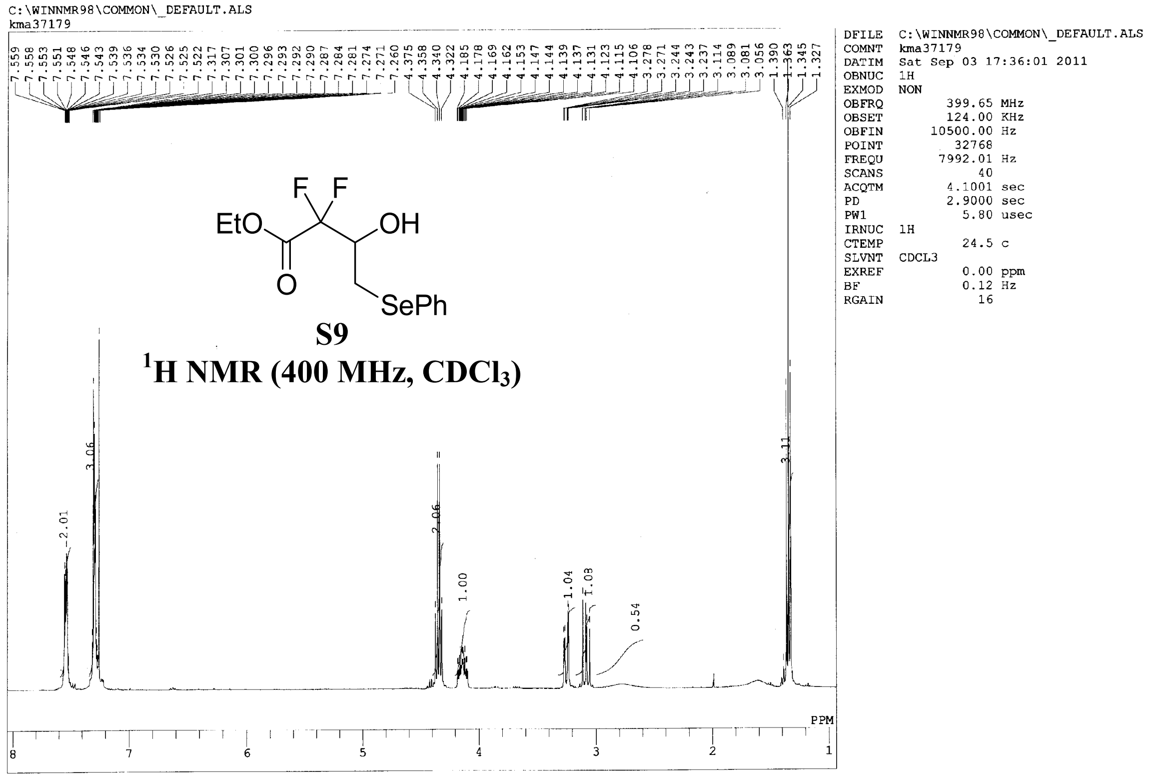
Revision Date      =  3-SEP-2011 14:27:23
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 6000
Total_scans        = 6000

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = METHYLENE-CHLORI
```

5b

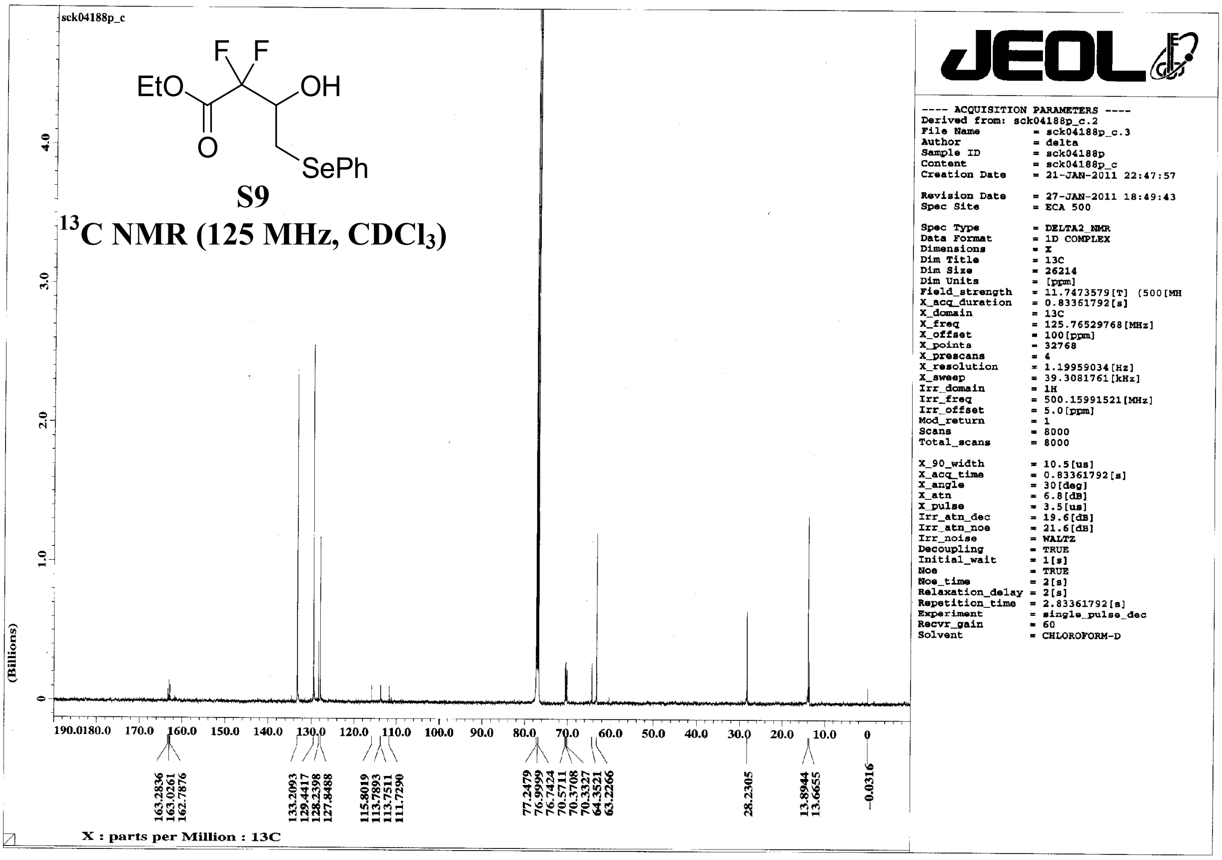
^{13}C NMR (125 MHz, CD_2Cl_2)



```
DFILE   C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT   kma37179
DATIM   Sat Sep 03 17:36:01 2011
OBNUC   1H
EXMOD   NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7992.01 Hz
SCANS            40
ACQTM        4.1001 sec
PD           2.9000 sec
PW1            5.80 usec
IRNUC   1H
CTEMP          24.5 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            16
```

S9

^{1}H NMR (400 MHz, CDCl$_3$)



```
---- ACQUISITION PARAMETERS ----
Derived from: sck04188p_c.2
File Name          = sck04188p_c.3
Author             = delta
Sample ID          = sck04188p
Content            = sck04188p_c
Creation Date      = 21-JAN-2011 22:47:57

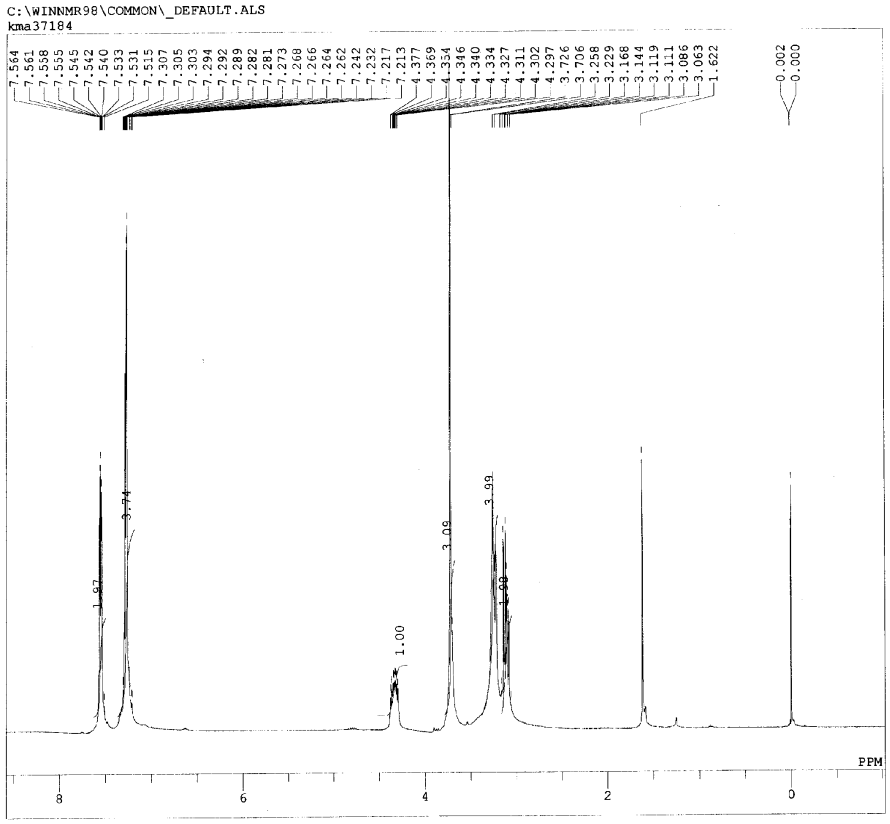
Revision Date      = 27-JAN-2011 18:49:43
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 8000
Total_scans        = 8000

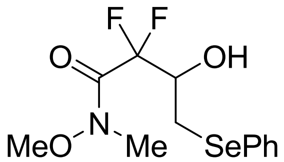
X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```

S9

^{13}C NMR (125 MHz, CDCl$_3$)

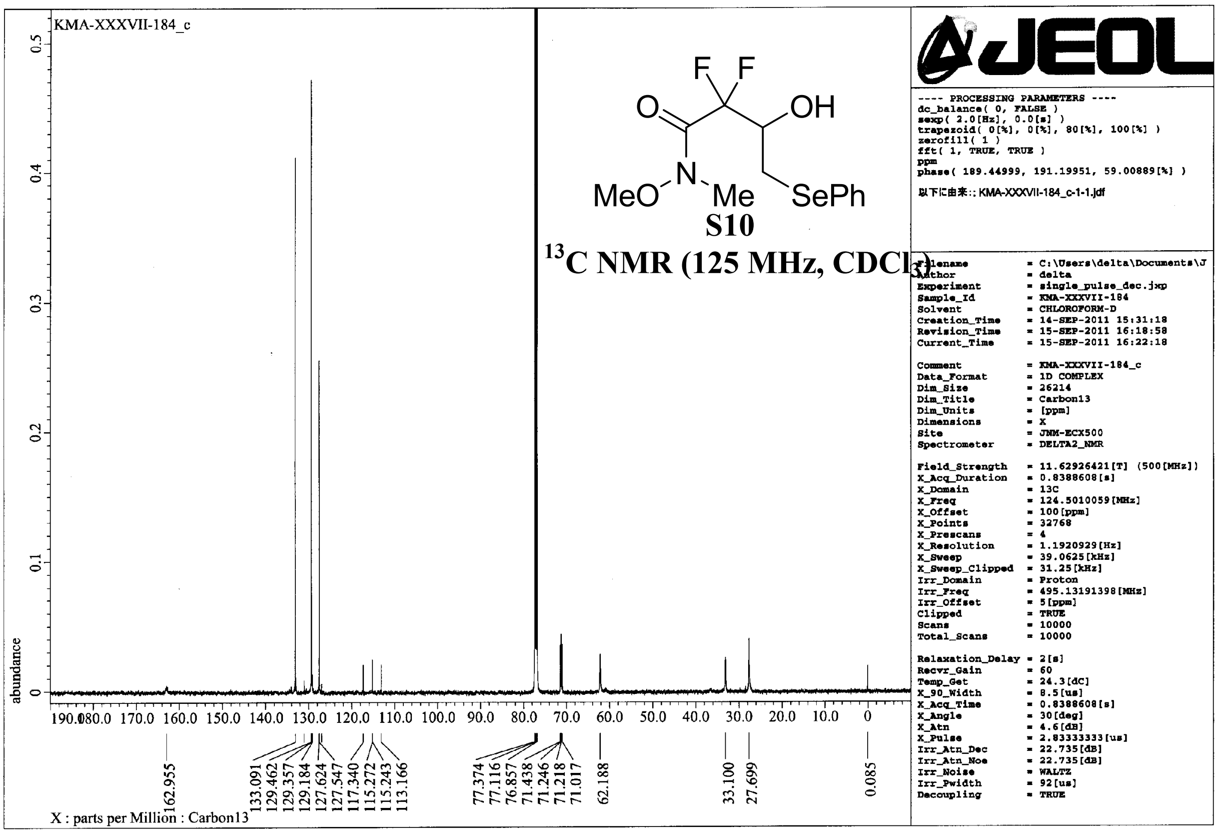


```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.AI
COMNT  kma37184
DATIM  Sat Sep 10 08:50:09 2011
OBNUC  1H
EXMOD  NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU      7992.01 Hz
SCANS           40
ACQTM       4.1001 sec
PD          2.9000 sec
PW1           5.80 usec
IRNUC  1H
CTEMP         24.5 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           14
```



S10

^{1}H NMR (400 MHz, CDCl$_3$)



S10

^{13}C NMR (125 MHz, CDCl$_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 189.44999, 191.19951, 59.00889[%] )

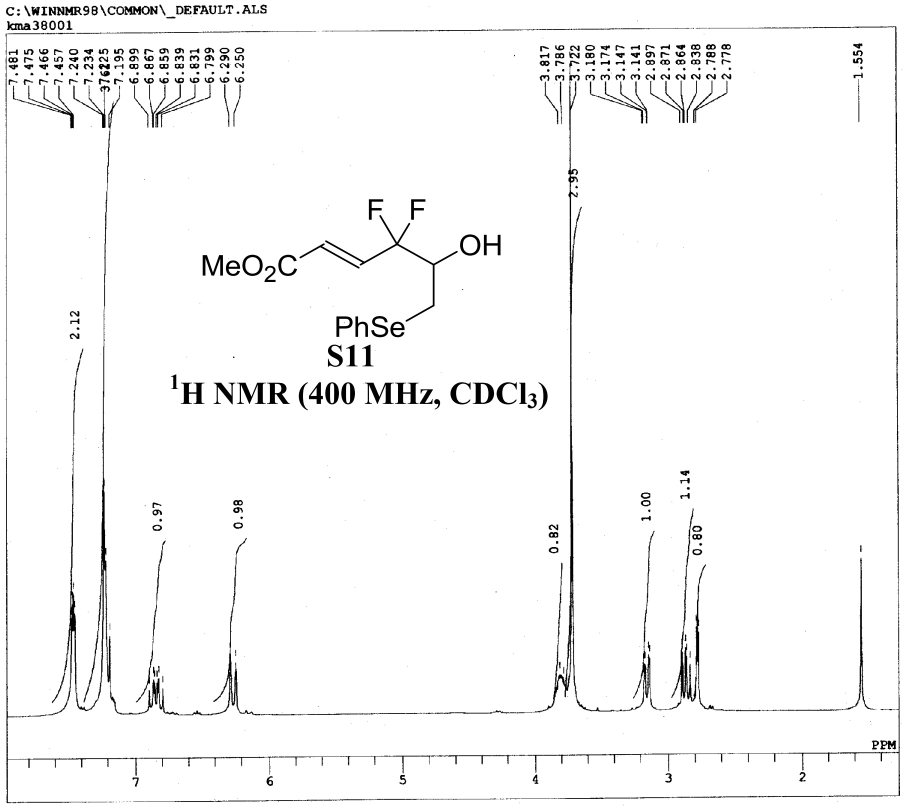
以下に由来:: KMA-XXXVII-184_c-1-1.jdf
```

```
Filename           = C:\Users\delta\Documents\J
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = KMA-XXXVII-184
Solvent            = CHLOROFORM-D
Creation_Time      = 14-SEP-2011 15:31:18
Revision_Time      = 15-SEP-2011 16:18:58
Current_Time       = 15-SEP-2011 16:22:18

Comment            = KMA-XXXVII-184_c
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.62926421[T] (500[MHz])
X_Acq_Duration     = 0.8388608[s]
X_Domain           = 13C
X_Freq             = 124.5010059[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.1920929[Hz]
X_Sweep            = 39.0625[kHz]
X_Sweep_Clipped    = 31.25[kHz]
Irr_Domain         = Proton
Irr_Freq           = 495.13191398[MHz]
Irr_Offset         = 5[ppm]
Clipped            = TRUE
Scans              = 10000
Total_Scans        = 10000

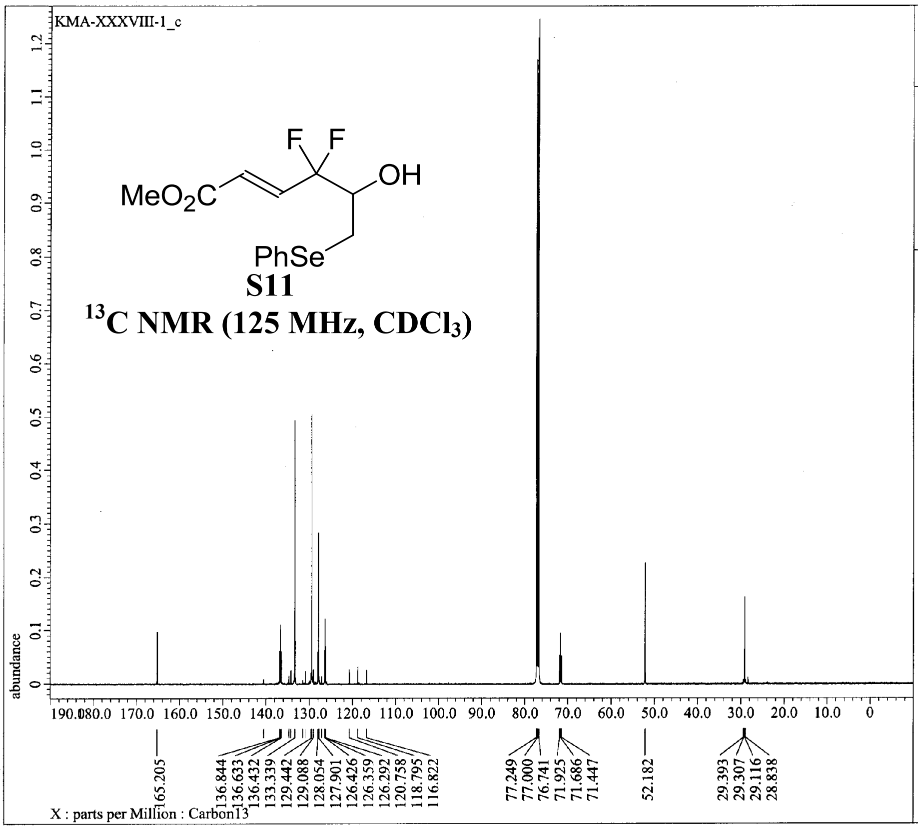
Relaxation_Delay   = 2[s]
Recvr_Gain         = 60
Temp_Get           = 24.3[dC]
X_90_Width         = 8.5[us]
X_Acq_Time         = 0.8388608[s]
X_Angle            = 30[deg]
X_Atn              = 4.6[dB]
X_Pulse            = 2.83333333[us]
Irr_Atn_Dec        = 22.735[dB]
Irr_Atn_Noe        = 22.735[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



S11

^{1}H NMR (400 MHz, $CDCl_3$)

```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT  kma38001
DATIM  Mon Sep 26 09:26:08 2011
OBNUC  1H
EXMOD  NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT          32768
FREQU        7992.01 Hz
SCANS             80
ACQTM         4.1001 sec
PD            2.9000 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           24.5 c
SLVNT  CDCL3
EXREF           7.24 ppm
BF              1.00 Hz
RGAIN             14
```



S11

^{13}C NMR (125 MHz, $CDCl_3$)

JEOL

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 195.65013, 191.18851, 59.37512[%] )

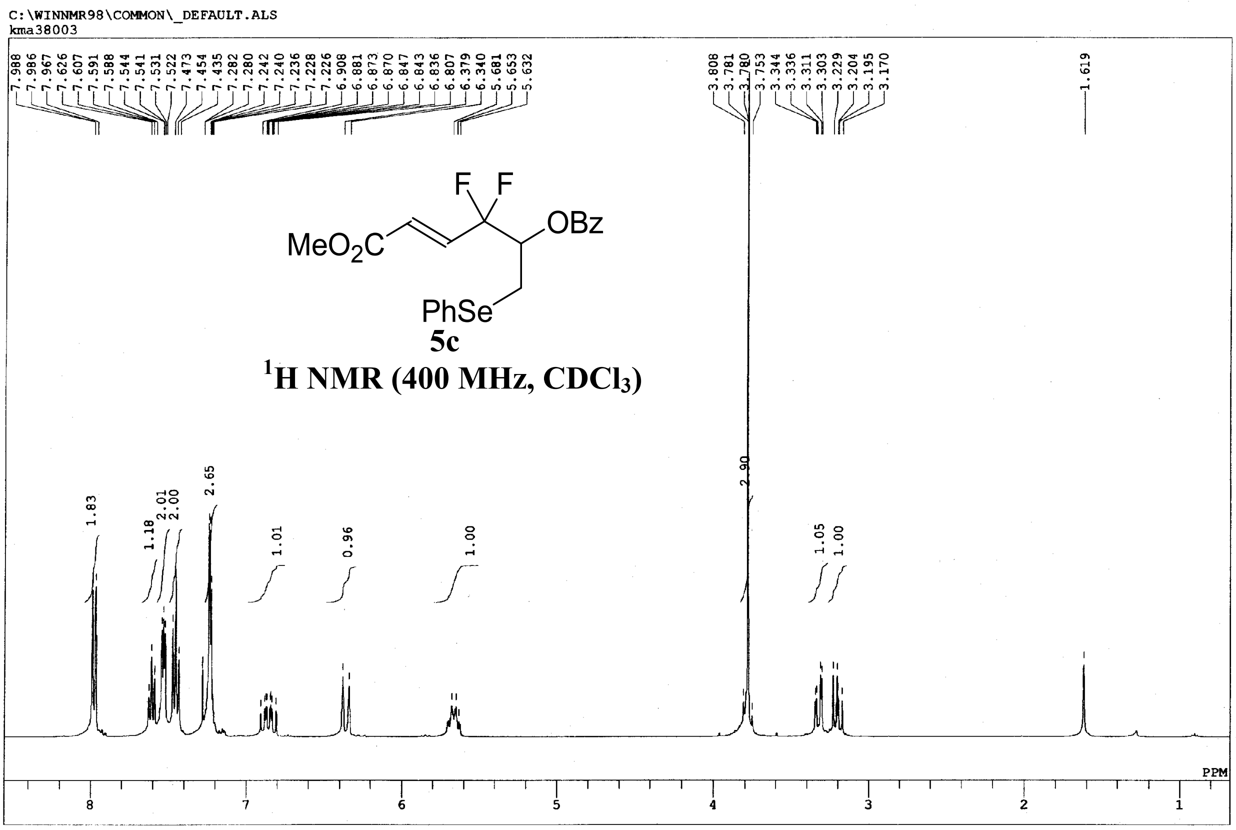
以下に由来:: KMA-XXXVIII-1_c-1-1.jdf
```

```
Filename            = C:\Users\delta\Documents\J
Author              = delta
Experiment          = single_pulse_dec.jxp
Sample_Id           = KMA-XXXVIII-1
Solvent             = CHLOROFORM-D
Creation_Time       =  1-OCT-2011 11:34:48
Revision_Time       =  3-OCT-2011 15:54:01
Current_Time        =  3-OCT-2011 15:55:52

Comment             = KMA-XXXVIII-1_c
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

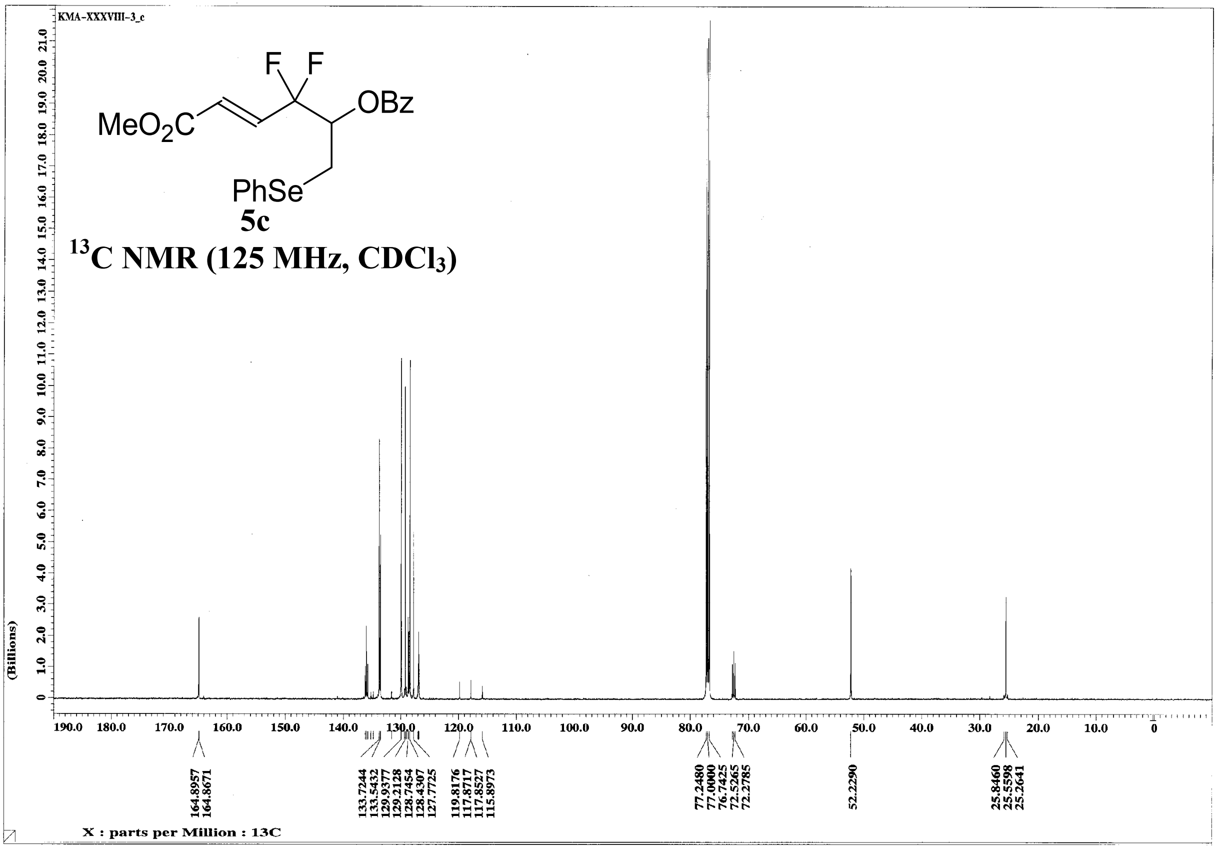
Field_Strength      = 11.62926421[T] (500[MHz])
X_Acq_Duration      = 0.8388608[s]
X_Domain            = 13C
X_Freq              = 124.5010059[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.1920929[Hz]
X_Sweep             = 39.0625[kHz]
X_Sweep_Clipped     = 31.25[kHz]
Irr_Domain          = Proton
Irr_Freq            = 495.13191398[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 20000
Total_Scans         = 20000

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 23.9[dC]
X_90_Width          = 8.5[us]
X_Acq_Time          = 0.8388608[s]
X_Angle             = 30[deg]
X_Atn               = 4.6[dB]
X_Pulse             = 2.83333333[us]
Irr_Atn_Dec         = 22.735[dB]
Irr_Atn_Noe         = 22.735[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```



