

Supporting Information

Novel Synthesis of (*Z*)-Difluoroacrylates via Highly Stereoselective Addition-elimination Reaction

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Experimental section

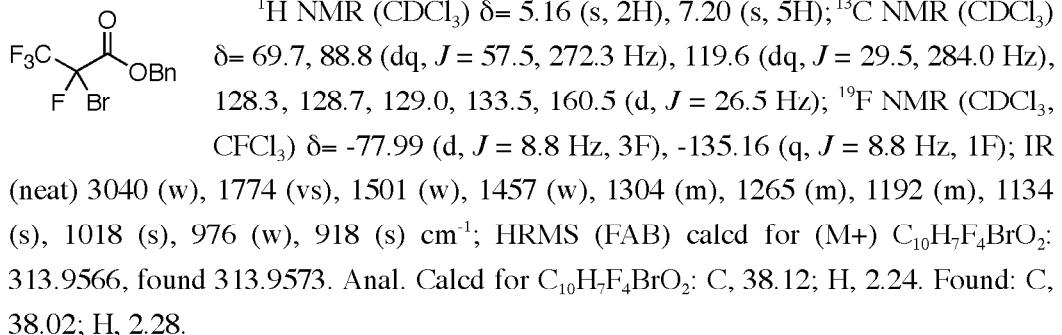
1. General Method.

All reactions were carried out in an oven-dried glassware under an atmosphere of argon, and all the reagents and anhydrous solvents were commercially available. The reagents were used without further purification or, if necessary, purified by distillation on appropriate drying agents. The isomeric mixtures of β -bromostyrene were employed in the reaction. Melting points were recorded on a Shimadzu MM-2 type instrument at atmospheric pressure. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 spectrometer operating at 500.13 MHz and 125.75 MHz, respectively. CDCl_3 was used as solvent in all NMR measurements and chemical shifts were recorded in ppm relative to internal tetramethylsilane. ^{19}F NMR spectra were measured for CDCl_3 solutions with a JEOL JNM-EX90A spectrometer operating at 84.10 MHz. All ^{19}F chemical shifts were reported in ppm relative to trichlorofluoromethane (CFCl_3) as an internal standard. IR spectra were determined with a Shimadzu FT-IR 8200 PC spectrophotometer. High resolution mass spectra were taken with a JEOL JMS-700 MS spectrometer. Elemental analyses were conducted with a Yanaco CHN CORDER MT-5 instrument. Column chromatography was carried out on silica gel (Wako gel C-200) and TLC analysis was performed on silica gel TLC plates (Merck, Silica gel 60 F₂₅₄).

2. Preparation of benzyl 2-bromo-2,3,3,3-tetrafluoropropanoate

A 50 mL-three necked round bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a solution of benzyl alcohol (3.244g, 30 mmol) and Et_3N (2.277 g, 22 mmol) in diethyl ether (26 mL). To this solution was slowly added 3.487 g (14 mmol) of 2-bromo-2,3,3,3-tetrafluoropropenoyl chloride in Et_2O (4 mL) *via* a syringe at 0 °C. After being stirred for 15 min. at 0 °C and then stirred for 20 h at room temperature. The reaction mixture was poured into ice-cooled water (50 mL), followed by extraction with ether (30 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (2:1) yielded pure product, benzyl 2-bromo-2,3,3,3-tetrafluoropropanoate (4.233g, 94%).

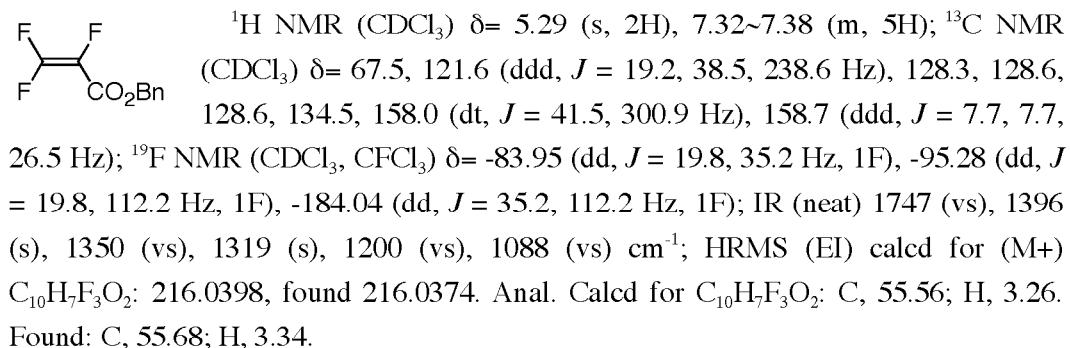
2.1. Benzyl 2-bromo-2,3,3,3-tetrafluoropropanoate



3. Preparation of benzyl 2,3,3-trifluoroacrylate (1)

A 50 mL-three necked round bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a suspended solution of Zn dust (0.420 g, 11 mmol) in diethyl ether (16 mL). To this suspended solution was slowly added diethylaluminum chloride in hexane (0.95 mL, 1.0 mmol) and benzyl 2-bromo-2,3,3,3-tetrafluoropropanoate (3.139 g, 10 mmol) in Et_2O . After being stirred for 30 min. at room temperature, the reaction mixture was poured into an ice-cooled saturated aqueous ammonium chloride (50 mL). The resultant mixture was extracted with ether (30 mL \times 5) and the organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator under reduced pressure. Column chromatography of the residue using hexane/benzene (5:1) gave pure product, benzyl 2,3,3-trifluoroacrylate.

3.1. Benzyl 2,3,3-trifluoroacrylate (1)



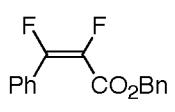
*4. Typical procedure for reaction of **1** with phenylmagnesium bromide (**3a**) in the presence of a catalytic amount of CuBr*

A 50 mL-three necked round bottomed flask equipped with a magnetic stirrer bar, a thermometer, a rubber septum and an inlet tube for argon was charged with a suspended solution of cuprous bromide (0.018 g, 0.125 mmol) in THF (0.5 mL). To this suspended solution was slowly dropwise added a solution of phenylmagnesium bromide (**a**, 1.5mmol) in THF at -78 °C. To the resulting solution was slowly added 0.108 g (0.50 mmol) of **1** in THF (1.5 mL) via a syringe at -78 °C. After being stirred for 1 h at -78 °C, the reaction mixture was poured into ice-cooled water (50 mL), followed by extraction with ether (30 mL × 5). The organic layers were dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. Column chromatography of the residue using hexane/benzene (2:1) yielded pure product, benzyl 2,3-difluoro-3-phenylacrylate (**2a**). The stereoisomers of all compounds except for **2e**, **2j**, **2m**, and **2n** could not be separated by silica gel column chromatography.

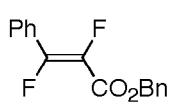
*4.1. Benzyl 2,3-difluoro-3-phenylacrylate (**2a**)*

M.P. 60~61 °C; IR (KBr) 3040 (w), 1736 (vs), 1666 (vs), 1447 (s), 1393 (s), 1277 (vs), 1165 (s), 1084 (vs), 1026 (s), 968 (vs), 945 (s) cm⁻¹; HRMS (EI) calcd for (M+) C₁₆H₁₂F₂O₂: 274.0805, found 274.0801. Anal. Calcd for C₁₆H₁₂F₂O₂: C, 70.07; H, 4.41. Found: C, 69.67; H, 4.27.

Z isomer

 ¹H NMR (CDCl₃) δ= 5.17 (s, 2H), 7.17-7.32 (m, 5H), 7.36~7.53 (m, 5H); ¹³C NMR (CDCl₃) δ= 67.2, 128.0, 128.5, 129.3 (dd, *J* = 3.3, 3.3 Hz), 314.1, 134.5, 135.1, 137.2 (dd, *J* = 21.9, 254.5 Hz), 156.3 (dd, *J* = 16.4, 267.1 Hz), 160.2 (dd, *J* = 8.0, 29.4 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -99.88 (d, *J* = 6.6 Hz, 1F), -148.73 (d, *J* = 6.6 Hz, 1F).

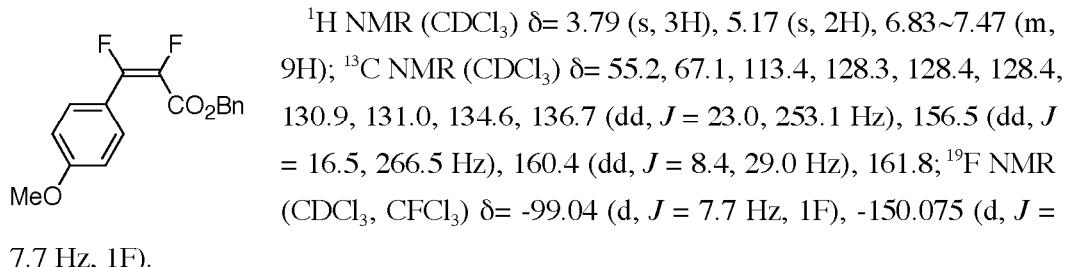
E isomer

 ¹H NMR (CDCl₃) δ= 5.15 (s, 2H), 7.15~7.32 (m, 5H), 7.34~7.51 (m, 5H); ¹³C NMR (CDCl₃) δ= 67.2, 128.0, 128.5, 129.3 (dd, *J* = 3.3, 3.3 Hz), 314.1, 134.5, 135.1, 137.2 (dd, *J* = 21.9, 254.5 Hz), 156.3 (dd, *J* = 16.4, 267.1 Hz), 160.2 (dd, *J* = 8.0, 29.4 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -133.85 (d, *J* = 127.6 Hz, 1F), -162.16 (d, *J* = 127.6 Hz, 1F).

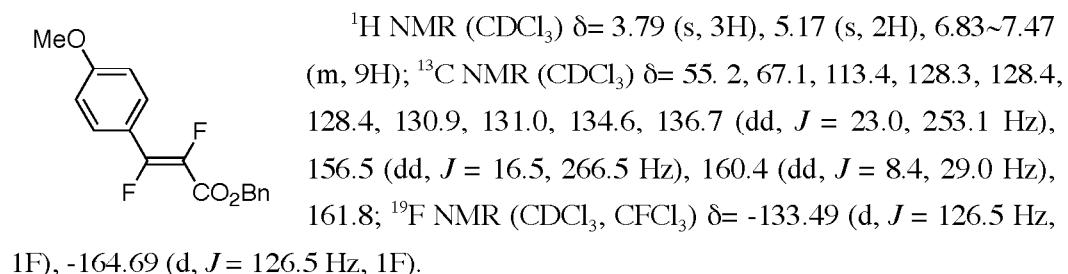
4.2. Benzyl 2,3-difluoro-3-(4-methoxyphenyl)acrylate (**2b**)

M.P. 47~49 °C; IR (KBr) 3506 (w), 1720 (vs), 1605 (vs), 1512 (s), 1462 (m), 1389 (s), 1258 (vs), 1180 (vs), 1088 (vs), 988 (m) cm⁻¹; HRMS (EI) calcd for (M+) C₁₇H₁₄F₂O₃: 304.0911, found 304.0909. Anal. Calcd for C₁₇H₁₄F₂O₃: C, 67.10; H, 4.64. Found: C, 67.37; H, 4.57.

Z isomer



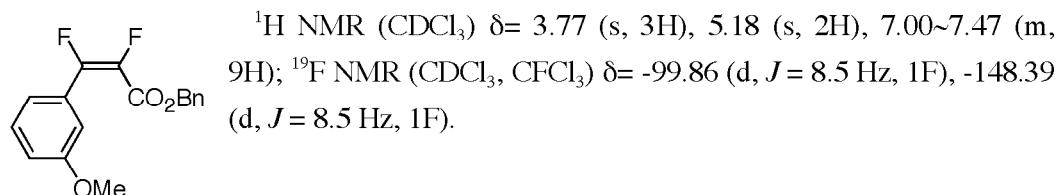
E isomer



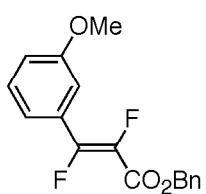
4.3. Benzyl 2,3-difluoro-3-(3-methoxyphenyl)acrylate (**2c**)

IR (KBr) 3067 (m), 2961 (m), 1732 (vs), 1686 (s), 1581 (s), 1492 (s), 1383 (s), 1294 (vs), 1165 (vs), 1095 (vs) cm⁻¹; HRMS (FAB) calcd for (M+) C₁₇H₁₄F₂O₃: 304.0911, found 304.0919.

Z isomer

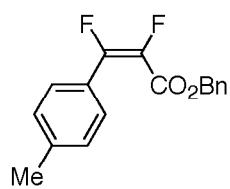


E isomer



¹H NMR (CDCl₃) δ= 3.84 (s, 3H), 5.38 (s, 2H), 7.00~7.47 (m, 9H); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -133.32 (d, *J* = 127.1 Hz, 1F), -161.29 (d, *J* = 127.1 Hz, 1F).

4.4. Benzyl (Z)-2,3-difluoro-3-(4-methylphenyl)acrylate (2e)

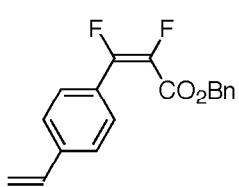


M.P. 58~59 °C; ¹H NMR (CDCl₃) δ= 2.38 (s, 3H), 5.17 (s, 2H), 7.16~7.20 (m, 4H), 7.30~7.42 (m, 5H); ¹³C NMR (CDCl₃) δ= 21.5, 67.2, 125.0, 158.2, 128.3, 128.43, 128.5, 128.8, 129.2 (dd, *J* = 3.3, 3.3 Hz), 134.6, 137.0 (dd, *J* = 22.9, 254.3 Hz), 156.6 (dd, *J* = 16.3, 267.0 Hz), 160.4 (dd, *J* = 8.3, 29.0 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -99.41 (d, *J* = 6.6 Hz, 1F), -149.46 (d, *J* = 6.6 Hz, 1F); IR (neat) 2920 (w), 1724 (vs), 1682 (s), 1497 (w), 1327 (s), 1281 (s), 1169 (vs), 1092 (vs), 984 (s) cm⁻¹; HRMS (EI) calcd for (M+) C₁₇H₁₄F₂O₂: 288.0962, found 288.0943. Anal. Calcd for C₁₇H₁₄F₂O₂: C, 70.83; H, 4.89. Found: C, 71.14; H, 4.93.

4.5. Benzyl 2,3-difluoro-3-(4-vinylphenyl)acrylate (2f)

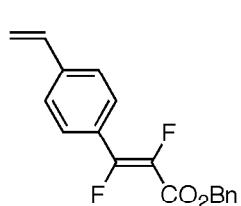
M.P. 54~55 °C; IR (KBr) 2372 (w), 1736 (vs), 1666 (s), 1454 (m), 1393 (m), 1277 (m), 1180 (m), 1084 (vs) cm⁻¹; HRMS (FAB) calcd for (M+) C₁₈H₁₄F₂O₂: 300.0962, found 300.0964.

