

## Supporting Information

# $\alpha$ -Fluorovinyl Weinreb Amides and $\alpha$ -Fluoroenones from a Common Fluorinated Building Block

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## GENERAL EXPERIMENTAL METHODS

THF was distilled over LiAlH<sub>4</sub> and then over sodium, CH<sub>2</sub>Cl<sub>2</sub> was distilled over CaCl<sub>2</sub> and toluene over sodium. DMF, DMPU and CH<sub>3</sub>CN were obtained from commercial sources and were used without further purification. For reactions that were performed under a nitrogen atmosphere, glassware was flame dried under vacuum. Dry sodium hydride (95%) was used for the reactions, fluorinating reagent NFSI was obtained from Honeywell (NFSI is also commercially available). All other reagents were obtained from commercial sources and used without further purification. Thin layer chromatography was performed on 250 μm silica plates and column chromatographic purifications were performed on 200-300 mesh silica gel. <sup>1</sup>H NMR spectra were recorded at 500 MHz in CDCl<sub>3</sub> and were referenced to residual CHCl<sub>3</sub> or to tetramethylsilane (TMS). <sup>13</sup>C NMR spectra were recorded at 125 MHz or at 75 MHz and were referenced to CDCl<sub>3</sub>. <sup>19</sup>F NMR spectra were recorded at 282 MHz using CFCI<sub>3</sub> as internal standard. Chemical shifts (δ) are reported in parts per million and coupling constants (J) are in hertz.

***N*-Methoxy-*N*-methyl-(1,3-benzothiazol-2-ylsulfanyl)acetamide (1).**<sup>1</sup> **Step 1. Synthesis of 2-Bromo-*N*-methoxy-*N*-methylacetamide.**<sup>2</sup> To a stirring mixture of *N*,*O*-dimethylhydroxylamine hydrochloride (6.00 g, 61.5 mmol, 1 molar equiv) and bromoacetyl bromide (13.66 g, 67.7 mmol, 1.1 molar equiv) in distilled CH<sub>2</sub>Cl<sub>2</sub> (154 mL) was added NEt<sub>3</sub> (19.0 mL, 13.7 g, 135 mmol, 2.2 molar equiv) at rt, and the reaction mixture was allowed to stir in an open reaction flask for 1 h at rt. Water was added to the reaction mixture and the layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were washed with 1N HCl, sat aq NaHCO<sub>3</sub>, water and brine. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated to yield 7.60 g of dark oily product that was subjected to the next step without further purification. Crude product: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 4.24, 4.00 (2 br s, 2H, CH<sub>2</sub>), 3.78, 3.74 (2 s, 3H, OCH<sub>3</sub>), 3.23 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 167.89, 61.83, 40.97, 32.71, 25.30. **Step 2.** To a stirring solution of crude 2-bromo-*N*-methoxy-*N*-methylacetamide (7.60 g, obtained in step 1) in DMF (175 mL), was added the sodium salt of 2-mercapto-1,3-benzothiazole (9.53 g, 50.4 mmol, 1.2 molar equiv) at rt. The reaction mixture was allowed to stir at rt for 4 h, water and EtOAc were added, the layers were separated and the aqueous layer was extracted with EtOAc (3 x). The combined organic layers were thoroughly washed with water and brine, dried over anhydrous

Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated in vacuo. The crude product was purified by column chromatography (SiO<sub>2</sub>, 20% EtOAc in hexanes, followed by 50% EtOAc in hexanes after elution of an impurity) to yield **1** as a yellow solid (10.1 g, 61% over two steps). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.83 (d, 1H, Ar-H, *J* = 8.3), 7.74 (d, 1H, Ar-H *J* = 7.8), 7.40 (t, 1H, Ar-H, *J* = 7.3), 7.29 (t, 1H, Ar-H, *J* = 7.0), 4.43 (s, 2H), 3.84 (s, 3H), 3.26 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 168.2, 165.6, 152.9, 135.5, 125.9, 124.3, 121.5, 121.0, 61.5, 34.9, 32.6.

***N*-Methoxy-*N*-methyl-(1,3-benzothiazol-2-ylsulfonyl)acetamide (**2**).**<sup>1</sup> To a vigorously stirred solution of **1** (2.50 g, 9.33 mmol, 1 molar equiv) in CHCl<sub>3</sub> (30.0 mL) at -10 °C (ice-salt cooling) a solution of *m*-CPBA (4.80 g, 28.0 mmol, 3 molar equiv) in CHCl<sub>3</sub> (90.0 mL) was added dropwise. After complete addition the mixture was stirred for an additional 5 min at -10 °C, allowed to warm to rt and stirred at rt overnight. The mixture was then poured into sat aq NaHCO<sub>3</sub> (150 mL) and vigorously stirred for 15 min. After layer separation, the aqueous layer was extracted with CHCl<sub>3</sub> (3 x), and the combined organic layer was washed with sat aq NaHCO<sub>3</sub>, water and brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO<sub>2</sub>, 30% EtOAc in hexanes, followed by 80% EtOAc in hexanes once product started eluting) to yield **2** as a white solid (2.48 g, 89%). Mp (sample recrystallized from EtOAc) 132.5–133 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.22 (d, 1H, Ar-H, *J* = 8.0), 8.00 (d, 1H, Ar-H, *J* = 8.0), 7.63 (td, 1H, *J* = 7.7; 1.3), 7.58 (td, 1H, *J* = 7.7; 1.1), 4.79 (s, 2H), 3.81 (s, 3H), 3.19 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 125.5, 161.4, 152.5, 137.1, 128.1, 127.6, 125.5, 122.4, 62.0, 56.3, 32.1.

### **General Procedures for Synthesis of 4-7 via DBU-Mediated Condensations of Aldehydes with *N*-Methoxy-*N*-methyl-(1,3-benzothiazol-2-ylsulfonyl)fluoroacetamide **3**.**

#### **Method A**

To a stirred solution of the aldehyde (1 molar equiv) and sulfone **3** (1.4 molar equiv) in dry THF (7.8 mL per mmol of aldehyde) at -78 °C was added a cooled (-75 °C) solution of DBU (4.0 molar equiv) in dry THF (7.8 mL per mmol of aldehyde). The reaction mixture was allowed to stir at -78 °C until complete consumption of aldehyde was observed by TLC (2.5-4.0 h), sat aq NH<sub>4</sub>Cl was added, the reaction mixture was brought to rt and extracted with Et<sub>2</sub>O (3 x). The combined organic layer was washed with 1N NaOH, water and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure and the *E/Z* ratio was analyzed by <sup>19</sup>F NMR. The crude product was purified by column chromatography (SiO<sub>2</sub>, 20% EtOAc in

hexanes). The yield of combined *E/Z* product mixture, the *E/Z* ratio, reaction time and  $^{19}\text{F}$  NMR data are shown in Table 2 of the manuscript. Condensation with *p*-nitrobenzaldehyde is shown as representative procedure in the Experimental Section of the manuscript.

### Method B

To a stirred solution of aldehyde (1.3 molar equiv) and **3** (1.0 molar equiv) in DMPU (7.8 mL per mmol of **3**) at rt was added solution of DBU (2 molar equiv) in DMPU (7.8 mL per mmol of **3**) dropwise. The reaction mixture was allowed to stir overnight until complete consumption of **3** was observed by TLC (16-17 h). The reaction was quenched with sat aq  $\text{NH}_4\text{Cl}$ , the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x), the combined organic layer was washed with 1N NaOH, water and brine, and then dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure and the *E/Z* ratio was analyzed by  $^{19}\text{F}$  NMR. The crude product was purified by column chromatography ( $\text{SiO}_2$ , 20% EtOAc in hexanes). The yield of the combined *E/Z* product mixture, the *E/Z* ratio, reaction time and  $^{19}\text{F}$  NMR data are shown in Table 2 of the manuscript. Condensation with 2-thiophenecarboxaldehyde is shown as representative procedure in the Experimental Section of the manuscript.

### General Procedure for Synthesis of 4–12 via NaH-Mediated Condensations of Carbonyl Compounds with Fluoro Sulfone **3** (Method C).

A suspension of NaH (4 molar equiv) and **3** (2 molar equiv) in dry THF (5.7 mL per mmol of **3**) was stirred at rt under a nitrogen atmosphere for 2 min. A solution of aldehyde (1 molar equiv) in dry THF (4.7 mL per mmol of aldehyde) was added dropwise. The reaction mixture was allowed to stir at rt for 1.5 h and then quenched with sat aq  $\text{NH}_4\text{Cl}$ . The mixture was extracted with  $\text{Et}_2\text{O}$  (3 x), the combined organic layers were washed with 1N NaOH, water and brine, dried over  $\text{Na}_2\text{SO}_4$ , and the product *E/Z* ratio was analyzed by  $^{19}\text{F}$  NMR. The crude product was purified by column chromatography ( $\text{SiO}_2$ , 20% EtOAc in hexanes), except in the case of **9**, where additional purification was required ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ). The yield, *E/Z* ratio and  $^{19}\text{F}$  NMR data are shown in Table 3 of the manuscript. In the case of *N*-benzylpiperidone, molar ratio of NaH, **3** and ketone was 2:1:2.5, respectively. Condensation with *p*-methoxybenzaldehyde is shown as representative procedure in the Experimental Section of the manuscript.

**(Z)-2-Fluoro-N-methoxy-N-methyl-3-(2-naphthyl)propenamide (4)**.<sup>3</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07(s, 1H, Ar-H), 7.86–7.75(m, 4H, Ar-H), 7.52–7.48 (m, 2H, Ar-H), 6.88 (d, 1H,  $^3J_{\text{FH}}$  = 37.1), 3.83 (s, 3H), 3.32 (s, 3H). HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{14}\text{FNO}_2\text{Na}$  [ $\text{M} + \text{Na}$ ]<sup>+</sup> 282.0900, found 282.0897.

**(Z)-2-Fluoro-N-methoxy-N-methyl-3-(2-methylphenyl)propenamide (9).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.78-7.76 (m, 1H, Ar-H), 7.29-7.25 (m, 3H, Ar-H), 6.92 (d, 1H,  $^3J_{\text{FH}} = 36.3$ ), 3.82 (s, 3H), 3.32 (s, 3H), 2.40 (s, 3H). HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{14}\text{FNO}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  246.0900, found 246.0892.

**(Z)-2-Fluoro-N-methoxy-N-methyl-3-(2-thienyl)propenamide (6).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (d, 1H, Ar-H,  $J = 4.9$ ), 7.29 (d, 1H, Ar-H,  $J = 3.4$ ), 7.13-7.06 (m, 2H, Ar-H overlapping with =CH), 3.80 (s, 3H), 3.29 (s, 3H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -119.7 (d,  $^2J_{\text{FH}} = 33.6$ ).

**(Z)-3-Ferrocenyl-2-fluoro-N-methoxy-N-methyl-propenamide (10).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.65 (d, 1H,  $^3J_{\text{FH}} = 36.9$ ), 4.58 (s, 2H, Cp-H), 4.36 (s, 2H, Cp-H), 4.16 (s, 5H, Cp-H), 3.78 (s, 3H), 3.26 (s, 3H). HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{16}\text{FeNO}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  340.0406, found 340.0405.

**(Z)-2-Fluoro-N-methoxy-N-methyl-2-decenamide (7).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.85 (dt, 1H,  $J = 35.4; 7.7$ ), 3.72 (s, 3H), 3.22 (s, 3H), 2.21 (br qd, 2H,  $J = 7.4; 1.6$ ), 1.45-1.40 (m, 2H), 1.30-1.26 (m, 8H), 0.87 (t, 3H,  $J = 7.0$ ). HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{22}\text{FNO}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  254.1526, found 254.1521.

**(Z)-4-Ethyl-2-fluoro-N-methoxy-N-methyl-2-hexenamide (11).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.61 (dd, 1H,  $J = 35.5; 10.5$ ), 3.72 (s, 3H), 3.23 (s, 3H), 2.47-2.39 (m, 1H), 1.55-1.47 (m, 2H), 1.33-1.24 (m, 2H), 0.87 (t, 6H,  $J = 7.3$ ). HRMS (ESI) calcd. for  $\text{C}_{10}\text{H}_{18}\text{FNO}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  226.1213, found 226.1210.

### **Representative Procedures for Condensations of Aldehydes with (1,3-Benzothiazol-2-ylsulfonyl)fluoromethyl Phenyl Ketone 16.**

**Synthesis of (Z)-2-Fluoro-3-(4-nitrophenyl)-1-phenyl-2-propen-1-one (20a).** To a refluxing solution of *p*-nitrobenzaldehyde (30.8 mg, 0.204 mmol, 1 molar equiv) and DBU (93.1 mg, 0.612 mmol, 3 molar equiv) in THF (5.6 mL) was added a solution of sulfone **16** (137 mg, 0.408 mmol, 2 molar equiv) in THF (1.8 mL) dropwise. After ca 15 min, TLC ( $\text{SiO}_2$ , 20% EtOAc in hexanes) showed presence of both, **16** and unreacted *p*-nitrobenzaldehyde. An additional 1 molar equiv of DBU (32.1 mg, 0.211 mmol) in THF (0.4 mL) was added and the stirring was continued at reflux for another 15 min. Complete consumption of aldehyde was observed by TLC, the reaction mixture was quenched with sat aq  $\text{NH}_4\text{Cl}$  (30 mL) and extracted with EtOAc (3 x 30 mL). The organic layer was washed with sat aq  $\text{NaHCO}_3$  (30 mL), brine (30 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic layer was concentrated and the crude product was purified by column chromatography ( $\text{SiO}_2$ , 10% EtOAc in hexanes) to afford **20a** (44.7 mg, 81%) as a

yellowish solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28 (d, 2H, Ar-H,  $J = 8.8$ ), 7.93 (d, 2H, Ar-H,  $J = 7.8$ ), 7.86 (d, 2H, Ar-H,  $J = 8.8$ ), 7.65 (t, 1H, Ar-H,  $J = 7.4$ ), 7.53 (t, 2H, Ar-H,  $J = 7.8$ ), 6.93 (d, 1H,  $^3J_{\text{HF}} = 35.5$ ).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -114.1 (d,  $^3J_{\text{FH}} = 33.6$ ). HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{10}\text{FNO}_3\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  294.0536, observed 294.0530.

**Synthesis of (Z)-2-Fluoro-1-phenyl-3-(2-thienyl)-2-propen-1-one (21a).** To a refluxing solution of thiophene-2-carboxaldehyde (56.1 mg, 0.500 mmol, 1 molar equiv) and DBU (228 mg, 1.50 mmol, 3 molar equiv) in THF (14.0 mL) was added a solution of sulfone **16** (335 mg, 1.00 mmol, 1.5 molar equiv) in THF (4.5 mL) dropwise. Upon addition, the color of the reaction mixture turned dark yellow. After ca 15 min, TLC ( $\text{SiO}_2$ , 20% EtOAc in hexanes) showed a complete consumption of **16** and unreacted starting thiophene-2-carboxaldehyde. An additional 1 molar equiv each of solid **16** (168 mg, 0.50 mmol) and DBU (76.1 mg, 0.500 mmol) in THF (1.00 mL) were added and the stirring was continued at reflux for another 15 min. Since TLC showed small amount of unreacted aldehyde, 1 molar equiv of solid **16** (168 mg, 0.50 mmol) was again added and after additional 10 min of reflux complete consumption of aldehyde was observed by TLC. The reaction mixture was quenched with sat aq  $\text{NH}_4\text{Cl}$  (30 mL) and extracted with EtOAc (3 x 30 mL). The organic layer was washed with sat aq  $\text{NaHCO}_3$  (30 mL), brine (30 mL), and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic layer was concentrated and the crude product was purified by column chromatography ( $\text{SiO}_2$ , 5% EtOAc in hexanes) to afford **21a** (82.3 mg, 71%) as a clear liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d, 2H, Ar-H,  $J = 7.8$ ), 7.57-7.63 (m, 2H, Ar-H), 7.50 (t, 2H, Ar-H,  $J = 7.4$ ), 7.42 (d, 1H, Ar-H,  $J = 2.8$ ), 7.21 (d, 1H,  $^3J_{\text{HF}} = 35.0$ ), 7.13 (br s, 1H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -118.9 (d,  $^3J_{\text{HF}} = 33.6$ ). HRMS (ESI) calcd. for  $\text{C}_{13}\text{H}_9\text{FOSNa}$  [ $\text{M} + \text{Na}$ ] $^+$  255.0250, found 255.0246.