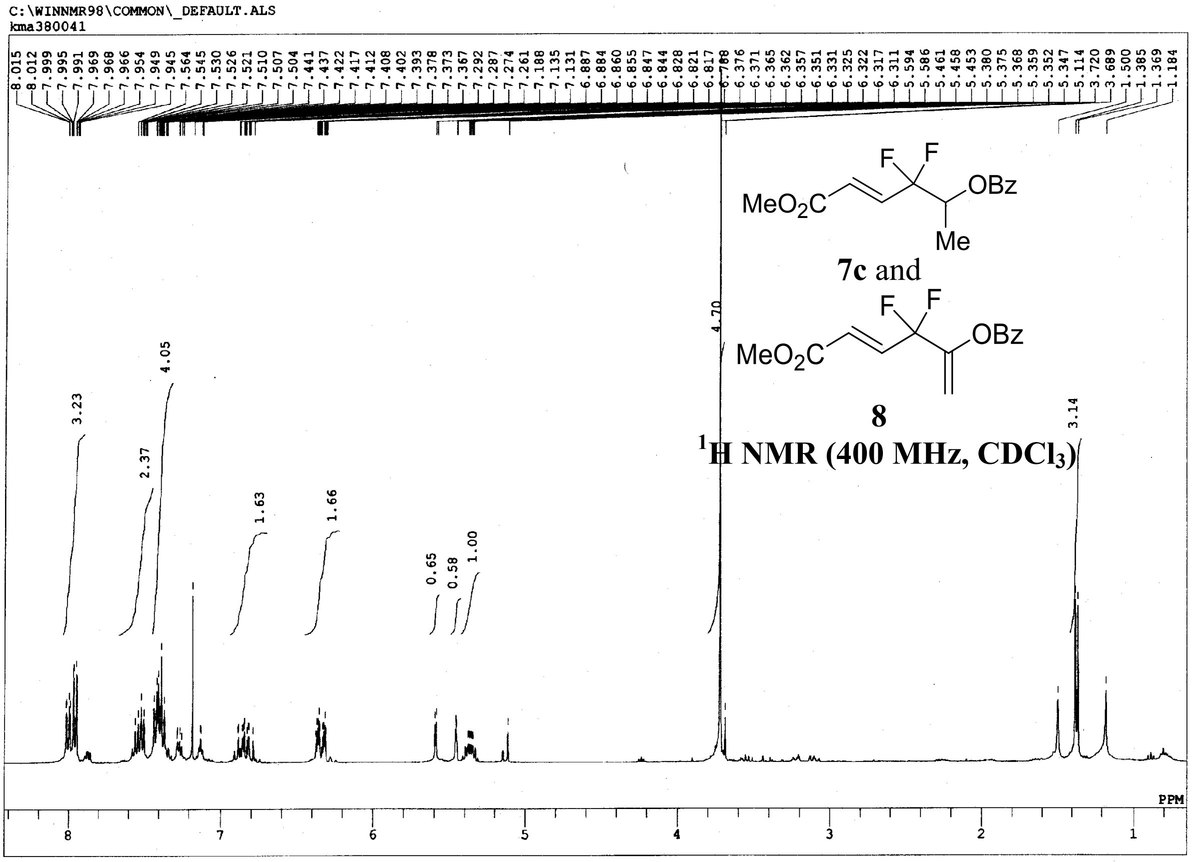
5c

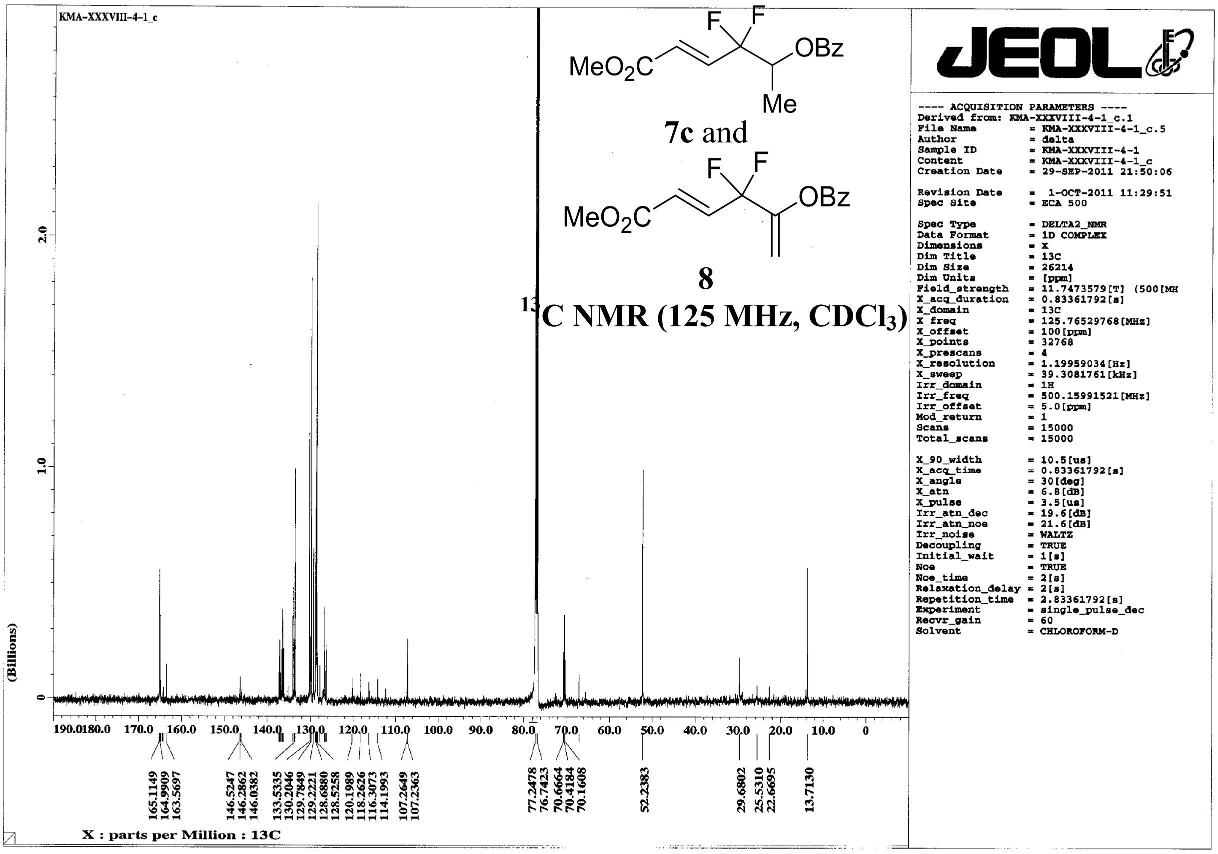
^{1}H NMR (400 MHz, CDCl$_3$)



5c

^{13}C NMR (125 MHz, CDCl$_3$)



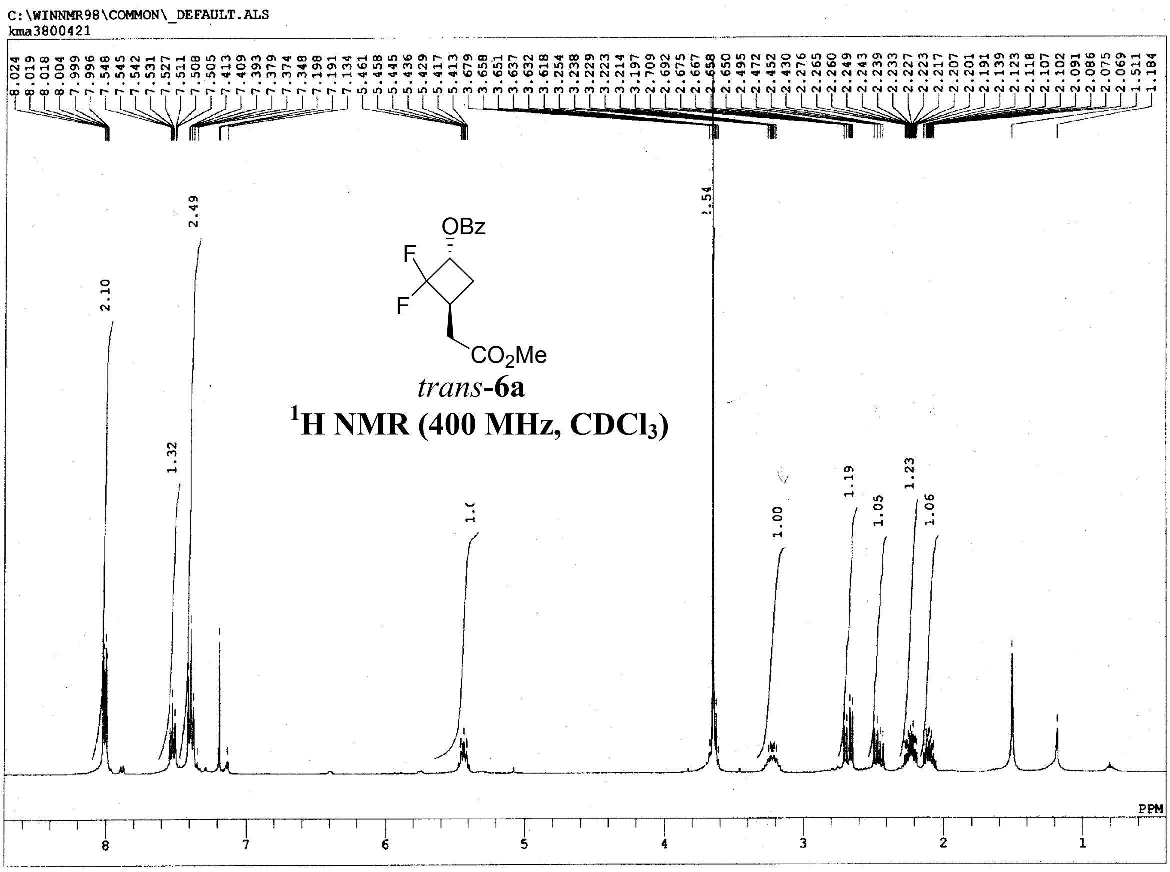


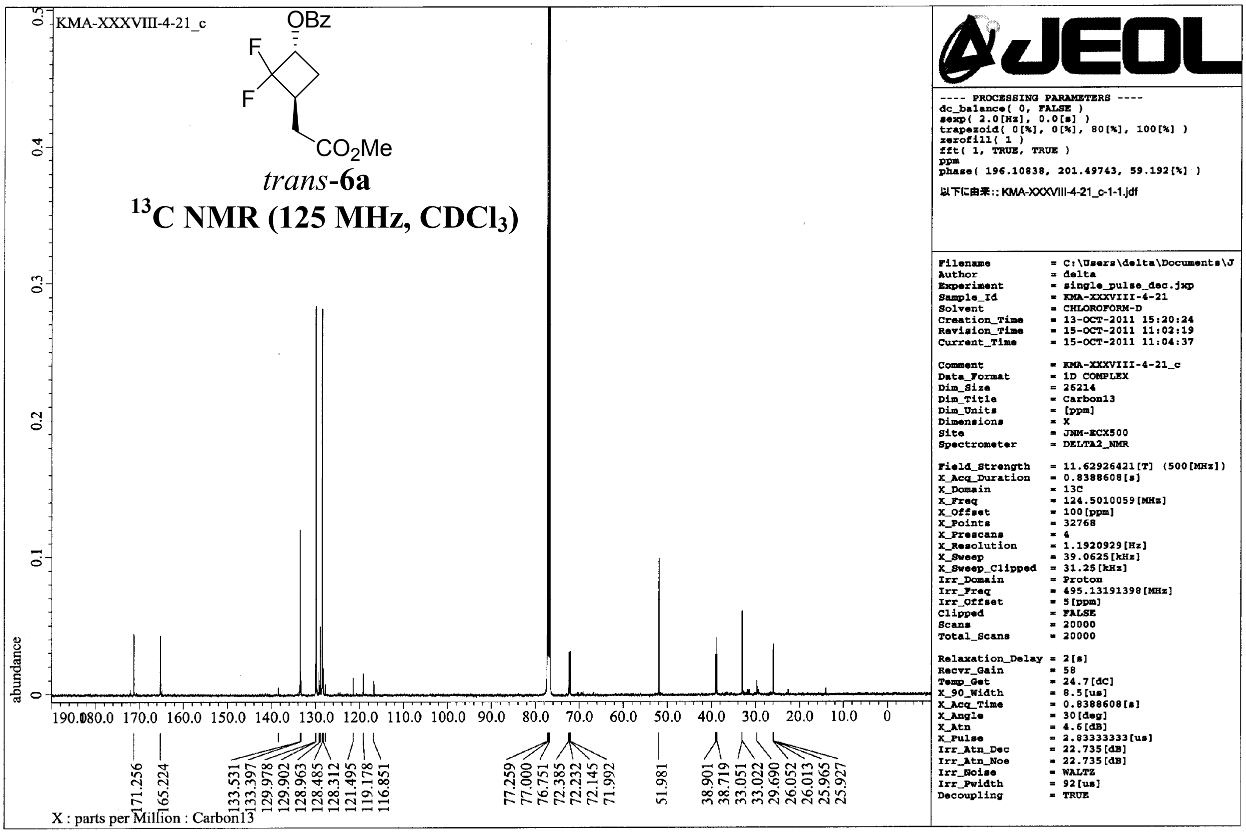
```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVIII-4-1_c.1
File Name             = KMA-XXXVIII-4-1_c.5
Author                = delta
Sample ID             = KMA-XXXVIII-4-1
Content               = KMA-XXXVIII-4-1_c
Creation Date         = 29-SEP-2011 21:50:06

Revision Date         =  1-OCT-2011 11:29:51
Spec Site             = ECA 500

Spec Type             = DELTA2_NMR
Data Format           = 1D COMPLEX
Dimensions            = X
Dim Title             = 13C
Dim Size              = 26214
Dim Units             = [ppm]
Field_strength        = 11.7473579[T] (500[MH
X_acq_duration        = 0.83361792[s]
X_domain              = 13C
X_freq                = 125.76529768[MHz]
X_offset              = 100[ppm]
X_points              = 32768
X_prescans            = 4
X_resolution          = 1.19959034[Hz]
X_sweep               = 39.3081761[kHz]
Irr_domain            = 1H
Irr_freq              = 500.15991521[MHz]
Irr_offset            = 5.0[ppm]
Mod_return            = 1
Scans                 = 15000
Total_scans           = 15000

X_90_width            = 10.5[us]
X_acq_time            = 0.83361792[s]
X_angle               = 30[deg]
X_atn                 = 6.8[dB]
X_pulse               = 3.5[us]
Irr_atn_dec           = 19.6[dB]
Irr_atn_noe           = 21.6[dB]
Irr_noise             = WALTZ
Decoupling            = TRUE
Initial_wait          = 1[s]
Noe                   = TRUE
Noe_time              = 2[s]
Relaxation_delay      = 2[s]
Repetition_time       = 2.83361792[s]
Experiment            = single_pulse_dec
Recvr_gain            = 60
Solvent               = CHLOROFORM-D
```





```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 196.10838, 201.49743, 59.192[%] )

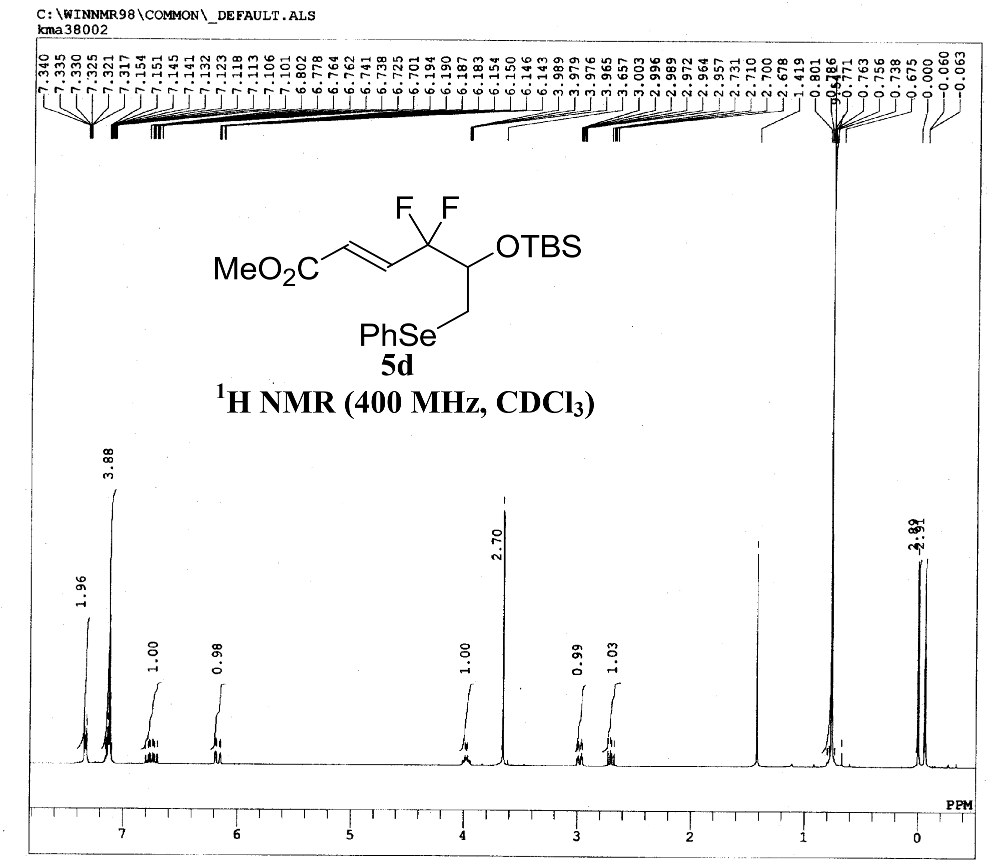
以下に由来:: KMA-XXXVIII-4-21_c-1-1.jdf
```

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = single_pulse_dec.jxp
Sample_Id         = KMA-XXXVIII-4-21
Solvent           = CHLOROFORM-D
Creation_Time     = 13-OCT-2011 15:20:24
Revision_Time     = 15-OCT-2011 11:02:19
Current_Time      = 15-OCT-2011 11:04:37

Comment           = KMA-XXXVIII-4-21_c
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
X_Sweep_Clipped   = 31.25[kHz]
Irr_Domain        = Proton
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 20000
Total_Scans       = 20000

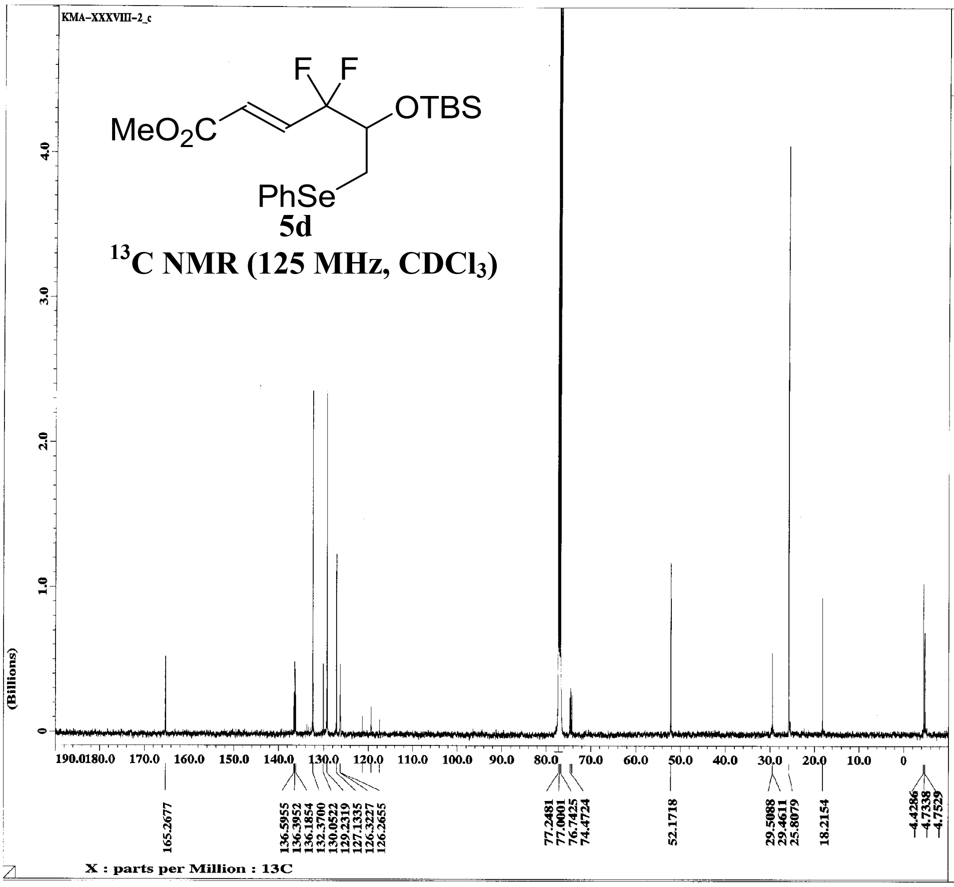
Relaxation_Delay = 2[s]
Recvr_Gain        = 58
Temp_Get          = 24.7[dC]
X_90_Width        = 8.5[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 4.6[dB]
X_Pulse           = 2.83333333[us]
Irr_Atn_Dec       = 22.735[dB]
Irr_Atn_Noe       = 22.735[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
```



5d

^{1}H NMR (400 MHz, $CDCl_3$)

```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT  kma38002
DATIM  Fri Sep 30 09:34:31 2011
OBNUC  1H
EXMOD  NON
OBFRQ       399.65 MHz
OBSET       124.00 KHz
OBFIN     10500.00 Hz
POINT        32768
FREQU      7992.01 Hz
SCANS           40
ACQTM       4.1001 sec
PD          2.9000 sec
PW1           5.80 usec
IRNUC  1H
CTEMP         23.9 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            0.12 Hz
RGAIN           16
```



5d

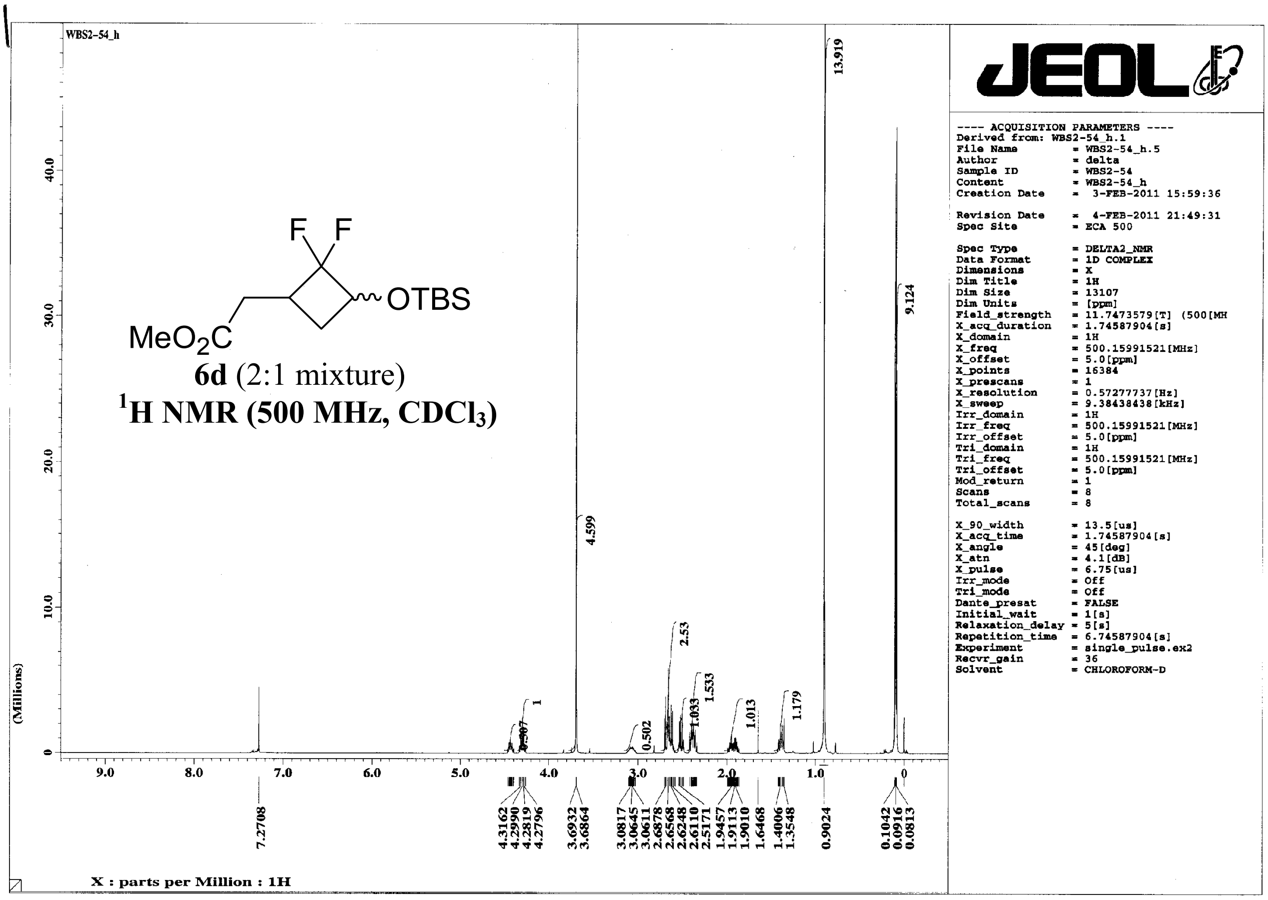
^{13}C NMR (125 MHz, $CDCl_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVIII-2_c.1
File Name          = KMA-XXXVIII-2_c.4
Author             = delta
Sample ID          = KMA-XXXVIII-2
Content            = KMA-XXXVIII-2_c
Creation Date      = 13-OCT-2011 04:56:26

Revision Date      = 13-OCT-2011 10:17:22
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 20000
Total_scans        = 20000

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```



6d (2:1 mixture)

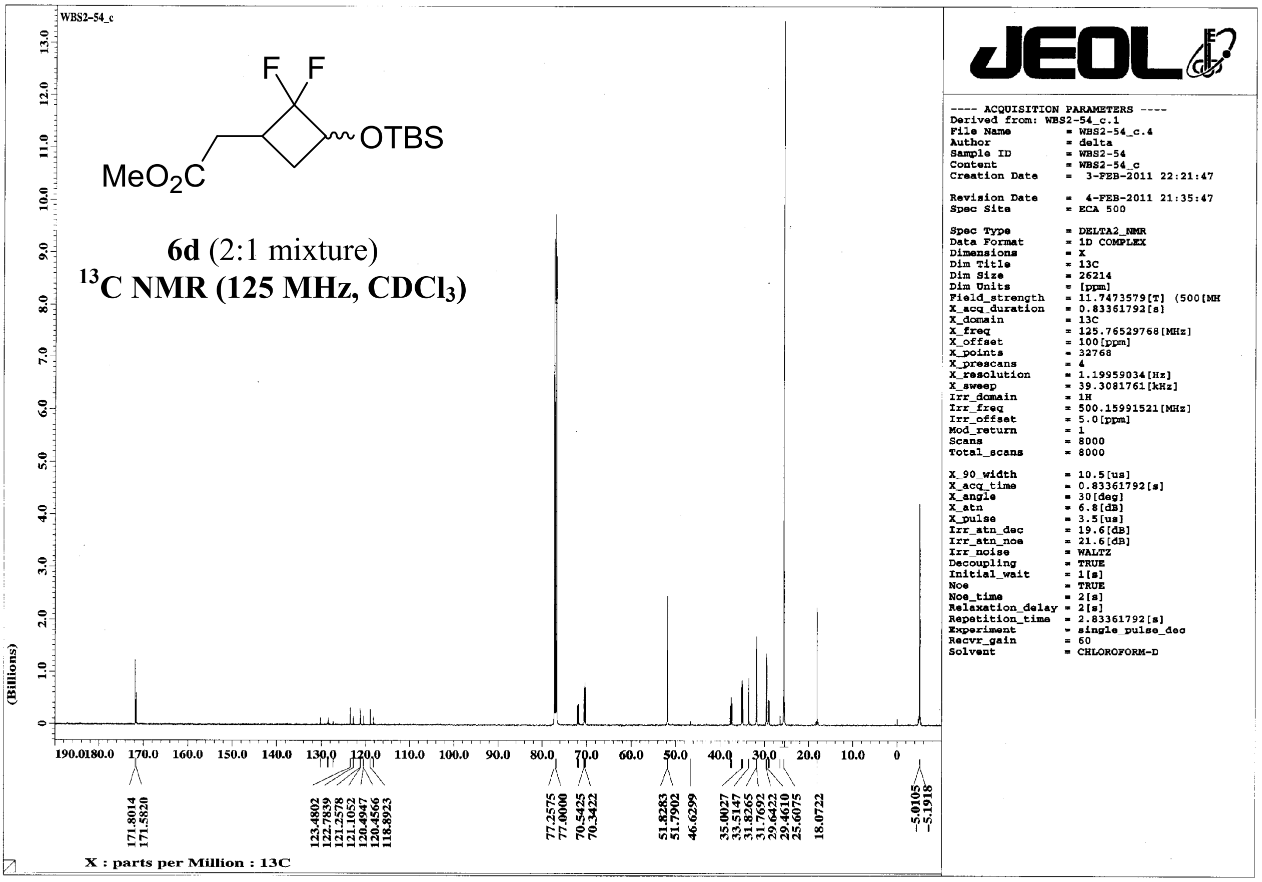
^{1}H NMR (500 MHz, $CDCl_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: WBS2-54_h.1
File Name           = WBS2-54_h.5
Author              = delta
Sample ID           = WBS2-54
Content             = WBS2-54_h
Creation Date       =  3-FEB-2011 15:59:36

Revision Date       =  4-FEB-2011 21:49:31
Spec Site           = ECA 500

Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 13107
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 1.74587904[s]
X_domain            = 1H
X_freq              = 500.15991521[MHz]
X_offset            = 5.0[ppm]
X_points            = 16384
X_prescans          = 1
X_resolution        = 0.57277737[Hz]
X_sweep             = 9.38438438[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Tri_domain          = 1H
Tri_freq            = 500.15991521[MHz]
Tri_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 8
Total_scans         = 8

X_90_width          = 13.5[us]
X_acq_time          = 1.74587904[s]
X_angle             = 45[deg]
X_atn               = 4.1[dB]
X_pulse             = 6.75[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Relaxation_delay    = 5[s]
Repetition_time     = 6.74587904[s]
Experiment          = single_pulse.ex2
Recvr_gain          = 36
Solvent             = CHLOROFORM-D
```