Z isomer



¹H NMR (CDCl₃) δ= 5.18 (s, 2H), 5.36 (d, *J* = 8.5 Hz, 1H), 5.82 (d, *J* = 17.7 Hz, 1H), 6.71 (dd, *J* = 10.8 Hz, 17.7 Hz, 1H), 7.17~7.49 (m, 9H); ¹³C NMR (CDCl₃) δ= 67.3, 116.1, 125.8, 128.3, 128.5, 129.6 (dd, *J* = 3.2, 3.2 Hz), 134.5, 135.7, 135.9, 137.2 (dd, *J* = 23.3, 255.0 Hz), 140.3, 140.4, 156.2 (dd, *J* = 16.9, 266.5 Hz), 160.2 (dd, *J* = 8.4, 29.1 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -100.84 (d, *J* = 4.4 Hz, 1F), -148.45 (d, *J* = 4.4 Hz, 1F).

E isomer

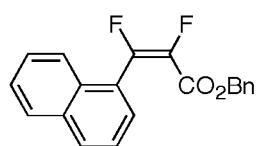


¹H NMR (CDCl₃) δ= 5.18 (s, 2H), 5.38 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 17.9 Hz, 1H), 6.71 (dd, *J* = 10.8 Hz, 17.9 Hz, 1H), 7.17~7.49 (m, 9H); ¹³C NMR (CDCl₃) δ= 67.2, 116.5, 126.4, 128.3, 128.5, 129.6 (dd, *J* = 3.2, 3.2 Hz), 134.5, 135.7, 135.9, 137.2 (dd, *J* = 23.3, 255.0 Hz), 140.3, 140.4, 156.2 (dd, *J* = 16.9, 266.5 Hz), 160.2 (dd, *J* = 8.4, 29.1 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -134.51 (d, *J* = 125.4 Hz, 1F), -161.85 (d, *J* = 125.4 Hz, 1F).

4.6. Benzyl 2,3-difluoro-3-(1-naphthyl)acrylate (2h)

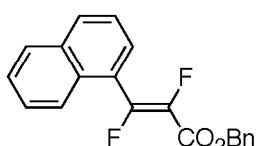
M.P. 36~38 °C; IR (KBr) 3063 (w), 2959 (w), 1732 (vs), 1686 (m), 1385 (m), 1319 (s), 1288 (m), 1169 (s), 1123 (s), 1042 (s) cm⁻¹; HRMS (FAB) calcd for (M+) C₂₀H₁₄F₂O₂: 324.0962, found 324.0965. Anal. Calcd for C₂₀H₁₄F₂O₂: C, 74.07; H, 4.35. Found: C, 73.97; H, 4.48.

Z isomer



¹H NMR (CDCl₃) δ= 4.94 (s, 2H), 6.76 (m, 2H), 7.11~7.22 (m, 3H), 7.39~7.42 (m, 1H), 7.51~7.55 (m, 3H), 7.86~7.93 (m, 3H); ¹³C NMR (CDCl₃) δ= 67.2, 124.3, 124.7, 126.5, 127.4, 127.8, 128.2, 128.3, 128.5, 129.5, 131.2, 131.61, 131.64, 133.3, 134.1, 138.5 (dd, *J* = 21.6, 254.5 Hz), 155.0 (dd, *J* = 15.9, 271.3 Hz), 160.0 (dd, *J* = 8.4, 30.2 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -94.87 (d, *J* = 11.0 Hz, 1F), -147.01 (d, *J* = 11.0 Hz, 1F).

E isomer

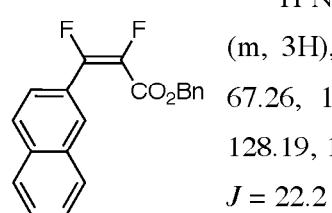


¹H NMR (CDCl₃) δ= 5.43 (s, 2H), 7.35~7.42 (m, 5H), 7.48~7.57 (m, 5H), 7.96~7.99 (m, 2H); ¹³C NMR (CDCl₃) δ= 67.2, 124.4, 124.7, 126.5, 127.4, 127.8, 128.2, 128.3, 128.5, 129.5, 131.2, 131.61, 131.64, 133.3, 134.1, 138.5 (dd, *J* = 21.6, 254.5 Hz), 155.0 (dd, *J* = 15.9, 271.3 Hz), 160.0 (dd, *J* = 8.4, 30.2 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -114.56 (d, *J* = 137.6 Hz, 1F), -160.00 (d, *J* = 137.6 Hz, 1F).

4.7. Benzyl 2,3-difluoro3-(2-naphthyl)acrylate (**2i**)

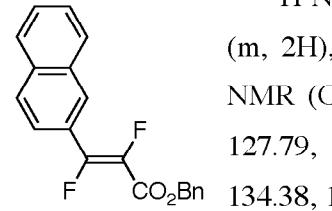
M.P. 79~80 °C; IR (KBr) 3063 (w), 1736 (s), 1678 (m), 1501 (w), 1454 (w), 1323 (m), 1231 (w), 1153 (w), 1080 (vs) cm⁻¹; HRMS (FAB) calcd for (M+) C₂₀H₁₄F₂O₂: 324.0962, found 324.0959. Anal. Calcd for C₂₀H₁₄F₂O₂: C, 74.07; H, 4.35. Found: C, 73.82; H, 4.58.

Z isomer



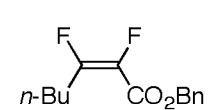
¹H NMR (CDCl₃) δ= 5.13 (s, 2H), 7.05-7.23 (m, 5H), 7.47-7.55 (m, 3H), 7.75-7.82 (m, 3H), 8.02 (s, 1H); ¹³C NMR (CDCl₃) δ= 67.26, 125.21, 125.35, 125.37, 126.69, 127.69, 127.79, 127.84, 128.19, 128.37, 128.71, 130.18, 132.22, 134.27, 134.38, 137.41 (dd, J = 22.2 Hz, 254.6 Hz), 156.44 (dd, J = 16.6 Hz, 267.3 Hz), 160.24 (dd, J = 8.1 Hz, 29.4 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -99.67 (d, J = 7.8 Hz, 1F), -147.96 (d, J = 7.8 Hz, 1F).

E isomer



¹H NMR (CDCl₃) δ= 5.40 (s, 2H), 7.34-7.42 (m, 3H), 7.46-7.47 (m, 2H), 7.50-7.59 (m, 2H), 7.79-7.91 (m, 4H), 8.29 (s, 1H); ¹³C NMR (CDCl₃) δ= 67.26, 125.21, 125.35, 125.37, 126.69, 127.69, 127.79, 127.84, 128.19, 128.37, 128.71, 130.18, 132.22, 134.27, 134.38, 137.41 (dd, J = 22.2 Hz, 254.6 Hz), 156.44 (dd, J = 16.6 Hz, 267.3 Hz), 160.24 (dd, J = 8.1 Hz, 29.4 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -133.51 (d, J = 127.7 Hz, 1F), -161.98 (d, J = 127.7 Hz, 1F).

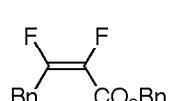
4.8. Benzyl (Z)-3-butyl-2,3-difluoroacrylate (**2j**)



¹H NMR (CDCl₃) δ= 0.89 (t, J = 7.3 Hz, 3H), 1.30-1.38 (m, 2H), 1.54~1.60 (m, 2H), 2.74 (ddt, J = 3.0 Hz, 8.0 Hz, 27.0 Hz, 2H), 5.26 (s, 2H), 7.32~7.39 (m, 5H); ¹³C NMR (CDCl₃) δ= 13.6, 22.0, 27.9 (d, J = 2.7 Hz), 27.7 (dd, J = 2.0, 20.5 Hz), 67.1, 128.4, 128.5, 128.6, 134.9, 136.8 (dd, J = 19.2, 251.5 Hz), 160.4 (dd, J = 11.6, 272.4 Hz), 160.9 (dd, J = 10.1, 27.5 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -106.17 (dt, J = 4.4 Hz, 27.0 Hz, 1F), -155.07 (d, J =

4.4 Hz, 1F); IR (neat) 3036 (w), 2874 (w), 1732 (s), 1686 (m), 1501 (w), 1431 (w), 1312 (s), 1157 (m), 1022 (m) cm^{-1} ; HRMS (EI) calcd for (M+) $\text{C}_{14}\text{H}_{16}\text{F}_2\text{O}_2$: 254.1118, found 254.1112. Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{O}_2$: C, 66.13; H, 6.34. Found: C, 66.52; H, 6.44.

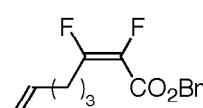
4.9. Benzyl (Z)-3-benzyl-2,3-difluoroacrylate (**2k**)

 ^1H NMR (CDCl_3) δ = 4.01 (dd, J = 2.8 Hz, 26.9 Hz, 2H), 5.24 (s, 2H), 7.16-7.33 (m, 10H); ^{13}C NMR (CDCl_3) δ = 34.59 (d, J = 20.6 Hz), 67.42, 127.35, 128.47, 128.69, 128.74, 128.83, 134.40, 134.42, 134.74, 136.92 (dd, J = 18.9 Hz, 254.7 Hz), 157.95 (dd, J = 13.0 Hz, 272.6 Hz), 160.90 (dd, J = 9.5 Hz, 27.7 Hz); ^{19}F NMR (CDCl_3 , CFCl_3) δ = -105.70 (dt, J = 2.0 Hz, 26.9 Hz, 1F), -153.65 (d, J = 2.0 Hz, 1F); IR (neat) 3067 (w), 3032 (w), 1732 (vs), 1690 (vs), 1605 (w), 1497 (m), 1454 (m), 1420 (w), 1385 (s), 1312 (vs), 1258 (w), 1181 (vs), 1146 (vs), 1076 (s), 1030 (vs), 799 (w), 764 (s), 706 (vs) cm^{-1} ; HRMS (EI) calcd for (M+) $\text{C}_{17}\text{H}_{14}\text{F}_2\text{O}_2$: 288.0962, found 288.0961. Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{F}_2\text{O}_2$: C, 70.83; H, 4.89. Found: C, 70.91; H, 5.07.

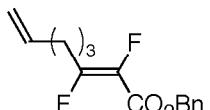
4.10. Benzyl 2,3-difluoro-3-(4-pentenyl)acrylate (**2l**)

IR (neat) 3069 (vs), 2939 (vs), 1685 (vs), 1609 (m), 1499 (vs), 1383 (vs), 1147 (vs), 1028 (vs) cm^{-1} ; HRMS (EI) calcd for (M+) $\text{C}_{15}\text{H}_{16}\text{F}_2\text{O}_2$: 266.1118, found 2666.1111.

Z isomer

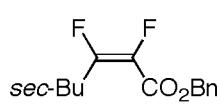
 ^1H NMR (CDCl_3) δ = 1.72 (tt, J = 7.5, 7.5 Hz, 2H), 2.09 (dt, J = 7.5, 7.5 Hz, 2H), 2.77 (dtd, J = 25.4, 7.5, 2.4 Hz, 2H), 4.99 (dd, J = 11.3, 1.6 Hz, 1H), 5.02 (dd, J = 17.1, 1.6 Hz, 1H), 5.28 (s, 2H), 5.76 (dt, J = 11.3, 7.5 Hz, 1H), 7.33~7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ = 15.20, 25.08, 27.93 (d, J = 20.3 Hz), 32.82, 65.78, 67.16, 115.43, 128.62, 129.37, 134.84, 136.85 (dd, J = 252.0, 19.1 Hz), 137.31, 160.03 (dd, J = 272.2, 12.6 Hz), 160.86 (dd, J = 27.5, 9.5 Hz); ^{19}F NMR (CDCl_3 , CFCl_3) δ = -106.49 (t, J = 25.4 Hz, 1F), -154.54 (s, 1F).

E isomer



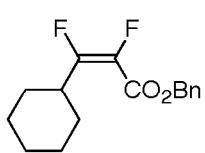
¹H NMR (CDCl₃) δ=1.70-1.80 (m, 2H), 2.15 (dt, *J* = 6.1, 6.1 Hz, 2H), 2.52 (ddt, *J* = 22.5, 6.1, 6.1 Hz, 2H), 5.00-5.10 (m, 2H), 5.31 (s, 2H), 5.72~5.85 (m, 1H), 7.33~7.45 (m, 5H); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -124.06 (dt, *J* = 129.9, 22.5 Hz, 1F), -167.08 (d, *J* = 129.9 Hz, 1F).

4.11. Benzyl (Z)-3-sec-butyl- 2,3-difluoroacrylate (2m)



¹H NMR (CDCl₃) δ= 0.82 (t, *J* = 7.5 Hz, 3H), 1.09 (d, *J* = 3.5 Hz, 3H), 1.46 (dq, *J* = 7.5 Hz, 42.5 Hz, 2H), 3.35 (dtq, *J* = 3.5 Hz, 30.8 Hz, 42.5Hz, 1H), 5.21 (d, *J* = 7.5 Hz, 2H), 7.26~7.32 (m, 5H); ¹³C NMR (CDCl₃) δ= 11.6, 16.6, 26.2, 34.1 (d, *J* = 19.8 Hz), 67.1, 128.3, 128.6, 128.7, 134.9, 136.8 (dd, *J* = 19.2, 251.5 Hz), 160.1 (dd, *J* = 11.6, 272.4 Hz), 161.3 (dd, *J* = 10.1, 27.5 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -121.14 (d, *J* = 30.8 Hz, 1F), -155.41 (s, 1F); IR (neat) 2970 (m), 2936 (w), 1732 (vs), 1682 (m), 1308 (vs), 1130 (m), 1022 (m) cm⁻¹; HRMS (FAB) calcd for (M+) C₁₄H₁₆F₂O₂: 254.1118, found 254.1120. Anal. Calcd for C₁₄H₁₆F₂O₂: C, 66.13; H, 6.34. Found: C, 65.95; H, 6.70.