**(Z)-2-Fluoro-3-(4-methoxyphenyl)-1-phenyl-2-propen-1-one (18a).**<sup>4</sup> Total amount of **16**: 3 molar equiv; DBU: 4 molar equiv; TLC:  $\text{SiO}_2$ , 15% EtOAc in hexanes; column chromatography:  $\text{SiO}_2$ , 4% EtOAc in hexanes; yield of **18a**: 61% (yellowish solid).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.86 (d, 2H, Ar-H,  $J = 7.6$ ), 7.67 (d, 2H, Ar-H,  $J = 8.9$ ), 7.59 (t, 1H, Ar-H,  $J = 7.3$ ), 7.49 (t, 2H, Ar-H,  $J = 7.6$ ), 6.95 (d, 2H, Ar-H,  $J = 8.9$ ), 6.83 (d, 1H,  $^3J_{\text{HF}} = 36.6$ ), 3.86 (s, 3H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -123.4 (d,  $^3J_{\text{HF}} = 36.6$ ). HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{13}\text{FO}_2\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  279.0792, observed 279.0783.

**(Z)-2-Fluoro-3-(2-methoxyphenyl)-1-phenyl-2-propen-1-one (19a).** Total amount of **16**: 4 molar equiv; DBU: 6 molar equiv; TLC:  $\text{SiO}_2$ , 20% EtOAc in hexanes; column chromatography:  $\text{SiO}_2$ , 10% EtOAc in hexanes; yield of **19a**: 64% (colorless liquid).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (dd, 1H, Ar-H,  $J = 7.9, 1.2$ ), 7.89 (d, 2H, Ar-H,  $J = 7.9$ ), 7.60 (t, 1H, Ar-H,  $J = 7.6$ ), 7.48 (t, 2H, Ar-H,  $J = 7.6$ ), 7.42-7.34 (m, 2H), 7.03 (t, 1H, Ar-H,  $J = 7.6$ ), 6.92 (d, 1H, Ar-H,  $J = 8.2$ ), 3.84

(s, 3H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -121.8 (d,  $^3J_{\text{HF}} = 36.6$ ). HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{13}\text{FO}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  279.0792, observed 279.0787.

**Representative Procedures for Condensations of Aldehydes with (1,3-Benzothiazol-2-ylsulfonyl)fluoromethyl *n*-Propyl Ketone (17).**

**Synthesis of (Z)-2-Fluoro-1-(4-nitrophenyl)-1-hexen-3-one (20b).** A solution of *p*-nitrobenzaldehyde (75.0 mg, 0.500 mmol, 1 molar equiv) and DBU (454 mg, 2.98 mmol, 6 molar equiv) in THF (15.0 mL) was cooled to 0 °C. A solution of **17** (299 mg, 0.992 mmol, 2 molar equiv) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added *slowly, dropwise* over 2 h to the reaction mixture. The reaction mixture was allowed to stir at 0 °C for an additional 6 h, at which time complete consumption of aldehyde was observed by TLC ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ). Sat aq  $\text{NH}_4\text{Cl}$  was added to the reaction mixture and the mixture was extracted with EtOAc (2 x 20 mL). The combined organic layer was washed with water, brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated. The crude product was purified by column chromatography ( $\text{SiO}_2$ , 5% EtOAc in hexanes) to afford **20b** as a yellow solid (101 mg, 86%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.26 (d, 2H, Ar-H,  $J = 8.5$ ), 7.81 (d, 2H, Ar-H,  $J = 8.8$ ), 6.86 (d, 1H,  $^3J_{\text{FH}} = 35.7$ ), 2.75 (dt, 2H,  $J = 7.3$ , 2.2), 1.73 (sext, 2H,  $J = 7.3$ ), 1.01 (t, 3H,  $J = 7.3$ ).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  -120.9 (d,  $^3J_{\text{FH}} = 36.6$ ). HRMS (ESI) calcd. for  $\text{C}_{12}\text{H}_{12}\text{FNO}_3\text{Na}$   $[\text{M} + \text{Na}]^+$  260.0693, found 260.0681.

**Synthesis of (Z)-5-Fluoro-8-phenyl-5-octen-4-one (23b).**<sup>5</sup> A solution of 3-phenylpropanal (70.0 mg, 0.522 mmol, 1 molar equiv) and DBU (477 mg, 3.13 mmol, 6 molar equiv) in THF (14.5 mL) was cooled to 0 °C. A solution of **17** (236 mg, 0.783 mmol, 2 molar equiv) in  $\text{CH}_2\text{Cl}_2$  (15.0 mL) was added *slowly, dropwise* over 1 h to the reaction mixture. The reaction mixture was allowed to stir at 0 °C for an additional 2 h, at which time complete consumption of aldehyde was observed by TLC ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ). Sat aq  $\text{NH}_4\text{Cl}$  was added to the reaction mixture and the mixture was extracted with EtOAc (2 x 20 mL). The combined organic layer was washed with water, brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated. The crude product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) to afford **23b** as yellow oil (84.0 mg, 73%).

**(Z)-2-Fluoro-1-(4-methoxyphenyl)-1-hexen-3-one (18b).**<sup>5</sup> Total amount of **22**: 3 molar equiv; reaction time: 16 h. Crude product was purified by column chromatography ( $\text{SiO}_2$ , 2.5% EtOAc in hexanes) to yield **18b** as an off white solid (90%).

**(Z)-2-Fluoro-1-(1-benzofuran-5-yl)-1-hexen-3-one (22b).** Total amount of **17**: 3 molar equiv; reaction time: 8 h. Crude product was purified by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) to yield **22b** as an off white solid (90%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.96 (s, 1H, Ar-H), 7.65 (d, 1H, Ar-H,  $J = 2.1$ ), 7.61 (d, 1H, Ar-H,  $J = 8.5$ ), 7.52 (d, 1H, Ar-H,  $J = 8.5$ ), 6.93 (d, 1H,  $^3J_{\text{FH}} =$



36.9), 6.80 (d, 1H, Ar-H,  $J = 1.2$ ), 2.73 (td, 2H,  $J = 7.3, 2.1$ ), 1.73 (sext, 2H,  $J = 7.3$ ), 1.01 (t, 3H,  $J = 7.3$ ).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta -127.7$  (d,  $^3J_{\text{FH}} = 36.6$ ). HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{13}\text{FO}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  255.0792, found 255.0788.

**Condensation of *N*-Benzylpiperidone with *N*-Methoxy-*N*-methyl-(1,3-benzothiazol-2-ylsulfonyl)fluoroacetamide (3). Synthesis of 12.** To a solution of sulfone **3** (0.150 g, 0.471 mmol, 1 molar equiv) in dry DMF (5.0 mL) was added  $\text{Cs}_2\text{CO}_3$  (0.769 g, 2.36 mmol, 5 molar equiv) and the color of the reaction mixture turned orange. The suspension was stirred at rt for 30 min, and a solution of *N*-benzylpiperidone (0.270 g, 1.43 mmol, 3 molar equiv) in dry DMF (2.0 mL) was added. The reaction mixture was stirred at rt for 30 h, sat aq  $\text{NH}_4\text{Cl}$  (30 mL) was added, and the mixture was extracted with EtOAc (3 x 30 mL). The combined organic layer was washed with aq NaOH (0.1 M, 30 mL, twice), brine (30 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed in vacuo and the crude product was purified by column chromatography ( $\text{SiO}_2$ , 25% EtOAc in hexanes) to give **12** as a clear liquid (81.1 mg, 59%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.31 (m, 5H, Ar-H), 3.73 (s, 3H), 3.52 (s, 2H), 3.23 (s, 3H), 2.49–2.40 (m, 8H).  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta -126.3$  (s). HRMS (ESI) calcd. for  $\text{C}_{16}\text{H}_{21}\text{FN}_2\text{O}_2\text{Na}$   $[\text{M} + \text{Na}]^+$  315.1479, found 315.1479.

## References

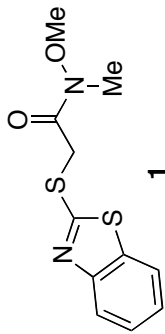
- (1) Manjunath, B. N.; Sane, N. P.; Aidhen, I. S. *Eur. J. Org. Chem.* **2006**, 2851-2855.
- (2) Procedure described for the synthesis of 2-chloro-*N*-methoxy-*N*-methylacetamide was used: Boumendjel, A.; Nuzillard, J.-M.; Massiot, G. *Tetrahedron Lett.* **1999**, *40*, 9033-9036. 2-Bromo-*N*-methoxy-*N*-methylacetamide: (a) Hirner, S.; Panknin, O.; Edefuhr, M.; Somfai, P. *Angew. Chem. Int. Ed.* **2008**, *47*, 1907-1909. (b) Mechelke, M. F.; Meyers, A. I. *Tetrahedron Lett.* **2000**, *41*, 4339-4342.
- (3) Alonso, D. A.; Fuensanta, M.; Gómez-Bengoa, E.; Nájera, C. *Adv. Synth. Catal.* **2008**, *350*, 1823-1829.
- (4) Hata, H.; Kobayashi, T.; Amii, H.; Uneyama, K.; Welch, J. T. *Tetrahedron Lett.* **2002**, *43*, 6099-6102.
- (5) Dutheuil, G.; Paturel, C.; Lei, X.; Couve-Bonnaire, S.; Pannecocke, X. *J. Org. Chem.* **2006**, *71*, 4316-4319.

1222-Ag-11-1002-sulfide-pure

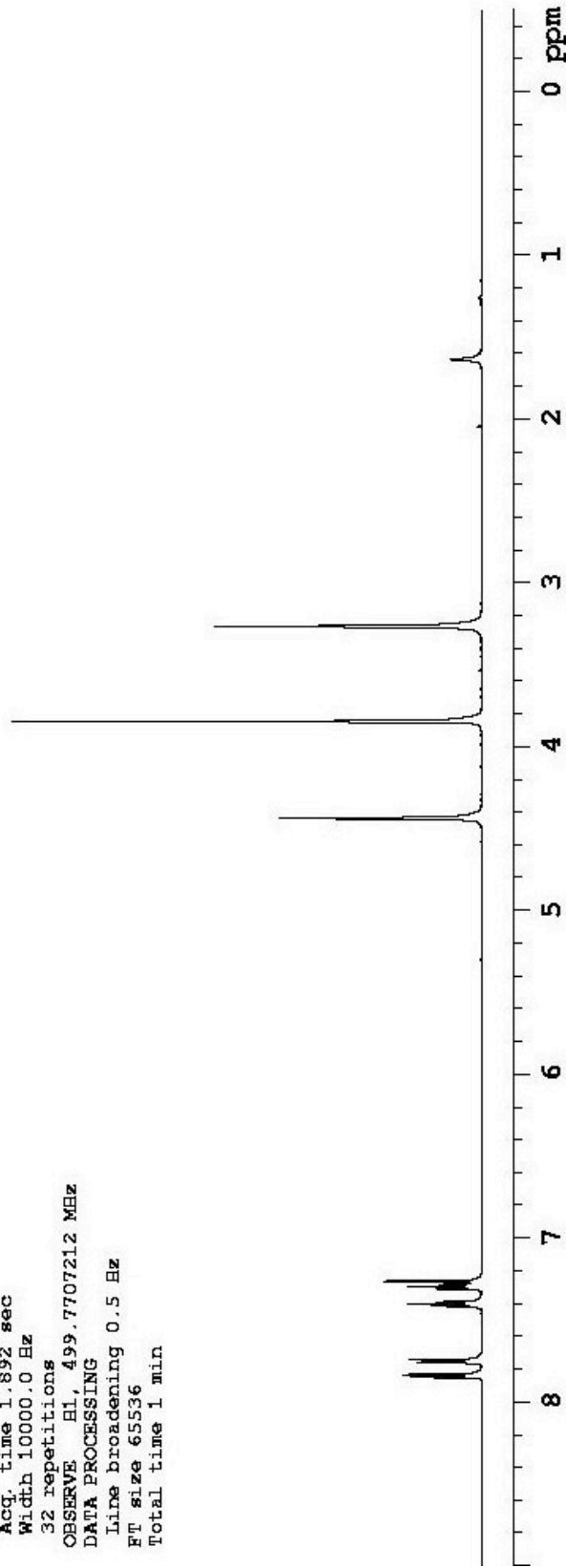
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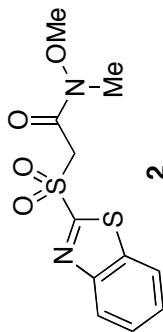
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32 repetitions  
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DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min



500 MHz; CDCl<sub>3</sub>



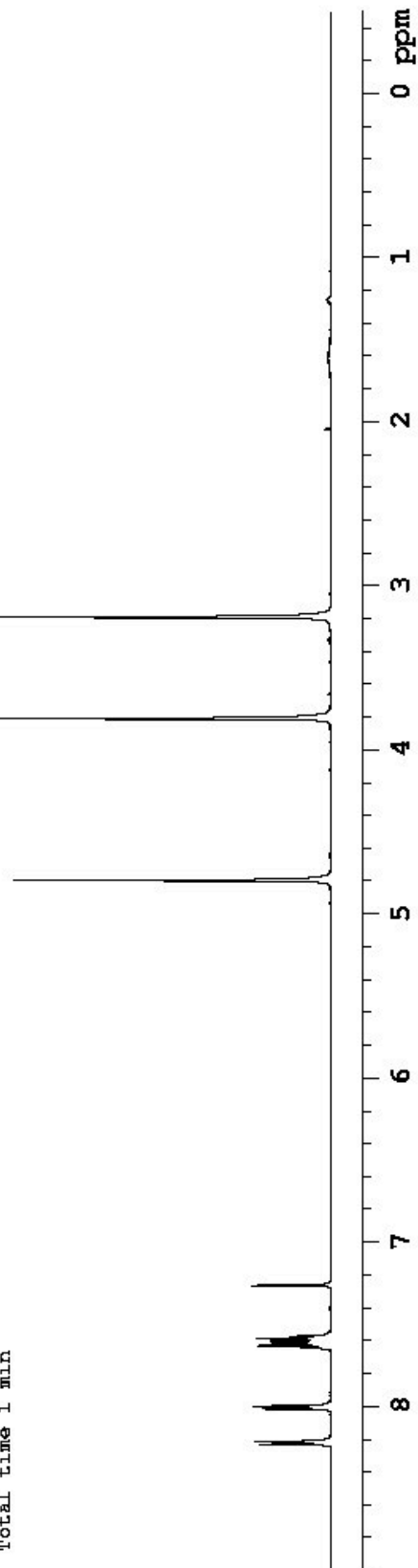


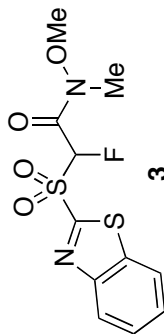
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 DATA PROCESSING  
 Line broadening 0.5 Hz  
 FT size 65536  
 Total time 1 min





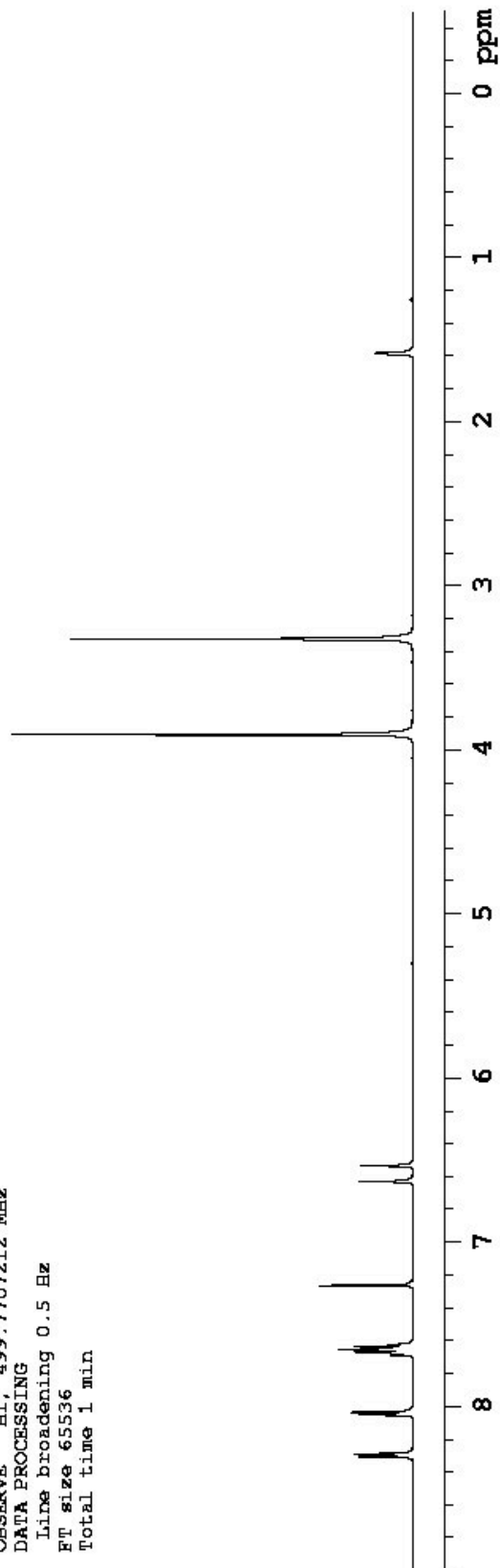
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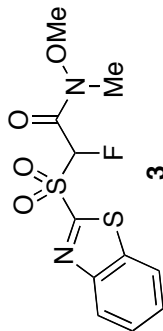
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Temp. 25.0 C / 298.1 K  
Operator: barbara