6d (2:1 mixture)

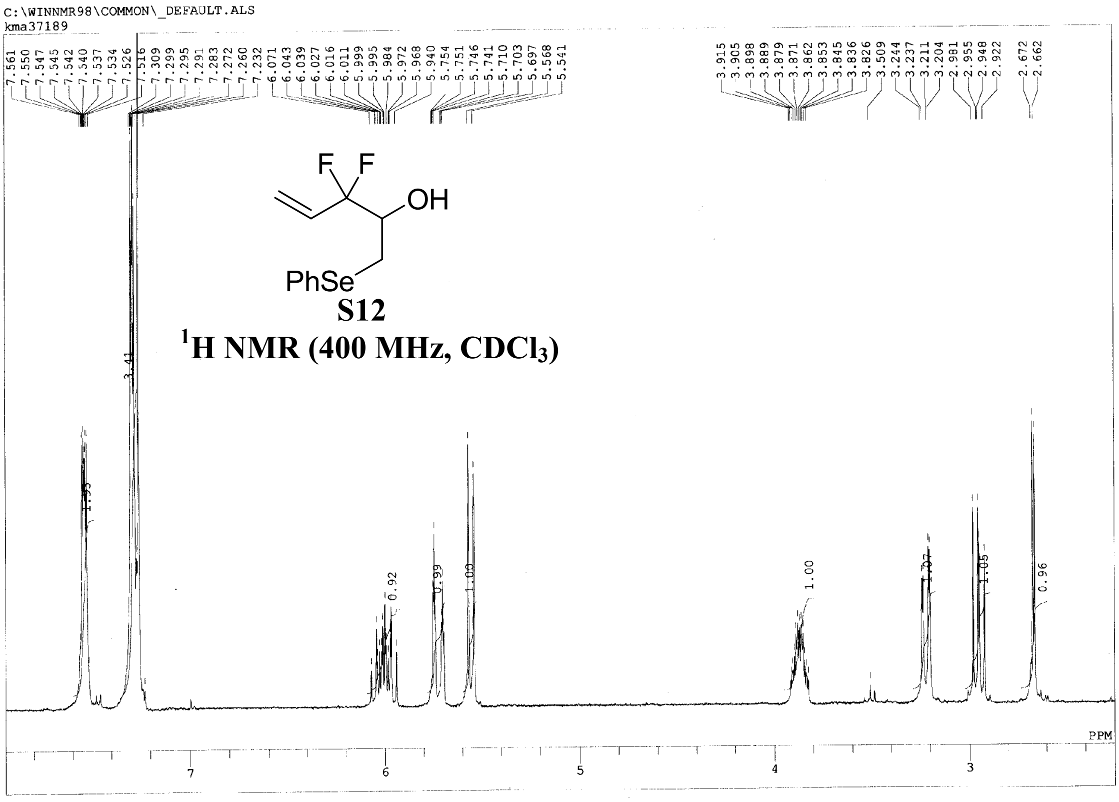
^{13}C NMR (125 MHz, $CDCl_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: WBS2-54_c.1
File Name           = WBS2-54_c.4
Author              = delta
Sample ID           = WBS2-54
Content             = WBS2-54_c
Creation Date       =  3-FEB-2011 22:21:47

Revision Date       =  4-FEB-2011 21:35:47
Spec Site           = ECA 500

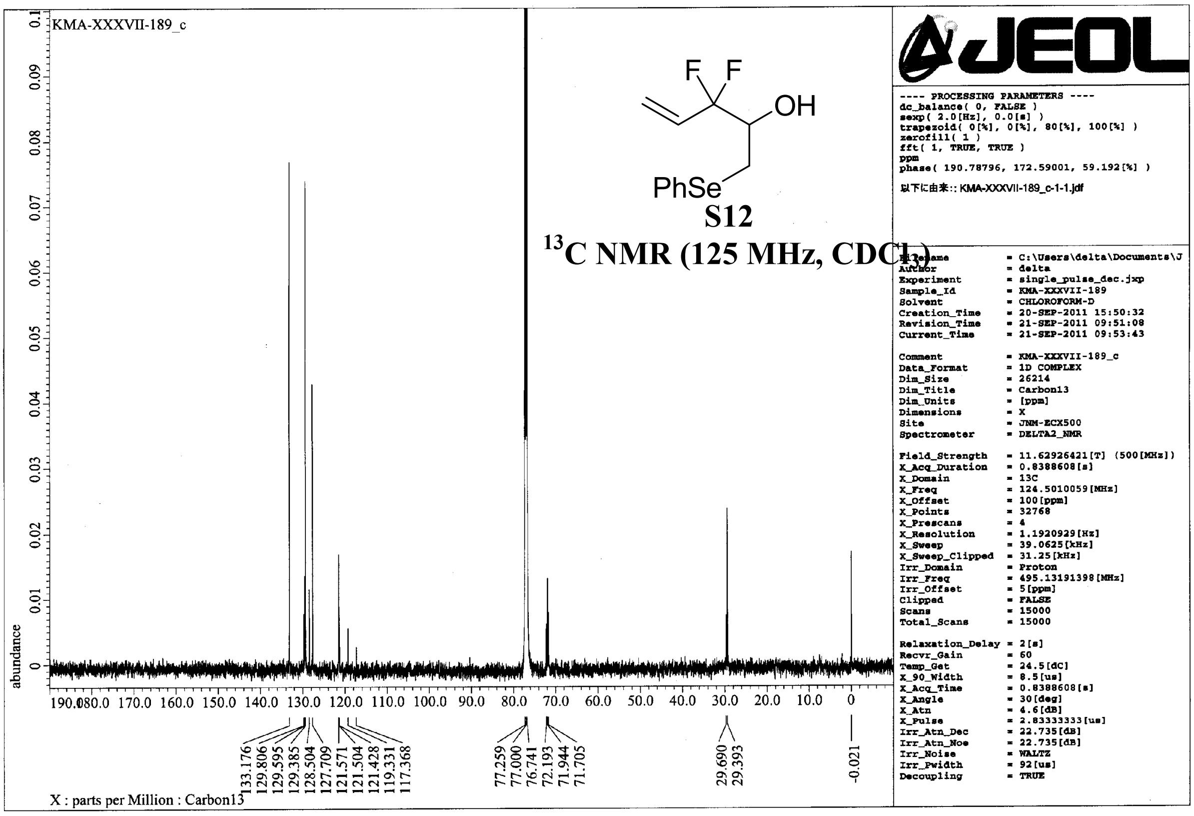
Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 26214
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 0.83361792[s]
X_domain            = 13C
X_freq              = 125.76529768[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 1.19959034[Hz]
X_sweep             = 39.3081761[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 8000
Total_scans         = 8000

X_90_width          = 10.5[us]
X_acq_time          = 0.83361792[s]
X_angle             = 30[deg]
X_atn               = 6.8[dB]
X_pulse             = 3.5[us]
Irr_atn_dec         = 19.6[dB]
Irr_atn_noe         = 21.6[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Relaxation_delay    = 2[s]
Repetition_time     = 2.83361792[s]
Experiment          = single_pulse_dec
Recvr_gain          = 60
Solvent             = CHLOROFORM-D
```



S12

^{1}H NMR (400 MHz, $CDCl_3$)



S12

^{13}C NMR (125 MHz, $CDCl_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 190.78796, 172.59001, 59.192[%] )

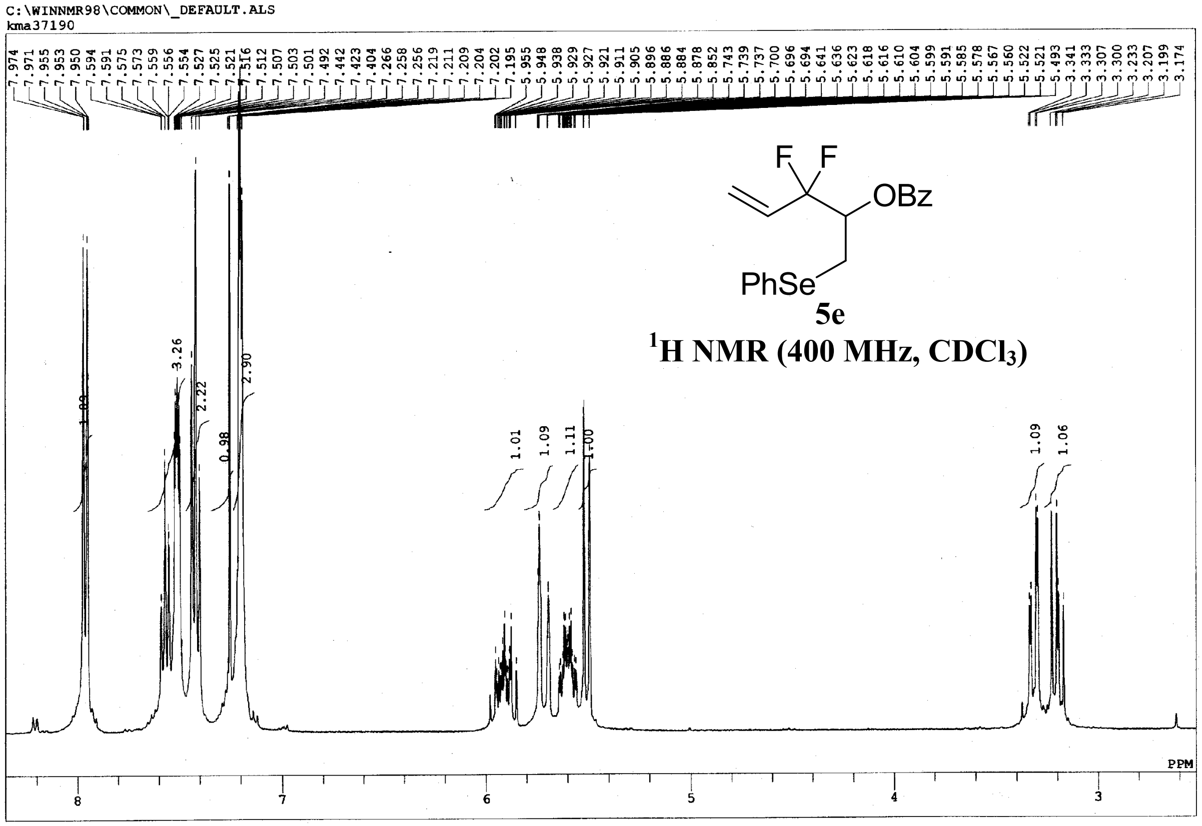
以下に由来:: KMA-XXXVII-189_c-1-1.jdf
```

```
Filename            = C:\Users\delta\Documents\J
Author              = delta
Experiment          = single_pulse_dec.jxp
Sample_Id           = KMA-XXXVII-189
Solvent             = CHLOROFORM-D
Creation_Time       = 20-SEP-2011 15:50:32
Revision_Time       = 21-SEP-2011 09:51:08
Current_Time        = 21-SEP-2011 09:53:43

Comment             = KMA-XXXVII-189_c
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

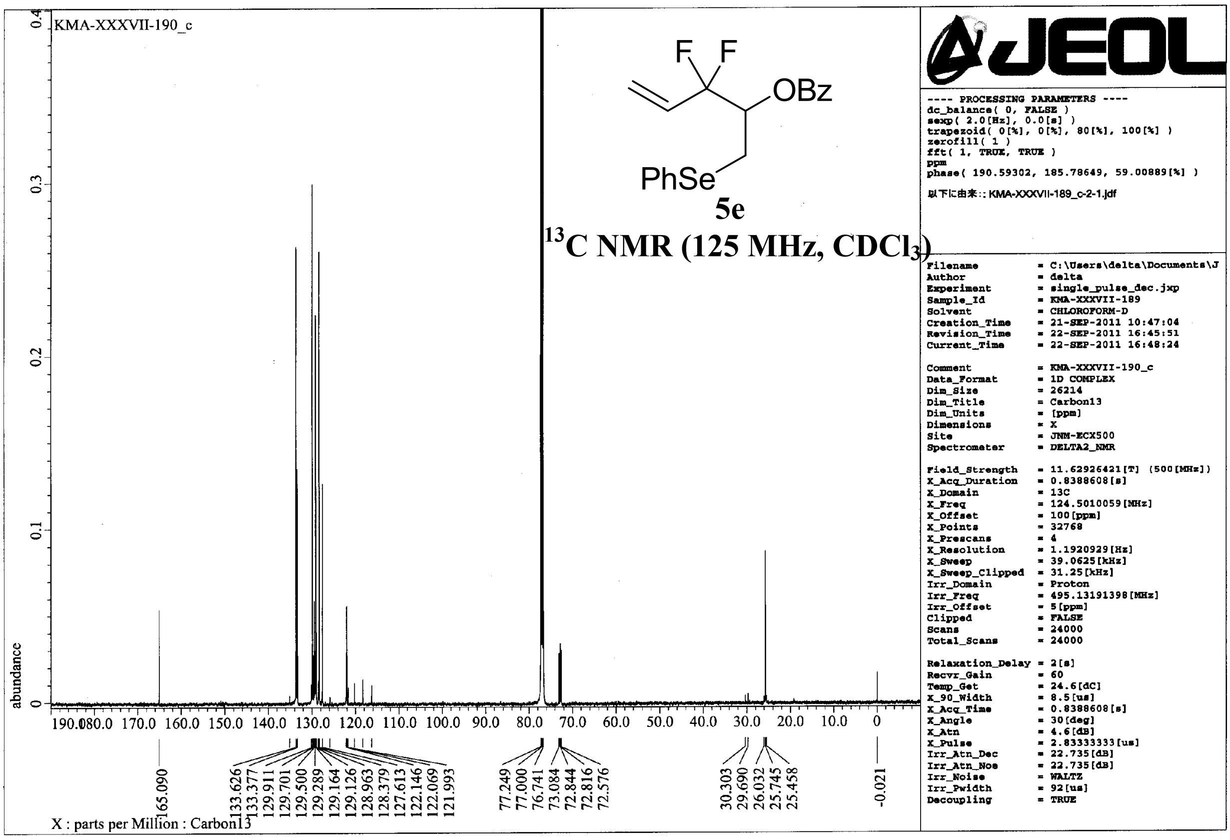
Field_Strength      = 11.62926421[T] (500[MHz])
X_Acq_Duration      = 0.8388608[s]
X_Domain            = 13C
X_Freq              = 124.5010059[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.1920929[Hz]
X_Sweep             = 39.0625[kHz]
X_Sweep_Clipped     = 31.25[kHz]
Irr_Domain          = Proton
Irr_Freq            = 495.13191398[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 15000
Total_Scans         = 15000

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 24.5[dC]
X_90_Width          = 8.5[us]
X_Acq_Time          = 0.8388608[s]
X_Angle             = 30[deg]
X_Atn               = 4.6[dB]
X_Pulse             = 2.83333333[us]
Irr_Atn_Dec         = 22.735[dB]
Irr_Atn_Noe         = 22.735[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```



5e

^{1}H NMR (400 MHz, CDCl$_3$)



5e

^{13}C NMR (125 MHz, CDCl$_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 190.59302, 185.78649, 59.00889[%] )

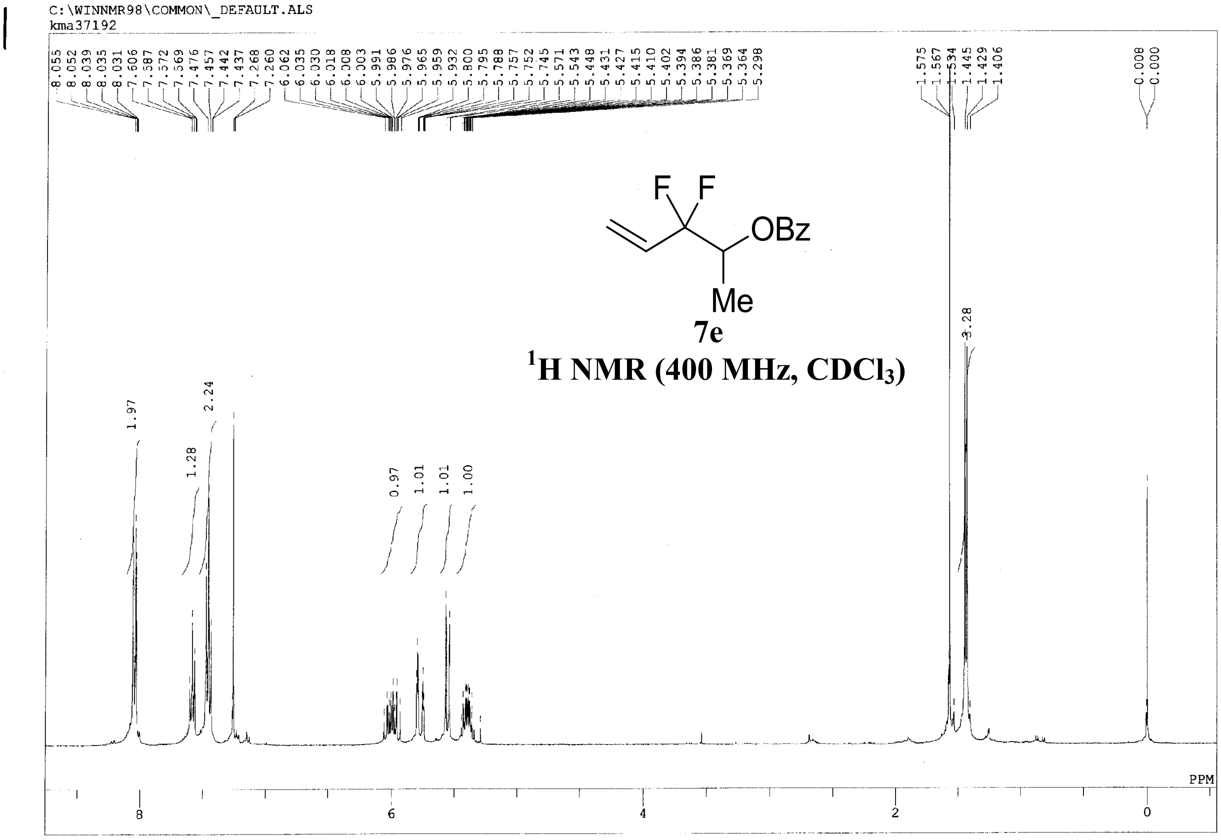
以下に由来:: KMA-XXXVII-189_c-2-1.jdf
```

```
Filename            = C:\Users\delta\Documents\J
Author              = delta
Experiment          = single_pulse_dec.jxp
Sample_Id           = KMA-XXXVII-189
Solvent             = CHLOROFORM-D
Creation_Time       = 21-SEP-2011 10:47:04
Revision_Time       = 22-SEP-2011 16:45:51
Current_Time        = 22-SEP-2011 16:48:24

Comment             = KMA-XXXVII-190_c
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

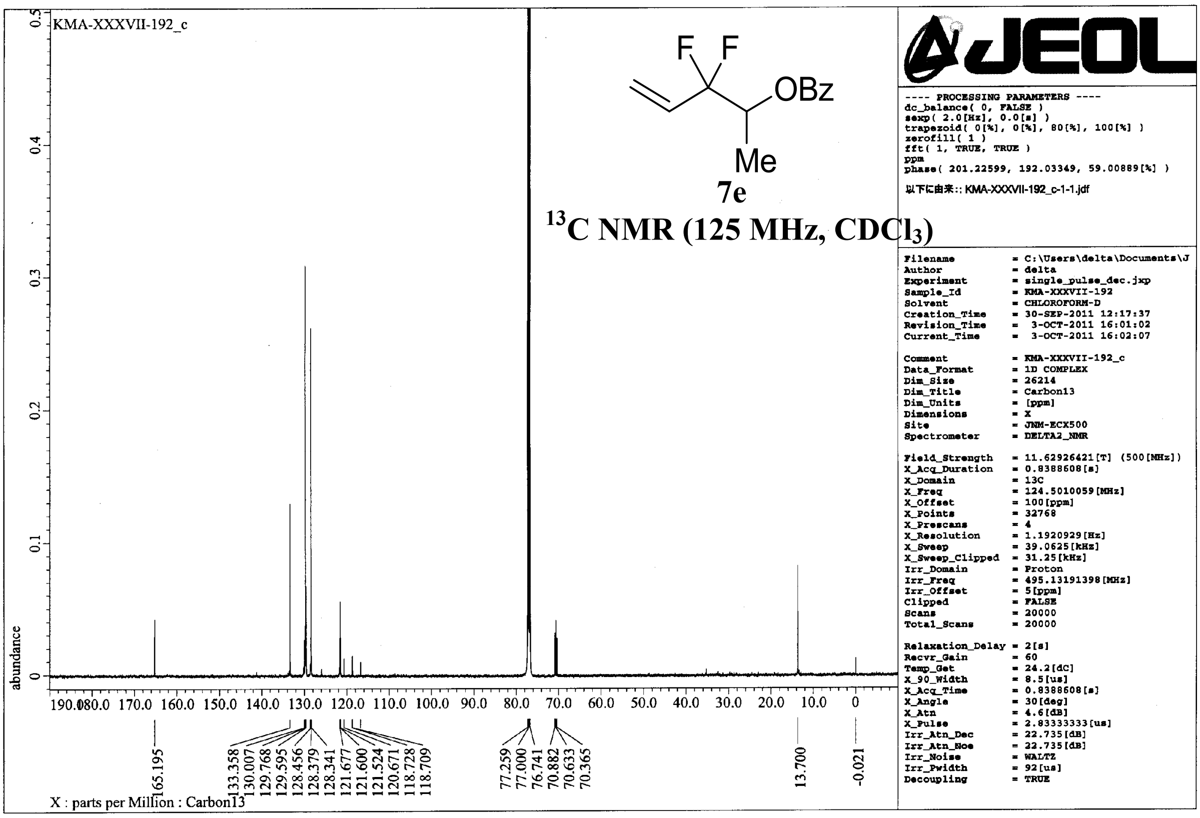
Field_Strength      = 11.62926421[T] (500[MHz])
X_Acq_Duration      = 0.8388608[s]
X_Domain            = 13C
X_Freq              = 124.5010059[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.1920929[Hz]
X_Sweep             = 39.0625[kHz]
X_Sweep_Clipped     = 31.25[kHz]
Irr_Domain          = Proton
Irr_Freq            = 495.13191398[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 24000
Total_Scans         = 24000

Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 24.6[dC]
X_90_Width          = 8.5[us]
X_Acq_Time          = 0.8388608[s]
X_Angle             = 30[deg]
X_Atn               = 4.6[dB]
X_Pulse             = 2.83333333[us]
Irr_Atn_Dec         = 22.735[dB]
Irr_Atn_Noe         = 22.735[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```



7e

^{1}H NMR (400 MHz, $CDCl_3$)



7e

^{13}C NMR (125 MHz, $CDCl_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 201.22599, 192.03349, 59.00889[%] )

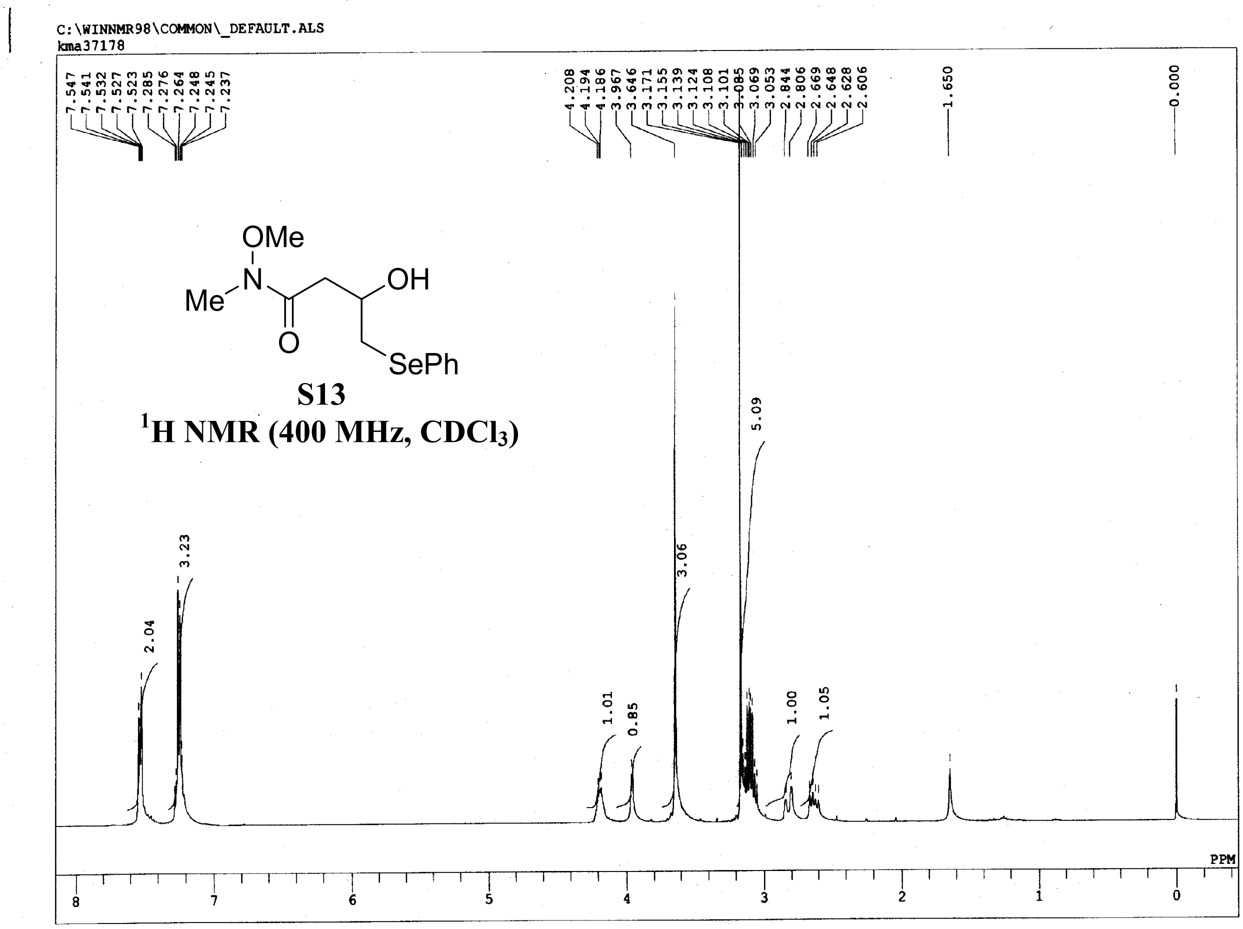
以下に由来:: KMA-XXXVII-192_c-1-1.jdf
```

```
Filename           = C:\Users\delta\Documents\J
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = KMA-XXXVII-192
Solvent            = CHLOROFORM-D
Creation_Time      = 30-SEP-2011 12:17:37
Revision_Time      =  3-OCT-2011 16:01:02
Current_Time       =  3-OCT-2011 16:02:07

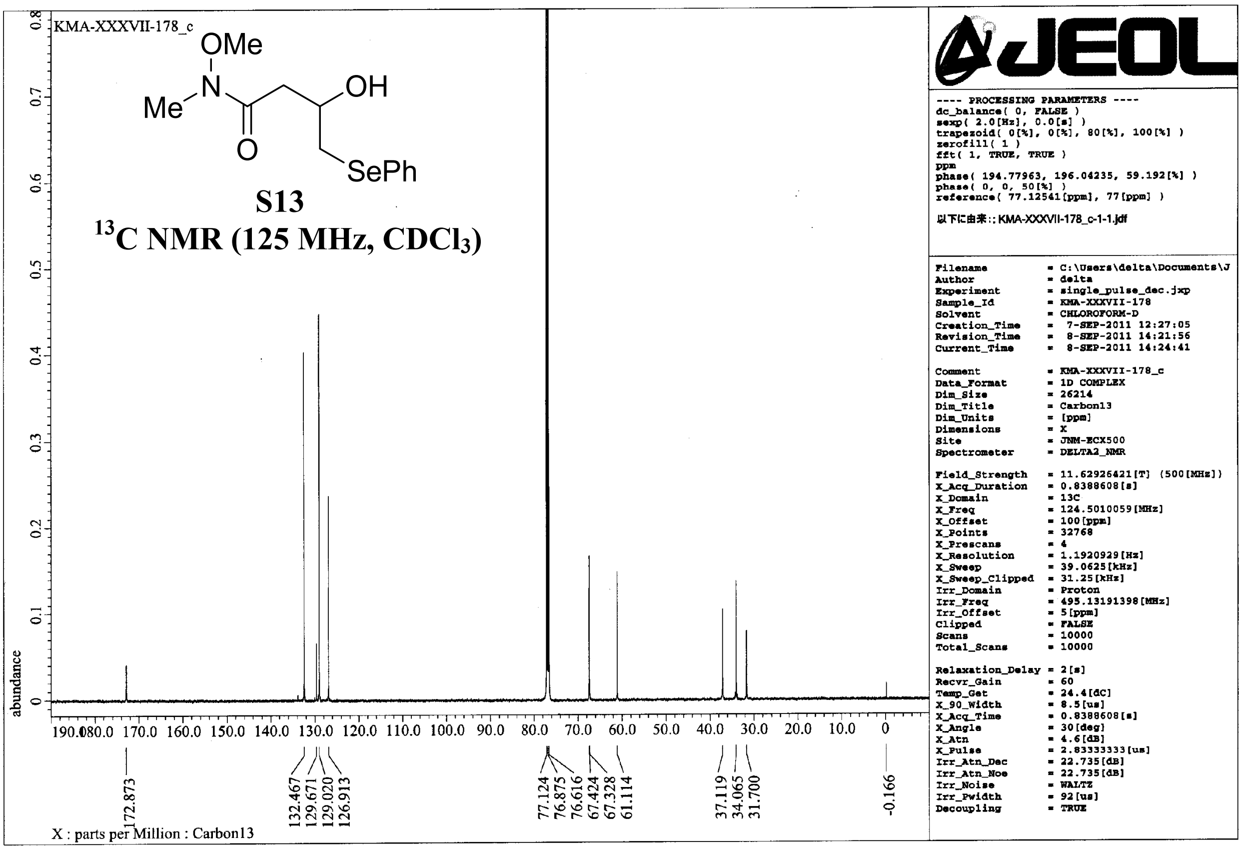
Comment            = KMA-XXXVII-192_c
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.62926421[T] (500[MHz])
X_Acq_Duration     = 0.8388608[s]
X_Domain           = 13C
X_Freq             = 124.5010059[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.1920929[Hz]
X_Sweep            = 39.0625[kHz]
X_Sweep_Clipped    = 31.25[kHz]
Irr_Domain         = Proton
Irr_Freq           = 495.13191398[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 20000
Total_Scans        = 20000

Relaxation_Delay   = 2[s]
Recvr_Gain         = 60
Temp_Get           = 24.2[dC]
X_90_Width         = 8.5[us]
X_Acq_Time         = 0.8388608[s]
X_Angle            = 30[deg]
X_Atn              = 4.6[dB]
X_Pulse            = 2.83333333[us]
Irr_Atn_Dec        = 22.735[dB]
Irr_Atn_Noe        = 22.735[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



S13
^{1}H NMR (400 MHz, CDCl$_3$)



S13
^{13}C NMR (125 MHz, CDCl$_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 194.77963, 196.04235, 59.192[%] )
phase( 0, 0, 50[%] )
reference( 77.12541[ppm], 77[ppm] )

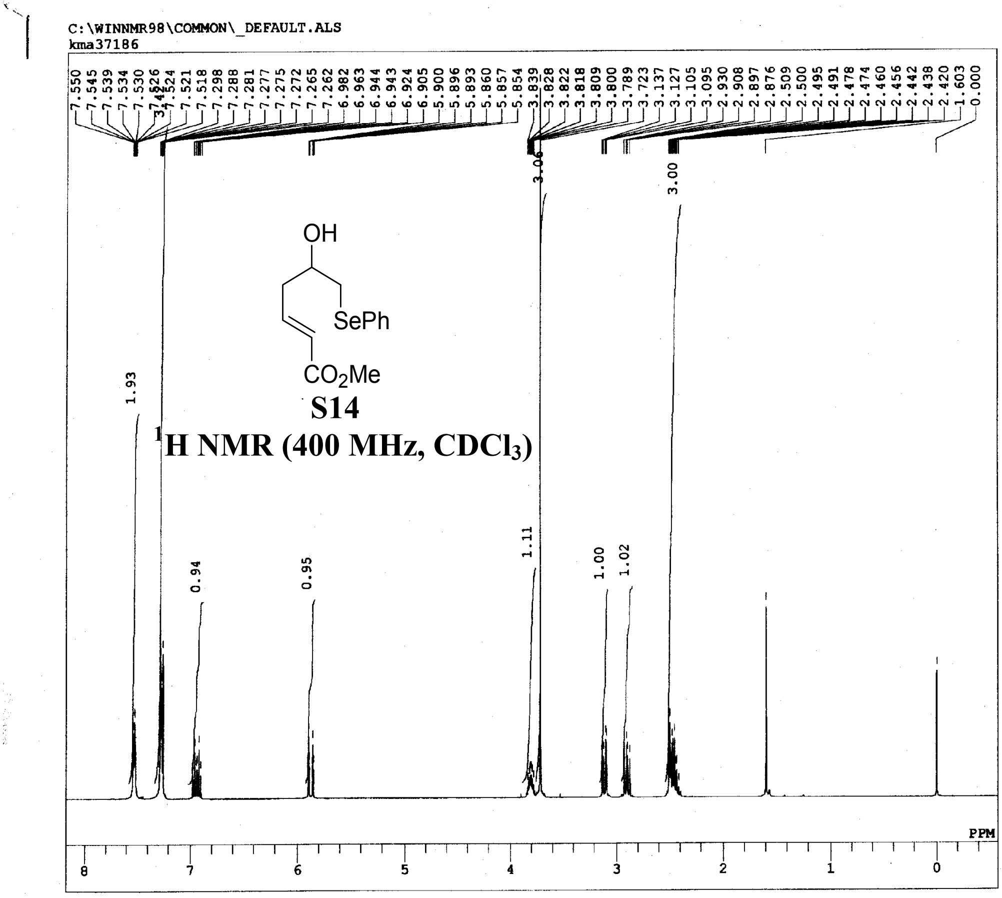
以下に由来:: KMA-XXXVII-178_c-1-1.jdf

Filename           = C:\Users\delta\Documents\J
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = KMA-XXXVII-178
Solvent            = CHLOROFORM-D
Creation_Time      =  7-SEP-2011 12:27:05
Revision_Time      =  8-SEP-2011 14:21:56
Current_Time       =  8-SEP-2011 14:24:41

Comment            = KMA-XXXVII-178_c
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.62926421[T] (500[MHz])
X_Acq_Duration     = 0.8388608[s]
X_Domain           = 13C
X_Freq             = 124.5010059[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.1920929[Hz]
X_Sweep            = 39.0625[kHz]
X_Sweep_Clipped    = 31.25[kHz]
Irr_Domain         = Proton
Irr_Freq           = 495.13191398[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 10000
Total_Scans        = 10000

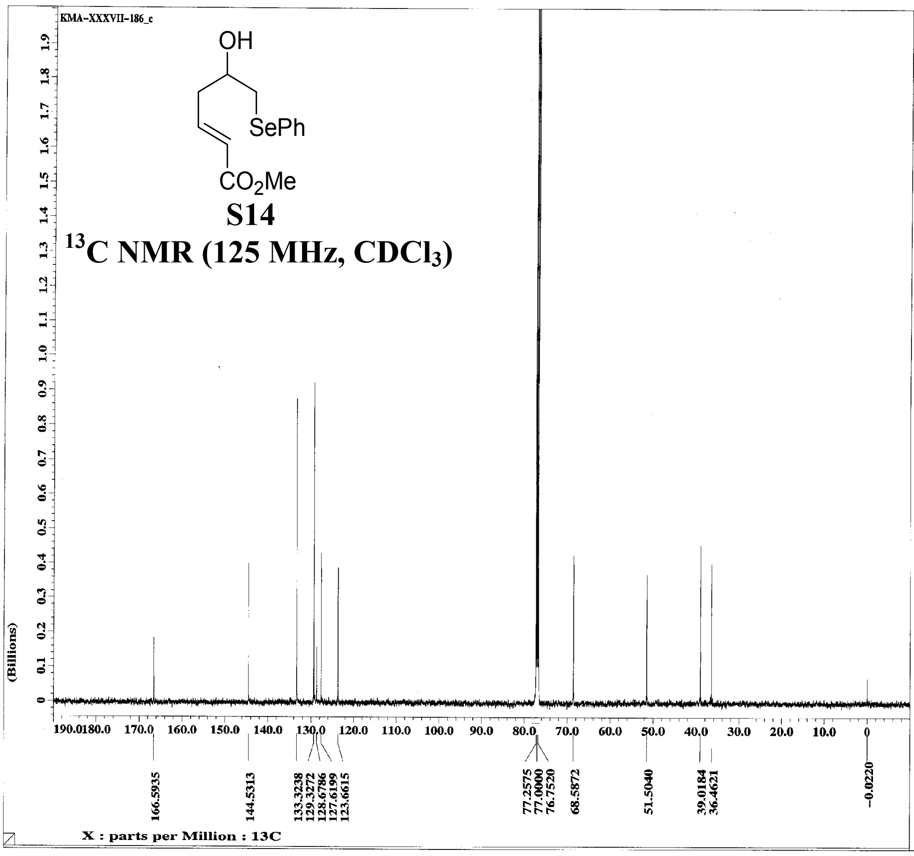
Relaxation_Delay   = 2[s]
Recvr_Gain         = 60
Temp_Get           = 24.4[dC]
X_90_Width         = 8.5[us]
X_Acq_Time         = 0.8388608[s]
X_Angle            = 30[deg]
X_Atn              = 4.6[dB]
X_Pulse            = 2.83333333[us]
Irr_Atn_Dec        = 22.735[dB]
Irr_Atn_Noe        = 22.735[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



S14

^{1}H NMR (400 MHz, CDCl$_3$)