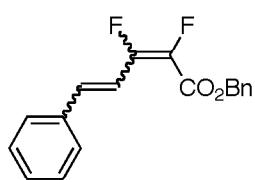
4.12. Benzyl (Z)-3-cyclohexyl- 2,3-difluoroacrylate (2n)



M.P. 60~62 °C; ¹H NMR (CDCl₃) δ= 1.13~1.31 (m, 4H), 1.46~1.54 (m, 2H), 1.67~1.80 (m, 4H), 3.33 (dtt, *J* = 12.0 Hz, 12.0 Hz, 32.7Hz, 1H), 5.27 (s, 2H), 7.34~7.39 (m, 5H); ¹³C NMR (CDCl₃) δ= 25.4, 25.6, 28.5 (d, *J* = 1.7 Hz), 37.0 (dd, *J* = 1.6, 19.3 Hz), 67.1, 128.3, 128.5, 128.6, 134.9, 136.9 (dd, *J* = 19.6 Hz, 257.3 Hz), 161.0 (dd, *J* = 10.0, 27.7 Hz), 163.3 (dd, *J* = 10.7, 275.5 Hz); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -117.31 (d, *J* = 32.7 Hz, 1F), -156.80 (s, 1F); IR (neat) 2932 (vs), 2855 (m), 1728 (vs), 1674 (vs), 1454 (s), 1327 (vs), 1258 (m), 1126 (vs), 1018 (vs) cm⁻¹; HRMS (EI) calcd for (M+) C₁₆H₁₈F₂O₂: 280.1275, found 280.1273. Anal. Calcd for C₁₆H₁₈F₂O₂: C, 68.56; H, 6.47. Found: C, 68.69; H, 6.24.

4.13. Benzyl 2,3-difluoro-3-(2-phenylethenyl)acrylate (2o**)**

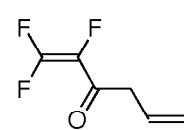
The products were obtained as an inseparable isomeric mixtures.



¹H NMR (CDCl₃) δ=5.34 (s, 3H), 5.35 (s, 3H), 5.37 (s, 3H), 6.65~6.75 (m, 4H), 6.80~7.00 (m, 4H), 7.15~7.65 (m, 4H); ¹⁹F NMR (CDCl₃, CFCl₃) δ=-113.33 (dd, *J* = 14.2, 14.2 Hz, 1F), -125.70 (dd, *J* = 25.3, 25.3 Hz, 1F), -140.07 (dd, *J* = 119.9, 25.3 Hz, 1F), -147.26 (s, 1F), -149.94 (s, 1F), -162.68 (d, *J* = 119.9 Hz, 1F); IR (neat) 3029 (w), 2359 (w), 1723 (vs), 1639 (s), 1496 (m), 1384 (s), 1319 (vs), 1165 (vs), 1075 (vs) cm⁻¹; HRMS (FAB) calcd for (M+Na) C₁₈H₁₄F₂O₂Na: 323.0860, found 323.0863.

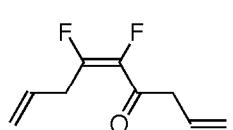
4.14. 1,1,2-Trifluorohexa-1,5-diene-3-one (4p**) and 5,6-Difluoronona-1,5-diene-4-one (**5p**)**

Products **4p** and **5p** could not be separated by a silica gel column chromatography as a sole product. Therefore, the chemical shifts of **4p** and **5p** are determined based on the ¹H and ¹⁹F NMR analyses of the mixture (**4p** and **5p**).



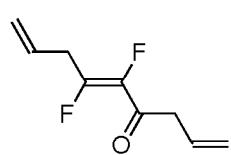
¹H NMR (CDCl₃) δ= 2.37 (dd, *J* = 8.3 Hz, 13.7 Hz, 1H), 2.55 (dd, *J* = 6.8 Hz, 13.7 Hz, 1H), 5.13-5.25 (m, 2H), 5.76-5.87 (m, 1H); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -101.11 (dd, *J* = 33.1 Hz, 83.6 Hz, 1F), -116.36 (dd, *J* = 83.6 Hz, 112.2 Hz, 1F), -178.044 (dd, *J* = 33.1 Hz, 112.2 Hz, 1F)

Z isomer



¹H NMR (CDCl₃) δ= 2.26 (dd, *J* = 8.5 Hz, 13.5 Hz, 1H), 2.37 (dd, *J* = 8.0 Hz, 13.5 Hz, 1H), 2.54 (dd, *J* = 6.5 Hz, 14.0 Hz, 1H), 2.57~2.62 (m, 1H), 3.22~3.28 (m, 1H), 5.09~5.24 (m, 2H), 5.75~5.85 (m, 1H); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -130.03 (t, *J* = 25.3 Hz, 1F), -143.27 (s, 1F).

E isomer

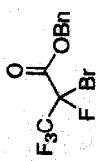


¹H NMR (CDCl₃) δ= 2.26 (dd, *J* = 8.5 Hz, 13.5 Hz, 1H), 2.37 (dd, *J* = 8.0 Hz, 13.5 Hz, 1H), 2.54 (dd, *J* = 6.5 Hz, 14.0 Hz, 1H), 2.57-2.62 (m, 1H), 3.06~3.13 (m, 1H), 5.09~5.24 (m, 2H), 5.75~5.85 (m, 1H); ¹⁹F NMR (CDCl₃, CFCl₃) δ= -15.056 (dt, *J* = 23.1 Hz, 127.6 Hz, 1F), -158.55 (d, *J* = 127.6 Hz, 1F).

Current Data Parameters
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Pulse: 1

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SF: 1.000000 Hz
SSB: 0
DPG: 100000000 Hz
T1: 1.000000 sec
TD: 1000000000 sec
R1: 1.000000 sec
R2: 1.000000 sec
P1: 1000.000000 Hz
PR1: 1.000000 sec
PL1: -6.00 dB

F2 - Processing parameters
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PC: 1.00



Current Data Parameters

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EXPNO : 3
PROCNO : 1

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NS : 2
SW(Hz) : 30000.00 Hz
FIDRES : 0.000007 Hz
AQ : 0.300000 sec
RG : 2048
DE : 7.00 ms
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P1 : 0.000000 sec
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T1 : 0.000000 sec
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Processor Parameters

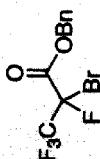
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F2 - Processing parameters

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1D NMR Plot Parameters

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F1 : 200 Hz, 50 sec
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PPPG : 0.00000 Hz
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69.6917

87.8240

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ppm

Current Data Parameters

Name: 4-28

Proton 1

P2 - Acquisition Parameter

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PROTON: 6 mm Helium

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T0: 30700

SL: VENT

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TD: 1000000

SW_VENT:

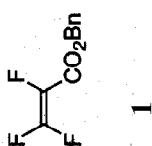
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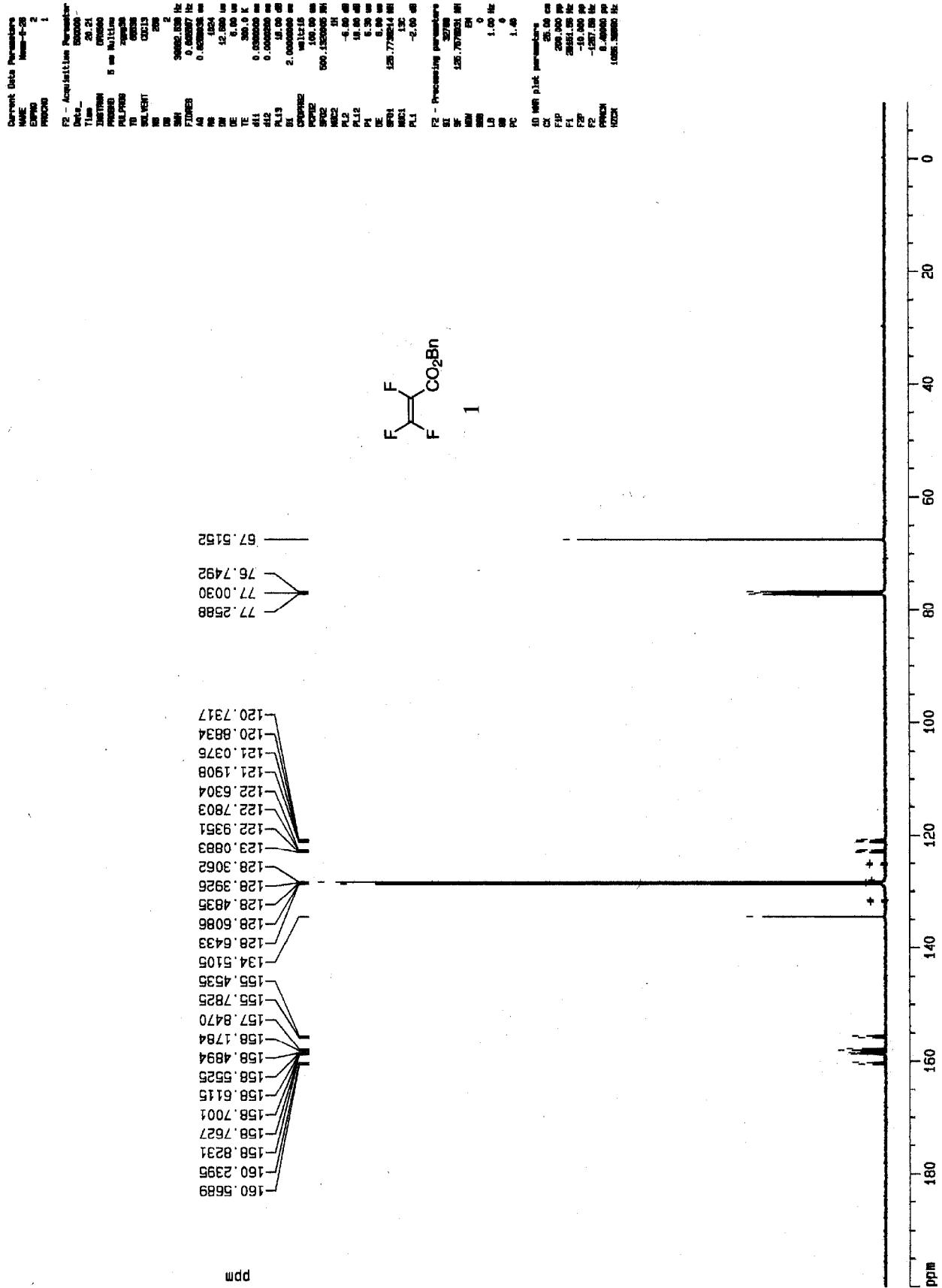
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TD: 30700

SW_VENT:

IR: 10000



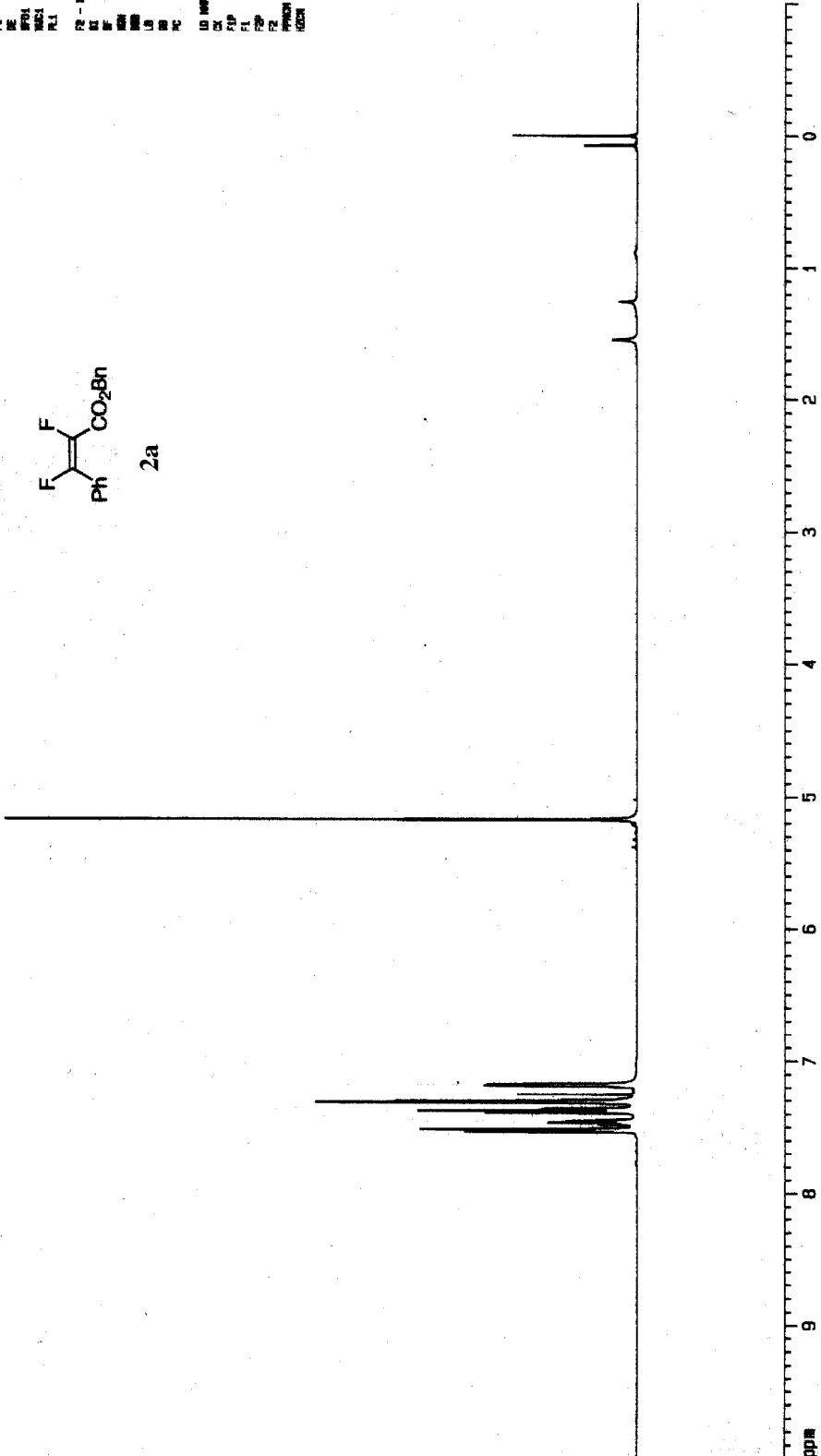
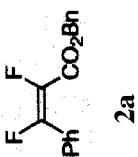


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NUC1: 1H
PL1: -0.00 dB

P2 - Acquisition Parameters
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DW: 100 us
TE: 1.3000000 sec
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P1: 0.30 us
DE: 0.00 us
FID1: 800.1532000 Hz
NUC1: 1H
PL1: -0.00 dB

P2 - Processing parameters
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D1: 0.0000000 sec
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RG: 1.00
TC: 1.00

TD NMR print parameters
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F1: 8000.00 Hz
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SI: 2048



Current Data Parameters
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EXPNO 1
PRODNO 1

F2 - Acquisition parameters

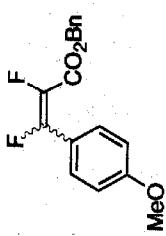
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F2 - Processing parameters