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Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707212 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min





**3**  
125 MHz; CDCl<sub>3</sub>

1222=Ag-11-1004-pure-monoF-13C

Data Collected on:  
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Archive directory:  
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Sample directory:

File: 1222=Ag-11-1004-pure-monoF-13C

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>

Temp. 25.0 C / 298.1 K

Operator: barbara

Relax. delay 4.000 sec

Pulse 52.1 degrees

Acq. time 1.300 sec

Width 29996.3 Hz

1620 repetitions

OBSERVE C13, 125.6674540 MHz

DECOUPLE H1, 499.7732084 MHz

Power 42 dB

on during acquisition

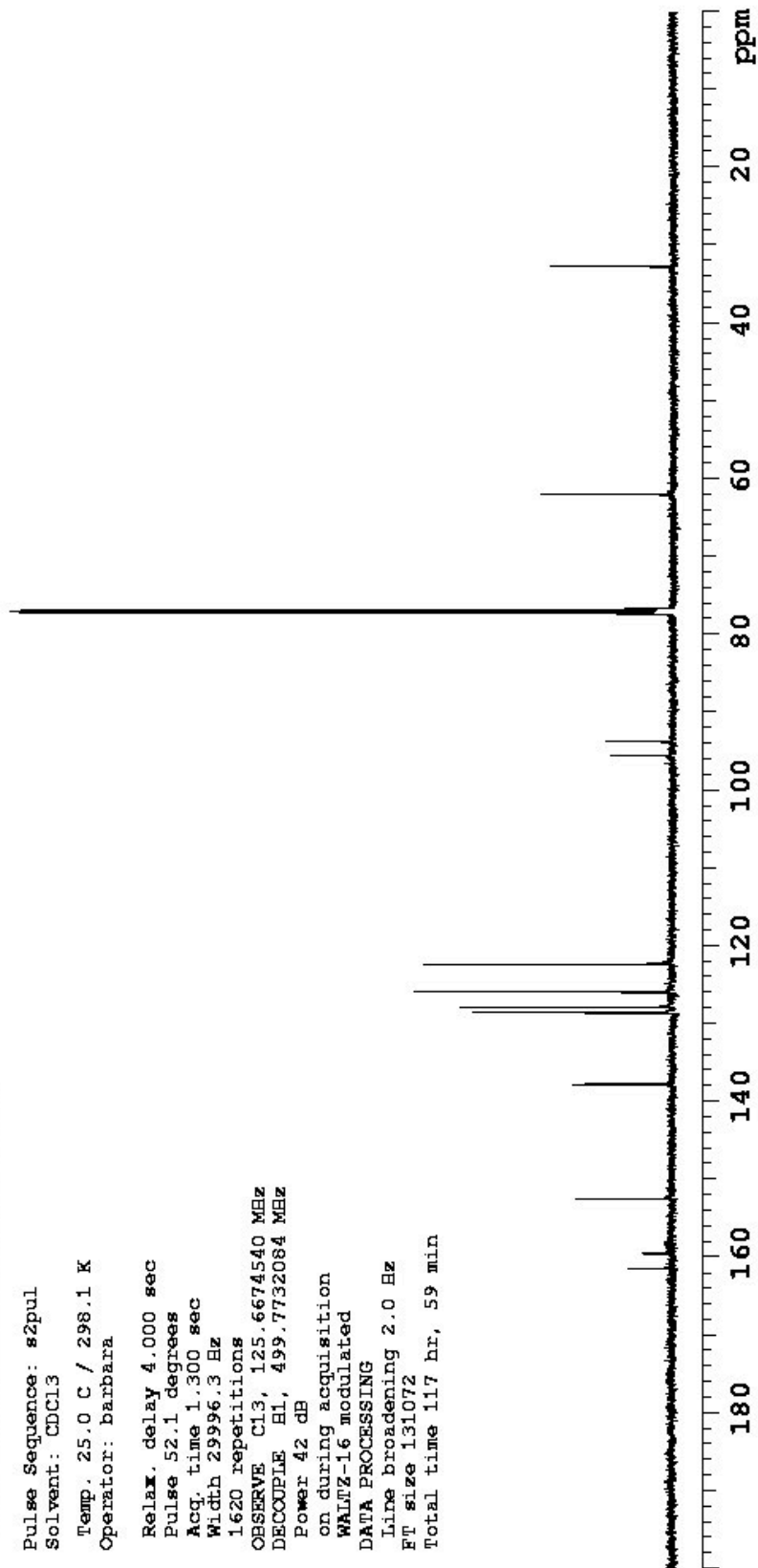
WALTZ-16 modulated

DATA PROCESSING

Line broadening 2.0 Hz

FT size 131072

Total time 117 hr, 59 min



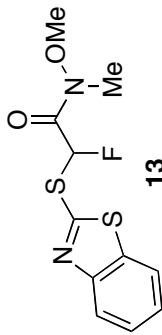
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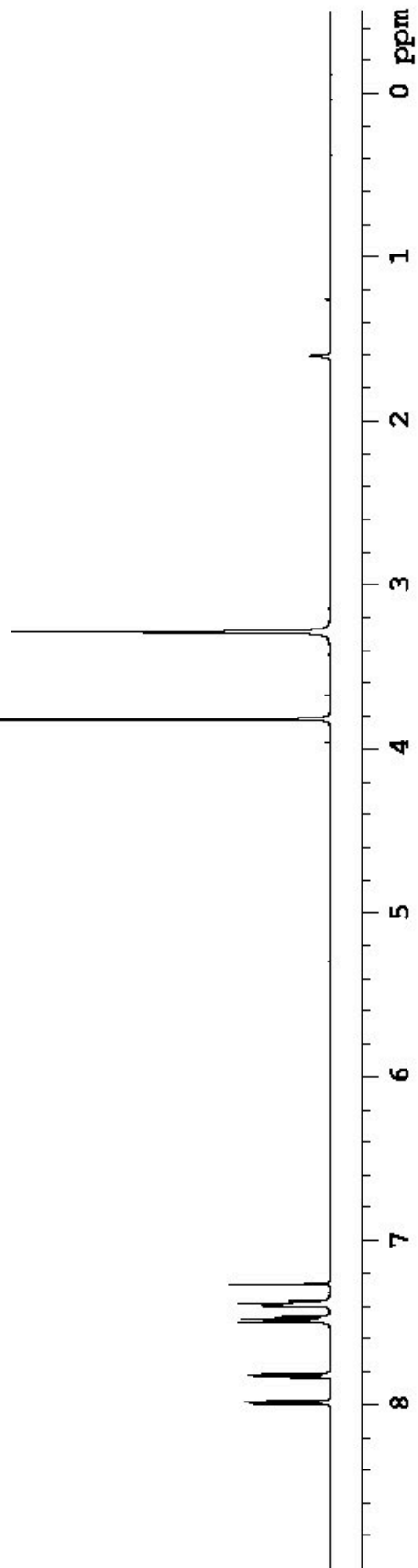
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INOVA-500 "riga"

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12 repetitions  
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DATA PROCESSING  
Line broadening 0.1 Hz  
Ft size 32768  
Total time 1 min, 32 sec



500 MHz; CDCl<sub>3</sub>



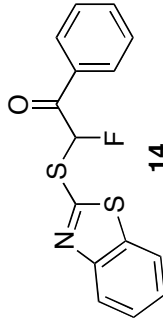
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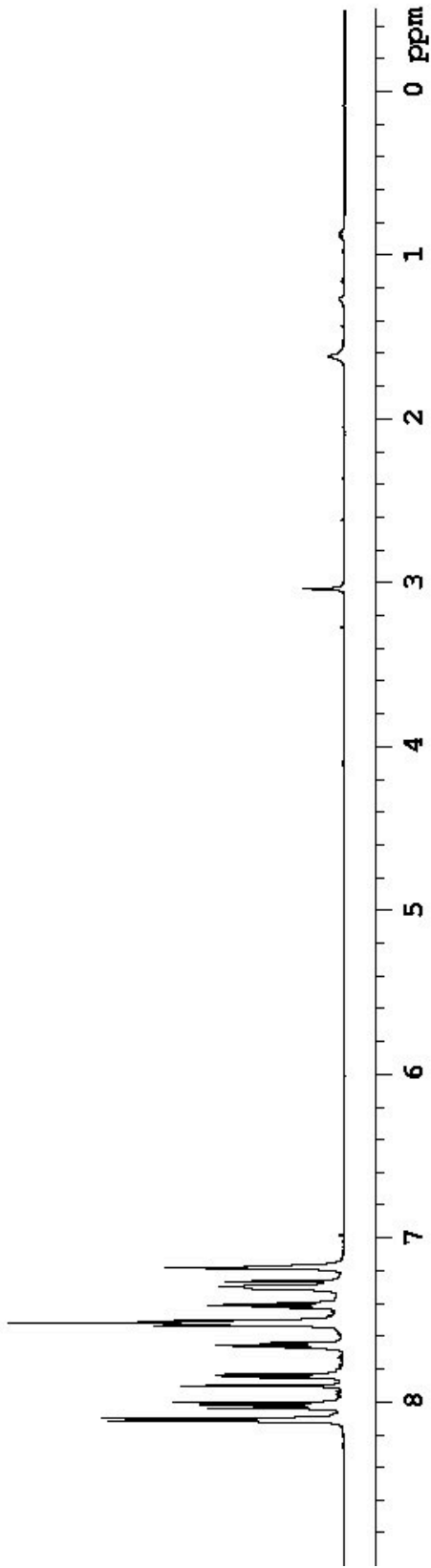
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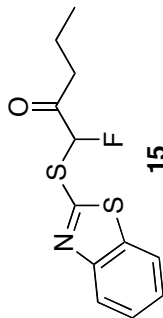
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Acq. time 1.892 sec  
Width 7544.3 Hz  
32 repetitions  
OBSERVE H1, 499.7707221 MHz  
DATA PROCESSING  
Line broadening 0.1 Hz  
F1 size 32768  
Total time 1 min, 32 sec



500 MHz; CDCl<sub>3</sub>





500 MHz; CDCl<sub>3</sub>

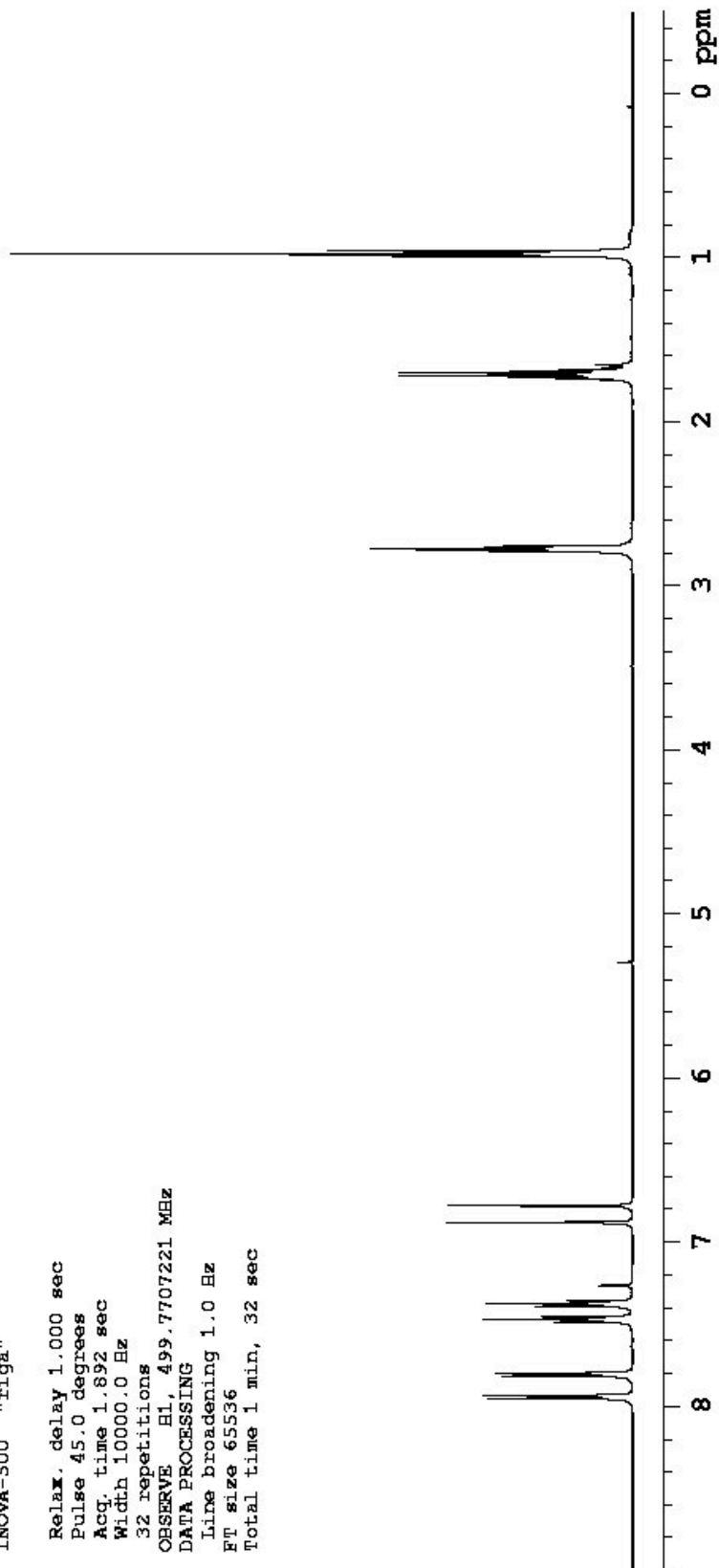
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Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1231-ss-02-158pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
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DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 1 min, 32 sec