```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT  kma37186
DATIM  Mon Sep 12 09:08:19 2011
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7992.01 Hz
SCANS            40
ACQTM        4.1001 sec
PD           2.9000 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          24.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            15
```



S14

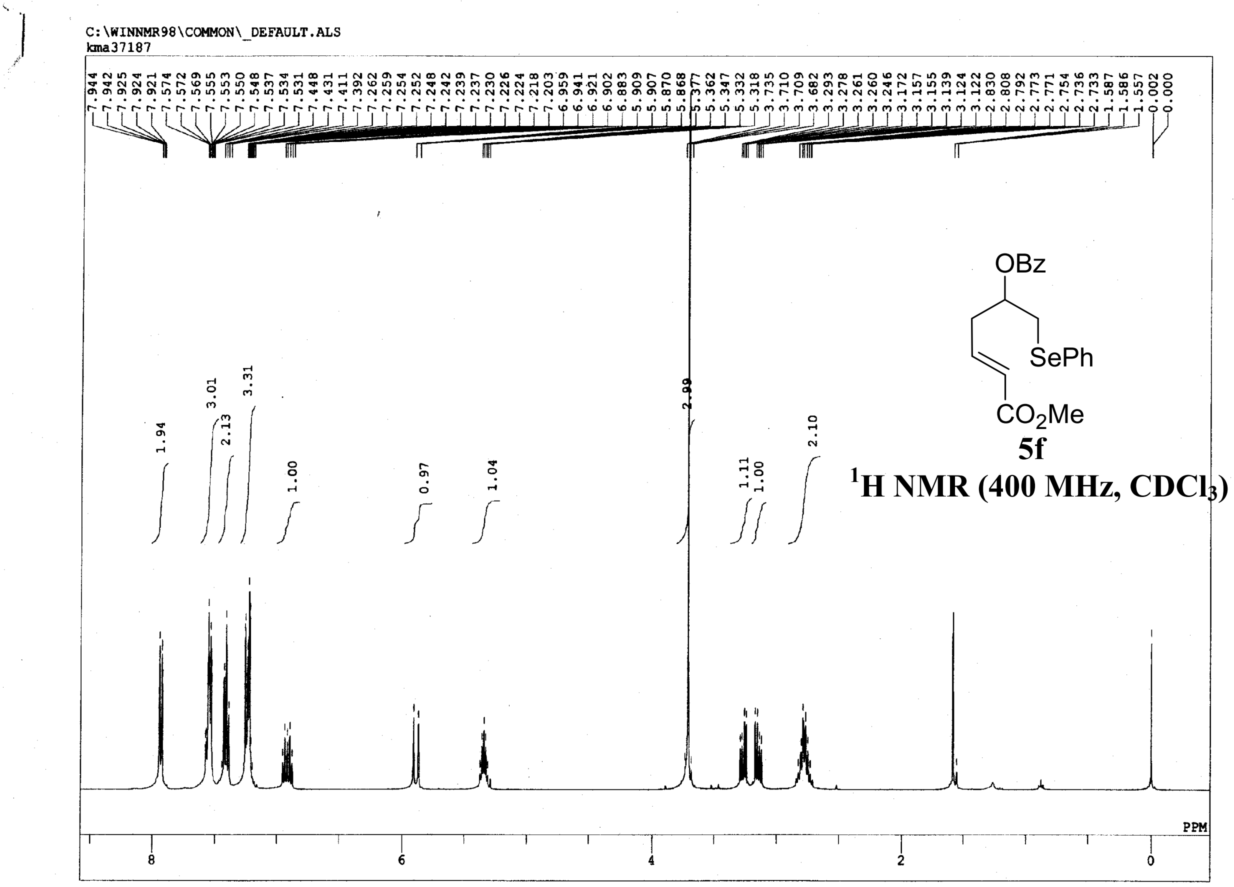
^{13}C NMR (125 MHz, CDCl$_3$)

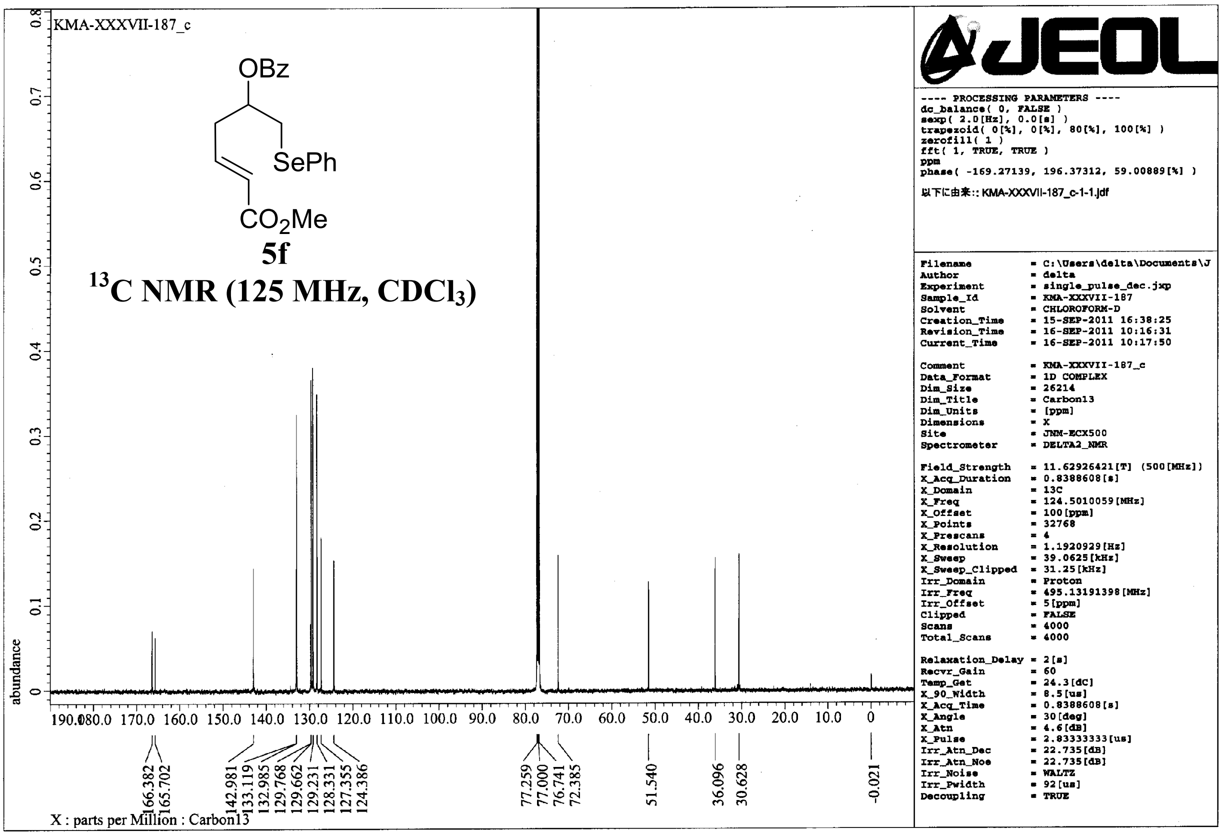
```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-186_c.1
File Name           = KMA-XXXVII-186_c.3
Author              = delta
Sample ID           = KMA-XXXVII-186
Content             = KMA-XXXVII-186_c
Creation Date       = 14-SEP-2011 15:02:39

Revision Date       = 15-SEP-2011 10:05:31
Spec Site           = ECA 500

Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 26214
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 0.83361792[s]
X_domain            = 13C
X_freq              = 125.76529768[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 1.19959034[Hz]
X_sweep             = 39.3081761[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 3801
Total_scans         = 3801

X_90_width          = 10.5[us]
X_acq_time          = 0.83361792[s]
X_angle             = 30[deg]
X_atn               = 6.8[dB]
X_pulse             = 3.5[us]
Irr_atn_dec         = 19.6[dB]
Irr_atn_noe         = 21.6[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Relaxation_delay    = 2[s]
Repetition_time     = 2.83361792[s]
Experiment          = single_pulse_dec
Recvr_gain          = 60
Solvent             = CHLOROFORM-D
```





```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( -169.27139, 196.37312, 59.00889[%] )

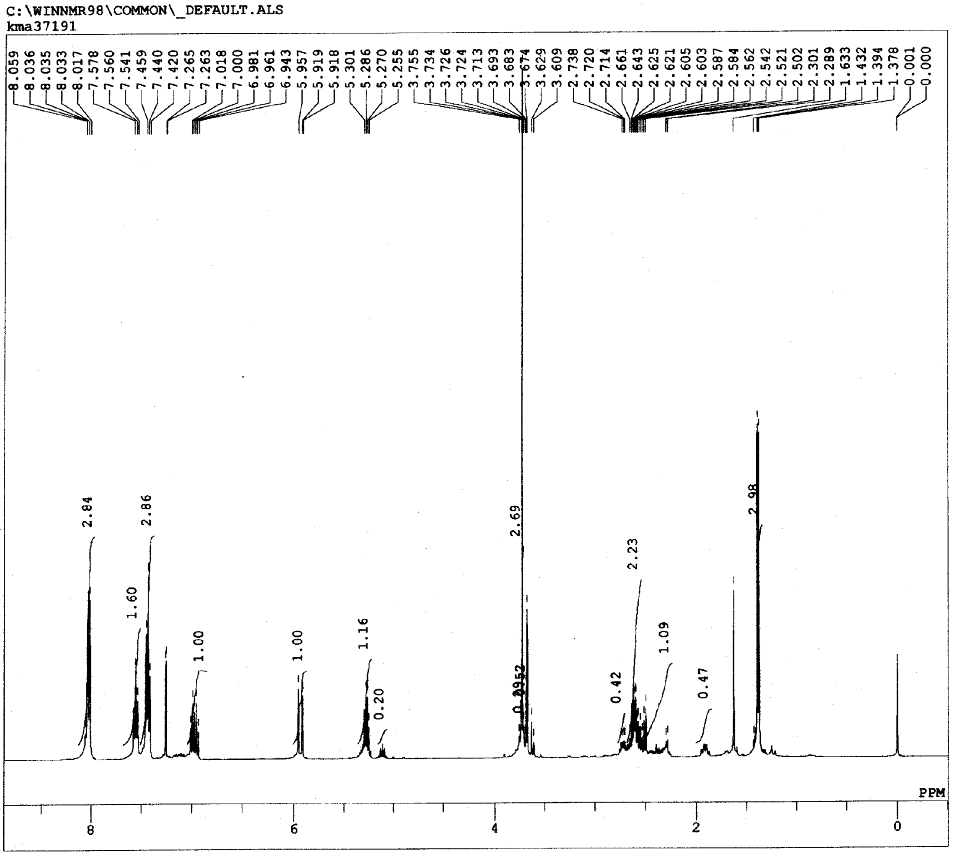
以下に由来:: KMA-XXXVII-187_c-1-1.jdf

Filename           = C:\Users\delta\Documents\J
Author             = delta
Experiment         = single_pulse_dec.jxp
Sample_Id          = KMA-XXXVII-187
Solvent            = CHLOROFORM-D
Creation_Time      = 15-SEP-2011 16:38:25
Revision_Time      = 16-SEP-2011 10:16:31
Current_Time       = 16-SEP-2011 10:17:50

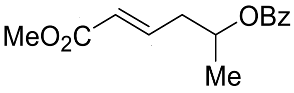
Comment            = KMA-XXXVII-187_c
Data_Format        = 1D COMPLEX
Dim_Size           = 26214
Dim_Title          = Carbon13
Dim_Units          = [ppm]
Dimensions         = X
Site               = JNM-ECX500
Spectrometer       = DELTA2_NMR

Field_Strength     = 11.62926421[T] (500[MHz])
X_Acq_Duration     = 0.8388608[s]
X_Domain           = 13C
X_Freq             = 124.5010059[MHz]
X_Offset           = 100[ppm]
X_Points           = 32768
X_Prescans         = 4
X_Resolution       = 1.1920929[Hz]
X_Sweep            = 39.0625[kHz]
X_Sweep_Clipped    = 31.25[kHz]
Irr_Domain         = Proton
Irr_Freq           = 495.13191398[MHz]
Irr_Offset         = 5[ppm]
Clipped            = FALSE
Scans              = 4000
Total_Scans        = 4000

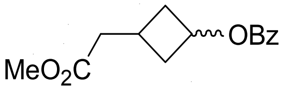
Relaxation_Delay   = 2[s]
Recvr_Gain         = 60
Temp_Get           = 24.3[dC]
X_90_Width         = 8.5[us]
X_Acq_Time         = 0.8388608[s]
X_Angle            = 30[deg]
X_Atn              = 4.6[dB]
X_Pulse            = 2.83333333[us]
Irr_Atn_Dec        = 22.735[dB]
Irr_Atn_Noe        = 22.735[dB]
Irr_Noise          = WALTZ
Irr_Pwidth         = 92[us]
Decoupling         = TRUE
```