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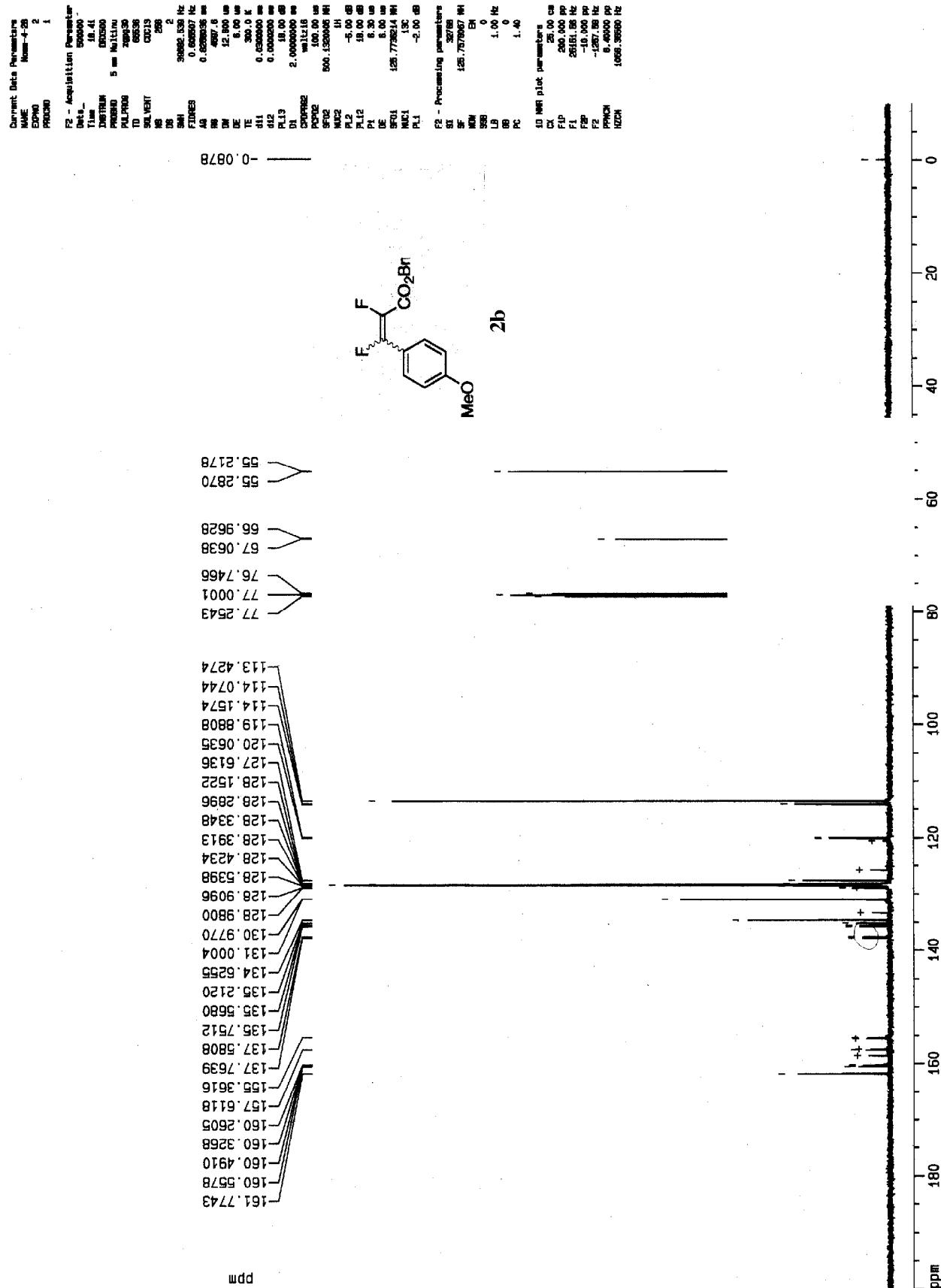
3D NMR plot parameters

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2b



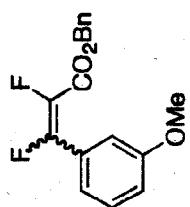


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 DS 2
 SWH 10330.578 Hz
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 AQ 3.1719923 sec
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 TE 295.3 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
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 LB 0.30 Hz
 GB 0
 PC 1.00

F2 - Processing parameters
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 EM 0
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 CX 20.00 cm
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Current Data Parameters

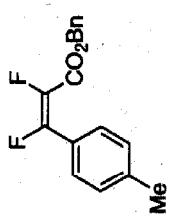
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TDZ2	1.000000000 ms
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F2 - Acquisition Parameter

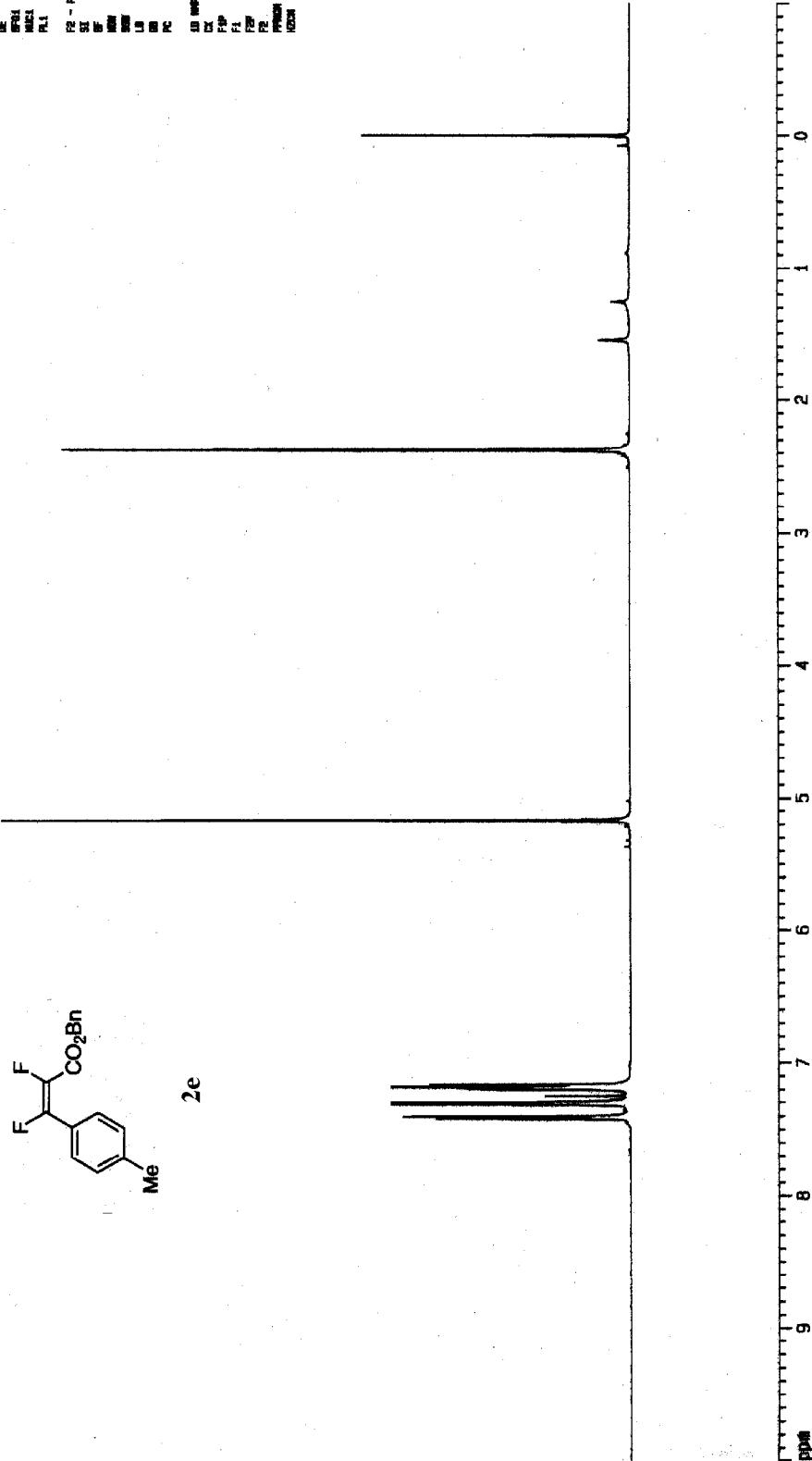
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F2 - Processing parameter

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2e



Current Data Parameters
NAME Name-2-23
EXPNO 1
PROCNO 2

P2 - Acquisition Parameter
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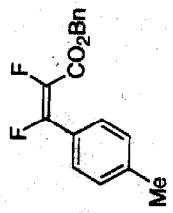
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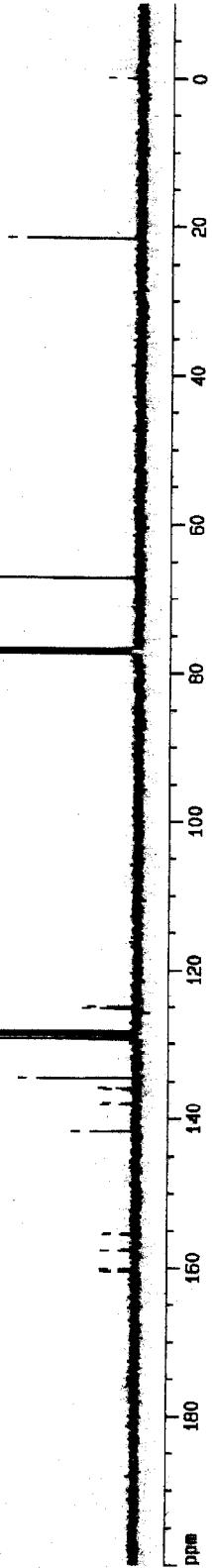
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137.9078
138.0903
141.7032
145.4631
155.5891
157.7154
160.2119
160.2781
160.4426
160.5063



P2 - Processing Parameter
Data-
Time 15.11
TE 1000
D1 5 sec
NUC1 1H
P1 10.00
TD 32768
SWH 2000
SF 1.0000000000000001

RO 1.00
RG 200
DW 1.00
DW1 0

-0.0323



Current Data Parameters
NAME name=11-20
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

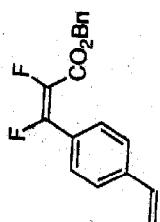
Data_2D 202109 -
Time 47.22
TECHNIQ NMR360
PROBOD 5 mm MAGNETIC
PULPROG zg32
TD 32768
S�ENT 16
DS 2
SWH 1.0590,576 Hz
FIDRES 0.312504 Hz
AQ 1.3880012 ms
RG 200.2
DM 400 us
DE 6.66 us
TE 300.0 K
TM 1.0000000 us
P1 6.38 us
SF01 590.1350000 MHz
NUC1 H
PL1 -6.00,40

F2 - Processing parameters

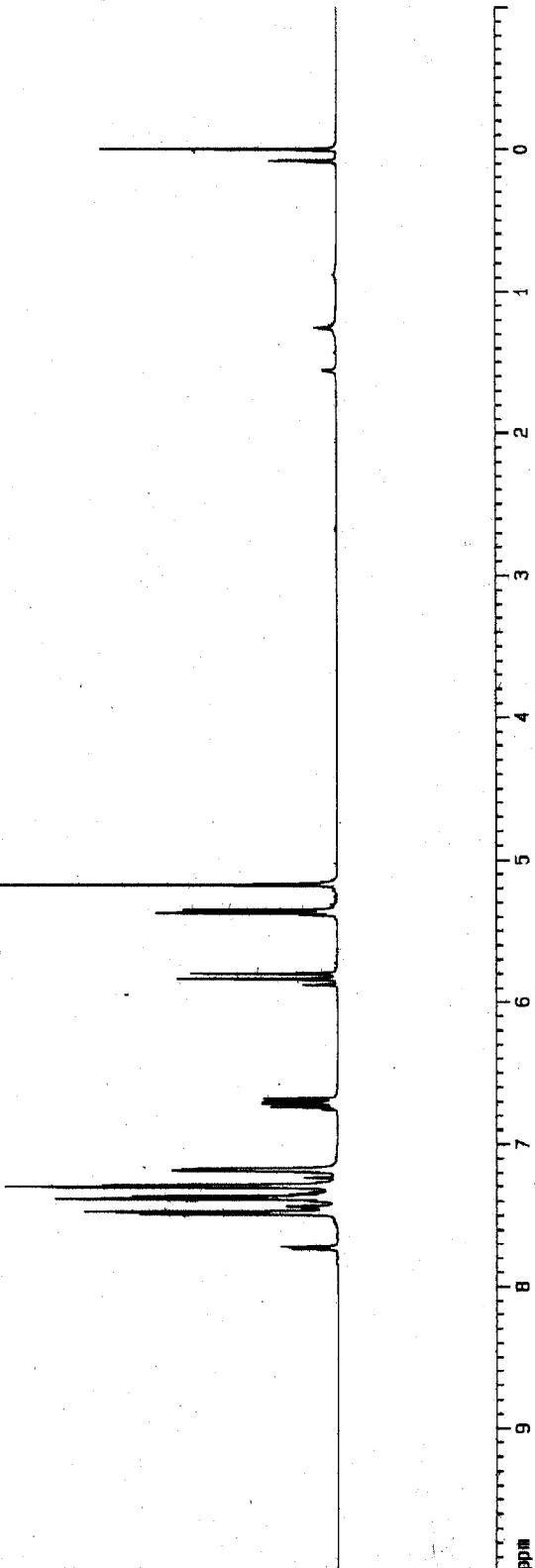
ST 10284
SF 590.1350000 MHz
NMW 1E1
SW 8500
LB 0
RR 0.30,40
RR 0.0
PC 1.00

1D NMR peak parameters

CS 25.00 cm
FP 30,000 pp
F1 500.1350 Hz
F2P -1.000 pp
F2 -200.13 Hz
PPM1 0.44000 pp
HDM 220.05722 Hz



2f



Current Data Parameters

NAME	name-11-29
EXPNO	1
PROBOD	

P2 - Acquisition Parameters

Date	20201229
Time	17:30
INSTRUM	5 mm NMR300
PRGRM	PRGRM
TD	32768
SOLVENT	CDCl ₃
NS	2
SWH	3200.000 Hz
ETR	0.000007 Hz
AB	0.000005 sec
DM	12.800 sec
TE	7.19 ms
TEC	200.0 K
PL1	0.000000 sec
PL2	0.000000 sec
PL3	18.00 dB
DL	0.000000 sec
CPDPR2	wait16
CPDP2	100.00 sec
SP2	600.130006 Hz
N1	3H
PL2	-0.00 dB
PL3	18.00 dB
PI	5.70 ms
SD	428.779234 Hz
ME1	452.
PL1	-1.00 dB

P2 - Processing parameters

SI	32768
SF	1201.7677934 Hz
NUC1	1H
SW	0
LB	1.00 sec
DS	0
PC	1.40

2D NMR plot parameters

CP

CPD

F1

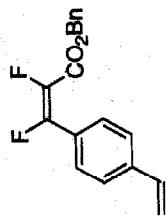
F2

PRGRM

RT2N

67.2671
75.7488
77.0023
77.2572

116.1416
125.7622
128.2503
128.3318
128.4875
128.6143
129.5524
129.5576
134.4698
135.8702
140.3611