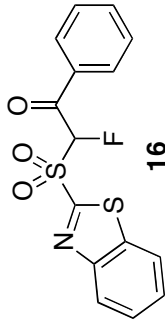
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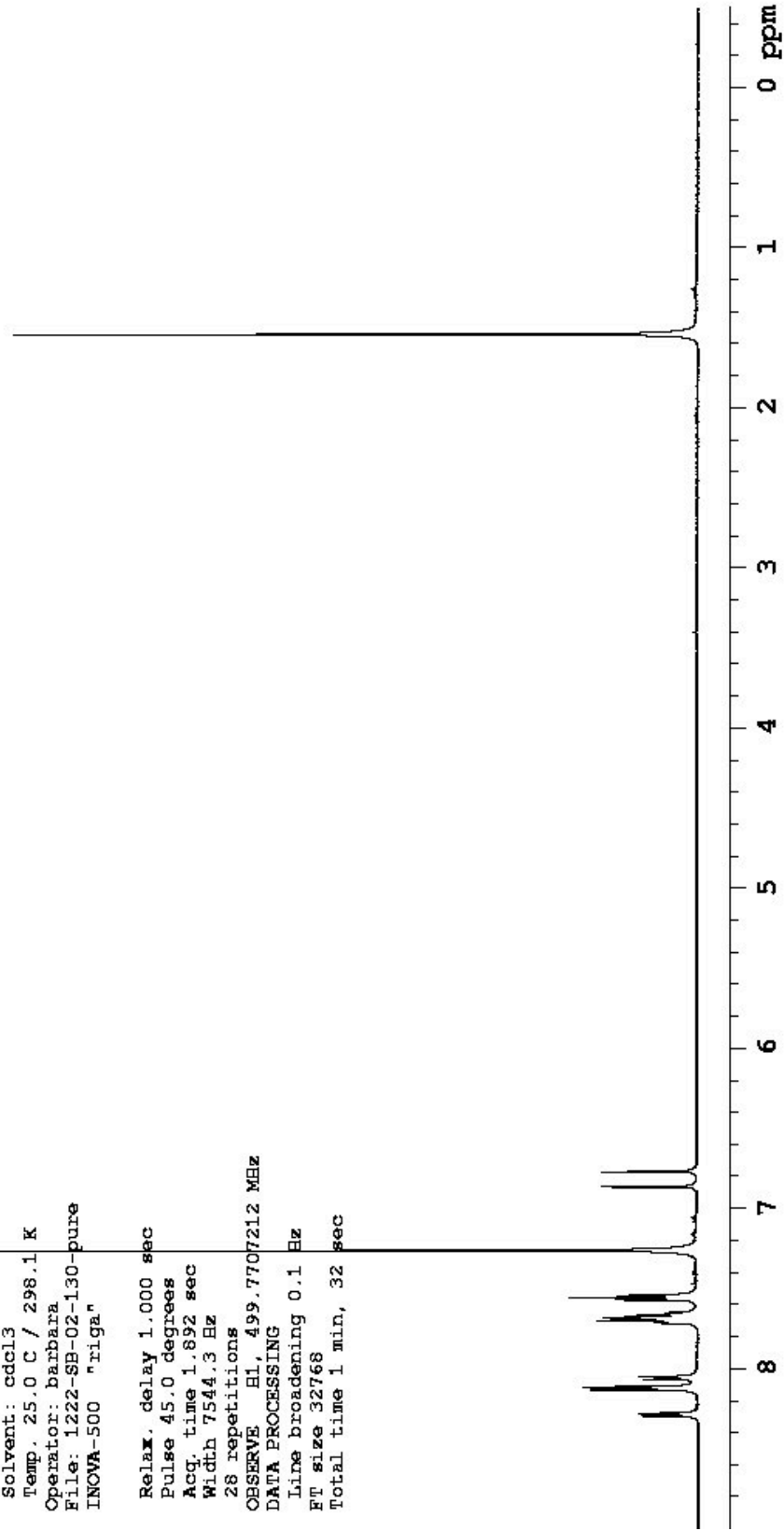
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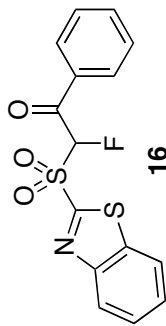
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500 MHz; CDCl<sub>3</sub>





125 MHz; CDCl<sub>3</sub>

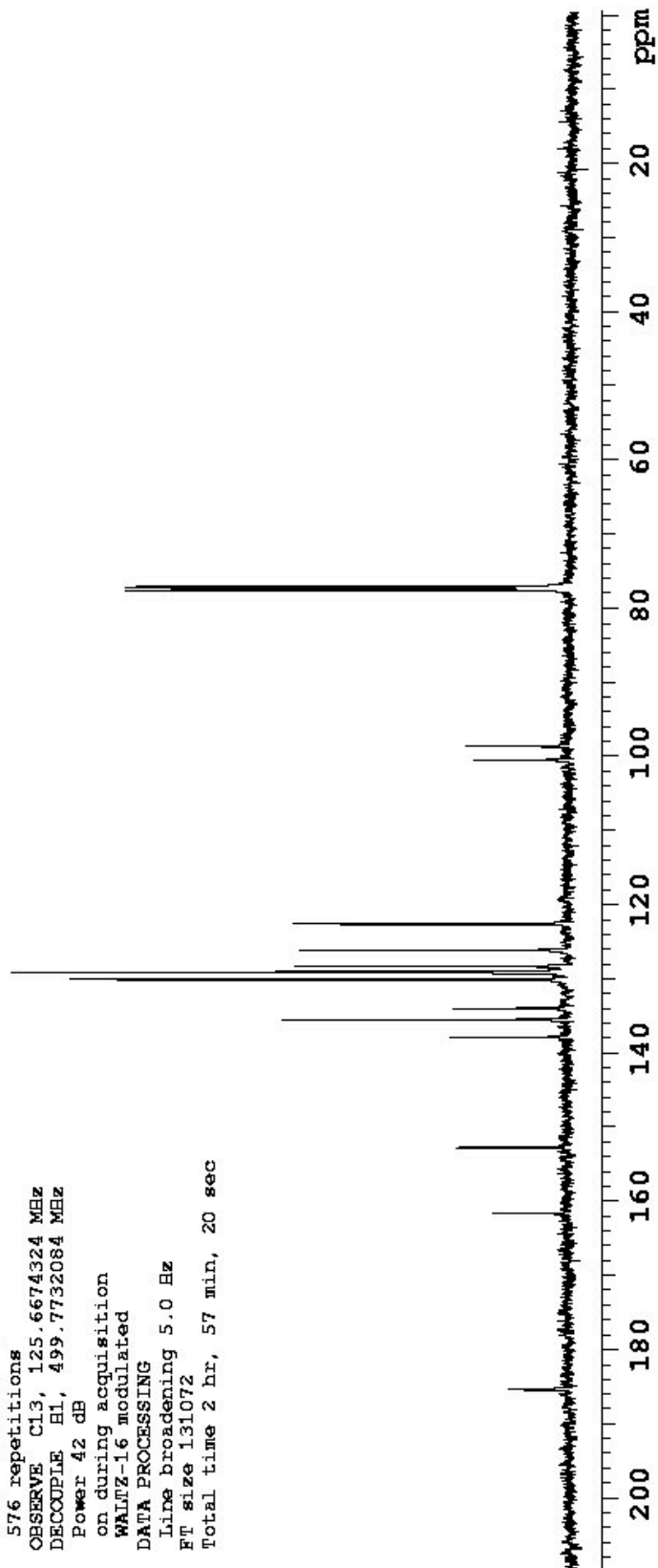
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 Temp. 25.0 C / 298.1 K  
 Operator: barbara  
 File: 1222-SB-03-135-pure-13C  
 INOVA-500 "riga"

Relax. delay 4.000 sec  
 Pulse 52.1 degrees  
 Acq. time 1.300 sec  
 Width 29996.3 Hz  
 576 repetitions  
 OBSERVE C13, 125.6674324 MHz  
 DECOUPLE H1, 499.7732084 MHz  
 Power 42 dB  
 on during acquisition  
 WALTZ-16 modulated  
 DATA PROCESSING  
 Line broadening 5.0 Hz  
 FT size 131072  
 Total time 2 hr, 57 min, 20 sec



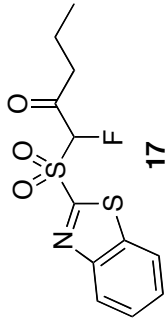
1231-ss-02-157pure

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

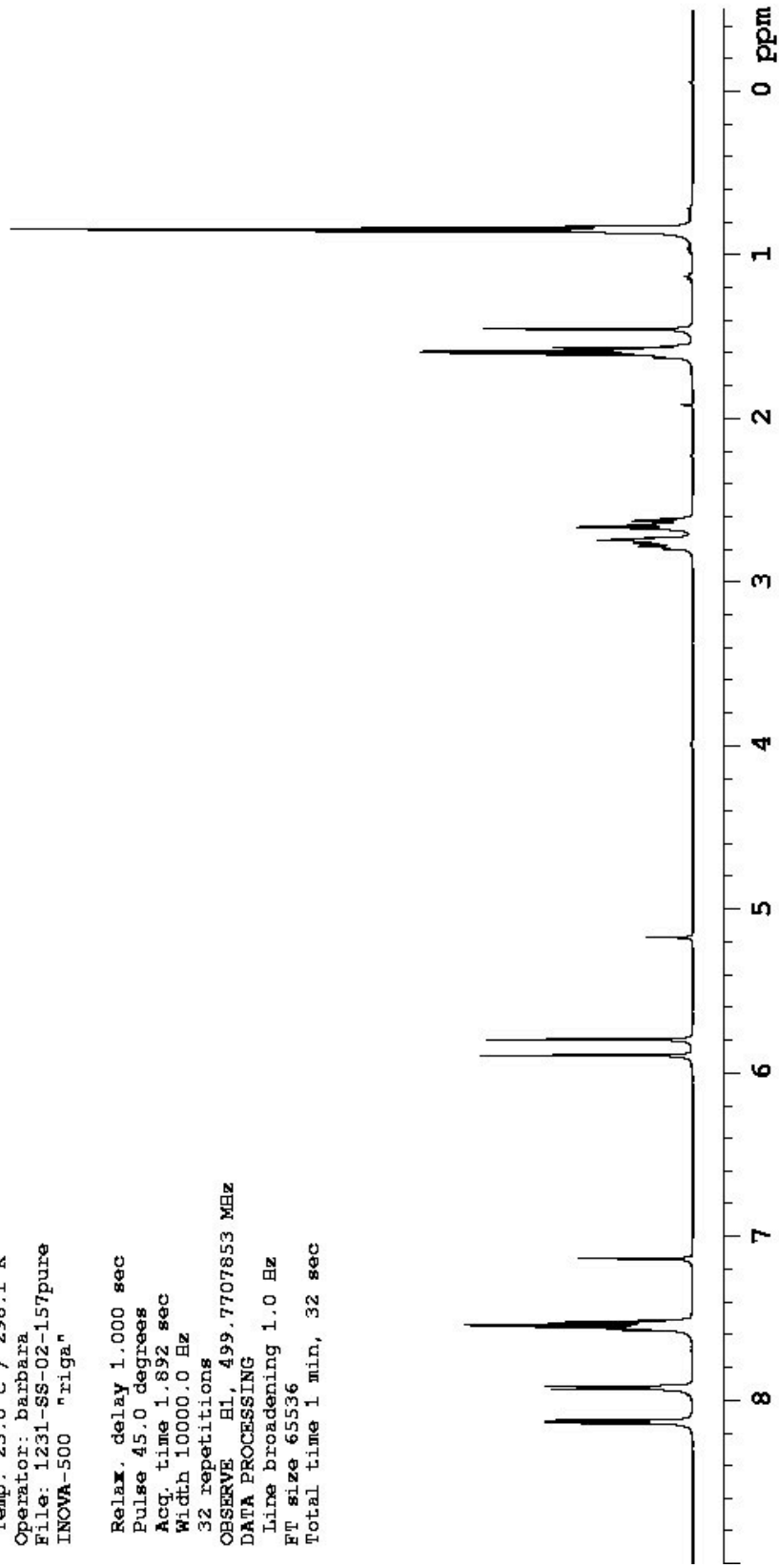
Pulse Sequence: s2pul

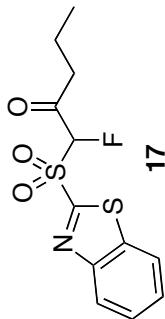
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1231-SS-02-157pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707853 MHz  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 1 min, 32 sec



500 MHz; CDCl<sub>3</sub>





**17**  
125 MHz; CDCl<sub>3</sub>

1222-SS-171-C13

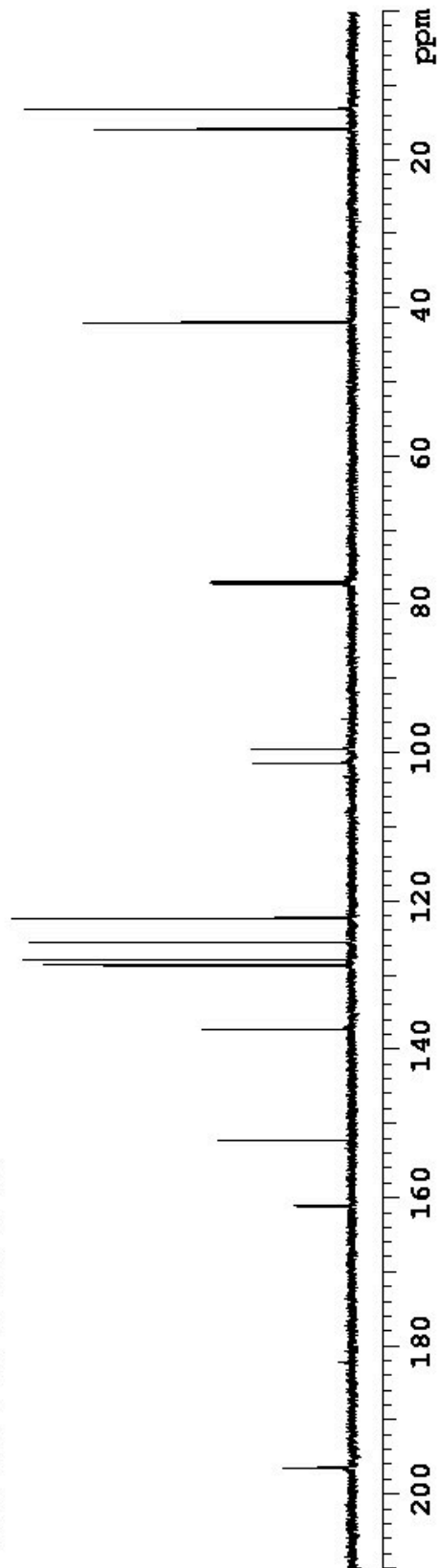
Archive directory: /export/home/barbara/vnmrSYS/data  
Sample directory:

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SS-171-C13  
INOVA-500 "riga"

Relax. delay 4.000 sec  
Pulse 52.1 degrees  
Acq. time 1.300 sec  
Width 29996.3 Hz  
48 repetitions  
OBSERVE C13, 125.6674778 MHz  
DECOUPLE H1, 499.7732084 MHz  
Power 42 dB

on during acquisition  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 2.0 Hz  
FT size 131072  
Total time 2 hr, 57 min, 20 sec



1222-Ag-11-1063-purified

Archive directory: /export/home/barbara/vnmrsys/data  
Sample directory:

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Operator: barbara

File: 1222-Ag-11-1063-purified  
INOVA-500 "riga"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 10000.0 Hz

32 repetitions

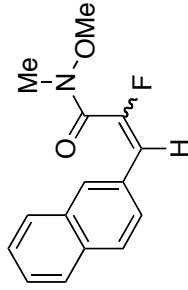
OBSERVE H1, 499.7707212 MHz

DATA PROCESSING

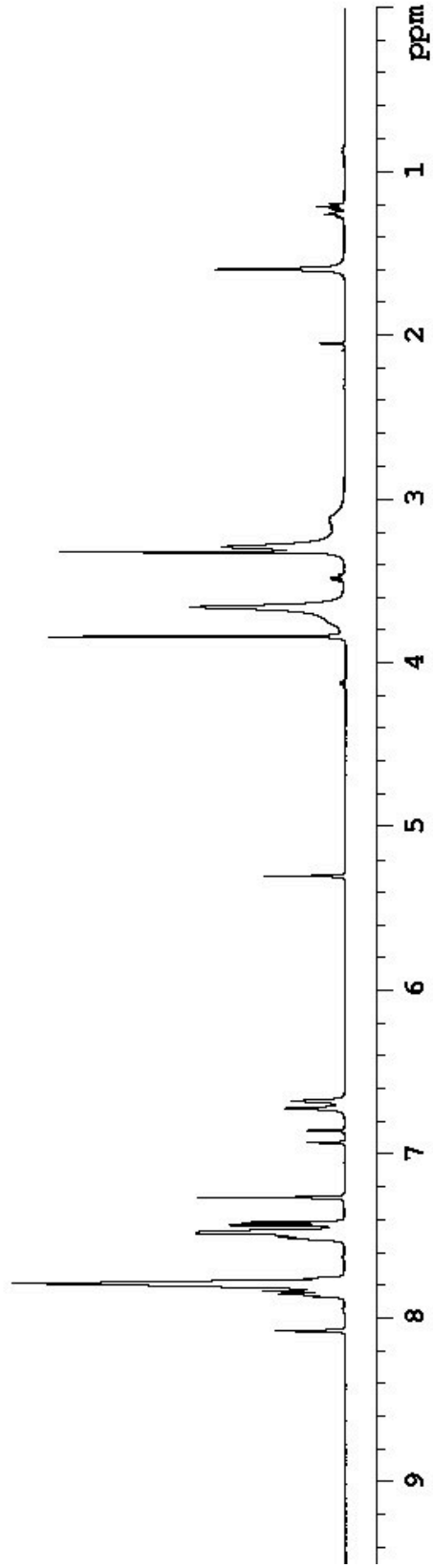
Line broadening 0.5 Hz

FT size 65536

Total time 1 min, 32 sec



4: E/Z78/22  
500 MHz; CDCl<sub>3</sub>

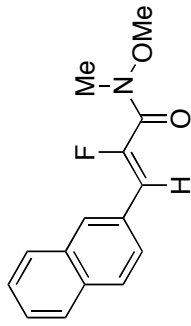


1222-Ag-11-1031-pure

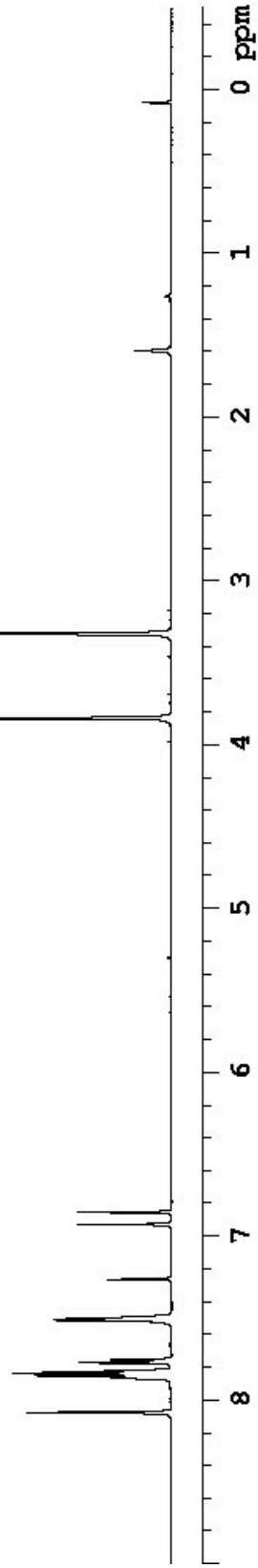
Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1031-pure