```
DFILE   C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT   kma37191
DATIM   Tue Sep 20 08:58:48 2011
OBNUC   1H
EXMOD   NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7992.01 Hz
SCANS            80
ACQTM        4.1001 sec
PD           2.9000 sec
PW1            5.80 usec
IRNUC   1H
CTEMP          23.8 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            14
```

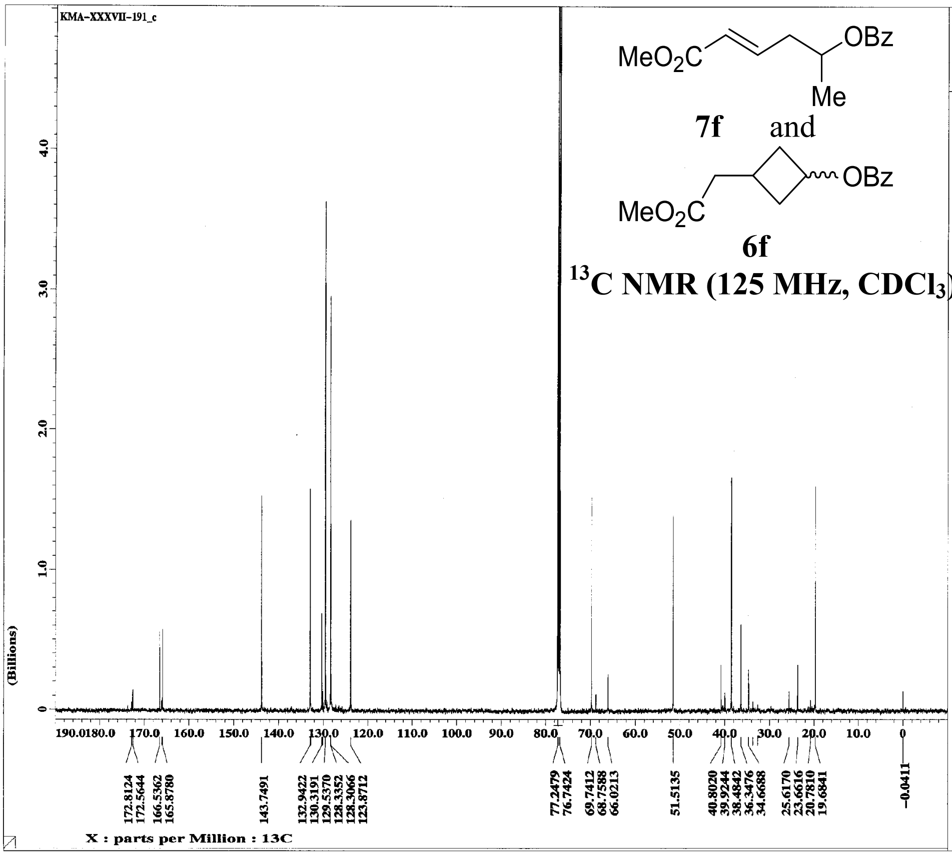


7f and



6f

^{1}H NMR (400 MHz, CDCl$_3$)



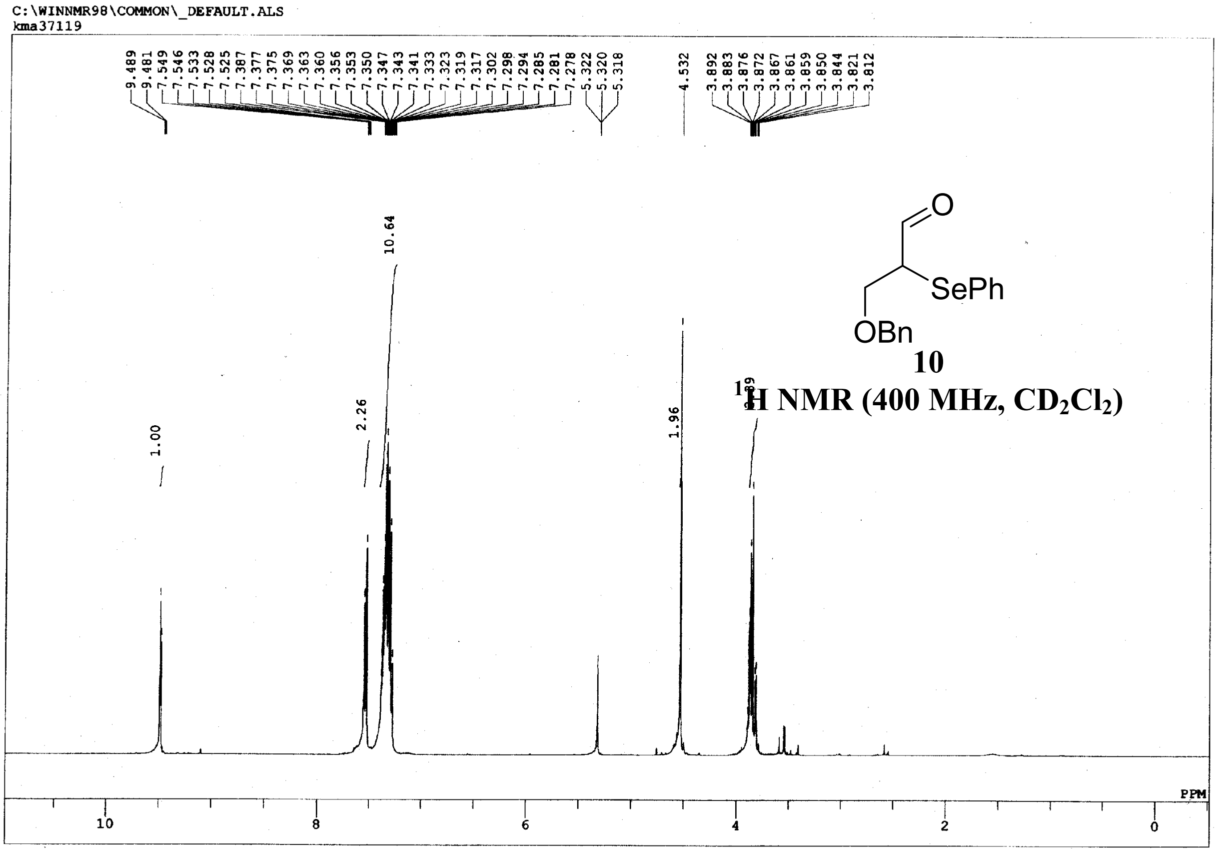
^{13}C NMR (125 MHz, CDCl$_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-191_c.1
File Name          = KMA-XXXVII-191_c.5
Author             = delta
Sample ID          = KMA-XXXVII-191
Content            = KMA-XXXVII-191_c
Creation Date      = 20-SEP-2011 22:09:34

Revision Date      = 21-SEP-2011 15:46:29
Spec Site          = ECA 500

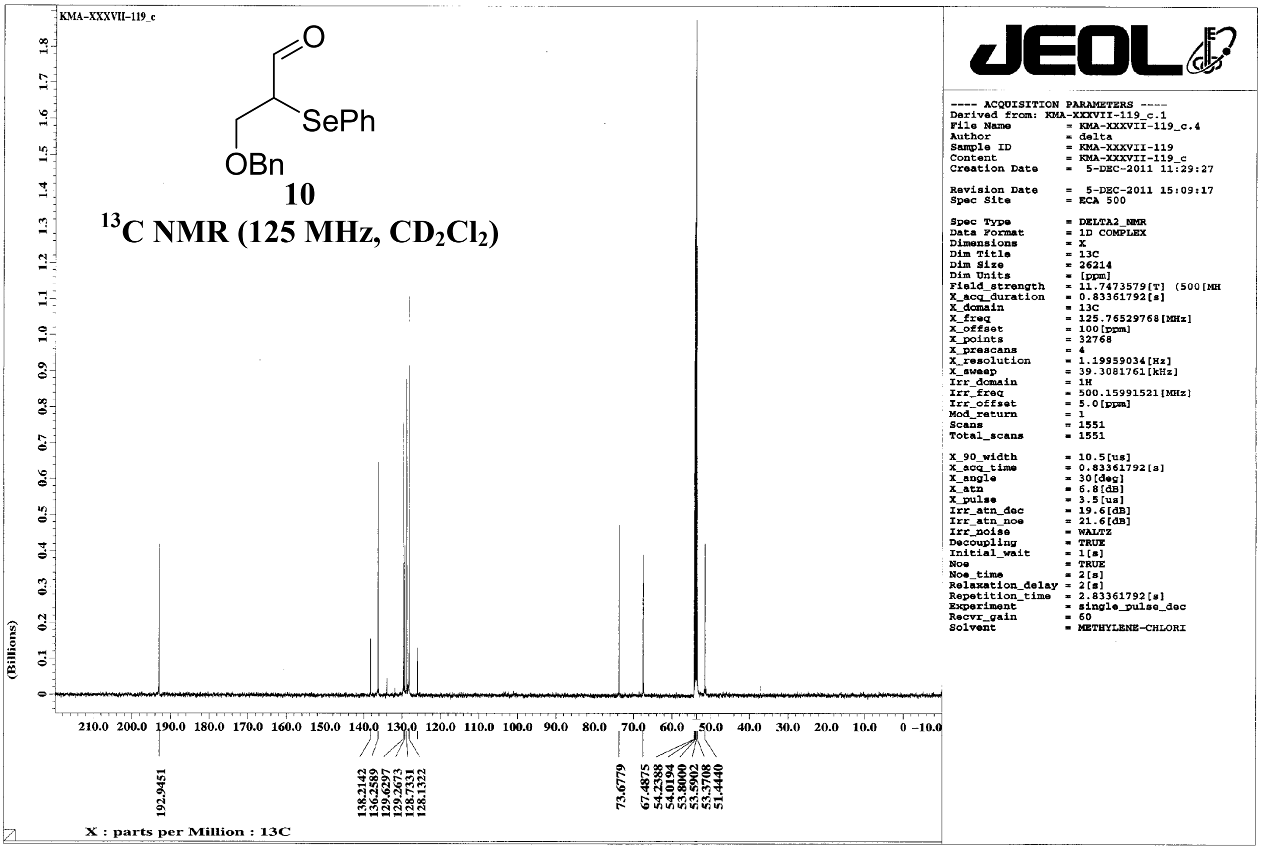
Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 10000
Total_scans        = 10000

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```



10

^{1}H NMR (400 MHz, CD$_2$Cl$_2$)



10

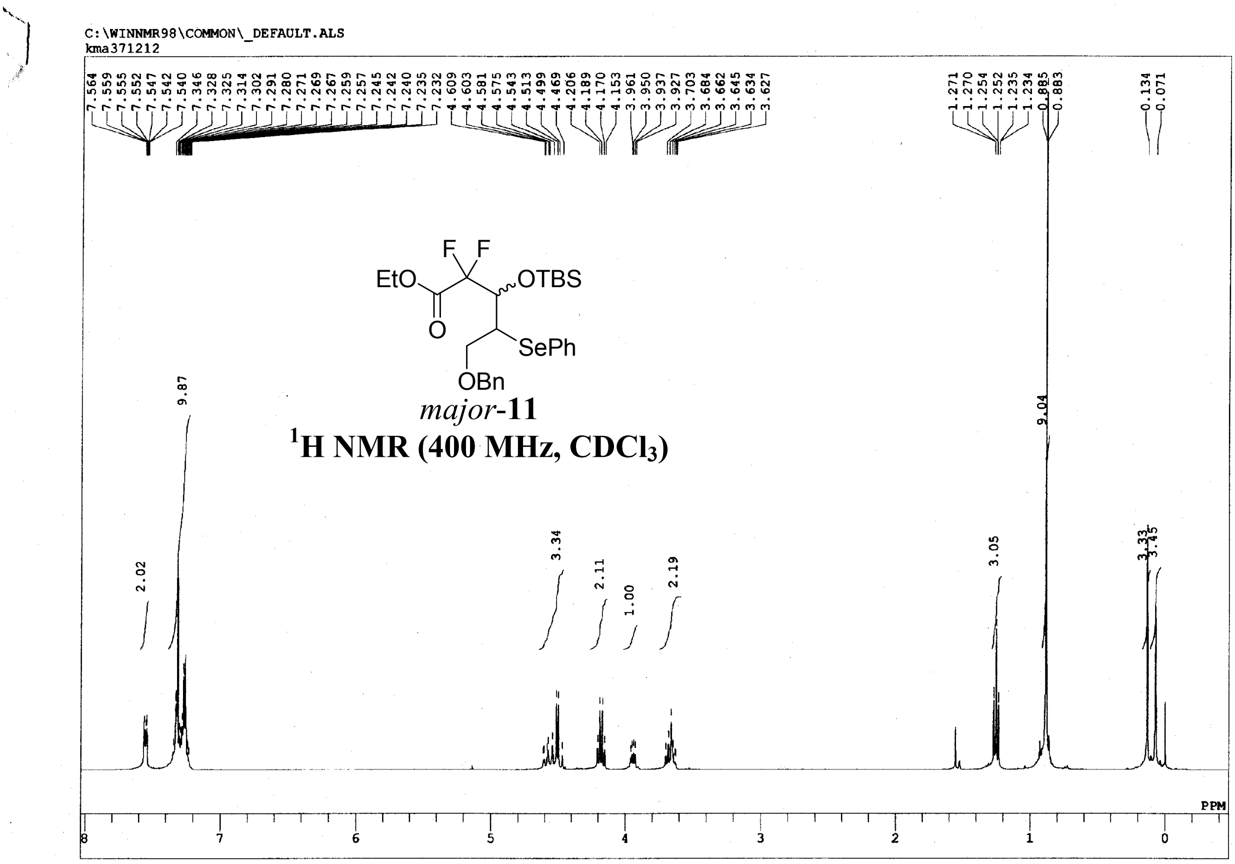
^{13}C NMR (125 MHz, CD$_2$Cl$_2$)

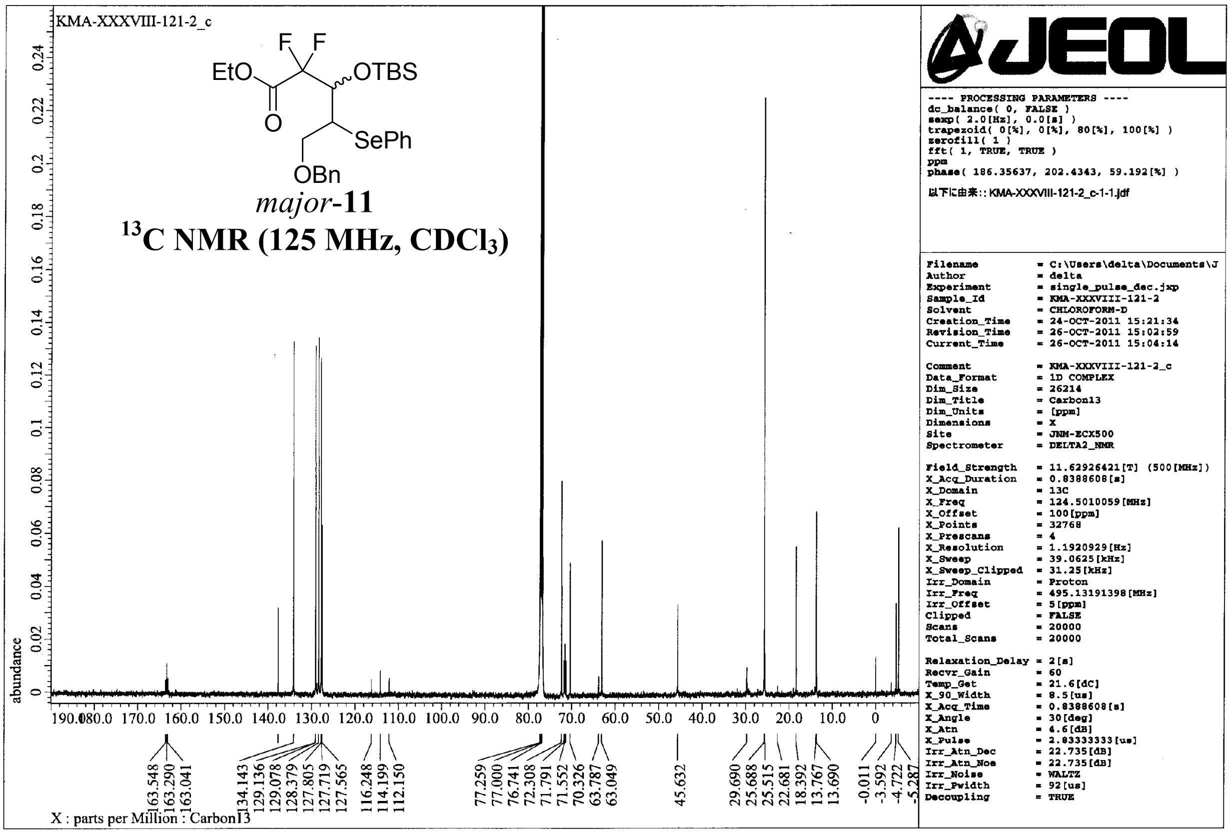
```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-119_c.1
File Name          = KMA-XXXVII-119_c.4
Author             = delta
Sample ID          = KMA-XXXVII-119
Content            = KMA-XXXVII-119_c
Creation Date      =  5-DEC-2011 11:29:27

Revision Date      =  5-DEC-2011 15:09:17
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 1551
Total_scans        = 1551

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = METHYLENE-CHLORI
```





```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 186.35637, 202.4343, 59.192[%] )

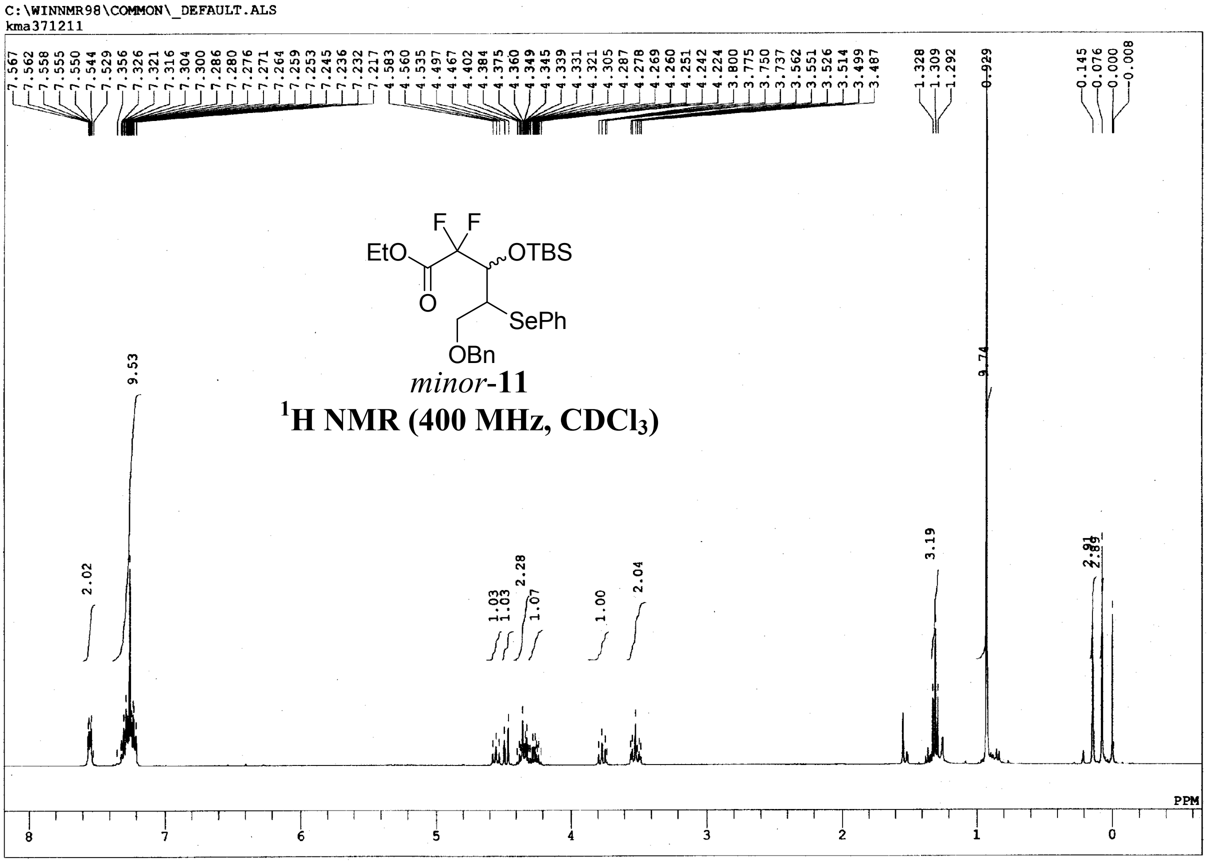
以下に由来:: KMA-XXXVIII-121-2_c-1-1.jdf
```

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = single_pulse_dec.jxp
Sample_Id         = KMA-XXXVIII-121-2
Solvent           = CHLOROFORM-D
Creation_Time     = 24-OCT-2011 15:21:34
Revision_Time     = 26-OCT-2011 15:02:59
Current_Time      = 26-OCT-2011 15:04:14

Comment           = KMA-XXXVIII-121-2_c
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

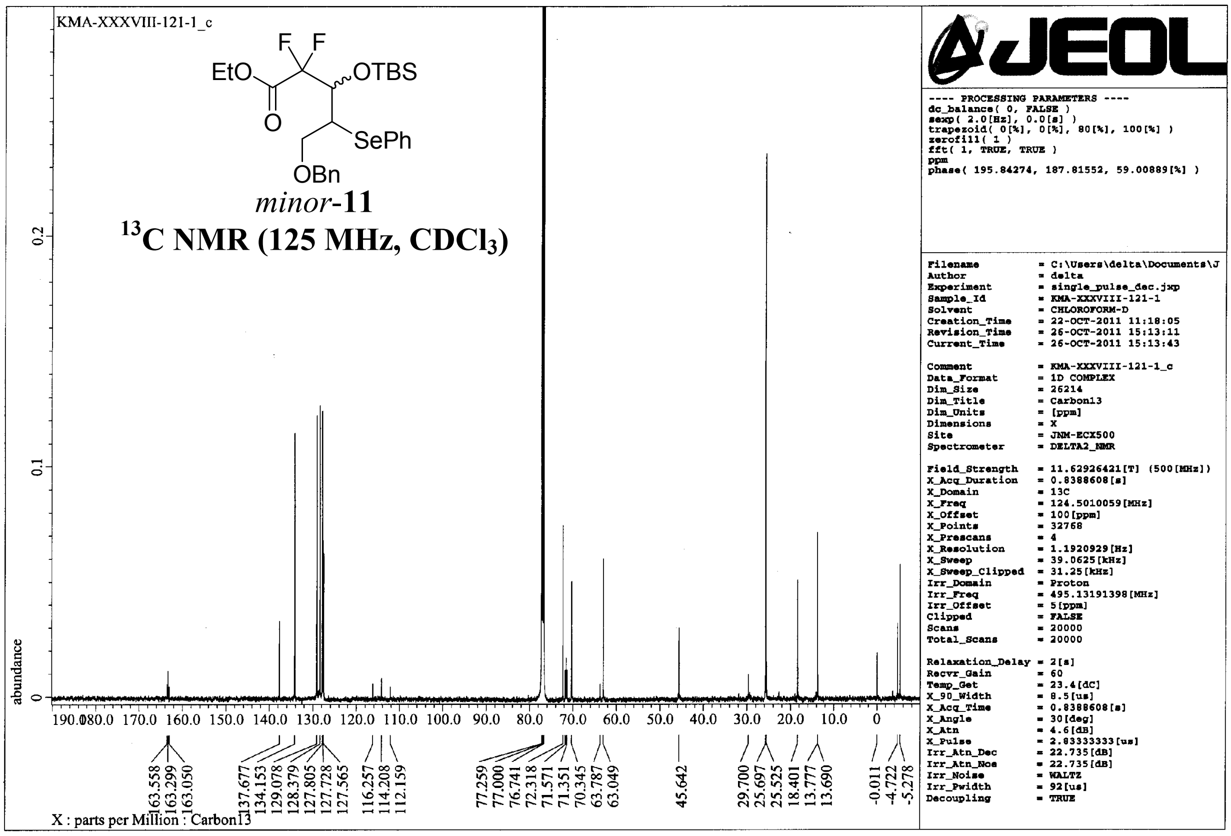
Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
X_Sweep_Clipped   = 31.25[kHz]
Irr_Domain        = Proton
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 20000
Total_Scans       = 20000

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 21.6[dC]
X_90_Width        = 8.5[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 4.6[dB]
X_Pulse           = 2.83333333[us]
Irr_Atn_Dec       = 22.735[dB]
Irr_Atn_Noe       = 22.735[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
```



minor-**11**

^{1}H NMR (400 MHz, $CDCl_3$)



minor-**11**

^{13}C NMR (125 MHz, $CDCl_3$)

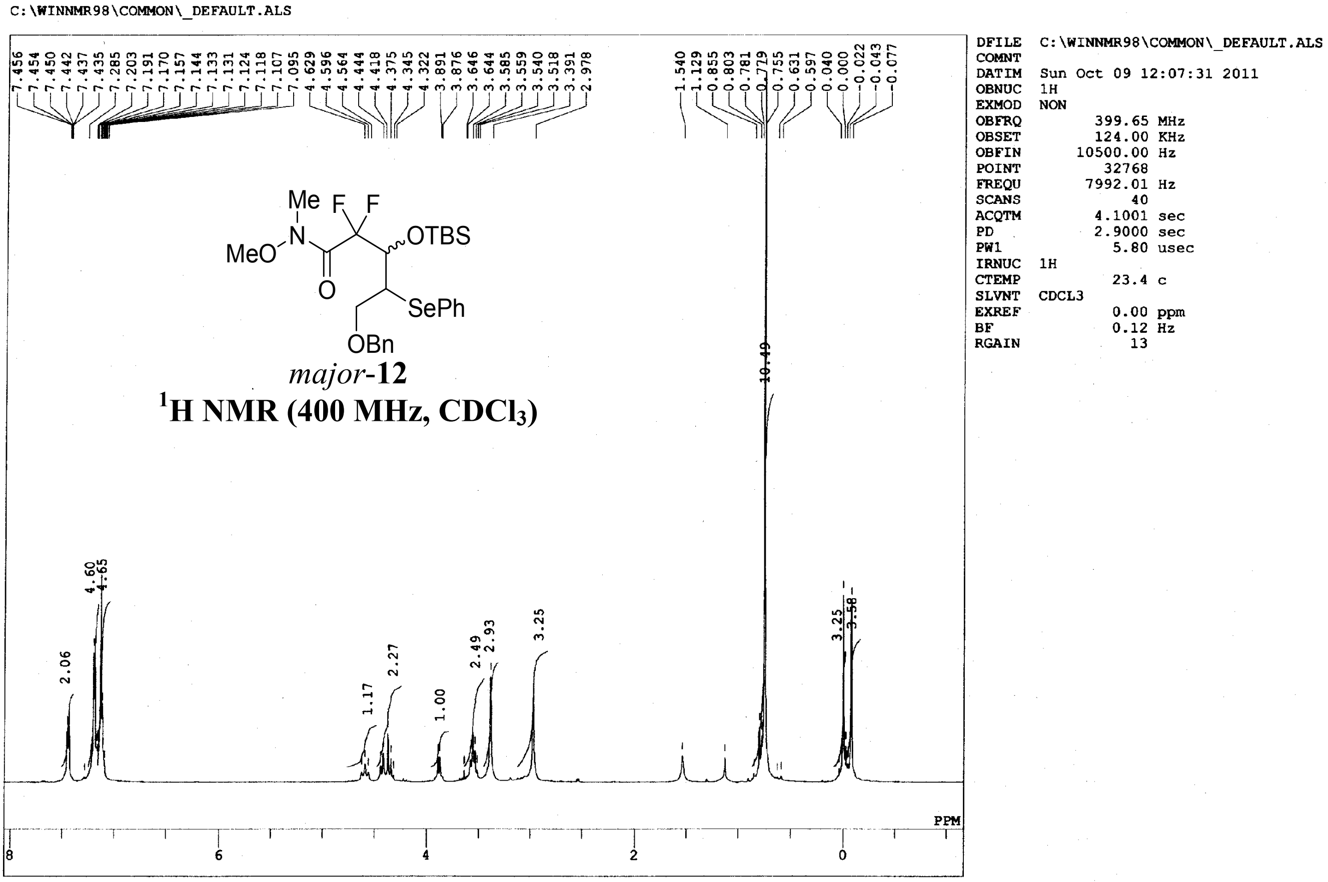
```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 195.84274, 187.81552, 59.00889[%] )

Filename            = C:\Users\delta\Documents\J
Author              = delta
Experiment          = single_pulse_dec.jxp
Sample_Id           = KMA-XXXVIII-121-1
Solvent             = CHLOROFORM-D
Creation_Time       = 22-OCT-2011 11:18:05
Revision_Time       = 26-OCT-2011 15:13:11
Current_Time        = 26-OCT-2011 15:13:43

Comment             = KMA-XXXVIII-121-1_c
Data_Format         = 1D COMPLEX
Dim_Size            = 26214
Dim_Title           = Carbon13
Dim_Units           = [ppm]
Dimensions          = X
Site                = JNM-ECX500
Spectrometer        = DELTA2_NMR

Field_Strength      = 11.62926421[T] (500[MHz])
X_Acq_Duration      = 0.8388608[s]
X_Domain            = 13C
X_Freq              = 124.5010059[MHz]
X_Offset            = 100[ppm]
X_Points            = 32768
X_Prescans          = 4
X_Resolution        = 1.1920929[Hz]
X_Sweep             = 39.0625[kHz]
X_Sweep_Clipped     = 31.25[kHz]
Irr_Domain          = Proton
Irr_Freq            = 495.13191398[MHz]
Irr_Offset          = 5[ppm]
Clipped             = FALSE
Scans               = 20000
Total_Scans         = 20000

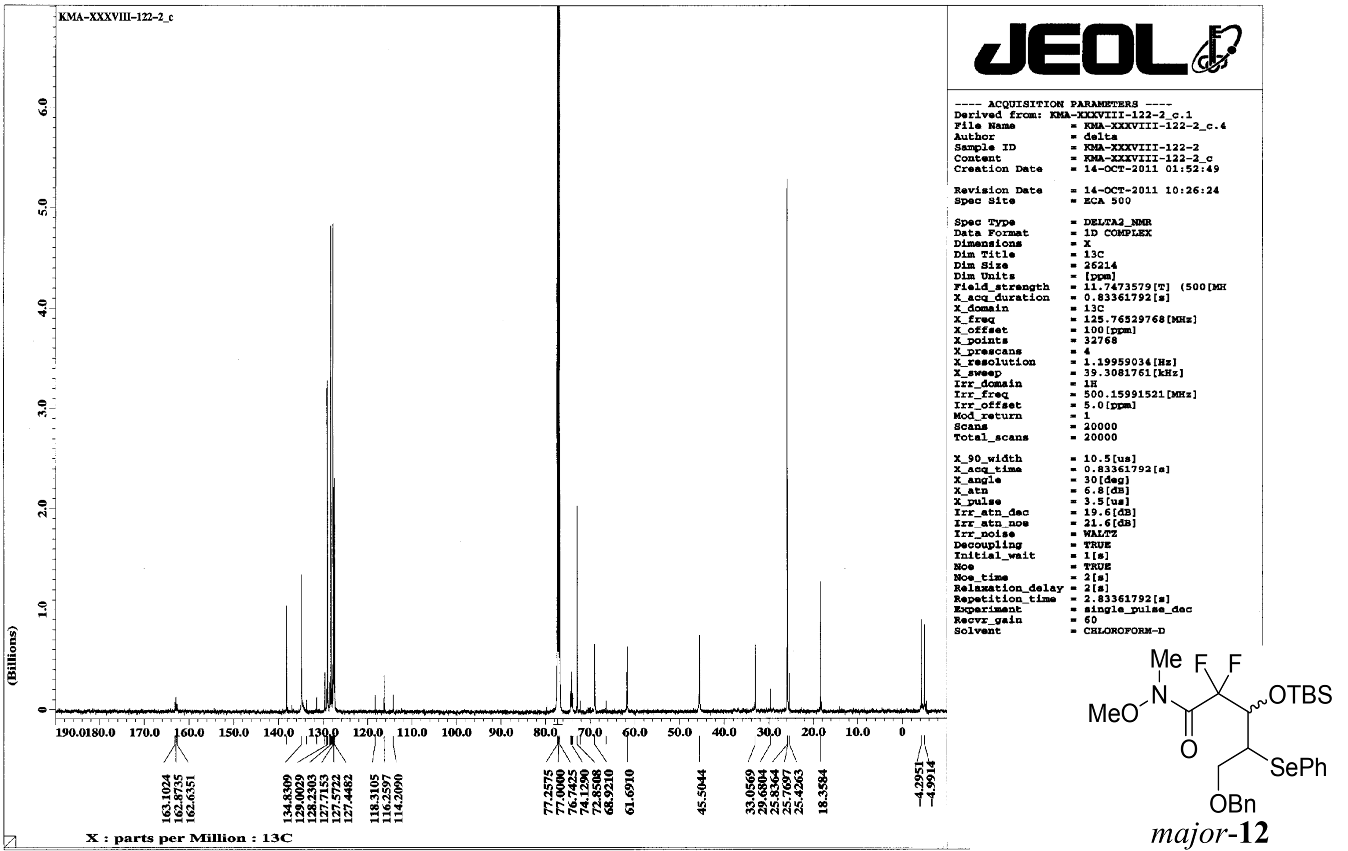
Relaxation_Delay    = 2[s]
Recvr_Gain          = 60
Temp_Get            = 23.4[dC]
X_90_Width          = 8.5[us]
X_Acq_Time          = 0.8388608[s]
X_Angle             = 30[deg]
X_Atn               = 4.6[dB]
X_Pulse             = 2.83333333[us]
Irr_Atn_Dec         = 22.735[dB]
Irr_Atn_Noe         = 22.735[dB]
Irr_Noise           = WALTZ
Irr_Pwidth          = 92[us]
Decoupling          = TRUE
```



```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT
DATIM  Sun Oct 09 12:07:31 2011
OBNUC  1H
EXMOD  NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT          32768
FREQU        7992.01 Hz
SCANS             40
ACQTM         4.1001 sec
PD            2.9000 sec
PW1             5.80 usec
IRNUC  1H
CTEMP           23.4 c
SLVNT  CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             13
```