2f

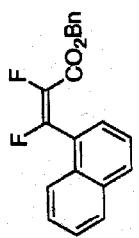


ppm

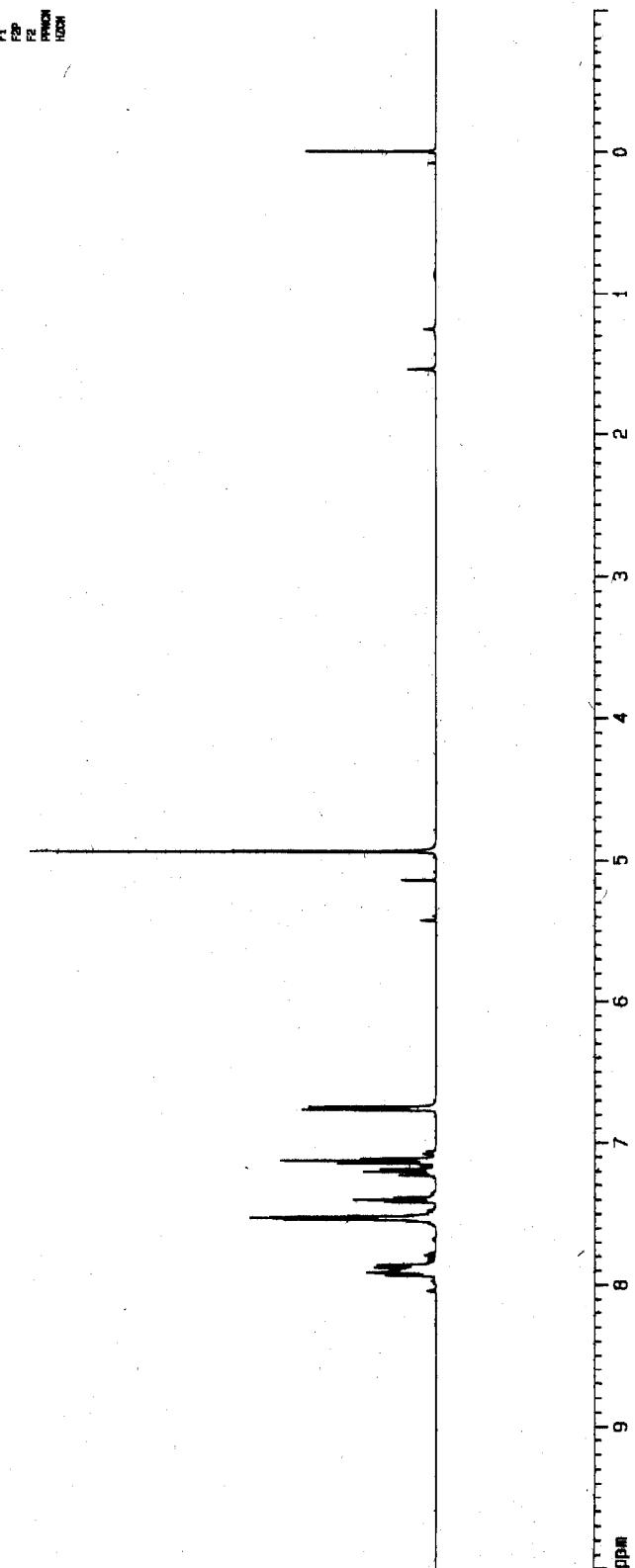
Current Data Parameters
NAME name-0-14
EXPNO 1
PRDNO 1

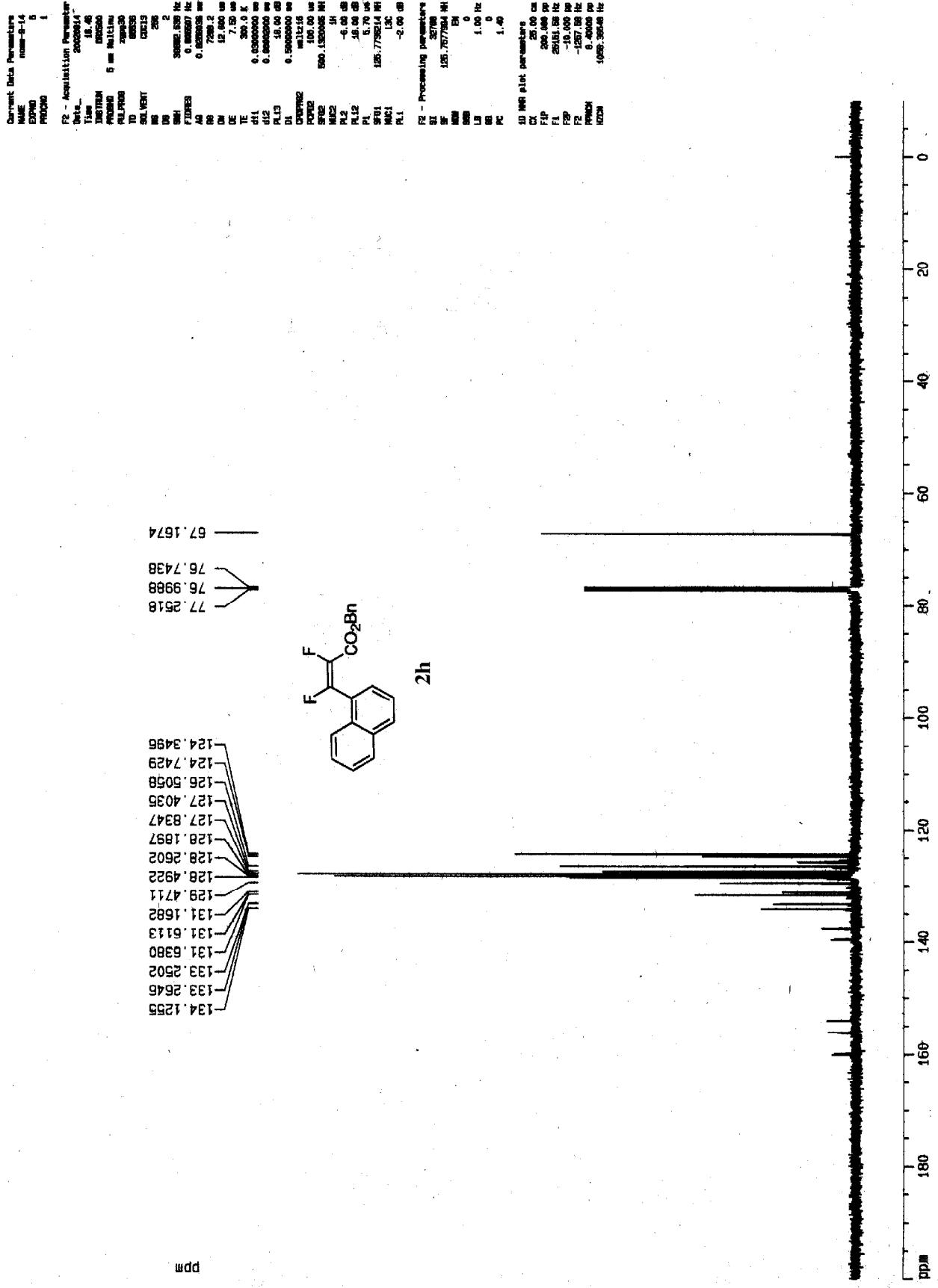
F2 - Acquisition Parameters
Date_ 20020514
Time 10:30
INSTRUM spect
PROBOD 5 mm MFTONE
PULPROG zg30
TD 32768
SWEV 16
NS 2
SWH 10236.876 Hz
SF 0.318284 Hz
DW 1.3880212 us
RG 205.2
IM 40400 us
DE 6.00 us
TE 300.1 K
D1 1.0000000 us
P1 0.30 us
SF01 500.1532000 Hz
NUC1 1H
PL1 -6.00 dB

F2 - Processing parameters
SI 102364
SF 500.1532000 Hz
NUC1 EH
SSB 0
LB 0.30 Hz
RR 0
PC 1.00



2h





Current Data Parameters

NAME:	name=6-i
EXPNO:	1
PROBOD:	

F2 - Acquisition Parameter

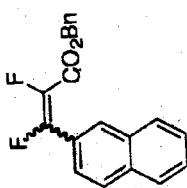
DATA1:	2000000
TIME:	12.40
DURATION:	0.00000
PROBOD:	0 mm Multico
PULPROG:	3230
TD:	32768
SW1:	2048 0.76 Hz
SW2:	0.50000000 Hz
TE:	10.00 us
TM:	0.00 us
TEC:	0.00 us
DRY:	1.00000000 us
PA:	9.38 us
SP01:	900.13300000 Hz
N1:	351
PL1:	-0.00 dB

F2 - Processing parameter

ST:	40964
SF:	100.13300000 Hz
WDW:	FT
SSB:	0
LB:	0.39 Hz
RR:	0
PC:	1.00

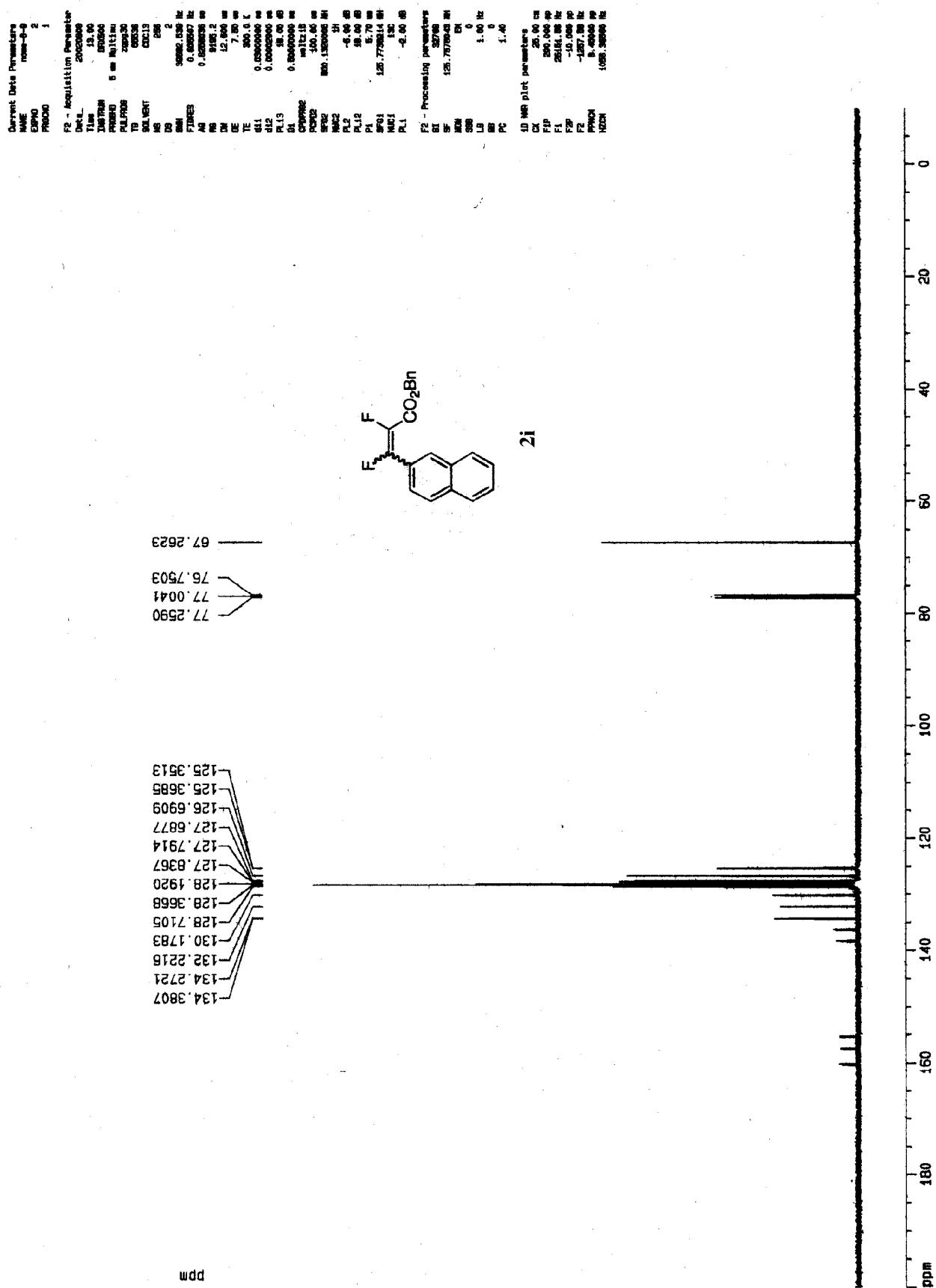
1D NMR plot parameters

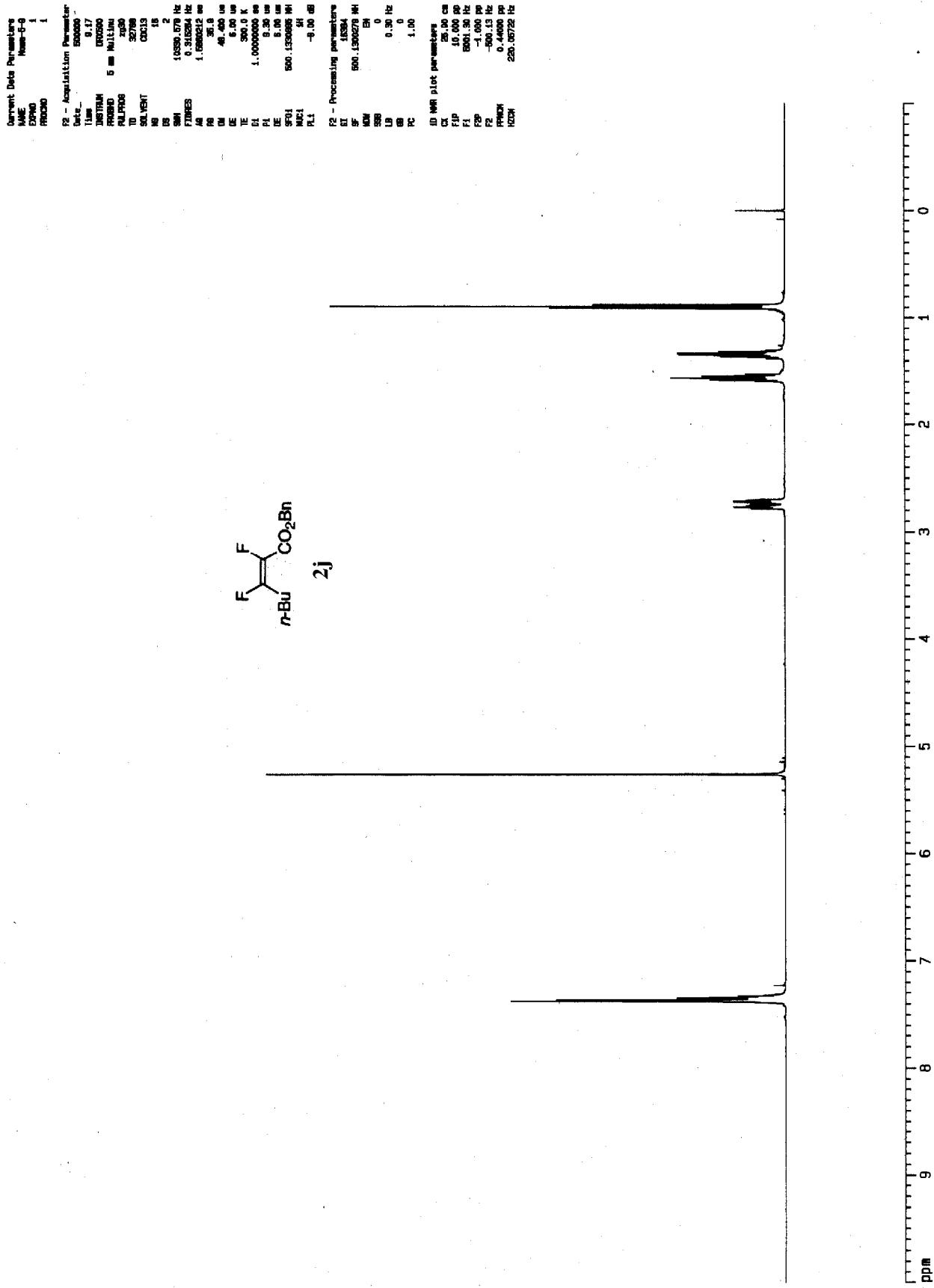
CX:	25.00 cm
FLP:	10.400179
F1:	6001.50 Hz
FP1:	-1.000179
F2:	-66.53 Hz
PPMCH:	0.44000179
PPDM:	229.48728179 Hz