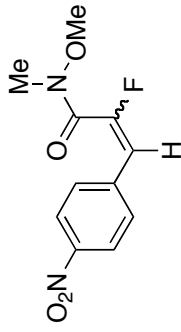
Pulse Sequence: s2pul  
Solvent: CDCl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707209 MHz  
DATA PROCESSING  
Line broadening 0.1 Hz  
Ft size 65536  
Total time 1 min



4: Z-isomer  
500 MHz; CDCl<sub>3</sub>





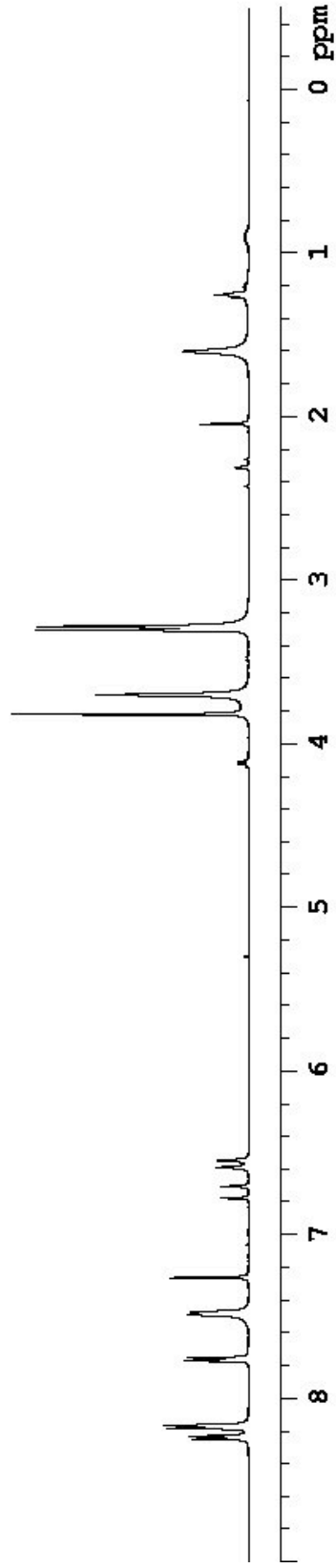
5: *E/Z* 67/33  
500 MHz; CDCl<sub>3</sub>

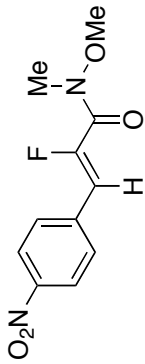
1222-Ag-12-1074-purified

Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-12-1074-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707206 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min





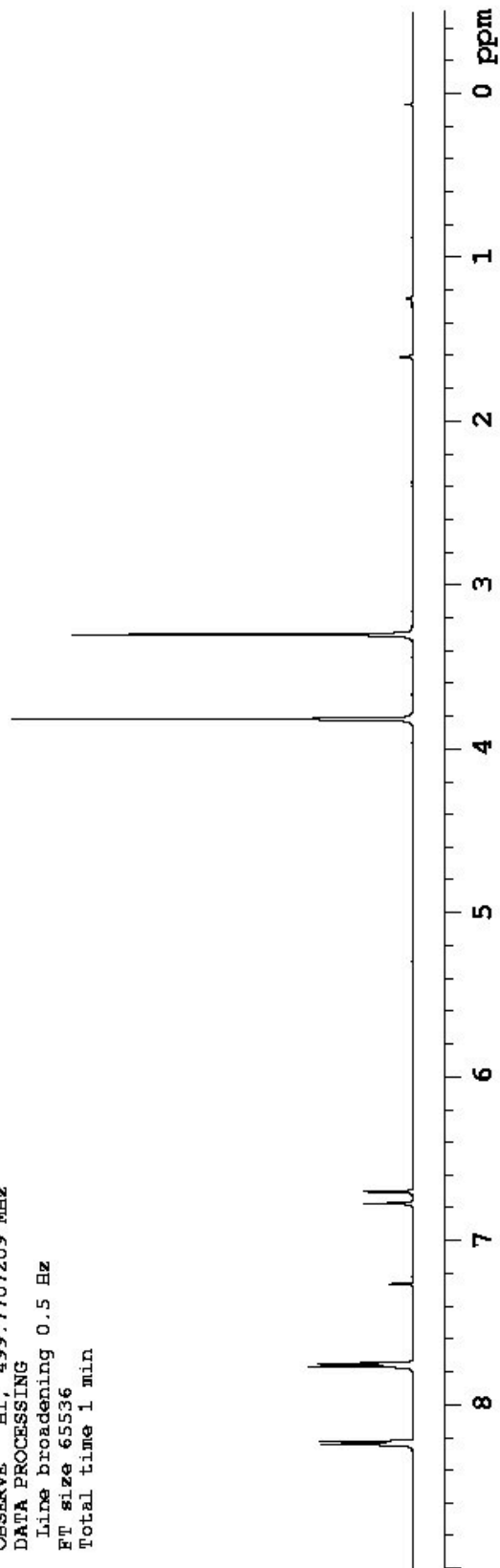
5: Z-isomer  
500 MHz; CDCl<sub>3</sub>

1222-Ag-11-1042-purified

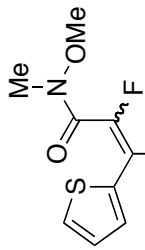
Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1042-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707209 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min







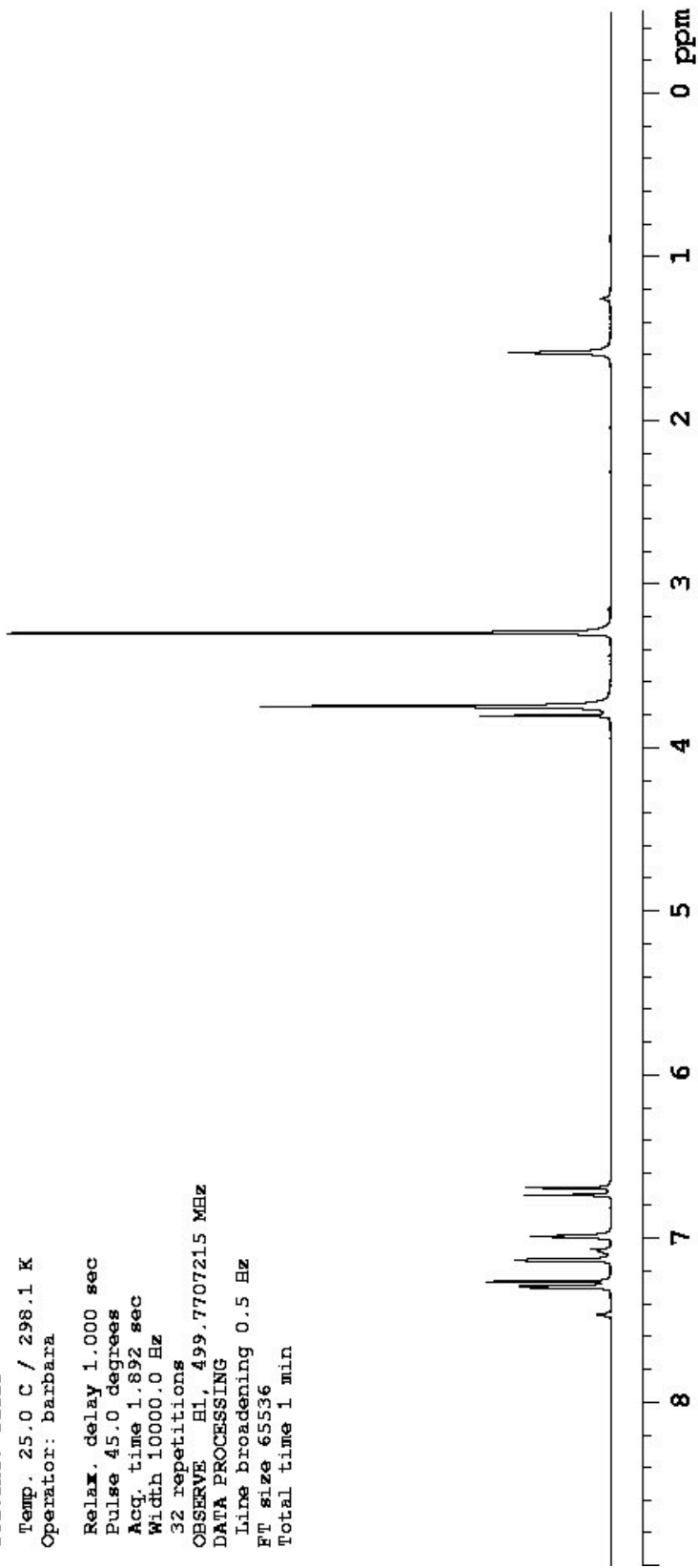
6: E/Z 86/14  
500 MHz; CDCl<sub>3</sub>

1222-Ag-12-1086-purified

Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-12-1086-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707215 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min



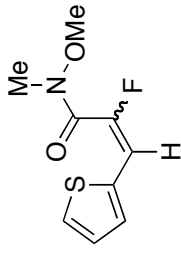
1222-AG-14-1146-pure

Archive directory: /export/home/barbara/vnmrSYS/data  
File: 1222-AG-14-1146-pure

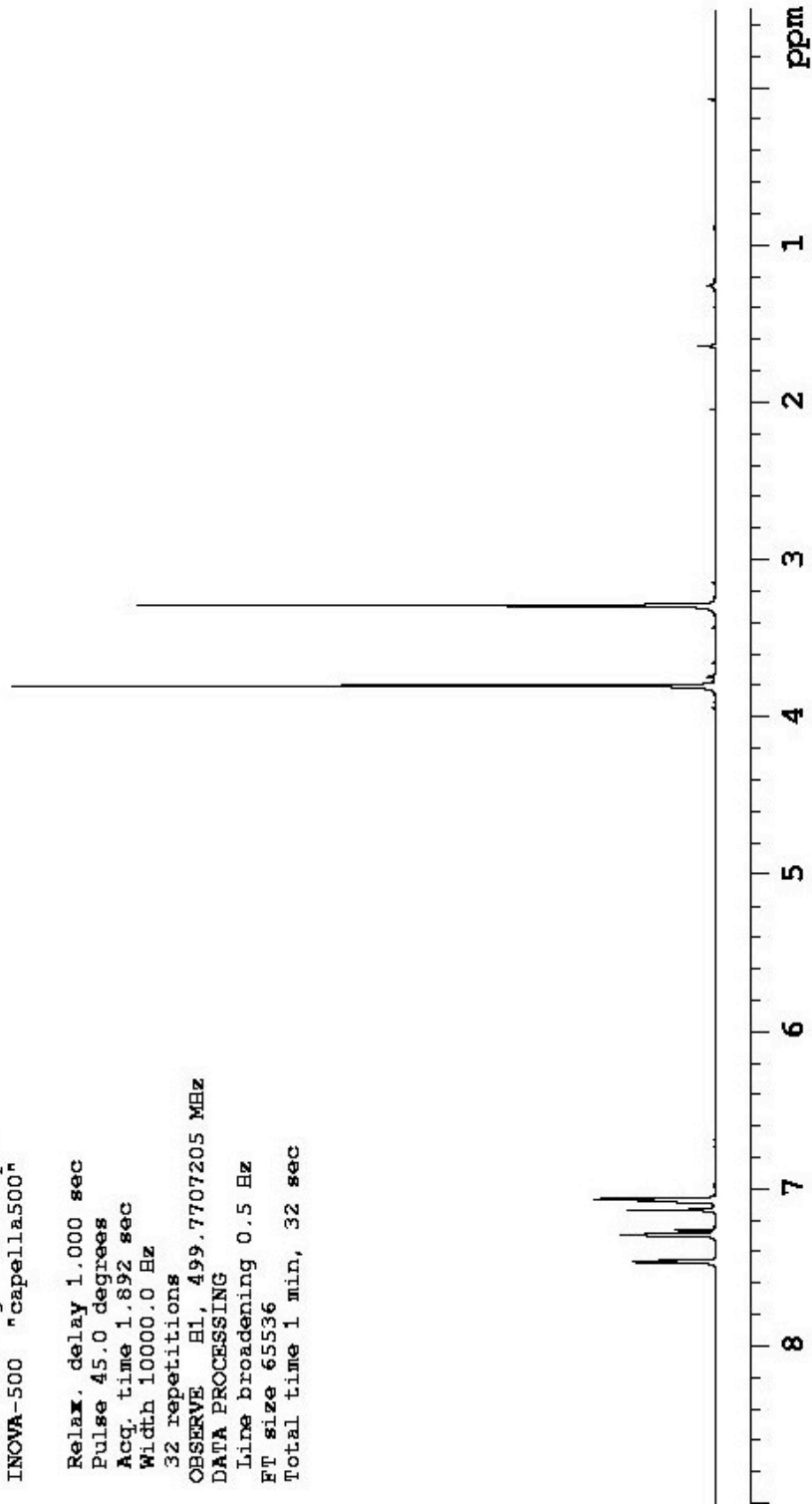
Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-AG-14-1146-pure  
INOVA-500 "capella500"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707205 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min, 32 sec



6: E/Z 2/98  
500 MHz; CDCl<sub>3</sub>



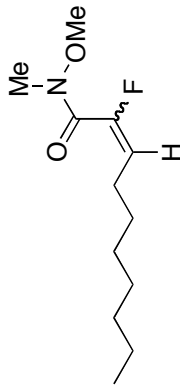
1222-Ag-12-1075-purified

Data Collected on:  
capella500-incova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-12-1075-purified

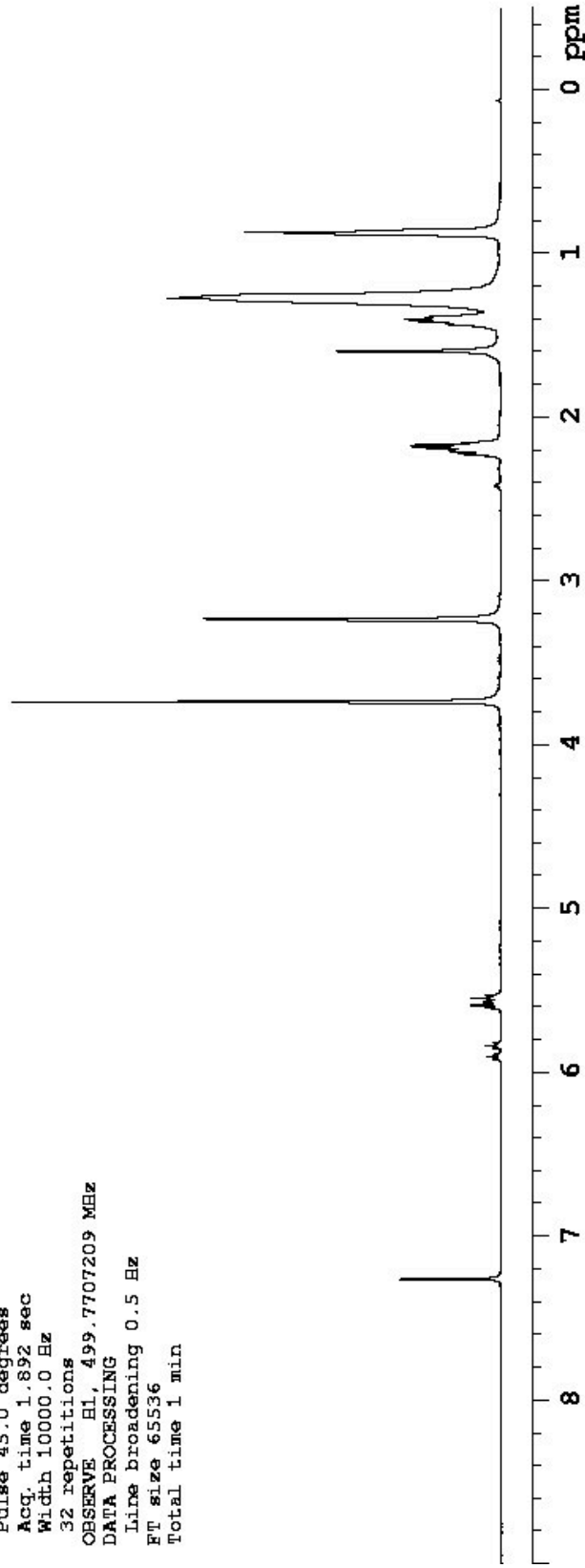
Pulse Sequence: s2pul  
Solvent: cdcl3

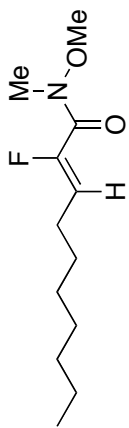
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707209 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min