major-**12**

^{1}H NMR (400 MHz, CDCl$_3$)



```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVIII-122-2_c.1
File Name          = KMA-XXXVIII-122-2_c.4
Author             = delta
Sample ID          = KMA-XXXVIII-122-2
Content            = KMA-XXXVIII-122-2_c
Creation Date      = 14-OCT-2011 01:52:49

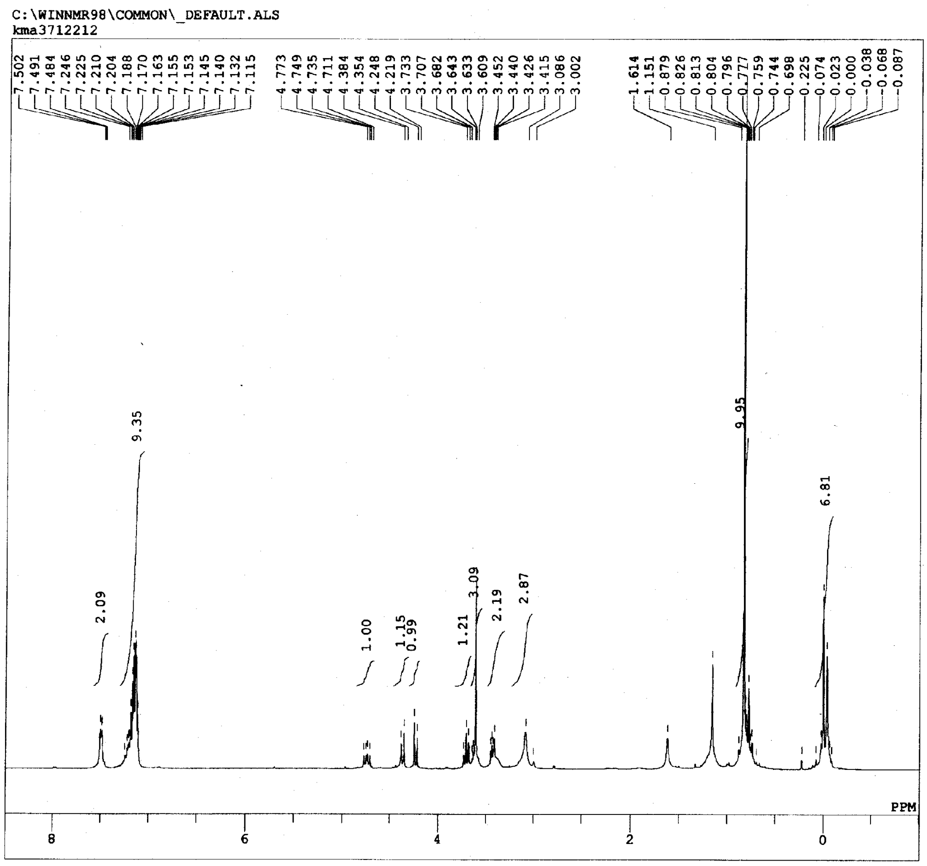
Revision Date      = 14-OCT-2011 10:26:24
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 20000
Total_scans        = 20000

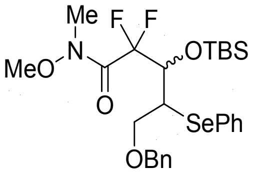
X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```

major-**12**

^{13}C NMR (125 MHz, CDCl$_3$)

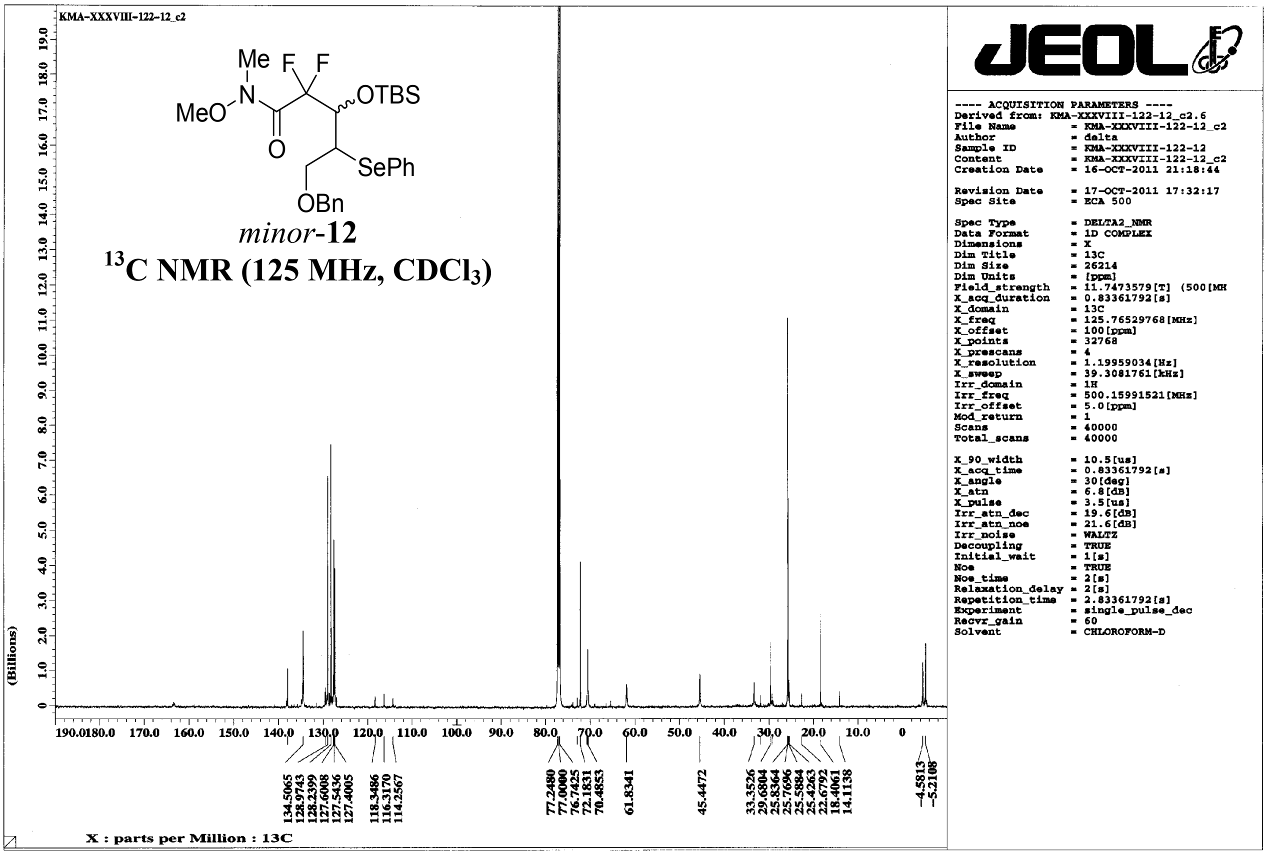


```
DFILE   C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT   kma3712212
DATIM   Mon Oct 10 12:51:21 2011
OBNUC   1H
EXMOD   NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7992.01 Hz
SCANS            40
ACQTM        4.1001 sec
PD           2.9000 sec
PW1            5.80 usec
IRNUC   1H
CTEMP          23.4 c
SLVNT   CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            13
```



minor-**12**

^{1}H NMR (400 MHz, CDCl$_3$)



minor-**12**

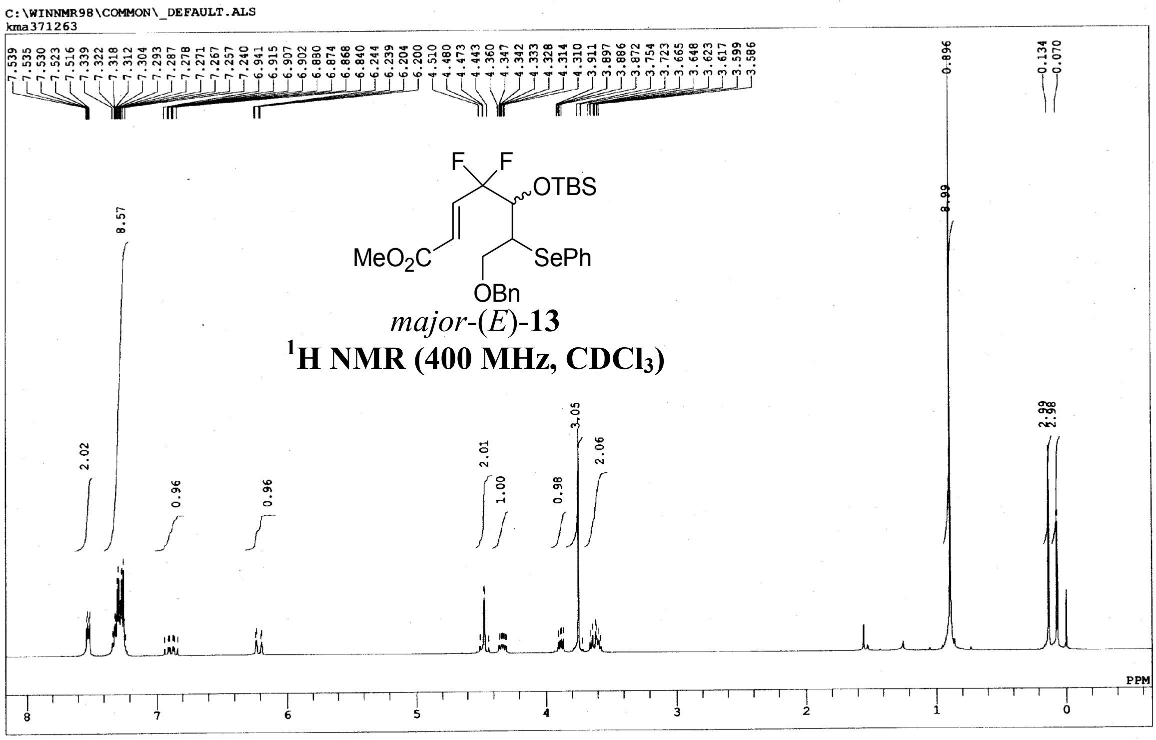
^{13}C NMR (125 MHz, CDCl$_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVIII-122-12_c2.6
File Name         = KMA-XXXVIII-122-12_c2
Author            = delta
Sample ID         = KMA-XXXVIII-122-12
Content           = KMA-XXXVIII-122-12_c2
Creation Date     = 16-OCT-2011 21:18:44

Revision Date     = 17-OCT-2011 17:32:17
Spec Site         = ECA 500

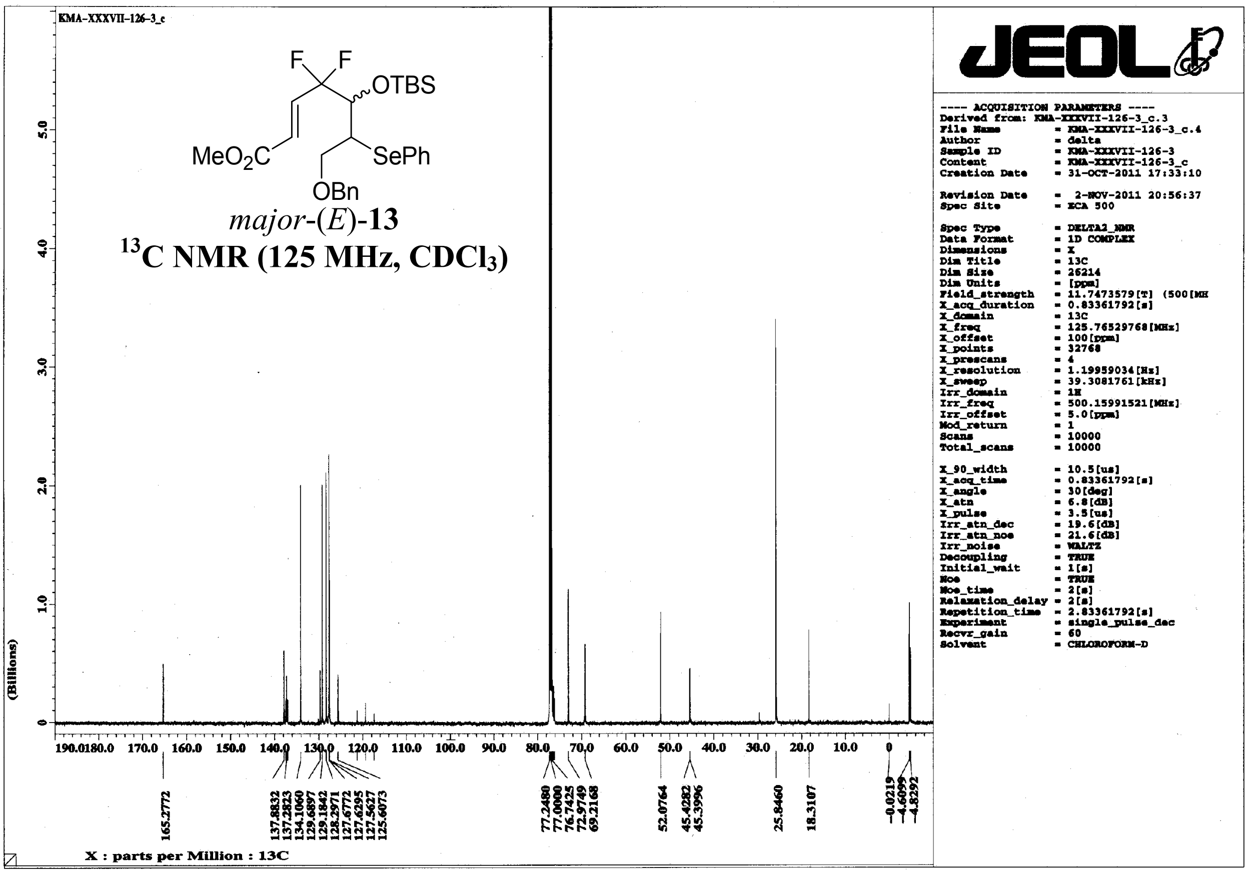
Spec Type         = DELTA2_NMR
Data Format       = 1D COMPLEX
Dimensions        = X
Dim Title         = 13C
Dim Size          = 26214
Dim Units         = [ppm]
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Mod_return        = 1
Scans             = 40000
Total_scans       = 40000

X_90_width        = 10.5[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 6.8[dB]
X_pulse           = 3.5[us]
Irr_atn_dec       = 19.6[dB]
Irr_atn_noe       = 21.6[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Experiment        = single_pulse_dec
Recvr_gain        = 60
Solvent           = CHLOROFORM-D
```



major-(*E*)-**13**

^{1}H NMR (400 MHz, CDCl$_3$)



major-(*E*)-**13**

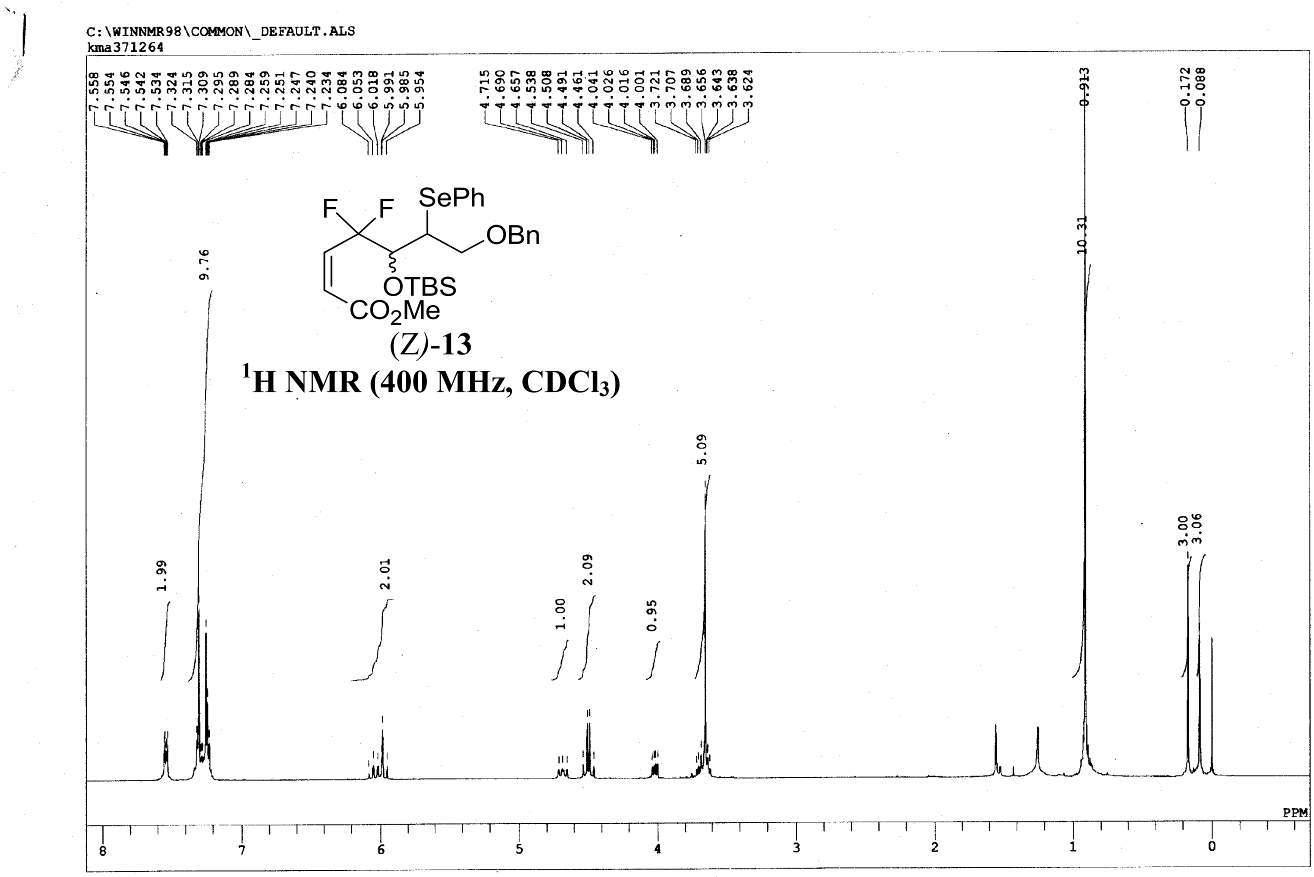
^{13}C NMR (125 MHz, CDCl$_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-126-3_c.3
File Name          = KMA-XXXVII-126-3_c.4
Author             = delta
Sample ID          = KMA-XXXVII-126-3
Content            = KMA-XXXVII-126-3_c
Creation Date      = 31-OCT-2011 17:33:10

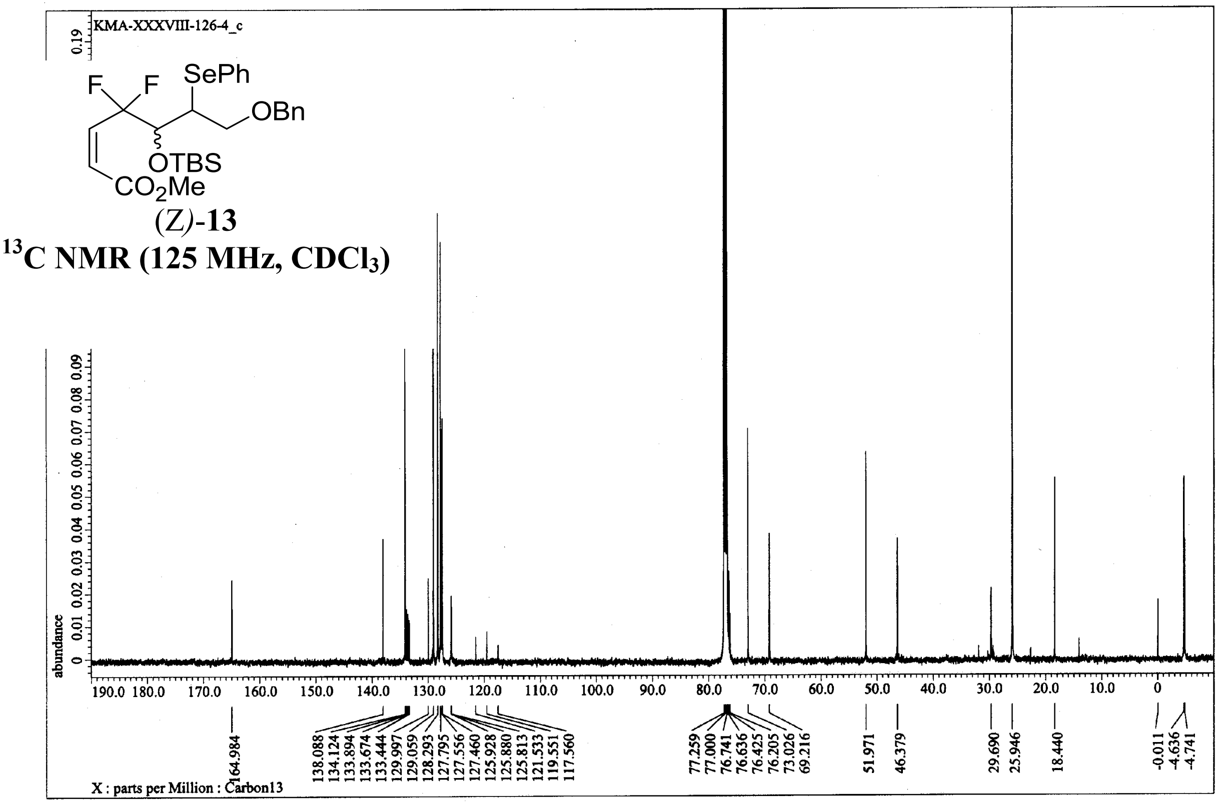
Revision Date      =  2-NOV-2011 20:56:37
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 10000
Total_scans        = 10000

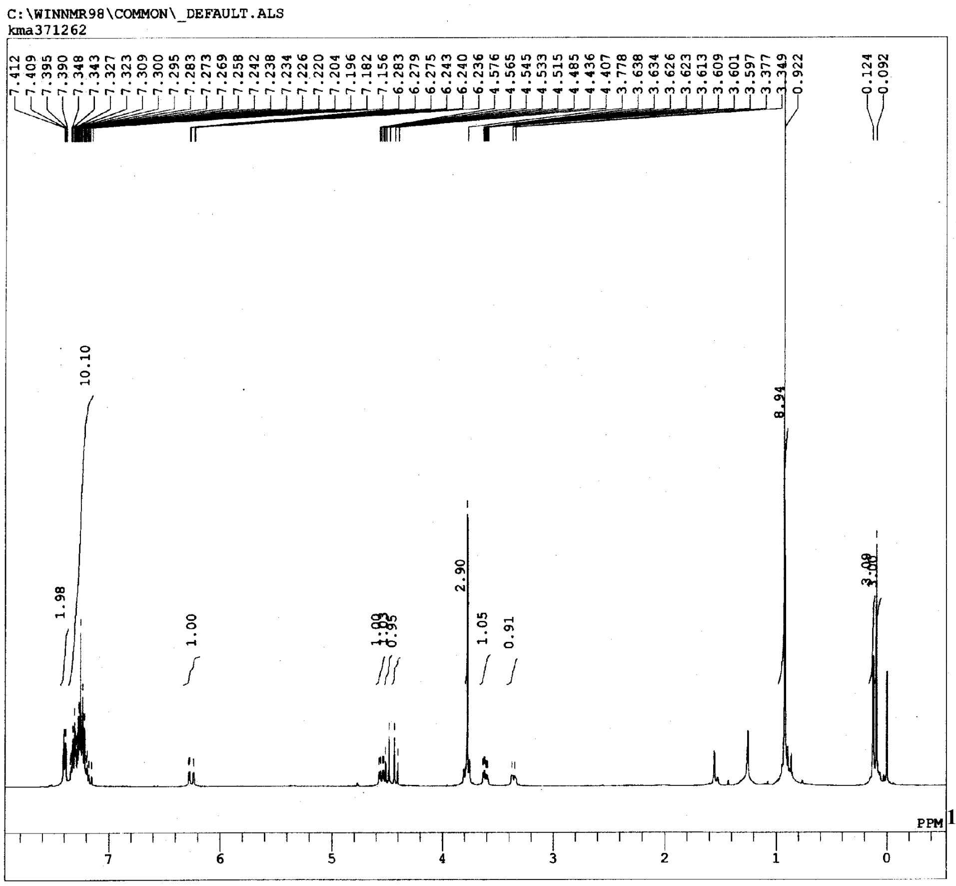
X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```


(*Z*)-**13**

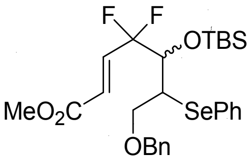
^{1}H NMR (400 MHz, CDCl$_3$)


(*Z*)-**13**

^{13}C NMR (125 MHz, CDCl$_3$)

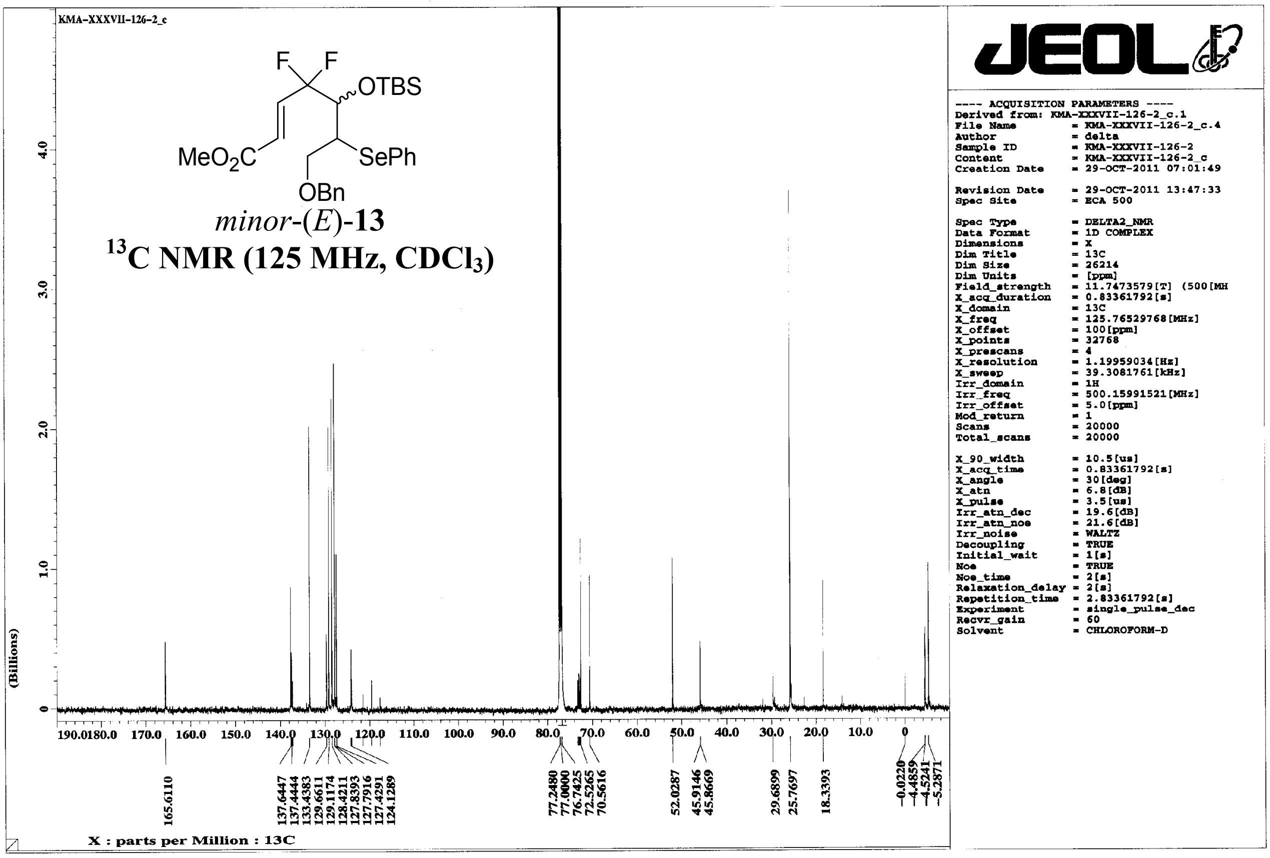


```
DFILE   C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT   kma371262
DATIM   Thu Oct 13 17:12:29 2011
OBNUC   1H
EXMOD   NON
OBFRQ         399.65 MHz
OBSET         124.00 KHz
OBFIN       10500.00 Hz
POINT          32768
FREQU        7992.01 Hz
SCANS             40
ACQTM         4.1001 sec
PD            2.9000 sec
PW1             5.80 usec
IRNUC   1H
CTEMP           24.1 c
SLVNT   CDCL3
EXREF           0.00 ppm
BF              0.12 Hz
RGAIN             15
```



minor-(*E*)-**13**

^{1}H NMR (400 MHz, CDCl$_3$)