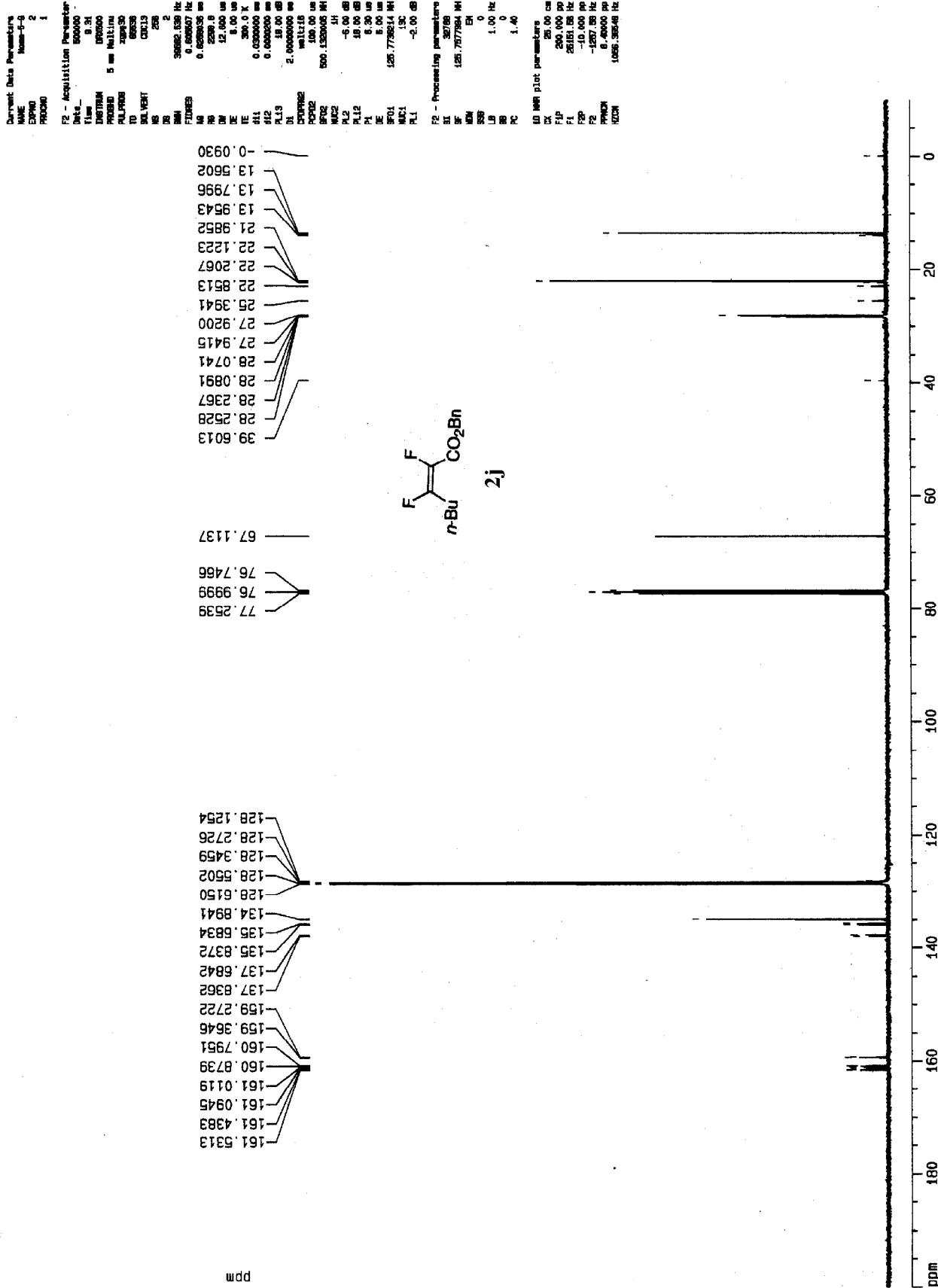


2i





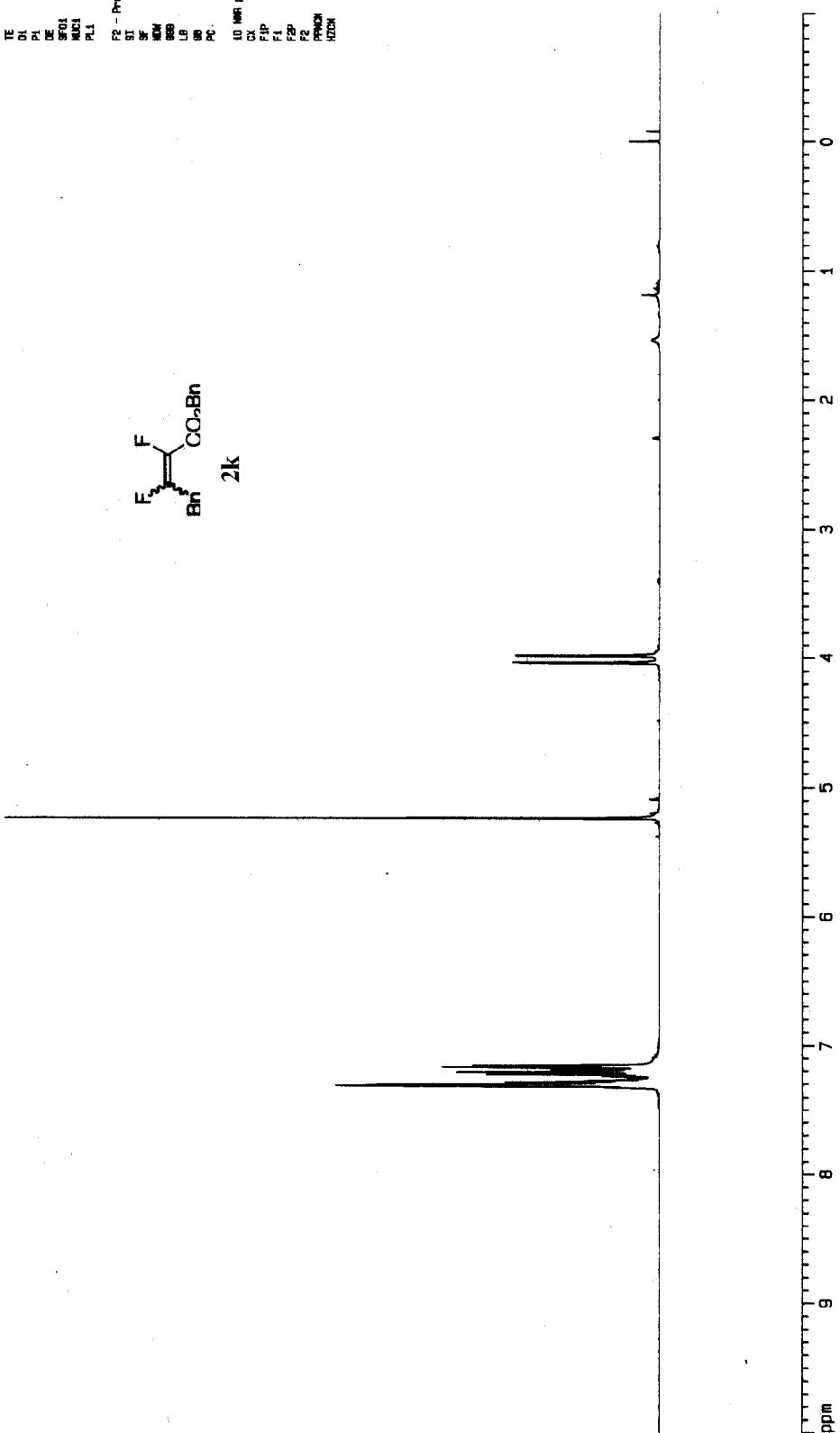
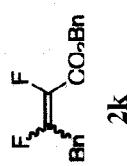




Current Data Parameters
 NAME Name-4-9
 PROB# 1
 P2 - Acquisition Parameter
 Date 500000
 Time 20:55
 INSTRUM QNP300
 PROBHD 5 mm Multin
 PLATES 2500
 T0 52.000
 SOLVENT CDCl₃
 NS 50
 DS 2
 SWH 10238.076 Hz
 FIDRES 0.312504 Hz
 AQ 1.000000 sec
 R0 181.
 DM 40,000 us
 DE 6.00 us
 TE 360.0 K
 D1 1.0000000 sec
 T1 0.30 us
 P1 0.30 us
 QF 0.30 us
 SF 500.1330035 MHz
 NCYC 161
 PT 1 -6.00 dB

P2 - Processing parameters
 ST 10384
 SF 500.1330035 MHz
 HMW EH
 BPP 0
 LB 0.30 Hz
 SB 0
 PC 1.00

AD NMR plot parameters
 CS 15.00 cm
 F1P 10,000 Hz
 F1 5001.30 Hz
 F2P -1,000 Hz
 F2 -500.13 Hz
 FPMIN 0.44000 PP
 HZDN 229.06724 Hz



Current Data Parameters

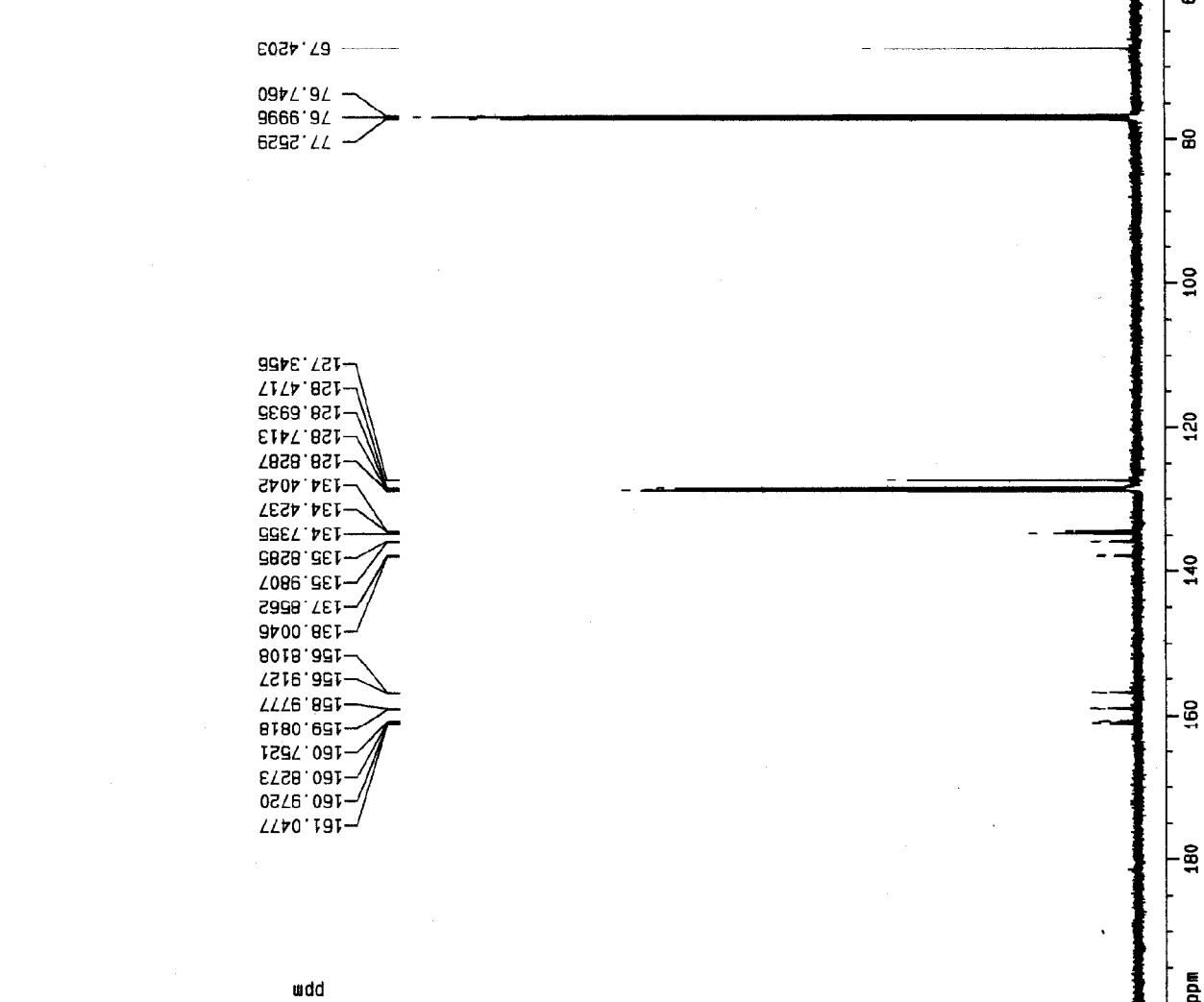
NAME Name-4-9
EDPNO 1
PRODNO 4

F2 - Acquisition Parameter

Date 800000
Time 21.00
INSTRUM DRX600
PROBOD 6 mm Multinu
PLATE96 409620
TO 65355
SOLVENT CDCl₃
NS 200
DS 2
SWH 10000.0 Hz
SFID 0.000007 Hz
TIME3 0.000007 Hz
A0 0.000000 Hz
IM 32
DE 6.00 ms
TE 0.00 ms
d1 0.00 ms
t1 0.000000 ms
RL 1.00 ms
D1 2.000000 ms
DW 100.00 us
PFG90 500.138005 Hz
NUC1 H1
P1 -6.00 Hz
T1 19.00 Hz
P1 6.30 us
DE 6.00 us
SFID 126.773834 Hz
NUC1 13C
R1 -2.00 Hz