7: E/Z 67/33  
500 MHz; CDCl<sub>3</sub>





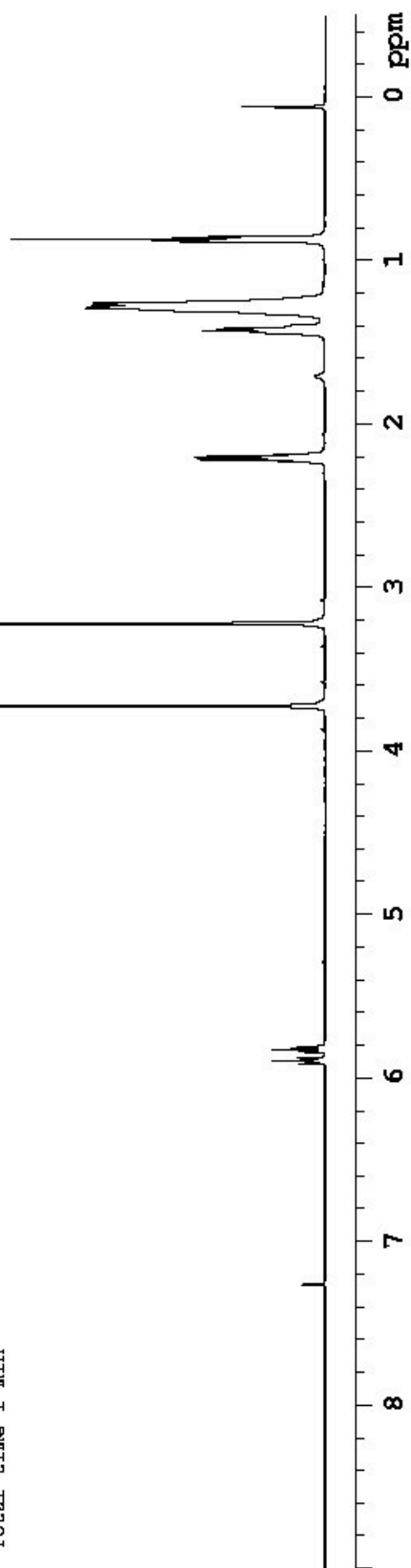
7: Z-isomer  
500 MHz; CDCl<sub>3</sub>

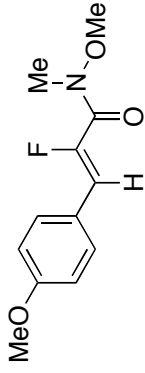
1222-Ag-11-1043-purified

Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1043-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707209 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min





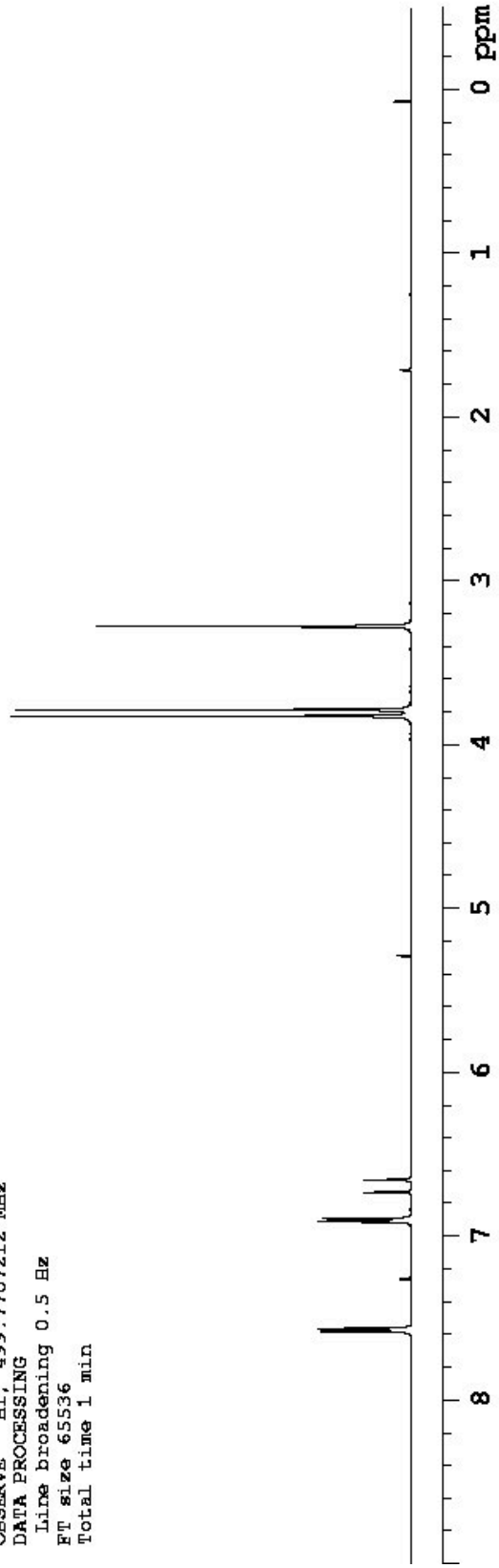
**8: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

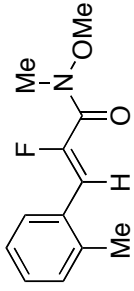
1222-Ag-11-1040-purified

Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1040-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707212 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min





**9: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

1222-Ag-11-1041-pure

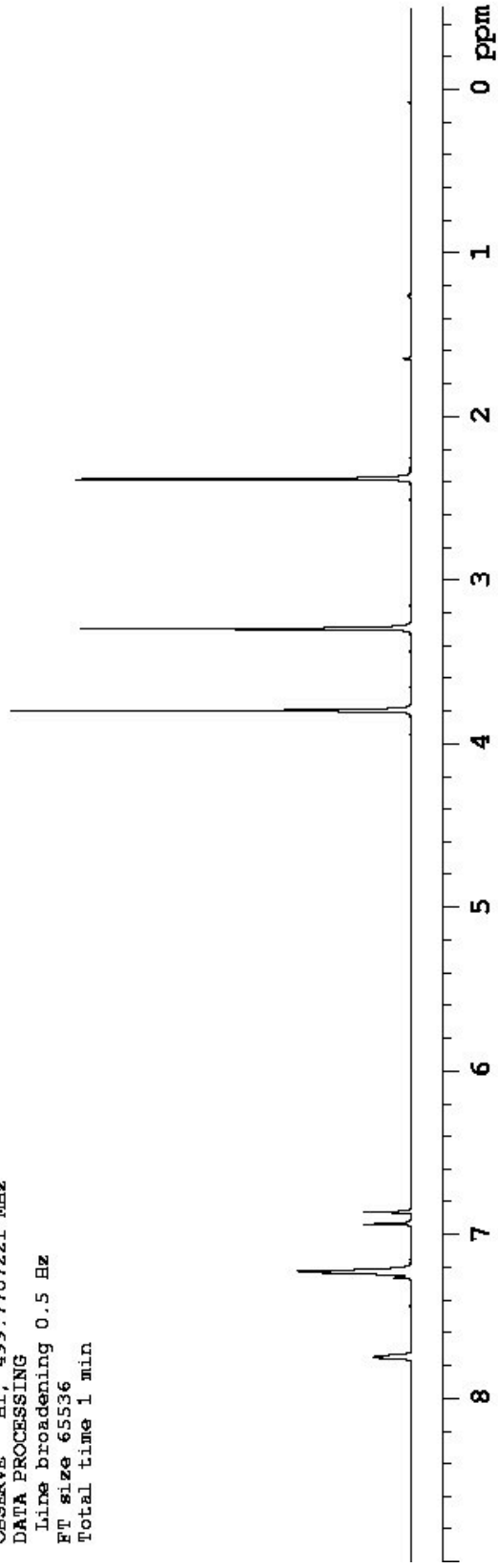
Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1041-pure

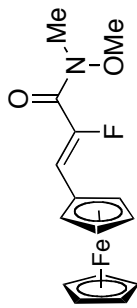
Pulse Sequence: s2pul  
Solvent: cdcl3

Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz

32 repetitions  
OBSERVE H1, 499.7707221 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min





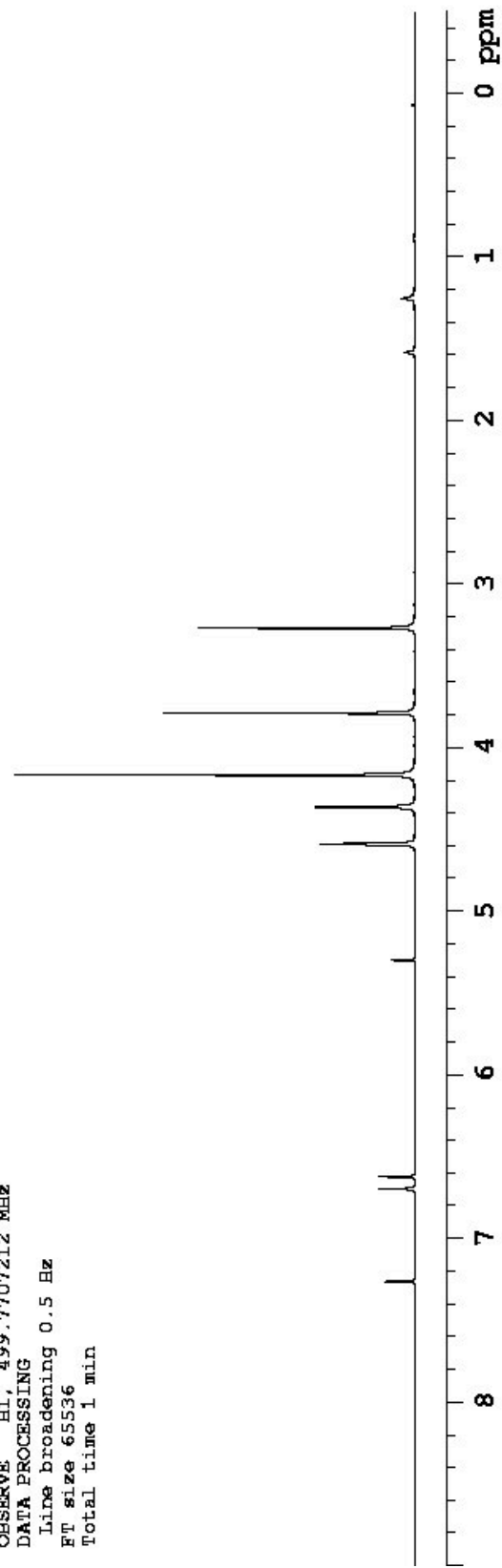
10: Z-isomer  
500 MHz; CDCl<sub>3</sub>

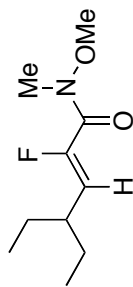
1222-Ag-11-1047-purified

Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1047-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707212 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min





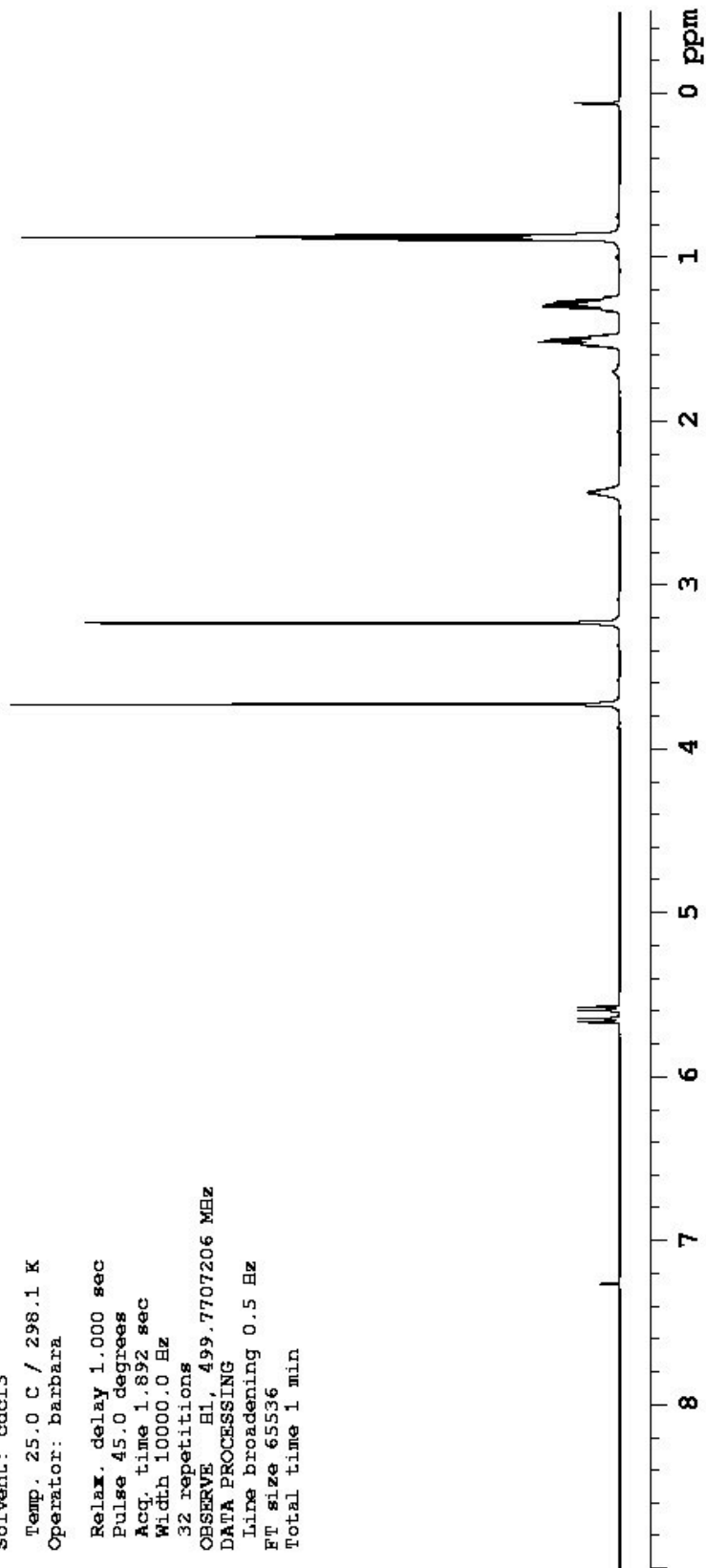
11: Z-isomer  
500 MHz; CDCl<sub>3</sub>

1222-Ag-11-1044-purified

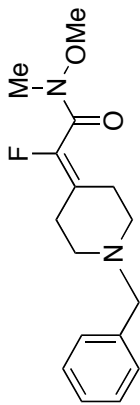
Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:  
auto\_13Dec2004  
File: 1222-Ag-11-1044-purified

Pulse Sequence: s2pul  
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707206 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
Ft size 65536  
Total time 1 min







12

500 MHz; CDCl<sub>3</sub>

1222-Ag-12-1102-purified

Data Collected on:  
capella500-inova500  
Archive directory:  
/export/home/mkl/vnmrSYS/data  
Sample directory:

File: 1222-Ag-12-1102-purified

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>

Temp. 25.0 C / 298.1 K

Operator: barbara

Relax. delay 6.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 7996.0 Hz

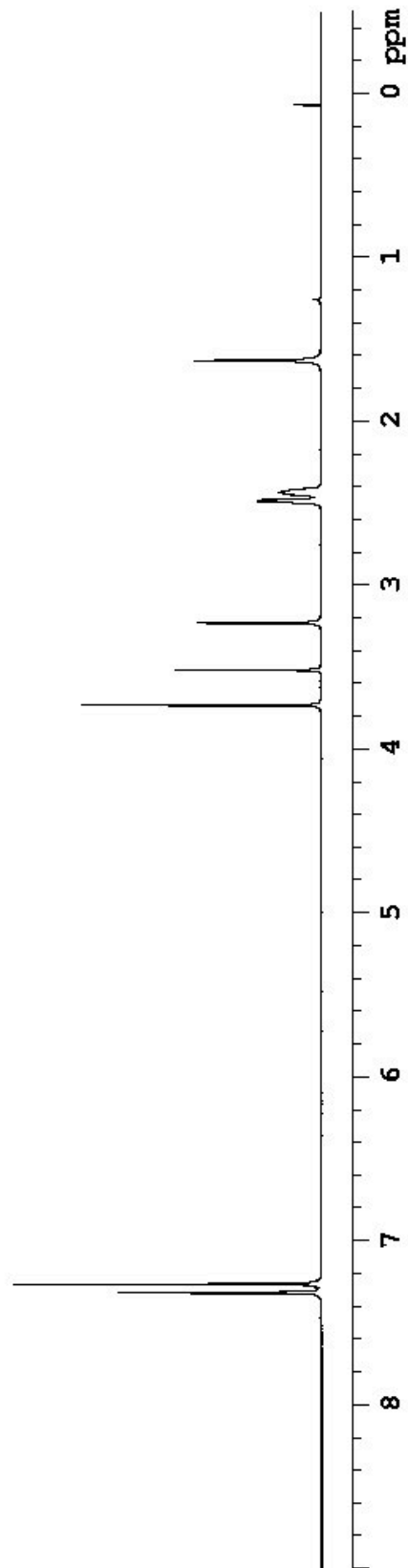
16 repetitions

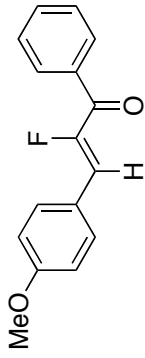
OBSERVE H1, 499.7707212 MHz

DATA PROCESSING

FT size 32768

Total time 2 min





**18a: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

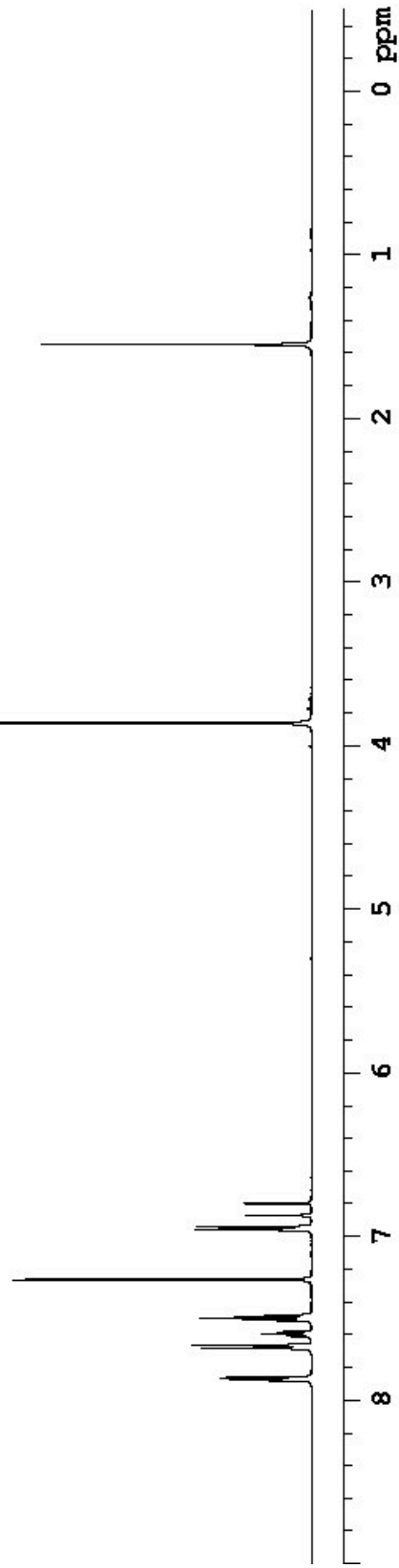
1222-SB-03-141-pure

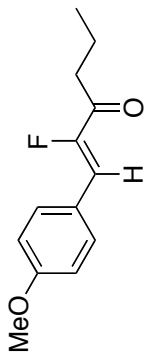
Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-141-pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707209 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min, 32 sec





**18b: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

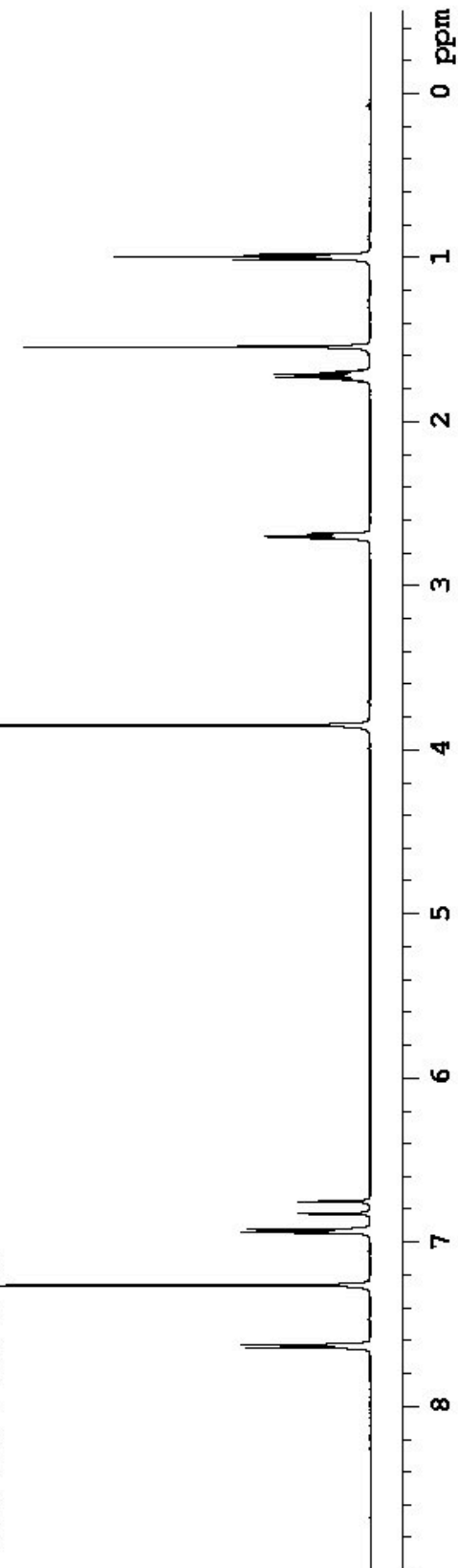
1231-SS-02-168pure

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1231-SS-02-168pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707212 MHz  
DATA PROCESSING  
Line broadening 1.0 Hz  
F1 size 65536  
Total time 1 min, 32 sec



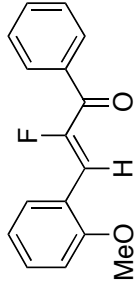
1222-SB-03-146-pure

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

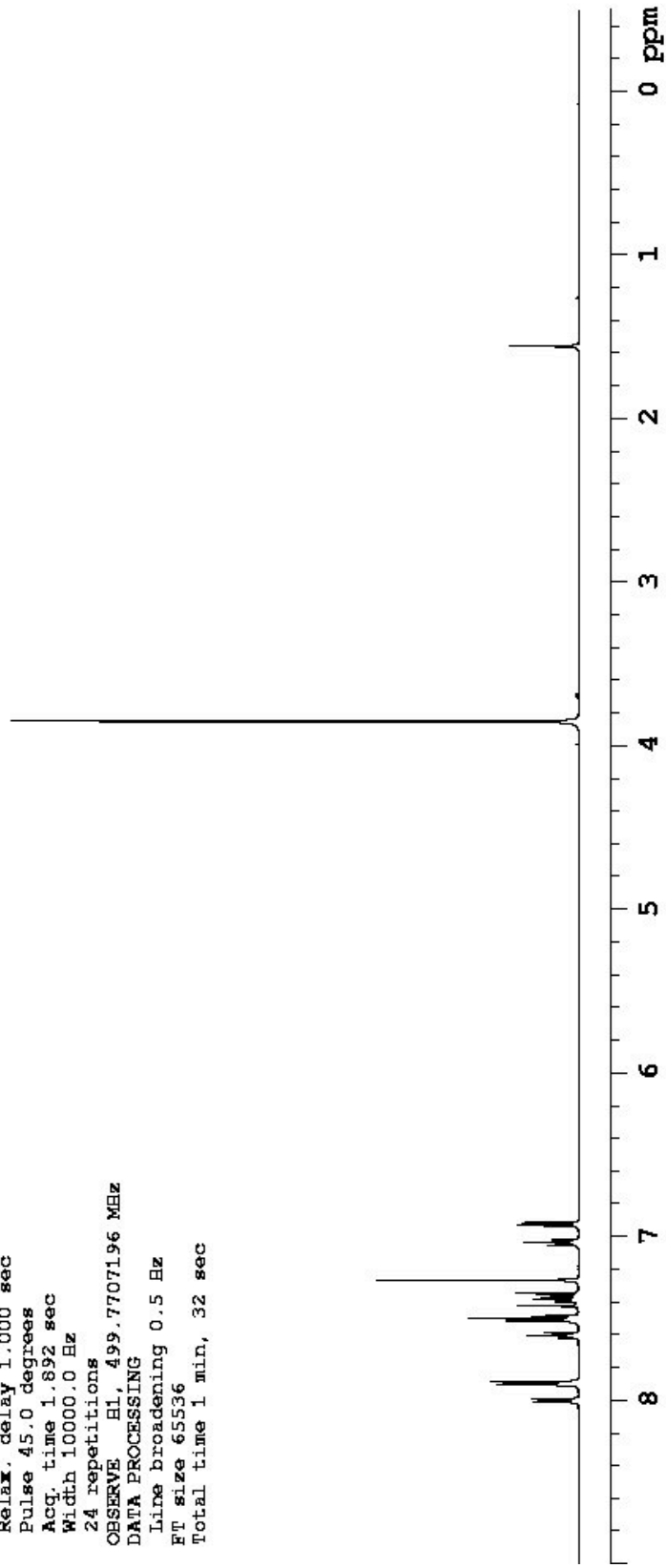
Pulse Sequence: s2pul

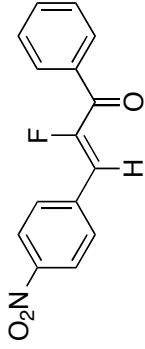
Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-146-pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
24 repetitions  
OBSERVE H1, 499.7707196 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min, 32 sec



19a: Z-isomer  
500 MHz; CDCl<sub>3</sub>





**20a: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

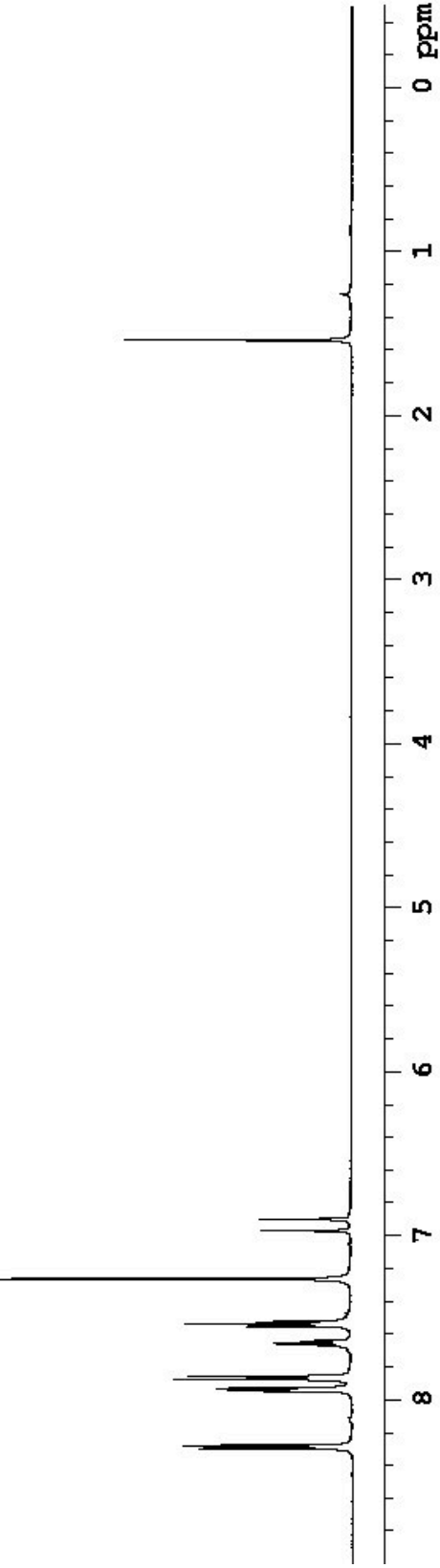
1222-SB-03-142-pure

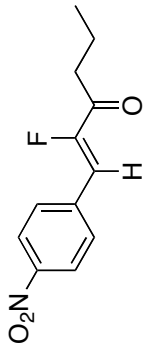
Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-142-pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 7544.3 Hz  
28 repetitions  
OBSERVE H1, 499.7707212 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
F1 size 32768  
Total time 1 min, 32 sec





**20b: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

1231-SS-02-165-2ndpurification

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

Operator: barbara

File: 1231-SS-02-165-2ndpurification

INOVA-500 "riga"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 10000.0 Hz

32 repetitions

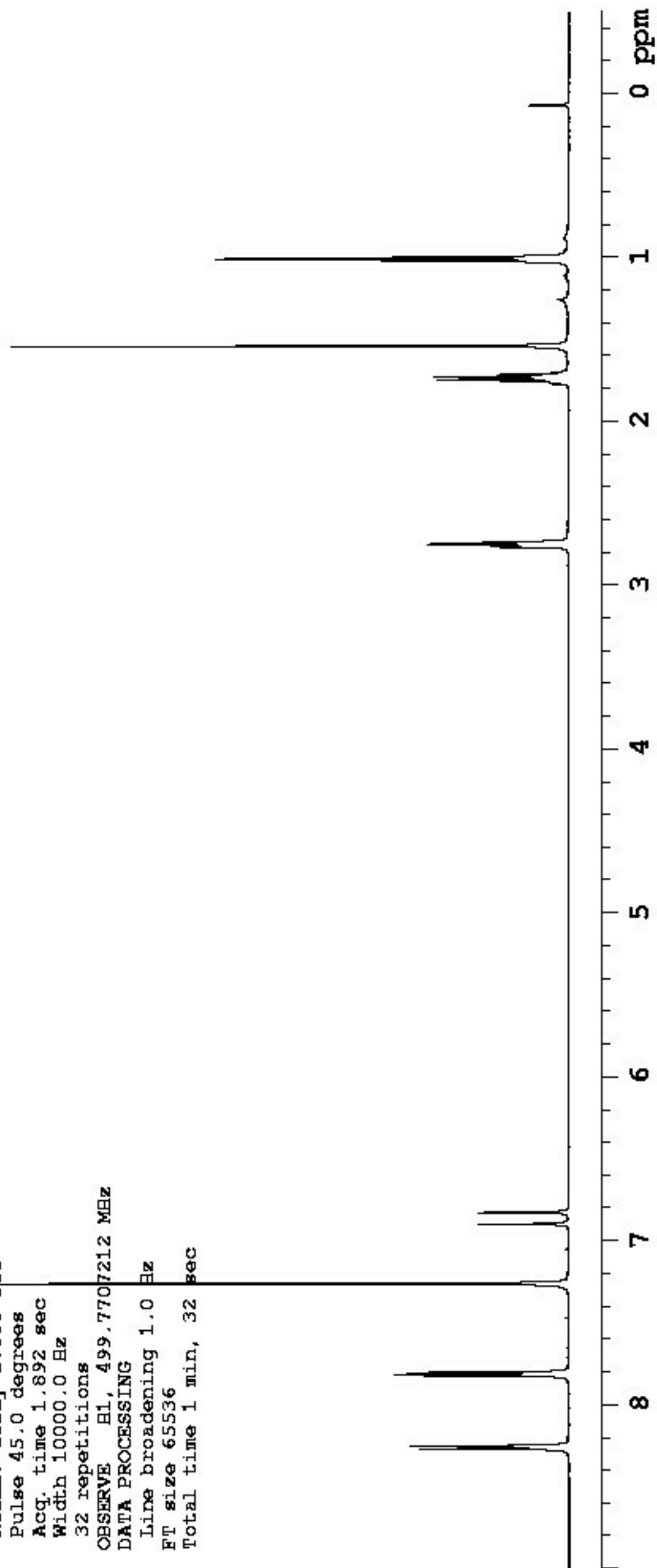
OBSERVE H1, 499.7707212 MHz

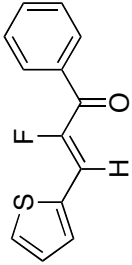
DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 min, 32 sec