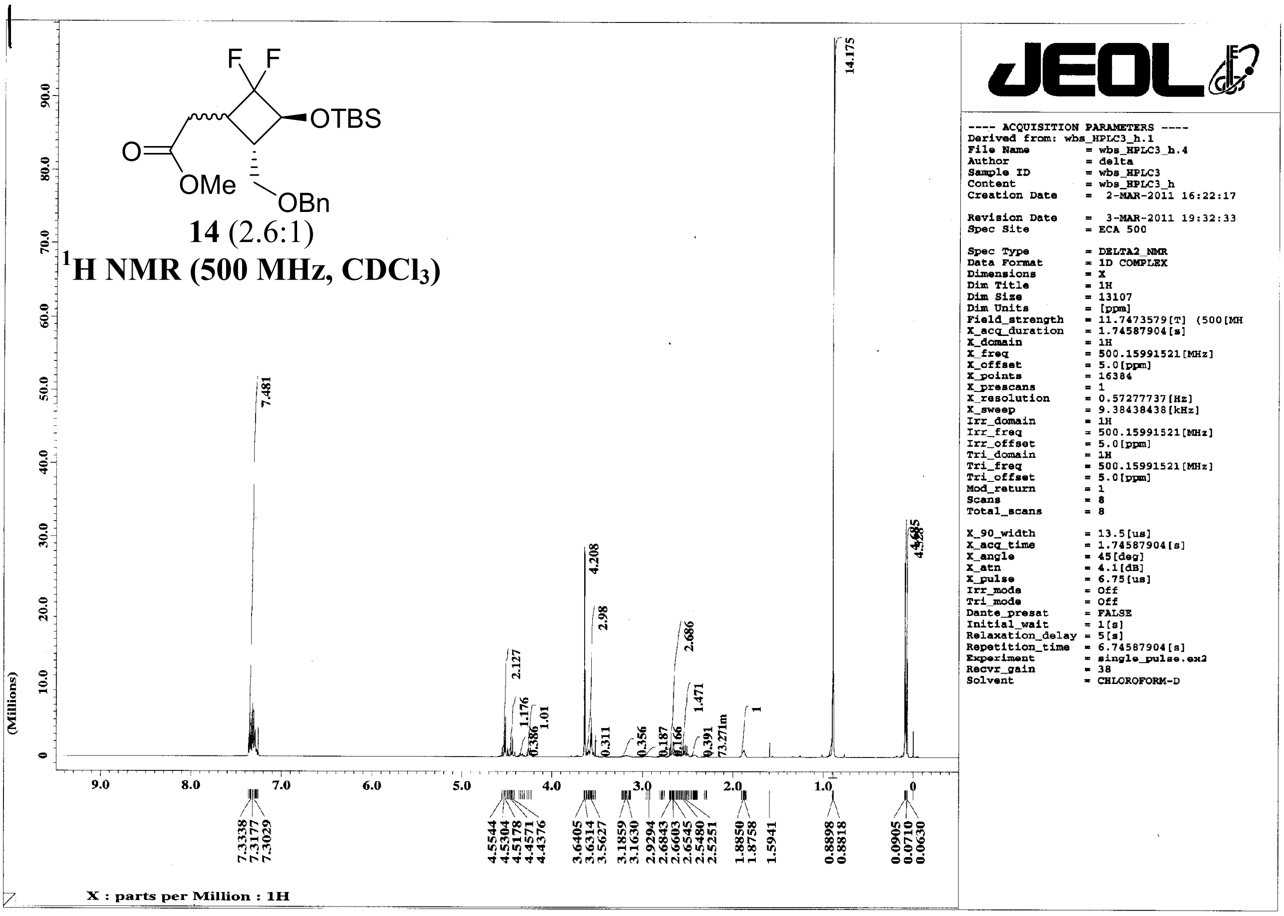


```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-126-2_c.1
File Name          = KMA-XXXVII-126-2_c.4
Author             = delta
Sample ID          = KMA-XXXVII-126-2
Content            = KMA-XXXVII-126-2_c
Creation Date      = 29-OCT-2011 07:01:49

Revision Date      = 29-OCT-2011 13:47:33
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 20000
Total_scans        = 20000

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```



14 (2.6:1)

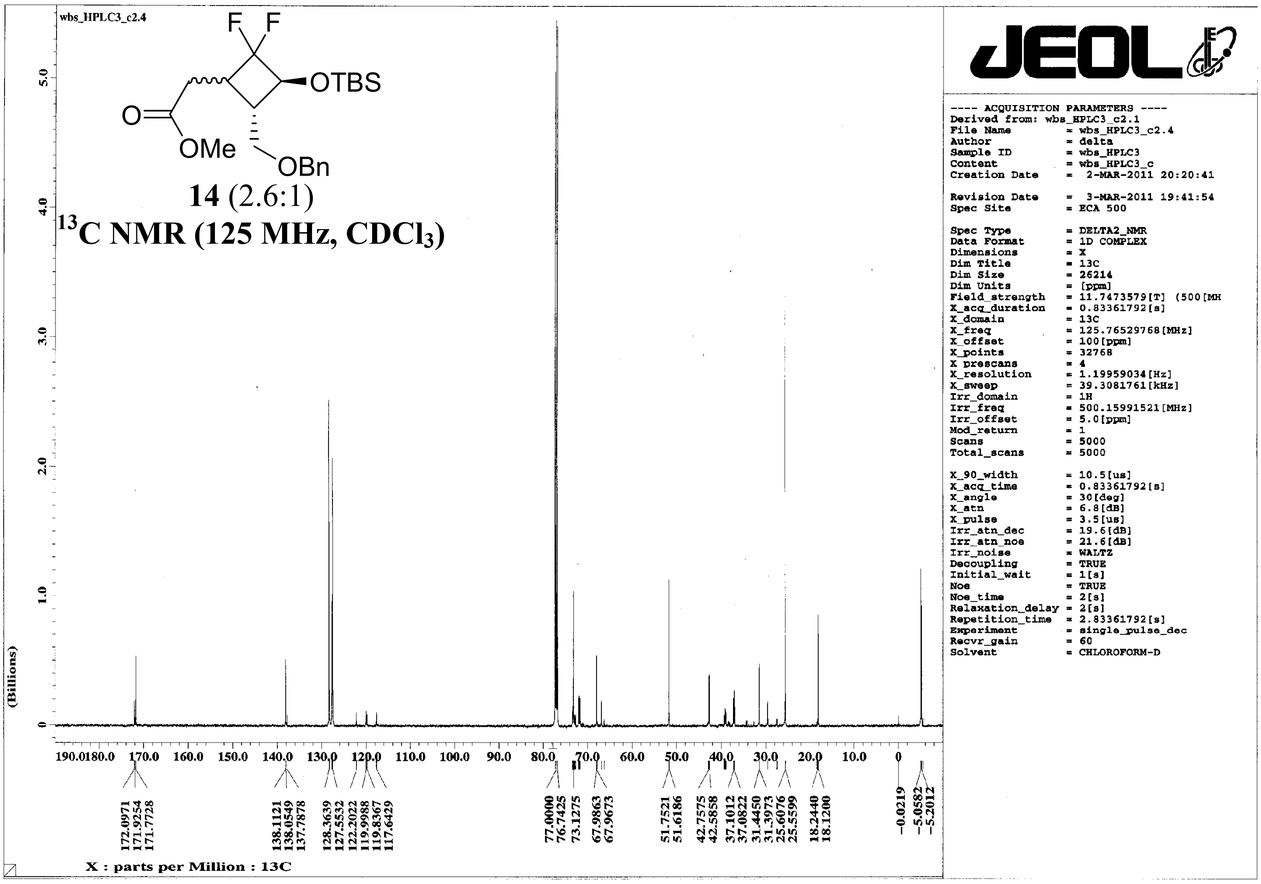
^{1}H NMR (500 MHz, CDCl$_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: wbs_HPLC3_h.1
File Name          = wbs_HPLC3_h.4
Author             = delta
Sample ID          = wbs_HPLC3
Content            = wbs_HPLC3_h
Creation Date      =  2-MAR-2011 16:22:17

Revision Date      =  3-MAR-2011 19:32:33
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 1H
Dim Size           = 13107
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 1.74587904[s]
X_domain           = 1H
X_freq             = 500.15991521[MHz]
X_offset           = 5.0[ppm]
X_points           = 16384
X_prescans         = 1
X_resolution       = 0.57277737[Hz]
X_sweep            = 9.38438438[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Tri_domain         = 1H
Tri_freq           = 500.15991521[MHz]
Tri_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 8
Total_scans        = 8

X_90_width         = 13.5[us]
X_acq_time         = 1.74587904[s]
X_angle            = 45[deg]
X_atn              = 4.1[dB]
X_pulse            = 6.75[us]
Irr_mode           = Off
Tri_mode           = Off
Dante_presat       = FALSE
Initial_wait       = 1[s]
Relaxation_delay   = 5[s]
Repetition_time    = 6.74587904[s]
Experiment         = single_pulse.ex2
Recvr_gain         = 38
Solvent            = CHLOROFORM-D
```



14 (2.6:1)

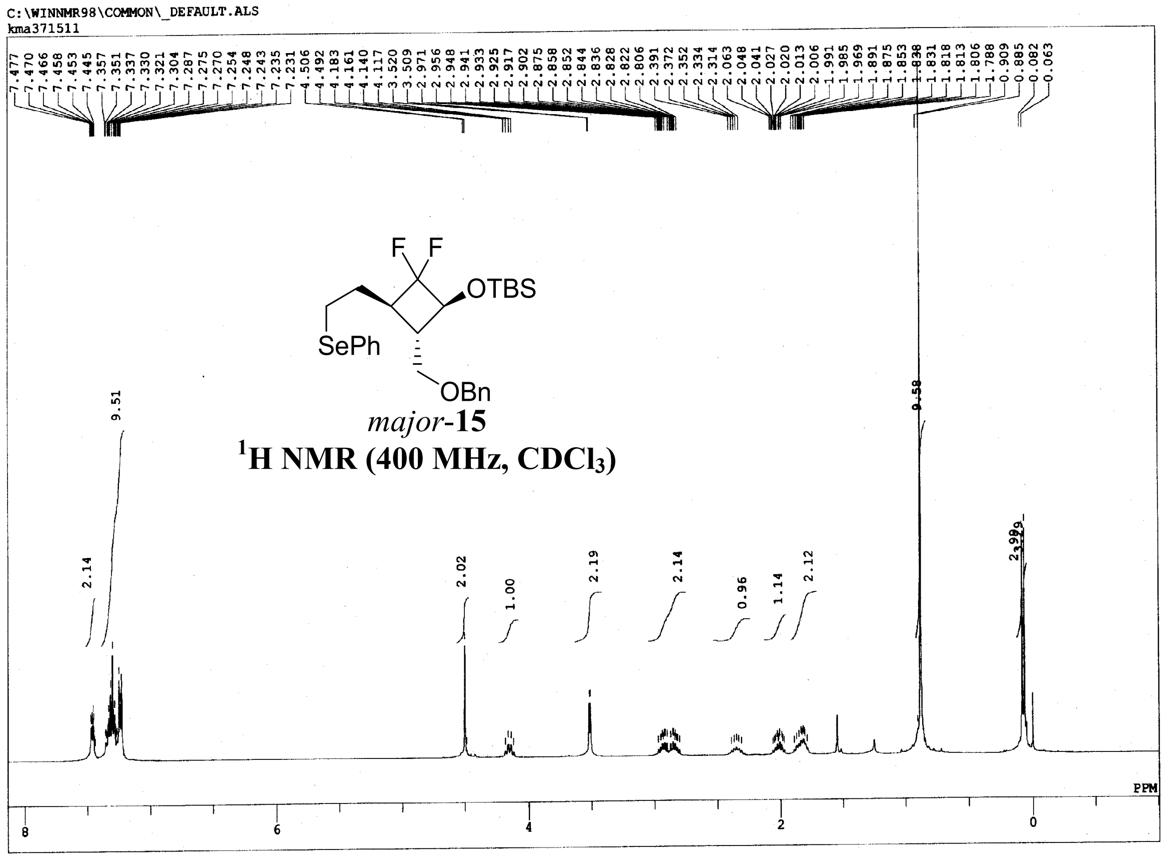
^{13}C NMR (125 MHz, CDCl$_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: wbs_HPLC3_c2.1
File Name          = wbs_HPLC3_c2.4
Author             = delta
Sample ID          = wbs_HPLC3
Content            = wbs_HPLC3_c
Creation Date      =  2-MAR-2011 20:20:41

Revision Date      =  3-MAR-2011 19:41:54
Spec Site          = ECA 500

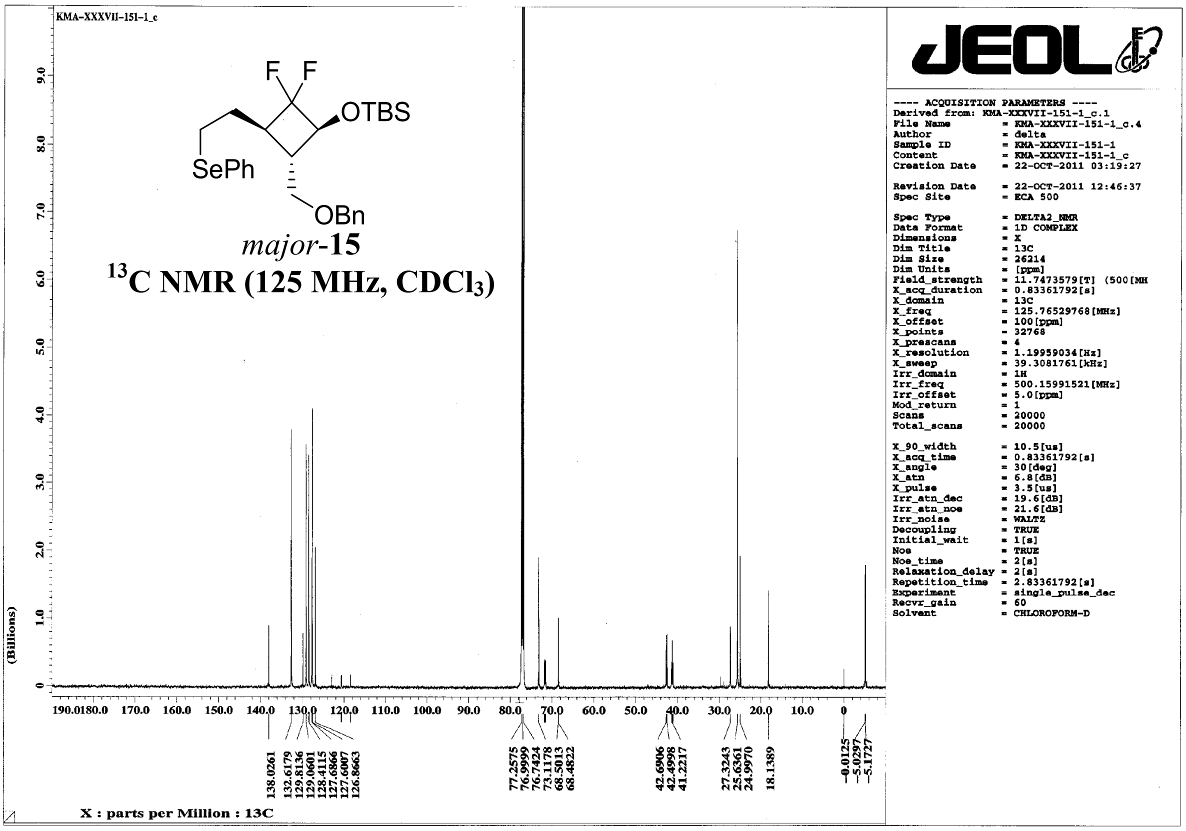
Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 5000
Total_scans        = 5000

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```



major-**15**

^{1}H NMR (400 MHz, CDCl$_3$)



major-**15**

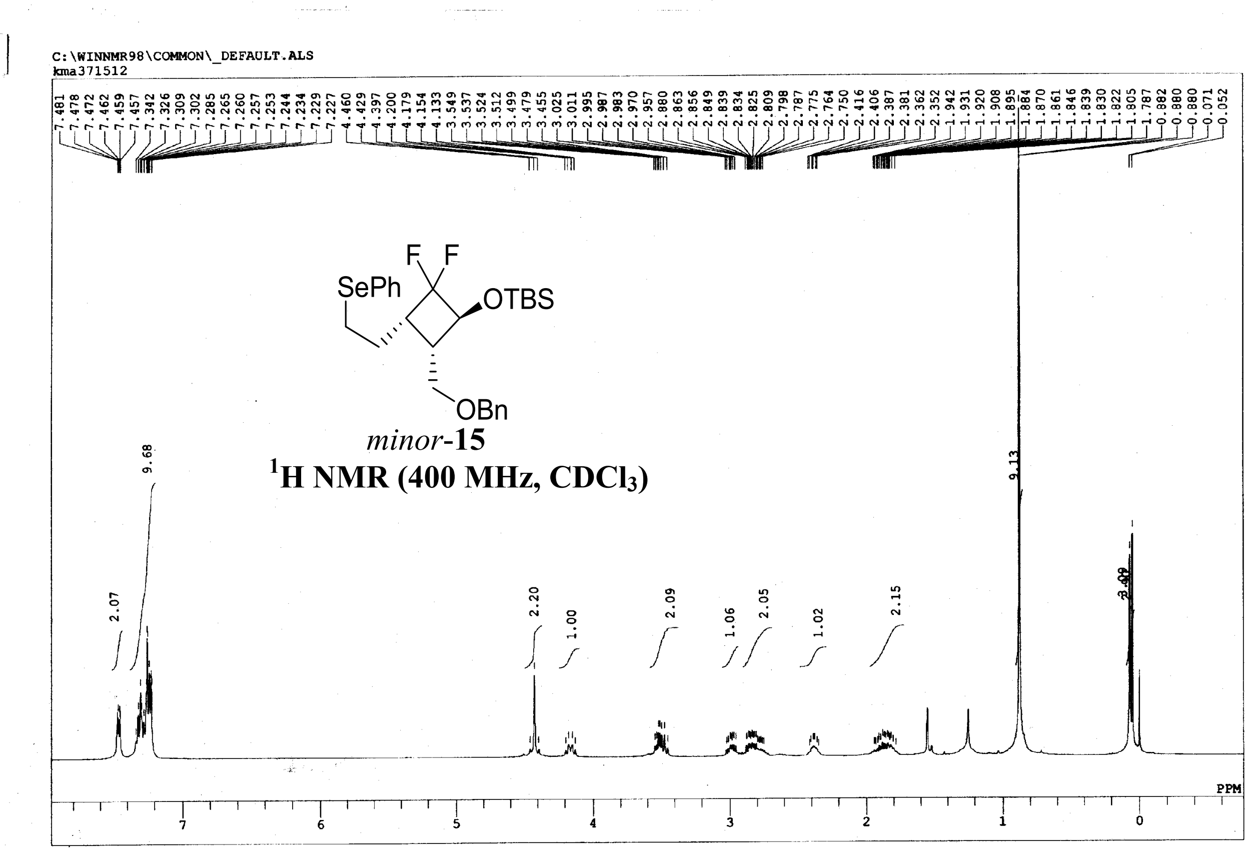
^{13}C NMR (125 MHz, CDCl$_3$)

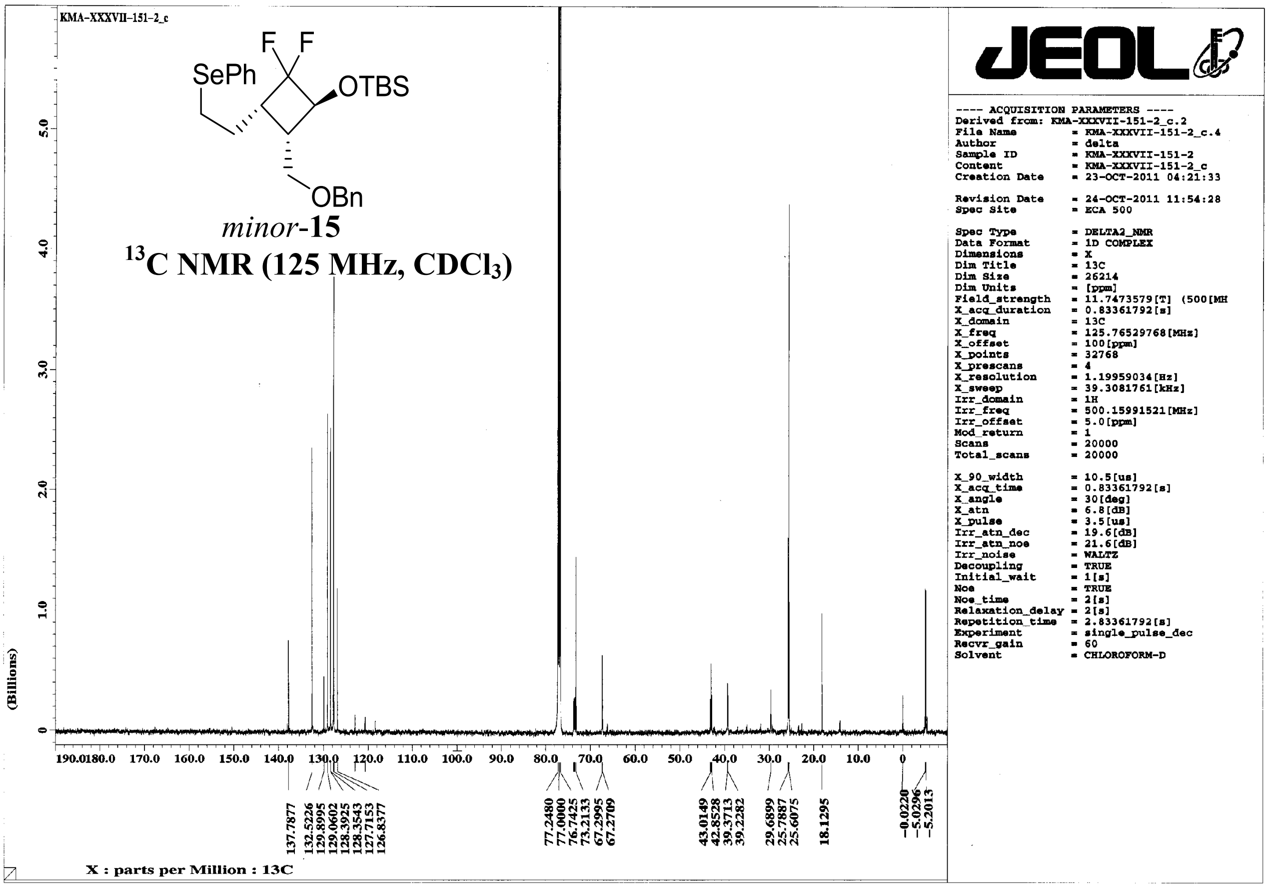
```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-151-1_c.1
File Name           = KMA-XXXVII-151-1_c.4
Author              = delta
Sample ID           = KMA-XXXVII-151-1
Content             = KMA-XXXVII-151-1_c
Creation Date       = 22-OCT-2011 03:19:27

Revision Date       = 22-OCT-2011 12:46:37
Spec Site           = ECA 500

Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 26214
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 0.83361792[s]
X_domain            = 13C
X_freq              = 125.76529768[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 1.19959034[Hz]
X_sweep             = 39.3081761[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 20000
Total_scans         = 20000

X_90_width          = 10.5[us]
X_acq_time          = 0.83361792[s]
X_angle             = 30[deg]
X_atn               = 6.8[dB]
X_pulse             = 3.5[us]
Irr_atn_dec         = 19.6[dB]
Irr_atn_noe         = 21.6[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Relaxation_delay    = 2[s]
Repetition_time     = 2.83361792[s]
Experiment          = single_pulse_dec
Recvr_gain          = 60
Solvent             = CHLOROFORM-D
```



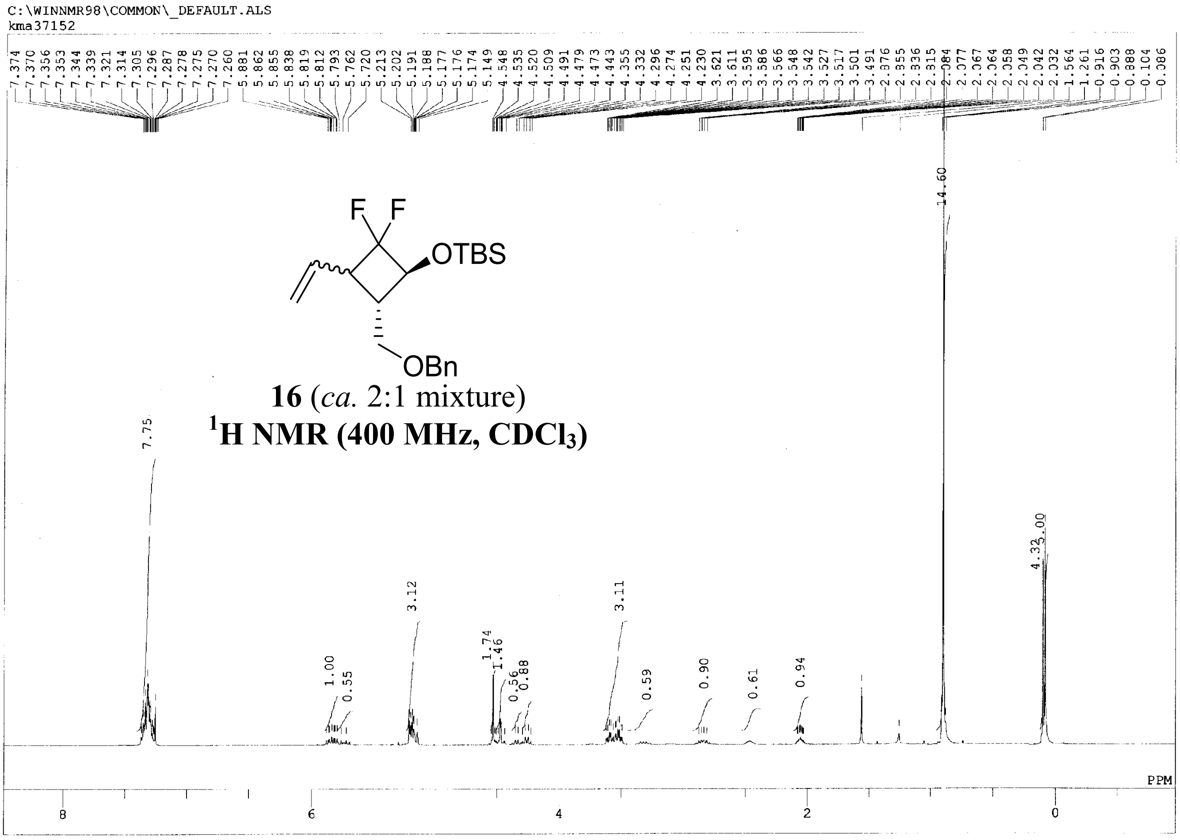


```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-151-2_c.2
File Name          = KMA-XXXVII-151-2_c.4
Author             = delta
Sample ID          = KMA-XXXVII-151-2
Content            = KMA-XXXVII-151-2_c
Creation Date      = 23-OCT-2011 04:21:33

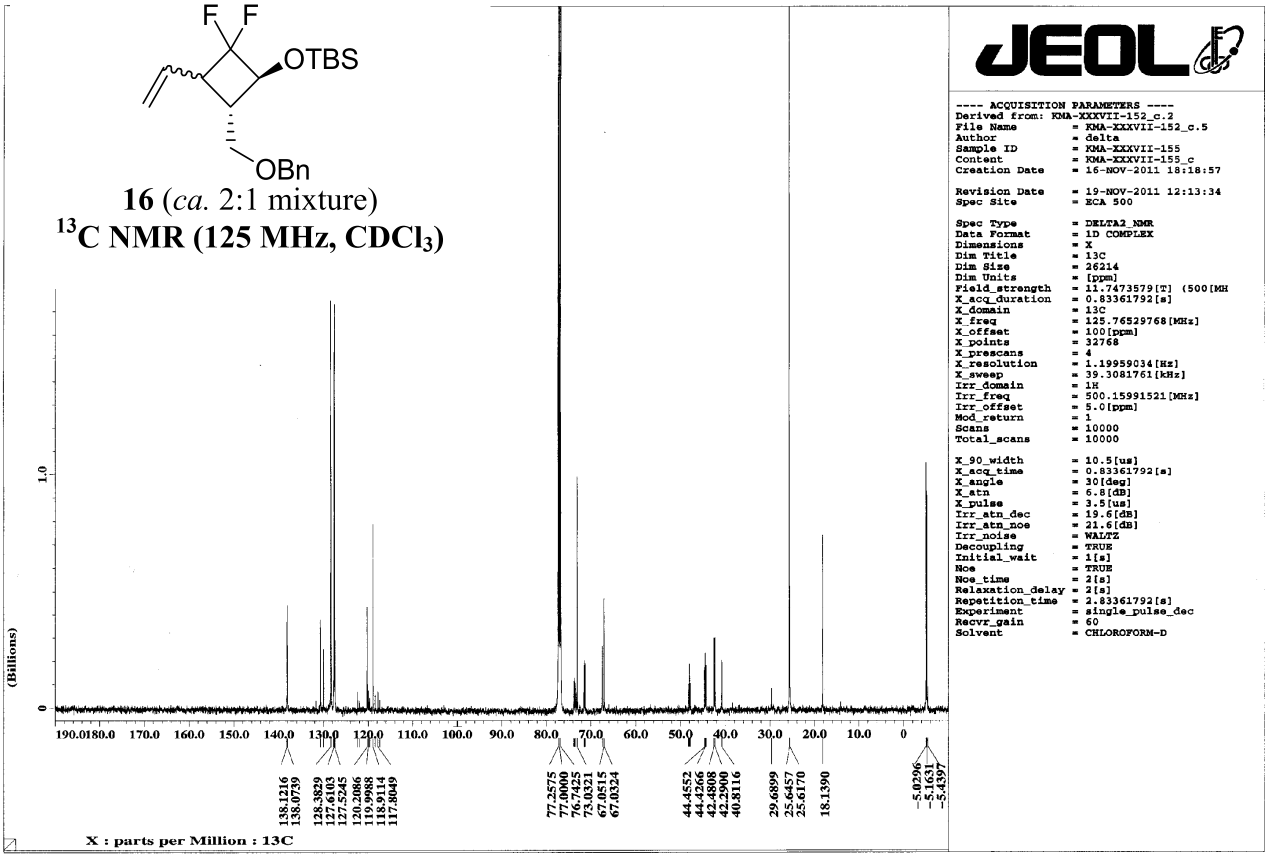
Revision Date      = 24-OCT-2011 11:54:28
Spec Site          = ECA 500

Spec Type          = DELTA2_NMR
Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 26214
Dim Units          = [ppm]
Field_strength     = 11.7473579[T] (500[MH
X_acq_duration     = 0.83361792[s]
X_domain           = 13C
X_freq             = 125.76529768[MHz]
X_offset           = 100[ppm]
X_points           = 32768
X_prescans         = 4
X_resolution       = 1.19959034[Hz]
X_sweep            = 39.3081761[kHz]
Irr_domain         = 1H
Irr_freq           = 500.15991521[MHz]
Irr_offset         = 5.0[ppm]
Mod_return         = 1
Scans              = 20000
Total_scans        = 20000

X_90_width         = 10.5[us]
X_acq_time         = 0.83361792[s]
X_angle            = 30[deg]
X_atn              = 6.8[dB]
X_pulse            = 3.5[us]
Irr_atn_dec        = 19.6[dB]
Irr_atn_noe        = 21.6[dB]
Irr_noise          = WALTZ
Decoupling         = TRUE
Initial_wait       = 1[s]
Noe                = TRUE
Noe_time           = 2[s]
Relaxation_delay   = 2[s]
Repetition_time    = 2.83361792[s]
Experiment         = single_pulse_dec
Recvr_gain         = 60
Solvent            = CHLOROFORM-D
```