F2 - Processing parameters

G1 25.00 cm
FID 200.000 Hz
F1 20161.00 Hz
F2P -10.000 Hz
F2 -1287.00 Hz
OPPCW 0.40000 Hz
TECD 1056.30048 Hz



Current Data Parameters
NAME yamada-05.11.10
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date 20051110
Time 15.20
INSTRUM drx500
PROBHD 5 mm Multinuc
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 57
DW 48.400 usec
DE 6.00 usec
TE 295.8 K
D1 1.0000000 sec
MOREST 0.0000000 sec
MCWRF 0.0150000 sec

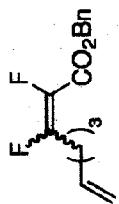
===== CHANNEL f1 =====

NUC1 1H
P1 10.30 usec
P_-1 -6.00 dB
SF01 500.1330885 MHz

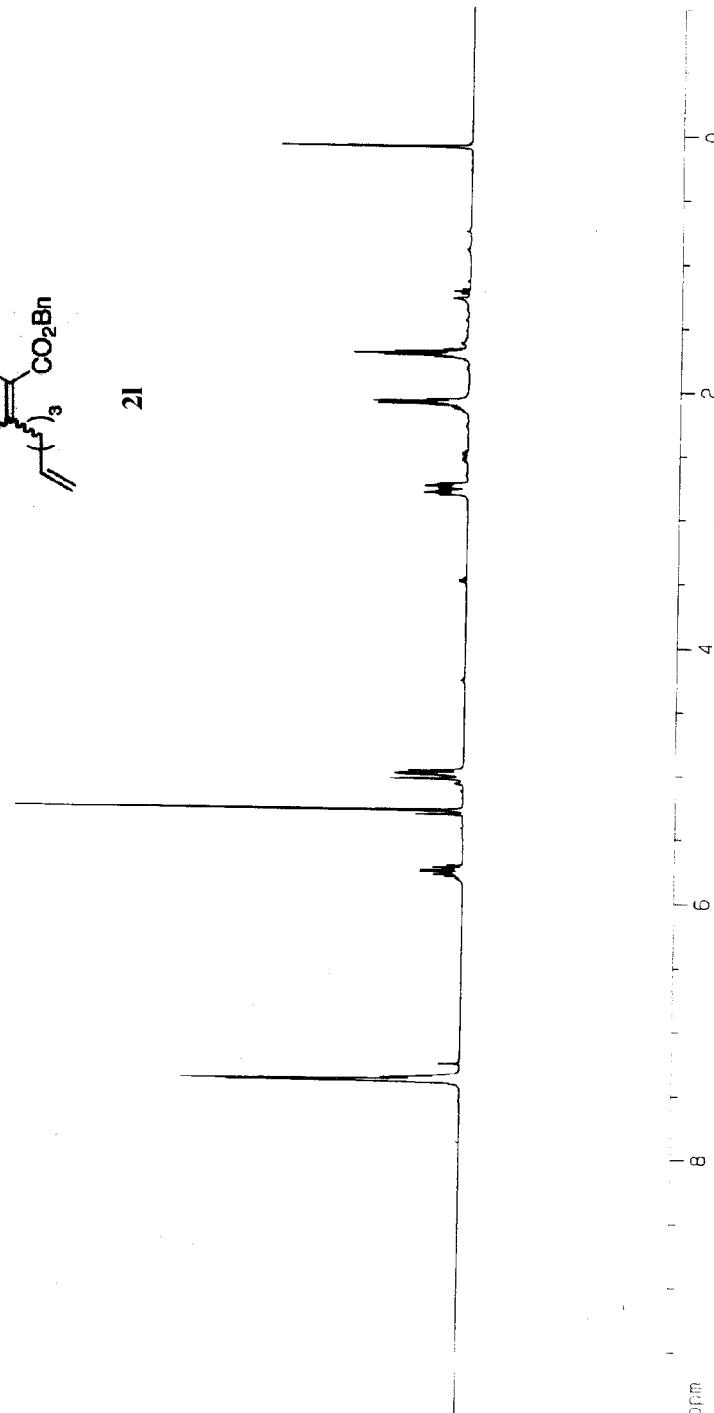
F2 - Processing parameters

SI 32768
SF 500.1300131 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 20.00 cm
CY 6.33 cm
F1P 10.000 ppm
F1 5001.30 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 275.07150 Hz/cm



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Current Data Parameters
NAME yamada-05.11.15
EXPNO 1
PROCND 1

F2 - Acquisition Parameters

Date 20051115
Time 21:33
INSTRUM dr500
PROBHD 5 mm Multinuc
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 256
DS 2
SWH 30030.059 Hz
FIDRES 0.458222 Hz
AQ 1.091224 sec
RG 9195.2
DW 16.650 usec
DE 6.00 usec
TE 297.2 K
D1 0.5000000 sec
d11 0.0300000 sec
t111 0.0000000 sec
t112 0.0150000 sec

***** CHANNEL f1 *****

NUC1 13C
P1 5.70 usec
PL1 -2.00 dB
SF01 125.7703643 MHz

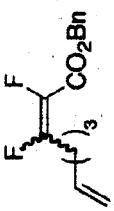
***** CHANNEL f2 *****

CFDR62
NUC2 1H
PP02 100.00 usec
PL2 -6.00 dB
PL12 13.74 dB
PL13 13.74 dB
SF02 500.1320005 MHz

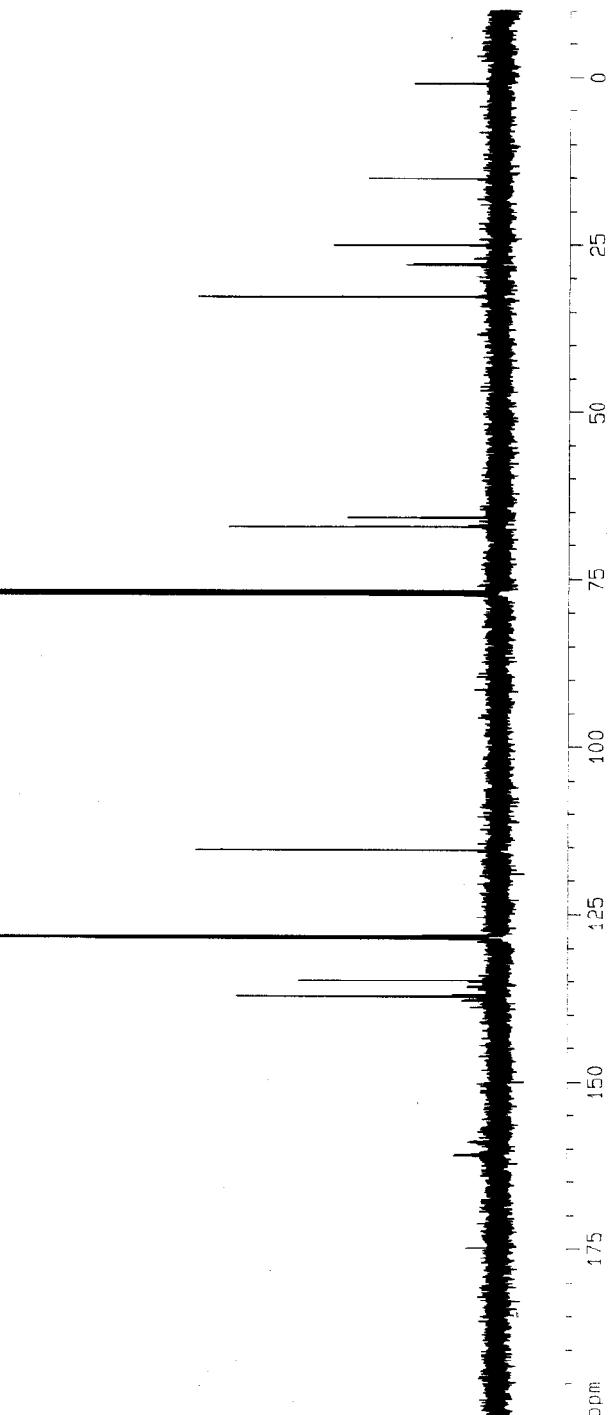
F2 - Processing parameters

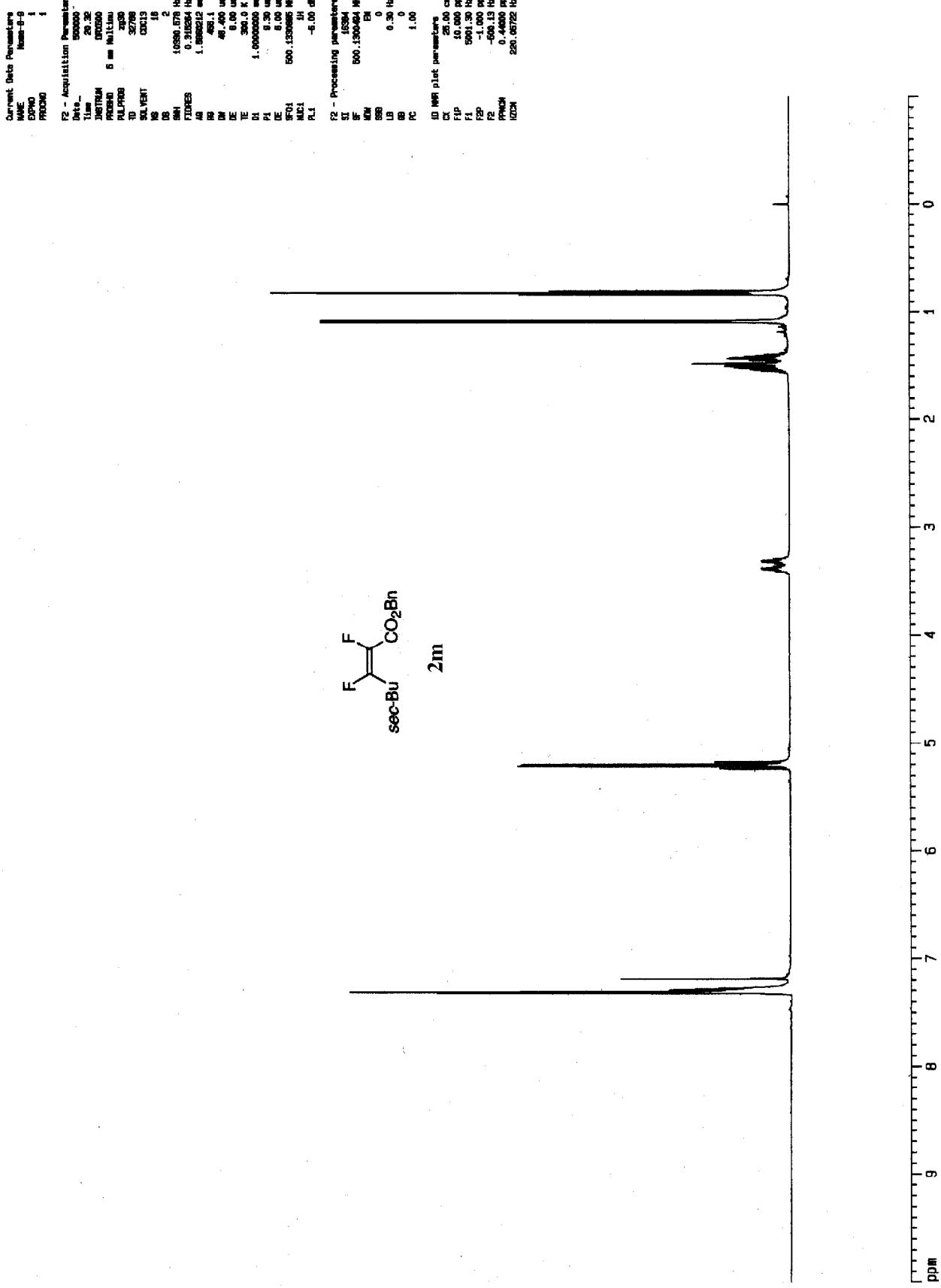
SJ 32768
SF 125.7577987 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

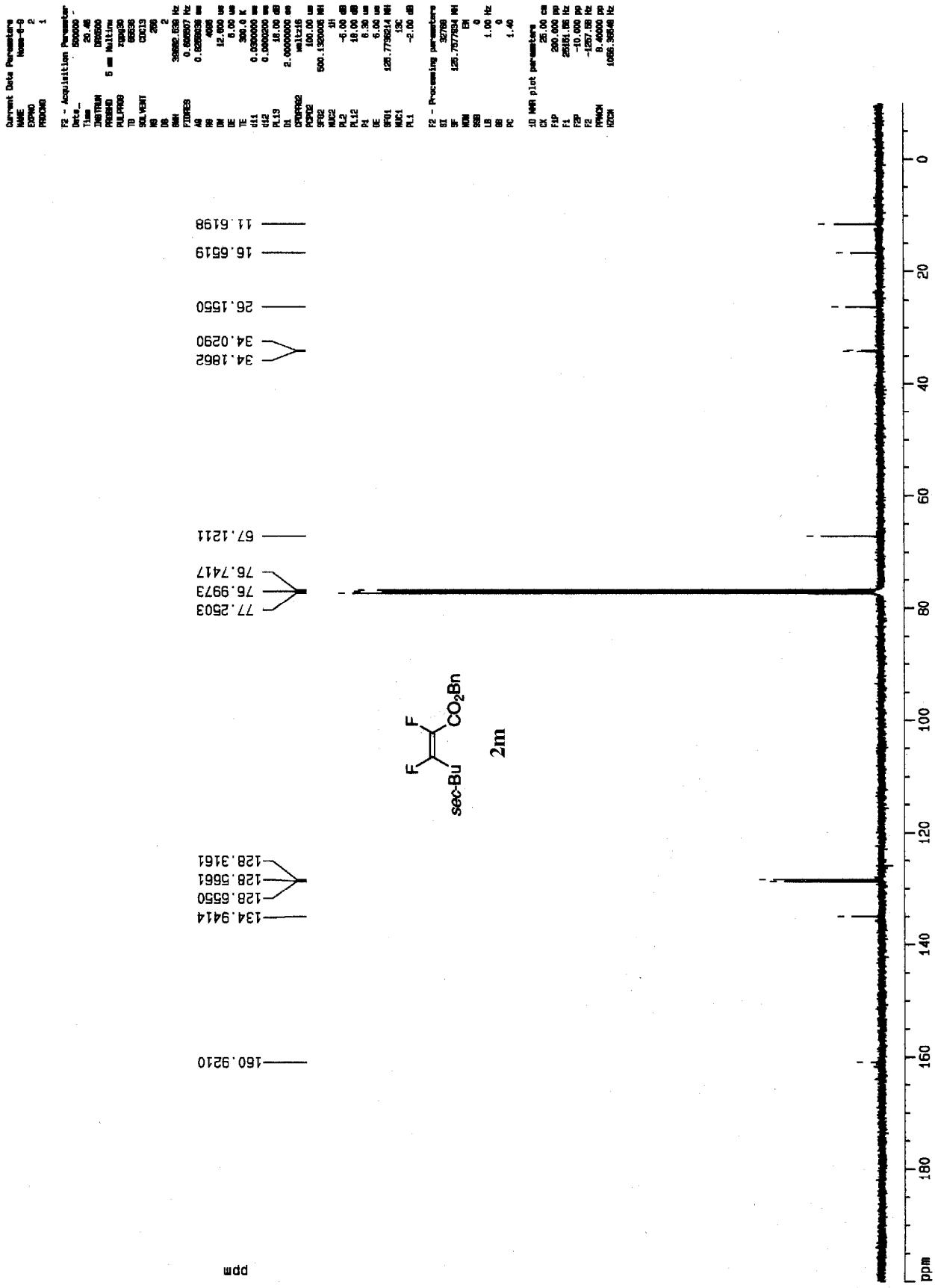
1D NMR plot parameters
CX 20.00 cm
CY 11.54 cm
F1P 200.000 ppm
F1 25151.56 Hz
F2P -10.000 ppm
F2 -1257.58 Hz
PPM 10.50000 ppm/cm
HZCM 1320.45679 Hz/cm