**21a: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

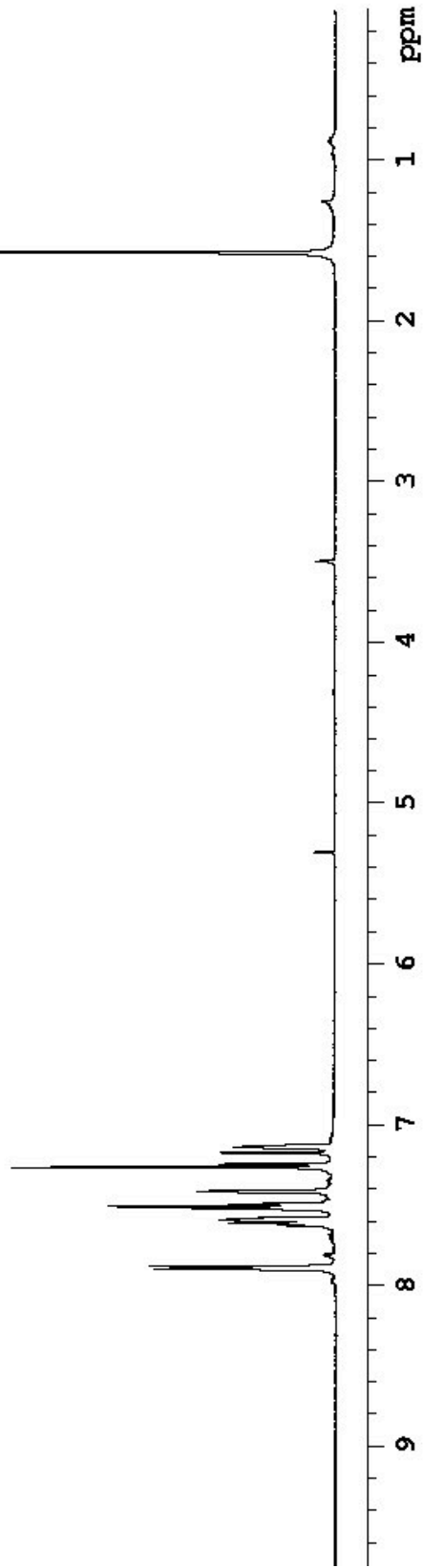
1222-03-177-pure

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-177-pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 7544.3 Hz  
16 repetitions  
OBSERVE H1, 499.7707239 MHz  
DATA PROCESSING  
Line broadening 0.1 Hz  
F1 size 32768  
Total time 1 min, 32 sec



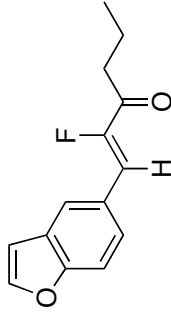
1231-SS-02-190pure

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

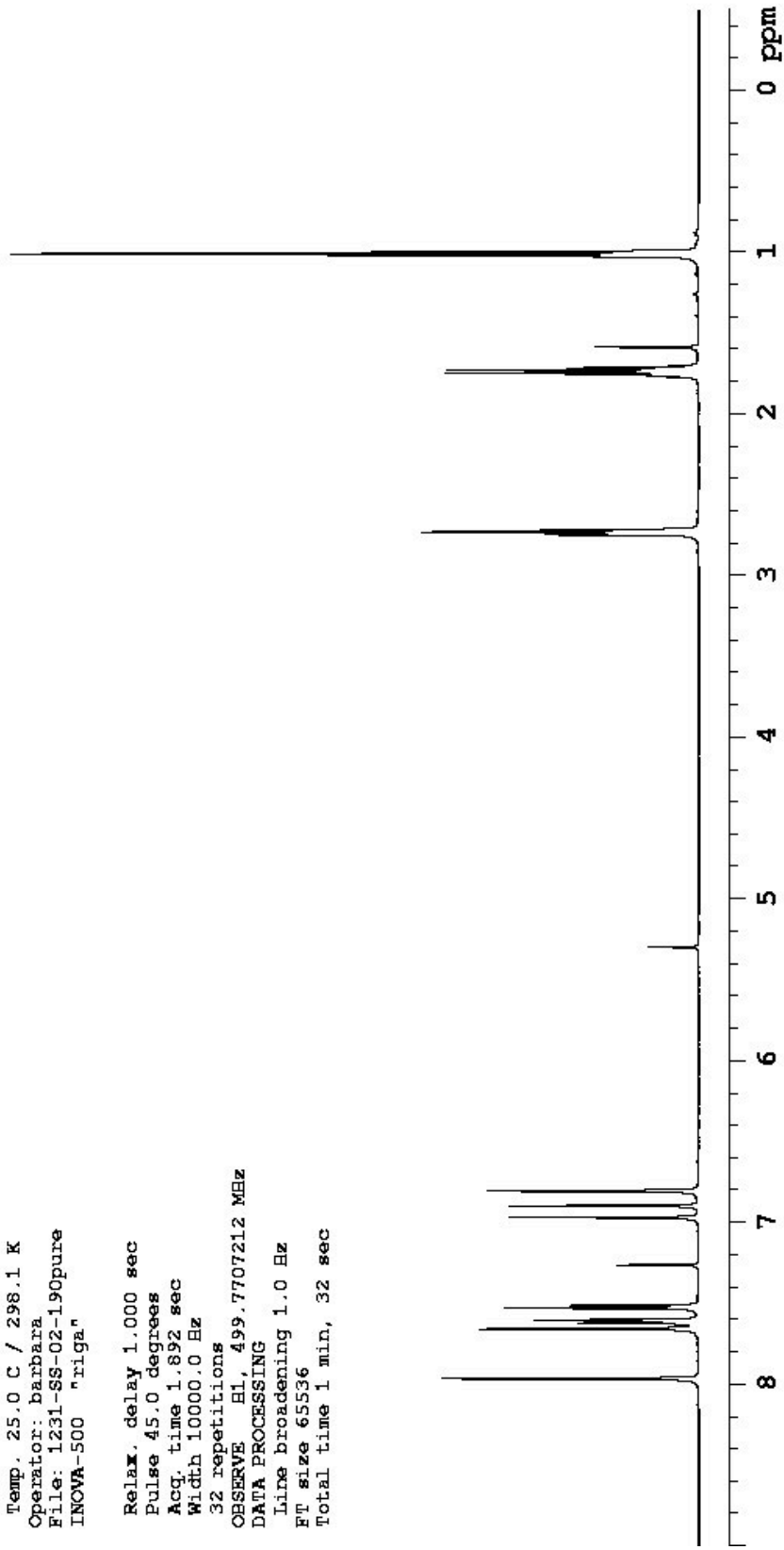
Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1231-SS-02-190pure  
INOVA-500 "riga"

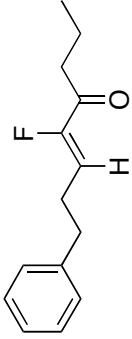
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707212 MHz  
DATA PROCESSING  
Line broadening 1.0 Hz  
F1 size 65536  
Total time 1 min, 32 sec



**22b: Z-isomer**  
500 MHz; CDCl<sub>3</sub>







**23b: Z-isomer**  
500 MHz; CDCl<sub>3</sub>

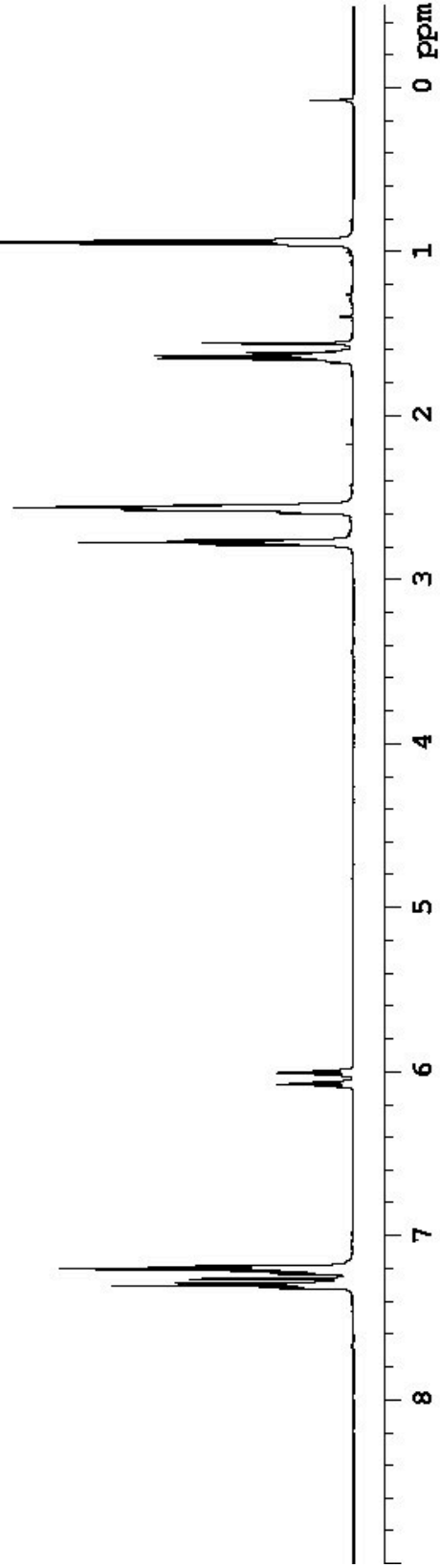
1231-SS-02-170-DCM-pure

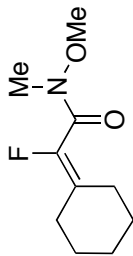
Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1231-SS-02-170-DCM-pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
24 repetitions  
OBSERVE H1, 499.7707215 MHz  
DATA PROCESSING  
Line broadening 1.0 Hz  
F1 size 65536  
Total time 1 min, 32 sec





24

500 MHz; CDCl<sub>3</sub>

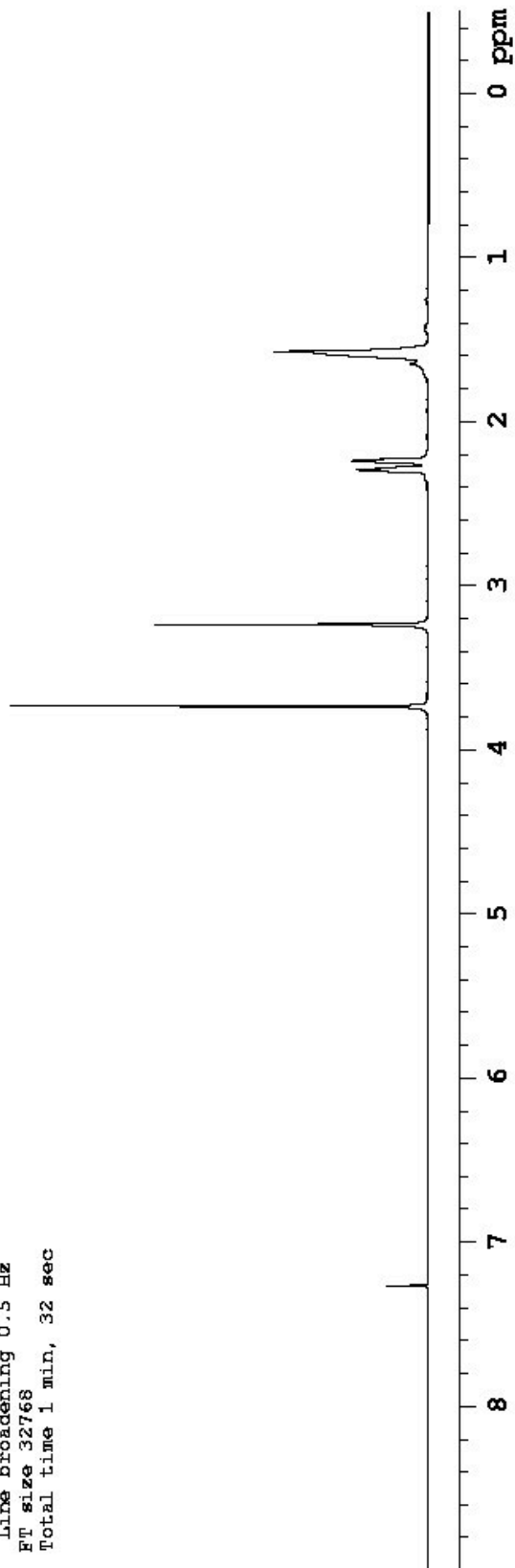
1222-SB-03-171-p

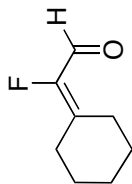
Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-171-p  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 7544.3 Hz  
32 repetitions  
OBSERVE H1, 499.7707226 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
F1 size 32768  
Total time 1 min, 32 sec





25

500 MHz; CDCl<sub>3</sub>

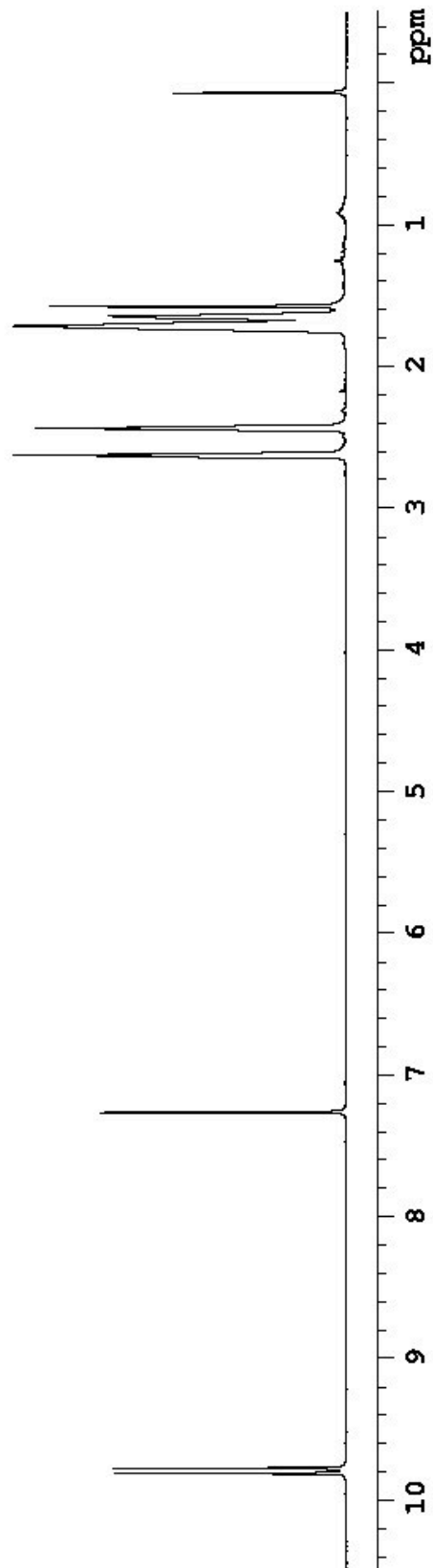
1222-SB-03-172-pure

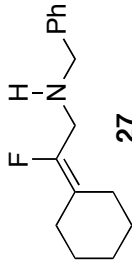
Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-172-pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 10000.0 Hz  
32 repetitions  
OBSERVE H1, 499.7707224 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min, 32 sec





500 MHz; CDCl<sub>3</sub>

1222-SB-03-174-pure

Archive directory: /export/home/mkl/vnmrSYS/data  
Sample directory: auto\_13Dec2004

Pulse Sequence: s2pul

Solvent: cdcl3  
Temp. 25.0 C / 298.1 K  
Operator: barbara  
File: 1222-SB-03-174pure  
INOVA-500 "riga"

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.892 sec  
Width 7544.3 Hz  
24 repetitions  
OBSERVE H1, 499.7707226 MHz  
DATA PROCESSING  
Line broadening 0.5 Hz  
F1 size 32768  
Total time 1 min, 32 sec