16 (*ca.* 2:1 mixture)
^{1}H NMR (400 MHz, CDCl$_3$)



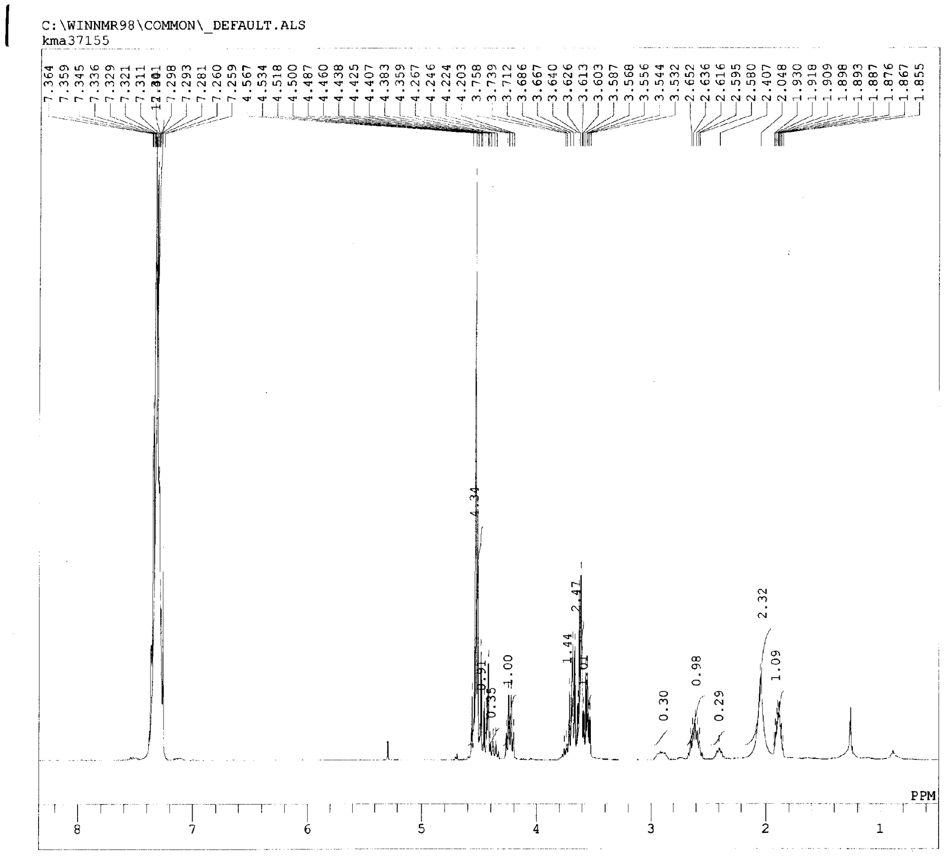
16 (*ca.* 2:1 mixture)
^{13}C NMR (125 MHz, CDCl$_3$)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-152_c.2
File Name         = KMA-XXXVII-152_c.5
Author            = delta
Sample ID         = KMA-XXXVII-155
Content           = KMA-XXXVII-155_c
Creation Date     = 16-NOV-2011 18:18:57

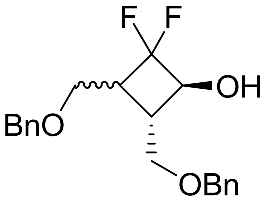
Revision Date     = 19-NOV-2011 12:13:34
Spec Site         = ECA 500

Spec Type         = DELTA2_NMR
Data Format       = 1D COMPLEX
Dimensions        = X
Dim Title         = 13C
Dim Size          = 26214
Dim Units         = [ppm]
Field_strength    = 11.7473579[T] (500[MH
X_acq_duration    = 0.83361792[s]
X_domain          = 13C
X_freq            = 125.76529768[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 1.19959034[Hz]
X_sweep           = 39.3081761[kHz]
Irr_domain        = 1H
Irr_freq          = 500.15991521[MHz]
Irr_offset        = 5.0[ppm]
Mod_return        = 1
Scans             = 10000
Total_scans       = 10000

X_90_width        = 10.5[us]
X_acq_time        = 0.83361792[s]
X_angle           = 30[deg]
X_atn             = 6.8[dB]
X_pulse           = 3.5[us]
Irr_atn_dec       = 19.6[dB]
Irr_atn_noe       = 21.6[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Relaxation_delay  = 2[s]
Repetition_time   = 2.83361792[s]
Experiment        = single_pulse_dec
Recvr_gain        = 60
Solvent           = CHLOROFORM-D
```

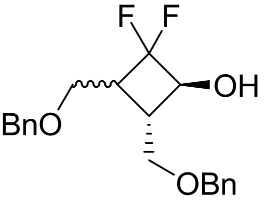


```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT  kma37155
DATIM  Tue Oct 11 08:31:26 2011
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7992.01 Hz
SCANS            40
ACQTM        4.1001 sec
PD           2.9000 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          23.4 c
SLVNT  CDCL3
EXREF          7.26 ppm
BF             0.12 Hz
RGAIN            15
```



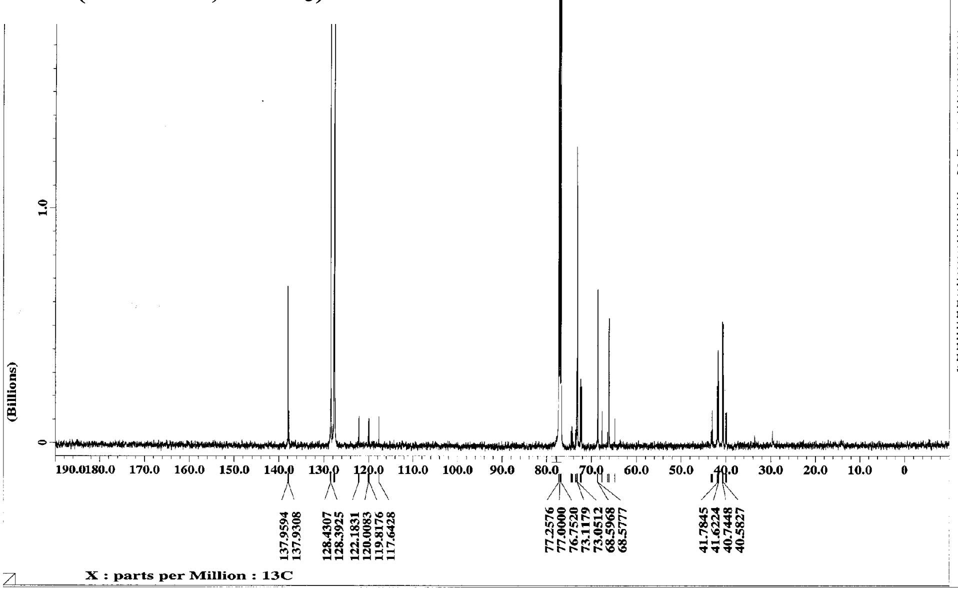
17 (*ca.* 3:1 mixture)

^{1}H NMR (400 MHz, CDCl$_3$)



17 (*ca.* 3:1 mixture)

^{13}C NMR (125 MHz, CDCl$_3$)



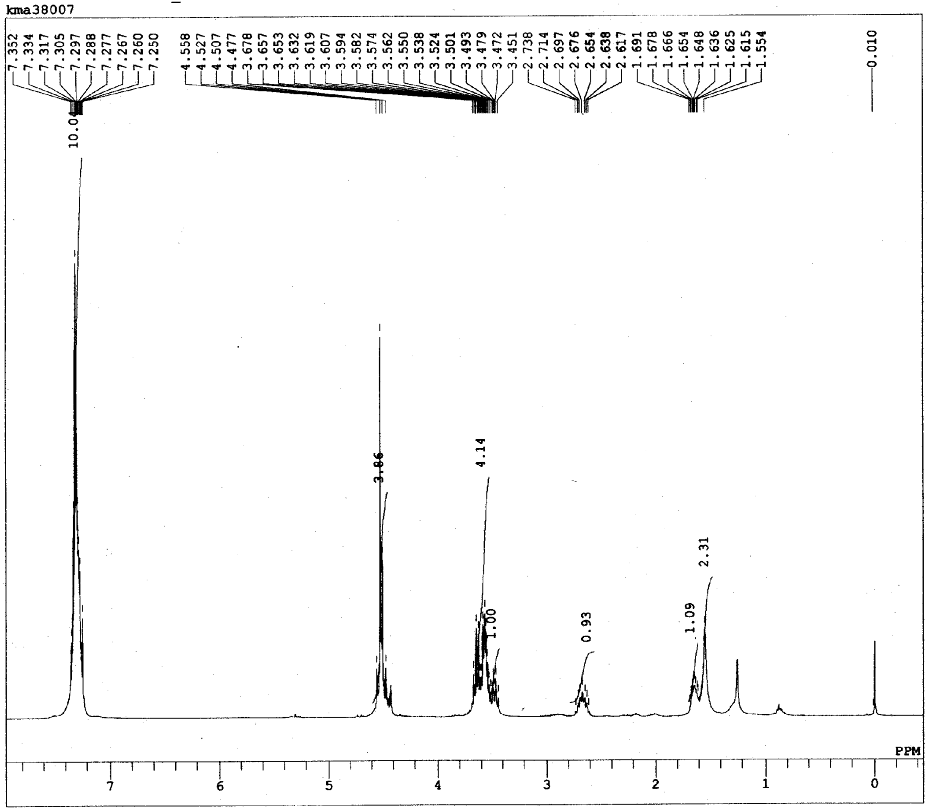
```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-155_c.1
File Name           = KMA-XXXVII-155_c.4
Author              = delta
Sample ID           = KMA-XXXVII-155
Content             = KMA-XXXVII-155_c
Creation Date       = 17-NOV-2011 18:21:18

Revision Date       = 19-NOV-2011 11:23:19
Spec Site           = ECA 500

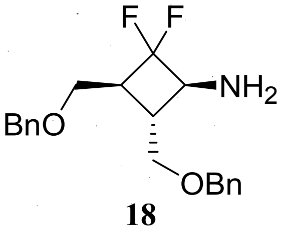
Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 26214
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 0.83361792[s]
X_domain            = 13C
X_freq              = 125.76529768[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 1.19959034[Hz]
X_sweep             = 39.3081761[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 10000
Total_scans         = 10000

X_90_width          = 10.5[us]
X_acq_time          = 0.83361792[s]
X_angle             = 30[deg]
X_atn               = 6.8[dB]
X_pulse             = 3.5[us]
Irr_atn_dec         = 19.6[dB]
Irr_atn_noe         = 21.6[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Relaxation_delay    = 2[s]
Repetition_time     = 2.83361792[s]
Experiment          = single_pulse_dec
Recvr_gain          = 60
Solvent             = CHLOROFORM-D
```

```
C:\WINNMR98\COMMON\_DEFAULT.ALS
kma38007
```

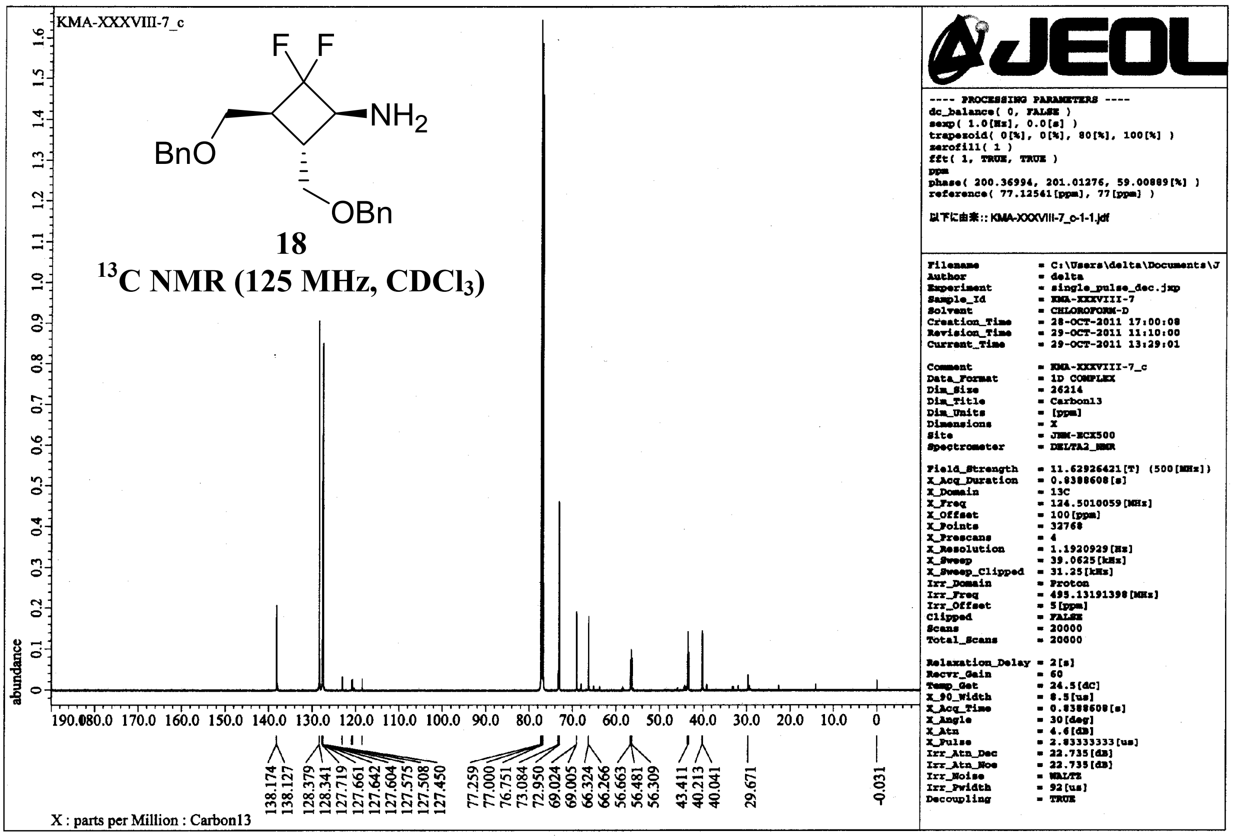


```
DFILE  C:\WINNMR98\COMMON\_DEFAULT.ALS
COMNT  kma38007
DATIM  Thu Oct 20 11:43:01 2011
OBNUC  1H
EXMOD  NON
OBFRQ        399.65 MHz
OBSET        124.00 KHz
OBFIN      10500.00 Hz
POINT         32768
FREQU       7992.01 Hz
SCANS            40
ACQTM        4.1001 sec
PD           2.9000 sec
PW1            5.80 usec
IRNUC  1H
CTEMP          24.5 c
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.12 Hz
RGAIN            12
```



18

^{1}H NMR (400 MHz, CDCl$_3$)



18

^{13}C NMR (125 MHz, CDCl$_3$)

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 1.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 200.36994, 201.01276, 59.00889[%] )
reference( 77.12541[ppm], 77[ppm] )

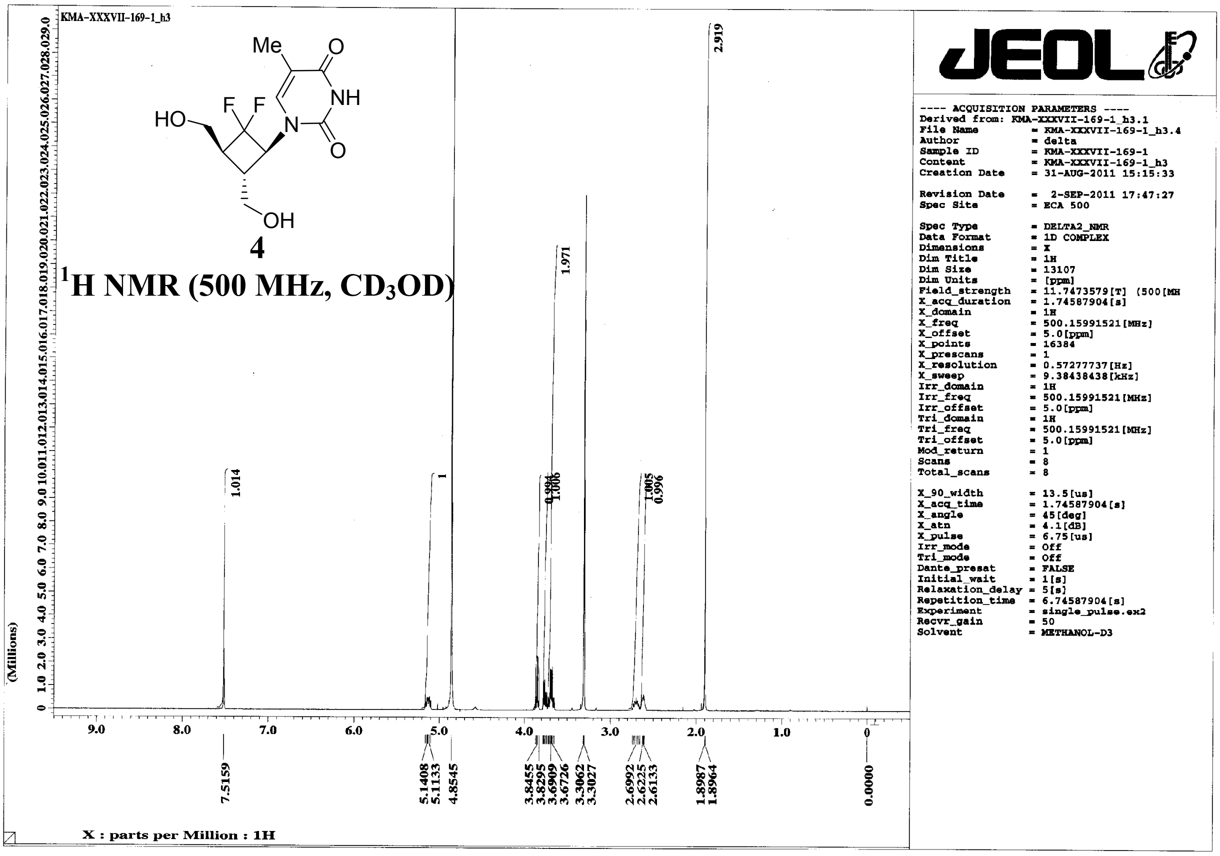
以下に由来:: KMA-XXXVIII-7_c-1-1.jdf
```

```
Filename          = C:\Users\delta\Documents\J
Author            = delta
Experiment        = single_pulse_dec.jxp
Sample_Id         = KMA-XXXVIII-7
Solvent           = CHLOROFORM-D
Creation_Time     = 28-OCT-2011 17:00:08
Revision_Time     = 29-OCT-2011 11:10:00
Current_Time      = 29-OCT-2011 13:29:01

Comment           = KMA-XXXVIII-7_c
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.62926421[T] (500[MHz])
X_Acq_Duration    = 0.8388608[s]
X_Domain          = 13C
X_Freq            = 124.5010059[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.1920929[Hz]
X_Sweep           = 39.0625[kHz]
X_Sweep_Clipped   = 31.25[kHz]
Irr_Domain        = Proton
Irr_Freq          = 495.13191398[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 20000
Total_Scans       = 20000

Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 24.5[dC]
X_90_Width        = 8.5[us]
X_Acq_Time        = 0.8388608[s]
X_Angle           = 30[deg]
X_Atn             = 4.6[dB]
X_Pulse           = 2.83333333[us]
Irr_Atn_Dec       = 22.735[dB]
Irr_Atn_Noe       = 22.735[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
```



4

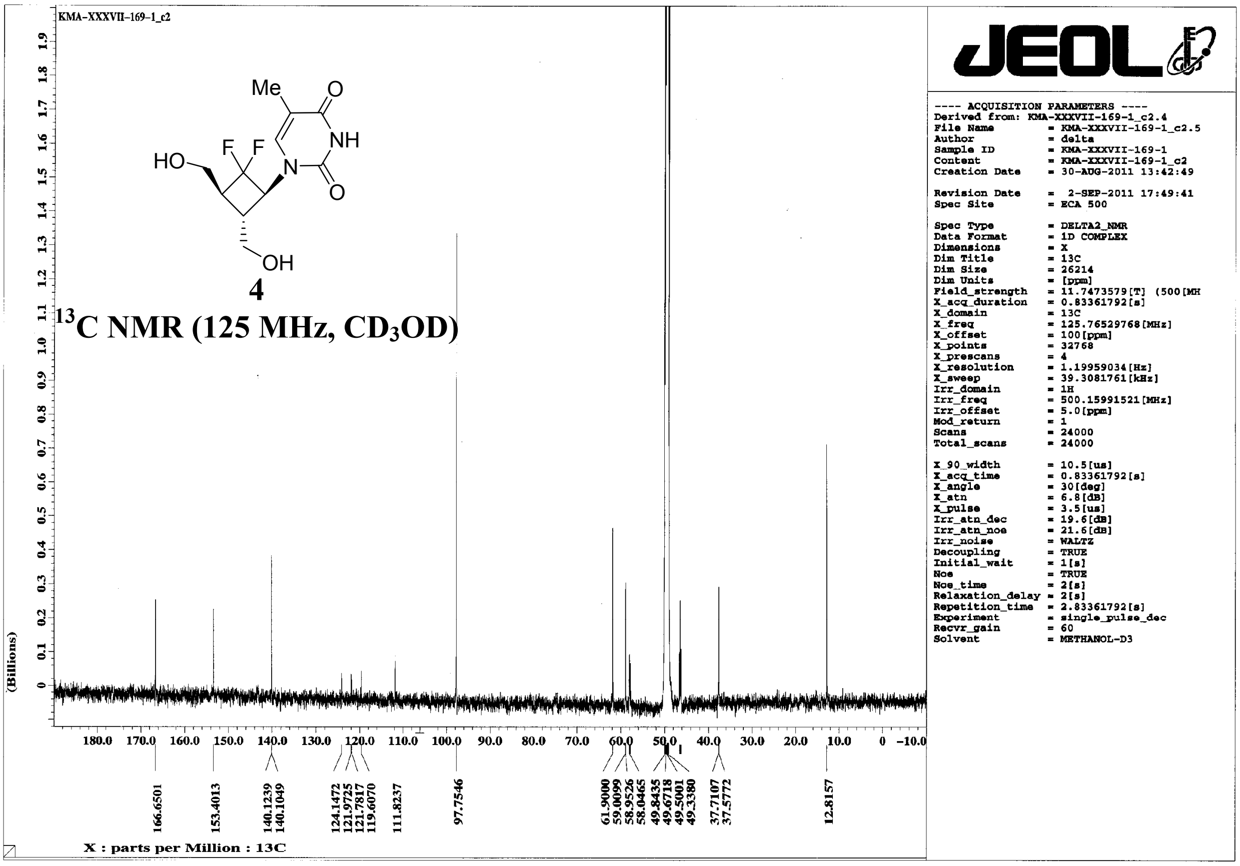
^{1}H NMR (500 MHz, CD$_3$OD)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-169-1_h3.1
File Name           = KMA-XXXVII-169-1_h3.4
Author              = delta
Sample ID           = KMA-XXXVII-169-1
Content             = KMA-XXXVII-169-1_h3
Creation Date       = 31-AUG-2011 15:15:33

Revision Date       =  2-SEP-2011 17:47:27
Spec Site           = ECA 500

Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 13107
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 1.74587904[s]
X_domain            = 1H
X_freq              = 500.15991521[MHz]
X_offset            = 5.0[ppm]
X_points            = 16384
X_prescans          = 1
X_resolution        = 0.57277737[Hz]
X_sweep             = 9.38438438[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Tri_domain          = 1H
Tri_freq            = 500.15991521[MHz]
Tri_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 8
Total_scans         = 8

X_90_width          = 13.5[us]
X_acq_time          = 1.74587904[s]
X_angle             = 45[deg]
X_atn               = 4.1[dB]
X_pulse             = 6.75[us]
Irr_mode            = Off
Tri_mode            = Off
Dante_presat        = FALSE
Initial_wait        = 1[s]
Relaxation_delay    = 5[s]
Repetition_time     = 6.74587904[s]
Experiment          = single_pulse.ex2
Recvr_gain          = 50
Solvent             = METHANOL-D3
```



4

^{13}C NMR (125 MHz, CD$_3$OD)

```
---- ACQUISITION PARAMETERS ----
Derived from: KMA-XXXVII-169-1_c2.4
File Name           = KMA-XXXVII-169-1_c2.5
Author              = delta
Sample ID           = KMA-XXXVII-169-1
Content             = KMA-XXXVII-169-1_c2
Creation Date       = 30-AUG-2011 13:42:49

Revision Date       =  2-SEP-2011 17:49:41
Spec Site           = ECA 500

Spec Type           = DELTA2_NMR
Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 26214
Dim Units           = [ppm]
Field_strength      = 11.7473579[T] (500[MH
X_acq_duration      = 0.83361792[s]
X_domain            = 13C
X_freq              = 125.76529768[MHz]
X_offset            = 100[ppm]
X_points            = 32768
X_prescans          = 4
X_resolution        = 1.19959034[Hz]
X_sweep             = 39.3081761[kHz]
Irr_domain          = 1H
Irr_freq            = 500.15991521[MHz]
Irr_offset          = 5.0[ppm]
Mod_return          = 1
Scans               = 24000
Total_scans         = 24000

X_90_width          = 10.5[us]
X_acq_time          = 0.83361792[s]
X_angle             = 30[deg]
X_atn               = 6.8[dB]
X_pulse             = 3.5[us]
Irr_atn_dec         = 19.6[dB]
Irr_atn_noe         = 21.6[dB]
Irr_noise           = WALTZ
Decoupling          = TRUE
Initial_wait        = 1[s]
Noe                 = TRUE
Noe_time            = 2[s]
Relaxation_delay    = 2[s]
Repetition_time     = 2.83361792[s]
Experiment          = single_pulse_dec
Recvr_gain          = 60
Solvent             = METHANOL-D3
```