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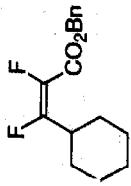


Connect Data Parameters
Name: -08
CPSIG: 1

P2 - Acquisition Parameters
Date: 06/06/06
Time: 21:46
INSTRUM: 6 mm Multin
PROBTD: 2500
PULPROG: 3071B
TD: 32768
SOLVENT: CDCl3
NS: 38
SW1: 14000.0 Hz
SF1: 0.000000 Hz
R1: 1.000000 sec
TE: 6.00 ms
D1: 300.0 K
P1: 1.000000 sec
DE: 8.30 ms
DW: 6.00 us
SF0L: 600.150000 Hz
NUC1: SH
PL1: -0.00 dB

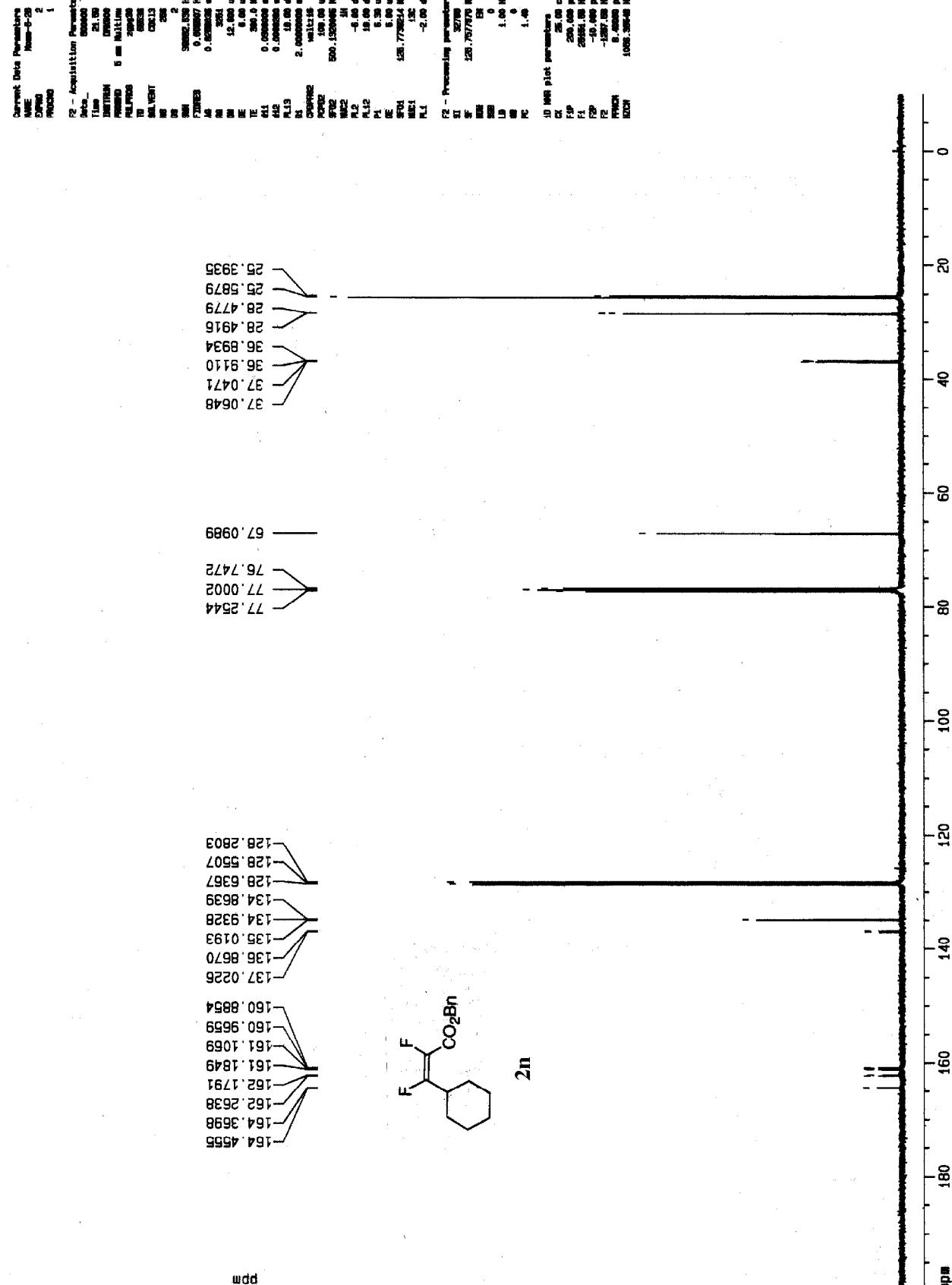
P2 - Processing parameters
SI: 65536
SF: 600.150000 Hz
WDW: FID
DE: 6.00 ms
TDC: 0
FC: 1.00

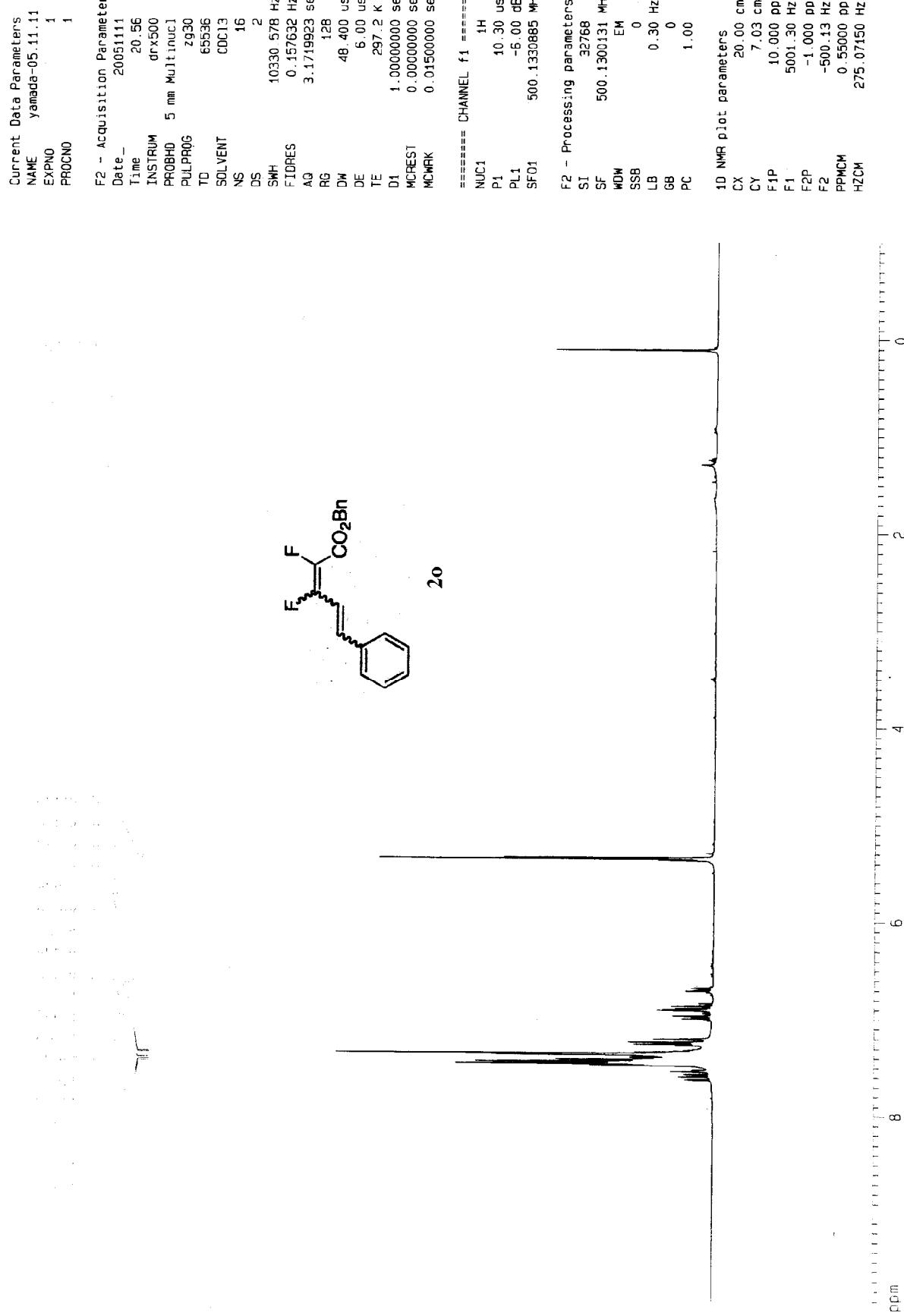
1D NMR stack parameters
SI: 65536
SF: 10.000 Hz
WDW: FID
DE: -1.000 ms
TDC: 0.40000 ms
FC: 200.000 Hz



2n







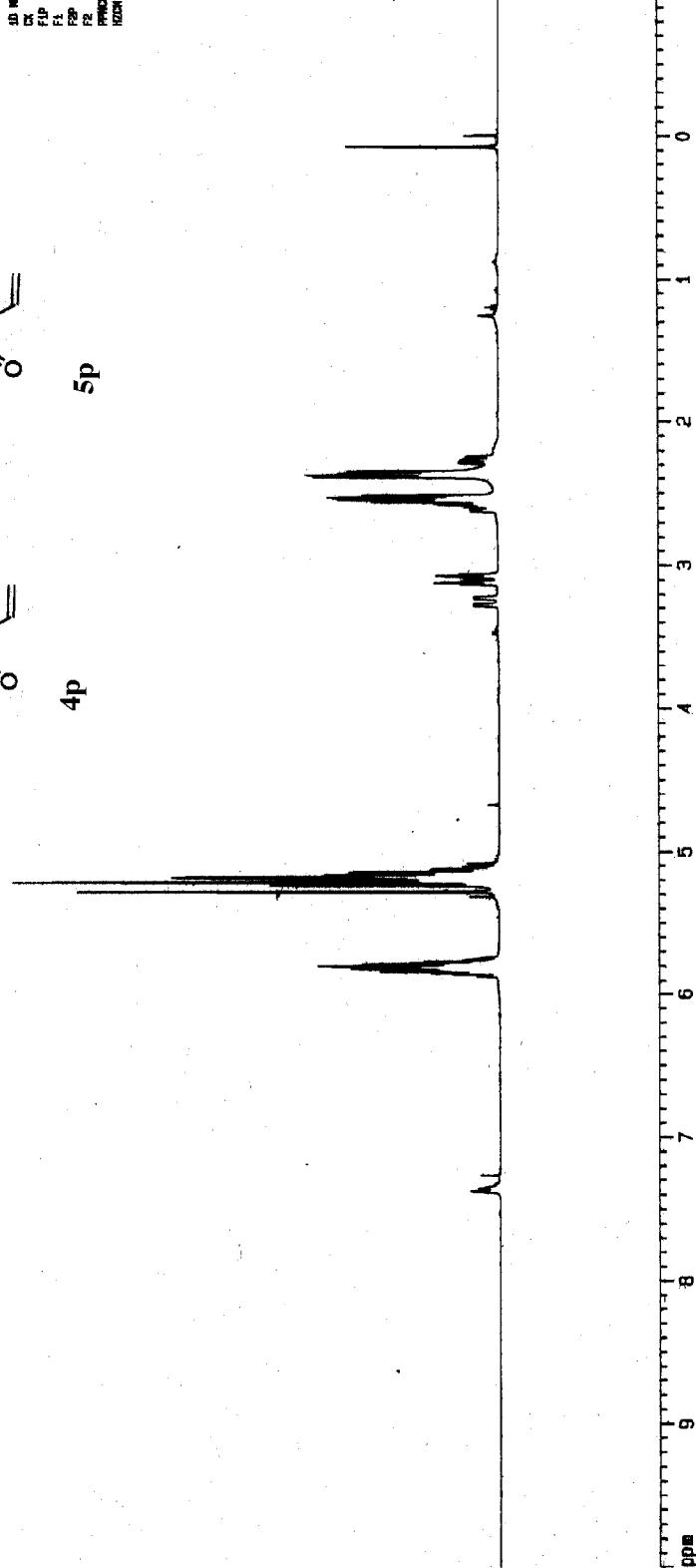
Current Date Parameters
NAME: name-12-4
EXPTID: 3
PRIMEN: 1

F2 - Acquisition Parameters

Date: 20200224
Time: 16:30
INSTRUM: DR600
PROBOD: 6 mm Multinucl
PULPROG: 3DFTB
TD: 32768
SOLVENT: CDCl3
NS: 16
DS: 2
SWH: 1000.076 Hz
FIDRES: 0.312500 Hz
AQ: 1.000000 sec
RG: 65.000
TE: 9.400 sec
TM: 0.00 sec
TEC: 300.0 K
PL: 1.000000 sec
SF01: 500.133000 MHz
NUC1: 1H
PL1: -6.00 dB

F2 - Processing parameters

ST: 16384
SF: 500.1330131 MHz
NMW: EH
SW: 0
LS: 0.30 Hz
GS: 0
PC: 1.00



4p 5p

